Australian Government
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National Measurement Institute

Proficiency Test Final Report AQA 25-14 Nutrients and Anions in Seawater and River Water

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

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

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Aaron Mamo

Wei Huang

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NATA WORLD RECOGNISED ACCREDITATION

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SUMMARY

This report presents the results of the proficiency test AQA 25-14 Nutrients and Anions in Seawater and River Water. The study focused on the measurement of pH and electrical conductivity (EC) at 25ºC, alkalinity to pH 4.5 (as $CaCO_3$), ammonia-N (NH_3-N), bromide, chloride, dissolved organic carbon-DOC (as dNPOC), fluoride, NOx as N (nitrate-N + nitrite-N), orthophosphate-P, silica (as SiO_2), sulphate, total hardness (as $CaCO_3$), total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), total Kjeldahl nitrogen (TKN), total nitrogen (TN), total phosphorus (TP), total organic carbon-TOC (as NPOC) and dissolved B, Ca, K, Mg and Na in seawater and river water.

The sample set consisted of three seawater samples and two river water samples.

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

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

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

i. *assess laboratory capabilities in measuring nutrients and anions in sea and river water;*

Of 663 z-scores, 598 (90%) returned an acceptable score of $|z| \leq 2.0$.

Of 663 E_n scores, 529 (80%) returned an acceptable score of $|E_n| < 1.0$.

Laboratories 16 and **22** reported results for all 40 tests for which a z-score was calculated, and **Laboratory 22** returned acceptable z-scores for every analyte.

Laboratory 22 had the highest number of acceptable E_n-scores with 36 out of 40 reported.

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

Low level TDP in seawater sample S1 challenged participants' analytical techniques. The methods they employed did not produce compatible results for this test.

Measurement of low level NH_3-N, nitrate-N + nitrite-N and orthophosphate-P in seawater sample S1 also challenged participants' analytical techniques. All results for these tests that returned unacceptable z-scores were biased high. High chloride concentrations can interfere with colour development, leading to exaggerated absorbance readings when calibration standards are prepared in deionised water instead of seawater. Contamination during sampling and analysis may also contribute to high bias. Optimising timing, temperature control and reagent handling is also very important for the measurement of these tests at low levels, because small variations in reagent volumes, timing, or temperature can disproportionately affect colour intensity.

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 676 numerical results, 663 (98%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0% to 240% of the reported value. An example of evaluating 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 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 NMIA Proficiency Testing Program

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

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

- per- and polyfluoroalkyl substances in soil, biosolid, water, biota, food, and consumables;
- hydrocarbons, phenols and other organic compounds in soil and water;
- pesticide residues in soil, water, fruit, vegetables, and herbs;
- metals in soil, water, food, filters, and paint;
- nutrients, anions and physical tests in water and soil;
- chlorophyll a in water; and
- controlled drug assay, drugs in wipes, and clandestine laboratory.

AQA 25-14 is the 20th NMIA PT study on nutrients, anions and physical tests in water.

1.2 Study Aims

The aims of the study were to:

- assess laboratory capability in measuring nutrients and anions in sea and river water;
- evaluate the laboratories' methods used in determination of nutrients and anions in sea and river water;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty evaluation; and
- produce materials that can be used in method validation and as control samples.

1.3 Study Conduct

The conduct of NMIA proficiency tests is described in the NMIA Study Protocol for Proficiency Testing.[2] The statistical methods used are described in the NMIA Chemical Proficiency Testing 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]

NMIA is accredited by National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043:2023 as a provider of proficiency testing schemes. This proficiency study is within the scope of NMIA'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 41 tests of the study 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-eight laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued:	01 September 2025
Samples dispatched:	29 September 2025
Results due:	24 October 2025
Interim report issued	29 October 2025
Preliminary report issued:	03 November 2025

2.3 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.4 Test Material Specification

Five samples were provided for analysis:
Sample S1 was two identical bottles of 200 mL of filtered and frozen seawater;
Sample S2 was two identical bottles of 200 mL of filtered and frozen river water;
Sample S3 was 200 mL of unfiltered and frozen seawater;
Sample S4 was 200 mL of unfiltered and frozen river water; and
Sample S5 was 200mL of unfiltered and chilled seawater.

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 ammonia-N, nitrate-N + nitrite-N, orthophosphate-P, TDN and TDP in Samples S1 and S2, and all tests in Samples S3 and S4. The results of partial homogeneity testing are reported in this study as the homogeneity value.

The preparation and analysis procedures are described in Appendix 1.

2.6 Stability of Analytes

A stability study was conducted for the less stable analytes (Ammonia-N, DOC, Nitrate-N + Nitrite-N, TDN, and TDP) in S1 and S2 to address issues associated with holding time and holding conditions. The stability study covered the entire period of the PT study. The set-up of this study and the results are presented in Appendix 2.

2.7 Sample Storage, Dispatch and Receipt

Samples S1, S2, S3 and S4 were frozen whilst S5 was refrigerated.

The samples were dispatched by courier on 29 September 2025.

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, S2, S3 and S4 frozen and Sample S5 chilled.
- Prior to testing, thaw samples S1, S2, S3 and S4 completely.

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

SAMPLE S1 **2 x 200 mL frozen, filtered seawater**		**SAMPLE S2** **2 x 200 mL frozen, filtered river water**	
Test	**Estimated Value* mg/L**	**Test**	**Estimated Value* mg/L**
Ammonia-N	<0.1	B (dissolved)	0.05-2
Nitrate-N + Nitrite-N	<0.1	Ca (dissolved)	5-200
Chloride	1000-40000	K (dissolved)	0.5-20
Fluoride	0.5-20	Mg (dissolved)	0.5-20
Sulphate	500-20000	Na (dissolved)	5-200
Dissolved Organic Carbon (as dNPOC)	0.5-20	Ammonia-N	<0.1
Orthophosphate-P (FRP)	<0.1	Nitrate-N + Nitrite-N	<1.0
Total Dissolved Nitrogen	<0.2	Bromide	0.05-2
Total Dissolved Phosphorus	<0.1	Chloride	5-200
SAMPLE S3 **200 mL frozen seawater**		Sulphate	0.5-20
Test	**Estimated Value* mg/L**	Dissolved Organic Carbon (as dNPOC)	0.5-20
Total Kjeldahl Nitrogen	0.05-2	Orthophosphate-P (FRP)	<0.1
Total Nitrogen	0.05-2	Total Dissolved Nitrogen	<1.0
Total Phosphorus	0.05-2	Total Dissolved Phosphorus	<0.1
Total Organic Carbon (as NPOC)	0.5-20	**SAMPLE S4** **200 mL frozen river water**	
SAMPLE S5 **200 mL chilled seawater**		**Test**	**Estimated Value* mg/L**
Test	**Estimated Value* mg/L**	Total Kjeldahl Nitrogen	0.05-2
B (dissolved)	0.5-20	Total Nitrogen	0.5-20
Ca (dissolved)	50-2000	Total Phosphorus	0.05-2
K (dissolved)	50-2000	Total Organic Carbon (as NPOC)	0.5-20
Mg (dissolved)	50-2000		
Na (dissolved)	500-20000		
Alkalinity to pH 4.5 (as $CaCO_3$)	5-200		
EC (at 25°C, µS/cm)	2500-100000		
pH (at 25°C)	2-14		
Silica (as SiO_2)	0.25-5		
Total Hardness (as $CaCO_3$)	500-20000		

- 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 evaluation.
- Please return the completed results sheet by 17 October 2025.

The results due date was extended to 24 October 2025 due to some labs experiencing instrument difficulties.

2.9 Interim and Preliminary Reports

An interim report was emailed to participants on 29 October 2025. A preliminary report was issued on 03 November 2025. 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, S4 and S5

Measurement methods and instrumental techniques used for the tests in Samples S1, S2, S3, S4 and S5 are presented in Appendices 6, 7, 8, 9 and 10 respectively.

3.2 Basis of Participants' Measurement Uncertainty Evaluation

Participants were requested to provide information about the basis of their uncertainty evaluation (Table 1).

Table 1 Basis of Uncertainty Evaluation

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation[a]		Guide Document for Evaluating MU
		Precision	Method Bias	
1	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
2	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - CRM	CRM Instrument Calibration	ISO/GUM
3*	Coverage factor not reported	Control samples - CRM Instrument Calibration	CRM	
4	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	Instrument Calibration	ISO/GUM
5	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration		Eurachem/CITAC Guide
6	Professional judgment k = 2	Control Samples Duplicate Analysis Instrument Calibration	Recoveries of SS	ISO/GUM
7	Top Down - reproducibility (standard deviation) from PT studies used directly k = 2	Standard deviation from PT Studies only		NATA Technical Report
		Instrument Calibration	CRM Instrument Calibration	
8	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) k = 2	Control samples - CRM	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	Eurachem 2000 / ISO1993A
9	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples Duplicate Analysis	Laboratory Bias from PT Studies	ISO/GUM
10	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
11	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - SS Duplicate Analysis	Recoveries of SS	Eurachem/CITAC Guide
12*	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Duplicate Analysis	Laboratory Bias from PT Studies	

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation[a]		Guide Document for Evaluating MU
		Precision	Method Bias	
13	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
14	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - SS Duplicate Analysis	CRM Laboratory Bias from PT Studies Recoveries of SS	ISO/GUM
15*	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM	CRM	NMIA Uncertainty Course
16	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration	Nordtest Report TR537
17	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
18	Top Down - precision and evaluations of the method and laboratory bias k = 2	Duplicate Analysis	CRM	Tech note
19	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	
20	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ASTM E2554-13
21	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - SS Duplicate Analysis		
22	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
23	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
24*	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM	CRM	NMIA Uncertainty Course
25*	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM	CRM	NMIA Uncertainty Course
26	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM	CRM Instrument Calibration	ISO/GUM
27	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) k = 2	Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	ISO/GUM
28	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537

[a] CRM = Certified Reference Material, SS = Spiked Samples. *Additional Information in Table 2

Table 2 Additional Information for Basis of Uncertainty Evaluation

Lab Code	Additional Information
3	Estimation of MU from within-laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques
12	Technical Guide 5: Chemical and Microbiological Testing Laboratories Measurement Uncertainty, Precision and Limits of Detection
15, 24 & 25	Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval)

3.3 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 3.

Table 3 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
We normally report our results as the molecule in umol/L. For this PT we have converted our umol/L results into mg/L by using the MW of the element and we are reporting the element in mg/L. For example the result is mg/L of P for the Orthophophate analysis.	Thank you for your feedback. We design our studies based on the most popular methods used by laboratories and on the reporting, format used by the majority of them.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 4 to 44 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 42. An example chart with an interpretation guide is shown in Figure 1.

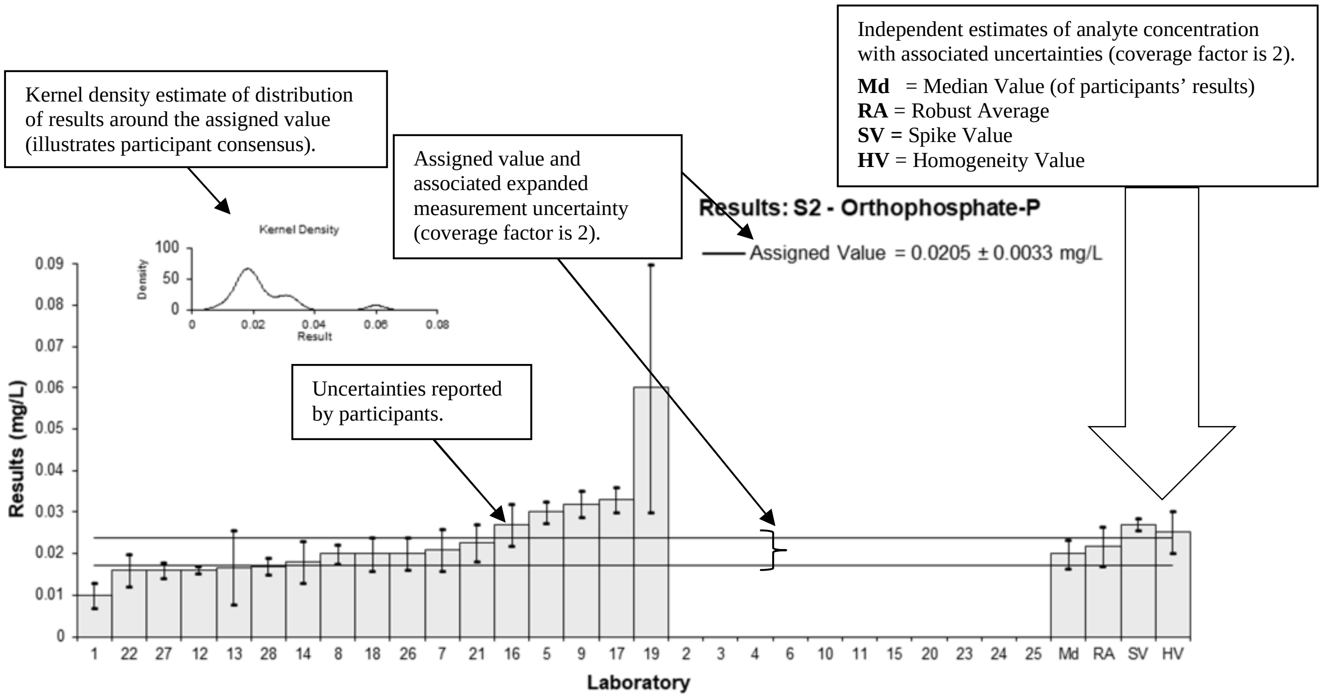


Figure 1 Guide to Presentation of Results

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 the 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 evaluated 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'.[6] The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528.[6]

4.5 Standard Deviation for Proficiency Assessment

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

$\sigma = (X) * PCV$ 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;
- χ is participants' result;
- X is the assigned value;
- σ is the standard deviation for proficiency assessment.

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

- |z| ≤ 2.0 is acceptable;
- 2.0 < |z| < 3.0 is questionable;
- |z| ≥ 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;
- χ is a participants' result;
- X is the assigned value;
- U_χ 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[8] must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[9]

5 TABLES AND FIGURES

Table 4

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	Ammonia-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	0.11	0.03	24.89	3.05
2*	0.034	0.009	4.24	1.70
3	0.025	0.0075	1.79	0.86
4	< 0.2	NR		
5	0.018	0.0027	-0.11	-0.13
6*	0.008	0.004	-2.83	-2.39
7	0.019	0.005	0.16	0.11
8*	0.034	0.0075	4.24	2.03
9*	0.033	0.0033	3.97	3.93
10**	0.5	0.028	130.87	17.17
11	NT	NT		
12	<0.005	NR		
13	<0.02	NR		
14	0.018	0.005	-0.11	-0.08
15	0.0175	0.0017	-0.24	-0.37
16	0.020	0.004	0.43	0.37
17	0.021	0.0005	0.71	1.47
18	0.011	0.002	-2.01	-2.82
19	NT	NT		
20	<0.1	NR		
21	0.0193	0.0035	0.24	0.23
22	0.013	0.006	-1.47	-0.87
23	<0.2	1.1		
24	0.0173	0.0017	-0.30	-0.46
25	0.0174	0.0017	-0.27	-0.42
26*	0.01	0.0035	-2.28	-2.16
27	0.02	0.01	0.43	0.16
28**	0.300	0.03	76.52	9.37

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0184	0.0017
Spike Value	Not Spiked	
Homogeneity Value	0.0182	0.0036
Robust Average	0.0205	0.0053
Median	0.0190	0.0017
Mean	0.025	
N	19	
Max	0.11	
Min	0.008	
Robust SD	0.0092	
Robust CV	45%	

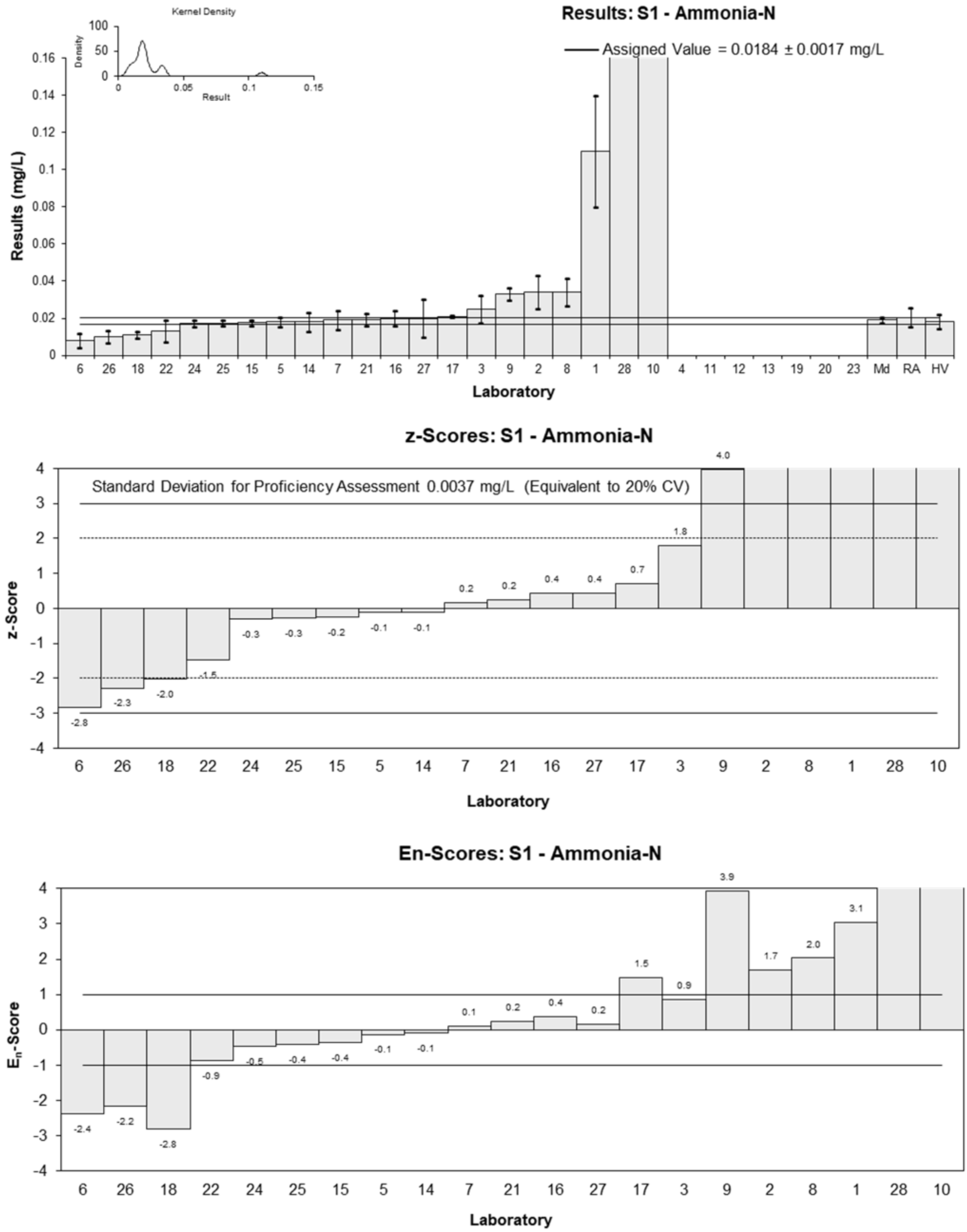

Kernel Density
Density
Result
Results: S1 - Ammonia-N
Assigned Value = 0.0184 ± 0.0017 mg/L
Results (mg/L)
Laboratory
z-Scores: S1 - Ammonia-N
Standard Deviation for Proficiency Assessment 0.0037 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
En-Scores: S1 - Ammonia-N
E_n-Score
Laboratory

Figure 2

Table 5

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	Chloride
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	21100	1190	0.14	0.21
2	20169.97	5042.49	-0.30	-0.12
3	22635	6790.5	0.88	0.27
4	19000	3800	-0.87	-0.46
5	20800	2354	0.00	0.00
6	25000	3100	2.02	1.31
7	NR	NR		
8	19800	732.6	-0.48	-0.92
9	20200	2020	-0.29	-0.28
10	NT	NT		
11	NT	NT		
12	20600	1000	-0.10	-0.16
13	17604.84	1578.2	-1.54	-1.81
14	16900	2535	-1.88	-1.47
15	NT	NT		
16	21500	3200	0.34	0.21
17	20500	2700	-0.14	-0.11
18	22370	3360	0.75	0.45
19	NT	NT		
20	19730	3219	-0.51	-0.32
21	21600	2600	0.38	0.29
22	21300	1910	0.24	0.24
23	20297	202	-0.24	-0.61
24	NT	NT		
25	NT	NT		
26**	1700	1700	-9.18	-10.17
27	20818	NR	0.01	0.02
28	22800	2500	0.96	0.76

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	20800	800
Spike Value	Not Spiked	
Robust Average	20800	800
Median	20700	700
Mean	20700	
N	20	
Max	25000	
Min	16900	
Robust SD	1500	
Robust CV	7.2%	

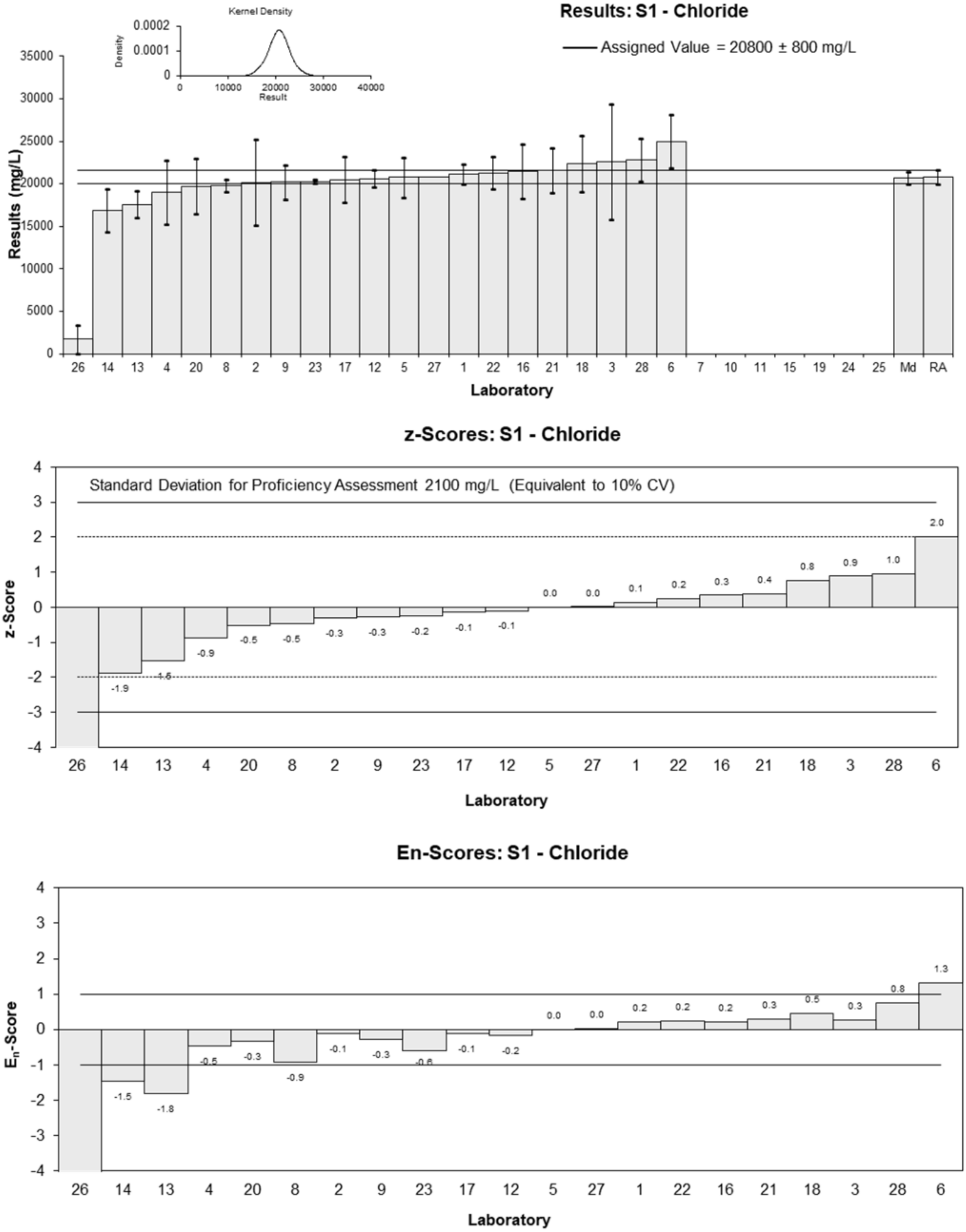

Results: S1 - Chloride
Assigned Value = 20800 ± 800 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
26 14 13 4 20 8 2 9 23 17 12 5 27 1 22 16 21 18 3 28 6 7 10 11 15 19 24 25 Md RA
z-Scores: S1 - Chloride
Standard Deviation for Proficiency Assessment 2100 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S1 - Chloride
En-Score
Laboratory

Figure 3

Table 6

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	DOC
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	<5	NT		
3	< 5	NR		
4	NT	NT		
5	1	0.236	-0.92	-0.53
6	1.1	0.3	-0.34	-0.17
7	NR	NR		
8	NT	NT		
9	1.3	0.13	0.80	0.61
10	NT	NT		
11	NT	NT		
12	1.5	0.0750	1.95	1.66
13*	3.07	1.84	10.98	1.03
14	<1.0	NR		
15	NT	NT		
16	0.9	0.2	-1.49	-0.94
17	1	0.41	-0.92	-0.35
18	1.3	0.01	0.80	0.74
19	NT	NT		
20	NT	NT		
21	1.32	0.26	0.92	0.50
22	0.9	0.2	-1.49	-0.94
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	1.3	0.247	0.80	0.45
27	NR	NR		
28	<1	NR		

* Outlier, see Section 4.2

Statistics

Assigned Value	1.16	0.19
Spike Value	Not Spiked	
Robust Average	1.20	0.20
Median	1.30	0.22
Mean	1.34	
N	11	
Max	3.07	
Min	0.9	
Robust SD	0.27	
Robust CV	23%	

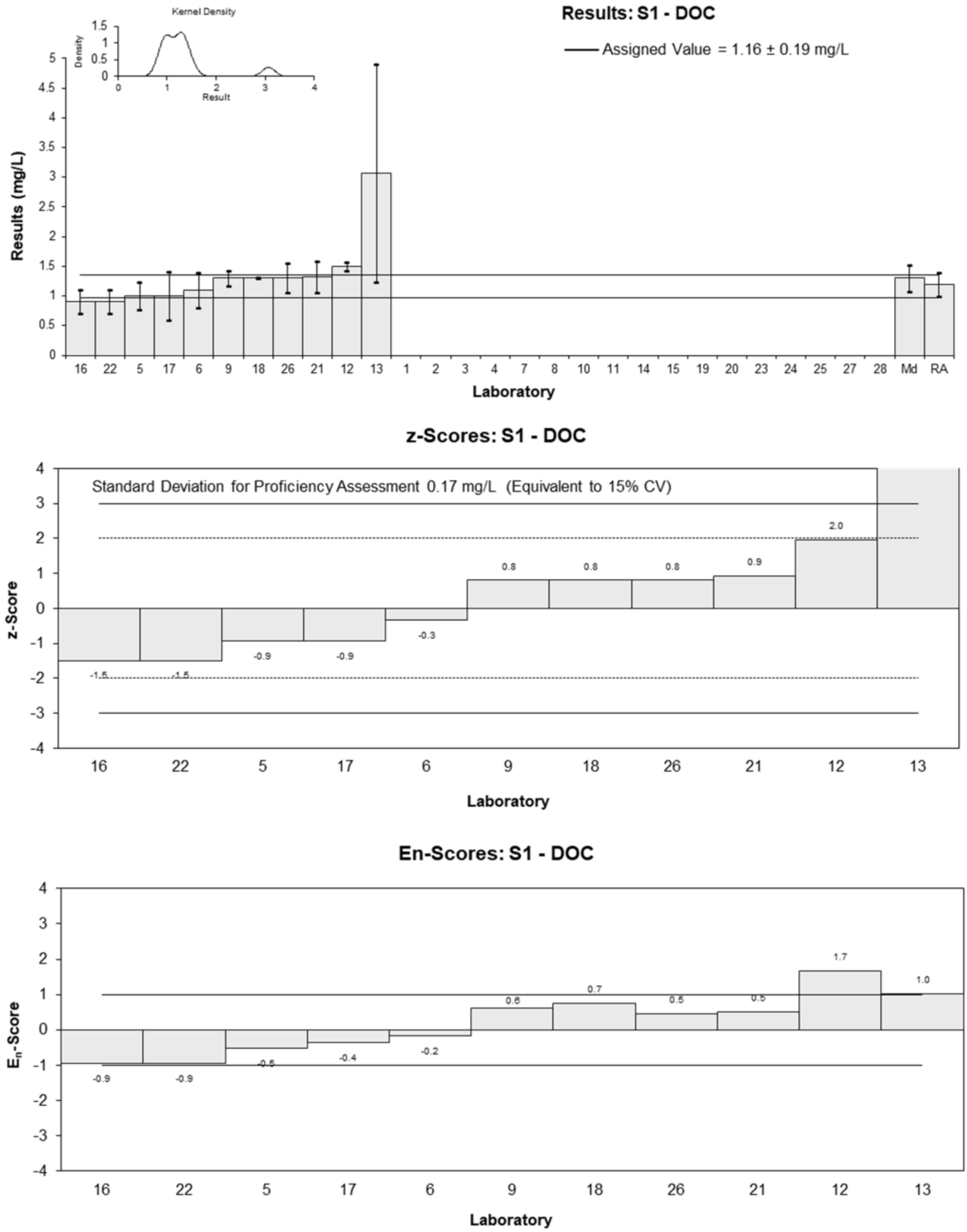

Results: S1 - DOC
Assigned Value = 1.16 ± 0.19 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
16 22 5 17 6 9 18 26 21 12 13 1 2 3 4 7 8 10 11 14 15 19 20 23 24 25 27 28 Md RA
z-Scores: S1 - DOC
Standard Deviation for Proficiency Assessment 0.17 mg/L (Equivalent to 15% CV)
z-Score
-1.5 -1.5 -0.9 -0.9 -0.3 0.8 0.8 0.8 0.9 2.0
16 22 5 17 6 9 18 26 21 12 13
Laboratory
En-Scores: S1 - DOC
En-Score
-0.9 -0.9 -0.5 -0.4 -0.2 0.6 0.7 0.5 0.5 1.7 1.0
16 22 5 17 6 9 18 26 21 12 13
Laboratory

Figure 4

Table 7

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	Fluoride
Unit	mg/L

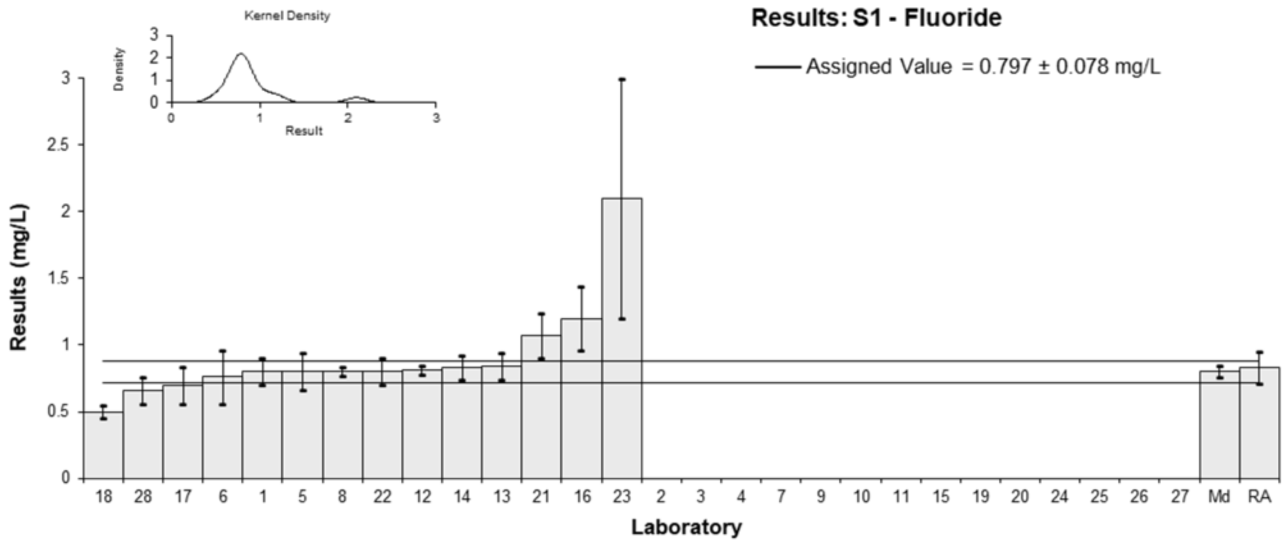
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.8	0.1	0.02	0.02
2	NT	NT		
3	< 10	NR		
4	< 10	NR		
5	0.8	0.14	0.02	0.02
6	0.76	0.2	-0.23	-0.17
7	NR	NR		
8	0.8	0.033	0.02	0.04
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	0.81	0.035	0.08	0.15
13	0.844	0.1	0.29	0.37
14	0.83	0.09	0.21	0.28
15	NT	NT		
16	1.2	0.24	2.53	1.60
17	0.7	0.14	-0.61	-0.61
18	0.5	0.05	-1.86	-3.21
19	NT	NT		
20	< 10	NR		
21	1.07	0.17	1.71	1.46
22	0.8	0.1	0.02	0.02
23*	2.1	0.9	8.17	1.44
24	NT	NT		
25	NT	NT		
26	<10	NR		
27	NR	NR		
28	0.66	0.1	-0.86	-1.08

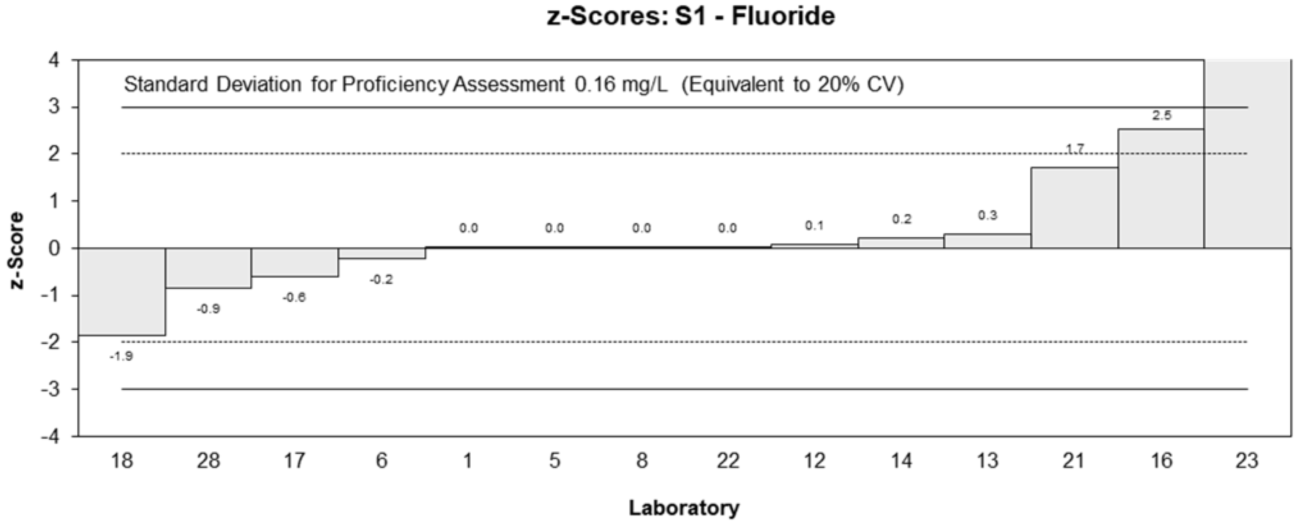
* Outlier, see Section 4.2

Statistics

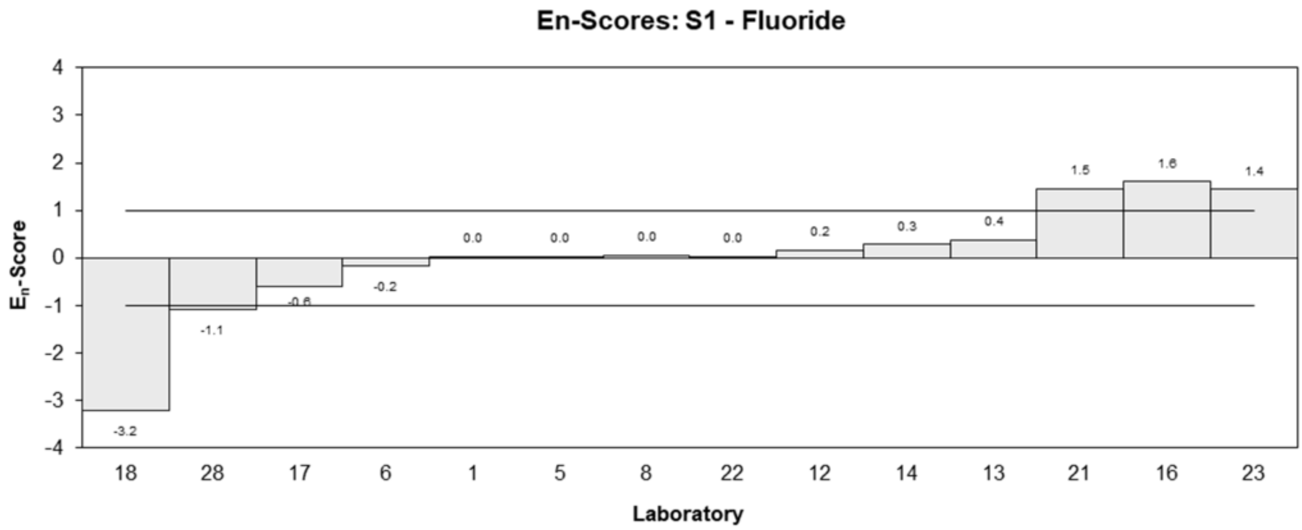
Assigned Value	0.797	0.078
Spike Value	Not Spiked	
Robust Average	0.83	0.12
Median	0.800	0.042
Mean	0.91	
N	14	
Max	2.1	
Min	0.5	
Robust SD	0.18	
Robust CV	22%	



Results: S1 - Fluoride
Assigned Value = 0.797 ± 0.078 mg/L
Kernel Density
Density
Result
Results (mg/L)
18 28 17 6 1 5 8 22 12 14 13 21 16 23 2 3 4 7 9 10 11 15 19 20 24 25 26 27 Md RA
Laboratory



z-Scores: S1 - Fluoride
Standard Deviation for Proficiency Assessment 0.16 mg/L (Equivalent to 20% CV)
z-Score
-1.9 -0.9 -0.6 -0.2 0.0 0.0 0.0 0.0 0.1 0.2 0.3 1.7 2.5
18 28 17 6 1 5 8 22 12 14 13 21 16 23
Laboratory



En-Scores: S1 - Fluoride
En-Score
-3.2 -1.1 -0.6 -0.2 0.0 0.0 0.0 0.0 0.2 0.3 0.4 1.5 1.6 1.4
18 28 17 6 1 5 8 22 12 14 13 21 16 23
Laboratory

Figure 5

Table 8

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	Nitrate-N + Nitrite-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.03	0.01	-0.70	-0.34
2	<0.02	NT		
3	< 0.05	NR		
4	< 0.1	NR		
5	0.036	0.0066	0.50	0.36
6	0.038	0.01	0.90	0.44
7	0.031	0.007	-0.50	-0.34
8	0.027	0.0018	-1.29	-2.23
9*	0.071	0.0071	7.46	5.02
10*	0.089	0.011	11.04	4.94
11	NT	NT		
12**	0.45	0.0045	82.89	82.41
13	0.043	0.01234	1.89	0.76
14	0.038	0.009	0.90	0.48
15	0.0319	0.0005	-0.32	-0.68
16	0.033	0.007	-0.10	-0.07
17	0.037	0.003	0.70	0.93
18	0.031	0.003	-0.50	-0.66
19	NT	NT		
20	< 0.1	NR		
21	0.0357	0.0075	0.44	0.28
22	0.033	0.003	-0.10	-0.13
23	NT	NT		
24	0.0314	0.0005	-0.42	-0.89
25	0.0312	0.0005	-0.46	-0.98
26	0.032	0.00576	-0.30	-0.24
27	0.03	0.01	-0.70	-0.34
28	0.037	0.005	0.70	0.64

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.0335	0.0023
Spike Value	Not Spiked	
Homogeneity Value	0.0330	0.0066
Robust Average	0.0344	0.0028
Median	0.0330	0.0025
Mean	0.0383	
N	20	
Max	0.089	
Min	0.027	
Robust SD	0.0049	
Robust CV	14%	

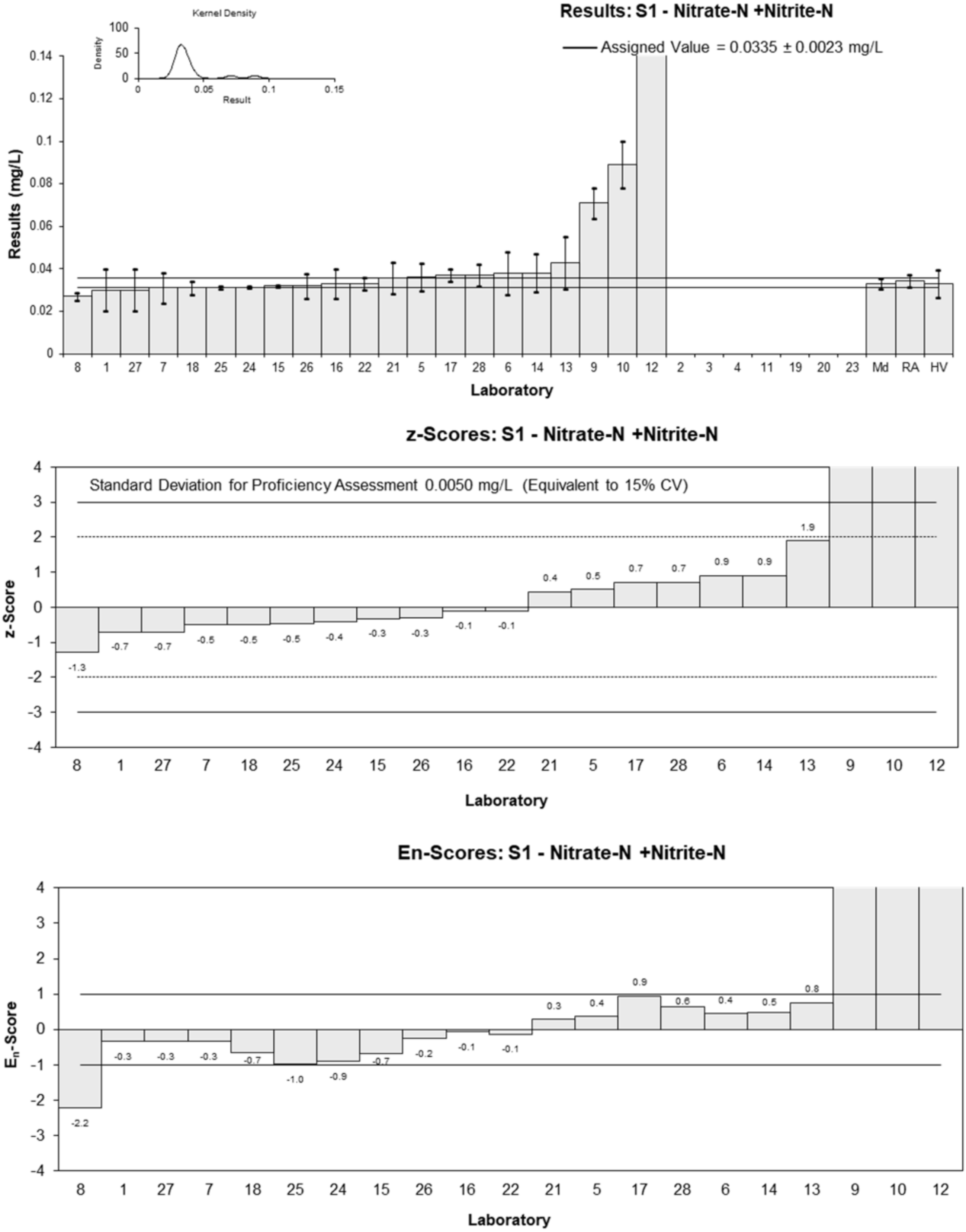

Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.0335 ± 0.0023 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 1 27 7 18 25 24 15 26 16 22 21 5 17 28 6 14 13 9 10 12 2 3 4 11 19 20 23 Md RA HV
z-Scores: S1 - Nitrate-N +Nitrite-N
Standard Deviation for Proficiency Assessment 0.0050 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
8 1 27 7 18 25 24 15 26 16 22 21 5 17 28 6 14 13 9 10 12
-1.3 -0.7 -0.7 -0.5 -0.5 -0.5 -0.4 -0.3 -0.3 -0.1 -0.1 0.4 0.5 0.7 0.7 0.9 0.9 1.9
En-Scores: S1 - Nitrate-N +Nitrite-N
E_n-Score
Laboratory
8 1 27 7 18 25 24 15 26 16 22 21 5 17 28 6 14 13 9 10 12
-2.2 -0.3 -0.3 -0.3 -0.7 -1.0 -0.9 -0.7 -0.2 -0.1 -0.1 0.3 0.4 0.9 0.6 0.4 0.5 0.8

Figure 6

Table 9

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	Orthophosphate-P
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<0.01	NR		
2	NT	NT		
3	< 0.05	NR		
4	< 0.1	NR		
5	0.006	0.0009	-0.07	-0.07
6	0.005	0.003	-0.72	-0.34
7	0.004	0.005	-1.38	-0.41
8	0.008	0.0009	1.25	1.27
9*	0.016	0.0016	6.49	4.95
10	0.004	0.0002	-1.38	-1.73
11	NT	NT		
12	0.0068	0.00034	0.46	0.56
13	<0.01	NR		
14	0.005	0.001	-0.72	-0.70
15	0.0050	0.0001	-0.72	-0.91
16	0.009	0.002	1.90	1.24
17*	0.013	0.002	4.52	2.96
18	0.008	0.002	1.25	0.81
19	NT	NT		
20	< 0.1	NR		
21	0.00867	0.00191	1.69	1.14
22	0.006	0.003	-0.07	-0.03
23	NT	NT		
24	0.0046	0.0001	-0.98	-1.25
25	0.0059	0.0001	-0.13	-0.17
26	0.006	0.00114	-0.07	-0.06
27	<0.002	NR		
28*	0.014	0.002	5.18	3.39

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0061	0.0012
Spike Value	Not Spiked	
Homogeneity Value	0.0060	0.0012
Robust Average	0.0069	0.0016
Median	0.0060	0.0015
Mean	0.0075	
N	18	
Max	0.016	
Min	0.004	
Robust SD	0.0027	
Robust CV	39%	

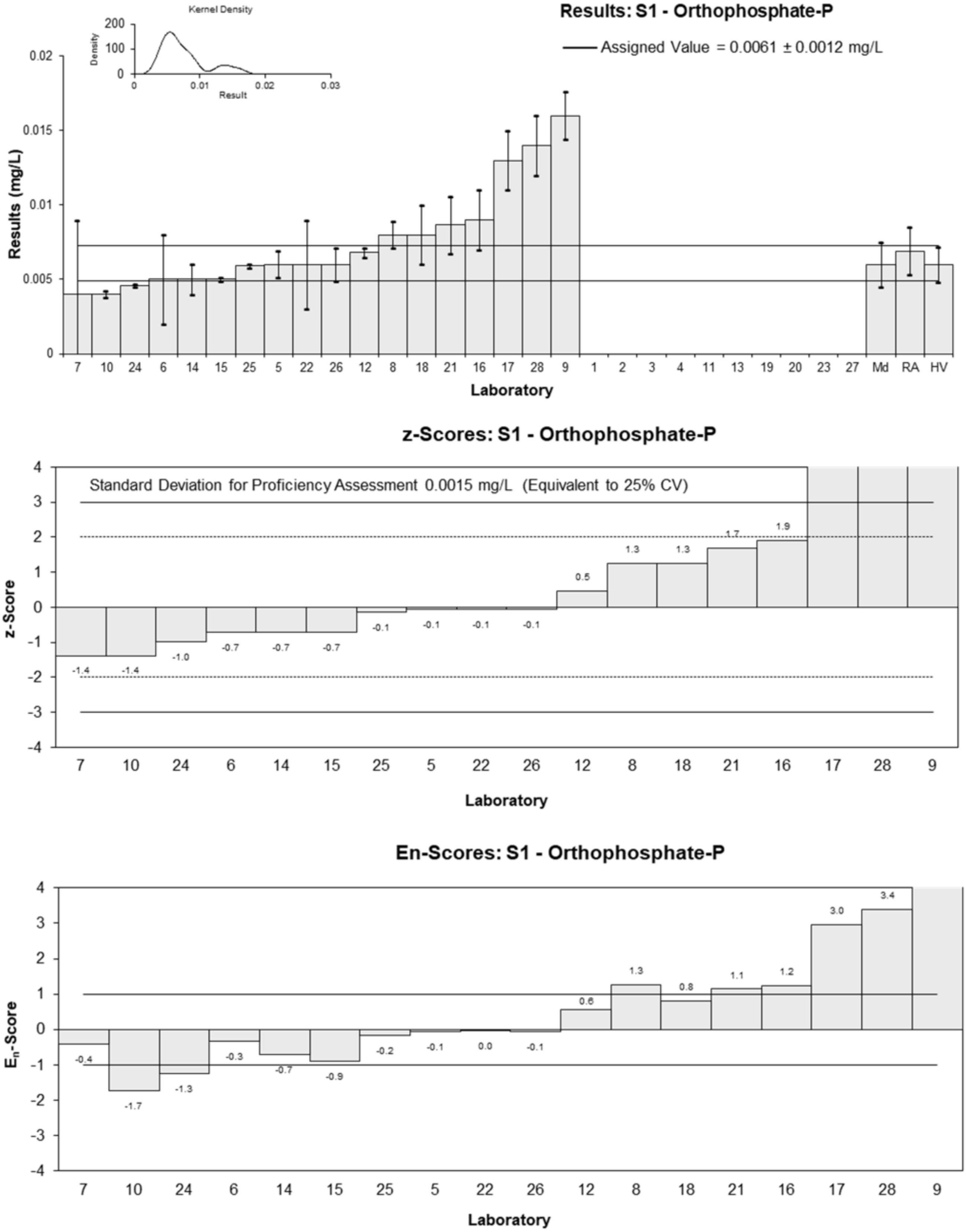

Kernel Density
Density
Result
Results: S1 - Orthophosphate-P
Assigned Value = 0.0061 ± 0.0012 mg/L
Results (mg/L)
Laboratory
7 10 24 6 14 15 25 5 22 26 12 8 18 21 16 17 28 9 1 2 3 4 11 13 19 20 23 27 Md RA HV
z-Scores: S1 - Orthophosphate-P
Standard Deviation for Proficiency Assessment 0.0015 mg/L (Equivalent to 25% CV)
z-Score
-1.4 -1.4 -1.0 -0.7 -0.7 -0.7 -0.1 -0.1 -0.1 -0.1 0.5 1.3 1.3 1.7 1.9
7 10 24 6 14 15 25 5 22 26 12 8 18 21 16 17 28 9
Laboratory
En-Scores: S1 - Orthophosphate-P
E_n-Score
-0.4 -1.7 -1.3 -0.3 -0.7 -0.9 -0.2 -0.1 0.0 -0.1 0.6 1.3 0.8 1.1 1.2 3.0 3.4
7 10 24 6 14 15 25 5 22 26 12 8 18 21 16 17 28 9
Laboratory

Figure 7

Table 10

Sample Details

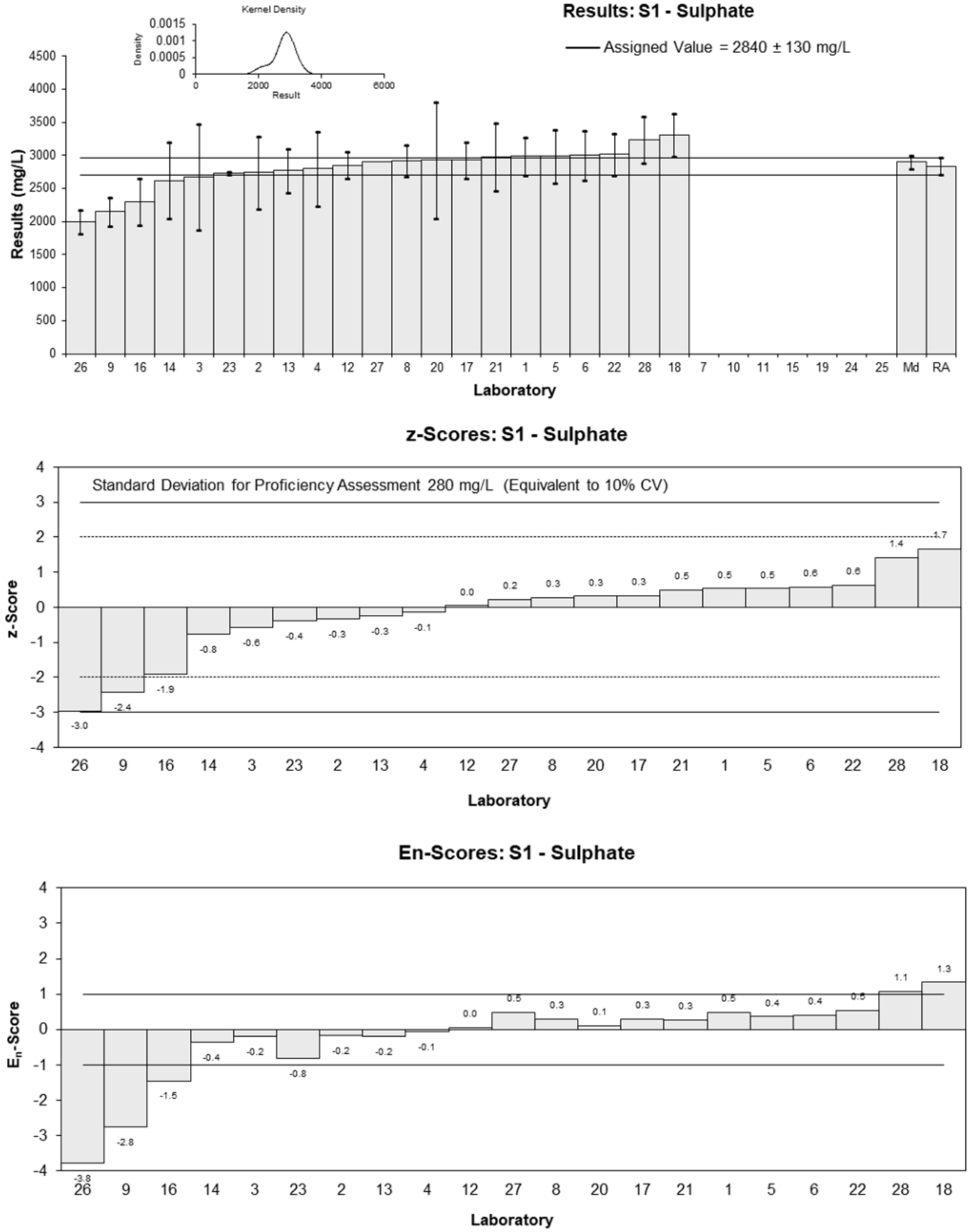
Sample No.	S1
Matrix	Seawater
Analyte	Sulphate
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2990	290	0.53	0.47
2	2744.07	548.81	-0.34	-0.17
3	2676	802.8	-0.58	-0.20
4	2800	560	-0.14	-0.07
5	2990	402	0.53	0.36
6	3000	380	0.56	0.40
7	NR	NR		
8	2920	242.4	0.28	0.29
9	2150	215	-2.43	-2.75
10	NT	NT		
11	NT	NT		
12	2850	200	0.04	0.04
13	2770.35	336.7	-0.25	-0.19
14	2620	576	-0.77	-0.37
15	NT	NT		
16	2300	350	-1.90	-1.45
17	2930	270	0.32	0.30
18	3310	330	1.65	1.33
19	NT	NT		
20	2929	879	0.31	0.10
21	2980	510	0.49	0.27
22	3020	317	0.63	0.53
23	2732	27	-0.38	-0.81
24	NT	NT		
25	NT	NT		
26	2000	180	-2.96	-3.78
27	2902	NR	0.22	0.48
28	3240	350	1.41	1.07

Statistics

Assigned Value	2840	130
Spike Value	Not Spiked	
Robust Average	2840	130
Median	2900	100
Mean	2800	
N	21	
Max	3310	
Min	2000	
Robust SD	240	
Robust CV	8.5%	



Results: S1 - Sulphate
Assigned Value = 2840 ± 130 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
26 9 16 14 3 23 2 13 4 12 27 8 20 17 21 1 5 6 22 28 18 7 10 11 15 19 24 25 Md RA
z-Scores: S1 - Sulphate
Standard Deviation for Proficiency Assessment 280 mg/L (Equivalent to 10% CV)
z-Score
-3.0 -2.4 -1.9 -0.8 -0.6 -0.4 -0.3 -0.3 -0.1 0.0 0.2 0.3 0.3 0.3 0.5 0.5 0.5 0.6 0.6 1.4 1.7
Laboratory
26 9 16 14 3 23 2 13 4 12 27 8 20 17 21 1 5 6 22 28 18
En-Scores: S1 - Sulphate
En-Score
-3.8 -2.8 -1.5 -0.4 -0.2 -0.8 -0.2 -0.2 -0.1 0.0 0.5 0.3 0.1 0.3 0.3 0.5 0.4 0.4 0.5 1.1 1.3
Laboratory
26 9 16 14 3 23 2 13 4 12 27 8 20 17 21 1 5 6 22 28 18

Figure 8

Table 11

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	TDN
Unit	mg/L

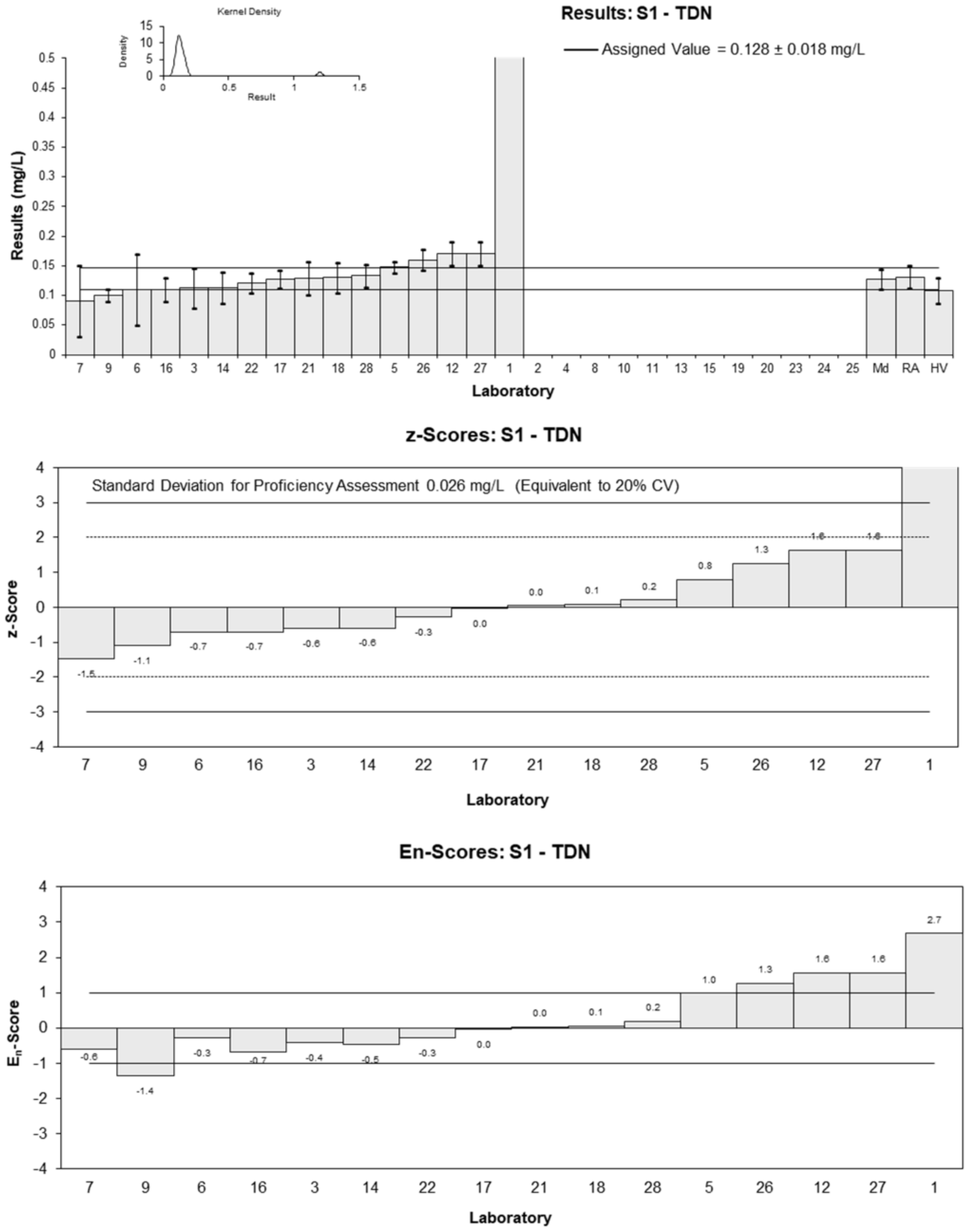
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	1.2	0.4	41.87	2.68
2	NT	NT		
3	0.1123	0.034	-0.61	-0.41
4	NT	NT		
5	0.148	0.0095	0.78	0.98
6	0.11	0.06	-0.70	-0.29
7	0.09	0.06	-1.48	-0.61
8	<0.1	<0.01		
9	0.1	0.01	-1.09	-1.36
10	NT	NT		
11	NT	NT		
12	0.17	0.02	1.64	1.56
13	<0.1	NR		
14	0.113	0.026	-0.59	-0.47
15	NT	NT		
16	0.11	0.02	-0.70	-0.67
17	0.127	0.0155	-0.04	-0.04
18	0.13	0.026	0.08	0.06
19	NT	NT		
20	NT	NT		
21	0.129	0.028	0.04	0.03
22	0.121	0.017	-0.27	-0.28
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	0.16	0.0176	1.25	1.27
27	0.17	0.02	1.64	1.56
28	0.133	0.02	0.20	0.19

* Outlier, see Section 4.2

Statistics

Assigned Value	0.128	0.018
Spike Value	Not Spiked	
Homogeneity Value	0.108	0.022
Robust Average	0.131	0.019
Median	0.128	0.017
Mean	0.20	
N	16	
Max	1.2	
Min	0.09	
Robust SD	0.03	
Robust CV	23%	



Results: S1 - TDN
Assigned Value = 0.128 ± 0.018 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
7 9 6 16 3 14 22 17 21 18 28 5 26 12 27 1 2 4 8 10 11 13 15 19 20 23 24 25 Md RA HV
z-Scores: S1 - TDN
Standard Deviation for Proficiency Assessment 0.026 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
7 9 6 16 3 14 22 17 21 18 28 5 26 12 27 1
En-Scores: S1 - TDN
E_n-Score
Laboratory
7 9 6 16 3 14 22 17 21 18 28 5 26 12 27 1

Figure 9

Table 12

Sample Details

Sample No.	S1
Matrix	Seawater
Analyte	TDP
Unit	mg/L

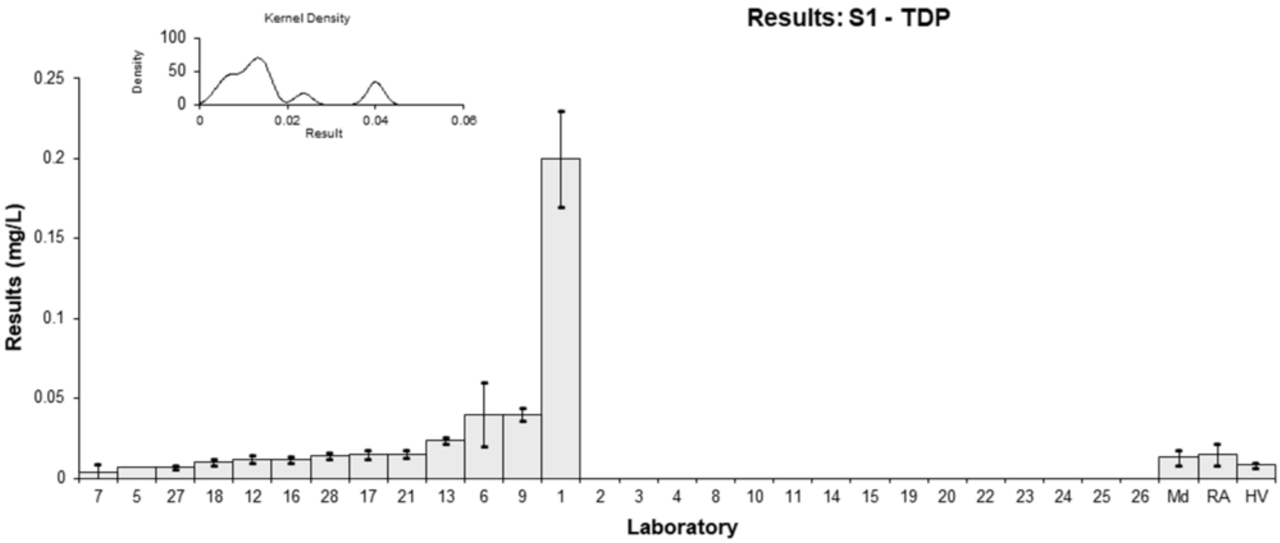
Participant Results

Lab. Code	Result	Uncertainty
1**	0.20	0.03
2	<0.5	NT
3	< 0.05	NR
4	NT	NT
5	0.007	NR
6	0.04	0.02
7	0.004	0.005
8	<0.005	<0.0006
9	0.04	0.004
10	NT	NT
11	NT	NT
12	0.012	0.0025
13	0.0236	0.0021
14	NR	NR
15	NT	NT
16	0.012	0.002
17	0.015	0.003
18	0.01	0.002
19	NT	NT
20	< 0.1	NR
21	0.0152	0.0026
22	<0.005	NR
23	NT	NT
24	NT	NT
25	NT	NT
26	<0.01	NR
27	0.007	0.001
28	0.014	0.002

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Homogeneity Value	0.0083	0.0017
Robust Average	0.0148	0.0067
Median	0.0130	0.0048
Mean	0.0167	
N	12	
Max	0.04	
Min	0.004	
Robust SD	0.0093	
Robust CV	63%	



Results: S1 - TDP
Kernel Density
Density
100
50
0
0
0.02
0.04
0.06
Result
Results (mg/L)
0.25
0.2
0.15
0.1
0.05
0
7
5
27
18
12
16
28
17
21
13
6
9
1
2
3
4
8
10
11
14
15
19
20
22
23
24
25
26
Md
RA
HV
Laboratory

Figure 10

Table 13

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	B
Unit	mg/L

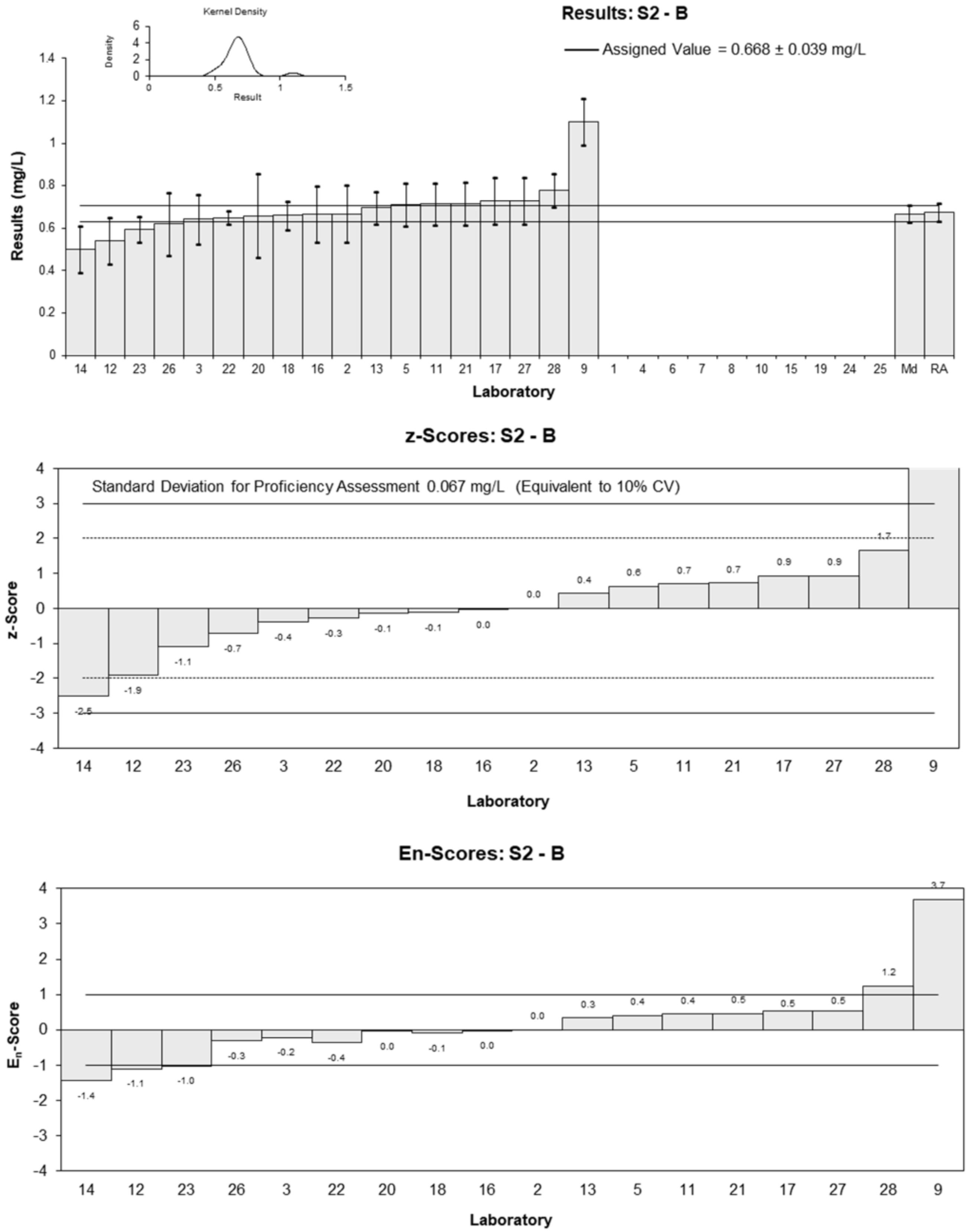
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.668	0.134	0.00	0.00
3	0.642	0.118	-0.39	-0.21
4	NT	NT		
5	0.71	0.10	0.63	0.39
6	NT	NT		
7	NR	NR		
8	NT	NT		
9*	1.1	0.11	6.47	3.70
10	NT	NT		
11	0.714	0.098	0.69	0.44
12	0.54	0.11	-1.92	-1.10
13	0.696	0.076	0.42	0.33
14	0.50	0.11	-2.51	-1.44
15	NT	NT		
16	0.665	0.133	-0.04	-0.02
17	0.73	0.11	0.93	0.53
18	0.66	0.066	-0.12	-0.10
19	NT	NT		
20	0.659	0.198	-0.13	-0.04
21	0.716	0.100	0.72	0.45
22	0.65	0.03	-0.27	-0.37
23	0.595	0.06	-1.09	-1.02
24	NT	NT		
25	NT	NT		
26	0.62	0.1488	-0.72	-0.31
27	0.73	0.11	0.93	0.53
28	0.778	0.08	1.65	1.24

* Outlier, see Section 4.2

Statistics

Assigned Value	0.668	0.039
Spike Value	Not Spiked	
Robust Average	0.675	0.042
Median	0.667	0.041
Mean	0.687	
N	18	
Max	1.1	
Min	0.5	
Robust SD	0.072	
Robust CV	11%	



Kernel Density
Density
Result
Results: S2 - B
Assigned Value = 0.668 ± 0.039 mg/L
Results (mg/L)
14 12 23 26 3 22 20 18 16 2 13 5 11 21 17 27 28 9 1 4 6 7 8 10 15 19 24 25 Md RA
Laboratory
z-Scores: S2 - B
Standard Deviation for Proficiency Assessment 0.067 mg/L (Equivalent to 10% CV)
z-Score
-2.5 -1.9 -1.1 -0.7 -0.4 -0.3 -0.1 -0.1 0.0 0.0 0.4 0.6 0.7 0.7 0.9 0.9 1.7
14 12 23 26 3 22 20 18 16 2 13 5 11 21 17 27 28 9
Laboratory
En-Scores: S2 - B
E_n-Score
-1.4 -1.1 -1.0 -0.3 -0.2 -0.4 0.0 -0.1 0.0 0.0 0.3 0.4 0.4 0.5 0.5 0.5 1.2 3.7
14 12 23 26 3 22 20 18 16 2 13 5 11 21 17 27 28 9
Laboratory

Figure 11

Table 14

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Ca
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	21.5	3.23	1.26	0.67
3	21.81	3.83	1.42	0.65
4	NT	NT		
5	20	2.1	0.47	0.34
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	15	1.5	-2.15	-1.87
10	NT	NT		
11	17.7	1.2	-0.73	-0.70
12	17	2.8	-1.10	-0.65
13	17.12	1.66	-1.04	-0.86
14	17.30	3.63	-0.94	-0.45
15	NT	NT		
16	21.3	4.3	1.15	0.48
17	23	2.4	2.04	1.35
18	23	2.3	2.04	1.39
19*	6.65	0.35	-6.52	-7.60
20	18.83	5.65	-0.14	-0.05
21	19.9	2.8	0.42	0.25
22	17	1	-1.10	-1.11
23	19	3	-0.05	-0.03
24	NT	NT		
25	NT	NT		
26	17	3.91	-1.10	-0.50
27	20.9	3.4	0.94	0.48
28	16.1	1.6	-1.57	-1.33

* Outlier, see Section 4.2

Statistics

Assigned Value	19.1	1.6
Spike Value	Not Spiked	
Robust Average	18.8	1.7
Median	18.8	1.6
Mean	18.4	
N	19	
Max	23	
Min	6.65	
Robust SD	3.0	
Robust CV	16%	

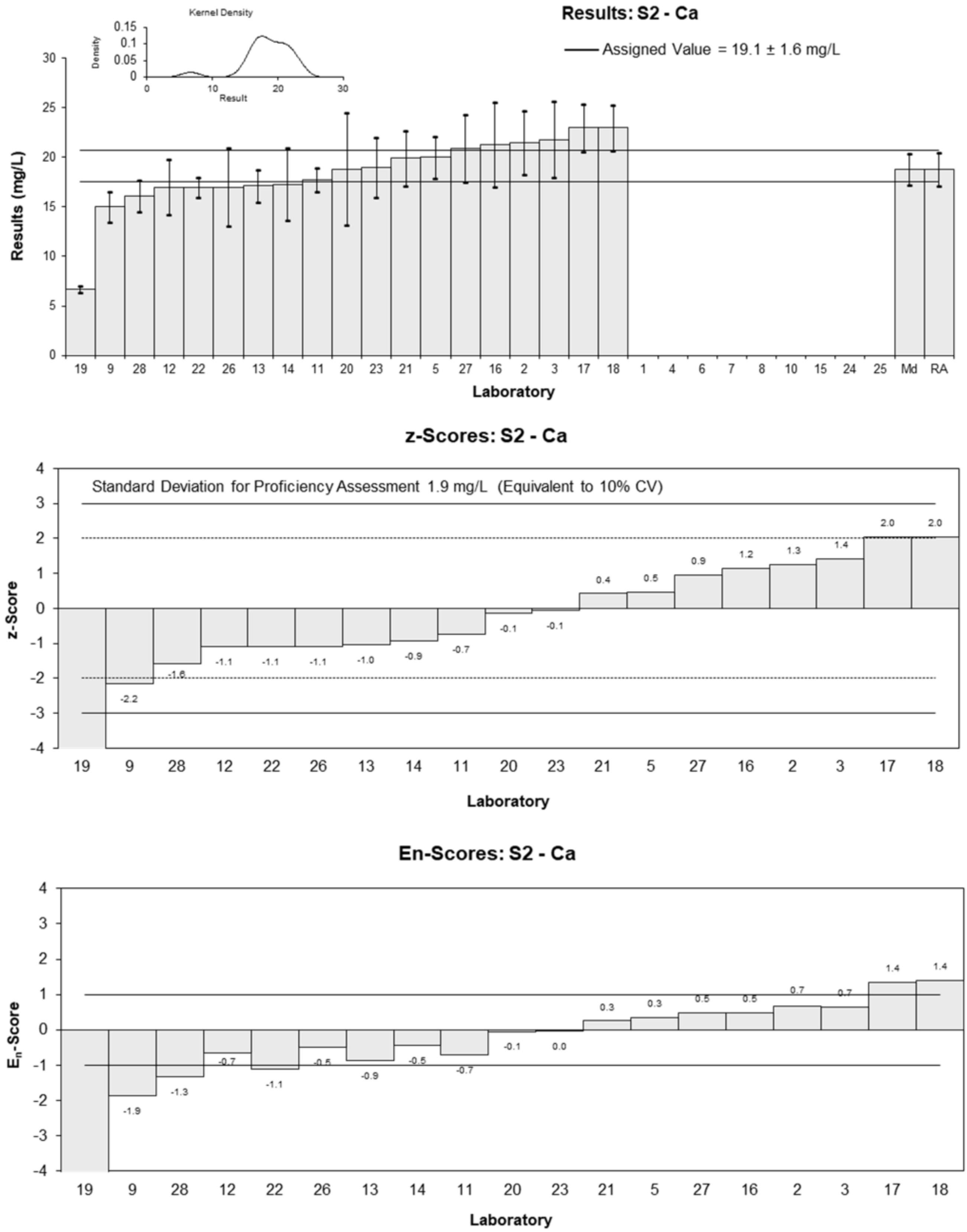

Results: S2 - Ca
Assigned Value = 19.1 ± 1.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
19 9 28 12 22 26 13 14 11 20 23 21 5 27 16 2 3 17 18 1 4 6 7 8 10 15 24 25 Md RA
z-Scores: S2 - Ca
Standard Deviation for Proficiency Assessment 1.9 mg/L (Equivalent to 10% CV)
z-Score
-2.2 -1.6 -1.1 -1.1 -1.1 -1.0 -0.9 -0.7 -0.1 -0.1 0.4 0.5 0.9 1.2 1.3 1.4 2.0 2.0
19 9 28 12 22 26 13 14 11 20 23 21 5 27 16 2 3 17 18
Laboratory
En-Scores: S2 - Ca
En-Score
-1.9 -1.3 -0.7 -1.1 -0.5 -0.9 -0.5 -0.7 -0.1 0.0 0.3 0.3 0.5 0.5 0.7 0.7 1.4 1.4
19 9 28 12 22 26 13 14 11 20 23 21 5 27 16 2 3 17 18
Laboratory

Figure 12

Table 15

Sample Details

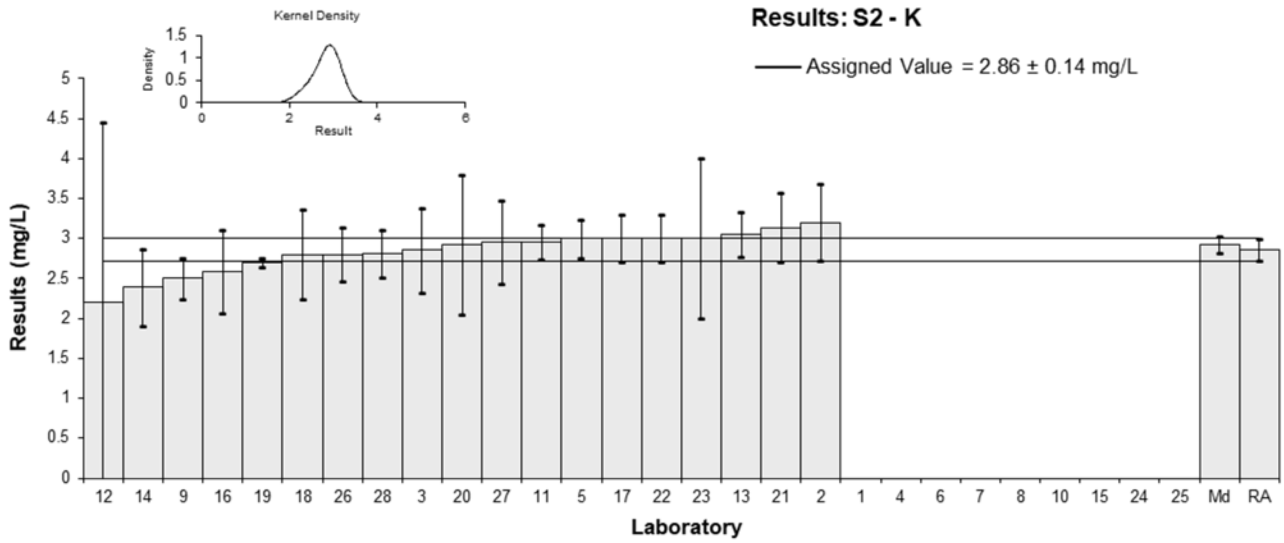
Sample No.	S2
Matrix	River Water
Analyte	K
Unit	mg/L

Participant Results

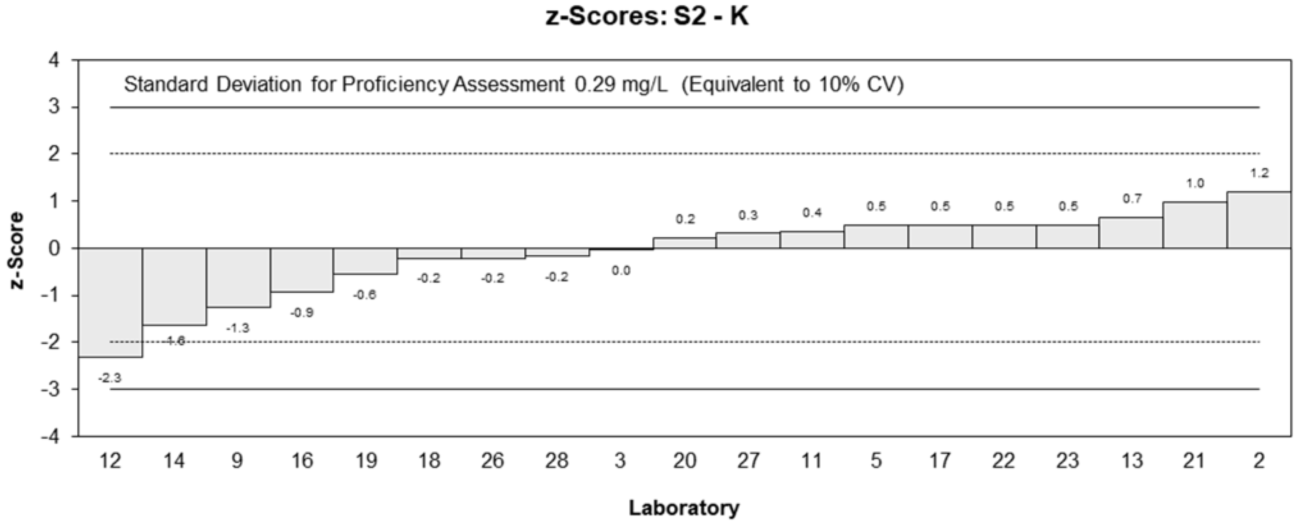
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	3.2	0.48	1.19	0.68
3	2.852	0.535	-0.03	-0.01
4	NT	NT		
5	3	0.24	0.49	0.50
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	2.5	0.25	-1.26	-1.26
10	NT	NT		
11	2.96	0.22	0.35	0.38
12	2.2	2.25	-2.31	-0.29
13	3.05	0.28	0.66	0.61
14	2.39	0.48	-1.64	-0.94
15	NT	NT		
16	2.59	0.52	-0.94	-0.50
17	3	0.3	0.49	0.42
18	2.8	0.56	-0.21	-0.10
19	2.70	0.05	-0.56	-1.08
20	2.92	0.876	0.21	0.07
21	3.14	0.44	0.98	0.61
22	3	0.3	0.49	0.42
23	3	1	0.49	0.14
24	NT	NT		
25	NT	NT		
26	2.8	0.336	-0.21	-0.16
27	2.95	0.52	0.31	0.17
28	2.81	0.3	-0.17	-0.15

Statistics

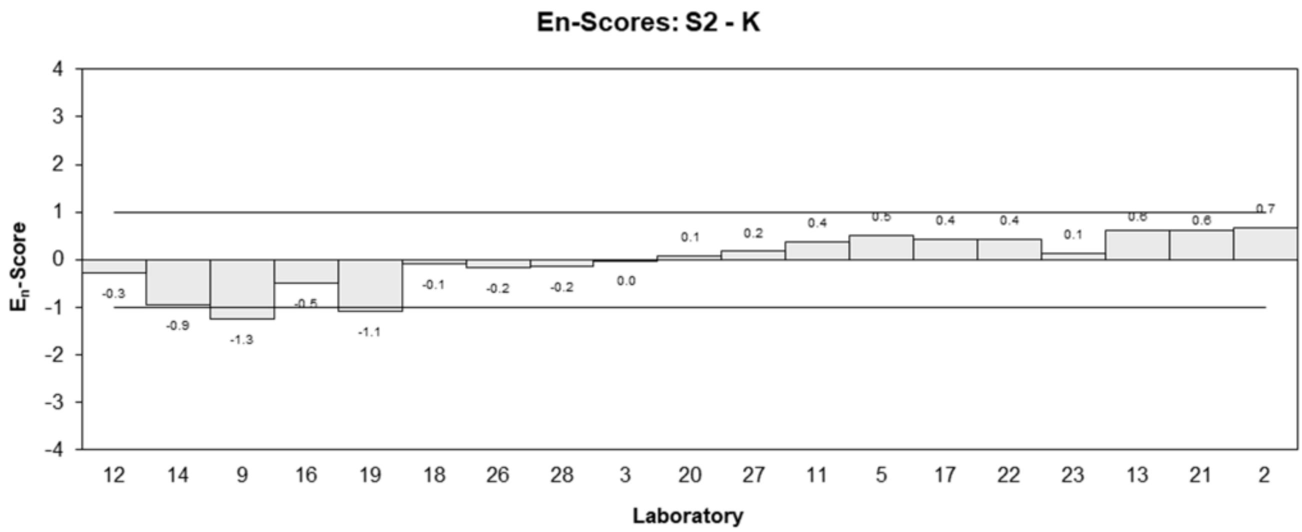
Assigned Value	2.86	0.14
Spike Value	Not Spiked	
Robust Average	2.86	0.14
Median	2.92	0.10
Mean	2.83	
N	19	
Max	3.2	
Min	2.2	
Robust SD	0.25	
Robust CV	8.6%	



Results: S2 - K
Assigned Value = 2.86 ± 0.14 mg/L
Kernel Density
Results (mg/L)
Laboratory



z-Scores: S2 - K
Standard Deviation for Proficiency Assessment 0.29 mg/L (Equivalent to 10% CV)
z-Score
Laboratory



En-Scores: S2 - K
En-Score
Laboratory

Figure 13

Table 16

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Mg
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	8.29	1.24	1.73	0.94
3	7.260	1.291	0.27	0.14
4	NT	NT		
5	7	0.56	-0.10	-0.10
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	6.4	0.64	-0.95	-0.89
10	NT	NT		
11	7.24	0.49	0.24	0.27
12	6.0	1.30	-1.51	-0.79
13	6.78	0.59	-0.41	-0.41
14	6.19	1.18	-1.24	-0.71
15	NT	NT		
16	7.14	1.43	0.10	0.05
17	8	0.7	1.32	1.16
18	7.8	0.78	1.03	0.84
19	7.73	0.10	0.93	1.64
20	7.10	2.13	0.04	0.01
21	7.38	1.03	0.44	0.28
22	6	0.4	-1.51	-1.92
23	7	1	-0.10	-0.07
24	NT	NT		
25	NT	NT		
26	6.9	1.311	-0.24	-0.12
27	7.26	0.99	0.27	0.18
28	6.94	0.7	-0.18	-0.16

Statistics

Assigned Value	7.07	0.39
Spike Value	Not Spiked	
Robust Average	7.07	0.39
Median	7.10	0.24
Mean	7.07	
N	19	
Max	8.29	
Min	6	
Robust SD	0.68	
Robust CV	9.7%	

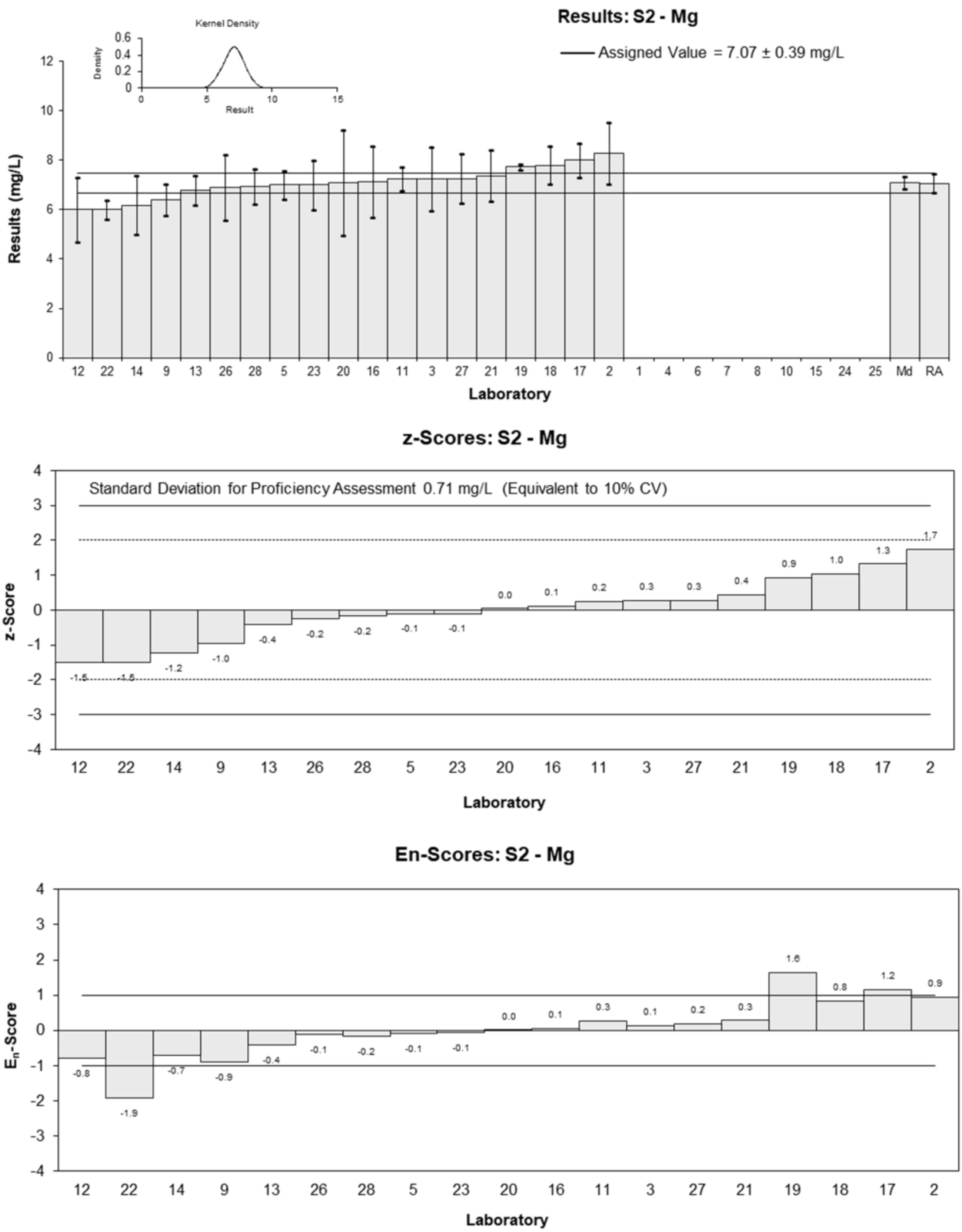

Results: S2 - Mg
Assigned Value = 7.07 ± 0.39 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
z-Scores: S2 - Mg
Standard Deviation for Proficiency Assessment 0.71 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S2 - Mg
E_n-Score
Laboratory

Figure 14

Table 17

Sample Details

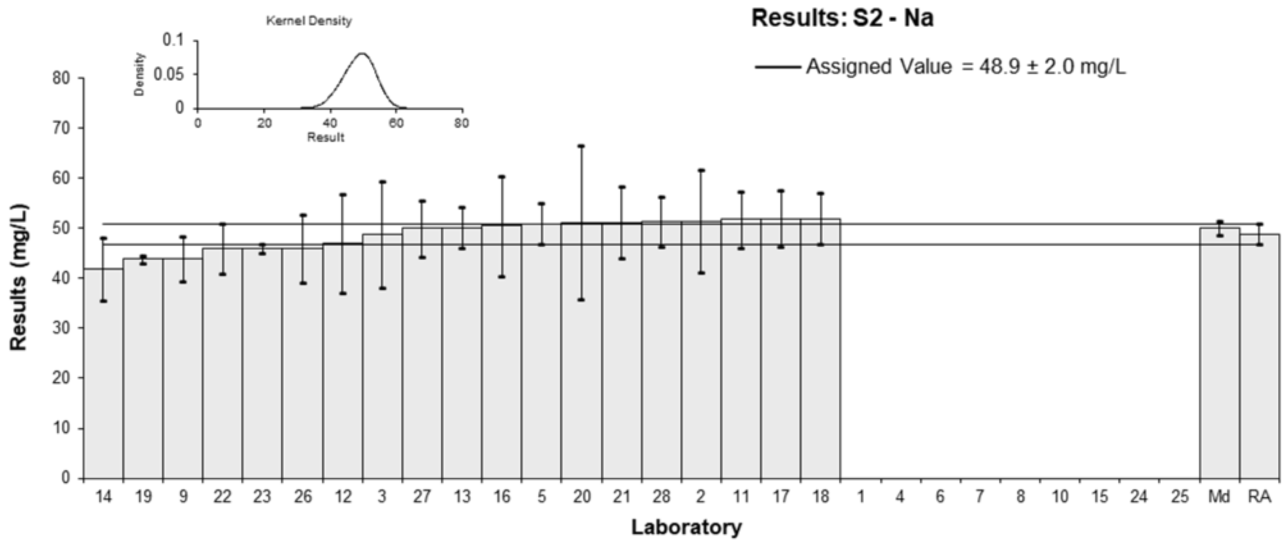
Sample No.	S2
Matrix	River Water
Analyte	Na
Unit	mg/L

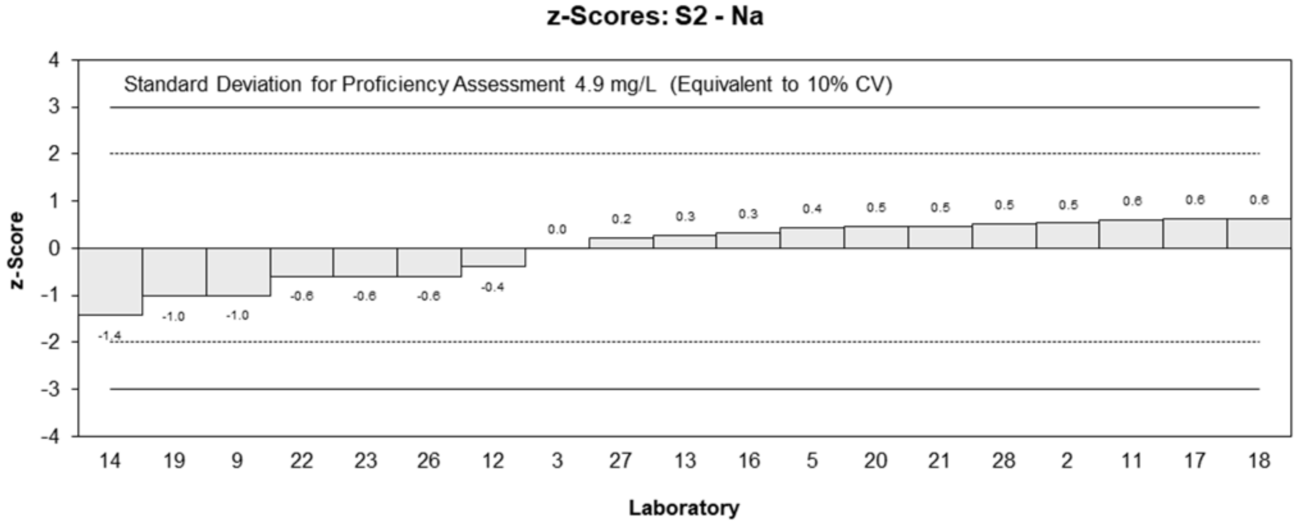
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	51.5	10.3	0.53	0.25
3	48.91	10.67	0.00	0.00
4	NT	NT		
5	51	4.0	0.43	0.47
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	44	4.4	-1.00	-1.01
10	NT	NT		
11	51.8	5.6	0.59	0.49
12	47	9.8	-0.39	-0.19
13	50.19	4.07	0.26	0.28
14	41.9	6.3	-1.43	-1.06
15	NT	NT		
16	50.5	10.1	0.33	0.16
17	52	5.7	0.63	0.51
18	52	5.2	0.63	0.56
19	43.93	0.80	-1.02	-2.31
20	51.2	15.36	0.47	0.15
21	51.2	7.2	0.47	0.31
22	46	5	-0.59	-0.54
23	46	1	-0.59	-1.30
24	NT	NT		
25	NT	NT		
26	46	6.9	-0.59	-0.40
27	50.0	5.6	0.22	0.18
28	51.4	5.1	0.51	0.46

Statistics

Assigned Value	48.9	2.0
Spike Value	Not Spiked	
Robust Average	48.9	2.0
Median	50.2	1.4
Mean	48.8	
N	19	
Max	52	
Min	41.9	
Robust SD	3.4	
Robust CV	7%	


Results: S2 - Na
Assigned Value = 48.9 ± 2.0 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
14 19 9 22 23 26 12 3 27 13 16 5 20 21 28 2 11 17 18 1 4 6 7 8 10 15 24 25 Md RA


z-Scores: S2 - Na
Standard Deviation for Proficiency Assessment 4.9 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
14 19 9 22 23 26 12 3 27 13 16 5 20 21 28 2 11 17 18

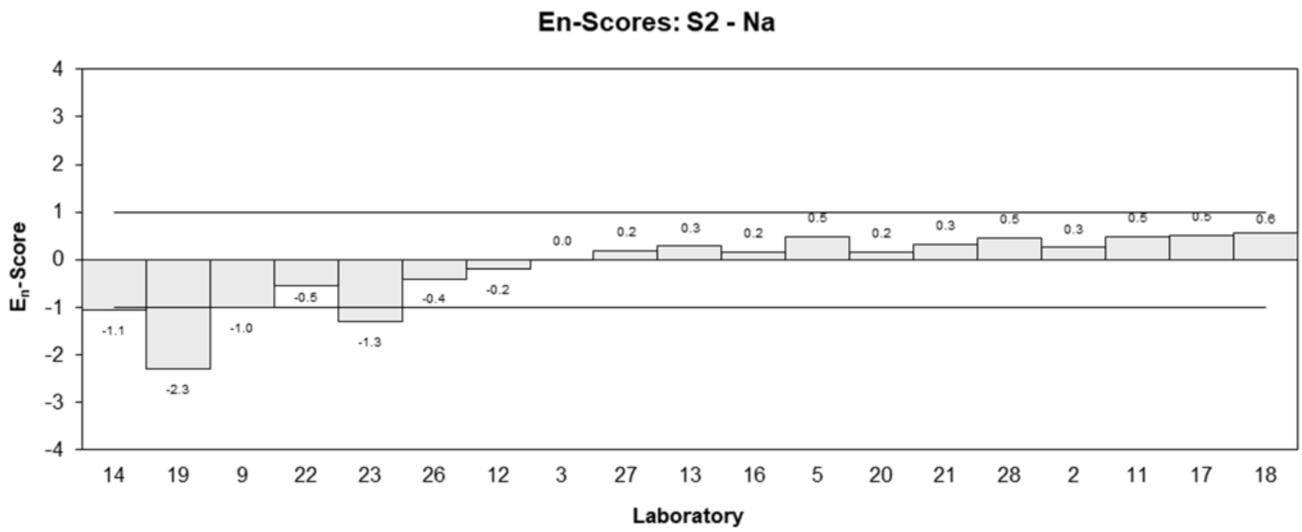

En-Scores: S2 - Na
En-Score
Laboratory
14 19 9 22 23 26 12 3 27 13 16 5 20 21 28 2 11 17 18

Figure 15

Table 18

Sample Details

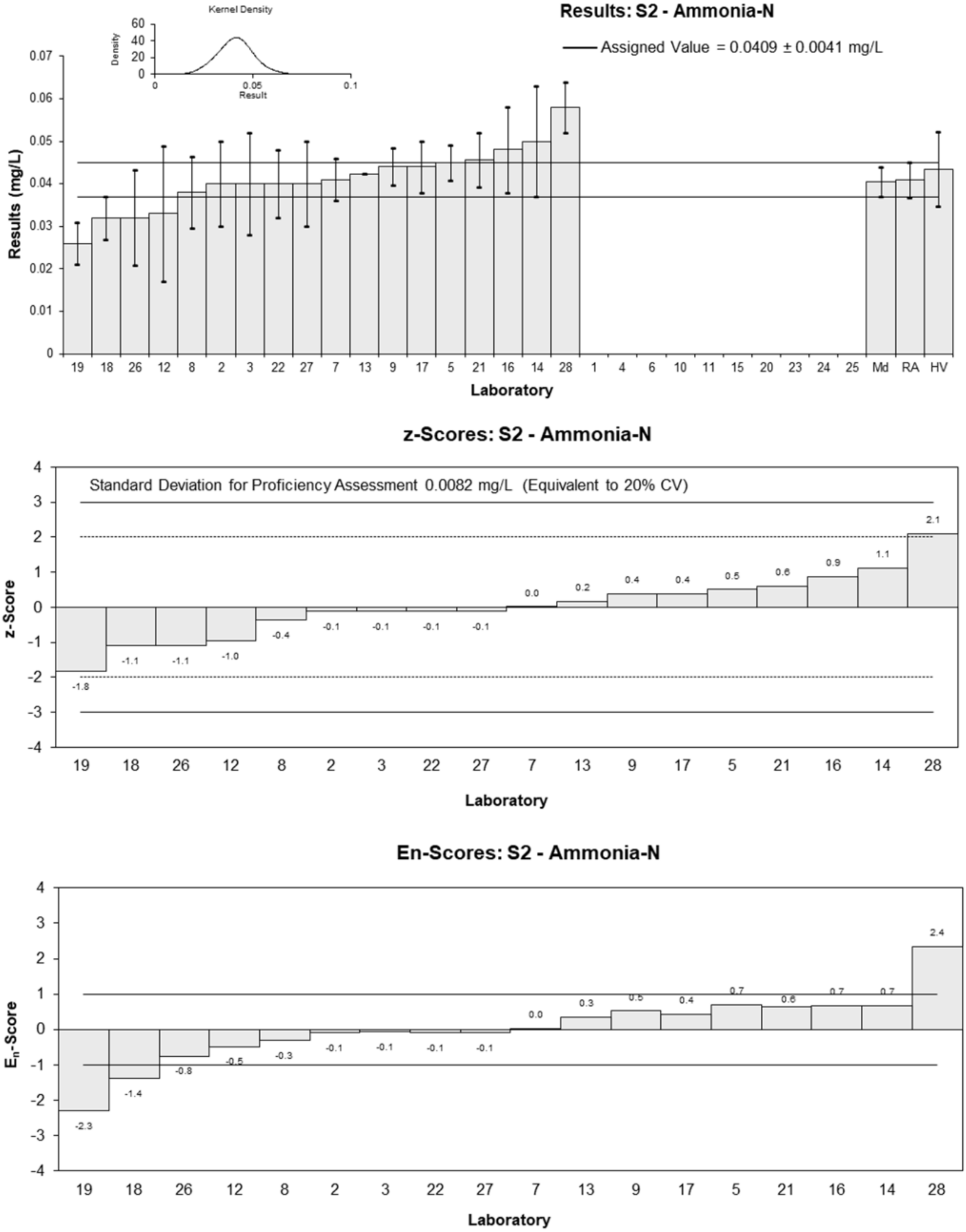
Sample No.	S2
Matrix	River Water
Analyte	Ammonia-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<0.01	NR		
2	0.04	0.01	-0.11	-0.08
3	0.04	0.012	-0.11	-0.07
4	NT	NT		
5	0.045	0.0042	0.50	0.70
6	NT	NT		
7	0.041	0.005	0.01	0.02
8	0.038	0.0084	-0.35	-0.31
9	0.044	0.0044	0.38	0.52
10	NT	NT		
11	NT	NT		
12	0.033	0.016	-0.97	-0.48
13	0.0423	0.0	0.17	0.34
14	0.050	0.013	1.11	0.67
15	NT	NT		
16	0.048	0.01	0.87	0.66
17	0.044	0.006	0.38	0.43
18	0.032	0.005	-1.09	-1.38
19	0.026	0.005	-1.82	-2.30
20	< 0.1	NR		
21	0.0457	0.0064	0.59	0.63
22	0.040	0.008	-0.11	-0.10
23	<0.2	1.1		
24	NT	NT		
25	NT	NT		
26	0.032	0.0112	-1.09	-0.75
27	0.04	0.01	-0.11	-0.08
28	0.058	0.006	2.09	2.35

Statistics

Assigned Value	0.0409	0.0041
Spike Value	Not Spiked	
Homogeneity Value	0.0435	0.0087
Robust Average	0.0409	0.0041
Median	0.0405	0.0035
Mean	0.0411	
N	18	
Max	0.058	
Min	0.026	
Robust SD	0.007	
Robust CV	17%	



Kernel Density
Density
Result
Results: S2 - Ammonia-N
Assigned Value = 0.0409 ± 0.0041 mg/L
Results (mg/L)
19 18 26 12 8 2 3 22 27 7 13 9 17 5 21 16 14 28 1 4 6 10 11 15 20 23 24 25 Md RA HV
Laboratory
z-Scores: S2 - Ammonia-N
Standard Deviation for Proficiency Assessment 0.0082 mg/L (Equivalent to 20% CV)
z-Score
-1.8 -1.1 -1.1 -1.0 -0.4 -0.1 -0.1 -0.1 -0.1 0.0 0.2 0.4 0.4 0.5 0.6 0.9 1.1 2.1
19 18 26 12 8 2 3 22 27 7 13 9 17 5 21 16 14 28
Laboratory
En-Scores: S2 - Ammonia-N
En-Score
-2.3 -1.4 -0.8 -0.5 -0.3 -0.1 -0.1 -0.1 -0.1 0.0 0.3 0.5 0.4 0.7 0.6 0.7 0.7 2.4
19 18 26 12 8 2 3 22 27 7 13 9 17 5 21 16 14 28
Laboratory

Figure 16

Table 19

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Bromide
Unit	mg/L

Participant Results

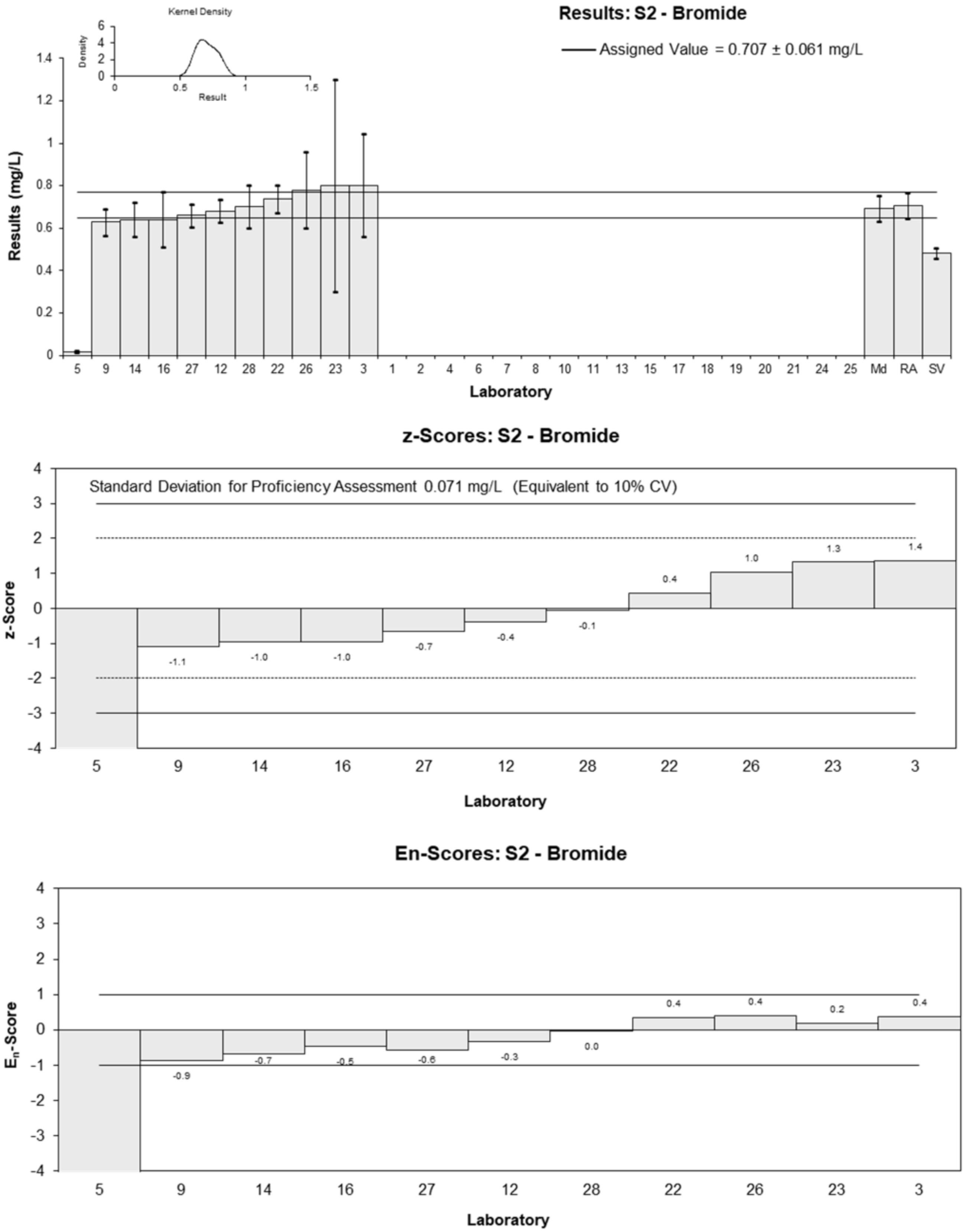
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	0.8023	0.241	1.35	0.38
4	NT	NT		
5**	0.018	0.003	-9.75	-11.28
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	0.63	0.063	-1.09	-0.88
10	NT	NT		
11	NT	NT		
12	0.68	0.054	-0.38	-0.33
13	NT	NT		
14	0.64	0.08	-0.95	-0.67
15	NT	NT		
16	0.64	0.13	-0.95	-0.47
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	< 1	NR		
21	NT	NT		
22	0.738	0.063	0.44	0.35
23	0.8	0.5	1.32	0.18
24	NT	NT		
25	NT	NT		
26	0.78	0.1794	1.03	0.39
27	0.66	0.055	-0.66	-0.57
28	0.703	0.1	-0.06	-0.03

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.707	0.061
Spike Value*	0.482	0.024
Robust Average	0.707	0.061
Median	0.692	0.060
Mean	0.707	
N	10	
Max	0.8023	
Min	0.63	
Robust SD	0.077	
Robust CV	11%	

*Incurred value not included.



Results: S2 - Bromide
Assigned Value = 0.707 ± 0.061 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5 9 14 16 27 12 28 22 26 23 3 1 2 4 6 7 8 10 11 13 15 17 18 19 20 21 24 25 Md RA SV
z-Scores: S2 - Bromide
Standard Deviation for Proficiency Assessment 0.071 mg/L (Equivalent to 10% CV)
z-Score
-1.1 -1.0 -1.0 -0.7 -0.4 -0.1 0.4 1.0 1.3 1.4
Laboratory
5 9 14 16 27 12 28 22 26 23 3
En-Scores: S2 - Bromide
En-Score
-0.9 -0.7 -0.5 -0.6 -0.3 0.0 0.4 0.4 0.2 0.4
Laboratory
5 9 14 16 27 12 28 22 26 23 3

Figure 17

Table 20

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Chloride
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	78	4	-0.92	-1.33
2	89.12	22.28	0.37	0.14
3	93.42	28.03	0.88	0.27
4	NT	NT		
5*	21.9	1.74	-7.45	-13.53
6	NT	NT		
7	NR	NR		
8	75	2.8	-1.27	-2.09
9	75	7.5	-1.27	-1.25
10	NT	NT		
11	NT	NT		
12	85	4.2	-0.10	-0.15
13	84.89	7.7	-0.12	-0.11
14	54	8	-3.71	-3.49
15	NT	NT		
16	87	17	0.13	0.06
17	89	12	0.36	0.24
18*	130	19.5	5.13	2.21
19	94.97	1.5	1.06	1.95
20	93	28	0.83	0.25
21	87.2	10.5	0.15	0.11
22	88	8	0.24	0.23
23	85	0.3	-0.10	-0.20
24	NT	NT		
25	NT	NT		
26	95	9.5	1.06	0.87
27	89	6.43	0.36	0.40
28	82.3	8.5	-0.42	-0.38

* Outlier, see Section 4.2

Statistics

Assigned Value	85.9	4.4
Spike Value	Not Spiked	
Robust Average	85.7	4.9
Median	87.1	4.4
Mean	83.8	
N	20	
Max	130	
Min	21.9	
Robust SD	8.8	
Robust CV	10%	

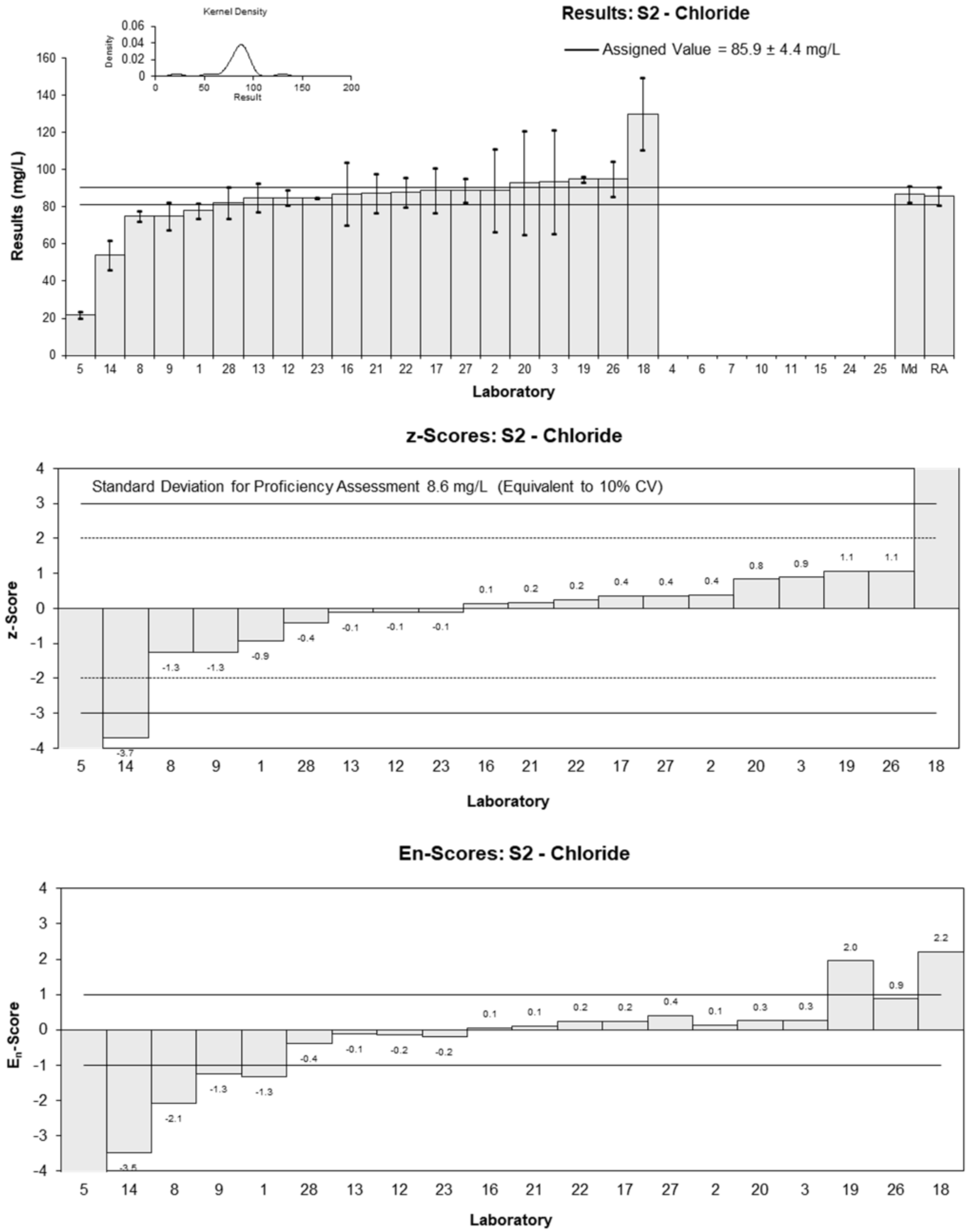

Results: S2 - Chloride
Assigned Value = 85.9 ± 4.4 mg/L
Kernel Density
Density
Result
Results (mg/L)
5 14 8 9 1 28 13 12 23 16 21 22 17 27 2 20 3 19 26 18 4 6 7 10 11 15 24 25 Md RA
Laboratory
z-Scores: S2 - Chloride
Standard Deviation for Proficiency Assessment 8.6 mg/L (Equivalent to 10% CV)
z-Score
-3.7 -1.3 -1.3 -0.9 -0.4 -0.1 -0.1 -0.1 0.1 0.2 0.2 0.4 0.4 0.4 0.8 0.9 1.1 1.1
5 14 8 9 1 28 13 12 23 16 21 22 17 27 2 20 3 19 26 18
Laboratory
En-Scores: S2 - Chloride
En-Score
-3.5 -2.1 -1.3 -1.3 -0.4 -0.1 -0.2 -0.2 0.1 0.1 0.2 0.2 0.4 0.1 0.3 0.3 2.0 0.9 2.2
5 14 8 9 1 28 13 12 23 16 21 22 17 27 2 20 3 19 26 18
Laboratory

Figure 18

Table 21

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	DOC
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	<5	NT		
3	< 5	NR		
4	NT	NT		
5	4	0.568	-0.73	-0.77
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	4.4	0.44	-0.13	-0.17
10	NT	NT		
11	4.21	0.86	-0.42	-0.31
12	5.1	0.25	0.91	1.59
13	3.72	1.92	-1.14	-0.40
14	4.6	0.8	0.16	0.13
15	NT	NT		
16	4.4	0.9	-0.13	-0.10
17	5	0.92	0.76	0.53
18	4.5	0.45	0.01	0.02
19	NT	NT		
20	NT	NT		
21	4.64	0.70	0.22	0.20
22	4.2	0.4	-0.43	-0.59
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	4.8	0.912	0.46	0.32
27	NR	NR		
28	4.65	0.5	0.24	0.28

Statistics

Assigned Value	4.49	0.29
Spike Value	Not Spiked	
Robust Average	4.49	0.29
Median	4.50	0.30
Mean	4.48	
N	13	
Max	5.1	
Min	3.72	
Robust SD	0.41	
Robust CV	9.2%	

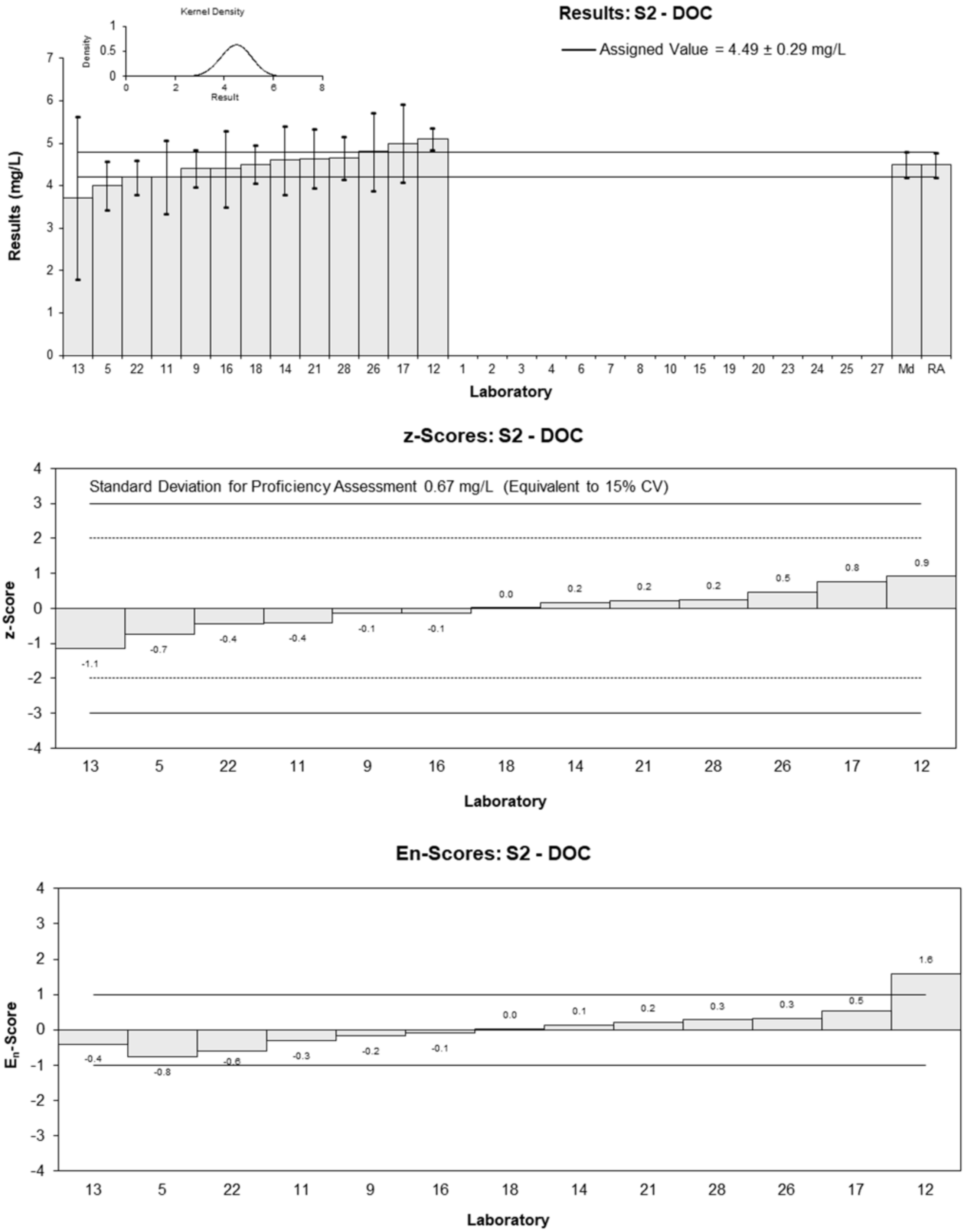

Results: S2 - DOC
Assigned Value = 4.49 ± 0.29 mg/L
Kernel Density
Density
Result
Results (mg/L)
13 5 22 11 9 16 18 14 21 28 26 17 12 1 2 3 4 6 7 8 10 15 19 20 23 24 25 27 Md RA
Laboratory
z-Scores: S2 - DOC
Standard Deviation for Proficiency Assessment 0.67 mg/L (Equivalent to 15% CV)
z-Score
-1.1 -0.7 -0.4 -0.4 -0.1 -0.1 0.0 0.2 0.2 0.2 0.5 0.8 0.9
13 5 22 11 9 16 18 14 21 28 26 17 12
Laboratory
En-Scores: S2 - DOC
En-Score
-0.4 -0.8 -0.6 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.3 0.3 0.5 1.6
13 5 22 11 9 16 18 14 21 28 26 17 12
Laboratory

Figure 19

Table 22

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Nitrate-N + Nitrite-N
Unit	mg/L

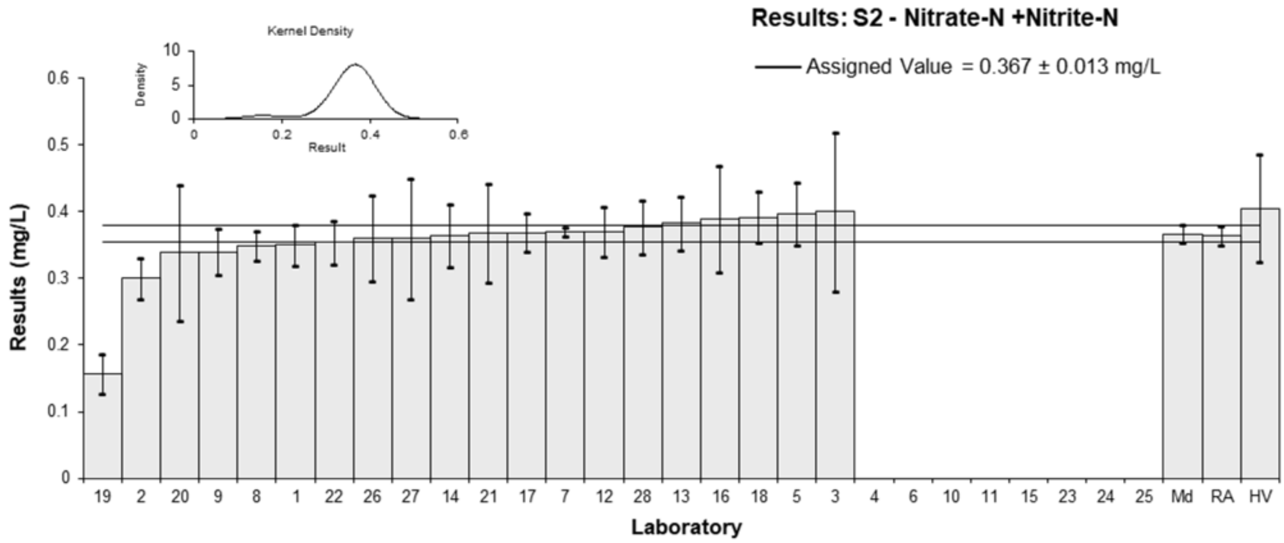
Participant Results

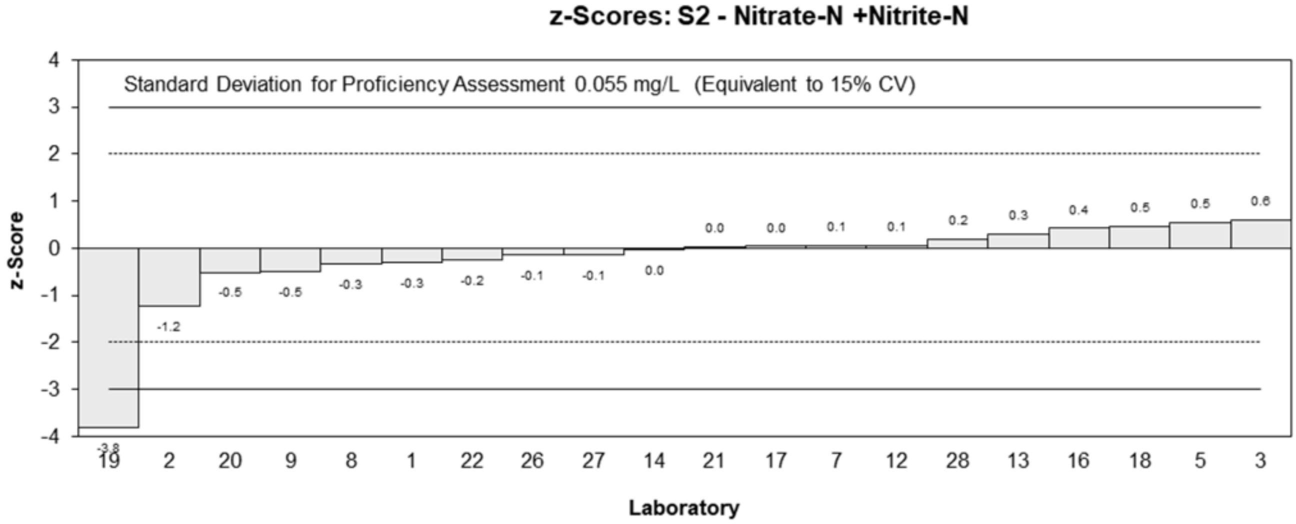
Lab. Code	Result	Uncertainty	z	E_n
1	0.35	0.03	-0.31	-0.52
2	0.3	0.03	-1.22	-2.05
3	0.40	0.12	0.60	0.27
4	NT	NT		
5	0.397	0.048	0.54	0.60
6	NT	NT		
7	0.37	0.007	0.05	0.20
8	0.349	0.0227	-0.33	-0.69
9	0.34	0.034	-0.49	-0.74
10	NT	NT		
11	NT	NT		
12	0.37	0.037	0.05	0.08
13	0.3827	0.0397	0.29	0.38
14	0.365	0.047	-0.04	-0.04
15	NT	NT		
16	0.39	0.08	0.42	0.28
17	0.369	0.029	0.04	0.06
18	0.392	0.039	0.45	0.61
19*	0.157	0.030	-3.81	-6.42
20	0.339	0.102	-0.51	-0.27
21	0.368	0.074	0.02	0.01
22	0.354	0.032	-0.24	-0.38
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	0.36	0.0648	-0.13	-0.11
27	0.36	0.09	-0.13	-0.08
28	0.377	0.04	0.18	0.24

* Outlier, see Section 4.2

Statistics

Assigned Value	0.367	0.013
Spike Value	Not Spiked	
Homogeneity Value	0.405	0.081
Robust Average	0.364	0.014
Median	0.367	0.014
Mean	0.354	
N	20	
Max	0.4	
Min	0.157	
Robust SD	0.024	
Robust CV	6.7%	


Results: S2 - Nitrate-N +Nitrite-N
Assigned Value = 0.367 ± 0.013 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
19 2 20 9 8 1 22 26 27 14 21 17 7 12 28 13 16 18 5 3 4 6 10 11 15 23 24 25 Md RA HV


z-Scores: S2 - Nitrate-N +Nitrite-N
Standard Deviation for Proficiency Assessment 0.055 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
-3.8 -1.2 -0.5 -0.5 -0.3 -0.3 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.1 0.1 0.2 0.3 0.4 0.5 0.5 0.6
19 2 20 9 8 1 22 26 27 14 21 17 7 12 28 13 16 18 5 3

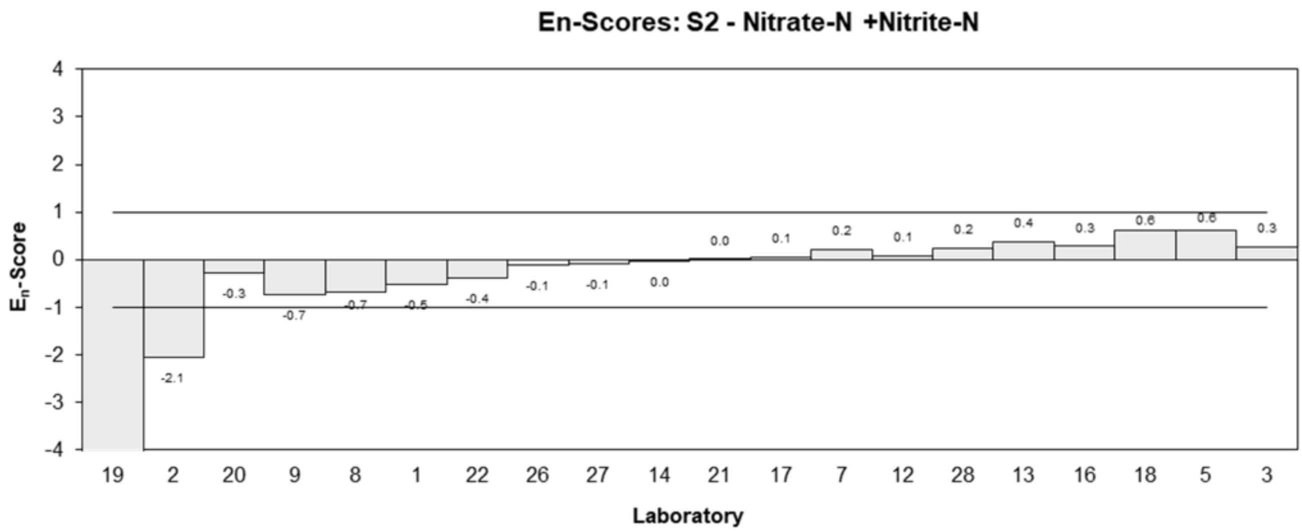

En-Scores: S2 - Nitrate-N +Nitrite-N
En-Score
Laboratory
-2.1 -0.3 -0.7 -0.7 -0.5 -0.4 -0.1 -0.1 0.0 0.0 0.1 0.2 0.1 0.2 0.4 0.3 0.6 0.6 0.3
19 2 20 9 8 1 22 26 27 14 21 17 7 12 28 13 16 18 5 3

Figure 20

Table 23

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Orthophosphate-P
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	0.01	0.003	-2.56	-2.35
2	NT	NT		
3	< 0.05	NR		
4	NT	NT		
5	0.030	0.0026	2.32	2.26
6	NT	NT		
7	0.021	0.005	0.12	0.08
8	0.020	0.0023	-0.12	-0.12
9	0.032	0.0032	2.80	2.50
10	NT	NT		
11	NT	NT		
12	0.0161	0.00081	-1.07	-1.29
13	0.0167	0.009	-0.93	-0.40
14	0.018	0.005	-0.61	-0.42
15	NT	NT		
16	0.027	0.005	1.59	1.08
17*	0.033	0.003	3.05	2.80
18	0.020	0.004	-0.12	-0.10
19*	0.06	0.03	9.63	1.31
20	<0.1	0.01		
21	0.0227	0.0045	0.54	0.39
22	0.016	0.004	-1.10	-0.87
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	0.02	0.0038	-0.12	-0.10
27	0.016	0.002	-1.10	-1.17
28	0.017	0.002	-0.85	-0.91

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0205	0.0033
Spike Value	0.0271	0.0015
Homogeneity Value	0.0252	0.0050
Robust Average	0.0217	0.0048
Median	0.0200	0.0035
Mean	0.0233	
N	17	
Max	0.06	
Min	0.01	
Robust SD	0.0079	
Robust CV	36%	

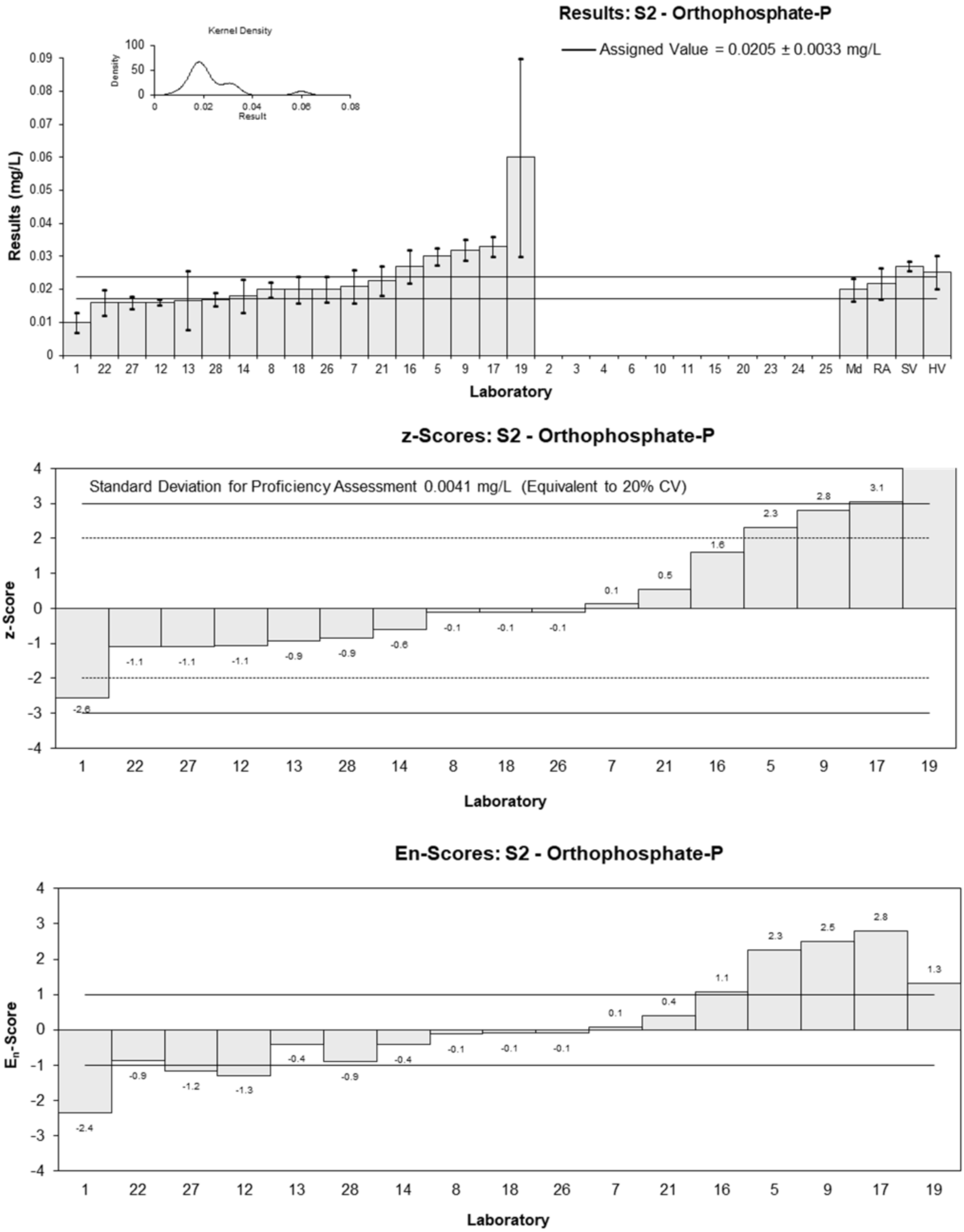

Results: S2 - Orthophosphate-P
Assigned Value = 0.0205 ± 0.0033 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
z-Scores: S2 - Orthophosphate-P
Standard Deviation for Proficiency Assessment 0.0041 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
En-Scores: S2 - Orthophosphate-P
En-Score
Laboratory

Figure 21

Table 24

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Sulphate
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	28	3	1.11	0.87
2	26.00	5.2	0.32	0.15
3	22.78	6.83	-0.96	-0.35
4	NT	NT		
5*	9.26	1.29	-6.33	-9.05
6	NT	NT		
7	NR	NR		
8	26	2.2	0.32	0.32
9	20	2.3	-2.06	-2.00
10	NT	NT		
11	NT	NT		
12	22.9	1.6	-0.91	-1.15
13	27.38	3.7	0.87	0.56
14	22.2	4.0	-1.19	-0.72
15	NT	NT		
16	27	5.4	0.71	0.33
17	26	5.3	0.32	0.15
18	26	2.6	0.32	0.28
19	24.5	0.75	-0.28	-0.49
20	23.1	6.93	-0.83	-0.30
21	27.7	4.7	0.99	0.52
22	26	3	0.32	0.25
23	25	0.7	-0.08	-0.14
24	NT	NT		
25	NT	NT		
26	26	2.34	0.32	0.30
27	25	1.47	-0.08	-0.11
28	24.8	3.0	-0.16	-0.12

* Outlier, see Section 4.2

Statistics

Assigned Value	25.2	1.2
Spike Value	Not Spiked	
Robust Average	25.0	1.3
Median	25.5	1.0
Mean	24.3	
N	20	
Max	28	
Min	9.26	
Robust SD	2.3	
Robust CV	9.1%	

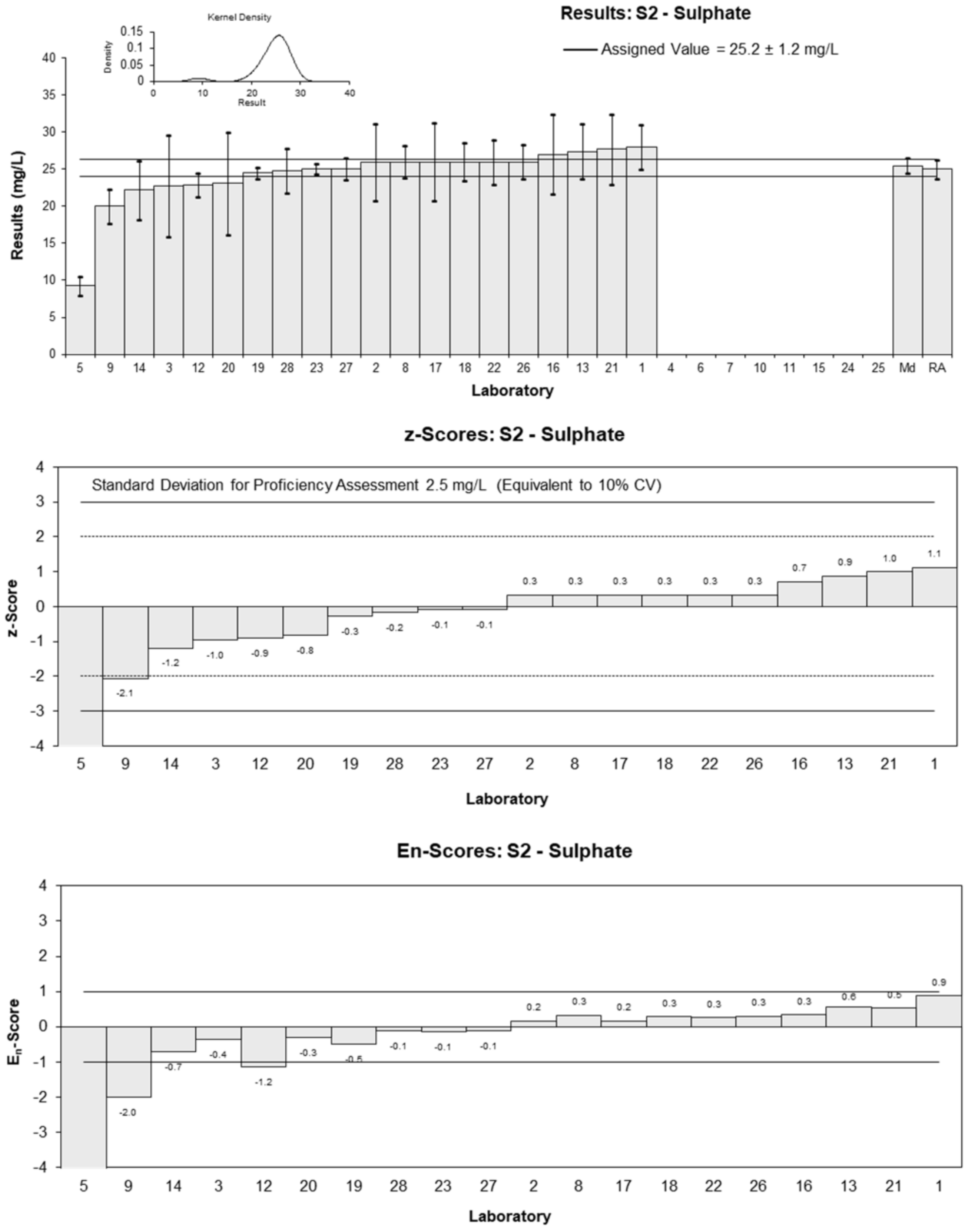

Results: S2 - Sulphate
Assigned Value = 25.2 ± 1.2 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5 9 14 3 12 20 19 28 23 27 2 8 17 18 22 26 16 13 21 1 4 6 7 10 11 15 24 25 Md RA
z-Scores: S2 - Sulphate
Standard Deviation for Proficiency Assessment 2.5 mg/L (Equivalent to 10% CV)
z-Score
-2.1 -1.2 -1.0 -0.9 -0.8 -0.3 -0.2 -0.1 -0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.7 0.9 1.0 1.1
Laboratory
5 9 14 3 12 20 19 28 23 27 2 8 17 18 22 26 16 13 21 1
En-Scores: S2 - Sulphate
En-Score
-2.0 -0.7 -0.4 -1.2 -0.3 -0.5 -0.1 -0.1 -0.1 0.2 0.3 0.2 0.3 0.3 0.3 0.3 0.6 0.5 0.9
Laboratory
5 9 14 3 12 20 19 28 23 27 2 8 17 18 22 26 16 13 21 1

Figure 22

Table 25

Sample Details

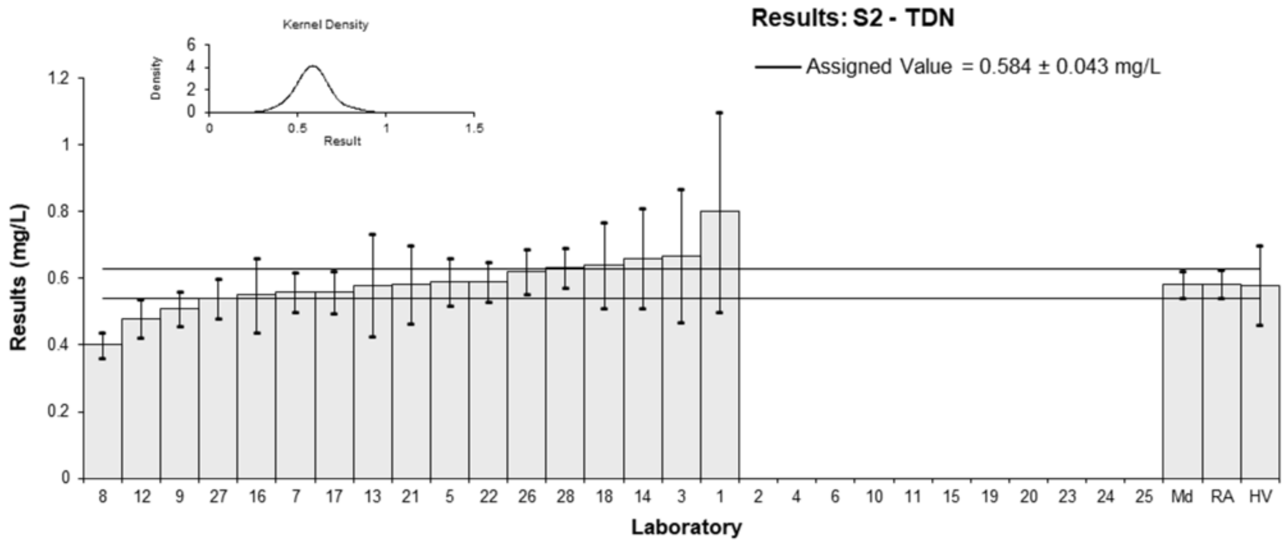
Sample No.	S2
Matrix	River Water
Analyte	TDN
Unit	mg/L

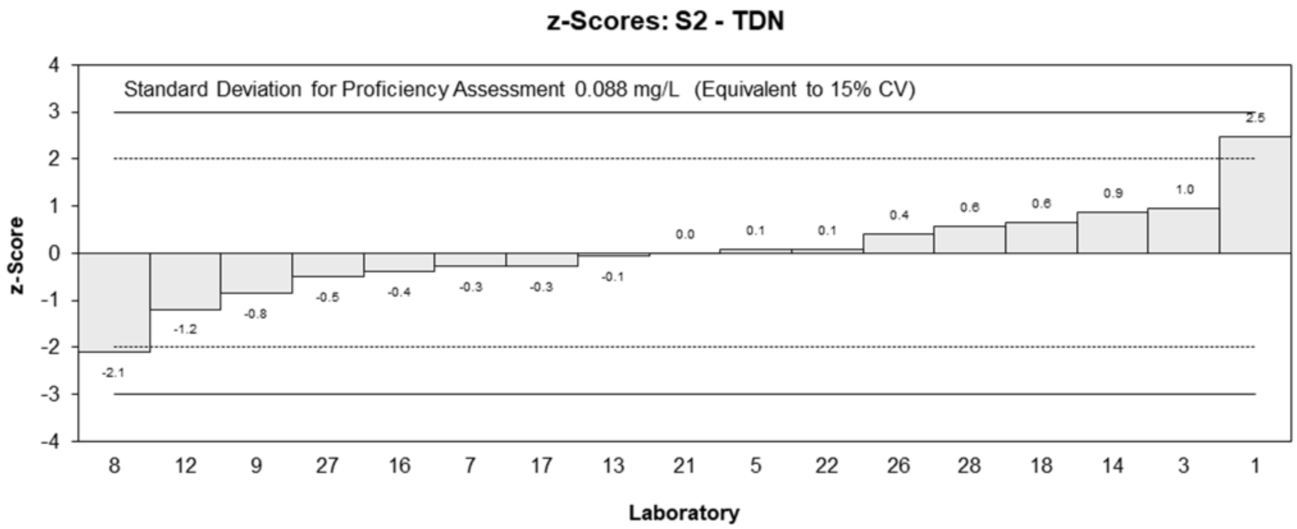
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.8	0.3	2.47	0.71
2	NT	NT		
3	0.668	0.2	0.96	0.41
4	NT	NT		
5	0.59	0.070	0.07	0.07
6	NT	NT		
7	0.56	0.06	-0.27	-0.33
8	0.4	0.04	-2.10	-3.13
9	0.51	0.051	-0.84	-1.11
10	NT	NT		
11	NT	NT		
12	0.48	0.058	-1.19	-1.44
13	0.58	0.153	-0.05	-0.03
14	0.66	0.15	0.87	0.49
15	NT	NT		
16	0.55	0.11	-0.39	-0.29
17	0.56	0.063	-0.27	-0.31
18	0.64	0.13	0.64	0.41
19	NT	NT		
20	NT	NT		
21	0.584	0.117	0.00	0.00
22	0.59	0.06	0.07	0.08
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	0.62	0.0682	0.41	0.45
27	0.54	0.06	-0.50	-0.60
28	0.633	0.06	0.56	0.66

Statistics

Assigned Value	0.584	0.043
Spike Value	Not Spiked	
Homogeneity Value	0.58	0.12
Robust Average	0.584	0.043
Median	0.584	0.040
Mean	0.586	
N	17	
Max	0.8	
Min	0.4	
Robust SD	0.071	
Robust CV	12%	


Results: S2 - TDN
Assigned Value = 0.584 ± 0.043 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 12 9 27 16 7 17 13 21 5 22 26 28 18 14 3 1 2 4 6 10 11 15 19 20 23 24 25 Md RA HV


z-Scores: S2 - TDN
Standard Deviation for Proficiency Assessment 0.088 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
8 12 9 27 16 7 17 13 21 5 22 26 28 18 14 3 1
-2.1 -1.2 -0.8 -0.5 -0.4 -0.3 -0.3 -0.1 0.0 0.1 0.1 0.4 0.6 0.6 0.9 1.0 2.5

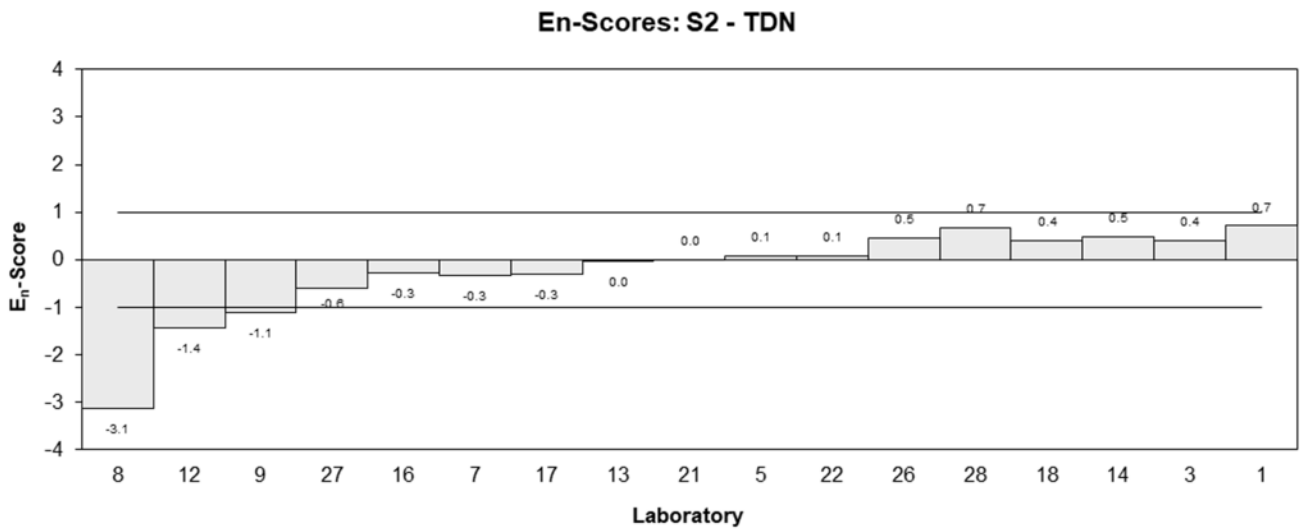

En-Scores: S2 - TDN
En-Score
Laboratory
8 12 9 27 16 7 17 13 21 5 22 26 28 18 14 3 1
-3.1 -1.4 -1.1 -0.6 -0.3 -0.3 -0.3 0.0 0.0 0.1 0.1 0.5 0.7 0.4 0.5 0.4 0.7

Figure 23

Table 26

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	TDP
Unit	mg/L

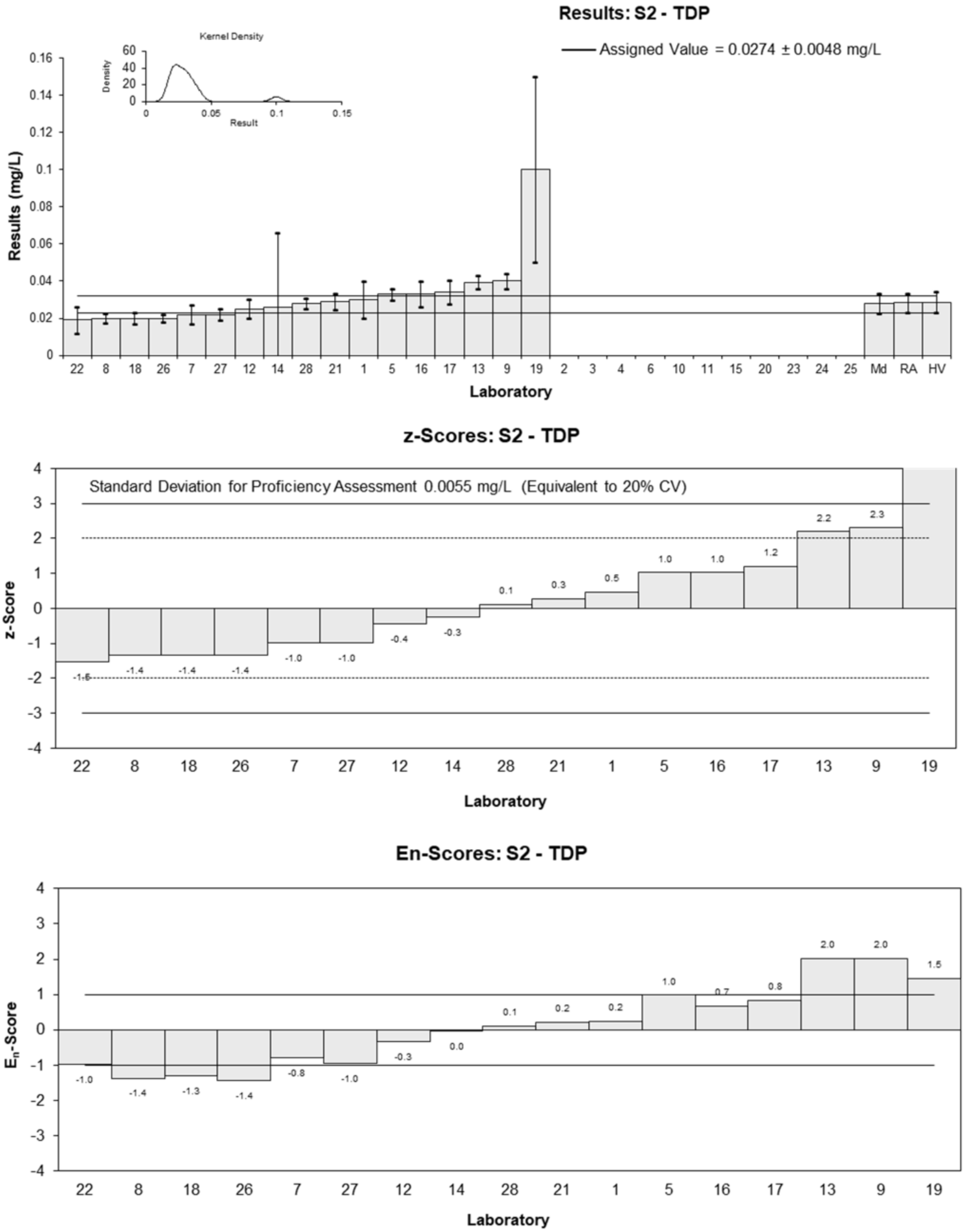
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.03	0.01	0.47	0.23
2	<0.5	NT		
3	< 0.05	NR		
4	NT	NT		
5	0.033	0.0031	1.02	0.98
6	NT	NT		
7	0.022	0.005	-0.99	-0.78
8	0.020	0.0025	-1.35	-1.37
9	0.04	0.004	2.30	2.02
10	NT	NT		
11	NT	NT		
12	0.025	0.0052	-0.44	-0.34
13	0.0394	0.0035	2.19	2.02
14	0.026	0.04	-0.26	-0.03
15	NT	NT		
16	0.033	0.007	1.02	0.66
17	0.034	0.0064	1.20	0.83
18	0.02	0.003	-1.35	-1.31
19*	0.10	0.05	13.25	1.45
20	< 0.1	NR		
21	0.0288	0.0043	0.26	0.22
22	0.019	0.007	-1.53	-0.99
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	0.02	0.0018	-1.35	-1.44
27	0.022	0.003	-0.99	-0.95
28	0.028	0.003	0.11	0.11

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0274	0.0048
Spike Value	Not Spiked	
Homogeneity Value	0.0287	0.0057
Robust Average	0.0283	0.0051
Median	0.0280	0.0054
Mean	0.0318	
N	17	
Max	0.1	
Min	0.019	
Robust SD	0.0085	
Robust CV	30%	



Results: S2 - TDP
Assigned Value = 0.0274 ± 0.0048 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
22 8 18 26 7 27 12 14 28 21 1 5 16 17 13 9 19 2 3 4 6 10 11 15 20 23 24 25 Md RA HV
z-Scores: S2 - TDP
Standard Deviation for Proficiency Assessment 0.0055 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.5 -1.4 -1.4 -1.4 -1.0 -1.0 -0.4 -0.3 0.1 0.3 0.5 1.0 1.0 1.2 2.2 2.3
22 8 18 26 7 27 12 14 28 21 1 5 16 17 13 9 19
En-Scores: S2 - TDP
E_n-Score
Laboratory
-1.0 -1.4 -1.3 -1.4 -0.8 -1.0 -0.3 0.0 0.1 0.2 0.2 1.0 0.7 0.8 2.0 2.0 1.5
22 8 18 26 7 27 12 14 28 21 1 5 16 17 13 9 19

Figure 24

Table 27

Sample Details

Sample No.	S3
Matrix	Seawater
Analyte	TKN
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	1.3	0.4	18.99	2.55
2	NR	NR		
3	< 1	NR		
4	< 2	NR		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	0.2	0.02	-1.31	-1.21
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	0.25	0.048	-0.39	-0.29
13	0.2318	0.1	-0.72	-0.34
14	0.19	0.05	-1.49	-1.09
15	NT	NT		
16	0.24	0.05	-0.57	-0.42
17	0.272	0.04	0.02	0.01
18	NT	NT		
19	NT	NT		
20	< 2	NR		
21	NT	NT		
22	0.321	0.044	0.92	0.71
23	NR	NR		
24	NT	NT		
25	NT	NT		
26	0.35	NR	1.46	1.44
27	0.43	0.11	2.93	1.29
28	0.280	0.03	0.17	0.14

* Outlier, see Section 4.2

Statistics

Assigned Value	0.271	0.055
Spike Value	0.210	0.022
Homogeneity Value	0.245	0.049
Robust Average	0.291	0.072
Median	0.272	0.055
Mean	0.37	
N	11	
Max	1.3	
Min	0.19	
Robust SD	0.095	
Robust CV	33%	

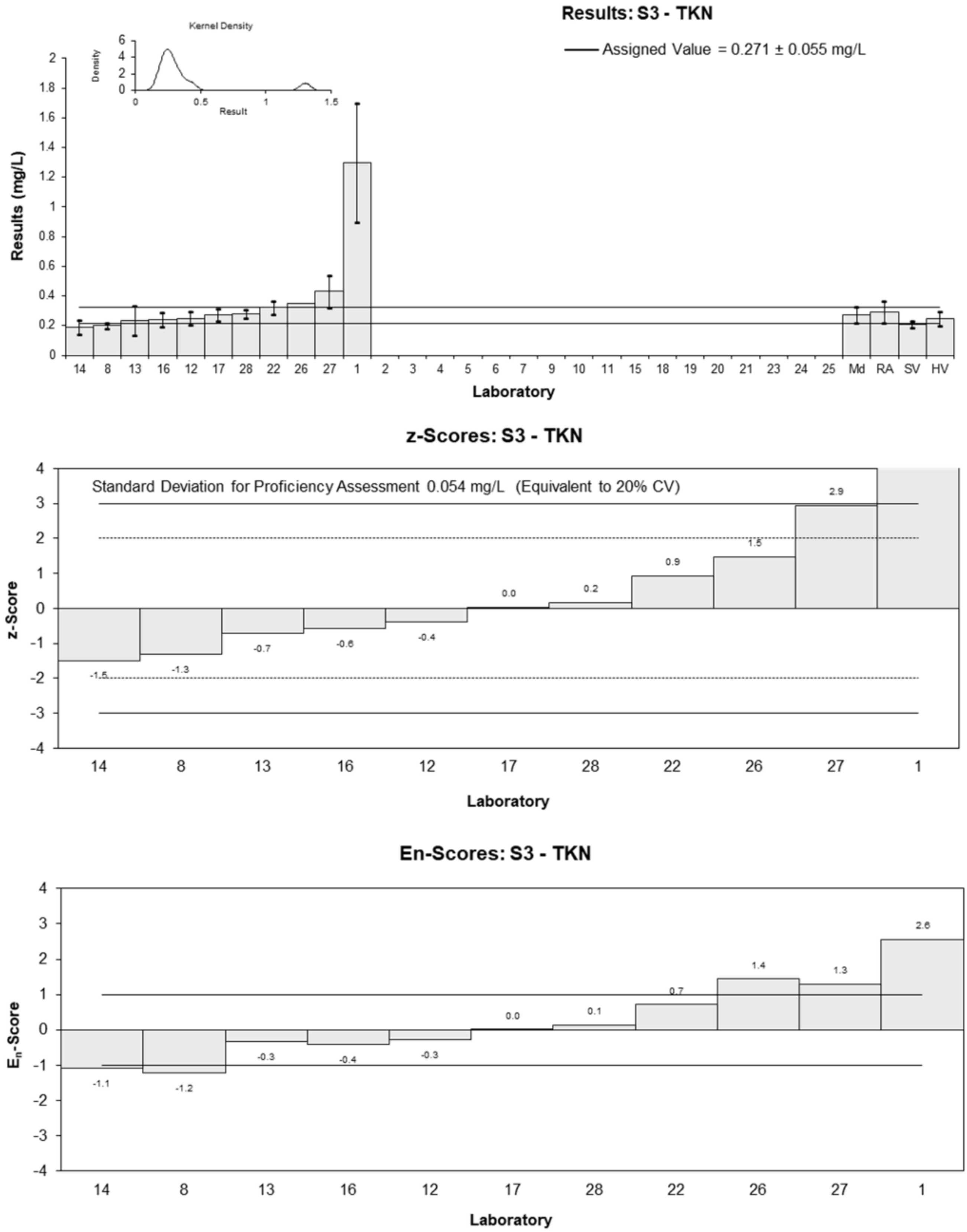

Results: S3 - TKN
Assigned Value = 0.271 ± 0.055 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
14 8 13 16 12 17 28 22 26 27 1 2 3 4 5 6 7 9 10 11 15 18 19 20 21 23 24 25 Md RA SV HV
z-Scores: S3 - TKN
Standard Deviation for Proficiency Assessment 0.054 mg/L (Equivalent to 20% CV)
z-Score
-1.5 -1.3 -0.7 -0.6 -0.4 0.0 0.2 0.9 1.5 2.9
14 8 13 16 12 17 28 22 26 27 1
Laboratory
En-Scores: S3 - TKN
E_n-Score
-1.1 -1.2 -0.3 -0.4 -0.3 0.0 0.1 0.7 1.4 1.3 2.6
14 8 13 16 12 17 28 22 26 27 1
Laboratory

Figure 25

Table 28

Sample Details

Sample No.	S3
Matrix	Seawater
Analyte	TN
Unit	mg/L

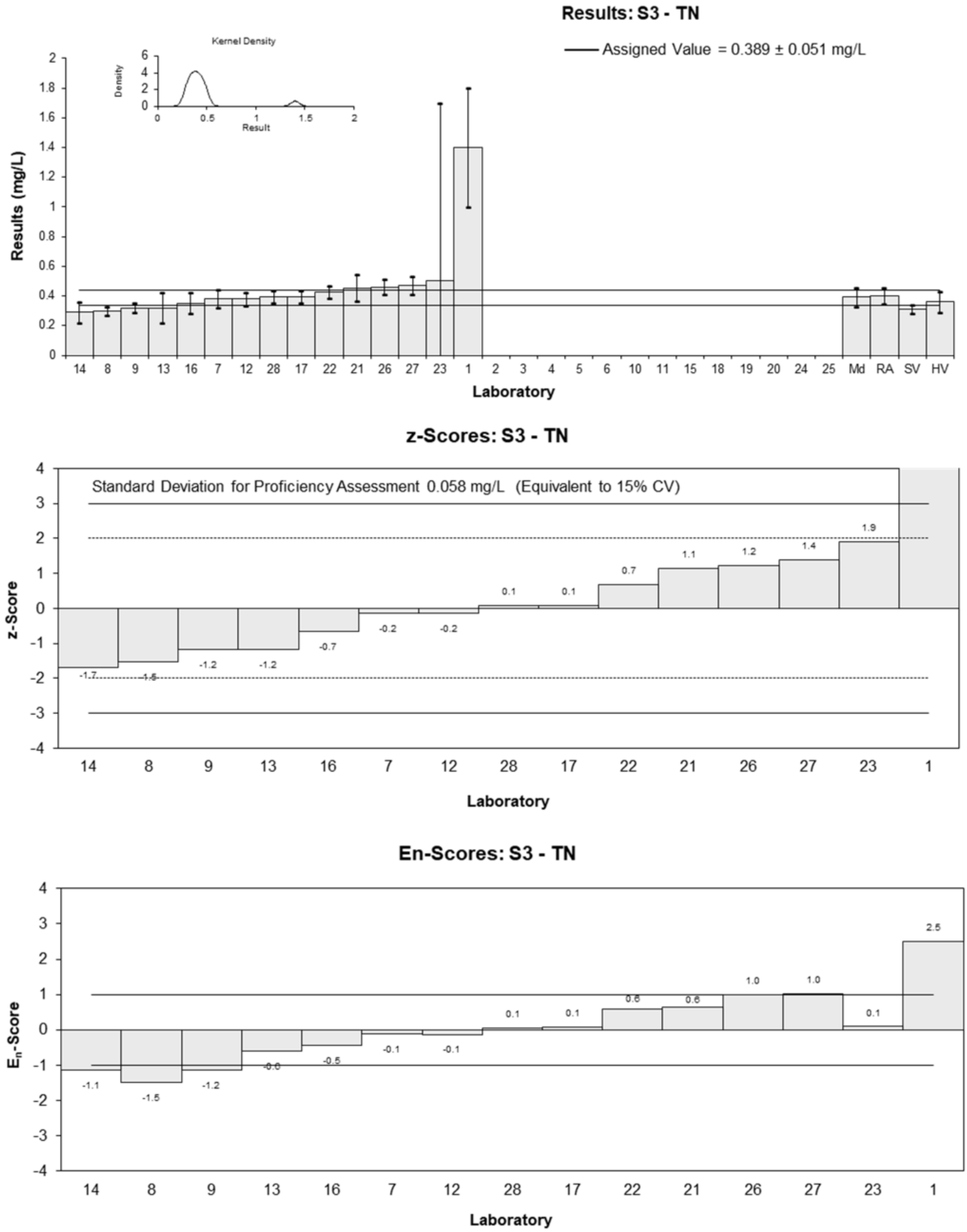
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	1.4	0.4	17.33	2.51
2	NR	NR		
3	< 1	NR		
4	< 2	NR		
5	NT	NT		
6	NT	NT		
7	0.38	0.06	-0.15	-0.11
8	0.3	0.03	-1.53	-1.50
9	0.32	0.032	-1.18	-1.15
10	NT	NT		
11	NT	NT		
12	0.38	0.046	-0.15	-0.13
13	0.32	0.1	-1.18	-0.61
14	0.29	0.07	-1.70	-1.14
15	NT	NT		
16	0.35	0.07	-0.67	-0.45
17	0.394	0.04	0.09	0.08
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	0.455	0.091	1.13	0.63
22	0.428	0.042	0.67	0.59
23	0.5	1.2	1.90	0.09
24	NT	NT		
25	NT	NT		
26	0.46	0.0506	1.22	0.99
27	0.47	0.06	1.39	1.03
28	0.393	0.04	0.07	0.06

* Outlier, see Section 4.2

Statistics

Assigned Value	0.389	0.051
Spike Value	0.309	0.030
Homogeneity Value	0.360	0.072
Robust Average	0.398	0.054
Median	0.393	0.064
Mean	0.46	
N	15	
Max	1.4	
Min	0.29	
Robust SD	0.083	
Robust CV	21%	



Results: S3 - TN
Assigned Value = 0.389 ± 0.051 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
14 8 9 13 16 7 12 28 17 22 21 26 27 23 1 2 3 4 5 6 10 11 15 18 19 20 24 25 Md RA SV HV
z-Scores: S3 - TN
Standard Deviation for Proficiency Assessment 0.058 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S3 - TN
En-Score
Laboratory

Figure 26

Table 29

Sample Details

Sample No.	S3
Matrix	Seawater
Analyte	TOC
Unit	mg/L

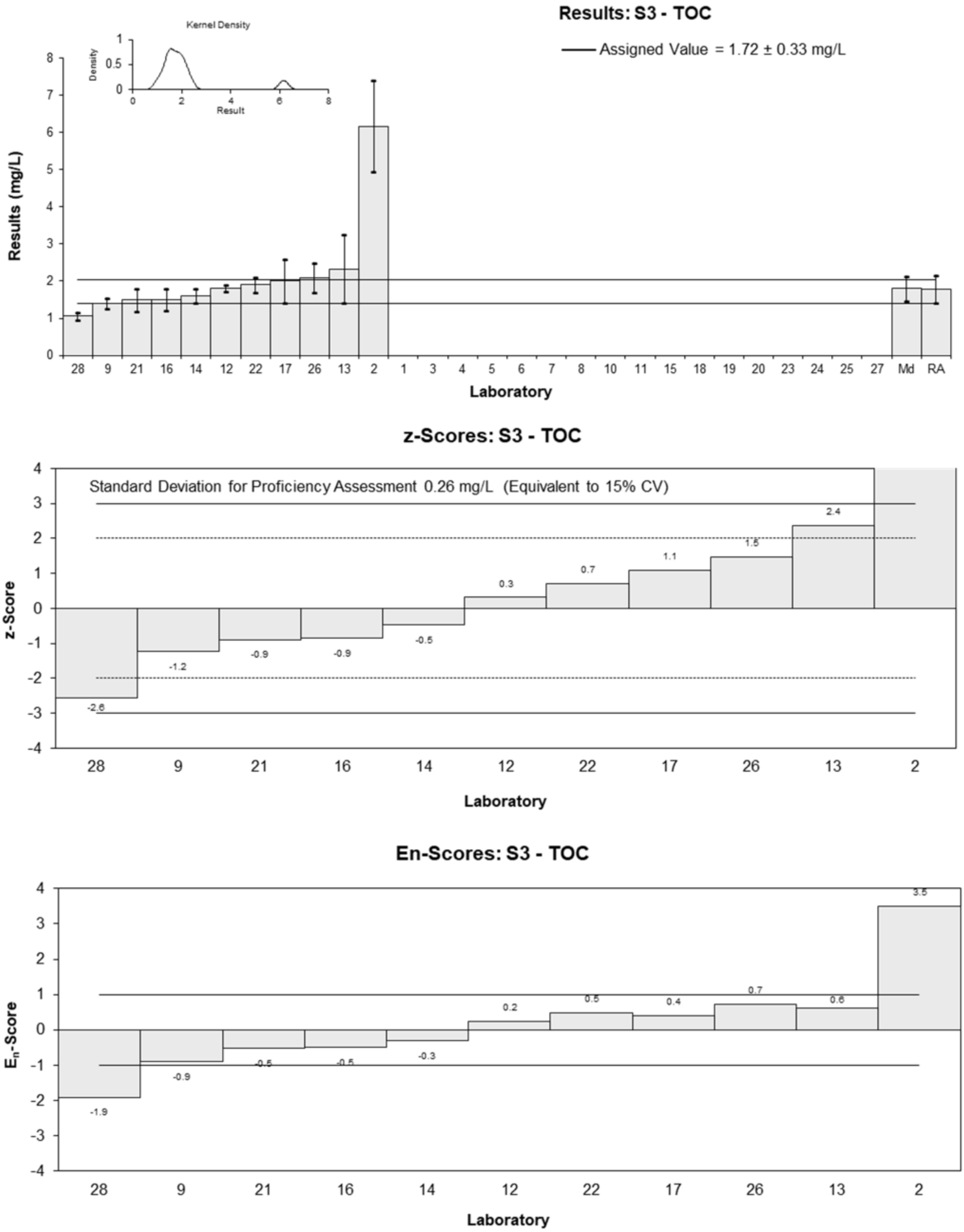
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2*	6.17	1.23	17.25	3.49
3	< 5	NR		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	1.4	0.14	-1.24	-0.89
10	NT	NT		
11	NT	NT		
12	1.8	0.089	0.31	0.23
13	2.33	0.92	2.36	0.62
14	1.6	0.2	-0.47	-0.31
15	NT	NT		
16	1.5	0.3	-0.85	-0.49
17	2	0.6	1.09	0.41
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	1.49	0.30	-0.89	-0.52
22	1.9	0.2	0.70	0.47
23	NR	NR		
24	NT	NT		
25	NT	NT		
26	2.1	0.399	1.47	0.73
27	NR	NR		
28	1.06	0.1	-2.56	-1.91

* Outlier, see Section 4.2

Statistics

Assigned Value	1.72	0.33
Spike Value	Not Spiked	
Robust Average	1.79	0.37
Median	1.80	0.34
Mean	2.12	
N	11	
Max	6.17	
Min	1.06	
Robust SD	0.49	
Robust CV	27%	



Results: S3 - TOC
Assigned Value = 1.72 ± 0.33 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
28 9 21 16 14 12 22 17 26 13 2 1 3 4 5 6 7 8 10 11 15 18 19 20 23 24 25 27 Md RA
z-Scores: S3 - TOC
Standard Deviation for Proficiency Assessment 0.26 mg/L (Equivalent to 15% CV)
z-Score
-2.6 -1.2 -0.9 -0.9 -0.5 0.3 0.7 1.1 1.5 2.4
28 9 21 16 14 12 22 17 26 13 2
Laboratory
En-Scores: S3 - TOC
E_n-Score
-1.9 -0.9 -0.5 -0.5 -0.3 0.2 0.5 0.4 0.7 0.6 3.5
28 9 21 16 14 12 22 17 26 13 2
Laboratory

Figure 27

Table 30

Sample Details

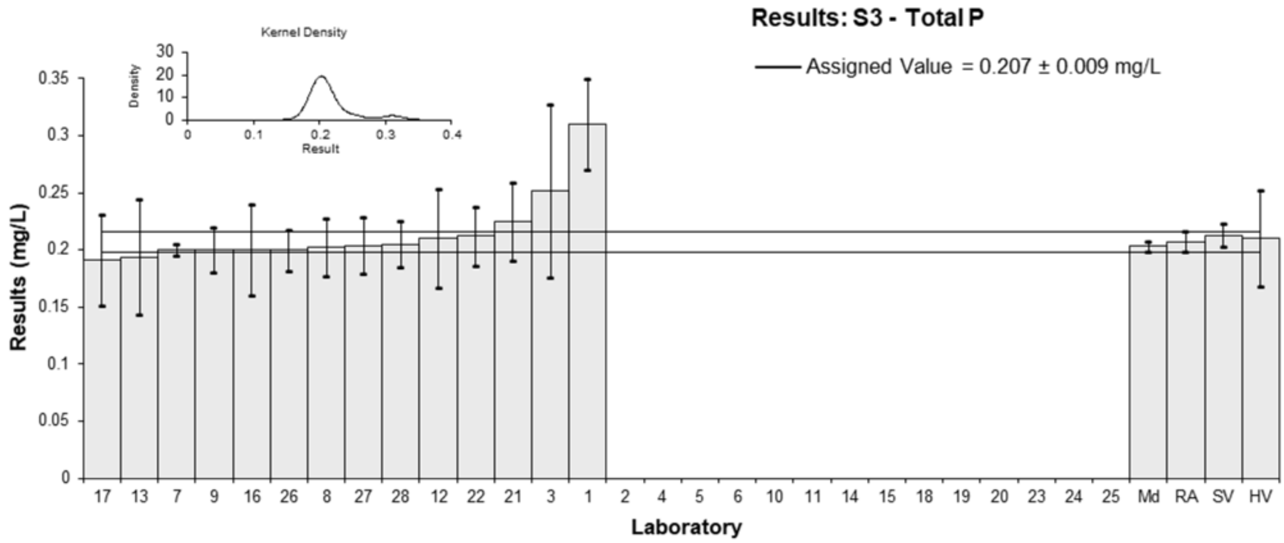
Sample No.	S3
Matrix	Seawater
Analyte	Total P
Unit	mg/L

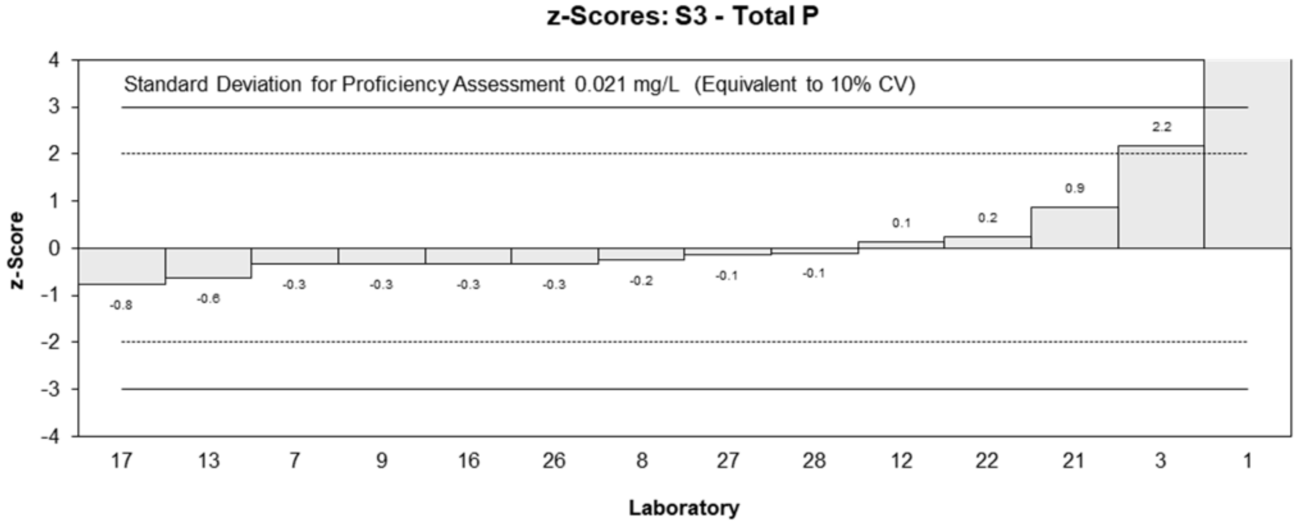
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.31	0.04	4.98	2.51
2	<0.5	NT		
3	0.252	0.0756	2.17	0.59
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	0.20	0.005	-0.34	-0.68
8	0.202	0.0252	-0.24	-0.19
9	0.2	0.02	-0.34	-0.32
10	NT	NT		
11	NT	NT		
12	0.21	0.043	0.14	0.07
13	0.194	0.05	-0.63	-0.26
14	NR	NR		
15	NT	NT		
16	0.20	0.04	-0.34	-0.17
17	0.191	0.04	-0.77	-0.39
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	0.225	0.034	0.87	0.51
22	0.212	0.026	0.24	0.18
23	<1.5	NR		
24	NT	NT		
25	NT	NT		
26	0.2	0.018	-0.34	-0.35
27	0.204	0.025	-0.14	-0.11
28	0.205	0.02	-0.10	-0.09

Statistics

Assigned Value	0.207	0.009
Spike Value	0.213	0.010
Homogeneity Value	0.210	0.042
Robust Average	0.207	0.009
Median	0.203	0.005
Mean	0.215	
N	14	
Max	0.31	
Min	0.191	
Robust SD	0.013	
Robust CV	6.5%	


Results: S3 - Total P
Assigned Value = 0.207 ± 0.009 mg/L
Kernel Density
Density
Result
Results (mg/L)
17 13 7 9 16 26 8 27 28 12 22 21 3 1 2 4 5 6 10 11 14 15 18 19 20 23 24 25 Md RA SV HV
Laboratory


z-Scores: S3 - Total P
Standard Deviation for Proficiency Assessment 0.021 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.6 -0.3 -0.3 -0.3 -0.3 -0.2 -0.1 -0.1 0.1 0.2 0.9 2.2
17 13 7 9 16 26 8 27 28 12 22 21 3 1
Laboratory

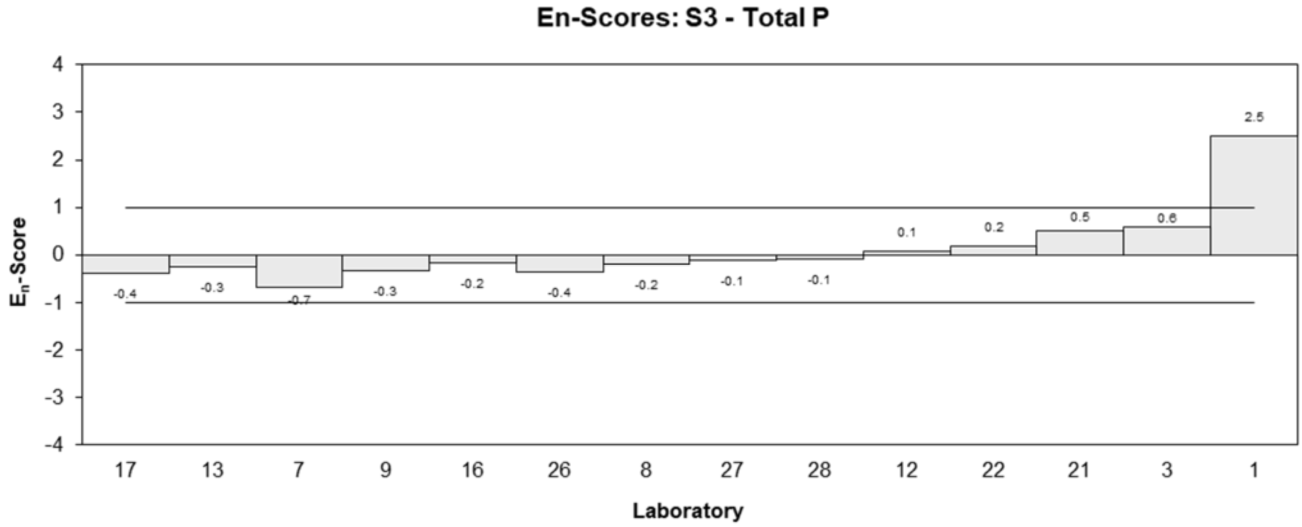

En-Scores: S3 - Total P
E_n-Score
-0.4 -0.3 -0.7 -0.3 -0.2 -0.4 -0.2 -0.1 -0.1 0.1 0.2 0.5 0.6 2.5
17 13 7 9 16 26 8 27 28 12 22 21 3 1
Laboratory

Figure 28

Table 31

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	NT	NT		
5	0.38	NR	-0.35	-0.41
6	NT	NT		
7	NR	NR		
8	0.3	0.03	-1.68	-1.71
9	NT	NT		
10	NT	NT		
11	NT	NT		
12*	0.17	0.11	-3.84	-1.91
13	0.414	0.1	0.22	0.12
14	0.46	0.06	0.98	0.75
15	NT	NT		
16	0.34	0.07	-1.01	-0.70
17	0.38	0.076	-0.35	-0.23
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	0.42	0.06	0.32	0.24
23	NR	NR		
24	NT	NT		
25	NT	NT		
26	0.47	NR	1.15	1.35
27	NR	NR		
28	0.438	0.05	0.62	0.52

* Outlier, see Section 4.2

Statistics

Assigned Value	0.401	0.051
Spike Value	0.414	0.047
Homogeneity Value	0.400	0.080
Robust Average	0.388	0.059
Median	0.397	0.057
Mean	0.377	
N	10	
Max	0.47	
Min	0.17	
Robust SD	0.074	
Robust CV	19%	

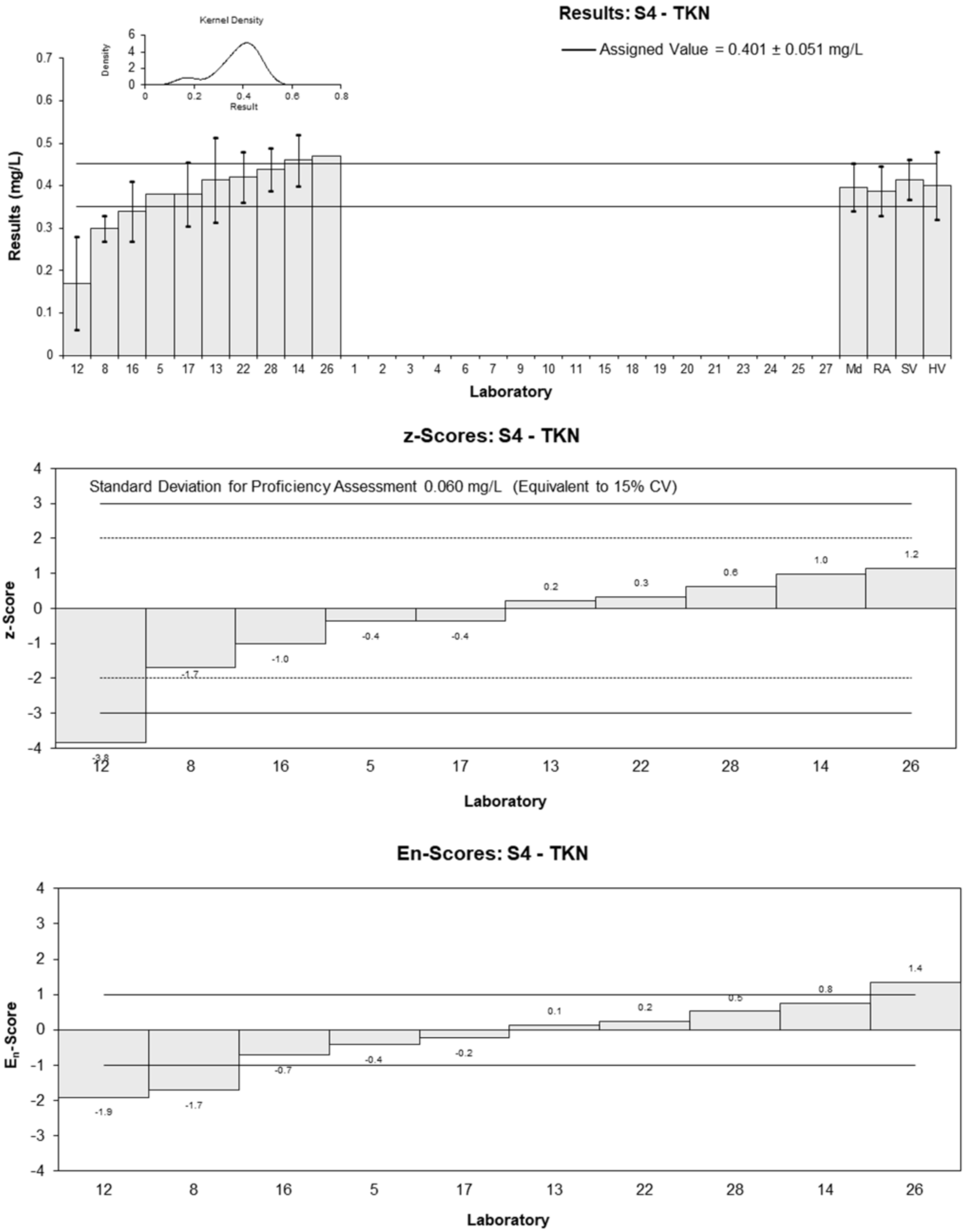

Results: S4 - TKN
Assigned Value = 0.401 ± 0.051 mg/L
Kernel Density
Density
Result
Results (mg/L)
12 8 16 5 17 13 22 28 14 26 1 2 3 4 6 7 9 10 11 15 18 19 20 21 23 24 25 27 Md RA SV HV
Laboratory
z-Scores: S4 - TKN
Standard Deviation for Proficiency Assessment 0.060 mg/L (Equivalent to 15% CV)
z-Score
-3.8 -1.7 -1.0 -0.4 -0.4 0.2 0.3 0.6 1.0 1.2
12 8 16 5 17 13 22 28 14 26
Laboratory
En-Scores: S4 - TKN
E_n-Score
-1.9 -1.7 -0.7 -0.4 -0.2 0.1 0.2 0.5 0.8 1.4
12 8 16 5 17 13 22 28 14 26
Laboratory

Figure 29

Table 32

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	NT	NT		
5	0.96	0.14	0.28	0.26
6	NT	NT		
7	0.91	0.06	-0.08	-0.14
8	0.8	0.08	-0.88	-1.29
9	0.85	0.085	-0.51	-0.72
10	NT	NT		
11	NT	NT		
12	0.74	0.090	-1.31	-1.77
13	0.96	0.2	0.28	0.19
14	0.9	0.2	-0.15	-0.10
15	NT	NT		
16	0.89	0.18	-0.22	-0.17
17	0.9	0.13	-0.15	-0.15
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	0.936	0.187	0.11	0.08
22	0.95	0.09	0.21	0.28
23	1.2	1.2	2.02	0.23
24	NT	NT		
25	NT	NT		
26	1	0.11	0.57	0.66
27	0.91	0.110	-0.08	-0.09
28	1.00	0.1	0.57	0.71

Statistics

Assigned Value	0.921	0.049
Spike Value	1.05	0.11
Homogeneity Value	0.92	0.18
Robust Average	0.921	0.049
Median	0.910	0.048
Mean	0.927	
N	15	
Max	1.2	
Min	0.74	
Robust SD	0.076	
Robust CV	8.2%	

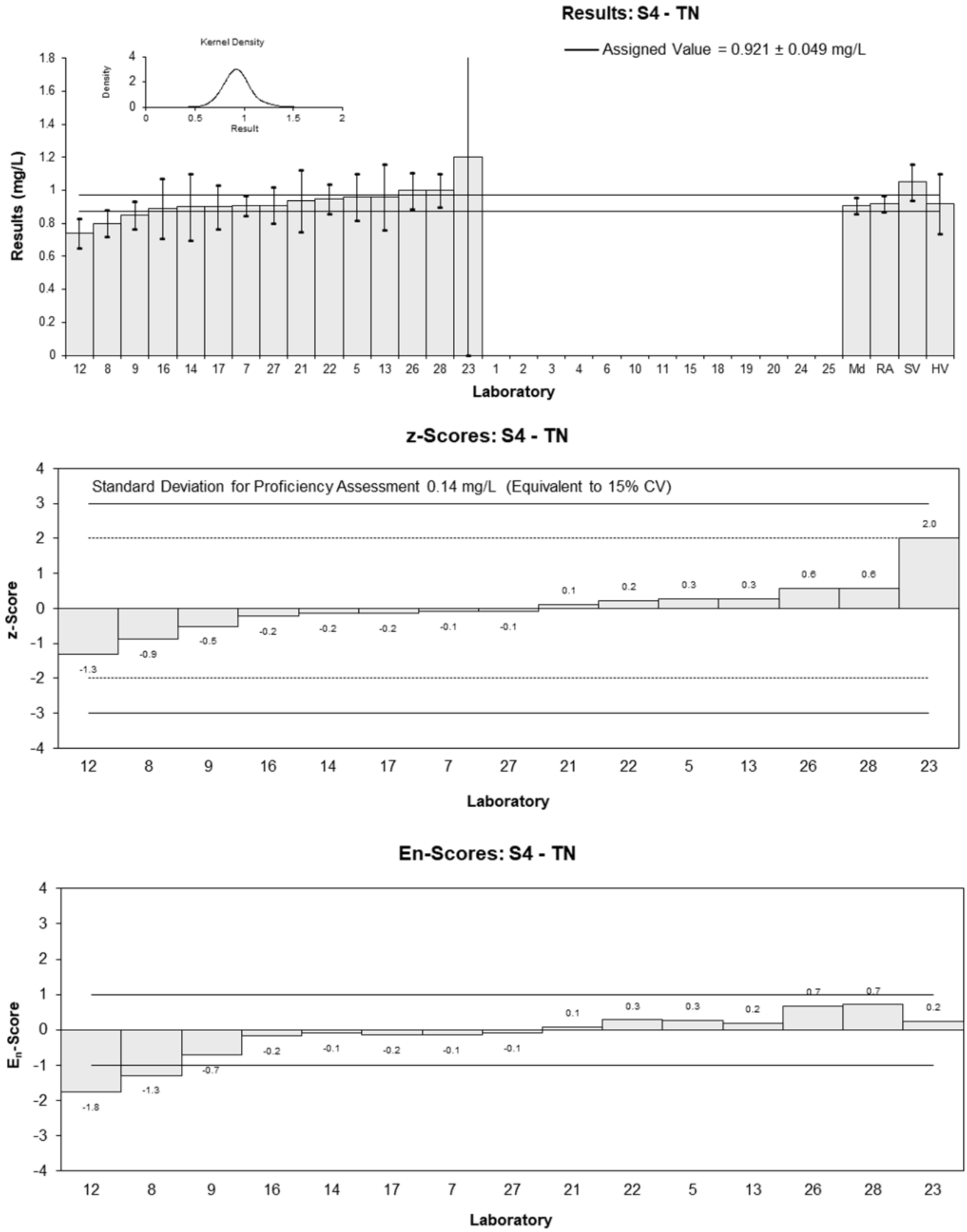

Results: S4 - TN
Assigned Value = 0.921 ± 0.049 mg/L
Kernel Density
Density
Result
Results (mg/L)
12 8 9 16 14 17 7 27 21 22 5 13 26 28 23 1 2 3 4 6 10 11 15 18 19 20 24 25 Md RA SV HV
Laboratory
z-Scores: S4 - TN
Standard Deviation for Proficiency Assessment 0.14 mg/L (Equivalent to 15% CV)
-1.3 -0.9 -0.5 -0.2 -0.2 -0.2 -0.1 -0.1 0.1 0.2 0.3 0.3 0.6 0.6 2.0
z-Score
12 8 9 16 14 17 7 27 21 22 5 13 26 28 23
Laboratory
En-Scores: S4 - TN
-1.8 -1.3 -0.7 -0.2 -0.1 -0.2 -0.1 -0.1 0.1 0.3 0.3 0.2 0.7 0.7 0.2
En-Score
12 8 9 16 14 17 7 27 21 22 5 13 26 28 23
Laboratory

Figure 30

Table 33

Sample Details

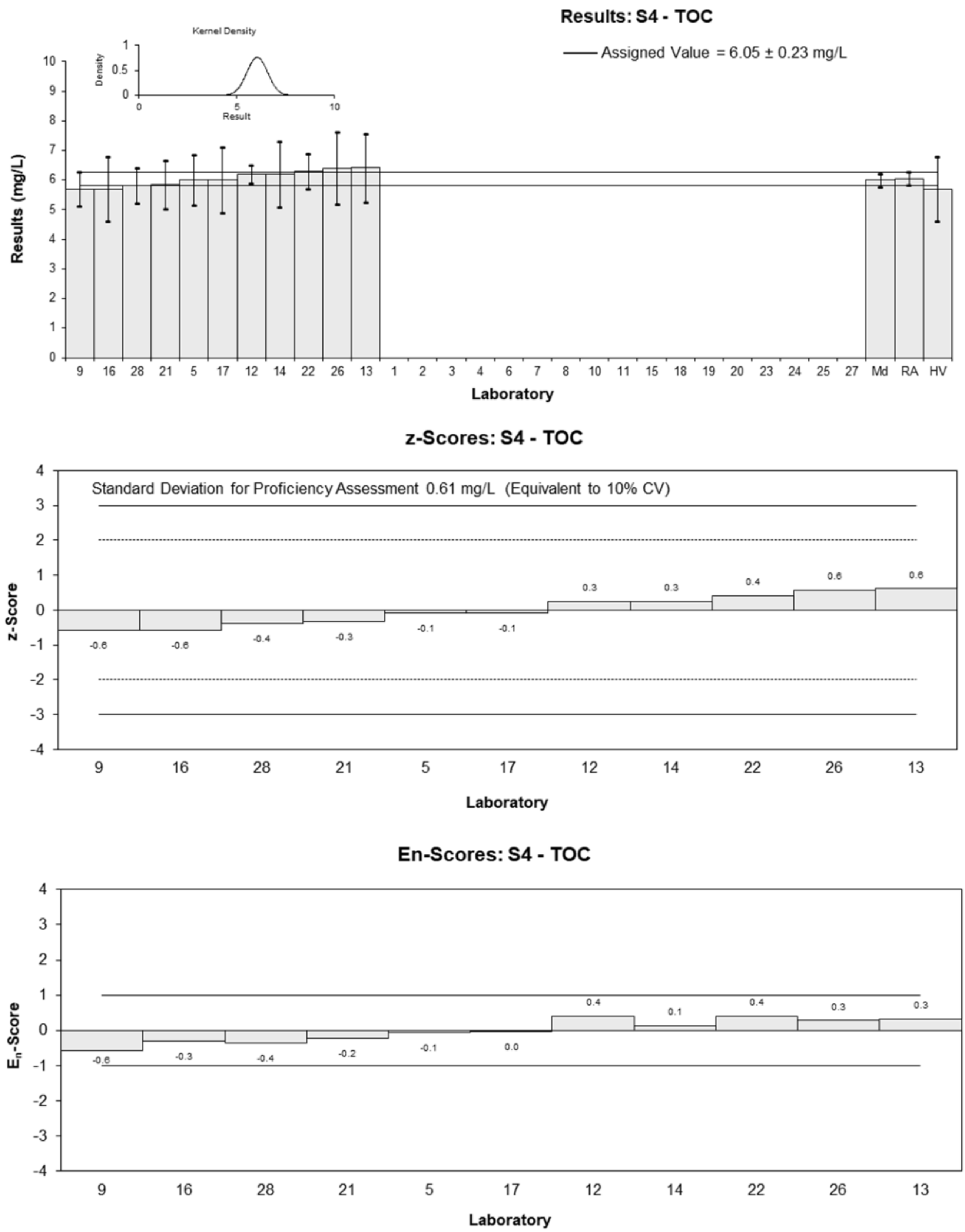
Sample No.	S4
Matrix	River Water
Analyte	TOC
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	NT	NT		
5	6	0.85	-0.08	-0.06
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	5.7	0.57	-0.58	-0.57
10	NT	NT		
11	NT	NT		
12	6.2	0.31	0.25	0.39
13	6.42	1.15	0.61	0.32
14	6.2	1.1	0.25	0.13
15	NT	NT		
16	5.7	1.1	-0.58	-0.31
17	6	1.1	-0.08	-0.04
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	5.85	0.82	-0.33	-0.23
22	6.3	0.6	0.41	0.39
23	NR	NR		
24	NT	NT		
25	NT	NT		
26	6.4	1.216	0.58	0.28
27	NR	NR		
28	5.82	0.6	-0.38	-0.36

Statistics

Assigned Value	6.05	0.23
Spike Value	Not Spiked	
Homogeneity Value	5.7	1.1
Robust Average	6.05	0.23
Median	6.00	0.22
Mean	6.05	
N	11	
Max	6.42	
Min	5.7	
Robust SD	0.3	
Robust CV	5%	



Results: S4 - TOC
Assigned Value = 6.05 ± 0.23 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
9 16 28 21 5 17 12 14 22 26 13 1 2 3 4 6 7 8 10 11 15 18 19 20 23 24 25 27 Md RA HV
z-Scores: S4 - TOC
Standard Deviation for Proficiency Assessment 0.61 mg/L (Equivalent to 10% CV)
z-Score
-0.6 -0.6 -0.4 -0.3 -0.1 -0.1 0.3 0.3 0.4 0.6 0.6
Laboratory
9 16 28 21 5 17 12 14 22 26 13
En-Scores: S4 - TOC
E_n-Score
-0.6 -0.3 -0.4 -0.2 -0.1 0.0 0.4 0.1 0.4 0.3 0.3
Laboratory
9 16 28 21 5 17 12 14 22 26 13

Figure 31

Table 34

Sample Details

Sample No.	S4
Matrix	River Water
Analyte	Total P
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	NT	NT		
5	0.158	0.018	0.39	0.32
6	NT	NT		
7	0.15	0.005	-0.13	-0.26
8	0.151	0.0189	-0.07	-0.05
9	0.16	0.016	0.53	0.47
10	NT	NT		
11	NT	NT		
12	0.16	0.033	0.53	0.24
13	0.129	0.04	-1.51	-0.57
14	0.140	0.021	-0.79	-0.55
15	NT	NT		
16	0.16	0.032	0.53	0.25
17	0.156	0.024	0.26	0.16
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	0.162	0.024	0.66	0.40
22	0.136	0.018	-1.05	-0.84
23	<1.5	NR		
24	NT	NT		
25	NT	NT		
26	0.15	0.0135	-0.13	-0.14
27	0.154	0.019	0.13	0.10
28	0.152	0.02	0.00	0.00

Statistics

Assigned Value	0.152	0.006
Spike Value	0.160	0.008
Homogeneity Value	0.157	0.031
Robust Average	0.152	0.006
Median	0.153	0.006
Mean	0.151	
N	14	
Max	0.162	
Min	0.129	
Robust SD	0.0094	
Robust CV	6.2%	

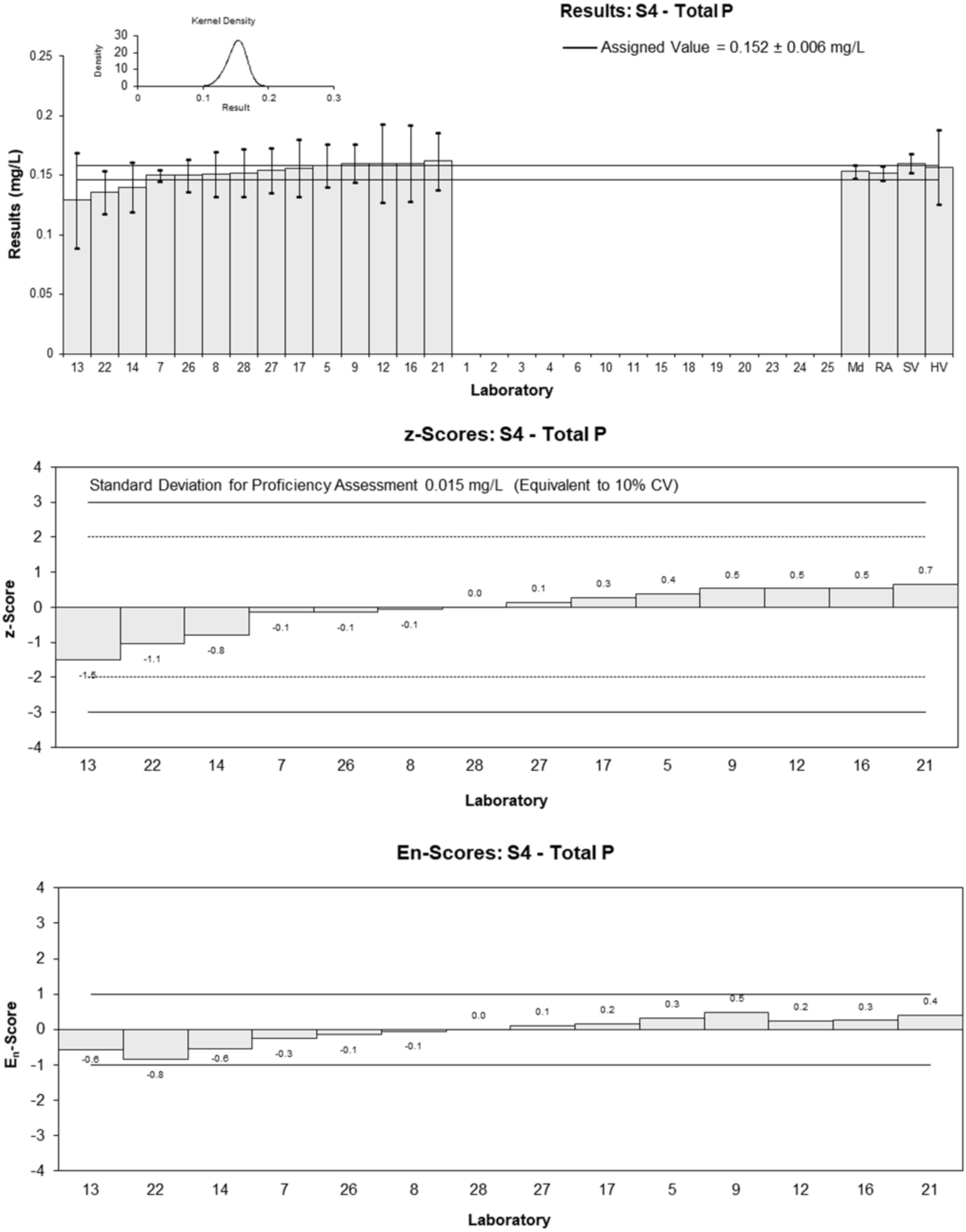

Results: S4 - Total P
Assigned Value = 0.152 ± 0.006 mg/L
Kernel Density
Density
Result
Results (mg/L)
13 22 14 7 26 8 28 27 17 5 9 12 16 21 1 2 3 4 6 10 11 15 18 19 20 23 24 25 Md RA SV HV
Laboratory
z-Scores: S4 - Total P
Standard Deviation for Proficiency Assessment 0.015 mg/L (Equivalent to 10% CV)
z-Score
-1.5 -1.1 -0.8 -0.1 -0.1 -0.1 0.0 0.1 0.3 0.4 0.5 0.5 0.5 0.7
13 22 14 7 26 8 28 27 17 5 9 12 16 21
Laboratory
En-Scores: S4 - Total P
En-Score
-0.6 -0.8 -0.6 -0.3 -0.1 -0.1 0.0 0.1 0.2 0.3 0.5 0.2 0.3 0.4
13 22 14 7 26 8 28 27 17 5 9 12 16 21
Laboratory

Figure 32

Table 35

Sample Details

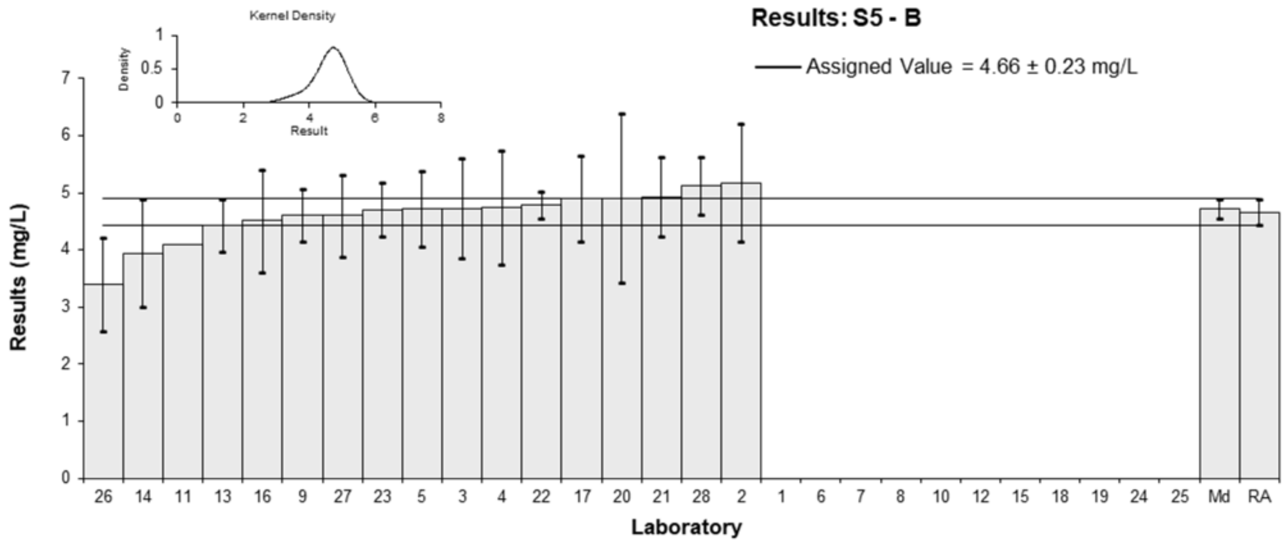
Sample No.	S5
Matrix	Seawater
Analyte	B
Unit	mg/L

Participant Results

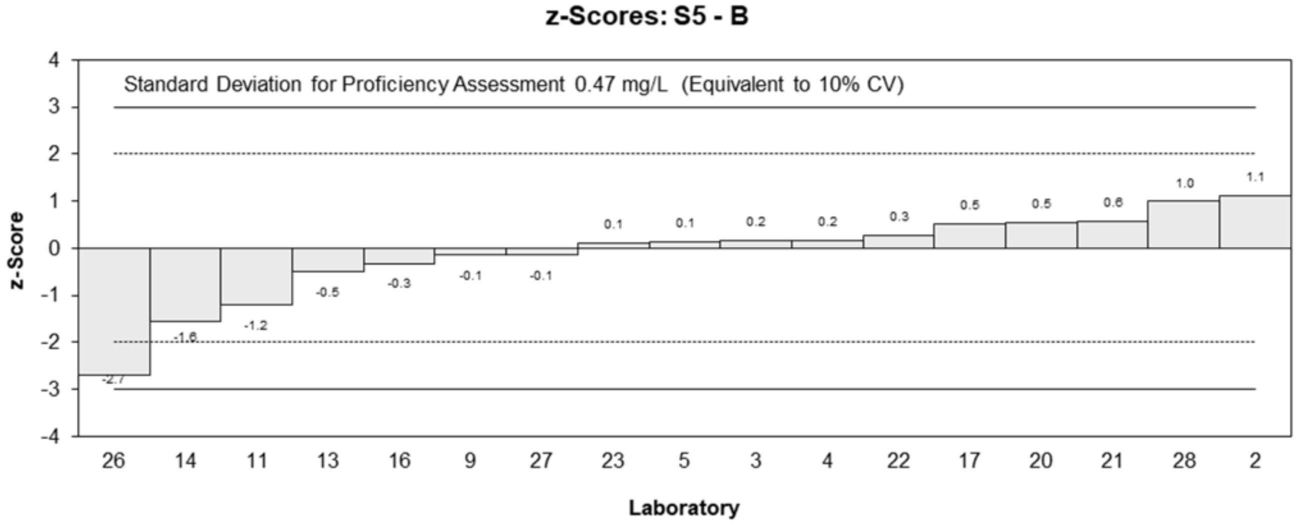
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	5.18	1.04	1.12	0.49
3	4.729	0.868	0.15	0.08
4	4.74	1.00	0.17	0.08
5	4.72	0.66	0.13	0.09
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	4.6	0.46	-0.13	-0.12
10	NT	NT		
11	4.1	NR	-1.20	-2.43
12	NT	NT		
13	4.43	0.468	-0.49	-0.44
14	3.94	0.94	-1.55	-0.74
15	NR	NR		
16	4.51	0.90	-0.32	-0.16
17	4.9	0.75	0.52	0.31
18	NT	NT		
19	NT	NT		
20	4.91	1.473	0.54	0.17
21	4.93	0.69	0.58	0.37
22	4.79	0.24	0.28	0.39
23	4.708	0.47	0.10	0.09
24	NT	NT		
25	NT	NT		
26	3.4	0.816	-2.70	-1.49
27	4.60	0.71	-0.13	-0.08
28	5.12	0.5	0.99	0.84

Statistics

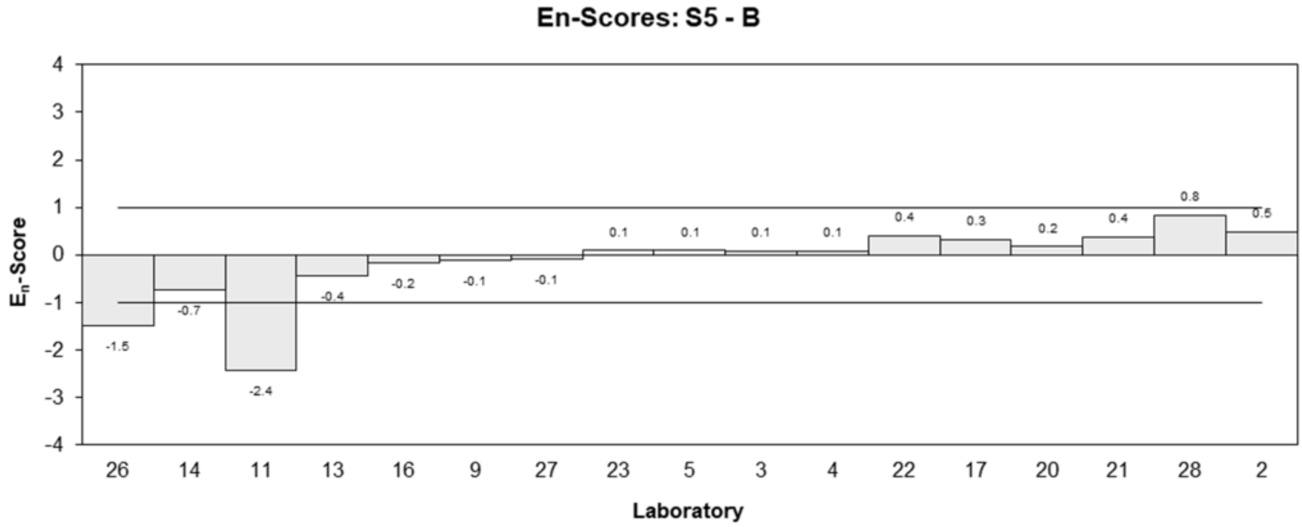
Assigned Value	4.66	0.23
Spike Value	Not Spiked	
Robust Average	4.66	0.23
Median	4.72	0.17
Mean	4.61	
N	17	
Max	5.18	
Min	3.4	
Robust SD	0.37	
Robust CV	8%	



Results: S5 - B
Assigned Value = 4.66 ± 0.23 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
26 14 11 13 16 9 27 23 5 3 4 22 17 20 21 28 2 1 6 7 8 10 12 15 18 19 24 25 Md RA



z-Scores: S5 - B
Standard Deviation for Proficiency Assessment 0.47 mg/L (Equivalent to 10% CV)
z-Score
-2.7 -1.6 -1.2 -0.5 -0.3 -0.1 -0.1 0.1 0.1 0.2 0.2 0.3 0.5 0.5 0.6 1.0 1.1
26 14 11 13 16 9 27 23 5 3 4 22 17 20 21 28 2
Laboratory



En-Scores: S5 - B
En-Score
-1.5 -0.7 -2.4 -0.4 -0.2 -0.1 -0.1 0.1 0.1 0.1 0.1 0.4 0.3 0.2 0.4 0.8 0.5
26 14 11 13 16 9 27 23 5 3 4 22 17 20 21 28 2
Laboratory

Figure 33

Table 36

Sample Details

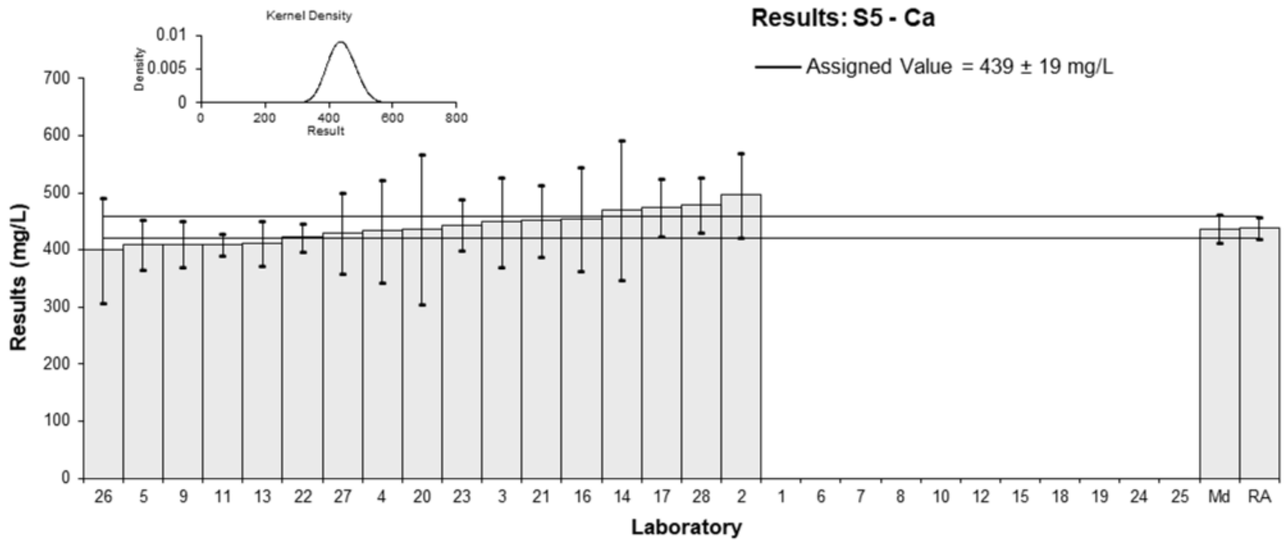
Sample No.	S5
Matrix	Seawater
Analyte	Ca
Unit	mg/L

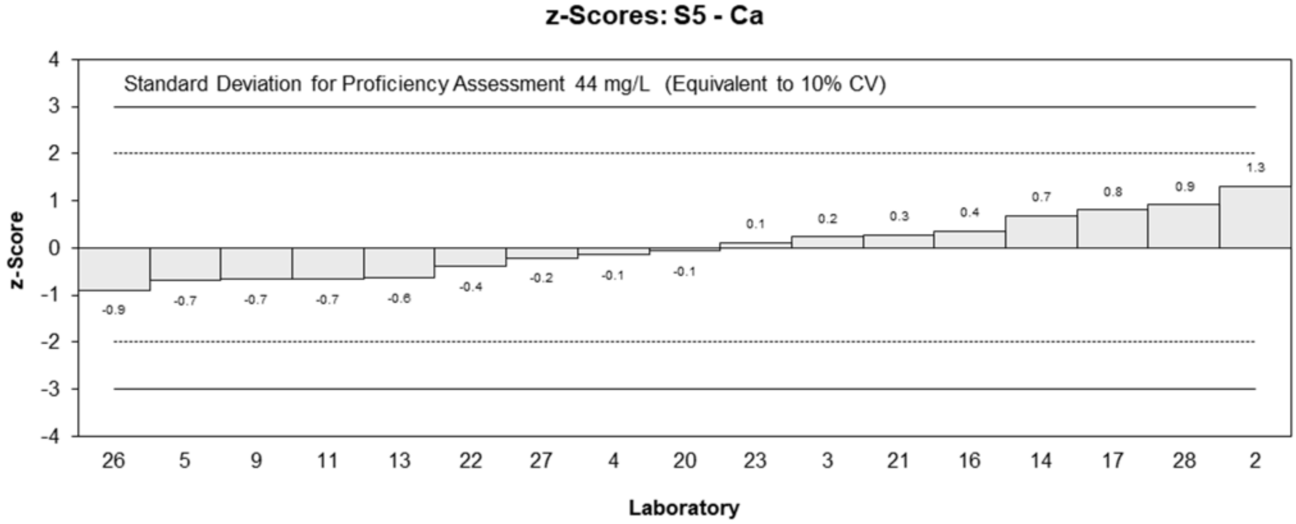
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	496	74.4	1.30	0.74
3	449	79	0.23	0.12
4	433	90	-0.14	-0.07
5	409	43.8	-0.68	-0.63
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	410	41	-0.66	-0.64
10	NT	NT		
11	410	19	-0.66	-1.08
12	NT	NT		
13	410.75	39.11	-0.64	-0.65
14	469	122	0.68	0.24
15	NR	NR		
16	455	91	0.36	0.17
17	474	50	0.80	0.65
18	NT	NT		
19	NT	NT		
20	437	131.1	-0.05	-0.02
21	451	63	0.27	0.18
22	422	24	-0.39	-0.56
23	444	44	0.11	0.10
24	NT	NT		
25	NT	NT		
26	400	92	-0.89	-0.42
27	430	71	-0.21	-0.12
28	479	48	0.91	0.77

Statistics

Assigned Value	439	19
Spike Value	Not Spiked	
Robust Average	439	19
Median	437	24
Mean	440	
N	17	
Max	496	
Min	400	
Robust SD	31	
Robust CV	7%	


Results: S5 - Ca
Assigned Value = 439 ± 19 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
26 5 9 11 13 22 27 4 20 23 3 21 16 14 17 28 2 1 6 7 8 10 12 15 18 19 24 25 Md RA


z-Scores: S5 - Ca
Standard Deviation for Proficiency Assessment 44 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
26 5 9 11 13 22 27 4 20 23 3 21 16 14 17 28 2
-0.9 -0.7 -0.7 -0.7 -0.6 -0.4 -0.2 -0.1 -0.1 0.1 0.2 0.3 0.4 0.7 0.8 0.9 1.3

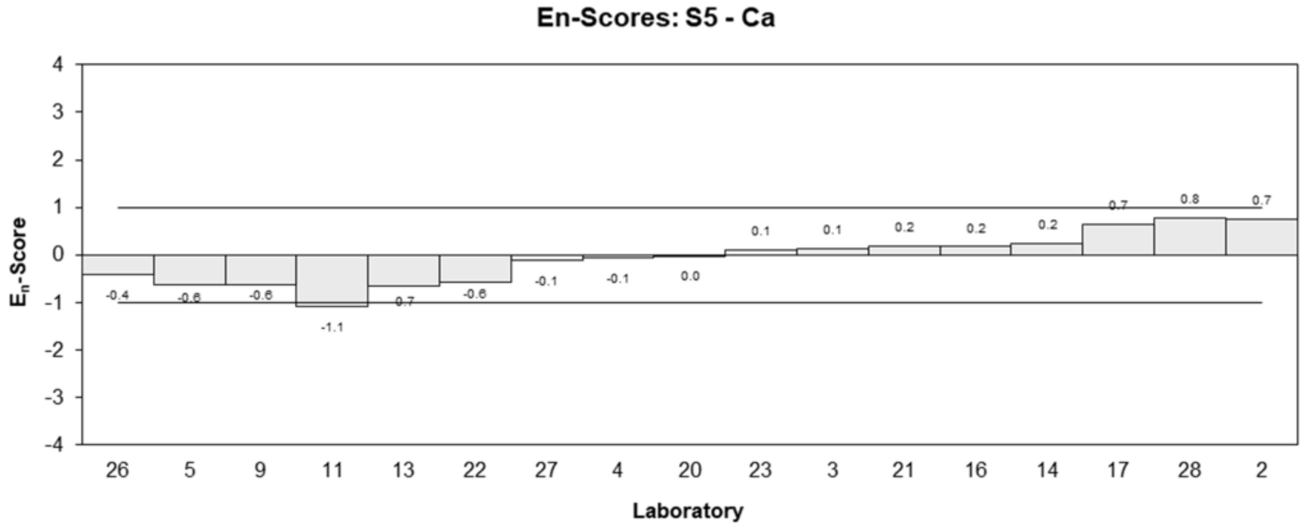

En-Scores: S5 - Ca
En-Score
Laboratory
26 5 9 11 13 22 27 4 20 23 3 21 16 14 17 28 2
-0.4 -0.6 -0.6 -1.1 -0.7 -0.6 -0.1 -0.1 0.0 0.1 0.1 0.2 0.2 0.2 0.7 0.8 0.7

Figure 34

Table 37

Sample Details

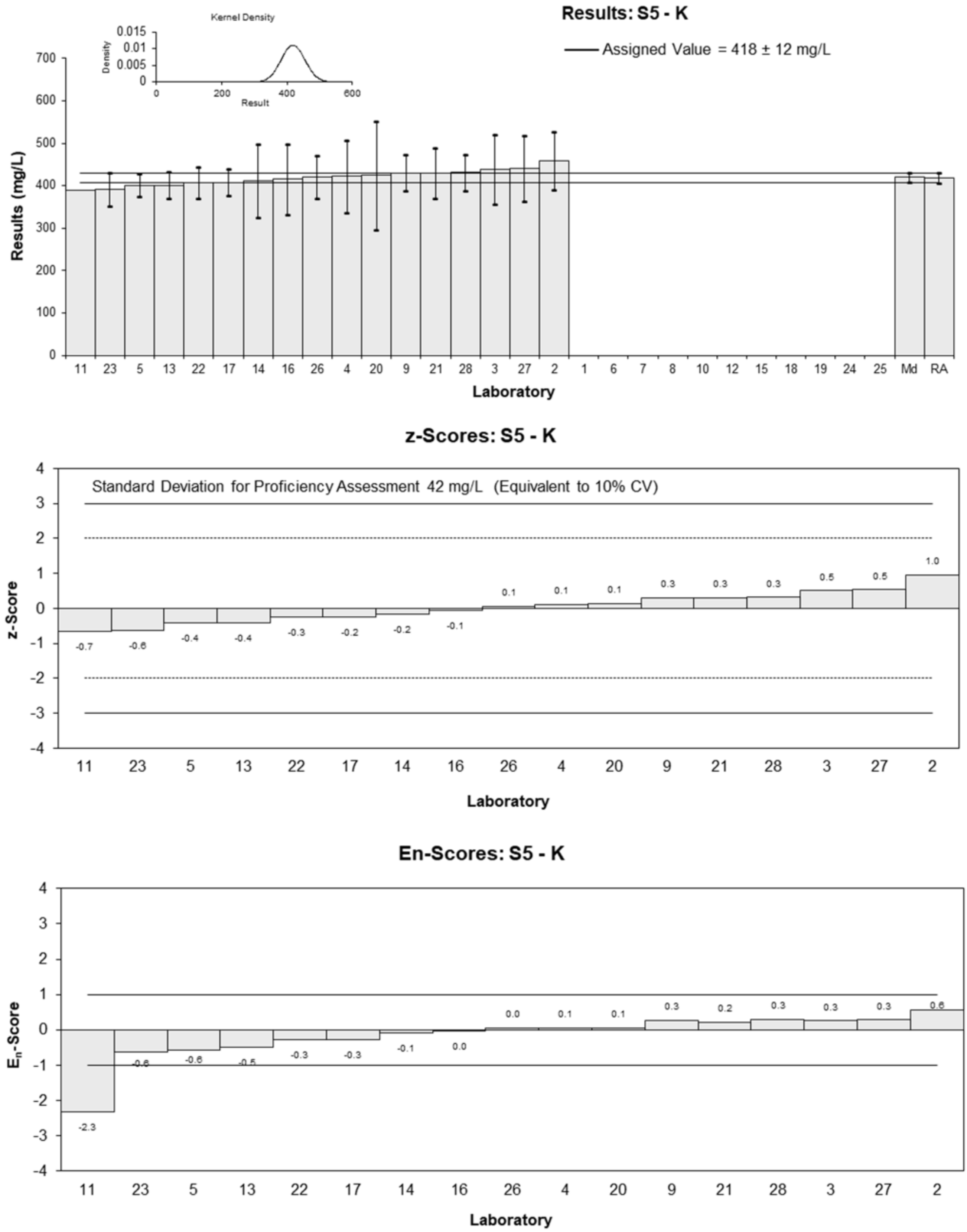
Sample No.	S5
Matrix	Seawater
Analyte	K
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	458	68.7	0.96	0.57
3	439	82	0.50	0.25
4	422	85	0.10	0.05
5	401	26.9	-0.41	-0.58
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	430	43	0.29	0.27
10	NT	NT		
11	390	NR	-0.67	-2.33
12	NT	NT		
13	401.02	31.83	-0.41	-0.50
14	411	86	-0.17	-0.08
15	NR	NR		
16	415	83	-0.07	-0.04
17	408	32	-0.24	-0.29
18	NT	NT		
19	NT	NT		
20	424	127.2	0.14	0.05
21	430	60	0.29	0.20
22	407	38	-0.26	-0.28
23	392	39	-0.62	-0.64
24	NT	NT		
25	NT	NT		
26	420	50.4	0.05	0.04
27	440	77	0.53	0.28
28	431	43	0.31	0.29

Statistics

Assigned Value	418	12
Spike Value	Not Spiked	
Robust Average	418	12
Median	420	11
Mean	419	
N	17	
Max	458	
Min	390	
Robust SD	19	
Robust CV	4.6%	



Results: S5 - K
Assigned Value = 418 ± 12 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
11 23 5 13 22 17 14 16 26 4 20 9 21 28 3 27 2 1 6 7 8 10 12 15 18 19 24 25 Md RA
z-Scores: S5 - K
Standard Deviation for Proficiency Assessment 42 mg/L (Equivalent to 10% CV)
z-Score
-0.7 -0.6 -0.4 -0.4 -0.3 -0.2 -0.2 -0.1 0.1 0.1 0.1 0.3 0.3 0.3 0.5 0.5 1.0
11 23 5 13 22 17 14 16 26 4 20 9 21 28 3 27 2
Laboratory
En-Scores: S5 - K
E_n-Score
-2.3 -0.6 -0.6 -0.5 -0.3 -0.3 -0.1 0.0 0.0 0.1 0.1 0.3 0.2 0.3 0.3 0.3 0.6
11 23 5 13 22 17 14 16 26 4 20 9 21 28 3 27 2
Laboratory

Figure 35

Table 38

Sample Details

Sample No.	S5
Matrix	Seawater
Analyte	Mg
Unit	mg/L

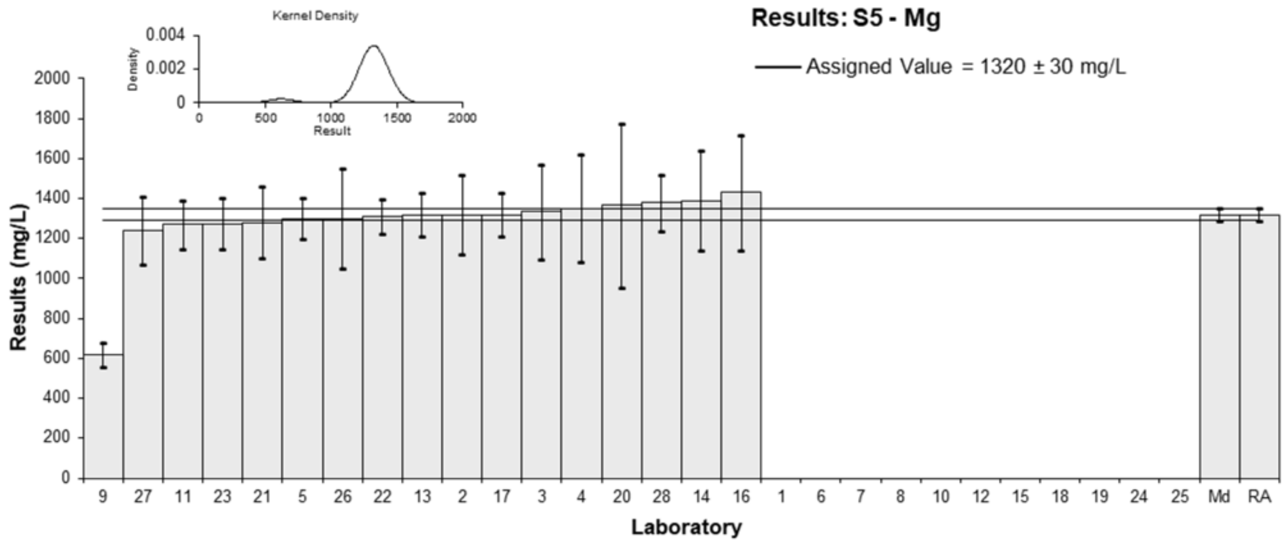
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	1320	198	0.00	0.00
3	1334	237	0.11	0.06
4	1352	270	0.24	0.12
5	1300	102.9	-0.15	-0.19
6	NT	NT		
7	NT	NT		
8	NT	NT		
9*	620	62	-5.30	-10.16
10	NT	NT		
11	1270	120	-0.38	-0.40
12	NT	NT		
13	1318.55	108.94	-0.01	-0.01
14	1390	250	0.53	0.28
15	NR	NR		
16	1430	290	0.83	0.38
17	1320	110	0.00	0.00
18	NT	NT		
19	NT	NT		
20	1365	410	0.34	0.11
21	1280	180	-0.30	-0.22
22	1310	85	-0.08	-0.11
23	1275	127	-0.34	-0.34
24	NT	NT		
25	NT	NT		
26	1300	250	-0.15	-0.08
27	1240	169	-0.61	-0.47
28	1380	140	0.45	0.42

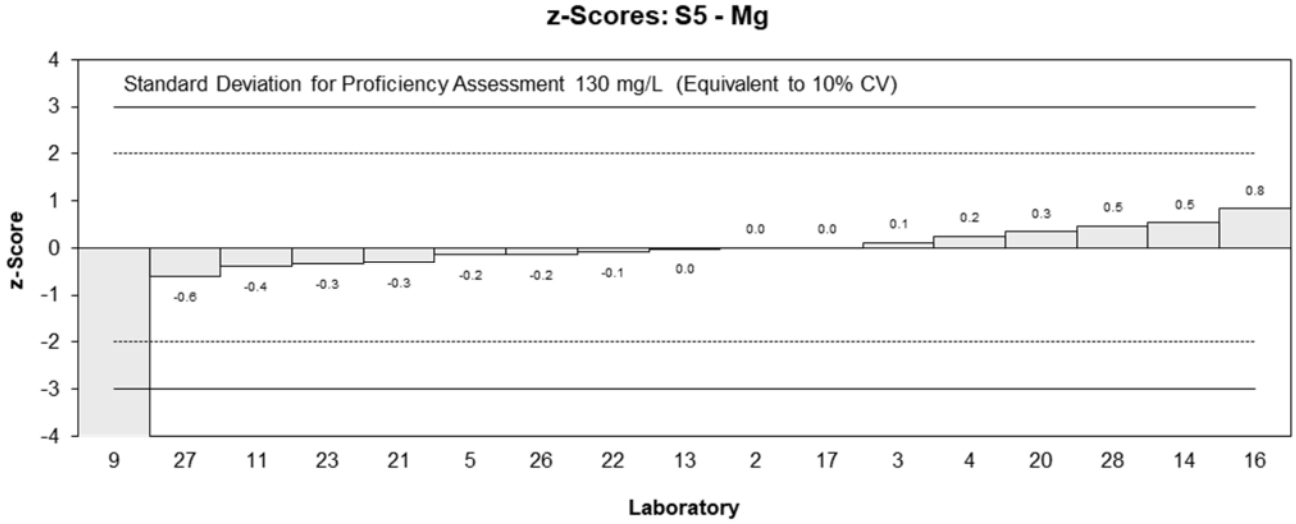
* Outlier, see Section 4.2

Statistics

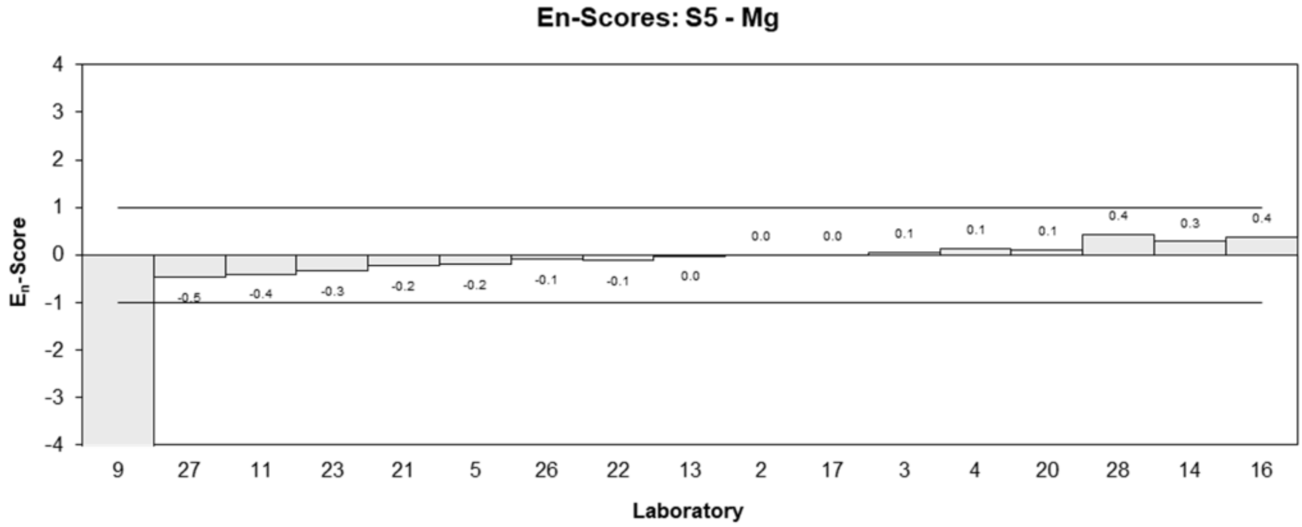
Assigned Value	1320	30
Spike Value	Not Spiked	
Robust Average	1320	30
Median	1320	30
Mean	1280	
N	17	
Max	1430	
Min	620	
Robust SD	56	
Robust CV	4.3%	



Results: S5 - Mg
Assigned Value = 1320 ± 30 mg/L
Kernel Density
Results (mg/L)
Laboratory
9 27 11 23 21 5 26 22 13 2 17 3 4 20 28 14 16 1 6 7 8 10 12 15 18 19 24 25 Md RA



z-Scores: S5 - Mg
Standard Deviation for Proficiency Assessment 130 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
9 27 11 23 21 5 26 22 13 2 17 3 4 20 28 14 16
-0.6 -0.4 -0.3 -0.3 -0.2 -0.2 -0.1 0.0 0.0 0.0 0.1 0.2 0.3 0.5 0.5 0.8



En-Scores: S5 - Mg
E_n-Score
Laboratory
9 27 11 23 21 5 26 22 13 2 17 3 4 20 28 14 16
-0.5 -0.4 -0.3 -0.2 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.1 0.1 0.1 0.4 0.3 0.4

Figure 36

Table 39

Sample Details

Sample No.	S5
Matrix	Seawater
Analyte	Na
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	12000	2400	0.71	0.33
3	11063	2413	-0.12	-0.06
4	12149	2500	0.85	0.37
5	11000	858	-0.18	-0.21
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	10500	105	-0.62	-1.69
10	NT	NT		
11	11000	NR	-0.18	-0.50
12	NT	NT		
13	10841.22	836.96	-0.32	-0.39
14	11400	1710	0.18	0.11
15	NR	NR		
16	11200	2200	0.00	0.00
17	11100	1200	-0.09	-0.08
18	NT	NT		
19	NT	NT		
20	12013	3603	0.73	0.22
21	10800	1500	-0.36	-0.26
22	10900	1240	-0.27	-0.23
23	10782	1078	-0.37	-0.36
24	NT	NT		
25	NT	NT		
26	11000	1700	-0.18	-0.11
27	10800	1210	-0.36	-0.31
28	12700	1270	1.34	1.13

Statistics

Assigned Value	11200	400
Spike Value	Not Spiked	
Robust Average	11200	400
Median	11000	200
Mean	11200	
N	17	
Max	12700	
Min	10500	
Robust SD	590	
Robust CV	5.2%	

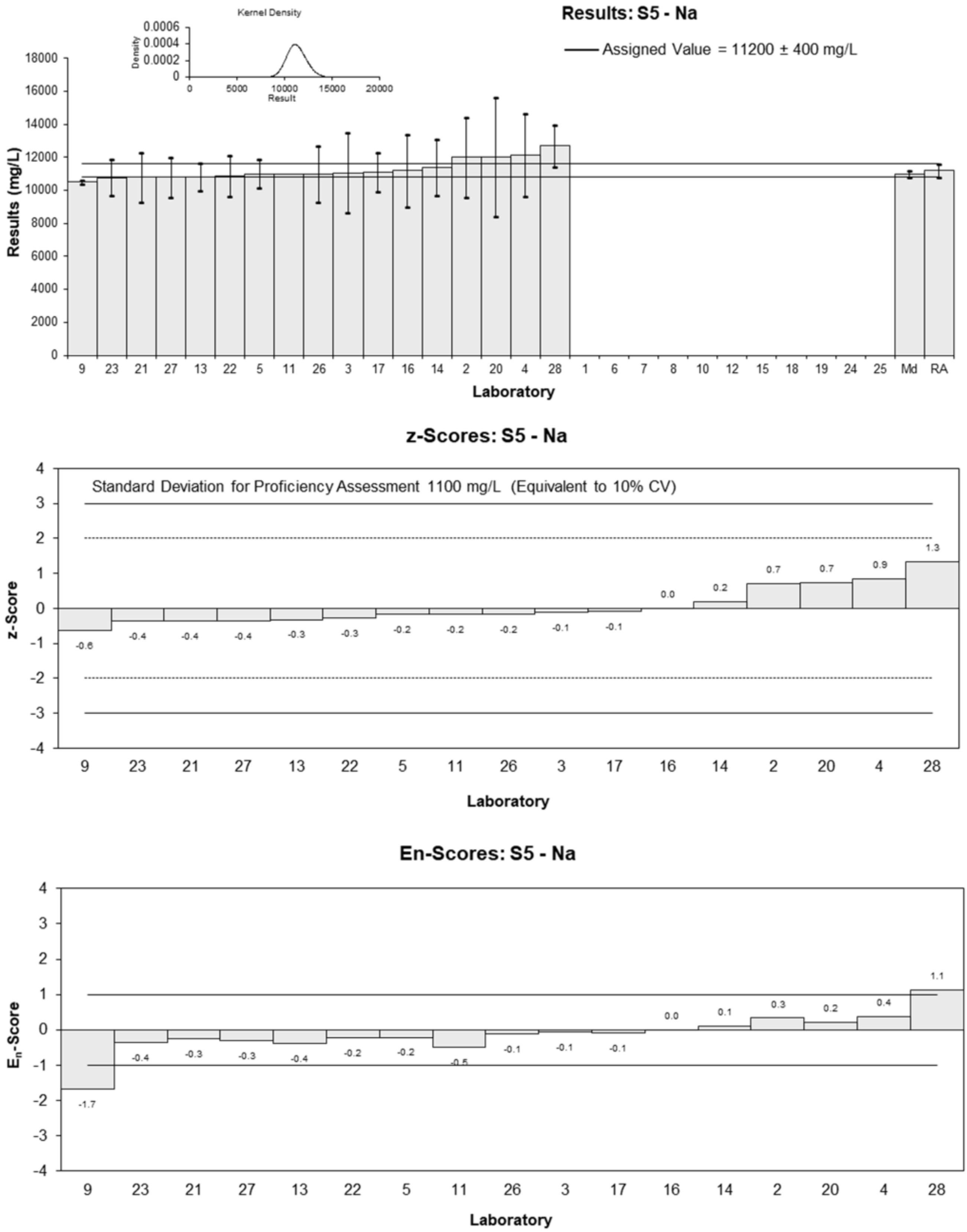

Results: S5 - Na
Assigned Value = 11200 ± 400 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
9 23 21 27 13 22 5 11 26 3 17 16 14 2 20 4 28 1 6 7 8 10 12 15 18 19 24 25 Md RA
z-Scores: S5 - Na
Standard Deviation for Proficiency Assessment 1100 mg/L (Equivalent to 10% CV)
z-Score
-0.6 -0.4 -0.4 -0.4 -0.3 -0.3 -0.2 -0.2 -0.2 -0.1 -0.1 0.0 0.2 0.7 0.7 0.9 1.3
9 23 21 27 13 22 5 11 26 3 17 16 14 2 20 4 28
Laboratory
En-Scores: S5 - Na
En-Score
-1.7 -0.4 -0.3 -0.3 -0.4 -0.2 -0.2 -0.5 -0.1 -0.1 -0.1 0.0 0.1 0.3 0.2 0.4 1.1
9 23 21 27 13 22 5 11 26 3 17 16 14 2 20 4 28
Laboratory

Figure 37

Table 40

Sample Details

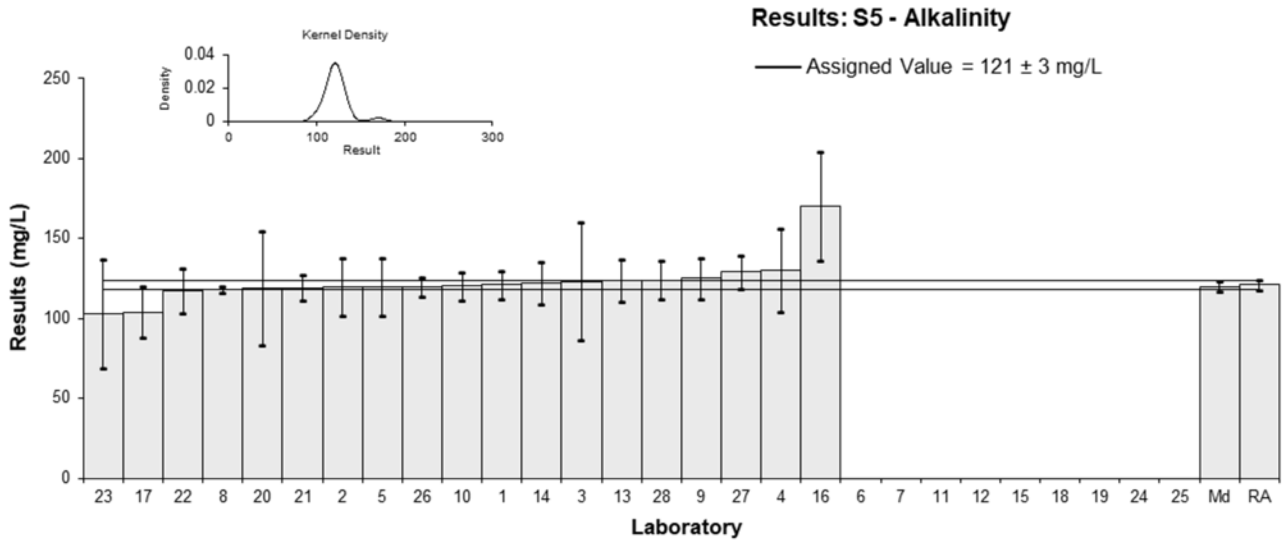
Sample No.	S5
Matrix	Seawater
Analyte	Alkalinity
Unit	mg/L

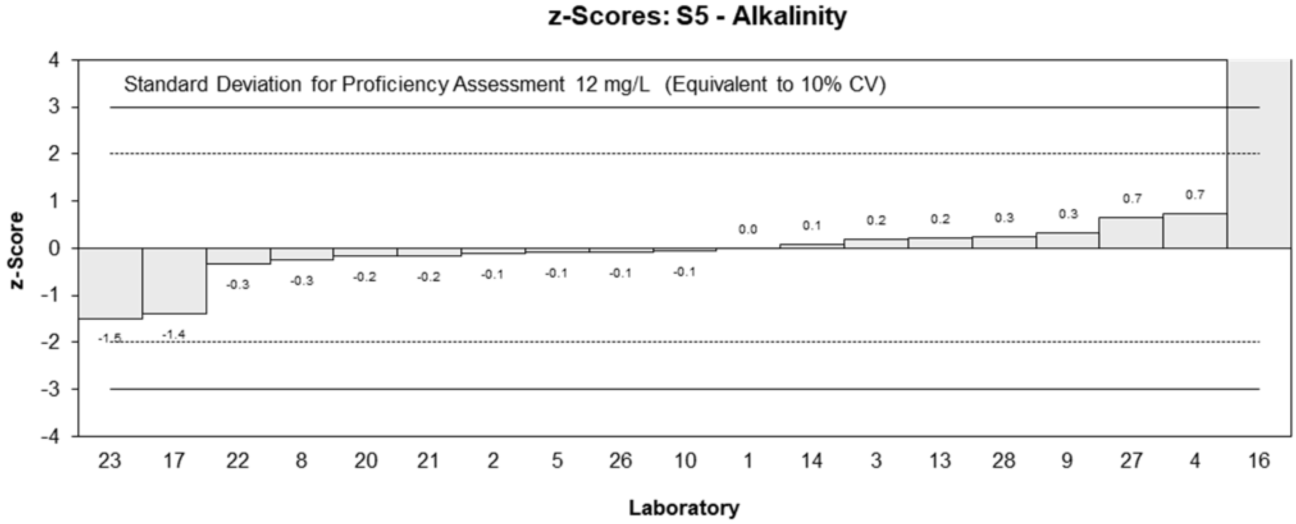
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	121	9	0.00	0.00
2	119.53	17.93	-0.12	-0.08
3	123.2	36.96	0.18	0.06
4	130	26	0.74	0.34
5	120	17.9	-0.08	-0.06
6	NT	NT		
7	NT	NT		
8	118	2.1	-0.25	-0.82
9	125	12.5	0.33	0.31
10	120.2	8.58	-0.07	-0.09
11	NT	NT		
12	NT	NT		
13	123.7	12.98	0.22	0.20
14	122	13	0.08	0.07
15	NR	NR		
16	170	34	4.05	1.44
17	104	16.1	-1.40	-1.04
18	NT	NT		
19	NT	NT		
20	119	35.7	-0.17	-0.06
21	119	8	-0.17	-0.23
22	117	14	-0.33	-0.28
23	103	34	-1.49	-0.53
24	NT	NT		
25	NT	NT		
26	120	6	-0.08	-0.15
27	129	10.3	0.66	0.75
28	124	12	0.25	0.24

Statistics

Assigned Value	121	3
Spike Value	Not Spiked	
Robust Average	121	3
Median	120	3
Mean	123	
N	19	
Max	170	
Min	103	
Robust SD	5.2	
Robust CV	4.3%	


Results: S5 - Alkalinity
Assigned Value = 121 ± 3 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
23 17 22 8 20 21 2 5 26 10 1 14 3 13 28 9 27 4 16 6 7 11 12 15 18 19 24 25 Md RA


z-Scores: S5 - Alkalinity
Standard Deviation for Proficiency Assessment 12 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
23 17 22 8 20 21 2 5 26 10 1 14 3 13 28 9 27 4 16

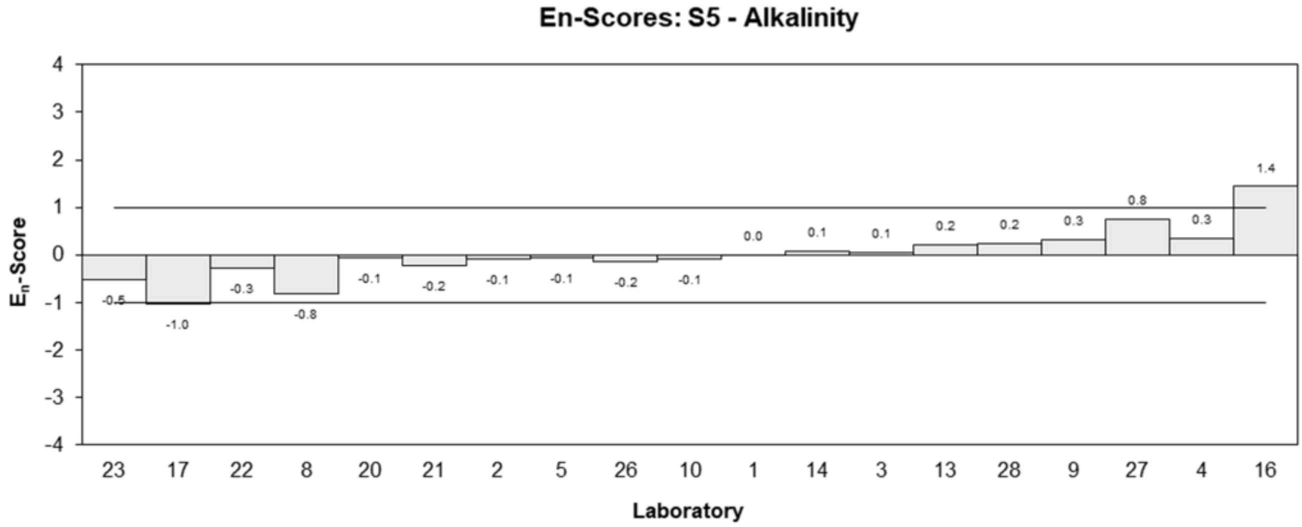

En-Scores: S5 - Alkalinity
En-Score
Laboratory
23 17 22 8 20 21 2 5 26 10 1 14 3 13 28 9 27 4 16

Figure 38

Table 41

Sample Details

Sample No.	S5
Matrix	Seawater
Analyte	EC
Unit	µS/cm

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	54900	1650	0.15	0.43
2	58300	5830	0.78	0.71
3	53307	15992	-0.15	-0.05
4	54000	10800	-0.02	-0.01
5	53600	4170	-0.09	-0.12
6	NT	NT		
7	NT	NT		
8	56000	2380	0.35	0.75
9	52820	5282	-0.24	-0.24
10	NT	NT		
11	NT	NT		
12	NT	NT		
13	53455.71	4048.6	-0.12	-0.16
14	52800	5808	-0.24	-0.22
15	NR	NR		
16	55000	8300	0.17	0.11
17	53100	10600	-0.18	-0.09
18	NT	NT		
19	NT	NT		
20	54669	16400	0.11	0.03
21	53200	2700	-0.17	-0.32
22	56000	3560	0.35	0.52
23	57550	5750	0.64	0.59
24	NT	NT		
25	NT	NT		
26	53300	530	-0.15	-0.77
27	52430	524.3	-0.31	-1.60
28	53000	5300	-0.20	-0.20

Statistics

Assigned Value	54100	900
Spike Value	Not Spiked	
Robust Average	54100	900
Median	53500	600
Mean	54300	
N	18	
Max	58300	
Min	52430	
Robust SD	1500	
Robust CV	2.8%	

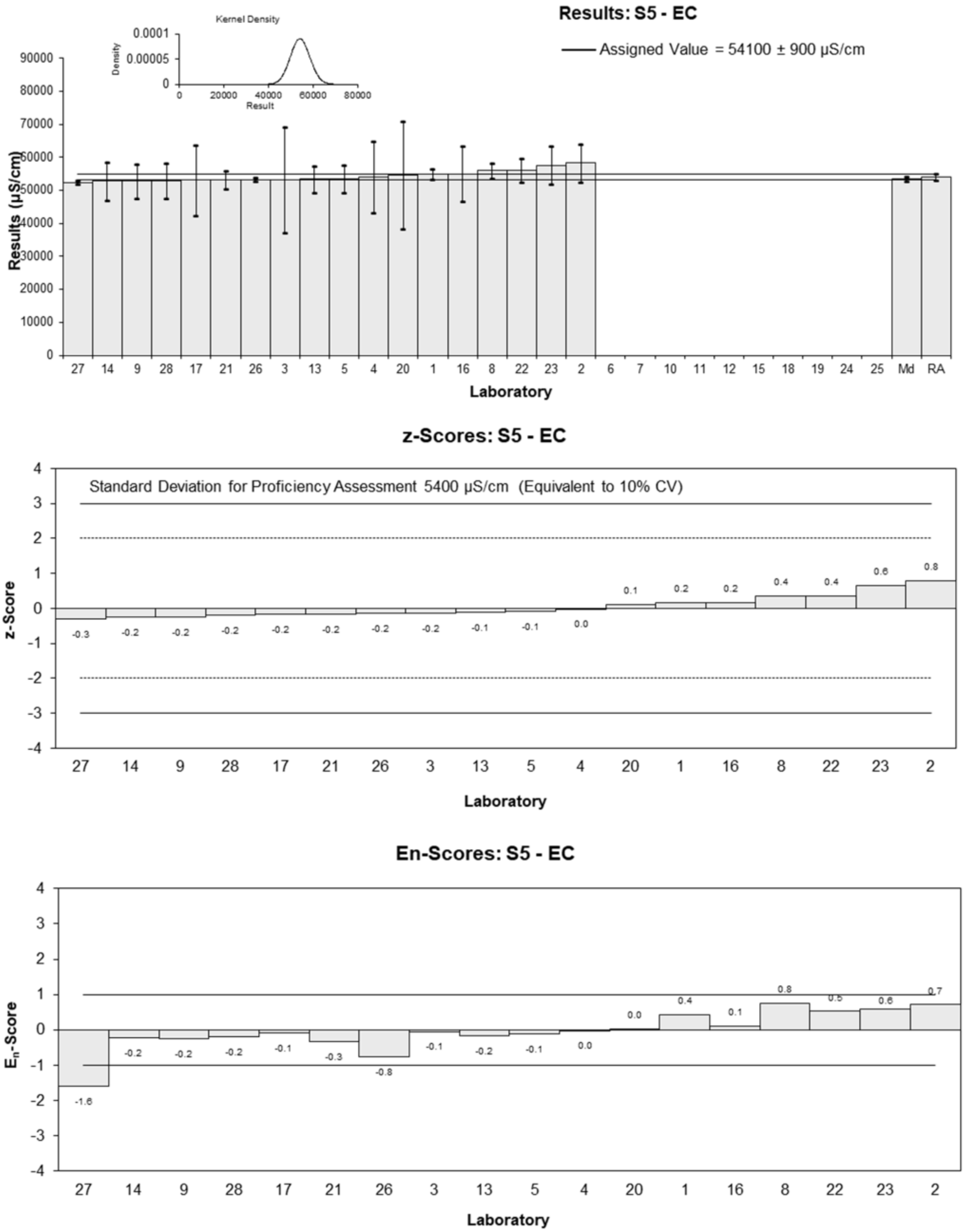

Results: S5 - EC
Assigned Value = 54100 ± 900 µS/cm
Kernel Density
Density
Result
Results (µS/cm)
Laboratory
27 14 9 28 17 21 26 3 13 5 4 20 1 16 8 22 23 2 6 7 10 11 12 15 18 19 24 25 Md RA
z-Scores: S5 - EC
Standard Deviation for Proficiency Assessment 5400 µS/cm (Equivalent to 10% CV)
z-Score
-0.3 -0.2 -0.2 -0.2 -0.2 -0.2 -0.2 -0.2 -0.1 -0.1 0.0 0.1 0.2 0.2 0.4 0.4 0.6 0.8
27 14 9 28 17 21 26 3 13 5 4 20 1 16 8 22 23 2
Laboratory
En-Scores: S5 - EC
En-Score
-1.6 -0.2 -0.2 -0.2 -0.1 -0.3 -0.8 -0.1 -0.2 -0.1 0.0 0.0 0.4 0.1 0.8 0.5 0.6 0.7
27 14 9 28 17 21 26 3 13 5 4 20 1 16 8 22 23 2
Laboratory

Figure 39

Table 42

Sample Details

Sample No.	S5
Matrix	Seawater
Analyte	pH

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	8.06	0.13	-0.04	-0.07
2	8.06	0.30	-0.04	-0.03
3	8.05	0.2	-0.07	-0.10
4	8.2	0.3	0.46	0.43
5	8.07	0.058	0.00	0.00
6	NT	NT		
7	NT	NT		
8	8.09	0.073	0.07	0.23
9	8.09	0.81	0.07	0.02
10	NT	NT		
11	NT	NT		
12	NT	NT		
13	8.03	0.13	-0.14	-0.29
14	8.2	0.2	0.46	0.63
15	NR	NR		
16	8.1	0.8	0.11	0.04
17	7.82	0.081	-0.89	-2.63
18	NT	NT		
19	NT	NT		
20	7.95	0.3	-0.42	-0.39
21	8.2	0.2	0.46	0.63
22	7.96	0.06	-0.39	-1.41
23	8.1	0.2	0.11	0.15
24	NT	NT		
25	NT	NT		
26	8	NR	-0.25	-1.40
27	8.1	0.06	0.11	0.38
28	8.07	0.2	0.00	0.00

Statistics

Assigned Value	8.07	0.05
Spike Value	Not Spiked	
Robust Average	8.07	0.05
Median	8.07	0.03
Mean	8.06	
N	18	
Max	8.2	
Min	7.82	
Robust SD	0.089	
Robust CV	1.1%	

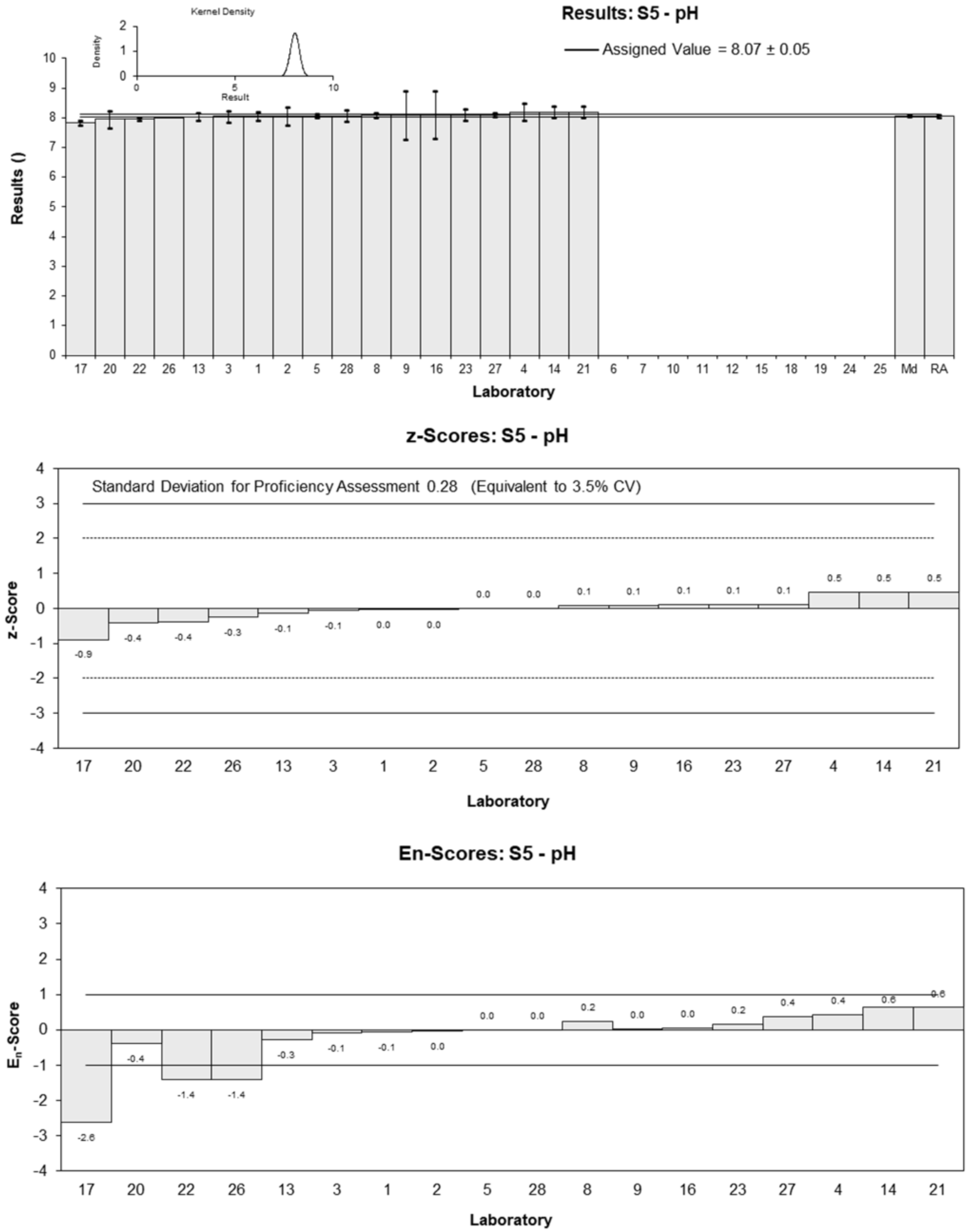

Results: S5 - pH
Assigned Value = 8.07 ± 0.05
Kernel Density
Density
Result
Results ()
Laboratory
17 20 22 26 13 3 1 2 5 28 8 9 16 23 27 4 14 21 6 7 10 11 12 15 18 19 24 25 Md RA
z-Scores: S5 - pH
Standard Deviation for Proficiency Assessment 0.28 (Equivalent to 3.5% CV)
-0.9 -0.4 -0.4 -0.3 -0.1 -0.1 0.0 0.0 0.0 0.0 0.1 0.1 0.1 0.1 0.1 0.5 0.5 0.5
z-Score
Laboratory
17 20 22 26 13 3 1 2 5 28 8 9 16 23 27 4 14 21
En-Scores: S5 - pH
-2.6 -0.4 -1.4 -1.4 -0.3 -0.1 -0.1 0.0 0.0 0.0 0.2 0.0 0.0 0.2 0.4 0.4 0.6 0.6
En-Score
Laboratory
17 20 22 26 13 3 1 2 5 28 8 9 16 23 27 4 14 21

Figure 40

Table 43

Sample Details

Sample No.	S5
Matrix	Seawater
Analyte	Silica (as SiO_2)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.52	0.04	-0.61	-0.91
2	NT	NT		
3	NT	NT		
4	0.5	0.1	-0.84	-0.67
5	0.61	0.072	0.44	0.46
6	NT	NT		
7	NT	NT		
8	0.61	0.041	0.44	0.66
9	0.5	0.05	-0.84	-1.11
10*	2.5	0.25	22.47	7.61
11	NT	NT		
12	NT	NT		
13	0.569	0.08	-0.03	-0.03
14*	1.1	0.2	6.15	2.59
15	0.5956	0.0088	0.28	0.56
16	0.774	0.155	2.35	1.26
17	0.58	0.12	0.09	0.06
18	NT	NT		
19	NT	NT		
20	< 10	NR		
21	NT	NT		
22	0.50	0.05	-0.84	-1.11
23	NT	NT		
24	0.5903	0.0088	0.21	0.44
25	0.6068	0.0090	0.41	0.83
26	<0.10	NR		
27	0.60	0.07	0.33	0.35
28	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.572	0.041
Spike Value*	0.301	0.015
Robust Average	0.602	0.063
Median	0.596	0.025
Mean	0.74	
N	15	
Max	2.5	
Min	0.5	
Robust SD	0.098	
Robust CV	16%	

*Incurred value not included.

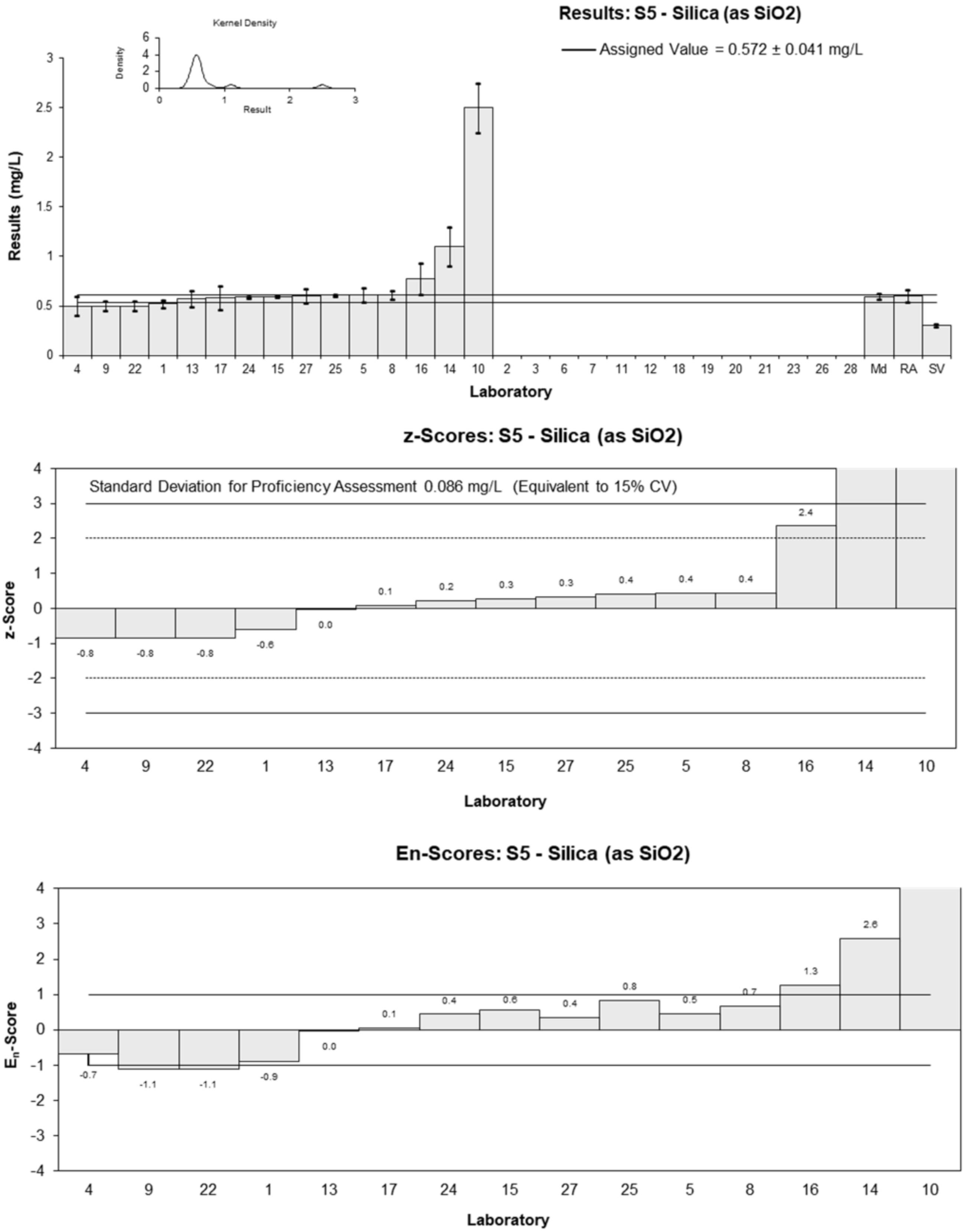

Results: S5 - Silica (as SiO2)
Assigned Value = 0.572 ± 0.041 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
4 9 22 1 13 17 24 15 27 25 5 8 16 14 10 2 3 6 7 11 12 18 19 20 21 23 26 28 Md RA SV
z-Scores: S5 - Silica (as SiO2)
Standard Deviation for Proficiency Assessment 0.086 mg/L (Equivalent to 15% CV)
z-Score
-0.8 -0.8 -0.8 -0.6 0.0 0.1 0.2 0.3 0.3 0.4 0.4 0.4 2.4
4 9 22 1 13 17 24 15 27 25 5 8 16 14 10
Laboratory
En-Scores: S5 - Silica (as SiO2)
En-Score
-0.7 -1.1 -1.1 -0.9 0.0 0.1 0.4 0.6 0.4 0.8 0.5 0.7 1.3 2.6
4 9 22 1 13 17 24 15 27 25 5 8 16 14 10
Laboratory

Figure 41

Table 44

Sample Details

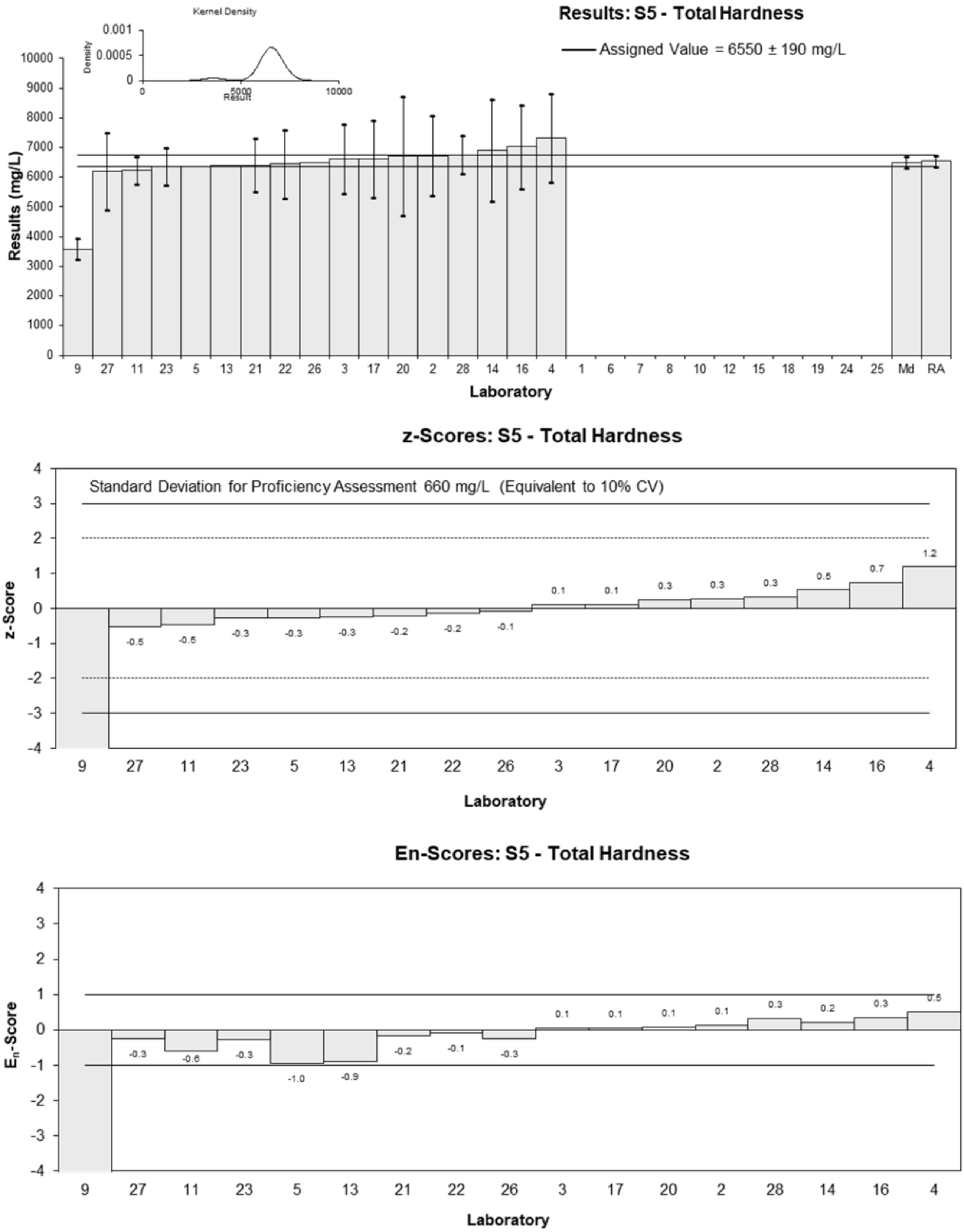
Sample No.	S5
Matrix	Seawater
Analyte	Total Hardness
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	6720	1340	0.26	0.13
3	6615	1169	0.10	0.05
4	7326	1500	1.18	0.51
5	6370	NR	-0.27	-0.95
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	3588	358	-4.52	-7.31
10	NT	NT		
11	6240	470	-0.47	-0.61
12	NT	NT		
13	6379.67	NR	-0.26	-0.90
14	6900	1725	0.53	0.20
15	NR	NR		
16	7025	1405	0.73	0.34
17	6620	1300	0.11	0.05
18	NT	NT		
19	NT	NT		
20	6715	2015	0.25	0.08
21	6400	900	-0.23	-0.16
22	6450	1150	-0.15	-0.09
23	6359	635	-0.29	-0.29
24	NT	NT		
25	NT	NT		
26	6500	NR	-0.08	-0.26
27	6200	1310	-0.53	-0.26
28	6760	650	0.32	0.31

Statistics

Assigned Value	6550	190
Spike Value	Not Spiked	
Robust Average	6550	190
Median	6500	190
Mean	6420	
N	17	
Max	7326	
Min	3588	
Robust SD	320	
Robust CV	4.9%	



Results: S5 - Total Hardness
Assigned Value = 6550 ± 190 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
z-Scores: S5 - Total Hardness
Standard Deviation for Proficiency Assessment 660 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S5 - Total Hardness
E_n-Score
Laboratory

Figure 42

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Assigned Values for the tests in this study 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'.[6] Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value (see subchapters 4.2 and 4.3).[3,6] Appendix 3 sets out the calculation for the assigned value of sulphate in Sample S1 and its associated uncertainty.

No assigned value was set for total dissolved phosphorus in S1 because the reported results were too variable. Participants may still compare their reported result for total dissolved phosphorus with other participants' results.

Spike Values where applicable, includes both the incurred value and the fortified value, except for bromide in Sample S2, and silica in Sample S5.

Traceability: The assigned values are not traceable to any external reference; they are traceable to the consensus of participants' results deriving from a variety of measurement methods and (presumably) a variety of calibrators. So, although expressed in SI units, the metrological traceability of the assigned values 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 676 numerical results, 663 (98%) 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 240% of the reported value. The participants used a wide variety of procedures to evaluate the expanded measurement uncertainty. These are presented in Table 1.

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 evaluations 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 42). 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 SDPA, then this should be reviewed as suspect. For example, 19 laboratories' results were included in the assessment of the assigned value for ammonia-N in S1. The uncertainty of the assigned value as determined from the robust standard deviation of the 19 laboratories' results is 0.0017 mg/L (9.2% of the assigned value). Laboratory 17 reported an uncertainty of 0.0005 mg/L (2.4% of their reported value) which may have been underestimated, as an uncertainty evaluated from one measurement cannot be smaller than the uncertainty evaluated from 19 measurements in different laboratories.
Alternatively, uncertainties for dissolved organic carbon in S1 larger than 0.54 mg/L (the uncertainty of the assigned value, 0.19 mg/L, plus the allowable variation from the assigned value, the SDPA of 0.174 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 13 for dissolved organic carbon in sample S1 (1.84 mg/L) might have been over-estimated.

Laboratories 8, 12 and 23 should assess their procedure used for evaluating measurement uncertainty, as some of their reported uncertainties were under-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.

For consistency, the result of .30 for the uncertainty of pH in Sample S3 reported by Laboratory 2 has been transcribed as 0.30.

Laboratory 26 reported values of 1,700 mg/L for S1 Chloride and 2,000 mg/L for S1 Sulphate. The study coordinator transcribed these results without commas, recording them as 1700 mg/L and 2000 mg/L. The associated uncertainties were provided without punctuation and were recorded as reported, without modification

Laboratories 7, 12, 14, 23 and 26 all reported measurement uncertainty greater than or equal to their reported result.

Laboratories 20 and 23 reported a measurement uncertainty for 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 3588 ± 358 mg/L, it is better to report 3590 ± 360 mg/L or, instead of 17.12 ± 1.66 mg/L, it is better to report 17.1 ± 1.7 mg/L.[9]

6.3 z-Score

The z-score compares the participant's deviation from the assigned value with the standard deviation for proficiency assessment (SDPA).

The SDPA defines acceptable performance in a proficiency test. SDPAs equivalent to 3.5% to 25% performance coefficient of variation (PCV) were used to calculate z-scores in this study. Unlike the standard deviation based on the between-laboratory CV, setting the SDPA as a realistic value enables z-scores to be used as fixed reference value points for the assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson/Horwitz equation[7] and the between-laboratory coefficient of variation from reported results in this study are presented for comparison in Table 45.

The dispersal of participants' z-scores is presented in Figure 43 (by laboratory code) and in Figure 45 (by analyte).

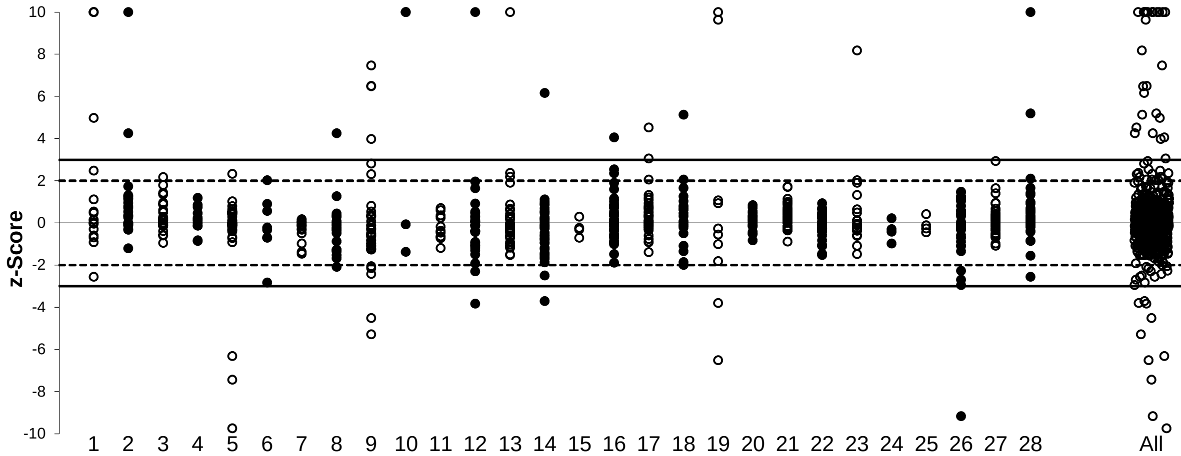
Of 663 results for which z-scores were calculated, 598 (90%) returned an acceptable score of $|z| \leq 2.0$ and 28 (4%) were questionable at $2.0 < |z| < 3.0$.

Participants with multiple z-scores greater than 2 or less than -2 should check for laboratory bias (Figure 43).

Laboratories **16** and **22** reported results for all 40 tests for which a z-score was calculated, and Laboratory **22** returned acceptable z-scores for all of these.

All results reported by Laboratories **21** (36), **20** (19), **7** (13), **4** (12), **11** (12), **15** (4), **24** (4), and **25** (4) also returned acceptable z scores.

A summary of participants' performance is presented in Figure 46.



Scores of >10 have been plotted as 10.

Figure 43 z-Score Dispersal by Laboratory

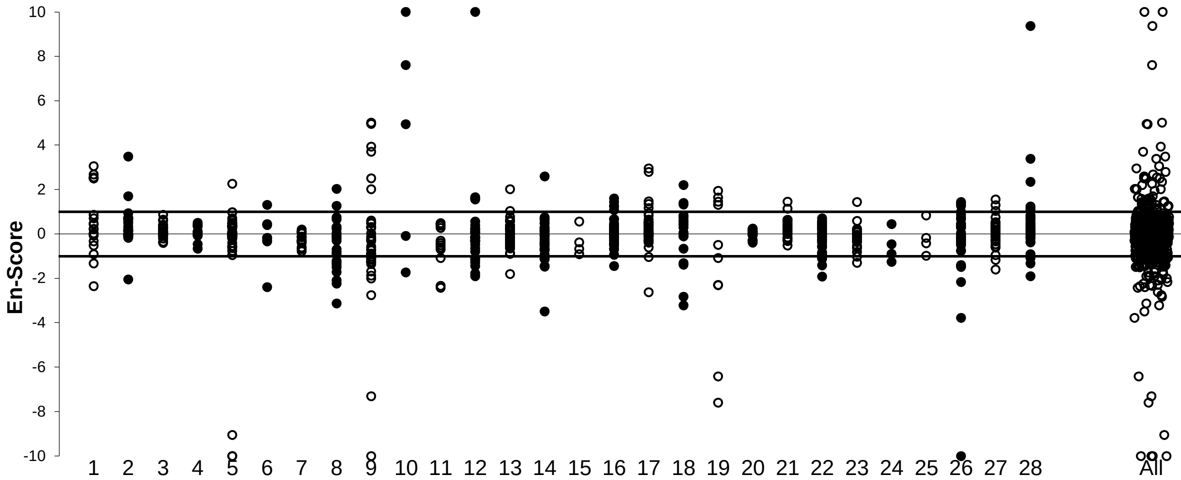
6.4 E_n-score

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 44. 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 663 results for which E_n-scores were calculated, 529 (80%) 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 **22** returned the highest number of acceptable E_n-scores (36). All results reported by Laboratories **3** (25), **20** (19), **7** (13), **4** (12), **15** (4), and **25** (4) returned acceptable E_n-scores.



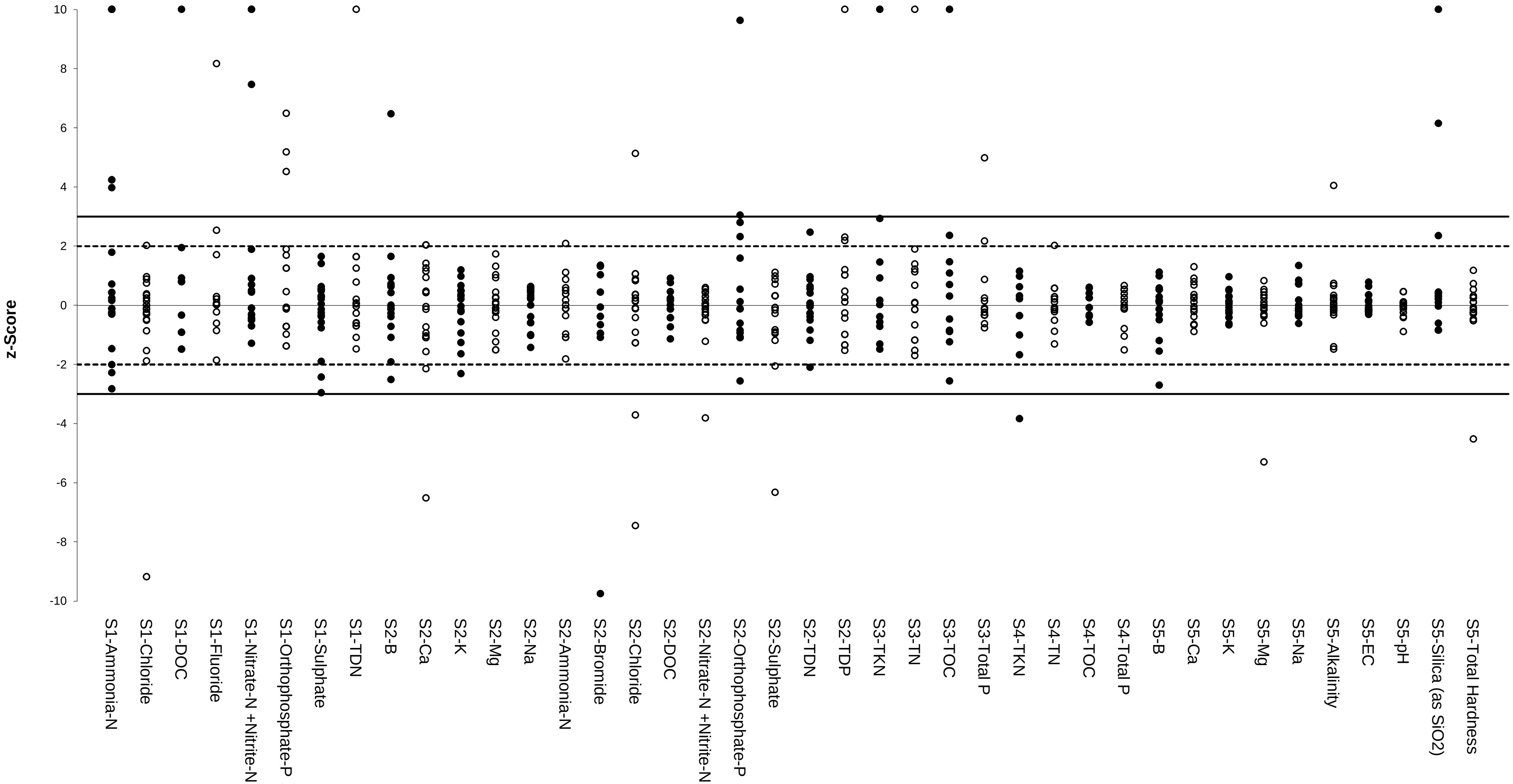
Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 44 E_n-Score Dispersal by Laboratory

Table 45 Standard Deviation for Proficiency Assessment, Thompson/Horwitz, and Between-Laboratory CV

Sample	Test	Assigned value (mg/L)	SDPA (as PCV, %)	Thompson/ Horwitz CV (%)	Between-Laboratory CV* (%)
S1	Ammonia-N	0.0184	20	22	14
S1	Chloride	20800	10	3.6	7.2
S1	DOC	1.16	15	16	20
S1	Fluoride	0.797	20	17	14
S1	Nitrate-N + Nitrite-N	0.0335	15	22	11
S1	Orthophosphate-P	0.0061	25	22	30
S1	Sulphate	2840	10	4.8	8.5
S1	TDN	0.128	20	22	22
S1	TDP	Not Set	Not Set	NA	63%
S2	B	0.668	10	17	9.6
S2	Ca	19.1	10	10	15
S2	K	2.86	10	14	8.6
S2	Mg	7.07	10	12	9.7
S2	Na	48.9	10	8.9	7
S2	Ammonia-N	0.0409	20	22	17
S2	Bromide	0.707	10	17	11
S2	Chloride	85.9	10	8.2	8.8
S2	DOC	4.49	15	13	9.2
S2	Nitrate-N + Nitrite-N	0.367	15	19	6.1
S2	Orthophosphate-P	0.0205	20	22	24
S2	Sulphate	25.2	10	9.8	8.3
S2	TDN	0.584	15	17	12
S2	TDP	0.0274	20	22	28
S3	TKN	0.271	20	19	26
S3	TN	0.389	15	18	20
S3	TOC	1.72	15	15	25
S3	Total P	0.207	10	20	6.5
S4	TKN	0.401	15	18	15
S4	TN	0.921	15	16	8.2
S4	TOC	6.05	10	12	5
S4	Total P	0.152	10	21	6.2
S5	B	4.66	10	13	8
S5	Ca	439	10	6.4	7
S5	K	418	10	6.4	4.6
S5	Mg	1320	10	5.4	3.9
S5	Na	11200	10	3.9	5.2
S5	Alkalinity	121	10	7.8	4.3
S5	EC	54100	10	NA	2.8
S5	pH	8.07	3.5	NA	1.1
S5	Silica (as SiO_2)	0.572	15	17	10
S5	Total Hardness	6550	10	4.3	4.9

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



Scores of >10 have been plotted as 10.

Figure 45 z-Score Dispersal by Analyte

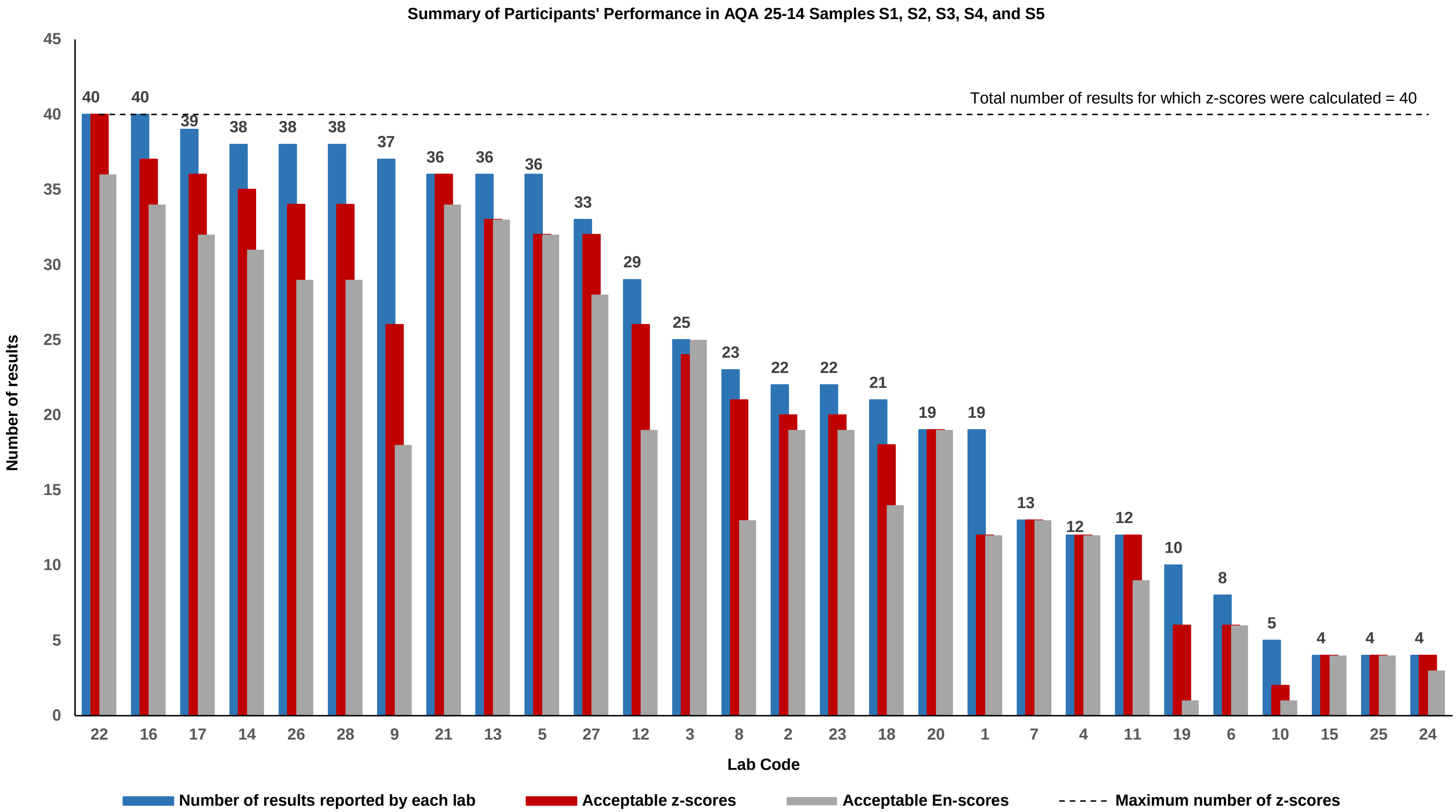


Figure 46 Summary of Participants' Performance

Table 46 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	0.0184	20800	1.16	0.797	0.0335	0.0061	2840	0.128	Not Set
HV	0.0182	NA	NA	NA	0.0330	0.0060	NA	0.108	0.0083
1	0.11	21100	NT	0.8	0.03	<0.01	2990	1.2	0.20
2	0.034	20169.97	<5	NT	<0.02	NT	2744.07	NT	<0.5
3	0.025	22635	< 5	< 10	< 0.05	< 0.05	2676	0.1123	< 0.05
4	< 0.2	19000	NT	< 10	< 0.1	< 0.1	2800	NT	NT
5	0.018	20800	1	0.8	0.036	0.006	2990	0.148	0.007
6	0.008	25000	1.1	0.76	0.038	0.005	3000	0.11	0.04
7	0.019	NR	NR	NR	0.031	0.004	NR	0.09	0.004
8	0.034	19800	NT	0.8	0.027	0.008	2920	<0.1	<0.005
9	0.033	20200	1.3	NT	0.071	0.016	2150	0.1	0.04
10	0.5	NT	NT	NT	0.089	0.004	NT	NT	NT
11	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	<0.005	20600	1.5	0.81	0.45	0.0068	2850	0.17	0.012
13	<0.02	17604.84	3.07	0.844	0.043	<0.01	2770.35	<0.1	0.0236
14	0.018	16900	<1.0	0.83	0.038	0.005	2620	0.113	NR
15	0.0175	NT	NT	NT	0.0319	0.0050	NT	NT	NT
16	0.020	21500	0.9	1.2	0.033	0.009	2300	0.11	0.012
17	0.021	20500	1	0.7	0.037	0.013	2930	0.127	0.015
18	0.011	22370	1.3	0.5	0.031	0.008	3310	0.13	0.01
19	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	<0.1	19730	NT	< 10	< 0.1	< 0.1	2929	NT	< 0.1
21	0.0193	21600	1.32	1.07	0.0357	0.00867	2980	0.129	0.0152
22	0.013	21300	0.9	0.8	0.033	0.006	3020	0.121	<0.005
23	<0.2	20297	NT	2.1	NT	NT	2732	NT	NT
24	0.0173	NT	NT	NT	0.0314	0.0046	NT	NT	NT
25	0.0174	NT	NT	NT	0.0312	0.0059	NT	NT	NT
26	0.01	1700	1.3	<10	0.032	0.006	2000	0.16	<0.01
27	0.02	20818	NR	NR	0.03	<0.002	2902	0.17	0.007
28	0.300	22800	<1	0.66	0.037	0.014	3240	0.133	0.014

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

Table 47 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)	Ammonia-N (mg/L)	Bromide (mg/L)	Chloride (mg/L)	DOC (mg/L)	Nitrate-N+Nitrite-N (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
AV	0.668	19.1	2.86	7.07	48.9	0.0409	0.707	85.9	4.49	0.367	0.0205	25.2	0.584	0.0274
HV	NA	NA	NA	NA	NA	0.0435	NA	NA	NA	0.405	0.0252	NA	0.58	0.0287
1	NT	NT	NT	NT	NT	<0.01	NT	78	NT	0.35	0.01	28	0.8	0.03
2	0.668	21.5	3.2	8.29	51.5	0.04	NT	89.12	<5	0.3	NT	26.00	NT	<0.5
3	0.642	21.81	2.852	7.260	48.91	0.04	0.8023	93.42	< 5	0.40	< 0.05	22.78	0.668	< 0.05
4	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
5	0.71	20	3	7	51	0.045	0.018	21.9	4	0.397	0.030	9.26	0.59	0.033
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NR	NR	NR	NR	NR	0.041	NR	NR	NR	0.37	0.021	NR	0.56	0.022
8	NT	NT	NT	NT	NT	0.038	NT	75	NT	0.349	0.020	26	0.4	0.020
9	1.1	15	2.5	6.4	44	0.044	0.63	75	4.4	0.34	0.032	20	0.51	0.04
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	0.714	17.7	2.96	7.24	51.8	NT	NT	NT	4.21	NT	NT	NT	NT	NT
12	0.54	17	2.2	6.0	47	0.033	0.68	85	5.1	0.37	0.0161	22.9	0.48	0.025
13	0.696	17.12	3.05	6.78	50.19	0.0423	NT	84.89	3.72	0.3827	0.0167	27.38	0.58	0.0394
14	0.50	17.30	2.39	6.19	41.9	0.050	0.64	54	4.6	0.365	0.018	22.2	0.66	0.026
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	0.665	21.3	2.59	7.14	50.5	0.048	0.64	87	4.4	0.39	0.027	27	0.55	0.033
17	0.73	23	3	8	52	0.044	NT	89	5	0.369	0.033	26	0.56	0.034
18	0.66	23	2.8	7.8	52	0.032	NT	130	4.5	0.392	0.020	26	0.64	0.02
19	NT	6.65	2.70	7.73	43.93	0.026	NT	94.97	NT	0.157	0.06	24.5	NT	0.10
20	0.659	18.83	2.92	7.10	51.2	< 0.1	< 1	93	NT	0.339	<0.1	23.1	NT	< 0.1
21	0.716	19.9	3.14	7.38	51.2	0.0457	NT	87.2	4.64	0.368	0.0227	27.7	0.584	0.0288
22	0.65	17	3	6	46	0.040	0.738	88	4.2	0.354	0.016	26	0.59	0.019
23	0.595	19	3	7	46	<0.2	0.8	85	NT	NT	NT	25	NT	NT
24	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
25	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
26	0.62	17	2.8	6.9	46	0.032	0.78	95	4.8	0.36	0.02	26	0.62	0.02
27	0.73	20.9	2.95	7.26	50.0	0.04	0.66	89	NR	0.36	0.016	25	0.54	0.022
28	0.778	16.1	2.81	6.94	51.4	0.058	0.703	82.3	4.65	0.377	0.017	24.8	0.633	0.028

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

Table 48 Summary of Participants' Results and Performance for Samples S3 and S4

Lab Code	S3-TKN (mg/L)	S3-TN (mg/L)	S3-TOC (mg/L)	S3-Total P (mg/L)	S4-TKN (mg/L)	S4-TN (mg/L)	S4-TOC (mg/L)	S4-Total P (mg/L)
AV	0.271	0.389	1.72	0.207	0.401	0.921	6.05	0.152
HV	0.245	0.360	NA	0.210	0.400	0.92	5.7	0.157
1	1.3	1.4	NT	0.31	NT	NT	NT	NT
2	NR	NR	6.17	<0.5	NT	NT	NT	NT
3	< 1	< 1	< 5	0.252	NT	NT	NT	NT
4	< 2	< 2	NT	NT	NT	NT	NT	NT
5	NT	NT	NT	NT	0.38	0.96	6	0.158
6	NT	NT	NT	NT	NT	NT	NT	NT
7	NR	0.38	NR	0.20	NR	0.91	NR	0.15
8	0.2	0.3	NT	0.202	0.3	0.8	NT	0.151
9	NT	0.32	1.40	0.2	NT	0.85	5.7	0.16
10	NT	NT	NT	NT	NT	NT	NT	NT
11	NT	NT	NT	NT	NT	NT	NT	NT
12	0.25	0.38	1.8	0.21	0.17	0.74	6.2	0.16
13	0.2318	0.32	2.33	0.194	0.414	0.96	6.42	0.129
14	0.19	0.29	1.6	NR	0.46	0.9	6.2	0.140
15	NT	NT	NT	NT	NT	NT	NT	NT
16	0.24	0.35	1.5	0.20	0.34	0.89	5.7	0.16
17	0.272	0.394	2	0.191	0.38	0.9	6	0.156
18	NT	NT	NT	NT	NT	NT	NT	NT
19	NT	NT	NT	NT	NT	NT	NT	NT
20	< 2	NT	NT	NT	NT	NT	NT	NT
21	NT	0.455	1.49	0.225	NT	0.936	5.85	0.162
22	0.321	0.428	1.9	0.212	0.42	0.95	6.3	0.136
23	NR	0.5	NR	<1.5	NR	1.2	NR	<1.5
24	NT	NT	NT	NT	NT	NT	NT	NT
25	NT	NT	NT	NT	NT	NT	NT	NT
26	0.35	0.46	2.1	0.2	0.47	1	6.4	0.15
27	0.43	0.47	NR	0.204	NR	0.91	NR	0.154
28	0.280	0.393	1.06	0.205	0.438	1.00	5.82	0.152

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

Table 49 Summary of Participants' Results and Performance for Sample S5

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 (as SiO_2) (mg/L)	Total Hardness (mg/L)
AV	4.66	439	418	1320	11200	121	54100	8.07	0.572	6550
1	NT	NT	NT	NT	NT	121	54900	8.06	0.52	NT
2	5.18	496	458	1320	12000	119.53	58300	8.06	NT	6720
3	4.729	449	439	1334	11063	123.2	53307	8.05	NT	6615
4	4.74	433	422	1352	12149	130	54000	8.2	0.5	7326
5	4.72	409	401	1300	11000	120	53600	8.07	0.61	6370
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	NT	NT	NT	NT	NT	118	56000	8.09	0.61	NT
9	4.6	410	430	620	10500	125	52820	8.09	0.5	3588
10	NT	NT	NT	NT	NT	120.2	NT	NT	2.5	NT
11	4.1	410	390	1270	11000	NT	NT	NT	NT	6240
12	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
13	4.43	410.75	401.02	1318.55	10841.22	123.7	53455.71	8.03	0.569	6379.67
14	3.94	469	411	1390	11400	122	52800	8.2	1.1	6900
15	NR	NR	NR	NR	NR	NR	NR	NR	0.5956	NR
16	4.51	455	415	1430	11200	170	55000	8.1	0.774	7025
17	4.9	474	408	1320	11100	104	53100	7.82	0.58	6620
18	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	4.91	437	424	1365	12013	119	54669	7.95	< 10	6715
21	4.93	451	430	1280	10800	119	53200	8.2	NT	6400
22	4.79	422	407	1310	10900	117	56000	7.96	0.50	6450
23	4.708	444	392	1275	10782	103	57550	8.1	NT	6359
24	NT	NT	NT	NT	NT	NT	NT	NT	0.5903	NT
25	NT	NT	NT	NT	NT	NT	NT	NT	0.6068	NT
26	3.4	400	420	1300	11000	120	53300	8	<0.10	6500
27	4.60	430	440	1240	10800	129	52430	8.1	0.60	6200
28	5.12	479	431	1380	12700	124	53000	8.07	NT	6760

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

6.5 Participants' Results and Analytical Methods

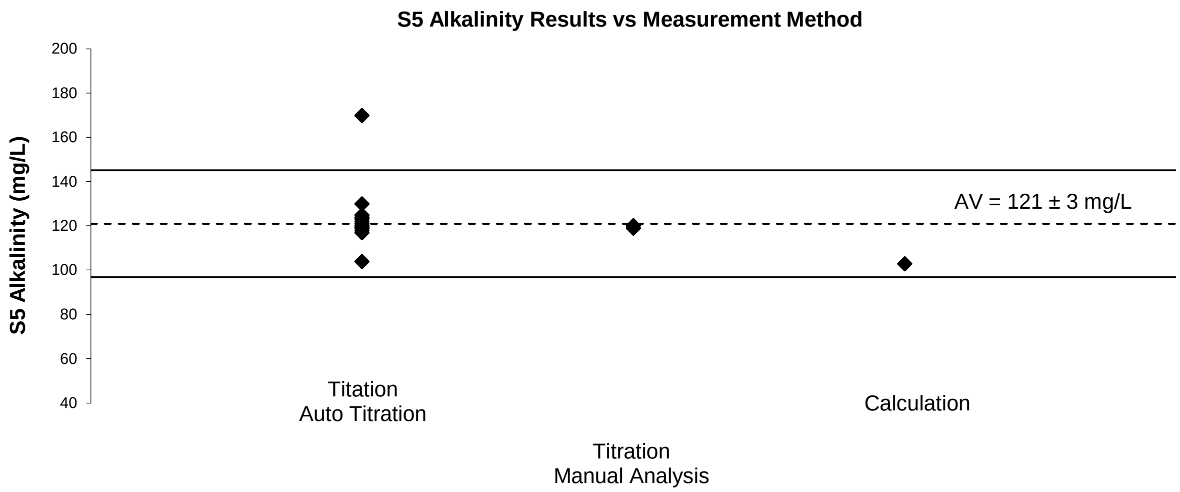
Samples S1, S3, and S5 were seawater samples while Samples S2 and S4 were river water samples. Participants were asked to analyse the samples using their normal test method. The measurement methods and instrumental techniques used are presented in Appendices 6 to 10.

Overall, participants' performance in the two matrices was similar. However, DOC, TOC, TN, and TKN in seawater posed the greatest challenge to most participants' analytical techniques compared with river water. The between-laboratory CVs for these parameters in seawater were two to five times higher than their river water counterparts.

Low level TDP in S1 followed by NH3-N in the same seawater sample, were the tests that challenged participants analytical techniques the most.

Individual Test Commentary

Alkalinity to pH 4.5 (as $CaCO_3$) Participants used auto-titration, manual titration or calculation to measure alkalinity in S5. All participants except one performed acceptably (Figure 47).



Horizontal lines correspond to z-scores of 2 and -2.

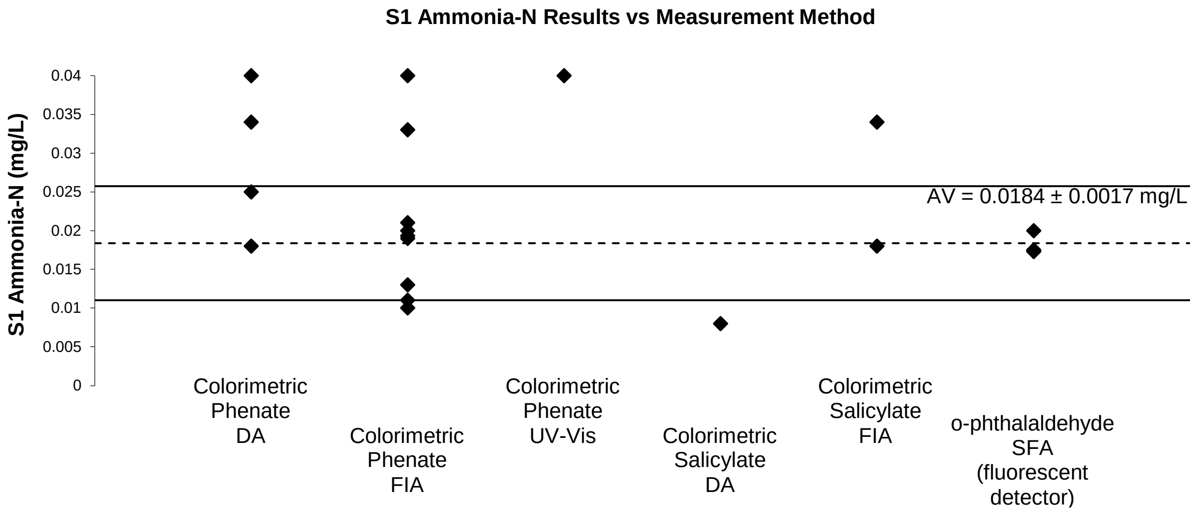
Figure 47 S5 Alkalinity Results vs. Measurement Method

Ammonia-Nitrogen level in the seawater sample (S1) was 0.0184 mg/L while in the river water sample (S2) was 0.0409 mg/L. Of the 21 results reported for ammonia in S1, 12 returned acceptable z-scores, while 17 out of 18 results reported for ammonia-N in river water, were acceptable. The lower ammonia concentration in seawater, combined with matrix interference from chloride and salinity, may explain the discrepancy in participants' performance between the two matrices.

With two exceptions, all unacceptable z-scores in S1 were biased high. Matrix effects and contamination during sample preparation are the most common causes of high bias for NH3-N results. High chloride concentrations can interfere with colour development, leading to exaggerated absorbance readings, while salinity can affect reagent activity and reaction kinetics when calibration standards are prepared in deionized water instead of seawater. Contamination during sampling and analysis may also contribute to high bias, as ammonia is highly sensitive to contamination from air, glassware, and containers. When ammonia is present at a low level in seawater small variations in reagent concentration, timing or temperature can also disproportionately affect colour intensity – particularly with salicylate method, which is more sensitive than phenate method. Furthermore, discrete analyser might not be the best choice for NH_3-N measurements at low level; the 10 mm absorption cell path length can limit sensitivity at the low ammonia level observed in S1.

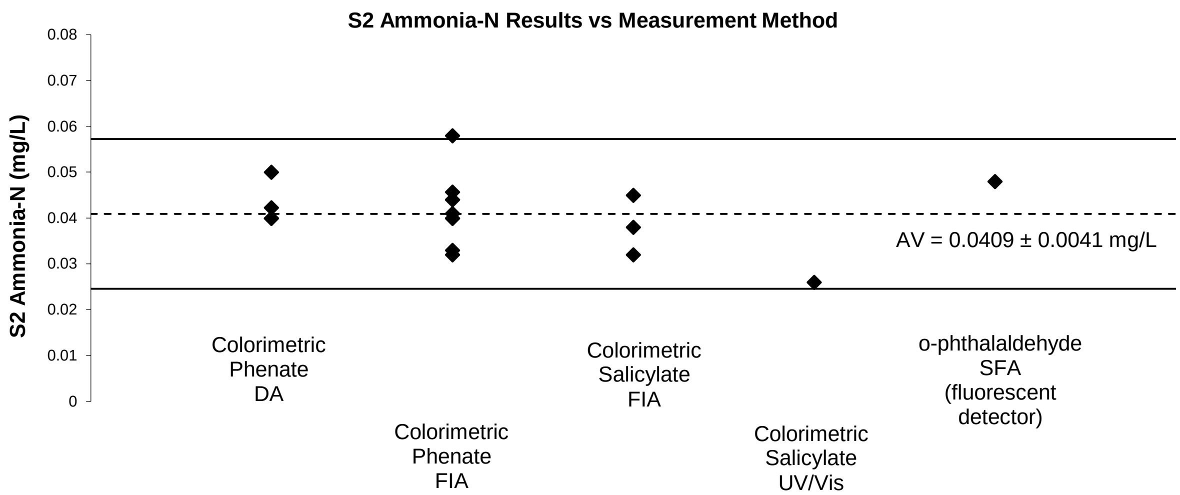
Matrix-matched calibration standards, the application of salinity correction factors, and better control of ammonia contamination in the laboratory may help improve performance in measuring ammonia-N in seawater. For trace-level ammonia analysis, consideration should also be given to optimizing the salicylate method or using segmented flow analysis (SFA) for greater sensitivity and reproducibility. [15, 16, 17]

Plots of participants' results in seawater and river water versus methods used for ammonia–N measurements are presented in Figures 48 and 49.



Horizontal lines correspond to z-scores of 2 and -2. Results larger than 0.04 mg/L have been set as 0.04 mg/L.

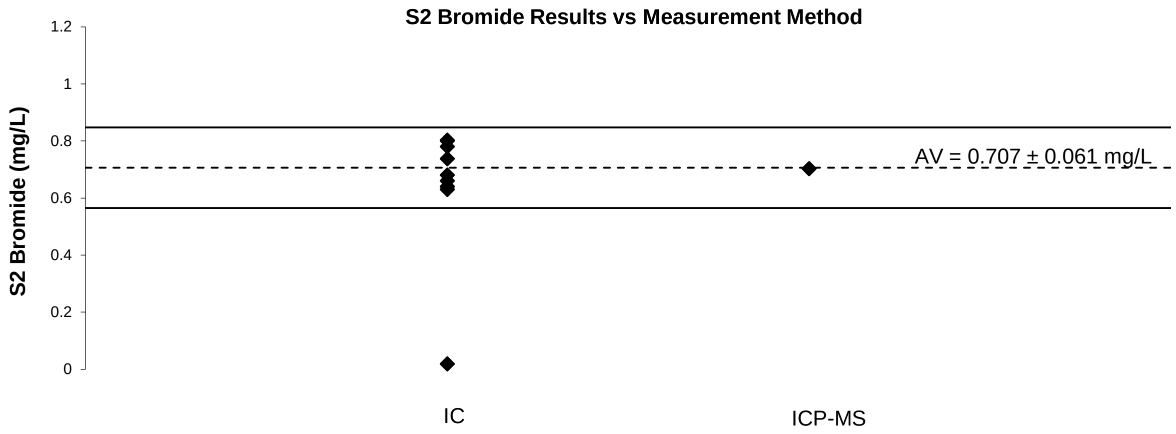
Figure 48 S1 Ammonia-N Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

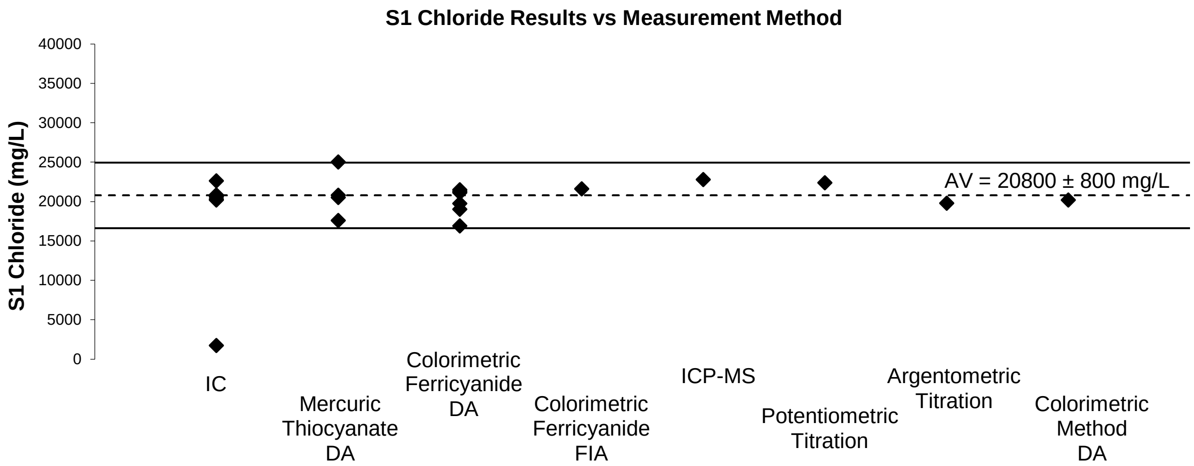
Figure 49 S2 Ammonia-N Results vs. Measurement Method

Bromide All but one of participating laboratories used an ion chromatographic (IC) method to measure bromide content in Sample S2. One laboratory reported an unacceptable result, despite using the IC method (Figure 50).



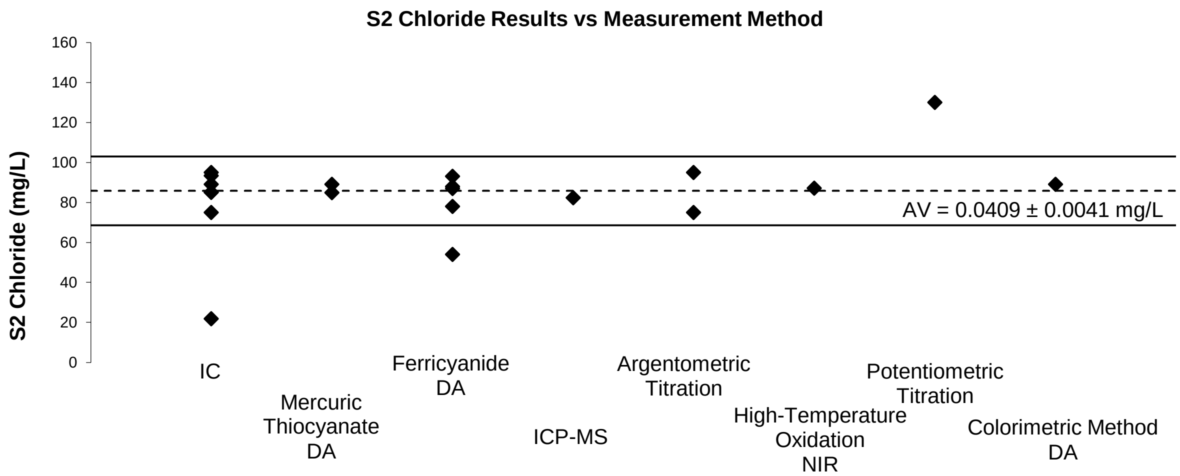
Horizontal lines correspond to z-scores of 2 and -2.

Figure 50 S2 Bromide Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

Figure 51 S1 Chloride Results vs. Measurement Method



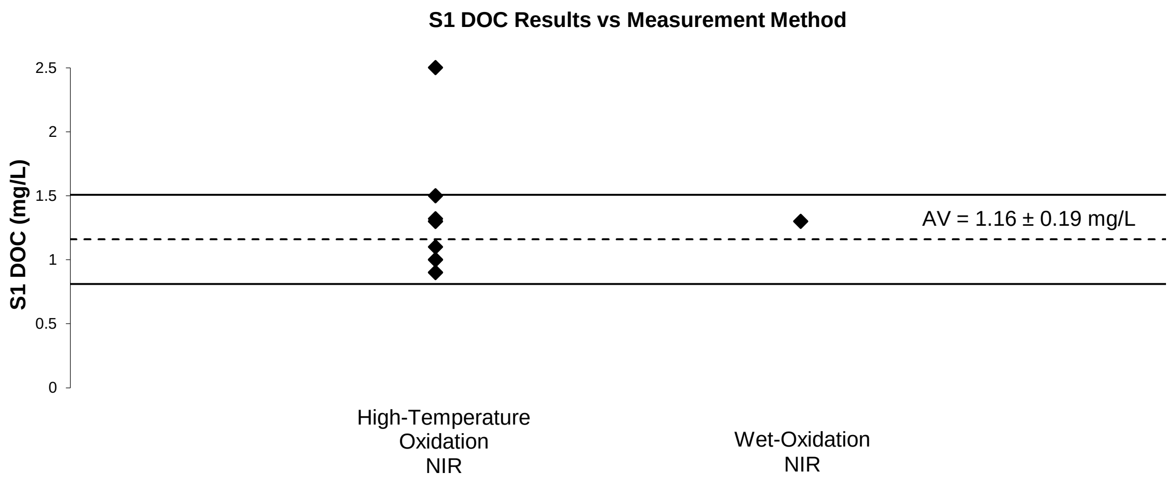
Horizontal lines correspond to z-scores of 2 and -2.

Figure 52 S2 Chloride Results vs. Measurement Method

Chloride was present in the seawater Sample S1 at 20800 mg/L, and in the river water Sample S2 at 85.9 mg/L. Two laboratories returned results that were not acceptable in S1, and three in S2. No laboratory received an unacceptable score for both samples. The measurement methods used are presented in Figures 51 and 52.

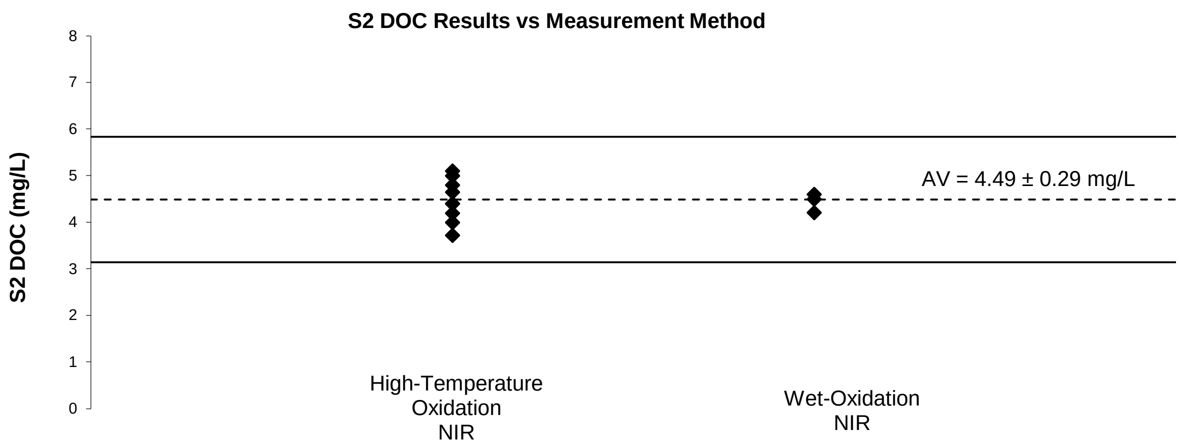
Caution should be exercised when using the potentiometric titration method, as it becomes less accurate at low chloride levels due to the reduced distinctness of the potential change at the endpoint.[18]

Dissolved Organic Carbon as dNPOC Participants were generally successful in measuring DOC in both the seawater sample (S1) and the river water sample (S2). Only one laboratory received an unacceptable score for S1, although this same laboratory achieved an acceptable score for S2. All participants, except four, reported using a high-temperature oxidation method for DOC measurements in both samples. Three laboratories employed wet oxidation. There was no significant difference between the results obtained using high-temperature oxidation and those obtained using wet oxidation (Figures 53 and 54).



Horizontal lines correspond to z-scores of 2 and -2. Results larger than 2.5 mg/L have been set as 2.5 mg/L.

Figure 53 S1 DOC Results vs. Measurement Method



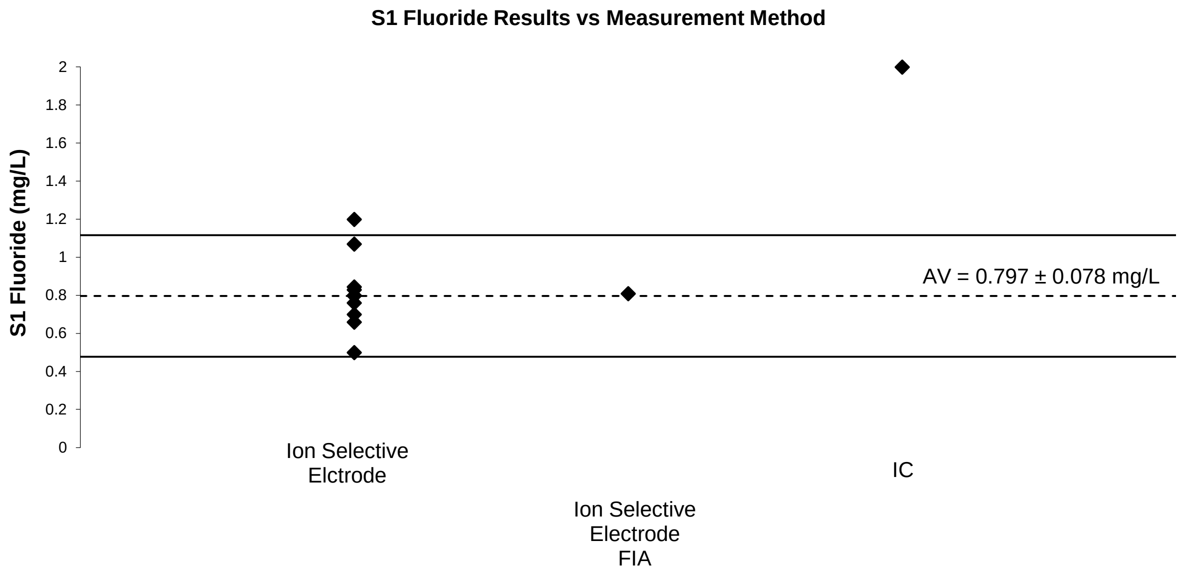
Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 54 S2 DOC Results vs. Measurement Method

EC measurements in seawater sample S5 did not challenge participants' analytical techniques, all reported results returned acceptable z-scores; the between-laboratory CV was very low at 2.8%.

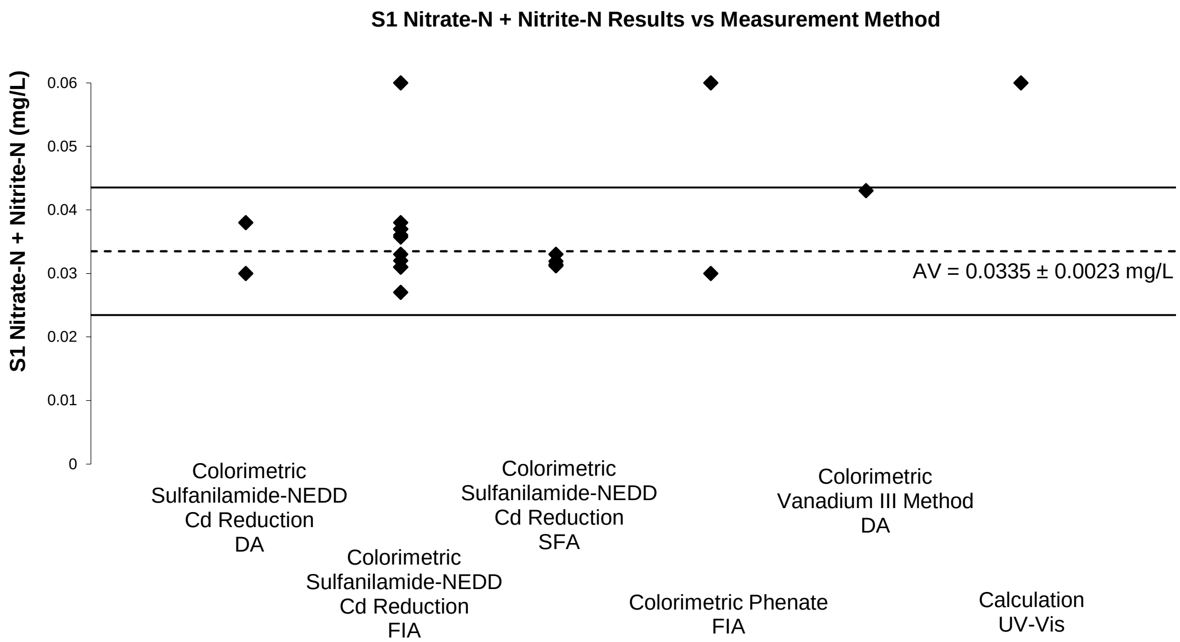
Fluoride was present in the seawater Sample S1. Plots of participants z-scores versus the measurement technique used are presented in Figure 55. All laboratories except two reported using an ion-selective electrode methodology. One laboratory reported using both FIA and selective electrode for fluoride measurements and one ion chromatography.

Participants should exercise caution when measuring low-level fluoride with the ion chromatographic method. Fluoride has a low molecular weight and valence charge and is not retained by columns in the normal elution times like other ions. Further, low-level fluoride may be difficult to quantify due to negative contribution of the "water dip" (corresponding to elution of water) or interference from organic acids eluting close to fluoride.[15]



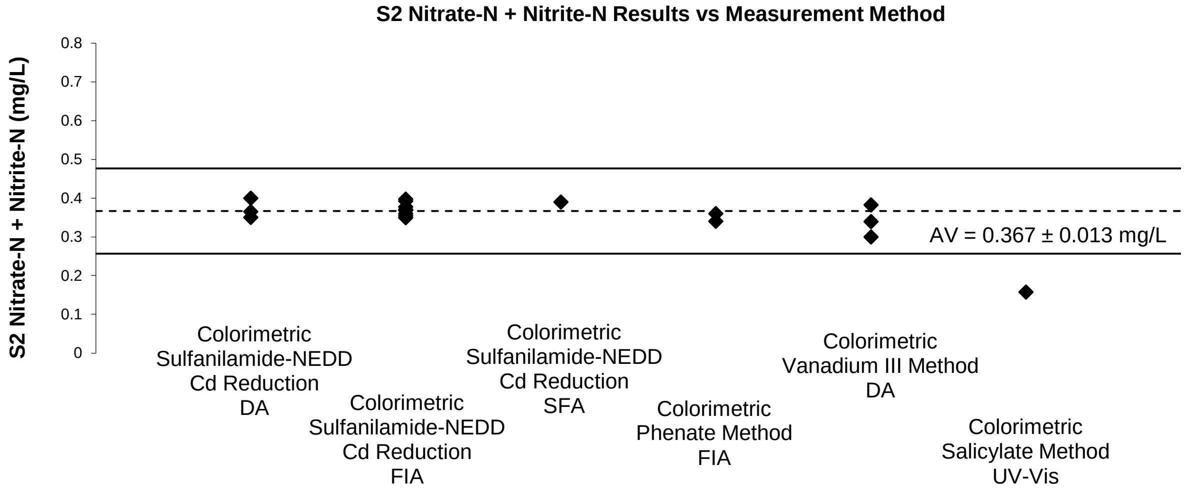
Horizontal lines correspond to z-scores of 2 and -2. Results larger than 2 mg/L have been set as 2 mg/L.

Figure 55 S1 Fluoride Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2. Results larger than 0.06 mg/L have been set as 0.06 mg/L.

Figure 56 S1 Nitrate-N+Nitrite-N Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

Figure 57 S2 Nitrate-N+Nitrite-N Results vs. Measurement Method

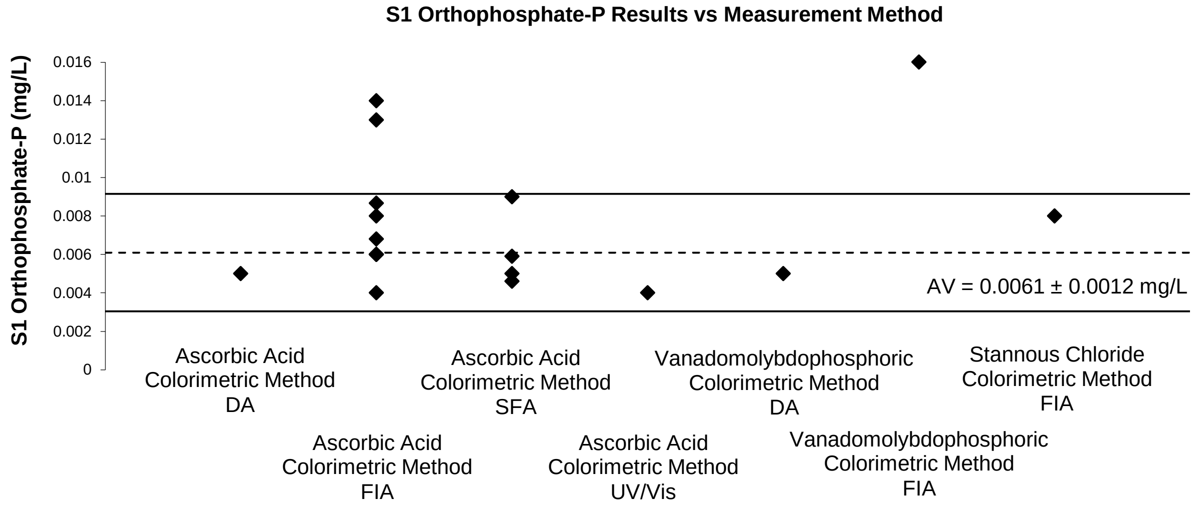
Nitrate-Nitrogen + Nitrite-Nitrogen level in the seawater sample S1 was 0.0335 mg/L, which is ten times lower than the 0.367 mg/L measured in river water sample S2. Of the 21 laboratories that reported results for NOx-N in S1, 18 performed acceptably, while 19 of 20 did so for S2. All 3 unacceptable z-scores for S1 were biased high.

Most laboratories used the colorimetric-sulfanilamide-NEDD Cd reduction method to convert NO_3-N to NO_2-N, and then measured NO_2-N by DA, FIA or SFA (Figures 56 and 57). High bias in low-level NOx-N (nitrate + nitrite) results in seawater is often attributed to matrix effects and contamination. As for ammonia-N, the high ionic strength of seawater can alter reaction kinetics and detector response, particularly when calibration standards are prepared in deionized water rather than seawater, creating a matrix mismatch. Chloride may interfere with reduction steps, such as those involving cadmium columns in flow-based methods, leading to incomplete or inconsistent reactions. Contamination from glassware, reagents, or laboratory air can also significantly impact trace-level measurements.[15, 19, 20]

Orthophosphate-P measurements in seawater (S1) and river water (S2) challenged participants analytical techniques. The between-laboratory coefficient of variation was high-30% for S1 and 24% for S2. Most participants preferred to use an ascorbic acid colorimetric method (Figures 58 and 59).

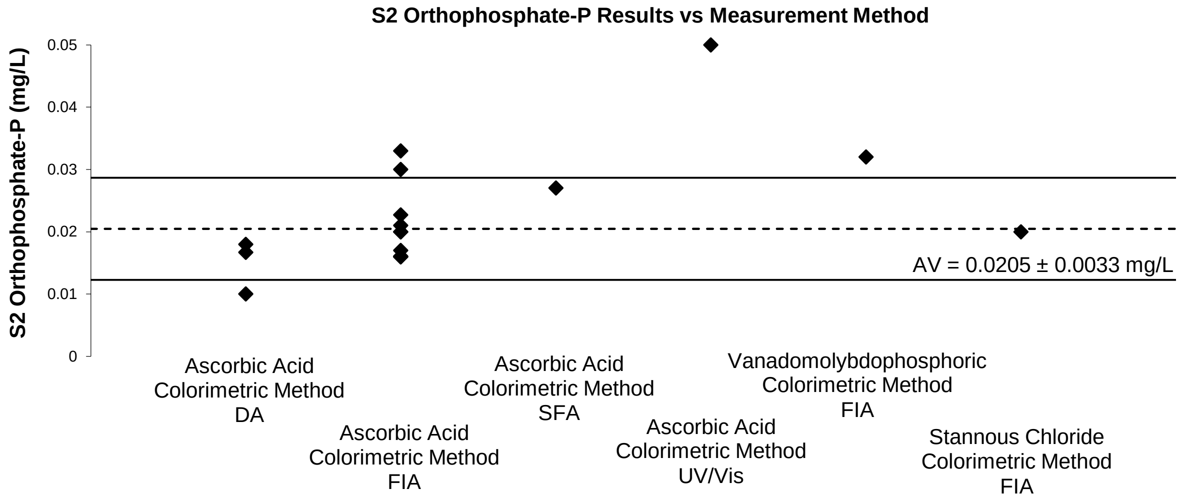
Orthophosphate-P concentrations in both samples were low, at 0.0061 mg/L in S1 and at 0.0205 mg/L in S2 which likely contributed to difficulty. All results that returned unacceptable z-scores for these samples were biased high.

Similarly to ammonia-N, orthophosphate-P results can be affected by high salinity in seawater and contamination from laboratory glassware or containers, reagents or wash water containing trace phosphate or dust particles from the air. Optimising timing or temperature and reagent handling is also very important for orthophosphate-P measurements at low level, because small variations in reagent volumes, timing, or temperature can disproportionately affect colour intensity. [15, 21]



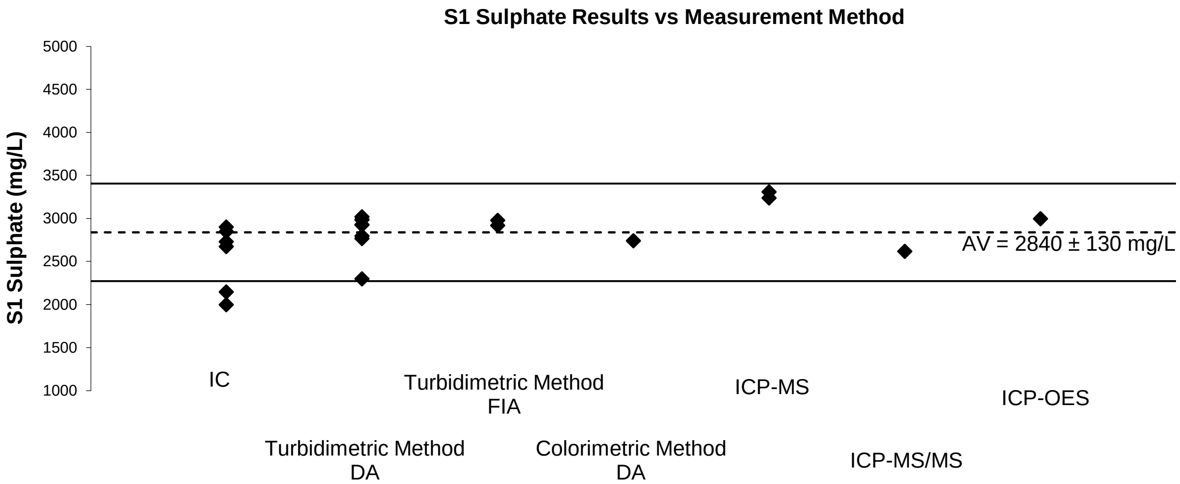
Horizontal lines correspond to z-scores of 2 and -2.

Figure 58 S1 Orthophosphate-P Results vs. Measurement Method



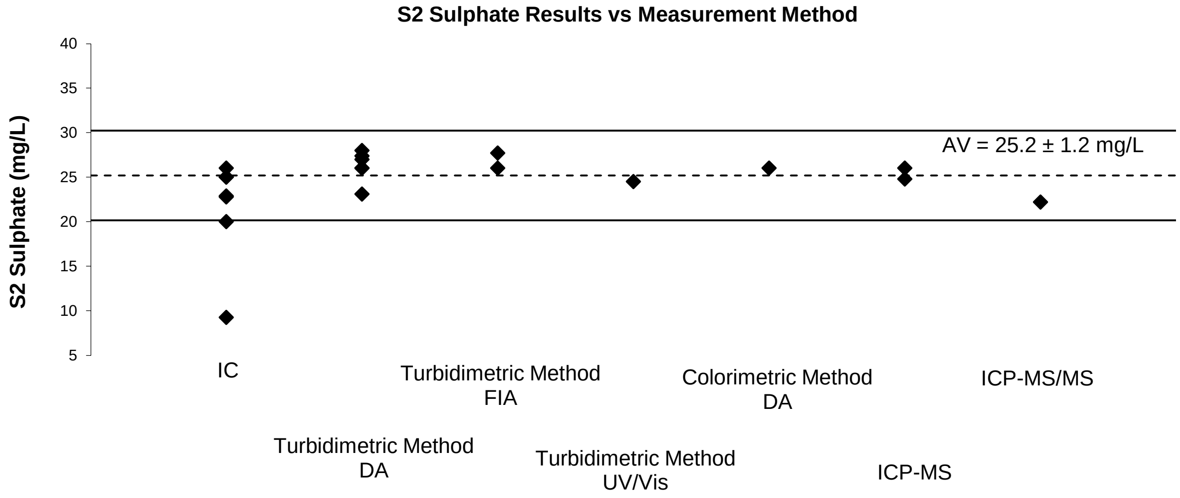
Horizontal lines correspond to z-scores of 2 and -2. Results larger than 0.05 mg//L have been set as 0.05 mg/L.

Figure 59 S2 Orthophosphate-P Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

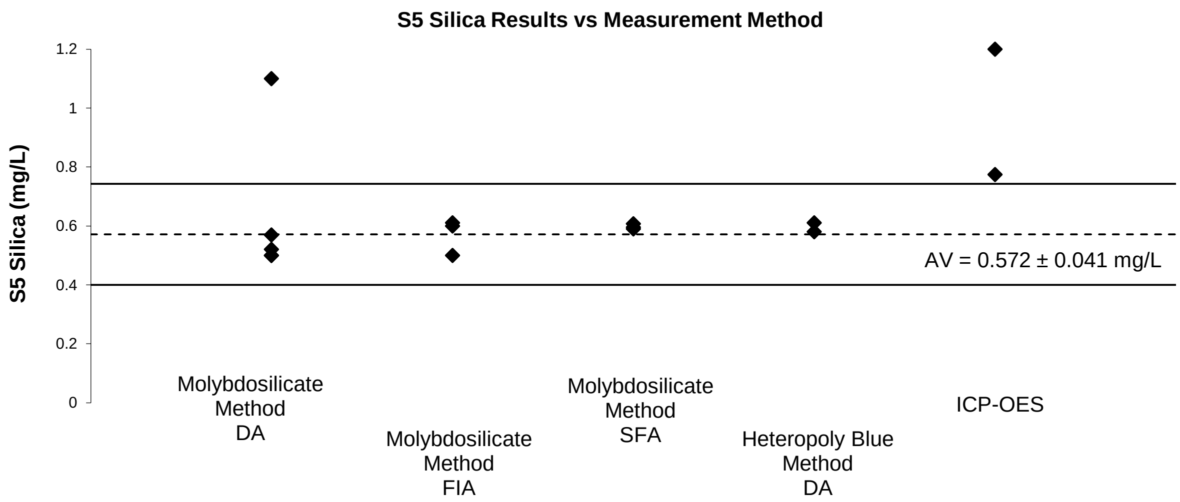
Figure 60 S1 Sulphate Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

Figure 61 S2 Sulphate Results vs. Measurement Method

Sulphate results reported in S1 and S2 were in an excellent agreement with each other, with between laboratory CVs of 8.5% and 8.3% respectively. All results that returned unacceptable z-scores in the two samples were biased low, and all were from IC measurements (Figures 61 and 62). High concentrations of chloride can distort or suppress the sulphate peak, leading to under-quantification when sulphate is measured by IC.



Horizontal lines correspond to z-scores of 2 and -2. Results larger than 1.2 mg/L have been set as 1.2 mg/L.

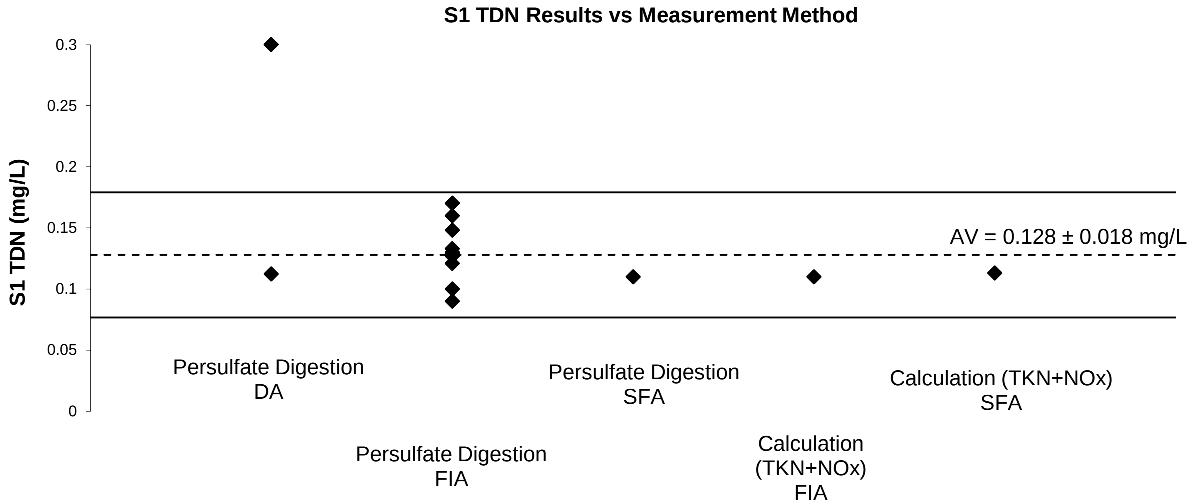
Figure 62 S5 Silica Results vs. Measurement Method

Silica (as SiO_2) Of the15 results reported for silica in seawater sample S5, 12 returned acceptable z-scores (Figure 62).

Seawater contains high concentrations of dissolved salts, which can cause signal suppression in ICP analysis. Significant dilution (up to 10-fold) can mitigate this, but this may also reduce the sample's silica concentration to a level outside the optimal calibration range, especially when ICP-OES is used. A high silica result from ICP determination may be also indicate the technique is measuring total silicon rather than only silica species that react with molybdate. [15]

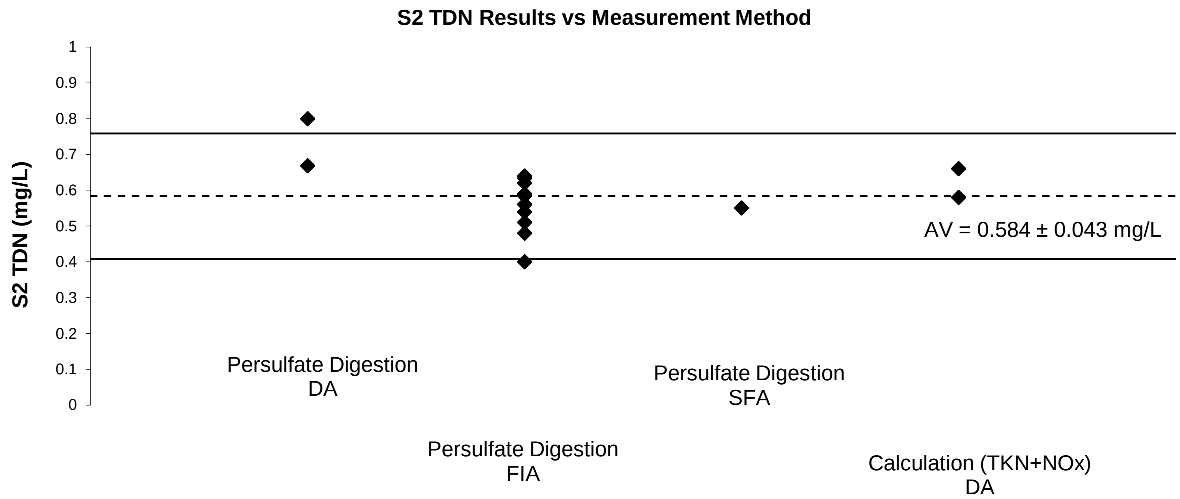
Total Dissolved Nitrogen (TDN) methodologies for Samples S1 and S2 are presented in Figures 63 and 64.

One laboratory reported high unacceptable results in both study samples, while another reported values as being below its level of reporting (0.1 mg/L), despite TDN levels being 0.128 mg/L in S1 and 0.584 mg/L in S2. These laboratories may need to review the method used for TDN measurements in water.



Horizontal lines correspond to z-scores of 2 and -2. Scores larger than 0.3 mg/L have been set as 0.3 mg/L.

Figure 63 S1 TDN Results vs. Measurement Method

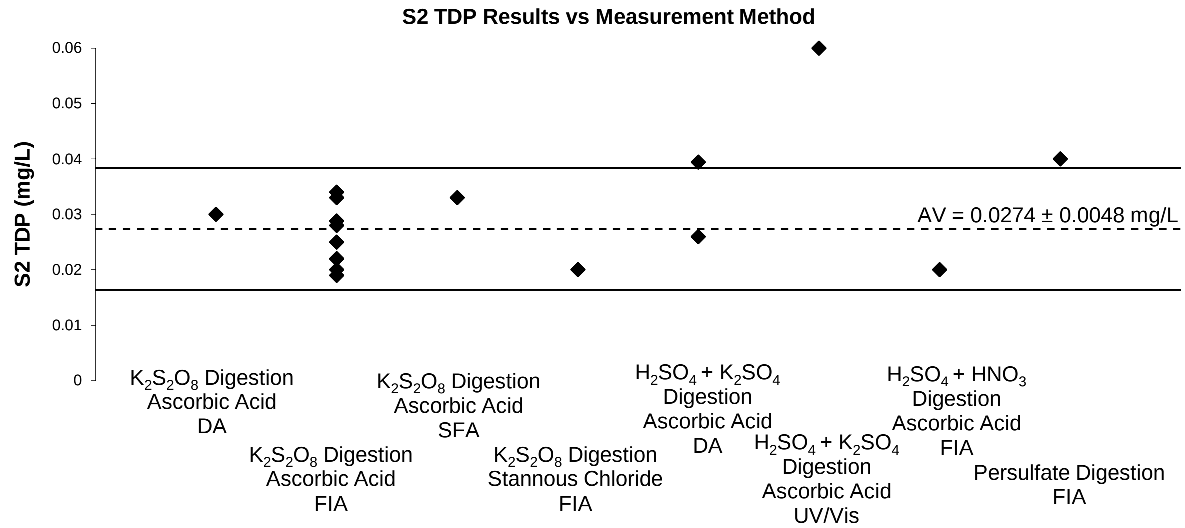


Horizontal lines correspond to z-scores of 2 and -2.

Figure 64 S2 TDN Results vs. Measurement Method

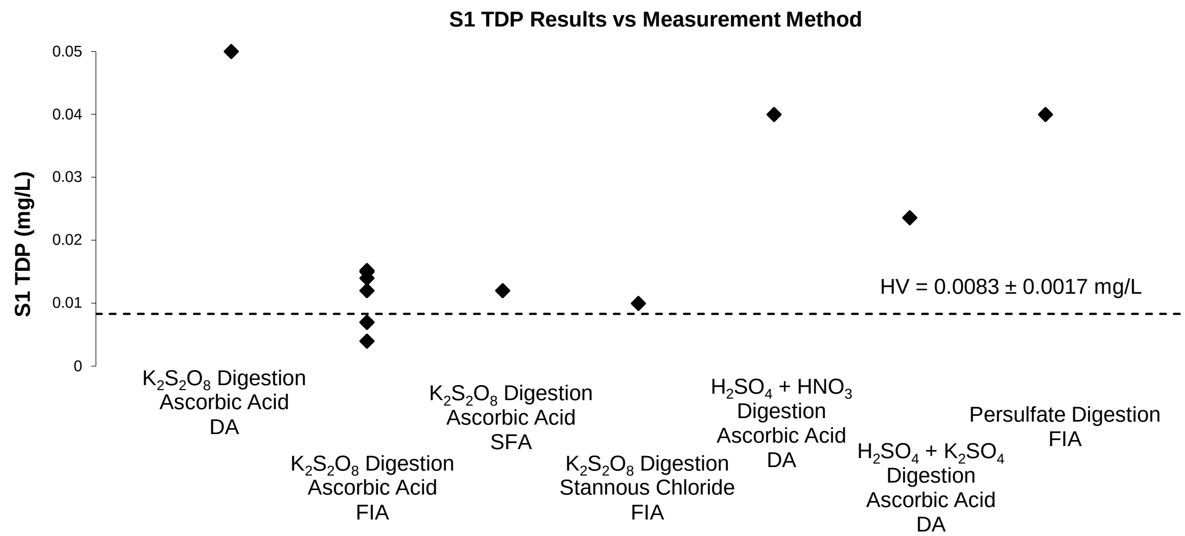
Total Dissolved Phosphorus (TDP) level in the river water sample S2 was 0.0274 mg/L. Of the 17 reported results, 14 returned acceptable z-scores. Most participants used the potassium persulfate digestion method followed by colorimetric determination by DA, FIA or SFA (Figure 65). All three unacceptable results were biased high. These laboratories may need to review their contamination-control procedures.

TDP results in seawater Sample S1 were too variable to set an assigned value (Figure 66). The reported results ranged from 0.004 mg/L to 0.2 mg/L. Contamination of the sample may explain some of the variability. However, it is well known that the high-salt matrix of seawater can significantly impact TDP measurements. High concentration of chloride, sulphate, magnesium, sodium can interfere with persulfate digestion efficiency, colour development and can contribute to baseline drift in spectrometric determination.[15]



Horizontal lines correspond to z-scores of 2 and -2. Results larger than 0.06 mg/L have been set as 0.06 mg/L.

Figure 65 S2 TDP Results vs. Measurement Method



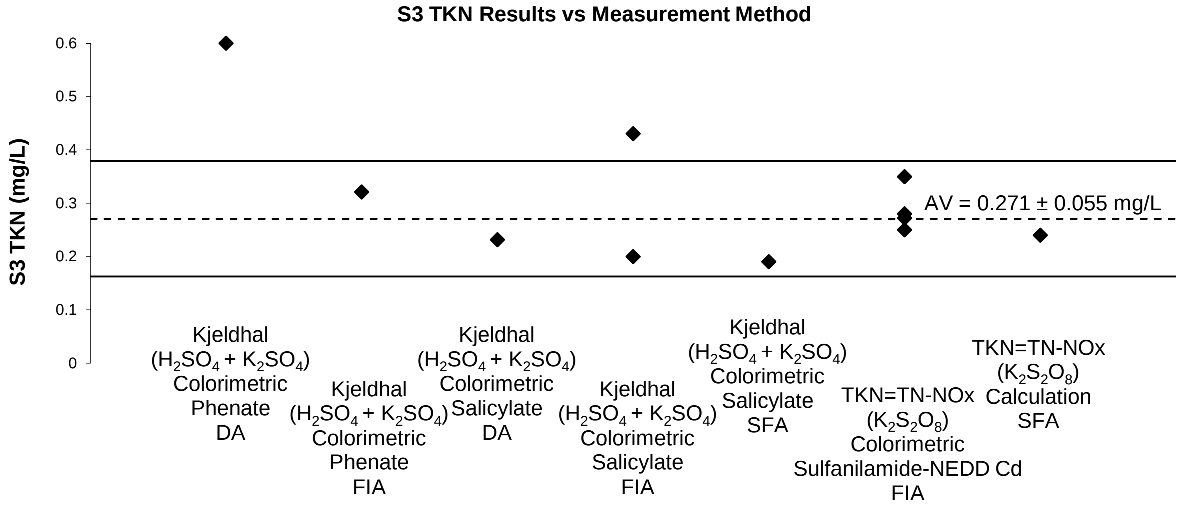
Results larger than 0.05 mg/L have been set as 0.05 mg/L.

Figure 66 S1 TDP Results vs. Measurement Method

Total Kjeldahl Nitrogen (TKN) and Total Nitrogen (TN) measurements in seawater (S3) challenged participants' techniques more than those in river water (S4). The between-laboratory CV in seawater was almost double that observed in river water.

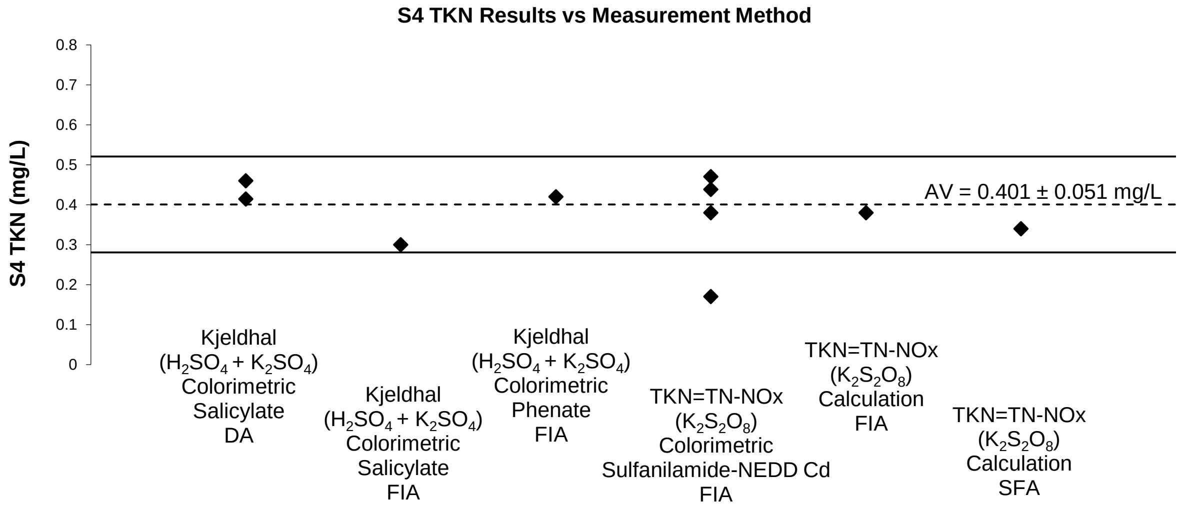
TKN and TN levels in seawater were approximately half and one-third respectively, of the concentration in river water. All results that returned unacceptable z-scores in seawater were biased high. As with ammonia-N, and nitrate-N +nitrate-N analysis, contamination and matrix complexity may explain the discrepancies in participants' performance across the two matrices.

Participants' methods for TKN and TN in S3 and S4 matrices are presented in Figures 67 to 70.



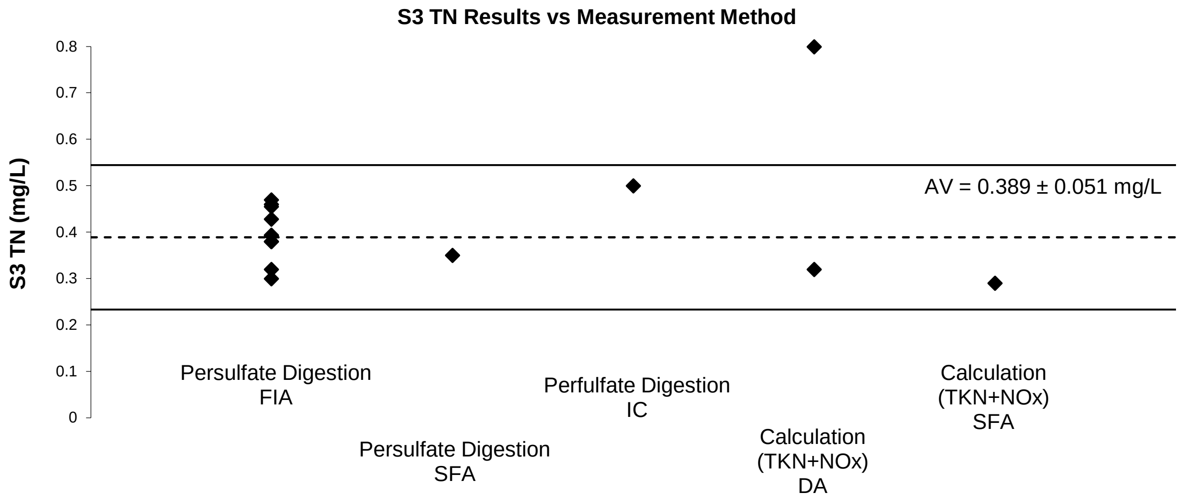
Horizontal lines correspond to z-scores of 2 and -2. Results larger than 0.6 mg/L have been set as 0.6 mg/L.

Figure 67 S3 TKN Results vs. Measurement Method



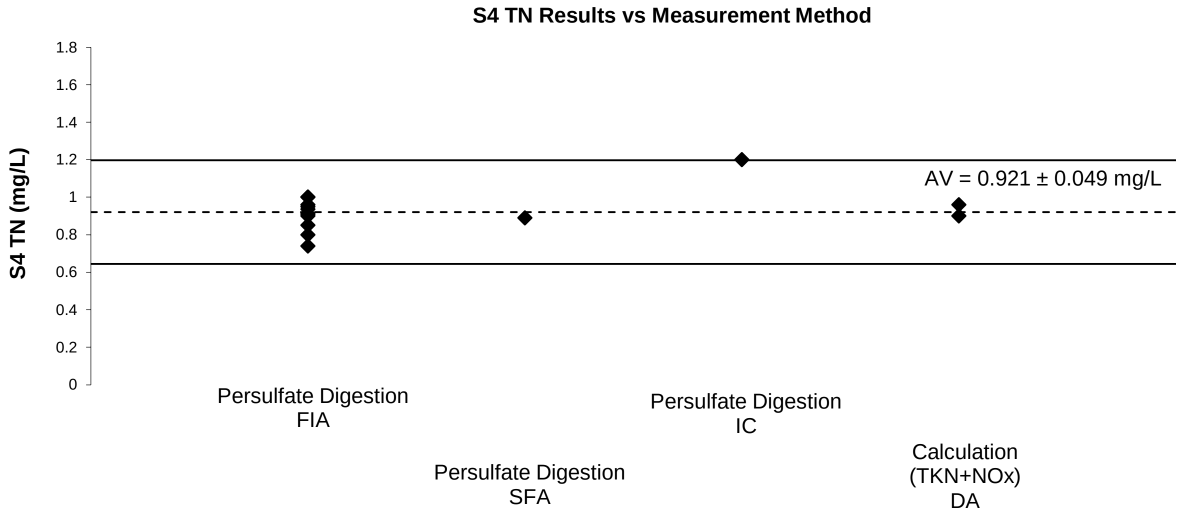
Horizontal lines correspond to z-scores of 2 and -2.

Figure 68 S4 TKN Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2. Results larger than 0.8 mg/L have been set as 0.8 mg/L.

Figure 69 S3 TN Results vs. Measurement Method



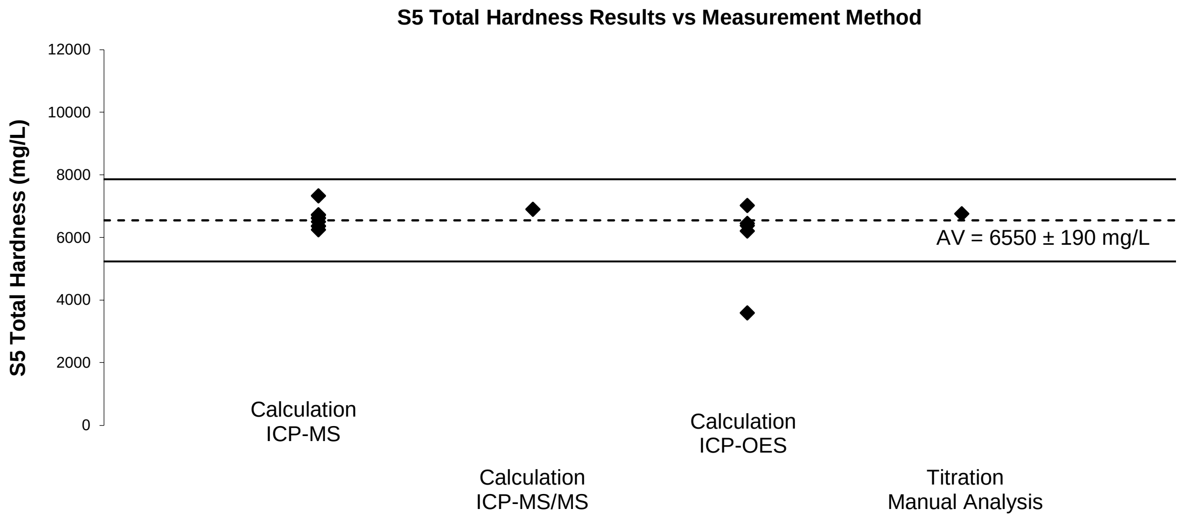
Horizontal lines correspond to z-scores of 2 and -2.

Figure 70 S4 TN Results vs. Measurement Method

Total Organic Carbon All participants except one reported using the high-temperature oxidation method for TOC measurements in S3 and S4. The between-laboratory CV in S3 was 25%, while in S4 less than half of this value at 8.2%.

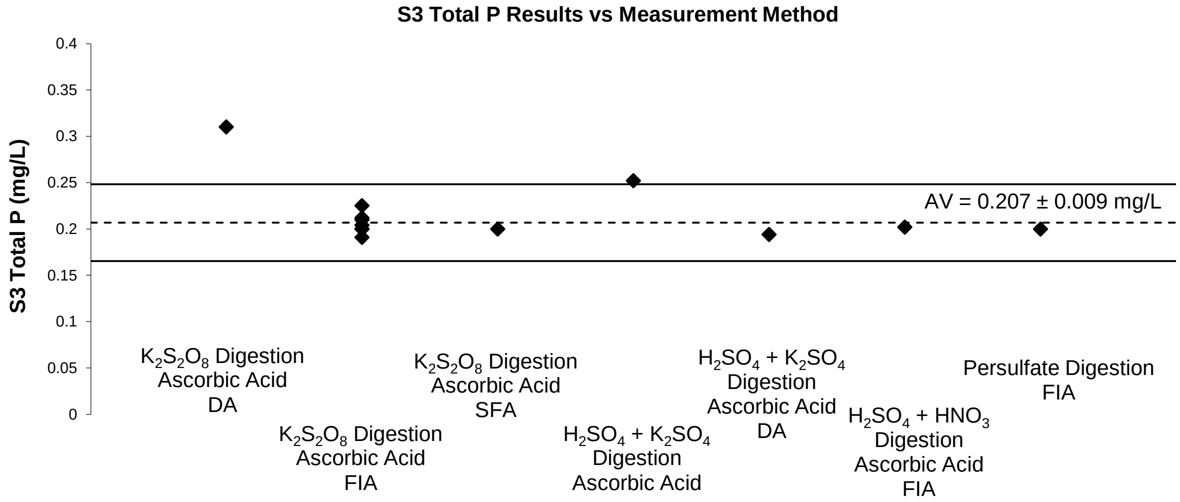
Total Hardness analysis in Sample S5 did not challenge participants' analytical techniques. All reported results returned acceptable z-scores, except one. Participants measured total hardness using either an ICP method or titration (Figure 71).

Total Phosphorus results in the seawater sample (S3) and in the river water sample (S4) were in an excellent agreement with each other. The between-laboratory CV was 6.5% in S3 and 6.3% in S4. The majority of participants used potassium persulfate digestion followed by colorimetric determination (Figures 72 and 73).



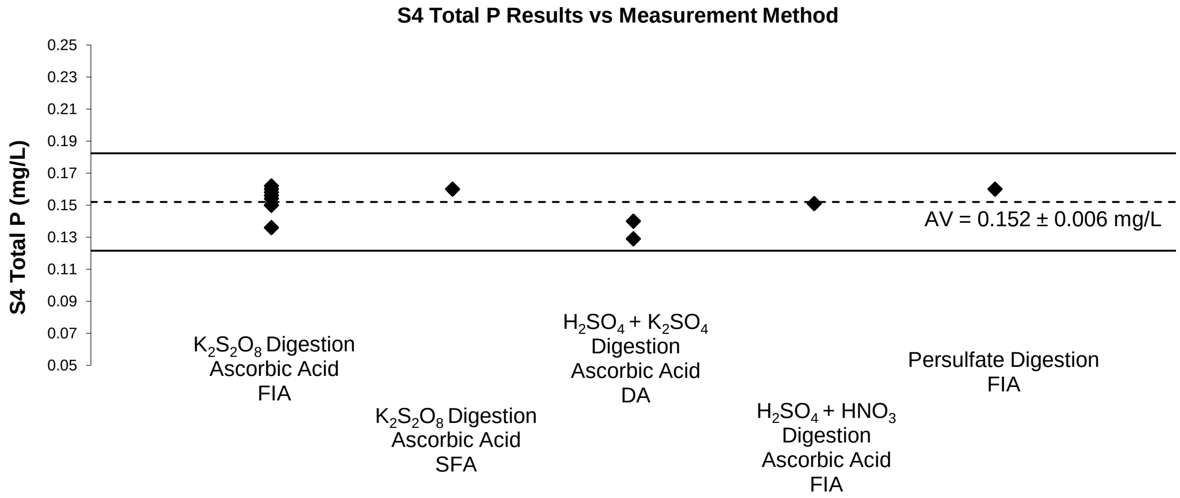
Horizontal lines correspond to z-scores of 2 and -2.

Figure 71 S5 Total Hardness Results vs. Measurement Method



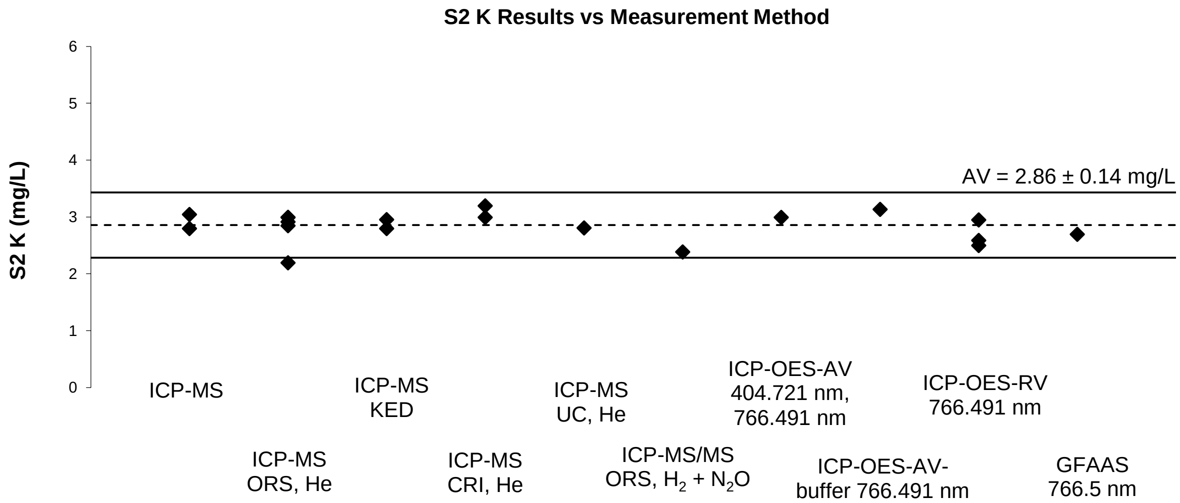
Horizontal lines correspond to z-scores of 2 and -2.

Figure 72 S3 Total P Results vs. Measurement Method



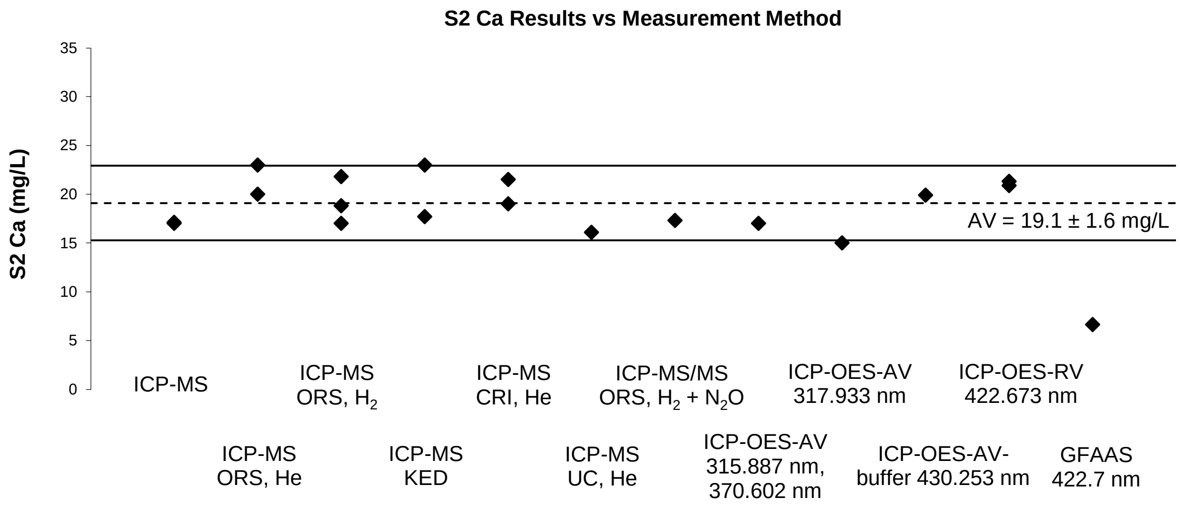
Horizontal lines correspond to z-scores of 2 and -2.

Figure 73 S4 Total P Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

Figure 74 S2 K Results vs. Measurement Method



Horizontal lines correspond to z-scores of 2 and -2.

Figure 75 S2 Ca Results vs. Measurement Method

Calcium, Potassium, and Sodium Participants used a wide variety of instrumental techniques for Ca, K, and Na measurements in river water sample S2 and seawater sample S5. All reported results returned acceptable z-scores in both matrices except for K and Ca in S2.

Plots of K and Ca result in S2 are presented in Figures 74 and 75 respectively.

6.6 Comparison with Previous NMIA Proficiency Tests of Water Characteristics

AQA 25-14 is the 20th NMIA proficiency test of water characteristics. Figure 76 presents participant performance over time. Despite different matrices and analyte concentrations, on average participant performance has remained consistent over time, with an average acceptable z-score rate of 92%, and an average acceptable E_n-score rate of 83%.

Over time laboratories should expect at least 95% of their scores to lay within the range |z| ≤ 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 and ex-PT samples) had been used (Table 50).

Table 50 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CRM
2	CRM
3	CRM: QCS-01-05 ICP Quality Control Standard #1; High Purity Standards CCV-1 Solution A; High Purity Standards CCV-1 Solution B; Australian Chemical Reagents Multi Element Standard
4	CRM

Lab. Code	Description of Control Samples
5	CRM
6	SS
7	RM / Ex PT Samples
8	CRM, SS
10	CRM
11	SS
13	CRM
14	SS, CRM
15	CRM: KANSO Certified Reference Material lot CR (Low range) was used for all samples. Bulk internal QC samples were also used for all samples.
16	CRM
17	CRM, SS
18	CRM
19	CRM
20	CRM, SS
21	SS
22	CRM
23	CRM, SS
24	CRM: KANSO Certified Reference Material lot CR (low range) and CS (medium range) was used for all samples. Bulk internal QC samples were also used for all samples.
25	CRM: KANSO Certified Reference Material lot CS (medium range) was used for all samples. Lot CQ (high range) was also used in the analysis of ammonia.
26	CRM
27	SS
28	CRM: CWW-TM-B and C (metals), Minerals 2 (salts)

Matrix matched control samples taken through all steps of the analytical process are the most valuable quality control tools for assessing a method's 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'*[22]

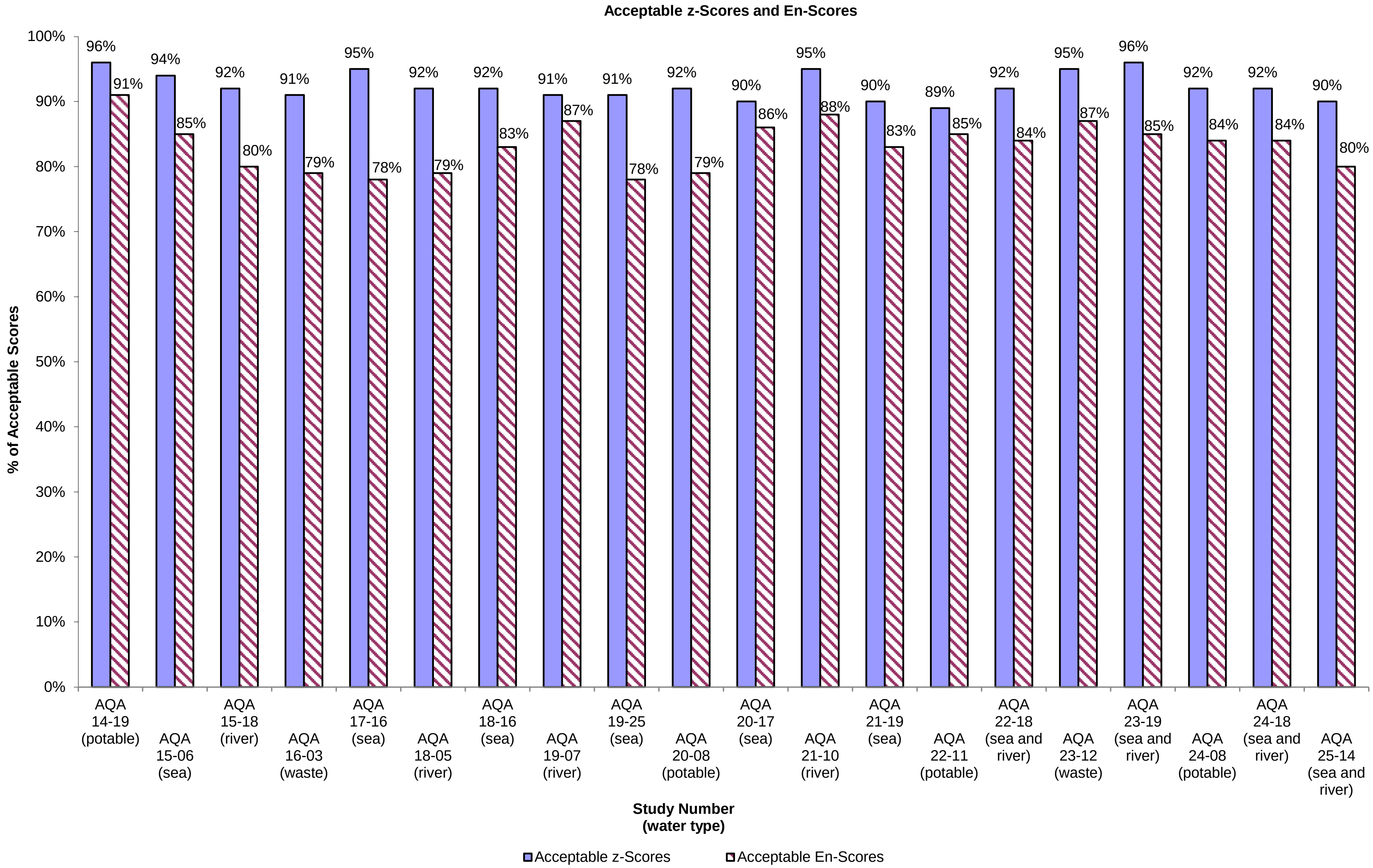


Figure 76 Participant Performance in Nutrients, Anions and Physical Tests in Water PT Studies over Time

7 REFERENCES

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

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared from approximately 20L of seawater that was, autoclaved and mixed thoroughly before being dispensed into 200 mL portions.

Sample S2 was prepared from approximately 20 L of river water that was autoclaved. This water was then fortified for two analytes, mixed thoroughly, and dispensed into 200 mL portions.

Sample S3 was prepared from approximately 20 L of seawater that was autoclaved and then fortified for three analytes, mixed thoroughly, and dispensed into 200 mL portions.

Sample S4 was prepared from approximately 20 L of autoclaved river water fortified for three analytes, mixed thoroughly, and dispensed into 200 mL portions.

Sample S5 was prepared from approximately 20 L of autoclaved seawater fortified for one analyte and mixed thoroughly before being dispensed into 200 mL portions.

Sample Analysis and Homogeneity Testing

A partial homogeneity test was conducted for ammonia-N, nitrate-N + nitrite-N, orthophosphate-P, TDN and TDP in Samples S1 and S2. Moreover, a partial homogeneity test was conducted on all analytes in Samples S3 and S4. For these tests, three bottles were analysed in duplicate, and the average of the results was reported as the homogeneity value.

Sample Analysis Methodology

Analyses were conducted by NMIA Analytical Services Branch, Inorganics section. A summary of the measurement methods and instrumental techniques used is presented in Table 51.

Table 51 Sample Analysis Methodology

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination – OPA Method	SFA
Nitrate-N + Nitrite-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA
Orthophosphate-P	Ascorbic Acid Colorimetric Method	DA
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 ($K_2S_2O_8$ Digestion)	SFA
Total Nitrogen	Persulfate Digestion	SFA
Total Organic Carbon	High Temperature Oxidation	NIR-detector
Total Phosphorus	$K_2S_2O_8$ Digestion; Ascorbic Acid Colorimetric Method	SFA

APPENDIX 2 - STABILITY STUDY

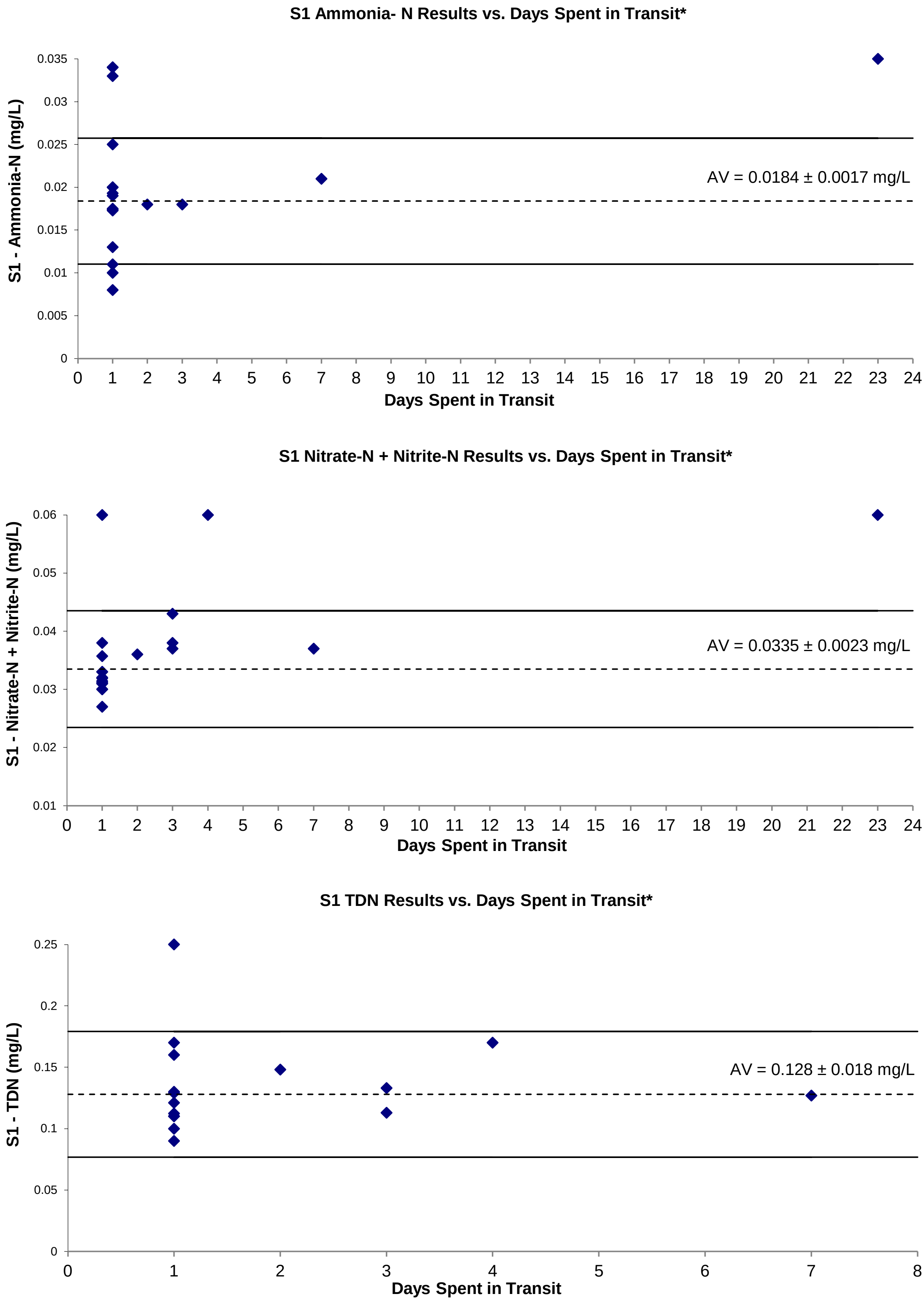
The test samples were dispatched on 29 September 2025. Participants were advised to store samples S1, S2, S3 and S4 frozen, if unable to commence analysis on the day of receipt. Samples' condition on receipt and the date when the samples were received and analysed by participants are presented in Table 52.

Table 52 Sample S1, S2, S3 and S4 Condition on Receipt and Dates When Sample was Received/Analysed

Lab Code	Received Date	S1		S2		S3		S4	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	30/09/2025	frozen	3/10/2025	frozen	3/10/2025	frozen	3/10/2025	NA	NA
2	30/09/2025	frozen	8/10/2025	frozen	8/10/2025	frozen	8/10/2025	NA	NA
3	30/09/2025	frozen	3/10/2025	frozen	3/10/2025	frozen	3/10/2025	NA	NA
4	30/09/2025	cold	3/10/2025	NA	NA	cold	3/10/2025	NA	NA
5	1/10/2025	frozen	1/10/2025	frozen	1/10/2025	NA	NA	frozen	1/10/2025
6	30/09/2025	frozen	2/10/2025	NA	NA	NA	NA	NA	NA
7	30/09/2025	frozen	2/10/2025	frozen	2/10/2025	frozen	3/10/2025	frozen	3/10/2025
8	30/09/2025	frozen	1/10/2025	frozen	1/10/2025	frozen	1/10/2025	frozen	1/10/2025
9	30/09/2025	frozen	1/10/2025	frozen	1/10/2025	frozen	1/10/2025	frozen	1/10/2025
10	22/10/2025	NR	16/10/2025	NA	NA	NA	NA	NA	NA
11	2/10/2025	NA	NA	frozen	02.10.25-13.10.25	NA	NA	NA	NA
12	3/10/2025	cold	Various	cold	Various	cold	Various	cold	Various
13	2/10/2025	frozen	3/10/2025	frozen	3/10/2025	frozen	3/10/2025	frozen	3/10/2025
14	2/10/2025	frozen	22/10/2025	frozen	22/10/2025	frozen	22/10/2025	frozen	22/10/2025
15	30/09/2025	Partially frozen	22/10/2025	NA	NA	NA	NA	NA	NA
16	30/09/2025	frozen	8/10/2025	frozen	8/10/2025	frozen	8/10/2025	frozen	8/10/2025
17	6/10/2025	cold	14/10/2025	cold	14/10/2025	cold	14/10/2025	cold	14/10/2025
18	30/09/2025	frozen	various	cold	various	NA	NA	NA	NA
19	6/10/2025	NA	NA	room temperature	07/10/25-08/10/25	NA	NA	NA	NA
20	30/09/2025	cold	3/10/2025	cold	6/10/2025	cold	9/10/2025	NA	NA
21	30/09/2025	partially thawed	Various	frozen	Various	partially thawed	Various	frozen	Various
22	30/09/2025	frozen	30/09/2025	frozen	30/09/2025	frozen	30/09/2025	frozen	30/09/2025
23	3/10/2025	cold	3/10/2025	cold	3/10/2025	frozen	3/10/2025	cold	3/10/2025
24	30/09/2025	partially frozen	10/09/2025	NA	NA	NA	NA	NA	NA
25	30/09/2025	partially frozen	10/09 & 13/09	NA	NA	NA	NA	NA	NA
26	30/09/2025	frozen	10/10/2025	frozen	8/10/2025	frozen	10/10/2025	frozen	10/10/2025
27	30/09/2025	frozen	10/10/2025	frozen	10/10/2025	cold	8/10/2025	cold	8/10/2025
28	2/10/2025	frozen	8/10/2025	frozen	8/10/2025	frozen	7/10/2025	frozen	7/10/2025

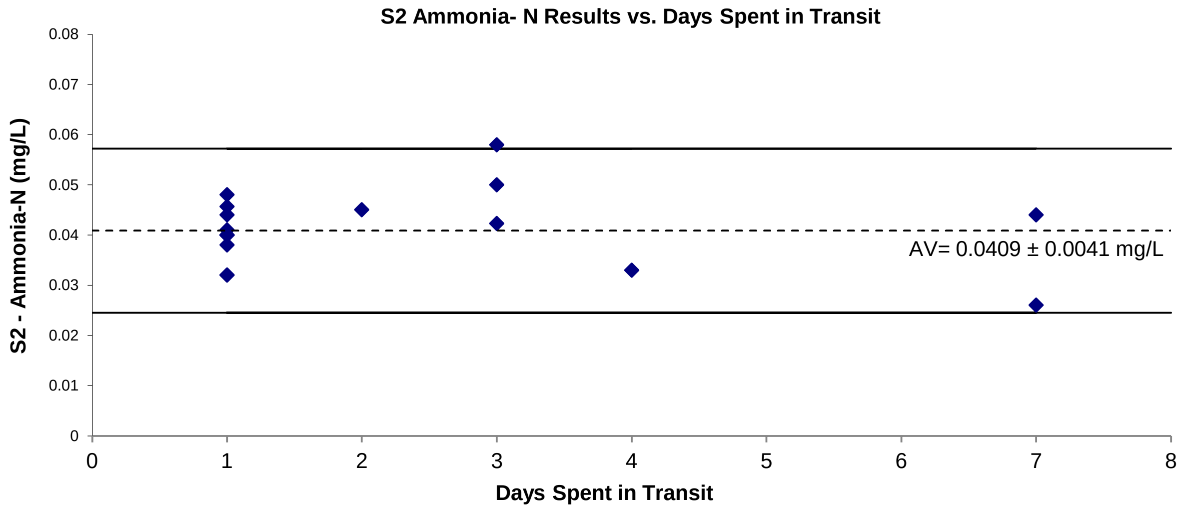
NA = Not Applicable, NR = Not Reported.

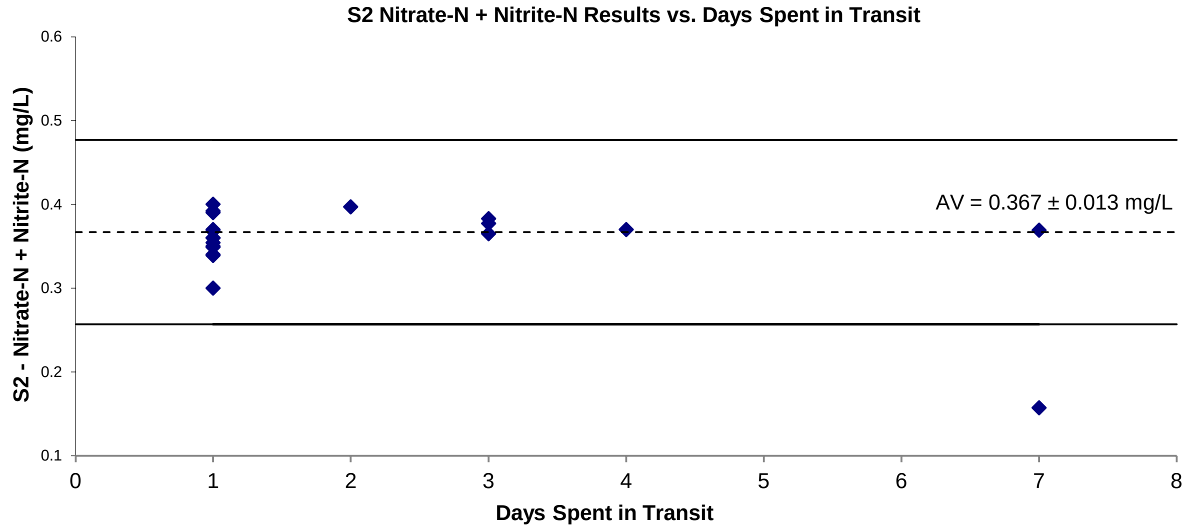
No relationship was evident between the participants' results reported for less stable analytes (ammonia-N, Nitrate-N + Nitrite-N, TDN), the samples' condition on receipt, or the number of days spent in transit (Figures 77 and 78).

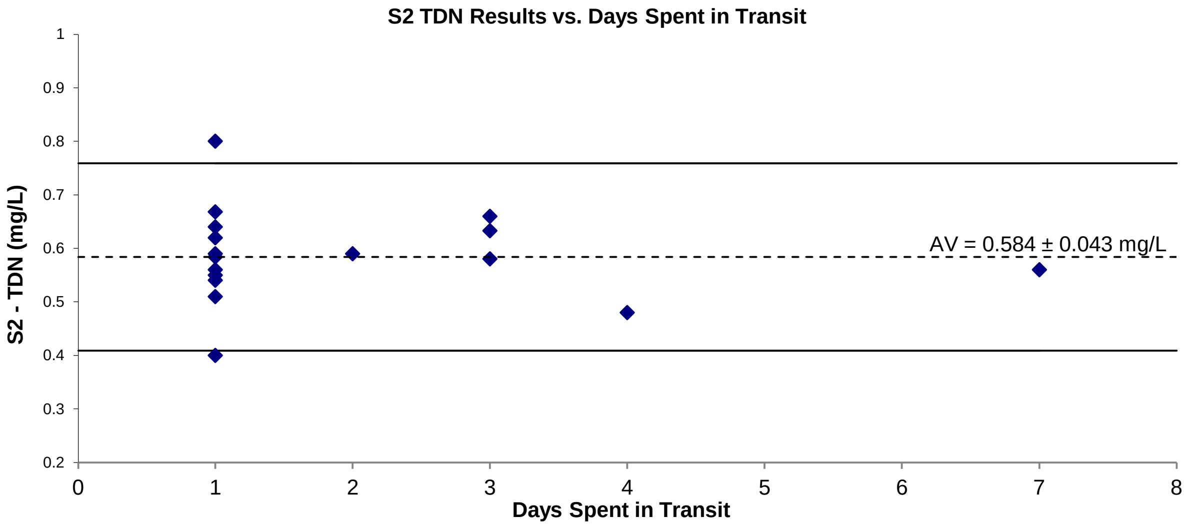


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.* Results larger than the maximum y-axis value have been set as the maximum y-axis value.

Figure 77 Results vs Days Spent in Transit

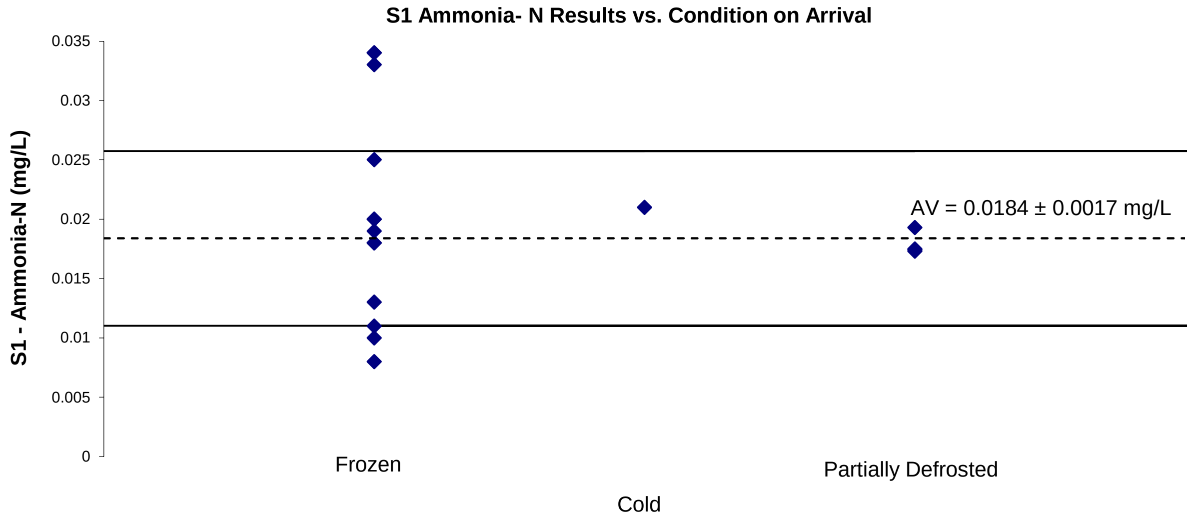


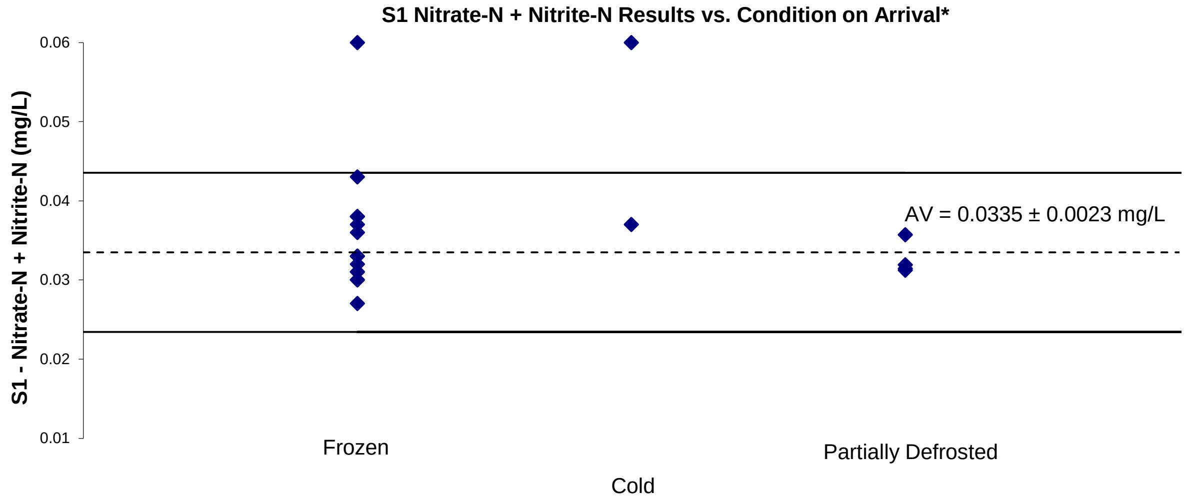


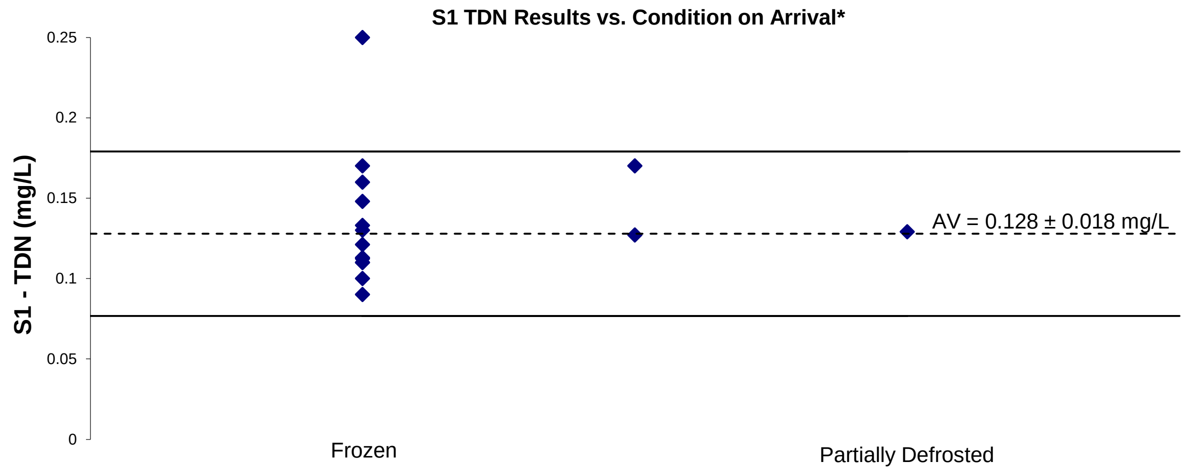


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 77 Results vs Days Spent in Transit (continued)

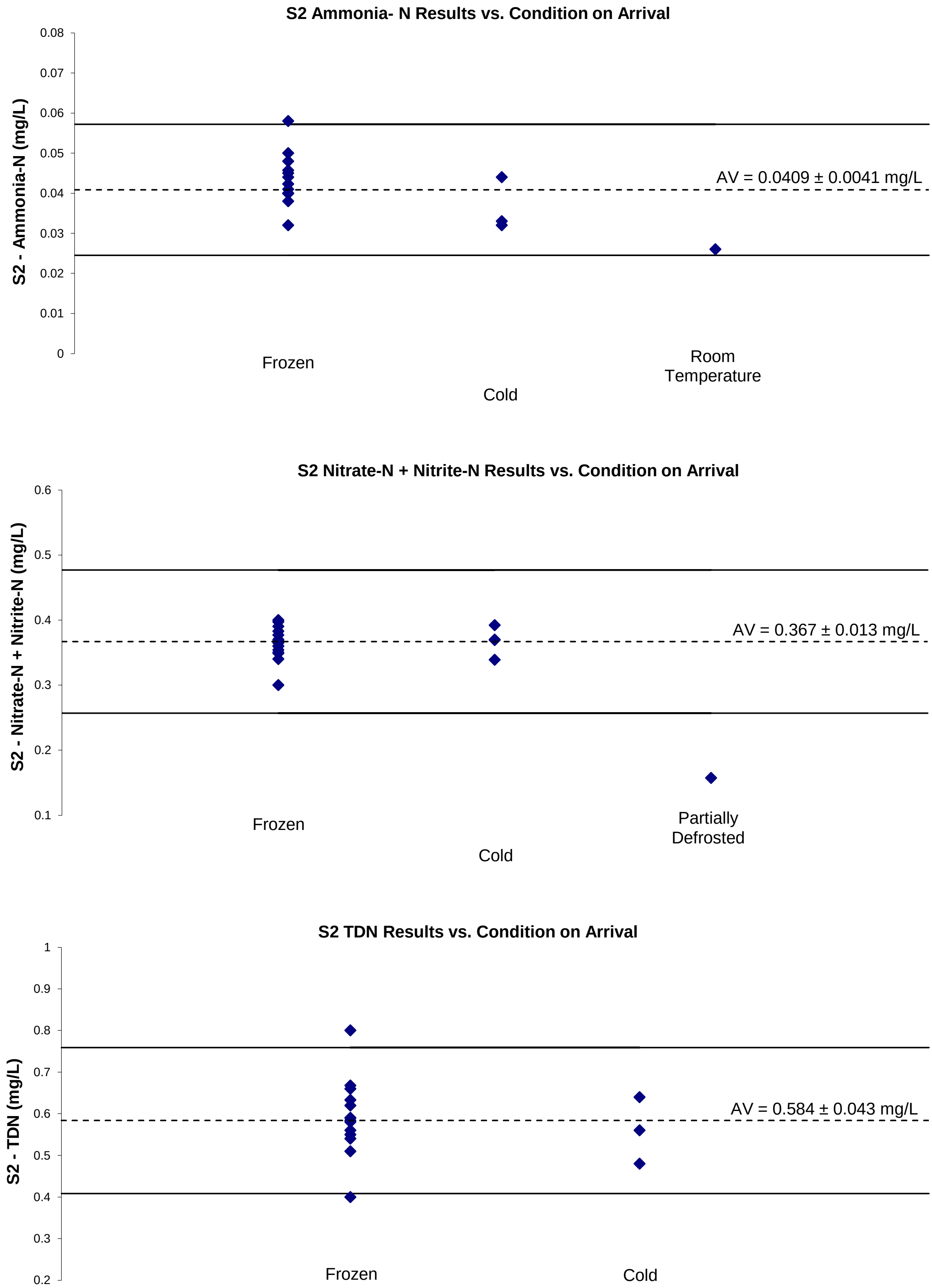






Horizontal lines on charts are the results corresponding to z-scores of 2 and -2. * Results larger than the maximum y-axis value have been set as the maximum y-axis value.

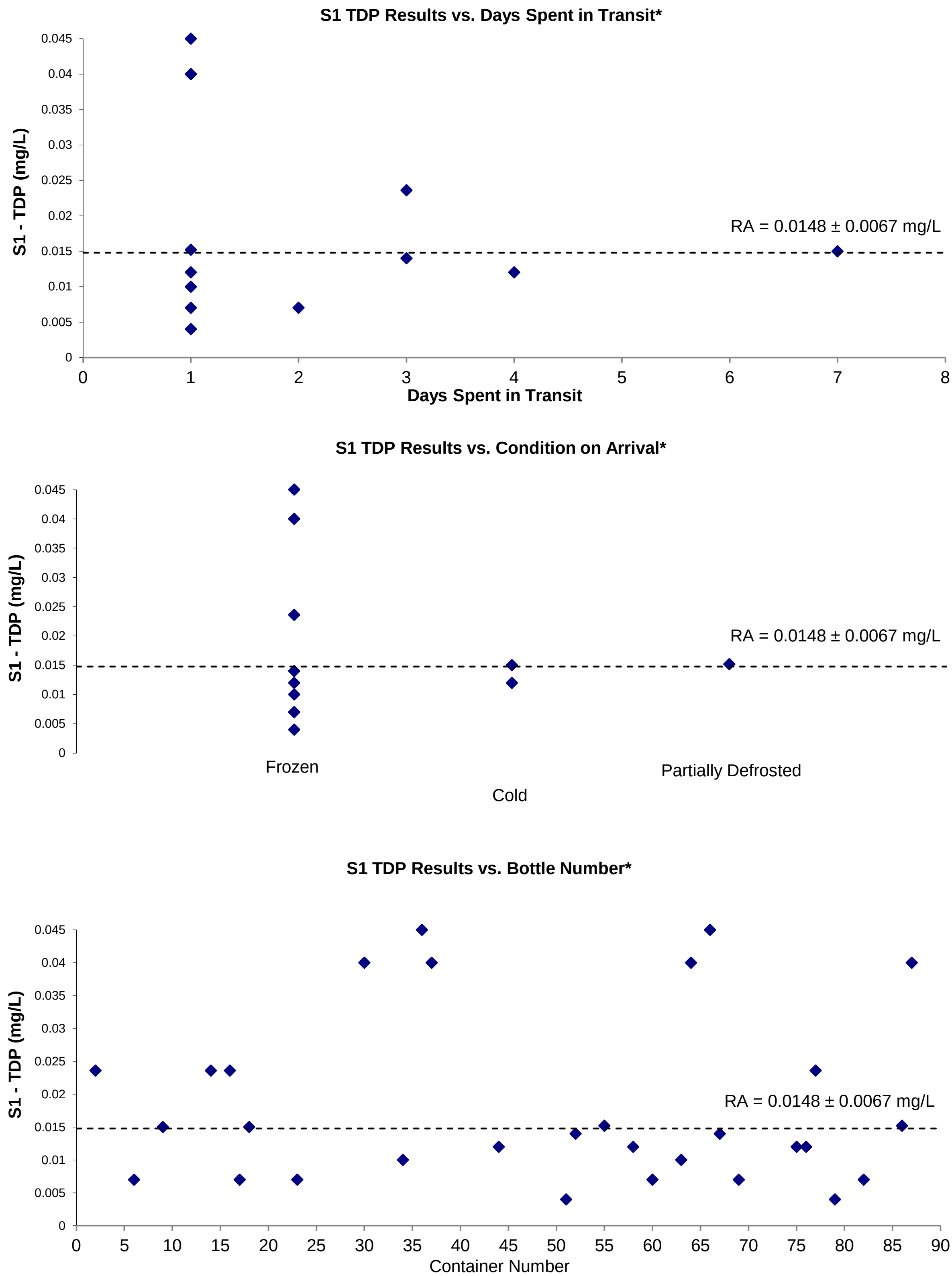
Figure 78 Results vs Condition on Arrival



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

Figure 78 Results vs Condition on Arrival (continued)

No relationship was also evident between the participants' results reported for TDP in S1 and samples' condition on receipt, the number of days spent in transit or the container number (Figure 79).



* Results larger than the maximum y-axis value have been set as the maximum y-axis value

Figure 79 S1 TDP Results vs Days in Transit, Arrival Condition, and Container Number

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 in Sample S1: ammonia-N, NOx-N, orthophosphate-P, total dissolved nitrogen and total dissolved phosphorus.

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 sample) 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 with the assigned value (Figure 80).

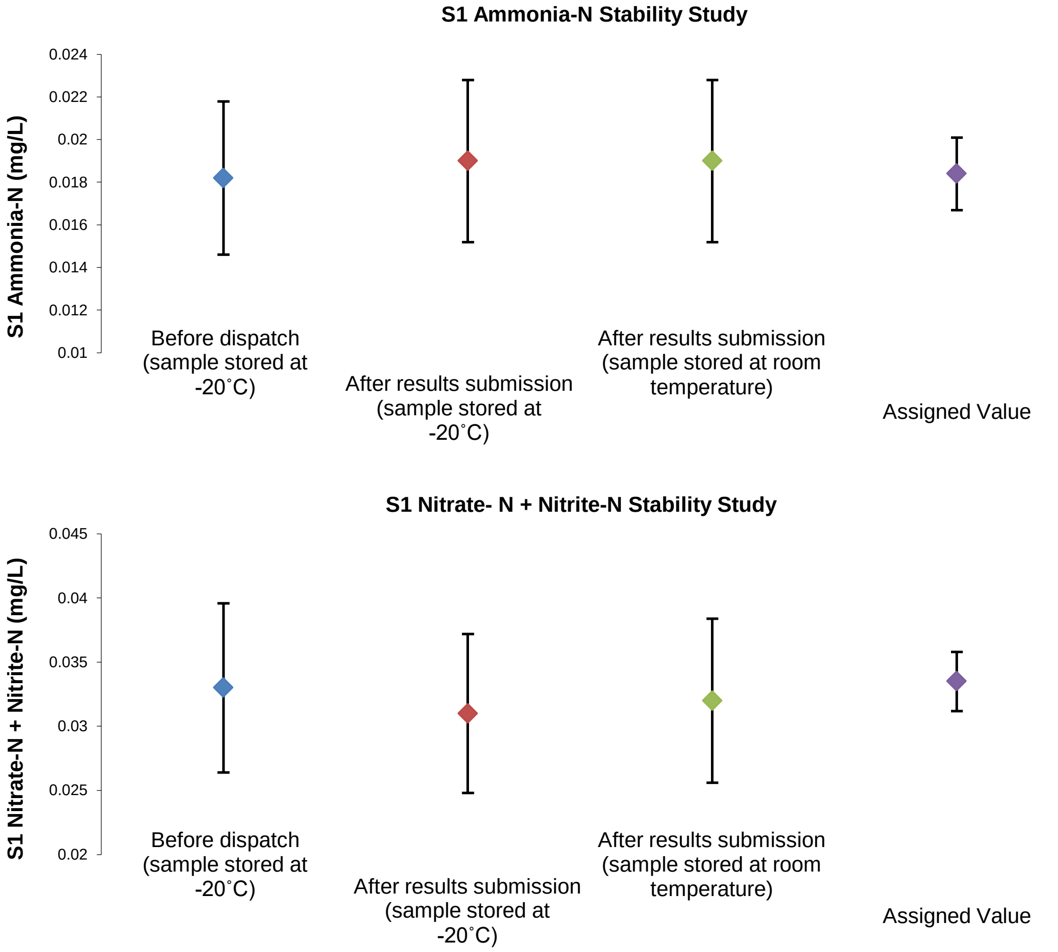


Figure 80 Stability Study Results

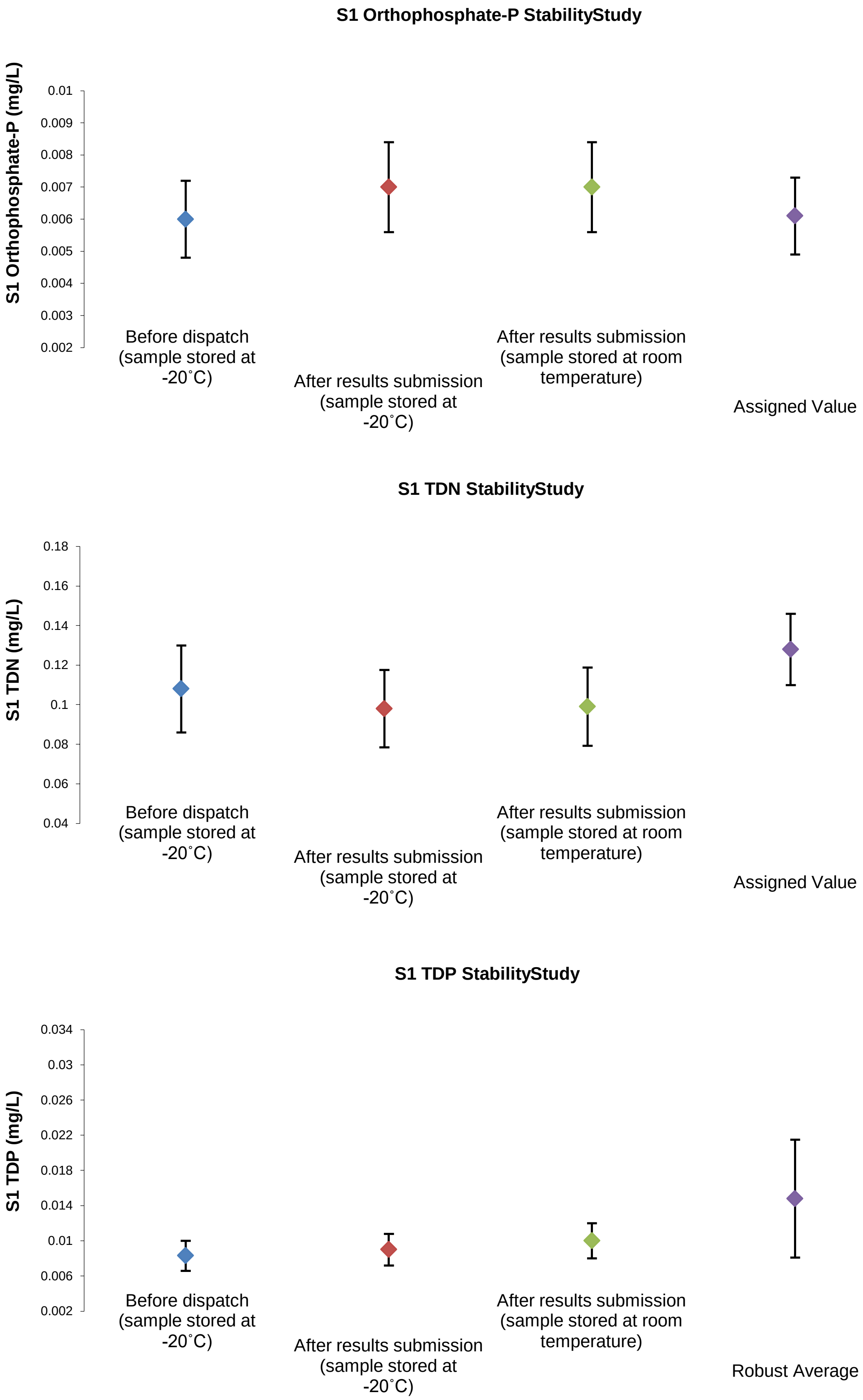


Figure 80 Stability Study Results (continued)

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 evaluated 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 53.

Table 53 Uncertainty of Assigned Value for Sulphate in Sample S1

No. results (p)	21
Robust Average	2843 mg/L
$S_{rob\ av}$	240 mg/L
$u_{rob\ av}$	65 mg/L
k	2
$U_{rob\ av}$	130 mg/L

The assigned value for **Sulphate** in Sample S1 is **2840 ± 130 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 54.

Table 54 z-Score and E_n-score for the Sample S1 Sulphate result reported by Laboratory 3

Result (mg/L)	Assigned Value (mg/L)	Standard Deviation for Proficiency Assessment	z-Score	E_n-Score
2676 ± 802.8	2840 ± 130	10% as CV or 0.1 x 2840 = = 284 mg/L	$z = \frac{(2676 - 2840)}{284}$ z = -0.58	$En = \frac{(2676 - 2840)}{\sqrt{802.8^2 + 130^2}}$ E_n = -0.20

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] Between 2014 and 2025, NMIA carried out 20 proficiency tests for nutrients, anions and physical tests in water. These studies involved measurements of 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 55 and 56).

Table 55 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
AQA 25-14	River	82.3 ± 8.5	85.9 ± 4.4	20	8.8
				Average	5.8*
$\boldsymbol{pooled\ s}\% = \sqrt{\frac{(\mathbf{8-1})\times\mathbf{2.9^2}+(\mathbf{10-1})\times\mathbf{6.5^2}+\cdots\cdots\cdots+(\mathbf{20-1})\times\mathbf{8.8^2})}{\mathbf{182-12}}}$					6.1

* The pooled standard deviation was used.

Table 56 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
AQA 25-14	Sea	22800 ± 2500	20800 ± 800	20	7.2
				Average	5.5*
$\boldsymbol{pooled\ s}\% = \sqrt{\frac{(\mathbf{8-1})\times\mathbf{6.3^2}+(\mathbf{10-1})\times\mathbf{4.1^2}+\cdots\cdots\cdots+(\mathbf{20-1})\times\mathbf{7.2^2})}{\mathbf{124-10}}}$					6.4

* The pooled standard deviation was used.

Taking the pooled standard deviation of these PT samples for each concentration range gives evaluations of the relative standard uncertainty of 6.1% and 6.4% 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 57 sets out the expanded uncertainty for results of the measurement of Chloride in potable, fresh, waste or seawater over the range 0.5 – 30000 mg/L.

Table 57 Uncertainty of Chloride results evaluated 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
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
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
KED	Kinetic Energy Discrimination
Max	Maximum Value in a Set of Results
Md	Median
Min	Minimum Value in a Set of Results
MU	Measurement Uncertainty
NEDD	N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride)
NIR	Near-infrared
NMIA	National Measurement Institute 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/σ	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 58 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Phenate Method	DA	APHA 4500-NH3
2	Colorimetric - Phenate Method	DA	In-House Method
3	Colorimetric - Phenate Method	DA	In-House Method
4	Colorimetric - Phenate Method	DA	In-House Method
5	Colorimetric - Salicylate Method	FIA	In-House Method
6	Colorimetric - Salicylate Method	DA	APHA4500NH3
7	Colorimetric - Phenate Method	FIA	APHA
8	Colorimetric - Salicylate Method	FIA	In-House Method based on APHA 4500-NH3 H
9	Colorimetric - Phenate Method	FIA	APHA
10	Colorimetric - Phenate Method	UV-Vis Spectrophotometer	SM 4500 NH3- F
12	Colorimetric - Phenate Method	FIA	APHA (4500-NH3 H
13	Colorimetric - Phenate Method	DA	In house
14	Colorimetric - Phenate Method	DA	APHA 4500-NH3 G
15	Fluorometric Determination - OPA Method		Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
16	Fluorometric Determination - OPA Method	SFA	SFA
17	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
18	Colorimetric - Phenate Method	FIA	APHA 4500-NH3
20	Colorimetric - Salicylate Method	DA	In-house
21	Colorimetric - Phenate Method	FIA	Inhouse
22	Colorimetric - Phenate Method	FIA	APHA 4500-NH3
23	Ion Selective Electrode Method		
24	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
25	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
26	Colorimetric - Phenate Method	FIA	Lachat QuikChem
27	Colorimetric - Phenate Method	FIA	In house
28	Colorimetric - Phenate Method	FIA	

Table 59 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl
2	Colorimetric	DA	In-House Method
3	Ion Chromatographic Method	IC	In-House Method
4	Ferricyanide Colorimetric Method	DA	In-House Method
5	Mercuric Thiocyanate	DA	
6	Mercuric Thiocyanate	DA	APHA4500Cl-
8	Argentometric Titration	Manual Analysis	In-House Method based on APHA, 4500-Cl- B
9	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	APHA (4110 B
13	Mercuric Thiocyanate	DA	In house
14	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl E
16	Ferricyanide Colorimetric Method	DA	APHA
17	Mercuric Thiocyanate	DA	APHA 4500 Cl-
18	Potentiometric-Titration	Auto Titration	APHA 4500-Cl D
20	Ferricyanide Colorimetric Method	DA	In-house
21	Ferricyanide Colorimetric Method	FIA	Inhouse
22	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl
23	Ion Chromatographic Method		
26	Ion Chromatographic Method	IC	APHA
27	Ion Chromatographic Method	IC	In house
28	ICP-Method	ICP-MS	In house

Table 60 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
2	High-Temperature Oxidation	TOC-L	In-House Method
3	High-Temperature Oxidation	NIR-detector	In-House Method
5	High-Temperature Oxidation	NIR-detector	APHA 5310 A, B and C
6	High-Temperature Oxidation	NIR-detector	APHA5310B
9	High-Temperature Oxidation	NIR-detector	APHA
12	High-Temperature Oxidation	NIR-detector	APHA (5310 B)
13	High-Temperature Oxidation		In house
14	High-Temperature Oxidation	NIR-detector	APHA5310B
16	High-Temperature Oxidation	NIR-detector	APHA
17	High-Temperature Oxidation	NIR-detector	APHA 5310 B
18	Wet-Oxidation	NDIR	APHA 5310 C
21	High-Temperature Oxidation	NIR-detector	Inhouse
22	High-Temperature Oxidation	NIR-detector	
26	High-Temperature Oxidation	NIR-detector	APHA
28	High-Temperature Oxidation	TOC-L	

Table 61 Measurement Methods and Instrument Techniques for Fluoride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F
3	Ion Chromatographic Method	IC	In-House Method
4	SPADNS Colorimetric Method	DA	In-House Method
5	Ion Selective Electrode Method	Auto Titration	APHA, 4500-F
6	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500F
8	Ion Selective Electrode Method	Ion Selective Electrode	In-House Method based on APHA, 4500-F- A,C
9	Ion Chromatographic Method	IC	APHA
12	Ion Selective Electrode Method	FIA	APHA (4500-F G)
13	Ion Selective Electrode Method	Ion Selective Electrode	In house
14	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F C
16	Ion Selective Electrode Method	Ion Selective Electrode	APHA
17	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F C
18	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500- F
20	Ion Chromatographic Method	IC	In-house
21	Ion Selective Electrode Method	Ion Selective Electrode	Inhouse
22	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F
23	Ion Chromatographic Method		
26	Ion Chromatographic Method	IC	APHA
27	Ion Chromatographic Method	IC	In house
28	Ion Selective Electrode Method	Ion Selective Electrode	

Table 62 Measurement Methods and Instrument Techniques for Nitrate-N + Nitrite-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	APHA 4500-NO3
2	Colorimetric -vanadium III method	DA	In-House Method
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	In-House Method
4	Colorimetric -vanadium III method	DA	In-House Method
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In-House Method
6	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO32
7	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In-House Method based on APHA, 4500-NO3 - A, E, I
9	Colorimetric - phenate method	FIA	APHA
10	Calculation	UV-Vis Spectrophotometer	SM 4500 NO3-(Nitrate) B + SM 4500 NO2 B(Nitrite)
12	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA (4500-NO3 I)
13	Colorimetric -vanadium III method	DA	In house
14	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	APHA 4500-NO3 I
15	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
16	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	SFA
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3- I
18	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3 I
20	Colorimetric -vanadium III method	DA	In-house
21	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Inhouse
22	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-N
24	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
25	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
26	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Lachat QuikChem
27	Colorimetric - phenate method	FIA	In house
28	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	

Table 63 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
3	Ascorbic Acid Colorimetric Method	DA	In-House Method
4	Ascorbic Acid Colorimetric Method	DA	In-House Method
5	Ascorbic Acid Colorimetric Method	FIA	In-House Method
6	Vanadomolybdophosphoric Colorimetric Method	DA	APHA4500P
7	Ascorbic Acid Colorimetric Method	FIA	APHA
8	Ascorbic Acid Colorimetric Method	FIA	In-House Method based on APHA, 4500-P A,B,E
9	Vanadomolybdophosphoric Colorimetric Method	FIA	APHA
10	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer	SM 4500 P E (Total Reactive Phosphorus)
12	Ascorbic Acid Colorimetric Method	FIA	APHA (4500-P G)
13	Ascorbic Acid Colorimetric Method	DA	In house
14	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P G
15	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
16	Ascorbic Acid Colorimetric Method	SFA	APHA
17	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P E
18	Stannous Chloride Colorimetric Method	FIA	APHA 4500-P-G
20	Vanadomolybdophosphoric Colorimetric Method	DA	In-house
21	Ascorbic Acid Colorimetric Method	FIA	Inhouse
22	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
24	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
25	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
26	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
27	Ascorbic Acid Colorimetric Method	FIA	In house
28	Ascorbic Acid Colorimetric Method	FIA	

Table 64 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1	Turbidimetric Method	DA	APHA 4500-SO4
2	Colorimetric Method	DA	In-House Method
3	Ion Chromatographic Method	IC	In-House Method
4	Turbidimetric Method	DA	In-House Method
5	Turbidimetric Method	DA	APHA, 4500-SO42- E
6	ICP Method	ICP-OES	APHA3120B
8	Turbidimetric Method	FIA	In-House Method based on APHA, 4500-SO4 2-
9	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	APHA (4110 B
13	Turbidimetric Method	DA	In house
14	ICP Method	ICP-MS/MS	USEPA200.8
16	Turbidimetric Method	DA	APHA
17	Turbidimetric Method	DA	APHA 4500-SO4
18	ICP Method	ICP-MS	APHA 3125B
20	Turbidimetric Method	DA	In-house
21	Turbidimetric Method	FIA	Inhouse
22	Turbidimetric Method	DA	APHA 4500-SO4
23	Ion Chromatographic Method		
26	Ion Chromatographic Method	IC	APHA
27	Ion Chromatographic Method	IC	In house
28	ICP Method	ICP-MS	In House

Table 65 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	DA	APHA 4500-N
3	Persulfate digestion	DA	In-House Method
5	Persulfate digestion	FIA	APHA, 4500-P J. & 4500-N C.
6	Calculation (TKN+NOx)	Not Applicable	NA
7	Persulfate digestion	FIA	APHA
8	Persulfate digestion	FIA	In-House Method based on APHA, 4500-N C
9	Persulfate digestion	FIA	APHA
12	Persulfate digestion	FIA	APHA (4500-NO3 I)
13	Calculation (TKN+NOx)	DA	In house
14	Calculation (TKN+NOx)	SFA	
16	Persulfate digestion	SFA	APHA
17	Persulfate digestion	FIA	APHA 4500-N B
18	Persulfate digestion	FIA	Inhouse
21	Persulfate digestion	FIA	Inhouse
22	Persulfate digestion	FIA	APHA 4500-N
26	Persulfate digestion	FIA	Lachat QuikChem
27	Persulfate digestion	FIA	In house
28	Persulfate digestion	FIA	

Table 66 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
2	No Digestion	ICP Method	ICP-MS	In-House Method
3	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In-House Method
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P J. & 4500-N C.
6	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA1500P
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
8	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-House Method based on APHA, 4500-P H
9	Persulfate digestion		FIA	APHA
12	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA (4500-P G)
13	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	SFA	USEPA365.4
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P I
18	K2S2O8-Digestion	Stannous Chloride Colorimetric Method	FIA	Inhouse
20	No Digestion	ICP Method	ICP-MS	in-house
21	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
26	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
27	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In house
28	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	

APPENDIX 7 - METHODOLOGY FOR S2

Table 67 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)
2	ICP-MS	Sc	CRI	He	x1	11
3	ICP-MS	Sc	ORS	He	1	11 (m/z)
5	ICP-MS	45	ORS	He		11
9	ICP-OES-AV	Te			100	249
11	ICP-MS	Sc	KED	He	1	10
12	ICP-MS	Y 89	ORS	Standard Mode	11.2	11
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	11(m/z)
14	ICP-MS/MS	Sc	ORS	NA	1	
16	ICP-OES-AV	Y	NA		2	249.678
17	ICP-MS	Sc	ORS	NA	NA	11
18	ICP-MS	Sc 45	KED	He	1	11
20	ICP-MS	Scandium			5	11
21	ICP-OES-AV-buffer	Lu				249.678
22	ICP-OES-AV	Eu & Cs	NA	He	1	249.773nm
26	ICP-MS					
27	ICP-OES-AV	Lu	NA	NA	1.05	208.956
28	ICP-MS	Sc	NA	NA	1	10

Table 68 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)
2	ICP-MS	Sc	CRI	He	x1	40
3	ICP-MS	Sc	ORS	H2	1	40 (m/z)
5	ICP-MS	45	ORS	He		44
9	ICP-OES-AV	Y			100	317.933
11	ICP-MS	Sc	KED	He	1	43
12	ICP-MS	Y 89	ORS	H2	11.2	40
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	44(m/z)
14	ICP-MS/MS	Sc	ORS	H2+N2O	1	
16	ICP-OES-RV	Y	NA		100	422.673
17	ICP-MS	Sc	ORS	He	NA	44
18	ICP-MS	Sc 45	KED	He	1	44
19	GFAAS		NA	NA	5	422.7
20	ICP-MS	Scandium	ORS	H2	1	40
21	ICP-OES-AV-buffer	Lu				430.253
22	ICP-OES-AV	Eu & Cs	NA	He	1	315.887, 370.602nm
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	1.05	422.673
28	ICP-MS	Sc	UC	He	1	44

Table 69 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)
2	ICP-MS	Sc	CRI	He	x1	39
3	ICP-MS	Sc	ORS	He	1	39 (m/z)
5	ICP-MS	45	ORS	He		39
9	ICP-OES-RV	Te			100	766.491
11	ICP-MS	Sc	KED	He	1	39
12	ICP-MS	Y 89	ORS	He	11.2	39
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	38(m/z)
14	ICP-MS/MS	Sc	ORS	H2+N2O	1	
16	ICP-OES-RV	Y	NA		100	766.491
17	ICP-MS	Sc	ORS	He	NA	39
18	ICP-MS	Sc 45	KED	He	1	39
19	GFAAS		NA	NA	5	766.5
20	ICP-MS	Scandium	ORS	He	1	39
21	ICP-OES-AV-buffer	Lu				766.491
22	ICP-OES-AV	Eu & Cs	NA	He	1	404.721nm, 766.491nm
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	1.05	766.491
28	ICP-MS	Sc	UC	He	1	39

Table 70 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)
2	ICP-MS	Sc	CRI	He	x1	24
3	ICP-MS	Sc	ORS	He	1	24 (m/z)
5	ICP-MS	45	ORS	He		25
9	ICP-OES-AV	Y			100	279.553
11	ICP-MS	Sc	KED	He	1	25
12	ICP-MS	Y 89	ORS	H2	11.2	24
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	24(m/z)
14	ICP-MS/MS	Sc	ORS	He	1	
16	ICP-OES-RV	Y	NA		100	279.078
17	ICP-MS	Sc	ORS	He	NA	24
18	ICP-MS	Sc 45	KED	He	1	25
19	GFAAS		NA	NA	5	285.2
20	ICP-MS	Scandium	ORS	He	1	24
21	ICP-OES-AV-buffer	Lu				279.078
22	ICP-OES-AV	Eu & Cs	NA	He	1	383.830 (nm)
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	1.05	285.213
28	ICP-MS	Sc	UC	He	1	25

Table 71 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)
2	ICP-MS	Sc	CRI	He	x1	23
3	ICP-MS	Sc	ORS	He	1	23 (m/z)
5	ICP-MS	45	ORS	He		23
9	ICP-OES-RV	Te			100 100	589.592
11	ICP-MS	Sc	KED	He	1	23
12	ICP-MS	Y 89	ORS	H2	1.12	23
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	23(m/z)
14	ICP-MS/MS	Sc	ORS	He	1	
16	ICP-OES-RV	Y	NA		100	589.592
17	ICP-MS	Sc	ORS	He	NA	23
18	ICP-MS	Sc 45	KED	He	1	23
19	GFAAS		NA	NA	50	589
20	ICP-MS	Scandium	ORS	He	1	23
21	ICP-OES-AV-buffer	Lu				589.592
22	ICP-OES-AV	Eu & Cs	NA	He	1	330.237, 589.592nm
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	1.05	589.592
28	ICP-MS	Sc	UC	He	1	23

Table 72 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Phenate Method	DA	APHA 4500-NH3
2	Colorimetric - Phenate Method	DA	In-House Method
3	Colorimetric - Phenate Method	DA	In-House Method
5	Colorimetric - Salicylate Method	FIA	In-House Method
7	Colorimetric - Phenate Method	FIA	APHA
8	Colorimetric - Salicylate Method	FIA	In-House Method based on APHA 4500-NH3 H
9	Colorimetric - Phenate Method	FIA	APHA
12	Colorimetric - Phenate Method	FIA	APHA (4500-NH3 H)
13	Colorimetric - Phenate Method	DA	In house
14	Colorimetric - Phenate Method	DA	APHA 4500-NH3 G
16	Fluorometric Determination - OPA Method	SFA	SFA
17	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
18	Colorimetric - Salicylate Method	FIA	APHA 4500-NH3
19	Colorimetric - Salicylate Method	UV-Vis Spectrophotometer	In-House Method
20	Colorimetric - Salicylate Method	DA	In-house
21	Colorimetric - Phenate Method	FIA	Inhouse
22	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
26	Colorimetric - Phenate Method	FIA	Lachat QuikChem
27	Colorimetric - Phenate Method	FIA	In House
28	Colorimetric - Phenate Method	FIA	

Table 73 Measurement Methods and Instrument Techniques for Bromide

Lab. Code	Measurement Method	Instrument	Method Reference
3	Ion Chromatographic Method	IC	In-House Method
5	Ion Chromatographic Method	IC	APHA 4110.
9	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	APHA (4110 B)
14	Ion Chromatographic Method	IC	USEPA Method 300.0
16	Ion Chromatographic Method	IC	APHA
20	Ion Chromatographic Method	IC	In-house
21	Ferricyanide Colorimetric Method	FIA	Inhouse
22	Ion Chromatographic Method	IC	APHA 4110
26	Ion Chromatographic Method	IC	APHA
27	Ion Chromatographic Method	IC	APHA 4110B
28		ICPMS	

Table 74 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl
2	Colorimetric Method	DA	In-House Method
3	Ion Chromatographic Method	IC	In-House Method
5	Ion Chromatographic Method	IC	APHA 4110.
8	Argentometric Titration	Manual Analysis	In-House Method based on APHA, 4500-Cl- B
9	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	APHA (4110 B)
13	Mercuric Thiocyanate	DA	In house
14	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl E
16	Ferricyanide Colorimetric Method	DA	APHA
17	Mercuric Thiocyanate	DA	APHA 4500 Cl-
18	Potentiometric-Titration	Auto Titration	APHA 4500-Cl D
19	Argentometric Titration	Manual Analysis	USEPA Method
20	Ferricyanide Colorimetric Method	DA	In-house
21	High-Temperature Oxidation	NIR-detector	Inhouse
22	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl E
26	Ion Chromatographic Method	IC	APHA
27	Ion Chromatographic Method	IC	APHA 4110B
28	ICP-Method	ICP-MS	In house

Table 75 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
2	High-Temperature Oxidation	TOC-L	In-House Method
3	High-Temperature Oxidation	NIR-detector	In-House Method
5	High-Temperature Oxidation	Other	APHA 5310 A, B and C
9	High-Temperature Oxidation	NIR-detector	APHA
11	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA5310C (modified)
12	High-Temperature Oxidation	NIR-detector	APHA (5310 B)
13	High-Temperature Oxidation		In house
14	Wet-Oxidation	NIR-detector	APHA5310C
16	High-Temperature Oxidation	NIR-detector	APHA
17	High-Temperature Oxidation	NIR-detector	APHA 5310 B
18	Wet-Oxidation	NDIR	APHA 5310 C
21	Ion Selective Electrode Method	Ion Selective Electrode	Inhouse
22	High-Temperature Oxidation	NIR-detector	APHA 5310 C
26	High-Temperature Oxidation	NIR-detector	APHA
28	High-Temperature Oxidation	TOC-L	

Table 76 Measurement Methods and Instrument Techniques for Nitrate-N + Nitrite-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	APHA 4500-NO3
2	Colorimetric -vanadium III method	DA	In-House Method
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	In-House Method
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In-House Method
7	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In-House Method based on APHA, 4500-NO3 - A, E, I
9	Colorimetric - phenate method	FIA	APHA
12	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA (4500-NO3 I)
13	Colorimetric -vanadium III method	DA	In house
14	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	APHA 4500-NO3 I
16	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3- I
18	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3 I
19	Colorimetric - salicylate method	UV-Vis Spectrophotometer	In-House Method
20	Colorimetric -vanadium III method	DA	In-house
21	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Inhouse
22	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-N
26	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Lachat QuikChem
27	Colorimetric - phenate method	FIA	In House
28	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	

Table 77 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
3	Ascorbic Acid Colorimetric Method	DA	In-House Method
5	Ascorbic Acid Colorimetric Method	FIA	In-House Method
7	Ascorbic Acid Colorimetric Method	FIA	APHA
8	Ascorbic Acid Colorimetric Method	FIA	In-House Method based on APHA, 4500-P A,B,E
9	Vanadomolybdophosphoric Colorimetric Method	FIA	APHA
12	Ascorbic Acid Colorimetric Method	FIA	APHA (4500-P G)
13	Ascorbic Acid Colorimetric Method	DA	In house
14	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P G
16	Ascorbic Acid Colorimetric Method	SFA	APHA
17	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P E
18	Stannous Chloride Colorimetric Method	FIA	APHA 4500-P-G
19	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer	USEPA Method
20	Vanadomolybdophosphoric Colorimetric Method	DA	In-house
21	Ascorbic Acid Colorimetric Method	FIA	Inhouse
22	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P E
26	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
27	Ascorbic Acid Colorimetric Method	FIA	In House
28	Ascorbic Acid Colorimetric Method	FIA	

Table 78 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1	Turbidimetric Method	DA	APHA 4500-SO4
2	Colorimetric Method	DA	In-House Method
3	Ion Chromatographic Method	IC	In-House Method
5	Ion Chromatographic Method	IC	APHA 4110.
8	Turbidimetric Method	FIA	In-House Method based on APHA, 4500-SO4 2-
9	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	APHA (4110 B)
13	Turbidimetric Method	DA	In house
14	ICP Method	ICP-MS/MS	USEPA200.8
16	Turbidimetric Method	DA	APHA
17	Turbidimetric Method	DA	APHA 4500-SO4
18	ICP Method	ICP-MS	APHA 3125B
19	Turbidimetric Method	UV-Vis Spectrophotometer	USEPA Method
20	Turbidimetric Method	DA	In-house
21	Turbidimetric Method	FIA	Inhouse
22	Turbidimetric Method	DA	APHA 4500-SO4 E
26	Ion Chromatographic Method	IC	APHA
27	Ion Chromatographic Method	IC	APHA 4110B
28	ICP Method	ICP-MS	In House

Table 79 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	DA	APHA 4500-N
3	Persulfate digestion	DA	In-House Method
5	Persulfate digestion	FIA	APHA, 4500-P J. & 4500-N C
7	Persulfate digestion	FIA	APHA
8	Persulfate digestion	FIA	In-House Method based on APHA, 4500-N C
9	Persulfate digestion	FIA	APHA
12	Persulfate digestion	FIA	APHA (4500-NO3 I)
13	Calculation (TKN+NOx)	DA	In house
14	Calculation (TKN+NOx)	DA	
16	Persulfate digestion	SFA	APHA
17	Persulfate digestion	FIA	APHA 4500-N B
18	Persulfate digestion	FIA	Inhouse
21	Persulfate digestion	FIA	Inhouse
22	Persulfate digestion	FIA	APHA 4500-N C
26	Persulfate digestion	FIA	Lachat QuikChem
27	Persulfate digestion	FIA	In House
28	Persulfate digestion	FIA	

Table 80 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
2	No Digestion	ICP Method	ICP-MS	In-House Method
3	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In-House Method
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P J. & 4500-N C
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
8	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-House Method based on APHA, 4500-P H
9	Persulfate digestion		FIA	APHA
12	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA (4500-P G)
13	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	USEPA365.4
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P I
18	K2S2O8-Digestion	Stannous Chloride Colorimetric Method	FIA	Inhouse
19	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer	USEPA Method
20	No Digestion	ICP Method	ICP-MS	in-house
21	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P J
26	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
27	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In House
28	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	

APPENDIX 8 – METHODOLOGY FOR S3

Table 81 Instrument Techniques for Total Kjeldahl Nitrogen

Lab. Code	Measurement Method		Instrument	Method Reference
1	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - phenate method	DA	APHA 4500-N
3	TKN=TN-NOx (K2S2O8 digestion)	Not Applicable	Not Applicable	In-House Method
4	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric - phenate method	DA	In-House Method
8	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	In-House Method based on APHA, 4500-N Org A,D
9	Kjeldahl (H2SO4+K2SO4 digestion)	Titrimetric method	Auto Titration	APHA
12	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA (4500-NO3 I)
13	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500 Norg-A
14	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	SFA	APHA 4500-N org A
16	TKN=TN-NOx (K2S2O8 digestion)	Calculation from TN and NOX	SFA	APHA
17	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-N C & 4500-NO3 I
20	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	In-house
22	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - phenate method	FIA	APHA 4500-N
26	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
27	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	In House
28	TKN=TN-NOx (K2S2O8 digestion)		FIA	

Table 82 Instrument Techniques for Total Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Calculation (TKN+NOx)		APHA 4500-N
3	Persulfate digestion	DA	In-House Method
4	Persulfate digestion	DA	In-House Method
7	Persulfate digestion	FIA	APHA
8	Persulfate digestion	FIA	In-House Method based on APHA, 4500-N C
9	Persulfate digestion	FIA	APHA
12	Persulfate digestion	FIA	APHA (4500-NO3 I)
13	Calculation (TKN+NOx)	DA	
14	Calculation (TKN+NOx)	SFA	
16	Persulfate digestion	SFA	APHA
17	Persulfate digestion	FIA	APHA 4500-N B
21	Persulfate digestion	FIA	Inhouse
22	Persulfate digestion	FIA	APHA 4500-N
26	Persulfate digestion	FIA	Lachat QuikChem
27	Persulfate digestion	FIA	In House
28	Persulfate digestion	FIA	

Table 83 Instrument Techniques for Total Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
2	High-Temperature Oxidation	TOC-L	In-House Method
3	High-Temperature Oxidation	NIR-detector	In-House Method
9	High-Temperature Oxidation	NIR-detector	APHA
12	High-Temperature Oxidation	NIR-detector	APHA (5310 B)
13	High-Temperature Oxidation	NIR-detector	APHA 5310
14	High-Temperature Oxidation	NIR-detector	APHA5310B
16	High-Temperature Oxidation	NIR-detector	APHA
17	High-Temperature Oxidation	NIR-detector	APHA 5310 B
21	High-Temperature Oxidation	NIR-detector	Inhouse
22	High-Temperature Oxidation	NIR-detector	APHA 5310-C
26	High-Temperature Oxidation	NIR-detector	APHA
28	High-Temperature Oxidation	TOC-L	

Table 84 Instrument Techniques for Total Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
2	No Digestion	ICP Method	ICP-MS	In-House Method
3	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method		In-House Method
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
8	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-House Method based on APHA, 4500-P H
9		Persulfate digestion	FIA	APHA
12	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA (4500-P G)
13	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	SFA	USEPA365.4
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P I
21	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
26	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
27	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In House
28			FIA	

APPENDIX 9 – METHODOLOGY FOR S4

Table 85 Instrument Techniques for Total Kjeldahl Nitrogen

Lab. Code	Measurement Method		Instrument	Method Reference
5	TKN=TN-NOx (K2S2O8 digestion)	Calculation	FIA	N/A
8	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	In-House Method based on APHA, 4500-N Org A,D
9	Kjeldahl (H2SO4+K2SO4 digestion)	Titrimetric method	Auto Titration	APHA
12	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA (4500-NO3 I)
13	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500 Norg-A
14	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500-N org A
16	TKN=TN-NOx (K2S2O8 digestion)	Calculation from TN and NOX	SFA	APHA
17	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-N C & 4500-NO3 I
22	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - phenate method	FIA	APHA 4500-N
26	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
27	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	In House
28	TKN=TN-NOx (K2S2O8 digestion)		FIA	

Table 86 Instrument Techniques for Total Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
5	Persulfate digestion	FIA	APHA, 4500-P J. & 4500-N C.
7	Persulfate digestion	FIA	APHA
8	Persulfate digestion	FIA	In-House Method based on APHA, 4500-N C
9	Persulfate digestion	FIA	APHA
12	Persulfate digestion	FIA	APHA (4500-NO3 I)
13	Calculation (TKN+NOx)	DA	
14	Calculation (TKN+NOx)	DA	
16	Persulfate digestion	SFA	APHA
17	Persulfate digestion	FIA	APHA 4500-N B
21	Persulfate digestion	FIA	Inhouse
22	Persulfate digestion	FIA	APHA 4500-N
26	Persulfate digestion	FIA	Lachat QuikChem
27	Persulfate digestion	FIA	In House
28	Persulfate digestion	FIA	

Table 87 Instrument Techniques for Total Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
5	High-Temperature Oxidation	Other	APHA 5310 A, B and C
9	High-Temperature Oxidation	NIR-detector	APHA
12	High-Temperature Oxidation	NIR-detector	APHA (5310 B)
13	High-Temperature Oxidation	NIR-detector	APHA 5310
14	Wet-Oxidation	NIR-detector	APHA5310C
16	High-Temperature Oxidation	NIR-detector	APHA
17	High-Temperature Oxidation	NIR-detector	APHA 5310 B
21	High-Temperature Oxidation	NIR-detector	Inhouse
22	High-Temperature Oxidation	NIR-detector	APHA 5310-C
26	High-Temperature Oxidation	NIR-detector	APHA
28	High-Temperature Oxidation	TOC-L	

Table 88 Instrument Techniques for Total Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P J. & 4500-N C.
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
8	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-House Method based on APHA, 4500-P H
9		Persulfate digestion	FIA	APHA
12	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA (4500-P G)
13	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	USEPA365.4
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P I
21	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
26	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
27	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In House
28			FIA	

APPENDIX 10 – METHODOLOGY FOR S5

Table 89 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)
2	ICP-MS	Sc	CRI	He	x1	11
3	ICP-MS	Sc	ORS	He	10	11 (m/z)
4	ICP-MS	Sc	NA	He	10	11
5	ICP-MS	45	ORS	He		11
9	ICP-OES-AV	Te			100	249
11	ICP-MS	Sc	KED	He	5	10
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	11(m/z)
14	ICP-MS/MS	Sc	ORS	NA	1	
16	ICP-OES-AV	Y	NA		2	249.678
17	ICP-MS	Sc	ORS	NA	NA	11
20	ICP-MS	Scandium			5	11
21	ICP-OES-AV-buffer	Lu				249.678
22	ICP-OES-AV	Eu & Cs	NA	He	1	249.773nm
26	ICP-MS					
27	ICP-OES-AV	Lu	NA	NA	10	208.956
28	ICP-MS	Sc	NA	NA	1	10

Table 90 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)
2	ICP-MS	Sc	CRI	He	x1	40
3	ICP-MS	Sc	ORS	H2	10	40 (m/z)
4	ICP-MS	Sc	NA	H2	10	40
5	ICP-MS	45	ORS	He		44
9	ICP-OES-AV	Y			100	317.933
11	ICP-MS	Sc	KED	He	5	43
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	44(m/z)
14	ICP-MS/MS	Sc	ORS	H2+N2O	1	
16	ICP-OES-RV	Y	NA		100	422.673
17	ICP-MS	Sc	ORS	He	NA	44
20	ICP-MS	Scandium	ORS	H2	20	40
21	ICP-OES-AV-buffer	Lu				430.253
22	ICP-OES-AV	Eu & Cs	NA	He	1	315.887, 370.602nm
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	50	422.673
28	ICP-MS	Sc	UC	He	1	44

Table 91 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)
2	ICP-MS	Sc	CRI	He	x1	39
3	ICP-MS	Sc	ORS	He	10	39 (m/z)
4	ICP-MS	Sc	NA	He	10	39
5	ICP-MS	45	ORS	He		39
9	ICP-OES-RV	Te			100	766.491
11	ICP-MS	Sc	KED	He	5	39
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	38(m/z)
14	ICP-MS/MS	Sc	ORS	H2+N2O	1	
16	ICP-OES-RV	Y	NA		100	766.491
17	ICP-MS	Sc	ORS	He	NA	39
20	ICP-MS	Scandium	ORS	He	20	39
21	ICP-OES-AV-buffer	Lu				766.491
22	ICP-OES-AV	Eu & Cs	NA	He	1	404.721nm, 766.491nm
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	50	766.491
28	ICP-MS	Sc	UC	He	1	39

Table 92 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)
2	ICP-MS	Sc	CRI	He	x10	24
3	ICP-MS	Sc	ORS	He	10	24 (m/z)
4	ICP-MS	Sc	NA	He	10	24
5	ICP-MS	45	ORS	He		25
9	ICP-OES-AV	Y			100	279.553
11	ICP-MS	Sc	KED	He	5	25
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	24(m/z)
14	ICP-MS/MS	Sc	ORS	He	1	
16	ICP-OES-RV	Y	NA		100	279.078
17	ICP-MS	Sc	ORS	He	NA	24
20	ICP-MS	Scandium	ORS	He	20	24
21	ICP-OES-AV-buffer	Lu				279.078
22	ICP-OES-AV	Eu & Cs	NA	He	1	383.830 (nm)
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	50	285.213
28	ICP-MS	Sc	UC	He	1	25

Table 93 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)
2	ICP-MS	Sc	CRI	He	x100	23
3	ICP-MS	Sc	ORS	He	100	23 (m/z)
4	ICP-MS	Sc	NA	He	10	23
5	ICP-MS	45	ORS	He		23
9	ICP-OES-RV	Te			100 100	589.592
11	ICP-MS	Sc	KED	He	5	23
13	ICP-MS	Sc,Rh,Ir	NA	He	NA	23(m/z)
14	ICP-MS/MS	Sc	ORS	He	1	
16	ICP-OES-RV	Y	NA		100	589.592
17	ICP-MS	Sc	ORS	He	NA	23
20	ICP-MS	Scandium	ORS	He	20	23
21	ICP-OES-AV-buffer	Lu				589.592
22	ICP-OES-AV	Eu & Cs	NA	He	1	330.237, 589.592nm
26	ICP-MS					
27	ICP-OES-RV	Lu	NA	NA	50	589.592
28	ICP-MS	Sc	UC	He	1	23

Table 94 Measurement Methods and Instrument Techniques for Alkalinity

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	APHA 2320
2	Titration	Auto Titration	In-House Method
3	Titration	Auto Titration	In-House Method
4	Titration	Auto Titration	In-House Method
5	Titration	Auto Titration	
8	Titration	Auto Titration	In-House Method based on APHA, 2320-Alkalinity – B
9	Titration	Auto Titration	APHA
10	Titration	Manual Analysis	SM 2320 B
13	Titration	Auto Titration	APHA 2320
14	Titration	Auto Titration	
16	Titration	Auto Titration	APHA
17	Titration	Auto Titration	APHA 2320 B
20	Titration	Auto Titration	in-house
21	Titration	Manual Analysis	Inhouse
22	Titration	Auto Titration	APHA 2320
23	Calculation		
26	Titration	Auto Titration	APHA
28	Titration	Auto Titration	

Table 95 Measurement Methods and Instrument Techniques for Silica

Lab. Code	Measurement Method	Instrument	Method Reference
1	Molybdosilicate Method	DA	APHA 4500-SiO2
4	Molybdosilicate Method	DA	In-House Method
5	Heteropoly Blue Method	DA	APHA, 4500- SiO2 D
8	Molybdosilicate Method	FIA	In-House Method based on APHA, 4500-SiO2 F
9	Molybdosilicate Method	FIA	APHA
10	ICP-Method	ICP-OES	EPA 200.7
13	Molybdosilicate Method	DA	APHA 4500 SIO2-D
14	Molybdosilicate Method	DA	APHA 4500-Si02
15	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
16	Calculation	ICP-OES	
17	Heteropoly Blue Method	DA	APHA 4500-SiO2 D
20	ICP-Method	ICP-MS	in-house
22	Molybdosilicate Method	DA	APHA 4500-SiO2
24	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
25	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
26	ICP-Method	ICP-MS	
27	Molybdosilicate Method	FIA	Inhouse

Table 96 Measurement Methods and Instrument Techniques for Total Hardness

Lab. Code	Measurement Method	Instrument	Method Reference
2	Calculation	NA	In-House Method
3	Calculation	ICP-MS	APHA 2340B
4	Calculation	ICP-MS	
5	Calculation	ICP-MS	
9	Calculation	ICP-OES	APHA
11	Calculation	ICP-MS	
13	Calculation	ICP-OES	APHA 2340
14	Calculation	ICP-MS/MS	USEPA200.8
16	Calculation	ICP-OES	APHA
17	Calculation	ICP-MS	APHA 3120 and 3125; USEPA SW 846 - 6010 and 6020
20	ICP-Method	ICP-MS	in-house
22	Calculation	ICP-OES	APHA 2340
23	Calculation		
26	Calculation		
27	Calculation	ICP-OES	Inhouse
28	Titration	Manual Analysis	

Table 97 Additional Information

Lab Code	Additional Information
16	pH and EC were done by OMNIS auto analyser

END OF REPORT