Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 23-19 Nutrients and Anions in River and Sea Water

February 2024

ACKNOWLEDGMENTS

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

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

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

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Accredited for compliance with ISO/IEC 17043

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SUMMARY

This report presents the results of the proficiency test AQA 23-19, Nutrients and Anions in River and Sea Water. The study focused on the measurement of pH and electrical conductivity at 25ºC, alkalinity to pH 4.5 (as $CaCO_3$), ammonia-N, bromide, chloride, dissolved organic carbon (as dNPOC), fluoride, iodide, nitrate-N, nitrite-N, NOx as N (nitrate-N + nitrite-N), orthophosphate-P, silica (as SiO_2), sulphate, total hardness (as $CaCO_3$), total dissolved nitrogen, total dissolved phosphorus, total Kjeldahl nitrogen, total nitrogen, total organic carbon (as NPOC) and dissolved B, Ca, K, Mg and Na in river water and sea water.

The sample set consisted of 2 sea water samples and 2 river water samples.

Eighteen laboratories registered to participate and sixteen submitted results.

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

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

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

Of 377 z-scores, 362 (96%) returned a satisfactory score of $|z| \leq 2.0$.

Of 377 E_n scores, 319 (85%) returned a satisfactory score of $|E_n| \leq 1.0$.

Laboratories 1 and **5** reported results for all 36 tests for which a z-score was calculated and returned satisfactory z-scores for all of them,

Laboratory 9 had the highest number of satisfactory E_n scores, 33 out of 36 reported.

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

Overall, the between-laboratory CVs of the sea water samples, and river water samples were comparable. Low level bromide was the test that most challenged participants' analytical techniques. Only four laboratories reported results.

TKN in S4 also challenged participants' analytical techniques. The reported results were not compatible with each other. When the NOx concentration approaches the TN concentration, the measurement error of TKN results, calculated as TN – NOx, increases.

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 traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates;*

Of 389 numerical results, 375 (96%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.29% to 900% of the reported value. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 4.

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

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

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

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

AQA 23-19 is the 17th NMI proficiency study of nutrients and anions in water.

1.2 Study Aims

The aims of the study were to:

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

1.3 Study Conduct

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

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

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The 39 tests were selected from those for which an investigation level is published in Australian and New Zealand Guidelines for Fresh and Marine Water Quality[5] and are commonly measured by water testing laboratories.

2.2 Participation

Eighteen laboratories participated and sixteen submitted results.

The timetable of the study was:

Invitation issued:	16 October 2023

Samples dispatched:	13 November 2023
Results due:	15 December 2023
Interim report issued	18 December 2023
Preliminary report issued:	20 December 2023

2.3 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.4 Test Material Specification

Four samples were provided for analysis:

Sample S1 was 400 mL of filtered, autoclaved and frozen sea water;

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

Sample S3 was two identical bottles of 200 mL filtered, autoclaved and frozen river water;

Sample S4 was 200 mL of autoclaved and frozen river water.

2.5 Sample Preparation, Analysis and Homogeneity Testing

Partial homogeneity testing was conducted in this study. The same validated preparation procedure was followed as in previous studies.[2] The test samples from the previous studies were demonstrated to be sufficiently homogeneous for evaluation of participants' performance. The results of partial homogeneity testing are reported in this study as the homogeneity value. The preparation and analysis are described in Appendix 1.

No partial homogeneity test was conducted for DOC and orthophosphate-P in S1, alkalinity, pH, silica, and total hardness in S2, ammonia-N, B, iodide and orthophosphate-P in S3, and TKN and TOC in S4.

2.6 Stability of Analytes

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

2.7 Sample Storage, Dispatch and Receipt

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

The samples were dispatched by courier on 13 November 2023.

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

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

2.8 Instructions to Participants

Participants were instructed as follows:

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

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

SAMPLE S1 **400 mL frozen sea water**		**SAMPLE S3** **2 x 200 mL frozen river water**	
Test	**Estimated Value mg/L**	**Test**	**Estimated Value mg/L**
Ammonia-N	0.05-2	Ammonia-N	0.05-2
Nitrate-N + Nitrite-N	0.005-0.2	Fluoride	0.05-2
Chloride	1000-40000	Iodide	Not available
Fluoride	0.1-4	Nitrate-N	0.5-20
Sulphate	200-8000	Nitrite-N	0.05-2
Dissolved Organic Carbon (as dNPOC)	0.5-20	Bromide	0.05-2
Orthophosphate-P (FRP)	0.05-2	Chloride	2-80
Total Dissolved Nitrogen	0.05-2	Sulphate	2-80
Total Dissolved Phosphorus	0.05-2	Dissolved Organic Carbon (as dNPOC)	0.5-20
SAMPLE S2 **2 x 200 mL chilled sea water**		Orthophosphate-P	0.05-2
Test	**Estimated Value mg/L**	Total Dissolved Nitrogen	0.5-20
B (dissolved)	0.5-20	Total Dissolved Phosphorus	0.025-1
Ca (dissolved)	>100	B (dissolved)	< 2
K (dissolved)	>100	Ca (dissolved)	1-40
Mg (dissolved)	>500	K (dissolved)	1-40
Na (dissolved)	>1000	Mg (dissolved)	1-40
Silica (as SiO2)	0.25-10	Na (dissolved)	2-80
Alkalinity to pH 4.5 (as CaCO3)	2-80	**SAMPLE S4** **200 mL frozen river water**	
Hardness, total (CaCO3)	200-8000	**Test**	**Estimated Value mg/L**
EC (at 25 °C, µS/cm)	>1000	Total Kjeldahl Nitrogen	0.5-20
pH (at 25 °C)	>3	Total Nitrogen	0.5-20
		Total Organic Carbon (as NPOC)	0.5-20

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (e.g. 5.23 ± 0.51 mg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.
- Please return the completed results sheet by 1 December 2023.

The due date for results was extended to 15 December 2023 due to staffing issues with some participants.

2.9 Interim and Preliminary Reports

An interim report was emailed to participants on 18 December 2023.A preliminary report was issued on 20 December 2023. 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. The following was changed from the Preliminary Report in the present Final Report: the assigned value for TKN in S1 was not set because the reported results were too variable.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Methodology for S1, S2, S3 and S4

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

3.2 Additional Information

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

Table 1 Additional Information

Lab Code	Additional Information
2	Sample S1: We have reported our results as mg/L of N in NOx, P in PO4 and N in NH4. NOTE: For Ammonia-N - our calibration curve tops out at 2uM (0.028mg/L) so the solution was measured as a 1:10 dilution as would be done on the occasional sample in the higher range. Calibration concentration for our lab was as follows: NOX-N (0-0.161mg/L), PO4-P (0-0.09mg/L) and NH4-N(0-0.028mg/L).
4	Samples S3 and S4: Sample analysed as received.
5	Sample S3 Lab does not perform bromide and iodide.
14	Sample S1: We have reported our results as mg/L of N in NOx, P in PO4 and N in NH4. NOTE: Phosphate and Ammonia was diluted by a factor of 10 to be within our calibration range. Sample S2: We have reported our results as mg/L as SiO2.

3.3 Basis of Participants' Measurement Uncertainty Estimates

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

Table 2 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
2*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NMI Uncertainty Course
3	Other (please type)	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis		Eurachem/CITAC Guide
5	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
6	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	CRM	NMI Uncertainty Course
7	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - RM Duplicate Analysis	CRM Instrument Calibration	Eurochem 2000/ISO1993A

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
		Instrument Calibration	Laboratory Bias from PT Studies Recoveries of SS	
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537
9	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis		
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
11	Top Down - reproducibility (standard deviation) from PT studies used directly	Standard deviation from PT studies only Control samples - RM Instrument Calibration	CRM Instrument Calibration	NATA Technical Report
12				
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
14*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NMI Uncertainty Course
15	Professional judgment	Control Samples - CRM	CRM Recoveries of SS	Inhouse Method
17*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis		

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

Table 3 Additional Information for Basis of Uncertainty Estimate

Lab Code	Additional Information
2	Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval)
14	Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval)
17	UoM is based on ISO 17025, XX Specific Criteria and EURACHEM /CITAC Guide. Some details have been removed from this comment to avoid laboratory identification.

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

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Such feedback may be useful in improving future studies. Participants’ comments are reproduced in Table 4.

Table 4 Participants’ Comments

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. The samples for Phosphate and Ammonia are in very high concentration compared to our normal work. It would be great to have low level nutrients.	The study samples have not been fortified for these tests. The phosphate and ammonia level in the study samples is the incurred level.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 42 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 39. An example chart with an interpretation guide is shown in Figure 1.

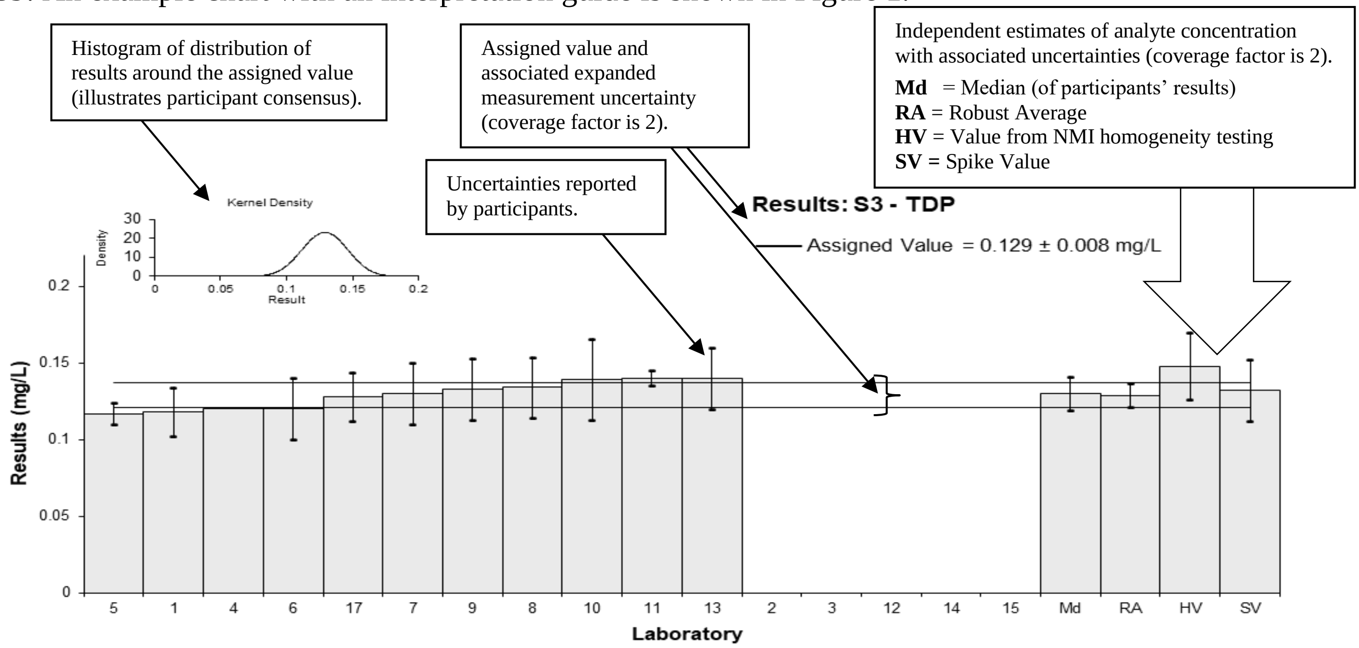


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

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

1.1 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 3. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'[1] In this study, the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, outliers removed; the expanded uncertainties were estimated from the associated robust standard deviations.[4,6]

1.2 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

4.3 Target Standard Deviation for Proficiency Assessment

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

$\sigma = (X) * PCV$ 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]

4.4 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 study assigned value;
σ is the target standard deviation.

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

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

1.3 E_n-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 satisfactory;
- $|E_n|$ >1.0 is unsatisfactory.

1.4 Traceability and Measurement Uncertainty

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

5 TABLES AND FIGURES

Table 5

Sample Details

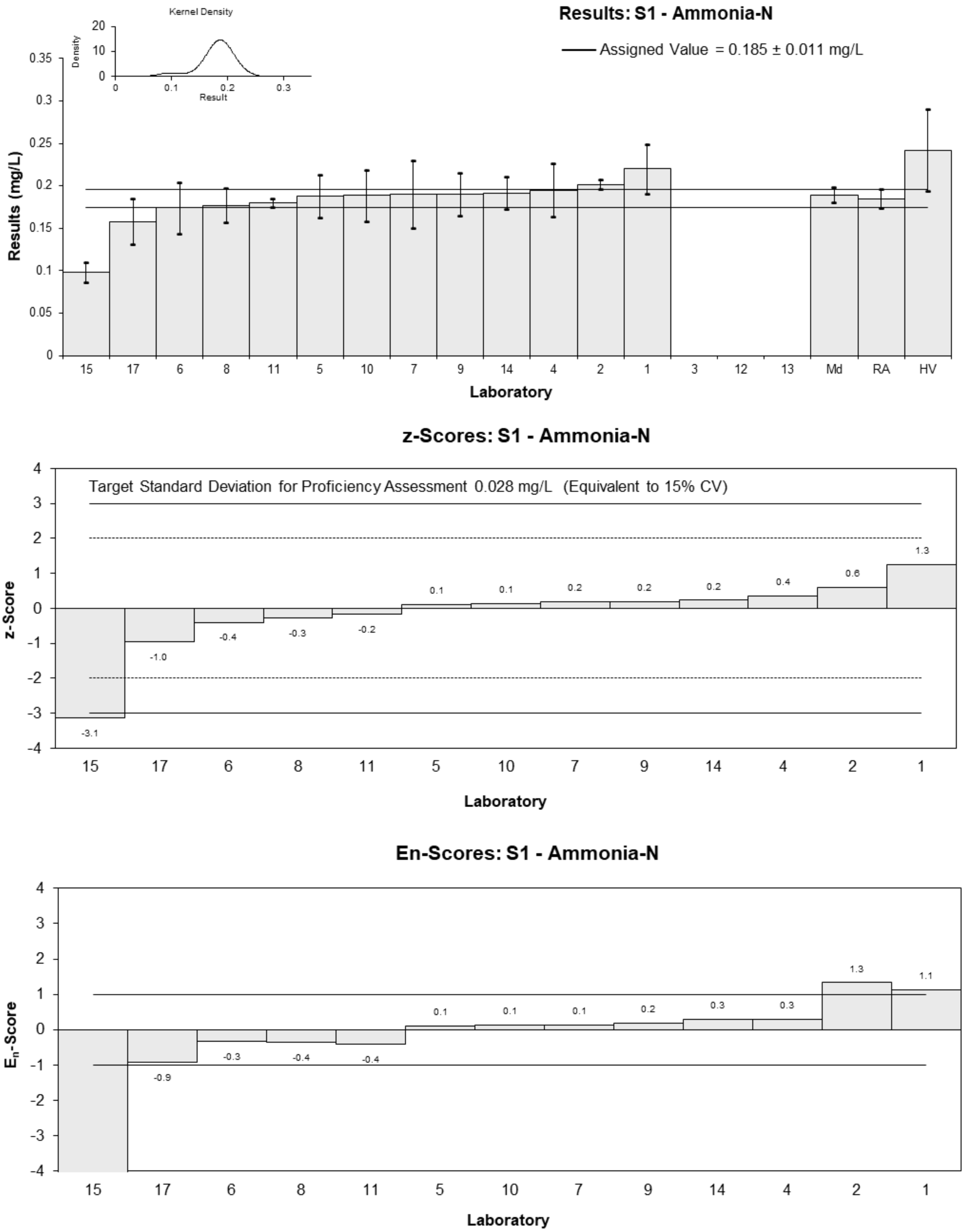
Sample No.	S1
Matrix	Sea Water
Analyte	Ammonia-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.220	0.029	1.26	1.13
2	0.2017	0.006	0.60	1.33
3	<0.2	1.12		
4	0.195	0.031	0.36	0.30
5	0.188	0.025	0.11	0.11
6	0.174	0.03	-0.40	-0.34
7	0.19	0.04	0.18	0.12
8	0.177	0.02	-0.29	-0.35
9	0.190	0.025	0.18	0.18
10	0.1889	0.0303	0.14	0.12
11	0.18	0.005	-0.18	-0.41
12	NT	NT		
13	<1	NR		
14	0.1914	0.01914	0.23	0.29
15	0.098	0.012	-3.14	-5.34
17	0.158	0.027	-0.97	-0.93

Statistics

Assigned Value	0.185	0.011
Spike Value	Not Spiked	
Homogeneity Value	0.240	0.048
Robust Average	0.185	0.011
Median	0.189	0.009
Mean	0.181	
N	13	
Max	0.22	
Min	0.098	
Robust SD	0.016	
Robust CV	8.8%	



Kernel Density
Density
Result
Results: S1 - Ammonia-N
Assigned Value = 0.185 ± 0.011 mg/L
Results (mg/L)
15 17 6 8 11 5 10 7 9 14 4 2 1 3 12 13 Md RA HV
Laboratory
z-Scores: S1 - Ammonia-N
Target Standard Deviation for Proficiency Assessment 0.028 mg/L (Equivalent to 15% CV)
z-Score
-3.1 -1.0 -0.4 -0.3 -0.2 0.1 0.1 0.2 0.2 0.2 0.4 0.6 1.3
15 17 6 8 11 5 10 7 9 14 4 2 1
Laboratory
En-Scores: S1 - Ammonia-N
En-Score
-0.9 -0.3 -0.4 -0.4 0.1 0.1 0.1 0.2 0.3 0.3 1.3 1.1
15 17 6 8 11 5 10 7 9 14 4 2 1
Laboratory

Figure 2

Table 6

Sample Details

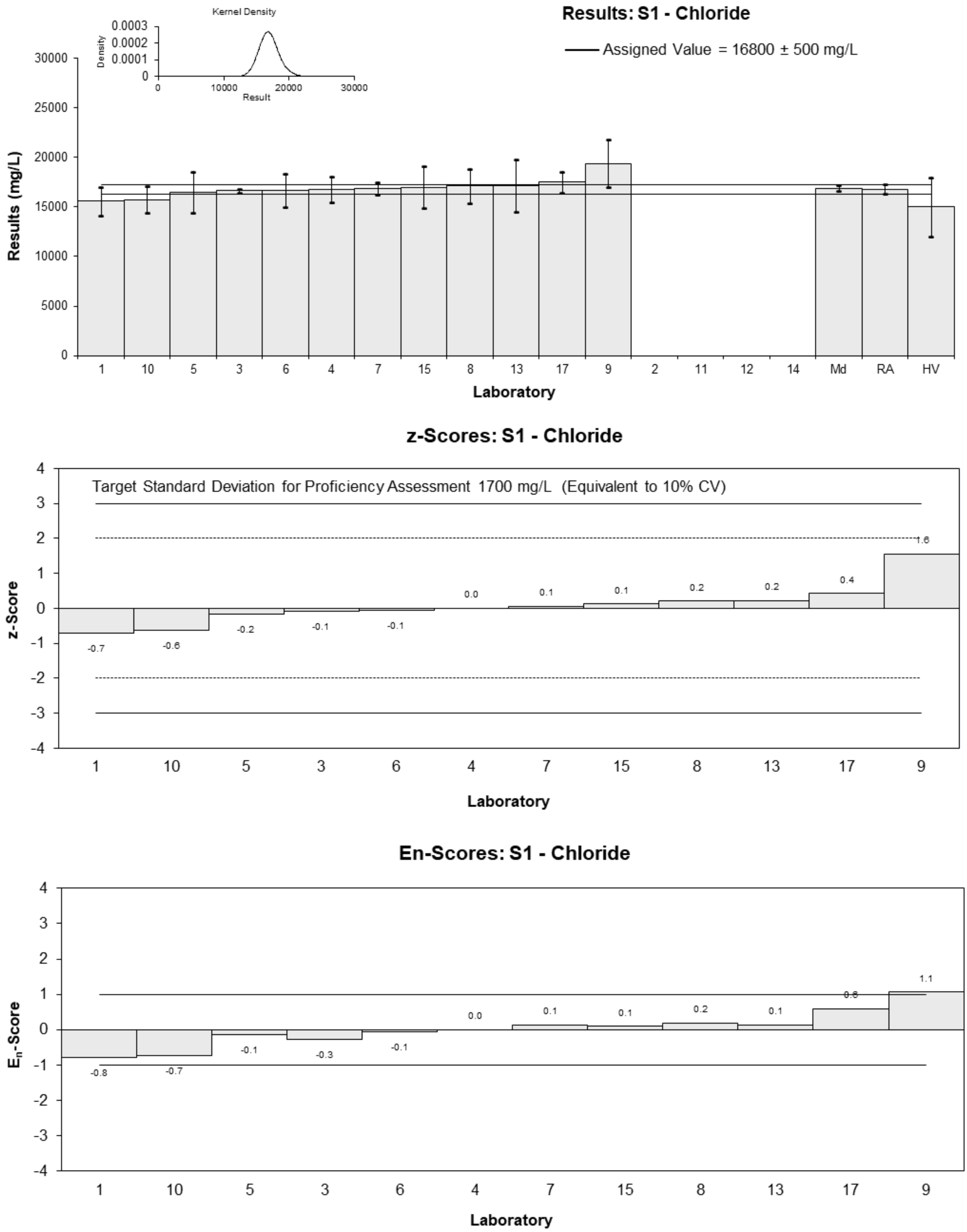
Sample No.	S1
Matrix	Sea Water
Analyte	Chloride
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	15600	1450	-0.71	-0.78
2	NR	NR		
3	16646	166	-0.09	-0.29
4	16800	1313	0.00	0.00
5	16500	2100	-0.18	-0.14
6	16700	1670	-0.06	-0.06
7	16900	608	0.06	0.13
8	17132	1750	0.20	0.18
9	19400	2400	1.55	1.06
10	15745.59	1357	-0.63	-0.73
11	NR	NR		
12	NT	NT		
13	17165	2678	0.22	0.13
14	NR	NR		
15	17000	2100	0.12	0.09
17	17500	1100	0.42	0.58

Statistics

Assigned Value	16800	500
Spike Value	Not Spiked	
Homogeneity Value	15000	3000
Robust Average	16800	500
Median	16900	300
Mean	16900	
N	12	
Max	19400	
Min	15600	
Robust SD	700	
Robust CV	4.2%	



Results: S1 - Chloride
Assigned Value = 16800 ± 500 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 10 5 3 6 4 7 15 8 13 17 9 2 11 12 14 Md RA HV
z-Scores: S1 - Chloride
Target Standard Deviation for Proficiency Assessment 1700 mg/L (Equivalent to 10% CV)
z-Score
-0.7 -0.6 -0.2 -0.1 -0.1 0.0 0.1 0.1 0.2 0.2 0.4 1.6
1 10 5 3 6 4 7 15 8 13 17 9
Laboratory
En-Scores: S1 - Chloride
E_n-Score
-0.8 -0.7 -0.1 -0.3 -0.1 0.0 0.1 0.1 0.2 0.1 0.6 1.1
1 10 5 3 6 4 7 15 8 13 17 9
Laboratory

Figure 3

Table 7

Sample Details

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

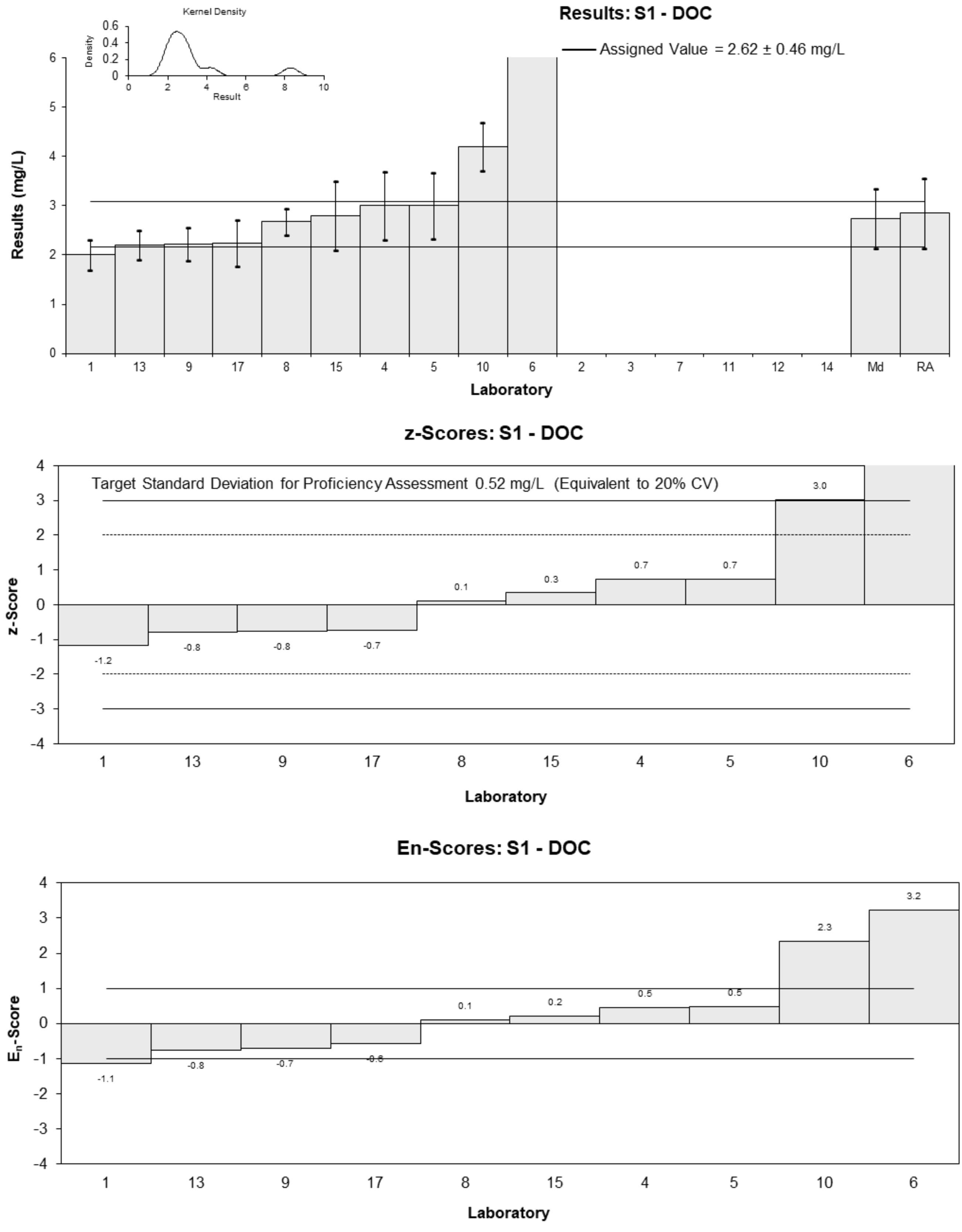
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2	0.3	-1.18	-1.13
2	NR	NR		
3	NT	NT		
4	3	0.7	0.73	0.45
5	3	0.67	0.73	0.47
6*	8.3	1.7	10.84	3.23
7	NT	NT		
8	2.68	0.27	0.11	0.11
9	2.22	0.33	-0.76	-0.71
10	4.20	0.496	3.02	2.34
11	NR	NR		
12	NT	NT		
13	2.2	0.3	-0.80	-0.76
14	NR	NR		
15	2.8	0.7	0.34	0.21
17	2.24	0.47	-0.73	-0.58

* Outlier, see Section 4.2

Statistics

Assigned Value	2.62	0.46
Spike Value	Not Spiked	
Robust Average	2.85	0.71
Median	2.74	0.60
Mean	3.3	
N	10	
Max	8.3	
Min	2	
Robust SD	0.89	
Robust CV	31%	



Results: S1 - DOC
Assigned Value = 2.62 ± 0.46 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 13 9 17 8 15 4 5 10 6 2 3 7 11 12 14 Md RA
z-Scores: S1 - DOC
Target Standard Deviation for Proficiency Assessment 0.52 mg/L (Equivalent to 20% CV)
z-Score
-1.2 -0.8 -0.8 -0.7 0.1 0.3 0.7 0.7 3.0
En-Scores: S1 - DOC
En-Score
-1.1 -0.8 -0.7 -0.6 0.1 0.2 0.5 0.5 2.3 3.2

Figure 4

Table 8

Sample Details

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

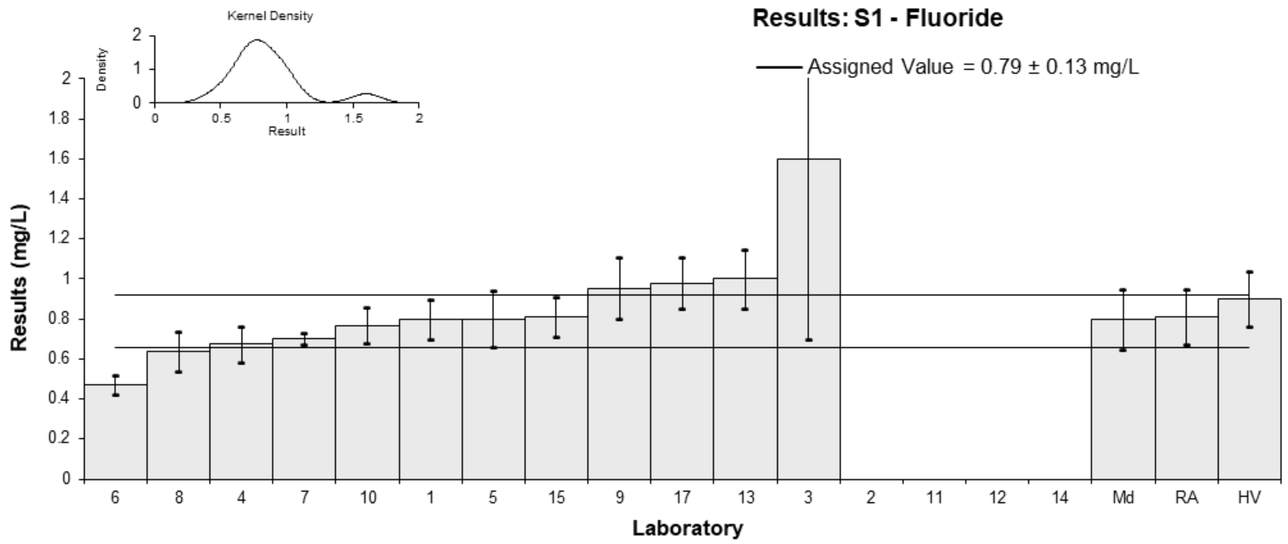
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.8	0.1	0.06	0.06
2	NR	NR		
3*	1.6	0.9	5.13	0.89
4	0.675	0.09	-0.73	-0.73
5	0.8	0.14	0.06	0.05
6	0.47	0.05	-2.03	-2.30
7	0.7	0.03	-0.57	-0.67
8	0.64	0.1	-0.95	-0.91
9	0.954	0.153	1.04	0.82
10	0.768	0.089	-0.14	-0.14
11	NR	NR		
12	NT	NT		
13	1.0	0.15	1.33	1.06
14	NR	NR		
15	0.81	0.1	0.13	0.12
17	0.98	0.13	1.20	1.03

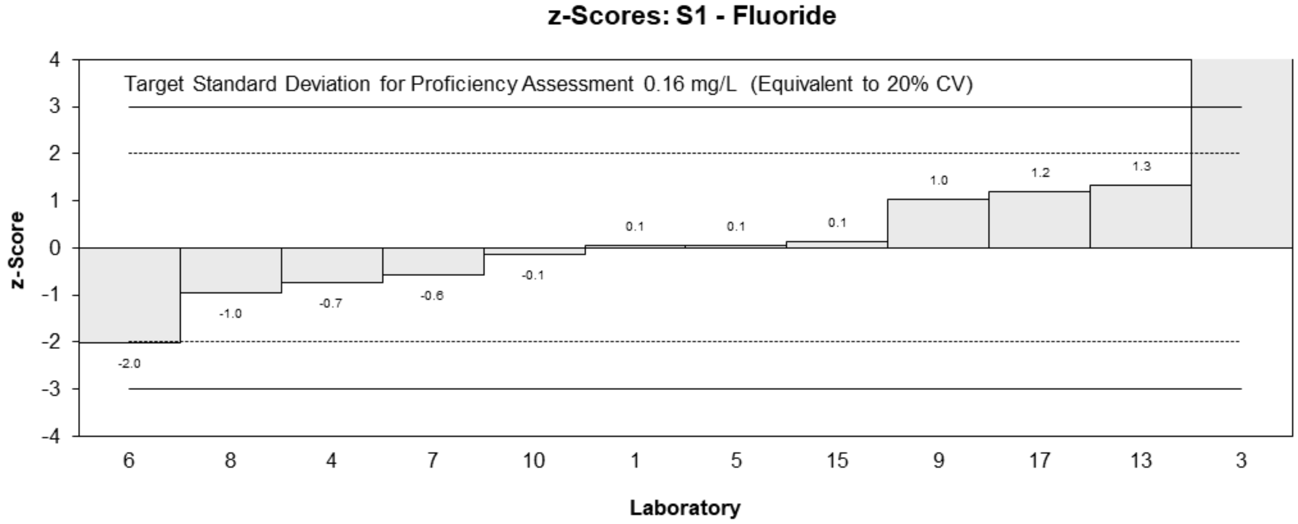
* Outlier, see Section 4.2

Statistics

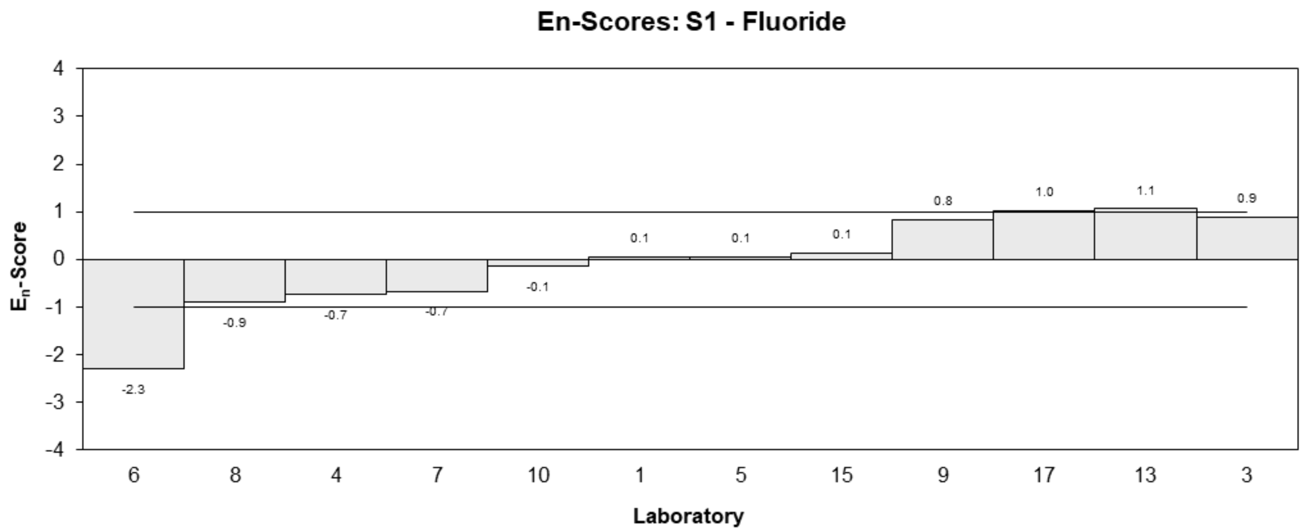
Assigned Value	0.79	0.13
Spike Value	Not Spiked	
Homogeneity Value	0.90	0.14
Robust Average	0.81	0.14
Median	0.80	0.15
Mean	0.85	
N	12	
Max	1.6	
Min	0.47	
Robust SD	0.19	
Robust CV	23%	



Results: S1 - Fluoride
Assigned Value = 0.79 ± 0.13 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6
8
4
7
10
1
5
15
9
17
13
3
2
11
12
14
Md
RA
HV



z-Scores: S1 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.16 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
-2.0
-1.0
-0.7
-0.6
-0.1
0.1
0.1
0.1
1.0
1.2
1.3



En-Scores: S1 - Fluoride
E_n-Score
Laboratory
-2.3
-0.9
-0.7
-0.7
-0.1
0.1
0.1
0.1
0.8
1.0
1.1
0.9

Figure 5

Table 9

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.10	0.01	-0.87	-1.34
2	0.1174	0.003	0.14	0.41
3	NT	NT		
4	0.109	0.018	-0.35	-0.32
5	0.12	0.011	0.29	0.41
6	0.112	0.011	-0.17	-0.25
7	0.11	0.01	-0.29	-0.45
8	0.122	0.02	0.41	0.34
9	0.123	0.025	0.46	0.31
10	0.1102	0.0166	-0.28	-0.28
11	0.12	0.007	0.29	0.58
12	NT	NT		
13	0.110	0.02	-0.29	-0.24
14	0.1191	0.0018	0.24	0.77
15	0.11	0.013	-0.29	-0.36
17	0.121	0.017	0.35	0.34

Statistics

Assigned Value	0.115	0.005
Spike Value	Not Spiked	
Homogeneity Value	0.117	0.018
Robust Average	0.115	0.005
Median	0.115	0.005
Mean	0.115	
N	14	
Max	0.123	
Min	0.1	
Robust SD	0.0068	
Robust CV	5.9%	

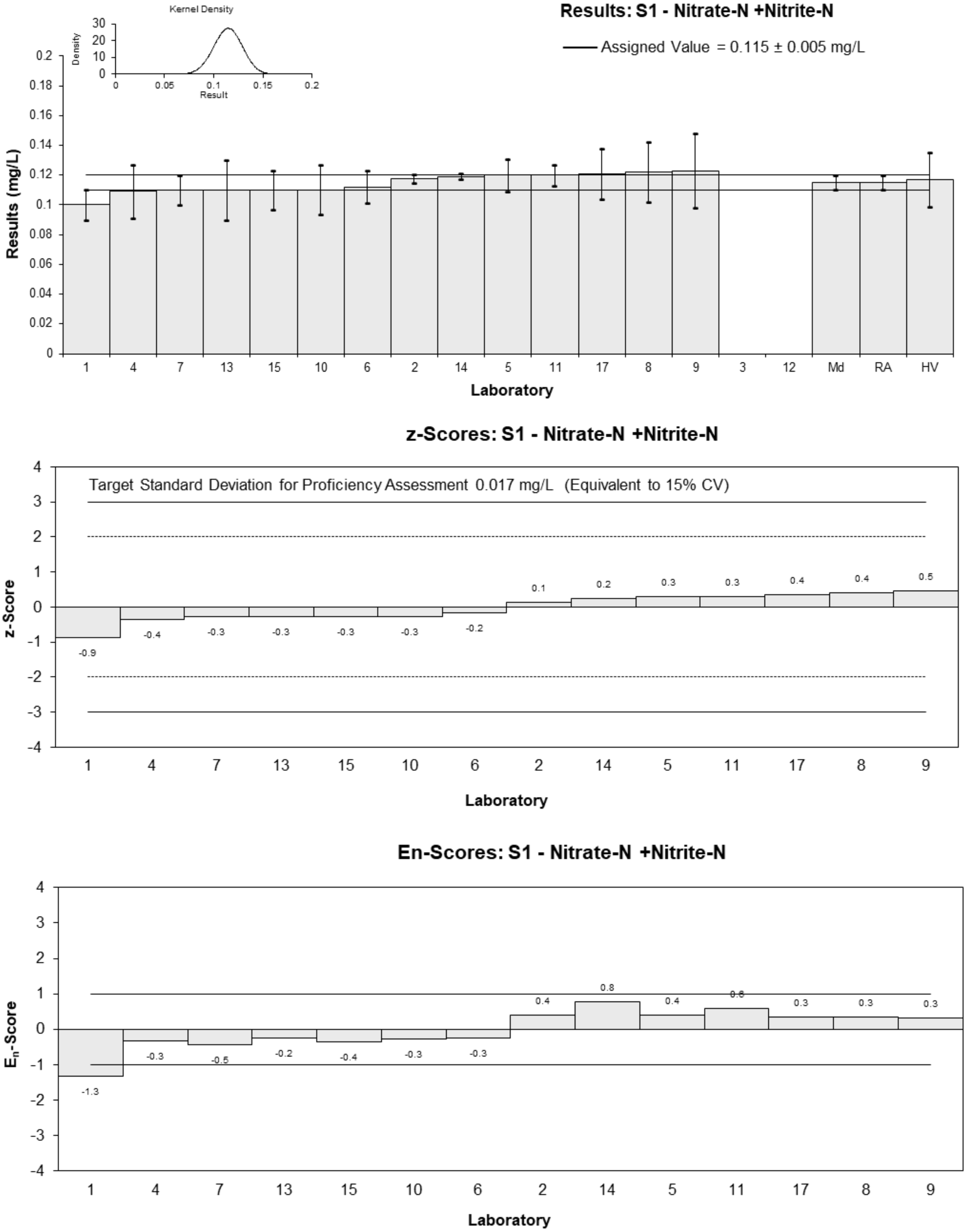

Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.115 ± 0.005 mg/L
Kernel Density
Density
Result
Results (mg/L)
1 4 7 13 15 10 6 2 14 5 11 17 8 9 3 12 Md RA HV
Laboratory
z-Scores: S1 - Nitrate-N +Nitrite-N
Target Standard Deviation for Proficiency Assessment 0.017 mg/L (Equivalent to 15% CV)
z-Score
-0.9 -0.4 -0.3 -0.3 -0.3 -0.3 -0.2 0.1 0.2 0.3 0.3 0.4 0.4 0.5
1 4 7 13 15 10 6 2 14 5 11 17 8 9
Laboratory
En-Scores: S1 - Nitrate-N +Nitrite-N
E_n-Score
-1.3 -0.3 -0.5 -0.2 -0.4 -0.3 -0.3 0.4 0.8 0.4 0.6 0.3 0.3 0.3
1 4 7 13 15 10 6 2 14 5 11 17 8 9
Laboratory

Figure 6

Table 10

Sample Details

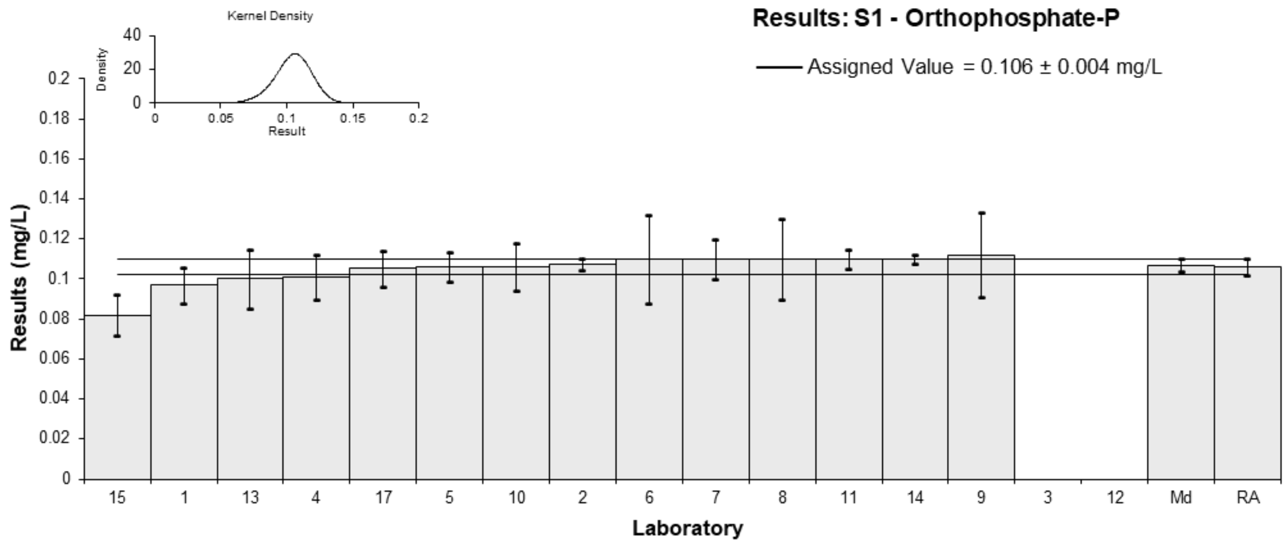
Sample No.	S1
Matrix	Sea Water
Analyte	Orthophosphate-P
Unit	mg/L

Participant Results

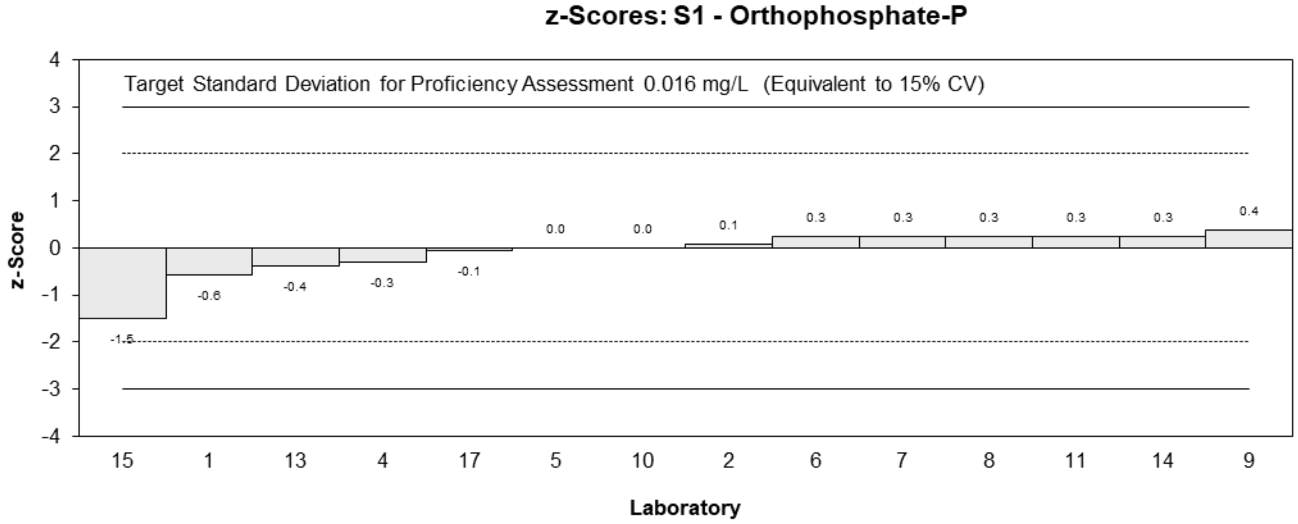
Lab. Code	Result	Uncertainty	z	E_n
1	0.097	0.009	-0.57	-0.91
2	0.1075	0.003	0.09	0.30
3	NT	NT		
4	0.101	0.011	-0.31	-0.43
5	0.106	0.0075	0.00	0.00
6	0.110	0.022	0.25	0.18
7	0.11	0.01	0.25	0.37
8	0.110	0.02	0.25	0.20
9	0.112	0.021	0.38	0.28
10	0.106	0.012	0.00	0.00
11	0.11	0.005	0.25	0.62
12	NT	NT		
13	0.10	0.015	-0.38	-0.39
14	0.11	0.002057	0.25	0.89
15	0.082	0.01	-1.51	-2.23
17	0.1052	0.0089	-0.05	-0.08

Statistics

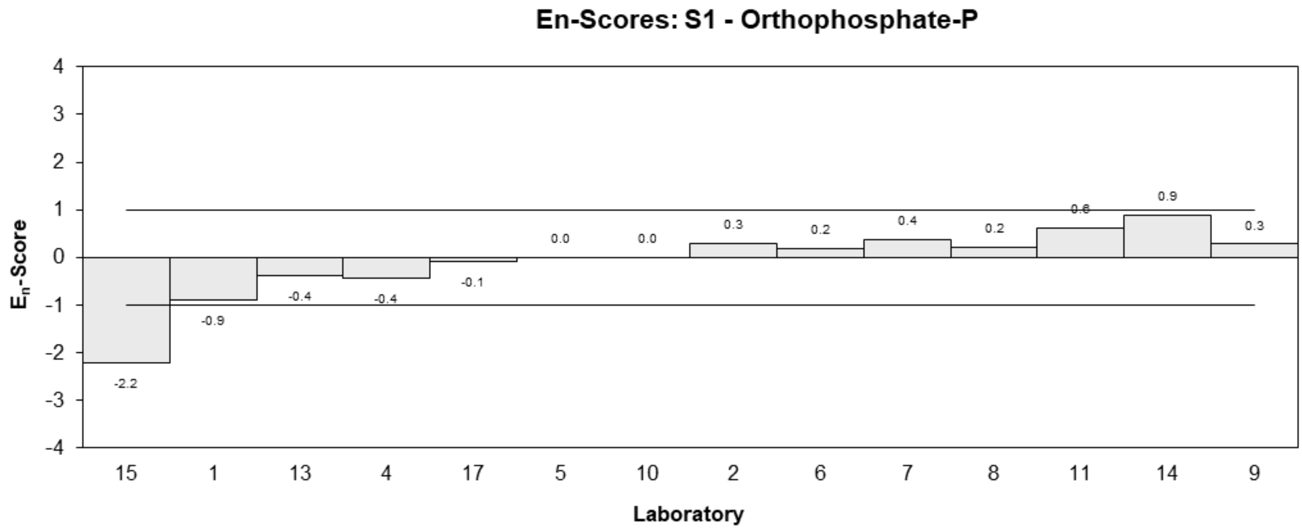
Assigned Value	0.106	0.004
Spike Value	Not Spiked	
Robust Average	0.106	0.004
Median	0.107	0.003
Mean	0.105	
N	14	
Max	0.112	
Min	0.082	
Robust SD	0.0057	
Robust CV	5.4%	



Results: S1 - Orthophosphate-P
Assigned Value = 0.106 ± 0.004 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15
1
13
4
17
5
10
2
6
7
8
11
14
9
3
12
Md
RA



z-Scores: S1 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.016 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.5
-0.6
-0.4
-0.3
-0.1
0.0
0.0
0.1
0.3
0.3
0.3
0.3
0.3
0.4



En-Scores: S1 - Orthophosphate-P
E_n-Score
Laboratory
-2.2
-0.9
-0.4
-0.4
-0.1
0.0
0.0
0.3
0.2
0.4
0.2
0.6
0.9
0.3

Figure 7

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2300	223	-0.21	-0.21
2	NR	NR		
3	2301	23	-0.21	-0.53
4	2380	325.6	0.13	0.09
5	2200	198	-0.64	-0.69
6	2640	264	1.23	1.04
7	2060	171	-1.23	-1.50
8	2440	280	0.38	0.31
9	2470	420	0.51	0.28
10	2271.3318	252	-0.33	-0.29
11	NR	NR		
12	NT	NT		
13	2365	530	0.06	0.03
14	NR	NR		
15	2400	300	0.21	0.16
17	2370	150	0.09	0.11

Statistics

Assigned Value	2350	90
Spike Value	Not Spiked	
Homogeneity Value	2000	300
Robust Average	2350	90
Median	2370	70
Mean	2350	
N	12	
Max	2640	
Min	2060	
Robust SD	120	
Robust CV	5.2%	

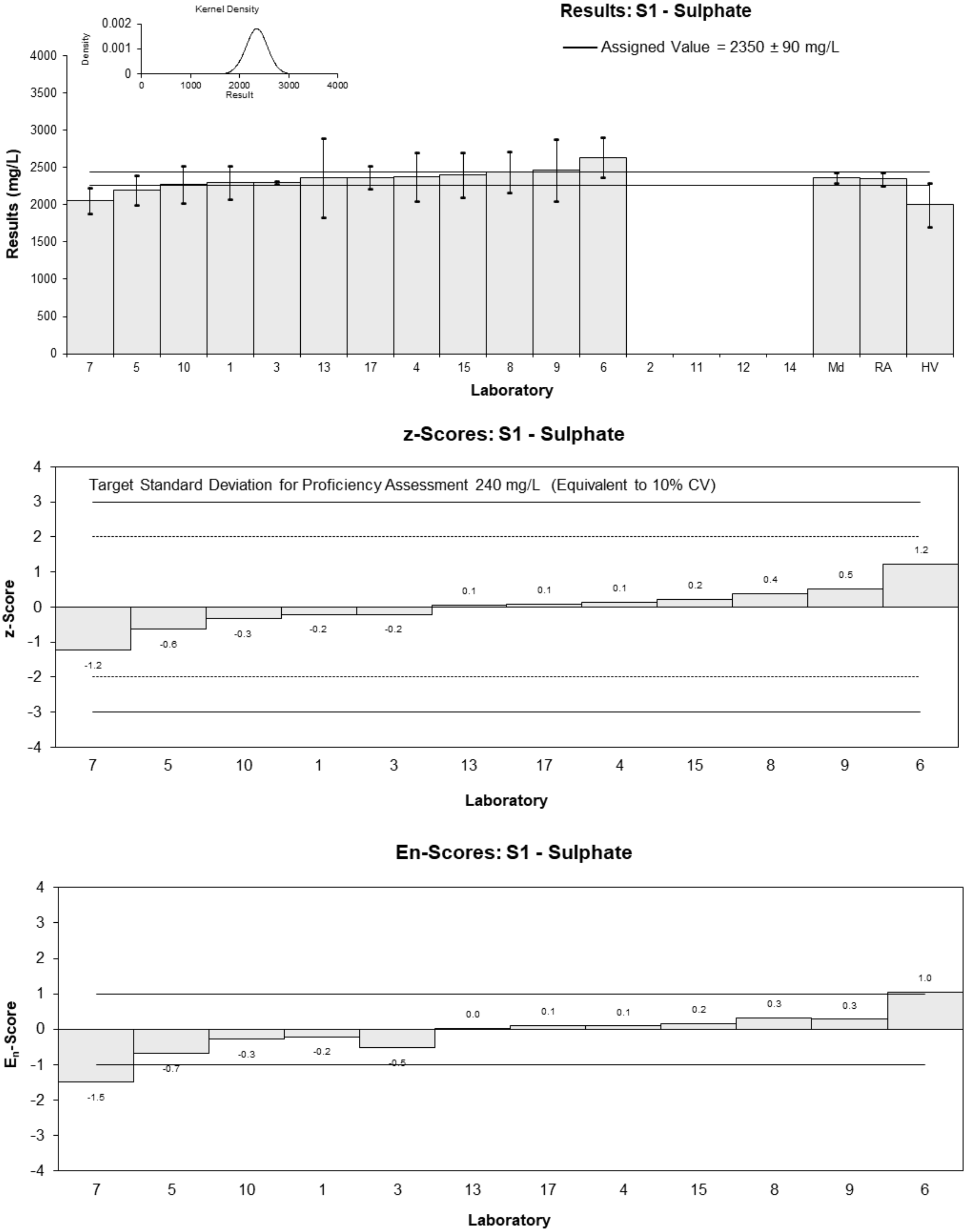

Results: S1 - Sulphate
Assigned Value = 2350 ± 90 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
7 5 10 1 3 13 17 4 15 8 9 6 2 11 12 14 Md RA HV
z-Scores: S1 - Sulphate
Target Standard Deviation for Proficiency Assessment 240 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S1 - Sulphate
E_n-Score
Laboratory

Figure 8

Table 12

Sample Details

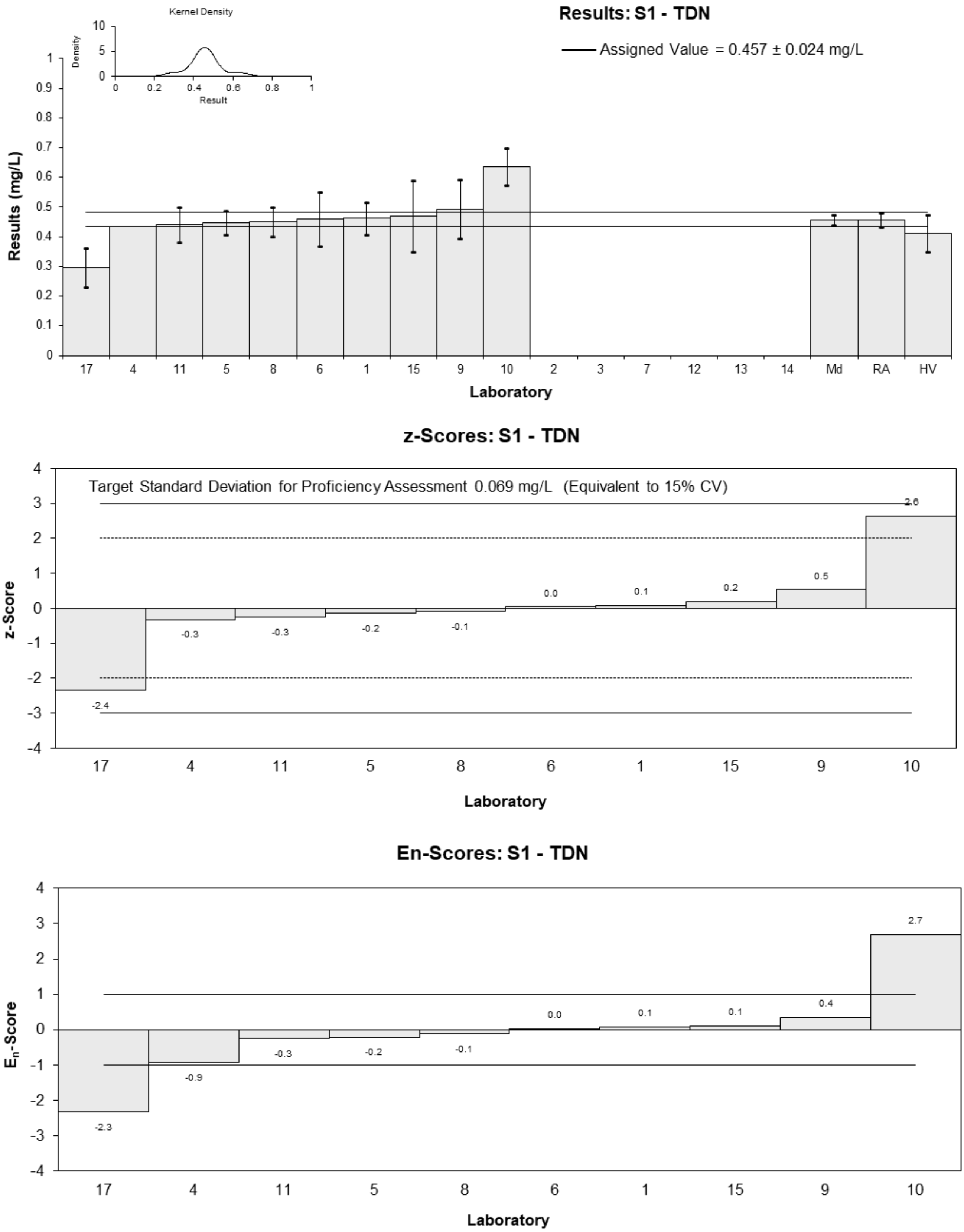
Sample No.	S1
Matrix	Sea Water
Analyte	TDN
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.462	0.055	0.07	0.08
2	NR	NR		
3	NT	NT		
4	0.435	NR	-0.32	-0.92
5	0.447	0.041	-0.15	-0.21
6	0.46	0.09	0.04	0.03
7	NT	NT		
8	0.451	0.05	-0.09	-0.11
9	0.493	0.099	0.53	0.35
10	0.6373	0.0624	2.63	2.70
11	0.44	0.06	-0.25	-0.26
12	NT	NT		
13	<0.1	NR		
14	NR	NR		
15	0.47	0.12	0.19	0.11
17	0.296	0.065	-2.35	-2.32

Statistics

Assigned Value	0.457	0.024
Spike Value	Not Spiked	
Homogeneity Value	0.412	0.062
Robust Average	0.457	0.024
Median	0.456	0.018
Mean	0.459	
N	10	
Max	0.6373	
Min	0.296	
Robust SD	0.031	
Robust CV	6.8%	



Results: S1 - TDN
Assigned Value = 0.457 ± 0.024 mg/L
Kernel Density
Density
Result
Results (mg/L)
17 4 11 5 8 6 1 15 9 10 2 3 7 12 13 14 Md RA HV
Laboratory
z-Scores: S1 - TDN
Target Standard Deviation for Proficiency Assessment 0.069 mg/L (Equivalent to 15% CV)
z-Score
-2.4 -0.3 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.5 2.6
17 4 11 5 8 6 1 15 9 10
Laboratory
En-Scores: S1 - TDN
E_n-Score
-2.3 -0.9 -0.3 -0.2 -0.1 0.0 0.1 0.1 0.4 2.7
17 4 11 5 8 6 1 15 9 10
Laboratory

Figure 9

Table 13

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.105	0.013	-0.58	-0.70
2	NR	NR		
3	NT	NT		
4	0.118	NR	0.17	0.50
5	0.113	0.034	-0.12	-0.06
6	0.11	0.02	-0.29	-0.24
7	0.11	0.01	-0.29	-0.43
8	0.145	0.02	1.74	1.44
9	0.124	0.019	0.52	0.45
10*	0.2006	0.0348	4.96	2.42
11	0.11	0.005	-0.29	-0.64
12	NT	NT		
13	<0.5	NR		
14	NR	NR		
15	0.12	0.03	0.29	0.16
17	0.1091	0.0041	-0.34	-0.81

* Outlier, see Section 4.2

Statistics

Assigned Value	0.115	0.006
Spike Value*	0.114	0.003
Homogeneity Value	0.117	0.018
Robust Average	0.117	0.009
Median	0.113	0.006
Mean	0.124	
N	11	
Max	0.2006	
Min	0.105	
Robust SD	0.011	
Robust CV	9.7%	

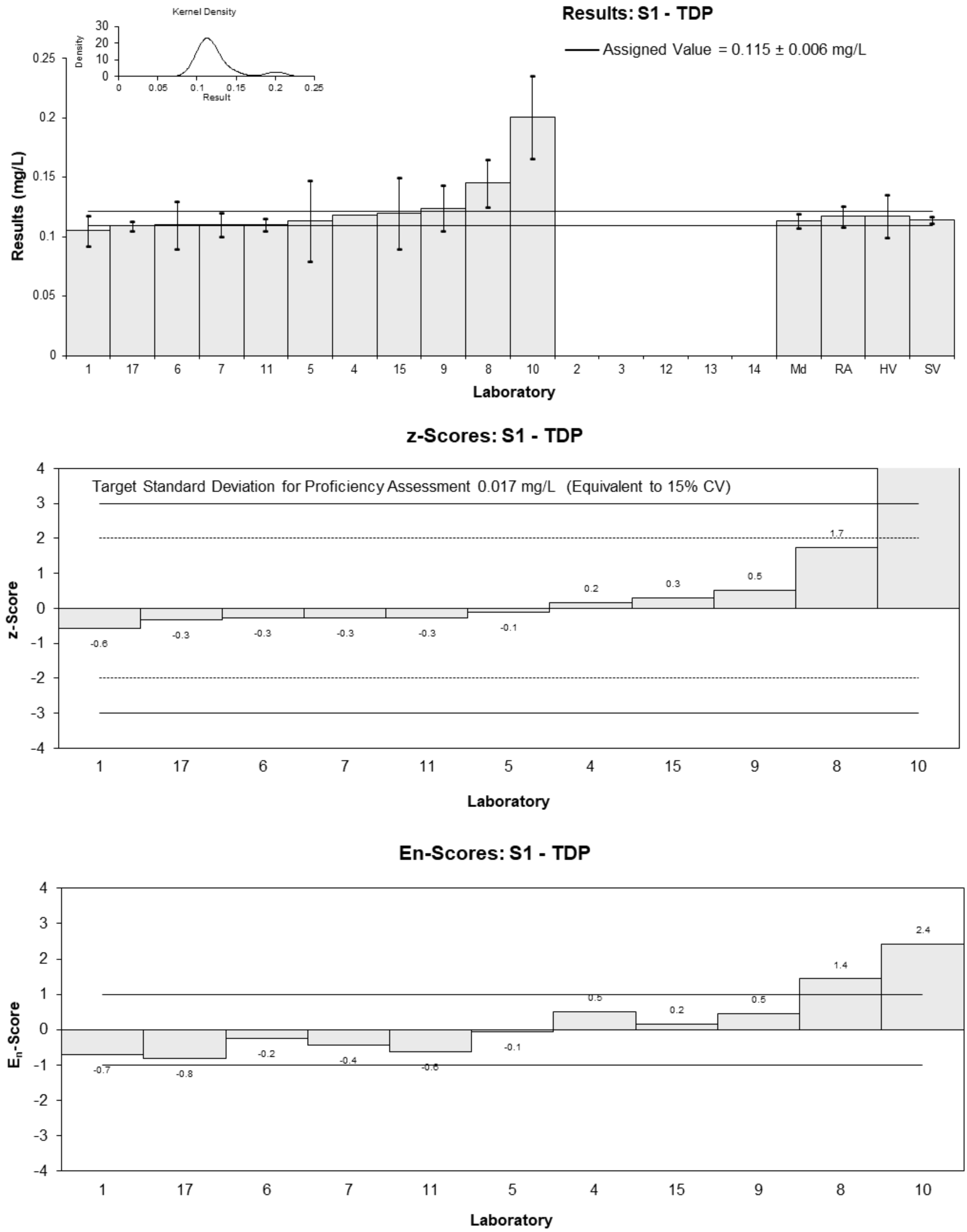

Results: S1 - TDP
Assigned Value = 0.115 ± 0.006 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 17 6 7 11 5 4 15 9 8 10 2 3 12 13 14 Md RA HV SV
z-Scores: S1 - TDP
Target Standard Deviation for Proficiency Assessment 0.017 mg/L (Equivalent to 15% CV)
z-Score
-0.6 -0.3 -0.3 -0.3 -0.3 -0.1 0.2 0.3 0.5 1.7
1 17 6 7 11 5 4 15 9 8 10
Laboratory
En-Scores: S1 - TDP
En-Score
-0.7 -0.8 -0.2 -0.4 -0.6 -0.1 0.5 0.2 0.5 1.4 2.4
1 17 6 7 11 5 4 15 9 8 10
Laboratory

Figure 10

Table 14

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.6	0.1	-0.08	-0.11
2	NR	NR		
3	3.116	0.03	1.89	3.05
4**	25.3	2.85	86.56	7.95
5	2.52	0.25	-0.38	-0.34
6	NT	NT		
7	NT	NT		
8	2.81	0.3	0.73	0.56
9	2.56	0.36	-0.23	-0.15
10	2.5820	0.2994	-0.15	-0.11
11	NR	NR		
12	NT	NT		
13	2.4	0.34	-0.84	-0.59
14	NR	NR		
15	2.6	0.33	-0.08	-0.05
17	NT	NT		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.62	0.16
Spike Value	Not Spiked	
Homogeneity Value	2.74	0.33
Robust Average	2.62	0.16
Median	2.59	0.07
Mean	2.65	
N	8	
Max	3.116	
Min	2.4	
Robust SD	0.18	
Robust CV	6.7%	

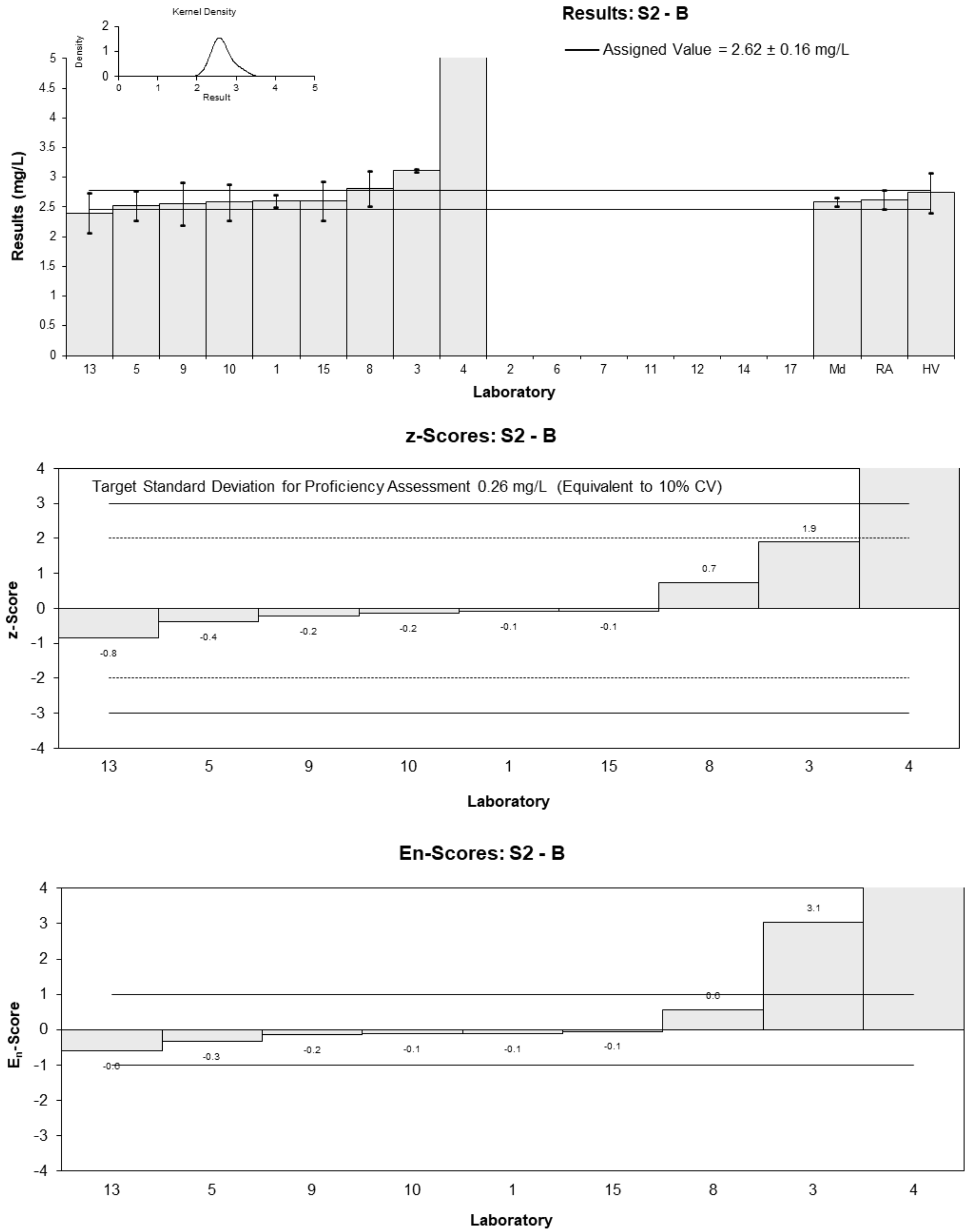

Results: S2 - B
Assigned Value = 2.62 ± 0.16 mg/L
Kernel Density
Density
Result
Results (mg/L)
13 5 9 10 1 15 8 3 4 2 6 7 11 12 14 17 Md RA HV
Laboratory
z-Scores: S2 - B
Target Standard Deviation for Proficiency Assessment 0.26 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.4 -0.2 -0.2 -0.1 -0.1 0.7 1.9
13 5 9 10 1 15 8 3 4
Laboratory
En-Scores: S2 - B
E_n-Score
-0.3 -0.2 -0.1 -0.1 -0.1 3.1
13 5 9 10 1 15 8 3 4
Laboratory

Figure 11

Table 15

Sample Details

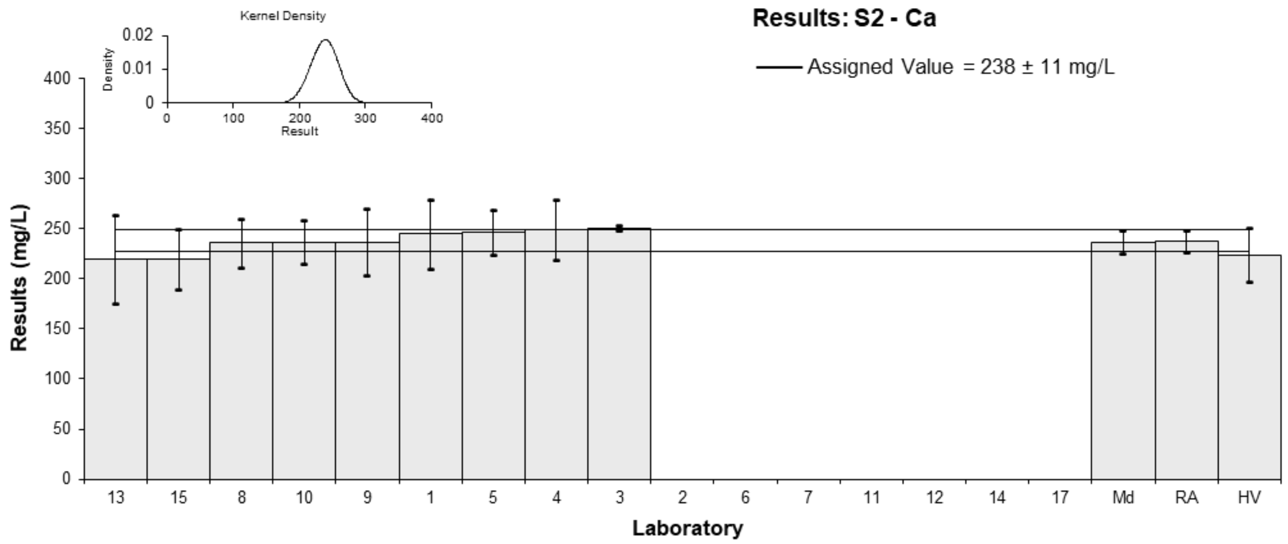
Sample No.	S2
Matrix	Sea Water
Analyte	Ca
Unit	mg/L

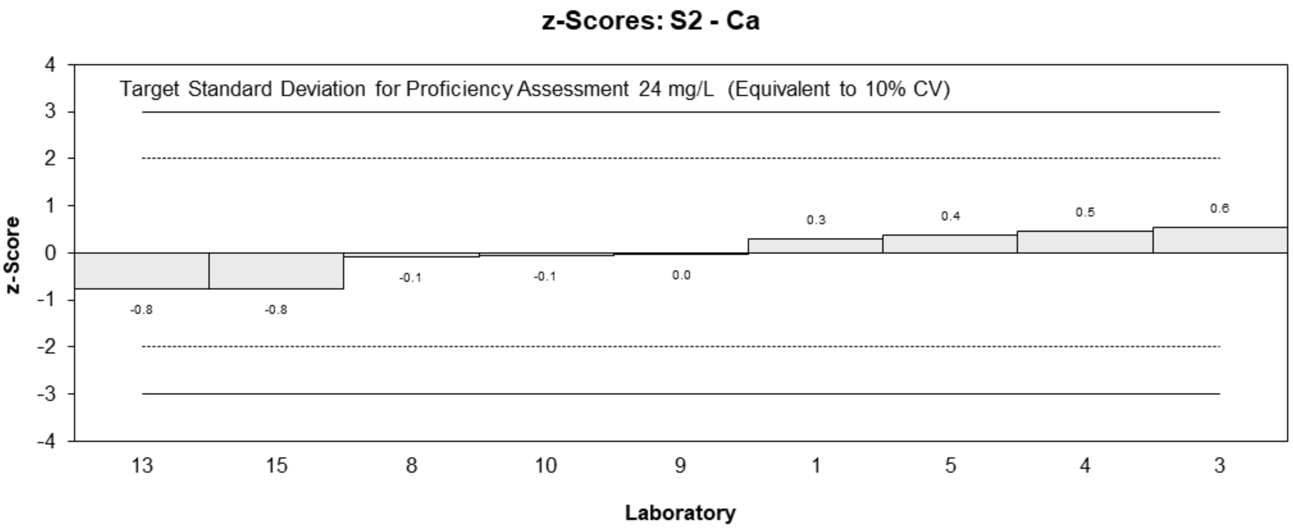
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	245	35	0.29	0.19
2	NR	NR		
3	251	2.5	0.55	1.15
4	249	30.3	0.46	0.34
5	247	22.7	0.38	0.36
6	NT	NT		
7	NT	NT		
8	236	24	-0.08	-0.08
9	237	33	-0.04	-0.03
10	236.921	21.776	-0.05	-0.04
11	NR	NR		
12	NT	NT		
13	220	44.4	-0.76	-0.39
14	NR	NR		
15	220	30	-0.76	-0.56
17	NT	NT		

Statistics

Assigned Value	238	11
Spike Value	Not Spiked	
Homogeneity Value	224	27
Robust Average	238	11
Median	237	12
Mean	238	
N	9	
Max	251	
Min	220	
Robust SD	13	
Robust CV	5.5%	


Kernel Density
0.02
0.01
0
Density
0
100
200
300
400
Result
Results: S2 - Ca
Assigned Value = 238 ± 11 mg/L
400
350
300
250
200
150
100
50
0
Results (mg/L)
13
15
8
10
9
1
5
4
3
2
6
7
11
12
14
17
Md
RA
HV
Laboratory


z-Scores: S2 - Ca
Target Standard Deviation for Proficiency Assessment 24 mg/L (Equivalent to 10% CV)
4
3
2
1
0
-1
-2
-3
-4
z-Score
-0.8
-0.8
-0.1
-0.1
0.0
0.3
0.4
0.5
0.6
13
15
8
10
9
1
5
4
3
Laboratory

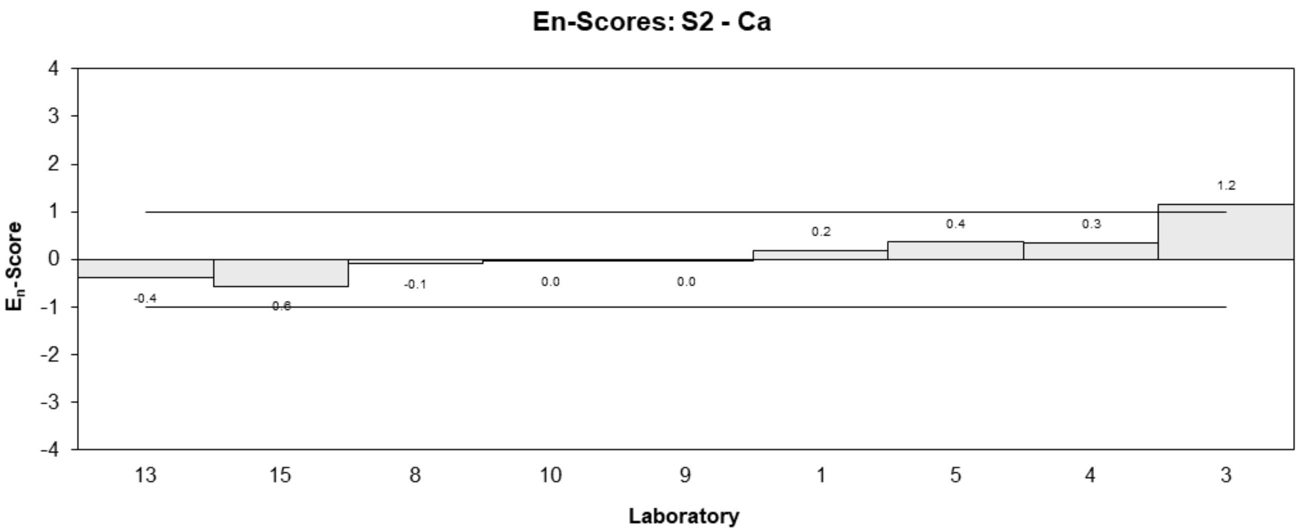

En-Scores: S2 - Ca
4
3
2
1
0
-1
-2
-3
-4
En-Score
-0.4
-0.6
-0.1
0.0
0.0
0.2
0.4
0.3
1.2
13
15
8
10
9
1
5
4
3
Laboratory

Figure 12

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	224	21	-0.13	-0.11
2	NR	NR		
3	245	2.4	0.79	1.05
4	223	16.2	-0.18	-0.17
5	214	14.8	-0.57	-0.58
6	NT	NT		
7	NT	NT		
8	185	19	-1.85	-1.65
9	251	35	1.06	0.62
10	248.268	19.039	0.94	0.83
11	NR	NR		
12	NT	NT		
13	220	38.3	-0.31	-0.17
14	NR	NR		
15	220	30	-0.31	-0.20
17	NT	NT		

Statistics

Assigned Value	227	17
Spike Value	Not Spiked	
Homogeneity Value	247	30
Robust Average	227	17
Median	223	11
Mean	226	
N	9	
Max	251	
Min	185	
Robust SD	20	
Robust CV	9%	

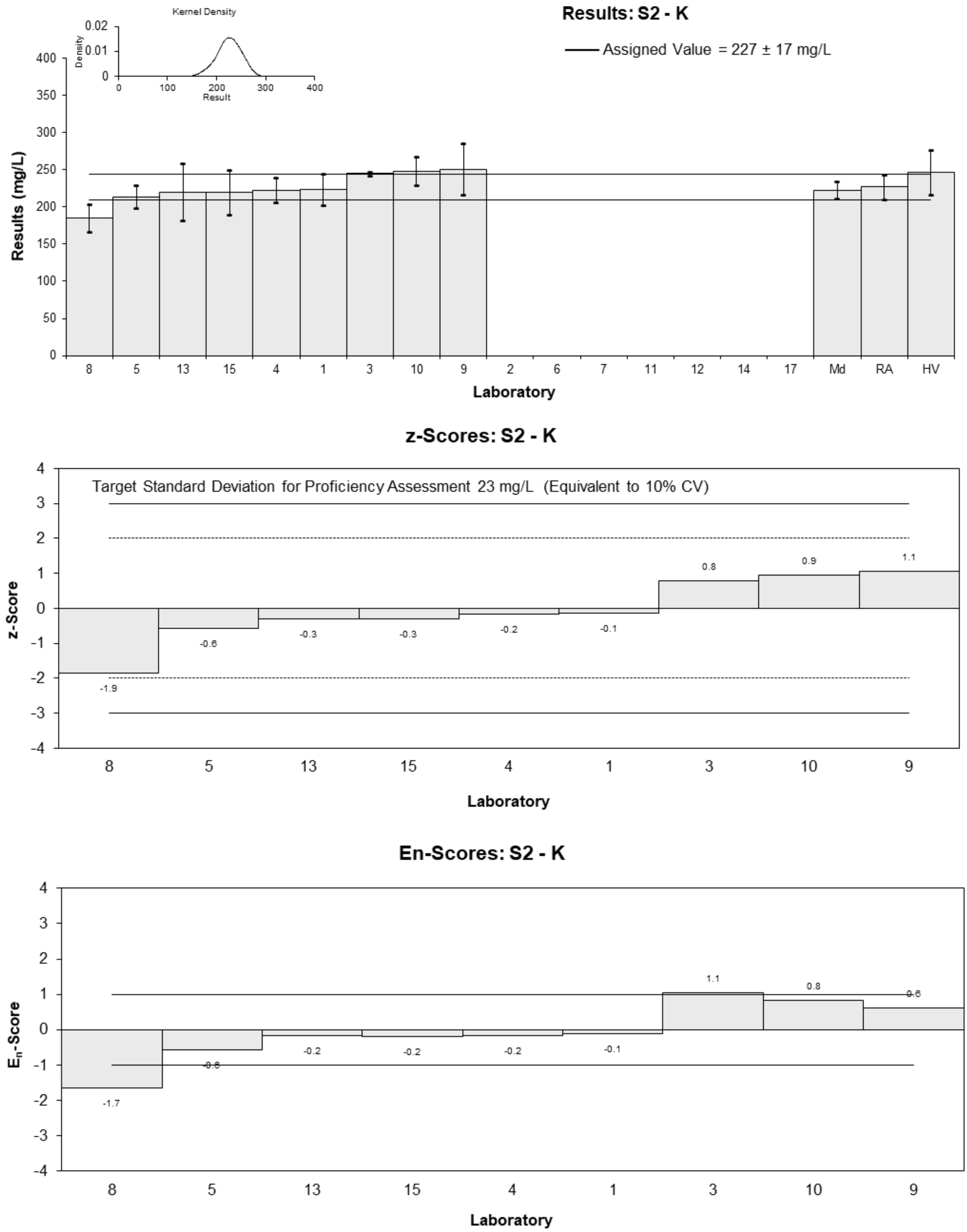

Kernel Density
Density
Result
Results: S2 - K
Assigned Value = 227 ± 17 mg/L
Results (mg/L)
Laboratory
8 5 13 15 4 1 3 10 9 2 6 7 11 12 14 17 Md RA HV
z-Scores: S2 - K
Target Standard Deviation for Proficiency Assessment 23 mg/L (Equivalent to 10% CV)
z-Score
-1.9 -0.6 -0.3 -0.3 -0.2 -0.1 0.8 0.9 1.1
Laboratory
8 5 13 15 4 1 3 10 9
En-Scores: S2 - K
E_n-Score
-1.7 -0.6 -0.2 -0.2 -0.2 -0.1 1.1 0.8 0.6
Laboratory
8 5 13 15 4 1 3 10 9

Figure 13

Table 17

Sample Details

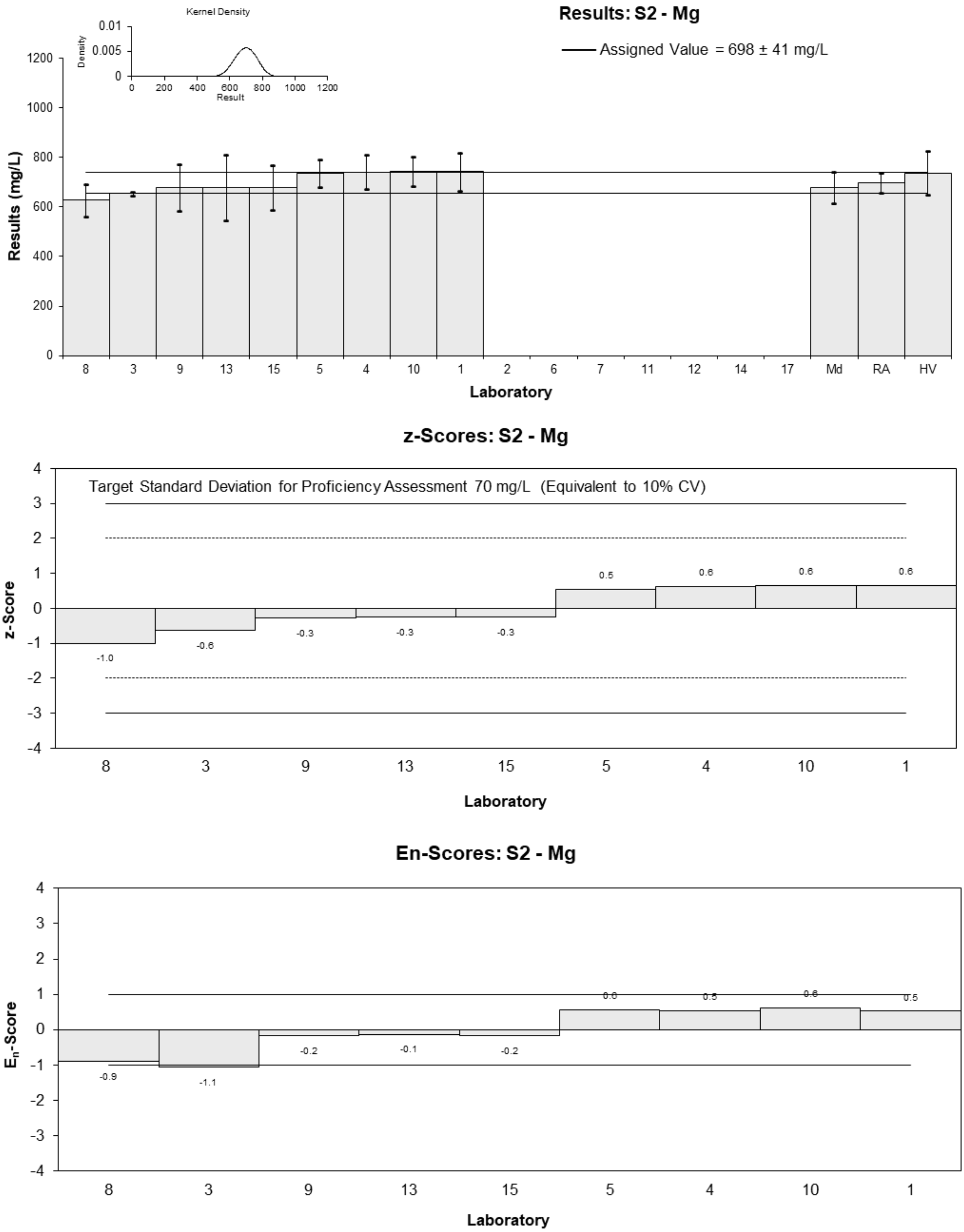
Sample No.	S2
Matrix	Sea Water
Analyte	Mg
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	743	77	0.64	0.52
2	NR	NR		
3	654	6.5	-0.63	-1.06
4	741	69.4	0.62	0.53
5	736	54.5	0.54	0.56
6	NT	NT		
7	NT	NT		
8	628	65	-1.00	-0.91
9	679	95	-0.27	-0.18
10	742.801	59.747	0.64	0.62
11	NR	NR		
12	NT	NT		
13	680	133	-0.26	-0.13
14	NR	NR		
15	680	90	-0.26	-0.18
17	NT	NT		

Statistics

Assigned Value	698	41
Spike Value	Not Spiked	
Homogeneity Value	737	88
Robust Average	698	41
Median	680	64
Mean	698	
N	9	
Max	743	
Min	628	
Robust SD	49	
Robust CV	7.1%	



Results: S2 - Mg
Assigned Value = 698 ± 41 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 3 9 13 15 5 4 10 1 2 6 7 11 12 14 17 Md RA HV
z-Scores: S2 - Mg
Target Standard Deviation for Proficiency Assessment 70 mg/L (Equivalent to 10% CV)
z-Score
-1.0 -0.6 -0.3 -0.3 -0.3 0.5 0.6 0.6 0.6
Laboratory
8 3 9 13 15 5 4 10 1
En-Scores: S2 - Mg
E_n-Score
-0.9 -1.1 -0.2 -0.1 -0.2
Laboratory
8 3 9 13 15 5 4 10 1

Figure 14

Table 18

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	5720	625	0.16	0.12
2	NR	NR		
3	6258	62	1.12	1.67
4	6020	553	0.69	0.59
5	5850	590	0.39	0.32
6	NT	NT		
7	NT	NT		
8	5376	540	-0.45	-0.39
9	5350	750	-0.50	-0.33
10	5692.731	427	0.11	0.11
11	NR	NR		
12	NT	NT		
13	5400	1199	-0.41	-0.18
14	NR	NR		
15	5000	630	-1.12	-0.86
17	NT	NT		

Statistics

Assigned Value	5630	370
Spike Value	Not Spiked	
Homogeneity Value	5310	640
Robust Average	5630	370
Median	5690	390
Mean	5630	
N	9	
Max	6258	
Min	5000	
Robust SD	440	
Robust CV	7.8%	

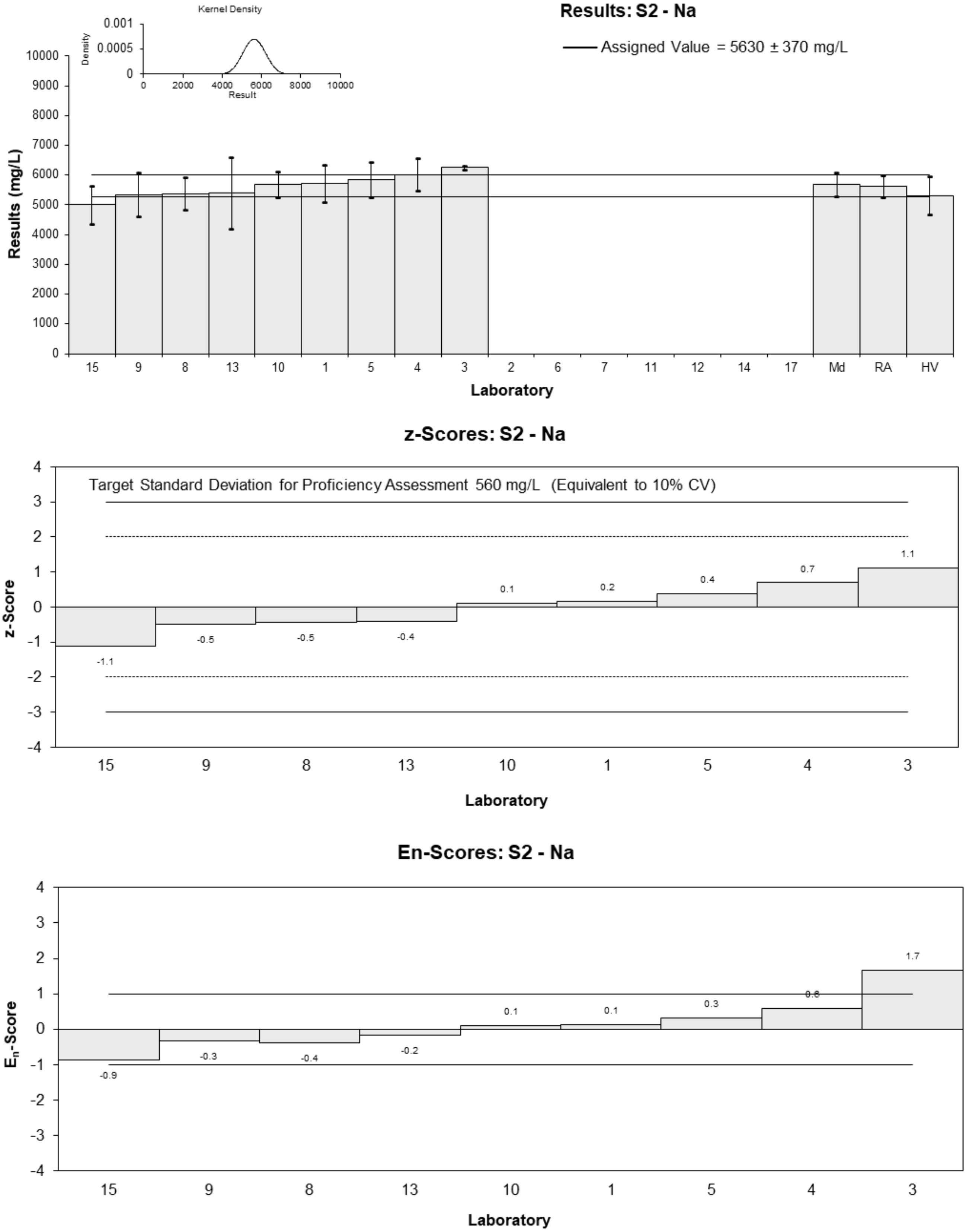

Results: S2 - Na
Assigned Value = 5630 ± 370 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15
9
8
13
10
1
5
4
3
2
6
7
11
12
14
17
Md
RA
HV
z-Scores: S2 - Na
Target Standard Deviation for Proficiency Assessment 560 mg/L (Equivalent to 10% CV)
z-Score
-1.1
-0.5
-0.5
-0.4
0.1
0.2
0.4
0.7
1.1
En-Scores: S2 - Na
En-Score
-0.9
-0.3
-0.4
-0.2
0.1
0.1
0.3
0.6
1.7

Figure 15

Table 19

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	84	10	-0.60	-0.47
2	NR	NR		
3	89	34	-0.04	-0.01
4	99	14.8	1.07	0.61
5	95	13.1	0.63	0.39
6	NT	NT		
7	87	5.05	-0.27	-0.32
8	88	9.0	-0.16	-0.13
9	85.3	5.4	-0.46	-0.52
10	79.07	7.67	-1.16	-1.08
11	NR	NR		
12	NT	NT		
13**	8.6	1.3	-9.04	-13.82
14	NR	NR		
15	98	12	0.96	0.65
17	89.7	3.7	0.03	0.04

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	89.4	5.7
Spike Value	Not Spiked	
Robust Average	89.4	5.7
Median	88.5	4.5
Mean	89.4	
N	10	
Max	99	
Min	79.07	
Robust SD	7.2	
Robust CV	8%	

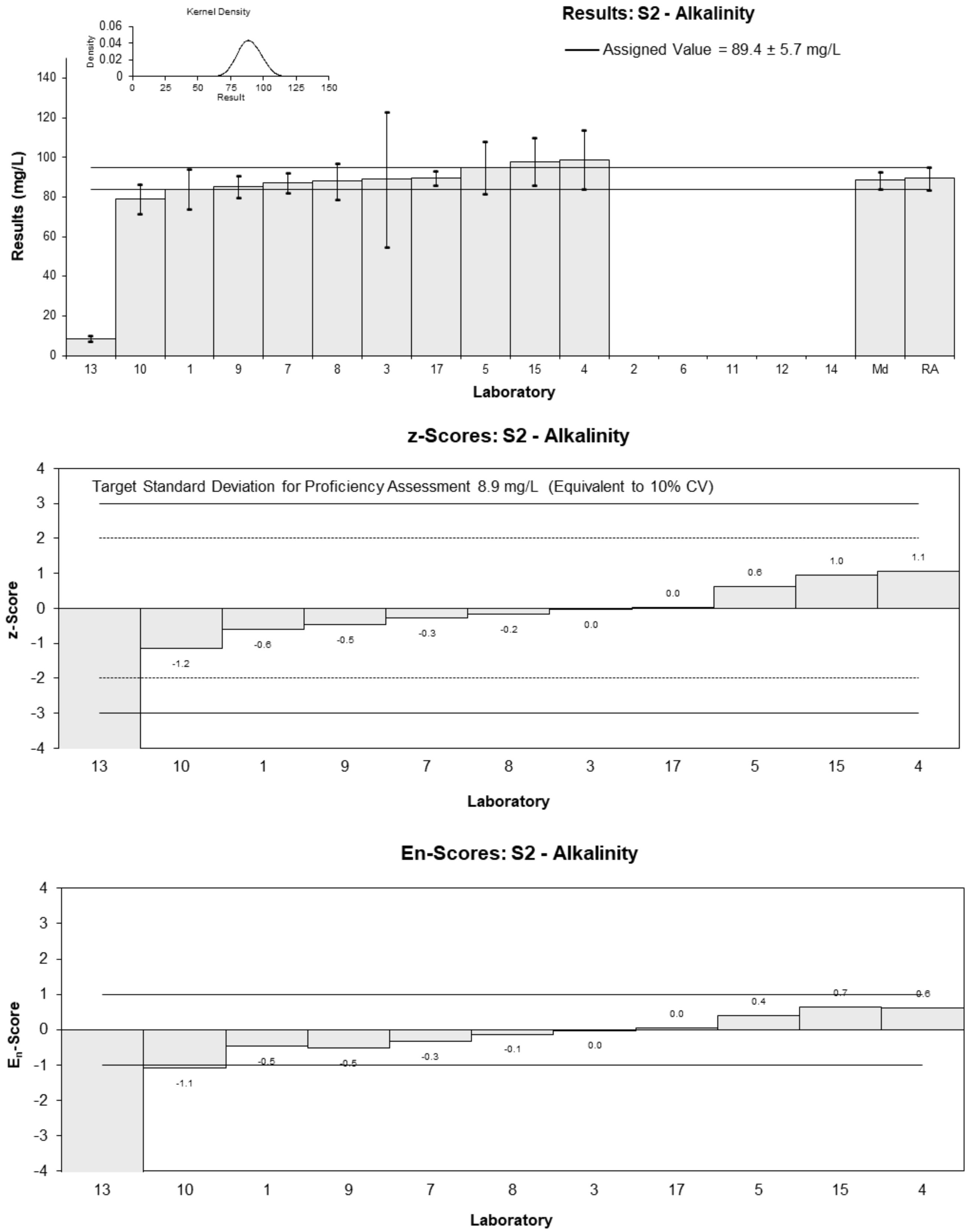

Results: S2 - Alkalinity
Assigned Value = 89.4 ± 5.7 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
13 10 1 9 7 8 3 17 5 15 4 2 6 11 12 14 Md RA
z-Scores: S2 - Alkalinity
Target Standard Deviation for Proficiency Assessment 8.9 mg/L (Equivalent to 10% CV)
z-Score
-1.2 -0.6 -0.5 -0.3 -0.2 0.0 0.0 0.6 1.0 1.1
Laboratory
13 10 1 9 7 8 3 17 5 15 4
En-Scores: S2 - Alkalinity
En-Score
-1.1 -0.5 -0.5 -0.3 -0.1 0.0 0.0 0.4 0.7 0.6
Laboratory
13 10 1 9 7 8 3 17 5 15 4

Figure 16

Table 20

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	31200	1880	0.10	0.14
2	NR	NR		
3	33650	336	0.89	2.39
4	31800	2474	0.29	0.33
5	31000	1500	0.03	0.05
6	NT	NT		
7	30000	1110	-0.29	-0.58
8	26160	2600	-1.53	-1.68
9	30600	1500	-0.10	-0.16
10	30913	2052.5	0.00	0.01
11	NR	NR		
12**	27.58	NR	-9.99	-28.07
13	32000	1600	0.36	0.57
14	NR	NR		
15	29000	3600	-0.61	-0.50
17	31170	630	0.09	0.21

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	30900	1100
Spike Value	Not Spiked	
Homogeneity Value	31000	2300
Robust Average	30900	1100
Median	31000	900
Mean	30700	
N	11	
Max	33650	
Min	26160	
Robust SD	1400	
Robust CV	4.6%	

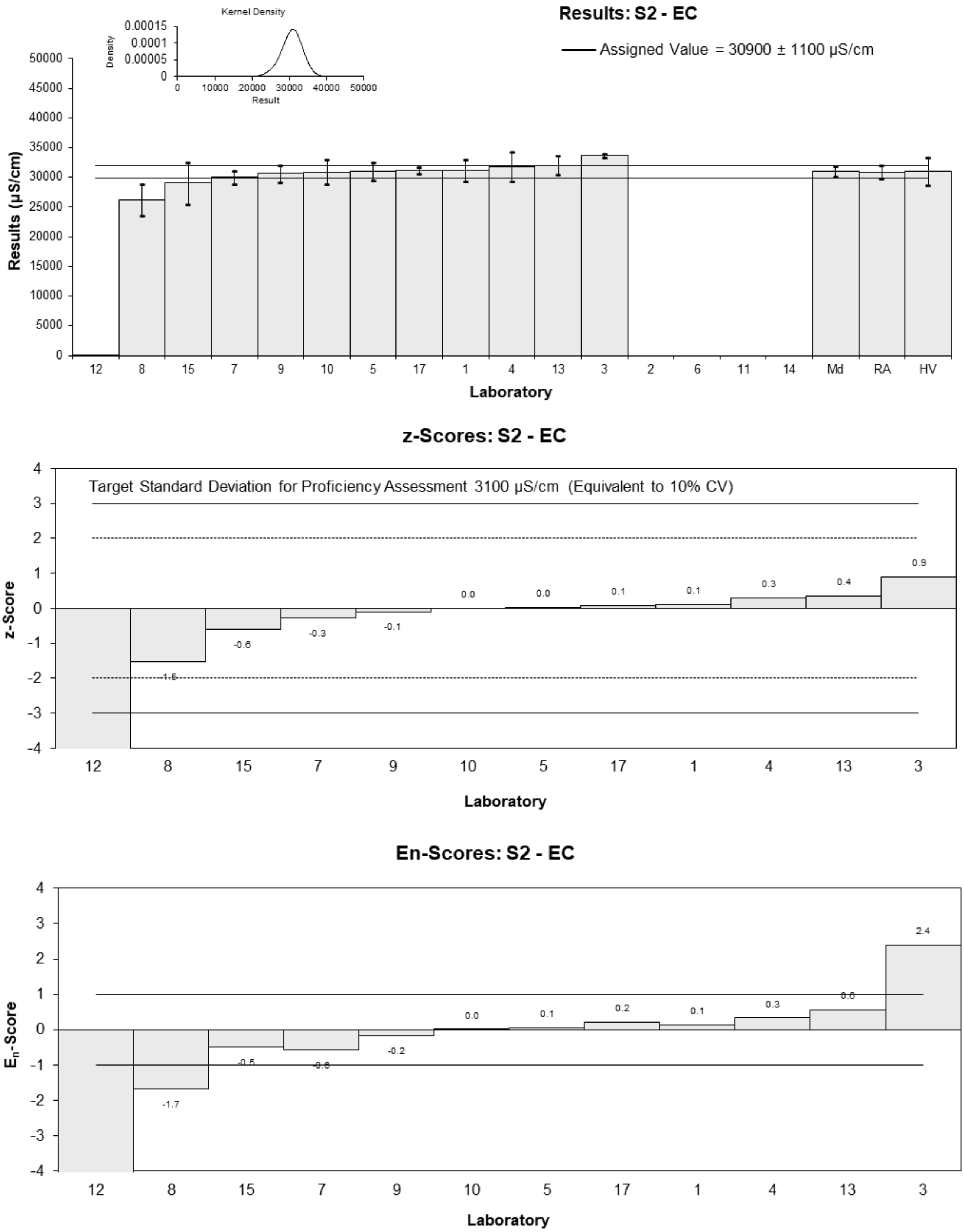

Results: S2 - EC
Assigned Value = 30900 ± 1100 µS/cm
Kernel Density
Density
Result
Results (µS/cm)
Laboratory
12 8 15 7 9 10 5 17 1 4 13 3 2 6 11 14 Md RA HV
z-Scores: S2 - EC
Target Standard Deviation for Proficiency Assessment 3100 µS/cm (Equivalent to 10% CV)
z-Score
Laboratory
12 8 15 7 9 10 5 17 1 4 13 3
En-Scores: S2 - EC
En-Score
Laboratory
12 8 15 7 9 10 5 17 1 4 13 3

Figure 17

Table 21

Sample Details

Sample No.	S2
Matrix	Sea Water
Analyte	pH

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	7.89	0.06	-0.25	-0.70
2	NR	NR		
3	8.1	0.17	0.50	0.75
4	7.86	0.098	-0.36	-0.79
5	7.88	0.052	-0.29	-0.84
6	NT	NT		
7	7.97	0.07	0.04	0.09
8	7.94	0.2	-0.07	-0.09
9	8.1	0.2	0.50	0.65
10	7.52	0.12	-1.58	-3.05
11	NR	NR		
12	7.901	NR	-0.21	-0.74
13	8.0	0.3	0.14	0.13
14	NR	NR		
15	8.1	1	0.50	0.14
17	8.0	0.2	0.14	0.19

Statistics

Assigned Value	7.96	0.08
Spike Value	Not Spiked	
Robust Average	7.96	0.08
Median	7.96	0.07
Mean	7.94	
N	12	
Max	8.1	
Min	7.52	
Robust SD	0.12	
Robust CV	1.5%	

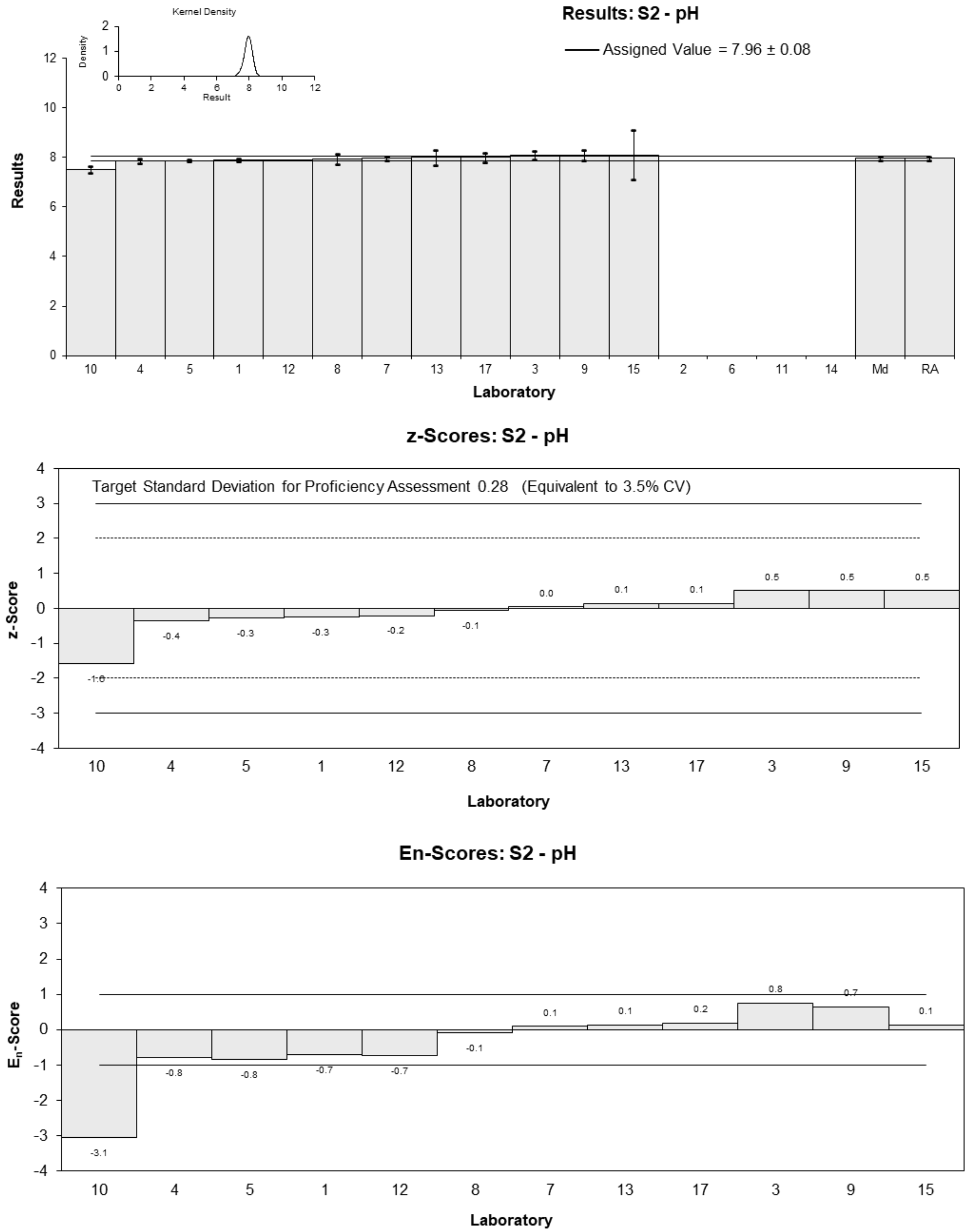

Results: S2 - pH
Assigned Value = 7.96 ± 0.08
Kernel Density
Density
Result
Results
Laboratory
10 4 5 1 12 8 7 13 17 3 9 15 2 6 11 14 Md RA
z-Scores: S2 - pH
Target Standard Deviation for Proficiency Assessment 0.28 (Equivalent to 3.5% CV)
z-Score
Laboratory
-1.6 -0.4 -0.3 -0.3 -0.2 -0.1 0.0 0.1 0.1 0.5 0.5 0.5
10 4 5 1 12 8 7 13 17 3 9 15
En-Scores: S2 - pH
E_n-Score
Laboratory
-3.1 -0.8 -0.8 -0.7 -0.7 -0.1 0.1 0.1 0.2 0.8 0.7 0.1
10 4 5 1 12 8 7 13 17 3 9 15

Figure 18

Table 22

Sample Details

Sample No.	S2
Matrix	Sea Water
Analyte	Silica (as SiO_2)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.24	0.03	-1.72	-2.33
2	0.39054	0.015	0.34	0.52
3	NT	NT		
4	NR	NR		
5	0.39	0.05	0.33	0.36
6	NT	NT		
7	0.33	0.02	-0.49	-0.73
8	NT	NT		
9	NT	NT		
10	0.3900	0.05	0.33	0.36
11	0.37	NR	0.05	0.09
12	NT	NT		
13	0.5	0.08	1.83	1.46
14	0.3901	0.005826	0.33	0.53
15	0.3	0.1	-0.90	-0.60
17	0.365	0.061	-0.01	-0.01

Statistics

Assigned Value	0.366	0.045
Spike Value	Not Spiked	
Robust Average	0.366	0.045
Median	0.380	0.015
Mean	0.367	
N	10	
Max	0.5	
Min	0.24	
Robust SD	0.057	
Robust CV	15%	

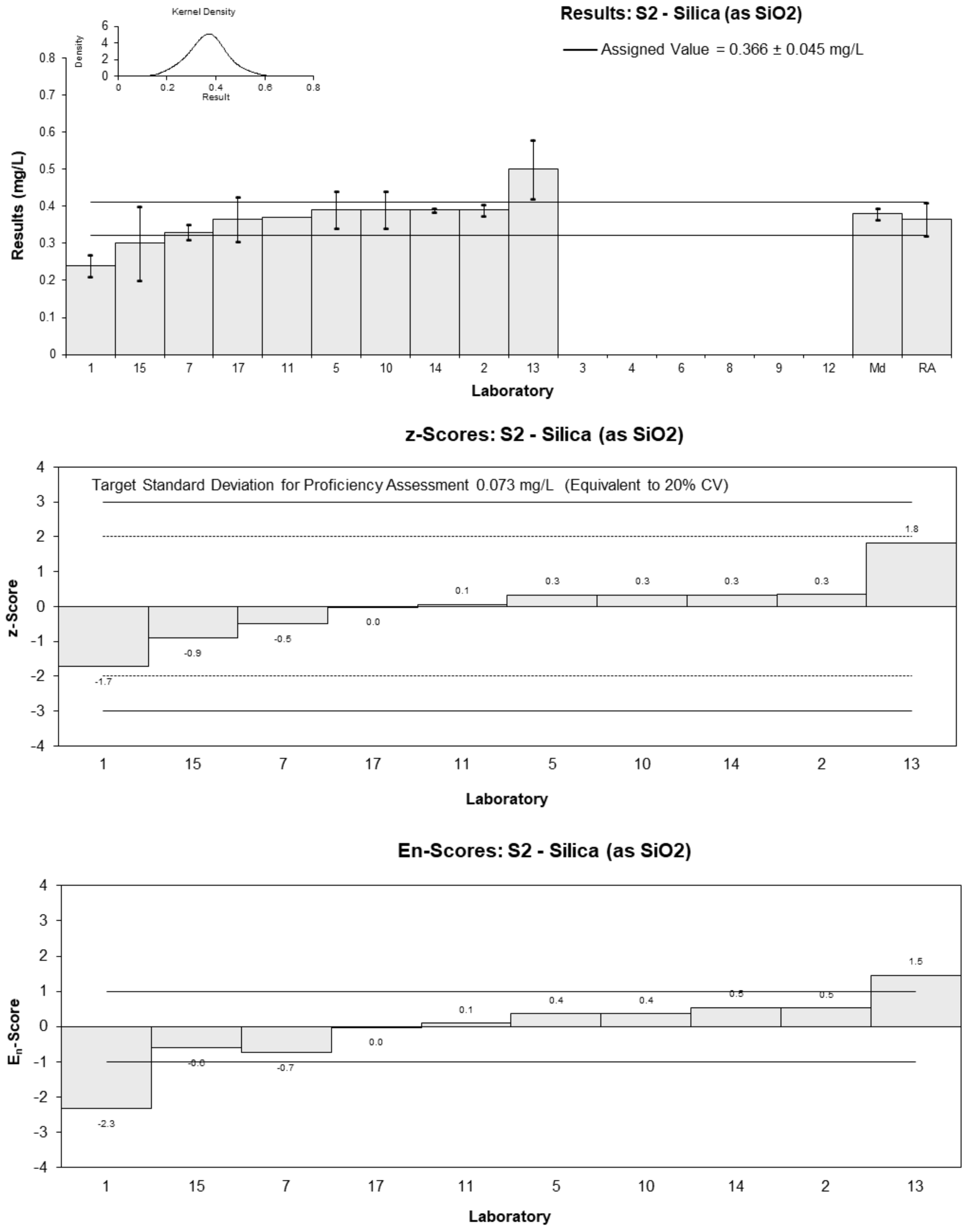

Results: S2 - Silica (as SiO2)
Assigned Value = 0.366 ± 0.045 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 15 7 17 11 5 10 14 2 13 3 4 6 8 9 12 Md RA
z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation for Proficiency Assessment 0.073 mg/L (Equivalent to 20% CV)
z-Score
-1.7 -0.9 -0.5 0.0 0.1 0.3 0.3 0.3 0.3 1.8
Laboratory
1 15 7 17 11 5 10 14 2 13
En-Scores: S2 - Silica (as SiO2)
En-Score
-2.3 -0.6 -0.7 0.0 0.1 0.4 0.4 0.5 0.5 1.5
Laboratory
1 15 7 17 11 5 10 14 2 13

Figure 19

Table 23

Sample Details

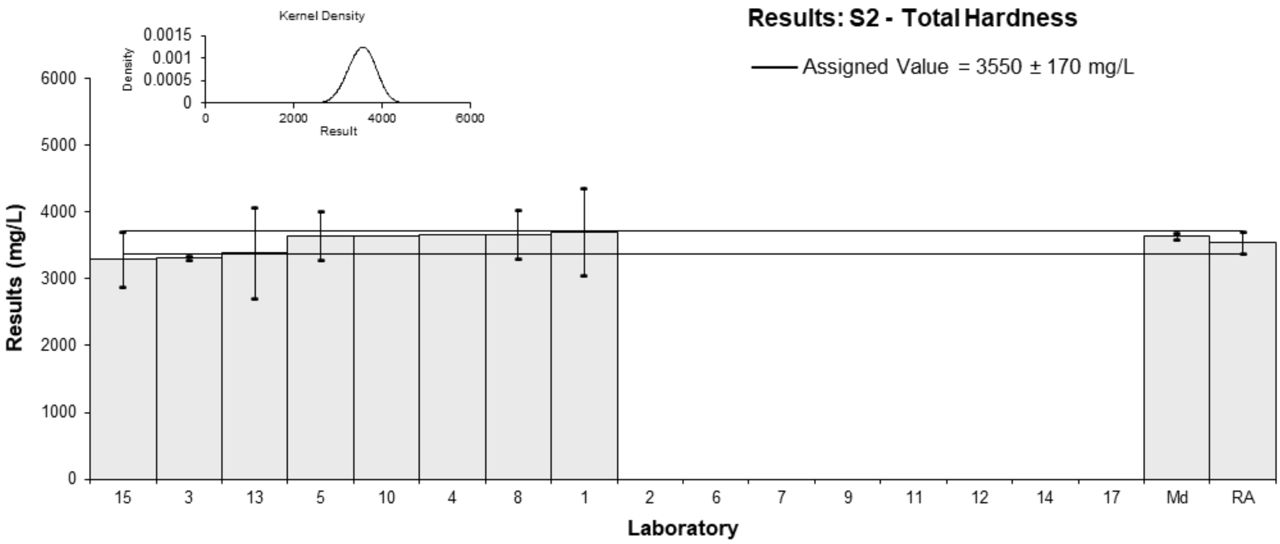
Sample No.	S2
Matrix	Sea Water
Analyte	Total Hardness
Unit	mg/L

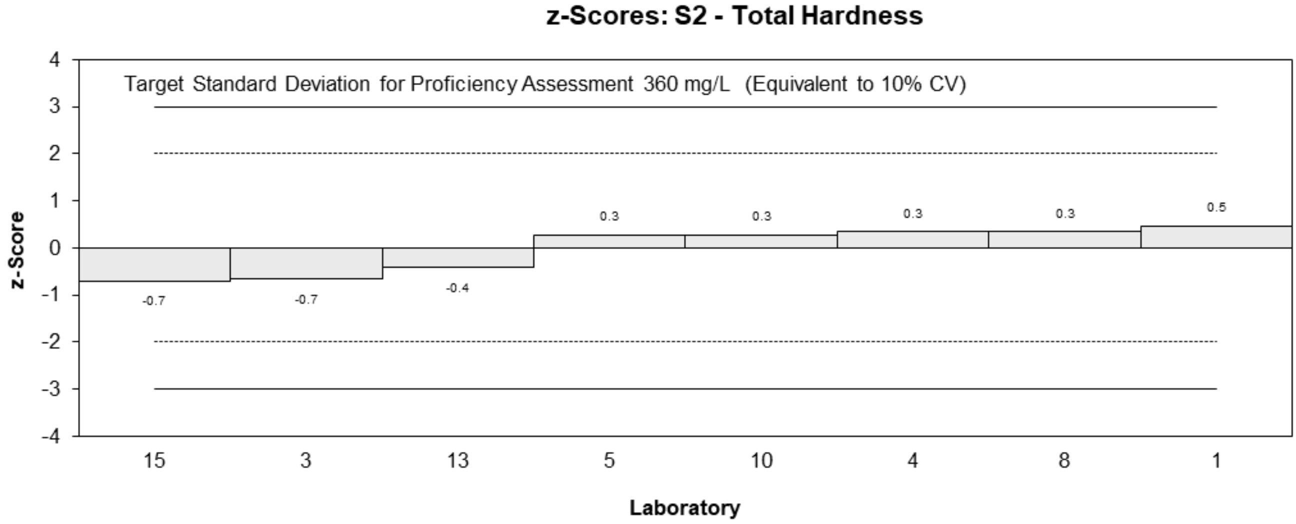
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3710	660	0.45	0.23
2	NR	NR		
3	3320	33.2	-0.65	-1.33
4	3670	NR	0.34	0.71
5	3650	365	0.28	0.25
6	NT	NT		
7	NT	NT		
8	3670	370	0.34	0.29
9	NT	NT		
10	3650.446	NR	0.28	0.59
11	NR	NR		
12	NT	NT		
13	3400	680	-0.42	-0.21
14	NR	NR		
15	3300	410	-0.70	-0.56
17	NT	NT		

Statistics

Assigned Value	3550	170
Spike Value	Not Spiked	
Robust Average	3550	170
Median	3650	50
Mean	3550	
N	8	
Max	3710	
Min	3300	
Robust SD	200	
Robust CV	5.6%	


Results: S2 - Total Hardness
Assigned Value = 3550 ± 170 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15
3
13
5
10
4
8
1
2
6
7
9
11
12
14
17
Md
RA


z-Scores: S2 - Total Hardness
Target Standard Deviation for Proficiency Assessment 360 mg/L (Equivalent to 10% CV)
z-Score
-0.7
-0.7
-0.4
0.3
0.3
0.3
0.3
0.5
Laboratory
15
3
13
5
10
4
8
1

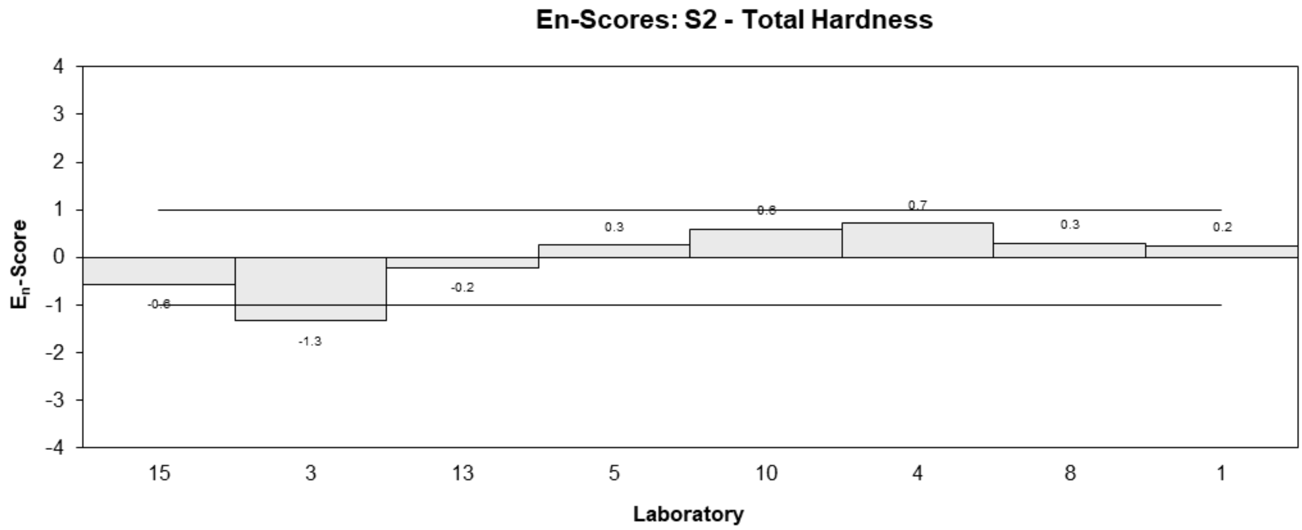

En-Scores: S2 - Total Hardness
En-Score
-0.6
-1.3
-0.2
0.3
0.6
0.7
0.3
0.2
Laboratory
15
3
13
5
10
4
8
1

Figure 20

Table 24

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.8	0.04	0.99	1.14
2	NT	NT		
3	0.662	0.01	-0.91	-1.32
4	0.7	0.08	-0.38	-0.30
5	0.73	0.073	0.03	0.02
6	0.68	0.07	-0.66	-0.56
7	NT	NT		
8	0.869	0.1	1.94	1.27
9	0.715	0.100	-0.18	-0.12
10	0.74757	0.0898	0.27	0.19
11	NR	NR		
12	NT	NT		
13	0.70	0.1	-0.38	-0.25
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	0.728	0.049
Spike Value	Not Spiked	
Robust Average	0.728	0.049
Median	0.715	0.040
Mean	0.734	
N	9	
Max	0.869	
Min	0.662	
Robust SD	0.059	
Robust CV	8.1%	

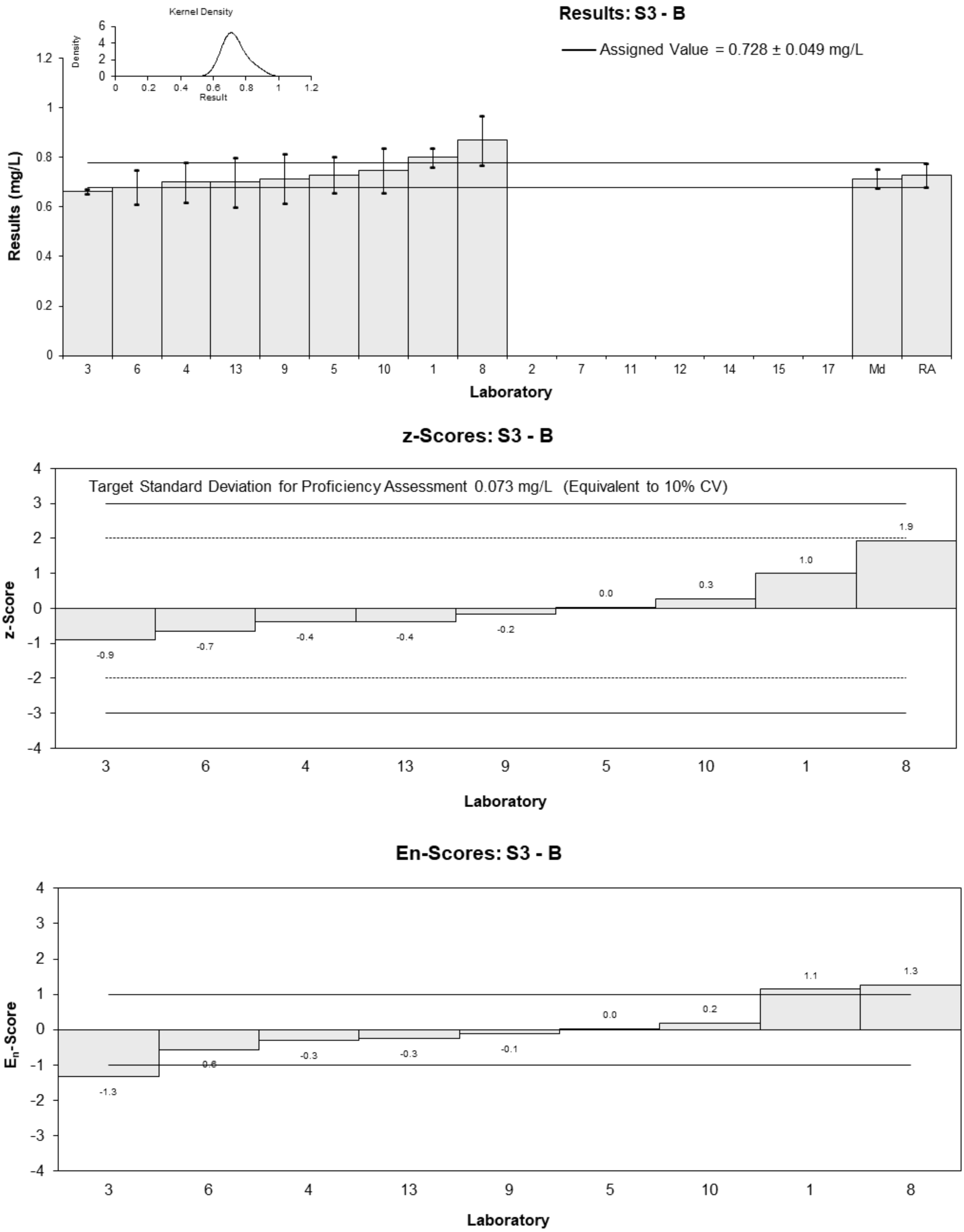

Kernel Density
Density
Result
Results: S3 - B
Assigned Value = 0.728 ± 0.049 mg/L
Results (mg/L)
3 6 4 13 9 5 10 1 8 2 7 11 12 14 15 17 Md RA
Laboratory
z-Scores: S3 - B
Target Standard Deviation for Proficiency Assessment 0.073 mg/L (Equivalent to 10% CV)
z-Score
-0.9 -0.7 -0.4 -0.4 -0.2 0.0 0.3 1.0 1.9
3 6 4 13 9 5 10 1 8
Laboratory
En-Scores: S3 - B
En-Score
-1.3 -0.6 -0.3 -0.3 -0.1 0.0 0.2 1.1 1.3
3 6 4 13 9 5 10 1 8
Laboratory

Figure 21

Table 25

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	13	2	-0.71	-0.48
2	NT	NT		
3	14	3	0.00	0.00
4	14	1.7	0.00	0.00
5	15	1.4	0.71	0.66
6	13	1.3	-0.71	-0.70
7	NT	NT		
8	14.2	1.5	0.14	0.12
9	14.3	2.0	0.21	0.14
10	14.442	1.357	0.32	0.30
11	NR	NR		
12	NT	NT		
13	14	2.8	0.00	0.00
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	14.0	0.6
Spike Value	Not Spiked	
Homogeneity Value	16.6	2.5
Robust Average	14.0	0.6
Median	14.0	0.4
Mean	14.0	
N	9	
Max	15	
Min	13	
Robust SD	0.73	
Robust CV	5.2%	

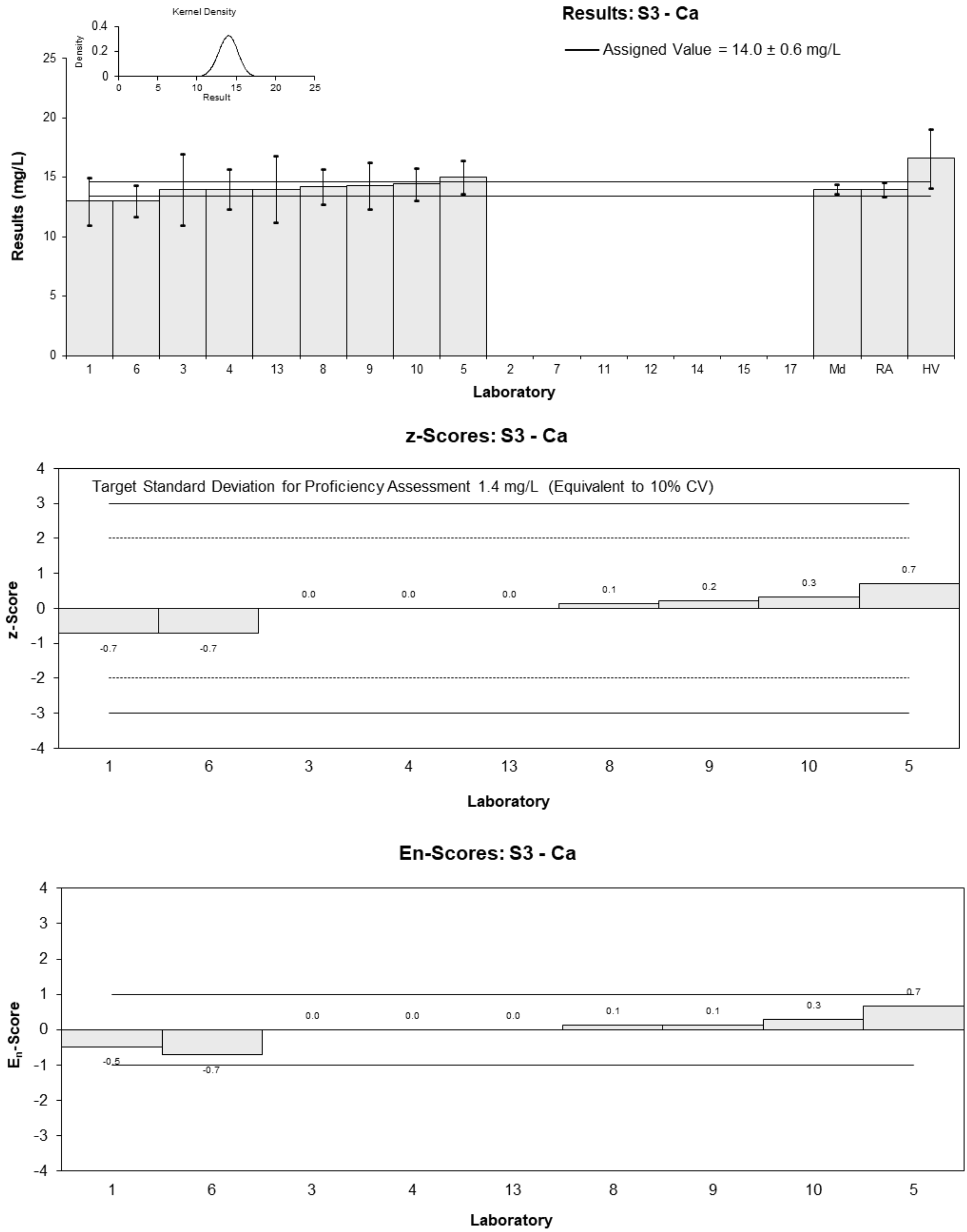

Results: S3 - Ca
Assigned Value = 14.0 ± 0.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 6 3 4 13 8 9 10 5 2 7 11 12 14 15 17 Md RA HV
z-Scores: S3 - Ca
Target Standard Deviation for Proficiency Assessment 1.4 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - Ca
E_n-Score
Laboratory

Figure 22

Table 26

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	7	0.7	0.04	0.03
2	NT	NT		
3	7	1	0.04	0.03
4	7	0.55	0.04	0.04
5	8	0.6	1.48	1.18
6	6.4	1.3	-0.82	-0.39
7	NT	NT		
8	5.82	0.6	-1.65	-1.32
9	6.94	0.97	-0.04	-0.03
10	7.856	0.629	1.27	1.00
11	NR	NR		
12	NT	NT		
13	6.7	1.2	-0.39	-0.20
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	6.97	0.63
Spike Value	Not Spiked	
Homogeneity Value	6.05	0.91
Robust Average	6.97	0.63
Median	7.00	0.37
Mean	6.97	
N	9	
Max	8	
Min	5.82	
Robust SD	0.75	
Robust CV	11%	

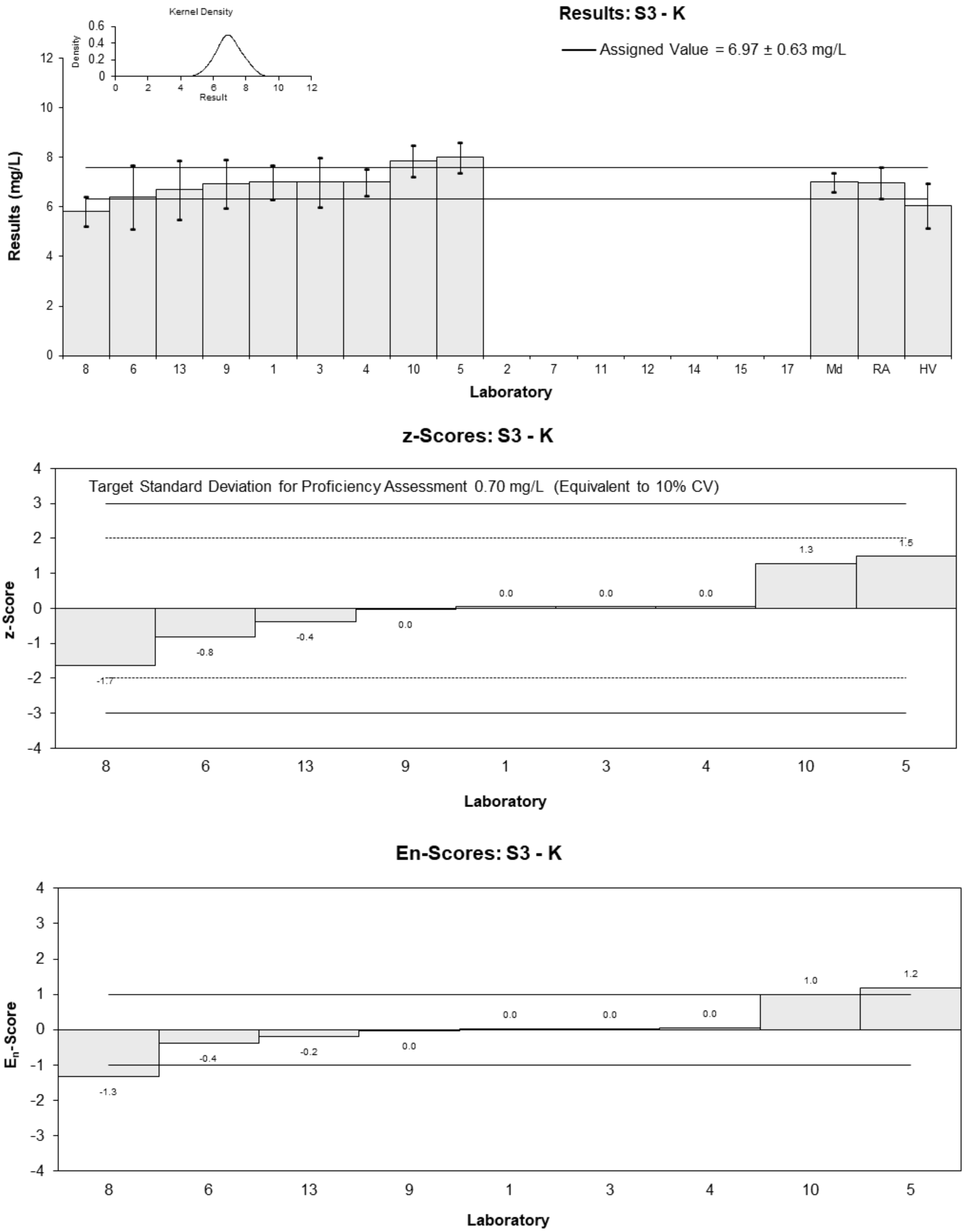

Results: S3 - K
Assigned Value = 6.97 ± 0.63 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8
6
13
9
1
3
4
10
5
2
7
11
12
14
15
17
Md
RA
HV
z-Scores: S3 - K
Target Standard Deviation for Proficiency Assessment 0.70 mg/L (Equivalent to 10% CV)
z-Score
-1.7
-0.8
-0.4
0.0
0.0
0.0
0.0
1.3
1.5
En-Scores: S3 - K
En-Score
-1.3
-0.4
-0.2
0.0
0.0
0.0
0.0
1.0
1.2

Figure 23

Table 27

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	6	0.6	-0.45	-0.38
2	NT	NT		
3	7	1	1.15	0.66
4	6	0.57	-0.45	-0.40
5	7	0.5	1.15	1.10
6	6.1	0.6	-0.29	-0.25
7	NT	NT		
8	5.75	0.6	-0.84	-0.72
9	6.26	0.88	-0.03	-0.02
10	6.41	0.055	0.21	0.31
11	NR	NR		
12	NT	NT		
13	6.0	1.2	-0.45	-0.22
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	6.28	0.42
Spike Value	Not Spiked	
Homogeneity Value	6.51	0.78
Robust Average	6.28	0.42
Median	6.10	0.20
Mean	6.28	
N	9	
Max	7	
Min	5.75	
Robust SD	0.51	
Robust CV	8.1%	

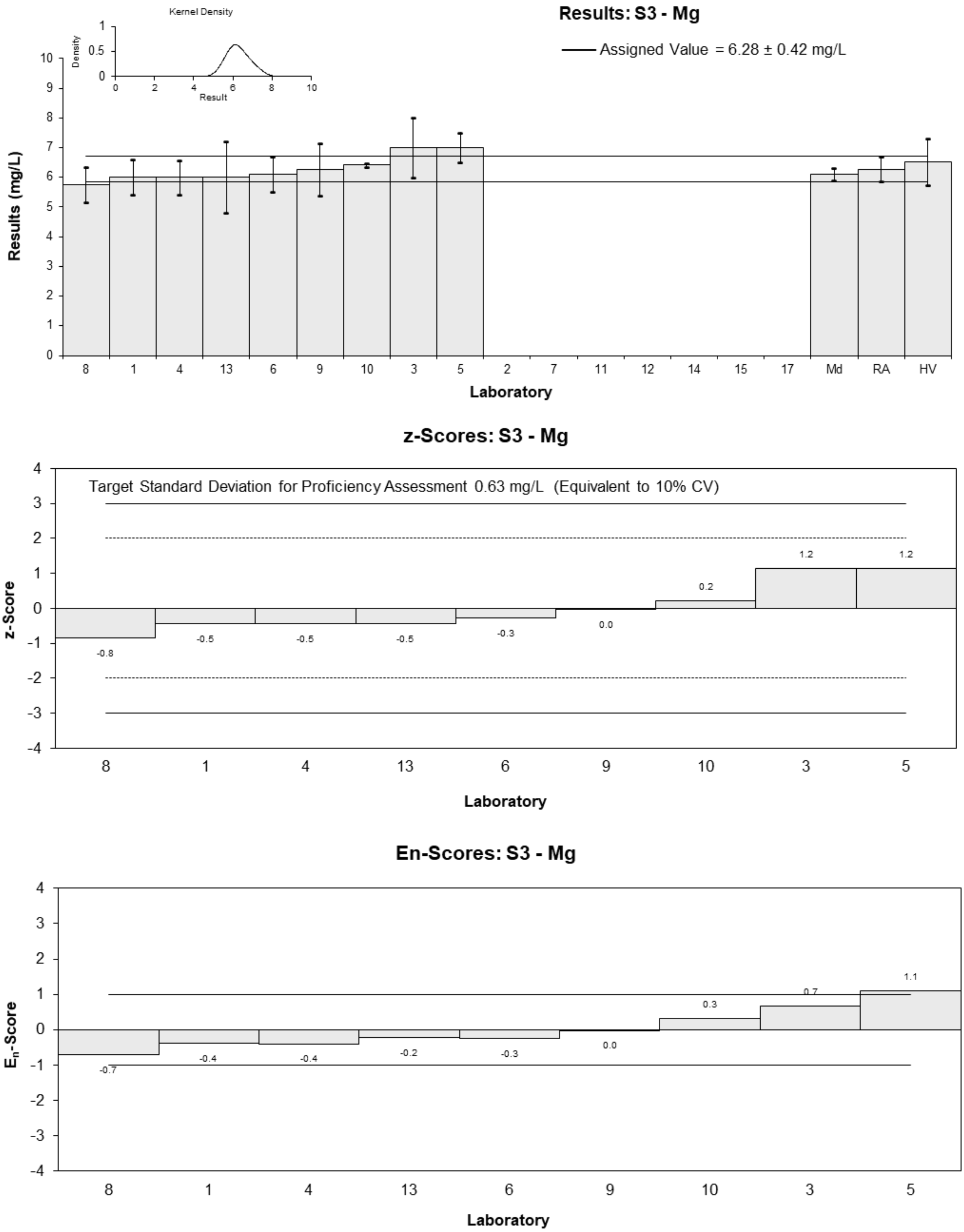

Results: S3 - Mg
Assigned Value = 6.28 ± 0.42 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 1 4 13 6 9 10 3 5 2 7 11 12 14 15 17 Md RA HV
z-Scores: S3 - Mg
Target Standard Deviation for Proficiency Assessment 0.63 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.5 -0.5 -0.5 -0.3 0.0 0.2 1.2 1.2
8 1 4 13 6 9 10 3 5
Laboratory
En-Scores: S3 - Mg
E_n-Score
-0.7 -0.4 -0.4 -0.2 -0.3 0.0 0.3 0.7 1.1
8 1 4 13 6 9 10 3 5
Laboratory

Figure 24

Table 28

Sample Details

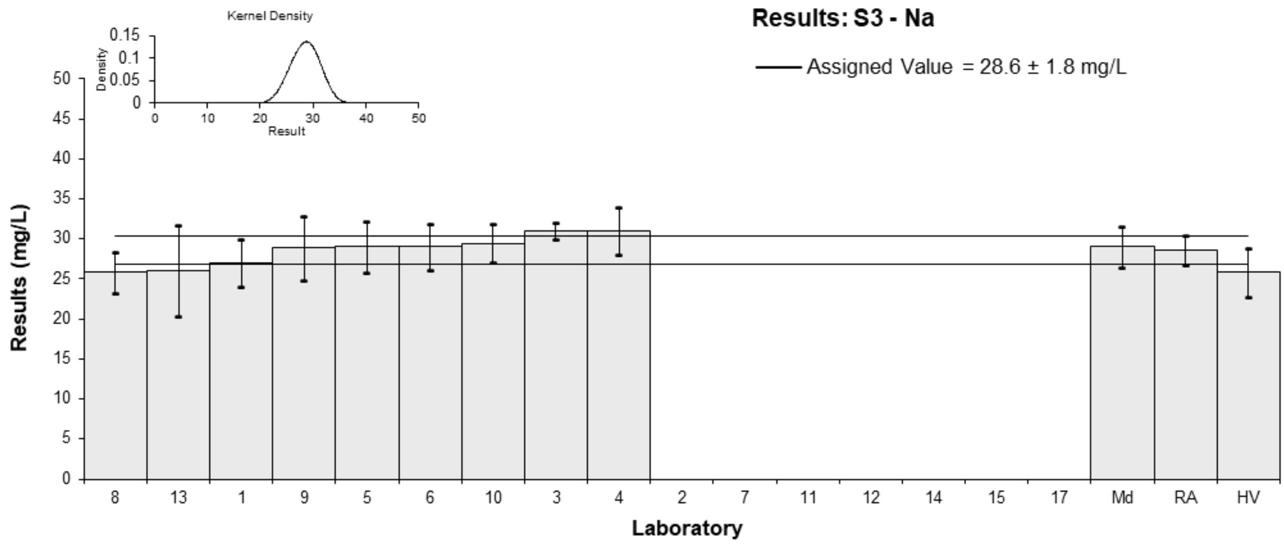
Sample No.	S3
Matrix	River Water
Analyte	Na
Unit	mg/L

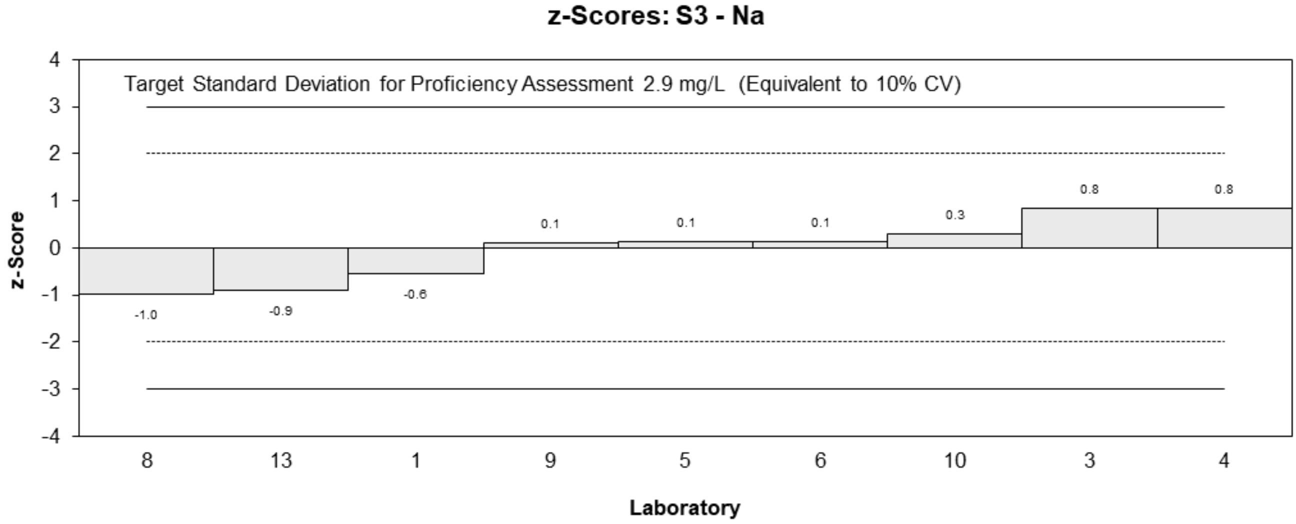
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	27	3	-0.56	-0.46
2	NT	NT		
3	31	1	0.84	1.17
4	31	2.9	0.84	0.70
5	29	3.2	0.14	0.11
6	29	2.9	0.14	0.12
7	NT	NT		
8	25.8	2.6	-0.98	-0.89
9	28.9	4.0	0.10	0.07
10	29.428	2.417	0.29	0.27
11	NR	NR		
12	NT	NT		
13	26	5.7	-0.91	-0.43
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	28.6	1.8
Spike Value	Not Spiked	
Homogeneity Value	25.8	3.1
Robust Average	28.6	1.8
Median	29.0	2.5
Mean	28.6	
N	9	
Max	31	
Min	25.8	
Robust SD	2.2	
Robust CV	7.7%	


Kernel Density
Results: S3 - Na
Assigned Value = 28.6 ± 1.8 mg/L
Results (mg/L)
Laboratory


z-Scores: S3 - Na
Target Standard Deviation for Proficiency Assessment 2.9 mg/L (Equivalent to 10% CV)
z-Score
Laboratory

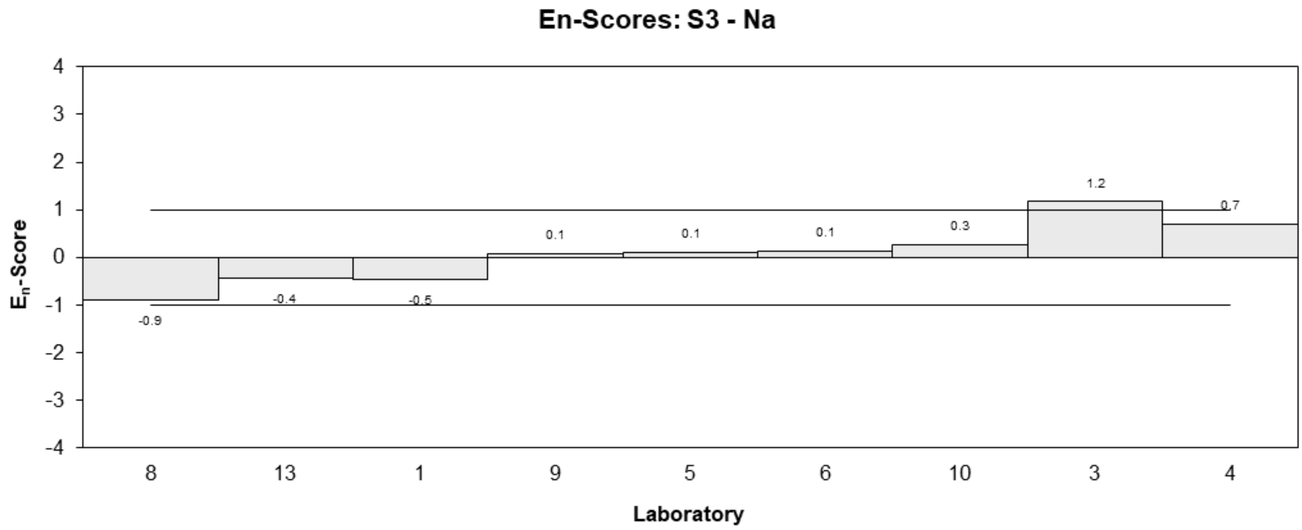

En-Scores: S3 - Na
E_n-Score
Laboratory

Figure 25

Table 29

Sample Details

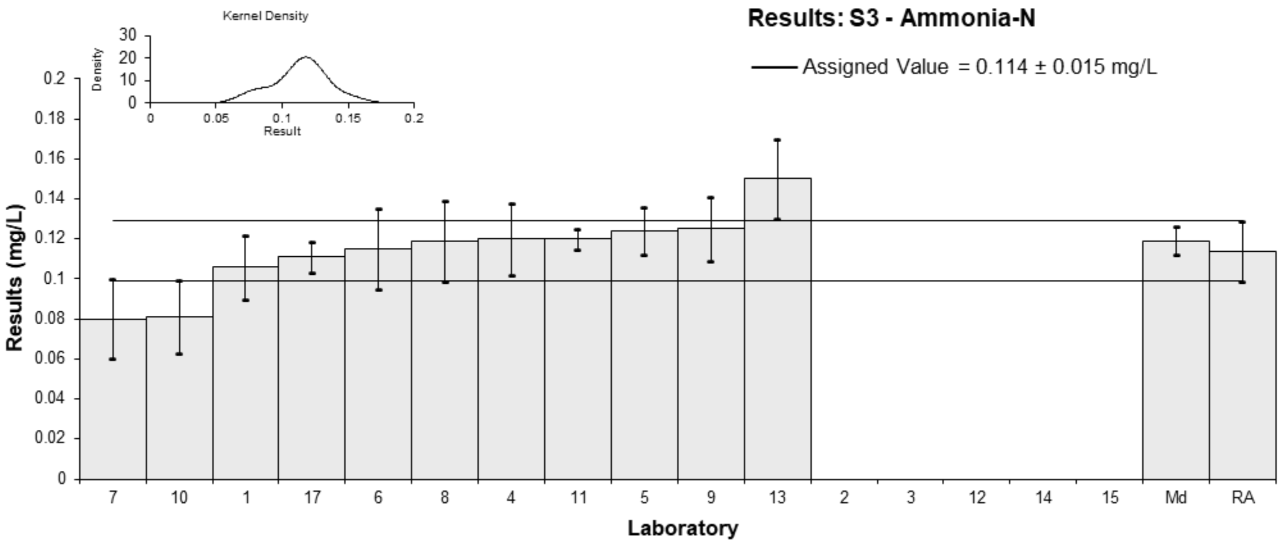
Sample No.	S3
Matrix	River Water
Analyte	Ammonia-N
Unit	mg/L

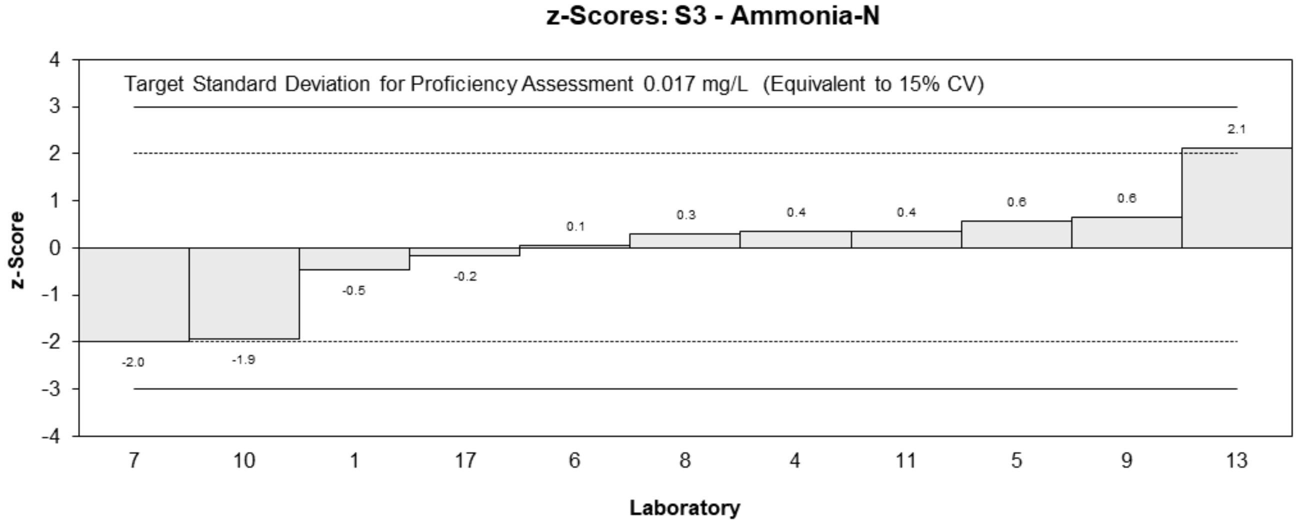
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.106	0.016	-0.47	-0.36
2	NT	NT		
3	<0.2	1.12		
4	0.120	0.018	0.35	0.26
5	0.124	0.012	0.58	0.52
6	0.115	0.02	0.06	0.04
7	0.08	0.02	-1.99	-1.36
8	0.119	0.02	0.29	0.20
9	0.125	0.016	0.64	0.50
10	0.0810	0.0185	-1.93	-1.39
11	0.12	0.005	0.35	0.38
12	NT	NT		
13	0.150	0.02	2.11	1.44
14	NT	NT		
15	NT	NT		
17	0.1110	0.0078	-0.18	-0.18

Statistics

Assigned Value	0.114	0.015
Spike Value	Not Spiked	
Robust Average	0.114	0.015
Median	0.119	0.007
Mean	0.114	
N	11	
Max	0.15	
Min	0.08	
Robust SD	0.019	
Robust CV	17%	


Results: S3 - Ammonia-N
Assigned Value = 0.114 ± 0.015 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
7 10 1 17 6 8 4 11 5 9 13 2 3 12 14 15 Md RA


z-Scores: S3 - Ammonia-N
Target Standard Deviation for Proficiency Assessment 0.017 mg/L (Equivalent to 15% CV)
z-Score
-2.0 -1.9 -0.5 -0.2 0.1 0.3 0.4 0.4 0.6 0.6 2.1
7 10 1 17 6 8 4 11 5 9 13
Laboratory

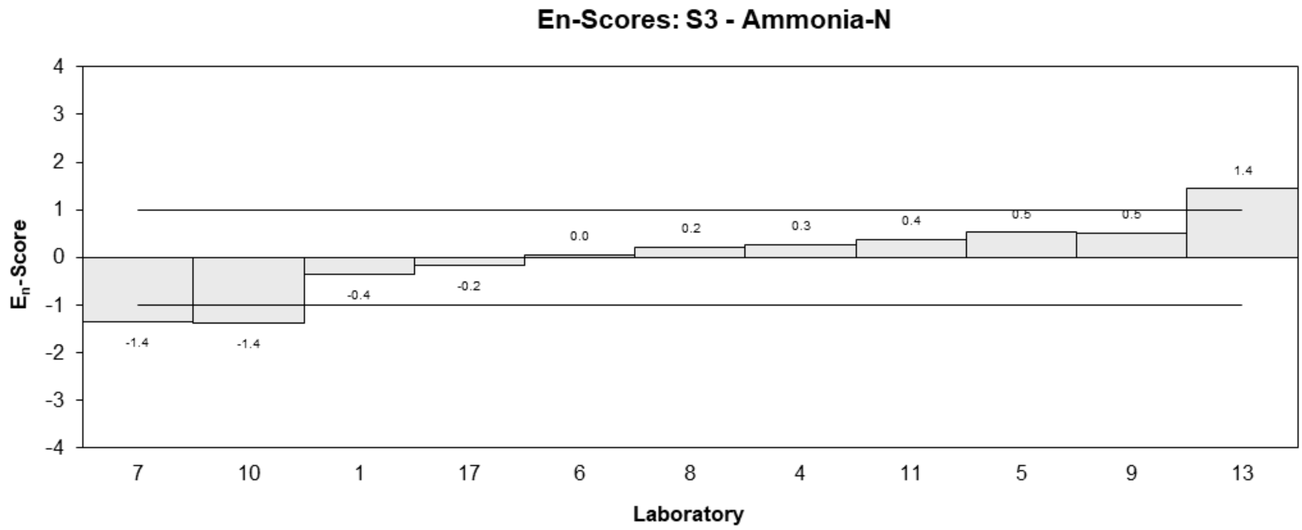

En-Scores: S3 - Ammonia-N
En-Score
-1.4 -1.4 -0.4 -0.2 0.0 0.2 0.3 0.4 0.5 0.5 1.4
7 10 1 17 6 8 4 11 5 9 13
Laboratory

Figure 26

Table 30

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	0.118	0.011
2	NT	NT
3	<0.2	0.5
4	0.179	0.02
5	NR	NR
6	NT	NT
7	NT	NT
8	<1	NR
9	NT	NT
10	NT	NT
11	NR	NR
12	NT	NT
13	0.14	0.021
14	NT	NT
15	NT	NT
17	0.107	0.045

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Homogeneity Value	0.100	0.015
Median	0.129	0.031
Mean	0.136	
N	4	
Max	0.179	
Min	0.107	

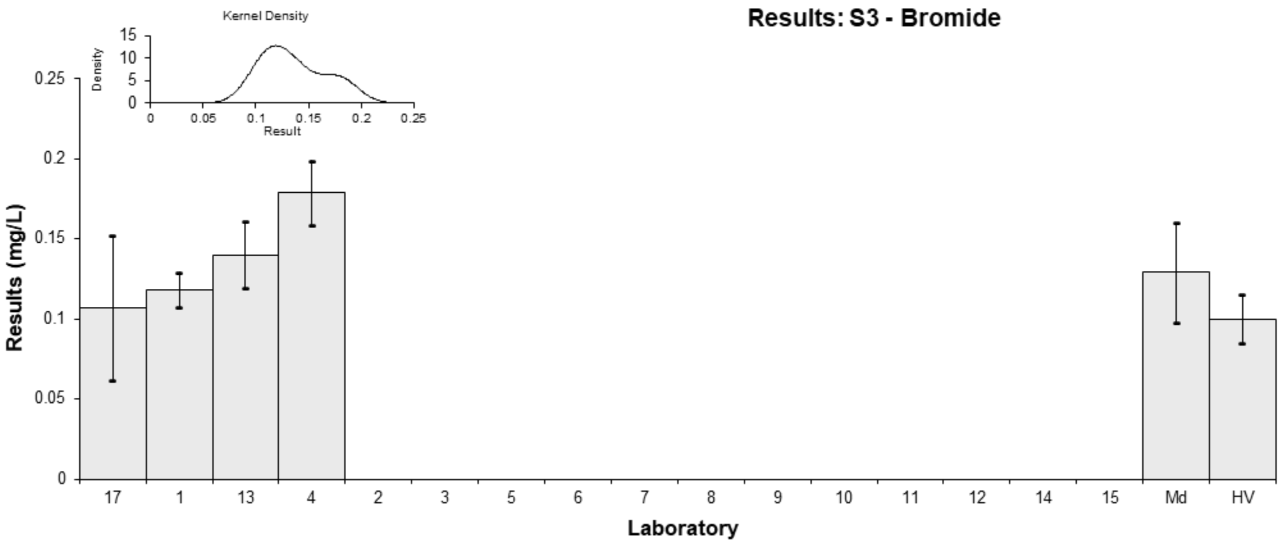

Results: S3 - Bromide
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17
1
13
4
2
3
5
6
7
8
9
10
11
12
14
15
Md
HV

Figure 27

Table 31

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	37	4	-0.70	-0.59
2	NT	NT		
3	38	0.3	-0.45	-0.69
4*	69.4	5.45	7.44	4.90
5	37	3.13	-0.70	-0.69
6	42	4.2	0.55	0.45
7	39	1.40	-0.20	-0.27
8	39.8	4.5	0.00	0.00
9	43.0	5.2	0.80	0.55
10	35.3361	3.1	-1.12	-1.10
11	NR	NR		
12	45.5	NR	1.43	2.19
13	43	6.7	0.80	0.45
14	NT	NT		
15	NT	NT		
17	38.2	2.4	-0.40	-0.45

* Outlier, see Section 4.2

Statistics

Assigned Value	39.8	2.6
Spike Value	Not Spiked	
Homogeneity Value	39.5	5.9
Robust Average	40.4	2.9
Median	39.4	2.7
Mean	42.3	
N	12	
Max	69.4	
Min	35.3361	
Robust SD	4.0	
Robust CV	10%	

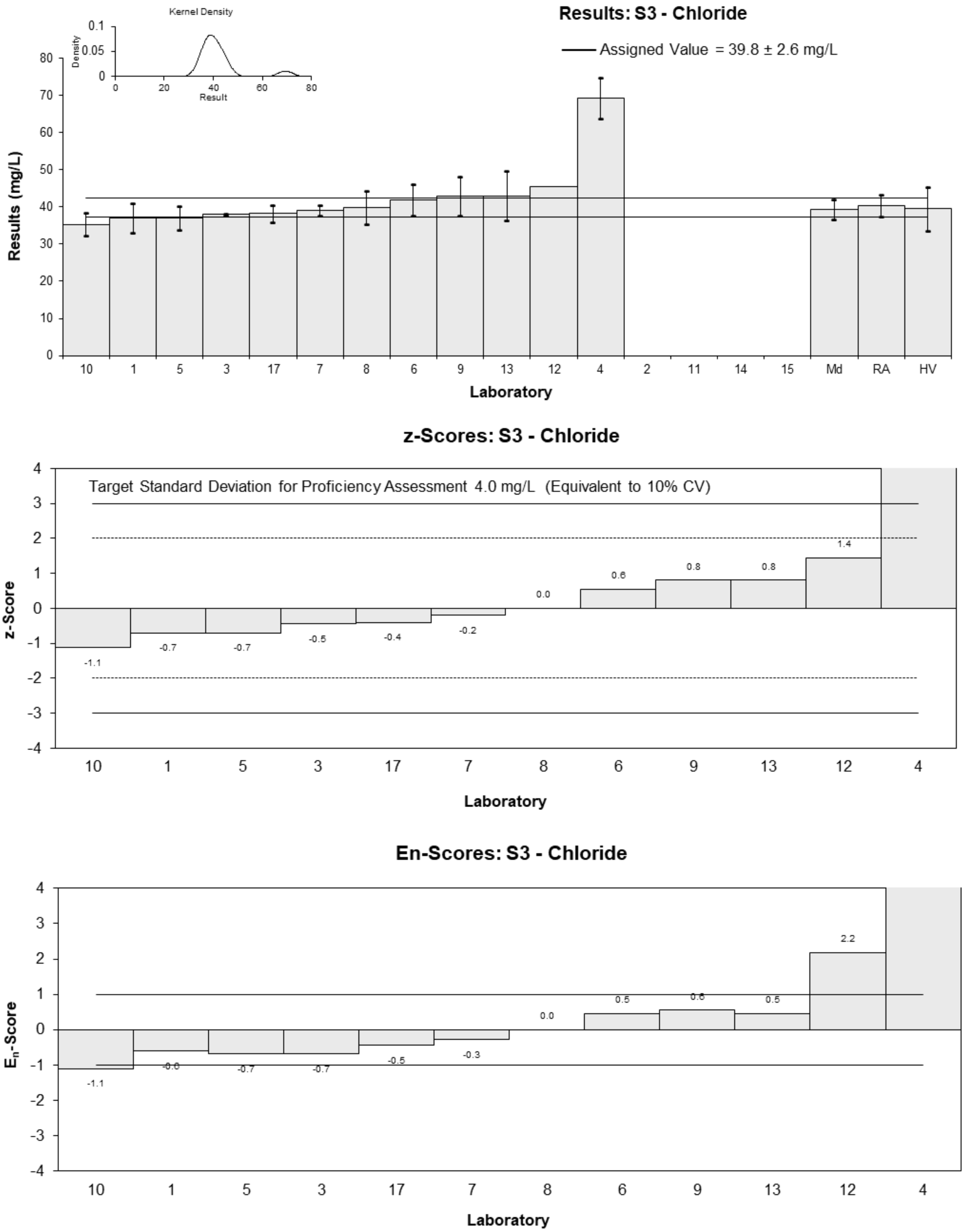

Results: S3 - Chloride
Assigned Value = 39.8 ± 2.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
10 1 5 3 17 7 8 6 9 13 12 4 2 11 14 15 Md RA HV
z-Scores: S3 - Chloride
Target Standard Deviation for Proficiency Assessment 4.0 mg/L (Equivalent to 10% CV)
z-Score
-1.1 -0.7 -0.7 -0.5 -0.4 -0.2 0.0 0.6 0.8 0.8 1.4
Laboratory
10 1 5 3 17 7 8 6 9 13 12 4
En-Scores: S3 - Chloride
E_n-Score
-1.1 -0.6 -0.7 -0.7 -0.5 -0.3 0.0 0.5 0.6 0.5 2.2
Laboratory
10 1 5 3 17 7 8 6 9 13 12 4

Figure 28

Table 32

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	5	0.4	-1.15	-1.04
2	NT	NT		
3	NT	NT		
4	6	1.1	0.62	0.29
5	6	0.69	0.62	0.42
6	5.4	1.1	-0.44	-0.21
7	NT	NT		
8	6.11	0.6	0.81	0.60
9	5.44	0.76	-0.37	-0.23
10	6.49	0.766	1.49	0.93
11	NR	NR		
12	NT	NT		
13	5.2	0.8	-0.80	-0.48
14	NT	NT		
15	NT	NT		
17	5.2	1.1	-0.80	-0.37

Statistics

Assigned Value	5.65	0.48
Spike Value	Not Spiked	
Homogeneity Value	5.43	0.82
Robust Average	5.65	0.48
Median	5.44	0.54
Mean	5.65	
N	9	
Max	6.49	
Min	5	
Robust SD	0.58	
Robust CV	10%	

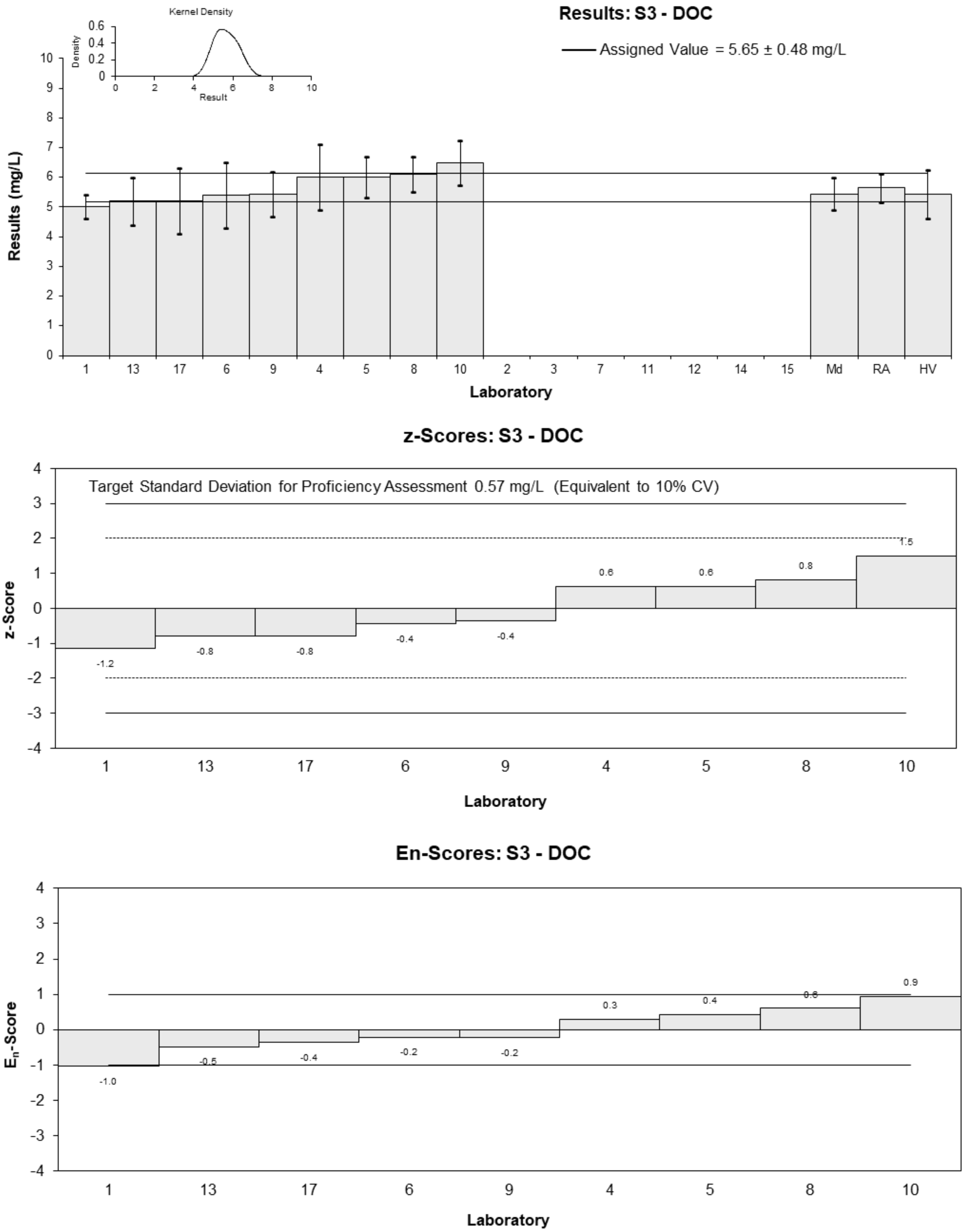

Results: S3 - DOC
Assigned Value = 5.65 ± 0.48 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 13 17 6 9 4 5 8 10 2 3 7 11 12 14 15 Md RA HV
z-Scores: S3 - DOC
Target Standard Deviation for Proficiency Assessment 0.57 mg/L (Equivalent to 10% CV)
z-Score
-1.2 -0.8 -0.8 -0.4 -0.4 0.6 0.6 0.8 1.5
Laboratory
1 13 17 6 9 4 5 8 10
En-Scores: S3 - DOC
E_n-Score
-1.0 -0.5 -0.4 -0.2 -0.2 0.3 0.4 0.6 0.9
Laboratory
1 13 17 6 9 4 5 8 10

Figure 29

Table 33

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.2	0.04	0.70	0.42
2	NT	NT		
3	0.1	0.9	-2.98	-0.09
4	0.153	0.02	-1.03	-0.99
5	0.2	0.028	0.70	0.55
6	0.18	0.02	-0.04	-0.04
7	0.2	0.01	0.70	0.85
8	0.17	0.03	-0.41	-0.31
9	0.175	0.039	-0.22	-0.14
10	0.165	0.029	-0.59	-0.45
11	NR	NR		
12	NT	NT		
13	0.22	0.03	1.44	1.08
14	NT	NT		
15	NT	NT		
17	0.188	0.046	0.26	0.14

Statistics

Assigned Value	0.181	0.020
Spike Value	Not Spiked	
Homogeneity Value	0.200	0.030
Robust Average	0.181	0.020
Median	0.180	0.022
Mean	0.177	
N	11	
Max	0.22	
Min	0.1	
Robust SD	0.026	
Robust CV	15%	

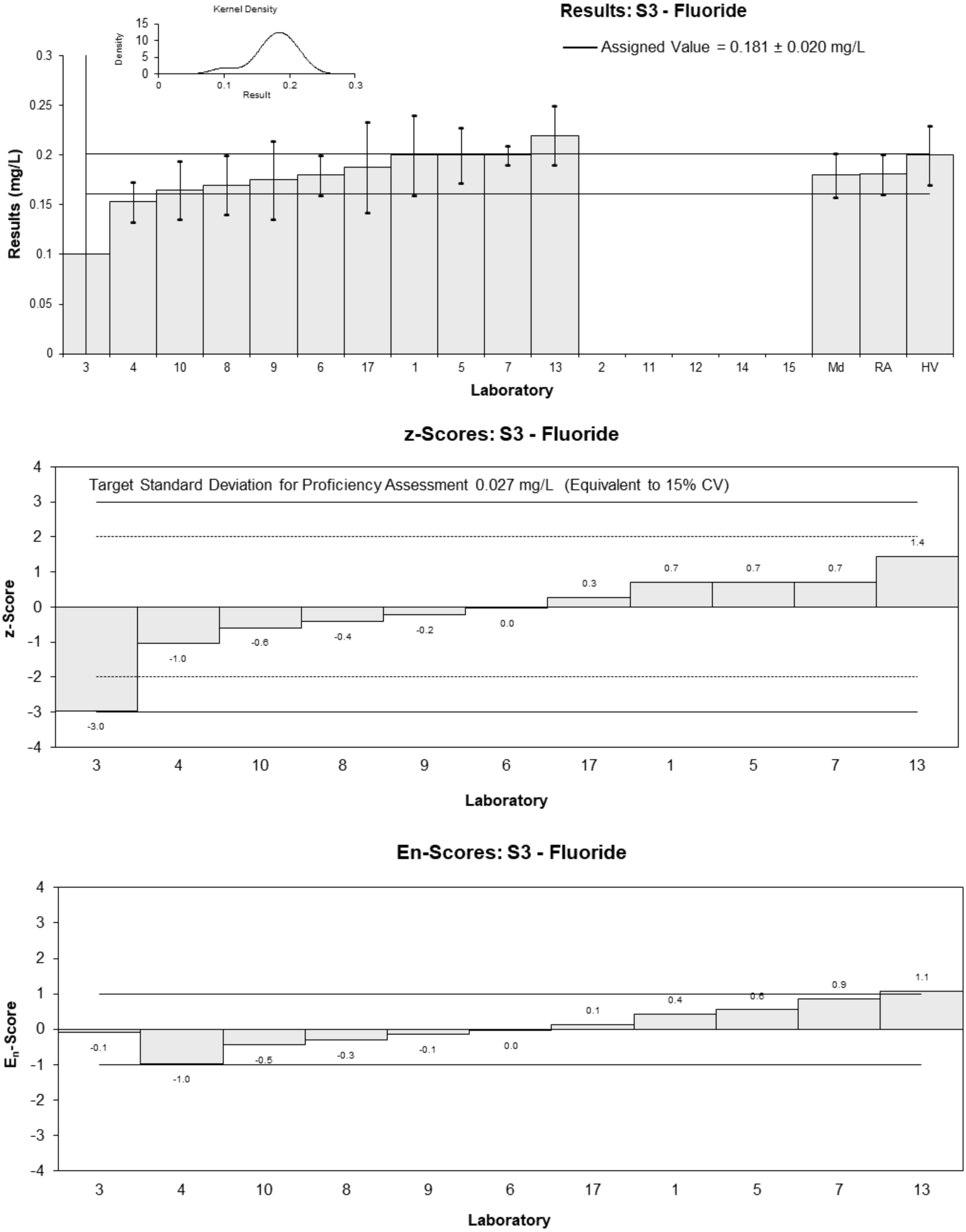

Results: S3 - Fluoride
Assigned Value = 0.181 ± 0.020 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3 4 10 8 9 6 17 1 5 7 13 2 11 12 14 15 Md RA HV
z-Scores: S3 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.027 mg/L (Equivalent to 15% CV)
z-Score
-3.0 -1.0 -0.6 -0.4 -0.2 0.0 0.3 0.7 0.7 0.7 1.4
Laboratory
3 4 10 8 9 6 17 1 5 7 13
En-Scores: S3 - Fluoride
E_n-Score
-0.1 -1.0 -0.5 -0.3 -0.1 0.0 0.1 0.4 0.6 0.9 1.1
Laboratory
3 4 10 8 9 6 17 1 5 7 13

Figure 30

Table 34

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.65	0.30	0.73	0.81
2	NT	NT		
3**	2368	135	6,598.63	17.52
4	2.34	NR	-0.14	-0.45
5	2.42	0.21	0.08	0.13
6	2.2	0.22	-0.53	-0.77
7	2.30	0.17	-0.25	-0.44
8	2.44	0.3	0.14	0.16
9	2.48	0.50	0.25	0.18
10	2.48	0.23	0.25	0.35
11	2.41	0.007	0.06	0.18
12	NT	NT		
13	2.120	0.32	-0.75	-0.80
14	NT	NT		
15	NT	NT		
17	2.46	0.32	0.20	0.21

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.39	0.11
Spike Value	Not Spiked	
Homogeneity Value	2.30	0.35
Robust Average	2.39	0.11
Median	2.42	0.07
Mean	2.39	
N	11	
Max	2.65	
Min	2.12	
Robust SD	0.15	
Robust CV	6.2%	

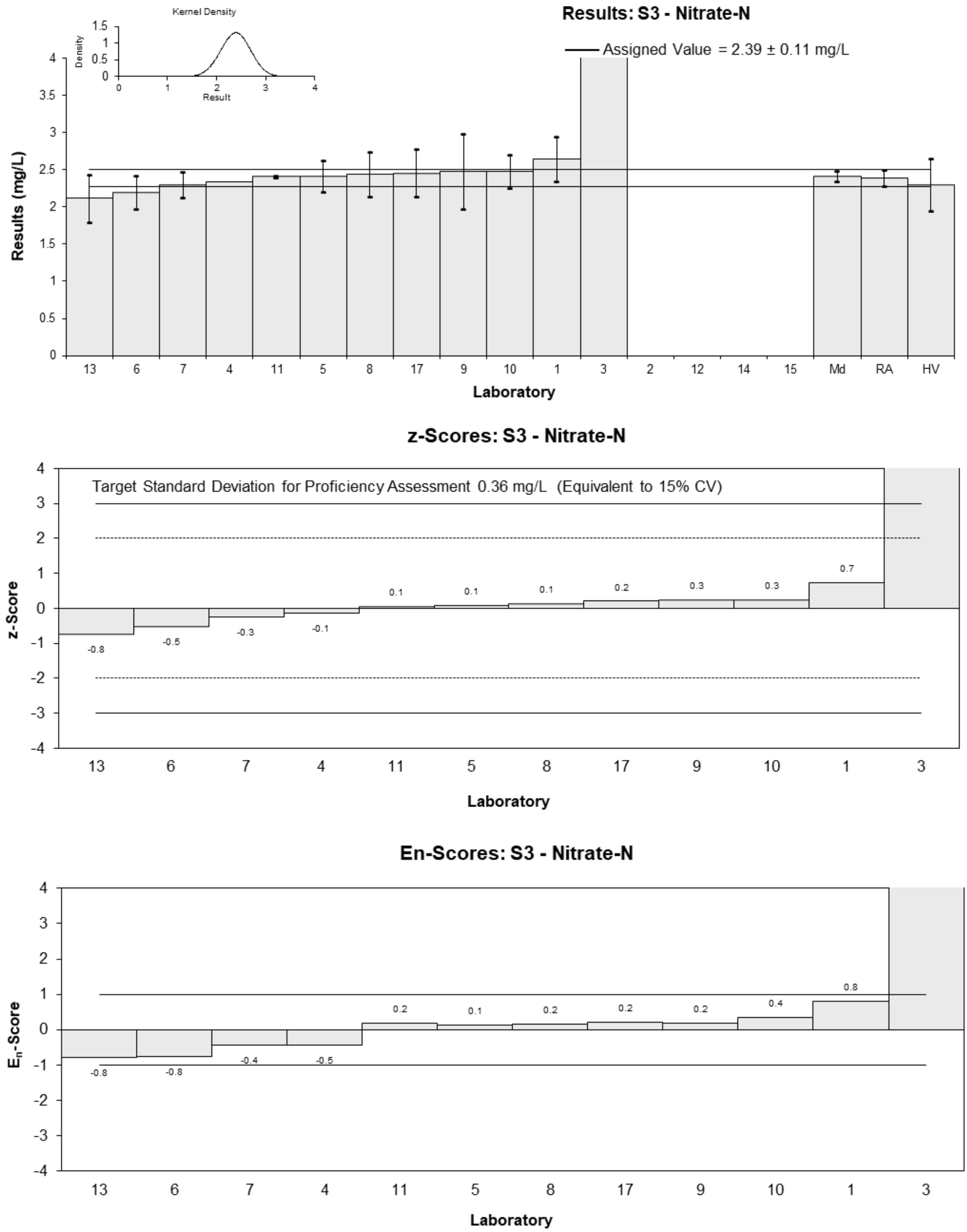

Results: S3 - Nitrate-N
Assigned Value = 2.39 ± 0.11 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
13 6 7 4 11 5 8 17 9 10 1 3 2 12 14 15 Md RA HV
z-Scores: S3 - Nitrate-N
Target Standard Deviation for Proficiency Assessment 0.36 mg/L (Equivalent to 15% CV)
z-Score
-0.8 -0.5 -0.3 -0.1 0.1 0.1 0.1 0.2 0.3 0.3 0.7
13 6 7 4 11 5 8 17 9 10 1 3
Laboratory
En-Scores: S3 - Nitrate-N
En-Score
-0.8 -0.8 -0.4 -0.5 0.2 0.1 0.2 0.2 0.2 0.4 0.8
13 6 7 4 11 5 8 17 9 10 1 3
Laboratory

Figure 31

Table 35

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.180	0.012	-0.35	-0.69
2	NT	NT		
3	NT	NT		
4	0.186	NR	-0.14	-0.50
5	0.202	0.02	0.42	0.56
6	0.20	0.01	0.35	0.78
7	0.18	0.01	-0.35	-0.78
8	0.202	0.03	0.42	0.39
9	0.197	0.026	0.25	0.26
10	0.19395	0.0215	0.14	0.17
11	0.19	0.007	0.00	0.00
12	NT	NT		
13	0.180	0.03	-0.35	-0.32
14	NT	NT		
15	NT	NT		
17	0.176	0.025	-0.49	-0.53

Statistics

Assigned Value	0.190	0.008
Spike Value	Not Spiked	
Homogeneity Value	0.190	0.029
Robust Average	0.190	0.008
Median	0.190	0.011
Mean	0.190	
N	11	
Max	0.202	
Min	0.176	
Robust SD	0.011	
Robust CV	5.9%	

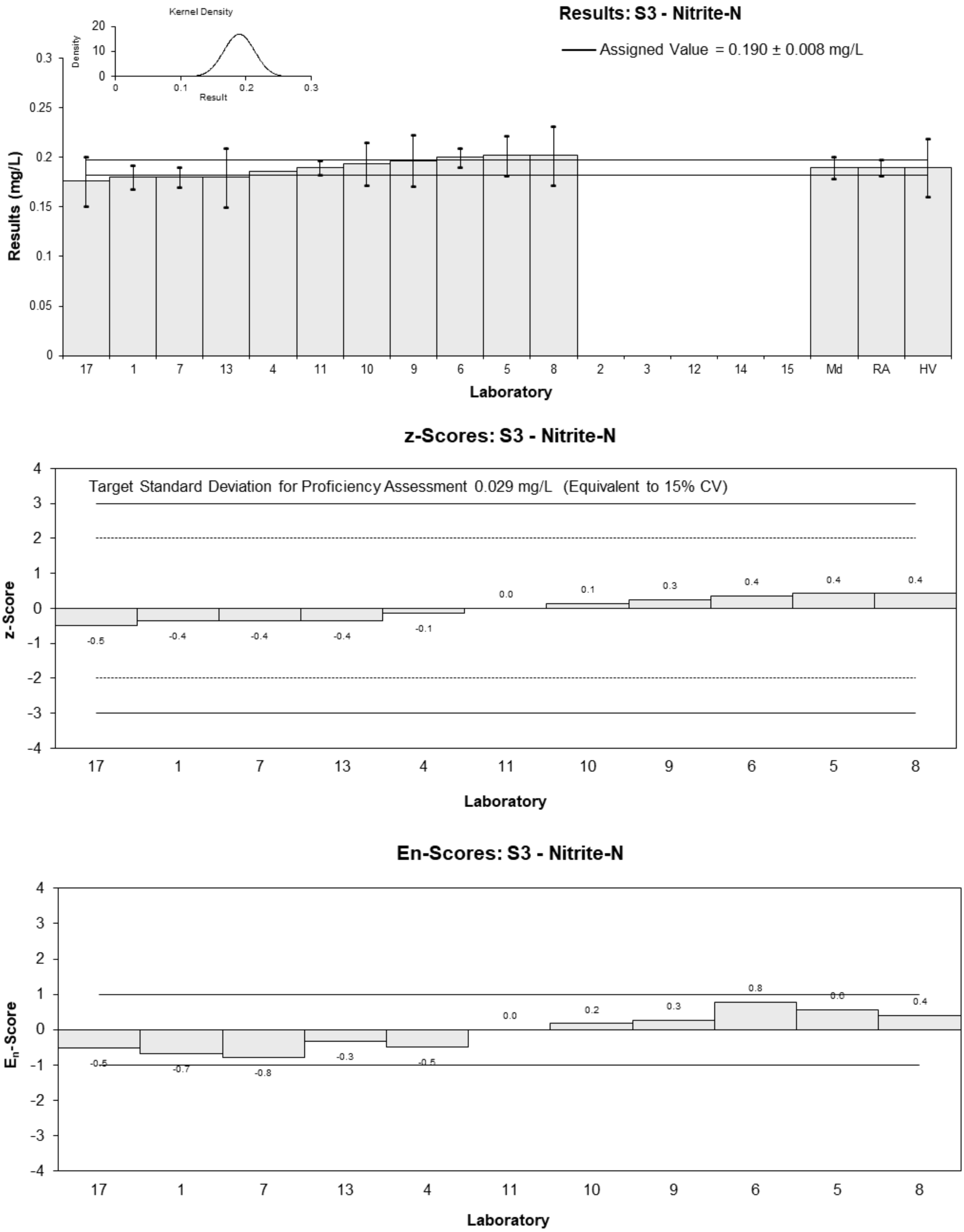

Results: S3 - Nitrite-N
Assigned Value = 0.190 ± 0.008 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 1 7 13 4 11 10 9 6 5 8 2 3 12 14 15 Md RA HV
z-Scores: S3 - Nitrite-N
Target Standard Deviation for Proficiency Assessment 0.029 mg/L (Equivalent to 15% CV)
z-Score
-0.5 -0.4 -0.4 -0.4 -0.1 0.0 0.1 0.3 0.4 0.4 0.4
17 1 7 13 4 11 10 9 6 5 8
Laboratory
En-Scores: S3 - Nitrite-N
E_n-Score
-0.5 -0.7 -0.8 -0.3 -0.5 0.0 0.2 0.3 0.8 0.4
17 1 7 13 4 11 10 9 6 5 8
Laboratory

Figure 32

Table 36

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.109	0.014	-0.56	-0.62
2	NT	NT		
3	NT	NT		
4	0.107	0.009	-0.67	-1.00
5	0.096	0.007	-1.29	-2.16
6	0.120	0.024	0.06	0.04
7	0.13	0.01	0.62	0.86
8	0.126	0.02	0.39	0.32
9	0.124	0.024	0.28	0.20
10	0.122	0.013	0.17	0.20
11	0.12	0.005	0.06	0.11
12	NT	NT		
13	0.130	0.0195	0.62	0.52
14	NT	NT		
15	NT	NT		
17	0.1164	0.0066	-0.15	-0.25

Statistics

Assigned Value	0.119	0.008
Spike Value	Not Spiked	
Robust Average	0.119	0.008
Median	0.120	0.007
Mean	0.118	
N	11	
Max	0.13	
Min	0.096	
Robust SD	0.010	
Robust CV	8.6%	

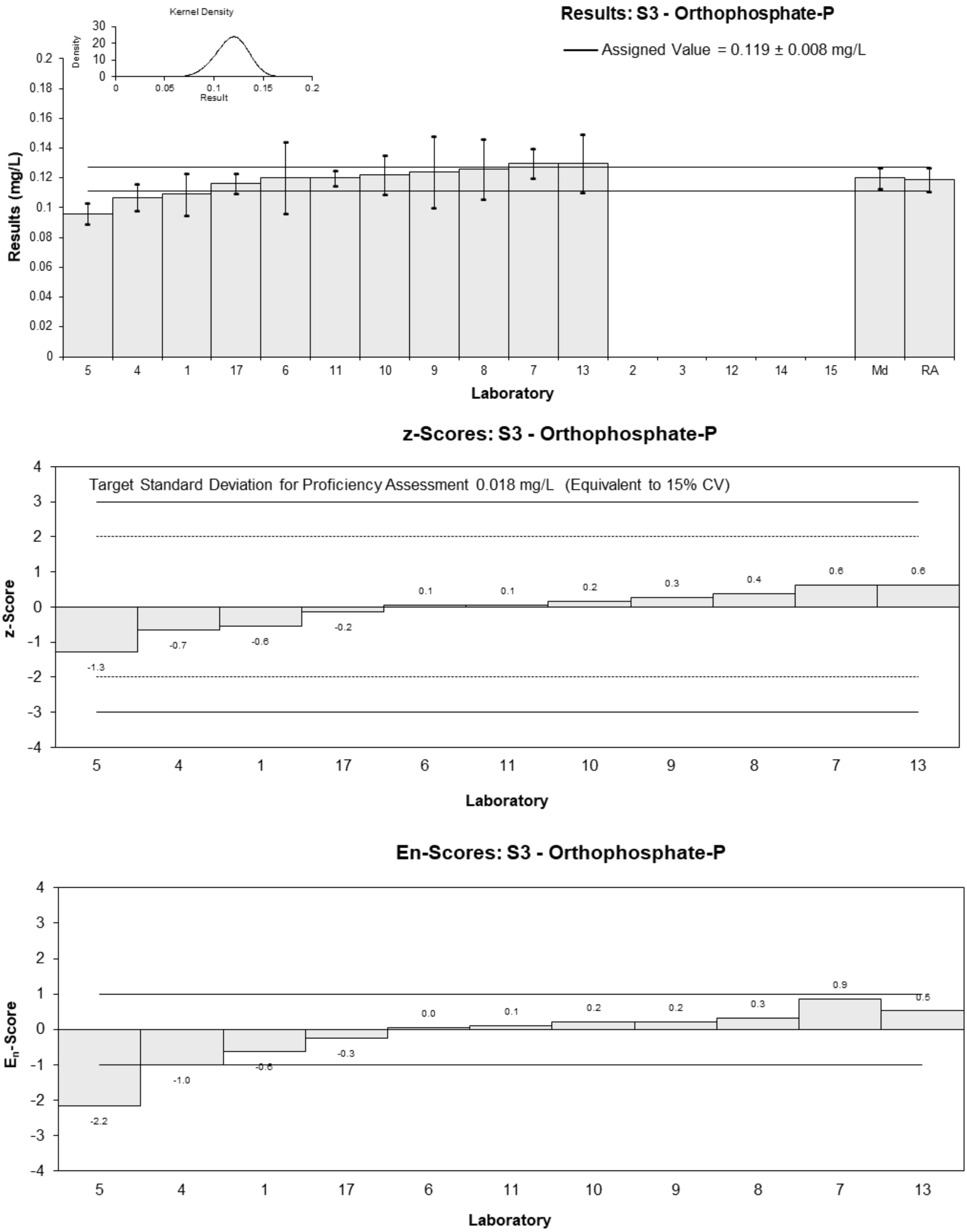

Kernel Density
Density
Result
Results: S3 - Orthophosphate-P
Assigned Value = 0.119 ± 0.008 mg/L
Results (mg/L)
5 4 1 17 6 11 10 9 8 7 13 2 3 12 14 15 Md RA
Laboratory
z-Scores: S3 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.018 mg/L (Equivalent to 15% CV)
z-Score
-1.3 -0.7 -0.6 -0.2 0.1 0.1 0.2 0.3 0.4 0.6 0.6
5 4 1 17 6 11 10 9 8 7 13
Laboratory
En-Scores: S3 - Orthophosphate-P
E_n-Score
-2.2 -1.0 -0.6 -0.3 0.0 0.1 0.2 0.2 0.3 0.9 0.5
5 4 1 17 6 11 10 9 8 7 13
Laboratory

Figure 33

Table 37

Sample Details

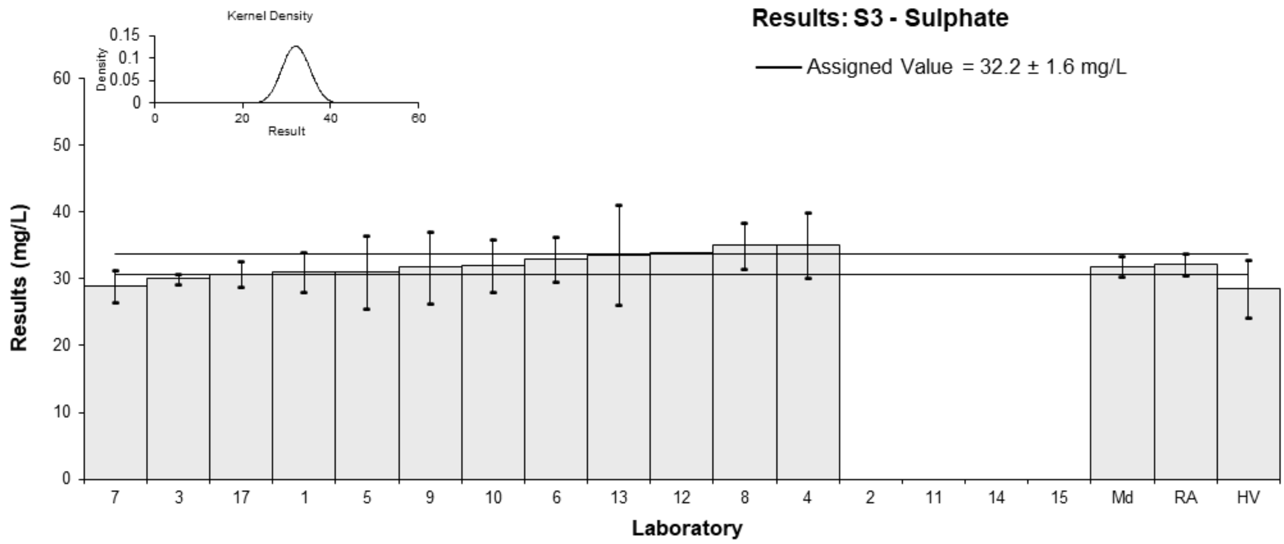
Sample No.	S3
Matrix	River Water
Analyte	Sulphate
Unit	mg/L

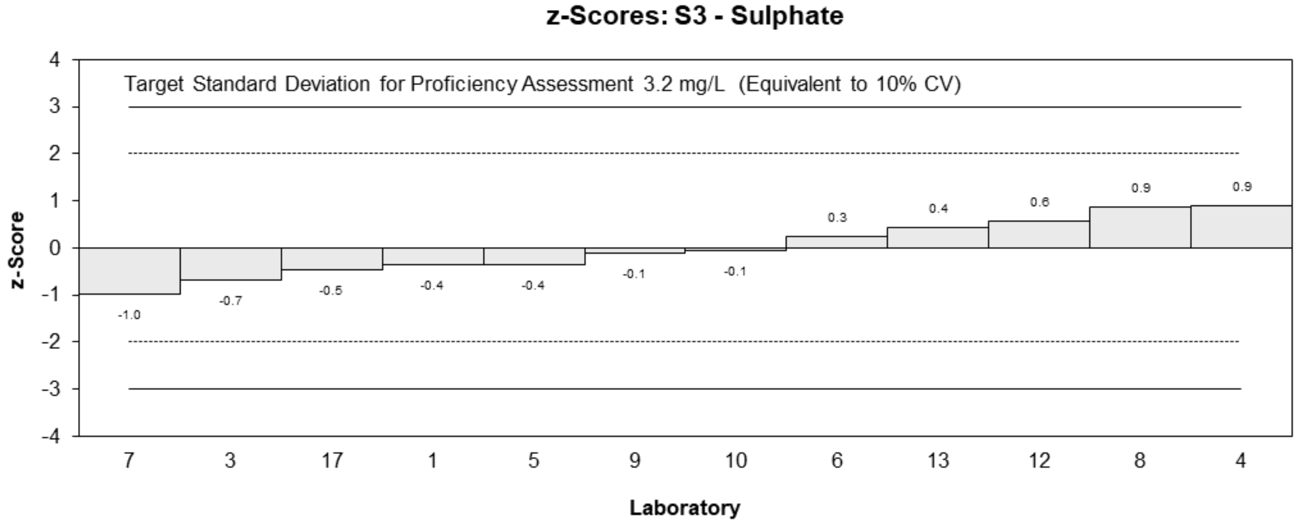
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	31	3	-0.37	-0.35
2	NT	NT		
3	30	0.7	-0.68	-1.26
4	35.1	4.83	0.90	0.57
5	31	5.48	-0.37	-0.21
6	33	3.3	0.25	0.22
7	29	2.41	-0.99	-1.11
8	35.0	3.5	0.87	0.73
9	31.8	5.4	-0.12	-0.07
10	31.994	4.0	-0.06	-0.05
11	NR	NR		
12	34	NR	0.56	1.12
13	33.6	7.5	0.43	0.18
14	NT	NT		
15	NT	NT		
17	30.7	1.9	-0.47	-0.60

Statistics

Assigned Value	32.2	1.6
Spike Value	Not Spiked	
Homogeneity Value	28.5	4.3
Robust Average	32.2	1.6
Median	31.9	1.6
Mean	32.2	
N	12	
Max	35.1	
Min	29	
Robust SD	2.2	
Robust CV	6.9%	


Results: S3 - Sulphate
Assigned Value = 32.2 ± 1.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
7 3 17 1 5 9 10 6 13 12 8 4 2 11 14 15 Md RA HV


z-Scores: S3 - Sulphate
Target Standard Deviation for Proficiency Assessment 3.2 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.0 -0.7 -0.5 -0.4 -0.4 -0.1 -0.1 0.3 0.4 0.6 0.9 0.9
7 3 17 1 5 9 10 6 13 12 8 4

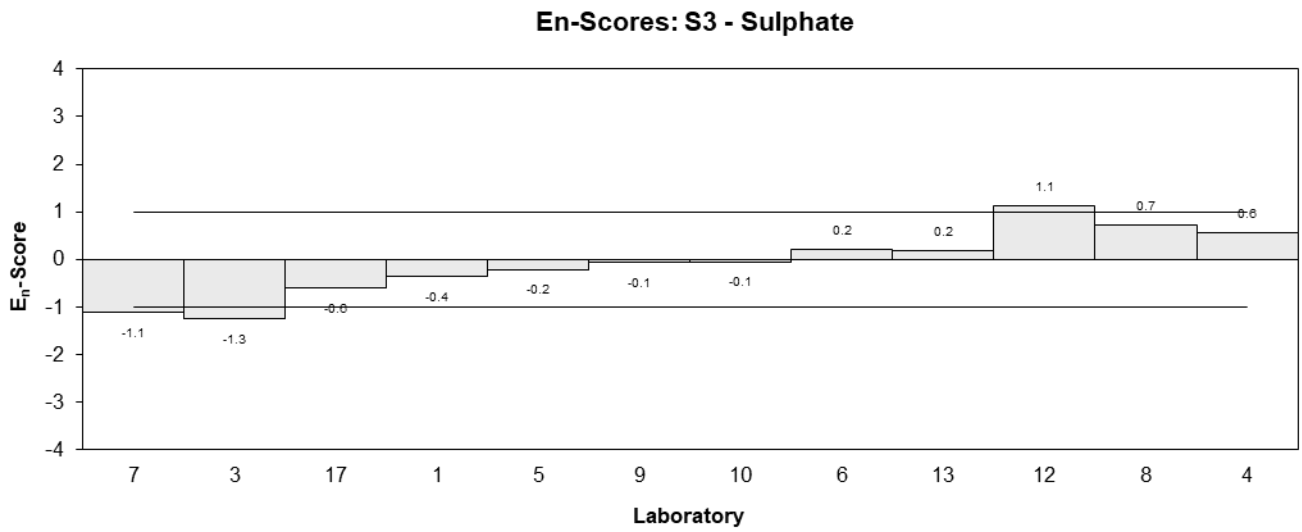

En-Scores: S3 - Sulphate
E_n-Score
Laboratory
-1.1 -1.3 -0.6 -0.4 -0.2 -0.1 -0.1 0.2 0.2 1.1 0.7 0.6
7 3 17 1 5 9 10 6 13 12 8 4

Figure 34

Table 38

Sample Details

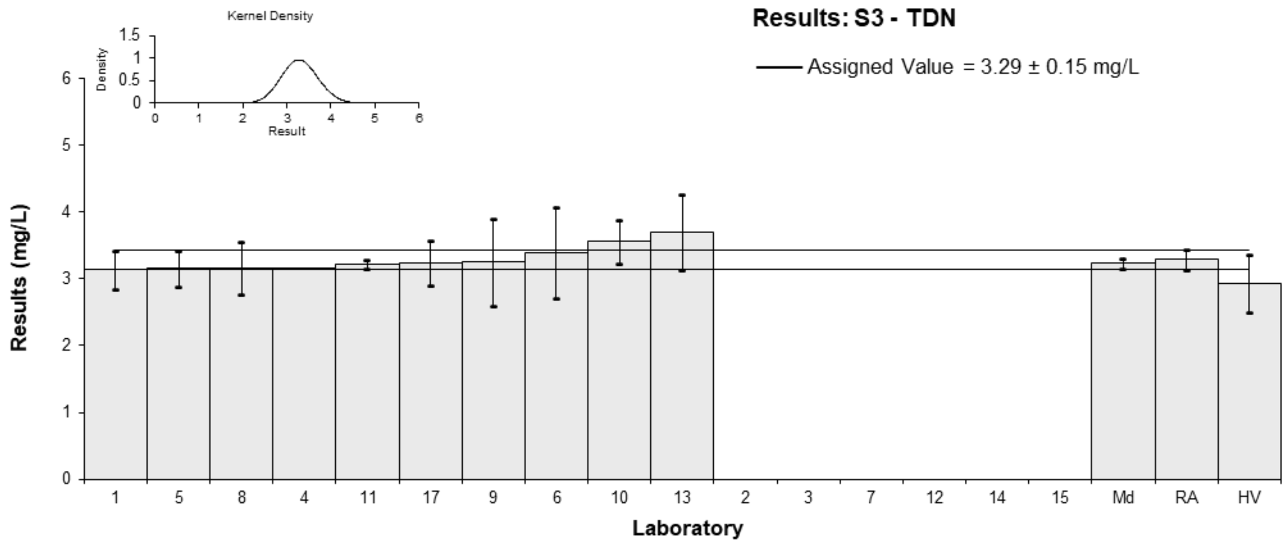
Sample No.	S3
Matrix	River Water
Analyte	TDN
Unit	mg/L

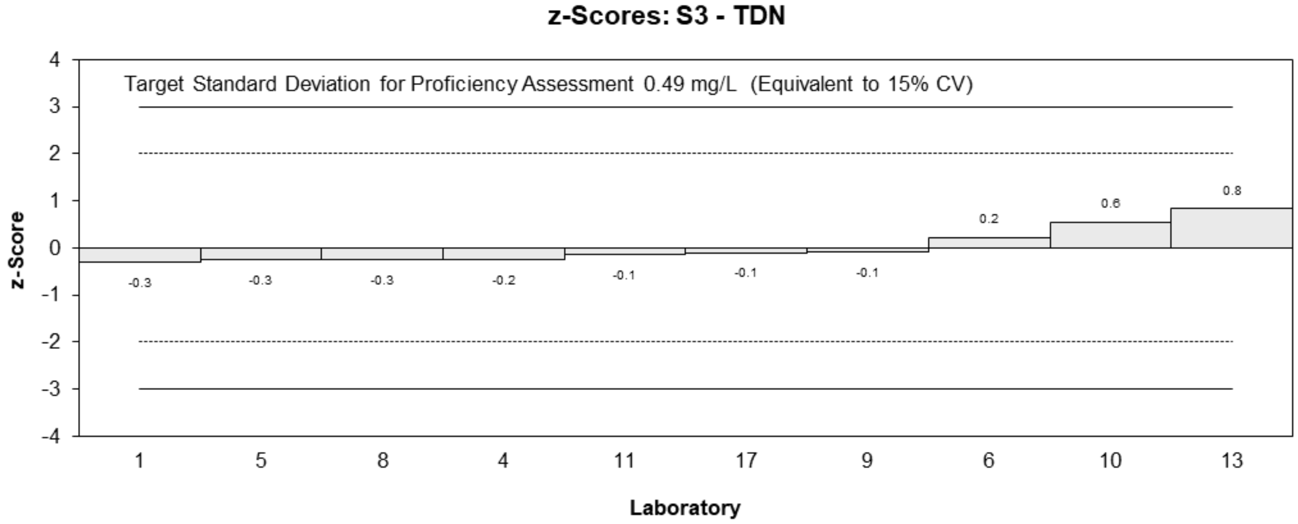
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.14	0.29	-0.30	-0.46
2	NT	NT		
3	NT	NT		
4	3.17	NR	-0.24	-0.80
5	3.16	0.27	-0.26	-0.42
6	3.4	0.68	0.22	0.16
7	NT	NT		
8	3.16	0.4	-0.26	-0.30
9	3.25	0.65	-0.08	-0.06
10	3.563	0.3254	0.55	0.76
11	3.22	0.06	-0.14	-0.43
12	NT	NT		
13	3.7	0.56	0.83	0.71
14	NT	NT		
15	NT	NT		
17	3.24	0.33	-0.10	-0.14

Statistics

Assigned Value	3.29	0.15
Spike Value	Not Spiked	
Homogeneity Value	2.93	0.44
Robust Average	3.29	0.15
Median	3.23	0.08
Mean	3.30	
N	10	
Max	3.7	
Min	3.14	
Robust SD	0.19	
Robust CV	5.7%	


Results: S3 - TDN
Assigned Value = 3.29 ± 0.15 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 5 8 4 11 17 9 6 10 13 2 3 7 12 14 15 Md RA HV


z-Scores: S3 - TDN
Target Standard Deviation for Proficiency Assessment 0.49 mg/L (Equivalent to 15% CV)
z-Score
-0.3 -0.3 -0.3 -0.2 -0.1 -0.1 -0.1 0.2 0.6 0.8
Laboratory
1 5 8 4 11 17 9 6 10 13

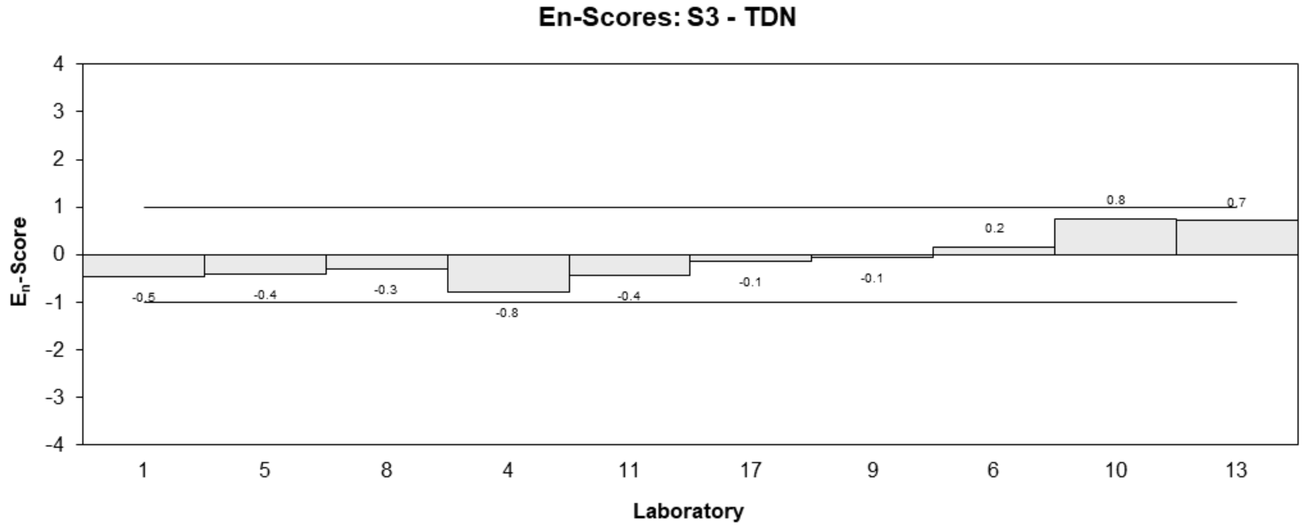

En-Scores: S3 - TDN
En-Score
-0.5 -0.4 -0.3 -0.8 -0.4 -0.1 -0.1 0.2 0.8 0.7
Laboratory
1 5 8 4 11 17 9 6 10 13

Figure 35

Table 39

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.118	0.016	-0.57	-0.61
2	NT	NT		
3	NT	NT		
4	0.120	NR	-0.47	-1.13
5	0.117	0.007	-0.62	-1.13
6	0.12	0.02	-0.47	-0.42
7	0.13	0.02	0.05	0.05
8	0.134	0.02	0.26	0.23
9	0.133	0.020	0.21	0.19
10	0.1394	0.0266	0.54	0.37
11	0.14	0.005	0.57	1.17
12	NT	NT		
13	0.140	0.02	0.57	0.51
14	NT	NT		
15	NT	NT		
17	0.128	0.016	-0.05	-0.06

Statistics

Assigned Value	0.129	0.008
Spike Value	0.132	0.020
Homogeneity Value	0.148	0.022
Robust Average	0.129	0.008
Median	0.130	0.011
Mean	0.129	
N	11	
Max	0.14	
Min	0.117	
Robust SD	0.010	
Robust CV	8%	

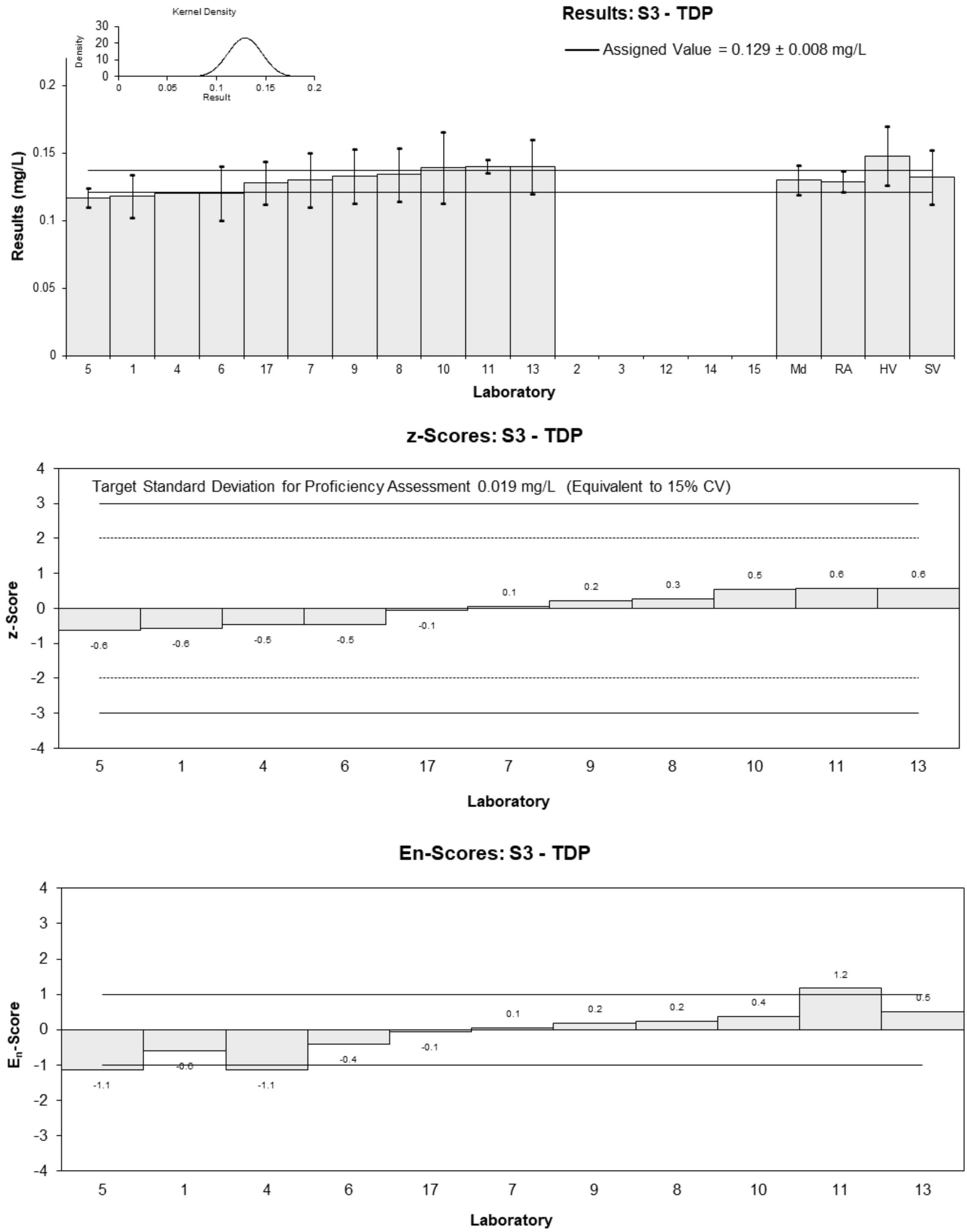

Kernel Density
Density
Result
Results: S3 - TDP
Assigned Value = 0.129 ± 0.008 mg/L
Results (mg/L)
5 1 4 6 17 7 9 8 10 11 13 2 3 12 14 15 Md RA HV SV
Laboratory
z-Scores: S3 - TDP
Target Standard Deviation for Proficiency Assessment 0.019 mg/L (Equivalent to 15% CV)
z-Score
-0.6 -0.6 -0.5 -0.5 -0.1 0.1 0.2 0.3 0.5 0.6 0.6
5 1 4 6 17 7 9 8 10 11 13
Laboratory
En-Scores: S3 - TDP
E_n-Score
-1.1 -0.6 -1.1 -0.4 -0.1 0.1 0.2 0.2 0.4 1.2 0.5
5 1 4 6 17 7 9 8 10 11 13
Laboratory

Figure 36

Table 40

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty
1	0.67	0.06
2	NT	NT
3	NT	NT
4	0.87	NR
5	0.8	0.15
6	NT	NT
7	0.8	0.08
8	0.45	0.05
9	NT	NT
10	0.9364	0.2318
11	NT	NT
12	NT	NT
13*	1.3	0.2
14	NT	NT
15	NT	NT
17	NT	NT

* Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	0.82	0.26
Median	0.80	0.18
Mean	0.83	
N	7	
Max	1.3	
Min	0.45	
Robust SD	0.27	
Robust CV	33%	

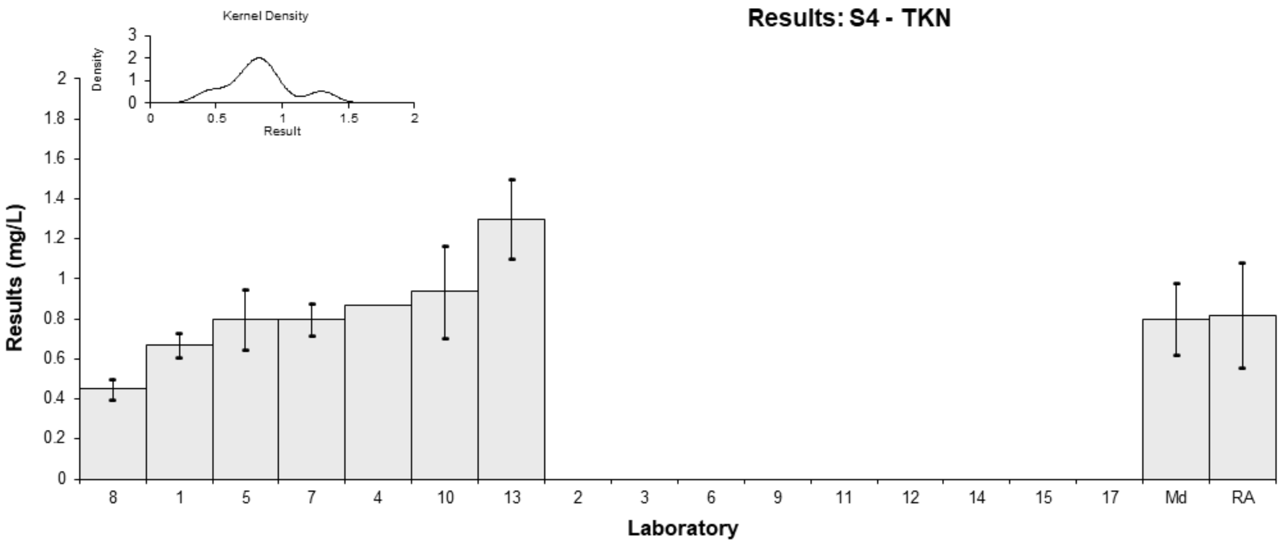

Results: S4 - TKN
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8
1
5
7
4
10
13
2
3
6
9
11
12
14
15
17
Md
RA

Figure 37

Table 41

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.23	0.30	-0.14	-0.18
2	NT	NT		
3	2.9	1.2	-0.81	-0.33
4	3.590	0.49	0.59	0.53
5	3.3	0.19	0.00	0.00
6	NT	NT		
7	3.1	0.31	-0.40	-0.50
8	3.07	0.3	-0.46	-0.59
9	3.26	0.65	-0.08	-0.06
10	3.5346	0.7161	0.47	0.31
11	NT	NT		
12	NT	NT		
13	3.7	0.5	0.81	0.72
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	3.30	0.25
Spike Value	Not Spiked	
Homogeneity Value	4.05	0.61
Robust Average	3.30	0.25
Median	3.26	0.23
Mean	3.30	
N	9	
Max	3.7	
Min	2.9	
Robust SD	0.30	
Robust CV	9.1%	

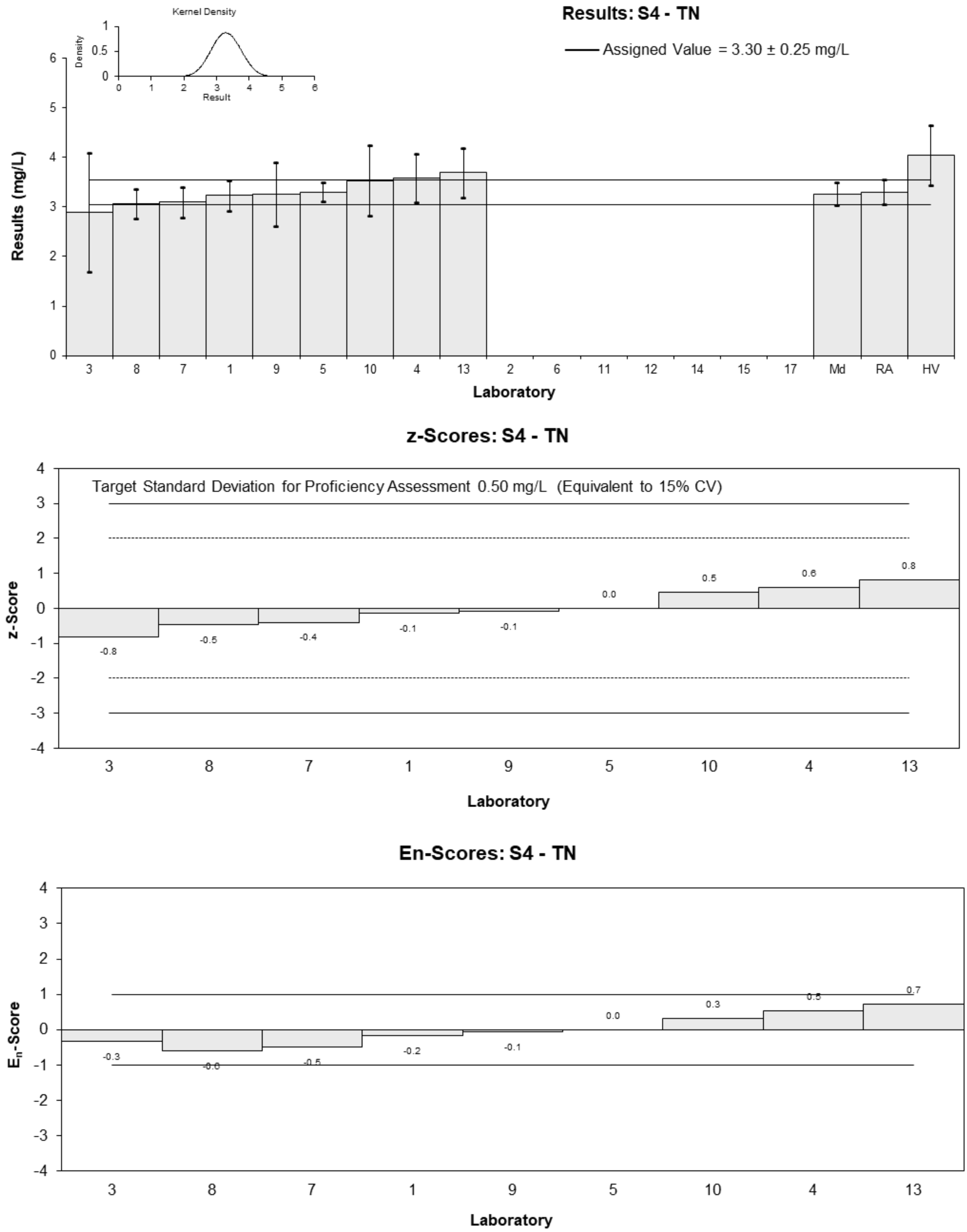

Results: S4 - TN
Assigned Value = 3.30 ± 0.25 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3 8 7 1 9 5 10 4 13 2 6 11 12 14 15 17 Md RA HV
z-Scores: S4 - TN
Target Standard Deviation for Proficiency Assessment 0.50 mg/L (Equivalent to 15% CV)
z-Score
-0.8 -0.5 -0.4 -0.1 -0.1 0.0 0.5 0.6 0.8
3 8 7 1 9 5 10 4 13
Laboratory
En-Scores: S4 - TN
En-Score
-0.3 -0.2 -0.1 0.0 0.3 0.7
3 8 7 1 9 5 10 4 13
Laboratory

Figure 38

Table 42

Sample Details

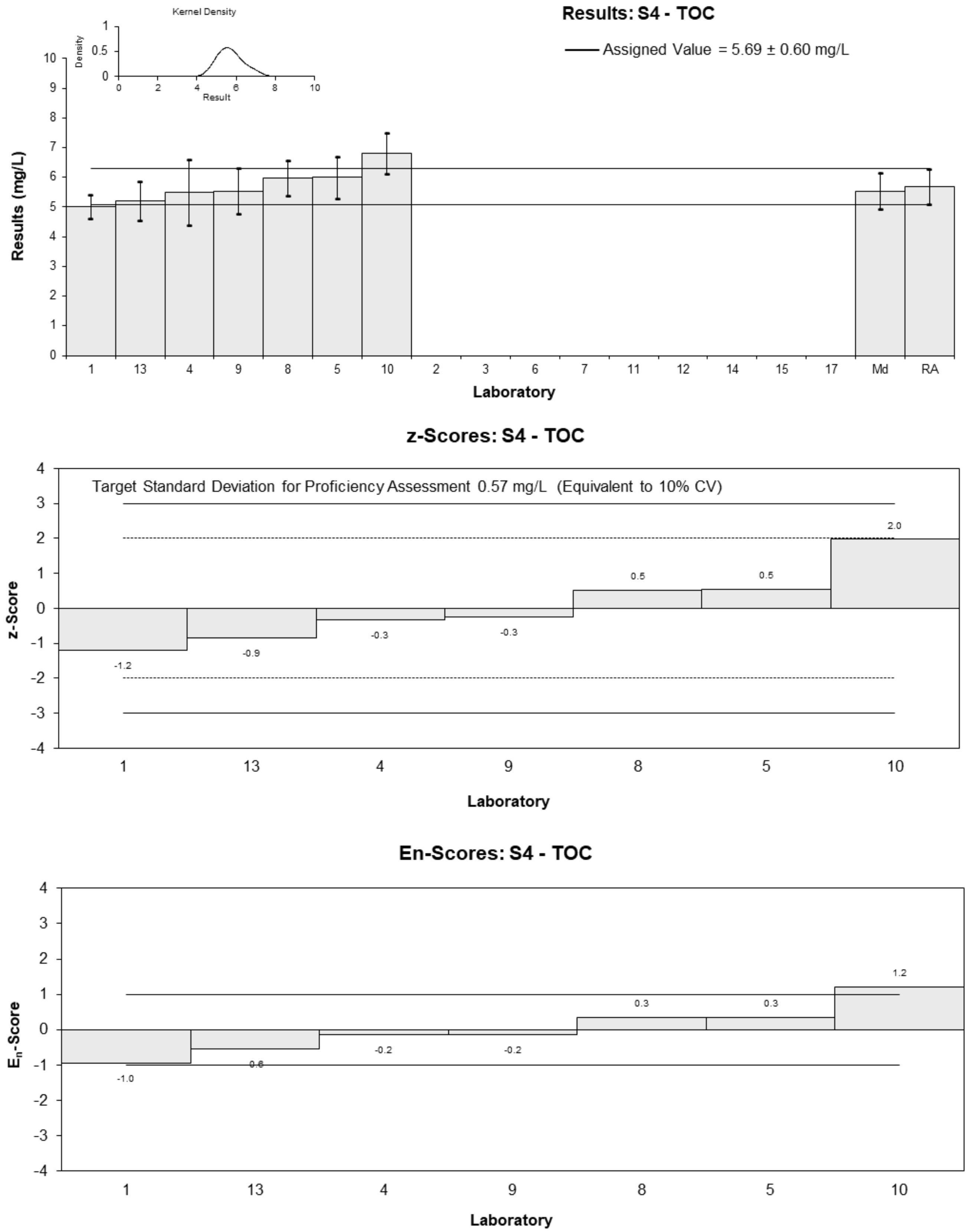
Sample No.	S4
Matrix	River Water
Analyte	TOC
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	5	0.4	-1.21	-0.96
2	NT	NT		
3	NT	NT		
4	5.5	1.1	-0.33	-0.15
5	6	0.7	0.54	0.34
6	NT	NT		
7	NT	NT		
8	5.98	0.6	0.51	0.34
9	5.54	0.77	-0.26	-0.15
10	6.81	0.701	1.97	1.21
11	NT	NT		
12	NT	NT		
13	5.2	0.65	-0.86	-0.55
14	NT	NT		
15	NT	NT		
17	NT	NT		

Statistics

Assigned Value	5.69	0.60
Spike Value	Not Spiked	
Robust Average	5.69	0.60
Median	5.54	0.62
Mean	5.72	
N	7	
Max	6.81	
Min	5	
Robust SD	0.63	
Robust CV	11%	



Results: S4 - TOC
Assigned Value = 5.69 ± 0.60 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 13 4 9 8 5 10 2 3 6 7 11 12 14 15 17 Md RA
z-Scores: S4 - TOC
Target Standard Deviation for Proficiency Assessment 0.57 mg/L (Equivalent to 10% CV)
z-Score
-1.2 -0.9 -0.3 -0.3 0.5 0.5 2.0
1 13 4 9 8 5 10
Laboratory
En-Scores: S4 - TOC
E_n-Score
-1.0 -0.6 -0.2 -0.2 0.3 0.3 1.2
1 13 4 9 8 5 10
Laboratory

Figure 39

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Assigned Values were the robust average of participants' results. The robust averages and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528, Statistical methods for use in proficiency testing by inter-laboratory comparisons'. Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value.[6] Appendix 3 sets out the calculation for the robust average of Ammonia-N in Sample S1 and its associated uncertainty.

No assigned value was set for bromide and iodide in S3 because the reported results were too few. Participants may still compare their reported result for bromide with other participants' results and homogeneity value. No descriptive statistics were presented for iodide in S3 due to only one result (0.03 mg/L) being reported. No assigned value was set for TKN in S4 because the results were too variable.

Spike Value where applicable, includes both the incurred value and the fortified value.

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

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

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 389 numerical results, 375 (96%) 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 0.29% to 900% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 2.

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

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded uncertainties are presented in the bar charts for each analyte (Figure 2 to 39). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 12 laboratories reported results for chloride in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 12 laboratories' results is 500 mg/L (3% of the assigned value). If Laboratory 3's result is coming from one measurement, they might have under-estimated its expanded measurement uncertainty reported for chloride in S1 (166 mg/L or 1%) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 12 measurements. Alternatively, estimates of uncertainties for alkalinity in S2 larger than 23.5 mg/L (the uncertainty of the assigned value, 5.7 mg/L plus the allowable variation from the assigned value, the target standard deviation of 8.9 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 3 for alkalinity in S1 (34 mg/L) might have been over-estimated.

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[10] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Laboratory 3 should assess their procedure used for estimating measurement uncertainty, as most of their reported estimates of uncertainty were under-estimated or over-estimated. They also reported an estimate of expanded uncertainty for fluoride in S3 which was larger than the result itself and attached estimates of the expanded measurement uncertainty to results reported as being less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

In some cases, the results were reported with an inappropriate number of significant figures. The recommended format is to write the uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 2990 ± 228 mg/L, it is better to report 2990 ± 230 mg/L or, instead of 4.60 ± 0.5 mg/L, it is better to report 4.6 ± 0.5 mg/L.[9]

For consistency, results reported by Laboratory 13 in format ".XX" were typed as "0.XX". This change will not affect any of Laboratory 13's z-scores or E_n-scores.

6.3 z-Score

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

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 3.5% to 25% PCV were used to calculate z-scores. A set target standard deviation enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation (outliers removed) resulted in this study are presented for comparison in Table 43.

The dispersal of participants' z-scores is presented in Figure 40 (by laboratory code) and in Figure 42 (by analyte). Of 377 results for which z-scores were calculated, 362 (96%) returned a satisfactory score of $|z| \le 2.0$ and 5 (1%) were questionable of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias (Figure 40).

Laboratories **1**, **5**, and **10** reported results for all 36 tests for which a z-score was calculated; Laboratories **1** and **5** also returned satisfactory z-scores for all analytes.

All results reported by laboratories **8** (35), **9** (34), **7** (20), **11** (12), **14** (4), and **2** (4) also returned satisfactory z scores.

Summary of participants' performance is presented in Figure 40.

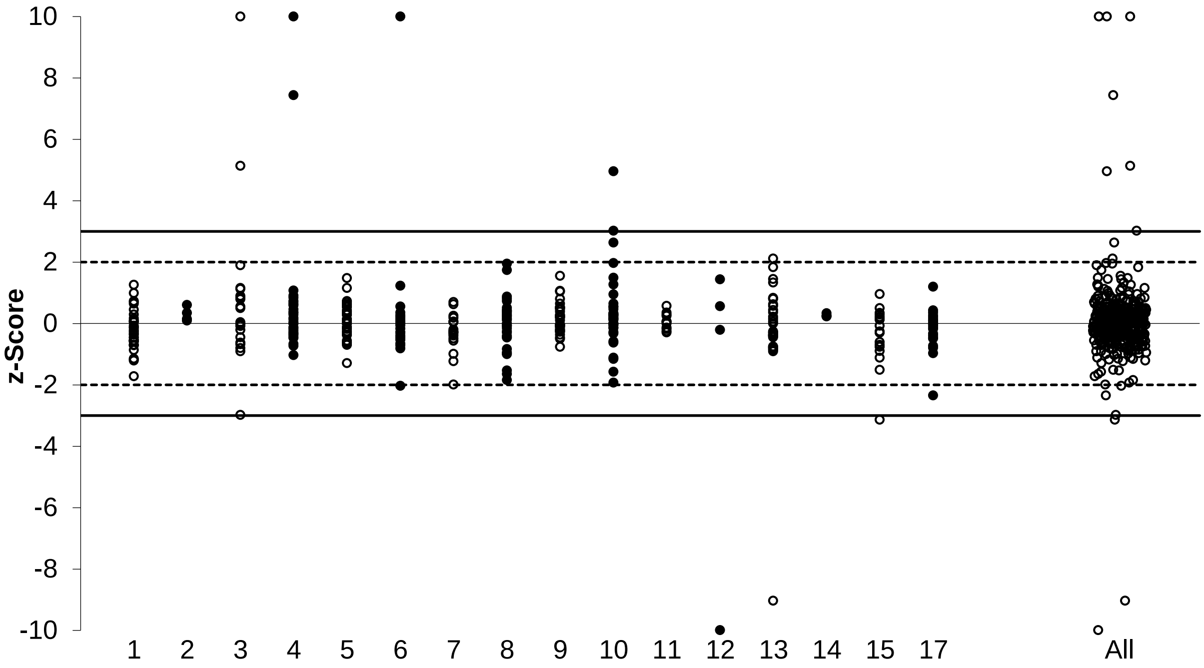
6.4 E_n-score

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

The dispersal of participants' E_n-scores is graphically presented in Figure 41. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

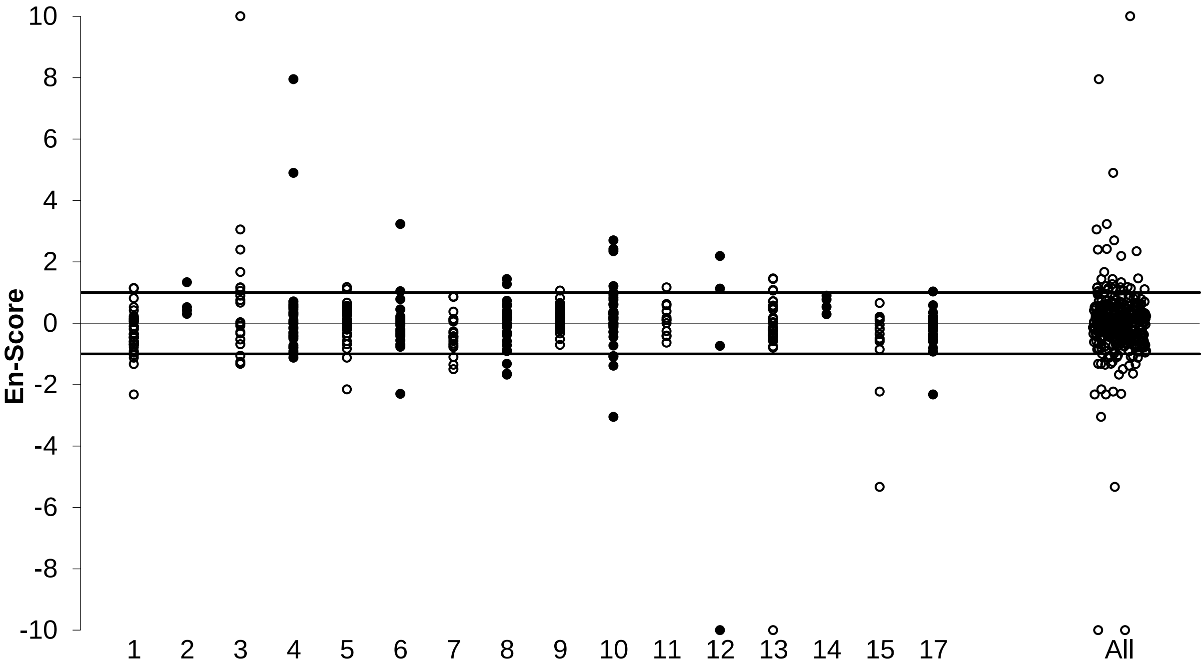
Of 377 results for which E_n-scores were calculated, 319 (85%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

Laboratory **9** returned the highest number of satisfactory E_n-scores (33). All results reported by laboratory **14** (4) returned satisfactory E_n-scores.



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

Figure 40 z-Score Dispersal by Laboratory



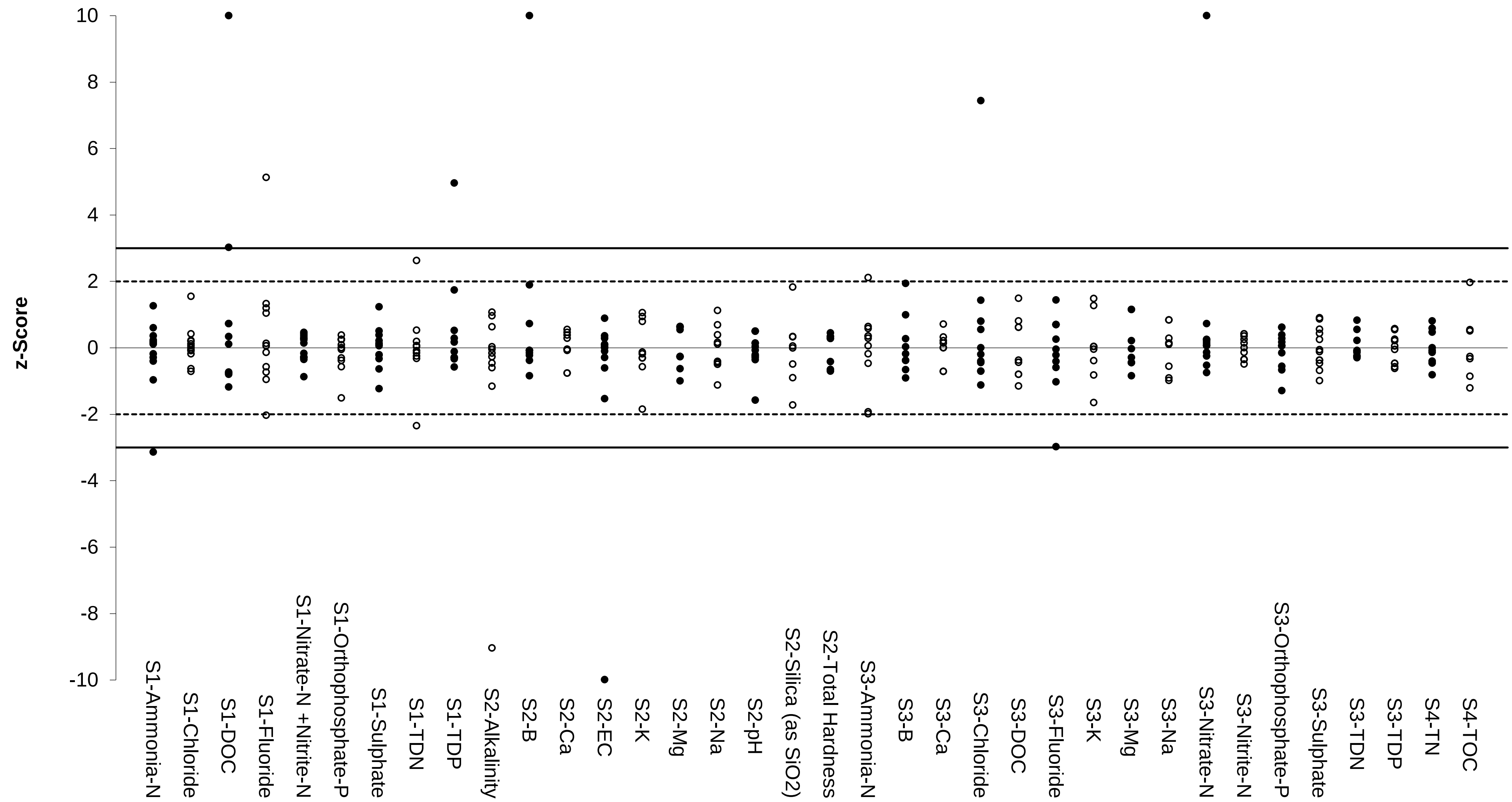
Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 41 E_n-Score Dispersal by Laboratory

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

Sample	Test	Assigned value (mg/L)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Ammonia-N	0.185	8.8%	21%	15%
S1	Chloride	16800	4.2%	3.7%	10%
S1	DOC	2.62	21%	14%	20%
S1	Fluoride	0.79	21%	17%	20%
S1	Nitrate-N +Nitrite-N	0.115	5.9%	22%	15%
S1	Orthophosphate-P	0.106	5.4%	22%	15%
S1	Sulphate	2350	5.2%	5%	10%
S1	TDN	0.457	6.8%	18%	15%
S1	TDP	0.115	7.1%	22%	15%
S2	B	2.62	6.7%	14%	10%
S2	Ca	238	5.5%	7%	10%
S2	K	227	9%	7.1%	10%
S2	Mg	698	7.1%	6%	10%
S2	Na	5630	7.8%	4.4%	10%
S2	Alkalinity	89.4	8%	8.1%	10%
S2	EC	30900 µS/cm	4.6%	3.4%	10%
S2	pH	7.96	1.5%	11.7%	3.5%
S2	Silica (as SiO2)	0.366	15%	19%	20%
S2	Total Hardness	3550	5.6%	4.7%	10%
S3	B	0.728	8.1%	17%	10%
S3	Ca	14.0	5.2%	11%	10%
S3	K	6.97	11%	12%	10%
S3	Mg	6.28	8.1%	12%	10%
S3	Na	28.6	7.7%	9.7%	10%
S3	Ammonia-N	0.114	17%	22%	15%
S3	Bromide	Not Set	26%	NA	Not Set
S3	Chloride	39.8	8.7%	9.2%	10%
S3	DOC	5.65	10%	12%	10%
S3	Fluoride	0.181	15%	21%	15%
S3	Nitrate-N	2.39	6.2%	14%	15%
S3	Nitrite-N	0.190	5.9%	21%	15%
S3	Orthophosphate-P	0.119	8.6%	22%	15%
S3	Sulphate	32.2	6.9%	9.5%	10%
S3	TDN	3.29	5.7%	13%	15%
S3	TDP	0.129	8%	22%	15%
S4	TKN	Not set	33%	NA	Not Set
S4	TN	3.30	9.1%	13%	15%
S4	TOC	5.69	11%	12%	10%

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



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

Figure 42 z-Score Dispersal by Analyte

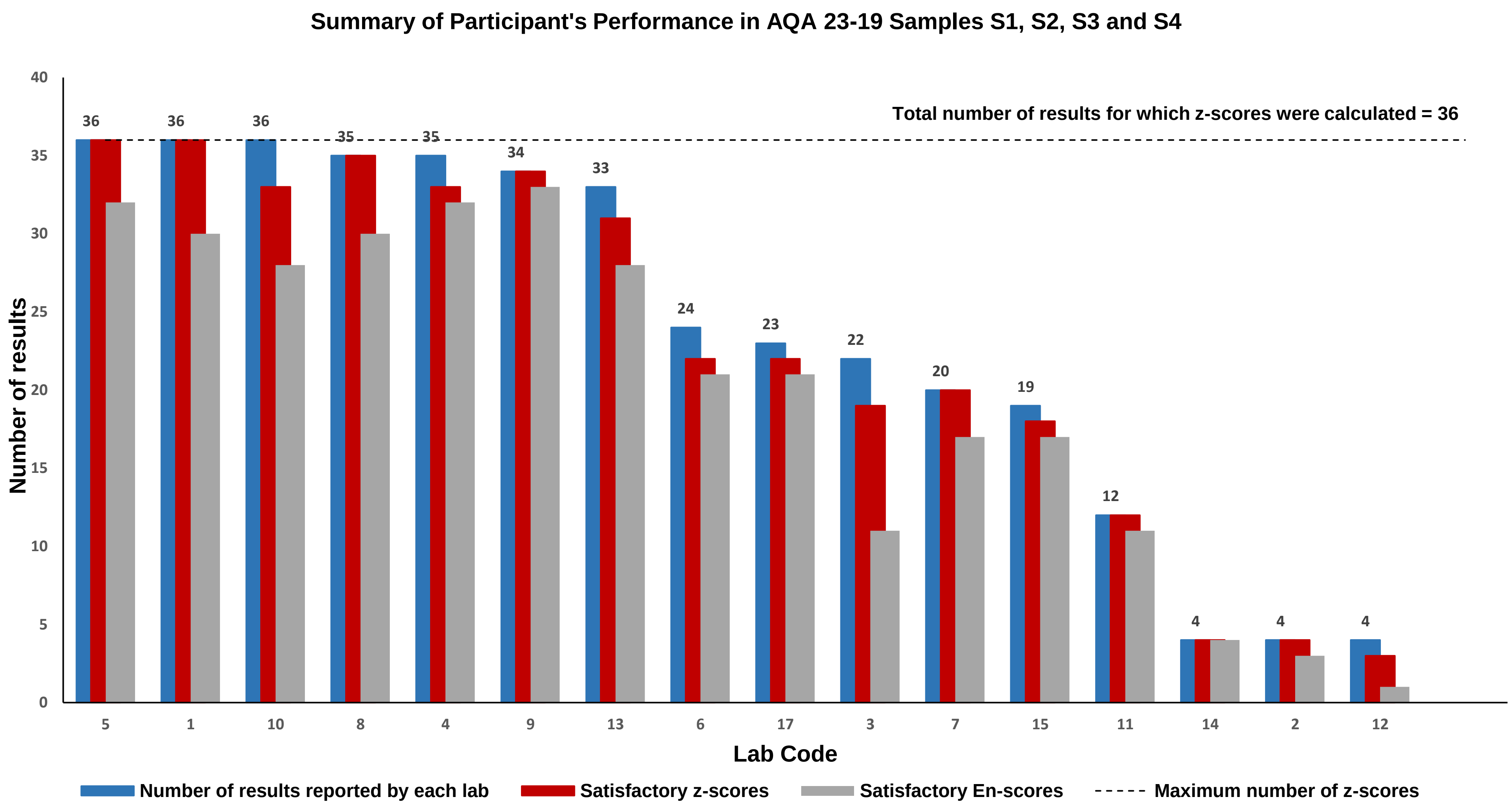


Figure 43 Summary of Participants' Performance

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

Lab Code	Ammonia-N (mg/L)	Chloride (mg/L)	DOC (mg/L)	Fluoride (mg/L)	Nitrate-N +Nitrite-N (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
AV	0.185	16800	2.62	0.79	0.115	0.106	2350	0.457	0.115
HV	0.240	15000	NA	0.90	0.117	NA	2000	0.412	0.117
1	0.220	15600	2	0.8	0.10	0.097	2300	0.462	0.105
2	0.2017	NR	NR	NR	0.1174	0.1075	NR	NR	NR
3	<0.2	16646	NT	1.6	NT	NT	2301	NT	NT
4	0.195	16800	3	0.675	0.109	0.101	2380	0.435	0.118
5	0.188	16500	3	0.8	0.12	0.106	2200	0.447	0.113
6	0.174	16700	8.3	0.47	0.112	0.110	2640	0.46	0.11
7	0.19	16900	NT	0.7	0.11	0.11	2060	NT	0.11
8	0.177	17132	2.68	0.64	0.122	0.110	2440	0.451	0.145
9	0.190	19400	2.22	0.954	0.123	0.112	2470	0.493	0.124
10	0.1889	15745.59	4.20	0.768	0.1102	0.106	2271.3318	0.6373	0.2006
11	0.18	NR	NR	NR	0.12	0.11	NR	0.44	0.11
12	NT	NT	NT	NT	NT	NT	NT	NT	NT
13	<1	17165	2.2	1.0	0.110	0.10	2365	<0.1	<0.5
14	0.1914	NR	NR	NR	0.1191	0.11	NR	NR	NR
15	0.098	17000	2.8	0.81	0.11	0.082	2400	0.47	0.12
17	0.158	17500	2.24	0.98	0.121	0.1052	2370	0.296	0.1091

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

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

Lab Code	B (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Alkalinity (mg/L)	EC (µS/cm)	pH	Silica (mg/L)	Total Hardness (mg/L)
AV	2.62	238	227	698	5630	89.4	30900	7.96	0.366	3550
HV	2.74	224	247	737	5310	NA	31000	NA	NA	NA
1	2.6	245	224	743	5720	84	31200	7.89	0.24	3710
2	NR	NR	NR	NR	NR	NR	NR	NR	0.39054	NR
3	3.116	251	245	654	6258	89	33650	8.1	NT	3320
4	25.3	249	223	741	6020	99	31800	7.86	NR	3670
5	2.52	247	214	736	5850	95	31000	7.88	0.39	3650
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	NT	NT	87	30000	7.97	0.33	NT
8	2.81	236	185	628	5376	88	26160	7.94	NT	3670
9	2.56	237	251	679	5350	85.3	30600	8.1	NT	NT
10	2.5820	236.921	248.268	742.801	5692.731	79.07	30913	7.52	0.3900	3650.446
11	NR	NR	NR	NR	NR	NR	NR	NR	0.37	NR
12	NT	NT	NT	NT	NT	NT	27.58	7.901	NT	NT
13	2.4	220	220	680	5400	8.6	32000	8.0	0.5	3400
14	NR	NR	NR	NR	NR	NR	NR	NR	0.3901	NR
15	2.6	220	220	680	5000	98	29000	8.1	0.3	3300
17	NT	NT	NT	NT	NT	89.7	31170	8.0	0.365	NT

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

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

Lab Code	S3-B (mg/L)	S3-Ca (mg/L)	S3-K (mg/L)	S3-Mg (mg/L)	S3-Na (mg/L)	S3-Ammonia-N (mg/L)	S3-Bromide (mg/L)	S3-Chloride (mg/L)	S3-DOC (mg/L)	S3-Fluoride (mg/L)
AV	0.728	14.0	6.97	6.28	28.6	0.114	Not Set	39.8	5.65	0.181
HV	NA	16.6	6.05	6.51	25.8	NA	0.100	39.5	5.43	0.200
1	0.8	13	7	6	27	0.106	0.118	37	5	0.2
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	0.662	14	7	7	31	<0.2	<0.2	38	NT	0.1
4	0.7	14	7	6	31	0.120	0.179	69.4	6	0.153
5	0.73	15	8	7	29	0.124	NR	37	6	0.2
6	0.68	13	6.4	6.1	29	0.115	NT	42	5.4	0.18
7	NT	NT	NT	NT	NT	0.08	NT	39	NT	0.2
8	0.869	14.2	5.82	5.75	25.8	0.119	<1	39.8	6.11	0.17
9	0.715	14.3	6.94	6.26	28.9	0.125	NT	43.0	5.44	0.175
10	0.74757	14.442	7.856	6.41	29.428	0.0810	NT	35.3361	6.49	0.165
11	NR	NR	NR	NR	NR	0.12	NR	NR	NR	NR
12	NT	NT	NT	NT	NT	NT	NT	45.5	NT	NT
13	0.70	14	6.7	6.0	26	0.150	0.14	43	5.2	0.22
14	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	NT	NT	NT	NT	0.1110	0.107	38.2	5.2	0.188

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

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

Lab Code	S3-Iodide (mg/L)	S3-Nitrate-N (mg/L)	S3-Nitrite-N (mg/L)	S3-Orthophosphate-P (mg/L)	S3-Sulphate (mg/L)	S3-TDN (mg/L)	S3-TDP (mg/L)	S4-TKN (mg/L)	S4-TN (mg/L)	S4-TOC (mg/L)
AV	Not Set	2.39	0.190	0.119	32.2	3.29	0.129	Not Set	3.30	5.69
HV	NA	2.30	0.190	NA	28.5	2.93	0.148	NA	4.05	NA
1	<0.020	2.65	0.180	0.109	31	3.14	0.118	0.67	3.23	5
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	NT	2368	NT	NT	30	NT	NT	NT	2.9	NT
4	<0.01	2.34	0.186	0.107	35.1	3.17	0.120	0.87	3.590	5.5
5	NR	2.42	0.202	0.096	31	3.16	0.117	0.8	3.3	6
6	NT	2.2	0.20	0.120	33	3.4	0.12	NT	NT	NT
7	NT	2.30	0.18	0.13	29	NT	0.13	0.8	3.1	NT
8	NT	2.44	0.202	0.126	35.0	3.16	0.134	0.45	3.07	5.98
9	NT	2.48	0.197	0.124	31.8	3.25	0.133	NT	3.26	5.54
10	<0.5	2.48	0.19395	0.122	31.994	3.563	0.1394	0.9364	3.5346	6.81
11	NR	2.41	0.19	0.12	NR	3.22	0.14	NT	NT	NT
12	NT	NT	NT	NT	34	NT	NT	NT	NT	NT
13	0.03	2.120	0.180	0.130	33.6	3.7	0.140	1.3	3.7	5.2
14	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	2.46	0.176	0.1164	30.7	3.24	0.128	NT	NT	NT

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

6.5 Participants' Results and Analytical Methods

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

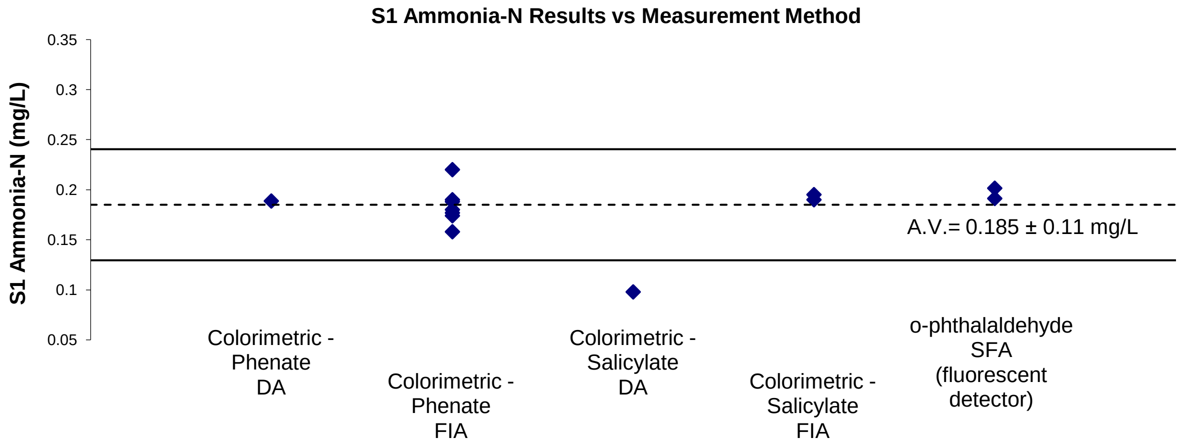
Bromide in S3 was the test that most challenged participants' analytical techniques. Only four laboratories reported results.

TKN in S4 also challenged participants' analytical techniques, between laboratory CV was high 33%.

Individual Test Commentary

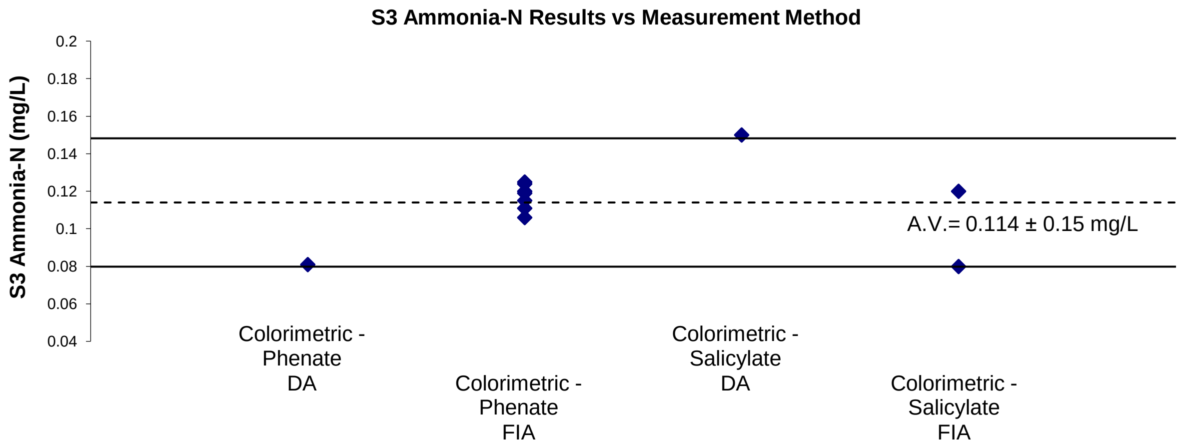
Alkalinity to pH 4.5 as ($CaCO_3$) Participants used auto-titration or manual titration to measure alkalinity in S2, and all but one performed satisfactorily.

Ammonia-Nitrogen Participants' performance in the sea water sample S1 and in the river water sample S3, were comparable, with CVs of 8.8% and 17% respectively.



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

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



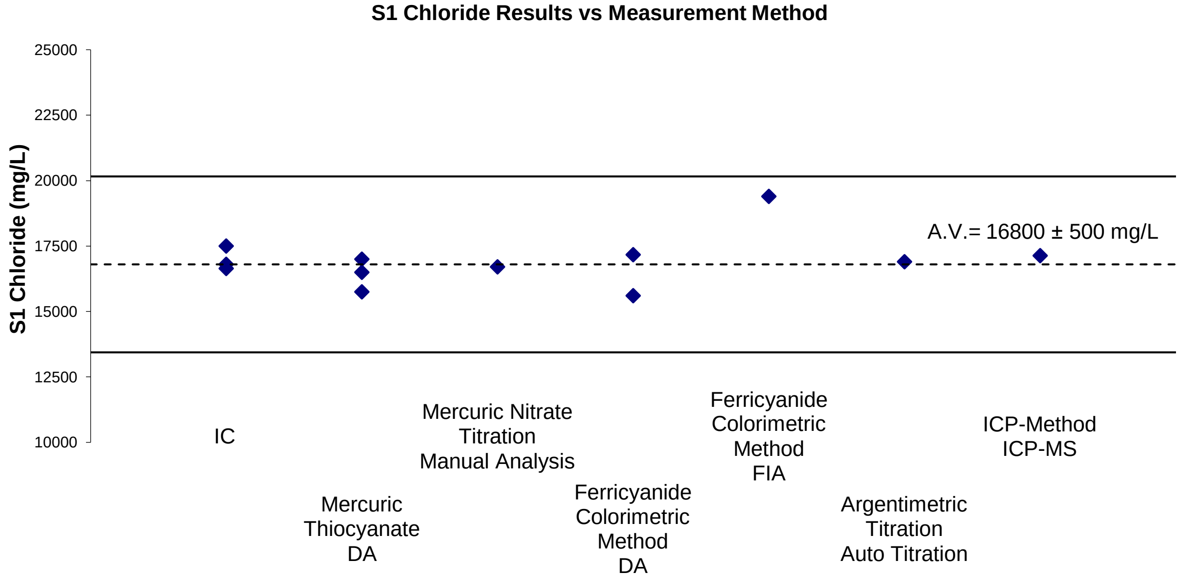
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

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

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

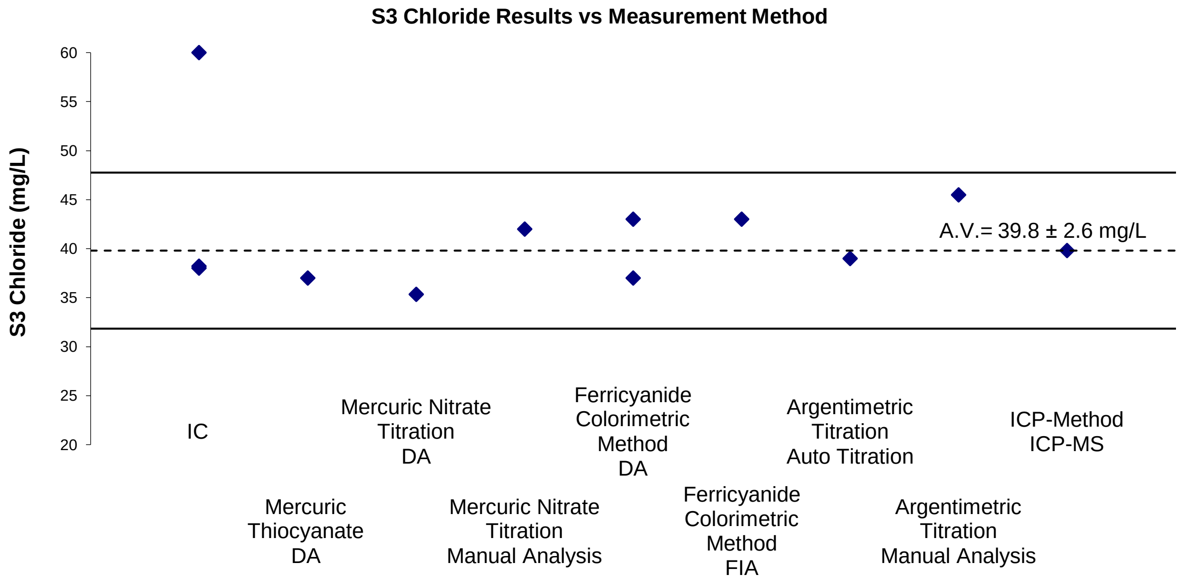
Bromide level in the river water sample S3 was low, which might have posted a challenge for participants' analytical techniques. Although a limited number of results were reported for this test, all were in good agreement with each other, as well as with the median of the reported results (0.129 mg/L) and with the homogeneity value of 0.100 mg/L. Three laboratories used Ion Chromatographic method and one ICP method.

Chloride level in the sea water sample S1 was 16800 mg/L and in S3 was 39.8 mg/L. All results returned satisfactory z-scores with the exception of one. Participants used a wide variety of methods; these are presented in Figures 46 and 47 versus participants' results.



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

Figure 46 S1-Chloride Results vs. Measurement Method

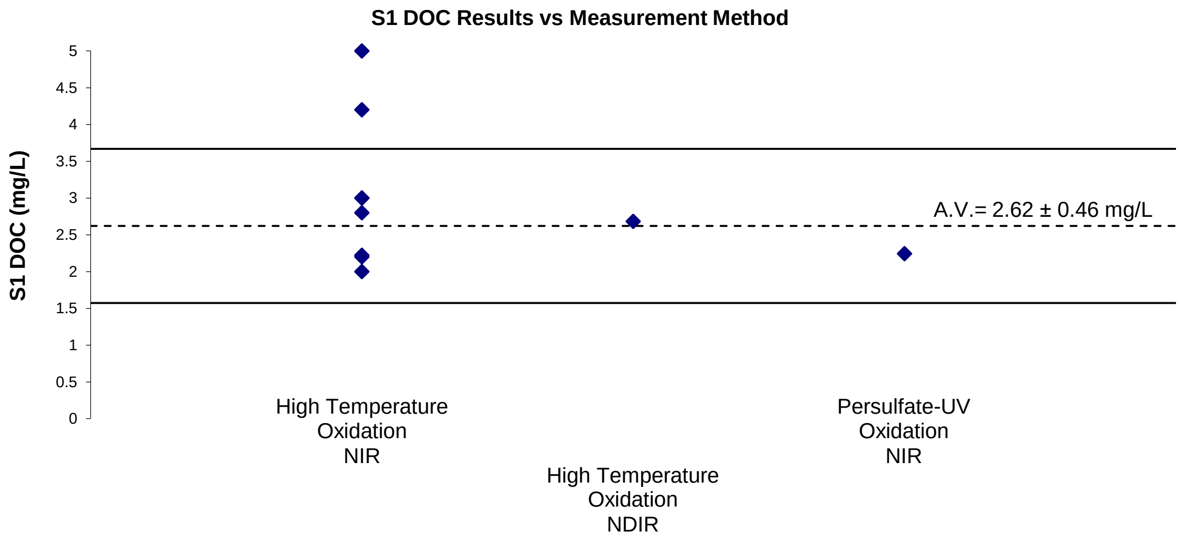


Laboratory 4 result of 69.4 mg/L has been plotted as 60 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 47 S3-Chloride Results vs. Measurement Method

Problems with calculation or sample preparation/dilution procedures may explain laboratory 4's unsatisfactory z-score in S3.

Dissolved Organic Carbon as dNPOC As in previous study AQA 22-18, measurements of DOC in sea water challenged participants' analytical methods, with a between-laboratory CV of 21% (Figure 48).

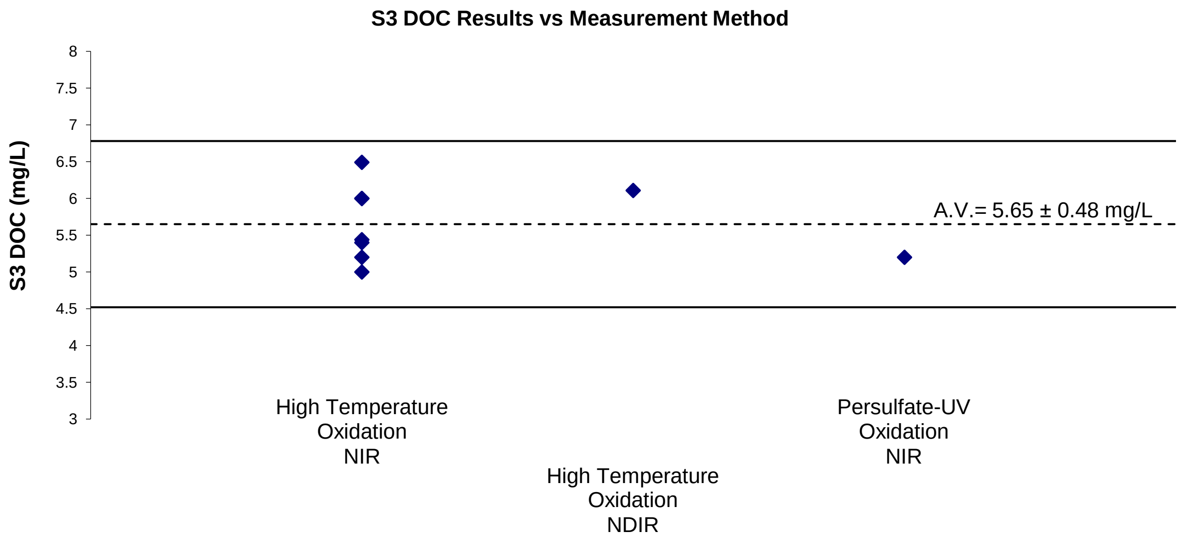


Laboratory 6 result of 8.3 mg/L has been plotted as 5 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 48 S1-DOC Results vs. Measurement Method

Chloride in sea water can interfere in the persulfate oxidation process of the organic molecules which may explain the variability of the results reported in S1. Sample dilution and increased digestion time can help to overcome this problem. [15]

All participants who reported results for DOC in river water S3 performed satisfactorily (Figure 49). The between-laboratory CV of 10% was in good agreement with the CV predicted by Thompson and Horwitz (12%).

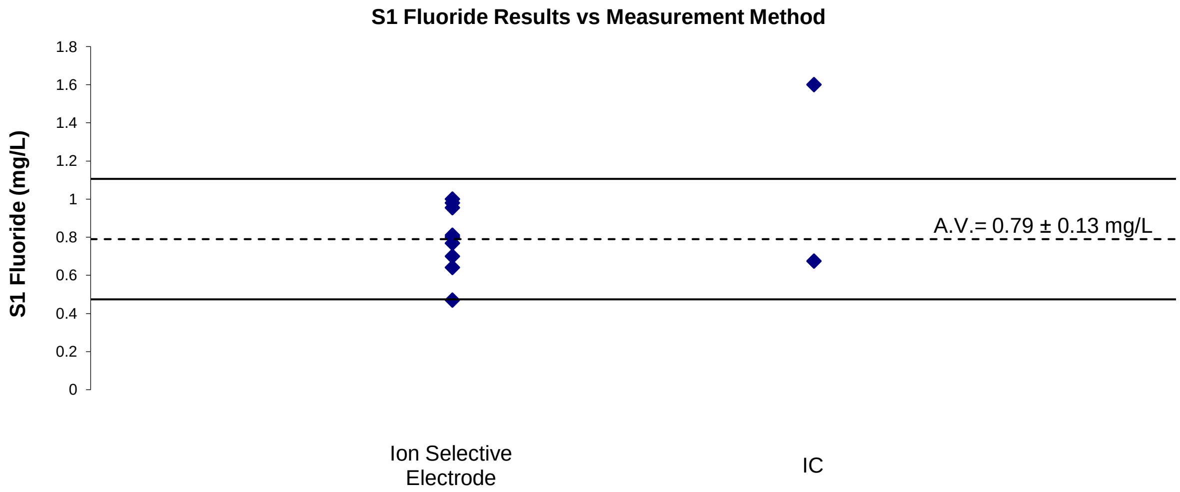


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 49 S3-DOC Results vs. Measurement Method

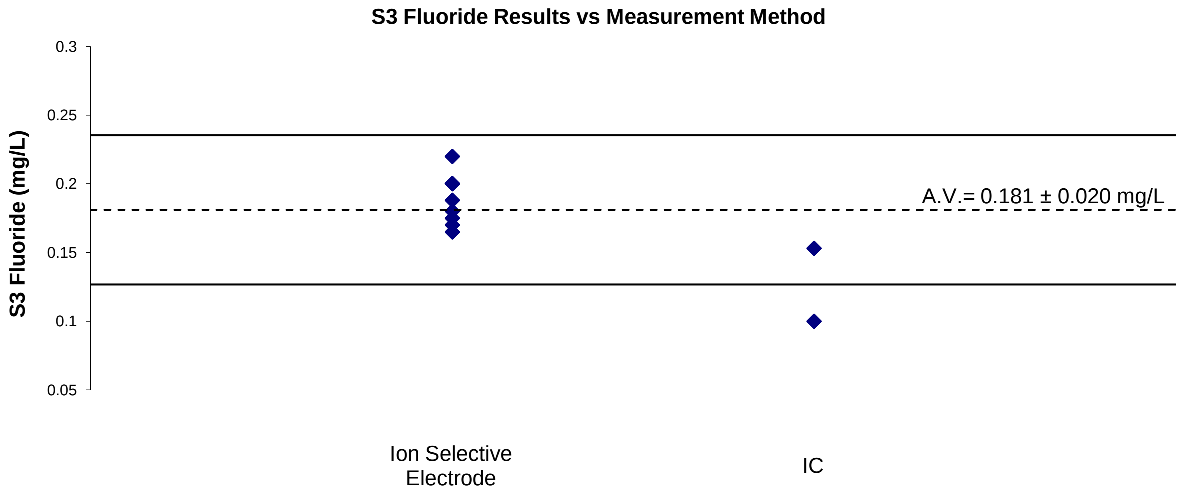
EC results in sample S2 were in good agreement except for laboratory 12 which correctly measured EC, but reported in the wrong units.

Fluoride Plots of participants z-scores versus the measurement technique used are presented in Figures 50 and 51. Caution should be exercised when the ion chromatographic method is used for low level fluoride measurements. Fluoride has a low molecular weight and valence charge and is not retained by the columns in the normal elution times like for the other ions. Low level fluoride may be difficult to quantify due to negative contribution of the "water dip" (corresponding to elution of water) or due to interference from the simple organic acids who may elute close to fluoride.[15]



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

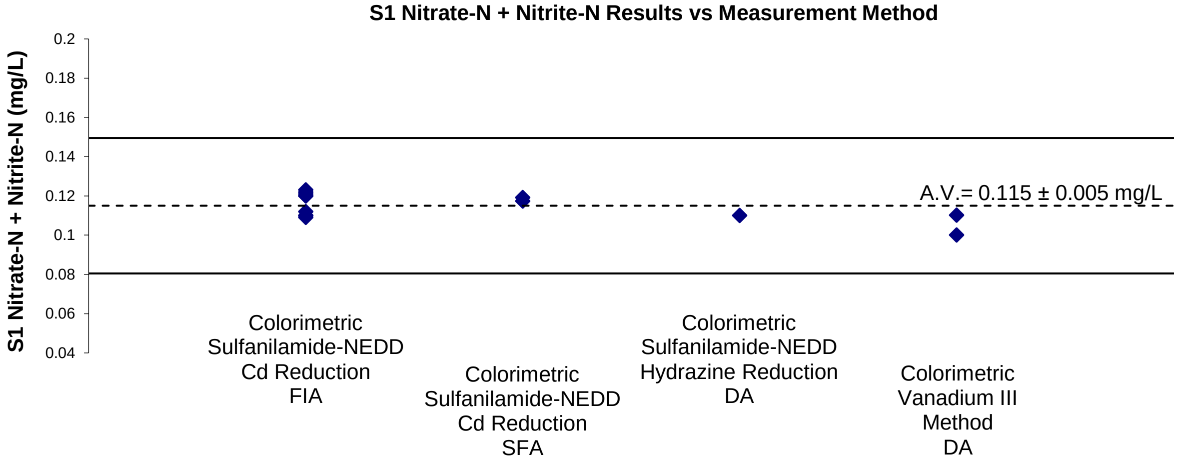
Figure 50 S1-Fluoride Results vs. Measurement Method



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

Figure 51 S3-Fluoride Results vs. Measurement Method

Nitrate-Nitrogen + Nitrite-Nitrogen level in the sea water samples S1 was the incurred level, 0.115 mg/L. Most laboratories used the colorimetric-sulfanilamide-NEDD Cd reduction method with FIA (Figures 52).

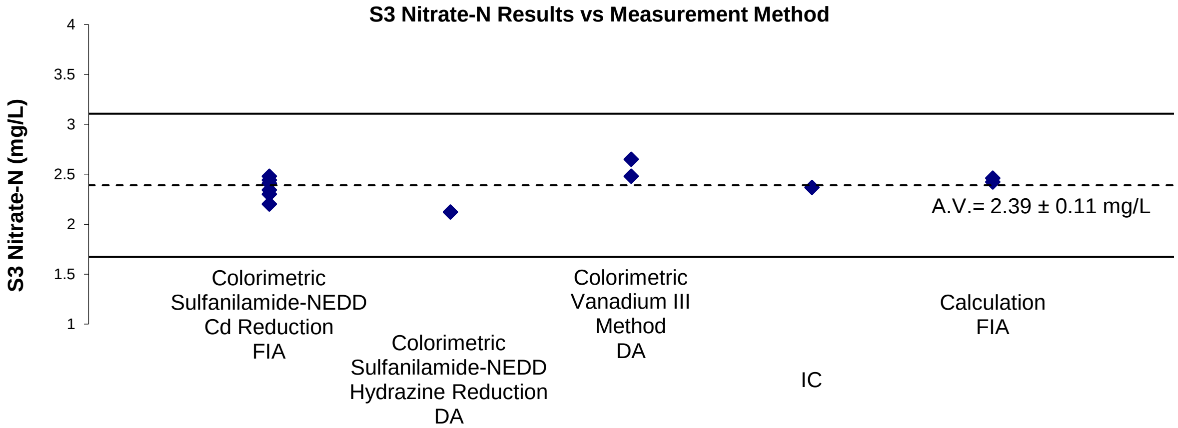


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 52 S1-Nitrate-N+Nitrite-N Results vs. Measurement Method

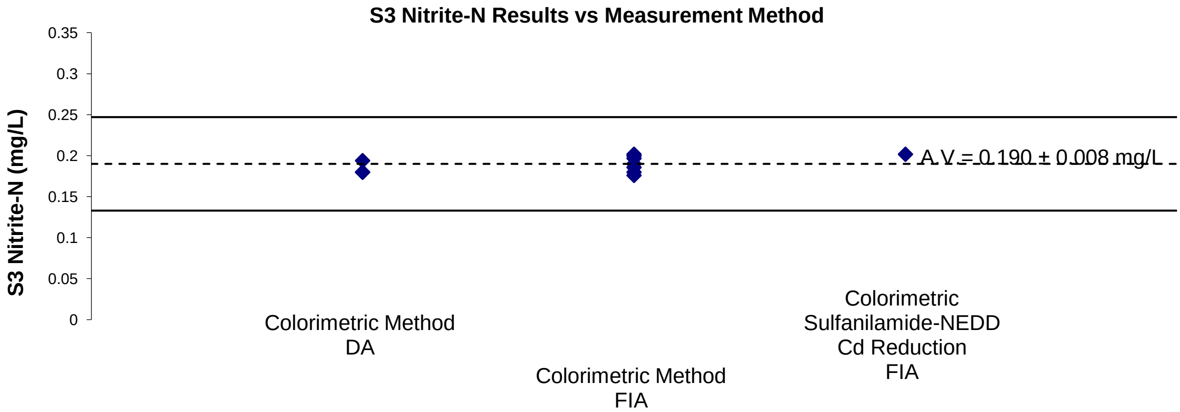
Nitrate-N results in S3 returned satisfactory z-scores, except for one. Laboratory 3 correctly measured NO_3-N in S3 but reported results in the wrong units (Figure 53).

Nitrite-N level in S3 was the incurred level, 0.190 mg/L. The reported results were in excellent agreement with each other, with a between-laboratory CV of only 5.9%. The colorimetric method with FIA determination was the most popular method used (Figure 54).



Laboratory 3's result of 2368 mg/L was plotted in correct units. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

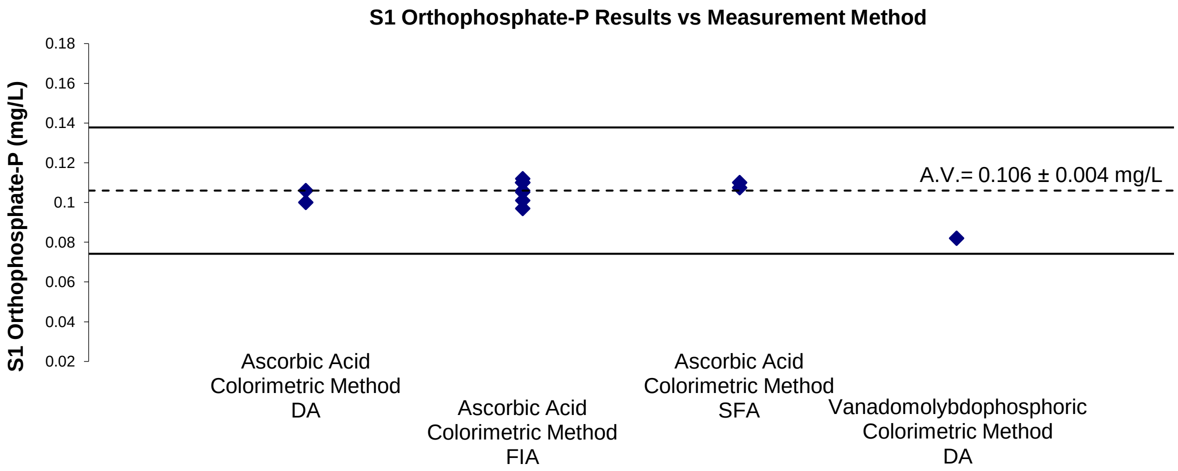
Figure 53 S3Nitrate-N Results vs. Measurement Method



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

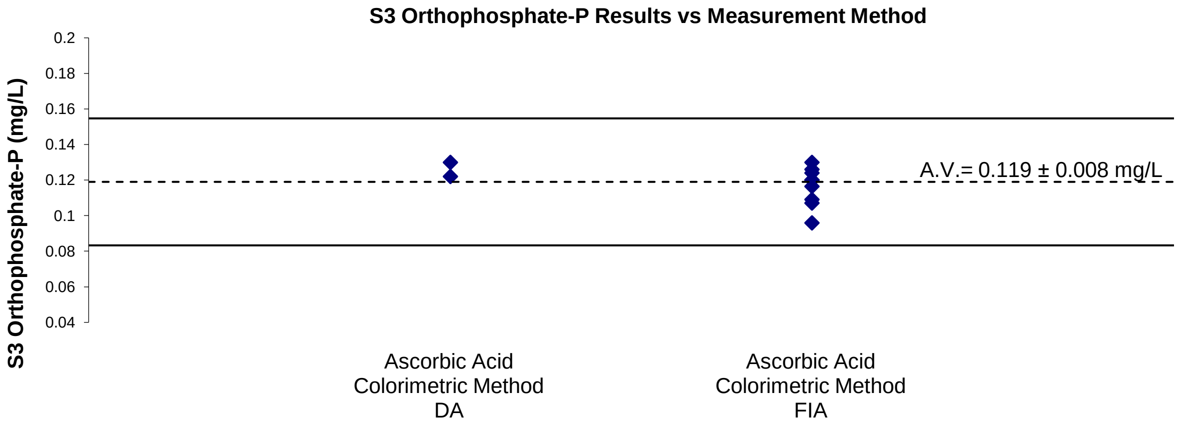
Figure 54 S3- Nitrite-N Results vs. Measurement Method

Orthophosphate-P level in in the sea water sample S1 and in the river water samples S3 was similar at 0.106 mg/L and 0.119 mg/L respectively. Ascorbic acid colorimetric method with FIA was the preferred method of measurement (Figures 55 and 56).



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

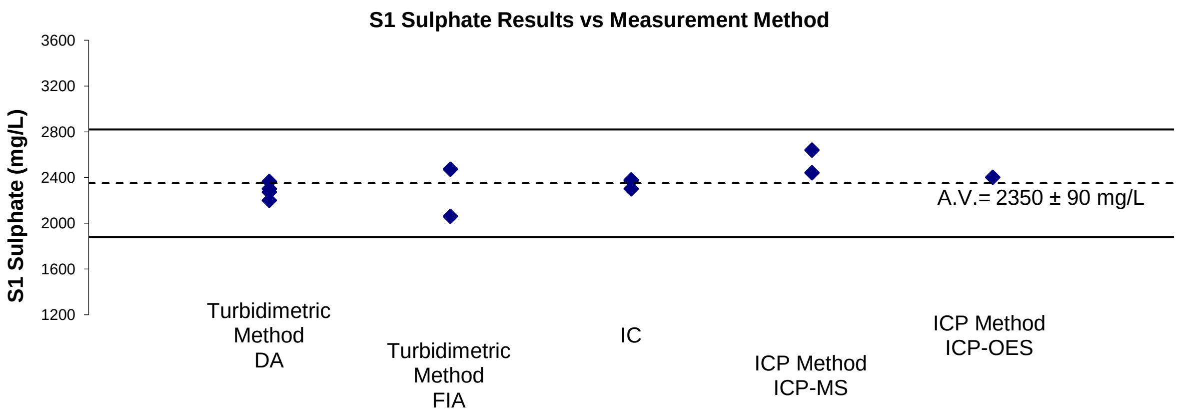
Figure 55 S1-Orthophosphate-P Results vs. Measurement Method



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

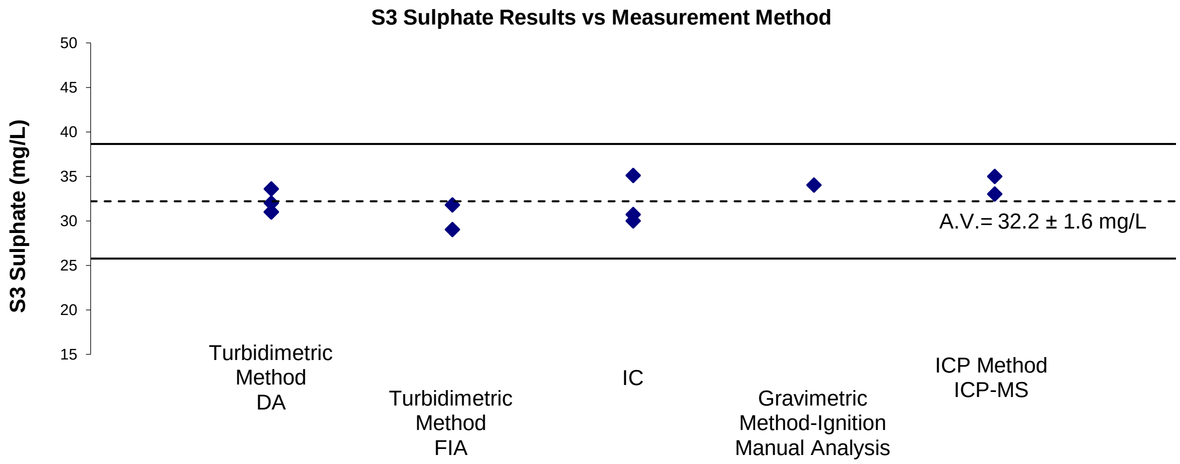
Figure 56 S3-Orthophosphate-P Results vs. Measurement Method

Sulphate measurements in sea water and river water did not challenge participants' analytical technics. Laboratories used various methods, and all produced comparable results. (Figures 57 and 58).



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

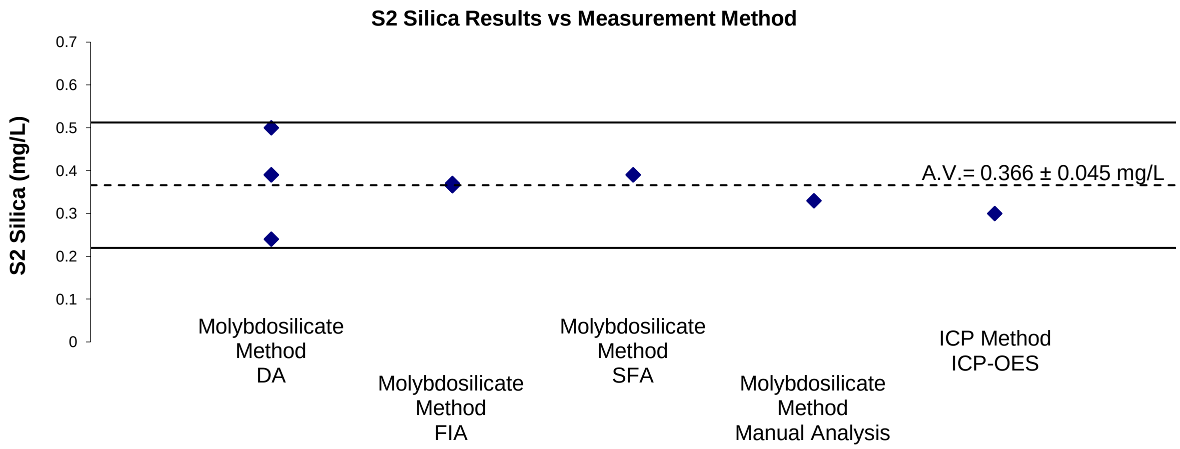
Figure 57 S1-Sulphate Results vs. Measurement Method



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

Figure 58 S3-Sulphate Results vs. Measurement Method

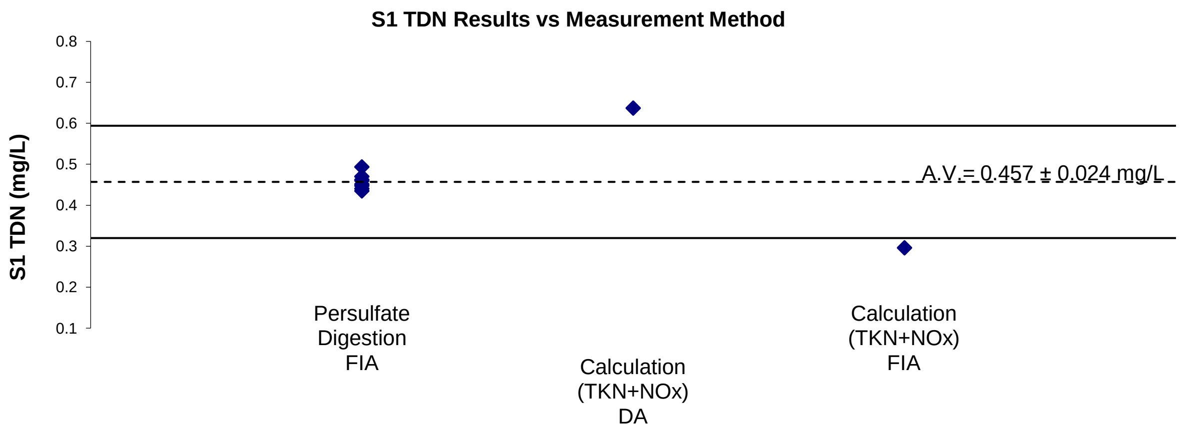
Silica (as SiO_2) Participants measured silica in S2 using a variety of methods (Figure 59). All reported results returned satisfactory z-scores.



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

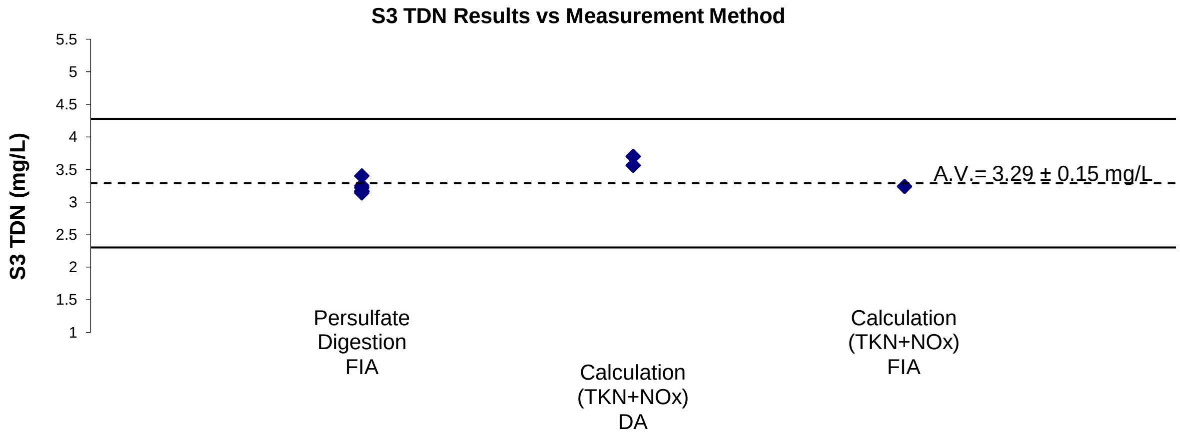
Figure 59 S2-Silica Results vs. Measurement Method

Total Dissolved Nitrogen With the exception of three, all participants determined total dissolved nitrogen in S1 and S3 by oxidation of all nitrogenous compounds to nitrate (Figures 60 and 61).



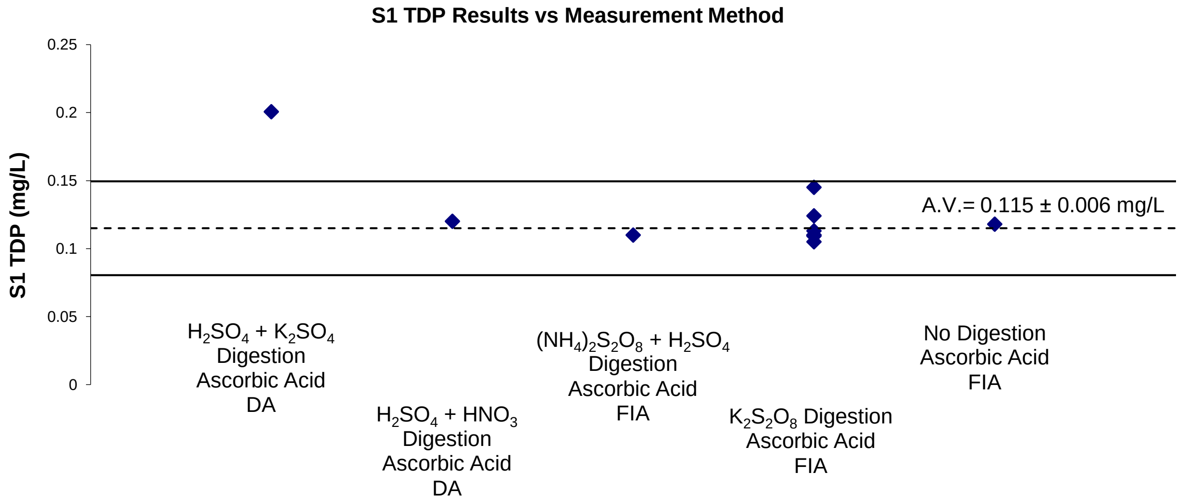
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 60 S1-TDN Results vs. Measurement Method



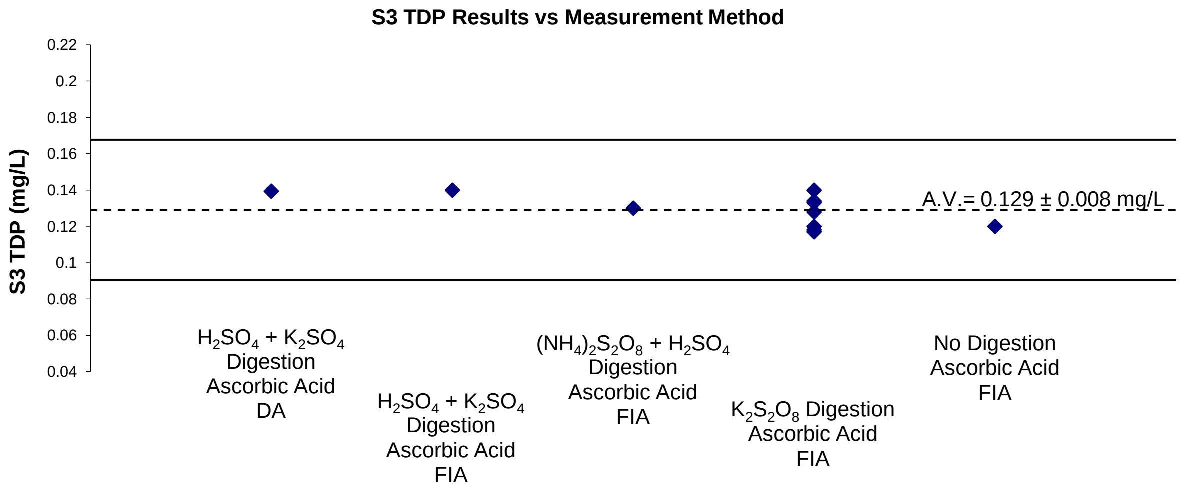
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 61 S3-TDN Results vs. Measurement Method



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

Figure 62 S1-TDP Results vs. Measurement Method



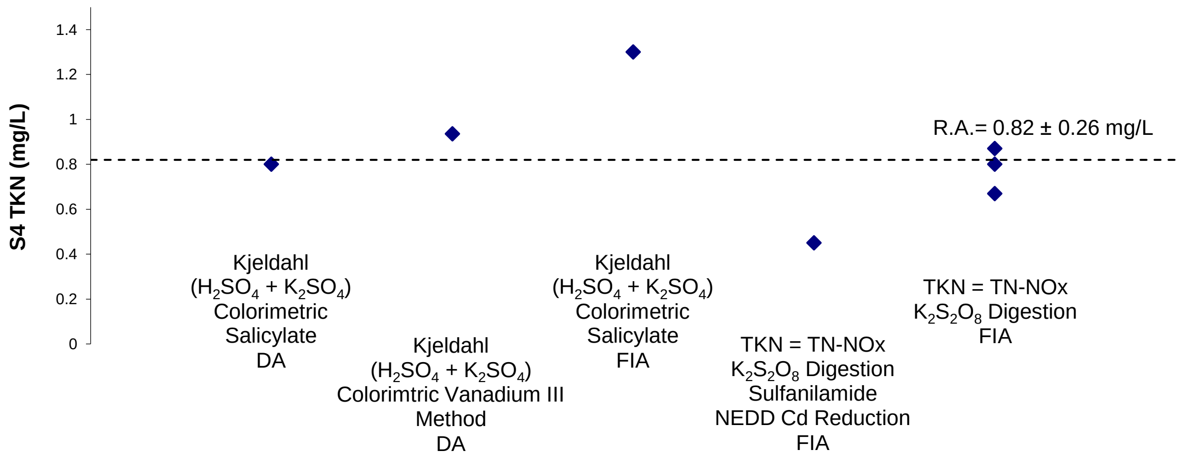
Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 63 S3-TDP Results vs. Measurement Method

Total Dissolved Phosphorus in the sea water Sample S1 and in the river water Sample S3 was at similar level, 0.115 mg/L and 0.129 mg/L respectively; the between-laboratory CV in the two samples was also similar, at 7.1% for S1 and 8% for S3. All reported results returned satisfactory z-scores with the exception of one. The most popular method used involved potassium persulphate digestion followed by FIA determination (Figures 62 and 63).

Total Kjeldahl Nitrogen measurements in the river water sample S4 challenged participants' analytical techniques. The between-laboratory CV was large, 33% and no assigned value was set for this test. When NOx exceeds TKN concentration in a sample, the TKN results determined as TN-NOx can be biased low.

Plots of participants results versus the measurement method used are presented in Figure 64.

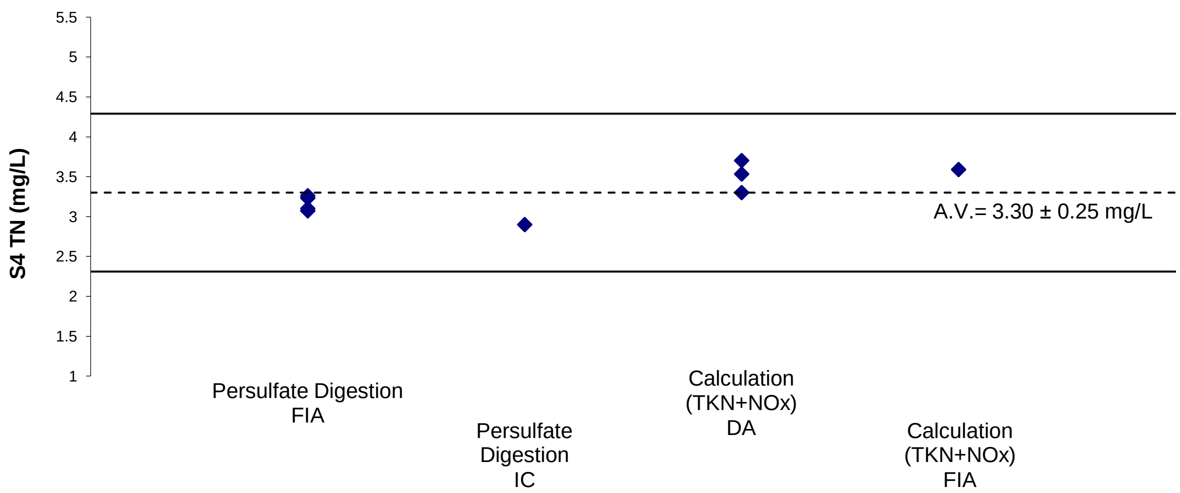


Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 64 S4-TKN Results vs. Measurement Method

Total Nitrogen Nine laboratories reported results for TN in S4, and all returned satisfactory z-scores.

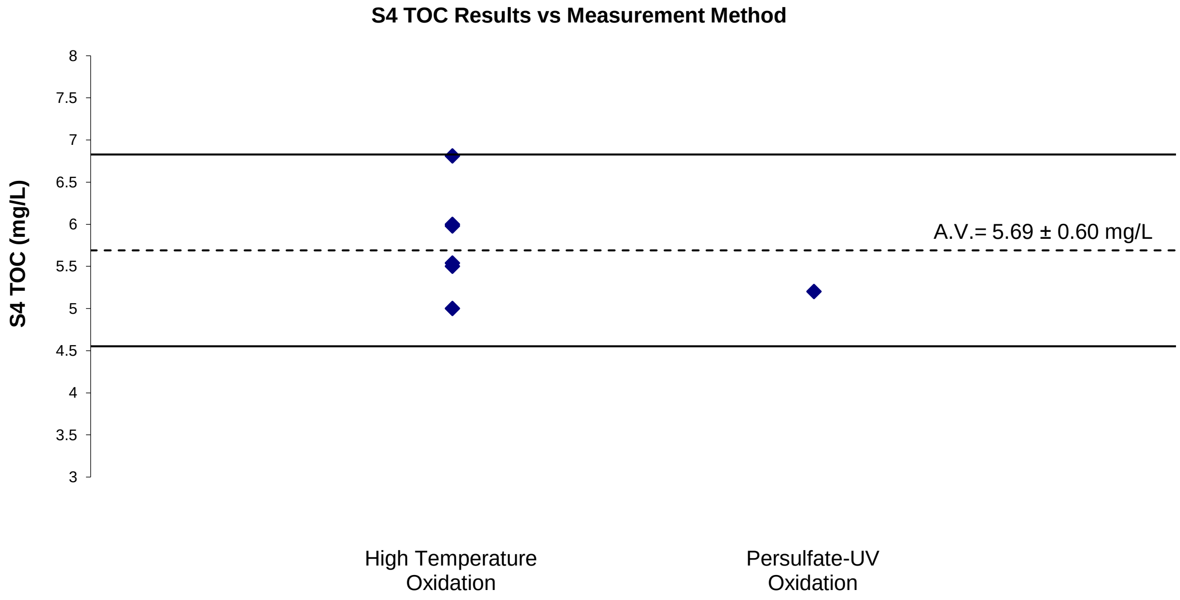
Plots of participants' results versus the instrumental technique used are presented in Figure 65. One laboratory measured total nitrogen as nitrate-N, using alkaline persulfate digestion followed by IC determination. (Figure 65).



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

Figure 65 S4-TN Results vs. Measurement Method

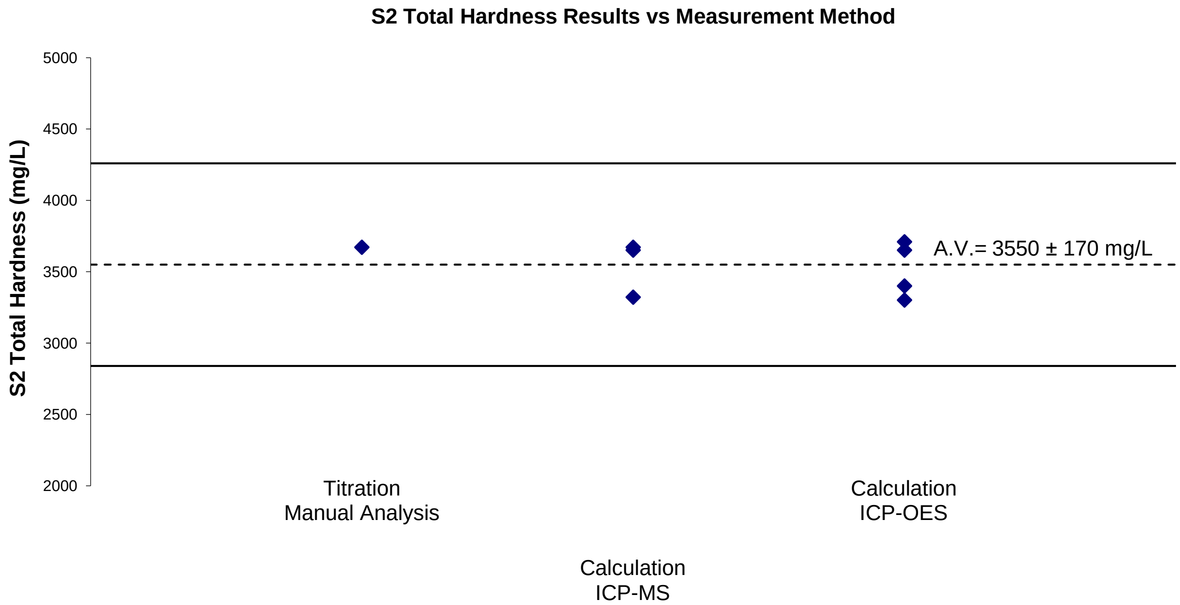
Total Organic Carbon. All participants but one reported using High Temperature Oxidation Method for TOC measurements in S4, and all performed satisfactorily (Figure 66).



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

Figure 66 S4-TOC Results vs. Measurement Method

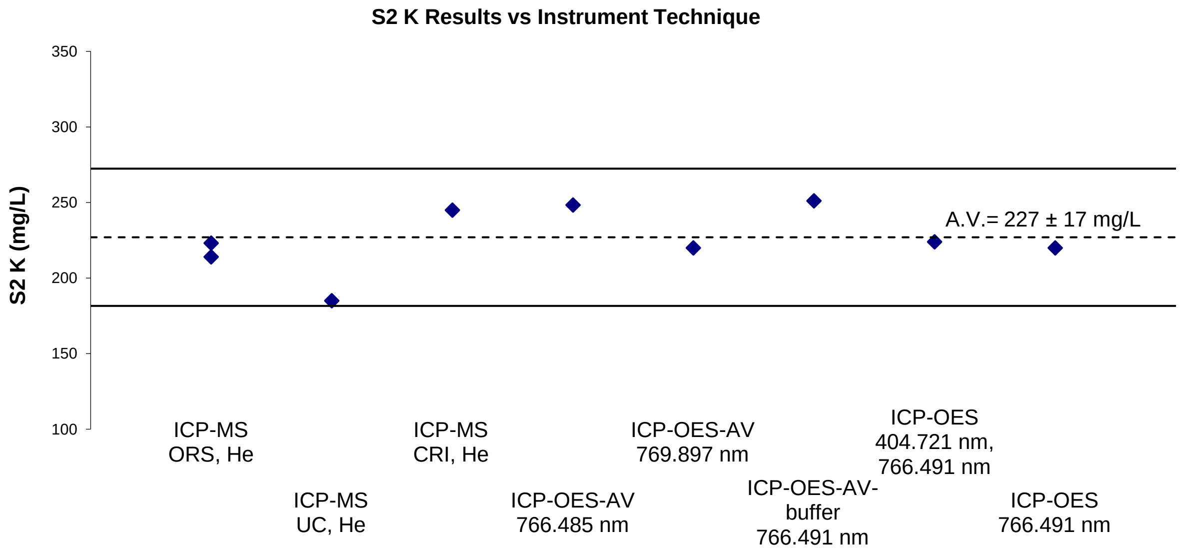
Total Hardness All reported results for total hardness in S2 returned satisfactory results. ICP was the preferred measurement technique (Figure 67).



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

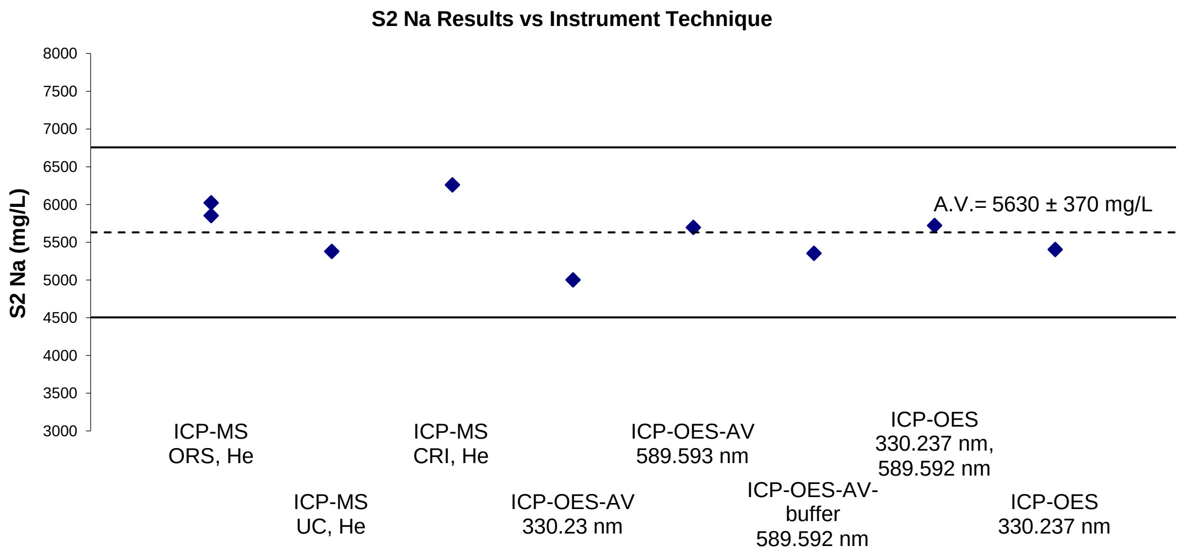
Figure 67 S2-Total Hardness Results vs. Measurement Method

Potassium and Sodium Participants used various instrumental techniques for K and Na measurement in S2 and S3 and all produced compatible results (Figures 68 and 69). ICP-OES was preferred instrumental technique.



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

Figure 68 S2-K Results vs. Instrument Technique



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

Figure 69 S2-Na Results vs. Instrument Technique

6.6 Comparison with Previous NMI Proficiency Tests of Water Characteristics

AQA 23-19 is the 17th NMI proficiency test of water characteristics. Figure 70 presents participant performance over time. Despite different matrices and analytes' concentrations, on average, participants' performance has remained consistent over time.

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

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

6.7 Reference Materials and Certified Reference Materials

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

Table 47 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CRM
2	CRM - Reference material for nutrients in seawater (RMNS): Ammonia is not part of the RMNS so an internal QC is implemented using an independent Ammonia standard solution.
3	CRM - EC AccuSPEC (lot S220225022), pH (AccuSPEC standards), Alkalinity (WQC-ALK HPS lot 2304750), Total N QCI-064 NSI lot 221129), IC (IC-7-1 NSI lot 230501), Ammonia (NSI lot 221014)
4	RM
7	RM
8	CRM – CWW-TM-A, B and C (metals) Minerals 1 and 2 (salts)
10	CRM
11	RM – AQA-22-18, S1 S3, AQA-21-19
13	SS
14	CRM - Reference material for nutrients in seawater (RMNS): This PT we used for the first time a new RMNS that is certified for Ammonia. We also used an internal QC for all.
15	CRM – Inorganic Venture-QCP MIN and Sulfur Standard
17	RM

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

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

> *' **a reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'*[16]

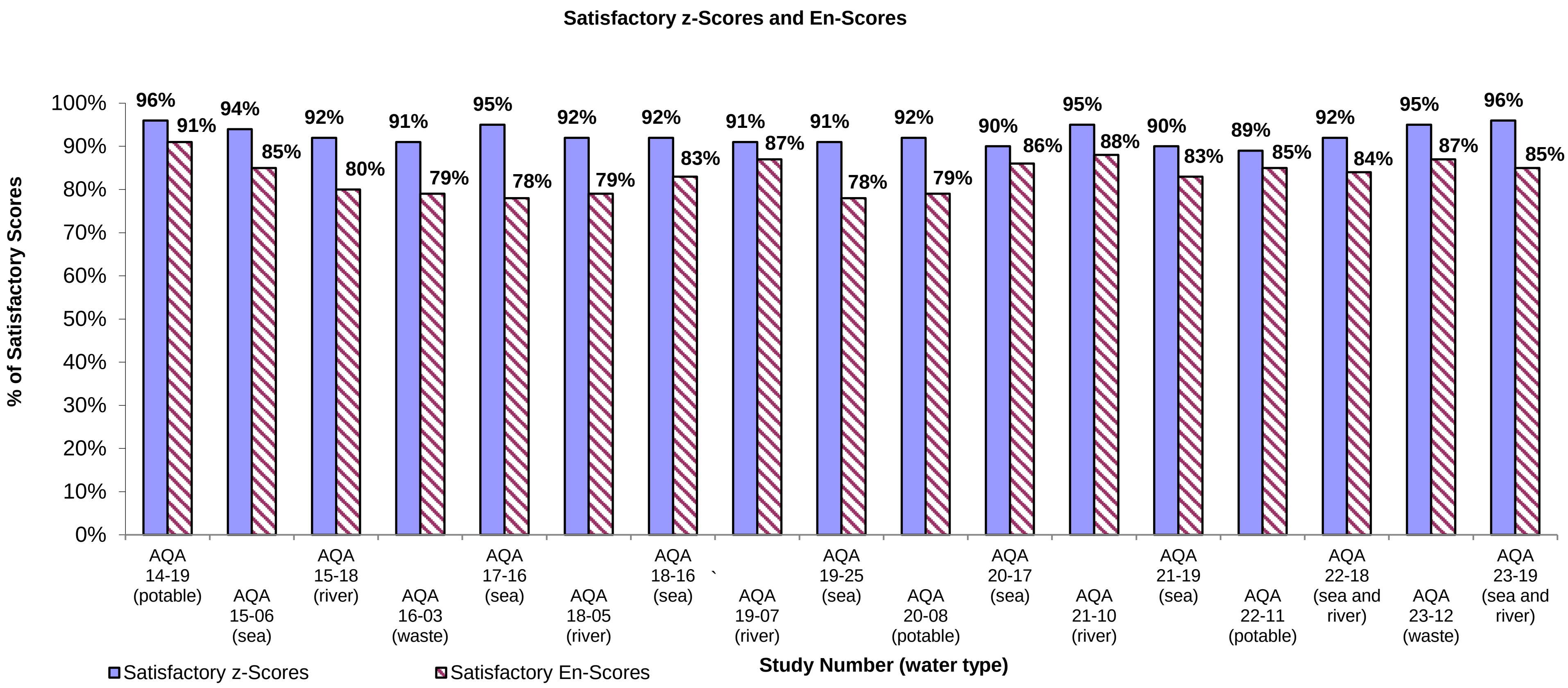


Figure 70 Participants' Performance in Nutrients, Anions and Physical Tests in Water PT Studies over Time

7 REFERENCES

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

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Plasma Mass Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry.

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was 400 mL of filtered and autoclaved sea water fortified for TDP.

Sample S2 was two identical bottles of 200 mL of low salinity sea water: unfiltered sea water mixed with milli-Q water in a ratio of 2:1.

Sample S3 was two identical bottles of 200 mL filtered and autoclaved river water fortified for TDP.

Sample S4 was 200 mL of autoclaved river water.

Sample Analysis and Homogeneity Testing

With the exception of DOC and orthophosphate-P in S1, alkalinity, pH, silica, and total hardness in S2, ammonia-N, B, iodide and orthophosphate-P in S3, and TKN and TOC in S4 a partial homogeneity test was conducted for all other analytes of interest. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Sample Analysis for Dissolved Elements

For analyses of dissolved elements in Samples S2 and S3, a test portion of 5 mL for S2 and 8 mL for S3 was transferred to a 14 mL graduated tube.[17]

Testing involved measurements using ICP-MS and ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates and sample matrix spikes was carried through the same set of procedures and analysed simultaneously with the samples.

A summary of the instrument conditions used for each analyte is given in Table 48.

Table 48 Methodology for Dissolved Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength/Ion
S2-B	ICP-OES	Y	NA	NA	2	249.678 nm
S2-Ca	ICP-OES	Y	NA	NA	2	317.933 nm
S2-K	ICP-OES	Y	NA	NA	2	766.491 nm
S2-Mg	ICP-OES	Y	NA	NA	2	279.078 nm
S2-Na	ICP-OES	Y	NA	NA	2	579 nm
S3-Ca	ICP-MS	Rh	ORS	He	1.25	44 m/z
S3-K	ICP-MS	Rh	ORS	He	1.25	39 m/z
S3-Mg	ICP-MS	Rh	ORS	He	1.25	24 m/z
S3-Na	ICP-MS	Rh	ORS	He	1.25	23 m/z

Methodology for Tests Other Than Dissolved Elements

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

Table 49 Methodology for Tests Other Than Dissolved Elements

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination – OPA Method	SFA

Bromide	Ion Chromatographic Method	IC
Chloride	Turbidimetric Method	DA
Dissolved Organic Carbon	High-Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	ISE
Nitrate-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Nitrite-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Sulphate	Ion Chromatographic Method	IC
Total Dissolved Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Dissolved Phosphorus	ICP-Method	ICP-MS
Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA

APPENDIX 2 - STABILITY STUDY

Samples S1, S3 and **S4** were dispatched on 13 November 2023 frozen. Participants were advised to store the samples frozen, if unable to commence analysis on the day of receipt. Samples condition on receipt and the date when the samples were received and analysed by participants are presented in Table 50. No relationship between participants' results, samples' condition on receipt and days spent in transit, were evident (Figures 71 and 72).

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

Lab Code	Received Date	S1		S3		S4	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	16/11/2023	Frozen	23/11/2023	Frozen	23/11/2023	Frozen	23/11/2023
2	14/11/2023	Cold	12/12/2023	NA	NA	NA	NA
3	15/11/2023	Frozen	16/11/2023	Frozen	17/11/2023	Frozen	16/11/2023
4	17/11/2023	Frozen	24/11/2023	Frozen	24/11/2023	Frozen	24/11/2023
5	14/11/2023	Frozen	28/11/2023	Frozen	28/11/2023	Frozen	28/11/2023
6	14/11/2023	Frozen	15/11/2023	Frozen	15/11/2023	NA	NA
7	15/11/2023	Frozen	15/11/2023	Frozen	15/11/2023	Frozen	15/11/2023
8	14/11/2023	Cold	22/11/2023	Cold	22/11/2023	Cold	22/11/2023
9	14/11/2023	Partially Thawed	Various	Frozen	Various	Frozen	Various
10	14/11/2023	Frozen	21/11/2023	Frozen	21/11/2023	Frozen	21/11/2023
11	15/11/2023	Frozen	24/11/2023	Frozen	24/11/2023	NA	NA
12	16/11/2023	NA	NA	Frozen	14/12/2023	NA	NA
13	17/11/2023	Frozen	21/11/2023	Cold	21/11/2023	Frozen	21/11/2023
14	14/11/2023	Partially Frozen	30/11/2023	NA	NA	NA	NA
15	14/11/2023	Frozen	15/11/2023	NA	NA	NA	NA
16	14/11/2023	NA	NA	Not Given	NA	NA	NA
17	14/11/2023	Frozen	20/11/2023	Frozen	20/11/2023	NA	NA
18	15/11/2023	NA	NA	Frozen	NA	NA	NA

NA = Not Applicable.

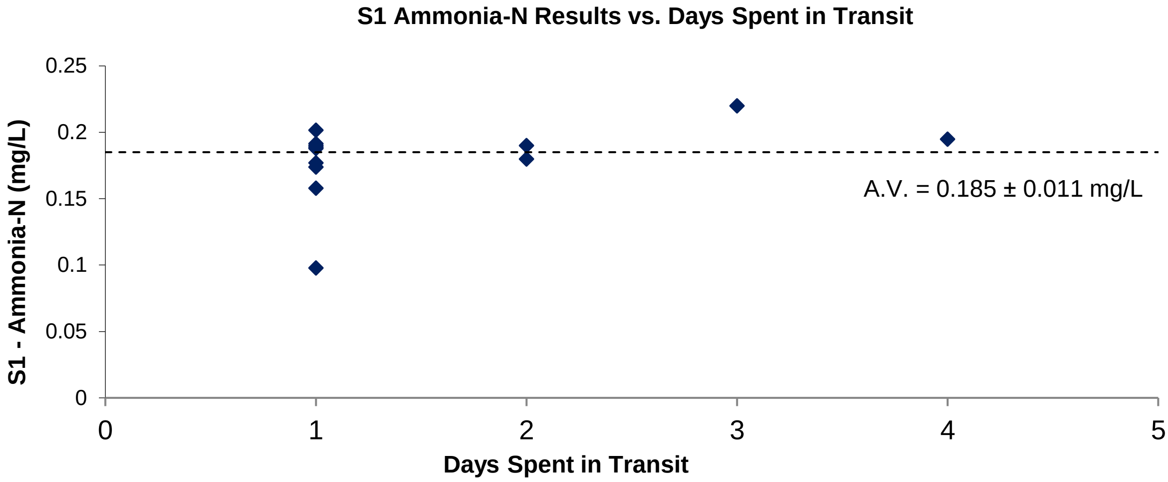
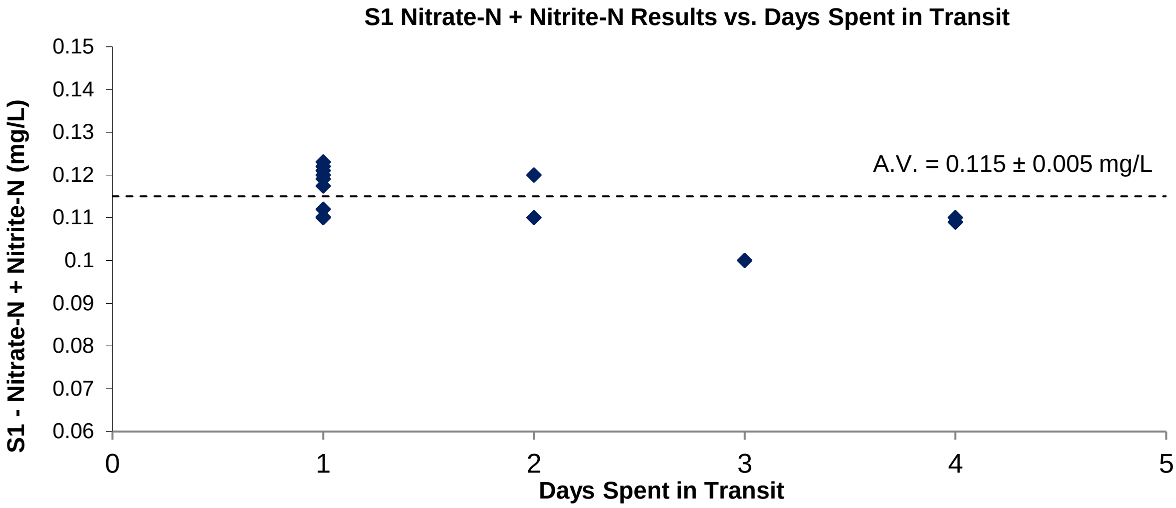
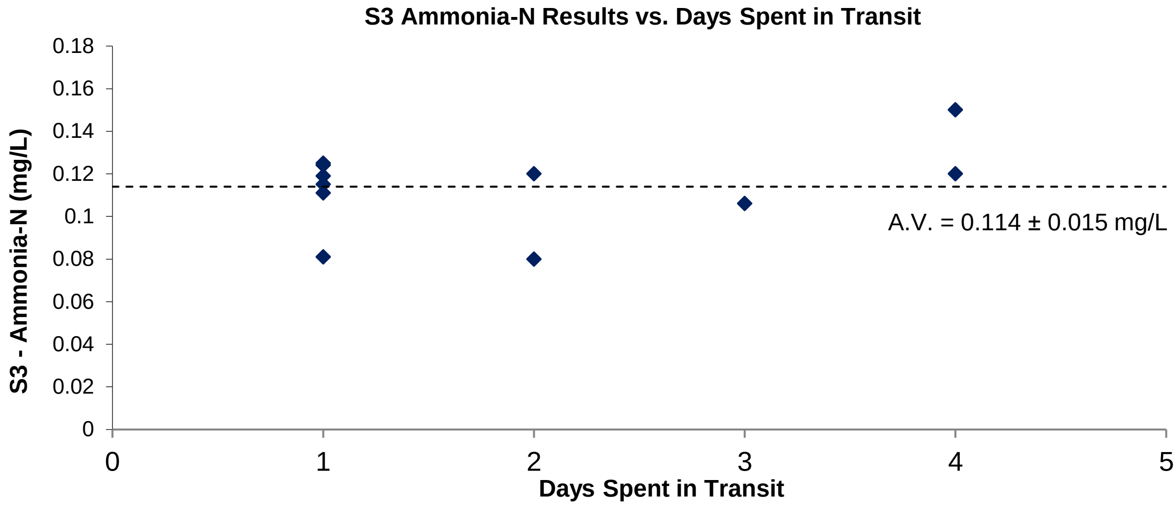
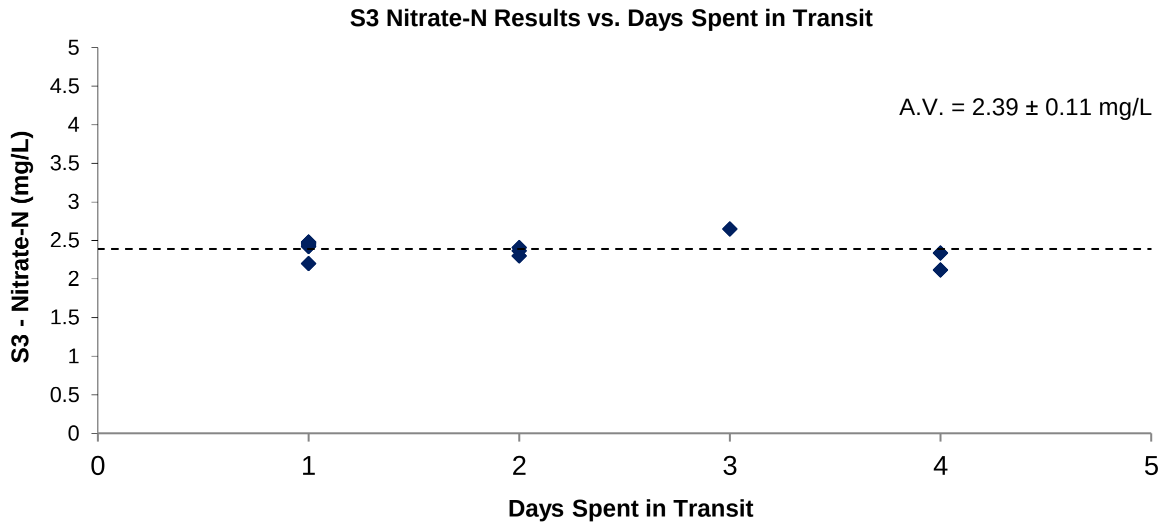


Figure 71 Results vs Days Spent in Transit (continued)







Laboratory 3's result of 2368 mg/L was plotted with correct units.

Figure 71 Results vs Days Spent in Transit (continued)

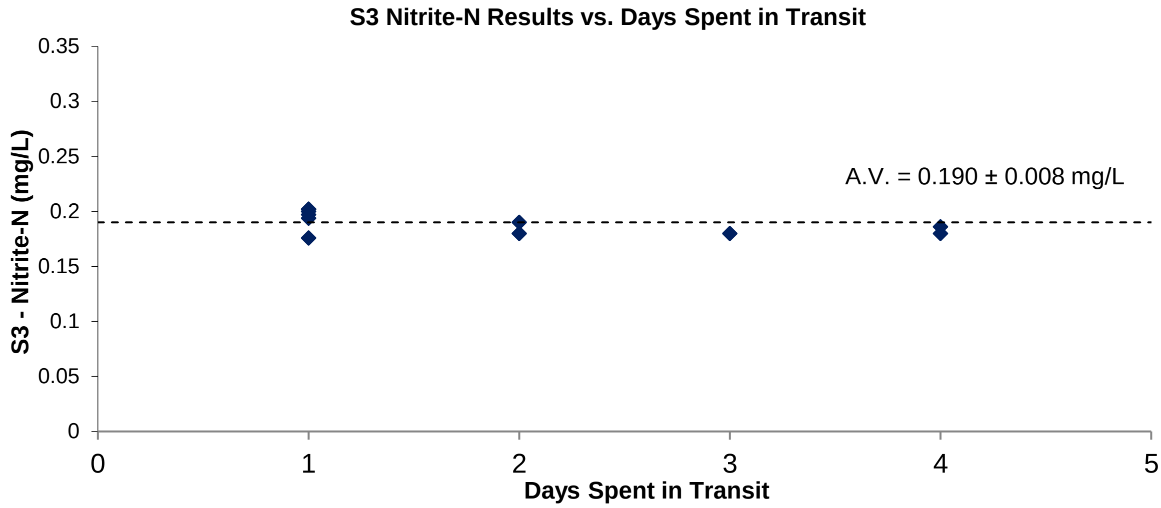
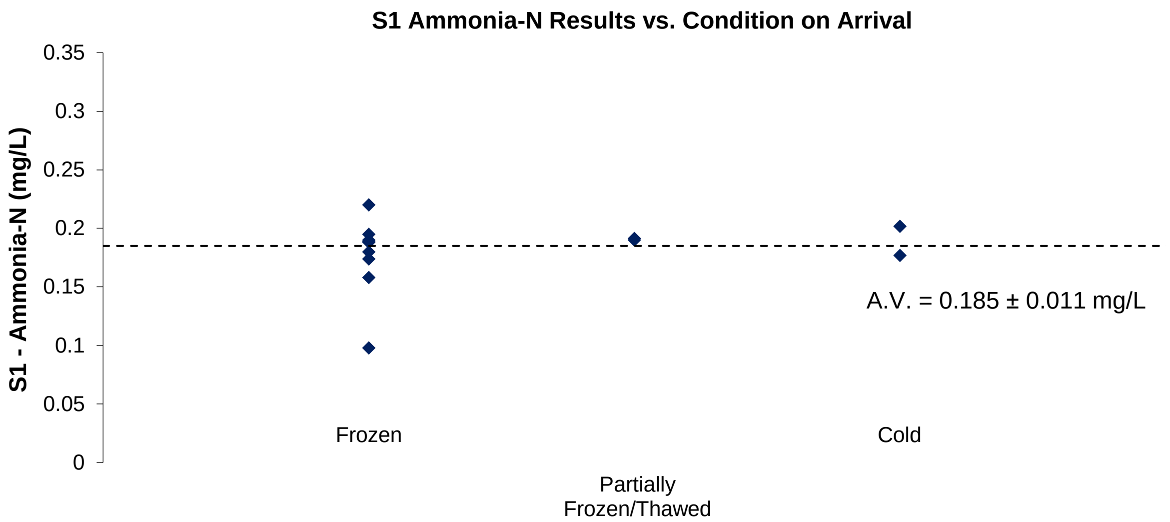


Figure 71 Results vs Days Spent in Transit (continued)



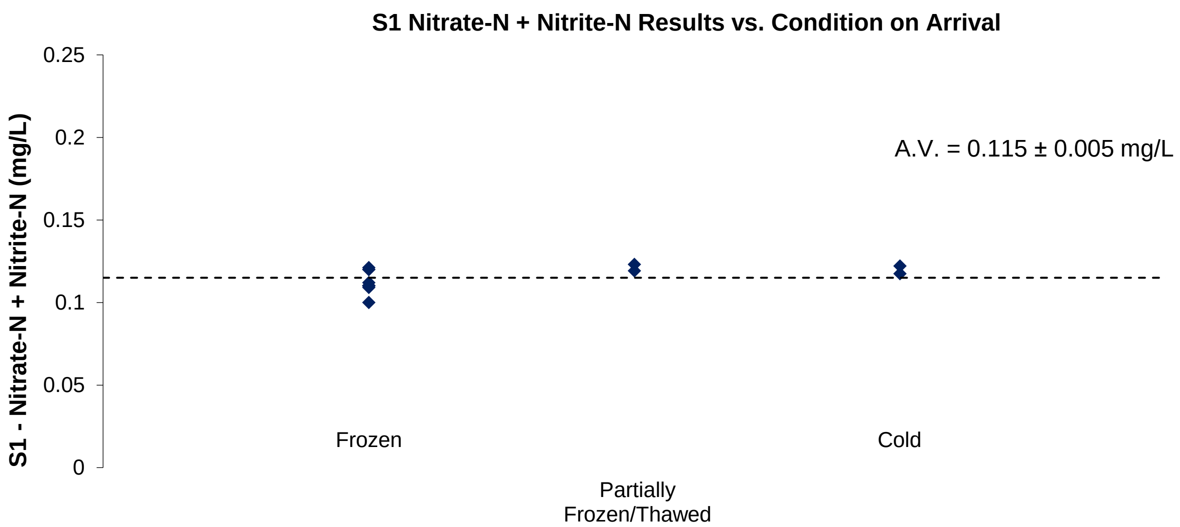
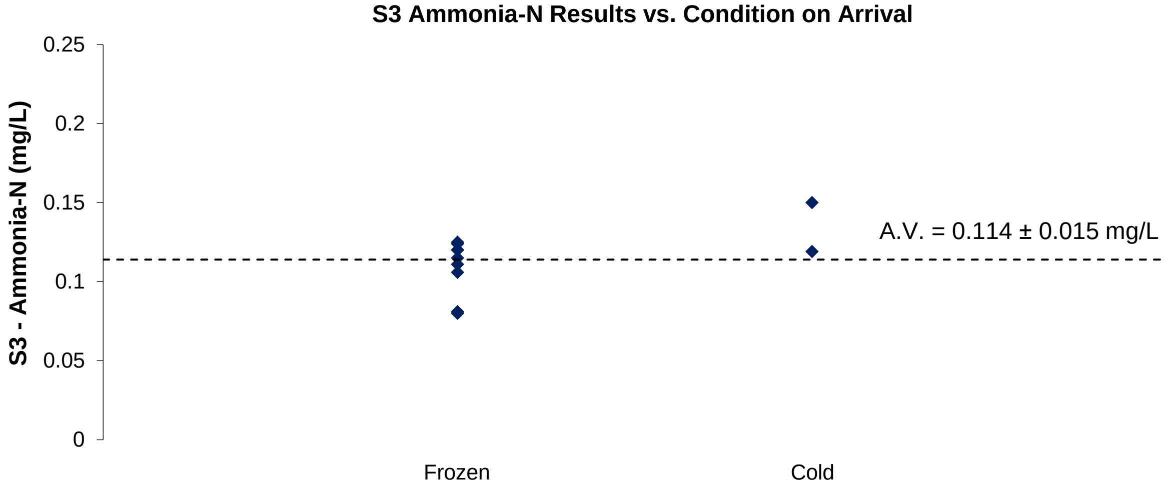
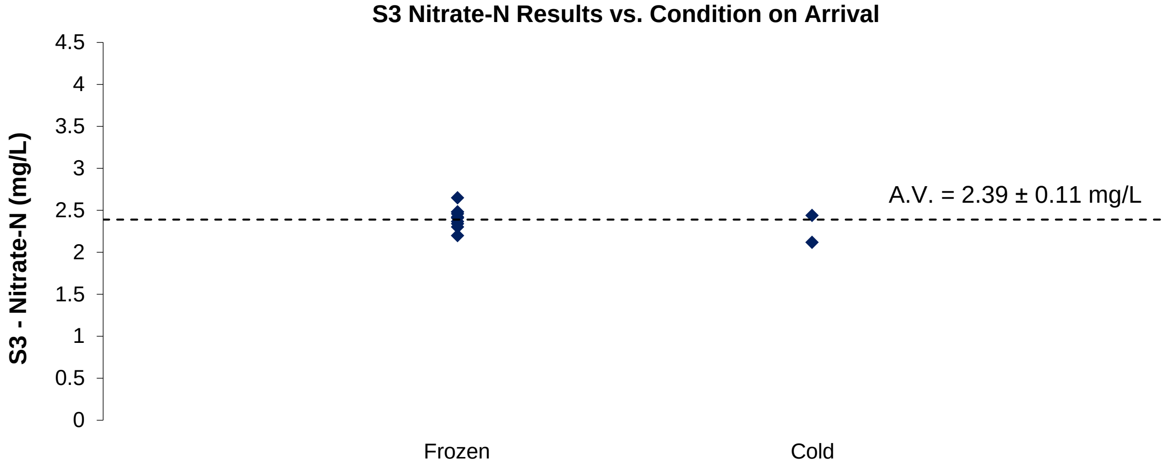


Figure 72 Results vs Condition on Arrival





Laboratory 3's result of 2368 mg/L was plotted with correct units.

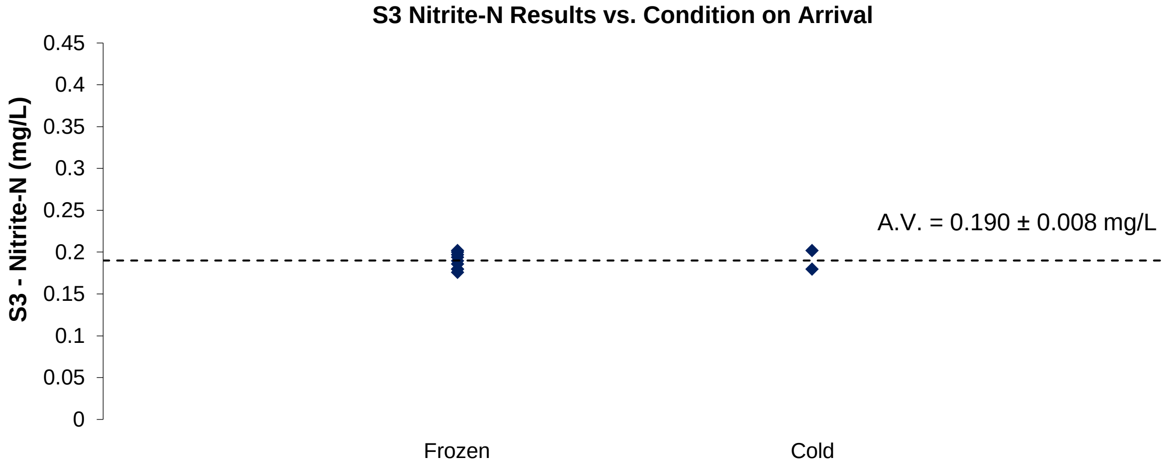


Figure 72 Results vs Condition on Arrival (continued)

In the previous study of ammonia and NOx-N in water AQA 21-19 one set of samples spent eight days in transit. To assess analytes' stability during transport, results from the "transport set of samples" with eight days in transit (T8) were compared with results from a set of samples sent to the same laboratory but with only two days in transit (T2). The results from this study are presented in Figure 73. The two sets of results were in good agreement with each other within their stated uncertainties.[18]

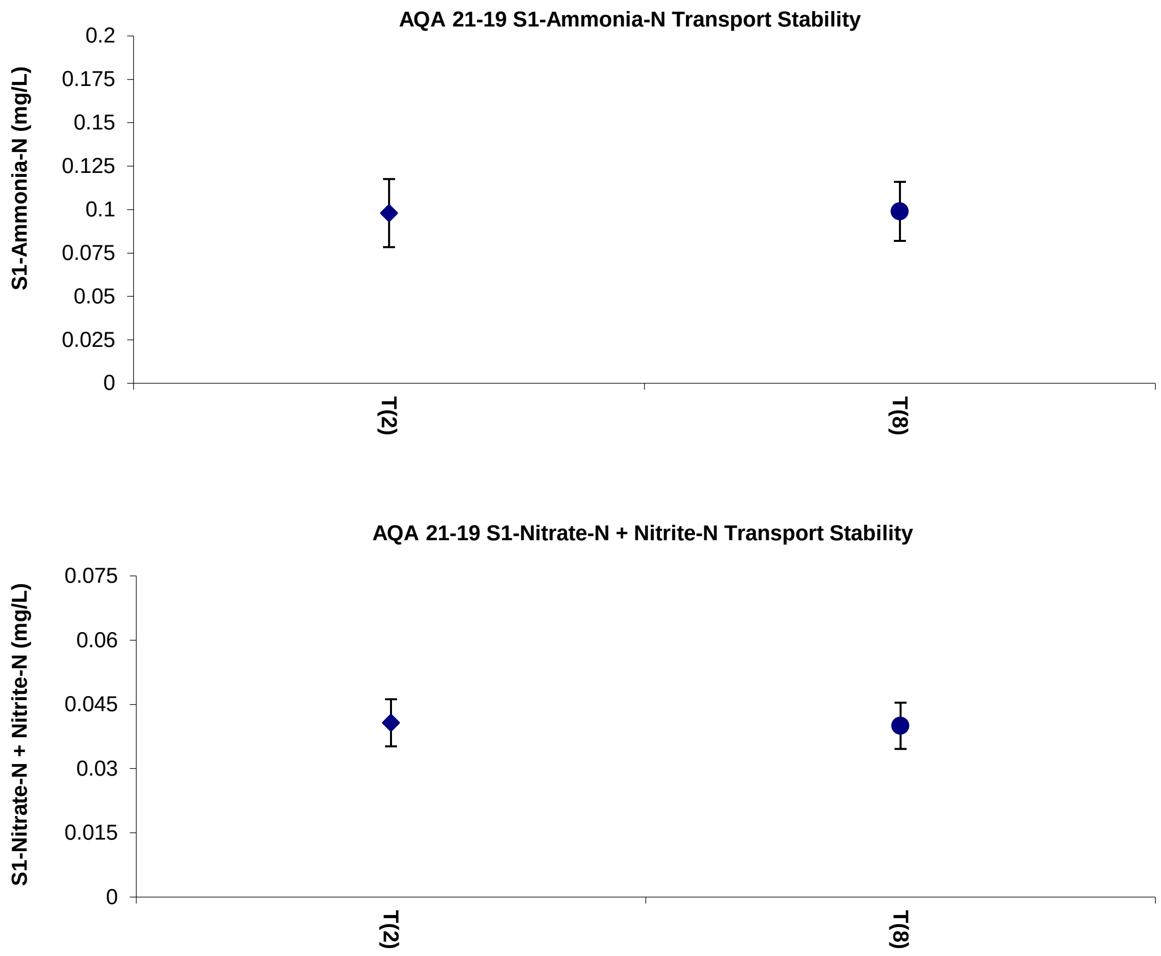


Figure 73 AQA 21-19 Transport Stability Results

Stability Study

In previous PT studies, stability studies conducted for nutrients and physical tests in water found no significant changes in any of the analytes' concentrations. A stability study was however conducted in the present study for the less stabile analytes: Ammonia-N and Nitrate-N + Nitrite-N in the low level water sample S1.

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

To check sample stability during the study, a comparison was conducted of the results from samples analysed before the samples' dispatch (T0) versus those analysed at the end of the study, after submission of results (T1). Each sample was analysed in duplicate together with a set of quality control samples consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes. Results from both studies were in good agreement with each other and the assigned value were within their stated uncertainties (Figure 74).

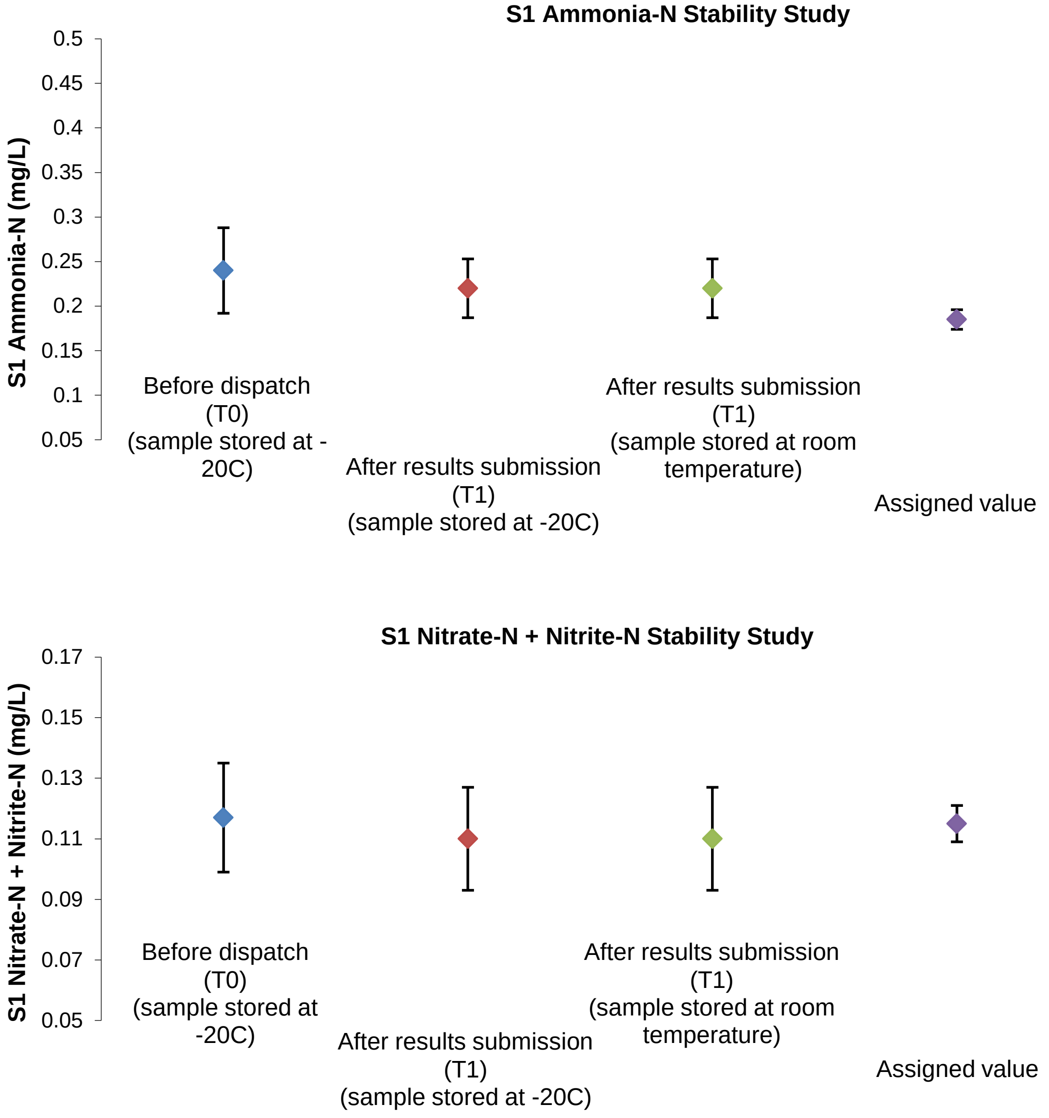


Figure 74 Stability Study Results

Participant's results, and the low between laboratory CV gave no indication of any possible issues with stability of these analyes in any of the study's samples.

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

The assigned value was calculated as the robust average using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] The uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 51.

Table 51 Uncertainty of Assigned Value for Ammonia-N in Sample S1

No. results (p)	13
Robust Average	0.185 mg/L
$S_{rob\ av}$	0.016 mg/L
$u_{rob\ av}$	0.0055 mg/L
k	2
$U_{rob\ av}$	0.011 mg/L

The assigned value for **Ammonia-N** in Sample S1 is **0.185 ± 0.011 mg/L.**

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 2 and Equation 3 respectively (see page 9).

A worked example is set out below in Table 52.

Table 52 z-Score and E_n-score for Ammonia-N result reported by Laboratory 4 in S1

Result mg/L	**Assigned Value mg/L**	**Set Target Standard Deviation**	**z-Score**	**E_n-Score**
0.195 ± 0.031	0.185 ± 0.011	15% as CV or 0.15 x 0.185 = =0.028 mg/L	$z = \frac{(0.195 - 0.185)}{0.028}$ z = 0.36	$En = \frac{(0.195 - 0.185)}{\sqrt{0.031^2 + 0.011^2}}$ E_n= 0.30

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10, 12] An example is given in Table 53. Between 2014 and 2023, NMI carried out 17 proficiency tests for nutrients, anions and physical tests in water. These studies involved measurements of these analytes in potable, fresh (river), waste and seawater.

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

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

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 14-19	Potable	51.9 ± 10	55.4 ± 1.4	2.9	8
AQA 15-18	River	65.7 ± 10	70.3 ± 3.6	6.5	10
AQA 18-05	River	68 ± 8.0	71.3 ± 1.5	3.4	17
AQA 19-07	River	57.0 ± 12	53.7 ± 2.0	4.7	10
AQA 20-08	Potable	33.4 ± 7.0	41.6 ± 1.9	6.7	13
AQA 21-10	River	81 ± 10	86.3 ± 2.7	5.7	20
AQA 22-11	Potable	22.3 ± 5.0	25.5 ± 0.8	5.5	19
AQA 22-18	River	60 ± 10	62.3 ± 1.5	4.1	19
AQA 23-12	Waste	152 ± 20	142 ± 6	6.3	16
AQA 23-19	River	39.8 ± 4.5	39.8 ± 2.6	8.7	11
Average				5.4**	

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

Table 54 Laboratory X Reported Results for Chloride at 1000 - 30000 mg/L Level

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 16-03	Waste	3099 ± 320	2990 ± 170	6.3	8
AQA 17-16	Sea	13100 ± 1300	12800 ± 420	4.1	10
AQA 18-16	Sea	16600 ± 1600	17300 ± 1600	13	13
AQA 19-25	Sea	20000 ± 2000	20500 ± 1000	2.2	13
AQA 20-17	Sea	9800 ± 980	10700 ± 400	4.9	10
AQA 21-19	Sea	19440 ± 1950	20100 ± 600	3.8	9
AQA 22-18	Sea	14073 ± 1400	13800 ± 500	5.3	14
AQA 23-19	Sea	17132 ± 1750	16800 ± 500	4.2	12
Average				5.4**	

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

Taking the average of the robust CV over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 5.4% and 5.4% respectively. Using a coverage factor of two gives a relative expanded uncertainty of 11% for both ranges, at a level of confidence of approximately 95%.

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

Table 55 Uncertainty of Chloride results estimated using PT data

Results mg/L	Uncertainty mg/L
20.0	2.2
500	55
1000	110
15000	1700
30000	3300

The MU estimates made using PT data is close to Laboratory X's own uncertainty estimates reported with their PT results. The estimate of 11% passes the test of being reasonable, and the analysis of the four different matrices over seven 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
CRM	Certified Reference Material
CV	Coefficient of Variation
CV_{rob}	Robust Coefficient of Variation
DA	Discrete Analyser
dNPOC	Dissolved non-purgeable organic carbon
FIA	Flow Injection Analyser
GUM	Guide to the Expression of Uncertainty in Measurement
H.V.	Homogeneity Value
ICP-MS	Inductively Coupled Plasma – Mass 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
ISE	Ion Selective Electrode
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
LOR	Limit of Reporting
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MU	Measurement Uncertainty
N	Number of Participants
NATA	National Association of Testing Authorities
NEDD	N-(1-naphthyl)-ethylenediamine dihhydrochloride (NED dihydrochloride)
NIR-Detector	Near-infrared Detector
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
OPA	o-Phthalaldehyde
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PFAS	Polyfluoroalkyl Substances
PT	Proficiency Test
R.A.	Robust Average
RM	Reference Material
SD_{rob}	Robust Standard Deviation
SFA	Segment Flow Analyser
SI	The International System of Units
SS	Spiked Sample
S.V.	Spiked or formulated concentration of a PT sample
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation (symbol: σ)
UV-Vis	Ultraviolet -visible spectroscopy

APPENDIX 6 - METHODOLOGY FOR S1

Table 56 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Phenate Method	FIA	APHA 4500-NH3
2	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
3	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-NH3 D
4	Colorimetric - Salicylate Method	FIA	EK255A
5	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
6	Colorimetric - Phenate Method	FIA	in house
7	Colorimetric - Salicylate Method	FIA	APHA 4500-NH3 H (EN/EK055A)
8	Colorimetric - Phenate Method	FIA	
9	Colorimetric - Phenate Method	FIA	Inhouse
10	Colorimetric - Phenate Method	DA	In house
11	Colorimetric - Phenate Method	FIA	APHA
13	Colorimetric - Salicylate Method	DA	QWI-EN.WK055G
14	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
15	Colorimetric - Salicylate Method	DA	APHA4500NH3
17	Colorimetric - Phenate Method	FIA	APHA4500-NH3

Table 57 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl-
3	Ion Chromatographic Method	IC	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
5	Mercuric Thiocyanate	DA	APHA 4500 Cl - E
6	Mercurric Nitrate Titration	Manual Analysis	in house
7	Argentometric Titration	Auto Titration	APHA, 4500-Cl- B (EN/ED045)
8	ICP-Method	ICP-MS	In house W33
9	Ferricyanide Colorimetric Method	FIA	Inhouse
10	Mercuric Thiocyanate	DA	In house
13	Ferricyanide Colorimetric Method	DA	QWI-EN.WD045G
15	Mercuric Thiocyanate	DA	APHA4500Cl-
17	Ion Chromatographic Method	IC	APHA4110B(modified)

Table 58 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	APHA 5310
4	High-Temperature Oxidation	NIR-detector	EP002
5	High-Temperature Oxidation	NIR-detector	APHA 5310 B
6	High-Temperature Oxidation	NIR-detector	in house
8	High-Temperature Oxidation	NDIR-detector	
9	High-Temperature Oxidation	NIR-detector	Inhouse
10	High-Temperature Oxidation	NIR-detector	In house
13	High-Temperature Oxidation	NIR-detector	QWI-EN.WP005SF002SF
15	High-Temperature Oxidation	NIR-detector	APHA5310B
17	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA5310C(modified)

Table 59 Measurement Methods and Instrument Techniques for Fluoride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F-
3	Ion Chromatographic Method	IC	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
5	Ion Selective Electrode Method	Auto Titration	APHA 4500-F C
6	Ion Selective Electrode Method	Ion Selective Electrode	in house
7	Ion Selective Electrode Method	Ion Selective Electrode	APHA, 4500-F- A,C (CEN/EK040&P)
8	Ion Selective Electrode Method	Ion Selective Electrode	
9	Ion Selective Electrode Method	Ion Selective Electrode	Inhouse
10	Ion Selective Electrode Method	Ion Selective Electrode	In house
13	Ion Selective Electrode Method	Ion Selective Electrode	QWI-EN.WK040LL
15	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500F
17	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500-F-C

Table 60 Measurement Methods and Instrument Techniques for NOx

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric -vanadium III method	DA	NEMI 9171
2	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
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	EK025A
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3- I
6	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	in house
7	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA, 4500-NO3 - A, E, I (EN/EK059A)
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
9	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Inhouse
10	Colorimetric -vanadium III method	DA	In house
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
13	Colorimetric-Sulfanilamide-NEDD hydrazine reduction	DA	QWI-EN.EK057G
14	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
15	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO32
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA-4500NO3(modified)

Table 61 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
2	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
4	Ascorbic Acid Colorimetric Method	FIA	EK271A
5	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P E
6	Ascorbic Acid Colorimetric Method	FIA	in house
7	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P A,B,E (EN/EK071A)
8	Ascorbic Acid Colorimetric Method	FIA	
9	Ascorbic Acid Colorimetric Method	FIA	Inhouse
10	Ascorbic Acid Colorimetric Method	DA	In house
11	Ascorbic Acid Colorimetric Method	FIA	APHA
13	Ascorbic Acid Colorimetric Method	DA	QWI-EN.WK071G
14	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
15	Vanadomolybdophosphoric Colorimetric Method	DA	APHA4500P
17	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PG

Table 62 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1	Turbidimetric Method	DA	APHA 4500-SO4
3	Ion Chromatographic Method	IC	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
5	Turbidimetric Method	DA	APHA 4500-SO4
6	ICP Method	ICP-MS	in house
7	Turbidimetric Method	FIA	APHA, 4500-SO4 2- (EN/ED041A)
8	ICP Method	ICP-MS	In House W32
9	Turbidimetric Method	FIA	Inhouse
10	Turbidimetric Method	DA	In house
12	Barium Sulfate method		APHA
13	Turbidimetric Method	DA	QWI-EN.WD041G
15	ICP Method	ICP-OES	APHA3120B
17	Ion Chromatographic Method	IC	APHA4110B(modified)

Table 63 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	APHA 4500-N
4	Persulfate digestion	FIA	EK262P-F
5	Persulfate digestion	FIA	APHA, 4500-N C
6	Persulfate digestion	FIA	in house
8	Persulfate digestion	FIA	
9	Persulfate digestion	FIA	Inhouse
10	Calculation (TKN+NOx)	Not Applicable	In house
11	Persulfate digestion	FIA	APHA
13	Calculation (TKN+NOx)	DA	QWI-EN.WK062
15	Persulfate digestion	Not Applicable	N/A
17	Calculation (TKN+NOx)		Inhouse

Table 64 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
4		Ascorbic Acid Colorimetric Method	FIA	EK267PA-F
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P J
6	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
7	Ammonium persulfate and concentrated sulfuric acid	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P H (EN/EK067A)
8	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
9	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
10	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house
11	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
13		Other (please type)	FIA	QWI-EN.WK061A
15	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA1500P
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PH

APPENDIX 7 - METHODOLOGY FOR S2

Table 65 Instrument Techniques for Boron

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	249.773nm
3	ICP-MS	Sc	CRI	He	100	
4	ICP-MS	SC,Rh,Ir	ORS	He	10	NA
5	ICP-MS	Sc	ORS	He	x1	11
8	ICP-MS	Sc	NA	NA	1	10
9	ICP-OES-AV-buffer	Lu			1	249.678
10	ICP-OES-AV	Eu				249.773
13	ICP-MS	Ga,Ge,Ph,Ir.	NA	He	10	11
15	ICP-OES-AV	Yb	NA		10	249.772nm

Table 66 Instrument Techniques for Calcium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	315.887, 370.602nm
3	ICP-MS	Sc	CRI	He	100	
4	ICP-MS	SC,Rh,Ir	ORS	He	10	NA
5	ICP-MS	Sc	ORS	He	x5	44
8	ICP-MS	Sc	UC	He	1	44
9	ICP-OES-AV-buffer	Lu			1	430.253
10	ICP-OES-AV	Eu				315.885
13	ICP-OES	Cs,Y	NA	NA	10	370.602
15	ICP-OES-AV	Yb	NA		10	317.93nm

Table 67 Instrument Techniques for Potassium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	404.721nm, 766.491nm
3	ICP-MS	Sc	CRI	He	100	
4	ICP-MS	SC,Rh,Ir	ORS	He	10	NA
5	ICP-MS	Sc	ORS	He	x5	39
8	ICP-MS	Sc	UC	He	1	39
9	ICP-OES-AV-buffer	Lu			1	766.491
10	ICP-OES-AV	Eu				766.485
13	ICP-OES	Cs,Y	NA	NA	10	766.491
15	ICP-OES-AV	Yb	NA		10	769.897nm

Table 68 Instrument Techniques for Magnesium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	383.830 (nm)
3	ICP-MS	Sc	CRI	He	100	
4	ICP-MS	SC,Rh,Ir	ORS	He	10	NA
5	ICP-MS	Sc	ORS	He	x5	24
8	ICP-MS	Sc	UC	He	1	25
9	ICP-OES-AV-buffer	Lu			1	279.078
10	ICP-OES-AV	Eu				383.83
13	ICP-OES	Cs,Y	NA	NA	100	285.213
15	ICP-OES-AV	Yb	NA		10	383.23nm

Table 69 Instrument Techniques for Sodium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	330.237, 589.592nm
3	ICP-MS	Sc	CRI	He	100	
4	ICP-MS	SC,Rh,Ir	ORS	He	10	NA
5	ICP-MS	Sc	ORS	He	x5	23
8	ICP-MS	Sc	UC	He	1	23
9	ICP-OES-AV-buffer	Lu			1	589.592
10	ICP-OES-AV	Eu				589.593
13	ICP-OES	Cs,Y	NA	NA	100	330.237
15	ICP-OES-AV	Yb	NA		10	330.23nm

Table 70 Measurement Methods and Instrument Techniques for Alkalinity

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	APHA 2320
3	Titration	Manual Analysis	APHA 2320-Alkalinity
4	Titration	Auto Titration	APHA
5	Titration	Auto Titration	APHA 2320 B
7	Titration	Auto Titration	APHA, 2320-Alkalinity – B (EN/ED036-037&P)
8	Titration	Auto Titration	
9	Titration	Manual Analysis	Inhouse
10	Titration	Auto Titration	In house
13	Titration	Ion Selective Electrode	QWI-EN.WD037
15	Titration	Ion Selective Electrode	APHA2320
17	Titration	Auto Titration	APHA2320B modified

Table 71 Measurement Methods and Instrument Techniques for Silica

Lab. Code	Measurement Method	Instrument	Method Reference
1	Molybdosilicate Method	DA	APHA 2120
2	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
4	ICP-Method	ICP-OES	APHA
5	Heteropoly Blue Method	DA	APHA, 4500- SiO2 D
7	Molybdosilicate Method	Manual Analysis	APHA, 4500-SiO2 F (EN/EG052A)
8	ICP-Method		
10	Heteropoly Blue Method	DA	In house
11	Molybdosilicate Method	FIA	APHA
13	Molybdosilicate Method	DA	
14	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
15	ICP-Method	ICP-OES	APHA3120B
17	Molybdosilicate Method	FIA	APHA4500-SiO2Fmodified

Table 72 Measurement Methods and Instrument Techniques for Total Hardness

Lab. Code	Measurement Method	Instrument	Method Reference
1	Calculation	ICP-OES	APHA 2340
3	Calculation	ICP-MS	APHA 2340 B-Hardness
4	Calculation	Auto Titration	APHA
5	Calculation	Not Applicable	APHA 2340 A and B
8	Titration	Manual Analysis	
10	Calculation	ICP-OES	In house
13	Calculation	ICP-OES	
15	Calculation	Not Applicable	APHA2340B

APPENDIX 8 – METHODOLOGY FOR S3

Table 73 Instrument Techniques for Boron

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	249.773nm
3	ICP-MS	Sc	CRI	He	1	
4	ICP-MS	Sc	ORS	He	1	11
5	ICP-MS	Sc	ORS	NA	x1	11
6	ICP-MS/MS					
8	ICP-MS	Sc	NA	NA	1	10
9	ICP-OES-AV-buffer	Lu			1	249.678
10	ICP-OES-AV	Eu				249.773
13	ICP-MS	Ga,Ge,Ph,Ir.	NA	He	10	11

Table 74 Instrument Techniques for Calcium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	315.887, 370.602nm
3	ICP-MS	Sc	CRI	He	1	
4	ICP-MS	Sc	ORS	He	1	44
5	ICP-MS	Sc	ORS	He	x1	44
6	ICP-MS/MS					
8	ICP-MS	Sc	UC	He	1	44
9	ICP-OES-AV-buffer	Lu			1	430.253
10	ICP-OES-AV	Eu				315.885
13	ICP-OES	Cs,Y	NA	NA	1	370.602

Table 75 Instrument Techniques for Potassium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	404.721nm, 766.491nm
3	ICP-MS	Sc	CRI	He	1	
4	ICP-MS	Sc	ORS	He	1	39
5	ICP-MS	Sc	ORS	He	x1	39
6	ICP-MS/MS					
8	ICP-MS	Sc	UC	He	1	39
9	ICP-OES-AV-buffer	Lu			1	766.491
10	ICP-OES-AV	Eu				766.485
13	ICP-OES	Cs,Y	NA	NA	1	766.491

Table 76 Instrument Techniques for Magnesium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	383.830 (nm)
3	ICP-MS	Sc	CRI	He	1	
4	ICP-MS	Sc	ORS	He	1	24
5	ICP-MS	Sc	ORS	He	x1	24
6	ICP-MS/MS					
8	ICP-MS	Sc	UC	He	1	25
9	ICP-OES-AV-buffer	Lu			1	279.078
10	ICP-OES-AV	Eu				383.83
13	ICP-OES	Cs,Y	NA	NA	1	285.213

Table 77 Instrument Techniques for Sodium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES	Eu & Cs	NA	NA	1	330.237, 589.592nm
3	ICP-MS	Sc	CRI	He	1	
4	ICP-MS	Sc	ORS	He	1	23
5	ICP-MS	Sc	ORS	He	x1	23
6	ICP-MS/MS					
8	ICP-MS	Sc	UC	He	1	23
9	ICP-OES-AV-buffer	Lu			1	589.592
10	ICP-OES-AV	Eu				589.593
13	ICP-OES	Cs,Y	NA	NA	1	330.237

Table 78 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Phenate Method	FIA	APHA 4500-NH3
3	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-NH3 D
4	Colorimetric - Salicylate Method	FIA	EK255A
5	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
6	Colorimetric - Phenate Method	FIA	in house
7	Colorimetric - Salicylate Method	FIA	APHA 4500-NH3 H (EN/EK055A)
8	Colorimetric - Phenate Method	FIA	
9	Colorimetric - Phenate Method	FIA	Inhouse
10	Colorimetric - Phenate Method	DA	In house
11	Colorimetric - Phenate Method	FIA	APHA
13	Colorimetric - Salicylate Method	DA	QWI-EN.WK055G
17	Colorimetric - Phenate Method	FIA	APHA4500-NH3

Table 79 Measurement Methods and Instrument Techniques for Bromide

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA 4110
3	Ion Chromatographic Method	IC	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
8	ICP Method	ICP-MS	
13	Ion Chromatographic Method	Ion Selective Electrode	
17	Ion Chromatographic Method	IC	APHA4110B(modified)

Table 80 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl-
3	Ion Chromatographic Method	IC	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
5	Mercuric Thiocyanate	DA	APHA 4500 Cl - E
6	Mercurric Nitrate Titration	Manual Analysis	in house
7	Argentometric Titration	Auto Titration	APHA, 4500-Cl- B (EN/ED045)
8	ICP-Method	ICP-MS	In house W33
9	Ferricyanide Colorimetric Method	FIA	Inhouse
10	Mercurric Nitrate Titration	DA	In house
12	Argentometric Titration	Manual Analysis	APHA
17	Ion Chromatographic Method	IC	APHA4110B(modified)

Table 81 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	APHA 5310
4	High-Temperature Oxidation	NIR-detector	EP002
5	High-Temperature Oxidation	NIR-detector	APHA 5310 B
6	High-Temperature Oxidation	NIR-detector	in house
8	High-Temperature Oxidation	NDIR-detector	
9	High-Temperature Oxidation	NIR-detector	Inhouse
10	High-Temperature Oxidation	NIR-detector	In house
17	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA4110B(modified)

Table 82 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	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
5	Ion Selective Electrode Method	Auto Titration	APHA 4500-F C
6	Ion Selective Electrode Method	Ion Selective Electrode	in house
7	Ion Selective Electrode Method	Ion Selective Electrode	APHA, 4500-F- A,C (CEN/EK040&P)
8	Ion Selective Electrode Method	Ion Selective Electrode	
9	Ion Selective Electrode Method	Ion Selective Electrode	Inhouse
10	Ion Selective Electrode Method	Auto Titration	In house
17	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500-F-C

Table 83 Measurement Methods and Instrument Techniques for Iodide

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA 4110
4	Ion Chromatographic Method	IC	ED009X
10	Ion Selective Electrode Method	Manual Analysis	In house

Table 84 Measurement Methods and Instrument Techniques for Nitrate-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric -vanadium III method	FIA	NEMI 9171
3	Ion Chromatographic Method	IC	APHA 411 B
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	EK258A
5	Calculation	FIA	APHA 4500-NO3- I
6	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	in house
7	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA, 4500-NO3- A,E,I (EN/EK058A)
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
9	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Inhouse
10	Colorimetric -vanadium III method	DA	In house
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
17	Calculation		In-house Method

Table 85 Measurement Methods and Instrument Techniques for Nitrite-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric Method	FIA	APHA 4500-NO2-
4	Colorimetric Method	FIA	EK257A
5	Colorimetric Method	FIA	APHA, 4500 - NO2 -
6	Colorimetric Method	FIA	in house
7	Colorimetric Method	FIA	APHA, 4500-NO2- (EN/EK057A)
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
9	Colorimetric Method	FIA	Inhouse
10	Colorimetric Method	DA	In house
11	Colorimetric Method	FIA	APHA
17	Colorimetric Method	FIA	APHA-4500NO3(modified)

Table 86 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
4	Ascorbic Acid Colorimetric Method	FIA	EK271A
5	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P E
6	Ascorbic Acid Colorimetric Method	FIA	in house
7	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P A,B,E (EN/EK071A)
8	Ascorbic Acid Colorimetric Method	FIA	
9	Ascorbic Acid Colorimetric Method	FIA	Inhouse
10	Ascorbic Acid Colorimetric Method	DA	In house
11	Ascorbic Acid Colorimetric Method	FIA	APHA
17	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PG

Table 87 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1	Turbidimetric Method	DA	APHA 4500-SO4
3	Ion Chromatographic Method	IC	APHA 411 B
4	Ion Chromatographic Method	IC	ED009X
5	Turbidimetric Method	DA	APHA 4500-SO4
6	ICP Method	ICP-MS	in house
7	Turbidimetric Method	FIA	APHA, 4500-SO4 2- (EN/ED041A)
8	ICP Method	ICP-MS	In House W32
9	Turbidimetric Method	FIA	Inhouse
10	Turbidimetric Method	DA	In house
12	Other (please type)	Manual Analysis	APHA
17	Ion Chromatographic Method	IC	APHA4110B(modified)

Table 88 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	APHA 4500-N
4	Persulfate digestion	FIA	EK262PA-F
5	Persulfate digestion	FIA	APHA, 4500-N C
6	Persulfate digestion	FIA	in house
8	Persulfate digestion	FIA	
9	Persulfate digestion	FIA	Inhouse
10	Calculation (TKN+NOx)	DA	In house
11	Persulfate digestion	FIA	APHA
17	Calculation (TKN+NOx)		In-house Method

Table 89 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P
4		Ascorbic Acid Colorimetric Method	FIA	EK267PA-F
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P J
6	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
7	Ammonium persulfate and concentrated sulfuric acid	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P H (EN/EK067A)
8	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
9	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
10	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house
11	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PH

APPENDIX 9 – METHODOLOGY FOR S4

Table 90 Measurement Methods and Instrument Techniques for Total Kjeldahl Nitrogen

Lab. Code	Measurement Method		Instrument	Method Reference
1	TKN=TN-NOx (K2S2O8 digestion)	Calculation	FIA	APHA 4500-N
4		Colorimetric - salicylate method	FIA	EK261PA
5	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500-Norg D
7	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric - salicylate method	FIA	APHA, 4500-N Org A,D (EN/EK061)
8	TKN=TN-NOx (K2S2O8 digestion)		FIA	
10	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric -vanadium III method	DA	In house
13	Kjeldahl (H2SO4+K2SO4 digestion)		FIA	WK261 62 67 PSF-A

Table 91 Measurement Methods and Instrument Techniques for Total Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	APHA 4500-N
3	Persulfate digestion	IC	ASTM D8001-16e1
4	Calculation (TKN+NOx)	FIA	EK262PA
5	Calculation (TKN+NOx)	DA	APHA 4500-Norg / 4500-NO3-
7	Persulfate digestion	FIA	APHA, 4500-N C (EN/EK062A)
8	Persulfate digestion	FIA	
9	Persulfate digestion	FIA	Inhouse
10	Calculation (TKN+NOx)	DA	
13	Calculation (TKN+NOx)	DA	EK060 EK063

Table 92 Measurement Methods and Instrument Techniques for Total Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	APHA 5310
4	High-Temperature Oxidation	NIR-detector	EP005
5	High-Temperature Oxidation	NIR-detector	APHA 5310 B
8	High-Temperature Oxidation	NDIR-detector	
9	High-Temperature Oxidation	NIR-detector	Inhouse
10	High-Temperature Oxidation	NIR-detector	In house
13	Persulfate-Ultraviolet Oxidation	SFA	WP005SF002SF

END OF REPORT