Australian Government
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National Measurement Institute

Proficiency Test Final Report AQA 21-19 Nutrients, Anions and Physical Tests in Seawater

March 2022

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

The assistance of the following NMI staff members and collaborators 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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1 SUMMARY

This report presents the results of the proficiency test AQA 21-19, Nutrients, Anions and Physical Tests in Seawater. Measurement of pH at 25ºC, electrical conductivity at 25ºC, alkalinity to pH 4.5 (as $CaCO_3$), ammonia-N, chloride, dissolved organic carbon (as dNPOC), fluoride, orthophosphate-P, sulphate, total hardness (as $CaCO_3$), NOx (nitrate-N + nitrite-N), total dissolved nitrogen, total dissolved phosphorus, total Kjeldahl nitrogen, total nitrogen, total organic carbon (as NPOC), total dissolved solids, total solids, total suspended solids, total P and dissolved B, Ca, K, Mg and Na were included in the program.

Fourteen laboratories registered to participate and all submitted results.

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

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

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

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

Of 180 z-scores, 162 (90%) returned a satisfactory score of $|z| \leq 2.0$.

Of 180 E_n scores, 150 (83%) returned a satisfactory score of $|E_n| \leq 1.0$.

Laboratories 3 and **7** returned the highest number of satisfactory z scores (19 out of 20 reported and 19 out of 19 reported respectively).

Laboratory 7 returned the highest number of satisfactory E_n scores (19 out of 19 reported).

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

Errors in sample preparation and/or standard preparation procedure are still the main causes of poor performance among participants.

The methods used by participants for NO_3-N+NO_2-N measurement in S1 produced accurate results. The results reported for NOx-N in S1 were in excellent agreement with each-other, (with a between laboratory CV of 7.8%).

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

Despite differences in matrices and concentrations, on average, participants' performance remained fairly 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 208 numerical results, 202 (97%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.24% to 350% of the reported value indicating that while most participants have a procedure in place for uncertainty estimation, some are still have problems with reporting realistic estimates of it.

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.

2 INTRODUCTION

2.1 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;
- allergens in food;
- controlled drug assay; and
- folic acid in flour

AQA 21-19 is the 13th NMI proficiency study of nutrients, anions and physical tests in water.

2.2 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 seawater;
- 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.

2.3 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.

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The 25 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.

3.2 Participation

Fourteen laboratories participated and submitted results.

The timetable of the study was:

Invitation issued:	8 November 2021
Samples dispatched:	29 November 2021
Results due:	24 January 2022
Interim report issued:	25 January 2022

3.3 Test Material Specification

Three samples were provided for analysis:

Sample S1 was two identical bottles of 200 mL filtered, autoclaved and frozen seawater;

Sample S2 was 400 mL of unfiltered, autoclaved and frozen seawater; and

Sample S3 was 750 mL of unfiltered low salinity seawater.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 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. No homogeneity test was conducted for B, Na, TDN, TP, TDS, TS and TSS.

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

A stability study was conducted for the less stable analytes (NH_3-N and NO_3-N +NO_2-N in S1 in order to address issues associated with holding time and holding conditions. The stability study, which also included transport samples, was conducted over the entire period of the PT study conduct. The set-up of this study together with the study results are presented in Appendix 2.

3.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were frozen.

The samples were dispatched by courier on 29 November 2021.

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.

3.8 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 and S2 frozen.
- Prior to testing, thaw samples S1 and S2 completely.

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

SAMPLE S1 filtered, seawater		**SAMPLE S2 unfiltered, seawater**		**SAMPLE S3 unfiltered low salinity seawater**	
Test	**Approximate Conc. Range mg/L**	**Test**	**Approximate Conc. Range mg/L**	**Test**	**Approximate Min Conc. mg/L**
Ammonia-N	0.025-0.75	P (total)	<0.5	TS (dried at 103-105°C)	>100
(Nitrate-N +Nitrite-N) NOx as N	0.005-0.125	Total Kjeldahl Nitrogen	0.025-1	TSS (dried at 103-105°C)	>15
Total Dissolved Nitrogen (TDN)	0.005-0.5	Total Nitrogen	0.025-1	TDS (dried at 180°C)	>100
Orthophosphate-P (FRP)	0.005-0.125	Total Organic Carbon	1-25		
Total Dissolved Phosphorus	0.005-0.125	Alkalinity to pH 4.5 as $CaCO_3$	<250		
Dissolved Organic Carbon (as dNPOC)	0.5-25	Total Hardness ($CaCO_3$)	>3000		
Chloride	<50000	pH (at 25°C)	>2.5		
Fluoride	0.25-5	EC (at 25°C)	>30000		
Sulphate	<5000				
B (dissolved)	0.5-15				
Ca (dissolved)	0.5-15				
K (dissolved)	0.5-15				
Mg (dissolved)	0.5-15				
Na (dissolved)	5-150				

NA – Not Available

- 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 e-mail (proficiency@measurement.gov.au) by 14 January 2022.

3.9 Interim Report

An interim report was emailed to participants on 25 January 2022.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for S1, S2 and S3

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

4.2 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
1	Sample S1: Ammonia-N: neat sample overrange for our method. Required 5x dilution with pure water. Methodology for S2: Open cell titration. Based on IOCCP Report No. 8 (2007) Method SOP-3b.
4	Methodology for S1: Fluoride analysed using standard addition.
7	Sample S3: TDS = TS – TSS
9	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 1:6 dilution as would be done on the occasional sample in the higher range. Calibration concentration was as follows: NOX-N (0-0.161 mg/L), PO4-P (0-0.09mg/L) and NH4-N(0-0.028 mg/L)
11	Sample S3: TDS dried to 103-105ºC Methodology for S3: All samples dried at 103-105ºC

4.3 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	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Standard Purity	NMI Uncertainty Course
2	Top Down - reproducibility (standard deviation) from PT studies used directly	Standard deviation from PT studies only Control Samples – RM Duplicate Analysis Instrument Calibration	Instrument Calibration Laboratory Bias from PT Studies	Nordtest Report TR537
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis	CRM	Nordtest Report TR537
4	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – SS Duplicate Analysis		other please type
5	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
6	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis	CRM Instrument Calibration	ISO/GUM

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
			Recoveries of SS Standard Purity	
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
8	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples – CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM
9*	Top Down - precision and estimates of the method and laboratory bias	Control Samples – CRM	CRM	NMI Uncertainty Course
11*	Top Down - precision and estimates of the method and laboratory bias	Control Samples – RM Duplicate Analysis		IANZ Technical Guide
12	Professional Judgment	Control Samples Duplicate Analysis Instrument Calibration	CRM	Eurachem/CITAC Guide
13	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM	Eurachem/CITAC Guide
14	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM

[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
9	Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval)
11	UoM is based on ISO 17025, IANZ Specific Criteria and EURACHEM / CITAC Guide

4.4 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 element 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.	Our study design is based on the most popular methods used by laboratories and on the report format used by the majority. The request in this study was for orthophosphate-P (FRP). Participants are welcome to contact the study coordinator if further clarification is needed. However, as PT is an attempt to assess laboratories' compliance with ISO 17025 (including their ability to report results in the format requested by their client), the study coordinator cannot help participants with their calculations for results conversion.
As mentioned last year, sending the samples on dry ice rather than ice bricks for in particular seawater sample would be a great improvement.	Thank you for your feedback for how to pack our samples. It would be great if we could use dry ice but it is considered a dangerous good and the quotation received from our couriers was prohibitive.

	A “transport stability study” was conducted when we first started running these studies. However for less stable analytes, stability studies are conducted each time.
A separate chilled sample for silicates of seawater would also be great.	Thank you for your suggestions. In our studies, we attempt to give our participants the best value for money. Silica was included in 2021 in AQA 21-10. We will run this test again this year.

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 5 to 29 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 26. An example chart with an interpretation guide is shown in Figure 1.

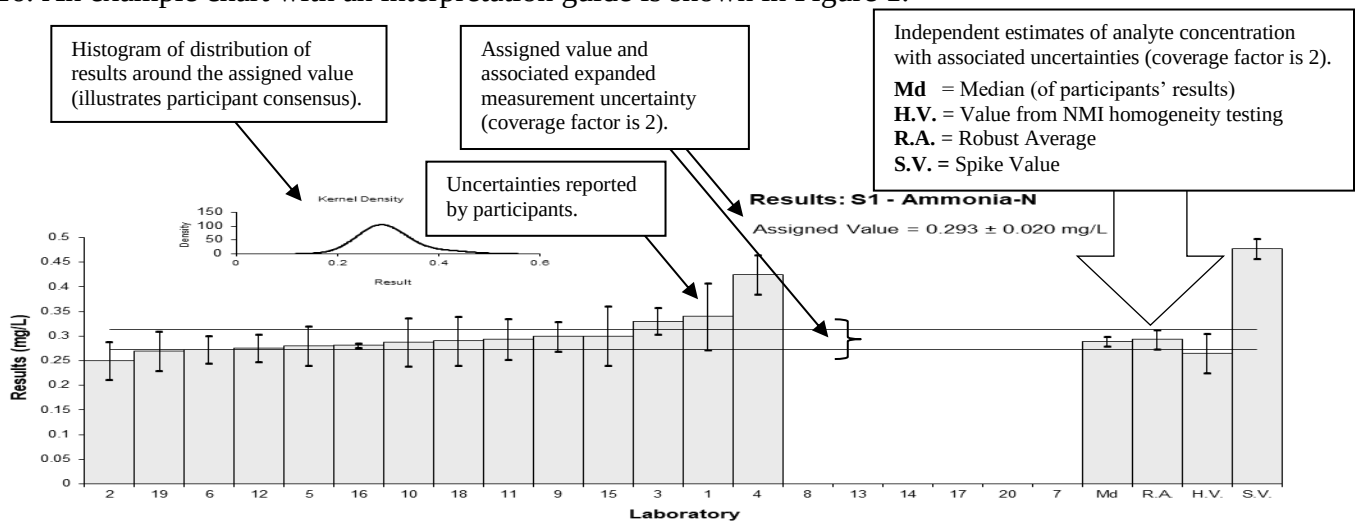


Figure 1 Guide to Presentation of Results

5.2 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 for calculation of summary statistics.[3-4]

5.3 Assigned Value

An example of an 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 concentration of analyte. Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.[4,6]

5.4 Robust Average

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, ISO13528:2015(E)'.[6]

5.5 Robust Between-Laboratory Coefficient of Variation

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 ISO13528:2015(E).[6]

5.6 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value *(X)* and the 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]

5.7 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:

$$z = \frac{(\chi - X)}{\sigma}$$ 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|):

- $|z| \leq 2.0$ is satisfactory;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ is unsatisfactory.

5.8 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:

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}}$$ 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 ($|E_n|$):

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

5.9 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]

6 TABLES AND FIGURES

Table 5

Sample Details

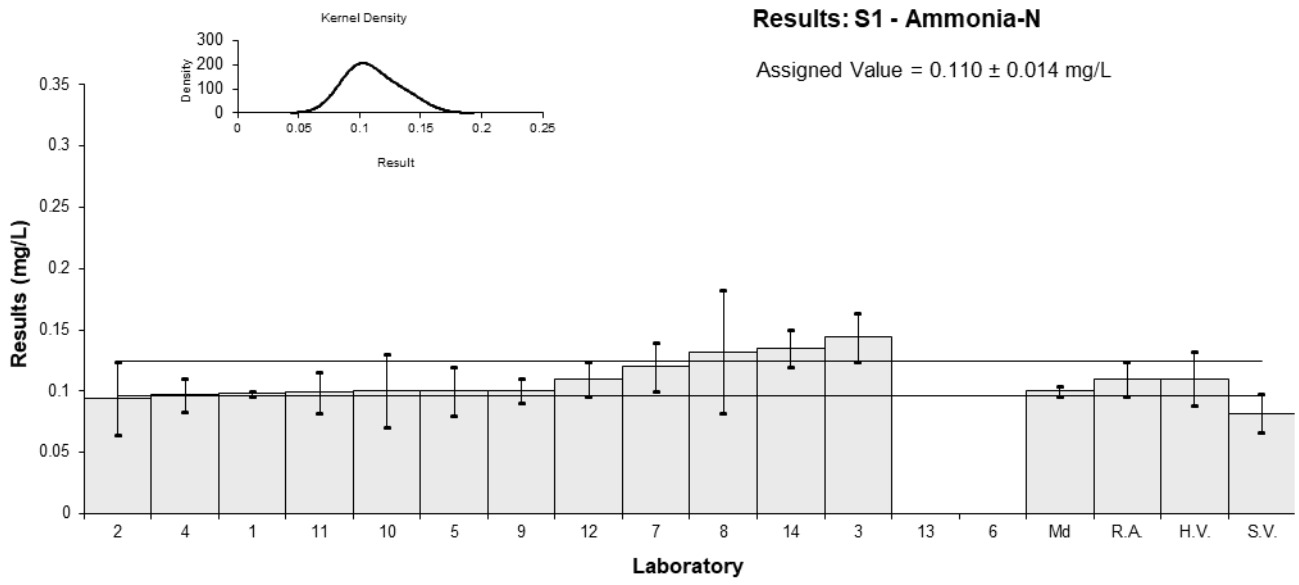
Sample No.	S1
Matrix.	Seawater
Analyte.	Ammonia-N
Units	mg/L

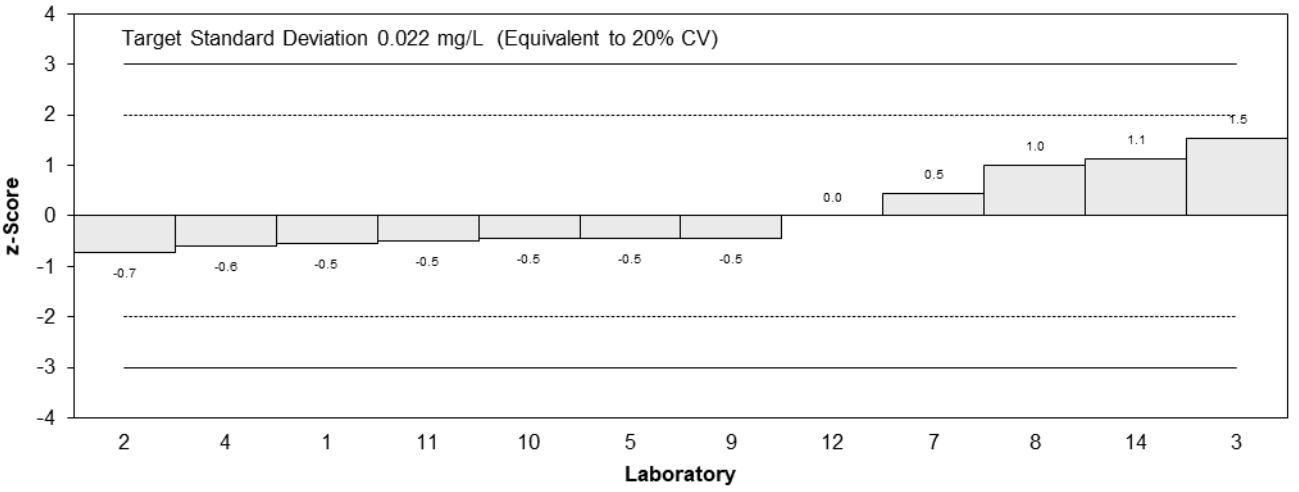
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.098	0.002	-0.55	-0.85
2	0.094	0.03	-0.73	-0.48
3	0.144	0.02	1.55	1.39
4	0.0967	0.0136	-0.60	-0.68
5	0.1	0.02	-0.45	-0.41
6	NT	NT		
7	0.12	0.02	0.45	0.41
8	0.132	0.05	1.00	0.42
9	0.1001	0.01	-0.45	-0.58
10	0.10	0.03	-0.45	-0.30
11	0.099	0.017	-0.50	-0.50
12	0.11	0.014	0.00	0.00
13	NT	NT		
14	0.135	0.015	1.14	1.22

Statistics

Assigned Value	0.110	0.014
Spike	0.082	0.016
Homogeneity Value	0.110	0.022
Robust Average	0.110	0.014
Median	0.100	0.004
Mean	0.111	
N	12	
Max.	0.144	
Min.	0.094	
Robust SD	0.019	
Robust CV	17%	


Kernel Density
Density
Result
Results: S1 - Ammonia-N
Assigned Value = 0.110 ± 0.014 mg/L
Results (mg/L)
Laboratory
2 4 1 11 10 5 9 12 7 8 14 3 13 6 Md R.A. H.V. S.V.


z-Scores: S1 - Ammonia-N
Target Standard Deviation 0.022 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
2 4 1 11 10 5 9 12 7 8 14 3
-0.7 -0.6 -0.5 -0.5 -0.5 -0.5 -0.5 0.0 0.5 1.0 1.1 1.5

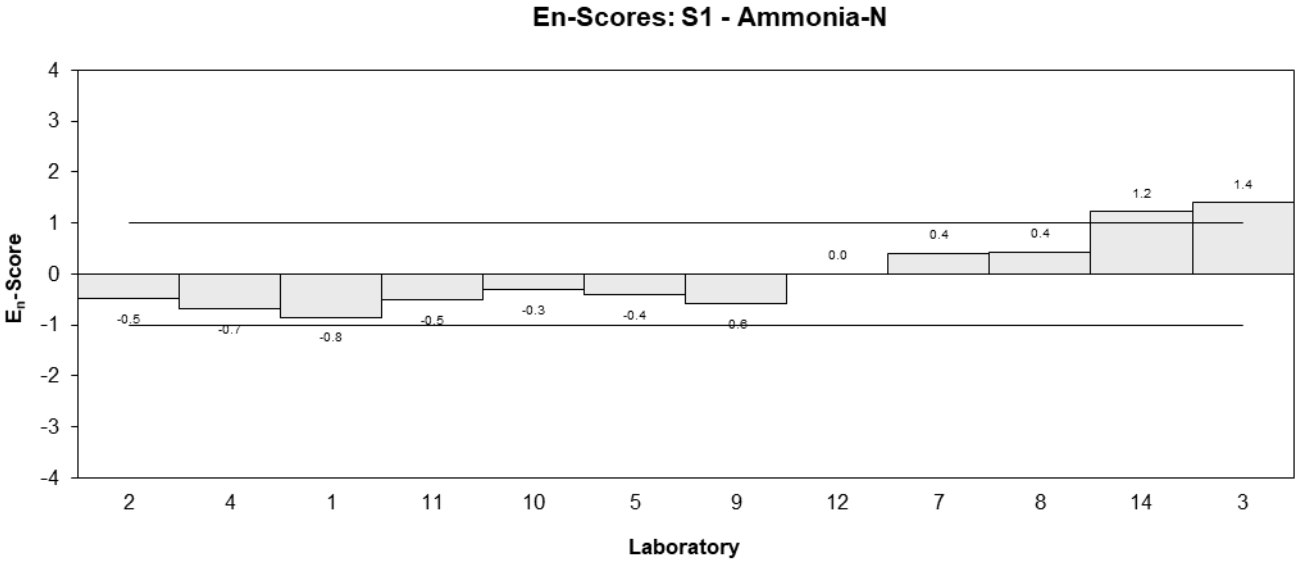

En-Scores: S1 - Ammonia-N
En-Score
Laboratory
2 4 1 11 10 5 9 12 7 8 14 3
-0.5 -0.7 -0.8 -0.5 -0.3 -0.4 -0.6 0.0 0.4 0.4 1.2 1.4

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	B
Units	mg/L

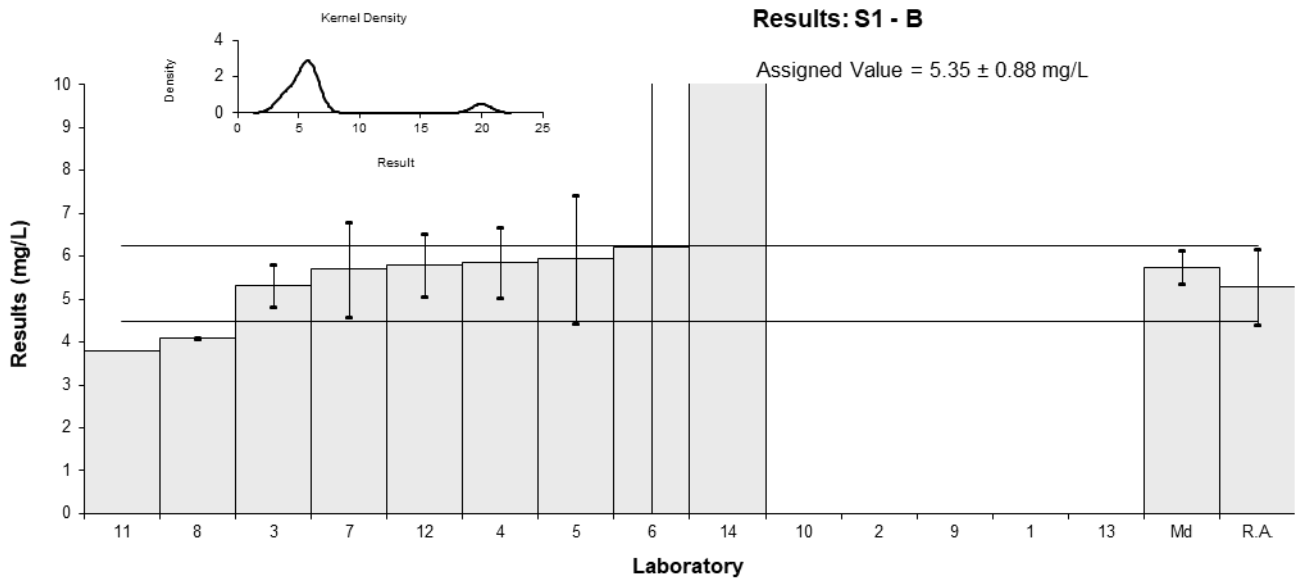
Participant Results

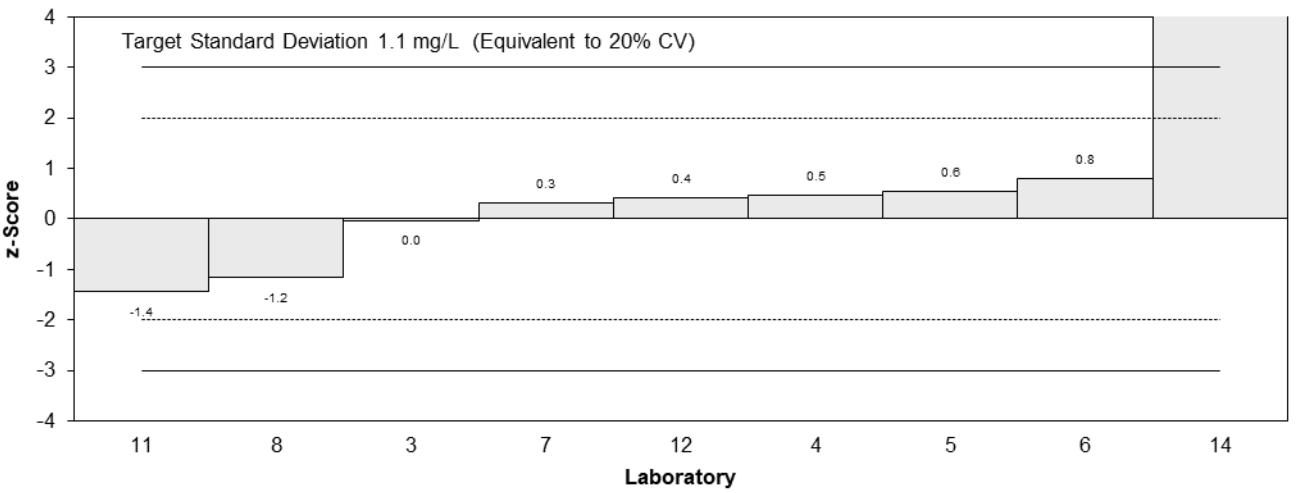
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	5.32	0.5	-0.03	-0.03
4	5.86	0.82	0.48	0.42
5	5.940	1.49	0.55	0.34
6	6.2	9.3	0.79	0.09
7	5.7	1.1	0.33	0.25
8	4.1	0.01	-1.17	-1.42
9	NR	NR		
10	NR	NR		
11	3.8	NR	-1.45	-1.76
12	5.8	0.73	0.42	0.39
13	NT	NT		
14	6353.8	700	5933.13	9.07

Statistics*

Assigned Value	5.35	0.88
Spike	Not Spiked	
Robust Average	5.35	0.88
Median	5.75	0.38
Mean	5.34	
N	8	
Max.	6.2	
Min.	3.8	
Robust SD	1.0	
Robust CV	19%	

*Laboratory 14 was excluded from statistical calculation (extreme outlier).


Kernel Density
Density
Result
Results: S1 - B
Assigned Value = 5.35 ± 0.88 mg/L
Results (mg/L)
Laboratory
11 8 3 7 12 4 5 6 14 10 2 9 1 13 Md R.A.


z-Scores: S1 - B
Target Standard Deviation 1.1 mg/L (Equivalent to 20% CV)
z-Score
-1.4
-1.2
0.0
0.3
0.4
0.5
0.6
0.8
Laboratory
11 8 3 7 12 4 5 6 14

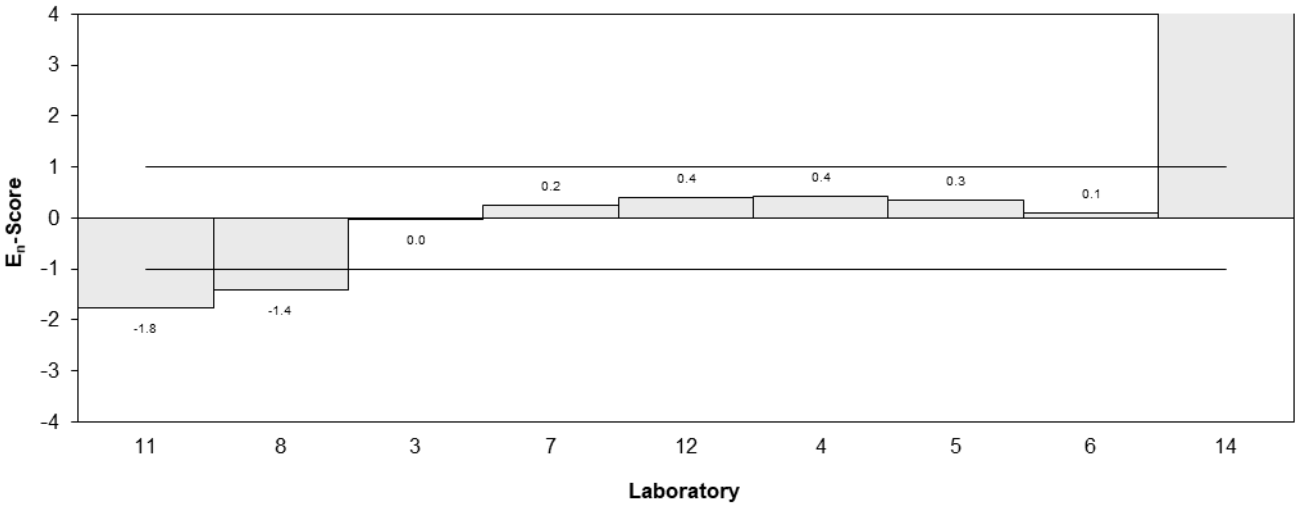

En-Scores: S1 - B
En-Score
-1.8
-1.4
0.0
0.2
0.4
0.4
0.3
0.1
Laboratory
11 8 3 7 12 4 5 6 14

Figure 3

Table 7

Sample Details

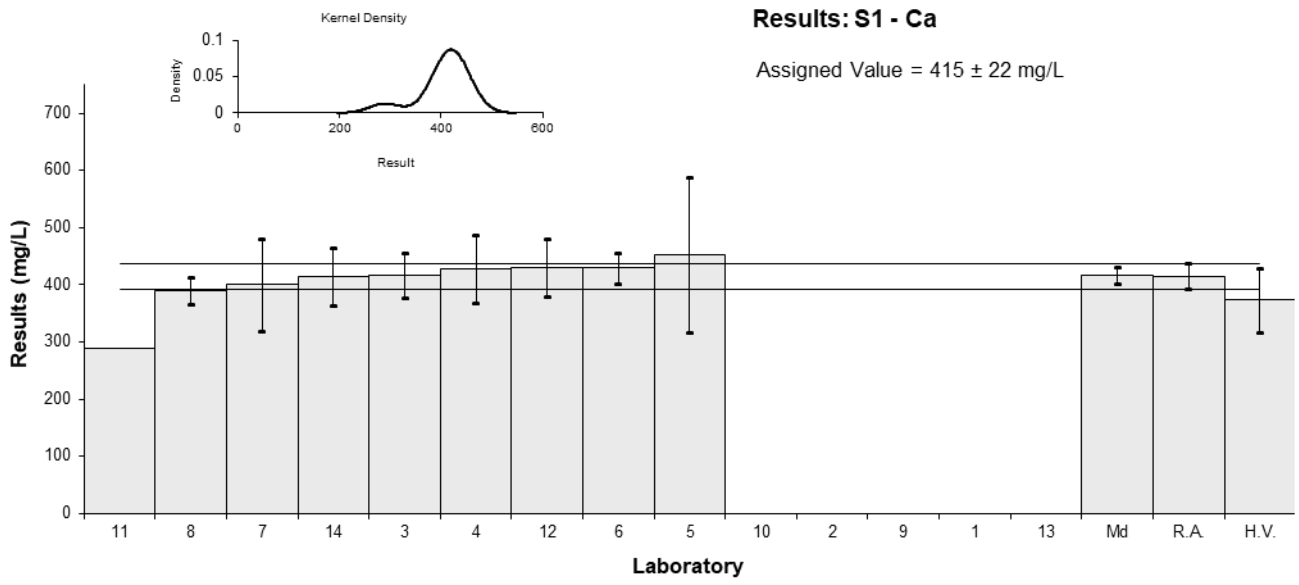
Sample No.	S1
Matrix.	Seawater
Analyte.	Ca
Units	mg/L

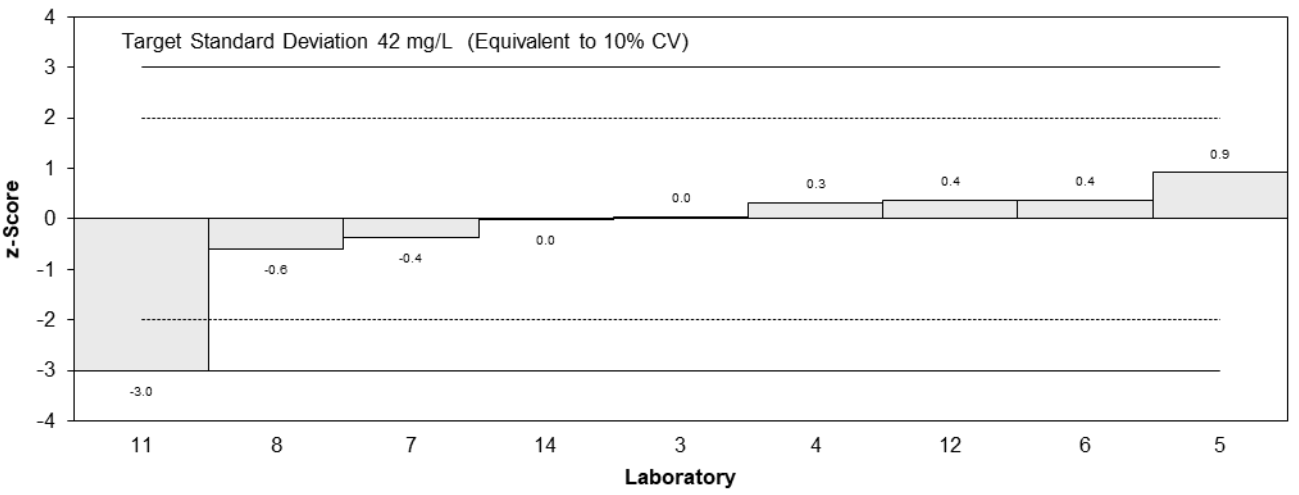
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	417	40	0.05	0.04
4	428	60	0.31	0.20
5	453	136	0.92	0.28
6	430	27	0.36	0.43
7	400	80	-0.36	-0.18
8	390	24	-0.60	-0.77
9	NR	NR		
10	NR	NR		
11	290	NR	-3.01	-5.68
12	430	50	0.36	0.27
13	NT	NT		
14	414.7	50	-0.01	-0.01

Statistics

Assigned Value	415	22
Spike	Not Spiked	
Homogeneity Value	374	56
Robust Average	415	22
Median	417	15
Mean	406	
N	9	
Max.	453	
Min.	290	
Robust SD	27	
Robust CV	6.5%	


Kernel Density
Density
Result
Results: S1 - Ca
Assigned Value = 415 ± 22 mg/L
Results (mg/L)
Laboratory
11 8 7 14 3 4 12 6 5 10 2 9 1 13 Md R.A. H.V.


z-Scores: S1 - Ca
Target Standard Deviation 42 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 8 7 14 3 4 12 6 5
-3.0 -0.6 -0.4 0.0 0.0 0.3 0.4 0.4 0.9

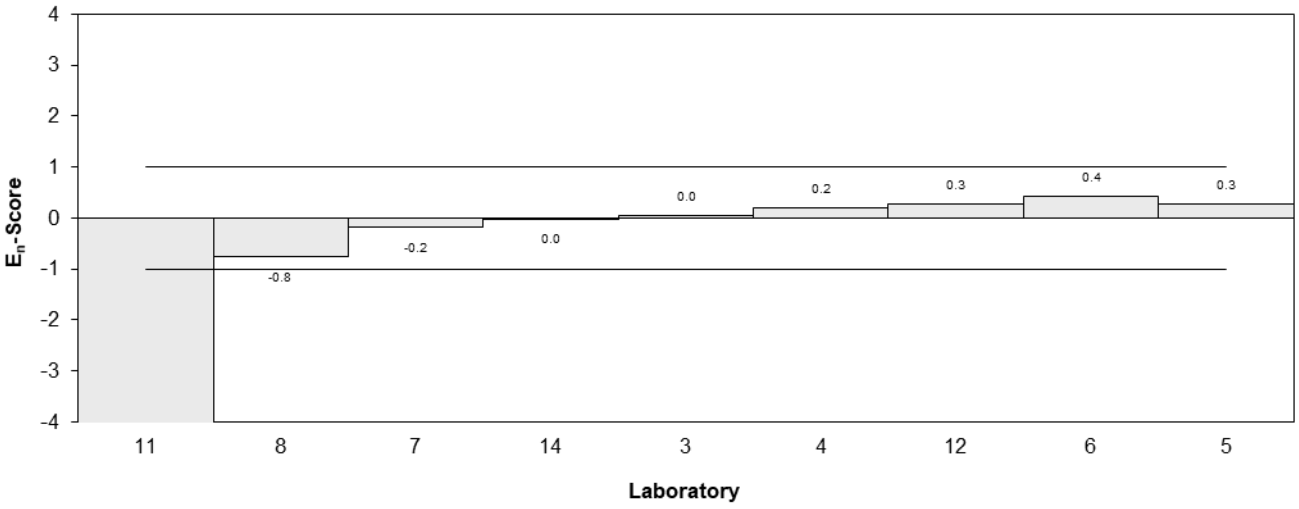

En-Scores: S1 - Ca
En-Score
Laboratory
11 8 7 14 3 4 12 6 5
-0.8 -0.2 0.0 0.0 0.2 0.3 0.4 0.3

Figure 4

Table 8

Sample Details

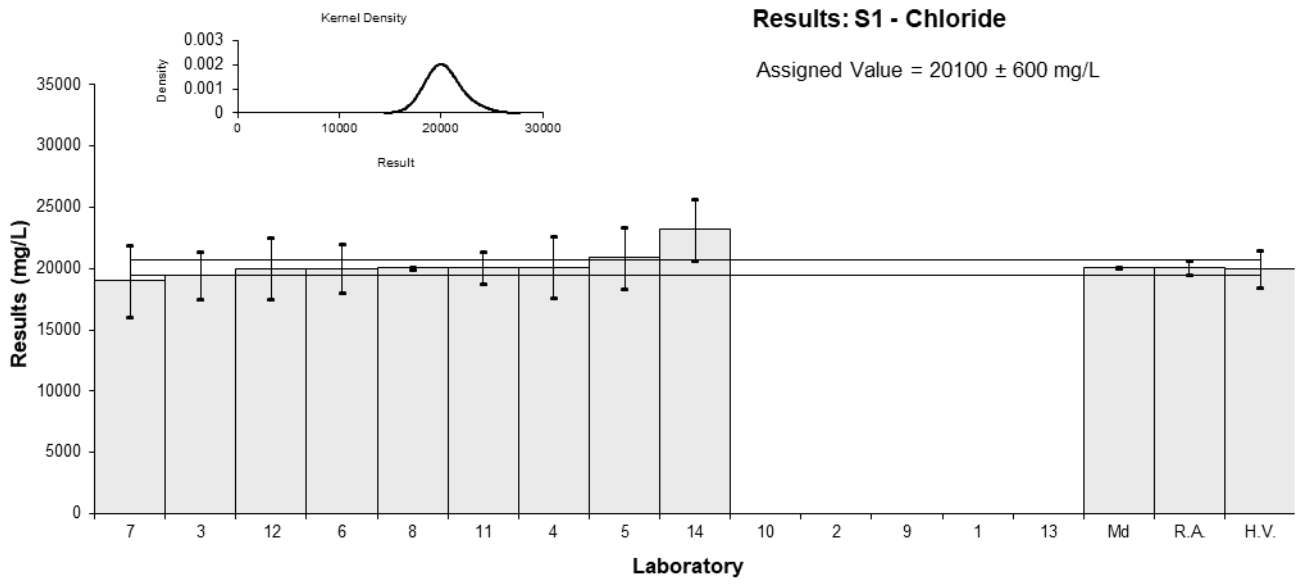
Sample No.	S1
Matrix.	Seawater
Analyte.	Chloride
Units	mg/L

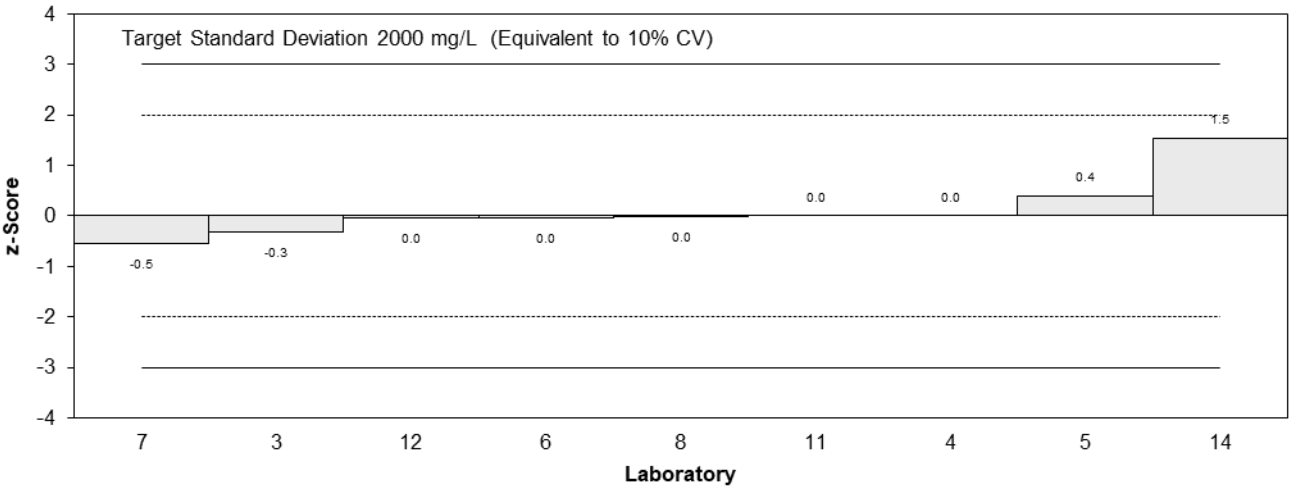
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	19440	1950	-0.33	-0.32
4	20100	2500	0.00	0.00
5	20900	2500	0.40	0.31
6	20000	2000	-0.05	-0.05
7	19000	2900	-0.55	-0.37
8	20061	100	-0.02	-0.06
9	NR	NR		
10	NR	NR		
11	20100	1300	0.00	0.00
12	20000	2500	-0.05	-0.04
13	NT	NT		
14	23198	2500	1.54	1.20

Statistics

Assigned Value	20100	600
Spike	Not Spiked	
Homogeneity Value	20000	1500
Robust Average	20100	600
Median	20100	70
Mean	20300	
N	9	
Max.	23198	
Min.	19000	
Robust SD	800	
Robust CV	3.8%	


Kernel Density
Density
0.003
0.002
0.001
0
0
10000
20000
30000
Result
Results: S1 - Chloride
Assigned Value = 20100 ± 600 mg/L
Results (mg/L)
35000
30000
25000
20000
15000
10000
5000
0
7
3
12
6
8
11
4
5
14
10
2
9
1
13
Md
R.A.
H.V.
Laboratory


z-Scores: S1 - Chloride
Target Standard Deviation 2000 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.3
0.0
0.0
0.0
0.0
0.0
0.4
1.5
7
3
12
6
8
11
4
5
14
Laboratory

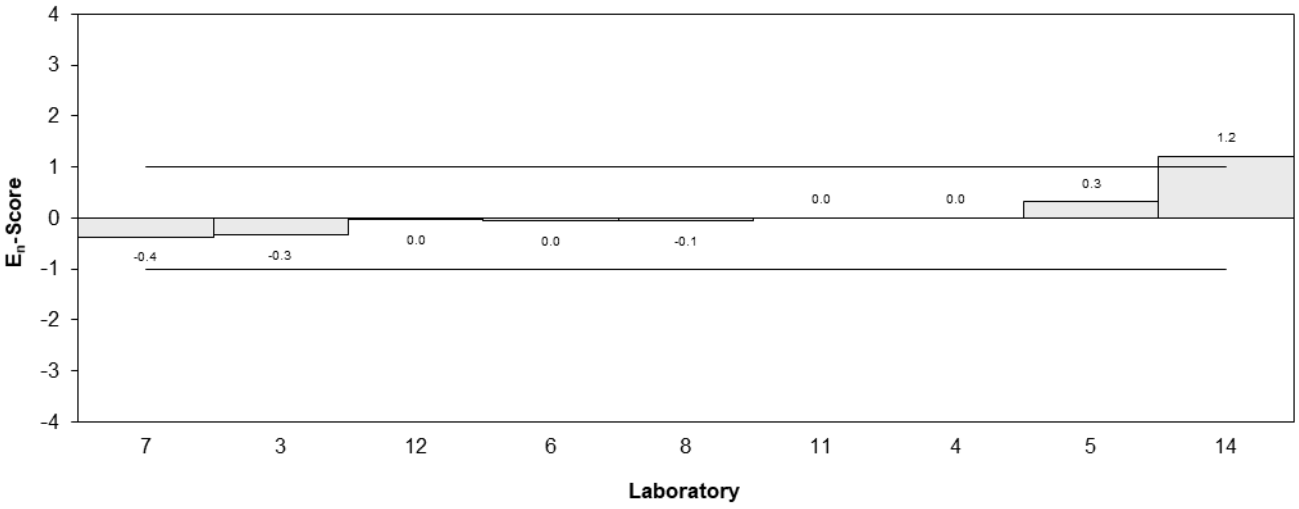

En-Scores: S1 - Chloride
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.4
-0.3
0.0
0.0
-0.1
0.0
0.0
0.3
1.2
7
3
12
6
8
11
4
5
14
Laboratory

Figure 5

Table 9

Sample Details

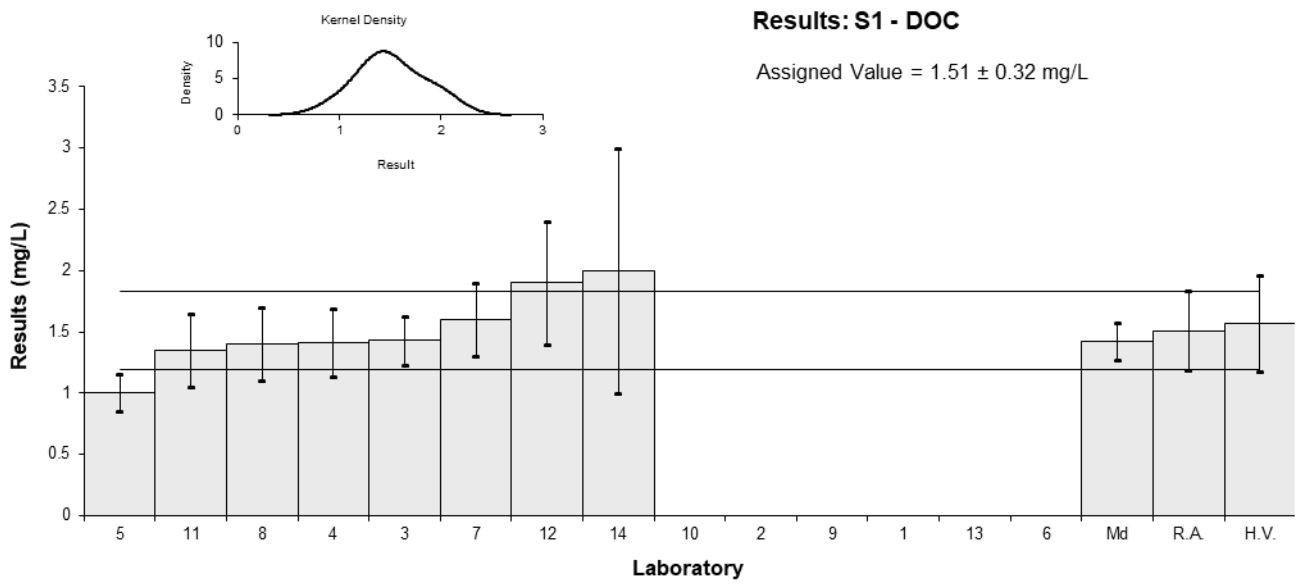
Sample No.	S1
Matrix.	Seawater
Analyte.	DOC
Units	mg/L

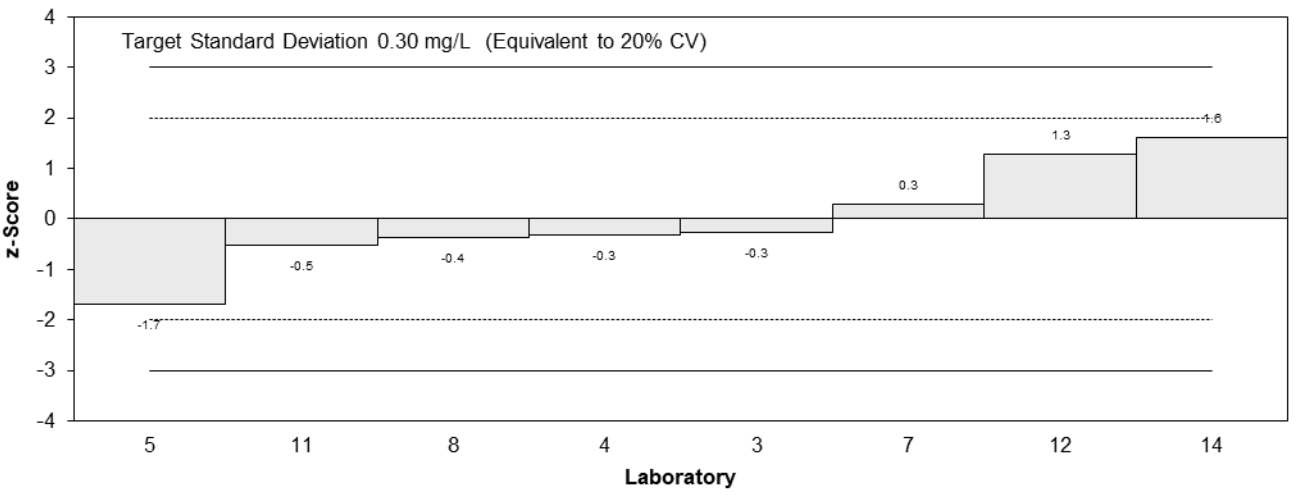
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	1.43	0.2	-0.26	-0.21
4	1.41	0.28	-0.33	-0.24
5	1.0	0.15	-1.69	-1.44
6	NT	NT		
7	1.6	0.3	0.30	0.21
8	1.4	0.3	-0.36	-0.25
9	NR	NR		
10	NR	NR		
11	1.35	0.30	-0.53	-0.36
12	1.9	0.5	1.29	0.66
13	NT	NT		
14	2	1	1.62	0.47

Statistics

Assigned Value	1.51	0.32
Spike	Not Spiked	
Homogeneity Value	1.57	0.39
Robust Average	1.51	0.32
Median	1.42	0.15
Mean	1.51	
N	8	
Max.	2	
Min.	1	
Robust SD	0.36	
Robust CV	24%	


Kernel Density
Density
Result
Results: S1 - DOC
Assigned Value = 1.51 ± 0.32 mg/L
Results (mg/L)
Laboratory
5 11 8 4 3 7 12 14 10 2 9 1 13 6 Md R.A. H.V.


z-Scores: S1 - DOC
Target Standard Deviation 0.30 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
5 11 8 4 3 7 12 14
-1.7
-0.5
-0.4
-0.3
-0.3
0.3
1.3
1.6

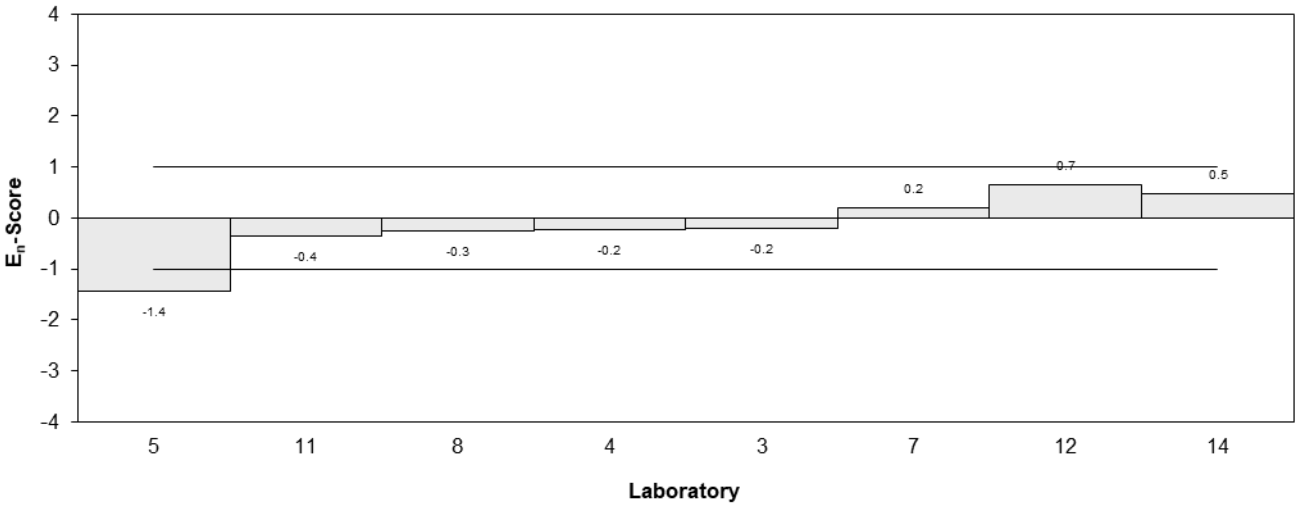

En-Scores: S1 - DOC
En-Score
Laboratory
5 11 8 4 3 7 12 14
-1.4
-0.4
-0.3
-0.2
-0.2
0.2
0.7
0.5

Figure 6

Table 10

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	NR	NR
3	1.7	0.2
4	1.13	0.14
5	<2.50	NR
6	NT	NT
7	1.0	0.15
8	NR	NR
9	NR	NR
10	NR	NR
11	1.07	0.14
12	0.7	0.18
13	NT	NT
14	1.2	0.2

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	1.10	0.22
Robust Average	1.13	0.36
Median	1.10	0.16
Mean	1.13	
N	6	
Max.	1.7	
Min.	0.7	
Robust SD	0.35	
Robust CV	31%	

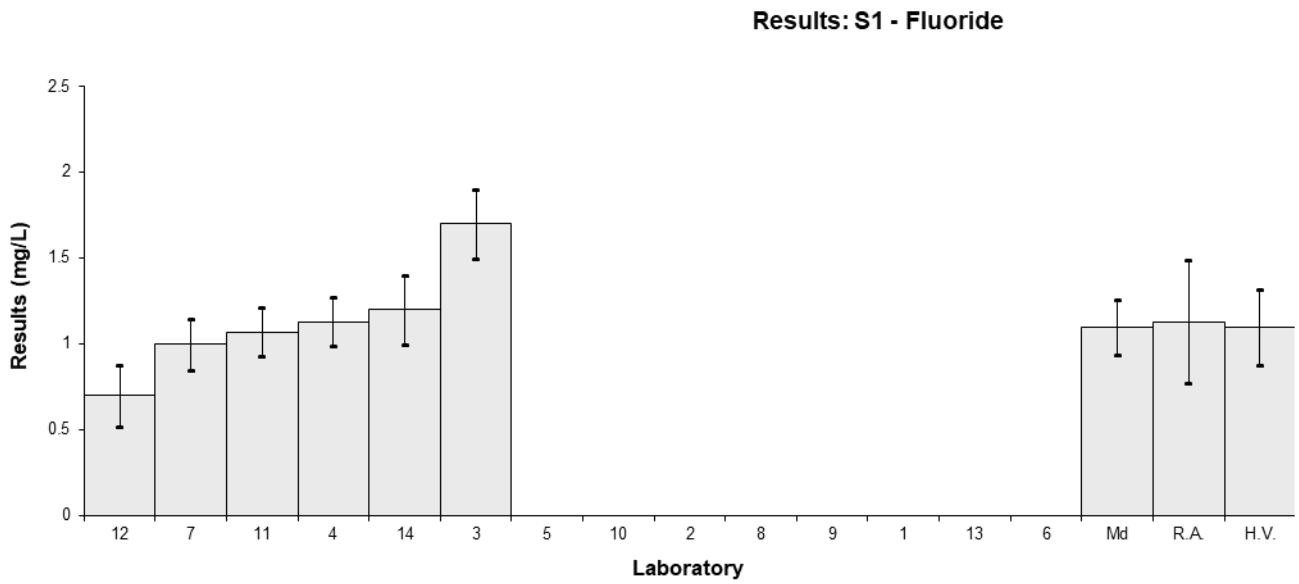

Results: S1 - Fluoride
Results (mg/L)
2.5
2
1.5
1
0.5
0
12
7
11
4
14
3
5
10
2
8
9
1
13
6
Md
R.A.
H.V.
Laboratory

Figure 7

Table 11

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	K
Units	mg/L

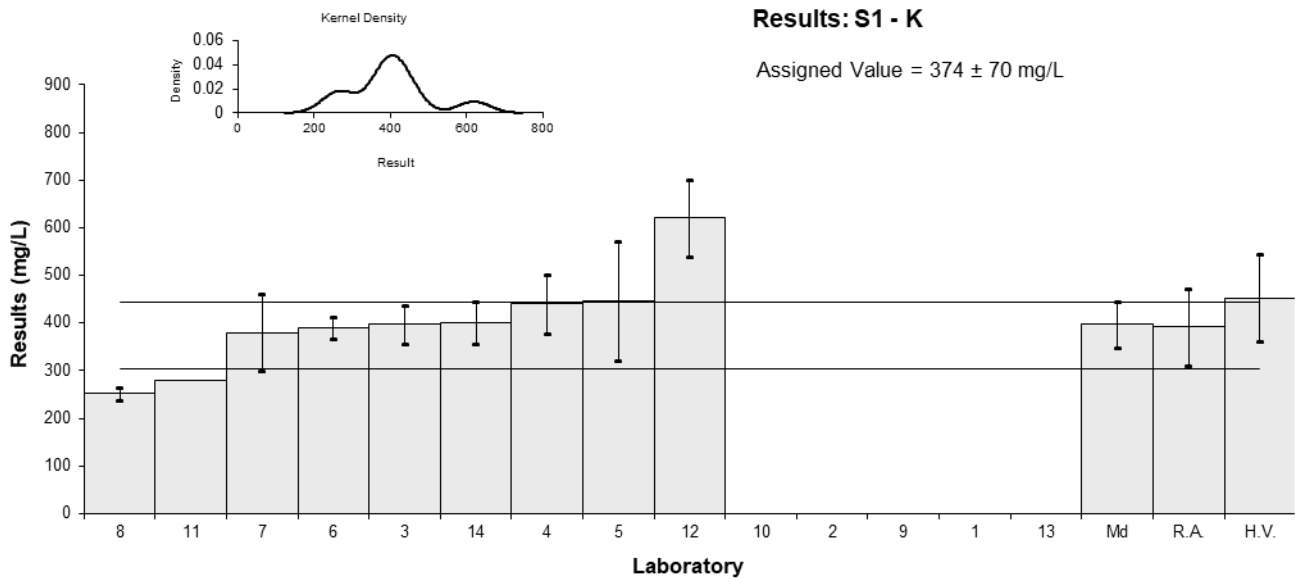
Participant Results

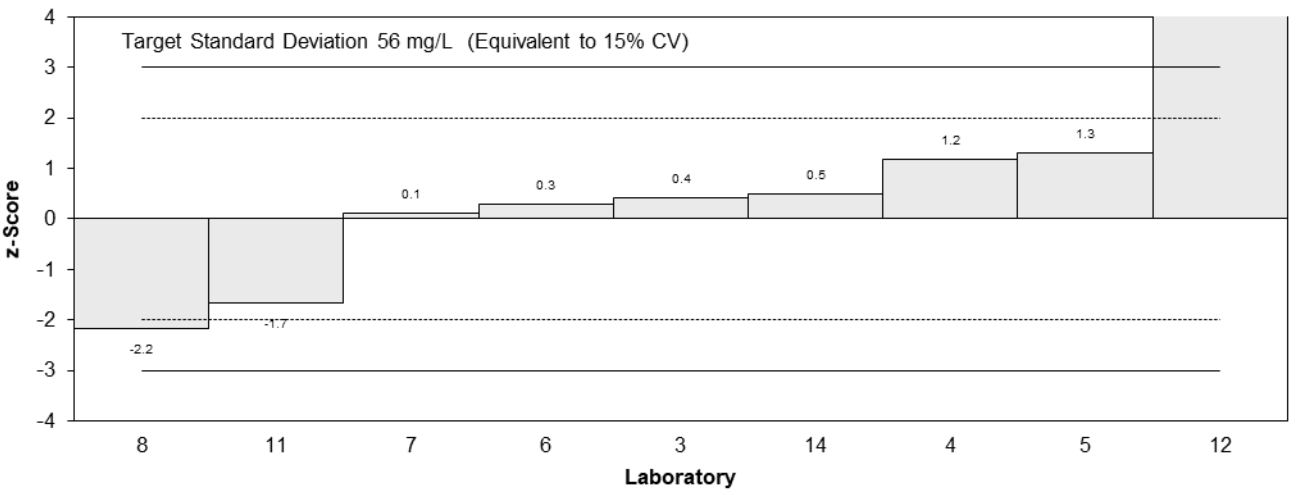
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	397	40	0.41	0.29
4	440	62	1.18	0.71
5	447	125	1.30	0.51
6	390	22	0.29	0.22
7	380	80	0.11	0.06
8	252	14	-2.17	-1.71
9	NR	NR		
10	NR	NR		
11	280	NR	-1.68	-1.34
12	620	80	4.39	2.31
13	NT	NT		
14	401.2	45	0.48	0.33

Statistics

Assigned Value*	374	70
Spike	Not Spiked	
Homogeneity Value	453	91
Robust Average	392	81
Median	397	49
Mean	401	
N	9	
Max.	620	
Min.	252	
Robust SD	97	
Robust CV	25%	

*Robust Average excluding laboratory 12.


Kernel Density
Density
Result
Results: S1 - K
Assigned Value = 374 ± 70 mg/L
Results (mg/L)
Laboratory
8
11
7
6
3
14
4
5
12
10
2
9
1
13
Md
R.A.
H.V.


z-Scores: S1 - K
Target Standard Deviation 56 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.2
-1.7
0.1
0.3
0.4
0.5
1.2
1.3

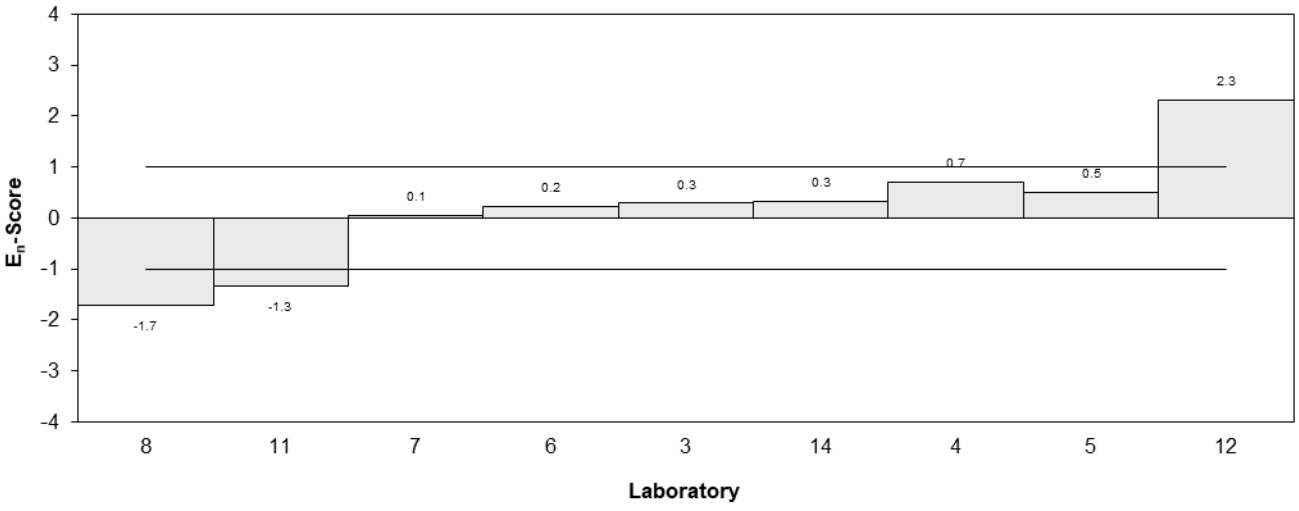

En-Scores: S1 - K
En-Score
Laboratory
-1.7
-1.3
0.1
0.2
0.3
0.3
0.7
0.5
2.3

Figure 8

Table 12

Sample Details

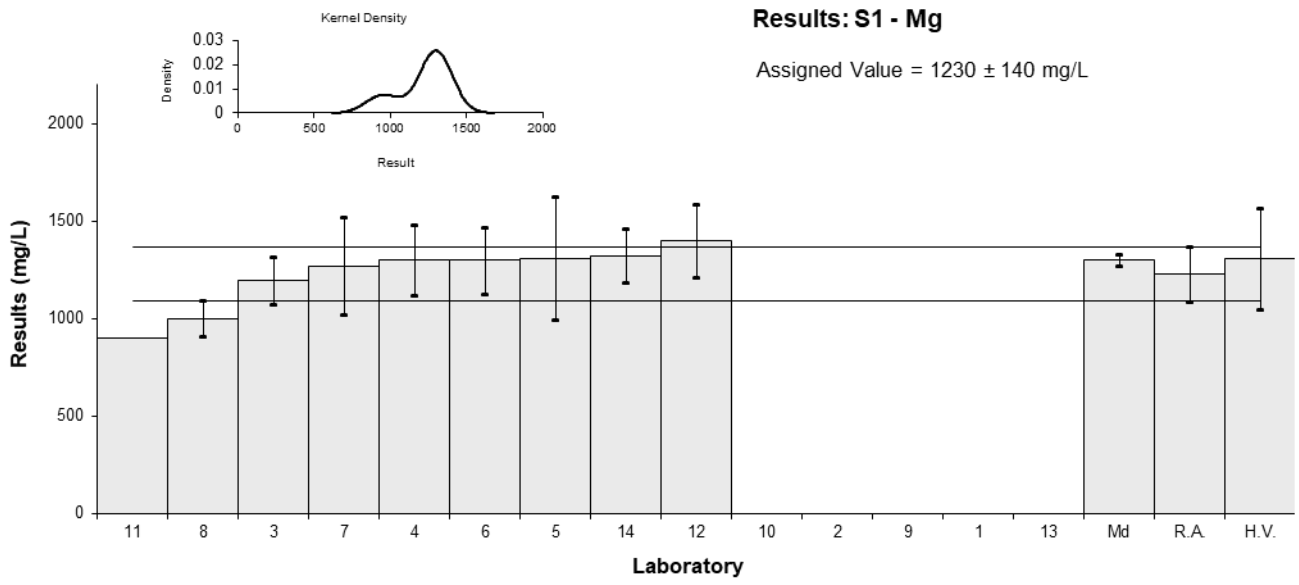
Sample No.	S1
Matrix.	Seawater
Analyte.	Mg
Units	mg/L

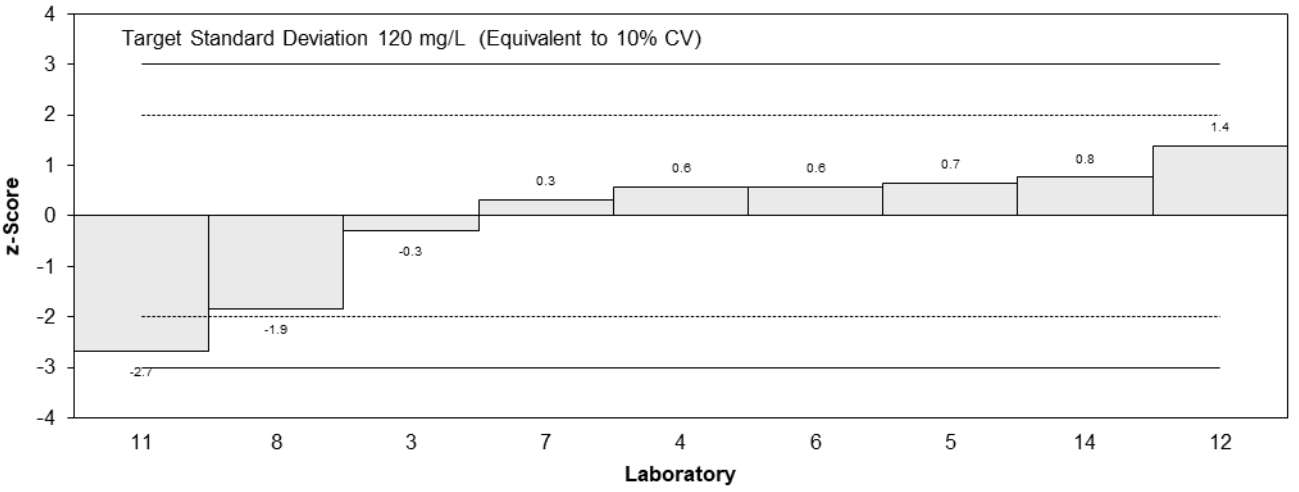
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	1195	120	-0.28	-0.19
4	1300	180	0.57	0.31
5	1310	314	0.65	0.23
6	1300	170	0.57	0.32
7	1270	250	0.33	0.14
8	1002	90	-1.85	-1.37
9	NR	NR		
10	NR	NR		
11	900	NR	-2.68	-2.36
12	1400	190	1.38	0.72
13	NT	NT		
14	1323.7	140	0.76	0.47

Statistics

Assigned Value	1230	140
Spike	Not Spiked	
Homogeneity Value	1310	260
Robust Average	1230	140
Median	1300	30
Mean	1220	
N	9	
Max.	1400	
Min.	900	
Robust SD	160	
Robust CV	13%	


Kernel Density
Density
0.03
0.02
0.01
0
0
500
1000
1500
2000
Result
Results: S1 - Mg
Assigned Value = 1230 ± 140 mg/L
Results (mg/L)
2000
1500
1000
500
0
11
8
3
7
4
6
5
14
12
10
2
9
1
13
Md
R.A.
H.V.
Laboratory


z-Scores: S1 - Mg
Target Standard Deviation 120 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
1.4
0.8
0.7
0.6
0.6
0.3
-0.3
-1.9
-2.7
11
8
3
7
4
6
5
14
12
Laboratory

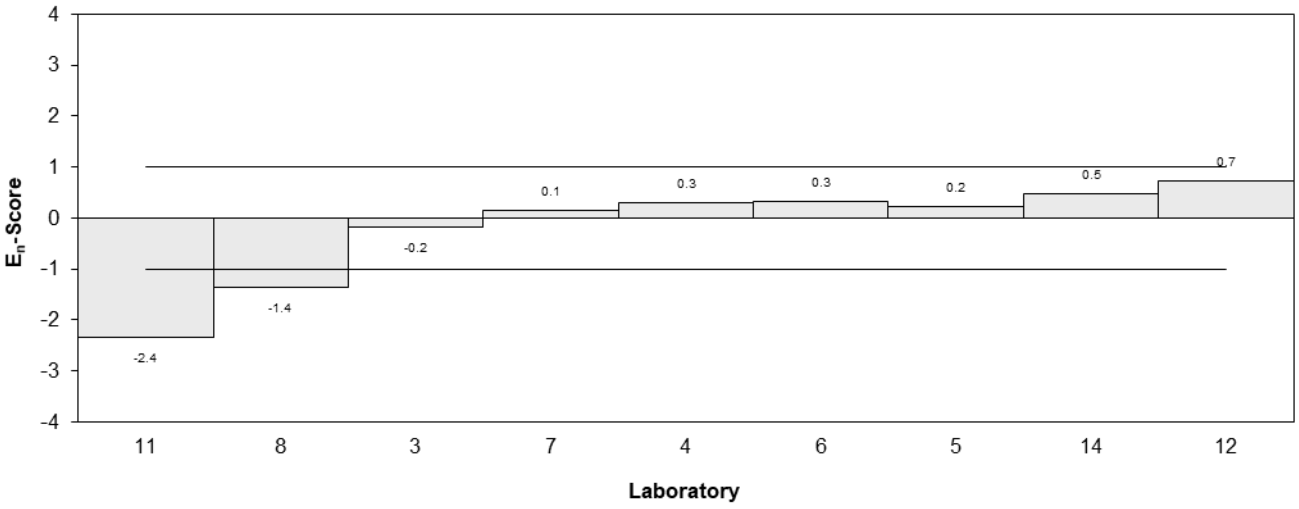

En-Scores: S1 - Mg
En-Score
4
3
2
1
0
-1
-2
-3
-4
0.7
0.5
0.3
0.3
0.2
0.1
-0.2
-1.4
-2.4
11
8
3
7
4
6
5
14
12
Laboratory

Figure 9

Table 13

Sample Details

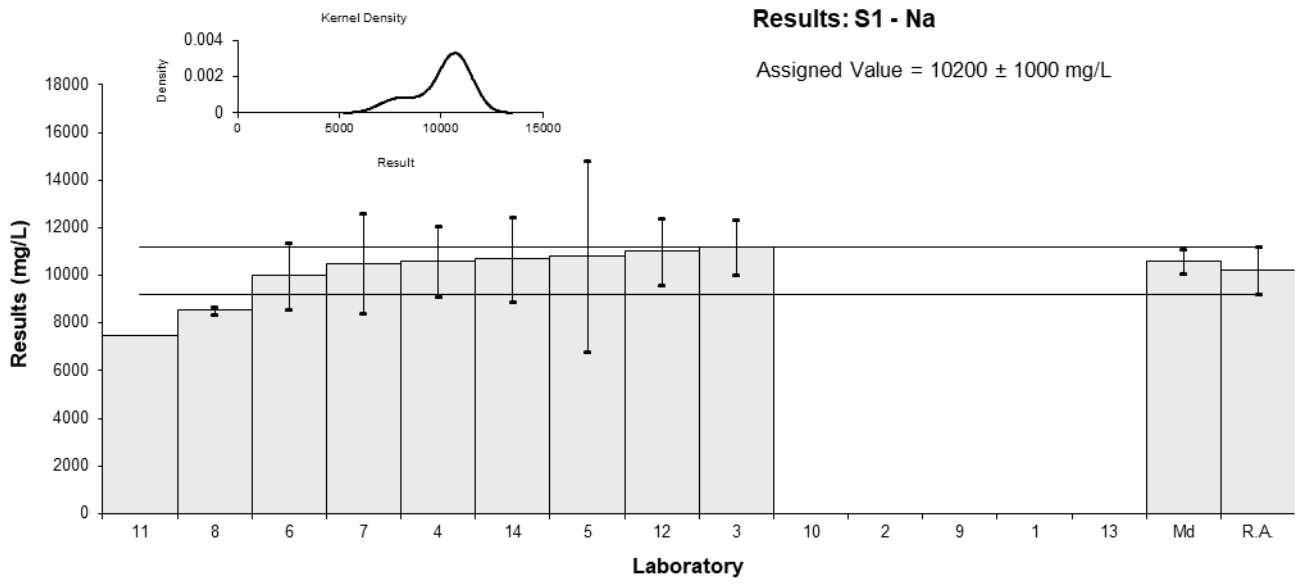
Sample No.	S1
Matrix.	Seawater
Analyte.	Na
Units	mg/L

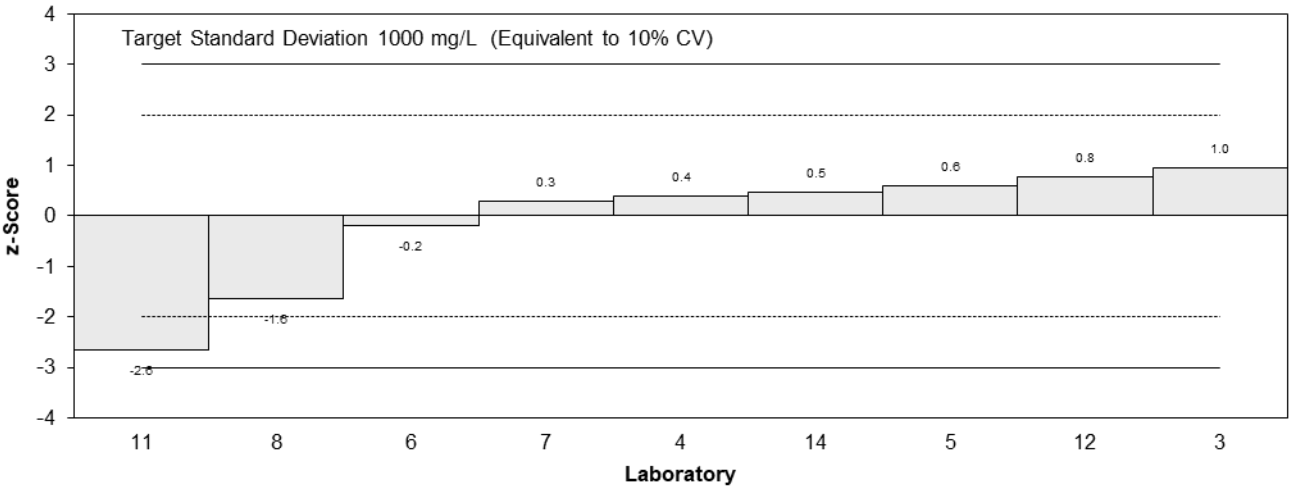
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	11180	1150	0.96	0.64
4	10600	1500	0.39	0.22
5	10800	4000	0.59	0.15
6	10000	1400	-0.20	-0.12
7	10500	2100	0.29	0.13
8	8528	170	-1.64	-1.65
9	NR	NR		
10	NR	NR		
11	7500	NR	-2.65	-2.70
12	11000	1400	0.78	0.46
13	NT	NT		
14	10675.9	1750	0.47	0.24

Statistics

Assigned Value	10200	1000
Spike	Not Spiked	
Robust Average	10200	1000
Median	10600	500
Mean	10100	
N	9	
Max.	11180	
Min.	7500	
Robust SD	1200	
Robust CV	11%	


Kernel Density
Density
0.004
0.002
0
0
5000
10000
15000
Result
Results: S1 - Na
Assigned Value = 10200 ± 1000 mg/L
Results (mg/L)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
11
8
6
7
4
14
5
12
3
10
2
9
1
13
Md
R.A.
Laboratory


z-Scores: S1 - Na
Target Standard Deviation 1000 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.6
-1.6
-0.2
0.3
0.4
0.5
0.6
0.8
1.0
11
8
6
7
4
14
5
12
3
Laboratory

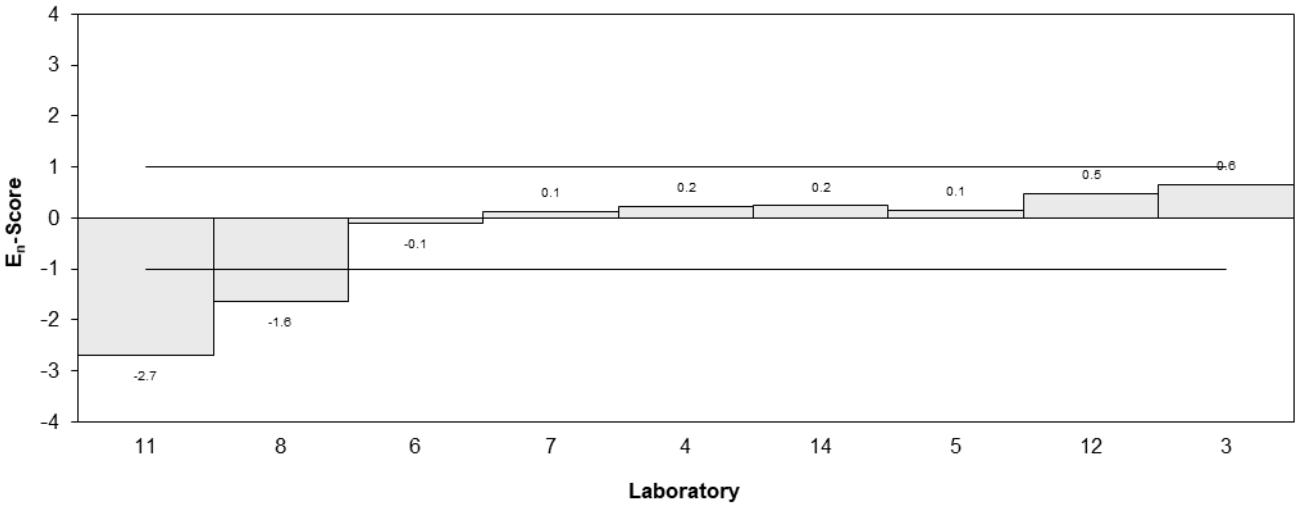

En-Scores: S1 - Na
En-Score
4
3
2
1
0
-1
-2
-3
-4
-2.7
-1.6
-0.1
0.1
0.2
0.2
0.1
0.5
0.6
11
8
6
7
4
14
5
12
3
Laboratory

Figure 10

Table 14

Sample Details

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

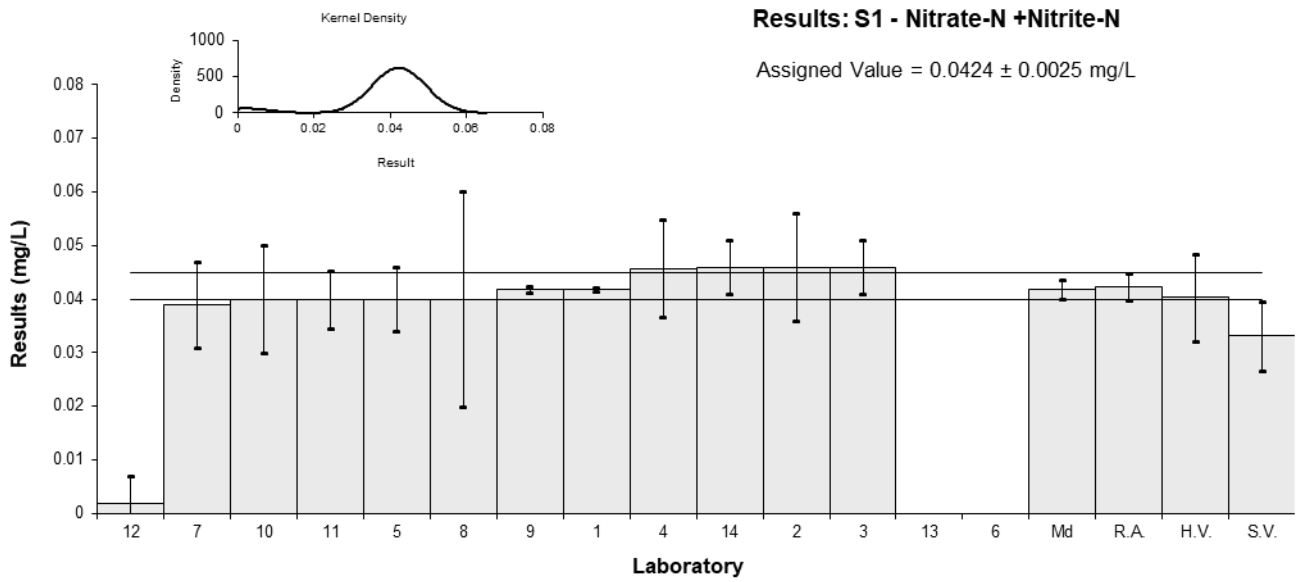
Participant Results

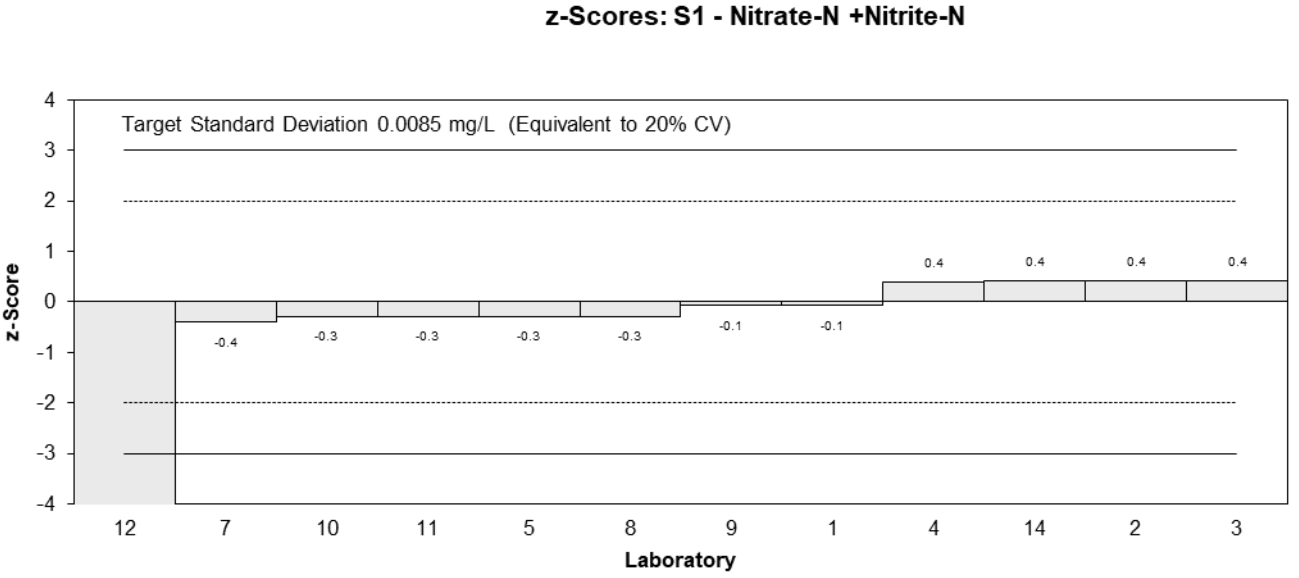
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.0419	0.0004	-0.06	-0.20
2	0.046	0.01	0.42	0.35
3	0.046	0.005	0.42	0.64
4	0.0457	0.0091	0.39	0.35
5	0.040	0.006	-0.28	-0.37
6	NT	NT		
7	0.039	0.008	-0.40	-0.41
8	0.04	0.02	-0.28	-0.12
9	0.0418	0.0006	-0.07	-0.23
10	0.04	0.01	-0.28	-0.23
11	0.0400	0.0054	-0.28	-0.40
12	0.002	0.005	-4.76	-7.23
13	NT	NT		
14	0.046	0.005	0.42	0.64

Statistics*

Assigned Value	0.0424	0.0025
Spike	0.0331	0.0065
Homogeneity Value	0.0403	0.0081
Robust Average	0.0424	0.0025
Median	0.0418	0.0018
Mean	0.0424	
N	11	
Max.	0.046	
Min.	0.039	
Robust SD	0.0033	
Robust CV	7.8%	

*Laboratory 12 excluded from statistical calculation (extreme outlier).


Kernel Density
Density
Result
Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.0424 ± 0.0025 mg/L
Results (mg/L)
Laboratory
12 7 10 11 5 8 9 1 4 14 2 3 13 6 Md R.A. H.V. S.V.


z-Scores: S1 - Nitrate-N +Nitrite-N
Target Standard Deviation 0.0085 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
12 7 10 11 5 8 9 1 4 14 2 3
-0.4 -0.3 -0.3 -0.3 -0.3 -0.1 -0.1 0.4 0.4 0.4 0.4

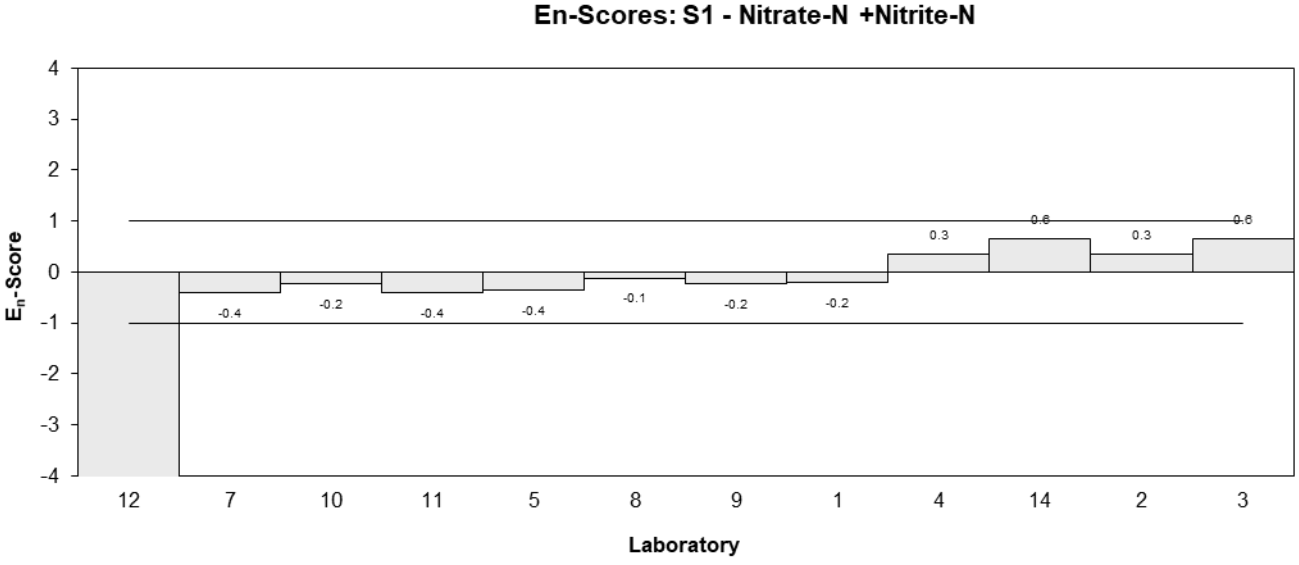

En-Scores: S1 - Nitrate-N +Nitrite-N
En-Score
Laboratory
12 7 10 11 5 8 9 1 4 14 2 3
-0.4 -0.2 -0.4 -0.4 -0.1 -0.2 -0.2 0.3 0.6 0.3 0.6

Figure 11

Table 15

Sample Details

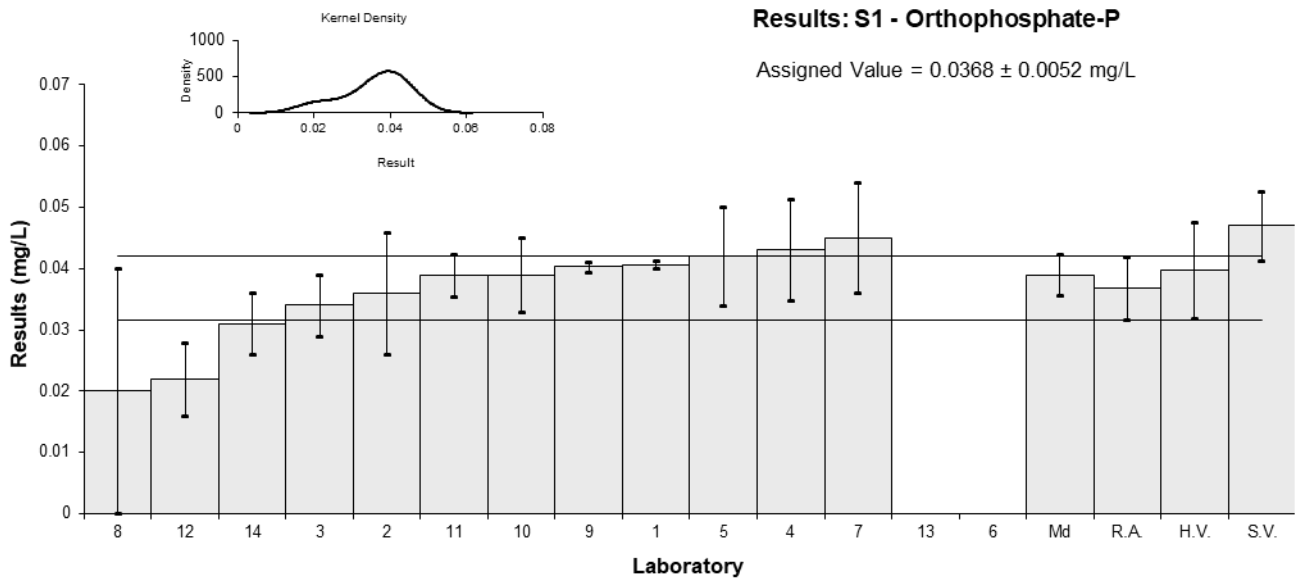
Sample No.	S1
Matrix.	Seawater
Analyte.	Orthophosphate-P
Units	mg/L

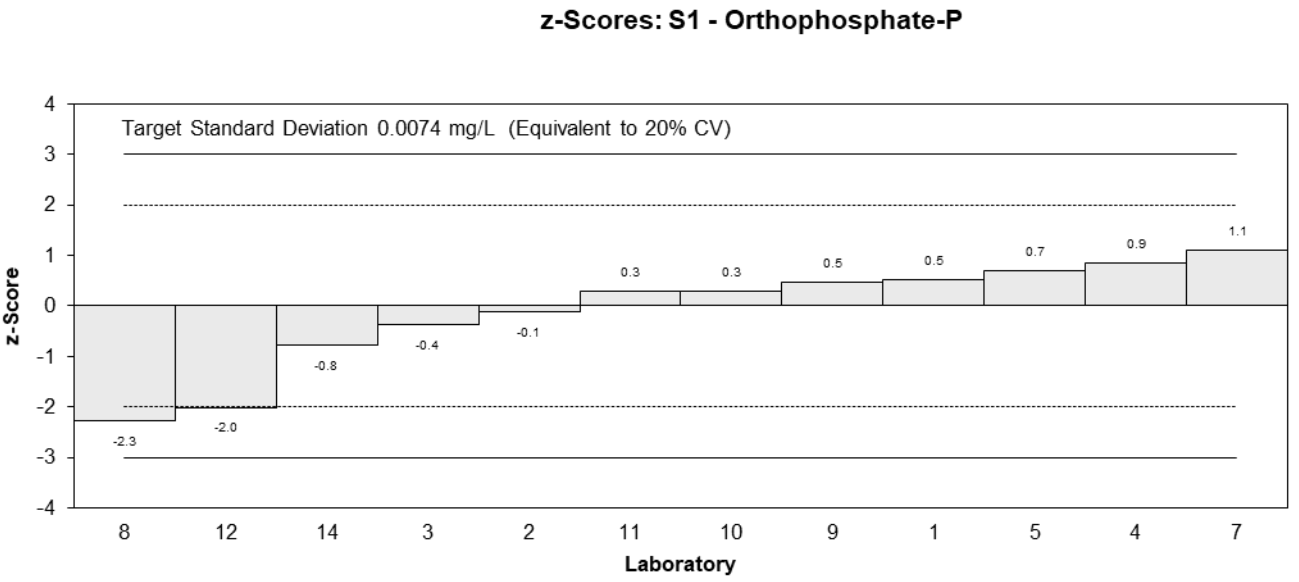
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.0406	0.0006	0.52	0.73
2	0.036	0.01	-0.11	-0.07
3	0.034	0.005	-0.38	-0.39
4	0.0431	0.0082	0.86	0.65
5	0.042	0.008	0.71	0.54
6	NT	NT		
7	0.045	0.009	1.11	0.79
8	0.02	0.02	-2.28	-0.81
9	0.0403	0.0008	0.48	0.67
10	0.039	0.006	0.30	0.28
11	0.0389	0.0034	0.29	0.34
12	0.022	0.006	-2.01	-1.86
13	NT	NT		
14	0.031	0.005	-0.79	-0.80

Statistics

Assigned Value	0.0368	0.0052
Spike	0.0470	0.0056
Homogeneity Value	0.0397	0.0079
Robust Average	0.0368	0.0052
Median	0.0390	0.0034
Mean	0.0360	
N	12	
Max.	0.045	
Min.	0.02	
Robust SD	0.0072	
Robust CV	20%	


Kernel Density
Density
Result
Results: S1 - Orthophosphate-P
Assigned Value = 0.0368 ± 0.0052 mg/L
Results (mg/L)
Laboratory
8 12 14 3 2 11 10 9 1 5 4 7 13 6 Md R.A. H.V. S.V.


z-Scores: S1 - Orthophosphate-P
Target Standard Deviation 0.0074 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
8 12 14 3 2 11 10 9 1 5 4 7
-2.3 -2.0 -0.8 -0.4 -0.1 0.3 0.3 0.5 0.5 0.7 0.9 1.1

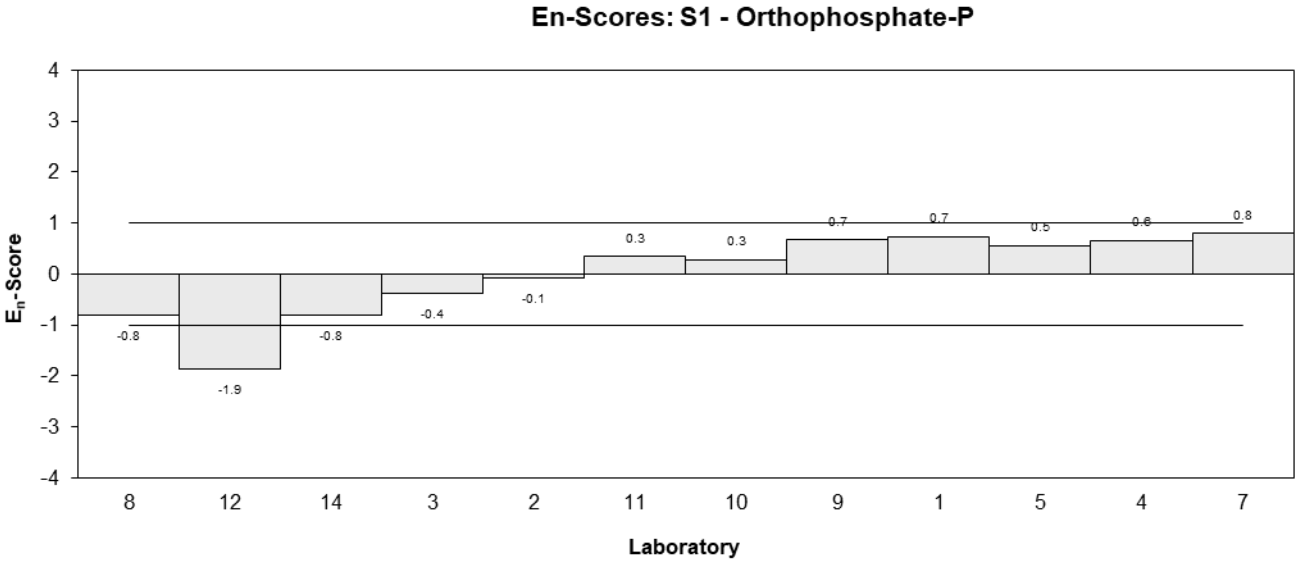

En-Scores: S1 - Orthophosphate-P
En-Score
Laboratory
8 12 14 3 2 11 10 9 1 5 4 7
-0.8 -1.9 -0.8 -0.4 -0.1 0.3 0.3 0.7 0.7 0.5 0.6 0.8

Figure 12

Table 16

Sample Details

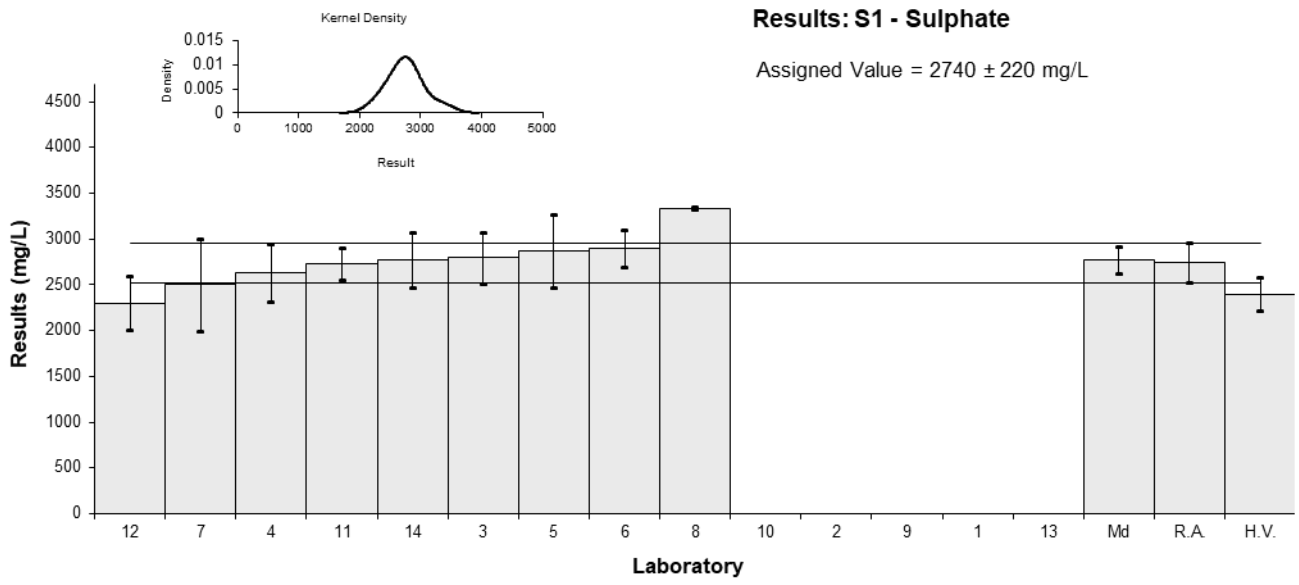
Sample No.	S1
Matrix.	Seawater
Analyte.	Sulphate
Units	mg/L

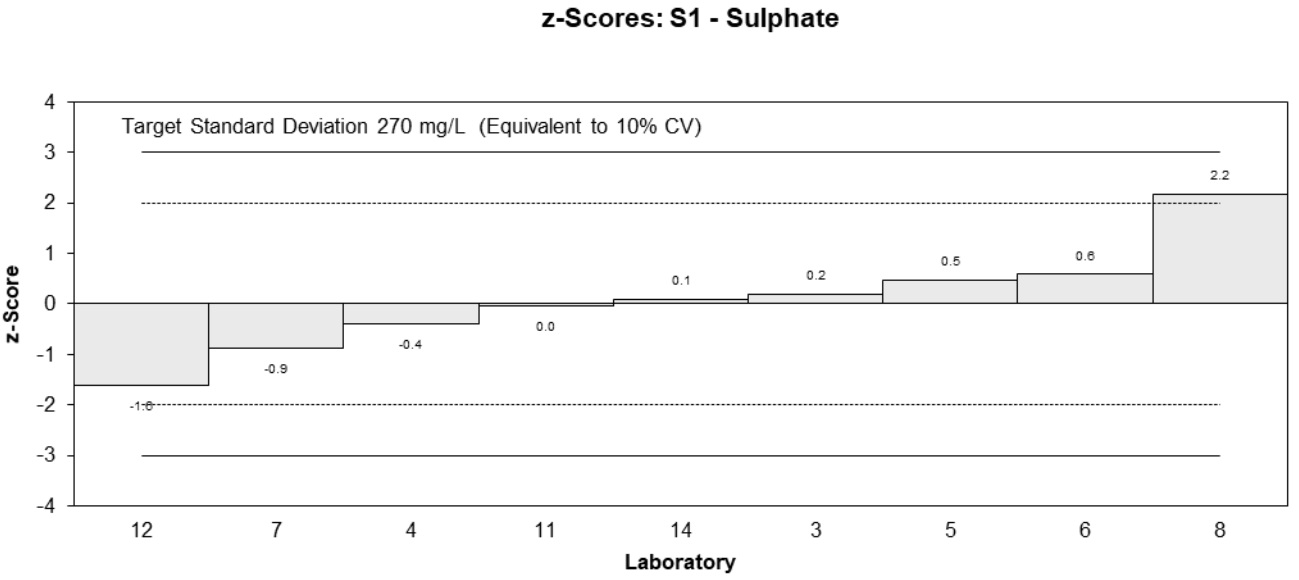
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	2793	280	0.19	0.15
4	2630	320	-0.40	-0.28
5	2870	402	0.47	0.28
6	2900	200	0.58	0.54
7	2500	500	-0.88	-0.44
8	3337	10	2.18	2.71
9	NR	NR		
10	NR	NR		
11	2730	170	-0.04	-0.04
12	2300	290	-1.61	-1.21
13	NT	NT		
14	2766.2	300	0.10	0.07

Statistics

Assigned Value	2740	220
Spike	Not Spiked	
Homogeneity Value	2400	180
Robust Average	2740	220
Median	2770	150
Mean	2760	
N	9	
Max.	3337	
Min.	2300	
Robust SD	260	
Robust CV	9.5%	


Kernel Density
Density
0.015
0.01
0.005
0
0
1000
2000
3000
4000
5000
Result
Results: S1 - Sulphate
Assigned Value = 2740 ± 220 mg/L
Results (mg/L)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
12
7
4
11
14
3
5
6
8
10
2
9
1
13
Md
R.A.
H.V.
Laboratory


z-Scores: S1 - Sulphate
Target Standard Deviation 270 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.6
-0.9
-0.4
0.0
0.1
0.2
0.5
0.6
2.2
12
7
4
11
14
3
5
6
8
Laboratory

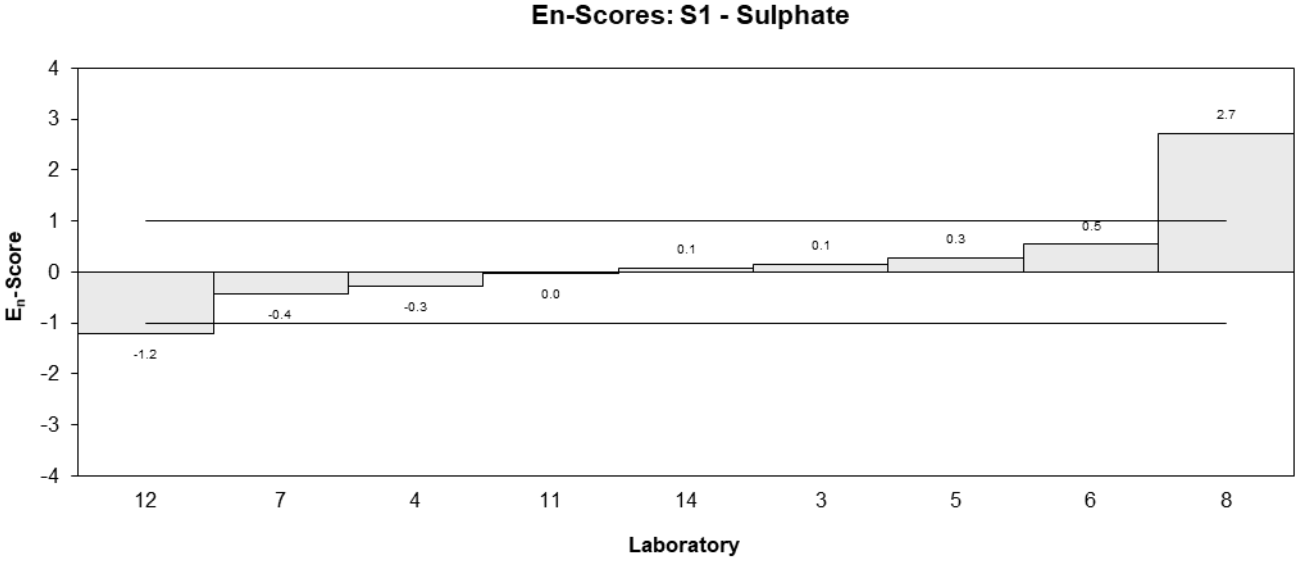

En-Scores: S1 - Sulphate
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.2
-0.4
-0.3
0.0
0.1
0.1
0.3
0.5
2.7
12
7
4
11
14
3
5
6
8
Laboratory

Figure 13

Table 17

Sample Details

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

Participant Results

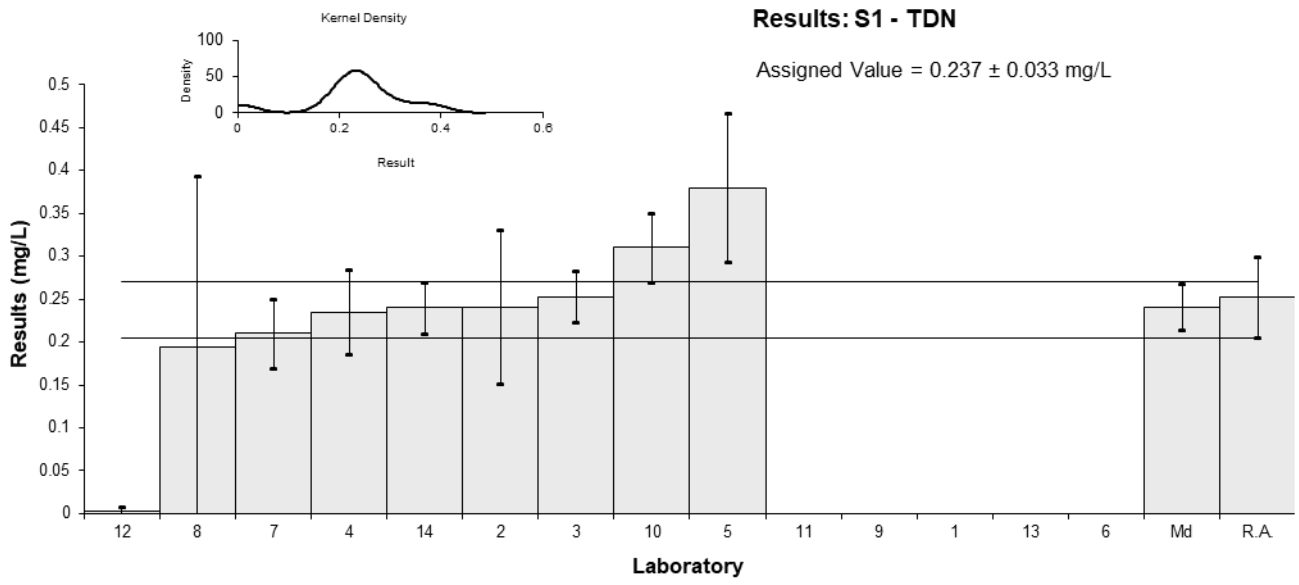
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.241	0.09	0.08	0.04
3	0.253	0.03	0.34	0.36
4	0.235	0.049	-0.04	-0.03
5	0.38	0.087	3.02	1.54
6	NT	NT		
7	0.21	0.04	-0.57	-0.52
8	0.194	0.2	-0.91	-0.21
9	NR	NR		
10	0.31	0.04	1.54	1.41
11	< 0.3	0.065		
12	0.003	0.005	-4.94	-7.01
13	NT	NT		
14	0.24	0.03	0.06	0.07

Statistics*

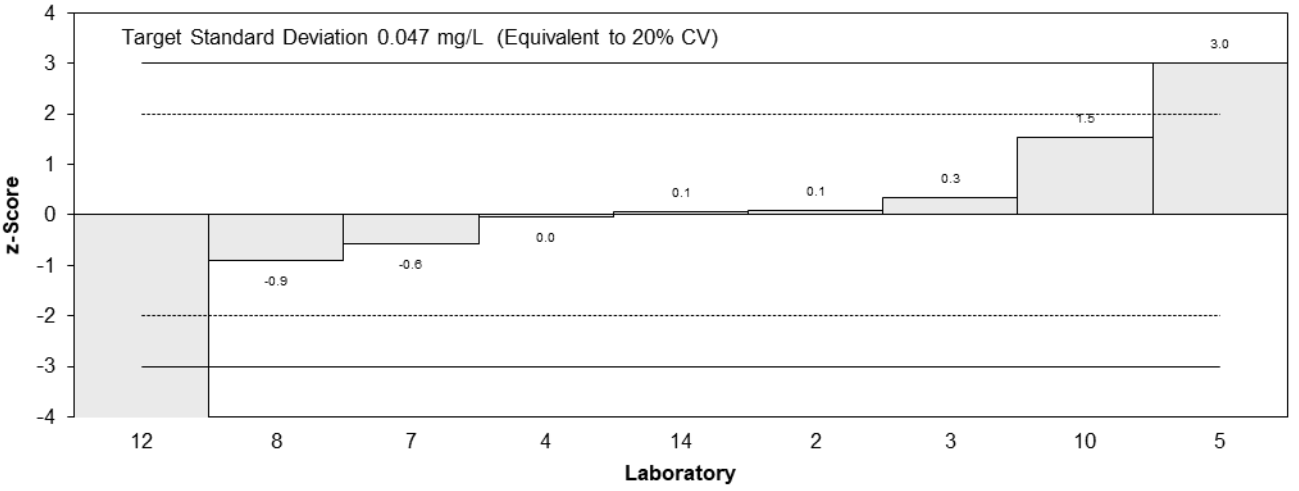
Assigned Value**	0.237	0.033
Spike	Not Spiked	
Robust Average	0.252	0.047
Median	0.241	0.027
Mean	0.258	
N	8	
Max.	0.38	
Min.	0.194	
Robust SD	0.053	
Robust CV	21%	

*Laboratory 12 was excluded from statistical calculation (extreme outlier).

**Robust Average excluding laboratory 5.



z-Scores: S1 - TDN



En-Scores: S1 - TDN

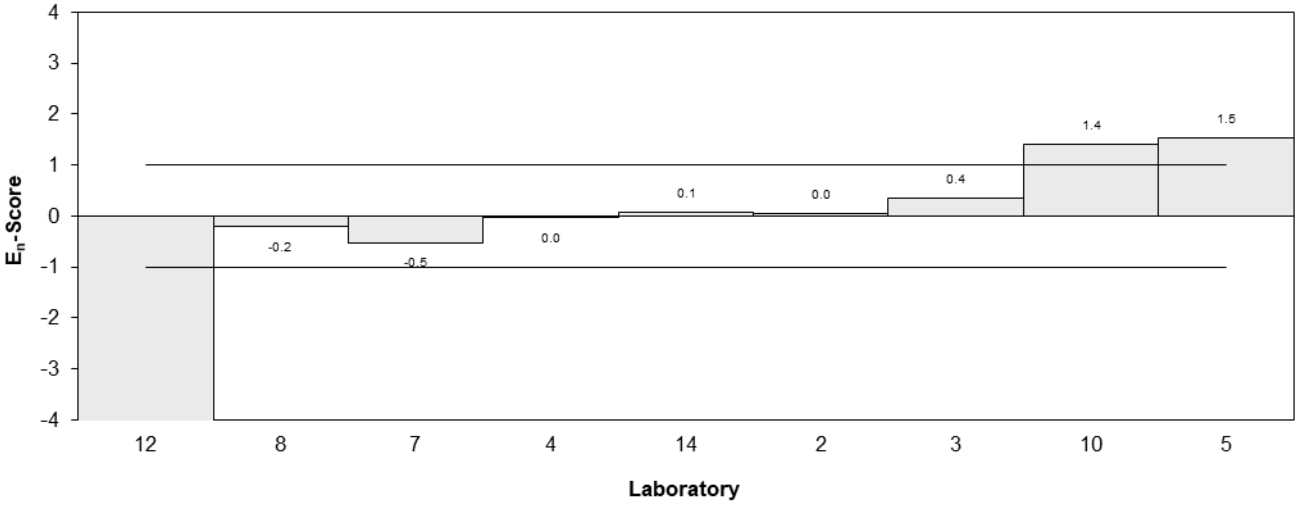


Figure 14

Table 18

Sample Details

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

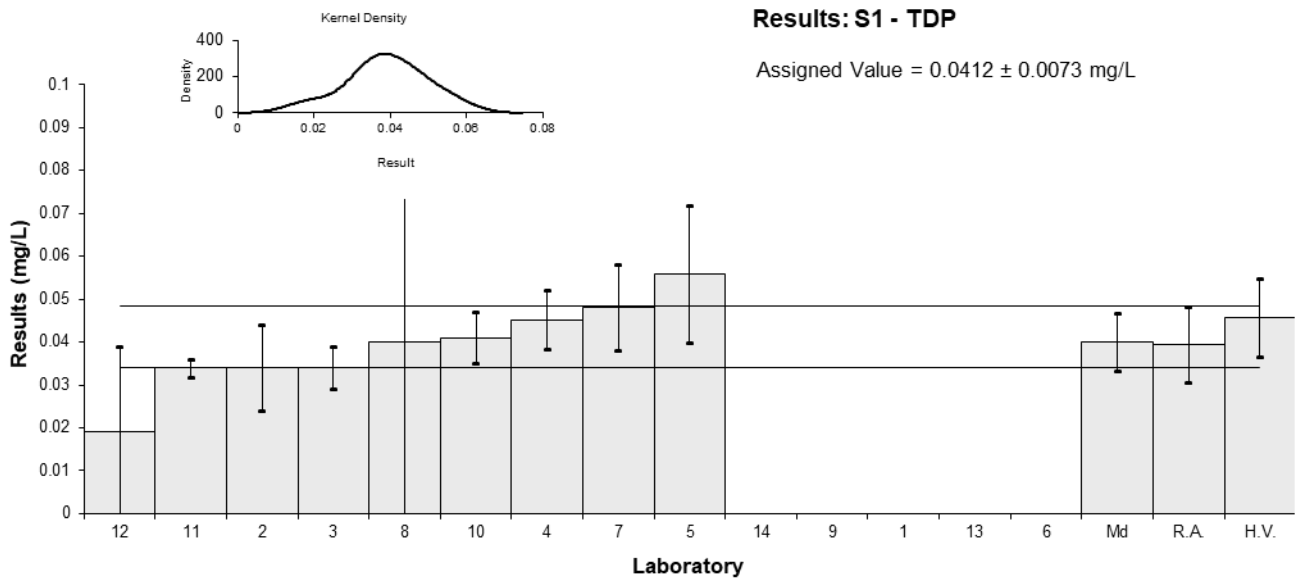
Participant Results

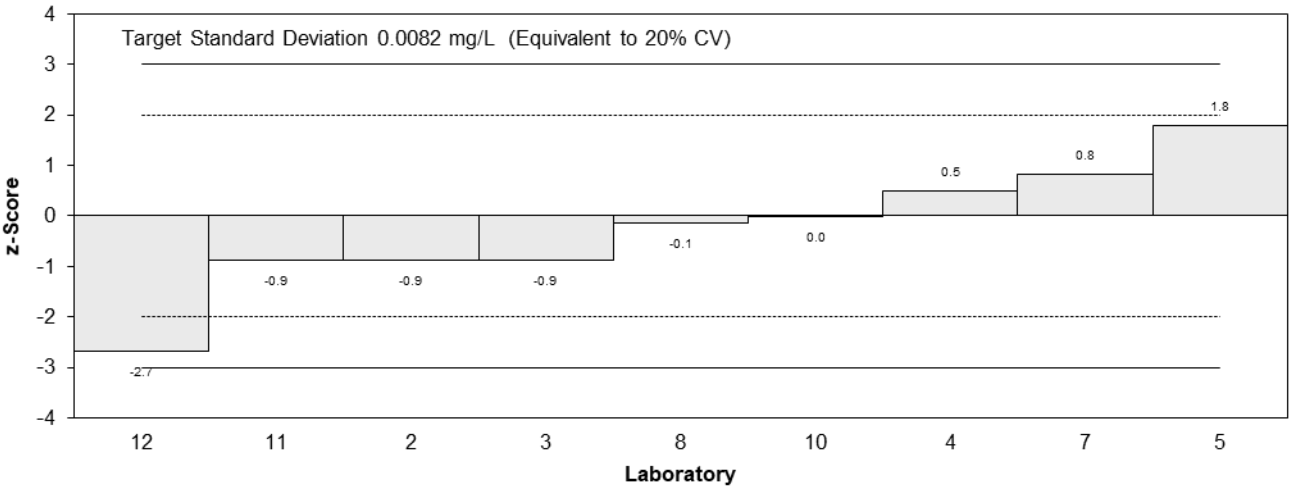
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.034	0.01	-0.87	-0.58
3	0.034	0.005	-0.87	-0.81
4	0.0452	0.0068	0.49	0.40
5	0.056	0.016	1.80	0.84
6	NT	NT		
7	0.048	0.010	0.83	0.55
8	0.04	0.14	-0.15	-0.01
9	NR	NR		
10	0.041	0.006	-0.02	-0.02
11	0.0340	0.0021	-0.87	-0.95
12	0.019	0.02	-2.69	-1.04
13	NT	NT		
14	<0.05	0.05		

Statistics

Assigned Value*	0.0412	0.0073
Spike	Not Spiked	
Homogeneity Value	0.0457	0.0091
Robust Average	0.0395	0.0088
Median	0.0400	0.0068
Mean	0.0390	
N	9	
Max.	0.056	
Min.	0.019	
Robust SD	0.011	
Robust CV	27%	

*Robust Average excluding laboratory 12.


Kernel Density
Density
Result
Results: S1 - TDP
Assigned Value = 0.0412 ± 0.0073 mg/L
Results (mg/L)
Laboratory
12
11
2
3
8
10
4
7
5
14
9
1
13
6
Md
R.A.
H.V.


z-Scores: S1 - TDP
Target Standard Deviation 0.0082 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
-2.7
-0.9
-0.9
-0.9
-0.1
0.0
0.5
0.8
1.8

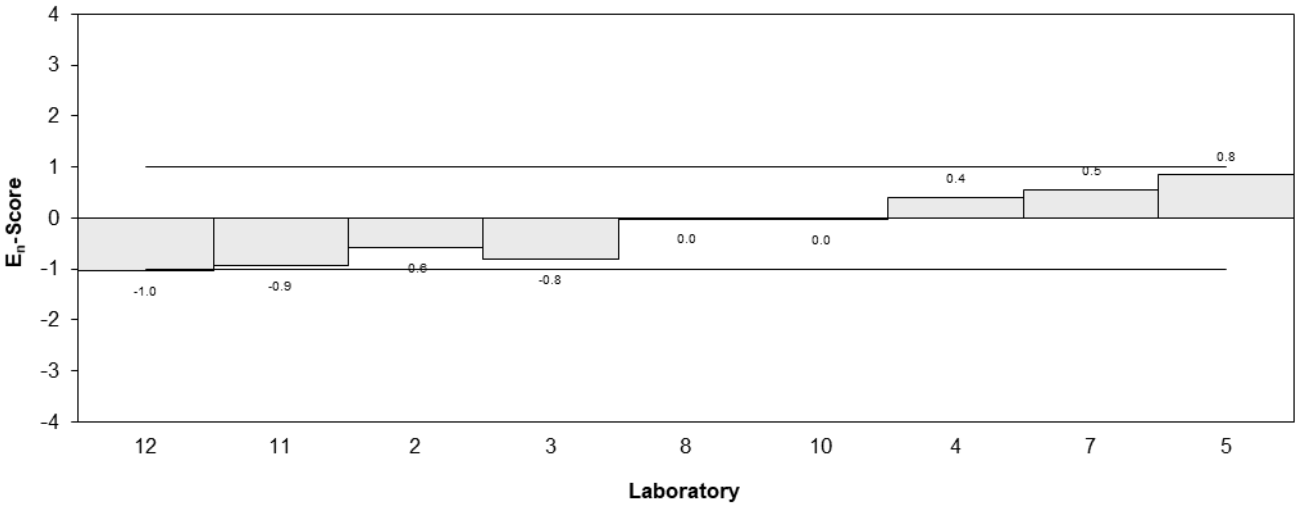

En-Scores: S1 - TDP
En-Score
Laboratory
-1.0
-0.9
-0.6
-0.8
0.0
0.0
0.4
0.5
0.8

Figure 15

Table 19

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	Alkalinity
Units	mg/L

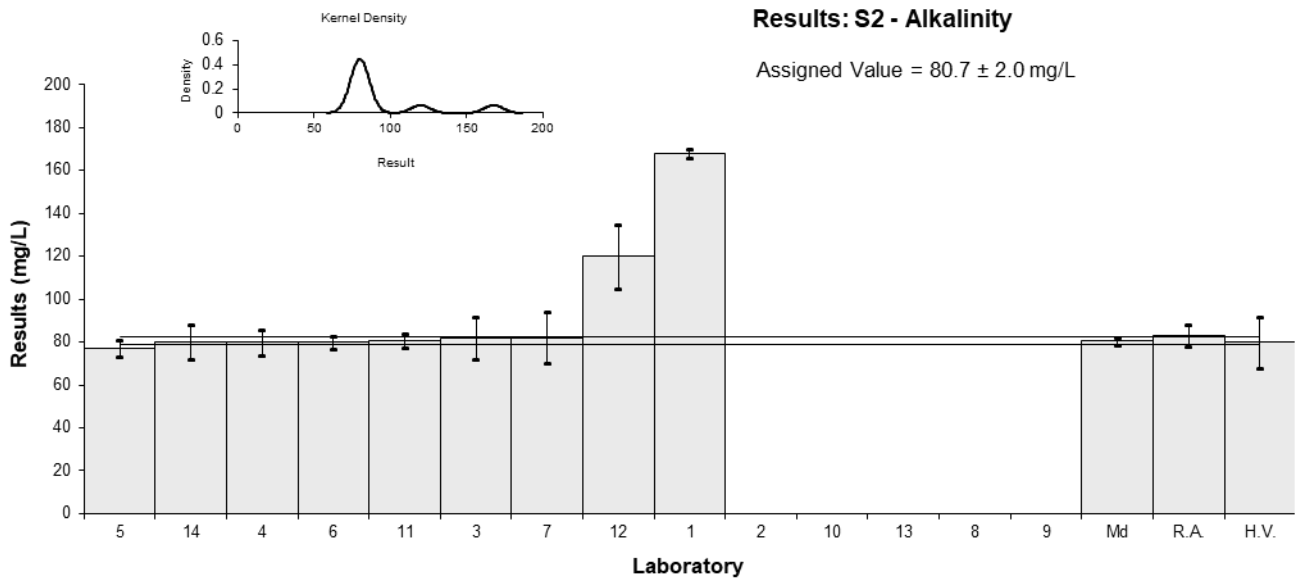
Participant Results

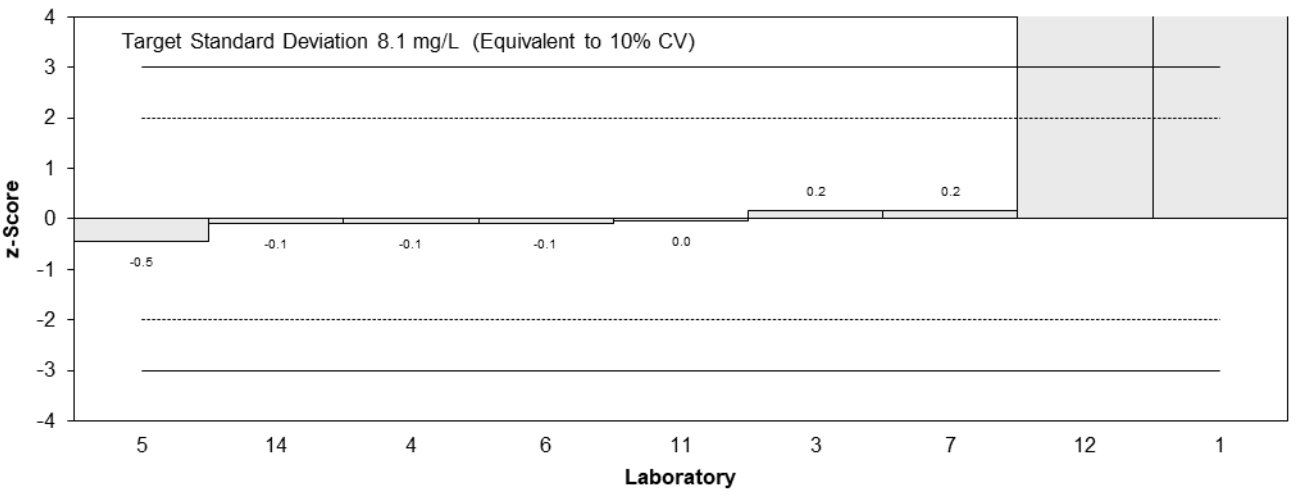
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	168	2	10.82	30.87
2	NR	NR		
3	82	10	0.16	0.13
4	80	6	-0.09	-0.11
5	77	4	-0.46	-0.83
6	80	3	-0.09	-0.19
7	82	12	0.16	0.11
8	NT	NT		
9	NT	NT		
10	NT	NT		
11	80.4	3.3	-0.04	-0.08
12	120	15	4.87	2.60
13	NT	NT		
14	80	8	-0.09	-0.08

Statistics

Assigned Value*	80.7	2.0
Spike	Not Spiked	
Homogeneity Value	80	12
Robust Average	82.8	5.1
Median	80.4	1.8
Mean	94.4	
N	9	
Max.	168	
Min.	77	
Robust SD	6.1	
Robust CV	7.4%	

*Robust Average excluding laboratory 1.


Kernel Density
Density
Result
Results: S2 - Alkalinity
Assigned Value = 80.7 ± 2.0 mg/L
Results (mg/L)
Laboratory
5 14 4 6 11 3 7 12 1 2 10 13 8 9 Md R.A. H.V.


z-Scores: S2 - Alkalinity
Target Standard Deviation 8.1 mg/L (Equivalent to 10% CV)
z-Score
-0.5 -0.1 -0.1 -0.1 0.0 0.2 0.2
Laboratory
5 14 4 6 11 3 7 12 1

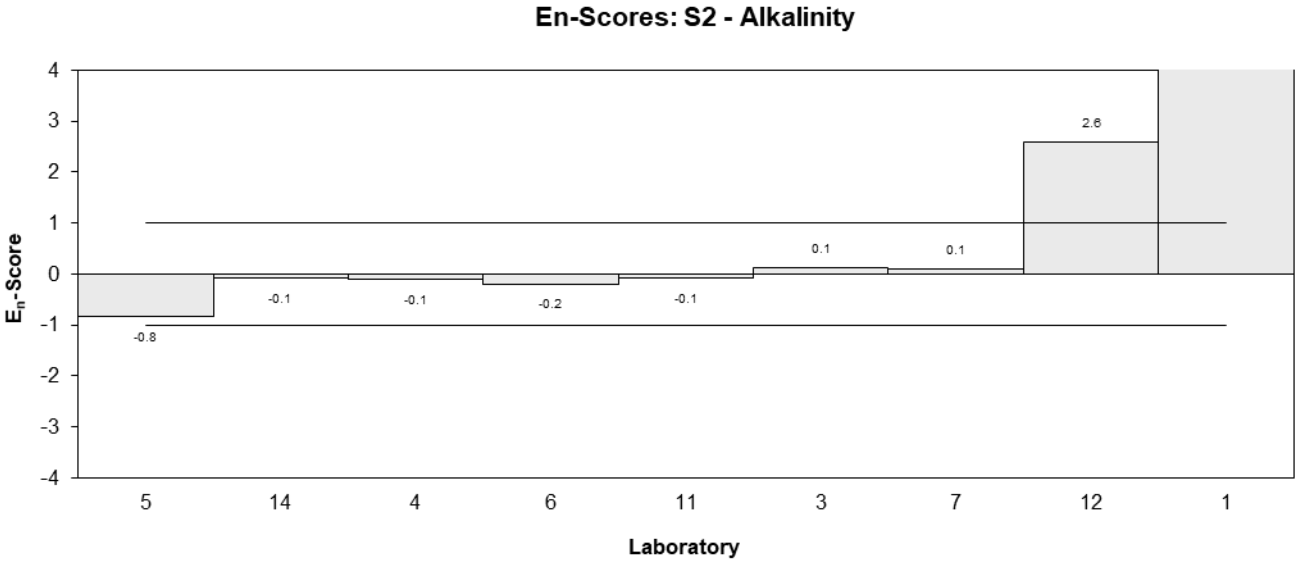

En-Scores: S2 - Alkalinity
En-Score
-0.8 -0.1 -0.1 -0.2 -0.1 0.1 0.1 2.6
Laboratory
5 14 4 6 11 3 7 12 1

Figure 16

Table 20

Sample Details

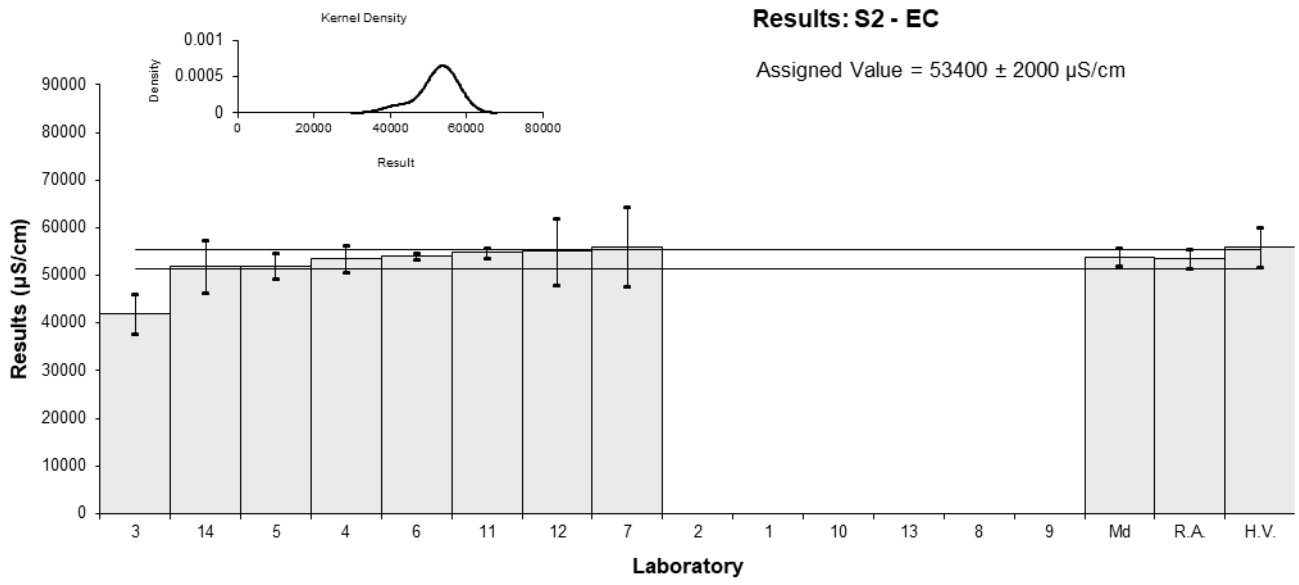
Sample No.	S2
Matrix.	Seawater
Analyte.	EC
Units	µS/cm

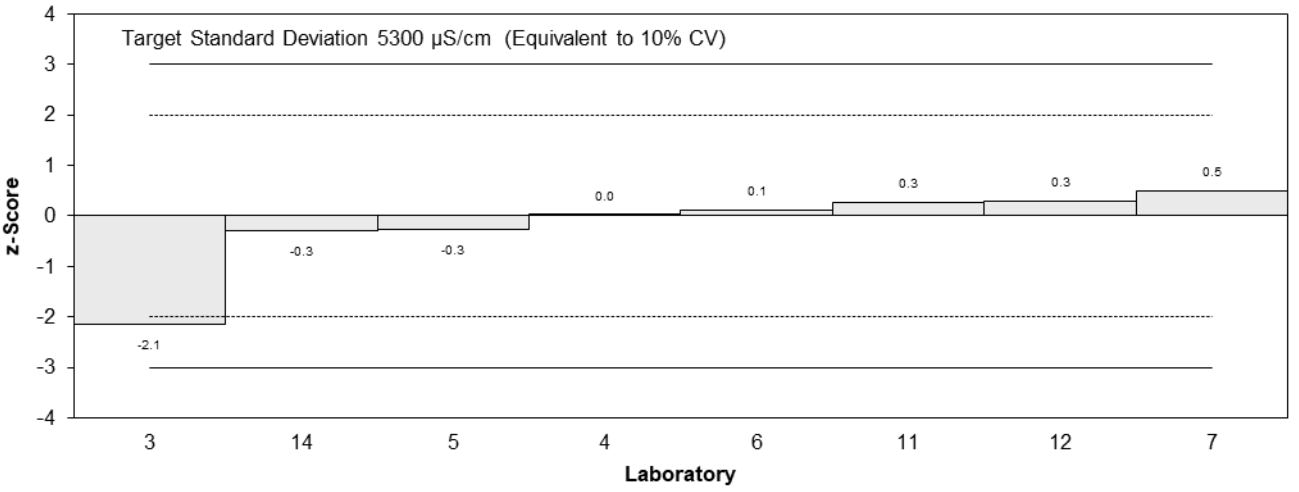
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NR	NR		
3	41982	4200	-2.14	-2.45
4	53500	2700	0.02	0.03
5	52000	2600	-0.26	-0.43
6	54000	660	0.11	0.28
7	56000	8400	0.49	0.30
8	NT	NT		
9	NT	NT		
10	NT	NT		
11	54800	1100	0.26	0.61
12	55000	6900	0.30	0.22
13	NT	NT		
14	51802	5500	-0.30	-0.27

Statistics

Assigned Value	53400	2000
Spike	Not Spiked	
Homogeneity Value	56000	4200
Robust Average	53400	2000
Median	53800	1900
Mean	52400	
N	8	
Max.	56000	
Min.	41982	
Robust SD	2300	
Robust CV	4.2%	


Kernel Density
Density
0.001
0.0005
0
0
20000
40000
60000
80000
Result
Results: S2 - EC
Assigned Value = 53400 ± 2000 µS/cm
Results (µS/cm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
3
14
5
4
6
11
12
7
2
1
10
13
8
9
Md
R.A.
H.V.
Laboratory


z-Scores: S2 - EC
Target Standard Deviation 5300 µS/cm (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.1
-0.3
-0.3
0.0
0.1
0.3
0.3
0.5
3
14
5
4
6
11
12
7
Laboratory

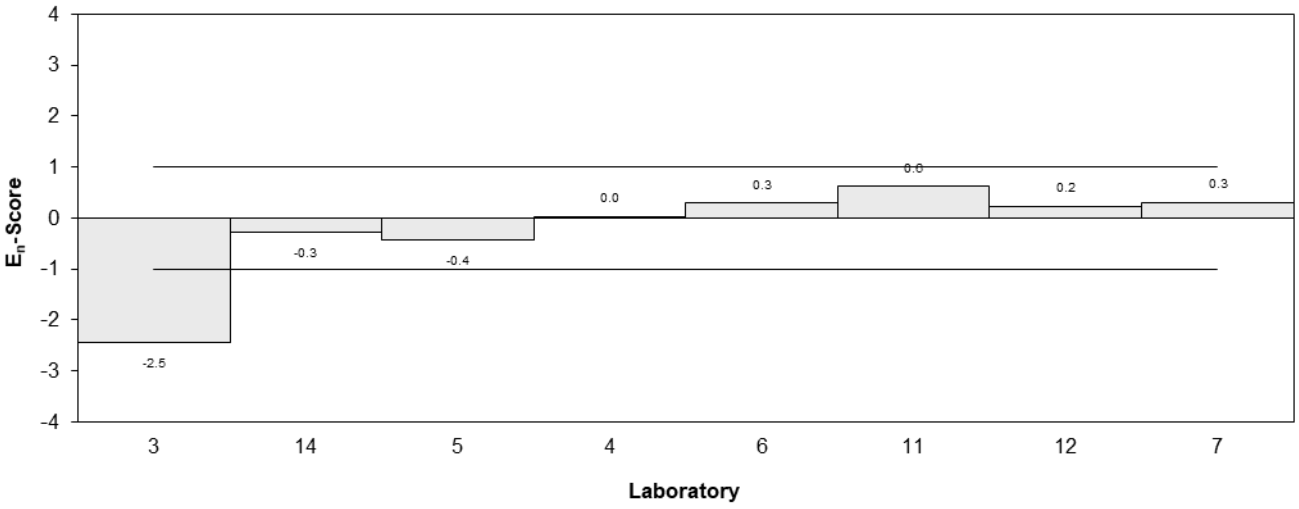

En-Scores: S2 - EC
En-Score
4
3
2
1
0
-1
-2
-3
-4
-2.5
-0.3
-0.4
0.0
0.3
0.6
0.2
0.3
3
14
5
4
6
11
12
7
Laboratory

Figure 17

Table 21

Sample Details

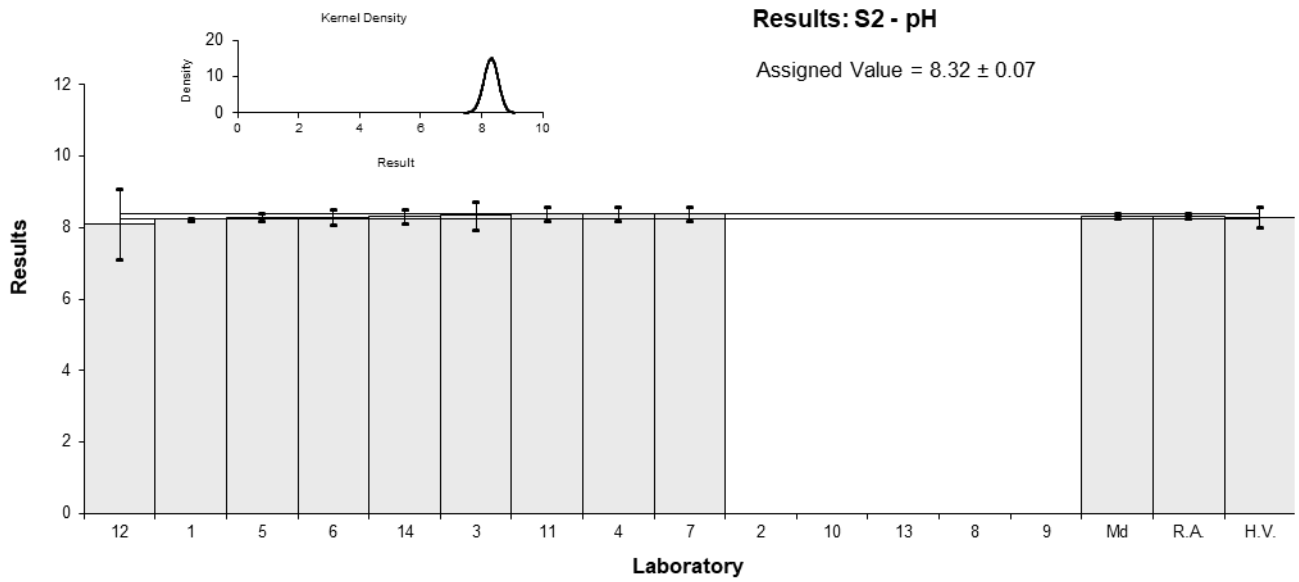
Sample No.	S2
Matrix.	Seawater
Analyte.	pH

Participant Results

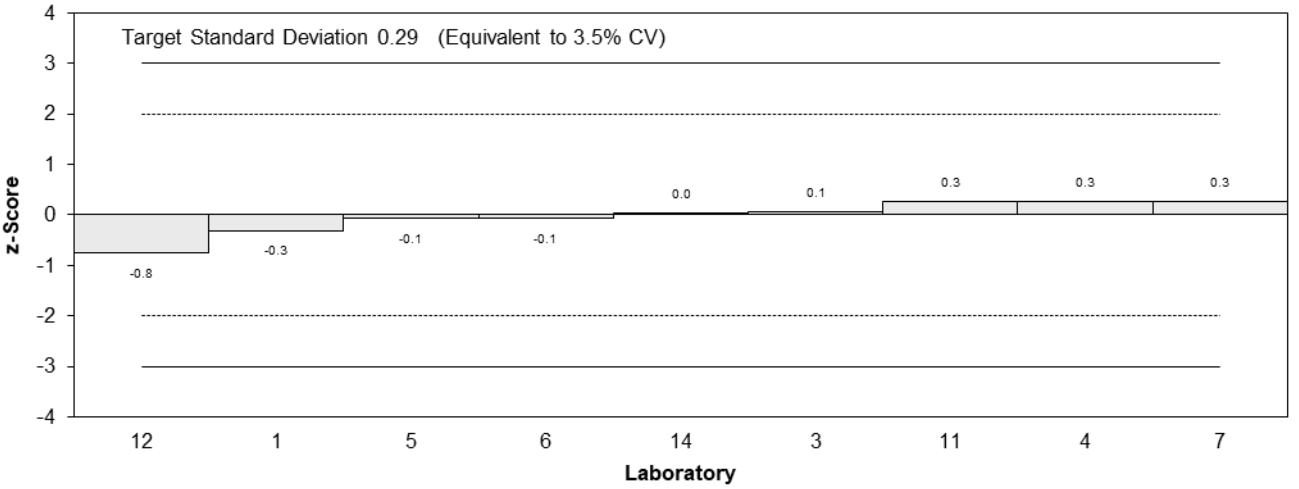
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	8.23	0.02	-0.31	-1.24
2	NR	NR		
3	8.34	0.4	0.07	0.05
4	8.4	0.2	0.27	0.38
5	8.3	0.1	-0.07	-0.16
6	8.3	0.2	-0.07	-0.09
7	8.4	0.2	0.27	0.38
8	NT	NT		
9	NT	NT		
10	NT	NT		
11	8.4	0.2	0.27	0.38
12	8.1	1	-0.76	-0.22
13	NT	NT		
14	8.33	0.2	0.03	0.05

Statistics

Assigned Value	8.32	0.07
Spike	Not Spiked	
Homogeneity Value	8.30	0.30
Robust Average	8.32	0.07
Median	8.33	0.08
Mean	8.31	
N	9	
Max.	8.4	
Min.	8.1	
Robust SD	0.084	
Robust CV	1%	



z-Scores: S2 - pH



En-Scores: S2 - pH

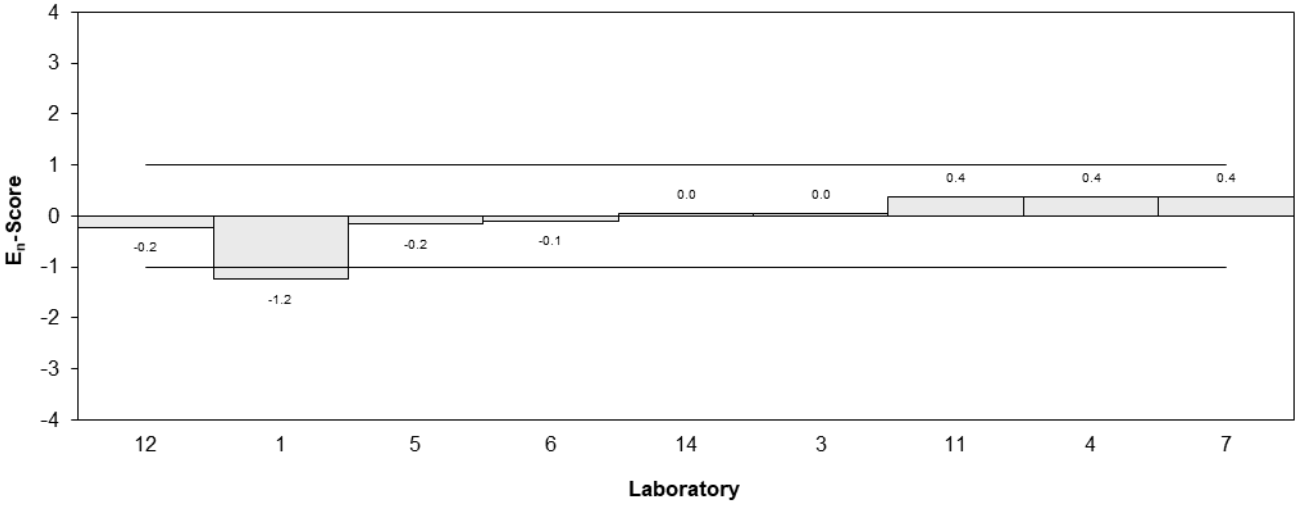


Figure 18

Table 22

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	TKN
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	NR	NR
3	0.81	0.1
4	NR	NR
5	0.71	0.16
6	NT	NT
7	0.60	0.12
8	NT	NT
9	NT	NT
10	NT	NT
11	0.341	0.069
12	0.57	0.14
13	NT	NT
14	NT	NT

Statistics

Assigned Value	Not Set	
Spike*	0.253	0.011
Homogeneity Value	0.589	0.088
Median	0.60	0.20
Mean	0.61	
N	5	
Max.	0.81	
Min.	0.341	

*Incurred value not included

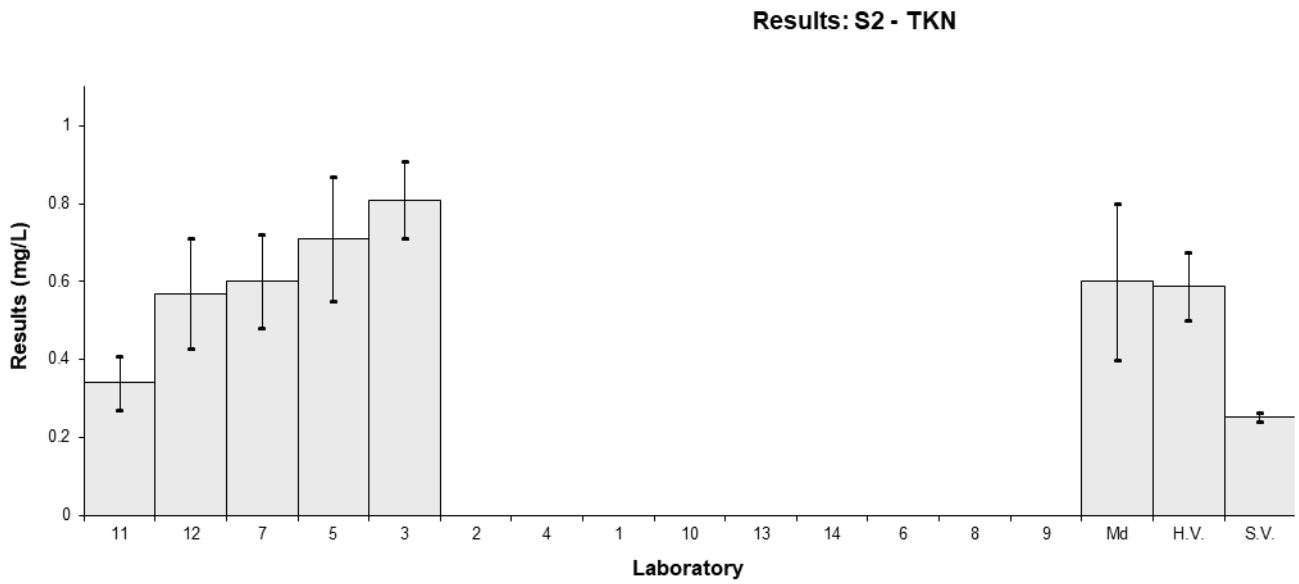

Results: S2 - TKN
Results (mg/L)
1
0.8
0.6
0.4
0.2
0
11
12
7
5
3
2
4
1
10
13
14
6
8
9
Md
H.V.
S.V.
Laboratory

Figure 19

Table 23

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	TN
Units	mg/L

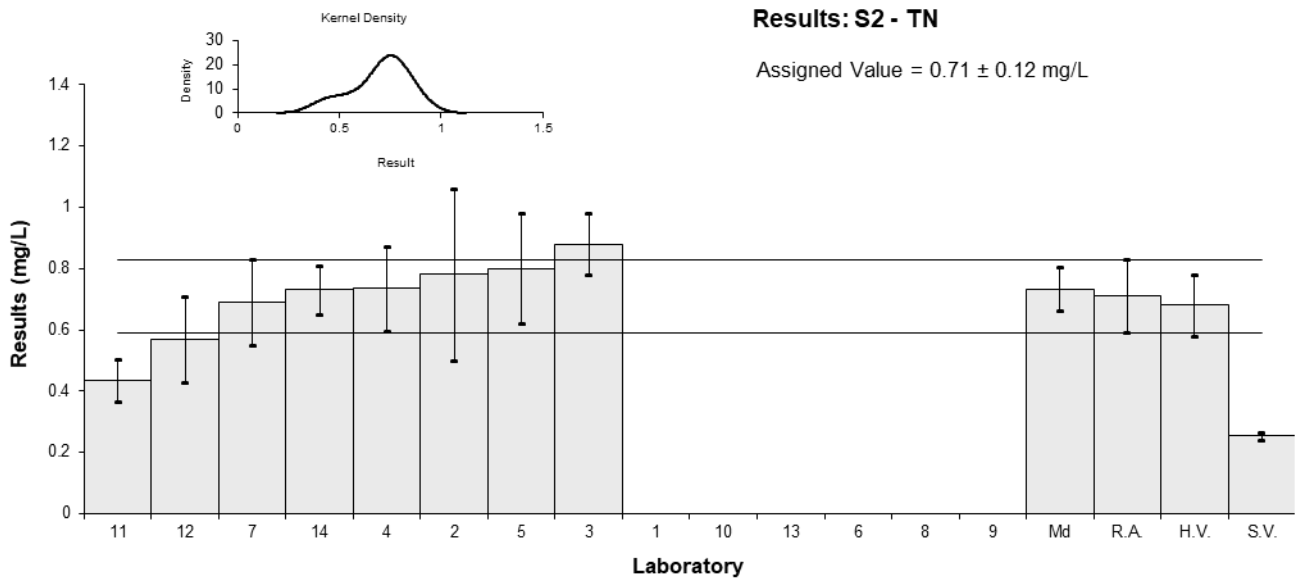
Participant Results

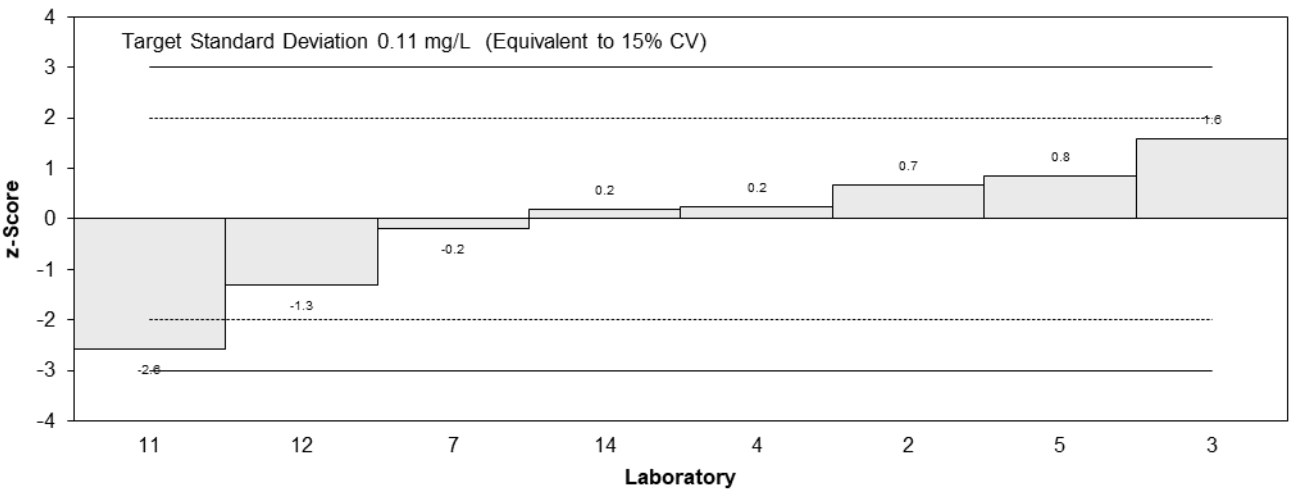
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.781	0.28	0.67	0.23
3	0.88	0.1	1.60	1.09
4	0.735	0.137	0.23	0.14
5	0.8	0.18	0.85	0.42
6	NT	NT		
7	0.69	0.14	-0.19	-0.11
8	NT	NT		
9	NT	NT		
10	NT	NT		
11	0.434	0.070	-2.59	-1.99
12	0.57	0.14	-1.31	-0.76
13	NT	NT		
14	0.73	0.08	0.19	0.14

Statistics

Assigned Value	0.71	0.12
Spike*	0.253	0.011
Homogeneity Value	0.68	0.10
Robust Average	0.71	0.12
Median	0.733	0.072
Mean	0.703	
N	8	
Max.	0.88	
Min.	0.434	
Robust SD	0.14	
Robust CV	20%	

*Incurred value not included


Kernel Density
Density
Result
Results: S2 - TN
Assigned Value = 0.71 ± 0.12 mg/L
Results (mg/L)
Laboratory
11 12 7 14 4 2 5 3 1 10 13 6 8 9 Md R.A. H.V. S.V.


z-Scores: S2 - TN
Target Standard Deviation 0.11 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 12 7 14 4 2 5 3
-2.6
-1.3
-0.2
0.2
0.2
0.7
0.8
1.6

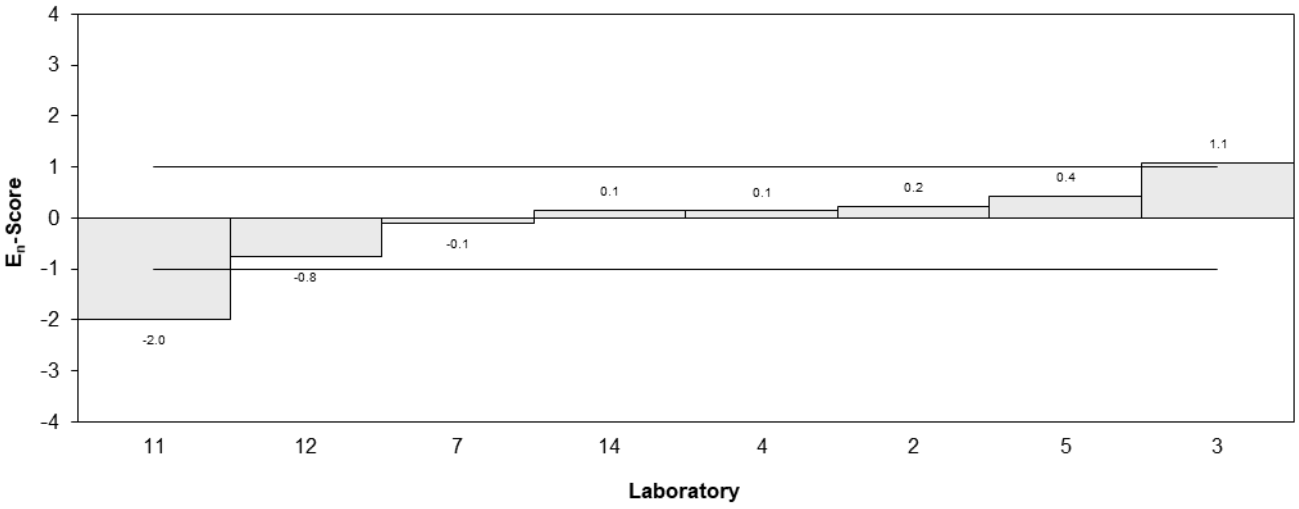

En-Scores: S2 - TN
En-Score
Laboratory
11 12 7 14 4 2 5 3
-2.0
-0.8
-0.1
0.1
0.1
0.2
0.4
1.1

Figure 20

Table 24

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	TOC
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	NR	NR
3	NT	NT
4	4.18	0.63
5	3.9	0.6
6	NT	NT
7	4.5	0.9
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	4.5	0.6
13	NT	NT
14	4	1

Statistics

Assigned Value	Not Set	
Spike	4.85	0.83
Homogeneity Value	4.53	0.68
Median	4.18	0.52
Mean	4.22	
N	5	
Max.	4.5	
Min.	3.9	

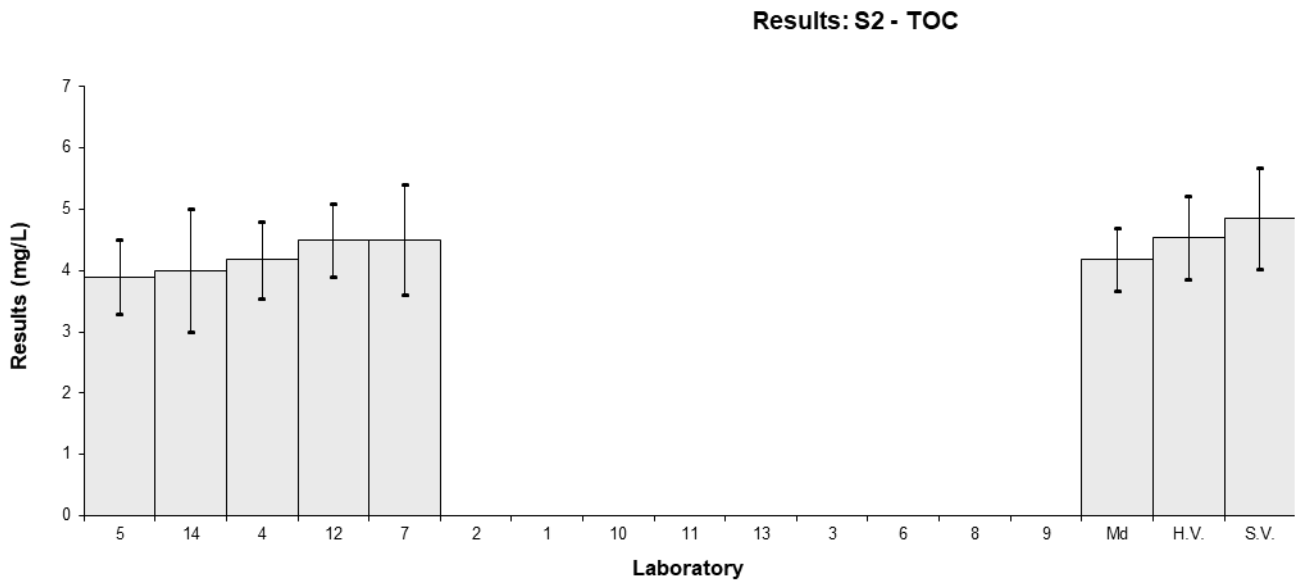

Results: S2 - TOC
Results (mg/L)
0
1
2
3
4
5
6
7
5
14
4
12
7
2
1
10
11
13
3
6
8
9
Md
H.V.
S.V.
Laboratory

Figure 21

Table 25

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	Total Hardness
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	NR	NR
3	6800	680
4	NR	NR
5	6440	1930
6	NT	NT
7	6000	1200
8	NT	NT
9	NT	NT
10	NT	NT
11	6100	NR
12	100	13
13	NT	NT
14	6440.4	700

Statistics*

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	6900	690
Median	6440	630
Mean	6360	
N	5	
Max.	6800	
Min.	6000	

*Laboratory 12 was excluded from statistical calculation (extreme outlier).

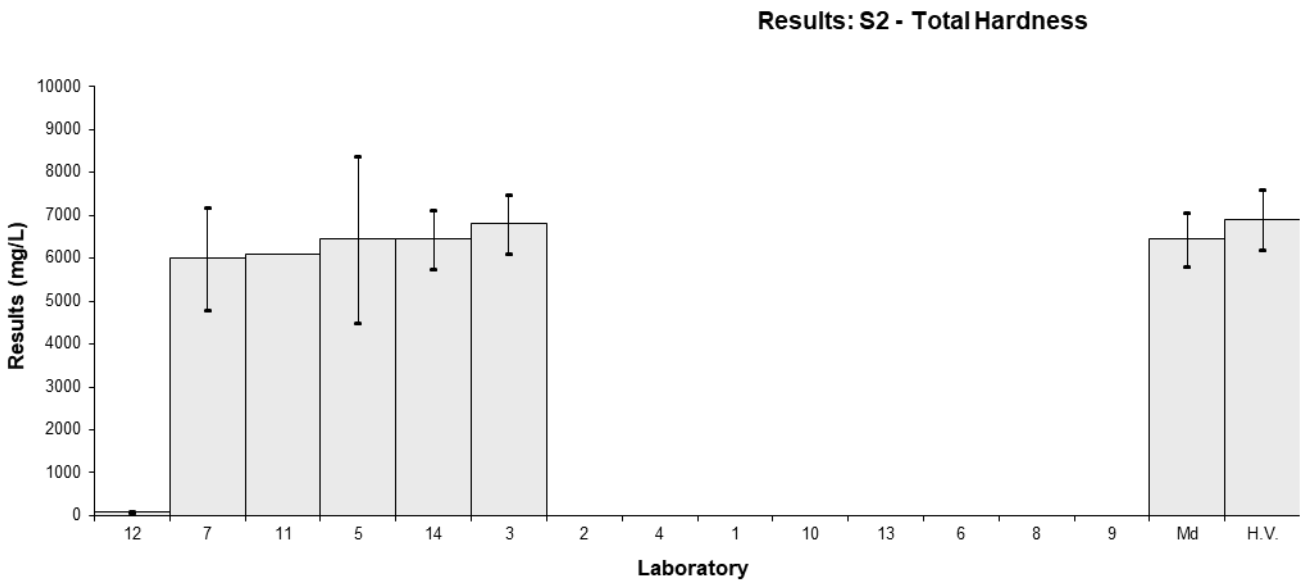

Results: S2 - Total Hardness
Results (mg/L)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
12
7
11
5
14
3
2
4
1
10
13
6
8
9
Md
H.V.
Laboratory

Figure 22

Table 26

Sample Details

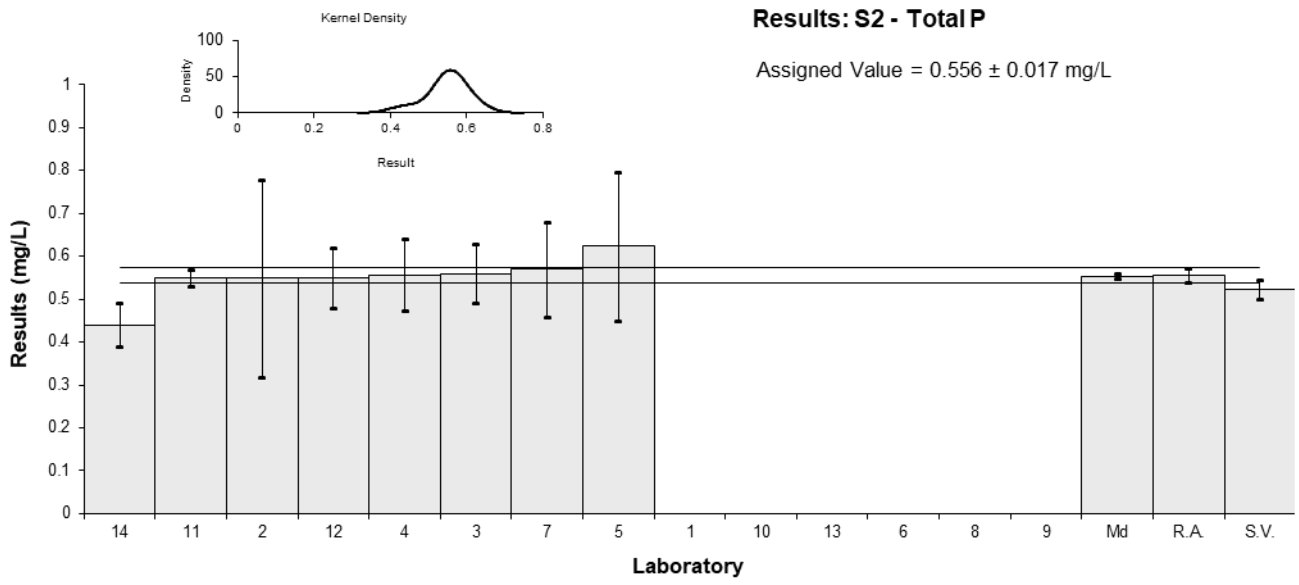
Sample No.	S2
Matrix.	Seawater
Analyte.	Total P
Units	mg/L

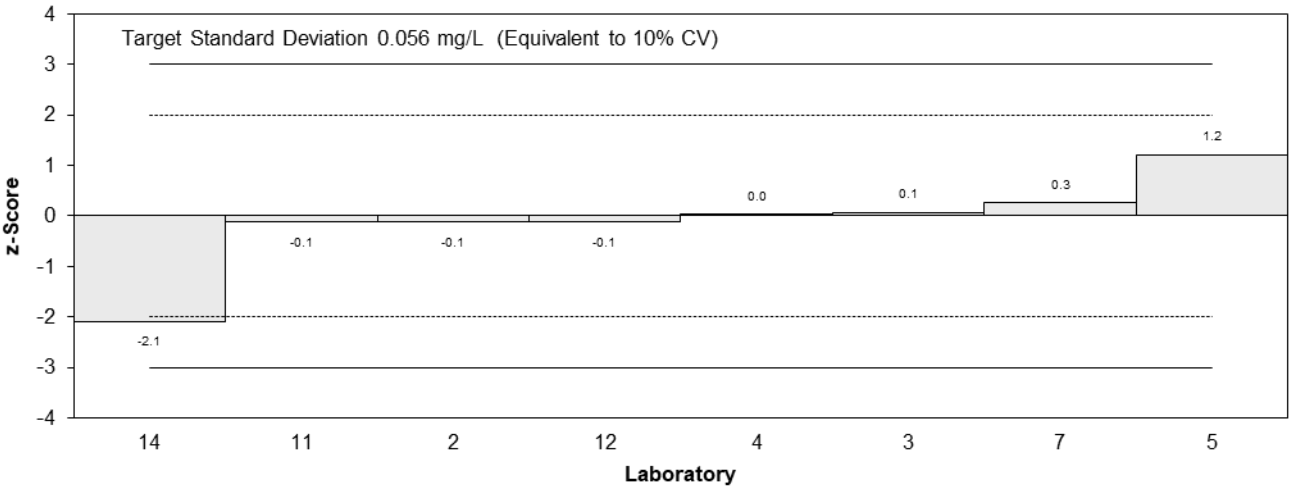
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.549	0.23	-0.13	-0.03
3	0.56	0.07	0.07	0.06
4	0.557	0.084	0.02	0.01
5	0.623	0.174	1.21	0.38
6	NT	NT		
7	0.57	0.11	0.25	0.13
8	NT	NT		
9	NT	NT		
10	NT	NT		
11	0.549	0.019	-0.13	-0.27
12	0.55	0.07	-0.11	-0.08
13	NT	NT		
14	0.44	0.05	-2.09	-2.20

Statistics

Assigned Value	0.556	0.017
Spike	0.523	0.022
Robust Average	0.556	0.017
Median	0.554	0.007
Mean	0.550	
N	8	
Max.	0.623	
Min.	0.44	
Robust SD	0.019	
Robust CV	3.4%	


Kernel Density
Density
Result
Results: S2 - Total P
Assigned Value = 0.556 ± 0.017 mg/L
Results (mg/L)
Laboratory
14 11 2 12 4 3 7 5 1 10 13 6 8 9 Md R.A. S.V.


z-Scores: S2 - Total P
Target Standard Deviation 0.056 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
14 11 2 12 4 3 7 5
-2.1 -0.1 -0.1 -0.1 0.0 0.1 0.3 1.2

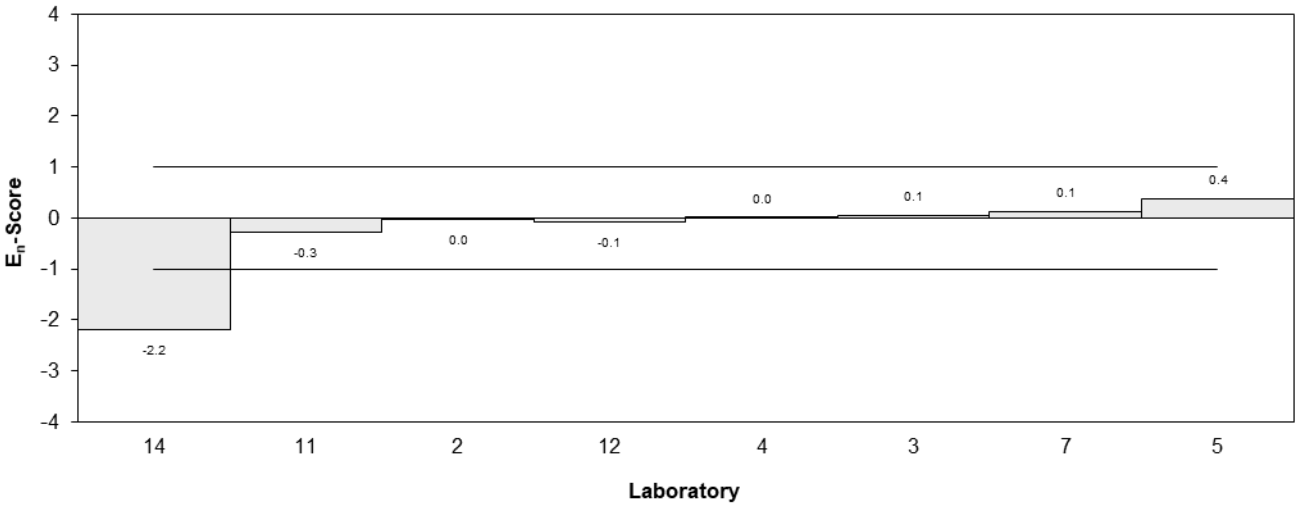

En-Scores: S2 - Total P
En-Score
Laboratory
14 11 2 12 4 3 7 5
-2.2 -0.3 0.0 -0.1 0.0 0.1 0.1 0.4

Figure 23

Table 27

Sample Details

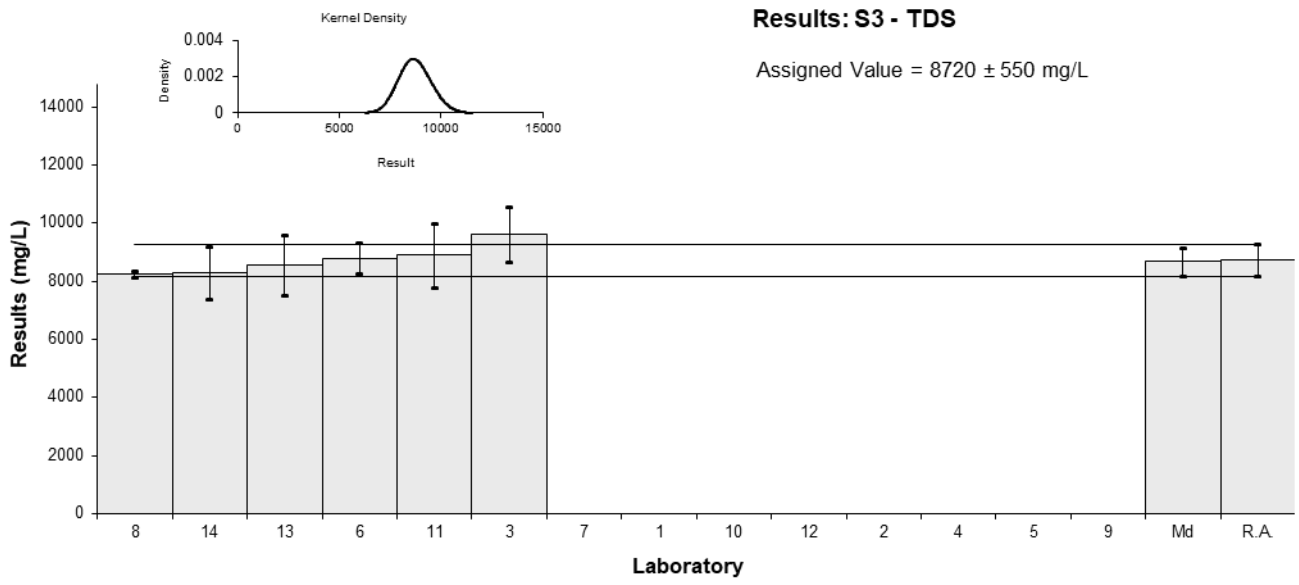
Sample No.	S3
Matrix.	Seawater
Analyte.	TDS
Units	mg/L

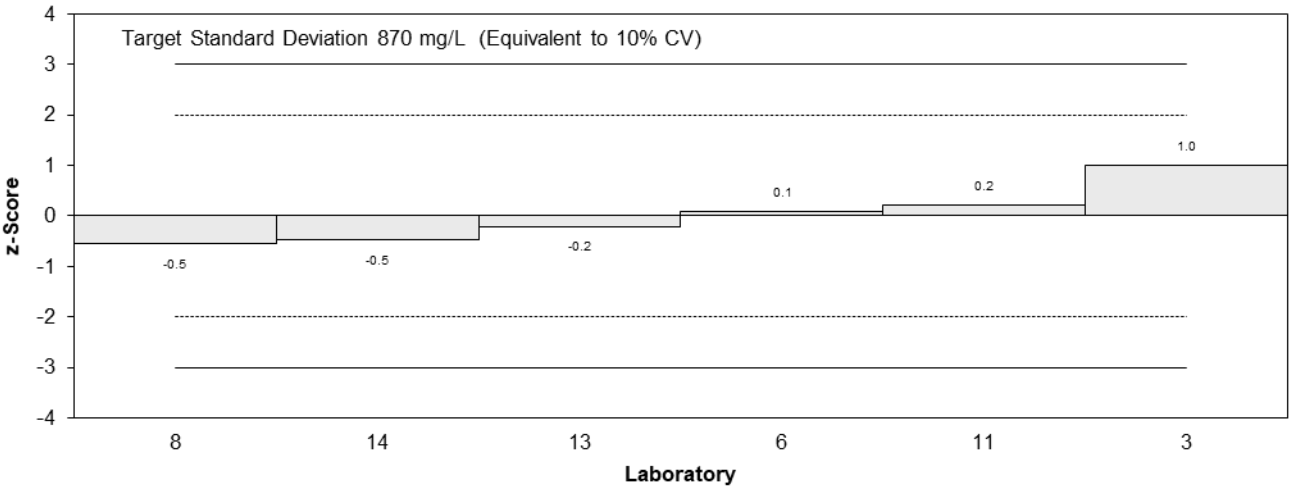
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	9596	950	1.00	0.80
4	NT	NT		
5	NT	NT		
6	8800	520	0.09	0.11
7	NR	NR		
8	8247	100	-0.54	-0.85
9	NT	NT		
10	NT	NT		
11	8900	1100	0.21	0.15
12	NT	NT		
13	8540	1033.3	-0.21	-0.15
14	8300	900	-0.48	-0.40

Statistics

Assigned Value	8720	550
Spike	Not Spiked	
Robust Average	8720	550
Median	8670	470
Mean	8730	
N	6	
Max.	9596	
Min.	8247	
Robust SD	530	
Robust CV	6.1%	


Kernel Density
Density
0.004
0.002
0
0
5000
10000
15000
Result
Results: S3 - TDS
Assigned Value = 8720 ± 550 mg/L
Results (mg/L)
14000
12000
10000
8000
6000
4000
2000
0
8
14
13
6
11
3
7
1
10
12
2
4
5
9
Md
R.A.
Laboratory


z-Scores: S3 - TDS
Target Standard Deviation 870 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.5
-0.2
0.1
0.2
1.0
8
14
13
6
11
3
Laboratory

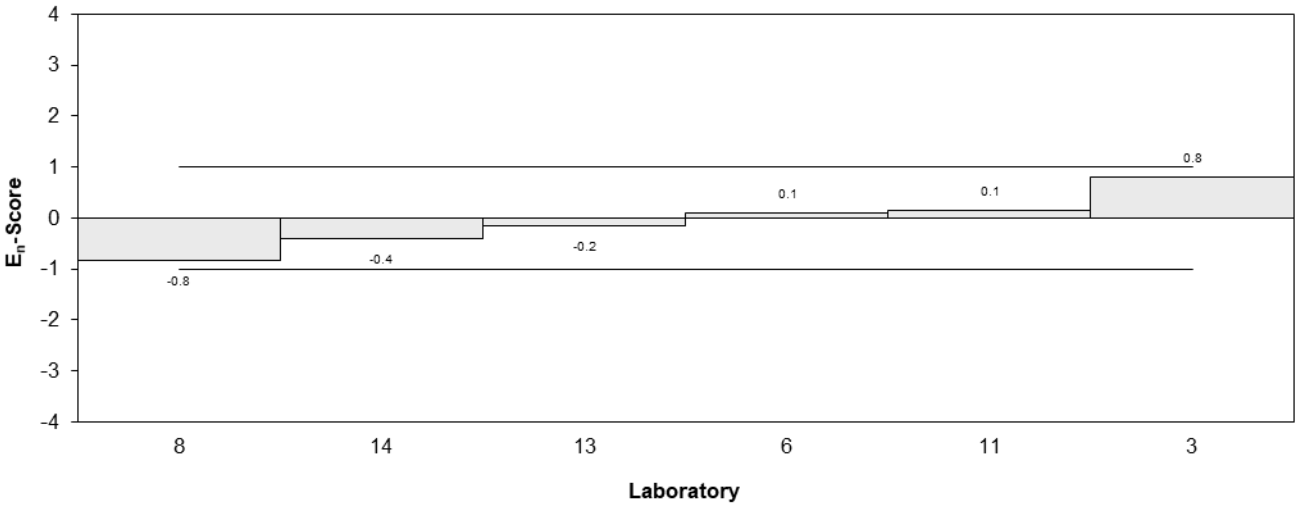

En-Scores: S3 - TDS
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.4
-0.2
0.1
0.1
0.8
8
14
13
6
11
3
Laboratory

Figure 24

Table 28

Sample Details

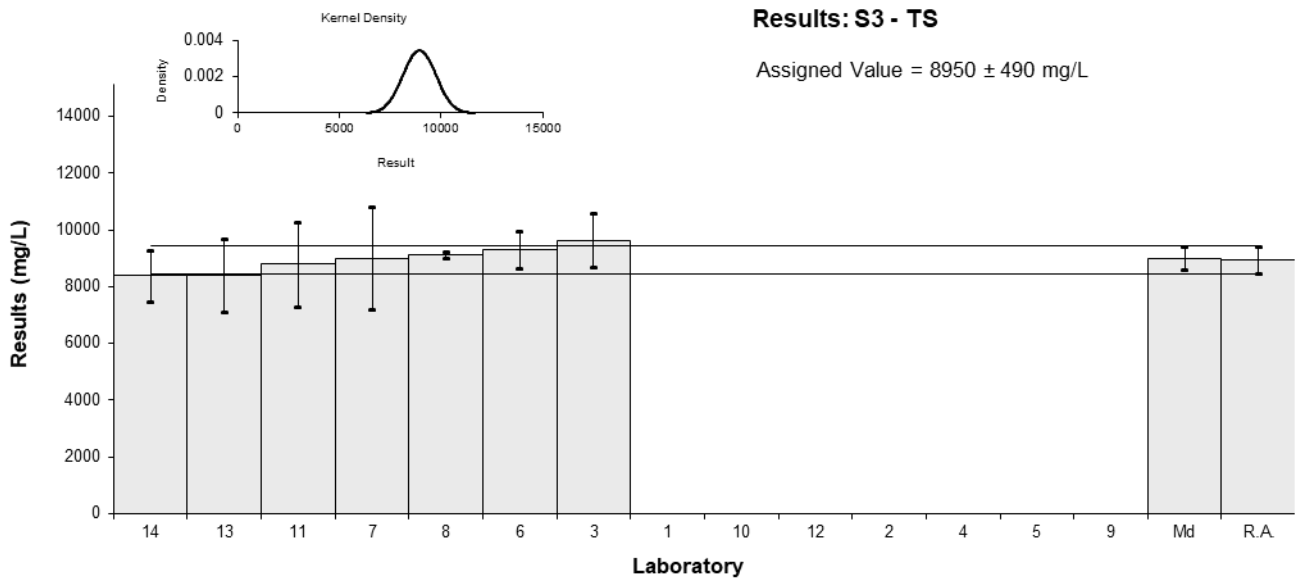
Sample No.	S3
Matrix.	Seawater
Analyte.	TS
Units	mg/L

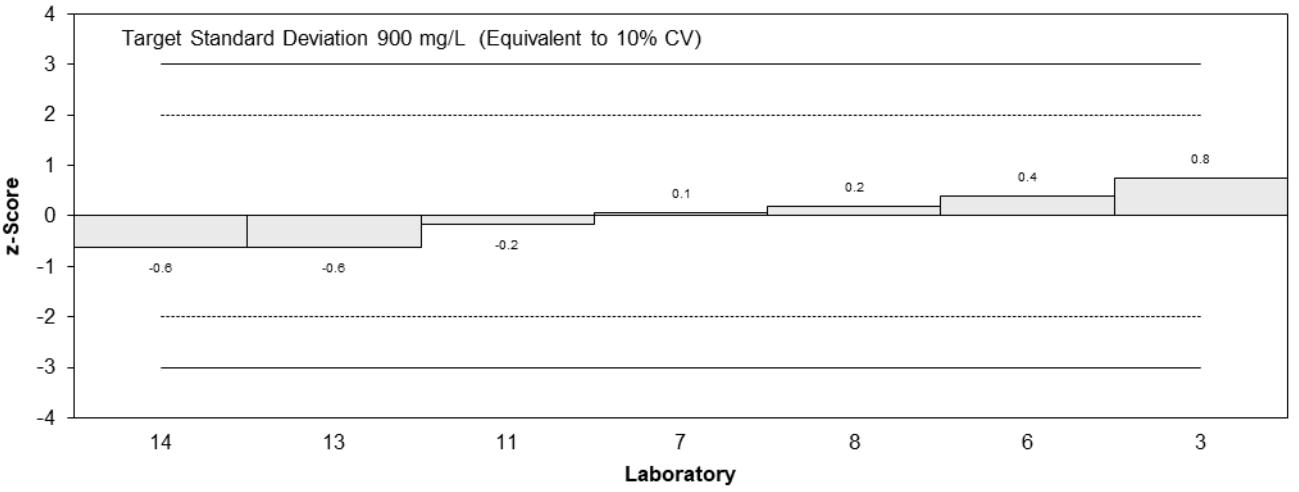
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	9628	950	0.76	0.63
4	NT	NT		
5	NT	NT		
6	9300	650	0.39	0.43
7	9000	1800	0.06	0.03
8	9120	100	0.19	0.34
9	NT	NT		
10	NT	NT		
11	8800	1500	-0.17	-0.10
12	NT	NT		
13	8400	1293.6	-0.61	-0.40
14	8380	900	-0.64	-0.56

Statistics

Assigned Value	8950	490
Spike	Not Spiked	
Robust Average	8950	490
Median	9000	410
Mean	8950	
N	7	
Max.	9628	
Min.	8380	
Robust SD	520	
Robust CV	5.8%	


Kernel Density
Density
0.004
0.002
0
0
5000
10000
15000
Result
Results: S3 - TS
Assigned Value = 8950 ± 490 mg/L
Results (mg/L)
14000
12000
10000
8000
6000
4000
2000
0
14
13
11
7
8
6
3
1
10
12
2
4
5
9
Md
R.A.
Laboratory


z-Scores: S3 - TS
Target Standard Deviation 900 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.6
-0.2
0.1
0.2
0.4
0.8
14
13
11
7
8
6
3
Laboratory

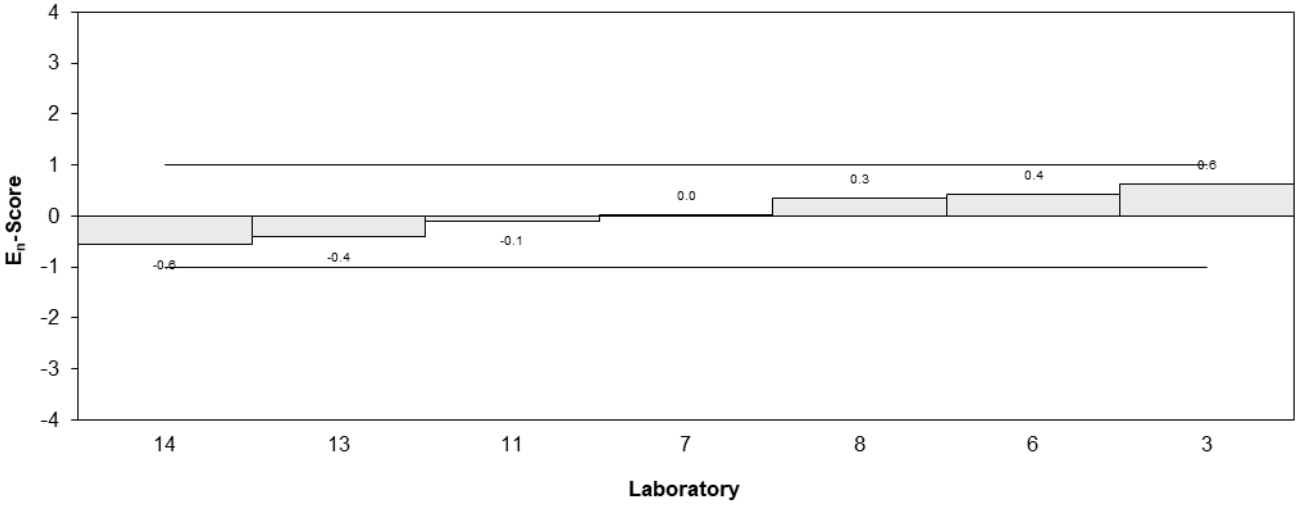

En-Scores: S3 - TS
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.4
-0.1
0.0
0.3
0.4
0.6
14
13
11
7
8
6
3
Laboratory

Figure 25

Table 29

Sample Details

Sample No.	S3
Matrix.	Seawater
Analyte.	TSS
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	NT	NT
3	31	3
4	NT	NT
5	NT	NT
6	31	2
7	27	4
8	NR	NR
9	NT	NT
10	NT	NT
11	31.6	4.6
12	NT	NT
13	25	4.7
14	50	10

Statistics

Assigned Value	Not Set	
Spike	34.1	1.4
Robust Average	30.7	5.5
Median	31.0	3.6
Mean	32.6	
N	6	
Max.	50	
Min.	25	
Robust SD	5.4	
Robust CV	18%	

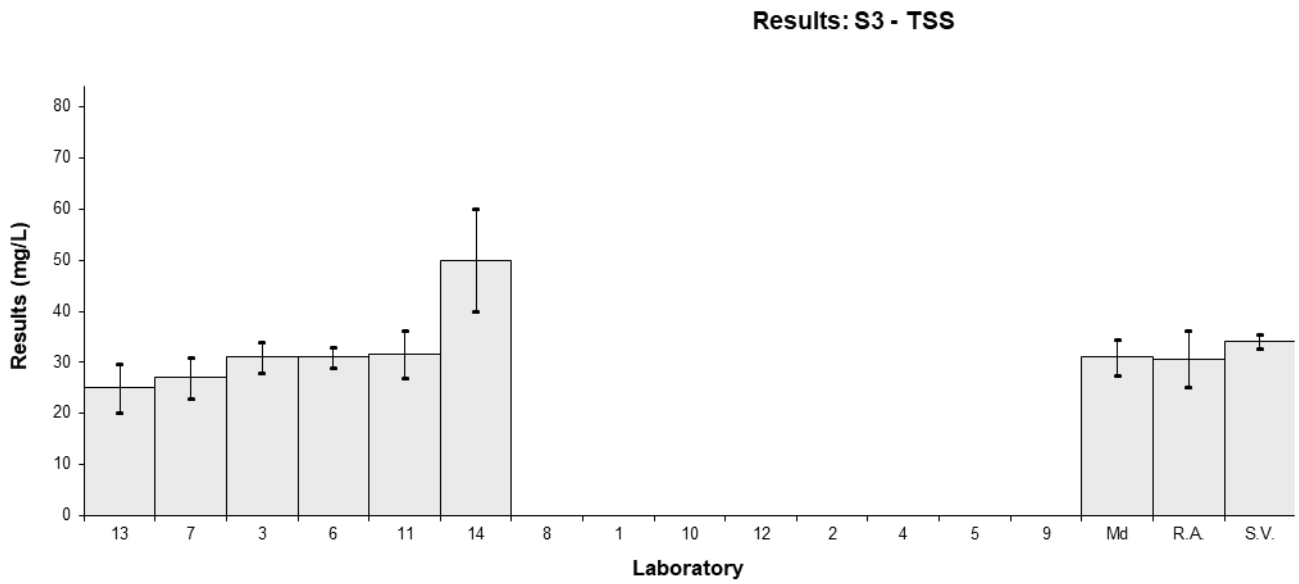

Results: S3 - TSS
Results (mg/L)
80
70
60
50
40
30
20
10
0
13
7
3
6
11
14
8
1
10
12
2
4
5
9
Md
R.A.
S.V.
Laboratory

Figure 26

7 DISCUSSION OF RESULTS

7.1 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 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory 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.

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

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 208 numerical results, 202 (97%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0.24% to 350% 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, 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 comparisons studies.[9-14]

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 26). 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, 9 laboratories reported results for B in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 9 laboratories' results is 0.88 mg/L (see equation 4, Appendix 3). Laboratory 8 might have under-estimated its expanded measurement uncertainties reported for B in S1 (0.01 mg/L) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 9 measurements. Alternatively, estimates of uncertainties for TDN in S1 larger than 0.127 mg/L (the uncertainty of the assigned value, 0.033 mg/L plus the allowable variation from the assigned value, the target standard deviation of 0.047 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 uncertainties reported by laboratory 8 for TDN in S1 (0.2 mg/L) might have been over-estimated.

Double counting the precision uncertainty components and overestimation of the laboratory or method bias are the most common errors seen in the laboratories' estimated uncertainty budgets. According to NORDTEST TR 537[10], the most common experimental data used for estimating the precision component for the measurement uncertainty calculation in the top down approach are from:

- Stable control samples that cover the whole analytical process (including extraction) and **have a matrix similar** to the samples; **or**
- Stable control samples **and** duplicate analyses if control samples do not cover whole analytical process (e.g. the control sample is a synthetic sample- we have to take into consideration uncertainties arising from different matrices); **or**

- When control samples are not stable, from analysis of natural duplicates (gives within-day variation for sampling and measurement) and long-term uncertainty component from the variation in the instrument calibration; **or**
- Replicate analyses performed on the same sample at different times to obtain estimates of intermediate precision; within-batch replication provides estimates of repeatability only.

The most common sources for estimating the method bias component for the measurement uncertainty calculation are from:

- Certified reference material recoveries; **or**
- Participation in PT studies (laboratory bias from at least 6 successful PT studies); **or**
- From sample spike recoveries.

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.

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 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]

7.3 E_n-score

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

The dispersal of participants' E_n-scores is graphically presented in Figure 27. 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 180 results for which E_n-scores were calculated, 150 (83%) 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.

7.4 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% to 20% PCV were used to calculate z-scores. A set target standard deviation enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

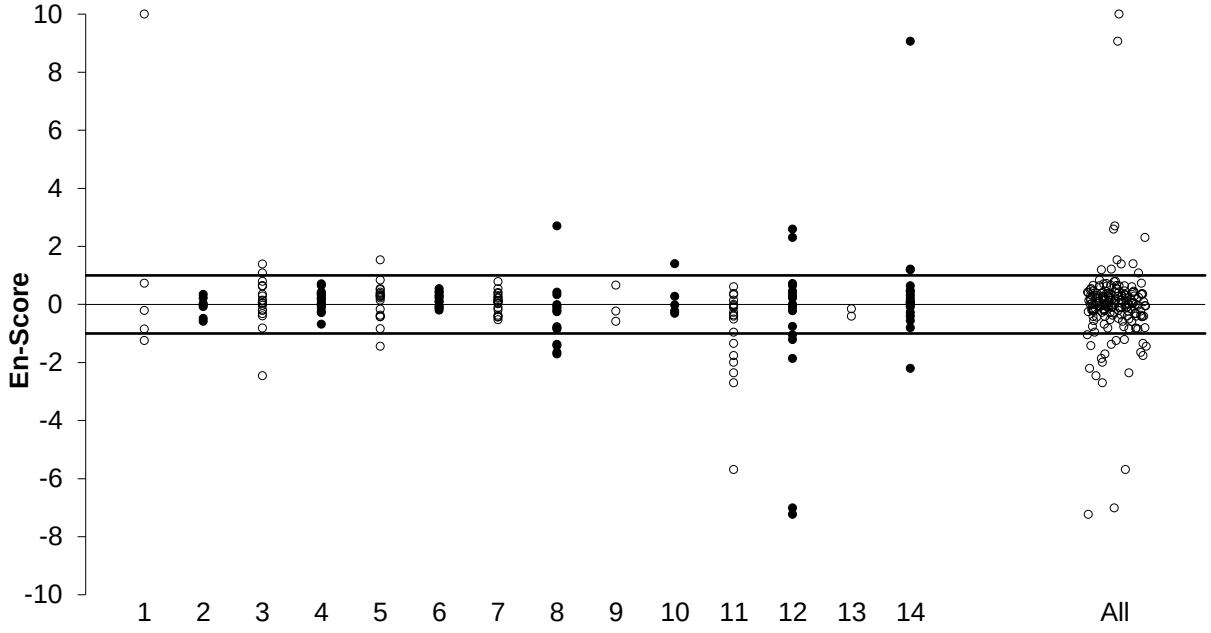
The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 30.

The dispersal of participants' z-scores is presented in Figure 28 (by laboratory code) and in Figure 29 (by test). Of 180 results for which z-scores were calculated, 162 (90%) returned a satisfactory score of $|z| \leq 2.0$ and 10 (6%) 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.

Five laboratories analysed all three samples. **Laboratory 3** reported results for all tests for which a z-score was calculated (20).

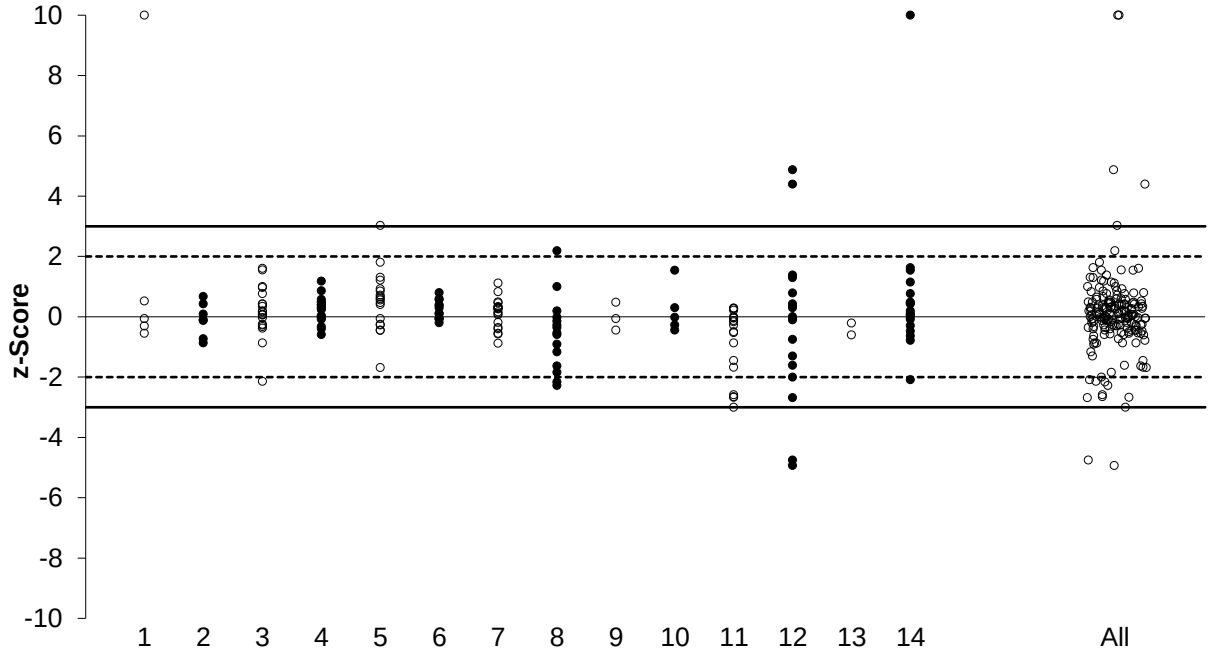
Summary of participants' performance is presented in Figure 30**. Laboratories 3** and **7** returned the highest number of satisfactory z scores (19 out of 20 reported and 19 out of 19 reported respectively). All results reported by **laboratories 7** (19), **4** (18), **6** (12), **2** (7), **10** (5), **9** (3) and **13** (2) also returned satisfactory z scores.

Laboratory 7 returned the highest number of satisfactory E_n scores (19 out of 19 reported). All results reported by **laboratories 7** (19), **4** (18), **6** (12), **2** (7), **9** (3) and **13** (2) returned satisfactory E_n scores.



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

Figure 27 E_n-Score Dispersal by Laboratory



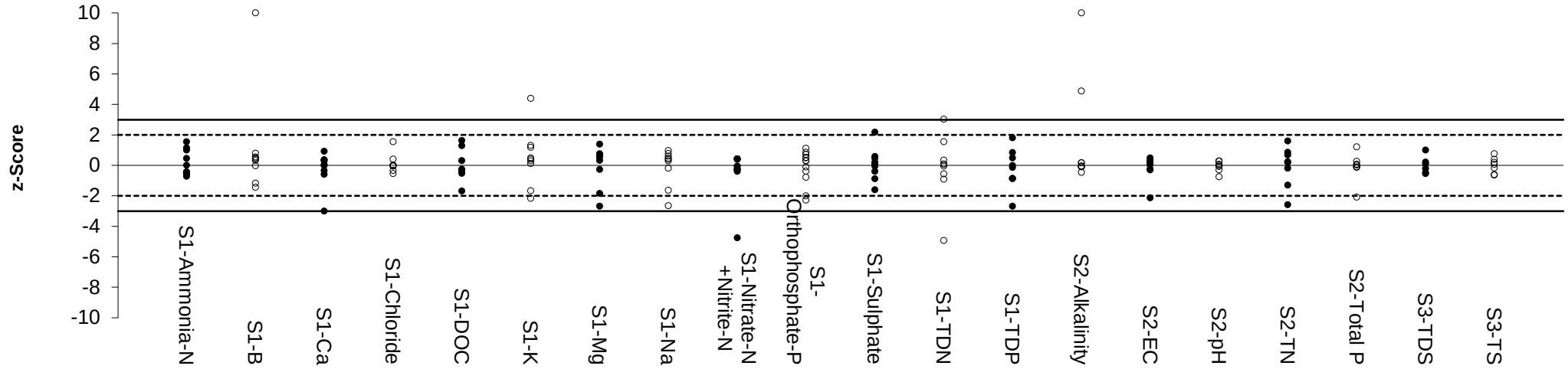
Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 28 z-Score Dispersal by Laboratory

Table 30 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	0.110	17%	22%	20%
S1	B	5.35	19%	12%	20%
S1	Ca	415	6.5%	6.5%	10%
S1	Chloride	20100	3.8%	3.6%	10%
S1	DOC	1.51	24%	15%	20%
S1	Fluoride	Not Set	31%	NA	Not Set
S1	K	374	21%	6.6%	15%
S1	Mg	1230	13%	5.5%	10%
S1	Na	10200	11%	4.0%	10%
S1	Nitrate-N +Nitrite-N	0.0424	7.8%	22%	20%
S1	Orthophosphate-P	0.0368	20%	22%	20%
S1	Sulphate	2740	9.5%	4.9%	10%
S1	TDN	0.237	15%	20%	20%
S1	TDP	0.0412	20%	22%	20%
S2	Alkalinity	80.7	2.8%	8.3%	10%
S2	EC	53400	4.2%	3.1%	10%
S2	pH	8.32	1%	12%	3.5%
S2	TKN	Not Set	NA	NA	Not Set
S2	TN	0.71	20%	17%	15%
S2	TOC	Not Set	NA	NA	Not Set
S2	Total Hardness	Not Set	NA	NA	Not Set
S2	Total P	0.556	3.4%	17%	10%
S3	TDS	8720	6.1%	4.1%	10%
S3	TS	8950	5.8%	4.1%	10%
S3	TSS	Not Set	18%	NA	Not Set

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



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

Figure 29 z-Score Dispersal by Analyte

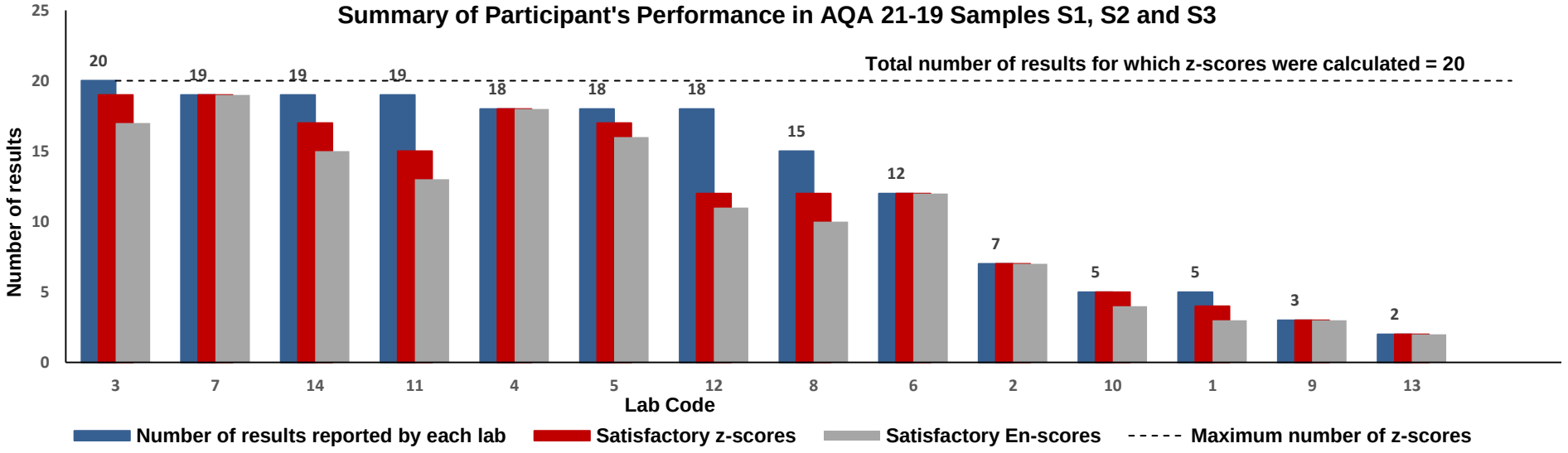


Figure 30 Summary of Participants' Performance

Table 31 Summary of Participants' Results and Performance for Sample S1

Lab Code	Ammonia-N (mg/L)	B (mg/L)	Ca (mg/L)	Chloride (mg/L)	DOC (mg/L)	Fluoride (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	NOx-N (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
A.V.	0.110	5.35	415	20100	1.51	Not Set	374	1230	10200	0.0424	0.0368	2740	0.237	0.0412
H.V.	0.110	NA	374	20000	1.57	1.10	453	1310	NA	0.0403	0.0397	2400	NA	0.0457
1	0.098	NT	NT	NT	NT	NT	NT	NT	NT	0.0419	0.0406	NT	NT	NT
2	0.094	NR	NR	NR	NR	NR	NR	NR	NR	0.046	0.036	NR	0.241	0.034
3	0.144	5.32	417	19440	1.43	1.7	397	1195	11180	0.046	0.034	2793	0.253	0.034
4	0.0967	5.86	428	20100	1.41	1.13	440	1300	10600	0.0457	0.0431	2630	0.235	0.0452
5	0.1	5.940	453	20900	1.0	<2.50	447	1310	10800	0.040	0.042	2870	0.38	0.056
6	NT	6.2	430	20000	NT	NT	390	1300	10000	NT	NT	2900	NT	NT
7	0.12	5.7	400	19000	1.6	1.0	380	1270	10500	0.039	0.045	2500	0.21	0.048
8	0.132	4.1	390	20061	1.4	NR	252	1002	8528	0.04	0.02	3337	0.194	0.04
9	0.1001	NR	NR	NR	NR	NR	NR	NR	NR	0.0418	0.0403	NR	NR	NR
10	0.10	NR	NR	NR	NR	NR	NR	NR	NR	0.04	0.039	NR	0.31	0.041
11	0.099	3.8	290	20100	1.35	1.07	280	900	7500	0.0400	0.0389	2730	< 0.3	0.0340
12	0.11	5.8	430	20000	1.9	0.7	620	1400	11000	0.002	0.022	2300	0.003	0.019
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	0.135	6353.8	414.7	23198	2	1.2	401.2	1323.7	10675.9	0.046	0.031	2766.2	0.24	<0.05

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

Table 32 Summary of Participants' Results and Performance for Samples S2 and S3

Lab Code	S2-Alkalinity (mg/L)	S2-EC (µS/cm)	S2-pH	S2-TKN (mg/L)	S2-TN (mg/L)	S2-TOC (mg/L)	S2-Total Hardness (mg/L)	S2-Total P (mg/L)	S3-TDS (mg/L)	S3-TS (mg/L)	S3-TSS (mg/L)
A.V.	80.7	53400	8.32	Not Set	0.71	Not Set	Not Set	0.556	8720	8950	Not Set
H.V.	80	56000	8.30	0.589	0.68	4.53	6900	NA	NA	NA	NA
1	168	NT	8.23	NT	NT	NT	NT	NT	NT	NT	NT
2	NR	NR	NR	NR	0.781	NR	NR	0.549	NT	NT	NT
3	82	41982	8.34	0.81	0.88	NT	6800	0.56	9596	9628	31
4	80	53500	8.4	NR	0.735	4.18	NR	0.557	NT	NT	NT
5	77	52000	8.3	0.71	0.8	3.9	6440	0.623	NT	NT	NT
6	80	54000	8.3	NT	NT	NT	NT	NT	8800	9300	31
7	82	56000	8.4	0.60	0.69	4.5	6000	0.57	NR	9000	27
8	NT	NT	NT	NT	NT	NT	NT	NT	8247	9120	NR
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	80.4	54800	8.4	0.341	0.434	NT	6100	0.549	8900	8800	31.6
12	120	55000	8.1	0.57	0.57	4.5	100	0.55	NT	NT	NT
13	NT	NT	NT	NT	NT	NT	NT	NT	8540	8400	25
14	80	51802	8.33	NT	0.73	4	6440.4	0.44	8300	8380	50

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

7.5 Participants' Results and Analytical Methods

Participants were asked to analyse the samples using their normal test method. The measurement methods and instrumental techniques used are presented in Appendices 6, 7 and 8.

Laboratory 11 confirmed pipetting error as the cause of their unsatisfactory results.

Most of the unsatisfactory results reported by laboratory 12 were lower or higher than the assigned value by a factor of approximately 2, 20 or 100. This laboratory may need to check their sample preparation, dilution factors and/or standard preparation procedure. Their unsatisfactory results were not included in the analysis of extraction methods and instrumental techniques employed by participants.

Individual Test Commentary

Ammonia-Nitrogen Plots of participants' results versus methods used for ammonia–N measurement are presented in Figure 31. All methods produced compatible results (Figure 31).

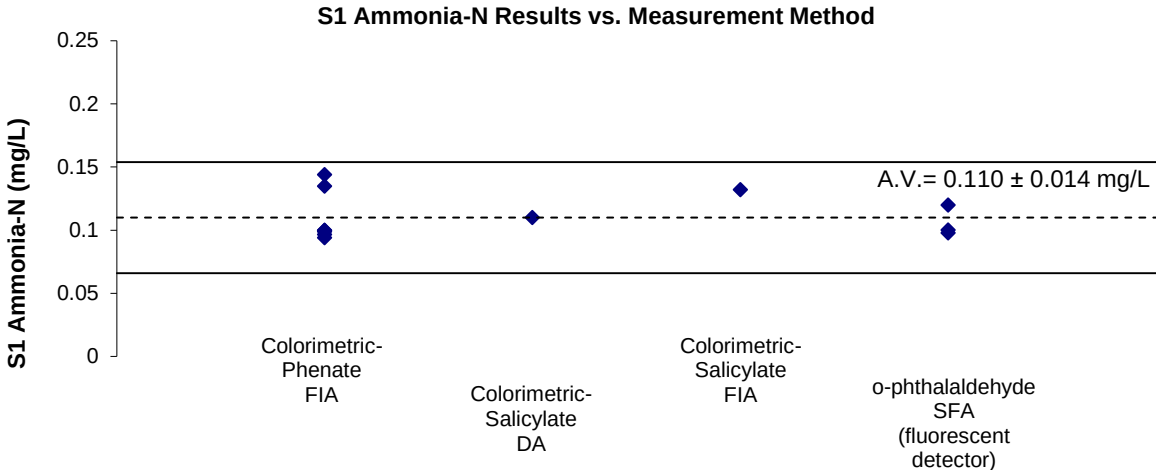
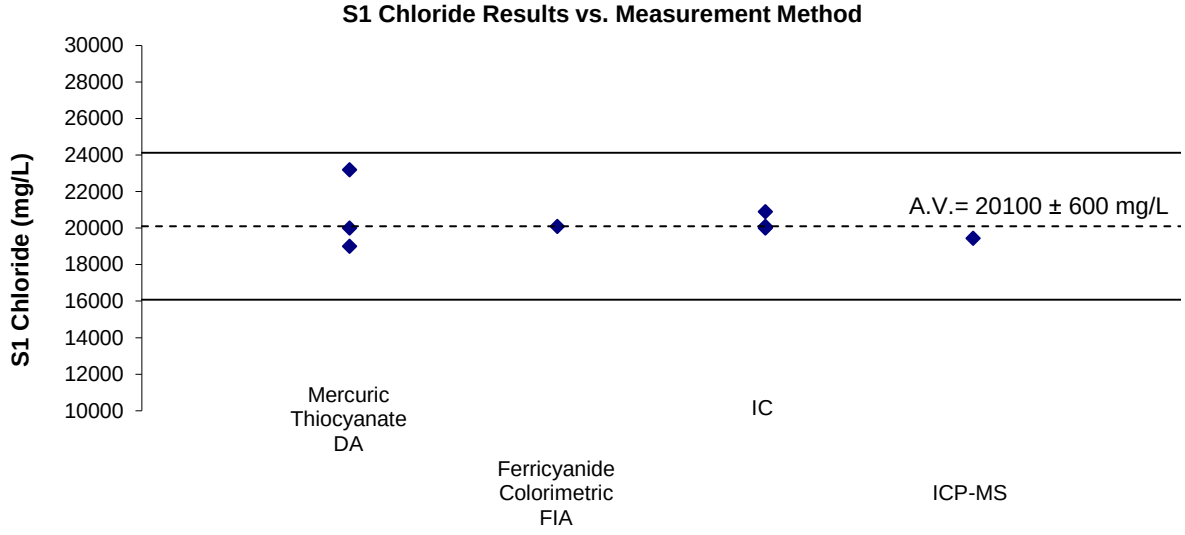


Figure 31 S1-NH_3-N Results vs. Measurement Method

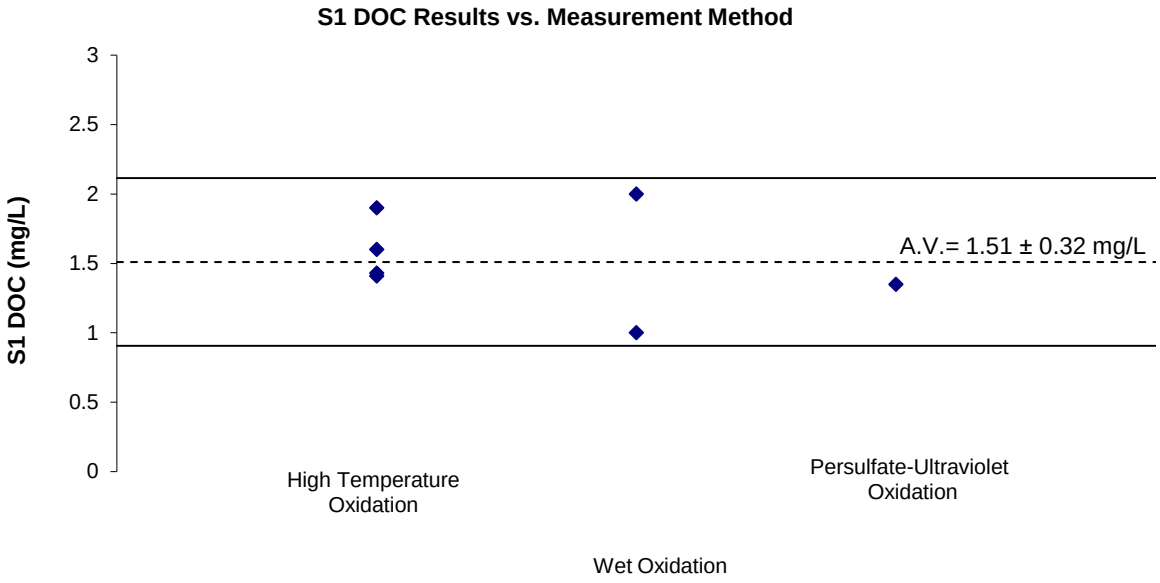
Chloride level in S1 was 20100 mg/L. All results returned satisfactory z-scores. (Figure 32).



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

Figure 32 S1-Chloride Results vs. Measurement Method

Dissolved Organic Carbon as dNPOC Participants used high-temperature oxidation (combustion) or persulfate oxidation for DOC measurement in sea water. All performed satisfactorily (Figure 33).



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

Figure 33 S1-DOC vs. Measurement Method

Fluoride Only 6 results were reported for fluoride in S1. All but one were compatible with each other (Figure 34). Caution should be exercised when fluoride in sea water is measured by the colorimetric method as it suffers from interference from chlorides.

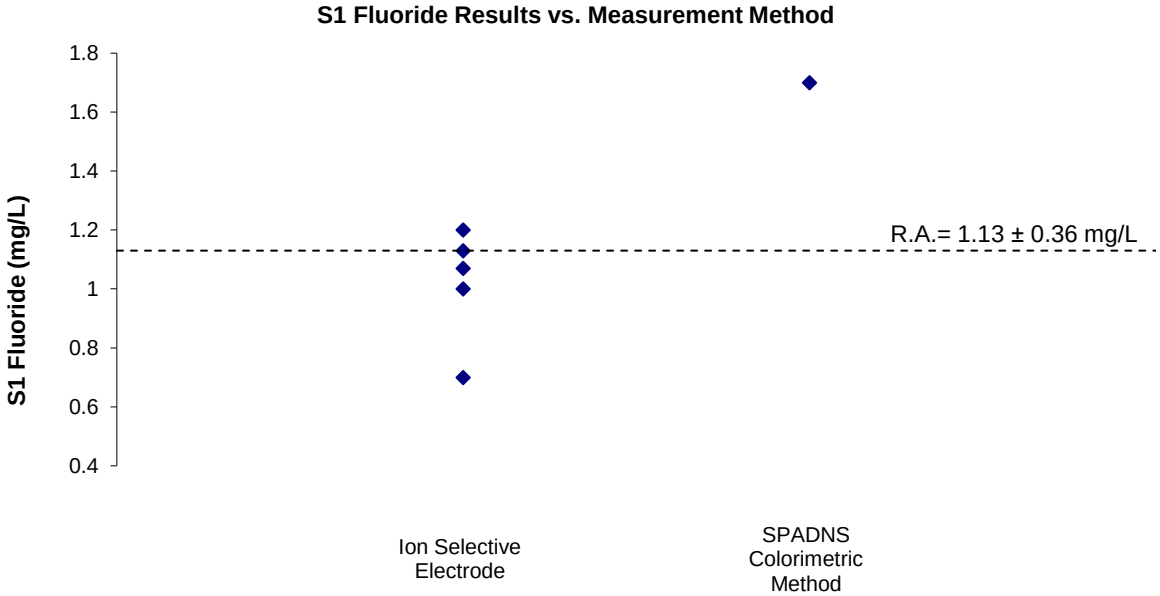
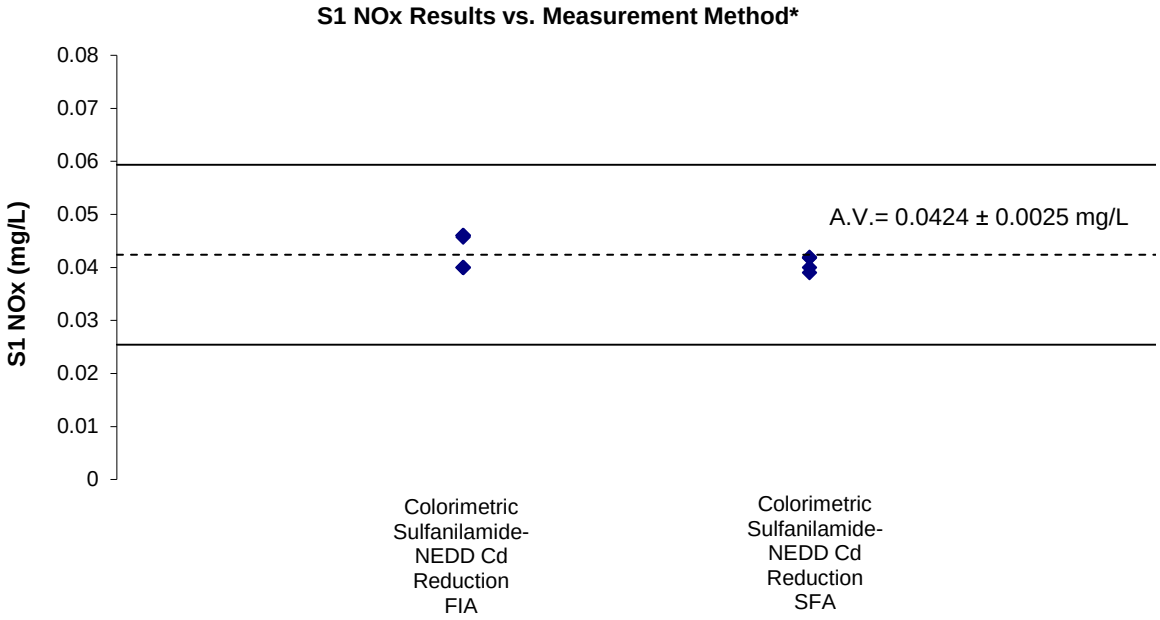


Figure 34 S1-Fluoride Results vs. Measurement Method

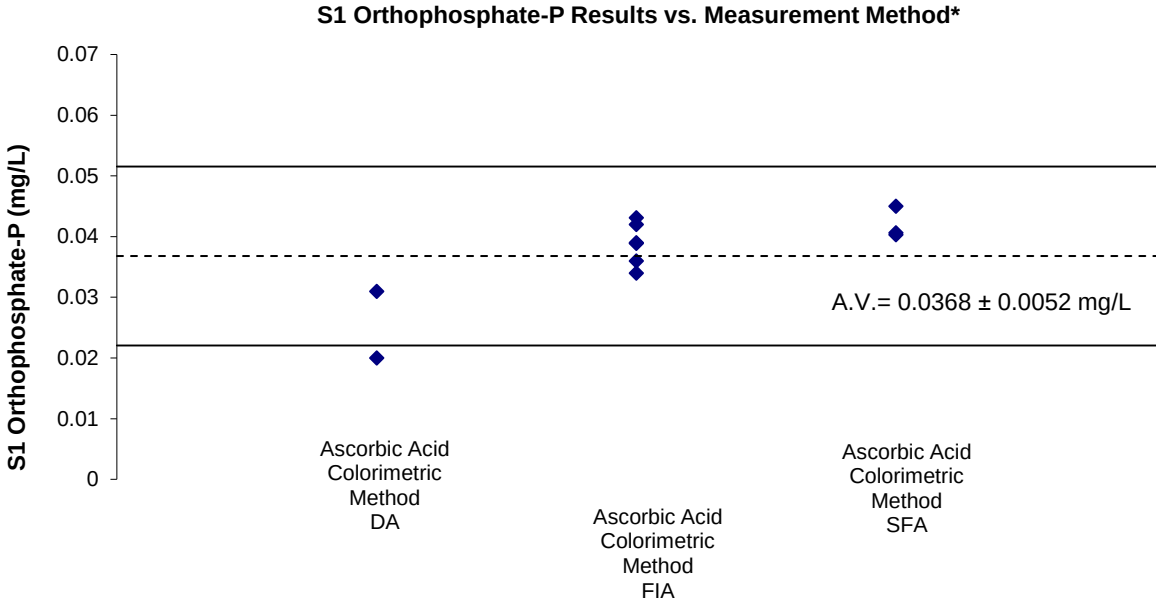
Nitrate-Nitrogen + Nitrite-Nitrogen All participants used colorimetric-sulfanilamide-NEDD Cd reduction with SFA or FIA (Figure 35). The reported results were in excellent agreement with each other, with a between-laboratory CV of 7.8%.



*The result reported by laboratory 12 not included. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 35 S1-Nitrate-N+Nitrite-N Results vs. Measurement Method and Instrumental Technique

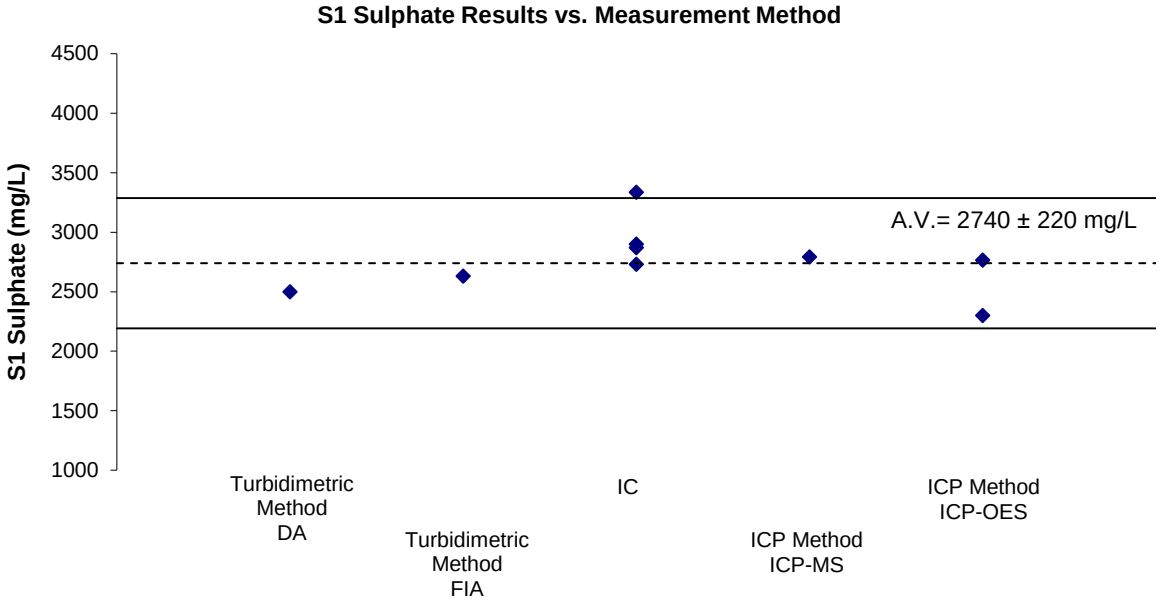
Orthophosphate-P level in S1 was 0.0368 mg/L and of 12 reported results, 10 returned satisfactory z-scores. Ascorbic acid colorimetric method with FIA was the preferred method of measurement (Figure 36).



*The result reported by laboratory 12 not included. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 36 S1-Orthophosphate-P Results vs. Measurement Method

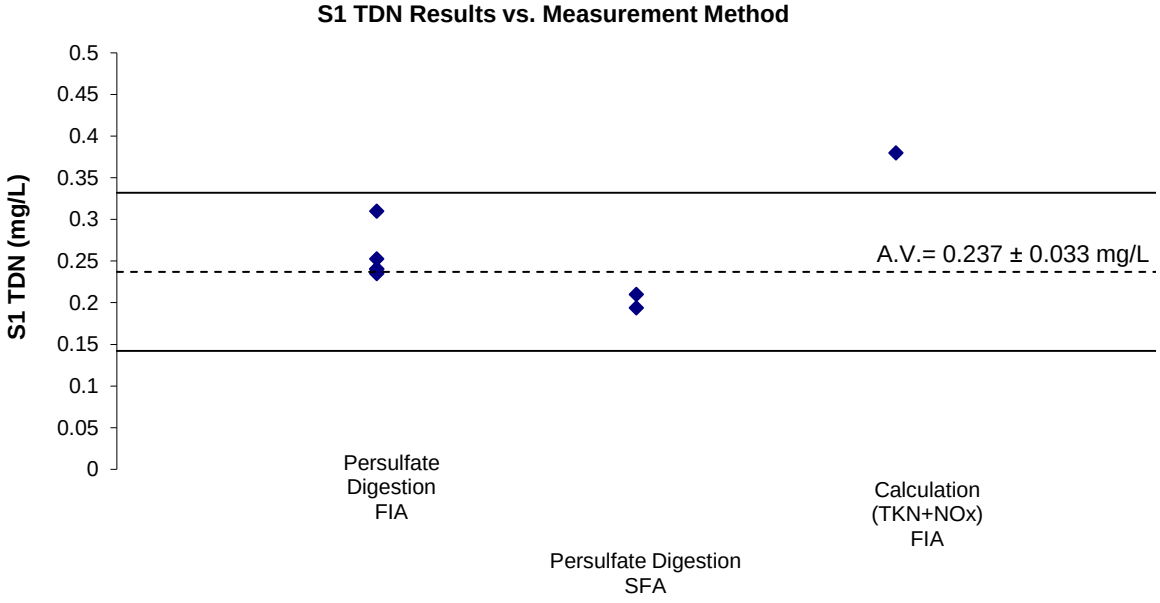
Sulphate Participants used various methods. All but one of the reported results returned a satisfactory z-score (Figure 37).



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

Figure 37 S1-Sulphate Results vs. Measurement Method

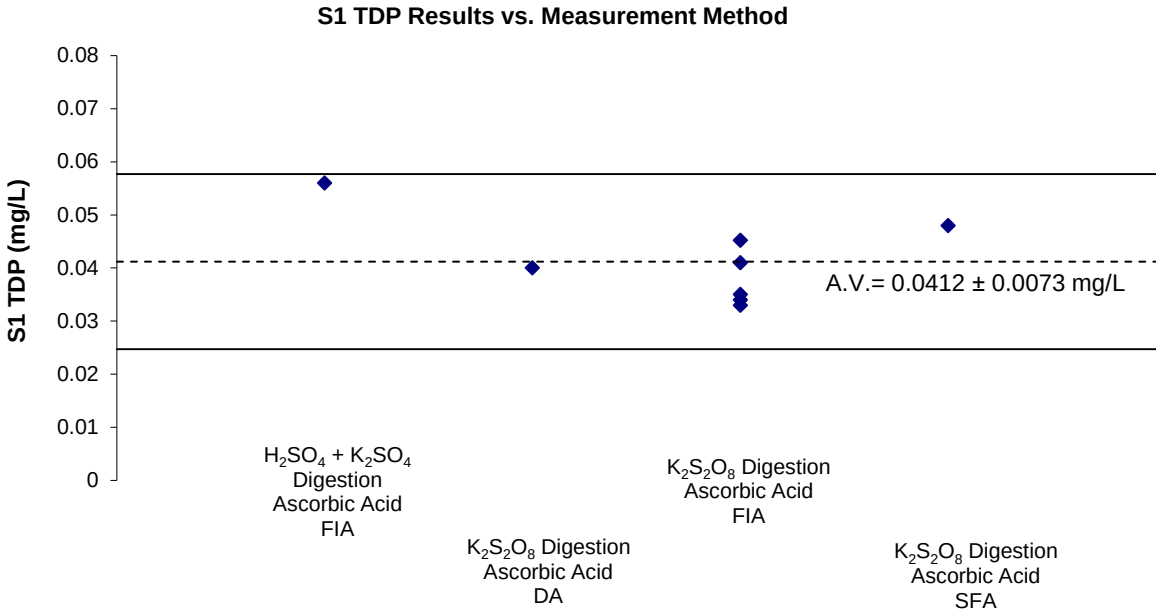
Total Dissolved Nitrogen With the exception of two, all participants determined total nitrogen by oxidation of all nitrogenous compounds to nitrate (Figure 38).



*The result reported by laboratory 12 not included. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 38 S1-TDN Results vs. Measurement Method and Instrumental Technique

Total Dissolved Phosphorus level in S1 was 0.0412 mg/L. Nine laboratories reported TDP results in S1, and all but one performed satisfactorily. The most popular method used for TDP measurements in S1 involved potassium persulphate digestion followed by FIA or DA determination (Figure 38).

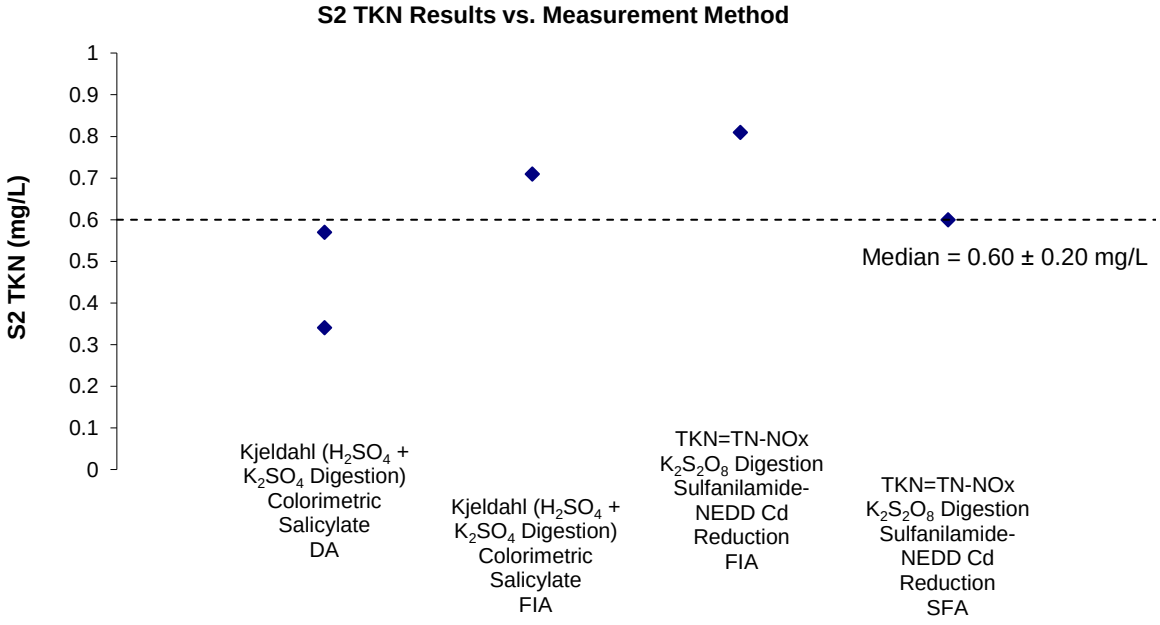


*The result reported by laboratory 12 not included. Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 39 S1-TDP Results vs. Measurement Method and Instrumental Technique

Alkalinity to pH 4.5 as ($CaCO_3$) Participants used auto-titration or manual titration to measure alkalinity in S2, and all but two performed satisfactorily. Electrodes close to the end of life, changes in titrant strength (due to variations in temperature or contamination) or contamination of solvents are typical causes of titration errors.

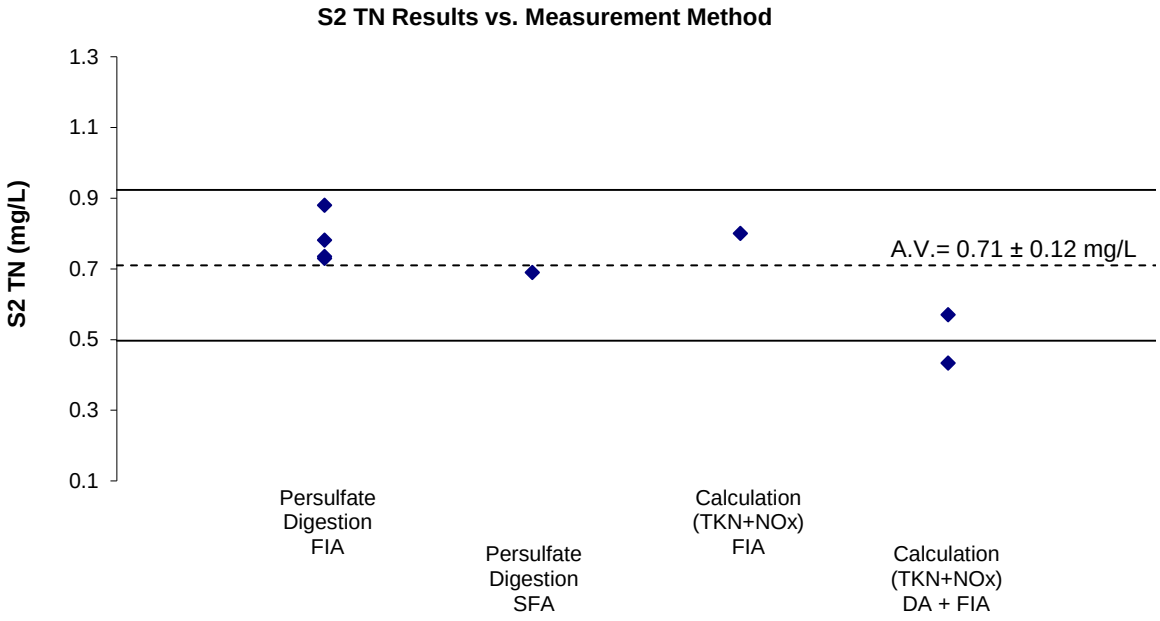
Total Kjeldahl Nitrogen Only 5 results were reported for TKN in S2. All results were in relatively good agreement with each other, with a median value of 0.60 mg/L and homogeneity value of 0.589 mg/L (Figure 40).



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

Figure 40 S2-TKN Results vs. Measurement Method

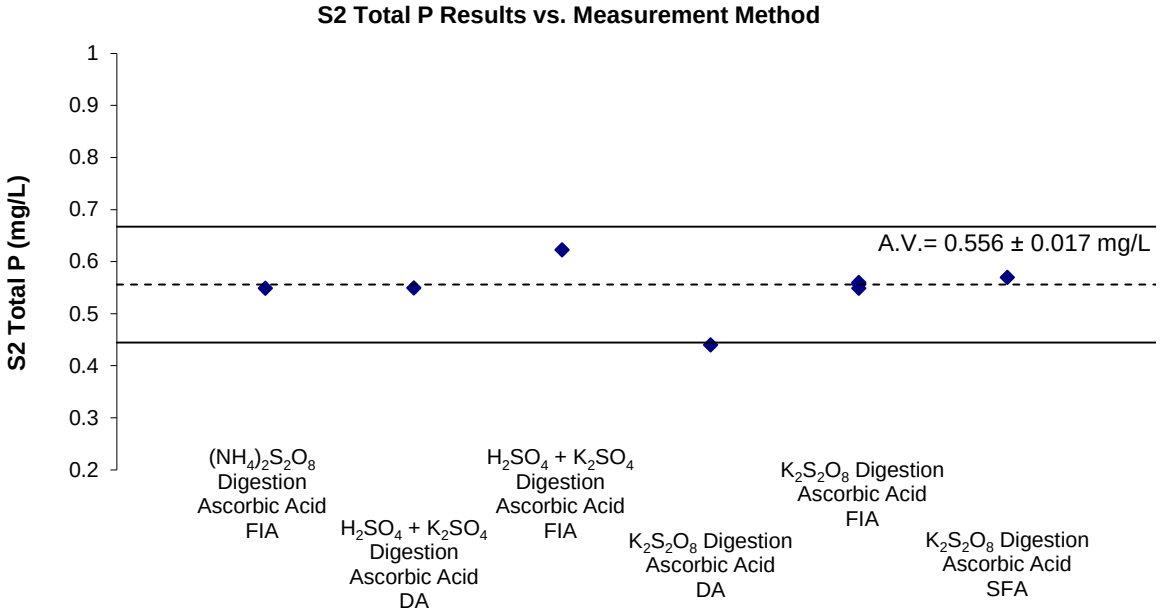
Total Nitrogen Of 8 reported results, 1 returned an unsatisfactory z-score, The unsatisfactory result was reported as the sum of TKN and NOx with the TKN result being produced via sulfuric acid and potassium sulfate digestion followed by DA determination.



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

Figure 41 S2-TN Results vs. Measurement Method

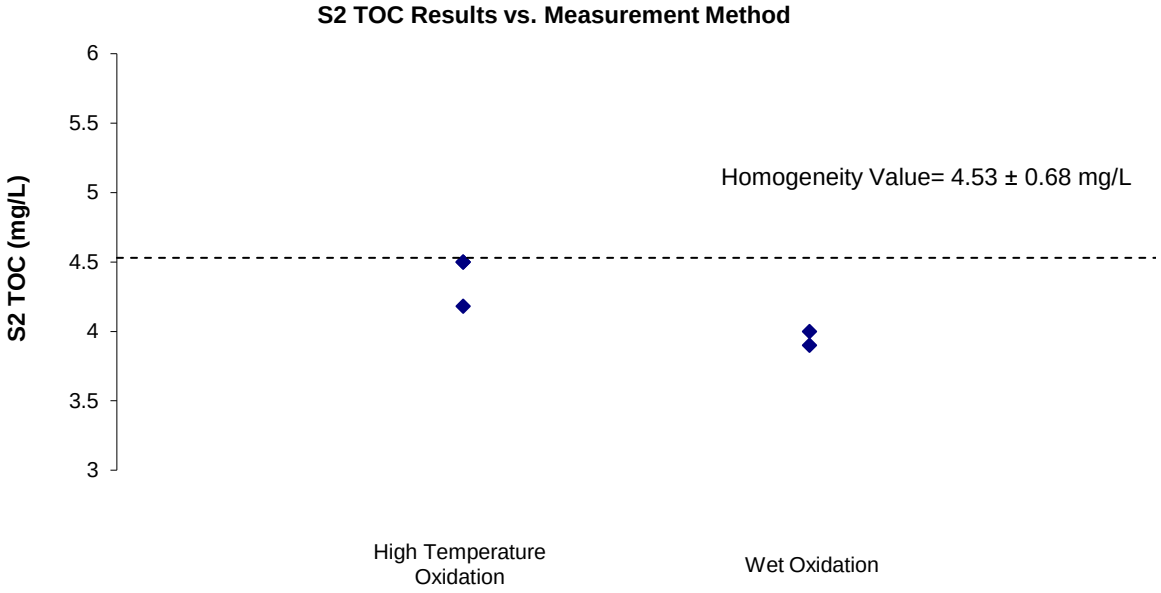
Total Phosphorus Participants used various methods for measurement of TP in S2 and all but one produced compatible results (Figure 42).



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

Figure 42 S2-TP Results vs. Measurement Method

Total Organic Carbon. All 5 results reported for TOC in S2 were compatible with each other and with the homogeneity value (4.53 mg/L) (Figure 43).

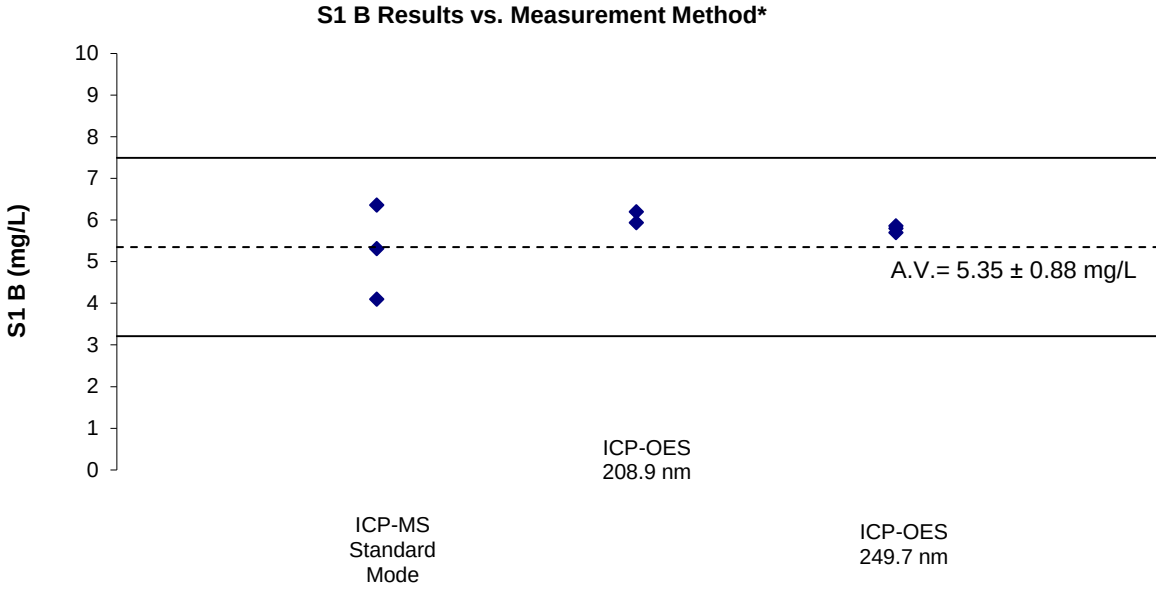


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 43 S2-TOC Results vs. Measurement Method

Total Hardness Five results were reported for total hardness in S2 and all were in excellent agreement with each other and with homogeneity value (6900 mg/L).

Boron level in S1 was 5.35 mg/L and did not present difficulty to participating laboratories (Figure 44).



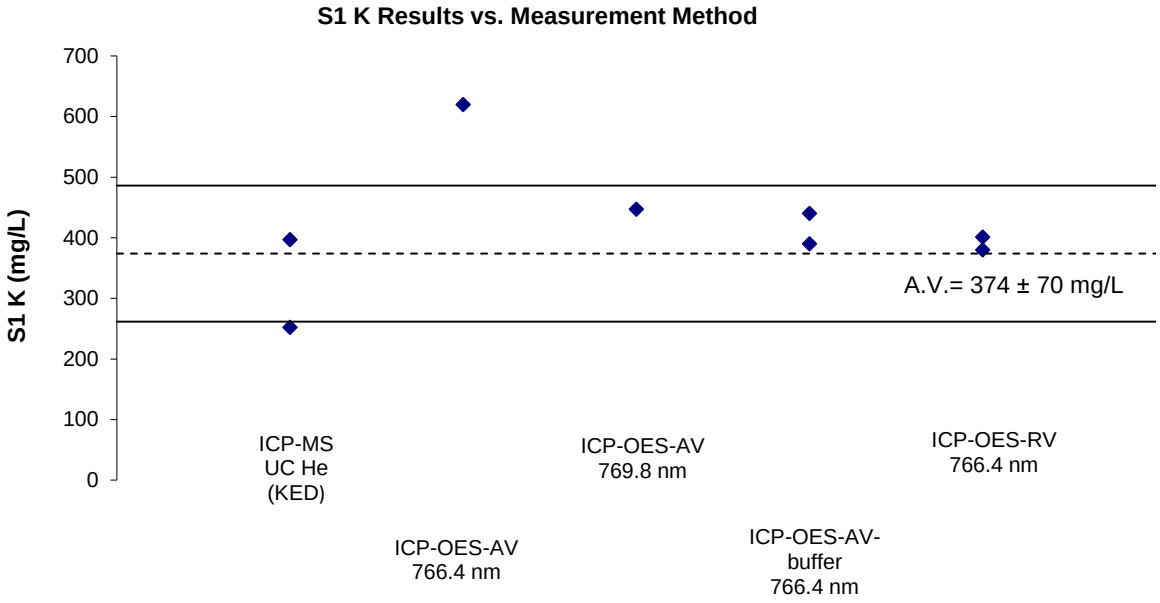
*Laboratory 14 result of 6356.8 mg/L has been plotted as 6.36 mg/L. The result reported by laboratory 11 not included.
Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 44 S1-B Results vs. Measurement Method

Laboratory 14 might have reported the result for B in S2 in the wrong units.

Potassium When K measurements are conducted using ICP-OES with axially-viewed plasma (ICP-OES-AV), the emission signal of K is significantly enhanced in the presence of other easily ionised elements such as Al, Ca, Mg and Na. [15]

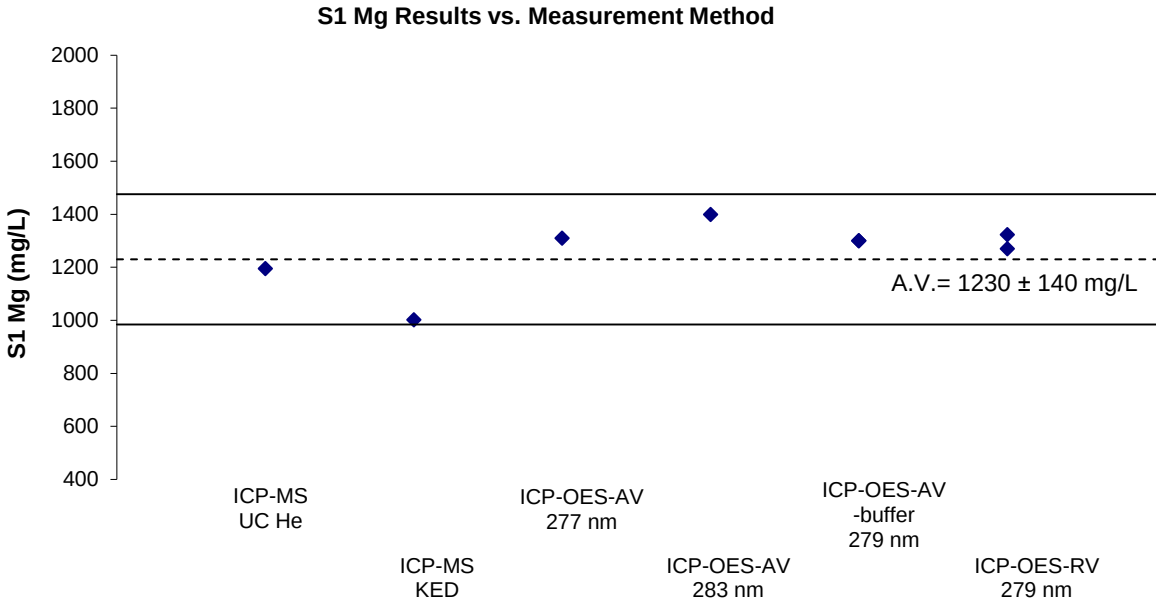
Plots of participant's performance and results versus instrumental technique used are presented in Figure 45.



*The result reported by laboratory 11 not included. Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 45 S1-K Results vs. Measurement Method

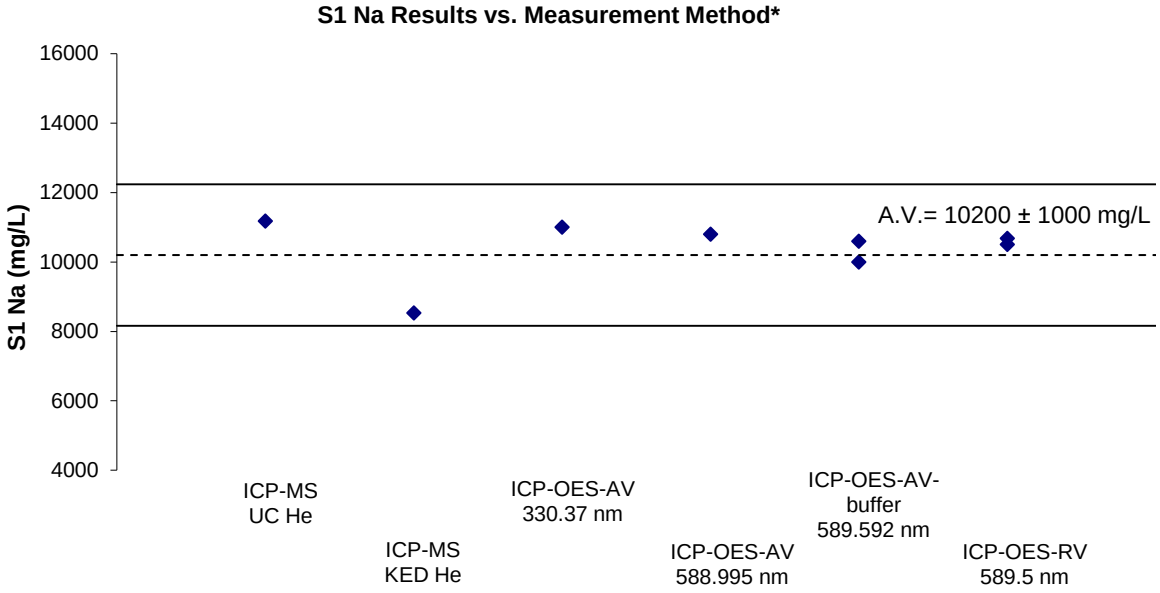
Magnesium For Mg measurements in S1 participants used ICP-MS in collision mode or ICP-OES with wavelengths 279 nm, 283 nm or 277 nm (Figure 46).



*The result reported by laboratory 11 not included. Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 46 S1-Mg Results vs. Measurement Method

Sodium Participants used various instrumental techniques for Na measurement in S1 and all produced satisfactory results (Figure 47).



*The result reported by laboratory 11 not included. Horizontal lines on charts are the results correspond to z-scores of 2 and -2.

Figure 47 S1-Na Results vs. Measurement Method

TDS, TS and TSS All reported results for TDS and TSS returned satisfactory z-scores. Of 6 results reported for TSS in S3, all but one were compatible with each other.

7.6 Comparison with Previous NMI Proficiency Tests of Water Characteristics

AQA 21-19 is the 13th NMI proficiency test of water characteristics. Figure 48 presents participant performance over time. Despite different matrices and analyte concentrations, on average, participants' performance has remained fairly 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.

7.7 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 33).

Table 33 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	Nutrients: Kanso Reference Material Seawater Nutrients (RMNS) Lot CD
2	RM – Reference samples from NMI
3	CRM – CWW-TM-A, B and C (metals)
4	SS
5	CRM
7	CRM
8	CRM

Lab. Code	Description of Control Samples
9	CRM – 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.
11	RM
13	CRM – Multi-Analyte Solids Standard Catalogue Number QCI-171 Lot number 210107. Manufacture Date: 01/07/21 Certification Date: 01/11/21, Expired Date: 31/01/23
14	CRM

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]

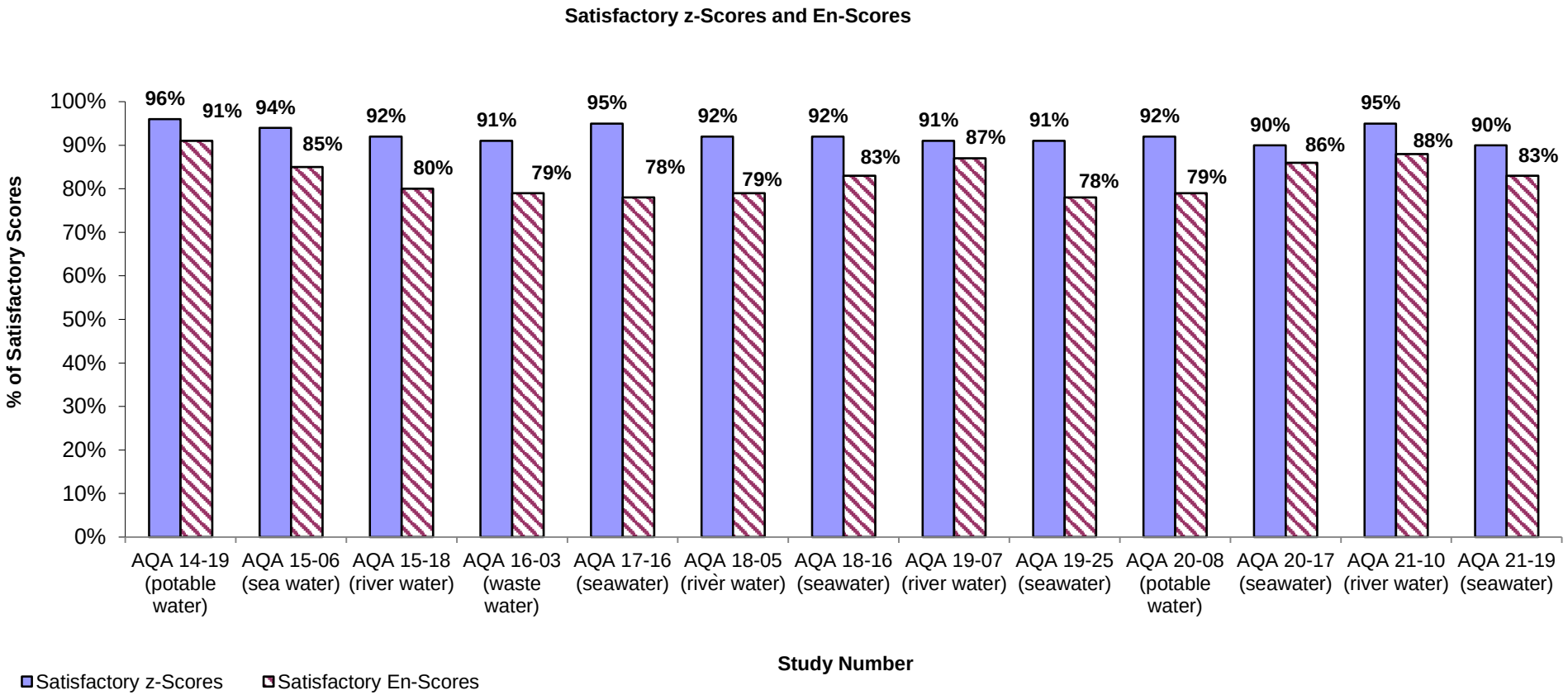


Figure 48 Participants' Performance in Nutrients, Anions and Physical Tests in Water PT Studies over Time

8 REFERENCES

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was two identical bottles of 200 mL filtered, autoclaved and frozen seawater fortified with ammonia-N, orthophosphate-P, and nitrate-N.

Sample S2 was 400 mL of unfiltered, autoclaved and frozen seawater fortified with total Kjeldahl nitrogen, total organic carbon and total phosphorus.

Sample S3 was 750 mL of unfiltered low salinity seawater. 1022 g of composite spike solution was added to 13978 g of low salinity sea water (3502 g filtered sea water and 10477 g ultra-high purity water).

Sample Analysis and Homogeneity Testing

With the exception of B, Na, TDN, TP, TDS, TS and TSS, a partial homogeneity test was conducted for all analytes of interest. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Sample Analysis for Total Elements

For analyses of dissolved elements in Sample S1, a test portion of 10 mL was transferred to a 14 mL graduated polystyrene round bottom tube.

Testing involved measurements using 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 wavelength and instrument conditions used for each analyte is given in Table 34.

Table 34 Methodology for Dissolved Elements

Analyte	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Ion/Wavelenght
Ca	ICP-OES	Y	NA	NA	NA	317.933 nm
K	ICP-OES	Y	NA	NA	NA	766.491 nm
Mg	ICP-OES	Y	NA	NA	NA	279.078 nm

Methodology for Tests Other Than Total Elements in S1 and S2

A summary of the measurement methods and instrumental techniques is presented in Tables 35 and 36.

Table 35 Methodology for S1

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination – OPA Method	SFA
Chloride	Turbidimetric Method	DA
Dissolved Organic Carbon	High-Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	ISE
Nitrate-N + Nitrite-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA

Sulphate	Turbidimetric Method	DA
Total Dissolved Phosphorus	ICP-Method	ICP-MS

Table 36 Methodology for S2

Test	Measurement Method	Instrument
Alkalinity to pH 4.5 (as $CaCO_3$)	Titration	Titration
Total Hardness (as $CaCO_3$)	Calculation	ICP-OES
Total Kjeldahl Nitrogen	TKN=TN-NOx, Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Organic Carbon	High-Temperature Oxidation	NIR-detector

APPENDIX 2 - STABILITY STUDY

Samples S1 and S2 were dispatched on 29 November 2021. Participants were advised to store both samples frozen, if unable to commence on the day of receipt. Sample condition on receipt and the date when the samples were received and analysed by the participants is presented in Table 37. No trends between participants' results, samples' condition on receipt and days spent in transit, were evident (Figures 49 and 50)

Table 37 Sample S1 and S2 Condition on Receipt and the Date When the Sample was Received and Analysed

Lab Code	Received Date	S1		S2	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	30/11/2021	cold	1/12/2021	cold	12/01/2022
2	1/12/2021	cold		frozen	13/12/2021
3	30/11/2021	cold	7/12/2021	cold	7/12/2021
4	30/11/2021	frozen	various	frozen	various
5	30/11/2021	frozen	6/12/2021	frozen	6/12/2021
6	30/11/2021	frozen	7/12/2021	frozen	1/12/2021
7	30/11/2021	cold	6/01/2022		
8	30/11/2021	frozen	2/12/2021	NA	NA
9	30/11/2021	partially frozen	16/12/2021	NA	NA
10	30/11/2021	frozen	30/11/2021	NA	NA
11*	15/12/2021	frozen	16/12/2021	frozen	16/12/2021
12	30/11/2021	frozen	7/12/2021	frozen	7/12/2021
13	NA	NA	NA	NA	NA
14	6/12/2021	cold	6/12/2021	cold	6/12/2021
Trip sample	08/12/2021	Room temperature	09/12/2021	Room temperature	09/12/2021

NA = Not Applicable. *Laboratory 11 S1 and S2 sample dispatched 13/12/2021

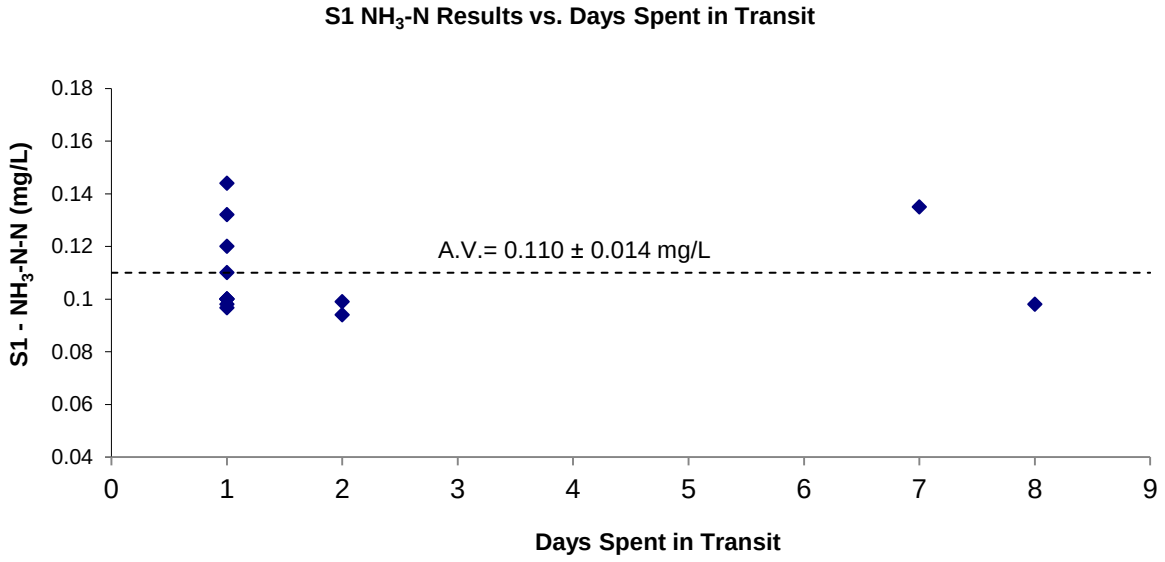
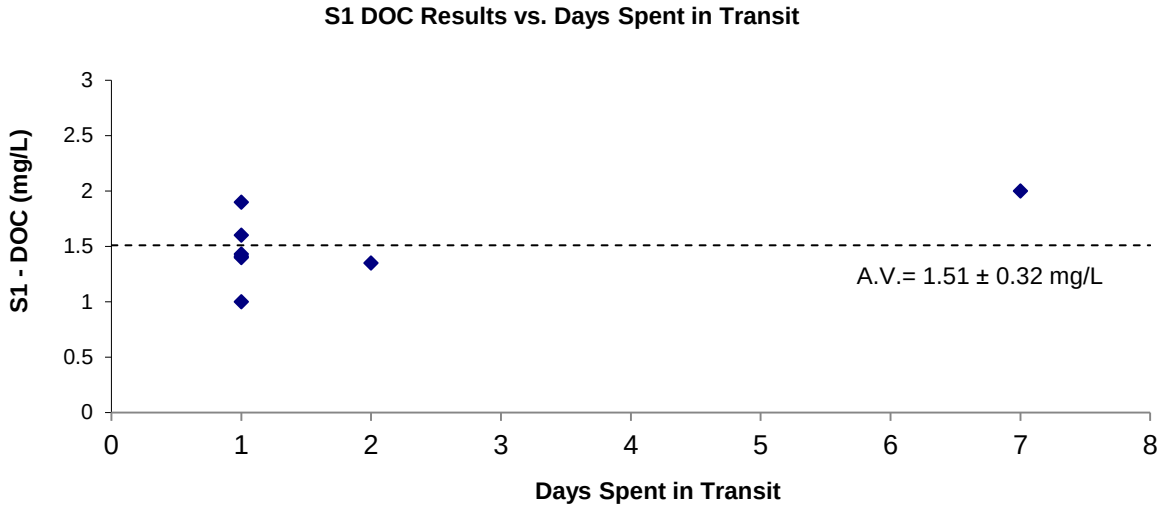
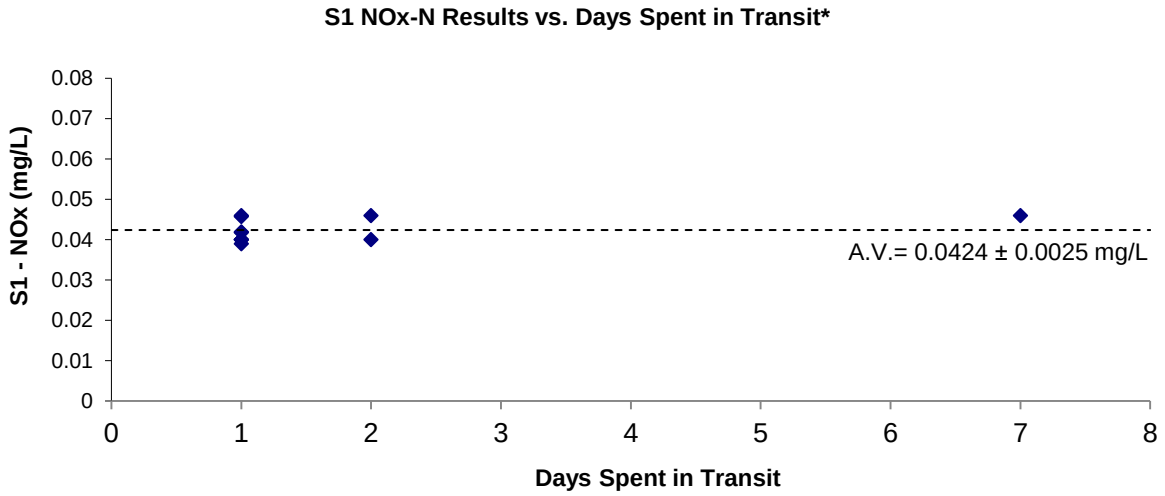
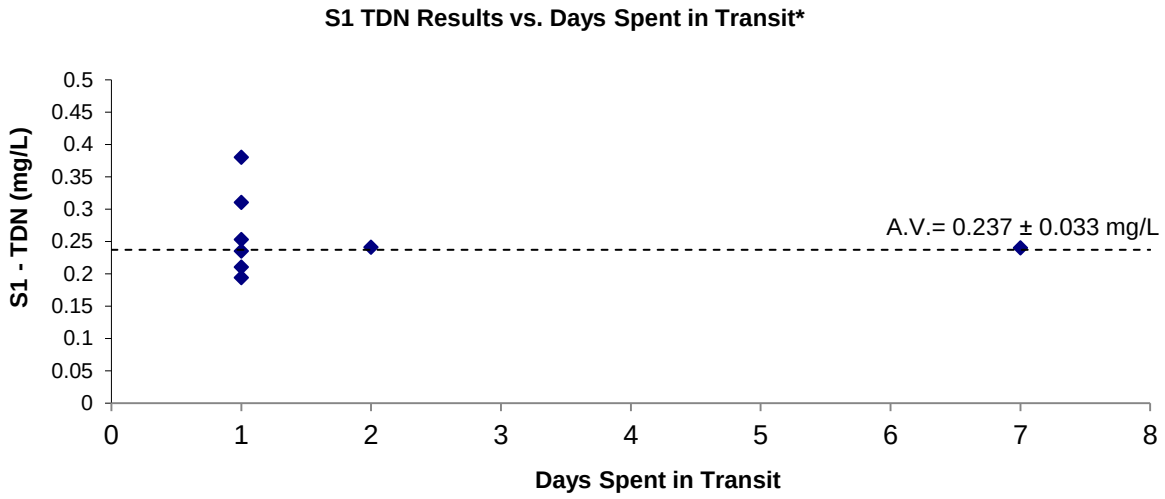


Figure 49 Results vs Days Spent in Transit

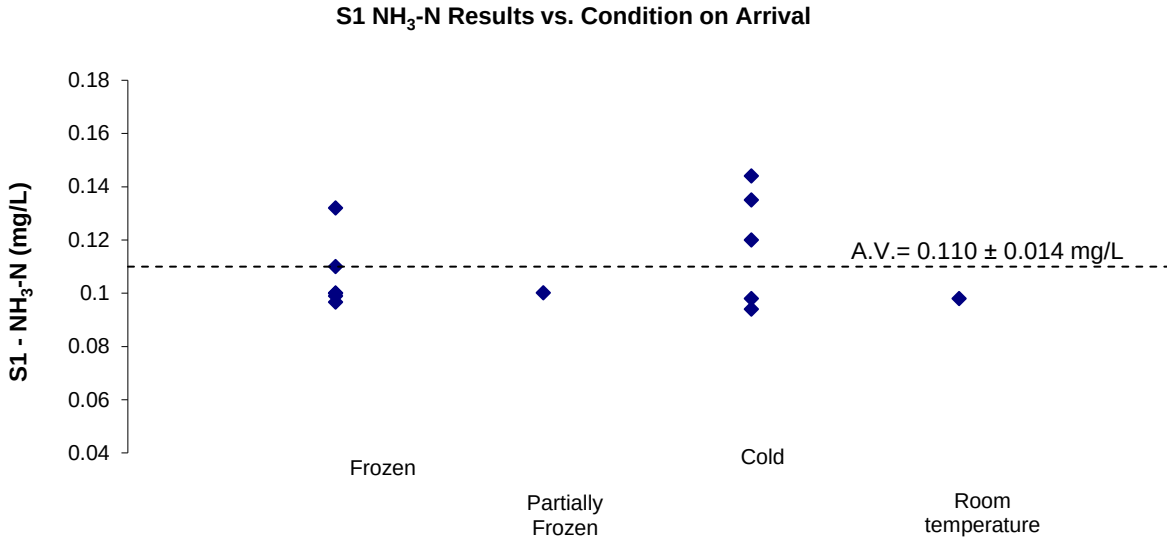


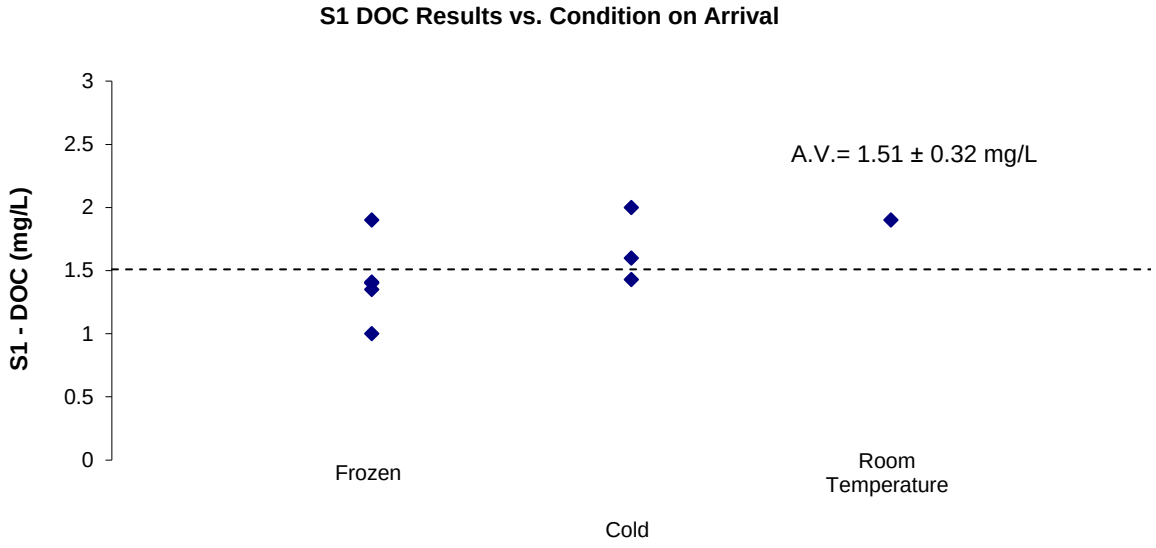


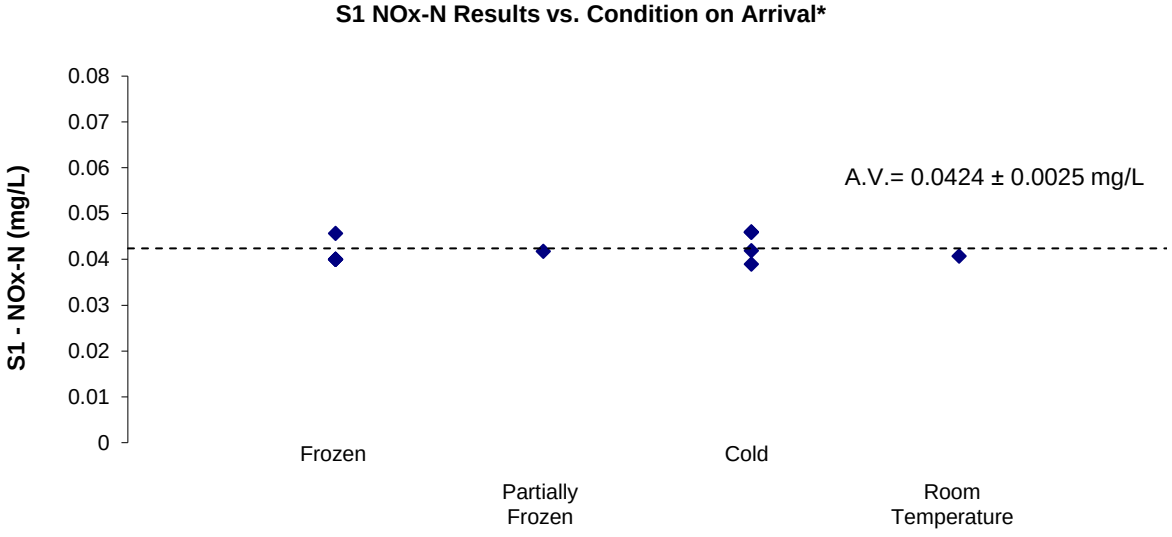


*The result reported by laboratory 11 not included.

Figure 49 Results vs Day Spent in Transit (continued)







*The result reported by laboratory 11 not included.

Figure 50 Results vs Condition on Arrival

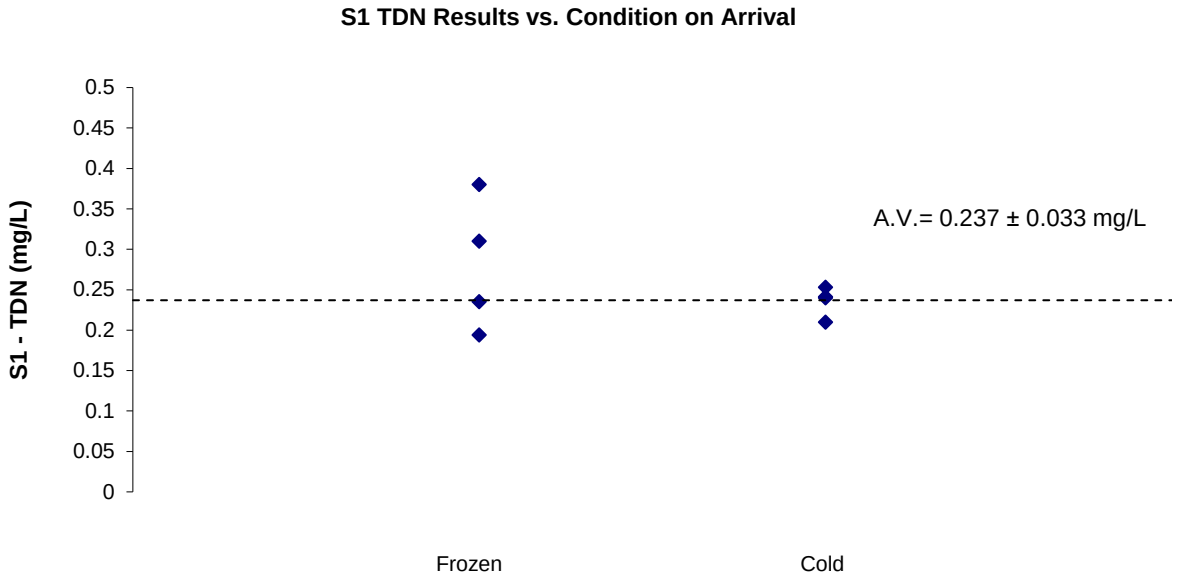


Figure 50 Results vs Condition on Arrival (continued)

With the exception of 3, all samples sets spent one day in transit. Two sample sets spent 2 days in transit and one spent 7 days. To assess analytes' stability during transport, results from a "transport set of samples" that spent 8 days in transit (T8) were compared with results from a set of samples sent to the same laboratory but with only 2 days in transit (T2). The two sets of results were in good agreement with each other within their stated uncertainties (Figure 51).

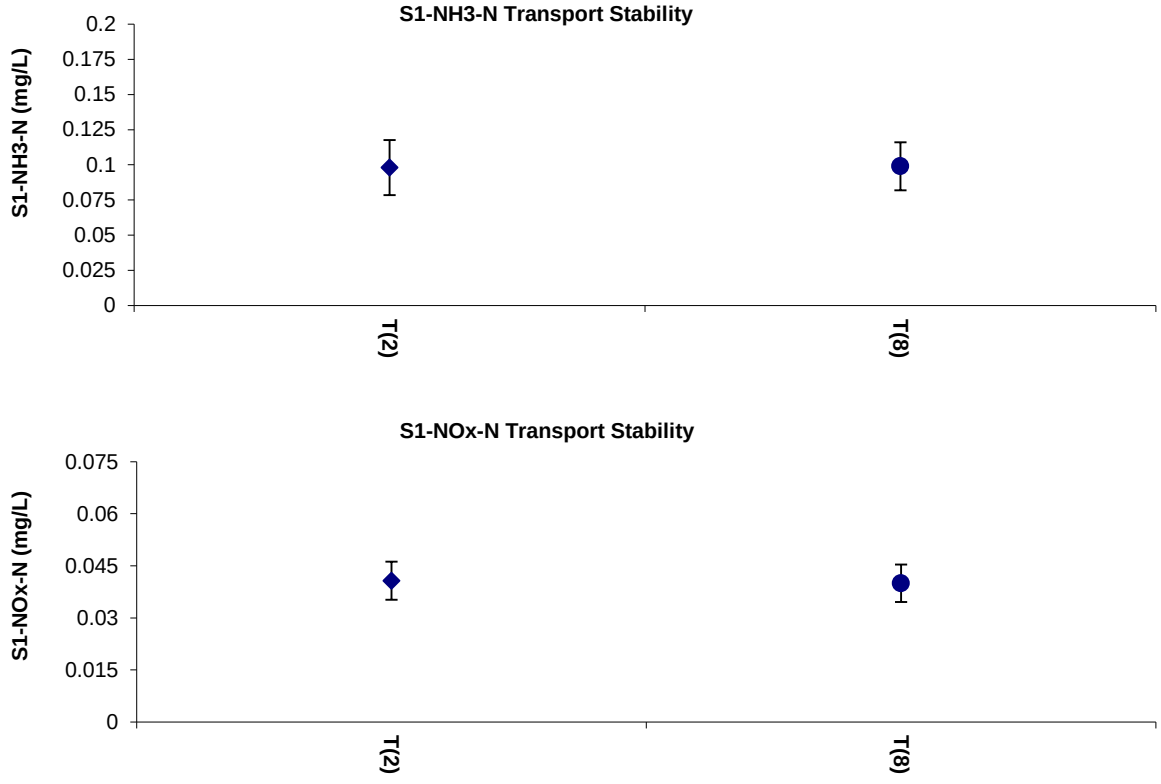


Figure 51 Transport Stability Results

Stability Study

In previous 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: NH_3-N and NO_3-N +NO_2-N in 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 two sets of samples kept at -20°C (reference samples) were compared with the results from two samples left out on a laboratory table for three days (room). Theses samples were analysed in duplicate and in random order 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 of these studies were in good agreement with each other and the assigned value were within their stated uncertainties (Figure 52).

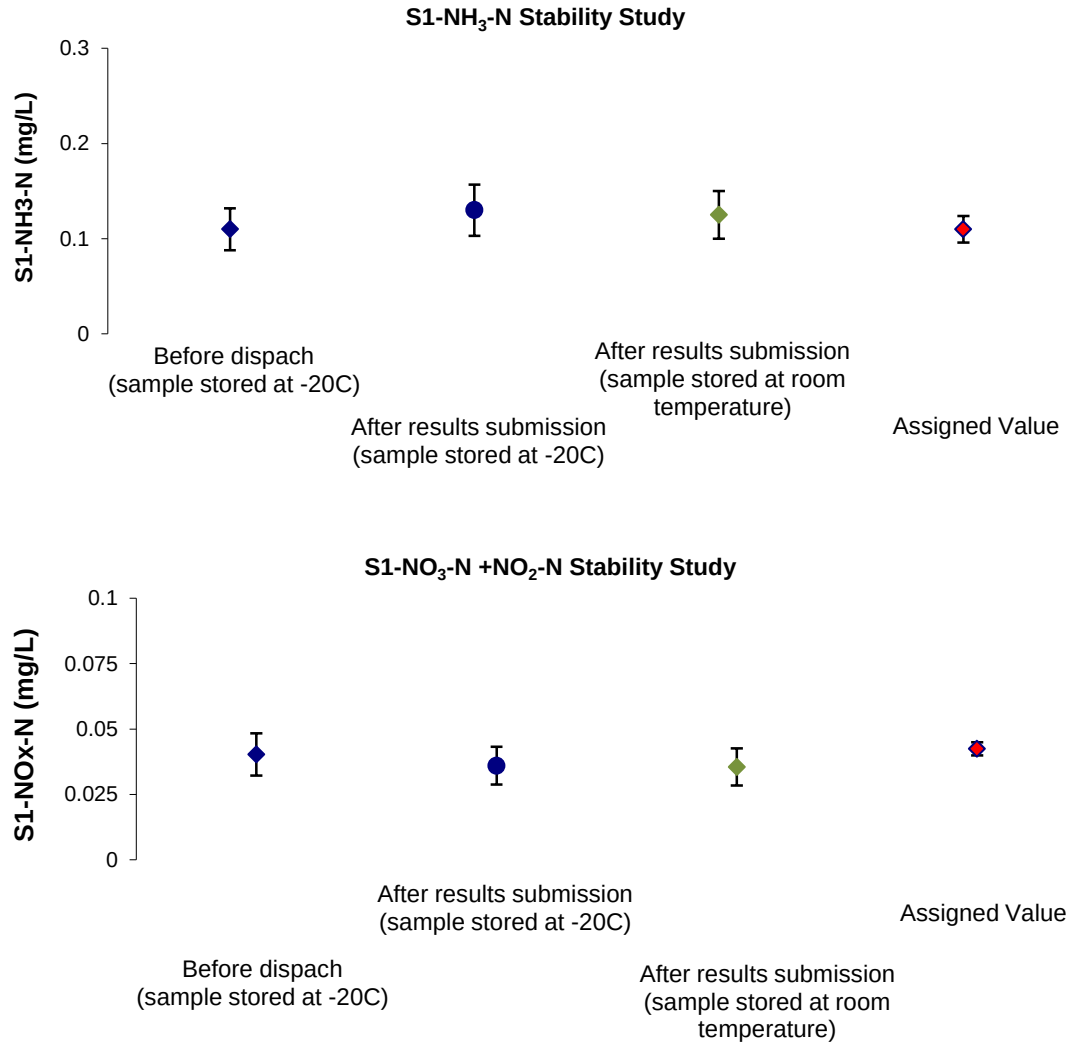


Figure 52 Stability Study Results

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, 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 38.

Table 38 Uncertainty of Assigned Value for Ammonia-N in Sample S1

No. results (p)	12
Robust Average	0.110 mg/L
$S_{rob\ av}$	0.019 mg/L
$u_{rob\ av}$	0.0069 mg/L
k	2
$U_{rob\ av}$	0.014 mg/L

The assigned value for **Ammonia-N** in Sample S1 is **0.110 ± 0.014 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 39.

Table 39 z-Score and E_n-score for Ammonia-N result reported by Laboratory 7 in S1

Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
0.12 ± 0.02	0.110 ± 0.014	20% as CV or 0.2 x 0.110 = =0.022 mg/L	$z = \frac{(0.12 - 0.110)}{0.022}$ z = 0.45	$En = \frac{(0.12 - 0.110)}{\sqrt{0.02^2 + 0.014^2}}$ E_n= 0.41

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. Between 2014 and 2021, NMI carried out twelve 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.

Table 40 Chloride Results for Laboratory X From Proficiency Testing Studies of Nutrients, Anions and Physical Tests in Water

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 16-03	Waste	3099 ± 320	2990 ± 170	6.3	8
AQA 17-16	Seawater	13100 ± 1300	12800 ± 420	4.1	10
AQA 18-05	River	68 ± 8.0	71.3 ± 1.5	3.4	17
AQA 18-16	Seawater	16600 ± 1600	17300 ± 1600	13	13
AQA 19-07	River	57.0 ± 12	53.7 ± 2.0	4.7	10
AQA 19-25	Seawater	20000 ± 2000	20500 ± 1000	2.2	13
AQA 20-08	Potable	33.4 ± 7.0	41.6 ± 1.9	6.7	13
AQA 20-17	Seawater	9800 ± 980	10700 ± 400	4.9	10
AQA 21-10	River	81 ± 10	86.3 ± 2.7	5.7	20
AQA 21-19	Seawater	19440 ± 1950	20100 ± 600	3.8	9
Average				5.3**	

* 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 gives an estimate of the relative standard uncertainty of 5.3%. Using a coverage factor of 2 gives a relative expanded uncertainty of 11%, at a level of confidence of approximately 95%. Table 41 sets out the expanded uncertainty for results of the measurement of Chloride in potable, fresh, waste or seawater over the range 20.0 – 20000 mg/L.

Table 41 Uncertainty of Chloride results estimated using PT data

Results mg/L	Uncertainty mg/L
20.0	2.2
500	55
1000	110
10000	1100
20000	2200

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
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 42 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						
2						
3	ICP-MS	Sc	NA	NA	10	10
4	ICP-OES-AV-buffer	Lu			5	249.678
5	ICP-OES-AV	Y 371.029				208.889
6	ICP-OES-AV-buffer	Yttrium			100	208.957
7	ICP-OES-AV	Y	NA	NA	50	249.678
8	ICP-MS	Y	NA			
9						
10						
11	ICP-MS	Sc	KED	He	100	10
12	ICP-OES-AV	Yb	NA		1	249.772
13	NA	NA	NA	NA	NA	NA
14	ICP-MS		CRI	NA	40	11

Table 43 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						
2						
3	ICP-MS	Sc	UC	He	10	44
4	ICP-OES-AV-buffer	Lu			100	422.673
5	ICP-OES-AV	Y 371.029				430.253
6	ICP-OES-AV-buffer	Yttrium			100	315.887
7	ICP-OES-RV	Y	NA	NA	50	422.673
8	ICP-MS	Y	KED			
9						
10						
11	ICP-MS	Sc	KED	He	20	43
12	ICP-OES-AV	Yb	NA		1	373.69
13	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV				40	315.8

Table 44 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						
2						
3	ICP-MS	Sc	UC	He	10	39
4	ICP-OES-AV-buffer	Lu			100	766.491
5	ICP-OES-AV	Y 371.029				769.897
6	ICP-OES-AV-buffer	Yttrium			100	766.49
7	ICP-OES-RV	Y	NA	NA	50	766.491
8	ICP-MS	Y	KED			
9						
10						
11	ICP-MS	Sc	KED	He	20	39
12	ICP-OES-AV	Yb	NA		1	766.491
13	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV				40	766.4

Table 45 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						
2						
3	ICP-MS	Sc	UC	He	10	25
4	ICP-OES-AV-buffer	Lu			100	279.078
5	ICP-OES-AV	Y 371.029				277.983
6	ICP-OES-AV-buffer	Yttrium			100	279.077
7	ICP-OES-RV	Y	NA	NA	50	279.078
8	ICP-MS	Y	KED			
9						
10						
11	ICP-MS	Sc	KED	He	100	25
12	ICP-OES-AV	Yb	NA		1	283.829
13	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV				40	279.8

Table 46 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						
2						
3	ICP-MS	Sc	UC	He	10	23
4	ICP-OES-AV-buffer	Lu			1000	589.592
5	ICP-OES-AV	Y 371.029				588.995
6	ICP-OES-AV-buffer	Yttrium			100	589.592
7	ICP-OES-RV	Y	NA	NA	100	589.592
8	ICP-MS	Y	KED			
9						
10						
11	ICP-MS	Sc	KED	He	100	13
12	ICP-OES-AV	Yb	NA		10	330.37
13	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV				40	589.5

Table 47 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Fluorometric Determination - OPA Method	SFA	In-house
2	Colorimetric - Phenate Method	FIA	APHA
3	Colorimetric - Phenate Method	FIA	
4	Colorimetric - Phenate Method	FIA	Inhouse
5	Colorimetric - Phenate Method	FIA	in house
6			
7	Fluorometric Determination - OPA Method	SFA	APHA
8	Colorimetric - Salicylate Method	SFA	EN ISO 11732
9	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
10	Colorimetric - Phenate Method	FIA	4500-NH3 H
11	Colorimetric - Phenate Method	FIA	APHA4500-NH3
12	Colorimetric - Salicylate Method	DA	APHA4500NH3G
13	Not Applicable	Not Applicable	Not Applicable
14	Colorimetric - Phenate Method	FIA	4500-NH3 H

Table 48 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2			
3	ICP-Method	ICP-MS	In house W33
4	Ferricyanide Colorimetric Method	FIA	Inhouse
5	Ion Chromatographic Method	IC	in house
6	Ion Chromatographic Method	IC	APHA 4110B
7	Mercuric Thiocyanate	DA	APHA
8	Ion Chromatographic Method	IC	APHA 4110 B
9			
10			
11	Ion Chromatographic Method	IC	APHA4110B(modified)
12	Mercuric Thiocyanate	DA	APHA4500CLE
13	Not Applicable	Not Applicable	Not Applicable
14	Mercuric Thiocyanate	DA	4500-CL G

Table 49 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2			
3	High-Temperature Oxidation	NIR-detector	
4	High-Temperature Oxidation	NIR-detector	Inhouse
5	Wet-Oxidation	NIR-detector	in house
6			
7	High-Temperature Oxidation	NIR-detector	APHA
8			
9			
10			
11	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA5310C(modified)
12	High-Temperature Oxidation	NIR-detector	APHA5310B
13	Not Applicable	Not Applicable	Not Applicable
14	Wet-Oxidation	NIR-detector	5310 C

Table 50 Measurement Methods and Instrument Techniques for Fluoride

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2			
3			
4	Ion Selective Electrode Method	Ion Selective Electrode	Inhouse
5	Ion Chromatographic Method	IC	in house
6			
7	Ion Selective Electrode Method	Ion Selective Electrode	APHA
8			
9			
10			
11	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500-F- C
12	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500FC
13	Not Applicable	Not Applicable	Not Applicable
14	Ion Selective Electrode Method	Ion Selective Electrode	4500-F C

Table 51 Measurement Methods and Instrument Techniques for NOx

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	In-house
2	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Inhouse
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	in house
6			
7	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	ISO 13395:1996
9	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
10	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500-NO3 I
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA-4500NO3(modified)
12	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO23
13	Not Applicable	Not Applicable	Not Applicable
14	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500-NO3 I

Table 52 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	SFA	In-house
2	Ascorbic Acid Colorimetric Method	FIA	APHA
3	Ascorbic Acid Colorimetric Method	FIA	
4	Ascorbic Acid Colorimetric Method	FIA	Inhouse
5	Ascorbic Acid Colorimetric Method	FIA	in house
6			
7	Ascorbic Acid Colorimetric Method	SFA	APHA
8	Ascorbic Acid Colorimetric Method	DA	USEPA 103,104,129
9	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
10	Ascorbic Acid Colorimetric Method	FIA	APHA 4500 P, G, H
11	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PG
12	Vanadomolybdophosphoric Colorimetric Method	DA	APHA4500PF
13	Not Applicable	Not Applicable	Not Applicable
14	Ascorbic Acid Colorimetric Method	DA	4500-P G

Table 53 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2			
3	ICP Method	ICP-MS	In House W32
4	Turbidimetric Method	FIA	Inhouse
5	Ion Chromatographic Method	IC	in house
6	Ion Chromatographic Method	IC	APHA 4110B
7	Turbidimetric Method	DA	APHA
8	Ion Chromatographic Method	IC	APHA 4110 B
9			
10			
11	Ion Chromatographic Method	IC	APHA4110B(modified)
12	ICP Method	ICP-OES	APHA3120B
13	Not Applicable	Not Applicable	Not Applicable
14	ICP Method	ICP-OES	3120 B

Table 54 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2	Persulfate digestion	FIA	APHA
3	Persulfate digestion	FIA	
4	Persulfate digestion	FIA	Inhouse
5	Calculation (TKN+NOx)	FIA	in house
6			
7	Persulfate digestion	SFA	APHA
8	Persulfate digestion	SFA	ISO 13395:1996
9			
10	Persulfate digestion	FIA	APHA 4500 P, G, H
11	Persulfate digestion	FIA	APHA4500NC&4500NO3
12	Calculation (TKN+NOx)	Not Applicable	
13	Not Applicable	Not Applicable	Not Applicable
14	Persulfate digestion	FIA	4500-P J

Table 55 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1				
2	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
3	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
4	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
5	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
6				
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
8	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500 P B G
9				
10	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500 P, G, H
11	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PH
12	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA4500P
13	NA	Not Applicable	Not Applicable	Not Applicable
14	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	4500-P J

APPENDIX 7 - METHODOLOGY FOR S2

Table 56 Measurement Methods and Instrument Techniques for Alkalinity

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	In-house
2			
3	Titration	Manual Analysis	
4	Titration	Ion Selective Electrode	APHA2320B
5	Titration	Auto Titration	in house
6	Titration	Ion Selective Electrode	APHA 2320 B
7	Titration	Auto Titration	APHA
8	Not Applicable	Not Applicable	Not Applicable
9	Not Applicable	Not Applicable	Not Applicable
10	Not Applicable	Not Applicable	Not Applicable
11	Titration	Auto Titration	APHA 2320 B
12	Titration	Auto Tritator	APHA2320
13	Not Applicable	Not Applicable	Not Applicable
14	Titration	Auto Titration	2320 B

Table 57 Measurement Methods and Instrument Techniques for Total Hardness in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2			
3	Titration	Manual Analysis	
4			
5	Calculation	ICP-OES	in house
6			
7	Calculation	ICP-OES	APHA
8	Not Applicable	Not Applicable	Not Applicable
9	Not Applicable	Not Applicable	Not Applicable
10	Not Applicable	Not Applicable	Not Applicable
11	Calculation	Not Applicable	
12	Calculation		
13	Not Applicable	Not Applicable	Not Applicable
14	Calculation	Not Applicable	2340 B

Table 58 Measurement Methods and Instrument Techniques for Total Kjeldahl Nitrogen in S2

Lab. Code	Measurement Method		Instrument	Method Reference
1				
2				
3	TKN=TN-NOx (K2S2O8 digestion)		FIA	
4				
5	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	in house
6				
7	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
8	NA	Not Applicable	Not Applicable	Not Applicable
9	NA	Not Applicable	Not Applicable	Not Applicable
10	NA	Not Applicable	Not Applicable	Not Applicable
11	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA4500Norg
12	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA4500NORG
13	NA	Not Applicable	Not Applicable	Not Applicable
14				

Table 59 Measurement Methods and Instrument Techniques for Total Nitrogen in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2	Persulfate digestion	FIA	APHA
3	Persulfate digestion	FIA	
4	Persulfate digestion	FIA	Inhouse
5	Calculation (TKN+NOx)	FIA	in house
6			
7	Persulfate digestion	SFA	APHA
8	Not Applicable	Not Applicable	Not Applicable
9	Not Applicable	Not Applicable	Not Applicable
10	Not Applicable	Not Applicable	Not Applicable
11	Calculation (TKN+NOx)	Not Applicable	
12	Calculation (TKN+NOx)	Not Applicable	
13	Not Applicable	Not Applicable	Not Applicable
14	Persulfate digestion	FIA	4500-P J

Table 60 Measurement Methods and Instrument Techniques for Total Organic Carbon in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2			
3			
4	High-Temperature Oxidation	NIR-detector	Inhouse
5	Wet-Oxidation	NIR-detector	in house
6			
7	High-Temperature Oxidation	NIR-detector	APHA
8	Not Applicable	Not Applicable	Not Applicable
9	Not Applicable	Not Applicable	Not Applicable
10	Not Applicable	Not Applicable	Not Applicable
11	NA		
12	High-Temperature Oxidation	NIR-detector	APHA5310B
13	Not Applicable	Not Applicable	Not Applicable
14	Wet-Oxidation	NIR-detector	5310 C

Table 61 Measurement Methods and Instrument Techniques for Total Phosphorus in S2

Lab. Code	Measurement Method		Instrument	Method Reference
1				
2	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
3	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
4	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
5	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
6				
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
8	NA	Not Applicable	Not Applicable	Not Applicable
9	NA	Not Applicable	Not Applicable	Not Applicable
10	NA	Not Applicable	Not Applicable	Not Applicable
11	(NH4)2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P H
12	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA4500P
13	NA	Not Applicable	Not Applicable	Not Applicable
14	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	4500-P J

APPENDIX 8 – METHODOLOGY FOR S3

Table 62 Measurement Methods and Instrument Techniques for TDS, TSS and Total Solids

Laboratory Code	Method Reference
6	APHA 2540 B, C &D, USEPA 160.1, 160.2, 160.3 and 160.4
8	APHA 2540 B, APHA 2540 C
11	APHA 2540
13	APHA 2540 B, C and D
14	Solids 2540 B, C & D

END OF REPORT