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Proficiency Test Final Report AQA 20-17 Nutrients, Anions and Physical Tests in Sea Water

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

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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 20-17, Nutrients, Anions and Physical Tests in Sea Water. 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 and total B, Ca, K, Mg, Na and P were included in the program.

Twenty laboratories registered to participate and all submitted results.

The assigned values were the robust average of participants' results with the exception of total dissolved solids in the water Sample S3. 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 222 z-scores, 200 (90%) returned a satisfactory score of $|z| \leq 2$.

Of 222 E_n scores, 191 (86%) returned a satisfactory score of $|E_n| \leq 1$.

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

A limited number of participants have capabilities to measure total phosphorus at low level in sea water. Only 4 participants reported results for this test. All reported results were in an excellent agreement with each other (with a between laboratory CV of 13%).

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 226 numerical results, 206 (91%) were reported with an expanded measurement uncertainty. 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; and
- controlled drug assay.

AQA 20-17 is the 11th 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 sea water;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

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

Twenty laboratories participated and submitted results.

The timetable of the study was:

Invitation issued:	12 October 2020
Samples dispatched:	9 November 2020
Results due:	8 December 2020
Interim report issued:	9 December 2020

3.3 Test Material Specification

Three samples were provided for analysis:

Sample S1 was 200 mL of filtered, autoclaved and frozen sea water;

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

Sample S3 was 750 mL of unfiltered sea water.

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 sulphate in S1 and alkalinity, Na and total P in S2.

Results returned by participants gave no reason to question the homogeneity of the test samples.

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

For Samples S1 and S2, to address issues associated with holding time and holding conditions, a stability study was conducted for the less stable analytes: NH_3-N and NO_3-N +NO_2-N in S1. The stability study was conducted over the entire period of the PT study and was carried out to simulate the conditions encountered by the samples during storage. Details of the study and results are given in Appendix 2.

3.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were frozen.

The samples were dispatched by courier on 9 November 2020.

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, sea water		SAMPLE S2 unfiltered, sea water		SAMPLE S3 unfiltered sea water	
Test	**Approximate Conc. Range mg/L**	**Test**	**Approximate Conc. Range mg/L**	**Test**	**Approximate Conc. Range mg/L**
Ammonia-N	0.025-0.75	B (total)	0.5-25	TDS (dried at 180°C)	>100
(Nitrate-N +Nitrite-N) NOx	0.005-0.125	Ca (total)	30-900	TSS (dried at 103-105°C)	>50
Total Dissolved Nitrogen (TDN)	0.025-0.75	K (total)	50-1500	TS (dried at 103-105°C)	>100
Orthophosphate-P (FRP)	0.005-0.125	Mg (total)	30-900		
Total Dissolved Phosphorus	0.005-0.125	Na (total)	30-900		
Dissolved Organic Carbon	0.5-25	P (total)	0.005-0.125		
Chloride	<50000	Total Kjeldahl Nitrogen	0.025-1		
Fluoride	0.25-5	Total Nitrogen	0.025-1		
Sulphate	<5000	Total Organic Carbon	1-25		
		Alkalinity to pH 4.5 as CaCO3	NA		
		Total Hardness (CaCO3)	<7500		
		pH (at 25°C)	>2.5		
		EC (at 25°C)	<75000		

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.

3.9 Interim Report

An interim report was emailed to participants on 9 December 2020.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for S1 and S2

Measurement methods and instrumental techniques used for the tests in Samples S1 and S2 are presented in Appendices 6 and 7 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
3	Sample S1: (1) Ammonia assay: S1 diluted by a factor of 17.67 with type 1 water to bring S1 within my calibration range. My top calibration standard is 0.035 mg/L NH4_N (2.5 umol/L N) (2) NOx and Orthophosphate-P assay: S1 neat. Methodology for S1: SFA instrument: Seal AA3HR.
6 and 12	Sample S1: We have reported our results as mg/L of N in NOx, P in PO4 and N in NH4. NOTE: For Ammonia-N – our calibration curve tops out at 2uM (0.028mg/L) so the solution was measured as a 1:10 dilution as would be done on the occasional sample in the higher range. Methodology for S1: Calibration concentration for our lab was as follows: NOx-N (0-0.588mg/L), PO4-P (0-0.09mg/L) and NH4-N (0-0.028mg/L).
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 1:10 dilution as would be done on the occasional sample in the higher range. Methodology for S1: Calibration concentration for our lab was as follows: NOx-N (0-0.161mg/L), PO4-P (0-0.09mg/L) and NH4-N (0-0.028mg/L).
10	Sample S1: It has been noted that the result for DRP (Orthophosphate-P) is higher than that of Total Dissolved P. Repeat testing has confirmed this discrepancy.

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 - CRM Duplicate Analysis Instrument Calibration		ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
3*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Standard Purity	NMI Uncertainty Course
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	Instrument Calibration	Nordtest Report TR537
5	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM Recoveries of SS	
6*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NMI Uncertainty Course

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Top Down Approach
9*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NMI Uncertainty Course
10*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	Recoveries of SS	IANZ technical guide
11	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	CRM	NATA Technical Note 33
12*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NMI Uncertainty Course
13	Top Down - precision and estimates of the method and laboratory bias		CRM	Nordtest Report TR537
14	Top Down - precision and estimates of the method and laboratory bias		CRM Laboratory Bias from PT Studies Recoveries of SS	NATA Technical Note 33
15	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	CRM Recoveries of SS	ISO/GUM
16	Top Down - reproducibility (standard deviation) from PT studies used directly	Control samples - CRM Duplicate Analysis Instrument Calibration	Laboratory Bias from PT Studies	
17	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM
18	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	NMI Uncertainty Course
19	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA Technical Note 33
20	Standard deviation of replicate analyses multiplied by 2 or 3			

[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
3, 6, 9,12	Measurement uncertainty is reported as an expanded uncertainty with a coverage factor of 2 (95% confidence interval).
10	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
Ammonia in blue ocean sea water is typically <0.02 mg/L NH4_N 0.3 mg/L is not representative of blue ocean concentrations and such samples usually need dilution to measure in ocean sea water labs.	We will include unspiked seawater samples and/or will spike seawater with lower levels of ammonia. The other participants are also invited to comment.
Suggest include nutrients: reactive silicate and nitrite in future studies.	These tests will be included in our next studies in fresh and saline water.
Please ship sea water on dry-ice to ensure sample remains frozen during transit.	Thank you for your feedback for how to pack our samples. A "transport stability study" was conducted when we first started running these studies. However for less stable analytes, stability studies are conducted each time. 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.
We normally report 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 Orthophosphate analysis. It would be great if the guide made this clear as to whether there was an expectation of mg/L of P or PO4.	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.
Make methods selection LETTER coded for reporting	Thank you for your feedback; a drop-down list with the codes for the most popular methods will be included in the results form. Participants will still have the option to type the name of their method if it is not included in the list.

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.

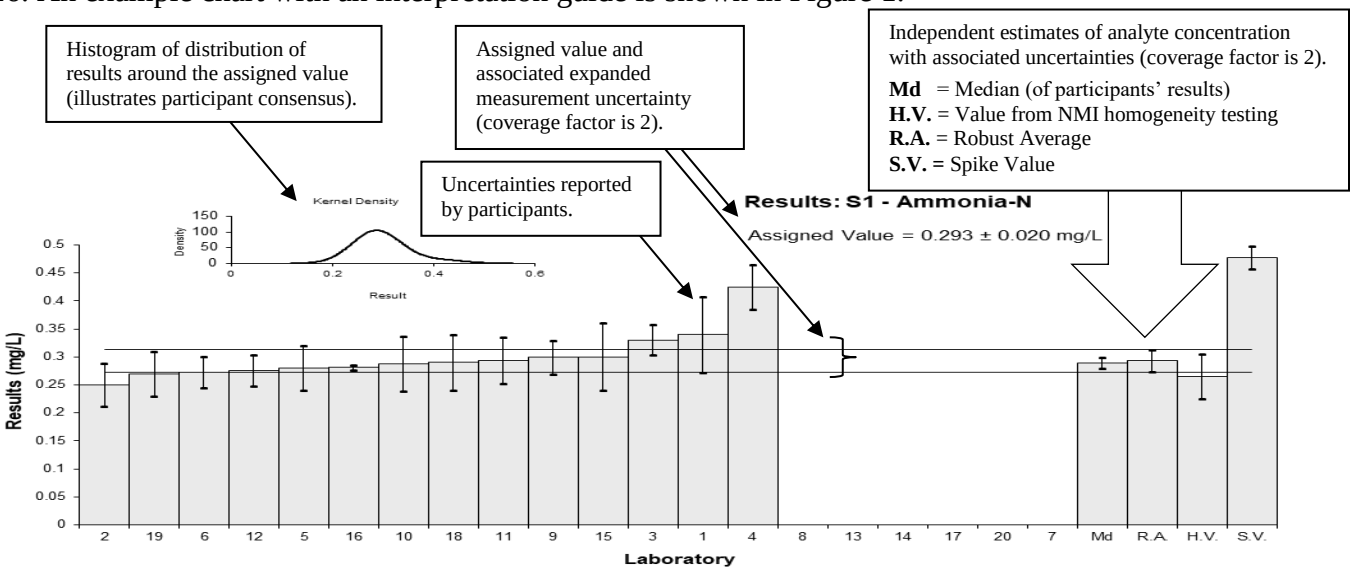


Figure 1 Guide to Presentation of Results

5.2 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.

5.3 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]

5.4 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]

5.5 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study coordinator would be expected from participants. It is important to note that is not the coefficient of variation of participant 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] By setting a fixed and realistic value for the PCV, the participant's performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value *(X)* and the performance coefficient of variation (PCV) as presented in Equation 1.

$\sigma = (X) * PCV$ Equation 1

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.	Sea Water
Analyte.	Ammonia-N
Units	mg/L

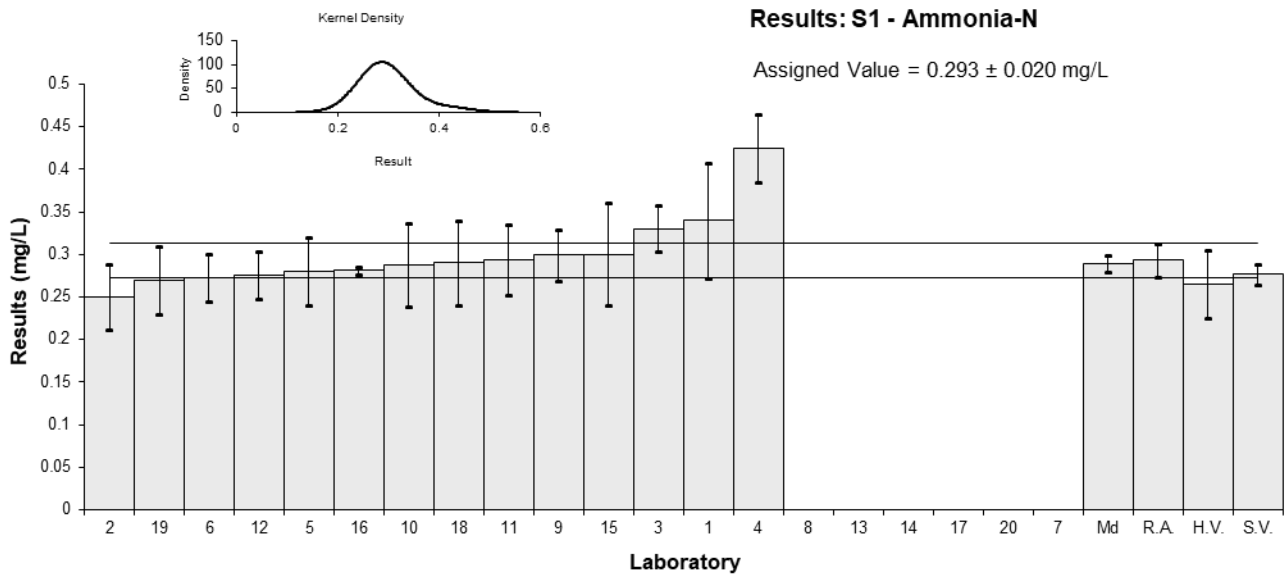
Participant Results

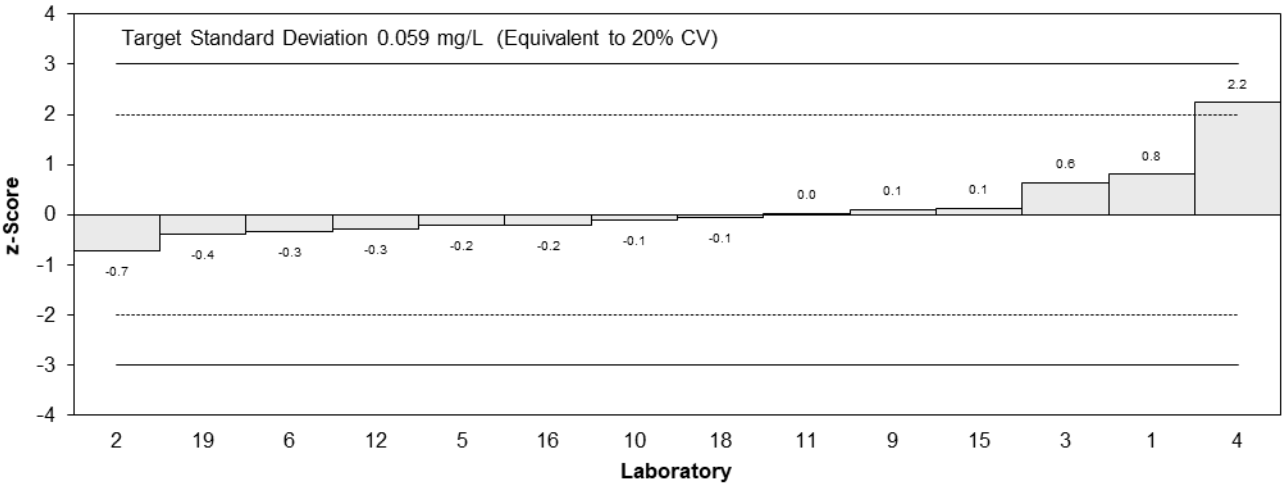
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.34	0.068	0.80	0.66
2	0.25	0.038	-0.73	-1.00
3	0.330	0.027	0.63	1.10
4	0.424	0.04	2.24	2.93
5	0.28	0.04	-0.22	-0.29
6	0.2726	0.0273	-0.35	-0.60
7	NT	NT		
8	NR	NR		
9	0.2990	0.0299	0.10	0.17
10	0.287	0.049	-0.10	-0.11
11	0.2939	0.041	0.02	0.02
12	0.2757	0.0276	-0.30	-0.51
13	NT	NT		
14	NT	NT		
15	0.3	0.06	0.12	0.11
16	0.281	0.005	-0.20	-0.58
17	NT	NT		
18	0.29	0.05	-0.05	-0.06
19	0.27	0.04	-0.39	-0.51
20	NT	NT		

Statistics

Assigned Value	0.293	0.020
Spike*	0.277	0.012
Homogeneity Value	0.265	0.040
Robust Average	0.293	0.020
Median	0.289	0.010
Mean	0.300	
N	14	
Max.	0.424	
Min.	0.25	
Robust SD	0.030	
Robust CV	10%	

*Incurred value not included


Kernel Density
Density
Result
Results: S1 - Ammonia-N
Assigned Value = 0.293 ± 0.020 mg/L
Results (mg/L)
Laboratory
2 19 6 12 5 16 10 18 11 9 15 3 1 4 8 13 14 17 20 7 Md R.A. H.V. S.V.


z-Scores: S1 - Ammonia-N
Target Standard Deviation 0.059 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
2 19 6 12 5 16 10 18 11 9 15 3 1 4
-0.7 -0.4 -0.3 -0.3 -0.2 -0.2 -0.1 -0.1 0.0 0.1 0.1 0.6 0.8 2.2

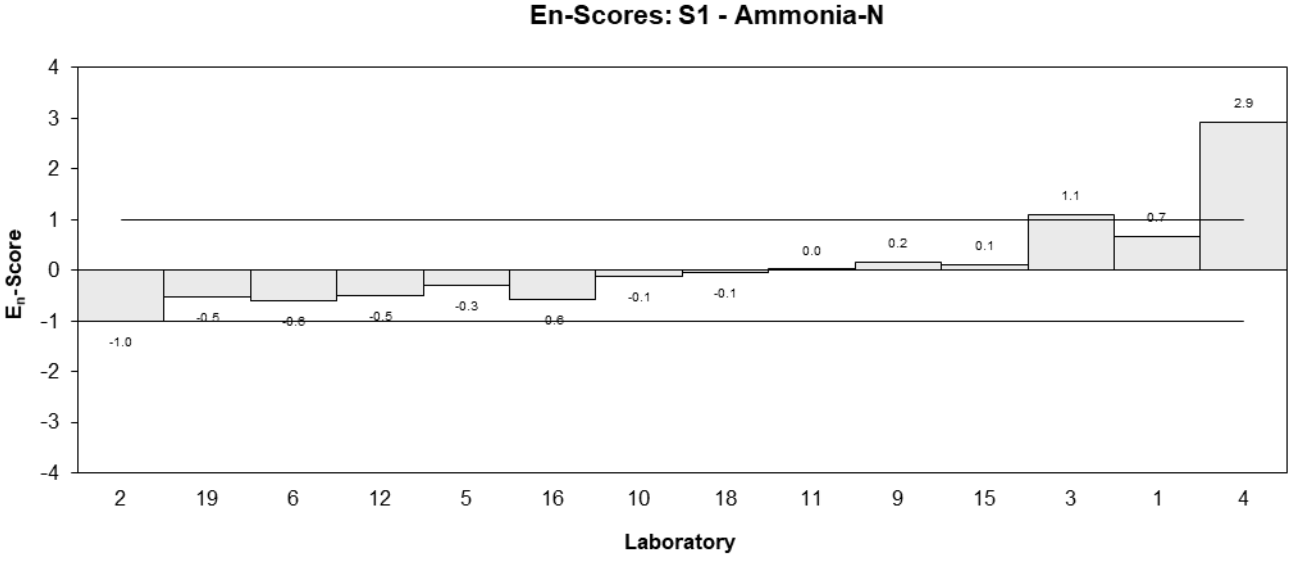

En-Scores: S1 - Ammonia-N
En-Score
Laboratory
2 19 6 12 5 16 10 18 11 9 15 3 1 4
-1.0 -0.5 -0.6 -0.5 -0.3 -0.6 -0.1 -0.1 0.0 0.2 0.1 1.1 0.7 2.9

Figure 2

Table 6

Sample Details

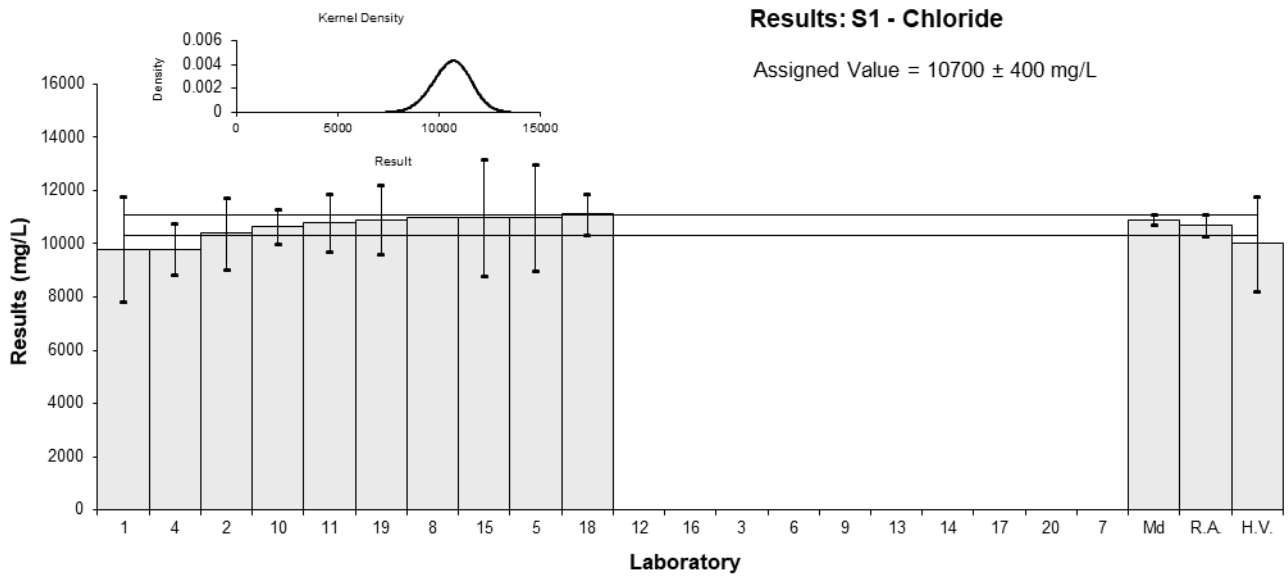
Sample No.	S1
Matrix.	Sea Water
Analyte.	Chloride
Units	mg/L

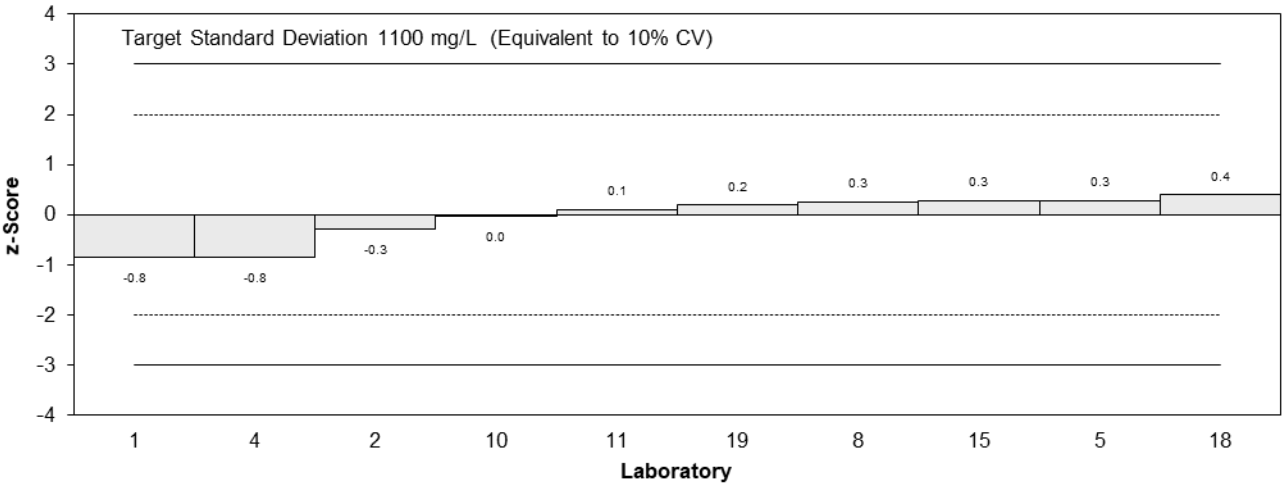
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	9800	1960	-0.84	-0.45
2	10400	1350	-0.28	-0.21
3	NR	NR		
4	9800	980	-0.84	-0.85
5	11000	2000	0.28	0.15
6	NR	NR		
7	NT	NT		
8	10978	NR	0.26	0.70
9	NR	NR		
10	10660	640	-0.04	-0.05
11	10810	1080	0.10	0.10
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	11000	2200	0.28	0.13
16	NR	NR		
17	NT	NT		
18	11120	780	0.39	0.48
19	10900	1310	0.19	0.15
20	NT	NT		

Statistics

Assigned Value	10700	400
Spike	Not Spiked	
Homogeneity Value	10000	1800
Robust Average	10700	400
Median	10900	200
Mean	10600	
N	10	
Max.	11120	
Min.	9800	
Robust SD	520	
Robust CV	4.9%	


Kernel Density
Density
0.006
0.004
0.002
0
0
5000
10000
15000
Result
Results: S1 - Chloride
Assigned Value = 10700 ± 400 mg/L
Results (mg/L)
16000
14000
12000
10000
8000
6000
4000
2000
0
1 4 2 10 11 19 8 15 5 18 12 16 3 6 9 13 14 17 20 7 Md R.A. H.V.
Laboratory


z-Scores: S1 - Chloride
Target Standard Deviation 1100 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.8
-0.3
0.0
0.1
0.2
0.3
0.3
0.3
0.4
1 4 2 10 11 19 8 15 5 18
Laboratory

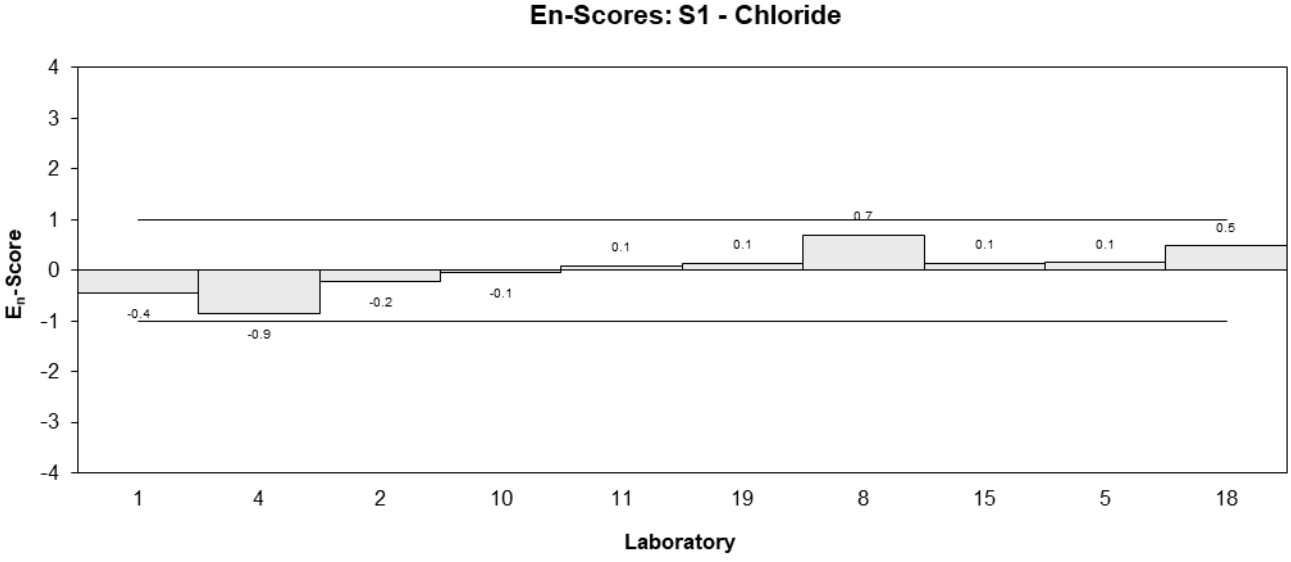

En-Scores: S1 - Chloride
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.4
-0.9
-0.2
-0.1
0.1
0.1
0.7
0.1
0.1
0.5
1 4 2 10 11 19 8 15 5 18
Laboratory

Figure 3

Table 7

Sample Details

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

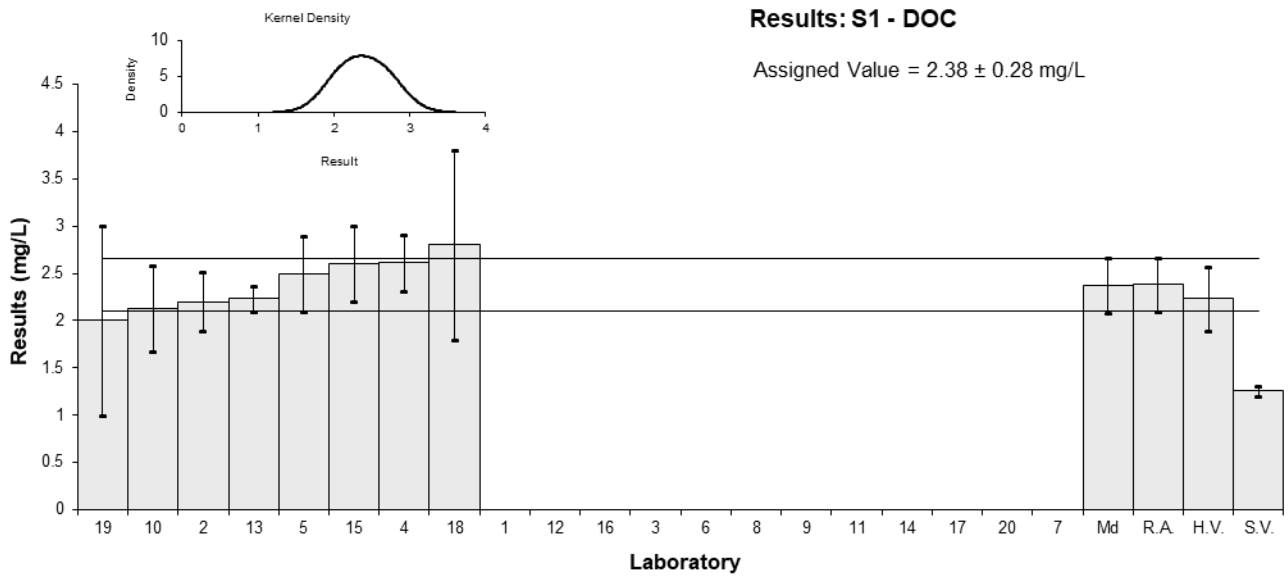
Participant Results

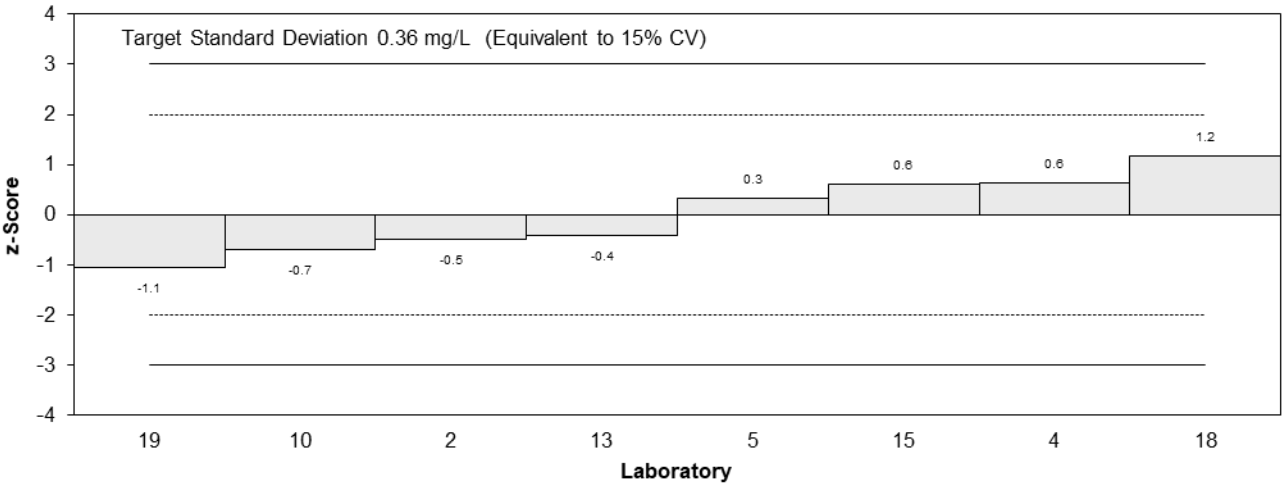
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	2.2	0.31	-0.50	-0.43
3	NR	NR		
4	2.61	0.3	0.64	0.56
5	2.5	0.4	0.34	0.25
6	NR	NR		
7	NT	NT		
8	NR	NR		
9	NR	NR		
10	2.13	0.45	-0.70	-0.47
11	NT	NT		
12	NR	NR		
13	2.23	0.13	-0.42	-0.49
14	NT	NT		
15	2.6	0.4	0.62	0.45
16	NR	NR		
17	NT	NT		
18	2.8	1	1.18	0.40
19	2.0	1	-1.06	-0.37
20	NT	NT		

Statistics

Assigned Value	2.38	0.28
Spike*	1.26	0.05
Homogeneity Value	2.23	0.34
Robust Average	2.38	0.28
Median	2.37	0.29
Mean	2.38	
N	8	
Max.	2.8	
Min.	2	
Robust SD	0.32	
Robust CV	13%	

*Incurred value not included.


Kernel Density
Density
Result
Results: S1 - DOC
Assigned Value = 2.38 ± 0.28 mg/L
Results (mg/L)
Laboratory
19 10 2 13 5 15 4 18 1 12 16 3 6 8 9 11 14 17 20 7 Md R.A. H.V. S.V.


z-Scores: S1 - DOC
Target Standard Deviation 0.36 mg/L (Equivalent to 15% CV)
z-Score
-1.1
-0.7
-0.5
-0.4
0.3
0.6
0.6
1.2
Laboratory
19 10 2 13 5 15 4 18

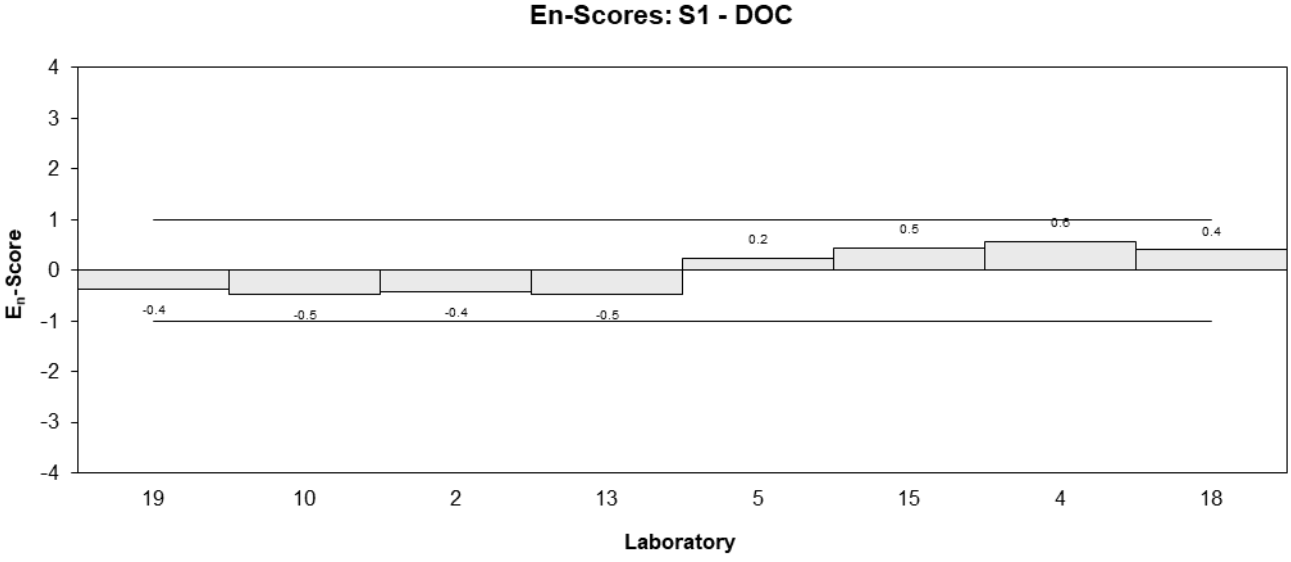

En-Scores: S1 - DOC
En-Score
-0.4
-0.5
-0.4
-0.5
0.2
0.5
0.6
0.4
Laboratory
19 10 2 13 5 15 4 18

Figure 4

Table 8

Sample Details

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

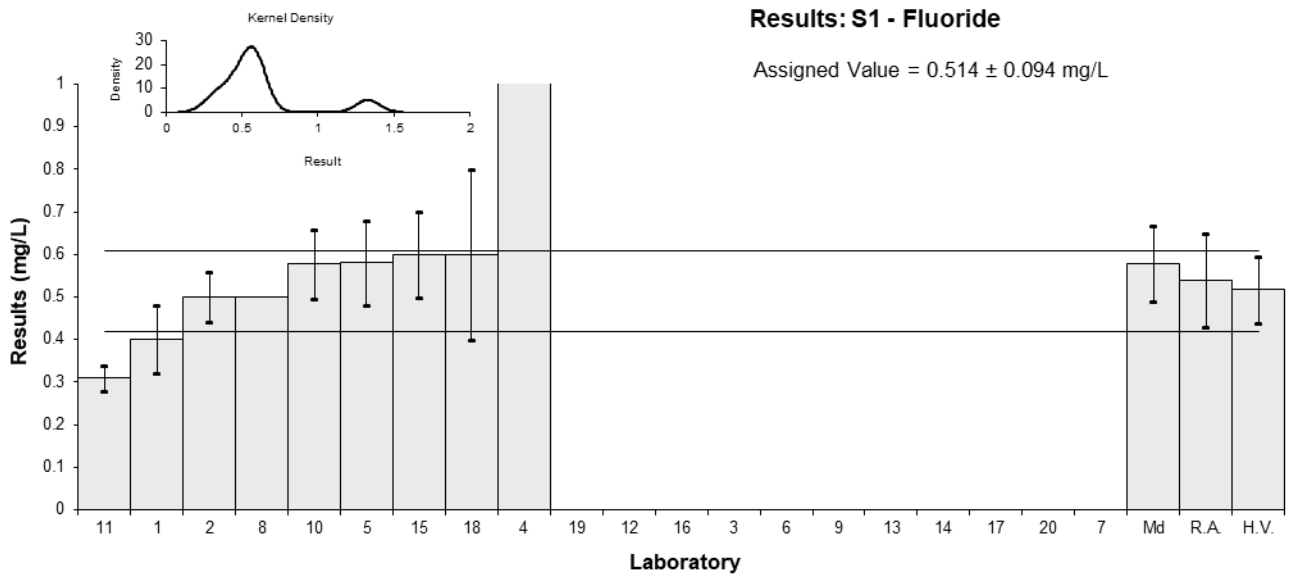
Participant Results

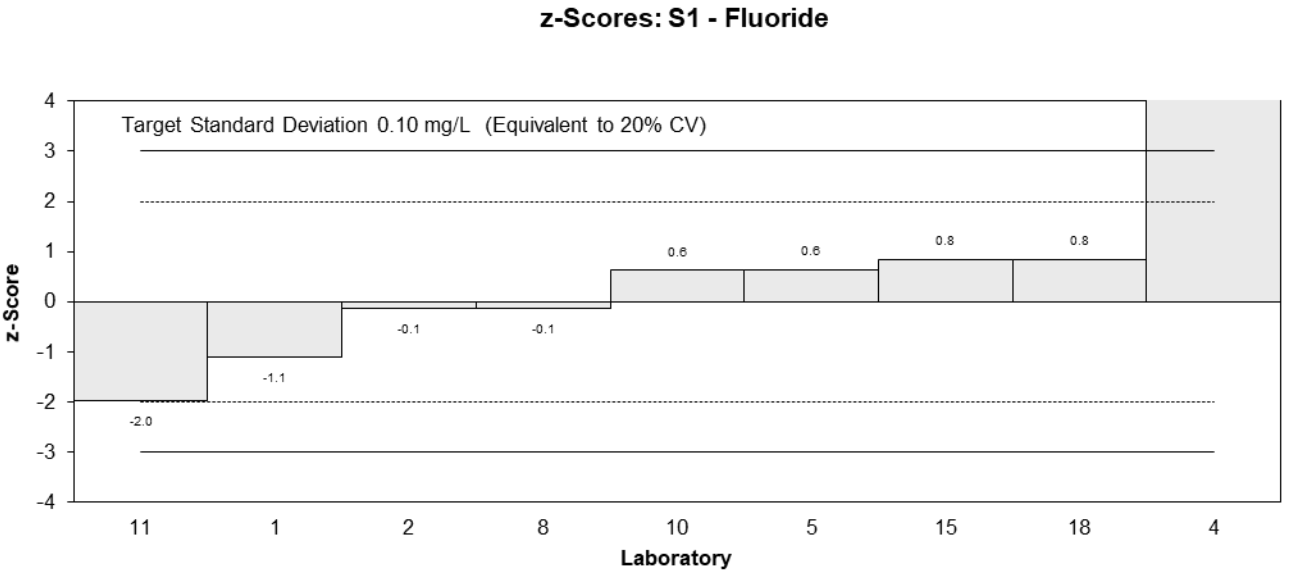
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.4	0.08	-1.11	-0.92
2	0.5	0.06	-0.14	-0.13
3	NR	NR		
4	1.33	0.13	7.94	5.09
5	0.58	0.1	0.64	0.48
6	NR	NR		
7	NT	NT		
8	0.5	NR	-0.14	-0.15
9	NR	NR		
10	0.578	0.081	0.62	0.52
11	0.31	0.03	-1.98	-2.07
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	0.6	0.1	0.84	0.63
16	NR	NR		
17	NT	NT		
18	0.6	0.2	0.84	0.39
19	<10	NR		
20	NT	NT		

Statistics

Assigned Value*	0.514	0.094
Spike	Not Spiked	
Homogeneity Value	0.517	0.078
Robust Average	0.54	0.11
Median	0.578	0.089
Mean	0.600	
N	9	
Max.	1.33	
Min.	0.31	
Robust SD	0.14	
Robust CV	26%	

*Robust Average excluding Laboratory 4.


Results: S1 - Fluoride
Assigned Value = 0.514 ± 0.094 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
11 1 2 8 10 5 15 18 4 19 12 16 3 6 9 13 14 17 20 7 Md R.A. H.V.


z-Scores: S1 - Fluoride
Target Standard Deviation 0.10 mg/L (Equivalent to 20% CV)
z-Score
-2.0
-1.1
-0.1
-0.1
0.6
0.6
0.8
0.8
Laboratory
11 1 2 8 10 5 15 18 4

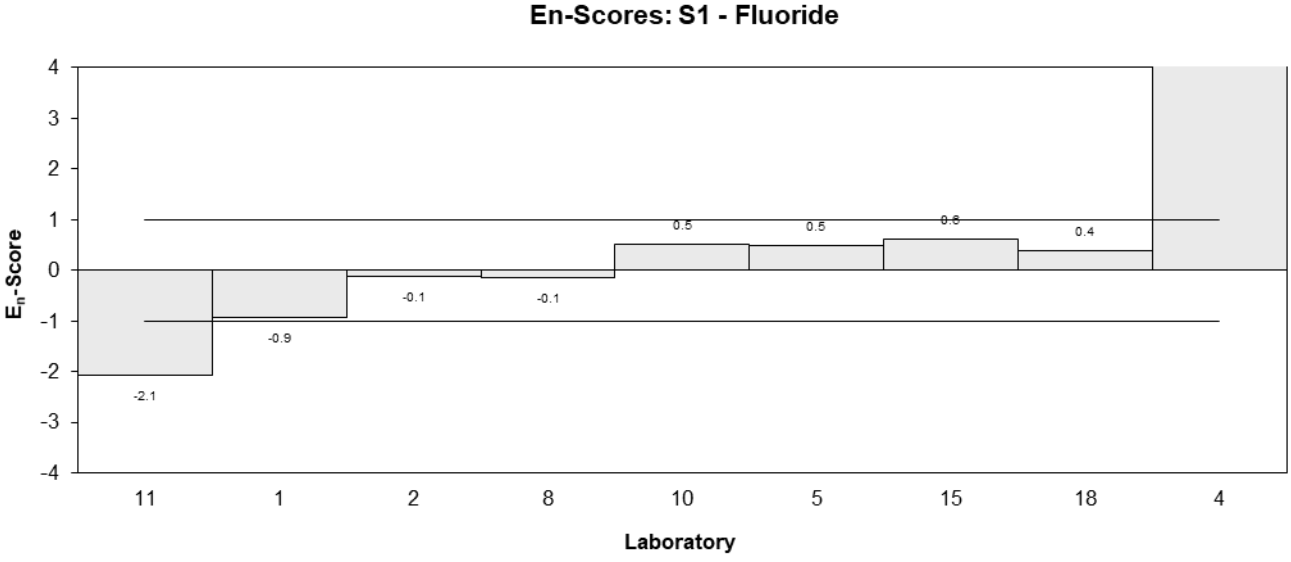

En-Scores: S1 - Fluoride
En-Score
-2.1
-0.9
-0.1
-0.1
0.5
0.5
0.6
0.4
Laboratory
11 1 2 8 10 5 15 18 4

Figure 5

Table 9

Sample Details

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

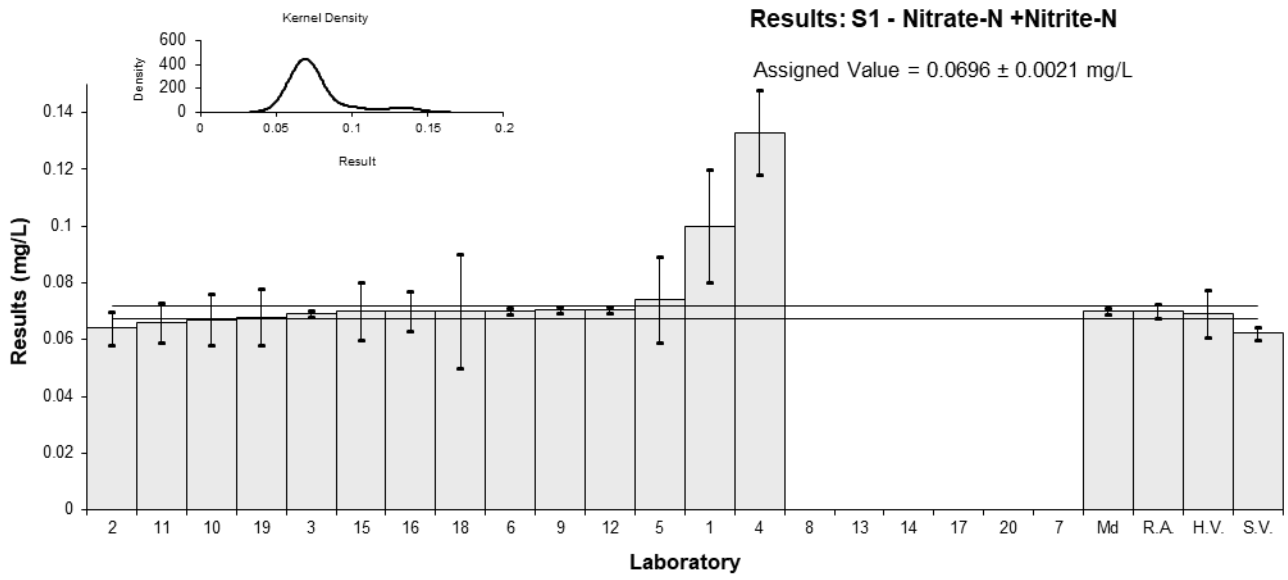
Participant Results

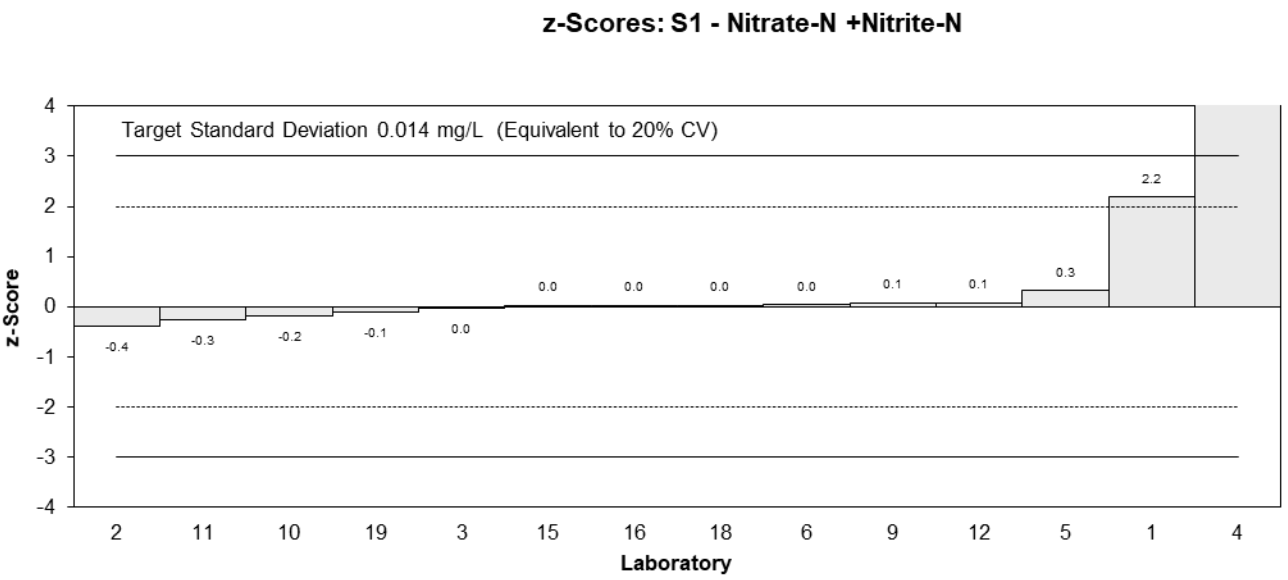
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.10	0.02	2.18	1.51
2	0.064	0.006	-0.40	-0.88
3	0.0690	0.0011	-0.04	-0.25
4	0.133	0.015	4.55	4.19
5	0.074	0.015	0.32	0.29
6	0.0701	0.0011	0.04	0.21
7	NT	NT		
8	NR	NR		
9	0.0705	0.0011	0.06	0.38
10	0.0671	0.0090	-0.18	-0.27
11	0.066	0.007	-0.26	-0.49
12	0.0706	0.0011	0.07	0.42
13	NT	NT		
14	NT	NT		
15	0.07	0.01	0.03	0.04
16	0.07	0.007	0.03	0.05
17	NT	NT		
18	0.07	0.02	0.03	0.02
19	0.068	0.01	-0.11	-0.16
20	NT	NT		

Statistics

Assigned Value*	0.0696	0.0021
Spike**	0.0622	0.0021
Homogeneity Value	0.0693	0.0083
Robust Average	0.0701	0.0025
Median	0.0700	0.0013
Mean	0.0759	
N	14	
Max.	0.133	
Min.	0.064	
Robust SD	0.0037	
Robust CV	5.3%	

*Robust Average excluding Laboratory 4. **Incurred value not included.


Kernel Density
Density
Result
Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.0696 ± 0.0021 mg/L
Results (mg/L)
Laboratory
2 11 10 19 3 15 16 18 6 9 12 5 1 4 8 13 14 17 20 7 Md R.A. H.V. S.V.


z-Scores: S1 - Nitrate-N +Nitrite-N
Target Standard Deviation 0.014 mg/L (Equivalent to 20% CV)
z-Score
-0.4 -0.3 -0.2 -0.1 0.0 0.0 0.0 0.0 0.0 0.1 0.1 0.3 2.2
Laboratory
2 11 10 19 3 15 16 18 6 9 12 5 1 4

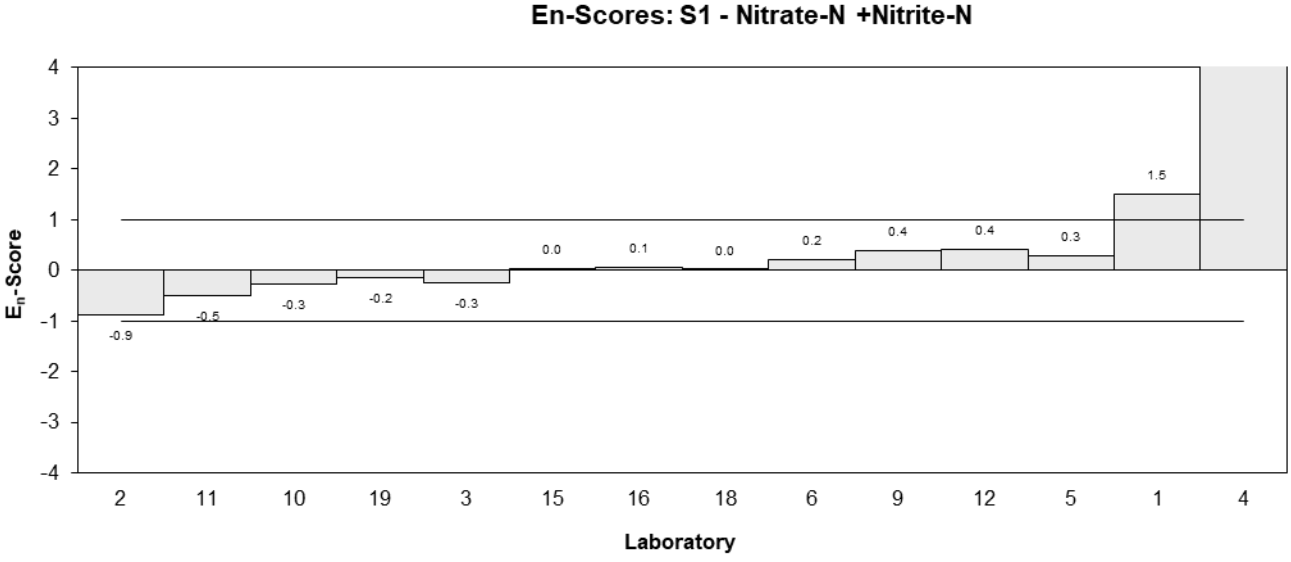

En-Scores: S1 - Nitrate-N +Nitrite-N
En-Score
-0.9 -0.5 -0.3 -0.2 -0.3 0.0 0.1 0.0 0.2 0.4 0.4 0.3 1.5
Laboratory
2 11 10 19 3 15 16 18 6 9 12 5 1 4

Figure 6

Table 10

Sample Details

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

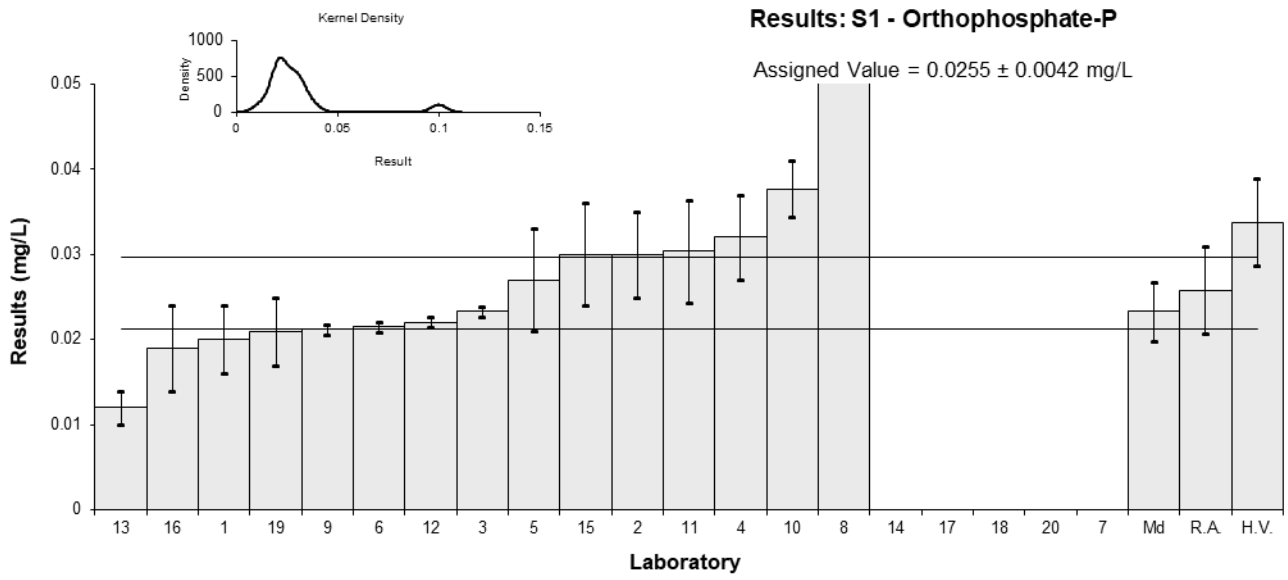
Participant Results

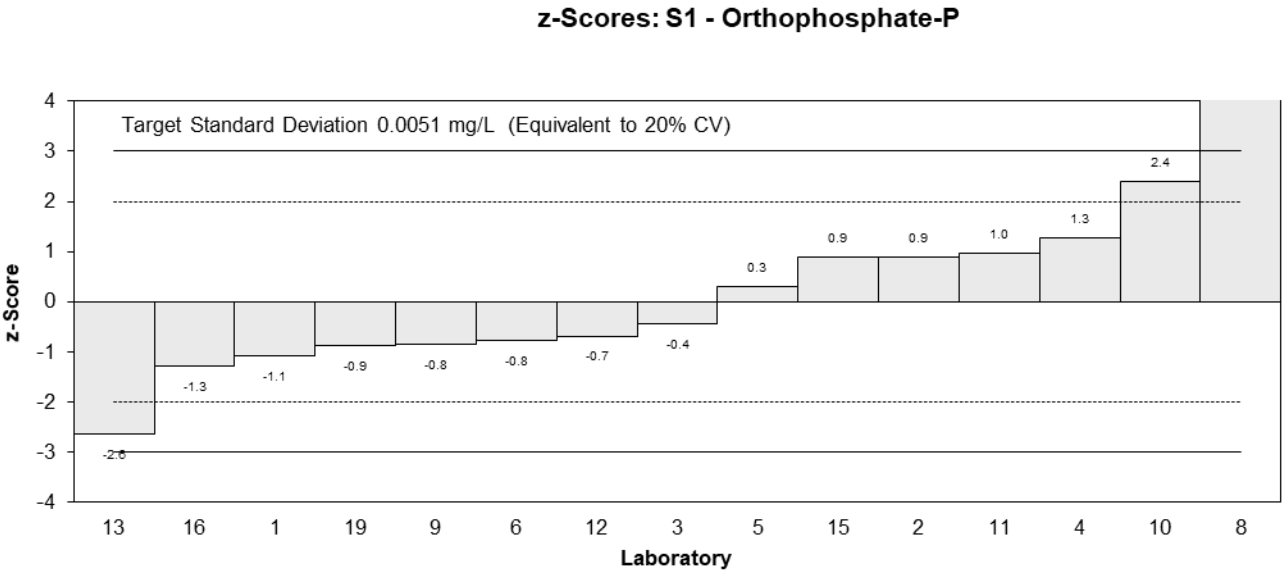
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.02	0.004	-1.08	-0.95
2	0.030	0.005	0.88	0.69
3	0.0233	0.0006	-0.43	-0.52
4	0.032	0.005	1.27	1.00
5	0.027	0.006	0.29	0.20
6	0.0215	0.0006	-0.78	-0.94
7	NT	NT		
8	0.10	NR	14.61	17.74
9	0.0212	0.0006	-0.84	-1.01
10	0.0377	0.0033	2.39	2.28
11	0.0304	0.006	0.96	0.67
12	0.0220	0.0006	-0.69	-0.82
13	0.012	0.002	-2.65	-2.90
14	NT	NT		
15	0.03	0.006	0.88	0.61
16	0.019	0.005	-1.27	-1.00
17	NT	NT		
18	NT	NT		
19	0.021	0.004	-0.88	-0.78
20	NT	NT		

Statistics

Assigned Value*	0.0255	0.0042
Spike	Not Spiked	
Homogeneity Value	0.0338	0.0051
Robust Average	0.0258	0.0051
Median	0.0233	0.0035
Mean	0.0298	
N	15	
Max.	0.1	
Min.	0.012	
Robust SD	0.0079	
Robust CV	31%	

*Robust Average excluding Laboratories 8 and 13.


Kernel Density
Density
Result
Results: S1 - Orthophosphate-P
Assigned Value = 0.0255 ± 0.0042 mg/L
Results (mg/L)
Laboratory
13 16 1 19 9 6 12 3 5 15 2 11 4 10 8 14 17 18 20 7 Md R.A. H.V.


z-Scores: S1 - Orthophosphate-P
Target Standard Deviation 0.0051 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
13 16 1 19 9 6 12 3 5 15 2 11 4 10 8
-2.6 -1.3 -1.1 -0.9 -0.8 -0.8 -0.7 -0.4 0.3 0.9 0.9 1.0 1.3 2.4

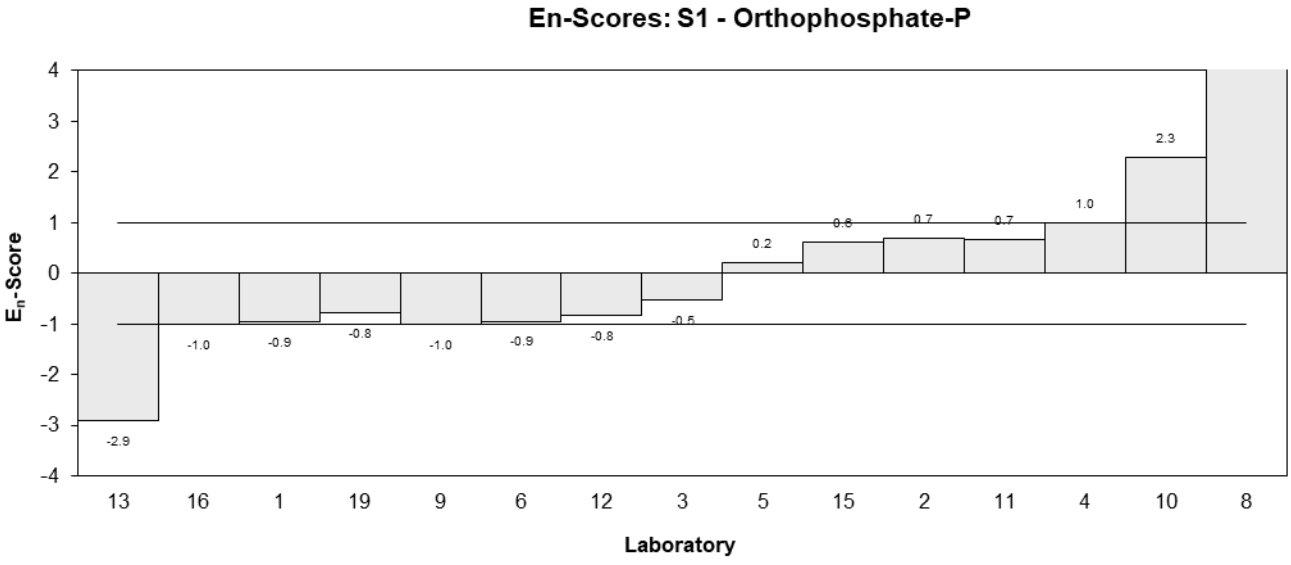

En-Scores: S1 - Orthophosphate-P
En-Score
Laboratory
13 16 1 19 9 6 12 3 5 15 2 11 4 10 8
-2.9 -1.0 -0.9 -0.8 -1.0 -0.9 -0.8 -0.5 0.2 0.6 0.7 0.7 1.0 2.3

Figure 7

Table 11

Sample Details

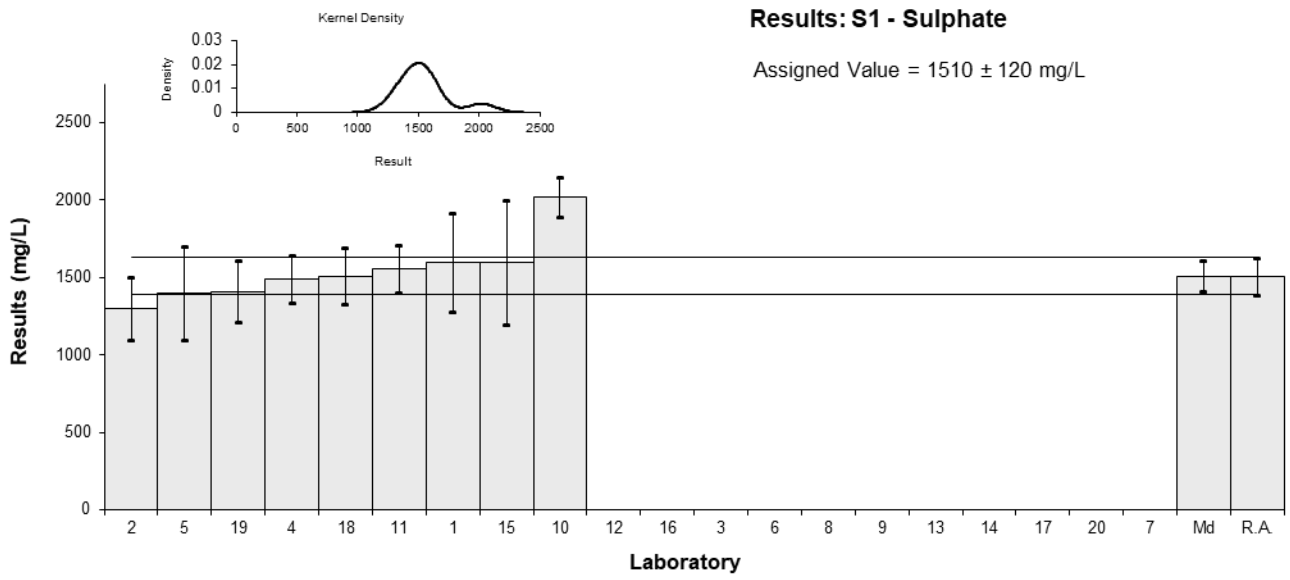
Sample No.	S1
Matrix.	Sea Water
Analyte.	Sulphate
Units	mg/L

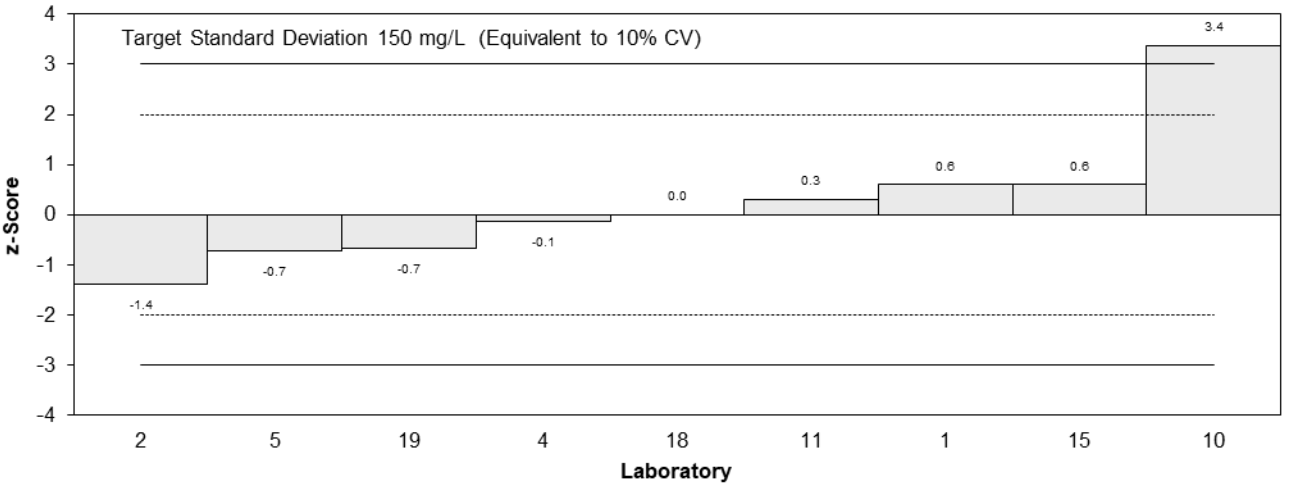
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1600	320	0.60	0.26
2	1300	200	-1.39	-0.90
3	NR	NR		
4	1490	150	-0.13	-0.10
5	1400	300	-0.73	-0.34
6	NR	NR		
7	NT	NT		
8	NR	NR		
9	NR	NR		
10	2020	130	3.38	2.88
11	1556	156	0.30	0.23
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	1600	400	0.60	0.22
16	NR	NR		
17	NT	NT		
18	1510	180	0.00	0.00
19	1410	200	-0.66	-0.43
20	NT	NT		

Statistics

Assigned Value	1510	120
Spike	Not Spiked	
Robust Average	1510	120
Median	1510	100
Mean	1540	
N	9	
Max.	2020	
Min.	1300	
Robust SD	150	
Robust CV	9.9%	


Kernel Density
Density
0.03
0.02
0.01
0
0
500
1000
1500
2000
2500
Result
Results: S1 - Sulphate
Assigned Value = 1510 ± 120 mg/L
Results (mg/L)
2500
2000
1500
1000
500
0
2
5
19
4
18
11
1
15
10
12
16
3
6
8
9
13
14
17
20
7
Md
R.A.
Laboratory


z-Scores: S1 - Sulphate
Target Standard Deviation 150 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.7
-0.7
-0.1
0.0
0.3
0.6
0.6
3.4
2
5
19
4
18
11
1
15
10
Laboratory

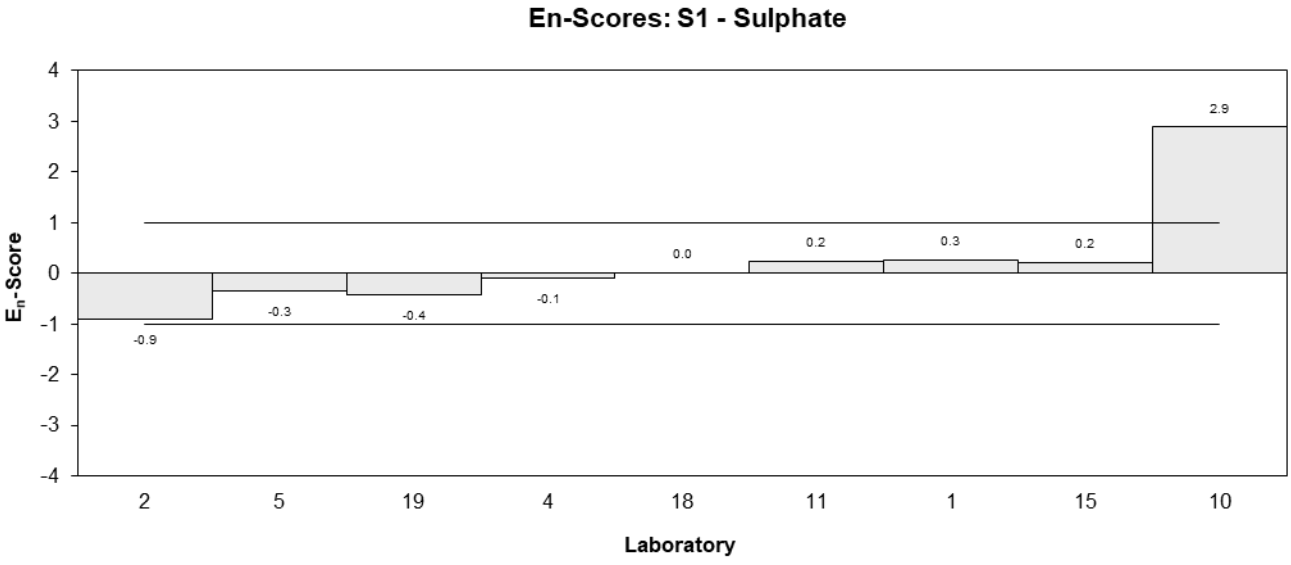

En-Scores: S1 - Sulphate
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.3
-0.4
-0.1
0.0
0.2
0.3
0.2
2.9
2
5
19
4
18
11
1
15
10
Laboratory

Figure 8

Table 12

Sample Details

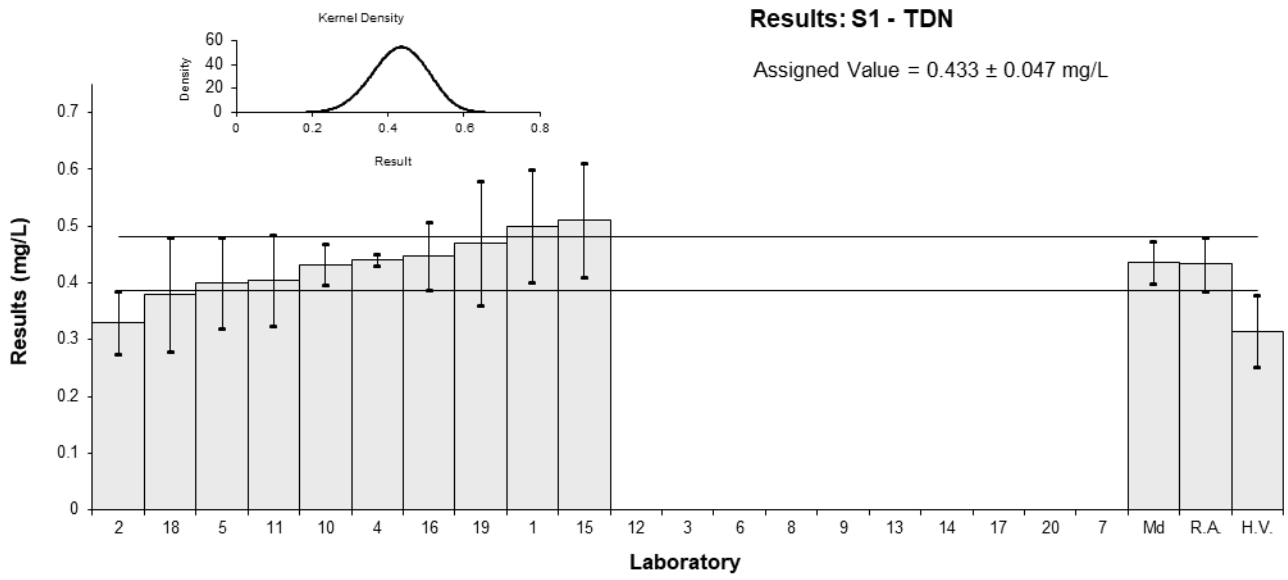
Sample No.	S1
Matrix.	Sea Water
Analyte.	TDN
Units	mg/L

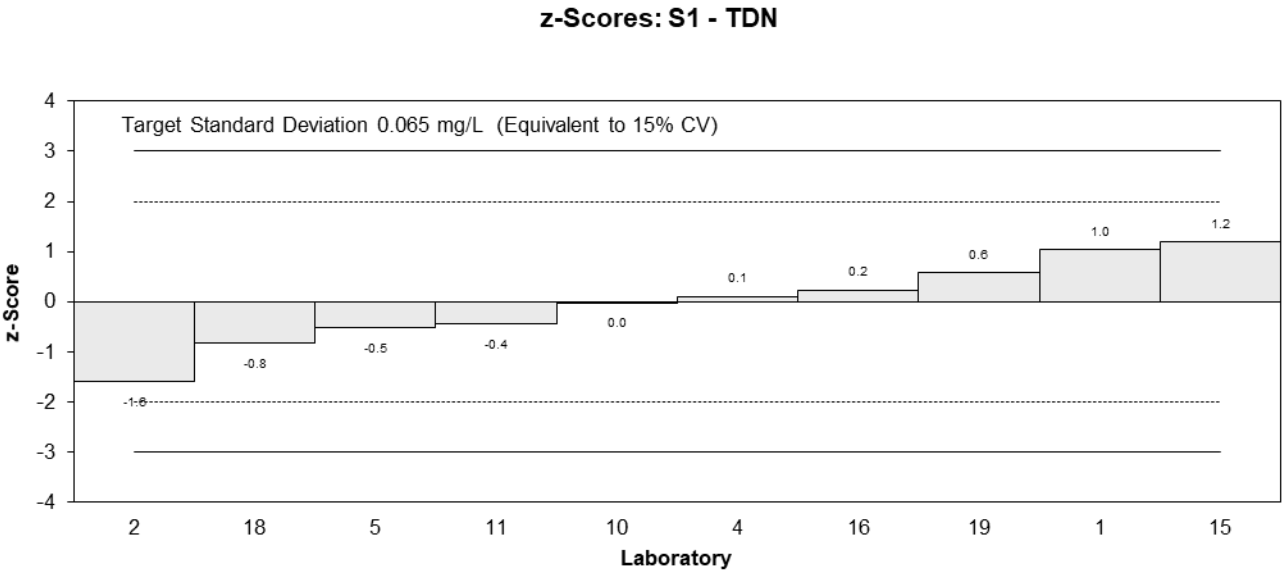
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.5	0.1	1.03	0.61
2	0.33	0.056	-1.59	-1.41
3	NR	NR		
4	0.44	0.01	0.11	0.15
5	0.40	0.08	-0.51	-0.36
6	NR	NR		
7	NT	NT		
8	NR	NR		
9	NR	NR		
10	0.432	0.036	-0.02	-0.02
11	0.404	0.08	-0.45	-0.31
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	0.51	0.1	1.19	0.70
16	0.448	0.06	0.23	0.20
17	NT	NT		
18	0.38	0.1	-0.82	-0.48
19	0.47	0.11	0.57	0.31
20	NT	NT		

Statistics

Assigned Value	0.433	0.047
Spike	Not Spiked	
Homogeneity Value	0.315	0.063
Robust Average	0.433	0.047
Median	0.436	0.037
Mean	0.431	
N	10	
Max.	0.51	
Min.	0.33	
Robust SD	0.060	
Robust CV	14%	


Kernel Density
Density
Result
Results: S1 - TDN
Assigned Value = 0.433 ± 0.047 mg/L
Results (mg/L)
Laboratory
2 18 5 11 10 4 16 19 1 15 12 3 6 8 9 13 14 17 20 7 Md R.A. H.V.


z-Scores: S1 - TDN
Target Standard Deviation 0.065 mg/L (Equivalent to 15% CV)
z-Score
-1.6 -0.8 -0.5 -0.4 0.0 0.1 0.2 0.6 1.0 1.2
Laboratory
2 18 5 11 10 4 16 19 1 15

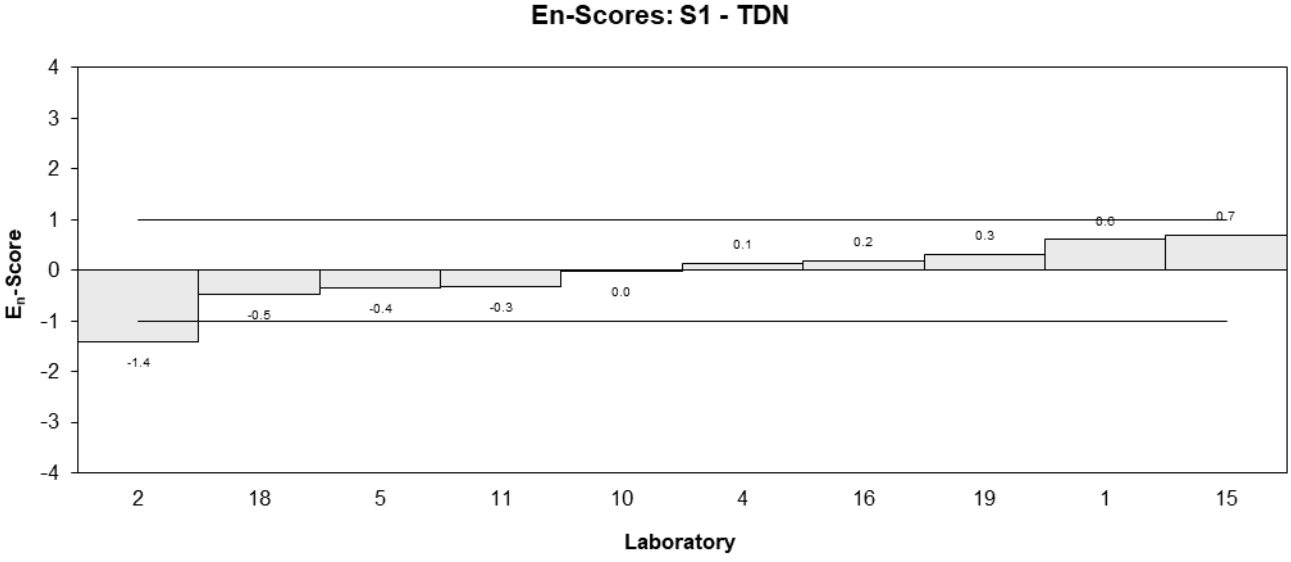

En-Scores: S1 - TDN
En-Score
-1.4 -0.5 -0.4 -0.3 0.0 0.1 0.2 0.3 0.6 0.7
Laboratory
2 18 5 11 10 4 16 19 1 15

Figure 9

Table 13

Sample Details

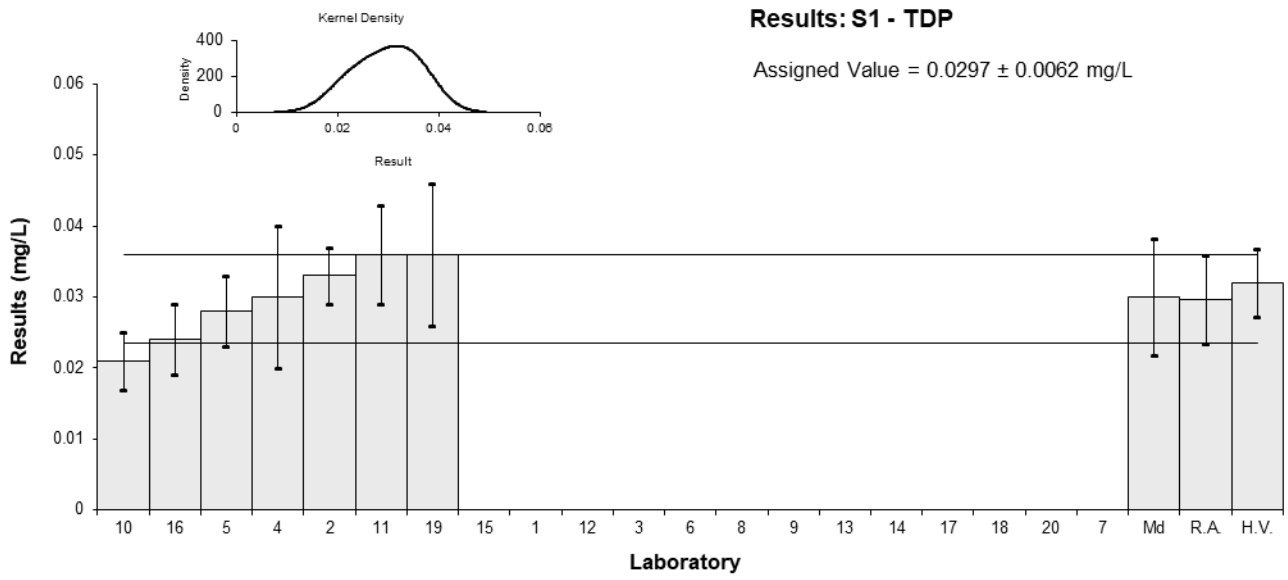
Sample No.	S1
Matrix.	Sea Water
Analyte.	TDP
Units	mg/L

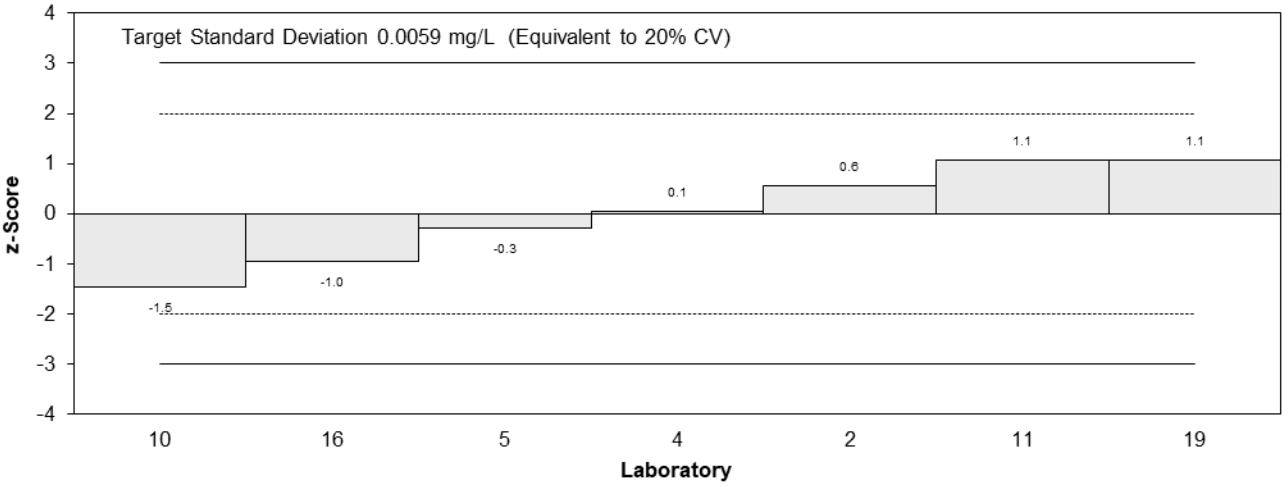
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	0.033	0.004	0.56	0.45
3	NR	NR		
4	0.03	0.01	0.05	0.03
5	0.028	0.005	-0.29	-0.21
6	NR	NR		
7	NT	NT		
8	NR	NR		
9	NR	NR		
10	0.0210	0.0040	-1.46	-1.18
11	0.036	0.007	1.06	0.67
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	<0.05	NR		
16	0.024	0.005	-0.96	-0.72
17	NT	NT		
18	NT	NT		
19	0.036	0.01	1.06	0.54
20	NT	NT		

Statistics

Assigned Value	0.0297	0.0062
Spike	Not Spiked	
Homogeneity Value	0.0320	0.0048
Robust Average	0.0297	0.0062
Median	0.0300	0.0082
Mean	0.0297	
N	7	
Max.	0.036	
Min.	0.021	
Robust SD	0.0066	
Robust CV	22%	


Kernel Density
Density
400
200
0
0
0.02
0.04
0.06
Result
Results: S1 - TDP
Assigned Value = 0.0297 ± 0.0062 mg/L
Results (mg/L)
0.06
0.05
0.04
0.03
0.02
0.01
0
10 16 5 4 2 11 19 15 1 12 3 6 8 9 13 14 17 18 20 7 Md R.A. H.V.
Laboratory


z-Scores: S1 - TDP
Target Standard Deviation 0.0059 mg/L (Equivalent to 20% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.5
-1.0
-0.3
0.1
0.6
1.1
1.1
10 16 5 4 2 11 19
Laboratory

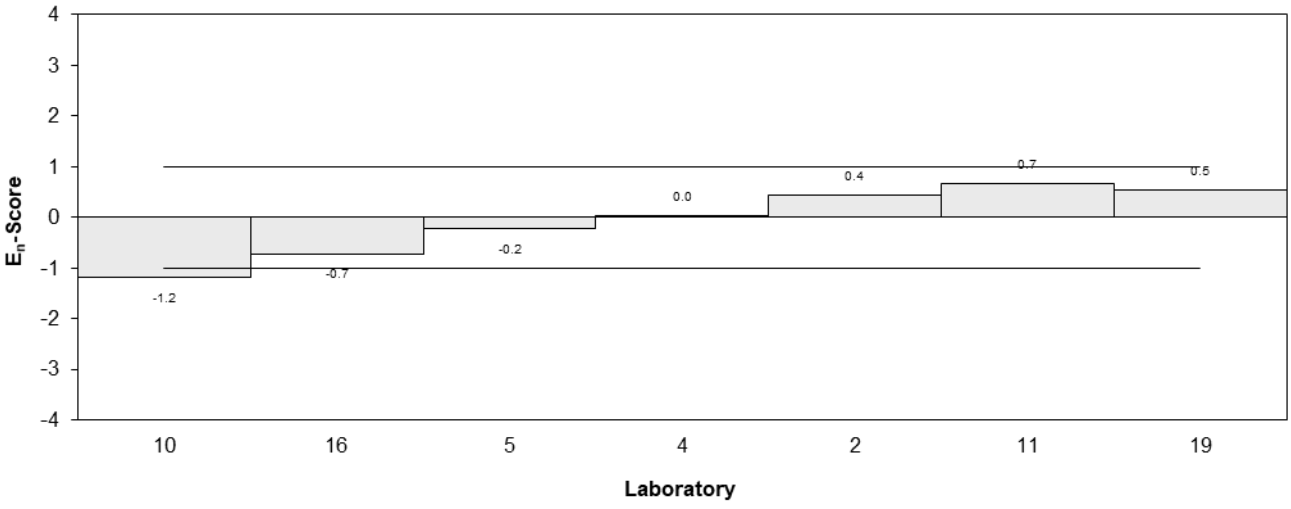

En-Scores: S1 - TDP
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.2
-0.7
-0.2
0.0
0.4
0.7
0.5
10 16 5 4 2 11 19
Laboratory

Figure 10

Table 14

Sample Details

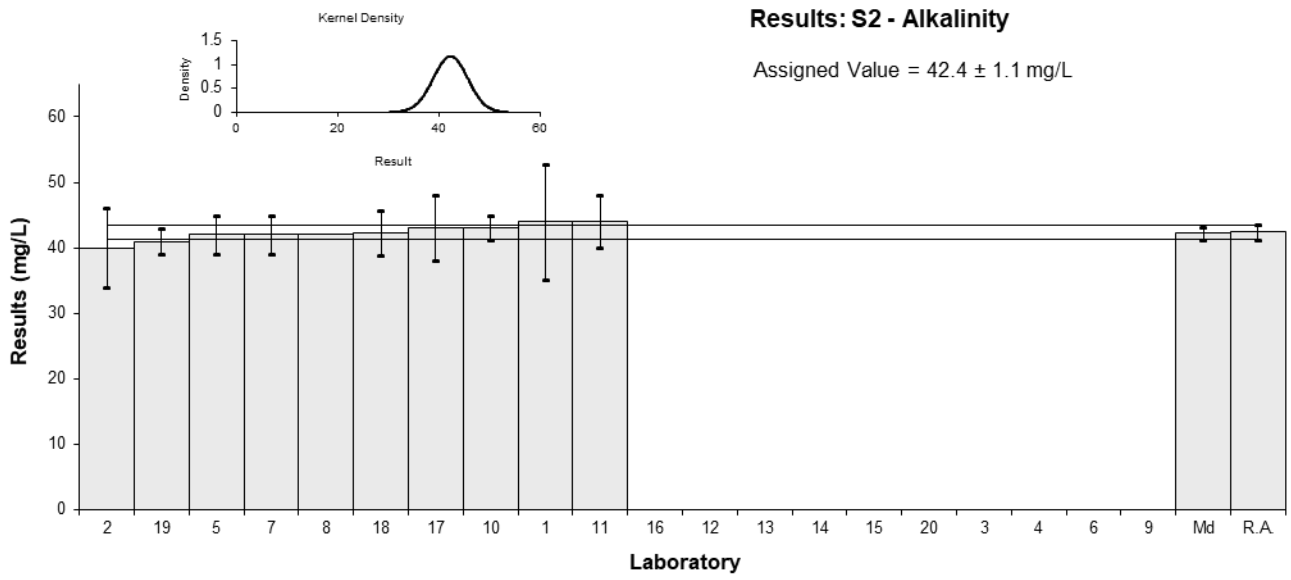
Sample No.	S2
Matrix.	Sea Water
Analyte.	Alkalinity
Units	mg/L

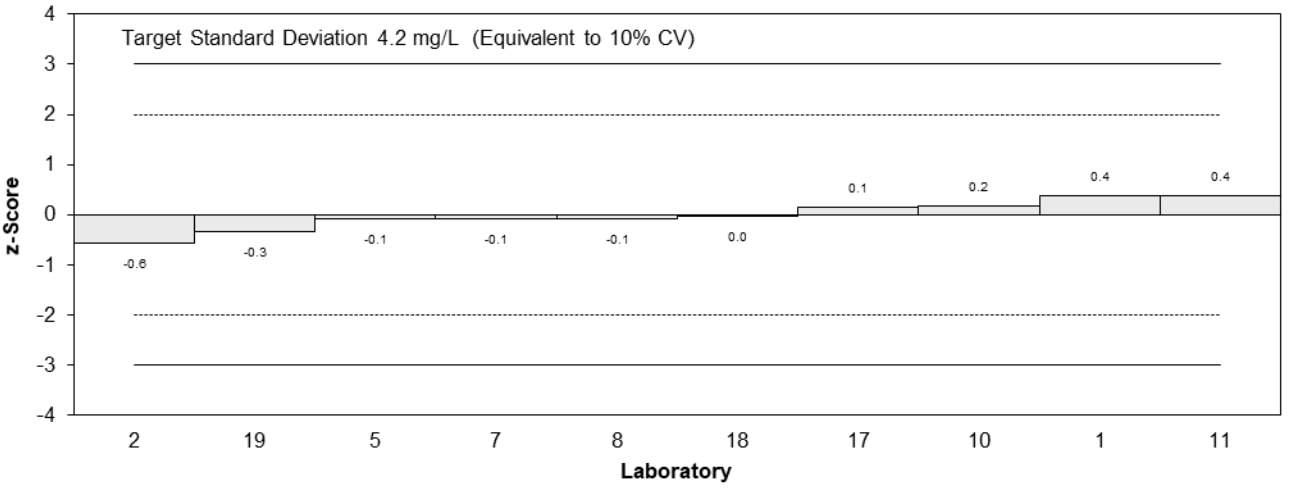
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	44	8.8	0.38	0.18
2	40	6	-0.57	-0.39
3	NT	NT		
4	NT	NT		
5	42	3	-0.09	-0.13
6	NT	NT		
7	42	3	-0.09	-0.13
8	42	NR	-0.09	-0.36
9	NT	NT		
10	43.1	1.9	0.17	0.32
11	44	4	0.38	0.39
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	43	5	0.14	0.12
18	42.3	3.4	-0.02	-0.03
19	41	2	-0.33	-0.61
20	NT	NT		

Statistics

Assigned Value	42.4	1.1
Spike	Not Spiked	
Robust Average	42.4	1.1
Median	42.2	1.0
Mean	42.3	
N	10	
Max.	44	
Min.	40	
Robust SD	1.3	
Robust CV	3.1%	


Kernel Density
Density
Result
Results: S2 - Alkalinity
Assigned Value = 42.4 ± 1.1 mg/L
Results (mg/L)
Laboratory
2 19 5 7 8 18 17 10 1 11 16 12 13 14 15 20 3 4 6 9 Md R.A.


z-Scores: S2 - Alkalinity
Target Standard Deviation 4.2 mg/L (Equivalent to 10% CV)
z-Score
-0.6 -0.3 -0.1 -0.1 -0.1 0.0 0.1 0.2 0.4 0.4
Laboratory
2 19 5 7 8 18 17 10 1 11

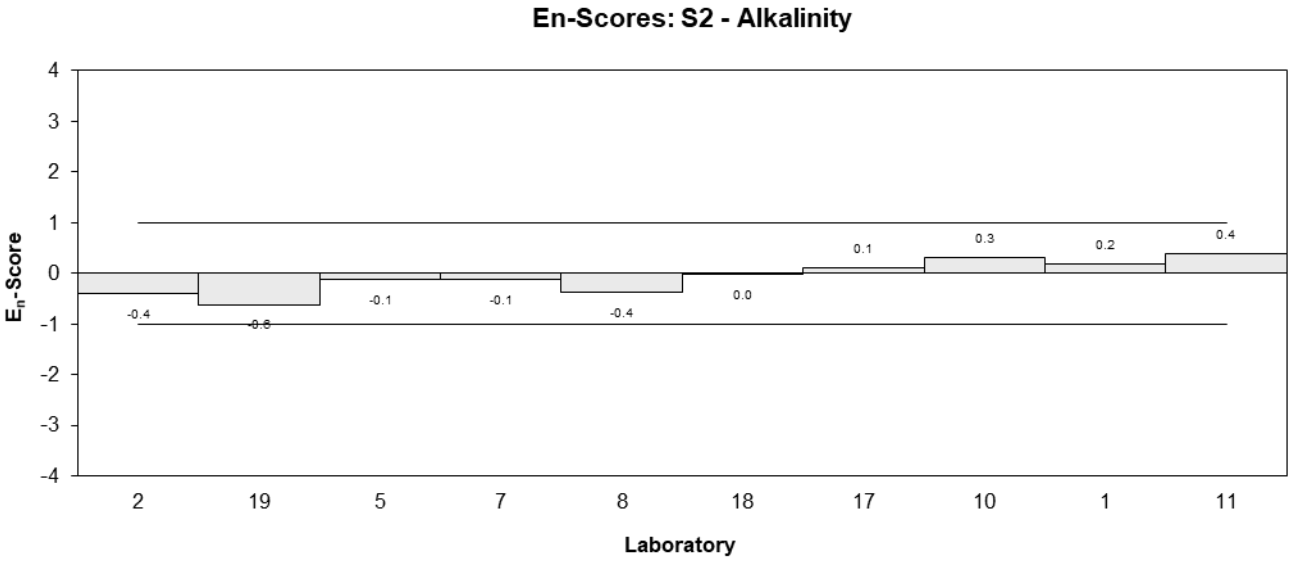

En-Scores: S2 - Alkalinity
En-Score
-0.4 -0.6 -0.1 -0.1 -0.4 0.0 0.1 0.3 0.2 0.4
Laboratory
2 19 5 7 8 18 17 10 1 11

Figure 11

Table 15

Sample Details

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

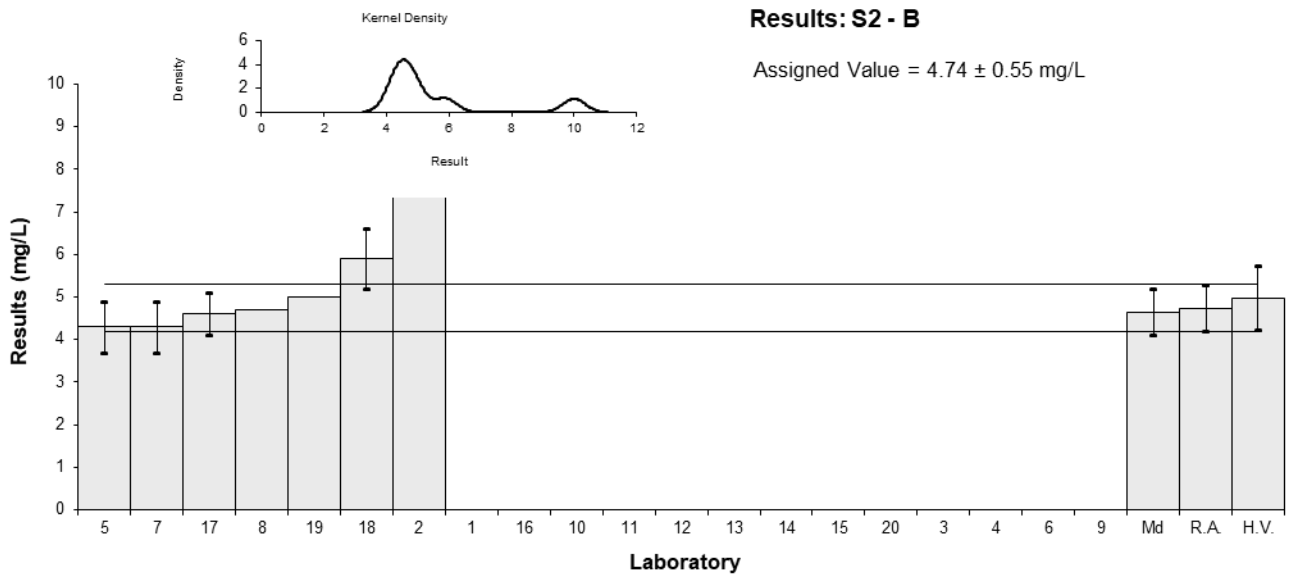
Participant Results

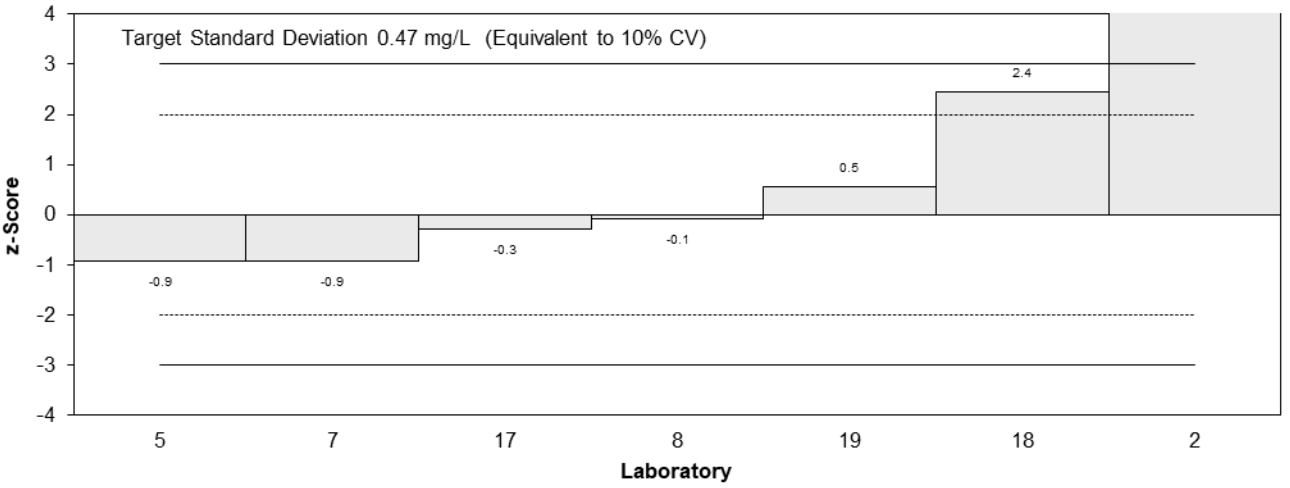
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	4000	800	8428.82	4.99
3	NT	NT		
4	NT	NT		
5	4.3	0.6	-0.93	-0.54
6	NT	NT		
7	4.3	0.6	-0.93	-0.54
8	4.7	NR	-0.08	-0.07
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	4.60	0.5	-0.30	-0.19
18	5.9	0.7	2.45	1.30
19	5	NR	0.55	0.47
20	NT	NT		

Statistics*

Assigned Value	4.74	0.55
Spike	Not Spiked	
Homogeneity Value	4.98	0.75
Robust Average	4.74	0.55
Median	4.65	0.54
Mean	4.80	
N	6	
Max.	4000	
Min.	4.3	
Robust SD	0.54	
Robust CV	11%	

*The result reported by Laboratory 2 was omitted from statistical calculation (gross error).


Kernel Density
Density
Result
Results: S2 - B
Assigned Value = 4.74 ± 0.55 mg/L
Results (mg/L)
Laboratory
5 7 17 8 19 18 2 1 16 10 11 12 13 14 15 20 3 4 6 9 Md R.A. H.V.


z-Scores: S2 - B
Target Standard Deviation 0.47 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
5 7 17 8 19 18 2
-0.9 -0.9 -0.3 -0.1 0.5 2.4

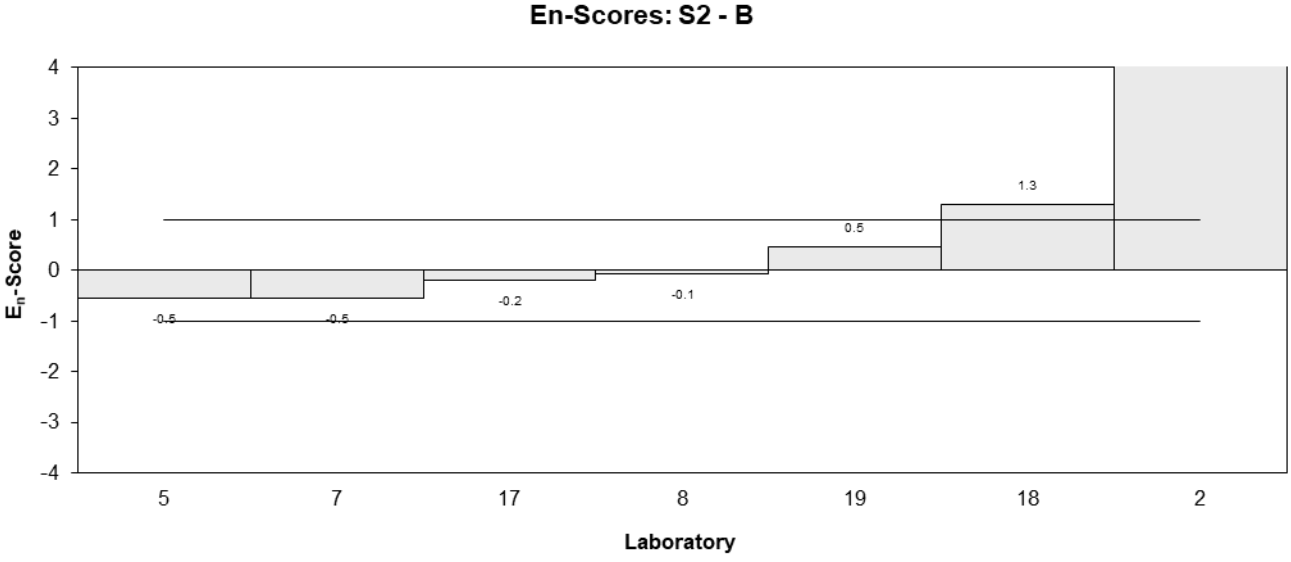

En-Scores: S2 - B
En-Score
Laboratory
5 7 17 8 19 18 2
-0.5 -0.5 -0.2 -0.1 0.5 1.3

Figure 12

Table 16

Sample Details

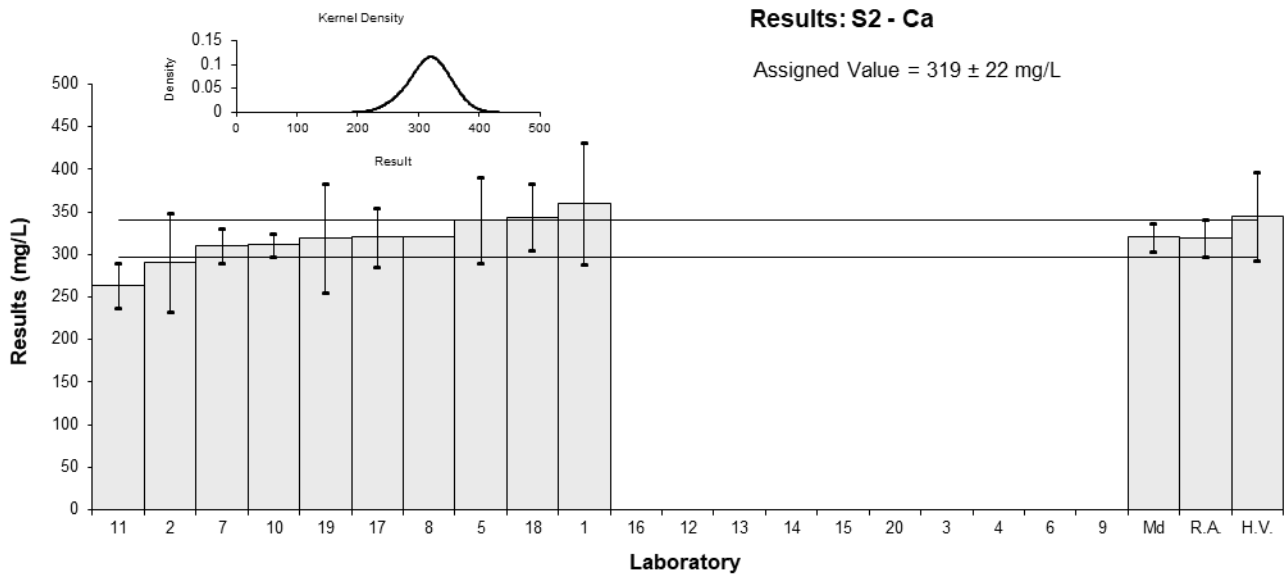
Sample No.	S2
Matrix.	Sea Water
Analyte.	Ca
Units	mg/L

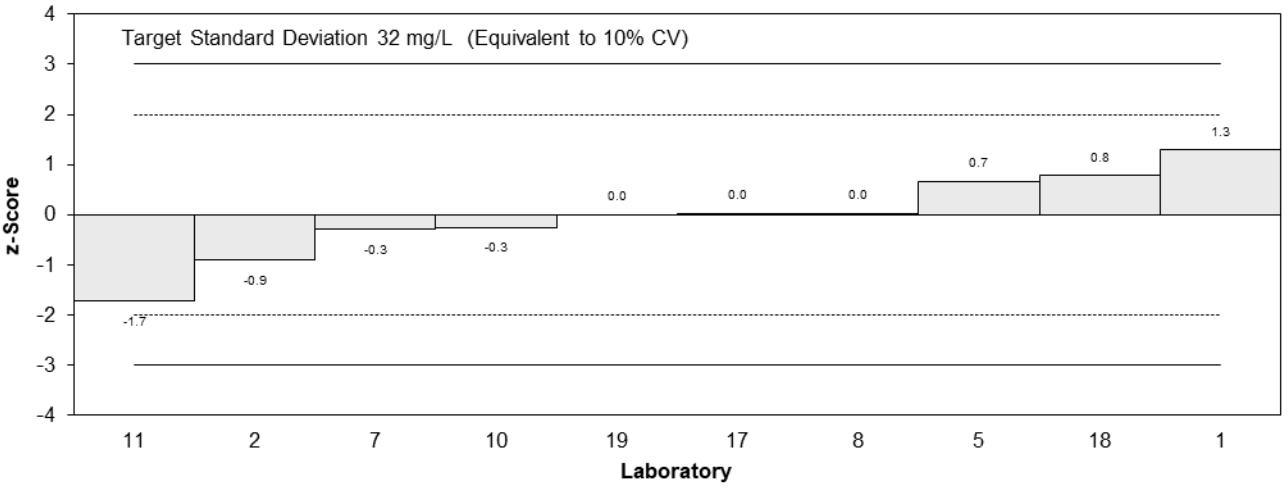
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	360	72	1.29	0.54
2	290	58	-0.91	-0.47
3	NT	NT		
4	NT	NT		
5	340	50	0.66	0.38
6	NT	NT		
7	310	20	-0.28	-0.30
8	320	NR	0.03	0.05
9	NT	NT		
10	311	13	-0.25	-0.31
11	264	26.4	-1.72	-1.60
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	320	35	0.03	0.02
18	343.7	39.5	0.77	0.55
19	319	64	0.00	0.00
20	NT	NT		

Statistics

Assigned Value	319	22
Spike	Not Spiked	
Homogeneity Value	345	52
Robust Average	319	22
Median	320	16
Mean	318	
N	10	
Max.	360	
Min.	264	
Robust SD	28	
Robust CV	8.8%	


Kernel Density
Density
Result
Results: S2 - Ca
Assigned Value = 319 ± 22 mg/L
Results (mg/L)
Laboratory
11 2 7 10 19 17 8 5 18 1 16 12 13 14 15 20 3 4 6 9 Md R.A. H.V.


z-Scores: S2 - Ca
Target Standard Deviation 32 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 2 7 10 19 17 8 5 18 1
-1.7 -0.9 -0.3 -0.3 0.0 0.0 0.0 0.7 0.8 1.3

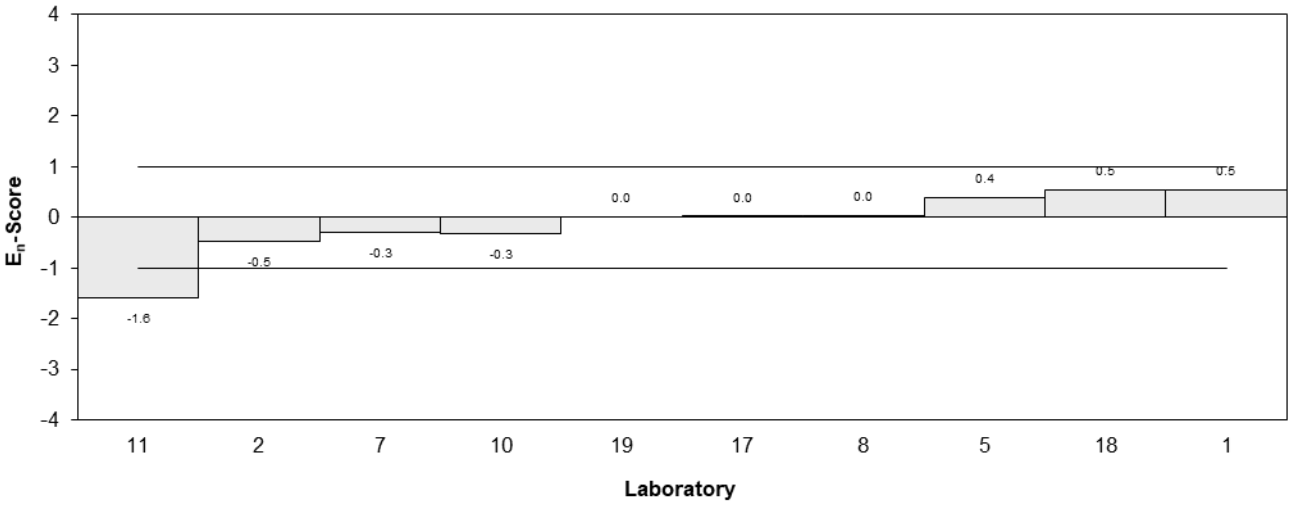

En-Scores: S2 - Ca
En-Score
Laboratory
11 2 7 10 19 17 8 5 18 1
-1.6 -0.5 -0.3 -0.3 0.0 0.0 0.0 0.4 0.5 0.5

Figure 13

Table 17

Sample Details

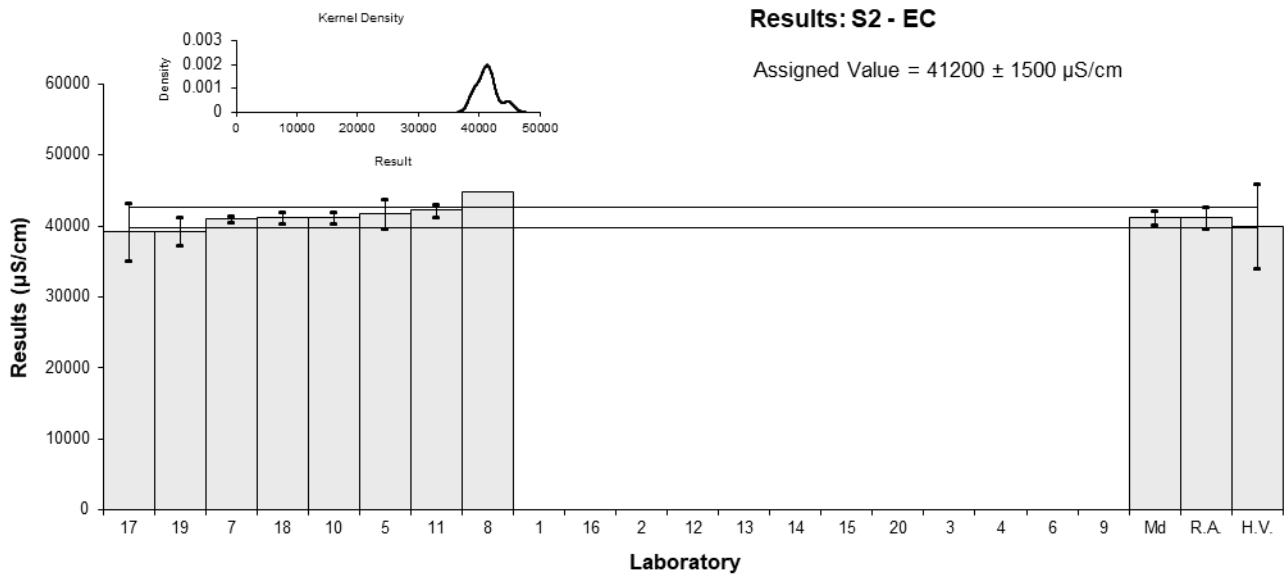
Sample No.	S2
Matrix.	Sea Water
Analyte.	EC
Units	µS/cm

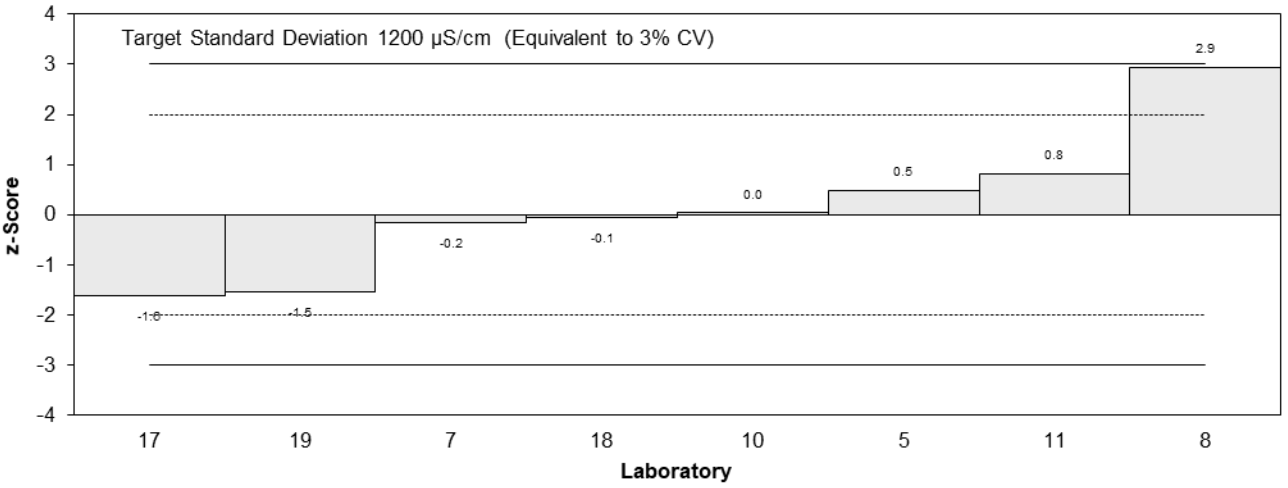
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NR	NR		
3	NT	NT		
4	NT	NT		
5	41800	2100	0.49	0.23
6	NT	NT		
7	41000	500	-0.16	-0.13
8	44824	NR	2.93	2.42
9	NT	NT		
10	41240	830	0.03	0.02
11	42200	840	0.81	0.58
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	39200	4000	-1.62	-0.47
18	41120	822	-0.06	-0.05
19	39300	1970	-1.54	-0.77
20	NT	NT		

Statistics

Assigned Value	41200	1500
Spike	Not Spiked	
Homogeneity Value	40000	6000
Robust Average	41200	1500
Median	41200	1000
Mean	41300	
N	8	
Max.	44824	
Min.	39200	
Robust SD	1700	
Robust CV	4.1%	


Kernel Density
Density
0.003
0.002
0.001
0
0
10000
20000
30000
40000
50000
Result
Results: S2 - EC
Assigned Value = 41200 ± 1500 µS/cm
Results (µS/cm)
60000
50000
40000
30000
20000
10000
0
17
19
7
18
10
5
11
8
1
16
2
12
13
14
15
20
3
4
6
9
Md
R.A.
H.V.
Laboratory


z-Scores: S2 - EC
Target Standard Deviation 1200 µS/cm (Equivalent to 3% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
2.9
0.8
0.5
0.0
-0.1
-0.2
-1.5
-1.6
17
19
7
18
10
5
11
8
Laboratory

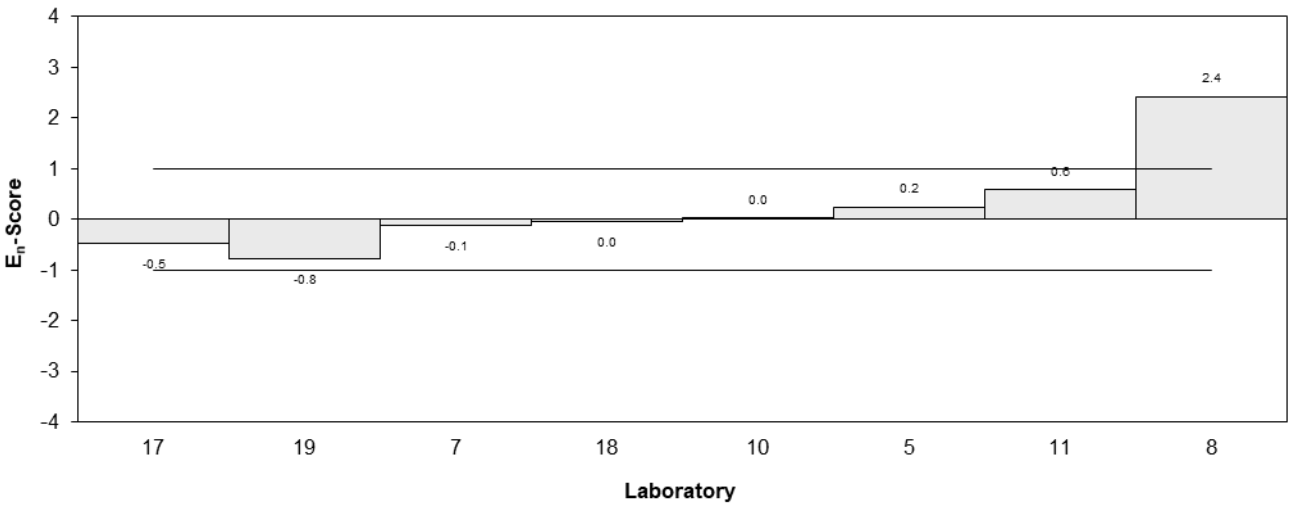

En-Scores: S2 - EC
En-Score
4
3
2
1
0
-1
-2
-3
-4
2.4
0.6
0.2
0.0
-0.1
0.0
-0.5
-0.8
17
19
7
18
10
5
11
8
Laboratory

Figure 14

Table 18

Sample Details

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

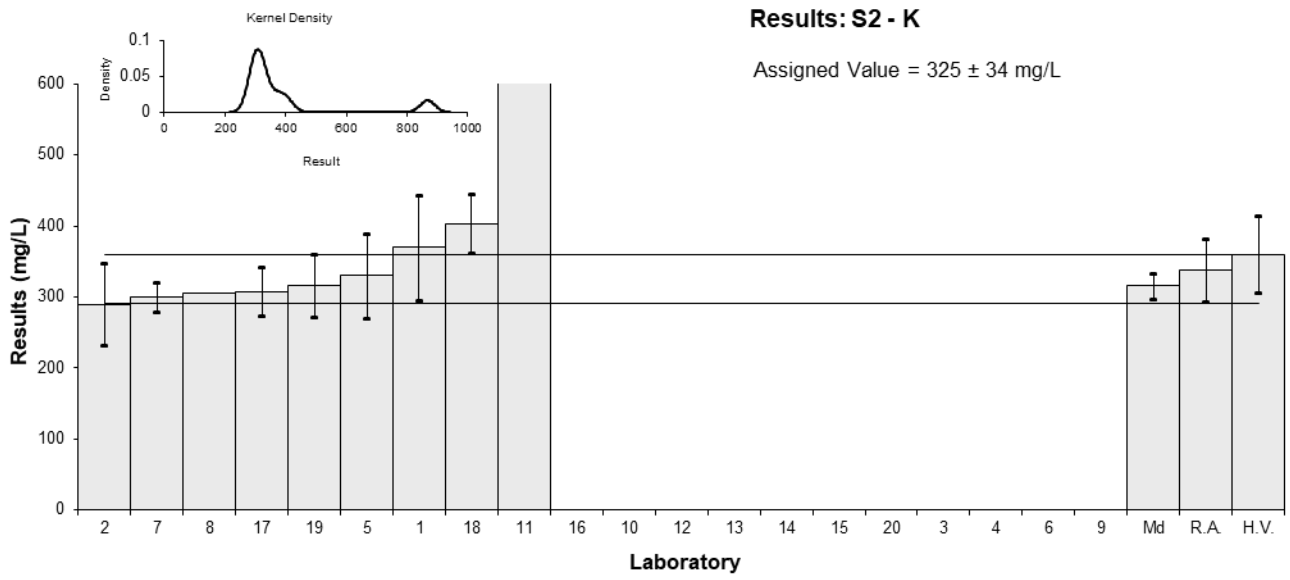
Participant Results

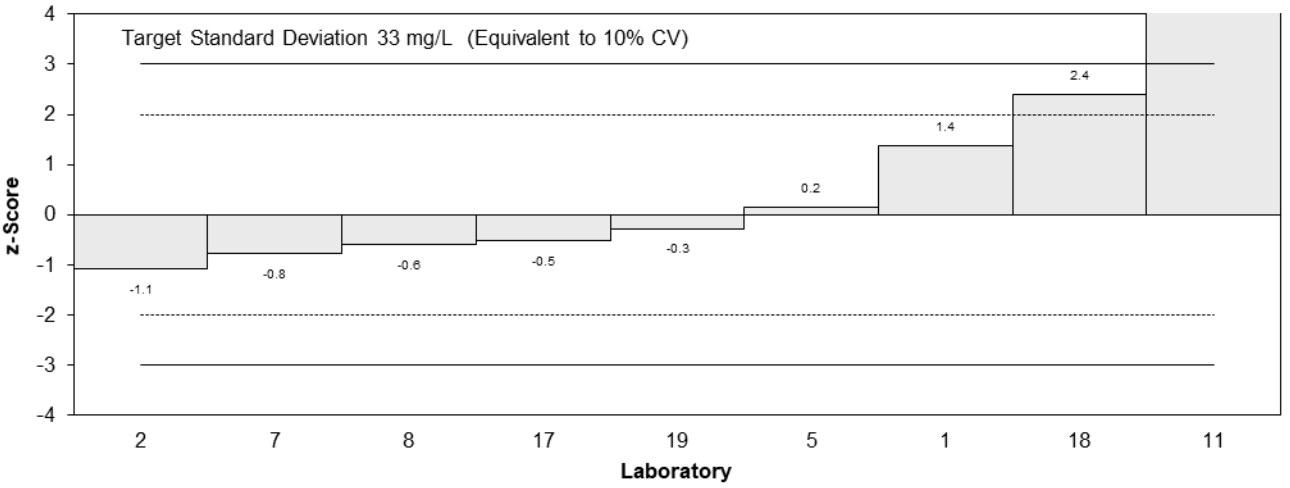
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	370	74	1.38	0.55
2	290	58	-1.08	-0.52
3	NT	NT		
4	NT	NT		
5	330	60	0.15	0.07
6	NT	NT		
7	300	20	-0.77	-0.63
8	306	NR	-0.58	-0.56
9	NT	NT		
10	NT	NT		
11	868	174	16.71	3.06
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	308	35	-0.52	-0.35
18	403	41.5	2.40	1.45
19	316	44	-0.28	-0.16
20	NT	NT		

Statistics

Assigned Value*	325	34
Spike	Not Spiked	
Homogeneity Value	360	54
Robust Average	338	45
Median	316	18
Mean	388	
N	9	
Max.	868	
Min.	290	
Robust SD	54	
Robust CV	16%	

*Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - K
Assigned Value = 325 ± 34 mg/L
Results (mg/L)
Laboratory
2 7 8 17 19 5 1 18 11 16 10 12 13 14 15 20 3 4 6 9 Md R.A. H.V.


z-Scores: S2 - K
Target Standard Deviation 33 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
2 7 8 17 19 5 1 18 11
-1.1 -0.8 -0.6 -0.5 -0.3 0.2 1.4 2.4

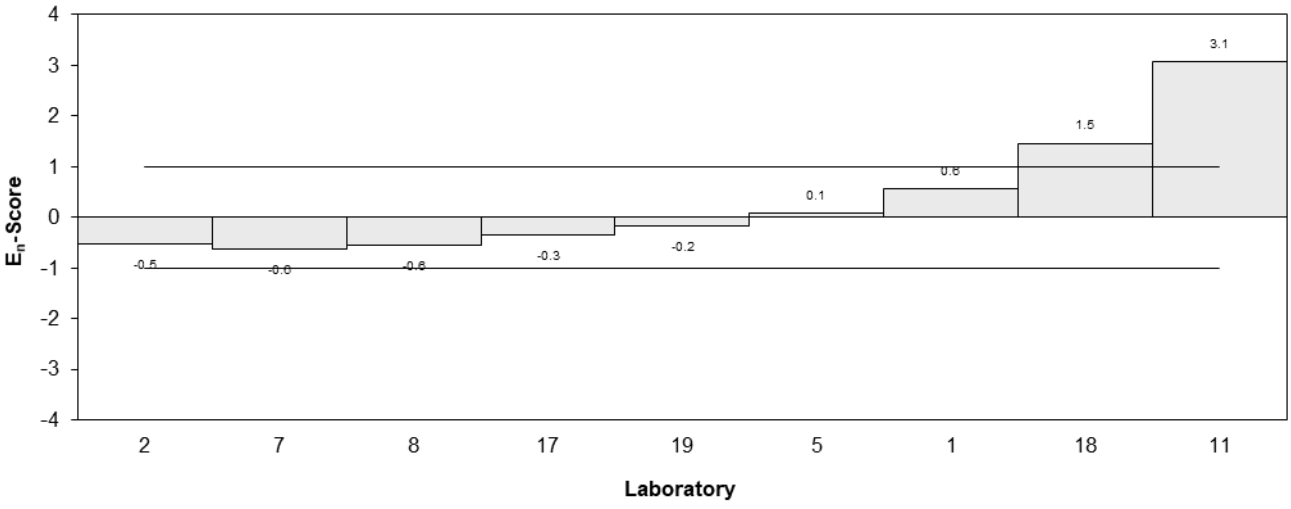

En-Scores: S2 - K
En-Score
Laboratory
2 7 8 17 19 5 1 18 11
-0.5 -0.6 -0.6 -0.3 -0.2 0.1 0.6 1.5 3.1

Figure 15

Table 19

Sample Details

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

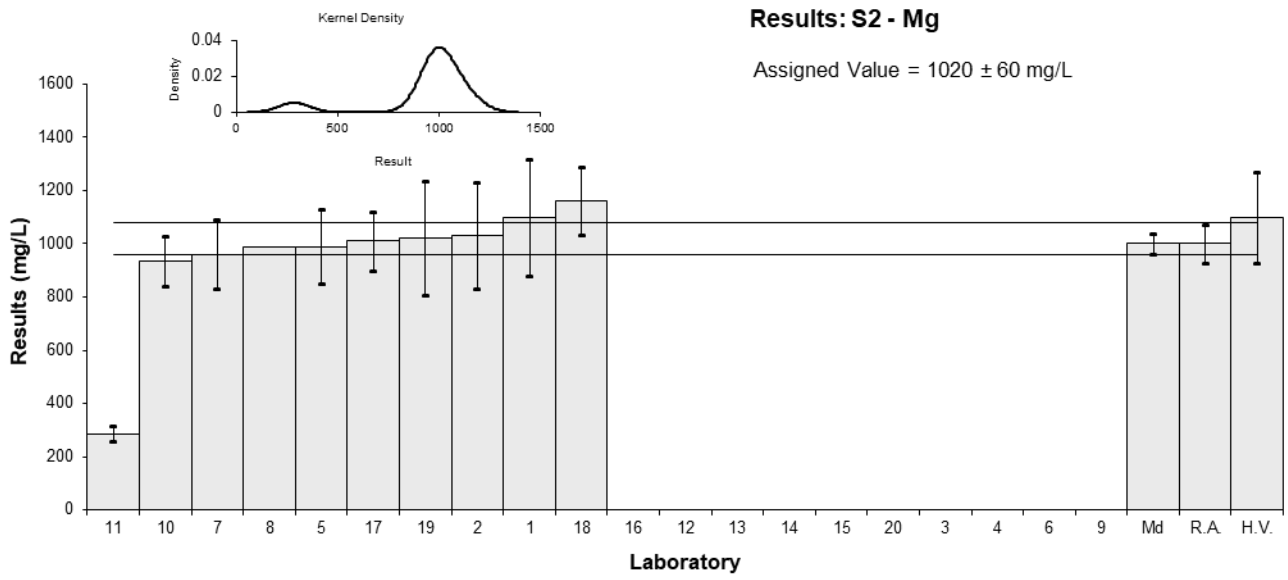
Participant Results

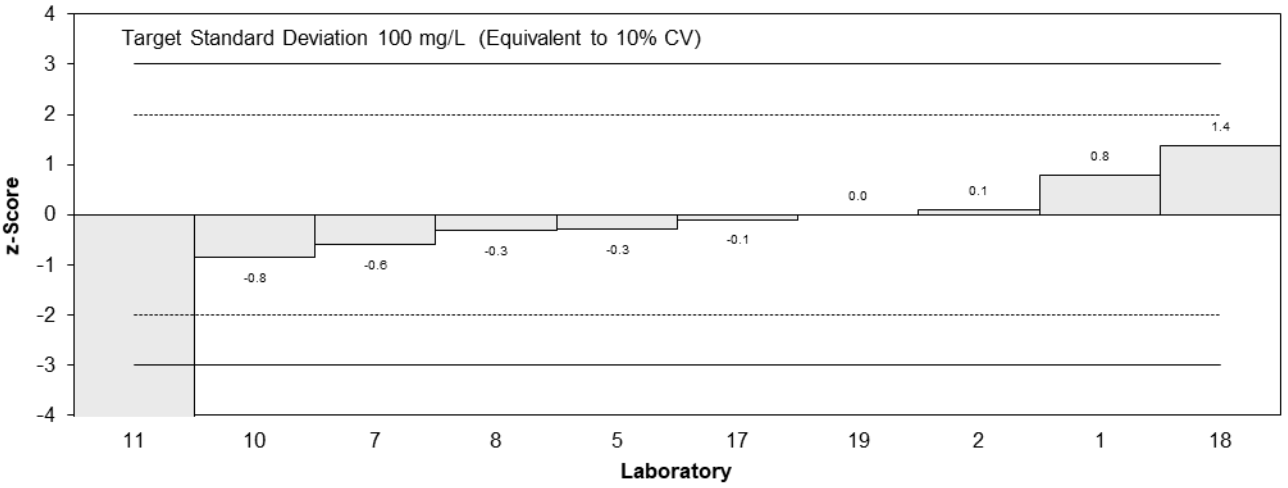
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1100	220	0.78	0.35
2	1030	200	0.10	0.05
3	NT	NT		
4	NT	NT		
5	990	140	-0.29	-0.20
6	NT	NT		
7	960	130	-0.59	-0.42
8	988	NR	-0.31	-0.53
9	NT	NT		
10	934	94	-0.84	-0.77
11	286	28.6	-7.20	-11.04
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	1010	110	-0.10	-0.08
18	1160	128	1.37	0.99
19	1020	214	0.00	0.00
20	NT	NT		

Statistics

Assigned Value*	1020	60
Spike	Not Spiked	
Homogeneity Value	1100	170
Robust Average	1000	70
Median	1000	37
Mean	948	
N	10	
Max.	1160	
Min.	286	
Robust SD	84	
Robust CV	8.4%	

*Robust Average excluding Laboratory 11.


Results: S2 - Mg
Assigned Value = 1020 ± 60 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
11 10 7 8 5 17 19 2 1 18 16 12 13 14 15 20 3 4 6 9 Md R.A. H.V.


z-Scores: S2 - Mg
Target Standard Deviation 100 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 10 7 8 5 17 19 2 1 18
-0.8 -0.6 -0.3 -0.3 -0.1 0.0 0.1 0.8 1.4

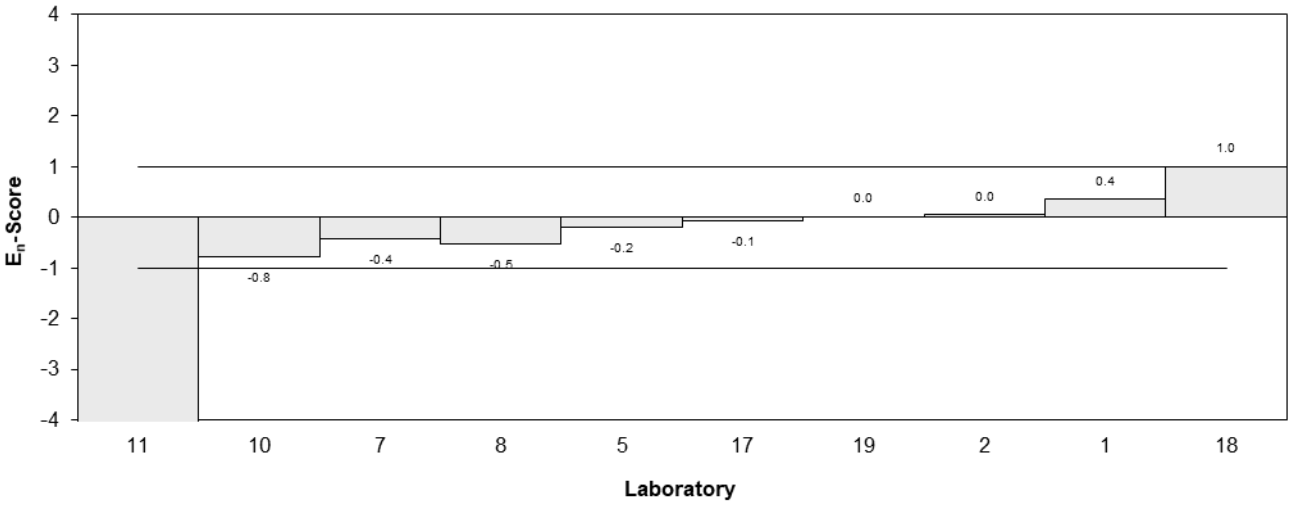

En-Scores: S2 - Mg
En-Score
Laboratory
11 10 7 8 5 17 19 2 1 18
-0.8 -0.4 -0.5 -0.2 -0.1 0.0 0.0 0.4 1.0

Figure 16

Table 20

Sample Details

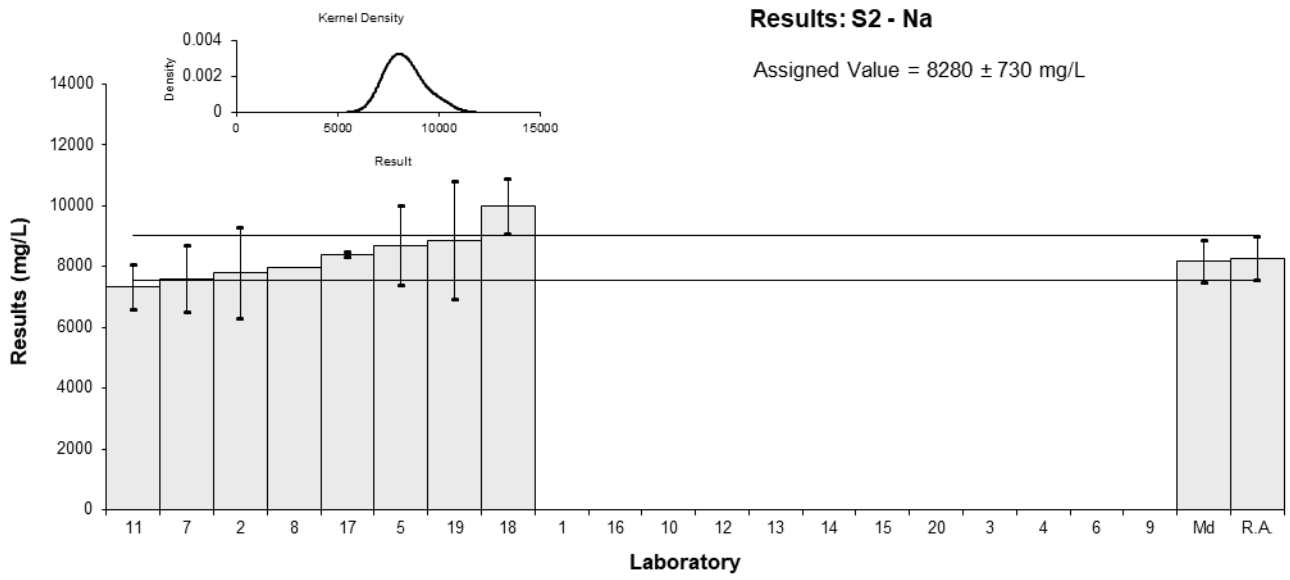
Sample No.	S2
Matrix.	Sea Water
Analyte.	Na
Units	mg/L

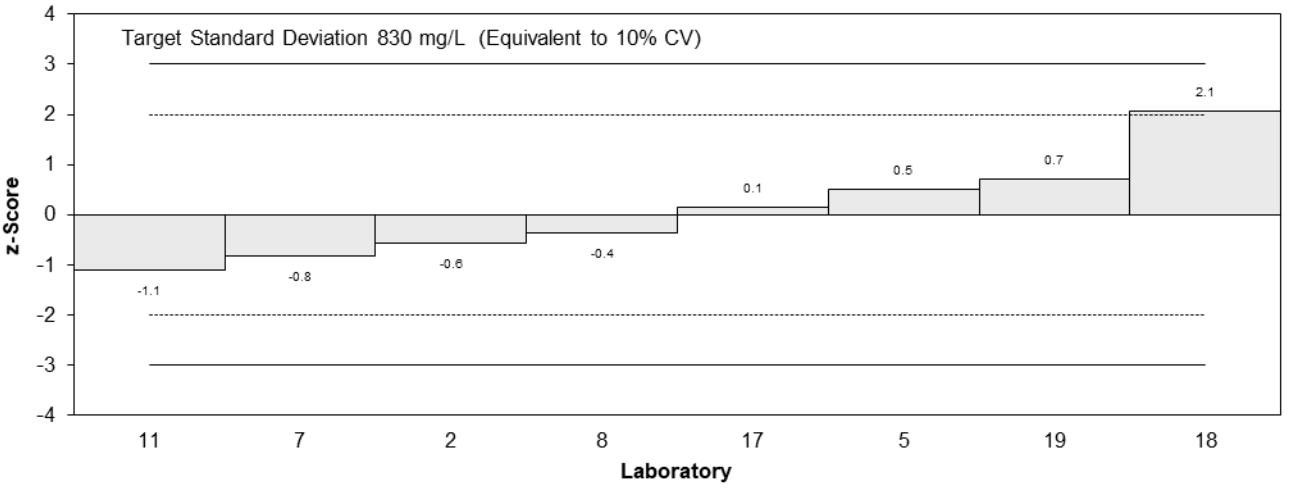
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	7800	1500	-0.58	-0.29
3	NT	NT		
4	NT	NT		
5	8700	1300	0.51	0.28
6	NT	NT		
7	7600	1100	-0.82	-0.52
8	7969	NR	-0.38	-0.43
9	NT	NT		
10	NT	NT		
11	7355	736	-1.12	-0.89
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	8400	90	0.14	0.16
18	9995	900	2.07	1.48
19	8870	1950	0.71	0.28
20	NT	NT		

Statistics

Assigned Value	8280	730
Spike	Not Spiked	
Robust Average	8280	730
Median	8180	680
Mean	8340	
N	8	
Max.	9995	
Min.	7355	
Robust SD	830	
Robust CV	10%	


Kernel Density
Density
0.004
0.002
0
0
5000
10000
15000
Result
Results: S2 - Na
Assigned Value = 8280 ± 730 mg/L
Results (mg/L)
14000
12000
10000
8000
6000
4000
2000
0
11
7
2
8
17
5
19
18
1
16
10
12
13
14
15
20
3
4
6
9
Md
R.A.
Laboratory


z-Scores: S2 - Na
Target Standard Deviation 830 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.1
-0.8
-0.6
-0.4
0.1
0.5
0.7
2.1
11
7
2
8
17
5
19
18
Laboratory

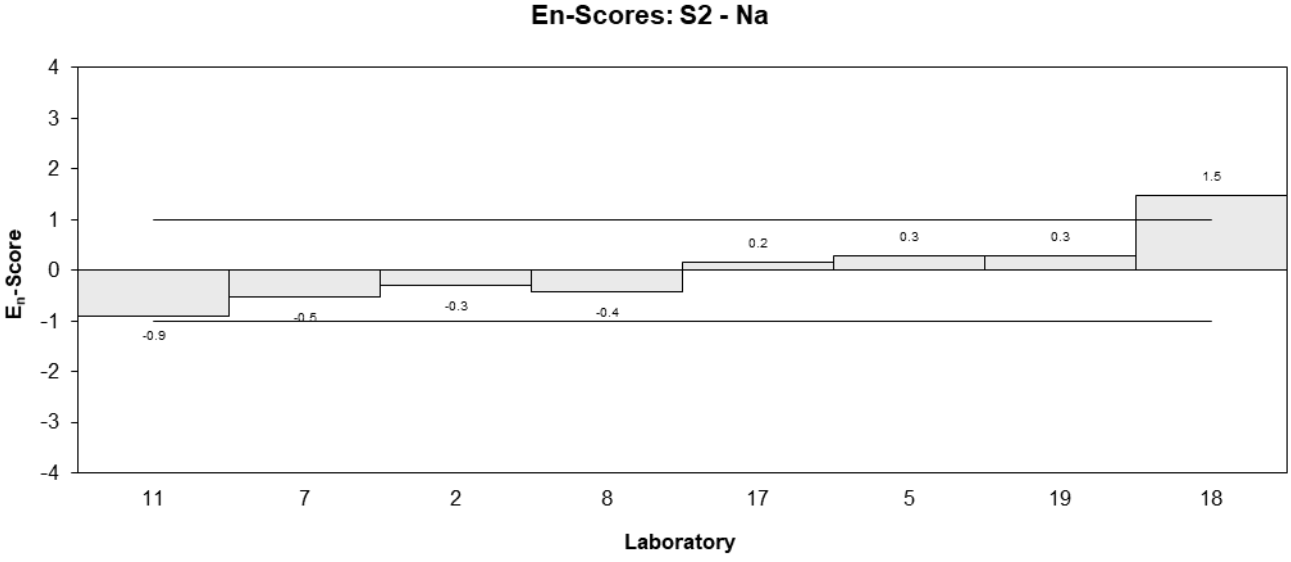

En-Scores: S2 - Na
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.5
-0.3
-0.4
0.2
0.3
0.3
1.5
11
7
2
8
17
5
19
18
Laboratory

Figure 17

Table 21

Sample Details

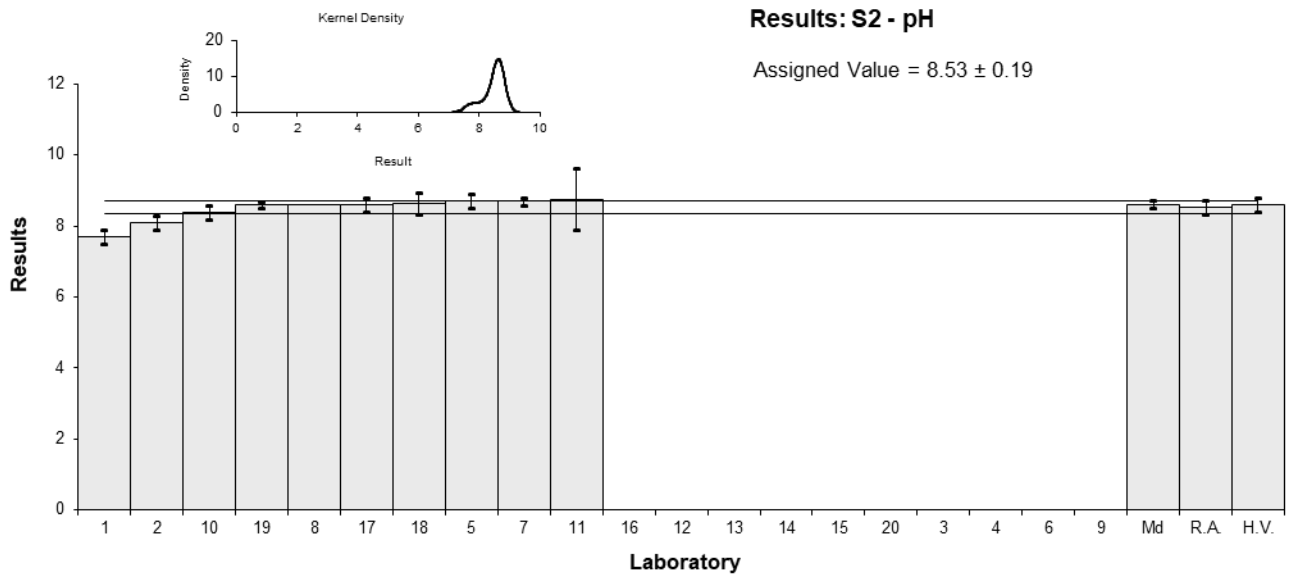
Sample No.	S2
Matrix.	Sea Water
Analyte.	pH

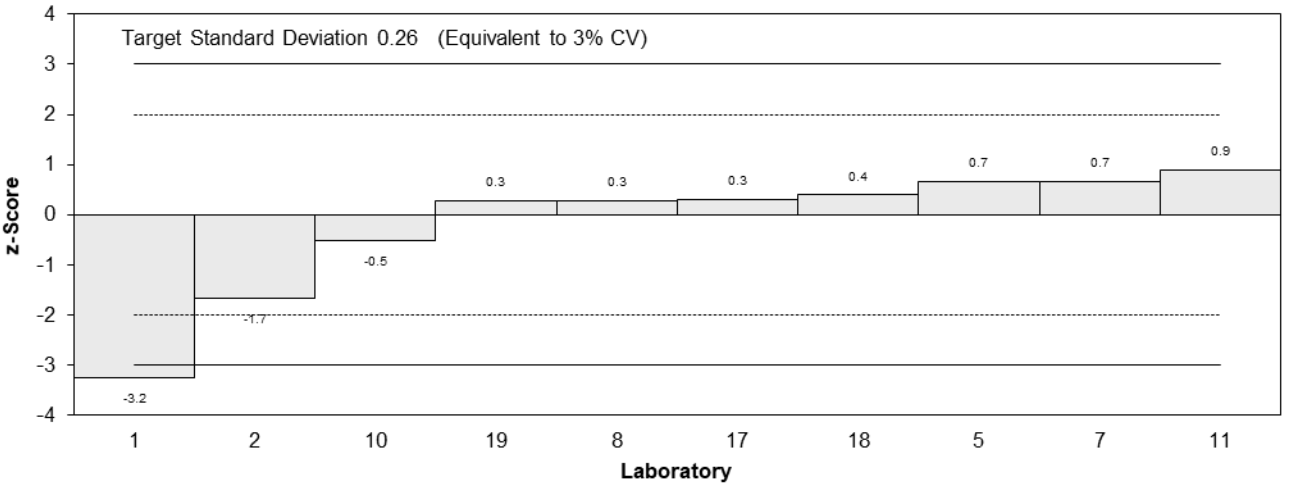
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.7	0.2	-3.24	-3.01
2	8.1	0.2	-1.68	-1.56
3	NT	NT		
4	NT	NT		
5	8.7	0.2	0.66	0.62
6	NT	NT		
7	8.7	0.1	0.66	0.79
8	8.6	NR	0.27	0.37
9	NT	NT		
10	8.4	0.2	-0.51	-0.47
11	8.76	0.88	0.90	0.26
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	8.61	0.2	0.31	0.29
18	8.63	0.3	0.39	0.28
19	8.6	0.1	0.27	0.33
20	NT	NT		

Statistics

Assigned Value	8.53	0.19
Spike	Not Spiked	
Homogeneity Value	8.60	0.20
Robust Average	8.53	0.19
Median	8.61	0.10
Mean	8.48	
N	10	
Max.	8.76	
Min.	7.7	
Robust SD	0.24	
Robust CV	2.8%	


Kernel Density
Density
Result
Results: S2 - pH
Assigned Value = 8.53 ± 0.19
Results
Laboratory
1 2 10 19 8 17 18 5 7 11 16 12 13 14 15 20 3 4 6 9 Md R.A. H.V.


z-Scores: S2 - pH
Target Standard Deviation 0.26 (Equivalent to 3% CV)
z-Score
Laboratory
1 2 10 19 8 17 18 5 7 11
-3.2
-1.7
-0.5
0.3
0.3
0.3
0.4
0.7
0.7
0.9

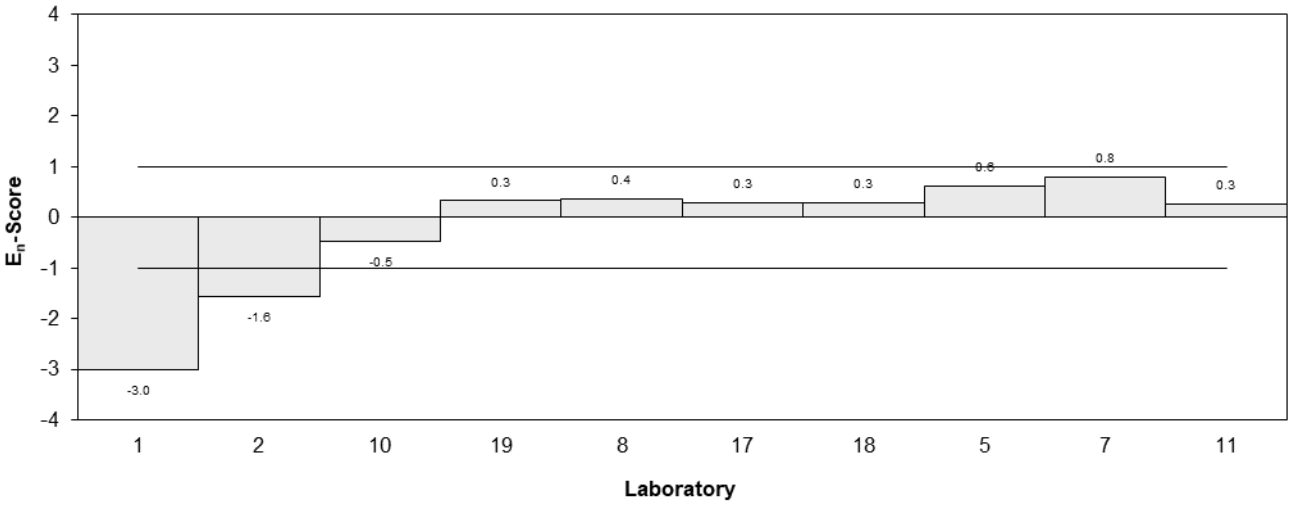

En-Scores: S2 - pH
En-Score
Laboratory
1 2 10 19 8 17 18 5 7 11
-3.0
-1.6
-0.5
0.3
0.4
0.3
0.3
0.6
0.8
0.3

Figure 18

Table 22

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	TKN
Units	mg/L

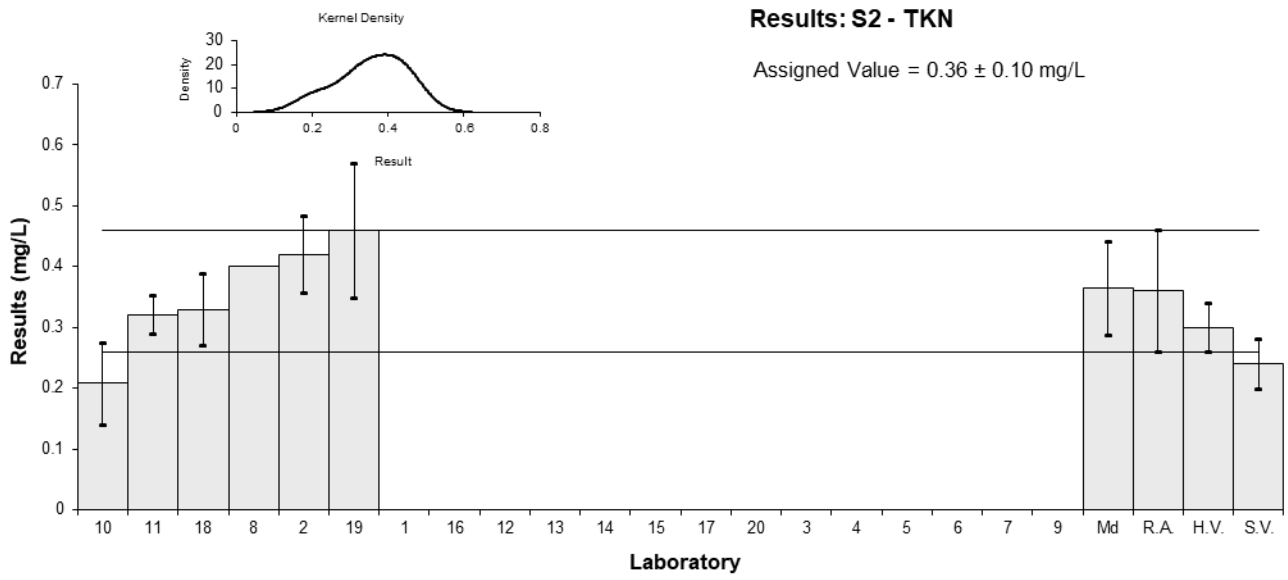
Participant Results

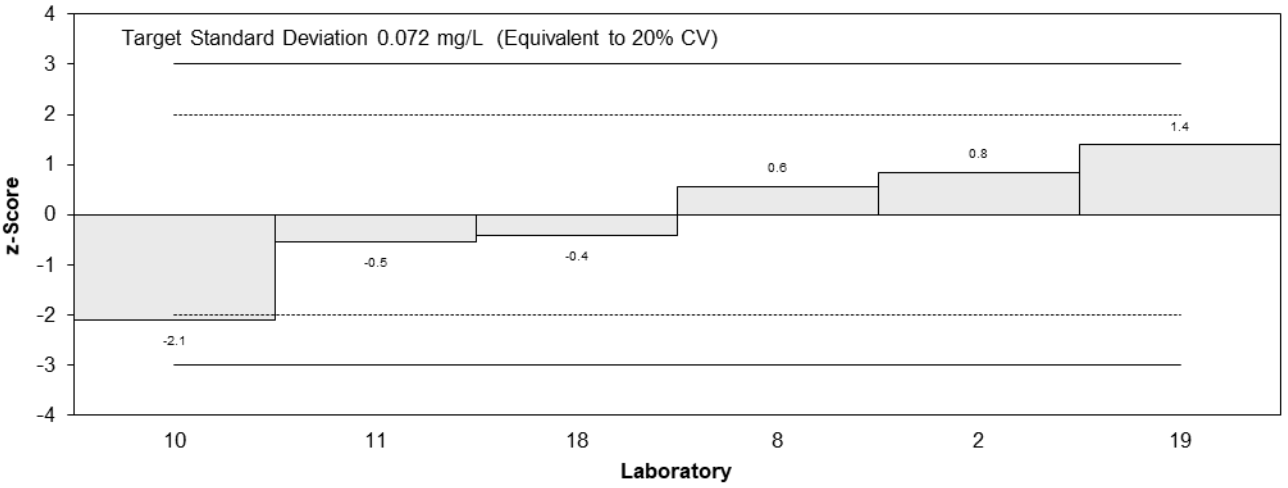
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	0.42	0.063	0.83	0.51
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	0.4	NR	0.56	0.40
9	NT	NT		
10	0.208	0.068	-2.11	-1.26
11	0.321	0.032	-0.54	-0.37
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	NT	NT		
18	0.33	0.06	-0.42	-0.26
19	0.46	0.11	1.39	0.67
20	NT	NT		

Statistics

Assigned Value	0.36	0.10
Spike*	0.24	0.04
Homogeneity Value	0.30	0.04
Robust Average	0.36	0.10
Median	0.365	0.077
Mean	0.36	
N	6	
Max.	0.46	
Min.	0.208	
Robust SD	0.10	
Robust CV	28%	

*Incurred Value not included


Kernel Density
Density
Result
Results: S2 - TKN
Assigned Value = 0.36 ± 0.10 mg/L
Results (mg/L)
Laboratory
10 11 18 8 2 19 1 16 12 13 14 15 17 20 3 4 5 6 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - TKN
Target Standard Deviation 0.072 mg/L (Equivalent to 20% CV)
z-Score
-2.1
-0.5
-0.4
0.6
0.8
1.4
Laboratory
10 11 18 8 2 19

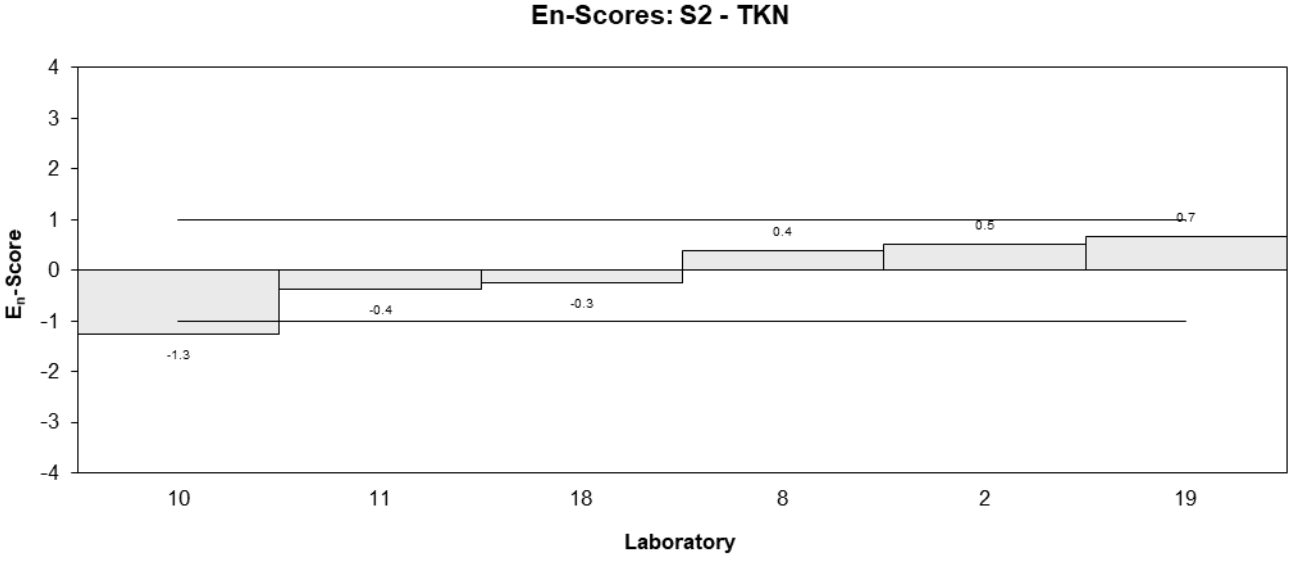

En-Scores: S2 - TKN
En-Score
-1.3
-0.4
-0.3
0.4
0.5
0.7
Laboratory
10 11 18 8 2 19

Figure 19

Table 23

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	TN
Units	mg/L

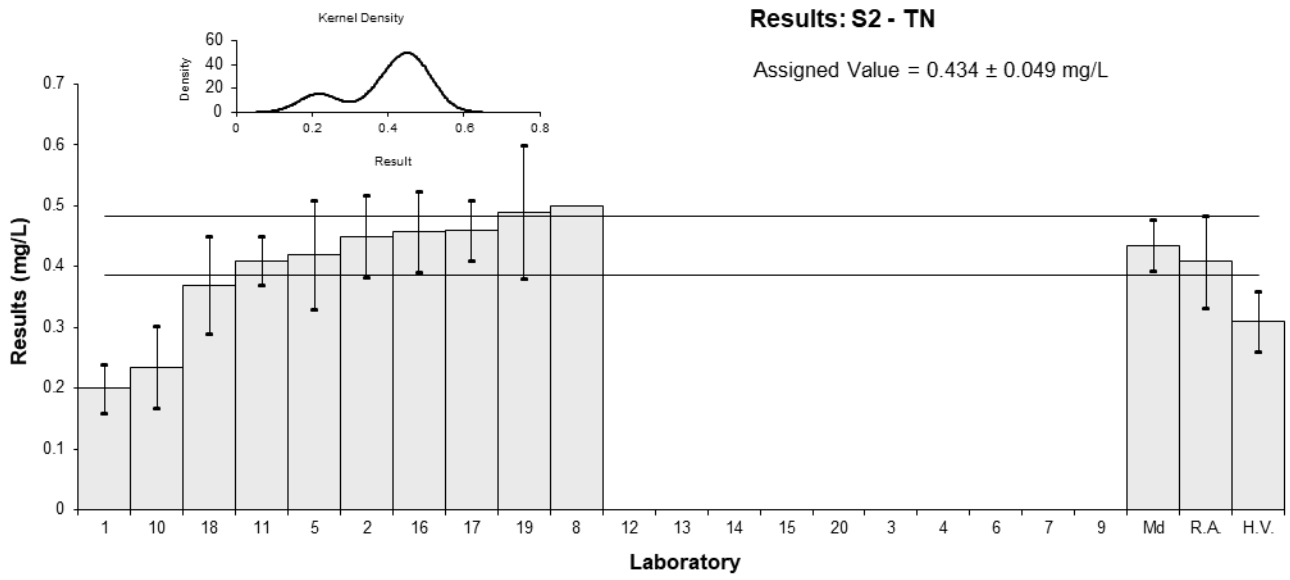
Participant Results

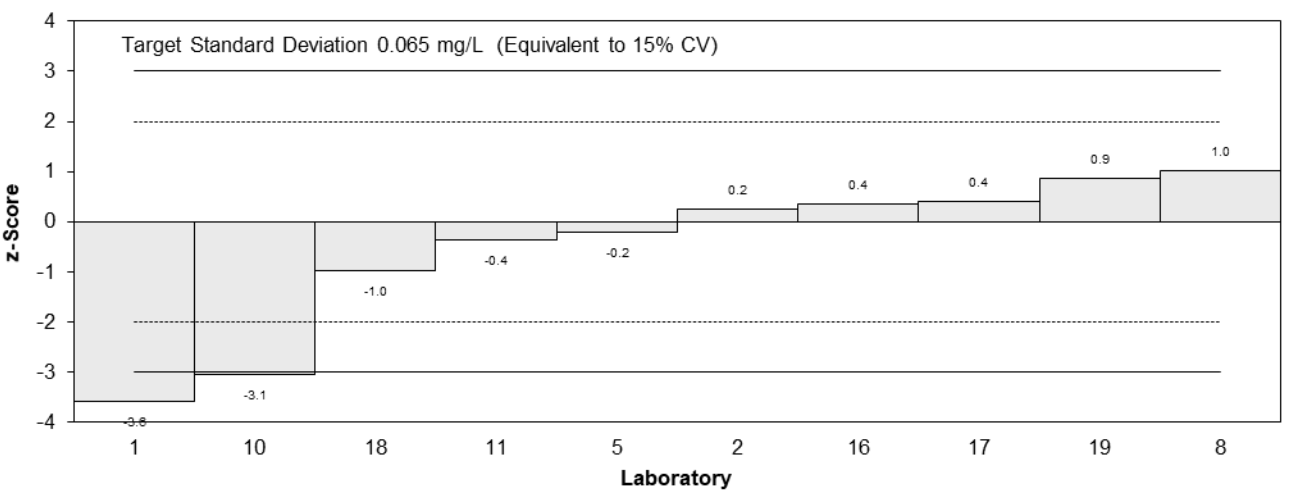
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.2	0.04	-3.59	-3.70
2	0.45	0.068	0.25	0.19
3	NT	NT		
4	NT	NT		
5	0.42	0.09	-0.22	-0.14
6	NT	NT		
7	NT	NT		
8	0.5	NR	1.01	1.35
9	NT	NT		
10	0.235	0.068	-3.06	-2.37
11	0.410	0.041	-0.37	-0.38
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	0.457	0.066	0.35	0.28
17	0.46	0.05	0.40	0.37
18	0.37	0.08	-0.98	-0.68
19	0.49	0.11	0.86	0.47
20	NT	NT		

Statistics

Assigned Value*	0.434	0.049
Spike	Not Spiked	
Homogeneity Value	0.310	0.062
Robust Average	0.408	0.076
Median	0.435	0.042
Mean	0.399	
N	10	
Max.	0.5	
Min.	0.2	
Robust SD	0.097	
Robust CV	24%	

*Robust Average excluding Laboratory 1.


Kernel Density
Density
Result
Results: S2 - TN
Assigned Value = 0.434 ± 0.049 mg/L
Results (mg/L)
Laboratory
1 10 18 11 5 2 16 17 19 8 12 13 14 15 20 3 4 6 7 9 Md R.A. H.V.


z-Scores: S2 - TN
Target Standard Deviation 0.065 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
1 10 18 11 5 2 16 17 19 8
-3.6 -3.1 -1.0 -0.4 -0.2 0.2 0.4 0.4 0.9 1.0

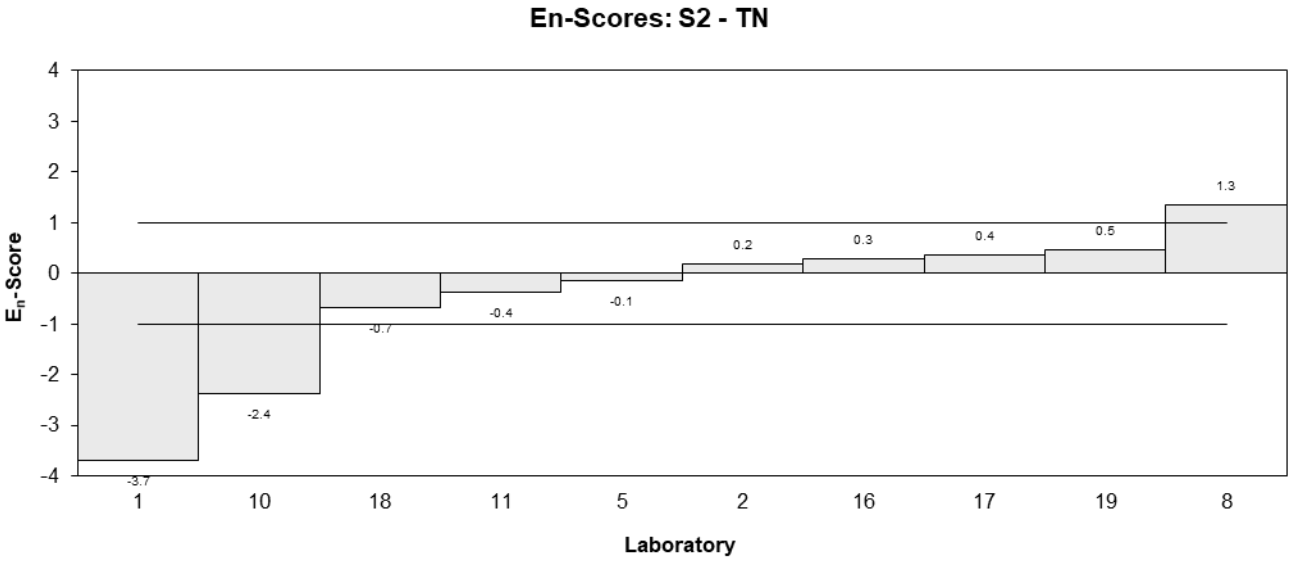

En-Scores: S2 - TN
En-Score
Laboratory
1 10 18 11 5 2 16 17 19 8
-3.7 -2.4 -0.7 -0.4 -0.1 0.2 0.3 0.4 0.5 1.3

Figure 20

Table 24

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	TOC
Units	mg/L

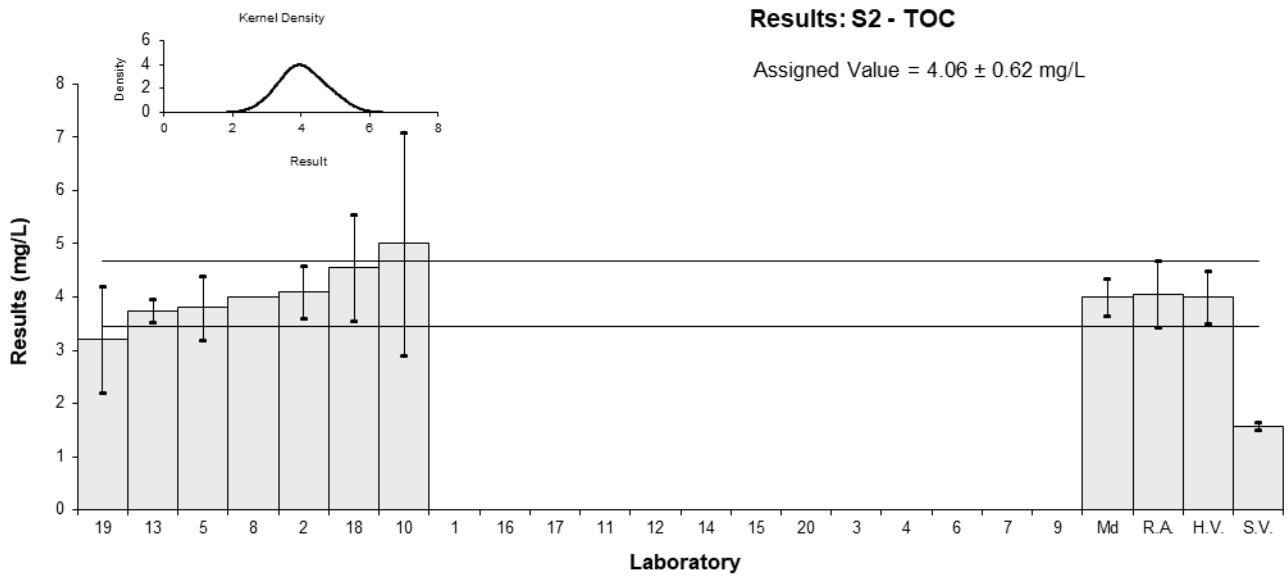
Participant Results

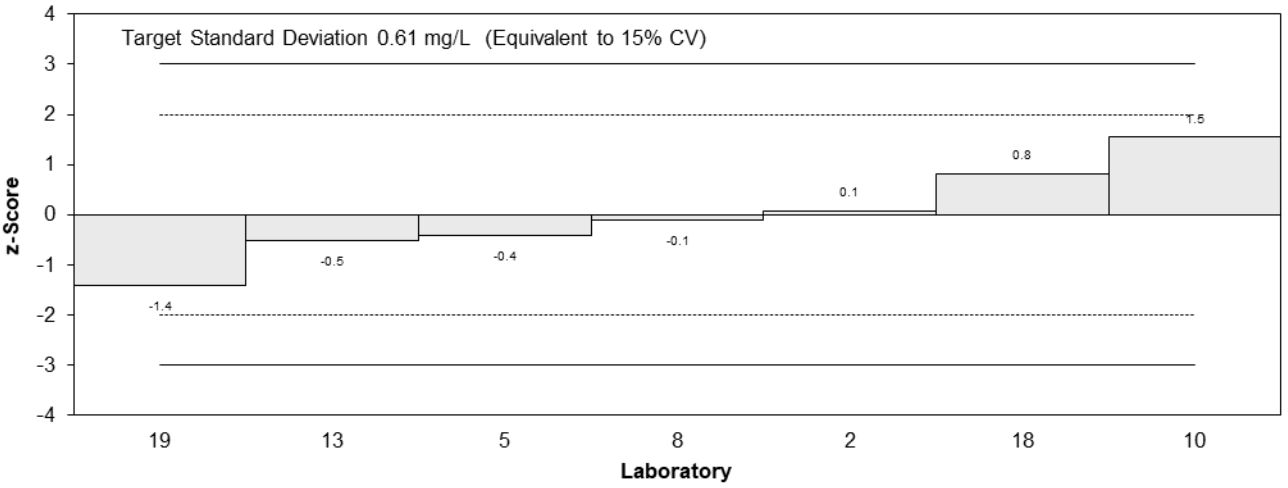
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	4.1	0.49	0.07	0.05
3	NT	NT		
4	NT	NT		
5	3.8	0.6	-0.43	-0.30
6	NT	NT		
7	NT	NT		
8	4	NR	-0.10	-0.10
9	NT	NT		
10	5.0	2.1	1.54	0.43
11	NT	NT		
12	NT	NT		
13	3.74	0.22	-0.53	-0.49
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	NR	1		
18	4.55	1	0.80	0.42
19	3.2	1	-1.41	-0.73
20	NT	NT		

Statistics

Assigned Value	4.06	0.62
Spike*	1.58	0.07
Homogeneity Value	4.00	0.50
Robust Average	4.06	0.62
Median	4.00	0.36
Mean	4.06	
N	7	
Max.	5	
Min.	3.2	
Robust SD	0.66	
Robust CV	16%	

*Incurred value not included.


Kernel Density
Density
Result
Results: S2 - TOC
Assigned Value = 4.06 ± 0.62 mg/L
Results (mg/L)
19 13 5 8 2 18 10 1 16 17 11 12 14 15 20 3 4 6 7 9 Md R.A. H.V. S.V.
Laboratory


z-Scores: S2 - TOC
Target Standard Deviation 0.61 mg/L (Equivalent to 15% CV)
z-Score
-1.4
-0.5
-0.4
-0.1
0.1
0.8
T.5
19 13 5 8 2 18 10
Laboratory

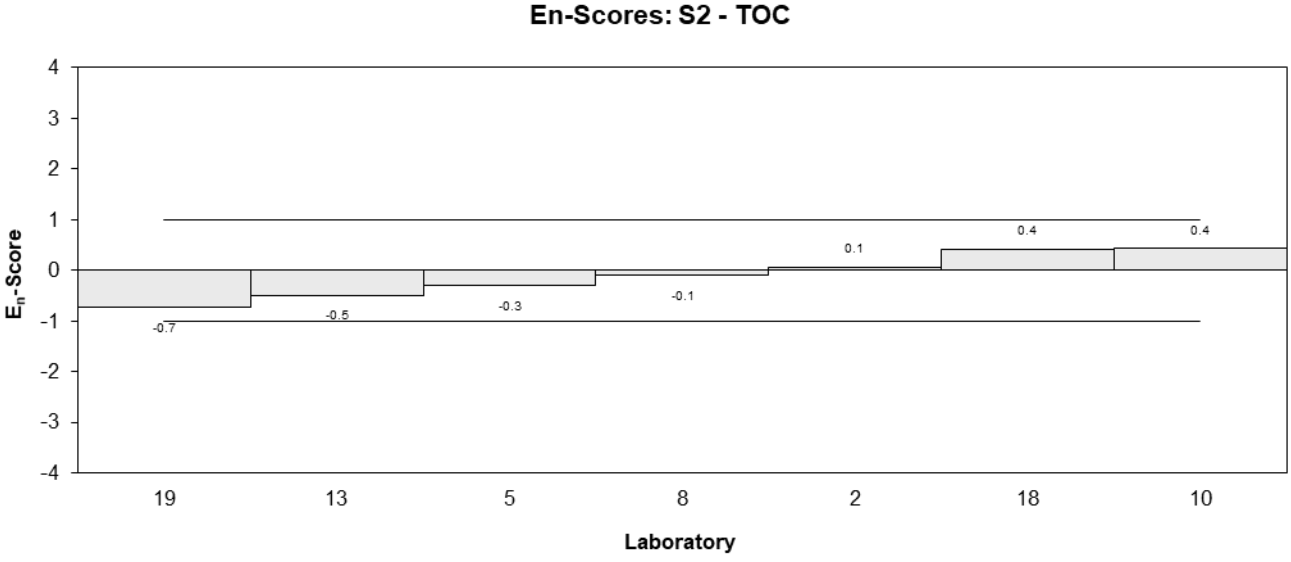

En-Scores: S2 - TOC
En-Score
-0.7
-0.5
-0.3
-0.1
0.1
0.4
0.4
19 13 5 8 2 18 10
Laboratory

Figure 21

Table 25

Sample Details

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

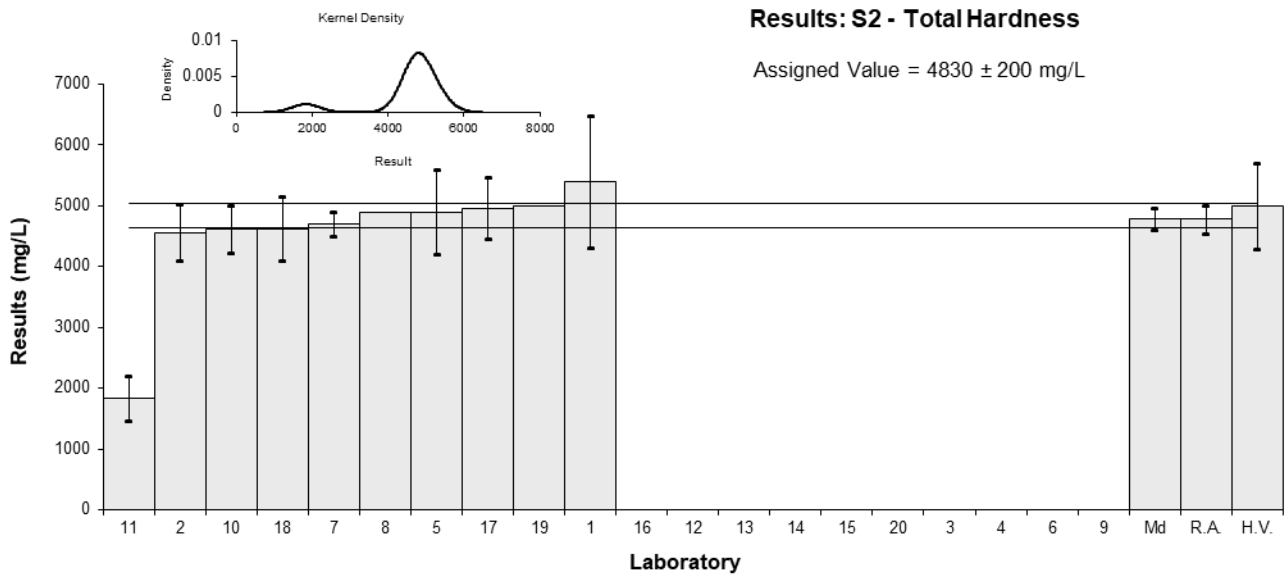
Participant Results

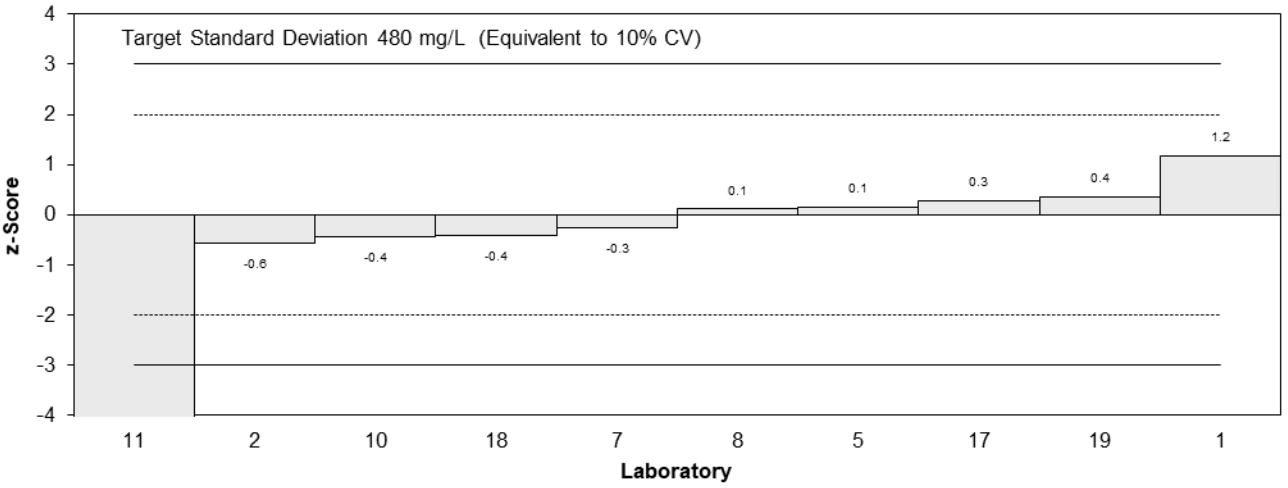
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5400	1080	1.18	0.52
2	4560	460	-0.56	-0.54
3	NT	NT		
4	NT	NT		
5	4900	700	0.14	0.10
6	NT	NT		
7	4700	200	-0.27	-0.46
8	4884	NR	0.11	0.27
9	NT	NT		
10	4620	390	-0.43	-0.48
11	1840	370	-6.19	-7.11
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NR	NR		
17	4960	500	0.27	0.24
18	4627	532	-0.42	-0.36
19	5000	NR	0.35	0.85
20	NT	NT		

Statistics

Assigned Value*	4830	200
Spike	Not Spiked	
Homogeneity Value	5000	700
Robust Average	4780	230
Median	4790	180
Mean	4550	
N	10	
Max.	5400	
Min.	1840	
Robust SD	290	
Robust CV	6.1%	

*Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Total Hardness
Assigned Value = 4830 ± 200 mg/L
Results (mg/L)
Laboratory
11 2 10 18 7 8 5 17 19 1 16 12 13 14 15 20 3 4 6 9 Md R.A. H.V.


z-Scores: S2 - Total Hardness
Target Standard Deviation 480 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 2 10 18 7 8 5 17 19 1
-0.6 -0.4 -0.4 -0.3 0.1 0.1 0.3 0.4 1.2

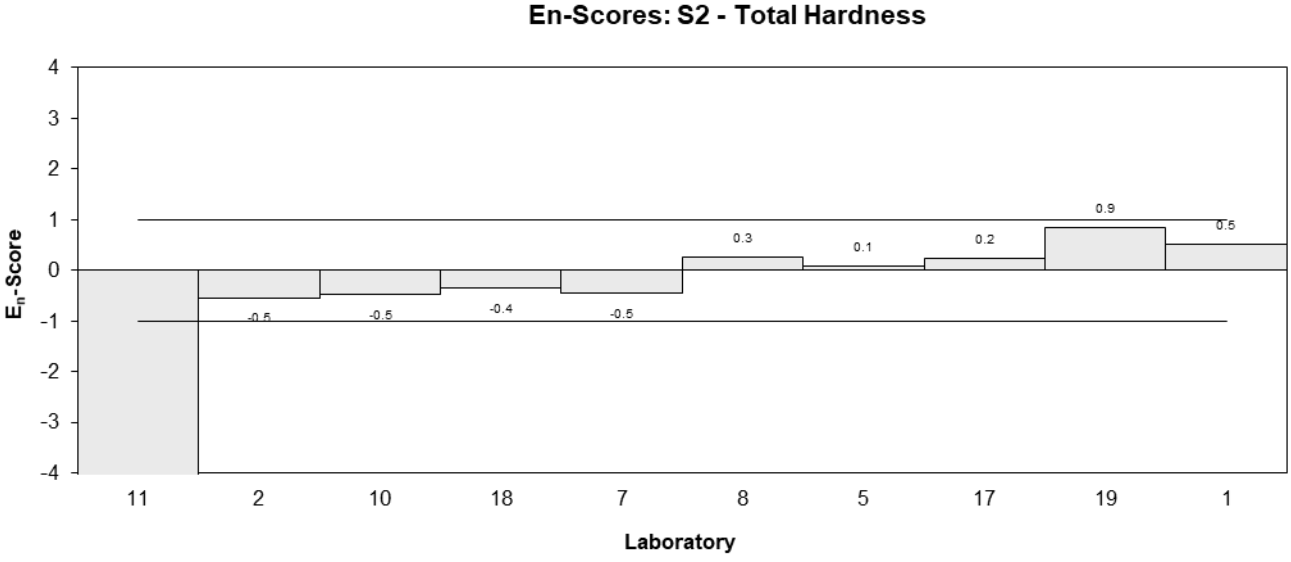

En-Scores: S2 - Total Hardness
En-Score
Laboratory
11 2 10 18 7 8 5 17 19 1
-0.5 -0.5 -0.4 -0.5 0.3 0.1 0.2 0.9 0.5

Figure 22

Table 26

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	NR	NR
2	0.010	0.001
3	NT	NT
4	NT	NT
5	0.012	0.003
6	NT	NT
7	NT	NT
8	NR	NR
9	NT	NT
10	NT	NT
11	0.012	0.002
12	NT	NT
13	NT	NT
14	NT	NT
15	NT	NT
16	0.007	0.005
17	NT	NT
18	<0.1	NR
19	<1	NR
20	NT	NT

Statistics*

Assigned Value	Not Set	
Spike	Not Spiked	
Median	0.0110	0.0024
Mean	0.0103	
N	4	
Max.	0.012	
Min.	0.007	
Robust SD	0.0015	
Robust CV	13%	

*Insufficient data to calculate statistics.

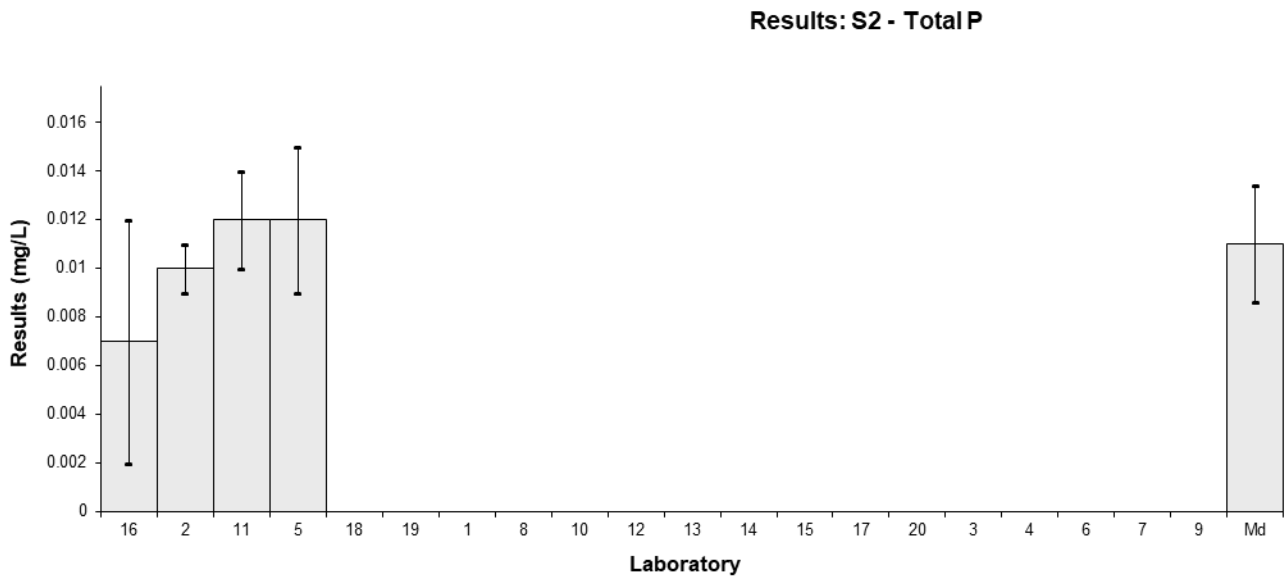

Results: S2 - Total P
Results (mg/L)
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
16
2
11
5
18
19
1
8
10
12
13
14
15
17
20
3
4
6
7
9
Md
Laboratory

Figure 23

Table 27

Sample Details

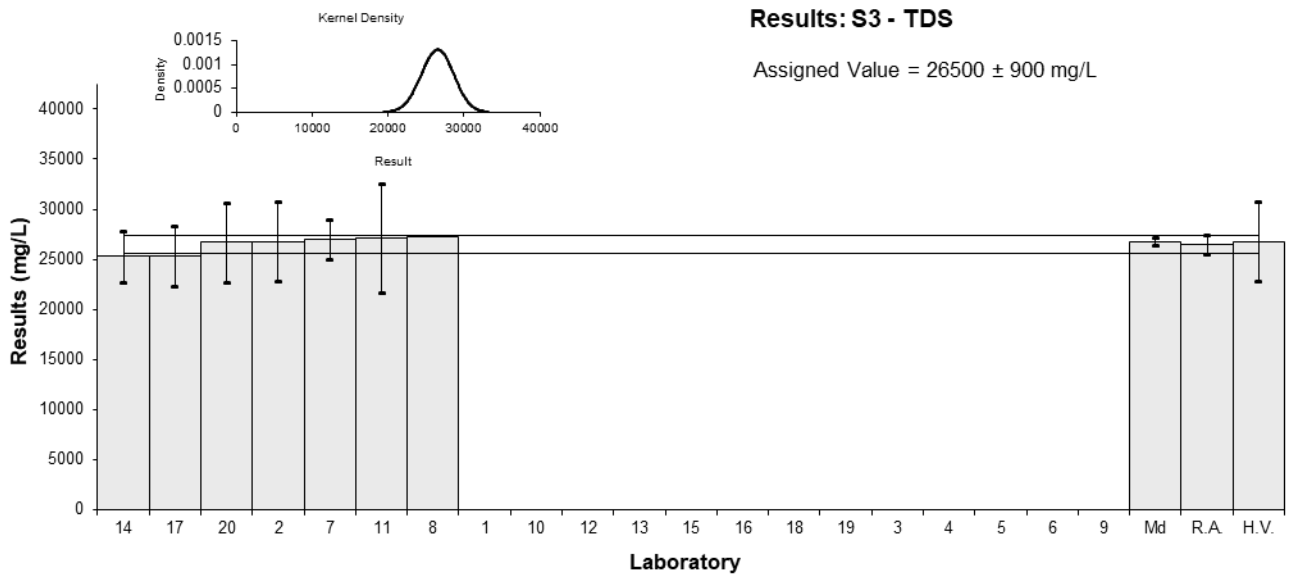
Sample No.	S3
Matrix.	Sea Water
Analyte.	TDS
Units	mg/L

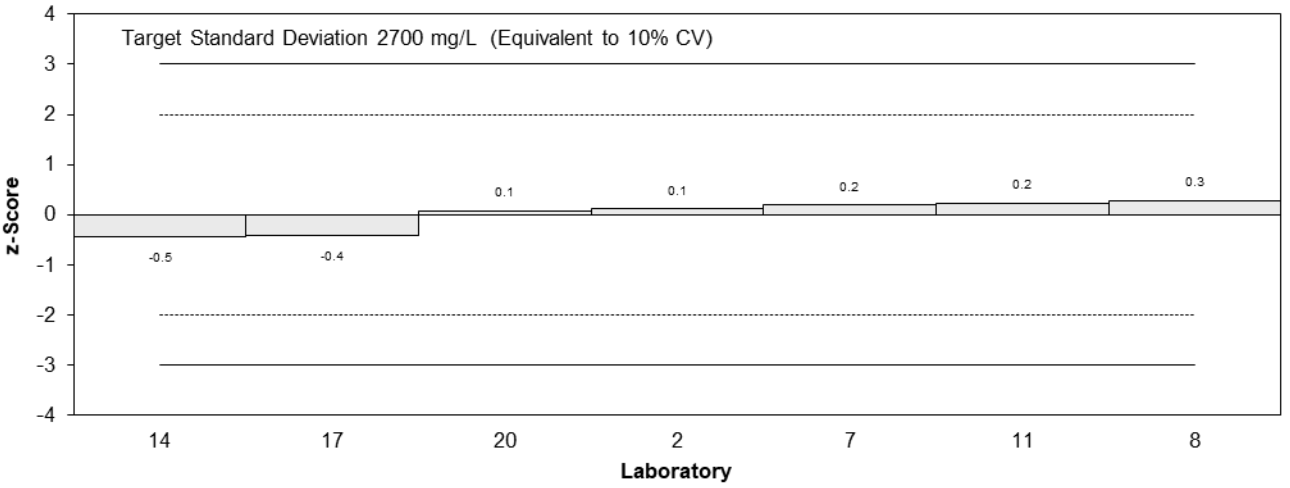
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	26800	4000	0.11	0.07
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	27000	2000	0.19	0.23
8	27215	NR	0.27	0.79
9	NT	NT		
10	NT	NT		
11	27120	5420	0.23	0.11
12	NT	NT		
13	NT	NT		
14	25300	2530	-0.45	-0.45
15	NT	NT		
16	NT	NT		
17	25400	3000	-0.42	-0.35
18	NT	NT		
19	NT	NT		
20	26700	4000	0.08	0.05

Statistics

Assigned Value	26500	900
Spike	Not Spiked	
Homogeneity Value	26800	4000
Robust Average	26500	900
Median	26800	400
Mean	26500	
N	7	
Max.	27215	
Min.	25300	
Robust SD	920	
Robust CV	3.5%	


Kernel Density
Density
0.0015
0.001
0.0005
0
0
10000
20000
30000
40000
Result
Results: S3 - TDS
Assigned Value = 26500 ± 900 mg/L
Results (mg/L)
40000
35000
30000
25000
20000
15000
10000
5000
0
14 17 20 2 7 11 8 1 10 12 13 15 16 18 19 3 4 5 6 9 Md R.A. H.V.
Laboratory


z-Scores: S3 - TDS
Target Standard Deviation 2700 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.4
0.1
0.1
0.2
0.2
0.3
14 17 20 2 7 11 8
Laboratory

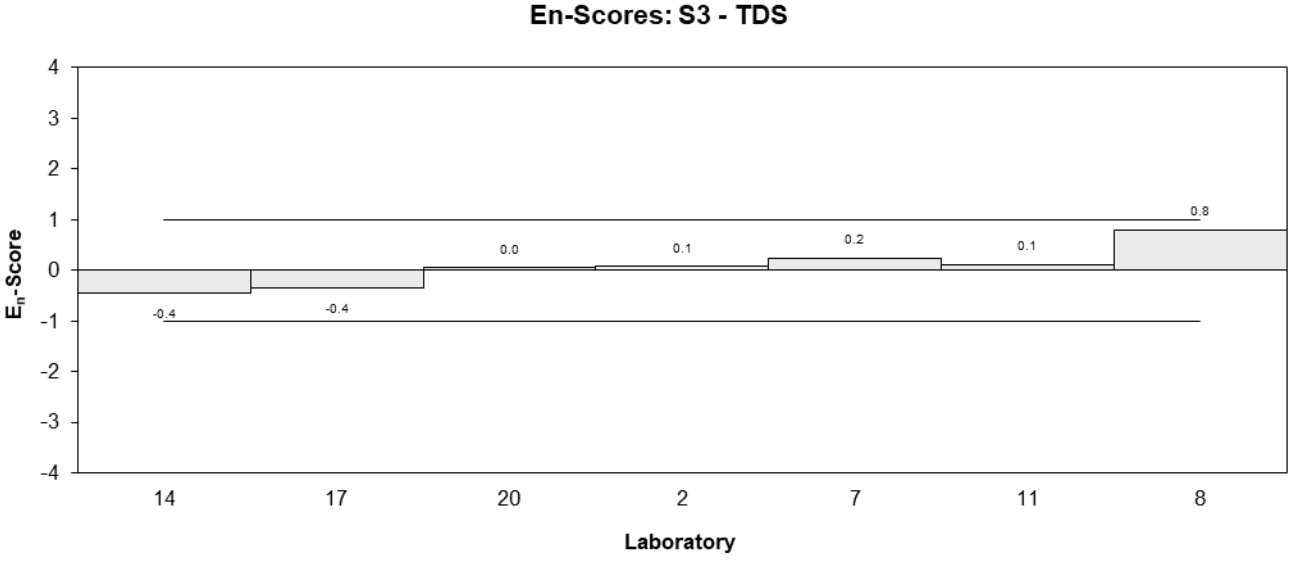

En-Scores: S3 - TDS
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.4
-0.4
0.0
0.1
0.2
0.1
0.8
14 17 20 2 7 11 8
Laboratory

Figure 24

Table 28

Sample Details

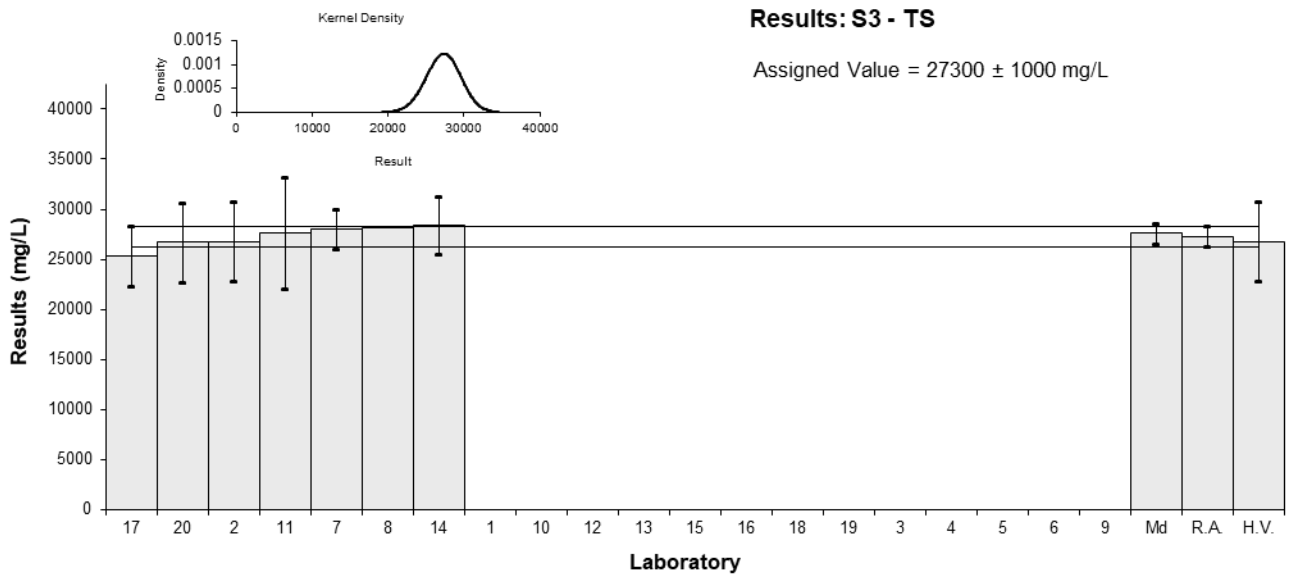
Sample No.	S3
Matrix.	Sea Water
Analyte.	TS
Units	mg/L

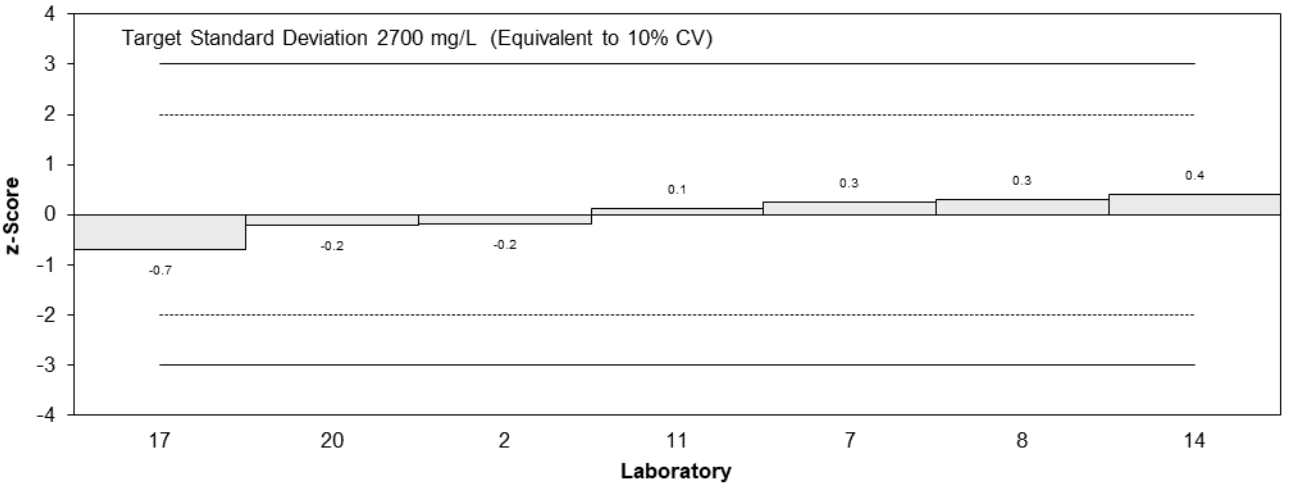
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	26800	4000	-0.18	-0.12
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	28000	2000	0.26	0.31
8	28108	NR	0.30	0.81
9	NT	NT		
10	NT	NT		
11	27640	5530	0.12	0.06
12	NT	NT		
13	NT	NT		
14	28400	2840	0.40	0.37
15	NT	NT		
16	NT	NT		
17	25400	3000	-0.70	-0.60
18	NT	NT		
19	NT	NT		
20	26700	4000	-0.22	-0.15

Statistics

Assigned Value	27300	1000
Spike	Not Spiked	
Homogeneity Value	26800	4000
Robust Average	27300	1000
Median	27600	1000
Mean	27300	
N	7	
Max.	28400	
Min.	25400	
Robust SD	1100	
Robust CV	4%	


Kernel Density
Density
Result
Results: S3 - TS
Assigned Value = 27300 ± 1000 mg/L
Results (mg/L)
Laboratory
17 20 2 11 7 8 14 1 10 12 13 15 16 18 19 3 4 5 6 9 Md R.A. H.V.


z-Scores: S3 - TS
Target Standard Deviation 2700 mg/L (Equivalent to 10% CV)
z-Score
-0.7
-0.2
-0.2
0.1
0.3
0.3
0.4
Laboratory
17 20 2 11 7 8 14

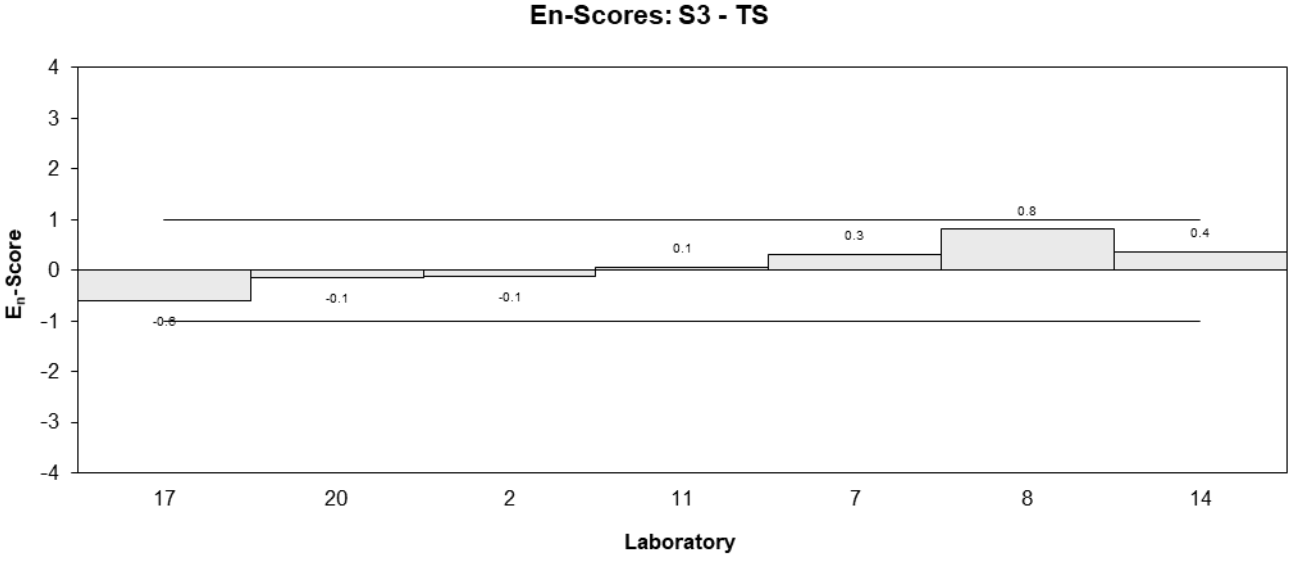

En-Scores: S3 - TS
En-Score
-0.6
-0.1
-0.1
0.1
0.3
0.8
0.4
Laboratory
17 20 2 11 7 8 14

Figure 25

Table 29

Sample Details

Sample No.	S3
Matrix.	Sea Water
Analyte.	TSS
Units	mg/L

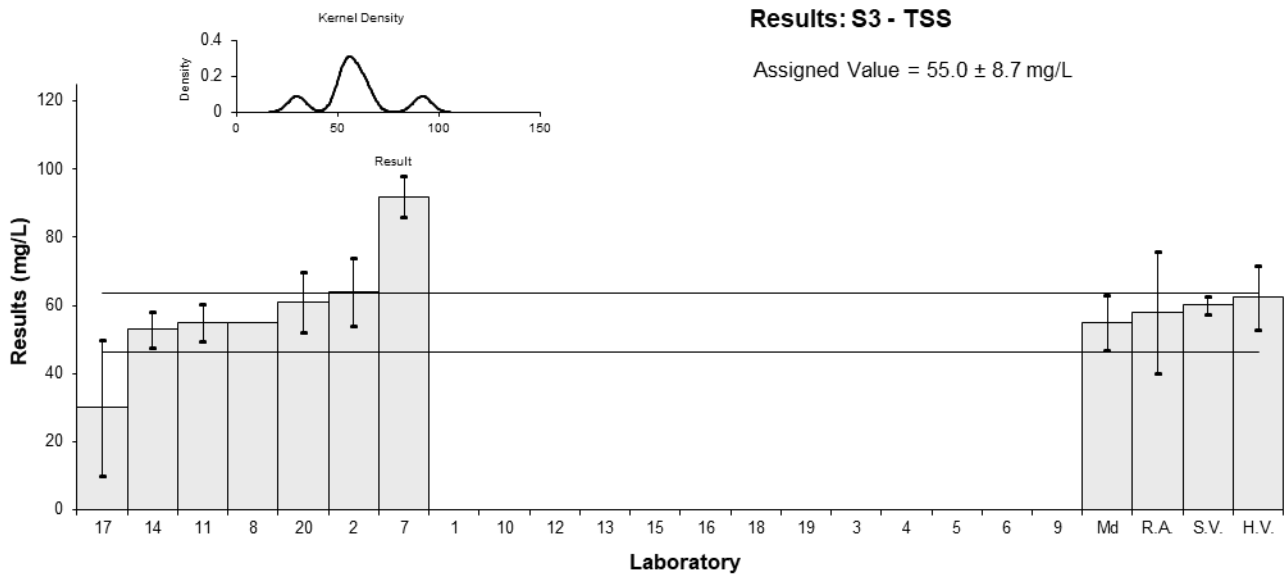
Participant Results

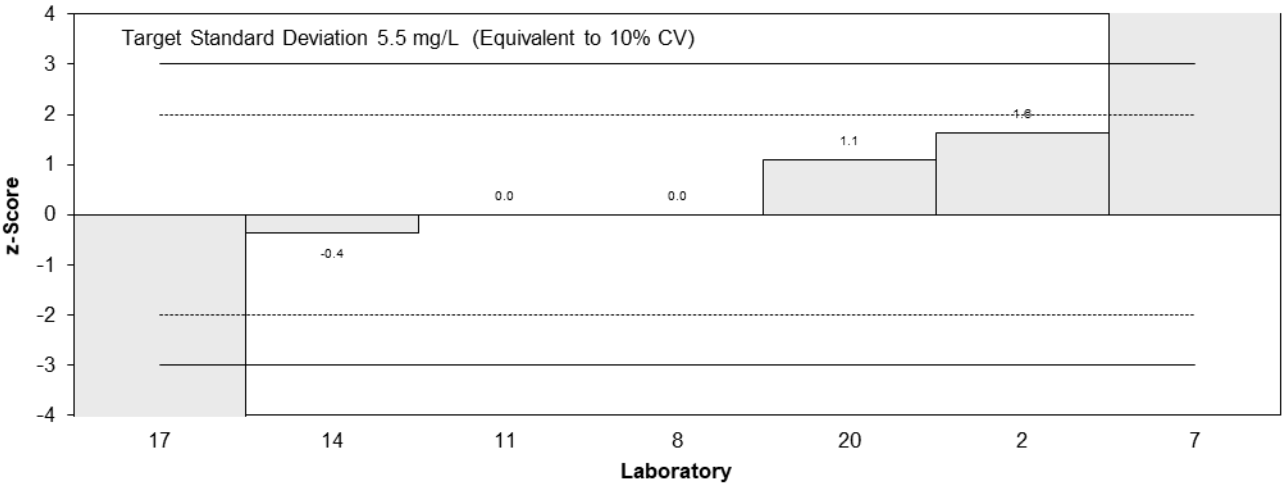
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	64	10	1.64	0.68
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	92	6	6.73	3.5
8	55	NR	0	0
9	NT	NT		
10	NT	NT		
11	55	5.5	0	0
12	NT	NT		
13	NT	NT		
14	53	5.3	-0.36	-0.2
15	NT	NT		
16	NT	NT		
17	30	20	-4.55	-1.15
18	NT	NT		
19	NT	NT		
20	61	9	1.09	0.48

Statistics

Assigned Value*	55.0	8.7
Spike	60.1	2.6
Homogeneity Value	62.5	9.4
Robust Average	58	18
Median	55.0	8.2
Mean	58.6	
N	7	
Max.	92	
Min.	30	
Robust SD	19	
Robust CV	33%	

*Robust Average excluding Laboratory 7.


Kernel Density
Density
Result
Results: S3 - TSS
Assigned Value = 55.0 ± 8.7 mg/L
Results (mg/L)
Laboratory
17 14 11 8 20 2 7 1 10 12 13 15 16 18 19 3 4 5 6 9 Md R.A. S.V. H.V.


z-Scores: S3 - TSS
Target Standard Deviation 5.5 mg/L (Equivalent to 10% CV)
z-Score
0.0
0.0
1.1
1.6
-0.4
Laboratory
17 14 11 8 20 2 7

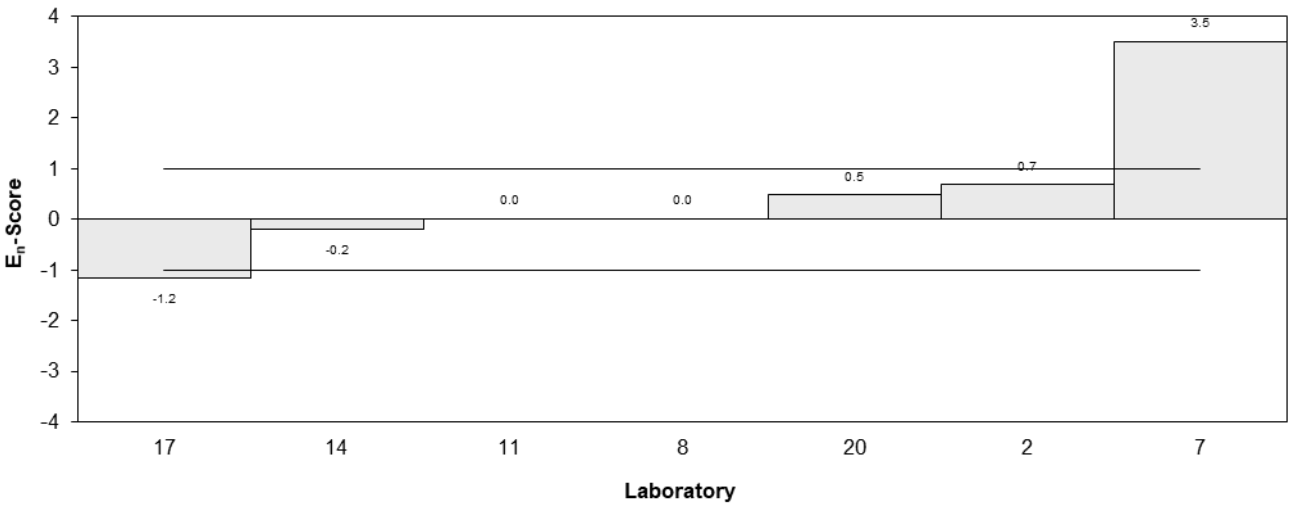

En-Scores: S3 - TSS
En-Score
3.5
0.7
0.5
0.0
0.0
-0.2
-1.2
Laboratory
17 14 11 8 20 2 7

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 DOC 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 226 numerical results, 206 (91%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.[8] 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.[9-15]

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 the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be viewed as suspect.

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 General Accreditation Guidance, Estimating and reporting measurement uncertainty of chemical test results[12] and 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, 12] 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 222 results for which E_n-scores were calculated, 191 (86%) returned a satisfactory score of $|E_n| \leq 1$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

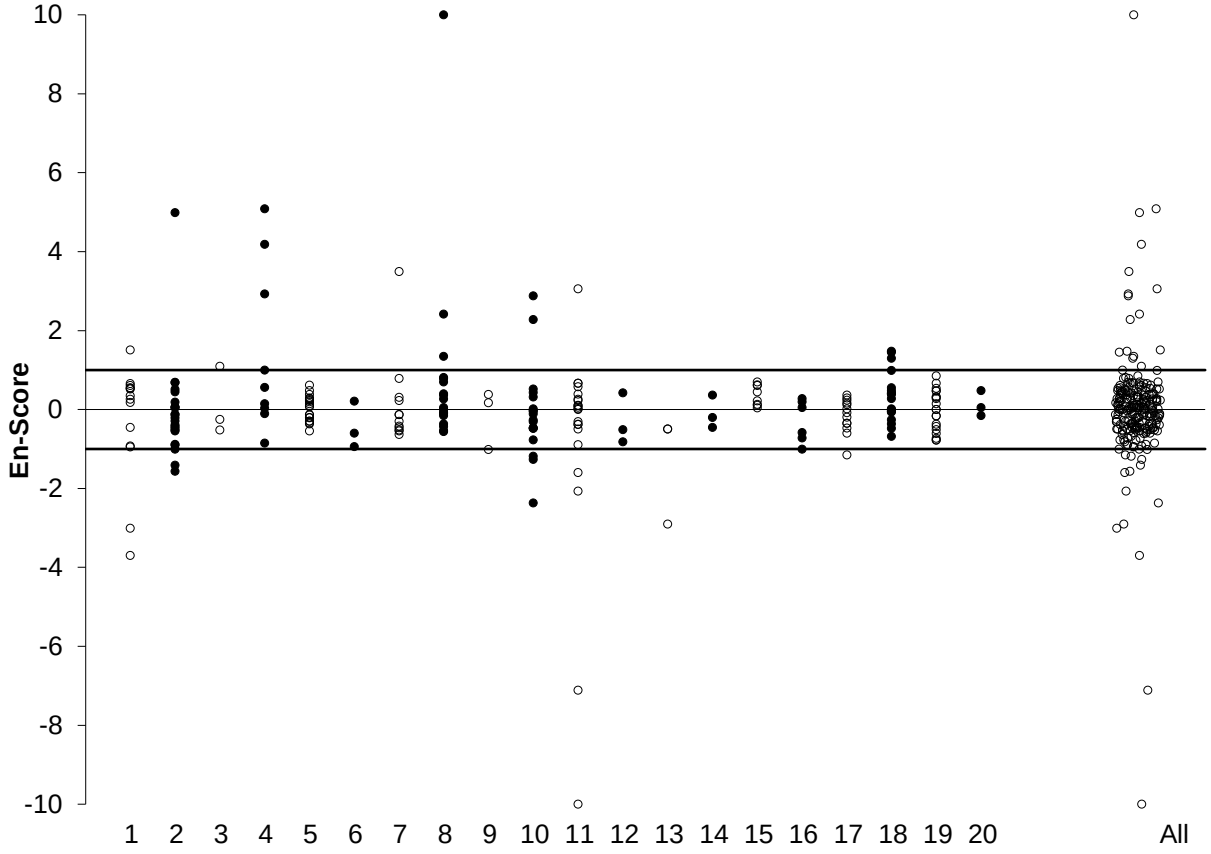
7.4 z-Score

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.

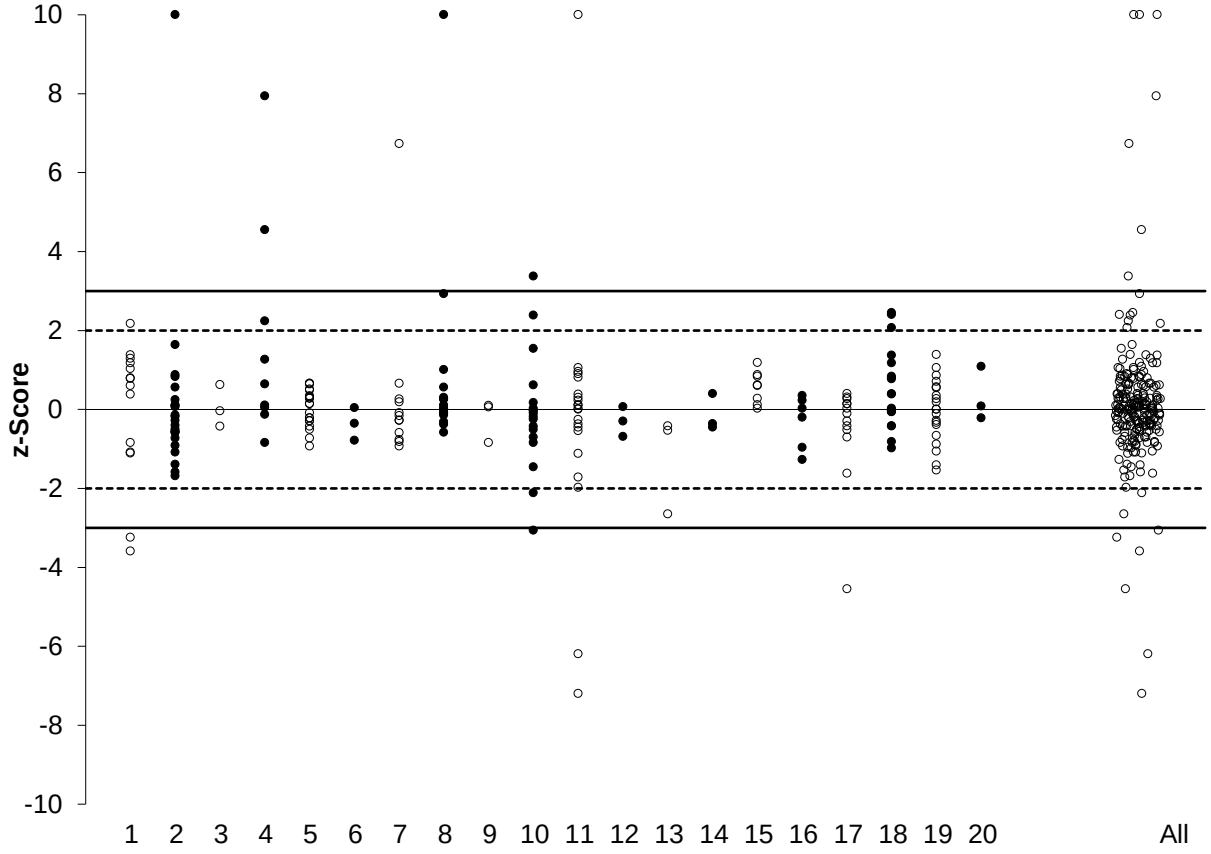
The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 30.

The dispersal of participants' z-scores is presented in Figure 28 (by laboratory code) and in Figure 29 (by test). Of 222 results for which z-scores were calculated, 200 (90%) returned a satisfactory score of $|z| \leq 2$ and 9 (4%) were questionable of $2 < |z| < 3$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.



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

Figure 27 E_n-Score Dispersal by Laboratory



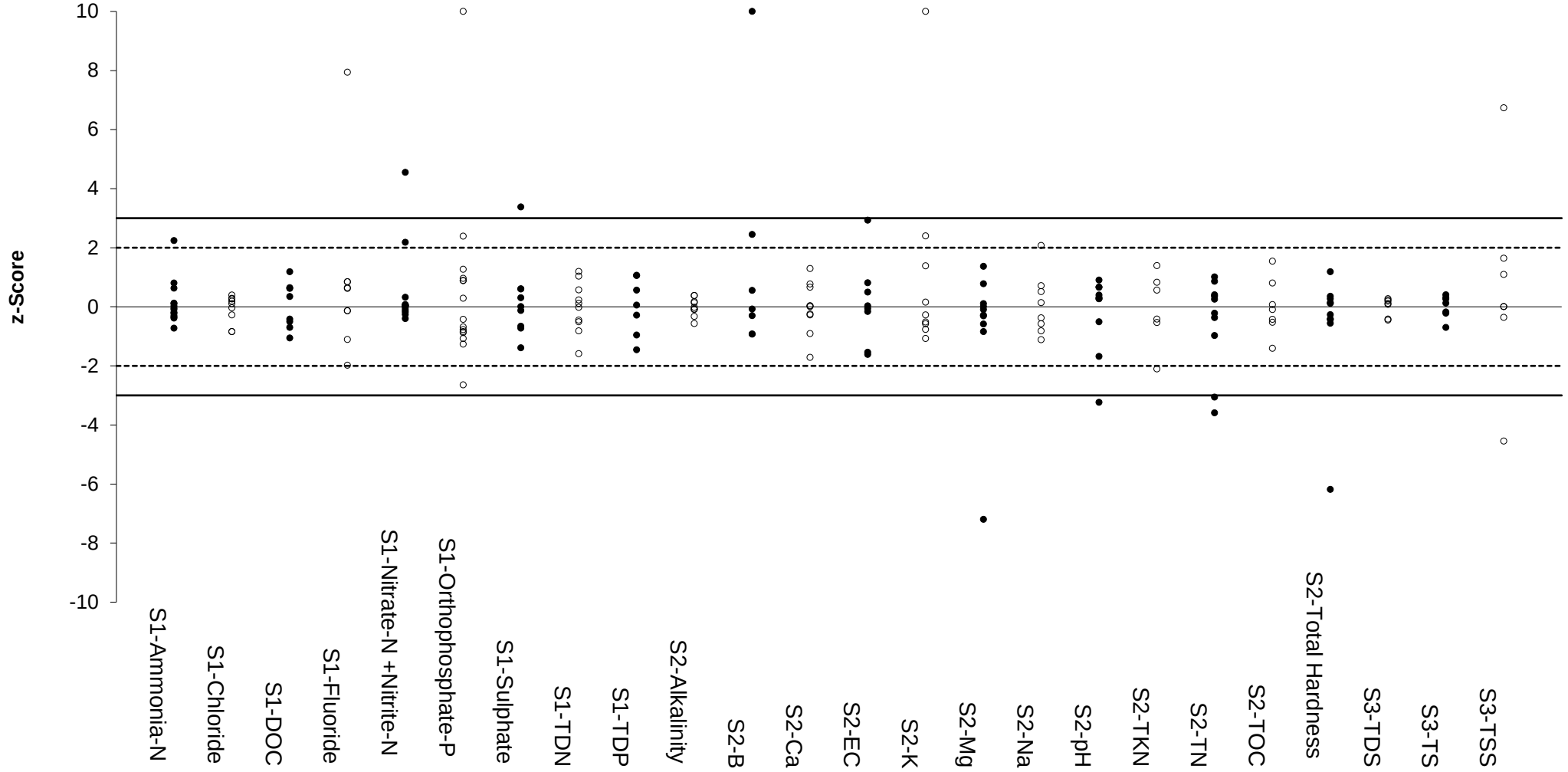
Scores of >10 or <-10 have been plotted as 10 or -10.

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	0.293	10%	19%	20%
S1	Chloride	10700	4.9%	4%	10%
S1	DOC	2.38	13%	14%	15%
S1	Fluoride	0.514	21%	18%	20%
S1	NOx	0.0696	4.3%	22%	20%
S1	Orthophosphate-P	0.0255	23%	22%	20%
S1	Sulphate	1510	9.9%	5.3%	10%
S1	TDN	0.433	14%	18%	15%
S1	TDP	0.0297	22%	22%	20%
S2	Alkalinity	42.4	3.1%	9.1%	10%
S2	B	4.74	11%	13%	10%
S2	Ca	319	8.8%	6.7%	10%
S2	EC	41200 µS/cm	4.1%	3.2%	3%
S2	K	325	12%	6.7%	10%
S2	Mg	1020	6.8%	5.6%	10%
S2	Na	8280	10%	4.1%	10%
S2	pH	8.53	2.8%	12%	3%
S2	TKN	0.36	28%	19%	20%
S2	TN	0.434	14%	18%	15%
S2	TOC	4.06	16%	13%	15%
S2	Total Hardness	4830	4.9%	4.5%	10%
S2	Total P	0.011*	13%	22%	Not Set
S3	TDS	26500	3.5%	3.5%	10%
S3	TS	27300	4%	3.4%	10%
S3	TSS	60.1	16%	8.6%	10%

NA = Not Available, *Robust between Laboratories CV with outliers removed. Median value of the reported results.



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

Figure 29 z-Score Dispersal by Analyte

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

Lab Code	Ammonia-N (mg/L)	Chloride (mg/L)	DOC (mg/L)	Fluoride (mg/L)	NOx (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
A.V.	0.293	10700	2.38	0.514	0.0696	0.0255	1510	0.433	0.0297
H.V.	0.265	10000	2.23	0.517	0.0693	0.0338	NA	0.315	0.0320
1	0.34	9800	NR	0.4	0.10	0.02	1600	0.5	NR
2	0.25	10400	2.2	0.5	0.064	0.030	1300	0.33	0.033
3	0.330	NR	NR	NR	0.0690	0.0233	NR	NR	NR
4	0.424	9800	2.61	1.33	0.133	0.032	1490	0.44	0.03
5	0.28	11000	2.5	0.58	0.074	0.027	1400	0.40	0.028
6	0.2726	NR	NR	NR	0.0701	0.0215	NR	NR	NR
7	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	NR	10978	NR	0.5	NR	0.10	NR	NR	NR
9	0.2990	NR	NR	NR	0.0705	0.0212	NR	NR	NR
10	0.287	10660	2.13	0.578	0.0671	0.0377	2020	0.432	0.0210
11	0.2939	10810	NT	0.31	0.066	0.0304	1556	0.404	0.036
12	0.2757	NR	NR	NR	0.0706	0.0220	NR	NR	NR
13	NT	NT	2.23	NT	NT	0.012	NT	NT	NT
14	NT	NT	NT	NT	NT	NT	NT	NT	NT
15	0.3	11000	2.6	0.6	0.07	0.03	1600	0.51	<0.05
16	0.281	NR	NR	NR	0.07	0.019	NR	0.448	0.024
17	NT	NT	NT	NT	NT	NT	NT	NT	NT
18	0.29	11120	2.8	0.6	0.07	NT	1510	0.38	NT
19	0.27	10900	2.0	<10	0.068	0.021	1410	0.47	0.036
20	NT	NT	NT	NT	NT	NT	NT	NT	NT

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

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

Lab Code	S2-Alkalinity (mg/L)	S2-B (mg/L)	S2-Ca (mg/L)	S2-EC (µS/cm)	S2-K (mg/L)	S2-Mg (mg/L)	S2-Na (mg/L)	S2-pH
A.V.	42.4	4.74	319	41200	325	1020	8280	8.53
H.V.	NA	4.98	345	40000	360	1100	NA	8.60
1	44	NR	360	NR	370	1100	NR	7.7
2	40	4000	290	NR	290	1030	7800	8.1
3	NT	NT	NT	NT	NT	NT	NT	NT
4	NT	NT	NT	NT	NT	NT	NT	NT
5	42	4.3	340	41800	330	990	8700	8.7
6	NT	NT	NT	NT	NT	NT	NT	NT
7	42	4.3	310	41000	300	960	7600	8.7
8	42	4.7	320	44824	306	988	7969	8.6
9	NT	NT	NT	NT	NT	NT	NT	NT
10	43.1	NT	311	41240	NT	934	NT	8.4
11	44	NT	264	42200	868	286	7355	8.76
12	NT	NT	NT	NT	NT	NT	NT	NT
13	NT	NT	NT	NT	NT	NT	NT	NT
14	NT	NT	NT	NT	NT	NT	NT	NT
15	NT	NT	NT	NT	NT	NT	NT	NT
16	NR	NR	NR	NR	NR	NR	NR	NR
17	43	4.60	320	39200	308	1010	8400	8.61
18	42.3	5.9	343.7	41120	403	1160	9995	8.63
19	41	5	319	39300	316	1020	8870	8.6
20	NT	NT	NT	NT	NT	NT	NT	NT

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

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

Lab Code	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.	0.36	0.434	4.06	4830	Not Set	26500	27300	60.1
H.V.	0.30	0.310	4.00	5000	NA	NA	NA	NA
1	NR	0.2	NR	5400	NR	NT	NT	NT
2	0.42	0.45	4.1	4560	0.010	26800	26800	64
3	NT	NT	NT	NT	NT	NT	NT	NT
4	NT	NT	NT	NT	NT	NT	NT	NT
5	NT	0.42	3.8	4900	0.012	NT	NT	NT
6	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	4700	NT	27000	28000	92
8	0.4	0.5	4	4884	NR	27215	28108	55
9	NT	NT	NT	NT	NT	NT	NT	NT
10	0.208	0.235	5.0	4620	NT	NT	NT	NT
11	0.321	0.410	NT	1840	0.012	27120	27640	55
12	NT	NT	NT	NT	NT	NT	NT	NT
13	NT	NT	3.74	NT	NT	NT	NT	NT
14	NT	NT	NT	NT	NT	25300	28400	53
15	NT	NT	NT	NT	NT	NT	NT	NT
16	NR	0.457	NR	NR	0.007	NT	NT	NT
17	NT	0.46	NR	4960	NT	25400	25400	30
18	0.33	0.37	4.55	4627	<0.1	NT	NT	NT
19	0.46	0.49	3.2	5000	<1	NT	NT	NT
20	NT	NT	NT	NT	NT	26700	26700	61

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

7.5 Participants' Results and Analytical Methods for Tests in Samples S1 and S2

Participants were asked to analyse samples S1 and S2 using their normal test method. The measurement methods and instrumental techniques used for analyses of S1 and S2 are presented in Appendices 6, 7 and 8.

Sample S1-Individual Test Commentary

Ammonia-Nitrogen With the exception of one laboratory, all results reported for NH_3-N returned satisfactory z-scores (Figure 30).

Poor buffering can cause interference for ammonia; using just phenol at a concentration of 0.06M can make system self-buffering. [16]

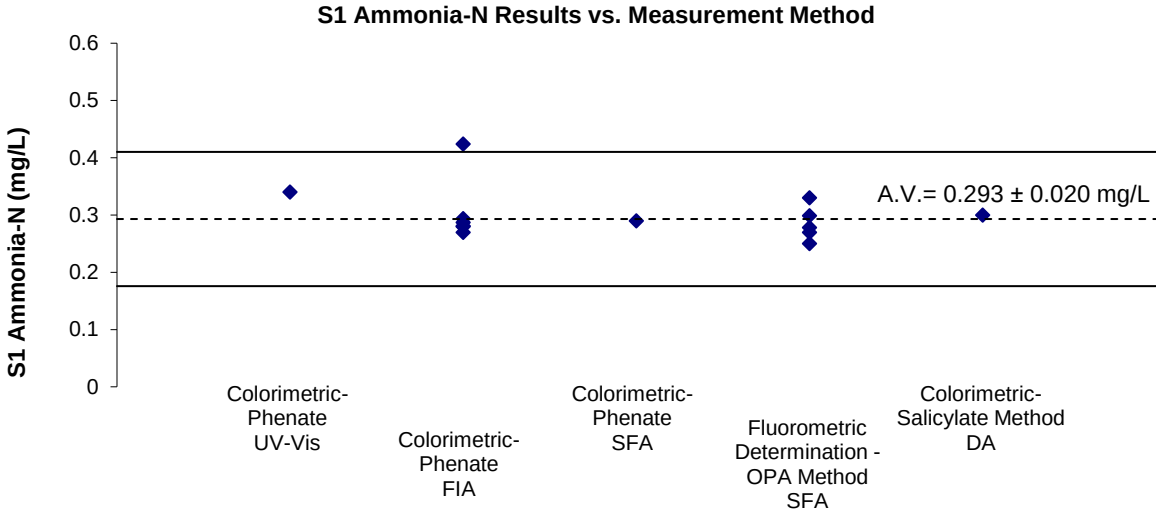
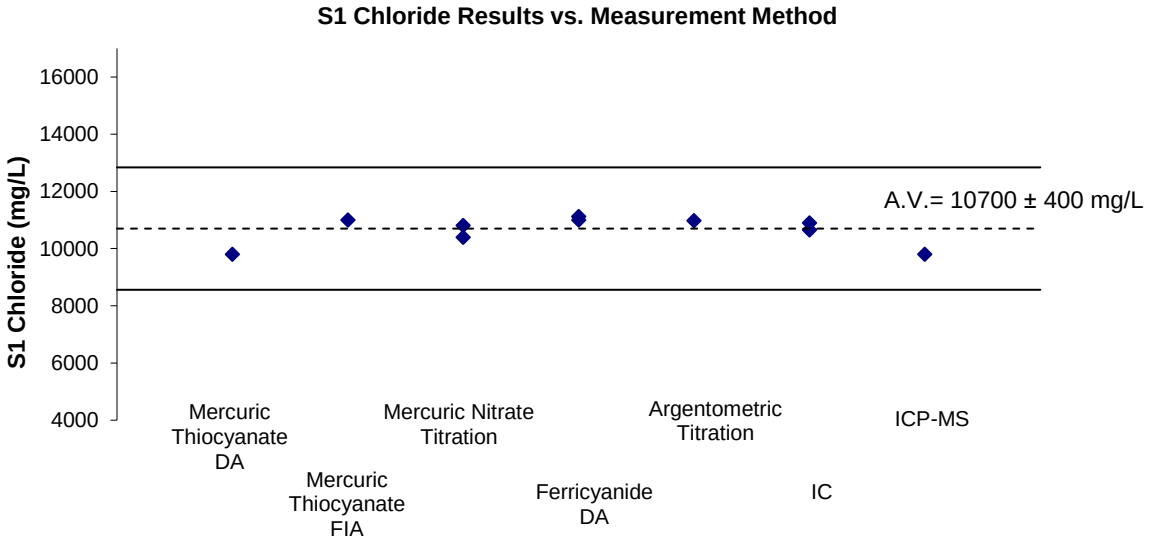


Figure 30 S1-NH_3-N Results vs. Measurement Method

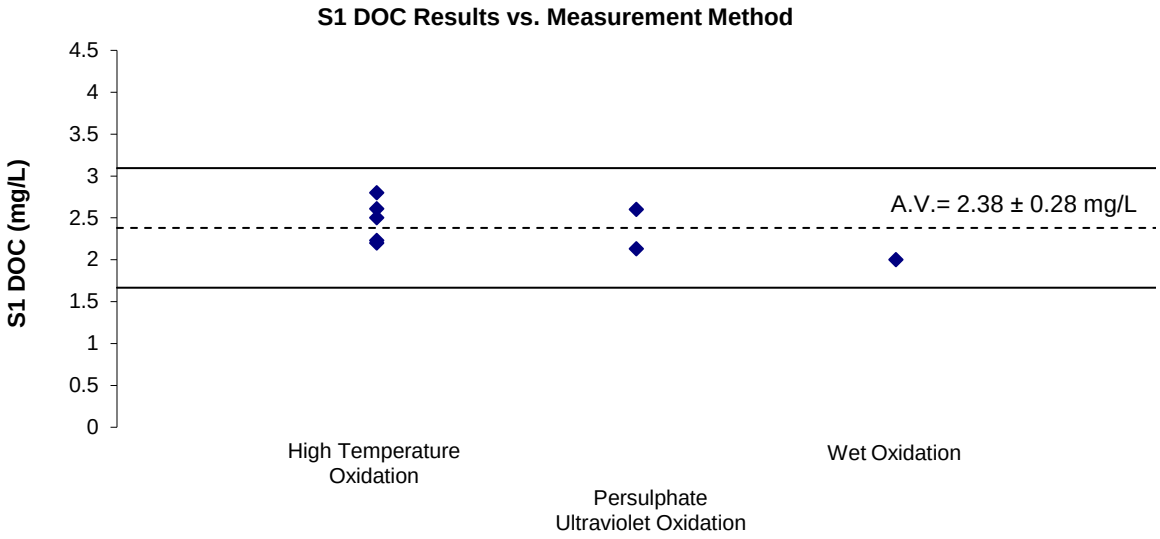
Chloride level in S1 was 10700 mg/L. Participants used a wide variety of methods for chloride analysis in S1; all produced results which were compatible with each other (Figure 31).



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

Figure 31 S1-Chloride Results vs. Measurement Method

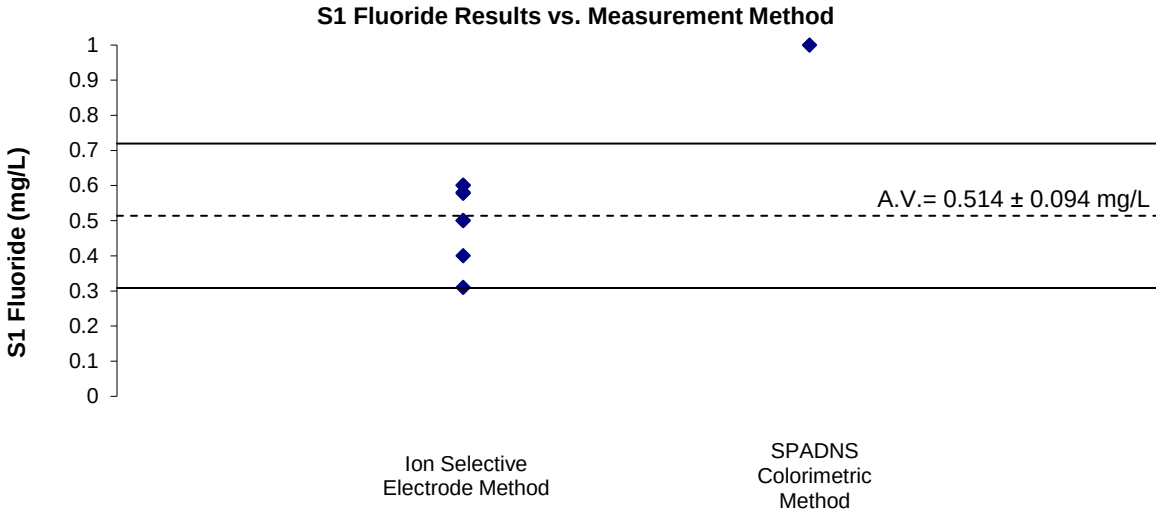
Dissolved Organic Carbon as dNPOC Participants used high-temperature oxidation (combustion), wet oxidation or persulfate-ultraviolet oxidation (Figure 32).



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

Figure 32 S1-DOC vs. Measurement Method

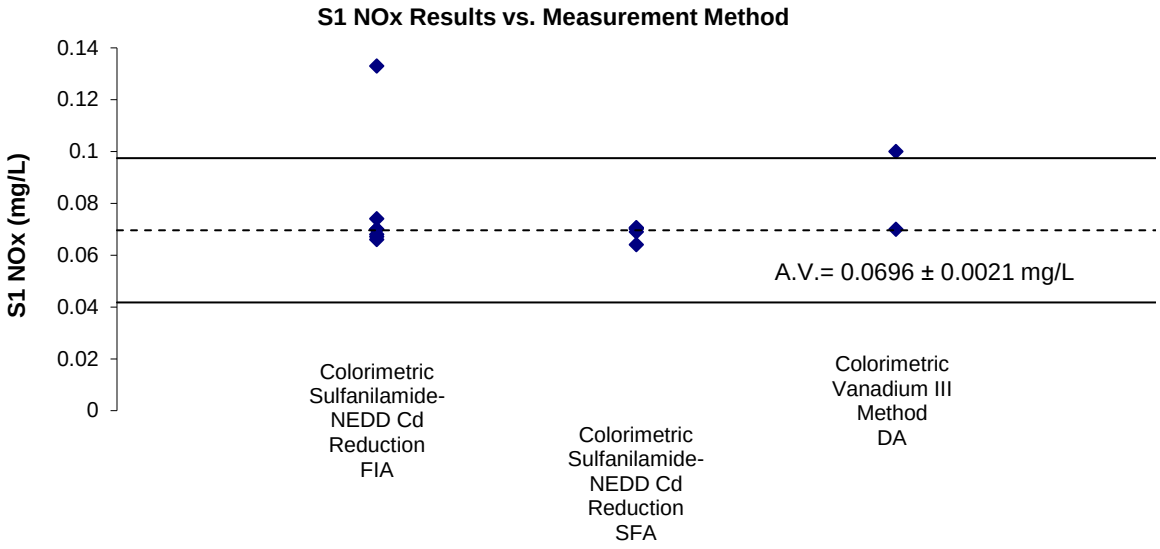
Fluoride One participant used the SPANDS colorimetric method; the results they reported were higher than the robust average of participants' results (Figure 33). Fluoride by the colorimetric method suffers from interference from chlorides, hence SPANDS might not be the best choice for fluoride measurement at low level in sea water.



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

Figure 33 S1-Fluoride Results vs. Measurement Method

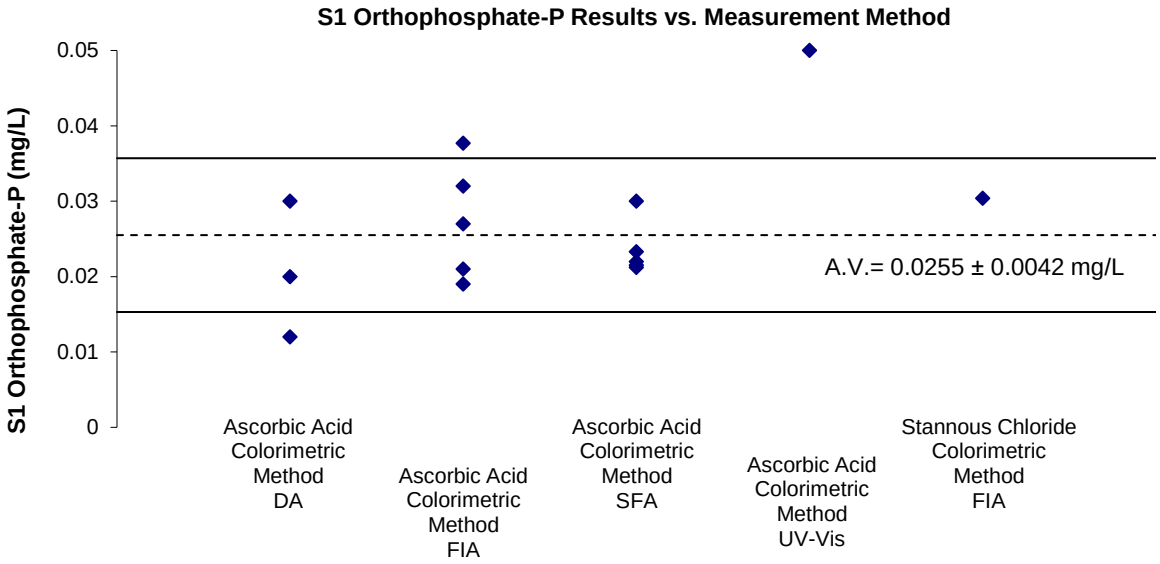
Nitrate-Nitrogen + Nitrite-Nitrogen Of 14 reported results, 12 returned satisfactory z-scores. Most participants used colorimetric-sulfanilamide-NEDD Cd reduction with SFA or FIA (Figure 34). Two laboratories reported using the Vanadium III colorimetric method with DA.



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

Figure 34 S1-Nitrate-N+Nitrite-N Results vs. Measurement Method and Instrumental Technique

Orthophosphate-P level in S1 was low (0.0255 mg/L), which may have presented difficulty to participating laboratories; the between laboratory CV was high, 23%. All participants used the ascorbic acid colorimetric method for orthophosphate-P measurement, with the exception of one laboratory (Figure 35).

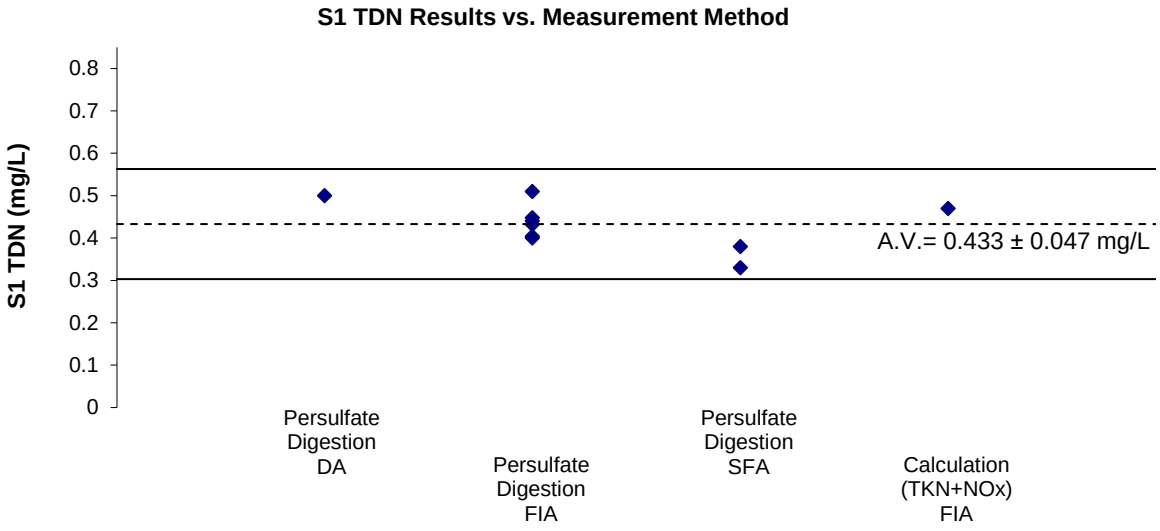


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 35 S1-Orthophosphate-P Results vs. Measurement Method

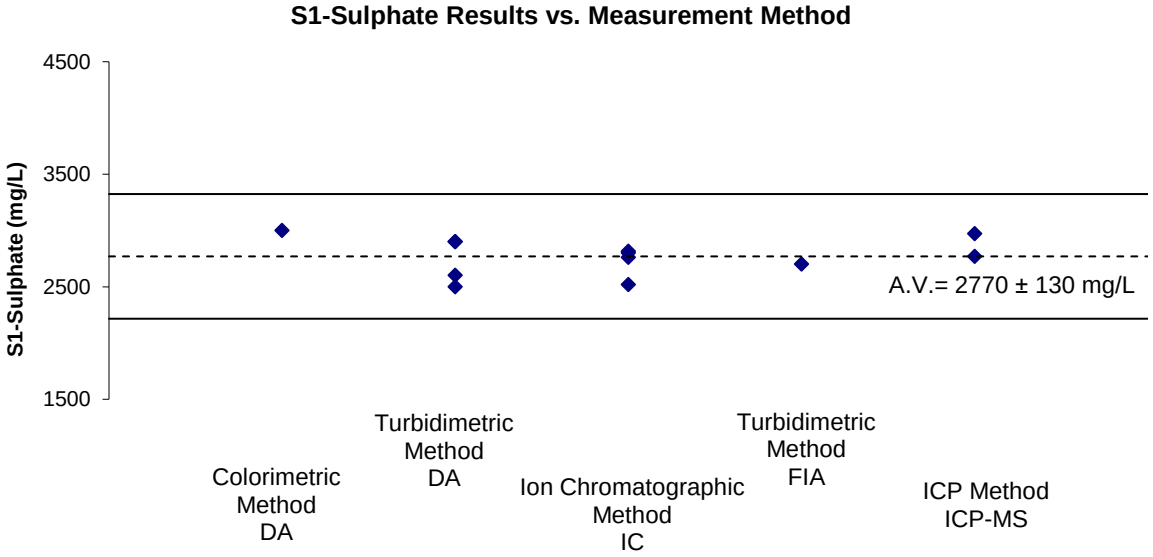
Total Dissolved Nitrogen With the exception of one, all participants determined total nitrogen by oxidation of all nitrogenous compounds to nitrate (Figure 36).

Sulphate Participants used various methods. All but one of the reported results were compatible with each other.



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

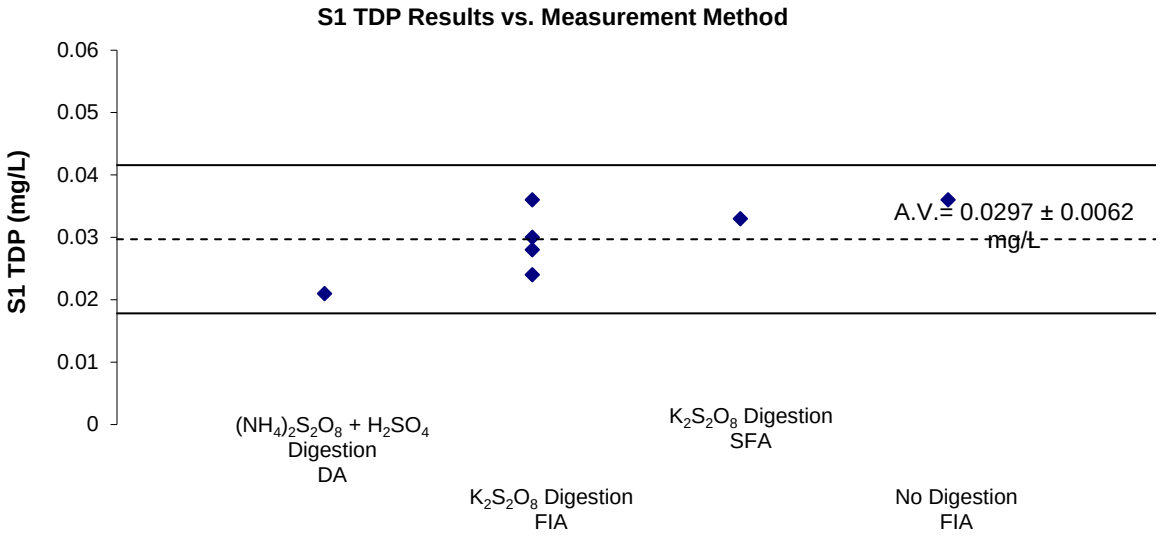
Figure 36 S1-TDN Results vs. Measurement Method and Instrumental Technique



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 Phosphorus level in S1 was low (0.0297 mg/L). Seven laboratories reported TDP results in S1, and all performed satisfactorily. Five laboratories used potassium persulphate for digestion and one used sulphuric acid and ammonium persulphate; these participants further measured the liberated orthophosphate colorimetrically by FIA or DA. One participant performed no digestion and instead measured TDP in the sample by FIA (Figure 38).

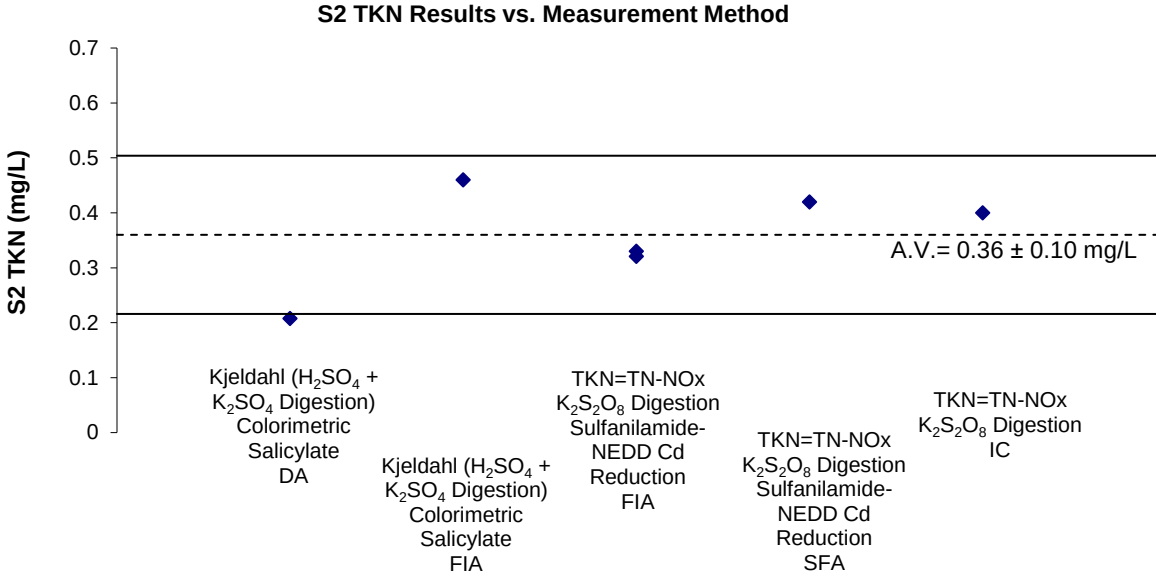


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

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

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

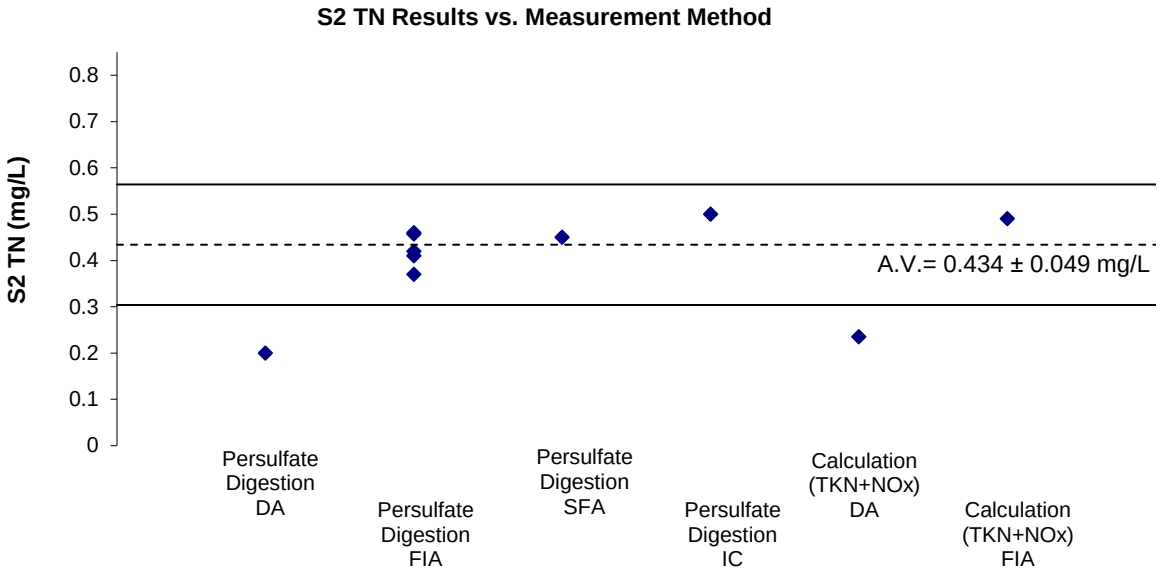
Total Kjeldahl Nitrogen As in the previous study in sea water, the unsatisfactory result was produced by the colorimetric salycilate or colorimetric phenate methods with DA as instrumental technique (Figure 39).



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

Figure 39 S2-TKN Results vs. Measurement Method

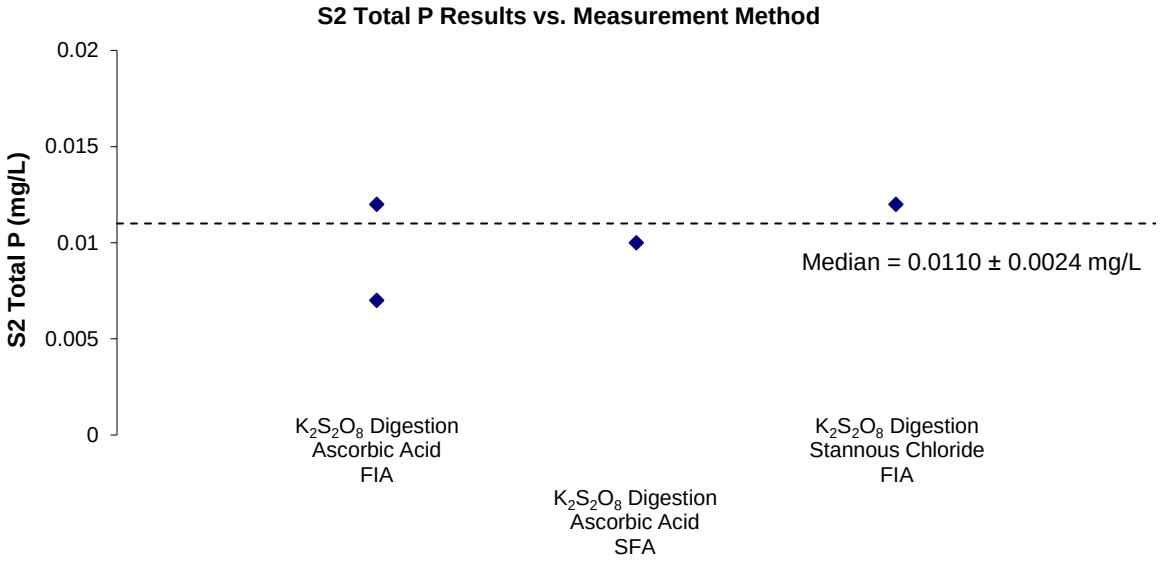
Total Nitrogen Of 10 reported results, 2 returned unsatisfactory z-scores. Of these two unsatisfactory results, one was produced by persulfate digestion followed by DA determination and one was reported as the sum of TKN and TN with the TKN result being produced via sulfuric acid and potassium sulfate digestion followed by DA determination.



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

Figure 40 S2-TN Results vs. Measurement Method

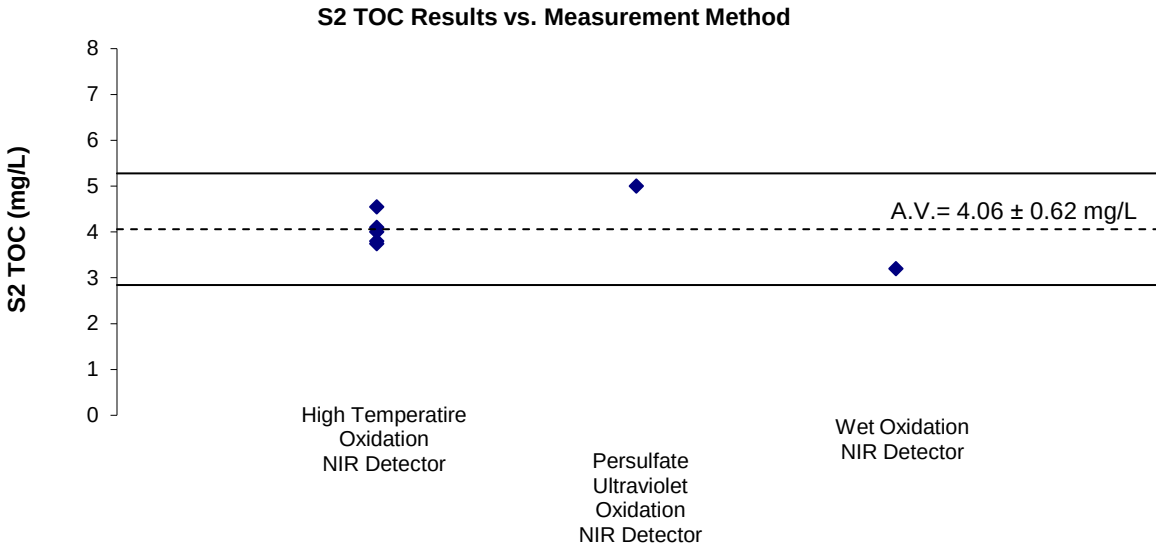
Total Phosphorus level in S2 was low, with the median of the reported results being 0.011 mg/L. Only 4 results were reported for TP in S2, and all were compatible with each other (Figure 41).



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

Figure 41 S2-TP Results vs. Measurement Method

Total Organic Carbon. All results reported for TOC in S2 returned satisfactory z-scores (Figure 42).

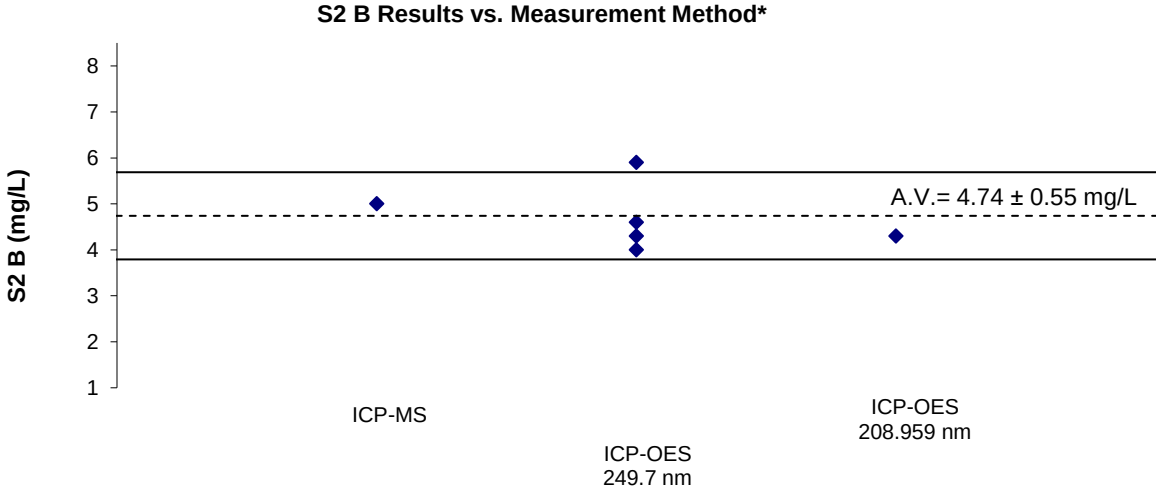


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 42 S2-TOC Results vs. Measurement Method

Total Hardness All reported results for total hardness in S2 returned satisfactory z-scores, with the exception of one. Laboratory 11 mixed up the reported results for Mg and K, and so used their K result in the hardness calculation instead of Mg.

Boron level in S2 was 4.74 mg/L and did not presented difficulties to the participating laboratories (Figure 43).



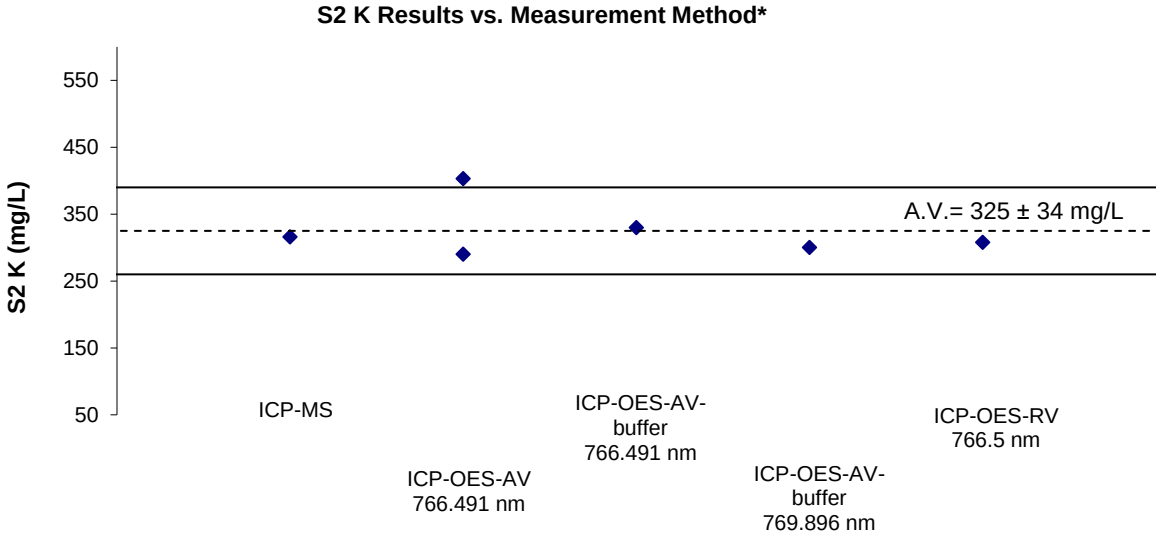
Horizontal lines on charts are the results correspond to z-scores of 2 and -2. Laboratory 2 result of 4000 mg/L has been plotted as 4 mg/L.

Figure 43 S2-B Results vs. Measurement Method

Laboratory 2 correctly measured B in S2 but reported result in the wrong units

Potassium When K measurements are conducted using an 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. [17]

Plots of participant's performance and results versus instrumental technique used are presented in Figure 40.



Horizontal lines on charts are the results correspond to z-scores of 2 and -2. Laboratory 11result was not plotted.

Figure 44 S2-K Results vs. Measurement Method

7.6 Comparison with Previous NMI Proficiency Tests of Water Characteristics

AQA 19-25 is the 11th NMI proficiency test of water characteristics. Figure 45 presents participant performance over time. Despite different matrices and analyte concentrations, on average, participants' performance remained consistent across time.

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.

Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally 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.

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	CRM
2	CRM
3	CRM – (1) CRM = KANSO, Reference Material Nutrient Seawater (RMNS), Lot BU & Lot CD. (http://www.kanso.co.jp/eng/production/). (2) RMNS certified for NOx ad PO4. Not certified for ammonia. (3) In-house independent spiked sea water used for ammonia QC.
4	CRM
6	CRM – CRM = Reference material for nutrients in sea water (RMNS): Ammonia is not part of the RMNS so an internal QC is implemented using an independent Ammonia standard solution.
7	CRM – CWWTMC
9	CRM – CRM = Reference material for nutrients in sea water (RMNS): Ammonia is not part of the RMNS so an internal QC was implemented using an independent Ammonia standard solution.
10	RM

Lab. Code	Description of Control Samples
12	CRM – CRM = Reference material for nutrients in sea water (RMNS): Ammonia is not part of the RMNS so an internal QC is implemented using an independent Ammonia standard solution.
15	RM
16	CRM
18	CRM
19	RM

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

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

> ***' a reference material****, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'*[18]

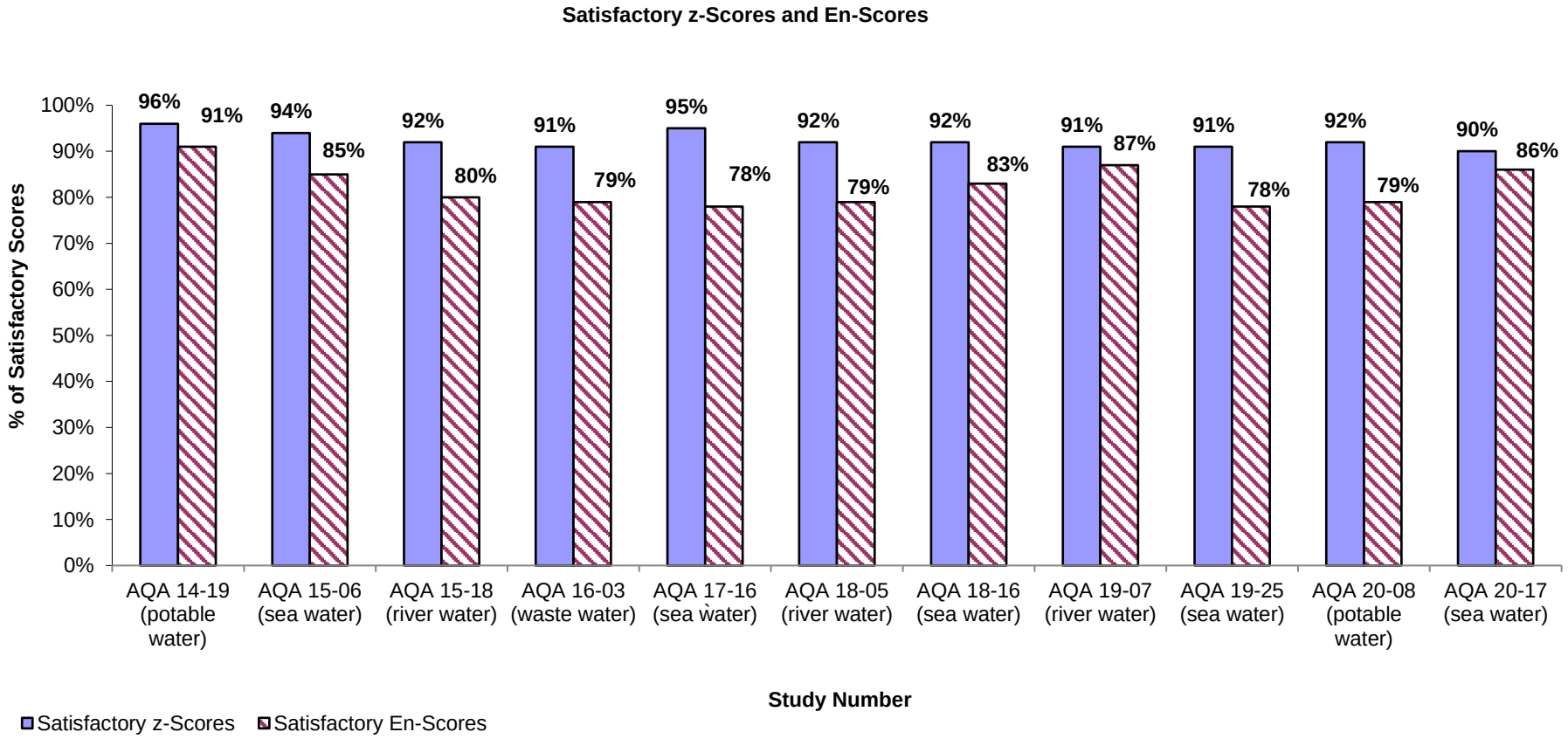


Figure 45 Participants' Performance in Nutrients, Anions and Physical Tests in Water PT Studies over Time

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was 200 mL of filtered, autoclaved and frozen sea water fortified with ammonia-N, dissolved organic carbon, and nitrate-N.

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

Sample S3 was unfiltered water. 0.60323 g of glass fibre filter was disintegrated and added to 10041 g of ultra-high purity water.

Sample Analysis and Homogeneity Testing

With the exception of sulphate in S1 and alkalinity, Na and total P in S2, 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 total elements in Sample S2, a test portion of 30 mL was transferred to a 50 mL graduated polypropylene centrifuge tube. The samples were digested using 2 mL of nitric acid on a hot block at 95 – 100^{o}C for 90 min.

Testing involved measurements using ICP-MS or 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 ion/wavelength and instrument conditions used for each analyte is given in Table 34.

Table 34 Methodology for Total Elements

Analyte	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Ion/Wavelenght
B	ICP-OES	Y	NA	NA	NA	208.965 nm
Ca	ICP-OES	Y	NA	NA	NA	422.491 nm
K	ICP-MS	Rh	ORS	He	NA	39 m/z
Mg	ICP-OES	Y	NA	NA	NA	279.8 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
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA
Nitrate-N + Nitrite-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA

Total Dissolved Nitrogen	Persulfate digestion	FIA
Total Dissolved Phosphorus	ICP-Method	ICP-MS

Table 36 Methodology for S2

Test	Measurement Method	Instrument
Total Hardness (as CaCO3)	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 9 November 2020. Participants were advised to store the Samples S1 and S2 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 46 and 47)

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	10/11/2020	Frozen	13/11/2020	Frozen	13/11/2020
2	10/11/2020	Frozen	10/11/2020	Cold	10/11/2020
3	10/11/2020	Partially Frozen	24/11/2020	NA	NA
4	12/11/2020	Frozen	13/11/2020	NA	NA
5	10/11/2020	Frozen, Partially Thawed	Various	Frozen, Partially Thawed	Various
6	10/11/2020	Unknown	14/11/2020	NA	NA
7	10/11/2020	NA	NA	Frozen	10/11/2020
8	10/11/2020				
9	10/11/2020	Unknown	25/11/2020	NA	NA
10	12/11/2020	Frozen	13/11/2020	Frozen	13/11/2020
11	10/11/2020	Frozen	11/11/2020	Frozen	11/11/2020
12	10/11/2020	Unknown	23/11/2020	NA	NA
13	11/11/2020	Frozen	20/11/2020	Frozen	20/11/2020
15	12/11/2020	Cold			
16	10/11/2020	Frozen	17/11/2020	Frozen	27/11/2020
17	11/11/2020	NA	NA	Cold	16/11/2020
18	10/11/2020	Frozen	19/11/2020	Frozen	19/11/2020
19	11/11/2020	Frozen		Frozen	

NA = Not Applicable

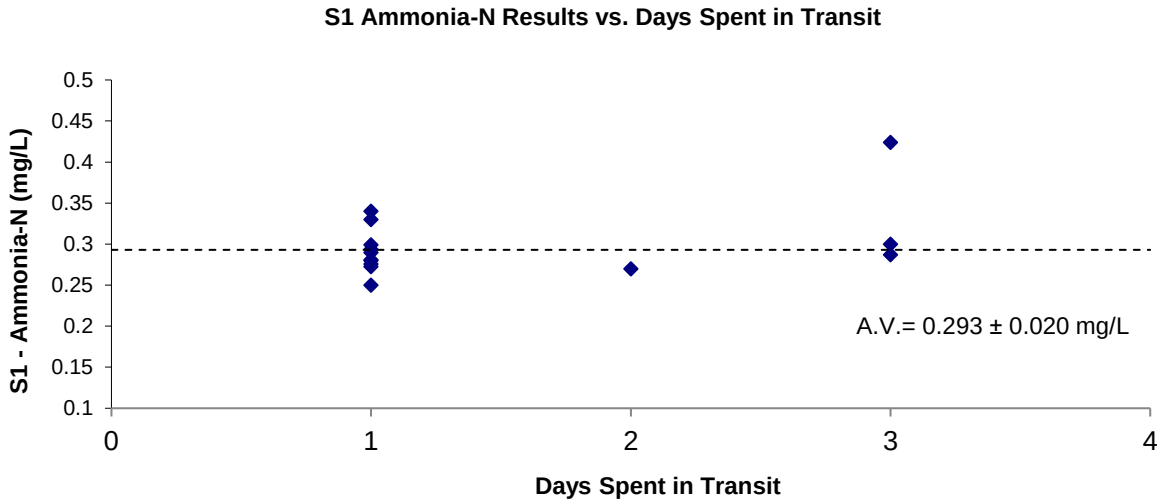
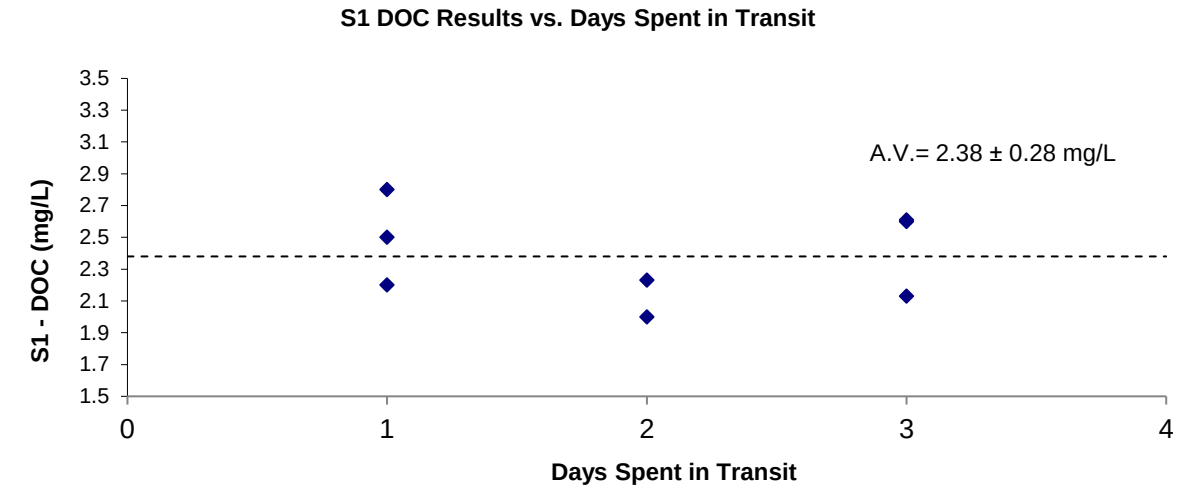
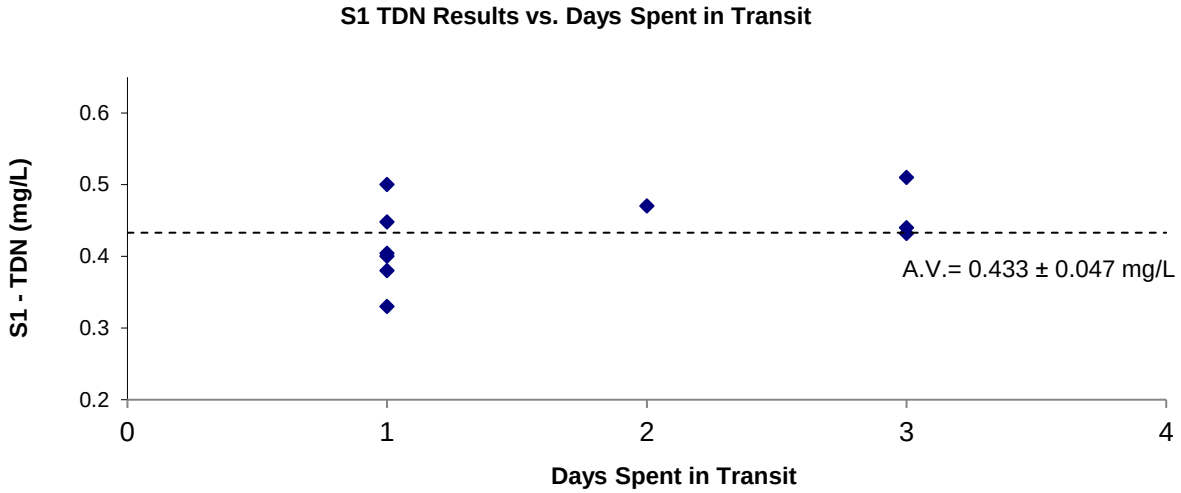


Figure 46 Results vs Day Spent in Transit





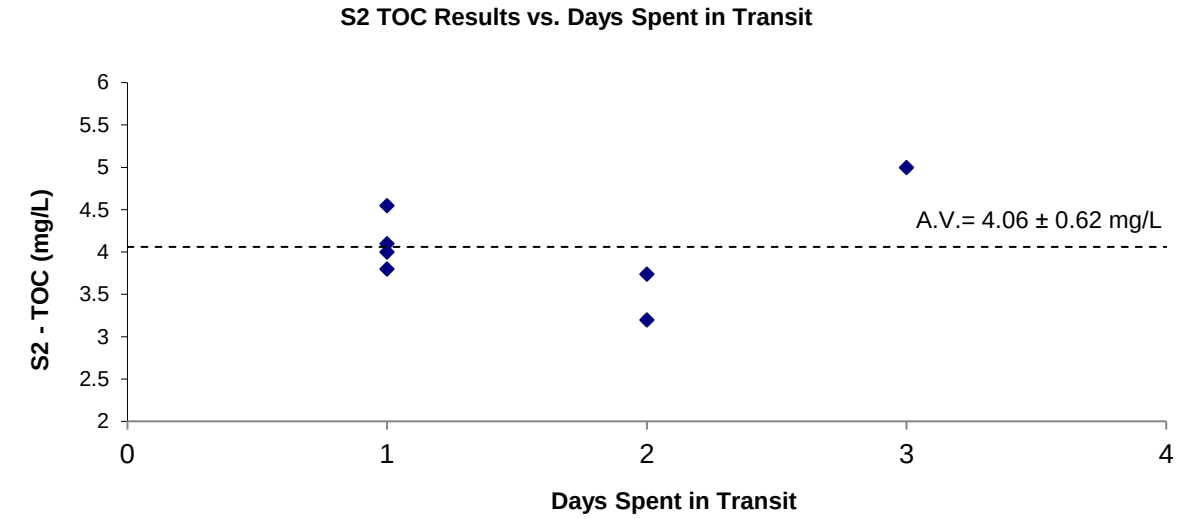


Figure 42 Results vs Day Spent in Transit (continued)

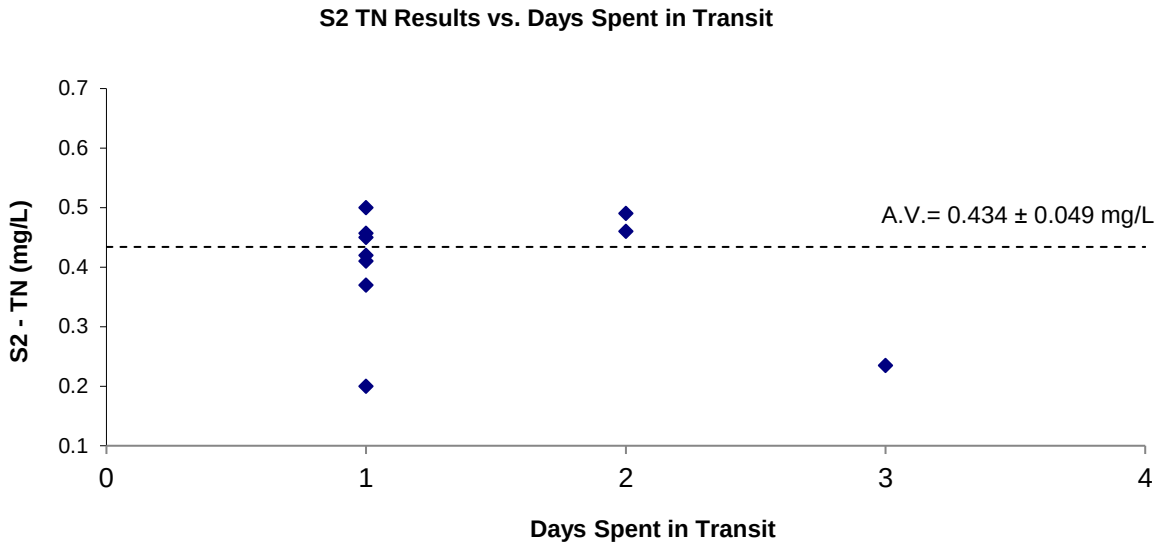
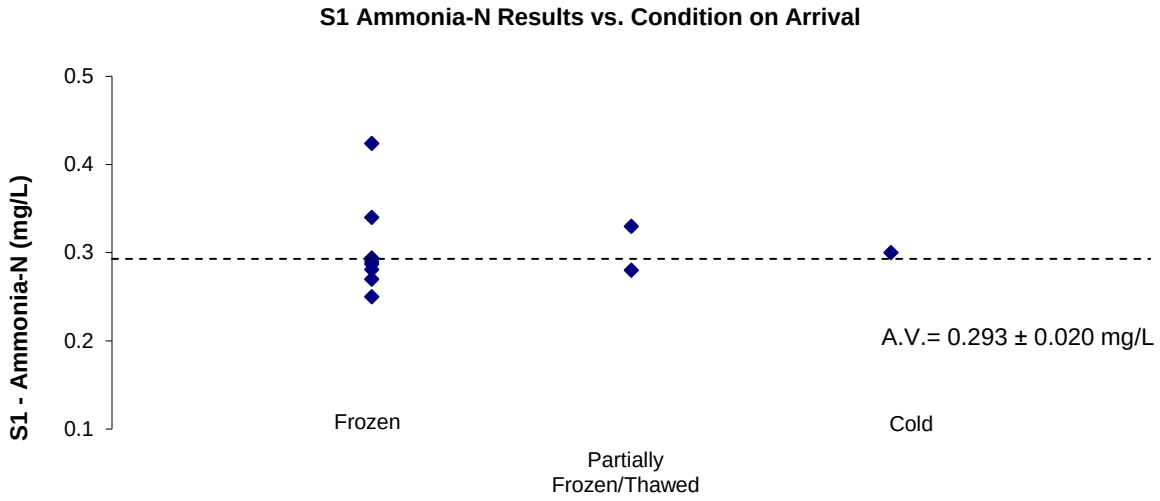


Figure 42 Results vs Day Spent in Transit (continued)



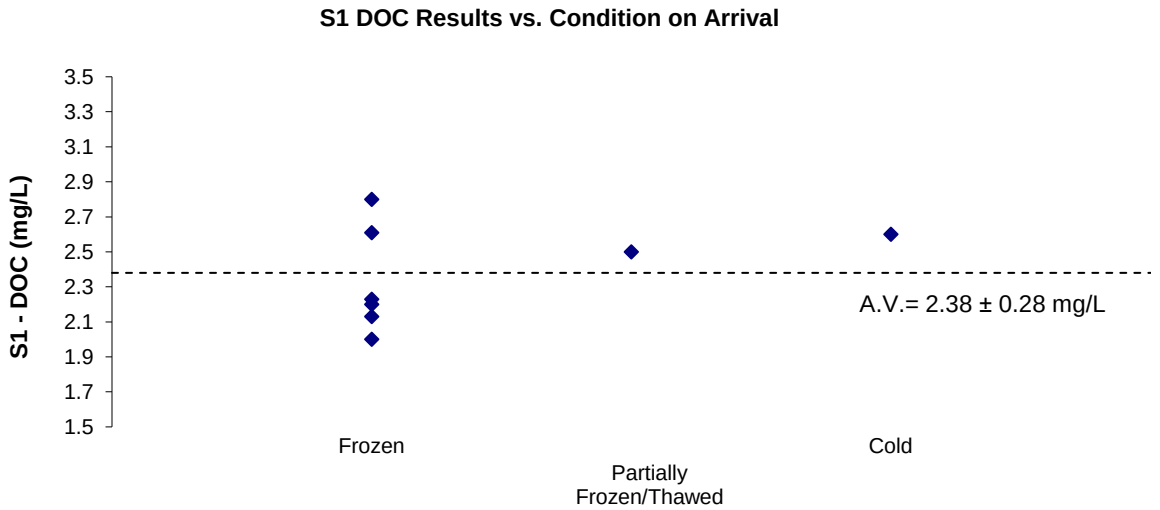
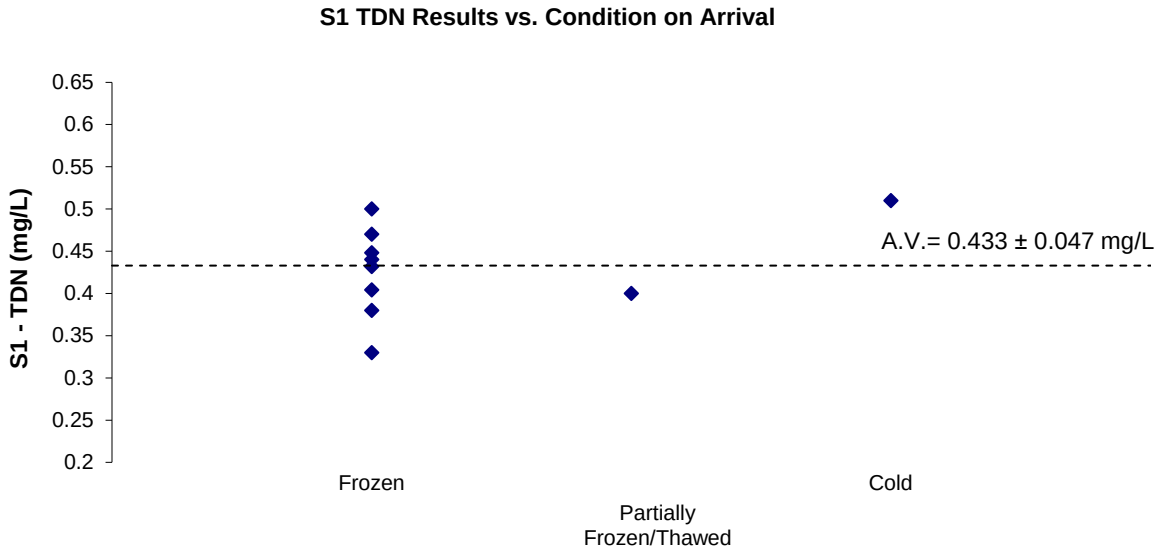
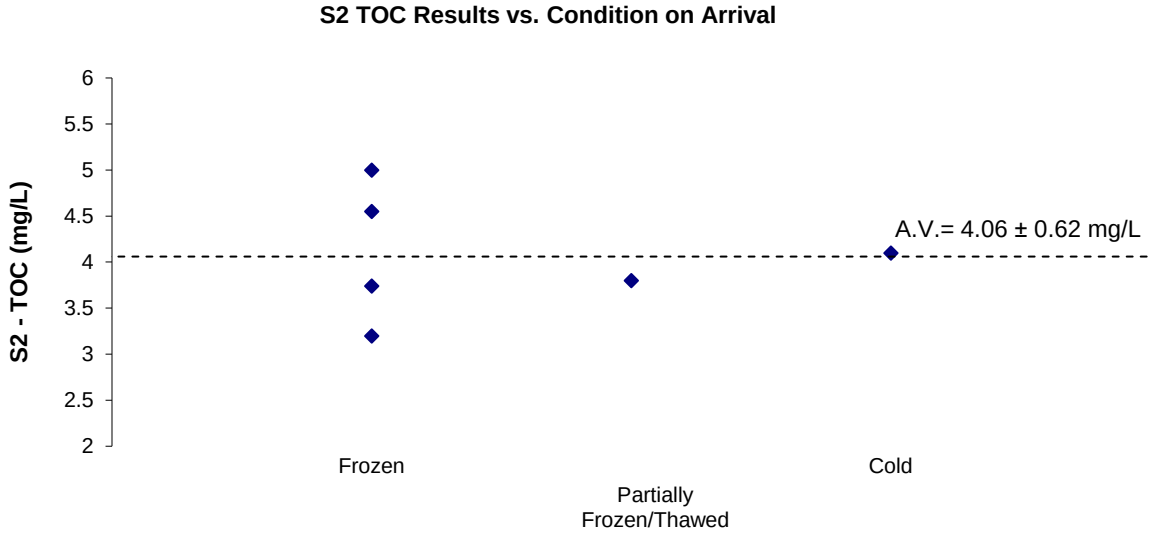


Figure 47 Results vs Condition on Arrival





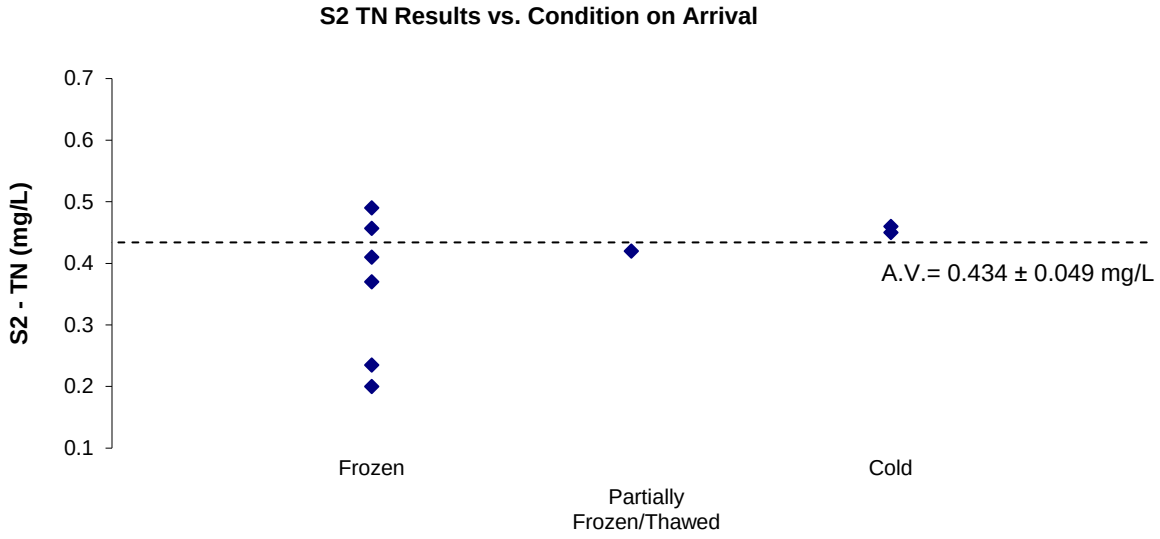


Figure 47 Results vs Condition on Arrival (continued)

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

Results from both of these studies were in good agreement with each other and the assigned value were within their stated uncertainties (Figure 48).

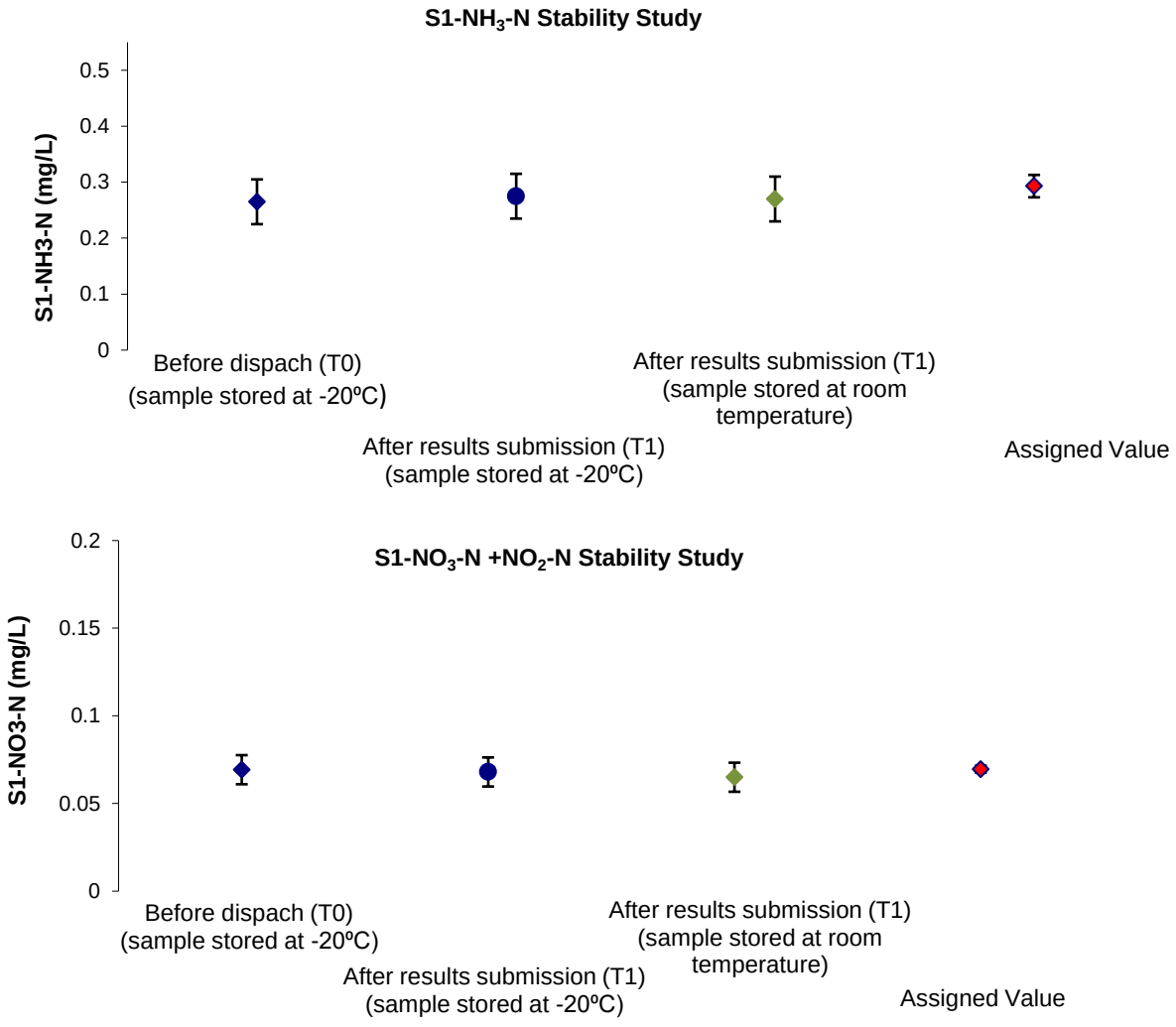


Figure 48 Stability Study Results

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 DOC in Sample S1

No. results (p)	8
Robust Average	2.38 mg/L
$S_{rob\ av}$	0.32 mg/L
$u_{rob\ av}$	0.14 mg/L
k	2
$U_{rob\ av}$	0.28 mg/L

The assigned value for **DOC** in Sample S1 is **2.38 ± 0.28 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 DOC result reported by Laboratory 10 in S1

DOC Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
2.03 ± 0.45	2.38 ± 0.28	15% as CV or 0.15 x 2.38 = =0.357 mg/L	$z = \frac{(2.13 - 2.38)}{0.357}$ z = -0.70	$En = \frac{(2.13 - 2.38)}{\sqrt{0.45^2 + 0.28^2}}$ E_n= -0.47

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 2020, NMI carried out eleven proficiency tests for nutrients, anions and physical tests in water. These studies involved measurements of these analytes in potable, fresh (river), waste and sea water. 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	Sea Water	13100 ± 1300	12800 ± 420	4.1	10
AQA 18-05	Fresh	68 ± 8.0	71.3 ± 1.5	3.4	17
AQA 18-16	Sea water	16600 ± 1600	17300 ± 1600	13	13
AQA 19-07	Fresh	57.0 ± 12	53.7 ± 2.0	4.7	10
AQA 19-25	Sea Water	20000 ± 2000	20500 ± 1000	2.2	13
AQA 20-08	Potable Water	33.4 ± 7	41.6 ± 1.9	6.7	13
AQA 20-17	Sea Water	9800 ± 980	10700 ± 400	4.9	10
Average				5.4**	

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

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 5.4%. 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 sea water 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 six 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
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
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
SPADNS	2-(4-Sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt
Target SD	Target standard deviation (symbol: σ)
UV-Vis	Ultraviolet -visible spectroscopy

APPENDIX 6 - METHODOLOGY FOR S1

Table 42 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Phenate Method	UV-Vis Spectrophotometer	
2	Fluorometric Determination - OPA Method	SFA	
3	Fluorometric Determination - OPA Method	SFA	Kerouel, R, Aminot, A. Marine Chemistry Vol 57, no. 3-4 pp. 265-275. Jul 1997.
4	Colorimetric - Phenate Method	FIA	
5	Colorimetric - Phenate Method	FIA	
6	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
7	NA	NA	NA
8			
9	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
10	Colorimetric - Phenate Method	FIA	APHA4500-NH3
11	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
12	Fluorometric Determination - OPA Method	SFA	Roger Kérouel and Alain Aminot, IFREMER (1997 Mar.Chem.57)
13			
14	NA	NA	NA
15	Colorimetric - Salicylate Method	DA	WK/055G WRG
16	Colorimetric - Phenate Method	FIA	
17	NA	NA	NA
18	Colorimetric - Phenate Method	SFA	
19	Colorimetric - Phenate Method	FIA	APHA Method 4500
20	NA	NA	NA

Table 43 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Mercuric Thiocyanate	DA	
2	Mercuric Nitrate Titration	DA	
3			
4	ICP-Method	ICP-MS	
5	Mercuric Thiocyanate	FIA	
6			
7	NA	NA	NA
8	Argentometric Titration	Auto Titration	APHA
9			
10	Ion Chromatographic Method	IC	APHA4110B(modified)
11	Mercurric Nitrate Titration	Manual Analysis	APHA 4500 ClC
12			
13			
14	NA	NA	NA
15	Ferricyanide Colorimetric Method	DA	WD/045G
16			
17	NA	NA	NA
18	Ferricyanide Colorimetric Method	DA	
19	Ion Chromatographic Method	IC	APHA Method 4110C
20	NA	NA	NA

Table 44 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2	High-Temperature Oxidation	NIR-detector	
3			
4	High-Temperature Oxidation	NIR-detector	
5	High-Temperature Oxidation	NIR-detector	
6			
7	NA	NA	NA
8			
9			
10	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA5310C (modified)
11			
12			
13	High-Temperature Oxidation	NIR-detector	APHA
14	NA	NA	NA
15	Persulfate-Ultraviolet Oxidation	Photo metric	WP/005SF 002SF
16			
17	NA	NA	NA
18	High-Temperature Oxidation	NIR-detector	
19	Wet-Oxidation	NIR-detector	APHA Method 5310 A and C
20	NA	NA	NA

Table 45 Measurement Methods and Instrument Techniques for Fluoride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ion Selective Electrode Method	Ion Selective Electrode	
2	Ion Selective Electrode Method	Ion Selective Electrode	
3			
4	SPADNS Colorimetric Method	UV-Vis Spectrophotometer	
5	Ion Selective Electrode Method	Ion Selective Electrode	
6			
7	NA	NA	NA
8	Ion Selective Electrode Method	Ion Selective Electrode	APHA
9			
10	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500-F-C
11	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500 F-C
12			
13			
14	NA	NA	NA
15	Ion Selective Electrode Method	Ion Selective Electrode	WK040LL
16			
17	NA	NA	NA
18	Ion Selective Electrode Method	Ion Selective Electrode	
19	Ion Chromatographic Method	IC	APHA Method 4110C
20	NA	NA	NA

Table 46 Measurement Methods and Instrument Techniques for NOx

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric -vanadium III method	DA	
2	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." Limnol. Oceanogr: Methods
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
6	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
7	NA	NA	NA
8			
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	APHA4500-NO3I(modified)
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500 NO3 I
12	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
13			
14	NA	NA	NA
15	Colorimetric -vanadium III method	DA	QWI-EN WK058GV059GV WRG
16	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
17	NA	NA	NA
18	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
19	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA Method 4500
20	NA	NA	NA

Table 47 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	DA	
2	Ascorbic Acid Colorimetric Method	SFA	
3	Ascorbic Acid Colorimetric Method	SFA	Rees, C., L. Pender, K. Sherrin, C. Schwanger, P. Hughes, S. Tibben, A. Marouchos, and M. Rayner. (2018) "Methods for reproducible shipboard SFA nutrient measurement using RMNS and automated data processing." Limnol. Oceanogr: Methods
4	Ascorbic Acid Colorimetric Method	FIA	
5	Ascorbic Acid Colorimetric Method	FIA	
6	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
7	NA	NA	NA
8	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer	APHA
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	APHA4500-PG
11	Stannous Chloride Colorimetric Method	FIA	in house
12	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
13	Ascorbic Acid Colorimetric Method	DA	APHA
14	NA	NA	NA
15	Ascorbic Acid Colorimetric Method	DA	QWI-EN.WK071G
16	Ascorbic Acid Colorimetric Method	FIA	
17	NA	NA	NA
18			
19	Ascorbic Acid Colorimetric Method	FIA	APHA Method 4500
20	NA	NA	NA

Table 48 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric Method	DA	
2	Turbidimetric Method	DA	
3			
4	ICP Method	ICP-MS	
5	Turbidimetric Method	FIA	
6			
7	NA	NA	NA
8			
9			
10	Ion Chromatographic Method	IC	APHA4110B(modified)
11	ICP Method	ICP-OES	APHA 3120 B
12			
13			
14	NA	NA	NA
15	Turbidimetric Method	DA	WD/041G
16			
17	NA	NA	NA
18	Turbidimetric Method	DA	
19	Ion Chromatographic Method	IC	APHA Method 4110C
20	NA	NA	NA

Table 49 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2	Persulfate digestion	SFA	
3			
4	Persulfate digestion	FIA	
5	Persulfate digestion	FIA	
6			
7	NA	NA	NA
8			
9			
10	Persulfate digestion	FIA	APHA-4500NC&4500NO3I modified
11	Persulfate digestion	FIA	inhouse
12			
13			
14	NA	NA	NA
15	Persulfate digestion	FIA	WK261 62 67 PSF-A
16	Persulfate digestion	FIA	
17	NA	NA	NA
18	Persulfate digestion	SFA	
19	Calculation (TKN+NOx)	FIA	APHA Method 4500
20	NA	NA	NA

Table 50 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1				
2	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	
3				
4	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
6				
7	NA	NA	NA	NA
8				
9				
10	(NH4)2S2O8+H2SO4 Digestion	Ascorbic Acid Colorimetric Method	DA	APHA4500-PE (modified)
11	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	inhouse
12				
13				
14	NA	NA	NA	NA
15	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	WK261 62 67 PSF-A
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
17	NA	NA	NA	NA
18				
19		Ascorbic Acid Colorimetric Method	FIA	APHA Method 4500
20	NA	NA	NA	NA

APPENDIX 7 - METHODOLOGY FOR S2

Table 51 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	ICP-OES-AV	Y	NA	NA	2	249.772
3	NA	NA	NA	NA	NA	NA
4	NA	NA	NA	NA	NA	NA
5	ICP-OES-AV-buffer	Lu			5	249.678
6	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV-buffer	Y	NA	NA	1	208.959
8	ICP-OES-AV	Lu			1	261
9	NA	NA	NA	NA	NA	NA
10						
11						
12	NA	NA	NA	NA	NA	NA
13						
14	NA	NA	NA	NA	NA	NA
15	NA	NA	NA	NA	NA	NA
16						
17	ICP-OES-RV	LU				249.6
18	ICP-OES-AV	Lu			1.1	
19	ICP-MS					11
20	NA	NA	NA	NA	NA	NA

Table 52 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	ICP-OES-AV	Y	NA	NA	100	315.887
3	NA	NA	NA	NA	NA	NA
4	NA	NA	NA	NA	NA	NA
5	ICP-OES-AV-buffer	Lu			10	430.253
6	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV-buffer	Y	NA	NA	1	317.933
8	ICP-OES-AV	Lu			1	261
9	NA	NA	NA	NA	NA	NA
10						
11	ICP-OES-RV					
12	NA	NA	NA	NA	NA	NA
13						
14	NA	NA	NA	NA	NA	NA
15	NA	NA	NA	NA	NA	NA
16						
17	ICP-OES-RV	LU				315.9
18	ICP-OES-AV	Lu			1.1	
19	ICP-MS	Yes			10	44
20	NA	NA	NA	NA	NA	NA

Table 53 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	ICP-OES-AV	Y	NA	NA	100	766.491
3	NA	NA	NA	NA	NA	NA
4	NA	NA	NA	NA	NA	NA
5	ICP-OES-AV-buffer	Lu			100	766.491
6	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV-buffer	Y	NA	NA	100	769.896
8	ICP-OES-AV	Lu			1	261
9	NA	NA	NA	NA	NA	NA
10						
11	ICP-OES-RV					
12	NA	NA	NA	NA	NA	NA
13						
14	NA	NA	NA	NA	NA	NA
15	NA	NA	NA	NA	NA	NA
16						
17	ICP-OES-RV	LU				766.5
18	ICP-OES-AV	Lu			1.1	
19	ICP-MS	Yes			10	39
20	NA	NA	NA	NA	NA	NA

Table 54 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	ICP-OES-AV	Y	NA	NA	100	279.8
3	NA	NA	NA	NA	NA	NA
4	NA	NA	NA	NA	NA	NA
5	ICP-OES-AV-buffer	Lu			100	279.078
6	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV-buffer	Y	NA	NA	10	279.079
8	ICP-OES-AV	Lu			1	261
9	NA	NA	NA	NA	NA	NA
10						
11	ICP-OES-RV					
12	NA	NA	NA	NA	NA	NA
13						
14	NA	NA	NA	NA	NA	NA
15	NA	NA	NA	NA	NA	NA
16						
17	ICP-OES-RV	LU				279.8
18	ICP-OES-AV	Lu			1.1	
19	ICP-MS	Yes			10	24
20	NA	NA	NA	NA	NA	NA

Table 55 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	ICP-OES-AV	Y	NA	NA	500	330.237
3	NA	NA	NA	NA	NA	NA
4	NA	NA	NA	NA	NA	NA
5	ICP-OES-AV-buffer	Lu			100	568.821
6	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV-buffer	Y	NA	NA	100	330.237
8	ICP-OES-AV	Lu			1	261
9	NA	NA	NA	NA	NA	NA
10						
11	ICP-OES-RV					
12	NA	NA	NA	NA	NA	NA
13						
14	NA	NA	NA	NA	NA	NA
15	NA	NA	NA	NA	NA	NA
16						
17	ICP-OES-RV	LU				589.6
18	ICP-OES-AV	Lu			1.1	
19	ICP-MS	Yes			10	23
20	NA	NA	NA	NA	NA	NA

Table 56 Measurement Methods and Instrument Techniques for Alkalinity

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Manual Analysis	
2	Titration	Auto Titration	
3	NA	NA	NA
4	NA	NA	NA
5	Titration	Manual Analysis	
6	NA	NA	NA
7	Titration	Auto Titration	
8	Titration	Auto Titration	APHA
9	NA	NA	NA
10	Titration	Auto Titration	APHA2320 Alkalinity B (modified)
11	Titration	manual titration	APHA 2320
12	NA	NA	NA
13			
14	NA	NA	NA
15	NA	NA	NA
16			
17	Titration		2320B
18	Titration	Auto Titration	
19	Titration	Auto Titration	APHA Method 2320B
20	NA	NA	NA

Table 57 Measurement Methods and Instrument Techniques for Total Hardness

Lab. Code	Measurement Method	Instrument	Method Reference
1	Calculation		
2	Calculation	ICP-OES	
3	NA	NA	NA
4	NA	NA	NA
5	Calculation	ICP-OES	
6	NA	NA	NA
7	Calculation	ICP-OES	
8	Calculation	ICP-OES	APHA
9	NA	NA	NA
10	Calculation		
11	Calculation	ICP-OES	APHA 2320
12	NA	NA	NA
13			
14	NA	NA	NA
15	NA	NA	NA
16			
17	Calculation	ICP-OES	
18	Calculation	Not Applicable	
19	Calculation	ICP-MS	APHA Method 2340
20	NA	NA	NA

Table 58 Measurement Methods and Instrument Techniques for Total Kjeldahl Nitrogen

Lab. Code	Measurement Method		Instrument	Method Reference
1				
2	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	
3	NA	NA	NA	NA
4	NA	NA	NA	NA
5				
6	NA	NA	NA	NA
7				
8	APHA4500	if other please type	IC	APHA
9	NA	NA	NA	NA
10	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA4500N org
11	TKN=TN-NOx (K2S2O8 digestion)		FIA	inhouse
12	NA	NA	NA	NA
13				
14	NA	NA	NA	NA
15	NA	NA	NA	NA
16				
17				
18	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
19		Colorimetric - salicylate method	FIA	APHA Method 4500
20	NA	NA	NA	NA

Table 59 Measurement Methods and Instrument Techniques for Total Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	DA	
2	Persulfate digestion	SFA	
3	NA	NA	NA
4	NA	NA	NA
5	Persulfate digestion	FIA	
6	NA	NA	NA
7			
8	APHA4500	IC	APHA
9	NA	NA	NA
10	Calculation (TKN+NOx)		
11	Persulfate digestion	FIA	inhouse
12	NA	NA	NA
13			
14	NA	NA	NA
15	NA	NA	NA
16	Persulfate digestion	FIA	
17	Persulfate digestion	FIA	4500-N C
18	Persulfate digestion	FIA	
19	Calculation (TKN+NOx)	FIA	APHA Method 4500
20	NA	NA	NA

Table 60 Measurement Methods and Instrument Techniques for Total Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
1				
2	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	
3	NA	NA	NA	NA
4	NA	NA	NA	NA
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
6	NA	NA	NA	NA
7				
8	H2SO4+HNO3-Digestion	if other please type	ICP-MS	APHA
9	NA	NA	NA	NA
10	(NH4)2S2O8+H2SO4 Digestion	Ascorbic Acid Colorimetric Method	DA	APHA4500-PB&E (modified)
11	K2S2O8-Digestion	Stannous Chloride Colorimetric Method	FIA	inhouse
12	NA	NA	NA	NA
13				
14	NA	NA	NA	NA
15	NA	NA	NA	NA
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	
17				
18	HNO3-Digestion	ICP Method	ICP-OES	
19		ICP Method	ICP-MS	USEPA Method 200.8
20	NA	NA	NA	NA

Table 61 Measurement Methods and Instrument Techniques for Total Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
1			
2	High-Temperature Oxidation	NIR-detector	
3	NA	NA	NA
4	NA	NA	NA
5	High-Temperature Oxidation	NIR-detector	
6	NA	NA	NA
7			
8	High-Temperature Oxidation	NIR-detector	APHA 5310B
9	NA	NA	NA
10	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA 5310C (modified)
11			
12	NA	NA	NA
13			
14	NA	NA	NA
15	NA	NA	NA
16			
17	Wet-Oxidation	NIR-detector	5310C
18	High-Temperature Oxidation	NIR-detector	
19	Wet-Oxidation	NIR-detector	APHA Method 5310 A and C
20	NA	NA	NA

APPENDIX 8 – METHODOLOGY FOR S3

Table 62 Measurement Methods and Instrument Techniques for Total Organic Carbon

Laboratory Code	Method Reference
7	APHA Method 2540 B, C, D
8	APHA Method 2540 B, C, D
11	APHA 2540 C, D and G
14	2540B, D; APHA AWWA (2017)
17	2540 B C D

END OF REPORT