Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report
AQA 22-11
Nutrients and Anions in Potable Water

October 2022

ACKNOWLEDGMENTS

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

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

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

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WORLD RECOGNISED
ACCREDITATION

Accredited for compliance with ISO/IEC 17043

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1 SUMMARY

This report presents the results of the proficiency test AQA 22-11, Nutrients and Anions in Potable Water. The study focused on the measurement of total: B, Ca, K, Mg, Na and P. Ammonia (as NH_3), bromide, chloride, dissolved organic carbon (as dNPOC), fluoride, iodide, nitrate (as NO_3), nitrite (as NO_2), orthophosphate-P, sulphate, total dissolved nitrogen, total dissolved phosphorus, alkalinity to pH 4.5 (as $CaCO_3$), electrical conductivity at 25ºC, total hardness (as $CaCO_3$), pH at 25ºC, silica (as SiO_2), and apparent colour (Pt-Co units) were also included in the program.

The sample set consisted of two water samples.

Twenty-two laboratories registered to participate and all submitted 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 300 z-scores, 268 (89%) returned a satisfactory score of $|z| \leq 2.0$.
Of 300 E_n-scores, 255 (85%) returned a satisfactory score of $|E_n| \leq 1.0$.

Laboratory 20 returned the highest number of satisfactory z-scores and E_n-scores (21 out of 21 reported).

ii. *evaluate the laboratories' methods used in determination of nutrients, anions and physical tests in potable water;*

Iodide and colour were the tests which presented the most analytical difficulty to participating laboratories

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

On average, over the last seven years, participants' performance in measuring nutrients, anions and physical tests in water has remained fairly consistent.

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 323 numerical results, 320 (99%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using the proficiency testing data only 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 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;
- PFOS/PFOA in water, soil, biota and food;
- allergens in food;
- controlled drug assay; and
- folic acid in flour.

AQA 22-11 is the 14th 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 potable 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 twenty-four tests were selected from those for which an investigation level is listed in the Australian Drinking Water Guidelines[5] and are commonly measured by water testing laboratories.

3.2 Participation

Twenty-two laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued:	28 June 2022
Samples dispatched:	26 July 2022
Results due:	26 August 2022
Interim report issued:	31 August 2022

3.3 Test Material Specification

Two samples were provided for analysis:

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

Sample S2 was 400 mL of unfiltered and chilled potable water.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

Test samples from previous studies have been demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. Therefore, only a partial homogeneity test was conducted for all analytes with the exception of alkalinity, chloride, colour, iodide, sulphate and total P.[1] The results of the partial homogeneity testing for these samples are reported in the present study as the homogeneity value.

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

To address issues associated with holding time and holding conditions, a stability study was conducted for the less stable analytes: ammonia, nitrate and nitrite in S1. The stability study was conducted over the entire period of the PT study and was designed to simulate the conditions encountered by the samples during storage. Details of the study and its results are given in Appendix 2. The test samples were stable for the period of the proficiency test.

3.7 Sample Storage, Dispatch and Receipt

Sample S2 was refrigerated before dispatch, while sample S1 was frozen.

The samples were dispatched by courier on 26 July 2022.

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 Sample S1 frozen.
- Prior to testing thaw sample S1 completely.
- Participants are asked to report results in units of mg/L except for pH, colour (Pt-Co units) and EC (µS/cm) for the following:

SAMPLE S1 Filtered, autoclaved, frozen potable water		**SAMPLE S2** unfiltered potable water	
Test	**Estimated Value mg/L**	**Test**	**Estimated Value mg/L**
Bromide	<5.0	B (total)	<5.0
Chloride	<100	Ca (total)	<50
Fluoride	<5.0	K (total)	<50
Iodide	<5.0	Mg (total)	<50
Dissolved Organic Carbon (as dNPOC)	<50	Na (total)	<50
Ammonia (as NH_3)	<5.0	P (total)	<5.0
Nitrate (as nitrate)	<5.0	Alkalinity to pH 4.5 (as $CaCO_3$)	<300
Nitrite (as nitrite)	<5.0	Colour, apparent (Pt-Co units)	<50
Total Dissolved Nitrogen	<5.0	Hardness, total ($CaCO_3$)	<300
Total Dissolved Phosphorus	<5.0	EC (at 25°C, µS/cm)	<50000
Orthophosphate-P	<5.0	pH (at 25 °C)	>2.5
Sulphate	<50	Silica (as SiO_2)	<50

- 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 31 August 2022.

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 together with the additional information for each sample analysed are presented in Appendices 6 and 7.

4.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 1 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	CRM	NMI Uncertainty Course
2	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	CRM	Eurachem/CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Standard Purity	Nordtest Report TR537
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NATA General Accreditation Guidance – Estimating and Reporting Measurement Uncertainty of Chemical Test Results
5	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	John Eames
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
7	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis	CRM Recoveries of SS	
8	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	Recoveries of SS	Eurachem/CITAC Guide
10	Top Down Approach	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurochem Guide 2007
11	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	Eurachem/CITAC Guide
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM Recoveries of SS	Eurachem/CITAC Guide
14	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis		NATA General Accreditation Guidance, Estimating and Reporting MU

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
15	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	Eurachem/CITAC Guide
16	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	Eurachem/CITAC Guide
17	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM	Recoveries of SS	Internal SOP 08
18	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	Recoveries of SS	Eurachem/CITAC Guide
19	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - SS Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
20	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM
21	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis Instrument Calibration	Instrument Calibration	
22	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies	Nordtest Report TR537

*RM= Reference Material, CRM = Certified Reference Material, SS =Spiked samples.

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

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Participants’ comments are reproduced in Table 2.

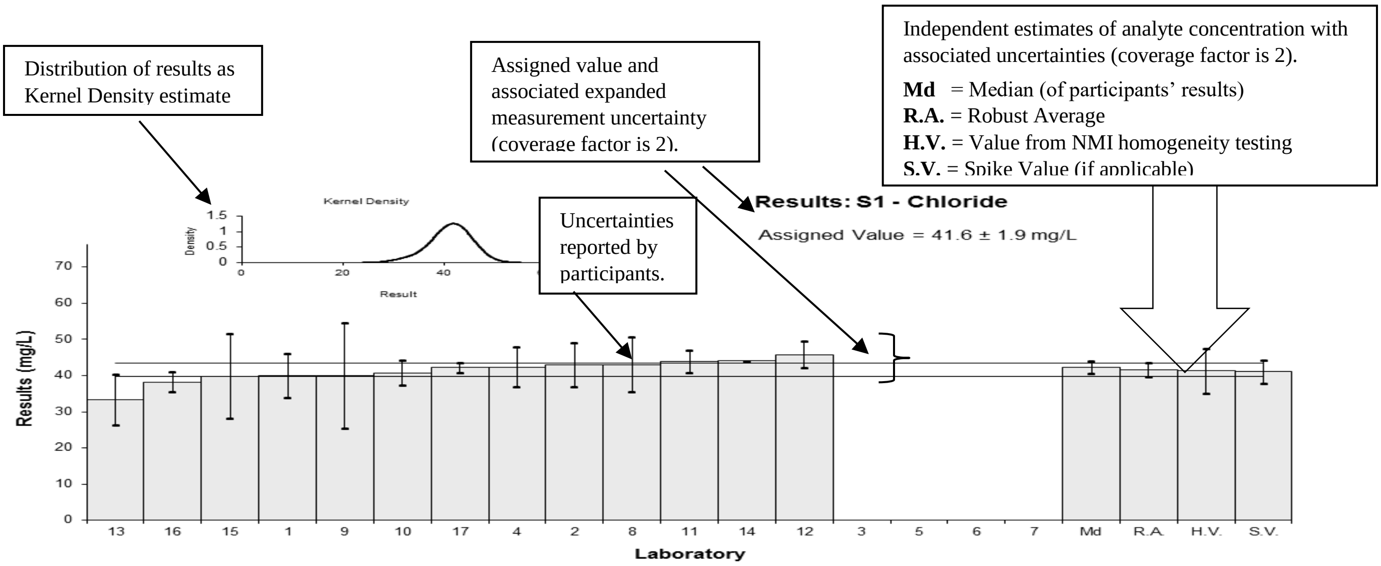
Table 2 Participants’ Comments

Participants’ Comments	Study Co-ordinator’s Response
Very useful study. Levels well within reach. Few more parameters like alkalies would have been good, which would have completed a normal full water balance.	Thank you for your feedback.

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 3 to 26 with resultant 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 25. An example chart with interpretation guide is shown in Figure 1.



Distribution of results as Kernel Density estimate

Assigned value and associated expanded measurement uncertainty (coverage factor is 2).

Uncertainties reported by participants.

Independent estimates of analyte concentration with associated uncertainties (coverage factor is 2).

Md = Median (of participants' results)
R.A. = Robust Average
H.V. = Value from NMI homogeneity testing
S.V. = Spike Value (if applicable)

Figure 1 Guide to Presentation of Results

5.2 Outliers and Extreme Outliers

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

5.3 Assigned Value

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

5.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'.[6]

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2015(E).[6]

5.5 Target Standard Deviation for Proficiency Assessment

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

$$\sigma = X * PCV \qquad \text{Equation 1}$$

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as the Thompson Horwitz equation.[7]

5.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 3. For each participants' result a z-score is calculated according to Equation 2 below:

$$z = \frac{(\chi - X)}{\sigma} \qquad \text{Equation 2}$$

Where:

z is z-score;
χ is participant's 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.

5.7 E_n-Score

An example of E_n-score calculation using data from the present study is given in Appendix 3. The E_n-score is complementary to the z-score in assessment of laboratory performance.

E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \qquad \text{Equation 3}$$

where:

E_n is E_n-score;
χ is a participant's result;
X is the study assigned value;
U_χ is the expanded uncertainty of the participant's 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.

5.8 Traceability and Measurement Uncertainty

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

6 TABLES AND FIGURES

Table 3

Sample Details

Sample	S1
Analyte	Bromide
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U	z	E_n
1	0.14	0.02	0.14	0.08
2	NT	NT		
3	<0.5	NR		
4	NT	NT		
5	<0.5	NR		
6	0.14	0.03	0.14	0.06
7	0.148	0.01	0.72	0.61
8	0.13	0.01	-0.58	-0.49
9	0.13	0.01	-0.58	-0.49
10	NT	NT		
11	<0.2	NR		
12	<0.2	NR		
13	NT	NT		
14	NT	NT		
15	<0.2	0.5		
16	<0.2	NR		
17	NT	NT		
18	<0.5	NR		
19	0.12	0.01	-1.30	-1.10
20	0.155	0.2	1.23	0.08
21	NT	NT		
22	NR	NR		

Statistics

Assigned Value	0.138	0.013
Spike Value	0.145	0.021
Homogeneity Value	0.147	0.022
Robust Average	0.138	0.013
Median	0.140	0.014
Mean	0.138	0.009
N	7	
Max	0.155	
Min	0.12	
Robust SD	0.013	
Robust CV	9.8%	

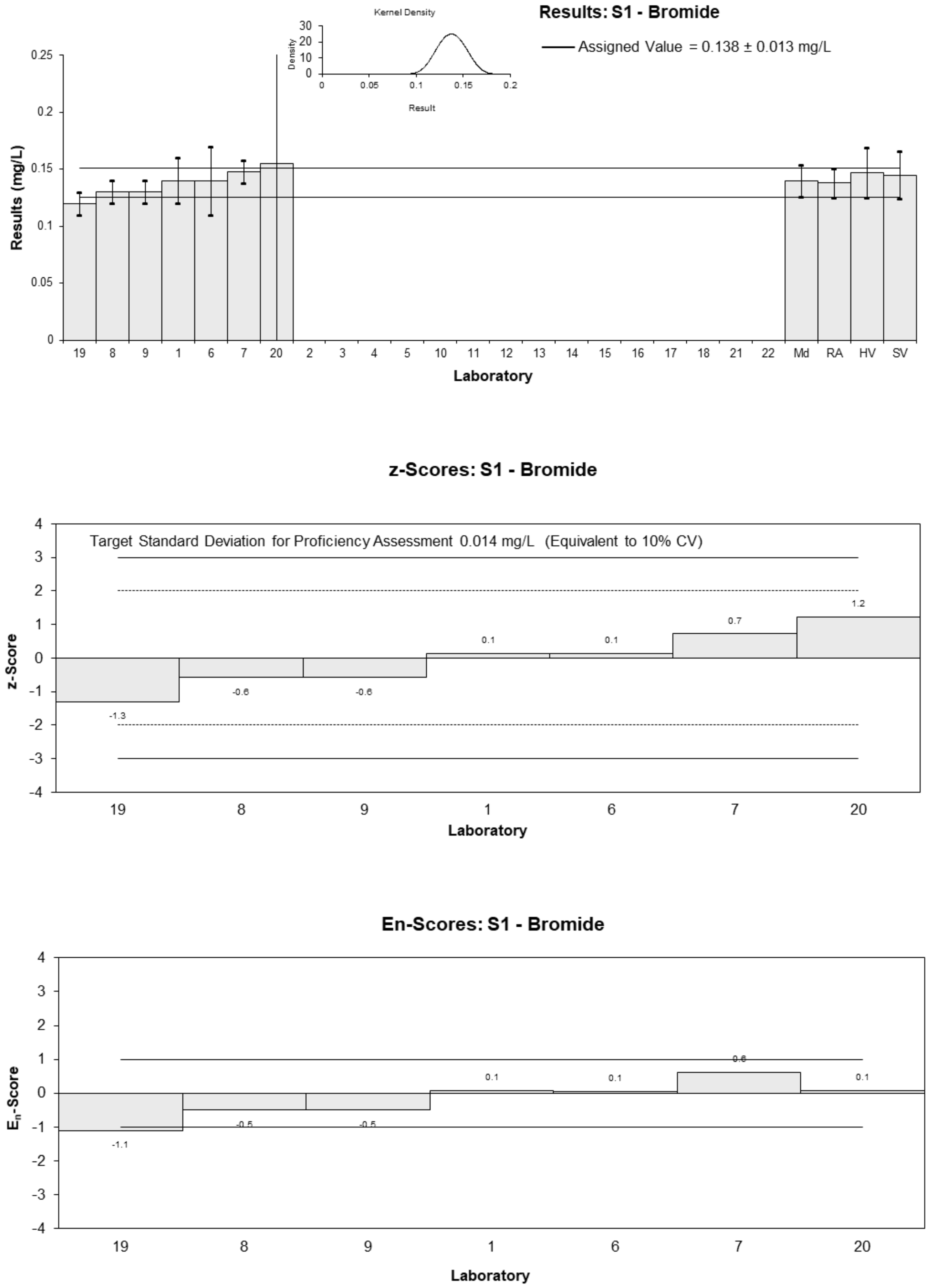

Results: S1 - Bromide
Assigned Value = 0.138 ± 0.013 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
19
8
9
1
6
7
20
2
3
4
5
10
11
12
13
14
15
16
17
18
21
22
Md
RA
HV
SV
z-Scores: S1 - Bromide
Target Standard Deviation for Proficiency Assessment 0.014 mg/L (Equivalent to 10% CV)
z-Score
-1.3
-0.6
-0.6
0.1
0.1
0.7
1.2
En-Scores: S1 - Bromide
E_n-Score
-1.1
-0.5
-0.5
0.1
0.1
0.6
0.1

Figure 2

Table 4

Sample Details

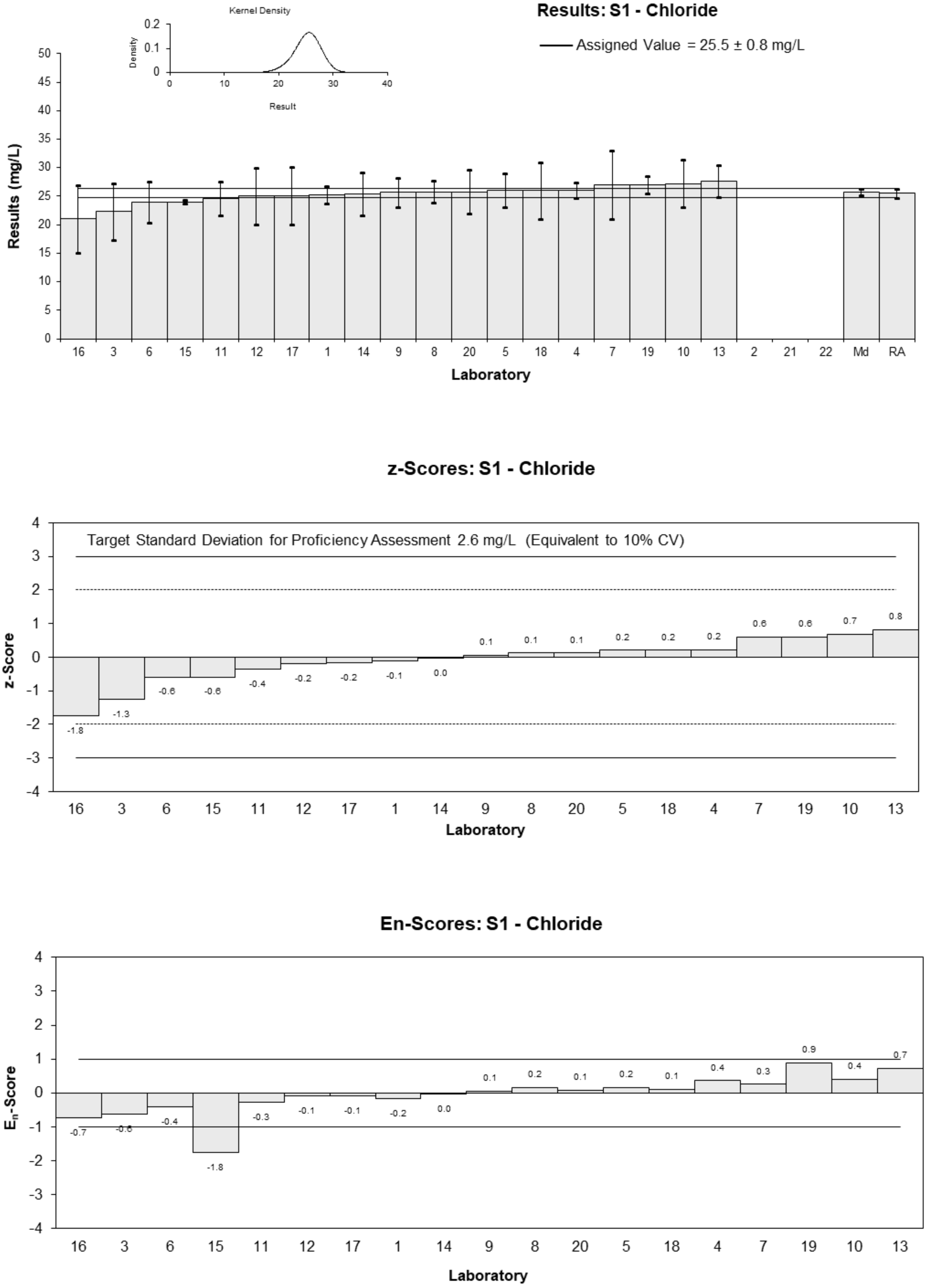
Sample	S1
Analyte	Chloride
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U	z	E_n
1	25.2	1.5	-0.12	-0.18
2	NT	NT		
3	22.3	5.0	-1.25	-0.63
4	26.0471	1.302355	0.21	0.36
5	26	3	0.20	0.16
6	24	3.6	-0.59	-0.41
7	27	6	0.59	0.25
8	25.8	1.9	0.12	0.15
9	25.65	2.57	0.06	0.06
10	27.2	4.2	0.67	0.40
11	24.6	3.0	-0.35	-0.29
12	25	5	-0.20	-0.10
13	27.6	2.8	0.82	0.72
14	25.4	3.81	-0.04	-0.03
15	24	0.3	-0.59	-1.76
16	21	6	-1.76	-0.74
17	25.10	5.02	-0.16	-0.08
18	26	5	0.20	0.10
19	27	1.5	0.59	0.88
20	25.8	3.8	0.12	0.08
21	NT	NT		
22	NR	NR		

Statistics

Assigned Value	25.5	0.8
Spike Value	Not Spiked	
Robust Average	25.5	0.8
Median	25.7	0.6
Mean	25.3	0.8
N	19	
Max	27.6	
Min	21	
Robust SD	1.4	
Robust CV	5.5%	



Results: S1 - Chloride

z-Scores: S1 - Chloride

En-Scores: S1 - Chloride

Figure 3

Table 5

Sample Details

Sample	S1
Analyte	Fluoride
Matrix	Potable Water
Unit	mg/L

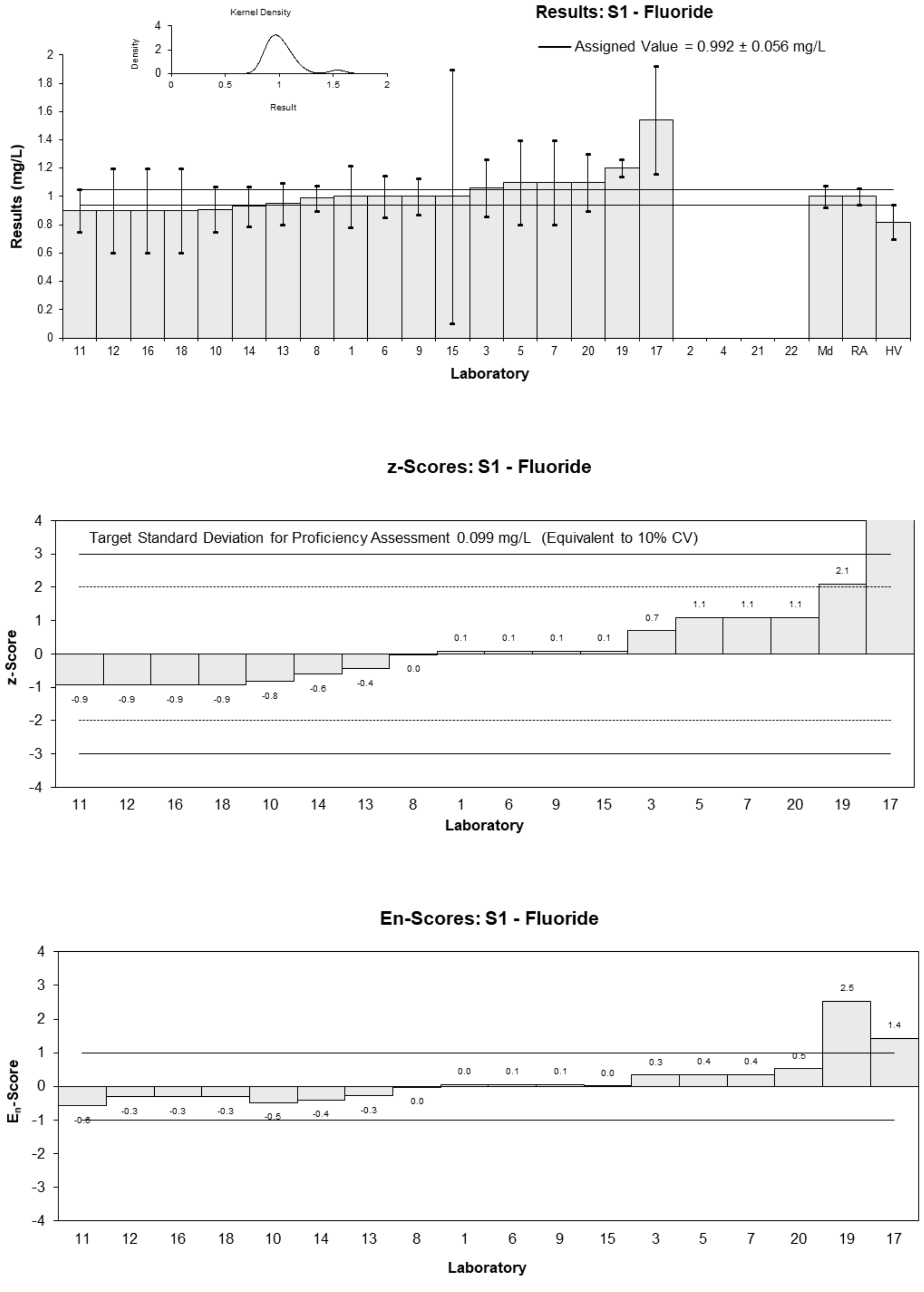
Participant Results

Lab. Code	Result	U	z	E_n
1	1	0.22	0.08	0.04
2	NT	NT		
3	1.06	0.2	0.69	0.33
4	NT	NT		
5	1.1	0.3	1.09	0.35
6	1.0	0.15	0.08	0.05
7	1.1	0.3	1.09	0.35
8	0.99	0.09	-0.02	-0.02
9	1.00	0.13	0.08	0.06
10	0.91	0.16	-0.83	-0.48
11	0.90	0.15	-0.93	-0.57
12	0.9	0.3	-0.93	-0.30
13	0.949	0.145	-0.43	-0.28
14	0.931	0.140	-0.61	-0.40
15	1	0.9	0.08	0.01
16	0.9	0.3	-0.93	-0.30
17*	1.54	0.38	5.52	1.43
18	0.9	0.3	-0.93	-0.30
19	1.2	0.06	2.10	2.53
20	1.1	0.2	1.09	0.52
21	NT	NT		
22	NR	NR		

* Outlier

Statistics

Assigned Value	0.992	0.056
Spike Value	Not Spiked	
Homogeneity Value	0.82	0.12
Robust Average	1.00	0.06
Median	1.00	0.08
Mean	1.03	0.07
N	18	
Max	1.54	
Min	0.9	
Robust SD	0.10	
Robust CV	10%	


Results: S1 - Fluoride
Assigned Value = 0.992 ± 0.056 mg/L
Kernel Density
Density
4
2
0
0
0.5
1
1.5
2
Result
Results (mg/L)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
11
12
16
18
10
14
13
8
1
6
9
15
3
5
7
20
19
17
2
4
21
22
Md
RA
HV
Laboratory
z-Scores: S1 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.099 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.9
-0.9
-0.9
-0.8
-0.6
-0.4
0.0
0.1
0.1
0.1
0.1
0.7
1.1
1.1
1.1
2.1
11
12
16
18
10
14
13
8
1
6
9
15
3
5
7
20
19
17
Laboratory
En-Scores: S1 - Fluoride
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.3
-0.3
-0.3
-0.5
-0.4
-0.3
0.0
0.0
0.1
0.1
0.0
0.3
0.4
0.4
0.5
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1.4
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13
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1
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9
15
3
5
7
20
19
17
Laboratory

Figure 4

Table 6

Sample Details

Sample	S1
Analyte	Iodide
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U
1	0.42	0.05
2	NT	NT
3	NT	NT
4	NT	NT
5	NT	NT
6	0.3	0.06
7	0.233	0.01
8	NR	NR
9	0.21	0.01
10	NT	NT
11	NT	NT
12	0.4	0.2
13	0.205	0.019
14	NT	NT
15	NT	NT
16	<0.5	NR
17	NT	NT
18	0.2	0.2
19	0.21	0.02
20	NR	NR
21	NT	NT
22	NR	NR

Statistics

Assigned Value	Not Set	
Spike Value	0.425	0.060
Robust Average	0.272	0.091
Median	0.222	0.025
Mean	0.272	0.064
N	8	
Max	0.42	
Min	0.2	
Robust SD	0.10	
Robust CV	38%	

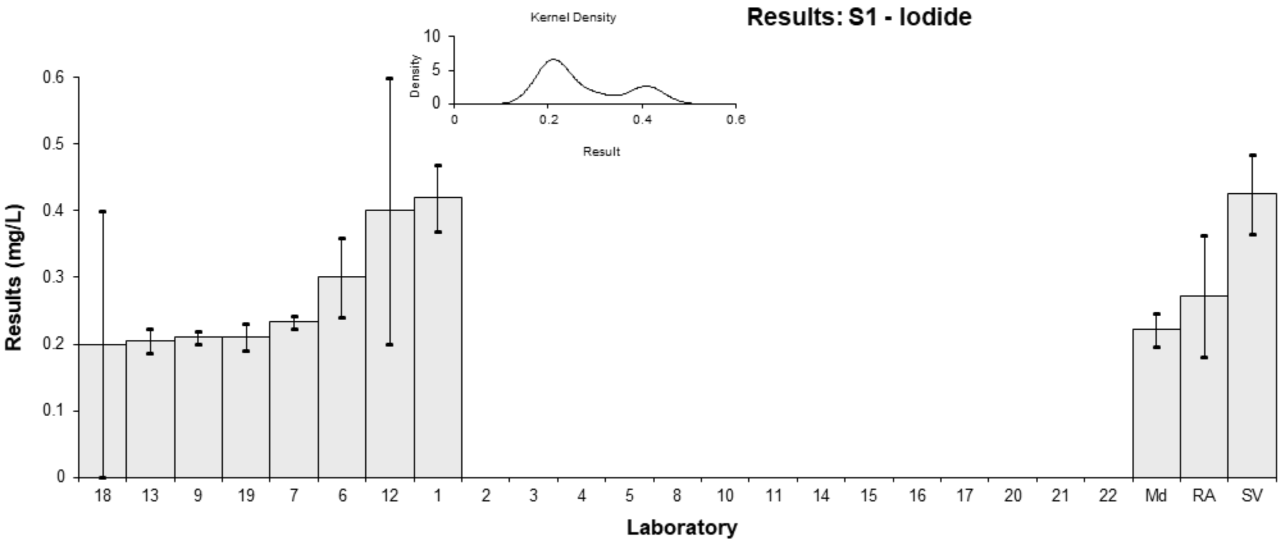

Results: S1 - Iodide
Kernel Density
Density
10
5
0
0
0.2
0.4
0.6
Result
Results (mg/L)
0.6
0.5
0.4
0.3
0.2
0.1
0
18
13
9
19
7
6
12
1
2
3
4
5
8
10
11
14
15
16
17
20
21
22
Md
RA
SV
Laboratory

Figure 5

Table 7

Sample Details

Sample	S1
Analyte	DOC
Matrix	Potable Water
Unit	mg/L

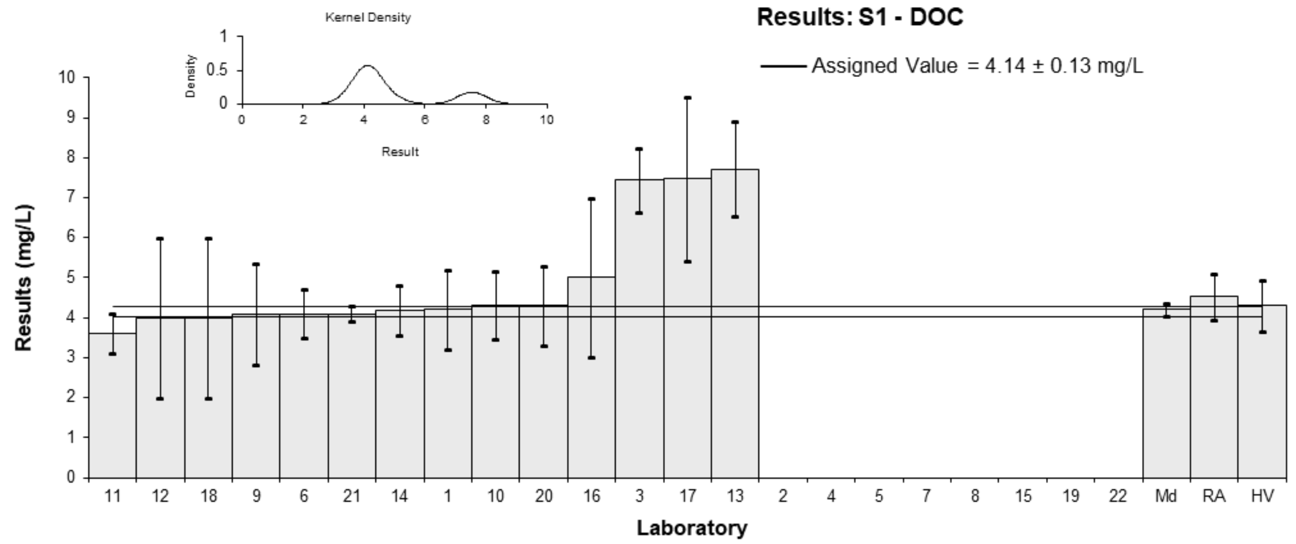
Participant Results

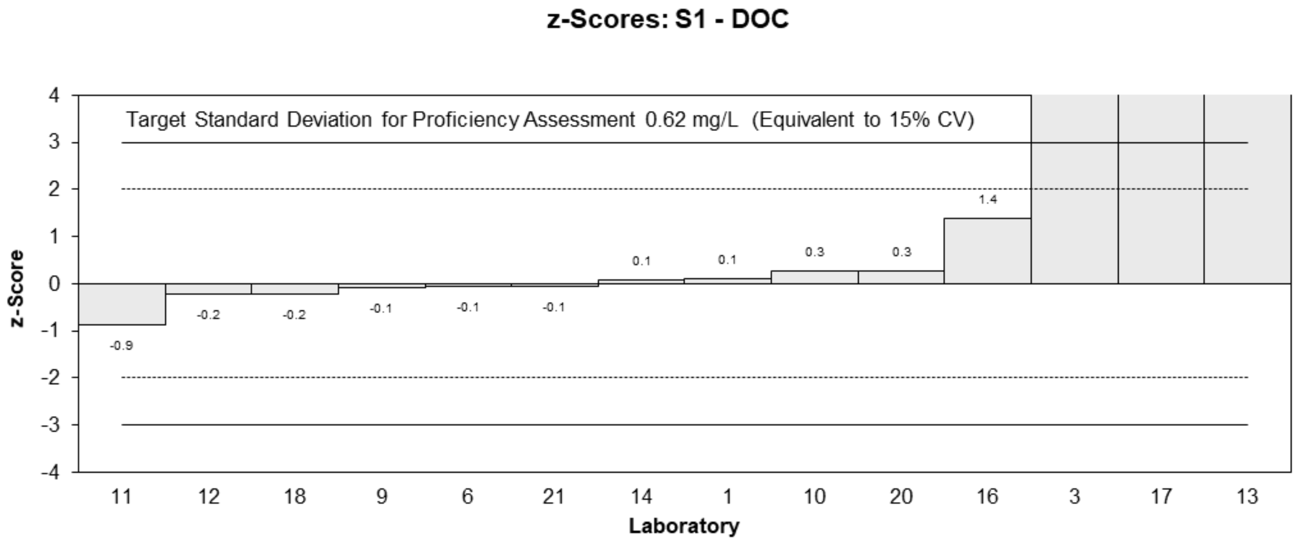
Lab. Code	Result	U	z	E_n
1	4.2	1	0.10	0.06
2	NT	NT		
3*	7.44	0.8	5.31	4.07
4	NT	NT		
5	NT	NT		
6	4.1	0.62	-0.06	-0.06
7	NT	NT		
8	NR	NR		
9	4.09	1.27	-0.08	-0.04
10	4.3	0.85	0.26	0.19
11	3.6	0.5	-0.87	-1.05
12	4	2	-0.23	-0.07
13*	7.72	1.19	5.76	2.99
14	4.19	0.629	0.08	0.08
15	NT	NT		
16	5	2	1.38	0.43
17*	7.48	2.05	5.38	1.63
18	4	2	-0.23	-0.07
19	NR	NR		
20	4.3	1	0.26	0.16
21	4.1	0.2	-0.06	-0.17
22	NR	NR		

* Outlier

Statistics

Assigned Value	4.14	0.13
Spike Value	Not Spiked	
Homogeneity Value	4.30	0.65
Robust Average	4.52	0.57
Median	4.20	0.15
Mean	4.89	0.78
N	14	
Max	7.72	
Min	3.6	
Robust SD	0.86	
Robust CV	19%	


Results: S1 - DOC
Assigned Value = 4.14 ± 0.13 mg/L
Kernel Density
Density
1
0.5
0
0
2
4
6
8
10
Result
Results (mg/L)
10
9
8
7
6
5
4
3
2
1
0
11
12
18
9
6
21
14
1
10
20
16
3
17
13
2
4
5
7
8
15
19
22
Md
RA
HV
Laboratory


z-Scores: S1 - DOC
Target Standard Deviation for Proficiency Assessment 0.62 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.2
-0.2
-0.1
-0.1
-0.1
0.1
0.1
0.3
0.3
1.4
11
12
18
9
6
21
14
1
10
20
16
3
17
13
Laboratory

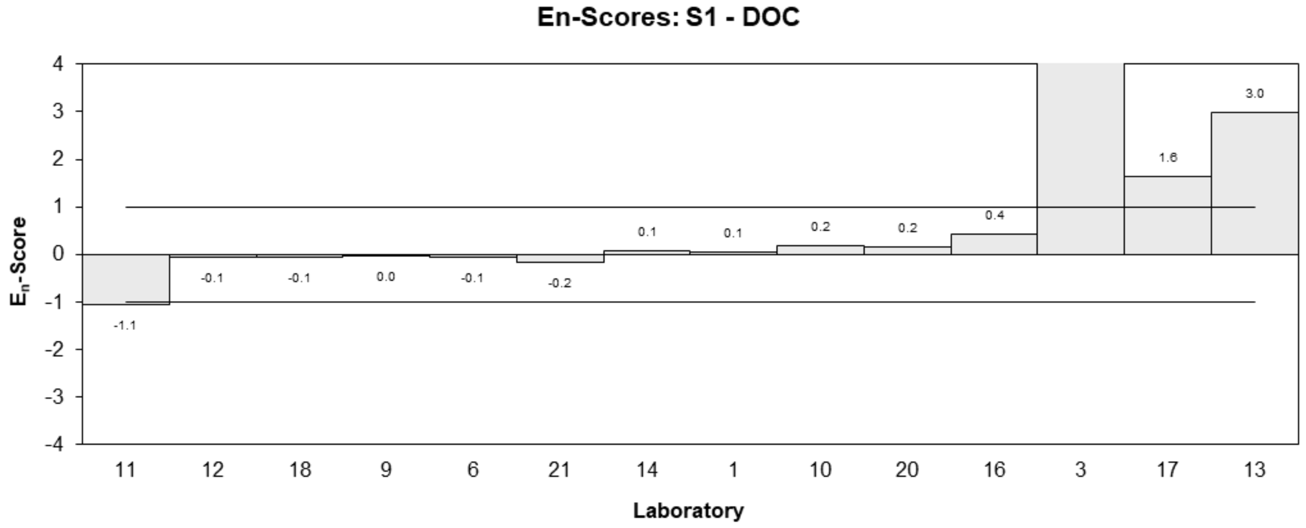

En-Scores: S1 - DOC
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-1.1
-0.1
-0.1
0.0
-0.1
-0.2
0.1
0.1
0.2
0.2
0.4
1.6
3.0
11
12
18
9
6
21
14
1
10
20
16
3
17
13
Laboratory

Figure 6

Table 8

Sample Details

Sample	S1
Analyte	Ammonia (as NH_3)
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U	z	E_n
1	NR	NR		
2	NT	NT		
3	0.209	0.03	-3.04	-4.34
4	0.3671379855	0.018356899275	-0.29	-0.52
5	NT	NT		
6	0.37	0.056	-0.24	-0.23
7	NT	NT		
8	NR	NR		
9	0.364	0.07	-0.35	-0.27
10	0.43	0.11	0.80	0.41
11	0.41	0.06	0.45	0.40
12	0.38	0.1	-0.07	-0.04
13	0.36	0.06	-0.42	-0.36
14	0.353	0.057	-0.54	-0.49
15	0.4	1.12	0.28	0.01
16	0.39	0.1	0.10	0.06
17	0.43	0.05	0.80	0.81
18	0.35	0.1	-0.59	-0.33
19	0.45	0.02	1.15	1.96
20	0.436	0.06	0.90	0.79
21	NT	NT		
22	0.34	0.005	-0.76	-1.60

Statistics

Assigned Value	0.384	0.027
Spike Value	0.362	0.062
Homogeneity Value	0.372	0.056
Robust Average	0.384	0.027
Median	0.375	0.023
Mean	0.377	0.028
N	16	
Max	0.45	
Min	0.209	
Robust SD	0.043	
Robust CV	11%	

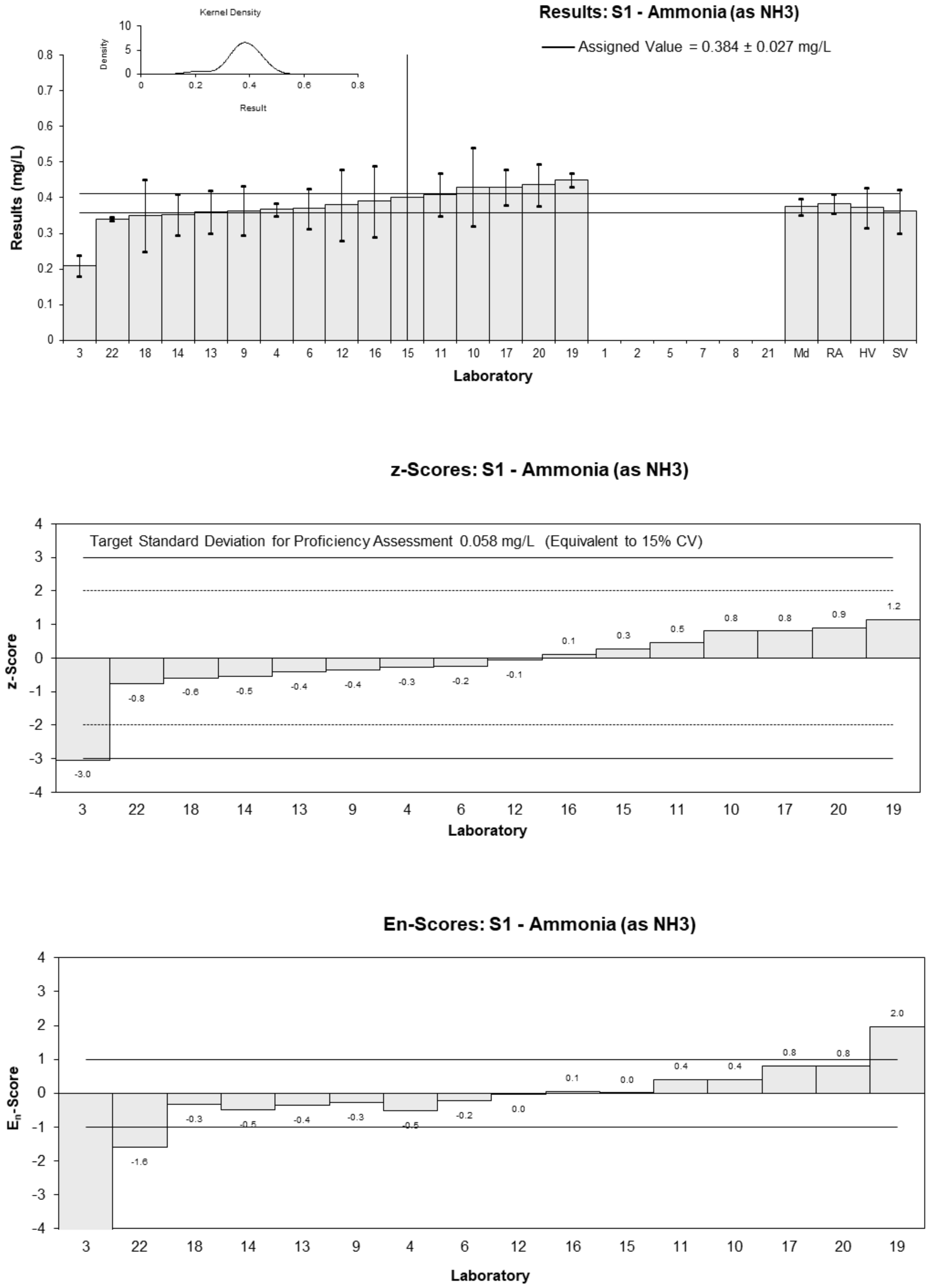

Results: S1 - Ammonia (as NH3)
Assigned Value = 0.384 ± 0.027 mg/L
Kernel Density
Density
Result
10
5
0
0.2
0.4
0.6
0.8
Results (mg/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
3
22
18
14
13
9
4
6
12
16
15
11
10
17
20
19
1
2
5
7
8
21
Md
RA
HV
SV
Laboratory
z-Scores: S1 - Ammonia (as NH3)
Target Standard Deviation for Proficiency Assessment 0.058 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-3.0
-0.8
-0.6
-0.5
-0.4
-0.4
-0.3
-0.2
-0.1
0.1
0.3
0.5
0.8
0.8
0.9
1.2
3
22
18
14
13
9
4
6
12
16
15
11
10
17
20
19
Laboratory
En-Scores: S1 - Ammonia (as NH3)
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.6
-0.3
-0.5
-0.4
-0.3
-0.5
-0.2
0.0
0.1
0.0
0.4
0.4
0.8
0.8
2.0
3
22
18
14
13
9
4
6
12
16
15
11
10
17
20
19
Laboratory

Figure 7

Table 9

Sample Details

Sample	S1
Analyte	Nitrate (as NO_3)
Matrix	Potable Water
Unit	mg/L

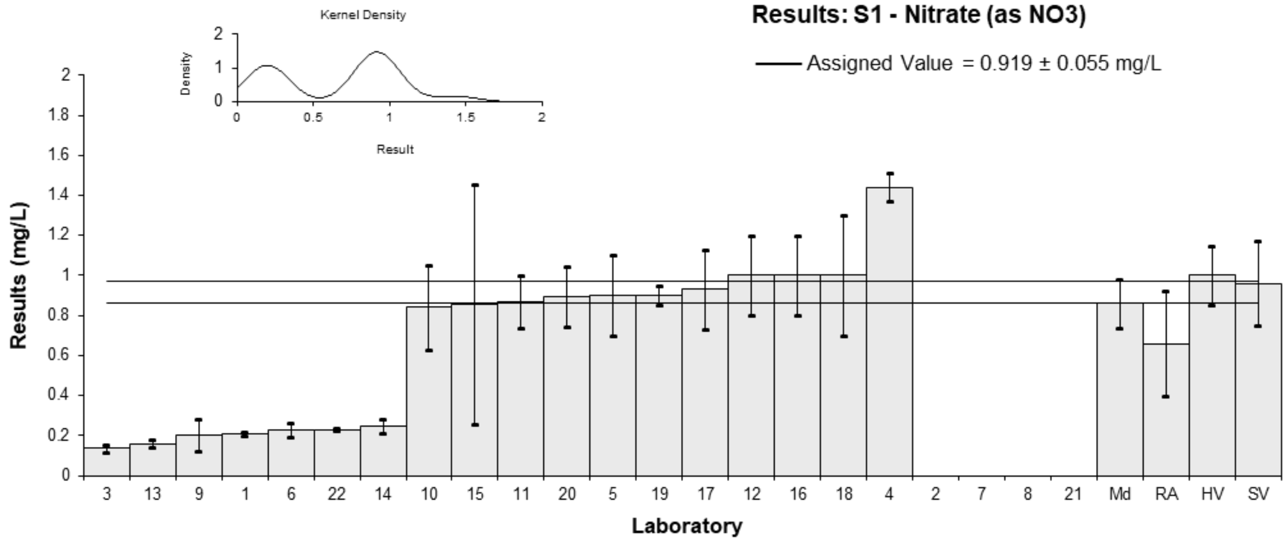
Participant Results

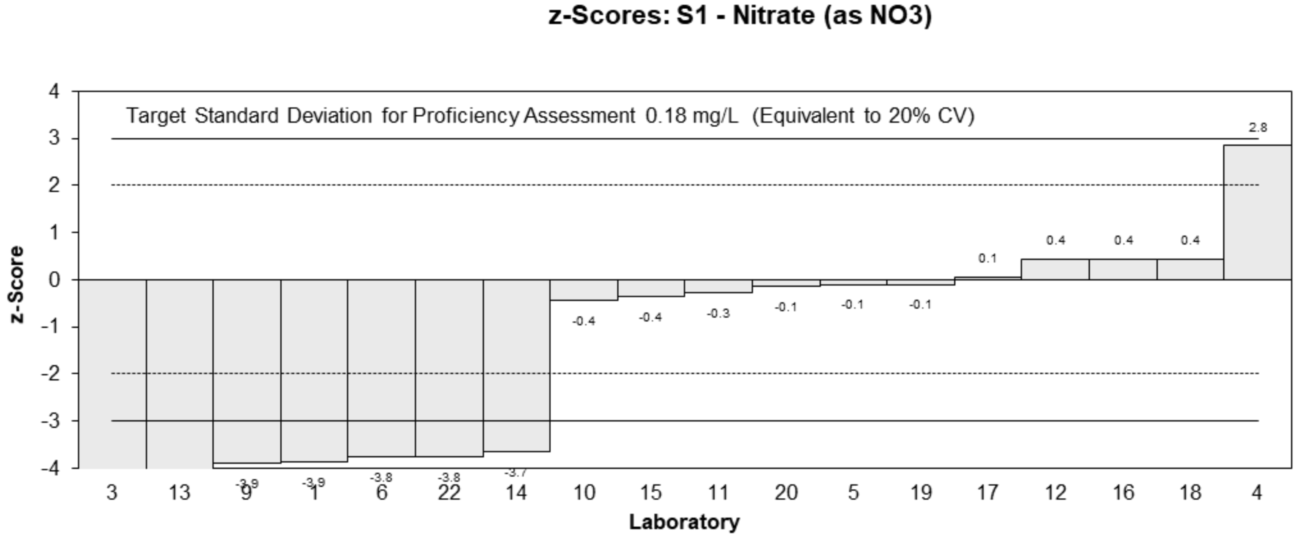
Lab. Code	Result	U	z	E_n
1*	0.21	0.01	-3.86	-12.68
2	NT	NT		
3*	0.137	0.02	-4.25	-13.36
4*	1.4409904	0.07204952	2.84	5.76
5	0.9	0.2	-0.10	-0.09
6*	0.23	0.035	-3.75	-10.57
7	NT	NT		
8	NR	NR		
9*	0.202	0.08	-3.90	-7.39
10	0.84	0.21	-0.43	-0.36
11	0.87	0.13	-0.27	-0.35
12	1.0	0.2	0.44	0.39
13*	0.16	0.02	-4.13	-12.97
14*	0.248	0.037	-3.65	-10.12
15	0.855	0.6	-0.35	-0.11
16	1.0	0.2	0.44	0.39
17	0.93	0.20	0.06	0.05
18	1.0	0.3	0.44	0.27
19	0.90	0.05	-0.10	-0.26
20	0.895	0.15	-0.13	-0.15
21	NT	NT		
22*	0.23	0.007	-3.75	-12.43

* Outlier

Statistics

Assigned Value	0.919	0.055
Spike Value	0.96	0.21
Homogeneity Value	1.00	0.15
Robust Average	0.66	0.26
Median	0.86	0.12
Mean	0.67	0.19
N	18	
Max	1.4409904	
Min	0.137	
Robust SD	0.45	
Robust CV	67%	


Results: S1 - Nitrate (as NO3)
Assigned Value = 0.919 ± 0.055 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3
13
9
1
6
22
14
10
15
11
20
5
19
17
12
16
18
4
2
7
8
21
Md
RA
HV
SV


z-Scores: S1 - Nitrate (as NO3)
Target Standard Deviation for Proficiency Assessment 0.18 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
-3.9
-3.9
-3.8
-3.8
-3.7
-0.4
-0.4
-0.3
-0.1
-0.1
-0.1
0.1
0.4
0.4
0.4
2.8
3
13
9
1
6
22
14
10
15
11
20
5
19
17
12
16
18
4

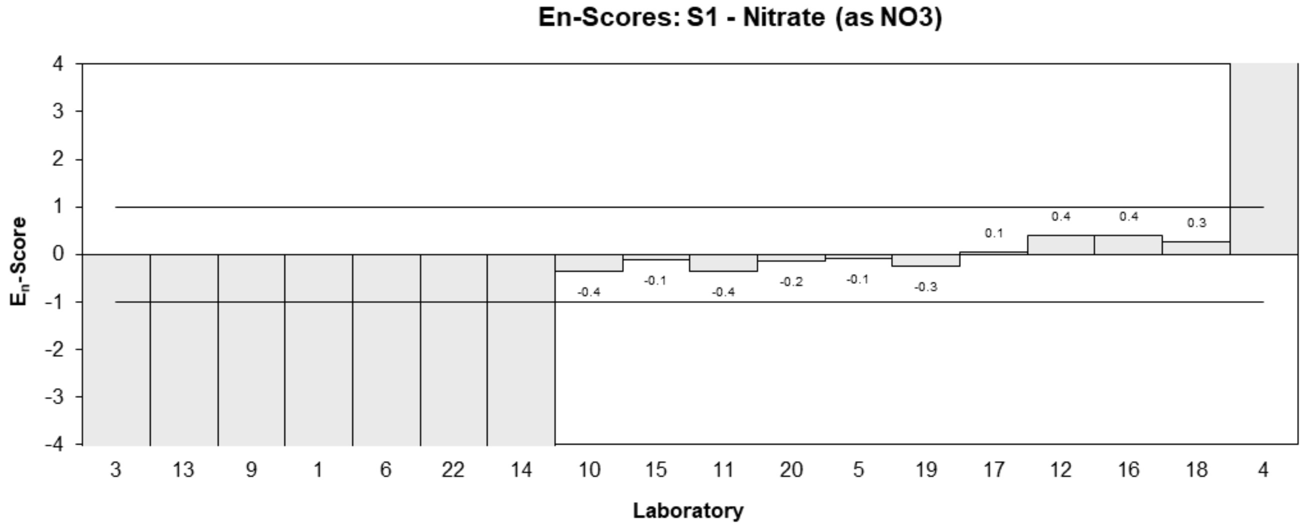

En-Scores: S1 - Nitrate (as NO3)
E_n-Score
Laboratory
-0.4
-0.1
-0.4
-0.2
-0.1
-0.3
0.1
0.4
0.4
0.3
3
13
9
1
6
22
14
10
15
11
20
5
19
17
12
16
18
4

Figure 8

Table 10

Sample Details

Sample	S1
Analyte	Nitrite (as NO_2)
Matrix	Potable Water
Unit	mg/L

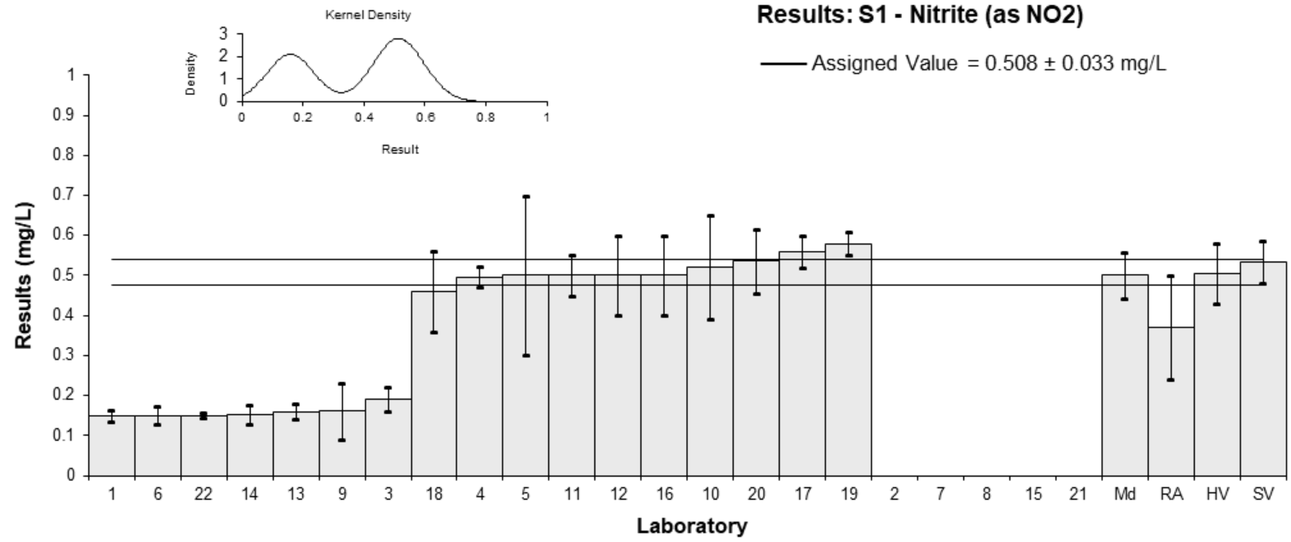
Participant Results

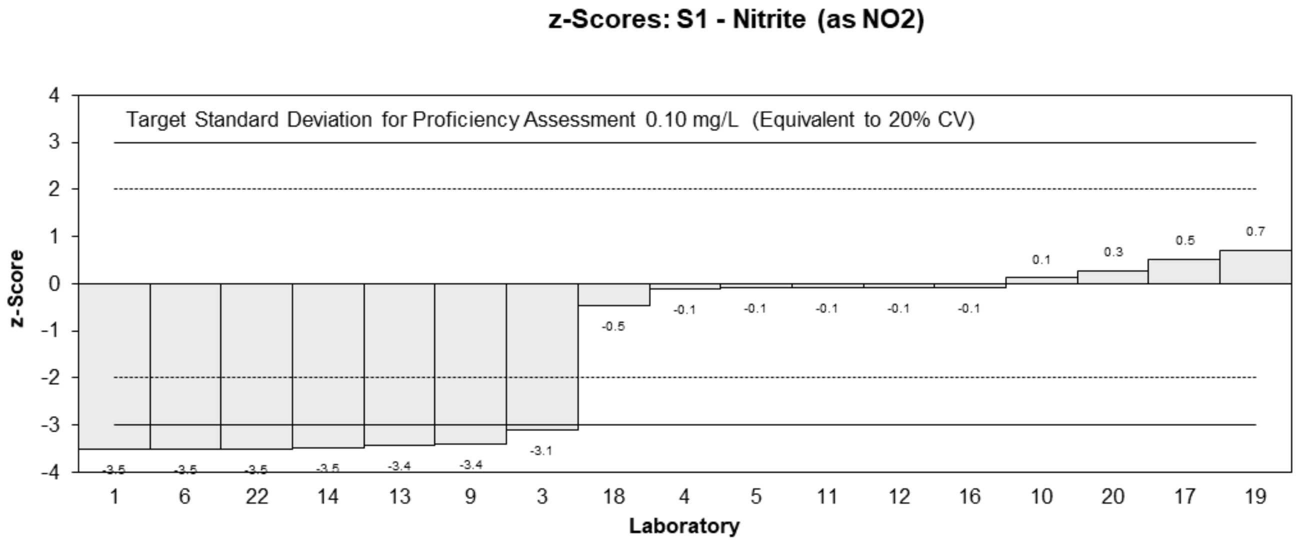
Lab. Code	Result	U	z	E_n
1*	0.15	0.014	-3.52	-9.99
2	NT	NT		
3	0.191	0.03	-3.12	-7.11
4	0.4961328	0.02480664	-0.12	-0.29
5	0.5	0.2	-0.08	-0.04
6*	0.15	0.023	-3.52	-8.90
7	NT	NT		
8	NR	NR		
9*	0.161	0.07	-3.42	-4.48
10	0.52	0.13	0.12	0.09
11	0.50	0.05	-0.08	-0.13
12	0.50	0.1	-0.08	-0.08
13*	0.16	0.02	-3.43	-9.02
14*	0.153	0.023	-3.49	-8.83
15	NT	NT		
16	0.50	0.1	-0.08	-0.08
17	0.56	0.04	0.51	1.00
18	0.46	0.1	-0.47	-0.46
19	0.58	0.03	0.71	1.61
20	0.536	0.08	0.28	0.32
21	NT	NT		
22*	0.15	0.007	-3.52	-10.61

* Outlier

Statistics

Assigned Value	0.508	0.033
Spike Value	0.533	0.052
Homogeneity Value	0.504	0.076
Robust Average	0.37	0.13
Median	0.496	0.057
Mean	0.369	0.089
N	17	
Max	0.58	
Min	0.15	
Robust SD	0.21	
Robust CV	56%	


Results: S1 - Nitrite (as NO2)
Assigned Value = 0.508 ± 0.033 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1
6
22
14
13
9
3
18
4
5
11
12
16
10
20
17
19
2
7
8
15
21
Md
RA
HV
SV


z-Scores: S1 - Nitrite (as NO2)
Target Standard Deviation for Proficiency Assessment 0.10 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
-3.5
-3.5
-3.5
-3.5
-3.4
-3.4
-3.1
-0.5
-0.1
-0.1
-0.1
-0.1
-0.1
0.1
0.3
0.5
0.7
1
6
22
14
13
9
3
18
4
5
11
12
16
10
20
17
19

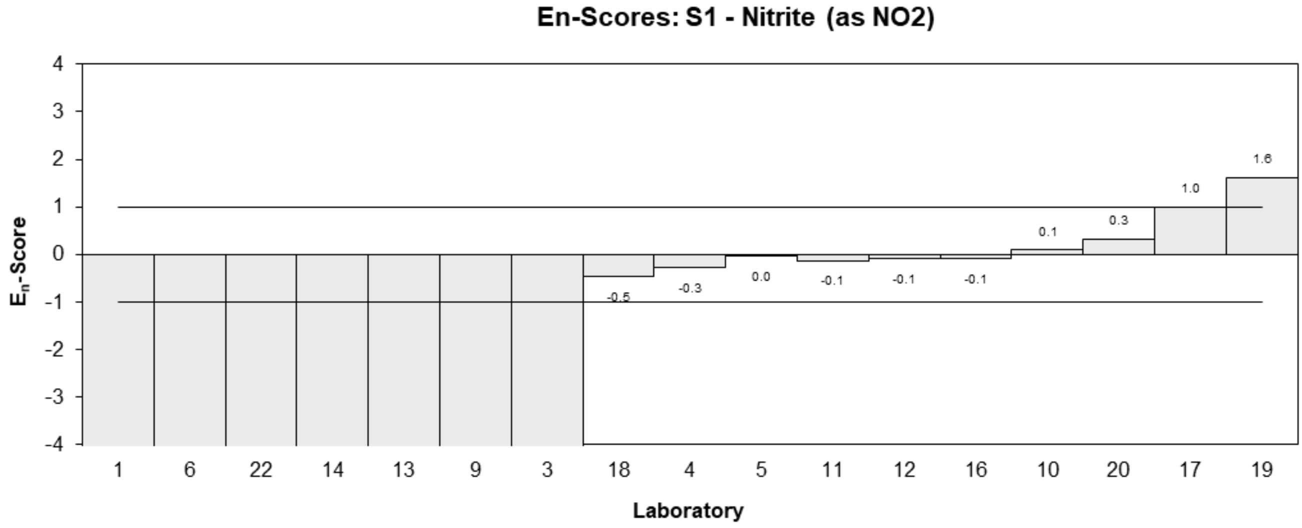

En-Scores: S1 - Nitrite (as NO2)
E_n-Score
Laboratory
-0.5
-0.3
0.0
-0.1
-0.1
-0.1
0.1
0.3
1.0
1.6
1
6
22
14
13
9
3
18
4
5
11
12
16
10
20
17
19

Figure 9

Table 11

Sample Details

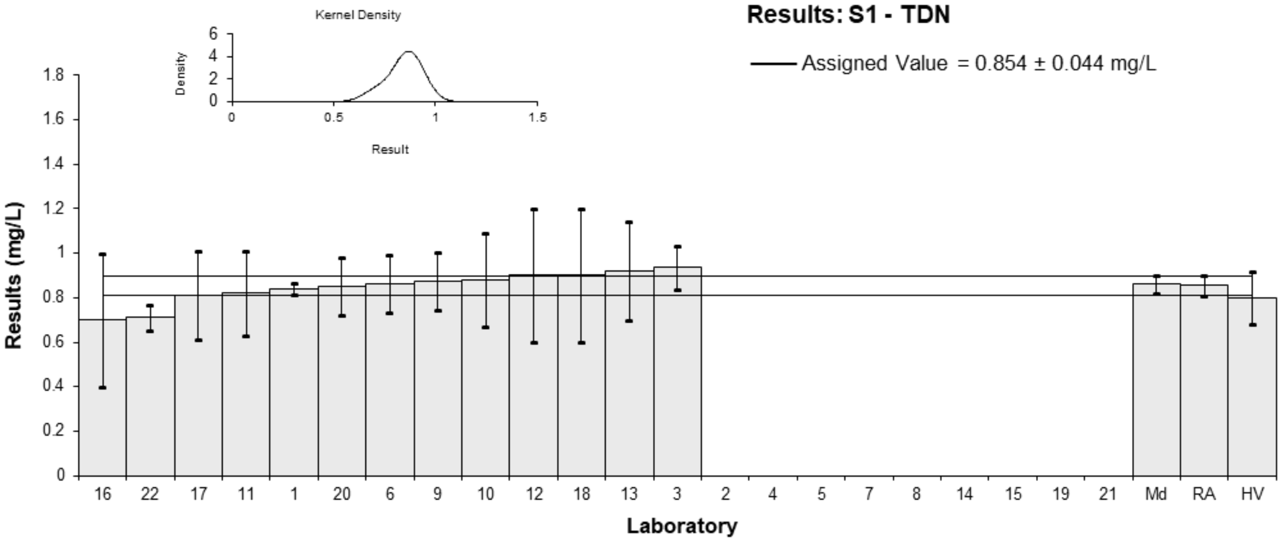
Sample	S1
Analyte	TDN
Matrix	Potable Water
Unit	mg/L

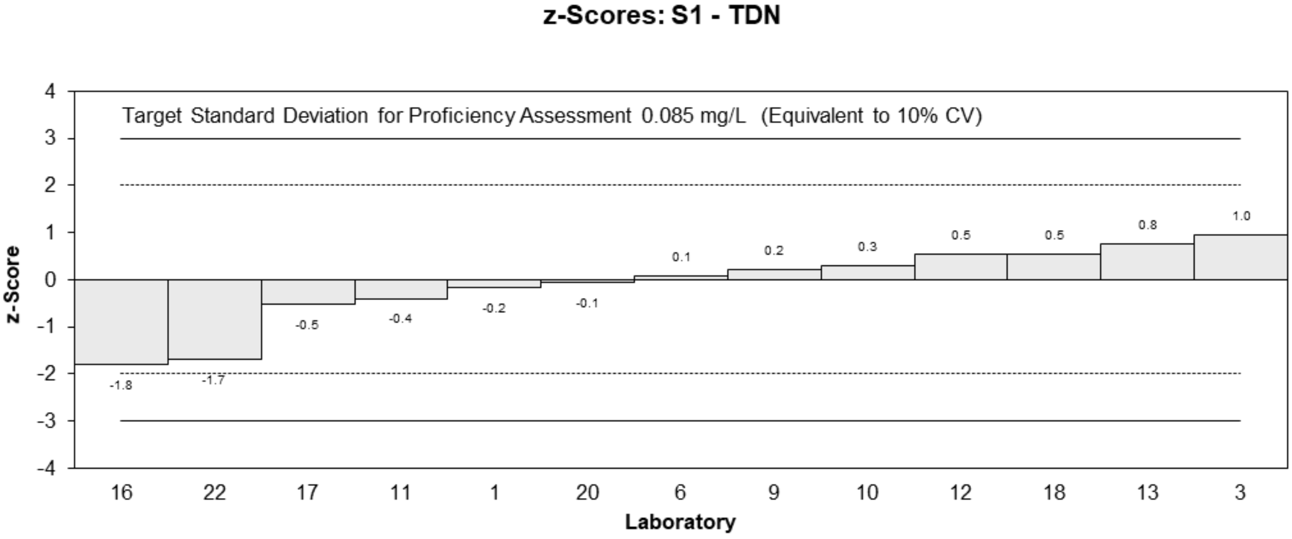
Participant Results

Lab. Code	Result	U	z	E_n
1	0.84	0.025	-0.16	-0.28
2	NT	NT		
3	0.935	0.1	0.95	0.74
4	NT	NT		
5	NT	NT		
6	0.86	0.13	0.07	0.04
7	NT	NT		
8	NR	NR		
9	0.873	0.13	0.22	0.14
10	0.88	0.21	0.30	0.12
11	0.82	0.19	-0.40	-0.17
12	0.9	0.3	0.54	0.15
13	0.92	0.22	0.77	0.29
14	NT	NT		
15	NT	NT		
16	0.7	0.3	-1.80	-0.51
17	0.81	0.20	-0.52	-0.21
18	0.9	0.3	0.54	0.15
19	NR	NR		
20	0.85	0.13	-0.05	-0.03
21	NT	NT		
22	0.71	0.06	-1.69	-1.94

Statistics

Assigned Value	0.854	0.044
Spike Value	Not Spiked	
Homogeneity Value	0.80	0.12
Robust Average	0.854	0.044
Median	0.860	0.041
Mean	0.846	0.040
N	13	
Max	0.935	
Min	0.7	
Robust SD	0.063	
Robust CV	7.4%	


Results: S1 - TDN
Assigned Value = 0.854 ± 0.044 mg/L
Kernel Density
Density
6
4
2
0
0
0.5
1
1.5
Result
Results (mg/L)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
16
22
17
11
1
20
6
9
10
12
18
13
3
2
4
5
7
8
14
15
19
21
Md
RA
HV
Laboratory


z-Scores: S1 - TDN
Target Standard Deviation for Proficiency Assessment 0.085 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.8
-1.7
-0.5
-0.4
-0.2
-0.1
0.1
0.2
0.3
0.5
0.5
0.8
1.0
16
22
17
11
1
20
6
9
10
12
18
13
3
Laboratory

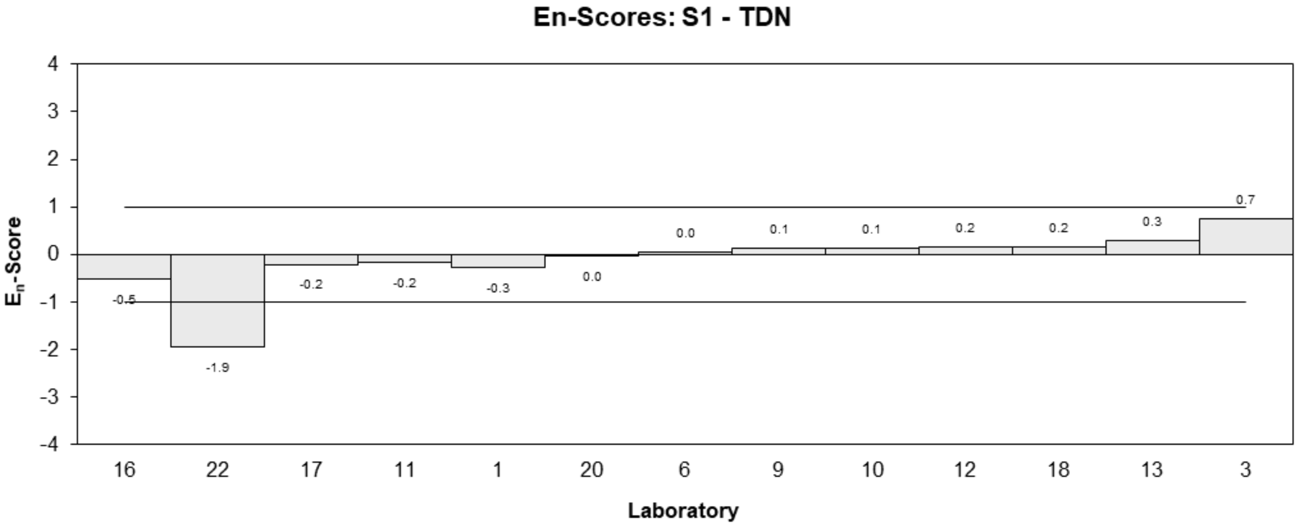

En-Scores: S1 - TDN
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-1.9
-0.2
-0.2
-0.3
0.0
0.0
0.1
0.1
0.2
0.2
0.3
0.7
16
22
17
11
1
20
6
9
10
12
18
13
3
Laboratory

Figure 10

Table 12

Sample Details

Sample	S1
Analyte	TDP
Matrix	Potable Water
Unit	mg/L

Participant Results

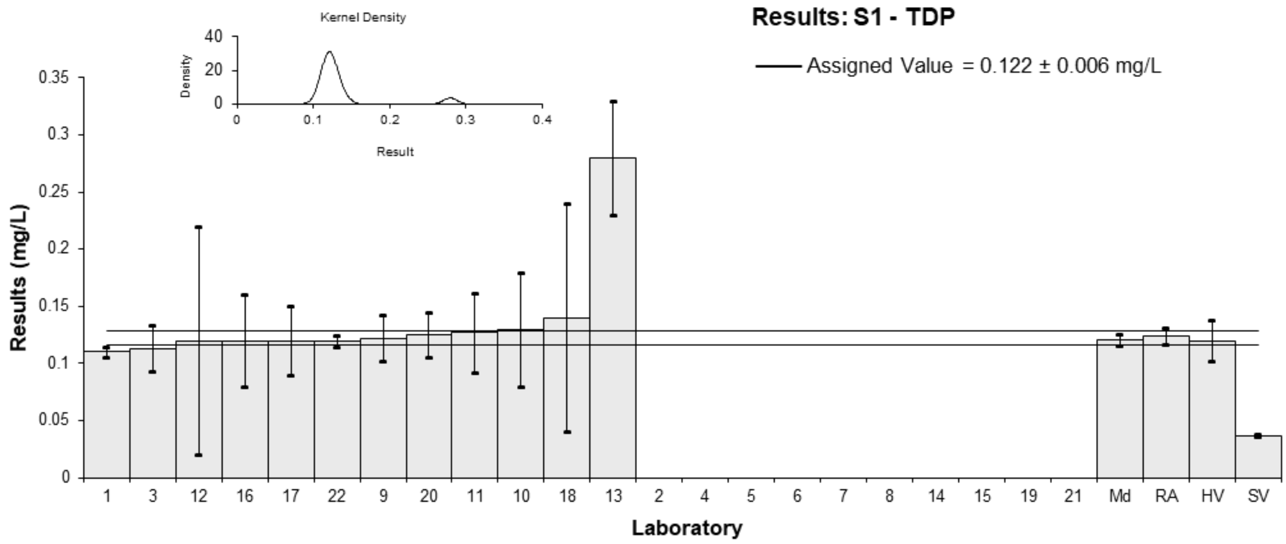
Lab. Code	Result	U	z	E_n
1	0.11	0.005	-0.98	-1.54
2	NT	NT		
3	0.113	0.02	-0.74	-0.43
4	NT	NT		
5	NT	NT		
6	NR	NR		
7	NT	NT		
8	NR	NR		
9	0.122	0.02	0.00	0.00
10	0.13	0.05	0.66	0.16
11	0.127	0.035	0.41	0.14
12	0.12	0.1	-0.16	-0.02
13*	0.28	0.05	12.95	3.14
14	NT	NT		
15	NT	NT		
16	0.12	0.04	-0.16	-0.05
17	0.12	0.03	-0.16	-0.07
18	0.14	0.1	1.48	0.18
19	NR	NR		
20	0.125	0.02	0.25	0.14
21	NT	NT		
22	0.12	0.005	-0.16	-0.26

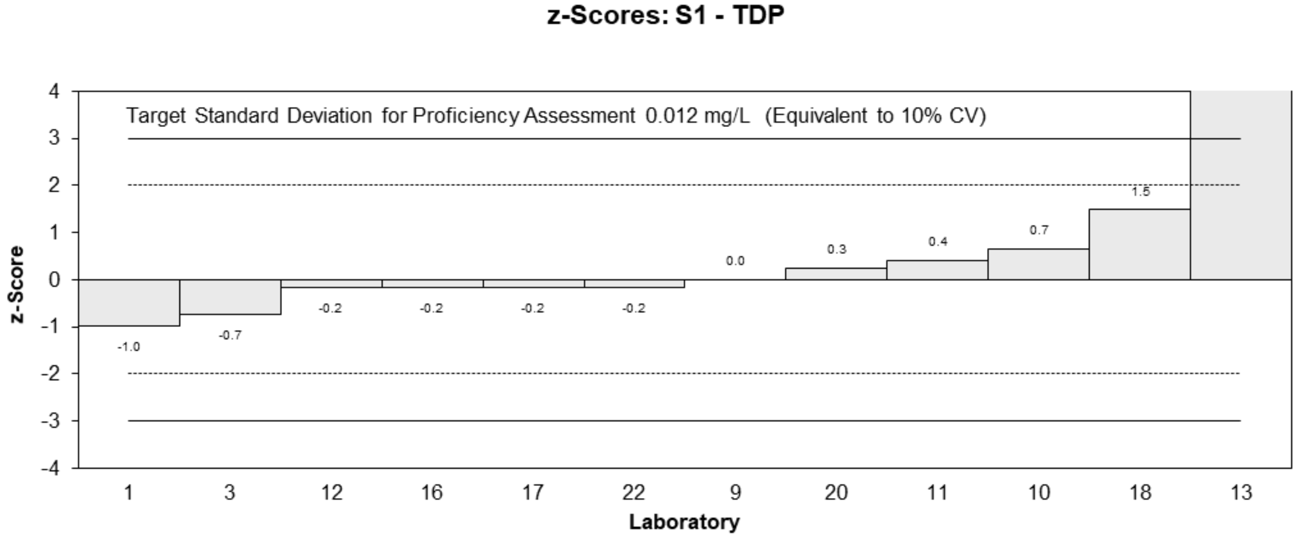
* Outlier

Statistics

Assigned Value	0.122	0.006
Spike Value*	0.0369	0.0011
Homogeneity Value	0.120	0.018
Robust Average	0.124	0.007
Median	0.121	0.005
Mean	0.136	0.027
N	12	
Max	0.28	
Min	0.11	
Robust SD	0.010	
Robust CV	8.1%	

*Incurred value not included


Results: S1 - TDP
Assigned Value = 0.122 ± 0.006 mg/L
Kernel Density
Density
40
20
0
0
0.1
0.2
0.3
0.4
Result
Results (mg/L)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
1
3
12
16
17
22
9
20
11
10
18
13
2
4
5
6
7
8
14
15
19
21
Md
RA
HV
SV
Laboratory


z-Scores: S1 - TDP
Target Standard Deviation for Proficiency Assessment 0.012 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.7
-0.2
-0.2
-0.2
-0.2
0.0
0.3
0.4
0.7
1.5
1
3
12
16
17
22
9
20
11
10
18
13
Laboratory

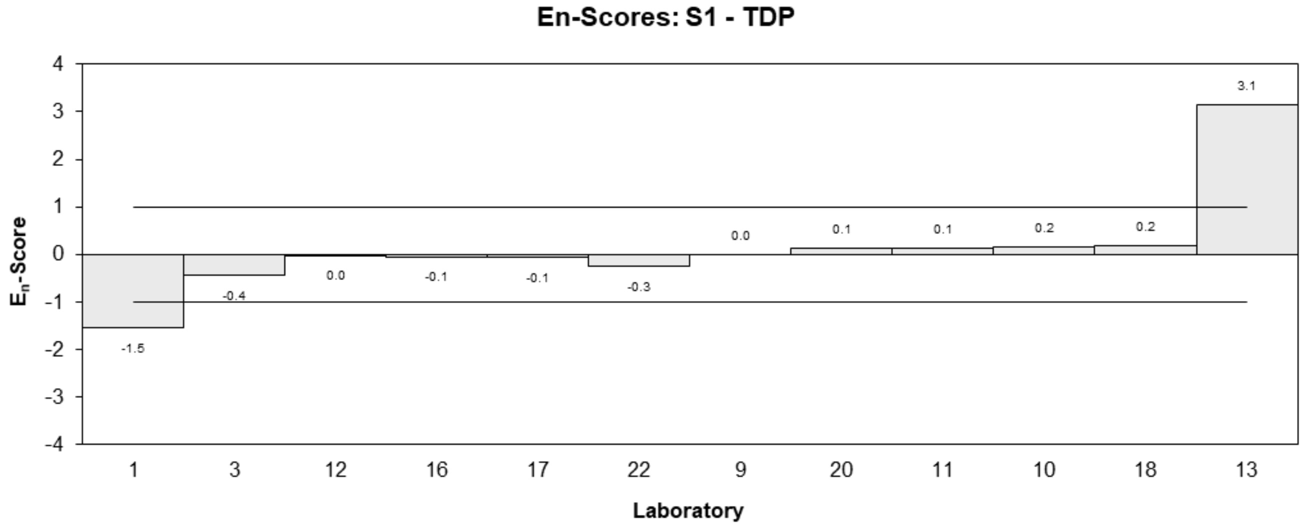

En-Scores: S1 - TDP
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-1.5
-0.4
0.0
-0.1
-0.1
-0.3
0.0
0.1
0.1
0.2
0.2
3.1
1
3
12
16
17
22
9
20
11
10
18
13
Laboratory

Figure 11

Table 13

Sample Details

Sample	S1
Analyte	Orthophosphate-P
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U	z	E_n
1	0.11	0.005	-0.52	-0.64
2	NT	NT		
3	0.113	0.02	-0.26	-0.14
4	NT	NT		
5	NT	NT		
6	0.12	0.018	0.34	0.20
7	0.13	0.02	1.21	0.65
8	NR	NR		
9	0.125	0.05	0.78	0.18
10	0.10	0.04	-1.38	-0.39
11	0.120	0.024	0.34	0.16
12	0.10	0.02	-1.38	-0.74
13	0.12	0.02	0.34	0.19
14	0.106	0.016	-0.86	-0.56
15	NT	NT		
16	0.10	0.05	-1.38	-0.32
17	0.12	0.03	0.34	0.13
18	0.12	0.1	0.34	0.04
19*	0.34	0.03	19.31	7.21
20	0.135	0.02	1.64	0.88
21	NT	NT		
22	0.12	0.005	0.34	0.42

* Outlier

Statistics

Assigned Value	0.116	0.008
Spike Value*	0.0829	0.0025
Homogeneity Value	0.120	0.018
Robust Average	0.117	0.008
Median	0.120	0.008
Mean	0.130	0.028
N	16	
Max	0.34	
Min	0.1	
Robust SD	0.013	
Robust CV	11%	

*Incurred value not included

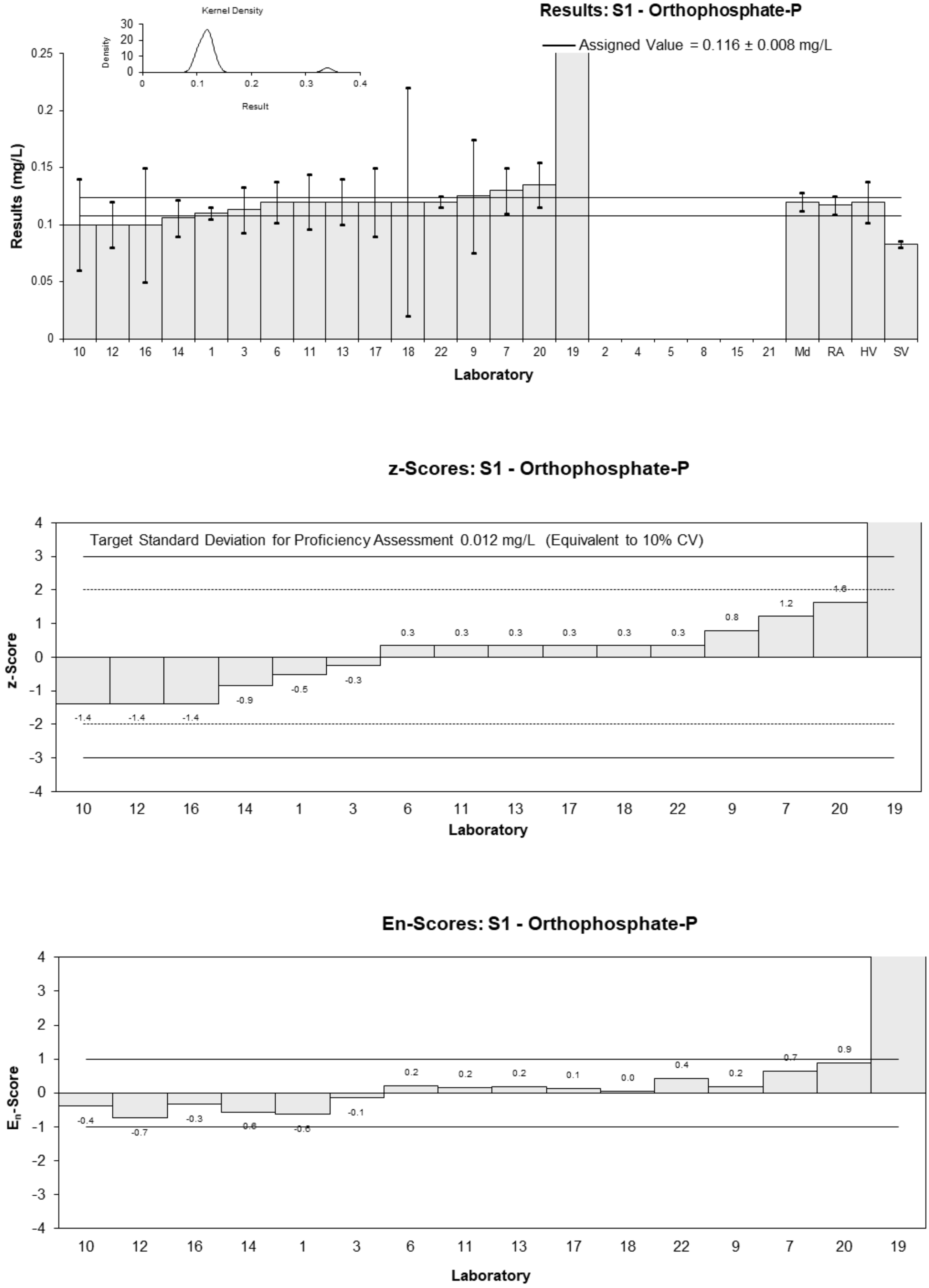

Results: S1 - Orthophosphate-P
Assigned Value = 0.116 ± 0.008 mg/L
Kernel Density
Density
30
20
10
0
0
0.1
0.2
0.3
0.4
Result
Results (mg/L)
0.25
0.2
0.15
0.1
0.05
0
10 12 16 14 1 3 6 11 13 17 18 22 9 7 20 19 2 4 5 8 15 21 Md RA HV SV
Laboratory
z-Scores: S1 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.012 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-1.4
-1.4
-0.9
-0.5
-0.3
0.3
0.3
0.3
0.3
0.3
0.3
0.8
1.2
1.6
10 12 16 14 1 3 6 11 13 17 18 22 9 7 20 19
Laboratory
En-Scores: S1 - Orthophosphate-P
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-0.4
-0.7
-0.3
-0.6
-0.6
-0.1
0.2
0.2
0.2
0.1
0.0
0.4
0.2
0.7
0.9
10 12 16 14 1 3 6 11 13 17 18 22 9 7 20 19
Laboratory

Figure 12

Table 14

Sample Details

Sample	S1
Analyte	Sulphate
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U	z	E_n
1	5.2	1.1	0.26	0.12
2	NT	NT		
3*	8.25	1.0	6.27	3.11
4	5.07966	0.253983	0.02	0.03
5	5.4	0.5	0.65	0.61
6	4.4	0.66	-1.32	-0.97
7	5.26	0.15	0.37	0.74
8	4.80	0.28	-0.53	-0.77
9	4.96	0.45	-0.22	-0.22
10	5.5	1.5	0.85	0.28
11	4.7	0.7	-0.73	-0.51
12	5	1	-0.14	-0.07
13	5.42	1.16	0.69	0.30
14	5.15	0.839	0.16	0.09
15	5.2	0.7	0.26	0.18
16	5	3	-0.14	-0.02
17	4.72	1.37	-0.69	-0.25
18	4	2	-2.11	-0.53
19	5.6	0.30	1.05	1.45
20	5.15	0.8	0.16	0.10
21	NT	NT		
22	NR	NR		

* Outlier

Statistics

Assigned Value	5.07	0.21
Spike Value	Not Spiked	
Robust Average	5.10	0.22
Median	5.15	0.21
Mean	5.20	0.38
N	19	
Max	8.25	
Min	4	
Robust SD	0.39	
Robust CV	7.6%	

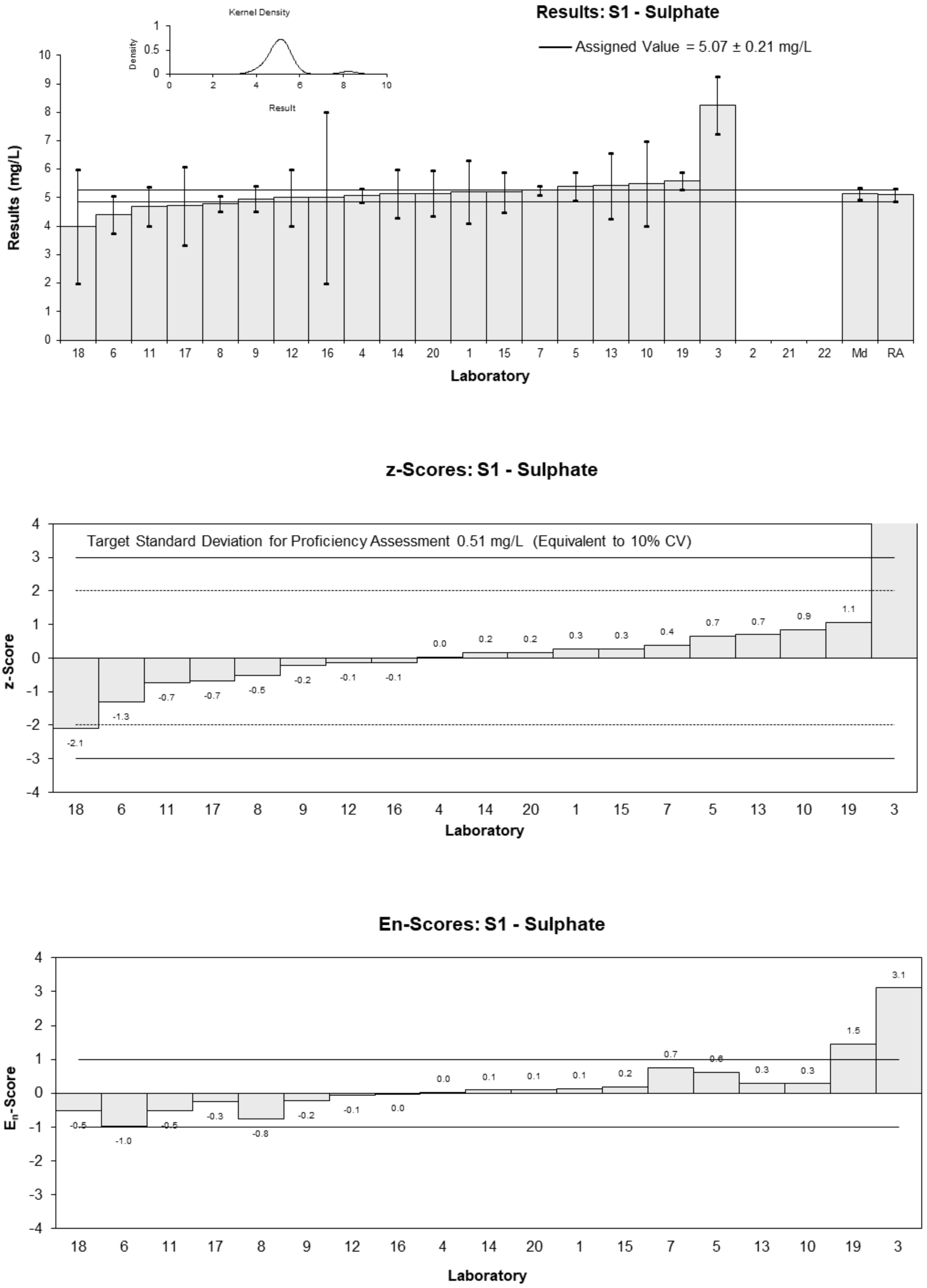

Results: S1 - Sulphate
Assigned Value = 5.07 ± 0.21 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
18 6 11 17 8 9 12 16 4 14 20 1 15 7 5 13 10 19 3 2 21 22 Md RA
z-Scores: S1 - Sulphate
Target Standard Deviation for Proficiency Assessment 0.51 mg/L (Equivalent to 10% CV)
z-Score
-2.1 -1.3 -0.7 -0.7 -0.5 -0.2 -0.1 -0.1 0.0 0.2 0.2 0.3 0.3 0.4 0.7 0.7 0.9 1.1
18 6 11 17 8 9 12 16 4 14 20 1 15 7 5 13 10 19 3
Laboratory
En-Scores: S1 - Sulphate
E_n-Score
-0.5 -1.0 -0.5 -0.3 -0.8 -0.2 -0.1 0.0 0.0 0.1 0.1 0.1 0.2 0.7 0.6 0.3 0.3 1.5 3.1
18 6 11 17 8 9 12 16 4 14 20 1 15 7 5 13 10 19 3
Laboratory

Figure 13

Table 15

Sample Details

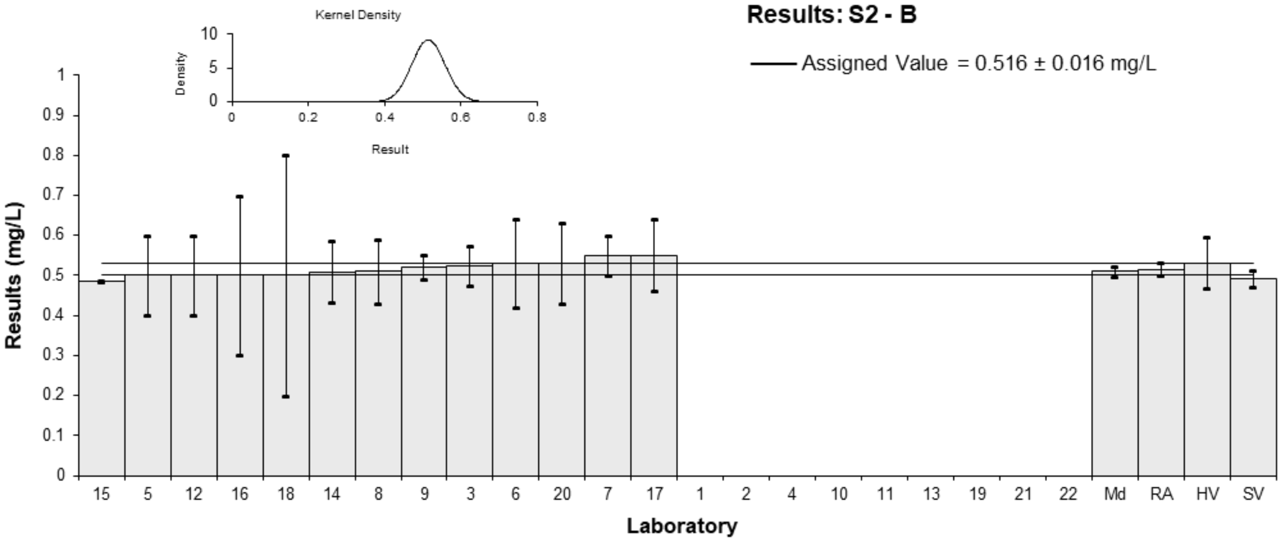
Sample	S2
Analyte	B
Matrix	Potable Water
Unit	mg/L

Participant Results

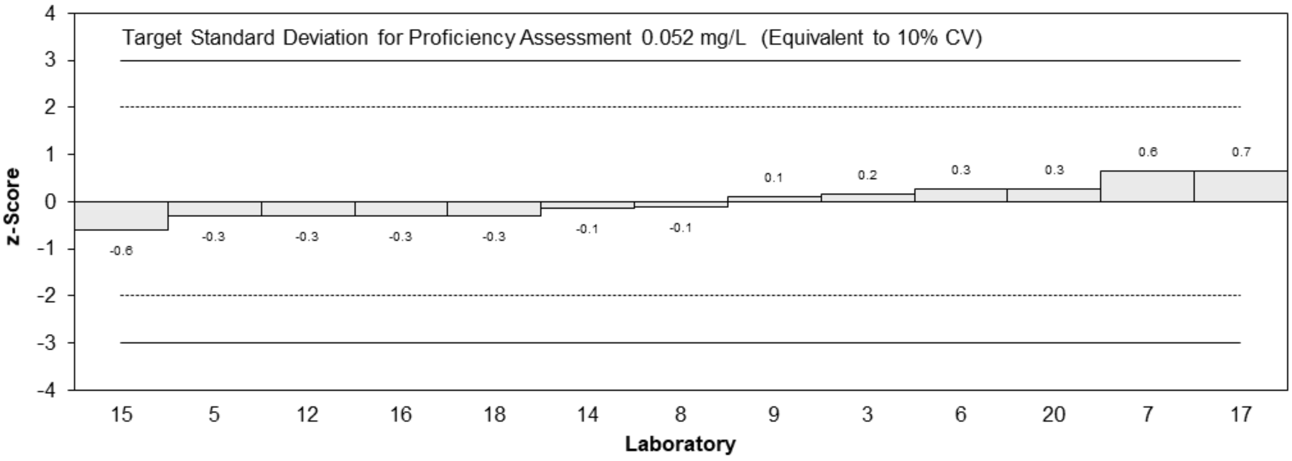
Lab. Code	Result	U	z	E_n
1	NT	NT		
2	NT	NT		
3	0.525	0.05	0.17	0.17
4	NT	NT		
5	0.5	0.1	-0.31	-0.16
6	0.53	0.11	0.27	0.13
7	0.549	0.05	0.64	0.63
8	0.51	0.08	-0.12	-0.07
9	0.5213	0.03	0.10	0.16
10	NT	NT		
11	NR	NR		
12	0.50	0.1	-0.31	-0.16
13	NT	NT		
14	0.509	0.076	-0.14	-0.09
15	0.485	0.002	-0.60	-1.92
16	0.50	0.2	-0.31	-0.08
17	0.55	0.09	0.66	0.37
18	0.5	0.3	-0.31	-0.05
19	NT	NT		
20	0.53	0.1	0.27	0.14
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	0.516	0.016
Spike Value	0.493	0.021
Homogeneity Value	0.532	0.064
Robust Average	0.516	0.016
Median	0.510	0.012
Mean	0.516	0.011
N	13	
Max	0.55	
Min	0.485	
Robust SD	0.023	
Robust CV	4.4%	



z-Scores: S2 - B



En-Scores: S2 - B

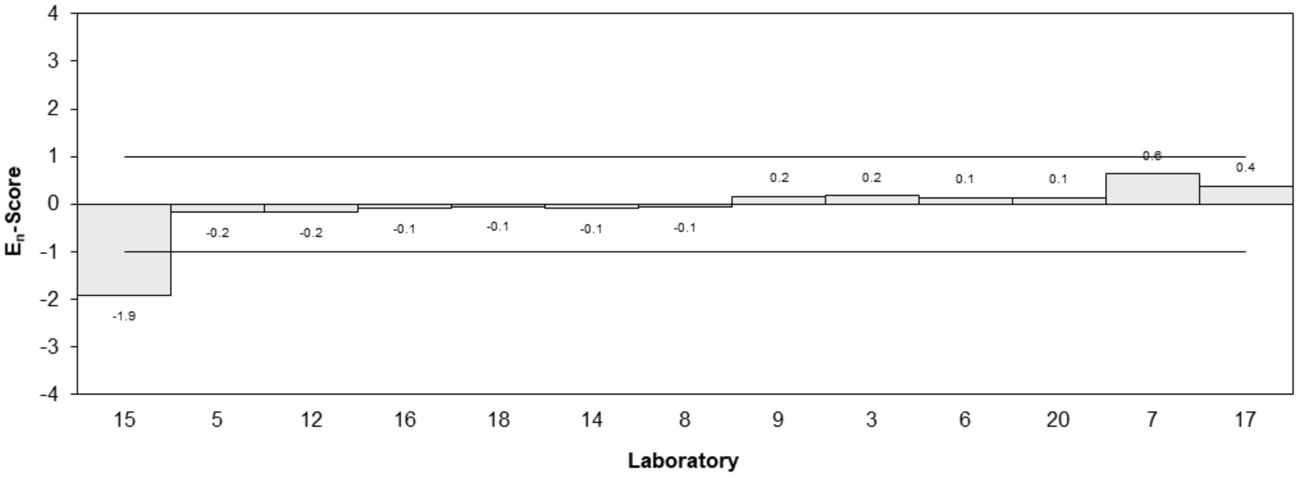


Figure 14

Table 16

Sample Details

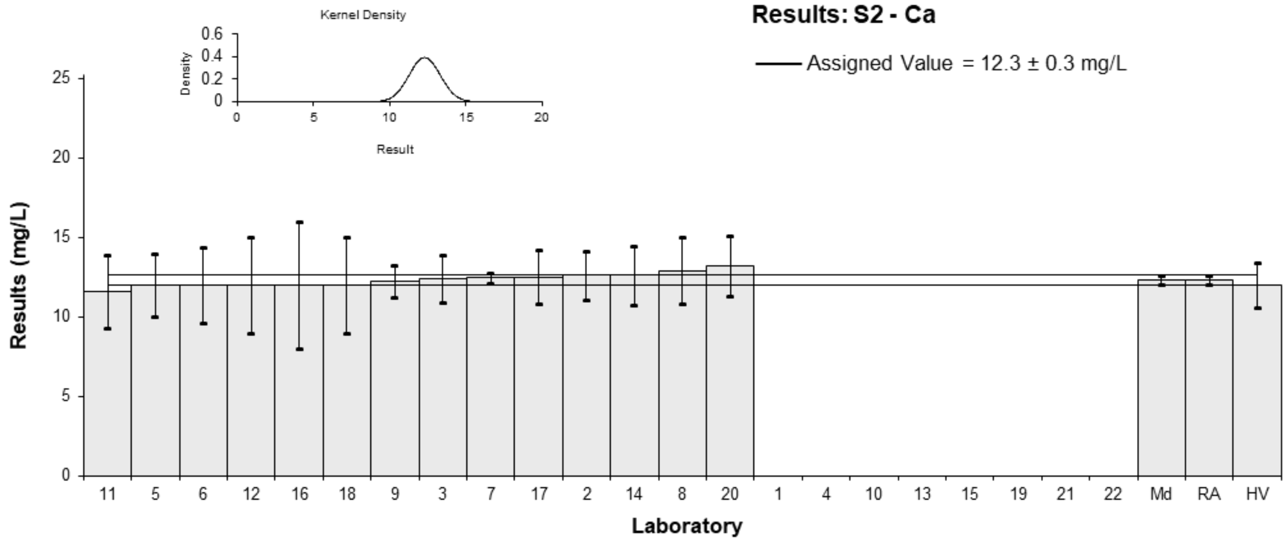
Sample	S2
Analyte	Ca
Matrix	Potable Water
Unit	mg/L

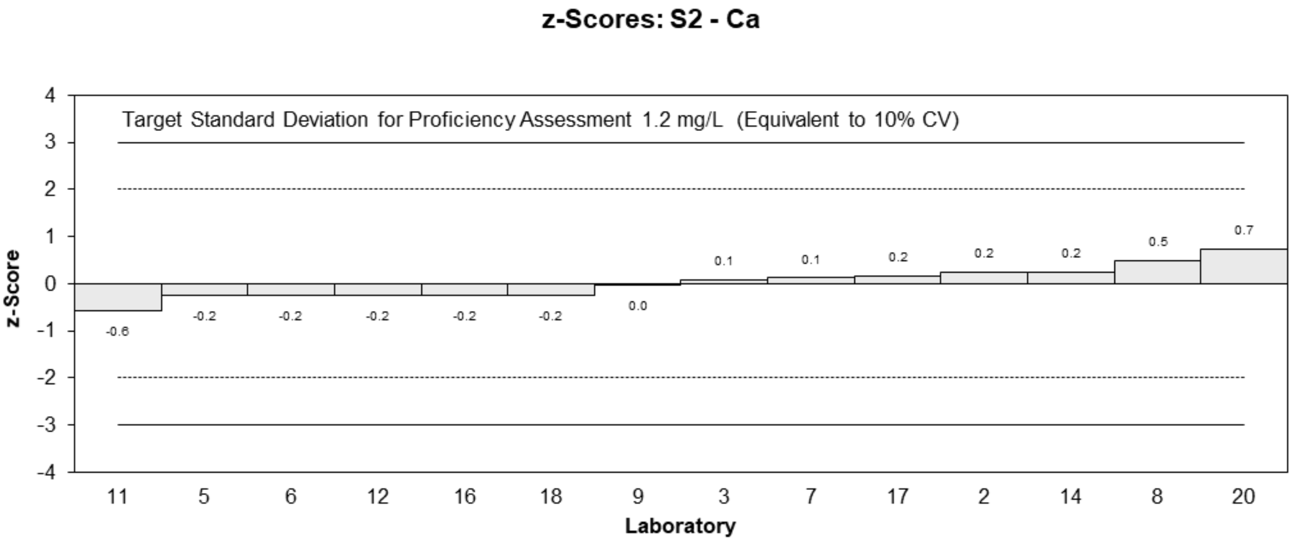
Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	12.6	1.5	0.24	0.20
3	12.4	1.5	0.08	0.07
4	NT	NT		
5	12	2	-0.24	-0.15
6	12	2.4	-0.24	-0.12
7	12.45	0.30	0.12	0.35
8	12.9	2.1	0.49	0.28
9	12.2473	0.98	-0.04	-0.05
10	NT	NT		
11	11.6	2.3	-0.57	-0.30
12	12	3	-0.24	-0.10
13	NT	NT		
14	12.6	1.89	0.24	0.16
15	NT	NT		
16	12	4	-0.24	-0.07
17	12.5	1.70	0.16	0.12
18	12	3	-0.24	-0.10
19	NT	NT		
20	13.2	1.9	0.73	0.47
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	12.3	0.3
Spike Value	Not Spiked	
Homogeneity Value	12.0	1.4
Robust Average	12.3	0.3
Median	12.3	0.3
Mean	12.3	0.2
N	14	
Max	13.2	
Min	11.6	
Robust SD	0.44	
Robust CV	3.5%	


Results: S2 - Ca
Assigned Value = 12.3 ± 0.3 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
11 5 6 12 16 18 9 3 7 17 2 14 8 20 1 4 10 13 15 19 21 22 Md RA HV


z-Scores: S2 - Ca
Target Standard Deviation for Proficiency Assessment 1.2 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 5 6 12 16 18 9 3 7 17 2 14 8 20
-0.6 -0.2 -0.2 -0.2 -0.2 -0.2 0.0 0.1 0.1 0.2 0.2 0.2 0.5 0.7

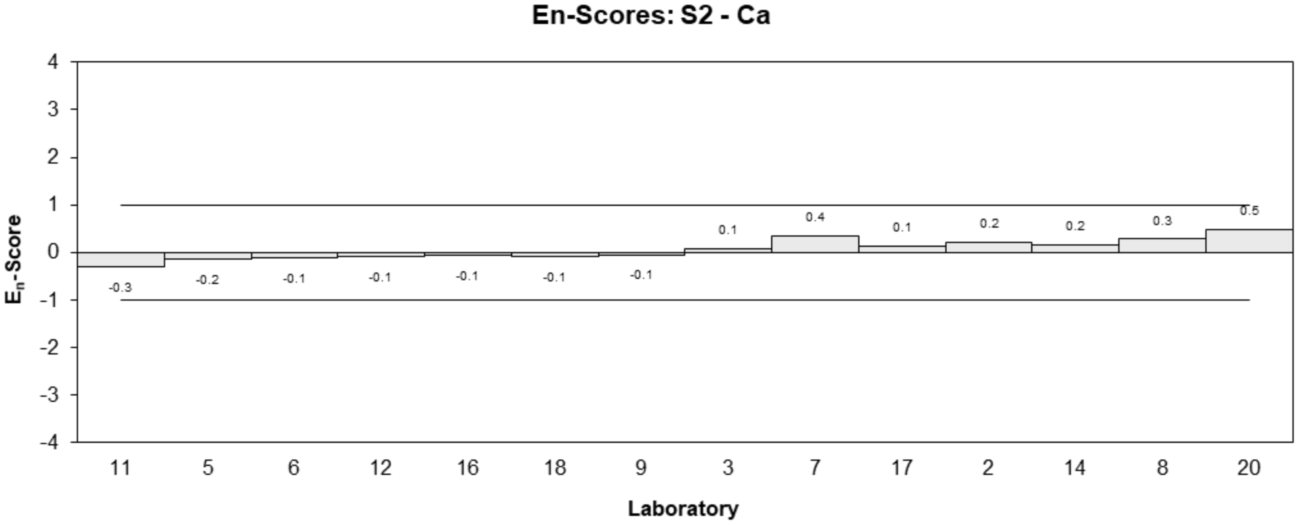

En-Scores: S2 - Ca
E_n-Score
Laboratory
11 5 6 12 16 18 9 3 7 17 2 14 8 20
-0.3 -0.2 -0.1 -0.1 -0.1 -0.1 -0.1 0.1 0.4 0.1 0.2 0.2 0.3 0.5

Figure 15

Table 17

Sample Details

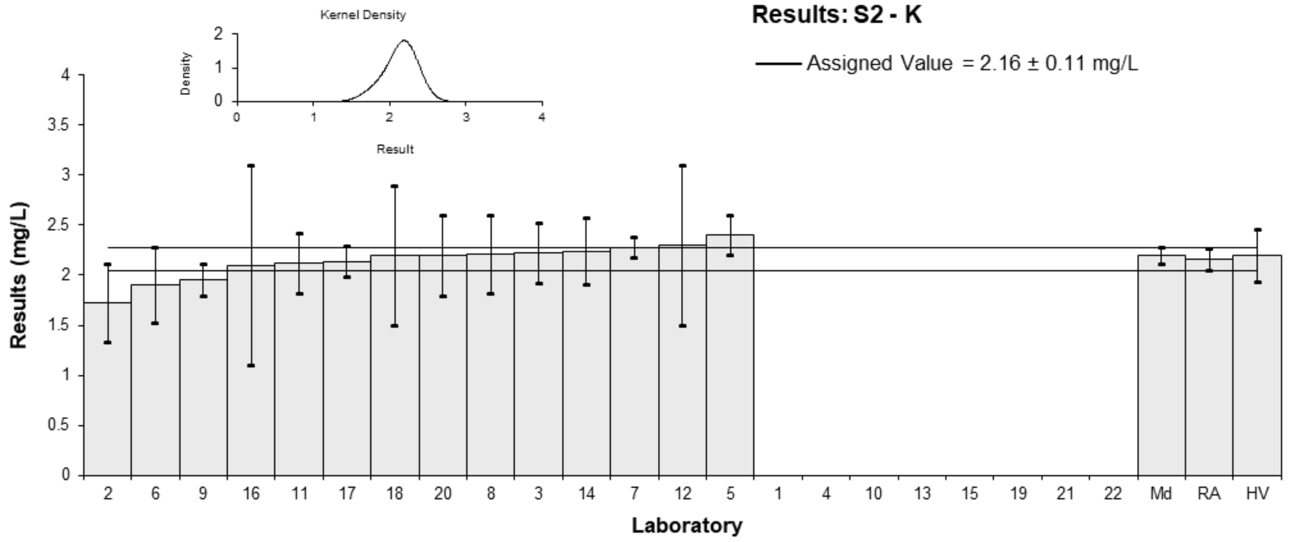
Sample	S2
Analyte	K
Matrix	Potable Water
Unit	mg/L

Participant Results

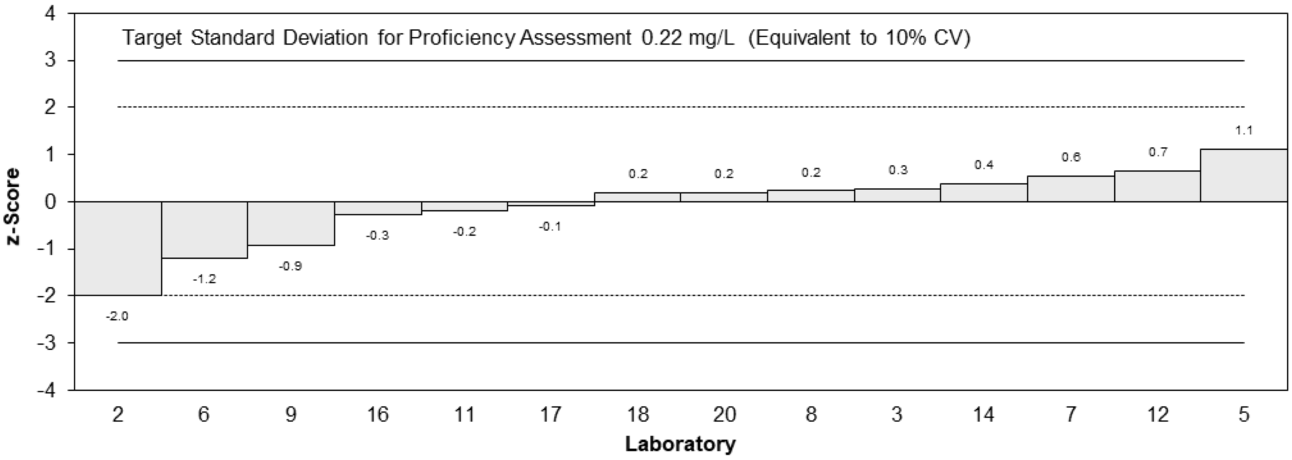
Lab. Code	Result	U	z	E_n
1	NT	NT		
2	1.73	0.39	-1.99	-1.06
3	2.22	0.3	0.28	0.19
4	NT	NT		
5	2.4	0.2	1.11	1.05
6	1.9	0.38	-1.20	-0.66
7	2.279	0.10	0.55	0.80
8	2.21	0.39	0.23	0.12
9	1.9593	0.16	-0.93	-1.03
10	NT	NT		
11	2.12	0.3	-0.19	-0.13
12	2.3	0.8	0.65	0.17
13	NT	NT		
14	2.24	0.336	0.37	0.23
15	NT	NT		
16	2.1	1	-0.28	-0.06
17	2.14	0.15	-0.09	-0.11
18	2.2	0.7	0.19	0.06
19	NT	NT		
20	2.2	0.4	0.19	0.10
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	2.16	0.11
Spike Value	Not Spiked	
Homogeneity Value	2.20	0.26
Robust Average	2.16	0.11
Median	2.20	0.08
Mean	2.14	0.09
N	14	
Max	2.4	
Min	1.73	
Robust SD	0.17	
Robust CV	7.7%	



z-Scores: S2 - K



En-Scores: S2 - K

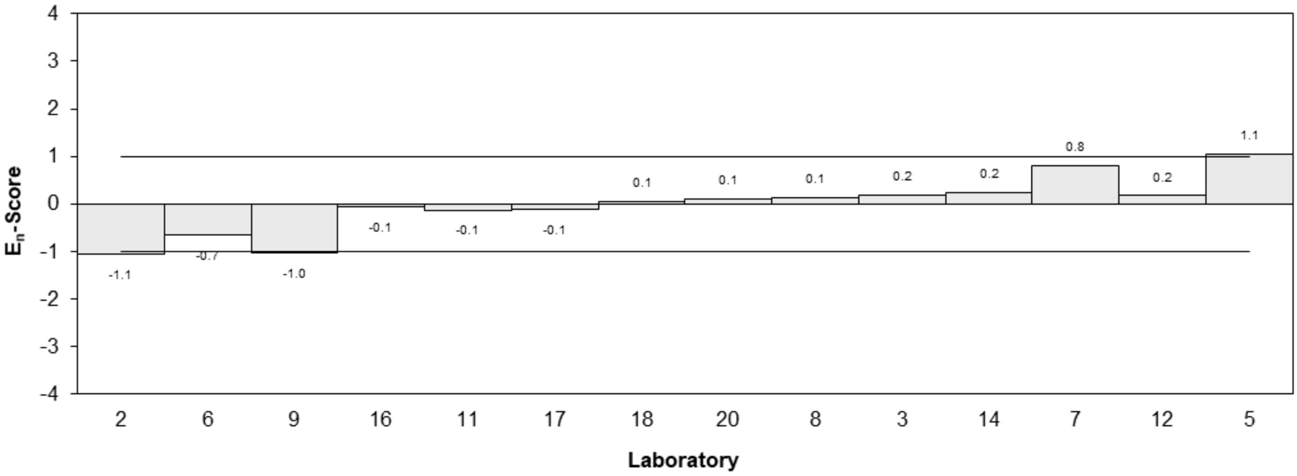


Figure 16

Table 18

Sample Details

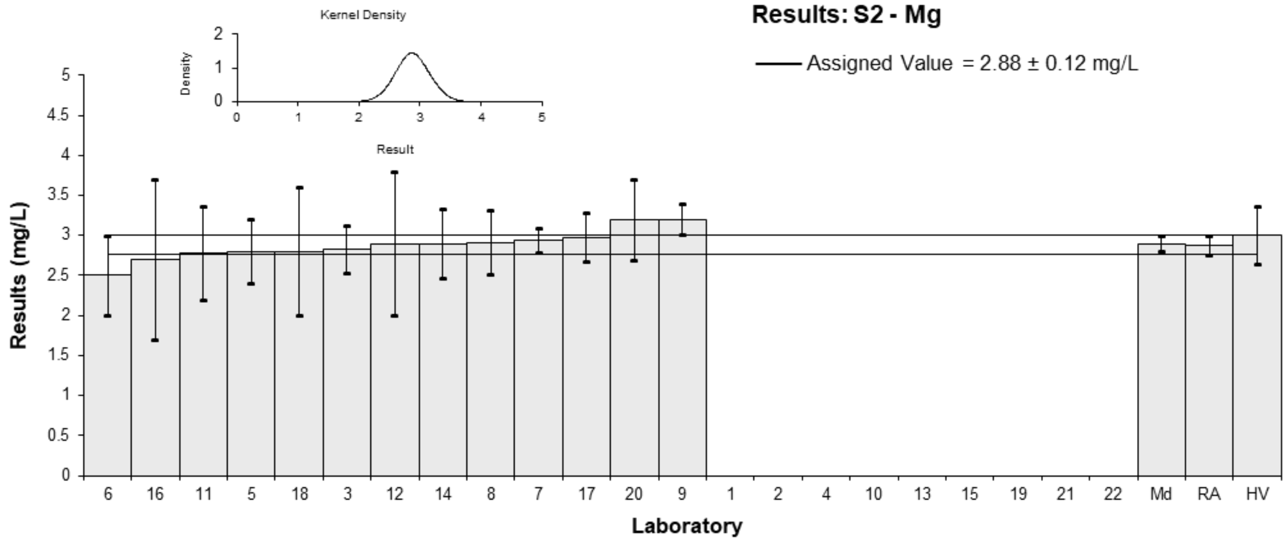
Sample	S2
Analyte	Mg
Matrix	Potable Water
Unit	mg/L

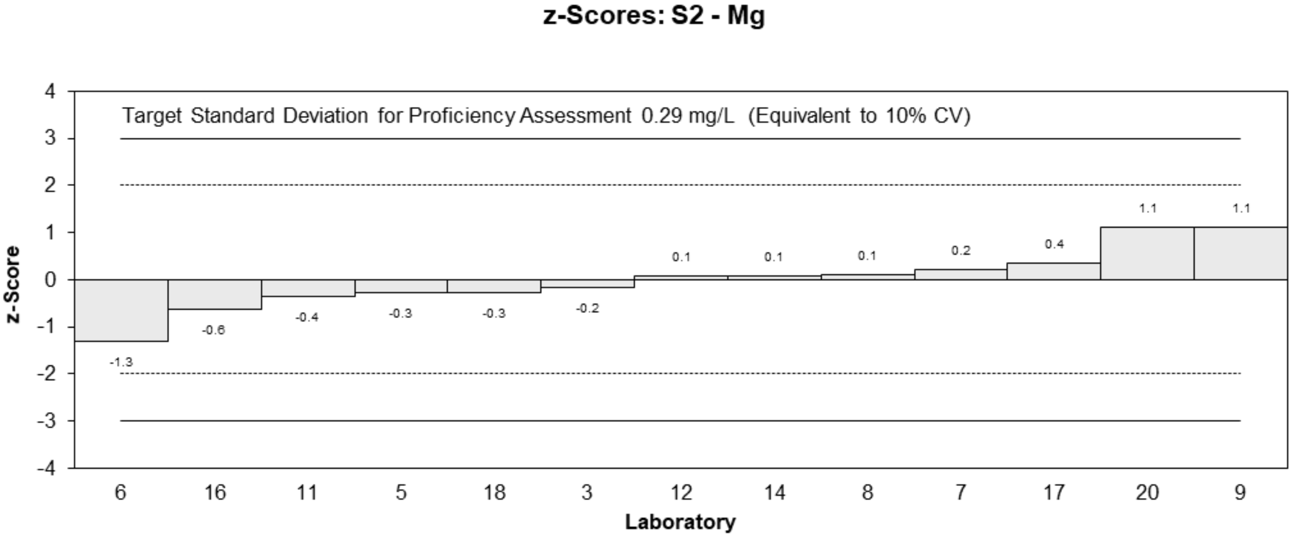
Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	NT	NT		
3	2.83	0.3	-0.17	-0.15
4	NT	NT		
5	2.8	0.4	-0.28	-0.19
6	2.5	0.50	-1.32	-0.74
7	2.941	0.15	0.21	0.32
8	2.91	0.40	0.10	0.07
9	3.201	0.19	1.11	1.43
10	NT	NT		
11	2.78	0.58	-0.35	-0.17
12	2.9	0.9	0.07	0.02
13	NT	NT		
14	2.90	0.435	0.07	0.04
15	NT	NT		
16	2.7	1	-0.62	-0.18
17	2.98	0.30	0.35	0.31
18	2.8	0.8	-0.28	-0.10
19	NT	NT		
20	3.2	0.5	1.11	0.62
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	2.88	0.12
Spike Value	Not Spiked	
Homogeneity Value	3.00	0.36
Robust Average	2.88	0.12
Median	2.90	0.10
Mean	2.88	0.10
N	13	
Max	3.201	
Min	2.5	
Robust SD	0.17	
Robust CV	5.8%	


Results: S2 - Mg
Assigned Value = 2.88 ± 0.12 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6
16
11
5
18
3
12
14
8
7
17
20
9
1
2
4
10
13
15
19
21
22
Md
RA
HV


z-Scores: S2 - Mg
Target Standard Deviation for Proficiency Assessment 0.29 mg/L (Equivalent to 10% CV)
z-Score
-1.3
-0.6
-0.4
-0.3
-0.3
-0.2
0.1
0.1
0.1
0.2
0.4
1.1
1.1
6
16
11
5
18
3
12
14
8
7
17
20
9
Laboratory

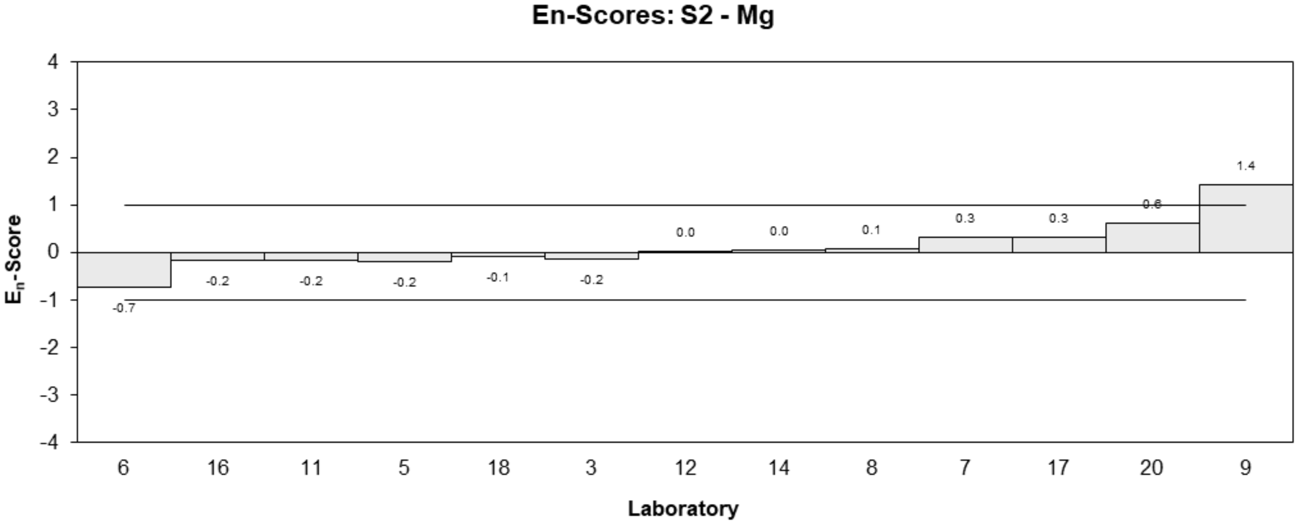

En-Scores: S2 - Mg
E_n-Score
-0.7
-0.2
-0.2
-0.2
-0.1
-0.2
0.0
0.0
0.1
0.3
0.3
0.6
1.4
6
16
11
5
18
3
12
14
8
7
17
20
9
Laboratory

Figure 17

Table 19

Sample Details

Sample	S2
Analyte	Na
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	10.1	0.9	-0.90	-0.97
3	10.4	1.2	-0.63	-0.54
4	NT	NT		
5	11	2	-0.09	-0.05
6	11	2.2	-0.09	-0.04
7	11.566	0.30	0.42	0.80
8	11.3	1.3	0.18	0.14
9	12.694	0.63	1.44	1.98
10	NT	NT		
11	11.0	2.4	-0.09	-0.04
12	10	2	-0.99	-0.53
13	NT	NT		
14	11.4	1.71	0.27	0.17
15	NT	NT		
16	11	3	-0.09	-0.03
17	11.00	1.67	-0.09	-0.06
18	11	3	-0.09	-0.03
19	NT	NT		
20	12.1	1.8	0.90	0.54
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	11.1	0.5
Spike Value	Not Spiked	
Homogeneity Value	11.0	1.3
Robust Average	11.1	0.5
Median	11.0	0.3
Mean	11.1	0.4
N	14	
Max	12.694	
Min	10	
Robust SD	0.72	
Robust CV	6.5%	

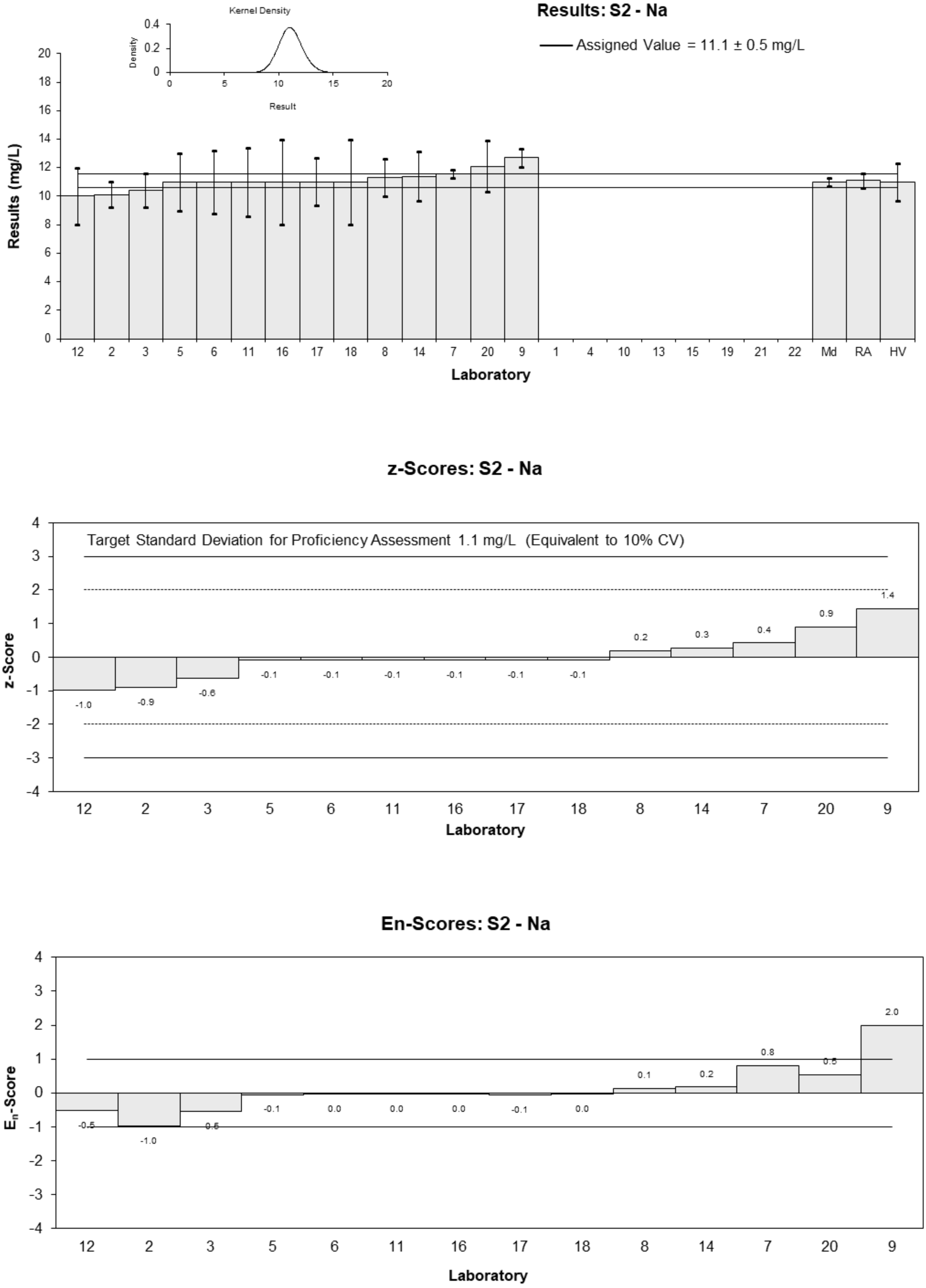

Results: S2 - Na
Assigned Value = 11.1 ± 0.5 mg/L
Kernel Density
Density
0.4
0.2
0
0
5
10
15
20
Result
Results (mg/L)
20
18
16
14
12
10
8
6
4
2
0
12
2
3
5
6
11
16
17
18
8
14
7
20
9
1
4
10
13
15
19
21
22
Md
RA
HV
Laboratory
z-Scores: S2 - Na
Target Standard Deviation for Proficiency Assessment 1.1 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.9
-0.6
-0.1
-0.1
-0.1
-0.1
-0.1
-0.1
0.2
0.3
0.4
0.9
1.4
12
2
3
5
6
11
16
17
18
8
14
7
20
9
Laboratory
En-Scores: S2 - Na
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-1.0
-0.5
-0.1
0.0
0.0
0.0
-0.1
0.0
0.1
0.2
0.8
0.5
2.0
12
2
3
5
6
11
16
17
18
8
14
7
20
9
Laboratory

Figure 18

Table 20

Sample Details

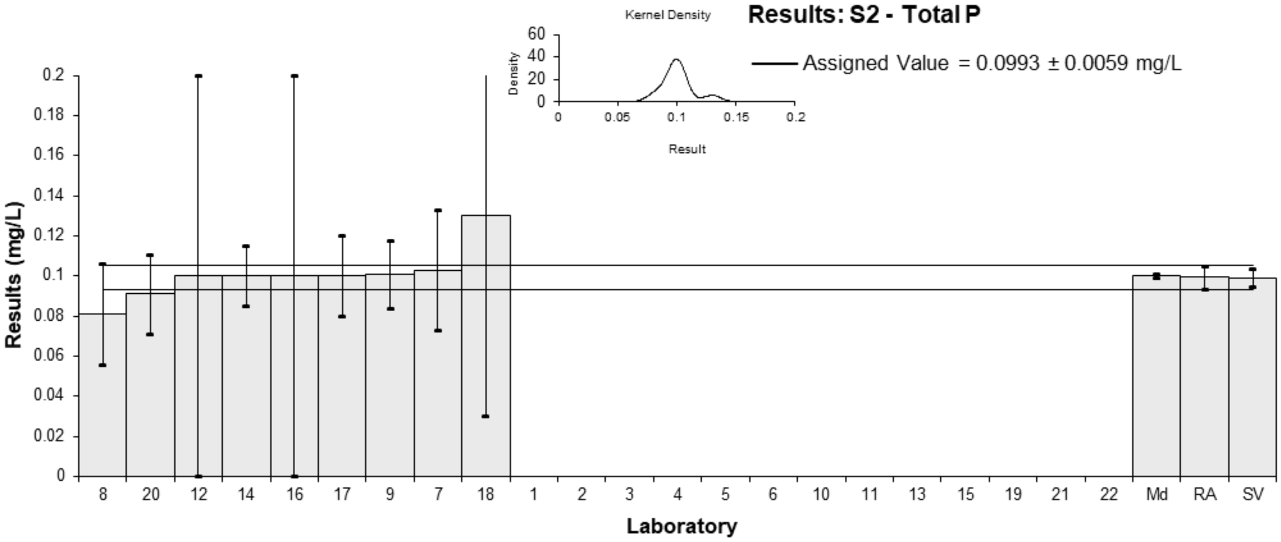
Sample	S2
Analyte	Total P
Matrix	Potable Water
Unit	mg/L

Participant Results

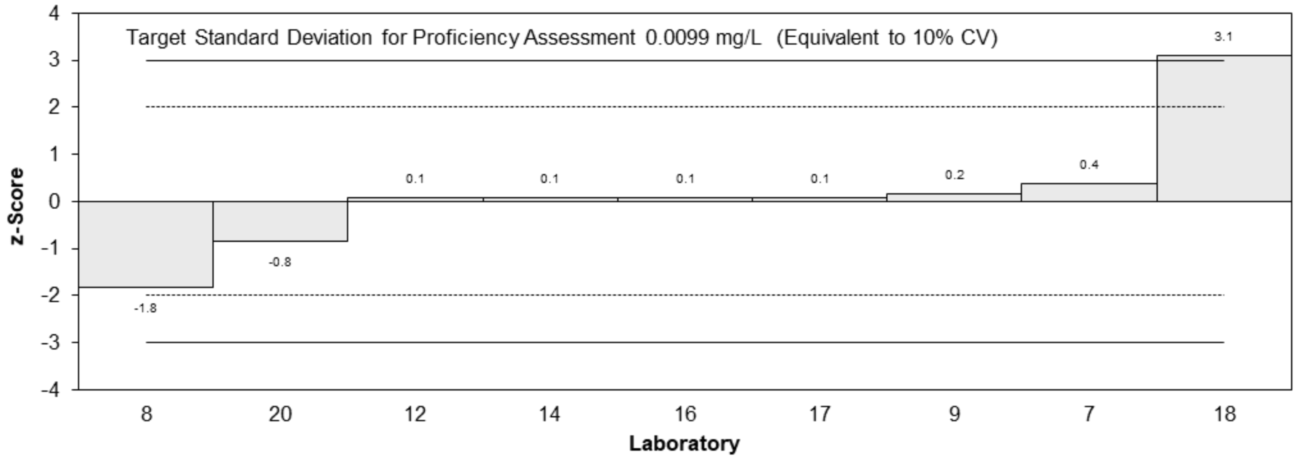
Lab. Code	Result	U	z	E_n
1	NT	NT		
2	NT	NT		
3	<0.5	NR		
4	NT	NT		
5	NT	NT		
6	NR	NR		
7	0.103	0.03	0.37	0.12
8	0.081	0.025	-1.84	-0.71
9	0.101	0.017	0.17	0.09
10	NT	NT		
11	NT	NT		
12	0.1	0.1	0.07	0.01
13	NT	NT		
14	0.100	0.015	0.07	0.04
15	<1.5	0.7		
16	0.1	0.1	0.07	0.01
17	0.10	0.02	0.07	0.03
18	0.13	0.1	3.09	0.31
19	NT	NT		
20	0.091	0.02	-0.84	-0.40
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	0.0993	0.0059
Spike Value	0.0992	0.0042
Robust Average	0.0993	0.0059
Median	0.100	0.001
Mean	0.101	0.009
N	9	
Max	0.13	
Min	0.081	
Robust SD	0.0071	
Robust CV	7.2%	



z-Scores: S2 - Total P



En-Scores: S2 - Total P

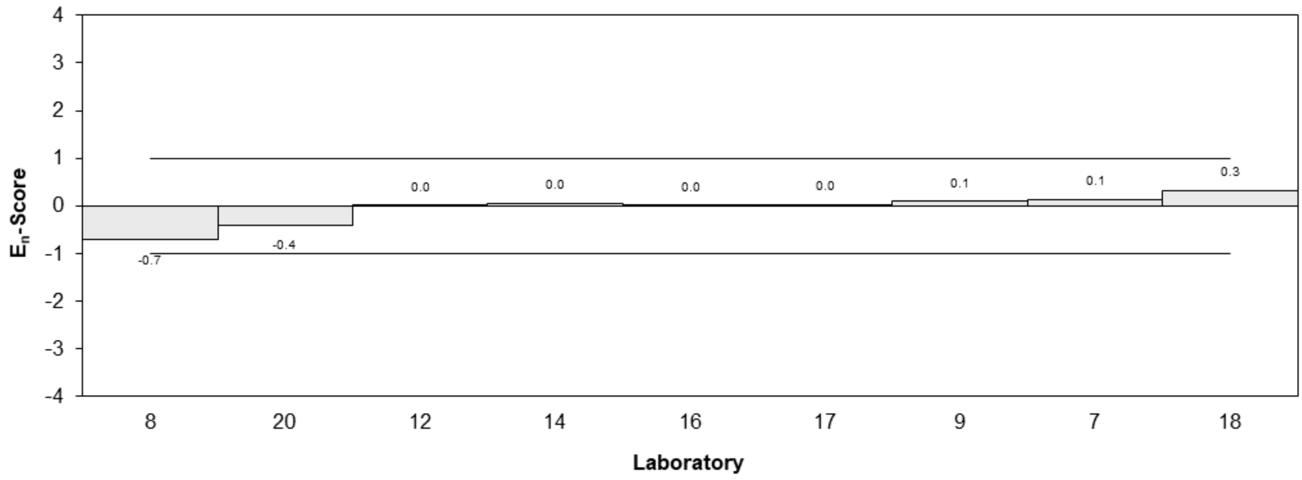


Figure 19

Table 21

Sample Details

Sample	S2
Analyte	Alkalinity
Matrix	Potable Water
Unit	mg/L

Participant Results

Lab. Code	Result	U
1	NT	NT
2	NT	NT
3	<1	NR
4	NT	NT
5	<6	NR
6	<5	1
7	<5	5
8	NR	NR
9	<1	NR
10	NT	NT
11	<2	NR
12	<5	NR
13	NT	NT
14	0	NR
15	<1	34
16	<5	NR
17	31.33	4.58
18	<5	NR
19	NT	NT
20	<1	<1
21	0	NR
22	NT	NT

Statistics*

Assigned Value	Not Set	
Spike Value	Not Spiked	
N	3	
Max	31.33	
Min	0	

*Insufficient data to calculate statistics

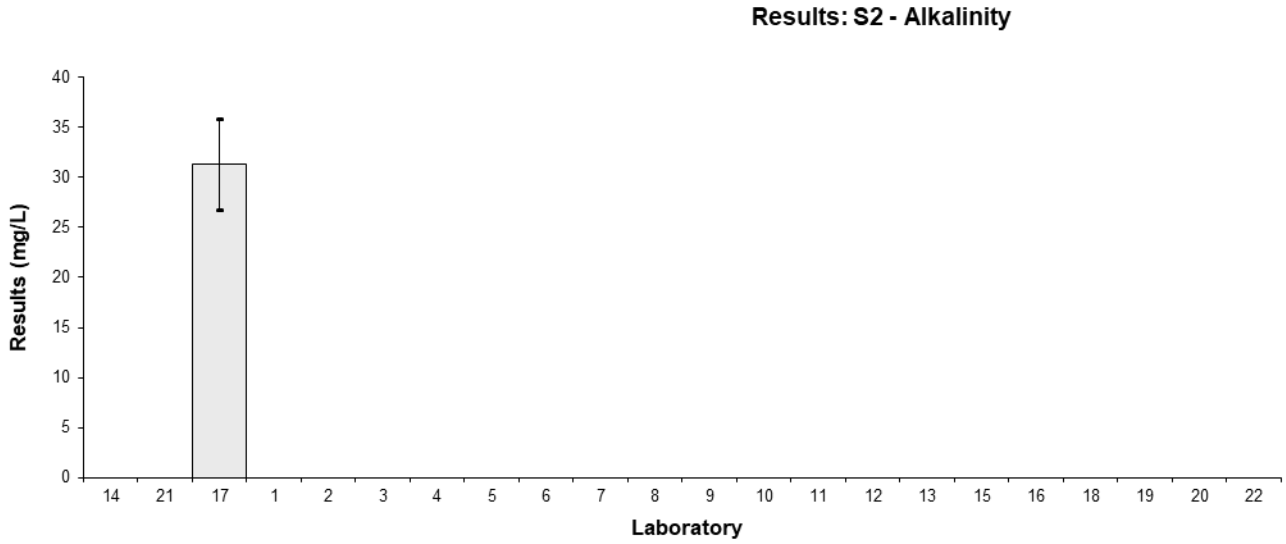

Results: S2 - Alkalinity
Results (mg/L)
40
35
30
25
20
15
10
5
0
14
21
17
1
2
3
4
5
6
7
8
9
10
11
12
13
15
16
18
19
20
22
Laboratory

Figure 20

Table 22

Sample Details

Sample	S2
Analyte	Colour
Matrix	Potable Water
Unit	Pt-Co units

Participant Results

Lab. Code	Result	U
1	NT	NT
2	NT	NT
3	7	1
4	NT	NT
5	<20	NR
6	4	0.8
7	15	3
8	NR	NR
9	5.4	1.13
10	NT	NT
11	10	1
12	7	2
13	NT	NT
14	5	1.5
15	NT	NT
16	5	2
17	7.08	0.55
18	6	5
19	NT	NT
20	3	5
21	4.3	0.2
22	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	8.3	1.5
Robust Average	6.1	1.7
Median	5.7	1.4
Mean	6.6	1.9
N	12	
Max	15	
Min	3	
Robust SD	2.3	
Robust CV	39%	

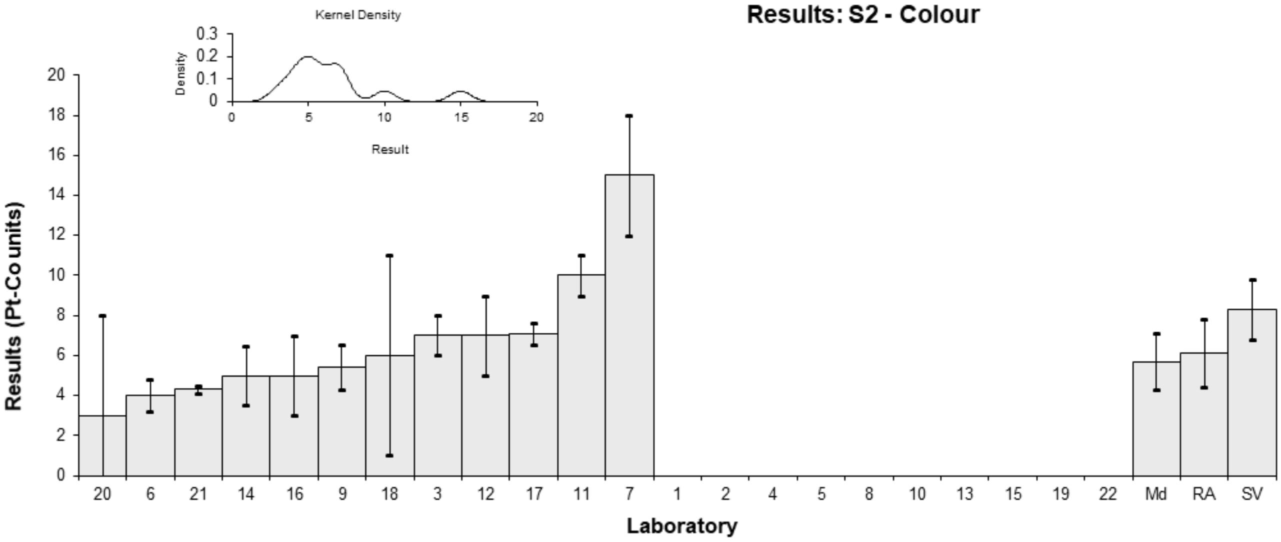

Results: S2 - Colour
Kernel Density
Density
0.3
0.2
0.1
0
0
5
10
15
20
Result
Results (Pt-Co units)
20
18
16
14
12
10
8
6
4
2
0
20
6
21
14
16
9
18
3
12
17
11
7
1
2
4
5
8
10
13
15
19
22
Md
RA
SV
Laboratory

Figure 21

Table 23

Sample Details

Sample	S2
Analyte	EC
Matrix	Potable Water
Unit	µS/cm

Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	NT	NT		
3	1584	150	-0.92	-0.49
4	NT	NT		
5	1680	40	0.24	0.35
6	1700	260	0.48	0.15
7	1415	30	-2.95	-4.90
8	NR	NR		
9	1622.1	129.76	-0.46	-0.28
10	NT	NT		
11	1650	80	-0.12	-0.11
12	1700	400	0.48	0.10
13	NT	NT		
14	1700	255	0.48	0.15
15	1664	33	0.05	0.08
16	1800	500	1.69	0.28
17*	317	44.22	-16.18	-22.52
18	1700	300	0.48	0.13
19	NT	NT		
20	1636	250	-0.29	-0.09
21	1658	33	-0.02	-0.04
22	NT	NT		

* Outlier

Statistics

Assigned Value	1660	40
Spike Value	Not Spiked	
Homogeneity Value	1700	260
Robust Average	1650	50
Median	1660	40
Mean	1560	200
N	14	
Max	1800	
Min	317	
Robust SD	68	
Robust CV	4.1%	

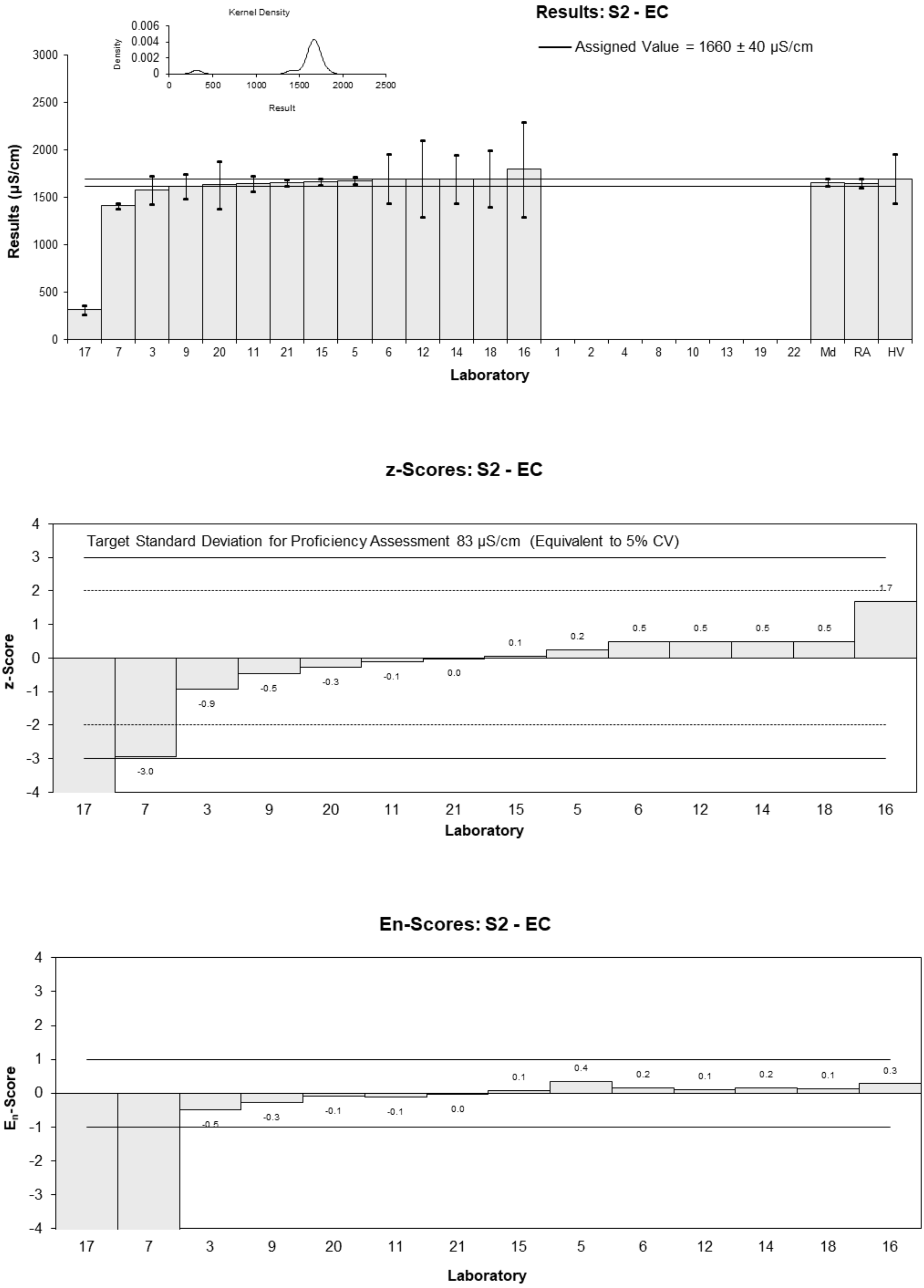

Results: S2 - EC
Assigned Value = 1660 ± 40 µS/cm
Kernel Density
Density
0.006
0.004
0.002
0
0
500
1000
1500
2000
2500
Result
Results (µS/cm)
3000
2500
2000
1500
1000
500
0
17
7
3
9
20
11
21
15
5
6
12
14
18
16
1
2
4
8
10
13
19
22
Md
RA
HV
Laboratory
z-Scores: S2 - EC
Target Standard Deviation for Proficiency Assessment 83 µS/cm (Equivalent to 5% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-3.0
-0.9
-0.5
-0.3
-0.1
0.0
0.1
0.2
0.5
0.5
0.5
0.5
1.7
17
7
3
9
20
11
21
15
5
6
12
14
18
16
Laboratory
En-Scores: S2 - EC
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.3
-0.1
-0.1
0.0
0.1
0.4
0.2
0.1
0.2
0.1
0.3
17
7
3
9
20
11
21
15
5
6
12
14
18
16
Laboratory

Figure 22

Table 24

Sample Details

Sample	S2
Analyte	pH
Matrix	Potable Water

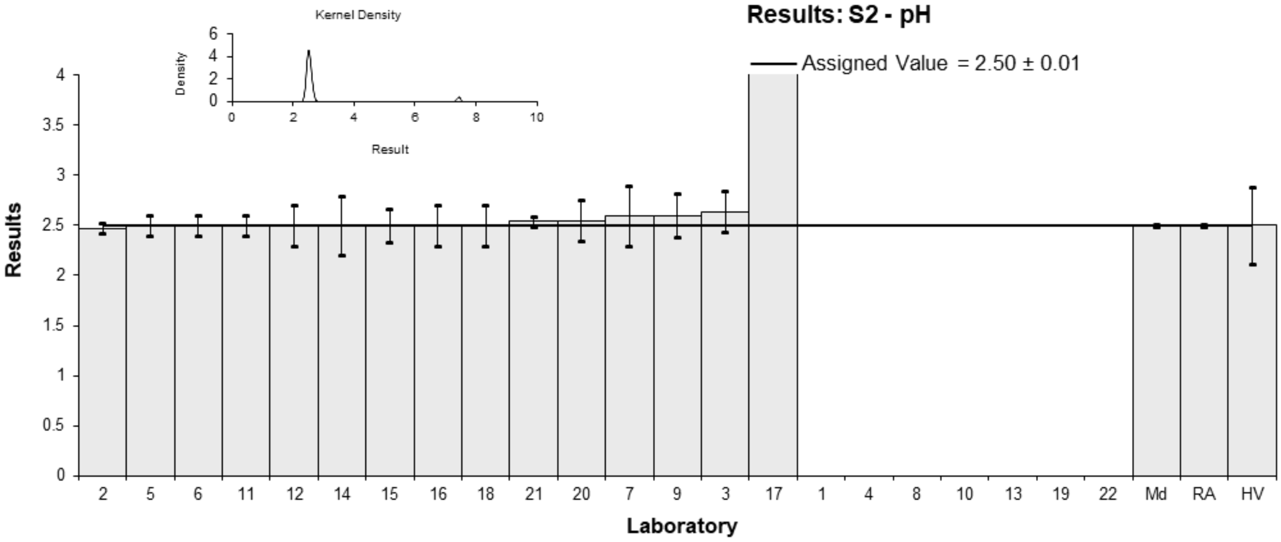
Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	2.47	0.05	-0.34	-0.59
3	2.64	0.2	1.60	0.70
4	NT	NT		
5	2.5	0.1	0.00	0.00
6	2.5	0.1	0.00	0.00
7	2.6	0.3	1.14	0.33
8	NR	NR		
9	2.6	0.22	1.14	0.45
10	NT	NT		
11	2.5	0.1	0.00	0.00
12	2.5	0.2	0.00	0.00
13	NT	NT		
14	2.5	0.3	0.00	0.00
15	2.5	0.17	0.00	0.00
16	2.5	0.2	0.00	0.00
17*	7.43	0.10	56.34	49.06
18	2.5	0.2	0.00	0.00
19	NT	NT		
20	2.55	0.2	0.57	0.25
21	2.54	0.05	0.46	0.78
22	NT	NT		

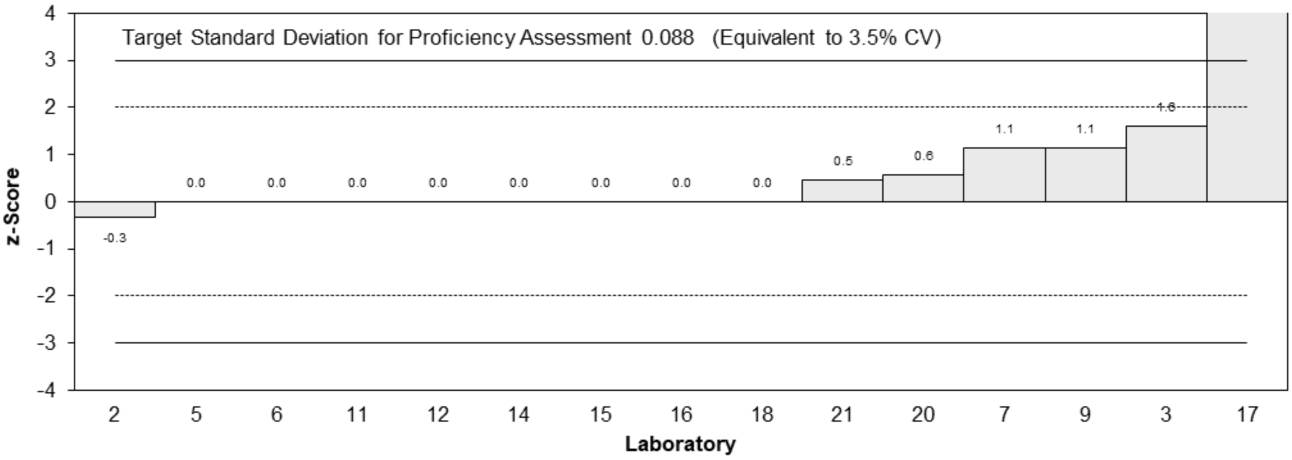
* Outlier

Statistics

Assigned Value	2.50	0.01
Spike Value	Not Spiked	
Homogeneity Value	2.50	0.38
Robust Average	2.50	0.01
Median	2.50	0.01
Mean	2.86	0.65
N	15	
Max	7.43	
Min	2.47	
Robust SD	0.025	
Robust CV	1%	



z-Scores: S2 - pH



En-Scores: S2 - pH

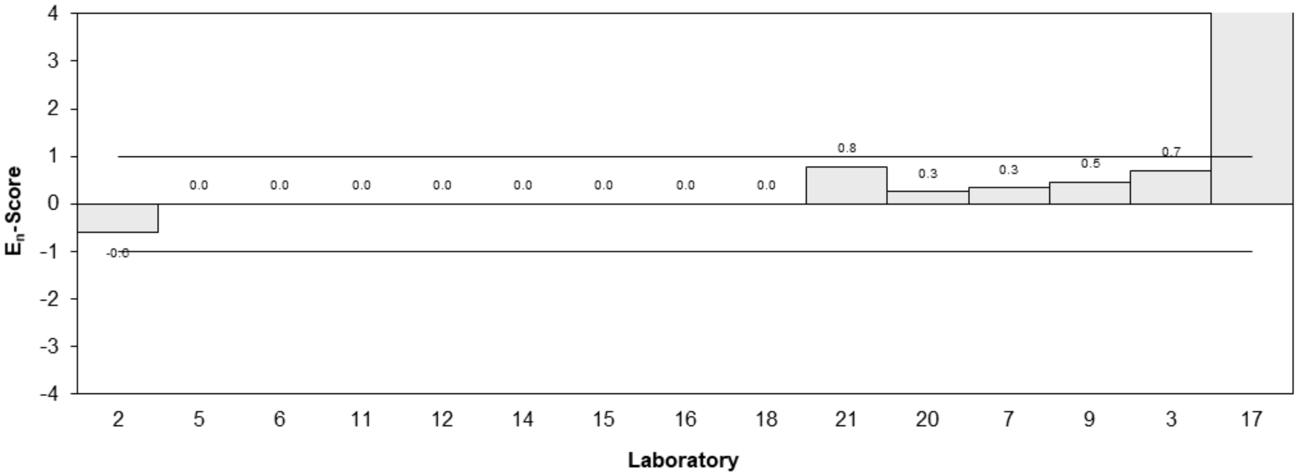


Figure 23

Table 25

Sample Details

Sample	S2
Analyte	Silica (as SiO2)
Matrix	Potable Water
Unit	mg/L

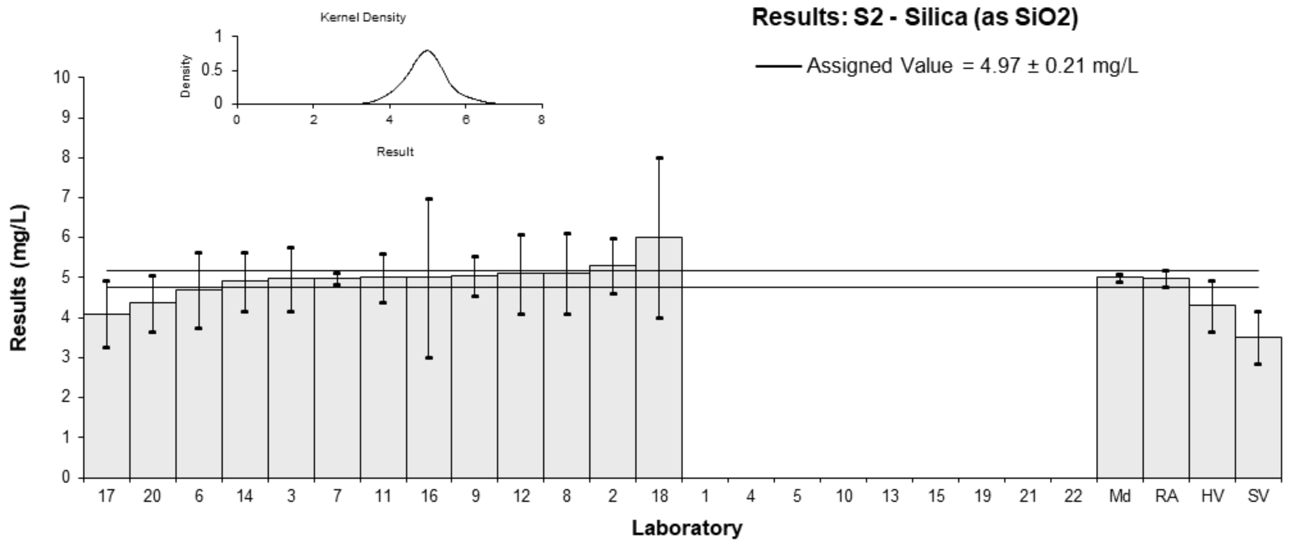
Participant Results

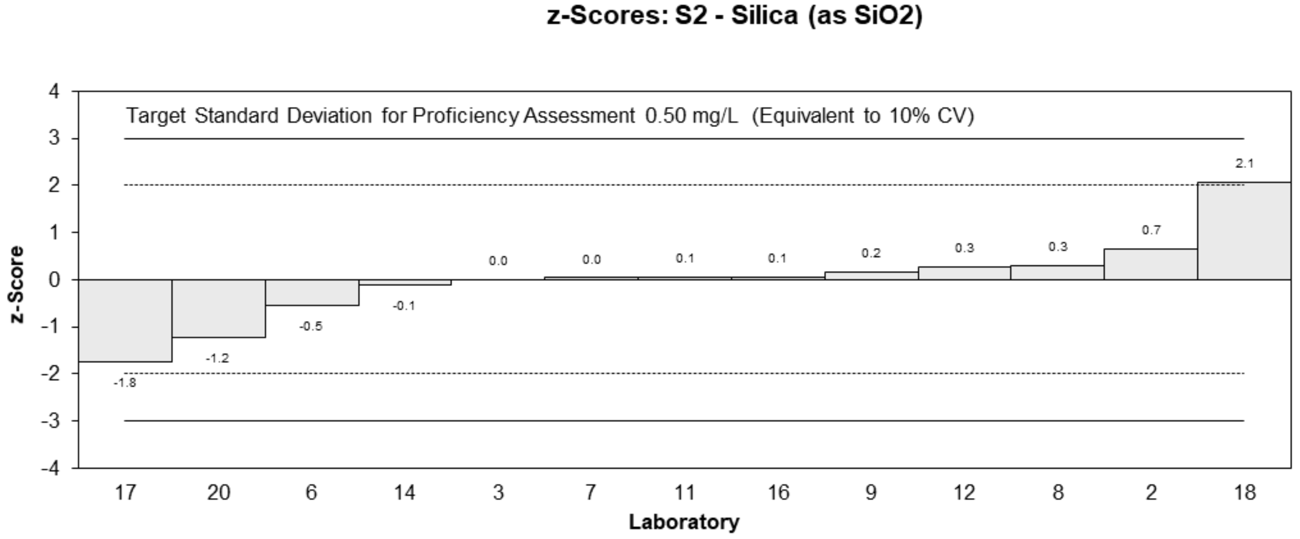
Lab. Code	Result	U	z	E_n
1	NT	NT		
2	5.3	0.7	0.66	0.45
3	4.97	0.8	0.00	0.00
4	NT	NT		
5	NT	NT		
6	4.7	0.94	-0.54	-0.28
7	4.99	0.15	0.04	0.08
8	5.12	1.01	0.30	0.15
9	5.044	0.50	0.15	0.14
10	NT	NT		
11	5.0	0.6	0.06	0.05
12	5.1	1	0.26	0.13
13	NT	NT		
14	4.91	0.737	-0.12	-0.08
15	NT	NT		
16	5.0	2	0.06	0.01
17	4.1	0.82	-1.75	-1.03
18	6	2	2.07	0.51
19	NT	NT		
20	4.36	0.7	-1.23	-0.83
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	4.97	0.21
Spike Value*	3.51	0.65
Homogeneity Value	4.30	0.65
Robust Average	4.97	0.21
Median	5.00	0.10
Mean	4.97	0.25
N	13	
Max	6	
Min	4.1	
Robust SD	0.30	
Robust CV	6%	

*Incurred value not included


Results: S2 - Silica (as SiO2)
Assigned Value = 4.97 ± 0.21 mg/L
Kernel Density
Density
1
0.5
0
0
2
4
6
8
Result
Results (mg/L)
10
9
8
7
6
5
4
3
2
1
0
17
20
6
14
3
7
11
16
9
12
8
2
18
1
4
5
10
13
15
19
21
22
Md
RA
HV
SV
Laboratory


z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation for Proficiency Assessment 0.50 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.8
-1.2
-0.5
-0.1
0.0
0.0
0.1
0.1
0.2
0.3
0.3
0.7
2.1
17
20
6
14
3
7
11
16
9
12
8
2
18
Laboratory

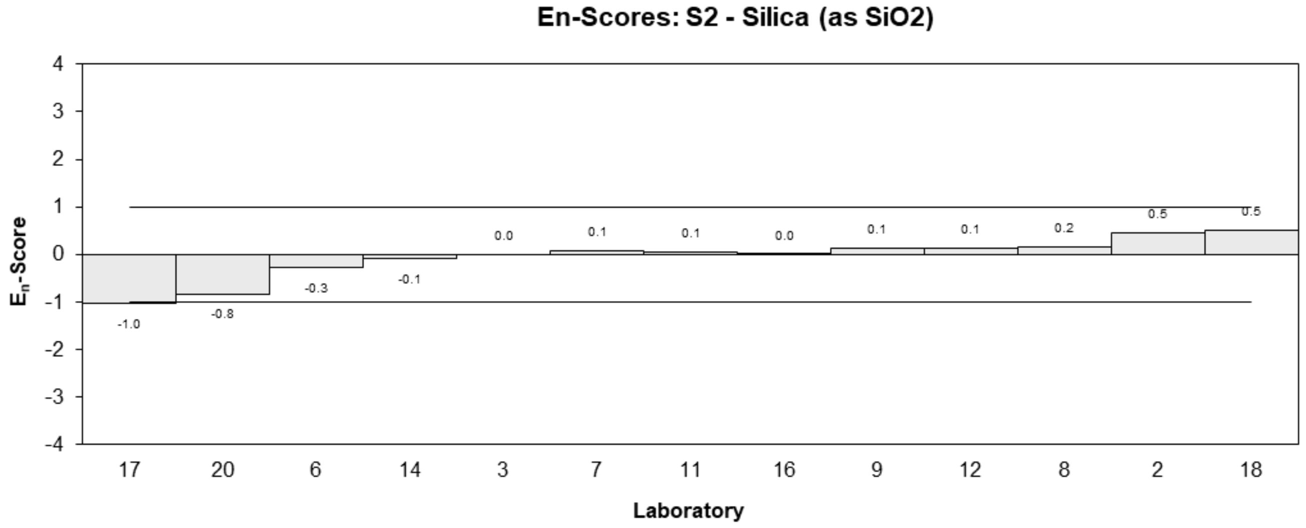

En-Scores: S2 - Silica (as SiO2)
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.8
-0.3
-0.1
0.0
0.1
0.1
0.0
0.1
0.1
0.2
0.5
0.5
17
20
6
14
3
7
11
16
9
12
8
2
18
Laboratory

Figure 24

Table 26

Sample Details

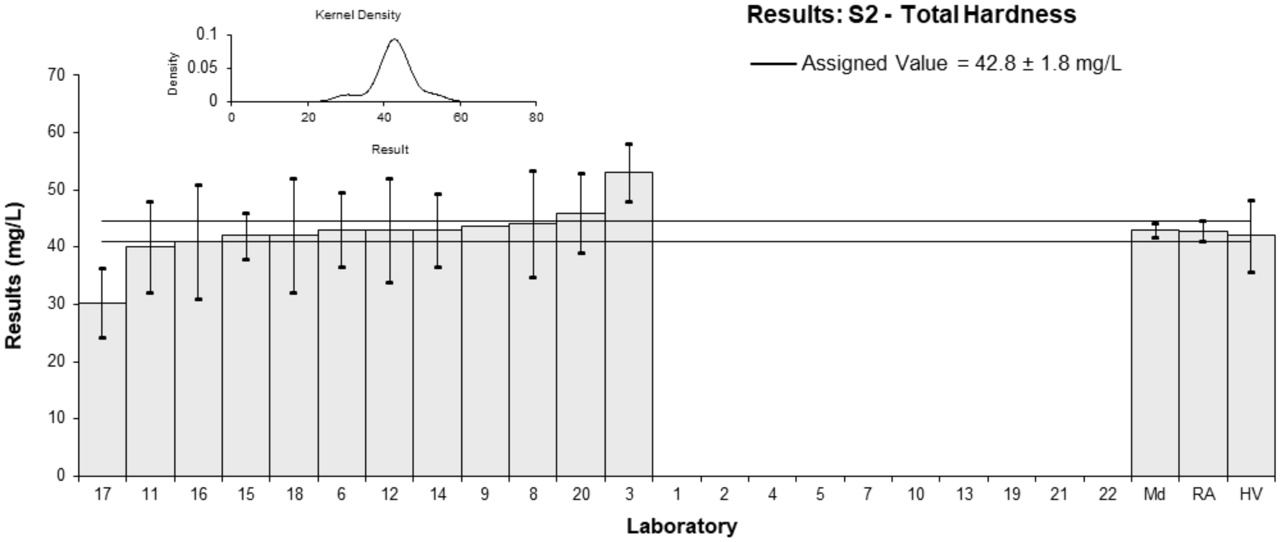
Sample	S2
Analyte	Total Hardness
Matrix	Potable Water
Unit	mg/L

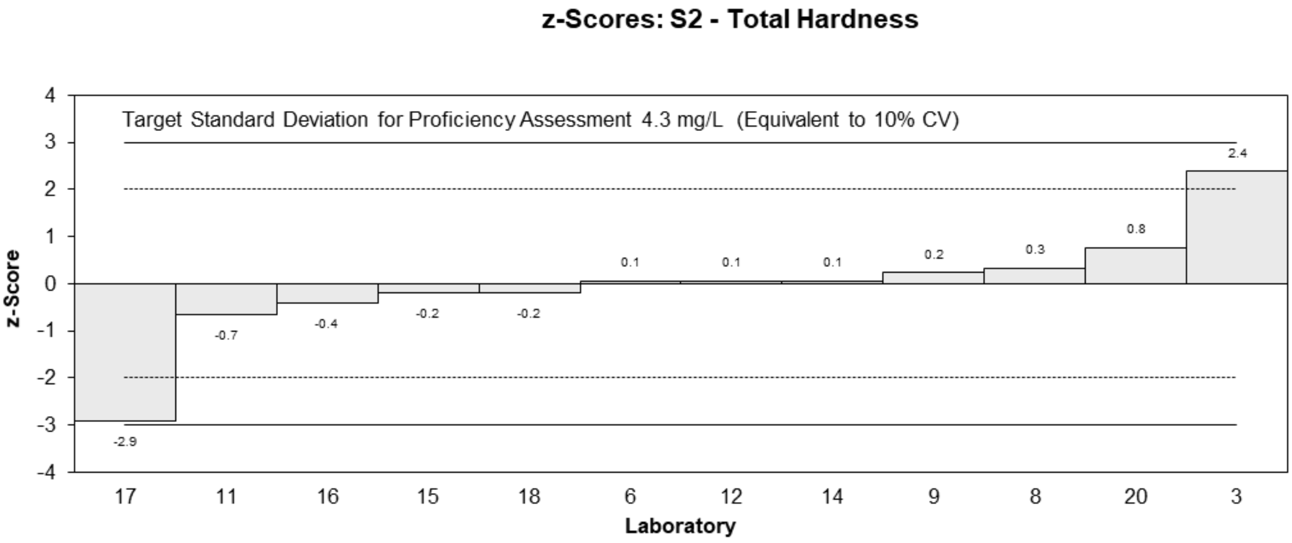
Participant Results

Lab. Code	Result	U	z	E_n
1	NT	NT		
2	NT	NT		
3	53	5.0	2.38	1.92
4	NT	NT		
5	NT	NT		
6	43	6.5	0.05	0.03
7	NT	NT		
8	44.2	9.3	0.33	0.15
9	43.7632	NR	0.23	0.54
10	NT	NT		
11	40	8	-0.65	-0.34
12	43	9	0.05	0.02
13	NT	NT		
14	43	6.45	0.05	0.03
15	42	4	-0.19	-0.18
16	41	10	-0.42	-0.18
17	30.29	6.06	-2.92	-1.98
18	42	10	-0.19	-0.08
19	NT	NT		
20	46.0	6.9	0.75	0.45
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	42.8	1.8
Spike Value	Not Spiked	
Homogeneity Value	42.0	6.3
Robust Average	42.8	1.8
Median	43.0	1.2
Mean	42.6	2.9
N	12	
Max	53	
Min	30.29	
Robust SD	2.5	
Robust CV	5.9%	


Results: S2 - Total Hardness
Assigned Value = 42.8 ± 1.8 mg/L
Kernel Density
Density
0.1
0.05
0
0
20
40
60
80
Result
Results (mg/L)
70
60
50
40
30
20
10
0
17
11
16
15
18
6
12
14
9
8
20
3
1
2
4
5
7
10
13
19
21
22
Md
RA
HV
Laboratory


z-Scores: S2 - Total Hardness
Target Standard Deviation for Proficiency Assessment 4.3 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.9
-0.7
-0.4
-0.2
-0.2
0.1
0.1
0.1
0.2
0.3
0.8
2.4
17
11
16
15
18
6
12
14
9
8
20
3
Laboratory

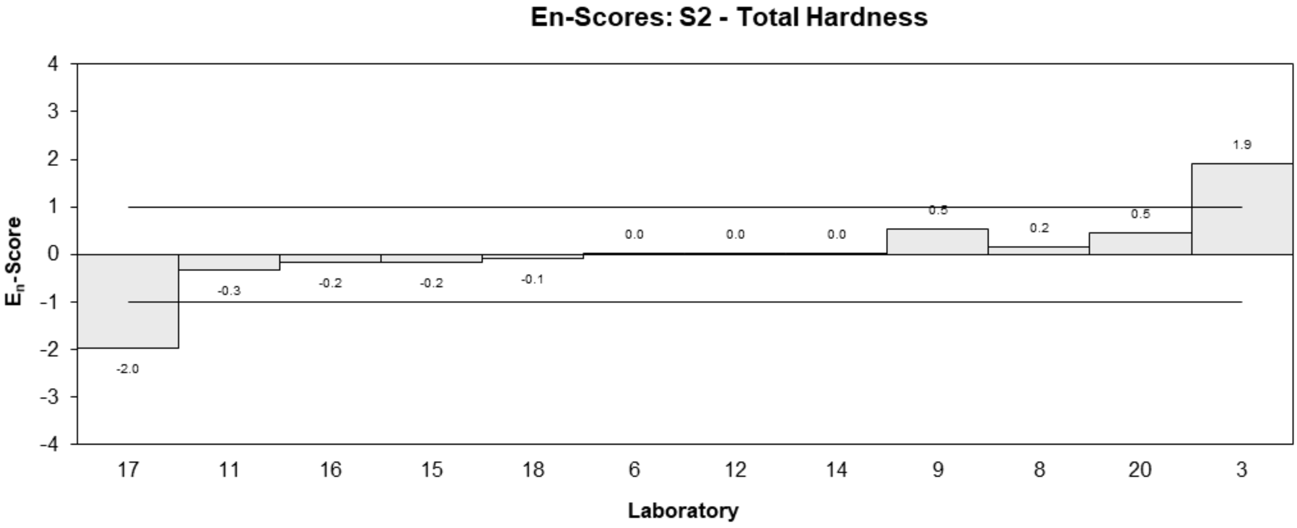

En-Scores: S2 - Total Hardness
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-2.0
-0.3
-0.2
-0.2
-0.1
0.0
0.0
0.0
0.5
0.2
0.5
1.9
17
11
16
15
18
6
12
14
9
8
20
3
Laboratory

Figure 25

7 DISCUSSION OF RESULTS

7.1 Assigned Value and Traceability

Assigned Value were the robust average of participants' results. The robust averages used as assigned values 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'.[6] 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 of the robust average and assigned value for chloride in Sample S1 and its associated uncertainty.

No assigned value was set for iodide in S1 and colour in S2 because the results were too variable. No assigned value was also set for alkalinity in S2 because the level of this test in S2 was below the reporting limit of most participants.

Spike Value where applicable, includes both the incurred value and the fortified value except for silica, orthophosphate-P and total dissolved phosphorus.

With the exception of silica, orthophosphate-P and total dissolved phosphorus, assigned values, spike values and homogeneity values were in agreement with each other within their estimates of uncertainty for all elements of interest.

Traceability The consensus of participants' results (robust average) is not traceable to any external reference. 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 323 numerical results, 320 (99%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0.41% to 280% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 1.

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 comparison studies.[9 – 14]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 25). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 13 laboratories reported results for B in S2. The uncertainty of the assigned value estimated from the robust standard deviation of the 13 laboratories' results is 0.016 mg/L (see equation 4, Appendix 3). Laboratory 15 might have under-estimated its expanded measurement uncertainties reported for B in S2 (0.002 mg/L) as an uncertainty estimated from one measurement should not be smaller than the uncertainty estimated from 13 measurements. Alternatively, estimates of uncertainties for Orthophosphate-P in S1 larger than 0.032 mg/L (the uncertainty of the assigned value, 0.008 mg/L plus the allowable variation from the assigned value, the target standard deviation of 0.012 mg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainties reported by laboratory 18 for orthophosphate-P in S1 (0.1 mg/L) might have been over-estimated.

Laboratory 15 should review their procedure for estimating measurement uncertainty as most of their estimated uncertainties were either under or over-estimated.

Laboratories 7 and 18 should also review their procedure for estimating measurement uncertainty. Most of the uncertainties reported by Laboratory 7 were under-estimated while most of the uncertainties reported by Laboratory 18 were over-estimated.

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

Laboratories 6, 7 and 15 attached an estimate of the expanded measurement uncertainty to a result reported as "less than". An estimate of uncertainty expressed as a numerical value cannot be attached to a result expressed as a range.[9]

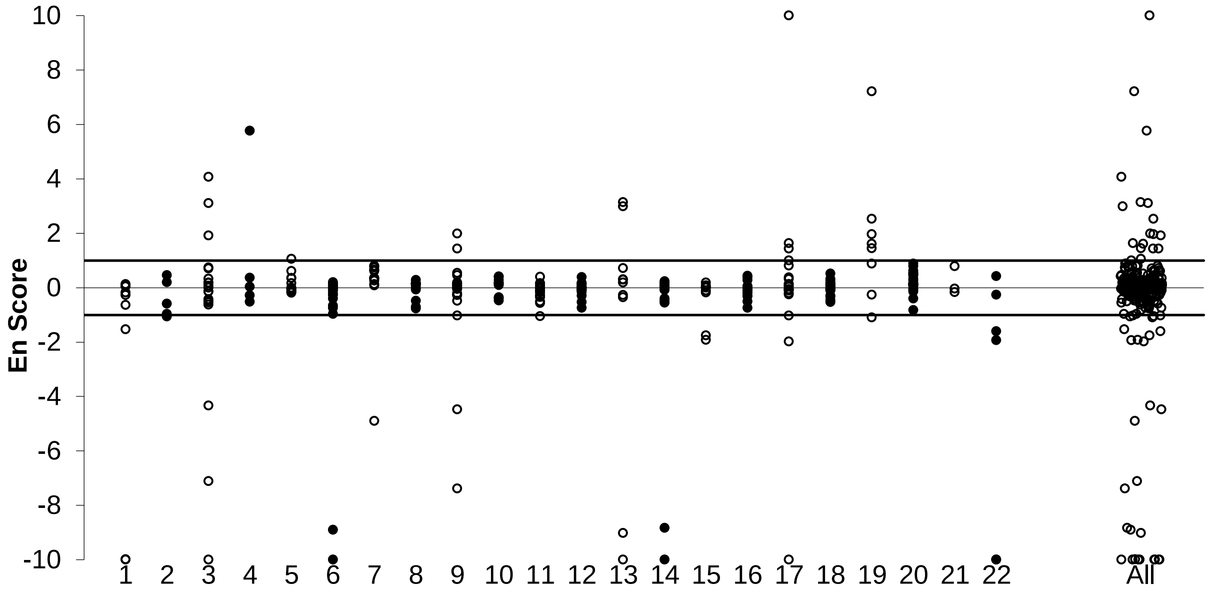
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 18.44 ± 3.42 mg/L, it is better to report 18.4 ± 3.4 mg/L.[9]

7.3 E_n-score

E_n-score can be interpreted in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value 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.

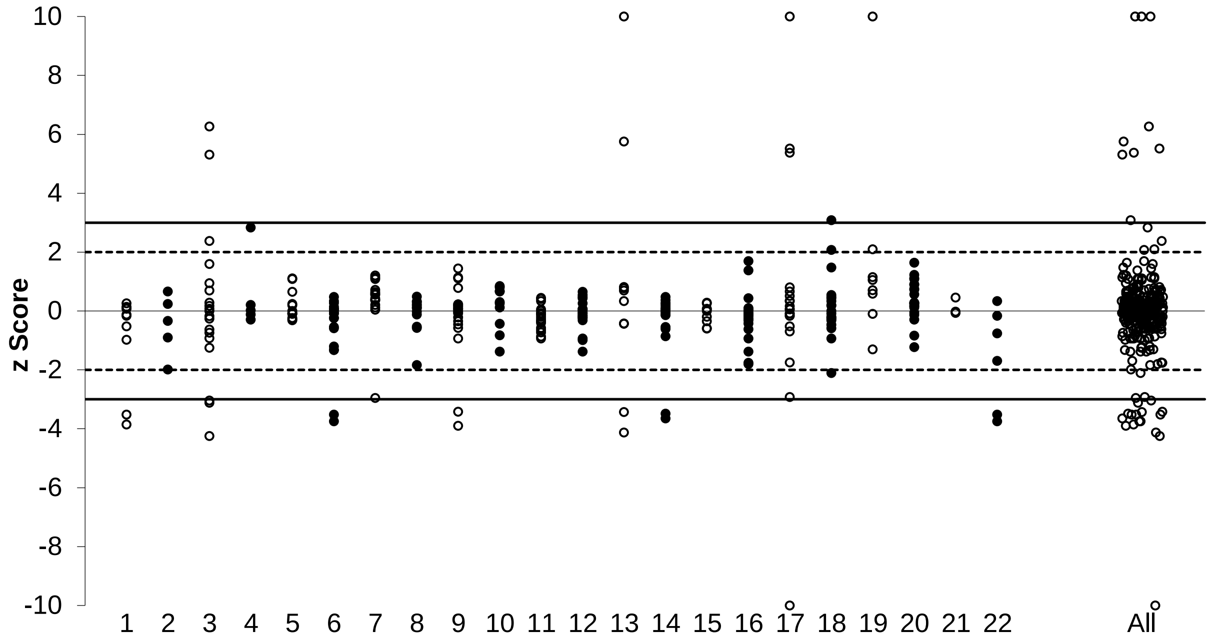
The dispersal of participants' E_n-scores is graphically presented in Figure 26. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 300 results for which E_n-scores were calculated, 255 (85%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.



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

Figure 26 E_n-Score Dispersal by Laboratory



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

Figure 27 z-Score Dispersal by Laboratory

7.4 z-Score

The z-score compares 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 for proficiency assessment equivalent to 3.5% to 20% performance coefficient of variation (PCV) were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation for proficiency assessment as a realistic, set value enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

The between laboratories coefficient of variation predicted by the Thompson equation[7] and the between laboratories coefficient of variation resulted in this study are presented for comparison in Table 27.

The dispersal of participants' z-scores is presented in Figure 28 (by laboratory code) and in Figure 29 (by test). Of 300 results for which z-scores were calculated, 268 (89%) returned a satisfactory score of $|z| \leq 2.0$ and 7 (2%) were questionable with a score of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

Summary of participants' reported results and performance is presented in Figure 29**.**

Laboratory 20 returned the highest number of satisfactory z-scores and En-scores (21 out of 21 reported).

All results reported by **laboratories 12** (20)**, 16** (20), **11** (18), **5** (12), **8** (12), **10** (10), 1**5** (9), **2** (5), and **21** (3) returned satisfactory z scores.

All results reported by **laboratories 12** (20), **16** (20), **18** (20), **8** (12), **10** (10) and **21** (3) returned satisfactory E_n scores

Table 27 Between Laboratories 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 CV)
S1	Ammonia (as NH3)	0.384	11%	18%	15%
S1	Bromide	0.138	9.8%	22%	10%
S1	Chloride	25.5	5.5%	9.8%	10%
S1	DOC	4.14	4.3%	13%	15%
S1	Fluoride	0.992	9.3%	16%	10%
S1	Iodide	Not Set	38%	NA	Not Set
S1	Nitrate (as NO3)	0.919	7.6%	16%	20%
S1	Nitrite (as NO2)	0.508	8.6%	18%	20%
S1	Orthophosphate-P	0.116	11%	22%	10%
S1	Sulphate	5.07	7.1%	13%	10%
S1	TDN	0.854	7.4%	16%	10%
S1	TDP	0.122	6.3%	22%	10%
S2	Alkalinity	Not Set	NA	NA	Not Set
S2	B	0.516	4.4%	18%	10%
S2	Ca	12.3	3.5%	11%	10%
S2	Colour	Not Set	39%	NA	Not Set
S2	EC	1660 µS/cm	3.3%	5.2%	5%
S2	K	2.16	7.7%	14%	10%
S2	Mg	2.88	5.8%	14%	10%
S2	Na	11.1	6.5%	11%	10%
S2	pH	2.50	0.1%	14%	3.5%
S2	Silica (as SiO2)	4.97	6%	13%	10%
S2	Total Hardness	42.8	5.9%	9.1%	10%
S2	Total P	0.0993	7.2%	22%	10%

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

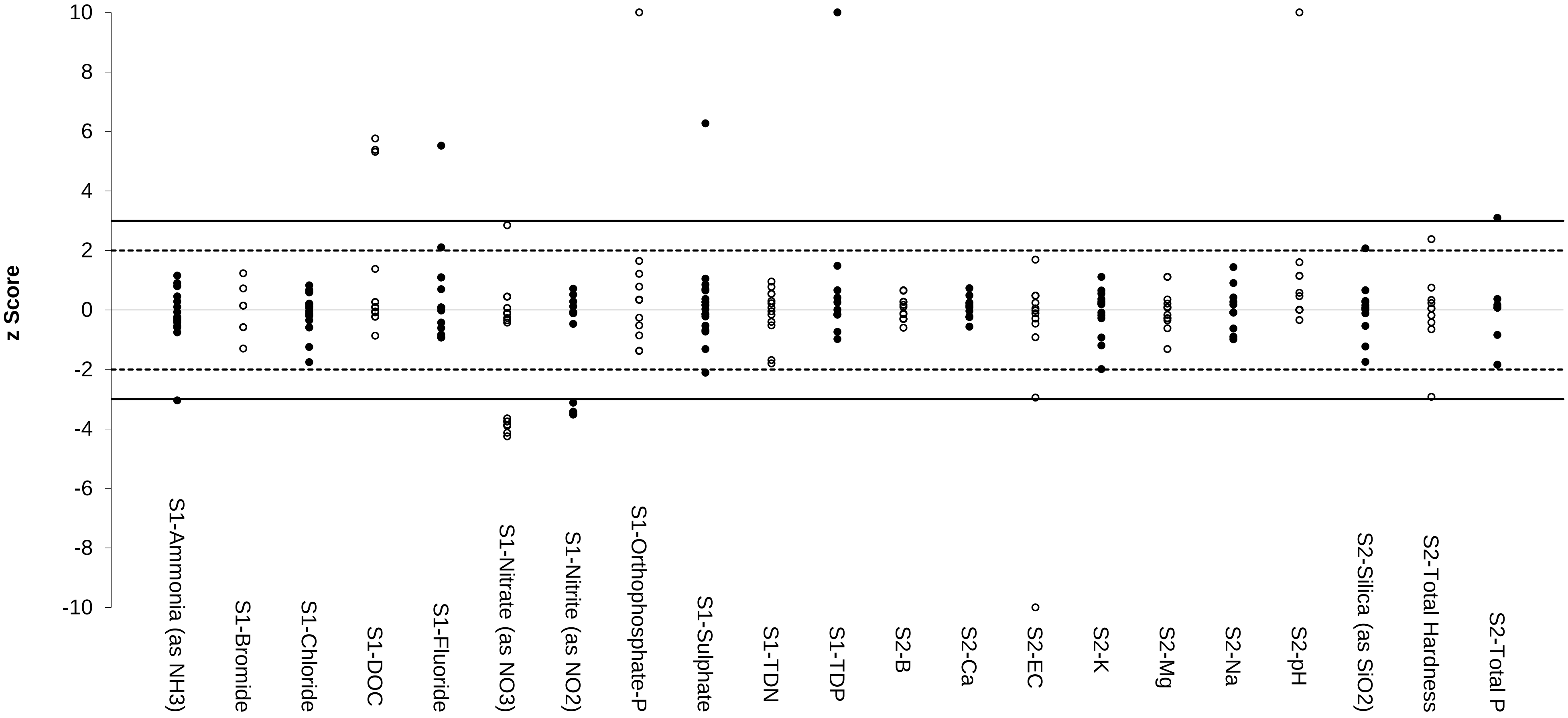


Figure 28 z-Score Dispersal by Test

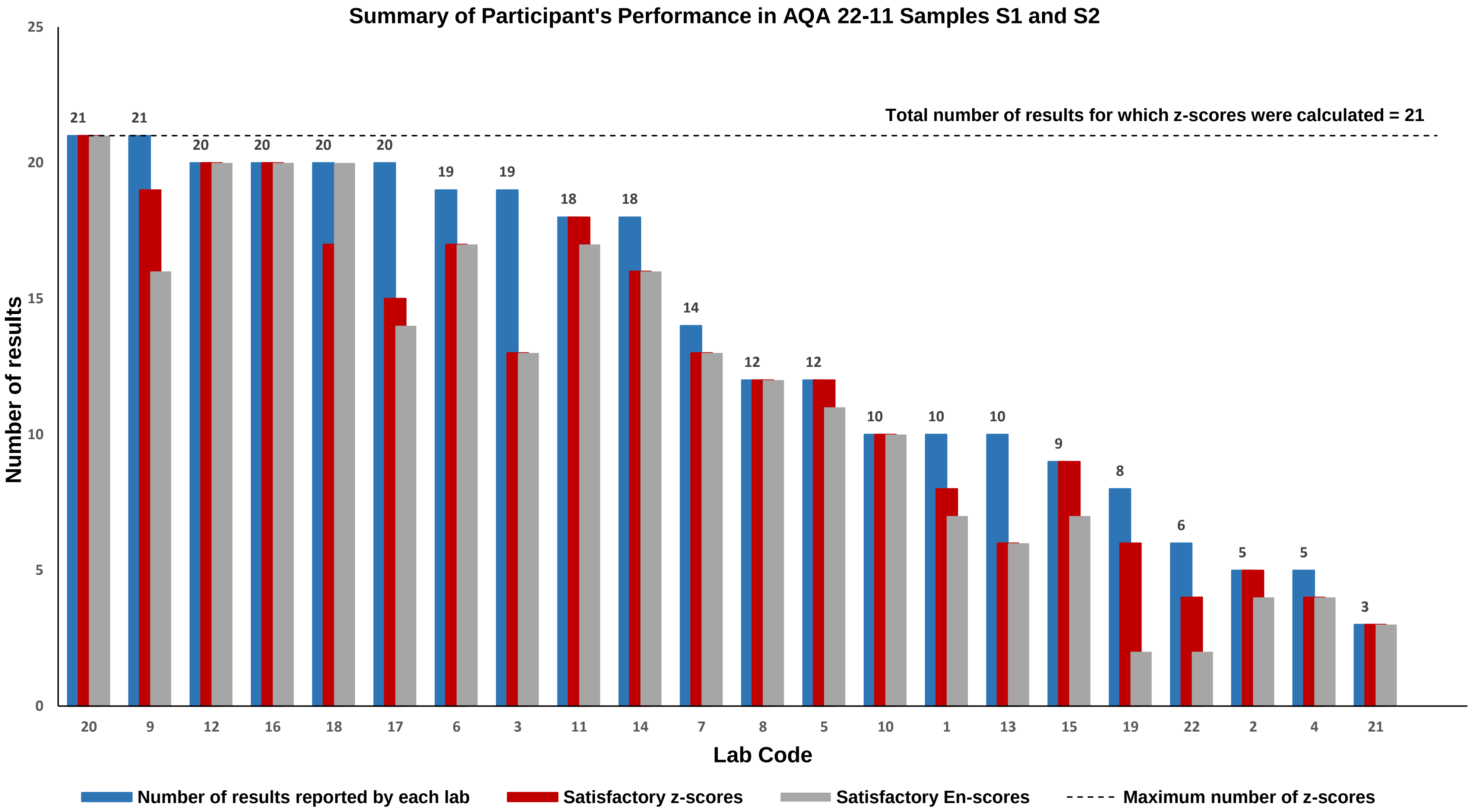


Figure 29: Summary of Participants Performance in AQA 22-11

Table 28 Summary of Participants' Results and Performance for S1

Lab Code	S1-Ammonia (mg/L)	S1-Bromide (mg/L)	S1-Chloride (mg/L)	S1-DOC (mg/L)	S1-Fluoride (mg/L)	S1-Iodide (mg/L)	S1-Nitrate (mg/L)	S1-Nitrite (mg/L)	S1-Orthophosphate-P (mg/L)	S1-Sulphate (mg/L)	S1-TDN (mg/L)	S1-TDP (mg/L)
A.V.	0.384	0.138	25.5	4.14	0.992	Not Set	0.919	0.508	0.116	5.07	0.854	0.122
H.V.	0.372	0.147	NA	4.30	0.82	NA	1.00	0.504	0.120	NA	0.80	0.120
1	NR	0.14	25.2	4.2	1	0.42	0.21	0.15	0.11	5.2	0.84	0.11
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	0.209	<0.5	22.3	7.44	1.06	NT	0.137	0.191	0.113	8.25	0.935	0.113
4	0.3671379855	NT	26.0471	NT	NT	NT	1.4409904	0.4961328	NT	5.07966	NT	NT
5	NT	<0.5	26	NT	1.1	NT	0.9	0.5	NT	5.4	NT	NT
6	0.37	0.14	24	4.1	1.0	0.3	0.23	0.15	0.12	4.4	0.86	NR
7	NT	0.148	27	NT	1.1	0.233	NT	NT	0.13	5.26	NT	NT
8	NR	0.13	25.8	NR	0.99	NR	NR	NR	NR	4.80	NR	NR
9	0.364	0.13	25.65	4.09	1.00	0.21	0.202	0.161	0.125	4.96	0.873	0.122
10	0.43	NT	27.2	4.3	0.91	NT	0.84	0.52	0.10	5.5	0.88	0.13
11	0.41	<0.2	24.6	3.6	0.90	NT	0.87	0.50	0.120	4.7	0.82	0.127
12	0.38	<0.2	25	4	0.9	0.4	1.0	0.50	0.10	5	0.9	0.12
13	0.36	NT	27.6	7.72	0.949	0.205	0.16	0.16	0.12	5.42	0.92	0.28
14	0.353	NT	25.4	4.19	0.931	NT	0.248	0.153	0.106	5.15	NT	NT
15	0.4	<0.2	24	NT	1	NT	0.855	NT	NT	5.2	NT	NT
16	0.39	<0.2	21	5	0.9	<0.5	1.0	0.50	0.10	5	0.7	0.12
17	0.43	NT	25.10	7.48	1.54	NT	0.93	0.56	0.12	4.72	0.81	0.12
18	0.35	<0.5	26	4	0.9	0.2	1.0	0.46	0.12	4	0.9	0.14
19	0.45	0.12	27	NR	1.2	0.21	0.90	0.58	0.34	5.6	NR	NR
20	0.436	0.155	25.8	4.3	1.1	NR	0.895	0.536	0.135	5.15	0.85	0.125
21	NT	NT	NT	4.1	NT	NT	NT	NT	NT	NT	NT	NT
22	0.34	NR	NR	NR	NR	NR	0.23	0.15	0.12	NR	0.71	0.12

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

Table 29 Summary of Participants' Results and Performance for S2

Lab Code	S2-Alkalinity (mg/L)	S2-B (mg/L)	S2-Ca (mg/L)	S2-Colour (Pt-Co units)	S2-EC (µS/cm)	S2-K (mg/L)	S2-Mg (mg/L)	S2-Na (mg/L)	S2-pH	S2-Silica (mg/L)	S2-Total Hardness (mg/L)	S2-Total P (mg/L)
A.V.	Not Set	0.516	12.3	Not Set	1660	2.16	2.88	11.1	2.50	4.97	42.8	0.0993
H.V.	NA	0.532	12.0	NA	1700	2.20	3.00	11.0	2.50	4.30	42.0	NA
1	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
2	NT	NT	12.6	NT	NT	1.73	NT	10.1	2.47	5.3	NT	NT
3	<1	0.525	12.4	7	1584	2.22	2.83	10.4	2.64	4.97	53	<0.5
4	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
5	<6	0.5	12	<20	1680	2.4	2.8	11	2.5	NT	NT	NT
6	<5	0.53	12	4	1700	1.9	2.5	11	2.5	4.7	43	NR
7	<5	0.549	12.45	15	1415	2.279	2.941	11.566	2.6	4.99	NT	0.103
8	NR	0.51	12.9	NR	NR	2.21	2.91	11.3	NR	5.12	44.2	0.081
9	<1	0.5213	12.2473	5.4	1622.1	1.9593	3.201	12.694	2.6	5.044	43.7632	0.101
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	<2	NR	11.6	10	1650	2.12	2.78	11.0	2.5	5.0	40	NT
12	<5	0.50	12	7	1700	2.3	2.9	10	2.5	5.1	43	0.1
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	0	0.509	12.6	5	1700	2.24	2.90	11.4	2.5	4.91	43	0.100
15	<1	0.485	NT	NT	1664	NT	NT	NT	2.5	NT	42	<1.5
16	<5	0.50	12	5	1800	2.1	2.7	11	2.5	5.0	41	0.1
17	31.33	0.55	12.5	7.08	317	2.14	2.98	11.00	7.43	4.1	30.29	0.10
18	<5	0.5	12	6	1700	2.2	2.8	11	2.5	6	42	0.13
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	<1	0.53	13.2	3	1636	2.2	3.2	12.1	2.55	4.36	46.0	0.091
21	0	NT	NT	4.3	1658	NT	NT	NT	2.54	NT	NT	NT
22	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

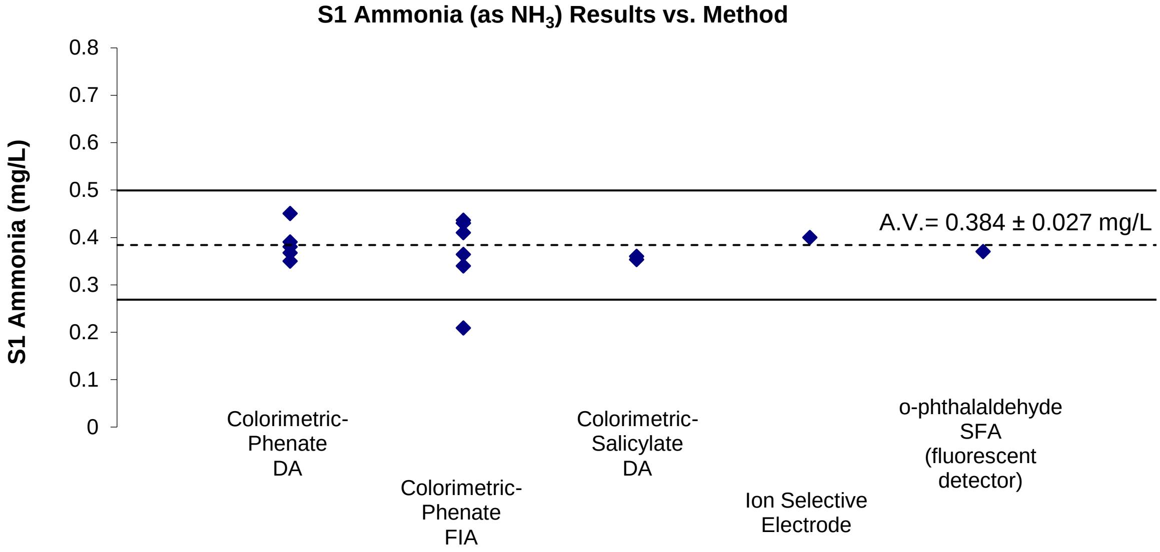
Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value; NA = Not Available

7.5 Participants' Results and Analytical Methods for Dissolved and Total Elements

A summary of participants' results and performance is presented in Tables 28 and 29 and in Figures 26 to 29. Participants were asked to analyse samples S1 and S2 using their normal test method. The measurement methods and instrumental techniques used are presented in Appendices 6 and 7.

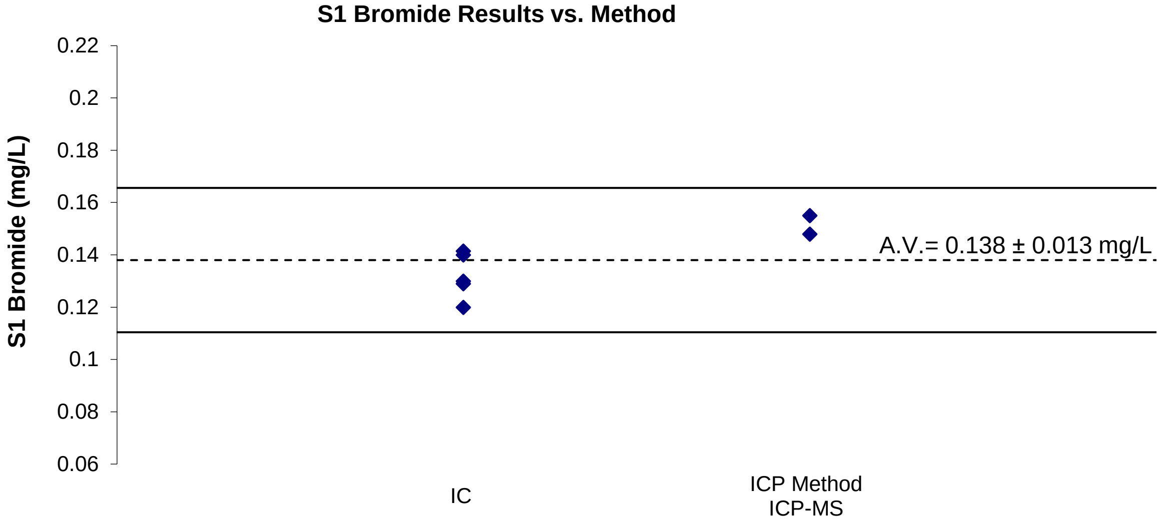
Individual Test Commentary

Ammonia (as NH_3) All results reported for NH_3 returned satisfactory z-scores. Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination. One laboratory reported using ISE and one used the *o*-phthalaldehyde method with SFA and fluorescent detector. Each of these methods produced comparable/satisfactory results (Figure 30).



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

Figure 30 S1-Ammonia Results vs. Measurement Method



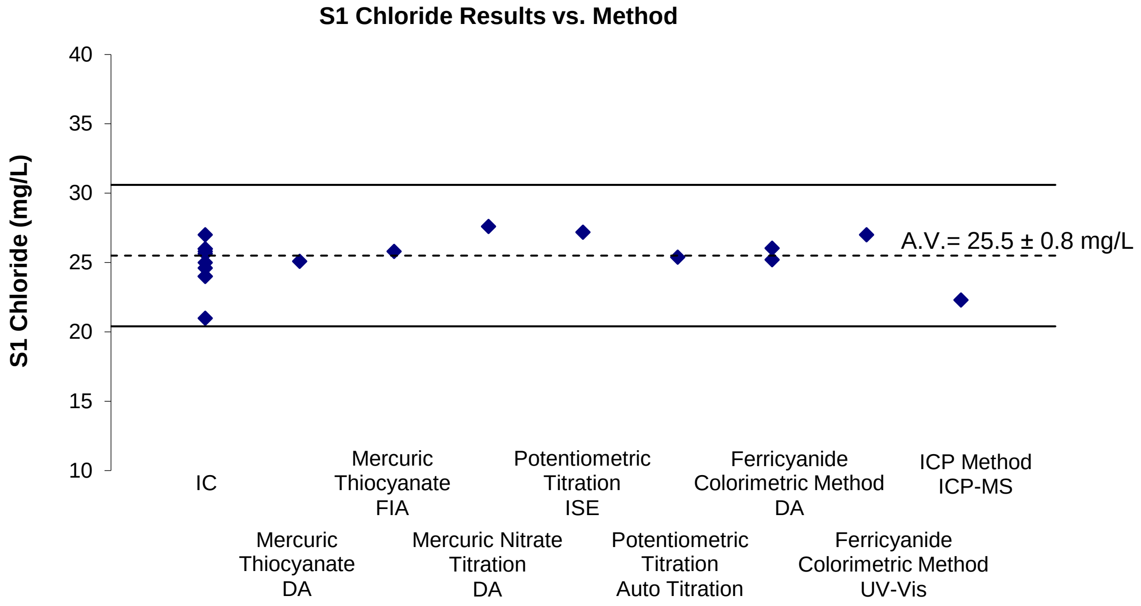
Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 31 S1-Bromide Results vs. Measurement Method

Bromide Although still compatible, bromide results produced using the ICP Method were higher than those from IC measurements (Figure 31).

During ozonation or chlorination, the by-product bromate is formed in water containing bromide. Caution should be exercised when using the ICP method because it measures both bromide and bromate.

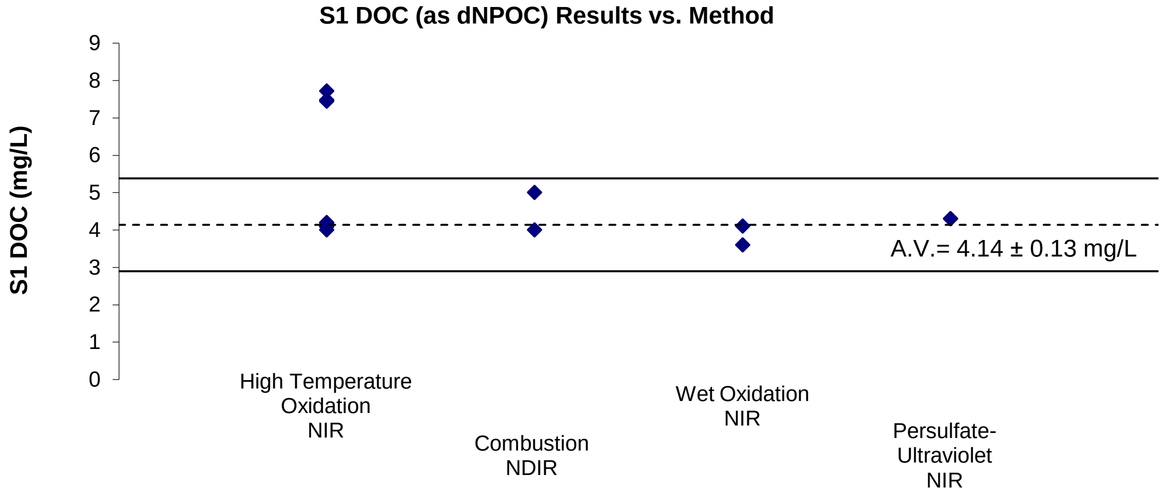
Chloride Participants used a wide variety of methods for chloride analysis in S1 and all produced compatible results (Figure 32).



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

Figure 32 S1-Chloride Results vs. Measurement Method

Dissolved Organic Carbon as dNPOC level in S1 was 4.14 mg/L. Three participants reported high unsatisfactory results. The results were similar, centred on a value of 7.55 mg/L. These laboratories may have measured and reported total dissolved carbon, and not the dNPOC fraction of total dissolved carbon (Figure 33).

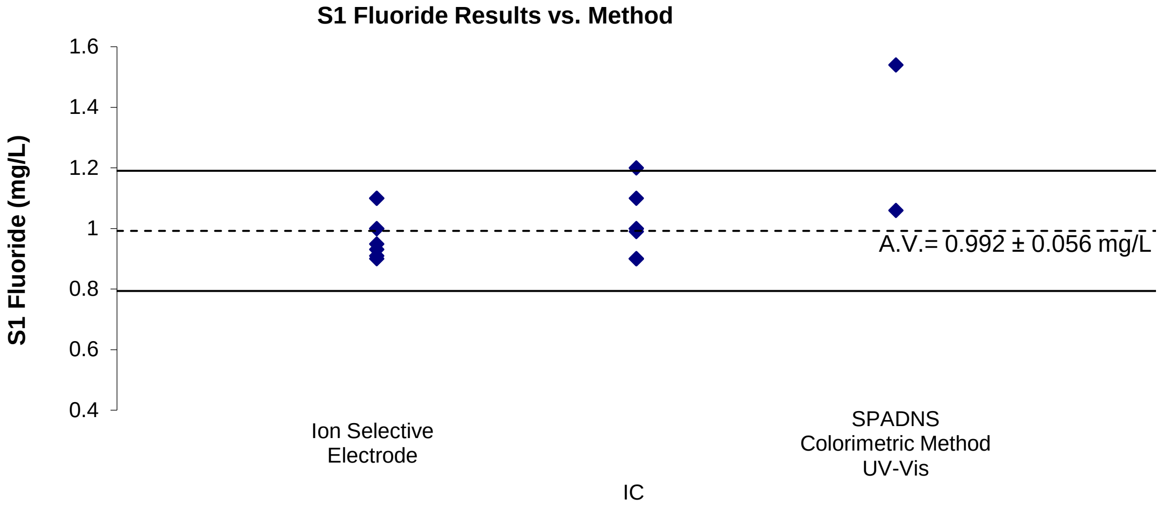


Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 33 S1-DOC (as dNPOC) Results vs. Measurement Method

Fluoride Most participants used either the ion selective electrode method or ion chromatographic method. Two laboratories used the SPADNS colorimetric method with UV-Vis determination (Figure 34).

Fluoride by SPANDS suffers from interference from chlorides.



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

Figure 34 S1-Fluoride Results vs. Measurement Method

Iodide Eight participants reported results for iodide in S1. No assigned value was set for iodide in S1 because the reported results were too variable with a between-laboratory coefficient of variation of 38%. One laboratory used ICP-MS for its iodide measurements (Figure 35).

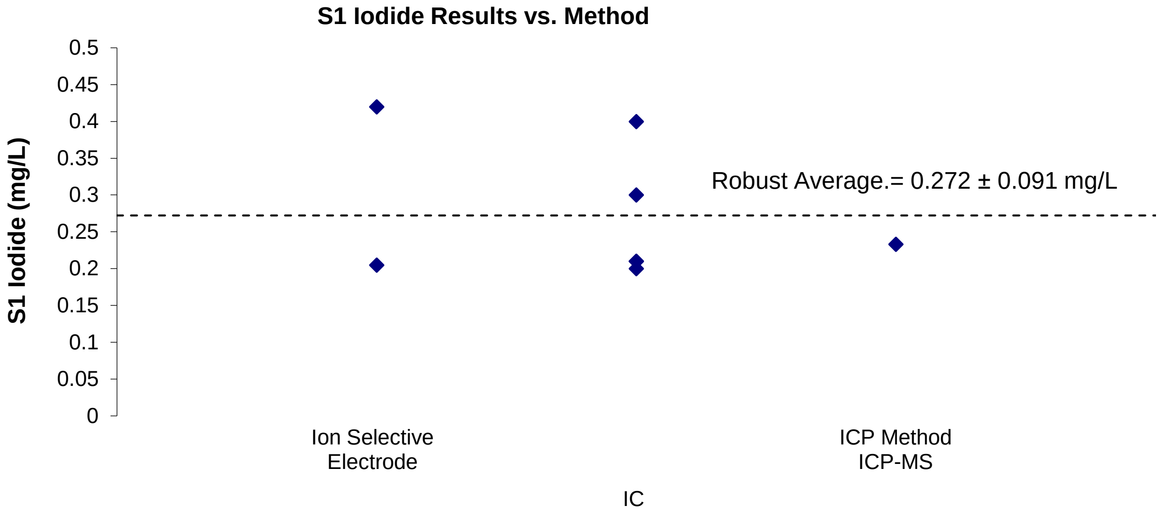
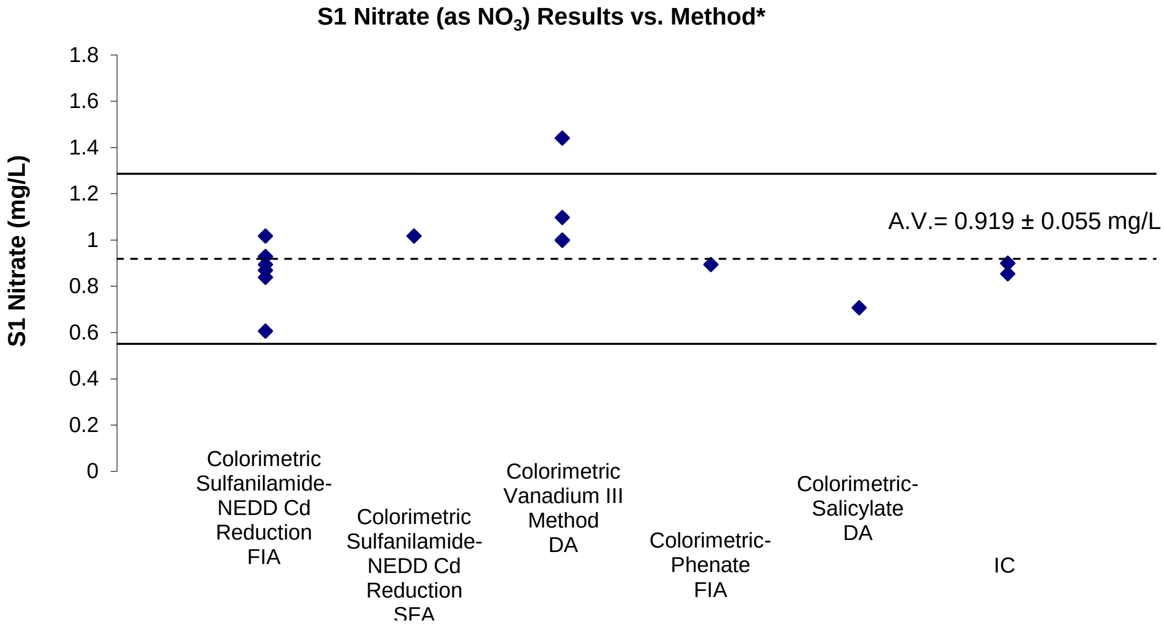


Figure 35 S1-Iodide Results vs. Measurement Method

Nitrate-(as NO_3) and Nitrite (as NO_2) The Australian Drinking Water Guidelines are specified for nitrate (as NO_3) and nitrite (as NO_2). The request in this study was for participants to use their routine methods but to report results for nitrate and nitrite.

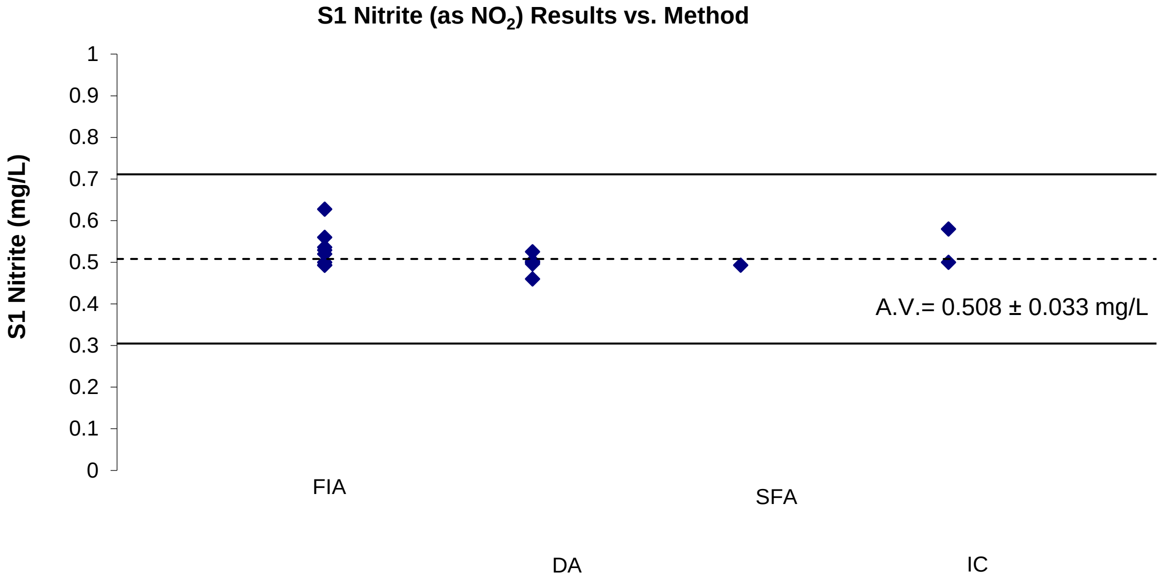
Laboratories 1, 3, 6, 9, 13, 14 and 22 correctly measured nitrate and nitrite in the potable water sample S1 but reported results as nitrate-N and nitrite-N. The assigned value for nitrate converted to nitrate –N is 0.208 mg/L and for nitrite converted to nitrite-N is 0.155 mg/L.

Figures 36 and 37 present plots of participants results for NO_3 and NO_2 in S1 respectively versus the instrumental techniques used. The results reported by laboratories 1, 3, 6, 9, 13, 14 and 22 were converted and plotted from NO_3-N or NO_3-N to NO_3 and NO_2 respectively in order to assess any trends with various measurement methods.



*The results reported by laboratories 1, 3, 6, 9, 13, 14 and 22 have been converted from NO_3-N to NO_3 and plotted as NO_3. Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 36 S1-Nitrate Results vs. Measurement Method

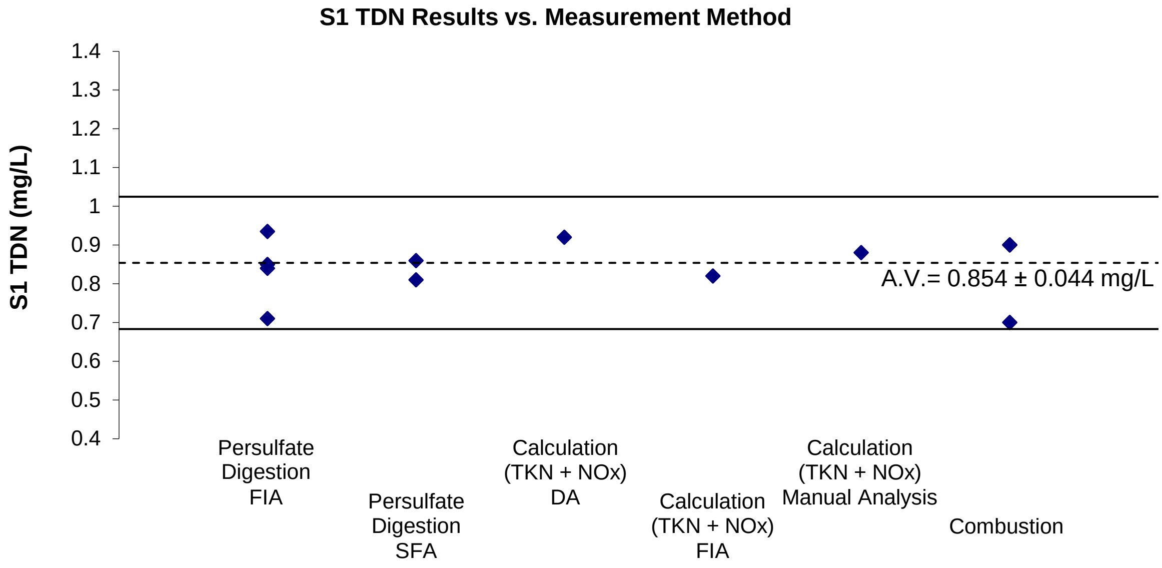


*The results reported by laboratories 1, 3, 6, 9, 13, 14 and 22 have been converted from NO_2-N to NO_2 and plotted as NO_2. Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 37 S1-Nitrite Results vs. Measurement Method

Most participants (eight) used colorimetric-sulfanilamide-NEDD Cd reduction for nitrate measurements; five used the Vanadium III colorimetric method with DA and three used the ion chromatographic method (Figure 36).

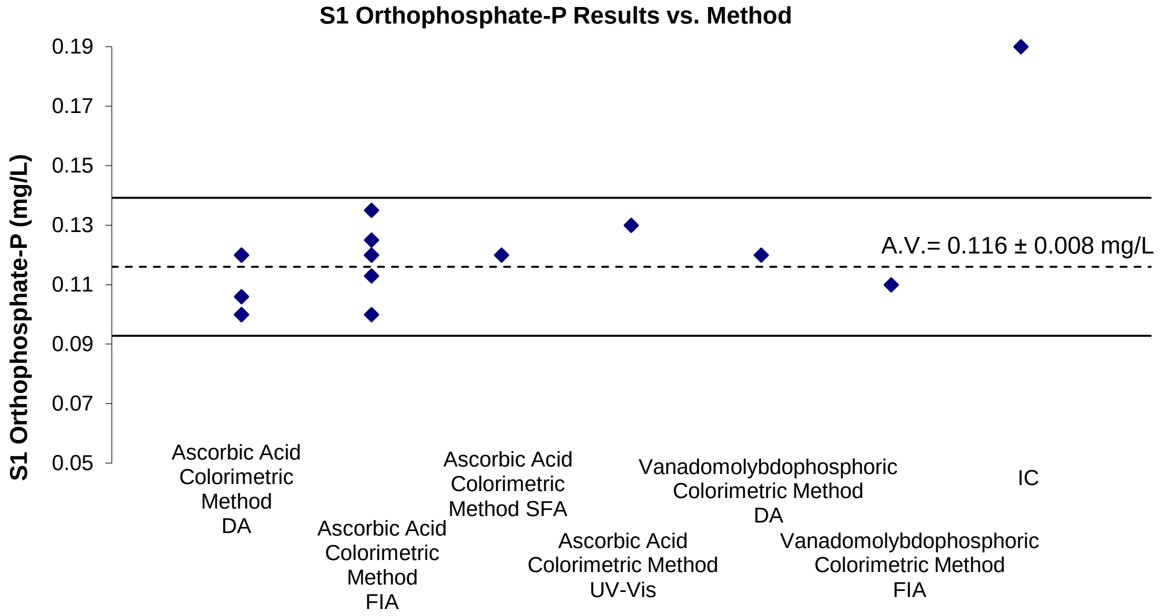
Total Dissolved Nitrogen All reported results for TDN were in agreement with each other and with the robust average of 0.854 ± 0.044 mg/L. Figure 38 presents plots of participants' results versus measurement method used for TDN determination in S1.



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

Figure 38 S1-TDN Results vs. Measurement Method

Orthophosphate-P One participant used IC for orthophosphate-P measurements in S1 and two reported using a vanadomolybdophosphoric acid method; all other participants used ascorbic acid colorimetric method with FIA, SFA, DA or UV-Vis determination (Figure 39).

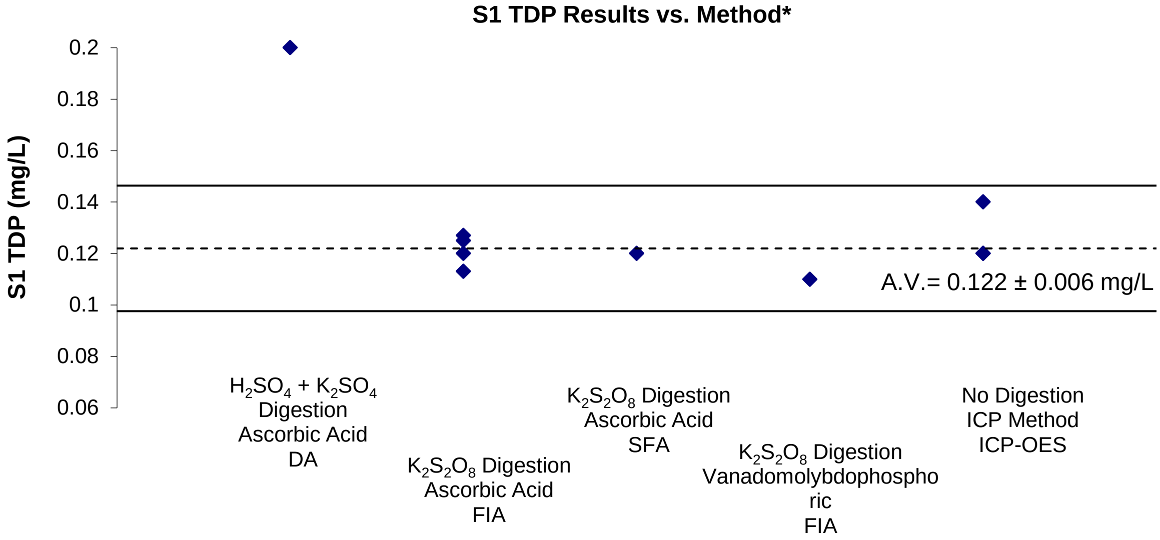


Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 39 S1-Orthophosphate-P Results vs. Method

The level of orthophosphate in S1 was 0.116 mg/L and the level of sulphate was 19.5 mg/L. Sulphate can interfere with low level phosphate when measured by IC and can cause false positive results. Old columns may also cause peak shifting which can result in misidentification.

Total dissolved phosphorus Most laboratories used potassium persulphate for digestion and then measured the liberated orthophosphate colorimetrically by FIA or SFA. Two participants did not perform any digestion, instead reporting measurement of TDP in the sample by an ICP method. All reported results returned satisfactory z-scores except for one (Figure 40).

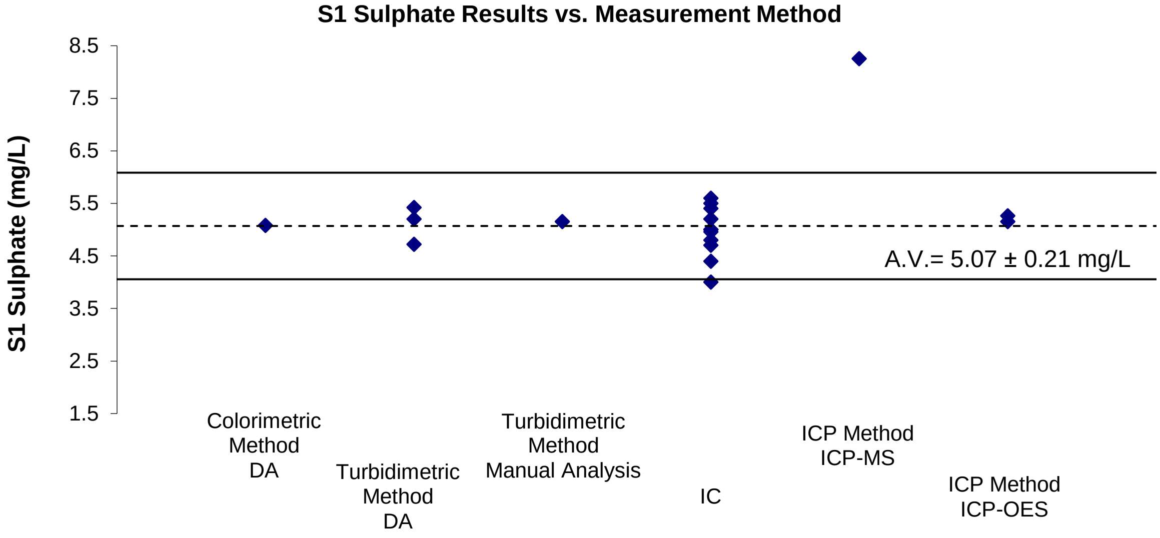


Laboratory 13 result of 0.28 mg/L has been plotted as 0.2 mg/L. Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 40 S1-TDP Results vs. Measurement Method

Sulphate Most participants used IC for sulphate measurements, and four reported using a turbidimetric method.

Two laboratories measured sulphate by ICP-OES as total sulphur, and one by ICP-MS (Figure 41).

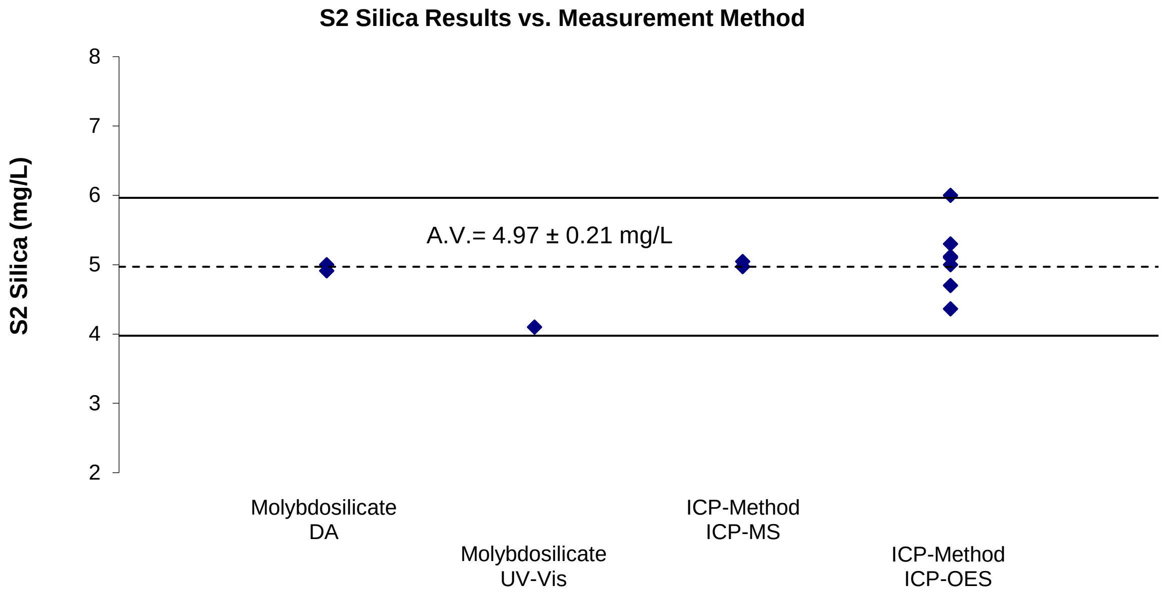


Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 41 S1-Sulphate Results vs. Measurement Method

Alkalinity to pH 4.5 as ($CaCO_3$) was below the reporting level of most participants. No assigned value was set for this test.

Silica (as SiO_2) Plots of participants' results versus measurement technique used are presented in Figure 42.



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

Figure 42 S2-Si (as SiO_2) Results vs. Measurement Method

Colour No assigned value could be set for colour in S2 because the measurement methods used did not produce compatible results (Figure 43). The least variable results were those produced using DA measurement.

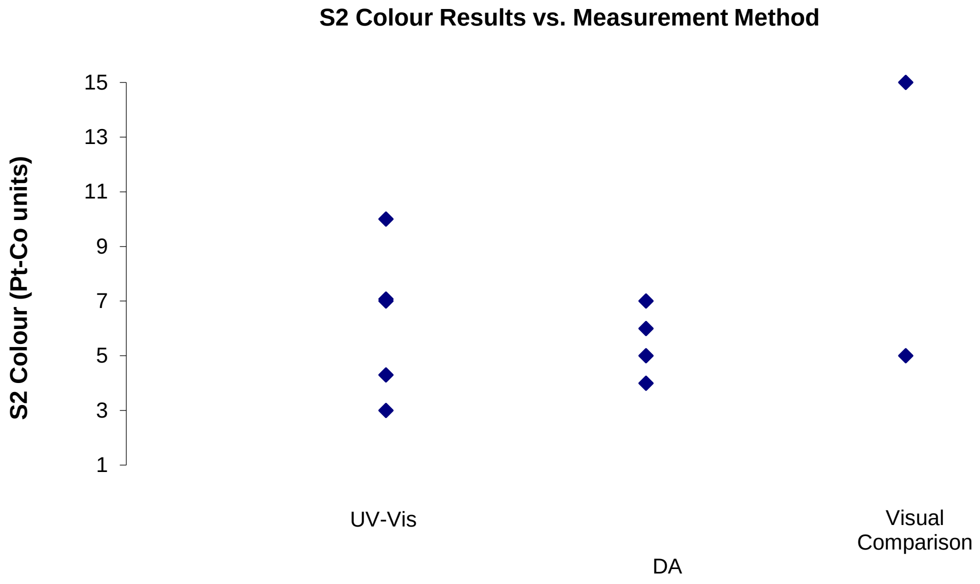
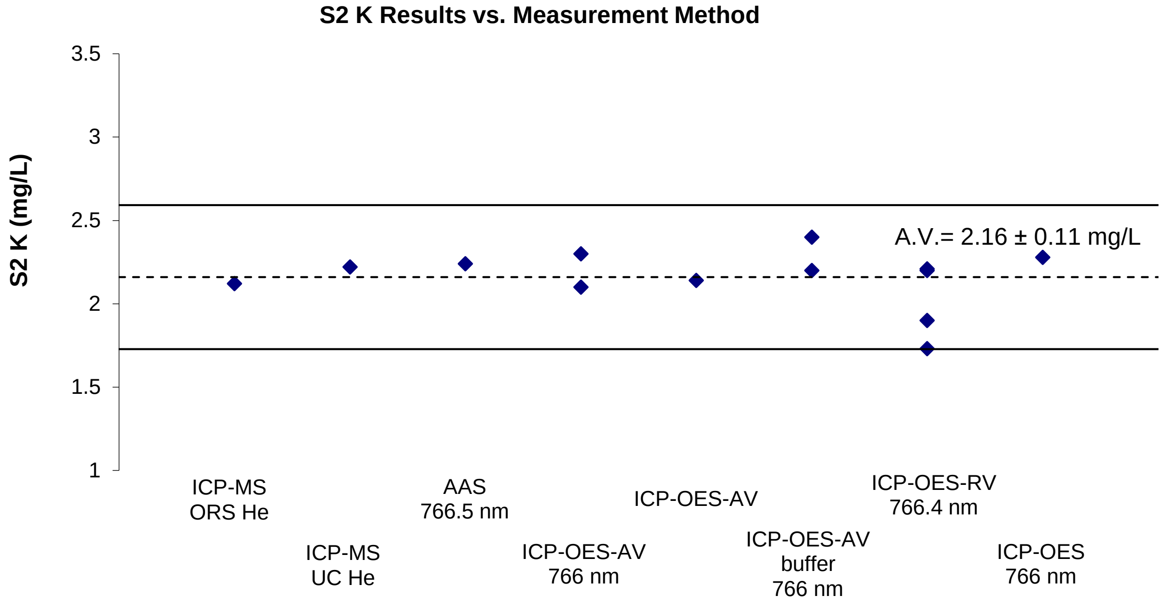


Figure 43 S2-Colour Results vs. Measurement Method

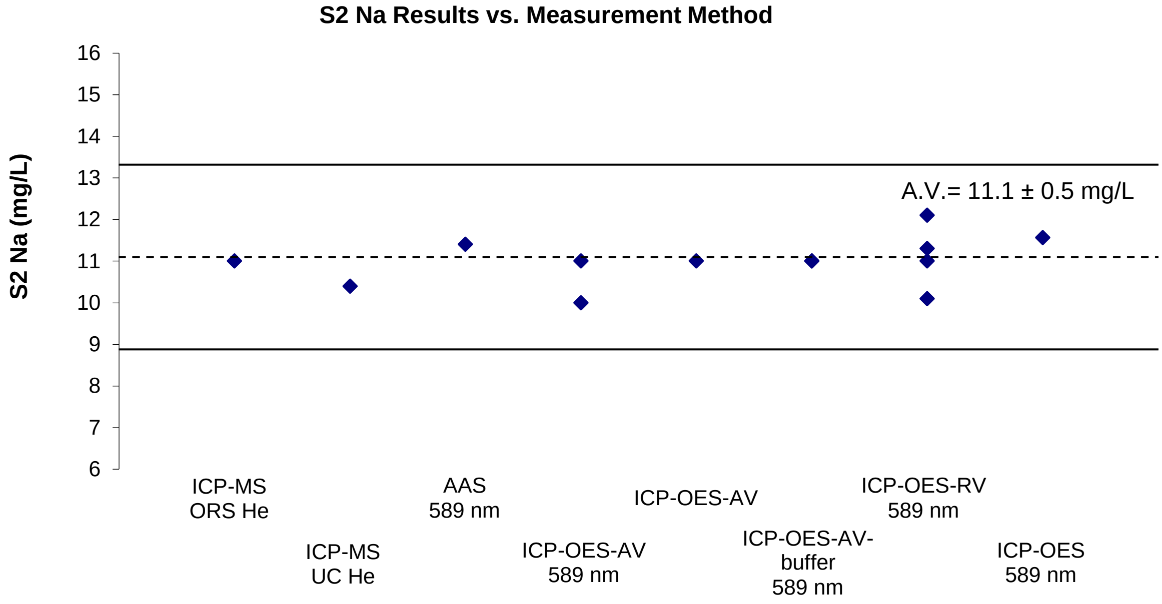
Potassium All results reported for K in S2 returned satisfactory z-scores. Participants used a wide variety of instrumental techniques, which are presented in Figure 44.



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

Figure 44 S2-K Results vs. Measurement Method

Sodium measurements in S2 did not present technical difficulty to participating laboratories. (Figure 45).



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

Figure 45 S2-Na Results vs. Measurement Method

7.6 Comparison with Previous NMI Proficiency Tests of Nutrients in Water

AQA 22-11 is the fourteenth NMI proficiency test of nutrients in water. On average, participants' performance in measuring nutrients, anions and physical tests in water has remained consistent over time with the percentage of satisfactory z-scores ranging from 89% to 96% (Figure 46).

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 its scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ 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 are 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 30).

Table 30 Control Samples Used by Participants

Lab. Code	Description of Control Samples
2	Elemental check standards sourced from LGC Standards (ISO 17034:2016 accredited Reference Materials Producer, A2LA Certificate No. 2848.02)
3	CWW-TM-A, B and C
4	Sigma-Aldrich - Ammonium Standard for IC, Sigma-Aldrich - Nitrite Standard for IC, Sigma-Aldrich - Nitrate Standard for IC, Sigma-Aldrich - Chloride Standard for IC, Sigma-Aldrich - Sulfate Standard for IC
5	CWWTMC, QCI-136 alkalinity, C02948 conductivity, C02838 pH, ICC-210 anions
7	ICP-AM-17, ICP-MS-68B-B, GWS-4 (In-house reference standard)
10	NSI Lab-Nutrients/BOD (H2O)-CRM QCI-084, HPS-TOC 100071-9-100
15	TMDW Trace metals in Drinking Water #2126004
22	NMI Reference standards

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*’[15]

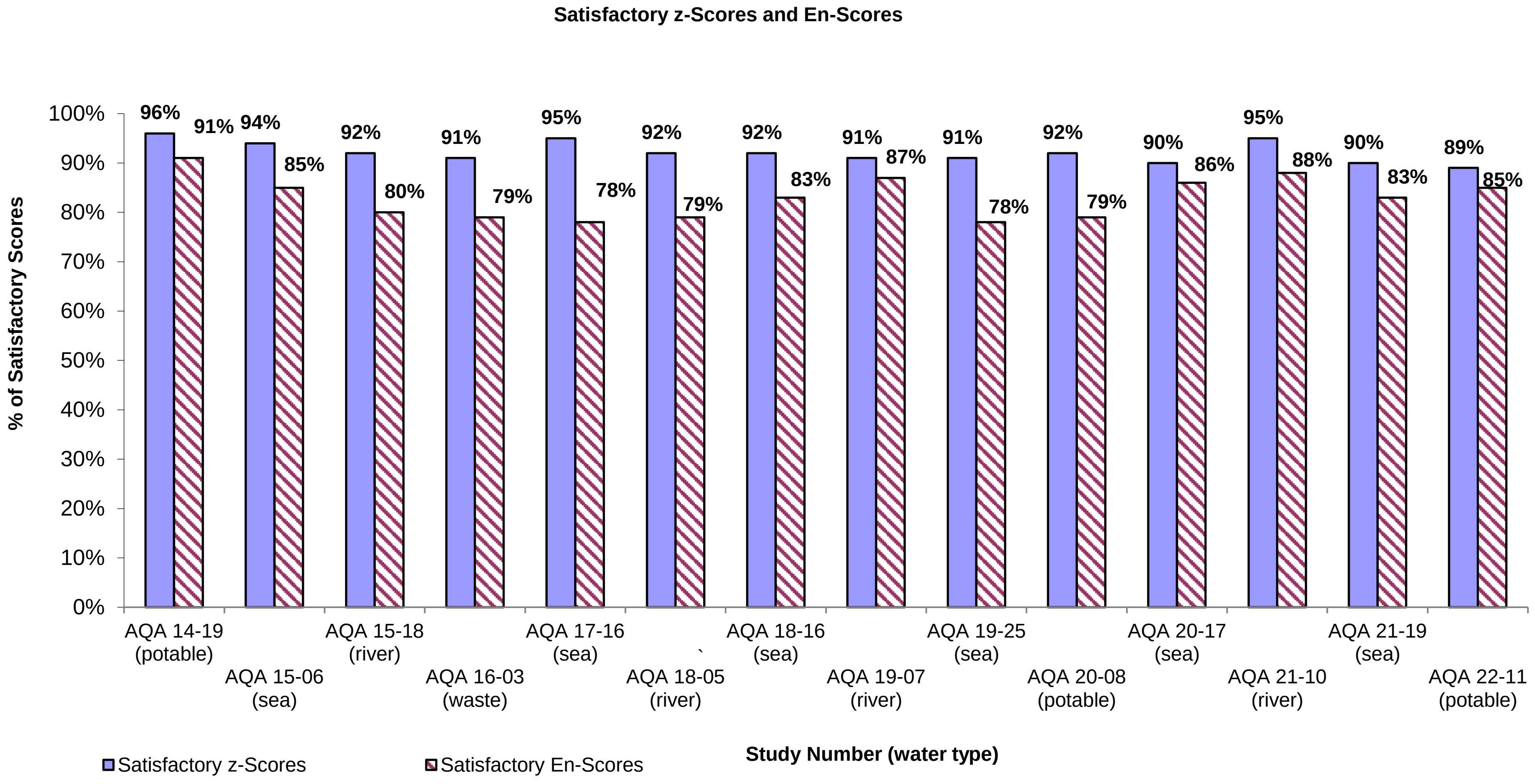


Figure 46 Participants' Performance in Nutrients and Anions in Water PT Studies over Time

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A 1.1 Sample Preparation

Sample S1 was prepared from approximately 16 L of autoclaved potable water. The water was fortified for seven analytes of interest, before mixing and dispensing into 400 mL portions.

Sample S2 was prepared from approximately 17 L of potable water which was fortified for four analytes of interest. The sample was then allowed to mix thoroughly prior to being bottled into 400 mL portions.

A 1.2 Sample Analysis and Homogeneity Testing

A partial homogeneity test was conducted for all the analytes of interest in samples S1 and S2 with the exception of alkalinity, chloride, colour, iodide, sulphate and total P.[1] Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Methodology for Total Elements

Measurement of total elements in S2 involved using ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, duplicates and sample matrix spikes was carried through the same set of procedures and analysed at the same time as the samples. A summary of the wavelength used for each analyte is given in Table 31.

Table 31 Instrumental Technique used for Total Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S2 Final Dilution Factor	Wavelength (nm)
B	ICP-OES	Y	NA	NA	1	249.772
Ca	ICP-OES	Y	NA	NA	1	318.127
K	ICP-OES	Y	NA	NA	1	766.491
Mg	ICP-OES	Y	NA	NA	1	279.800
Na	ICP-OES	Y	NA	NA	1	588.995
P	ICP-OES	Y	NA	NA	1	177.434

Methodology for Tests Other Than Total Elements in S1 and S2

A summary of the measurement methods and instrumental techniques for analytes in Samples S1 and S2 are presented in Tables 32 and 33.

Table 32 Methodology for S1

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination - OPA Method	SFA
Bromide	Ion Chromatographic Method	IC
Dissolved Organic Carbon	High Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	ISE
NO_3	Colorimetric-Sulphanilamide-NEDD Cd Reduction	FIA
NO_2	Colorimetric	FIA
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA

Sulphate	Turbidimetric Method	DA
Total Dissolved Nitrogen	Persulfate digestion	FIA
Total Dissolved Phosphorus	ICP-Method	ICP-MS

Table 33 Methodology for S2

Test	Measurement Method	Instrument
Silica (as SiO_2)	ICP-Method	ICP-OES
Total Hardness (as $CaCO_3$)	Calculation	ICP-OES

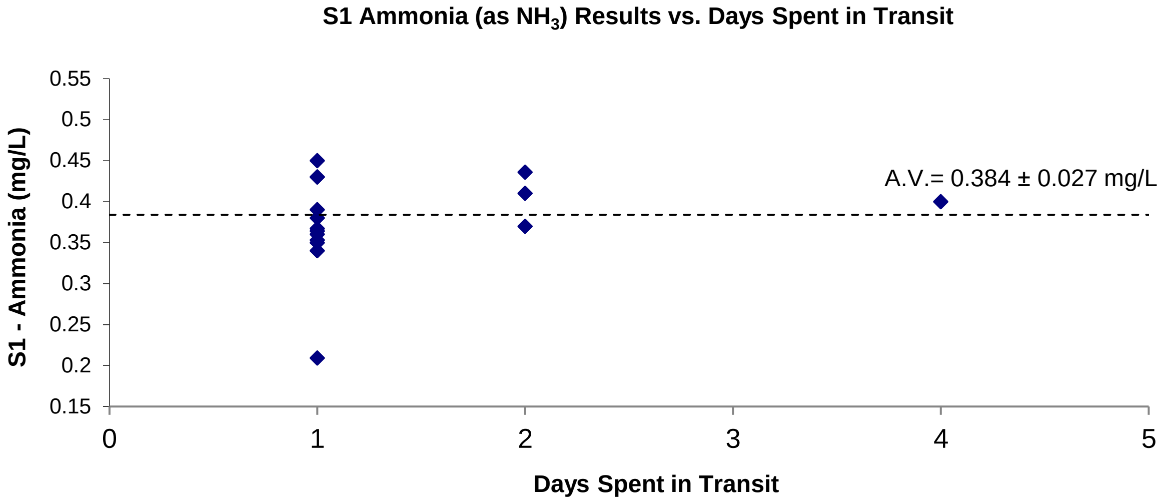
APPENDIX 2 - STABILITY STUDY

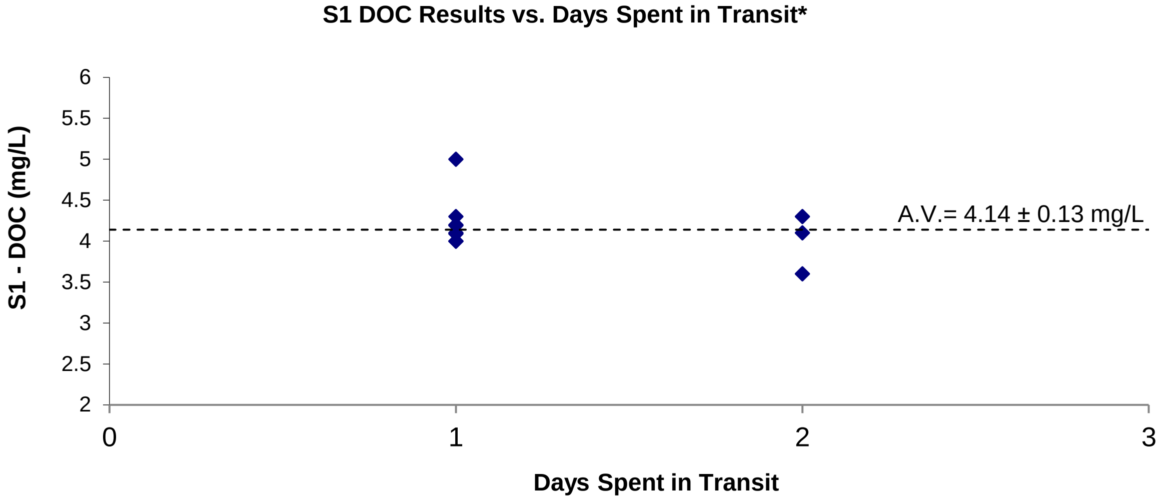
Samples S1 and S2 were dispatched on 26 July 2022. Participants were advised to store sample S1 frozen if analyses cannot be commenced on the day of receipt. Sample's condition on receipt and the date when the samples were received and analysed by the participants are presented in Table 34. No significant trends between participants' results and sample's condition on receipt and date of analysis were evident (Figures 45 to 46).

Table 34 Sample S1 and S2 Condition on Receipt and the Date When the Samples were Received and Analysed

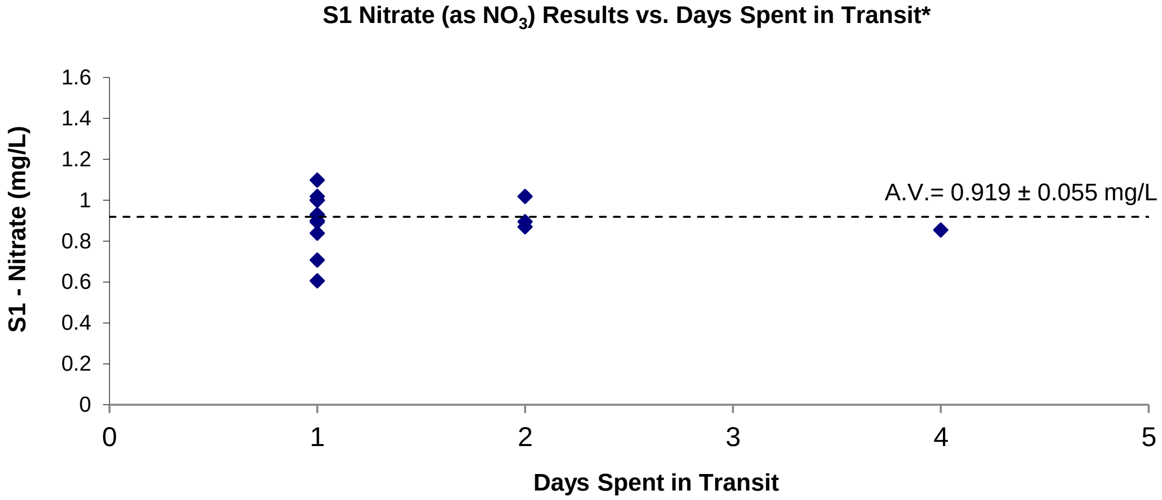
Lab Code	Received Date	S1		S2	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	27/07/2022	Frozen	4/08/2022		
2	28/07/2022			Cold	25/08/2022
3	27/07/2022	Frozen	8/08/2022	Cold	10/08/2022
4	27/07/2022	Frozen	28/07/2022		
5	27/07/2022	Frozen	28/07/2022	Cold	28/07/2022
6	28/07/2022			Refrigerated	2/08/2022
7	27/07/2022	Frozen	18/08/2022	Frozen	18/08/2022
8	27/07/2022	At room temperature	17/08/2022	At room temperature	17/08/2022
9	27/07/2022	Cold	31/07/2022	Frozen	29/07/2022
10	27/07/2022	Cold	27/07/22 - 26/08/22		
11	28/07/2022	Frozen	2/08/2022	Cold	2/08/2022
12	27/07/2022	Cold	29/07/2022	Cold	29/07/2022
13	27/07/2022	Frozen	15/08/2022		
14	27/07/2022	Frozen	1/08/2022	Cold	1/08/2022
15	30/07/2022	Cold	1/08/2022	Cold	1/08/2022
16	27/07/2022	Cold	29/07/2022	Cold	29/07/2022
17	27/07/2022	Cold	2/08/2022	Frozen	2/08/2022
18	27/07/2022	Cold	24/08/2022	Frozen	24/08/2022
19	27/07/2022	Frozen	22/08/2022		
20*	29/07/2022	Cold	3/08/2022	Cold	3/08/2022
21*	28/07/2022	Frozen	18/08/2022	Cold	29/07/2022
22*	3/08/2022	Frozen	22/08/2022		

*The samples have been dispatched on 26/07/2022 except for laboratories 20, 21 and 22. The samples for laboratories 20 and 21 were dispatched on 27.07.2022 while for laboratory 22 were dispatched on 02.08.2022.



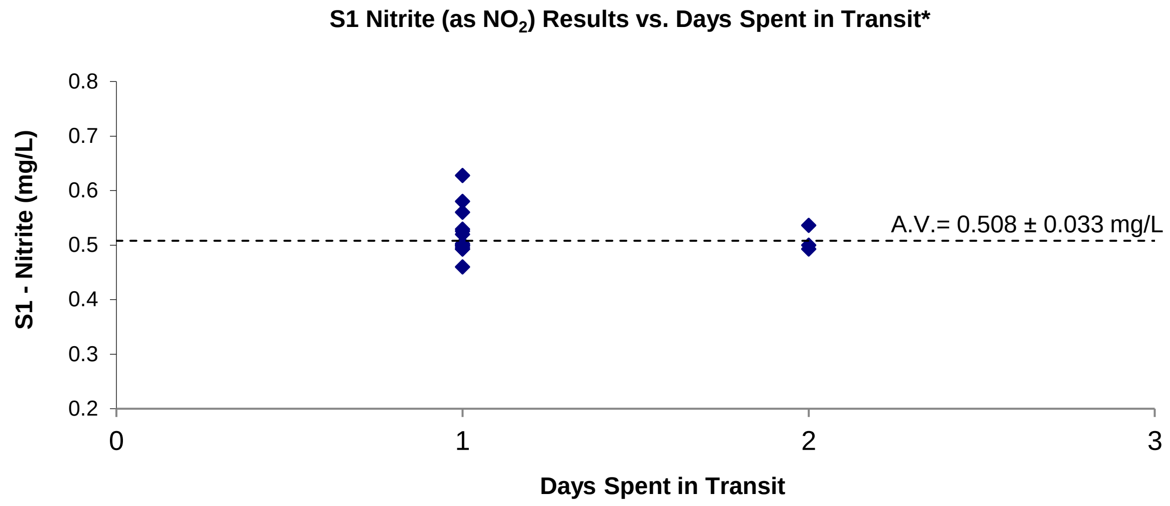


*The result reported by laboratories 3, 13 and 17 were not included.



*The results reported by laboratories 1, 3, 6, 9, 13, 14 and 22 were converted from NO_3-N to NO_3 and plotted as NO_3. The result reported by laboratory 4 was not included.

Figure 47 Results vs Days Spent in Transit



*The results for laboratories 1, 3, 6, 9, 13, 14 and 22 were converted from NO_2-N to NO_2 and plotted as NO_2.

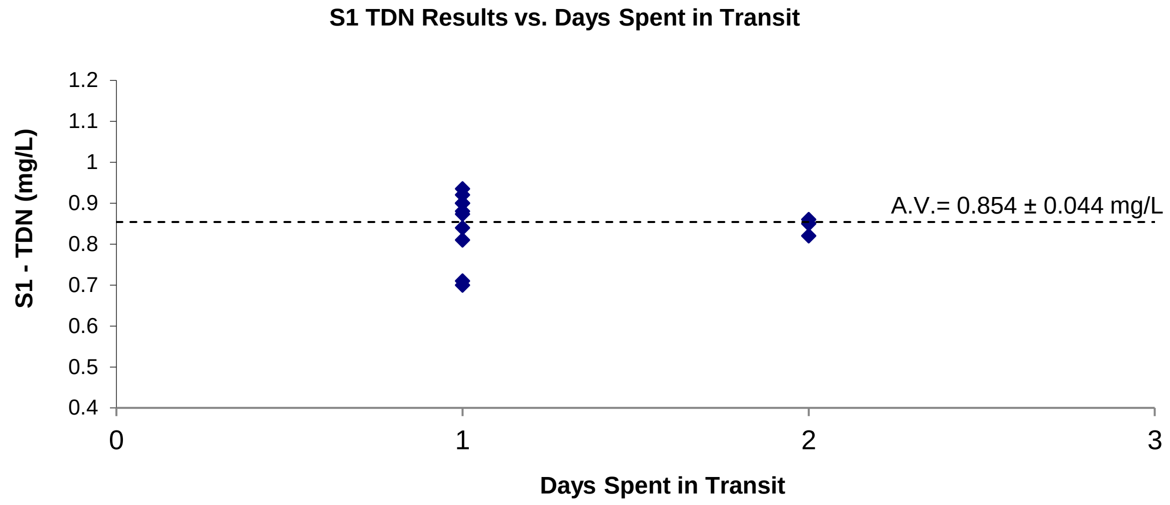


Figure 45 Results vs Days Spent in Transit (continued)

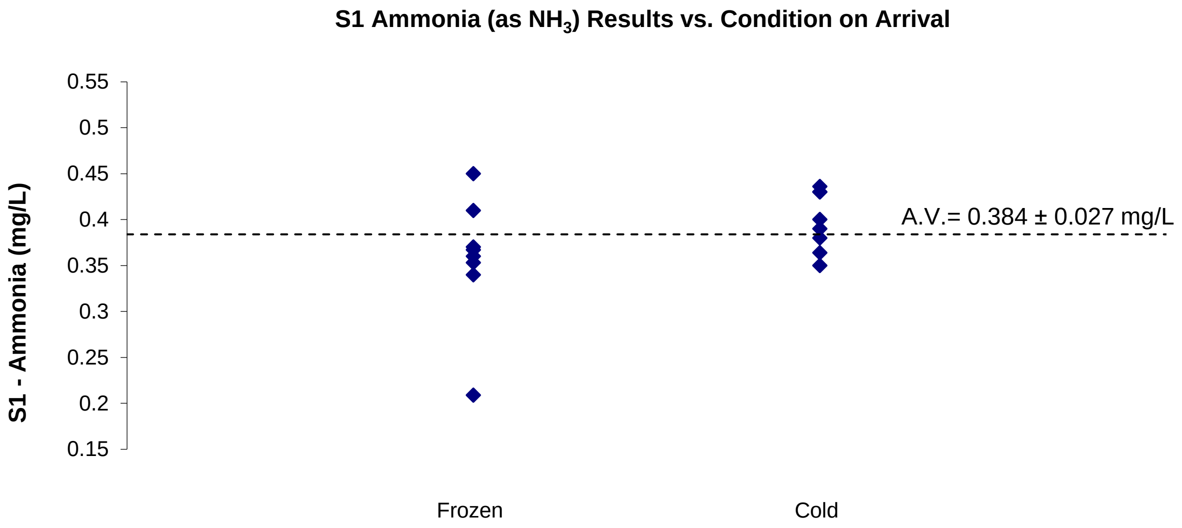
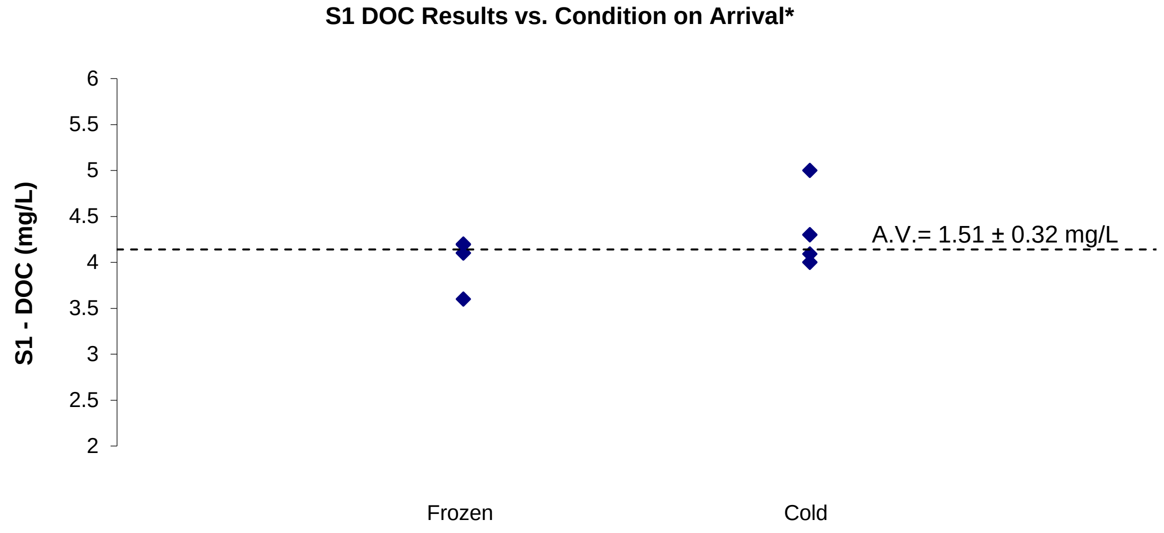
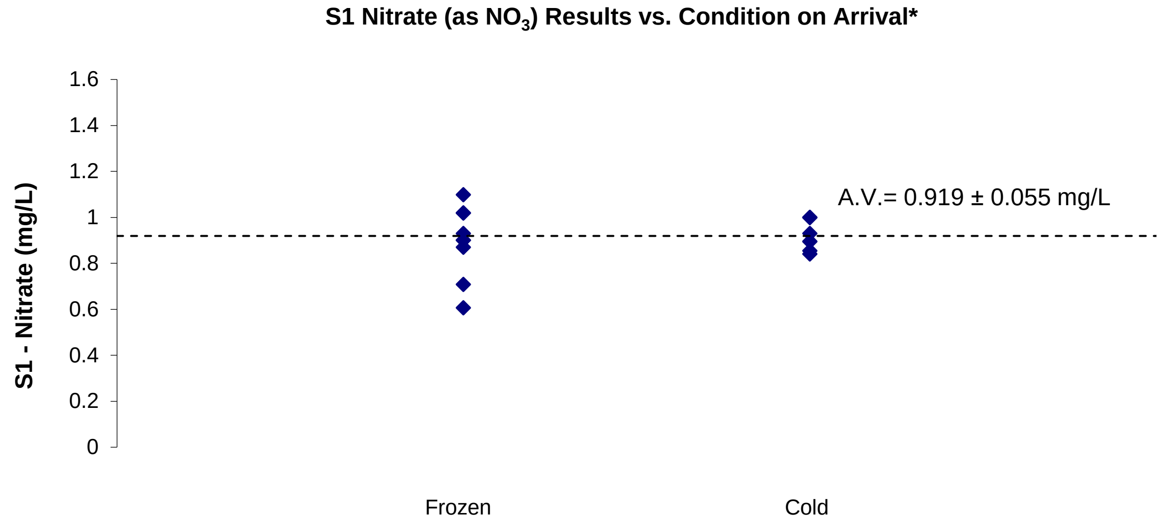


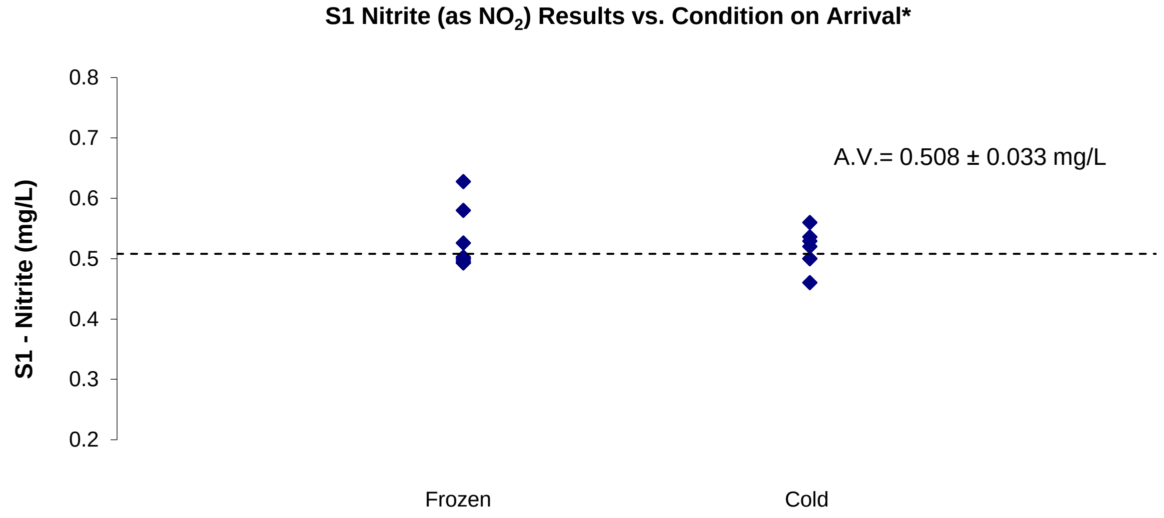
Figure 48 Results vs Condition on Arrival


S1 DOC Results vs. Condition on Arrival*

*The results reported by laboratories 3, 13 and 17 were not included.


S1 Nitrate (as NO_3) Results vs. Condition on Arrival*

*The results reported by laboratories 1, 3, 6, 9, 13, 14 and 22 were converted from NO_3-N to NO_3 and plotted as NO_3. The result reported by laboratory 4 was not included.


S1 Nitrite (as NO_2) Results vs. Condition on Arrival*

*The results for laboratories 1, 3, 6, 9, 13, 14 and 22 were converted from NO_2-N to NO_2 and plotted as NO_2.

Figure 46 Results vs Condition on Arrival (continued)

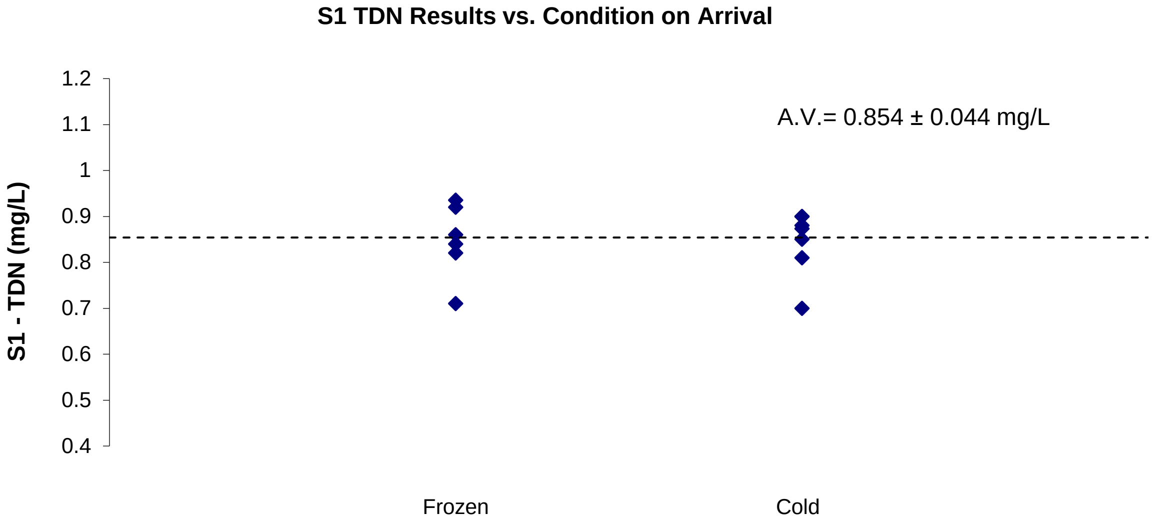


Figure 46 Results vs Condition on Arrival (continued)

Stability Study

Stability studies conducted for nutrients and physical tests in water in previous PT studies found no significant changes in any of the analytes' concentration. A stability study was however conducted in the present study for the less stabile analytes: Ammonia (as NH_3), Nitrate (as NO_3) and Nitrite (as NO_2) in S1.

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

To test for storage stability, the results from two sets of samples kept at -20°C (reference samples) were compared to the results from two samples left out on a laboratory table for three days (room samples). These samples were analysed in duplicate and in random order at the same time.

To check sample stability during the study conduct, a comparison was undertaken of 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 within their respective uncertainties (Figure 47).

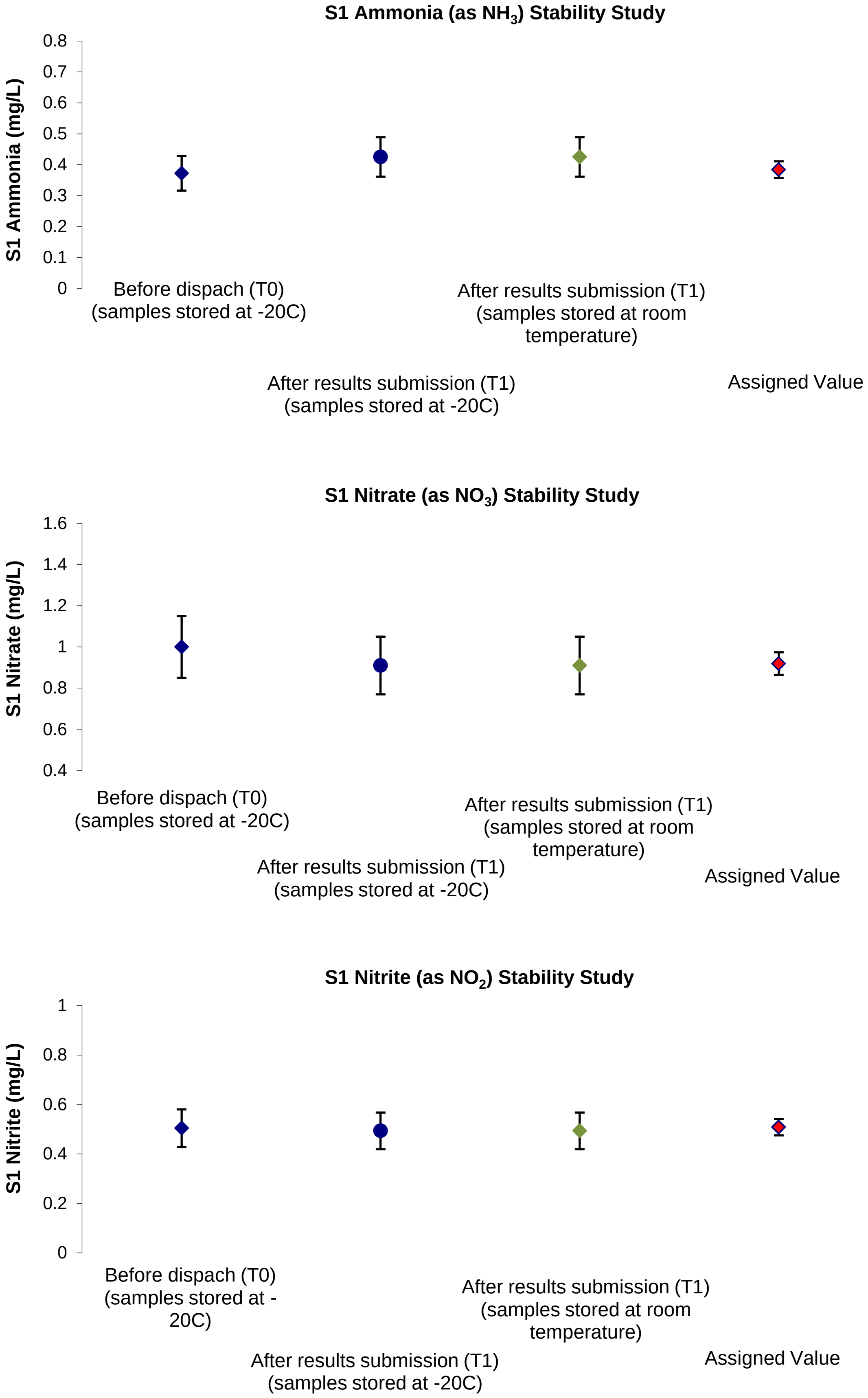


Figure 49 Stability Study Results

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 ‘ISO13258:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C’.[6] The uncertainty was estimated as:

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

where:

$u_{\text{rob av}}$ 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 35.

Table 35 Uncertainty of Assigned Value for Chloride in Sample S1

No. results (p)	19
Robust Average	25.5 mg/L
$S_{rob\ av}$	1.40 mg/L
$u_{rob\ av}$	0.40 mg/L
k	2
$U_{rob\ av}$	0.80 mg/L

The assigned value for Chloride in Sample S1 is **25.5 ± 0.8 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 8).

A worked example is set out below in Table 36.

Table 36 z-Score and E_n-score for Chloride result reported by Laboratory 11 in S1

Chloride Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
24.6 ± 3	25.5 ± 0.8	10% as CV or 0.10 x 25.5 = = 2.25 mg/L	$z = \frac{(24.6 - 25.5)}{2.25}$ z = -0.35	$En = \frac{(24.6 - 25.5)}{\sqrt{3^2 + 0.8^2}}$ E_n = -0.29

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 be used to estimate the uncertainty of their measurement results.[10] Between 2014 and 2022, NMI carried out fourteen proficiency tests for nutrients, anions and physical tests in water. These studies involved measurements of these analytes in potable, fresh (river), waste and seawater. Laboratory X participated and submitted satisfactory results for 13 of these studies. Results are presented in Table 37.

Table 37 Laboratory X Reported Results for Chloride

Study No.	Sample	Laboratory result[*] mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 14-19	Potable	51.9 ± 10	55.4 ± 1.4	2.9	8
AQA 15-18	River	65.7 ± 10	70.3 ± 3.6	6.5	10
AQA 16-03	Waste	3099 ± 320	2990 ± 170	6.3	8
AQA 17-16	Seawater	13100 ± 1300	12800 ± 420	4.1	10
AQA 18-05	River	68 ± 8.0	71.3 ± 1.5	3.4	17
AQA 18-16	Seawater	16600 ± 1600	17300 ± 1600	13	13
AQA 19-07	River	57.0 ± 12	53.7 ± 2.0	4.7	10
AQA 19-25	Seawater	20000 ± 2000	20500 ± 1000	2.2	13
AQA 20-08	Potable	33.4 ± 7.0	41.6 ± 1.9	6.7	13
AQA 20-17	Seawater	9800 ± 980	10700 ± 400	4.9	10
AQA 21-10	River	81 ± 10	86.3 ± 2.7	5.7	20
AQA 21-19	Seawater	19440 ± 1950	20100 ± 600	3.8	9
AQA 22-11	Potable	22.3 ± 5.0	25.5 ± 0.8	5.5	19
Average				5.3[**]	

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

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 5.3%. Using a coverage factor of two gives a relative expanded uncertainty of 11%, at a level of confidence of approximately 95%. Table 38 sets out the expanded uncertainty for results of the measurement of Chloride in potable, fresh, waste or seawater over the range 20.0 – 20000 mg/L.

Table 38 Uncertainty of chloride results estimated using PT data

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

The estimate of 11% passes the test of being reasonable, and the analysis of the four different matrices over eight years can safely be assumed to include all the relevant uncertainty components (different operators, reagents, calibrants etc), and so complies with ISO 17025.[8]

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
AAS	Atomic Absorption Spectrometry
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
DA	Discreet Analyser
dNPOC	Dissolved non-purgeable organic carbon
FIA	Flow Injection Analyser
GUM	Guide to the Expression of Uncertainty in Measurement
IC	Ion Chromatograph
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-MS/MS	Inductively Coupled Plasma - Tandem Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma - Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma - Optical Emission Spectrometry- radial view
ISE	Ion Selective Electrode
Max	Maximum Value in a Set of Results
Md	Median
Min	Minimum Value in a Set of Results
MU	Measurement Uncertainty
NEDD	N-(1-naphthyl)-ethylenediamine dihhydrochloride (NED dihydrochloride)
NIST	National Institute of Standards and Technology
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NIR	Near-infrared
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PT	Proficiency Test
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S.V.	Spiked or Formulated Concentration of a PT Sample
SFA	Segment Flow Analyser
SI	The International System of Units
SPANDS	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
s^2_{sam}	Sampling Variance
s_a/σ	Analytical Standard Deviation Divided by the Target Standard Deviation
Target SD	Target Standard Deviation
σ	Target Standard Deviation
UV-Vis	Ultraviolet and Visible Spectroscopy

APPENDIX 6 - METHODOLOGY FOR S1

Table 39 Measurement Methods and Instrument Techniques for Ammonia-N

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Phenate Method		
2	Not Applicable	Not Applcable	Not Applicable
3	Colorimetric - Phenate Method	FIA	APHA4500NH3-H
4	Colorimetric - Phenate Method	DA	4500-NH3
6	Fluorometric Determination - OPA Method	SFA	Seal
9	Colorimetric - Phenate Method	FIA	
10	Colorimetric - Phenate Method	FIA	4500G
11	Colorimetric - Phenate Method	FIA	in house
12	Colorimetric - Phenate Method	DA	APHA 4500-NH3
13	Colorimetric - Salicylate Method	DA	In house
14	Colorimetric - Salicylate Method	DA	In house method based on APHA 4500-NH3 B
15	Ion Selective Electrode Method	Ion Selective Electrode	APHA
16	Colorimetric - Phenate Method	DA	APHA 4500-NH3
17	Colorimetric - Phenate Method	FIA	APHA 4500
18	Colorimetric - Phenate Method	DA	APHA 4500-NH3
19	Colorimetric - Phenate Method	DA	
20	Colorimetric - Phenate Method	FIA	4500-NH3 H
22	Colorimetric - Phenate Method	FIA	APHA

Table 40 Measurement Methods and Instrument Techniques for Bromide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method		
2	Not Applicable	Not Applcable	Not Applicable
3	ICP-Method	ICP-MS	W32
5	Ion Chromatographic Method	IC	APHA 4110 B
6	Ion Chromatographic Method	IC	apha
7	ICP Method	ICP-MS	
8	Ion Chromatographic Method	IC	Inhouse
9	Ion Chromatographic Method	IC	
10	Not Tested	Not Tested	Not Tested
11	Ion Chromatographic Method	IC	in house
12	Ion Chromatographic Method	IC	APHA 4110B
15	Ion Chromatographic Method	IC	APHA
16	Ion Chromatographic Method	IC	APHA 4110B
18	Ion Chromatographic Method	IC	APHA 4110B
19	Ion Chromatographic Method	IC	
20	ICP Method	ICP-MS	

Table 41 Measurement Methods and Instrument Techniques for Chloride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ferricyanide Colorimetric Method		
2	Not Applicable	Not Applcable	Not Applicable
3	ICP-Method	ICP-MS	W32
4	Ferricyanide Colorimetric Method	DA	4500-Cl
5	Ion Chromatographic Method	IC	APHA 4110 B
6	Ion Chromatographic Method	IC	apha
7	Ferricyanide Colorimetric Method	UV-Vis Spectrophotometer	
8	Ion Chromatographic Method	IC	Inhouse
9	Ion Chromatographic Method	IC	
10	Potentiometric-Titration	Ion Selective Electrode	4500D
11	Ion Chromatographic Method	IC	in house
12	Ion Chromatographic Method	IC	APHA 4110B
13	Mercurric Nitrate Titration	DA	In house
14	Potentiometric-Titration	Auto Titration	In House method based on APHA 4500-Cl D
15	Ion Chromatographic Method	IC	APHA
16	Ion Chromatographic Method	IC	APHA 4110B
17	Mercuric Thiocyanate	DA	APHA 4500
18	Ion Chromatographic Method	IC	APHA 4110B
19	Ion Chromatographic Method	IC	
20	Mercuric Thiocyanate	FIA	4500-CL G

Table 42 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Laboratory Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation		
2	Not Applicable	Not Applcable	Not Applicable
3	High-Temperature Oxidation	NIR-detector	APHA5310-B
6	High-Temperature Oxidation	NIR-detector	apha
9	High-Temperature Oxidation	NIR-detector	
10	Persulfate-Ultraviolet Oxidation	NIR-detector	5310C
11	Wet-Oxidation	NIR-detector	in house
12	combustion NDIR		APHA 5310B
13	High-Temperature Oxidation	NIR-detector	In house
14	High-Temperature Oxidation	NIR-detector	In house method based on APHA 5310-TOC B
16	combustion NDIR		APHA 5310B
17	High-Temperature Oxidation	NIR-detector	APHA 4500
18	High-Temperature Oxidation		APHA 5310B
20	Persulfate-Ultraviolet Oxidation	NIR-detector	5310 C
21	Wet-Oxidation	NIR-detector	

Table 43 Measurement Methods and Instrument Techniques for Fluoride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Selective Electrode Method		
2	Not Applicable	Not Applcable	Not Applicable
3		UV-Vis Spectrophotometer	
5	Ion Chromatographic Method	IC	APHA 4110 B
6	Ion Selective Electrode Method	Ion Selective Electrode	apha
7	Ion Selective Electrode Method	Ion Selective Electrode	
8	Ion Chromatographic Method	IC	Inhouse
9	Ion Chromatographic Method	IC	
10	Ion Selective Electrode Method	Ion Selective Electrode	4500C
11	Ion Chromatographic Method	IC	in house
12	Ion Chromatographic Method	IC	APHA 4110B
13	Ion Selective Electrode Method	Auto Titration	In house
14	Ion Selective Electrode Method	Ion Selective Electrode	In house method based on APHA 4500-F C
15	Ion Chromatographic Method	IC	APHA
16	Ion Chromatographic Method	IC	APHA 4110B
17	SPADNS Colorimetric Method	DA	APHA 4500
18	Ion Selective Electrode Method	IC	APHA 4110B
19	Ion Chromatographic Method	IC	
20	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F C

Table 44 Measurement Methods and Instrument Techniques for Iodide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Selective Electrode Method		
2	Not Applicable	Not Applcable	Not Applicable
6	Ion Chromatographic Method	IC	apha
7	ICP Method	ICP-MS	
9	Ion Chromatographic Method	IC	
12	Ion Chromatographic Method	IC	APHA 4110B
13	Ion Selective Electrode Method	Ion Selective Electrode	In house
16	Ion Chromatographic Method	IC	APHA 4110B
18	Ion Chromatographic Method	IC	APHA 4110B
19	Ion Chromatographic Method	IC	

Table 45 Measurement Methods and Instrument Techniques for Nitrate

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction		
2	Not Applicable	Not Applcable	Not Applicable
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO3-F
4	Colorimetric -vanadium III method	DA	ISO 15923-1:2013
5	Ion Chromatographic Method	IC	APHA 4110 B
6	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	apha
9	Colorimetric - phenate method	FIA	
10	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500G
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	in house
12	Colorimetric -vanadium III method	DA	APHA
13	Colorimetric - salicylate method	DA	In house
14	Colorimetric -vanadium III method	DA	In house method based on APHA 4500-NO3 H
15	Ion Chromatographic Method	IC	APHA
16	Colorimetric -vanadium III method	DA	APHA
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500
18	Colorimetric -vanadium III method	DA	APHA
19	Ion Chromatographic Method	IC	
20	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500-NO3 I
22	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA

Table 46 Measurement Methods and Instrument Techniques for Nitrite

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric Method		
2	Not Applicable	Not Applcable	Not Applicable
3		FIA	APHA4500NO3-F
4	Colorimetric Method	DA	ISO 15923-1:2013
5	Ion Chromatographic Method	IC	APHA 4110 B
6	Colorimetric Method	SFA	apha
9	Colorimetric Method	FIA	
10	Colorimetric Method	FIA	4500B
11	Colorimetric Method	FIA	in house
12	Colorimetric-Sulfanilamide-NEDD hydrazine reduction	DA	APHA 4500-NO2
13	Colorimetric Method	DA	In house
14	Colorimetric Method	DA	In house method based on APHA 4500-NO2 B
16	Colorimetric-Sulfanilamide-NEDD hydrazine reduction	DA	APHA 4500-NO2
17	Colorimetric Method	FIA	APHA 4500
18	Colorimetric Method	DA	APHA 4500-NO2
19	Ion Chromatographic Method	IC	
20	Colorimetric Method	FIA	4500-NO3 I
22	Colorimetric Method	FIA	APHA

.Table 47 Measurement Methods and Instrument Techniques for Orthophosphate-P

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Vanadomolybdophosphoric Colorimetric Method		
2	Not Applicable	Not Applcable	Not Applicable
3	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-G
6	Ascorbic Acid Colorimetric Method	SFA	apha
7	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer	
9	Ascorbic Acid Colorimetric Method		
10	Ascorbic Acid Colorimetric Method	FIA	4500F
11	Ascorbic Acid Colorimetric Method	FIA	in house
12	Ascorbic Acid Colorimetric Method	DA	APHA-P C
13	Ascorbic Acid Colorimetric Method	DA	In house
14	Ascorbic Acid Colorimetric Method	DA	In house method based on APHA 4500-P B & F
16	Ascorbic Acid Colorimetric Method	DA	APHA-P C
17	Ascorbic Acid Colorimetric Method	DA	APHA 4500
18	Vanadomolybdophosphoric Colorimetric Method	DA	APHA-P C
19	Ion Chromatographic Method	IC	
20	Ascorbic Acid Colorimetric Method	FIA	4500-P G
22	Ascorbic Acid Colorimetric Method	FIA	APHA

Table 48 Measurement Methods and Instrument Techniques for Sulphate

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Turbidimetric Method		
3	ICP Method	ICP-MS	W32
4	Colorimetric Method	DA	4500-SO4
5	Ion Chromatographic Method	IC	APHA 4110 B
6	Ion Chromatographic Method	IC	apha
7	ICP Method	ICP-OES	
8	Ion Chromatographic Method	IC	Inhouse
9	Ion Chromatographic Method	IC	
10	Ion Chromatographic Method	IC	4110B
11	Ion Chromatographic Method	IC	in house
12	Ion Chromatographic Method	IC	APHA 4110B
13	Turbidimetric Method	DA	In house
14	Turbidimetric Method	Manual Analysis	In house method based on USEPA method 9038 rev 0
15	Ion Chromatographic Method	IC	APHA
16	Ion Chromatographic Method	IC	APHA 4110B
17	Turbidimetric Method	DA	APHA 4500
18	Ion Chromatographic Method	IC	APHA 4110B
19	Ion Chromatographic Method	IC	
20	ICP Method	ICP-OES	3120 B

Table 49 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion		
2	Not Applicable	Not Applcable	Not Applicable
3	Persulfate digestion	FIA	APHA4500P-J
6	Persulfate digestion	SFA	apha
10	Calculation (TKN+NOx)	Manual Analysis	4500B
11	Calculation (TKN+NOx)	FIA	in house
12	Combustion chemiluminescence		ISO
13	Calculation (TKN+NOx)	DA	In house
16	Combustion chemiluminescence		ISO
17	Persulfate digestion	SFA	APHA 4500
18	Combustion		ISO
20	Persulfate digestion	FIA	4500-P J
22	Persulfate digestion	FIA	APHA

Table 50 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Laboratory Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Vanadomolybdophosphoric Colorimetric Method		
3	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
10		Ascorbic Acid Colorimetric Method	ICP-OES	3120B
11		Ascorbic Acid Colorimetric Method	FIA	in house
12	No Digestion	ICP Method	ICP-OES	USEPA 6010
13	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house
16	No Digestion	ICP Method	ICP-OES	USEPA 6010
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA 4500
18		ICP Method	ICP-OES	USEPA 6010
20	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	4500-P J
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA

APPENDIX 7 - METHODOLOGY FOR S2

Table 51 Instrument Techniques for Boron

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
3	ICP-MS	Sc	NA	NA	1	10
5	ICP-OES-AV-buffer	Y	NA		1	208.957
6	ICP-OES-AV	Y	NA	NA	2	249.678
7	ICP-OES	Lu			1.05	B208ax
8	ICP-OES-AV	Lu			1.05	182.577
9	ICP-MS/MS	YES		He		
11	ICP-MS	Sc45	NA	NA	1	11
12	ICP-MS	Lu			1	11
14	ICP-OES-AV	NA	NA	NA	Neat	249.772
15	ICP-MS	Ir, Rh				
16	ICP-MS	Lu			1	11
17	ICP-MS		DRC	He		
18	ICP-OES-AV-buffer	Lu			1	11
20	ICP-MS					11

Table 52 Instrument Techniques for Calcium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-OES-RV	Lu			1	317.933
3	ICP-MS	Sc	UC	He	1	44
5	ICP-OES-AV-buffer	Y	NA		1	315.887
6	ICP-OES-RV	Y	NA	NA	2	422.673
7	ICP-OES	Lu			1.05	Ca317
8	ICP-OES-RV	Lu			1.05	422.673
9	ICP-MS/MS	YES		He		
11	ICP-MS	Sc45	ORS	He	1	44
12	ICP-OES-AV	Lu			1	422
14	AAS	NA	NA	NA	2	422.7
16	ICP-OES-AV	Lu			1	422
17	ICP-OES-AV					
18	ICP-OES-AV-buffer	Lu			1	422
20	ICP-OES-RV					315.8

Table 53 Instrument Techniques for Potassium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-OES-RV	Lu			1	766.49
3	ICP-MS	Sc	UC	He	1	39
5	ICP-OES-AV-buffer	Y	NA		1	766.49
6	ICP-OES-RV	Y	NA	NA	2	766.491
7	ICP-OES	Lu			1.05	K766
8	ICP-OES-RV	Lu			1.05	766.491
9	ICP-MS/MS	YES		He		
11	ICP-MS	Sc45	ORS	He	1	39
12	ICP-OES-AV	Lu			1	766
14	AAS	NA	NA	NA	Neat	766.5
16	ICP-OES-AV	Lu			1	766
17	ICP-OES-AV					
18	ICP-OES-AV-buffer	Lu			1	766
20	ICP-OES-RV					766.4

Table 54 Instrument Techniques for Magnesium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
3	ICP-MS	Sc	UC	He	1	25
5	ICP-OES-AV-buffer	Y	NA		1	279.077
6	ICP-OES-RV	Y	NA	NA	2	279.078
7	ICP-OES	Lu			1.05	Mg280
8	ICP-OES-RV	Lu			1.05	285.213
9	ICP-MS/MS	YES		He		
11	ICP-MS	Sc45	ORS	He	1	24
12	ICP-OES-AV	Lu			1	
14	AAS	NA	NA	NA	Neat	285.2
16	ICP-OES-AV	Lu			1	280
17	ICP-OES-AV					
18	ICP-OES-AV-buffer	Lu			1	
20	ICP-OES-RV					279.8

Table 55 Instrument Techniques for Sodium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-OES-RV	Lu			1	589.592
3	ICP-MS	Sc	UC	He	1	23
5	ICP-OES-AV-buffer	Y	NA		1	588.995
6	ICP-OES-RV	Y	NA	NA	2	589.592
7	ICP-OES	Lu			1.05	Na589
8	ICP-OES-RV	Lu			1.05	589.592
9	ICP-MS/MS	YES		He		
11	ICP-MS	Sc45	ORS	He	1	23
12	ICP-OES-AV	Lu			1	589
14	AAS	NA	NA	NA	10	589
16	ICP-OES-AV	Lu			1	589
17	ICP-OES-AV					
18	ICP-OES-AV-buffer	Lu			1	589
20	ICP-OES-RV					589.5

Table 56 Measurement Methods and Instrument Techniques for Alkalinity

Laboratory Code	Measurement Method	Instrument	Method Reference
3	Titration	Auto Titration	APHA2320B
5	Titration		APHA 2320 B
6	Titration	Auto Titration	apha
7	Titration	Auto Titration	
9	Titration		
11	Titration	Auto Titration	in house
12	titration	Auto Titration	APHA 2320
14	Titration	Auto Titration	In house method based on APHA 2320 B
15	Titration	Manual Analysis	APHA
16	titration	Auto Titration	APHA 2320
17	Titration	Auto Titration	APHA 4500
18	Titration	Auto Titration	APHA 2320
20	Titration	Auto Titration	2320 B
21	Titration	Manual Analysis	

Table 577 Measurement Methods and Instrument Techniques for Colour, apparent

Laboratory Code	Measurement Method	Instrument	Method Reference
3	Spectrophotometric Method	UV-Vis Spectrophotometer	In House - W1
5	Spectrophotometric Method	UV-Vis Spectrophotometer	APHA 2120 C
6	Spectrophotometric Method	DA	apha
7	Visual Comparison Method	Manual Analysis	
9	Spectrophotometric Method		
11	Spectrophotometric Method	UV-Vis Spectrophotometer	in house
12	Spectrophotometric Method	DA	APHA 2120 B
14	Visual Comparison Method	Not Applicable	In house method based on APHA 2120 B
16	Spectrophotometric Method	DA	APHA 2120 B
17	Spectrophotometric Method	UV-Vis Spectrophotometer	APHA 4500
18	Spectrophotometric Method	DA	APHA 2120 B
20	Spectrophotometric Method	UV-Vis Spectrophotometer	2120 B
21	Spectrophotometric Method	UV-Vis Spectrophotometer	

Table 588 Measurement Methods and Instrument Techniques for Silica

Laboratory Code	Measurement Method	Instrument	Method Reference
2	ICP-Method	ICP-OES	In-house method
3	ICP-Method	ICP-MS	In House - W32
6	ICP-Method	ICP-OES	apha
8	ICP-Method	ICP-OES	Inhouse
9	ICP-Method	ICP-MS	
11	Molybdosilicate Method	DA	in house
12	ICP-Method	DA	USEPA 6010
14	Molybdosilicate Method	DA	In house method based on APHA 4500-SiO2 E
16	ICP-Method	DA	USEPA 6010
17	Molybdosilicate Method	UV-Vis Spectrophotometer	APHA 4500
18	ICP-Method	DA	USEPA 6010
20	ICP-Method	ICP-OES	3120 B

Table 59 Measurement Methods and Instrument Techniques for Total Hardness

Laboratory Code	Measurement Method	Instrument	Method Reference
3	Titration	Manual Analysis	In House - W21
6	Calculation	ICP-OES	apha
9	Calculation		
11	Calculation	ICP-MS	in house
12	Calculation	DA	USEPA 6010
14	Calculation	Not Applicable	In house method based on APHA 2340 B
15	Calculation	ICP-MS	APHA
16	Calculation	DA	USEPA 6010
17	Calculation	ICP-OES	APHA 4500
18	Calculation	DA	USEPA 6010
20	Calculation	ICP-OES	2340 B

Table 60 Measurement Methods and Instrument Techniques for Total P

Laboratory Code	Measurement Method		Instrument	Method Reference
3	No Digestion	ICP Method	ICP-MS	In House - W32
7		ICP Method	ICP-OES	
8	HNO3/HCL	ICP Method	ICP-OES	Inhouse
11	HNO3-Digestion	ICP Method	ICP-MS	in house
12	No Digestion	ICP Method	ICP-OES	USEPA 6010
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house method based on APHA 5310-P F
15	K2S2O8-Digestion	Ion Chromatographic Method	IC	ASTM
16	No Digestion	ICP Method	ICP-OES	USEPA 6010
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA 4500
18		ICP Method	ICP-OES	USEPA 6010
20	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	4500-P J

END OF REPORT