Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report
AQA 24-08
Nutrients and Anions in Potable Water

July 2024

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

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

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Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

SUMMARY

This report presents the results of the proficiency test AQA 24-08, 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, and silica (as SiO_2) were also included in the program.

The sample set consisted of two water samples. The assigned values were the robust average of participants' results. The associated uncertainties were estimated from the robust standard deviation of the participants' results. The results from Laboratories 1, 4, 6, 10, 11, and 21 for NH_3, NO_3 and NO_2 in Sample S1, were consistently lower than the spiked value by the same factor. These laboratories might have reported results for NH_3-N, NO_3-N, and NO_2-N instead. To avoid unfair scoring, these results were excluded from robust average calculations as they would unduly bias the assigned value, making it appear lower than its actual value; they were subsequently also excluded from the calculation of all summary statistics.

Twenty-three 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 359 z-scores, 329 (92%) returned an acceptable score of $|z| \leq 2.0$.
Of 359 E_n-scores, 301 (84%) returned an acceptable score of $|E_n| < 1.0$.

No laboratory reported results for all 23 tests scored in this study.

Laboratories 7 and **17** returned the highest number of acceptable z-scores (21).

Laboratories 5, 7 and **8** returned the highest number of acceptable E_n-scores (20).

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

Sulphate was the analyte with the largest number of unacceptable z-scores, not including those labs who potentially misreported their results for NO_3 and NO_2.

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

On average, over the last eleven years, participants' performance in measuring nutrients, anions and physical tests in water has remained 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 359 numerical results, 349 (97%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was between 0.34% to 275% of the reported value. 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.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

- inorganic analytes in soil, water, food and pharmaceuticals;
- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- PFAS in water, soil, biota and food;
- chlorophyll a in water; and
- controlled drug assay, drugs in wipes and clandestine laboratory.

AQA 24-08 is the 18th NMI proficiency study of nutrients, anions and physical tests in water.

1.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories' methods used in determination of nutrients, anions and physical tests in 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.

1.3 Study Conduct

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

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

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The twenty-three 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.

2.2 Participation

Twenty-three laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued:	8 April 2024
Samples dispatched:	6 May 2024
Results due:	31 May 2024
Interim report issued:	4 June 2024
Preliminary report issued:	11 June 2024

2.3 Test Material Specification

Two samples were provided for analysis:

Sample S1 was two 200 mL bottles of filtered, autoclaved and frozen potable water; and

Sample S2 was 400 mL of chilled potable water.

2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.5 Sample Preparation, Analysis and Homogeneity Testing

The same preparation procedure was followed as in previous studies. A partial homogeneity test was conducted for all tests.[1] The test samples from previous studies were demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. Results from partial homogeneity testing are reported in this study as homogeneity values.

The preparation, analysis and homogeneity testing of the study samples are described in Appendix 1. In the present study, the test samples were demonstrated to be sufficiently homogeneous for all the analytes assessed.

2.6 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. Details of the study and its results are given in Appendix 2. The test samples were stable for the period of the proficiency test.

2.7 Sample Storage, Dispatch and Receipt

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

The samples were dispatched by courier on 6 May 2024.

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

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

2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- If analyses cannot be commenced on the day of receipt, please store Sample S1 frozen.
- Prior to testing thaw sample S1 completely.
- Participants are asked to report results in units of mg/L except for pH 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	0.05-2	B (total)	0.05-2
Chloride	1-40	Ca (total)	1-40
Fluoride	0.5-20	K (total)	1-40
Iodide	0.05-2	Mg (total)	1-40
Dissolved Organic Carbon (as dNPOC)	0.5-20	Na (total)	1-40
Ammonia (as NH_3)	0.05-2	P (total)	0.05-2
Nitrate (as NO_3)	0.05-2	Alkalinity to pH 4.5 (as $CaCO_3$)	1-40
Nitrite (as NO_2)	0.05-2	Hardness, total ($CaCO_3$)	5-200
Total Dissolved Nitrogen	0.05-2	EC (at 25°C, µS/cm)	100-4000
Total Dissolved Phosphorus	0.05-2	pH (at 25 °C)	3-12
Orthophosphate-P	0.05-2	Silica (as SiO_2)	1-40
Sulphate	0.5-20		

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty (e.g. 5.23 ± 0.51 mg/L).
- Please send us the requested details regarding the test method.
- Please return the completed results sheet by 24 May 2024.

The due date for this study was extended to 31 May 2024 due to delays in sample delivery.

2.9 Interim and Preliminary Reports

An interim report was emailed to participants on 4 June 2024.

A preliminary report was issued on 11 June 2024. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants.

No data has been changed from the Preliminary Report in this Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Methodology for S1 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.

3.2 Additional Information

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

Table 1 Additional Information

Lab Code	Additional Information
16	Methodology for S2: Total Phosphorous analysis was performed by Discrete Analyser.
18	Methodology for S2: Total P - H2SO4+K2SO4-Digestion, Ascorbic Acid Colorimetric Method
20	Methodology for S2: P was analysed via IC after Persulphate Digestion

3.3 Basis of Participants' Measurement Uncertainty Estimates

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

Table 2 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - RM Duplicate Analysis		Eurachem/CITAC Guide
2	Coverage factor not reported			
3	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
5	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM
6	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM
7	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
8	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples Duplicate Analysis Instrument Calibration	CRM Recoveries of SS	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS	ASTM E2254-13
10	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
11	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
12	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - SS	Recoveries of SS	ISO/GUM
13	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Standard deviation from PT studies only		ISO/GUM
			Laboratory Bias from PT Studies	
14	Top Down - reproducibility (standard deviation) from PT studies used directly k = 2	Standard deviation from PT studies only		
		Control samples - RM Instrument Calibration	CRM Instrument Calibration	
15	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported		CRM Recoveries of SS	NMI Uncertainty Course
16*	See 'Additional Information' section below k = 2	Control samples - CRM Instrument Calibration	CRM	See 'Additional Information' section below
17	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples Duplicate Analysis	CRM	Nordtest Report TR537
18	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - SS Duplicate Analysis	Recoveries of SS	
19	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples - CRM Instrument Calibration	CRM Instrument Calibration	ISO/GUM
20	Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies	Eurachem/CITAC Guide
21	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) k = 2	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	Eurachem 2000 / ISO1993A
22	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
23	Coverage factor not reported	Control Samples	Recoveries of SS	

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

Table 3 Additional Information for Basis of Uncertainty Estimate

Lab Code	Additional Information
16	Estimation of MU from within-laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

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

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

There were no comments given in this study.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 4 to 26 with resultant summary statistics: robust average, median, mean, number of numeric results, 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 24. An example chart with interpretation guide is shown in Figure 1.

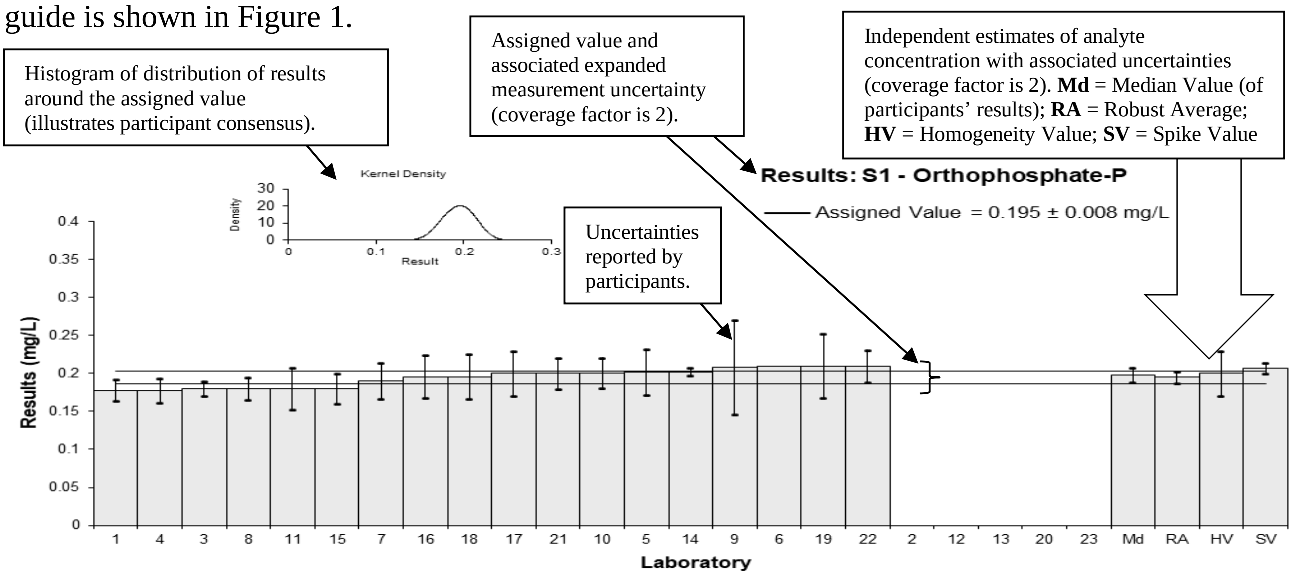


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

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

4.3 Assigned Value

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

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

4.5 Target Standard Deviation for Proficiency Assessment

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

$\sigma = X * PCV$ Equation 1

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

4.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 3. For each participant's 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 a participant's result;
X is the assigned value;
σ is the target standard deviation.

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

- $|z| \le 2.0$ is acceptable;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \ge 3.0$ is unacceptable.

4.7 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 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 ($|E_n|$):

- $|E_n| < 1.0$ is acceptable;
- $|E_n| \ge 1.0$ is unacceptable.

The acceptance criteria for E_n-score has been changed from an acceptable $|E_n|$ score of ≤ 1 to an acceptable $|E_n|$ score of < 1.0 as per new IS0/IEC 17043:2023 requirements.[1]

4.8 Traceability and Measurement Uncertainty

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

5 TABLES AND FIGURES

Table 4

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Ammonia (as NH3)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1**	0.330	0.046	-1.11	-0.80
2	NT	NT		
3	0.32	0.05	-1.37	-0.93
4**	0.2561	0.0387	-3.10	-2.55
5	0.394	0.059	0.62	0.36
6**	0.3	0.1	-1.91	-0.69
7	0.425	0.055	1.46	0.91
8	0.35	0.044	-0.57	-0.42
9	0.369	0.111	-0.05	-0.02
10**	0.373	0.02	0.05	0.07
11**	0.3	0.042	-1.91	-1.48
12	0.3579	0.0577	-0.35	-0.21
13	0.25	0.05	-3.26	-2.20
14	0.384	0.005	0.35	0.55
15	0.36	0.03	-0.30	-0.29
16	0.373	0.05	0.05	0.04
17	0.40	0.06	0.78	0.45
18	0.402	0.065	0.84	0.45
19	0.33	0.07	-1.11	-0.56
20	0.4	1.1	0.78	0.03
21**	0.32	0.02	-1.37	-1.67
22	0.383	0.038	0.32	0.27
23	NR	NR		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.371	0.023
Spike Value	0.365	0.080
Homogeneity Value	0.51	0.10
Robust Average	0.371	0.023
Median	0.373	0.022
Mean	0.367	
N	15	
Max	0.425	
Min	0.25	
Robust SD	0.036	
Robust CV	9.8%	

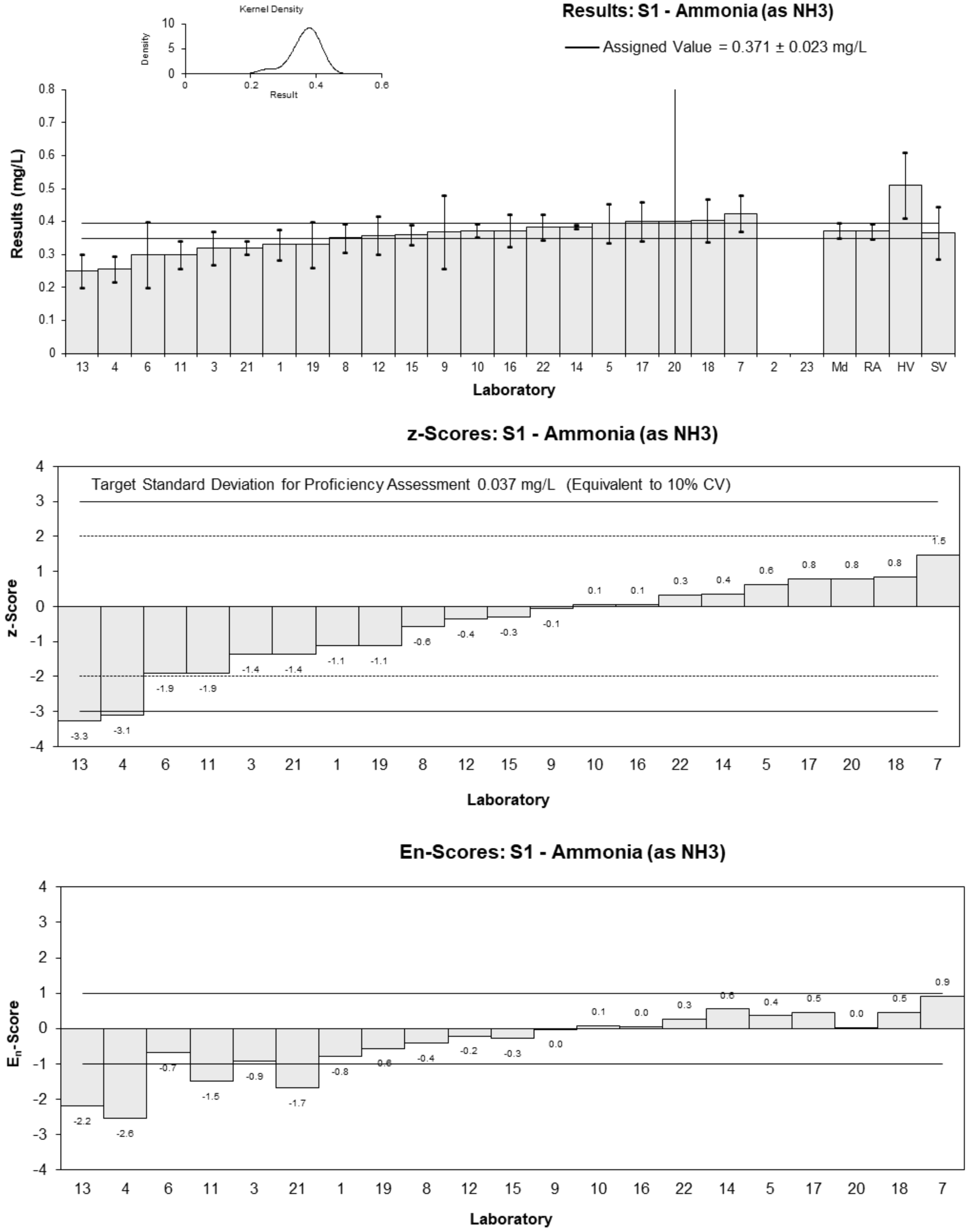

Kernel Density
Density
10
5
0
0
0.2
0.4
0.6
Result
Results: S1 - Ammonia (as NH3)
Assigned Value = 0.371 ± 0.023 mg/L
Results (mg/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
13
4
6
11
3
21
1
19
8
12
15
9
10
16
22
14
5
17
20
18
7
2
23
Md
RA
HV
SV
Laboratory
z-Scores: S1 - Ammonia (as NH3)
Target Standard Deviation for Proficiency Assessment 0.037 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-3.3
-3.1
-1.9
-1.9
-1.4
-1.4
-1.1
-1.1
-0.6
-0.4
-0.3
-0.1
0.1
0.1
0.3
0.4
0.6
0.8
0.8
0.8
1.5
13
4
6
11
3
21
1
19
8
12
15
9
10
16
22
14
5
17
20
18
7
Laboratory
En-Scores: S1 - Ammonia (as NH3)
En-Score
4
3
2
1
0
-1
-2
-3
-4
-2.2
-2.6
-0.7
-1.5
-0.9
-1.7
-0.8
-0.6
-0.4
-0.2
-0.3
0.0
0.1
0.0
0.3
0.6
0.4
0.5
0.0
0.5
0.9
13
4
6
11
3
21
1
19
8
12
15
9
10
16
22
14
5
17
20
18
7
Laboratory

Figure 2

Table 5

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Bromide
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.124	0.0121	-0.16	-0.14
2	NT	NT		
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	0.12	0.02	-0.48	-0.28
7	0.159	0.016	2.62	1.89
8	NT	NT		
9	<1	NR		
10	0.13	0.03	0.32	0.13
11	0.12	0.02	-0.48	-0.28
12	NT	NT		
13	NT	NT		
14	NR	NR		
15	0.13	0.02	0.32	0.19
16	< 0.5	NR		
17	0.12	0.02	-0.48	-0.28
18	NT	NT		
19	NT	NT		
20	<0.2	0.5		
21	NR	NR		
22	<0.20	0.1		
23	NR	NR		

Statistics

Assigned Value	0.126	0.007
Spike Value	0.119	0.021
Homogeneity Value	0.117	0.018
Robust Average	0.126	0.007
Median	0.124	0.006
Mean	0.129	
N	7	
Max	0.159	
Min	0.12	
Robust SD	0.0077	
Robust CV	6.1%	

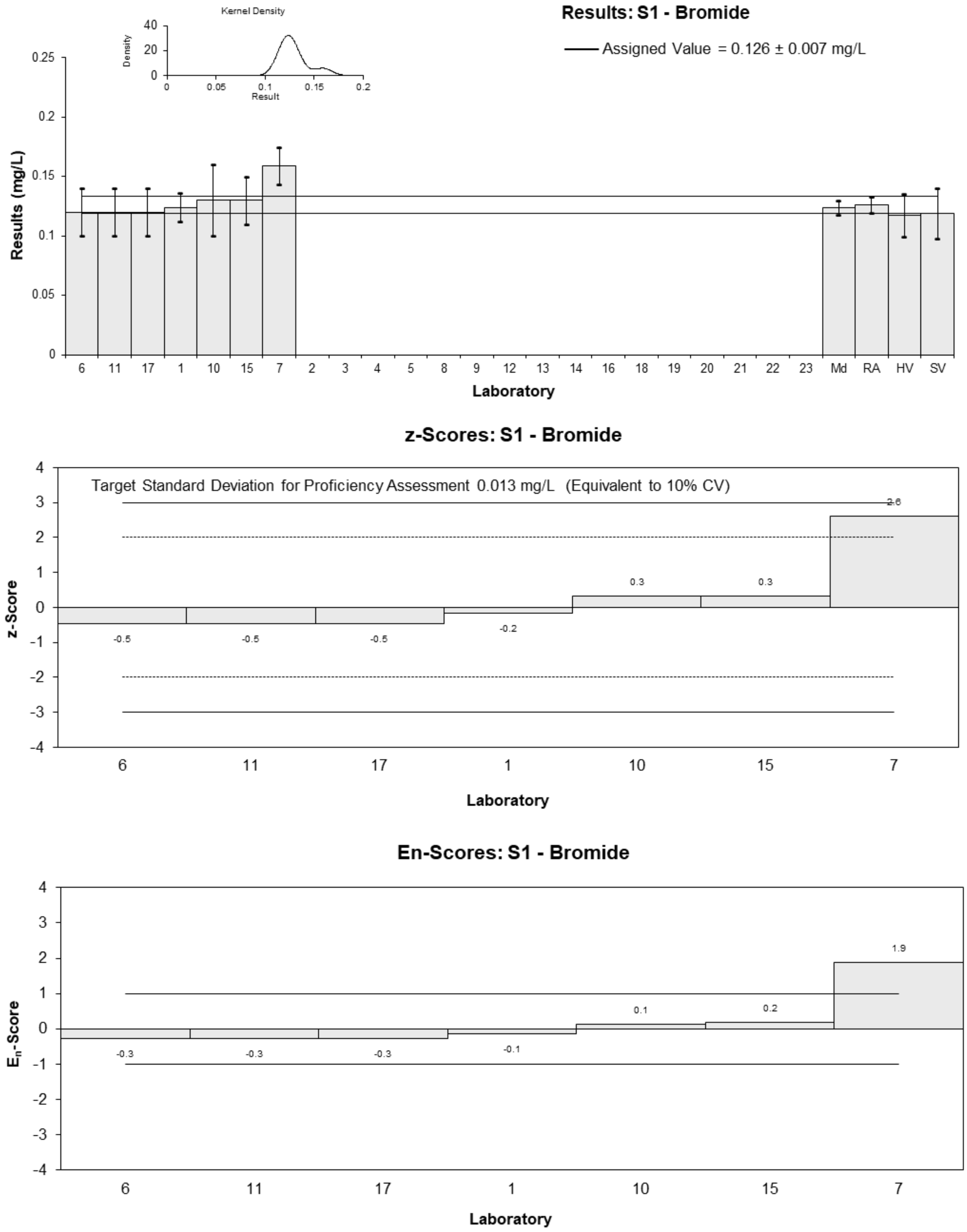

Results: S1 - Bromide
Assigned Value = 0.126 ± 0.007 mg/L
Kernel Density
Density
40
20
0
0
0.05
0.1
0.15
0.2
Result
Results (mg/L)
0.25
0.2
0.15
0.1
0.05
0
6
11
17
1
10
15
7
2
3
4
5
8
9
12
13
14
16
18
19
20
21
22
23
Md
RA
HV
SV
Laboratory
z-Scores: S1 - Bromide
Target Standard Deviation for Proficiency Assessment 0.013 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.5
-0.5
-0.2
0.3
0.3
2.6
6
11
17
1
10
15
7
Laboratory
En-Scores: S1 - Bromide
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-0.3
-0.3
-0.3
-0.1
0.1
0.2
1.9
6
11
17
1
10
15
7
Laboratory

Figure 3

Table 6

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	30.8	2.431	0.66	0.72
2	NT	NT		
3	25	1	-1.35	-2.76
4	26.96	2.71	-0.67	-0.67
5	29	4.5	0.03	0.02
6	33	6	1.42	0.67
7	28	3	-0.31	-0.28
8	29	2.52	0.03	0.04
9	28.4	8.5	-0.17	-0.06
10	33.3	5.0	1.52	0.86
11	27.0	4.212	-0.66	-0.44
12	30.35	3.005	0.50	0.46
13	NT	NT		
14	NR	NR		
15	28.8	1.7	-0.03	-0.05
16	28.3	4.45	-0.21	-0.13
17	29	4	0.03	0.02
18	29.8	4.47	0.31	0.20
19	29	5.8	0.03	0.02
20	29	0.3	0.03	0.10
21	25	0.90	-1.35	-2.90
22	30	3.6	0.38	0.29
23	NR	NR		

Statistics

Assigned Value	28.9	1.0
Spike Value	Not Spiked	
Homogeneity Value	33.2	5.0
Robust Average	28.9	1.0
Median	29.0	0.9
Mean	28.9	
N	19	
Max	33.3	
Min	25	
Robust SD	1.8	
Robust CV	6.3%	

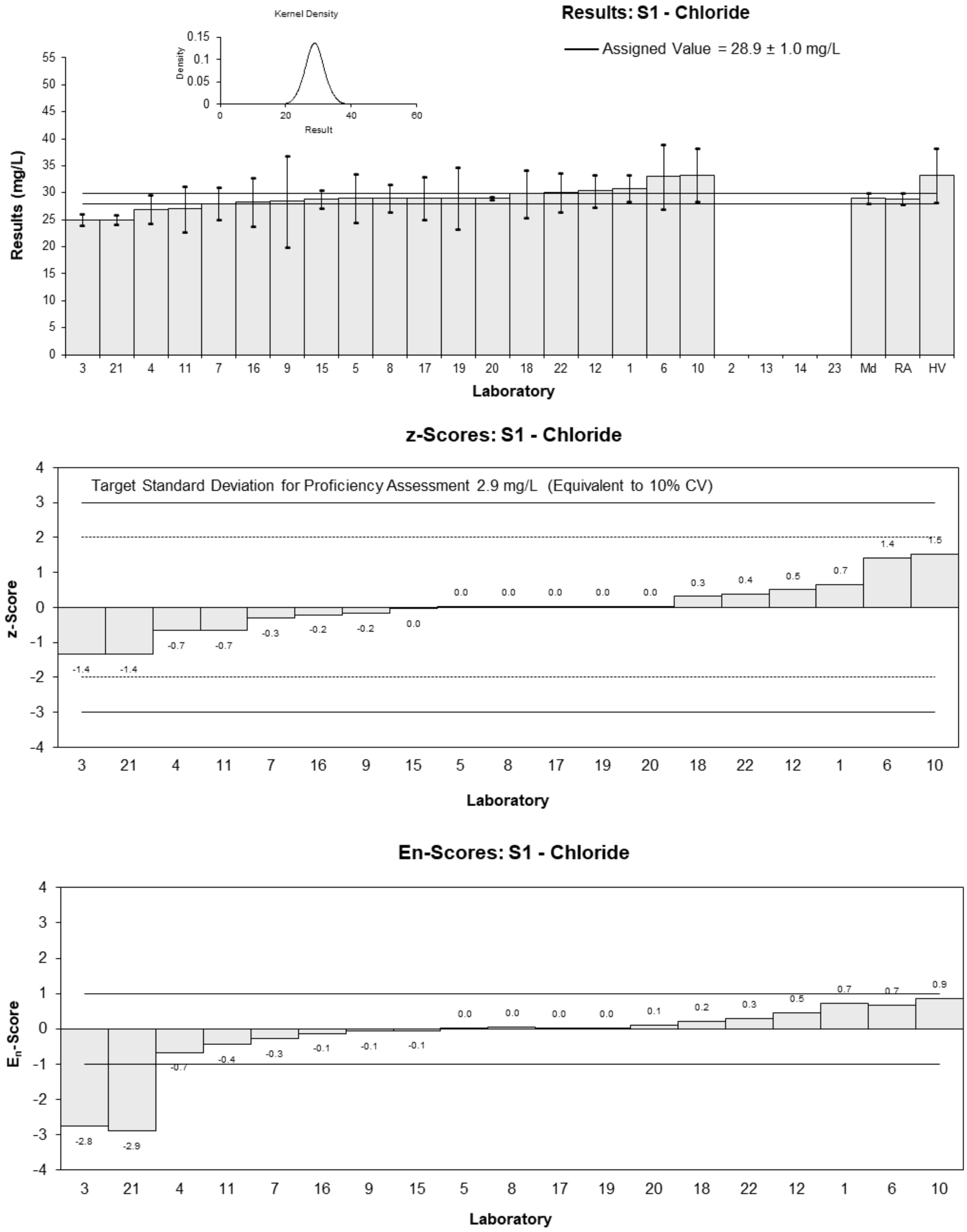

Results: S1 - Chloride
Assigned Value = 28.9 ± 1.0 mg/L
Kernel Density
Density
Result
0.15
0.1
0.05
0
0
20
40
60
Results (mg/L)
Laboratory
3
21
4
11
7
16
9
15
5
8
17
19
20
18
22
12
1
6
10
2
13
14
23
Md
RA
HV
z-Scores: S1 - Chloride
Target Standard Deviation for Proficiency Assessment 2.9 mg/L (Equivalent to 10% CV)
z-Score
-1.4
-1.4
-0.7
-0.7
-0.3
-0.2
-0.2
0.0
0.0
0.0
0.0
0.0
0.0
0.3
0.4
0.5
0.7
1.4
1.5
En-Scores: S1 - Chloride
E_n-Score
-2.8
-2.9
-0.7
-0.4
-0.3
-0.1
-0.1
-0.1
0.0
0.0
0.0
0.0
0.1
0.2
0.3
0.5
0.7
0.7
0.9

Figure 4

Table 7

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.0	0.8	-0.69	-0.48
2	NT	NT		
3	NT	NT		
4	6.29	1.31	2.74	1.29
5	NT	NT		
6	NT	NT		
7	4	1	-0.69	-0.41
8	4	0.55	-0.69	-0.60
9	NT	NT		
10	3.56	0.4	-1.35	-1.36
11	4.6	0.7	0.21	0.16
12	5.231	.5231	1.15	1.04
13	NT	NT		
14	NR	NR		
15	4.7	1	0.36	0.21
16	< 5	NR		
17	NR	NR		
18	4.61	0.692	0.22	0.17
19	NT	NT		
20	NT	NT		
21	NR	NR		
22	4.4	0.7	-0.09	-0.07
23	NR	NR		

Statistics

Assigned Value	4.46	0.53
Spike Value	Not Spiked	
Homogeneity Value	4.80	0.72
Robust Average	4.46	0.53
Median	4.50	0.59
Mean	4.54	
N	10	
Max	6.29	
Min	3.56	
Robust SD	0.67	
Robust CV	15%	

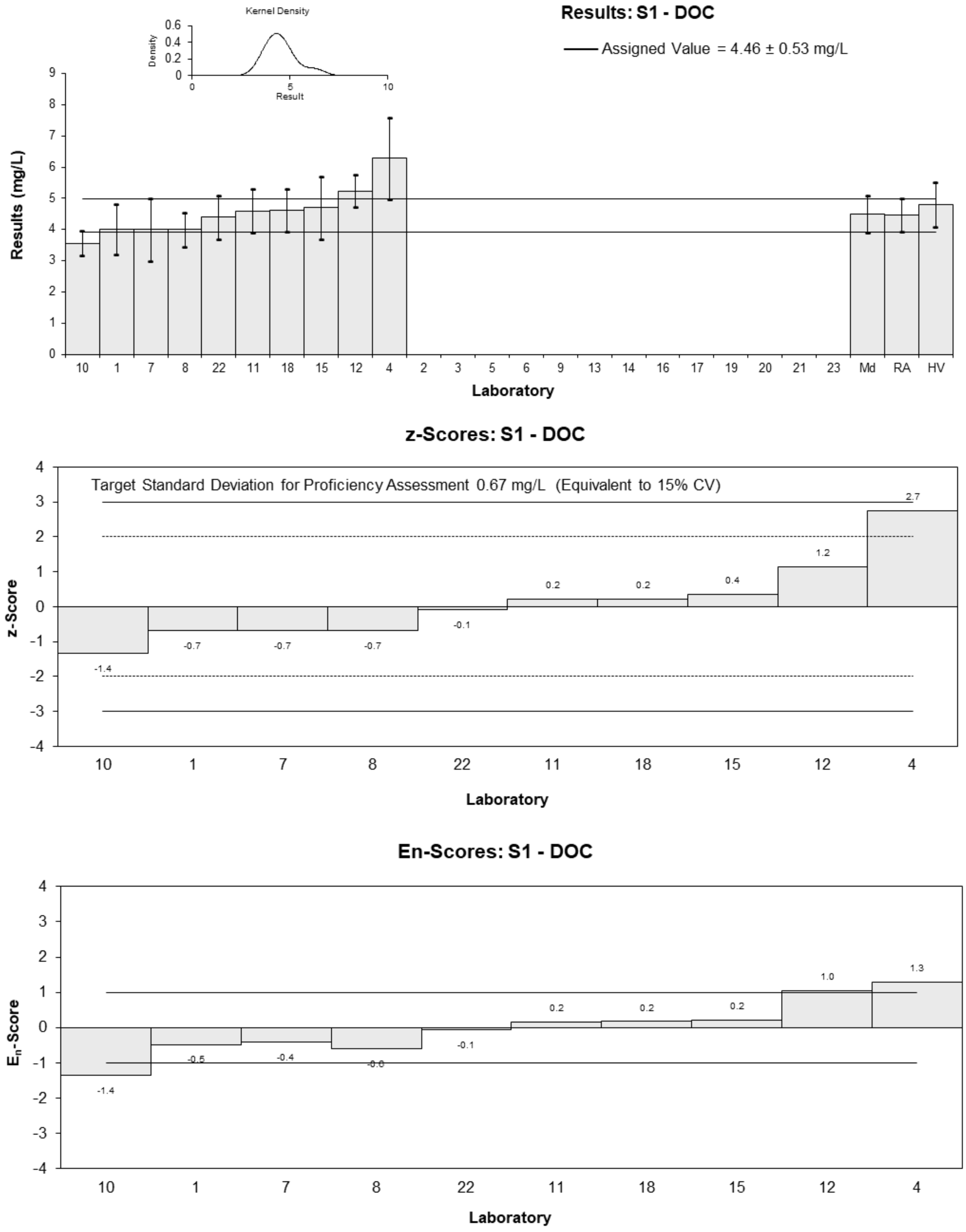

Results: S1 - DOC
Assigned Value = 4.46 ± 0.53 mg/L
Kernel Density
Density
0.6
0.4
0.2
0
0
5
10
Result
Results (mg/L)
9
8
7
6
5
4
3
2
1
0
10
1
7
8
22
11
18
15
12
4
2
3
5
6
9
13
14
16
17
19
20
21
23
Md
RA
HV
Laboratory
z-Scores: S1 - DOC
Target Standard Deviation for Proficiency Assessment 0.67 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.7
-0.7
-0.7
-0.1
0.2
0.2
0.4
1.2
2.7
10
1
7
8
22
11
18
15
12
4
Laboratory
En-Scores: S1 - DOC
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.5
-0.4
-0.6
-0.1
0.2
0.2
0.2
1.0
1.3
10
1
7
8
22
11
18
15
12
4
Laboratory

Figure 5

Table 8

Sample Details

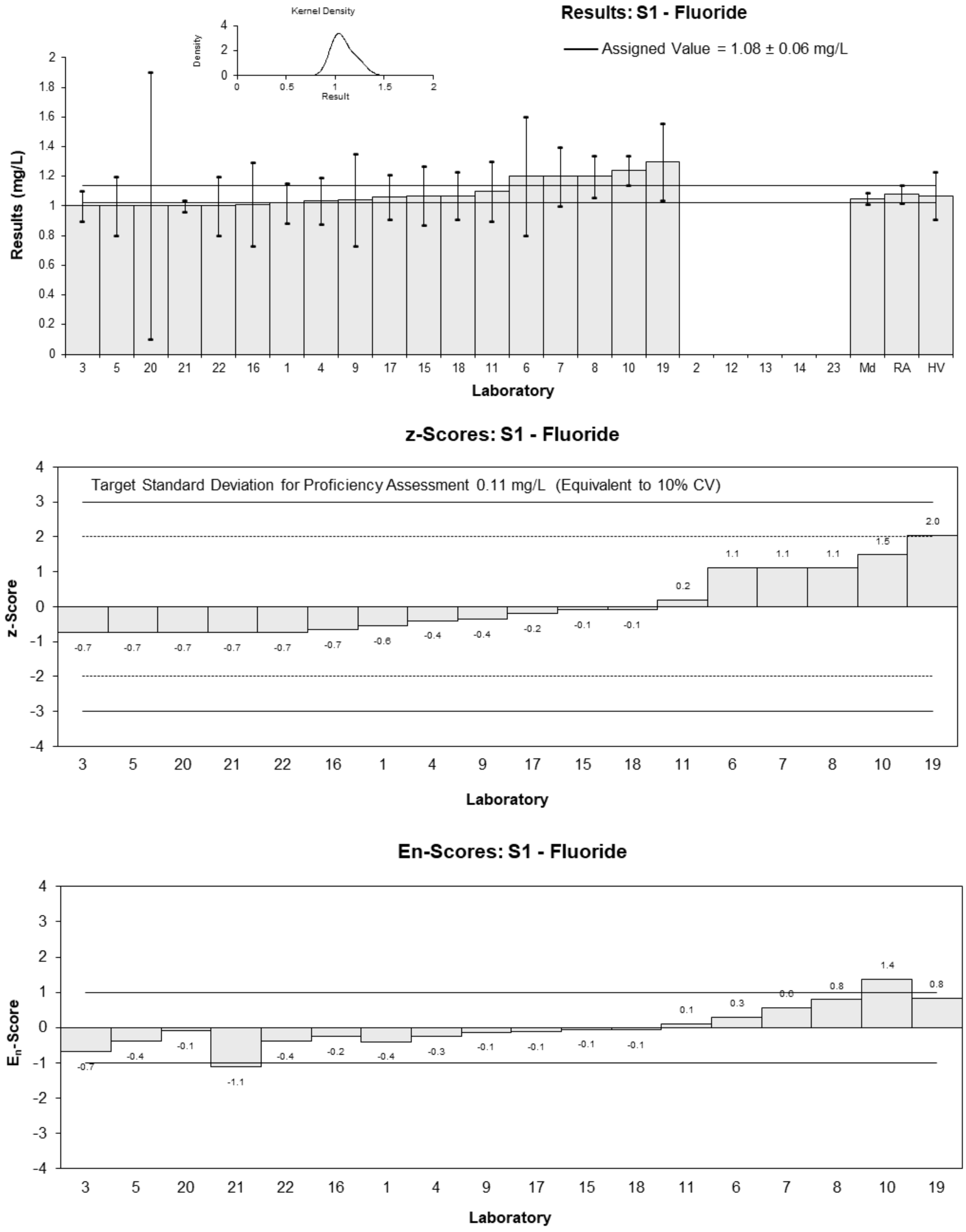
Sample No.	S1
Matrix	Potable Water
Analyte	Fluoride
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.02	0.136	-0.56	-0.40
2	NT	NT		
3	1.0	0.1	-0.74	-0.69
4	1.037	0.158	-0.40	-0.25
5	1	0.2	-0.74	-0.38
6	1.2	0.4	1.11	0.30
7	1.2	0.2	1.11	0.57
8	1.2	0.14	1.11	0.79
9	1.04	0.31	-0.37	-0.13
10	1.24	0.1	1.48	1.37
11	1.1	0.2	0.19	0.10
12	NT	NT		
13	NT	NT		
14	NR	NR		
15	1.07	0.2	-0.09	-0.05
16	1.01	0.282	-0.65	-0.24
17	1.06	0.15	-0.19	-0.12
18	1.07	0.161	-0.09	-0.06
19	1.3	0.26	2.04	0.82
20	1	0.9	-0.74	-0.09
21	1.0	0.04	-0.74	-1.11
22	1	0.2	-0.74	-0.38
23	NR	NR		

Statistics

Assigned Value	1.08	0.06
Spike Value	Not Spiked	
Homogeneity Value	1.07	0.16
Robust Average	1.08	0.06
Median	1.05	0.04
Mean	1.09	
N	18	
Max	1.3	
Min	1	
Robust SD	0.10	
Robust CV	9.3%	



Results: S1 - Fluoride
Assigned Value = 1.08 ± 0.06 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
3
5
20
21
22
16
1
4
9
17
15
18
11
6
7
8
10
19
2
12
13
14
23
Md
RA
HV
Laboratory
z-Scores: S1 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.11 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.7
-0.7
-0.7
-0.7
-0.7
-0.7
-0.6
-0.4
-0.4
-0.2
-0.1
-0.1
0.2
1.1
1.1
1.1
1.5
2.0
3
5
20
21
22
16
1
4
9
17
15
18
11
6
7
8
10
19
Laboratory
En-Scores: S1 - Fluoride
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.7
-0.4
-0.1
-1.1
-0.4
-0.2
-0.4
-0.3
-0.1
-0.1
-0.1
-0.1
0.1
0.3
0.6
0.8
1.4
0.8
3
5
20
21
22
16
1
4
9
17
15
18
11
6
7
8
10
19
Laboratory

Figure 6

Table 9

Sample Details

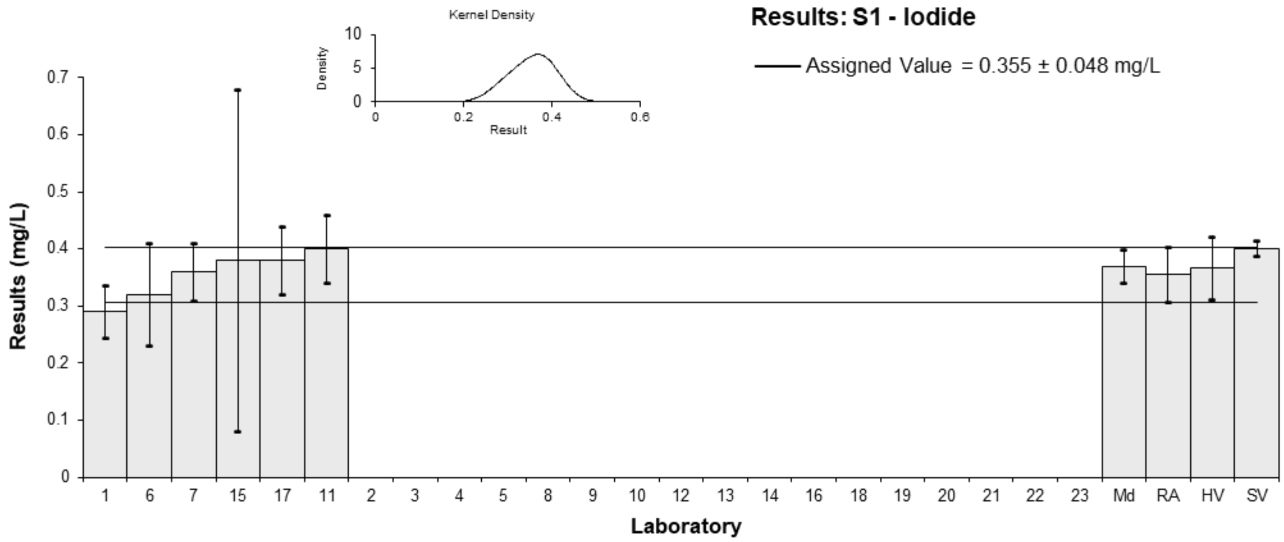
Sample No.	S1
Matrix	Potable Water
Analyte	Iodide
Unit	mg/L

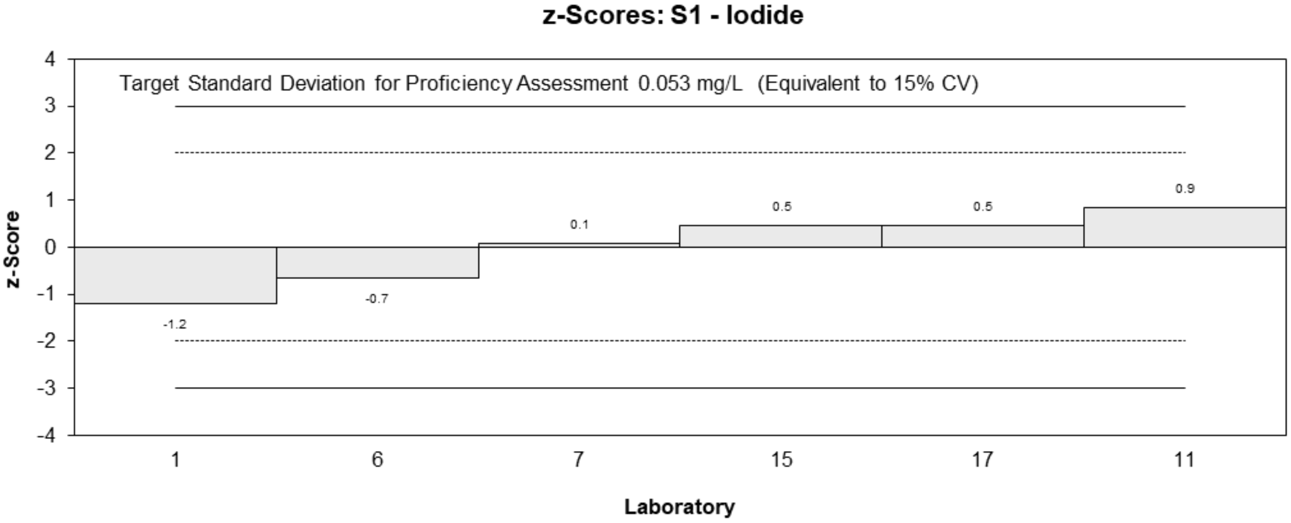
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.291	0.046	-1.20	-0.96
2	NT	NT		
3	NT	NT		
4	<0.5	NR		
5	NT	NT		
6	0.32	0.09	-0.66	-0.34
7	0.360	0.050	0.09	0.07
8	NT	NT		
9	<1	NR		
10	NT	NT		
11	0.4	0.06	0.85	0.59
12	NT	NT		
13	NT	NT		
14	NR	NR		
15	0.38	0.3	0.47	0.08
16	< 1	NR		
17	0.38	0.06	0.47	0.33
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	0.355	0.048
Spike Value	0.401	0.013
Homogeneity Value	0.367	0.055
Robust Average	0.355	0.048
Median	0.370	0.030
Mean	0.355	
N	6	
Max	0.4	
Min	0.291	
Robust SD	0.047	
Robust CV	13%	


Results: S1 - Iodide
Assigned Value = 0.355 ± 0.048 mg/L
Kernel Density
Density
10
5
0
0
0.2
0.4
0.6
Result
Results (mg/L)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
6
7
15
17
11
2
3
4
5
8
9
10
12
13
14
16
18
19
20
21
22
23
Md
RA
HV
SV
Laboratory


z-Scores: S1 - Iodide
Target Standard Deviation for Proficiency Assessment 0.053 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.2
-0.7
0.1
0.5
0.5
0.9
1
6
7
15
17
11
Laboratory

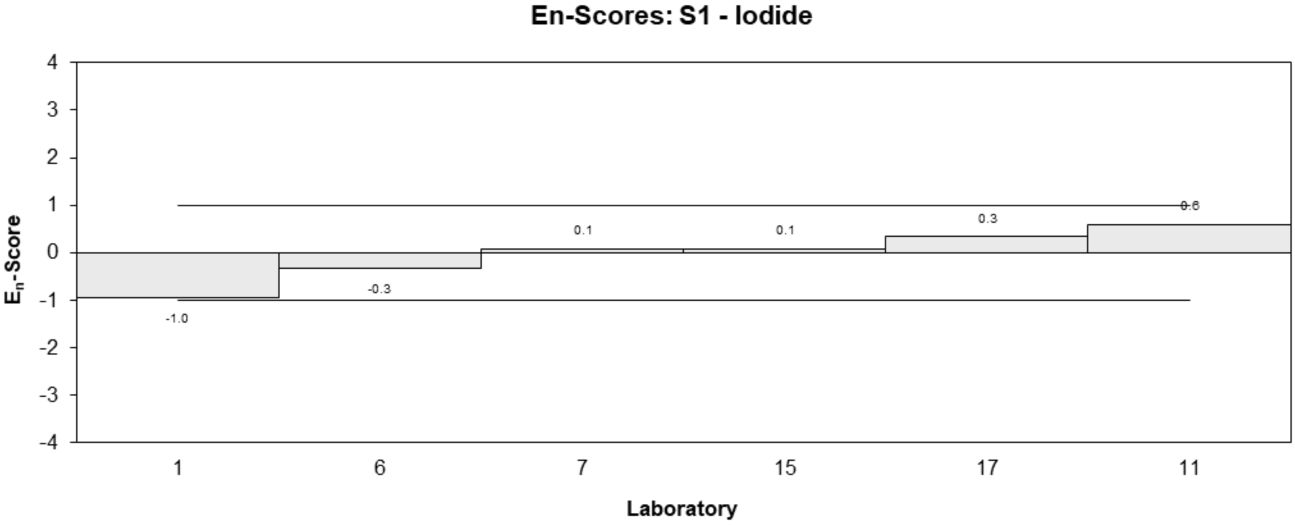

En-Scores: S1 - Iodide
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.3
0.1
0.1
0.3
0.6
1
6
7
15
17
11
Laboratory

Figure 7

Table 10

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Nitrate (as NO3)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1**	0.453	NR	-7.76	-17.41
2	NT	NT		
3	1.99	0.30	-0.15	-0.10
4**	0.48	0.05	-7.62	-14.96
5	1.94	0.29	-0.40	-0.26
6**	0.46	NR	-7.72	-17.33
7	2.16	0.24	0.69	0.55
8	2.08	0.12	0.30	0.40
9	2.19	0.66	0.84	0.26
10**	0.457	0.02	-7.74	-16.95
11**	0.44	0.054	-7.82	-15.05
12	2.067286	0.2212	0.23	0.20
13	<0.5	NR		
14	2.04	0.007	0.10	0.22
15	1.99	0.13	-0.15	-0.19
16	2.07	0.621	0.25	0.08
17	1.9	0.29	-0.59	-0.40
18	2.30	0.345	1.39	0.79
19	1.8	0.36	-1.09	-0.59
20	1.9	0.6	-0.59	-0.20
21**	0.38	0.03	-8.12	-17.29
22	1.96	0.196	-0.30	-0.28
23	NR	NR		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.02	0.09
Spike Value	1.86	0.40
Homogeneity Value	1.93	0.29
Robust Average	2.02	0.09
Median	2.02	0.07
Mean	2.03	
N	14	
Max	2.3	
Min	1.8	
Robust SD	0.13	
Robust CV	6.5%	

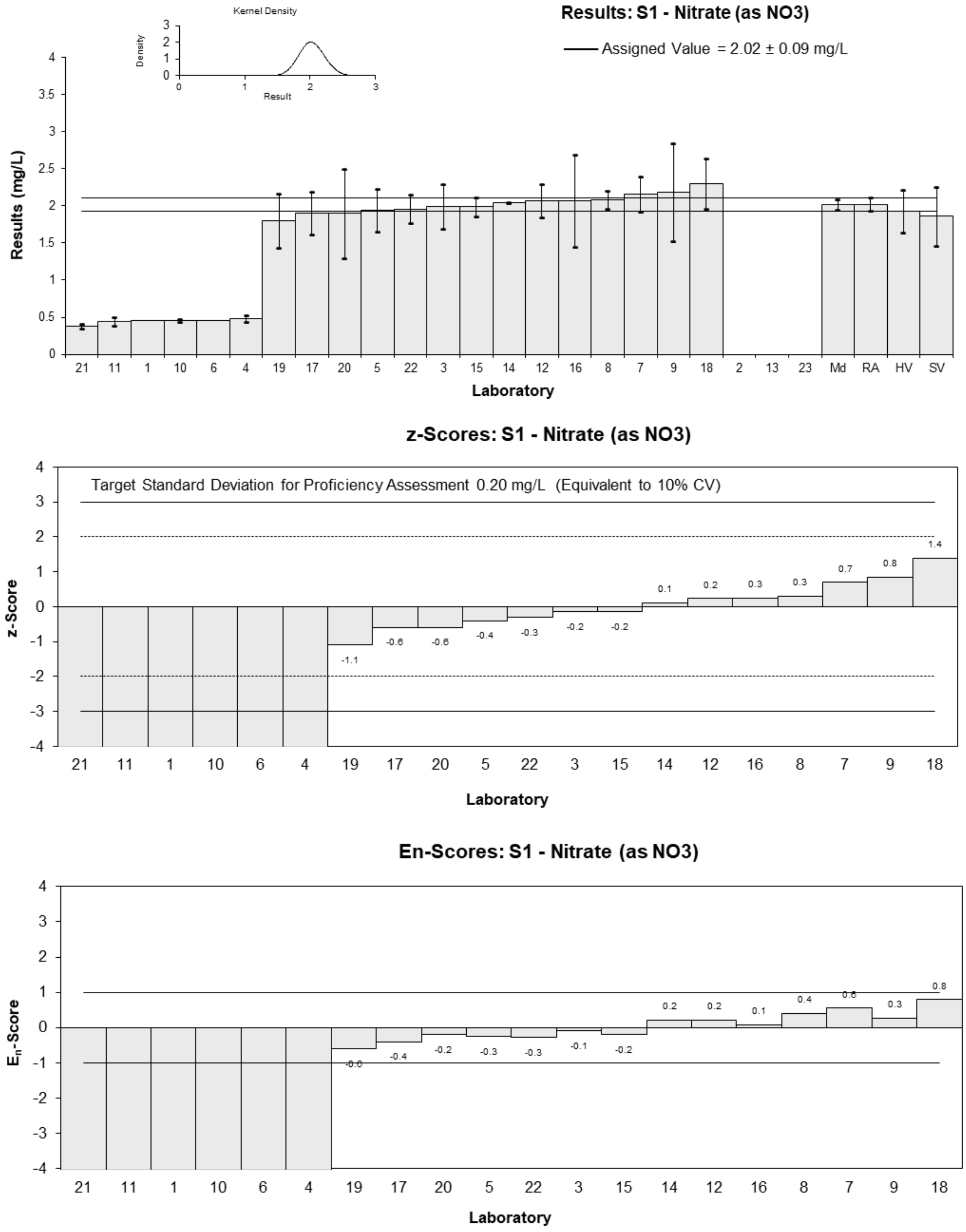

Results: S1 - Nitrate (as NO3)
Assigned Value = 2.02 ± 0.09 mg/L
Kernel Density
Density
Result
Results (mg/L)
0
0.5
1
1.5
2
2.5
3
3.5
4
21
11
1
10
6
4
19
17
20
5
22
3
15
14
12
16
8
7
9
18
2
13
23
Md
RA
HV
SV
Laboratory
z-Scores: S1 - Nitrate (as NO3)
Target Standard Deviation for Proficiency Assessment 0.20 mg/L (Equivalent to 10% CV)
z-Score
-1.1
-0.6
-0.6
-0.4
-0.3
-0.2
-0.2
0.1
0.2
0.3
0.3
0.7
0.8
1.4
Laboratory
En-Scores: S1 - Nitrate (as NO3)
E_n-Score
-0.6
-0.4
-0.2
-0.3
-0.3
-0.1
-0.2
0.2
0.2
0.1
0.4
0.6
0.3
0.8
Laboratory

Figure 8

Table 11

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Nitrite (as NO2)
Unit	mg/L

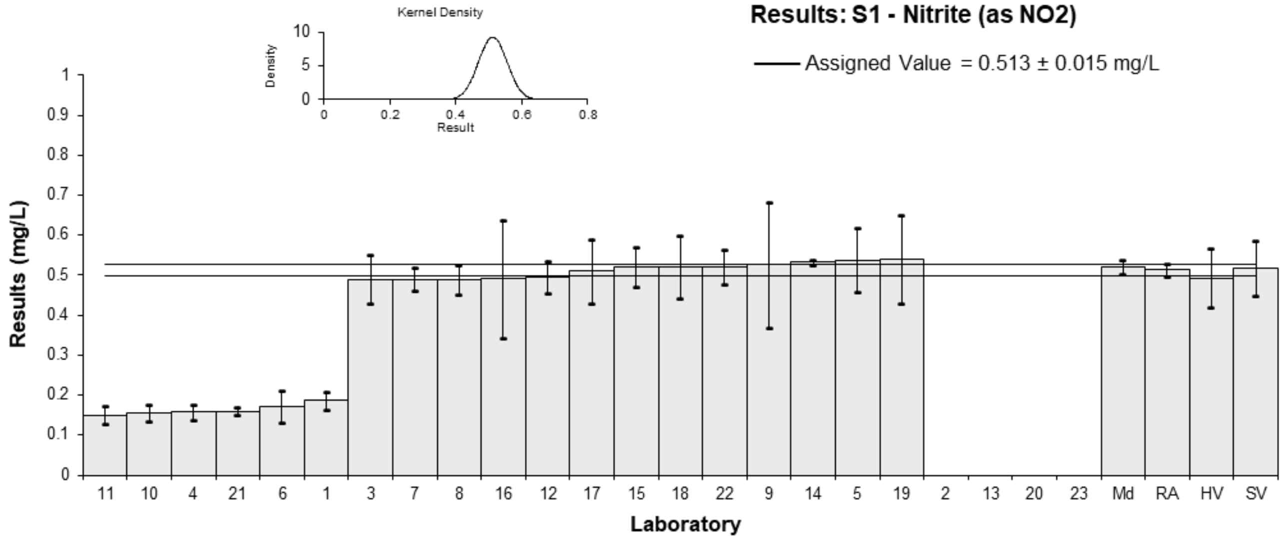
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1**	0.186	0.0237	-6.37	-11.66
2	NT	NT		
3	0.49	0.06	-0.45	-0.37
4**	0.1571	0.0184	-6.94	-14.99
5	0.537	0.08	0.47	0.29
6**	0.17	0.04	-6.69	-8.03
7	0.49	0.03	-0.45	-0.69
8	0.49	0.037	-0.45	-0.58
9	0.526	0.158	0.25	0.08
10**	0.156	0.02	-6.96	-14.28
11**	0.15	0.0225	-7.08	-13.42
12	0.4956	0.0396	-0.34	-0.41
13	<0.5	NR		
14	0.532	0.007	0.37	1.15
15	0.52	0.05	0.14	0.13
16	0.491	0.147	-0.43	-0.15
17	0.51	0.08	-0.06	-0.04
18	0.521	0.078	0.16	0.10
19	0.54	0.11	0.53	0.24
20	NT	NT		
21**	0.16	0.01	-6.88	-19.58
22	0.521	0.042	0.16	0.18
23	NR	NR		

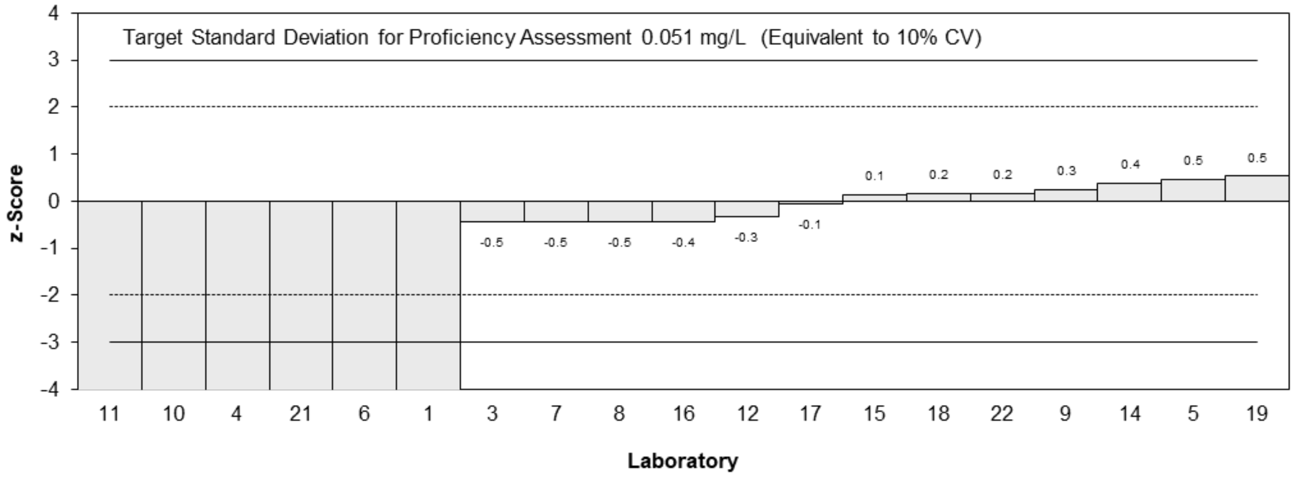
** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.513	0.015
Spike Value	0.517	0.068
Homogeneity Value	0.493	0.074
Robust Average	0.513	0.015
Median	0.520	0.017
Mean	0.513	
N	13	
Max	0.54	
Min	0.49	
Robust SD	0.022	
Robust CV	4.2%	



z-Scores: S1 - Nitrite (as NO2)



En-Scores: S1 - Nitrite (as NO2)

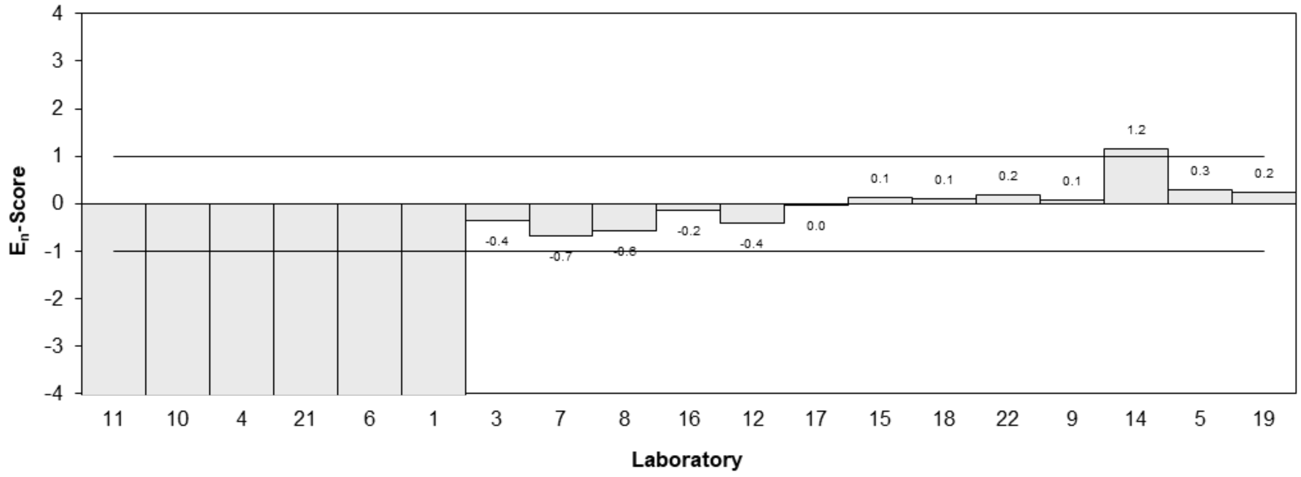


Figure 9

Table 12

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.178	0.014	-0.87	-1.05
2	NT	NT		
3	0.18	0.01	-0.77	-1.17
4	0.178	0.016	-0.87	-0.95
5	0.202	0.03	0.36	0.23
6	0.21	NR	0.77	1.87
7	0.190	0.024	-0.26	-0.20
8	0.18	0.015	-0.77	-0.88
9	0.208	0.062	0.67	0.21
10	0.201	0.02	0.31	0.28
11	0.18	0.027	-0.77	-0.53
12	NT	NT		
13	<0.25	NR		
14	0.202	0.005	0.36	0.74
15	0.18	0.02	-0.77	-0.70
16	0.196	0.028	0.05	0.03
17	0.20	0.03	0.26	0.16
18	0.196	0.029	0.05	0.03
19	0.21	0.042	0.77	0.35
20	NT	NT		
21	0.20	0.02	0.26	0.23
22	0.210	0.021	0.77	0.67
23	NR	NR		

Statistics

Assigned Value	0.195	0.008
Spike Value	0.207	0.007
Homogeneity Value	0.200	0.030
Robust Average	0.195	0.008
Median	0.198	0.010
Mean	0.195	
N	18	
Max	0.21	
Min	0.178	
Robust SD	0.014	
Robust CV	7.1%	

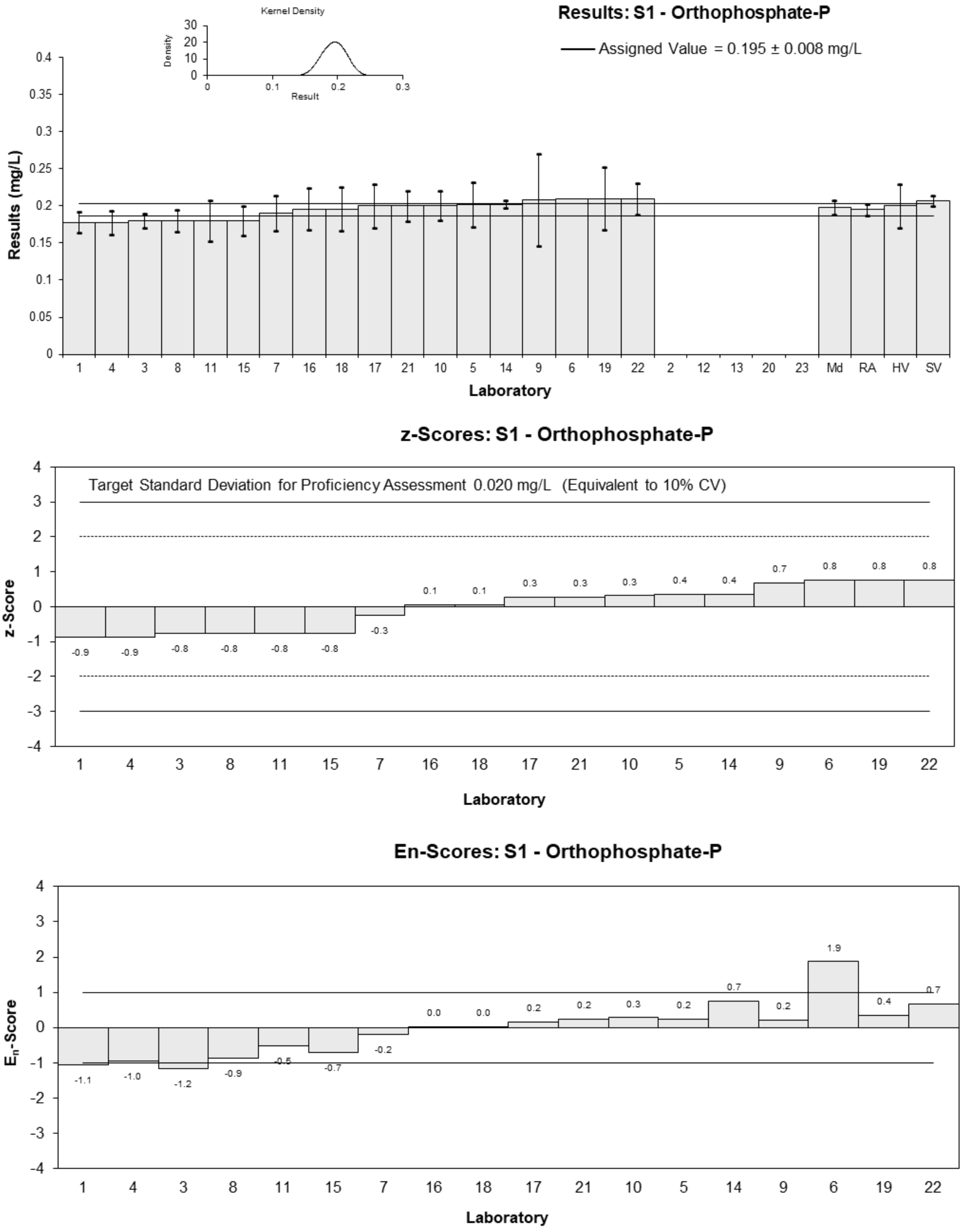

Results: S1 - Orthophosphate-P
Assigned Value = 0.195 ± 0.008 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 4 3 8 11 15 7 16 18 17 21 10 5 14 9 6 19 22 2 12 13 20 23 Md RA HV SV
z-Scores: S1 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.020 mg/L (Equivalent to 10% CV)
-0.9 -0.9 -0.8 -0.8 -0.8 -0.8 -0.3 0.1 0.1 0.3 0.3 0.3 0.4 0.4 0.7 0.8 0.8 0.8
z-Score
Laboratory
1 4 3 8 11 15 7 16 18 17 21 10 5 14 9 6 19 22
En-Scores: S1 - Orthophosphate-P
-1.1 -1.0 -1.2 -0.9 -0.5 -0.7 -0.2 0.0 0.0 0.2 0.2 0.3 0.2 0.7 0.2 1.9 0.4 0.7
En-Score
Laboratory
1 4 3 8 11 15 7 16 18 17 21 10 5 14 9 6 19 22

Figure 10

Table 13

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	10.4	1.44	-0.37	-0.27
2	NT	NT		
3	11	1	0.19	0.19
4	11.37	1.74	0.53	0.32
5	10.8	1.6	0.00	0.00
6	11	2	0.19	0.10
7	11	1	0.19	0.19
8	10	4.78	-0.74	-0.17
9	13.2	4.0	2.22	0.60
10*	21.4	3.0	9.81	3.50
11	10.0	1.5	-0.74	-0.52
12	11.03214	0.7061	0.21	0.29
13*	4.8625	0.9725	-5.50	-5.65
14	NR	NR		
15	10.6	2.5	-0.19	-0.08
16	10.6	3.17	-0.19	-0.06
17	11	1.7	0.19	0.11
18	11.3	1.84	0.46	0.27
19	12	2.4	1.11	0.49
20	11	0.7	0.19	0.25
21	9	0.75	-1.67	-2.12
22	10.6	1.5	-0.19	-0.13
23	NR	NR		

* Outlier, see Section 4.2

Statistics

Assigned Value	10.8	0.4
Spike Value	Not Spiked	
Homogeneity Value	11.0	1.7
Robust Average	10.9	0.5
Median	11.0	0.3
Mean	11.1	
N	20	
Max	21.4	
Min	4.8625	
Robust SD	0.81	
Robust CV	7.4%	

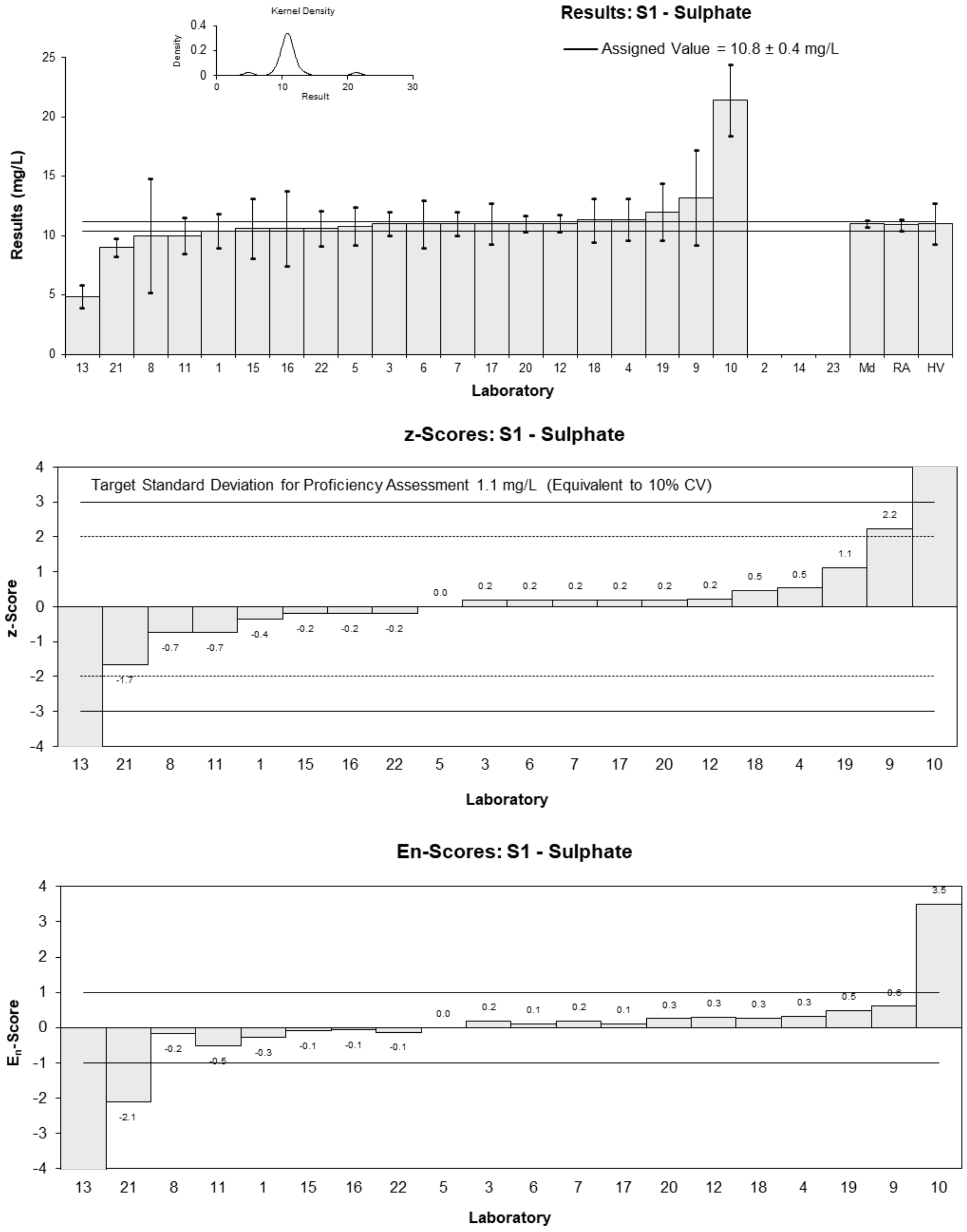

Kernel Density
Density
0.4
0.2
0
0
10
20
30
Result
Results: S1 - Sulphate
Assigned Value = 10.8 ± 0.4 mg/L
Results (mg/L)
25
20
15
10
5
0
13 21 8 11 1 15 16 22 5 3 6 7 17 20 12 18 4 19 9 10 2 14 23 Md RA HV
Laboratory
z-Scores: S1 - Sulphate
Target Standard Deviation for Proficiency Assessment 1.1 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.7
-0.7
-0.7
-0.4
-0.2
-0.2
-0.2
0.0
0.2
0.2
0.2
0.2
0.2
0.2
0.5
0.5
1.1
2.2
13 21 8 11 1 15 16 22 5 3 6 7 17 20 12 18 4 19 9 10
Laboratory
En-Scores: S1 - Sulphate
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-2.1
-0.2
-0.5
-0.3
-0.1
-0.1
-0.1
0.0
0.2
0.1
0.2
0.1
0.3
0.3
0.3
0.3
0.5
0.6
3.5
13 21 8 11 1 15 16 22 5 3 6 7 17 20 12 18 4 19 9 10
Laboratory

Figure 11

Table 14

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.20	0.144	0.62	0.42
2	NT	NT		
3	NT	NT		
4	1.14	0.27	0.09	0.04
5	0.996	0.2	-1.19	-0.62
6	NT	NT		
7	1.07	0.10	-0.53	-0.47
8	1.2	0.18	0.62	0.36
9	NT	NT		
10	1.13	0.1	0.00	0.00
11	1.3	0.2	1.50	0.79
12	NT	NT		
13	NT	NT		
14	1.1	0.06	-0.27	-0.30
15	1.06	0.07	-0.62	-0.66
16	1.3	0.389	1.50	0.43
17	1.0	0.15	-1.15	-0.76
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	1.0	0.10	-1.15	-1.02
22	1.14	0.21	0.09	0.04
23	NR	NR		

Statistics

Assigned Value	1.13	0.08
Spike Value	Not Spiked	
Homogeneity Value	0.99	0.15
Robust Average	1.13	0.08
Median	1.13	0.07
Mean	1.13	
N	13	
Max	1.3	
Min	0.996	
Robust SD	0.12	
Robust CV	10%	

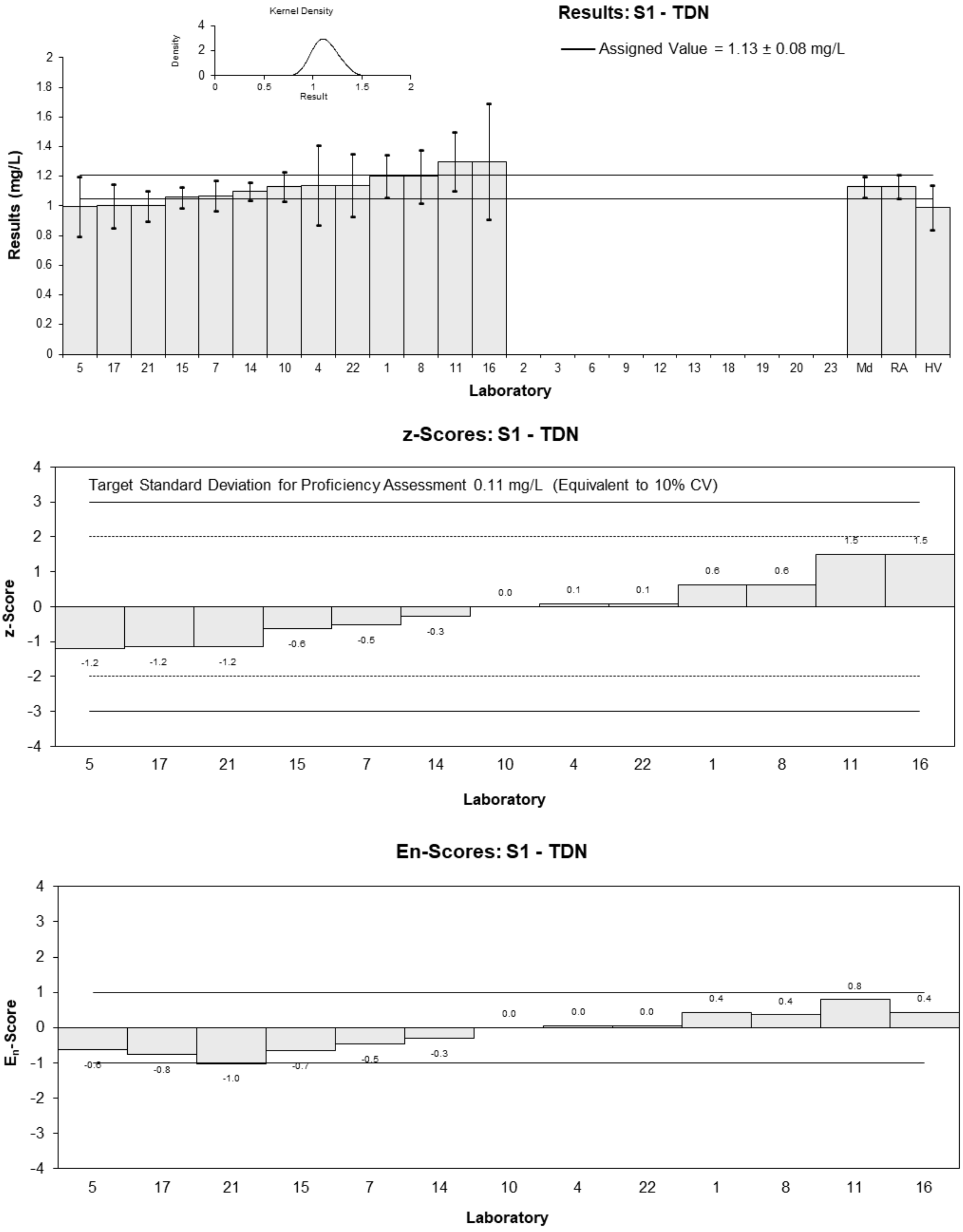

Results: S1 - TDN
Assigned Value = 1.13 ± 0.08 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5
17
21
15
7
14
10
4
22
1
8
11
16
2
3
6
9
12
13
18
19
20
23
Md
RA
HV
z-Scores: S1 - TDN
Target Standard Deviation for Proficiency Assessment 0.11 mg/L (Equivalent to 10% CV)
z-Score
-1.2
-1.2
-1.2
-0.6
-0.5
-0.3
0.0
0.1
0.1
0.6
0.6
1.5
1.5
En-Scores: S1 - TDN
E_n-Score
-0.6
-0.8
-1.0
-0.7
-0.5
-0.3
0.0
0.0
0.0
0.4
0.4
0.8
0.4

Figure 12

Table 15

Sample Details

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

Participant Results

Lab. Code	**Result**	**Uncertainty**	**z**	**E_n**
1	0.2	0.019	0.05	0.05
2	NT	NT		
3	NT	NT		
4	0.171	0.016	-1.41	-1.53
5	0.206	0.03	0.35	0.22
6	NT	NT		
7	0.206	0.026	0.35	0.25
8	0.19	0.031	-0.45	-0.28
9	< 0.5	NR		
10	0.20	0.02	0.05	0.05
11	0.21	0.03	0.55	0.35
12	0.186	.0373	-0.65	-0.34
13	NT	NT		
14	0.21	0.005	0.55	1.07
15	0.199	0.02	0.00	0.00
16	0.181	0.046	-0.90	-0.38
17	0.20	0.03	0.05	0.03
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	0.28	0.03	4.07	2.59
22	0.198	0.03	-0.05	-0.03
23	NR	NR		

Statistics

Assigned Value	0.199	0.009
Spike Value	0.207	0.007
Homogeneity Value	0.200	0.030
Robust Average	0.199	0.009
Median	0.200	0.008
Mean	0.203	
N	14	
Max	0.28	
Min	0.171	
Robust SD	0.013	
Robust CV	6.4%	

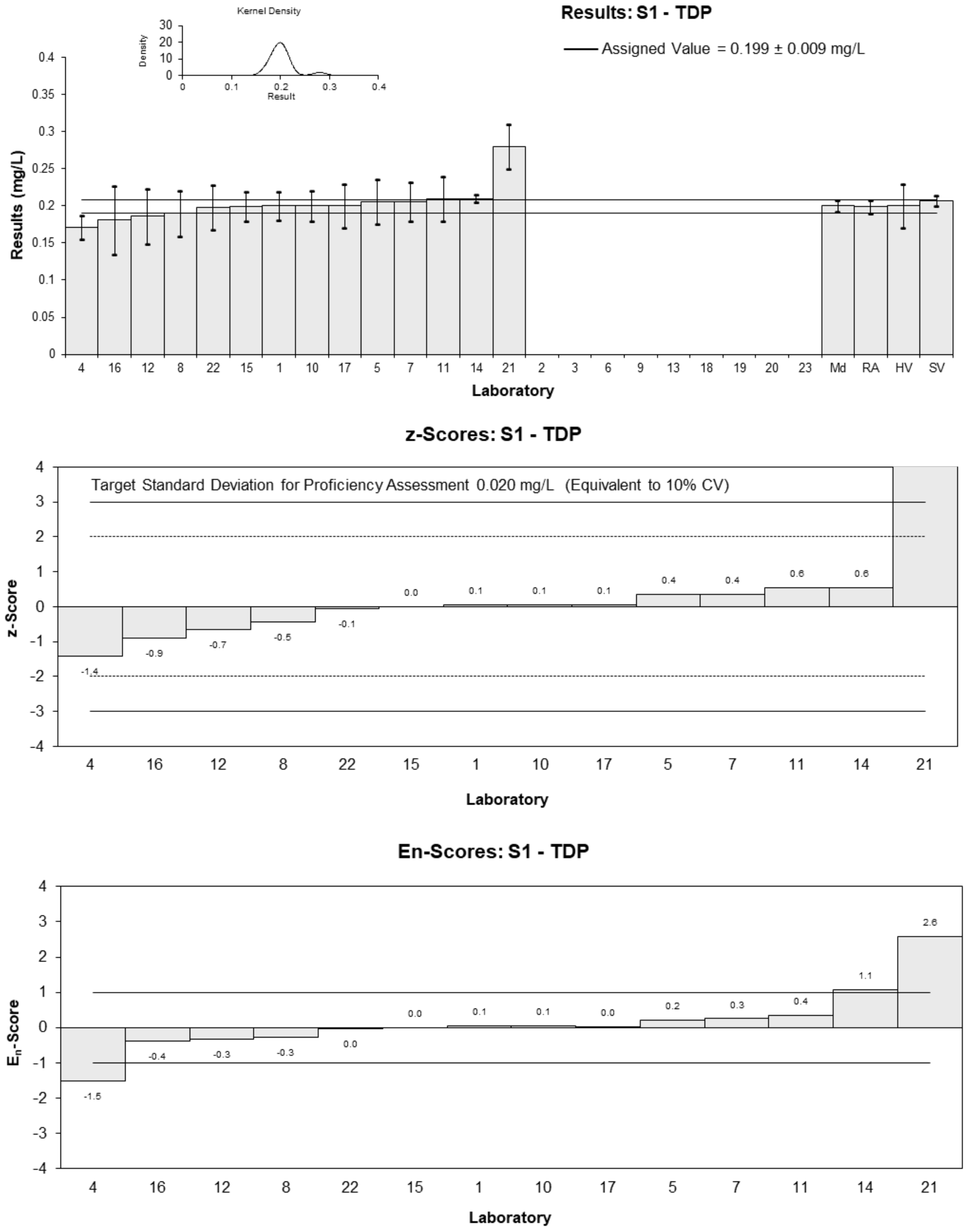

Results: S1 - TDP
Assigned Value = 0.199 ± 0.009 mg/L
Kernel Density
Density
30
20
10
0
0
0.1
0.2
0.3
0.4
Result
Results (mg/L)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
4
16
12
8
22
15
1
10
17
5
7
11
14
21
2
3
6
9
13
18
19
20
23
Md
RA
HV
SV
Laboratory
z-Scores: S1 - TDP
Target Standard Deviation for Proficiency Assessment 0.020 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.9
-0.7
-0.5
-0.1
0.0
0.1
0.1
0.1
0.4
0.4
0.6
0.6
4
16
12
8
22
15
1
10
17
5
7
11
14
21
Laboratory
En-Scores: S1 - TDP
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-1.5
-0.4
-0.3
-0.3
0.0
0.0
0.1
0.1
0.0
0.2
0.3
0.4
1.1
2.6
4
16
12
8
22
15
1
10
17
5
7
11
14
21
Laboratory

Figure 13

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.4	0.039	-0.41	-0.40
2	0.42	0.02	0.07	0.11
3	NT	NT		
4	0.437	0.05	0.48	0.38
5	0.45	0.07	0.79	0.46
6	0.42	0.06	0.07	0.05
7	0.39	0.07	-0.65	-0.37
8	0.44	0.056	0.55	0.39
9	0.41	0.12	-0.17	-0.06
10	0.412	0.05	-0.12	-0.09
11	NR	NR		
12	0.353	0.0706	-1.53	-0.88
13	0.42	0.084	0.07	0.03
14	NR	NR		
15	NT	NT		
16	0.38	0.05	-0.89	-0.70
17	0.44	0.09	0.55	0.25
18	0.433	0.065	0.38	0.24
19	0.388	0.078	-0.70	-0.36
20	0.504	0.0504	2.09	1.63
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	0.417	0.018
Spike Value	0.415	0.017
Homogeneity Value	0.398	0.048
Robust Average	0.417	0.018
Median	0.420	0.019
Mean	0.419	
N	16	
Max	0.504	
Min	0.353	
Robust SD	0.029	
Robust CV	7.0%	

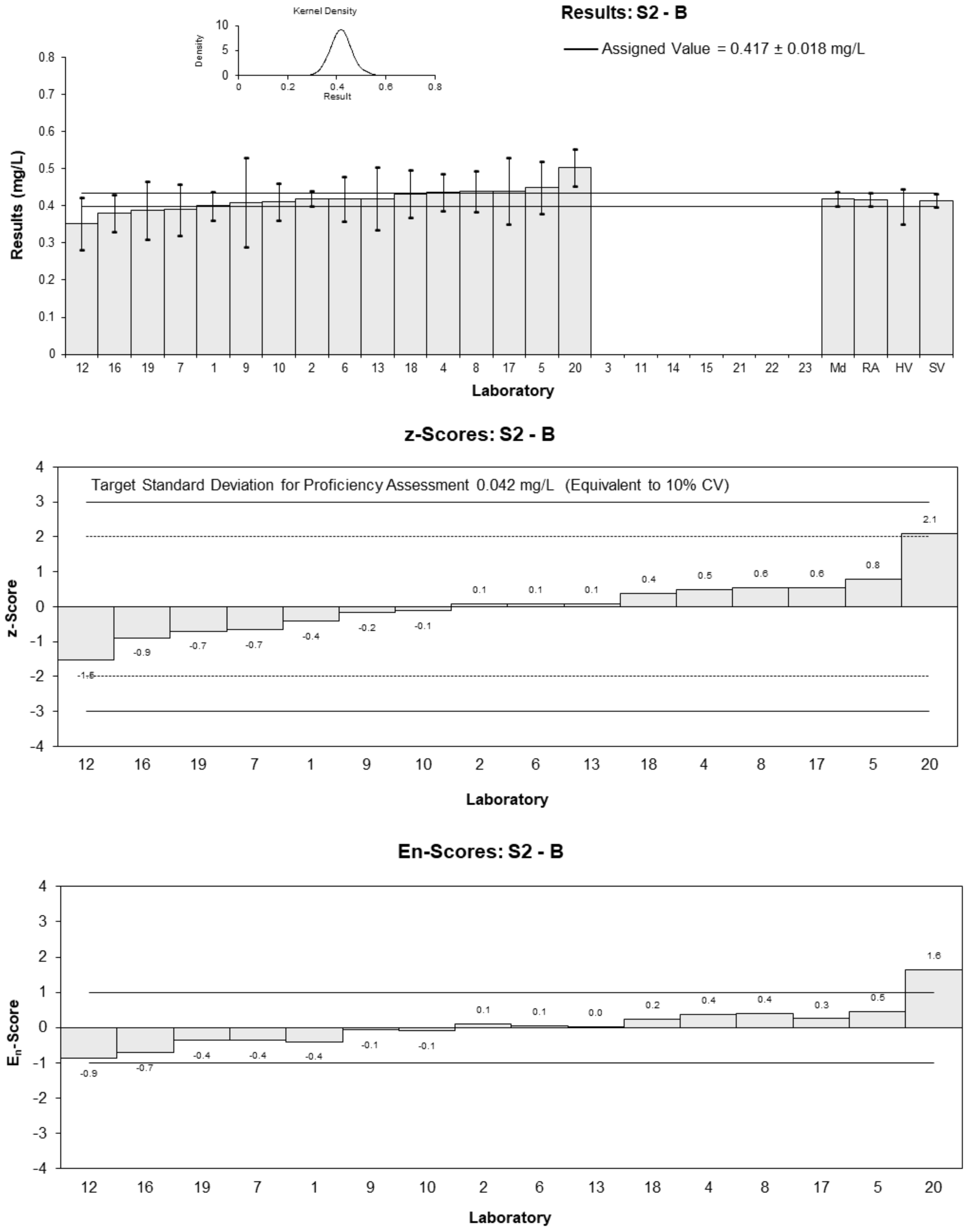

Results: S2 - B
Assigned Value = 0.417 ± 0.018 mg/L
Kernel Density
Density
10
5
0
0
0.2
0.4
0.6
0.8
Result
Results (mg/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
12
16
19
7
1
9
10
2
6
13
18
4
8
17
5
20
3
11
14
15
21
22
23
Md
RA
HV
SV
Laboratory
z-Scores: S2 - B
Target Standard Deviation for Proficiency Assessment 0.042 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.5
-0.9
-0.7
-0.7
-0.4
-0.2
-0.1
0.1
0.1
0.1
0.4
0.5
0.6
0.6
0.8
2.1
12
16
19
7
1
9
10
2
6
13
18
4
8
17
5
20
Laboratory
En-Scores: S2 - B
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.7
-0.4
-0.4
-0.4
-0.1
-0.1
0.1
0.1
0.0
0.2
0.4
0.4
0.3
0.5
1.6
12
16
19
7
1
9
10
2
6
13
18
4
8
17
5
20
Laboratory

Figure 14

Table 17

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	17	1.95	0.49	0.39
2	16.05	0.80	-0.09	-0.15
3	NT	NT		
4	16.329	1.873	0.08	0.07
5	16.6	2.5	0.25	0.16
6	14	1	-1.36	-1.89
7	17	1	0.49	0.69
8	17	1.6	0.49	0.47
9	15.9	4.7	-0.19	-0.06
10	16.4	2.0	0.12	0.10
11	NR	NR		
12	15.3	2.3	-0.56	-0.38
13	16.7	3.34	0.31	0.15
14	NR	NR		
15	NT	NT		
16	15.3	1.9	-0.56	-0.45
17	16	3.2	-0.12	-0.06
18	17.9	2.69	1.05	0.62
19	15.3	2.30	-0.56	-0.38
20	NT	NT		
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	16.2	0.6
Spike Value	Not Spiked	
Homogeneity Value	16.7	2.0
Robust Average	16.2	0.6
Median	16.3	0.6
Mean	16.2	
N	15	
Max	17.9	
Min	14	
Robust SD	0.88	
Robust CV	5.4%	

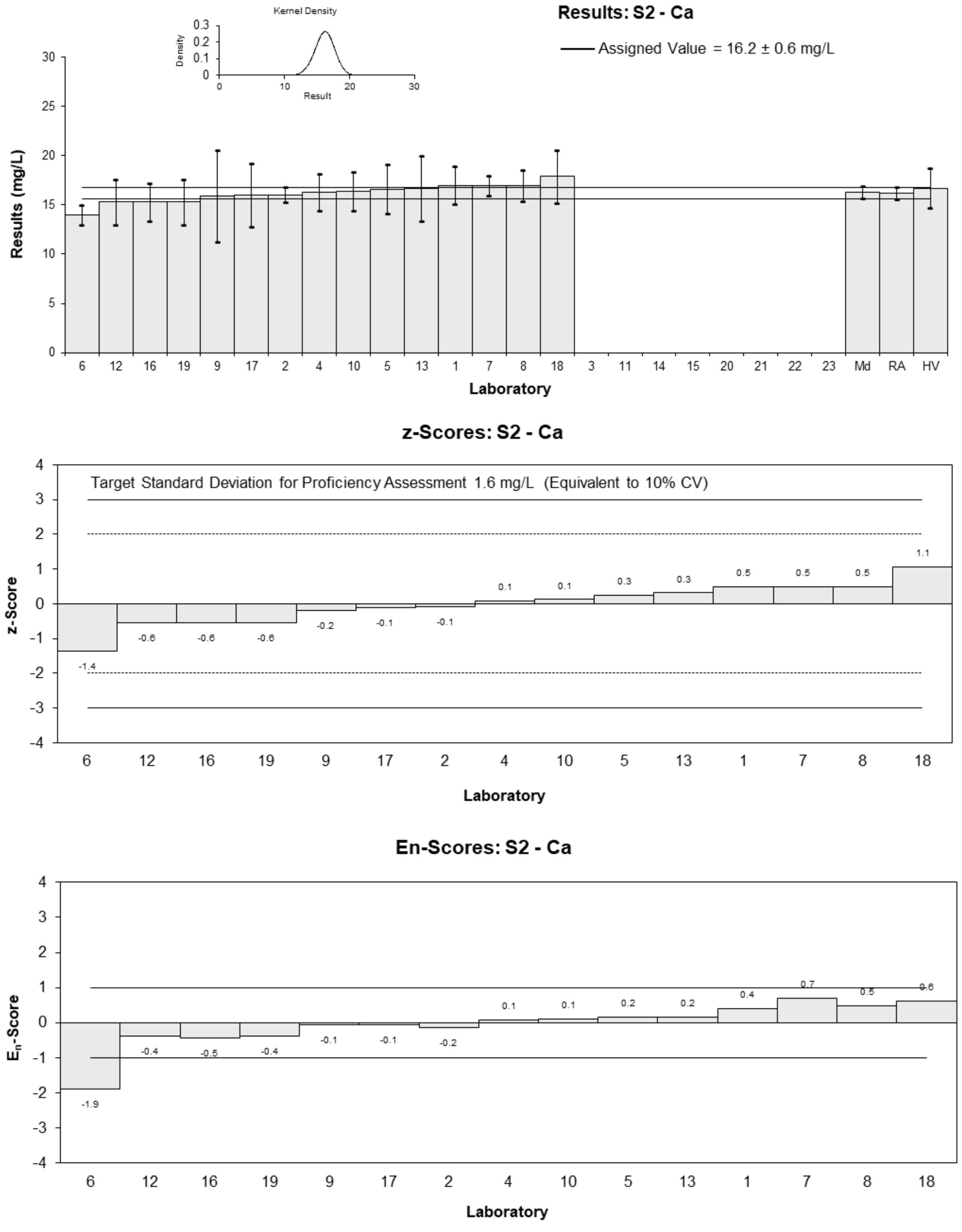

Results: S2 - Ca
Assigned Value = 16.2 ± 0.6 mg/L
Kernel Density
Density
0.3
0.2
0.1
0
0
10
20
30
Result
Results (mg/L)
30
25
20
15
10
5
0
6
12
16
19
9
17
2
4
10
5
13
1
7
8
18
3
11
14
15
20
21
22
23
Md
RA
HV
Laboratory
z-Scores: S2 - Ca
Target Standard Deviation for Proficiency Assessment 1.6 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.6
-0.6
-0.6
-0.2
-0.1
-0.1
0.1
0.1
0.3
0.3
0.5
0.5
0.5
1.1
6
12
16
19
9
17
2
4
10
5
13
1
7
8
18
Laboratory
En-Scores: S2 - Ca
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.9
-0.4
-0.5
-0.4
-0.1
-0.1
-0.2
0.1
0.1
0.2
0.2
0.4
0.7
0.5
0.6
6
12
16
19
9
17
2
4
10
5
13
1
7
8
18
Laboratory

Figure 15

Table 18

Sample Details

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

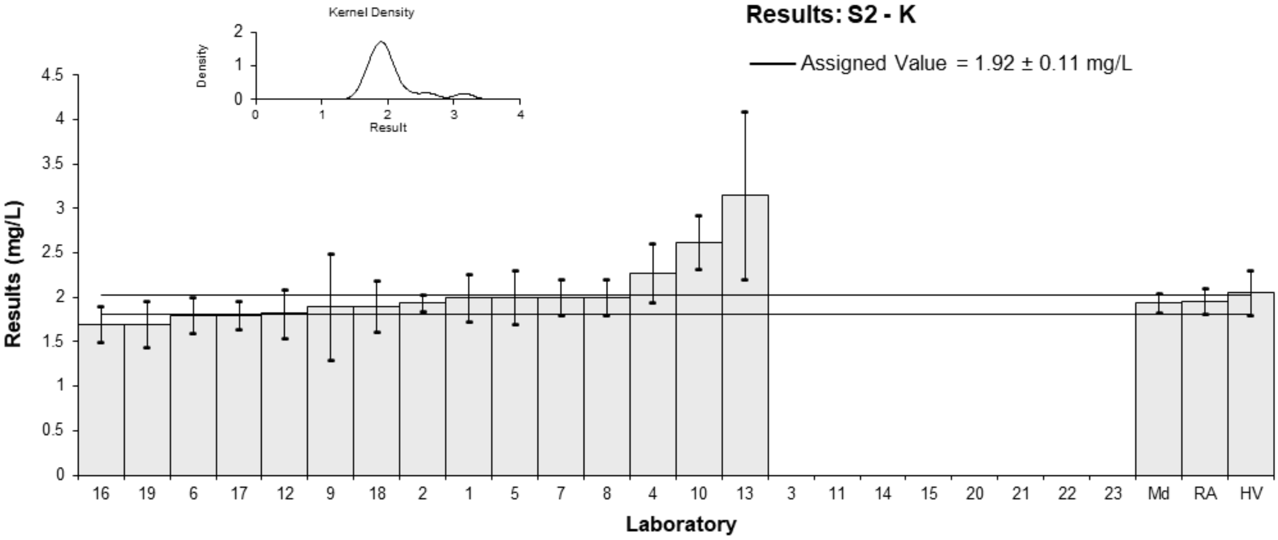
Participant Results

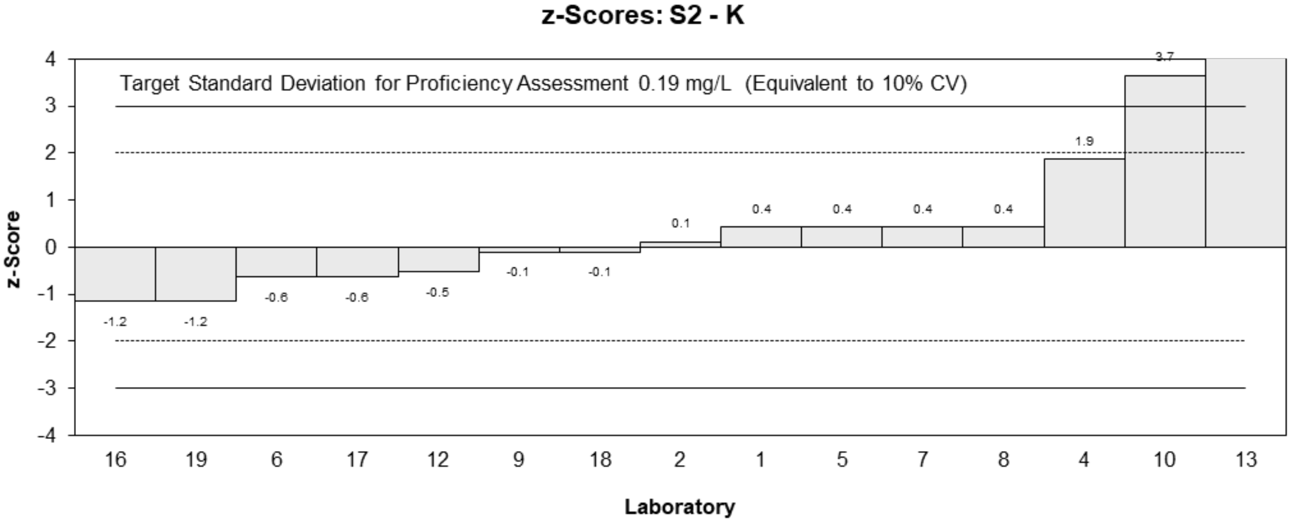
Lab. Code	Result	Uncertainty	z	E_n
1	2.0	0.268	0.42	0.28
2	1.94	0.10	0.10	0.13
3	NT	NT		
4	2.278	0.335	1.86	1.02
5	2.0	0.3	0.42	0.25
6	1.8	0.2	-0.62	-0.53
7	2	0.2	0.42	0.35
8	2	0.2	0.42	0.35
9	1.9	0.6	-0.10	-0.03
10	2.62	0.3	3.65	2.19
11	NR	NR		
12	1.82	0.273	-0.52	-0.34
13*	3.155	0.9465	6.43	1.30
14	NR	NR		
15	NT	NT		
16	1.7	0.2	-1.15	-0.96
17	1.8	0.16	-0.62	-0.62
18	1.90	0.285	-0.10	-0.07
19	1.70	0.255	-1.15	-0.79
20	NT	NT		
21	NR	NR		
22	NT	NT		
23	NR	NR		

* Outlier, see Section 4.2

Statistics

Assigned Value	1.92	0.11
Spike Value	Not Spiked	
Homogeneity Value	2.05	0.25
Robust Average	1.96	0.15
Median	1.94	0.11
Mean	2.04	
N	15	
Max	3.155	
Min	1.7	
Robust SD	0.22	
Robust CV	11%	


Results: S2 - K
Assigned Value = 1.92 ± 0.11 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
16 19 6 17 12 9 18 2 1 5 7 8 4 10 13 3 11 14 15 20 21 22 23 Md RA HV


z-Scores: S2 - K
Target Standard Deviation for Proficiency Assessment 0.19 mg/L (Equivalent to 10% CV)
z-Score
-1.2 -1.2 -0.6 -0.6 -0.5 -0.1 -0.1 0.1 0.4 0.4 0.4 0.4 1.9 3.7
Laboratory
16 19 6 17 12 9 18 2 1 5 7 8 4 10 13

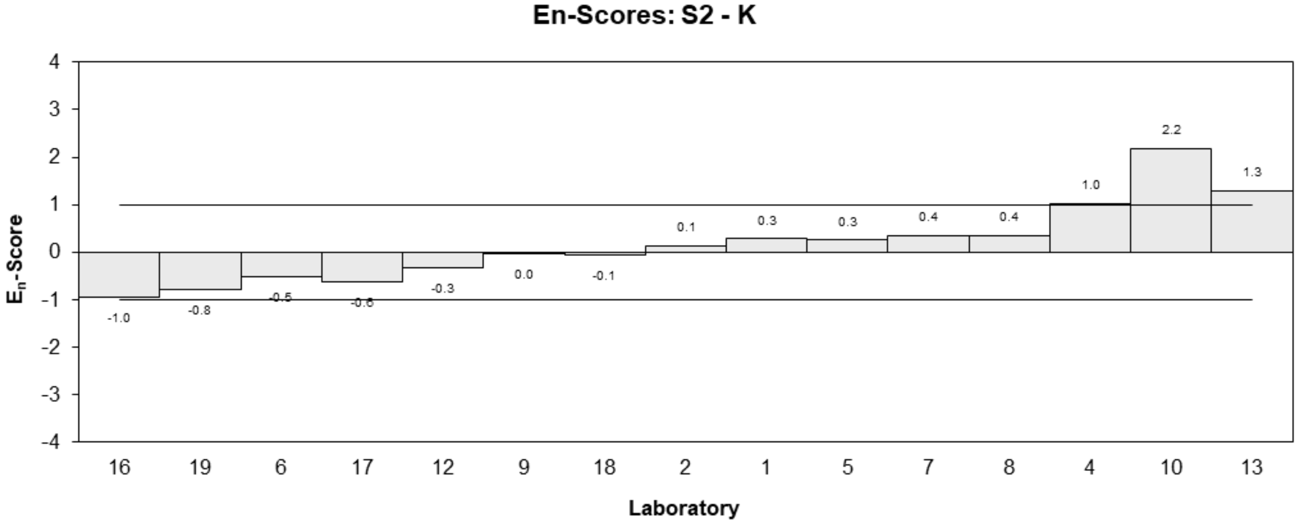

En-Scores: S2 - K
En-Score
-1.0 -0.8 -0.5 -0.6 -0.3 0.0 -0.1 0.1 0.3 0.3 0.4 0.4 1.0 2.2 1.3
Laboratory
16 19 6 17 12 9 18 2 1 5 7 8 4 10 13

Figure 16

Table 19

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	6.0	0.726	-0.34	-0.28
2	6.12	0.31	-0.14	-0.24
3	NT	NT		
4	6.379	0.813	0.27	0.20
5	6.0	0.9	-0.34	-0.23
6	6	1	-0.34	-0.21
7	6	0.4	-0.34	-0.46
8	6	0.5	-0.34	-0.39
9	6	1.8	-0.34	-0.12
10	6.24	0.7	0.05	0.04
11	NR	NR		
12	6	1.2	-0.34	-0.17
13	6.69	1.338	0.77	0.35
14	NR	NR		
15	NT	NT		
16	6.4	0.8	0.31	0.23
17	5.9	1.2	-0.50	-0.25
18	6.94	1.04	1.18	0.69
19	6.74	1.01	0.85	0.51
20	NT	NT		
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	6.21	0.21
Spike Value	Not Spiked	
Homogeneity Value	6.24	0.75
Robust Average	6.21	0.21
Median	6.00	0.10
Mean	6.23	
N	15	
Max	6.94	
Min	5.9	
Robust SD	0.33	
Robust CV	5.4%	

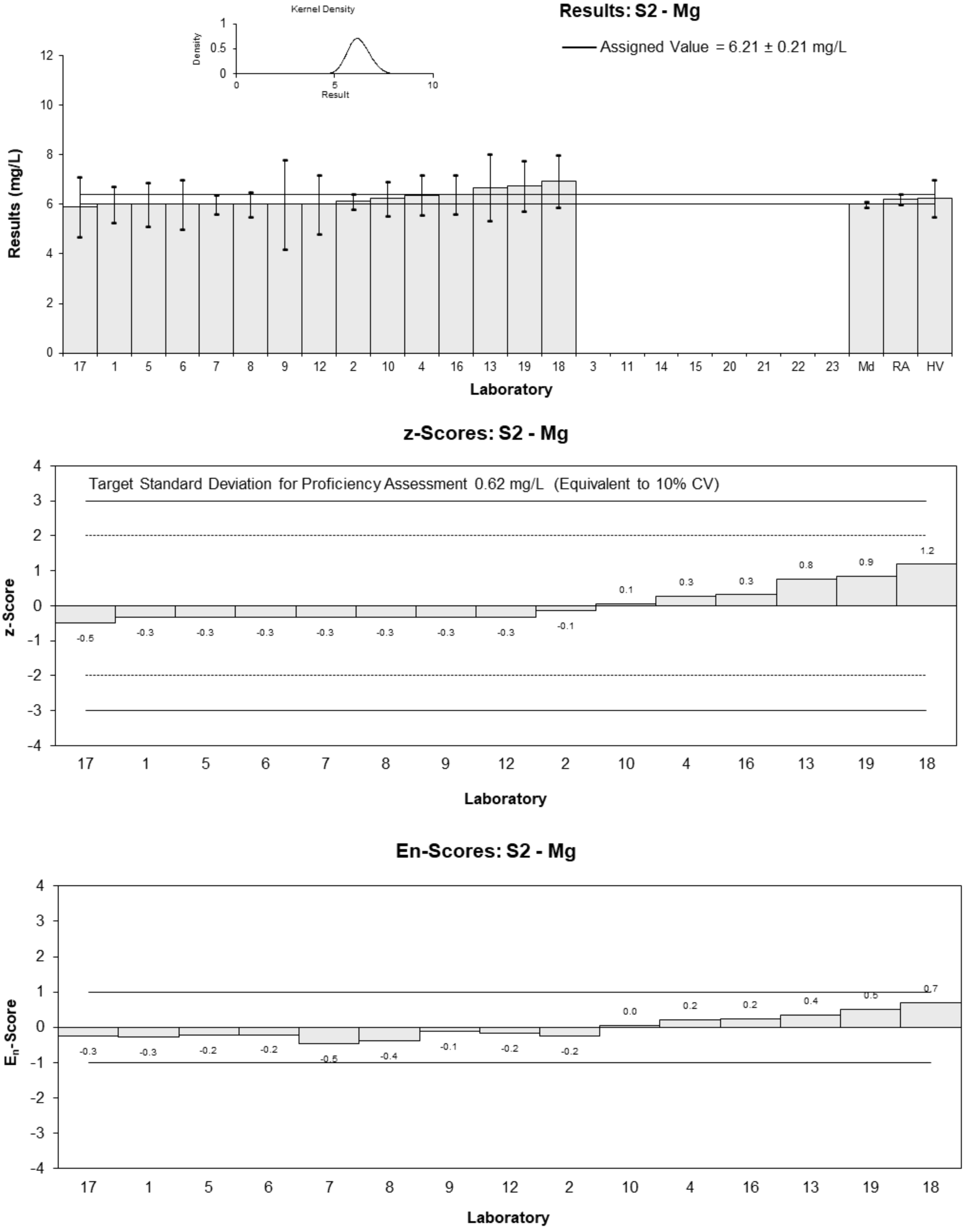

Kernel Density
Density
Result
Results: S2 - Mg
Assigned Value = 6.21 ± 0.21 mg/L
Results (mg/L)
Laboratory
17 1 5 6 7 8 9 12 2 10 4 16 13 19 18 3 11 14 15 20 21 22 23 Md RA HV
z-Scores: S2 - Mg
Target Standard Deviation for Proficiency Assessment 0.62 mg/L (Equivalent to 10% CV)
z-Score
17 1 5 6 7 8 9 12 2 10 4 16 13 19 18
-0.5 -0.3 -0.3 -0.3 -0.3 -0.3 -0.3 -0.3 -0.1 0.1 0.3 0.3 0.8 0.9 1.2
En-Scores: S2 - Mg
E_n-Score
17 1 5 6 7 8 9 12 2 10 4 16 13 19 18
-0.3 -0.3 -0.2 -0.2 -0.5 -0.4 -0.1 -0.2 -0.2 0.0 0.2 0.2 0.4 0.5 0.7
Laboratory

Figure 17

Table 20

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	15.0	1.885	0.27	0.21
2	14.45	0.72	-0.10	-0.17
3	NT	NT		
4	13.545	1.784	-0.72	-0.57
5	15.1	2.3	0.34	0.21
6	14	2	-0.41	-0.29
7	14	1	-0.41	-0.54
8	16	1.9	0.96	0.71
9	15.5	4.6	0.62	0.19
10	13.8	1.5	-0.55	-0.51
11	NR	NR		
12	13.5	2.7	-0.75	-0.40
13	14.84	4.452	0.16	0.05
14	NR	NR		
15	NT	NT		
16	14.9	1.6	0.21	0.18
17	14	2.8	-0.41	-0.21
18	14.7	2.21	0.07	0.04
19	15.5	2.33	0.62	0.38
20	NT	NT		
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	14.6	0.5
Spike Value	Not Spiked	
Homogeneity Value	15.0	1.8
Robust Average	14.6	0.5
Median	14.7	0.7
Mean	14.6	
N	15	
Max	16	
Min	13.5	
Robust SD	0.85	
Robust CV	5.8%	

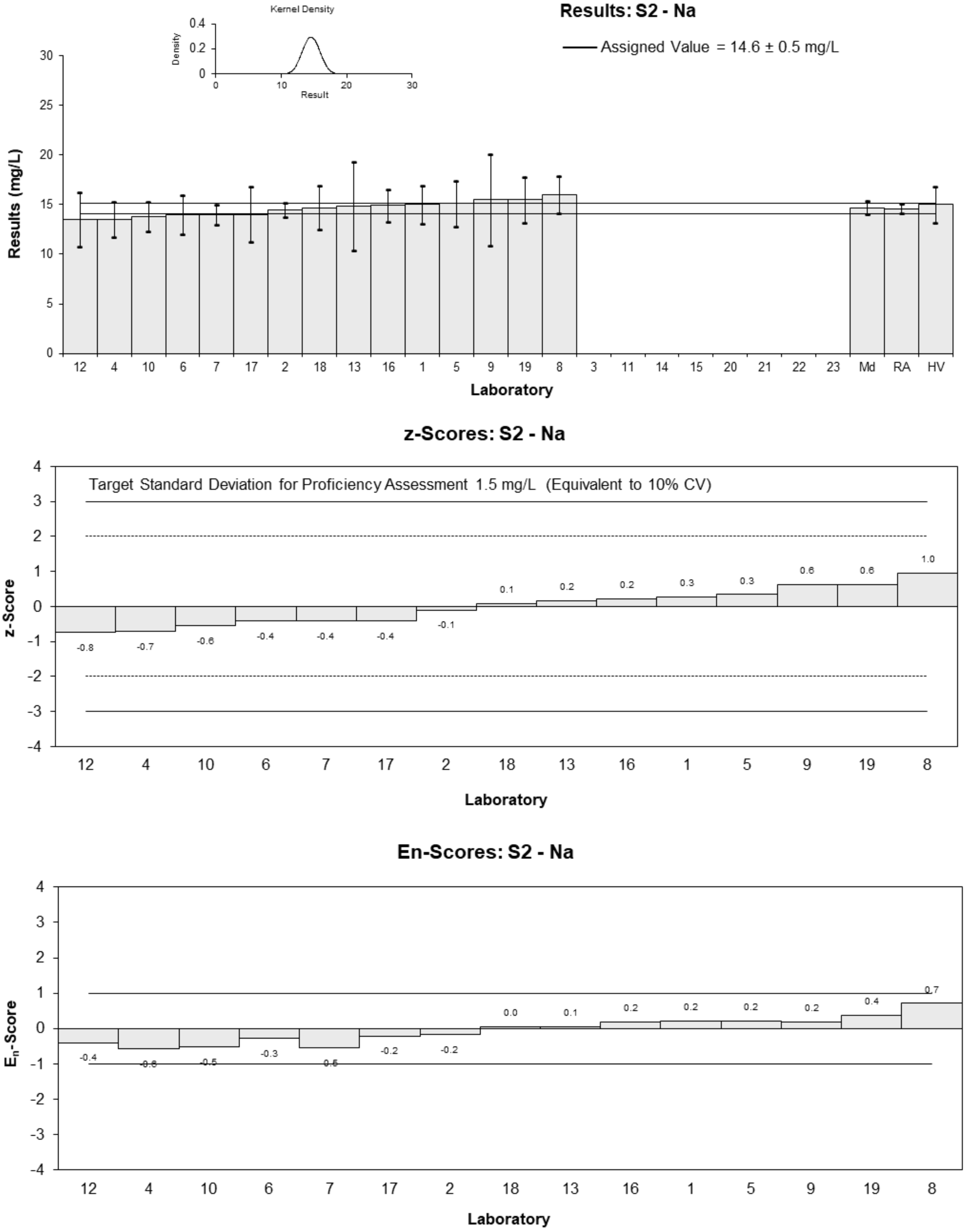

Kernel Density
Density
Result
Results: S2 - Na
Assigned Value = 14.6 ± 0.5 mg/L
Results (mg/L)
Laboratory
12 4 10 6 7 17 2 18 13 16 1 5 9 19 8 3 11 14 15 20 21 22 23 Md RA HV
z-Scores: S2 - Na
Target Standard Deviation for Proficiency Assessment 1.5 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.7 -0.6 -0.4 -0.4 -0.4 -0.1 0.1 0.2 0.2 0.3 0.3 0.6 0.6 1.0
12 4 10 6 7 17 2 18 13 16 1 5 9 19 8
Laboratory
En-Scores: S2 - Na
E_n-Score
-0.4 -0.6 -0.5 -0.3 -0.5 -0.2 -0.2 0.0 0.1 0.2 0.2 0.2 0.2 0.4 0.7
12 4 10 6 7 17 2 18 13 16 1 5 9 19 8
Laboratory

Figure 18

Table 21

Sample Details

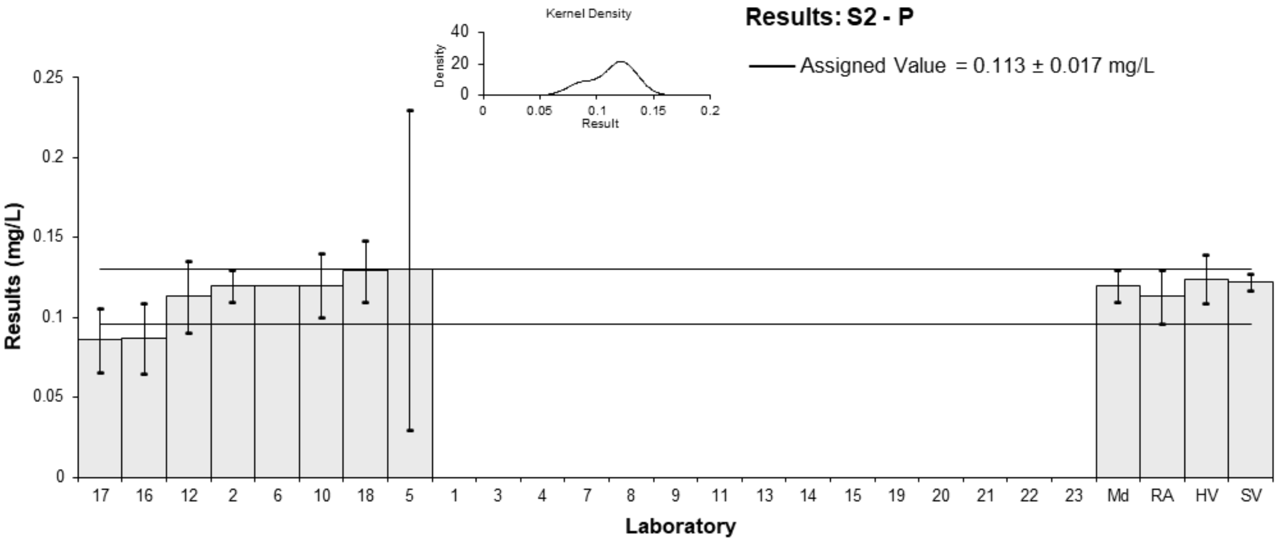
Sample No.	S2
Matrix	Potable Water
Analyte	P
Unit	mg/L

Participant Results

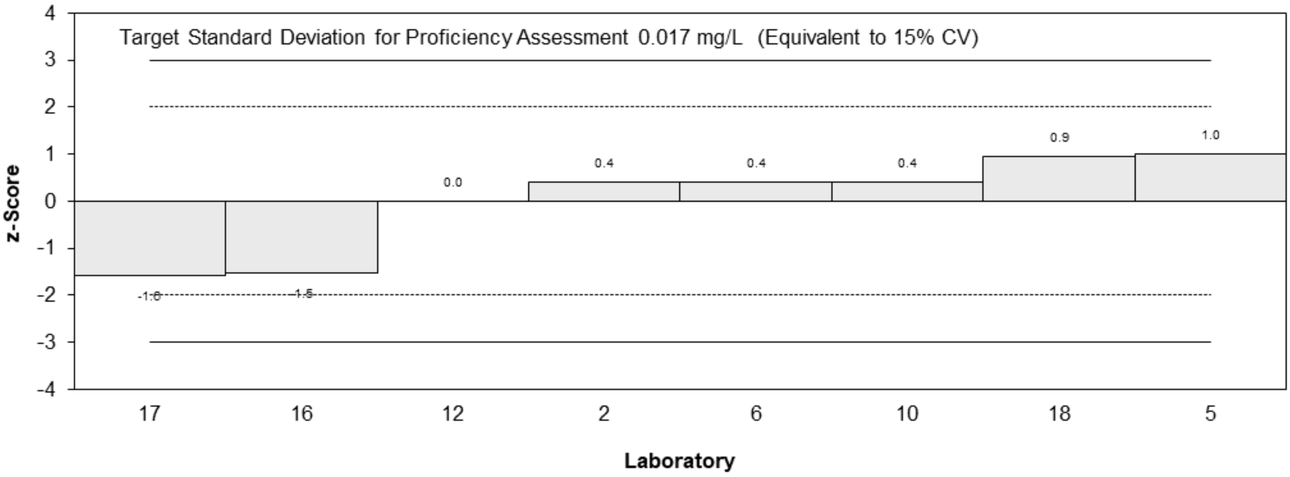
Lab. Code	Result	Uncertainty	z	E_n
1	<1	NR		
2	0.12	0.01	0.41	0.35
3	NT	NT		
4	<1	NR		
5	0.13	0.1	1.00	0.17
6	0.12	NR	0.41	0.41
7	<1	NR		
8	<1	0.11		
9	< 0.5	NR		
10	0.12	0.02	0.41	0.27
11	NR	NR		
12	0.113	0.0226	0.00	0.00
13	<0.25	NR		
14	NR	NR		
15	NT	NT		
16	0.087	0.022	-1.53	-0.94
17	0.086	0.02	-1.59	-1.03
18	0.129	0.019	0.94	0.63
19	NT	NT		
20	<1.5	0.7		
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	0.113	0.017
Spike Value	0.122	0.005
Homogeneity Value	0.124	0.015
Robust Average	0.113	0.017
Median	0.120	0.010
Mean	0.113	
N	8	
Max	0.13	
Min	0.086	
Robust SD	0.020	
Robust CV	17%	


Results: S2 - P

z-Scores: S2 - P



En-Scores: S2 - P

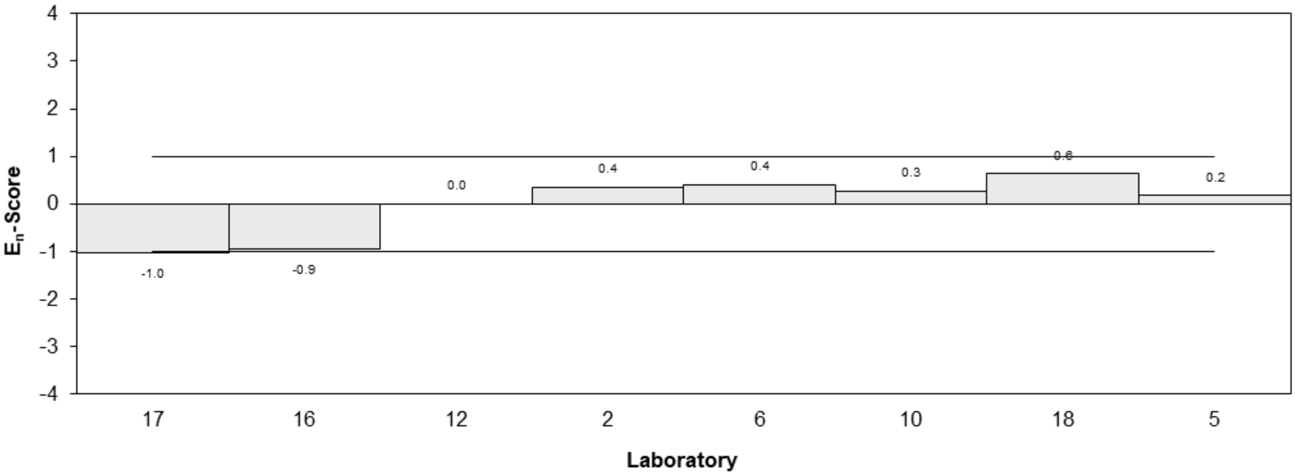


Figure 19

Table 22

Sample Details

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

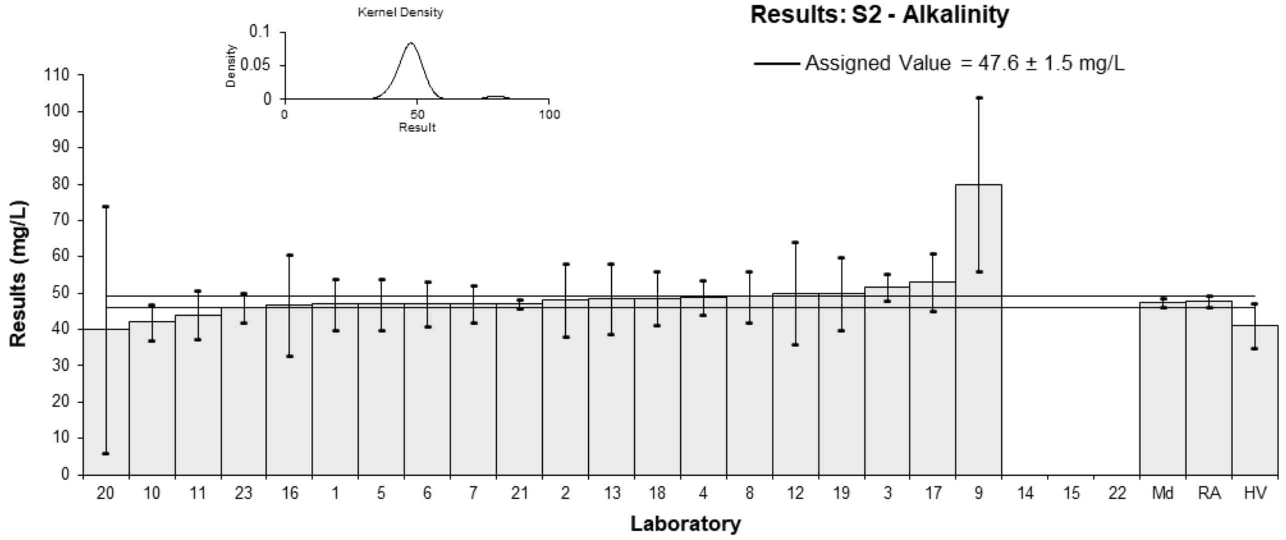
Participant Results

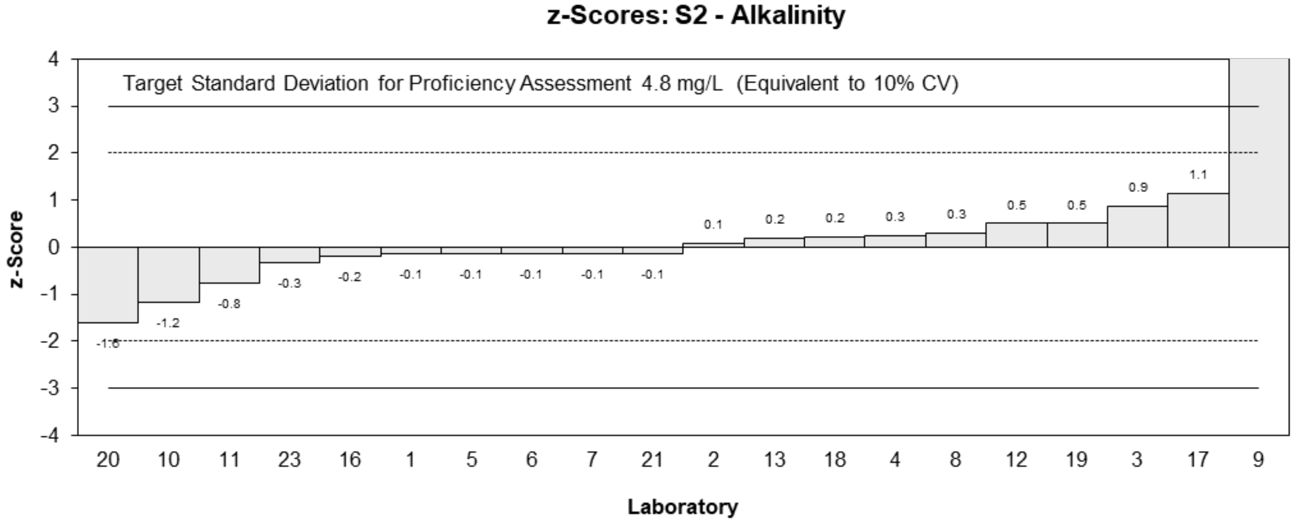
Lab. Code	Result	Uncertainty	z	E_n
1	47	7.03	-0.13	-0.08
2	48.0	10	0.08	0.04
3	51.7	3.8	0.86	1.00
4	48.78	4.73	0.25	0.24
5	47	7	-0.13	-0.08
6	47	6.1	-0.13	-0.10
7	47	5	-0.13	-0.11
8	49	6.9	0.29	0.20
9*	80	24	6.81	1.35
10	42	5.0	-1.18	-1.07
11	44.0	6.6	-0.76	-0.53
12	50	14	0.50	0.17
13	48.5	9.7	0.19	0.09
14	NR	NR		
15	NT	NT		
16	46.7	14	-0.19	-0.06
17	53	8	1.13	0.66
18	48.6	7.29	0.21	0.13
19	50	10	0.50	0.24
20	40	34	-1.60	-0.22
21	47	1.31	-0.13	-0.30
22	NT	NT		
23	46	3.9	-0.34	-0.38

* Outlier, see Section 4.2

Statistics

Assigned Value	47.6	1.5
Spike Value	Not Spiked	
Homogeneity Value	41.0	6.2
Robust Average	47.9	1.6
Median	47.5	1.2
Mean	49.1	
N	20	
Max	80	
Min	40	
Robust SD	2.9	
Robust CV	6.2%	


Results: S2 - Alkalinity
Assigned Value = 47.6 ± 1.5 mg/L
Kernel Density
Density
0.1
0.05
0
0
50
100
Result
Results (mg/L)
110
100
90
80
70
60
50
40
30
20
10
0
20
10
11
23
16
1
5
6
7
21
2
13
18
4
8
12
19
3
17
9
14
15
22
Md
RA
HV
Laboratory


z-Scores: S2 - Alkalinity
Target Standard Deviation for Proficiency Assessment 4.8 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.6
-1.2
-0.8
-0.3
-0.2
-0.1
-0.1
-0.1
-0.1
-0.1
0.1
0.2
0.2
0.3
0.3
0.5
0.5
0.9
1.1
20
10
11
23
16
1
5
6
7
21
2
13
18
4
8
12
19
3
17
9
Laboratory

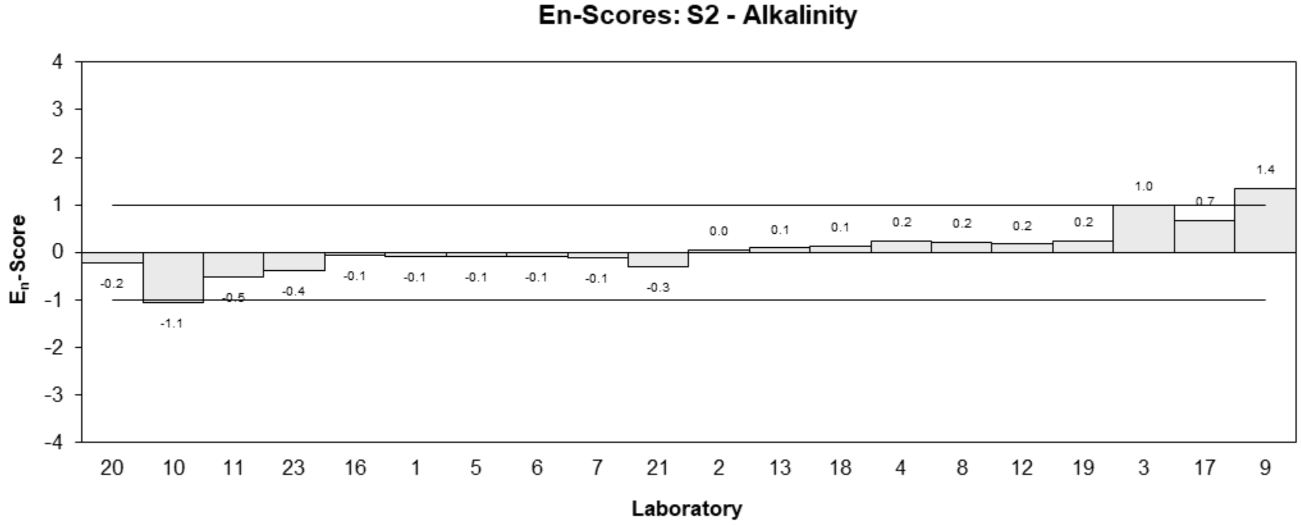

En-Scores: S2 - Alkalinity
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.2
-1.1
-0.5
-0.4
-0.1
-0.1
-0.1
-0.1
-0.1
-0.3
0.0
0.1
0.1
0.2
0.2
0.2
0.2
1.0
0.7
1.4
20
10
11
23
16
1
5
6
7
21
2
13
18
4
8
12
19
3
17
9
Laboratory

Figure 20

Table 23

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	208	16.6	-0.56	-0.35
2	205	20	-0.84	-0.44
3	213	6	-0.09	-0.14
4	204.51	14.35	-0.89	-0.64
5	218	33	0.37	0.12
6	210	8.5	-0.37	-0.43
7	207	13	-0.65	-0.51
8	208	10.67	-0.56	-0.53
9	217	65	0.28	0.05
10	241	25	2.52	1.07
11	210	10.5	-0.37	-0.36
12	221	11.934	0.65	0.56
13**	0.226	0.0226	-19.98	-53.44
14	NR	NR		
15	NT	NT		
16	219	15.2	0.47	0.32
17	220	33	0.56	0.18
18	219	32.9	0.47	0.15
19	220	44	0.56	0.14
20	212	33	-0.19	-0.06
21	210	7.77	-0.37	-0.46
22	NT	NT		
23	257	3.5	4.02	8.09

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	214	4
Spike Value	Not Spiked	
Homogeneity Value	220	17
Robust Average	214	4
Median	213	5
Mean	217	
N	19	
Max	257	
Min	204.51	
Robust SD	7.7	
Robust CV	3.6%	

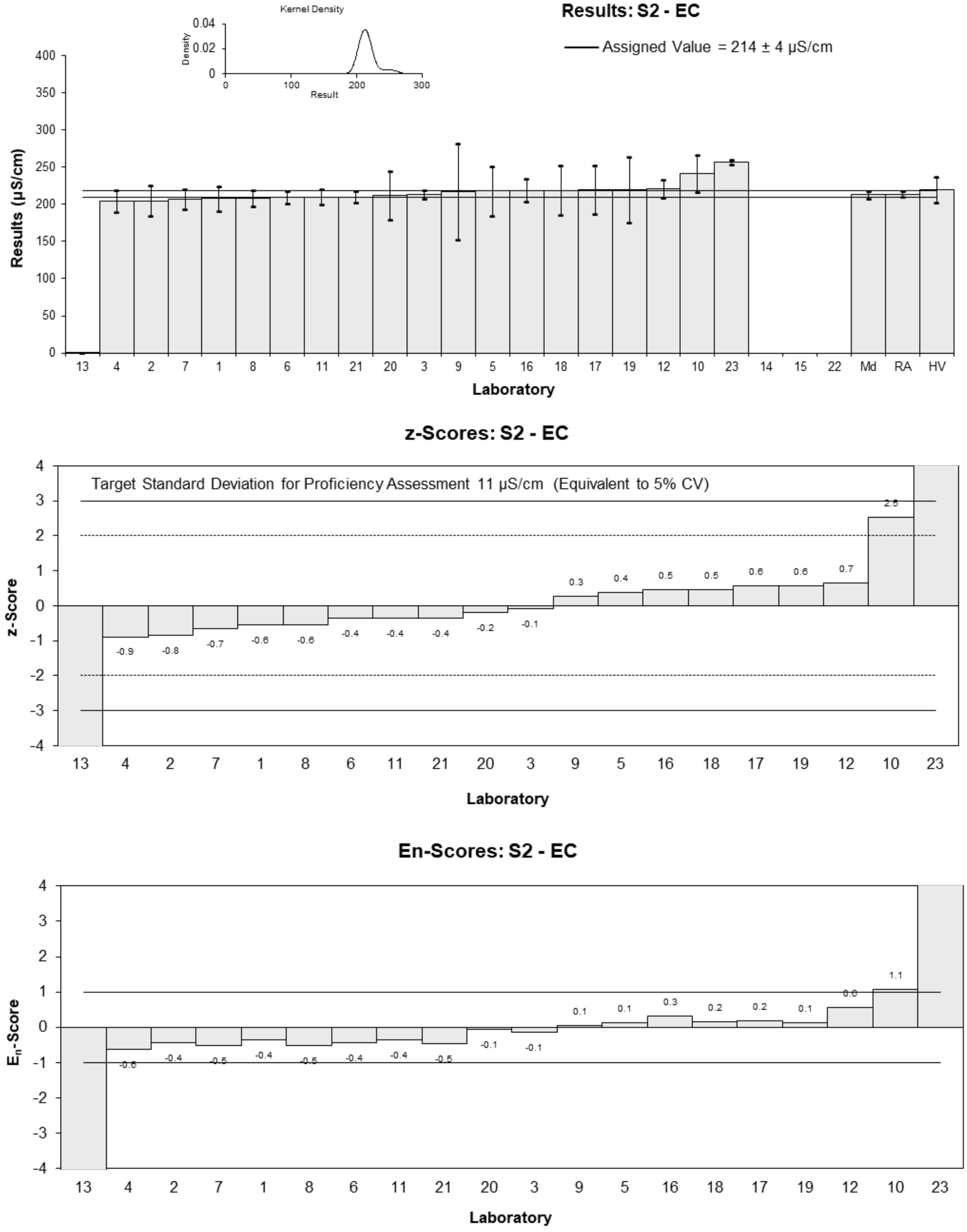

Results: S2 - EC
Assigned Value = 214 ± 4 µS/cm
Kernel Density
Density
0.04
0.02
0
0
100
200
300
Result
Results (µS/cm)
400
350
300
250
200
150
100
50
0
13
4
2
7
1
8
6
11
21
20
3
9
5
16
18
17
19
12
10
23
14
15
22
Md
RA
HV
Laboratory
z-Scores: S2 - EC
Target Standard Deviation for Proficiency Assessment 11 µS/cm (Equivalent to 5% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.8
-0.7
-0.6
-0.6
-0.4
-0.4
-0.4
-0.2
-0.1
0.3
0.4
0.5
0.5
0.6
0.6
0.7
2.5
13
4
2
7
1
8
6
11
21
20
3
9
5
16
18
17
19
12
10
23
Laboratory
En-Scores: S2 - EC
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.4
-0.5
-0.4
-0.5
-0.4
-0.4
-0.5
-0.1
-0.1
0.1
0.1
0.3
0.2
0.2
0.1
0.6
1.1
13
4
2
7
1
8
6
11
21
20
3
9
5
16
18
17
19
12
10
23
Laboratory

Figure 21

Table 24

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	pH

Participant Results

Lab. Code	**Result**	**Uncertainty**	**z**	**E_n**
1	7.41	0.12	-0.34	-0.45
2	7.7	0.2	0.76	0.78
3	7.60	0.09	0.38	0.54
4	6.93	0.11	-2.17	-2.94
5	7.68	0.2	0.69	0.70
6	7.8	0.4	1.14	0.70
7	7.08	0.11	-1.60	-2.16
8	7.64	0.050	0.53	0.84
9	7.22	0.2	-1.07	-1.09
10	7.86	0.1	1.37	1.91
11	7.8	0.3	1.14	0.88
12	7.7	0.094	0.76	1.08
13	7.48	NR	-0.08	-0.12
14	NR	NR		
15	NT	NT		
16	7.64	0.2	0.53	0.55
17	7.2	0.1	-1.14	-1.59
18	7.71	0.3	0.80	0.62
19	7.1	0.3	-1.52	-1.18
20	7.5	0.17	0.00	0.00
21	7.32	0.07	-0.69	-1.03
22	NT	NT		
23	7.50	0.465	0.00	0.00

Statistics

Assigned Value	7.50	0.16
Spike Value	Not Spiked	
Homogeneity Value	7.17	0.14
Robust Average	7.50	0.16
Median	7.55	0.13
Mean	7.49	
N	20	
Max	7.86	
Min	6.93	
Robust SD	0.29	
Robust CV	3.9%	

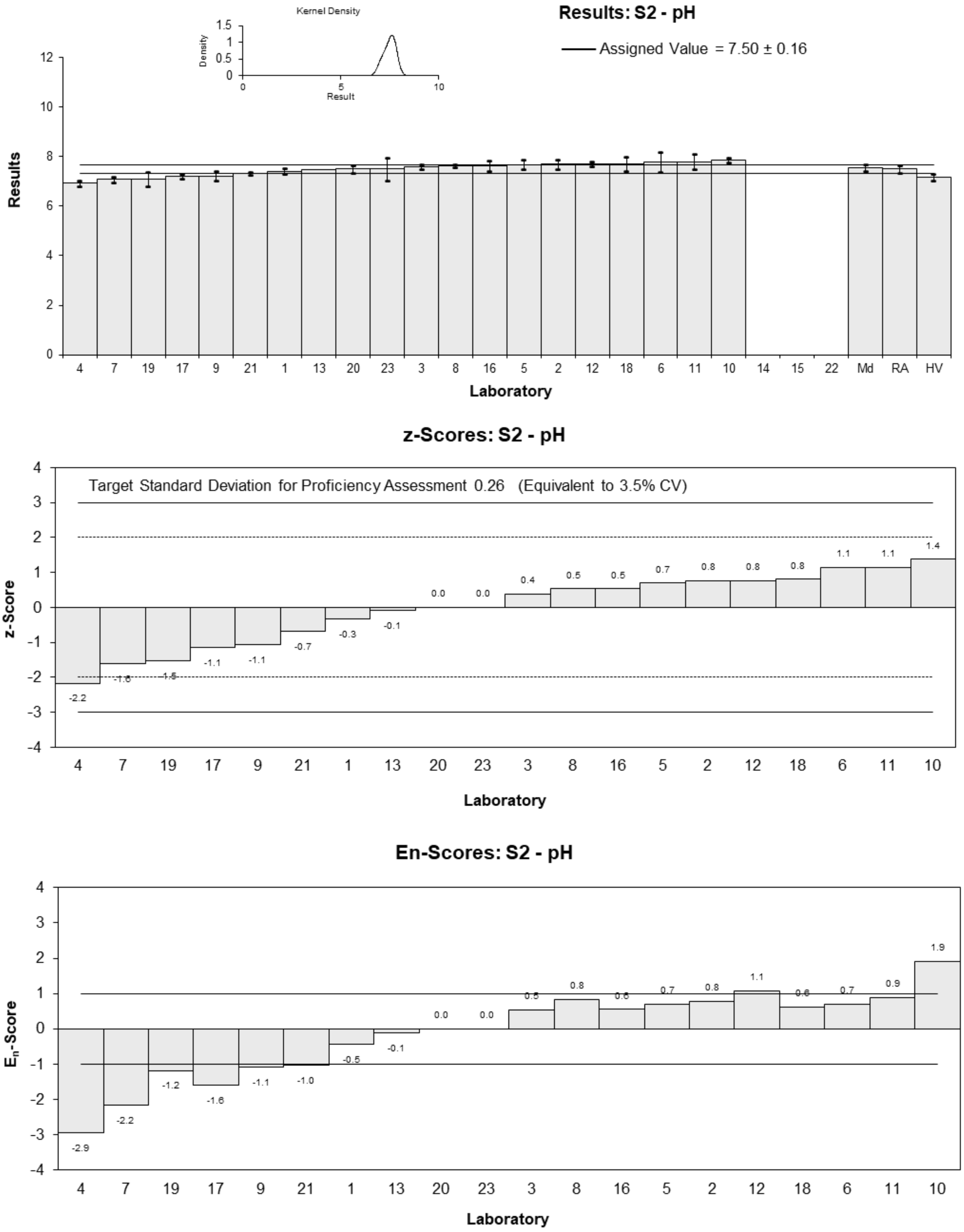

Kernel Density
Density
1.5
1
0.5
0
0
5
10
Result
Results: S2 - pH
Assigned Value = 7.50 ± 0.16
Results
12
10
8
6
4
2
0
4 7 19 17 9 21 1 13 20 23 3 8 16 5 2 12 18 6 11 10 14 15 22 Md RA HV
Laboratory
z-Scores: S2 - pH
Target Standard Deviation for Proficiency Assessment 0.26 (Equivalent to 3.5% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.2 -1.6 -1.5 -1.1 -1.1 -0.7 -0.3 -0.1 0.0 0.0 0.4 0.5 0.5 0.7 0.8 0.8 0.8 1.1 1.1 1.4
4 7 19 17 9 21 1 13 20 23 3 8 16 5 2 12 18 6 11 10
Laboratory
En-Scores: S2 - pH
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-2.9 -2.2 -1.2 -1.6 -1.1 -1.0 -0.5 -0.1 0.0 0.0 0.5 0.8 0.6 0.7 0.8 1.1 0.6 0.7 0.9 1.9
4 7 19 17 9 21 1 13 20 23 3 8 16 5 2 12 18 6 11 10
Laboratory

Figure 22

Table 25

Sample Details

Sample No.	S2
Matrix	Potable Water
Analyte	Silica (as SiO2)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.91	0.414	0.36	0.37
2	4.61	0.23	-0.27	-0.43
3	4.53	0.26	-0.44	-0.64
4	4.78	0.62	0.08	0.06
5	4.6	0.7	-0.30	-0.19
6	4.4	NR	-0.72	-1.70
7	4.73	0.22	-0.02	-0.03
8	4.6	0.92	-0.30	-0.15
9	4.5	1.4	-0.51	-0.17
10	5.16	0.8	0.89	0.51
11	NR	NR		
12	NT	NT		
13	NT	NT		
14	4.77	NR	0.06	0.15
15	NT	NT		
16	NT	NT		
17	4.2	0.84	-1.14	-0.63
18	4.94	0.741	0.42	0.26
19	5.1	1.0	0.76	0.35
20	NT	NT		
21	5.12	0.34	0.80	0.96
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	4.74	0.20
Spike Value	Not Spiked	
Homogeneity Value	4.30	0.65
Robust Average	4.74	0.20
Median	4.73	0.19
Mean	4.73	
N	15	
Max	5.16	
Min	4.2	
Robust SD	0.30	
Robust CV	6.4%	

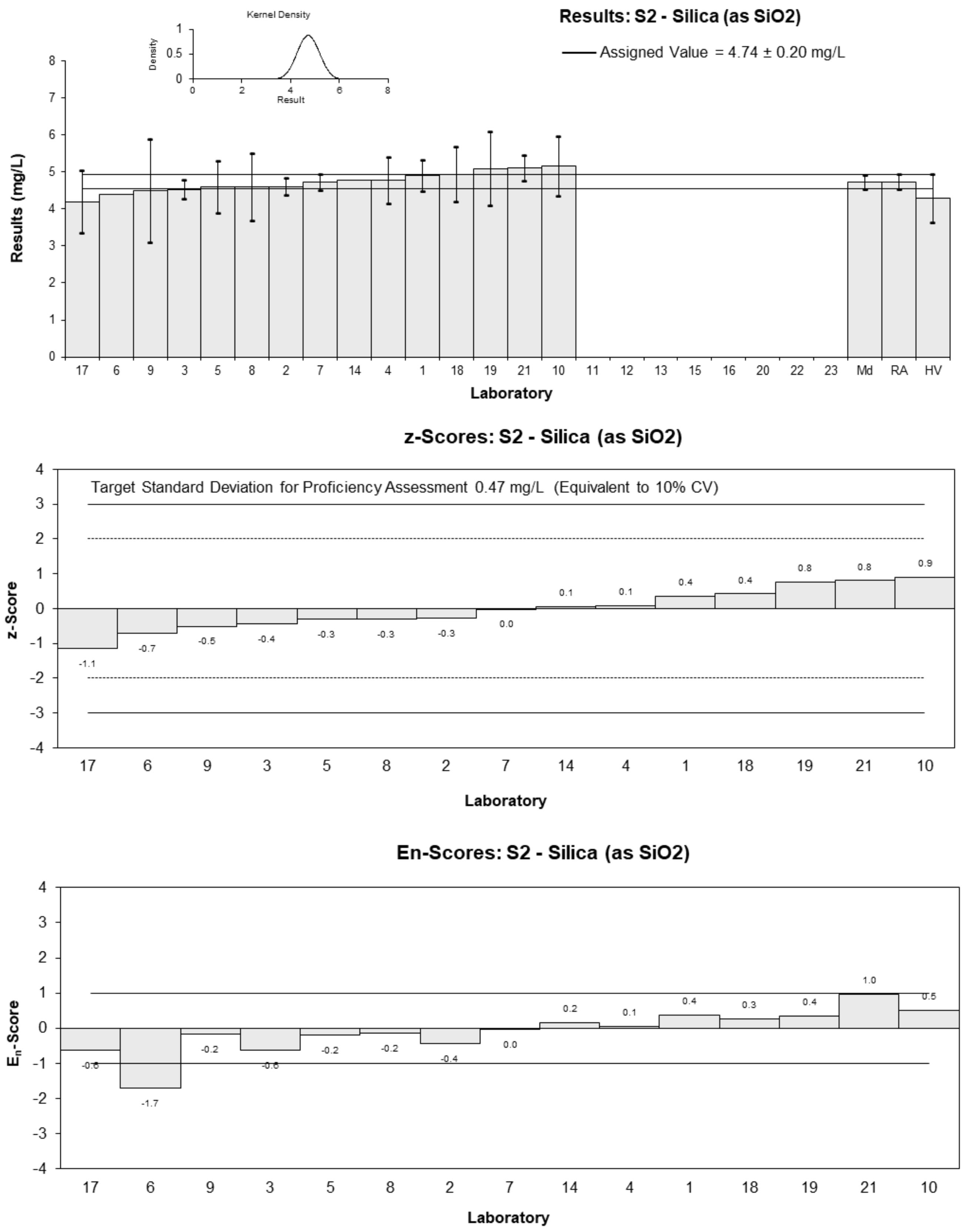

Results: S2 - Silica (as SiO2)
Assigned Value = 4.74 ± 0.20 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
17 6 9 3 5 8 2 7 14 4 1 18 19 21 10 11 12 13 15 16 20 22 23 Md RA HV
z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation for Proficiency Assessment 0.47 mg/L (Equivalent to 10% CV)
z-Score
-1.1 -0.7 -0.5 -0.4 -0.3 -0.3 -0.3 0.0 0.1 0.1 0.4 0.4 0.8 0.8 0.9
17 6 9 3 5 8 2 7 14 4 1 18 19 21 10
Laboratory
En-Scores: S2 - Silica (as SiO2)
E_n-Score
-0.6 -1.7 -0.2 -0.6 -0.2 -0.2 -0.4 0.0 0.2 0.1 0.4 0.3 0.4 1.0 0.5
17 6 9 3 5 8 2 7 14 4 1 18 19 21 10
Laboratory

Figure 23

Table 26

Sample Details

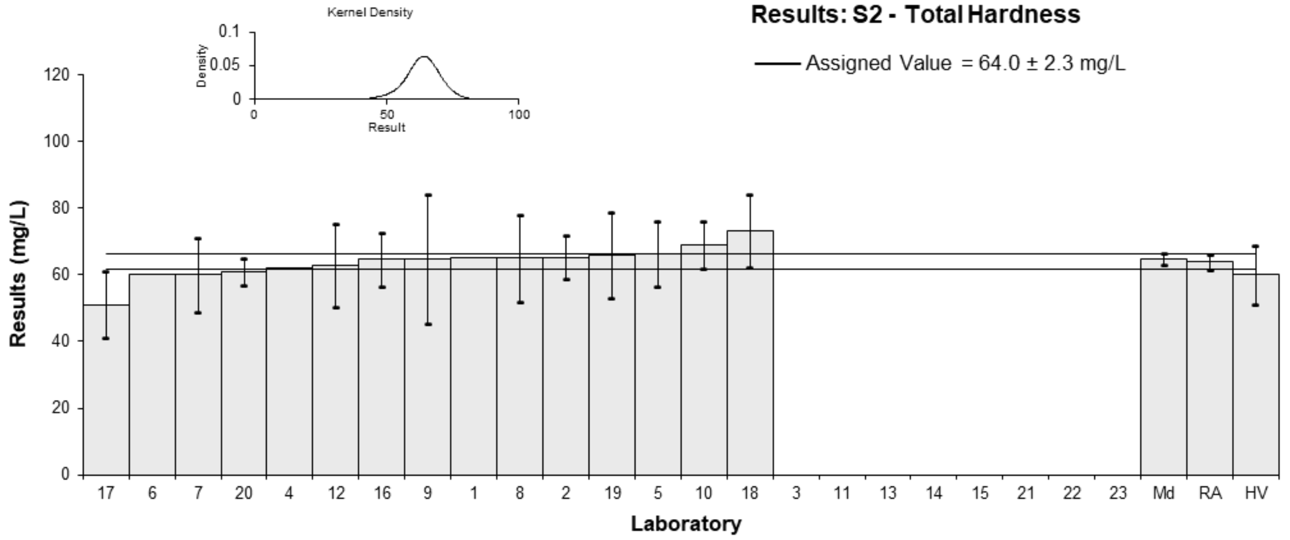
Sample No.	S2
Matrix	Potable Water
Analyte	Total Hardness
Unit	mg/L

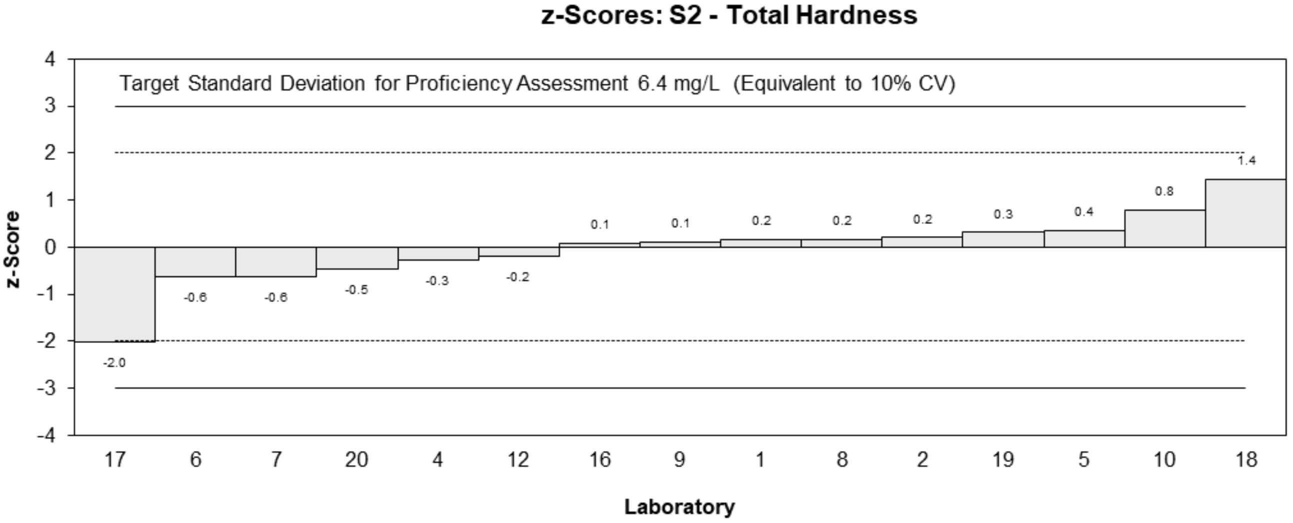
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	65	NR	0.16	0.43
2	65.27	6.52	0.20	0.18
3	NT	NT		
4	62.16	NR	-0.29	-0.80
5	66.3	9.9	0.36	0.23
6	60	NR	-0.62	-1.74
7	60	11	-0.62	-0.36
8	65	13	0.16	0.08
9	64.7	19.4	0.11	0.04
10	69	7.0	0.78	0.68
11	NR	NR		
12	62.8	12.6	-0.19	-0.09
13	NT	NT		
14	NR	NR		
15	NT	NT		
16	64.6	7.9	0.09	0.07
17	51	10	-2.03	-1.27
18	73.2	10.98	1.44	0.82
19	66	13	0.31	0.15
20	61	4	-0.47	-0.65
21	NR	NR		
22	NT	NT		
23	NR	NR		

Statistics

Assigned Value	64.0	2.3
Spike Value	Not Spiked	
Homogeneity Value	60.0	9.0
Robust Average	64.0	2.3
Median	64.7	1.8
Mean	63.7	
N	15	
Max	73.2	
Min	51	
Robust SD	3.6	
Robust CV	5.7%	


Results: S2 - Total Hardness
Assigned Value = 64.0 ± 2.3 mg/L
Kernel Density
Density
0.1
0.05
0
0
50
100
Result
Results (mg/L)
120
100
80
60
40
20
0
17
6
7
20
4
12
16
9
1
8
2
19
5
10
18
3
11
13
14
15
21
22
23
Md
RA
HV
Laboratory


z-Scores: S2 - Total Hardness
Target Standard Deviation for Proficiency Assessment 6.4 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.0
-0.6
-0.6
-0.5
-0.3
-0.2
0.1
0.1
0.2
0.2
0.2
0.3
0.4
0.8
1.4
17
6
7
20
4
12
16
9
1
8
2
19
5
10
18
Laboratory

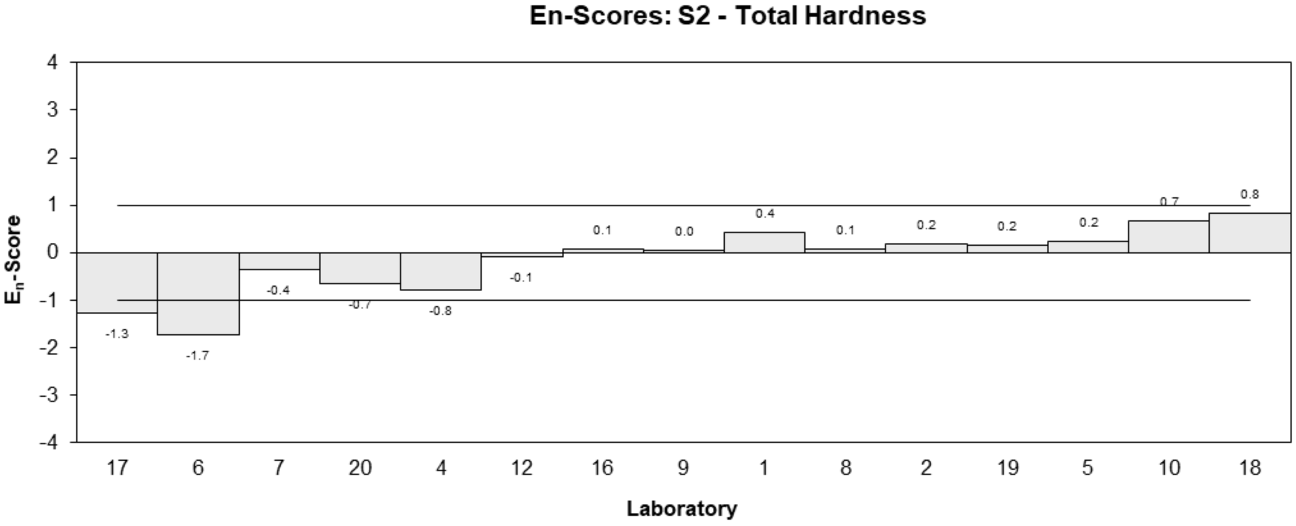

En-Scores: S2 - Total Hardness
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.3
-1.7
-0.4
-0.7
-0.8
-0.1
0.1
0.0
0.4
0.1
0.2
0.2
0.2
0.7
0.8
17
6
7
20
4
12
16
9
1
8
2
19
5
10
18
Laboratory

Figure 24

6 DISCUSSION OF RESULTS

6.1 Assigned Value and Traceability

Sample S1 was prepared from autoclaved potable water fortified with 7 analytes of interest, whilst **Sample S2** was unfiltered potable water fortified with 2 analytes.

Assigned values for the 23 tests in the study samples were calculated as the robust averages of participants' results. The robust averages and their associated expanded uncertainties were calculated using the procedure described in ISO13528.[6] Extreme outliers and results less than 50% and more than 150% of the robust average were excluded prior to the calculation of each assigned value (see subchapters 4.2 and 4.3). Appendix 3 sets out the calculation of the robust average and assigned value for chloride in Sample S1 and its associated uncertainty.

The results from Laboratories 1, 4, 6, 10, 11, and 21 for NH_3, NO_3 and NO_2 in Sample S1, were consistently lower than the spiked value by the same factor. To avoid unfair scoring, these results were excluded from robust average calculations as they would unduly bias the assigned value, making it appear lower than its actual value; they were subsequently also excluded from the calculation of all summary statistics.

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

Traceability The assigned values are not traceable to any external reference; they are traceable to the consensus of participants' results derived from a variety of measurement methods and (presumably) a variety of calibrators. So, although expressed in SI units, the metrological traceability of the assigned values has not been established.

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 359 numerical results, 349 (97%) were reported with an expanded measurement uncertainty, indicating that most laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0.34% to 275% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 2.

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

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 24).

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, 19 laboratories reported results for EC in S2. The uncertainty of the assigned value estimated from the robust standard deviation of the 19 laboratories' results is 4 µS/cm (see equation 4, Appendix 3). Laboratory 23 might have under-estimated its expanded measurement uncertainties reported for EC in S2 (3.5 µS/cm) as an uncertainty estimated from one measurement should not be smaller than the uncertainty estimated from 19 measurements. Alternatively, estimates of uncertainties for Mg in S2 larger than 1.45 mg/L (the uncertainty of the assigned value, 0.21 mg/L plus the allowable variation from the assigned value, the target standard deviation of 0.621 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 9 for Mg in S2 (1.8 mg/L) might have been over-estimated.

Laboratory 20 should review their procedure for estimating measurement uncertainty as some of their estimated uncertainties were either under or over-estimated.

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

Laboratory 20 reported an estimate of expanded uncertainty for one measurement result larger than the result itself.

Laboratories 8, 20 and 22 attached estimates of the expanded measurement uncertainty to results reported as less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[10]

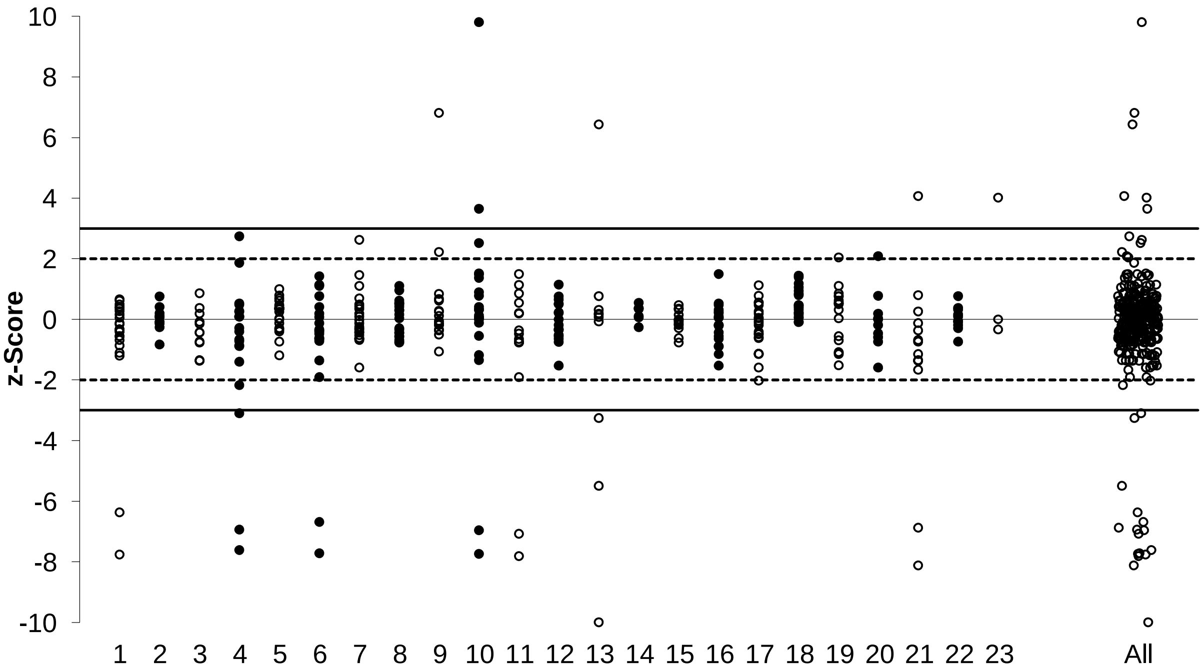
In some cases, the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 18.44 ± 3.42 mg/L,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

6.3 z-Score

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

The target standard deviation defines acceptable performance in a proficiency test. Target standard deviations for proficiency assessment equivalent to 3.5% to 15% performance coefficient of variation (PCV) were used to calculate z-scores. Unlike the standard deviation based on between-laboratory 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-laboratory coefficient of variation predicted by the Thompson-Horwitz equation[7] and the between-laboratory coefficient of variation resulted in this study are presented for comparison in Table 27.



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

Figure 25 z-Score Dispersal by Laboratory

The dispersal of participants' z-scores is presented in Figure 25 (by laboratory code) and in Figure 27 (by test). Of 359 results for which z-scores were calculated, 329 (92%) returned an acceptable score of $|z| \leq 2.0$ and 8 (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.

A summary of participants' performance is presented in Figure 28, and in Tables 28 and 29.

Laboratories 7 and **17** returned the highest number of acceptable z-scores (21 out of 22 reported).

All results reported by **Laboratories 5** (20)**, 8** (20), **16** (19), **18** (19), **12** (17), **15** (12), **2** (11), **3** (11), **22** (10) and **14** (7) returned acceptable z-scores.

Table 27 Between-Laboratory CV of this Study, Thompson/Horwitz CV and Set Target CV

Sample	Test	Assigned value (mg/L)	Between-Laboratory CV*	Thompson/ Horwitz CV	Target SD (as CV)
S1	Ammonia (as NH3)	0.371	9.8%	19%	10%
S1	Bromide	0.126	6.1%	22%	10%
S1	Chloride	28.9	6.3%	9.6%	10%
S1	DOC	4.46	15%	13%	15%
S1	Fluoride	1.08	9.3%	16%	10%
S1	Iodide	0.355	13%	19%	15%
S1	Nitrate (as NO3)	2.02	6.5%	14%	10%
S1	Nitrite (as NO2)	0.513	4.2%	18%	10%
S1	Orthophosphate-P	0.195	7.1%	20%	10%
S1	Sulphate	10.8	5.7%	11%	10%
S1	TDN	1.13	10%	16%	10%
S1	TDP	0.199	6.4%	20%	10%
S2	Alkalinity	47.6	5.5%	8.9%	10%
S2	B	0.417	7.0%	18%	10%
S2	Ca	16.2	5.4%	11%	10%
S2	EC	214	3.6%	7.1%	5%
S2	K	1.92	8.9%	15%	10%
S2	Mg	6.21	5.4%	12%	10%
S2	Na	14.6	5.8%	11%	10%
S2	P	0.113	17%	22%	15%
S2	pH	7.50	3.9%	12%	3.5%
S2	Silica (as SiO2)	4.74	6.4%	13%	10%
S2	Total Hardness	64.0	5.7%	8.6%	10%

*Robust between-laboratories CV with outliers removed

6.4 E_n-score

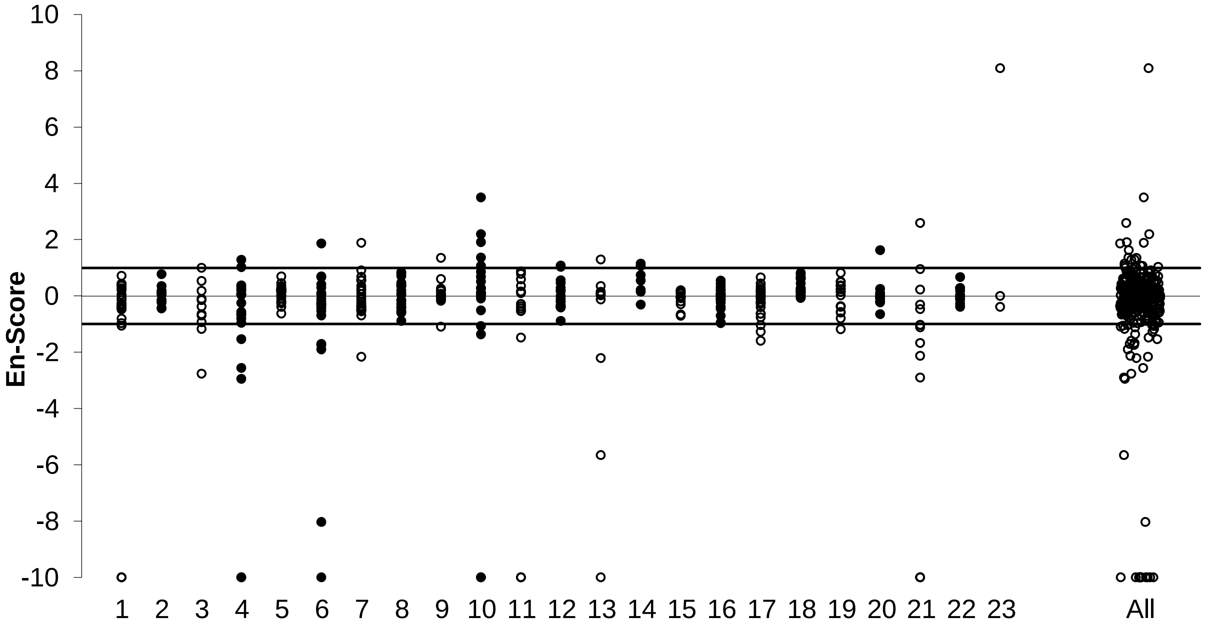
E_n-score can be interpreted in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value considering the respective uncertainties. An unacceptable E_n -score for an analyte can either be caused by an inappropriate measurement, an inappropriate estimation 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 359 results for which E_n-scores were calculated, 301 (84%) returned an acceptable score of $|E_n| < 1.0$, indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

Laboratories 7, **5** and **8** returned the highest number of acceptable E_n-scores with 20.

All results reported by **Laboratories 5** (20), **8** (20), **16** (19), **18** (19), **15** (12), **2** (11), and **22** (10) returned acceptable E_n-scores.



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

Figure 26 E_n-Score Dispersal by Laboratory

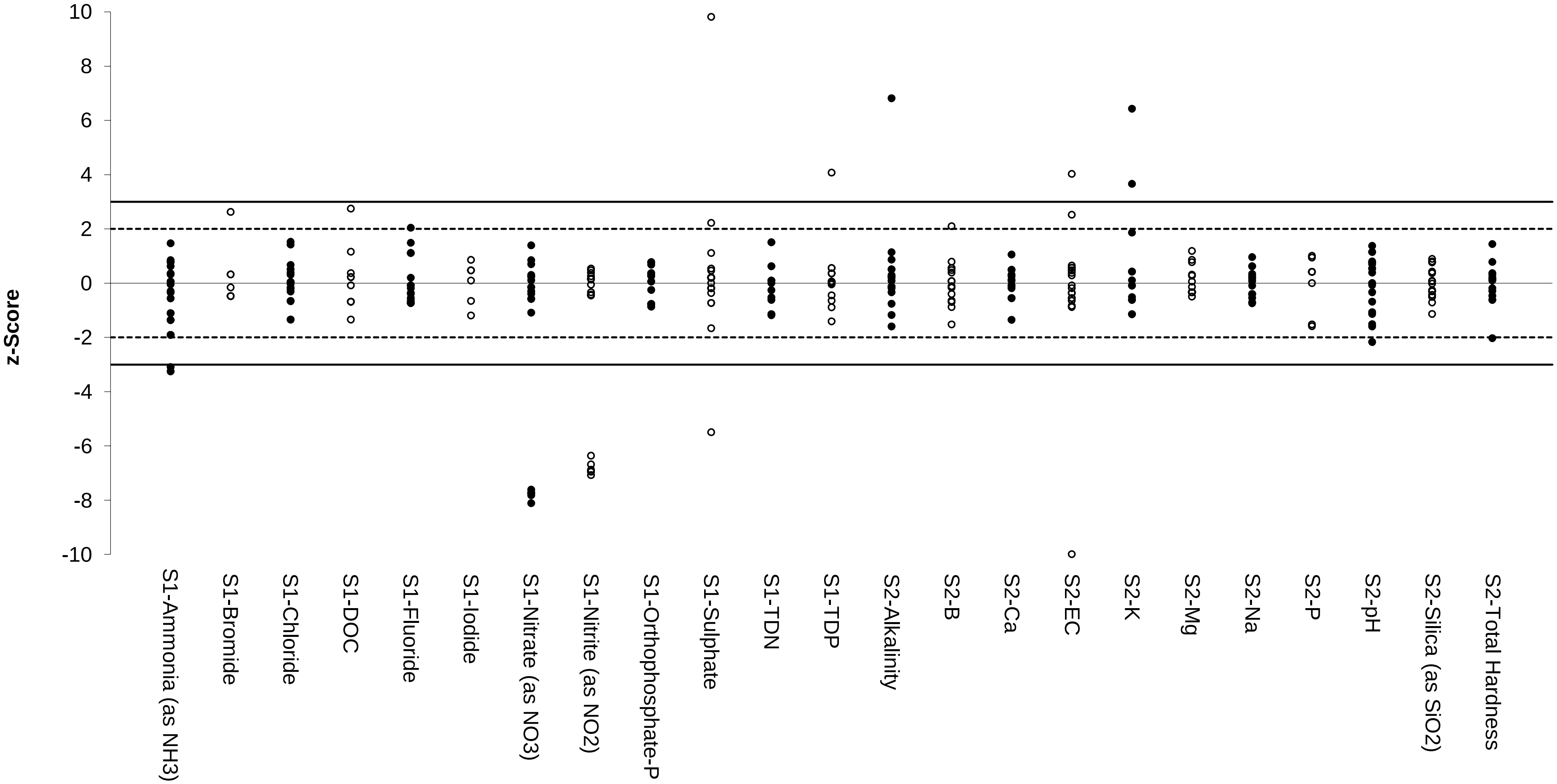


Figure 27 z-Score Dispersal by Test

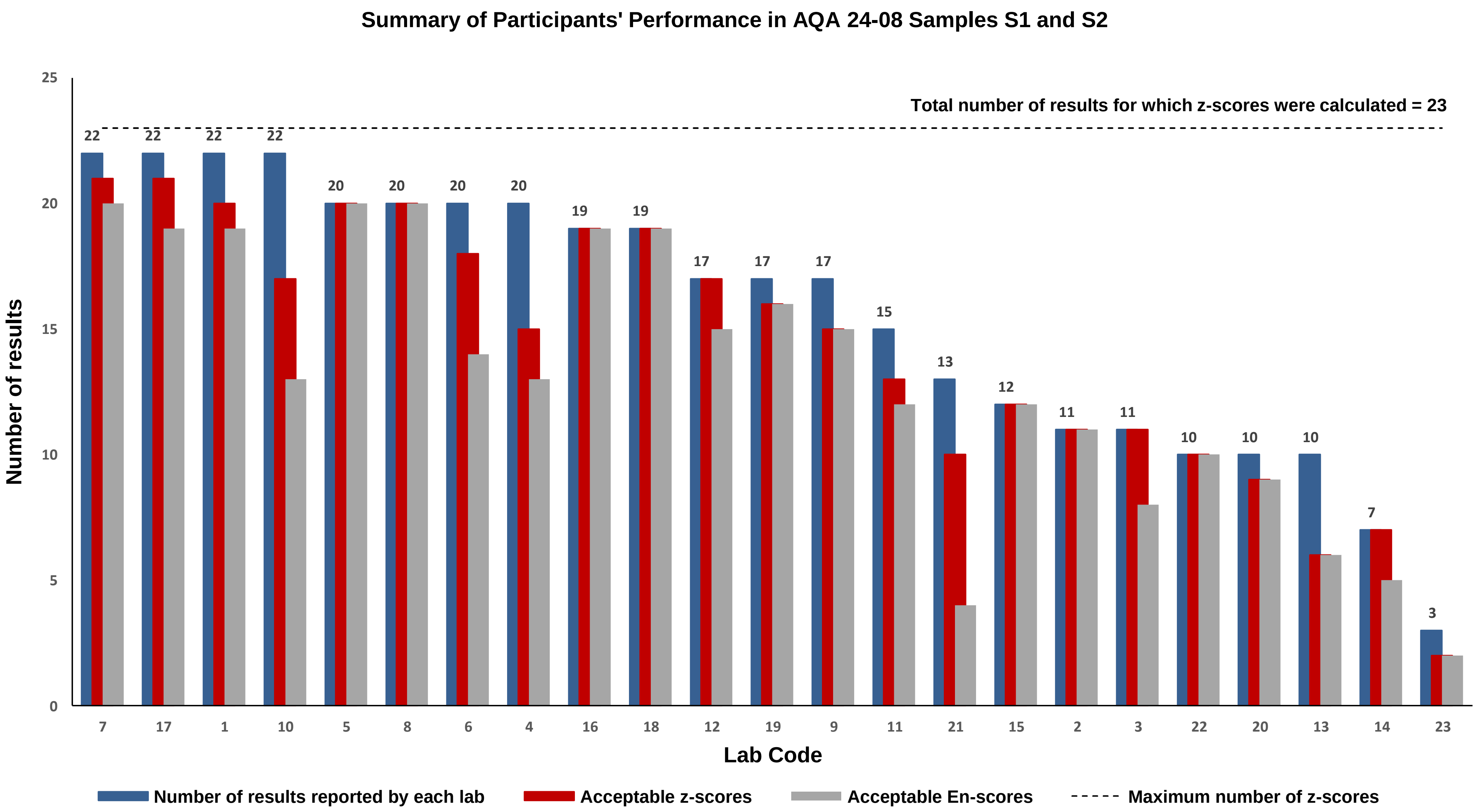


Figure 28 Summary of Participants Performance in AQA 24-08

Table 28 Summary of Participants' Results and Performance for S1

Lab Code	S1-Ammonia (as NH_3) (mg/L)	S1-Bromide (mg/L)	S1-Chloride (mg/L)	S1-DOC (mg/L)	S1-Fluoride (mg/L)	S1-Iodide (mg/L)	S1-Nitrate (as NO_3) (mg/L)	S1-Nitrite (as NO_2) (mg/L)	S1-Orthophosphate-P (mg/L)	S1-Sulphate (mg/L)	S1-TDN (mg/L)	S1-TDP (mg/L)
AV	0.371	0.126	28.9	4.46	1.08	0.355	2.02	0.513	0.195	10.8	1.13	0.199
HV	0.51	0.117	33.2	4.80	1.07	0.367	1.93	0.493	0.200	11.0	0.99	0.200
1	0.330	0.124	30.8	4.0	1.02	0.291	0.453	0.186	0.178	10.4	1.20	0.2
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	0.32	NT	25	NT	1.0	NT	1.99	0.49	0.18	11	NT	NT
4	0.2561	NT	26.96	6.29	1.037	<0.5	0.48	0.1571	0.178	11.37	1.14	0.171
5	0.394	NT	29	NT	1	NT	1.94	0.537	0.202	10.8	0.996	0.206
6	0.3	0.12	33	NT	1.2	0.32	0.46	0.17	0.21	11	NT	NT
7	0.425	0.159	28	4	1.2	0.360	2.16	0.49	0.190	11	1.07	0.206
8	0.35	NT	29	4	1.2	NT	2.08	0.49	0.18	10	1.2	0.19
9	0.369	<1	28.4	NT	1.04	<1	2.19	0.526	0.208	13.2	NT	< 0.5
10	0.373	0.13	33.3	3.56	1.24	NT	0.457	0.156	0.201	21.4	1.13	0.20
11	0.3	0.12	27.0	4.6	1.1	0.4	0.44	0.15	0.18	10.0	1.3	0.21
12	0.3579	NT	30.35	5.231	NT	NT	2.067286	0.4956	NT	11.03214	NT	0.186
13	0.25	NT	NT	NT	NT	NT	<0.5	<0.5	<0.25	4.8625	NT	NT
14	0.384	NR	NR	NR	NR	NR	2.04	0.532	0.202	NR	1.1	0.21
15	0.36	0.13	28.8	4.7	1.07	0.38	1.99	0.52	0.18	10.6	1.06	0.199
16	0.373	< 0.5	28.3	< 5	1.01	< 1	2.07	0.491	0.196	10.6	1.3	0.181
17	0.40	0.12	29	NR	1.06	0.38	1.9	0.51	0.20	11	1.0	0.20
18	0.402	NT	29.8	4.61	1.07	NT	2.30	0.521	0.196	11.3	NT	NT
19	0.33	NT	29	NT	1.3	NT	1.8	0.54	0.21	12	NT	NT
20	0.4	<0.2	29	NT	1	NT	1.9	NT	NT	11	NT	NT
21	0.32	NR	25	NR	1.0	NR	0.38	0.16	0.20	9	1.0	0.28
22	0.383	<0.20	30	4.4	1	NT	1.96	0.521	0.210	10.6	1.14	0.198
23	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR

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

Table 29 Summary of Participants' Results and Performance for S2

Lab Code	S2-B (mg/L)	S2-Ca (mg/L)	S2-K (mg/L)	S2-Mg (mg/L)	S2-Na (mg/L)	S2-P (mg/L)	S2-Alkalinity (mg/L)	S2-EC (µS/cm)	S2-pH	S2-Silica (mg/L)	S2-Total Hardness (mg/L)
AV	0.417	16.2	1.92	6.21	14.6	0.113	47.6	214	7.50	4.74	64.0
HV	0.398	16.7	2.05	6.24	15.0	0.124	41.0	220	7.17	4.30	60.0
1	0.4	17	2.0	6.0	15.0	<1	47	208	7.41	4.91	65
2	0.42	16.05	1.94	6.12	14.45	0.12	48.0	205	7.7	4.61	65.27
3	NT	NT	NT	NT	NT	NT	51.7	213	7.60	4.53	NT
4	0.437	16.329	2.278	6.379	13.545	<1	48.78	204.51	6.93	4.78	62.16
5	0.45	16.6	2.0	6.0	15.1	0.13	47	218	7.68	4.6	66.3
6	0.42	14	1.8	6	14	0.12	47	210	7.8	4.4	60
7	0.39	17	2	6	14	<1	47	207	7.08	4.73	60
8	0.44	17	2	6	16	<1	49	208	7.64	4.6	65
9	0.41	15.9	1.9	6	15.5	< 0.5	80	217	7.22	4.5	64.7
10	0.412	16.4	2.62	6.24	13.8	0.12	42	241	7.86	5.16	69
11	NR	NR	NR	NR	NR	NR	44.0	210	7.8	NR	NR
12	0.353	15.3	1.82	6	13.5	0.113	50	221	7.7	NT	62.8
13	0.42	16.7	3.155	6.69	14.84	<0.25	48.5	0.226	7.48	NT	NT
14	NR	NR	NR	NR	NR	NR	NR	NR	NR	4.77	NR
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	0.38	15.3	1.7	6.4	14.9	0.087	46.7	219	7.64	NT	64.6
17	0.44	16	1.8	5.9	14	0.086	53	220	7.2	4.2	51
18	0.433	17.9	1.90	6.94	14.7	0.129	48.6	219	7.71	4.94	73.2
19	0.388	15.3	1.70	6.74	15.5	NT	50	220	7.1	5.1	66
20	0.504	NT	NT	NT	NT	<1.5	40	212	7.5	NT	61
21	NR	NR	NR	NR	NR	NR	47	210	7.32	5.12	NR
22	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
23	NR	NR	NR	NR	NR	NR	46	257	7.5	NR	NR

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

6.5 Participants' Results and Analytical Methods

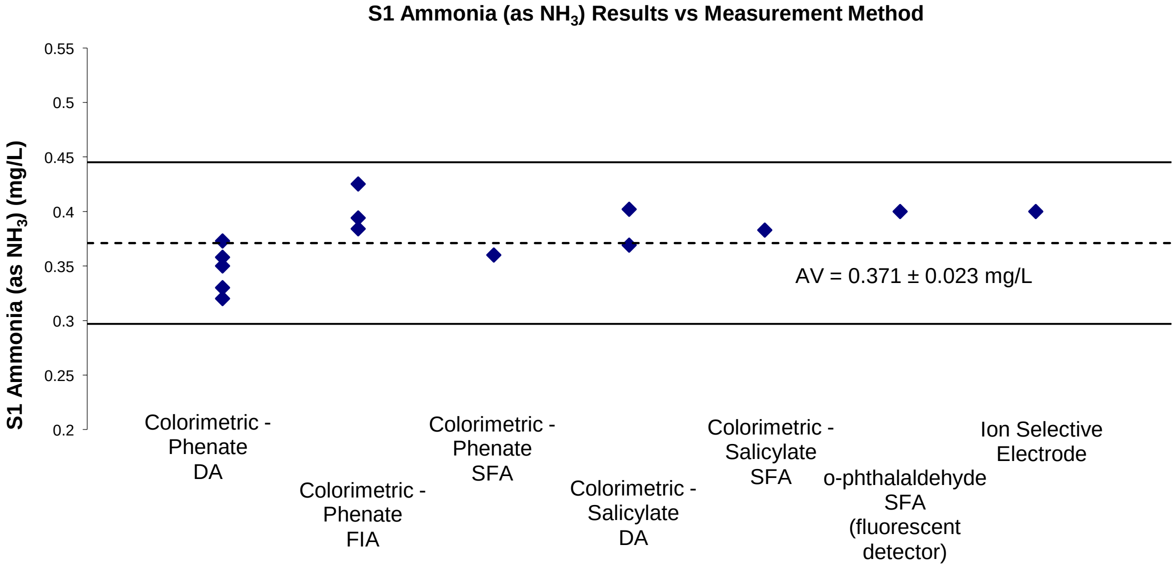
A summary of participants' results and performance is presented in Tables 28 and 29 and in Figures 25 to 28.

The measurement methods and instrumental techniques used are presented in Appendices 6 and 7.

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. The results reported by Laboratories 1, 4, 6, 10, 11, and 21 for NH_3, NO_3 and NO_2 in Sample S1, were lower than the spike value by a factor consistent with the ratios of nitrogen to ammonia, nitrogen to nitrate and nitrogen to nitrite respectively. These participants may have reported results as ammonia-nitrogen, nitrate-nitrogen, and nitrite-nitrogen instead. The results reported by them for these tests were not included in the analysis of methods employed by participants.

Individual Test Commentary

Ammonia (as NH_3) Most participants used the colorimetric-phenate method with FIA, SFA or DA determination, while others used a colourimetric-salicylate method with DA or SFA. One laboratory reported using ISE and one used the *o*-phthalaldehyde method with SFA and fluorescent detector. Each of these methods produced comparable/acceptable results (Figure 29).



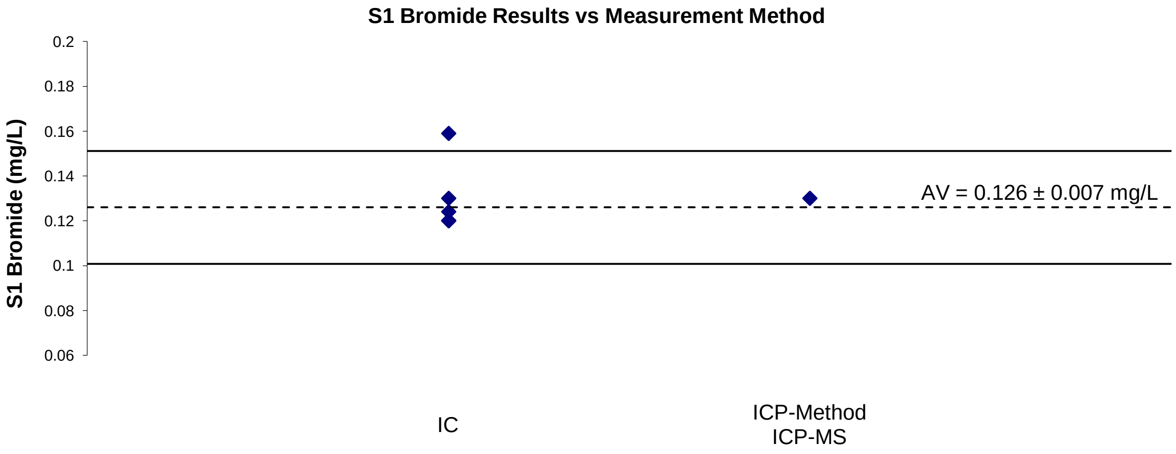
Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 29 S1-Ammonia Results vs. Measurement Method

Bromide level in S1 was below the level of reporting of many participants. Of 7 reported results 6 returned acceptable z-scores. All laboratories but one used IC for bromide measurements. One participant reported using the ICP Method (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.

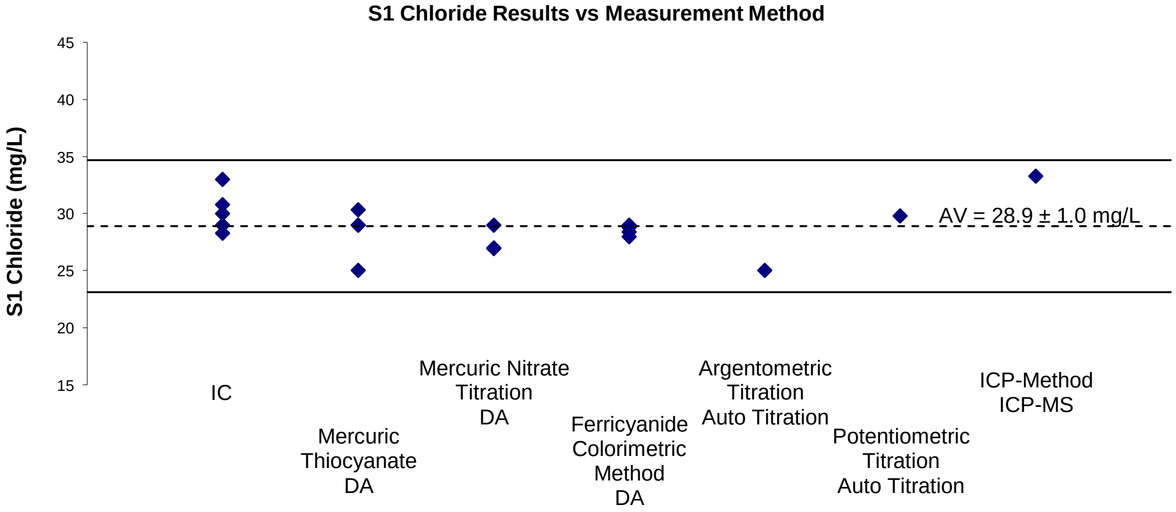
Chloride Participants used a wide variety of methods for chloride analysis in S1 and all produced compatible results (Figure 31).

Dissolved Organic Carbon as dNPOC level in S1 was 4.46 mg/L. All but one participant performed acceptably (Figure 32).



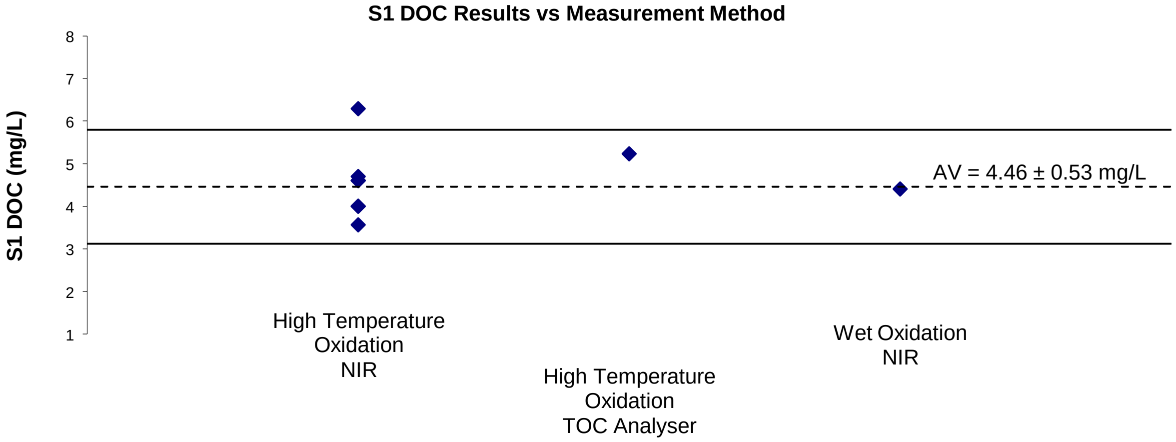
Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 30 S1-Bromide Results vs. Measurement Method



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

Figure 31 S1-Chloride Results vs. Measurement Method

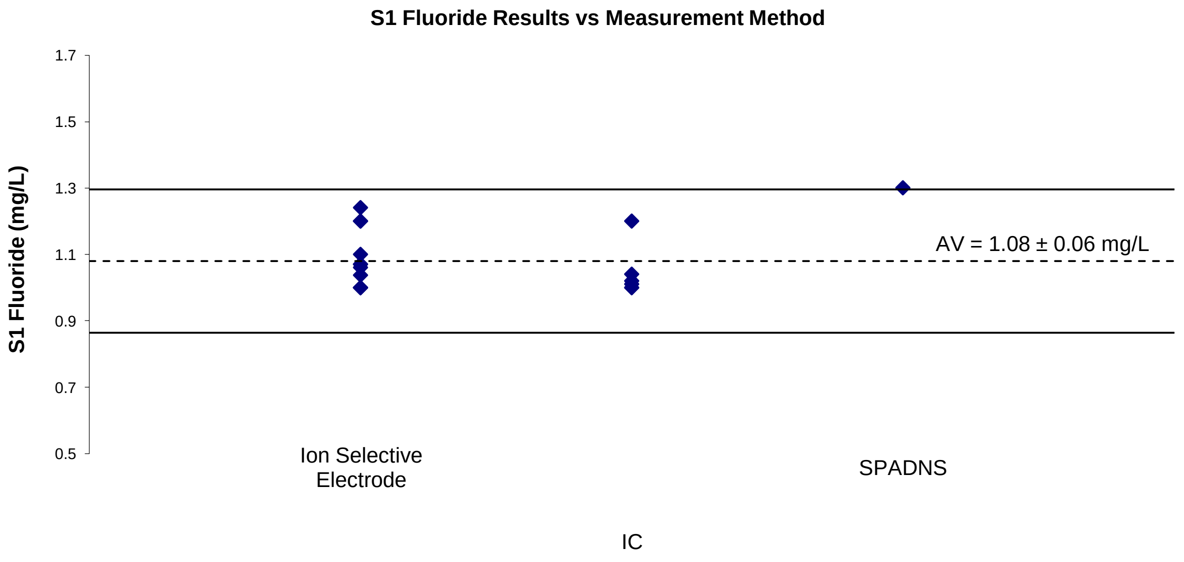


Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 32 S1-DOC (as dNPOC) Results vs. Measurement Method

Fluoride Most participants used either the ion selective electrode method or ion chromatographic method. One laboratory used the SPADNS colorimetric method with UV-Vis determination (Figure 33).

Fluoride by SPADNS suffers from interference from chlorides which may produce elevated results.



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

Figure 33 S1-Fluoride Results vs. Measurement Method

Iodide Six participants reported results for iodide in S1 and all performed acceptably. One laboratory used an ion selective electrode for its iodide measurements (Figure 34).

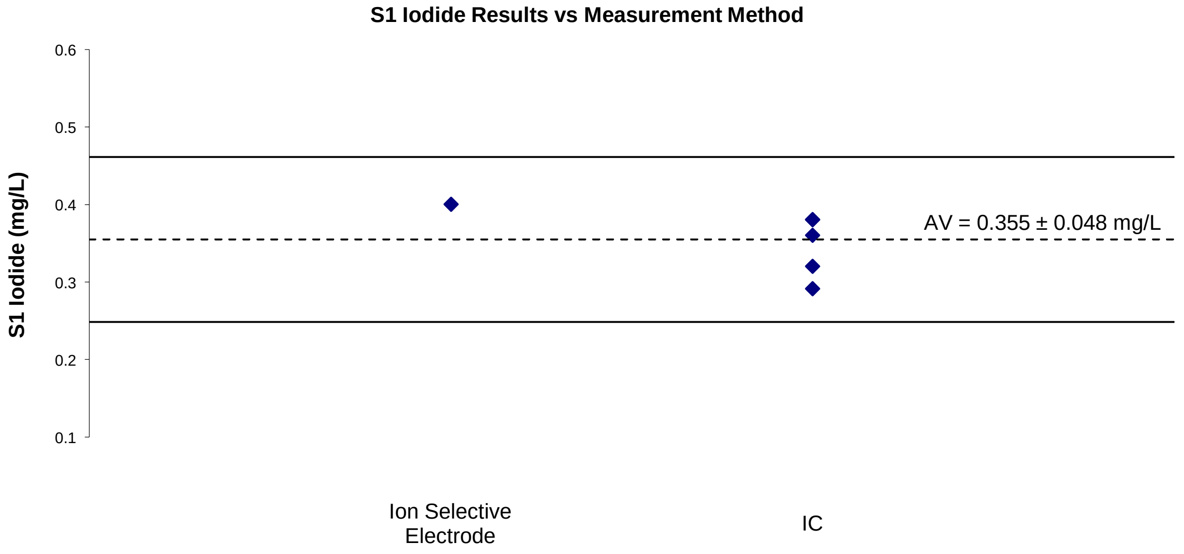
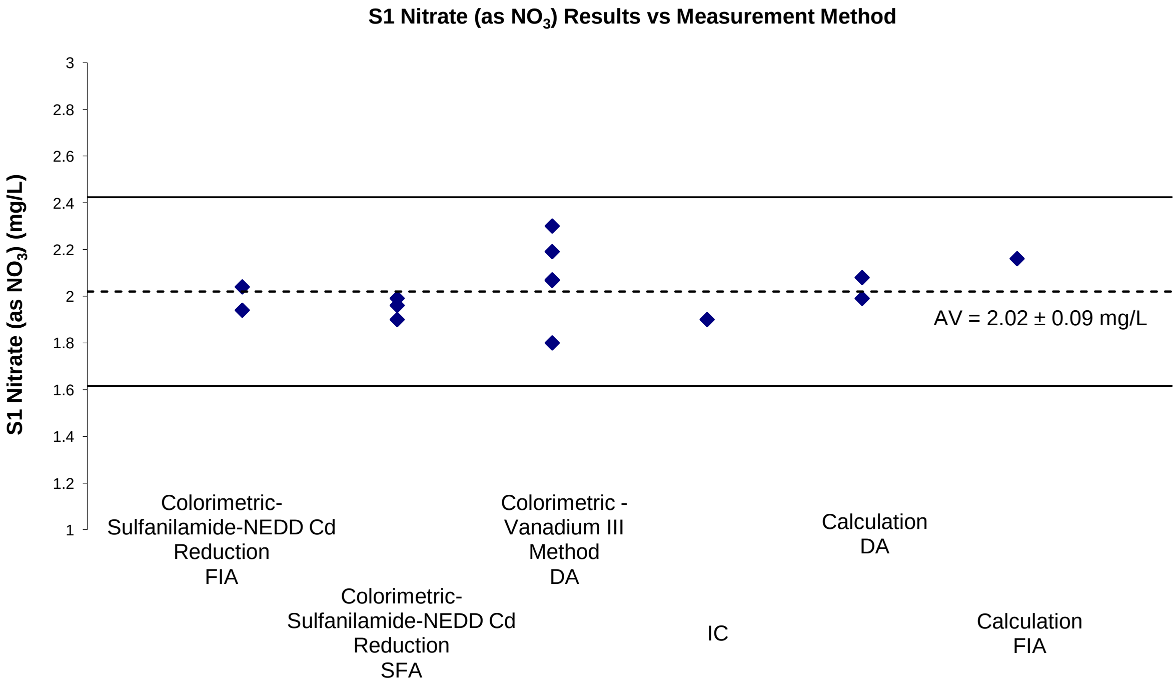


Figure 34 S1-Iodide Results vs. Measurement Method

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.

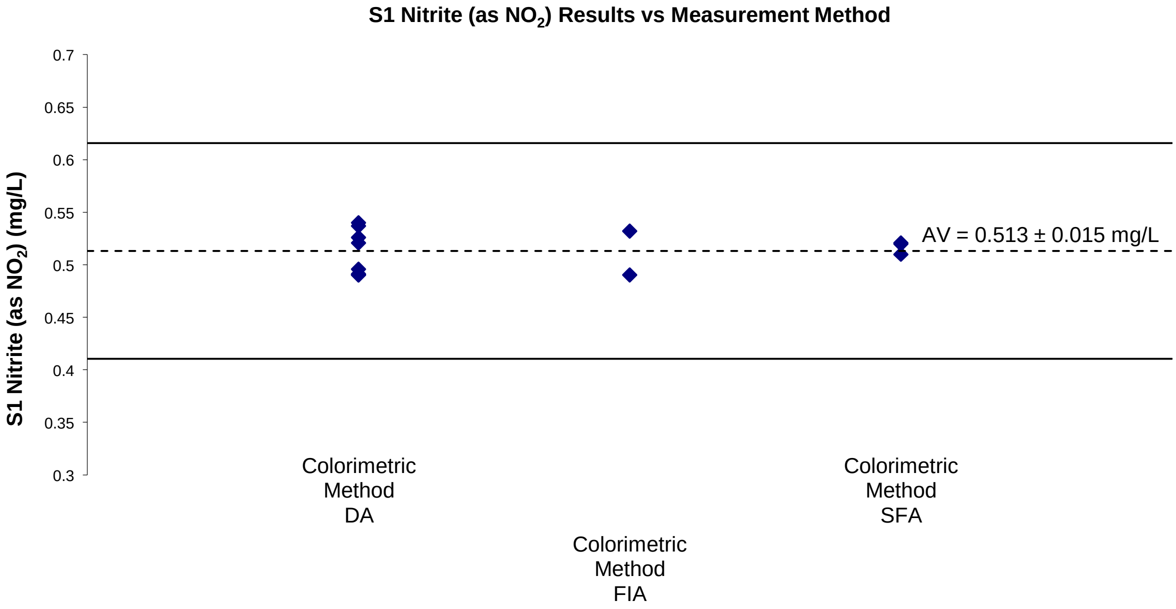
Laboratories 1, 4, 6, 10, 11 and 21 may have reported results as nitrate-nitrogen and nitrite-nitrogen. To allow these labs to compare their results to other participants, the assigned value for nitrate converted to nitrate-nitrogen is 0.456 mg/L, and for nitrite converted to nitrite-nitrogen it is 0.156 mg/L.

Figures 35 and 36 present plots of participants' results for NO_3 and NO_2 in S1 respectively versus instrumental techniques. Results reported by laboratories 1, 4, 6, 10, 11, and 21 were not included in order to assess any trends associated with the measurement methods used.



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

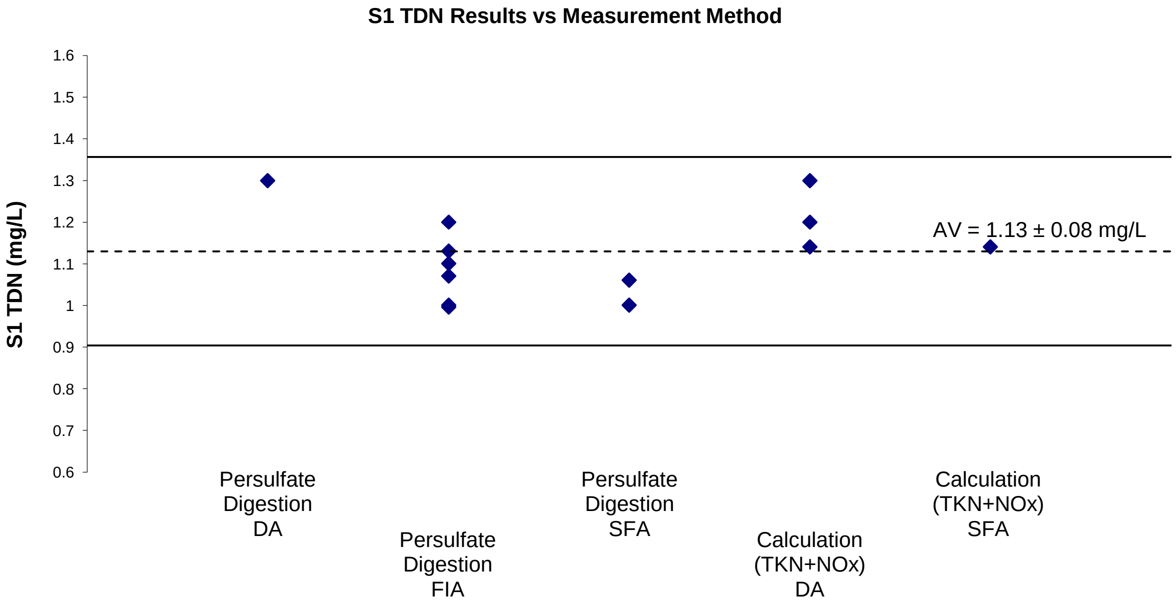
Figure 35 S1-Nitrate (as NO_3) Results vs. Measurement Method



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

Figure 36 S1-Nitrite (as NO_2) Results vs. Measurement Method

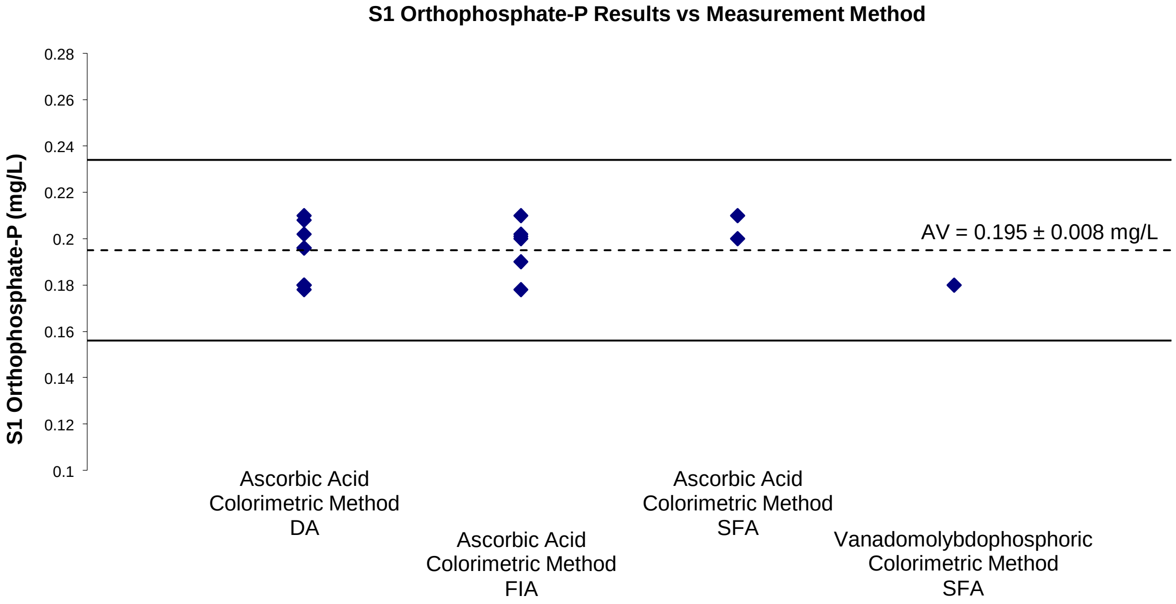
Total Dissolved Nitrogen All reported results for TDN agreed with each other and with the robust average of 1.13 ± 0.08 mg/L. Figure 37 presents plots of participants' results versus measurement method used for TDN determination in S1.



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

Figure 37 S1-TDN Results vs. Measurement Method

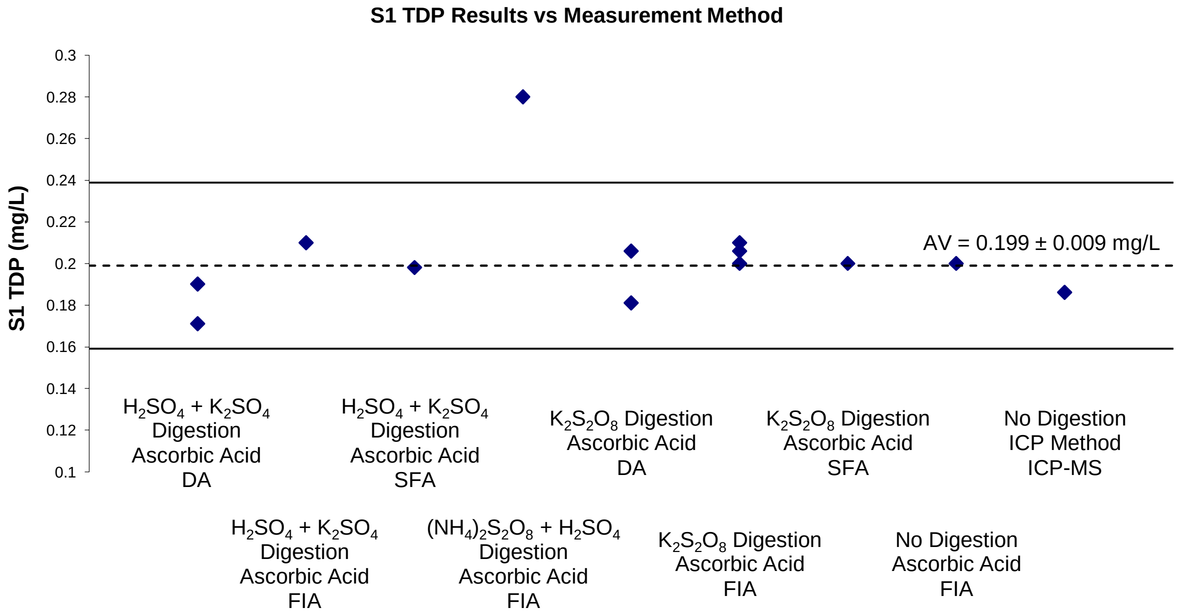
Orthophosphate-P One participant employed the vanadomolybdophosphoric acid method; all other participants used the ascorbic acid colorimetric method with FIA, SFA or DA determination (Figure 38).



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

Figure 38 S1-Orthophosphate-P Results vs. Method

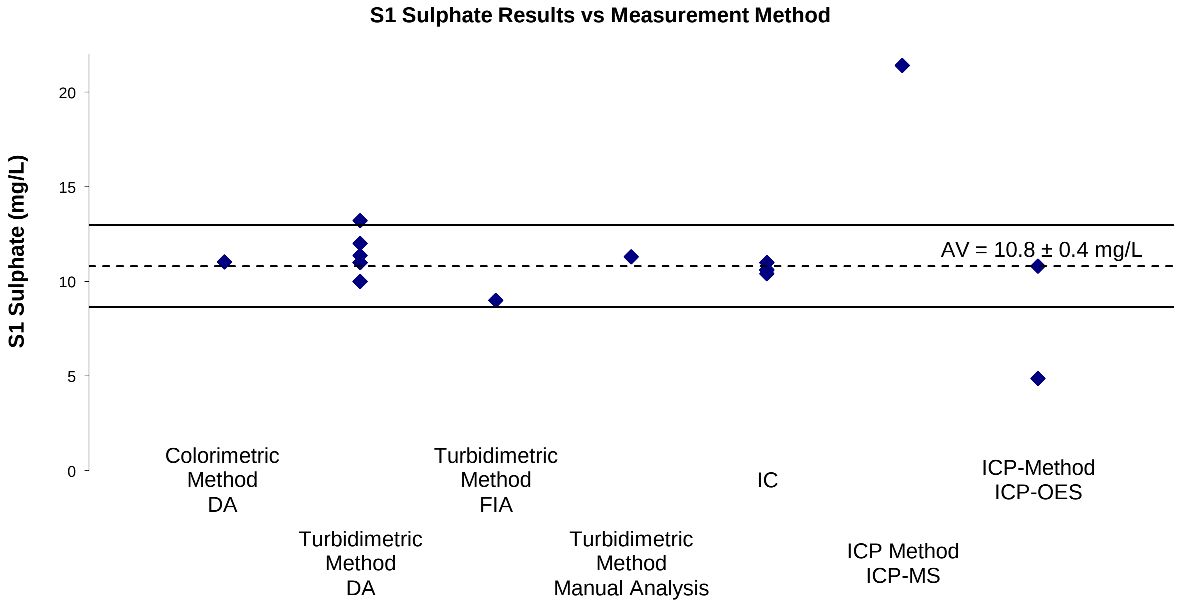
Total dissolved phosphorus Most laboratories used potassium persulphate for digestion and then measured the liberated orthophosphate colorimetrically by either DA, FIA or SFA. Two participants did not perform any digestion, instead reporting measurement of TDP in the sample from FIA or ICP determination. All reported results returned acceptable z-scores with the exception of one (Figure 39).



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

Figure 39 S1-TDP Results vs. Measurement Method

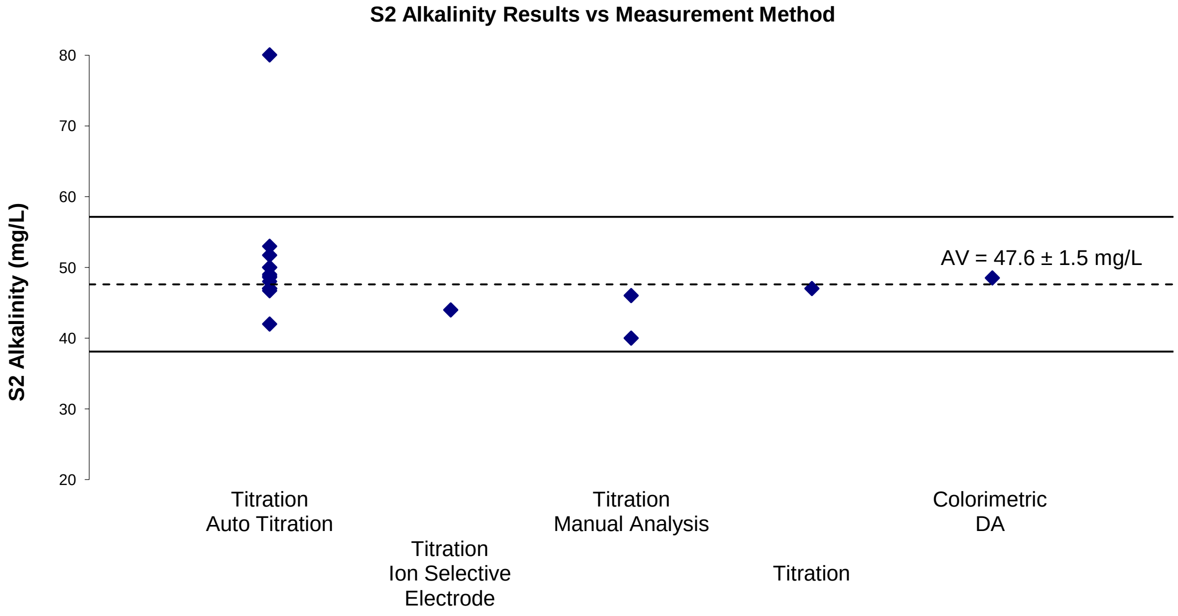
Sulphate Most participants used IC for sulphate measurements or a turbidimetric method. Two laboratories measured sulphate by ICP-OES as total sulphur, and one by ICP-MS (Figure 41). Caution should be exercised when the ICP method is used for sulphate measurement in water; false positive results can be produced because this technique measures total S and not just S from sulphate compounds.



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

Figure 40 S1-Sulphate Results vs. Measurement Method

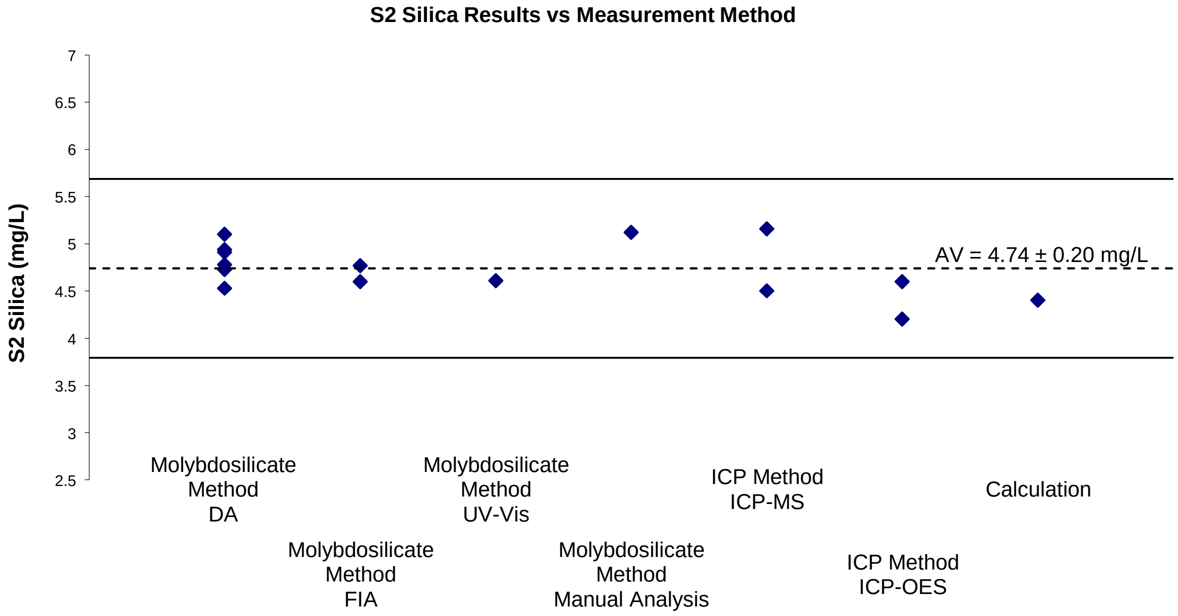
Alkalinity All reported results but one returned acceptable z-scores. Titration was the preferred method of most participants for alkalinity measurements in the potable water sample S2.



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

Figure 41 S2-Alkalinity Results vs. Measurement Method

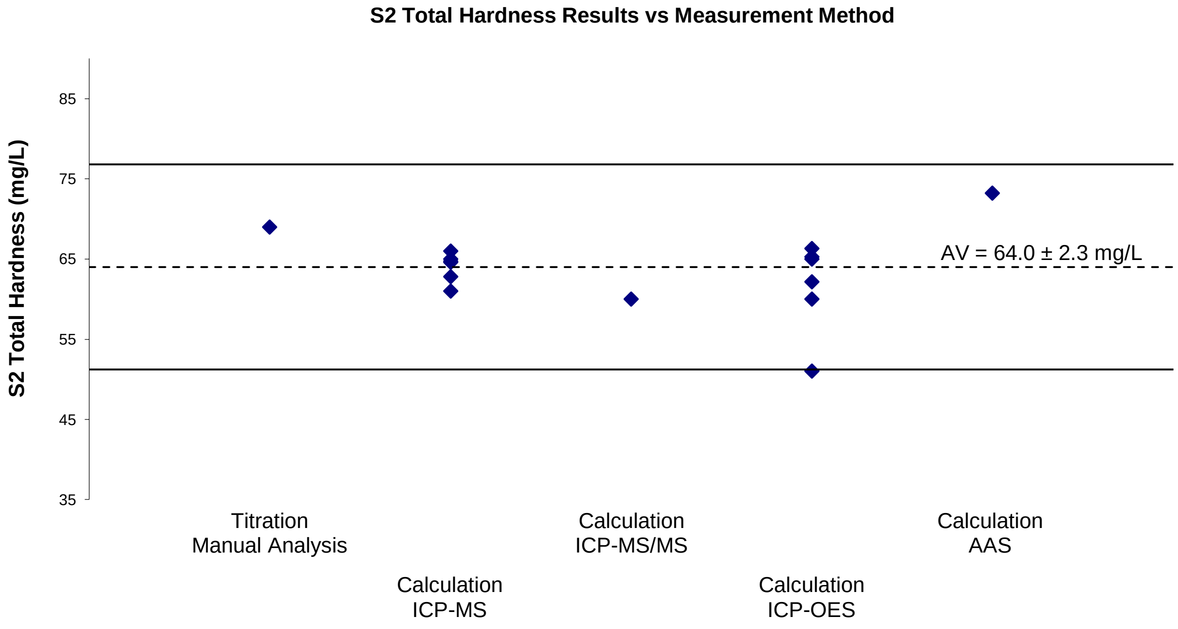
Silica (as SiO_2) Fifteen participants reported results for silica in S2 and all performed acceptably. Plots of participants' results versus measurement technique used are presented in Figure 42.



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

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

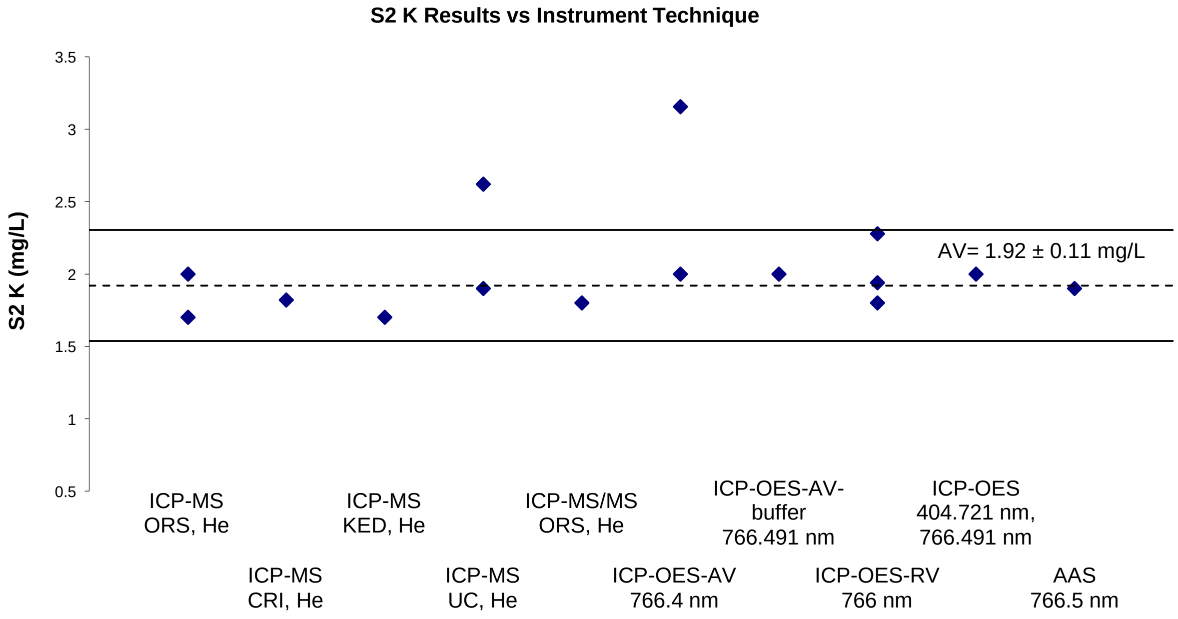
Total Hardness measurements in S2 did not challenge participants' analytical techniques; most used calculation from the ICP method, one used titration and one used calculation from AAS determination. All performed acceptably (Figure 43)**.**



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

Figure 43 S2-Total Hardness Results vs. Measurement Method

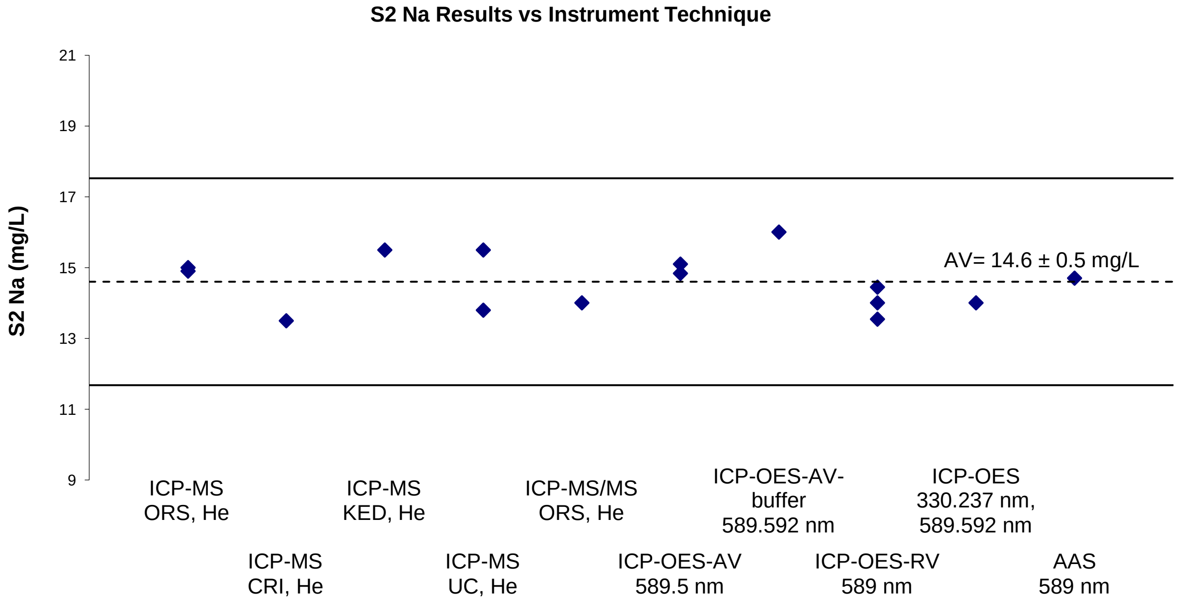
Potassium For K measurements most participants used ICP-MS in collision mode or ICP-OES with wavelength 766.491 nm (Figure 44).



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, all reported results returned acceptable z-scores. For Na measurements in S2, the majority of participants used ICP-OES with wavelength 589.592 nm (Figure 45).



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

Figure 45 S2-Na Results vs. Measurement Method

6.6 Comparison with Previous NMI Proficiency Tests of Nutrients in Water

AQA 24-08 is the 18th 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 acceptable 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 potential method or laboratory bias, even if all scores are acceptable.

6.7 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 30).

Table 30 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	RM
3	CRM
4	CRM
6	CRM
7	CRM
9	CRM
10	CRM – CWW-TM-B and CWW-TM-C (metals) Minerals 1 and 2 (Salts)

Lab. Code	Description of Control Samples
12	Spiked Sample
14	RM – AQA 23-19S1, AQA 22-11 S1, AQA 21-19 S2, AQA 22-18 S1
16	CRM – QCS-01-05 ICP Quality Control Standard #1; High Purity Standards CCV-1 Solution A; High Purity Standards CCV-1 Solution B; NMI AGAL-12 Biosoil; Australian Chemical Reagents Multi Element Standard; Australian Chemical Reagents Mixed Anion Standard; ERA Mercury WasteWatR; N (Ammonium Chloride) CRM; NO3 as N CRM, NO2 as N CRM; Certipur pH 7 CRM; Fluoride standard for IC; Chloride Standard for IC; Bromide standard for IC; Sulfate Standard for IC; Iodide Standard for IC; Alkalinity, CaCO3 500 mg/L; Conductivity Standard - 1412 µmhos/cm; Phosphate Standard for IC;TOC 1000mg/L CRM;Phosphate standard for IC 1000 mg/L
18	Spiked Sample
19	CRM
20	CRM – WQC-ALK (HPS CRM) FOR ALKALINITY, NSI STANDARD FOR AMMONIA, PH EC ACCUSPEC CRM
21	RM
22	CRM

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]

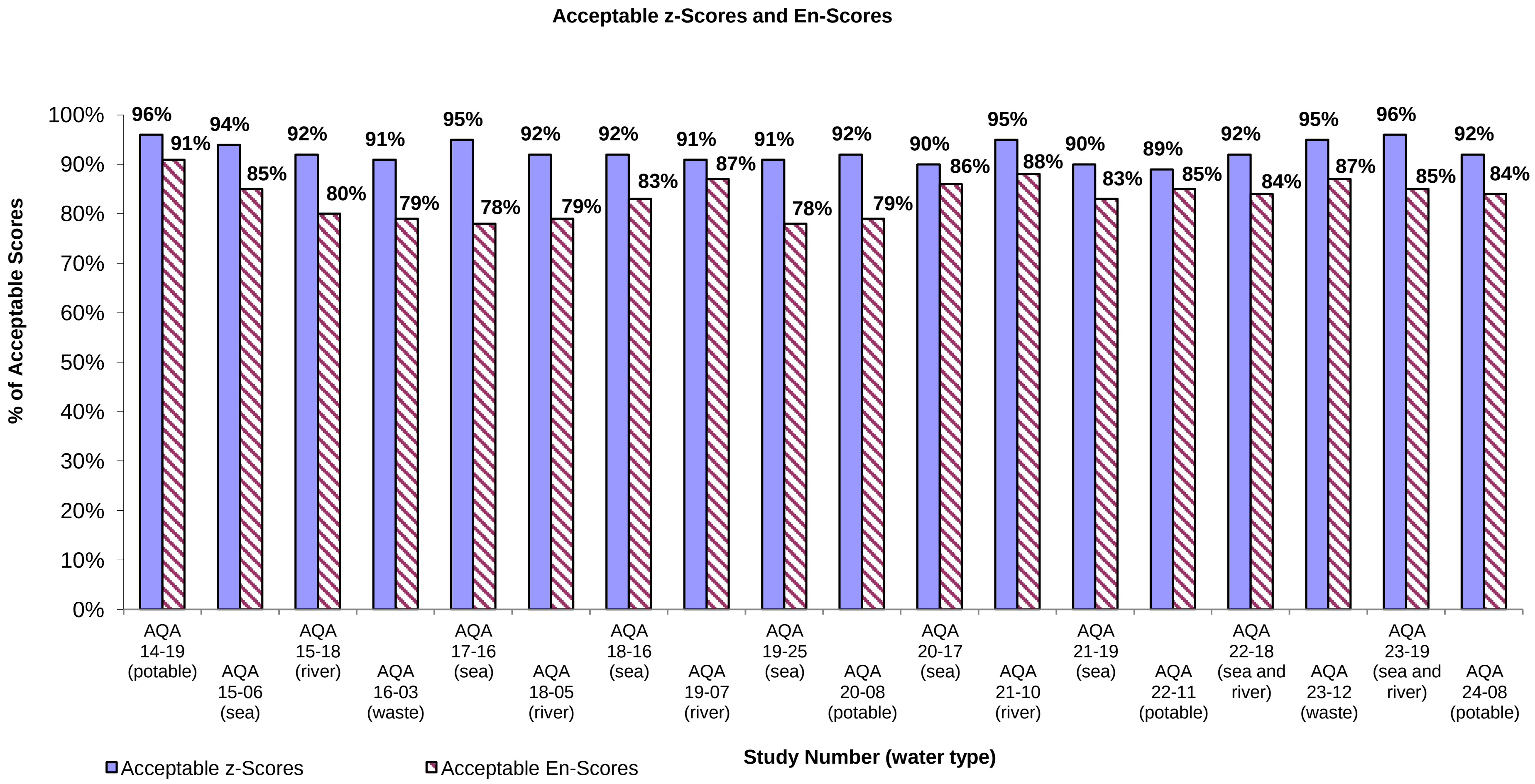


Figure 46 Participants' Performance in Nutrients and Anions in Water PT Studies over Time

7 REFERENCES

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

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[15] JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms* (VIM), 3rd edition.

[16] National Measurement Institute, Method Number NT2.47: Determination of Total Acid Extractable Metals and Dissolved Elements in Water using Inductively Coupled Plasma Mass Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry.

APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A 1.1 Sample Preparation

Sample S1 was prepared from approximately 20 L of autoclaved potable water. The water was fortified with seven analytes of interest, before mixing and dispensing into 200 mL portions.

Sample S2 was prepared from approximately 18 L of potable water which was fortified with two 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.[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-MS.[16] 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 were carried through the same set of procedures and analysed at the same time as the samples. A summary of the mass/charge ratio 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	Ion (m/z)
B	ICP-MS	Rh	NA	NA	2	11
Ca	ICP-MS	Rh	ORS	He	2	43
K	ICP-MS	Rh	ORS	He	2	39
Mg	ICP-MS	Rh	ORS	He	2	24
Na	ICP-MS	Rh	ORS	He	2	23
P	ICP-MS	Ir	ORS	HEHe	2	31

Methodology for Tests Other Than Total Elements in S1 and S2

Analyses for all the tests other than dissolved elements were conducted by NMI Inorganics section. 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 (as NH3)	Fluorometric Determination - OPA Method	SFA
Bromide	Ion Chromatographic Method	IC
Chloride	Mercuric Nitrate Titration	DA
Dissolved Organic Carbon	High Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	ISE
Iodide	Ion Chromatographic Method	IC

Nitrate (as NO3)	Colorimetric-Sulphanilamide-NEDD Cd Reduction	SFA
Nitrite (as NO2)	Colorimetric Method	SFA
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	SFA
Sulphate	Turbidimetric Method	DA
Total Dissolved Nitrogen	Persulfate digestion	SFA
Total Dissolved Phosphorus	K2S2O8 Digestion - Ascorbic Acid Colorimetric Method	SFA

Table 33 Methodology for S2

Test	Measurement Method	Instrument
Alkalinity	Titration	Auto Titration
Silica (as SiO2)	ICP-Method	ICP-OES
Total Hardness (as CaCO3)	Calculation	ICP-OES

APPENDIX 2 - STABILITY STUDY

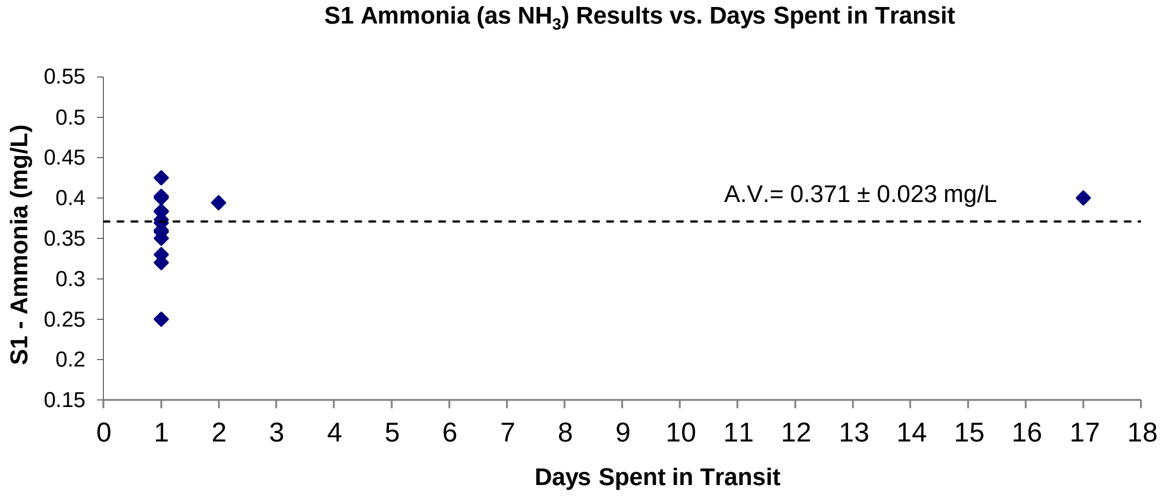
Samples S1 and S2 were dispatched on 6 May 2024. Participants were advised to store sample S1 frozen if analyses cannot be commenced on the day of receipt. The samples' condition on receipt, and the date when they were received and analysed by the participants, are presented in Table 34.

No significant trends between participants' results, samples' condition on receipt and date of analysis were evident (Figures 47 to 48).

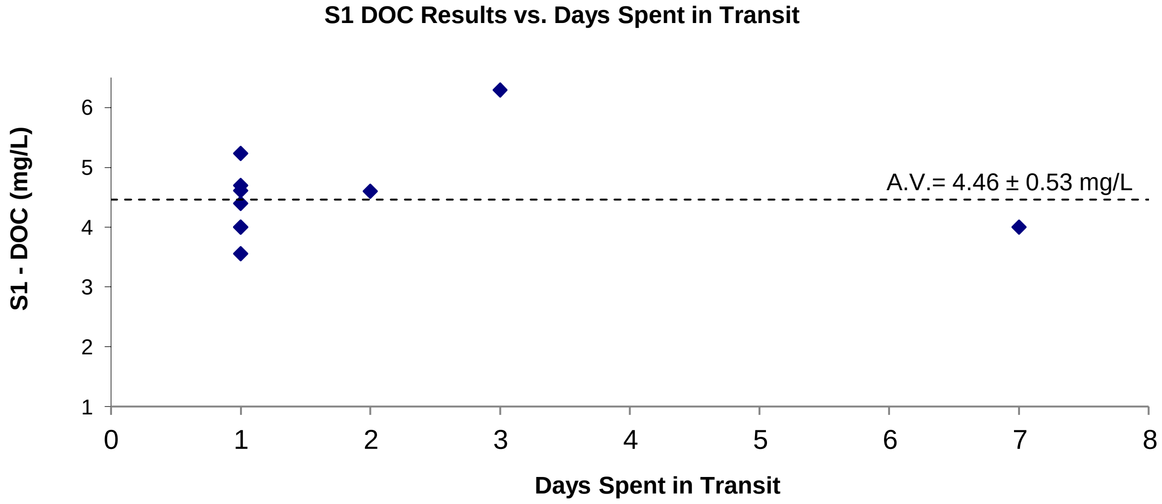
Table 34 Sample S1 and S2 Condition on Receipt and the Date When the Samples were Received and Analysed

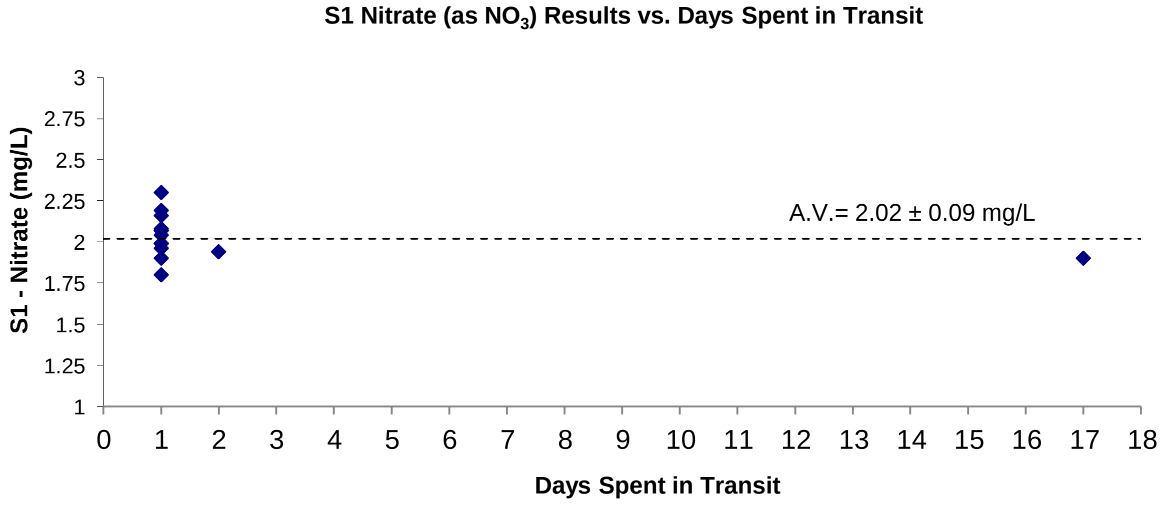
Lab Code	**Received Date**	**S1**		**S2**	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	13/05/2024	Frozen	16/05/2024	Cold	16/05/2024
2	07/05/2024	NT	NT		
3	07/05/2024	Frozen	14/05/2024	Cold	14/05/2024
4	09/05/2024	Frozen	14/05/2024	Cold	16/05/2024
5	08/05/2024	Cold	27/05/2024	Cold	27/05/2024
6	07/05/2024	Frozen	14/05/2024	Cold	15/05/2024
7	07/05/2024	Frozen	15/05/2024	Cold	15/05/2024
8	07/05/2024	Frozen	17/05/2024	Cold	17/05/2024
9	07/05/2024	Cold	19/05/2024	Cold	19/05/2024
10	07/05/2024	Cold	09/05/2024	Cold	09/05/2024
11	08/05/2024	Frozen	20/05/2024	Cold	09/05/2024
12	07/05/2024	Frozen	09/05/2024	Cold	09/05/2024
13	07/05/2024	Frozen	17/05/2024	Cold	17/05/2024
14	07/05/2024	Frozen	17/05/2024	Cold	10/05/2024
15	07/05/2024	Frozen		NT	NT
16	07/05/2024	Frozen	14/05/2024	Cold	14/05/2024
17	07/05/2024	Frozen		Cold	08/05/2024
18	07/05/2024	Frozen	10/05/2024	Cold	10/05/2024
19	07/05/2024	Cold	10/05/2024	Cold	10/05/2024
20	23/05/2024	Frozen	24/05/2024	Cold	24/05/2024
21	07/05/2024	Frozen	07/05/2024	Frozen	07/05/2024
22	07/05/2024	Frozen		NT	NT
23	07/05/2024	NT	NT	Cold	22/05/2024

NT = Not Tested



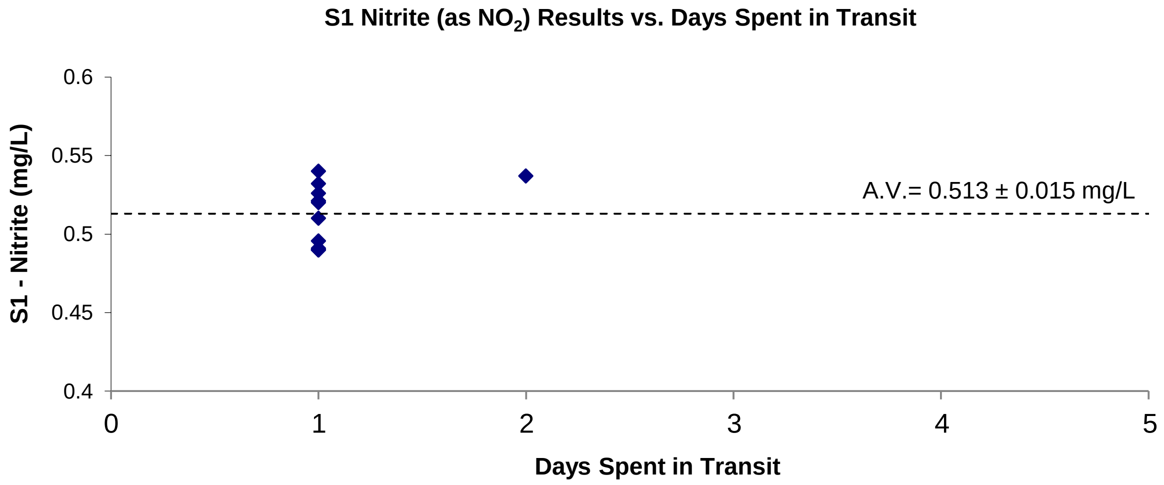
*The results reported by Labs 1, 4, 6, 10, 11 and 21 were extreme outliers and are not included in this graph.





*The results reported by Labs 1, 4, 6, 10, 11 and 21 were extreme outliers and are not included in this graph.

Figure 47 Results vs Days Spent in Transit



*The results reported by Labs 1, 4, 6, 10, 11 and 21 were extreme outliers and are not included in this graph.

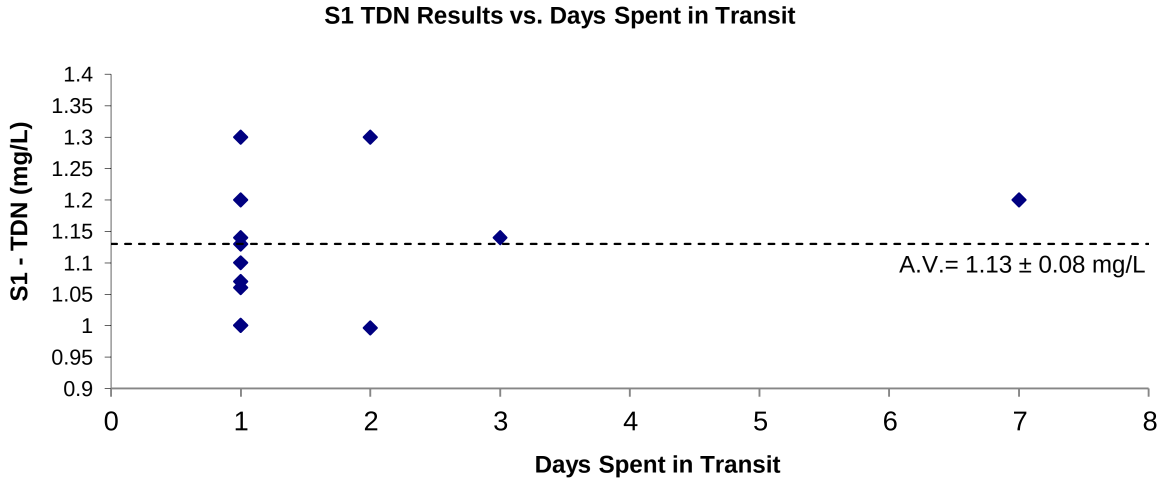
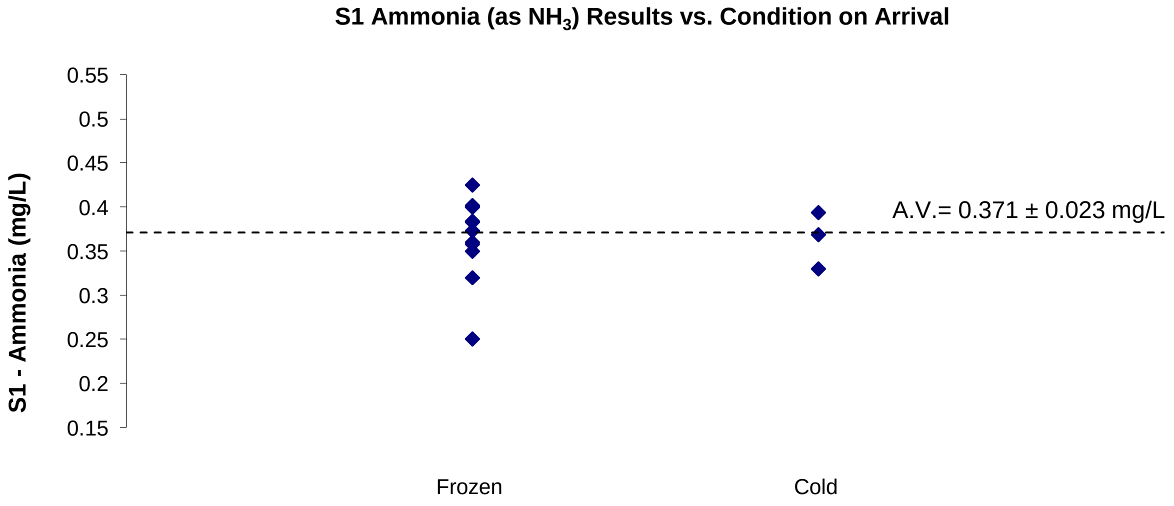
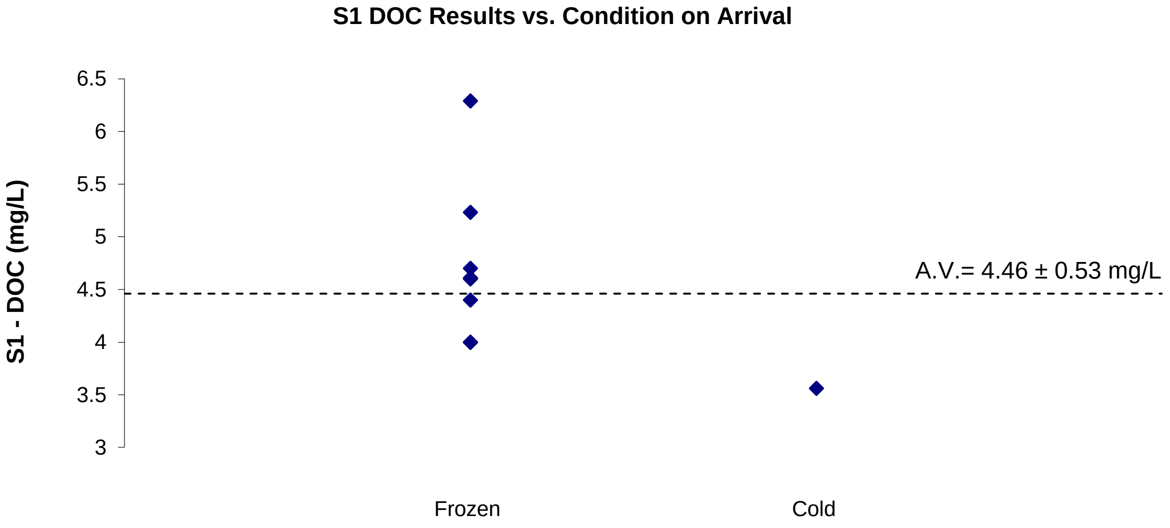


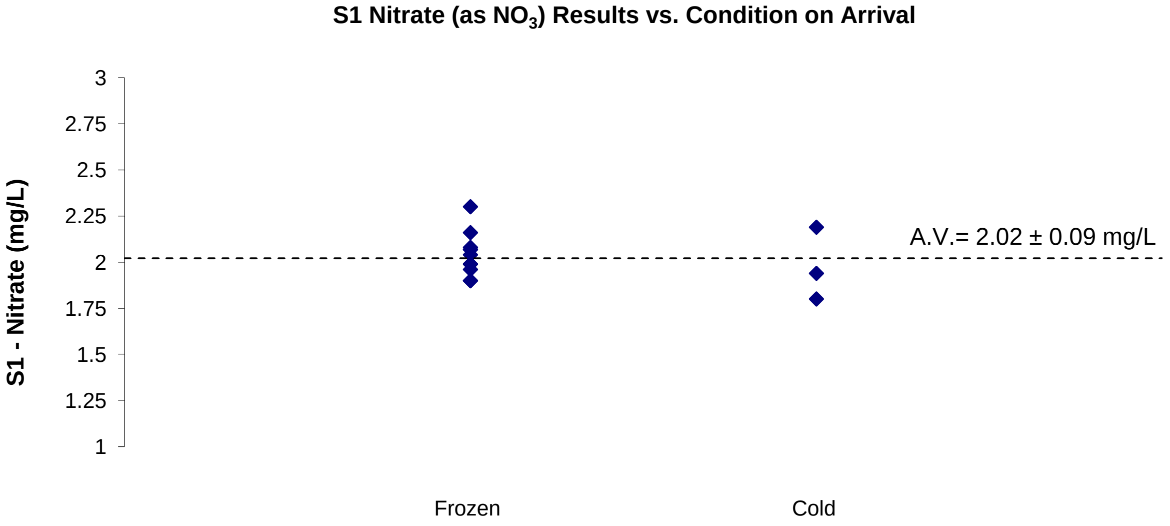
Figure 47 Results vs Days Spent in Transit (continued)



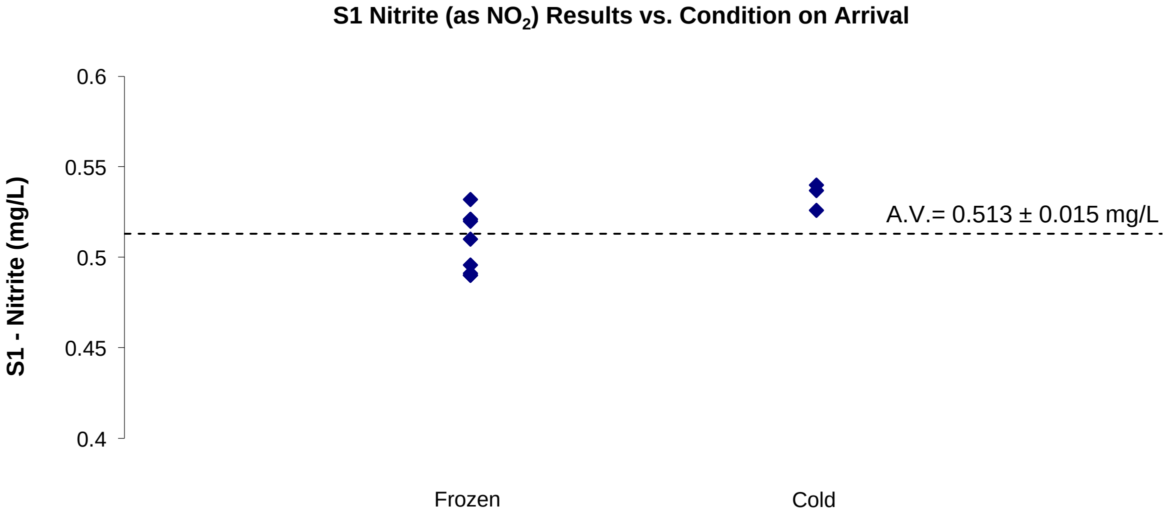
*The results reported by Labs 1, 4, 6, 10, 11 and 21 were extreme outliers and are not included in this graph.

Figure 48 Results vs Condition on Arrival





*The results reported by Labs 1, 4, 6, 10, 11 and 21 were extreme outliers and are not included in this graph.



*The results reported by Labs 1, 4, 6, 10, 11 and 21 were extreme outliers and are not included in this graph.

Figure 48 Results vs Condition on Arrival (continued)

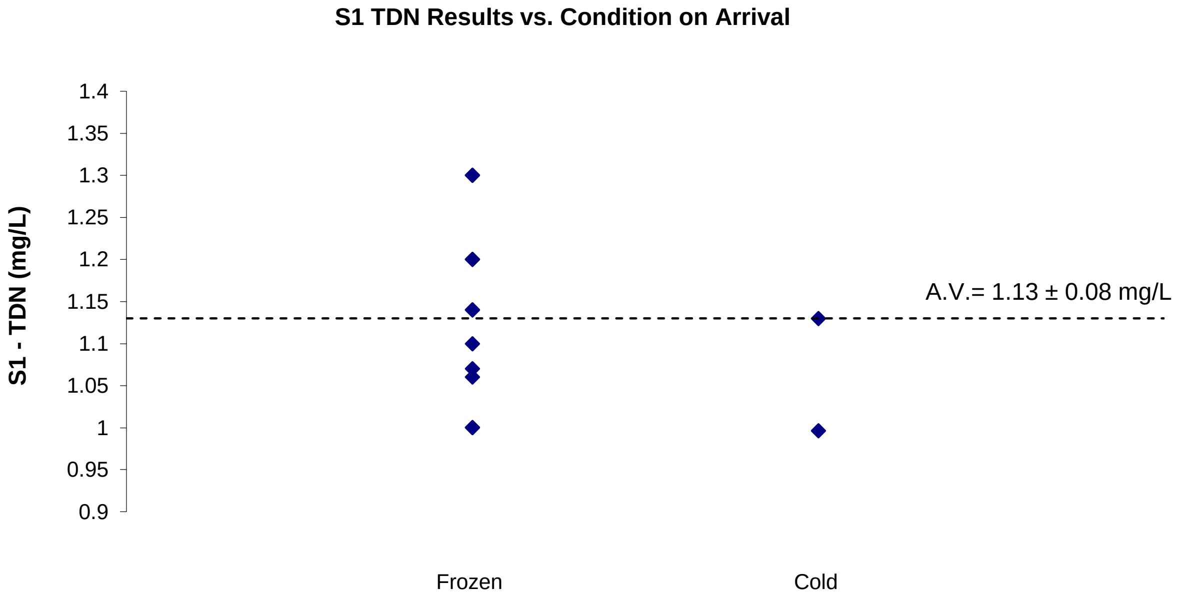


Figure 48 Results vs Condition on Arrival (continued)

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 stable 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 a sample kept at -20°C (reference sample) were compared to the results from a sample left out on a laboratory table for three days (room sample). 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, equivalent to the homogeneity value) 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 and sample matrix spikes.

Results were in good agreement with each other and the assigned value within their respective uncertainties (Figure 49).

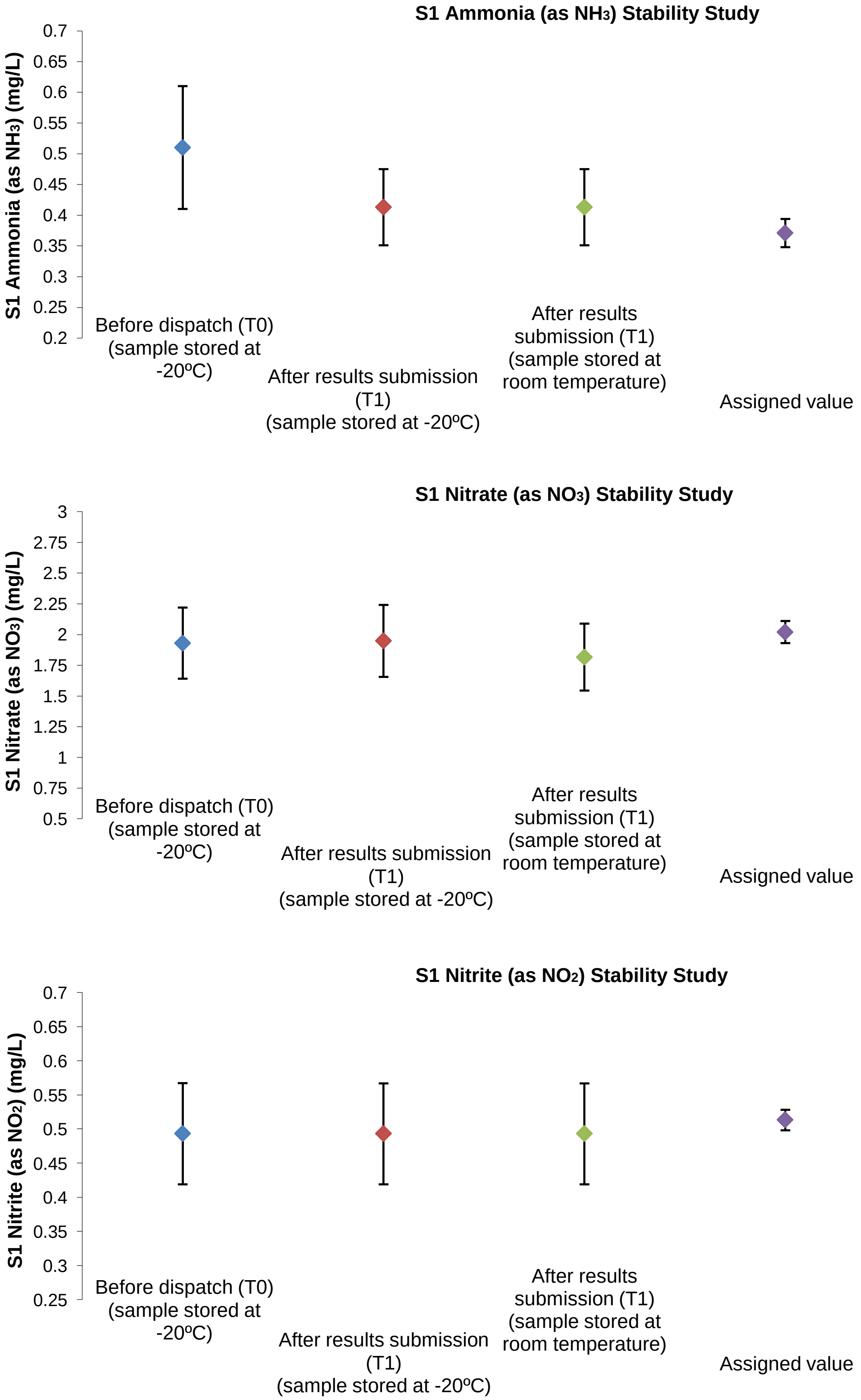


Figure 49 Stability Study Results

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 'ISO 13258' [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	28.9 mg/L
$S_{rob\ av}$	1.81 mg/L
$u_{rob\ av}$	0.50 mg/L
k	2
$U_{rob\ av}$	1.0 mg/L

The assigned value for Chloride in Sample S1 is **28.9 ± 1.0 mg/L.**

z-Score and E_n-score

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

A worked example is set out below in Table 36.

Table 36 z-Score and E_n-score for Chloride Result Reported by Laboratory 5 in S1

Chloride Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
29 ± 4.5	28.9 ± 1.0	10% as CV or 0.10 x 28.9 = 2.89 mg/L	$z = \frac{(29 - 28.9)}{2.89}$ $z = 0.03$	$En = \frac{(29 - 28.9)}{\sqrt{4.5^2 + 1.0^2}}$ $E_n = 0.02$

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION OR VERIFICATION

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 2024, NMI carried out 17 proficiency studies for nutrients, anions and physical tests in water. These studies involved measurements of these analytes in potable, river, waste and sea water.

Laboratory X participated in and submitted acceptable results for all of these studies that included chloride as an analyte. This data can be separated into two ranges of results: 0.5 mg/L to 1000 mg/L, and greater than 1000 mg/L (Tables 37 and 38).

Table 37 Laboratory X Reported Results for Chloride at 0.5 to 1000 mg/L Level

Study No.	Sample	Laboratory result mg/L	Assigned value mg/L	Number of Results	Robust CV of all results (%)
AQA 14-19	Potable	51.9 ± 10	55.4 ± 1.4	8	2.9
AQA 15-18	River	65.7 ± 10	70.3 ± 3.6	10	6.5
AQA 18-05	River	68 ± 8.0	71.3 ± 1.5	17	3.4
AQA 19-07	River	57.0 ± 12	53.7 ± 2.0	10	4.7
AQA 20-08	Potable	33.4 ± 7.0	41.6 ± 1.9	13	6.7
AQA 21-10	River	81 ± 10	86.3 ± 2.7	20	5.7
AQA 22-11	Potable	22.3 ± 5.0	25.5 ± 0.8	19	5.5
AQA 22-18	River	60 ± 10	62.3 ± 1.5	19	4.1
AQA 23-12	Waste	152 ± 20	142 ± 6	16	6.3
AQA 23-19	River	39.8 ± 4.5	39.8 ± 2.6	11	8.7
AQA 24-08	Potable	33.3 ± 5.0	28.9 ± 1.0	19	6.3
Average					5.5*
$\boldsymbol{pooled\ s\%} = \sqrt{\frac{\mathbf{(8-1)\times 2.9^2+(10-1)\times 6.5^2+\cdots\ldots\ldots\ldots\ldots.+(19-1)\times 6.3^2)}}{\mathbf{143-10}}}$					5.7

* The pooled standard deviation was used.

Table 38 Laboratory X Reported Results for Chloride at >1000 mg/L Level

Study No.	Sample	Laboratory result mg/L	Assigned value mg/L	Number of Results	Robust CV of all results (%)
AQA 16-03	Waste	3099 ± 320	2990 ± 170	8	6.3
AQA 17-16	Sea	13100 ± 1300	12800 ± 420	10	4.1
AQA 18-16	Sea	16600 ± 1600	17300 ± 1600	13	13
AQA 19-25	Sea	20000 ± 2000	20500 ± 1000	13	2.2
AQA 20-17	Sea	9800 ± 980	10700 ± 400	10	4.9
AQA 21-19	Sea	19440 ± 1950	20100 ± 600	9	3.8
AQA 22-18	Sea	14073 ± 1400	13800 ± 500	14	5.3
AQA 23-19	Sea	17132 ± 1750	16800 ± 500	12	4.2
Average					5.5*
$\boldsymbol{pooled\ s\%} = \sqrt{\frac{\mathbf{(8-1)\times 6.3^2+(10-1)\times 4.1^2+\cdots\ldots\ldots\ldots\ldots.+(12-1)\times 4.2^2)}}{\mathbf{89-8}}}$					6.5

* The pooled standard deviation was used.

Taking the pooled standard deviation of these PT samples gives an estimate of relative standard uncertainty of 5.7% for chloride concentrations at 0.5 to 1000 mg/L, and 6.5% at concentrations greater than 1000 mg/L. Using a coverage factor of two gives relative expanded uncertainties of 12% and 13% respectively, at a level of confidence of approximately 95%.

Table 39 sets out the subsequent estimated expanded uncertainty for results measuring chloride in potable, fresh, waste or seawater at levels of 20.0 – 20000 mg/L.

Table 39 Uncertainty of Chloride Results Estimated Using PT Data

Results mg/L	Uncertainty mg/L
20.0	2.4
500	60
1000	120
7500	980
20000	2600

These estimates of 12% and 13% passes the test of being reasonable, and the analysis of the four different matrices over eleven years can safely be assumed to include all the relevant uncertainty components (different operators, reagents, calibrants etc), and so complies with ISO 17025 requirements.[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
DRC	Dynamic Reaction Cell
FIA	Flow Injection Analyser
GUM	Guide to the Expression of Uncertainty in Measurement
HV	Homogeneity Value
IC	Ion Chromatograph
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-MS/MS	Inductively Coupled Plasma - Tandem Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
ICP-OES-AV	Inductively Coupled Plasma - Optical Emission Spectrometry- axial view
ICP-OES-AV-buffer	Inductively Coupled Plasma - Optical Emission Spectrometry- axial view with buffer
ICP-OES-RV	Inductively Coupled Plasma - Optical Emission Spectrometry- radial view
Max	Maximum Value in a Set of Results
Md	Median
Min	Minimum Value in a Set of Results
MU	Measurement Uncertainty
NEDD	N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride)
NIR	Near-infrared
NMI	National Measurement Institute (of Australia)
NOx	Nitrous Oxides
NR	Not Reported
NT	Not Tested
OPA	Orthophtaldialdehyde
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PT	Proficiency Test
RA	Robust Average
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
SV	Spiked or Formulated Concentration of a PT Sample
SFA	Segment Flow Analyser
SI	The International System of Units
SS	Spiked Samples
s_a/σ	Analytical Standard Deviation Divided by the Target Standard Deviation
Target SD	Target Standard Deviation

σ	Target Standard Deviation
TKN	Total Kjeldahl Nitrogen
UC	Universal Cell
UV-Vis	Ultraviolet and Visible Spectroscopy

APPENDIX 6 - METHODOLOGY FOR S1

Table 40 Measurement Methods and Instrument Techniques for Ammonia

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Salicylate Method	FIA	APHA
3	Colorimetric - Phenate Method	DA	APHA 4500-NH3 G
4	Colorimetric - Salicylate Method	DA	In house
5	Colorimetric - Phenate Method	FIA	4500-NH3 H
6		FIA	
7	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
8	Colorimetric - Phenate Method	DA	APHA 4500-NH3 G
9	Colorimetric - Salicylate Method	DA	In-House Method
10	Colorimetric - Phenate Method	FIA	APHA4500NH3-H
11	Colorimetric - Salicylate Method	DA	In-House Method
12	Colorimetric - Phenate Method	DA	In-House Method
13	Colormetric	DA	In-House Method
14	Colorimetric - Phenate Method	FIA	APHA
15		SFA	
16	Colorimetric - Phenate Method	DA	In-House Method
17	Fluorometric Determination - OPA Method	SFA	
18	Colorimetric - Salicylate Method	DA	In house method based on APHA 4500-NH3 B
19	Colorimetric - Phenate Method	DA	APHA
20	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500
21	Colorimetric - Salicylate Method	FIA	APHA 4500-NH3 H (In-House Method)
22	Colorimetric - Salicylate Method	SFA	in house

Table 41 Measurement Methods and Instrument Techniques for Bromide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA
6	Ion Chromatographic Method	IC	
7	Ion Chromatographic Method	IC	APHA 4110
9	Ion Chromatographic Method	IC	In-House Method
10	ICP-Method	ICP-MS	In-House Method
11	Ion Chromatographic Method	IC	In-House Method
15		IC	
16	Ion Chromatographic Method	IC	In-House Method
17	Ion Chromatographic Method	IC	APHA
20	Ion Chromatographic Method	IC	APHA 411 B
22	Ion Chromatographic Method	IC	in house

Table 42 Measurement Methods and Instrument Techniques for Chloride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA
3	Mercuric Thiocyanate	DA	APHA 4500-Cl E
4	Mercurric Nitrate Titration	DA	In house
5	Mercuric Thiocyanate	DA	4500-CL G
6	Ion Chromatographic Method	IC	
7	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl E
8	Mercuric Thiocyanate	DA	APHA 4500 Cl G
9	Ferricyanide Colorimetric Method	DA	In-House Method
10	ICP-Method	ICP-MS	In-House Method
11	Mercurric Nitrate Titration	DA	In-House Method
12	Mercuric Thiocyanate	DA	In-House Method
15		DA	
16	Ion Chromatographic Method	IC	In-House Method
17	Mercurric Nitrate Titration	DA	APHA
18	Potentiometric-Titration	Auto Titration	In House method based on APHA 4500-Cl D
19	Ferricyanide Colorimetric Method	DA	APHA
20	Ion Chromatographic Method	IC	APHA 411 B
21	Argentometric Titration	Auto Titration	APHA, 4500-Cl- B (In-House Method)
22	Ion Chromatographic Method	IC	in house

Table 43 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Other	Other	APHA
4	High-Temperature Oxidation	NIR-detector	In house
7	High-Temperature Oxidation	NIR-detector	APHA 5310 C
8	High-Temperature Oxidation	NIR-detector	APHA 5310 B
10	High-Temperature Oxidation	NIR-detector	APHA5310-B
11	High-Temperature Oxidation	NIR-detector	In-House Method
12	High-Temperature Oxidation	Total Organic Carbon analyser	In-House Method
15		NIR-detector	
16	High-Temperature Oxidation	TOC-L	In-House Method
17	High-Temperature Oxidation		
18	High-Temperature Oxidation	NIR-detector	In house method based on APHA 5310-TOC B
22	Wet-Oxidation	NIR-detector	in house

Table 44 Measurement Methods and Instrument Techniques for Fluoride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA
3	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F C
4	Ion Selective Electrode Method	Auto Titration	In house
5	Ion Selective Electrode Method	Ion Selective Electrode	4500-F C
6	Ion Chromatographic Method	IC	
7	Ion Selective Electrode Method	Ion Selective Electrode	4500-F C
8	Ion Selective Electrode Method	Auto Titration	APHA 4500-F C
9	Ion Chromatographic Method	IC	In-House Method
10	Ion Selective Electrode Method	Ion Selective Electrode	
11	Ion Selective Electrode Method	Ion Selective Electrode	In-House Method
15		Ion Selective Electrode	
16	Ion Chromatographic Method	IC	In-House Method
17	Ion Selective Electrode Method	Ion Selective Electrode	
18	Ion Selective Electrode Method	Ion Selective Electrode	In house method based on APHA 4500-F C
19	SPADNS Colorimetric Method	DA	APHA
20	Ion Selective Electrode Method	IC	APHA 411 B
21	Ion Selective Electrode Method	Ion Selective Electrode	APHA, 4500-F- A,C (In-House Method)
22	Ion Chromatographic Method	IC	in house

Table 45 Measurement Methods and Instrument Techniques for Iodide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Selective Electrode Method	IC	APHA
4	Ion Selective Electrode Method	Auto Titration	In house
6	Ion Chromatographic Method	IC	
7	Ion Chromatographic Method	IC	APHA 4110
9	Ion Chromatographic Method	IC	In-House Method
11	Ion Selective Electrode Method	Ion Selective Electrode	In-House Method
15		IC	
16	Ion Chromatographic Method	IC	In-House Method
17	Ion Chromatographic Method	IC	

Table 46 Measurement Methods and Instrument Techniques for Nitrate

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
3	Calculation	DA	NEMI 9171
4	Colorimetric - salicylate method	DA	In house
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500-NO3 I
6	Calculation		
7	Calculation	FIA	APHA 4500-NO3
8	Calculation	DA	APHA 4500-NO3-F
9	Colorimetric -vanadium III method	DA	In-House Method
10	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO3-F
11	Calculation	calculation	In-House Method
12	Colorimetric -vanadium III method	DA	In-House Method
13	Colorimetric -vanadium III method	DA	In-House Method
14	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
15		SFA	
16	Colorimetric -vanadium III method	DA	In-House Method
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	
18	Colorimetric -vanadium III method	DA	In house method based on APHA 4500-NO3 H
19	Colorimetric -vanadium III method	DA	APHA
20	Ion Chromatographic Method	IC	APHA 411 B
21	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA, 4500-NO3 – (In-House Method)
22	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	in house

Table 47 Measurement Methods and Instrument Techniques for Nitrite

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric Method	FIA	APHA
3	Colorimetric Method	DA	APHA 4500-NO2 B
4	Colorimetric Method	DA	In house
5	Colorimetric Method	DA	4500-NO3 I
6		FIA	
7	Colorimetric Method	FIA	APHA 4500-NO2
8	Colorimetric Method	DA	APHA 4500-NO2-B
9	Colorimetric Method	DA	In-House Method
10	Colorimetric Method	FIA	APHA4500NO2-F
11	Colorimetric Method	DA	In-House Method
12	Colorimetric Method	DA	In-House Method
13	Colorimetric Method	DA	In-House Method
14	Colorimetric Method	FIA	APHA
15		SFA	
16	Colorimetric Method	DA	In-House Method
17	Colorimetric Method	SFA	
18	Colorimetric Method	DA	In house method based on APHA 4500-NO2 B
19	Colorimetric Method	DA	APHA
21	Colorimetric Method	FIA	APHA, 4500-NO2 - (In-House Method)
22	Colorimetric Method	SFA	in house

Table 48 Measurement Methods and Instrument Techniques for Orthophosphate-P

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	FIA	APHA
3	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P F
4	Ascorbic Acid Colorimetric Method	DA	In house
5	Ascorbic Acid Colorimetric Method	DA	4500-P G
6		FIA	
7	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P E
8	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P F
9	Ascorbic Acid Colorimetric Method	DA	In-House Method
10	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-G
11	Ascorbic Acid Colorimetric Method	DA	In-House Method
13	Ascorbic Acid Colorimetric Method	DA	In-House Method
14	Ascorbic Acid Colorimetric Method	FIA	APHA
15		SFA	
16	Ascorbic Acid Colorimetric Method	DA	In-House Method
17	Ascorbic Acid Colorimetric Method	SFA	
18	Ascorbic Acid Colorimetric Method	DA	In house method based on APHA 4500-P B & F
19	Ascorbic Acid Colorimetric Method	DA	APHA
21	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P A,B,E (In-House Method)
22	Ascorbic Acid Colorimetric Method	SFA	in house

Table 49 Measurement Methods and Instrument Techniques for Sulphate

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA
3	Turbidimetric Method	DA	APHA 4500-SO4 E
4	Turbidimetric Method	DA	In house
5	ICP Method	ICP-OES	3120 B
6	Ion Chromatographic Method	IC	
7	Turbidimetric Method	DA	APHA 4500-SO4 E
8	Turbidimetric Method	DA	APHA 4500-SO4
9	Turbidimetric Method	DA	In-House Method
10	ICP Method	ICP-MS	In-House Method
11	Turbidimetric Method	DA	In-House Method
12	Colorimetric Method	DA	In-House Method
13	ICP Method	ICP-OES	In-House Method
15		IC	
16	Ion Chromatographic Method	IC	In-House Method
17	Turbidimetric Method	DA	
18	Turbidimetric Method	Manual Analysis	In house method based on USEPA method 9038 rev 0
19	Turbidimetric Method	DA	APHA
20	Ion Chromatographic Method	IC	APHA 411 B
21	Turbidimetric Method	FIA	APHA, 4500-SO4 2- (In-House Method)
22	Ion Chromatographic Method	IC	in house

Table 50 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	APHA
4	Calculation (TKN+NOx)	DA	In house
5	Persulfate digestion	FIA	4500-P J
7	Persulfate digestion	FIA	APHA 4500-N C
8	Calculation (TKN+NOx)	DA	APHA 4500-Norg/4500-NO3-
10	Persulfate digestion	FIA	APHA4500P-J
11	Calculation (TKN+NOx)	Calculation	In-House Method
14	Persulfate digestion	FIA	APHA
15		SFA	
16	Persulfate digestion	DA	APHA 4500-N
17	Persulfate digestion	SFA	
22	Calculation (TKN+NOx)	SFA	in house

Table 51 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Laboratory Code	Measurement Method		Instrument	Method Reference
1		Ascorbic Acid Colorimetric Method	FIA	APHA
4	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	4500-P J
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P J
8	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P H
9	No Digestion	ICP Method	ICP-MS	In-House Method
10	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
11	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-House Method
12	No Digestion	ICP Method	ICP-MS	In-House Method
13	HNO3-Digestion	ICP Method	ICP-OES	In-House Method
14	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
15			SFA	
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	In-House Method
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	
21	(NH4)2S2O8+H2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P H (In-House Method)
22	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	SFA	in house

APPENDIX 7 - METHODOLOGY FOR S2

Table 52 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)
1	ICP-MS	SC,Rh,Ir		He	10	NA
2	ICP OES	Lu			1	208
4	ICP-MS					
5	ICP-OES-AV					208.8
6	ICP-MS/MS					
7	ICP-OES	Eu & Cs	NA	He	1	249.773nm
8	ICP-OES-AV-buffer	CsCl	NA	NA	1	249.772nm
9	ICP-MS	45 Sc	DRC	NA	1	11
10	ICP-MS	Sc	NA	NA	1	10
12	ICP-MS	Sc	CRI	NA	1	11
13	ICP-OES-AV	Y			1:10	249.677
16	ICP-MS	Sc	ORS	He	1	11
17	ICP-OES-RV	Y	NA	NA		249.678
18	ICP-OES-AV	NA	NA	NA	1	249.772
19	ICP-MS	Sc		He	1	11
20	ICP-MS	Sc	NA	Standard Mode	10	

Table 53 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)
1	ICP-MS	SC,Rh,Ir		He	10	NA
2	ICP OES	Lu			1	315
4	ICP-OES-RV	Eu	NA	NA	NA	315.887
5	ICP-OES-AV					315.8
6	ICP-MS/MS					
7	ICP-OES	Eu & Cs	NA	He	1	315.887, 370.602nm
8	ICP-OES-AV-buffer	CsCl	NA	NA	1	315.887nm
9	ICP-MS	72 Ge	DRC	He	1	40
10	ICP-MS	Sc	UC	He	1	44
12	ICP-MS	Sc	CRI	He	1	40
13	ICP-OES-AV	Y			1:10	315.887
16	ICP-MS	Sc	ORS	H2	1	40
17	ICP-OES-RV	Y	NA	NA		422.673
18	AAS	NA	NA	NA	10	422.7
19	ICP-MS	Sc		H2	1	40

Table 54 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)
1	ICP-MS	SC,Rh,Ir		He	10	NA
2	ICP OES	Lu			1	766
4	ICP-OES-RV	Eu	NA	NA	NA	766.491
5	ICP-OES-AV					766.4
6	ICP-MS/MS					
7	ICP-OES	Eu & Cs	NA	He	1	404.721nm, 766.491nm
8	ICP-OES-AV-buffer	CsCl	NA	NA	1	766.491nm
9	ICP-MS	72 Ge	DRC	He	1	39
10	ICP-MS	Sc	UC	He	1	39
12	ICP-MS	Sc	CRI	He	1	39
13	ICP-OES-AV	Y			1:10	766.49
16	ICP-MS	Sc	ORS	He	1	39
17	ICP-OES-RV	Y	NA	NA		766.491
18	AAS	NA	NA	NA	1	766.5
19	ICP-MS	Sc		He	1	39

Table 55 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)
1	ICP-MS	SC,Rh,Ir		He	10	NA
2	ICP OES	Lu			1	280
4	ICP-OES-RV	Eu	NA	NA	NA	383.829
5	ICP-OES-AV					279.8
6	ICP-MS/MS					
7	ICP-OES	Eu & Cs	NA	He	1	383.830 (nm)
8	ICP-OES-AV-buffer	CsCl	NA	NA	1	383.829nm
9	ICP-MS	72 Ge	DRC	He	1	24
10	ICP-MS	Sc	UC	He	1	25
12	ICP-MS	Sc	CRI	He	1	24
13	ICP-OES-AV	Y			1:10	279.077
16	ICP-MS	Sc	ORS	He	1	24
17	ICP-OES-RV	Y	NA	NA		279.078
18	AAS	NA	NA	NA	10	285.2
19	ICP-MS	Sc		He	1	24

Table 56 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)
1	ICP-MS	SC,Rh,Ir		He	10	NA
2	ICP OES	Lu			1	589
4	ICP-OES-RV	Eu	NA	NA	NA	589.592
5	ICP-OES-AV					589.5
6	ICP-MS/MS					
7	ICP-OES	Eu & Cs	NA	He	1	330.237, 589.592nm
8	ICP-OES-AV-buffer	CsCl	NA	NA	1	589.592nm
9	ICP-MS	72 Ge	DRC	He	1	23
10	ICP-MS	Sc	UC	He	1	23
12	ICP-MS	Sc	CRI	He	1	23
13	ICP-OES-AV	Y			1:10	589.582
16	ICP-MS	Sc	ORS	He	1	23
17	ICP-OES-RV	Y	NA	NA		589.592
18	AAS	NA	NA	NA	10	589
19	ICP-MS	Sc		He	1	23

Table 57 Instrument Techniques for Phosphorous

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	SC,Rh,Ir		He	10	NA
2	ICP OES	Lu			1	178
4	ICP-OES-RV	Eu	NA	NA	NA	
5	ICP-OES-AV					177.4
6	FIA					
7	ICP-OES	Eu & Cs	NA	He	1	185.827 (nm)
8	ICP-OES-AV-buffer	CsCl	NA	NA	1	185.827nm
9	ICP-MS	72 Ge	DRC	He	1	31
10	ICP-MS	Sc	UC	He	1	31
12	ICP-MS	Sc	CRI	He	1	31
13	ICP-OES-AV	Y			1:10	178.221
17	ICP-OES-RV	Y	NA	NA		213.618
18	DA	NA	NA	NA	1	880
20	Other		NA	Other	15	

Table 58 Measurement Methods and Instrument Techniques for Alkalinity

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	APHA
2	Titration	Auto Titration	APHA-Y2017
3	Titration	Auto Titration	APHA 2320-Alkalinity B
4	Titration	Auto Titration	APHA 2320
5	Titration	Auto Titration	2320 B
7	Titration	Auto Titration	APHA 2320
8	Titration	Auto Titration	APHA 2320 B
9	Titration	Auto Titration	In-House Method
10	Titration	Auto Titration	APHA2320B
11	Titration	Ion Selective Electrode	In-House Method
13	Colormetric	DA	In-House Method
16	Titration	Auto Titration	In-House Method
17	Titration		
18	Titration	Auto Titration	In house method based on APHA 2320 B
19	Titration	Auto Titration	APHA
20	Titration	Manual Analysis	APHA 2320-Alkalinity
21	Titration	Auto Titration	APHA, 2320-Alkalinity – B (In-House Method)
23	Titration	Manual Analysis	APHA 2320

Table 59 Measurement Methods and Instrument Techniques for Silica

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Molybdosilicate Method	DA	APHA
2	Molybdosilicate Method	UV-Vis Spectrophotometer	4500-SiO2 C&D
3	Molybdosilicate Method	DA	APHA 4500-SiO2 D
4	Molybdosilicate Method	DA	APHA 4500 SIO2-D
5	Molybdosilicate Method	FIA	2120 B
6	Calculation		
7	Molybdosilicate Method	DA	APHA 4500-SiO2
8	ICP-Method	ICP-OES	APHA 4500-SiO2
9	ICP-Method	ICP-MS	In-House Method
10	ICP-Method	ICP-MS	In House
14	Molybdosilicate Method	FIA	APHA
17	ICP-Method	ICP-OES	In-House Method
18	Molybdosilicate Method	DA	In house method based on APHA 4500-SiO2 E
19	Molybdosilicate Method	DA	APHA
21	Molybdosilicate Method	Manual Analysis	APHA, 4500-SiO2 F (In-House Method)

Table 60 Measurement Methods and Instrument Techniques for Total Hardness

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Calculation	Auto Titration	APHA
2	Calculation	Other	CALC
4	Calculation	ICP-OES	APHA 2340
5	Calculation	ICP-OES	2340 B
6	Calculation		
7	Calculation	ICP-OES	APHA 2340
8	Calculation	ICP-OES	APHA 2340 B
9	Calculation	ICP-MS	In-House Method
10	Titration	Manual Analysis	In House
16	Calculation	ICP-MS	APHA Part 2340B
18	Calculation	NA	In house method based on APHA 2340 B
20	Calculation	ICP-MS	APHA 2340 B-Hardness

END OF REPORT