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Proficiency Test Final Report AQA 26-09 Nutrients and Anions in Potable Water

July 2026

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EXECUTIVE SUMMARY

This report presents the results of the proficiency test AQA 26-09 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 2 water samples. The assigned values were the robust average of participants' results. The associated uncertainties were evaluated from the robust standard deviation of the participants' results. The results reported by some laboratories for NH_3, NO_3, and NO_2 in Sample S1 were consistently lower than the assigned value by the same factor. These laboratories might have reported results for NH_3-N, NO_3-N, and NO_2-N. To avoid unfair scoring, these results were excluded from robust average calculations as it will bias low the assigned value; they were also excluded from the calculation of all summary statistics.

Twenty-two laboratories registered to participate, and all submitted results.

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

i. assess laboratory capability in measuring nutrients and anions in potable water;

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

Of 380 z-scores, 345 (91%) returned an acceptable score of $|z| \leq 2.0$.

Of 380 E_n-scores, 320 (84%) returned an acceptable score of $|E_n| < 1.0$.

Laboratories 5 and 16 returned the highest number of acceptable z-scores (21).

Laboratories 11 and 18 returned the highest number of acceptable E_n-scores (20).

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

Phosphorus measurements at the 100 µg/L level continue to challenge participants' analytical techniques. It was one of the analytes with largest number of unsatisfactory z-scores.

iii. assess participants' ability to determine compliance of water samples with the Australian Drinking Water Guidelines;

Most participants' results correctly reflected that Sample S1 complies with the Australian Drinking Water Guideline values when considering uncertainty for fluoride and iodide. However, the results reported by some laboratories, when considered together with their associated measurement uncertainties, would have led to an inconclusive compliance assessment. These laboratories should investigate the bias of their reported results and if their uncertainty is fit for purpose.

Some participants should also consider reviewing their laboratory reporting limit for measurement of iodide in potable water as they may not be fit for purpose.

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

Despite different matrices and analyte concentrations, on average participants' performance has remained consistent over the last 13 years.

v. develop the practical application of measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty evaluation;

Of 380 numerical results, 379 (99%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was between 0.83% to 100% of the reported value.

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

The study samples are homogeneous and stable and are well characterised, both by in-house testing and from the results of the proficiency round. Surplus of these test samples are available for purchase from NMIA and can be used for quality control and method validation purposes.

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1 INTRODUCTION

1.1 NMIA Proficiency Testing Program

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

Proficiency testing (PT) is the 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons.'[1] NMIA PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement, and food safety. NMIA offers studies in:

- per- and polyfluoroalkyl substances in soil, biosolid, water, biota, food, and consumables;
- hydrocarbons, phenols, and other organic compounds in soil and water;
- pesticide residues in soil, water, fruit, vegetables, and herbs;
- metals in soil, water, food, filters, and paint;
- nutrients, anions and physical tests in water and soil;
- chlorophyll a in water; and
- controlled drug assay, drugs in wipes, and clandestine laboratory.

AQA 26-09 is the 21st NMIA PT study on nutrients, anions, and physical tests in water.

1.2 Study Aims

The aims of the study were to:

- assess laboratory capability in measuring nutrients and anions in potable water;
- evaluate the laboratories' methods used in determination of nutrients and anions in potable water;
- assess participants' ability to determine compliance of water samples with the Australian Drinking Water Guidelines (ADWG);
- compare the performance of participant laboratories with their past performance;
- develop the practical application of measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty evaluation; and
- produce materials that can be used in method validation and as control samples.

1.3 Study Conduct

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

NMIA is accredited by the National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes. This study falls within the scope of NMIA's accreditation (Accreditation No. 198; Site No. 14485).

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

2 STUDY INFORMATION

2.1 Study Timetable

The timetable of the study was:

Invitation issued:	07 April 2026
Samples dispatched:	04 May 2026
Results due:	22 May 2026
Interim report issued:	26 May 2026
Preliminary report issued:	28 May 2026

2.2 Participation and Laboratory Code

Twenty-two laboratories participated and submitted results. All participant laboratories were assigned a confidential code number for this study.

2.3 Selection of Matrices and Inorganic Analytes, and Test Material Specification

The 23 tests were selected from those for which a guideline value is listed in the Australian Drinking Water Guidelines (ADWG)[5] and are commonly measured by water testing laboratories.

Two samples were provided for analysis:

- Sample S1 consisted of two identical 200 mL bottles of filtered, autoclaved, and frozen potable water; and
- Sample S2 was 400 mL of chilled potable water

2.4 Test Material Preparation, Analysis, Homogeneity, and Stability

The same validated preparation procedure was followed as in previous studies.[2] Test samples from previous studies were demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. Therefore, only a partial homogeneity test was conducted for chloride, fluoride, iodide, nitrate, nitrite, orthophosphate-P, and TDN in Sample S1. The results from the partial homogeneity test are reported in the present study as the homogeneity value.

To address issues associated with holding time and storage 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.

The preparation and analysis methods of the study samples are described in Appendix 1.

2.5 Sample Storage, Dispatch, and Receipt

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

The samples were dispatched by courier on 4 May 2026.

The following items were packaged with the samples:

- a covering letter which included a description of the test samples and instructions for participants; and
- a form to confirm the receipt and condition of the samples.

An Excel spreadsheet for the electronic reporting of the results was emailed to participants.

2.6 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your routine test method.
- If analyses cannot be commenced on the day of receipt, please store Sample S1 frozen and Sample S2 refrigerated.
- Prior to testing, thaw Sample S1 completely.
- These samples contain the following analytes in the displayed concentration ranges:

SAMPLE S1 **2 x 200 mL frozen, filtered potable water**		**SAMPLE S2** **400 mL potable water**	
Test	**Estimated Value* mg/L**	**Test**	**Estimated Value* mg/L**
Ammonia (as NH_3)	0.05-2	B (total)	0.05-2
Nitrate (as NO_3)	0.5-20	Ca (total)	5-200
Nitrite (as NO_2)	0.05-2	K (total)	0.5-20
Bromide	0.005-0.2	Mg (total)	0.5-20
Chloride	5-200	Na (total)	5-200
Fluoride	0.5-20	P (total)	0.05-2
Iodide	0.05-2	Alkalinity to pH 4.5 (as $CaCO_3$)	5-200
Sulphate	0.5-20	Total Hardness (as $CaCO_3$)	5-200
Dissolved Organic Carbon (as dNPOC)	0.5-20	EC (at 25˚C, µs/cm)	50-2000
Orthophosphate-P (FRP)	0.005-0.2	pH (at 25˚C)	3-12
Total Dissolved Nitrogen	NA	Silica (as SiO_2)	0.5-20
Total Dissolved Phosphorus	0.05-2		

- Participants need not test for all listed analytes.
- Participants are asked to report results in units of mg/L except for pH and EC (µS/cm).
- For each analyte in each sample, report a single result. This figure will be used in all statistical analysis in the study report.
- Report results as you would report to a client and applying the limit of reporting of the method used for analysis (no limit of reporting has been set for this study).
- For each analyte in each sample, report the associated expanded uncertainty (e.g. 0.50 ± 0.02 mg/L).
- Report any listed analyte not tested as NT as the result.
- Report the basis of your uncertainty evaluations as requested in the results sheet (e.g. uncertainty budget, repeatability precision, long term result variability).
- Please complete the method details as requested in the Methodology sheet.
- Return the completed results sheet by email (proficiency@measurement.gov.au).
- Please return results by 22 May 2026. Late results may not be included in the study report.

2.7 Interim Report and Preliminary Reports

An Interim Report was emailed to participants on 26 May 2026.

A Preliminary Report was issued on 28 May 2026. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and E_n-scores for each analyte tested by participants. No data from the Preliminary Report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summaries

Participants were requested to provide information about their measurement methods and instrumental techniques. Responses reported by participants for each sample analysed are presented in Appendix 6. Some responses may have been modified so that the participant cannot be identified.

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
7	S1 and S2: Accredited for all except B, Ca, Mg, Na & K - currently being assessed.

3.3 Basis of Participants' Measurement Uncertainty Evaluations

Participants were requested to provide information about the basis of their uncertainty evaluation (Table 2). Some responses may be modified so that the participant cannot be identified.

Table 2 Basis of Uncertainty Evaluation

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation[a]		Guide Document for Evaluating MU
		Precision	Method Bias	
1	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	Instrument Calibration	ISO/GUM
2	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	
3	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - SS Duplicate Analysis	CRM Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
4*	Other Coverage factor not reported	Control samples - CRM Instrument Calibration	CRM	ASTM E2554-13
5	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - SS Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	ISO/GUM
6	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM	CRM	ISO/GUM
7	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
8	Top Down - reproducibility (standard deviation) from PT studies used directly Coverage factor not reported	Standard deviation from PT studies only		
		Instrument Calibration	CRM Instrument Calibration	
9	Top Down - precision and evaluations of the method and	Control Samples - CRM	CRM Instrument Calibration	ISO/GUM

Lab. Code	Approach to Evaluating MU	Information Sources for MU Evaluation[a]		Guide Document for Evaluating MU
		Precision	Method Bias	
	laboratory bias Coverage factor not reported			
10	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - Reference Material / Ex PT Sample	CRM Instrument Calibration Recoveries of SS Standard Purity	
11	Coverage factor not reported	Control Samples - Reference Material / Ex PT Sample Duplicate Analysis		
12	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - Reference Material / Ex PT Sample Duplicate Analysis	CRM	ASTM E2254-13
13	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Duplicate Analysis	Recoveries of SS	NATA General Accreditation Guidance, Estimating and Reporting MU
14	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - SS Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
15	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537
16	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control Samples - CRM Duplicate Analysis	CRM	Eurachem/CITAC Guide
17	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
18	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	Eurachem/CITAC Guide
19	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	Eurachem/CITAC Guide
20	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Duplicate Analysis	Recoveries of SS	ISO/GUM
21	Top Down - precision and evaluations of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	NMIA Uncertainty Course
22	Top Down - precision and evaluations of the method and laboratory bias Coverage factor not reported	Control Samples	CRM	ISO/GUM

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

Table 3 Additional Information for Basis of Uncertainty Evaluation

Lab Code	Additional Information
4	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 Participants' 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 summary statistics and other estimates of analyte mass fraction. Bar charts of the results and performance scores are presented in Figures 2 to 24. An example chart with interpretation guide is shown in Figure 1.

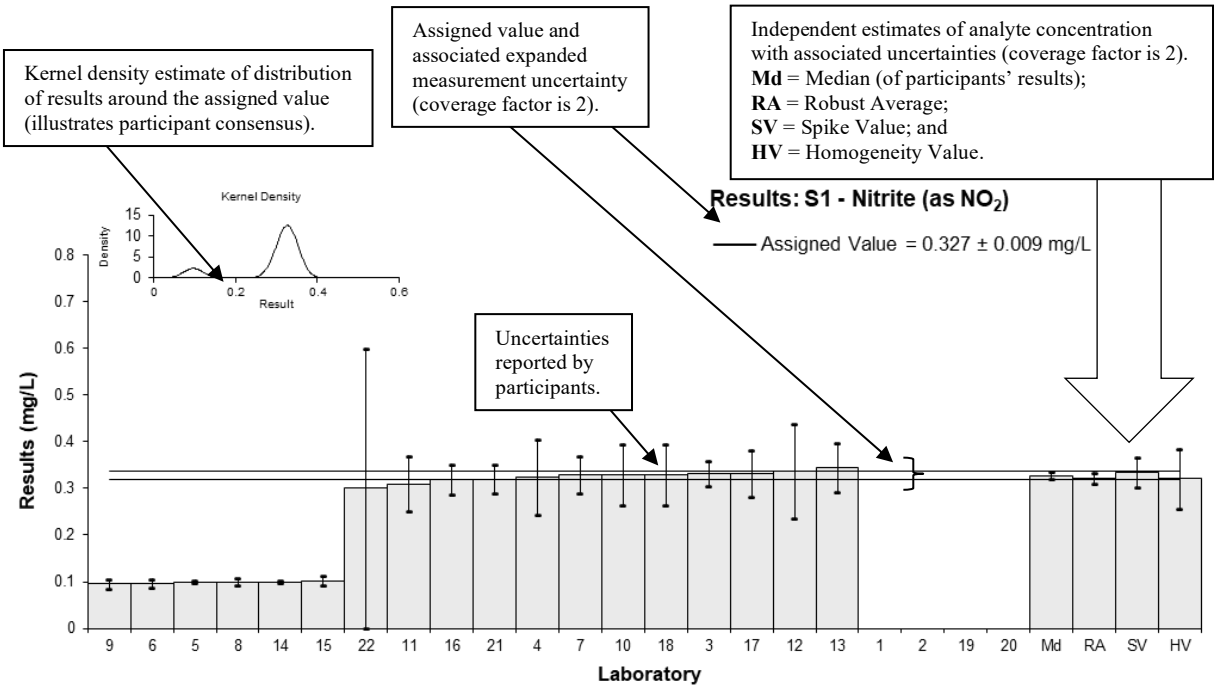


Figure 1 Guide to Presentation of Results

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.[3,4] 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 or characteristic of a proficiency testing item.'[1] In this study, the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, outliers removed; the expanded uncertainties were evaluated 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 uncertainties, and robust CVs (a measure of the variability of participants' results) were calculated as described in ISO 13528.[6]

The robust CVs as presented in the Section 5 Statistics Tables are the robust between-laboratory CV including outliers but excluding extreme outliers. Everywhere else in the report, the robust between-laboratory CV refers to the robust CV calculated with both outliers and extreme outliers removed.

4.5 Standard Deviation for Proficiency Assessment

The standard deviation for proficiency assessment (SDPA, 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-scores and provides scaling for laboratory deviation from the assigned value.

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

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The 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:

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

Where:

z is z-score;

χ is a participant's result;

X is the assigned value;

σ is the SDPA from Equation 1.

A z-score with absolute value (|z|): $|z| \leq 2.0$ is acceptable, $2.0 < |z| < 3.0$ is questionable, and $|z| \geq 3.0$ is not acceptable.

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 assessing laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

E_n is E_n-score;

χ is a 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 and $|E_n| \geq 1.0$ is not acceptable.

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 NH_3)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	0.249	0.025	-0.24	-0.21
4	0.268	0.067	0.51	0.19
5	0.24	0.034	-0.59	-0.41
6**	0.24	0.024	-0.59	-0.54
7	NT	NT		
8**	0.21	0.005	-1.76	-3.03
9	0.23	0.069	-0.98	-0.36
10	NT	NT		
11	0.25	0.05	-0.20	-0.10
12	0.22	0.066	-1.37	-0.52
13	0.274	0.0411	0.75	0.44
14**	0.2	0.003	-2.16	-3.84
15**	0.218	0.02	-1.45	-1.52
16	0.27	0.027	0.59	0.49
17	0.26	0.07	0.20	0.07
18	0.265	0.04	0.39	0.24
19	<0.2	1.12		
20	NR	NR		
21	0.25	0.02	-0.20	-0.20
22	0.282	0.2	1.06	0.13

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.255	0.014
Spike Value	Not Spiked	
Robust Average	0.255	0.014
Median	0.255	0.015
Mean	0.255	
N	12	
Max	0.282	
Min	0.22	
Robust SD	0.02	
Robust CV	7.8%	

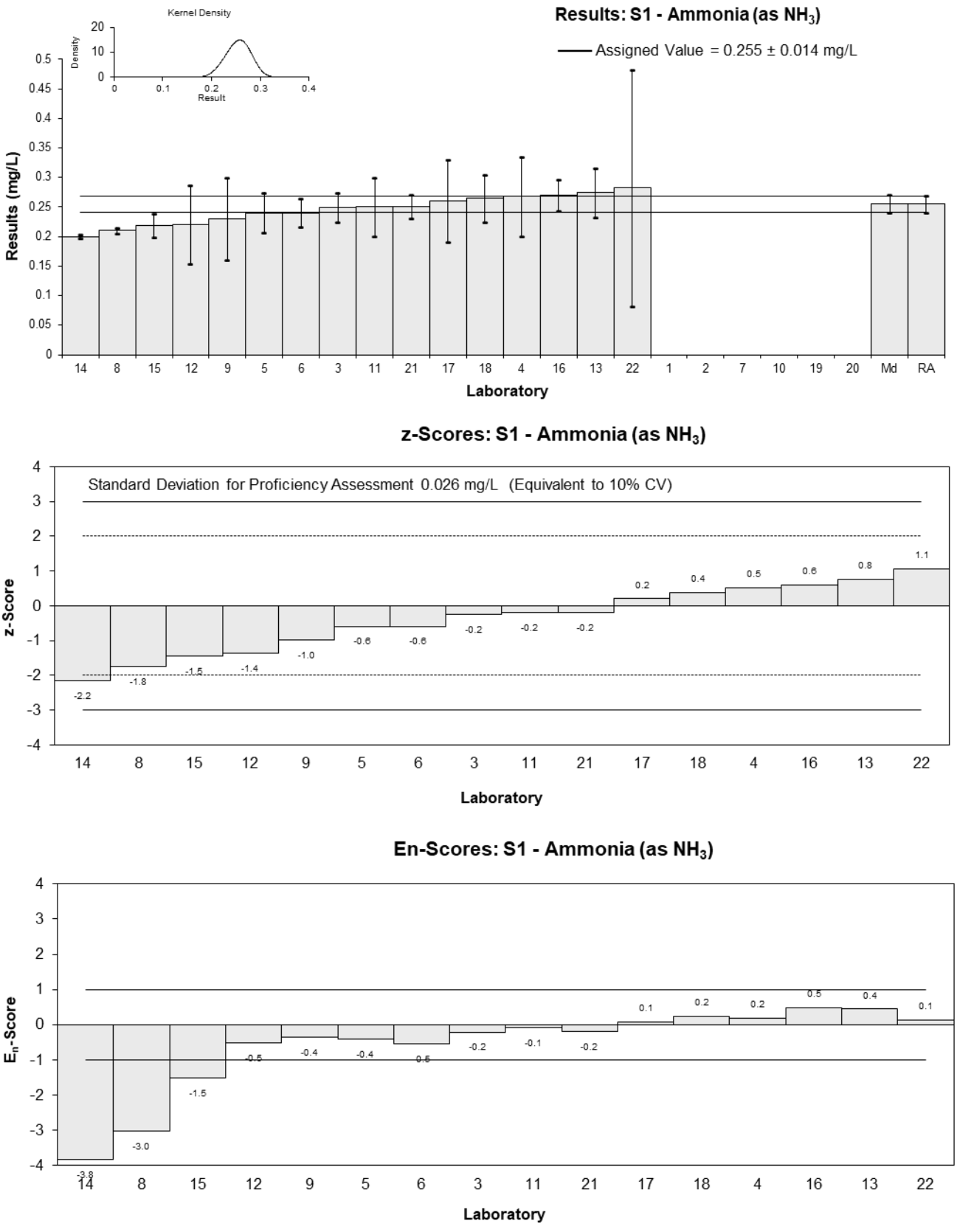

Kernel Density
Density
Result
Results: S1 - Ammonia (as NH3)
Assigned Value = 0.255 ± 0.014 mg/L
Results (mg/L)
Laboratory
14 8 15 12 9 5 6 3 11 21 17 18 4 16 13 22 1 2 7 10 19 20 Md RA
z-Scores: S1 - Ammonia (as NH3)
Standard Deviation for Proficiency Assessment 0.026 mg/L (Equivalent to 10% CV)
z-Score
-2.2 -1.8 -1.5 -1.4 -1.0 -0.6 -0.6 -0.2 -0.2 -0.2 0.2 0.4 0.5 0.6 0.8 1.1
Laboratory
14 8 15 12 9 5 6 3 11 21 17 18 4 16 13 22
En-Scores: S1 - Ammonia (as NH3)
En-Score
-3.8 -3.0 -1.5 -0.5 -0.4 -0.4 -0.5 -0.2 -0.1 -0.2 0.1 0.2 0.2 0.5 0.4 0.1
Laboratory
14 8 15 12 9 5 6 3 11 21 17 18 4 16 13 22

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	NT	NT		
2	<0.5	NR		
3	<0.1	NR		
4	< 0.5	NR		
5	0.06	0.0084	-1.23	-0.79
6	0.06	0.0066	-1.23	-0.90
7	NT	NT		
8	NR	NR		
9	NT	NT		
10	0.073	0.0146	0.67	0.29
11	<0.1	NR		
12	< 1	NR		
13	NT	NT		
14	0.07	0.011	0.23	0.12
15	<0.5	NR		
16	0.07	0.01	0.23	0.13
17	<0.10	NR		
18	NR	NR		
19	<0.2	0.05		
20	0.076	0.004	1.11	0.98
21	0.07	0.02	0.23	0.08
22*	0.18	0.1	16.32	1.11

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0684	0.0066
Spike Value	Not Spiked	
Robust Average	0.0703	0.0079
Median	0.0700	0.0059
Mean	0.082	
N	8	
Max	0.18	
Min	0.06	
Robust SD	0.0089	
Robust CV	13%	

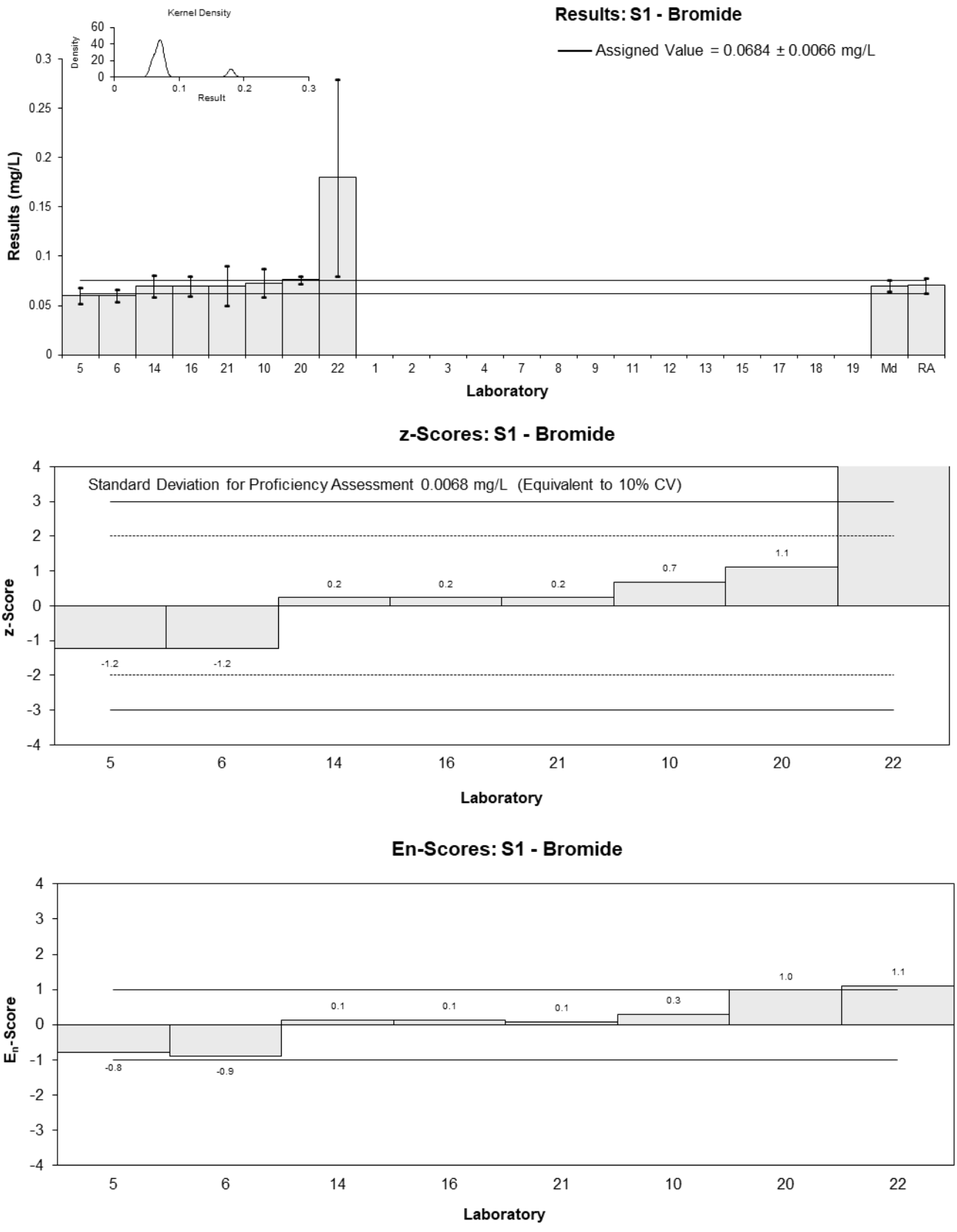

Results: S1 - Bromide
Assigned Value = 0.0684 ± 0.0066 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5 6 14 16 21 10 20 22 1 2 3 4 7 8 9 11 12 13 15 17 18 19 Md RA
z-Scores: S1 - Bromide
Standard Deviation for Proficiency Assessment 0.0068 mg/L (Equivalent to 10% CV)
z-Score
-1.2 -1.2 0.2 0.2 0.2 0.7 1.1
Laboratory
5 6 14 16 21 10 20 22
En-Scores: S1 - Bromide
En-Score
-0.8 -0.9 0.1 0.1 0.1 0.3 1.0 1.1
Laboratory
5 6 14 16 21 10 20 22

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	28.5	8.55	0.14	0.05
2	28.4	2.7	0.11	0.11
3	26	3	-0.75	-0.68
4	26.2	6.55	-0.68	-0.29
5	26	2.5	-0.75	-0.80
6	27	2.7	-0.39	-0.39
7	29	2	0.32	0.42
8	NR	NR		
9	28.09	5.62	0.00	0.00
10	28	5.6	-0.04	-0.02
11	30	6	0.68	0.31
12	29.1	8.73	0.36	0.11
13	30	4.50	0.68	0.42
14	29	0.464	0.32	0.97
15	31.3	4.0	1.14	0.78
16	29	0.3	0.32	1.05
17	28.0	2.0	-0.04	-0.05
18	28	3.7	-0.04	-0.03
19	28	0.3	-0.04	-0.12
20	28	2	-0.04	-0.05
21	27.4	1.9	-0.25	-0.34
22	27.0	4.0	-0.39	-0.27

Statistics

Assigned Value	28.1	0.8
Spike Value	Not Spiked	
Homogeneity Value	29.0	4.4
Robust Average	28.1	0.8
Median	28.0	0.8
Mean	28.2	
N	21	
Max	31.3	
Min	26	
Robust SD	1.4	
Robust CV	5%	

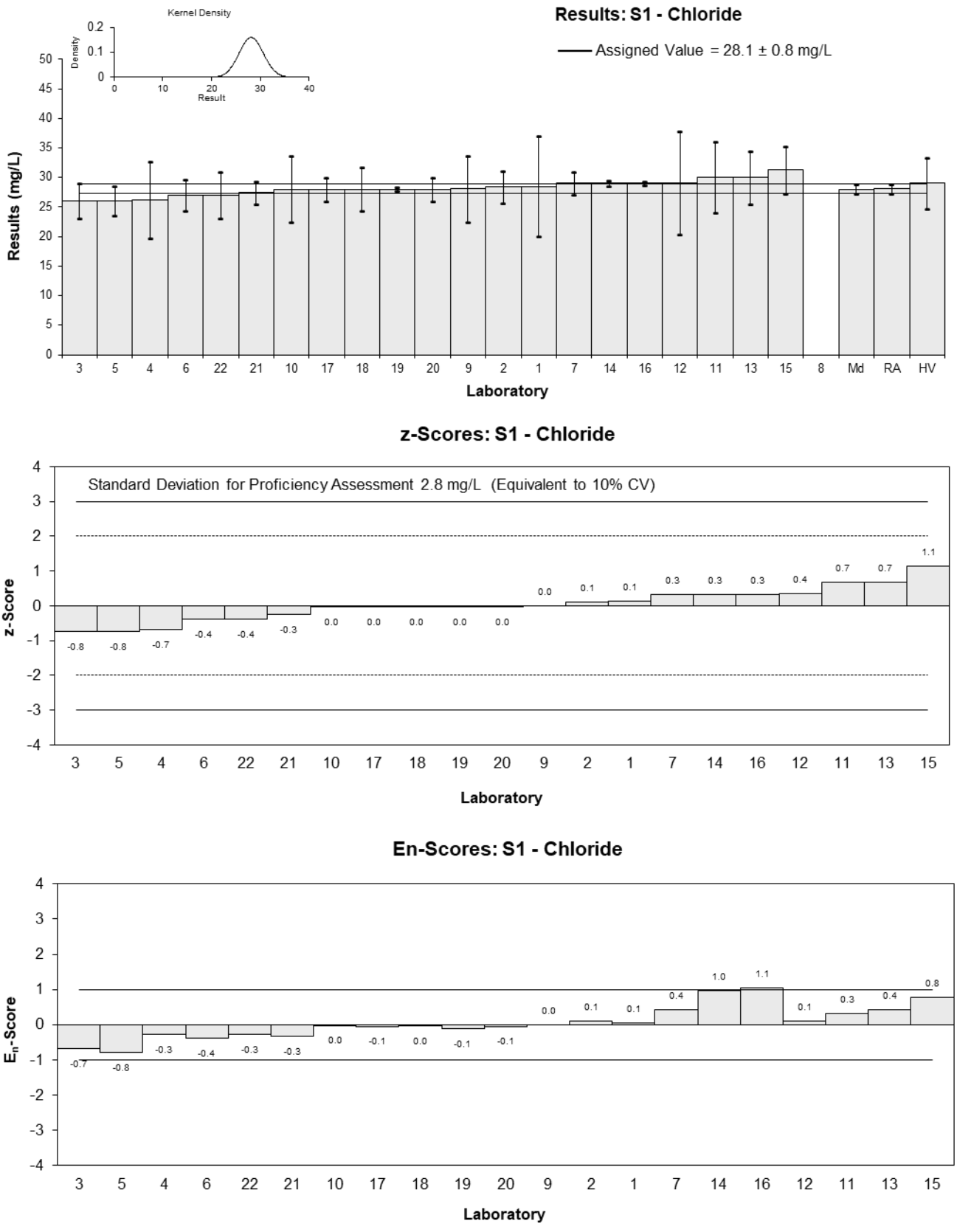

Kernel Density
Density
Result
Results: S1 - Chloride
Assigned Value = 28.1 ± 0.8 mg/L
Results (mg/L)
Laboratory
3 5 4 6 22 21 10 17 18 19 20 9 2 1 7 14 16 12 11 13 15 8 Md RA HV
z-Scores: S1 - Chloride
Standard Deviation for Proficiency Assessment 2.8 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.8 -0.7 -0.4 -0.4 -0.3 0.0 0.0 0.0 0.0 0.0 0.0 0.1 0.1 0.3 0.3 0.3 0.4 0.7 0.7 1.1
Laboratory
3 5 4 6 22 21 10 17 18 19 20 9 2 1 7 14 16 12 11 13 15
En-Scores: S1 - Chloride
En-Score
-0.7 -0.8 -0.3 -0.4 -0.3 -0.3 0.0 -0.1 0.0 -0.1 -0.1 0.0 0.1 0.1 0.4 1.0 1.1 0.1 0.3 0.4 0.8
Laboratory
3 5 4 6 22 21 10 17 18 19 20 9 2 1 7 14 16 12 11 13 15

Figure 4

Table 7

Sample Details

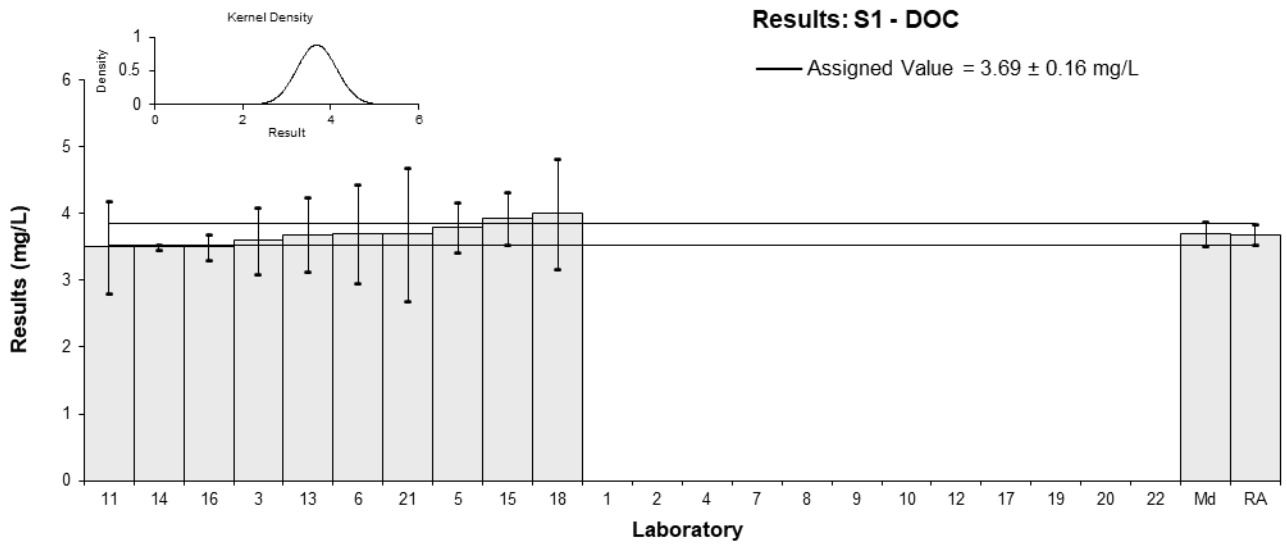
Sample No.	S1
Matrix	Potable Water
Analyte	DOC
Unit	mg/L

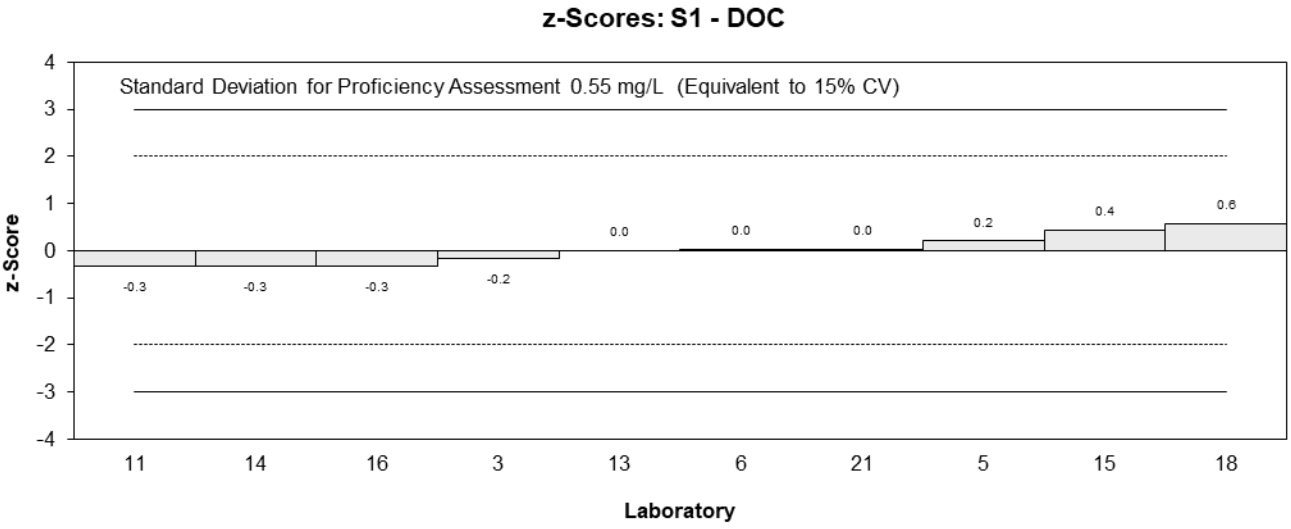
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	3.6	0.5	-0.16	-0.17
4	< 5	NR		
5	3.8	0.38	0.20	0.27
6	3.7	0.74	0.02	0.01
7	NT	NT		
8	NR	NR		
9	< 5	NR		
10	NT	NT		
11	3.5	0.7	-0.34	-0.26
12	NT	NT		
13	3.69	0.554	0.00	0.00
14	3.5	0.045	-0.34	-1.14
15	3.93	0.4	0.43	0.56
16	3.5	0.2	-0.34	-0.74
17	NR	NR		
18	4	0.82	0.56	0.37
19	NT	NT		
20	NR	NR		
21	3.7	1.0	0.02	0.01
22	NT	NT		

Statistics

Assigned Value	3.69	0.16
Spike Value	Not Spiked	
Robust Average	3.69	0.16
Median	3.70	0.18
Mean	3.69	
N	10	
Max	4	
Min	3.5	
Robust SD	0.2	
Robust CV	5.4%	


Kernel Density
Density
Result
Results: S1 - DOC
Assigned Value = 3.69 ± 0.16 mg/L
Results (mg/L)
Laboratory
11 14 16 3 13 6 21 5 15 18 1 2 4 7 8 9 10 12 17 19 20 22 Md RA


z-Scores: S1 - DOC
Standard Deviation for Proficiency Assessment 0.55 mg/L (Equivalent to 15% CV)
z-Score
-0.3 -0.3 -0.3 -0.2 0.0 0.0 0.0 0.2 0.4 0.6
Laboratory
11 14 16 3 13 6 21 5 15 18

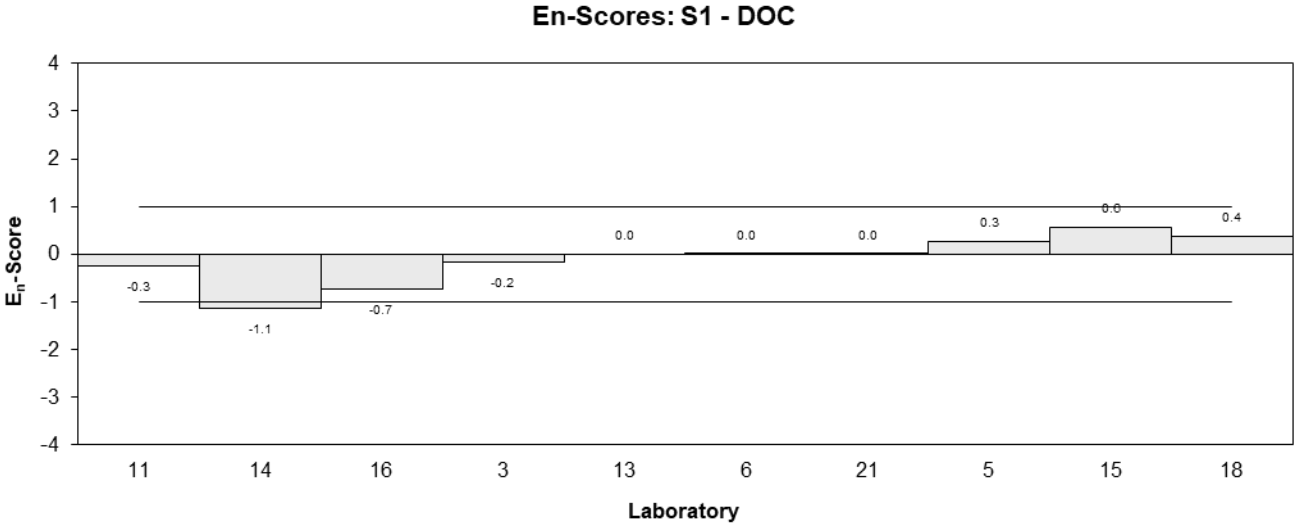

En-Scores: S1 - DOC
En-Score
-0.3 -1.1 -0.7 -0.2 0.0 0.0 0.0 0.3 0.6 0.4
Laboratory
11 14 16 3 13 6 21 5 15 18

Figure 5

Table 8

Sample Details

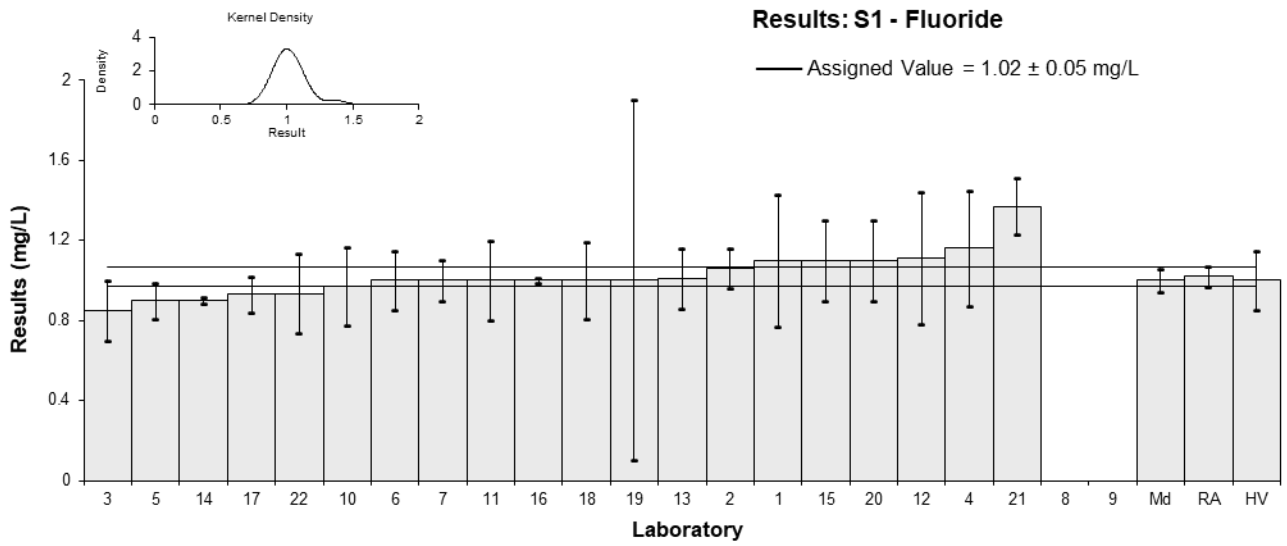
Sample No.	S1
Matrix	Potable Water
Analyte	Fluoride
Unit	mg/L

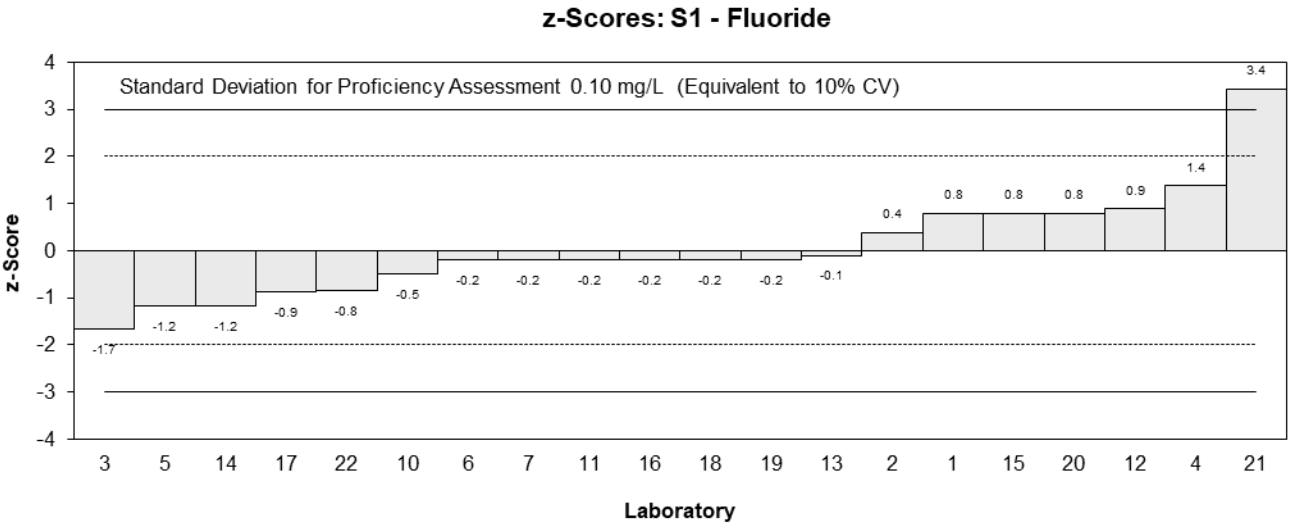
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.1	0.33	0.78	0.24
2	1.06	0.1	0.39	0.36
3	0.85	0.15	-1.67	-1.08
4	1.16	0.29	1.37	0.48
5	0.9	0.09	-1.18	-1.17
6	1	0.15	-0.20	-0.13
7	1.0	0.1	-0.20	-0.18
8	NR	NR		
9	NT	NT		
10	0.97	0.194	-0.49	-0.25
11	1.0	0.2	-0.20	-0.10
12	1.11	0.33	0.88	0.27
13	1.01	0.152	-0.10	-0.06
14	0.9	0.014	-1.18	-2.31
15	1.1	0.2	0.78	0.39
16	1.0	0.01	-0.20	-0.39
17	0.93	0.09	-0.88	-0.87
18	1.0	0.19	-0.20	-0.10
19	1	0.9	-0.20	-0.02
20	1.1	0.2	0.78	0.39
21	1.37	0.14	3.43	2.35
22	0.934	0.2	-0.84	-0.42

Statistics

Assigned Value	1.02	0.05
Spike Value	Not Spiked	
Homogeneity Value	1.00	0.15
Robust Average	1.02	0.05
Median	1.00	0.06
Mean	1.02	
N	20	
Max	1.37	
Min	0.85	
Robust SD	0.097	
Robust CV	9.6%	


Kernel Density
Density
Result
Results: S1 - Fluoride
Assigned Value = 1.02 ± 0.05 mg/L
Results (mg/L)
Laboratory
3 5 14 17 22 10 6 7 11 16 18 19 13 2 1 15 20 12 4 21 8 9 Md RA HV


z-Scores: S1 - Fluoride
Standard Deviation for Proficiency Assessment 0.10 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
3 5 14 17 22 10 6 7 11 16 18 19 13 2 1 15 20 12 4 21

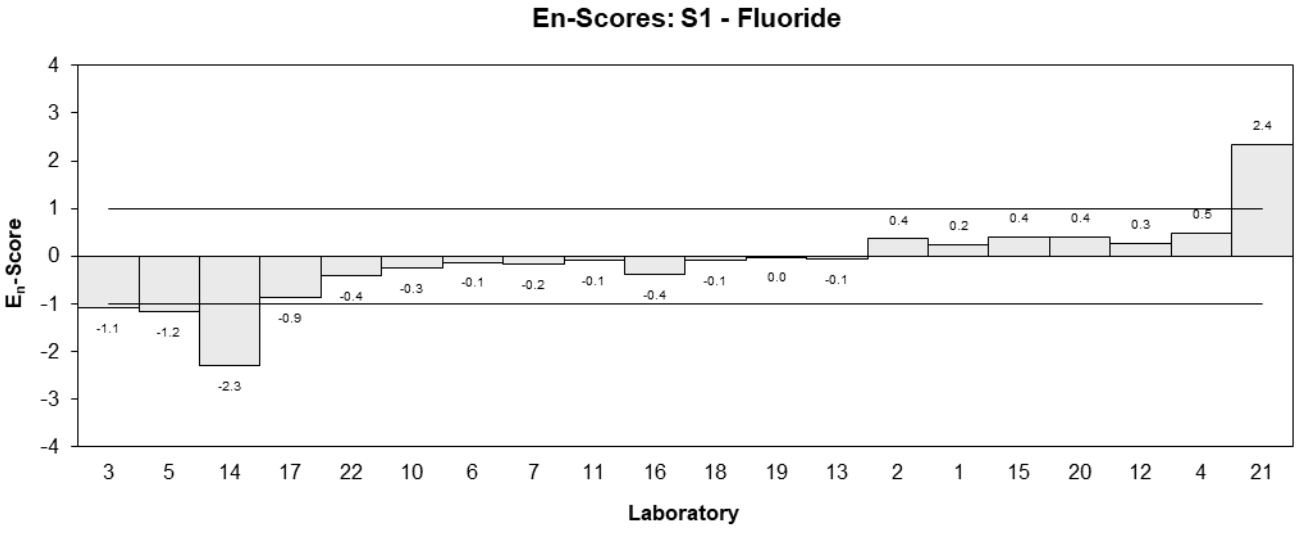

En-Scores: S1 - Fluoride
En-Score
Laboratory
3 5 14 17 22 10 6 7 11 16 18 19 13 2 1 15 20 12 4 21

Figure 6

Table 9

Sample Details

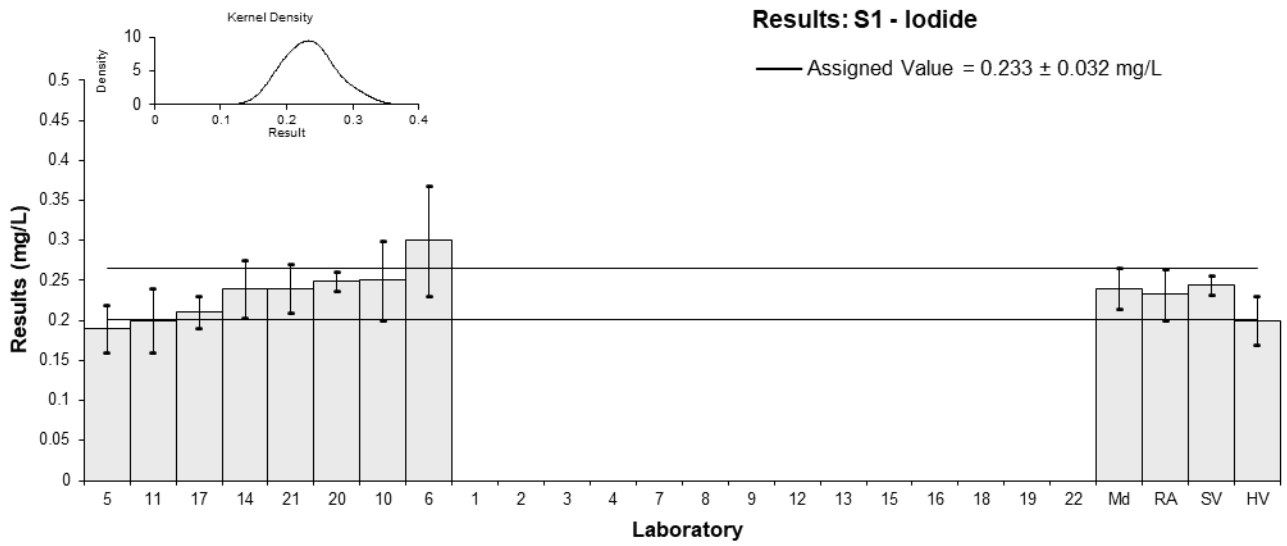
Sample No.	S1
Matrix	Potable Water
Analyte	Iodide
Unit	mg/L

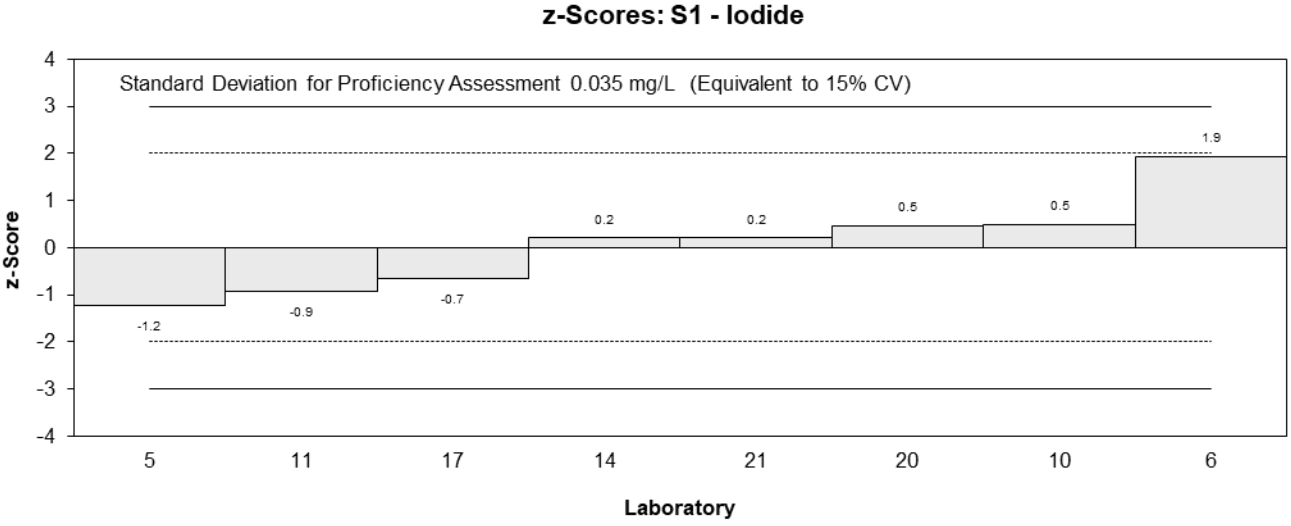
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	< 2	NR		
5	0.19	0.03	-1.23	-0.98
6	0.3	0.069	1.92	0.88
7	NT	NT		
8	NR	NR		
9	NT	NT		
10	0.25	0.05	0.49	0.29
11	0.2	0.04	-0.94	-0.64
12	< 1	NR		
13	NT	NT		
14	0.24	0.036	0.20	0.15
15	NT	NT		
16	< 0.3	NR		
17	0.21	0.02	-0.66	-0.61
18	NR	NR		
19	NT	NT		
20	0.249	0.0125	0.46	0.47
21	0.24	0.03	0.20	0.16
22	NT	NT		

Statistics

Assigned Value	0.233	0.032
Spike Value	0.245	0.012
Homogeneity Value	0.200	0.030
Robust Average	0.233	0.032
Median	0.240	0.026
Mean	0.235	
N	8	
Max	0.3	
Min	0.19	
Robust SD	0.036	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - Iodide
Assigned Value = 0.233 ± 0.032 mg/L
Results (mg/L)
Laboratory
5 11 17 14 21 20 10 6 1 2 3 4 7 8 9 12 13 15 16 18 19 22 Md RA SV HV


z-Scores: S1 - Iodide
Standard Deviation for Proficiency Assessment 0.035 mg/L (Equivalent to 15% CV)
z-Score
-1.2
-0.9
-0.7
0.2
0.2
0.5
0.5
1.9
Laboratory
5 11 17 14 21 20 10 6

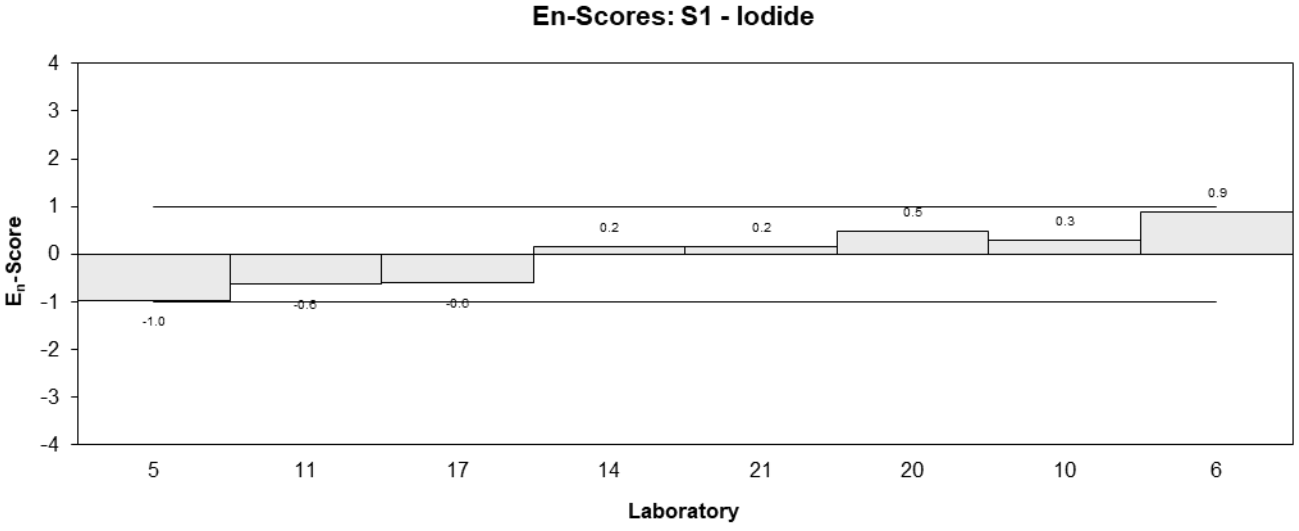

En-Scores: S1 - Iodide
En-Score
-1.0
-0.6
-0.0
0.2
0.2
0.5
0.3
0.9
Laboratory
5 11 17 14 21 20 10 6

Figure 7

Table 10

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Nitrate (as NO_3)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	1.30	0.130	0.24	0.21
4	1.51	0.378	1.89	0.63
5*	0.17	0.017	-8.66	-17.64
6**	0.3	0.03	-7.64	-14.46
7	NT	NT		
8**	0.30	0.007	-7.64	-16.06
9*	0.40	0.06	-6.85	-10.25
10	1.3	0.26	0.24	0.11
11	1.3	0.26	0.24	0.11
12	0.95	0.285	-2.52	-1.10
13	1.27	0.191	0.00	0.00
14**	0.3	0.005	-7.64	-16.11
15**	0.315	0.03	-7.52	-14.24
16	1.2	0.01	-0.55	-1.15
17	1.21	0.30	-0.47	-0.20
18	1.35	0.12	0.63	0.60
19	1.29	0.6	0.16	0.03
20	NR	NR		
21	1.30	0.09	0.24	0.28
22	1.18	0.7	-0.71	-0.13

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.27	0.06
Spike Value	Not Spiked	
Homogeneity Value	1.39	0.28
Robust Average	1.21	0.13
Median	1.28	0.07
Mean	1.12	
N	14	
Max	1.51	
Min	0.17	
Robust SD	0.19	
Robust CV	16%	

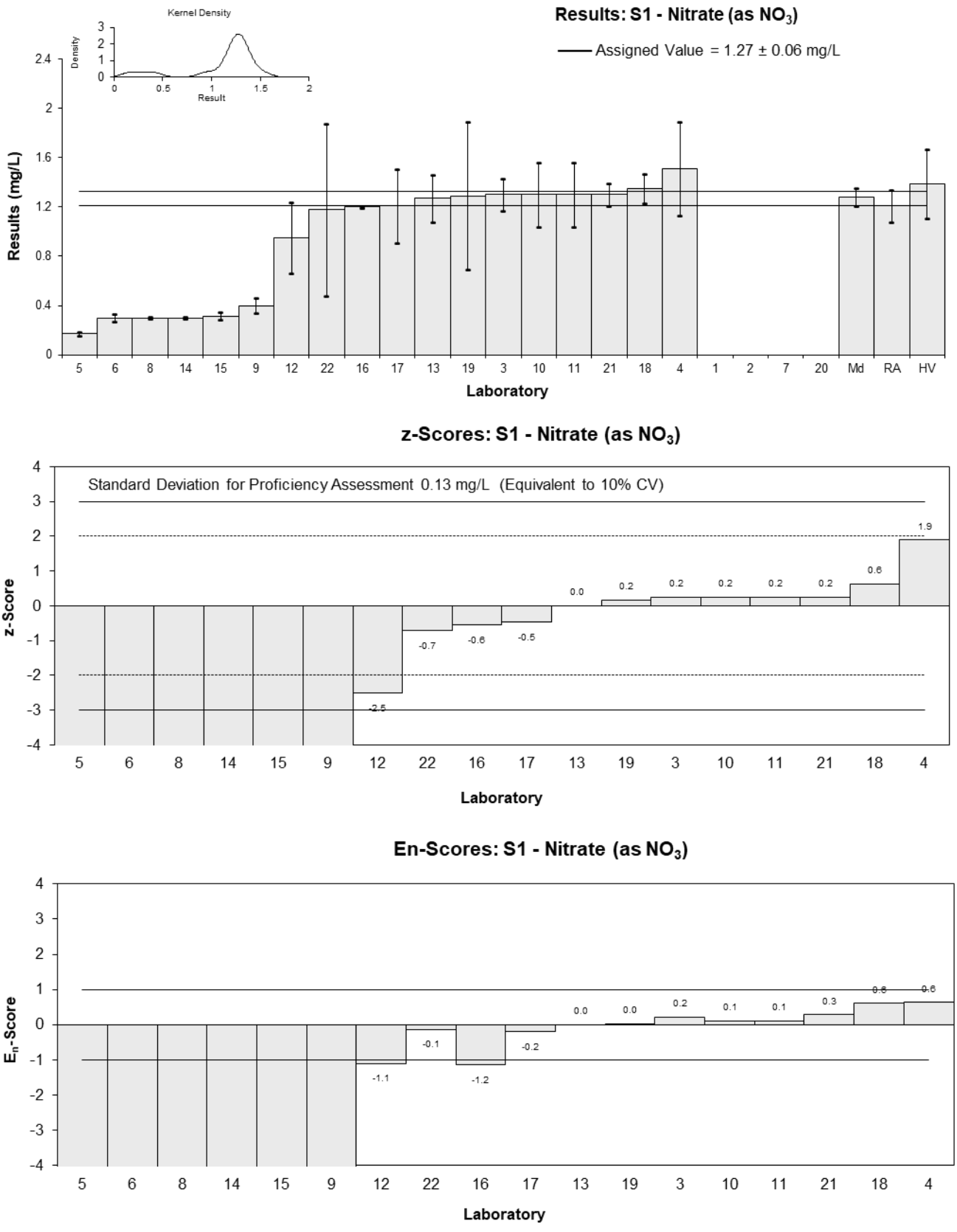

Kernel Density
Density
Result
Results: S1 - Nitrate (as NO3)
Assigned Value = 1.27 ± 0.06 mg/L
Results (mg/L)
Laboratory
5 6 8 14 15 9 12 22 16 17 13 19 3 10 11 21 18 4 1 2 7 20 Md RA HV
z-Scores: S1 - Nitrate (as NO3)
Standard Deviation for Proficiency Assessment 0.13 mg/L (Equivalent to 10% CV)
z-Score
0.0 0.2 0.2 0.2 0.2 0.2 0.6 1.9
-0.7 -0.6 -0.5
-2.5
Laboratory
5 6 8 14 15 9 12 22 16 17 13 19 3 10 11 21 18 4
En-Scores: S1 - Nitrate (as NO3)
En-Score
0.0 0.0 0.2 0.1 0.1 0.3 0.6 0.6
-0.1 -0.2
-1.1 -1.2
Laboratory
5 6 8 14 15 9 12 22 16 17 13 19 3 10 11 21 18 4

Figure 8

Table 11

Sample Details

Sample No.	S1
Matrix	Potable Water
Analyte	Nitrite (as NO_2)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	0.333	0.027	0.18	0.21
4	0.325	0.081	-0.06	-0.02
5*	0.10	0.003	-6.94	-23.93
6**	0.096	0.0096	-7.06	-17.55
7	0.33	0.04	0.09	0.07
8**	0.10	0.007	-6.94	-19.91
9*	0.095	0.0095	-7.09	-17.73
10	0.33	0.066	0.09	0.05
11	0.31	0.06	-0.52	-0.28
12	0.337	0.101	0.31	0.10
13	0.345	0.0518	0.55	0.34
14**	0.1	0.0015	-6.94	-24.88
15**	0.102	0.01	-6.88	-16.72
16	0.32	0.032	-0.21	-0.21
17	0.333	0.050	0.18	0.12
18	0.33	0.066	0.09	0.05
19	NT	NT		
20	NR	NR		
21	0.32	0.03	-0.21	-0.22
22	0.30	0.3	-0.83	-0.09

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.327	0.009
Spike Value	0.335	0.032
Homogeneity Value	0.321	0.064
Robust Average	0.322	0.012
Median	0.328	0.007
Mean	0.293	
N	14	
Max	0.345	
Min	0.095	
Robust SD	0.018	
Robust CV	5.7%	

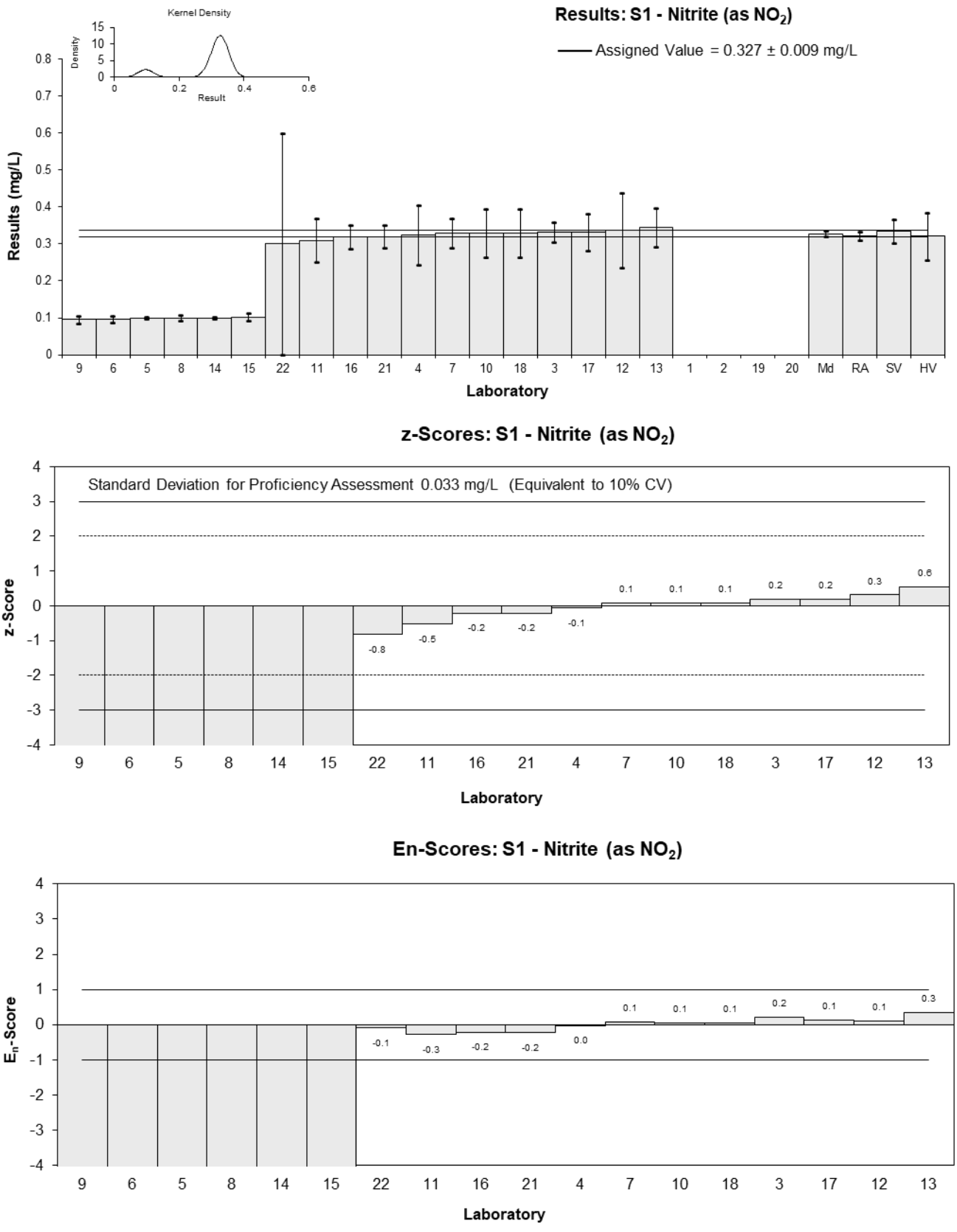

Kernel Density
Density
Result
Results: S1 - Nitrite (as NO2)
Assigned Value = 0.327 ± 0.009 mg/L
Results (mg/L)
Laboratory
9 6 5 8 14 15 22 11 16 21 4 7 10 18 3 17 12 13 1 2 19 20 Md RA SV HV
z-Scores: S1 - Nitrite (as NO2)
Standard Deviation for Proficiency Assessment 0.033 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.5 -0.2 -0.2 -0.1 0.1 0.1 0.1 0.2 0.2 0.3 0.6
Laboratory
9 6 5 8 14 15 22 11 16 21 4 7 10 18 3 17 12 13
En-Scores: S1 - Nitrite (as NO2)
En-Score
-0.1 -0.3 -0.2 -0.2 0.0 0.1 0.1 0.1 0.2 0.1 0.1 0.3
Laboratory
9 6 5 8 14 15 22 11 16 21 4 7 10 18 3 17 12 13

Figure 9

Table 12

Sample Details

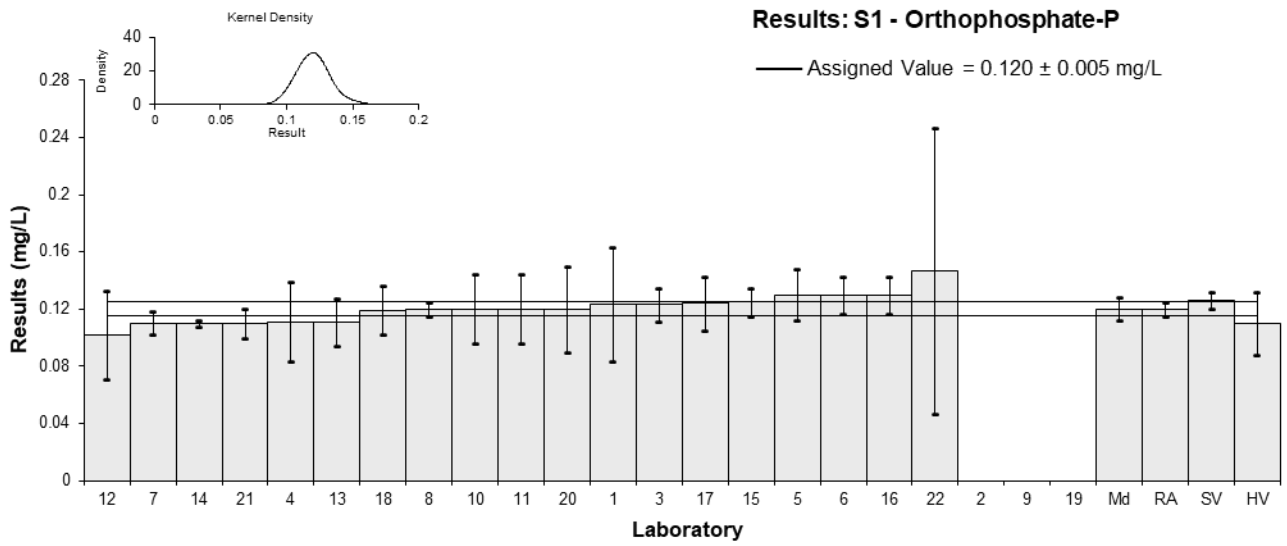
Sample No.	S1
Matrix	Potable Water
Analyte	Orthophosphate-P
Unit	mg/L

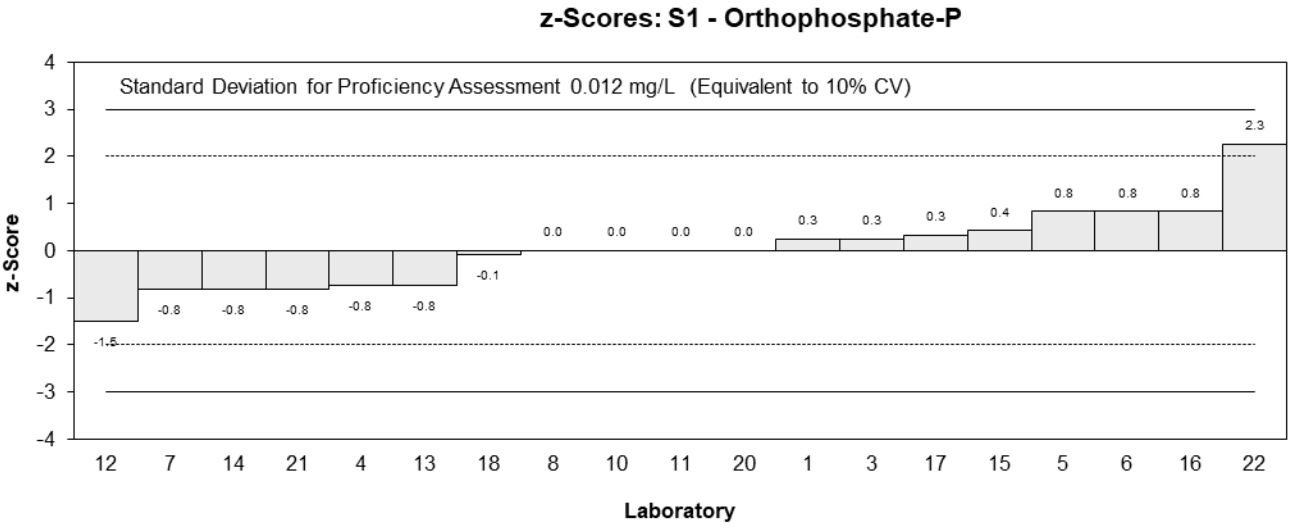
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.123	0.04	0.25	0.07
2	NT	NT		
3	0.123	0.012	0.25	0.23
4	0.111	0.028	-0.75	-0.32
5	0.13	0.018	0.83	0.54
6	0.13	0.013	0.83	0.72
7	0.11	0.008	-0.83	-1.06
8	0.12	0.005	0.00	0.00
9	NT	NT		
10	0.12	0.024	0.00	0.00
11	0.12	0.024	0.00	0.00
12	0.102	0.031	-1.50	-0.57
13	0.111	0.0167	-0.75	-0.52
14	0.11	0.002	-0.83	-1.86
15	0.125	0.01	0.42	0.45
16	0.13	0.013	0.83	0.72
17	0.124	0.019	0.33	0.20
18	0.119	0.017	-0.08	-0.06
19	NT	NT		
20	0.12	0.03	0.00	0.00
21	0.11	0.01	-0.83	-0.89
22	0.147	0.1	2.25	0.27

Statistics

Assigned Value	0.120	0.005
Spike Value	0.126	0.006
Homogeneity Value	0.110	0.022
Robust Average	0.120	0.005
Median	0.120	0.008
Mean	0.120	
N	19	
Max	0.147	
Min	0.102	
Robust SD	0.0093	
Robust CV	7.8%	


Kernel Density
Density
Result
Results: S1 - Orthophosphate-P
Assigned Value = 0.120 ± 0.005 mg/L
Results (mg/L)
Laboratory
12 7 14 21 4 13 18 8 10 11 20 1 3 17 15 5 6 16 22 2 9 19 Md RA SV HV


z-Scores: S1 - Orthophosphate-P
Standard Deviation for Proficiency Assessment 0.012 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
12 7 14 21 4 13 18 8 10 11 20 1 3 17 15 5 6 16 22

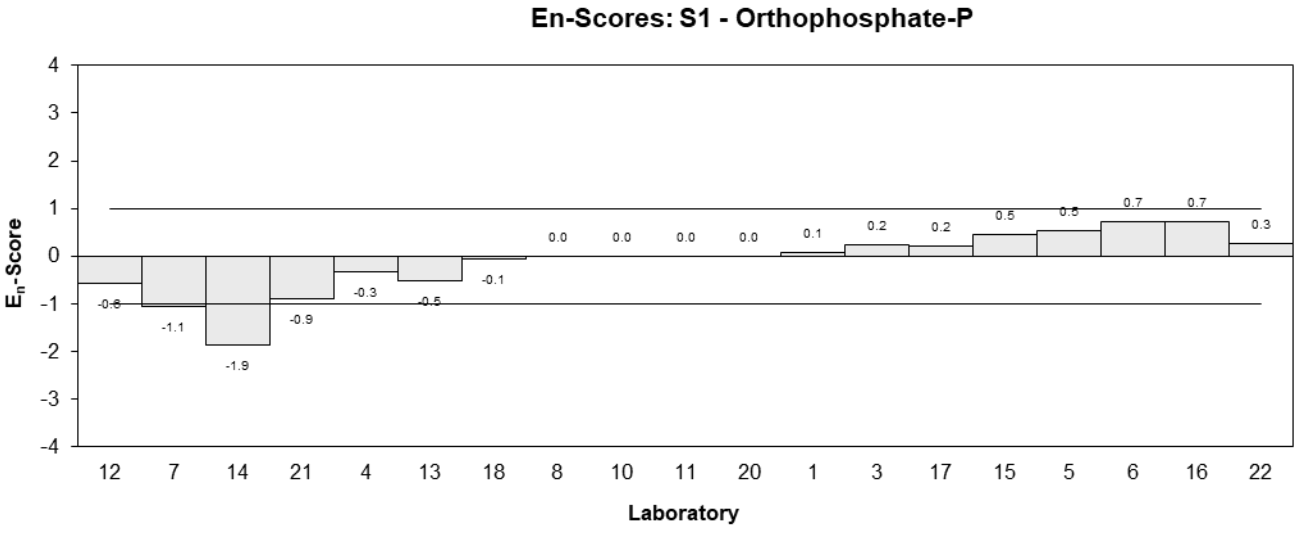

En-Scores: S1 - Orthophosphate-P
En-Score
Laboratory
12 7 14 21 4 13 18 8 10 11 20 1 3 17 15 5 6 16 22

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	10.7	3.21	0.79	0.24
2	9.88	1.21	-0.04	-0.03
3	8.3	1.2	-1.63	-1.31
4	10.1	2.52	0.18	0.07
5	11	1.24	1.09	0.85
6	9.2	0.37	-0.73	-1.53
7	10	1	0.08	0.08
8	NR	NR		
9	9.67	1.93	-0.25	-0.13
10	9.6	1.92	-0.32	-0.16
11	9.8	2.0	-0.12	-0.06
12	10.24	3.07	0.32	0.10
13	<2	NR		
14	10	0.22	0.08	0.22
15	14.1	2.0	4.21	2.07
16	9.7	0.1	-0.22	-0.72
17	8.90	0.52	-1.03	-1.71
18	10	1.05	0.08	0.07
19	9.8	0.7	-0.12	-0.16
20	9.89	0.495	-0.03	-0.05
21	10	2.3	0.08	0.03
22	10.1	1.5	0.18	0.12

Statistics

Assigned Value	9.92	0.29
Spike Value	Not Spiked	
Robust Average	9.92	0.29
Median	9.95	0.17
Mean	10.0	
N	20	
Max	14.1	
Min	8.3	
Robust SD	0.52	
Robust CV	5.2%	

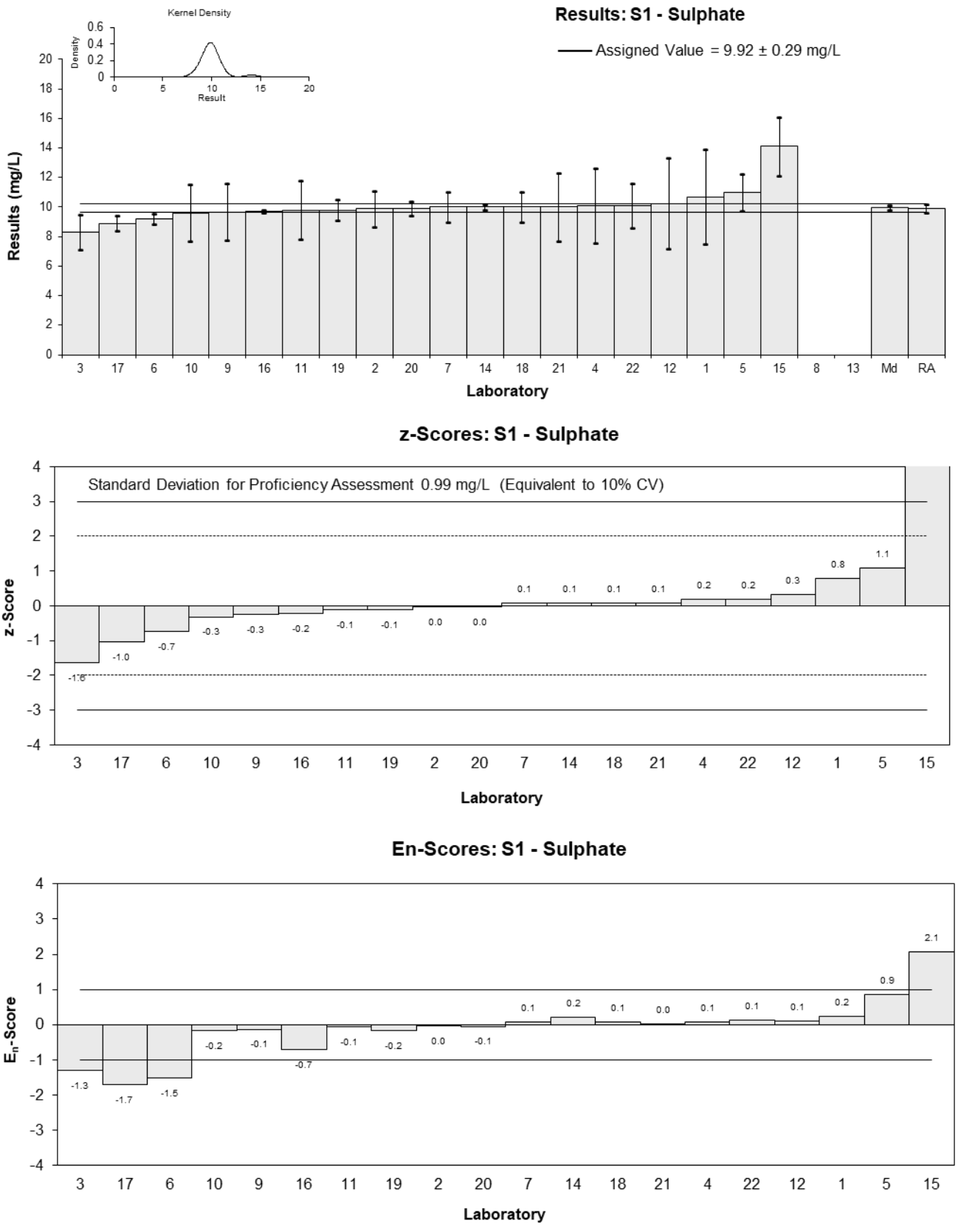

Kernel Density
Density
Result
Results: S1 - Sulphate
Assigned Value = 9.92 ± 0.29 mg/L
Results (mg/L)
Laboratory
3 17 6 10 9 16 11 19 2 20 7 14 18 21 4 22 12 1 5 15 8 13 Md RA
z-Scores: S1 - Sulphate
Standard Deviation for Proficiency Assessment 0.99 mg/L (Equivalent to 10% CV)
z-Score
-1.6 -1.0 -0.7 -0.3 -0.3 -0.2 -0.1 -0.1 0.0 0.0 0.1 0.1 0.1 0.1 0.2 0.2 0.3 0.8 1.1
Laboratory
3 17 6 10 9 16 11 19 2 20 7 14 18 21 4 22 12 1 5 15
En-Scores: S1 - Sulphate
En-Score
-1.3 -1.7 -1.5 -0.2 -0.1 -0.7 -0.1 -0.2 0.0 -0.1 0.1 0.2 0.1 0.0 0.1 0.1 0.1 0.2 0.9 2.1
Laboratory
3 17 6 10 9 16 11 19 2 20 7 14 18 21 4 22 12 1 5 15

Figure 11

Table 14

Sample Details

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

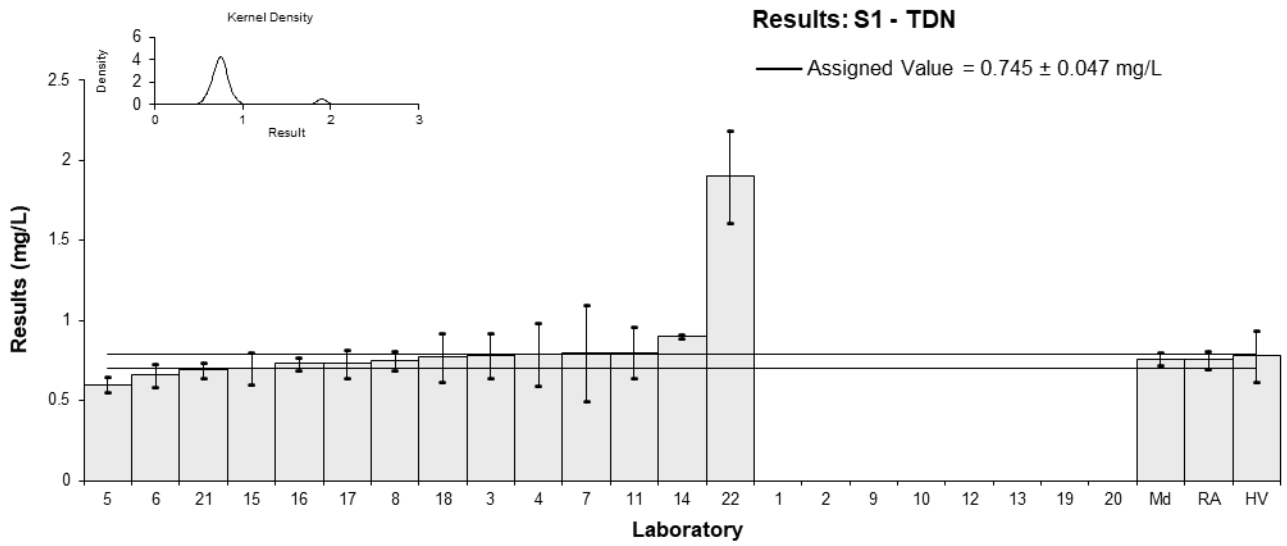
Participant Results

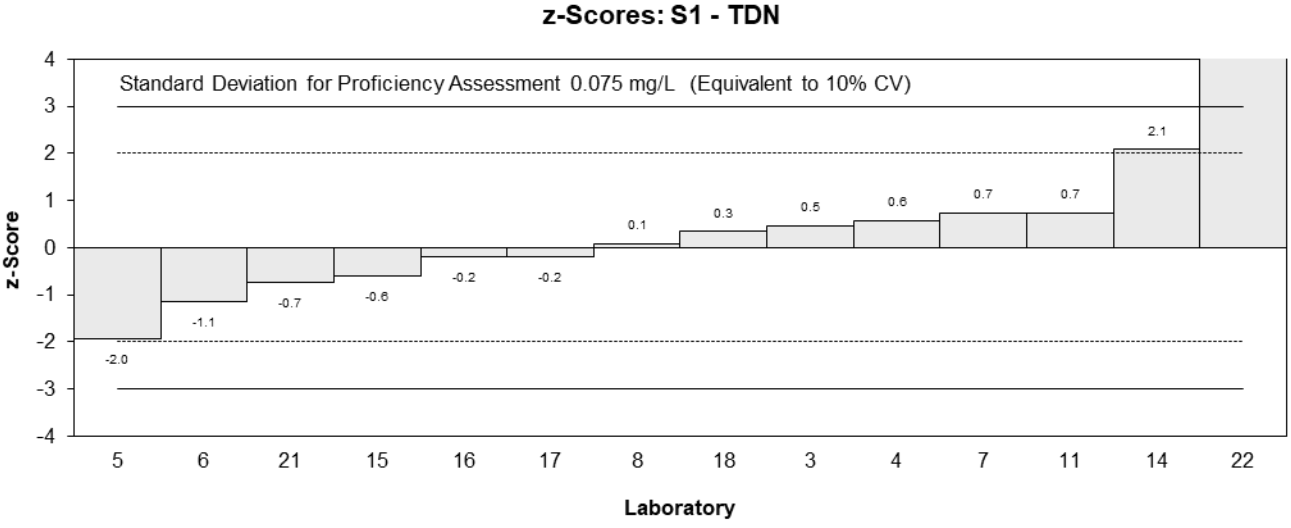
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	0.78	0.14	0.47	0.24
4	0.788	0.197	0.58	0.21
5	0.6	0.05	-1.95	-2.11
6	0.66	0.073	-1.14	-0.98
7	0.8	0.3	0.74	0.18
8	0.75	0.06	0.07	0.07
9	NT	NT		
10	NT	NT		
11	0.8	0.16	0.74	0.33
12	NT	NT		
13	NT	NT		
14	0.9	0.0135	2.08	3.17
15	0.70	0.1	-0.60	-0.41
16	0.73	0.04	-0.20	-0.24
17	0.73	0.09	-0.20	-0.15
18	0.77	0.15	0.34	0.16
19	NT	NT		
20	NR	NR		
21	0.69	0.05	-0.74	-0.80
22*	1.90	0.29	15.50	3.93

* Outlier, see Section 4.2

Statistics

Assigned Value	0.745	0.047
Spike Value	Not Spiked	
Homogeneity Value	0.78	0.16
Robust Average	0.757	0.056
Median	0.760	0.040
Mean	0.83	
N	14	
Max	1.90	
Min	0.6	
Robust SD	0.084	
Robust CV	11%	


Results: S1 - TDN
Assigned Value = 0.745 ± 0.047 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5 6 21 15 16 17 8 18 3 4 7 11 14 22 1 2 9 10 12 13 19 20 Md RA HV


z-Scores: S1 - TDN
Standard Deviation for Proficiency Assessment 0.075 mg/L (Equivalent to 10% CV)
z-Score
-2.0 -1.1 -0.7 -0.6 -0.2 -0.2 0.1 0.3 0.5 0.6 0.7 0.7 2.1
Laboratory
5 6 21 15 16 17 8 18 3 4 7 11 14 22

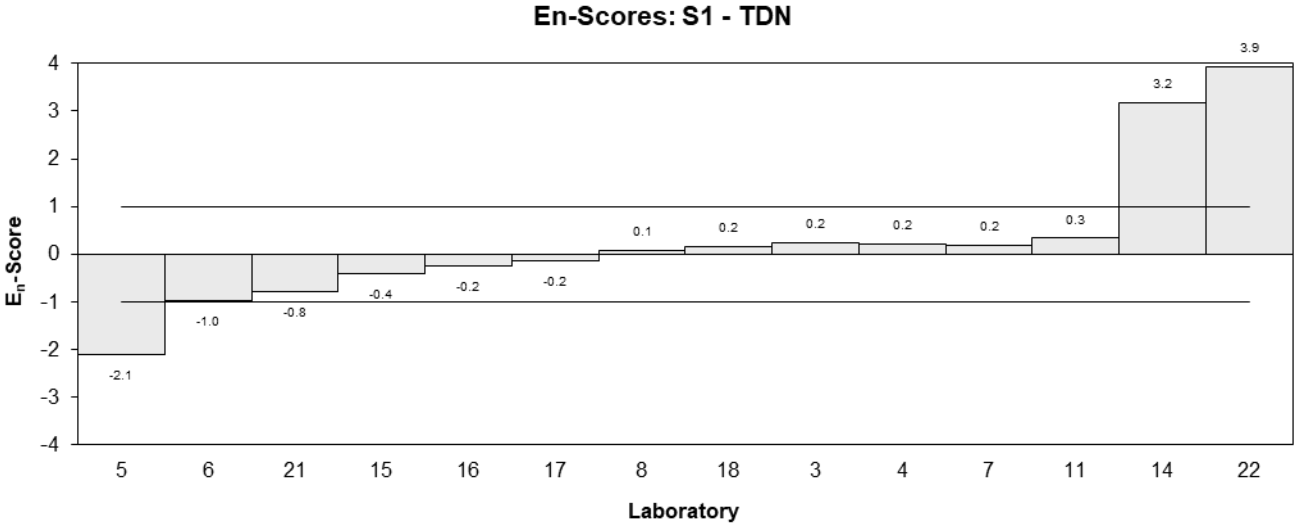

En-Scores: S1 - TDN
En-Score
-2.1 -1.0 -0.8 -0.4 -0.2 -0.2 0.1 0.2 0.2 0.2 0.2 0.3 3.2 3.9
Laboratory
5 6 21 15 16 17 8 18 3 4 7 11 14 22

Figure 12

Table 15

Sample Details

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

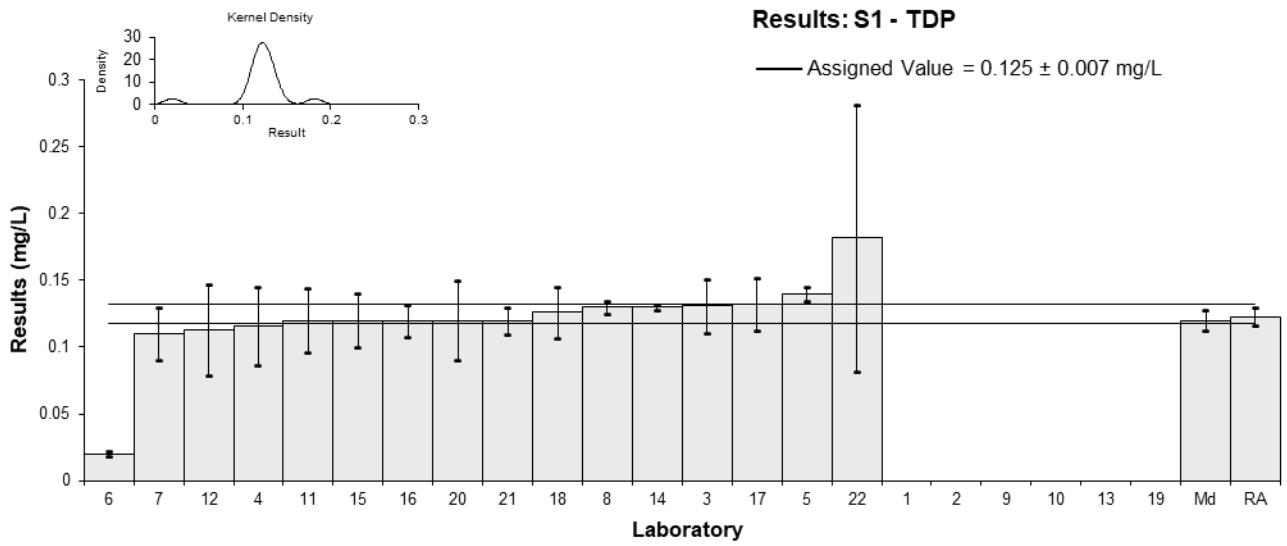
Participant Results

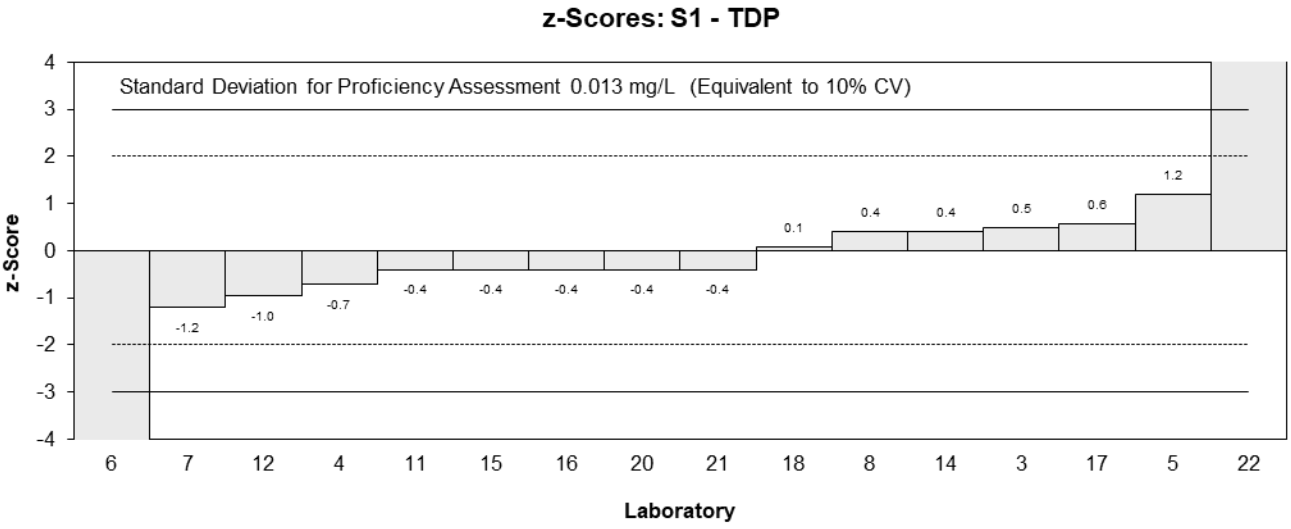
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	0.131	0.020	0.48	0.28
4	0.116	0.029	-0.72	-0.30
5	0.14	0.005	1.20	1.74
6*	0.02	0.002	-8.40	-14.42
7	0.11	0.02	-1.20	-0.71
8	0.13	0.005	0.40	0.58
9	NT	NT		
10	NT	NT		
11	0.12	0.024	-0.40	-0.20
12	0.113	0.0339	-0.96	-0.35
13	NT	NT		
14	0.13	0.002	0.40	0.69
15	0.12	0.02	-0.40	-0.24
16	0.12	0.012	-0.40	-0.36
17	0.132	0.020	0.56	0.33
18	0.126	0.019	0.08	0.05
19	NT	NT		
20	0.12	0.03	-0.40	-0.16
21	0.12	0.01	-0.40	-0.41
22	0.182	0.1	4.56	0.57

* Outlier, see Section 4.2

Statistics

Assigned Value	0.125	0.007
Spike Value	Not Spiked	
Robust Average	0.123	0.007
Median	0.120	0.008
Mean	0.121	
N	16	
Max	0.182	
Min	0.02	
Robust SD	0.011	
Robust CV	9.1%	


Results: S1 - TDP
Assigned Value = 0.125 ± 0.007 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6 7 12 4 11 15 16 20 21 18 8 14 3 17 5 22 1 2 9 10 13 19 Md RA


z-Scores: S1 - TDP
Standard Deviation for Proficiency Assessment 0.013 mg/L (Equivalent to 10% CV)
z-Score
-1.2 -1.0 -0.7 -0.4 -0.4 -0.4 -0.4 -0.4 0.1 0.4 0.4 0.5 0.6 1.2
Laboratory
6 7 12 4 11 15 16 20 21 18 8 14 3 17 5 22

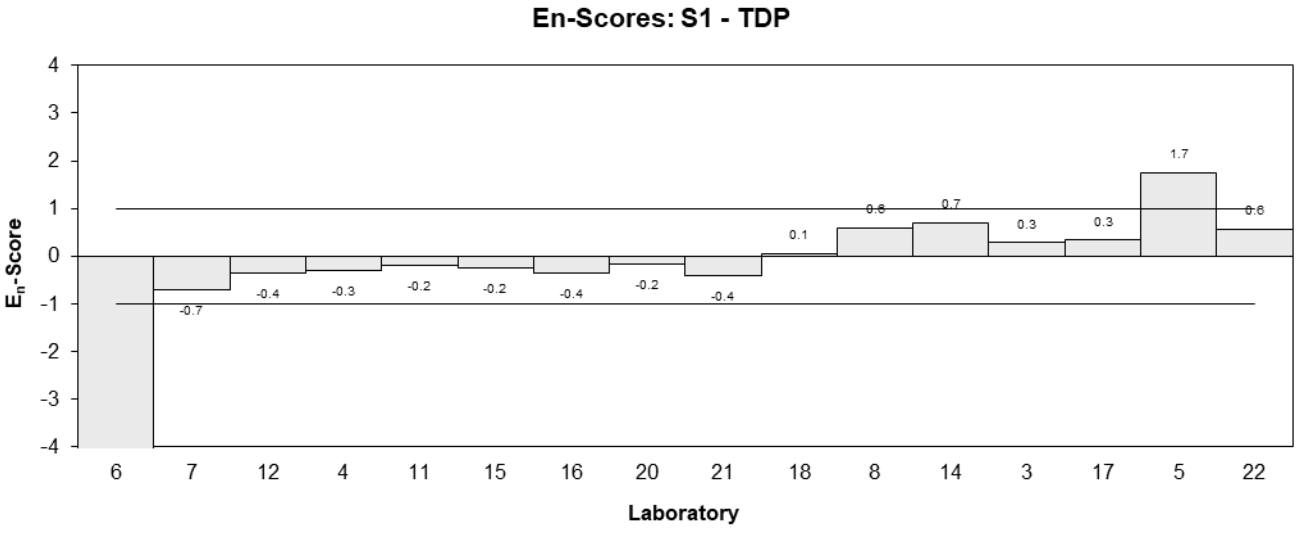

En-Scores: S1 - TDP
En-Score
-0.7 -0.4 -0.3 -0.2 -0.2 -0.4 -0.2 -0.4 0.1 0.6 0.7 0.3 0.3 1.7 0.6
Laboratory
6 7 12 4 11 15 16 20 21 18 8 14 3 17 5 22

Figure 13

Table 16

Sample Details

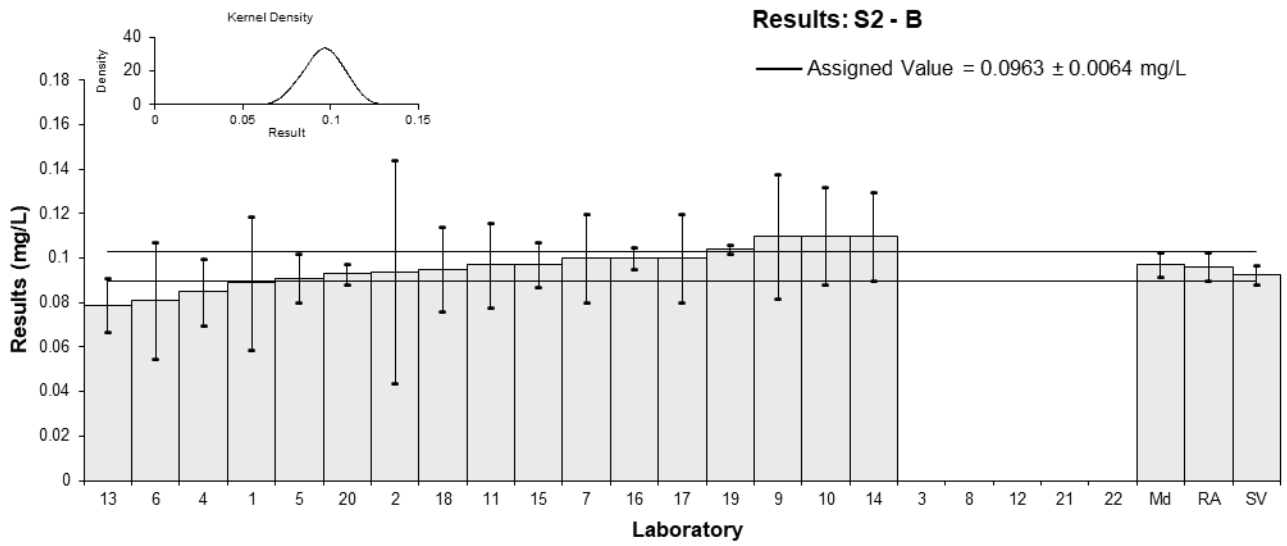
Sample No.	S2
Matrix	Potable Water
Analyte	B
Unit	mg/L

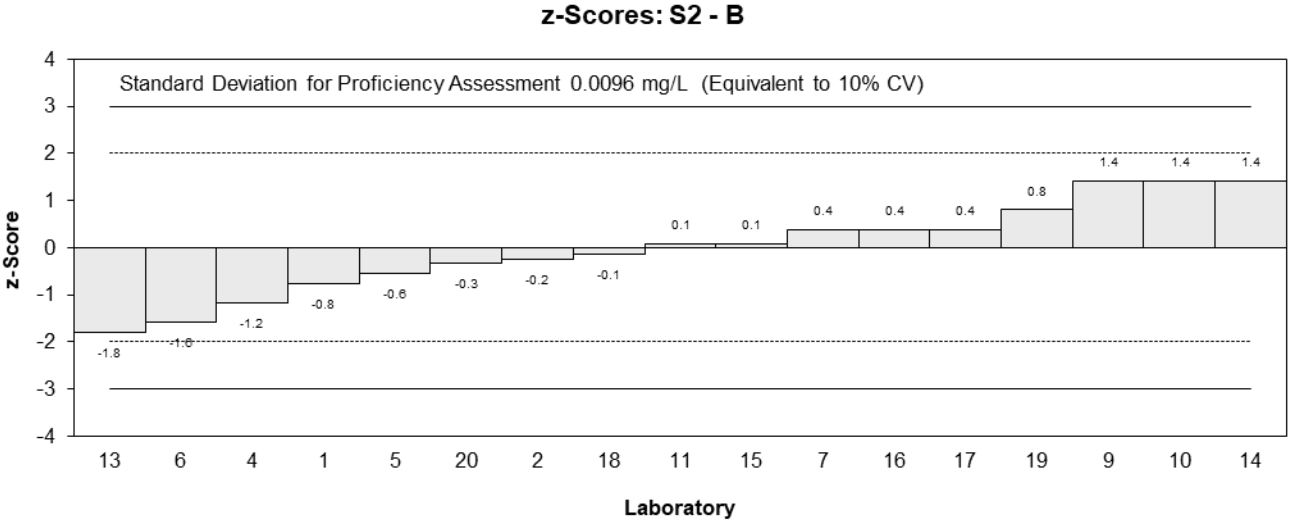
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.089	0.03	-0.76	-0.24
2	0.094	0.05	-0.24	-0.05
3	NT	NT		
4	0.085	0.015	-1.17	-0.69
5	0.091	0.011	-0.55	-0.42
6	0.081	0.026	-1.59	-0.57
7	0.10	0.02	0.38	0.18
8	NR	NR		
9	0.11	0.028	1.42	0.48
10	0.11	0.022	1.42	0.60
11	0.097	0.019	0.07	0.03
12	< 0.5	NR		
13	0.079	0.0119	-1.80	-1.28
14	0.11	0.02	1.42	0.65
15	0.097	0.01	0.07	0.06
16	0.10	0.005	0.38	0.46
17	0.10	0.02	0.38	0.18
18	0.095	0.019	-0.13	-0.06
19	0.104	0.002	0.80	1.15
20	0.093	0.00465	-0.34	-0.42
21	NT	NT		
22	NT	NT		

Statistics

Assigned Value	0.0963	0.0064
Spike Value	0.0924	0.0043
Robust Average	0.0963	0.0064
Median	0.0970	0.0054
Mean	0.0962	
N	17	
Max	0.11	
Min	0.079	
Robust SD	0.01	
Robust CV	11%	


Results: S2 - B
Assigned Value = 0.0963 ± 0.0064 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
13 6 4 1 5 20 2 18 11 15 7 16 17 19 9 10 14 3 8 12 21 22 Md RA SV


z-Scores: S2 - B
Standard Deviation for Proficiency Assessment 0.0096 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
13 6 4 1 5 20 2 18 11 15 7 16 17 19 9 10 14
-1.8 -1.6 -1.2 -0.8 -0.6 -0.3 -0.2 -0.1 0.1 0.1 0.4 0.4 0.4 0.8 1.4 1.4 1.4

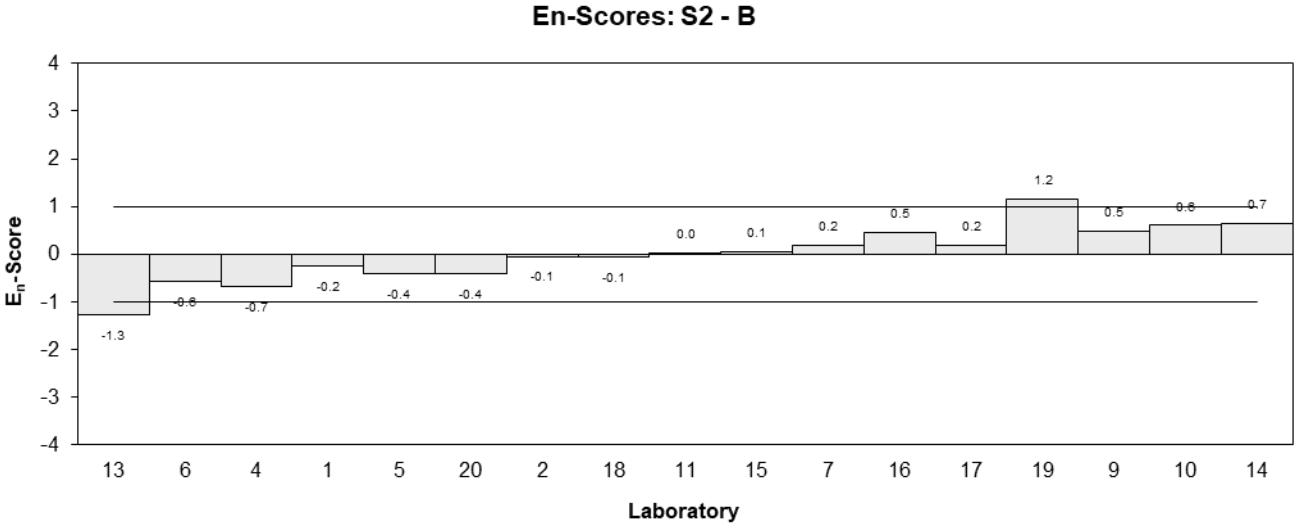

En-Scores: S2 - B
En-Score
Laboratory
13 6 4 1 5 20 2 18 11 15 7 16 17 19 9 10 14
-1.3 -0.6 -0.7 -0.2 -0.4 -0.4 -0.1 -0.1 0.0 0.1 0.2 0.5 0.2 1.2 0.5 0.6 0.7

Figure 14

Table 17

Sample Details

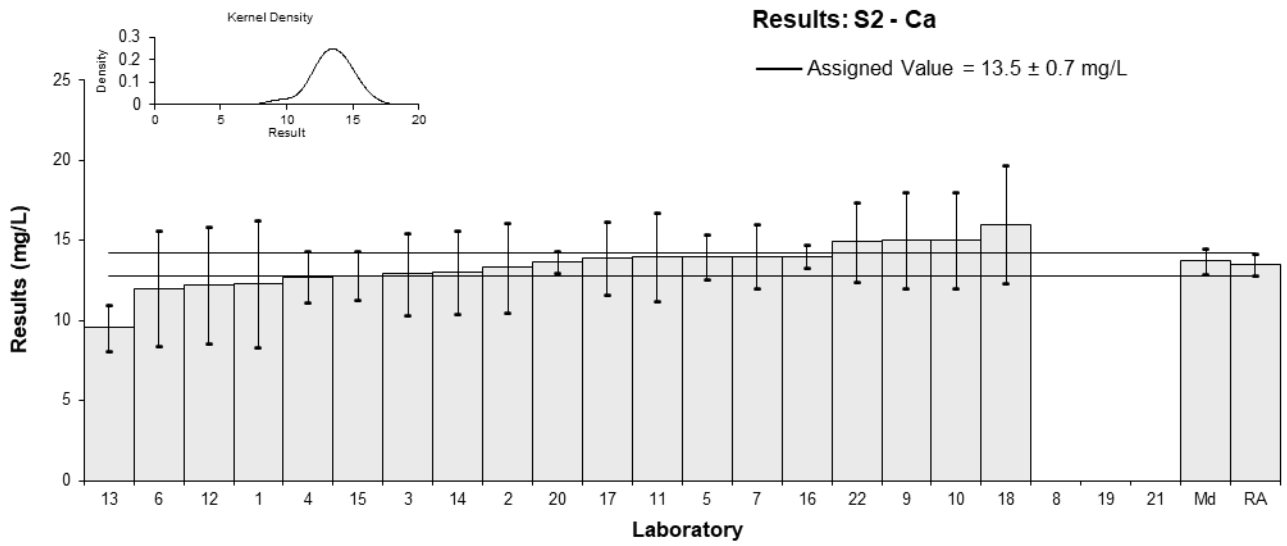
Sample No.	S2
Matrix	Potable Water
Analyte	Ca
Unit	mg/L

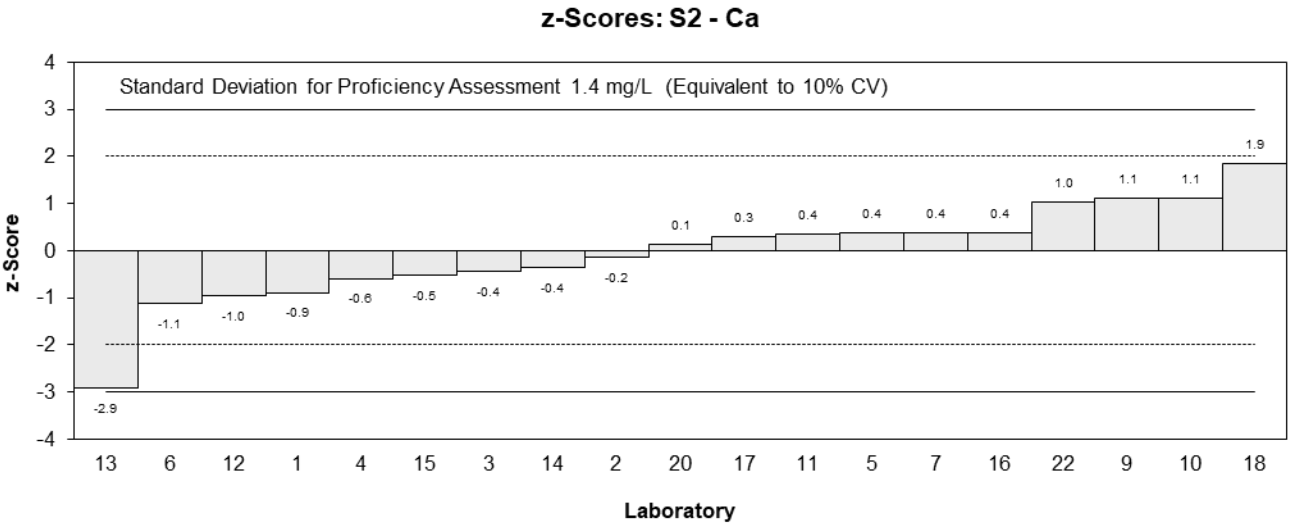
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	12.3	4	-0.89	-0.30
2	13.3	2.8	-0.15	-0.07
3	12.9	2.6	-0.44	-0.22
4	12.7	1.6	-0.59	-0.46
5	14	1.4	0.37	0.32
6	12	3.6	-1.11	-0.41
7	14	2	0.37	0.24
8	NR	NR		
9	15	3.0	1.11	0.49
10	15	3	1.11	0.49
11	13.97	2.79	0.35	0.16
12	12.2	3.66	-0.96	-0.35
13	9.55	1.43	-2.93	-2.48
14	13	2.6	-0.37	-0.19
15	12.8	1.5	-0.52	-0.42
16	14	0.7	0.37	0.51
17	13.9	2.3	0.30	0.17
18	16	3.7	1.85	0.66
19	NT	NT		
20	13.69	0.685	0.14	0.19
21	NT	NT		
22	14.9	2.5	1.04	0.54

Statistics

Assigned Value	13.5	0.7
Spike Value	Not Spiked	
Robust Average	13.5	0.7
Median	13.7	0.8
Mean	13.4	
N	19	
Max	16	
Min	9.55	
Robust SD	1.2	
Robust CV	9.2%	


Kernel Density
Density
Result
Results: S2 - Ca
Assigned Value = 13.5 ± 0.7 mg/L
Results (mg/L)
13 6 12 1 4 15 3 14 2 20 17 11 5 7 16 22 9 10 18 8 19 21 Md RA
Laboratory


z-Scores: S2 - Ca
Standard Deviation for Proficiency Assessment 1.4 mg/L (Equivalent to 10% CV)
z-Score
-2.9 -1.1 -1.0 -0.9 -0.6 -0.5 -0.4 -0.4 -0.2 0.1 0.3 0.4 0.4 0.4 0.4 1.0 1.1 1.1 1.9
13 6 12 1 4 15 3 14 2 20 17 11 5 7 16 22 9 10 18
Laboratory

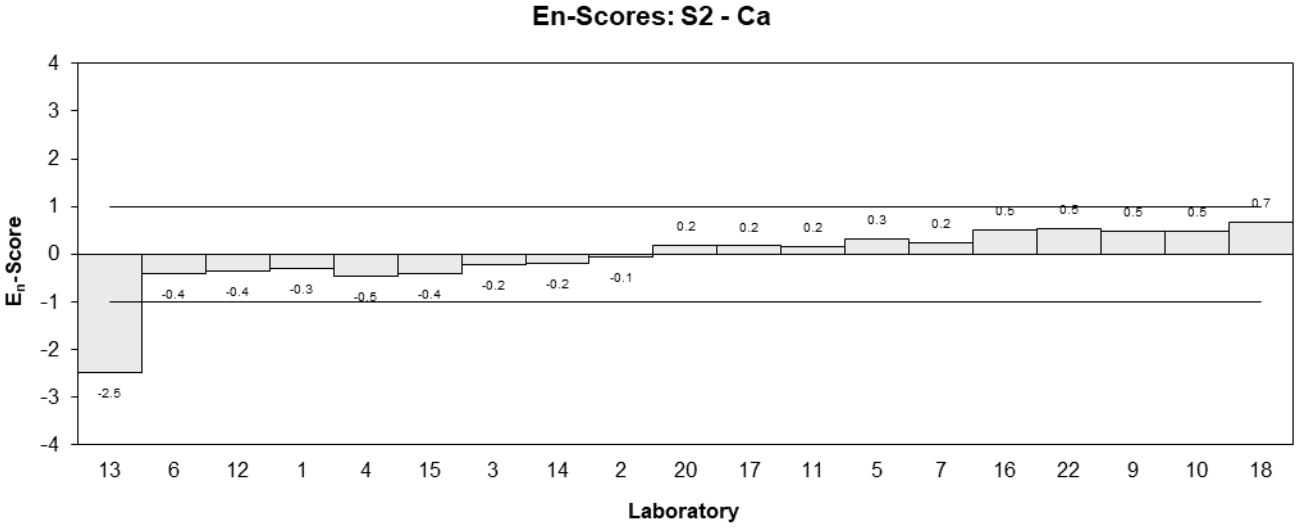

En-Scores: S2 - Ca
En-Score
-2.5 -0.4 -0.4 -0.3 -0.5 -0.4 -0.2 -0.2 -0.1 0.2 0.2 0.2 0.3 0.2 0.5 0.5 0.5 0.5 0.7
13 6 12 1 4 15 3 14 2 20 17 11 5 7 16 22 9 10 18
Laboratory

Figure 15

Table 18

Sample Details

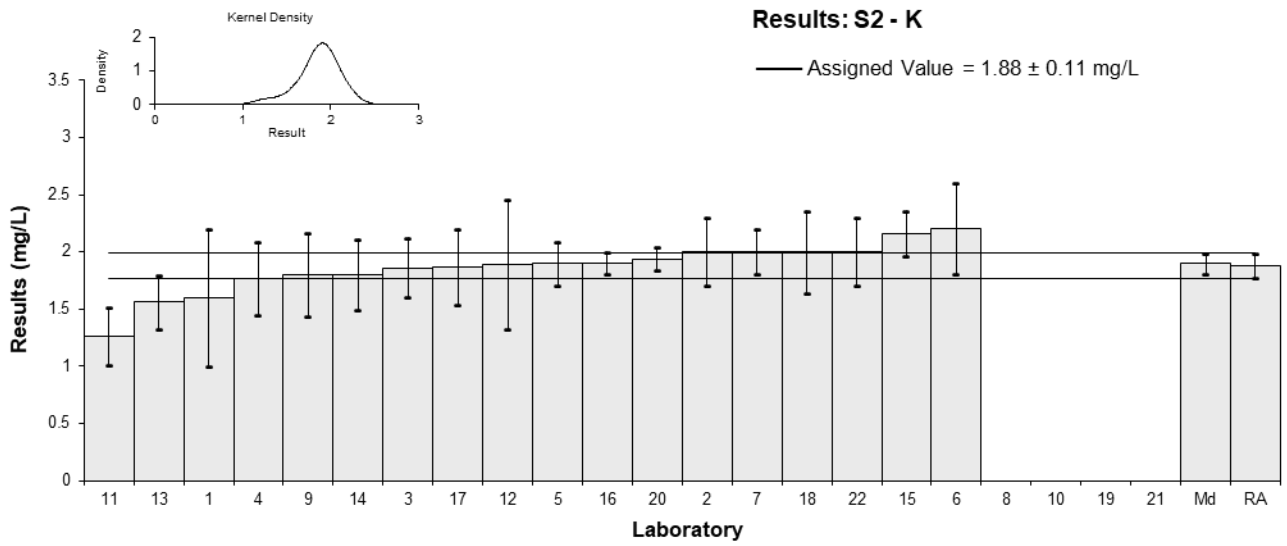
Sample No.	S2
Matrix	Potable Water
Analyte	K
Unit	mg/L

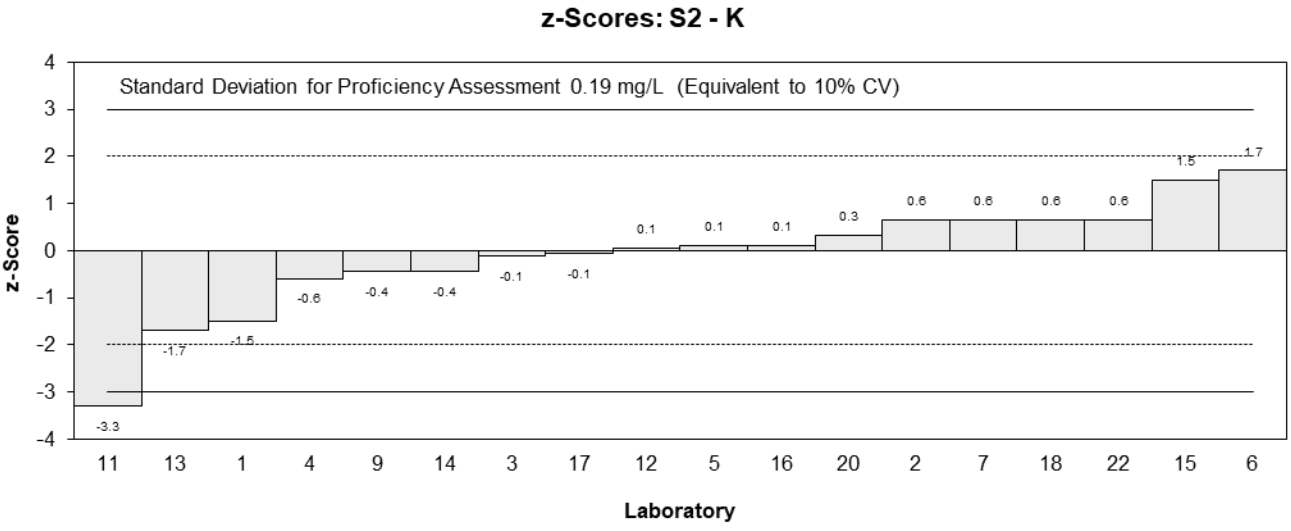
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.6	0.6	-1.49	-0.46
2	2.00	0.30	0.64	0.38
3	1.86	0.26	-0.11	-0.07
4	1.77	0.32	-0.59	-0.33
5	1.9	0.19	0.11	0.09
6	2.2	0.4	1.70	0.77
7	2	0.2	0.64	0.53
8	NR	NR		
9	1.8	0.36	-0.43	-0.21
10	NT	NT		
11	1.26	0.25	-3.30	-2.27
12	1.89	0.567	0.05	0.02
13	1.56	0.234	-1.70	-1.24
14	1.8	0.313	-0.43	-0.24
15	2.16	0.2	1.49	1.23
16	1.9	0.10	0.11	0.13
17	1.87	0.33	-0.05	-0.03
18	2	0.36	0.64	0.32
19	NT	NT		
20	1.94	0.097	0.32	0.41
21	NT	NT		
22	2.0	0.3	0.64	0.38

Statistics

Assigned Value	1.88	0.11
Spike Value	Not Spiked	
Robust Average	1.88	0.11
Median	1.90	0.09
Mean	1.86	
N	18	
Max	2.2	
Min	1.26	
Robust SD	0.19	
Robust CV	10%	


Kernel Density
Density
Result
Results: S2 - K
Assigned Value = 1.88 ± 0.11 mg/L
Results (mg/L)
Laboratory
11 13 1 4 9 14 3 17 12 5 16 20 2 7 18 22 15 6 8 10 19 21 Md RA


z-Scores: S2 - K
Standard Deviation for Proficiency Assessment 0.19 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 13 1 4 9 14 3 17 12 5 16 20 2 7 18 22 15 6
-3.3 -1.7 -1.5 -0.6 -0.4 -0.4 -0.1 -0.1 0.1 0.1 0.1 0.3 0.6 0.6 0.6 0.6 1.5 1.7

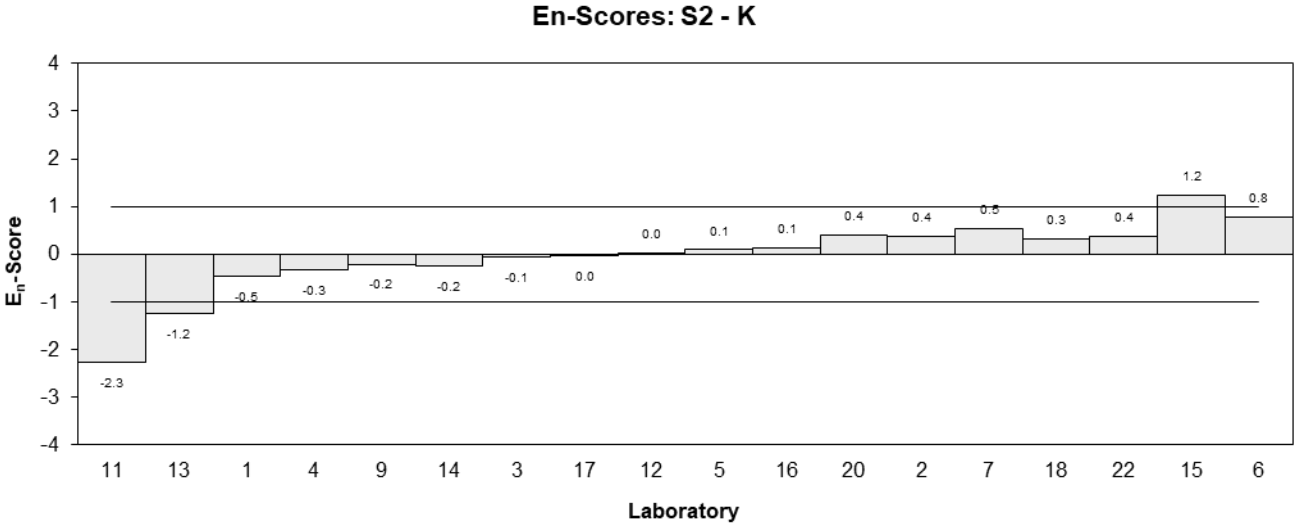

En-Scores: S2 - K
En-Score
Laboratory
11 13 1 4 9 14 3 17 12 5 16 20 2 7 18 22 15 6
-2.3 -1.2 -0.5 -0.3 -0.2 -0.2 -0.1 0.0 0.0 0.1 0.1 0.4 0.4 0.5 0.3 0.4 1.2 0.8

Figure 16

Table 19

Sample Details

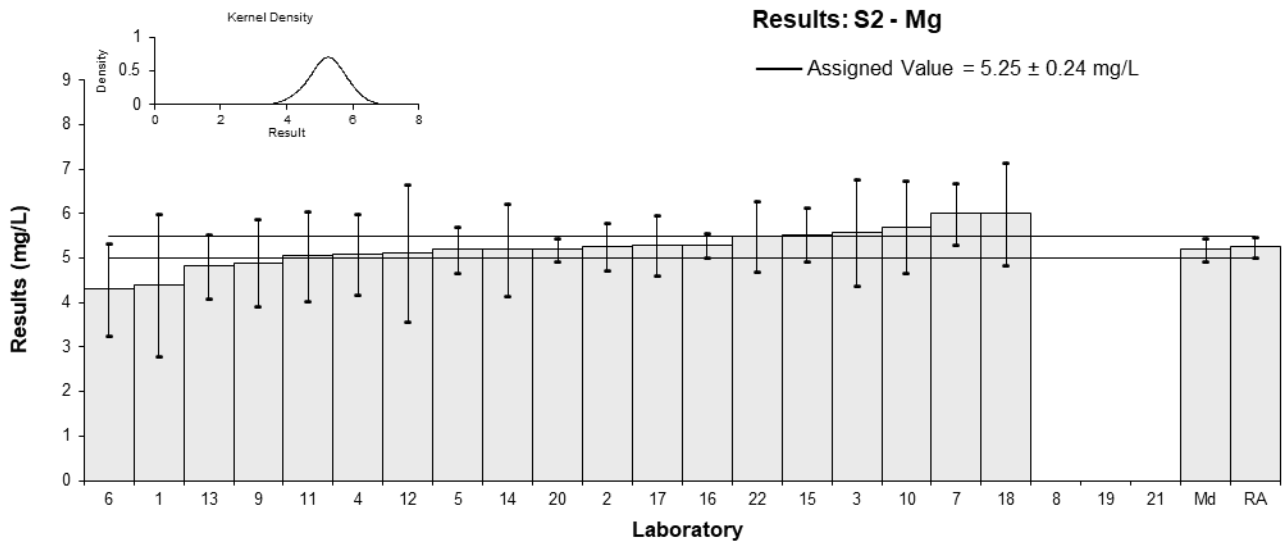
Sample No.	S2
Matrix	Potable Water
Analyte	Mg
Unit	mg/L

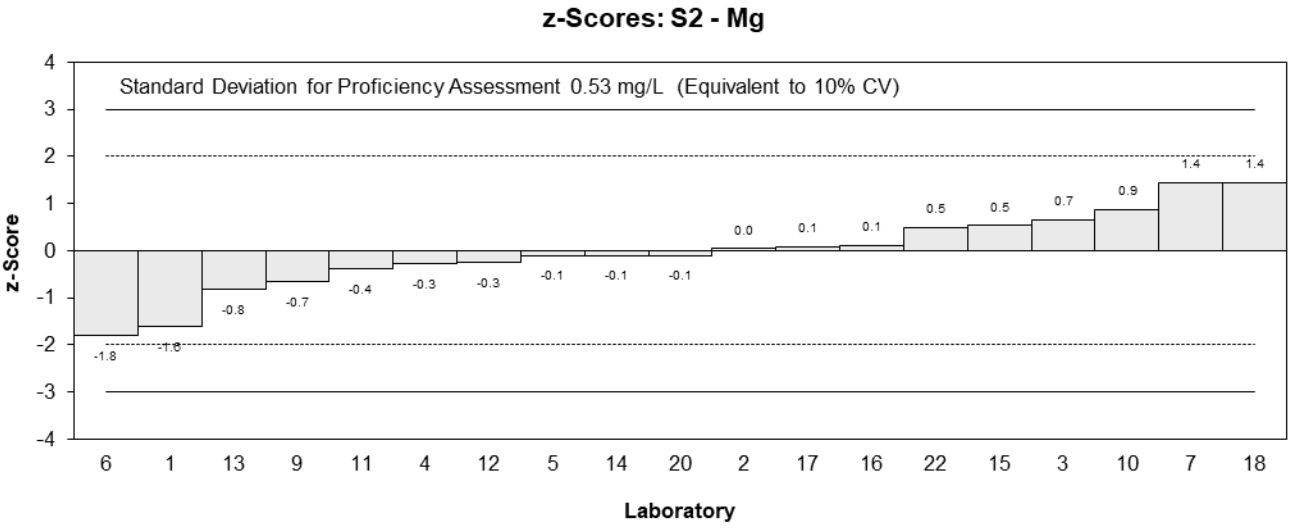
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.4	1.6	-1.62	-0.53
2	5.27	0.53	0.04	0.03
3	5.59	1.2	0.65	0.28
4	5.10	0.91	-0.29	-0.16
5	5.2	0.52	-0.10	-0.09
6	4.3	1.03	-1.81	-0.90
7	6	0.7	1.43	1.01
8	NR	NR		
9	4.9	0.97	-0.67	-0.35
10	5.7	1.04	0.86	0.42
11	5.05	1.01	-0.38	-0.19
12	5.12	1.536	-0.25	-0.08
13	4.82	0.723	-0.82	-0.56
14	5.2	1.04	-0.10	-0.05
15	5.53	0.6	0.53	0.43
16	5.3	0.27	0.10	0.14
17	5.29	0.68	0.08	0.06
18	6	1.16	1.43	0.63
19	NT	NT		
20	5.20	0.26	-0.10	-0.14
21	NT	NT		
22	5.5	0.8	0.48	0.30

Statistics

Assigned Value	5.25	0.24
Spike Value	Not Spiked	
Robust Average	5.25	0.24
Median	5.20	0.26
Mean	5.24	
N	19	
Max	6	
Min	4.3	
Robust SD	0.41	
Robust CV	7.9%	


Results: S2 - Mg
Assigned Value = 5.25 ± 0.24 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6 1 13 9 11 4 12 5 14 20 2 17 16 22 15 3 10 7 18 8 19 21 Md RA


z-Scores: S2 - Mg
Standard Deviation for Proficiency Assessment 0.53 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
6 1 13 9 11 4 12 5 14 20 2 17 16 22 15 3 10 7 18
-1.8 -1.6 -0.8 -0.7 -0.4 -0.3 -0.3 -0.1 -0.1 -0.1 0.0 0.1 0.1 0.5 0.5 0.7 0.9 1.4 1.4

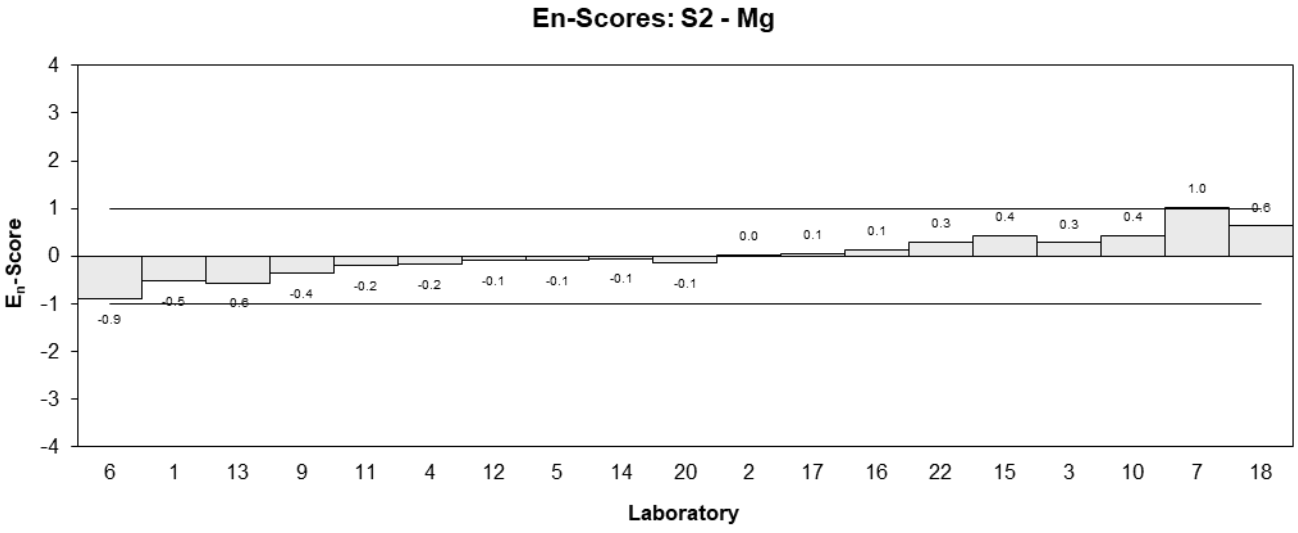

En-Scores: S2 - Mg
En-Score
Laboratory
6 1 13 9 11 4 12 5 14 20 2 17 16 22 15 3 10 7 18
-0.9 -0.5 -0.6 -0.4 -0.2 -0.2 -0.1 -0.1 -0.1 -0.1 0.0 0.1 0.1 0.3 0.4 0.3 0.4 1.0 0.6

Figure 17

Table 20

Sample Details

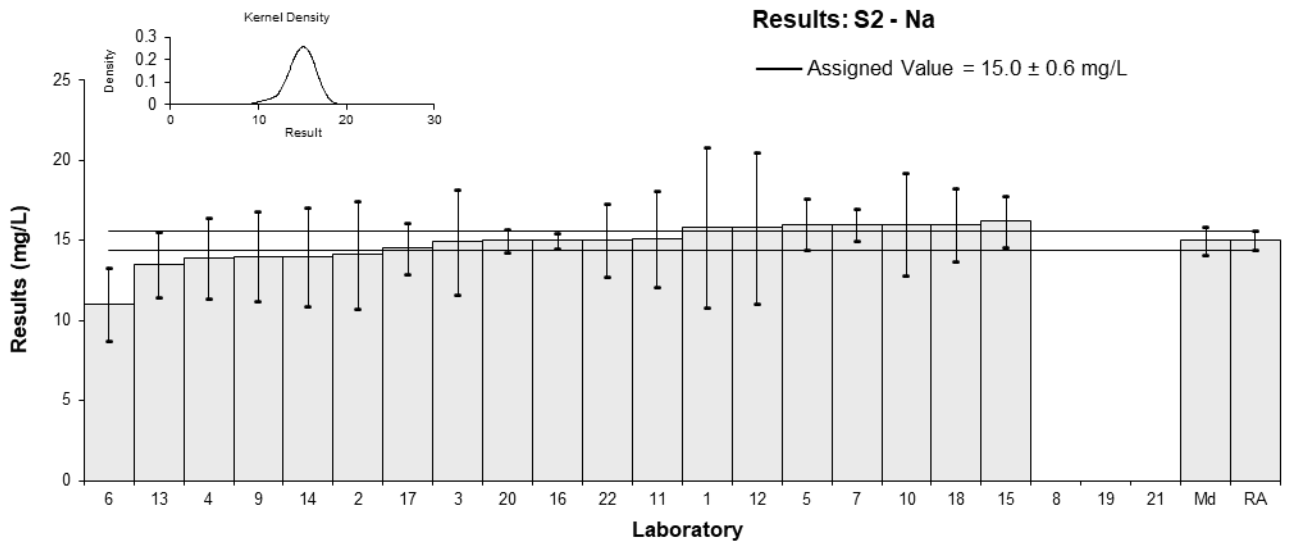
Sample No.	S2
Matrix	Potable Water
Analyte	Na
Unit	mg/L

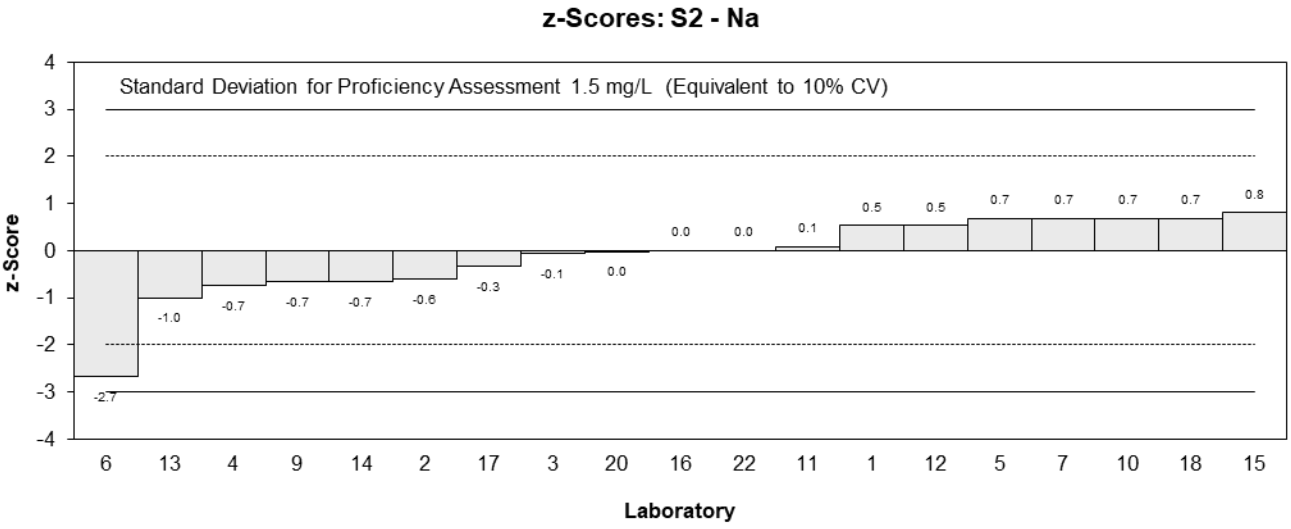
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	15.8	5	0.53	0.16
2	14.1	3.4	-0.60	-0.26
3	14.9	3.3	-0.07	-0.03
4	13.9	2.5	-0.73	-0.43
5	16	1.6	0.67	0.59
6	11	2.3	-2.67	-1.68
7	16	1	0.67	0.86
8	NR	NR		
9	14	2.81	-0.67	-0.35
10	16	3.2	0.67	0.31
11	15.1	3.0	0.07	0.03
12	15.8	4.74	0.53	0.17
13	13.5	2.03	-1.00	-0.71
14	14	3.1	-0.67	-0.32
15	16.2	1.6	0.80	0.70
16	15	0.5	0.00	0.00
17	14.5	1.6	-0.33	-0.29
18	16	2.3	0.67	0.42
19	NT	NT		
20	14.99	0.750	-0.01	-0.01
21	NT	NT		
22	15.0	2.3	0.00	0.00

Statistics

Assigned Value	15.0	0.6
Spike Value	Not Spiked	
Robust Average	15.0	0.6
Median	15.0	0.9
Mean	14.8	
N	19	
Max	16.2	
Min	11	
Robust SD	1.1	
Robust CV	7.1%	


Kernel Density
Density
Result
Results: S2 - Na
Assigned Value = 15.0 ± 0.6 mg/L
Results (mg/L)
Laboratory
6 13 4 9 14 2 17 3 20 16 22 11 1 12 5 7 10 18 15 8 19 21 Md RA


z-Scores: S2 - Na
Standard Deviation for Proficiency Assessment 1.5 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
6 13 4 9 14 2 17 3 20 16 22 11 1 12 5 7 10 18 15
-2.7 -1.0 -0.7 -0.7 -0.7 -0.6 -0.3 -0.1 0.0 0.0 0.0 0.1 0.5 0.5 0.7 0.7 0.7 0.7 0.8

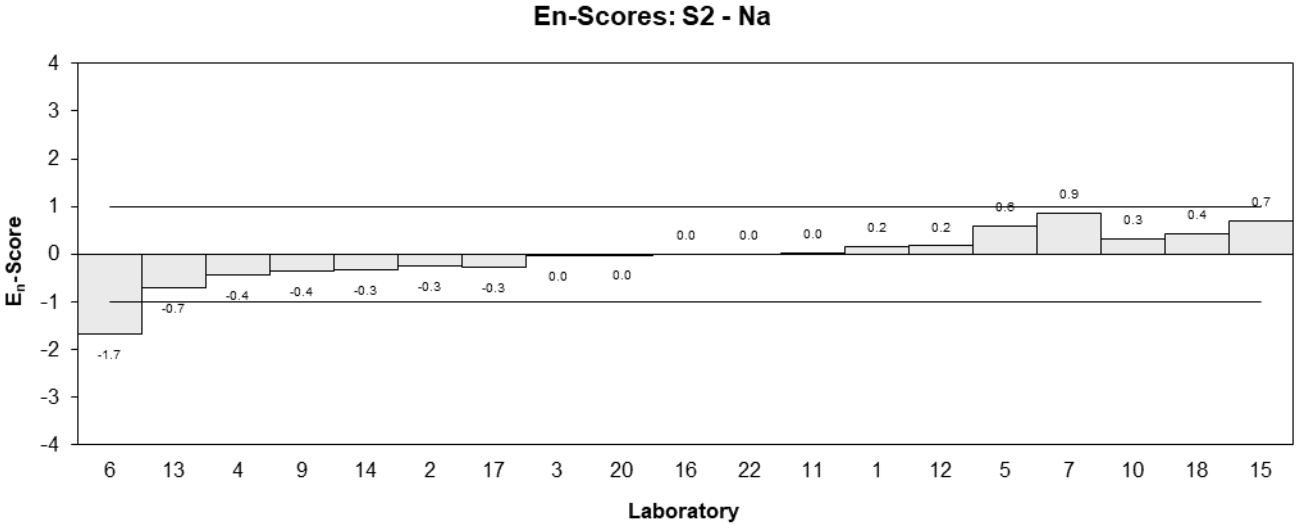

En-Scores: S2 - Na
En-Score
Laboratory
6 13 4 9 14 2 17 3 20 16 22 11 1 12 5 7 10 18 15
-1.7 -0.7 -0.4 -0.4 -0.3 -0.3 -0.3 0.0 0.0 0.0 0.0 0.0 0.2 0.2 0.6 0.9 0.3 0.4 0.7

Figure 18

Table 21

Sample Details

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

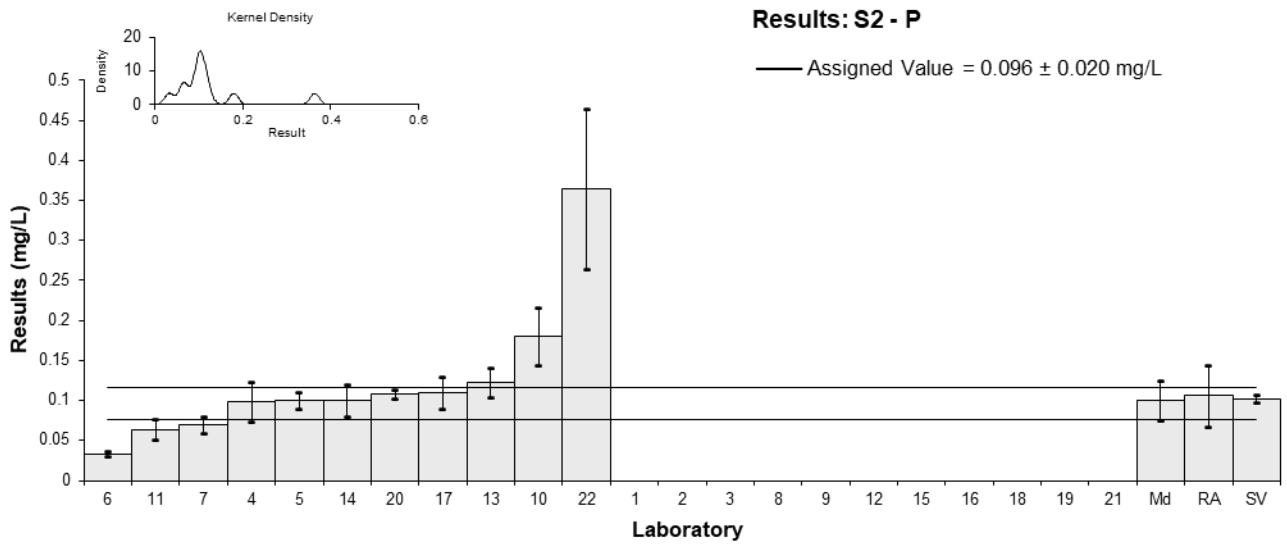
Participant Results

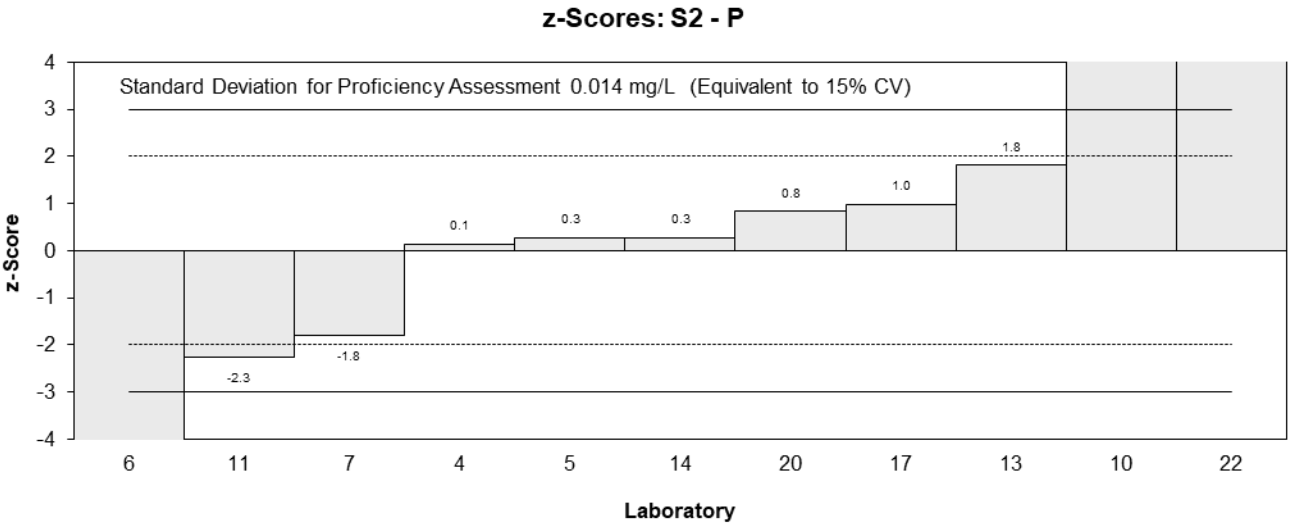
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	<0.1	NR		
3	NT	NT		
4	0.098	0.025	0.14	0.06
5	0.10	0.01	0.28	0.18
6*	0.033	0.0033	-4.38	-3.11
7	0.07	0.01	-1.81	-1.16
8	NR	NR		
9	< 0.5	NR		
10*	0.18	0.036	5.83	2.04
11	0.0635	0.013	-2.26	-1.36
12	< 0.5	NR		
13	0.122	0.0183	1.81	0.96
14	0.1	0.02	0.28	0.14
15	NT	NT		
16	<0.5	NR		
17	0.11	0.02	0.97	0.49
18	<1	0.2		
19	<1.5	0.7		
20	0.108	0.005	0.83	0.58
21	NT	NT		
22*	0.364	0.1	18.61	2.63

* Outlier, see Section 4.2

Statistics

Assigned Value	0.096	0.020
Spike Value	0.102	0.005
Robust Average	0.106	0.038
Median	0.100	0.025
Mean	0.123	
N	11	
Max	0.364	
Min	0.033	
Robust SD	0.051	
Robust CV	48%	


Results: S2 - P
Assigned Value = 0.096 ± 0.020 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6 11 7 4 5 14 20 17 13 10 22 1 2 3 8 9 12 15 16 18 19 21 Md RA SV


z-Scores: S2 - P
Standard Deviation for Proficiency Assessment 0.014 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
6 11 7 4 5 14 20 17 13 10 22
-2.3
-1.8
0.1
0.3
0.3
0.8
1.0
1.8

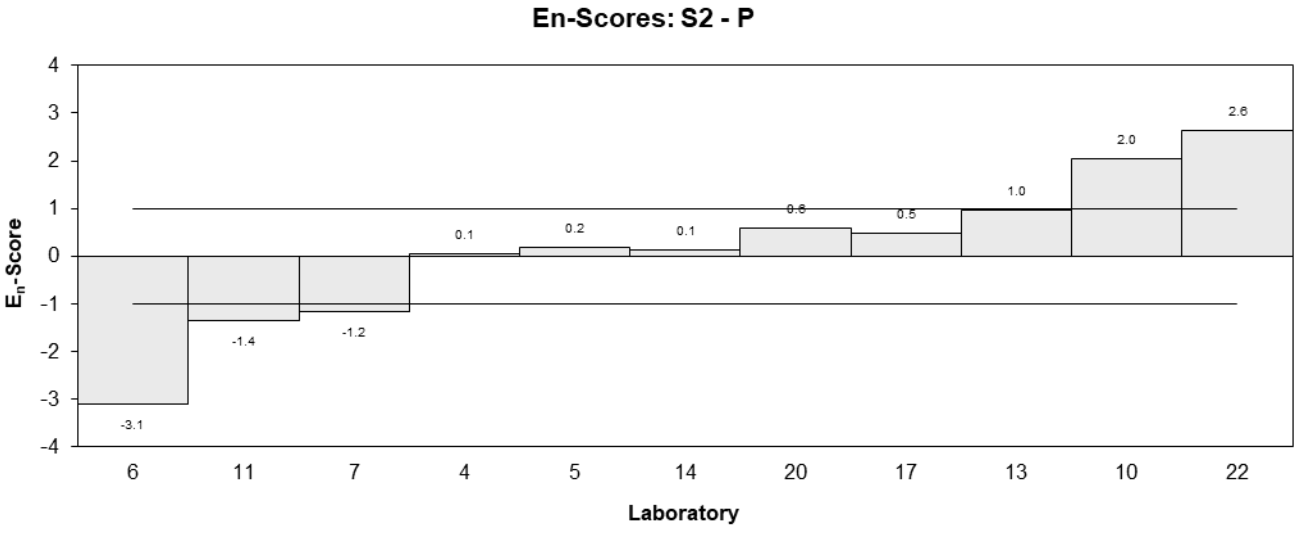

En-Scores: S2 - P
En-Score
Laboratory
6 11 7 4 5 14 20 17 13 10 22
-3.1
-1.4
-1.2
0.1
0.2
0.1
0.6
0.5
1.0
2.0
2.6

Figure 19

Table 22

Sample Details

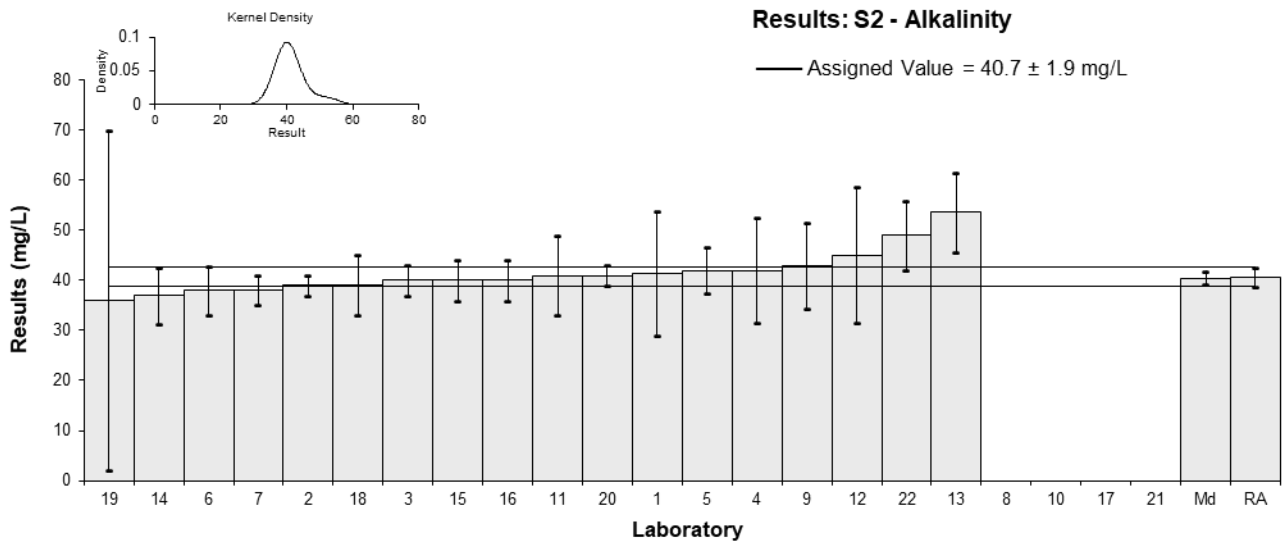
Sample No.	S2
Matrix	Potable Water
Analyte	Alkalinity
Unit	mg/L

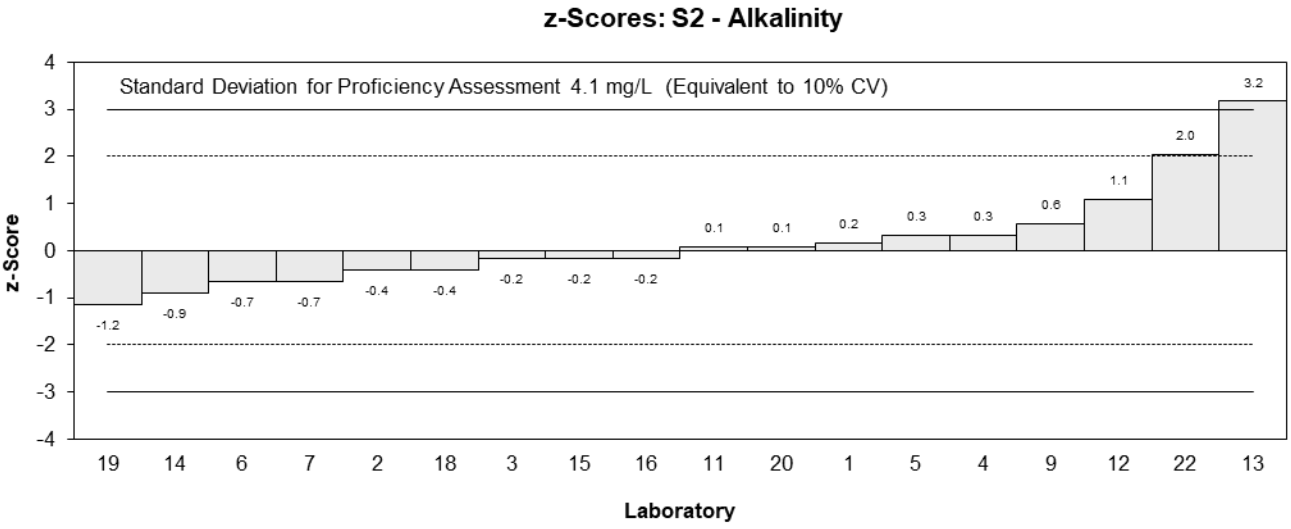
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	41.4	12.42	0.17	0.06
2	39	2	-0.42	-0.62
3	40	3	-0.17	-0.20
4	42.01	10.5	0.32	0.12
5	42	4.6	0.32	0.26
6	38	4.9	-0.66	-0.51
7	38	3	-0.66	-0.76
8	NR	NR		
9	43.00	8.6	0.57	0.26
10	NT	NT		
11	41	8	0.07	0.04
12	45.1	13.5	1.08	0.32
13	53.6	8.04	3.17	1.56
14	37	5.6	-0.91	-0.63
15	40	4.0	-0.17	-0.16
16	40	4	-0.17	-0.16
17	NR	NR		
18	39	6	-0.42	-0.27
19	36	34	-1.15	-0.14
20	41	2	0.07	0.11
21	NT	NT		
22	49	7	2.04	1.14

Statistics

Assigned Value	40.7	1.9
Spike Value	Not Spiked	
Robust Average	40.7	1.9
Median	40.5	1.3
Mean	41.4	
N	18	
Max	53.6	
Min	36	
Robust SD	3.2	
Robust CV	7.8%	


Results: S2 - Alkalinity
Assigned Value = 40.7 ± 1.9 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
19 14 6 7 2 18 3 15 16 11 20 1 5 4 9 12 22 13 8 10 17 21 Md RA


z-Scores: S2 - Alkalinity
Standard Deviation for Proficiency Assessment 4.1 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
19 14 6 7 2 18 3 15 16 11 20 1 5 4 9 12 22 13
-1.2 -0.9 -0.7 -0.7 -0.4 -0.4 -0.2 -0.2 -0.2 0.1 0.1 0.2 0.3 0.3 0.6 1.1 2.0 3.2

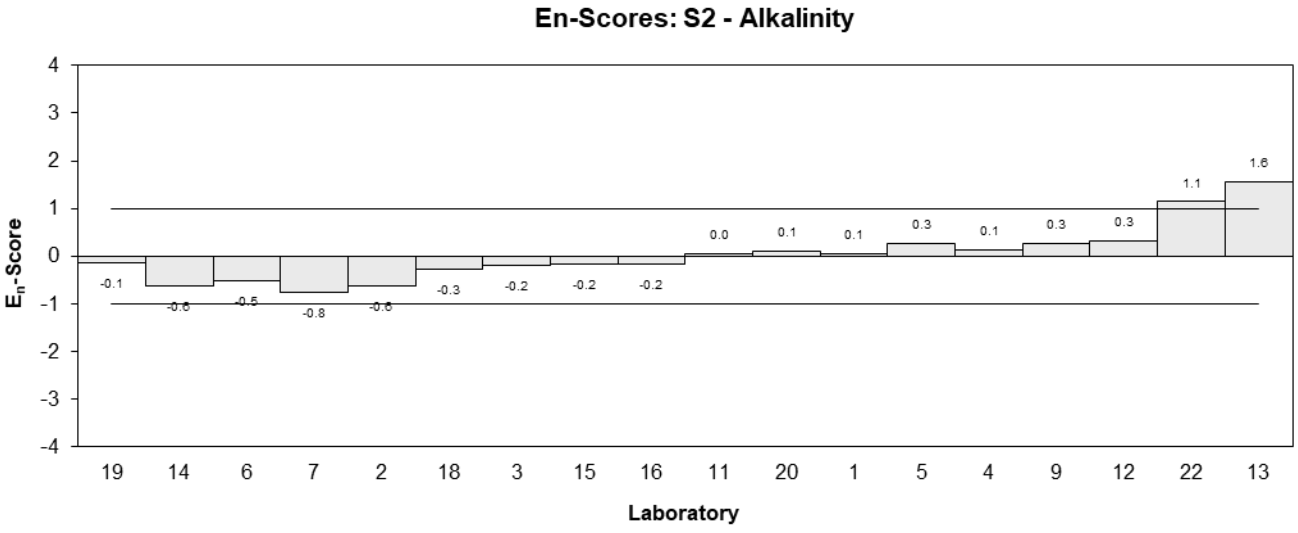

En-Scores: S2 - Alkalinity
En-Score
Laboratory
19 14 6 7 2 18 3 15 16 11 20 1 5 4 9 12 22 13
-0.1 -0.6 -0.5 -0.8 -0.6 -0.3 -0.2 -0.2 -0.2 0.0 0.1 0.1 0.3 0.1 0.3 0.3 1.1 1.6

Figure 20

Table 23

Sample Details

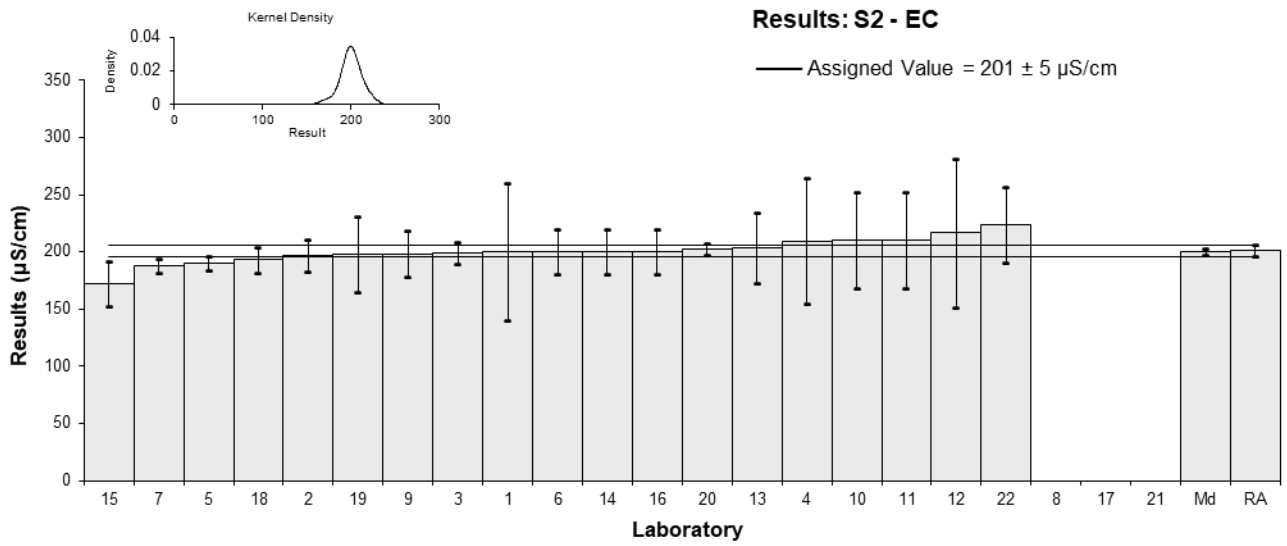
Sample No.	S2
Matrix	Potable Water
Analyte	EC
Unit	µS/cm

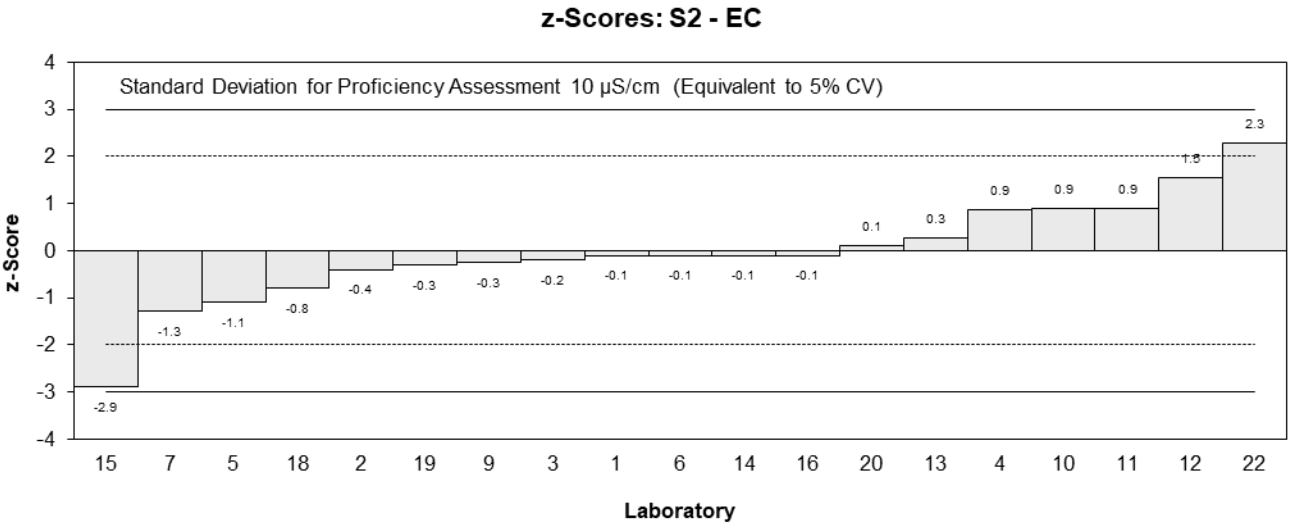
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	200	60	-0.10	-0.02
2	197	14	-0.40	-0.27
3	199	10	-0.20	-0.18
4	209.71	54.43	0.87	0.16
5	190	6.6	-1.09	-1.33
6	200	20	-0.10	-0.05
7	188	6	-1.29	-1.66
8	NR	NR		
9	198.4	19.8	-0.26	-0.13
10	210	42	0.90	0.21
11	210	42	0.90	0.21
12	216.5	64.95	1.54	0.24
13	203.7	30.56	0.27	0.09
14	200	20	-0.10	-0.05
15	172	20	-2.89	-1.41
16	200	20	-0.10	-0.05
17	NR	NR		
18	193	11	-0.80	-0.66
19	198	33	-0.30	-0.09
20	202	5	0.10	0.14
21	NT	NT		
22	224	33	2.29	0.69

Statistics

Assigned Value	201	5
Spike Value	Not Spiked	
Robust Average	201	5
Median	200	3
Mean	201	
N	19	
Max	224	
Min	172	
Robust SD	9.3	
Robust CV	4.7%	


Kernel Density
Density
0.04
0.02
0
0
100
200
300
Result
Results: S2 - EC
Assigned Value = 201 ± 5 µS/cm
Results (µS/cm)
350
300
250
200
150
100
50
0
15 7 5 18 2 19 9 3 1 6 14 16 20 13 4 10 11 12 22 8 17 21 Md RA
Laboratory


z-Scores: S2 - EC
Standard Deviation for Proficiency Assessment 10 µS/cm (Equivalent to 5% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.9
-1.3
-1.1
-0.8
-0.4
-0.3
-0.3
-0.2
-0.1
-0.1
-0.1
-0.1
0.1
0.3
0.9
0.9
0.9
1.6
2.3
15 7 5 18 2 19 9 3 1 6 14 16 20 13 4 10 11 12 22
Laboratory

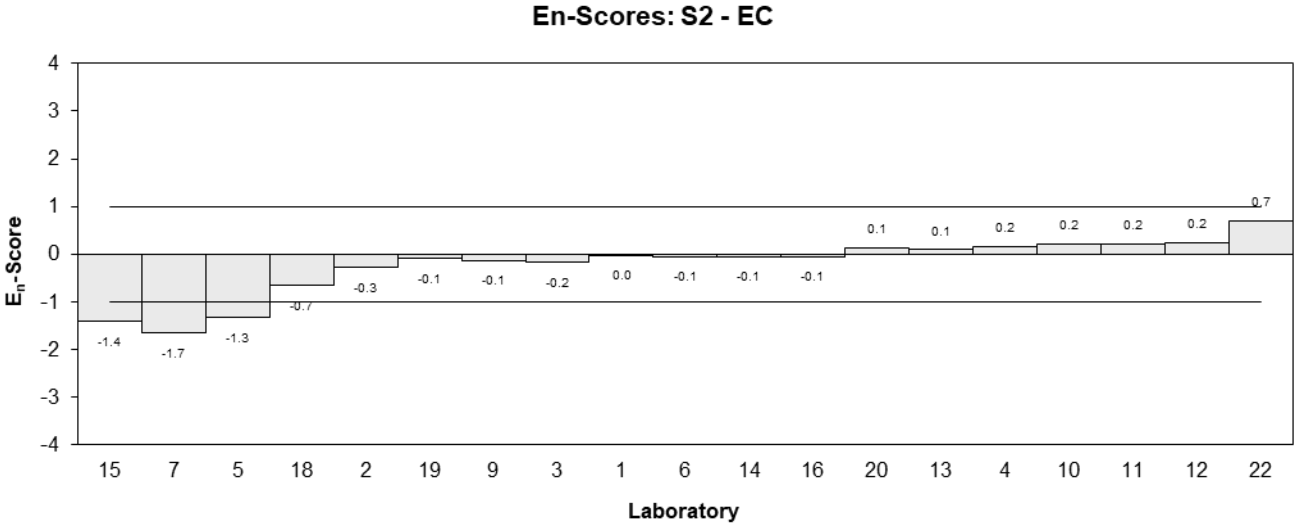

En-Scores: S2 - EC
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-1.7
-1.3
-0.7
-0.3
-0.1
-0.1
-0.2
0.0
-0.1
-0.1
-0.1
0.1
0.1
0.2
0.2
0.2
0.2
0.7
15 7 5 18 2 19 9 3 1 6 14 16 20 13 4 10 11 12 22
Laboratory

Figure 21

Table 24

Sample Details

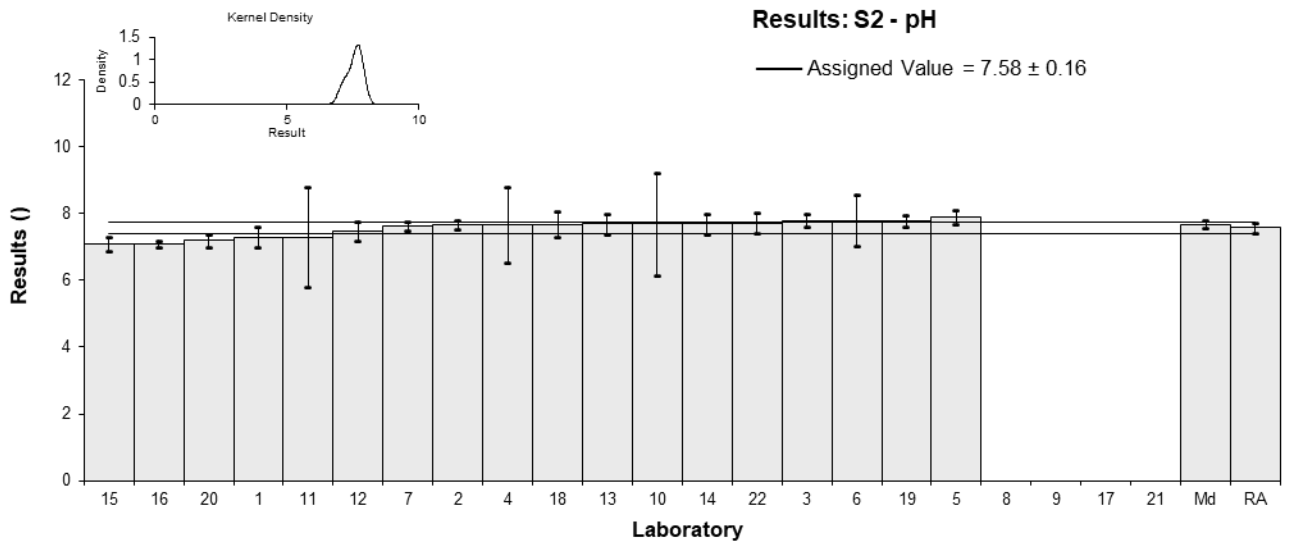
Sample No.	S2
Matrix	Potable Water
Analyte	pH

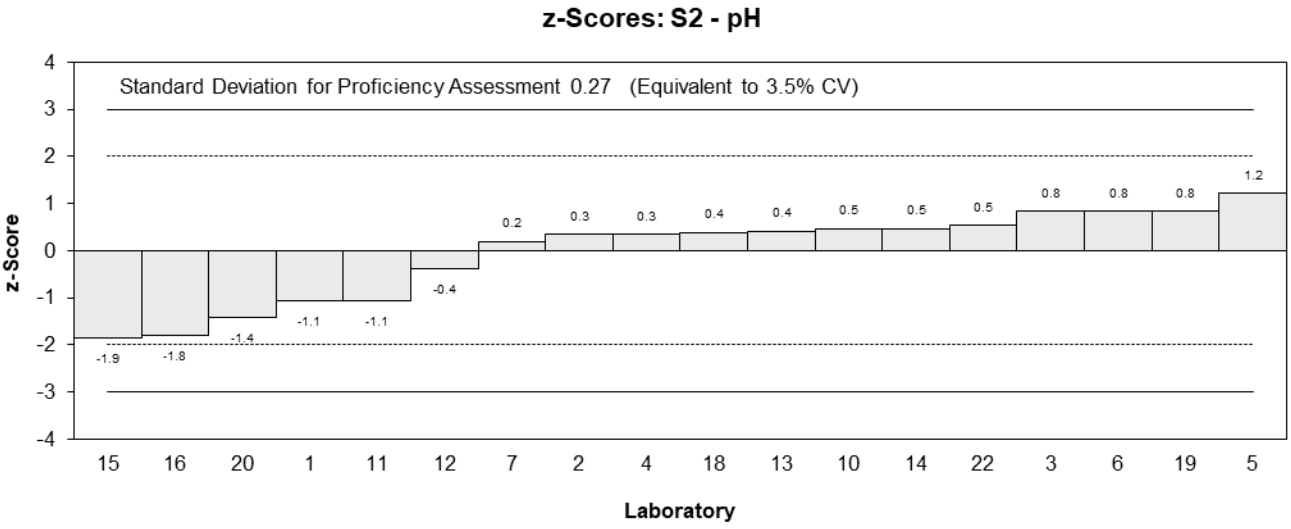
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	7.3	0.3	-1.06	-0.82
2	7.67	0.14	0.34	0.42
3	7.8	0.2	0.83	0.86
4	7.67	1.15	0.34	0.08
5	7.9	0.2	1.21	1.25
6	7.8	0.78	0.83	0.28
7	7.63	0.12	0.19	0.25
8	NR	NR		
9	NT	NT		
10	7.7	1.54	0.45	0.08
11	7.3	1.5	-1.06	-0.19
12	7.48	0.3	-0.38	-0.29
13	7.69	0.3	0.41	0.32
14	7.7	0.3	0.45	0.35
15	7.09	0.2	-1.85	-1.91
16	7.1	0.1	-1.81	-2.54
17	NR	NR		
18	7.68	0.38	0.38	0.24
19	7.8	0.17	0.83	0.94
20	7.2	0.2	-1.43	-1.48
21	NT	NT		
22	7.72	0.3	0.53	0.41

Statistics

Assigned Value	7.58	0.16
Spike Value	Not Spiked	
Robust Average	7.58	0.16
Median	7.68	0.11
Mean	7.57	
N	18	
Max	7.9	
Min	7.09	
Robust SD	0.27	
Robust CV	3.6%	


Kernel Density
Density
Result
Results: S2 - pH
Assigned Value = 7.58 ± 0.16
Results ()
Laboratory
15 16 20 1 11 12 7 2 4 18 13 10 14 22 3 6 19 5 8 9 17 21 Md RA


z-Scores: S2 - pH
Standard Deviation for Proficiency Assessment 0.27 (Equivalent to 3.5% CV)
z-Score
Laboratory
15 16 20 1 11 12 7 2 4 18 13 10 14 22 3 6 19 5
-1.9 -1.8 -1.4 -1.1 -1.1 -0.4 0.2 0.3 0.3 0.4 0.4 0.5 0.5 0.5 0.8 0.8 0.8 1.2

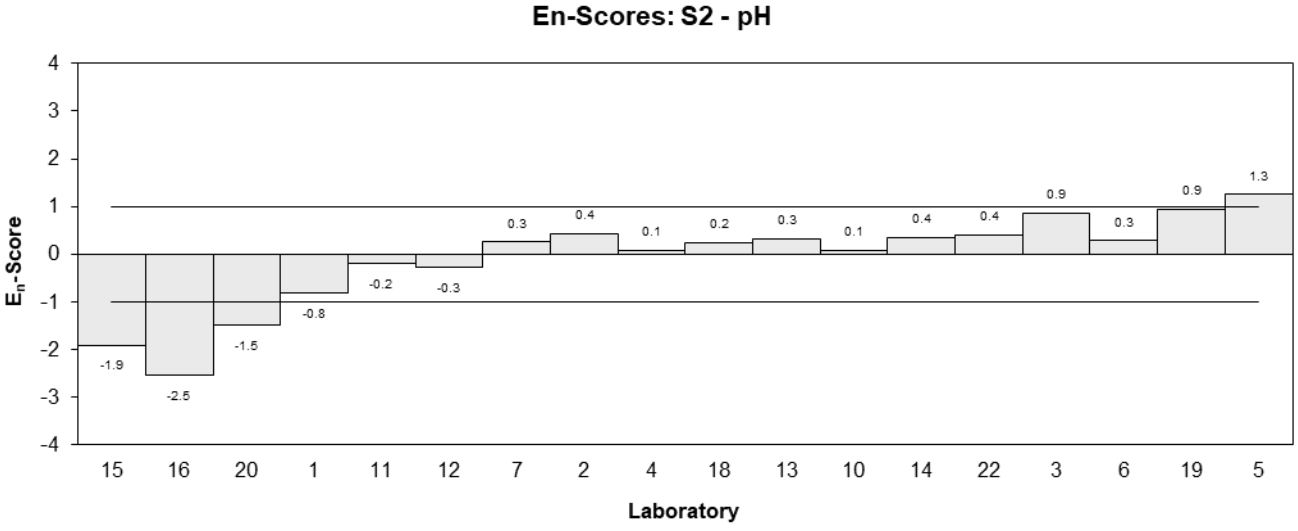

En-Scores: S2 - pH
En-Score
Laboratory
15 16 20 1 11 12 7 2 4 18 13 10 14 22 3 6 19 5
-1.9 -2.5 -1.5 -0.8 -0.2 -0.3 0.3 0.4 0.1 0.2 0.3 0.1 0.4 0.4 0.9 0.3 0.9 1.3

Figure 22

Table 25

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.9	1.17	0.43	0.14
2	NT	NT		
3	3.7	0.4	-0.11	-0.10
4	NT	NT		
5	3.4	0.34	-0.91	-0.93
6**	25	6.5	56.84	3.27
7	3.70	0.22	-0.11	-0.16
8	3.84	NR	0.27	0.77
9	NT	NT		
10	4.1	0.82	0.96	0.43
11	3.61	0.72	-0.35	-0.18
12	3.56	1.068	-0.48	-0.17
13	3.86	0.579	0.32	0.20
14	3.7	0.56	-0.11	-0.07
15	NT	NT		
16	3.7	0.2	-0.11	-0.17
17	3.71	0.37	-0.08	-0.08
18	4.04	0.81	0.80	0.37
19	NT	NT		
20	3.75	0.185	0.03	0.04
21	NT	NT		
22	3.5	0.5	-0.64	-0.46

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	3.74	0.13
Spike Value	Not Spiked	
Robust Average	3.74	0.13
Median	3.70	0.13
Mean	3.74	
N	15	
Max	4.1	
Min	3.4	
Robust SD	0.2	
Robust CV	5.3%	

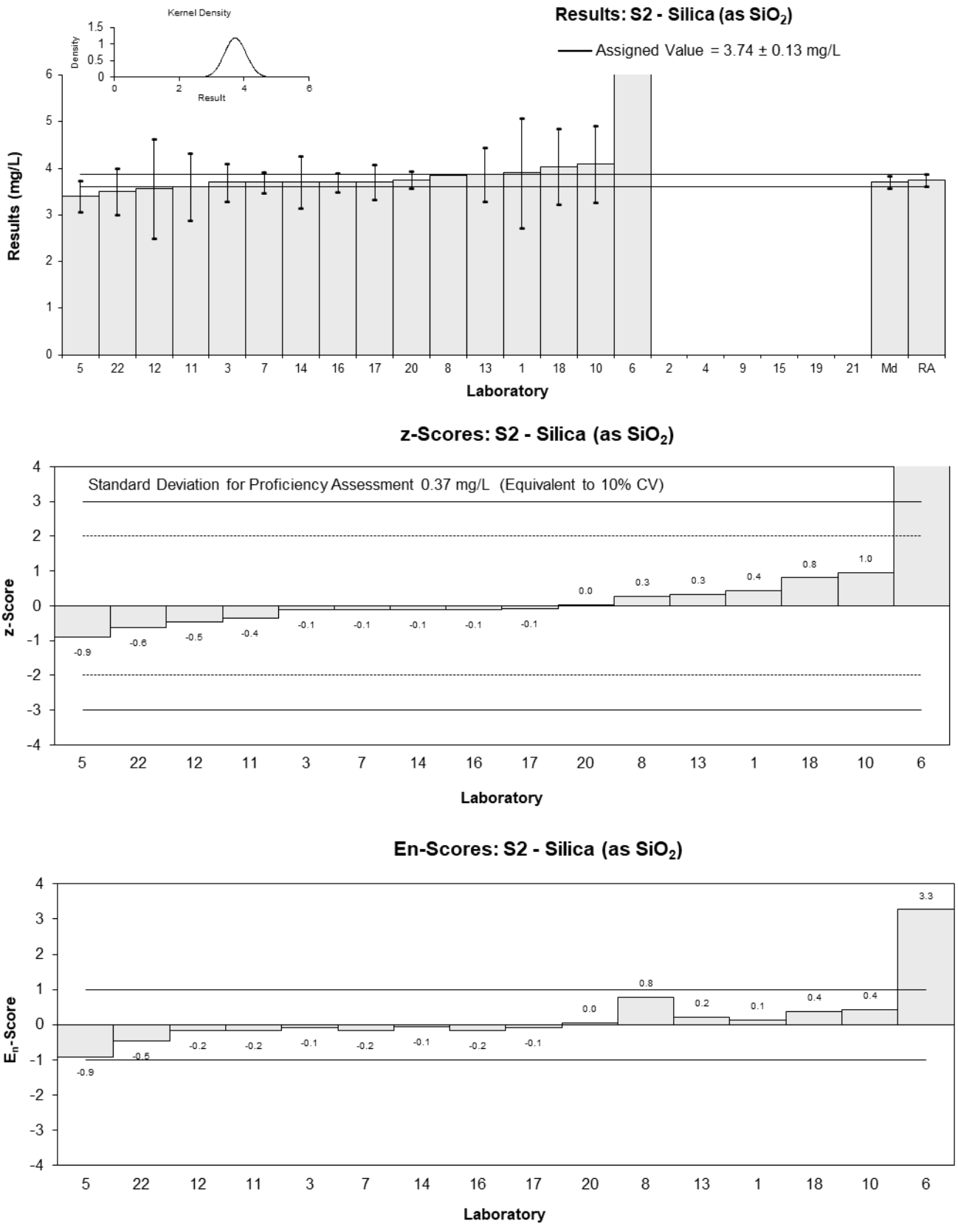

Kernel Density
Density
Result
Results: S2 - Silica (as SiO2)
Assigned Value = 3.74 ± 0.13 mg/L
Results (mg/L)
Laboratory
5 22 12 11 3 7 14 16 17 20 8 13 1 18 10 6 2 4 9 15 19 21 Md RA
z-Scores: S2 - Silica (as SiO2)
Standard Deviation for Proficiency Assessment 0.37 mg/L (Equivalent to 10% CV)
z-Score
-0.9 -0.6 -0.5 -0.4 -0.1 -0.1 -0.1 -0.1 -0.1 0.0 0.3 0.3 0.4 0.8 1.0
5 22 12 11 3 7 14 16 17 20 8 13 1 18 10 6
Laboratory
En-Scores: S2 - Silica (as SiO2)
En-Score
-0.9 -0.5 -0.2 -0.2 -0.1 -0.2 -0.1 -0.2 -0.1 0.0 0.8 0.2 0.1 0.4 0.4 3.3
5 22 12 11 3 7 14 16 17 20 8 13 1 18 10 6
Laboratory

Figure 23

Table 26

Sample Details

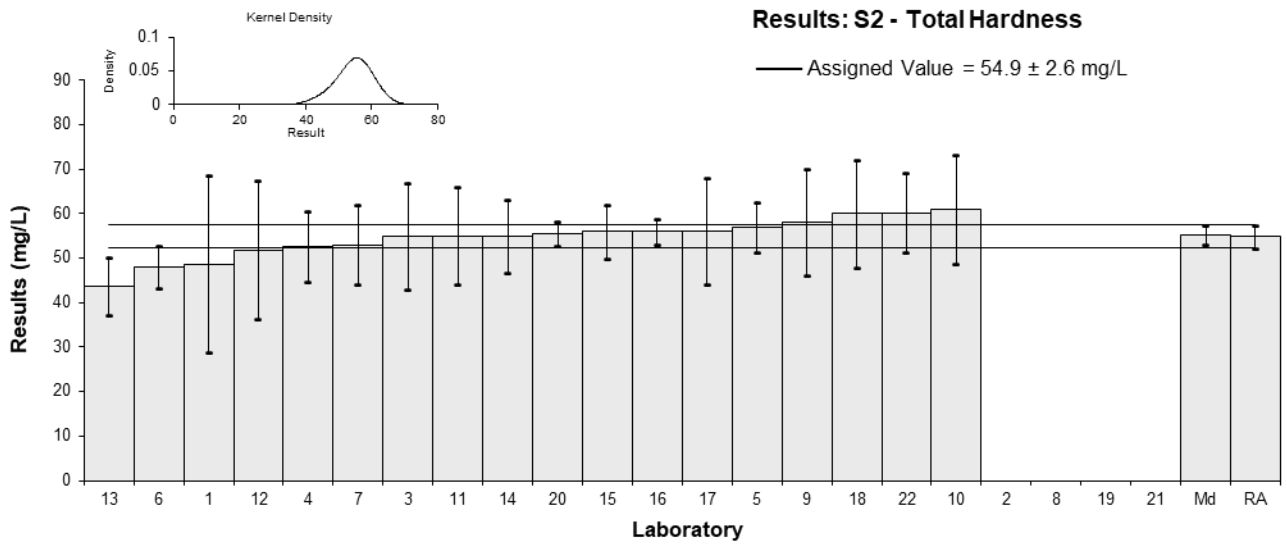
Sample No.	S2
Matrix	Potable Water
Analyte	Total Hardness
Unit	mg/L

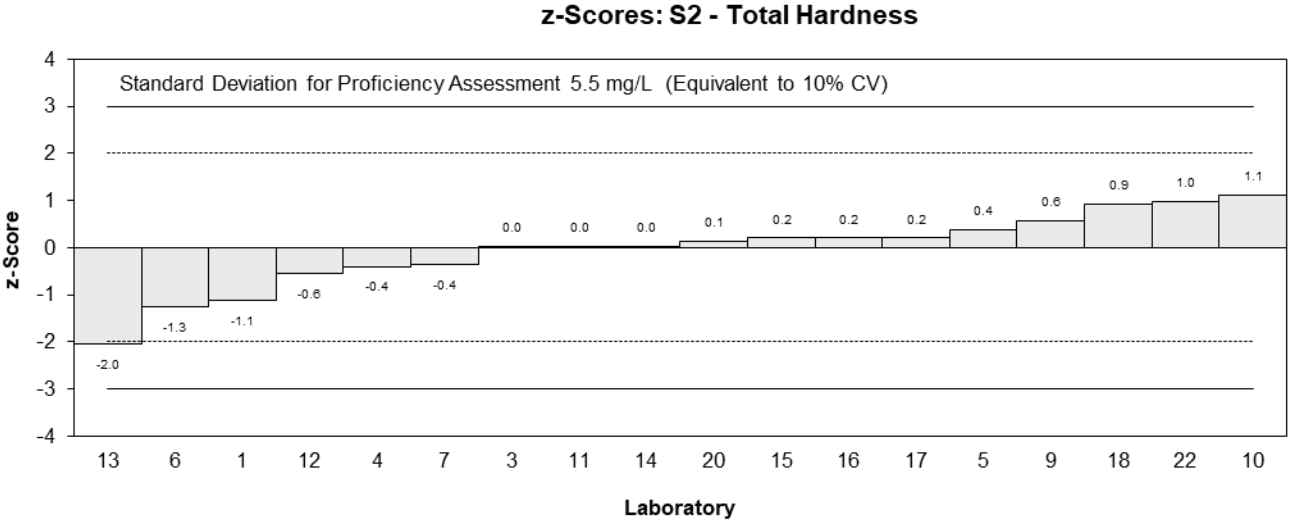
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	48.7	20	-1.13	-0.31
2	NT	NT		
3	55	12	0.02	0.01
4	52.7	7.9	-0.40	-0.26
5	57	5.7	0.38	0.34
6	48	4.8	-1.26	-1.26
7	53	9	-0.35	-0.20
8	NR	NR		
9	58	12	0.56	0.25
10	61	12.2	1.11	0.49
11	55	11	0.02	0.01
12	51.8	15.54	-0.56	-0.20
13	43.7	6.56	-2.04	-1.59
14	55	8.25	0.02	0.01
15	56	6.0	0.20	0.17
16	56	2.8	0.20	0.29
17	56	12	0.20	0.09
18	60	12	0.93	0.42
19	NT	NT		
20	55.6	2.78	0.13	0.18
21	NT	NT		
22	60.2	9.0	0.97	0.57

Statistics

Assigned Value	54.9	2.6
Spike Value	Not Spiked	
Robust Average	54.9	2.6
Median	55.3	2.1
Mean	54.6	
N	18	
Max	61	
Min	43.7	
Robust SD	4.4	
Robust CV	8%	


Kernel Density
Density
Result
Results: S2 - Total Hardness
Assigned Value = 54.9 ± 2.6 mg/L
Results (mg/L)
Laboratory
13 6 1 12 4 7 3 11 14 20 15 16 17 5 9 18 22 10 2 8 19 21 Md RA


z-Scores: S2 - Total Hardness
Standard Deviation for Proficiency Assessment 5.5 mg/L (Equivalent to 10% CV)
z-Score
-2.0 -1.3 -1.1 -0.6 -0.4 -0.4 0.0 0.0 0.0 0.1 0.2 0.2 0.2 0.4 0.6 0.9 1.0 1.1
Laboratory
13 6 1 12 4 7 3 11 14 20 15 16 17 5 9 18 22 10

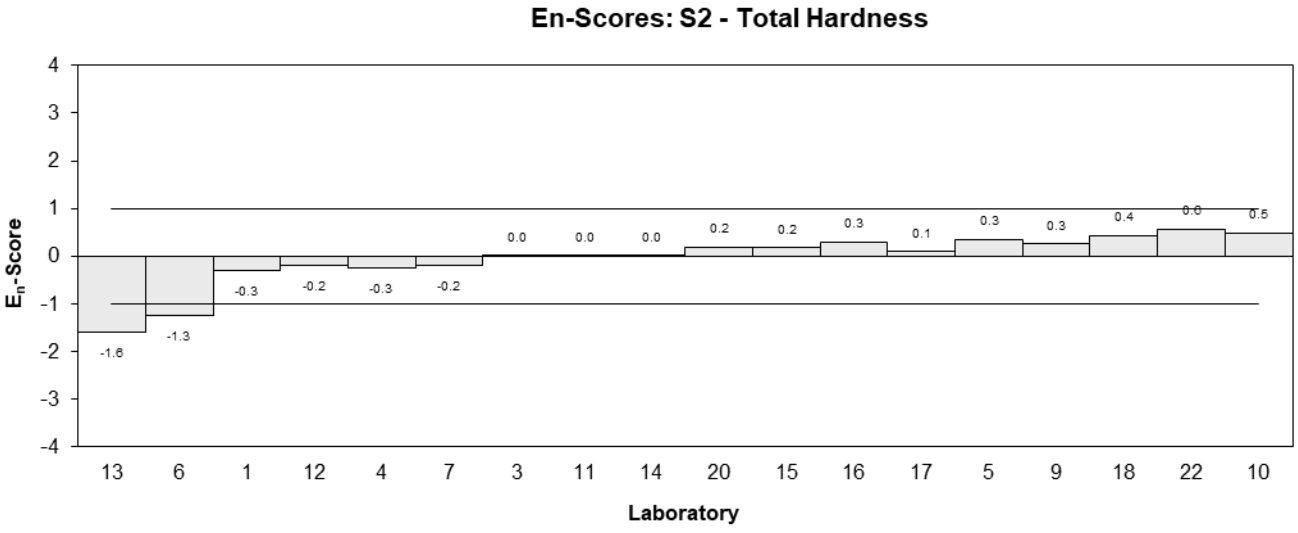

En-Scores: S2 - Total Hardness
En-Score
-1.6 -1.3 -0.3 -0.2 -0.3 -0.2 0.0 0.0 0.0 0.2 0.2 0.3 0.1 0.3 0.3 0.4 0.6 0.5
Laboratory
13 6 1 12 4 7 3 11 14 20 15 16 17 5 9 18 22 10

Figure 24

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The assigned values for all scored analytes were the robust averages of participants' results. Results that were less than 50% or greater than 150% of the robust average were excluded from the calculation of each assigned value.[4,6] The robust averages used as assigned values, and their associated expanded uncertainties were calculated using the procedure described in ISO 13528.[6] Appendix 3 sets out the calculation of the robust average and assigned value for chloride in Sample S1 and its associated uncertainty.

The results reported by Laboratories 6, 8, 14, and 15 for ammonia, nitrate, and nitrite in Sample S1, were consistently lower than the assigned value by the same factor. These laboratories might have reported results for NH_3-N, NO_3-N, and NO_2-N. To avoid unfair scoring, these results were excluded from robust average calculations as it will bias low the assigned value; they were also excluded from the calculation of all summary statistics.

For consistency, the result of ".11 mg/L" reported by Laboratory 14 for orthophosphate-P in Sample S1 was transcribed as 0.11 mg/L.

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

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

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an evaluation of the expanded measurement uncertainty associated with their results. Of 380 numerical results, 379 (99%) 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 0.83% to 100% of the reported value. The participants used a wide variety of procedures to evaluate the expanded measurement uncertainty. These are presented in Table 2. Two participants reported using the NATA GAG Estimating and Reporting MU as their guide; this document has been officially removed from the NATA website and is considered obsolete.

Approaches to evaluating 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 – 15]

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

As a simple rule of thumb, when the uncertainty is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the SDPA, then this should be reviewed as suspect. For example, 21 results were included in the calculation of the assigned value for chloride in S1. The uncertainty of the assigned value as determined from the robust standard deviation of the 21 results is 0.8 mg/L (2.8% of the assigned value). Laboratory 16 reported an uncertainty of 0.3 mg/L (1% of their reported value) which may have been underestimated, as an uncertainty evaluated from one measurement cannot be smaller than the uncertainty evaluated from 21 measurements.

Alternatively, uncertainties for chloride in S1 larger than 6.42 mg/L (the uncertainty of the assigned value, 0.8 mg/L, plus the allowable variation from the assigned value, the SDPA of 2.81 mg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also

be viewed as suspect. For example, the expanded measurement uncertainty reported by Laboratory 12 for chloride in S1 (8.73 mg/L) might have been overestimated.

Uncertainties associated with results returning an acceptable z-score, but a not acceptable E_n-score may have been underestimated.

Laboratories 1 and 12 should review their procedure for evaluating measurement uncertainty as most of their reported uncertainties were overestimated.

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 evaluate the uncertainty of their measurement results.[10] An example of evaluating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Laboratory 22 reported an evaluation of expanded uncertainty for one measurement result equal to the result itself. They may need to review the procedure for evaluation of measurement uncertainty as it is not fit for purpose.

Laboratories 18 and 19 attached an evaluation of the expanded measurement uncertainty for some results that they reported as less than their limit of detection. An evaluation of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

In some cases, the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than 2 significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 0.073 ± 0.0146 mg/L, it is better to report 0.073 ± 0.015 mg/L.[9]

6.3 z-Score

The z-score compares a participant's deviation from the assigned value with the standard deviation for proficiency assessment (SDPA). The SDPA defines acceptable performance in a proficiency test. SDPAs equivalent to 3.5%-15% PCV were used to calculate z-scores in this study. Unlike the standard deviation based on between-laboratory CV, setting the SDPA as a realistic set value enables z-scores to be used as reference value points for assessment of laboratory performance, independent of group's performance.

The between-laboratory coefficient of variation predicted by the Thompson-Horwitz equation and the between-laboratory coefficient of variation from reported results in this study are presented for comparison in Table 27.[4]

The dispersal of participants' z-scores is presented in Figure 25 (by laboratory code) and in Figure 26 (by test).

Of 380 results for which z-scores were calculated, 345 (91%) returned an acceptable score of $|z| \leq 2.0$ and 11 (3%) were questionable with a score of $2.0 < |z| < 3.0$.

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

Laboratories 5, 6, and 14 reported numeric results for all 23 scored analytes across both samples.

Laboratories 5 and 16 returned the highest number of acceptable z-scores with 21 each.

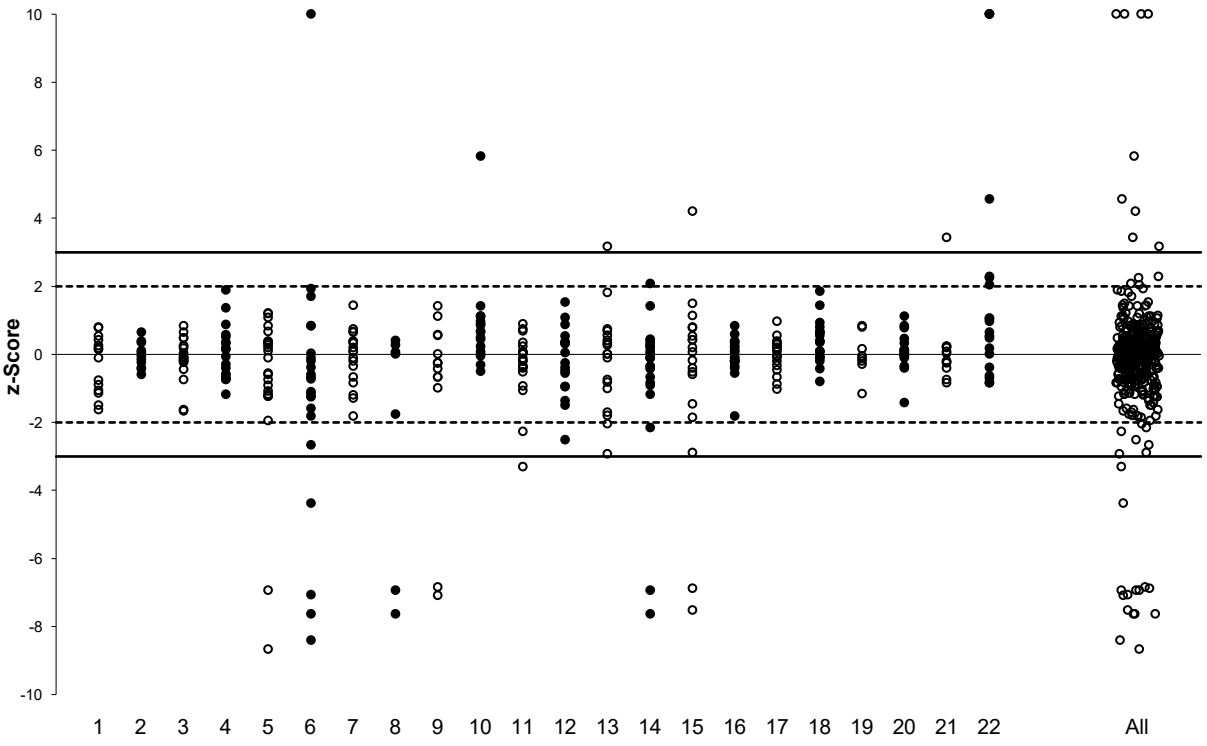
All results reported by Laboratories 18 (20), 4 (19), 3 (19), 17 (18), 20 (18), 7 (18), 1 (14), 2 (11), and 19 (8) returned acceptable z-scores.

Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

Table 27 Between-Laboratory CV of this Study, Thompson-Horwitz CV and SDPA

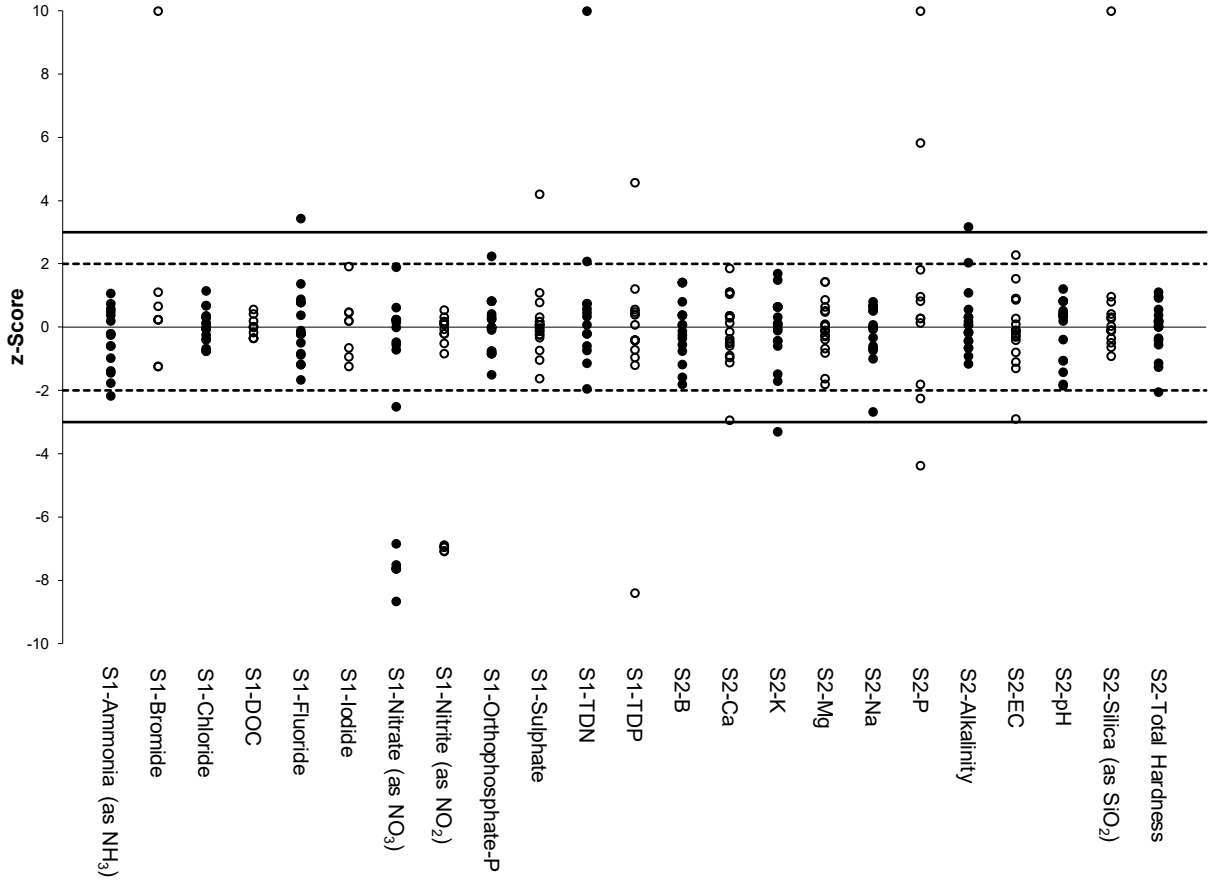
Sample	Analyte	Numeric Results Reported*	Assigned Value (mg/L)	Between-Laboratory CV* (%)	Thompson-Horwitz CV (%)	SDPA (as PCV, %)
S1	Ammonia (as NH_3)	12	0.255	7.8	20	10
S1	Bromide	7	0.0684	10	22	10
S1	Chloride	21	28.1	5	9.7	10
S1	DOC	10	3.69	5.4	13	15
S1	Fluoride	20	1.02	9.6	16	10
S1	Iodide	8	0.233	15	20	15
S1	Nitrate (as NO_3)	12	1.27	6.4	15	10
S1	Nitrite (as NO_2)	12	0.327	3.7	19	10
S1	Orthophosphate-P	19	0.120	7.8	22	10
S1	Sulphate	20	9.92	5.2	11	10
S1	TDN	13	0.745	9.2	17	10
S1	TDP	15	0.125	8.2	22	10
S2	B	17	0.0963	11	22	10
S2	Ca	19	13.5	9.2	11	10
S2	K	18	1.88	10	15	10
S2	Mg	19	5.25	7.9	13	10
S2	Na	19	15.0	7.1	11	10
S2	P	8	0.096	23	22	15
S2	Alkalinity	18	40.7	7.8	9.2	10
S2	EC	19	201 (µS/cm)	4.7	NA	5
S2	pH	18	7.58	3.6	NA	3.5
S2	Silica (as SiO_2)	15	3.74	5.3	13	10
S2	Total Hardness	18	54.9	8	8.8	10

*Values exclude outliers if applicable. Shaded cells represent between-laboratory CVs higher than both the SDPA and Thompson-Horwitz CV for scored analytes; NA = Not Applicable.



Scores >10 have been plotted as 10.

Figure 25 z-Score Dispersal by Laboratory



Scores of >10 have been plotted as 10.

Figure 26 z-Score Dispersal by Test

6.4 E_n-Score

The E_n-score indicates how closely a result agrees with the assigned value taking in consideration their respective uncertainties.

E_n-scores can be interpreted in conjunction with z-scores, as a not acceptable E_n-score for an analyte can either be caused by an inappropriate measurement, an inappropriate evaluation of measurement uncertainty, or both.

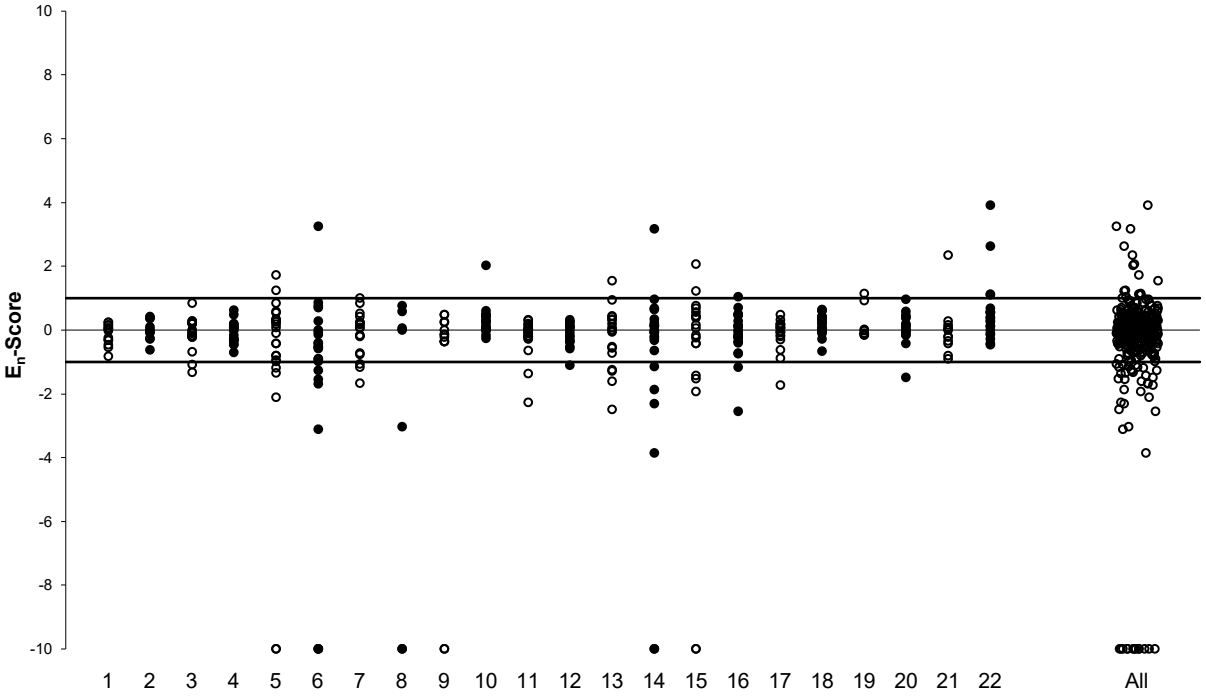
Where a participant did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

The dispersal of participants' E_n-scores is graphically presented in Figure 27.

Of 380 results for which E_n-scores were calculated, 320 (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 11 and 18 returned the highest number of acceptable E_n-scores with 20.

All results reported by Laboratories 4 (19), 1 (14), and 2 (11) returned acceptable E_n-scores.



Scores < -10 have been plotted as -10.

Figure 27 E_n-Score Dispersal by Laboratory

6.5 Participants' Results and Analytical Methods

Sample S1 was filtered potable water whilst Sample S2 was unfiltered potable water. Participants were asked to analyse the samples using their normal test method. The measurement methods and instrumental techniques used are presented in Appendix 6. A summary of participants' results and performance is presented in Tables 28 and 29 and in Figures 25 to 28.

The ADWG are specified for ammonia (as NH_3), nitrate (as NO_3), and nitrite (as NO_2).[5] The request in this study was for participants to use their routine methods but to report results for NH_3, NO_3,and NO_2. The results reported by Laboratories 6, 8, 14, and 15 for NH_3, NO_3 and NO_2 in Sample S1, were lower than the assigned 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 NH_3-N, NO_3-N, and NO_2 -N instead. The results reported by them for these tests were not included in the analysis of methods employed by participants.

Analytical test results are rounded to avoid presenting a misleading impression of precision. Most of the instrumental techniques and methods used by participants in the present study should be capable of producing results with a reasonable degree of certainty to up to two significant figures at ppb levels for most tests in potable water. Caution should be exercised when a rounding protocol is designed by a laboratory in order to avoid inadvertent loss of important information. According to Eurachem/CITAC Guide, "The reported result has to provide enough information in case a decision has to be made (e.g. when the result is close to the accepted guideline)".[9]

Of 23 numeric results reported by Laboratory 14, 7 were rounded to one significant figure. This laboratory should consider revising tthe reporting protocol.

Total P in Sample S2 was the test that most challenged participants' analytical techniques with the largest number of not acceptable z-scores. Of 11 reported results, 4 were not acceptable.

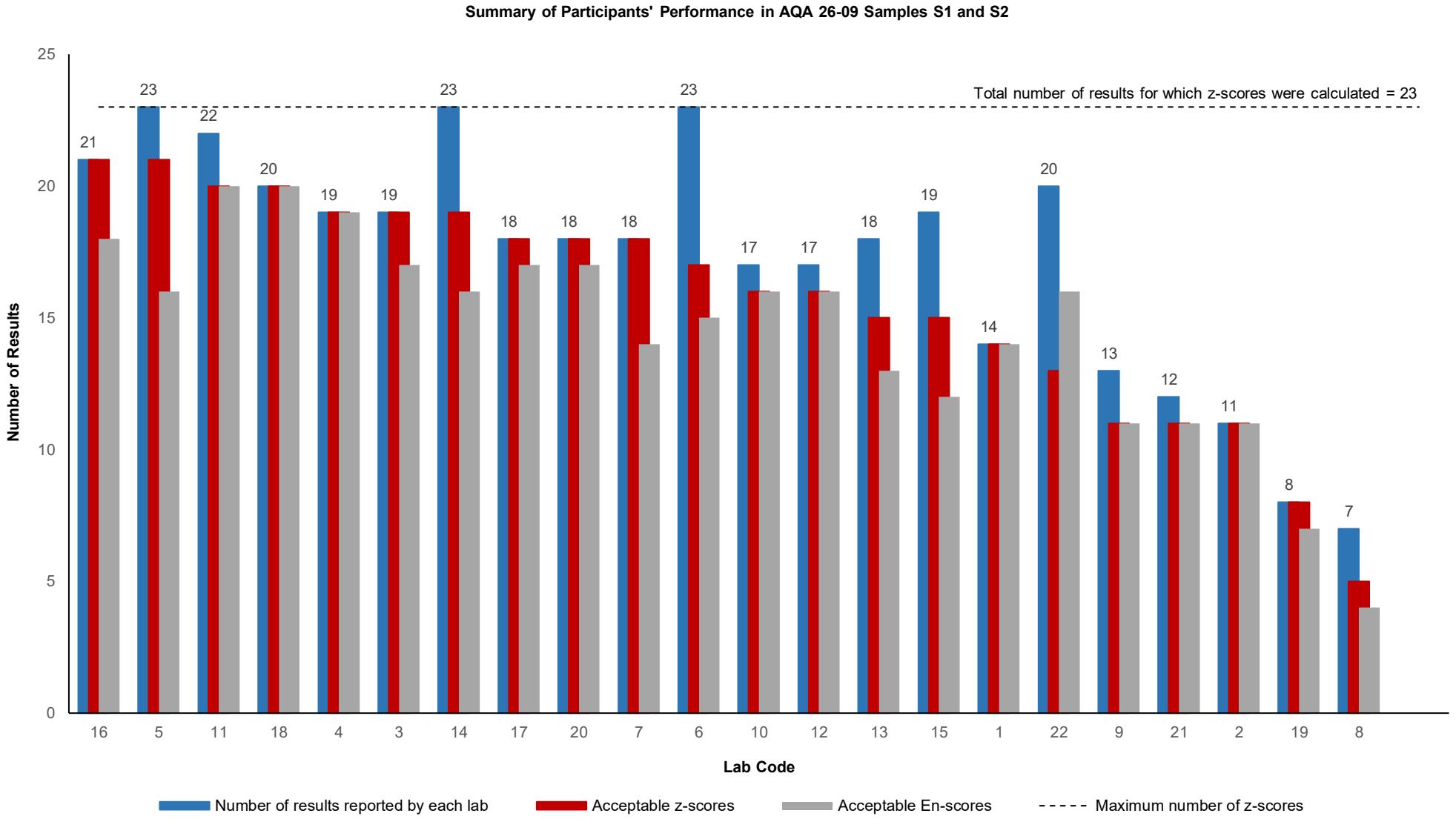


Figure 28 Summary of Participants' Performance in AQA 26-09

Table 28 Summary of Participants' Results and Performance in Sample S1

Lab Code	Ammonia (as NH_3) (mg/L)	Bromide (mg/L)	Chloride (mg/L)	DOC (mg/L)	Fluoride (mg/L)	Iodide (mg/L)	Nitrate (as NO_3) (mg/L)	Nitrite (as NO_2) (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
AV	0.255	0.0684	28.1	3.69	1.02	0.233	1.27	0.327	0.120	9.92	0.745	0.125
HV	NA	NA	29.0	NA	1.00	0.200	1.39	0.321	0.110	NA	0.78	NA
1	NT	NT	28.5	NT	1.1	NT	NT	NT	0.123	10.7	NT	NT
2	NT	<0.5	28.4	NT	1.06	NT	NT	NT	NT	9.88	NT	NT
3	0.249	<0.1	26	3.6	0.85	NT	1.30	0.333	0.123	8.3	0.78	0.131
4	0.268	< 0.5	26.2	< 5	1.16	< 2	1.51	0.325	0.111	10.1	0.788	0.116
5	0.24	0.06	26	3.8	0.9	0.19	0.17	0.10	0.13	11	0.6	0.14
6	0.24	0.06	27	3.7	1	0.3	0.3	0.096	0.13	9.2	0.66	0.02
7	NT	NT	29	NT	1.0	NT	NT	0.33	0.11	10	0.8	0.11
8	0.21	NR	NR	NR	NR	NR	0.30	0.10	0.12	NR	0.75	0.13
9	0.23	NT	28.09	< 5	NT	NT	0.40	0.095	NT	9.67	NT	NT
10	NT	0.073	28	NT	0.97	0.25	1.3	0.33	0.12	9.6	NT	NT
11	0.25	<0.1	30	3.5	1.0	0.2	1.3	0.31	0.12	9.8	0.8	0.12
12	0.22	< 1	29.1	NT	1.11	< 1	0.95	0.337	0.102	10.24	NT	0.113
13	0.274	NT	30	3.69	1.01	NT	1.27	0.345	0.111	<2	NT	NT
14	0.2	0.07	29	3.5	0.9	0.24	0.3	0.1	0.11	10	0.9	0.13
15	0.218	<0.5	31.3	3.93	1.1	NT	0.315	0.102	0.125	14.1	0.70	0.12
16	0.27	0.07	29	3.5	1.0	< 0.3	1.2	0.32	0.13	9.7	0.73	0.12
17	0.26	<0.10	28.0	NR	0.93	0.21	1.21	0.333	0.124	8.90	0.73	0.132
18	0.265	NR	28	4	1.0	NR	1.35	0.33	0.119	10	0.77	0.126
19	<0.2	<0.2	28	NT	1	NT	1.29	NT	NT	9.8	NT	NT
20	NR	0.076	28	NR	1.1	0.249	NR	NR	0.12	9.89	NR	0.12
21	0.25	0.07	27.4	3.7	1.37	0.24	1.30	0.32	0.11	10	0.69	0.12
22	0.282	0.18	27.0	NT	0.934	NT	1.18	0.30	0.147	10.1	1.90	0.182

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

Table 29 Summary of Participants' Results and Performance in Sample S2

Lab Code	B (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	P (mg/L)	Alkalinity (mg/L)	EC (µS/cm)	pH	Silica (as SiO_2) (mg/L)	Total Hardness (mg/L)
AV	0.0963	13.5	1.88	5.25	15.0	0.096	40.7	201	7.58	3.74	54.9
1	0.089	12.3	1.6	4.4	15.8	NT	41.4	200	7.3	3.9	48.7
2	0.094	13.3	2.00	5.27	14.1	<0.1	39	197	7.67	NT	NT
3	NT	12.9	1.86	5.59	14.9	NT	40	199	7.8	3.7	55
4	0.085	12.7	1.77	5.10	13.9	0.098	42.01	209.71	7.67	NT	52.7
5	0.091	14	1.9	5.2	16	0.10	42	190	7.9	3.4	57
6	0.081	12	2.2	4.3	11	0.033	38	200	7.8	25	48
7	0.10	14	2	6	16	0.07	38	188	7.63	3.70	53
8	NR	NR	NR	NR	NR	NR	NR	NR	NR	3.84	NR
9	0.11	15	1.8	4.9	14	< 0.5	43.00	198.4	NT	NT	58
10	0.11	15	NT	5.7	16	0.18	NT	210	7.7	4.1	61
11	0.097	13.97	1.26	5.05	15.1	0.0635	41	210	7.3	3.61	55
12	< 0.5	12.2	1.89	5.12	15.8	< 0.5	45.1	216.5	7.48	3.56	51.8
13	0.079	9.55	1.56	4.82	13.5	0.122	53.6	203.7	7.69	3.86	43.7
14	0.11	13	1.8	5.2	14	0.1	37	200	7.7	3.7	55
15	0.097	12.8	2.16	5.53	16.2	NT	40	172	7.09	NT	56
16	0.10	14	1.9	5.3	15	<0.5	40	200	7.1	3.7	56
17	0.10	13.9	1.87	5.29	14.5	0.11	NR	NR	NR	3.71	56
18	0.095	16	2	6	16	<1	39	193	7.68	4.04	60
19	0.104	NT	NT	NT	NT	<1.5	36	198	7.8	NT	NT
20	0.093	13.69	1.94	5.20	14.99	0.108	41	202	7.2	3.75	55.6
21	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
22	NT	14.9	2.0	5.5	15.0	0.364	49	224	7.72	3.5	60.2

Shaded cells are results which returned a questionable or not acceptable z-score; AV = Assigned Value; NR = Not Reported; NT = Not Tested.

Individual Test Commentary

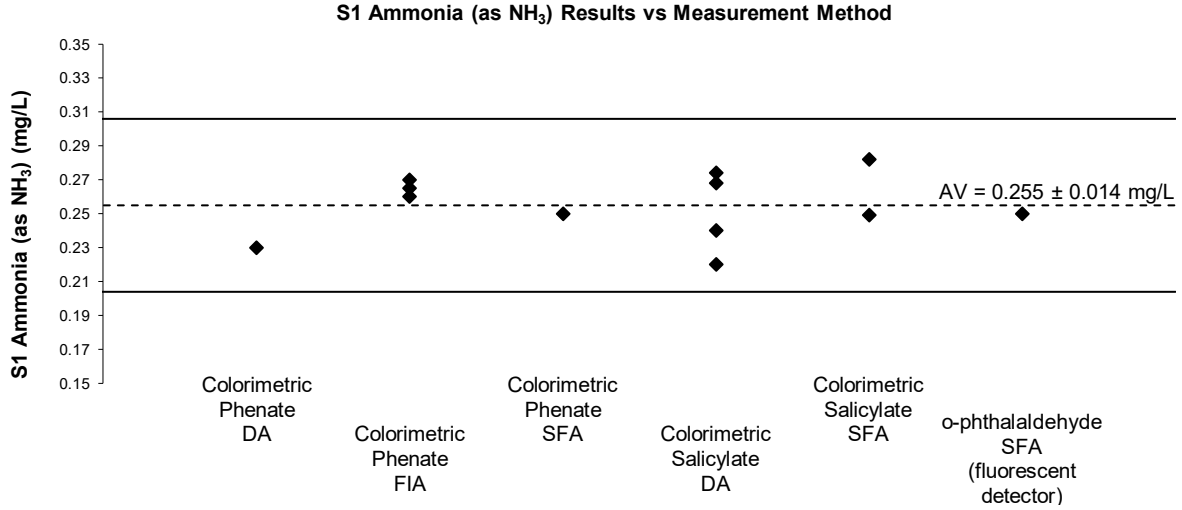
Ammonia (as NH_3) All laboratories reported using the colorimetric-phenate or colorimetric-salicylate method for NH_3 determination except for Laboratory 11. This laboratory reported using the *o*-phthalaldehyde method with SFA and fluorescent detector (Figure 29).

Bromide level in S1 was below the level of reporting of many participants. Of 8 reported results, 7 returned acceptable z-scores. Most laboratories used IC for bromide measurements. One participant reported using the ICP Method (Figure 30). During ozonation or chlorination, the by-product bromate is formed in water containing bromide.[16] Caution should be exercised when using the ICP method because it measures both bromide and bromate.

Laboratory 22 should check sample and standard preparation procedure as their results were higher than the assigned value by a factor of approximately 2.5.

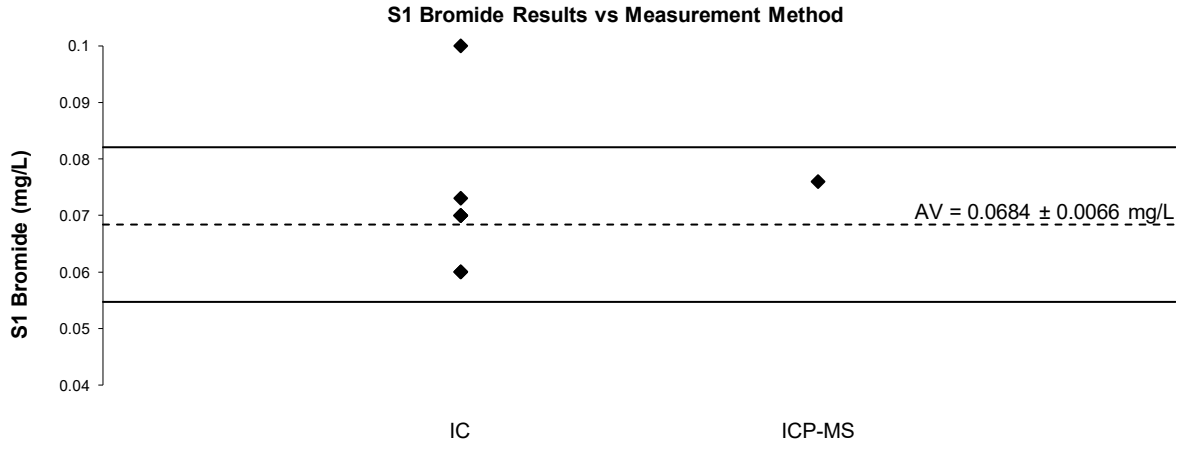
Chloride Participants used a wide variety of methods for chloride analysis in Sample S1, with IC being the most employed technique. All produced acceptable results (Figure 31).

Dissolved Organic Carbon as dNPOC level in S1 was 3.69 mg/L. All participants performed acceptably (Figure 32).



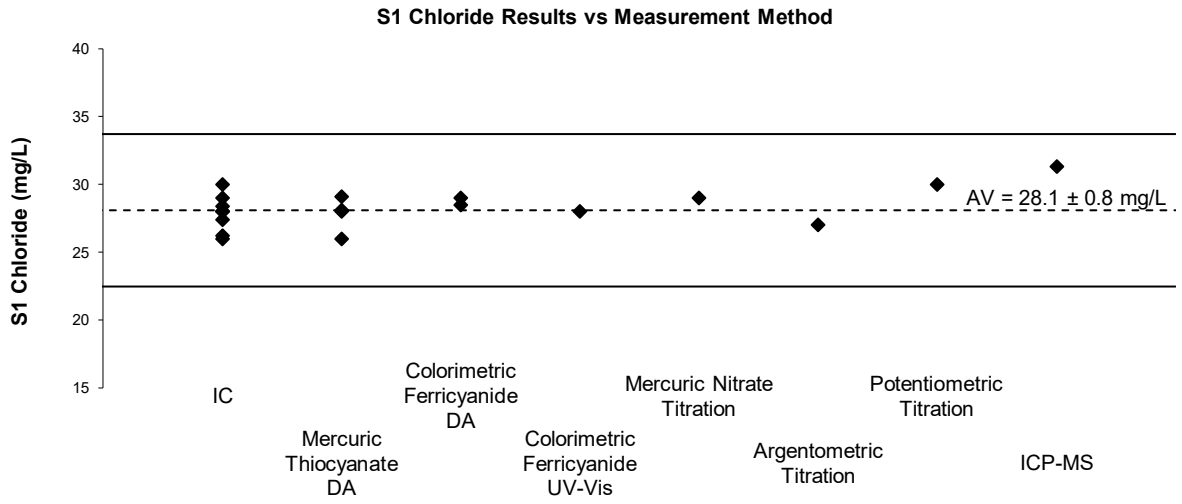
Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 29 S1 Ammonia (as NH_3) Results vs Measurement Method



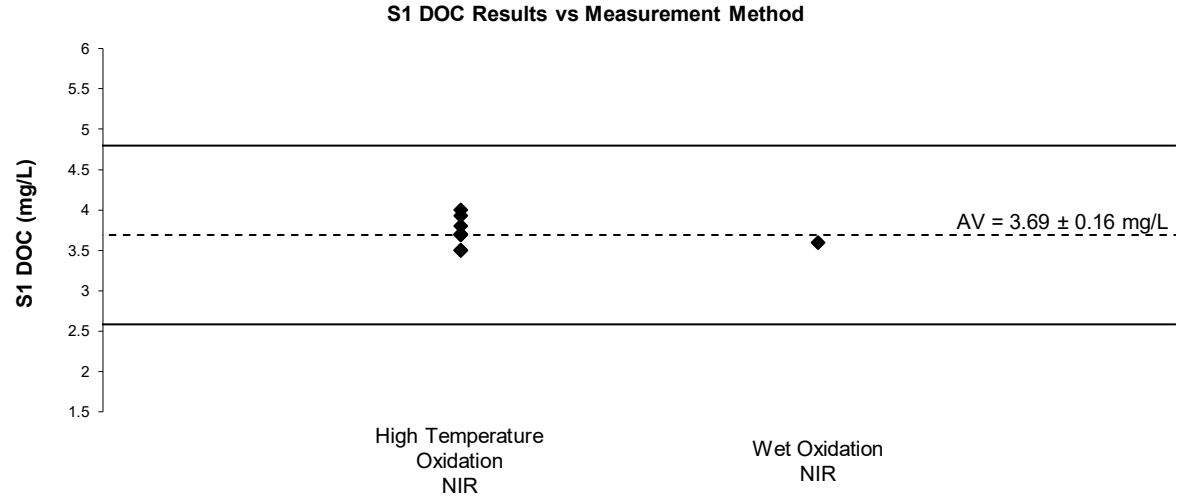
Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results > 0.1 mg/L plotted as 0.1 mg/L.

Figure 30 S1 Bromide Results vs Measurement Method



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 31 S1 Chloride Results vs Measurement Method

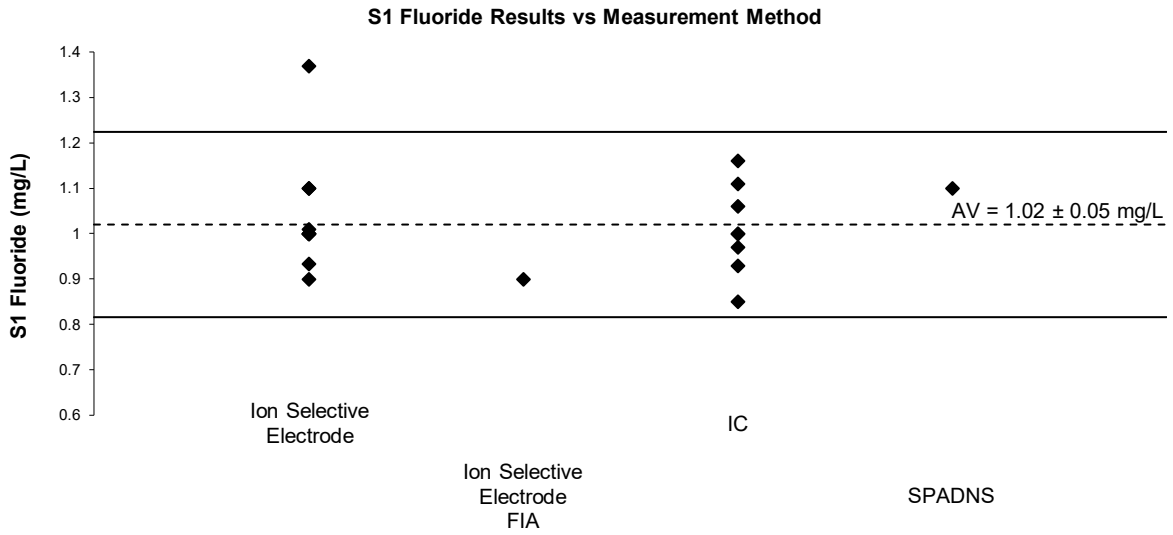


Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

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

Fluoride Most participants used either the ion selective electrode (ISE) method or IC method. One laboratory reported using both FIA and ISE method, and one laboratory used the SPADNS colorimetric method with UV-Vis determination (Figure 33).

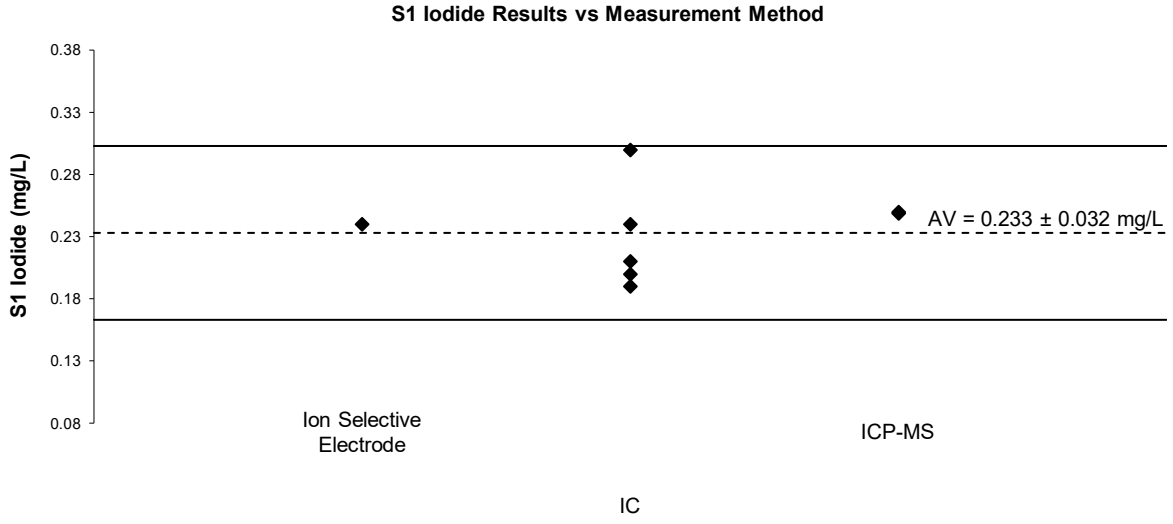
Chloride levels at 150 mg/L are not uncommon in drinking water, with concentrations ranging up to 350 mg/L.[5] Caution should be exercised when SPADNS is used for fluoride determination as it suffers from interference from chlorides and elevated results might be produced.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 33 S1 Fluoride Results vs Measurement Method

Iodide Eight participants reported results for iodide in Sample S1. Most participants used the IC method for analysis (Figure 34). One laboratory used an ion selective electrode for its iodide measurements and one reported using ICP-MS. All results produced acceptable scores.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

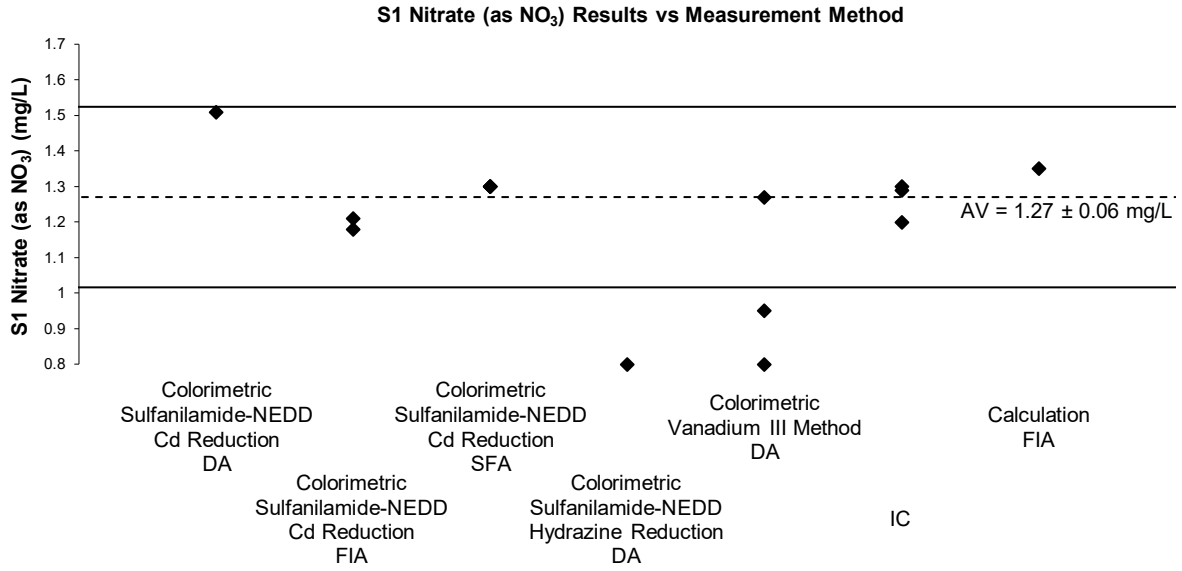
Figure 34 S1 Iodide Results vs Measurement Method

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).[5] The request in this study was for participants to use their routine methods but to report results for nitrate and nitrite.

Figures 35 and 36 present plots of participants' results for nitrate and nitrite in Sample S1 versus measurement method. Laboratories 6, 8, 14, and 15 may have reported results as nitrate-nitrogen and nitrite-nitrogen and were not included in these figures. To allow these labs to compare their results to other participants, the assigned value for nitrate converted to nitrate-nitrogen is 0.287 mg/L, and for nitrite converted to nitrite-nitrogen it is 0.0996 mg/L.

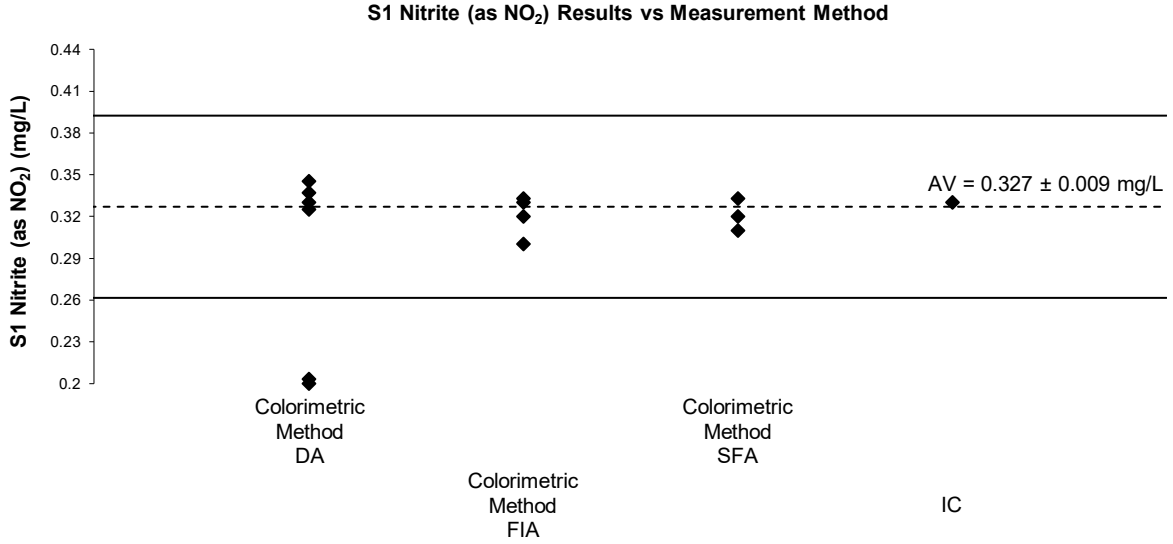
Laboratories 5 and 9 returned unacceptably low results for both analytes. These results may have been reported as nitrate-nitrogen and nitrite-nitrogen, but the study coordinator found

insufficient evidence to support this. These laboratories may want to review their calculation/reporting procedures or calibration standards to identify potential sources of error.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results < 0.8 mg/L plotted as 0.8 mg/L.

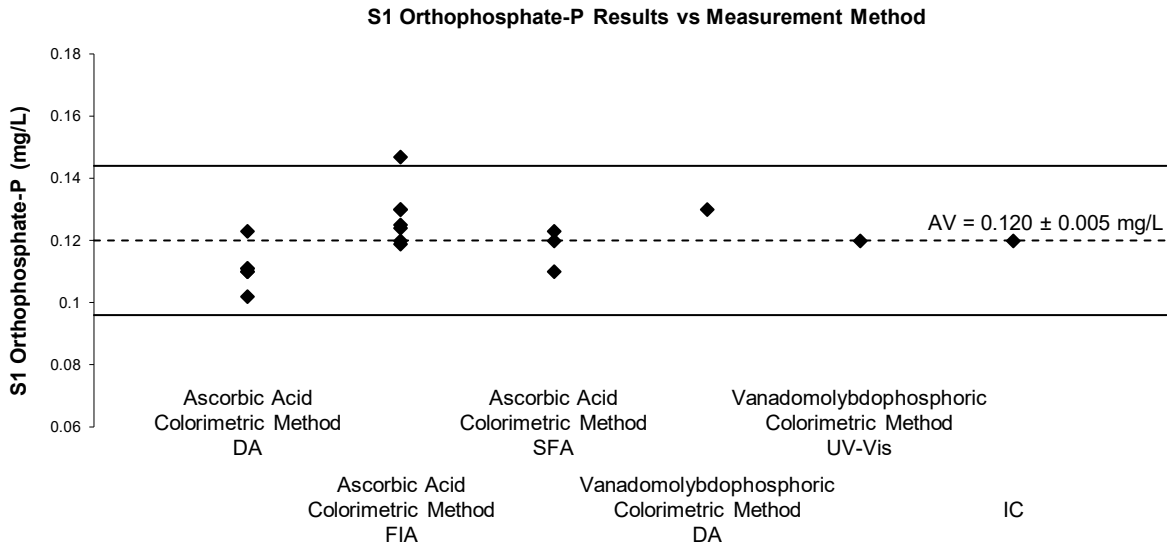
Figure 35 S1 Nitrate (as NO_3) Results vs Measurement Method



Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results < 0.2 mg/L plotted as 0.2 mg/L.

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

Orthophosphate-P Most participants used the ascorbic acid colorimetric method with FIA, DA or SFA determination (Figure 37). Two laboratories reported using the vanadomolybdophosphoric colorimetric method, and one reported using IC.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

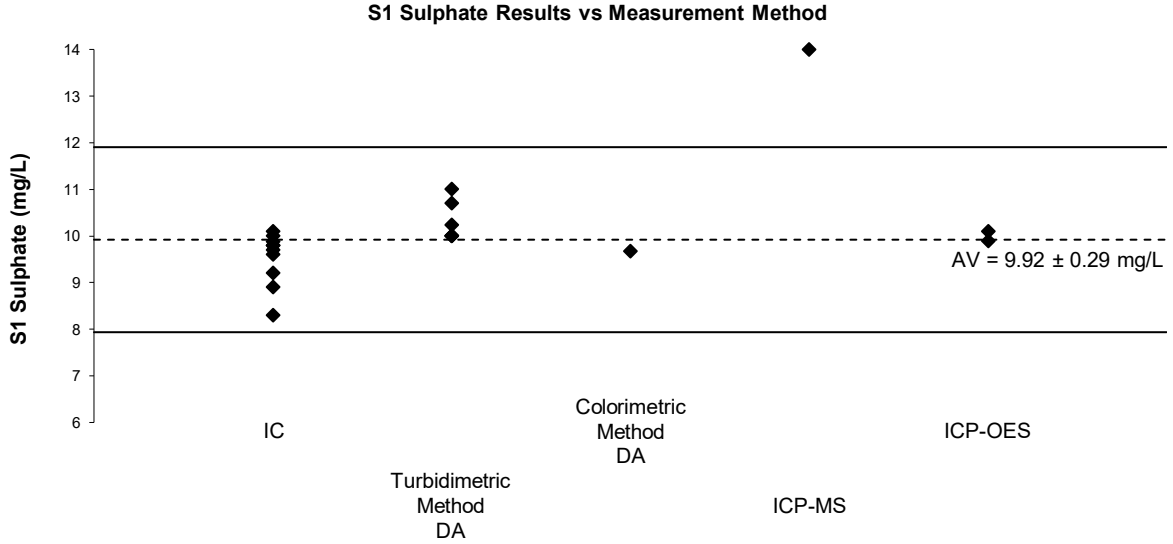
Figure 37 S1 Orthophosphate-P Results vs Measurement Method

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 38). 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.

Sulphur is one of the most difficult elements to measure by ICP-MS because it has a high ionisation potential and suffers from significant polyatomic interference on all naturally occurring isotopes. Unsolved interferences might explain the high unsatisfactory sulphate result.

The assigned value for sulphate in Sample S1 was 9.92 mg/L. Laboratory 13 reported a non-numeric result (< 2 mg/L) for this analyte. The laboratory may wish to review their method as the assigned value was well above their level of reporting.

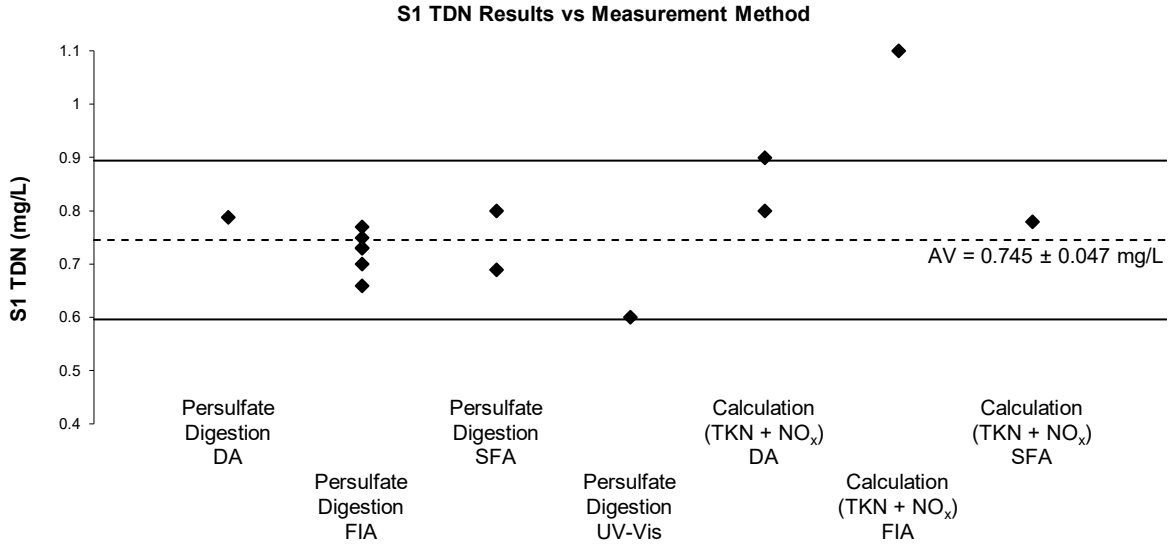


Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results > 14 mg/L plotted as 14 mg/L.

Figure 38 S1 Sulphate Results vs Measurement Method

Total Dissolved Nitrogen Four participants reported TDN as the sum of TKN and NO_x (Figure 39). All 4 results were biased high, with two participants returning questionable or not acceptable z-scores.

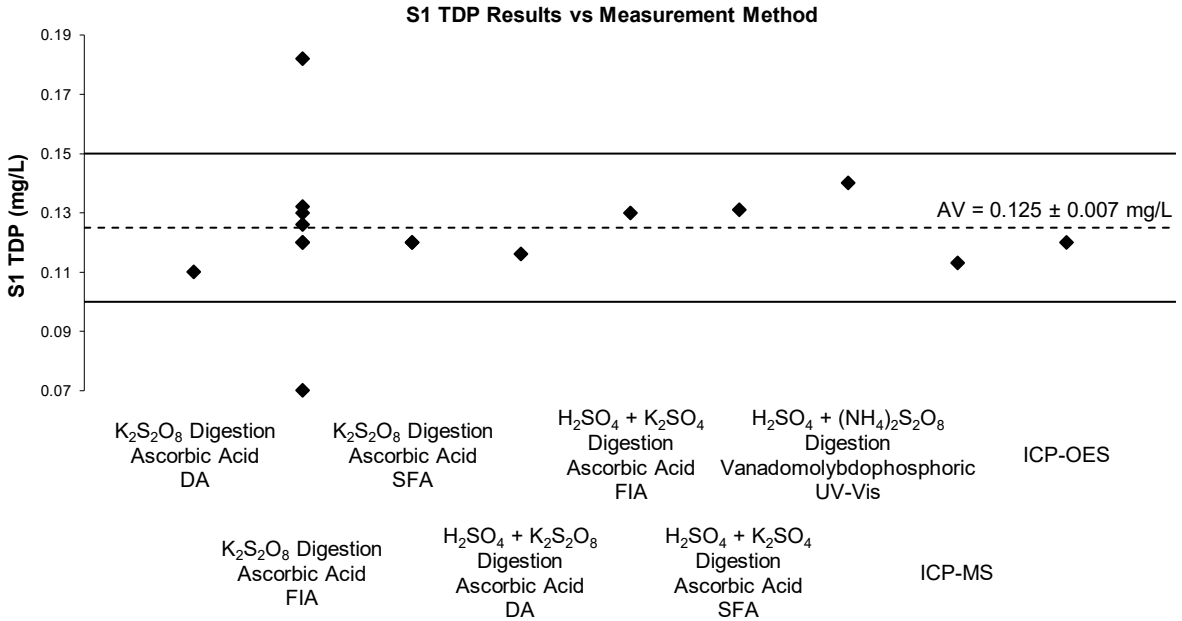
Laboratory 22 reported acceptable results for nitrate (as NO_3) and nitrite (as NO_2) but received a not acceptable result for TDN. They may want to review their calculation/reporting procedure.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results > 1.1 mg/L plotted as 1.1 mg/L.

Figure 39 S1 TDN Results vs Measurement Method

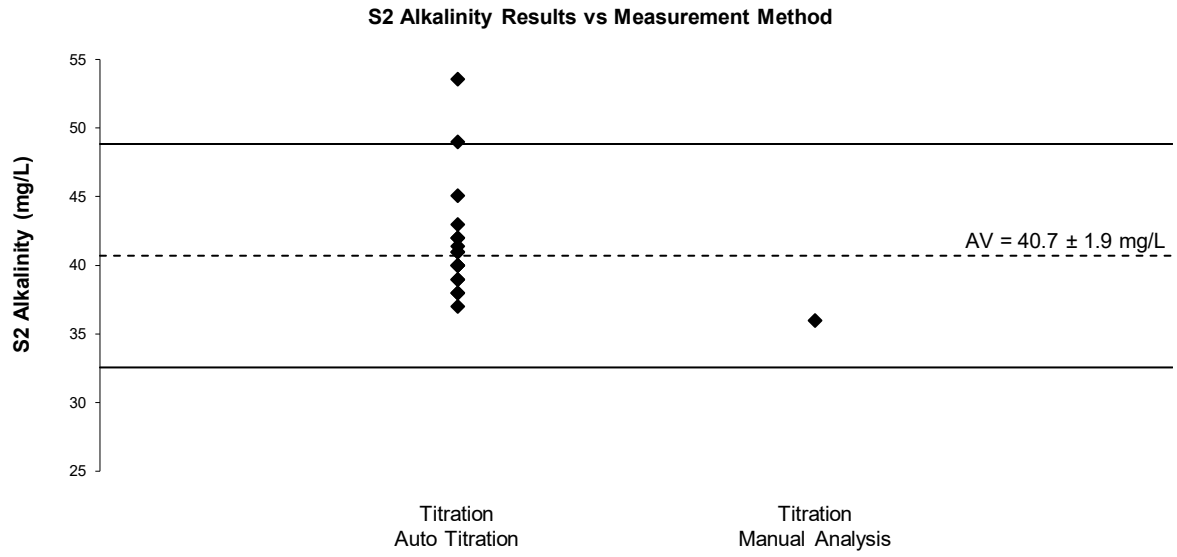
Total Dissolved Phosphorus Most laboratories used potassium persulphate for digestion and then measured the liberated orthophosphate colorimetrically by either FIA, SFA, or DA (Figure 40). Two participants reported using the ICP method for determination of TDP. All reported results returned acceptable z-scores with the exception of 2.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results < 0.07 mg/L plotted as 0.07 mg/L.

Figure 40 S1 TDP Results vs Measurement Method

Alkalinity One participant reported manually titrating the sample to determine alkalinity (Figure 41). All reported results returned acceptable z-scores except for 2.

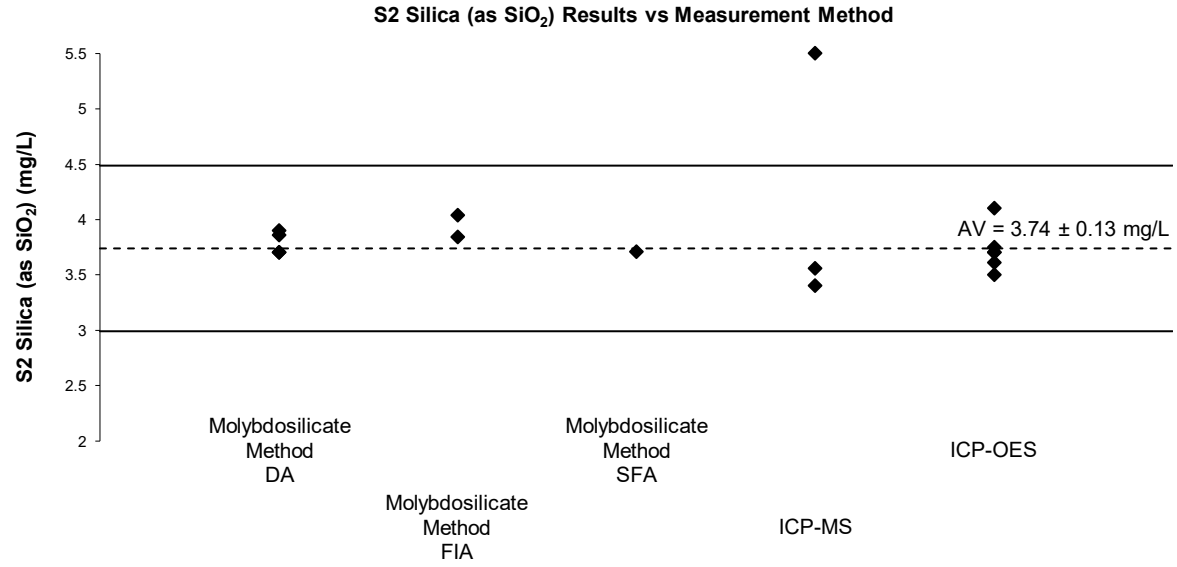


Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 41 S2 Alkalinity Results vs Measurement Method

Silica (as SiO_2) Sixteen participants reported results for silica in Sample S2 and all but one performed acceptably (Figure 42).

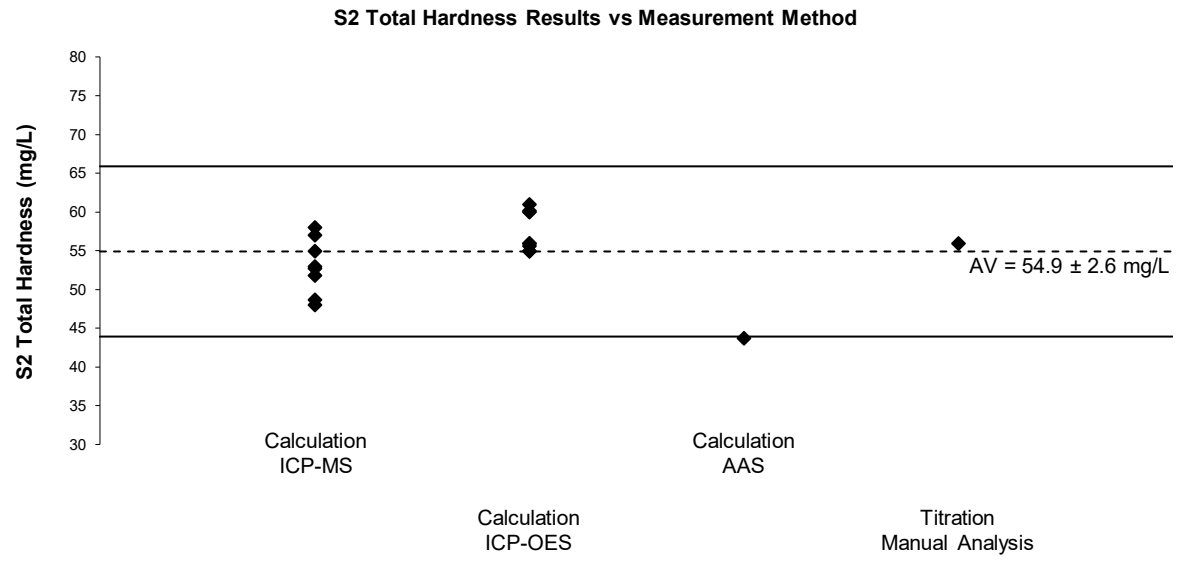
A similar number of participants used the molybdosilicate method and the ICP method for analysis.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results > 5.5 mg/L plotted as 5.5 mg/L.

Figure 42 S2 Silica (as SiO_2) Results vs Measurement Method

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

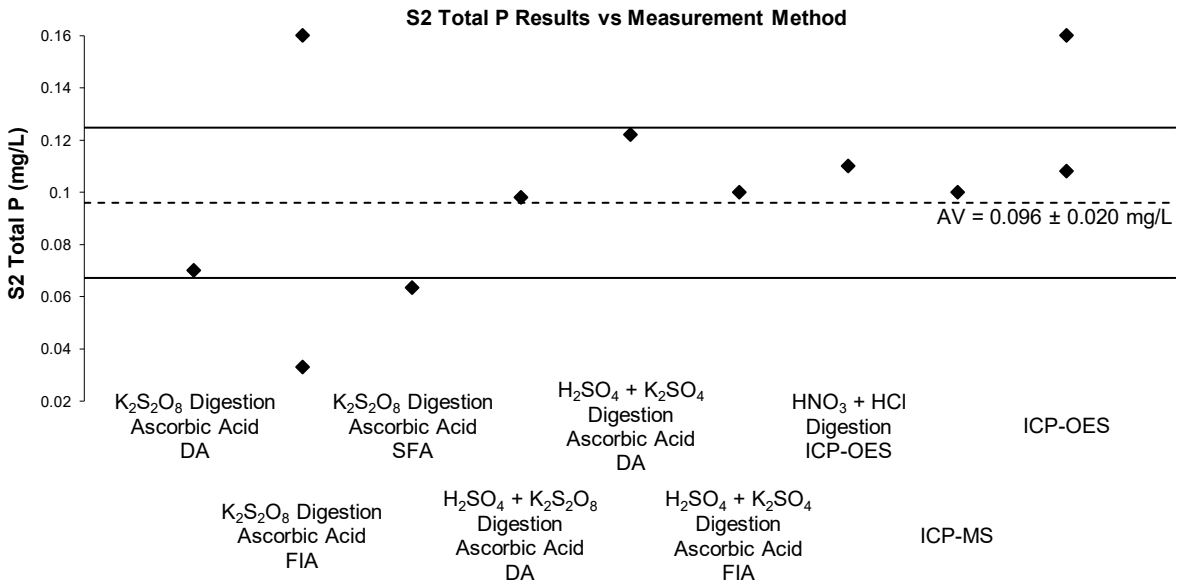


Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 43 S2 Total Hardness Results vs Measurement Method

Total P measurement in Sample S2 challenged participants' analytical techniques. Most laboratories used a colorimetric method, whilst 4 reported using an ICP method (Figure 44). All participants who reported the addition of acid during digestion and used a colorimetric method for total P determination returned acceptable z-scores. Laboratory 6 reported a value of 0.033 mg/L, approximately 3 times lower than the assigned value.

The results reported by Laboratories 10 and 22 were 2 and 4 times respectively higher than the assigned value. These laboratories may need to review their calculation procedures.

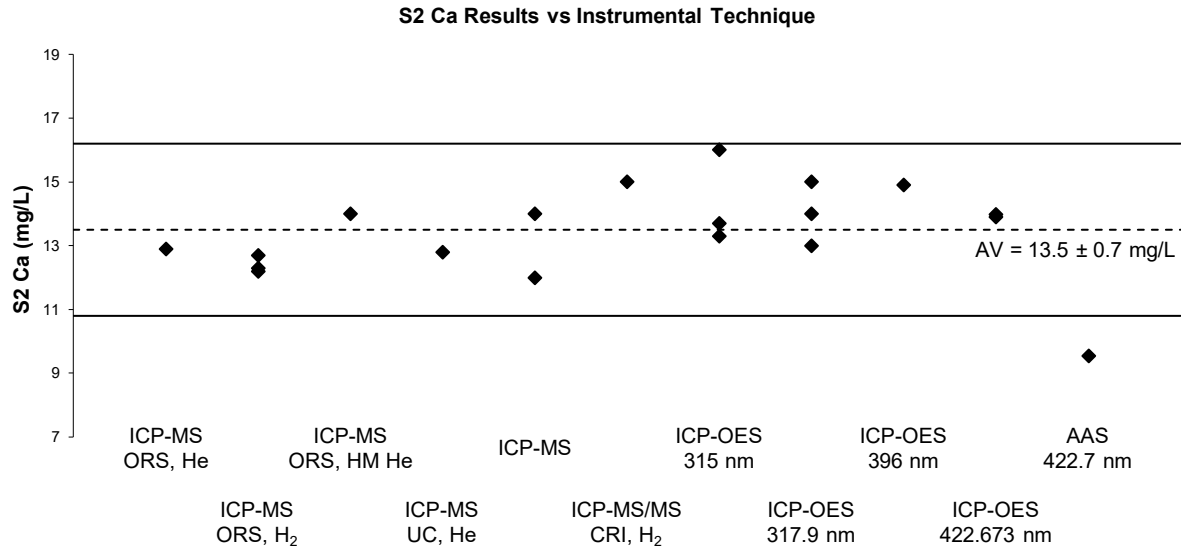


Horizontal lines are equivalent to z-scores of 2 and -2 respectively. Results > 0.16 mg/L plotted as 0.16 mg/L.

Figure 44 S2 Total P Results vs Measurement Method

Calcium Participants used a wide variety of instrumental techniques for Ca analysis in Sample S2 (Figure 45). One participant reported using ICP-MS with High Matrix Introduction (HM) Accessory in collision mode. Four laboratories used ICP-MS or ICP-MS/MS in reaction mode with H_2. All results returned acceptable z-scores except for one.

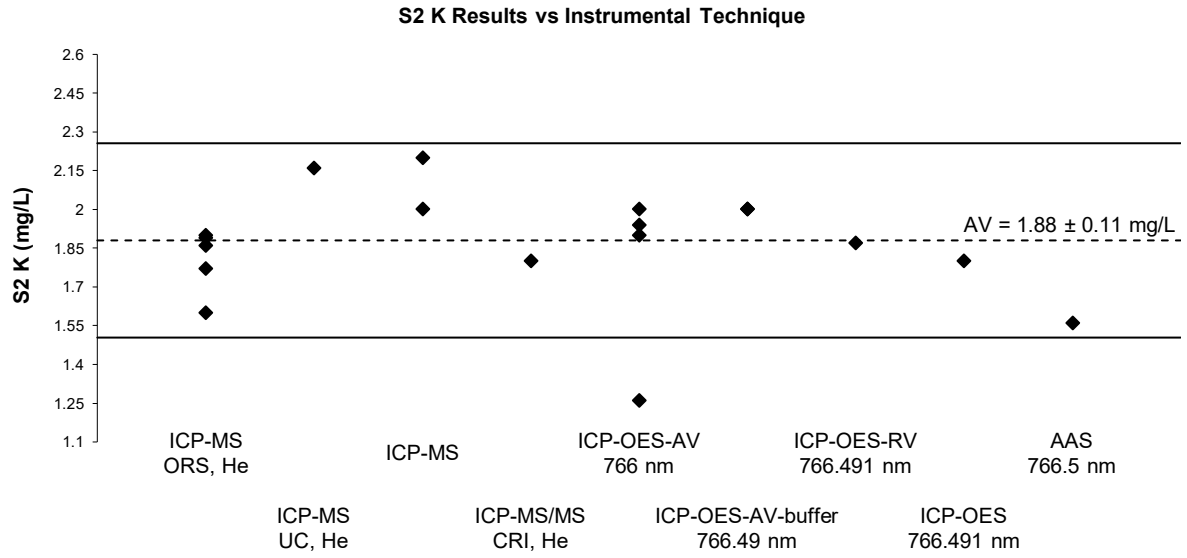
Typical values for pH in drinking water range between 6 and 10.8.[5] The assigned value for pH Sample S2 was 7.58. Caution should be used when using the AAS method for determination of calcium as low results can be obtained if the pH of a sample is above 7.[17]



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 45 S2 Ca Results vs Instrumental Technique

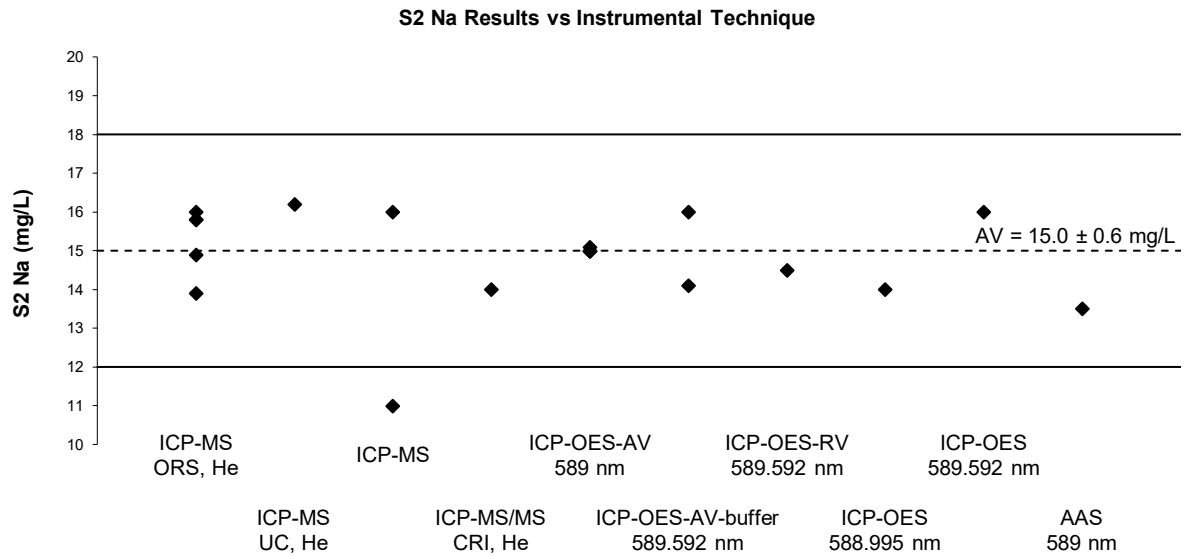
Potassium Most participants used ICP-MS in collision mode and ICP-OES with wavelength 766 nm for K measurements in Sample S2 (Figure 46). One laboratory reported using ICP-OES in axial view with buffer. All reported results returned acceptable z-scores except for one.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 46 S2 K Results vs Instrumental Technique

Sodium measurements in Sample S2 did not present technical difficulty to participating laboratories, all reported results returned acceptable z-scores except for one (Figure 47). Most participants used ICP-OES with wavelength 589 nm.



Horizontal lines are equivalent to z-scores of 2 and -2 respectively.

Figure 47 S2 Na Results vs Instrumental Technique

6.6 Fitness for Purpose of Participants' Results

The Australian Drinking Water Guidelines (ADWG) provide a nationally recognised framework for assessing and managing drinking water quality to protect public health and ensure water is safe for consumption.[5] These levels are set on either a health or aesthetic basis. Accurate measurement of nutrients and anions in potable water is essential, as analytical results must reliably indicate whether a water sample complies with the relevant guideline values. Analytes in Samples S1 or S2 that have a health guideline value are presented below in Table 30 along with their assigned values.

When a test result is used to determine whether a sample complies with an upper control limit, the measurement uncertainty of that result is critical. ISO/IEC 17025 defines a decision rule for such assessments as a 'rule that describes how measurement uncertainty is accounted for when stating conformity with a specified requirement'.[8] To determine whether a sample meets a regulatory limit, considering the reported result and its associated uncertainty, decision rules generally provide three possible outcomes: Pass, Fail, or Inconclusive when further testing may be required (Figure 48).[9]

Table 30 ADWG Values and Assigned Values

Analyte	Health Guideline Value (mg/L)[5]	Assigned Value (mg/L)
Fluoride	1.5	1.02
Iodide	0.5	0.233
Nitrate (as NO_3)	50	1.27
Nitrite (as NO_2)	3	0.327
B	4	0.0963

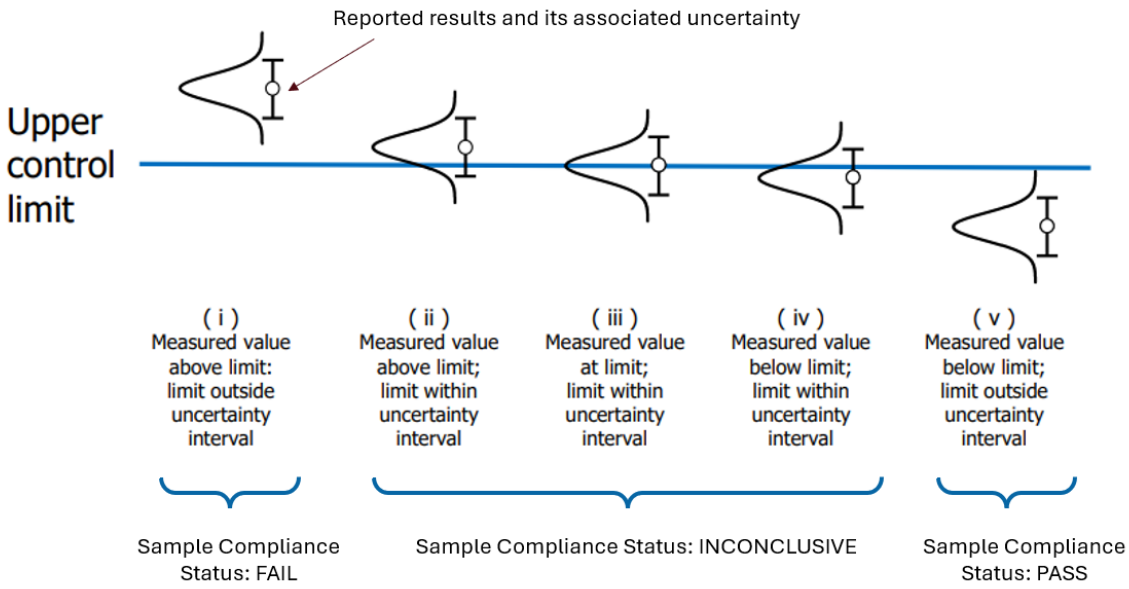


Image adapted from: Eurachem/CITAC Guide Use of Uncertainty Information in Compliance Assessment.[9]

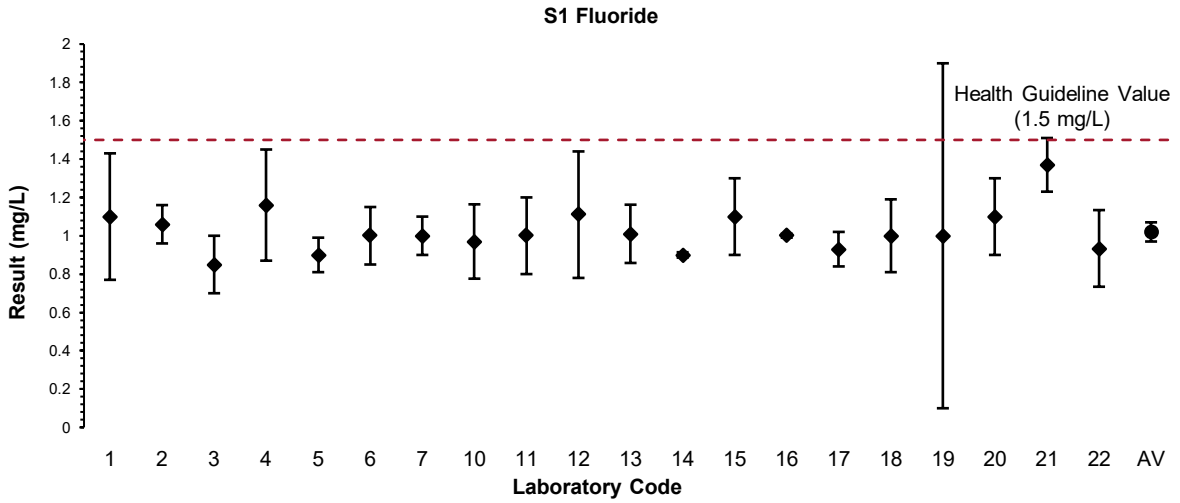
Figure 48 Assessment of Compliance with an Upper Limit

Figures 49 and 50 show comparisons of the spiked value (SV, where applicable), assigned value (AV), participants' results, and guideline values for fluoride and iodide respectively in Sample S1.

Fluoride is often added to drinking water at up to 1 mg/L to protect against dental cavities.[5] The health guideline value is set at 1.5 mg/L as levels of fluoride above this concentration can cause dental fluorosis in children up to about 6 to 8 years.[5] Fluoride in Sample S1 was at the incurred level, 1.02 mg/L. Most participants' results correctly reflected that the sample complies with the ADWG value when considering uncertainty.

Laboratory 21 received a not acceptable z-score for fluoride. Their result incorrectly classified the sample status as inconclusive which may lead to unnecessarily testing and they may want to investigate their method for a potential high bias.

Laboratory 19 reported an acceptable result for fluoride with an uncertainty of 90% of their reported value, which may have been overestimated. When assessed against the guideline value, the sample was also incorrectly classified as inconclusive. The laboratory may need to review their uncertainty evaluation procedures as their reported uncertainty is not fit for purpose.

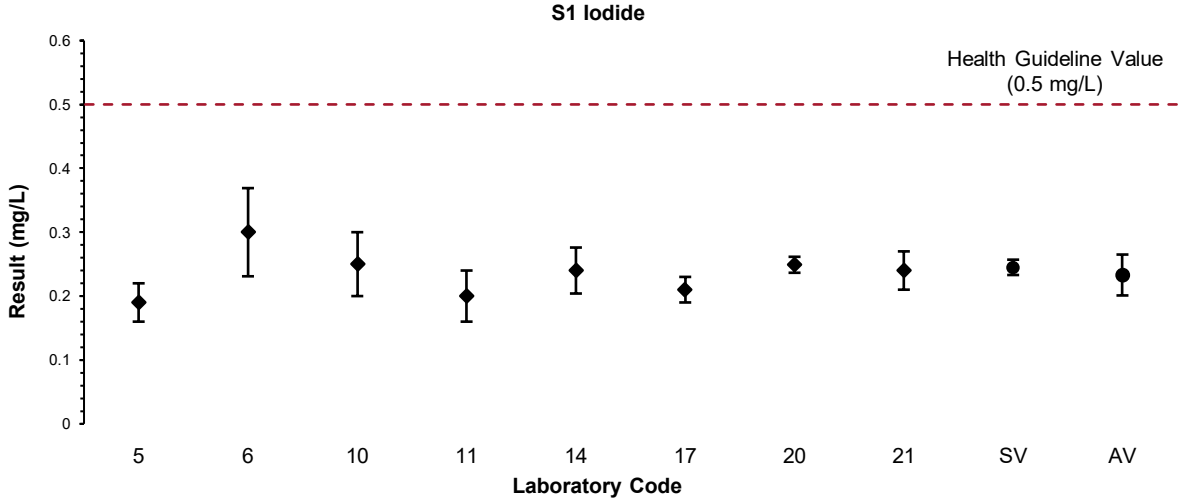


AV = Assigned Value.

Figure 49 Sample S1 Fluoride Results and Guideline Value

Iodide in Sample S1 was spiked at 0.245 mg/L, approximately half the health guideline value of 0.5 mg/L. All participants that reported numeric results correctly reflected sample compliance with the guideline value.

Laboratories 4 and 12 both reported LOR values above the health guideline value, at < 2 mg/L and <1 mg/L respectively. These laboratories should consider reviewing the fitness for purpose of their LORs for measurement of iodide in potable water.



SV = Spike Value, AV = Assigned Value.

Figure 50 Sample S1 Iodide Results and Guideline Value

6.7 Comparison with Previous NMIA Proficiency Tests of Water Characteristics

AQA 26-09 is the 21st NMIA proficiency test of water characteristics.

A summary of participants' performance in measurement of nutrients and anions in water over the last 13 years is presented in Figure 51. Despite different matrices and analyte concentrations, on average participants' performance has remained consistent over time.

Individual performance history reports are emailed to each participant at the end of the study; the consideration of z-scores for an analyte over time provides much more useful information than a single z-score. Over time, laboratories should expect at least 95% of 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.

6.8 Reference Materials and Certified Reference Materials

Proficiency testing and matrix matched control samples taken through all steps of the analytical process are highly valuable quality control tools for assessing extraction efficiency. Control samples used by participants in this study are presented in Table 31.

Table 31 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CRM
2	SS, CRM - CWWTMC; ICC-210; QCI-136;
3	SS, CRM
4	CRM - QCS-01-05 ICP Quality Control Standard #1; High Purity Standards CCV-1 Solution A; High Purity Standards CCV-1 Solution B; Australian Chemical Reagents Multi Element Standard
5	SS
6	CRM
7	CRM
8	RM / Ex PT Sample - AQA 21-10 S2, AQA24-08 S1, AQA 23-19 S1, AQA 24-18 S1, AQA 22-18 S3
9	CRM
10	SS, RM / Ex PT Sample
11	RM / Ex PT Sample
12	RM / Ex PT Sample
13	SS
14	SS, CRM
15	CRM - CWW-TM-B and CWW-TM-C (metals)
16	CRM
17	SS
18	SS, CRM
19	SS, CRM - NSI STANDARD FOR AMMONIA, PH EC ACCUSPEC CRM, NSI STANDARD 7 ANION CRM1 FOR ION CHROMATOGRAPHY
20	SS
21	SS, CRM
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*'[18]

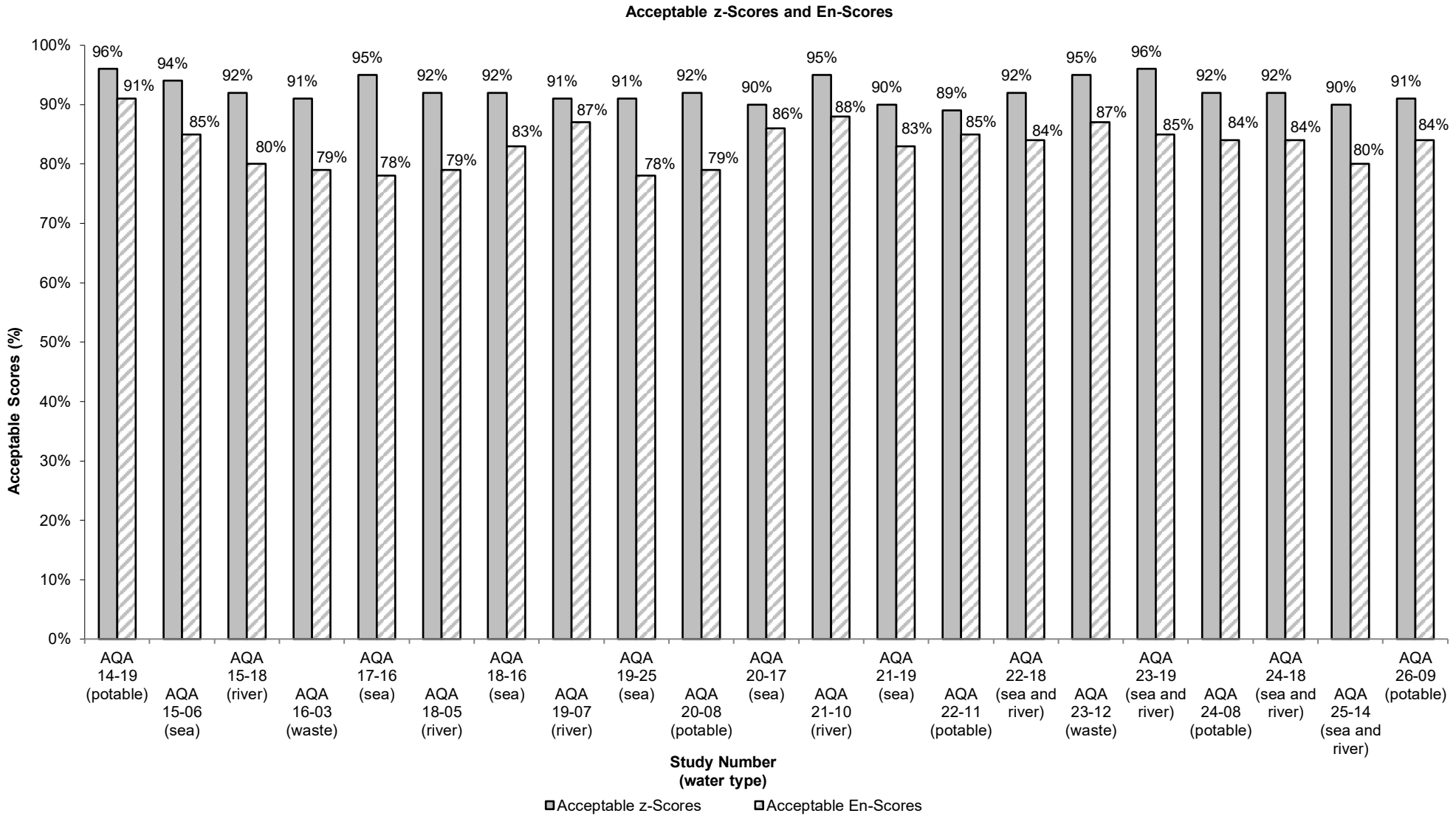


Figure 51 Participants' Performance over Time (2014 – 2026)

7 REFERENCES

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

[1] ISO/IEC 17043, *Conformity assessment – General requirements for the competence of proficiency testing providers.*

[2] Commonwealth of Australia, Department of Industry, Science and Resources, NMIA, 2026, *Study Protocol for Proficiency Testing,* viewed July 2026, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

[3] Commonwealth of Australia, Department of Industry, Science and Resources, NMIA, 2026, *Chemical Proficiency Testing Statistical Manual*, viewed July 2026, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

[4] Thompson, M., Ellison, S.L.R. and Wood, R., 2006, 'The International Harmonized Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories', *Pure Appl. Chem.,* vol. 78, pp. 145-196.

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[14] NMIA, *Estimating Measurement Uncertainty for Chemists*, viewed July 2026, <https://www.industry.gov.au/client-services/training-and-assessment>.

[15] ASTM E2554, *Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques*.

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[17] Fishman, M. and Downs, S.C., 1966, ‘Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water Supply Paper 1540’, pp 23 – 45.

[18] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition, viewed July 2026, <https://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf>.

APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A1.1 Sample Preparation

Sample S1 was prepared from approximately 20 L of autoclaved potable water, fortified with 3 analytes of interest, before mixing and dispensing into 200 mL portions.

Sample S2 was prepared from approximately 20 L of potable water which was fortified with 2 analytes of interest. The sample was then allowed to mix thoroughly prior to being bottled into 400 mL portions.

A1.2 Sample Analysis and Homogeneity Testing

A partial homogeneity test was conducted for 7 of the analytes of interest in Sample S1.[1] Three bottles were analysed in duplicate, and the average of the results was reported as the homogeneity value.

Methodology for Partial Homogeneity Testing of Sample S1

Analyses were conducted by the NMIA Analytical Services Branch, Inorganics section. A summary of the measurement methods and instrumental techniques used is presented in Table 32.

Table 32 Methodology for Sample S1

Test	Measurement Method	Instrument
Chloride	Mercuric Nitrate Titration	DA
Fluoride	Ion Selective Electrode Method	ISE
Iodide	Ion Chromatographic Method	IC
Nitrate (as NO_3)	Colorimetric-Sulphanilamide-NEDD Cd Reduction	SFA
Nitrite (as NO_2)	Colorimetric Method	SFA
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	SFA
Total Dissolved Nitrogen	Persulfate digestion	SFA

APPENDIX 2 - STABILITY STUDY

The test samples were dispatched on 4 May 2026. Participants were advised to store Sample S1 frozen if unable to commence analysis on the day of receipt. Samples' condition on receipt, the date when they were received, and the date of analysis reported by participants, are presented in Table 33.

Table 33 Samples S1 and S2 Condition on Receipt and Dates When Samples were Received and Analysed

Lab Code	Received Date	S1		S2	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	5/05/2026	cold	7/05/2026	cold	7/05/2026
2	5/05/2026	frozen	7/05/2026	cold	7/05/2026
3	5/05/2026	frozen	8/05/2026	cold	9/05/2026
4	5/05/2026	cold	8/05/2026	cold	8/05/2026
5	5/05/2026	frozen	7/05/2026	cold	7/05/2026
6	5/05/2026	cold	19/05/2026	cold	15/05/2026
7	5/05/2026	frozen	11/05/2026	cold	11/05/2026
8	5/05/2026	frozen	8/05/2026	cold	11/05/2026
9	5/05/2026	cold	14/05/2026	cold	14/05/2026
10	5/05/2026	frozen	11/05/2026	frozen	11/05/2026
11	5/05/2026	frozen	6/05/2026	cold	7/05/2026
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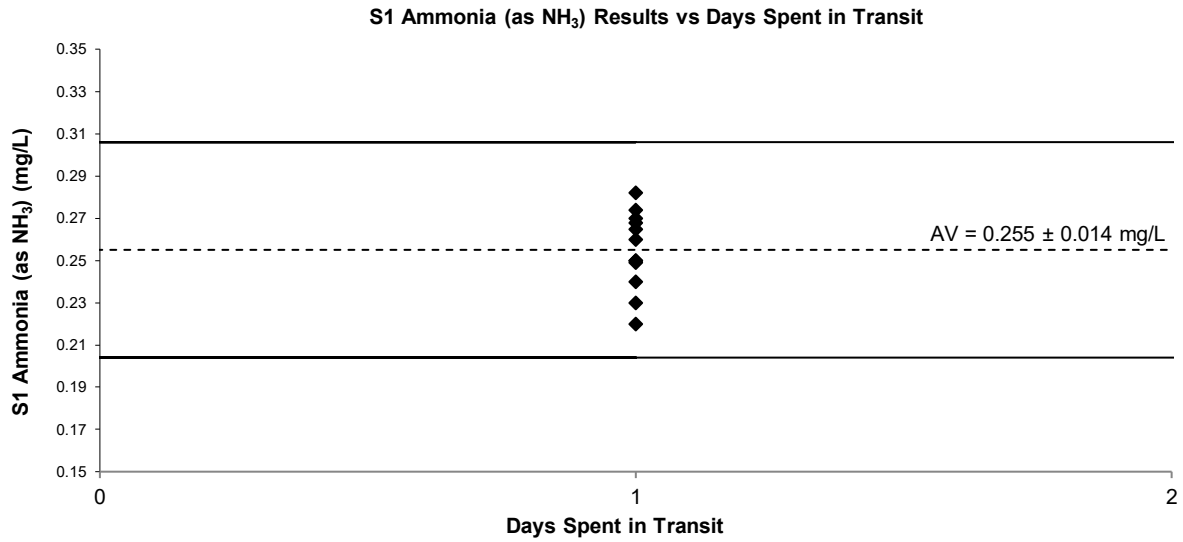
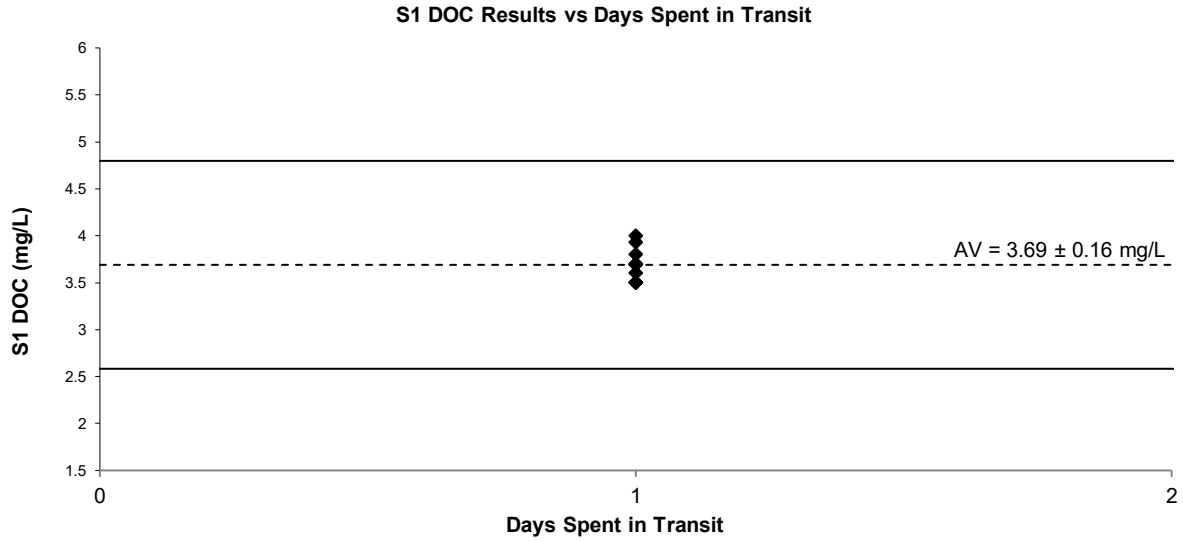
14	5/05/2026	frozen	14/05/2026	cold	12/05/2026
15	5/05/2026	frozen	13/05/2026	frozen	12/05/2026
16	5/05/2026	frozen	6/05/2026	cold	6/05/2026
17	5/05/2026	cold	6/05/2026	cold	5/05/2026
18	5/05/2026	cold	14/05/2026	cold	14/05/2026
19	6/05/2026	frozen	15/05/2026	cold	15/05/2026
20	5/05/2026	frozen	11/05/2026	frozen	21/05/2026
21	5/05/2026	frozen	7/05/2026	NA	NA
22	5/05/2026	frozen	6/05/2026	cold	6/05/2026

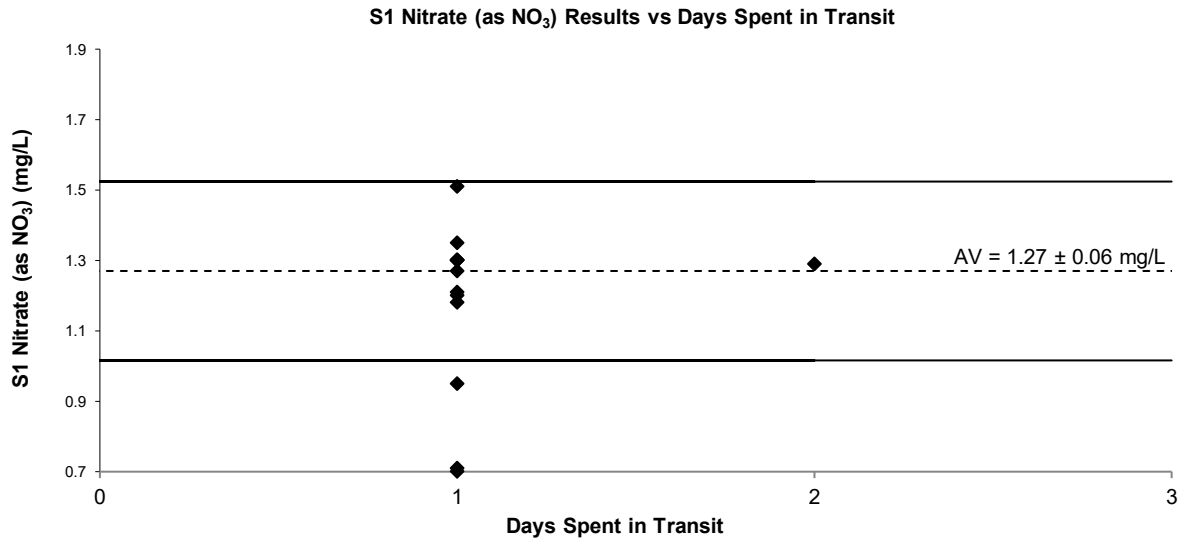
NA = Not Applicable

No significant trends between participants' results, samples' condition on receipt, and date of analysis were evident (Figures 52 to 53).



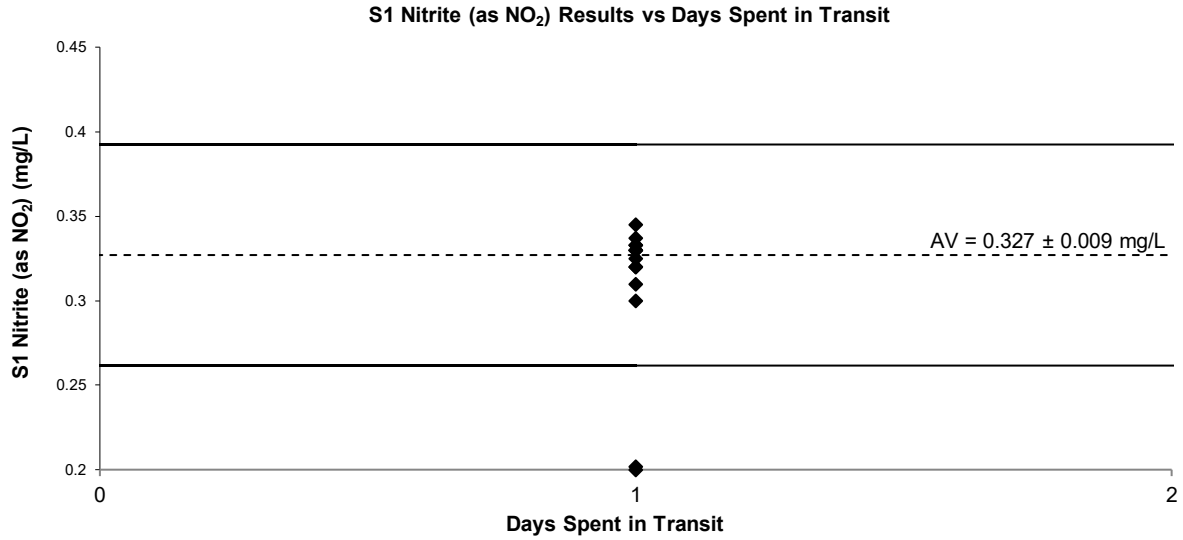
The results reported by Labs 6, 8, 14, and 15 were extreme outliers and are not included in this graph.



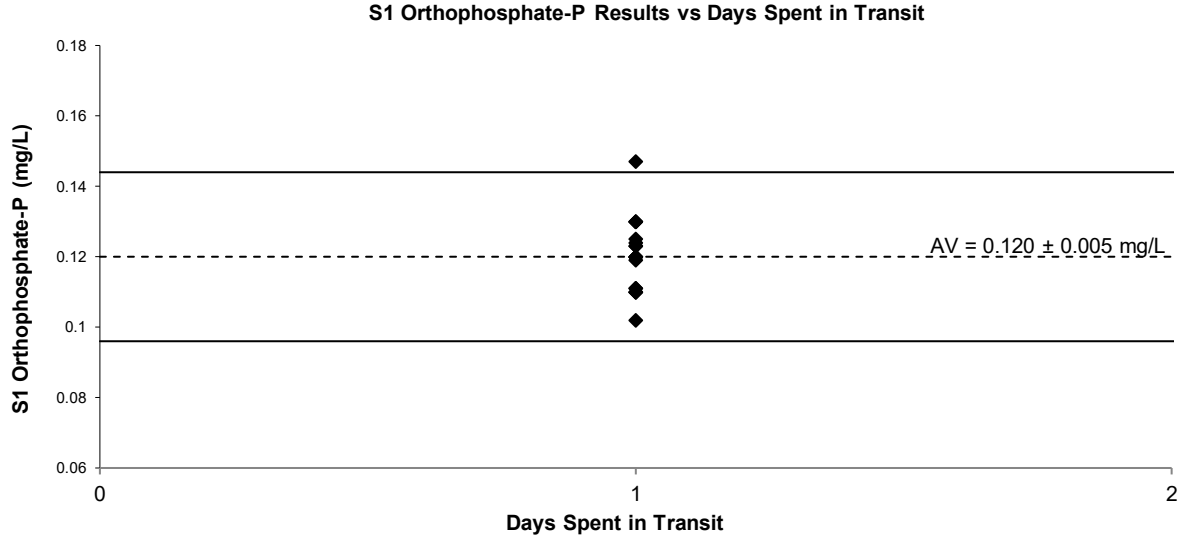


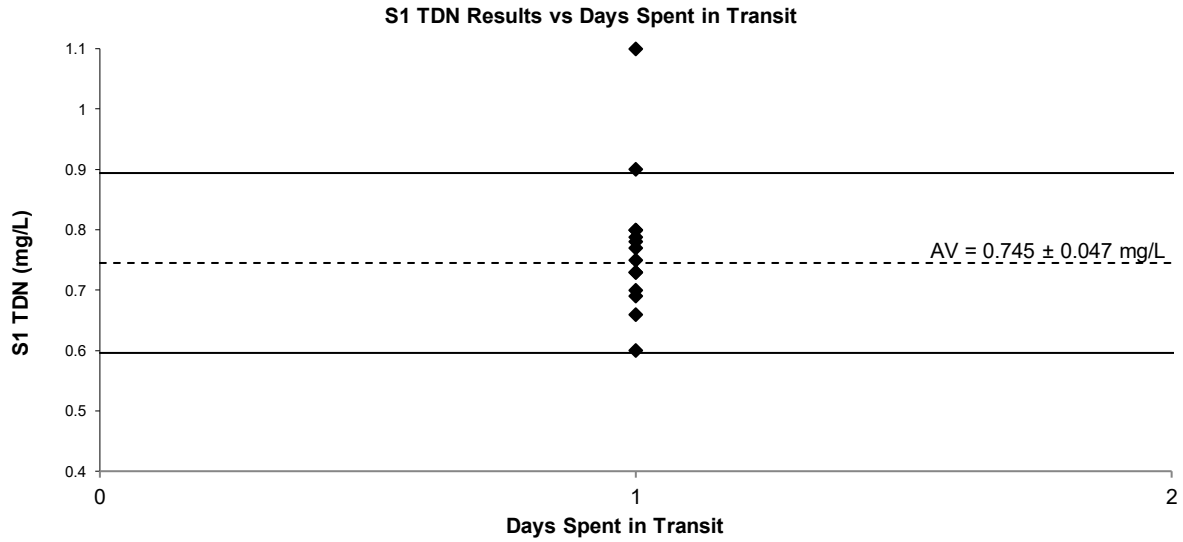
The results reported by Labs 6, 8, 14, and 15 were extreme outliers and are not included in this graph. Results < 0.7 mg/L plotted as 0.7 mg/L.

Figure 52 Results vs Days Spent in Transit



The results reported by Labs 6, 8, 14, and 15 were extreme outliers and are not included in this graph. Results < 0.2 mg/L plotted as 0.2 mg/L.





Results > 1.1 mg/L plotted as 1.1 mg/L.

Figure 52 Results vs Days Spent in Transit (continued)

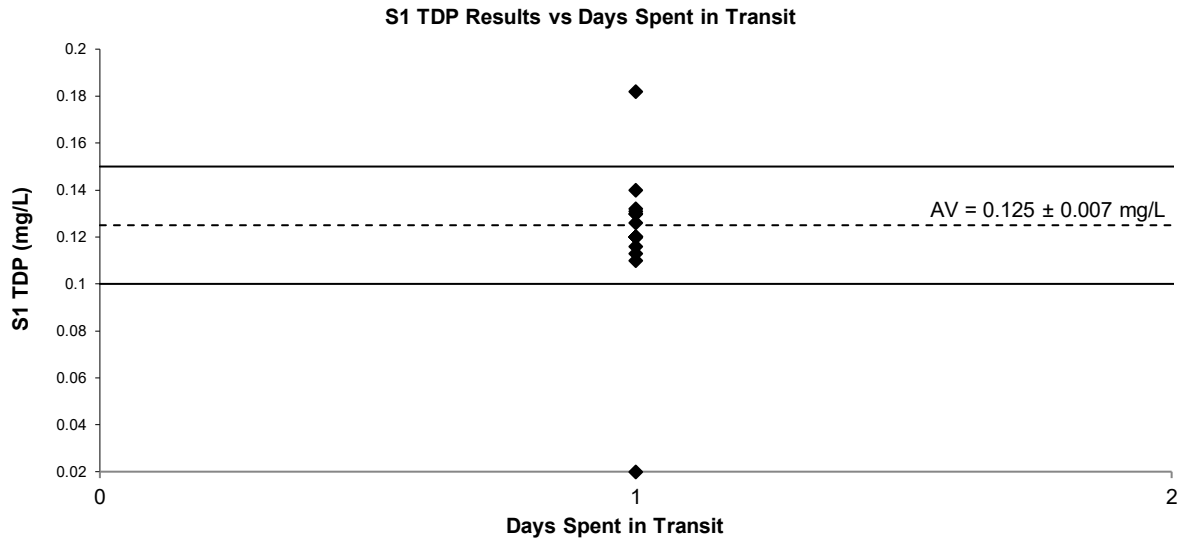
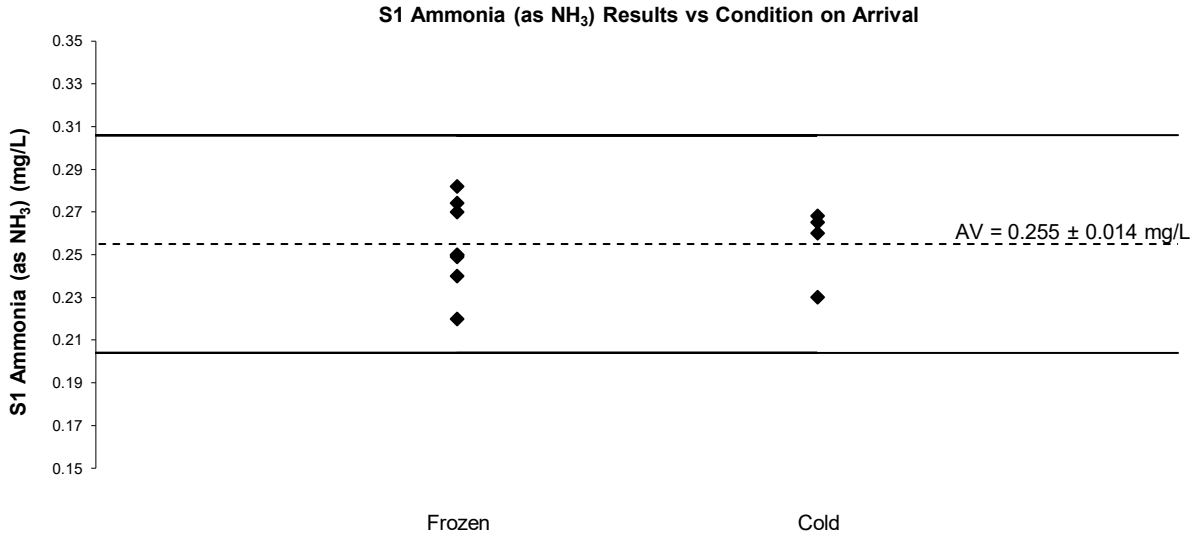


Figure 52 Results vs Days Spent in Transit (continued)



The results reported by Labs 6, 8, 14, and 15 were extreme outliers and are not included in this graph.

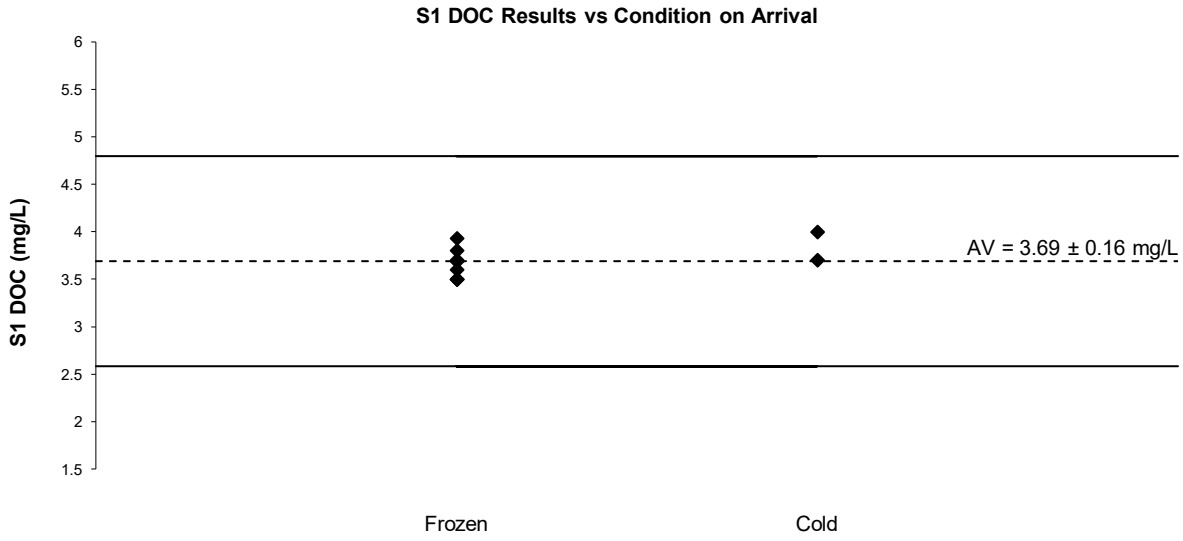
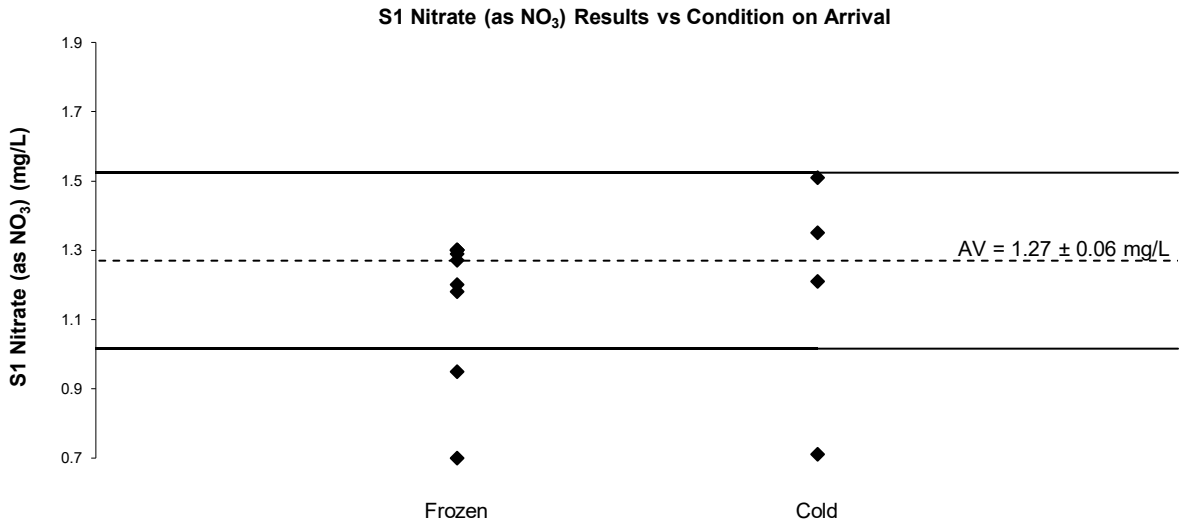
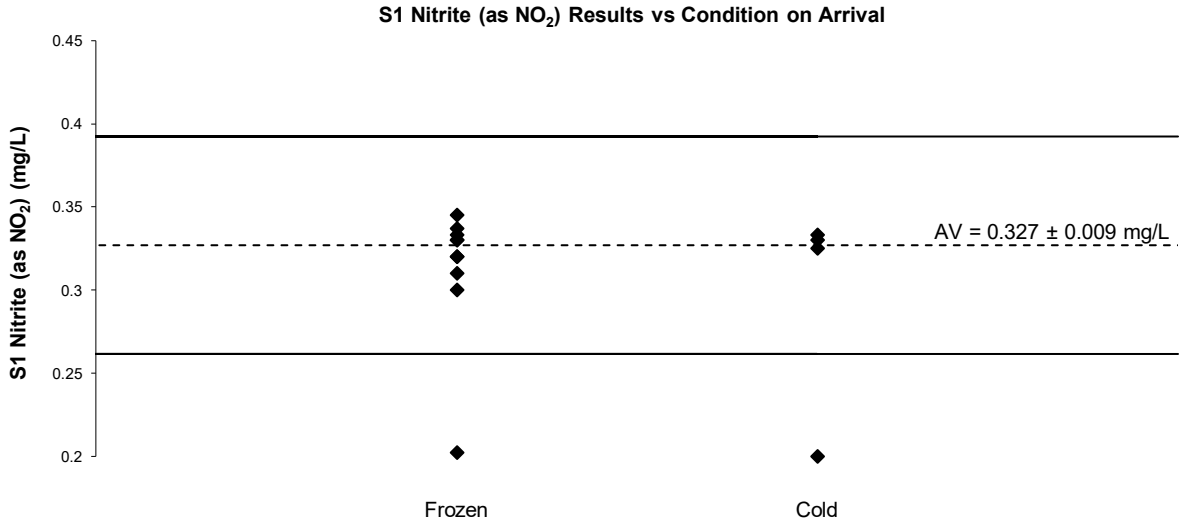


Figure 53 Results vs Condition on Arrival



The results reported by Labs 6, 8, 14, and 15 were extreme outliers and are not included in this graph. Results < 0.7 mg/L plotted as 0.7 mg/L.



The results reported by Labs 6, 8, 14, and 15 were extreme outliers and are not included in this graph. Results < 0.2 mg/L plotted as 0.2 mg/L.

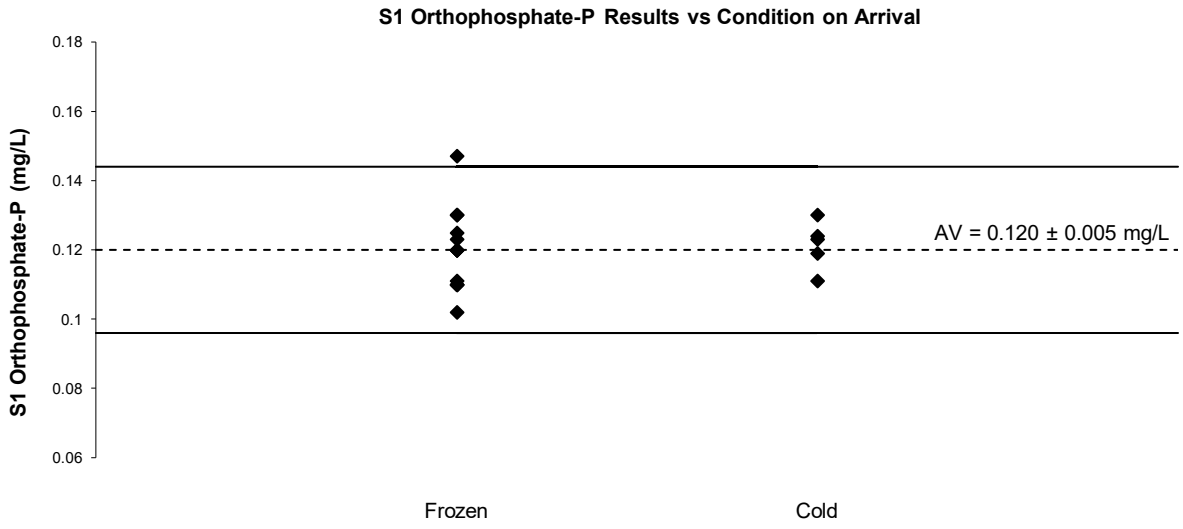
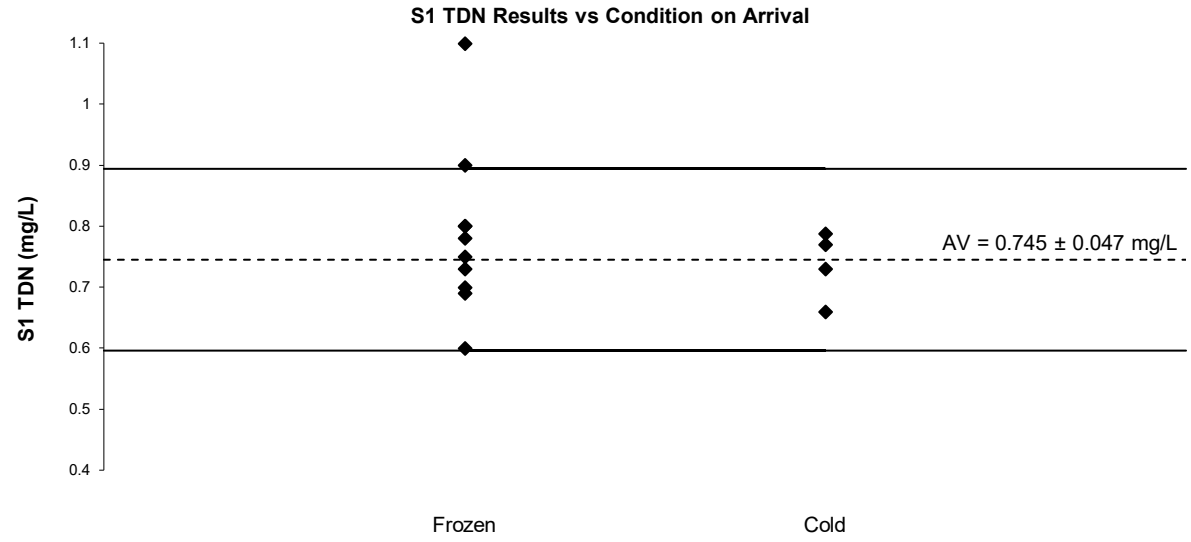


Figure 53 Results vs Condition on Arrival (continued)



Results > 1.1 mg/L plotted as 1.1 mg/L.

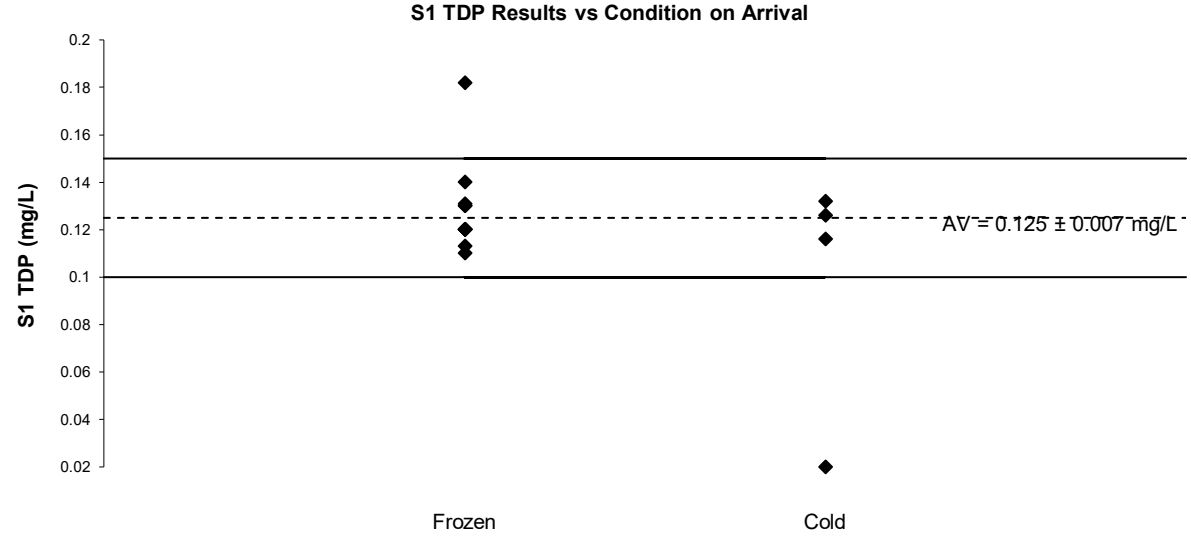


Figure 53 Results vs Condition on Arrival (continued)

A2.1 Storage 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' concentrations. 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 Sample 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 two 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 54).

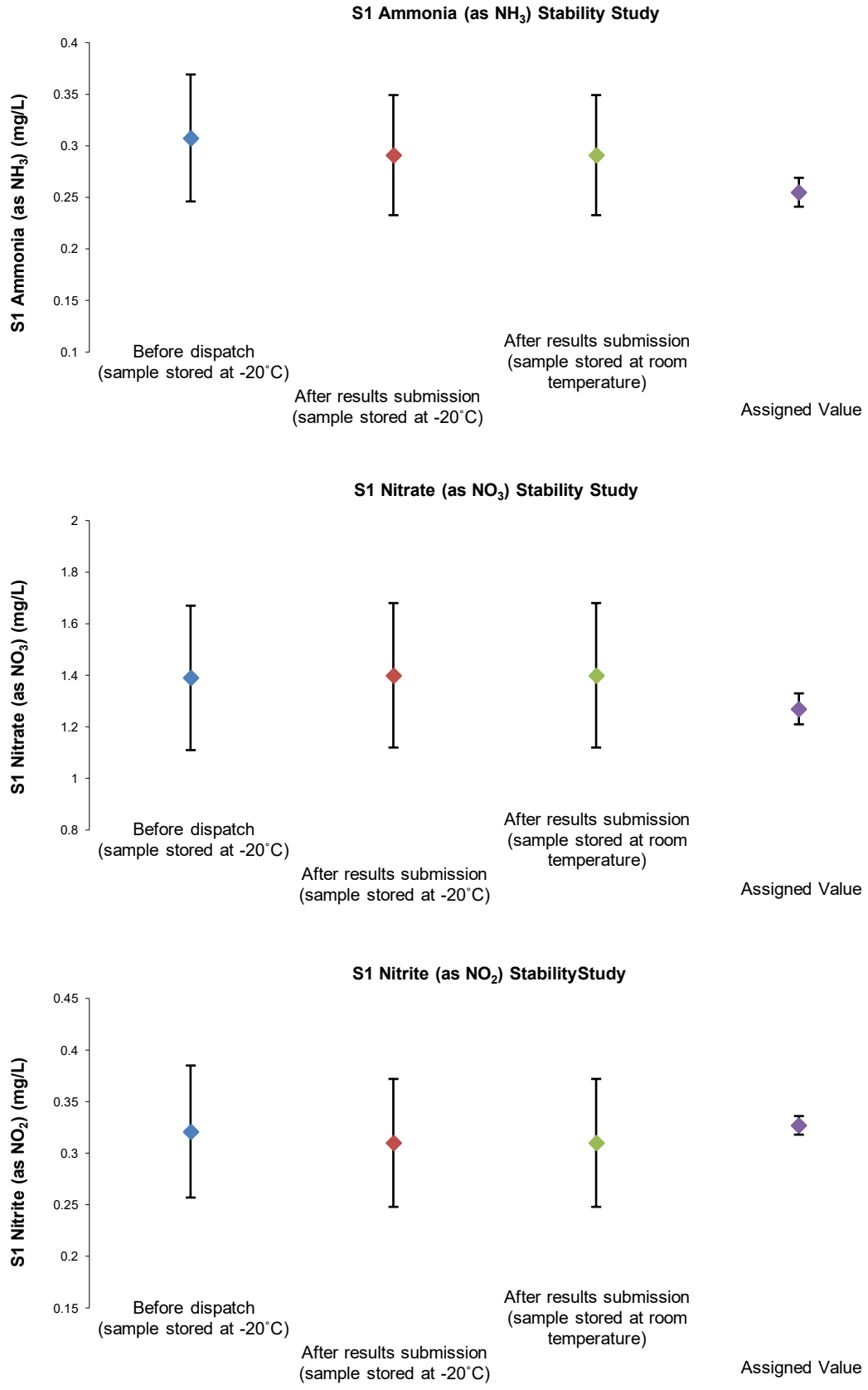


Figure 54 Stability Study Results

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

A3.1 Assigned Value

The assigned value was calculated as the robust average using the procedure described in ISO 13258.[6] The uncertainty was evaluated as:

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

where:

$u_{rob\ av}$ robust average standard uncertainty

$S_{rob\ av}$ robust average standard deviation

p number of results

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

A worked example is set out below in Table 34.

Table 34 Uncertainty of Assigned Value for Chloride in Sample S1

No. results (p)	21
Robust Average	28.1 mg/L
$S_{rob\ av}$	1.4 mg/L
$u_{rob\ av}$	0.38 mg/L
k	2
$U_{rob\ av}$	0.8 mg/kg

The assigned value for Chloride in Sample S1 is 28.1 ± 0.8 mg/L.

A3.2 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 Section 4).

A worked example is set out below in Table 35.

Table 35 z-Score and E_n-score for Chloride result Reported by Laboratory 15 in S1

Chloride Result (mg/L)	Assigned Value (mg/L)	Standard Deviation for Proficiency Assessment	z-Score	E_n-Score
31.3 ± 4.0	28.1 ± 0.8	10% as PCV or 0.10 x 28.1= 2.81 mg/L	$z = \frac{(31.3 - 28.1)}{2.81}$ z = 1.14	$En = \frac{(31.3 - 28.1)}{\sqrt{4.0^2 + 0.8^2}}$ $E_n = 0.78$

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY EVALUATION

When a laboratory has successfully participated in at least 6 proficiency testing studies (e.g. is demonstrating control of bias and verification of repeatability), the standard deviation from proficiency testing studies (the reproducibility between-laboratory variation) can be used to evaluate the uncertainty of their measurement results.[10,12]

Between 2014 and 2026, NMIA carried out 21 proficiency studies for nutrients, anions, and physical tests in water. These studies involved analysis of nutrients, anions, and physical tests in potable, fresh (river), waste, and seawater. Laboratory X participated in and submitted acceptable results for all these studies that included chloride as an analyte. This data can be separated into 2 ranges of results: 0.5 mg/L to 1000 mg/L, and greater than 1000 mg/L (Tables 36 and 37).

The pooled standard deviation of the robust CV over these PT samples for each concentration range gives evaluations of the relative standard uncertainty of 6% and 6.3% respectively. Using a coverage factor of 2 gives relative expanded uncertainties of 12% and 13% respectively, at a level of confidence of approximately 95%.

Table 36 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
AQA 25-14	River	82.3 ± 8.5	85.9 ± 4.4	20	8.8
AQA 26-09	Potable	31.3 ± 4.0	28.1 ± 0.8	21	5
				Average	5.7*
$\text{pooled s\%} = \sqrt{\frac{(8-1)\times 2.9^2 + (10-1)\times 6.5^2 + \cdots\cdots\cdots + (21-1)\times 5^2)}{203-13}}$					6

* The pooled standard deviation was used.

Table 37 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
AQA 24-18	Sea	22659 ± 2270	21600 ± 500	15	3.9
AQA 25-14	Sea	22800 ± 2500	20800 ± 800	20	7.2
				Average	5.5*
pooled s% $= \sqrt{\frac{(8-1)\times 6.3^2 + (10-1)\times 4.1^2 + \cdots\cdots\cdots + (20-1)\times 7.2^2)}{124-10}}$					6.4

* The pooled standard deviation was used.

Table 38 sets out the expanded uncertainty for results of the measurement of chloride in potable, fresh (river), waste, and seawater at levels of 0.5 – 30000 mg/L.

Table 38 Uncertainty of Chloride results evaluated using PT data

Results mg/L	Uncertainty mg/L
20.0	2.4
500	60
1000	120
7500	980
15000	2000
30000	3900

The evaluations of 12% and 13% relative pass the test of being reasonable, and the analysis of the 23 different PT samples over 12 years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrants etc.), and so complies with ISO 17025 requirements.[8]

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
ADWG	Australian Drinking Water Guidelines
APHA	American Public Health Association
ASTM	Australian Society for Testing and Materials
AV	Assigned Value
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
EC	Electrical conductivity
FIA	Flow Injection Analyser
GAG	General Accreditation Guidance
GUM	Guide to the Expression of Uncertainty in Measurement
HM	High Matrix Introduction Accessory
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
IEC	International Electrotechnical Commission
ISO	International Organisation for Standardisation
K	Coverage factor
LOR	Limit of Reporting
Max	Maximum
Md	Median
Min	Minimum
MU	Measurement Uncertainty
N	Number of numeric results
NATA	National Association of Testing Authorities, Australia
NEDD	N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride)
NIR	Near-infrared
NMIA	National Measurement Institute Australia
NOx	Nitrous Oxides
NR	Not Reported
NT	Not Tested
OPA	Orthophtaldialdehyde
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation

PT	Proficiency Testing
RA	Robust Average
RM	Reference Material
SD	Standard Deviation
SDPA	Standard Deviation for Proficiency Assessment
SFA	Segment Flow Analyser
SI	International System of Units
SPADNS	Sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate
SS	Spiked Samples
SV	Spiked Value (or formulated concentration)
TDN	Total Dissolved Nitrogen
TDN	Total Dissolved Phosphorous
TKN	Total Kjeldahl Nitrogen
UC	Universal Cell
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet and Visible Spectroscopy

APPENDIX 6 - METHODOLOGIES REPORTED BY PARTICIPANTS

A6.1 Methodology for Sample S1

Table 39 Measurement Methods and Instrument Techniques for Ammonia (as NH_3)

Lab. Code	Measurement Method	Instrument	Method Reference
3	Colorimetric - Salicylate Method	SFA	In-house
4	Colorimetric - Salicylate Method	DA	In-house
5	Colorimetric - Salicylate Method	DA	in house
6	Colorimetric - Phenate Method	FIA	Lachat QuikChem
8	Colorimetric - Phenate Method	FIA	APHA
9	Colorimetric - Phenate Method	DA	In-house
11	Fluorometric Determination - OPA Method	SFA	SFA
12	Colorimetric - Salicylate Method	DA	In-house
13	Colorimetric - Salicylate Method	DA	In house method based on APHA 4500-NH3 B
14	Colorimetric - Salicylate Method	DA	In-house
15	Colorimetric - Phenate Method	FIA	In House
16	Colorimetric - Phenate Method	FIA	In-House method
17	Colorimetric - Phenate Method	FIA	Inhouse
18	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
19	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500
21		SFA	
22	Colorimetric - Salicylate Method	SFA	APHA 4500 NH3 B

Table 40 Measurement Methods and Instrument Techniques for Bromide

Lab. Code	Measurement Method	Instrument	Method Reference
2	Ion Chromatographic Method	IC	APHA 4110 B
3	Ion Chromatographic Method	IC	APHA 4110 C
4	Ion Chromatographic Method	IC	In-house
5	Ion Chromatographic Method	IC	APHA 4110
6	Ion Chromatographic Method	IC	APHA
10	Ion Chromatographic Method	IC	
11	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	In-house
15	ICP-Method	ICP-MS	In House
16	Ion Chromatographic Method	IC	In-House method
17	Ion Chromatographic Method	IC	Inhouse
19	Ion Chromatographic Method	IC	APHA 4110 B
20	ICP-Method	ICP-MS	
21		IC	
22	Ion Chromatographic Method	IC	

Table 41 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ferricyanide Colorimetric Method	DA	In-house
2	Ion Chromatographic Method	IC	APHA 4110 B
3	Ion Chromatographic Method	IC	APHA 4110 C
4	Ion Chromatographic Method	IC	In-house
5	Mercuric Thiocyanate	DA	APHA 4500
6		FIA	
7	Ferricyanide Colorimetric Method	DA	APHA 4500-Cl
9	Colorimetric	DA	In-house
10	Ion Chromatographic Method	IC	
11	Ion Chromatographic Method	IC	APHA
12	Mercuric Thiocyanate	DA	In-house
13	Potentiometric-Titration	Auto Titration	In House method based on APHA 4500-Cl D
14	Mercurric Nitrate Titration	DA	In-house
15	ICP-Method	ICP-MS	In House
16	Ion Chromatographic Method	IC	In-House method
17	Ion Chromatographic Method	IC	Inhouse
18	Mercuric Thiocyanate	DA	APHA 4500-Cl E
19	Ion Chromatographic Method	IC	APHA 4110 B
20	Ferricyanide Colorimetric Method	UV-Vis Spectrophotometer	
21		IC	
22	Argentometric Titration	Auto Titration	APHA 4500-CL D

Table 42 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
3	Wet-Oxidation	NIR-detector	In-house
4	High-Temperature Oxidation	NIR-detector	In-house
5	High-Temperature Oxidation	NIR-detector	APHA 5310
6	High-Temperature Oxidation	NIR-detector	APHA
9	High-Temperature Oxidation	TOC-L	In-house
11	High-Temperature Oxidation	NIR-detector	APHA
13	High-Temperature Oxidation	NIR-detector	In house method based on APHA 5310-TOC B
15	High-Temperature Oxidation	Shimadzu TOC-L	In House
16	High-Temperature Oxidation	NDIR - detector	In-House method
18	High-Temperature Oxidation	NIR-detector	APHA 5310 B
21		NIR-detector	

Table 43 Measurement Methods and Instrument Techniques for Fluoride

Lab. Code	Measurement Method	Instrument	Method Reference
1	SPADNS Colorimetric Method	DA	In-house
2	Ion Chromatographic Method	IC	APHA 4110 B
3	Ion Chromatographic Method	IC	APHA 4110 C
4	Ion Chromatographic Method	IC	In-house
5	Ion Selective Electrode Method	FIA	QuickChem Method 10-109-12-2-D
6	Ion Selective Electrode Method	Ion Selective Electrode	APHA
7	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F
10	Ion Chromatographic Method	IC	
11	Ion Selective Electrode Method	Ion Selective Electrode	APHA
12	Ion Chromatographic Method	IC	In-house
13	Ion Selective Electrode Method	Ion Selective Electrode	In house method based on APHA 4500-F C
14	Ion Selective Electrode Method	Ion Selective Electrode	In-house
15	Ion Selective Electrode Method	Ion Selective Electrode	
16	Ion Chromatographic Method	IC	In-House method
17	Ion Chromatographic Method	IC	Inhouse
18	Ion Selective Electrode Method	Auto Titration	APHA 4500-F C
19	Ion Chromatographic Method	IC	APHA 4110 B
20	Ion Selective Electrode Method	Ion Selective Electrode	
21		Ion Selective Electrode	
22	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F C

Table 44 Measurement Methods and Instrument Techniques for Iodide

Lab. Code	Measurement Method	Instrument	Method Reference
4	Ion Chromatographic Method	IC	In-house
5	Ion Chromatographic Method	IC	APHA 4110
6	Ion Chromatographic Method	IC	APHA
10	ICP-Method	ICP-MS	
11	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	In-house
16	Ion Chromatographic Method	IC	In-House method
17	Ion Chromatographic Method	IC	Inhouse
20	ICP-Method	ICP-MS	
21		IC	

Table 45 Measurement Methods and Instrument Techniques for Nitrate (as NO_3)

Lab. Code	Measurement Method	Instrument	Method Reference
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	In-house
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	In-house
5	Colorimetric-Sulfanilamide-NEDD hydrazine reduction	DA	in house (based on APHA4500)
6	Calculation	FIA	Lachat QuikChem
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
9	Colorimetric -vanadium III method	DA	In-house
10	Ion Chromatographic Method	IC	
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
12	Colorimetric -vanadium III method	DA	In-house
13	Colorimetric -vanadium III method	DA	In house method based on APHA 4500-NO3 H
14	Calculation	calculation	In-house
15	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In House
16	Ion Chromatographic Method	IC	In-House method
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Inhouse
18	Calculation	FIA	APHA 4500-NO3-F
19	Ion Chromatographic Method	IC	APHA 4110 B
21		SFA	
22	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3 I

Table 46 Measurement Methods and Instrument Techniques for Nitrite (as NO_2)

Lab. Code	Measurement Method	Instrument	Method Reference
3	Colorimetric Method	SFA	In-house
4	Colorimetric Method	DA	In-house
5	Colorimetric Method	DA	in house (based on APHA4500)
6	Colorimetric Method	FIA	Lachat QuikChem
7	Colorimetric Method	DA	APHA 4500-NO2
8	Colorimetric Method	FIA	APHA
9	Colorimetric -vanadium III method	DA	In-house
10	Ion Chromatographic Method	IC	
11	Colorimetric Method	SFA	APHA
12	Colorimetric Method	DA	In-house
13	Colorimetric Method	DA	In house method based on APHA 4500-NO2 B
14	Colorimetric Method	DA	In-house
15	Colorimetric Method	FIA	In House
16	Colorimetric Method	FIA	In-House method
17	Colorimetric Method	FIA	Inhouse
18	Colorimetric Method	FIA	APHA 4500-NO2-B
21		SFA	
22	Colorimetric Method	FIA	APHA 4500-NO3 I

Table 47 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	DA	In-house
3	Ascorbic Acid Colorimetric Method	SFA	In-house
4	Ascorbic Acid Colorimetric Method	DA	In-house
5	Vanadomolybdophosphoric Colorimetric Method	DA	APHA 4500
6	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
7	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
8	Ascorbic Acid Colorimetric Method	FIA	APHA
10	Ion Chromatographic Method	IC	
11	Ascorbic Acid Colorimetric Method	SFA	APHA
12	Ascorbic Acid Colorimetric Method	DA	In-house
13	Ascorbic Acid Colorimetric Method	DA	In house method based on APHA 4500-P B & F
14	Ascorbic Acid Colorimetric Method	DA	In-house
15	Ascorbic Acid Colorimetric Method	FIA	In House
16	Ascorbic Acid Colorimetric Method	FIA	In-House method
17	Ascorbic Acid Colorimetric Method	FIA	Inhouse
18	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P E
20	Vanadomolybdophosphoric Colorimetric Method	UV-Vis Spectrophotometer	
21		SFA	
22	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P F

Table 48 Measurement Methods and Instrument Techniques for Sulphate

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

Table 49 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
3	Calculation (TKN+NOx)	SFA	In-house
4	Persulfate digestion	DA	In-house
5	Persulfate digestion	UV-Vis Spectrophotometer	APHA 4500
6	Persulfate digestion	FIA	Lachat QuikChem
7	Calculation (TKN+NOx)	DA	APHA 4500-N
8	Persulfate digestion	FIA	APHA
11	Persulfate digestion	SFA	APHA
14	Calculation (TKN+NOx)	Calculation	In-house
15	Persulfate digestion	FIA	In House
16	Persulfate digestion	FIA	In-House method
17	Persulfate digestion	FIA	Inhouse
18	Persulfate digestion	FIA	APHA 4500-N B
21		SFA	
22	Calculation (TKN+NOx)	FIA	APHA 4500-Norg B

Table 50 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
3	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	SFA	In-house
4	H2SO4 + persulfate digestion	In-house method	DA	In-house
5	(NH4)2S2O8+H2SO4-Digestion	Vanadomolybdophosphoric Colorimetric Method	UV-Vis Spectrophotometer	APHA 4500
6	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Lachat QuikChem
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
8	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
11	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA
12	No Digestion	ICP Method	ICP-MS	In-house
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-house
15	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In House
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-House method
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	Inhouse
18	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P I
20		ICP Method	ICP-OES	
21			SFA	
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P F

A6.2 Methodology for Sample S2

Table 51 Instrument Techniques for B

Lab. Code	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	Sc		He	1	11
2	ICP-MS	Sc			1	208.957
4	ICP-MS	Sc	ORS	He	1	11 (m/z)
5	ICP-MS	Sc	ORS	He	1	11
6	ICP-MS					
7	ICP-MS	Ir, Rh & Sc	NA	NA	1	11 (m/z)
9	ICP-MS/MS	Sc	CRI	No Gas	500	11
10	ICP-MS	YES	NA	He	100	11
11	ICP-MS	Sc Rh Ir	ORS	He	2	11
12	ICP-MS	45 Sc	ORS	NA	1	11
13	ICP-OES-AV	NA	NA	NA	1	249.772
14	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	11
15	ICP-MS	Sc	NA	NA	1	10
16	ICP-OES-AV	Bi 223.061			1	249.678
17	ICP-OES-AV	Lu	NA	NA	1.05	208.956
18	ICP-MS/MS	Sc	ORS	Standard Mode	NA	11
19	ICP-MS	Sc	CRI	Standard Mode	10	
20	ICP-OES-AV					208

Table 52 Instrument Techniques for Ca

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	Sc		H2	1	40
2	ICP-OES-AV-buffer	Y			1	315.887
3	ICP-MS	Sc45	ORS	He	1	44(m/z)
4	ICP-MS	Sc	ORS	H2	1	40 (m/z)
5	ICP-MS	Sc	ORS	HMHe	10	44
6	ICP-MS					
7	ICP-MS	Ir, Rh & Sc	NA	NA	1	44 (m/z)
9	ICP-MS/MS	Sc	CRI	H2	500	40
10	ICP-OES	YES	NA	NA	100	317.933
11	ICP-OES-AV	Y	NA	NA	3	422.673
12	ICP-MS	72 Ge	ORS	H2	1	40
13	AAS	NA	NA	NA	1	422.7
14	ICP-OES	Cs,Y	NA	NA	1	317.993
15	ICP-MS	Sc	UC	He	1	44
16	ICP-OES-AV	Eu 290.667			1	317.933
17	ICP-OES-RV	Lu	NA	NA	1.05	422.673
18	ICP-OES-AV-buffer	Eu			NA	315.887nm
20	ICP-OES-AV					315
22	ICP-OES-AV					396

Table 53 Instrument Techniques for K

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	Sc		He	1	39
2	ICP-OES-AV-buffer	Y			1	766.49
3	ICP-MS	Sc45	ORS	He	1	39(m/z)
4	ICP-MS	Sc	ORS	He	1	39 (m/z)
5	ICP-MS	Sc	ORS	He	1	39
6	ICP-MS					
7	ICP-MS	Ir, Rh & Sc	NA	NA	1	39 (m/z)
9	ICP-MS/MS	Sc	CRI	He	500	39
10	ICP-OES	YES	NA	NA	100	766.491
11	ICP-OES-AV	Y	NA	NA	4	766.491
12	ICP-MS	72 Ge	ORS	He	1	39
13	AAS	NA	NA	NA	1	766.5
14	ICP-OES	Cs,Y	NA	NA	1	766.491
15	ICP-MS	Sc	UC	He	1	39
16	ICP-OES-AV	In 410.176			1	766.491
17	ICP-OES-RV	Lu	NA	NA	1.05	766.491
18	ICP-OES-AV-buffer	Eu			NA	766.491nm
20	ICP-OES-AV					766
22	ICP-OES-AV					766

Table 54 Instrument Techniques for Mg

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	Sc		He	1	24
2	ICP-OES-AV-buffer	Y			1	285.213
3	ICP-MS	Sc45	ORS	He	1	24(m/z)
4	ICP-MS	Sc	ORS	He	1	24 (m/z)
5	ICP-MS	Sc	ORS	He	1	24
6	ICP-MS					
7	ICP-MS	Ir, Rh & Sc	NA	NA	1	24 (m/z)
9	ICP-MS/MS	Sc	CRI	He	500	24
10	ICP-OES	YES	NA	NA	100	383.829
11	ICP-OES-AV	Y	NA	NA	5	279.078
12	ICP-MS	72 Ge	ORS	He	1	24
13	AAS	NA	NA	NA	1	285.2
14	ICP-OES	Cs,Y	NA	NA	1	285.213
15	ICP-MS	Sc	UC	He	1	25
16	ICP-OES-RV	In 303.936			1	285.213
17	ICP-OES-RV	Lu	NA	NA	1.05	285.213
18	ICP-OES-AV-buffer	Eu			NA	383.829nm
20	ICP-OES-AV					279
22	ICP-OES-AV					279

Table 55 Instrument Techniques for Na

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	Sc		He	1	23
2	ICP-OES-AV-buffer	Y			1	589.592
3	ICP-MS	Sc45	ORS	He	1	23(m/z)
4	ICP-MS	Sc	ORS	He	1	23 (m/z)
5	ICP-MS	Sc	ORS	He	10	23
6	ICP-MS					
7	ICP-MS	Ir, Rh & Sc	NA	NA	1	23 (m/z)
9	ICP-MS/MS	Sc	CRI	He	500	23
10	ICP-OES	YES	NA	NA	100	589.592
11	ICP-OES-AV	Y	NA	NA	6	589.592
12	ICP-MS	72 Ge	ORS	He	1	23
13	AAS	NA	NA	NA	1	589
14	ICP-OES	Cs,Y	NA	NA	1	588.995
15	ICP-MS	Sc	UC	He	1	23
16	ICP-OES-AV	In 410.176			1	589.592
17	ICP-OES-RV	Lu	NA	NA	1.05	589.592
18	ICP-OES-AV-buffer	Eu			NA	589.592nm
20	ICP-OES-AV					589
22	ICP-OES-AV					589

Table 56 Measurement Methods and Instrument Techniques for Total P

Lab. Code	Measurement Method		Instrument	Method Reference
4	H2SO4 + persulfate digestion	Ascorbic Acid Colorimetric Method	DA	In-house
5	NA	ICP Method	ICP-MS	USEPA SW846 - 6020
6			FIA	Lachat QuikChem
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
9	No Digestion	ICP Method	ICP-MS	In-house
12	No Digestion	ICP Method	ICP-MS	In-house
13	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house method based on APHA 4500-P B & F
16	No Digestion	ICP Method	ICP-OES	In-House method
17	HNO3/HCL digestion	ICP Method	ICP-OES	Inhouse
18	HCl+HNO3	ICP Method	ICP-OES	USEPA 3005, APHA 3120
19	K2S2O8-Digestion	Ion Chromatographic Method	IC	APHA 4110 B
20		ICP Method	ICP-OES	
22	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P F

Table 57 Measurement Methods and Instrument Techniques for Alkalinity

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	In-house
2	Titration	Auto Titration	APHA 2320 B
3	Titration	Auto Titration	In-house
4	Titration	Auto Titration	In-house
5	Titration	Auto Titration	APHA 2320
6	Titration	Auto Titration	APHA
7	Titration	Auto Titration	APHA 2320
9	Titration	Auto Titration	In-house
11	Titration	Auto Titration	
12	Titration	Auto Titration	In-house
13	Titration	Auto Titration	In house method based on APHA 2320 B
14	Titration	Ion Selective Electrode	In-house
15	Titration	Auto Titration	In House
16	Titration	Auto Titration	In-House method
18	Titration	Auto Titration	APHA 2320 B
19	Titration	Manual Analysis	APHA 2320 - ALKALINITY
20	Titration	Auto Titration	2320B APHA23rd
22	Titration	Auto Titration	APHA 2320B

Table 58 Measurement Methods and Instrument Techniques for Silica (as SiO_2)

Lab. Code	Measurement Method	Instrument	Method Reference
1	Molybdosilicate Method	DA	In-house
3	Molybdosilicate Method	DA	In-house
5	ICP-Method	ICP-MS	USEPA SW846 - 6020
6	ICP-Method	ICP-MS	APHA
7	Molybdosilicate Method	DA	APHA 4500-SiO2
8	Molybdosilicate Method	FIA	APHA
10	ICP-Method	ICP-OES	
11	ICP-Method	ICP-OES	
12	ICP-Method	ICP-MS	In-house
13	Molybdosilicate Method	DA	In house method based on APHA 4500-SiO2 E
14	ICP-Method	ICP-OES	
16	ICP-Method	ICP-OES	In-House method
17	Molybdosilicate Method	SFA	Inhouse
18	Molybdosilicate Method	FIA	APHA 4500-SiO2 D
20	ICP-Method	ICP-OES	
22	ICP-Method	ICP-OES	APHA 3120 B

Table 59 Measurement Methods and Instrument Techniques for Total Hardness

Lab. Code	Measurement Method	Instrument	Method Reference
3	Calculation	ICP-MS	APHA 2340 B
4	Calculation	ICP-MS	APHA 2340B
5	Calculation	ICP-MS	USEPA SW846 - 6020
6	Calculation	ICP-MS	APHA
7	Calculation	NA	APHA 2340
9	Calculation	ICP-MS	In-house
10	Calculation	ICP-OES	
11	Calculation	ICP-OES	
12	Calculation	ICP-MS	In-house
13	Calculation	NA	In house method based on APHA 2340 B
14	Calculation	ICP-OES	
15	Titration	Manual Analysis	In House
16	Calculation	ICP-OES	In-House method
17	Calculation	ICP-OES	Inhouse
18	Calculation	ICP-OES	APHA 2340B
20	Calculation	ICP-OES	
22	Calculation	ICP-OES	APHA 2340 B

END OF REPORT