Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Report AQA 20-08 Nutrients, Anions and Physical Tests in Water

August 2020

ACKNOWLEDGMENTS

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

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

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

Luminita Antin

Dr Andrew Evans

Hamish Lenton

Wei Huang

I would also like to thank Geoff Firns from CHEMCENTRE for reviewing this report.

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Accredited for compliance with ISO/IEC 17043

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1 SUMMARY

This report presents the results of the proficiency test AQA 20-08, Nutrients, Anions and Physical Tests in Potable Water. The study focused on the measurement of total: B, Ca, K, Mg, Na and P. Ammonia-N, bromide, chloride, dissolved organic carbon (as dNPOC), fluoride, iodide, (nitrate-N + nitrite-N) NOx, orthophosphate-P, sulphate, total dissolved nitrogen, total dissolved phosphorus, alkalinity to pH 4.5 (as $CaCO_3$), electrical conductivity at 25ºC, total hardness (as $CaCO_3$), pH at 25ºC, silica (as SiO_2), total dissolved solids at 180ºC, total solids at 103-105°C, total suspended solids at 103-105ºC and turbidity (NTU) were also included in the program.

The sample set consisted of three water samples.

Seventeen laboratories registered to participate and sixteen submitted results.

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

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

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

Of 311 z-scores, 287 (92%) returned a satisfactory score of $|z| \leq 2.0$.
Of 311 E_n-scores, 248 (80%) returned a satisfactory score of $|E_n| \leq 1.0$.

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

Low level bromide and iodide were the tests which presented the most analytical difficulty to participating laboratories

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

On average, over the last seven years, participants' performance in measuring nutrients, anions and physical tests in water has remained consistent, with the percentage of satisfactory z-scores ranging from 91% to 96%. However laboratories are encountering difficulty in estimating the uncertainty of their measurement result; the number of satisfactory E_n-scores decreased from 91% to 79%.

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

Of 311 numerical results, 304 (98%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 4.

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

The study samples were checked for homogeneity and stability and are well characterised, both by in-house testing and from the results of the proficiency round. Surplus test samples are available for sale.

2 INTRODUCTION

2.1 NMI Proficiency Testing Program

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

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

- inorganic analytes in soil, water, food and pharmaceuticals;
- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- PFOS/PFOA in water, soil, biota and food;
- allergens in food;
- controlled drug assay; and
- folic acid in flour.

AQA 20-08 is the 10th NMI proficiency study of nutrients, anions and physical tests in water.

2.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories' methods used in determination of nutrients, anions and physical tests in potable water;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

2.3 Study Conduct

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

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

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

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The twenty-six tests were selected from those for which an investigation level is listed in the Australian Drinking Water Guidelines[5] and are commonly measured by water testing laboratories.

3.2 Participation

Seventeen laboratories participated and sixteen submitted results.

The timetable of the study was:

Invitation issued:	4 May 2020
Samples dispatched:	25 May 2020
Results due:	23 June 2020
Interim report issued:	24 June 2020

3.3 Test Material Specification

Three samples were provided for analysis:

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

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

Sample S3 was 500 mL of unfiltered potable water.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

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

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

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

To address issues associated with holding time and holding conditions, a stability study was conducted for the less stable analytes: NH_3-N and NO_x in S1. The stability study was conducted over the entire period of the PT study and was designed to simulate the conditions encountered by the samples during storage. Details of the study and its results are given in Appendix 2. The test samples were stable for the period of the proficiency test.

3.7 Sample Storage, Dispatch and Receipt

Sample S3 was stored at room temperature, Sample S2 was refrigerated before dispatch, while sample S1 was frozen.

The samples were dispatched by courier on 25 May 2020.

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

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

3.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- If analyses cannot be commenced on the day of receipt, please store Sample S1 frozen.

- Prior to testing thaw sample S1 completely.
- Turbidity in S3 should be measured after TS, TDS and TSS analyses.
- Participants are asked to report results in units of mg/L except for turbidity, pH and EC. Report turbidity result in nephelometric turbidity units (NTU) and the result for EC in units of µS/cm.

SAMPLE S1 filtered, autoclaved and frozen potable water		**SAMPLE S2 unfiltered and chilled potable water**		**SAMPLE S3 unfiltered potable water**	
Test	**Approximate Conc. Range mg/L**	**Test**	**Approximate Conc. Range mg/L**	**Test**	**Approximate Conc. Range mg/L**
Bromide	<0.75	B (total)	<2.5	TS (dried at 103-105°C)	<400
Chloride	<15	Ca (total)	<25	TSS (dried at 103-105°C)	<150
Fluoride	<5	K (total)	<25	TDS (dried at 180°C)	<250
Iodide	<0.5	Mg (total)	<25	Turbidity (NTU)	<50
Dissolved Organic Carbon as (dNPOC)	<10	Na (total)	<250		
Ammonia-N	<2.5	P (total)	<5		
(Nitrate-N +Nitrite-N) NOx	<2.5	Alkalinity to pH 4.5 as CaCO3	<250		
Total Dissolved Nitrogen	<10	Total Hardness (CaCO3)	<250		
Total Dissolved Phosphorus	<1	pH (at 25°C)	>5		
Orthophosphate-P	<0.25	Silica (as SiO2)	<25		
Sulphate	<25	EC (at 25°)	<2000 µS/cm		

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (e.g. 5.23 ± 0.51 mg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.

3.9 Interim Report

An interim report was emailed to participants on 24 June 2020.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for S1, S2 and S3

Measurement methods and instrumental techniques used for the tests in Samples S1, S2 and S3 together with the additional information for each sample analysed are presented in Appendices 6, 7 and 8 respectively.

4.2 Basis of Participants' Measurement Uncertainty Estimates

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

Table 1 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down – precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis	Instrument Calibration Recoveries of SS	Nordtest Report TR537
2	Top Down – precision and estimates of the method and laboratory bias	Control Samples – SS	CRM Laboratory Bias from PT Studies Recoveries of SS	NATA Technical Note 33
3	Top Down – precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA Technical Note 33
4	Top Down – precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
5	Top Down – precision and estimates of the method and laboratory bias	Control Samples – CRM Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ASTM E2254-13
6	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – CRM Duplicate Analysis	CRM	ISO/GUM
8	Top Down – precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis	CRM Instrument Calibration	Eurachem/CITAC Guide
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples – CRM Duplicate Analysis	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	NATA Technical Note 33
10	Top Down – precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis Instrument Calibration	Recoveries of SS	NATA Technical Note 33
11	Top Down – precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis	CRM	NMI Uncertainty Course
12	Top Down – precision and estimates of the method and laboratory bias	Control Samples – RM Duplicate Analysis		NATA Technical Note 33
13	Top Down – precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis	CRM Instrument Calibration Standard Purity	Nordtest Report TR537
14	Standard deviation of replicate analyses multiplied by 2 or 3	Standard Deviation from PT Studies Only		Eurachem/CITAC Guide
			Laboratory Bias from PT Studies	
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis	CRM	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
16	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	ISO/GUM
17	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – RM Duplicate Analysis	Recoveries of SS	NATA Technical Note 33

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

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

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

Table 2 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
The amount received was insufficient for testing TSS, TDS and TS on the same sample (S3).	Thank you for your feedback! We apologise for any inconvenience caused. We will review the design of our study and will provide more samples for analysis in our next studies.
More volume of sample is needed – we had insufficient sample to complete all tests for Sample 1. We had insufficient sample last participation too.	
Good program only limiting factor was amount of sample volume supply as it makes it hard to repeat some of the analysis if something goes wrong. Also some of the traditional methods require a bigger volume especially to obtain the limits for potable waters. (In future, you may consider supplying at least 500mL sample for S1).	

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 3 to 28 with resultant summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 27. An example chart with interpretation guide is shown in Figure 1.

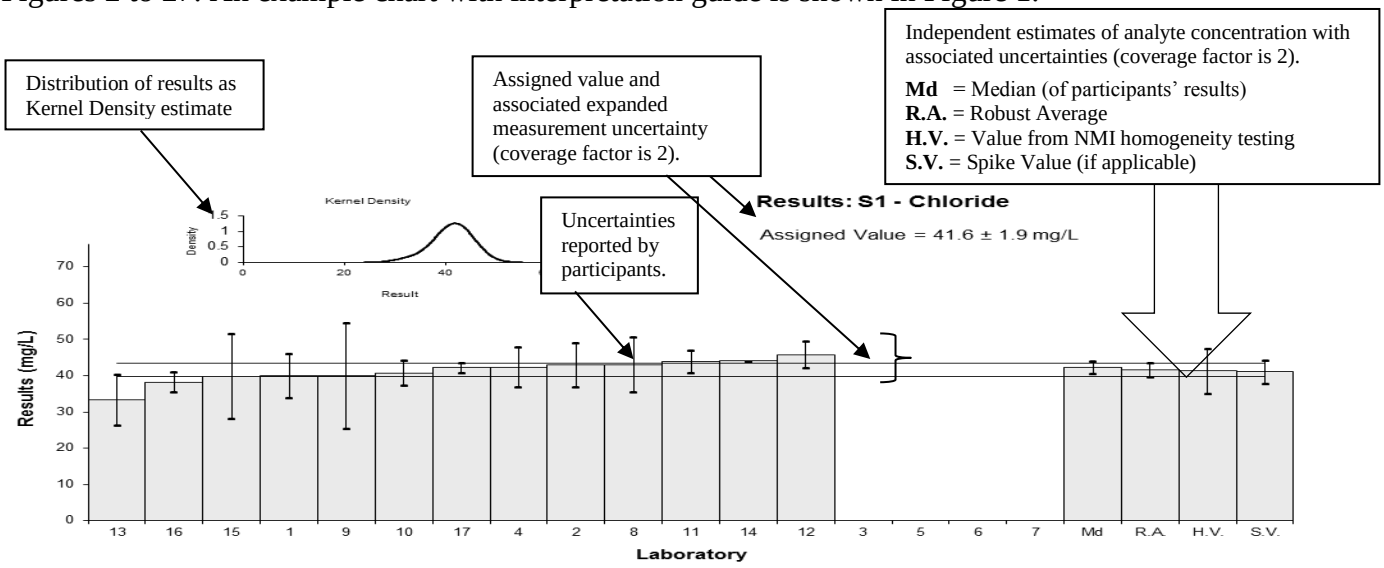


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

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

5.3 Robust Average

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

5.4 Robust Between-Laboratory Coefficient of Variation

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

5.5 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study coordinator would be expected from participants. It is important to note that is not the coefficient of variation of participant results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.[7] By setting a fixed and realistic value for the PCV, the participant's performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 Target Standard Deviation

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

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

This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

5.7 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 participants' result
X is the study assigned value
σ is the target standard deviation

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

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

5.8 E_n-Score

An example of E_n-score calculation using data from the present study is given in Appendix 3.

The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

E_n is E_n-score
χ is participants' result
X is the study assigned value
U_χ is the expanded uncertainty of the participants' result
U_X is the expanded uncertainty of the assigned value

An E_n-score with absolute value ($|E_n|$):

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

5.9 Traceability and Measurement Uncertainty

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

6 TABLES AND FIGURES

Table 3

Sample Details

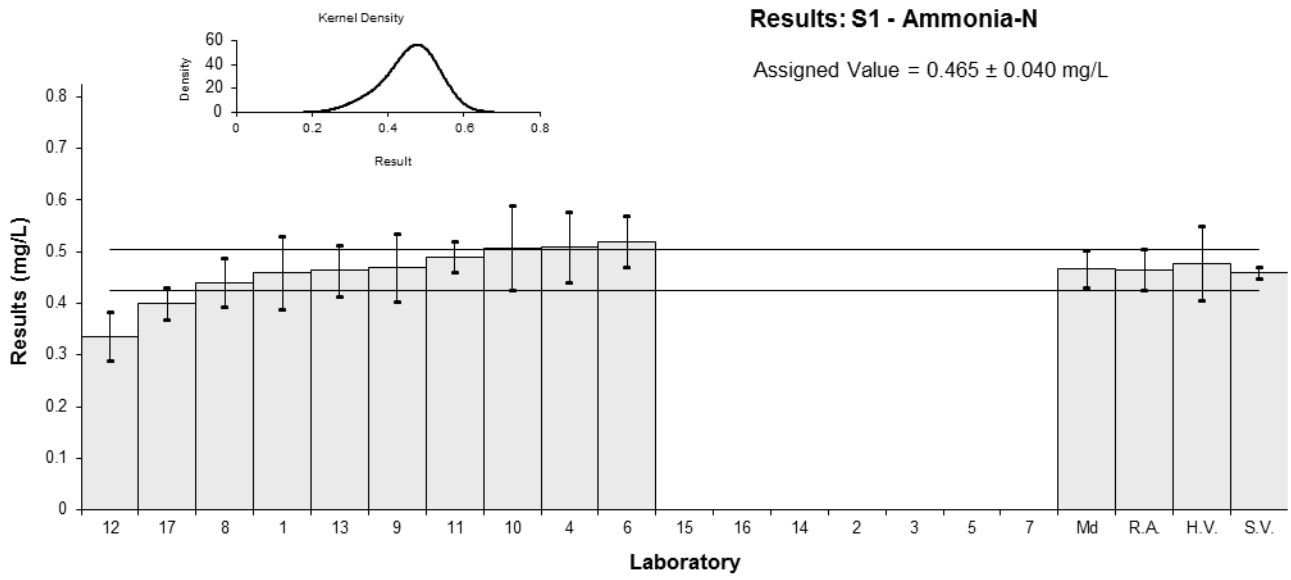
Sample No.	S1
Matrix.	Potable Water
Analyte.	Ammonia-N
Units	mg/L

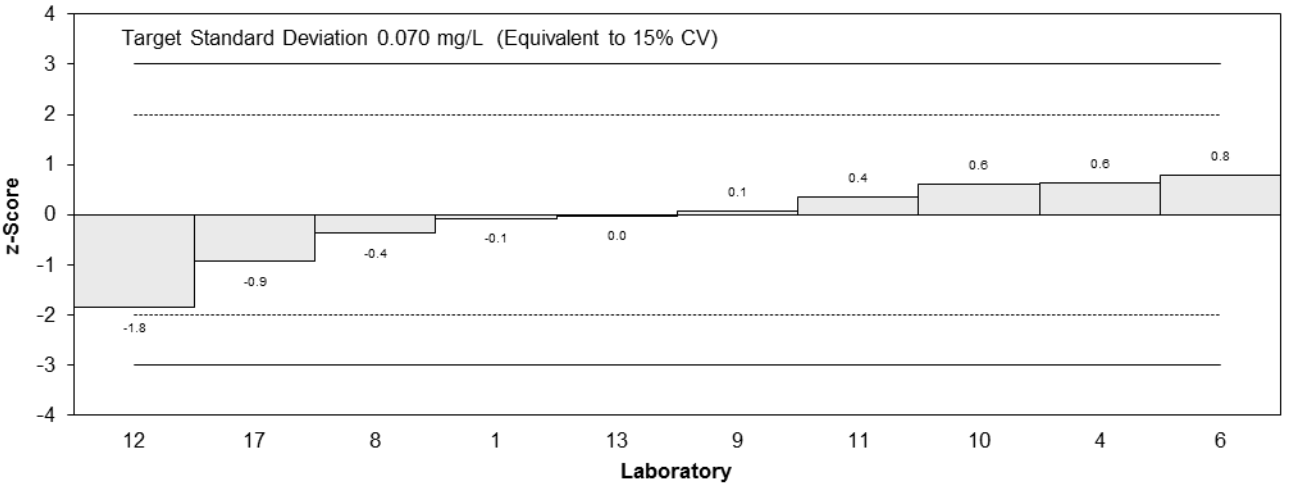
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.46	0.07	-0.07	-0.06
2	NT	NT		
3	NT	NT		
4	0.509	0.0676	0.63	0.56
5	NT	NT		
6	0.520	0.05	0.79	0.86
8	0.44	0.047	-0.36	-0.41
9	0.47	0.066	0.07	0.06
10	0.507	0.082	0.60	0.46
11	0.49	0.03	0.36	0.50
12	0.336	0.0476	-1.85	-2.07
13	0.464	0.05	-0.01	-0.02
14	NT	NT		
15	NR	NR		
16	NR	NR		
17	0.400	0.030	-0.93	-1.30

Statistics

Assigned Value	0.465	0.040
Spike	0.459	0.011
Homogeneity Value	0.477	0.072
Robust Average	0.465	0.040
Median	0.467	0.036
Mean	0.460	
N	10	
Max.	0.52	
Min.	0.336	
Robust SD	0.051	
Robust CV	11%	


Kernel Density
Density
Result
Results: S1 - Ammonia-N
Assigned Value = 0.465 ± 0.040 mg/L
Results (mg/L)
Laboratory
12 17 8 1 13 9 11 10 4 6 15 16 14 2 3 5 7 Md R.A. H.V. S.V.


z-Scores: S1 - Ammonia-N
Target Standard Deviation 0.070 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
12 17 8 1 13 9 11 10 4 6
-1.8 -0.9 -0.4 -0.1 0.0 0.1 0.4 0.6 0.6 0.8

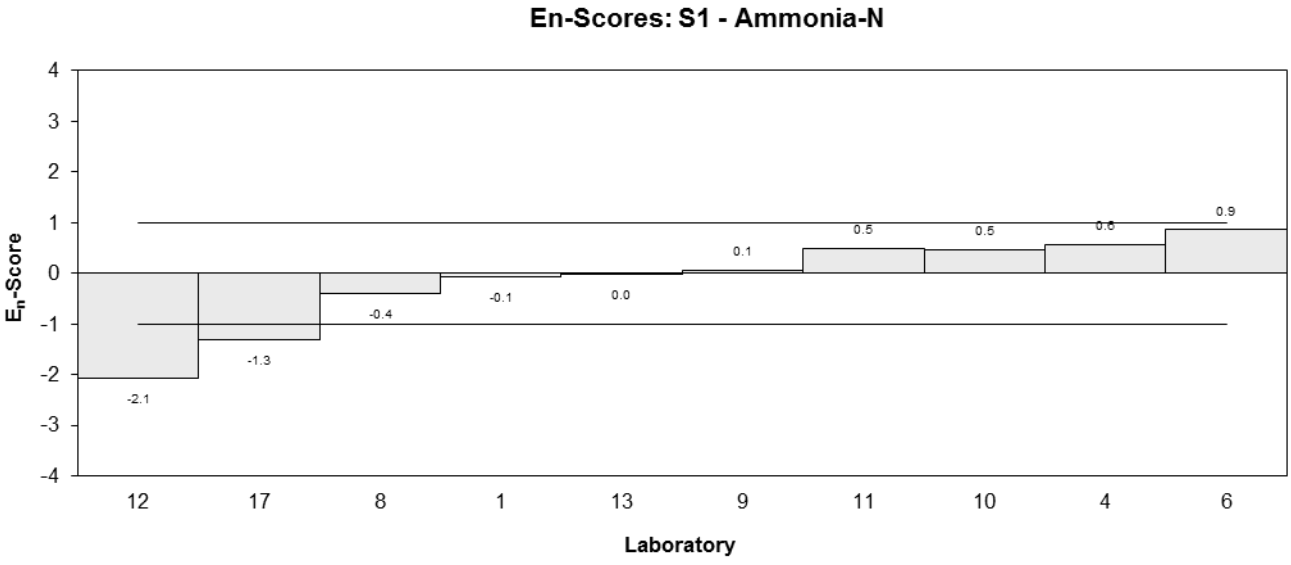

En-Scores: S1 - Ammonia-N
En-Score
Laboratory
12 17 8 1 13 9 11 10 4 6
-2.1 -1.3 -0.4 -0.1 0.0 0.1 0.5 0.5 0.6 0.9

Figure 2

Table 4

Sample Details

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

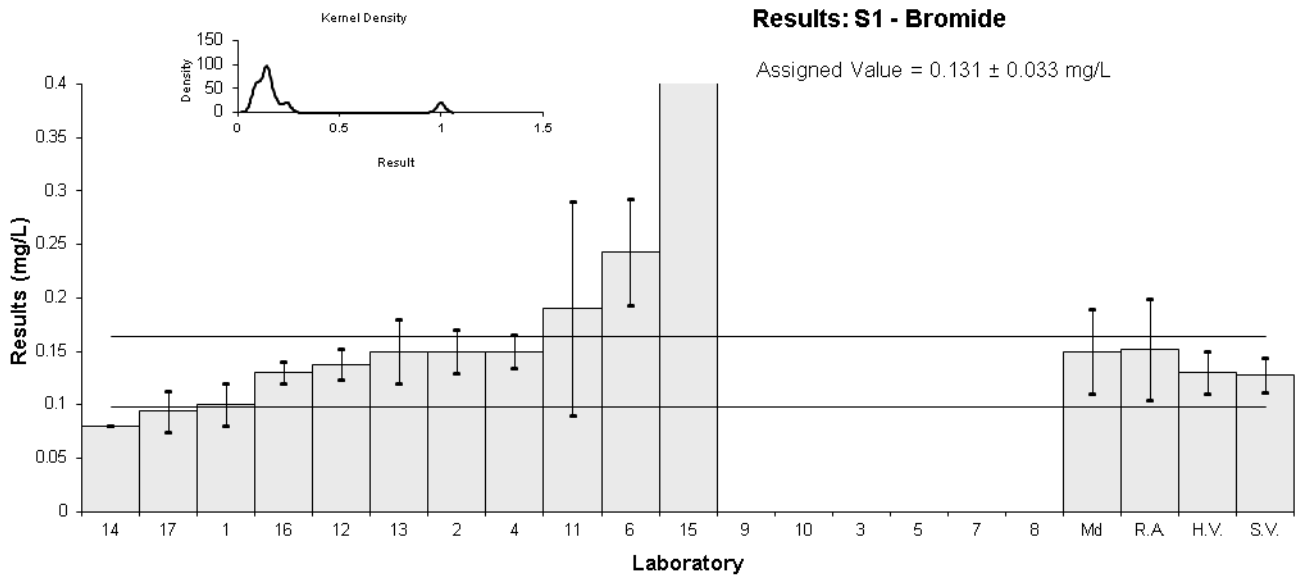
Participant Results

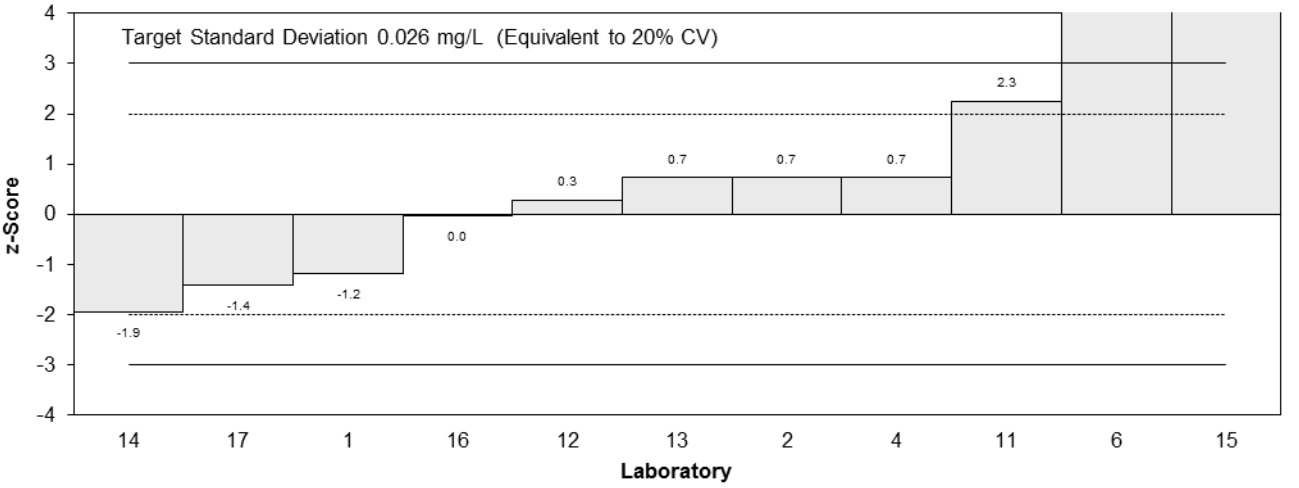
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.10	0.02	-1.18	-0.80
2	0.15	0.02	0.73	0.49
3	NT	NT		
4	0.150	0.0157	0.73	0.52
5	NT	NT		
6	0.243	0.05	4.27	1.87
8	NT	NT		
9	NR	NR		
10	NT	NT		
11	0.19	0.1	2.25	0.56
12	0.138	0.0139	0.27	0.20
13	0.15	0.03	0.73	0.43
14	0.08	0.00	-1.95	-1.55
15	4.47	1.15	165.61	3.77
16	0.13	0.01	-0.04	-0.03
17	0.094	0.019	-1.41	-0.97

Statistics

Assigned Value*	0.131	0.033
Spike	0.128	0.016
Homogeneity Value	0.130	0.020
Robust Average	0.152	0.047
Median	0.150	0.040
Mean	0.536	
N	11	
Max.	4.47	
Min.	0.08	
Robust SD	0.063	
Robust CV	41%	

*Robust Average excluding Laboratories 6 and 15.


Kernel Density
Density
Result
Results: S1 - Bromide
Assigned Value = 0.131 ± 0.033 mg/L
Results (mg/L)
Laboratory
14 17 1 16 12 13 2 4 11 6 15 9 10 3 5 7 8 Md R.A. H.V. S.V.


z-Scores: S1 - Bromide
Target Standard Deviation 0.026 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
14 17 1 16 12 13 2 4 11 6 15
-1.9 -1.4 -1.2 0.0 0.3 0.7 0.7 0.7 2.3

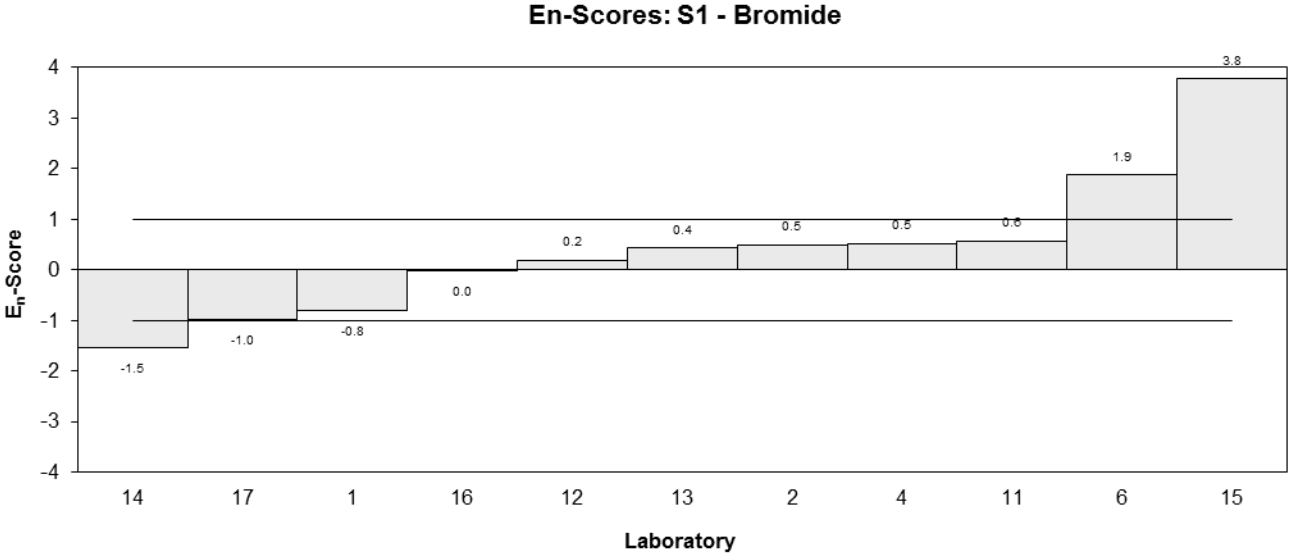

En-Scores: S1 - Bromide
En-Score
Laboratory
14 17 1 16 12 13 2 4 11 6 15
-1.5 -1.0 -0.8 0.0 0.2 0.4 0.5 0.5 0.6 1.9 3.8

Figure 3

Table 5

Sample Details

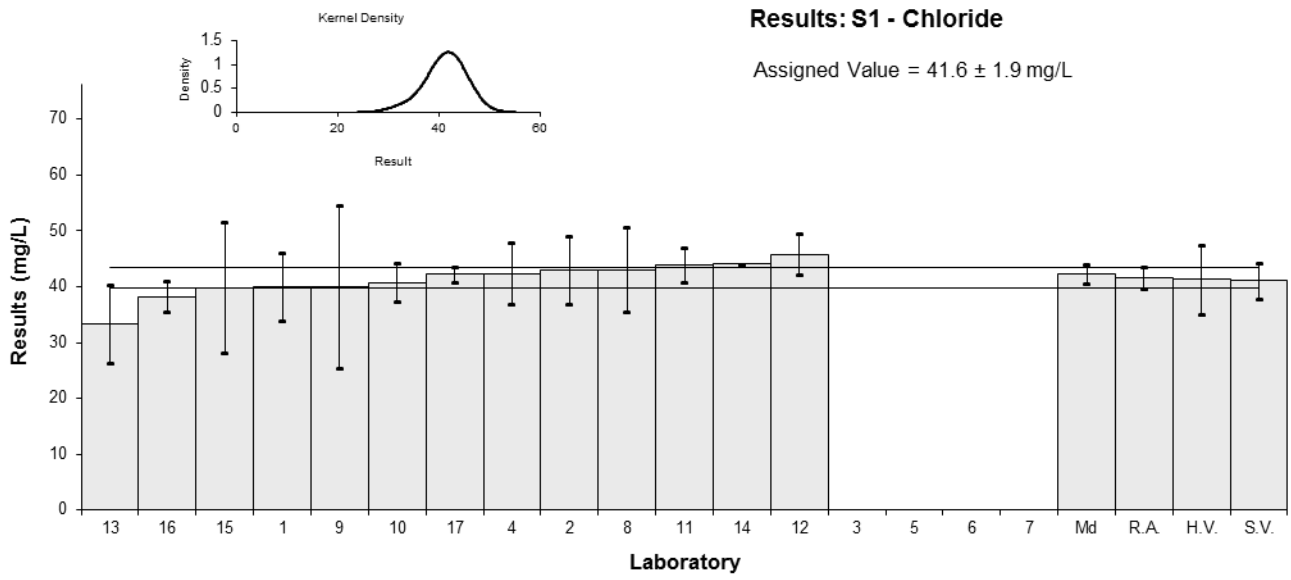
Sample No.	S1
Matrix.	Potable Water
Analyte.	Chloride
Units	mg/L

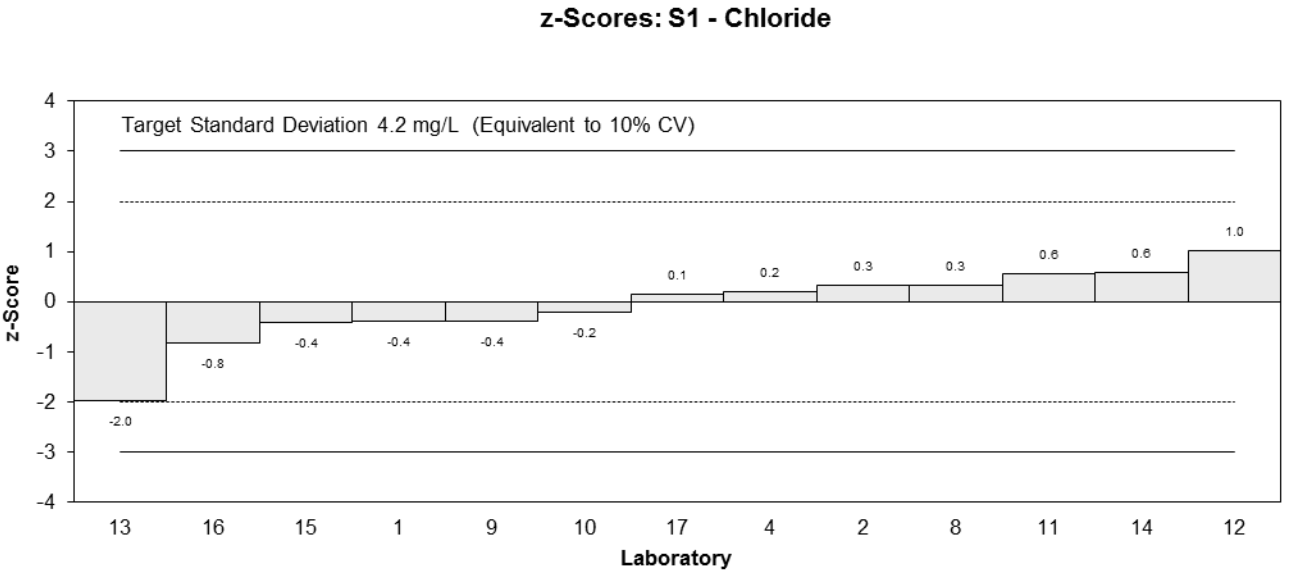
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	40	6	-0.38	-0.25
2	43	6	0.34	0.22
3	NT	NT		
4	42.4	5.49	0.19	0.14
5	NT	NT		
6	NT	NT		
8	43	7.6	0.34	0.18
9	40	14.5	-0.38	-0.11
10	40.7	3.46	-0.22	-0.23
11	43.9	3.1	0.55	0.63
12	45.8	3.734	1.01	1.00
13	33.4	7.0	-1.97	-1.13
14	44.07	0.05	0.59	1.30
15	39.87	11.7	-0.42	-0.15
16	38.2	2.8	-0.82	-1.00
17	42.2	1.35	0.14	0.26

Statistics

Assigned Value	41.6	1.9
Spike	41.1	3.2
Homogeneity Value	41.3	6.2
Robust Average	41.6	1.9
Median	42.2	1.7
Mean	41.3	
N	13	
Max.	45.8	
Min.	33.4	
Robust SD	2.8	
Robust CV	6.7%	


Kernel Density
Density
Result
Results: S1 - Chloride
Assigned Value = 41.6 ± 1.9 mg/L
Results (mg/L)
Laboratory
13 16 15 1 9 10 17 4 2 8 11 14 12 3 5 6 7 Md R.A. H.V. S.V.


z-Scores: S1 - Chloride
Target Standard Deviation 4.2 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
13 16 15 1 9 10 17 4 2 8 11 14 12
-2.0 -0.8 -0.4 -0.4 -0.4 -0.2 0.1 0.2 0.3 0.3 0.6 0.6 1.0

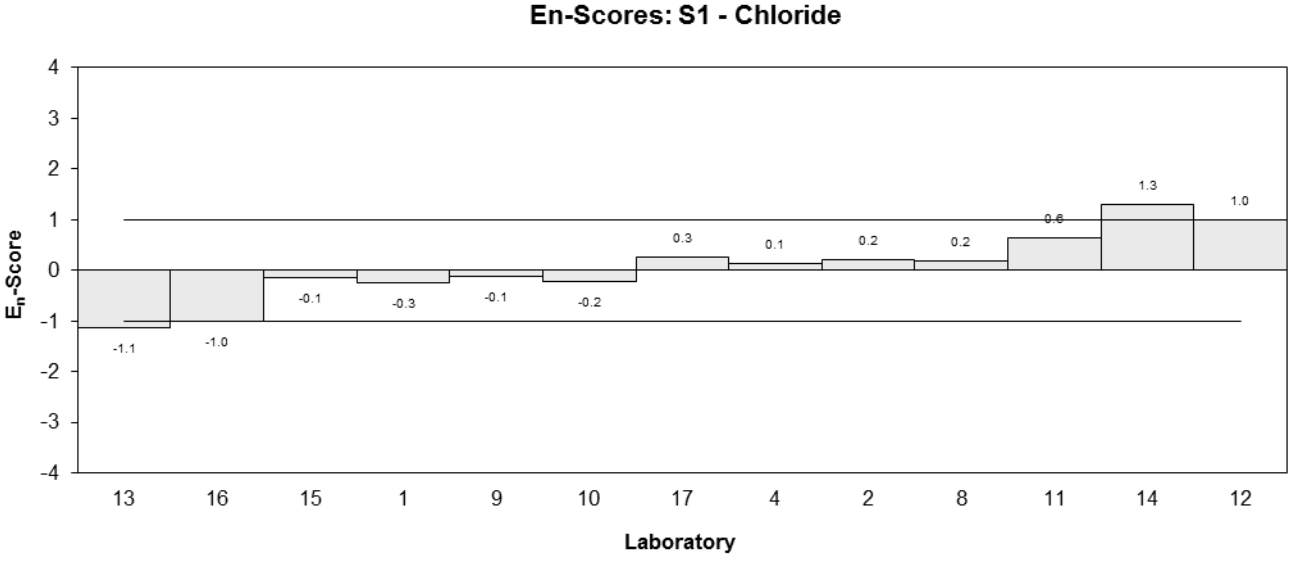

En-Scores: S1 - Chloride
En-Score
Laboratory
13 16 15 1 9 10 17 4 2 8 11 14 12
-1.1 -1.0 -0.1 -0.3 -0.1 -0.2 0.3 0.1 0.2 0.2 0.6 1.3 1.0

Figure 4

Table 6

Sample Details

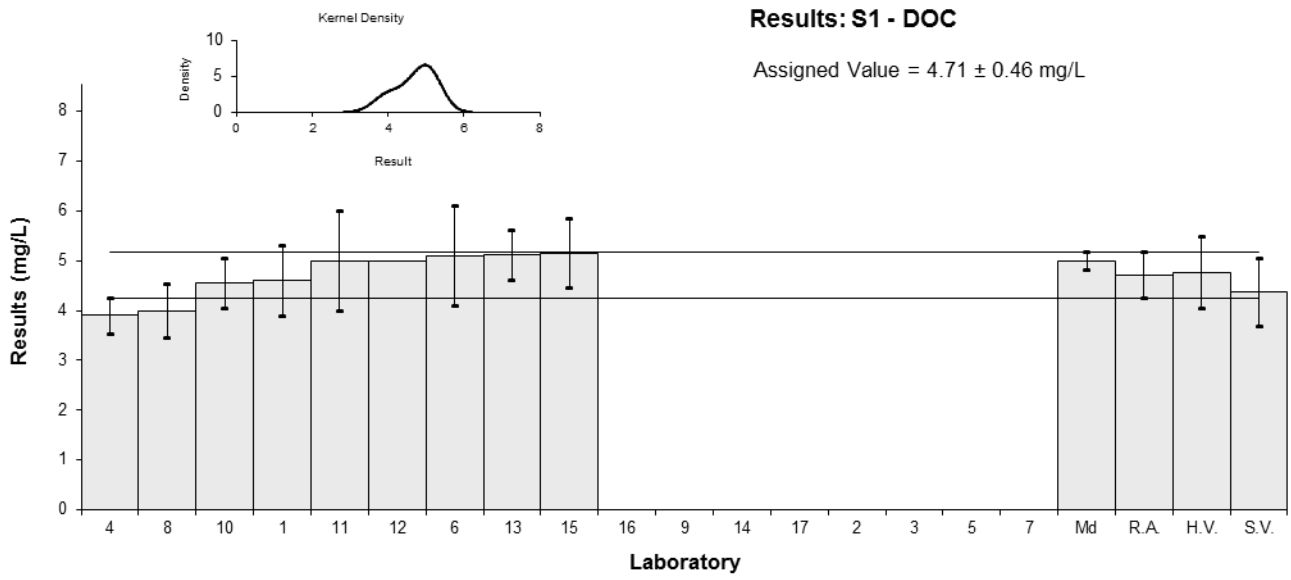
Sample No.	S1
Matrix.	Potable Water
Analyte.	DOC
Units	mg/L

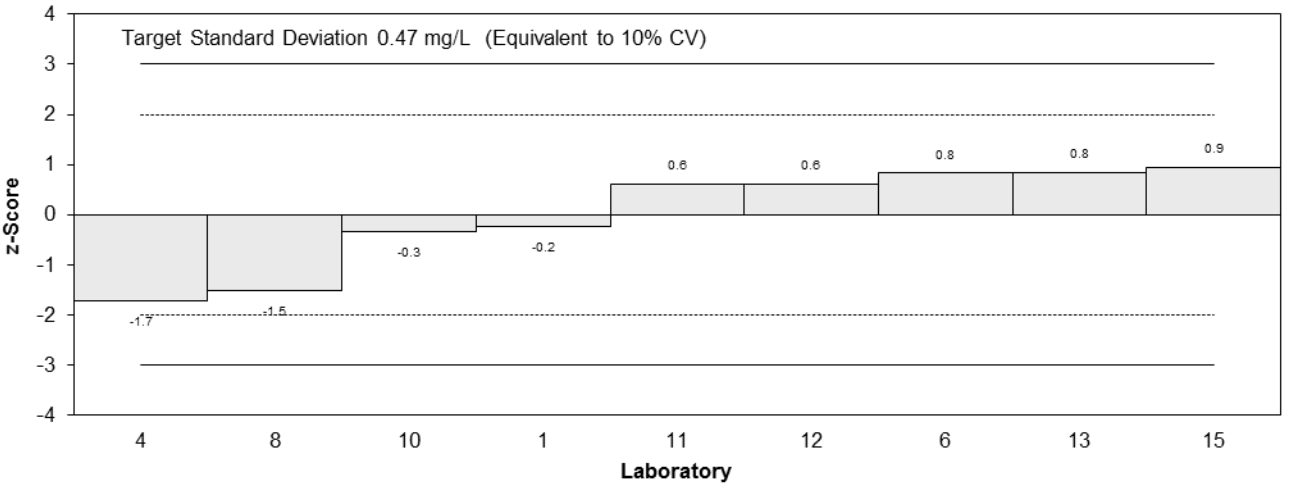
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.6	0.7	-0.23	-0.13
2	NT	NT		
3	NT	NT		
4	3.9	0.36	-1.72	-1.39
5	NT	NT		
6	5.1	1	0.83	0.35
8	4	0.55	-1.51	-0.99
9	NR	NR		
10	4.55	0.496	-0.34	-0.24
11	5.0	1	0.62	0.26
12	5	NR	0.62	0.63
13	5.11	0.5	0.85	0.59
14	NT	NT		
15	5.15	0.69	0.93	0.53
16	NR	NR		
17	NT	NT		

Statistics

Assigned Value	4.71	0.46
Spike	4.37	0.68
Homogeneity Value	4.77	0.72
Robust Average	4.71	0.46
Median	5.00	0.17
Mean	4.71	
N	9	
Max.	5.15	
Min.	3.9	
Robust SD	0.55	
Robust CV	12%	


Kernel Density
Density
Result
Results: S1 - DOC
Assigned Value = 4.71 ± 0.46 mg/L
Results (mg/L)
Laboratory
4 8 10 1 11 12 6 13 15 16 9 14 17 2 3 5 7 Md R.A. H.V. S.V.


z-Scores: S1 - DOC
Target Standard Deviation 0.47 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
4 8 10 1 11 12 6 13 15
-1.7
-1.5
-0.3
-0.2
0.6
0.6
0.8
0.8
0.9

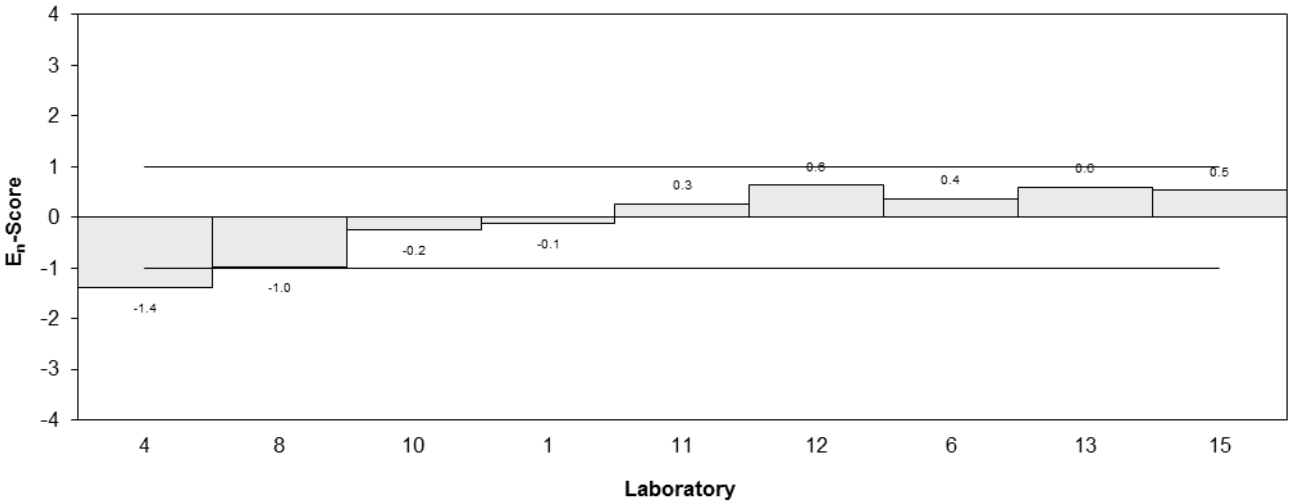

En-Scores: S1 - DOC
En-Score
Laboratory
4 8 10 1 11 12 6 13 15
-1.4
-1.0
-0.2
-0.1
0.3
0.6
0.4
0.6
0.5

Figure 5

Table 7

Sample Details

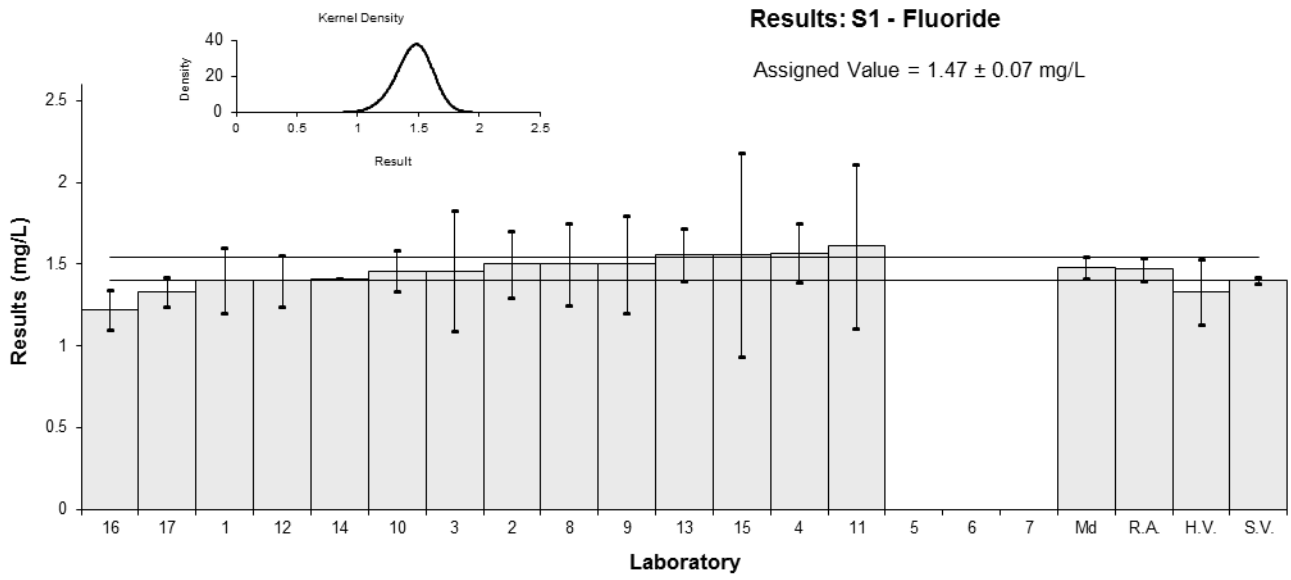
Sample No.	S1
Matrix.	Potable Water
Analyte.	Fluoride
Units	mg/L

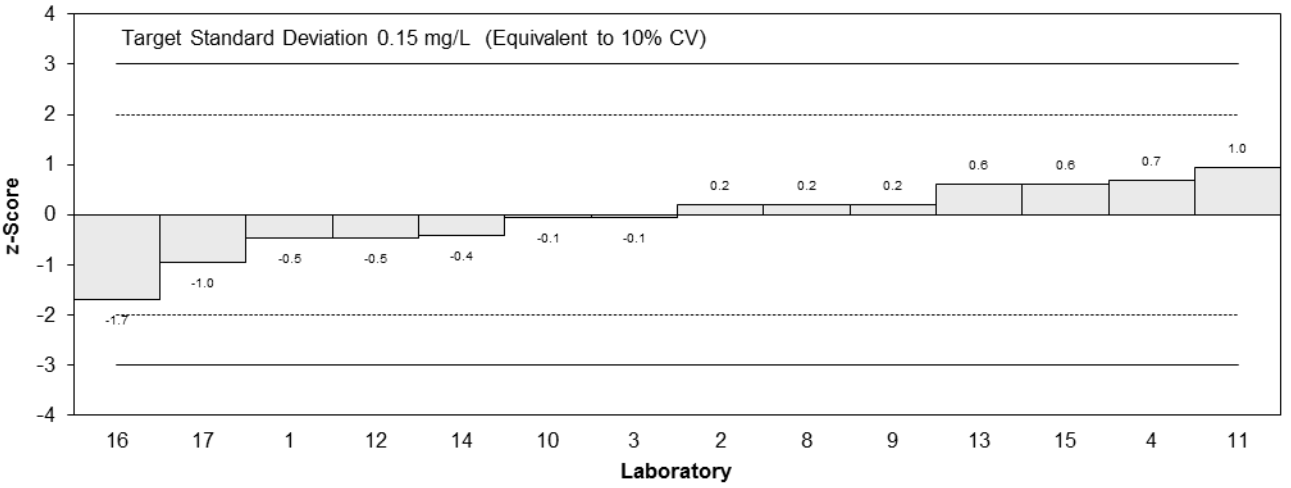
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.2	-0.48	-0.33
2	1.5	0.2	0.20	0.14
3	1.46	0.37	-0.07	-0.03
4	1.57	0.183	0.68	0.51
5	NT	NT		
6	NT	NT		
8	1.5	0.25	0.20	0.12
9	1.5	0.3	0.20	0.10
10	1.46	0.124	-0.07	-0.07
11	1.61	0.5	0.95	0.28
12	1.4	0.158	-0.48	-0.41
13	1.56	0.16	0.61	0.52
14	1.41	0.00	-0.41	-0.86
15	1.56	0.62	0.61	0.14
16	1.22	0.12	-1.70	-1.80
17	1.33	0.092	-0.95	-1.21

Statistics

Assigned Value	1.47	0.07
Spike	1.40	0.02
Homogeneity Value	1.33	0.20
Robust Average	1.47	0.07
Median	1.48	0.07
Mean	1.46	
N	14	
Max.	1.61	
Min.	1.22	
Robust SD	0.10	
Robust CV	6.8%	


Kernel Density
Density
Result
Results: S1 - Fluoride
Assigned Value = 1.47 ± 0.07 mg/L
Results (mg/L)
Laboratory
16 17 1 12 14 10 3 2 8 9 13 15 4 11 5 6 7 Md R.A. H.V. S.V.


z-Scores: S1 - Fluoride
Target Standard Deviation 0.15 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
16 17 1 12 14 10 3 2 8 9 13 15 4 11
-1.7 -1.0 -0.5 -0.5 -0.4 -0.1 -0.1 0.2 0.2 0.2 0.6 0.6 0.7 1.0

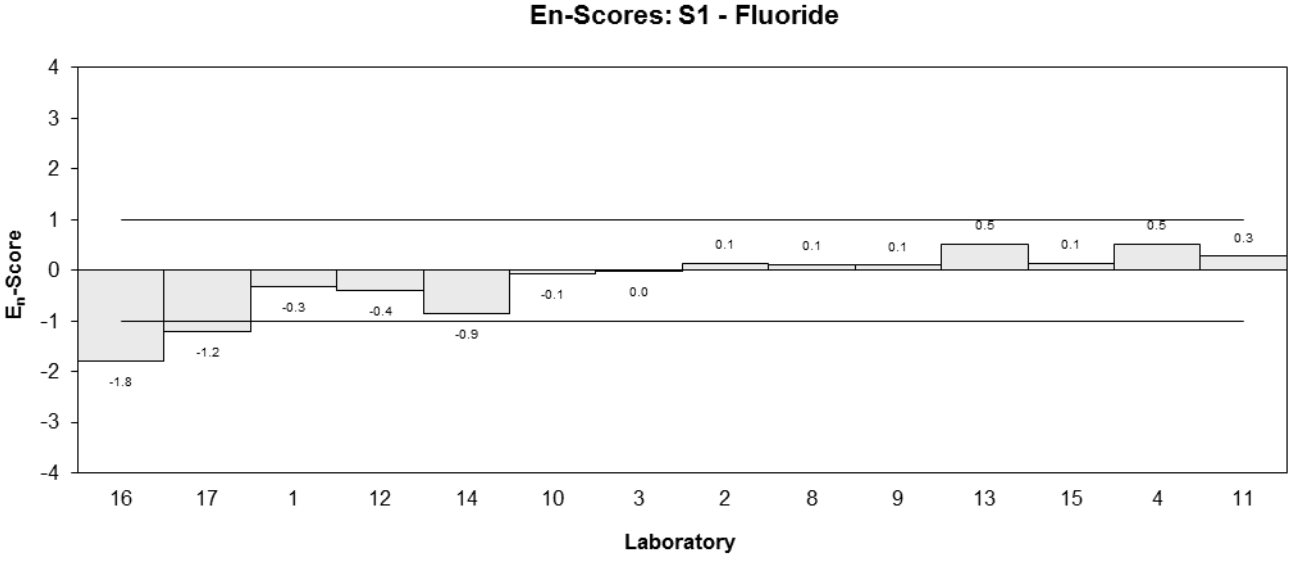

En-Scores: S1 - Fluoride
En-Score
Laboratory
16 17 1 12 14 10 3 2 8 9 13 15 4 11
-1.8 -1.2 -0.3 -0.4 -0.9 -0.1 0.0 0.1 0.1 0.1 0.5 0.1 0.5 0.3

Figure 6

Table 8

Sample Details

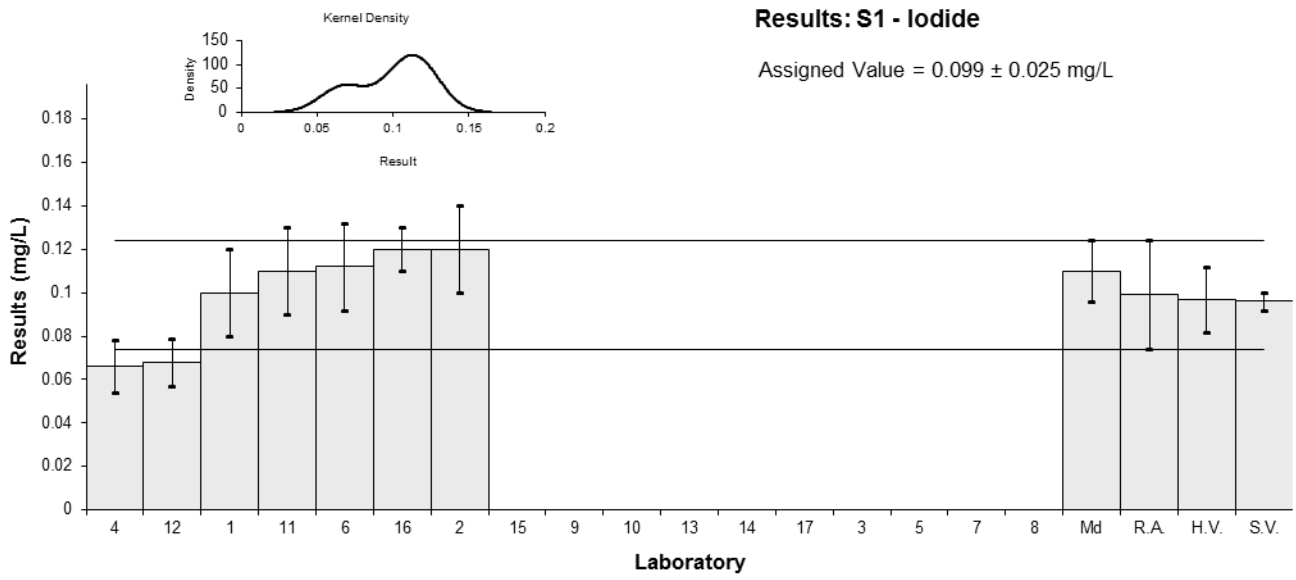
Sample No.	S1
Matrix.	Potable Water
Analyte.	Iodide
Units	mg/L

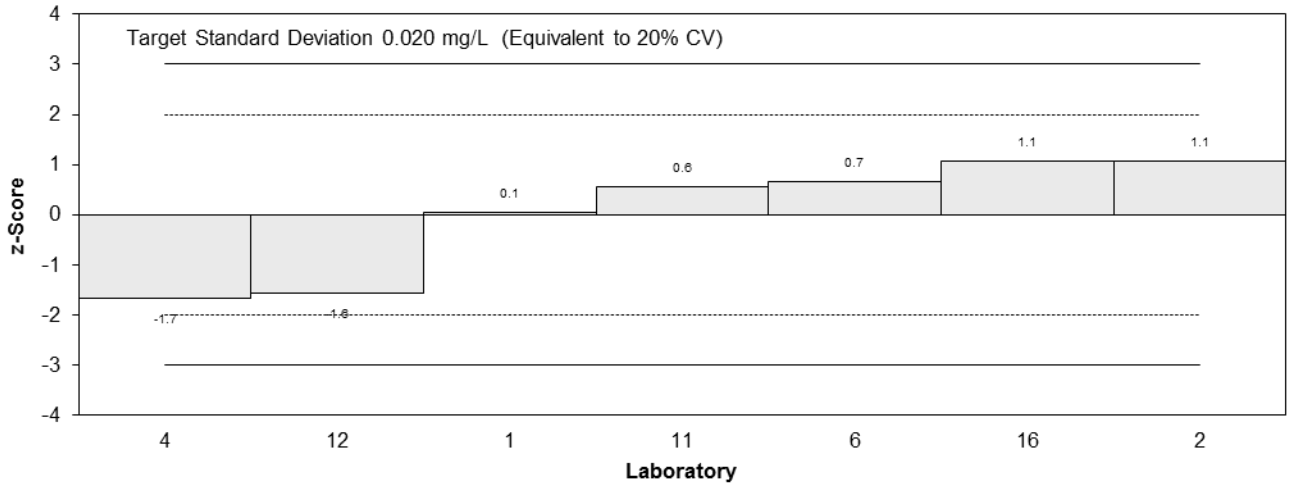
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.10	0.02	0.05	0.03
2	0.12	0.02	1.06	0.66
3	NT	NT		
4	0.066	0.0122	-1.67	-1.19
5	NT	NT		
6	0.112	0.02	0.66	0.41
8	NT	NT		
9	NR	NR		
10	NT	NT		
11	0.11	0.02	0.56	0.34
12	0.068	0.011	-1.57	-1.13
13	NT	NT		
14	NT	NT		
15	NR	NR		
16	0.12	0.01	1.06	0.78
17	NT	NT		

Statistics

Assigned Value	0.099	0.025
Spike	0.096	0.004
Homogeneity Value	0.097	0.015
Robust Average	0.099	0.025
Median	0.110	0.014
Mean	0.099	
N	7	
Max.	0.12	
Min.	0.066	
Robust SD	0.026	
Robust CV	26%	


Kernel Density
Density
150
100
50
0
0
0.05
0.1
0.15
0.2
Result
Results: S1 - Iodide
Assigned Value = 0.099 ± 0.025 mg/L
Results (mg/L)
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
4
12
1
11
6
16
2
15
9
10
13
14
17
3
5
7
8
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S1 - Iodide
Target Standard Deviation 0.020 mg/L (Equivalent to 20% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.7
-1.6
0.1
0.6
0.7
1.1
1.1
4
12
1
11
6
16
2
Laboratory

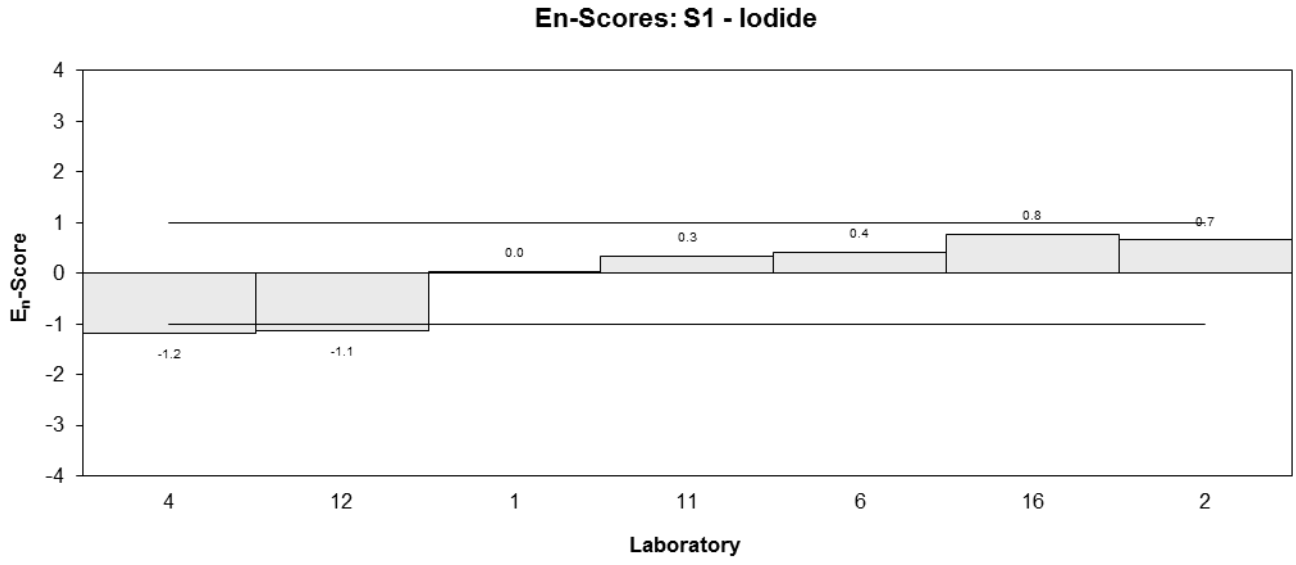

En-Scores: S1 - Iodide
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.2
-1.1
0.0
0.3
0.4
0.8
0.7
4
12
1
11
6
16
2
Laboratory

Figure 7

Table 9

Sample Details

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

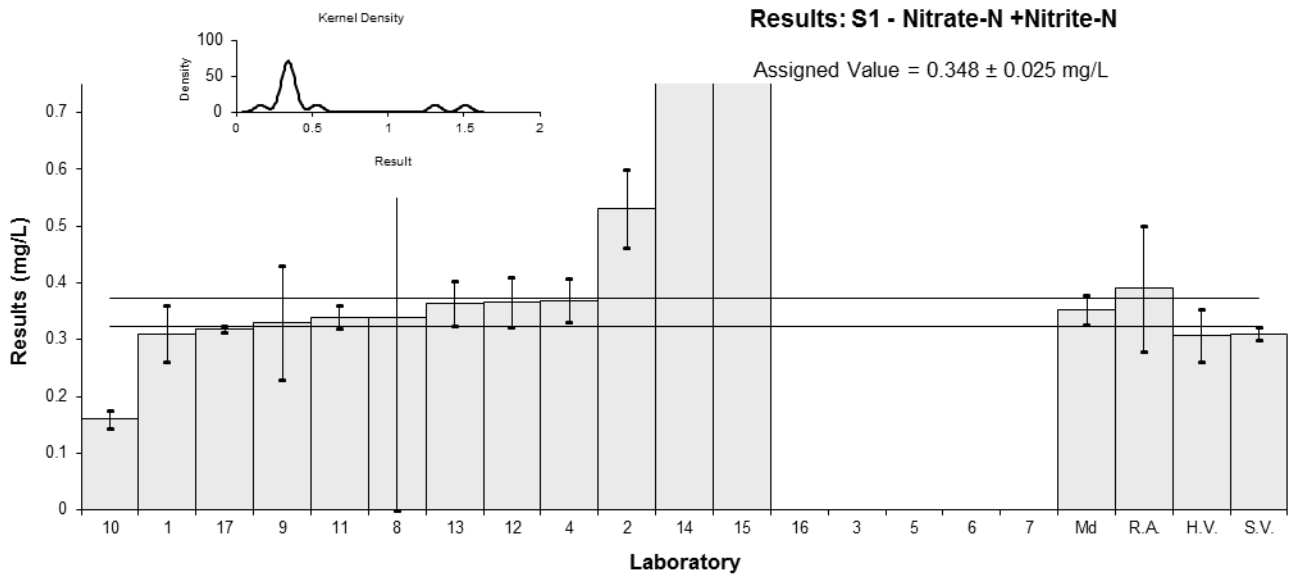
Participant Results

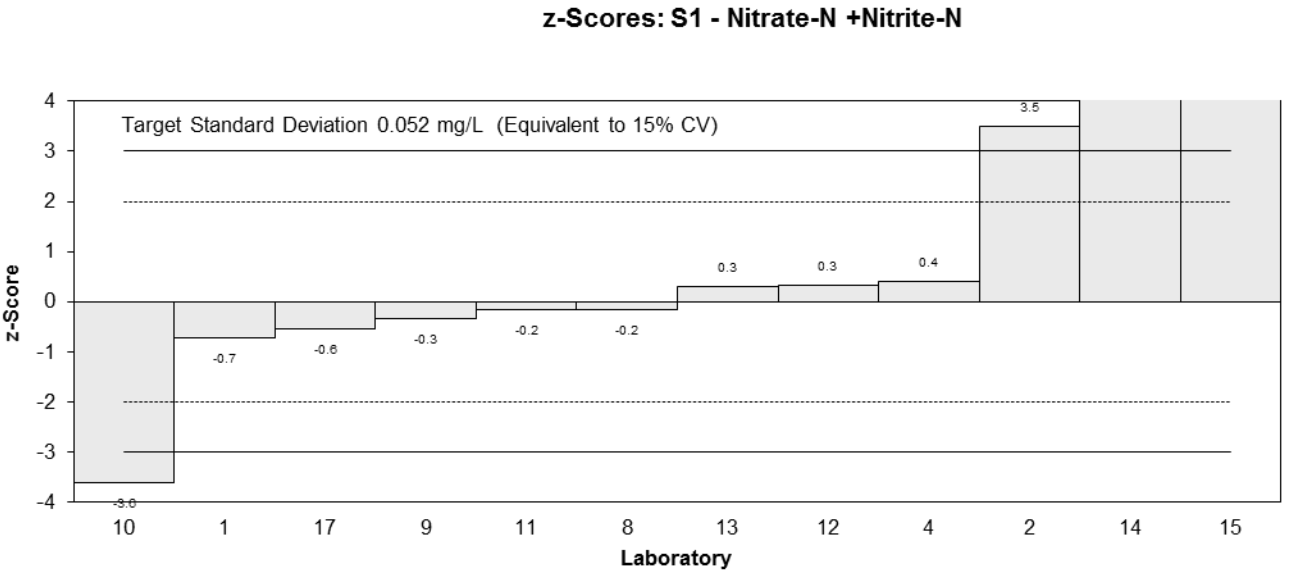
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.31	0.05	-0.73	-0.68
2	0.531	0.069	3.51	2.49
3	NT	NT		
4	0.369	0.0381	0.40	0.46
5	NT	NT		
6	NT	NT		
8	0.34	0.34	-0.15	-0.02
9	0.33	0.1	-0.34	-0.17
10	0.160	0.016	-3.60	-6.33
11	0.34	0.02	-0.15	-0.25
12	0.365	0.044	0.33	0.34
13	0.364	0.04	0.31	0.34
14	1.31	0.02	18.43	30.05
15	1.51	0.38	22.26	3.05
16	NR	NR		
17	0.319	0.006	-0.56	-1.13

Statistics

Assigned Value*	0.348	0.025
Spike	0.310	0.011
Homogeneity Value	0.307	0.061
Robust Average	0.39	0.11
Median	0.352	0.026
Mean	0.521	
N	12	
Max.	1.51	
Min.	0.16	
Robust SD	0.15	
Robust CV	38%	

*Robust Average excluding Laboratories 10, 14 and 15.


Kernel Density
Density
Result
Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.348 ± 0.025 mg/L
Results (mg/L)
Laboratory
10 1 17 9 11 8 13 12 4 2 14 15 16 3 5 6 7 Md R.A. H.V. S.V.


z-Scores: S1 - Nitrate-N +Nitrite-N
Target Standard Deviation 0.052 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
10 1 17 9 11 8 13 12 4 2 14 15

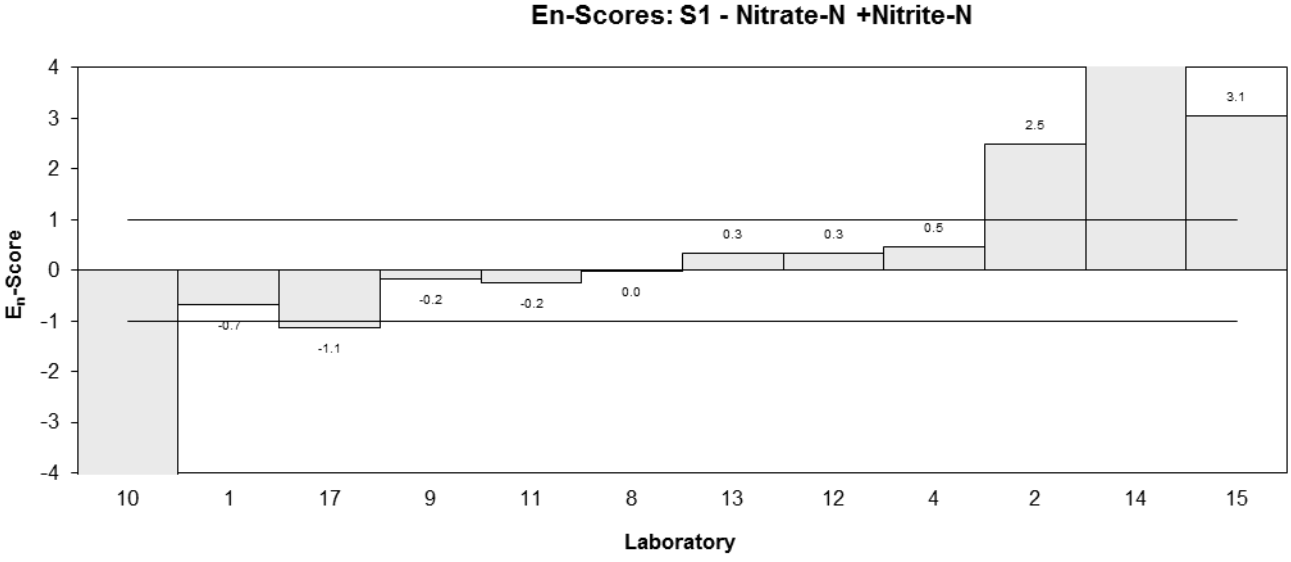

En-Scores: S1 - Nitrate-N +Nitrite-N
En-Score
Laboratory
10 1 17 9 11 8 13 12 4 2 14 15

Figure 8

Table 10

Sample Details

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

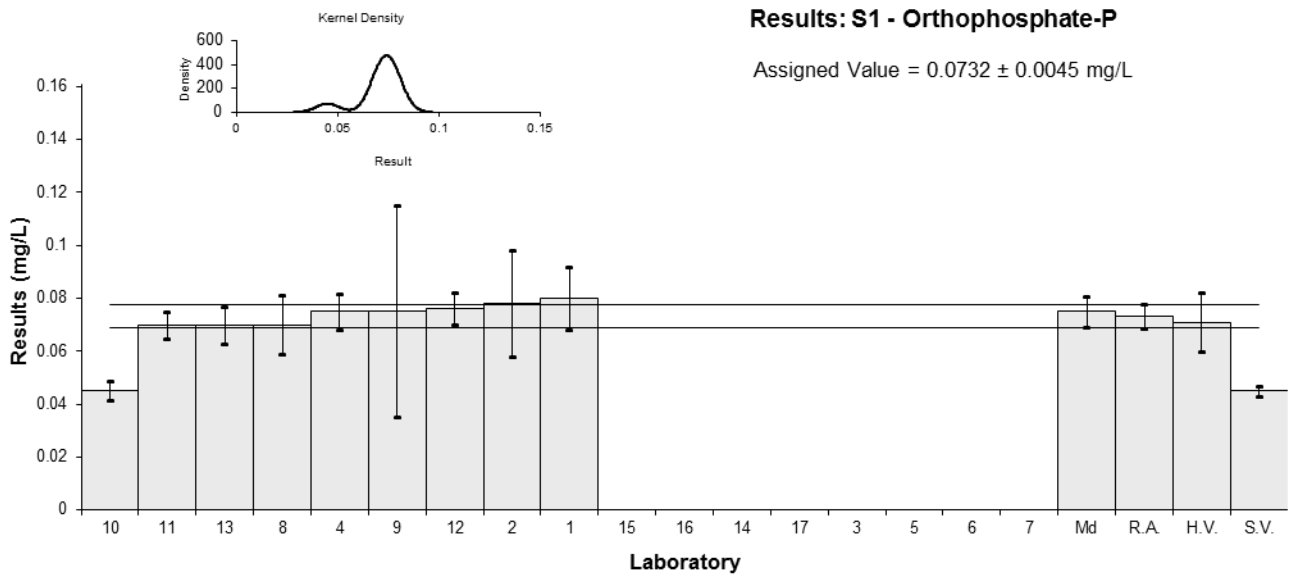
Participant Results

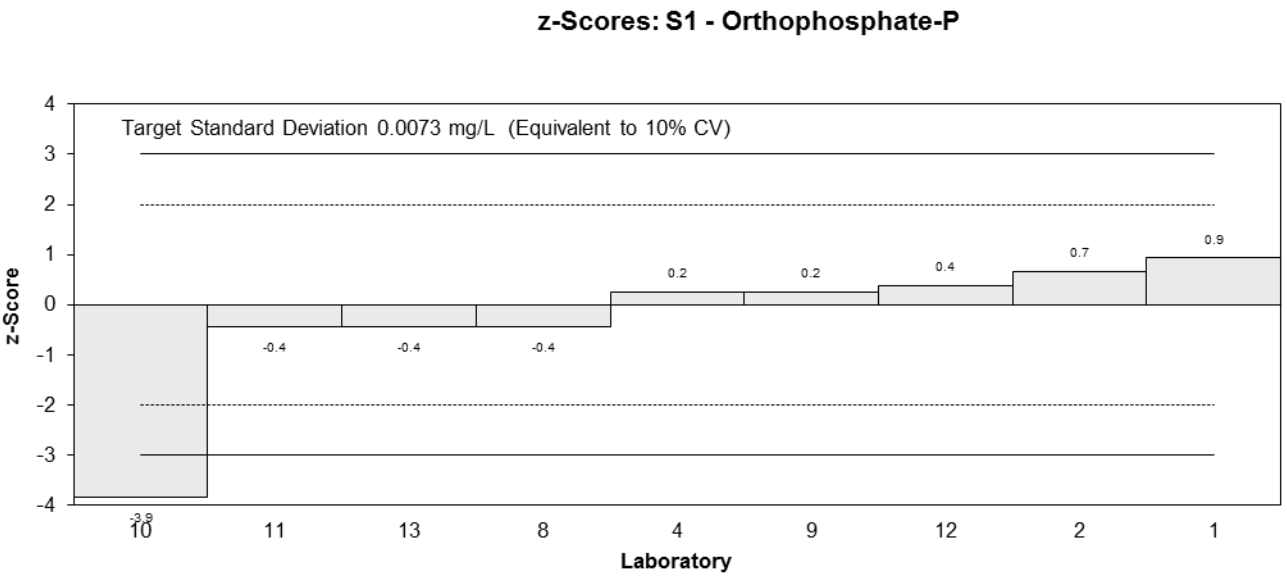
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.080	0.012	0.93	0.53
2	0.078	0.020	0.66	0.23
3	NT	NT		
4	0.075	0.0069	0.25	0.22
5	NT	NT		
6	NT	NT		
8	0.07	0.011	-0.44	-0.27
9	0.075	0.04	0.25	0.04
10	0.045	0.0037	-3.85	-4.84
11	0.07	0.005	-0.44	-0.48
12	0.076	0.006	0.38	0.37
13	0.070	0.007	-0.44	-0.38
14	NT	NT		
15	NR	NR		
16	NR	NR		
17	NT	NT		

Statistics

Assigned Value	0.0732	0.0045
Spike*	0.045	0.002
Homogeneity Value	0.071	0.011
Robust Average	0.0732	0.0045
Median	0.0750	0.0057
Mean	0.0710	
N	9	
Max.	0.08	
Min.	0.045	
Robust SD	0.0054	
Robust CV	7.4%	

*Spike Value does not include incurred value.


Kernel Density
Density
Result
Results: S1 - Orthophosphate-P
Assigned Value = 0.0732 ± 0.0045 mg/L
Results (mg/L)
Laboratory
10 11 13 8 4 9 12 2 1 15 16 14 17 3 5 6 7 Md R.A. H.V. S.V.


z-Scores: S1 - Orthophosphate-P
Target Standard Deviation 0.0073 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
10 11 13 8 4 9 12 2 1

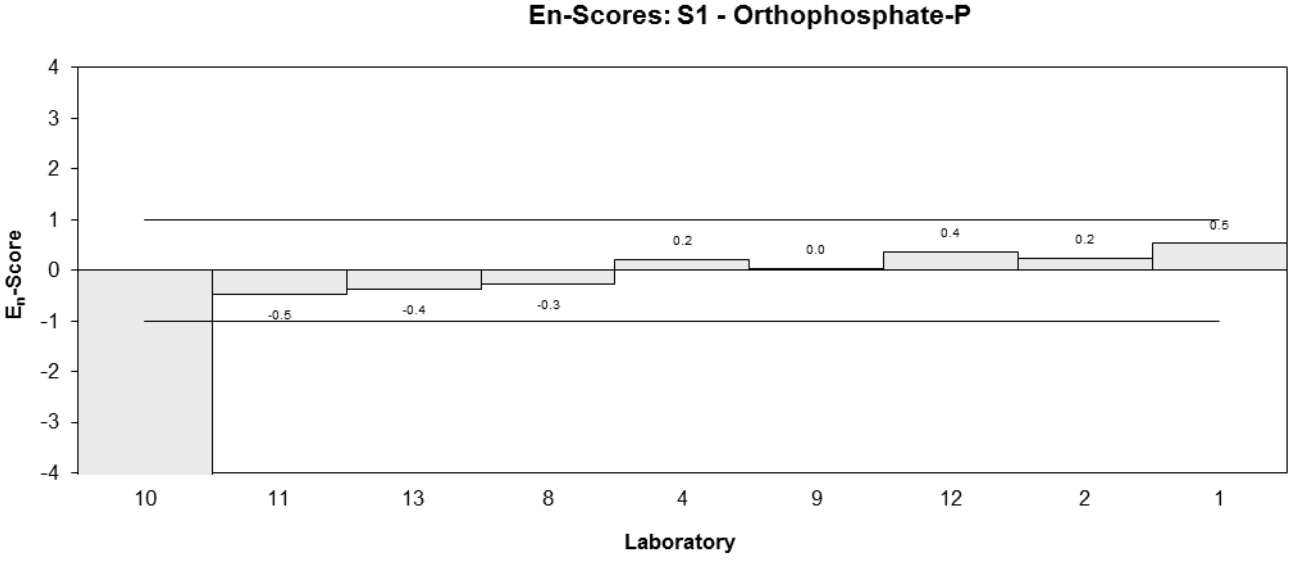

En-Scores: S1 - Orthophosphate-P
En-Score
Laboratory
10 11 13 8 4 9 12 2 1

Figure 9

Table 11

Sample Details

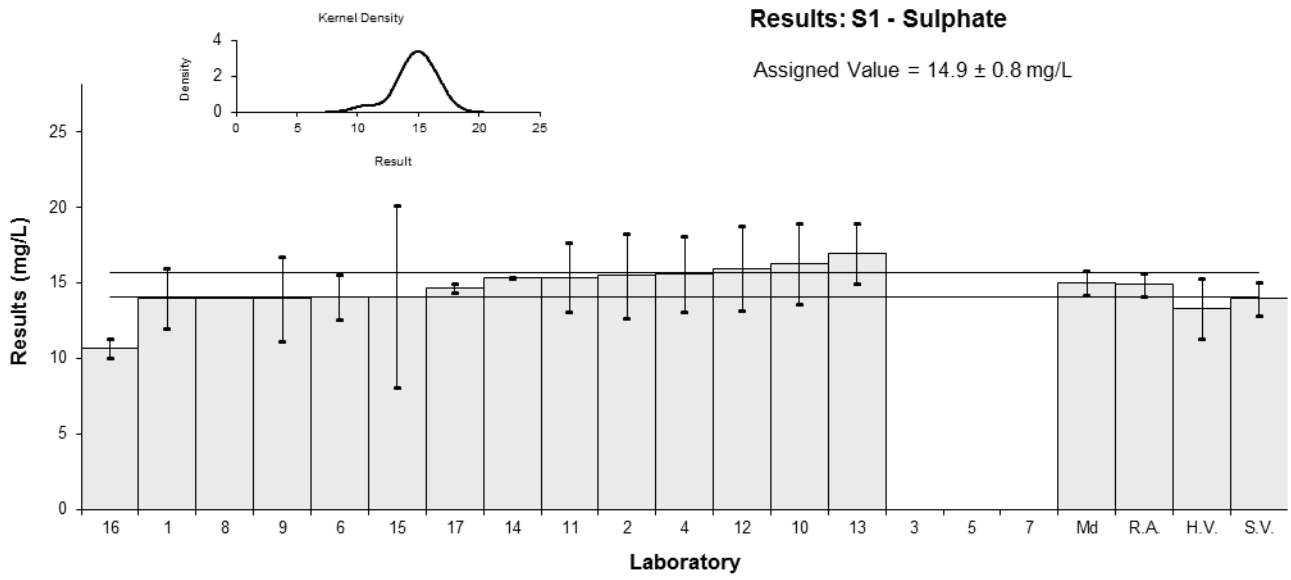
Sample No.	S1
Matrix.	Potable Water
Analyte.	Sulphate
Units	mg/L

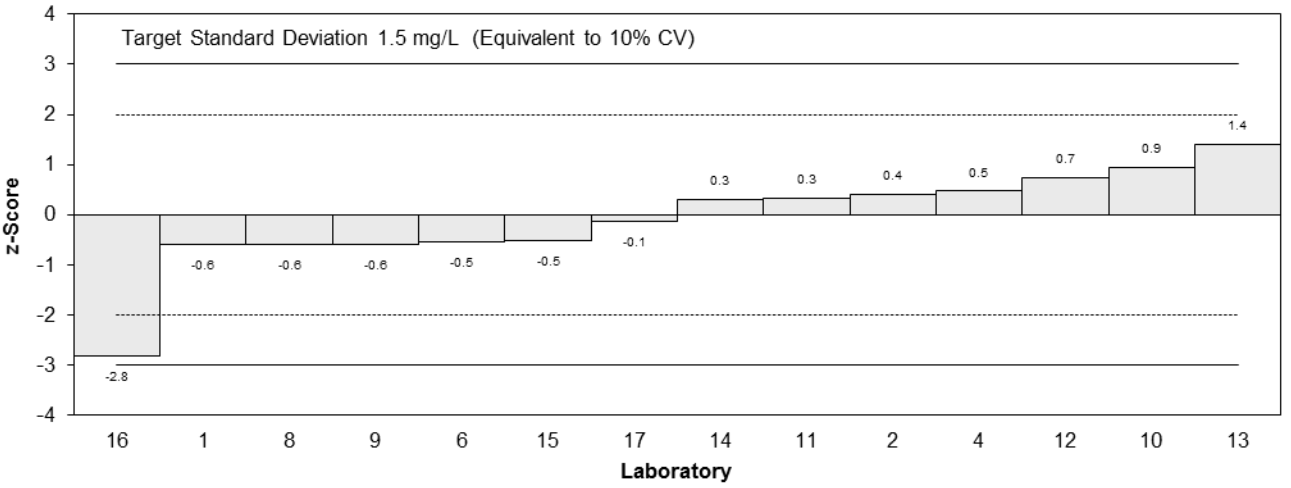
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	14	2	-0.60	-0.42
2	15.5	2.8	0.40	0.21
3	NT	NT		
4	15.6	2.48	0.47	0.27
5	NT	NT		
6	14.1	1.5	-0.54	-0.47
8	14	NR	-0.60	-1.13
9	14	2.8	-0.60	-0.31
10	16.3	2.66	0.94	0.50
11	15.4	2.3	0.34	0.21
12	16	2.813	0.74	0.38
13	17.0	2.0	1.41	0.97
14	15.34	0.06	0.30	0.55
15	14.13	6.00	-0.52	-0.13
16	10.7	0.6	-2.82	-4.20
17	14.7	0.304	-0.13	-0.23

Statistics

Assigned Value	14.9	0.8
Spike	14.0	1.1
Homogeneity Value	13.3	2.0
Robust Average	14.9	0.8
Median	15.0	0.8
Mean	14.8	
N	14	
Max.	17	
Min.	10.7	
Robust SD	1.2	
Robust CV	8.1%	


Kernel Density
Density
Result
Results: S1 - Sulphate
Assigned Value = 14.9 ± 0.8 mg/L
Results (mg/L)
Laboratory
16 1 8 9 6 15 17 14 11 2 4 12 10 13 3 5 7 Md R.A. H.V. S.V.


z-Scores: S1 - Sulphate
Target Standard Deviation 1.5 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
16 1 8 9 6 15 17 14 11 2 4 12 10 13
-2.8 -0.6 -0.6 -0.6 -0.5 -0.5 -0.1 0.3 0.3 0.4 0.5 0.7 0.9 1.4

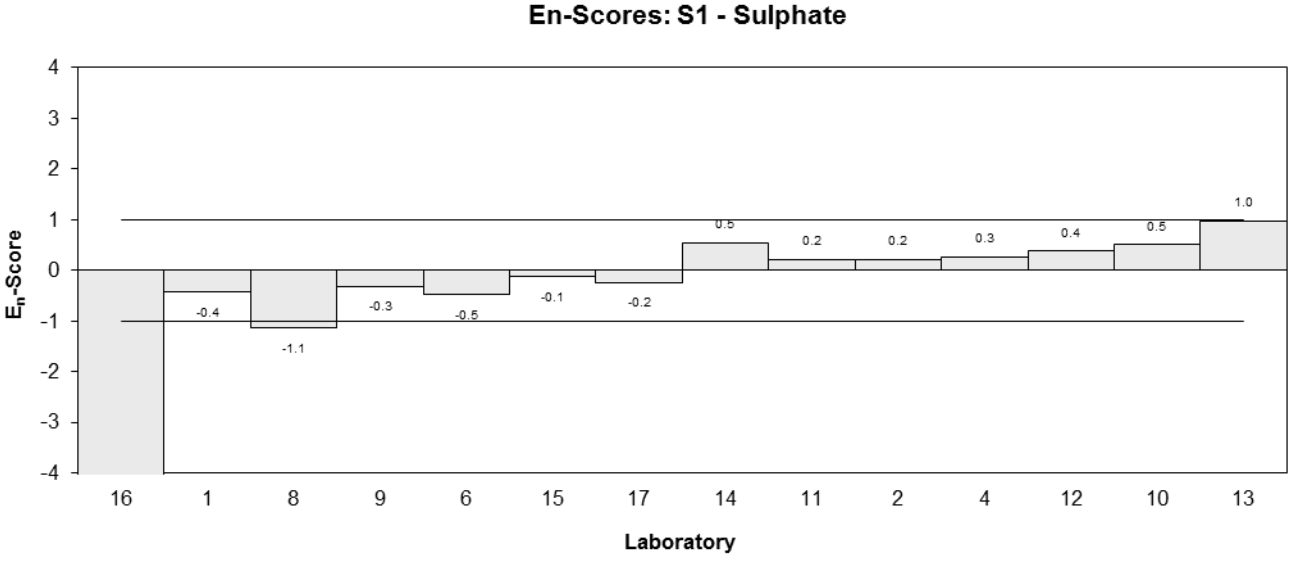

En-Scores: S1 - Sulphate
En-Score
Laboratory
16 1 8 9 6 15 17 14 11 2 4 12 10 13
-0.4 -1.1 -0.3 -0.5 -0.1 -0.2 0.5 0.2 0.2 0.3 0.4 0.5 1.0

Figure 10

Table 12

Sample Details

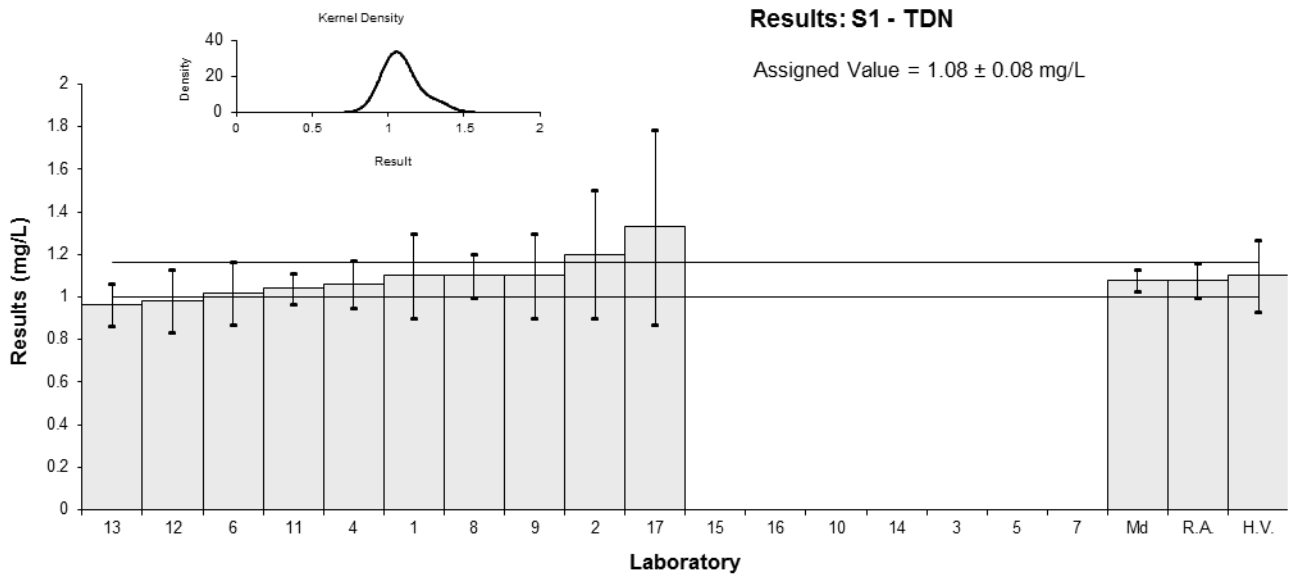
Sample No.	S1
Matrix.	Potable Water
Analyte.	TDN
Units	mg/L

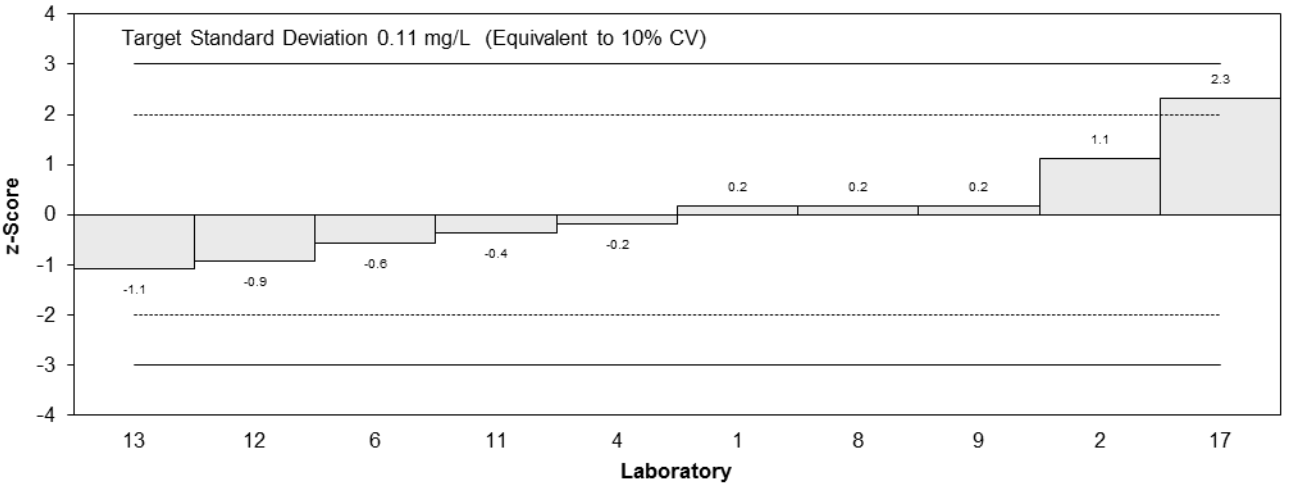
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.1	0.2	0.19	0.09
2	1.2	0.3	1.11	0.39
3	NT	NT		
4	1.06	0.111	-0.19	-0.15
5	NT	NT		
6	1.018	0.15	-0.57	-0.36
8	1.1	0.1	0.19	0.16
9	1.1	0.2	0.19	0.09
10	NT	NT		
11	1.04	0.07	-0.37	-0.38
12	0.98	0.147	-0.93	-0.60
13	0.962	0.1	-1.09	-0.92
14	NT	NT		
15	NR	NR		
16	NR	NR		
17	1.33	0.458	2.31	0.54

Statistics

Assigned Value	1.08	0.08
Spike	Not Spiked	
Homogeneity Value	1.10	0.17
Robust Average	1.08	0.08
Median	1.08	0.05
Mean	1.09	
N	10	
Max.	1.33	
Min.	0.962	
Robust SD	0.10	
Robust CV	9.3%	


Kernel Density
Density
Result
Results: S1 - TDN
Assigned Value = 1.08 ± 0.08 mg/L
Results (mg/L)
Laboratory
13 12 6 11 4 1 8 9 2 17 15 16 10 14 3 5 7 Md R.A. H.V.


z-Scores: S1 - TDN
Target Standard Deviation 0.11 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
13 12 6 11 4 1 8 9 2 17
-1.1 -0.9 -0.6 -0.4 -0.2 0.2 0.2 0.2 1.1 2.3

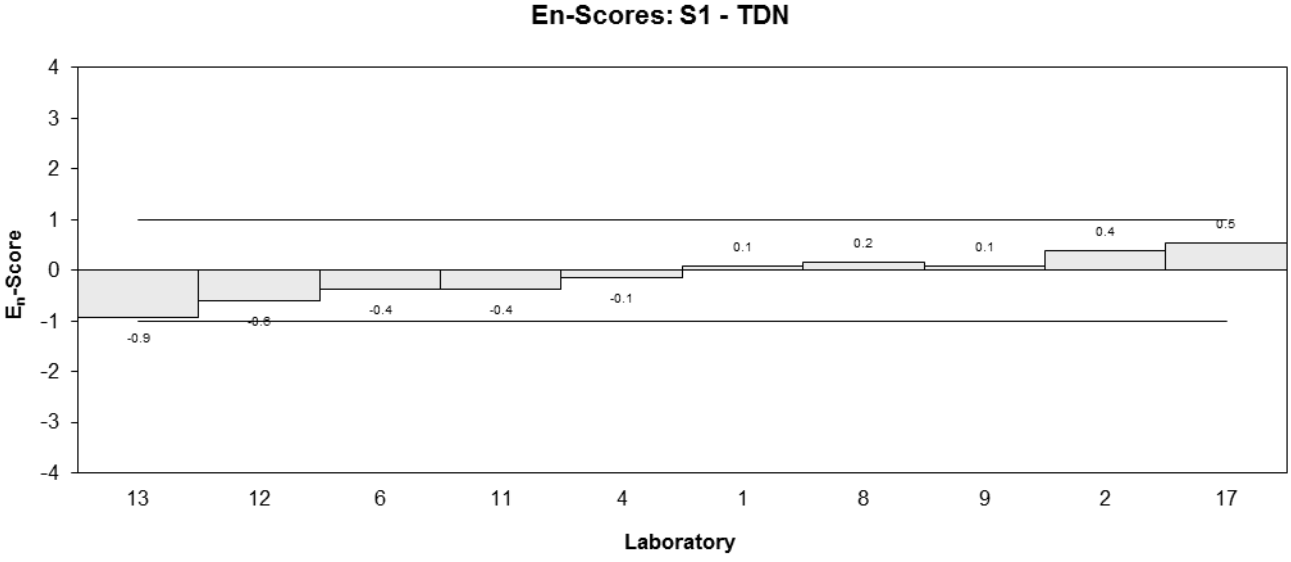

En-Scores: S1 - TDN
En-Score
Laboratory
13 12 6 11 4 1 8 9 2 17
-0.9 -0.6 -0.4 -0.4 -0.1 0.1 0.2 0.1 0.4 0.5

Figure 11

Table 13

Sample Details

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

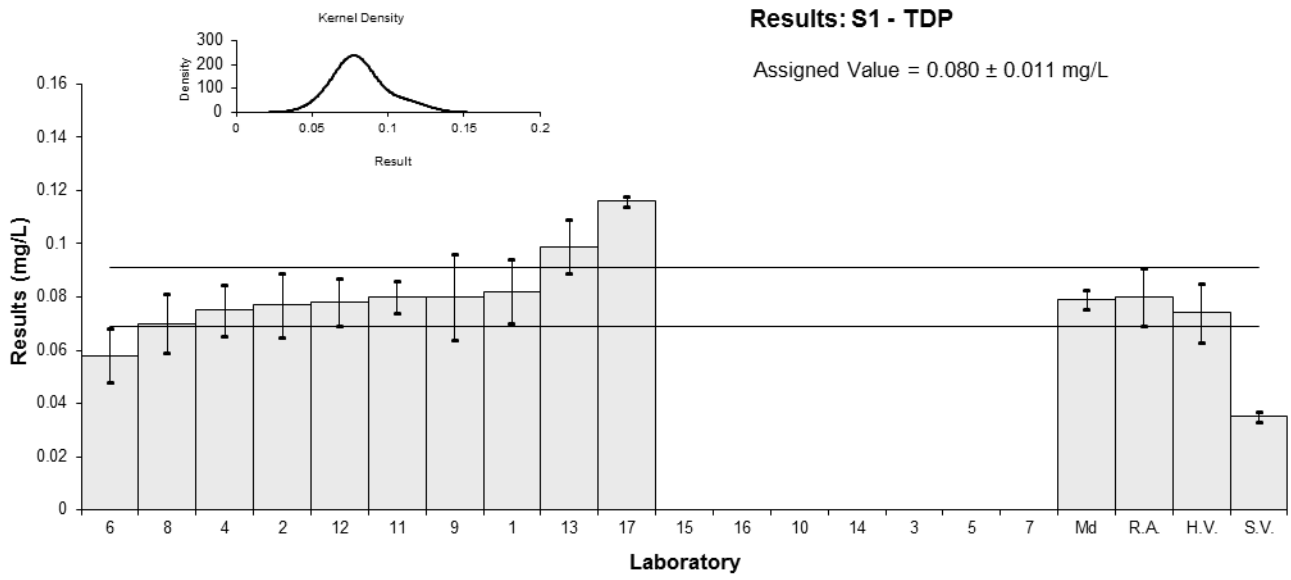
Participant Results

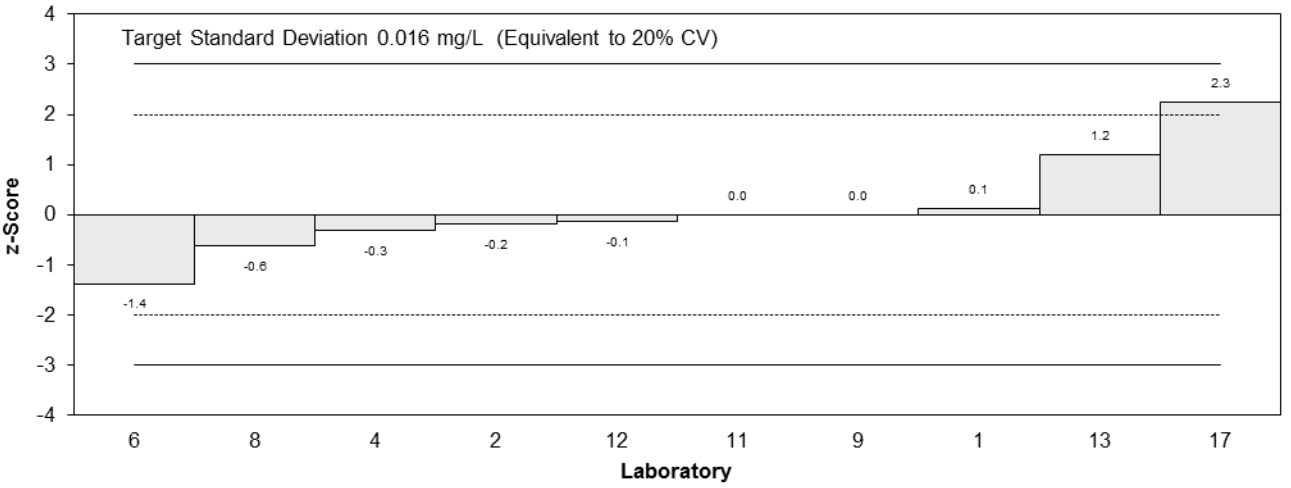
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.082	0.012	0.13	0.12
2	0.077	0.012	-0.19	-0.18
3	NT	NT		
4	0.075	0.0096	-0.31	-0.34
5	NT	NT		
6	0.058	0.01	-1.38	-1.48
8	0.07	0.011	-0.62	-0.64
9	0.08	0.016	0.00	0.00
10	NT	NT		
11	0.08	0.006	0.00	0.00
12	0.078	0.009	-0.13	-0.14
13	0.099	0.01	1.19	1.28
14	NT	NT		
15	NR	NR		
16	NR	NR		
17	0.116	0.002	2.25	3.22

Statistics

Assigned Value	0.080	0.011
Spike*	0.035	0.002
Homogeneity Value	0.074	0.011
Robust Average	0.080	0.011
Median	0.0790	0.0037
Mean	0.0815	
N	10	
Max.	0.116	
Min.	0.058	
Robust SD	0.014	
Robust CV	18%	

*Spike Value does not include incurred value.


Kernel Density
Density
Result
Results: S1 - TDP
Assigned Value = 0.080 ± 0.011 mg/L
Results (mg/L)
Laboratory
6 8 4 2 12 11 9 1 13 17 15 16 10 14 3 5 7 Md R.A. H.V. S.V.


z-Scores: S1 - TDP
Target Standard Deviation 0.016 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
6 8 4 2 12 11 9 1 13 17
-1.4 -0.6 -0.3 -0.2 -0.1 0.0 0.0 0.1 1.2 2.3

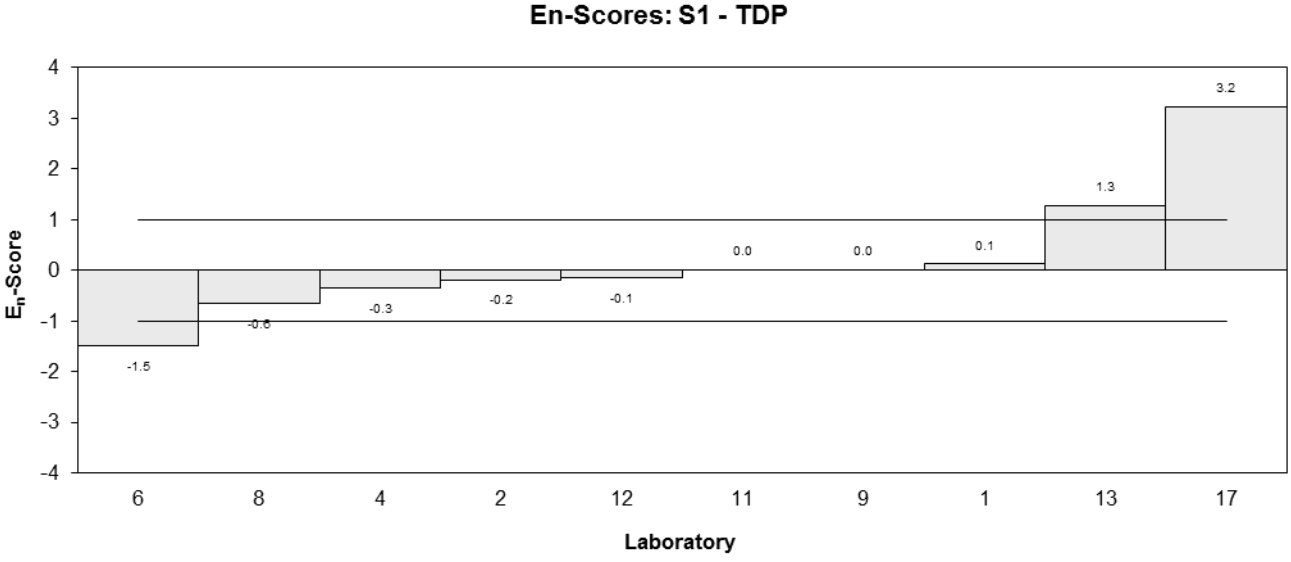

En-Scores: S1 - TDP
En-Score
Laboratory
6 8 4 2 12 11 9 1 13 17
-1.5 -0.6 -0.3 -0.2 -0.1 0.0 0.0 0.1 1.3 3.2

Figure 12

Table 14

Sample Details

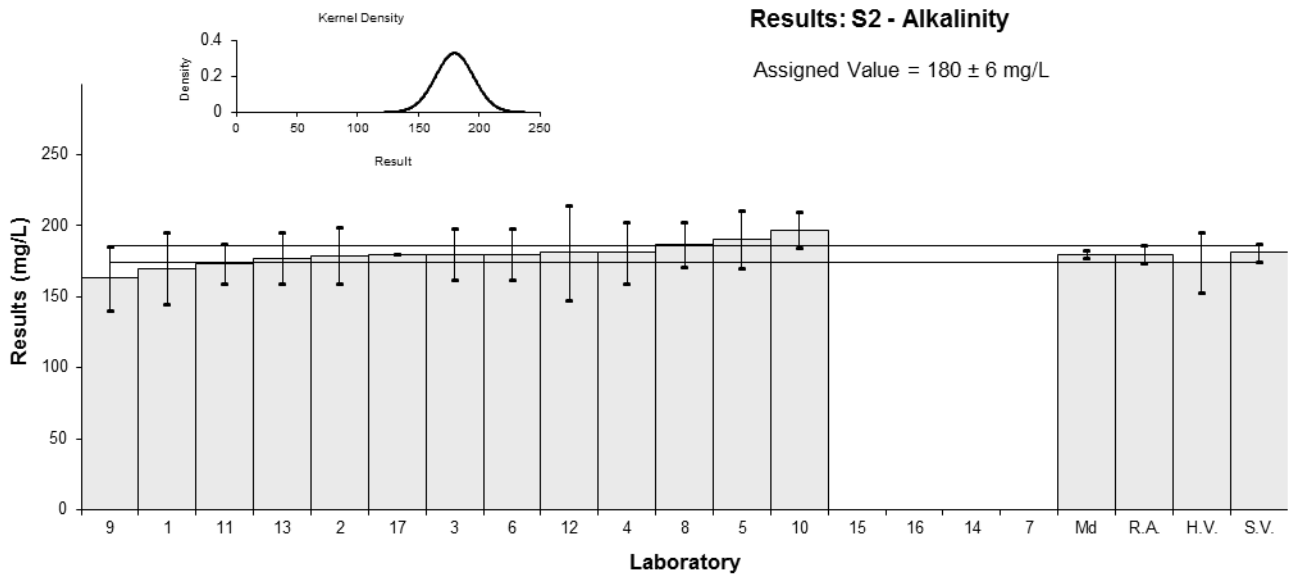
Sample No.	S2
Matrix.	Potable Water
Analyte.	Alkalinity
Units	mg/L

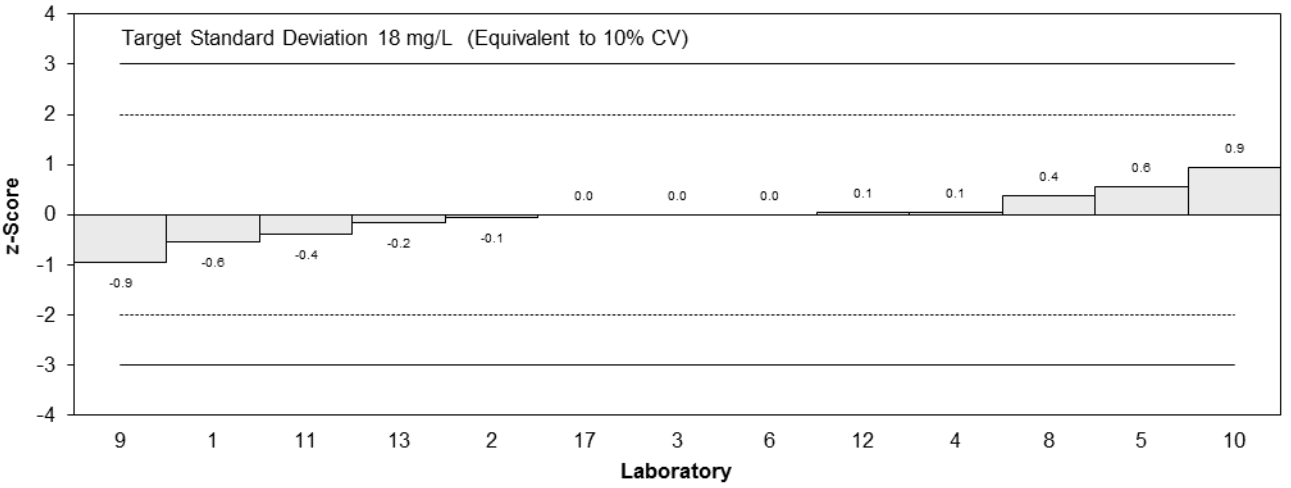
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	170	25	-0.56	-0.39
2	179	20	-0.06	-0.05
3	180	18.0	0.00	0.00
4	181	22.0	0.06	0.04
5	190	20.3	0.56	0.47
6	180	18	0.00	0.00
8	187	15.9	0.39	0.41
9	163	22.53	-0.94	-0.73
10	197	12.61	0.94	1.22
11	173	14	-0.39	-0.46
12	181	33	0.06	0.03
13	177	18	-0.17	-0.16
14	NT	NT		
15	NR	NR		
16	NR	NR		
17	180	0.001	0.00	0.00

Statistics

Assigned Value	180	6
Spike	181	6
Homogeneity Value	174	21
Robust Average	180	6
Median	180	3
Mean	180	
N	13	
Max.	197	
Min.	163	
Robust SD	8.0	
Robust CV	4.4%	


Kernel Density
Density
Result
Results: S2 - Alkalinity
Assigned Value = 180 ± 6 mg/L
Results (mg/L)
Laboratory
9 1 11 13 2 17 3 6 12 4 8 5 10 15 16 14 7 Md R.A. H.V. S.V.


z-Scores: S2 - Alkalinity
Target Standard Deviation 18 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
9 1 11 13 2 17 3 6 12 4 8 5 10
-0.9 -0.6 -0.4 -0.2 -0.1 0.0 0.0 0.0 0.1 0.1 0.4 0.6 0.9

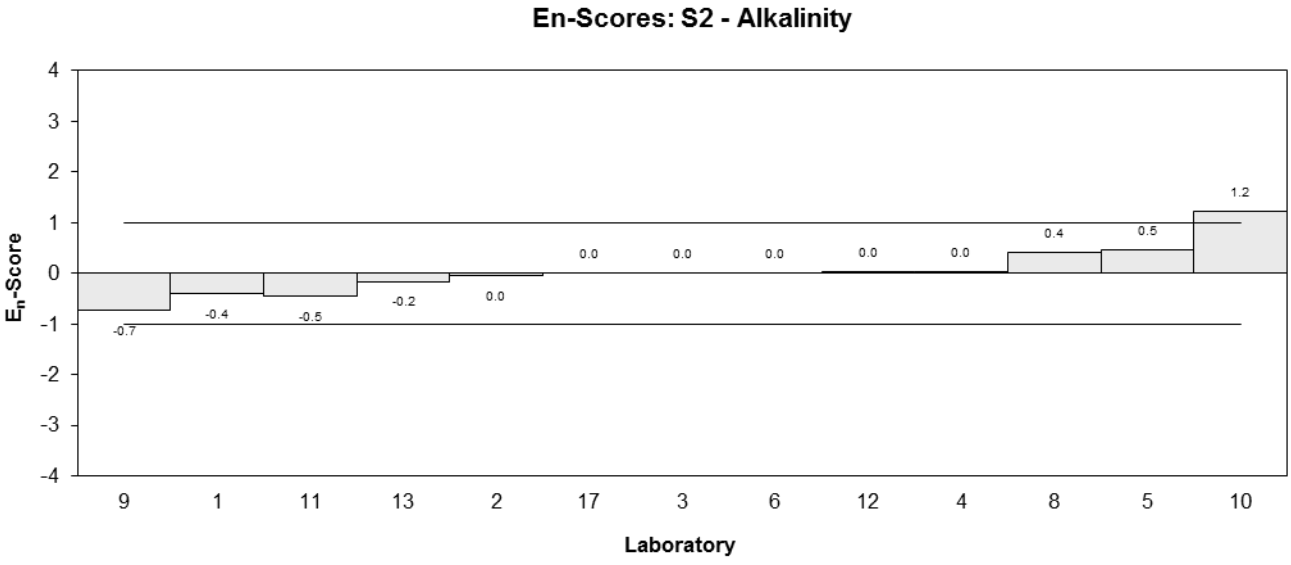

En-Scores: S2 - Alkalinity
En-Score
Laboratory
9 1 11 13 2 17 3 6 12 4 8 5 10
-0.7 -0.4 -0.5 -0.2 0.0 0.0 0.0 0.0 0.0 0.0 0.4 0.5 1.2

Figure 13

Table 15

Sample Details

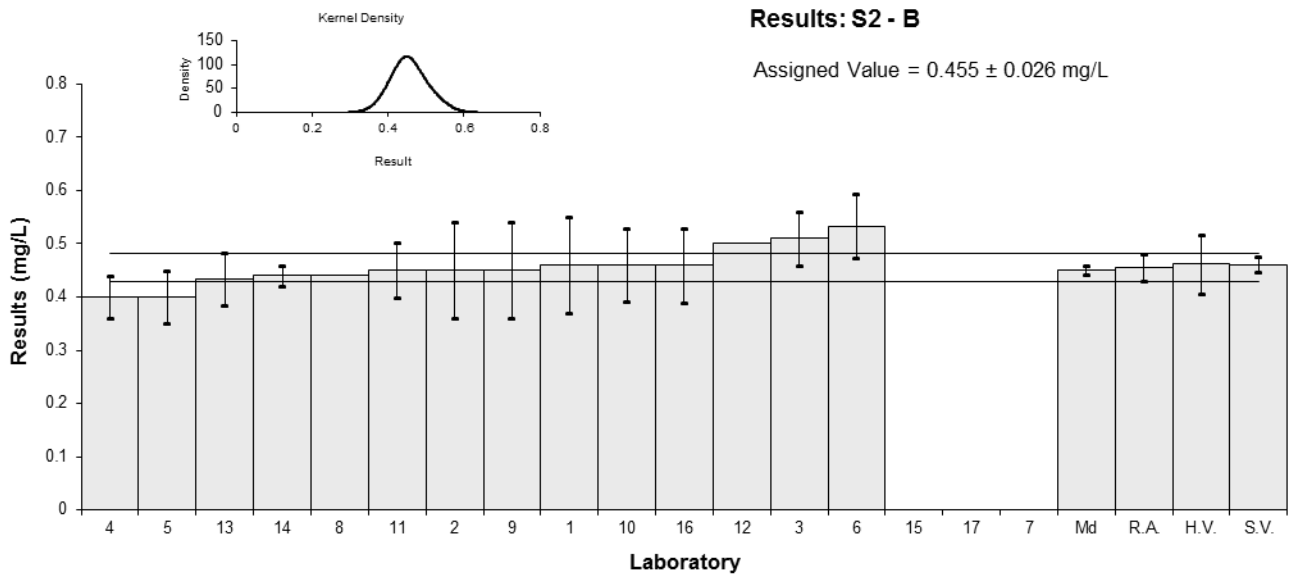
Sample No.	S2
Matrix.	Potable Water
Analyte.	B
Units	mg/L

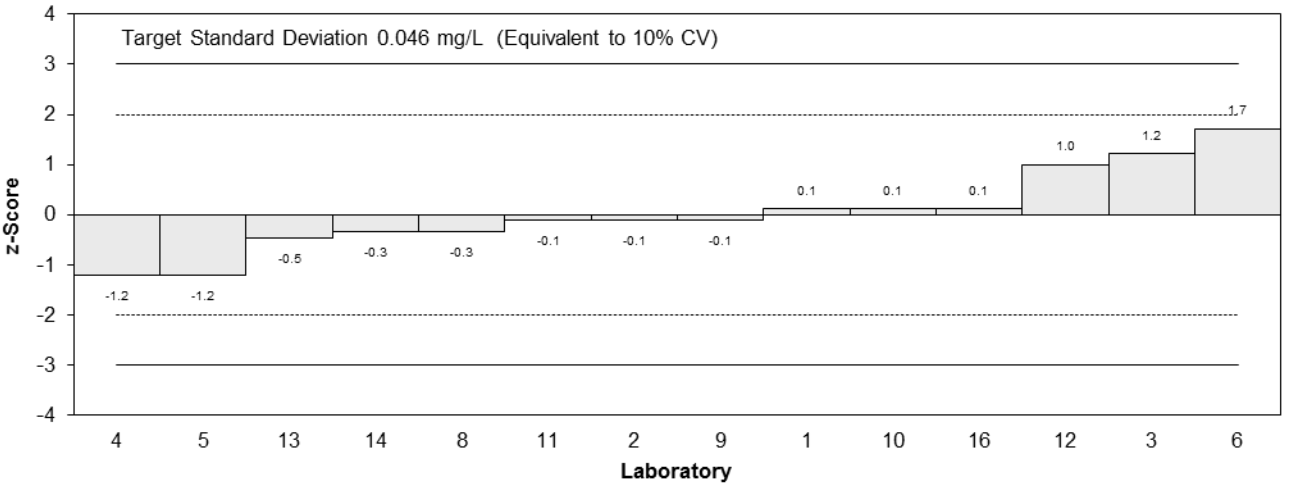
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.46	0.09	0.11	0.05
2	0.45	0.09	-0.11	-0.05
3	0.51	0.05	1.21	0.98
4	0.4	0.04	-1.21	-1.15
5	0.4	0.05	-1.21	-0.98
6	0.533	0.06	1.71	1.19
8	0.44	NR	-0.33	-0.58
9	0.45	0.09	-0.11	-0.05
10	0.460	0.068	0.11	0.07
11	0.45	0.052	-0.11	-0.09
12	0.5	NR	0.99	1.73
13	0.434	0.05	-0.46	-0.37
14	0.44	0.02	-0.33	-0.46
15	NR	NR		
16	0.46	0.07	0.11	0.07
17	NT	NT		

Statistics

Assigned Value	0.455	0.026
Spike	0.461	0.014
Homogeneity Value	0.462	0.055
Robust Average	0.455	0.026
Median	0.450	0.009
Mean	0.456	
N	14	
Max.	0.533	
Min.	0.4	
Robust SD	0.039	
Robust CV	8.6%	


Kernel Density
Density
Result
Results: S2 - B
Assigned Value = 0.455 ± 0.026 mg/L
Results (mg/L)
Laboratory
4 5 13 14 8 11 2 9 1 10 16 12 3 6 15 17 7 Md R.A. H.V. S.V.


z-Scores: S2 - B
Target Standard Deviation 0.046 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
4 5 13 14 8 11 2 9 1 10 16 12 3 6
-1.2 -1.2 -0.5 -0.3 -0.3 -0.1 -0.1 -0.1 0.1 0.1 0.1 1.0 1.2 1.7

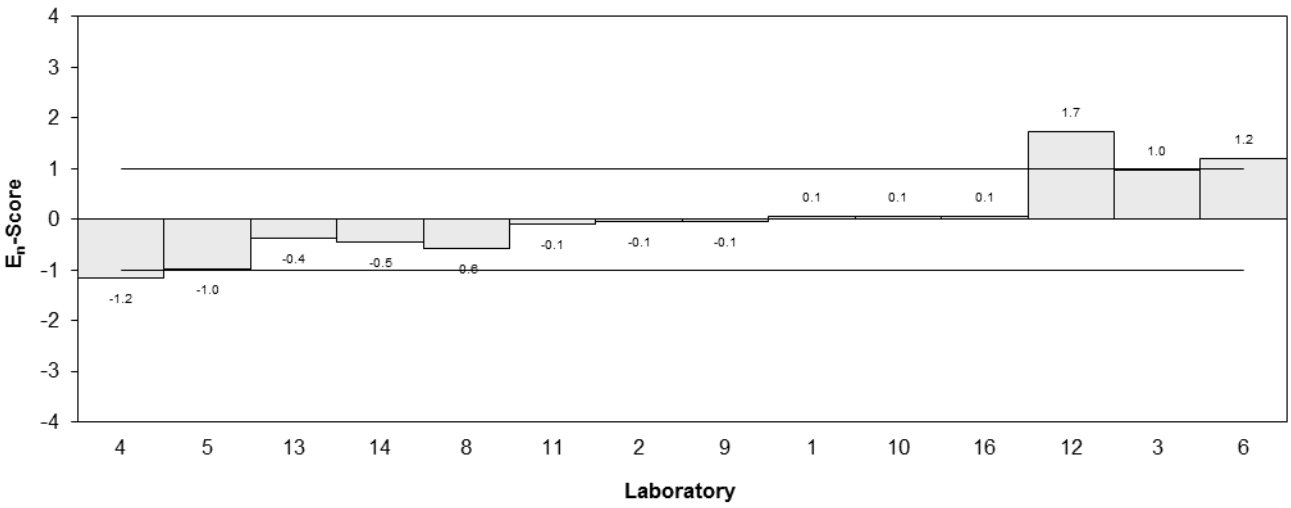

En-Scores: S2 - B
En-Score
Laboratory
4 5 13 14 8 11 2 9 1 10 16 12 3 6
-1.2 -1.0 -0.4 -0.5 -0.6 -0.1 -0.1 -0.1 0.1 0.1 0.1 1.7 1.0 1.2

Figure 14

Table 16

Sample Details

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

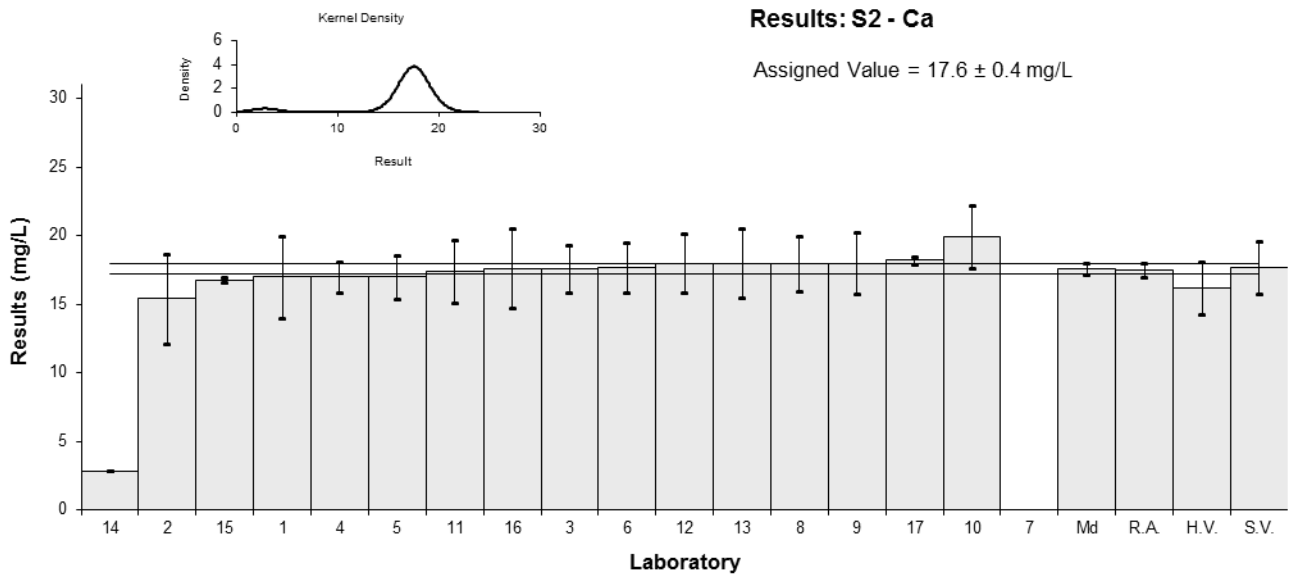
Participant Results

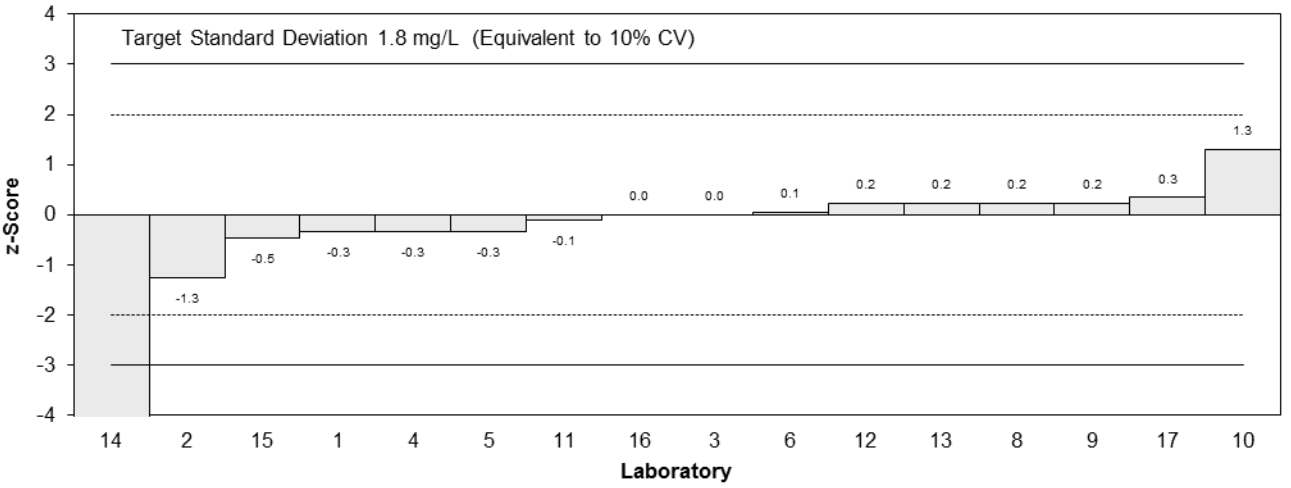
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	17	3	-0.34	-0.20
2	15.4	3.3	-1.25	-0.66
3	17.6	1.76	0.00	0.00
4	17	1.1	-0.34	-0.51
5	17	1.6	-0.34	-0.36
6	17.7	1.8	0.06	0.05
8	18	2	0.23	0.20
9	18	2.24	0.23	0.18
10	19.9	2.29	1.31	0.99
11	17.4	2.3	-0.11	-0.09
12	18	2.118	0.23	0.19
13	18.0	2.5	0.23	0.16
14	2.85	0.02	-8.38	-36.83
15	16.78	0.18	-0.47	-1.87
16	17.6	2.9	0.00	0.00
17	18.2	0.300	0.34	1.20

Statistics

Assigned Value*	17.6	0.4
Spike	17.7	1.9
Homogeneity Value	16.2	1.9
Robust Average	17.5	0.5
Median	17.6	0.4
Mean	16.7	
N	16	
Max.	19.9	
Min.	2.85	
Robust SD	0.77	
Robust CV	4.4%	

*Robust Average excluding Laboratory 14.


Kernel Density
Density
Result
Results: S2 - Ca
Assigned Value = 17.6 ± 0.4 mg/L
Results (mg/L)
Laboratory
14 2 15 1 4 5 11 16 3 6 12 13 8 9 17 10 7 Md R.A. H.V. S.V.


z-Scores: S2 - Ca
Target Standard Deviation 1.8 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
14 2 15 1 4 5 11 16 3 6 12 13 8 9 17 10
-1.3 -0.5 -0.3 -0.3 -0.3 -0.1 0.0 0.0 0.1 0.2 0.2 0.2 0.2 0.3 1.3

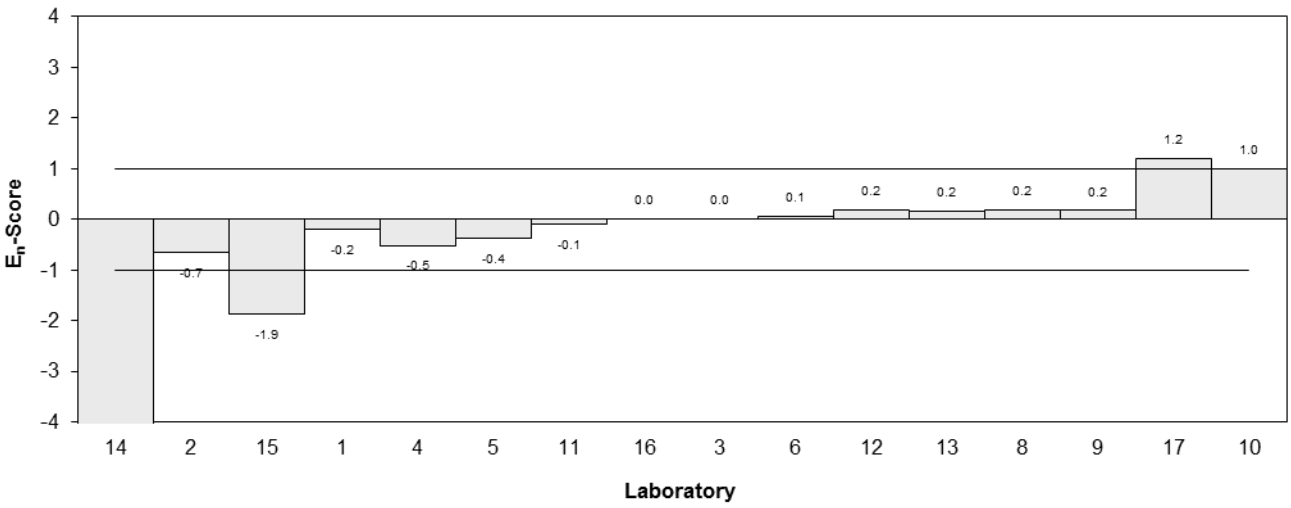

En-Scores: S2 - Ca
En-Score
Laboratory
14 2 15 1 4 5 11 16 3 6 12 13 8 9 17 10
-0.7 -1.9 -0.2 -0.5 -0.4 -0.1 0.0 0.0 0.1 0.2 0.2 0.2 0.2 1.2 1.0

Figure 15

Table 17

Sample Details

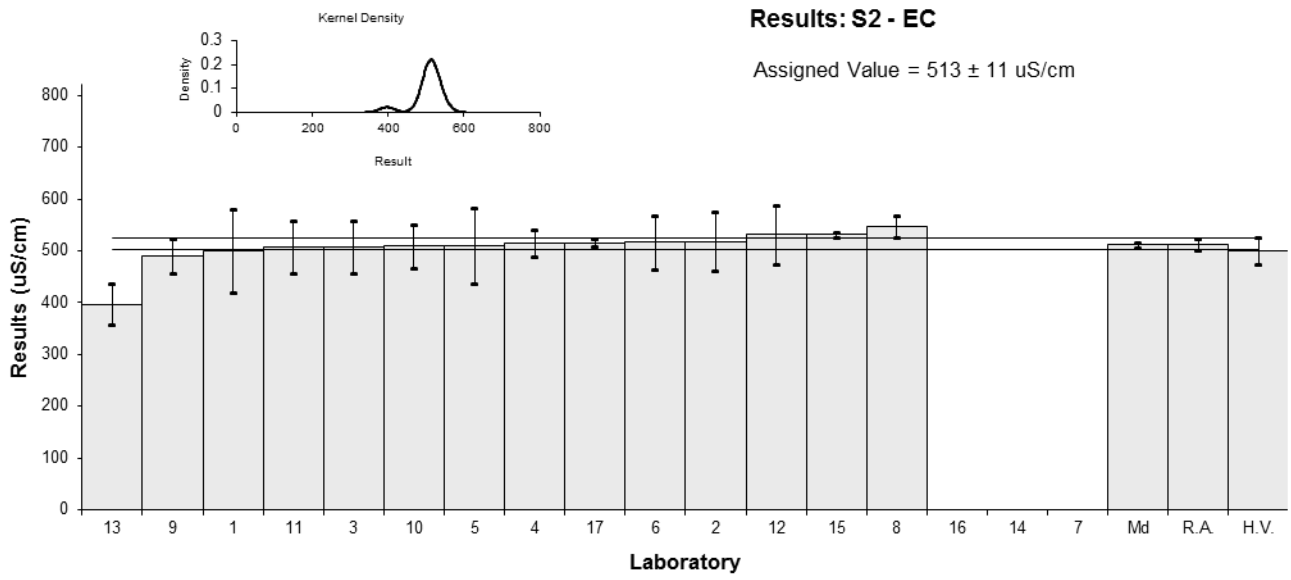
Sample No.	S2
Matrix.	Potable Water
Analyte.	EC
Units	uS/cm

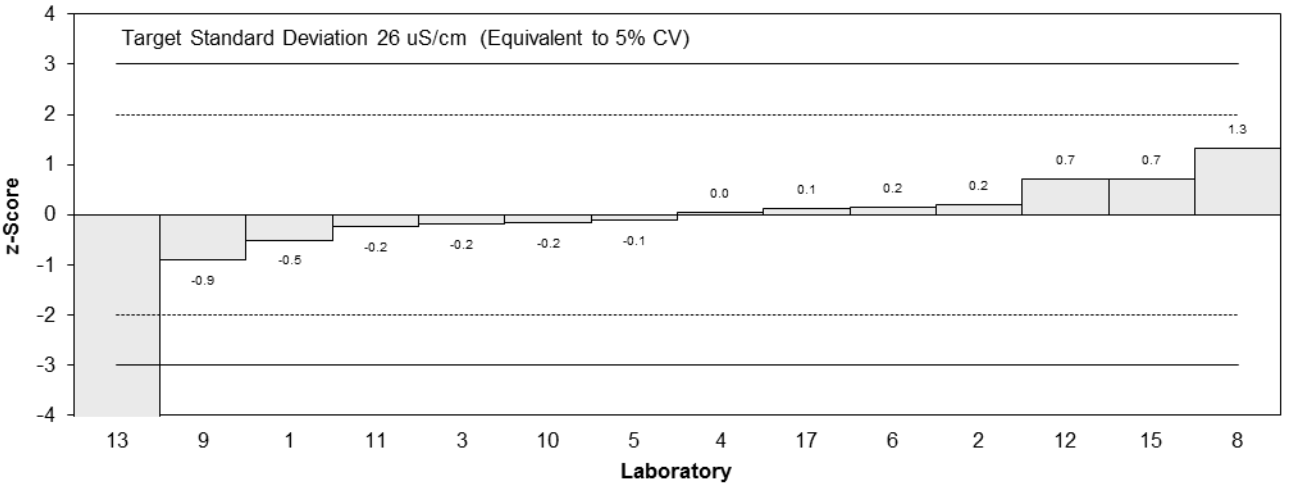
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	500	80	-0.51	-0.16
2	518	57	0.19	0.09
3	508	50.8	-0.19	-0.10
4	514	25.7	0.04	0.04
5	510	74	-0.12	-0.04
6	517	52	0.16	0.08
8	547	21.2	1.33	1.42
9	490	34.4	-0.90	-0.64
10	509	42.8	-0.16	-0.09
11	507	51	-0.23	-0.12
12	531	56	0.70	0.32
13	397	40	-4.52	-2.80
14	NT	NT		
15	531	4.6	0.70	1.51
16	NR	NR		
17	516	7.55	0.12	0.22

Statistics

Assigned Value	513	11
Spike	Not Spiked	
Homogeneity Value	500	25
Robust Average	513	11
Median	512	5
Mean	507	
N	14	
Max.	547	
Min.	397	
Robust SD	16	
Robust CV	3.1%	


Kernel Density
Density
Result
Results: S2 - EC
Assigned Value = 513 ± 11 uS/cm
Results (uS/cm)
Laboratory
13 9 1 11 3 10 5 4 17 6 2 12 15 8 16 14 7 Md R.A. H.V.


z-Scores: S2 - EC
Target Standard Deviation 26 uS/cm (Equivalent to 5% CV)
z-Score
Laboratory
13 9 1 11 3 10 5 4 17 6 2 12 15 8
-0.9 -0.5 -0.2 -0.2 -0.2 -0.1 0.0 0.1 0.2 0.2 0.7 0.7 1.3

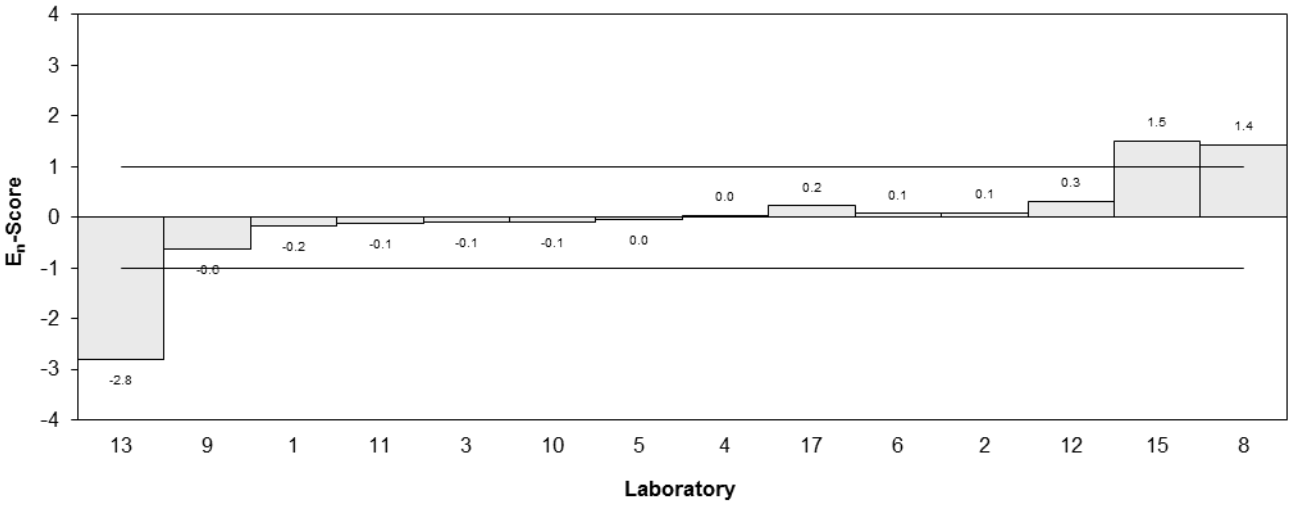

En-Scores: S2 - EC
En-Score
Laboratory
13 9 1 11 3 10 5 4 17 6 2 12 15 8
-2.8 -0.6 -0.2 -0.1 -0.1 -0.1 0.0 0.0 0.2 0.1 0.1 0.3 1.5 1.4

Figure 16

Table 18

Sample Details

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

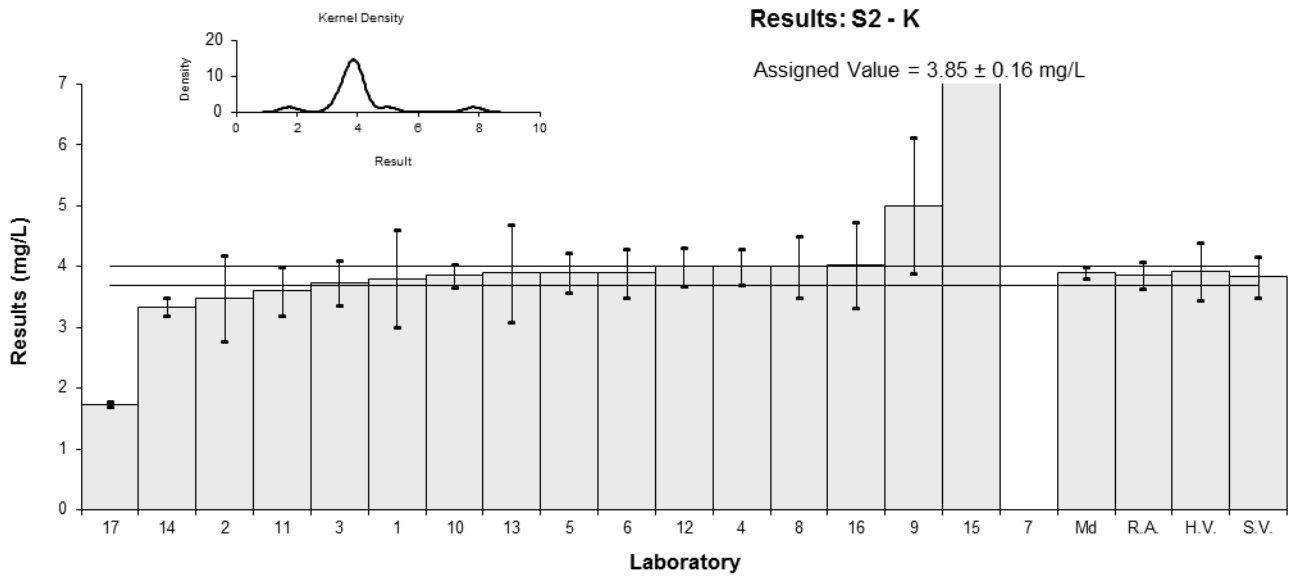
Participant Results

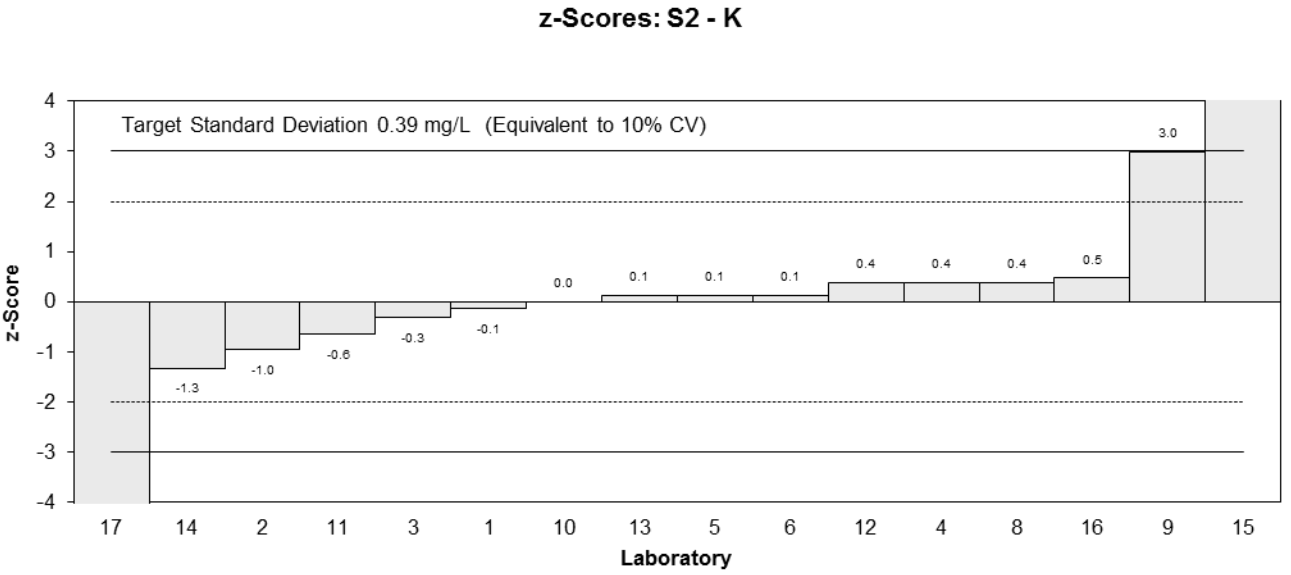
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.8	0.8	-0.13	-0.06
2	3.48	0.70	-0.96	-0.52
3	3.73	0.37	-0.31	-0.30
4	4	0.3	0.39	0.44
5	3.9	0.32	0.13	0.14
6	3.9	0.4	0.13	0.12
8	4	0.5	0.39	0.29
9	5	1.12	2.99	1.02
10	3.85	0.189	0.00	0.00
11	3.6	0.4	-0.65	-0.58
12	4	0.311	0.39	0.43
13	3.90	0.8	0.13	0.06
14	3.34	0.14	-1.32	-2.40
15	7.82	0.17	10.31	17.01
16	4.03	0.71	0.47	0.25
17	1.74	0.045	-5.48	-12.69

Statistics

Assigned Value*	3.85	0.16
Spike	3.83	0.33
Homogeneity Value	3.92	0.47
Robust Average	3.85	0.22
Median	3.90	0.09
Mean	4.01	
N	16	
Max.	7.82	
Min.	1.74	
Robust SD	0.34	
Robust CV	8.8%	

*Robust Average excluding Laboratories 15 and 17.


Kernel Density
Density
Result
Results: S2 - K
Assigned Value = 3.85 ± 0.16 mg/L
Results (mg/L)
17 14 2 11 3 1 10 13 5 6 12 4 8 16 9 15 7 Md R.A. H.V. S.V.
Laboratory


z-Scores: S2 - K
Target Standard Deviation 0.39 mg/L (Equivalent to 10% CV)
z-Score
17 14 2 11 3 1 10 13 5 6 12 4 8 16 9 15
Laboratory

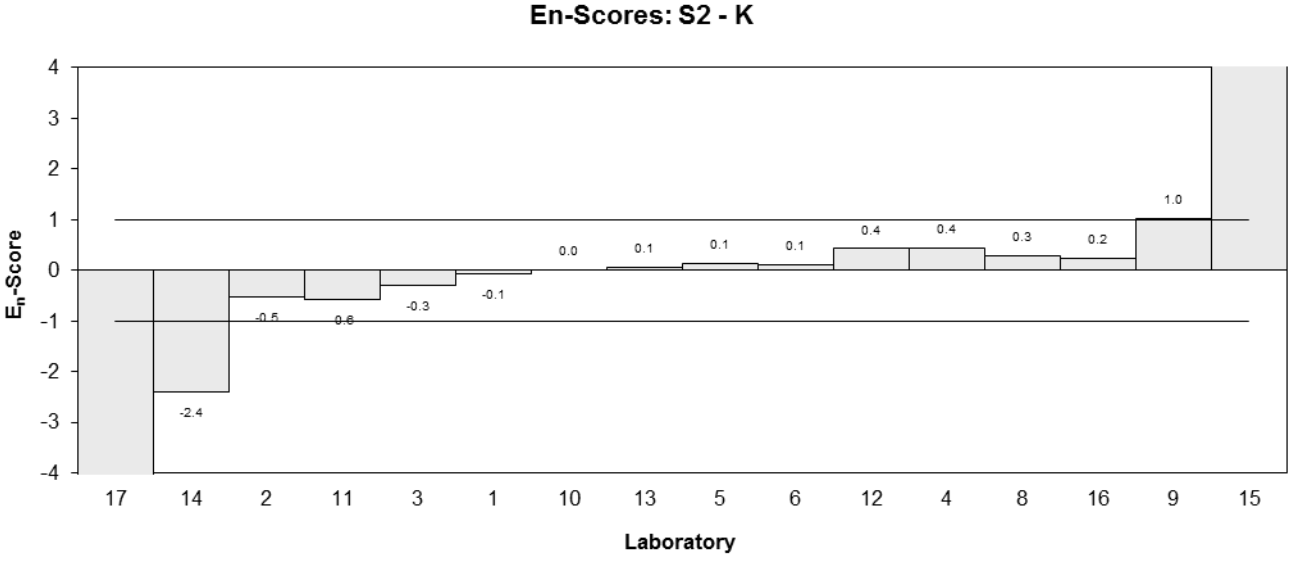

En-Scores: S2 - K
En-Score
17 14 2 11 3 1 10 13 5 6 12 4 8 16 9 15
Laboratory

Figure 17

Table 19

Sample Details

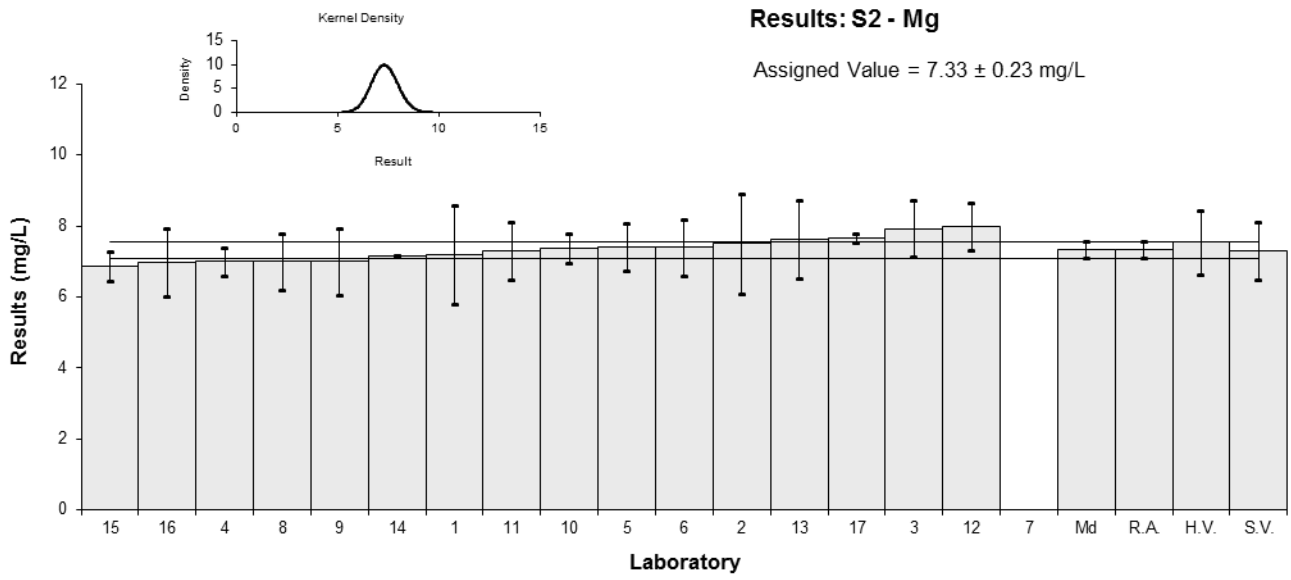
Sample No.	S2
Matrix.	Potable Water
Analyte.	Mg
Units	mg/L

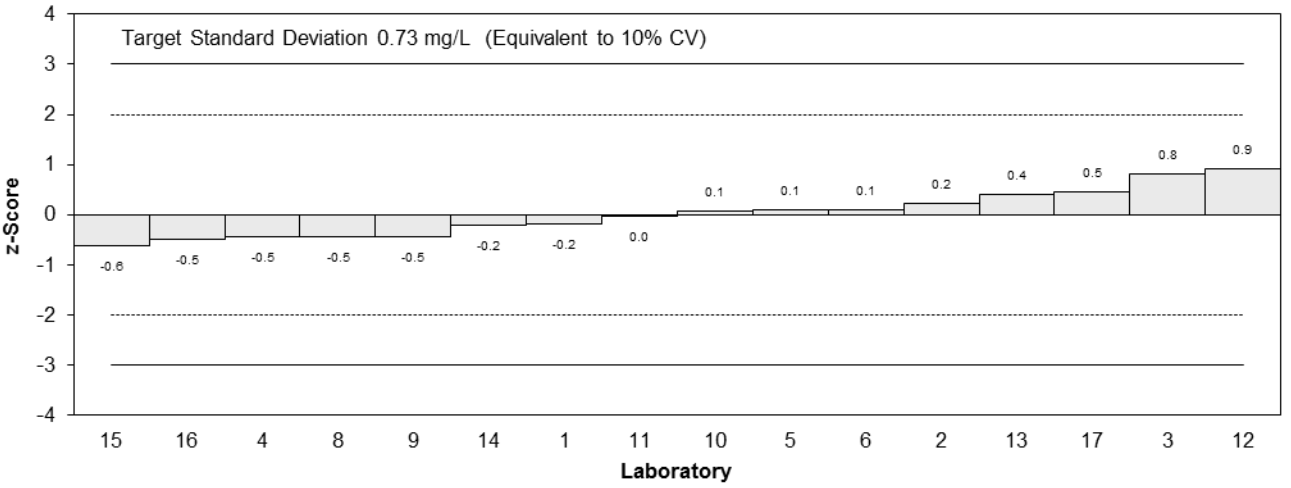
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.2	1.4	-0.18	-0.09
2	7.5	1.4	0.23	0.12
3	7.92	0.79	0.80	0.72
4	7	0.4	-0.45	-0.72
5	7.4	0.67	0.10	0.10
6	7.4	0.8	0.10	0.08
8	7	0.8	-0.45	-0.40
9	7	0.94	-0.45	-0.34
10	7.38	0.421	0.07	0.10
11	7.3	0.8	-0.04	-0.04
12	8	0.666	0.91	0.95
13	7.62	1.1	0.40	0.26
14	7.17	0.01	-0.22	-0.69
15	6.88	0.42	-0.61	-0.94
16	6.97	0.95	-0.49	-0.37
17	7.67	0.123	0.46	1.30

Statistics

Assigned Value	7.33	0.23
Spike	7.30	0.80
Homogeneity Value	7.54	0.90
Robust Average	7.33	0.23
Median	7.34	0.24
Mean	7.34	
N	16	
Max.	8	
Min.	6.88	
Robust SD	0.36	
Robust CV	4.9%	


Kernel Density
Density
Result
Results: S2 - Mg
Assigned Value = 7.33 ± 0.23 mg/L
Results (mg/L)
Laboratory
15 16 4 8 9 14 1 11 10 5 6 2 13 17 3 12 7 Md R.A. H.V. S.V.


z-Scores: S2 - Mg
Target Standard Deviation 0.73 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
15 16 4 8 9 14 1 11 10 5 6 2 13 17 3 12
-0.6 -0.5 -0.5 -0.5 -0.5 -0.2 -0.2 0.0 0.1 0.1 0.1 0.2 0.4 0.5 0.8 0.9

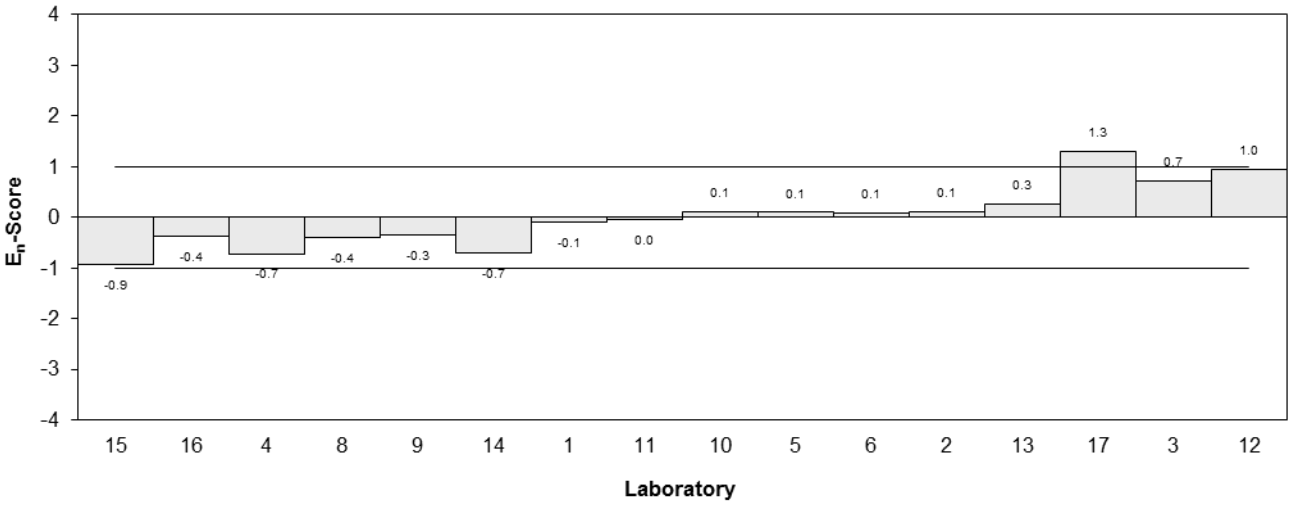

En-Scores: S2 - Mg
En-Score
Laboratory
15 16 4 8 9 14 1 11 10 5 6 2 13 17 3 12
-0.9 -0.4 -0.7 -0.4 -0.3 -0.7 -0.1 0.0 0.1 0.1 0.1 0.1 0.3 1.3 0.7 1.0

Figure 18

Table 20

Sample Details

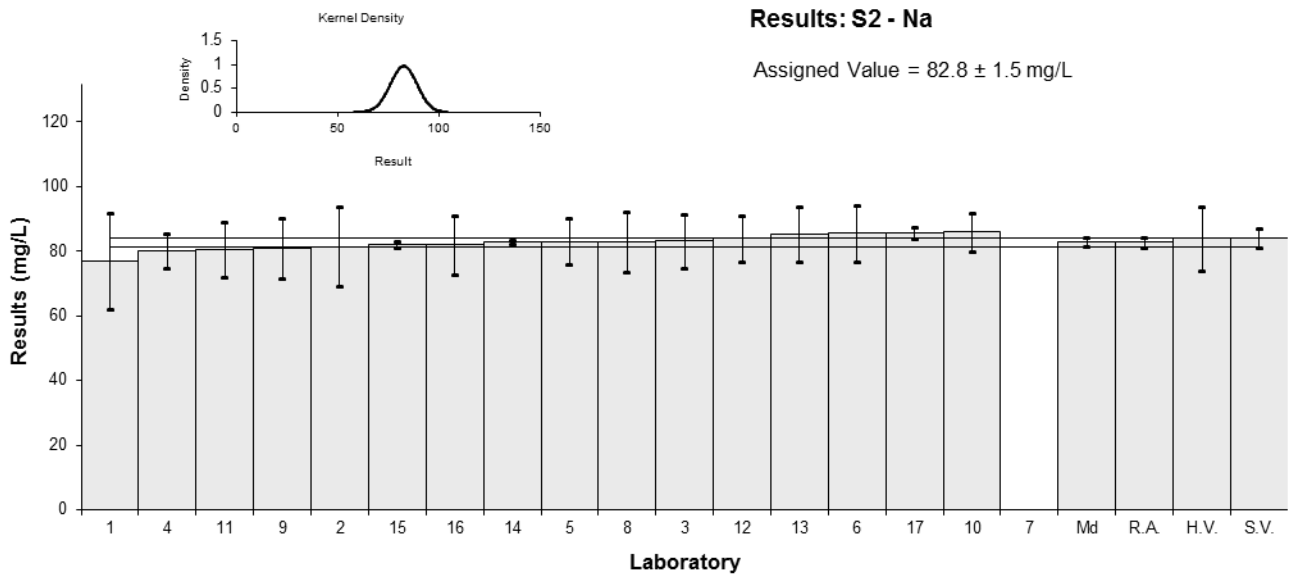
Sample No.	S2
Matrix.	Potable Water
Analyte.	Na
Units	mg/L

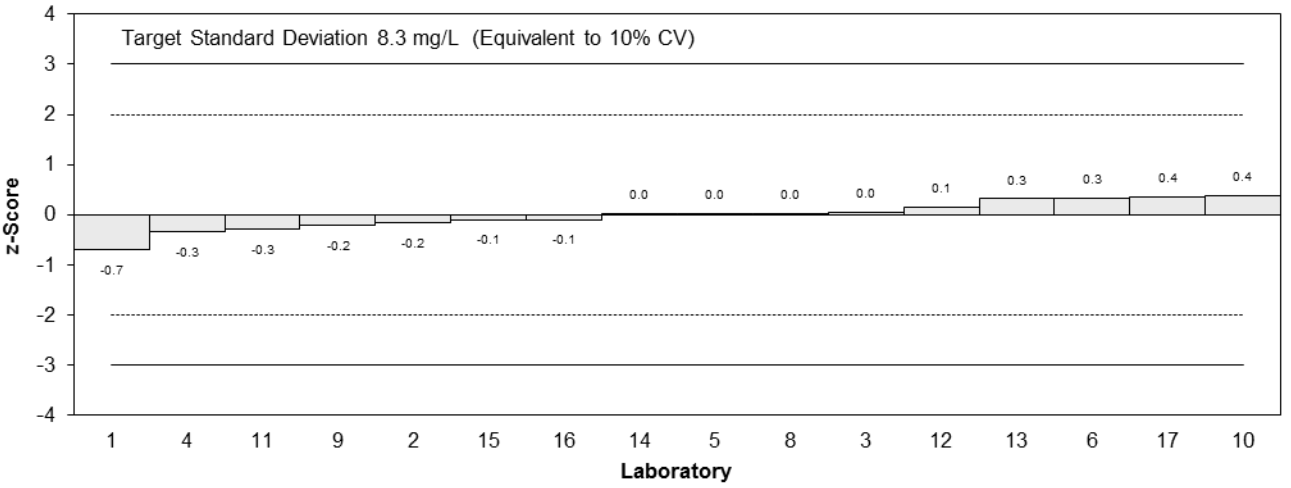
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	77	15	-0.70	-0.38
2	81.5	12.2	-0.16	-0.11
3	83.2	8.32	0.05	0.05
4	80	5.4	-0.34	-0.50
5	83	7.2	0.02	0.03
6	85.5	8.6	0.33	0.31
8	83	9.4	0.02	0.02
9	81	9.19	-0.22	-0.19
10	85.9	5.76	0.37	0.52
11	80.5	8.4	-0.28	-0.27
12	84	7.085	0.14	0.17
13	85.4	8.5	0.31	0.30
14	82.91	0.42	0.01	0.07
15	82.0	0.98	-0.10	-0.45
16	82.0	9.2	-0.10	-0.09
17	85.7	1.66	0.35	1.30

Statistics

Assigned Value	82.8	1.5
Spike	84.0	3.0
Homogeneity Value	84	10
Robust Average	82.8	1.5
Median	83.0	1.3
Mean	82.7	
N	16	
Max.	85.9	
Min.	77	
Robust SD	2.4	
Robust CV	2.9%	


Kernel Density
Density
Result
Results: S2 - Na
Assigned Value = 82.8 ± 1.5 mg/L
Results (mg/L)
Laboratory
1 4 11 9 2 15 16 14 5 8 3 12 13 6 17 10 7 Md R.A. H.V. S.V.


z-Scores: S2 - Na
Target Standard Deviation 8.3 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
1 4 11 9 2 15 16 14 5 8 3 12 13 6 17 10
-0.7 -0.3 -0.3 -0.2 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.0 0.1 0.3 0.3 0.4 0.4

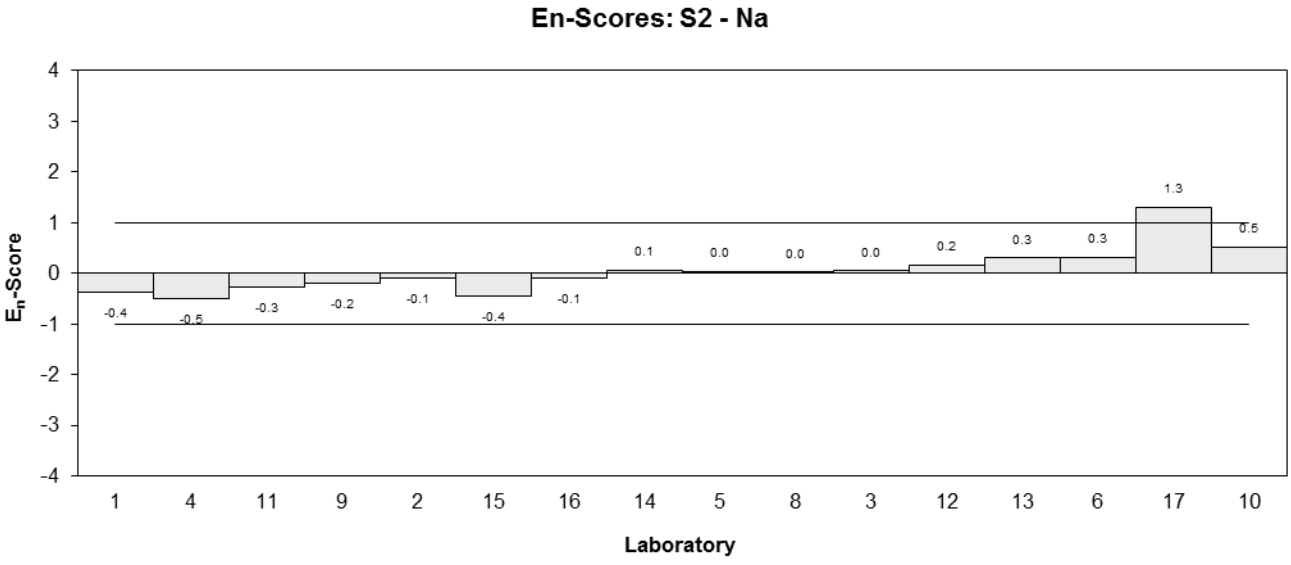

En-Scores: S2 - Na
En-Score
Laboratory
1 4 11 9 2 15 16 14 5 8 3 12 13 6 17 10
-0.4 -0.5 -0.3 -0.2 -0.1 -0.4 -0.1 0.1 0.0 0.0 0.0 0.2 0.3 0.3 1.3 0.5

Figure 19

Table 21

Sample Details

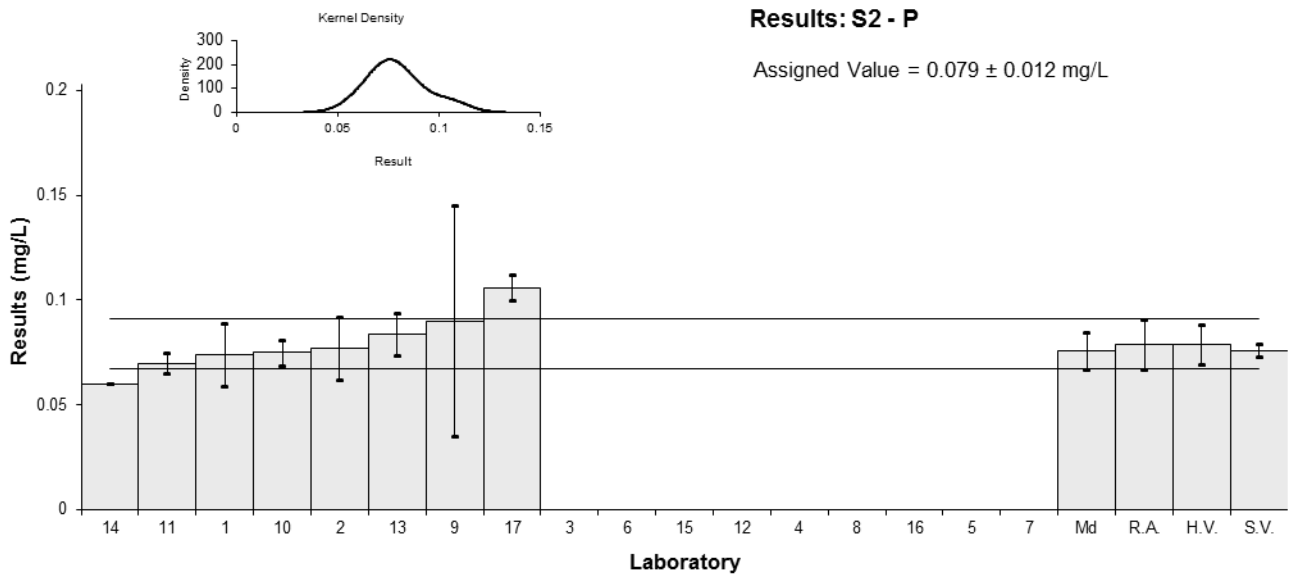
Sample No.	S2
Matrix.	Potable Water
Analyte.	P
Units	mg/L

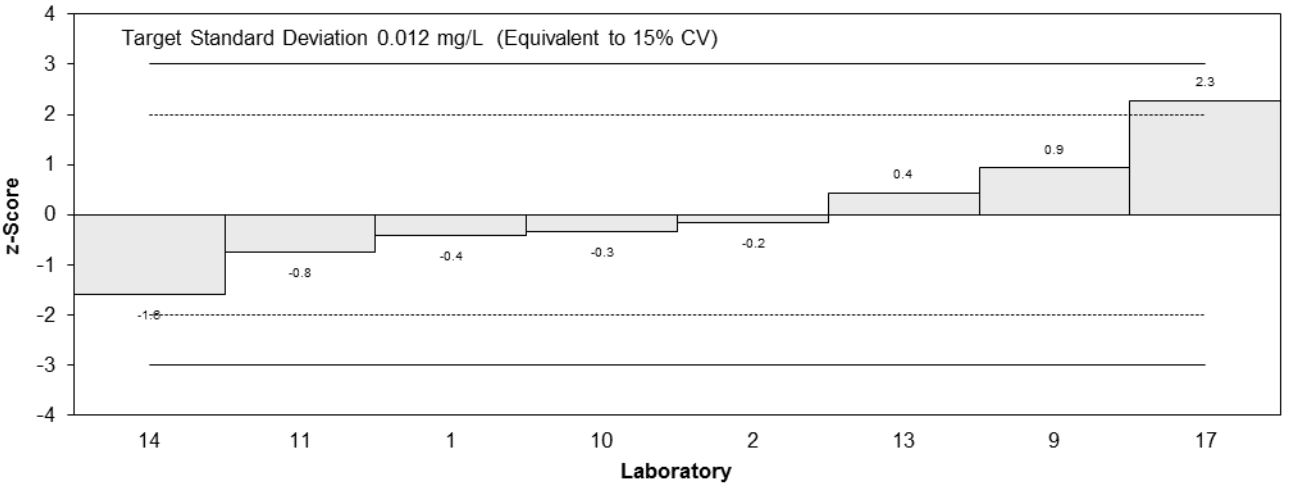
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.074	0.015	-0.42	-0.26
2	0.077	0.015	-0.17	-0.10
3	<0.02	NR		
4	<1	0.1		
5	NT	NT		
6	<0.1	NR		
8	<1	NR		
9	0.09	0.055	0.93	0.20
10	0.075	0.006	-0.34	-0.30
11	0.07	0.005	-0.76	-0.69
12	<1	NR		
13	0.084	0.01	0.42	0.32
14	0.06	0.00	-1.60	-1.58
15	<0.5	0.1		
16	NR	NR		
17	0.106	0.006	2.28	2.01

Statistics

Assigned Value	0.079	0.012
Spike	0.076	0.003
Homogeneity Value	0.0791	0.0095
Robust Average	0.079	0.012
Median	0.076	0.009
Mean	0.0795	
N	8	
Max.	0.106	
Min.	0.06	
Robust SD	0.014	
Robust CV	18%	


Kernel Density
Density
300
200
100
0
0
0.05
0.1
0.15
Result
Results: S2 - P
Assigned Value = 0.079 ± 0.012 mg/L
Results (mg/L)
0.2
0.15
0.1
0.05
0
14
11
1
10
2
13
9
17
3
6
15
12
4
8
16
5
7
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - P
Target Standard Deviation 0.012 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.6
-0.8
-0.4
-0.3
-0.2
0.4
0.9
2.3
14
11
1
10
2
13
9
17
Laboratory

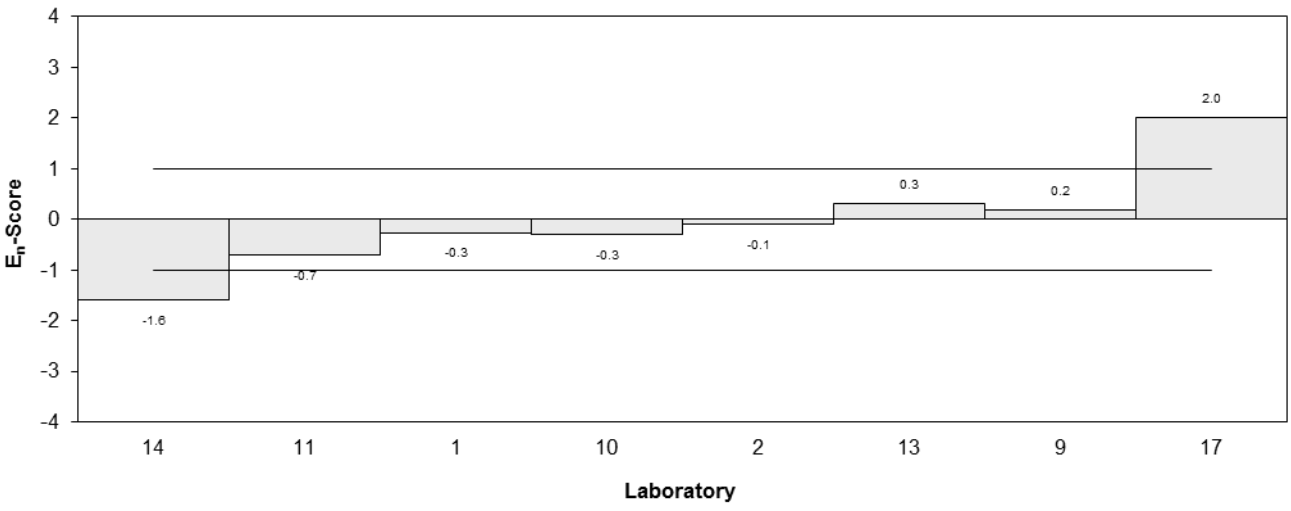

En-Scores: S2 - P
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.6
-0.7
-0.3
-0.3
-0.1
0.3
0.2
2.0
14
11
1
10
2
13
9
17
Laboratory

Figure 20

Table 22

Sample Details

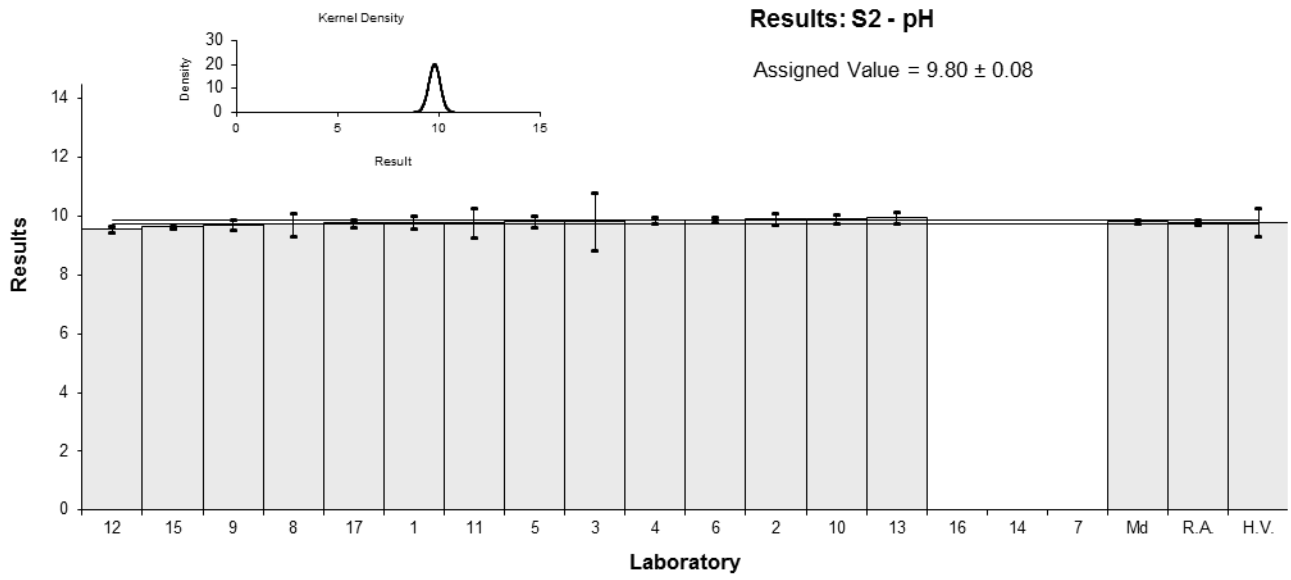
Sample No.	S2
Matrix.	Potable Water
Analyte.	pH

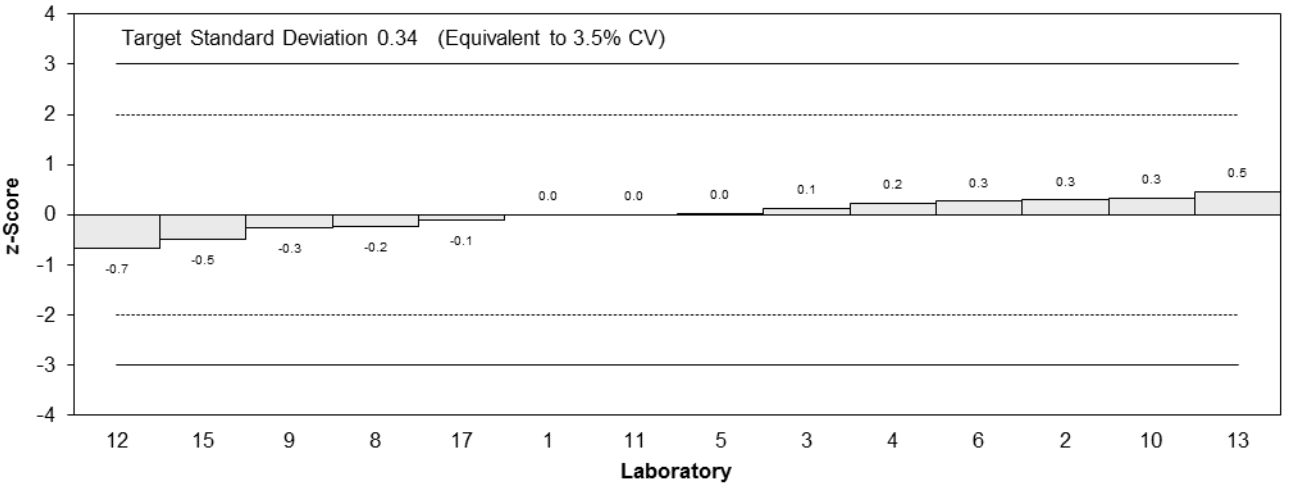
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	9.8	0.2	0.00	0.00
2	9.9	0.2	0.29	0.46
3	9.84	0.98	0.12	0.04
4	9.88	0.119	0.23	0.56
5	9.81	0.2	0.03	0.05
6	9.89	0.1	0.26	0.70
8	9.72	0.39	-0.23	-0.20
9	9.71	0.168	-0.26	-0.48
10	9.91	0.159	0.32	0.62
11	9.8	0.5	0.00	0.00
12	9.57	0.11	-0.67	-1.69
13	9.96	0.2	0.47	0.74
14	NT	NT		
15	9.63	0.03	-0.50	-1.99
16	NR	NR		
17	9.76	0.121	-0.12	-0.28

Statistics

Assigned Value	9.80	0.08
Spike	Not Spiked	
Homogeneity Value	9.80	0.49
Robust Average	9.80	0.08
Median	9.81	0.07
Mean	9.80	
N	14	
Max.	9.96	
Min.	9.57	
Robust SD	0.12	
Robust CV	1.2%	


Kernel Density
Density
Result
Results: S2 - pH
Assigned Value = 9.80 ± 0.08
Results
Laboratory
12 15 9 8 17 1 11 5 3 4 6 2 10 13 16 14 7 Md R.A. H.V.


z-Scores: S2 - pH
Target Standard Deviation 0.34 (Equivalent to 3.5% CV)
z-Score
Laboratory
12 15 9 8 17 1 11 5 3 4 6 2 10 13
-0.7 -0.5 -0.3 -0.2 -0.1 0.0 0.0 0.0 0.1 0.2 0.3 0.3 0.3 0.5

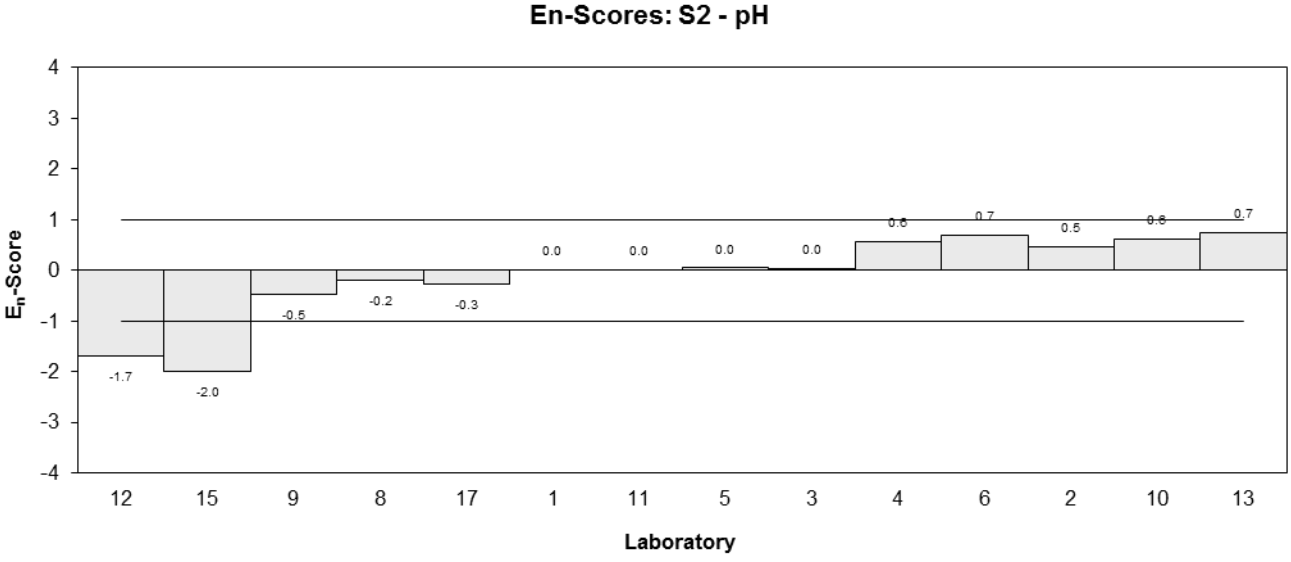

En-Scores: S2 - pH
En-Score
Laboratory
12 15 9 8 17 1 11 5 3 4 6 2 10 13
-1.7 -2.0 -0.5 -0.2 -0.3 0.0 0.0 0.0 0.0 0.6 0.7 0.5 0.6 0.7

Figure 21

Table 23

Sample Details

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

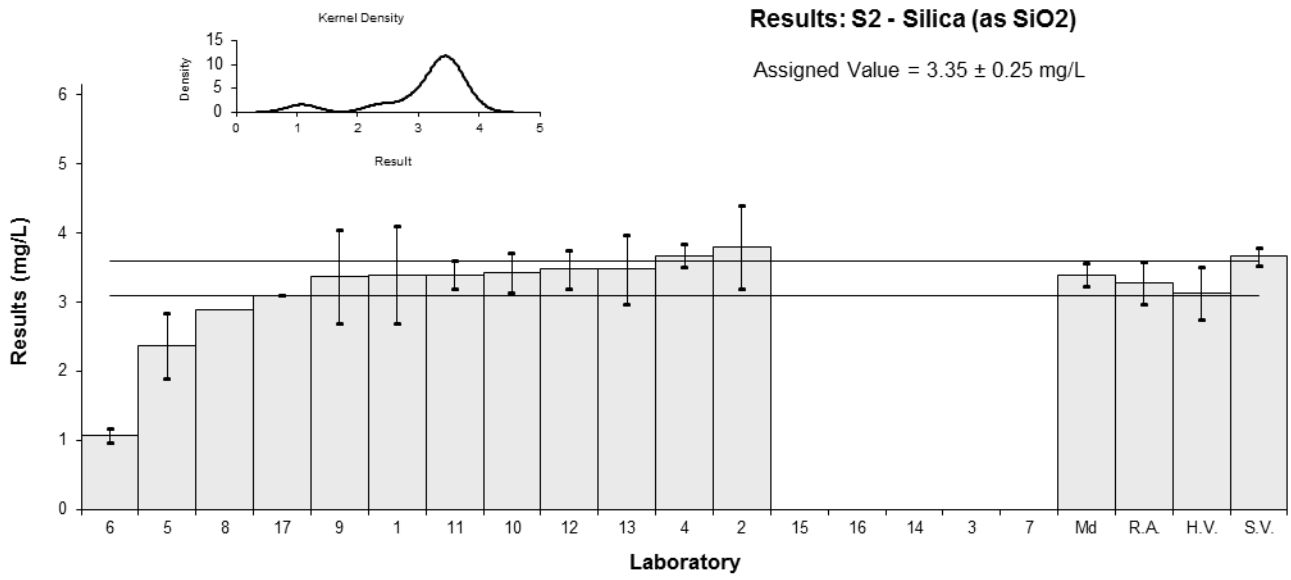
Participant Results

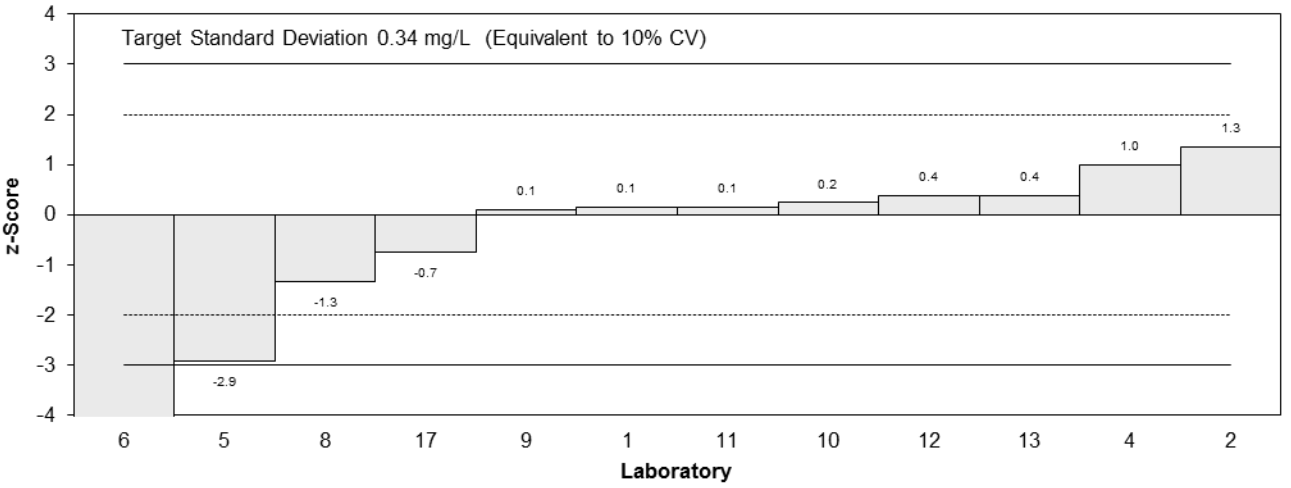
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.4	0.7	0.15	0.07
2	3.8	0.6	1.34	0.69
3	NT	NT		
4	3.68	0.173	0.99	1.09
5	2.37	0.47	-2.93	-1.84
6	1.08	0.1	-6.78	-8.43
8	2.9	NR	-1.34	-1.80
9	3.38	0.68	0.09	0.04
10	3.43	0.288	0.24	0.21
11	3.4	0.2	0.15	0.16
12	3.48	0.28	0.39	0.35
13	3.48	0.5	0.39	0.23
14	NT	NT		
15	NR	NR		
16	NR	NR		
17	3.10	0.001	-0.75	-1.00

Statistics

Assigned Value*	3.35	0.25
Spike	3.67	0.13
Homogeneity Value	3.14	0.38
Robust Average	3.28	0.31
Median	3.40	0.17
Mean	3.13	
N	12	
Max.	3.8	
Min.	1.08	
Robust SD	0.43	
Robust CV	13%	

*Robust Average excluding Laboratory 6.


Kernel Density
Density
Result
Results: S2 - Silica (as SiO2)
Assigned Value = 3.35 ± 0.25 mg/L
Results (mg/L)
Laboratory
6 5 8 17 9 1 11 10 12 13 4 2 15 16 14 3 7 Md R.A. H.V. S.V.


z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation 0.34 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
6 5 8 17 9 1 11 10 12 13 4 2
-2.9
-1.3
-0.7
0.1
0.1
0.1
0.2
0.4
0.4
1.0
1.3

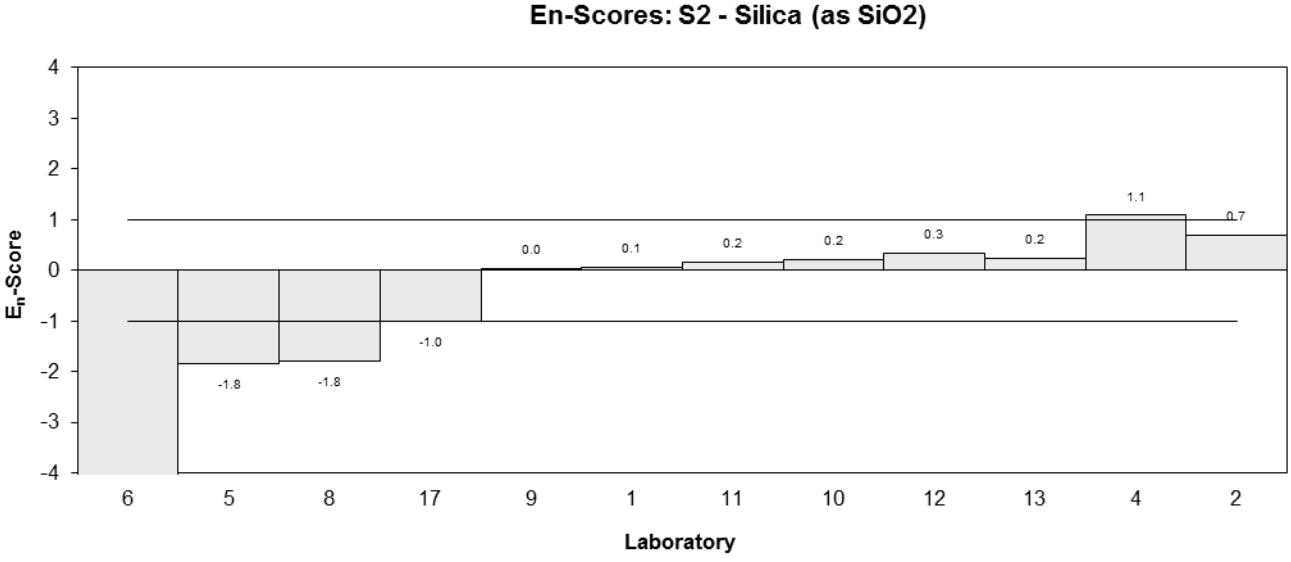

En-Scores: S2 - Silica (as SiO2)
En-Score
Laboratory
6 5 8 17 9 1 11 10 12 13 4 2
-1.8
-1.8
-1.0
0.0
0.1
0.2
0.2
0.3
0.2
1.1
0.7

Figure 22

Table 24

Sample Details

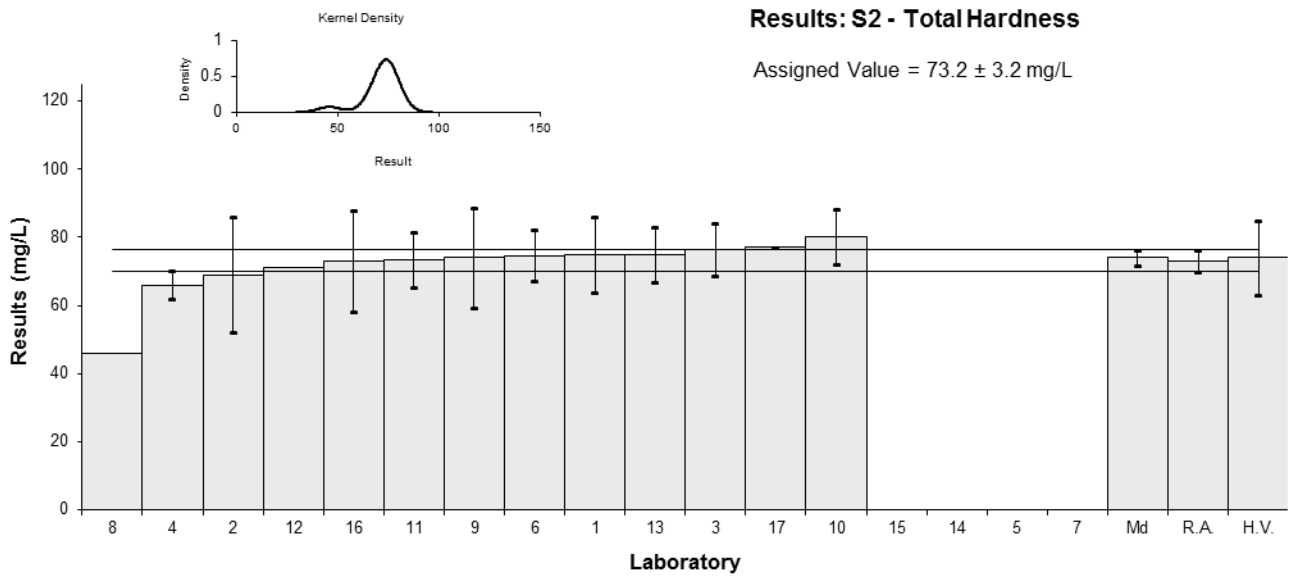
Sample No.	S2
Matrix.	Potable Water
Analyte.	Total Hardness
Units	mg/L

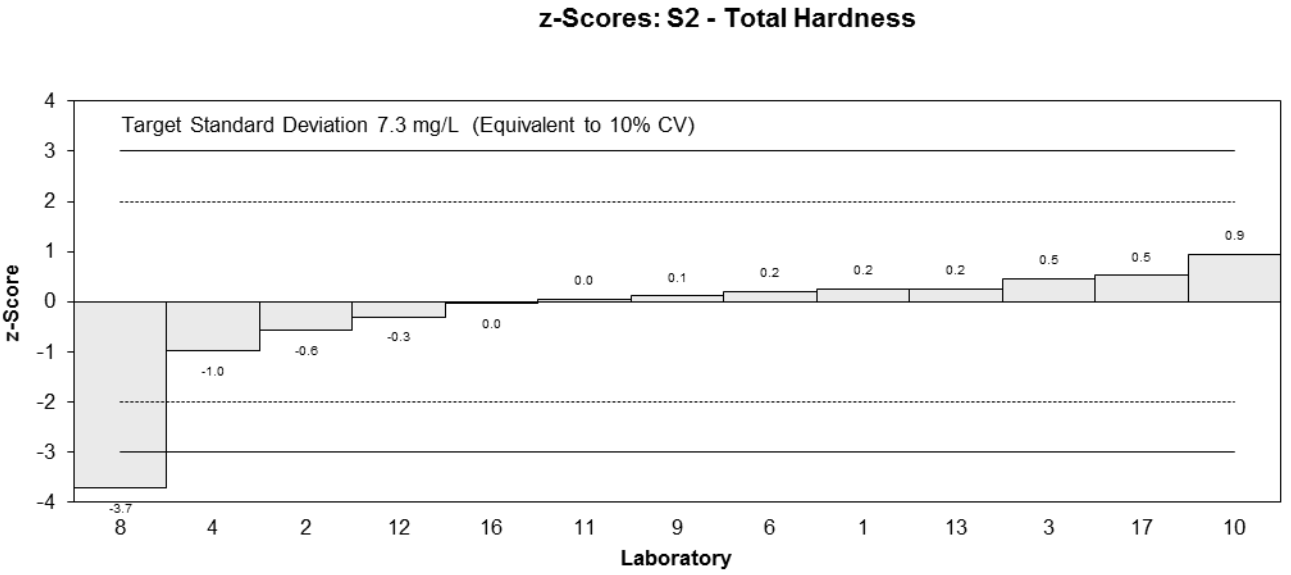
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	75	11	0.25	0.16
2	69	17	-0.57	-0.24
3	76.5	7.65	0.45	0.40
4	66	4.1	-0.98	-1.38
5	NT	NT		
6	74.7	7.5	0.20	0.18
8	46	NR	-3.72	-8.50
9	74	14.8	0.11	0.05
10	80.1	8.01	0.94	0.80
11	73.5	8.1	0.04	0.03
12	71	NR	-0.30	-0.69
13	75	8.0	0.25	0.21
14	NT	NT		
15	NR	NR		
16	73	15	-0.03	-0.01
17	77	0.001	0.52	1.19

Statistics

Assigned Value	73.2	3.2
Spike	Not Spiked	
Homogeneity Value	74	11
Robust Average	73.2	3.2
Median	74.0	2.2
Mean	71.6	
N	13	
Max.	80.1	
Min.	46	
Robust SD	4.7	
Robust CV	6.4%	


Kernel Density
Density
Result
Results: S2 - Total Hardness
Assigned Value = 73.2 ± 3.2 mg/L
Results (mg/L)
Laboratory
8 4 2 12 16 11 9 6 1 13 3 17 10 15 14 5 7 Md R.A. H.V.


z-Scores: S2 - Total Hardness
Target Standard Deviation 7.3 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
8 4 2 12 16 11 9 6 1 13 3 17 10
-3.7 -1.0 -0.6 -0.3 0.0 0.0 0.1 0.2 0.2 0.2 0.5 0.5 0.9

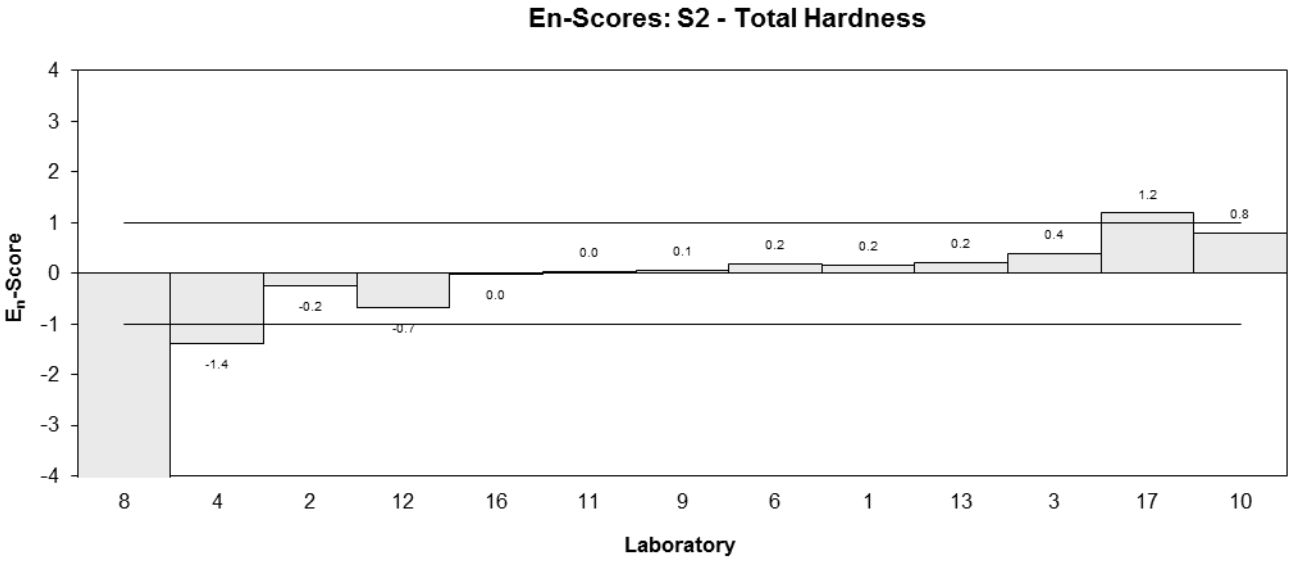

En-Scores: S2 - Total Hardness
En-Score
Laboratory
8 4 2 12 16 11 9 6 1 13 3 17 10
-1.4 -0.2 -0.7 0.0 0.0 0.1 0.2 0.2 0.2 0.4 1.2 0.8

Figure 23

Table 25

Sample Details

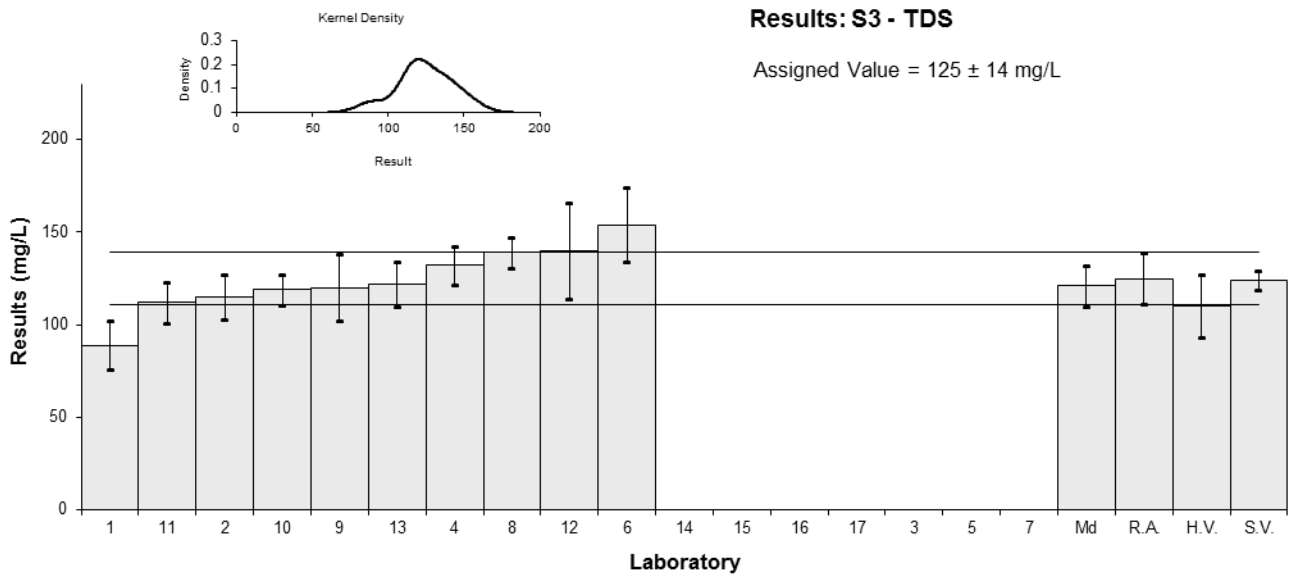
Sample No.	S3
Matrix.	Potable Water
Analyte.	TDS
Units	mg/L

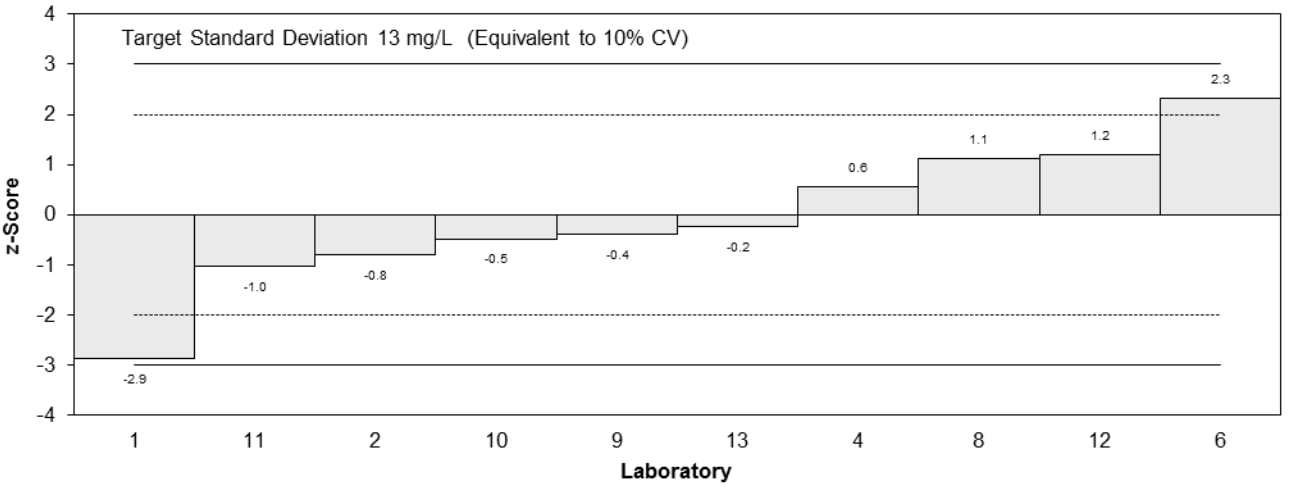
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	89	13	-2.88	-1.88
2	115	12	-0.80	-0.54
3	NT	NT		
4	132	10.4	0.56	0.40
5	NT	NT		
6	154	20	2.32	1.19
8	139	8.1	1.12	0.87
9	120	18.1	-0.40	-0.22
10	119	8.33	-0.48	-0.37
11	112	11.2	-1.04	-0.73
12	140	26	1.20	0.51
13	122	12	-0.24	-0.16
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	125	14
Spike	124	5
Homogeneity Value	110	17
Robust Average	125	14
Median	121	11
Mean	124	
N	10	
Max.	154	
Min.	89	
Robust SD	18	
Robust CV	14%	


Kernel Density
Density
Result
Results: S3 - TDS
Assigned Value = 125 ± 14 mg/L
Results (mg/L)
Laboratory
1 11 2 10 9 13 4 8 12 6 14 15 16 17 3 5 7 Md R.A. H.V. S.V.


z-Scores: S3 - TDS
Target Standard Deviation 13 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
1 11 2 10 9 13 4 8 12 6
-2.9 -1.0 -0.8 -0.5 -0.4 -0.2 0.6 1.1 1.2 2.3

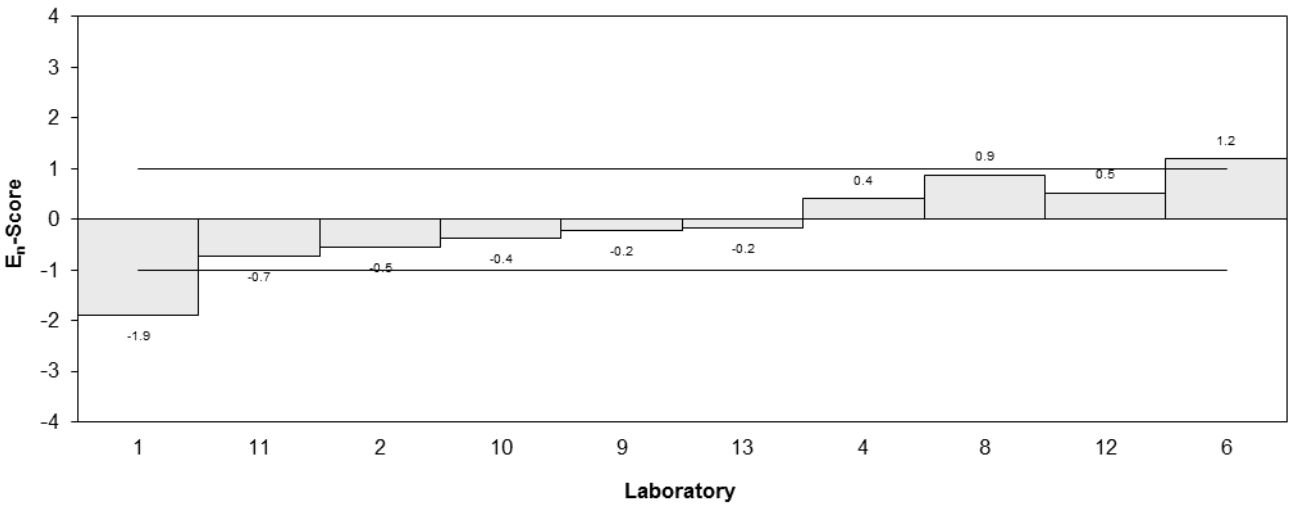

En-Scores: S3 - TDS
En-Score
Laboratory
1 11 2 10 9 13 4 8 12 6
-1.9 -0.7 -0.5 -0.4 -0.2 -0.2 0.4 0.9 0.5 1.2

Figure 24

Table 26

Sample Details

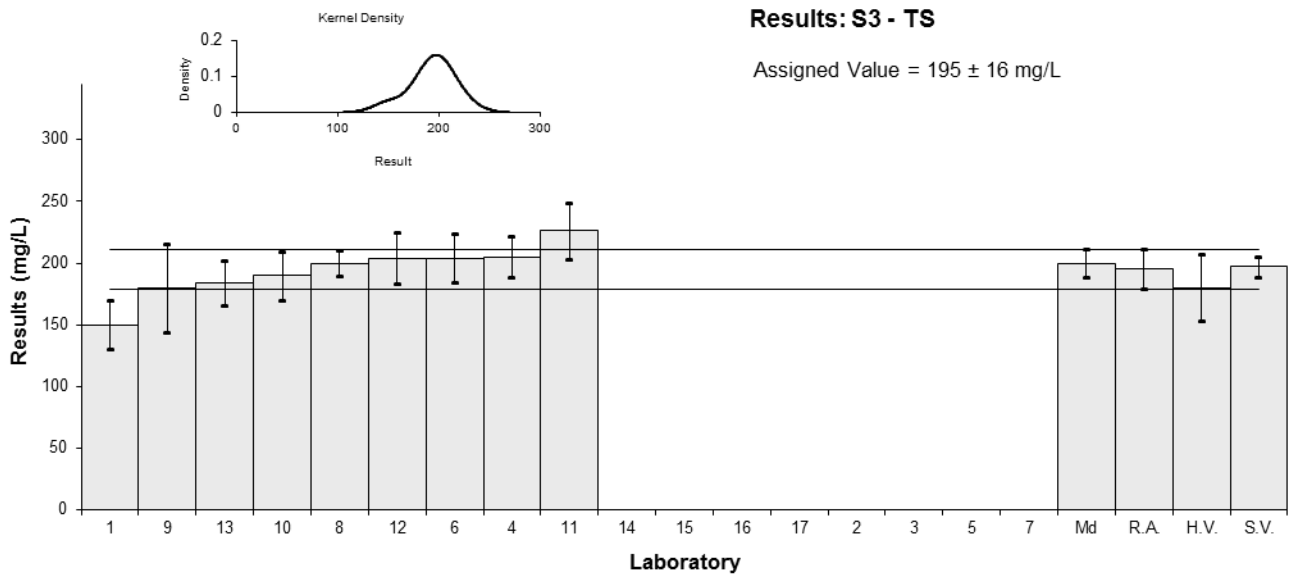
Sample No.	S3
Matrix.	Potable Water
Analyte.	TS
Units	mg/L

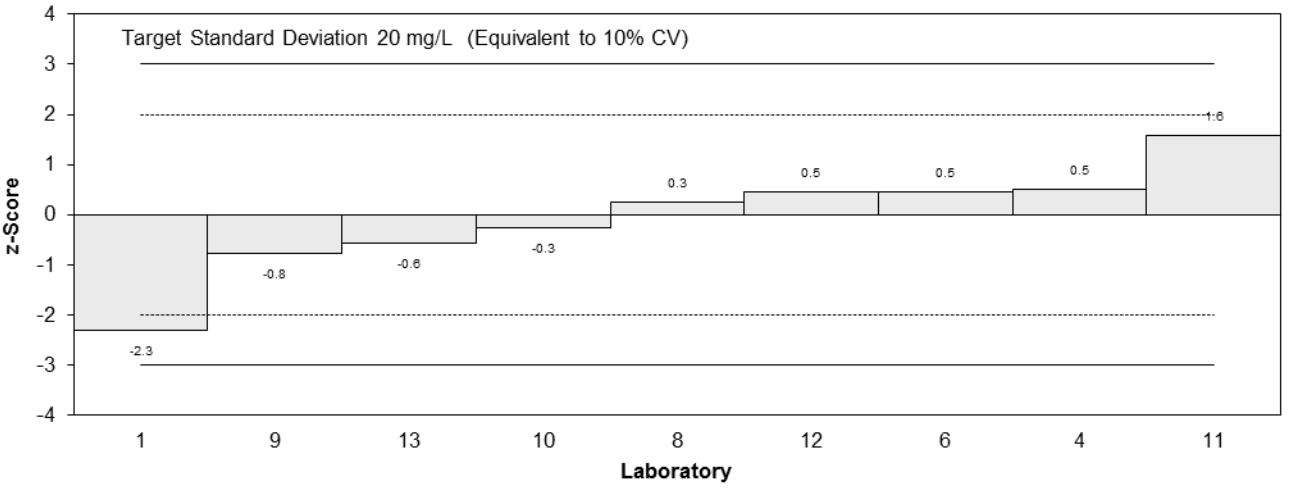
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	150	20	-2.31	-1.76
2	NT	NT		
3	NT	NT		
4	205	16.5	0.51	0.44
5	NT	NT		
6	204	20	0.46	0.35
8	200	10.2	0.26	0.26
9	180	36	-0.77	-0.38
10	190	19.8	-0.26	-0.20
11	226	23	1.59	1.11
12	204	20.57	0.46	0.35
13	184	18	-0.56	-0.46
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	195	16
Spike	197	8
Homogeneity Value	180	27
Robust Average	195	16
Median	200	11
Mean	194	
N	9	
Max.	226	
Min.	150	
Robust SD	19	
Robust CV	9.7%	


Kernel Density
Density
Result
Results: S3 - TS
Assigned Value = 195 ± 16 mg/L
Results (mg/L)
Laboratory
1 9 13 10 8 12 6 4 11 14 15 16 17 2 3 5 7 Md R.A. H.V. S.V.


z-Scores: S3 - TS
Target Standard Deviation 20 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
1 9 13 10 8 12 6 4 11
-2.3
-0.8
-0.6
-0.3
0.3
0.5
0.5
0.5
1.6

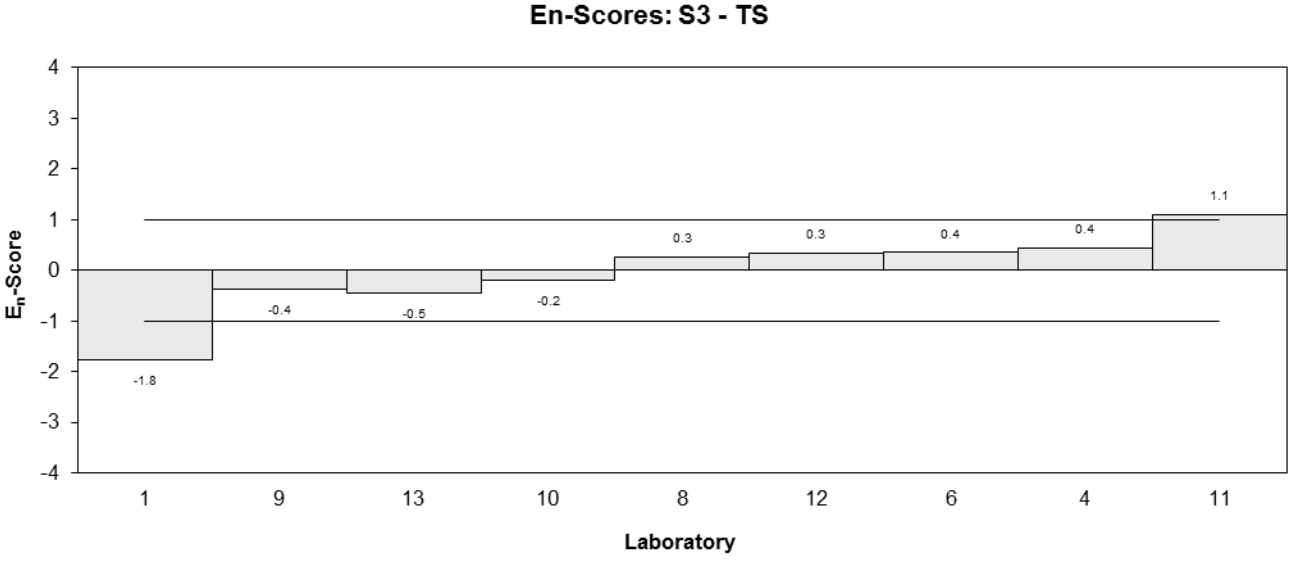

En-Scores: S3 - TS
En-Score
Laboratory
1 9 13 10 8 12 6 4 11
-1.8
-0.4
-0.5
-0.2
0.3
0.3
0.4
0.4
1.1

Figure 25

Table 27

Sample Details

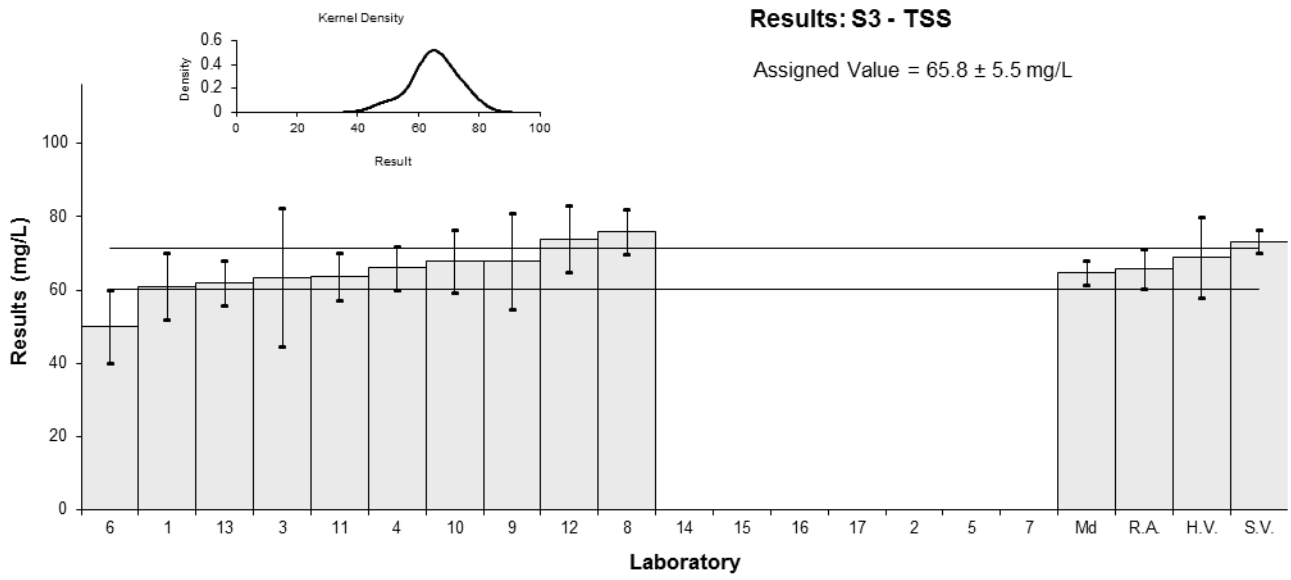
Sample No.	S3
Matrix.	Potable Water
Analyte.	TSS
Units	mg/L

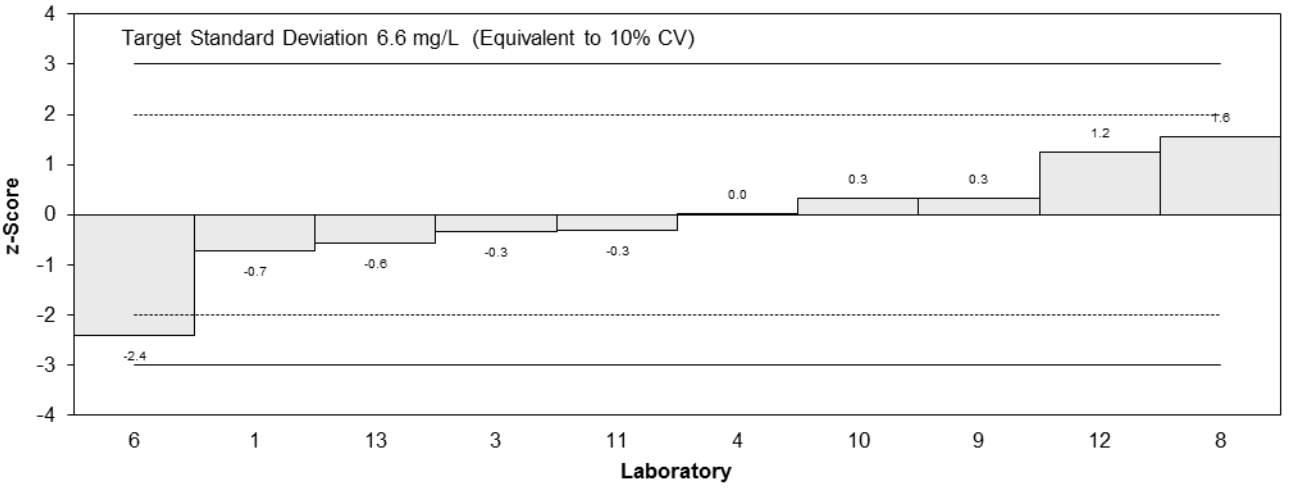
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	61	9	-0.73	-0.46
2	NT	NT		
3	63.5	19.0	-0.35	-0.12
4	66	5.9	0.03	0.02
5	NT	NT		
6	50	10	-2.40	-1.38
8	76	6.2	1.55	1.23
9	68	13.1	0.33	0.15
10	68.0	8.57	0.33	0.22
11	63.7	6.4	-0.32	-0.25
12	74	9	1.25	0.78
13	62	6	-0.58	-0.47
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	65.8	5.5
Spike	73.2	3.1
Homogeneity Value	69	11
Robust Average	65.8	5.5
Median	64.9	3.3
Mean	65.2	
N	10	
Max.	76	
Min.	50	
Robust SD	6.9	
Robust CV	10%	


Kernel Density
Density
Result
Results: S3 - TSS
Assigned Value = 65.8 ± 5.5 mg/L
Results (mg/L)
Laboratory
6 1 13 3 11 4 10 9 12 8 14 15 16 17 2 5 7 Md R.A. H.V. S.V.


z-Scores: S3 - TSS
Target Standard Deviation 6.6 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
6 1 13 3 11 4 10 9 12 8
-2.4 -0.7 -0.6 -0.3 -0.3 0.0 0.3 0.3 1.2 1.6

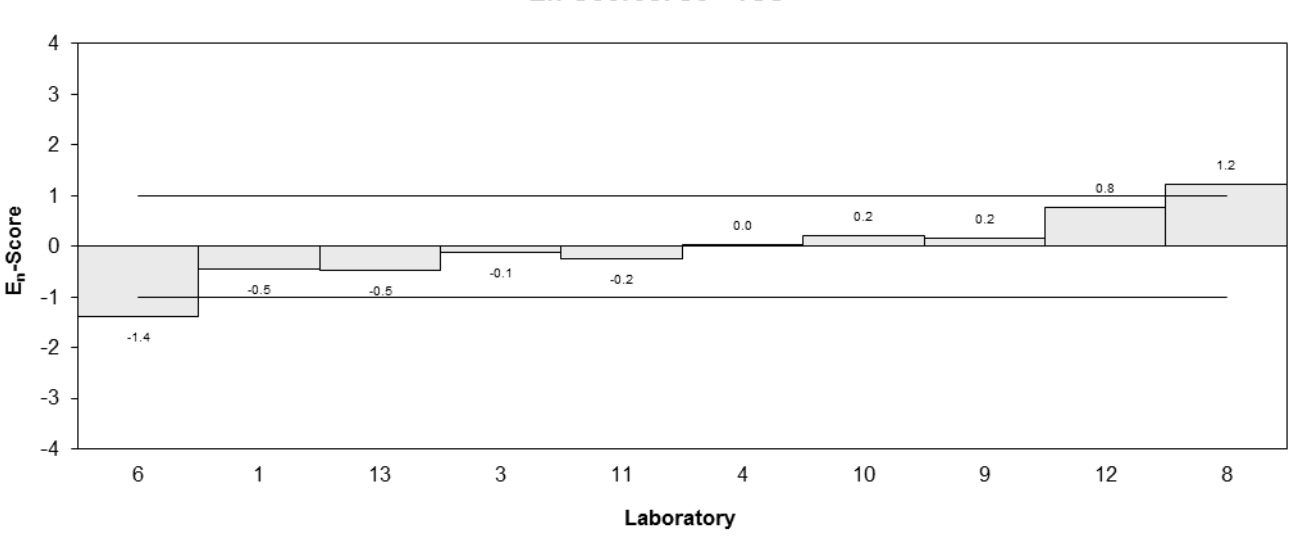

En-Scores: S3 - TSS
En-Score
Laboratory
6 1 13 3 11 4 10 9 12 8
-1.4 -0.5 -0.5 -0.1 -0.2 0.0 0.2 0.2 0.8 1.2

Figure 26

Table 28

Sample Details

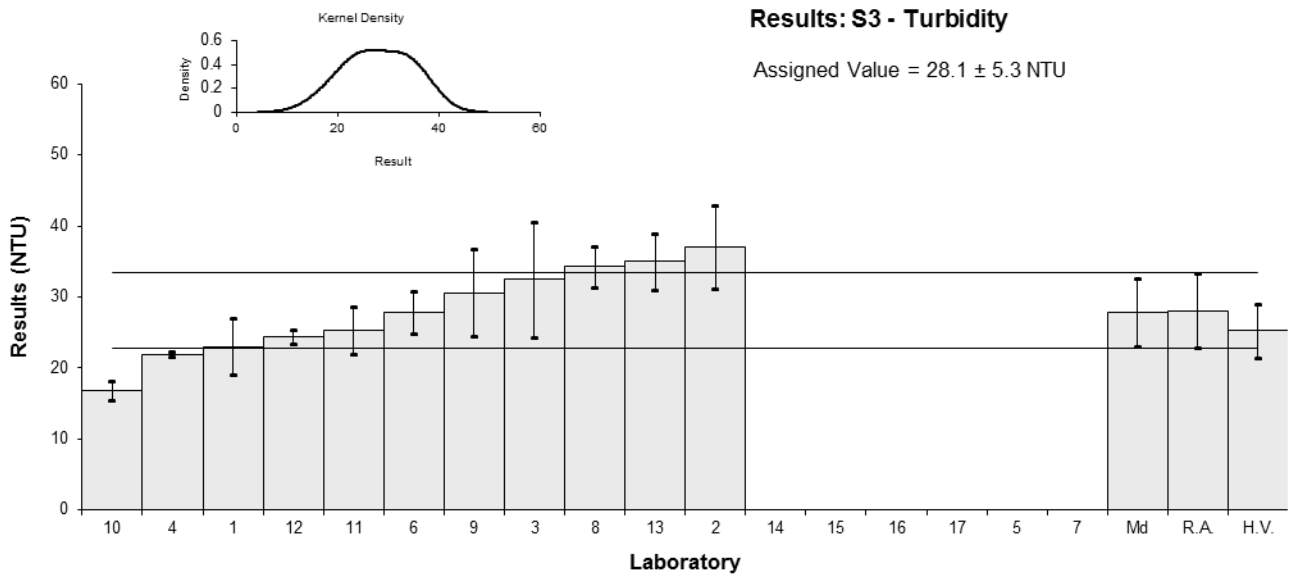
Sample No.	S3
Matrix.	Potable Water
Analyte.	Turbidity
Units	NTU

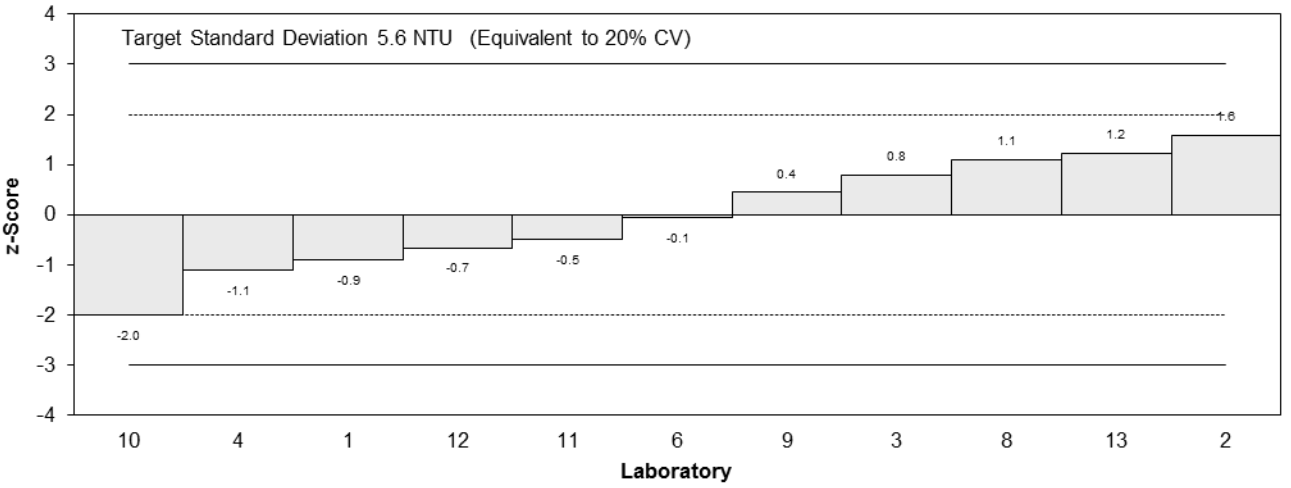
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	23	4	-0.91	-0.77
2	37	5.9	1.58	1.12
3	32.5	8.12	0.78	0.45
4	21.9	0.34	-1.10	-1.17
5	NT	NT		
6	27.8	3	-0.05	-0.05
8	34.3	2.9	1.10	1.03
9	30.6	6.12	0.44	0.31
10	16.9	1.35	-1.99	-2.05
11	25.3	3.3	-0.50	-0.45
12	24.4	1.070	-0.66	-0.68
13	35	4	1.23	1.04
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	28.1	5.3
Spike	Not Spiked	
Homogeneity Value	25.3	3.8
Robust Average	28.1	5.3
Median	27.8	4.8
Mean	28.1	
N	11	
Max.	37	
Min.	16.9	
Robust SD	7.1	
Robust CV	25%	


Kernel Density
Density
Result
Results: S3 - Turbidity
Assigned Value = 28.1 ± 5.3 NTU
Results (NTU)
Laboratory
10 4 1 12 11 6 9 3 8 13 2 14 15 16 17 5 7 Md R.A. H.V.


z-Scores: S3 - Turbidity
Target Standard Deviation 5.6 NTU (Equivalent to 20% CV)
z-Score
Laboratory
10 4 1 12 11 6 9 3 8 13 2
-2.0 -1.1 -0.9 -0.7 -0.5 -0.1 0.4 0.8 1.1 1.2 1.6

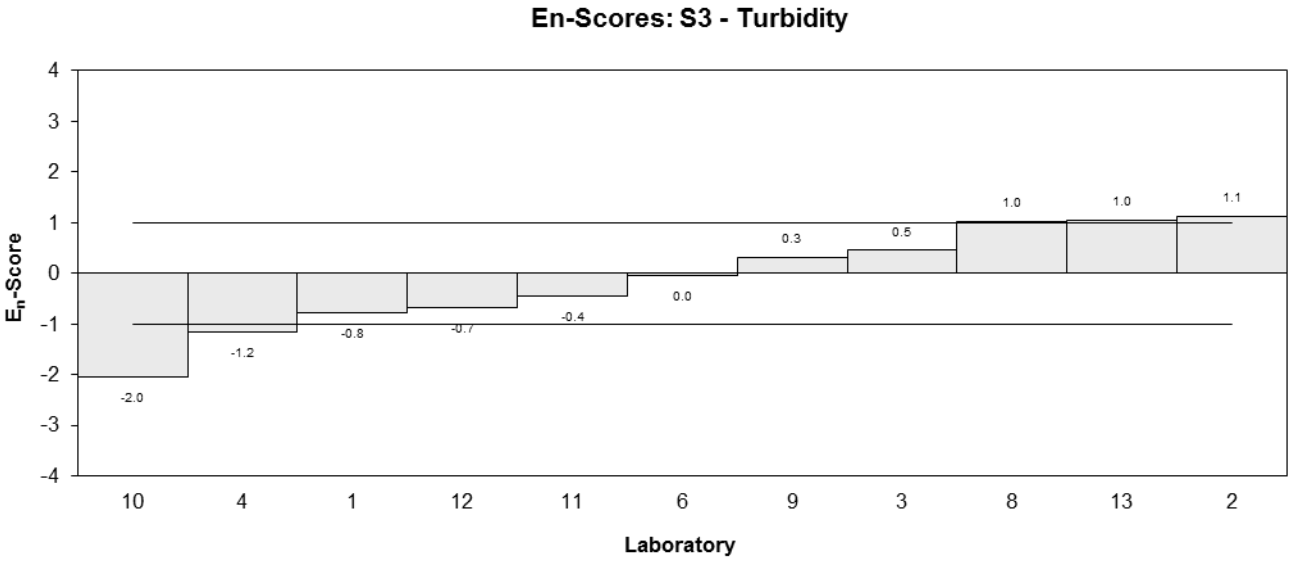

En-Scores: S3 - Turbidity
En-Score
Laboratory
10 4 1 12 11 6 9 3 8 13 2
-2.0 -1.2 -0.8 -0.7 -0.4 0.0 0.3 0.5 1.0 1.0 1.1

Figure 27

7 DISCUSSION OF RESULTS

7.1 Assigned Value and Traceability

Assigned Value were the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'.[6] Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value.[6] Appendix 3 sets out the calculation of the robust average and assigned value for Chloride in Sample S1 and its associated uncertainty.

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

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

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

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 311 numerical results, 304 (98%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0% to 100% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 1.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias and top down approach using only the reproducibility from inter-laboratory comparison studies.[9 – 15]

Proficiency tests allow a check of participants' uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 27).). In this study the reported expanded measurement uncertainty has been over-estimated in some cases (e.g. Lab 8 for NOx in S1) or under-estimated (e.g. Lab 14 for bromide in S1). As a simple rule of thumb, when the uncertainty estimate is smaller than the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be viewed as suspect.

Double counting the precision uncertainty components and overestimation of the laboratory or method bias are the most common errors seen in the laboratories' estimated uncertainty budgets. According to General Accreditation Guidance, Estimating and reporting measurement uncertainty of chemical test results[12] and to NORDTEST TR 537 [10] the most common experimental data used for estimating the precision component for the measurement uncertainty calculation in the top down approach are from:

- Stable control samples that cover the whole analytical process (including extraction) and **have a matrix similar** to the samples; **or**

- Stable control samples **and** duplicate analyses if control samples do not cover whole analytical process (e.g. the control sample is a synthetic sample- we have to take into consideration uncertainties arising from different matrices); **or**
- When control samples are not stable, from analysis of natural duplicates (gives within-day variation for sampling and measurement) and long-term uncertainty component from the variation in the instrument calibration ; **or**
- Replicate analyses performed on the same sample at different times to obtain estimates of intermediate precision; within-batch replication provides estimates of repeatability only.

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

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[10, 12] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Some laboratories may need to reassess their procedure for estimating measurement uncertainty. Laboratory 8 reported and estimated uncertainty for the measurement of NOx in S1 which was as large as the result itself.

Laboratory 14 estimated an uncertainty of 0 for its measurement results for P, bromide and fluoride. A measurement made without an associated uncertainty does not exist.

Laboratories 4 and 15 attached an estimate of the expanded measurement uncertainty to a P result reported as less than their limit of detection. An estimate of uncertainty expressed as a numerical value cannot be attached to a result expressed as a range.[9]

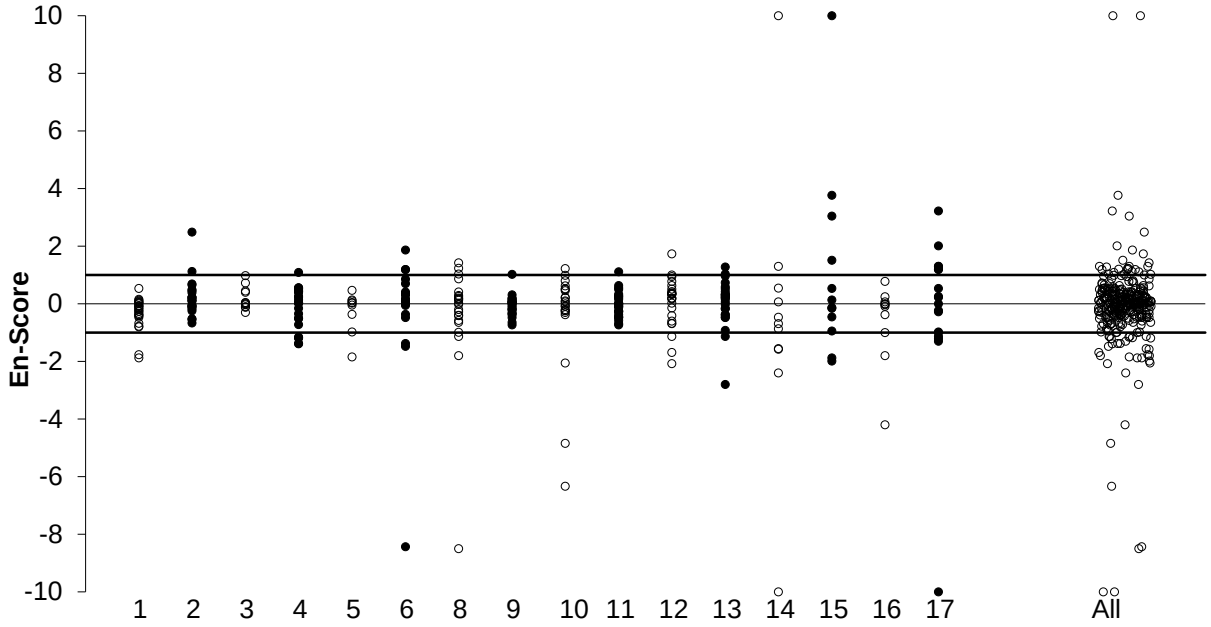
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 18.44 ± 3.42 mg/L,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

7.3 E_n-score

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

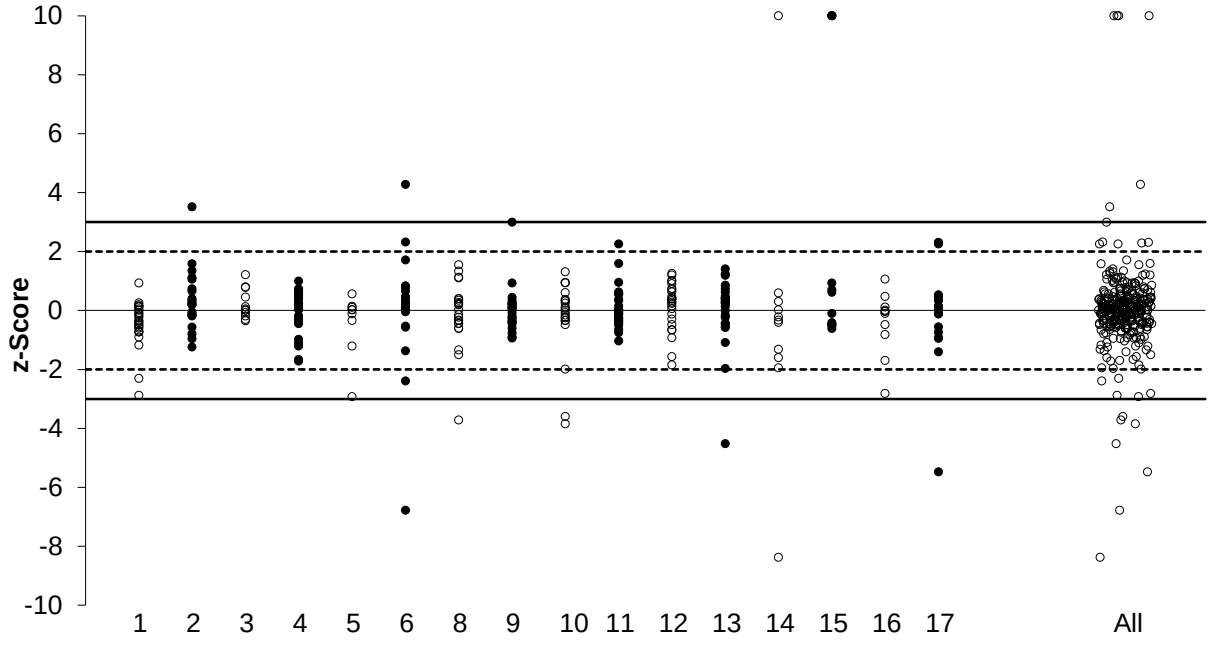
The dispersal of participants' E_n-scores is graphically presented in Figure 28. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 311 results for which E_n-scores were calculated, 248 (80%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.



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

Figure 28 E_n-Score Dispersal by Laboratory



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

Figure 29 z-Score Dispersal by Laboratory

7.4 z-Score

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

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

The between laboratories coefficient of variation predicted by the Thompson equation[7] and the between laboratories coefficient of variation resulted in this study are presented for comparison in Table 29.

The dispersal of participants' z-scores is presented in Figure 29 (by laboratory code) and in Figure 30 (by test). Of 311 results for which z-scores were calculated, 287 (92%) returned a satisfactory score of $|z| \leq 2.0$ and 11 (4%) were questionable with a score of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

Laboratories **3, 4** and **12** returned satisfactory z-scores for all analytes reported.

Table 29 Between Laboratories CV of this study, Thompson CV and Set Target CV

Sample	Test	Assigned value (mg/L)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as CV)
S1	Ammonia-N	0.465	11%	18%	15%
S1	Bromide	0.131	30%	22%	20%
S1	Chloride	41.6	6.7%	9.1%	10%
S1	Dissolved Organic Carbon	4.71	12%	13%	10%
S1	Fluoride	1.47	6.8%	15%	10%
S1	Iodide	0.099	26%	22%	20%
S1	NOx	0.348	8.8%	19%	15%
S1	Orthophosphate-P	0.0732	7.4%	22%	10%
S1	Sulphate	14.9	8.1%	11%	10%
S1	Total Dissolved Nitrogen	1.08	9.3%	16%	10%
S1	Total Dissolved Phosphorus	0.080	18%	22%	20%
S2	Alkalinity	180	4.4%	7.3%	10%
S2	B	0.455	8.6%	18%	10%
S2	Ca	17.6	3.8%	10%	10%
S2	EC	513 µS/cm	3.1%	6.3%	5%
S2	K	3.85	6.1%	13%	10%
S2	Mg	7.33	4.9%	12%	10%
S2	Na	82.8	2.9%	8.2%	10%
S2	P	0.079	18%	22%	15%
S2	pH	9.80	1.2%	11%	3.5%
S2	Silica	3.35	10%	13%	10%
S2	Total Hardness	73.2	6.4%	8.4%	10%
S3	TDS	125	14%	7.7%	10%
S3	TS	195	9.7%	7.2%	10%
S3	TSS	65.8	10%	8.5%	10%
S3	Turbidity	28.1 NTU	25%	9.7%	20%

*Robust between Laboratories CV with outliers removed

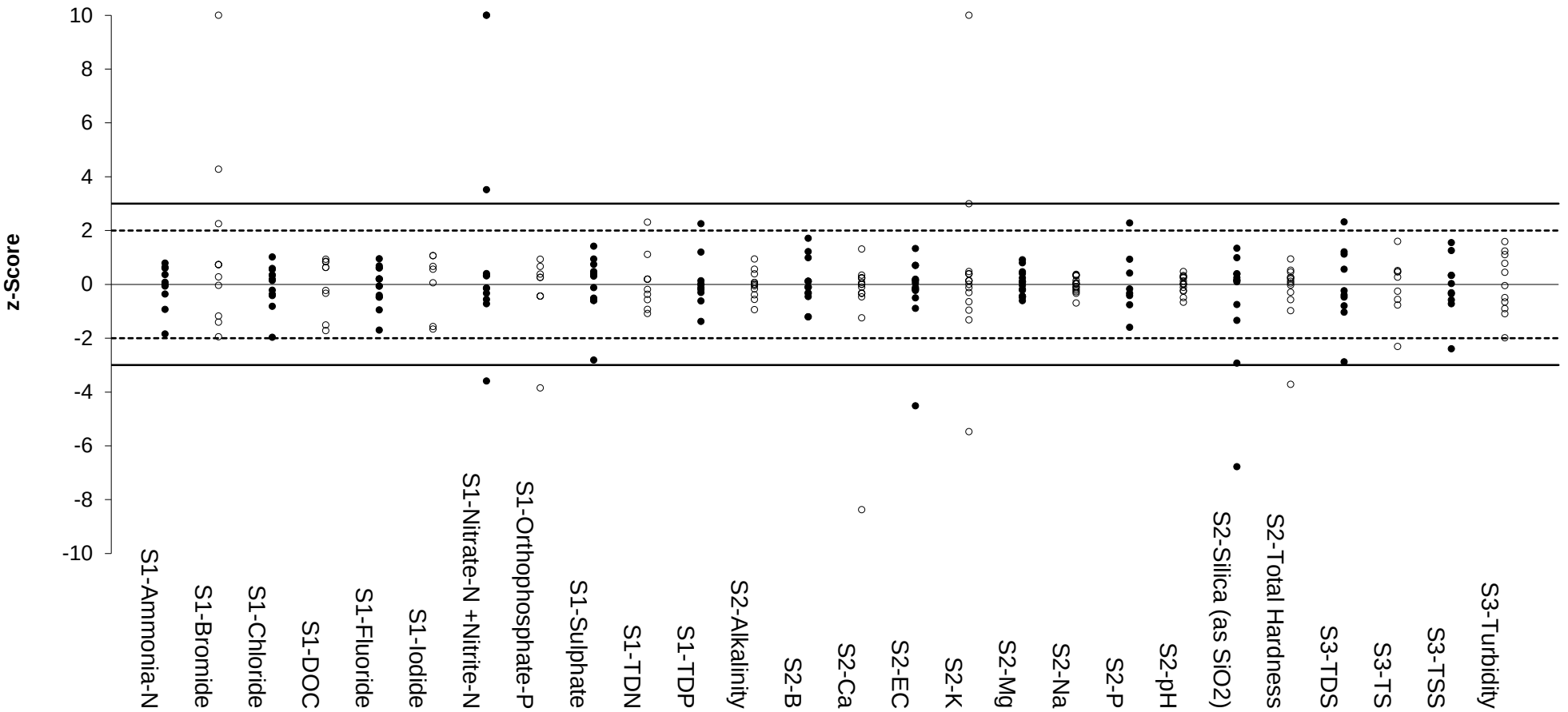


Figure 30 z-Score Dispersal by Test

Table 30 Summary of Participants' Results and Performance for S1

Lab Code	Ammonia-N (mg/L)	Bromide (mg/L)	Chloride (mg/L)	DOC (mg/L)	Fluoride (mg/L)	Iodide (mg/L)	NOx (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
A.V.	0.465	0.131	41.6	4.71	1.47	0.099	0.348	0.0732	14.9	1.08	0.080
H.V.	0.477	0.130	41.3	4.77	1.33	0.097	0.307	0.071	13.3	1.10	0.074
S.V.	0.459	0.128	41.1	4.37	1.40	0.096	0.310	0.045	14.0	Not Spiked	0.035
1	0.46	0.10	40	4.6	1.4	0.10	0.31	0.080	14	1.1	0.082
2	NT	0.15	43	NT	1.5	0.12	0.531	0.078	15.5	1.2	0.077
3	NT	NT	NT	NT	1.46	NT	NT	NT	NT	NT	NT
4	0.509	0.150	42.4	3.9	1.57	0.066	0.369	0.075	15.6	1.06	0.075
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	0.520	0.243	NT	5.1	NT	0.112	NT	NT	14.1	1.018	0.058
8	0.44	NT	43	4	1.5	NT	0.34	0.07	14	1.1	0.07
9	0.47	NR	40	NR	1.5	NR	0.33	0.075	14	1.1	0.08
10	0.507	NT	40.7	4.55	1.46	NT	0.160	0.045	16.3	NT	NT
11	0.49	0.19	43.9	5.0	1.61	0.11	0.34	0.07	15.4	1.04	0.08
12	0.336	0.138	45.8	5	1.4	0.068	0.365	0.076	16	0.98	0.078
13	0.464	0.15	33.4	5.11	1.56	NT	0.364	0.070	17.0	0.962	0.099
14	NT	0.08	44.07	NT	1.41	NT	1.31	NT	15.34	NT	NT
15	NR	4.47	39.87	5.15	1.56	NR	1.51	NR	14.13	NR	NR
16	NR	0.13	38.2	NR	1.22	0.12	NR	NR	10.7	NR	NR
17	0.400	0.094	42.2	NT	1.33	NT	0.319	NT	14.7	1.33	0.116

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, S.V. = Spike Value

Table 31 Summary of Participants' Results and Performance for S2 and S3

Lab Code	S2-Alkalinity (mg/L)	S2-B (mg/L)	S2-Ca (mg/L)	S2-EC (µS/cm)	S2-K (mg/L)	S2-Mg (mg/L)	S2-Na (mg/L)	S2-P (mg/L)	S2-pH	S2-Silica (mg/L)	S2-Total Hardness (mg/L)	S3-TDS (mg/L)	S3-TS (mg/L)	S3-TSS (mg/L)	S3-Turbidity (NTU)
A.V.	180	0.455	17.6	513	3.85	7.33	82.8	0.079	9.80	3.35	73.2	125	195	65.8	28.1
H.V.	174	0.462	16.2	500	3.92	7.54	84	0.0791	9.80	3.14	74	110	180	69	25.3
S.V.	181	0.461	17.7	Not Spiked	3.83	7.30	84.0	0.076	Not Spiked	3.67	Not Spiked	124	197	73.2	Not Spiked
1	170	0.46	17	500	3.8	7.2	77	0.074	9.8	3.4	75	89	150	61	23
2	179	0.45	15.4	518	3.48	7.5	81.5	0.077	9.9	3.8	69	115	NT	NT	37
3	180	0.51	17.6	508	3.73	7.92	83.2	<0.02	9.84	NT	76.5	NT	NT	63.5	32.5
4	181	0.4	17	514	4	7	80	<1	9.88	3.68	66	132	205	66	21.9
5	190	0.4	17	510	3.9	7.4	83	NT	9.81	2.37	NT	NT	NT	NT	NT
6	180	0.533	17.7	517	3.9	7.4	85.5	<0.1	9.89	1.08	74.7	154	204	50	27.8
8	187	0.44	18	547	4	7	83	<1	9.72	2.9	46	139	200	76	34.3
9	163	0.45	18	490	5	7	81	0.09	9.71	3.38	74	120	180	68	30.6
10	197	0.460	19.9	509	3.85	7.38	85.9	0.075	9.91	3.43	80.1	119	190	68.0	16.9
11	173	0.45	17.4	507	3.6	7.3	80.5	0.07	9.8	3.4	73.5	112	226	63.7	25.3
12	181	0.5	18	531	4	8	84	<1	9.57	3.48	71	140	204	74	24.4
13	177	0.434	18.0	397	3.90	7.62	85.4	0.084	9.96	3.48	75	122	184	62	35
14	NT	0.44	2.85	NT	3.34	7.17	82.91	0.06	NT	NT	NT	NT	NT	NT	NT
15	NR	NR	16.78	531	7.82	6.88	82.0	<0.5	9.63	NR	NR	NT	NT	NT	NT
16	NR	0.46	17.6	NR	4.03	6.97	82.0	NR	NR	NR	73	NT	NT	NT	NT
17	180	NT	18.2	516	1.74	7.67	85.7	0.106	9.76	3.10	77	NT	NT	NT	NT

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, S.V. = Spike Value

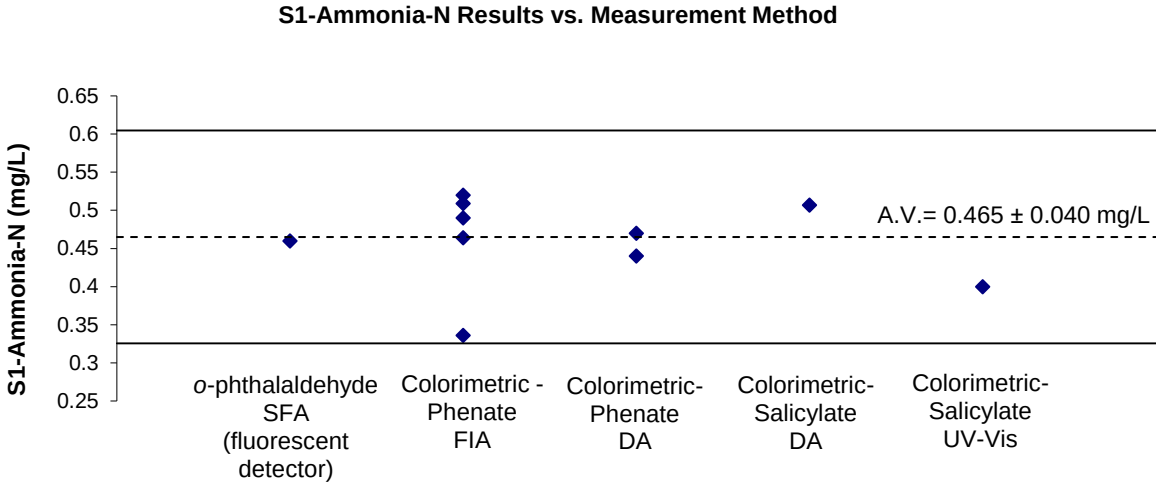
7.5 Participants' Results and Analytical Methods for Dissolved and Total Elements

A summary of participants' results and performance is presented in Tables 30 and 31 and in Figures 29 and 30.

Participants were asked to analyse samples S1, S2 and S3 using their normal test method. The measurement methods and instrumental techniques used are presented in Appendices 6, 7 and 8. .

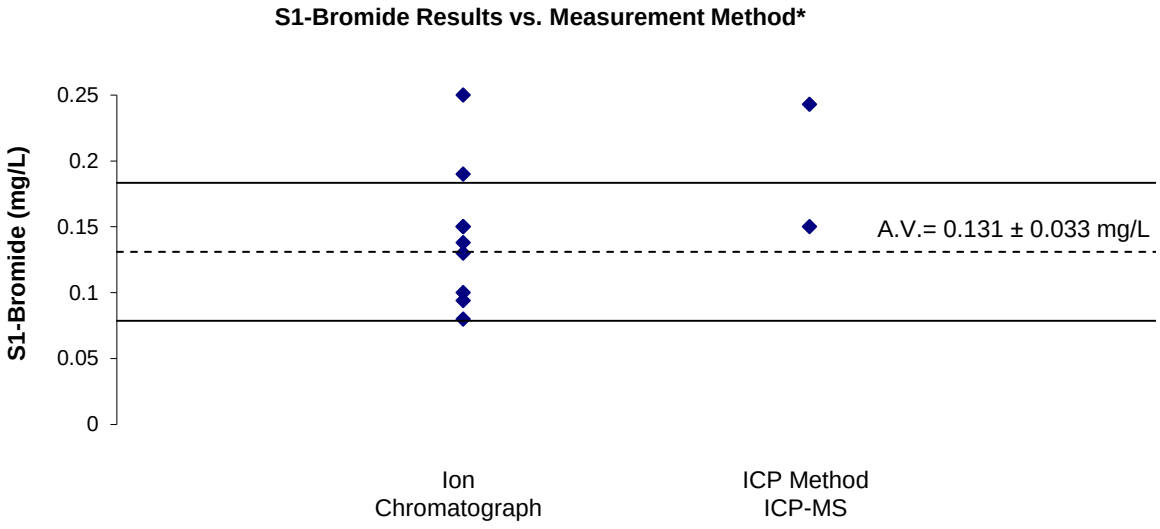
Individual Test Commentary

Ammonia-Nitrogen All results reported for NH_3-N returned satisfactory z-scores. Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination. One laboratory reported using UV-Vis and one used the *o*-phthalaldehyde method with SFA and fluorescent detector. Each of these methods produced comparable/satisfactory results (Figure 31).



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

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

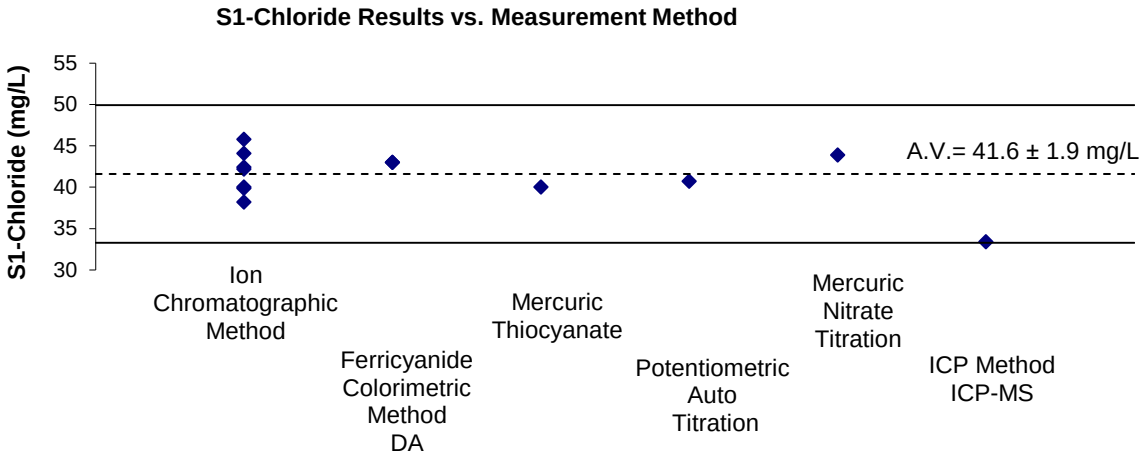


Horizontal lines on charts correspond to z-scores of 2 and -2.
*Result larger than 0.25 mg/L has been plotted as 0.25 mg/L.

Figure 32 S1-Bromide Results vs. Measurement Method

Bromide level in S1 was low (0.131 mg/L) which may have presented difficulties to participating laboratories. The between- laboratory CV was large at 30%. Ion chromatography was the method which the majority of laboratories chose to measure bromide. Two participants reported using the ICP method (Figure 32).

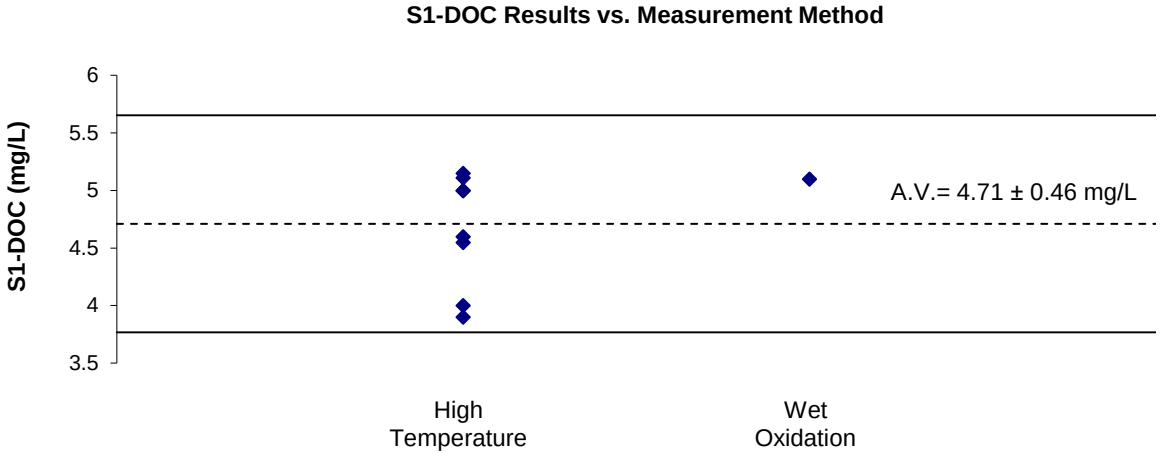
Chloride level in S1 was 41.6 mg/L. Participants used a wide variety of methods for chloride analysis in S1; all produced comparable results (Figure 33).



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

Figure 33 S1-Chloride Results vs. Measurement Method

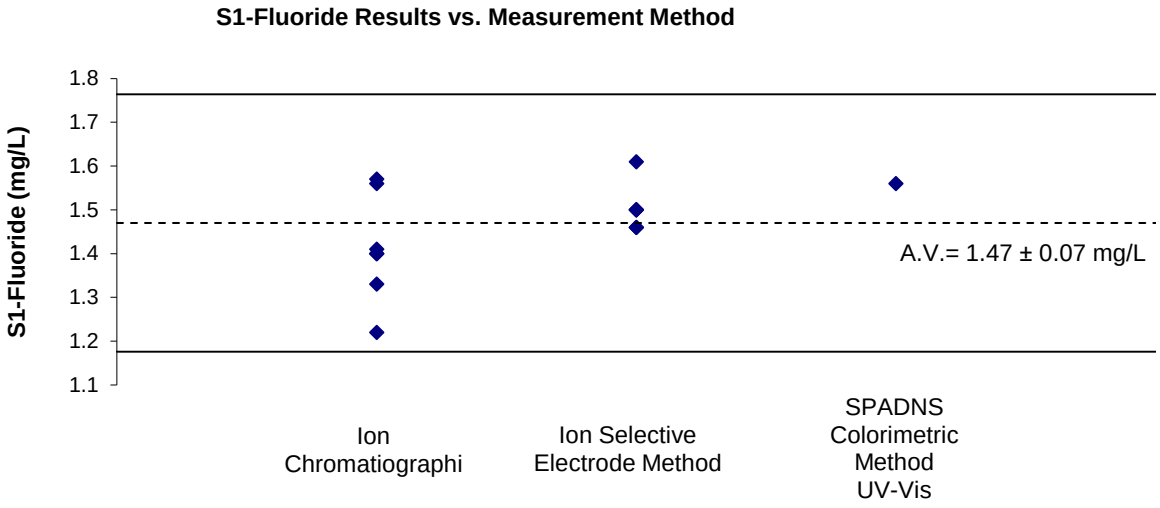
Dissolved Organic Carbon as dNPOC All DOC results were in agreement with each other. Participants used high temperature oxidation or wet oxidation; no significant difference was noticed between DOC results produced by these two methods (Figure 34).



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

Figure 34 S1-DOC Results vs. Measurement Method

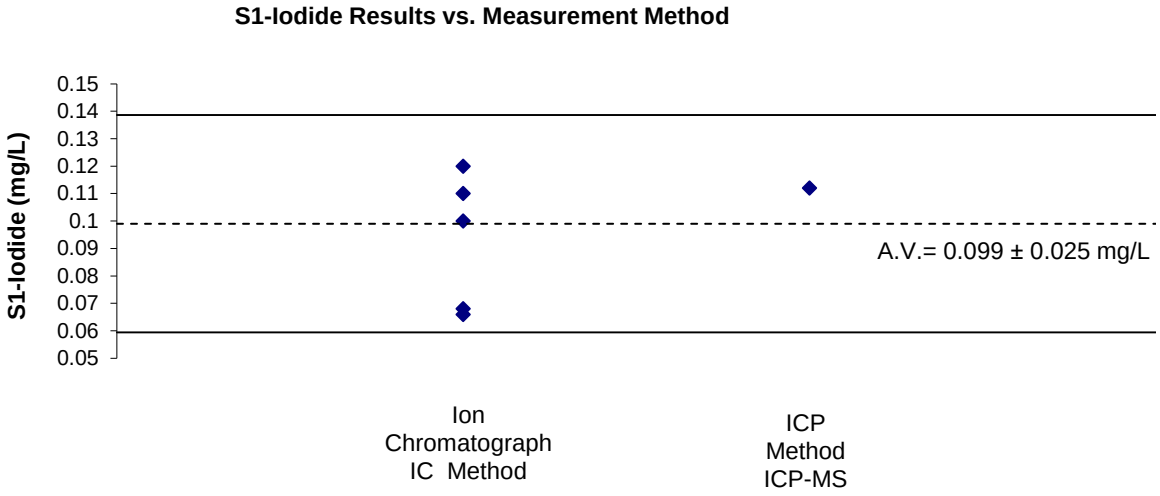
Fluoride Most participants used either the ion selective electrode method or ion chromatographic method. One laboratory used the SPADNS colorimetric method with UV-Vis determination (Figure 35).



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

Figure 35 S3-Fluoride Results vs. Measurement Method

Iodide level in S1 was 0.099 mg/L, which may explain the large between-laboratory coefficient of variation of 25%. One laboratory used ICP-MS for its iodide measurements (Figure 36).

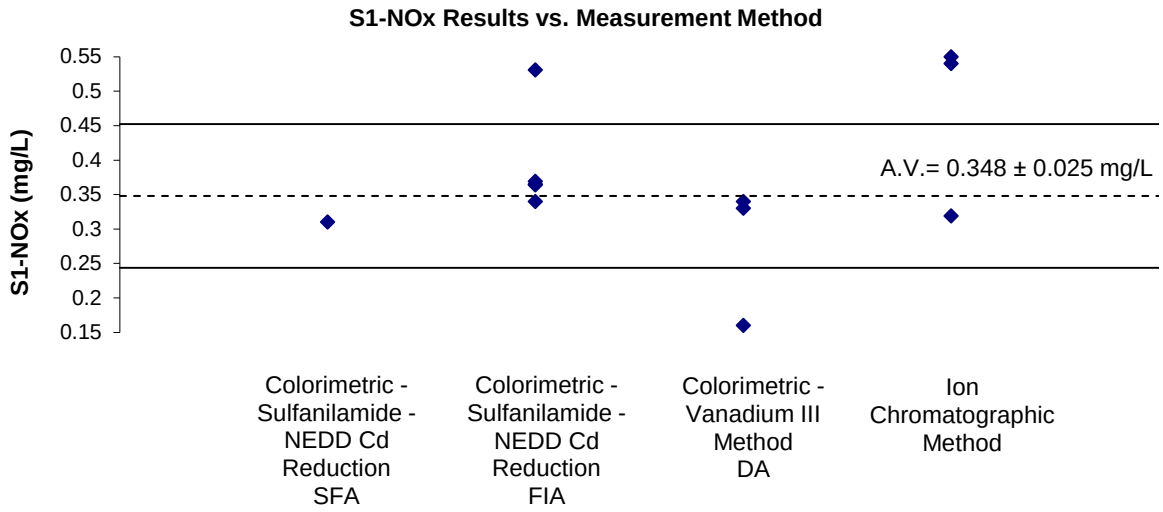


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 36 S3-Iodide Results vs. Measurement Method

Nitrate-Nitrogen + Nitrite-Nitrogen had the largest number of unsatisfactory results. Of 12 results reported for NOx, 4 returned unsatisfactory z-scores. Six participants used colorimetric-sulfanilamide-NEDD Cd reduction, three used the ion chromatographic method, and three the Vanadium III colorimetric method with DA. A plot of participants' results versus analytical method and instrumental technique used is presented in Figure 37.

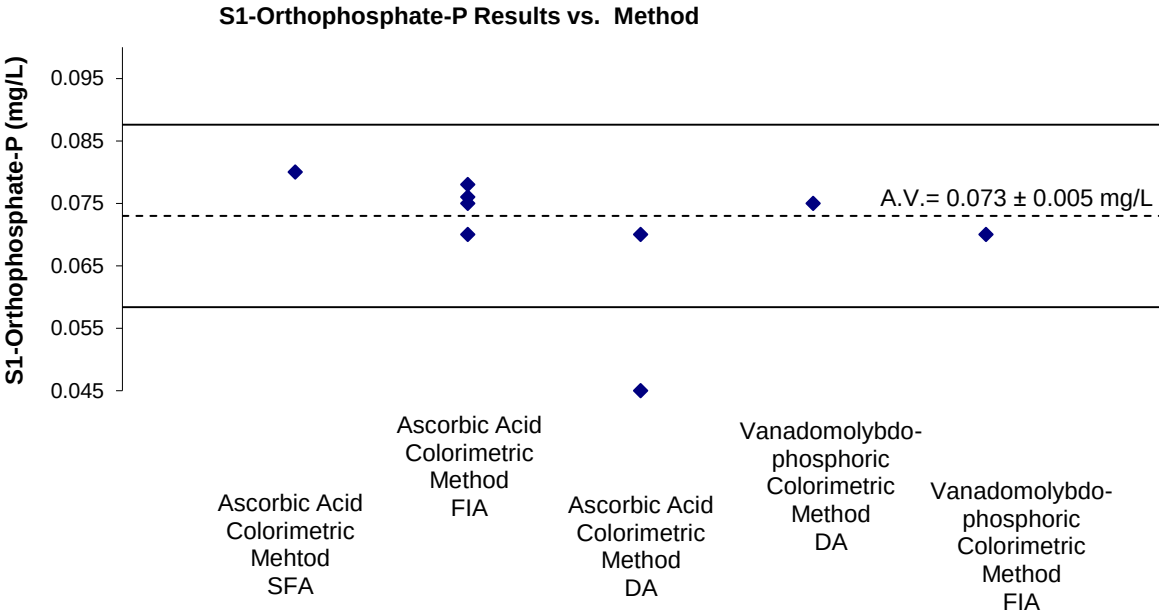
Laboratories 14 and 15 might have reported the nitrate-nitrogen + nitrite-nitrogen results as nitrate; the assigned value for NOx converted to NO_3 is 1.5 mg/L.



Horizontal lines on charts are the results correspond to z-scores of 2 and -2. *Laboratories 14 and 15 results have been plotted as 0.55 mg/L and 0.54 mg/L respectively.

Figure 37 S1-NOx Results vs. Measurement Method

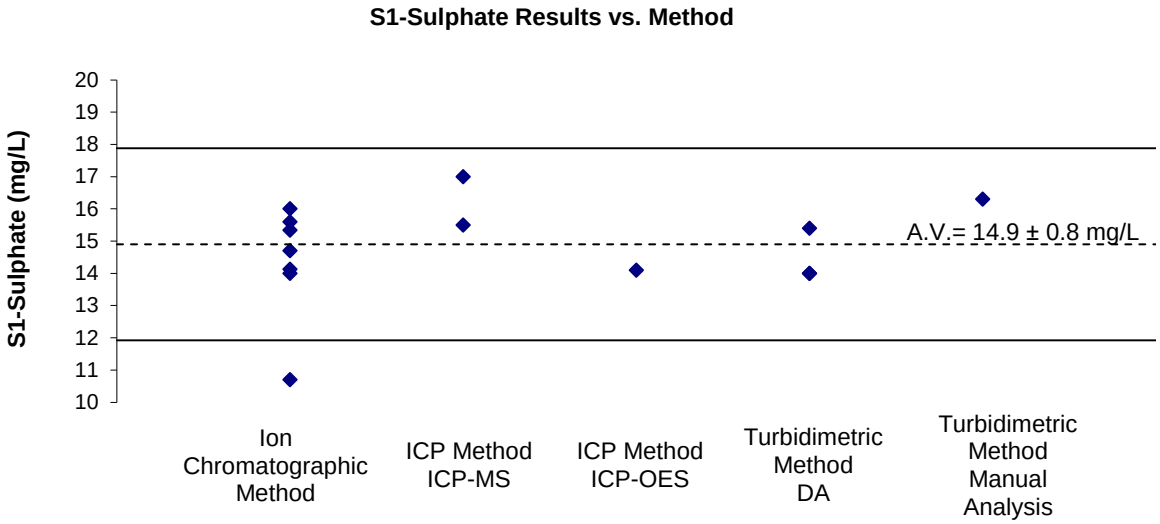
Orthophosphate-P Two participants reported using a vanadomolybdophosphoric method for orthophosphate-P measurements in S1; all other participants used ascorbic acid colorimetric method with FIA, SFA or DA determination (Figure 38). All results were in good agreement with each other, except for one.



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

Figure 38 S1-Orthophosphate-P Results vs. Method

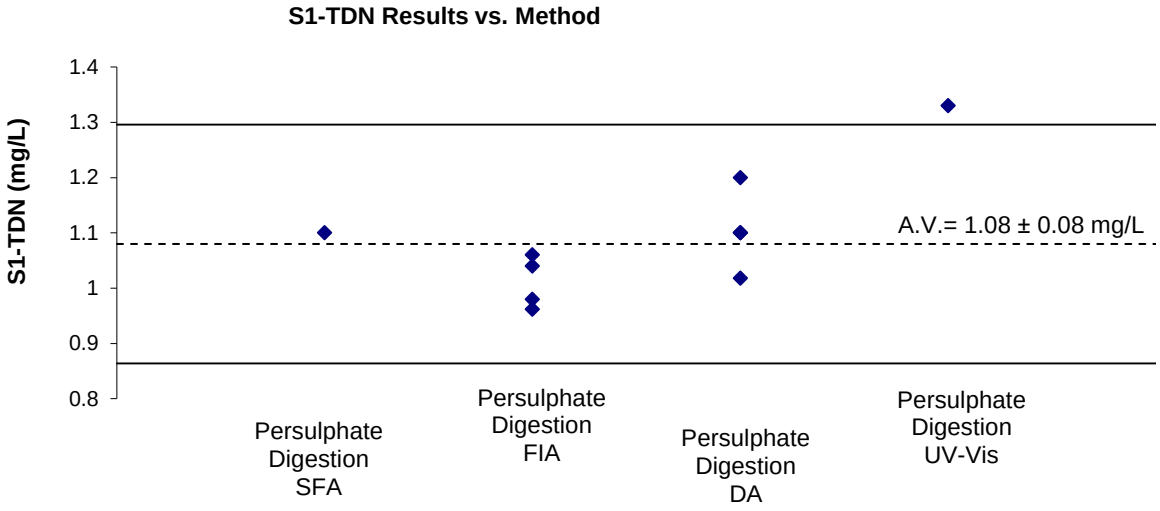
Sulphate Three participants reported using ICP-MS or ICP-OES for sulphate measurements in S1. Caution should be exercised when using the ICP method because it measures total S and not just S from sulphate compounds (Figure 39).



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

Figure 39 S3-Sulphate Results vs. Measurement Method

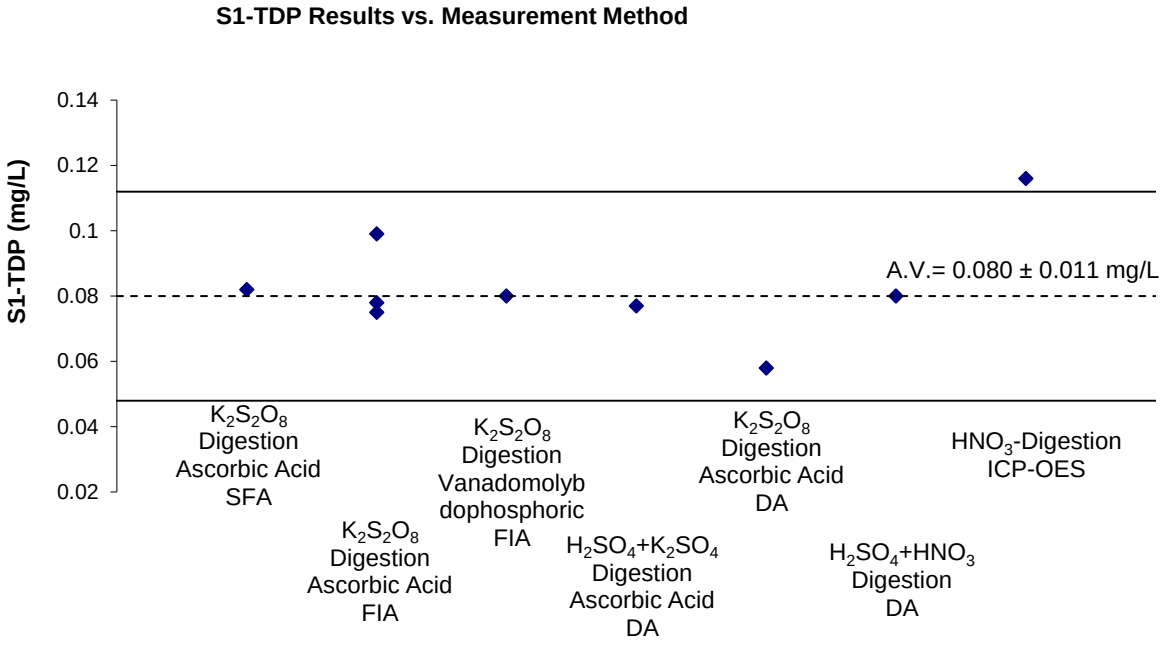
Total Dissolved Nitrogen With one exception, all reported results for TDN were in agreement with each other and with the robust average of 1.08 ± 0.08 mg/L. Figure 40 presents plots of participants' results vs the measurement method used for TDN determination in S1.



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

Figure 40 S1-TDN Results vs. Measurement Method

Total dissolved phosphorus level in S1 was low (0.080 mg/L) which may have presented difficulty to some laboratories. The reported results were variable with a high between- laboratory coefficient of variation (18%). Most laboratories used potassium persulphate for digestion and then measured the liberated orthophosphate colorimetrically by FIA or SFA. Nitric acid digestion was performed by one participant who also reported measuring TDP in the sample by ICP-OES (Figure 41).

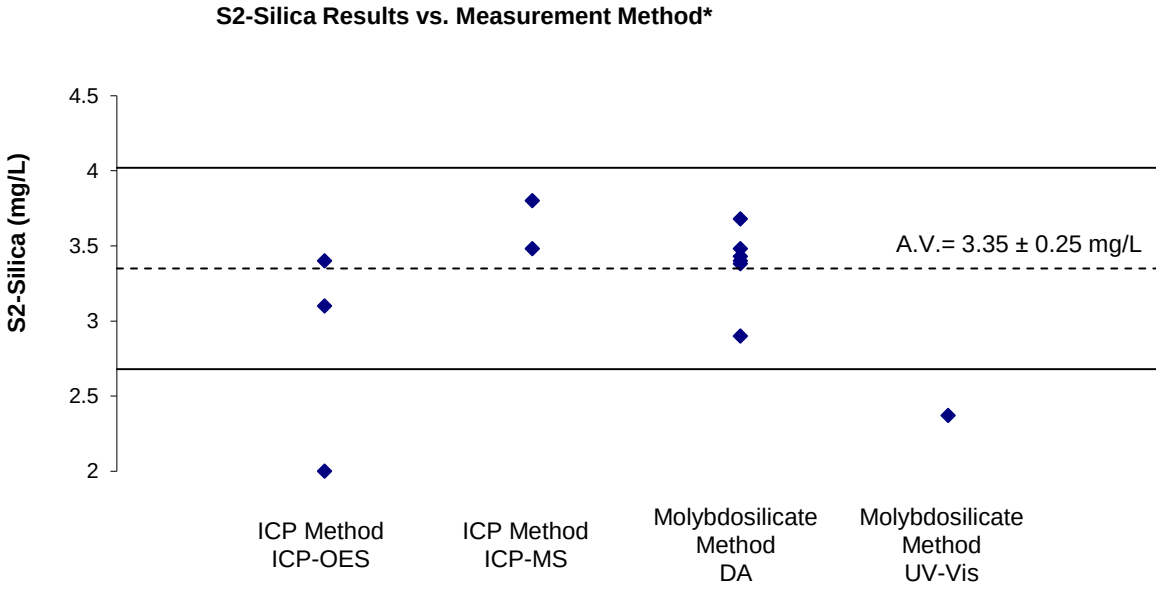


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 41 S1-TDP Results vs. Measurement Method

Alkalinity to pH 4.5 as ($CaCO_3$) did not present analytical difficulty to participants. All reported results returned satisfactory z-scores (Table 31).

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

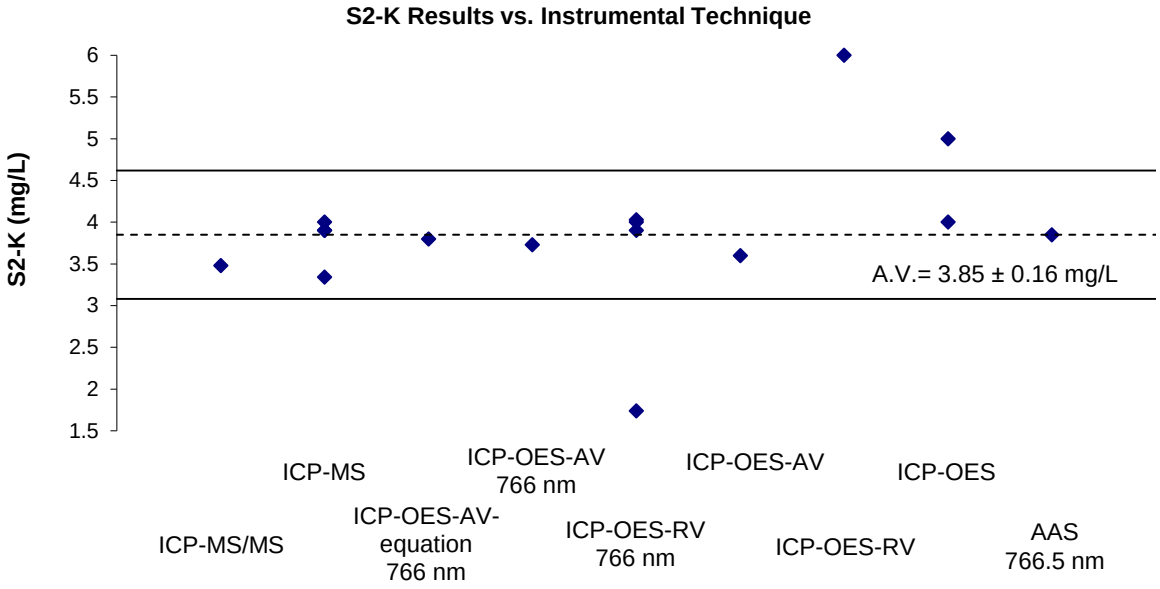


Horizontal lines on charts are the results correspond to z-scores of 2 and -2
*Result <2 mg/L has been plotted as 2 mg/L.

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

Laboratory 6 might have reported the Silica (as SiO2) result as Silicon (Si).

Potassium Of 17 results reported for K in S2, 14 returned satisfactory z-scores. Participants used a wide variety of instrumental techniques, which are presented in Figure 43.



Result >6 mg/L has been plotted as 6 mg/L

Figure 43 S2-K Results vs. Measurement Method

Sodium measurements in S2 did not present technical difficulty to participating laboratories. All reported results returned satisfactory z-scores (Figure 44).

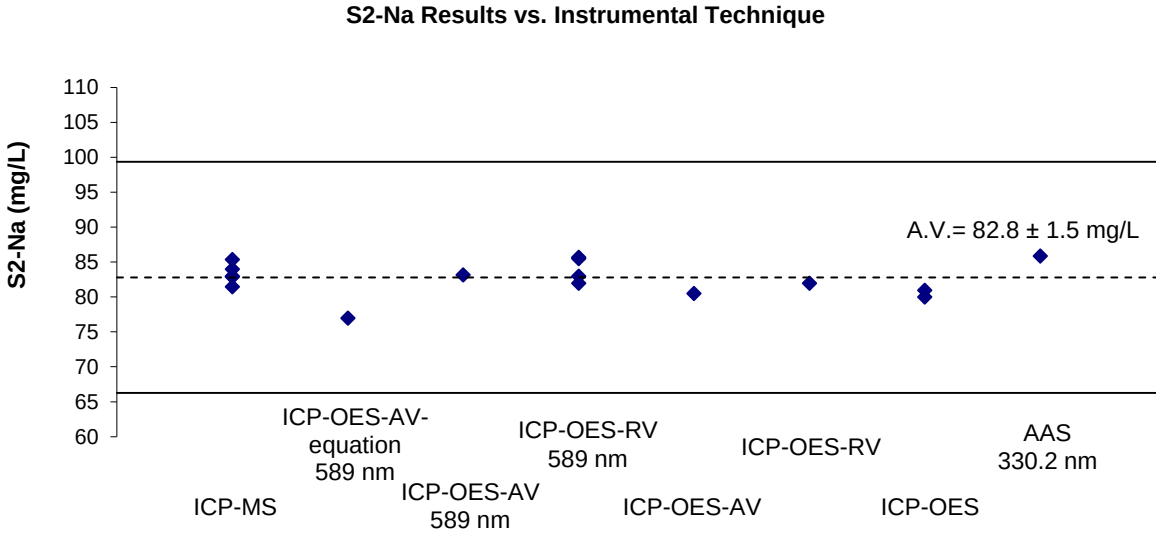


Figure 44 S2-Na Results vs. Measurement Method

7.6 Comparison with Previous NMI Proficiency Tests of Nutrients in Water

AQA 20-08 is the tenth NMI proficiency test of nutrients in water. On average, participants' performance in measuring nutrients, anions and physical tests in water has remained consistent over time with the percentage of satisfactory z-scores ranging from 91% to 96% Some laboratories are encountering difficulty in estimating the uncertainty of their

measurement results; the number of satisfactory E_n-scores decreased from 91% to 79%. (Figure 45).

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 can occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line are an indication of method or laboratory bias.

7.7 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 32).

Table 32 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	Spiked Sample
2	Spiked Sample
3	CRM
4	CRM – Choice Analytical High Purity Standards
5	CRM – Sigma Aldrich Alkalinity 500mg Caco3 /L Standard; CPA Chem Trace Metals CRM
6	CRM
7	CRM
8	Spiked Sample
9	CRM
10	Spiked Sample
11	CRM
12	RM
13	CRM – CWW-TM-A, B and C. Minerals 1 and 2
15	Internal QC sample for S1 and NIST SRM 1640a for S2
17	RM

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

> *'a reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures*'[16]

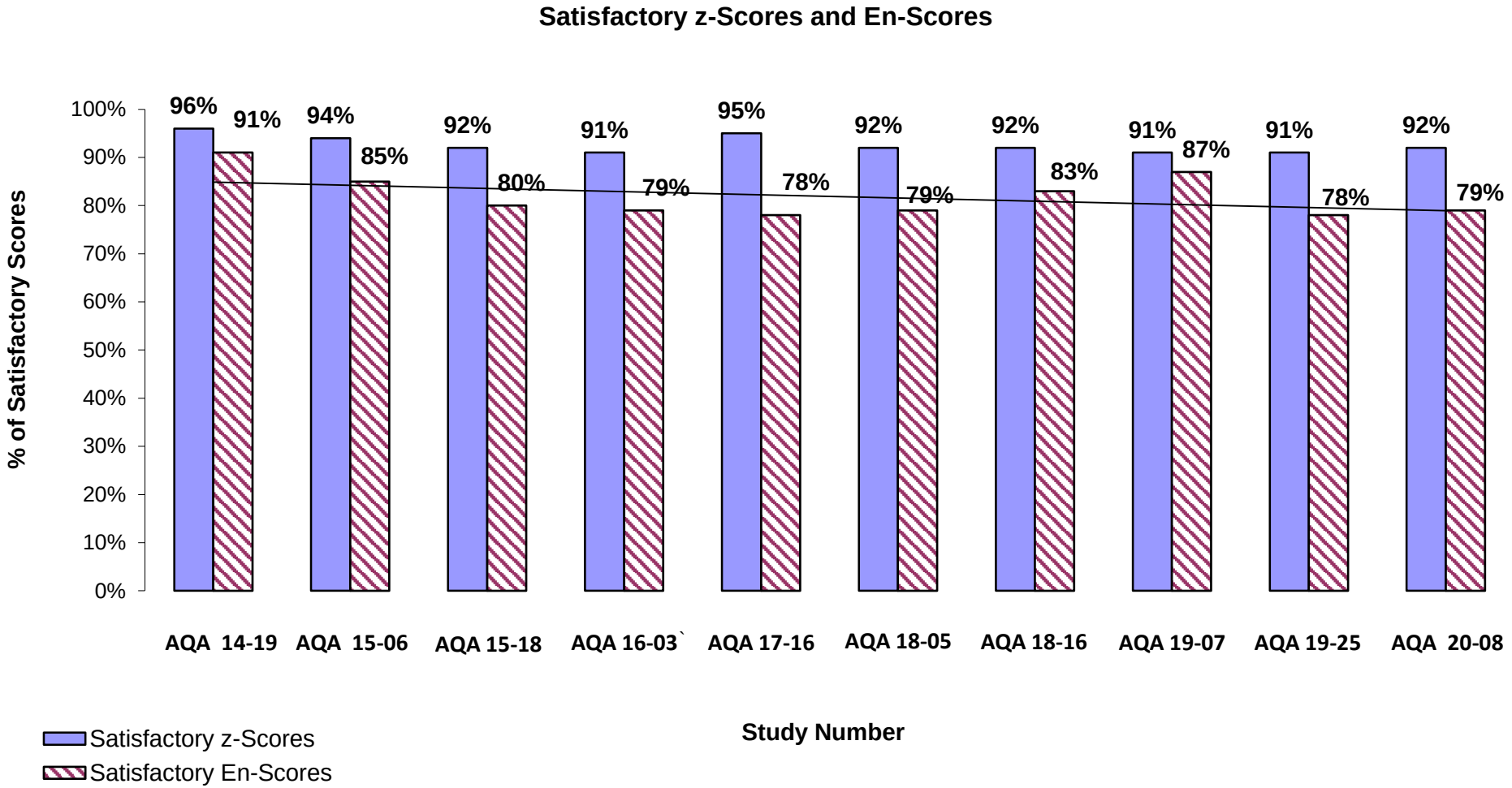


Figure 45 Participants' Performance in Nutrients and Anions in Water PT Studies over Time

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A 1.1 Sample Preparation

Sample S1 was prepared from approximately 10 L of potable water which was filtered and autoclaved. The water was further fortified for the analytes of interest, before mixing and dispensing into 200 mL portions.

Sample S2 was prepared from approximately 30 L of potable water which was fortified for the analytes of interest. The sample was then allowed to mix thoroughly prior to being bottled into 400 mL portions.

Sample S3 was unfiltered water. To 10016.93 g of ultra-high purity water has been added a known amount of glass fibre filter, potassium chloride and turbidity standard.

A 1.2 Sample Analysis and Homogeneity Testing

A partial homogeneity test was conducted for all the analytes of interest in samples S1, S2 and S3.[1] Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Methodology for Total Elements

For analysis of total elements in S2, a test portion of 30 mL was transferred to a 50 mL graduated polypropylene centrifuge tube. The samples were digested using 2 mL of nitric on a hot block at 90±100ºC for 90 min.

Measurement of total elements in S2 involved using ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, duplicates and sample matrix spikes was carried through the same set of procedures and analysed at the same time as the samples. A summary of the wavelength used for each analyte is given in Table 33.

Table 33 Instrumental Technique used for Total Elements

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

Methodology for Tests Other Than Total Elements in S1, S2 and S3

A summary of the measurement methods and instrumental techniques for analytes in Samples S1 and S2 are presented in Tables 34 and 35.

For sample S3, a well-mixed sample was filtered through a pre-weighed glass fibre filter; the residue retained on the filter was dried at 104°C weighed and reported as TSS. The filtrate was collected in a pre-weighed container then dried at 180ºC weighed and reported as TDS.

For TS measurements the unfiltered sample was dried at 104ºC into a pre-weighed container. After drying the residue was weighed and reported as TS.

Table 34 Methodology for S1

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination - OPA Method	SFA
Bromide	Ion Chromatographic Method	IC
Chloride	Turbidimetric Method	DA
Dissolved Organic Carbon	High Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	ISE
Iodide	Ion Chromatographic Method	IC
NOx	Colorimetric-Sulphanilamide-NEDD Cd Reduction	FIA
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA
Sulphate	Turbidimetric Method	DA
Total Dissolved Nitrogen	Persulfate digestion	FIA
Total Dissolved Phosphorus	ICP-Method	ICP-MS

Table 35 Methodology for S2

Test	Measurement Method	Instrument
Alkalinity to pH 4.5 (as $CaCO_3$)	Titration	Titration
Silica (as SiO_2)	ICP-Method	ICP-OES
Total Hardness (as $CaCO_3$)	Calculation	ICP-OES

APPENDIX 2 - STABILITY STUDY

Participants were advised to store Sample S1 frozen if analyses cannot be commenced on the day of receipt. Sample's condition on receipt and the date when the sample was received and analysed by the participants are presented in Table 36. No significant trends between participants' results and sample's condition on receipt were noticed (Figures 46 to 49)

Table 36 Sample S1 Condition on Receipt and the Date When the Sample was Received and Analysed

Lab Code	Received Date	S1	
		Condition on Receipt	Date of Analysis
1	27/05/2020	Frozen	25/05/2020
2	26/05/2020	Frozen	17/06/2020
3	26/05/2020	Frozen	11/06/2020
4	27/05/2020	satisfactory	28/05/2020
6	27/05/2020	cold	16/06/2020
8	26/05/2020	Frozen	29/05/2020
9	05/06/2020	Frozen	06/06/2020
10	26/05/2020	Frozen	28/05/2020
11	27/05/2020	Frozen	04/06/2020
12	26/05/2020	Frozen	01/06/2020
13	27/05/2020	Frozen	03/06/2020
14	05/06/2020	Cold	08/06/2020
15	30/05/2020	Cold	05/06/2020
16	26/05/2020	Cold	29/05/2020
17*	02/06/2020	Cold	05/06/2020

*The samples have been dispatched on 01/06/2020.

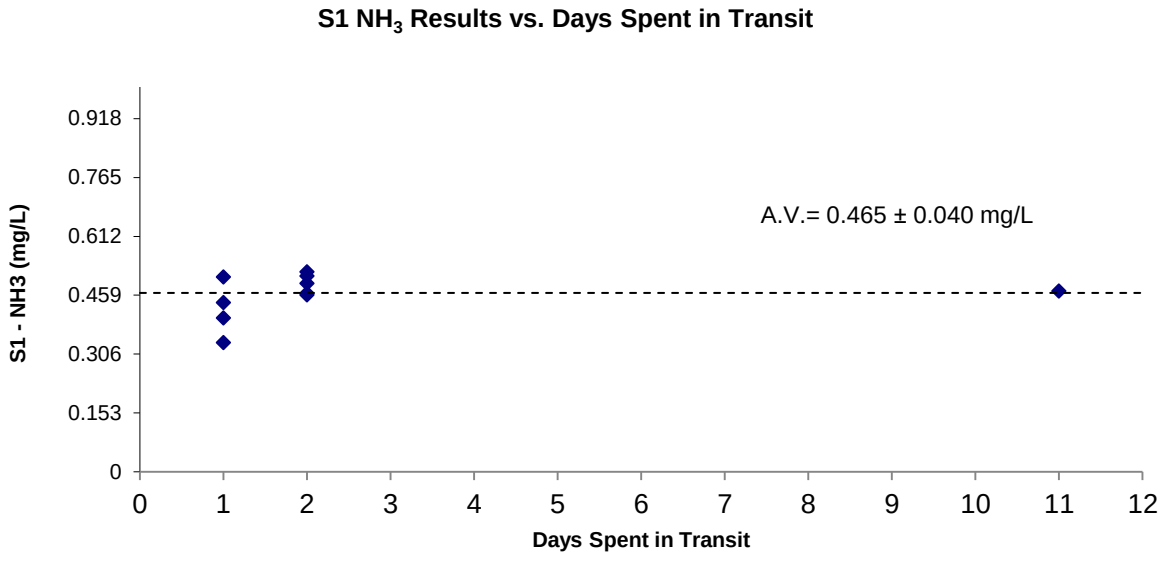

Figure 46 S1- NH3 Results vs Day Spent in Transit

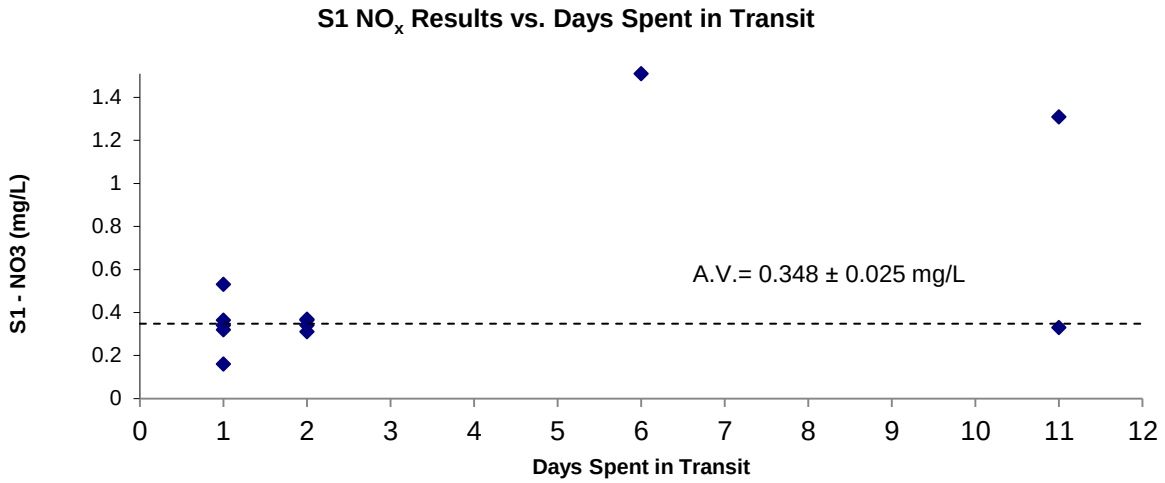

Figure 47 S1-NOx Results vs Day Spent in Transit

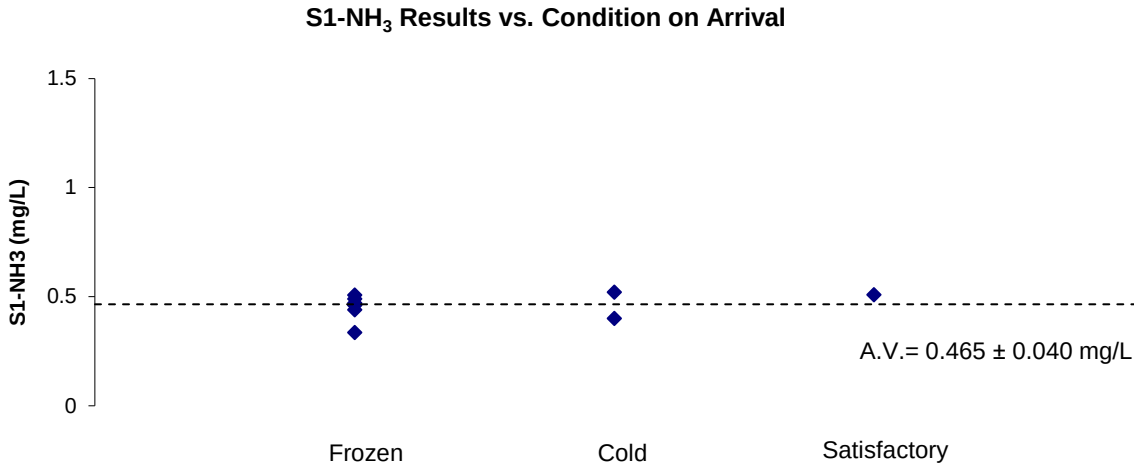

Figure 48 S1-NH3 Results vs Condition on Arrival

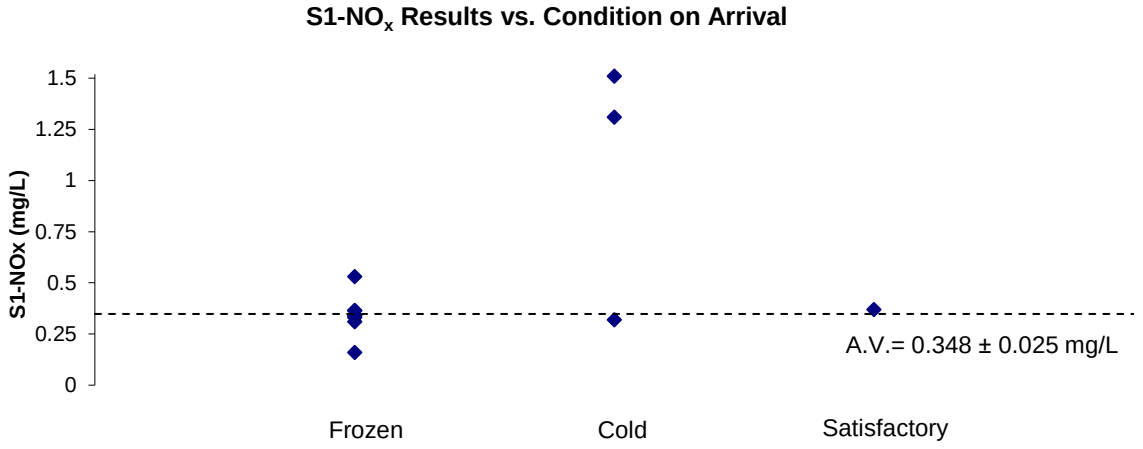

Figure 49 S1-NO_x Results vs Condition on Arrival

Stability Study

Stability studies conducted for nutrients and physical tests in water in previous studies found no significant changes in any of the analytes' concentration. A stability study was however conducted in the present study for the less stabile analytes: NH_3-N and NOx in S1.

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

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

To test for short term stability results from samples analysed over the study period from both before the samples' dispatch (T0) and the end of the study after result submission (T1) were compared. Each sample was analysed in duplicate together with a set of quality control samples consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes.

Results were in good agreement with each other as well as with the assigned value within their stated uncertainties (Figure 50).

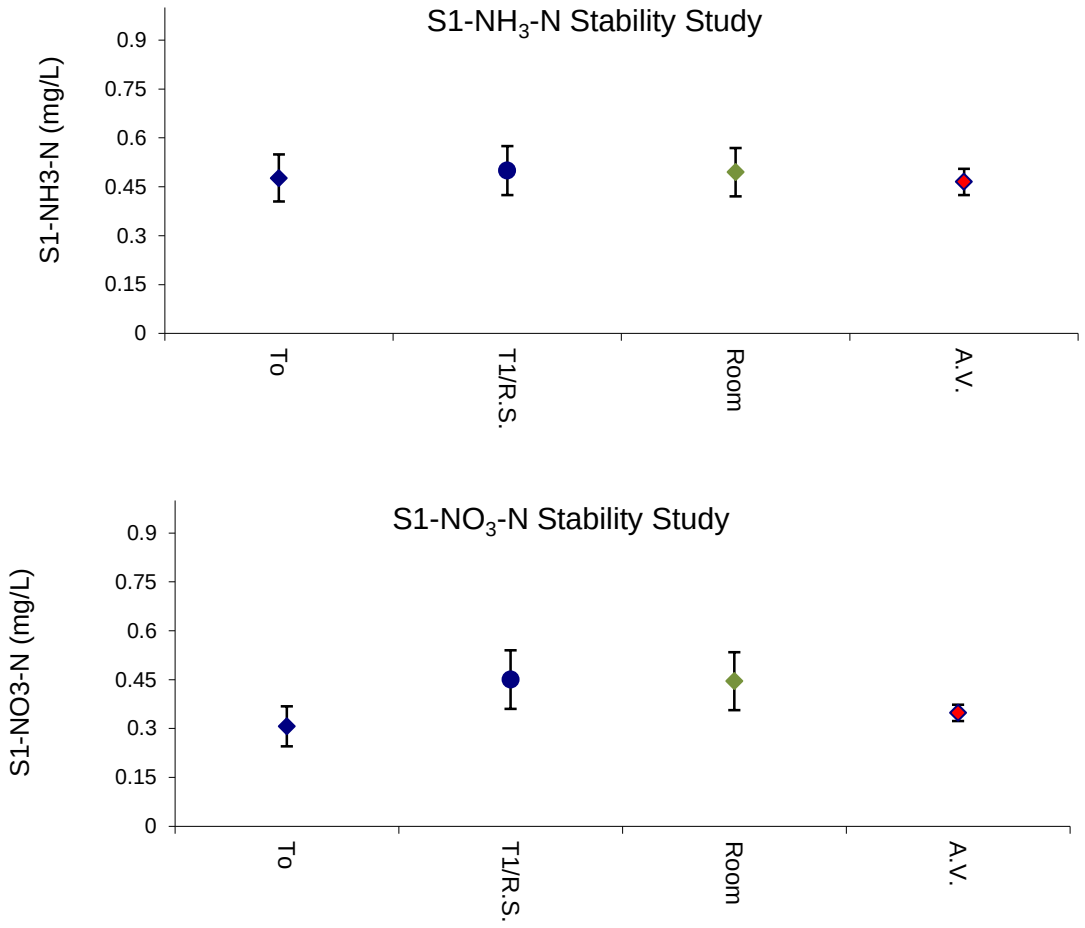

Figure 50 Stability Study Results

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

The assigned value was calculated as the robust average using the procedure described in 'ISO13258:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] The uncertainty was estimated as:

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

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 37.

Table 37 Uncertainty of Assigned Value for Chloride in Sample S1

No. results (p)	13
Robust Average	41.6 mg/L
$S_{rob\ av}$	2.75 mg/L
$u_{rob\ av}$	0.95 mg/L
k	2
$U_{rob\ av}$	1.9 mg/L

The assigned value for Chloride in Sample S1 is **41.6 ± 1.9 mg/L.**

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 2 and Equation 3 respectively (see page 8).

A worked example is set out below in Table 38.

Table 38 z-Score and E_n-score for Chloride result reported by Laboratory 11 in S1

Chloride Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
43.9 ± 3.1	41.6 ± 1.9	10% as CV or 0.10 x 41.6 = = 4.16 mg/L	$z = \frac{(43.9 - 41.6)}{4.16}$ z = 0.55	$En = \frac{(43.9 - 41.6)}{\sqrt{3.1^2 + 1.9^2}}$ $E_n = 0.63$

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can be used to estimate the uncertainty of their measurement results.[10, 12] Between 2014 and 2020, NMI carried out ten proficiency tests for nutrients, anions and physical tests in water. These studies involved analyses of anions, nutrients and physical tests in potable, fresh (river), waste and sea water. Laboratory X participated and submitted satisfactory results in 9 of these PTs. Results are presented in Table 39.

Table 39 Laboratory X Reported Results for Chloride

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 14-19	Potable	51.9 ± 10	55.4 ± 1.4	2.9	8
AQA 15-18	River	65.7 ± 10	70.3 ± 3.6	6.5	10
AQA 16-03	Waste	3099 ± 320	2990 ± 170	6.3	8
AQA 17-16	Sea water	13100 ± 1300	12800 ± 420	4.1	10
AQA 18-05	River	68 ± 8.0	71.3 ± 1.5	3.4	17
AQA 18-16	Sea water	16600 ± 1600	17300 ± 1600	13	13
AQA 19-07	River	57.0 ± 12	53.7 ± 2.0	4.7	10
AQA 19-25	Sea Water	20000 ± 2000	20500 ± 1000	2.2	13
AQA 20-08	Potable	33.4 ± 7.0	41.6 ± 1.9	6.7	13
Average				5.5**	

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

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 5.5%. Using a coverage factor of two gives a relative expanded uncertainty of 11%, at a level of confidence of approximately 95%.

Table 40 sets out the expanded uncertainty for results of the measurement of chloride in fresh, saline, waste or potable water over the range 40 – 20000 mg/L.

Table 40 Uncertainty of chloride results estimated using PT data

Results mg/L	Uncertainty mg/L
40.0	4.4
500	55
1000	110
15000	1700

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

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
AAS	Atomic Absorption Spectrometry
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
DA	Discreet Analyser
dNPOC	Dissolved non-purgeable organic carbon
FIA	Flow Injection Analyser
GUM	Guide to the Expression of Uncertainty in Measurement
IC	Ion Chromatograph
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-MS/MS	Inductively Coupled Plasma - Tandem Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma - Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma - Optical Emission Spectrometry- radial view
IEC	International Electrotechnical Commission
ISE	Ion Selective Electrode
ISO	International Organisation for Standardisation
Max	Maximum Value in a Set of Results
Md	Median
Min	Minimum Value in a Set of Results
MU	Measurement Uncertainty
NATA	National Association of Testing Authorities
NEDD	N-(1-naphthyl)-ethylenediamine dihhydrochloride (NED dihydrochloride)
NIST	National Institute of Standards and Technology
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NIR	Near-infrared
NT	Not Tested
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PT	Proficiency Test
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S.V.	Spiked or Formulated Concentration of a PT Sample
SFA	Segment Flow Analyser
SI	The International System of Units
SPANDS	2-(4-Sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt
SRM	Standard Reference Material (Trademark of NIST)
s^2_{sam}	Sampling Variance
s_a/σ	Analytical Standard Deviation Divided by the Target Standard Deviation
Target SD	Target Standard Deviation

σ	Target Standard Deviation
UC	Universal Cell
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet and Visible Spectroscopy

APPENDIX 6 - METHODOLOGY FOR S1

Table 41 Measurement Methods and Instrument Techniques for Ammonia-N

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Fluorometric Determination - OPA Method	SFA	
2			
3			
4	Colorimetric - Phenate Method	FIA	APHA 4500
5	NA	NA	NA
6	Colorimetric - Phenate Method	FIA	4500-NH3 H
7	NA	NA	NA
8	Colorimetric - Phenate Method	DA	In house
9	Colorimetric - Phenate Method	DA	in House
10	Colorimetric - Salicylate Method	DA	In-house method based on APHA 23rd edition 4500 NH3 B
11	Colorimetric - Phenate Method	FIA	
12	Colorimetric - Phenate Method	FIA	APHA
13	Colorimetric - Phenate Method	FIA	APHA4500NH3-H
14	NT	NT	NT
15			
16			
17	Colorimetric - Salicylate Method	UV-Vis Spectrophotometer	APHA4500 F

Table 42 Measurement Methods and Instrument Techniques for Bromide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	
2	Ion Chromatographic Method	IC	USEPA
3			
4	Ion Chromatographic Method	IC	APHA 4110
5	NA	NA	NA
6	ICP Method	ICP-MS	3030 B
7	NA	NA	NA
8			
9			
10			
11	Ion Chromatographic Method	IC	
12	Ion Chromatographic Method	IC	APHA
13	ICP Method	ICP-MS	W32
14	Ion Chromatographic Method	IC	ASTM D4327-17
15	Ion Chromatographic Method	IC	
16	Ion Chromatographic Method	IC	In house
17			

Table 43 Measurement Methods and Instrument Techniques for Chloride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	
2	Ferricyanide Colorimetric Method	DA	APHA
3			
4	Ion Chromatographic Method	IC	APHA 4110
5	NA	NA	NA
6	Insufficient volume to complete all the tests – we do Cl, NOx & OP on routine basis & would have included results.		
7	NA	NA	NA
8	Ferricyanide Colorimetric Method	DA	In house
9	Mercuric Thiocyanate	DA	in House
10	Potentiometric-Titration	Auto Titration	In-house method based on APHA 23rd edition 4500 Cl D
11	Mercurric Nitrate Titration	DA	
12	Ion Chromatographic Method	IC	APHA
13	ICP-Method	ICP-MS	W32
14	Ion Chromatographic Method	IC	ASTM D4327-17
15	Ion Chromatographic Method	IC	
16	Ion Chromatographic Method	IC	Inhouse
17	Ion Chromatographic Method	IC	APHA4110 B

Table 44 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Laboratory Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	
2			
3			
4	High-Temperature Oxidation	NIR-detector	APHA 5310
5	NA	NA	NA
6	Wet-Oxidation	NIR-detector	5310 C
7	NA	NA	NA
8	High-Temperature Oxidation	NIR-detector	In house
9			
10	High-Temperature Oxidation	FI-detector	In-house method based on APHA 23rd edition 5310-TOC B
11	High-Temperature Oxidation	NIR-detector	
12	High-Temperature Oxidation	DOC	APHA
13	High-Temperature Oxidation	NIR-detector	APHA5310-B
14	NT	NT	NT
15	High-Temperature Oxidation	if other please type	
16			
17			

Table 45 Measurement Methods and Instrument Techniques for Fluoride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	
2	Ion Selective Electrode Method	Ion Selective Electrode	APHA
3	Ion Selective Electrode Method	Ion Selective Electrode	APHA Method 4500-F- C
4	Ion Chromatographic Method	IC	APHA 4110
5	NA	NA	NA
6			
7	NA	NA	NA
8	Ion Selective Electrode Method	Ion Selective Electrode	In house
9	Ion Selective Electrode Method	Ion Selective Electrode	in House
10	Ion Selective Electrode Method	Ion Selective Electrode	In-house method based on APHA 23rd edition 4500-F C
11	Ion Selective Electrode Method	Ion Selective Electrode	
12	Ion Chromatographic Method	IC	APHA
13	SPADNS Colorimetric Method	UV-Vis Spectrophotometer	W1
14	Ion Chromatographic Method	IC	ASTM D4327-17
15	Ion Chromatographic Method	IC	
16	Ion Chromatographic Method	IC	Inhouse
17	Ion Chromatographic Method	IC	APHA4110 B

Table 46 Measurement Methods and Instrument Techniques for Iodide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	
2	Ion Chromatographic Method	IC	USEPA
3			
4	Ion Chromatographic Method	IC	APHA 4110
5	NA	NA	NA
6	ICP Method	ICP-MS	
7	NA	NA	NA
8			
9			
10			
11	Ion Chromatographic Method	IC	
12	Ion Chromatographic Method	IC	APHA
13			
14	NT	NT	NT
15			
16	Ion Chromatographic Method	IC	
17			

Table 47 Measurement Methods and Instrument Techniques for NOx

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	
2	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
3			
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500
5	NA	NA	NA
6	Insufficient volume to complete all the tests – we do Cl, NOx & OP on routine basis & would have included results.		
7	NA	NA	NA
8	Calculation	DA	In house
9	Colorimetric -vanadium III method	DA	in House
10	Calculation	DA	In-house method based on Aquakem Total Oxidised Nitrogen method
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
12	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
13	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO3-F
14	Ion Chromatographic Method	IC	ASTM D4327-17
15	Ion Chromatographic Method	IC	
16			
17	Ion Chromatographic Method	IC	APHA4110 B

Table 48 Measurement Methods and Instrument Techniques for Orthophosphate-P

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	SFA	
2	Ascorbic Acid Colorimetric Method	FIA	APHA
3			
4	Ascorbic Acid Colorimetric Method	FIA	APHA 4500
5	NA	NA	NA
6	Insufficient volume to complete all the tests – we do Cl, NOx & OP on routine basis & would have included results.		
7	NA	NA	NA
8	Ascorbic Acid Colorimetric Method	DA	In house
9	Vanadomolybdophosphoric Colorimetric Method	DA	in House
10	Ascorbic Acid Colorimetric Method	DA	In-house method based on APHA 23rd edition 4500-P F
11	Vanadomolybdophosphoric Colorimetric Method	FIA	
12	Ascorbic Acid Colorimetric Method	FIA	APHA
13	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-G
14	NT	NT	NT
15			
16			
17			

Table 49 Measurement Methods and Instrument Techniques for Sulphate

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	
2	ICP Method	ICP-MS	USEPA
3			
4	Ion Chromatographic Method	IC	USEPA 300
5	NA	NA	NA
6	ICP Method	ICPOES	3030 B
7	NA	NA	NA
8	Turbidimetric Method	DA	In house
9	Turbidimetric Method	DA	in House
10	Turbidimetric Method	Manual Analysis	In-house method based on USEPA method 9038, Sept 1986
11	Turbidimetric Method	DA	
12	Ion Chromatographic Method	IC	APHA
13	ICP Method	ICP-MS	W32
14	Ion Chromatographic Method	IC	ASTM D4327-17
15	Ion Chromatographic Method	IC	
16	Ion Chromatographic Method	IC	Inhouse
17	Ion Chromatographic Method	IC	APHA4110 B

Table 50 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	SFA	
2	Calculation (TKN+NOx)	DA	APHA
3			
4	Persulfate digestion	FIA	APHA 4500
5	NA	NA	NA
6	Persulfate digestion	DA	4500-P J
7	NA	NA	NA
8	Calculation (TKN+NOx)	DA	In house
9	Calculation (TKN+NOx)	DA	in House
10	We chose not to analyse Total Dissolved Nitrogen and Total Dissolved Phosphorus because of lack of sample volume. Most of our methods are traditional methods which may require around 100 mL per test for potable waters.		
11	Persulfate digestion	FIA	
12	Persulfate digestion	FIA	APHA
13	Persulfate digestion	FIA	APHA4500P-J
14	NT	NT	NT
15			
16			
17	Persulfate digestion	UV-Vis Spectrophotometer	APHA4500 C

Table 51 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Laboratory Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	
2	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA
3				
4	Persulfate digestion		FIA	APHA 4500
5	NA	NA	NA	NA
6	K2S2O8-Digestion		DA	4500-P J
7	NA	NA	NA	NA
8		Ascorbic Acid Colorimetric Method	DA	In house
9	H2SO4+HNO3-Digestion	In House	DA	in House
10	We chose not to analyse Total Dissolved Nitrogen and Total Dissolved Phosphorus because of lack of sample volume. Most of our methods are traditional methods which may require around 100 mL per test for potable waters.			
11		Vanadomolybdophosphoric Colorimetric Method	FIA	
12		Ascorbic Acid Colorimetric Method	FIA	APHA
13	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
14	NT	NT	NT	NT
15				
16				
17	HNO3-Digestion	ICP Method	ICP-OES	APHA3120

Table 52 Additional Information

Lab Code	Additional Information
6	S1: Insufficient volume to complete all the tests – we do Cl, NOx & OP on routine basis & would have included results.

APPENDIX 7 - METHODOLOGY FOR S2

Table 53 Instrument Techniques for Boron

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-MS	Sc	ORS	NA	1.25	11
2	ICP-MS/MS	Ge	ORS	NA	1	11
3	ICP-OES-AV	Te 214.282 / Y 371.029			1	249.678 nm
4	ICP-OES	Eu & Cs	NA	NA	1	249.773 (nm)
5	ICP-MS	Scandium	ORS	He	1	
6	ICP-MS		CRI	NA		11
8	ICP-MS	Rh, Sc, Ir		NA	NA	11 (m/z)
9	ICP-MS					
10*	ICP-OES-AV	NA	NA	NA	Neat	249.772
11	ICP-OES-AV					
12	ICP-MS	SC,Rh,Ir		He	10	NA
13	ICP-MS	Sc	NA	NA	1	10
14	ICP-MS	Agilent, P/N:5188-6525	NA	NA	1	m/z 11
15						
16	ICP-OES-AV	Lu			1.05	208.957
17						

*Additional Information in Table

Table 54 Instrument Techniques for Calcium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES-AV	Y			2	315.887
2	ICP-MS/MS	Sc	ORS	H2-N2O	1	40
3	ICP-OES-AV	Te 214.282 / Y 371.029			1	315.887 nm
4	ICP-OES	Eu & Cs	NA	NA	1	315.887, 370.602nm
5	ICP-MS	Scandium	ORS	He	1	
6	ICP-OES-RV					315.8
7	NA	NA	NA	NA	NA	NA
8	ICP-OES-RV				NA	315.885
9	ICP OES					
10	AAS	NA	NA	NA	2	422.7
11	ICP-OES-AV					
12	ICP-MS	SC,Rh,Ir		He	10	NA
13	ICP-MS	Sc	UC	He	1	44
14	ICP-MS	Agilent, P/N:5188-6525	NA	NA	1	m/z 44
15	ICP-OES-RV	Y				
16	ICP-OES-RV	Lu			1.05	422.668
17	ICP-OES-RV	NA	NA	NA	NA	317.933nm

Table 55 Instrument Techniques for Potassium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES-AV	Y			2	766.491
2	ICP-MS/MS	Sc	ORS	H2-N2O	1	39
3	ICP-OES-AV	Te 214.282 / Y 371.029			1	766.491 nm
4	ICP-OES	Eu & Cs	NA	NA	1	404.721nm, 766.491nm
5	ICP-MS	Scandium	ORS	He	1	
6	ICP-OES-RV					766.4
7	NA	NA	NA	NA	NA	NA
8	ICP-OES-RV				NA	766.485
9	ICP OES					
10	AAS	NA	NA	NA	Neat	766.5
11	ICP-OES-AV					
12	ICP-MS	SC,Rh,Ir		He	10	NA
13	ICP-MS	Sc	UC	He	1	39
14	ICP-MS	Agilent, P/N:5188-6525	NA	NA	1	m/z 39
15	ICP-OES-RV	Y				
16	ICP-OES-RV	Lu			1.05	766.49
17	ICP-OES-RV	NA	NA	NA	NA	766.496nm

Table 56 Instrument Techniques for Magnesium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES-AV	Y			2	279.8
2	ICP-MS	Sc	ORS	He	1	24
3	ICP-OES-AV	Te 214.282 / Y 371.029			1	280.270 nm
4	ICP-OES	Eu & Cs	NA	NA	1	383.830 (nm)
5	ICP-MS	Scandium	ORS	He	1	
6	ICP-OES-RV					279.8
7	NA	NA	NA	NA	NA	NA
8	ICP-OES-RV				NA	383.83
9	ICP OES					
10	AAS	NA	NA	NA	2	285.2
11	ICP-OES-AV					
12	ICP-MS	SC,Rh,Ir		He	10	NA
13	ICP-MS	Sc	UC	He	1	25
14	ICP-MS	Agilent, P/N:5188-6525	NA	NA	1	m/z 24
15	ICP-OES-RV	Y				
16	ICP-OES-RV	Lu			1.05	285.213
17	ICP-OES-RV	NA	NA	NA	NA	285.215nm

Table 57 Instrument Techniques for Sodium

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES-AV	Y			50	588.995
2	ICP-MS	Sc	ORS	He	1	23
3	ICP-OES-AV	Te 214.282 / Y 371.029			10	588.995 nm
4	ICP-OES	Eu & Cs	NA	NA	1	330.237, 589.592nm
5	ICP-MS	Scandium	ORS	He	1	
6	ICP-OES-RV					589.5
7	NA	NA	NA	NA	NA	NA
8	ICP-OES-RV				NA	589.593
9	ICP OES					
10	AAS	NA	NA	NA	Neat	330.2
11	ICP-OES-AV					
12	ICP-MS	SC,Rh,Ir		He	10	NA
13	ICP-MS	Sc	UC	He	1	23
14	ICP-MS	Agilent, P/N:5188-6525	NA	NA	1	m/z 23
15	ICP-OES-RV	Y				
16	ICP-OES-RV	Lu			1.05	589.592
17	ICP-OES-RV	NA	NA	NA	NA	589.591nm

Table 58 Instrument Techniques for Phosphorus

Laboratory Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
1	ICP-OES-AV	Y			2	213.618
2	ICP-MS/MS	Ge	ORS	H2-N2O	1	31->47
3	ICP-OES-AV	Te 214.282 / Y 371.029			1	213.618 nm
4	ICP-OES	Eu & Cs	NA	NA	1	185.827 (nm)
5	ICP-MS	Scandium	ORS	He	1	
6	ICP-OES-RV					
7	NA	NA	NA	NA	NA	NA
8	ICP-OES-RV				NA	185.827
9	ICP OES					
10*	DA	NA	NA	NA		NA
11	FIA					
12	ICP-MS	SC,Rh,Ir		He	10	NA
13	ICP-MS	Sc	UC	He	1	31
14	ICP-MS	Agilent, P/N:5188-6525	NA	NA	1	m/z 31
15	ICP-OES-RV	Y				
16						
17	ICP-OES-RV	NA	NA	NA	NA	213.617nm

*Additional Information in Table

Table 59 Measurement Methods and Instrument Techniques for Alkalinity

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	
2	Titration	Auto Titration	APHA
3	Titration		APHA 2320 B
4	Titration	Auto Titration	APHA 2320
5	Titration	Auto Titration	APHA2320
6	Titration	Auto Titrator	2320 B
7	NA	NA	NA
8	Titration	Auto Titration	In house
9	Titration	Auto Titration	in House
10	Titration	Auto Titration	In-house method based on APHA 23rd edition 2320 B
11	Titration	Auto Titration	
12	Titration	Auto Titration	APHA
13	Titration	Auto Titration	APHA2320B
14	NT	NT	NT
15			
16			
17	Titration	Manual Analysis	APHA2320 B

Table 60 Measurement Methods and Instrument Techniques for Silica

Laboratory Code	Measurement Method	Instrument	Method Reference
1	ICP-Method	ICP-OES	
2	ICP-Method	ICP-MS	USEPA
3			
4	Molybdosilicate Method	DA	APHA 4500
5	Molybdosilicate method	UV-Vis Spectrophotometer	APHA Method 4500-Si C
6	ICP-Method	ICP-OES	3030 B
7	NA	NA	NA
8	Molybdosilicate Method	DA	In house
9	Molybdosilicate Method	DA	in House
10	Molybdosilicate Method	DA	In-house method based on APHA 23rd edition 4500-SiO2 E
11	Molybdosilicate Method	DA	
12	Molybdosilicate Method	DA	APHA
13	ICP-Method	ICP-MS	W32
14	NT	NT	NT
15			
16			
17	ICP-Method	ICP-OES	APHA 3120

Table 61 Measurement Methods and Instrument Techniques for Total Hardness

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Calculation	ICP-OES	
2	Calculation	ICP-MS	APHA
3	Calculation		APHA 2340 B
4	Calculation	ICP-OES	APHA 2340
5	NA	NA	NA
6	Calculation	ICP-OES	2340 B
7	NA	NA	NA
8	Calculation	ICP-OES	In house
9	Calculation	DA	in House
10	Calculation	NA	In-house method based on APHA 23rd edition 2340 B
11	Calculation	ICP-OES	
12	Calculation	Auto Titration	APHA
13	Titration	Manual Analysis	W21
14	NT	NT	NT
15			
16	Calculation	ICP-OES	APHA_2340B
17	Calculation	ICP-OES	APHA 3120

Table 62 Additional Information

Lab Code	Additional Information
10	S2: The laboratory does not hold NATA accreditation for Total Boron. Methodology for S2: To be able to obtain the low limits required for Total P in Potable water, we analysed the samples using Ascorbic Acid colorimetric method using DA as instrument.

APPENDIX 8 - METHODOLOGY FOR S3

Table 63 Method References for Sample S3

Laboratory Code	Method Reference
1	
2	APHA
3	APHA 2540 D, APHA 2130 B
4	APHA 2540 / APHA 2130
5	NA
6	Solids 2540 B, C & D – Turbidity 2130 B
8	APHA 2450 and in-house
9	In House
10	Total Dissolved Solid – In house method based on APHA 23rd edition 2540 C, Total Solids – In house method based on APHA 23rd edition 2540 B, Total Suspended Solids – In house method based on APHA 23rd edition 2540 D, Turbidity – In house method based on APHA 23rd edition 2130 B
11	TSS only reported off one replicate, insufficient sample to perform the test in duplicate.
12	APHA 2540C, APHA 2540D, APHA 2540B
13	APHA 2540
14	NA
15	NA
16	NA

END OF STUDY