Australian Government
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National Measurement Institute

Proficiency Test Final Report AQA 21-10 Nutrients and Anions in River Water

October 2021

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.

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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 21-10, Nutrients and Anions in River Water. The study covers the measurement of total: B, Ca, K, Mg, Na and P. Ammonia-N, apparent colour (Pt-Co units), bromide, chloride, dissolved organic carbon (as dNPOC), (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 kjeldahl nitrogen (TKN), total nitrogen (TN) and total organic carbon (as NPOC), were also included in the program.

The sample set consisted of three water samples.

Twenty-five laboratories registered to participate and all submitted results.

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

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

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

Of 394 z-scores, 373 (95%) returned a satisfactory score of $|z| \leq 2.0$.
Of 394 E_n-scores, 347 (88%) returned a satisfactory score of $|E_n| \leq 1.0$.

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

Low level bromide and total dissolved phosphorus 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, 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 90% to 96% .

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 398 numerical results, 393 (99%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.35% to 316% of the reported value. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 4.

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

The study samples were checked for homogeneity and are well characterised, both by in-house testing and from the results of the proficiency round. These samples can be used for quality control, method development and method validation. Surplus test samples are available for sale.

2 INTRODUCTION

2.1 NMI Proficiency Testing Program

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

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

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

AQA 21-10 is the 12th 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 river water;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty;
- provide participants with information that will be useful in assessing their uncertainty estimates; 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

were selected from those for which an investigation level is published in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality[5] and are commonly measured by water testing laboratories.

3.2 Participation

Twenty-five laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued:	1 June 2021
Samples dispatched:	28 June 2021
Results due:	9 August 2021
Interim report issued:	11 August 2021

3.3 Test Material Specification

Three samples were provided for analysis:

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

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

Sample S3 was 200 mL of unfiltered, autoclaved and frozen river water.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

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

The preparation, analysis and homogeneity testing of the study samples 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 in time and 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

Samples S1 and S3 were frozen, while Sample S2 was refrigerated before dispatch.

The samples were dispatched by courier on 28 June 2021.

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

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

3.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- If analyses cannot be commenced on the day of receipt, please store Samples S1 and S3 frozen.

- Prior to testing, thaw samples S1 and S3 completely.
- Participants are asked to report results in units of mg/L except for pH and EC. Report EC in units of µS/cm.

SAMPLE S1 filtered, frozen river water		SAMPLE S2 unfiltered, chilled river water		SAMPLE S3 unfiltered, frozen river water	
Test	Approximate Conc. Range mg/L	Test	Approximate Conc. Range mg/L	Test	Approximate Min Conc. mg/L
Bromide	0.1-5	B (total)	0.02-2	Total Kjeldahl Nitrogen	0.025-1
Chloride	5-100	Ca (total)	0.5-50	Total Nitrogen	0.025-1
Sulphate	5-100	K (total)	0.5-50	Total Organic Carbon (as NPOC)	1-25
Ammonia-N	0.025-0.5	Mg (total)	0.2-20		
(Nitrate-N +Nitrite-N) NOx	0.025-0.5	Na (total)	5-500		
Total Dissolved Nitrogen (TDN)	0.02-5	P (total)	0.05-50		
Orthophosphate-P (FRP)	0.005-0.125	Silica (as SiO_2)	0.5-50		
Total Dissolved Phosphorus	0.005-0.125	Alkalinity to pH 4.5 as $CaCO_3$	5-500		
Dissolved Organic Carbon (as dNPOC)	0.5-25	Colour, apparent (Pt-Co units)	0.5-50		
		Total Hardness ($CaCO_3$)	5-500		
		pH (at 25°C)	>2.5		
		EC (at 25°C, µs/cm units)	100-2500		

- 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 11 August 2021.

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 Duplicate Analysis	CRM Recoveries of SS	Top Down approach
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	ASTM E2254-13
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration		Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Standard deviation from PT studies only		ISO/GUM
		Control Samples - CRM	CRM	
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	NMI Uncertainty Course
7	Estimation of MU from within-laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques	Control Samples - CRM Duplicate Analysis	CRM	ASTM E2254-13
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples	CRM	ISO/GUM
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	Eurachem 2000/ISO 1993A
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Standard Purity	Nordtest Report TR537
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM Recoveries of SS	Eurachem/CITAC Guide
13*	Top Down - precision and estimates of the method and laboratory bias	Control samples - CRM	CRM	Eurachem/CITAC Guide
14	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples - CRM Duplicate Analysis Instrument Calibration		NMI Uncertainty Course
15	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results
16*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis		
17	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis	Recoveries of SS	NATA General Accreditation Guidance, Estimating and Reporting MU
18	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis Instrument Calibration	Instrument Calibration	
19	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
20*	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	ISO/GUM
21	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS	Nordtest Report TR537
22	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Standard Purity	Eurachem/CITAC Guide
23	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM	NATA Technical Note 33
24	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	Recoveries of SS	Eurachem/CITAC Guide
25	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM

[a]RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples. *Additional information in Table 2.

4.3 Additional Uncertainty Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 2.

Table 2 Additional Uncertainty Information

Lab Code	Additional Information
13	NATA recommendations.
16	UoM is based on ISO 17025, EURACHEM / CITAC Guide.
20	NATA General Accreditation Guidance Estimating and Reporting Measurement Uncertainty of Chemical Test Results.

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

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Participants' comments are reproduced in Table 3.

Table 3 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
Please include filtered Na, Ca, K and Mg as we do not report total for those elements.	Thank you for your feedback.

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 4 to 27 with resultant summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 25. An example chart with interpretation guide is shown in Figure 1.

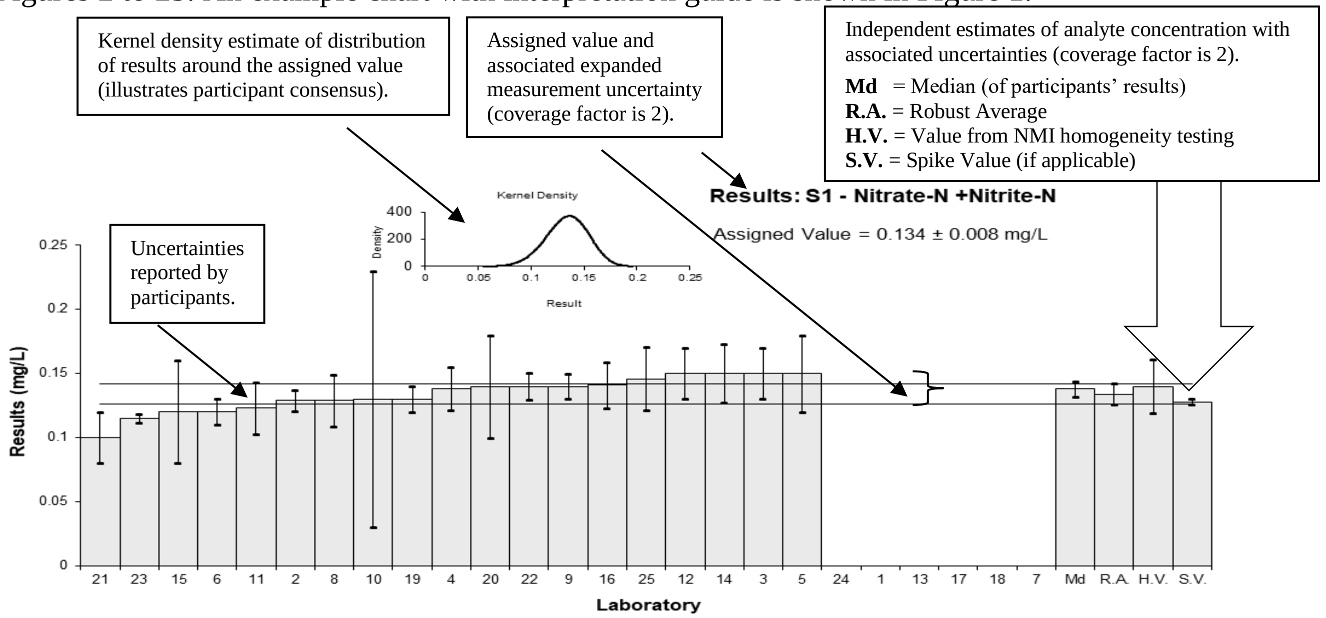


Figure 1 Guide to Presentation of Results

5.2 Outliers and Extreme Outliers

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

5.3 Assigned Value

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

5.4 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 interlaboratory comparisons, ISO13528:2015(E)'.[6]

5.5 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]

5.6 Target Standard Deviation for Proficiency Assessment

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

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

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

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:

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

where:

z is z-score;
χ is a participant's result;
X is the assigned value;
σ is the target standard deviation.

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

- $|z| \leq 2.0$ 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:

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

where:

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

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

- $|E_n| \leq 1.0$ 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 4

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.166	0.0142	0.43	0.59
3	0.16	0.02	0.17	0.18
4	0.142	0.021	-0.60	-0.61
5	0.19	0.038	1.45	0.87
6	0.14	0.01	-0.68	-1.19
7	0.158	0.033	0.09	0.06
8	0.1435	0.04305	-0.53	-0.28
9	0.150	0.033	-0.26	-0.18
10	0.13	0.2	-1.11	-0.13
11	0.165	0.02	0.38	0.41
12	0.15	0.04	-0.26	-0.15
13	<0.2	1.12		
14	0.162	0.024	0.26	0.23
15	0.16	0.06	0.17	0.07
16	0.1419	0.0084	-0.60	-1.15
17	NT	NT		
18	NT	NT		
19	0.149	0.022	-0.30	-0.29
20	0.19	0.6	1.45	0.06
21	0.034	0.007	-5.21	-10.70
22	0.165	0.023	0.38	0.36
23	0.148	0.005	-0.34	-0.78
24	NR	NR		
25	0.173	0.026	0.73	0.62

Statistics

Assigned Value*	0.156	0.009
Spike	Not spiked	
Homogeneity Value	0.157	0.024
Robust Average	0.155	0.009
Median	0.154	0.008
Mean	0.151	
N	20	
Max.	0.19	
Min.	0.034	
Robust SD	0.016	
Robust CV	11%	

*Robust Average excluding laboratory 21.

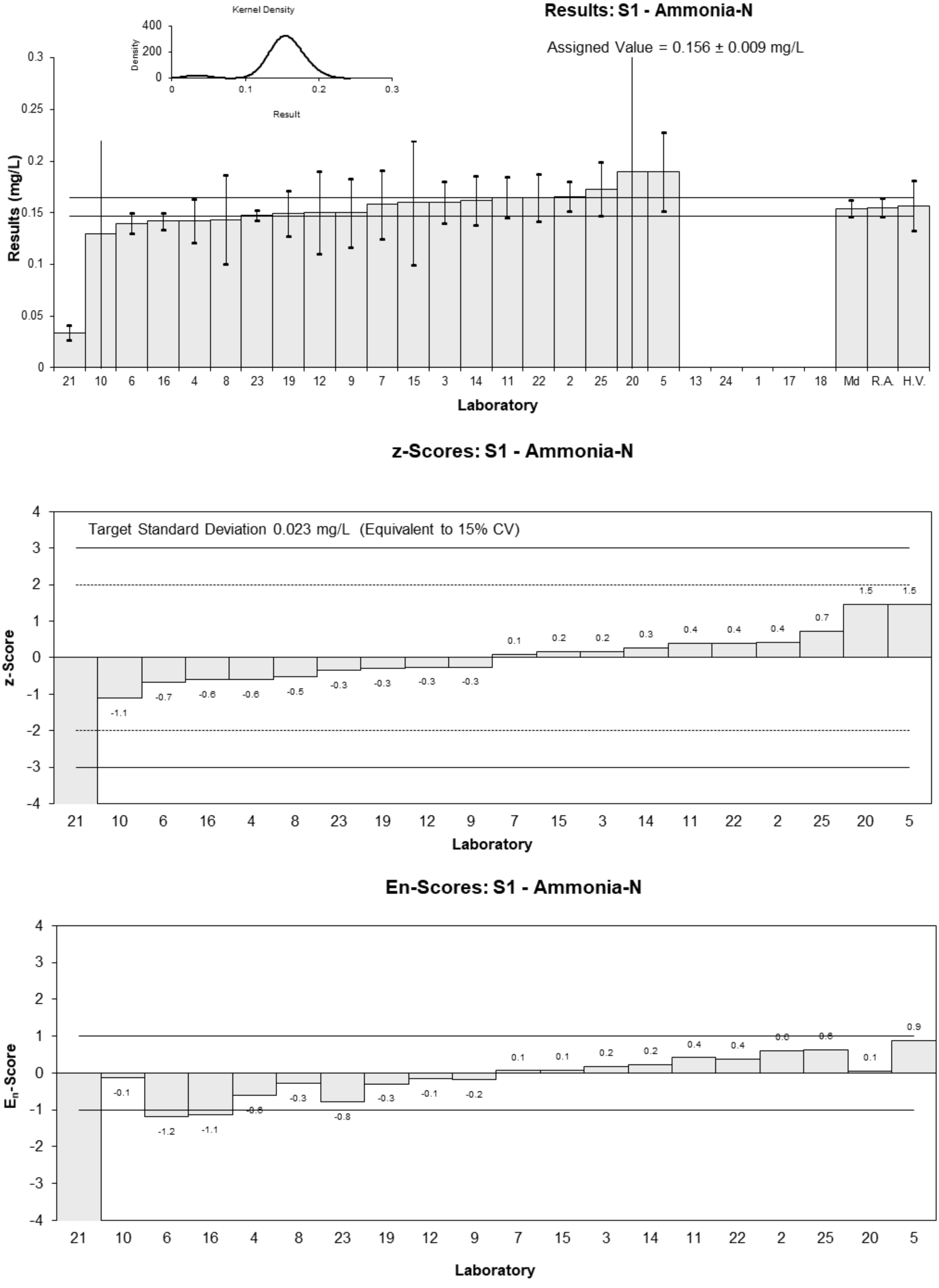

Results: S1 - Ammonia-N
Assigned Value = 0.156 ± 0.009 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
21 10 6 16 4 8 23 19 12 9 7 15 3 14 11 22 2 25 20 5 13 24 1 17 18 Md R.A. H.V.
z-Scores: S1 - Ammonia-N
Target Standard Deviation 0.023 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.1 -0.7 -0.6 -0.6 -0.5 -0.3 -0.3 -0.3 -0.3 0.1 0.2 0.2 0.3 0.4 0.4 0.4 0.7 1.5 1.5
En-Scores: S1 - Ammonia-N
E_n-Score
Laboratory
-0.1 -1.2 -1.1 -0.6 -0.3 -0.8 -0.3 -0.1 -0.2 0.1 0.1 0.2 0.2 0.4 0.4 0.6 0.6 0.1 0.9

Figure 2

Table 5

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<0.5	NR		
2	NT	NT		
3	0.2	0.1	-1.24	-0.60
4	0.201	0.024	-1.22	-1.25
5	NT	NT		
6	0.26	0.1	-0.11	-0.05
7	0.216	0.045	-0.94	-0.78
8	NT	NT		
9	NT	NT		
10	0.24	0.2	-0.49	-0.13
11	<1	NR		
12	NT	NT		
13	0.3	0.5	0.64	0.07
14	0.3	0.045	0.64	0.53
15	<0.5	NR		
16	0.351	0.075	1.60	0.97
17	NT	NT		
18	NT	NT		
19	0.282	0.026	0.30	0.30
20	<0.5	NR		
21	0.31	0.005	0.83	0.95
22	NR	NR		
23	NR	NR		
24	NR	NR		
25	NT	NT		

Statistics

Assigned Value	0.266	0.046
Spike	Not Spiked	
Homogeneity Value	0.200	0.040
Robust Average	0.266	0.046
Median	0.271	0.037
Mean	0.266	
N	10	
Max.	0.351	
Min.	0.2	
Robust SD	0.058	
Robust CV	22%	

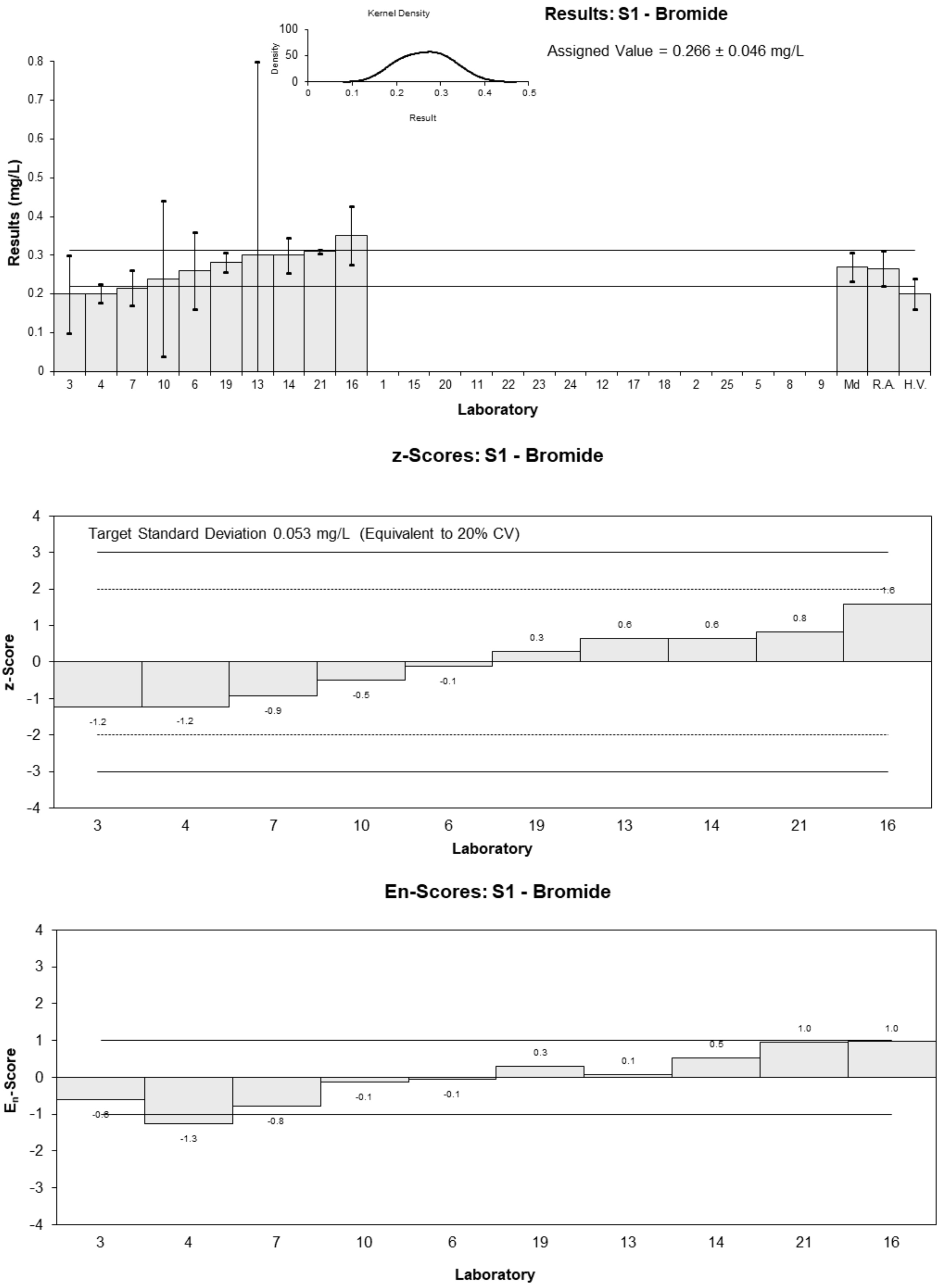

Results: S1 - Bromide
Assigned Value = 0.266 ± 0.046 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3 4 7 10 6 19 13 14 21 16 1 15 20 11 22 23 24 12 17 18 2 25 5 8 9 Md R.A. H.V.
z-Scores: S1 - Bromide
Target Standard Deviation 0.053 mg/L (Equivalent to 20% CV)
z-Score
-1.2 -1.2 -0.9 -0.5 -0.1 0.3 0.6 0.6 0.8 1.6
3 4 7 10 6 19 13 14 21 16
Laboratory
En-Scores: S1 - Bromide
E_n-Score
-0.6 -1.3 -0.8 -0.1 -0.1 0.3 0.1 0.5 1.0 1.0
3 4 7 10 6 19 13 14 21 16
Laboratory

Figure 3

Table 6

Sample Details

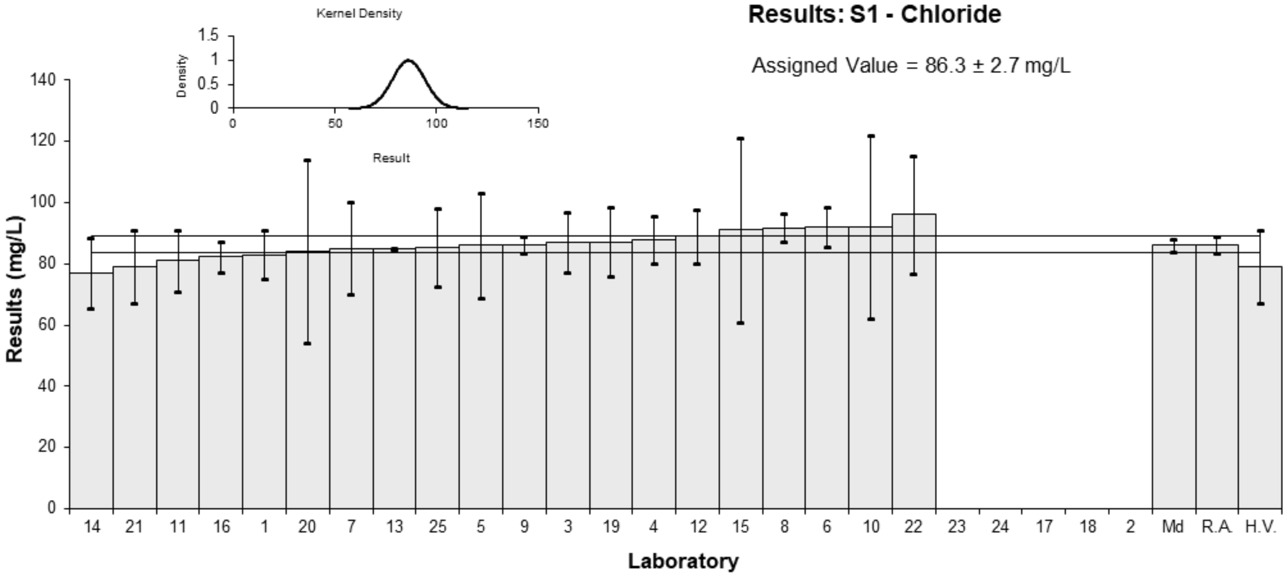
Sample No.	S1
Matrix.	River Water
Analyte.	Chloride
Units	mg/L

Participant Results

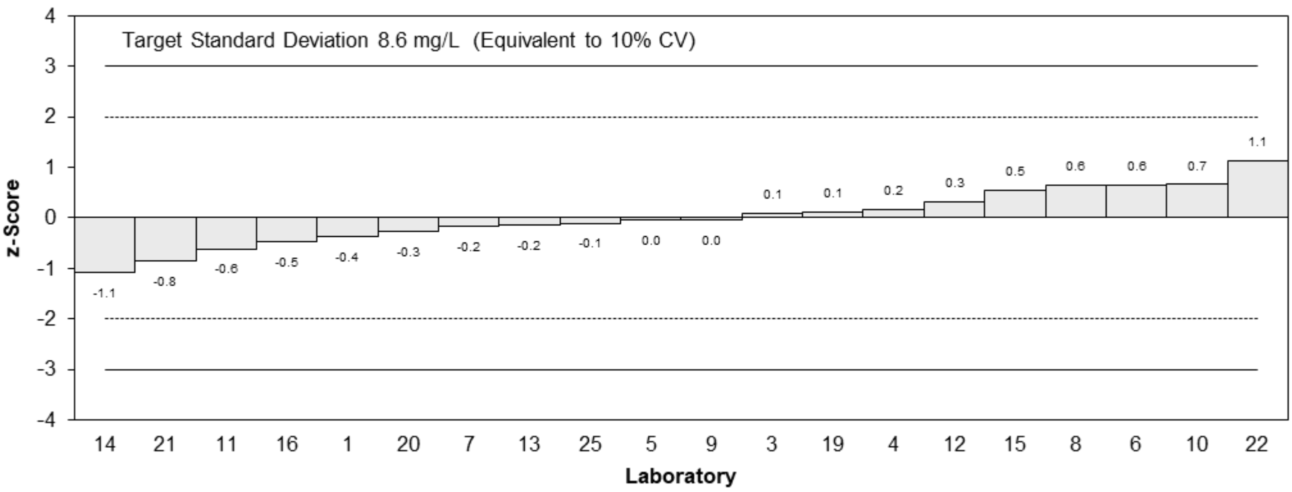
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	83	8	-0.38	-0.39
2	NT	NT		
3	87	10	0.08	0.07
4	87.8	7.66	0.17	0.18
5	86	17	-0.03	-0.02
6	91.9	6.4	0.65	0.81
7	84.941	15.035	-0.16	-0.09
8	91.8	4.59	0.64	1.03
9	86	2.7	-0.03	-0.08
10	92	30	0.66	0.19
11	81	10	-0.61	-0.51
12	89	8.8	0.31	0.29
13	85	0.3	-0.15	-0.48
14	77	11.6	-1.08	-0.78
15	91	30	0.54	0.16
16	82.2	5.0	-0.48	-0.72
17	NT	NT		
18	NT	NT		
19	87.2	11.3	0.10	0.08
20	84	30	-0.27	-0.08
21	79	12	-0.85	-0.59
22	96	19.2	1.12	0.50
23	NR	NR		
24	NR	NR		
25	85.4	12.8	-0.10	-0.07

Statistics

Assigned Value	86.3	2.7
Spike	Not Spiked	
Homogeneity Value	79	12
Robust Average	86.3	2.7
Median	86.0	2.1
Mean	86.4	
N	20	
Max.	96	
Min.	77	
Robust SD	4.9	
Robust CV	5.7%	



z-Scores: S1 - Chloride



En-Scores: S1 - Chloride

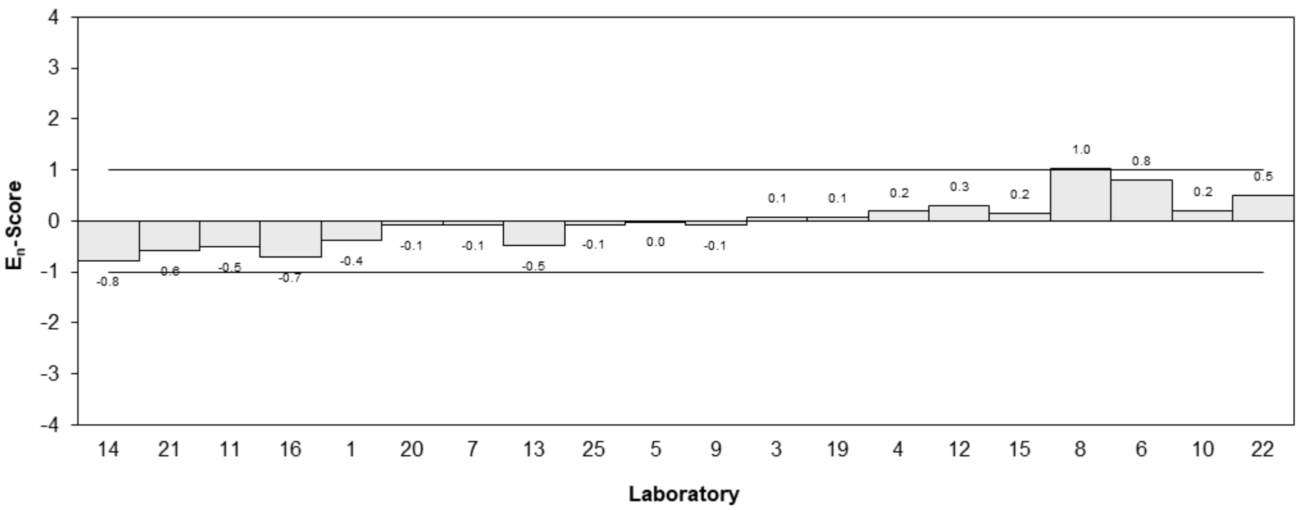


Figure 4

Table 7

Sample Details

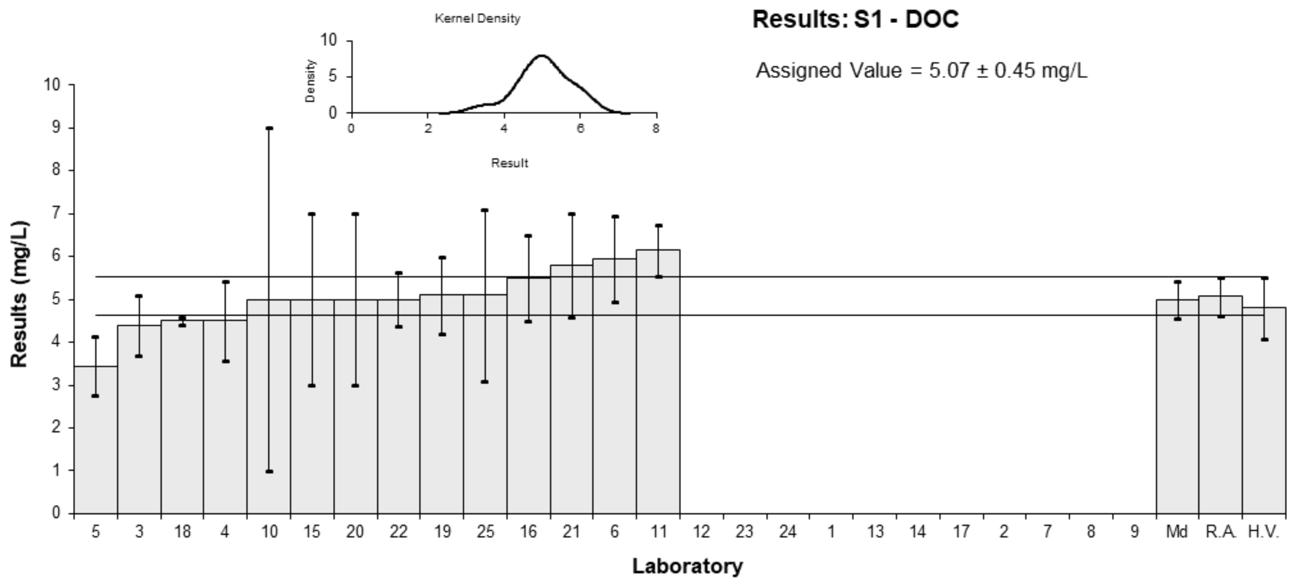
Sample No.	S1
Matrix.	River Water
Analyte.	DOC
Units	mg/L

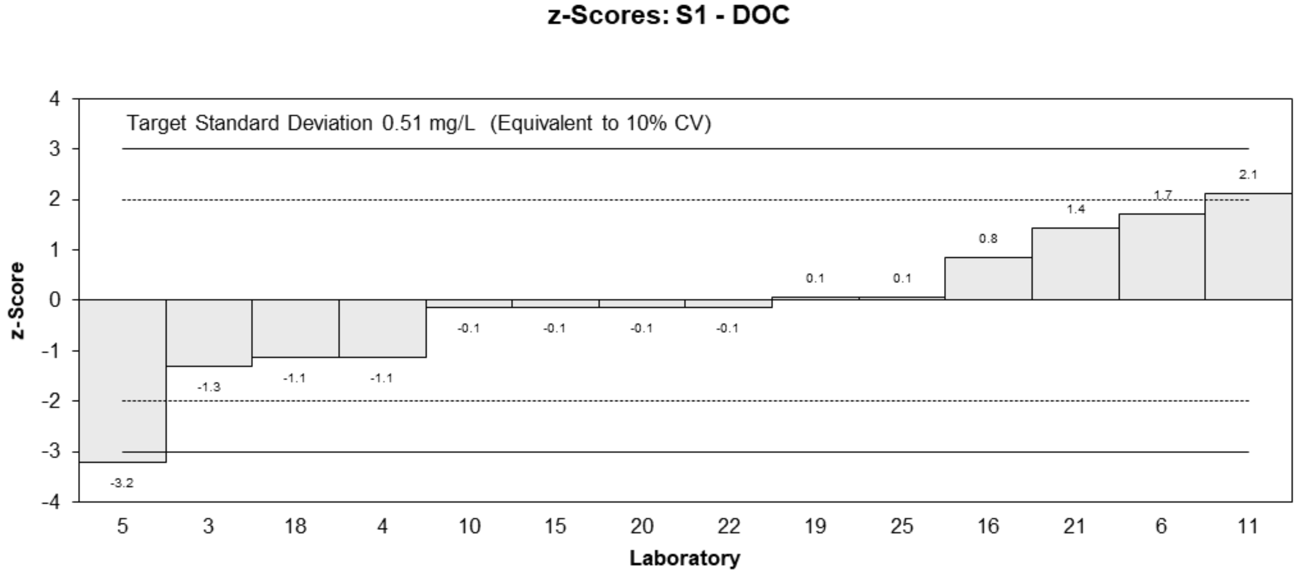
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	4.4	0.7	-1.32	-0.81
4	4.5	0.92	-1.12	-0.56
5	3.44	0.69	-3.21	-1.98
6	5.94	1	1.72	0.79
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	5	4	-0.14	-0.02
11	6.15	0.6	2.13	1.44
12	<1	NR		
13	NT	NT		
14	NT	NT		
15	5	2	-0.14	-0.03
16	5.5	1.0	0.85	0.39
17	NT	NT		
18	4.5	0.1	-1.12	-1.24
19	5.1	0.9	0.06	0.03
20	5	2.0	-0.14	-0.03
21	5.8	1.2	1.44	0.57
22	5	0.62	-0.14	-0.09
23	NR	NR		
24	NR	NR		
25	5.1	2	0.06	0.01

Statistics

Assigned Value	5.07	0.45
Spike	Not Spiked	
Homogeneity Value	4.80	0.72
Robust Average	5.07	0.45
Median	5.00	0.43
Mean	5.03	
N	14	
Max.	6.15	
Min.	3.44	
Robust SD	0.68	
Robust CV	13%	


Results: S1 - DOC
Assigned Value = 5.07 ± 0.45 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5
3
18
4
10
15
20
22
19
25
16
21
6
11
12
23
24
1
13
14
17
2
7
8
9
Md
R.A.
H.V.


z-Scores: S1 - DOC
Target Standard Deviation 0.51 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
-3.2
-1.3
-1.1
-1.1
-0.1
-0.1
-0.1
-0.1
0.1
0.1
0.8
1.4
1.7
2.1

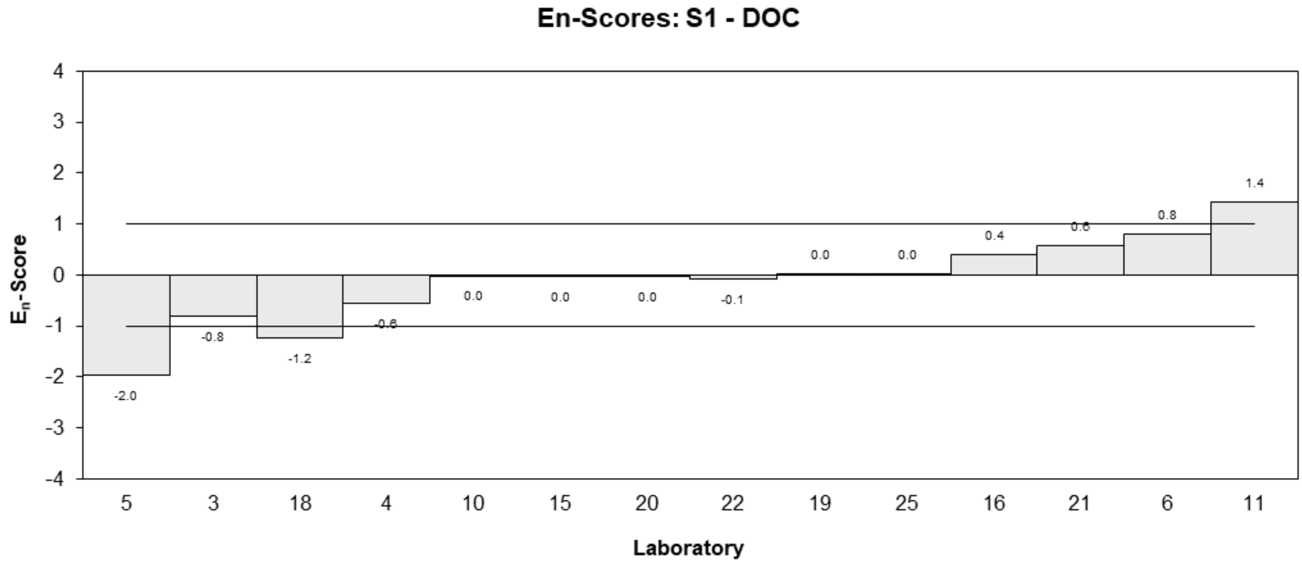

En-Scores: S1 - DOC
En-Score
Laboratory
-2.0
-0.8
-1.2
-0.6
0.0
0.0
0.0
-0.1
0.0
0.0
0.4
0.6
0.8
1.4

Figure 5

Table 8

Sample Details

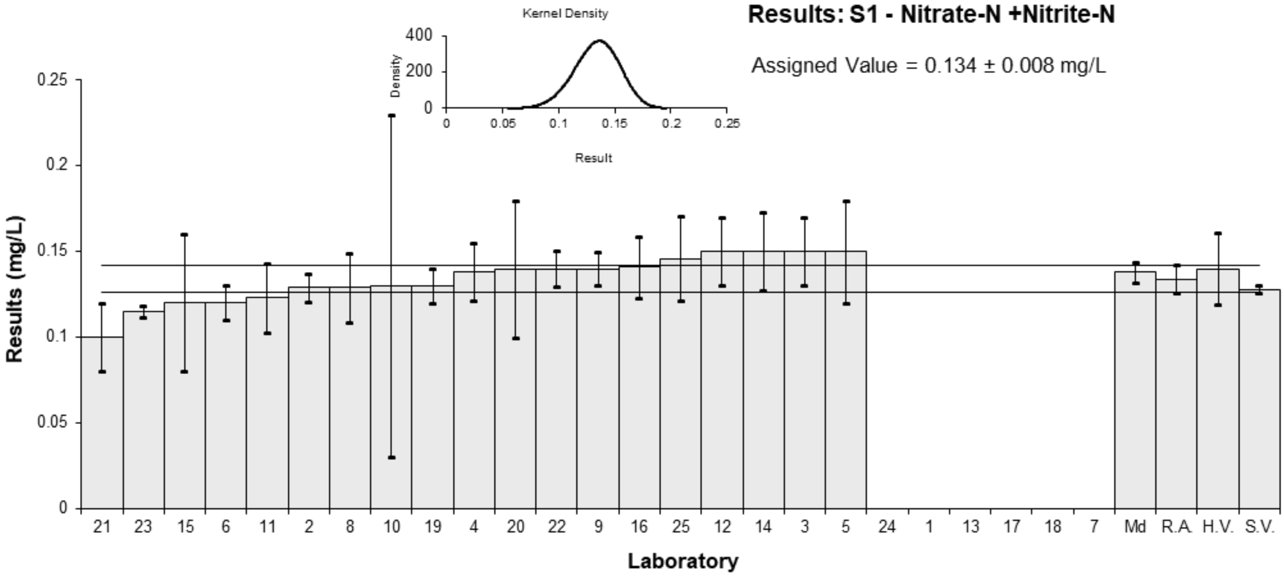
Sample No.	S1
Matrix.	River Water
Analyte.	Nitrate-N +Nitrite-N
Units	mg/L

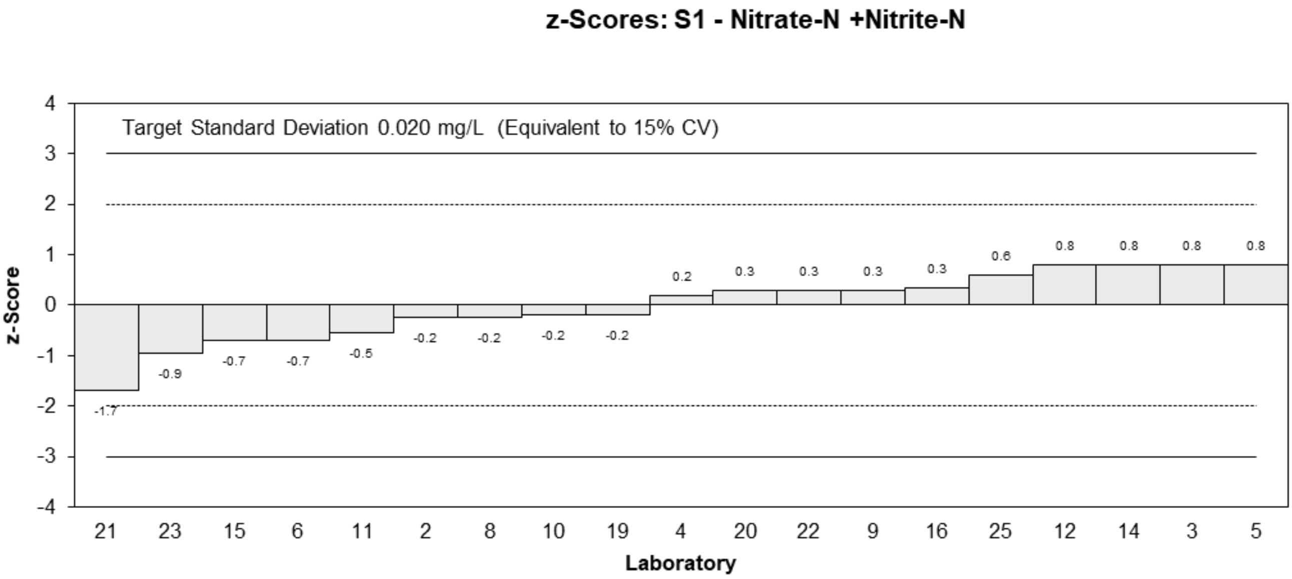
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.129	0.00816	-0.25	-0.44
3	0.15	0.02	0.80	0.74
4	0.138	0.017	0.20	0.21
5	0.15	0.03	0.80	0.52
6	0.12	0.01	-0.70	-1.09
7	NT	NT		
8	0.129	0.02	-0.25	-0.23
9	0.140	0.01	0.30	0.47
10	0.13	0.1	-0.20	-0.04
11	0.123	0.02	-0.55	-0.51
12	0.15	0.02	0.80	0.74
13	NT	NT		
14	0.150	0.023	0.80	0.66
15	0.12	0.04	-0.70	-0.34
16	0.141	0.018	0.35	0.36
17	NT	NT		
18	NT	NT		
19	0.13	0.01	-0.20	-0.31
20	0.14	0.04	0.30	0.15
21	0.10	0.02	-1.69	-1.58
22	0.14	0.0104	0.30	0.46
23	0.115	0.003	-0.95	-2.22
24	NR	NR		
25	0.146	0.025	0.60	0.46

Statistics

Assigned Value	0.134	0.008
Spike	0.128	0.002
Homogeneity Value	0.140	0.021
Robust Average	0.134	0.008
Median	0.138	0.006
Mean	0.134	
N	19	
Max.	0.15	
Min.	0.1	
Robust SD	0.014	
Robust CV	10%	


Results: S1 - Nitrate-N +Nitrite-N
Assigned Value = 0.134 ± 0.008 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory


z-Scores: S1 - Nitrate-N +Nitrite-N
Target Standard Deviation 0.020 mg/L (Equivalent to 15% CV)
z-Score
Laboratory

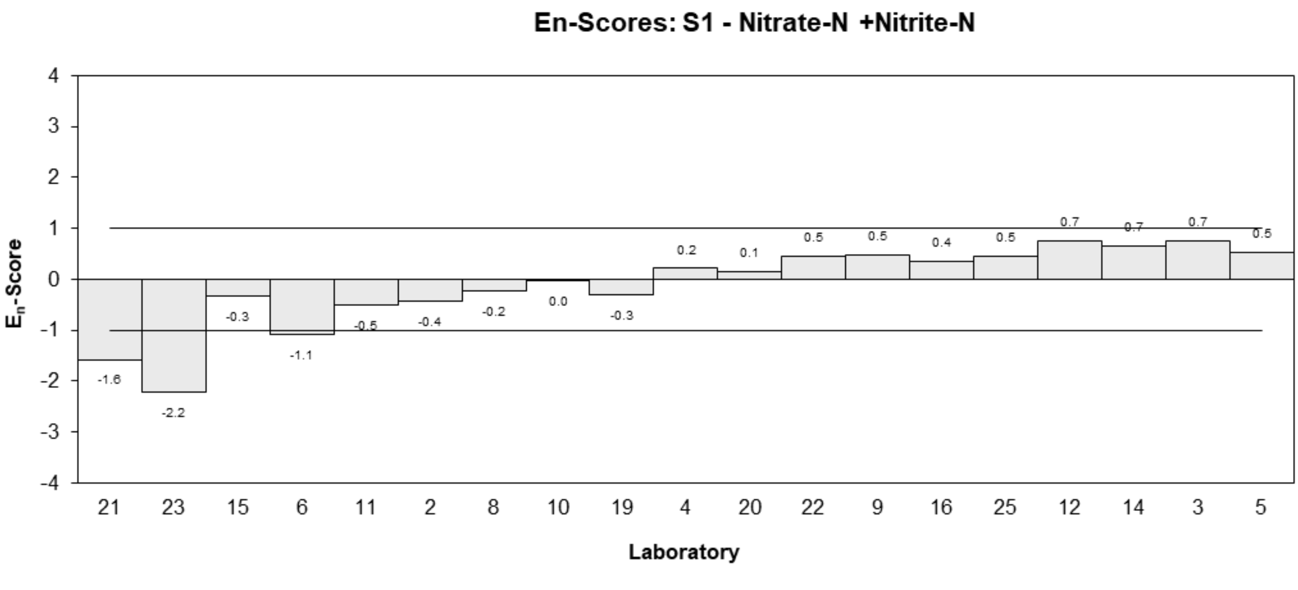

En-Scores: S1 - Nitrate-N +Nitrite-N
En-Score
Laboratory

Figure 6

Table 9

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	0.037	0.007	0.81	0.54
4	0.035	0.003	0.40	0.50
5	0.029	0.005	-0.81	-0.71
6	0.03	0.01	-0.61	-0.29
7	0.032	0.004	-0.20	-0.21
8	NT	NT		
9	0.037	0.004	0.81	0.84
10	0.029	0.02	-0.81	-0.20
11	0.032	0.008	-0.20	-0.12
12	0.04	0.04	1.41	0.17
13	NT	NT		
14	0.037	0.007	0.81	0.54
15	0.03	0.01	-0.61	-0.29
16	0.0224	0.0029	-2.14	-2.72
17	NT	NT		
18	NT	NT		
19	0.032	0.004	-0.20	-0.21
20	0.03	0.01	-0.61	-0.29
21	0.039	0.008	1.21	0.71
22	0.03	0.0028	-0.61	-0.79
23	0.035	0.002	0.40	0.61
24	NR	NR		
25	0.034	0.005	0.20	0.18

Statistics

Assigned Value	0.0330	0.0026
Spike	0.0300	0.0013
Homogeneity Value	0.0377	0.0057
Robust Average	0.0330	0.0026
Median	0.0320	0.0022
Mean	0.0328	
N	18	
Max.	0.04	
Min.	0.0224	
Robust SD	0.0043	
Robust CV	13%	

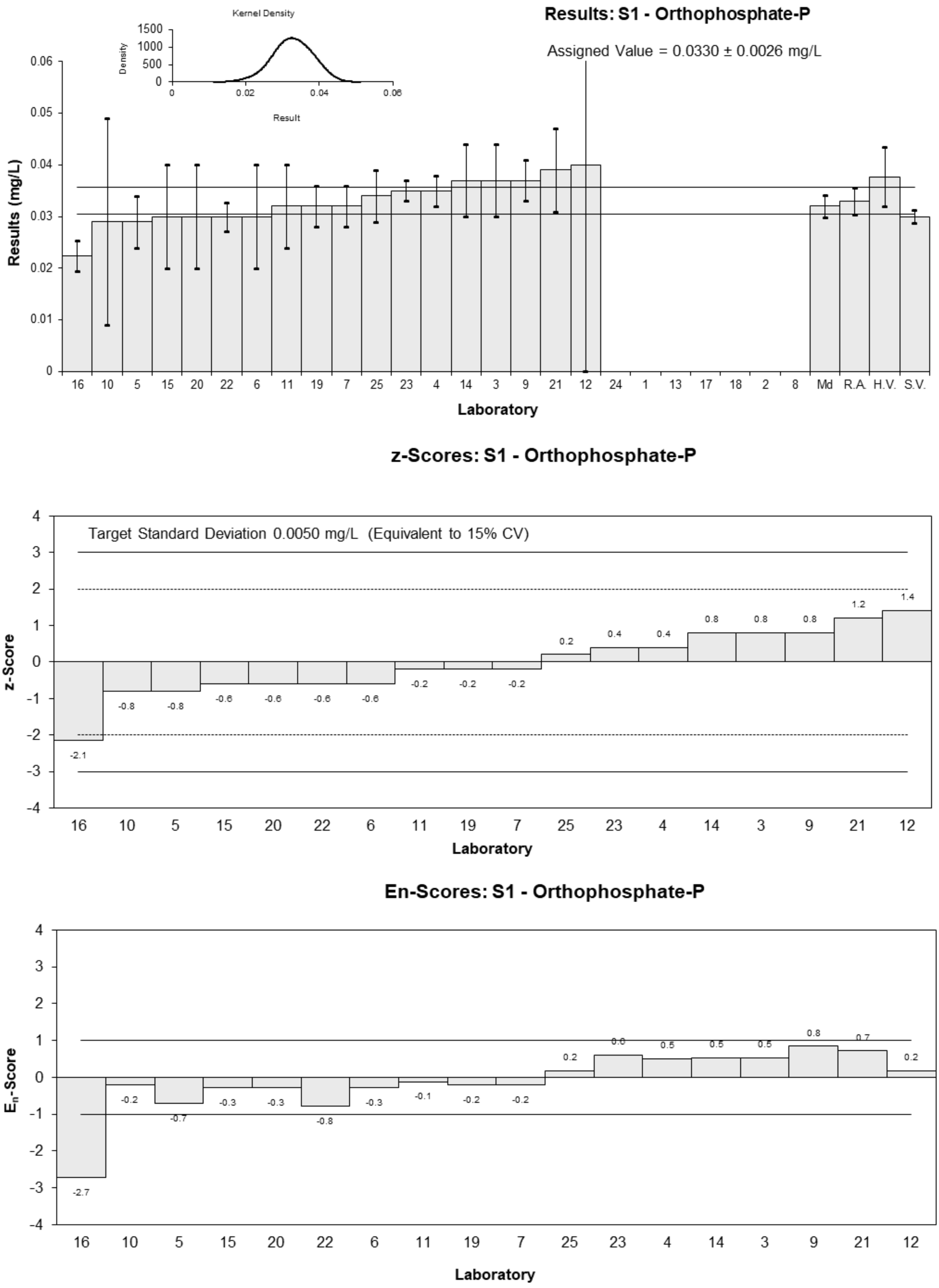

Results: S1 - Orthophosphate-P
Assigned Value = 0.0330 ± 0.0026 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
16 10 5 15 20 22 6 11 19 7 25 23 4 14 3 9 21 12 24 1 13 17 18 2 8 Md R.A. H.V. S.V.
z-Scores: S1 - Orthophosphate-P
Target Standard Deviation 0.0050 mg/L (Equivalent to 15% CV)
z-Score
-2.1 -0.8 -0.8 -0.6 -0.6 -0.6 -0.6 -0.2 -0.2 -0.2 0.2 0.4 0.4 0.8 0.8 0.8 1.2 1.4
16 10 5 15 20 22 6 11 19 7 25 23 4 14 3 9 21 12
Laboratory
En-Scores: S1 - Orthophosphate-P
E_n-Score
-2.7 -0.2 -0.7 -0.3 -0.3 -0.8 -0.3 -0.1 -0.2 -0.2 0.2 0.5 0.5 0.5 0.8 0.7 0.2
16 10 5 15 20 22 6 11 19 7 25 23 4 14 3 9 21 12
Laboratory

Figure 7

Table 10

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	19	2	-0.26	-0.23
2	NT	NT		
3	18.4	2.6	-0.56	-0.40
4	20.2	3.1	0.36	0.22
5	17.43	5.2	-1.06	-0.39
6	19.7	3.0	0.10	0.06
7	17.0	2.41	-1.28	-0.97
8	20	1	0.26	0.37
9	17	1.4	-1.28	-1.50
10	20	7	0.26	0.07
11	21	2.0	0.77	0.68
12	20	2.7	0.26	0.18
13	19	0.7	-0.26	-0.44
14	19.6	2.94	0.05	0.03
15	21	7	0.77	0.21
16	17.8	1.2	-0.87	-1.13
17	NT	NT		
18	NT	NT		
19	20	2	0.26	0.23
20	22	7.0	1.28	0.35
21	21	3	0.77	0.48
22	19	1.98	-0.26	-0.23
23	NR	NR		
24	27	4.1	3.85	1.79
25	19.0	2.8	-0.26	-0.17

Statistics

Assigned Value	19.5	0.9
Spike	Not Spiked	
Homogeneity Value	19.3	2.9
Robust Average	19.5	0.9
Median	19.7	0.5
Mean	19.8	
N	21	
Max.	27	
Min.	17	
Robust SD	1.6	
Robust CV	8.4%	

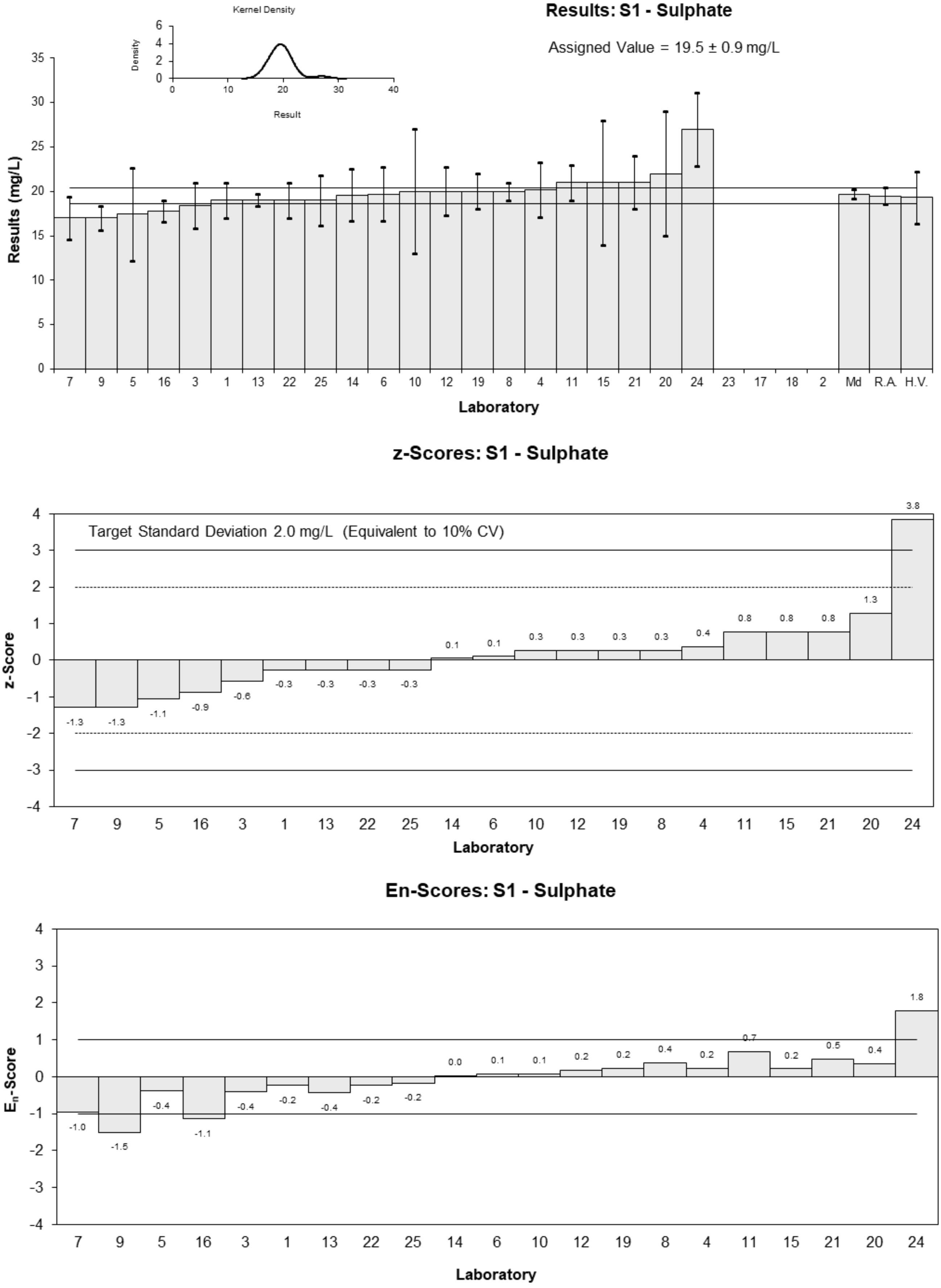

Results: S1 - Sulphate
Assigned Value = 19.5 ± 0.9 mg/L
Kernel Density
Density
Result
Results (mg/L)
7 9 5 16 3 1 13 22 25 14 6 10 12 19 8 4 11 15 21 20 24 23 17 18 2 Md R.A. H.V.
Laboratory
z-Scores: S1 - Sulphate
Target Standard Deviation 2.0 mg/L (Equivalent to 10% CV)
z-Score
-1.3 -1.3 -1.1 -0.9 -0.6 -0.3 -0.3 -0.3 -0.3 0.1 0.1 0.3 0.3 0.3 0.3 0.4 0.8 0.8 0.8 1.3 3.8
7 9 5 16 3 1 13 22 25 14 6 10 12 19 8 4 11 15 21 20 24
Laboratory
En-Scores: S1 - Sulphate
En-Score
-1.0 -1.5 -0.4 -1.1 -0.4 -0.2 -0.4 -0.2 -0.2 0.0 0.1 0.1 0.2 0.2 0.4 0.2 0.7 0.2 0.5 0.4 1.8
7 9 5 16 3 1 13 22 25 14 6 10 12 19 8 4 11 15 21 20 24
Laboratory

Figure 8

Table 11

Sample Details

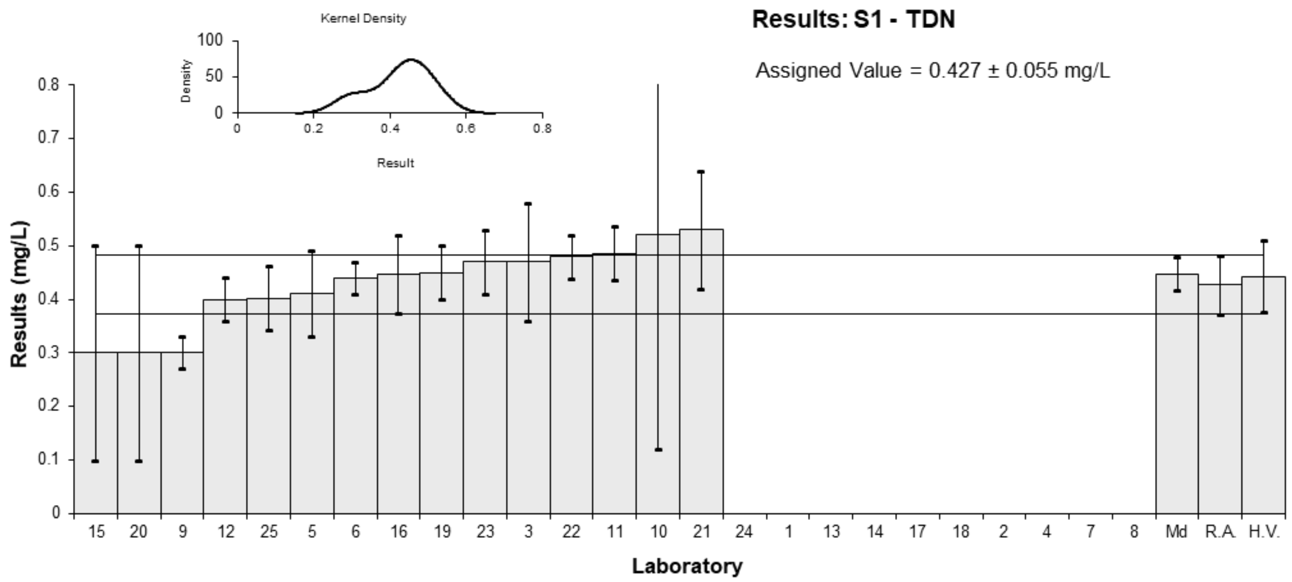
Sample No.	S1
Matrix.	River Water
Analyte.	TDN
Units	mg/L

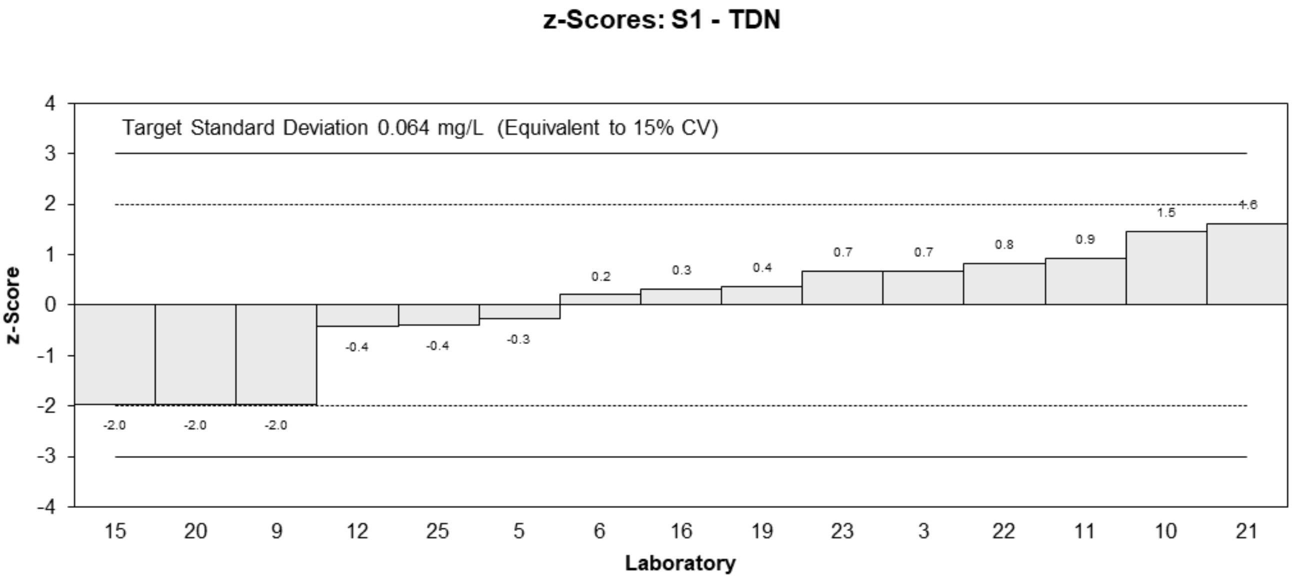
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	0.47	0.11	0.67	0.35
4	NT	NT		
5	0.41	0.08	-0.27	-0.18
6	0.44	0.03	0.20	0.21
7	NT	NT		
8	NT	NT		
9	0.3	0.03	-1.98	-2.03
10	0.52	0.4	1.45	0.23
11	0.486	0.05	0.92	0.79
12	0.4	0.04	-0.42	-0.40
13	NT	NT		
14	NT	NT		
15	0.3	0.2	-1.98	-0.61
16	0.448	0.073	0.33	0.23
17	NT	NT		
18	NT	NT		
19	0.45	0.05	0.36	0.31
20	0.3	0.2	-1.98	-0.61
21	0.53	0.11	1.61	0.84
22	0.48	0.041	0.83	0.77
23	0.47	0.06	0.67	0.53
24	NR	NR		
25	0.402	0.06	-0.39	-0.31

Statistics

Assigned Value	0.427	0.055
Spike	Not Spiked	
Homogeneity Value	0.443	0.067
Robust Average	0.427	0.055
Median	0.448	0.031
Mean	0.427	
N	15	
Max.	0.53	
Min.	0.3	
Robust SD	0.086	
Robust CV	20%	


Results: S1 - TDN
Assigned Value = 0.427 ± 0.055 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15 20 9 12 25 5 6 16 19 23 3 22 11 10 21 24 1 13 14 17 18 2 4 7 8 Md R.A. H.V.


z-Scores: S1 - TDN
Target Standard Deviation 0.064 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
15 20 9 12 25 5 6 16 19 23 3 22 11 10 21
-2.0 -2.0 -2.0 -0.4 -0.4 -0.3 0.2 0.3 0.4 0.7 0.7 0.8 0.9 1.5 1.6

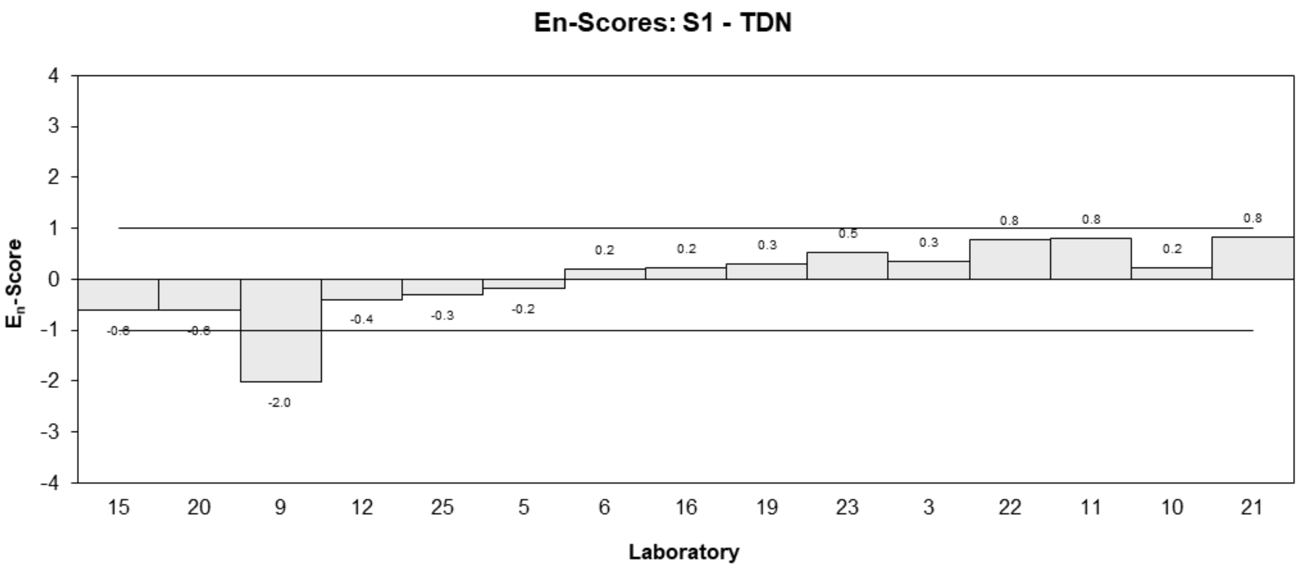

En-Scores: S1 - TDN
En-Score
Laboratory
15 20 9 12 25 5 6 16 19 23 3 22 11 10 21
-0.6 -0.6 -2.0 -0.4 -0.3 -0.2 0.2 0.2 0.3 0.5 0.3 0.8 0.8 0.2 0.8

Figure 9

Table 12

Sample Details

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

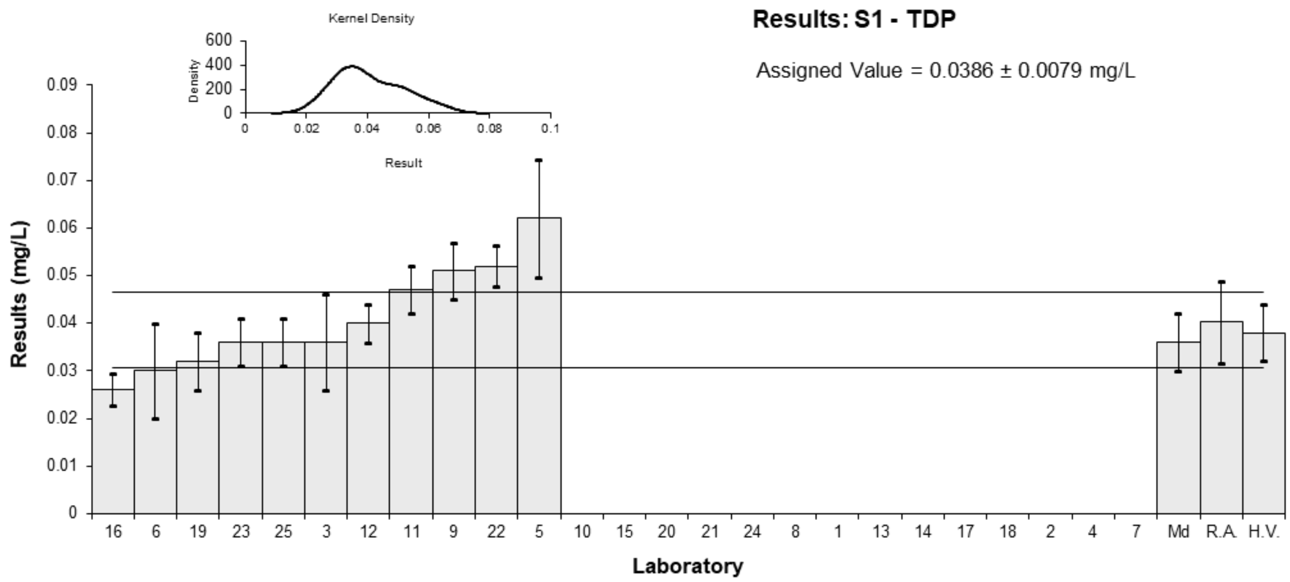
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	0.036	0.010	-0.34	-0.20
4	NT	NT		
5	0.062	0.0124	3.03	1.59
6	0.03	0.01	-1.11	-0.67
7	NT	NT		
8	NR	NR		
9	0.051	0.006	1.61	1.25
10	<0.1	NR		
11	0.047	0.005	1.09	0.90
12	0.04	0.004	0.18	0.16
13	NT	NT		
14	NT	NT		
15	<0.1	NR		
16	0.0261	0.0034	-1.62	-1.45
17	NT	NT		
18	NT	NT		
19	0.032	0.006	-0.85	-0.67
20	<0.1	NR		
21	NR	NR		
22	0.052	0.0043	1.74	1.49
23	0.036	0.005	-0.34	-0.28
24	NR	NR		
25	0.036	0.005	-0.34	-0.28

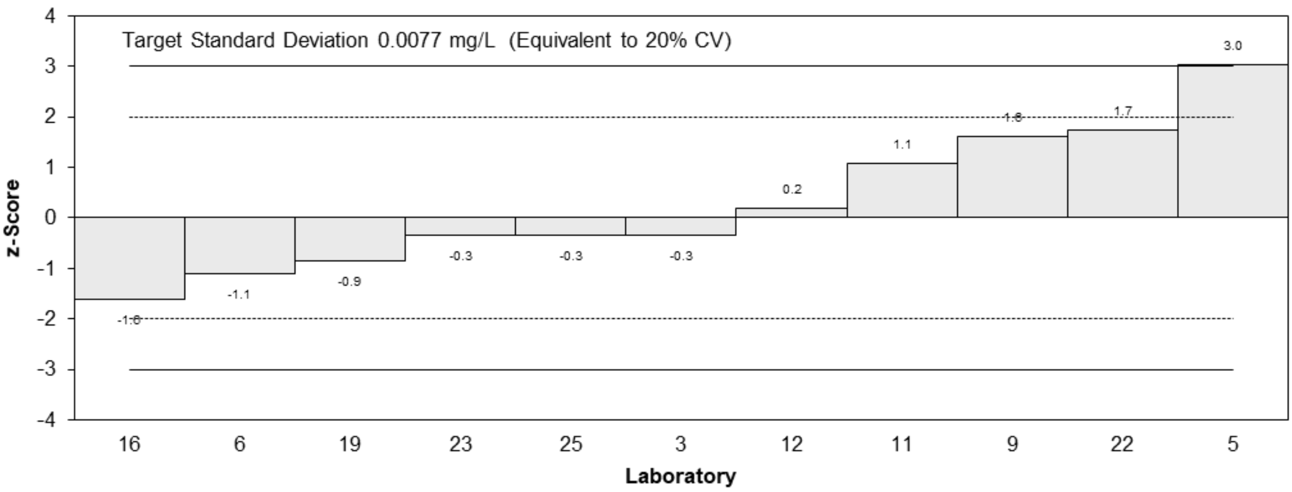
Statistics

Assigned Value*	0.0386	0.0079
Spike	Not Spiked	
Homogeneity Value	0.0380	0.0060
Robust Average	0.0403	0.0086
Median	0.0360	0.0060
Mean	0.0407	
N	11	
Max.	0.062	
Min.	0.0261	
Robust SD	0.011	
Robust CV	28%	

*Robust Average excluding laboratory 5.



z-Scores: S1 - TDP



En-Scores: S1 - TDP

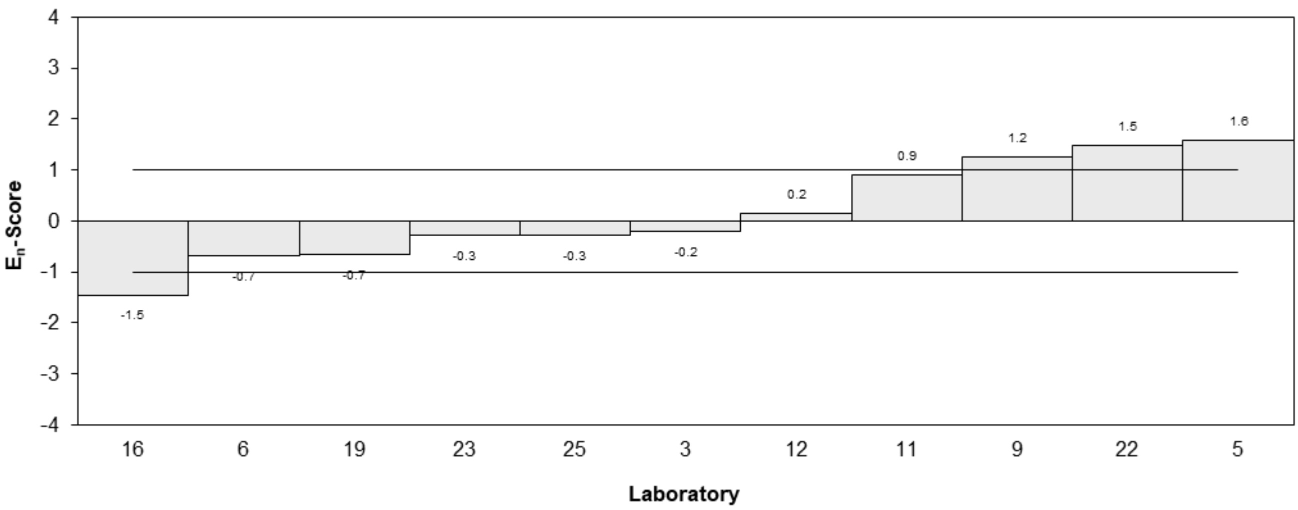


Figure 10

Table 13

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	48	3	-0.20	-0.31
2	53.9	10.2	1.00	0.48
3	47	2	-0.41	-0.86
4	47	8.6	-0.41	-0.23
5	49	9.8	0.00	0.00
6	48.3	3.9	-0.14	-0.17
7	51.4	3.54	0.49	0.64
8	50.43	7.56	0.29	0.19
9	52	2.9	0.61	0.96
10	51	20	0.41	0.10
11	50	5	0.20	0.19
12	48	4.7	-0.20	-0.21
13	46	34	-0.61	-0.09
14	52.5	7.88	0.71	0.44
15	50	20	0.20	0.05
16	NT	NT		
17	46	2.94	-0.61	-0.94
18	50	1	0.20	0.64
19	48	6	-0.20	-0.16
20	50	20	0.20	0.05
21	47	7	-0.41	-0.28
22	48	5.5	-0.20	-0.18
23	NT	NT		
24	48	4	-0.20	-0.24
25	48	7	-0.20	-0.14

Statistics

Assigned Value	49.0	1.2
Spike	Not Spiked	
Robust Average	49.0	1.2
Median	48.3	1.1
Mean	49.1	
N	23	
Max.	53.9	
Min.	46	
Robust SD	2.2	
Robust CV	4.5%	

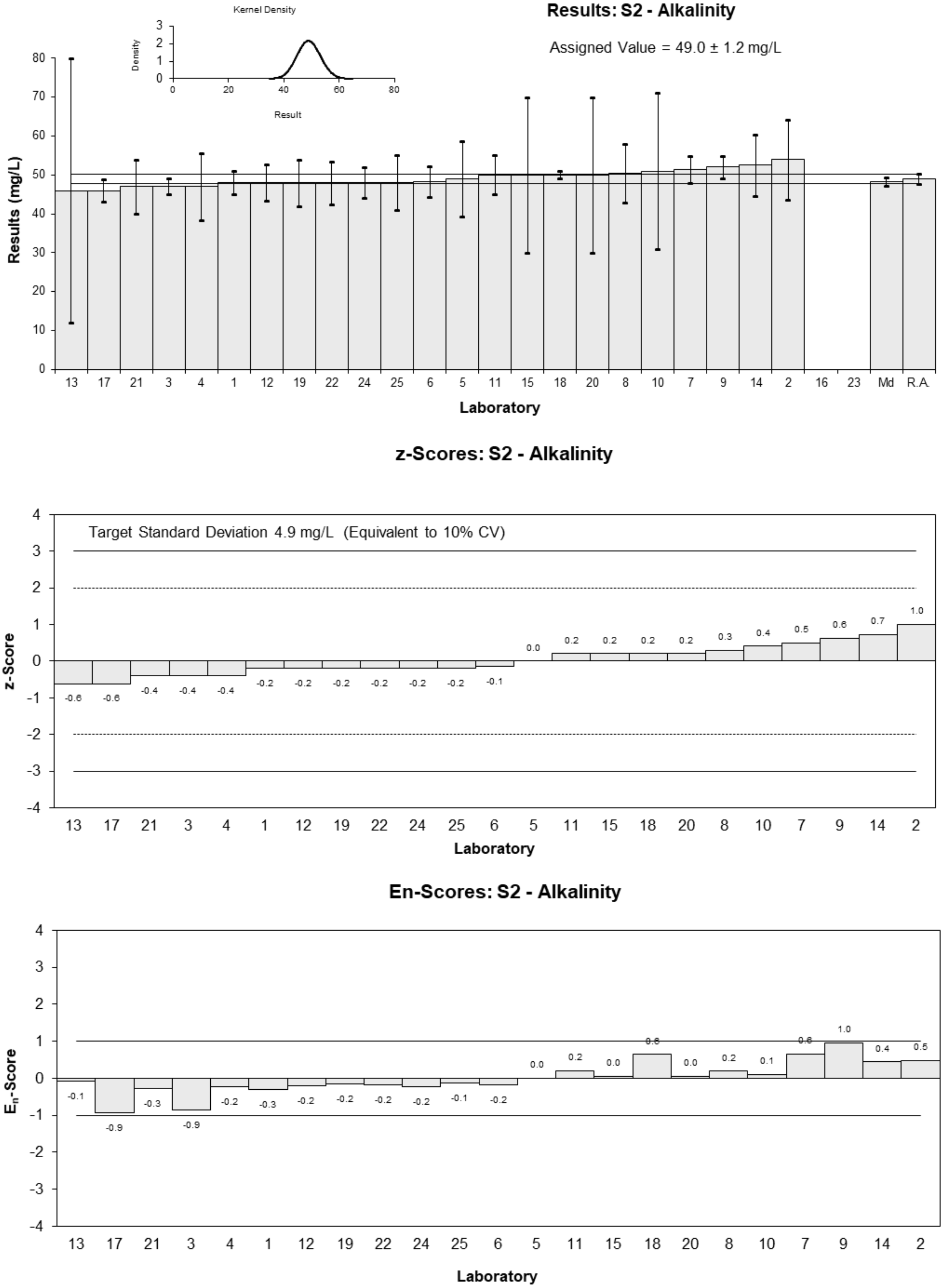

Results: S2 - Alkalinity
Assigned Value = 49.0 ± 1.2 mg/L
Kernel Density
Density
Result
Results (mg/L)
13 17 21 3 4 1 12 19 22 24 25 6 5 11 15 18 20 8 10 7 9 14 2 16 23 Md R.A.
Laboratory
z-Scores: S2 - Alkalinity
Target Standard Deviation 4.9 mg/L (Equivalent to 10% CV)
z-Score
-0.6 -0.6 -0.4 -0.4 -0.4 -0.2 -0.2 -0.2 -0.2 -0.2 -0.2 -0.1 0.0 0.2 0.2 0.2 0.2 0.3 0.4 0.5 0.6 0.7 1.0
13 17 21 3 4 1 12 19 22 24 25 6 5 11 15 18 20 8 10 7 9 14 2
Laboratory
En-Scores: S2 - Alkalinity
E_n-Score
-0.1 -0.9 -0.3 -0.9 -0.2 -0.3 -0.2 -0.2 -0.2 -0.2 -0.1 -0.2 0.0 0.2 0.0 0.6 0.0 0.2 0.1 0.6 1.0 0.4 0.5
13 17 21 3 4 1 12 19 22 24 25 6 5 11 15 18 20 8 10 7 9 14 2
Laboratory

Figure 11

Table 14

Sample Details

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

Participant Results

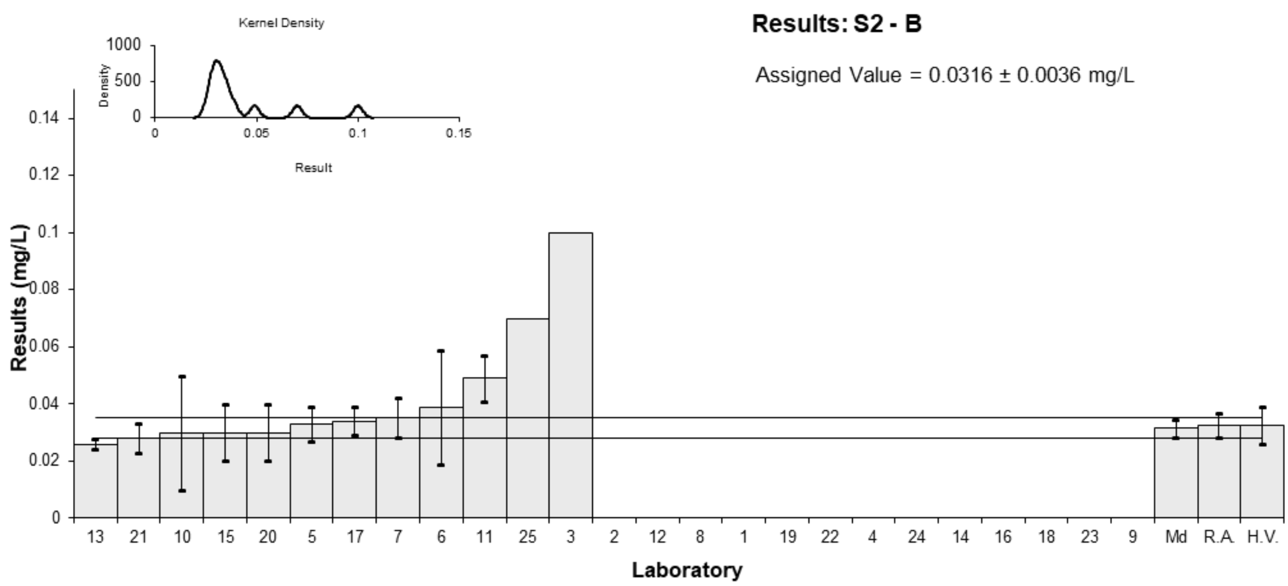
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<0.1	NR		
2	< 0.05	NR		
3	136	34	43028	4.00
4	<0.1	NR		
5	0.033	0.006	0.44	0.20
6	0.039	0.02	2.34	0.36
7	0.0352	0.0070	1.14	0.46
8	<0.05	0.01		
9	NT	NT		
10	0.03	0.02	-0.51	-0.08
11	0.049	0.008	5.51	1.98
12	<0.05	NR		
13	0.026	0.002	-1.77	-1.36
14	NT	NT		
15	0.03	0.01	-0.51	-0.15
16	NT	NT		
17	0.034	0.005	0.76	0.39
18	NT	NT		
19	<0.1	NR		
20	0.03	0.01	-0.51	-0.15
21	0.028	0.005	-1.14	-0.58
22	<0.1	NR		
23	NT	NT		
24	NR	NR		
25	35	5	11066	6.99

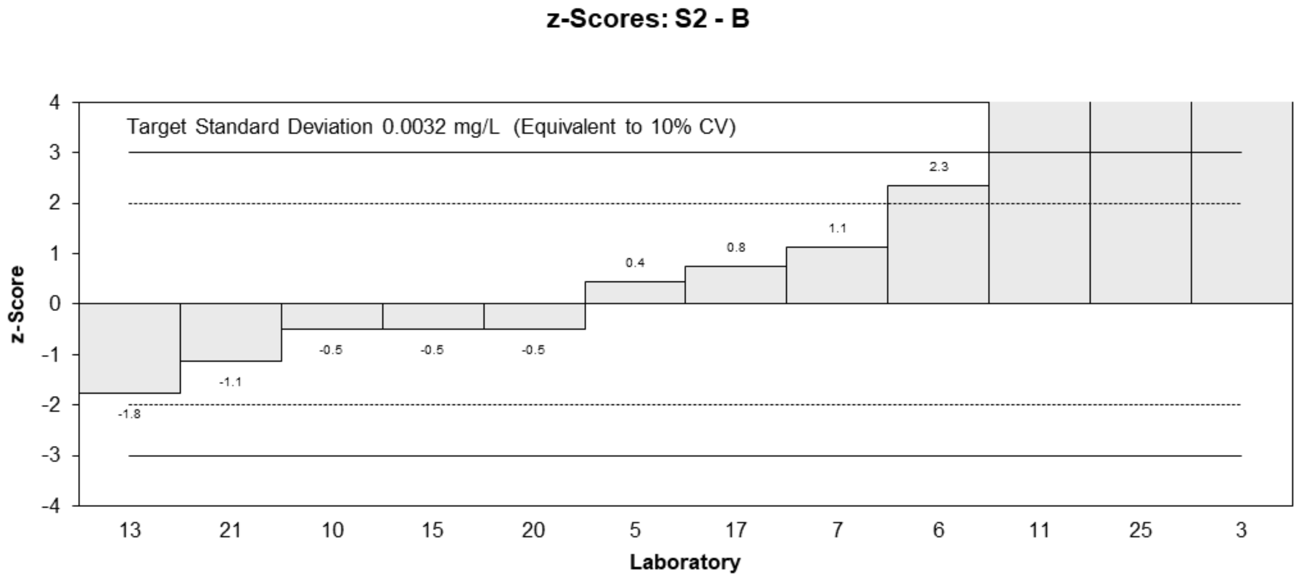
Statistics*

Assigned Value**	0.0316	0.0036
Spike	Not Spiked	
Homogeneity Value	0.0325	0.0065
Robust Average	0.0326	0.0042
Median	0.0315	0.0032
Mean	0.0334	
N	10	
Max.	0.049	
Min.	0.026	
Robust SD	0.0053	
Robust CV	16%	

*Laboratories 3 and 25 were excluded from statistical calculation (extreme outlier).

**Robust Average excluding laboratory 11.


Results: S2 - B
Assigned Value = 0.0316 ± 0.0036 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
13 21 10 15 20 5 17 7 6 11 25 3 2 12 8 1 19 22 4 24 14 16 18 23 9 Md R.A. H.V.


z-Scores: S2 - B
Target Standard Deviation 0.0032 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.8 -1.1 -0.5 -0.5 -0.5 0.4 0.8 1.1 2.3
13 21 10 15 20 5 17 7 6 11 25 3

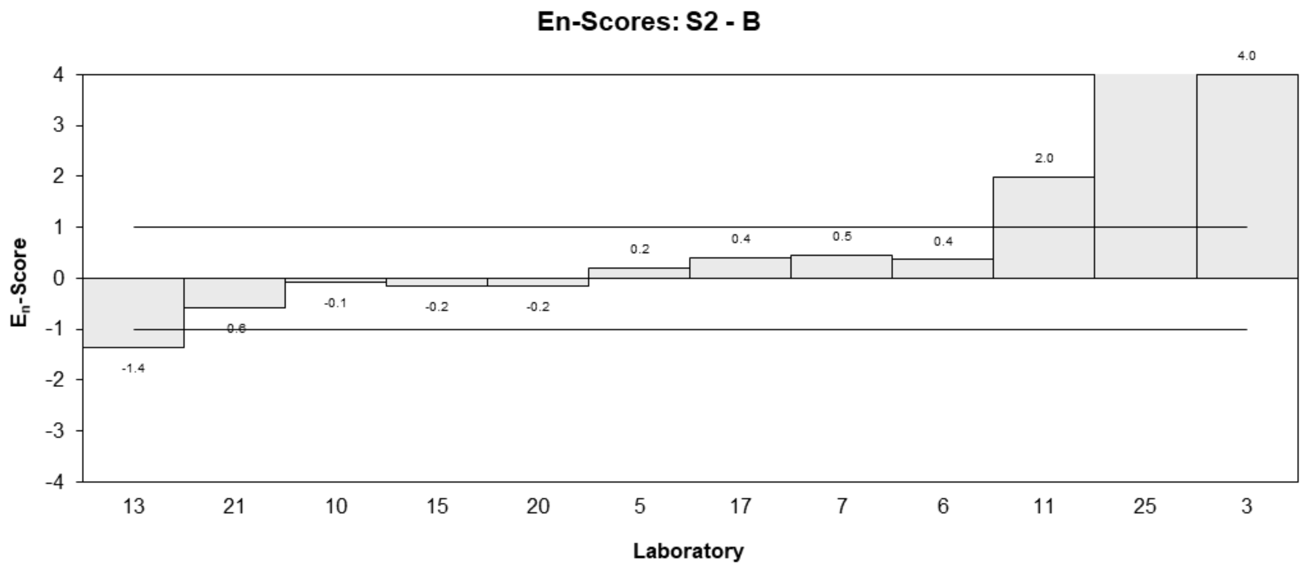

En-Scores: S2 - B
En-Score
Laboratory
-1.4 -0.6 -0.1 -0.2 -0.2 0.2 0.4 0.5 0.4 2.0 4.0
13 21 10 15 20 5 17 7 6 11 25 3

Figure 12

Table 15

Sample Details

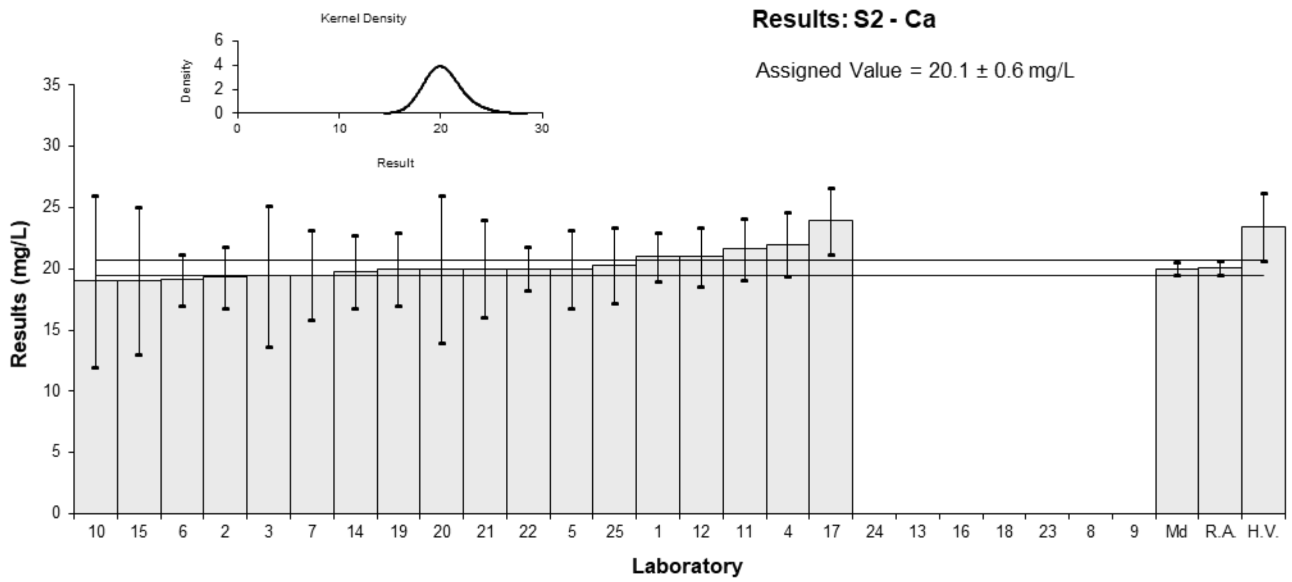
Sample No.	S2
Matrix.	River Water
Analyte.	Ca
Units	mg/L

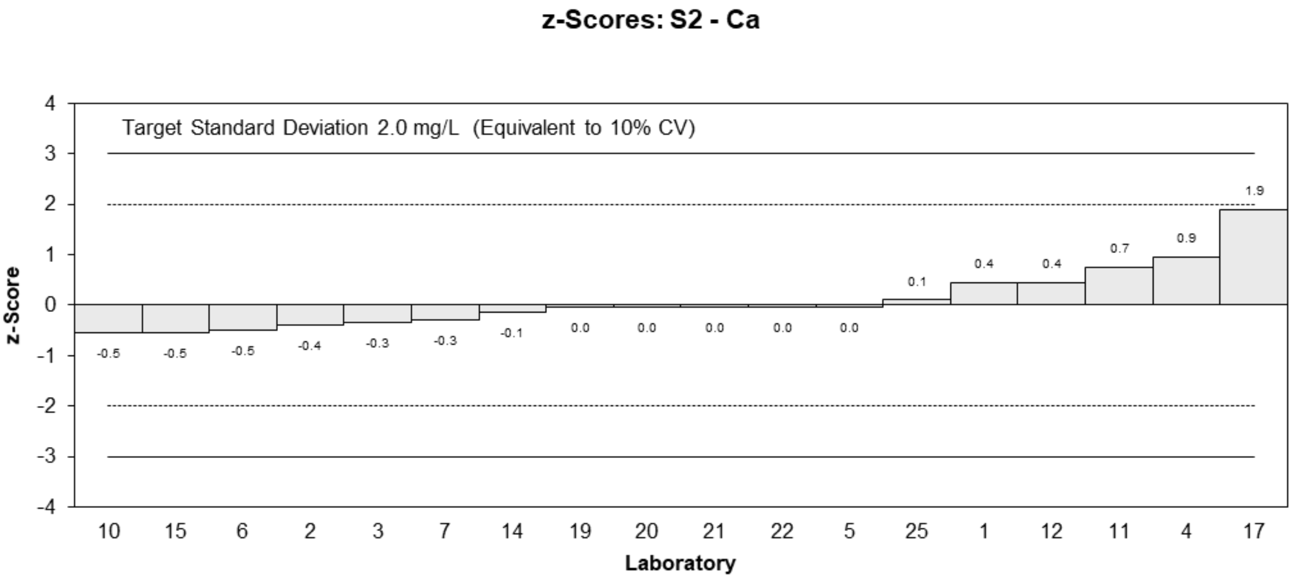
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	21	2	0.45	0.43
2	19.3	2.50	-0.40	-0.31
3	19.4	5.8	-0.35	-0.12
4	22	2.58	0.95	0.72
5	20	3.2	-0.05	-0.03
6	19.1	2.1	-0.50	-0.46
7	19.5	3.68	-0.30	-0.16
8	NT	NT		
9	NT	NT		
10	19	7	-0.55	-0.16
11	21.6	2.5	0.75	0.58
12	21	2.4	0.45	0.36
13	NT	NT		
14	19.8	2.97	-0.15	-0.10
15	19	6	-0.55	-0.18
16	NT	NT		
17	23.9	2.75	1.89	1.35
18	NT	NT		
19	20	3	-0.05	-0.03
20	20	6	-0.05	-0.02
21	20	4.0	-0.05	-0.02
22	20	1.8	-0.05	-0.05
23	NT	NT		
24	NR	NR		
25	20.3	3.1	0.10	0.06

Statistics

Assigned Value	20.1	0.6
Spike	Not Spiked	
Homogeneity Value	23.4	2.8
Robust Average	20.1	0.6
Median	20.0	0.5
Mean	20.3	
N	18	
Max.	23.9	
Min.	19	
Robust SD	1.0	
Robust CV	5.1%	


Results: S2 - Ca
Assigned Value = 20.1 ± 0.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
10 15 6 2 3 7 14 19 20 21 22 5 25 1 12 11 4 17 24 13 16 18 23 8 9 Md R.A. H.V.


z-Scores: S2 - Ca
Target Standard Deviation 2.0 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
10 15 6 2 3 7 14 19 20 21 22 5 25 1 12 11 4 17
-0.5 -0.5 -0.5 -0.4 -0.3 -0.3 -0.1 0.0 0.0 0.0 0.0 0.0 0.1 0.4 0.4 0.7 0.9 1.9

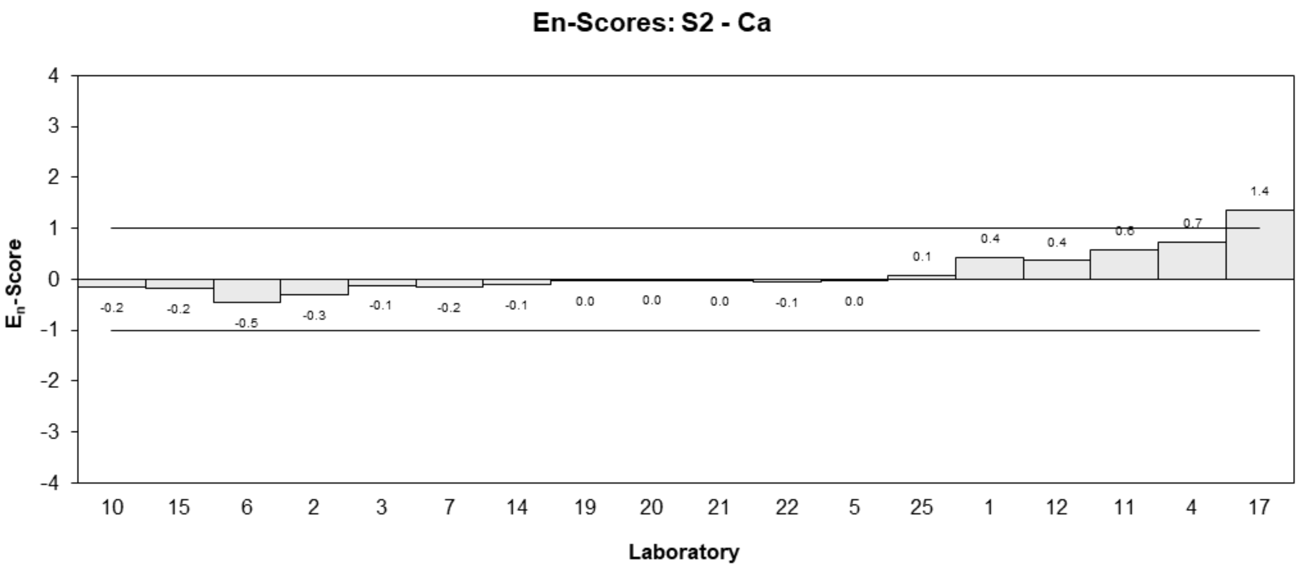

En-Scores: S2 - Ca
En-Score
Laboratory
10 15 6 2 3 7 14 19 20 21 22 5 25 1 12 11 4 17
-0.2 -0.2 -0.5 -0.3 -0.1 -0.2 -0.1 0.0 0.0 0.0 -0.1 0.0 0.1 0.4 0.4 0.6 0.7 1.4

Figure 13

Table 16

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Colour
Units	Pt-Co units

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	21	5	0.10	0.06
2	NT	NT		
3	23	2	0.74	0.79
4	20	NR	-0.23	-0.33
5	NT	NT		
6	22.2	4.4	0.48	0.31
7	NT	NT		
8	NT	NT		
9	20	1	-0.23	-0.30
10	20	10	-0.23	-0.07
11	19	2.0	-0.55	-0.59
12	25	NR	1.38	2.05
13	NT	NT		
14	NT	NT		
15	20	10	-0.23	-0.07
16	NT	NT		
17	25	7.5	1.38	0.55
18	13.1	0.1	-2.45	-3.61
19	20	2	-0.23	-0.24
20	30	10	3.00	0.91
21	18	4	-0.87	-0.60
22	20	2	-0.23	-0.24
23	NT	NT		
24	NR	NR		
25	16	5	-1.51	-0.87

Statistics

Assigned Value	20.7	2.1
Spike	Not Spiked	
Robust Average	20.7	2.1
Median	20.0	1.2
Mean	20.8	
N	16	
Max.	30	
Min.	13.1	
Robust SD	3.3	
Robust CV	16%	

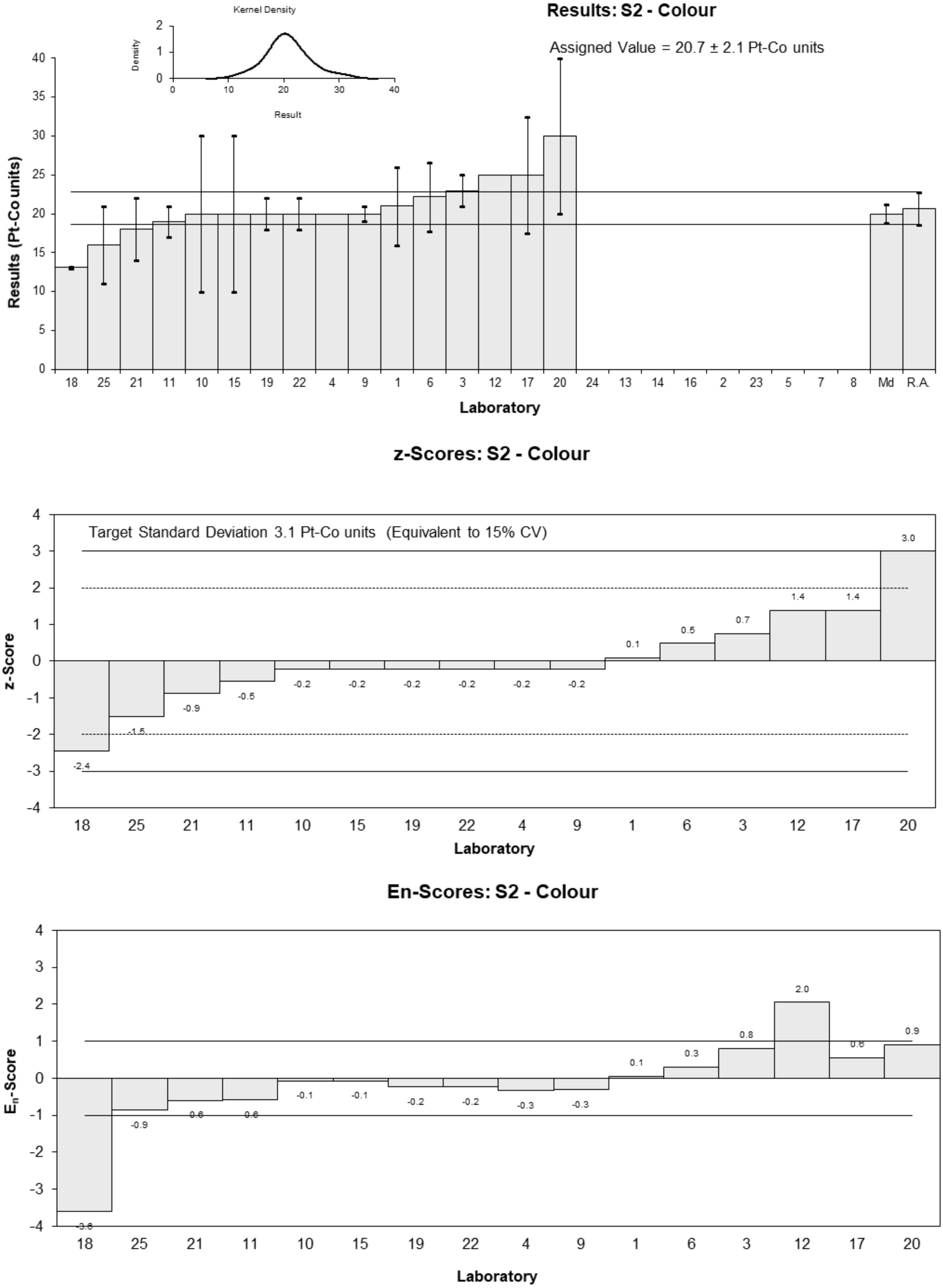

Results: S2 - Colour
Assigned Value = 20.7 ± 2.1 Pt-Co units
Kernel Density
Density
Result
Results (Pt-Co units)
Laboratory
18 25 21 11 10 15 19 22 4 9 1 6 3 12 17 20 24 13 14 16 2 23 5 7 8 Md R.A.
z-Scores: S2 - Colour
Target Standard Deviation 3.1 Pt-Co units (Equivalent to 15% CV)
z-Score
-2.4 -1.5 -0.9 -0.5 -0.2 -0.2 -0.2 -0.2 -0.2 -0.2 0.1 0.5 0.7 1.4 1.4 3.0
Laboratory
18 25 21 11 10 15 19 22 4 9 1 6 3 12 17 20
En-Scores: S2 - Colour
E_n-Score
-3.6 -0.9 -0.6 -0.6 -0.1 -0.1 -0.2 -0.2 -0.3 -0.3 0.1 0.3 0.8 2.0 0.6 0.9
Laboratory
18 25 21 11 10 15 19 22 4 9 1 6 3 12 17 20

Figure 14

Table 17

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	400	36	0.00	0.00
2	377	42.3	-1.64	-0.53
3	415	21	1.07	0.66
4	386	41	-1.00	-0.33
5	350	70	-3.57	-0.71
6	400.4	40.0	0.03	0.01
7	415	80.3	1.07	0.19
8	420	21	1.43	0.88
9	415	15.4	1.07	0.84
10	400	100	0.00	0.00
11	415	40	1.07	0.37
12	397	8.3	-0.21	-0.25
13	392	33	-0.57	-0.23
14	399	59.9	-0.07	-0.02
15	400	100	0.00	0.00
16	NT	NT		
17	406	34	0.43	0.17
18	378	39	-1.57	-0.55
19	382	19	-1.29	-0.86
20	420	100	1.43	0.20
21	400	80	0.00	0.00
22	386	77.2	-1.00	-0.18
23	NT	NT		
24	435	6	2.50	3.24
25	406	60	0.43	0.10

Statistics

Assigned Value	400	9
Spike	Not Spiked	
Homogeneity Value	380	57
Robust Average	400	9
Median	400	9
Mean	400	
N	23	
Max.	435	
Min.	350	
Robust SD	17	
Robust CV	4.2%	

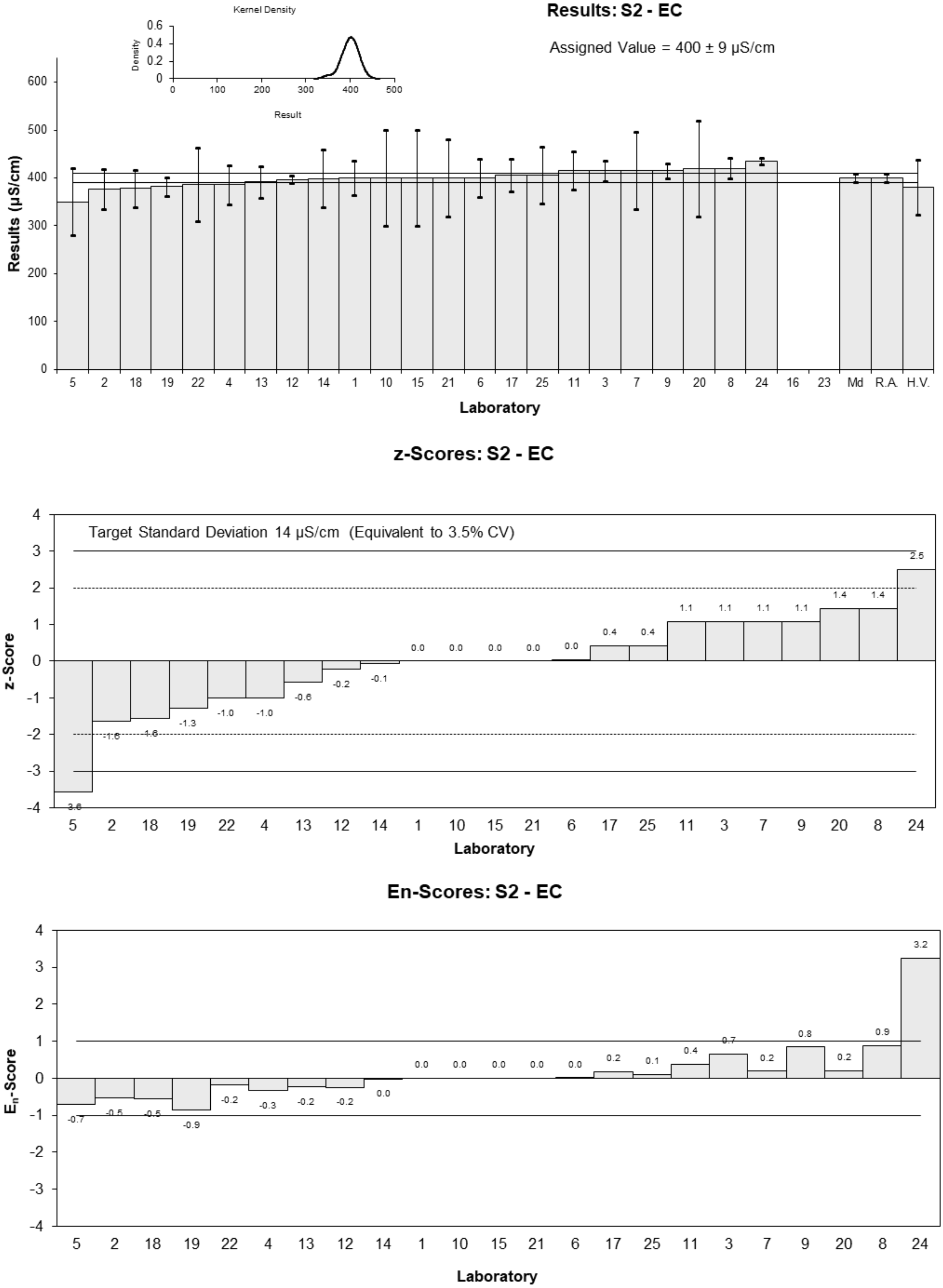

Results: S2 - EC
Assigned Value = 400 ± 9 µS/cm
Kernel Density
Density
Result
Results (µS/cm)
Laboratory
5 2 18 19 22 4 13 12 14 1 10 15 21 6 17 25 11 3 7 9 20 8 24 16 23 Md R.A. H.V.
z-Scores: S2 - EC
Target Standard Deviation 14 µS/cm (Equivalent to 3.5% CV)
z-Score
Laboratory
5 2 18 19 22 4 13 12 14 1 10 15 21 6 17 25 11 3 7 9 20 8 24
En-Scores: S2 - EC
En-Score
Laboratory
5 2 18 19 22 4 13 12 14 1 10 15 21 6 17 25 11 3 7 9 20 8 24

Figure 15

Table 18

Sample Details

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

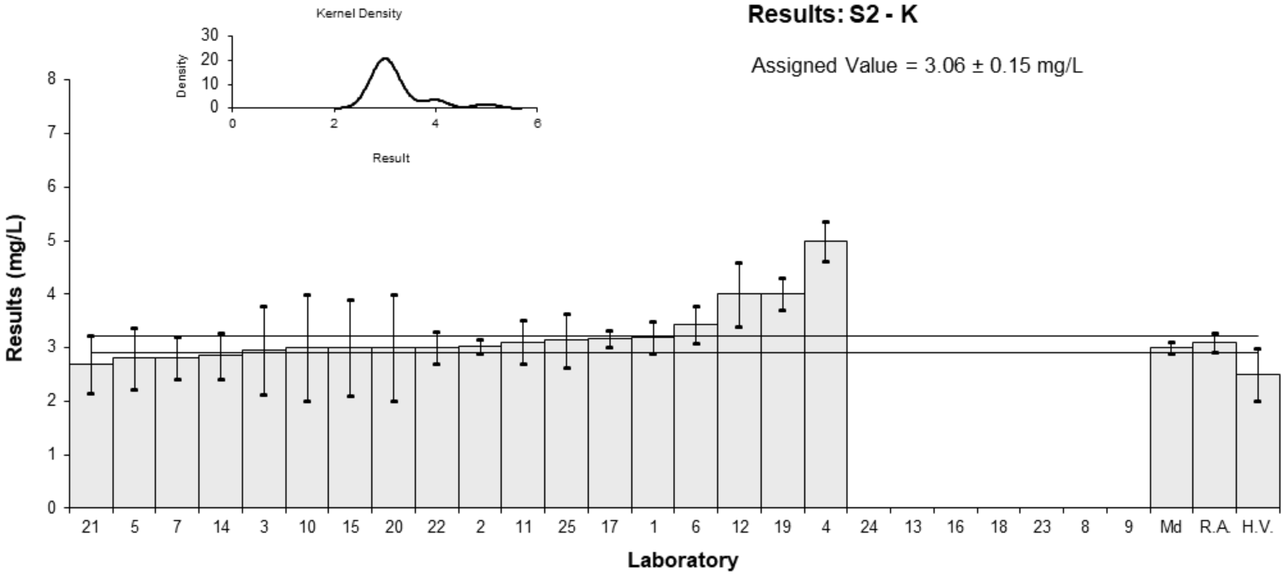
Participant Results

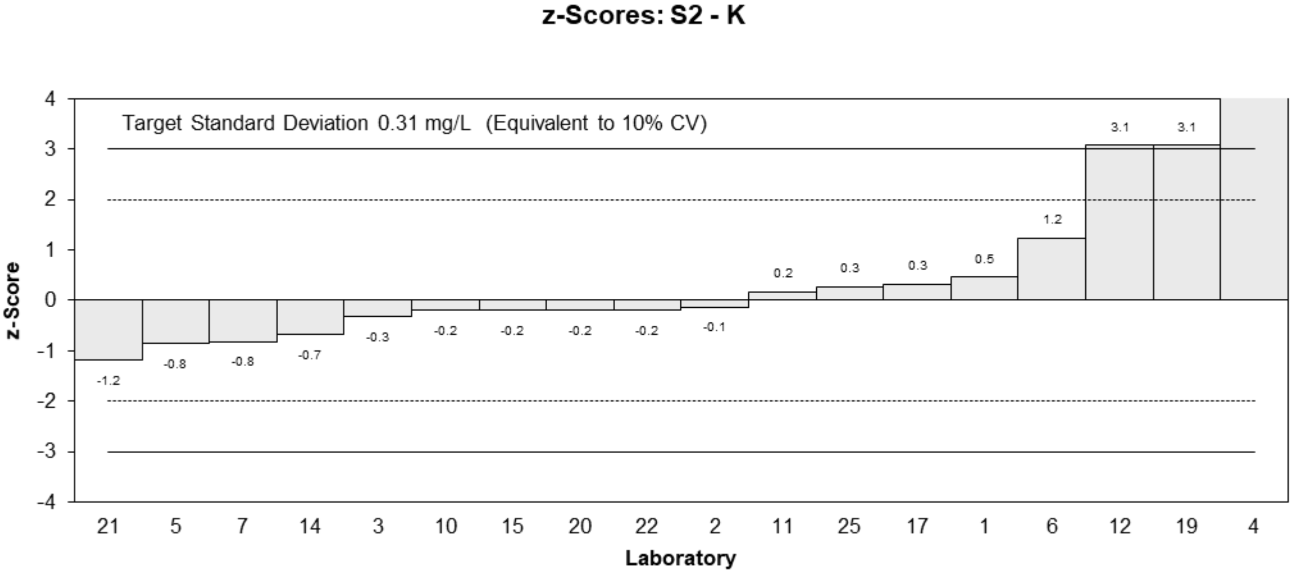
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.2	0.3	0.46	0.42
2	3.02	0.133	-0.13	-0.20
3	2.96	0.83	-0.33	-0.12
4	5	0.37	6.34	4.86
5	2.8	0.58	-0.85	-0.43
6	3.44	0.35	1.24	1.00
7	2.81	0.39	-0.82	-0.60
8	NT	NT		
9	NT	NT		
10	3	1	-0.20	-0.06
11	3.11	0.4	0.16	0.12
12	4	0.6	3.07	1.52
13	NT	NT		
14	2.85	.43	-0.69	-0.46
15	3	0.9	-0.20	-0.07
16	NT	NT		
17	3.16	0.155	0.33	0.46
18	NT	NT		
19	4	0.3	3.07	2.80
20	3	1	-0.20	-0.06
21	2.7	0.54	-1.18	-0.64
22	3	0.3	-0.20	-0.18
23	NT	NT		
24	NR	NR		
25	3.14	0.5	0.26	0.15

Statistics

Assigned Value*	3.06	0.15
Spike	Not Spiked	
Homogeneity Value	2.49	0.50
Robust Average	3.10	0.18
Median	3.01	0.11
Mean	3.23	
N	18	
Max.	5	
Min.	2.7	
Robust SD	0.30	
Robust CV	9.8%	

*Robust Average excluding laboratory 4.


Results: S2 - K
Assigned Value = 3.06 ± 0.15 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
21 5 7 14 3 10 15 20 22 2 11 25 17 1 6 12 19 4 24 13 16 18 23 8 9 Md R.A. H.V.


z-Scores: S2 - K
Target Standard Deviation 0.31 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
21 5 7 14 3 10 15 20 22 2 11 25 17 1 6 12 19 4

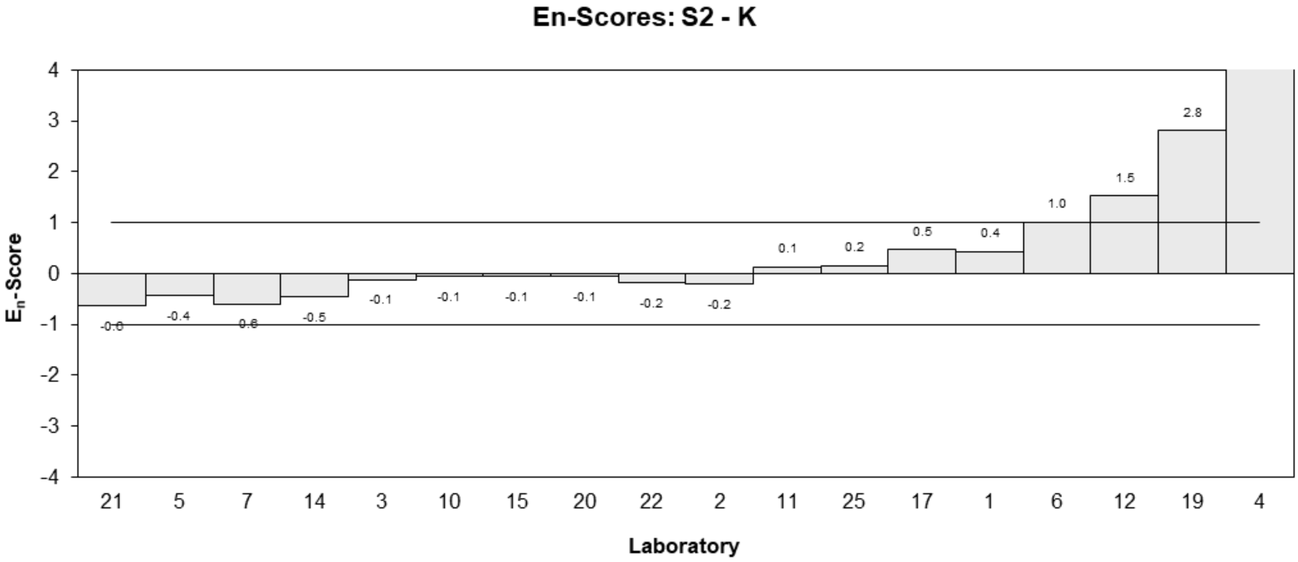

En-Scores: S2 - K
E_n-Score
Laboratory
21 5 7 14 3 10 15 20 22 2 11 25 17 1 6 12 19 4

Figure 16

Table 19

Sample Details

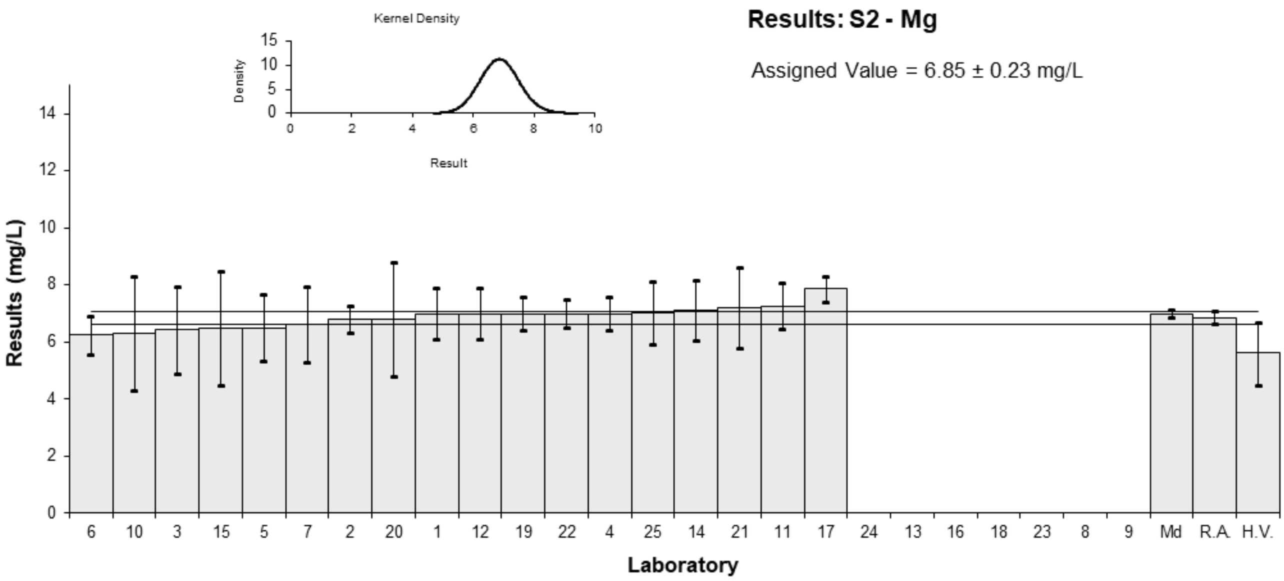
Sample No.	S2
Matrix.	River Water
Analyte.	Mg
Units	mg/L

Participant Results

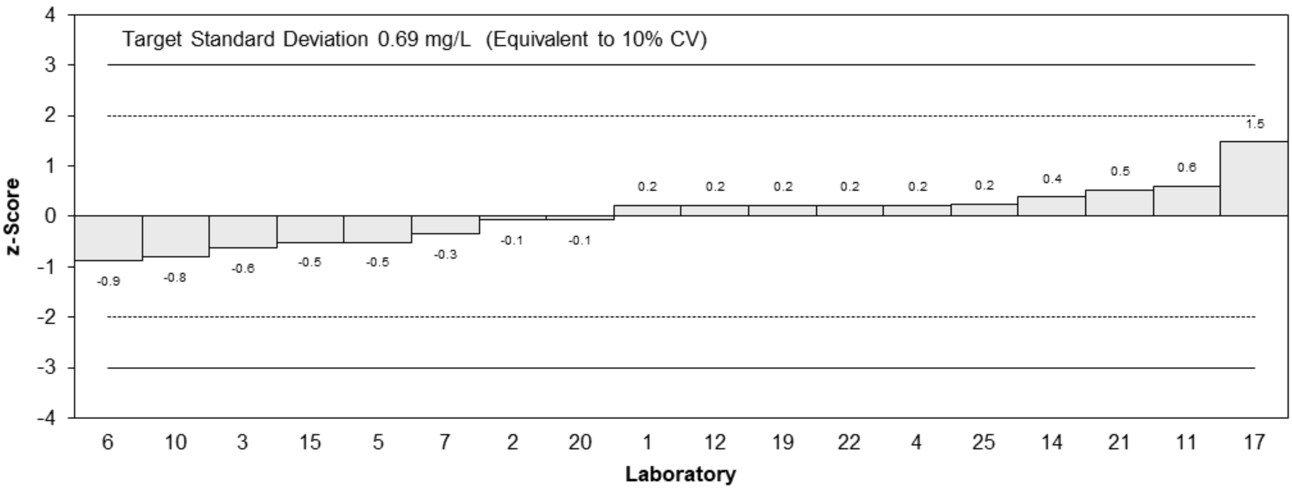
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.0	0.9	0.22	0.16
2	6.80	0.472	-0.07	-0.10
3	6.42	1.54	-0.63	-0.28
4	7	0.58	0.22	0.24
5	6.5	1.16	-0.51	-0.30
6	6.25	0.68	-0.88	-0.84
7	6.62	1.32	-0.34	-0.17
8	NT	NT		
9	NT	NT		
10	6.3	2	-0.80	-0.27
11	7.26	0.8	0.60	0.49
12	7	0.9	0.22	0.16
13	NT	NT		
14	7.11	1.07	0.38	0.24
15	6.5	2	-0.51	-0.17
16	NT	NT		
17	7.86	0.448	1.47	2.01
18	NT	NT		
19	7	0.6	0.22	0.23
20	6.8	2	-0.07	-0.02
21	7.2	1.4	0.51	0.25
22	7	0.5	0.22	0.27
23	NT	NT		
24	NR	NR		
25	7.01	1.1	0.23	0.14

Statistics

Assigned Value	6.85	0.23
Spike	Not Spiked	
Homogeneity Value	5.6	1.1
Robust Average	6.85	0.23
Median	7.00	0.15
Mean	6.87	
N	18	
Max.	7.86	
Min.	6.25	
Robust SD	0.38	
Robust CV	5.6%	



z-Scores: S2 - Mg



En-Scores: S2 - Mg

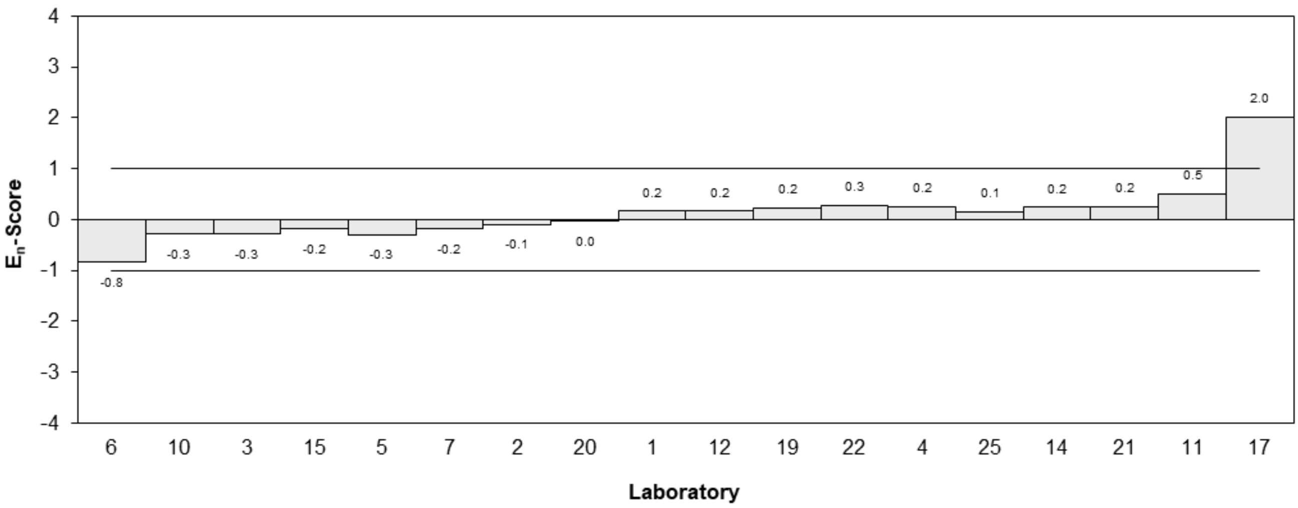


Figure 17

Table 20

Sample Details

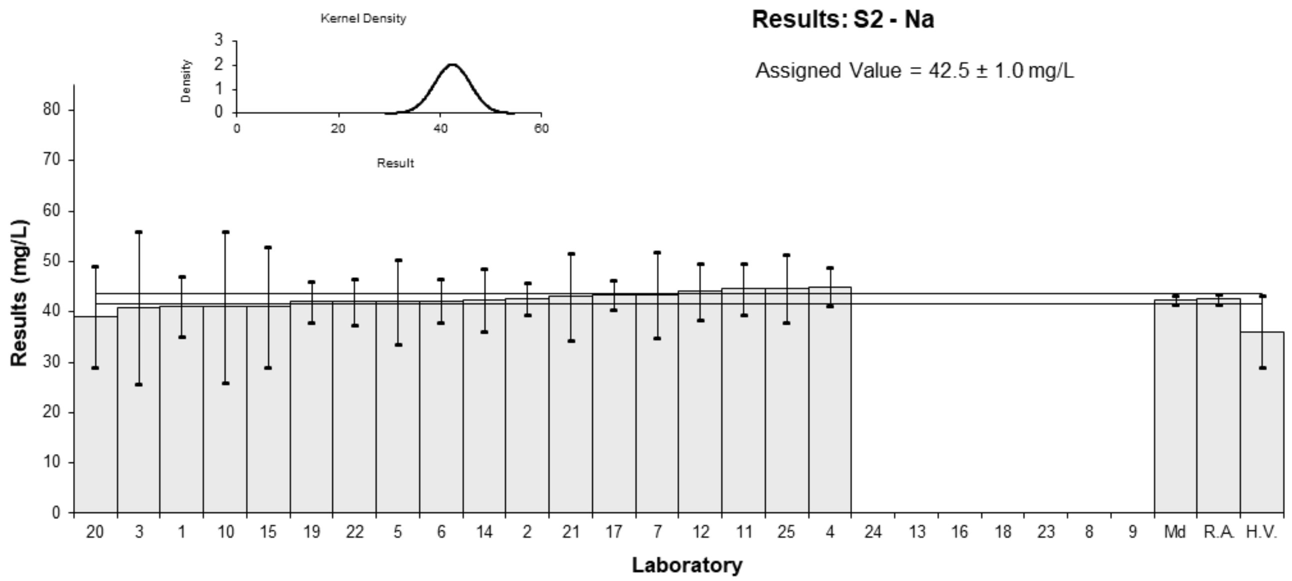
Sample No.	S2
Matrix.	River Water
Analyte.	Na
Units	mg/L

Participant Results

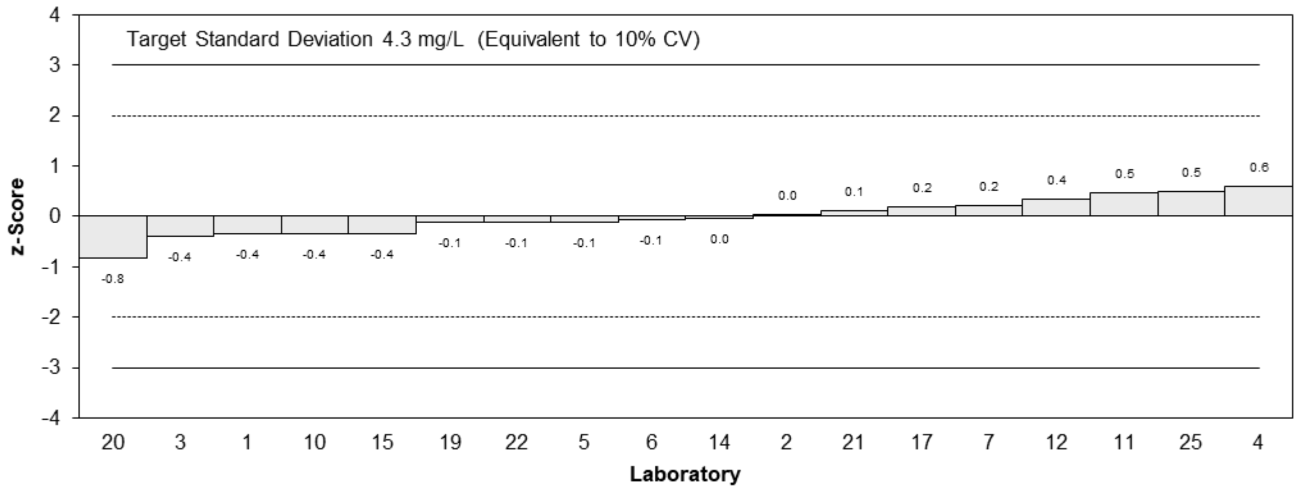
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	41	6	-0.35	-0.25
2	42.7	3.17	0.05	0.06
3	40.8	15.1	-0.40	-0.11
4	45	3.8	0.59	0.64
5	42	8.4	-0.12	-0.06
6	42.2	4.4	-0.07	-0.07
7	43.4	8.47	0.21	0.11
8	NT	NT		
9	NT	NT		
10	41	15	-0.35	-0.10
11	44.5	5.0	0.47	0.39
12	44	5.5	0.35	0.27
13	NT	NT		
14	42.3	6.3	-0.05	-0.03
15	41	12	-0.35	-0.12
16	NT	NT		
17	43.3	2.9	0.19	0.26
18	NT	NT		
19	42	4	-0.12	-0.12
20	39	10	-0.82	-0.35
21	43	8.6	0.12	0.06
22	42	4.5	-0.12	-0.11
23	NT	NT		
24	NR	NR		
25	44.6	6.7	0.49	0.31

Statistics

Assigned Value	42.5	1.0
Spike	Not Spiked	
Homogeneity Value	36.1	7.2
Robust Average	42.5	1.0
Median	42.3	0.9
Mean	42.4	
N	18	
Max.	45	
Min.	39	
Robust SD	1.6	
Robust CV	3.8%	



z-Scores: S2 - Na



En-Scores: S2 - Na

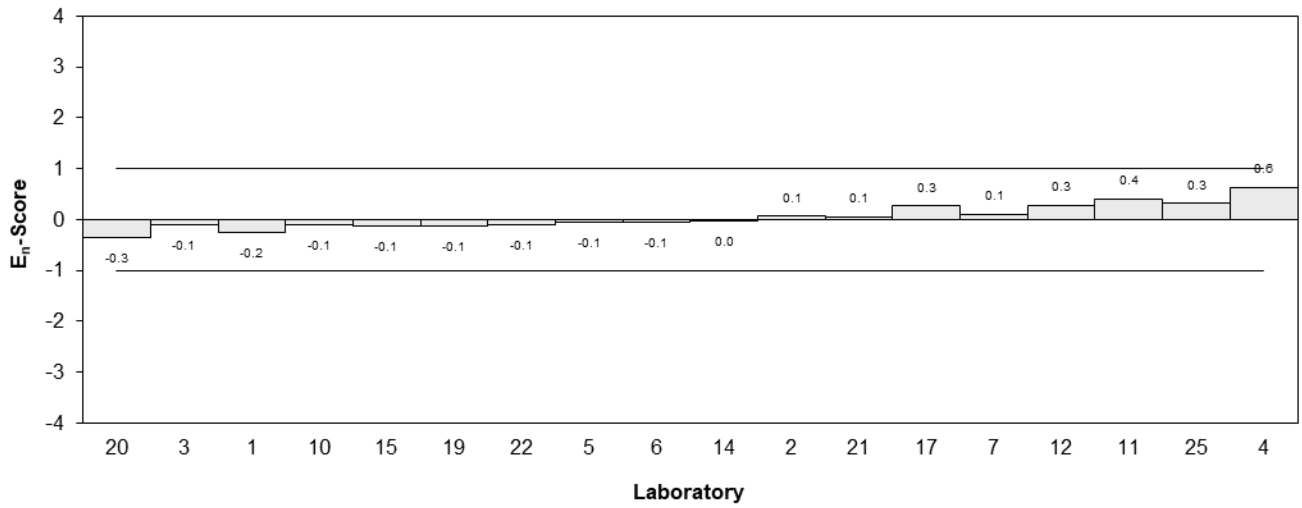


Figure 18

Table 21

Sample Details

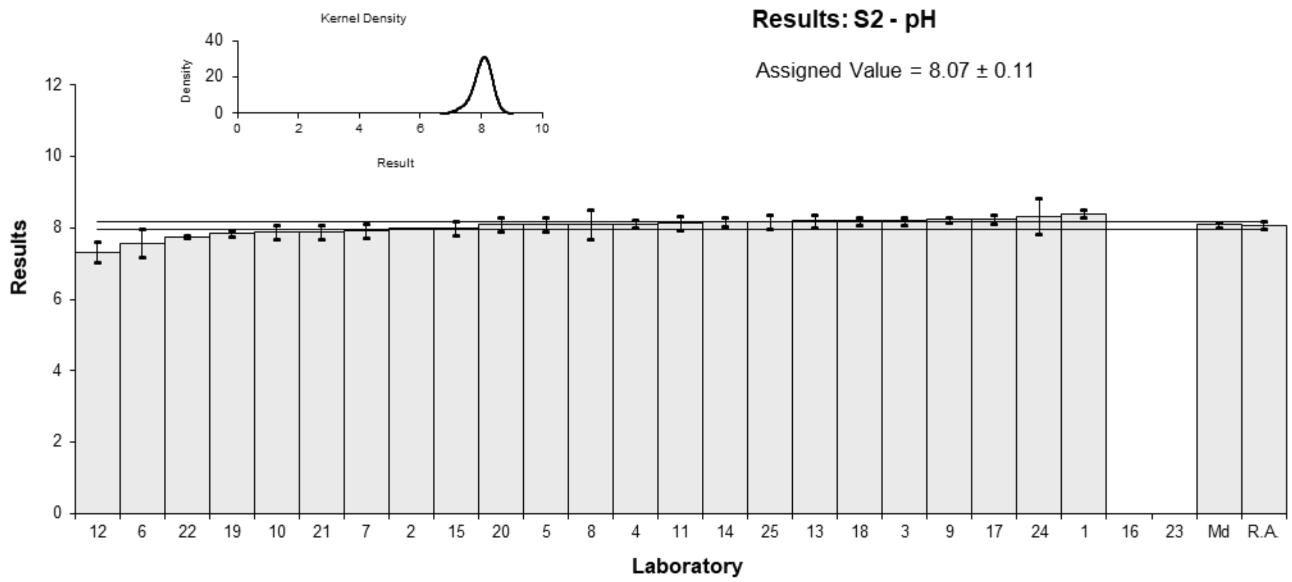
Sample No.	S2
Matrix.	River Water
Analyte.	pH

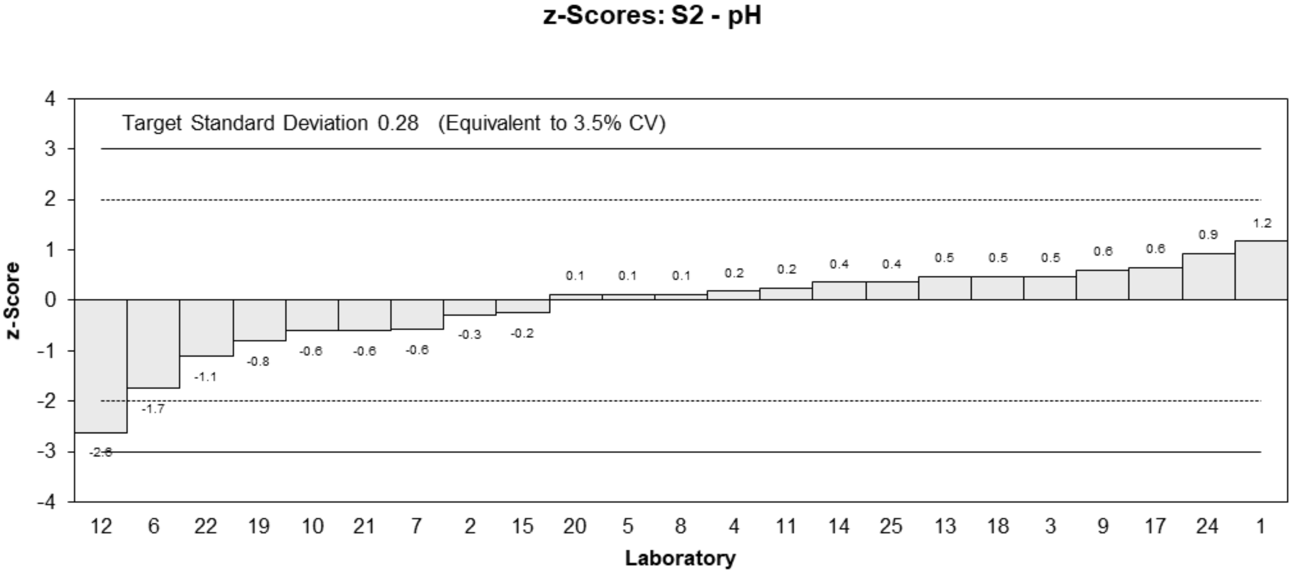
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	8.4	0.1	1.17	2.22
2	7.99	NR	-0.28	-0.73
3	8.2	0.1	0.46	0.87
4	8.12	0.1	0.18	0.34
5	8.1	0.2	0.11	0.13
6	7.58	0.38	-1.73	-1.24
7	7.91	0.2	-0.57	-0.70
8	8.1	0.4	0.11	0.07
9	8.24	0.07	0.60	1.30
10	7.9	0.2	-0.60	-0.74
11	8.14	0.2	0.25	0.31
12	7.33	0.3	-2.62	-2.32
13	8.2	0.17	0.46	0.64
14	8.17	0.13	0.35	0.59
15	8	0.2	-0.25	-0.31
16	NT	NT		
17	8.25	0.132	0.64	1.05
18	8.2	0.1	0.46	0.87
19	7.84	0.09	-0.81	-1.62
20	8.1	0.2	0.11	0.13
21	7.9	0.2	-0.60	-0.74
22	7.76	0.051	-1.10	-2.56
23	NT	NT		
24	8.33	0.5	0.92	0.51
25	8.17	0.2	0.35	0.44

Statistics

Assigned Value	8.07	0.11
Spike	Not Spiked	
Robust Average	8.07	0.11
Median	8.10	0.07
Mean	8.04	
N	23	
Max.	8.4	
Min.	7.33	
Robust SD	0.21	
Robust CV	2.6%	


Results: S2 - pH
Assigned Value = 8.07 ± 0.11
Kernel Density
Density
Result
Results
Laboratory
12
6
22
19
10
21
7
2
15
20
5
8
4
11
14
25
13
18
3
9
17
24
1
16
23
Md
R.A.


z-Scores: S2 - pH
Target Standard Deviation 0.28 (Equivalent to 3.5% CV)
z-Score
Laboratory
-2.6
-1.7
-1.1
-0.8
-0.6
-0.6
-0.6
-0.3
-0.2
0.1
0.1
0.1
0.2
0.2
0.4
0.4
0.5
0.5
0.5
0.6
0.6
0.9
1.2

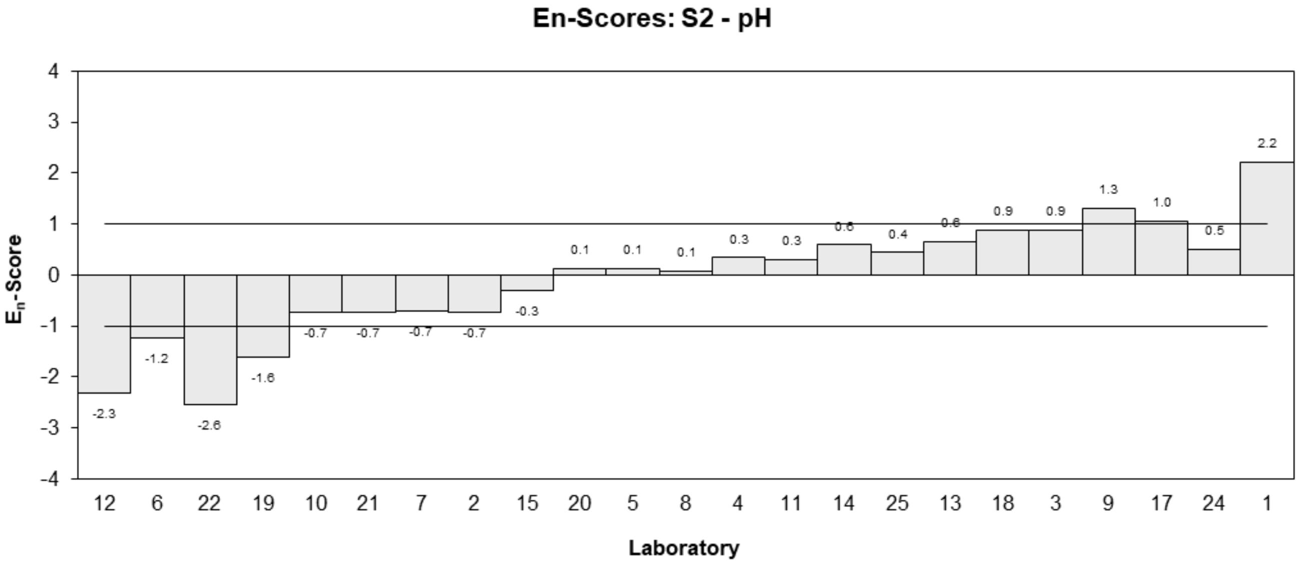

En-Scores: S2 - pH
E_n-Score
Laboratory
-2.3
-1.2
-2.6
-1.6
-0.7
-0.7
-0.7
-0.7
-0.3
0.1
0.1
0.1
0.3
0.3
0.6
0.4
0.6
0.9
0.9
1.3
1.0
0.5
2.2

Figure 19

Table 22

Sample Details

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

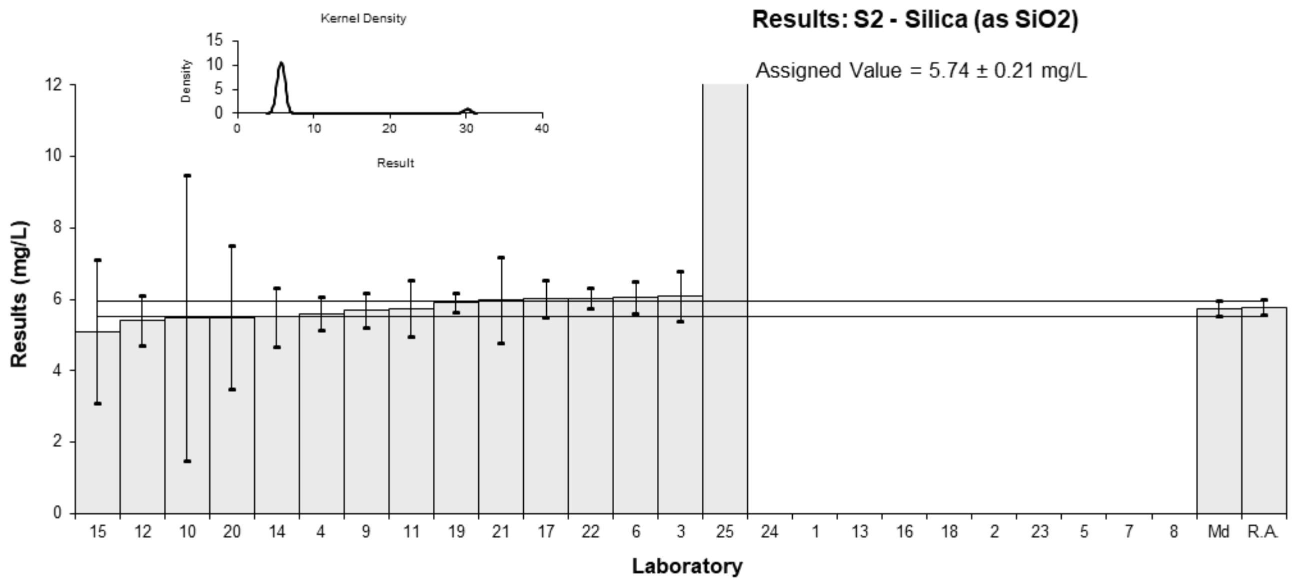
Participant Results

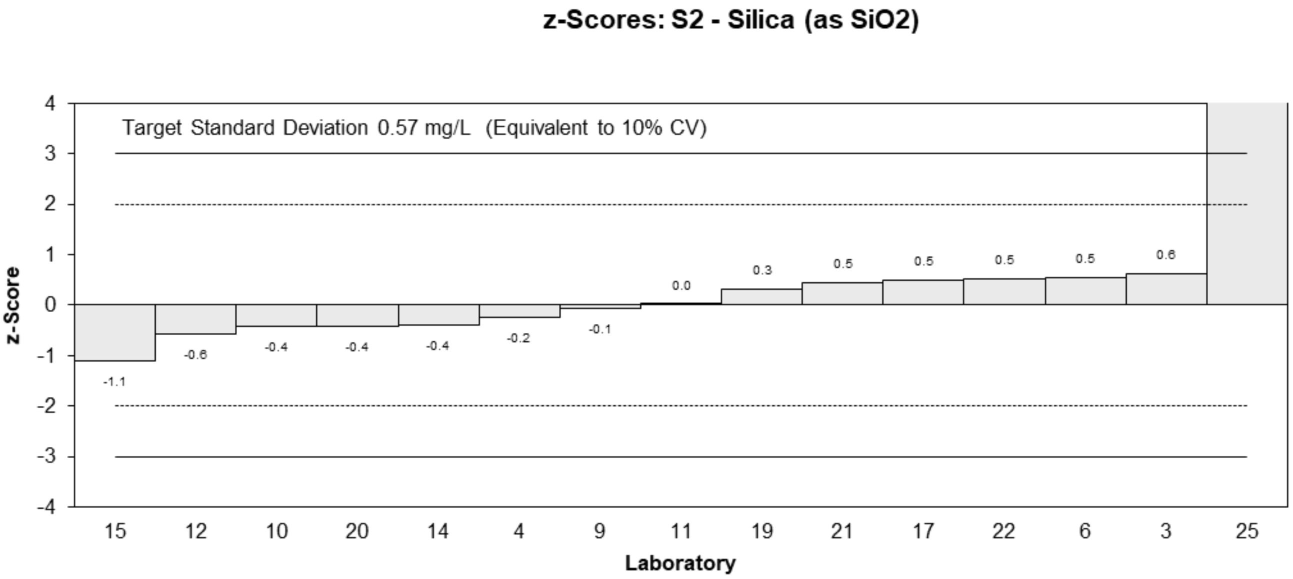
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	6.1	0.7	0.63	0.49
4	5.6	0.46	-0.24	-0.28
5	NT	NT		
6	6.05	0.44	0.54	0.64
7	NT	NT		
8	NT	NT		
9	5.70	0.48	-0.07	-0.08
10	5.5	4	-0.42	-0.06
11	5.75	0.8	0.02	0.01
12	5.41	0.7	-0.57	-0.45
13	NT	NT		
14	5.51	0.83	-0.40	-0.27
15	5.1	2	-1.11	-0.32
16	NT	NT		
17	6.02	0.506	0.49	0.51
18	NT	NT		
19	5.92	0.27	0.31	0.53
20	5.5	2	-0.42	-0.12
21	6.0	1.2	0.45	0.21
22	6.04	0.3	0.52	0.82
23	NT	NT		
24	NR	NR		
25	30.2	4.5	42.61	5.43

Statistics

Assigned Value*	5.74	0.21
Spike	Not Spiked	
Robust Average	5.78	0.22
Median	5.75	0.21
Mean	7.36	
N	15	
Max.	30.2	
Min.	5.1	
Robust SD	0.35	
Robust CV	6%	

*Robust Average excluding laboratory 25.


Results: S2 - Silica (as SiO2)
Assigned Value = 5.74 ± 0.21 mg/L
Kernel Density
Density
Result
Results (mg/L)
15 12 10 20 14 4 9 11 19 21 17 22 6 3 25 24 1 13 16 18 2 23 5 7 8 Md R.A.
Laboratory


z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation 0.57 mg/L (Equivalent to 10% CV)
z-Score
-1.1 -0.6 -0.4 -0.4 -0.4 -0.2 -0.1 0.0 0.3 0.5 0.5 0.5 0.5 0.6
15 12 10 20 14 4 9 11 19 21 17 22 6 3 25
Laboratory

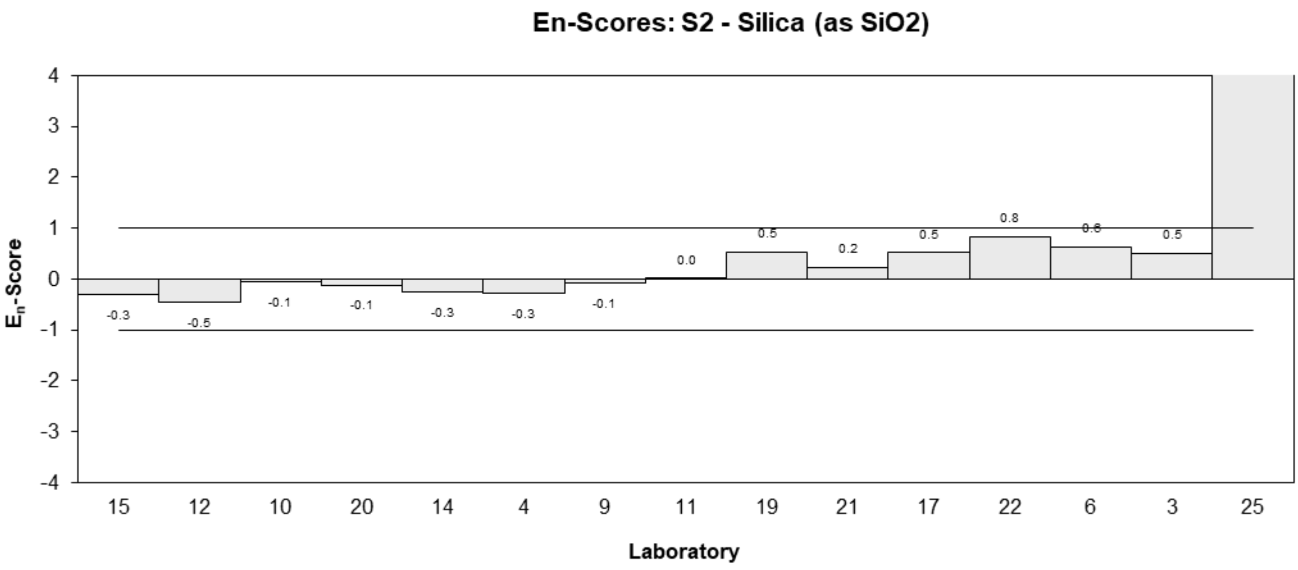

En-Scores: S2 - Silica (as SiO2)
En-Score
-0.3 -0.5 -0.1 -0.1 -0.3 -0.3 -0.1 0.0 0.5 0.2 0.5 0.8 0.6 0.5
15 12 10 20 14 4 9 11 19 21 17 22 6 3 25
Laboratory

Figure 20

Table 23

Sample Details

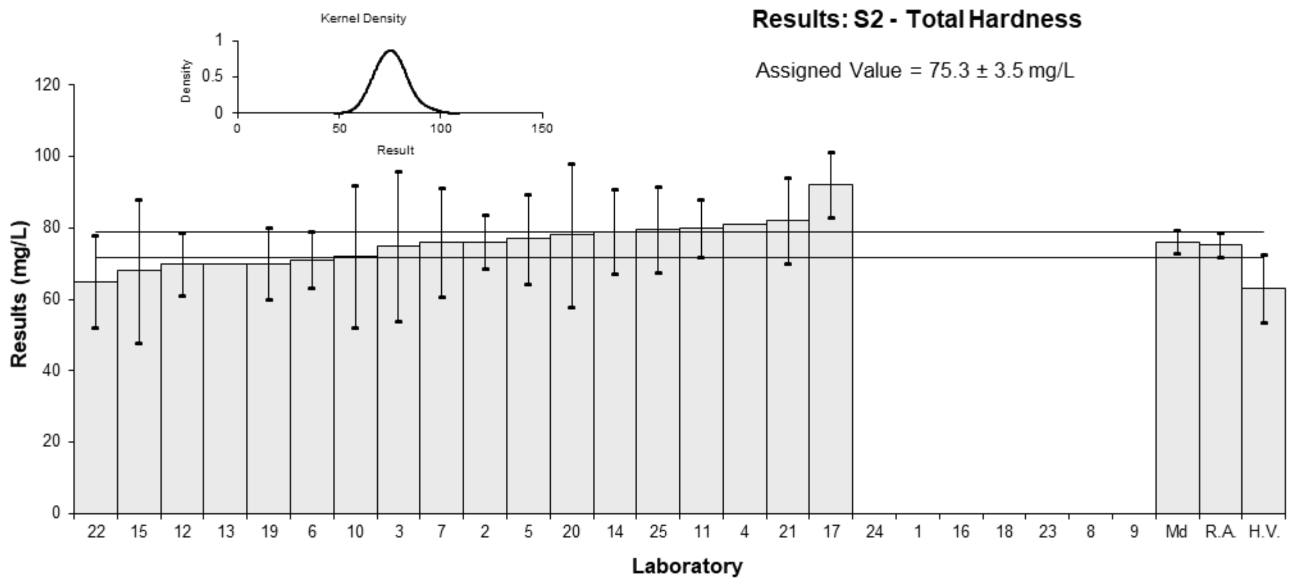
Sample No.	S2
Matrix.	River Water
Analyte.	Total Hardness
Units	mg/L

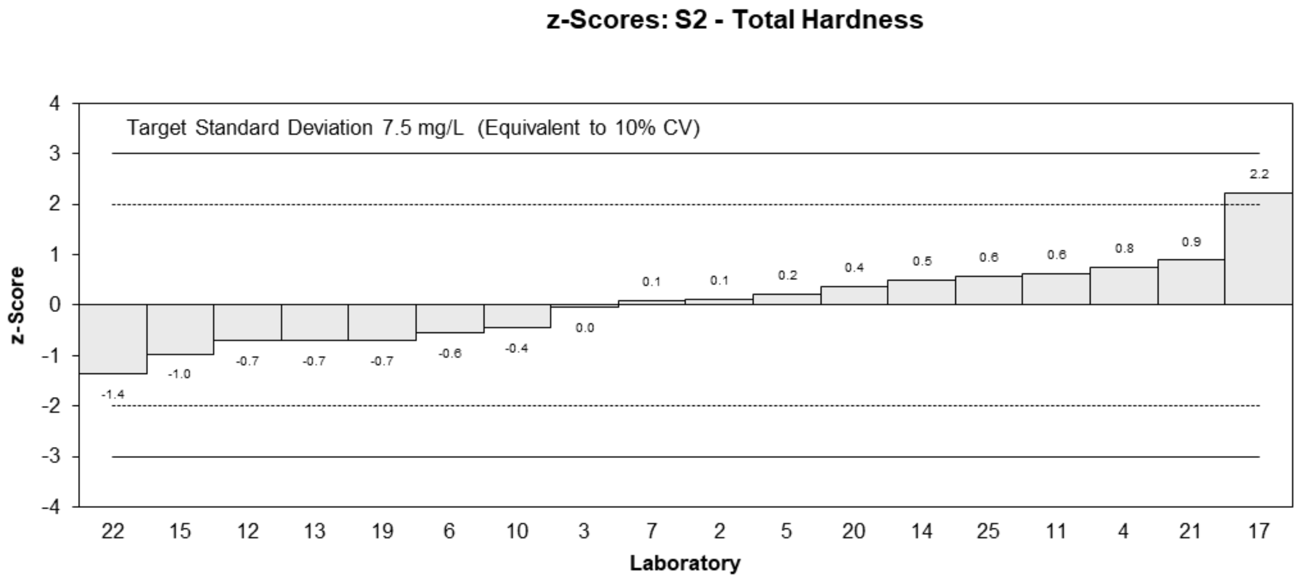
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	76.1	7.61	0.11	0.10
3	75	21	-0.04	-0.01
4	81	NR	0.76	1.63
5	77	12.6	0.23	0.13
6	71.1	7.82	-0.56	-0.49
7	76	15.2	0.09	0.04
8	NT	NT		
9	NT	NT		
10	72	20	-0.44	-0.16
11	80	8.0	0.62	0.54
12	70	8.7	-0.70	-0.57
13	70	NR	-0.70	-1.51
14	79	11.8	0.49	0.30
15	68	20	-0.97	-0.36
16	NT	NT		
17	92.1	9.2	2.23	1.71
18	NT	NT		
19	70	10	-0.70	-0.50
20	78	20	0.36	0.13
21	82	12	0.89	0.54
22	65	13	-1.37	-0.77
23	NT	NT		
24	NR	NR		
25	79.6	11.9	0.57	0.35

Statistics

Assigned Value	75.3	3.5
Spike	Not Spiked	
Homogeneity Value	63.0	9.5
Robust Average	75.3	3.5
Median	76.1	3.3
Mean	75.7	
N	18	
Max.	92.1	
Min.	65	
Robust SD	6.0	
Robust CV	7.9%	


Results: S2 - Total Hardness
Assigned Value = 75.3 ± 3.5 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
22 15 12 13 19 6 10 3 7 2 5 20 14 25 11 4 21 17 24 1 16 18 23 8 9 Md R.A. H.V.


z-Scores: S2 - Total Hardness
Target Standard Deviation 7.5 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
22 15 12 13 19 6 10 3 7 2 5 20 14 25 11 4 21 17
-1.4 -1.0 -0.7 -0.7 -0.7 -0.6 -0.4 0.0 0.1 0.1 0.2 0.4 0.5 0.6 0.6 0.8 0.9 2.2

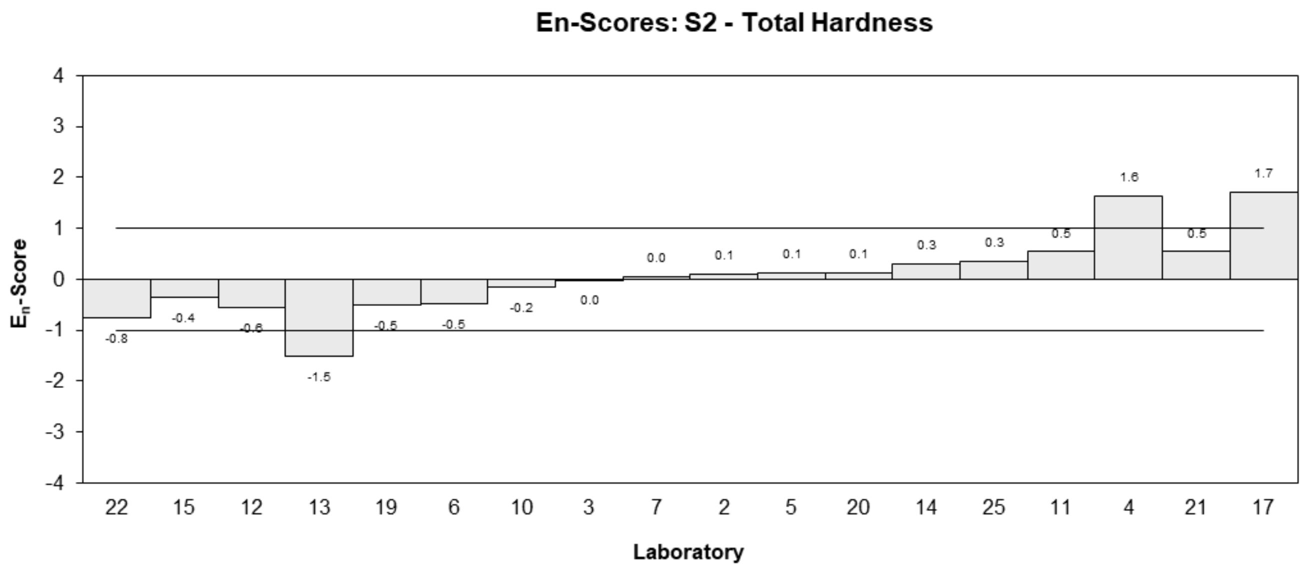

En-Scores: S2 - Total Hardness
E_n-Score
Laboratory
22 15 12 13 19 6 10 3 7 2 5 20 14 25 11 4 21 17
-0.8 -0.4 -0.6 -1.5 -0.5 -0.5 -0.2 0.0 0.0 0.1 0.1 0.1 0.3 0.3 0.5 1.6 0.5 1.7

Figure 21

Table 24

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<0.04	NR
2	NT	NT
3	<50	NR
4	<1	NR
5	0.031	0.006
6	NT	NT
7	0.041	0.010
8	NT	NT
9	NT	NT
10	<0.5	NR
11	<0.1	NR
12	<0.1	NR
13	<1.5	0.7
14	0.045	0.007
15	<0.5	NR
16	NT	NT
17	0.035	0.003
18	NT	NT
19	<1	NR
20	<0.5	NR
21	<0.05	NR
22	<1	NR
23	NT	NT
24	NR	NR
25	<0.1	0.1

Statistics

Assigned Value	Not Set	
Spike	0.078	0.002
Median	0.038	0.012
Mean	0.038	
N	4	
Max.	0.045	
Min.	0.031	
Robust SD	0.0071	
Robust CV	19%	

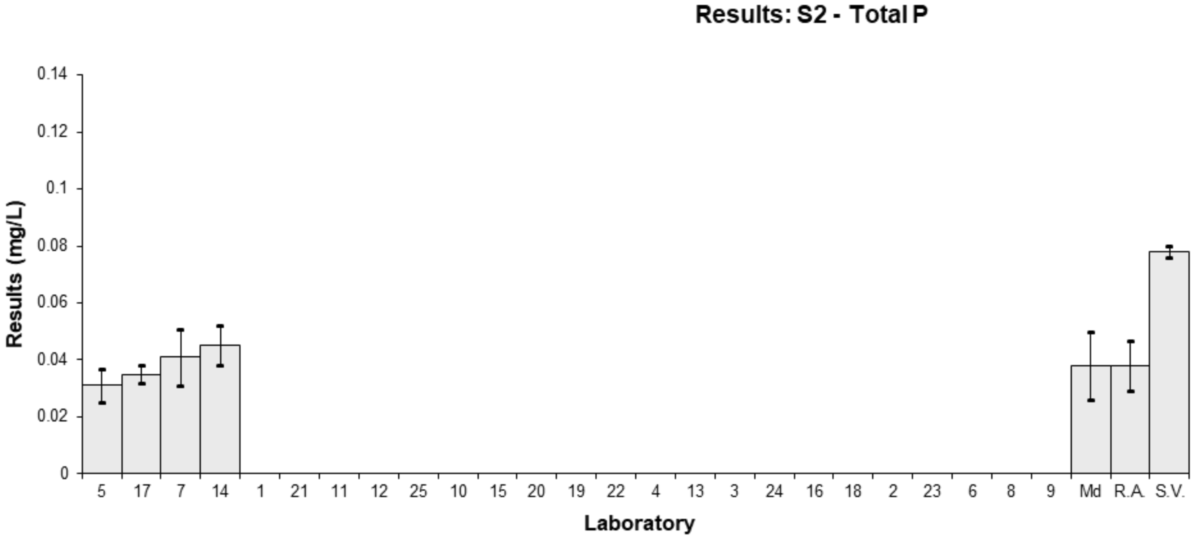

Results: S2 - Total P
Results (mg/L)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
5 17 7 14 1 21 11 12 25 10 15 20 19 22 4 13 3 24 16 18 2 23 6 8 9 Md R.A. S.V.
Laboratory

Figure 22

Table 25

Sample Details

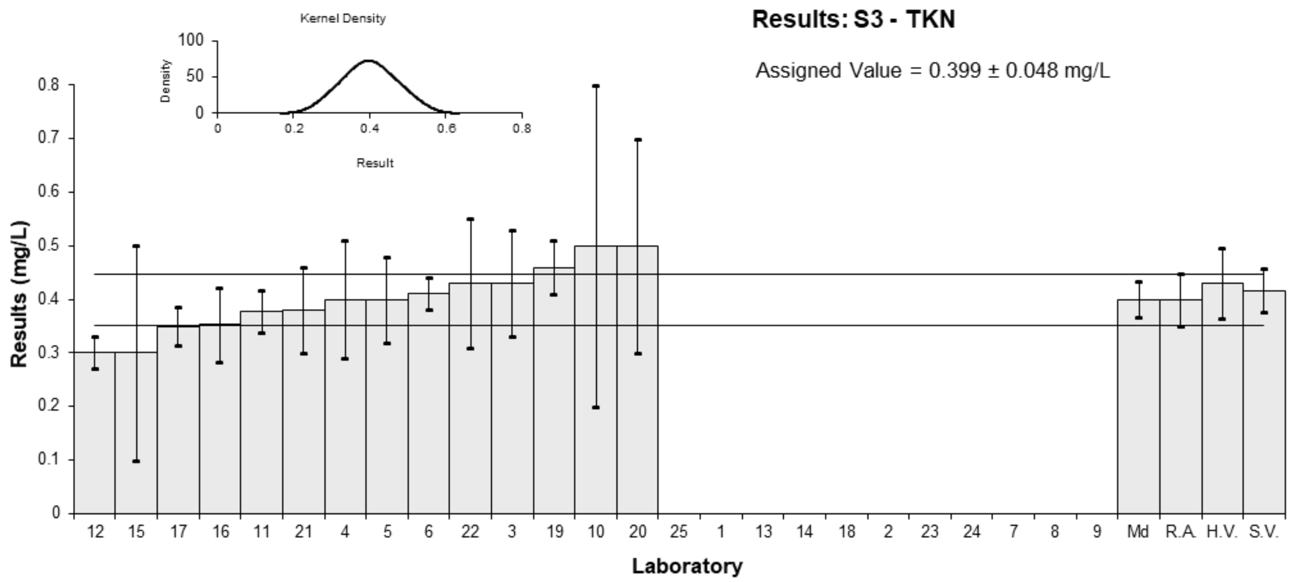
Sample No.	S3
Matrix.	River Water
Analyte.	TKN
Units	mg/L

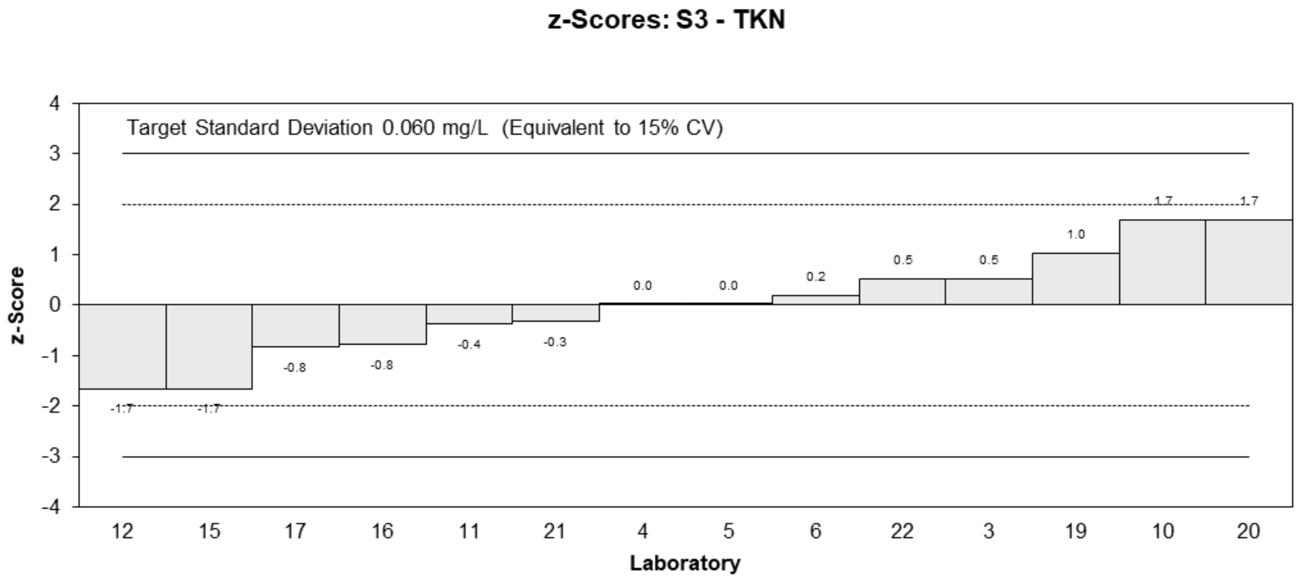
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	0.43	0.1	0.52	0.28
4	0.4	0.11	0.02	0.01
5	0.40	0.08	0.02	0.01
6	0.41	0.03	0.18	0.19
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	0.5	0.3	1.69	0.33
11	0.377	0.04	-0.37	-0.35
12	0.3	0.03	-1.65	-1.75
13	NT	NT		
14	NT	NT		
15	0.3	0.2	-1.65	-0.48
16	0.353	0.069	-0.77	-0.55
17	0.350	0.035	-0.82	-0.82
18	NT	NT		
19	0.46	0.05	1.02	0.88
20	0.5	0.2	1.69	0.49
21	0.38	0.08	-0.32	-0.20
22	0.43	0.12	0.52	0.24
23	NT	NT		
24	NT	NT		
25	NR	NR		

Statistics

Assigned Value	0.399	0.048
Spike	0.417	0.041
Homogeneity Value	0.430	0.065
Robust Average	0.399	0.048
Median	0.400	0.033
Mean	0.399	
N	14	
Max.	0.5	
Min.	0.3	
Robust SD	0.071	
Robust CV	18%	


Kernel Density
Density
Result
Results: S3 - TKN
Assigned Value = 0.399 ± 0.048 mg/L
Results (mg/L)
Laboratory
12 15 17 16 11 21 4 5 6 22 3 19 10 20 25 1 13 14 18 2 23 24 7 8 9 Md R.A. H.V. S.V.


z-Scores: S3 - TKN
Target Standard Deviation 0.060 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
12 15 17 16 11 21 4 5 6 22 3 19 10 20
-1.7 -1.7 -0.8 -0.8 -0.4 -0.3 0.0 0.0 0.2 0.5 0.5 1.0 1.7 1.7

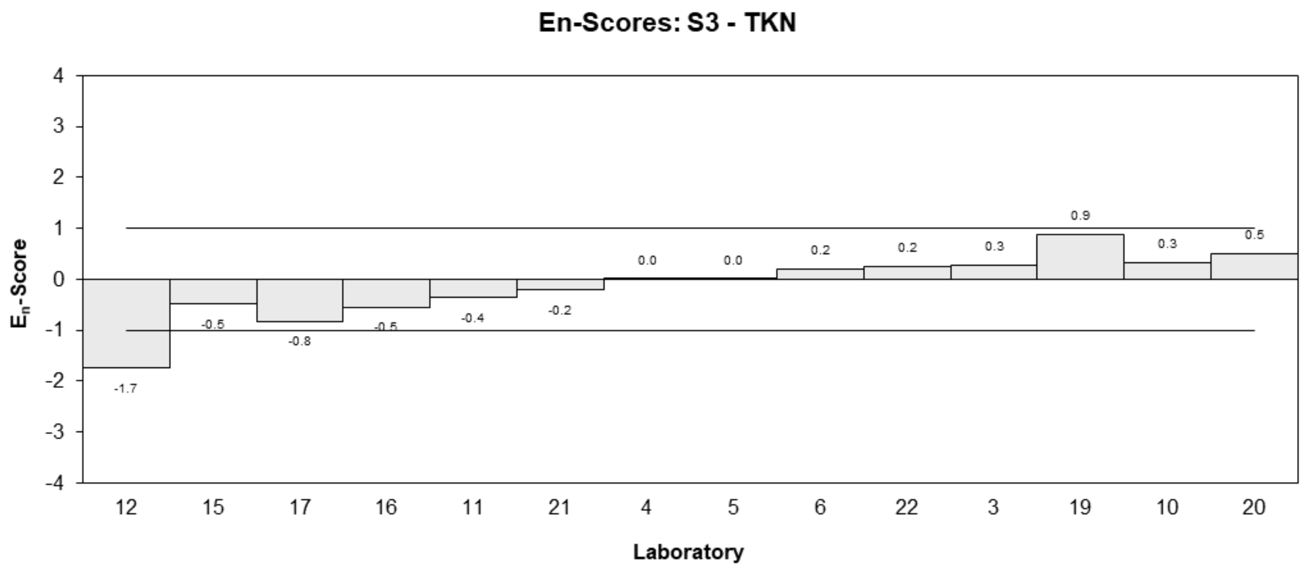

En-Scores: S3 - TKN
En-Score
Laboratory
12 15 17 16 11 21 4 5 6 22 3 19 10 20
-1.7 -0.5 -0.8 -0.5 -0.4 -0.2 0.0 0.0 0.2 0.2 0.3 0.9 0.3 0.5

Figure 23

Table 26

Sample Details

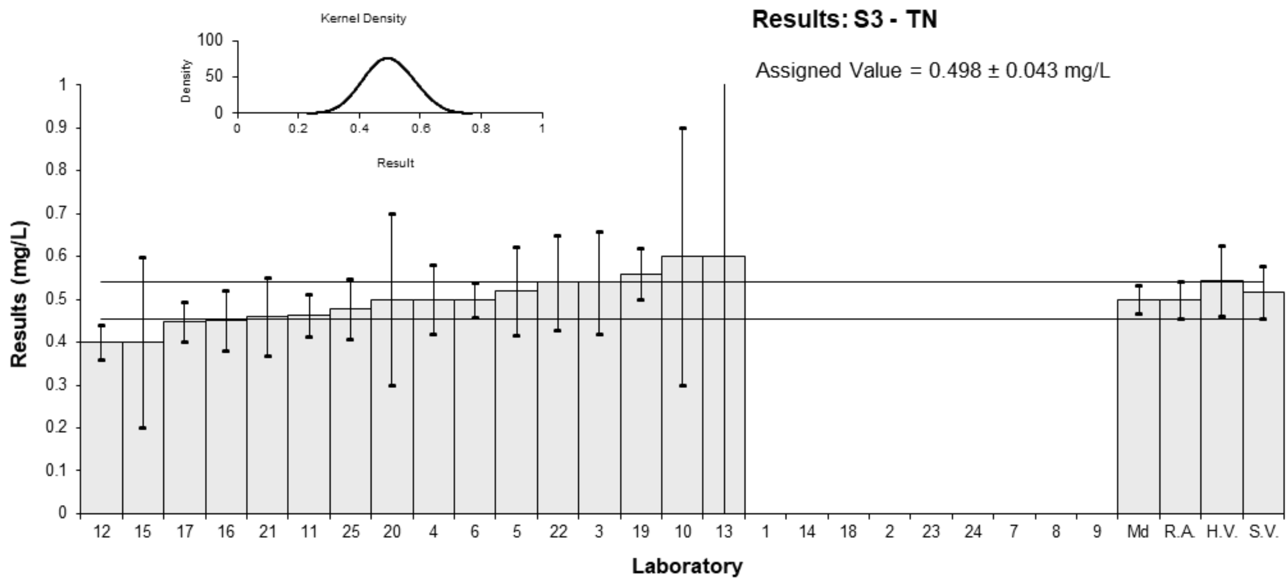
Sample No.	S3
Matrix.	River Water
Analyte.	TN
Units	mg/L

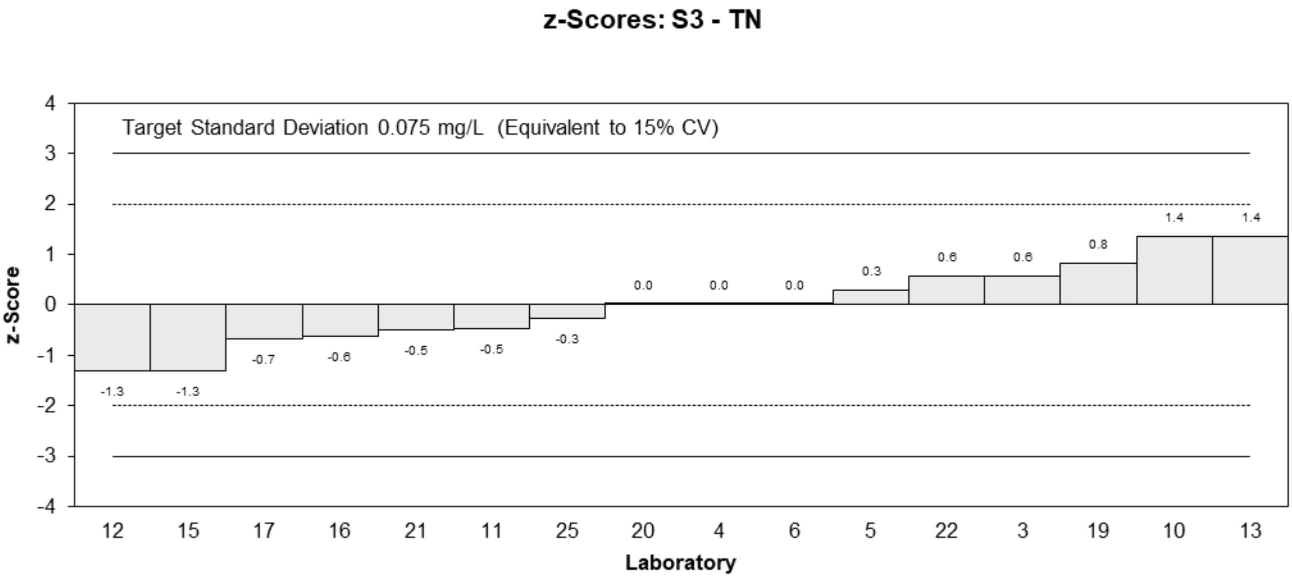
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	0.54	0.12	0.56	0.33
4	0.5	0.08	0.03	0.02
5	0.52	0.104	0.29	0.20
6	0.50	0.04	0.03	0.03
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	0.6	0.3	1.37	0.34
11	0.463	0.05	-0.47	-0.53
12	0.4	0.04	-1.31	-1.67
13	0.6	1.2	1.37	0.08
14	NT	NT		
15	0.4	0.2	-1.31	-0.48
16	0.452	0.070	-0.62	-0.56
17	0.448	0.045	-0.67	-0.80
18	NT	NT		
19	0.56	0.06	0.83	0.84
20	0.5	0.2	0.03	0.01
21	0.46	0.09	-0.51	-0.38
22	0.54	0.11	0.56	0.36
23	NT	NT		
24	NT	NT		
25	0.478	0.07	-0.27	-0.24

Statistics

Assigned Value	0.498	0.043
Spike	0.517	0.061
Homogeneity Value	0.543	0.082
Robust Average	0.498	0.043
Median	0.500	0.032
Mean	0.498	
N	16	
Max.	0.6	
Min.	0.4	
Robust SD	0.069	
Robust CV	14%	


Results: S3 - TN
Assigned Value = 0.498 ± 0.043 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
12 15 17 16 21 11 25 20 4 6 5 22 3 19 10 13 1 14 18 2 23 24 7 8 9 Md R.A. H.V. S.V.


z-Scores: S3 - TN
Target Standard Deviation 0.075 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
12 15 17 16 21 11 25 20 4 6 5 22 3 19 10 13
-1.3 -1.3 -0.7 -0.6 -0.5 -0.5 -0.3 0.0 0.0 0.0 0.3 0.6 0.6 0.8 1.4 1.4

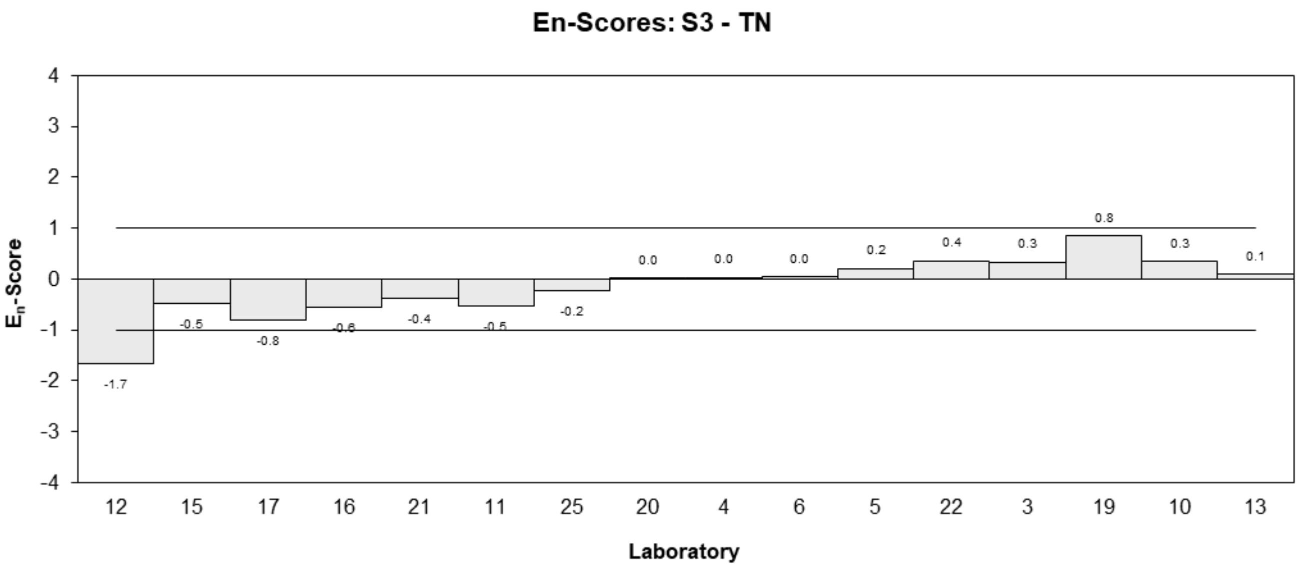

En-Scores: S3 - TN
En-Score
Laboratory
12 15 17 16 21 11 25 20 4 6 5 22 3 19 10 13
-1.7 -0.5 -0.8 -0.6 -0.4 -0.5 -0.2 0.0 0.0 0.0 0.2 0.4 0.3 0.8 0.3 0.1

Figure 24

Table 27

Sample Details

Sample No.	S3
Matrix.	River Water
Analyte.	TOC
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	NT	NT		
3	9.6	1.4	-0.11	-0.07
4	9.0	1.64	-0.73	-0.41
5	18.44	2.2	8.99	3.86
6	9.9	1.0	0.20	0.17
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	10	4	0.30	0.07
11	10.1	1.0	0.40	0.34
12	<1	NR		
13	NT	NT		
14	NT	NT		
15	9.2	3	-0.53	-0.17
16	11.6	3.5	1.95	0.53
17	9.38	1.02	-0.34	-0.29
18	NT	NT		
19	8.7	0.6	-1.04	-1.26
20	9	3	-0.73	-0.23
21	11	2	1.33	0.62
22	10	2	0.30	0.14
23	NT	NT		
24	NT	NT		
25	9.7	2	-0.01	0.00

Statistics

Assigned Value*	9.71	0.53
Spike	10.2	0.2
Homogeneity Value	9.2	1.4
Robust Average	9.87	0.63
Median	9.80	0.44
Mean	10.4	
N	14	
Max.	18.44	
Min.	8.7	
Robust SD	0.95	
Robust CV	9.6%	

*Robust Average excluding laboratory 5.

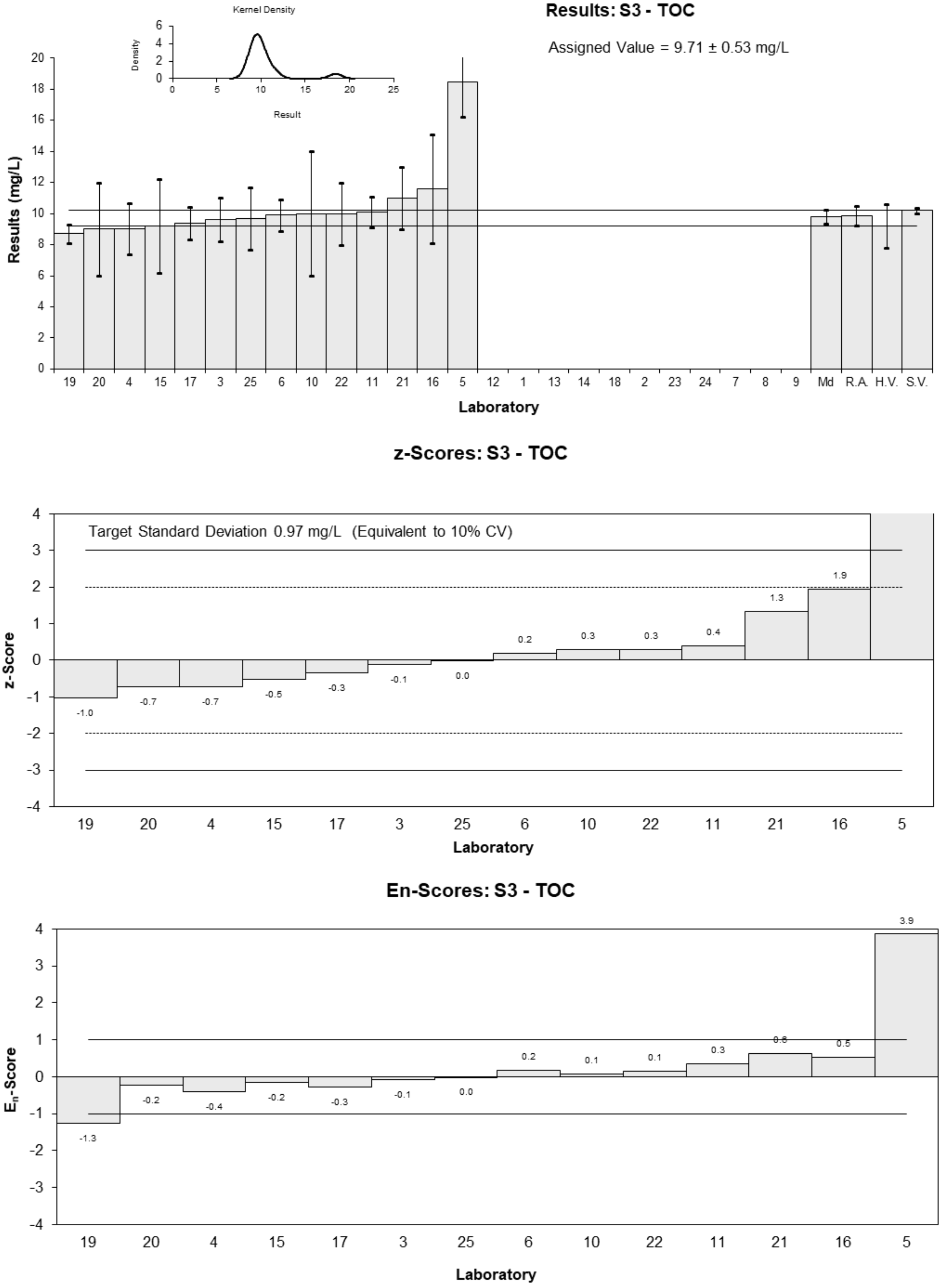

Results: S3 - TOC
Assigned Value = 9.71 ± 0.53 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
19 20 4 15 17 3 25 6 10 22 11 21 16 5 12 1 13 14 18 2 23 24 7 8 9 Md R.A. H.V. S.V.
z-Scores: S3 - TOC
Target Standard Deviation 0.97 mg/L (Equivalent to 10% CV)
z-Score
-1.0 -0.7 -0.7 -0.5 -0.3 -0.1 0.0 0.2 0.3 0.3 0.4 1.3 1.9
19 20 4 15 17 3 25 6 10 22 11 21 16 5
Laboratory
En-Scores: S3 - TOC
En-Score
-1.3 -0.2 -0.4 -0.2 -0.3 -0.1 0.0 0.2 0.1 0.1 0.3 0.6 0.5 3.9
19 20 4 15 17 3 25 6 10 22 11 21 16 5
Laboratory

Figure 25

7 DISCUSSION OF RESULTS

7.1 Assigned Value and Traceability

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

Assigned values, spike values and/or homogeneity values were in agreement with each other within their estimates of uncertainty for all analytes of interest.

No assigned value was set for total P in S2 because too few results were reported for this test.

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

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 398 numerical results, 393 (99%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0.35% to 316% 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, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[9 – 15]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 25). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 20 laboratories reported results for chloride in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 20 laboratories' results is 2.7 mg/L (see equation 4, page 83). Laboratory 13 might have under-estimated its expanded measurement uncertainties reported for chloride in S1 as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 20 measurements. Alternatively, estimates of uncertainties for chloride larger than 19.9 mg/L (the uncertainty of the assigned value, 2.7 mg/L plus the allowable variation from the assigned value, the target standard deviation of 8.6 mg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainties reported by laboratories 10, 15 and 20 for chloride in S1might have been over-estimated.

Laboratory 13 should review the procedure they have used for estimating measurement uncertainty as most of their estimated uncertainties were over or under-estimated.

Laboratories 10 and 23 should also review their procedure for estimating measurement uncertainty as most of their estimated uncertainties were over-estimated and under-estimated respectively.

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 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. [12] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Some laboratories estimated uncertainties for measurement results larger than the reported results themselves.

Laboratories 8, 13 and 25 attached estimates of the expanded measurement uncertainty to results 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]

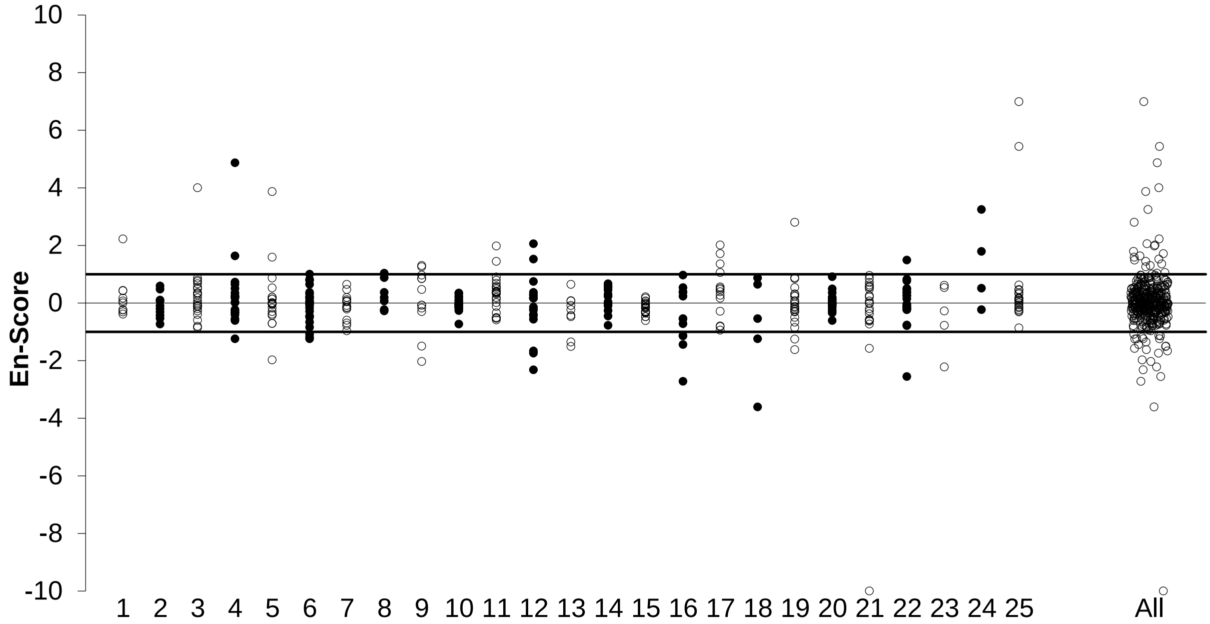
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 18.44 ± 3.4 mg/L, it is better to report 18.4 ± 3.4 mg/L or instead of 0.0023 ± 0.00048 mg/L, it is better to report 0.0023 ± 0.0005 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.

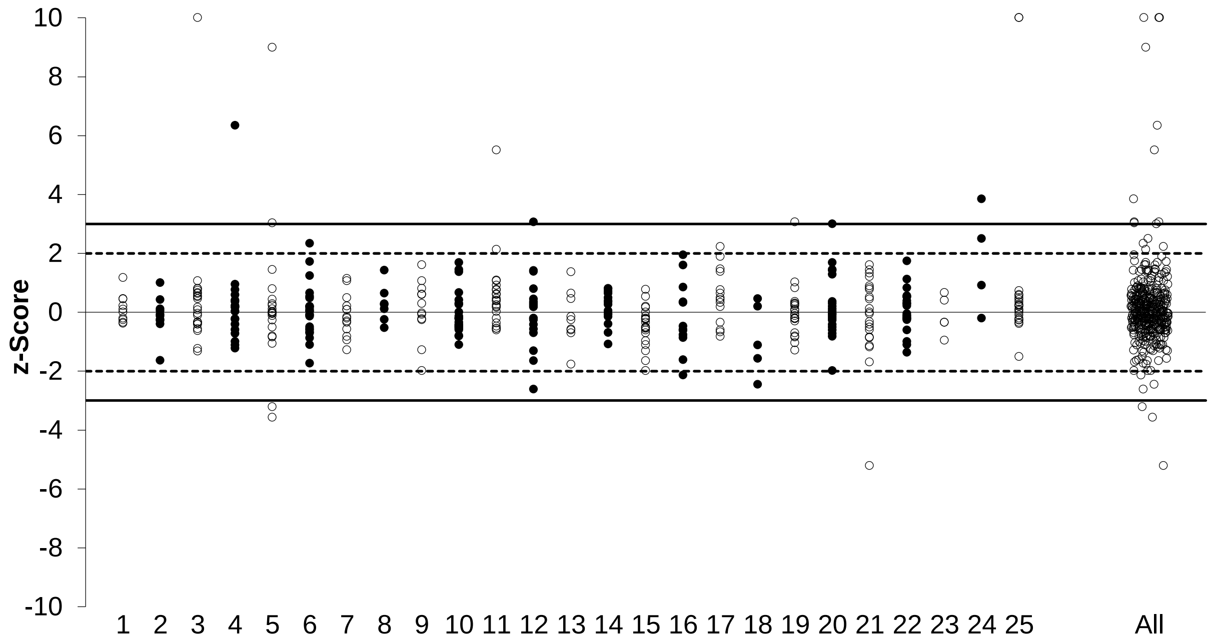
The dispersal of participants' E_n-scores is graphically presented in Figure 26. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 394 results for which E_n-scores were calculated, 347 (88%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.



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

Figure 26 E_n-Score Dispersal by Laboratory



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

Figure 27 z-Score Dispersal by Laboratory

7.4 z-Score

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

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 3.5%, 10%, 15% and 20% 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 28.

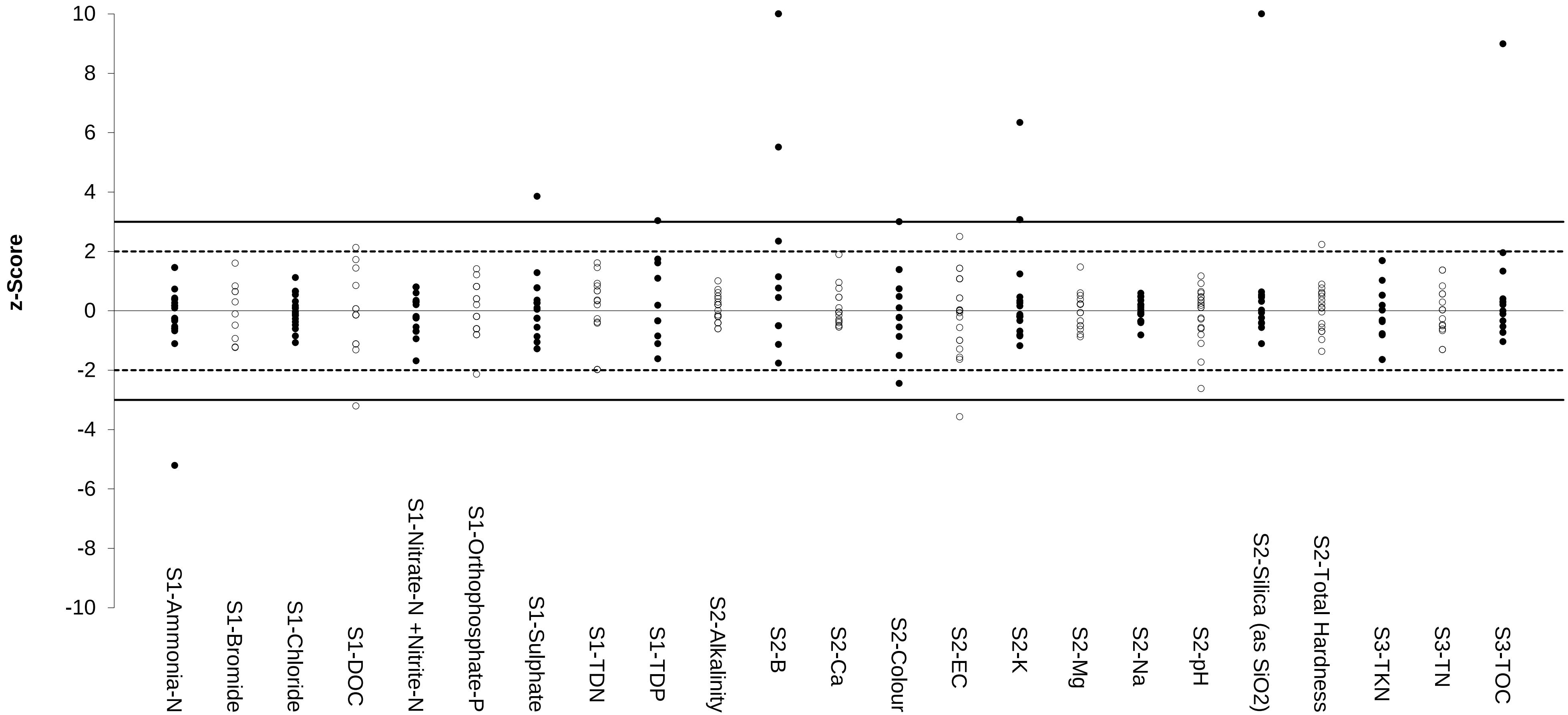
The dispersal of participants' z-scores is presented in Figure 27 (by laboratory code) and in Figure 28 (by test). Of 394 results for which z-scores were calculated, 373 (95%) returned a satisfactory score of $|z| \leq 2.0$ and 8 (2%) were questionable with a score of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2.0 or smaller than -2.0 should check for methoid or laboratory bias.

Laboratories 10, 15 and 22 reported results for all analytes except for two or three and all were satisfactory.

Table 28 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 PCV)
S1	Ammonia-N	0.156	9.6%	21%	15%
S1	Bromide	0.266	22%	20%	20%
S1	Chloride	86.3	5.7%	8.2%	10%
S1	DOC	5.07	13%	13%	10%
S1	NOx	0.134	10%	22%	15%
S1	Orthophosphate-P	0.0330	13%	22%	15%
S1	Sulphate	19.5	8.4%	10%	10%
S1	TDN	0.427	20%	18%	15%
S1	TDP	0.0386	26%	22%	20%
S2	Alkalinity	49.0	4.5%	8.9%	10%
S2	B	0.0316	14%	22%	10%
S2	Ca	20.1	5.1%	10%	10%
S2	Colour	20.7 Pt-Co units	16%	10%	15%
S2	EC	400 µS/cm	4.2%	6.5%	3.5%
S2	K	3.06	8.3%	14%	10%
S2	Mg	6.85	5.6%	12%	10%
S2	Na	42.5	3.8%	9.1%	10%
S2	pH	8.07	2.6%	12%	3.5%
S2	Silica	5.74	5.5%	12%	10%
S2	Total Hardness	75.3	7.9%	8.4%	10%
S2	Total P	Not Set	19%	NA	NA
S3	TKN	0.399	18%	18%	15%
S3	TN	0.498	14%	18%	15%
S3	TOC	9.71	7.8%	11%	10%

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



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

Figure 28 z-Score Dispersal by Test

Table 29 Summary of Participants' Results and Performance for S1

Lab Code	Ammonia-N (mg/L)	Bromide (mg/L)	Chloride (mg/L)	DOC (mg/L)	NO_3-N+NO_2-N (mg/L)	Orthophosphate-P (mg/L)	Sulphate (mg/L)	TDN (mg/L)	TDP (mg/L)
A.V.	0.156	0.266	86.3	5.07	0.134	0.0330	19.5	0.427	0.0386
H.V.	0.157	0.200	79	4.80	0.140	0.0377	19.3	0.443	0.0380
1	NT	<0.5	83	NT	NT	NT	19	NT	NT
2	0.166	NT	NT	NT	0.129	NT	NT	NT	NT
3	0.16	0.2	87	4.4	0.15	0.037	18.4	0.47	0.036
4	0.142	0.201	87.8	4.5	0.138	0.035	20.2	NT	NT
5	0.19	NT	86	3.44	0.15	0.029	17.43	0.41	0.062
6	0.14	0.26	91.9	5.94	0.12	0.03	19.7	0.44	0.03
7	0.158	0.216	84.941	NT	NT	0.032	17.0	NT	NT
8	0.1435	NT	91.8	NT	0.129	NT	20	NT	NR
9	0.150	NT	86	NT	0.140	0.037	17	0.3	0.051
10	0.13	0.24	92	5	0.13	0.029	20	0.52	<0.1
11	0.165	<1	81	6.15	0.123	0.032	21	0.486	0.047
12	0.15	NT	89	<1	0.15	0.04	20	0.4	0.04
13	<0.2	0.3	85	NT	NT	NT	19	NT	NT
14	0.162	0.3	77	NT	0.150	0.037	19.6	NT	NT
15	0.16	<0.5	91	5	0.12	0.03	21	0.3	<0.1
16	0.1419	0.351	82.2	5.5	0.141	0.0224	17.8	0.448	0.0261
17	NT	NT	NT	NT	NT	NT	NT	NT	NT
18	NT	NT	NT	4.5	NT	NT	NT	NT	NT
19	0.149	0.282	87.2	5.1	0.13	0.032	20	0.45	0.032
20	0.19	<0.5	84	5	0.14	0.03	22	0.3	<0.1
21	0.034	0.31	79	5.8	0.10	0.039	21	0.53	NR
22	0.165	NR	96	5	0.14	0.03	19	0.48	0.052
23	0.148	NR	NR	NR	0.115	0.035	NR	0.47	0.036
24	NR	NR	NR	NR	NR	NR	27	NR	NR
25	0.173	NT	85.4	5.1	0.146	0.034	19.0	0.402	0.036

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 30 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-Colour (Pt-Co units))	S2-EC (µS/cm)	S2-K (mg/L)	S2-Mg (mg/L)	S2-Na (mg/L)	S2-pH	S2-Silica (mg/L)	S2-Total Hardness (mg/L)	S2-Total P (mg/L)	S3-TKN (mg/L)	S3-TN (mg/L)	S3-TOC (mg/L)
A.V.	49.0	0.0316	20.1	20.7	400	3.06	6.85	42.5	8.07	5.74	75.3	Not Set	0.399	0.498	9.71
H.V.	NA	0.0325	23.4	NA	380	2.49	5.64	36.1	NA	NA	63.0	NA	0.430	0.543	9.2
1	48	<0.1	21	21	400	3.2	7.0	41	8.4	NT	NT	<0.04	NT	NT	NT
2	53.9	< 0.05	19.3	NT	377	3.02	6.80	42.7	7.99	NT	76.1	NT	NT	NT	NT
3	47	136	19.4	23	415	2.96	6.42	40.8	8.2	6.1	75	<50	0.43	0.54	9.6
4	47	<0.1	22	20	386	5	7	45	8.12	5.6	81	<1	0.4	0.5	9.0
5	49	0.033	20	NT	350	2.8	6.5	42	8.1	NT	77	0.031	0.40	0.52	18.44
6	48.3	0.039	19.1	22.2	400.4	3.44	6.25	42.2	7.58	6.05	71.1	NT	0.41	0.50	9.9
7	51.4	0.0352	19.5	NT	415	2.81	6.62	43.4	7.91	NT	76	0.041	NT	NT	NT
8	50.43	<0.05	NT	NT	420	NT	NT	NT	8.1	NT	NT	NT	NT	NT	NT
9	52	NT	NT	20	415	NT	NT	NT	8.24	5.70	NT	NT	NT	NT	NT
10	51	0.03	19	20	400	3	6.3	41	7.9	5.5	72	<0.5	0.5	0.6	10
11	50	0.049	21.6	19	415	3.11	7.26	44.5	8.14	5.75	80	<0.1	0.377	0.463	10.1
12	48	<0.05	21	25	397	4	7	44	7.33	5.41	70	<0.1	0.3	0.4	<1
13	46	0.026	NT	NT	392	NT	NT	NT	8.2	NT	70	<1.5	NT	0.6	NT
14	52.5	NT	19.8	NT	399	2.85	7.11	42.3	8.17	5.51	79	0.045	NT	NT	NT
15	50	0.03	19	20	400	3	6.5	41	8	5.1	68	<0.5	0.3	0.4	9.2
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0.353	0.452	11.6
17	46	0.034	23.9	25	406	3.16	7.86	43.3	8.25	6.02	92.1	0.035	0.350	0.448	9.38
18	50	NT	NT	13.1	378	NT	NT	NT	8.2	NT	NT	NT	NT	NT	NT
19	48	<0.1	20	20	382	4	7	42	7.84	5.92	70	<1	0.46	0.56	8.7
20	50	0.03	20	30	420	3	6.8	39	8.1	5.5	78	<0.5	0.5	0.5	9
21	47	0.028	20	18	400	2.7	7.2	43	7.9	6.0	82	<0.05	0.38	0.46	11
22	48	<0.1	20	20	386	3	7	42	7.76	6.04	65	<1	0.43	0.54	10
23	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
24	48	NR	NR	NR	435	NR	NR	NR	8.33	NR	NR	NR	NT	NT	NT
25	48	35	20.3	16	406	3.14	7.01	44.6	8.17	30.2	79.6	<0.1	NR	0.478	9.7

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

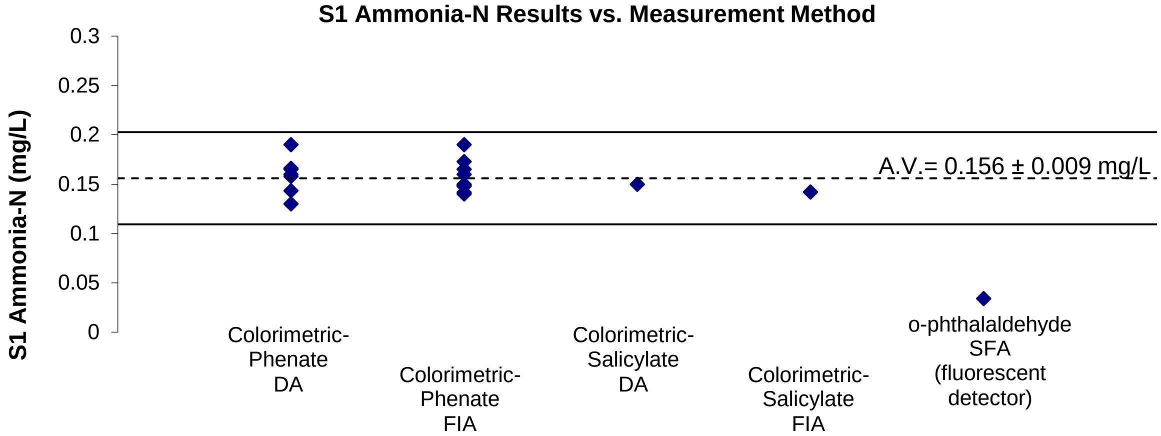
7.5 Participants' Results and Analytical Methods for Analyets

A summary of participants' results and performance is presented in Tables 29 and 30 and in Figures 27 and 28.

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 except for one. That laboratory confirmed the use of the wrong dilution factor as the cause of their unsatisfactory result, which was 5 times lower than the assigned value. Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination. One laboratory reported using the *o*-phthalaldehyde method with SFA and fluorescent detector (Figure 29).

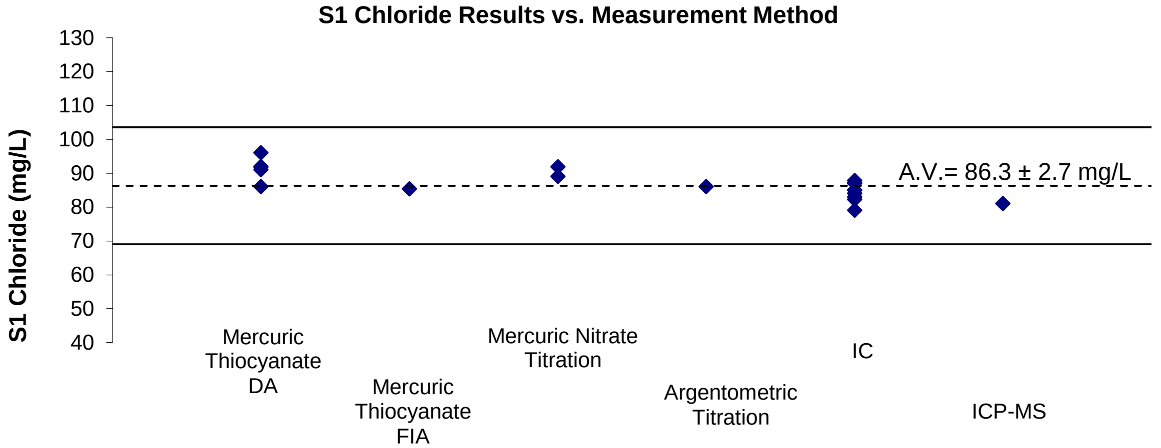


Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 29 S1-NH_3-N Results vs. Measurement Method

Bromide level in S1 was low at 0.266 mg/L, which was below the level of reporting of 4 laboratories. All laboratories who reported results used the ion chromatographic method for bromide measurement in S1.

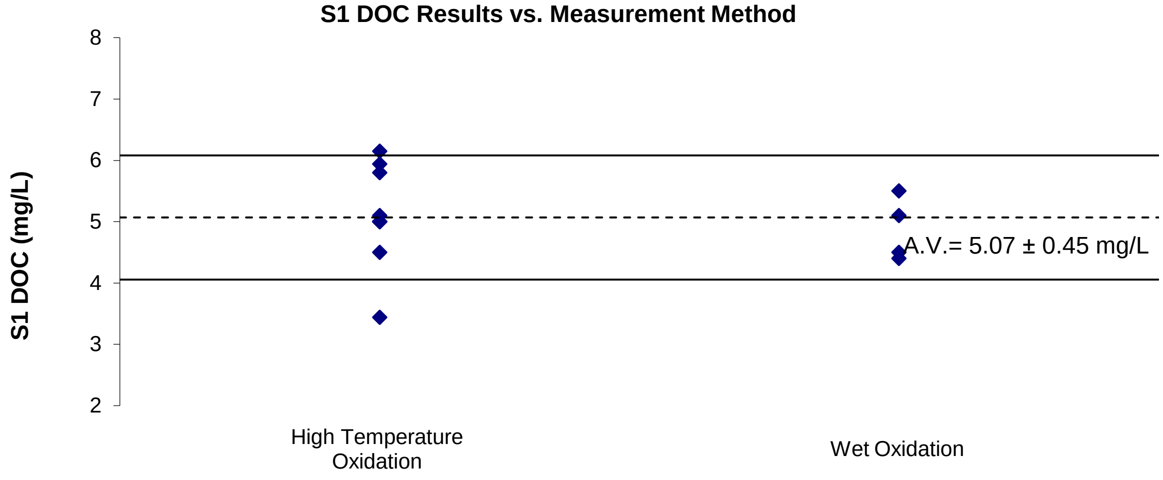
Chloride level in S1 was 86.3 mg/L. Participants used a wide variety of methods for chloride analysis in S1 and all produced compatible results (Figure 30).



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

Figure 30 S1-Chloride Results vs. Measurement Method

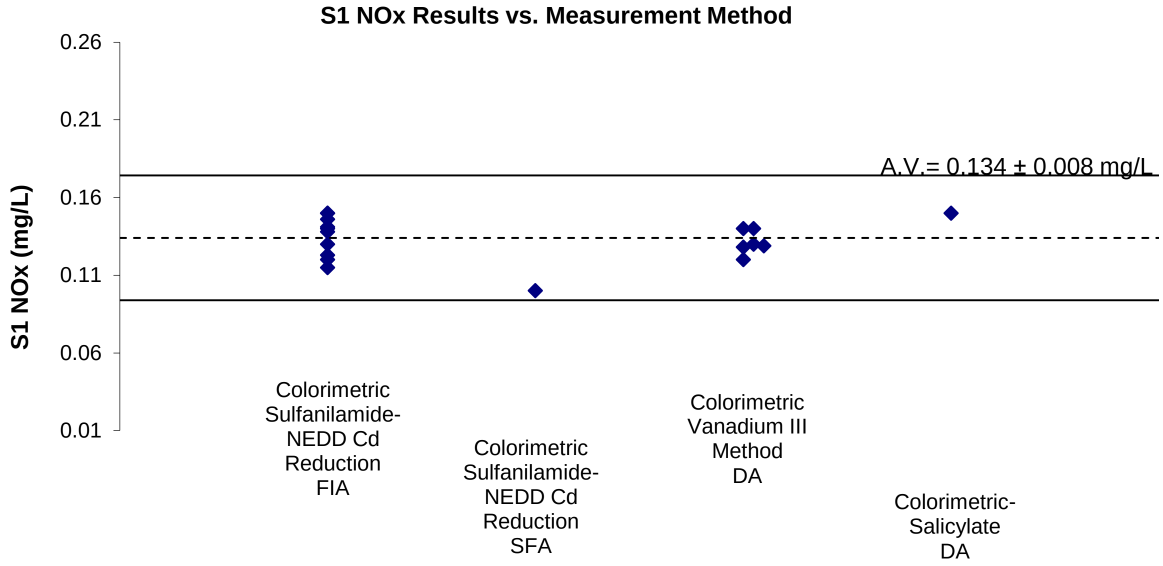
Dissolved Organic Carbon as dNPOC Participants used high temperature oxidation or wet oxidation; no significant difference was noticed between DOC results produced by these two methods (Figure 31).



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

Figure 31 S1-DOC Results vs. Measurement Method

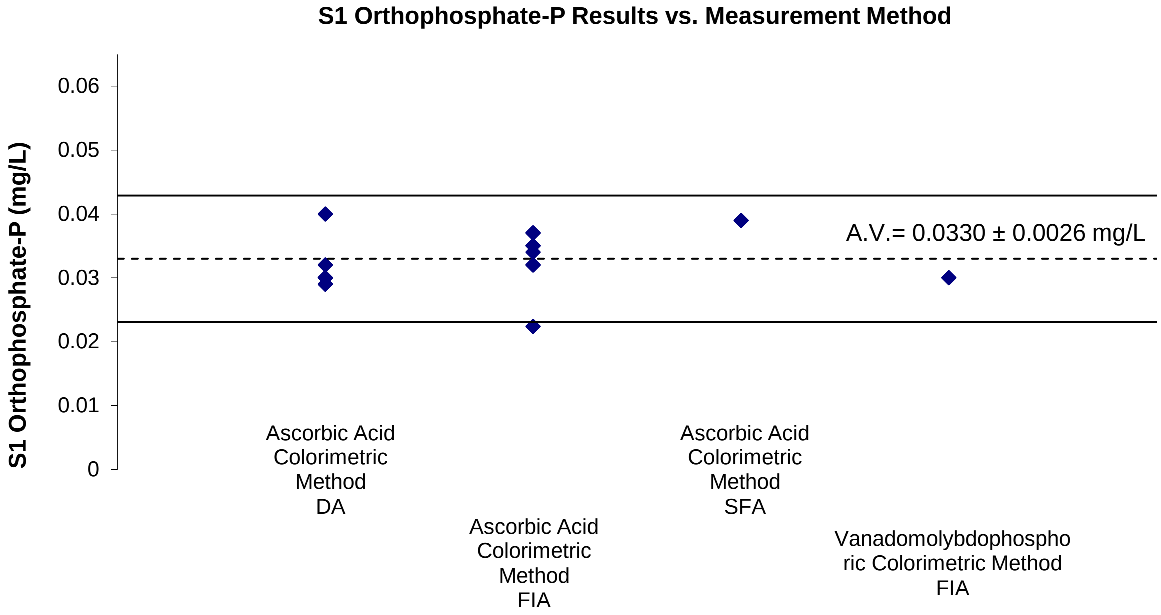
Nitrate-Nitrogen + Nitrite-Nitrogen Nineteen participants reported results for NO_3-N+NO_2-N and all performed satisfactorily. Eleven participants used colorimetric-sulfanilamide-NEDD Cd reduction, six used the Vanadium III colorimetric method with DA and one used the colorimetric salycilate method (Figure 32).



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

Figure 32 S1-NOx Results vs. Measurement Method

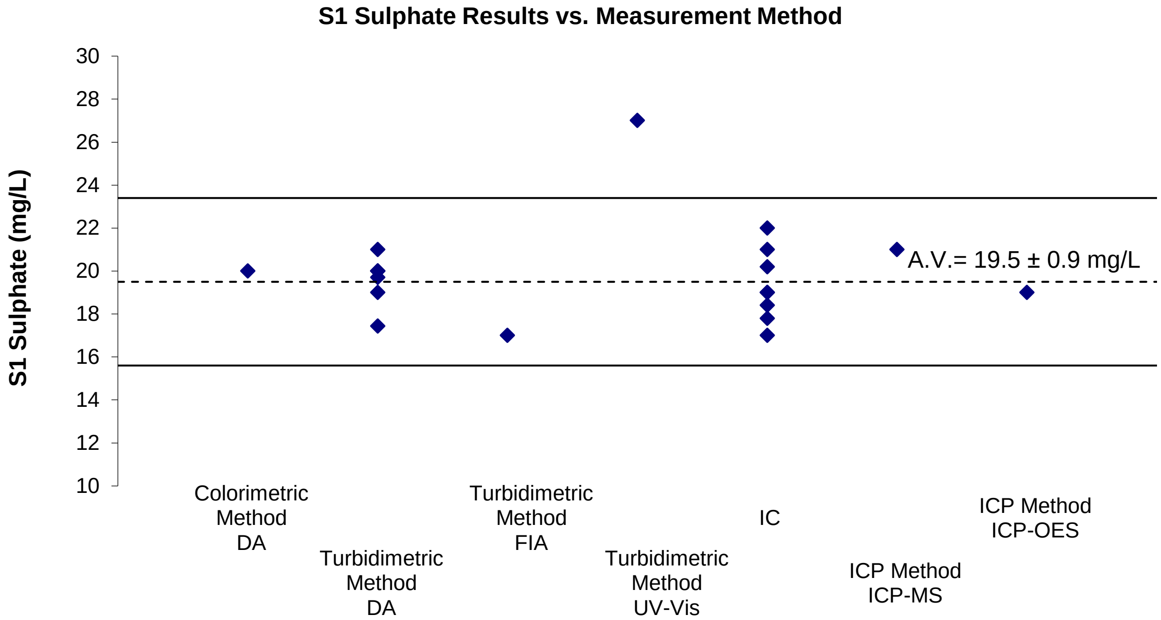
Orthophosphate-P One participant used a vanadomolybdophosphoric method for the measurement of orthophosphate-P in S1; all other participants used the ascorbic acid colorimetric method with FIA, SFA or DA determination (Figure 33). With the exception of one, all results were compatible with each other.



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

Figure 33 S1-Orthophosphate-P Results vs. Method

Sulphate participants used various methods and instrumental techniques for sulphate measurement in S1 and all produced compatible results, with the exception of one (Figure 34). Caution should be exercised when using the turbidimetric method in water with high organic content as it may not be possible to satisfactorily precipitate $BaSO_4$.[16]

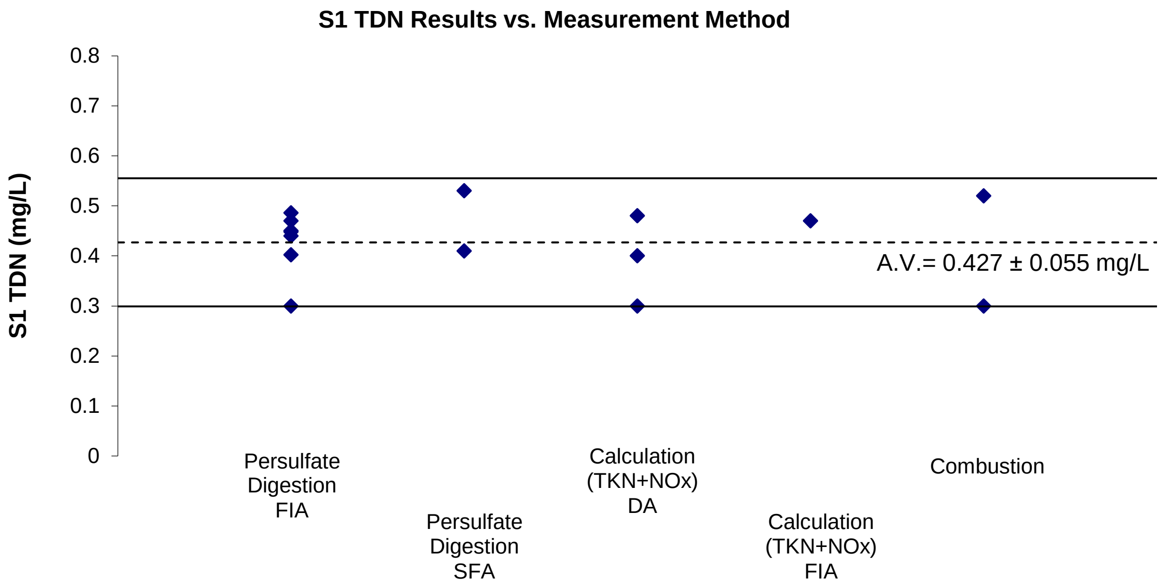


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 34 S1-Sulphate Results vs. Measurement Method

Although most of the S in soil samples is from sulphate compounds, false positive results can be produced when this is measured by ICP-OES and ICP-MS: these techniques measure total S and not only S from sulphate compounds.

Total Dissolved Nitrogen All reported results for TDN were compatible with each other and with the robust average of 0.427 ± 0.055 mg/L. Figure 35 presents plots of participants' results vs the measurement method used for TDN determination in S1.

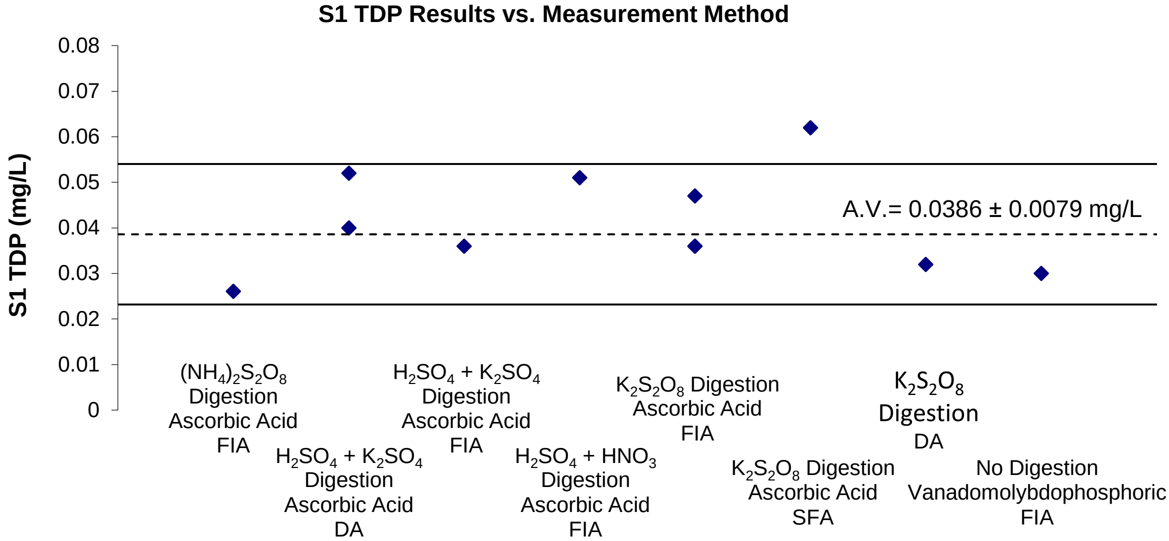


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 35 S1-TDN Results vs. Measurement Method

Total dissolved phosphorus level in S1 was low (0.0386 mg/L) which may have presented difficulty to some laboratories. The reported results were quite variable, with a high between-laboratory coefficient of variation of 26%.

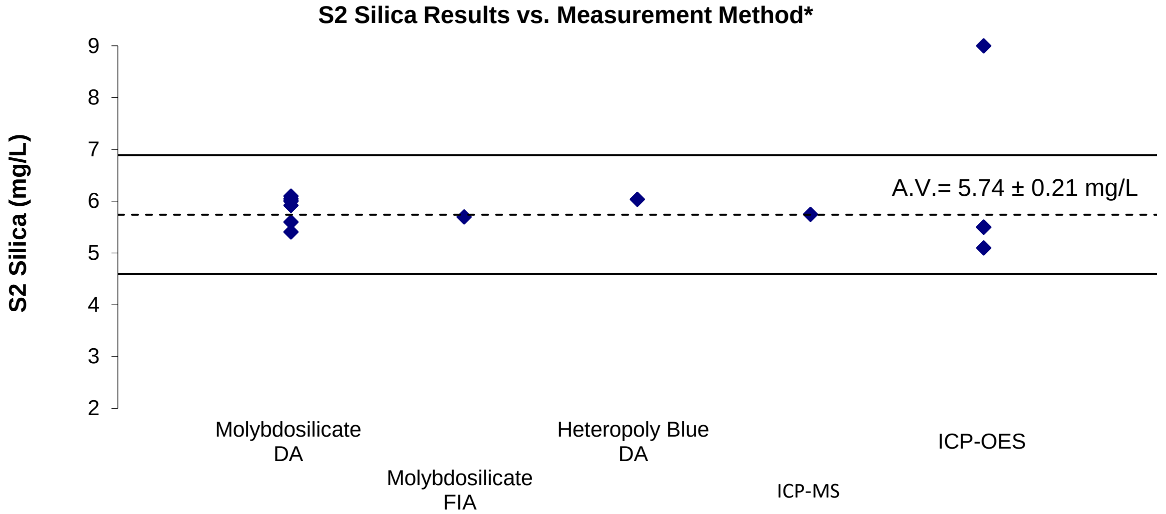
The dissolved phosphorus test measures the fraction of total phosphorus which is in the water (as opposed to being attached to suspended particles). It is determined by first filtering the sample, and then analysing the filtered sample for total phosphorus. The total dissolved phosphorus test measures all the forms of phosphorus in the sample: orthophosphate, condensed phosphate, and organic phosphate. This is accomplished by first by filtering then "digesting" (heating and acidifying) the sample to convert all the other forms to orthophosphate, and then measuring the orthophosphate by the ascorbic acid method. Laboratories used potassium persulphate, ammonium persulphate, sulphuric acid with potassium sulphate, or conducted a nitric acid and sulfuric acid digestion. The liberated orthophosphate was further measured colorimetrically by FIA or SFA. One laboratory measured orthophosphate in S1 directly using the vanadomolybdophosphoric method (Figure 36).
ICP-MS and ICP-OES techniques can also be used for TDP measurement, but these techniques would be unlikely to have the required sensitivity for such a low concentration.



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

Figure 36 S1-TDP Results vs. Measurement Method

Silica (as SiO_2) Plots of participants' results versus measurement technique used are presented in Figure 37.

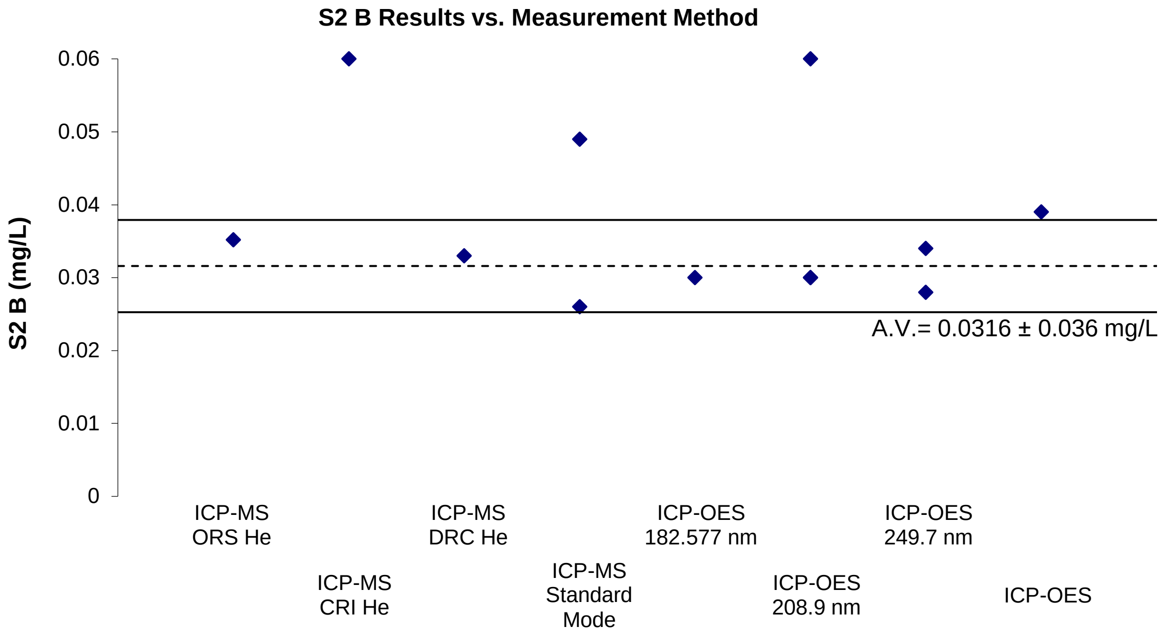


*Laboratory 25 result of 30.2 mg/L was plotted as 9 mg/L. Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 37 S2-Si (as SiO_2) Results vs. Measurement Method

Alkalinity to pH 4.5 as ($CaCO_3$) in S2 did not present analytical difficulty to participants. All reported results returned satisfactory z-scores (Table 30).

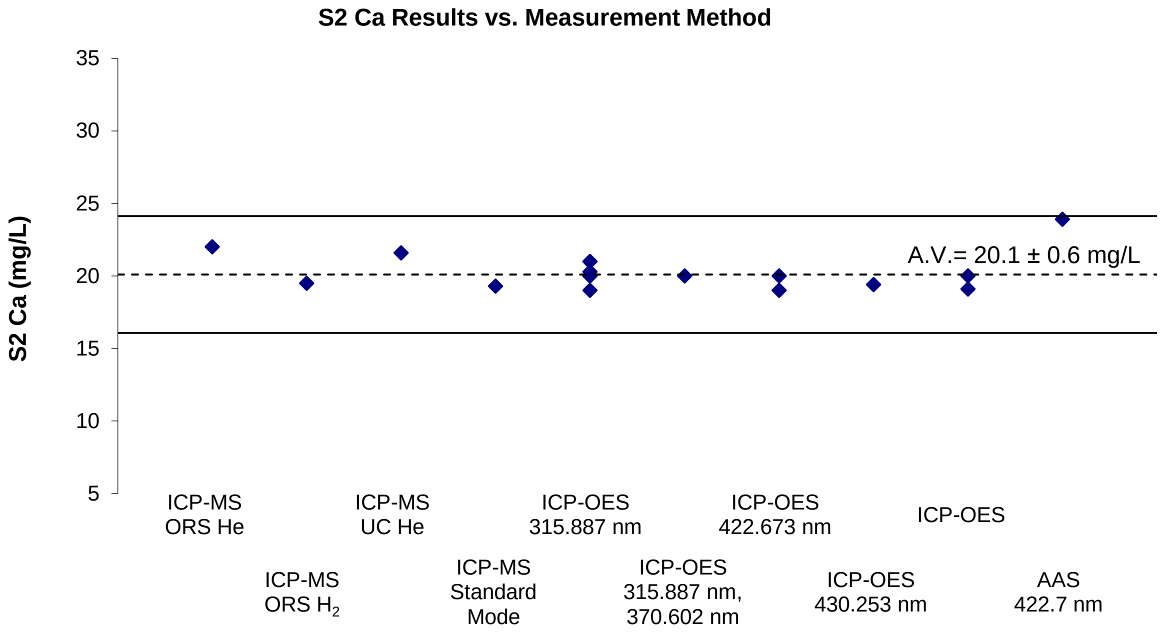
Boron level in S2 was low (0.0316 mg/L) which may have presented difficulty to some laboratories. Of 12 reported results, 8 returned satisfactory z-scores. All unsatisfactory results were higher than the assigned value (Figure 38). Boron is an element prone to contamination and suffers from the memory effect and tends to carry over to the next samples giving false positive results. If low level B has to be measured then the sampling system should be thoroughly cleaned and/or longer wash time should be used.



*Laboratories 3 and 25 results of 136 mg/L and of 35 mg/L respectively were plotted as 0.06 mg/L. Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 38 S2-B Results vs. Measurement Method

Calcium Participants used various instrumental techniques for Ca measurements in S2 and all produced compatible results (Figure 39).



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

Figure 39 S2-Ca Results vs. Measurement Method

Potassium Of 18 results reported for K in S2, 15 returned satisfactory z-scores. Participants used a wide variety of instrumental techniques, which are presented in Figure 40.

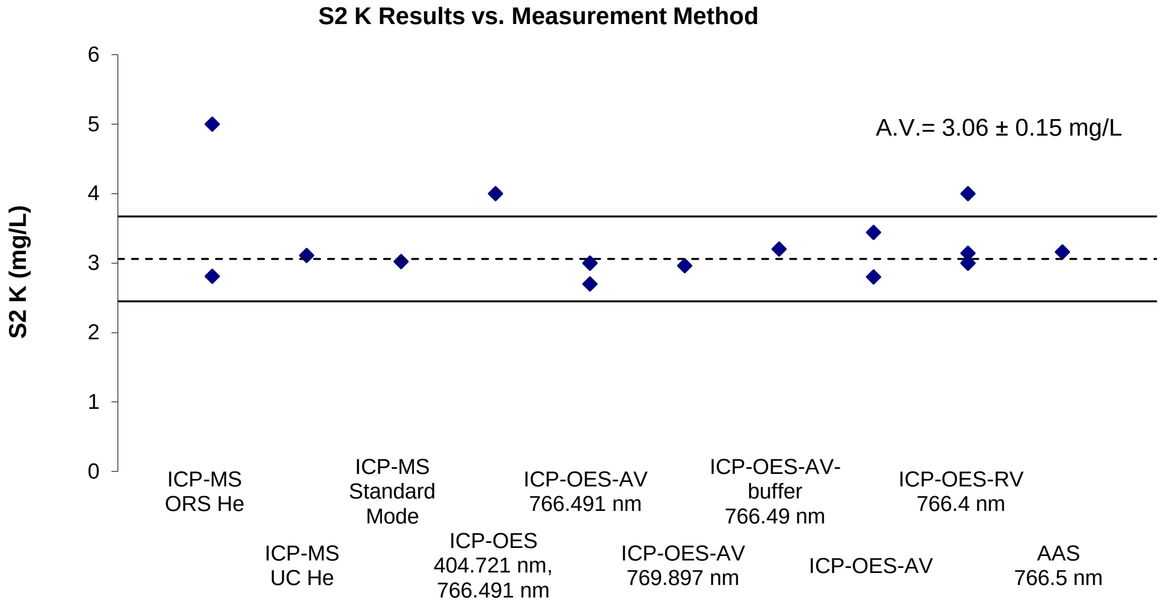


Figure 40 S2-K Results vs. Measurement Method

Sodium measurements in S2 did not present technical difficulty to participating laboratories. All reported results returned satisfactory z-scores (Figure 41).

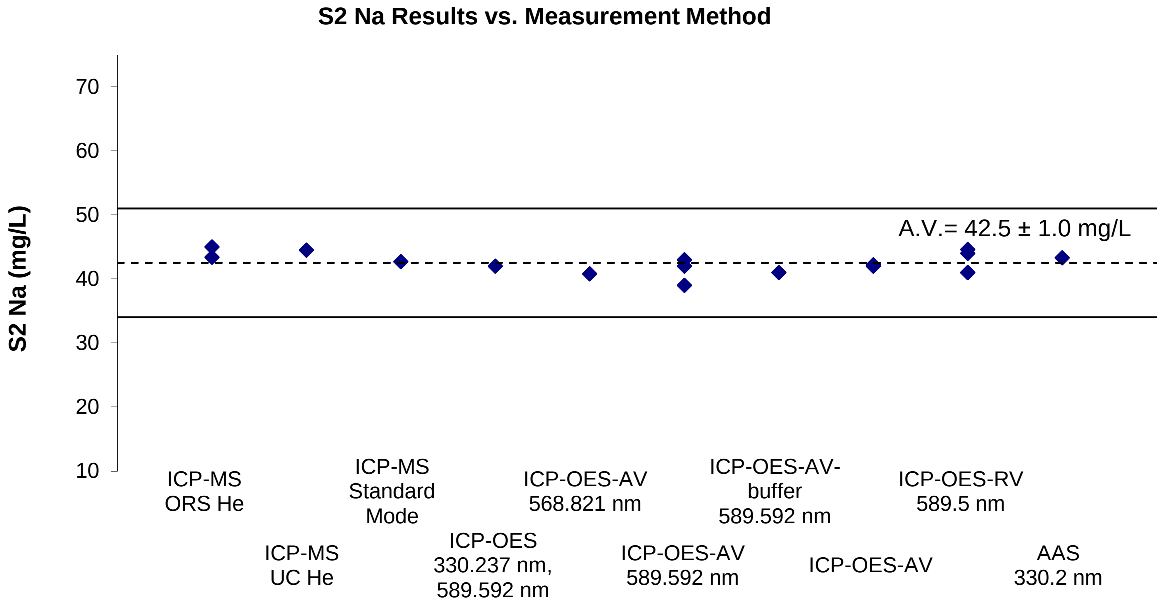


Figure 41 S2-Na Results vs. Measurement Method

Total Phosphorus level in S2 was low, with the median of the reported results being 0.038 mg/L. Only 4 results were reported for TP in S2, and all were compatible with each other (Figure 42).

One laboratory used the method of "no digestion" followed by ICP-MS determination, which measures only soluble P and not total P

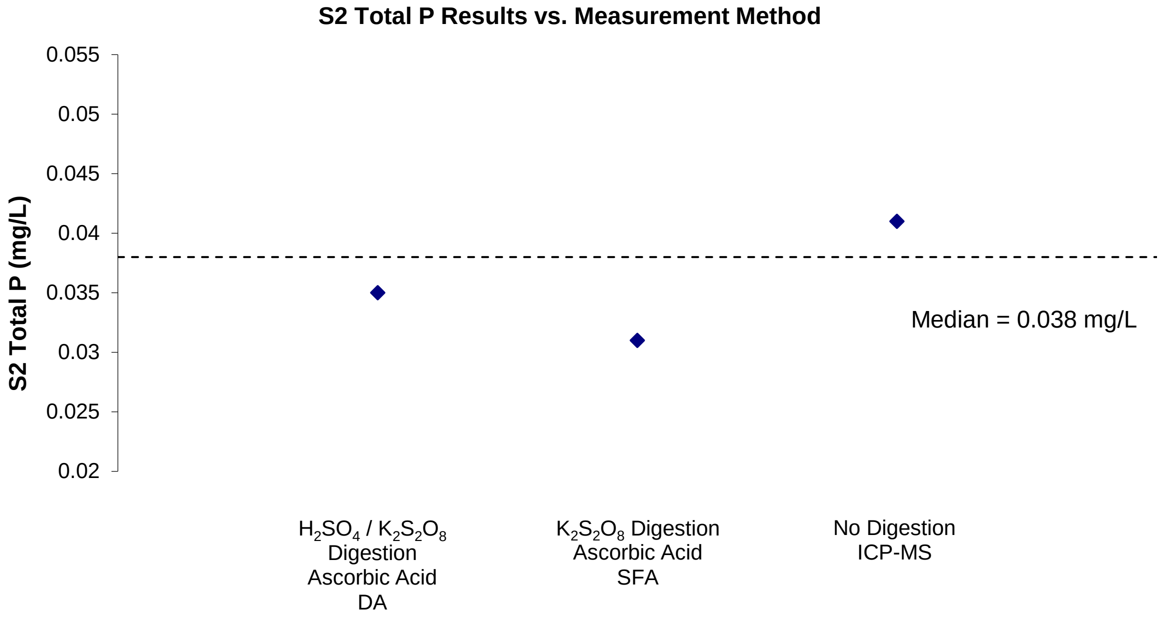
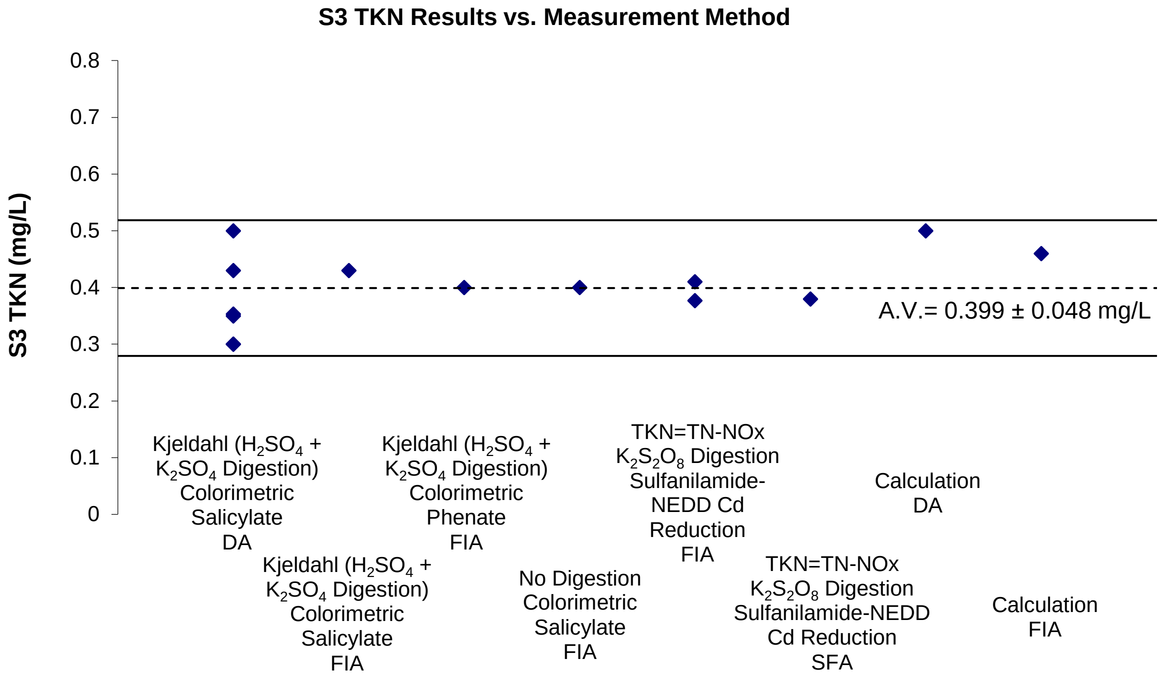


Figure 42 S2-P Results vs. Measurement Method

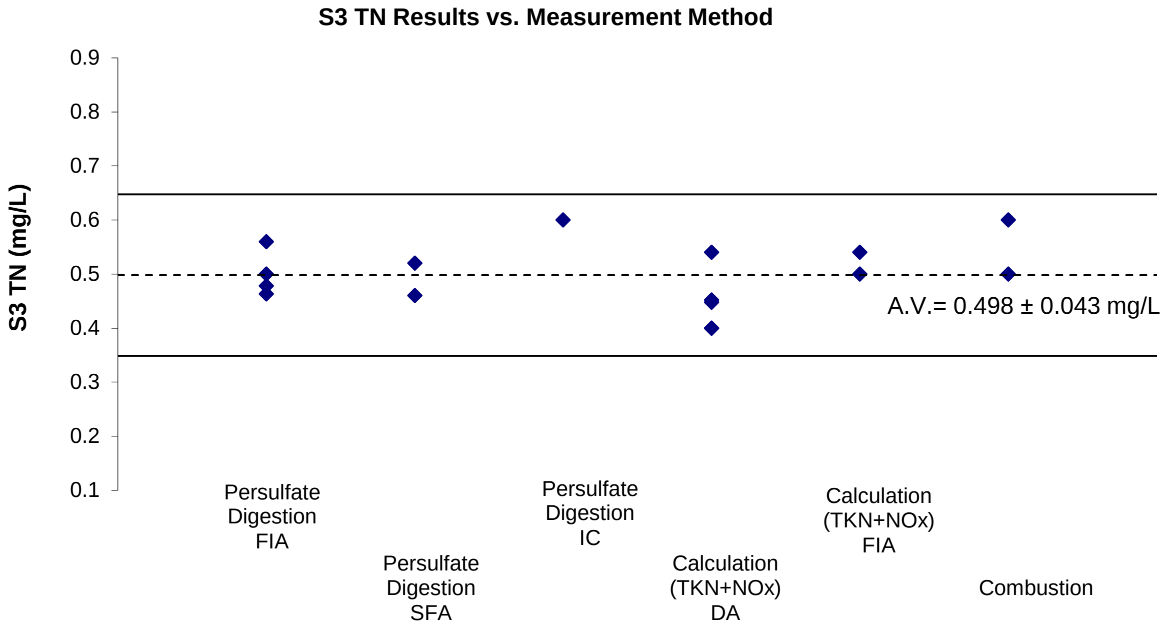
Total Kjeldahl Nitrogen Plots of participants results versus instrumental technique used are presented in Figure 43. Participants used various methods and all produced compatible results.



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

Figure 43 S3-TKN Results vs. Measurement Method

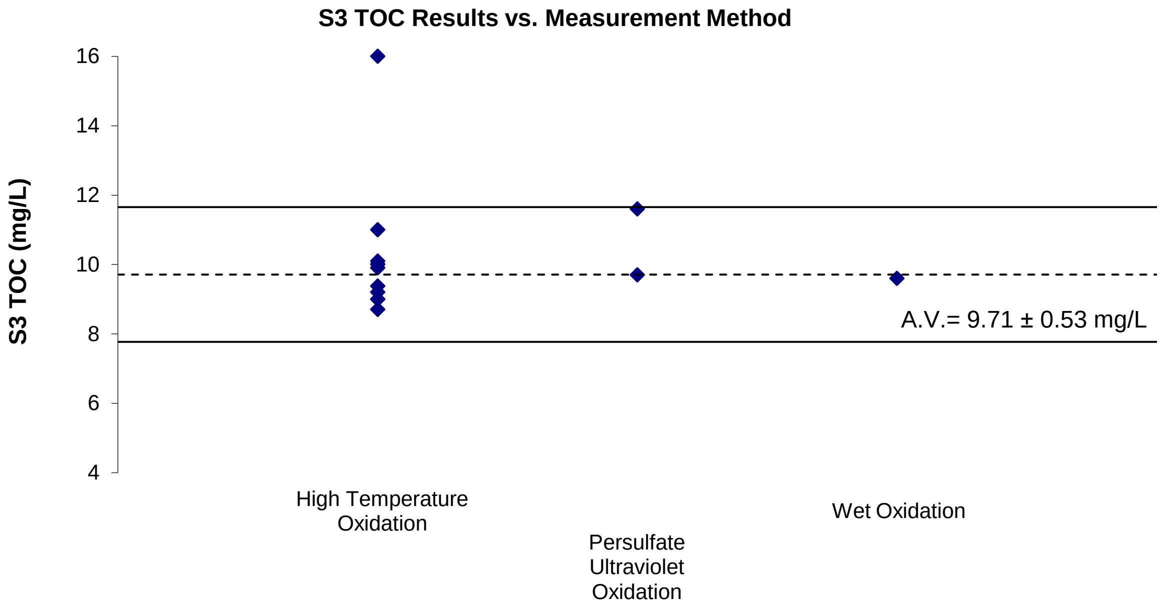
Total Nitrogen All 14 results reported for TN in S3 returned satisfactory z-scores. Plots of participants results versus the methods used are presented in Figure 44.



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

Figure 44 S3-TKN Results vs. Measurement Method

Total Organic Carbon. All results reported for TOC in S3 returned satisfactory z-scores except for one (Figure 45).



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

Figure 45 S3-TOC Results vs. Measurement Method

7.6 Comparison with Previous NMI Proficiency Tests of Nutrients in Water

AQA 21-10 is the 12th NMI proficiency test of nutrients in water. For most analytes, the same fixed target standard deviation was used in the present study as in previous studies of metals in water. This allowed for a comparison of participants' performance (z-scores) over time and provided a benchmark for progressive improvement.

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 90% to 96% (Figure 46).

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

Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \le 2.0$. Scores in the range $2.0 < |z| < 3.0$ may occasionally occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line are an indication of method or laboratory bias.

7.7 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 31).

Table 31 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CWWTMC; VHG-QWPMIN; QCI-136; pH C02745; Cat 141453 (colour); CRM-conductivity-C02741
2	CRM – CCV-1-A-100, CCV-1-B-100, Ammonium/Nitrate/Nitrite Standards for IC (Sigma)
3	CRM
4	RM
5	CRM
6	CRM
7	CRM – ICPMS CRM, ICV1-2, ICV3-1, HG CRM, ICV1-1, NH3 CRM, TDS CRM, BR CRM, ANIONS CRM
9	RM
11	CRM – CWW-TM-A, B and C
12	CRM
13	CRM – TMDW Trace Metals in Drinking Water #2025917
14	CRM
16	RM
17	SS
19	CRM – Choice Analytical CRMs
21	RM
22	CRM
23	RM – ex-PT reference samples
24	SS

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*'[17]

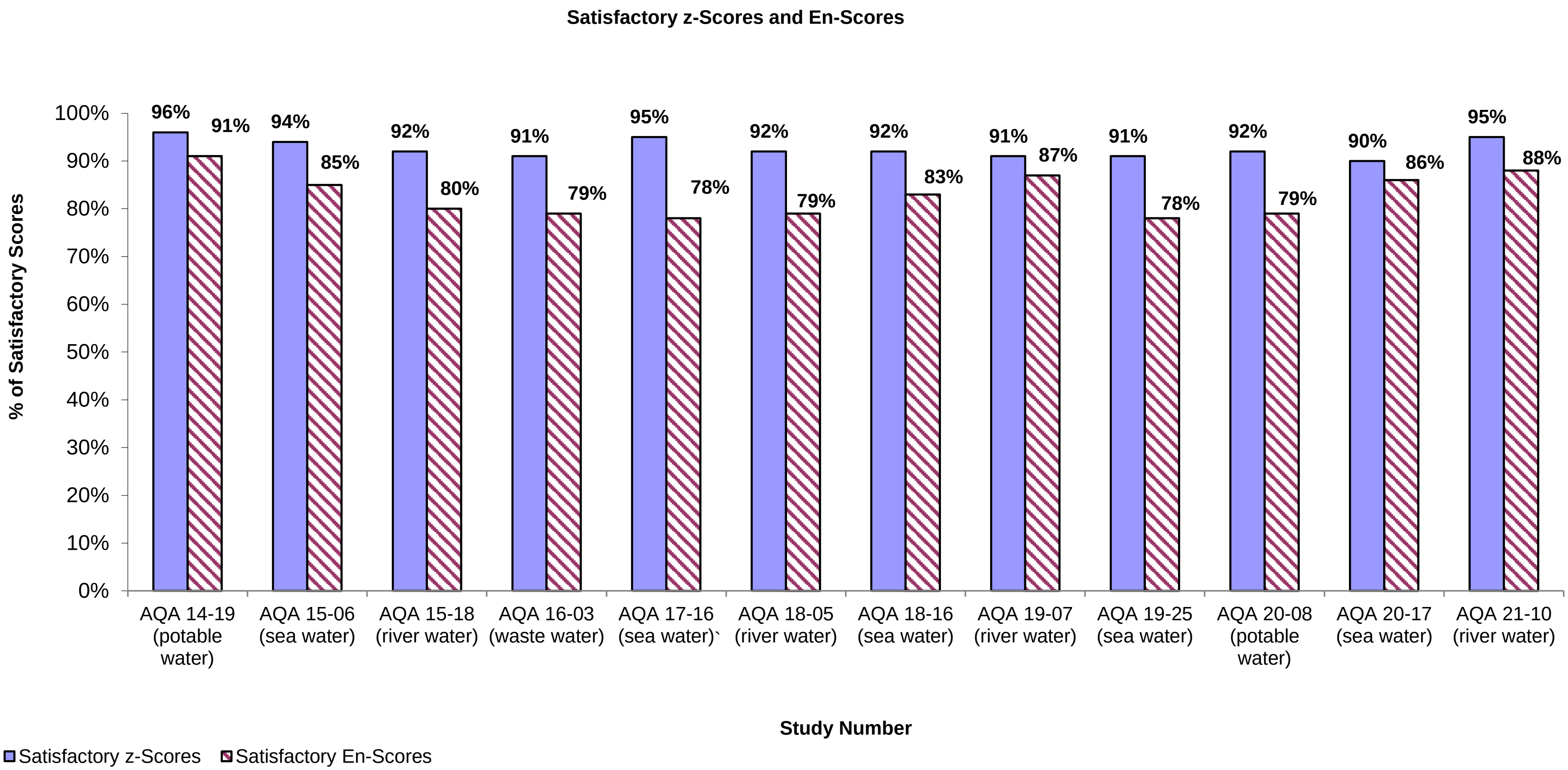


Figure 46 Participants’ Performance in Nutrients and Anions in Water PT Studies over Time

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A 1.1 Sample Preparation

Sample S1 was 400 mL of filtered, autoclaved and frozen river water fortified with orthophosphate-P, nitrate-N.

Sample S2 was 400 mL of unfiltered, river water fortified with P.

Sample S3 was 200 mL of unfiltered, autoclaved and frozen river water fortified with total nitrogen, total Kjeldahl nitrogen and total organic carbon.

A 1.2 Sample Analysis and Homogeneity Testing

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

Methodology for Total Elements

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±100^{o}C for 90 min.

Measurement of total elements in S2 involved using ICP-MS. 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 instrumental technique used for each analyte is given in Table 32.

Table 32 Instrumental Technique used for Total Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S2 Final Dilution Factor	Ion (m/z)
B	ICP-MS	Y	ORS	He	1	11
Ca	ICP-MS	Y	ORS	He	1	43
K	ICP-MS	Y	ORS	He	1	39
Mg	ICP-MS	Y	ORS	He	1	24
Na	ICP-MS	Y	ORS	He	1	23

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 Table 33.

Table 33 Methodology for test other than total elements in S1, S2 and S3

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
NO_3-N+NO_2-N	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
Total Hardness (as $CaCO_3$)	Calculation	ICP-OES
Total Kjeldahl Nitrogen	TKN=TN-NOx, Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Organic Carbon	High-Temperature Oxidation	NIR-detector

APPENDIX 2 - STABILITY STUDY

Samples S1 and S3 were dispatched on 28 June 2021. Participants were advised to store the Samples S1 and S3 frozen, if unable to commence analysis on the day of receipt. Sample condition on receipt and the date when the samples were received and analysed by the participants are presented in Table 34. No trends were evident between participants' results, samples' condition on receipt and days spent in transit (Figures 47 to 50).

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

Lab Code	Received Date	S1		S3	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	29/06/2021	Frozen	01/07/2021	NA	NA
2	30/06/2021	Good	08/07/2021	NA	NA
3	29/06/2021	Frozen		Frozen	
4	30/06/2021	Frozen	30/06/2021	Frozen	30/06/2021
5	29/06/2021	Cold	30/06/2021	Cold	30/06/2021
6	29/06/2021	Frozen	01/07/2021	Frozen	02/07/2021
7	29/06/2021	Frozen	22/07/2021	NA	NA
8	29/06/2021	Frozen	28/07/2021	NA	NA
9	30/06/2021	Frozen	08/07/2021	NA	NA
10	29/06/2021	Frozen	05/07/2021	Frozen	05/07/2021
11	29/06/2021	Frozen	07/07/2021	Frozen	07/07/2021
12	29/06/2021	Frozen	30/06/2021	Frozen	30/06/2021
13	30/06/2021	Chilled	02/07/2021	Chilled	02/07/2021
14	29/06/2021	Frozen	16/07/2021	NA	NA
15	29/06/2021	Frozen	05/07/2021	Frozen	05/07/2021
16	02/07/2021	Frozen	05/07/2021	Frozen	05/07/2021
17	29/06/2021	NA	NA	Frozen	05/07/2021
18	29/06/2021	Frozen	03/07/2021	NA	NA
19	29/06/2021	Satisfactory	02/07/2021	Satisfactory	02/07/2021
20	29/06/2021	Frozen	01/07/2021	Frozen	01/07/2021
21	29/06/2021	Frozen	13/07/2021	Frozen	13/07/2021
22	01/07/2021	Frozen	08/07/2021	Frozen	08/07/2021
23	29/06/2021	Frozen	15/07/2021	NA	NA
24*	28/07/2021	Frozen	31/07/2021	NA	NA
25	08/07/2021	Cold	13/07/2021	Cold	29/07/2021

NA = Not Applicable; * Laboratory 24 S1 sample dispatched 27/07/2021.

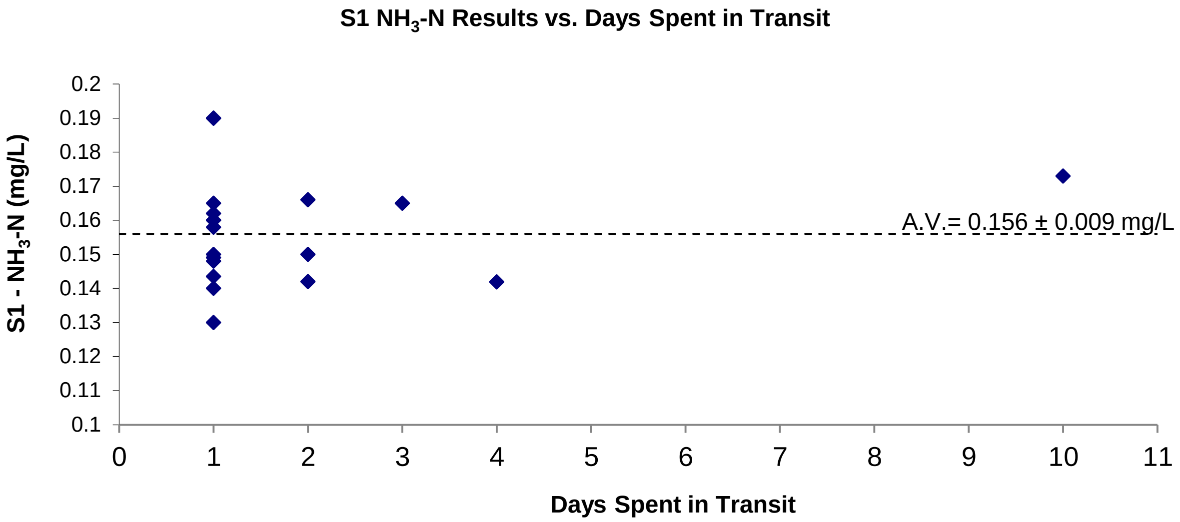


Figure 47 S1- NH3 Results vs Day Spent in Transit

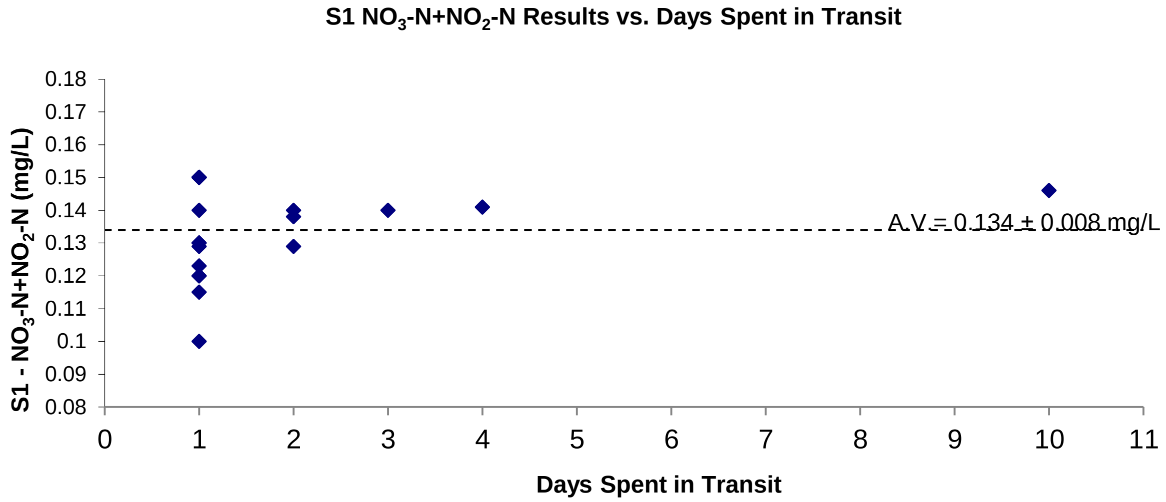


Figure 48 S1-NO_3-N+NO_2-N Results vs Day Spent in Transit

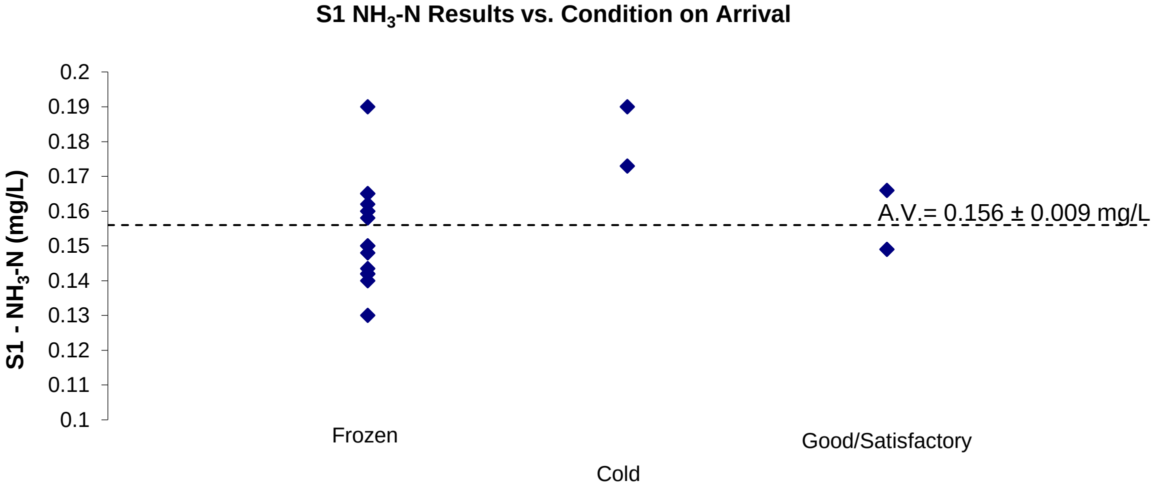


Figure 49 S1-NH_3-N Results vs Condition on Arrival

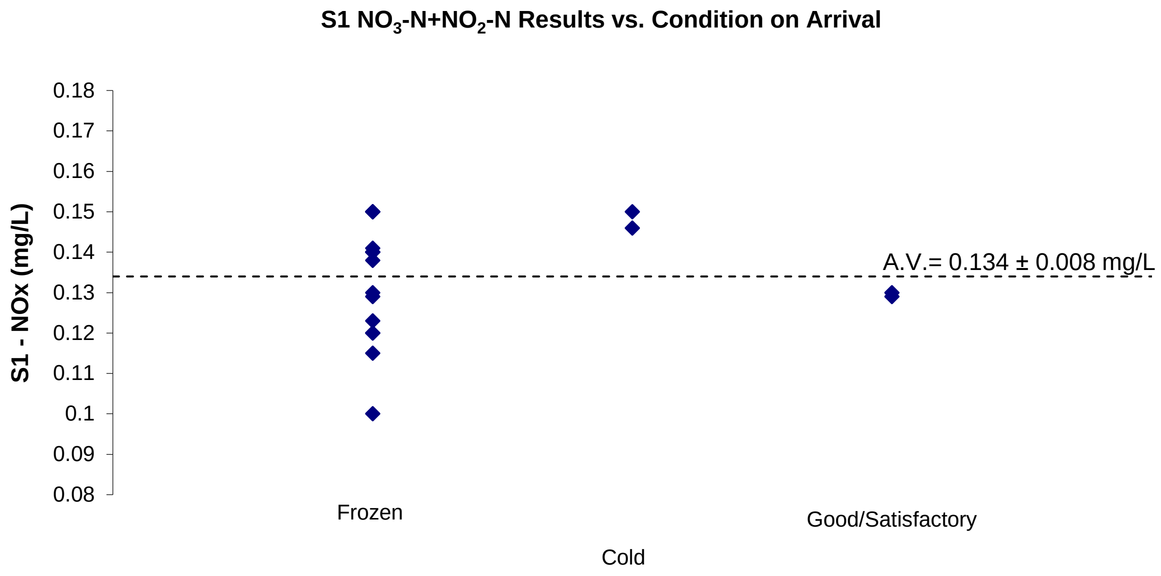


Figure 50 S1-NO_x Results vs Condition on Arrival

Stability Study

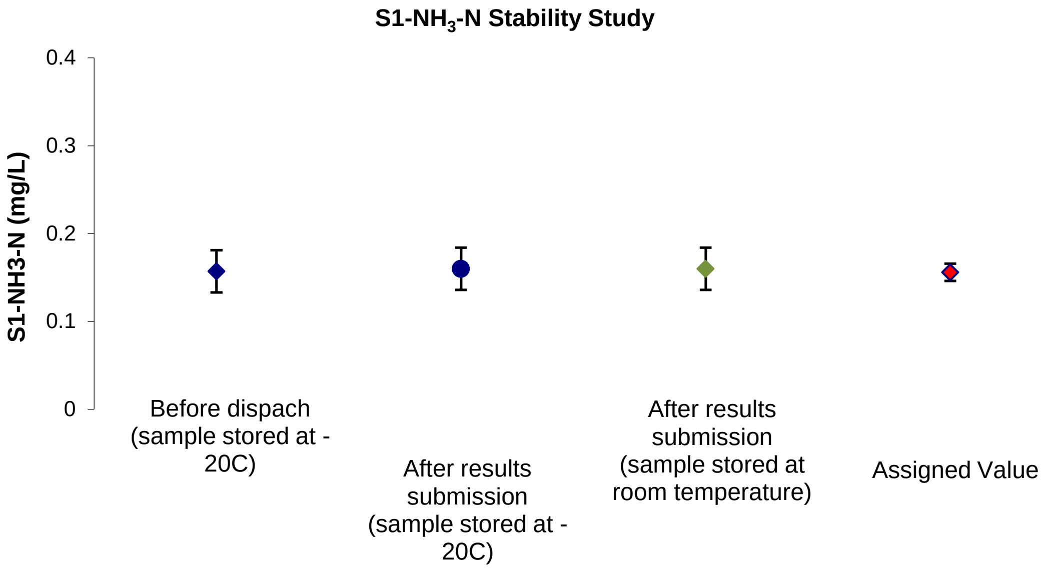
Stability studies conducted for nutrients and physical tests in water in previous studies found no significant changes in any of the analytes' concentration. A stability study was however conducted in the present study for the less stable analytes: NH_3-N and NO_3-N+NO_2-N in S1.

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

To test for storage stability, the results from two sets of samples were kept at -20°C (reference samples-RS) and were compared to the results from two samples 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 were compared from samples analysed before the samples' dispatch (T0) and the end of the study after result submission (T1). Each sample was analysed in duplicate together with a set of quality control samples consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes.

Results were in good agreement with each other as well as with the assigned value within their stated uncertainties (Figure 51).



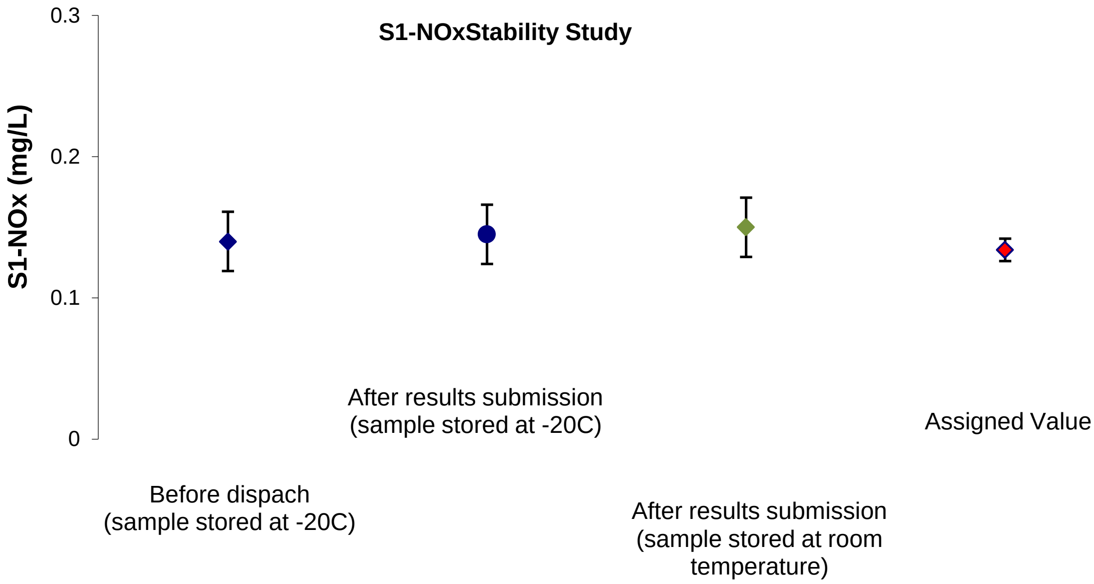


Figure 51 Stability Study Results

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 35.

Table 35 Uncertainty of Assigned Value for Chloride in Sample S1

No. results (p)	20
Robust Average	86.3 mg/L
$S_{rob\ av}$	4.9 mg/L
$u_{rob\ av}$	1.4 mg/L
k	2
$U_{rob\ av}$	2.7 mg/L

The assigned value for Chloride in Sample S1 is **86.3 ± 2.7 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 10).

A worked example is set out below in Table 36.

Table 36 z-Score and E_n-score for Chloride result reported by Laboratory 1 in S1

Chloride Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
83 ± 8	86.3 ± 2.7	10% as CV or 0.10 x 86.3 = = 8.63 mg/L	$z = \frac{(83 - 86.3)}{8.63}$ z = -0.38	$En = \frac{(83 - 86.3)}{\sqrt{8^2 + 2.7^2}}$ E_n = -0.39

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] An example is given. Between 2014 and 2021, NMI carried out twelve 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 for all studies with chloride in these PTs.

Table 37 Chloride Results for Laboratory X From Proficiency Testing Studies of Nutrients, Anions and Physical Tests in Water.

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 14-19	Potable	51.9 ± 10	55.4 ± 1.4	2.9	8
AQA 15-18	River	65.7 ± 10	70.3 ± 3.6	6.5	10
AQA 16-03	Waste	3099 ± 320	2990 ± 170	6.3	8
AQA 17-16	Sea water	13100 ± 1300	12800 ± 420	4.1	10
AQA 18-05	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
AQA 20-17	Sea Water	9800 ± 980	10700 ± 400	4.9	10
AQA 21-10	River	81 ± 10	86.3 ± 2.7	5.7	20
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 38 sets out the expanded uncertainty for results of the measurement of Chloride in potable, fresh, waste or sea water over the range 20.0 – 20000 mg/L.

Table 38 Uncertainty of chloride results estimated using PT data

Results mg/L	Uncertainty mg/L
20.0	2.2
500	55
1000	110
10000	1100
20000	2200

The 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
DRC	Dynamic Reaction Cell
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	Inductively Coupled Plasma - Optical Emission 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 39 Measurement Methods and Instrument Techniques for Ammonia-N

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2	Colorimetric - Phenate Method	DA	
3	Colorimetric - Phenate Method	FIA	in house
4	Colorimetric - Salicylate Method	FIA	APHA
5	Colorimetric - Phenate Method	FIA	APHA 4500
6	Colorimetric - Phenate Method	FIA	
7	Colorimetric - Phenate Method	DA	4200_R3
8	Colorimetric - Phenate Method	DA	APHA.4500
9	Colorimetric - Phenate Method	FIA	APHA 4500-NH3 H
10	Colorimetric - Phenate Method	DA	
11	Colorimetric - Phenate Method	FIA	APHA4500NH3-H
12	Colorimetric - Salicylate Method	DA	APHA 4500-NH3
13	Ion Selective Electrode Method	Ion Selective Electrode	APHA
14			
15	Colorimetric - Phenate Method	DA	
16	Colorimetric - Phenate Method	FIA	APHA4500-NH3
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Colorimetric - Phenate Method	FIA	APHA 4500
20	Colorimetric - Phenate Method	DA	
21	Fluorometric Determination - OPA Method	SFA	
22	Colorimetric - Phenate Method	DA	APHA, 4500-NH3 G
23	Colorimetric - Phenate Method	FIA	APHA
24			
25	Colorimetric - Phenate Method	FIA	4500-NH3 H

Table 40 Measurement Methods and Instrument Techniques for Bromide

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA 4110B
2			
3	Ion Chromatographic Method	IC	in house
4	Ion Chromatographic Method	IC	APHA
5	NT	N/A	N/A
6	Ion Chromatographic Method	IC	
7	Ion Chromatographic Method	IC	4270_R3
8	NT	NT	NT
9	NT	NT	NT
10	Ion Chromatographic Method	IC	
11	ICP-Method	ICP-MS	W32
12			
13	Ion Chromatographic Method	IC	APHA
14			
15	Ion Chromatographic Method	IC	
16	Ion Chromatographic Method	IC	APHA4110B(modified)
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Ion Chromatographic Method	IC	APHA 4110
20	Ion Chromatographic Method	IC	
21	Ion Chromatographic Method	IC	APHA
22			
23			
24			
25	NT		

Table 41 Measurement Methods and Instrument Techniques for Chloride

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA 4110B
2			
3	Ion Chromatographic Method	IC	in house
4	Ion Chromatographic Method	IC	APHA
5	Mercuric Thiocyanate	DA	APHA 4500
6	Mercurric Nitrate Titration	DA	
7	Ion Chromatographic Method	IC	4270_R3
8	Mercuric Thiocyanate	DA	APHA.4500
9	Argentometric Titration	Manual Analysis	APHA 4500-Cl B
10	Mercuric Thiocyanate	DA	
11	ICP-Method	ICP-MS	W32
12	Mercurric Nitrate Titration	DA	APHA 4500
13	Ion Chromatographic Method	IC	APHA
14			
15	Mercuric Thiocyanate	DA	
16	Ion Chromatographic Method	IC	APHA4110B(modified)
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Ion Chromatographic Method	IC	APHA 4110
20	Ion Chromatographic Method	IC	
21	Ion Chromatographic Method	IC	APHA
22	Mercuric Thiocyanate	DA	APHA 4500 Cl- E
23			
24			
25	Mercuric Thiocyanate	FIA	4500-CL G

Table 42 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2			
3	Wet-Oxidation	NIR-detector	in house
4	if other method please type	if other technique please type	APHA
5	High-Temperature Oxidation	NIR-detector	APHA 4500
6	High-Temperature Oxidation	NIR-detector	
7			
8	NT	NT	NT
9	NT	NT	NT
10	High-Temperature Oxidation	NIR-detector	
11	High-Temperature Oxidation	NIR-detector	APHA5310-B
12	High-Temperature Oxidation	NIR-detector	APHA 5310
13			
14			
15	High-Temperature Oxidation	NIR-detector	
16	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA5310C(modified)
17	Not Applicable	Not Applicable	Not Applicable
18	Wet-Oxidation	NIR-detector	
19	High-Temperature Oxidation	NIR-detector	APHA 5310
20	High-Temperature Oxidation	NIR-detector	
21	High-Temperature Oxidation	NIR-detector	APHA
22	High-Temperature Oxidation	NIR-detector	APHA 5310 A, B & C
23			
24			
25	Persulfate-Ultraviolet Oxidation	NIR-detector	5310 C

Table 43 Measurement Methods and Instrument Techniques for NOx

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2	Colorimetric -vanadium III method	DA	
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	in house
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
5	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500
6	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
7			
8	Colorimetric -vanadium III method	DA	ISO 15923-1:2013
9	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500-NO3 A,E,I
10	Colorimetric -vanadium III method	DA	
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO3-F
12	Colorimetric - salicylate method	DA	
13			
14			
15	Colorimetric -vanadium III method	DA	
16	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA-4500NO3(modified)
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA 4500
20	Colorimetric -vanadium III method	DA	
21	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
22	Colorimetric -vanadium III method	DA	NEMI METHOD ID: 9171
23	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
24			
25	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500-NO3 I

Table 44 Measurement Methods and Instrument Techniques for Orthophosphate-P

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2			
3	Ascorbic Acid Colorimetric Method	FIA	in house
4	Ascorbic Acid Colorimetric Method	FIA	APHA
5	Ascorbic Acid Colorimetric Method	DA	APHA 4500
6	Vanadomolybdophosphoric Colorimetric Method	FIA	
7	Ascorbic Acid Colorimetric Method	DA	052.1_R5
8	NT	NT	NT
9	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P A,B + E
10	Ascorbic Acid Colorimetric Method	DA	
11	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-G
12	Ascorbic Acid Colorimetric Method	DA	APHA 4500
13			
14			
15	Ascorbic Acid Colorimetric Method	DA	
16	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PG
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Ascorbic Acid Colorimetric Method	FIA	APHA 4500
20	Ascorbic Acid Colorimetric Method	DA	
21	Ascorbic Acid Colorimetric Method	SFA	APHA
22	Ascorbic Acid Colorimetric Method	DA	APHA 4500 - P A, B & F
23	Ascorbic Acid Colorimetric Method	FIA	APHA
24			
25	Ascorbic Acid Colorimetric Method	FIA	4500-P G

Table 45 Measurement Methods and Instrument Techniques for Sulphate

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Ion Chromatographic Method	IC	APHA 4110B
2			
3	Ion Chromatographic Method	IC	in house
4	Ion Chromatographic Method	IC	APHA
5	Turbidimetric Method	DA	APHA 4500
6	Turbidimetric Method	DA	
7	Ion Chromatographic Method	IC	4270_R3
8	Colorimetric Method	DA	APHA.4500
9	Turbidimetric Method	FIA	APHA 4500-SO4
10	Turbidimetric Method	DA	
11	ICP Method	ICP-MS	W32
12	Turbidimetric Method	DA	
13	Ion Chromatographic Method	IC	APHA
14			
15	Turbidimetric Method	DA	
16	Ion Chromatographic Method	IC	APHA4110B(modified)
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Turbidimetric Method	DA	USEPA 300
20	Ion Chromatographic Method	IC	
21	Ion Chromatographic Method	IC	APHA
22	Turbidimetric Method	DA	APHA 4500-SO4 2-
23			
24	Turbidimetric Method	UV-Vis Spectrophotometer	APHA 4500 E
25	ICP Method	ICP-OES	3120 B

Table 46 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2			
3	Calculation (TKN+NOx)	FIA	in house
4	Persulfate digestion	FIA	APHA
5	Persulfate digestion	SFA	APHA 4500
6	Persulfate digestion	FIA	
7			
8	NT	NT	NT
9	Persulfate digestion	FIA	APHA 4500-N C
10	Combustion	DA	
11	Persulfate digestion	FIA	APHA4500P-J
12	Calculation (TKN+NOx)	DA	
13			
14			
15	Calculation (TKN+NOx)	DA	
16	Persulfate digestion	FIA	APHA4500NC&4500NO3
17	Not Applicable	Not Applicable	Not Applicable
18			
19	Persulfate digestion	FIA	APHA 4500
20	Combustion	Chemiluminescence detection	
21	Persulfate digestion	SFA	APHA
22	Calculation (TKN+NOx)	DA	APHA 4500 N A & D
23	Persulfate digestion	FIA	APHA
24			
25	Persulfate digestion	FIA	4500-P J

Table 47 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Laboratory Code	Measurement Method		Instrument	Method Reference
1				
2				
3	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
4		Ascorbic Acid Colorimetric Method	FIA	APHA
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA 4500
6		Vanadomolybdophosphoric Colorimetric Method	FIA	
7				
8	NT	NT	NT	NT
9	H2SO4+HNO3-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA 4500-P H
10	HNO3-Digestion	ICP Method	ICP-OES	
11	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
12	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500 Norg-D
13				
14				
15	HNO3-Digestion	ICP Method	ICP-OES	
16	(NH4)2S2O8 Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PH
17	NA	Not Applicable	Not Applicable	Not Applicable
18				
19		Persulfate digestion	DA	APHA 4500
20	HNO3-Digestion	ICP Method	ICP-OES	
21				
22	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500 N-D
23	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
24				
25	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	4500-P J

APPENDIX 7 - METHODOLOGY FOR S2

Table 48 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-OES-AV-buffer	Y			1	208.957
2	ICP-MS					
3	ICP-OES-AV	Y 371.029	NA	NA	1	208.889
4	ICP-MS	SC,Rh,Ir		He	10	NA
5	ICP-MS		DRC	He		
6	ICP-OES-AV					
7	ICP-MS	Sc	ORS	He	1	11
8	NT	NT	NT	NT	NT	NT
9	NT	NT	NT	NT	NT	NT
10	ICP-OES-RV	Lu	NA		NA	208.956
11	ICP-MS	Sc	NA	NA	1	10
12						
13	ICP-MS					
14						
15	ICP-OES-RV	Lu	NA		NA	182.577
16	NA	NA	NA	NA	NA	NA
17	ICP-OES-AV	NA	NA	NA	neat	249.772
18						
19	ICP-OES	Eu & Cs	NA	NA	1	249.773 (nm)
20	ICP-OES-AV	Lu/Cs	NA		NA	208.956
21	ICP-OES-AV	Y	NA	NA	2	
22	ICP-MS	Sc	ORS	NA	1	11
23	NA	NA	NA	NA	NA	NA
24						
25	ICP-MS		CRI	He		11

Table 49 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-buffer	Y			1	315.887
2	ICP-MS					
3	ICP-OES-AV	Y 371.029	NA	NA	1	430.253
4	ICP-MS	SC,Rh,Ir		He	10	NA
5	ICP-OES-AV					
6	ICP-OES-AV					
7	ICP-MS	Sc	ORS	H2	1	40
8	NT	NT	NT	NT	NT	NT
9	NT	NT	NT	NT	NT	NT
10	ICP-OES-RV	Lu	NA		NA	422.673
11	ICP-MS	Sc	UC	He	1	44
12	ICP-OES-RV	Eu	NA	NA	NA	315.887
13						
14						
15	ICP-OES-RV	Lu	NA		NA	315.887
16	NA	NA	NA	NA	NA	NA
17	AAS	NA	NA	NA	2	422.7
18						
19	ICP-OES	Eu & Cs	NA	NA	1	315.887, 370.602nm
20	ICP-OES-AV	Lu/Cs	NA		NA	315.887
21	ICP-OES-AV	Y	NA	NA	3	
22	ICP-OES-AV	Eu	NA	NA	1	315.887
23	NA	NA	NA	NA	NA	NA
24						
25	ICP-OES-RV					315.8

Table 50 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-buffer	Y			1	766.49
2	ICP-MS					
3	ICP-OES-AV	Y 371.029	NA	NA	1	769.897
4	ICP-MS	SC,Rh,Ir		He	10	NA
5	ICP-OES-AV					
6	ICP-OES-AV					
7	ICP-MS	Sc	ORS	He	1	39
8	NT	NT	NT	NT	NT	NT
9	NT	NT	NT	NT	NT	NT
10	ICP-OES-RV	Lu	NA		NA	766.491
11	ICP-MS	Sc	UC	He	1	39
12	ICP-OES-RV	Eu	NA	NA	NA	766.491
13						
14						
15	ICP-OES-RV	Lu	NA		NA	766.491
16	NA	NA	NA	NA	NA	NA
17	AAS	NA	NA	NA	neat	766.5
18						
19	ICP-OES	Eu & Cs	NA	NA	1	404.721nm, 766.491nm
20	ICP-OES-AV	Lu/Cs	NA		NA	766.491
21	ICP-OES-AV	Y	NA	NA	4	
22	ICP-OES-AV	Eu	NA	NA	1	766.491
23	NA	NA	NA	NA	NA	NA
24						
25	ICP-OES-RV					766.4

Table 51 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-buffer	Y			1	279.077
2	ICP-MS					
3	ICP-OES-AV	Y 371.029	NA	NA	1	277.983
4	ICP-MS	SC,Rh,Ir		He	10	NA
5	ICP-OES-AV					
6	ICP-OES-AV					
7	ICP-MS	Sc	ORS	He	1	24
8	NT	NT	NT	NT	NT	NT
9	NT	NT	NT	NT	NT	NT
10	ICP-OES-RV	Lu	NA		NA	285.213
11	ICP-MS	Sc	UC	He	1	25
12	ICP-OES-RV	Eu	NA	NA	NA	383.829
13						
14						
15	ICP-OES-RV	Lu	NA		NA	279.8
16	NA	NA	NA	NA	NA	NA
17	AAS	NA	NA	NA	2	285.5
18						
19	ICP-OES	Eu & Cs	NA	NA	1	383.830 (nm)
20	ICP-OES-AV	Lu/Cs	NA		NA	279.8
21	ICP-OES-AV	Y	NA	NA	5	
22	ICP-OES-AV	Eu	NA	NA	1	383.829
23	NA	NA	NA	NA	NA	NA
24						
25	ICP-OES-RV					279.8

Table 52 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-buffer	Y			1	589.592
2	ICP-MS					
3	ICP-OES-AV	Y 371.029	NA	NA	1	568.821
4	ICP-MS	SC,Rh,Ir		He	10	NA
5	ICP-OES-AV					
6	ICP-OES-AV					
7	ICP-MS	Sc	ORS	He	1	23
8	NT	NT	NT	NT	NT	NT
9	NT	NT	NT	NT	NT	NT
10	ICP-OES-RV	Lu	NA		NA	589.592
11	ICP-MS	Sc	UC	He	1	23
12	ICP-OES-RV	Eu	NA	NA	NA	589.592
13						
14						
15	ICP-OES-RV	Lu	NA		NA	589.592
16	NA	NA	NA	NA	NA	NA
17	AAS	NA	NA	NA	neat	330.2
18						
19	ICP-OES	Eu & Cs	NA	NA	1	330.237, 589.592nm
20	ICP-OES-AV	Lu/Cs	NA		NA	589.592
21	ICP-OES-AV	Y	NA	NA	6	
22	ICP-OES-AV	Eu	NA	NA	1	589.592
23	NA	NA	NA	NA	NA	NA
24						
25	ICP-OES-RV					589.5

Table 53 Measurement Methods and Instrument Techniques for Alkalinity

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	APHA 2320 B
2	Titration	Auto Titration	
3	Titration	Auto Titration	in house
4	Titration	Auto Titration	APHA
5	Titration	Auto Titration	APHA 4500
6	Titration	Auto Titration	
7	Titration	Auto Titration	
8	Titration	Auto Titration	APHA 2320 B
9	Titration	Manual Analysis	APHA 2320 A+B
10	Titration	Auto Titration	
11	Titration	Auto Titration	APHA2320B
12	Titration	Auto Titration	APHA 2320
13	Titration	Manual Analysis	APHA
14			
15	Titration	Auto Titration	
16	Not Applicable	Not Applicable	Not Applicable
17	Titration	Auto Titration	In-house method based on APHA 23rd edition 2320 B
18	Titration	Manual Analysis	
19	Titration	Auto Titration	APHA 2320
20	Titration	Auto Titration	
21	Titration	Auto Titration	APHA
22	Titration	Auto Titration	APHA 2320 Alkalinity - A & B
23	Not Applicable	Not Applicable	Not Applicable
24	Titration	Manual Analysis	APHA 2320 B
25	Titration	Auto Titration	2320 B

Table 54 Measurement Methods and Instrument Techniques for Colour

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Visual Comparison Method	UV-Vis Spectrophotometer	APHA 2120 C
2			
3	Spectrophotometric Method	UV-Vis Spectrophotometer	in house
4	Visual Comparison Method	Not Applicable	APHA
5	Spectrophotometric Method	UV-Vis Spectrophotometer	APHA 4500
6	Spectrophotometric Method	UV-Vis Spectrophotometer	
7			
8	NT	NT	NT
9	Visual Comparison Method	Manual Analysis	APHA 2120 A+B
10	Spectrophotometric Method	DA	
11	Spectrophotometric Method	UV-Vis Spectrophotometer	W1
12	Visual Comparison Method	Manual Analysis	APHA 2120
13			
14			
15	Spectrophotometric Method	DA	
16	Not Applicable	Not Applicable	Not Applicable
17	Visual Comparison Method	Manual Analysis	In-house method based on APHA 23rd edition 2120 B
18	Spectrophotometric Method	UV-Vis Spectrophotometer	
19	Visual Comparison Method	NA	APHA 2120
20	Spectrophotometric Method	DA	
21	Spectrophotometric Method	DA	APHA
22	Visual Comparison Method	Not Applicable	APHA 2120 A & B
23	Not Applicable	Not Applicable	Not Applicable
24			
25	Spectrophotometric Method	UV-Vis Spectrophotometer	2120 B

Table 55 Measurement Methods and Instrument Techniques for Total Hardness

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2	Calculation	ICP-MS	
3	Calculation	ICP-OES	in house
4	Calculation	Auto Titration	APHA
5	Calculation	ICP-OES	APHA 4500
6	Calculation	ICP-OES	
7	Calculation	ICP-MS	APHA Part 2340 B
8	NT	NT	NT
9	NT	NT	NT
10	Calculation	ICP-OES	
11	Titration	Manual Analysis	W21
12	Calculation	ICP-OES	APHA 2340
13	Calculation	ICP-MS	APHA
14			
15	Calculation	ICP-OES	
16	Not Applicable	Not Applicable	Not Applicable
17	Calculation	Not Applicable	In-house method based on APHA 23rd edition 2340 B
18			
19	Calculation	ICP-OES	APHA 2320
20	Calculation	ICP-OES	
21	Calculation	ICP-OES	APHA
22	Calculation	ICP-OES	USEPA 3005
23	Not Applicable	Not Applicable	Not Applicable
24			
25	Calculation	ICP-OES	2340 B

Table 56 Measurement Methods and Instrument Techniques for Total Phosphorus

Laboratory Code	Measurement Method		Instrument	Method Reference
1	No Digestion	ICP Method	ICP-OES	USEPA 200.7
2				
3	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
4		ICP Method	ICP-MS	APHA
5	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	APHA 4500
6				
7	No Digestion	ICP Method	ICP-MS	USEPA6020
8	NT	NT	NT	NT
9	NT		NT	NT
10	HNO3-Digestion	ICP Method	ICP-OES	
11			ICP-MS	W32
12	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500 Norg-D
13	K2S2O8-Digestion	Ion Chromatographic Method	IC	ASTM
14				
15	HNO3-Digestion	ICP Method	ICP-OES	
16	NA	Not Applicable	Not Applicable	Not Applicable
17	H2SO4/K2S2O8	Ascorbic Acid Colorimetric Method	DA	In-house method based on APHA 23rd edition 4500 F
18				
19		ICP Method	ICP-OES	USEPA 3005
20	HNO3-Digestion	ICP Method	ICP-OES	
21				
22	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500 N-D
23	NA	Not Applicable	Not Applicable	Not Applicable
24				
25	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	4500-P J

Table 57 Measurement Methods and Instrument Techniques for Silica

Laboratory Code	Measurement Method	Instrument	Method Reference
1			
2			
3	Molybdosilicate Method	DA	in house
4	Molybdosilicate Method	DA	APHA
5	ICP-Method	ICP-OES	APHA 4500
6	Molybdosilicate Method	DA	
7			
8	NT	NT	NT
9	Molybdosilicate Method	FIA	APHA 4500- Si02 F
10	ICP-Method	ICP-OES	
11	ICP-Method	ICP-MS	W32
12	Molybdosilicate Method	DA	APHA 4500 SIO2-D
13			
14			
15	ICP-Method	ICP-OES	
16	Not Applicable	Not Applicable	Not Applicable
17	Molybdosilicate Method	DA	In-house method based on APHA 23rd edition 4500-SiO2 E
18			
19	Molybdosilicate Method	DA	APHA 4500
20	ICP-Method	ICP-OES	
21			
22	Heteropoly Blue Method	DA	APHA 4500 SiO2 D
23	Not Applicable	Not Applicable	Not Applicable
24			
25	ICP-Method	ICP-OES	3120 B

Table 58 Additional Information

Lab Code	Additional Information
25	S2: Reported total Silica (SiO2) not reactive silicate.

APPENDIX 8 - METHODOLOGY FOR S3

Table 59 Measurement Methods and Instrument Techniques for Total Kjeldahl Nitrogen

Laboratory Code	Measurement Method		Instrument	Method Reference
1	NA	Not Applicable	Not Applicable	Not Applicable
2	NA	Not Applicable	Not Applicable	Not Applicable
3	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	in house
4		Colorimetric - salicylate method	FIA	APHA
5	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - phenate method	FIA	
6	TKN=TN-NOx (K2S2O8 digestion)		FIA	
7	NA	Not Applicable	Not Applicable	Not Applicable
8	NA	Not Applicable	Not Applicable	Not Applicable
9	NA	Not Applicable	Not Applicable	Not Applicable
10		Calculation	DA	
11	TKN = TN – NOx		FIA	
12	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500 Norg-A
13				
14	NA	Not Applicable	Not Applicable	Not Applicable
15	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	
16	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA4500Norg
17	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	In-house method based on APHA 23rd edition 4500-Norg B
18	NA	Not Applicable	Not Applicable	Not Applicable
19		Calculation	FIA	APHA 4500
20	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	
21	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
22	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500 N A & D with Jirka modification (Jirka et al. 1976)
23	NA	Not Applicable	Not Applicable	Not Applicable
24	NA	Not Applicable	Not Applicable	Not Applicable
25	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	4500 OrgN

Table 60 Measurement Methods and Instrument Techniques for Total Nitrogen

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Not Applicable	Not Applicable	Not Applicable
2	Not Applicable	Not Applicable	Not Applicable
3	Calculation (TKN+NOx)	FIA	in house
4	Calculation (TKN+NOx)	FIA	APHA
5	Persulfate digestion	SFA	
6	Persulfate digestion	FIA	
7	Not Applicable	Not Applicable	Not Applicable
8	Not Applicable	Not Applicable	Not Applicable
9	Not Applicable	Not Applicable	Not Applicable
10	Combustion	Combustion	
11	Persulfate digestion	FIA	APHA4500P-J
12	Calculation (TKN+NOx)	DA	
13	Persulfate digestion	IC	ASTM
14	Not Applicable	Not Applicable	Not Applicable
15	Calculation (TKN+NOx)	DA	
16	Calculation (TKN+NOx)		
17	Calculation (TKN+NOx)	DA	In-house method
18	Not Applicable	Not Applicable	Not Applicable
19	Persulfate digestion	FIA	APHA 4500
20	Combustion	chemiluminescence detection	
21	Persulfate digestion	SFA	APHA
22	Calculation (TKN+NOx)	DA	APHA 4500 N A & D
23	Not Applicable	Not Applicable	Not Applicable
24	Not Applicable	Not Applicable	Not Applicable
25	Persulfate digestion	FIA	4500-P J

Table 61 Measurement Methods and Instrument Techniques for Total Organic Carbon

Laboratory Code	Measurement Method	Instrument	Method Reference
1	Not Applicable	Not Applicable	Not Applicable
2	Not Applicable	Not Applicable	Not Applicable
3	Wet-Oxidation	NIR-detector	in house
4	High-Temperature Oxidation	TOC	APHA
5	High-Temperature Oxidation	NIR-detector	
6	High-Temperature Oxidation	NIR-detector	
7	Not Applicable	Not Applicable	Not Applicable
8	Not Applicable	Not Applicable	Not Applicable
9	Not Applicable	Not Applicable	Not Applicable
10	High-Temperature Oxidation	NIR-detector	
11	High-Temperature Oxidation	NIR-detector	APHA5310-B
12	High-Temperature Oxidation	NIR-detector	APHA 5310
13			
14	Not Applicable	Not Applicable	Not Applicable
15	High-Temperature Oxidation	NIR-detector	
16	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA5310(modified)
17	High-Temperature Oxidation	NIR-detector	In-house method based on APHA 23rd edition 5310 B
18	Not Applicable	Not Applicable	Not Applicable
19	High-Temperature Oxidation	NIR-detector	APHA 5310
20	High-Temperature Oxidation	NIR-detector	
21	High-Temperature Oxidation	NIR-detector	APHA
22	High-Temperature Oxidation	NIR-detector	APHA 5310 A, B & C
23	Not Applicable	Not Applicable	Not Applicable
24	Not Applicable	Not Applicable	Not Applicable
25	Persulfate-Ultraviolet Oxidation	NIR-detector	5310 C

Table 62 Additional Information

Lab Code	Additional Information
11	Methodology for S3: TKN = TN-Nox.
17	Methodology for S3: NOx – In-house method based on Aquakem Total Oxidised Nitrogen method.

END OF STUDY