Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 23-12 Nutrients and Anions in Wastewater

November 2023

ACKNOWLEDGMENTS

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

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

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NATA WORLD RECOGNISED ACCREDITATION

Accredited for compliance with ISO/IEC 17043

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SUMMARY

This report presents the results of the proficiency test AQA 23-12, Nutrients and Anions in Wastewater. The study focused on the measurement of pH and electrical conductivity at 25ºC, alkalinity to pH 4.5 (as $CaCO_3$), ammonia-N, bromide, chloride, colour apparent (Pt-Co units), chemical oxygen dissolved (COD), dissolved organic carbon (as dNPOC), fluoride, nitrate-N, nitrite-N, orthophosphate-P, silica (as SiO_2), sulphate, sulphide, total hardness (as $CaCO_3$), total dissolved nitrogen, total phosphorus, total Kjeldahl nitrogen, total nitrogen, total organic carbon (as NPOC) and dissolved B, Ca, K, Mg, Na and P in trade wastewater.

The sample set consisted of 3 trade wastewater samples.

Twenty laboratories registered to participate and ninteen submitted results.

The assigned values were the robust average of participants' result. The associated uncertainties were estimated from the robust standard deviation of the participants' 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;*

Of 338 z-scores, 321 (95%) returned a satisfactory score of $|z| \leq 2.0$.

Of 338 E_n scores, 294 (87%) returned a satisfactory score of $|E_n| \leq 1.0$.

Laboratory 6 reported results for all 26 tests for which a z-score was calculated and returned satisfactory z-scores for 25 of them.

Laboratories 9, 14 15, 17, and 18 reported results for 25 tests each and retuned satisfactory z-scores for all of them.

Laboratory 9 had the highest number of satisfactory E_n-scores (25 out of 25 reported).

ii. *evaluate the laboratories' methods used in determination of inorganic analytes in wastewater;*

The measurements of colour challenged participants' analytical methods. Most participants used the Spectrophotometric method or the Visual Comparison method. The results reported were not compatible with each-other.

A small number of laboratories reported results for TP and TDP in the wastewater samples; however, the reported results were in good agreement with each other.

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

Despite differences in matrices and concentrations, on average, participants' performance remained consistent over time.

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 356 numerical results, 338 (95%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.013% to 180% of the reported value. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 4.

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

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

Surplus test samples from this study are available for sale.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

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

AQA 23-12 is the 16th NMI proficiency study of nutrients, anions and physical tests in water.

1.2 Study Aims

The aims of the study were to:

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

1.3 Study Conduct

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

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

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The 29 tests were selected from those for which an investigation level is published in the Liquid Trade Waste Management Guidelines,[5] and are commonly measured by water testing laboratories.

2.2 Participation

Twenty laboratories participated and nineteen submitted results.

The timetable of the study was:

Invitation issued:	13 June 2023
Samples dispatched:	3 July 2023
Results due:	4 August 2023
Interim report issued:	7 August 2023
Preliminary report issued	8 August 2023

2.3 Test Material Specification

Three samples were provided for analysis:

Sample S1 was 400 mL of filtered, autoclaved and frozen trade wastewater.

Sample S2 was two identical bottles of 200 mL each of chilled, autoclaved trade wastewater;

Sample S3 was 200 mL of autoclaved and frozen trade wastewater.

None of the study samples have been fortified with any of the analytes of interest.

2.4 Sample Preparation, Analysis and Homogeneity Testing

Partial homogeneity testing was conducted in this study. The same validated preparation procedure was followed as in previous studies.[2] The test samples from the previous studies were demonstrated to be sufficiently homogeneous for evaluation of participants' performance. The results of partial homogeneity testing are reported in this study as the homogeneity value. No homogeneity test was conducted for bromide, fluoride, orthophosphate-P, sulphide and TDP in S1, colour, EC and silica in S2, and TKN and total P in S3. The preparation and analysis are described in Appendix 1.

2.5 Stability of Analytes

A stability study was conducted for the less stable analytes (NH_3-N and NO_3-N) in S1 in order to address issues associated with holding time and holding conditions. The stability study was conducted over the entire period of the PT study conduct. The set-up of this study, together with the study results are presented in Appendix 2.

2.6 Sample Storage, Dispatch and Receipt

Samples S1 and S3 were frozen whilst S2 was refrigerated.

The samples were dispatched by courier on 3 July 2023.

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

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

2.7 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 and sample S2 chilled.
- Prior to testing, thaw samples S1 and S3 completely.
- Participants are asked to report results in units of mg/L, except for pH, colour (Pt-Co Units) and EC (µS/cm), for the following:

SAMPLE S1 frozen wastewater		SAMPLE S2 chilled wastewater		SAMPLE S3 frozen wastewater	
Test	**Estimated Conc. Range***	**Test**	**Estimated Conc. Range***	**Test**	**Estimated Conc. Range***
Bromide	>0.1	B (total)	>0.1	Total Kjeldahl Nitrogen	NA
Chloride	>50	Ca (total)	>1	Total Nitrogen	>10
Fluoride	>0.1	K (total)	>1	Total Phosphorus	>1
Chemical Oxygen Demand (COD)	>50	Mg (total)	>1	Total Organic Carbon (as NPOC)	>10
Ammonia-N	>10	Na (total)	>1		
Nitrite-N	NA	P (total)	>1		
Nitrate-N	NA	Alkalinity to pH 4.5 (as $CaCO_3$)	>50		
Total Dissolved Nitrogen	>10	Colour, apparent (Pt-Co units)	>10		
Total Dissolved Phosphorus	>1	Hardness, total ($CaCO_3$)	>100		
Orthophosphate-P	>1	EC (at 25°C, µS/cm)	>1000		
Sulphate (as SO_4)	>10	pH (at 25 °C)	>5		
Sulphide (as S)	>5	Silica (as SiO_2)	NA		
DOC	>10				

*As these samples are real samples, the values given are indicative; NA - the estimated concentration range is not available.

- Report results using the electronic results sheet emailed to you:
- Report results as you would report to a client. For each analyte, report the expanded measurement uncertainty.
- Please send us all the requested details regarding the test method.
- Please return the completed results sheet by e-mail (proficiency@measurement.gov.au), by 31 July 2023.

The due date for results was extended to 4 August 2023 due to delays in sample delivery to one of our overseas participants.

2.8 Interim and Preliminary Reports

An Interim Report was emailed to participants on 7 August 2023.

A Preliminary Report was issued on 8 August 20203. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants.

No data from the preliminary report has been changed in the present Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Methodology for S1, S2, and S3

Measurement methods and instrumental techniques used for the tests in Samples S1, S2, and S3 are presented in Appendices 6, 7, and 8 respectively.

3.2 Basis of Participants' Measurement Uncertainty Estimates

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

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	Standard deviation of replicate analyses multiplied by 2 or 3	Control samples - CRM Duplicate Analysis	CRM Instrument Calibration	other
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	Nordtest Report TR537
3	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis Instrument Calibration	Instrument Calibration	Eurachem/CITAC Guide
4	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
5	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis	CRM	Eurachem/CITAC Guide
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
7	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	ASTM E2254-13
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	CRM	IANZ Technical Guide
9	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
10	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	other
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
12	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)
13	if other please type	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide

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

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

Table 2 Additional Information for Basis of Uncertainty Estimate

Lab Code	Additional Information
8	UoM is based on ISO 17025, IANZ Specific Criteria and EURACHEM/ CITAC Guide
10	Eurochem 2000/ISO1993A

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

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Such feedback may be useful in improving future studies. Participants’ comments are reproduced in Table 4.

Table 3 Participants’ Comments

Participants’ Comments	Study Co-ordinator’s Response
Samples are analysed over a range of days for the different methods allocated.	Please specify the date of analyses for the less stable analytes: ammonia, nitrate-N, nitrite-N.
We suggest lithium be included as an analyte in future PT studies.	Thank you for your suggestion, Li will be added in our future studies.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 32 with results' 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 29. An example chart with an interpretation guide is shown in Figure 1.

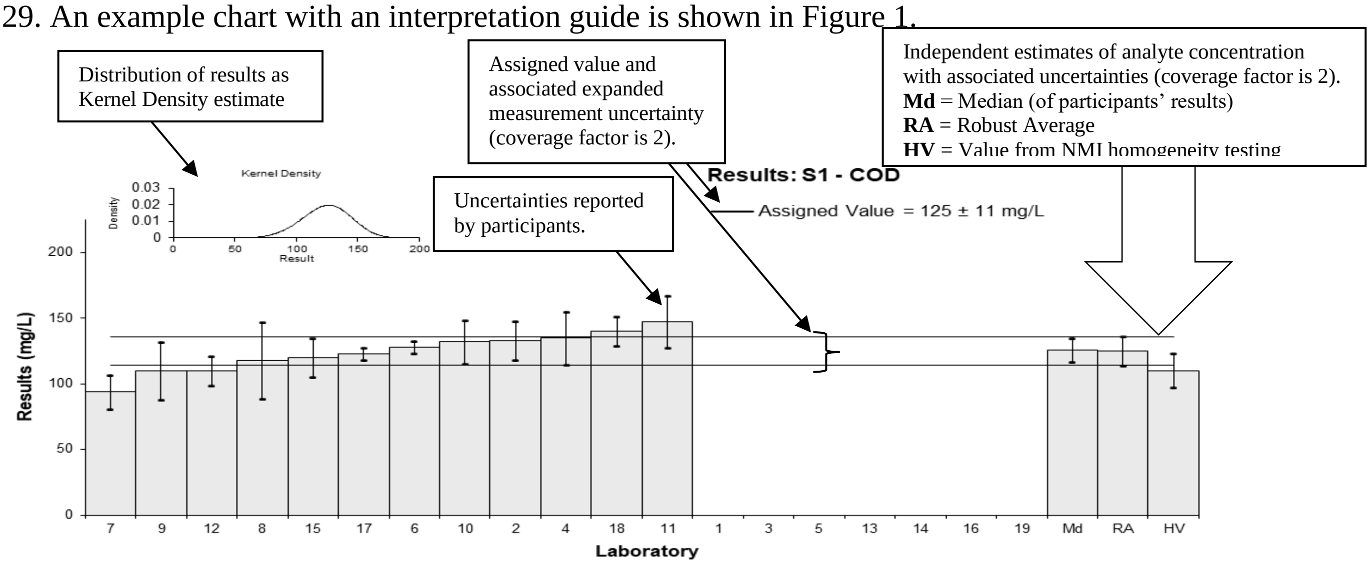


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

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

4.3 Assigned Value

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

4.4 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 inter-laboratory comparisons, ISO13528.[6]

4.5 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.[6]

4.6 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 on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.[7]

4.7 z-Score

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

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

where:

- z is z-score;
- χ is participants' result;
- X is the study assigned value;
- σ is the target standard deviation.

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

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

4.8 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:

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

where:

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

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

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

4.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025[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]

5 TABLES AND FIGURES

Table 4

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	Ammonia-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	47.18	0.28	2.05	6.43
2	36.5	4.0	0.07	0.09
3	NR	NR		
4	46.9	7.60	1.99	1.39
5	NT	NT		
6	34.7	3.7	-0.26	-0.34
7	NT	NT		
8	35.3	1.3	-0.15	-0.37
9	37	5.6	0.17	0.15
10	34.9	2.48	-0.22	-0.40
11	37.5	4.7	0.26	0.28
12	38	5.7	0.35	0.32
13	34.9	3.5	-0.22	-0.31
14	30.8	2.1	-0.98	-1.96
15	35	4.9	-0.20	-0.21
16	38.1	0.005	0.37	1.18
17	36.7	5.0	0.11	0.11
18	31.617	4.245	-0.83	-0.98
19	34.7	2.3	-0.26	-0.49

Statistics

Assigned Value	36.1	1.7
Homogeneity Value	37.7	5.7
Robust Average	36.1	1.7
Median	35.9	1.1
Mean	36.9	
N	16	
Max	47.18	
Min	30.8	
Robust SD	2.7	
Robust CV	7.5%	

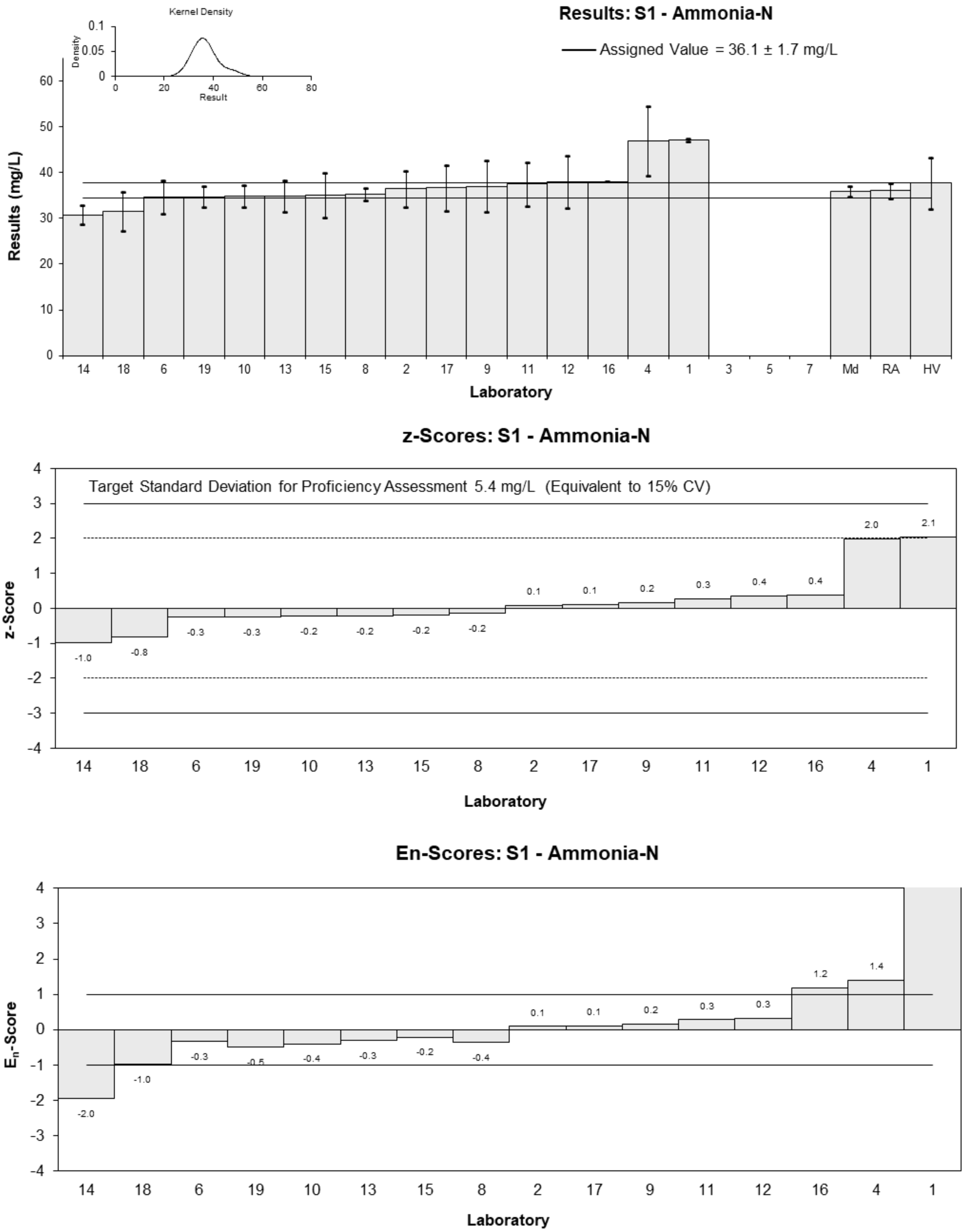

Kernel Density
Density
Result
Results: S1 - Ammonia-N
Assigned Value = 36.1 ± 1.7 mg/L
Results (mg/L)
Laboratory
14 18 6 19 10 13 15 8 2 17 9 11 12 16 4 1 3 5 7 Md RA HV
z-Scores: S1 - Ammonia-N
Target Standard Deviation for Proficiency Assessment 5.4 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Ammonia-N
En-Score
Laboratory

Figure 2

Table 5

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	Bromide
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty
1	NR	NR
2	<1	NR
3	0.15	0.01
4	NT	NT
5	NT	NT
6	0.180	0.017
7	NT	NT
8	NT	NT
9	0.2	0.04
10	NT	NT
11	NT	NT
12	<0.3	0.3
13	<0.2	0.5
14	NR	NR
15	0.19	0.0285
16	NR	NR
17	0.182	0.017
18	NT	NT
19	NT	NT

Statistics

Assigned Value	Not Set	
Median	0.182	0.013
Mean	0.180	
N	5	
Max	0.2	
Min	0.15	

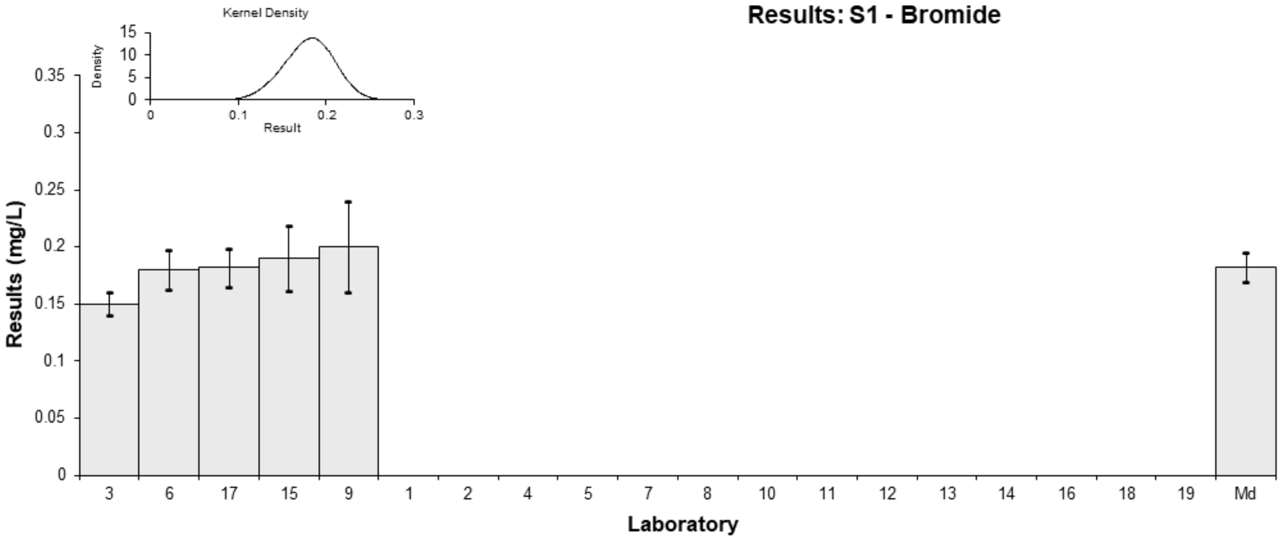

Results: S1 - Bromide
Kernel Density
Density
Result
Results (mg/L)
Laboratory
3
6
17
15
9
1
2
4
5
7
8
10
11
12
13
14
16
18
19
Md

Figure 3

Table 6

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	COD
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	133	15	0.43	0.43
3	NR	NR		
4	135	20.3	0.53	0.43
5	NT	NT		
6	128	5	0.16	0.25
7	94	13	-1.65	-1.82
8	118	29	-0.37	-0.23
9	110	22	-0.80	-0.61
10	132	16.50	0.37	0.35
11	147.6	20	1.21	0.99
12	110	11	-0.80	-0.96
13	NT	NT		
14	NR	NR		
15	120	14.64	-0.27	-0.27
16	NR	NR		
17	123	4.5	-0.11	-0.17
18	140	11.1	0.80	0.96
19	NT	NT		

Statistics

Assigned Value	125	11
Homogeneity Value	110	13
Robust Average	125	11
Median	126	9
Mean	124	
N	12	
Max	147.6	
Min	94	
Robust SD	15	
Robust CV	12%	

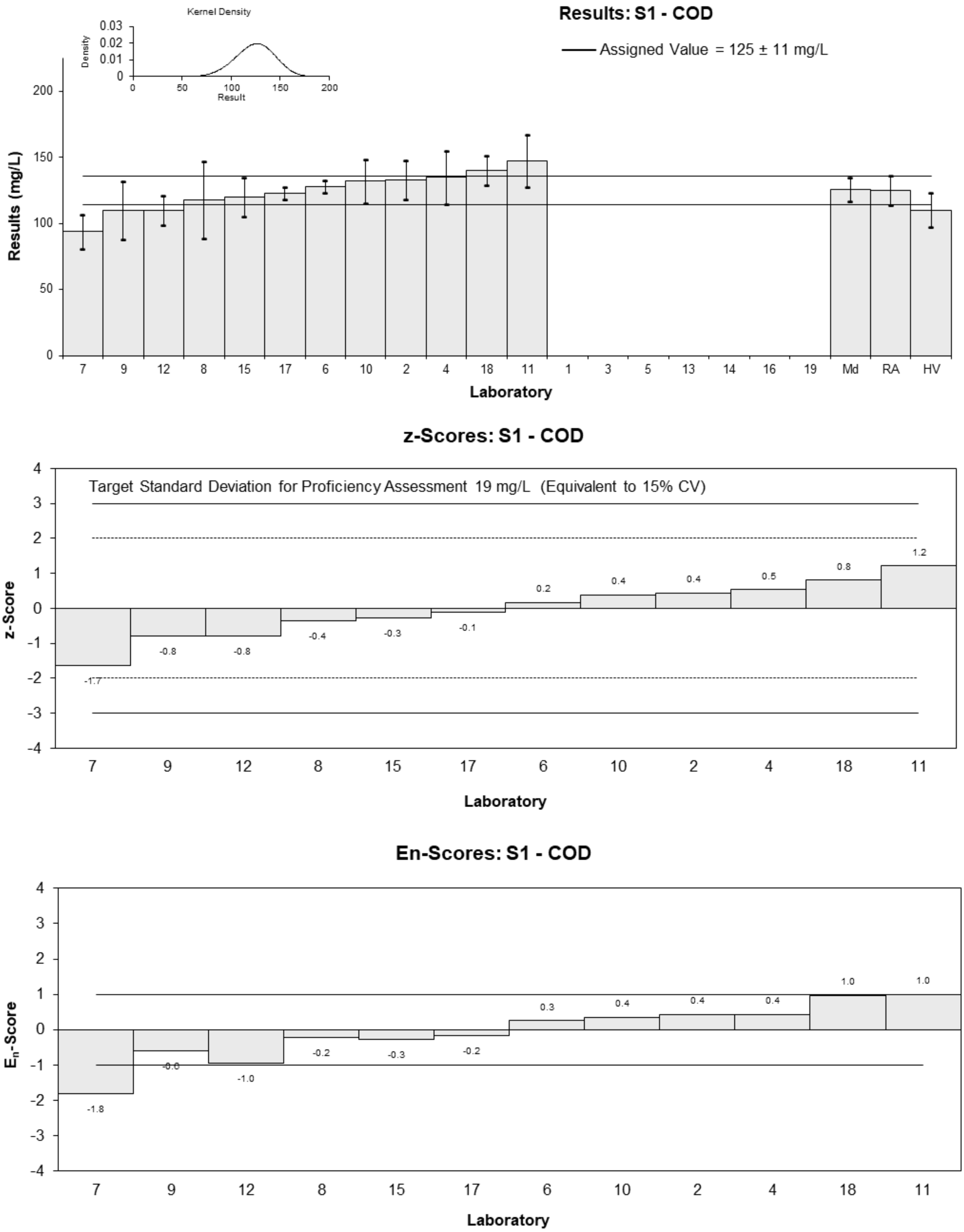

Results: S1 - COD
Assigned Value = 125 ± 11 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
7 9 12 8 15 17 6 10 2 4 18 11 1 3 5 13 14 16 19 Md RA HV
z-Scores: S1 - COD
Target Standard Deviation for Proficiency Assessment 19 mg/L (Equivalent to 15% CV)
z-Score
-1.7 -0.8 -0.8 -0.4 -0.3 -0.1 0.2 0.4 0.4 0.5 0.8 1.2
Laboratory
7 9 12 8 15 17 6 10 2 4 18 11
En-Scores: S1 - COD
E_n-Score
-1.8 -0.6 -1.0 -0.2 -0.3 -0.2 0.3 0.4 0.4 0.4 1.0 1.0
Laboratory
7 9 12 8 15 17 6 10 2 4 18 11

Figure 4

Table 7

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	Chloride
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	118	2	-1.69	-3.79
2	152	20	0.70	0.48
3	140	10	-0.14	-0.17
4	133	19.95	-0.63	-0.43
5	NT	NT		
6	151	14	0.63	0.59
7	140	13	-0.14	-0.14
8	137.1	8.3	-0.35	-0.48
9	140	28	-0.14	-0.07
10	162	5.83	1.41	2.39
11	NT	NT		
12	138	16.6	-0.28	-0.23
13	137	13	-0.35	-0.35
14	157	21	1.06	0.69
15	142	21.3	0.00	0.00
16	NR	NR		
17	147	11.5	0.35	0.39
18	141.36	12.24	-0.05	-0.05
19	137	4.0	-0.35	-0.69

Statistics

Assigned Value	142	6
Homogeneity Value	140	17
Robust Average	142	6
Median	140	3
Mean	142	
N	16	
Max	162	
Min	118	
Robust SD	9	
Robust CV	6.3%	

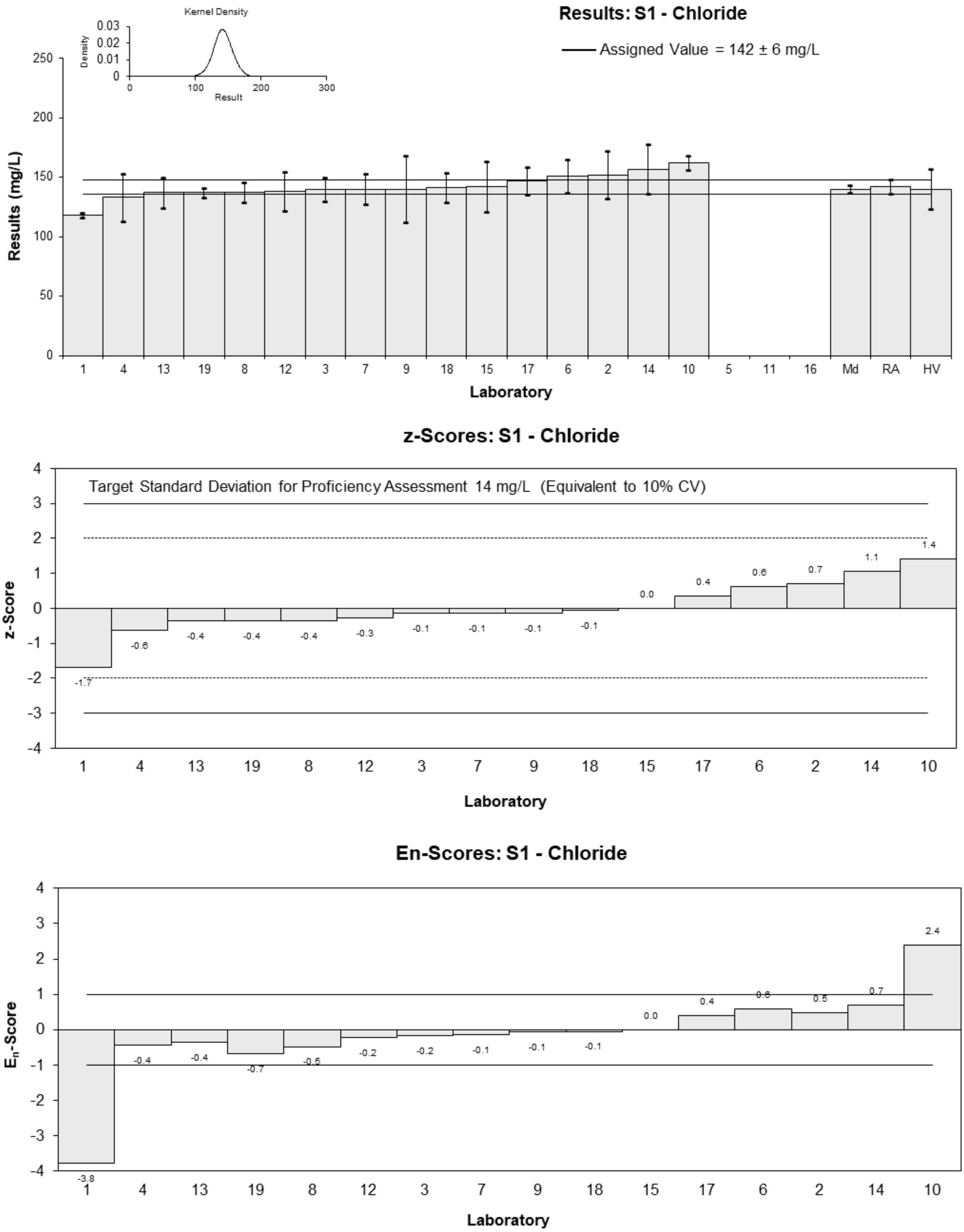

Results: S1 - Chloride
Assigned Value = 142 ± 6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1 4 13 19 8 12 3 7 9 18 15 17 6 2 14 10 5 11 16 Md RA HV
z-Scores: S1 - Chloride
Target Standard Deviation for Proficiency Assessment 14 mg/L (Equivalent to 10% CV)
z-Score
-1.7 -0.6 -0.4 -0.4 -0.4 -0.3 -0.1 -0.1 -0.1 -0.1 0.0 0.4 0.6 0.7 1.1 1.4
1 4 13 19 8 12 3 7 9 18 15 17 6 2 14 10
Laboratory
En-Scores: S1 - Chloride
E_n-Score
-3.8 -0.4 -0.4 -0.7 -0.5 -0.2 -0.2 -0.1 -0.1 -0.1 0.0 0.4 0.6 0.5 0.7 2.4
1 4 13 19 8 12 3 7 9 18 15 17 6 2 14 10
Laboratory

Figure 5

Table 8

Sample Details

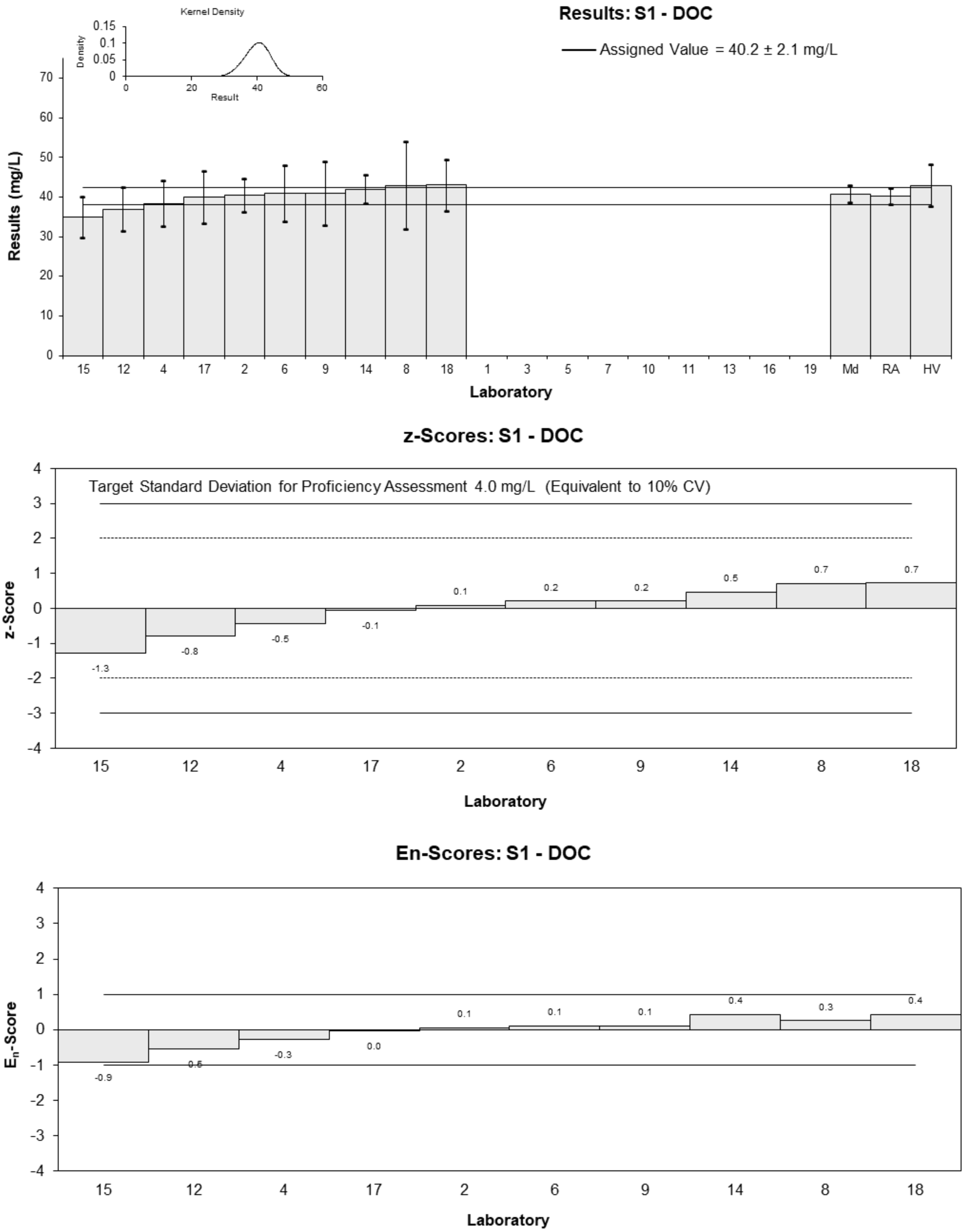
Sample No.	S1
Matrix	Wastewater
Analyte	DOC
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	40.5	4.2	0.07	0.06
3	NR	NR		
4	38.4	5.76	-0.45	-0.29
5	NT	NT		
6	41	7	0.20	0.11
7	NT	NT		
8	43	11	0.70	0.25
9	41	8	0.20	0.10
10	NT	NT		
11	NT	NT		
12	37	5.6	-0.80	-0.54
13	NT	NT		
14	42	3.6	0.45	0.43
15	35	5.25	-1.29	-0.92
16	NR	NR		
17	40	6.6	-0.05	-0.03
18	43.08	6.49	0.72	0.42
19	NT	NT		

Statistics

Assigned Value	40.2	2.1
Homogeneity Value	43.0	5.2
Robust Average	40.2	2.1
Median	40.8	2.1
Mean	40.1	
N	10	
Max	43.08	
Min	35	
Robust SD	2.7	
Robust CV	6.7%	



Kernel Density
Density
Result
Results: S1 - DOC
Assigned Value = 40.2 ± 2.1 mg/L
Results (mg/L)
15 12 4 17 2 6 9 14 8 18 1 3 5 7 10 11 13 16 19 Md RA HV
Laboratory
z-Scores: S1 - DOC
Target Standard Deviation for Proficiency Assessment 4.0 mg/L (Equivalent to 10% CV)
z-Score
-1.3 -0.8 -0.5 -0.1 0.1 0.2 0.2 0.5 0.7 0.7
15 12 4 17 2 6 9 14 8 18
Laboratory
En-Scores: S1 - DOC
En-Score
-0.9 -0.5 -0.3 0.0 0.1 0.1 0.1 0.4 0.3 0.4
15 12 4 17 2 6 9 14 8 18
Laboratory

Figure 6

Table 9

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	Fluoride
Unit	mg/L

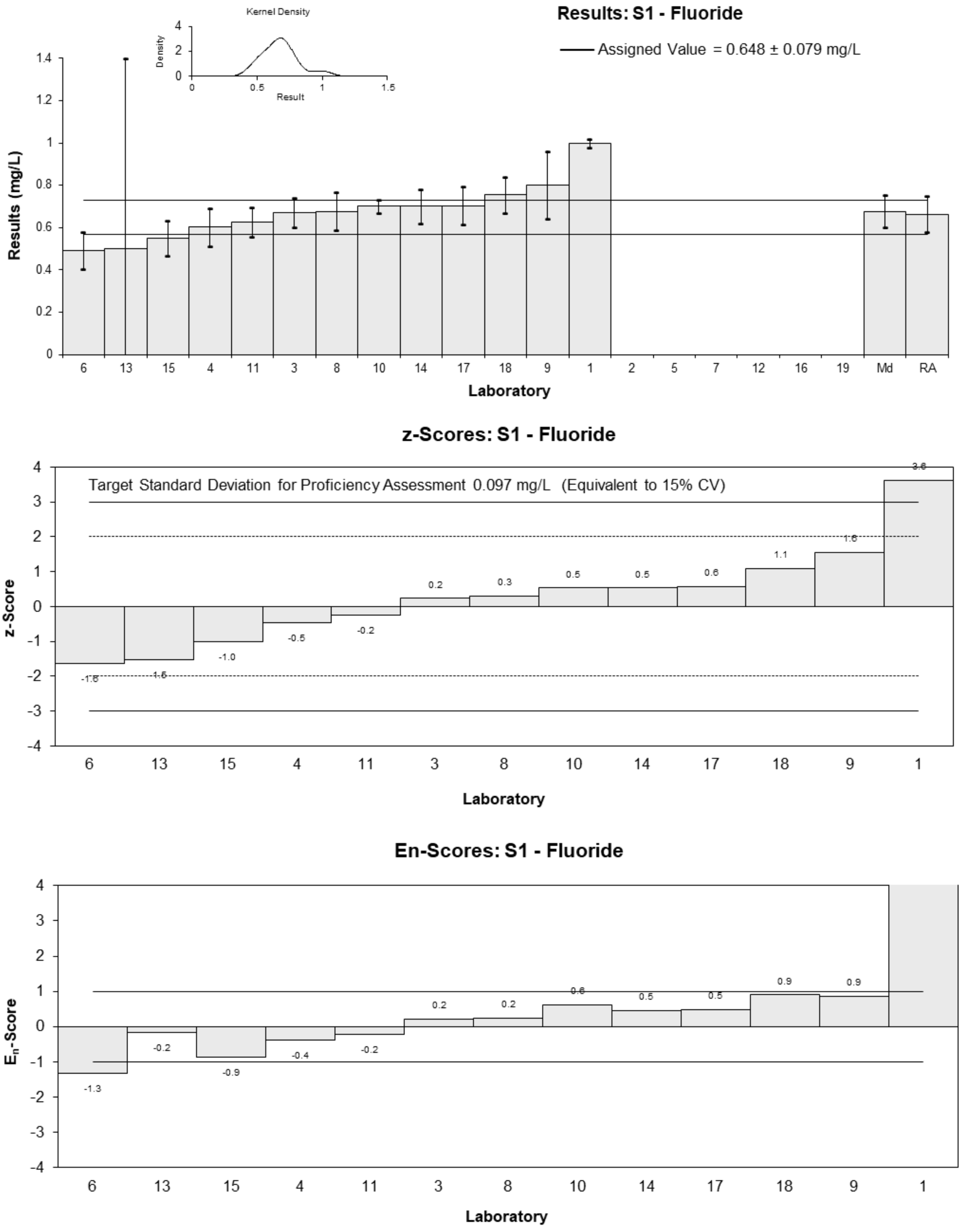
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	1.00	0.02	3.62	4.32
2	NT	NT		
3	0.67	0.07	0.23	0.21
4	0.602	0.09	-0.47	-0.38
5	NT	NT		
6	0.490	0.087	-1.63	-1.34
7	NT	NT		
8	0.677	0.091	0.30	0.24
9	0.8	0.16	1.56	0.85
10	0.7	0.03	0.53	0.62
11	0.6249	0.0687	-0.24	-0.22
12	<0.15	0.15		
13	0.5	0.9	-1.52	-0.16
14	0.7	0.08	0.53	0.46
15	0.55	0.0825	-1.01	-0.86
16	NR	NR		
17	0.704	0.09	0.58	0.47
18	0.754	0.087	1.09	0.90
19	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	0.648	0.079
Robust Average	0.663	0.085
Median	0.677	0.077
Mean	0.675	
N	13	
Max	1	
Min	0.49	
Robust SD	0.12	
Robust CV	18%	



Results: S1 - Fluoride
Assigned Value = 0.648 ± 0.079 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6 13 15 4 11 3 8 10 14 17 18 9 1 2 5 7 12 16 19 Md RA
z-Scores: S1 - Fluoride
Target Standard Deviation for Proficiency Assessment 0.097 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
6 13 15 4 11 3 8 10 14 17 18 9 1
En-Scores: S1 - Fluoride
E_n-Score
Laboratory
6 13 15 4 11 3 8 10 14 17 18 9 1

Figure 7

Table 10

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	Nitrate-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.4	0.2	2.70	1.98
2	0.934	0.1	-0.41	-0.58
3	NR	NR		
4*	4.00	0.60	20.11	5.00
5	NT	NT		
6	0.99	0.11	-0.04	-0.05
7	NT	NT		
8	1.04	0.20	0.29	0.22
9	0.97	0.19	-0.17	-0.13
10	0.97	0.07	-0.17	-0.32
11	1.055	0.432	0.39	0.14
12	1.0	0.15	0.03	0.03
13	0.985	0.14	-0.07	-0.08
14	0.98	0.057	-0.11	-0.23
15	0.8	0.12	-1.31	-1.55
16	0.957	0.007	-0.26	-0.96
17	1.03	NR	0.23	0.85
18	0.95	0.0877	-0.31	-0.48
19	1.18	0.06	1.23	2.55

* Outlier, see Section 4.2

Statistics

Assigned Value	0.996	0.040
Homogeneity Value	0.96	0.14
Robust Average	1.01	0.06
Median	0.988	0.037
Mean	1.20	
N	16	
Max	4	
Min	0.8	
Robust SD	0.089	
Robust CV	8.8%	

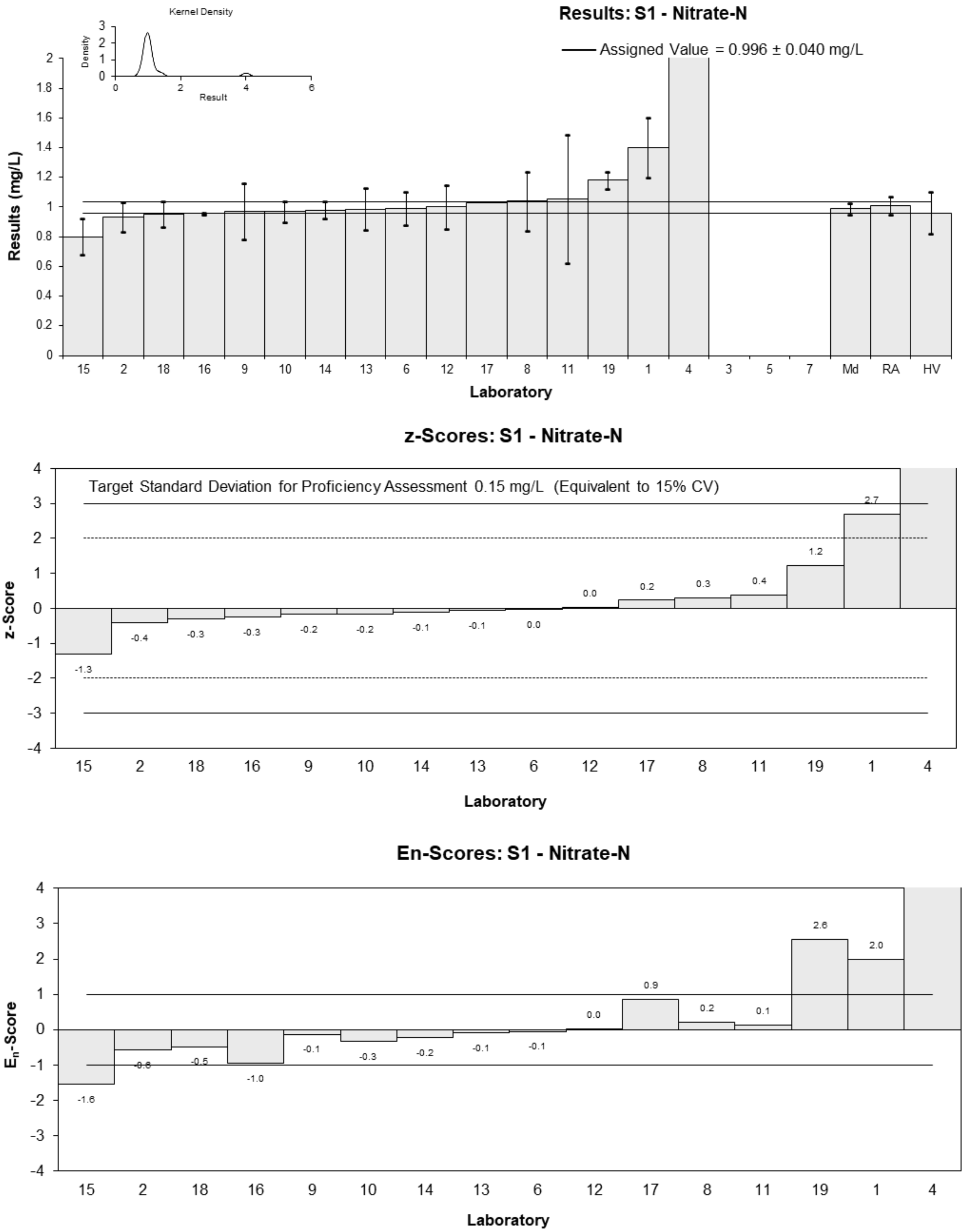

Results: S1 - Nitrate-N
Assigned Value = 0.996 ± 0.040 mg/L
Kernel Density
Density
Result
Results (mg/L)
15 2 18 16 9 10 14 13 6 12 17 8 11 19 1 4 3 5 7 Md RA HV
Laboratory
z-Scores: S1 - Nitrate-N
Target Standard Deviation for Proficiency Assessment 0.15 mg/L (Equivalent to 15% CV)
-1.3 -0.4 -0.3 -0.3 -0.2 -0.2 -0.1 -0.1 0.0 0.0 0.2 0.3 0.4 1.2 2.7
z-Score
15 2 18 16 9 10 14 13 6 12 17 8 11 19 1 4
Laboratory
En-Scores: S1 - Nitrate-N
-1.6 -0.6 -0.5 -1.0 -0.1 -0.3 -0.2 -0.1 -0.1 0.0 0.9 0.2 0.1 2.6 2.0
E_n-Score
15 2 18 16 9 10 14 13 6 12 17 8 11 19 1 4
Laboratory

Figure 8

Table 11

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	Nitrite-N
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	0.203	0.021	-3.89	-11.74
2	0.485	0.06	-0.03	-0.03
3	NR	NR		
4*	1.45	0.22	13.18	4.37
5	NT	NT		
6	0.47	0.03	-0.23	-0.53
7	NT	NT		
8	0.464	0.066	-0.31	-0.34
9	0.49	0.10	0.04	0.03
10	0.49	0.04	0.04	0.07
11	0.435	0.190	-0.71	-0.27
12	0.5	0.05	0.18	0.25
13	NT	NT		
14	0.50	0.037	0.18	0.33
15	0.5	0.075	0.18	0.17
16	0.497	0.007	0.14	0.72
17	0.480	NR	-0.10	-0.58
18	0.5159	0.0495	0.40	0.57
19	0.48	0.03	-0.10	-0.22

* Outlier, see Section 4.2

Statistics

Assigned Value	0.487	0.012
Homogeneity Value	0.487	0.073
Robust Average	0.486	0.016
Median	0.490	0.010
Mean	0.53	
N	15	
Max	1.45	
Min	0.203	
Robust SD	0.024	
Robust CV	5%	

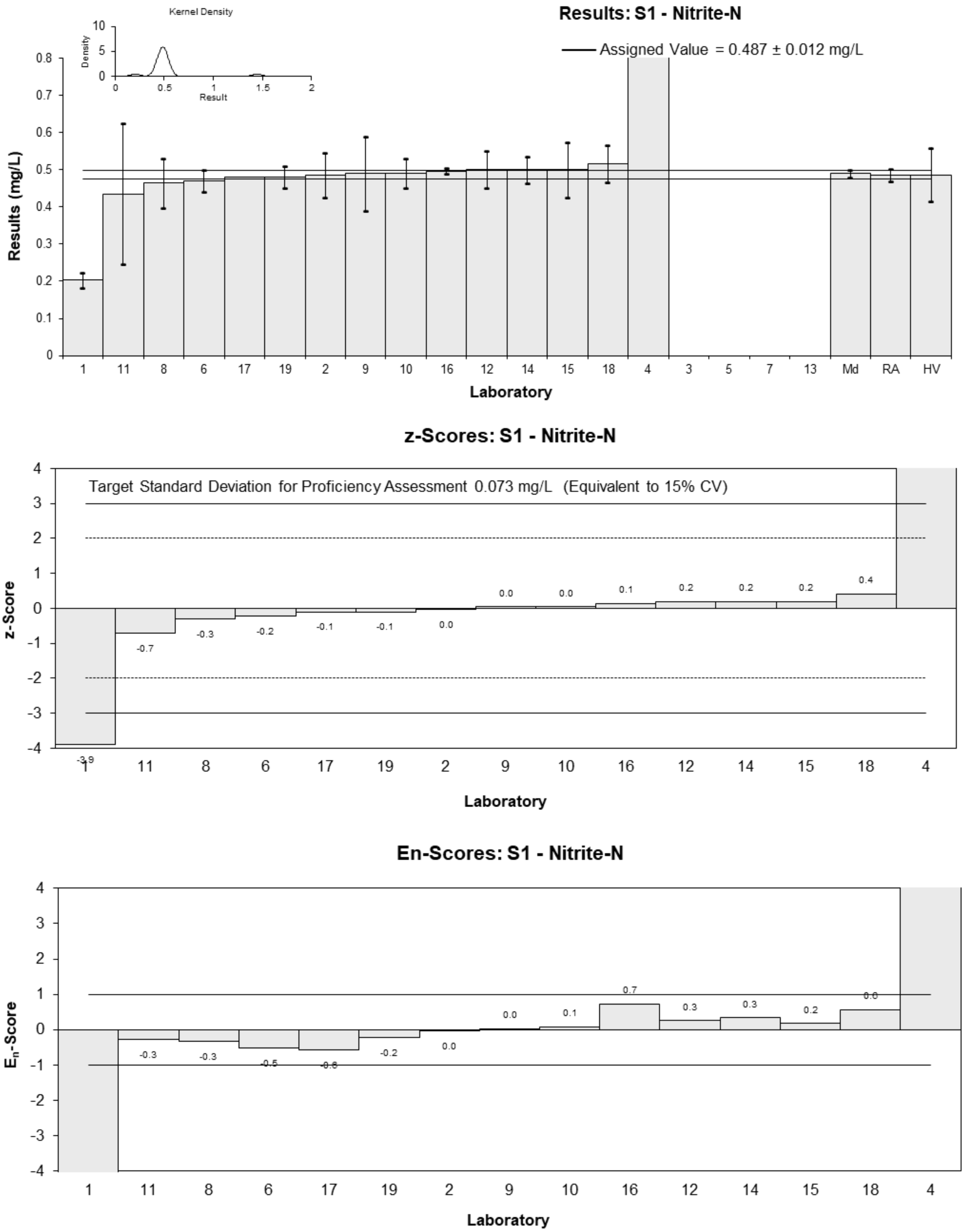

Results: S1 - Nitrite-N
Assigned Value = 0.487 ± 0.012 mg/L
Kernel Density
Density
Result
Results (mg/L)
1 11 8 6 17 19 2 9 10 16 12 14 15 18 4 3 5 7 13 Md RA HV
Laboratory
z-Scores: S1 - Nitrite-N
Target Standard Deviation for Proficiency Assessment 0.073 mg/L (Equivalent to 15% CV)
z-Score
-3.9 -0.7 -0.3 -0.2 -0.1 -0.1 0.0 0.0 0.0 0.1 0.2 0.2 0.2 0.4
1 11 8 6 17 19 2 9 10 16 12 14 15 18 4
Laboratory
En-Scores: S1 - Nitrite-N
E_n-Score
-0.3 -0.3 -0.5 -0.6 -0.2 0.0 0.0 0.1 0.7 0.3 0.3 0.2 0.6
1 11 8 6 17 19 2 9 10 16 12 14 15 18 4
Laboratory

Figure 9

Table 12

Sample Details

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

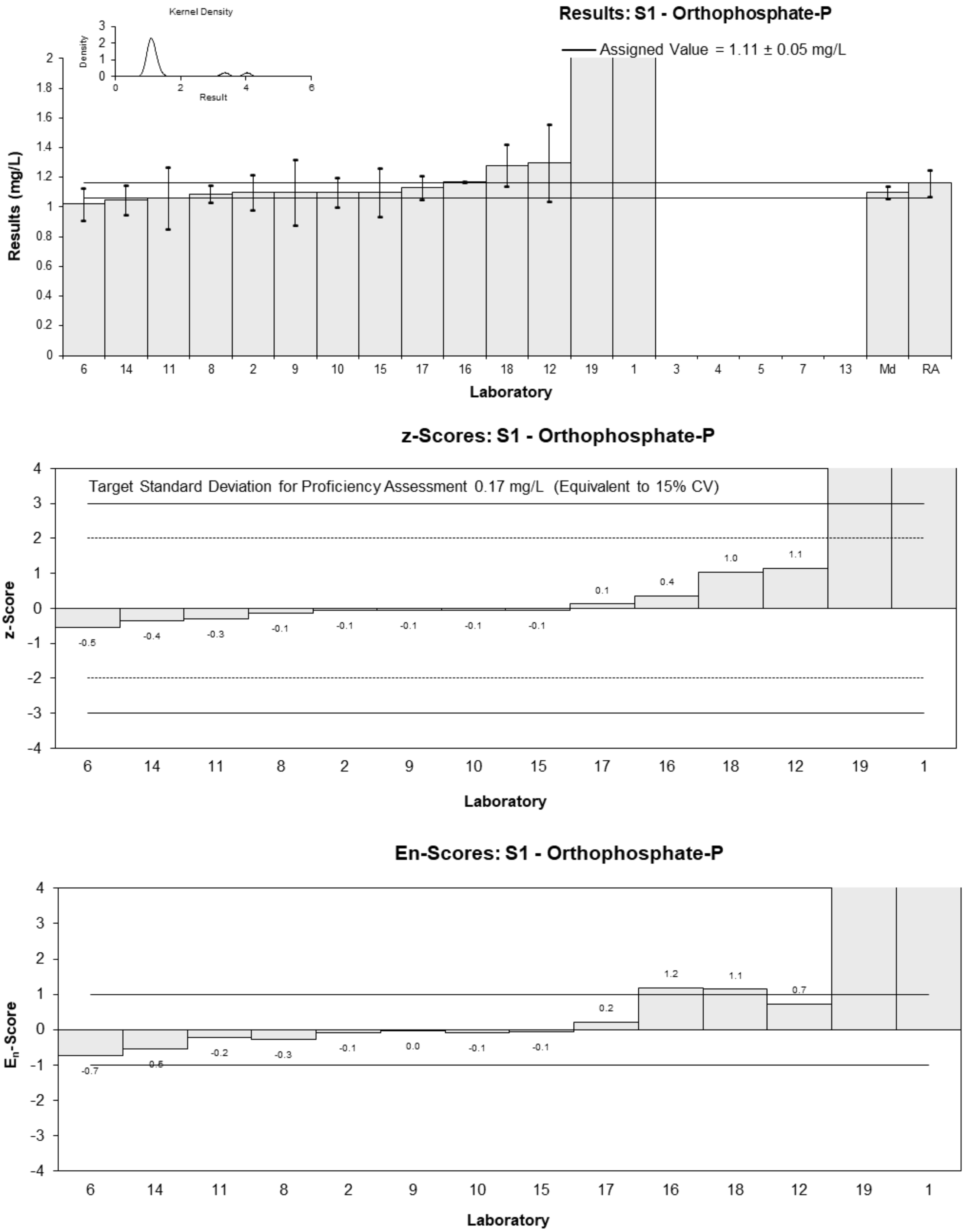
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1*	4.04	0.04	17.60	45.76
2	1.10	0.12	-0.06	-0.08
3	NR	NR		
4	NT	NT		
5	NT	NT		
6	1.02	0.11	-0.54	-0.74
7	NT	NT		
8	1.089	0.056	-0.13	-0.28
9	1.1	0.22	-0.06	-0.04
10	1.10	0.10	-0.06	-0.09
11	1.06	0.21	-0.30	-0.23
12	1.3	0.26	1.14	0.72
13	NT	NT		
14	1.05	0.1	-0.36	-0.54
15	1.1	0.165	-0.06	-0.06
16	1.170	0.005	0.36	1.19
17	1.13	0.08	0.12	0.21
18	1.281	0.141	1.03	1.14
19*	3.36	0.13	13.51	16.15

* Outlier, see Section 4.2

Statistics

Assigned Value	1.11	0.05
Robust Average	1.16	0.09
Median	1.10	0.04
Mean	1.49	
N	14	
Max	4.04	
Min	1.02	
Robust SD	0.13	
Robust CV	11%	



Results: S1 - Orthophosphate-P
Assigned Value = 1.11 ± 0.05 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
6 14 11 8 2 9 10 15 17 16 18 12 19 1 3 4 5 7 13 Md RA
z-Scores: S1 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 0.17 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Orthophosphate-P
En-Score
Laboratory

Figure 10

Table 13

Sample Details

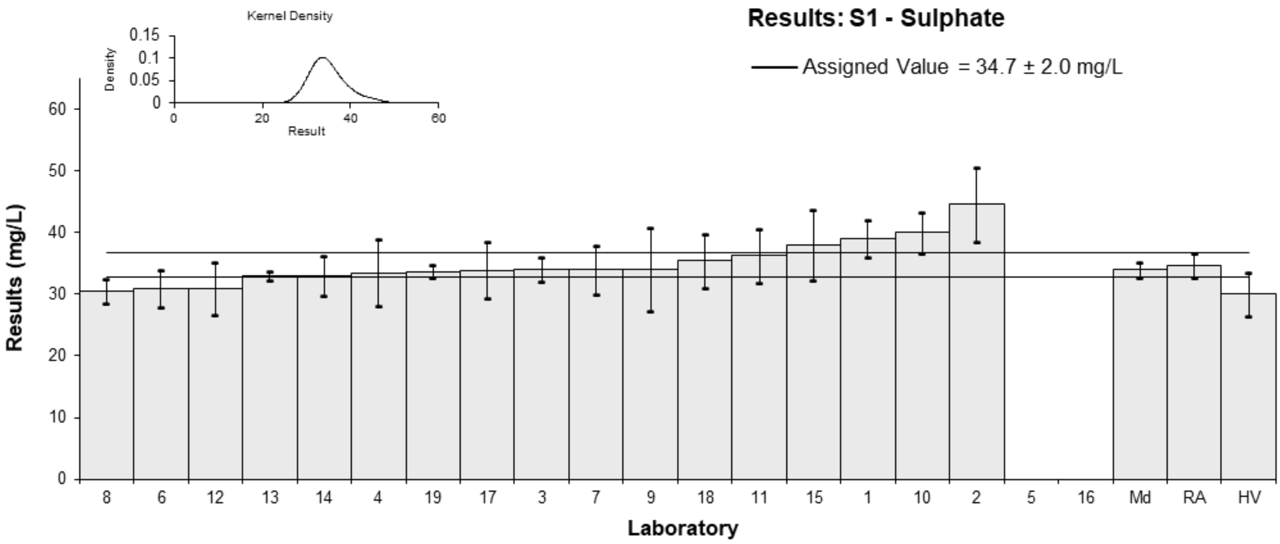
Sample No.	S1
Matrix	Wastewater
Analyte	Sulphate
Unit	mg/L

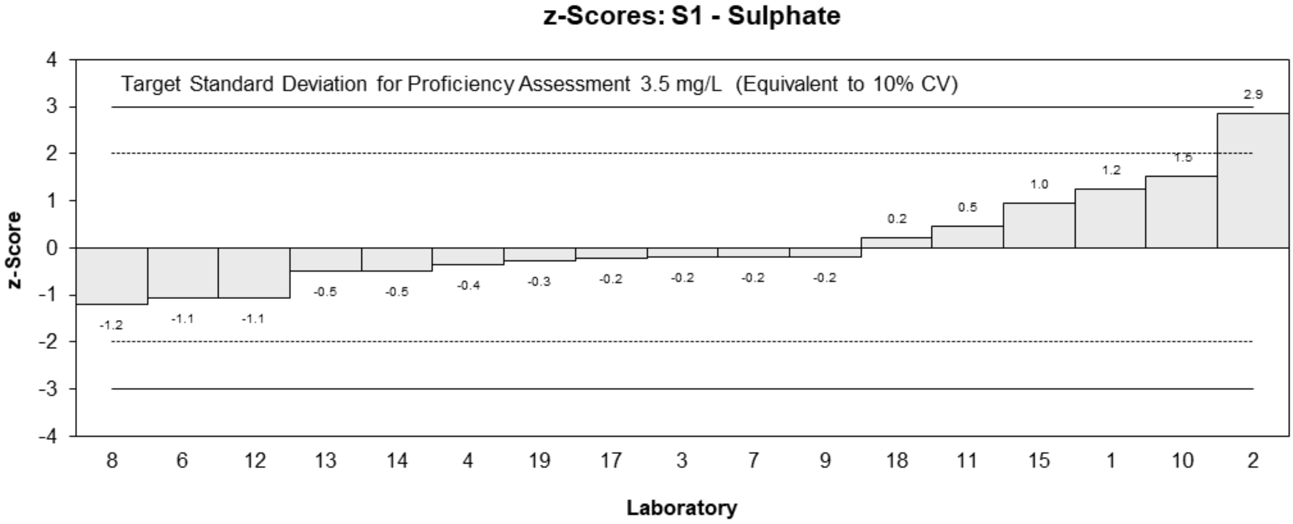
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	39	3	1.24	1.19
2	44.6	6.0	2.85	1.57
3	34.0	2.0	-0.20	-0.25
4	33.5	5.46	-0.35	-0.21
5	NT	NT		
6	31	3	-1.07	-1.03
7	34	4	-0.20	-0.16
8	30.5	1.9	-1.21	-1.52
9	34	6.8	-0.20	-0.10
10	40	3.32	1.53	1.37
11	36.2532	4.3504	0.45	0.32
12	31.0	4.3	-1.07	-0.78
13	33	0.7	-0.49	-0.80
14	33	3.2	-0.49	-0.45
15	38	5.7	0.95	0.55
16	NR	NR		
17	33.9	4.6	-0.23	-0.16
18	35.428	4.345	0.21	0.15
19	33.7	1.1	-0.29	-0.44

Statistics

Assigned Value	34.7	2.0
Homogeneity Value	30.0	3.6
Robust Average	34.7	2.0
Median	34.0	1.3
Mean	35.0	
N	17	
Max	44.6	
Min	30.5	
Robust SD	3.3	
Robust CV	9.6%	


Results: S1 - Sulphate
Assigned Value = 34.7 ± 2.0 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 6 12 13 14 4 19 17 3 7 9 18 11 15 1 10 2 5 16 Md RA HV


z-Scores: S1 - Sulphate
Target Standard Deviation for Proficiency Assessment 3.5 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
8 6 12 13 14 4 19 17 3 7 9 18 11 15 1 10 2

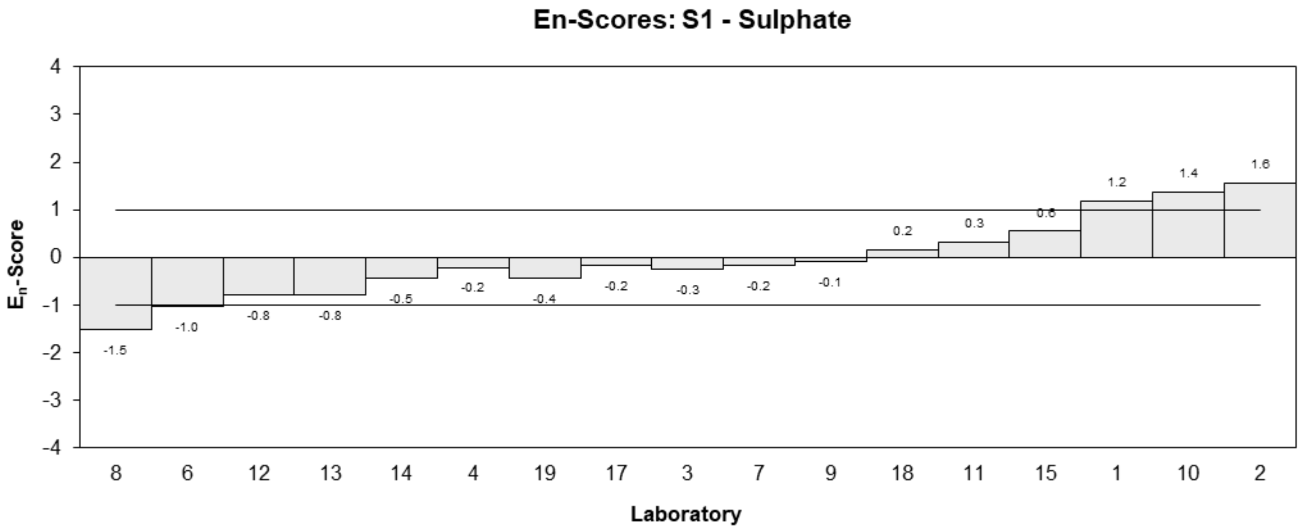

En-Scores: S1 - Sulphate
En-Score
Laboratory
8 6 12 13 14 4 19 17 3 7 9 18 11 15 1 10 2

Figure 11

Table 14

Sample Details

Sample No.	S1
Matrix	Wastewater
Analyte	TDN
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	44.4	5.0	0.70	0.49
3	NR	NR		
4	NT	NT		
5	NT	NT		
6	39.6	8.8	-0.46	-0.20
7	NT	NT		
8	41.0	4.0	-0.12	-0.10
9	42	8.4	0.12	0.06
10	NT	NT		
11	49.1	NR	1.83	2.45
12	43	9.9	0.36	0.14
13	NT	NT		
14	38.1	7.62	-0.82	-0.41
15	46	6.9	1.08	0.59
16	41	0.06	-0.12	-0.16
17	38.6	NR	-0.70	-0.94
18	35.07	6.88	-1.55	-0.85
19	NT	NT		

Statistics

Assigned Value	41.5	3.1
Homogeneity Value	41.0	4.9
Robust Average	41.5	3.1
Median	41.0	2.7
Mean	41.6	
N	11	
Max	49.1	
Min	35.07	
Robust SD	4.1	
Robust CV	9.9%	

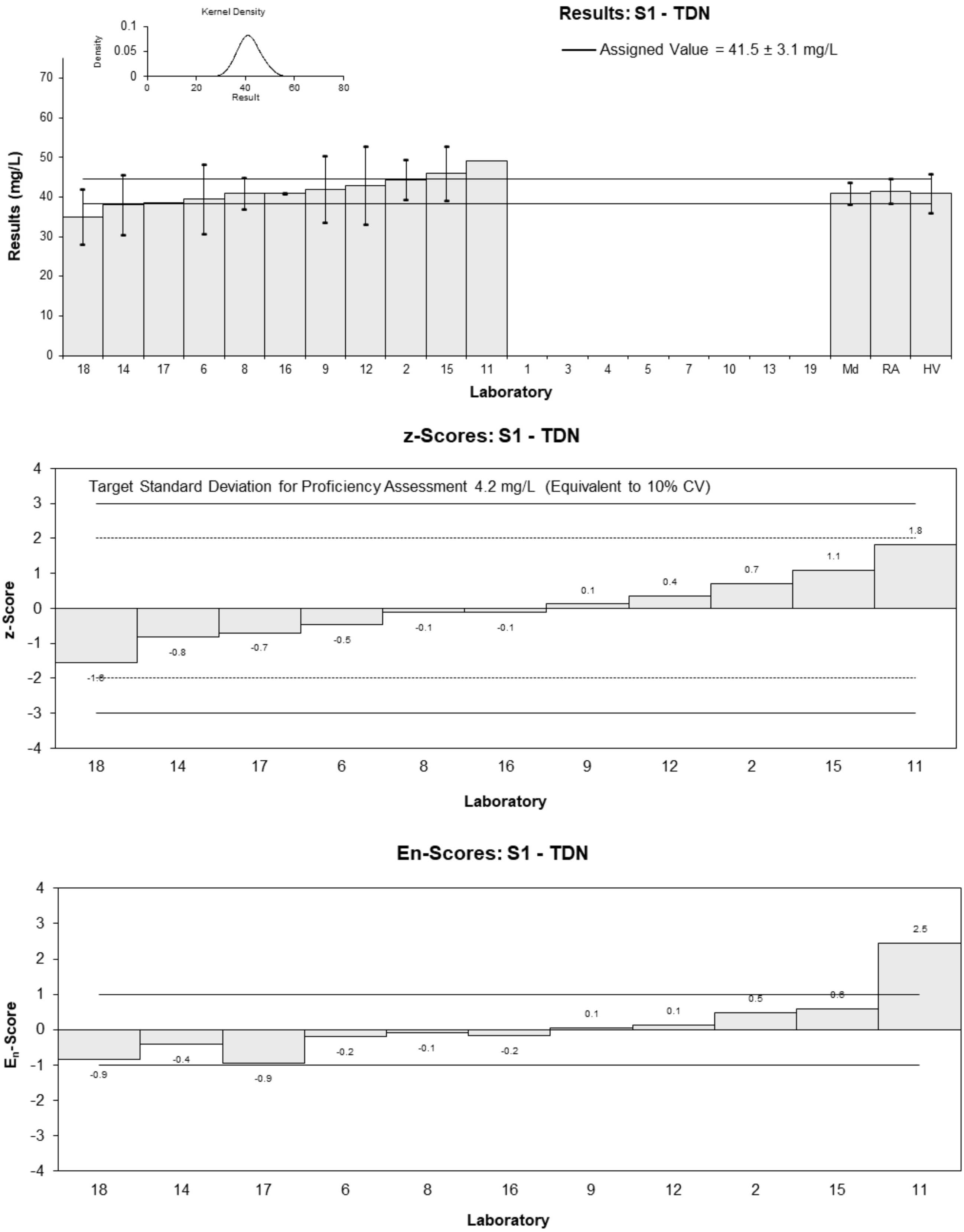

Results: S1 - TDN
Assigned Value = 41.5 ± 3.1 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
18 14 17 6 8 16 9 12 2 15 11 1 3 4 5 7 10 13 19 Md RA HV
z-Scores: S1 - TDN
Target Standard Deviation for Proficiency Assessment 4.2 mg/L (Equivalent to 10% CV)
z-Score
-1.6 -0.8 -0.7 -0.5 -0.1 -0.1 0.1 0.4 0.7 1.1 1.8
18 14 17 6 8 16 9 12 2 15 11
Laboratory
En-Scores: S1 - TDN
E_n-Score
-0.9 -0.4 -0.9 -0.2 -0.1 -0.2 0.1 0.1 0.5 0.6 2.5
18 14 17 6 8 16 9 12 2 15 11
Laboratory

Figure 12

Table 15

Sample Details

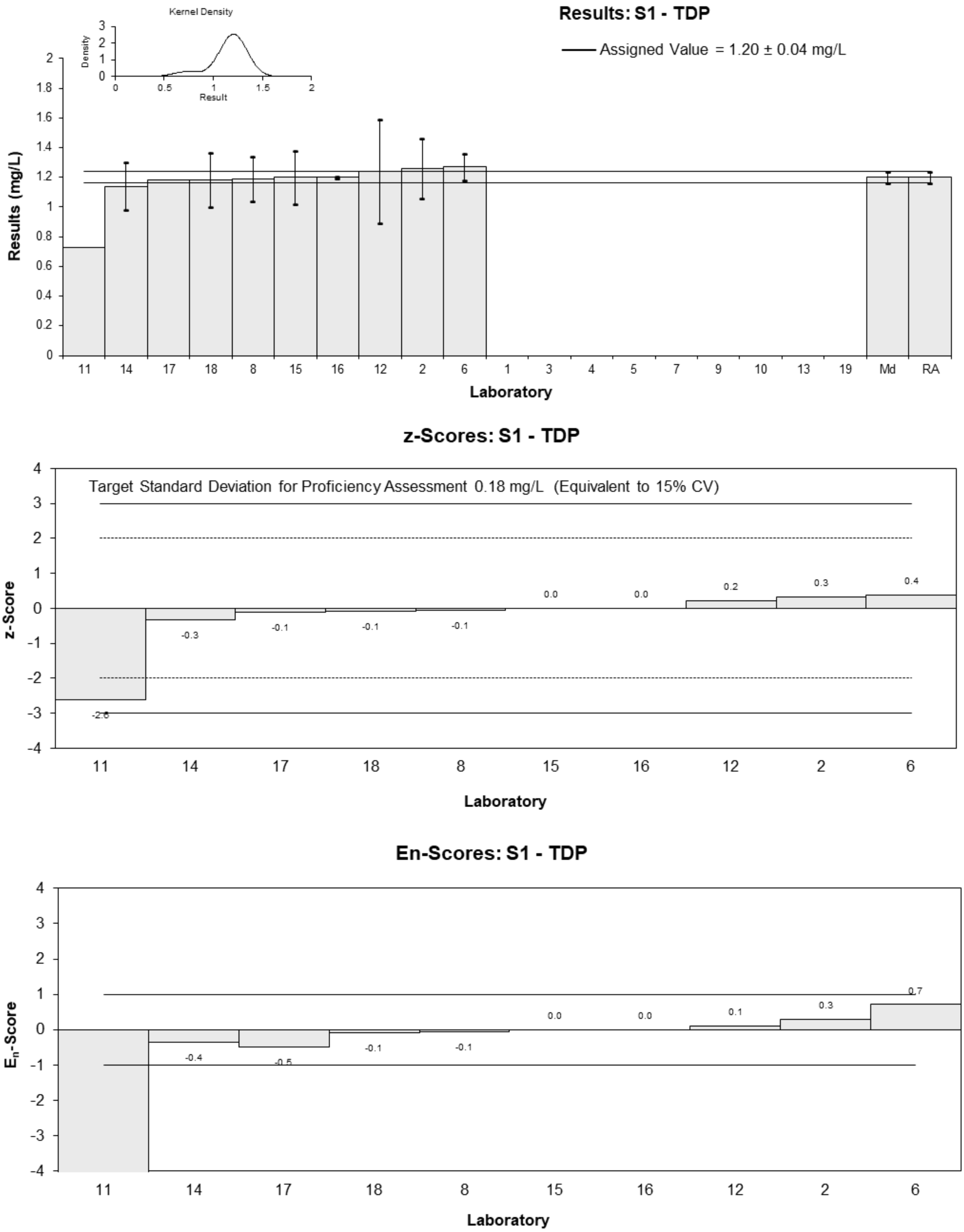
Sample No.	S1
Matrix	Wastewater
Analyte	TDP
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NR	NR		
2	1.26	0.2	0.33	0.29
3	NR	NR		
4	NT	NT		
5	NT	NT		
6	1.27	0.09	0.39	0.71
7	NT	NT		
8	1.19	0.15	-0.06	-0.06
9	NR	NR		
10	NT	NT		
11	0.726	NR	-2.63	-11.85
12	1.24	0.35	0.22	0.11
13	NT	NT		
14	1.14	0.16	-0.33	-0.36
15	1.2	0.18	0.00	0.00
16	1.2	0.005	0.00	0.00
17	1.18	NR	-0.11	-0.50
18	1.185	0.183	-0.08	-0.08
19	NT	NT		

Statistics

Assigned Value	1.20	0.04
Robust Average	1.20	0.04
Median	1.20	0.04
Mean	1.16	
N	10	
Max	1.27	
Min	0.726	
Robust SD	0.056	
Robust CV	4.6%	



Results: S1 - TDP
Assigned Value = 1.20 ± 0.04 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
z-Scores: S1 - TDP
Target Standard Deviation for Proficiency Assessment 0.18 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - TDP
En-Score
Laboratory

Figure 13

Table 16

Sample Details

Sample No.	S2
Matrix	Wastewater
Analyte	B
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.596	0.08	-0.45	-0.31
3	0.60	0.10	-0.38	-0.22
4	0.624	0.09	0.00	0.00
5	0.667	0.034	0.69	0.83
6	0.7	0.06	1.22	1.06
7	0.54	0.09	-1.35	-0.86
8	NT	NT		
9	0.66	0.13	0.58	0.27
10	NT	NT		
11	0.675	0.2903	0.82	0.17
12	NT	NT		
13	0.585	0.058	-0.63	-0.56
14	0.58	0.07	-0.71	-0.55
15	NR	NR		
16	NR	NR		
17	0.6	NR	-0.38	-0.62
18	0.663	0.062	0.63	0.53
19	NT	NT		

Statistics

Assigned Value	0.624	0.039
Homogeneity Value	0.631	0.076
Robust Average	0.624	0.039
Median	0.612	0.043
Mean	0.624	
N	12	
Max	0.7	
Min	0.54	
Robust SD	0.054	
Robust CV	8.6%	

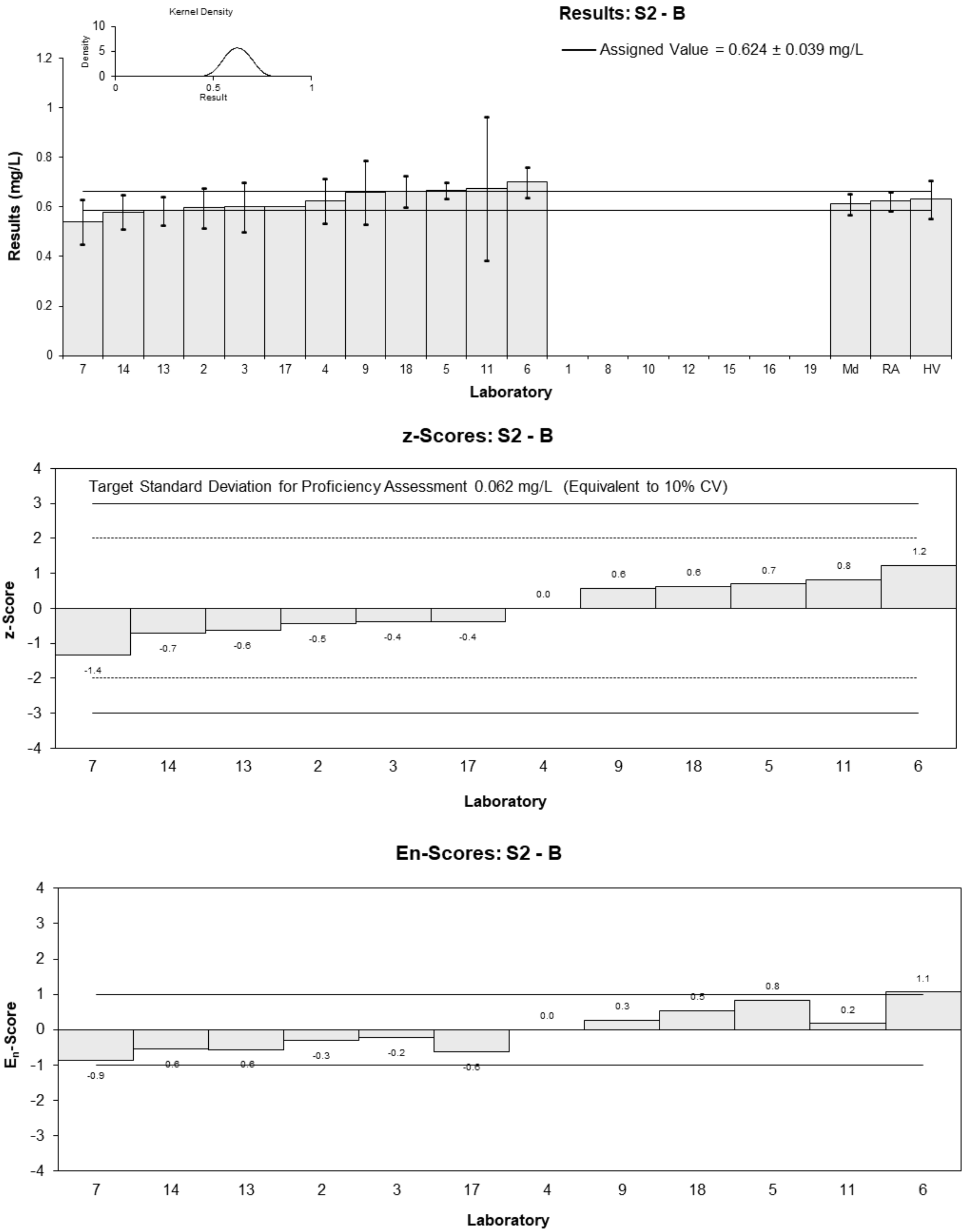

Kernel Density
Density
Result
Results: S2 - B
Assigned Value = 0.624 ± 0.039 mg/L
Results (mg/L)
Laboratory
7
14
13
2
3
17
4
9
18
5
11
6
1
8
10
12
15
16
19
Md
RA
HV
z-Scores: S2 - B
Target Standard Deviation for Proficiency Assessment 0.062 mg/L (Equivalent to 10% CV)
z-Score
-1.4
-0.7
-0.6
-0.5
-0.4
-0.4
0.0
0.6
0.6
0.7
0.8
1.2
En-Scores: S2 - B
E_n-Score
-0.9
-0.6
-0.6
-0.3
-0.2
-0.6
0.0
0.3
0.5
0.8
0.2
1.1

Figure 14

Table 17

Sample Details

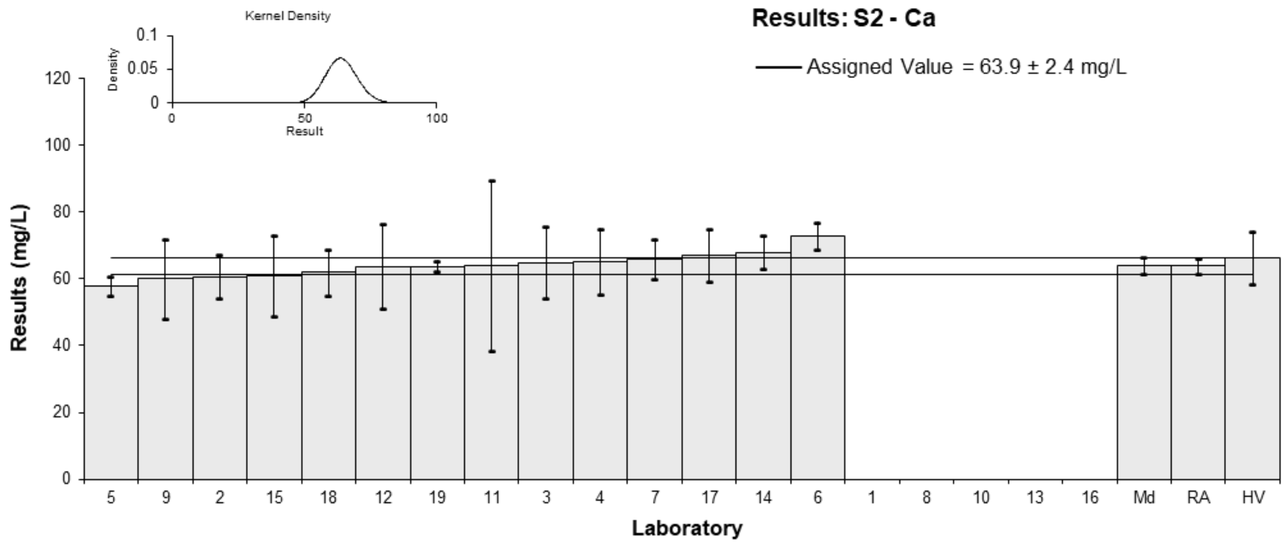
Sample No.	S2
Matrix	Wastewater
Analyte	Ca
Unit	mg/L

Participant Results

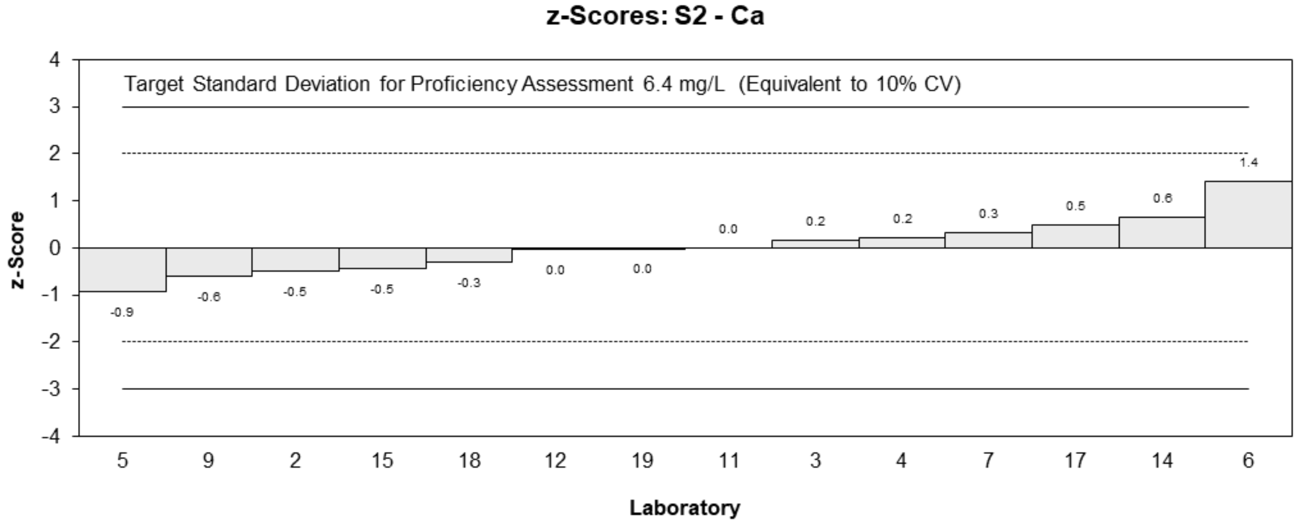
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	60.7	6.5	-0.50	-0.46
3	64.9	10.7	0.16	0.09
4	65.3	9.80	0.22	0.14
5	58.029	2.900	-0.92	-1.56
6	73	4	1.42	1.95
7	66	6	0.33	0.32
8	NT	NT		
9	60	12	-0.61	-0.32
10	NT	NT		
11	63.9	25.6	0.00	0.00
12	63.7	12.7	-0.03	-0.02
13	NT	NT		
14	68	5	0.64	0.74
15	61	12.2	-0.45	-0.23
16	NR	NR		
17	67	7.8	0.49	0.38
18	61.916	6.817	-0.31	-0.27
19	63.8	1.6	-0.02	-0.03

Statistics

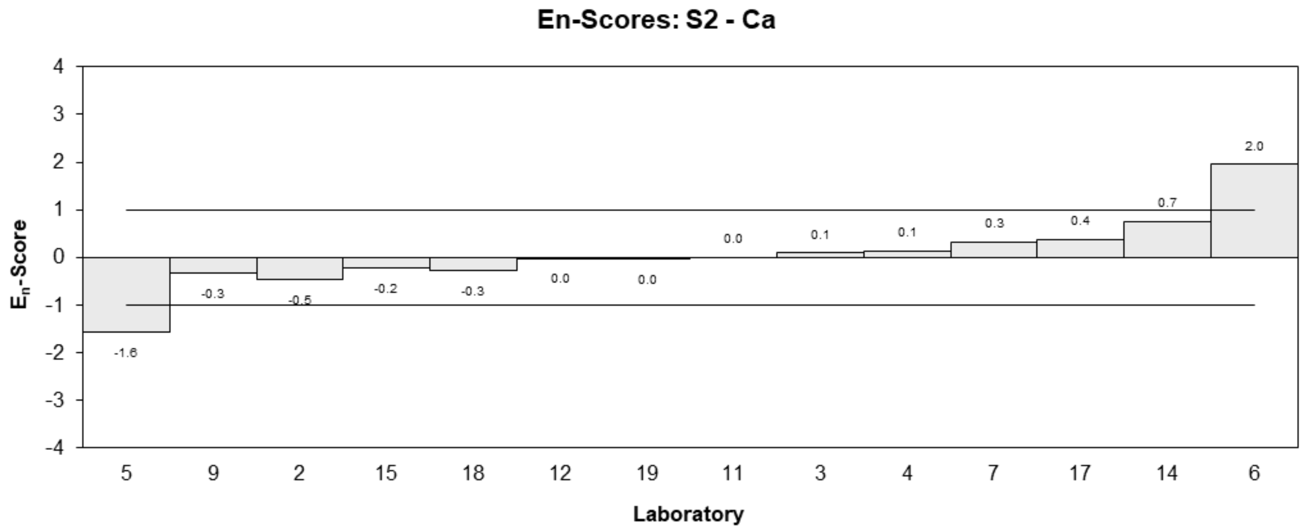
Assigned Value	63.9	2.4
Homogeneity Value	66.3	8.0
Robust Average	63.9	2.4
Median	63.9	2.5
Mean	64.1	
N	14	
Max	73	
Min	58.029	
Robust SD	3.6	
Robust CV	5.6%	



Results: S2 - Ca
Assigned Value = 63.9 ± 2.4 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
5
9
2
15
18
12
19
11
3
4
7
17
14
6
1
8
10
13
16
Md
RA
HV



z-Scores: S2 - Ca
Target Standard Deviation for Proficiency Assessment 6.4 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.9
-0.6
-0.5
-0.5
-0.3
0.0
0.0
0.0
0.2
0.2
0.3
0.5
0.6
1.4
5
9
2
15
18
12
19
11
3
4
7
17
14
6



En-Scores: S2 - Ca
E_n-Score
Laboratory
-1.6
-0.3
-0.5
-0.2
-0.3
0.0
0.0
0.0
0.1
0.1
0.3
0.4
0.7
2.0
5
9
2
15
18
12
19
11
3
4
7
17
14
6

Figure 15

Table 18

Sample Details

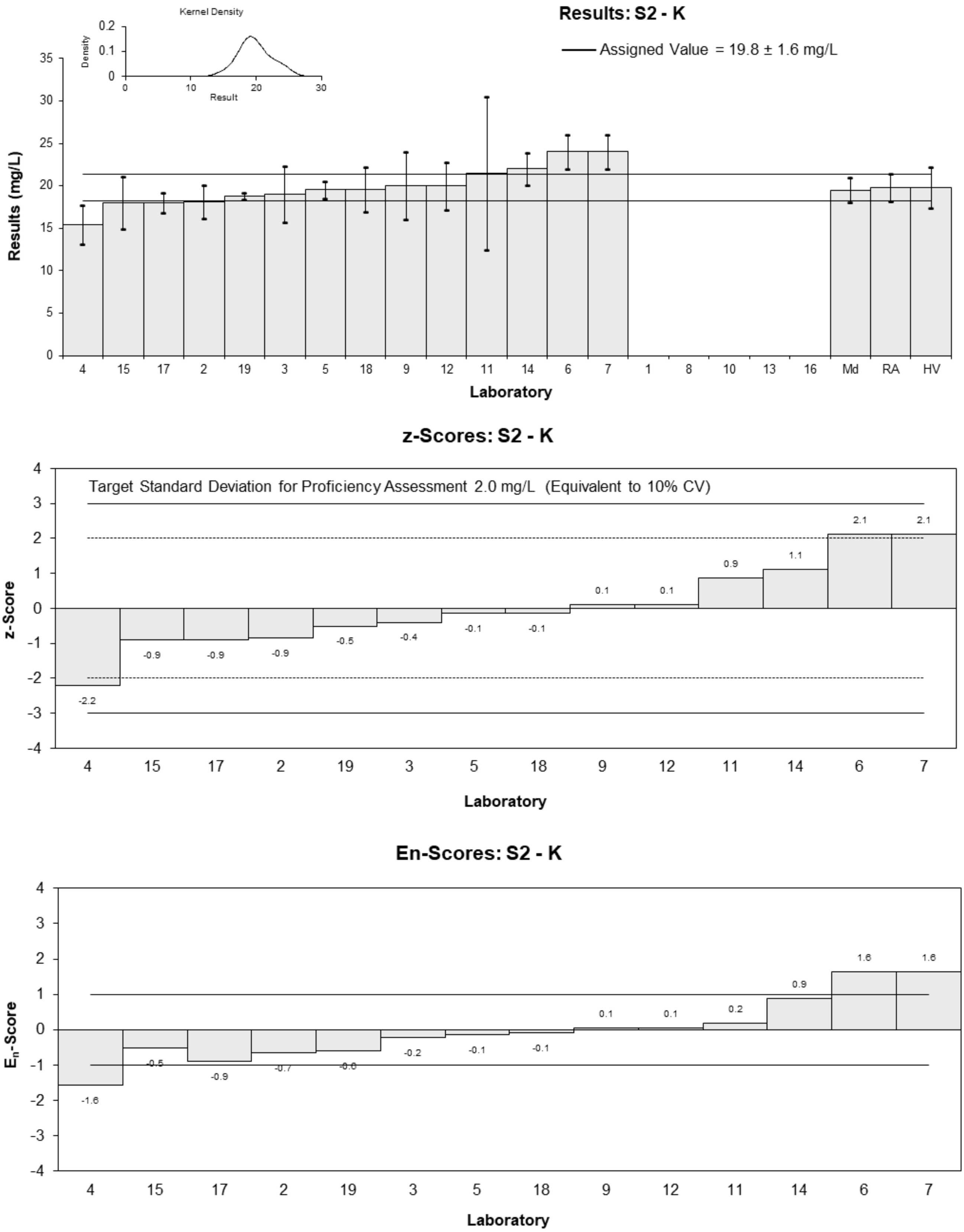
Sample No.	S2
Matrix	Wastewater
Analyte	K
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	18.1	2.0	-0.86	-0.66
3	19.0	3.3	-0.40	-0.22
4	15.4	2.31	-2.22	-1.57
5	19.532	0.977	-0.14	-0.14
6	24	2	2.12	1.64
7	24	2	2.12	1.64
8	NT	NT		
9	20	4	0.10	0.05
10	NT	NT		
11	21.5	9.0	0.86	0.19
12	20.0	2.8	0.10	0.06
13	NT	NT		
14	22	1.9	1.11	0.89
15	18	3.132	-0.91	-0.51
16	NR	NR		
17	18	1.2	-0.91	-0.90
18	19.537	2.641	-0.13	-0.09
19	18.8	0.4	-0.51	-0.61

Statistics

Assigned Value	19.8	1.6
Homogeneity Value	19.8	2.4
Robust Average	19.8	1.6
Median	19.5	1.5
Mean	19.8	
N	14	
Max	24	
Min	15.4	
Robust SD	2.4	
Robust CV	12%	



Results: S2 - K
Assigned Value = 19.8 ± 1.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
4 15 17 2 19 3 5 18 9 12 11 14 6 7 1 8 10 13 16 Md RA HV
z-Scores: S2 - K
Target Standard Deviation for Proficiency Assessment 2.0 mg/L (Equivalent to 10% CV)
z-Score
-2.2 -0.9 -0.9 -0.9 -0.5 -0.4 -0.1 -0.1 0.1 0.1 0.9 1.1 2.1 2.1
4 15 17 2 19 3 5 18 9 12 11 14 6 7
Laboratory
En-Scores: S2 - K
E_n-Score
-1.6 -0.5 -0.9 -0.7 -0.6 -0.2 -0.1 -0.1 0.1 0.1 0.2 0.9 1.6 1.6
4 15 17 2 19 3 5 18 9 12 11 14 6 7
Laboratory

Figure 16

Table 19

Sample Details

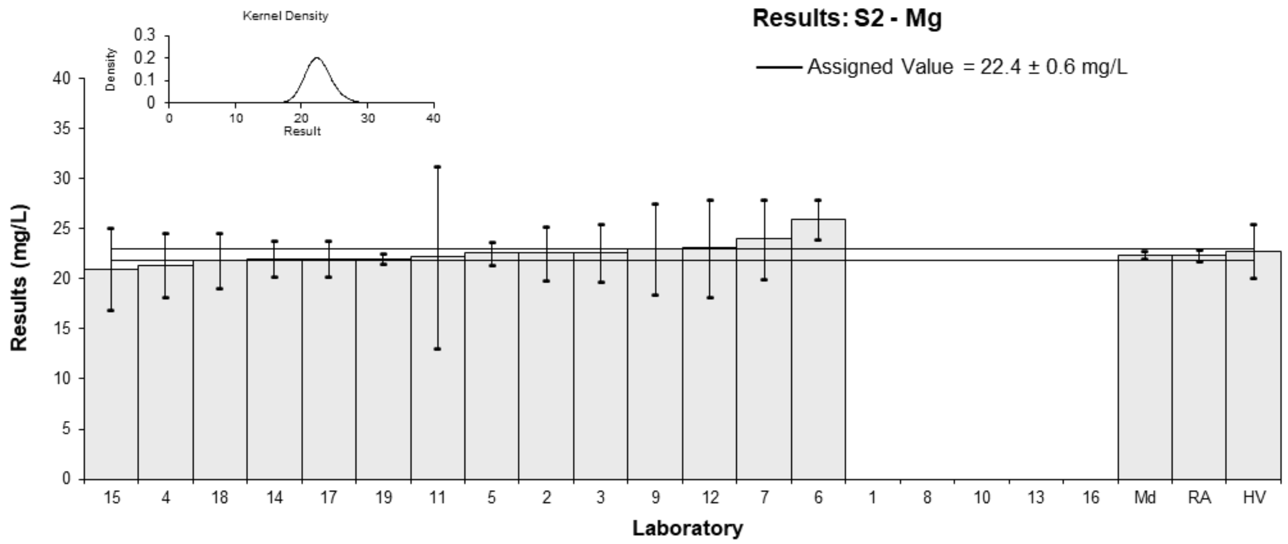
Sample No.	S2
Matrix	Wastewater
Analyte	Mg
Unit	mg/L

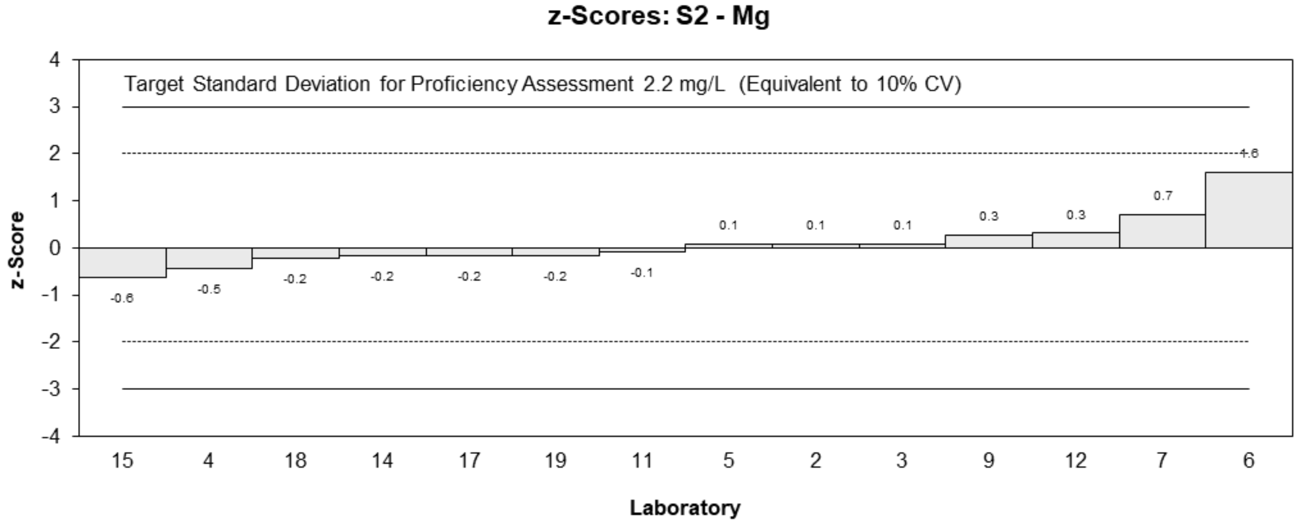
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	22.6	2.7	0.09	0.07
3	22.6	2.9	0.09	0.07
4	21.4	3.21	-0.45	-0.31
5	22.562	1.128	0.07	0.13
6	26	2	1.61	1.72
7	24	4	0.71	0.40
8	NT	NT		
9	23	4.6	0.27	0.13
10	NT	NT		
11	22.2	9.1	-0.09	-0.02
12	23.1	4.9	0.31	0.14
13	NT	NT		
14	22	1.8	-0.18	-0.21
15	21	4.095	-0.62	-0.34
16	NR	NR		
17	22	1.8	-0.18	-0.21
18	21.880	2.725	-0.23	-0.19
19	22.0	0.5	-0.18	-0.51

Statistics

Assigned Value	22.4	0.6
Homogeneity Value	22.8	2.7
Robust Average	22.4	0.6
Median	22.4	0.4
Mean	22.6	
N	14	
Max	26	
Min	21	
Robust SD	0.91	
Robust CV	4.1%	


Results: S2 - Mg
Assigned Value = 22.4 ± 0.6 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15 4 18 14 17 19 11 5 2 3 9 12 7 6 1 8 10 13 16 Md RA HV


z-Scores: S2 - Mg
Target Standard Deviation for Proficiency Assessment 2.2 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
15 4 18 14 17 19 11 5 2 3 9 12 7 6

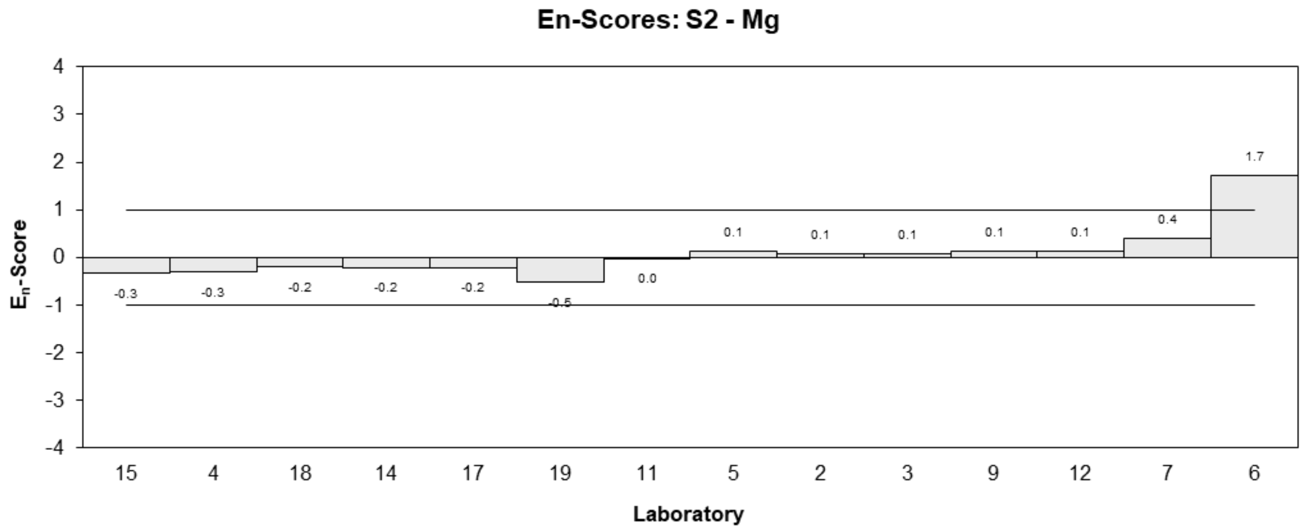

En-Scores: S2 - Mg
En-Score
Laboratory
15 4 18 14 17 19 11 5 2 3 9 12 7 6

Figure 17

Table 20

Sample Details

Sample No.	S2
Matrix	Wastewater
Analyte	Na
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	238	25	0.62	0.53
3	233	26	0.40	0.33
4	207	31.1	-0.76	-0.53
5	225.776	11.289	0.08	0.13
6	216	14	-0.36	-0.50
7	256	37	1.43	0.85
8	NT	NT		
9	220	44	-0.18	-0.09
10	NT	NT		
11	218	92	-0.27	-0.06
12	223	49	-0.04	-0.02
13	NT	NT		
14	213	25	-0.49	-0.42
15	220	48.84	-0.18	-0.08
16	NR	NR		
17	231	19.3	0.31	0.34
18	211.8	26.3	-0.54	-0.44
19	232	5	0.36	0.85

Statistics

Assigned Value	224	8
Homogeneity Value	215	26
Robust Average	224	8
Median	222	9
Mean	225	
N	14	
Max	256	
Min	207	
Robust SD	12	
Robust CV	5.2%	

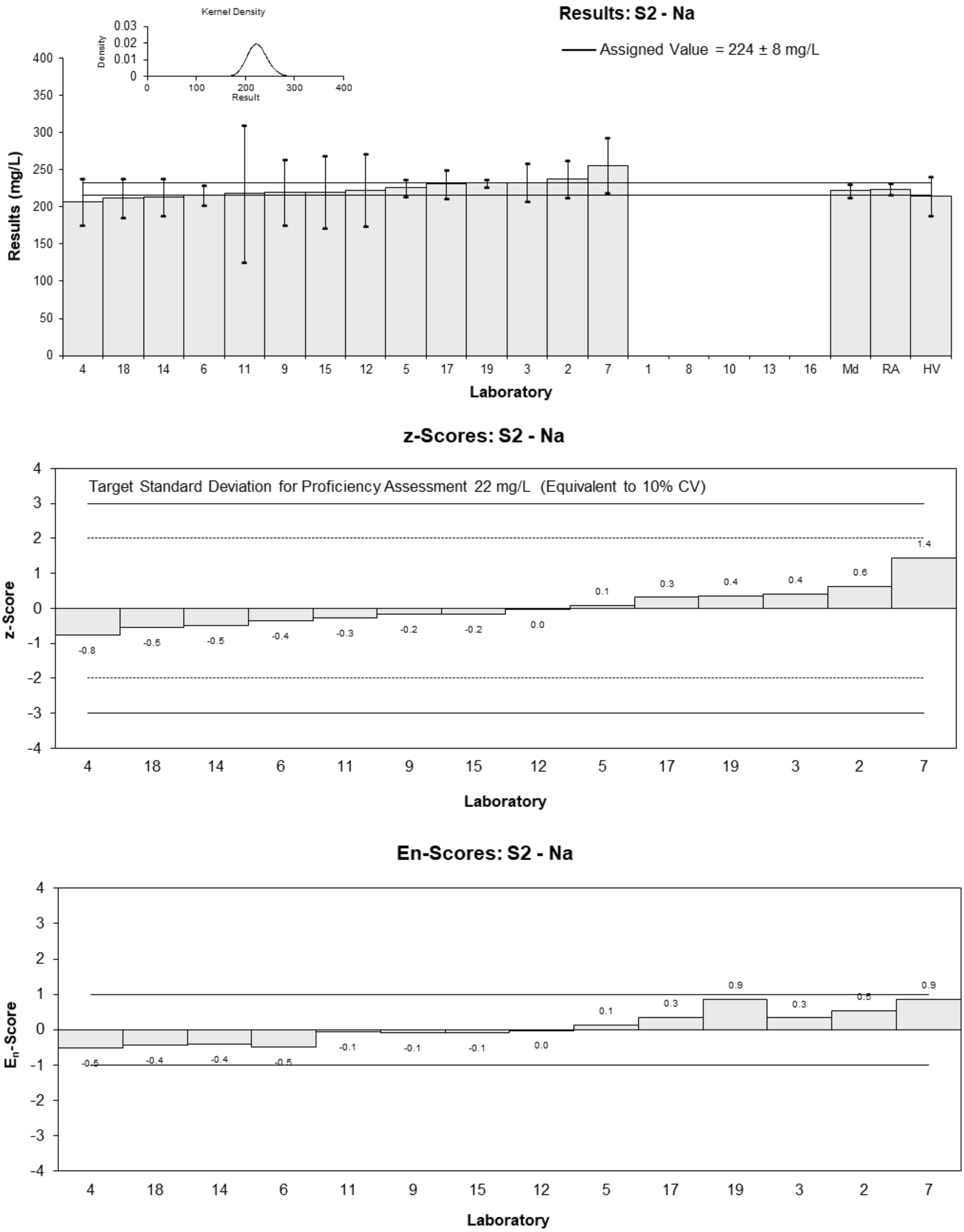

Results: S2 - Na
Assigned Value = 224 ± 8 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
4 18 14 6 11 9 15 12 5 17 19 3 2 7 1 8 10 13 16 Md RA HV
z-Scores: S2 - Na
Target Standard Deviation for Proficiency Assessment 22 mg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.5 -0.5 -0.4 -0.3 -0.2 -0.2 0.0 0.1 0.3 0.4 0.4 0.6 1.4
Laboratory
4 18 14 6 11 9 15 12 5 17 19 3 2 7
En-Scores: S2 - Na
En-Score
-0.5 -0.4 -0.4 -0.5 -0.1 -0.1 -0.1 0.0 0.1 0.3 0.9 0.3 0.5 0.9
Laboratory
4 18 14 6 11 9 15 12 5 17 19 3 2 7

Figure 18

Table 21

Sample Details

Sample No.	S2
Matrix	Wastewater
Analyte	P
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.82	0.1	-0.81	-0.58
3	0.90	0.22	0.09	0.03
4	NT	NT		
5	0.842	0.042	-0.56	-0.58
6	1	0.1	1.21	0.86
7	0.86	0.17	-0.36	-0.17
8	NT	NT		
9	0.81	0.16	-0.92	-0.46
10	NT	NT		
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	1	0.1	1.21	0.86
15	0.9	0.144	0.09	0.05
16	NR	NR		
17	<1	NR		
18	<1	NR		
19	NT	NT		

Statistics

Assigned Value	0.892	0.075
Homogeneity Value	0.86	0.10
Robust Average	0.892	0.075
Median	0.880	0.064
Mean	0.892	
N	8	
Max	1	
Min	0.81	
Robust SD	0.085	
Robust CV	9.5%	

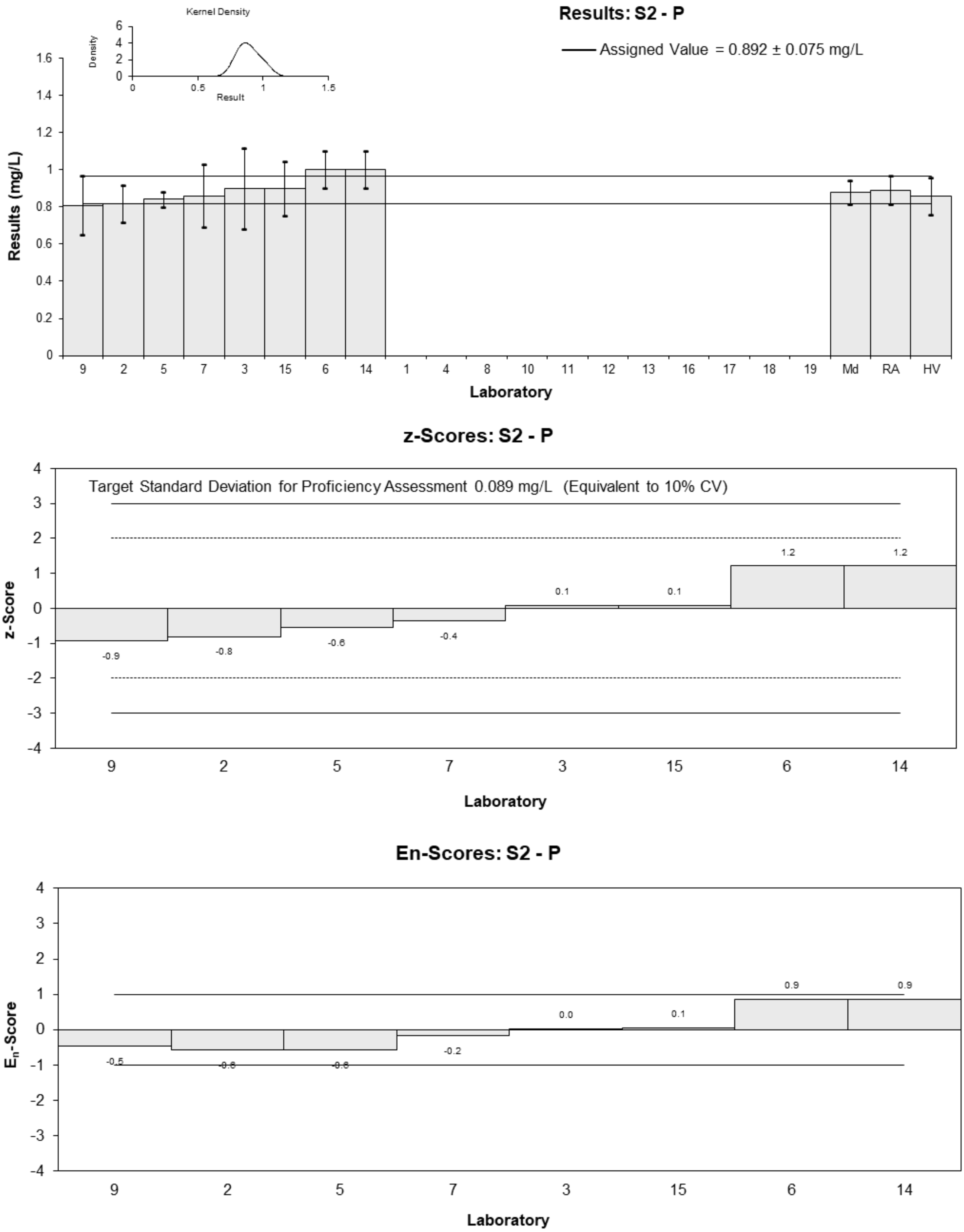

Results: S2 - P
Assigned Value = 0.892 ± 0.075 mg/L
Kernel Density
Density
Result
Results (mg/L)
9 2 5 7 3 15 6 14 1 4 8 10 11 12 13 16 17 18 19 Md RA HV
Laboratory
z-Scores: S2 - P
Target Standard Deviation for Proficiency Assessment 0.089 mg/L (Equivalent to 10% CV)
z-Score
-0.9 -0.8 -0.6 -0.4 0.1 0.1 1.2 1.2
9 2 5 7 3 15 6 14
Laboratory
En-Scores: S2 - P
E_n-Score
-0.5 -0.6 -0.6 -0.2 0.0 0.1 0.9 0.9
9 2 5 7 3 15 6 14
Laboratory

Figure 19

Table 22

Sample Details

Sample No.	S2
Matrix	Wastewater
Analyte	Alkalinity
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	184	20	-0.47	-0.42
3	NR	NR		
4	196	29.4	0.16	0.10
5*	90	6	-5.34	-10.30
6	205	25	0.62	0.46
7	200	8	0.36	0.62
8	NT	NT		
9	160	32	-1.71	-1.00
10	200	5.60	0.36	0.72
11	201.3	9.7	0.43	0.66
12	192	10	-0.05	-0.08
13	191	34	-0.10	-0.06
14	212	29	0.98	0.63
15	184	27.6	-0.47	-0.31
16	NR	NR		
17	188	28.1	-0.26	-0.17
18	185.26	17.97	-0.40	-0.39
19	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	193	8
Homogeneity Value	180	22
Robust Average	192	9
Median	192	8
Mean	185	
N	14	
Max	212	
Min	90	
Robust SD	13	
Robust CV	7%	

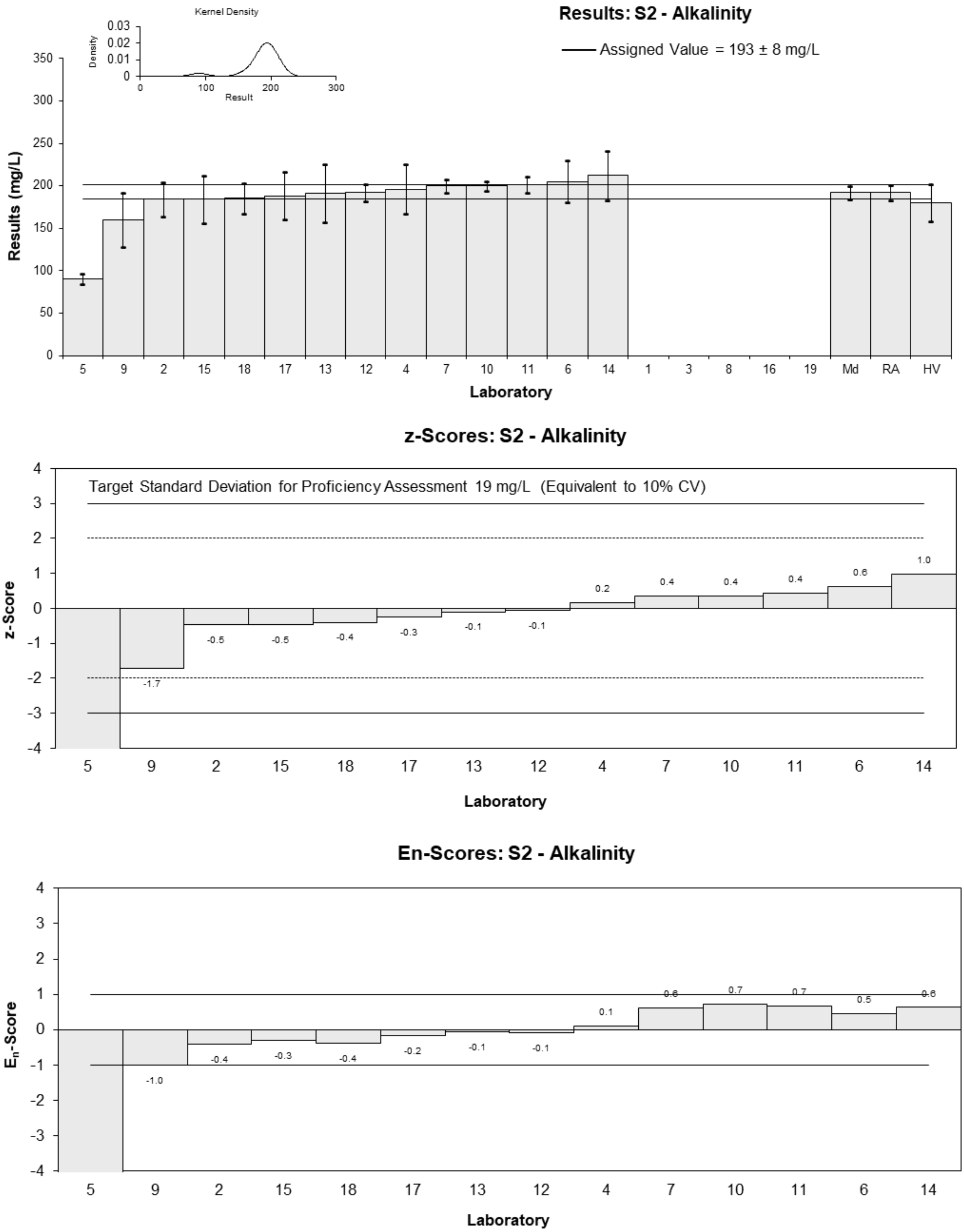

Kernel Density
Density
Result
Results: S2 - Alkalinity
Assigned Value = 193 ± 8 mg/L
Results (mg/L)
Laboratory
5 9 2 15 18 17 13 12 4 7 10 11 6 14 1 3 8 16 19 Md RA HV
z-Scores: S2 - Alkalinity
Target Standard Deviation for Proficiency Assessment 19 mg/L (Equivalent to 10% CV)
z-Score
-1.7 -0.5 -0.5 -0.4 -0.3 -0.1 -0.1 0.2 0.4 0.4 0.4 0.6 1.0
Laboratory
En-Scores: S2 - Alkalinity
E_n-Score
-1.0 -0.4 -0.3 -0.4 -0.2 -0.1 -0.1 0.1 0.6 0.7 0.7 0.5 0.6
Laboratory

Figure 20

Table 23

Sample Details

Sample No.	S2
Matrix	Wastewater
Analyte	Colour
Unit	Pt-Co units

Participant Results

Lab. Code	Result	Uncertainty
1	NT	NT
2	188	20
3	NR	NR
4	50	15
5	NT	NT
6	45	5
7	240	42
8	NT	NT
9	71	14
10	70	3.5
11	453	95
12	226	11
13	NT	NT
14	40	8
15	45	6.75
16	NR	NR
17	45	NR
18	40	NR
19	NT	NT

Statistics

Assigned Value	Not Set	
Robust Average	110	74
Median	60	19
Mean	126	
N	12	
Max	453	
Min	40	
Robust SD	100	
Robust CV	93%	

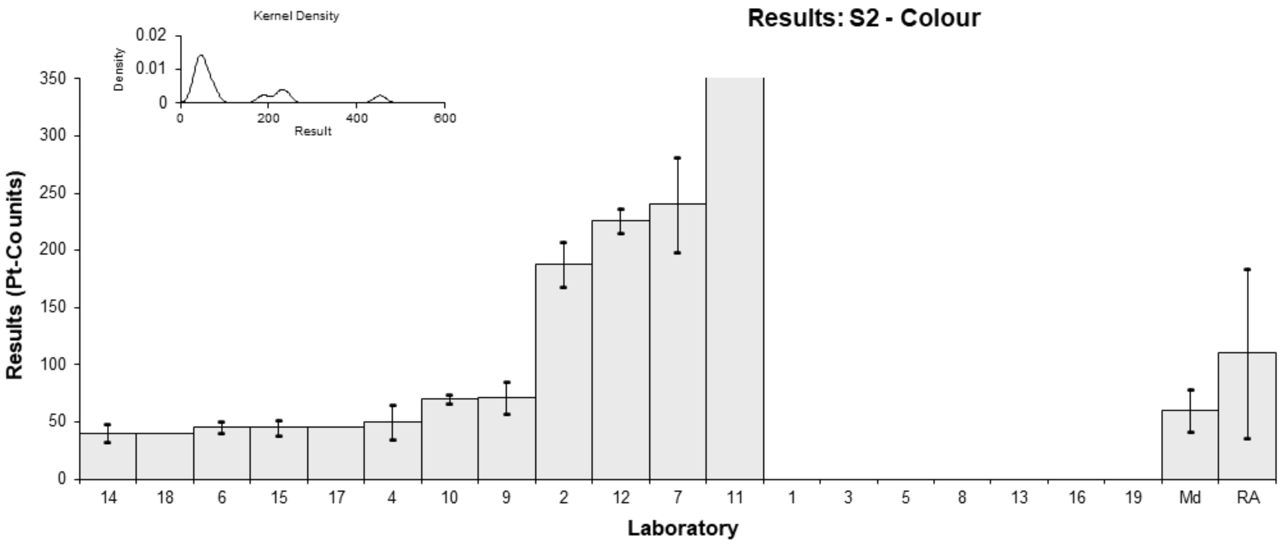

Results: S2 - Colour
Kernel Density
0.02
0.01
0
Density
0
200
400
600
Result
Results (Pt-Co units)
350
300
250
200
150
100
50
0
14
18
6
15
17
4
10
9
2
12
7
11
1
3
5
8
13
16
19
Md
RA
Laboratory

Figure 21

Table 24

Sample Details

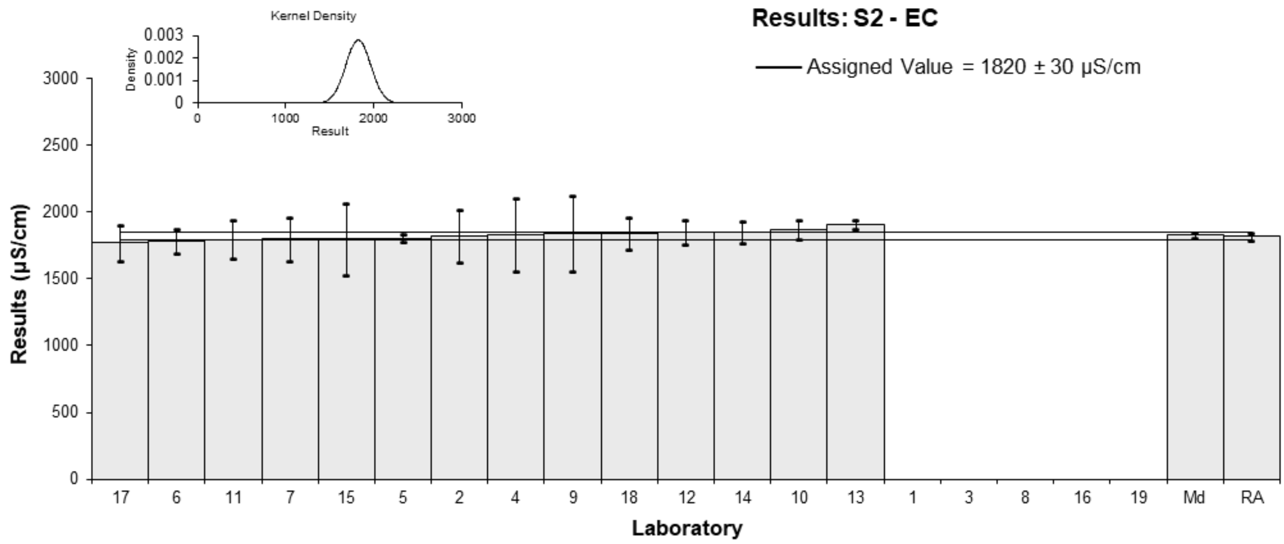
Sample No.	S2
Matrix	Wastewater
Analyte	EC
Unit	µS/cm

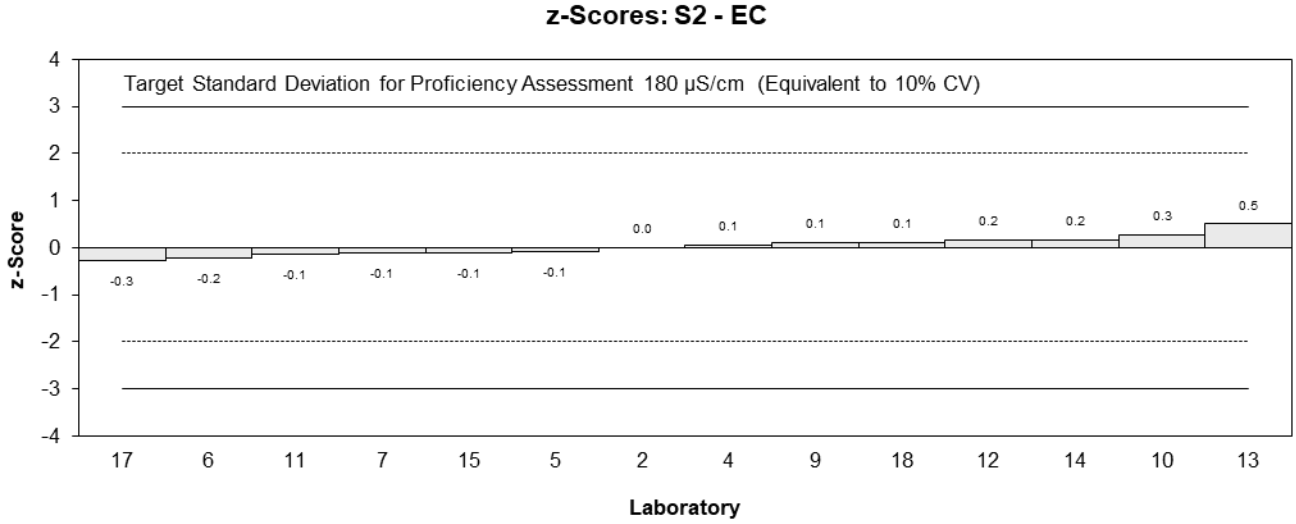
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	1820	200	0.00	0.00
3	NR	NR		
4	1830	274.5	0.05	0.04
5	1806	30	-0.08	-0.33
6	1780	90	-0.22	-0.42
7	1800	162	-0.11	-0.12
8	NT	NT		
9	1840	280	0.11	0.07
10	1870	69.19	0.27	0.66
11	1795.30	145.4	-0.14	-0.17
12	1850	93	0.16	0.31
13	1911	33	0.50	2.04
14	1850	84	0.16	0.34
15	1800	270	-0.11	-0.07
16	NR	NR		
17	1770	138	-0.27	-0.35
18	1840	123	0.11	0.16
19	NT	NT		

Statistics

Assigned Value	1820	30
Robust Average	1820	30
Median	1830	20
Mean	1830	
N	14	
Max	1911	
Min	1770	
Robust SD	38	
Robust CV	2.1%	


Results: S2 - EC
Assigned Value = 1820 ± 30 µS/cm
Kernel Density
Density
Result
Results (µS/cm)
Laboratory
17 6 11 7 15 5 2 4 9 18 12 14 10 13 1 3 8 16 19 Md RA


z-Scores: S2 - EC
Target Standard Deviation for Proficiency Assessment 180 µS/cm (Equivalent to 10% CV)
z-Score
-0.3 -0.2 -0.1 -0.1 -0.1 -0.1 0.0 0.1 0.1 0.1 0.2 0.2 0.3 0.5
17 6 11 7 15 5 2 4 9 18 12 14 10 13
Laboratory

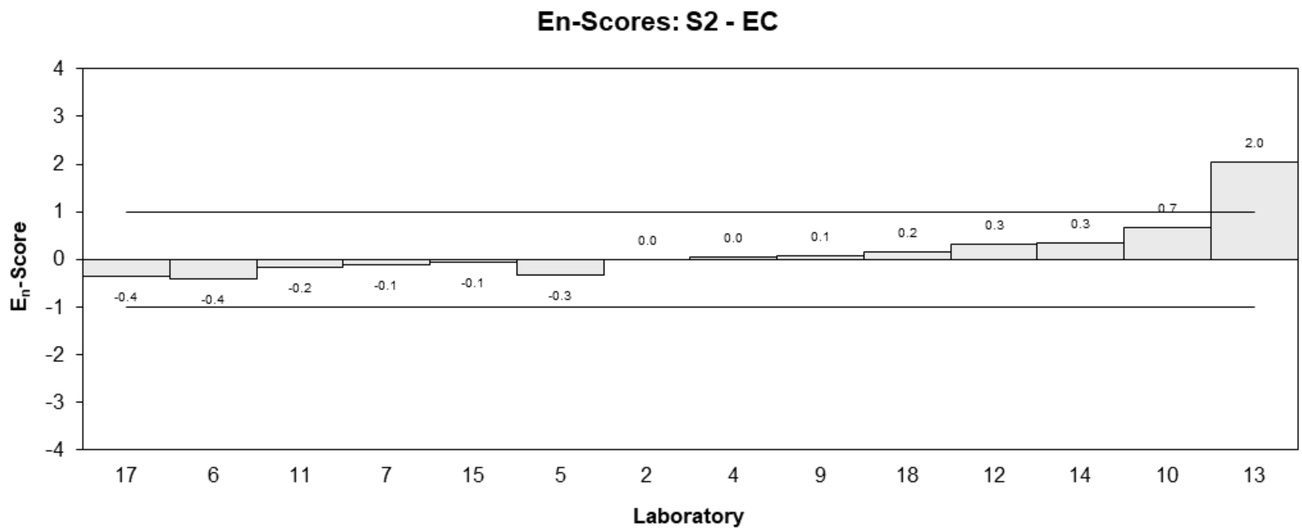

En-Scores: S2 - EC
En-Score
-0.4 -0.4 -0.2 -0.1 -0.1 -0.3 0.0 0.0 0.1 0.2 0.3 0.3 0.7 2.0
17 6 11 7 15 5 2 4 9 18 12 14 10 13
Laboratory

Figure 22

Table 25

Sample Details

Sample No.	S2
Matrix	Wastewater
Analyte	pH

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	8.57	0.2	-0.17	-0.22
3	NR	NR		
4	8.83	0.3	0.70	0.66
5	8.5	0.3	-0.40	-0.38
6	8.61	0.06	-0.03	-0.08
7	8.7	0.1	0.27	0.54
8	NT	NT		
9	8.4	1.7	-0.73	-0.13
10	8.76	0.08	0.46	1.03
11	8.74	0.7	0.40	0.17
12	8.7	0.1	0.27	0.54
13	8.8	0.17	0.60	0.89
14	8.52	0.56	-0.33	-0.18
15	8.6	1.29	-0.07	-0.02
16	NR	NR		
17	8.44	0.14	-0.60	-1.01
18	8.46	0.14	-0.53	-0.90
19	NT	NT		

Statistics

Assigned Value	8.62	0.11
Homogeneity Value	8.60	0.17
Robust Average	8.62	0.11
Median	8.61	0.12
Mean	8.62	
N	14	
Max	8.83	
Min	8.4	
Robust SD	0.16	
Robust CV	1.9%	

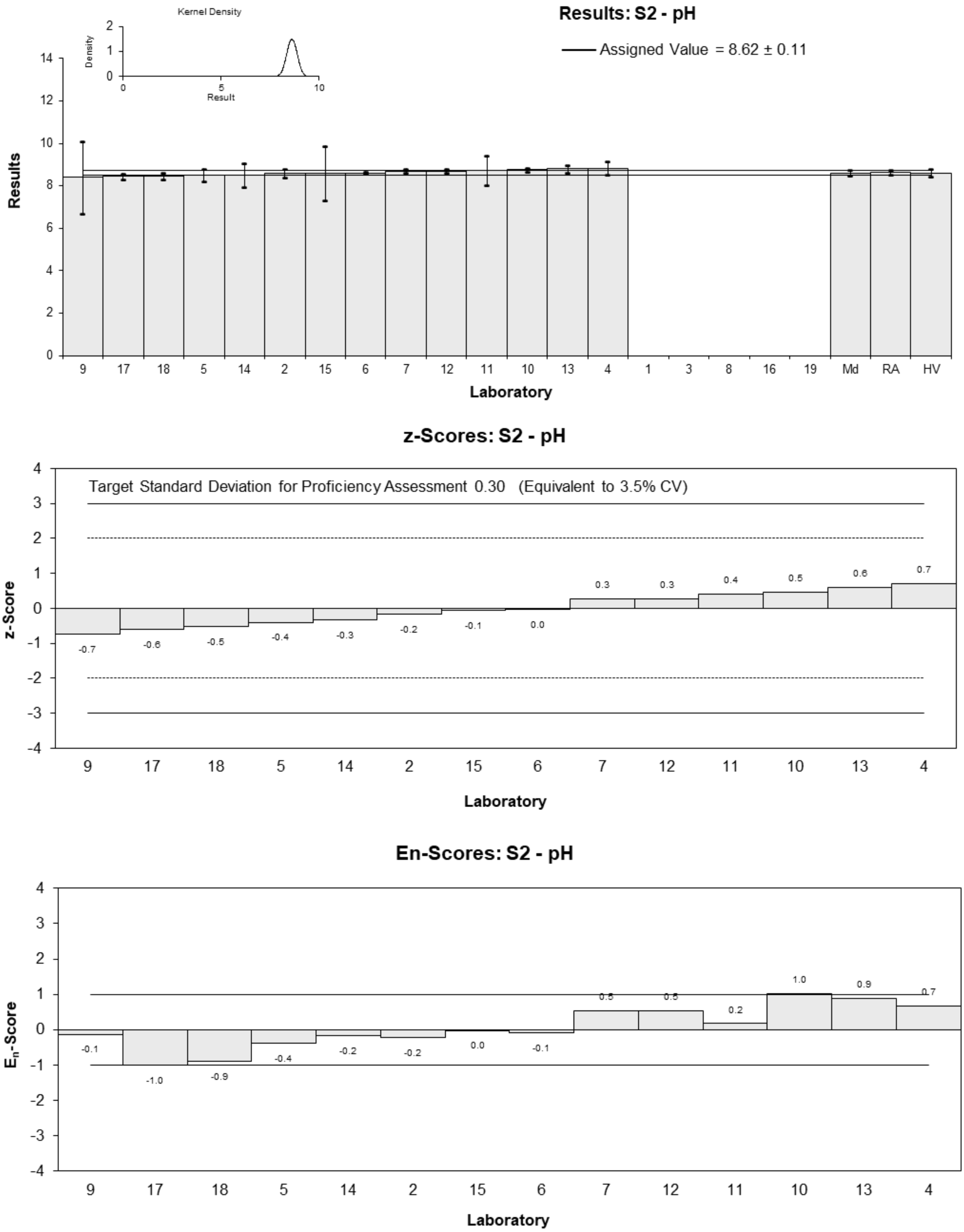

Results: S2 - pH
Assigned Value = 8.62 ± 0.11
Kernel Density
Density
Result
Results
Laboratory
9 17 18 5 14 2 15 6 7 12 11 10 13 4 1 3 8 16 19 Md RA HV
z-Scores: S2 - pH
Target Standard Deviation for Proficiency Assessment 0.30 (Equivalent to 3.5% CV)
z-Score
-0.7 -0.6 -0.5 -0.4 -0.3 -0.2 -0.1 0.0 0.3 0.3 0.4 0.5 0.6 0.7
9 17 18 5 14 2 15 6 7 12 11 10 13 4
Laboratory
En-Scores: S2 - pH
En-Score
-0.1 -1.0 -0.9 -0.4 -0.2 -0.2 0.0 -0.1 0.5 0.5 0.2 1.0 0.9 0.7
9 17 18 5 14 2 15 6 7 12 11 10 13 4
Laboratory

Figure 23

Table 26

Sample Details

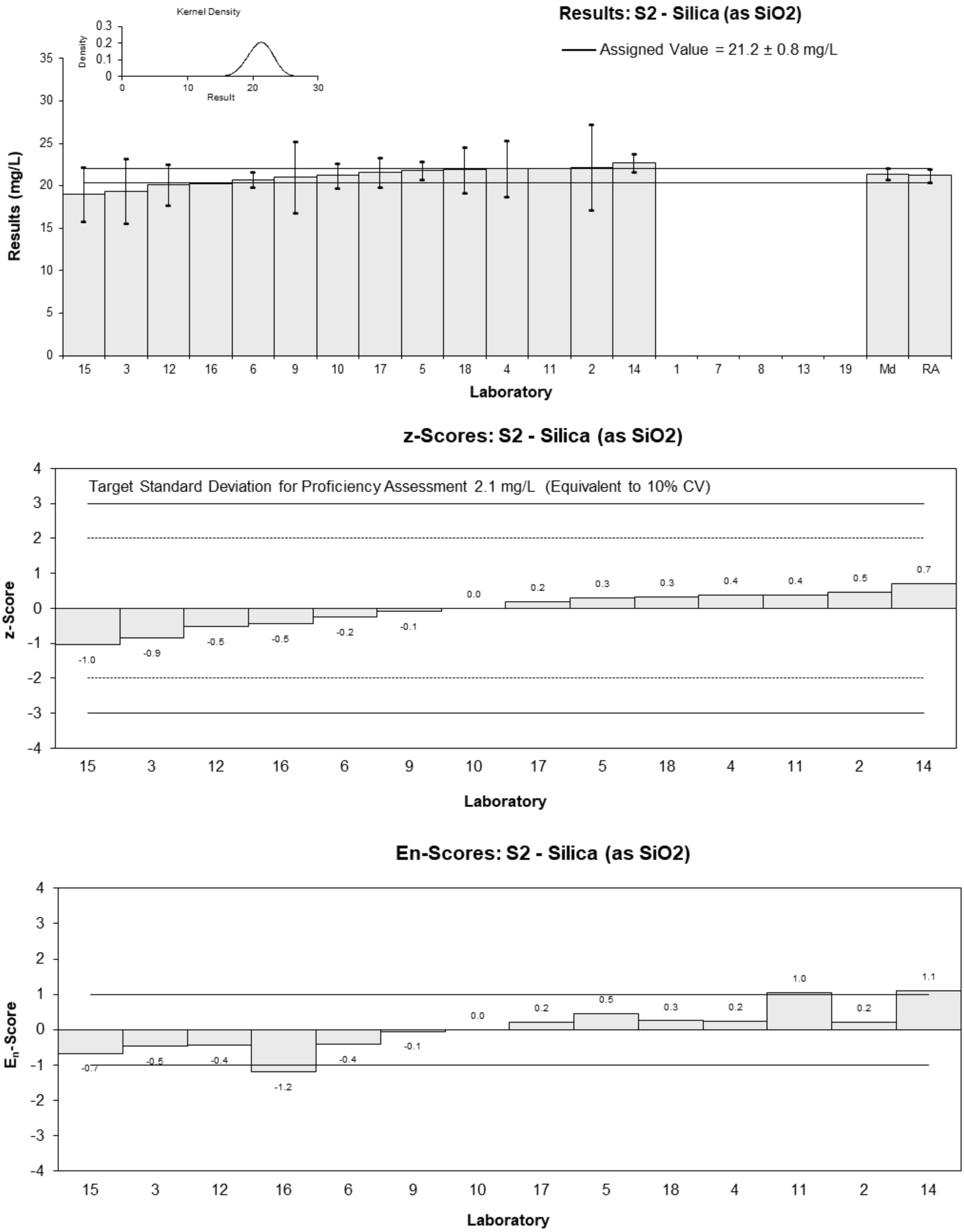
Sample No.	S2
Matrix	Wastewater
Analyte	Silica (as SiO_2)
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	22.2	5.0	0.47	0.20
3	19.4	3.8	-0.85	-0.46
4	22.0	3.30	0.38	0.24
5	21.829	1.091	0.30	0.46
6	20.7	0.9	-0.24	-0.42
7	NT	NT		
8	NT	NT		
9	21	4.2	-0.09	-0.05
10	21.2	1.42	0.00	0.00
11	22.0347	NT	0.39	1.04
12	20.1	2.4	-0.52	-0.43
13	NT	NT		
14	22.7	1.11	0.71	1.10
15	19	3.192	-1.04	-0.67
16	20.24	NR	-0.45	-1.20
17	21.6	1.7	0.19	0.21
18	21.894	2.667	0.33	0.25
19	NT	NT		

Statistics

Assigned Value	21.2	0.8
Robust Average	21.2	0.8
Median	21.4	0.7
Mean	21.1	
N	14	
Max	22.7	
Min	19	
Robust SD	1.2	
Robust CV	5.7%	



Results: S2 - Silica (as SiO2)
Assigned Value = 21.2 ± 0.8 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15 3 12 16 6 9 10 17 5 18 4 11 2 14 1 7 8 13 19 Md RA
z-Scores: S2 - Silica (as SiO2)
Target Standard Deviation for Proficiency Assessment 2.1 mg/L (Equivalent to 10% CV)
z-Score
-1.0 -0.9 -0.5 -0.5 -0.2 -0.1 0.0 0.2 0.3 0.3 0.4 0.4 0.5 0.7
15 3 12 16 6 9 10 17 5 18 4 11 2 14
Laboratory
En-Scores: S2 - Silica (as SiO2)
En-Score
-0.7 -0.5 -0.4 -1.2 -0.4 -0.1 0.0 0.2 0.5 0.3 0.2 1.0 0.2 1.1
15 3 12 16 6 9 10 17 5 18 4 11 2 14
Laboratory

Figure 24

Table 27

Sample Details

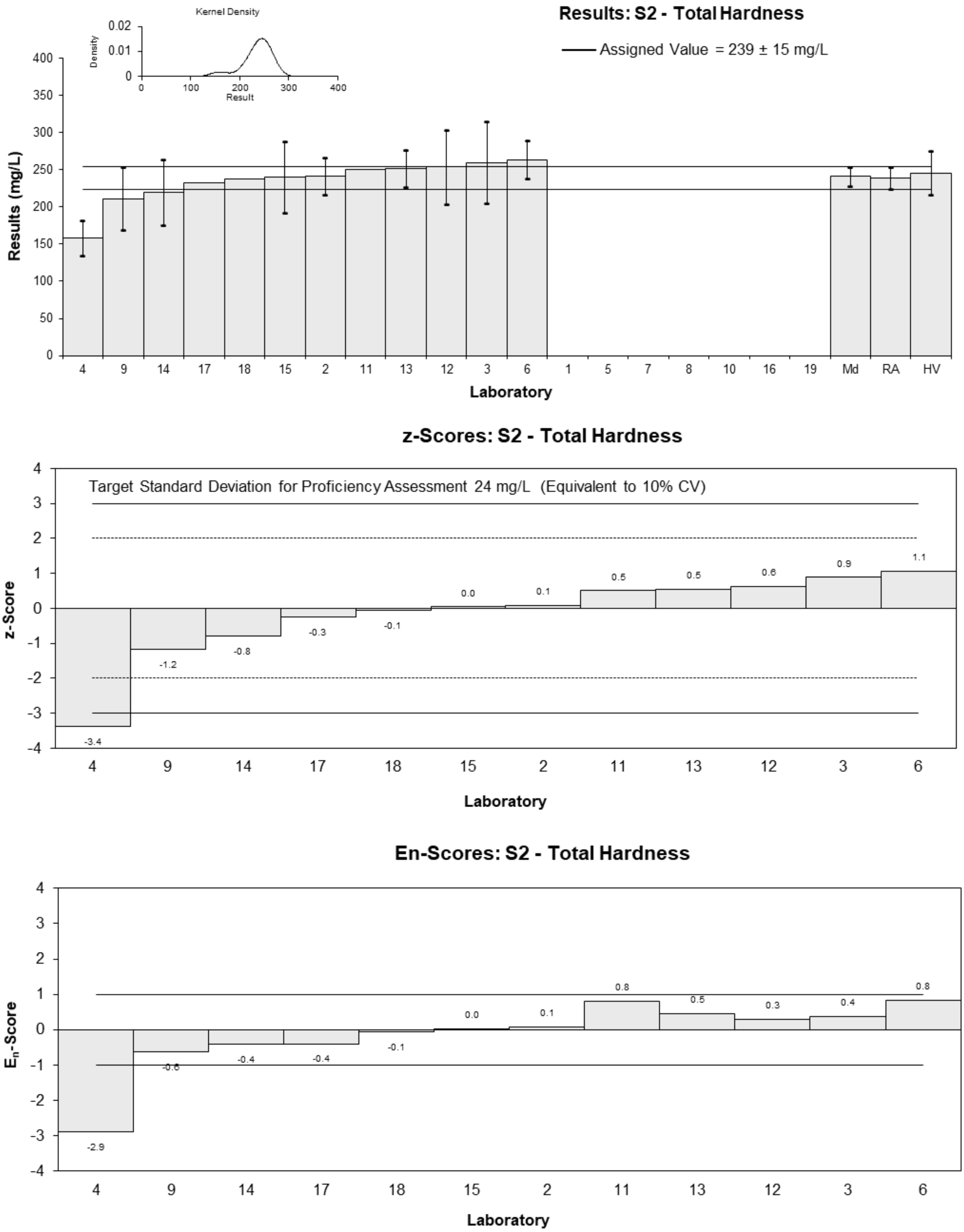
Sample No.	S2
Matrix	Wastewater
Analyte	Total Hardness
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	241	25	0.08	0.07
3	260	55	0.88	0.37
4	158	23.7	-3.39	-2.89
5	NT	NT		
6	264	26	1.05	0.83
7	NT	NT		
8	NT	NT		
9	211	42.2	-1.17	-0.63
10	NT	NT		
11	250.9779	NT	0.50	0.80
12	254	50	0.63	0.29
13	252	25	0.54	0.45
14	220	44	-0.79	-0.41
15	240	48	0.04	0.02
16	NR	NR		
17	233	NR	-0.25	-0.40
18	237.92	NR	-0.05	-0.07
19	NT	NT		

Statistics

Assigned Value	239	15
Homogeneity Value	246	30
Robust Average	239	15
Median	241	13
Mean	235	
N	12	
Max	264	
Min	158	
Robust SD	21	
Robust CV	8.8%	



Results: S2 - Total Hardness
Assigned Value = 239 ± 15 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
z-Scores: S2 - Total Hardness
Target Standard Deviation for Proficiency Assessment 24 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S2 - Total Hardness
E_n-Score
Laboratory

Figure 25

Table 28

Sample Details

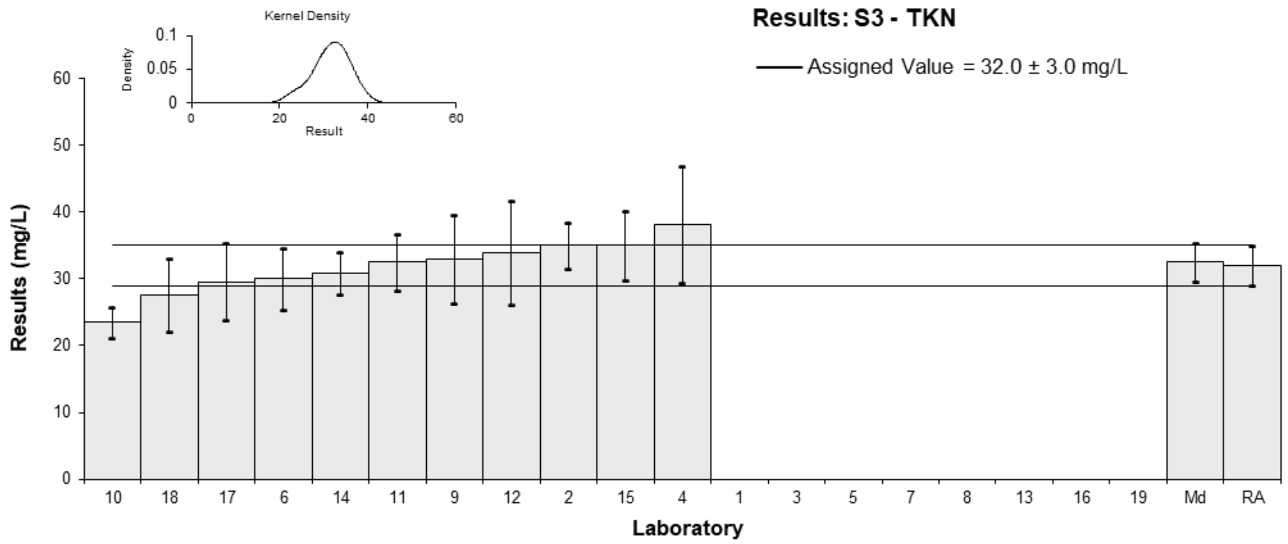
Sample No.	S3
Matrix	Wastewater
Analyte	TKN
Unit	mg/L

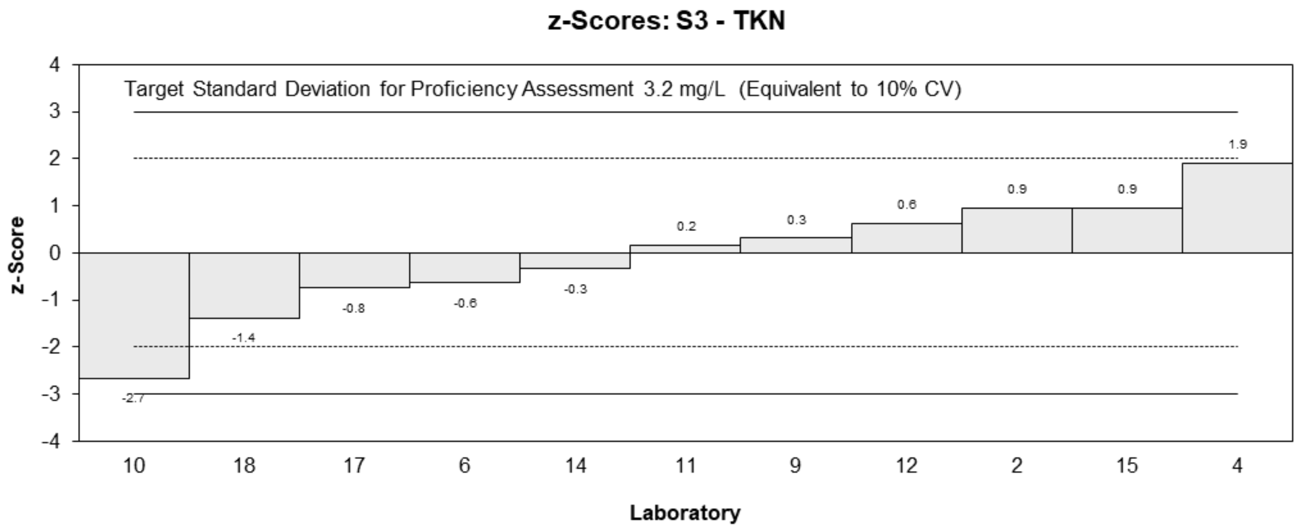
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	35.0	3.5	0.94	0.65
3	NT	NT		
4	38.1	8.76	1.91	0.66
5	NT	NT		
6	30.0	4.6	-0.62	-0.36
7	NT	NT		
8	NT	NT		
9	33	6.6	0.31	0.14
10	23.5	2.33	-2.66	-2.24
11	32.5	4.2	0.16	0.10
12	34	7.8	0.62	0.24
13	NT	NT		
14	30.9	3.2	-0.34	-0.25
15	35	5.25	0.94	0.50
16	NR	NR		
17	29.6	5.8	-0.75	-0.37
18	27.577	5.415	-1.38	-0.71
19	NT	NT		

Statistics

Assigned Value	32.0	3.0
Robust Average	32.0	3.0
Median	32.5	2.8
Mean	31.7	
N	11	
Max	38.1	
Min	23.5	
Robust SD	4	
Robust CV	13%	


Results: S3 - TKN
Assigned Value = 32.0 ± 3.0 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
10 18 17 6 14 11 9 12 2 15 4 1 3 5 7 8 13 16 19 Md RA


z-Scores: S3 - TKN
Target Standard Deviation for Proficiency Assessment 3.2 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
-2.7 -1.4 -0.8 -0.6 -0.3 0.2 0.3 0.6 0.9 0.9 1.9
10 18 17 6 14 11 9 12 2 15 4

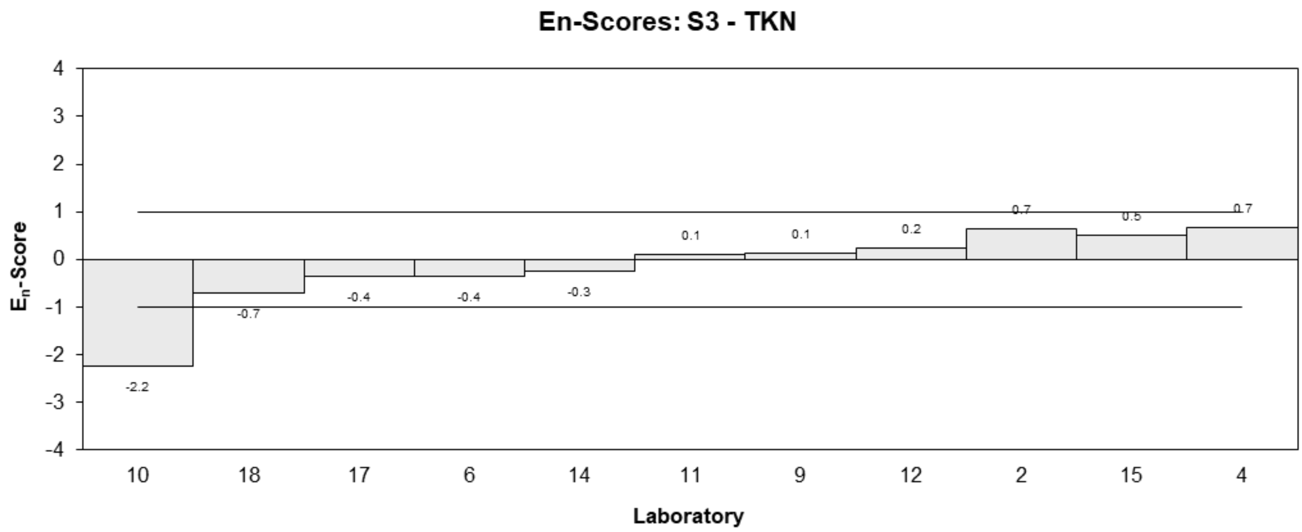

En-Scores: S3 - TKN
En-Score
Laboratory
-2.2 -0.7 -0.4 -0.4 -0.3 0.1 0.1 0.2 0.7 0.5 0.7
10 18 17 6 14 11 9 12 2 15 4

Figure 26

Table 29

Sample Details

Sample No.	S3
Matrix	Wastewater
Analyte	TN
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	35.0	3.5	1.11	0.86
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	30.0	6.6	-0.48	-0.22
7	NT	NT		
8	NT	NT		
9	33	6.6	0.48	0.22
10	23.5	2.33	-2.54	-2.55
11	32.5	4.9	0.32	0.19
12	34	7.8	0.79	0.31
13	31.3	NR	-0.06	-0.10
14	30.9	3.2	-0.19	-0.16
15	35	5.25	1.11	0.62
16	32	0.06	0.16	0.24
17	29.6	NR	-0.60	-0.90
18	27.596	5.419	-1.24	-0.67
19	NT	NT		

Statistics

Assigned Value	31.5	2.1
Homogeneity Value	33.0	4.0
Robust Average	31.5	2.1
Median	31.7	2.0
Mean	31.2	
N	12	
Max	35	
Min	23.5	
Robust SD	3	
Robust CV	9.4%	

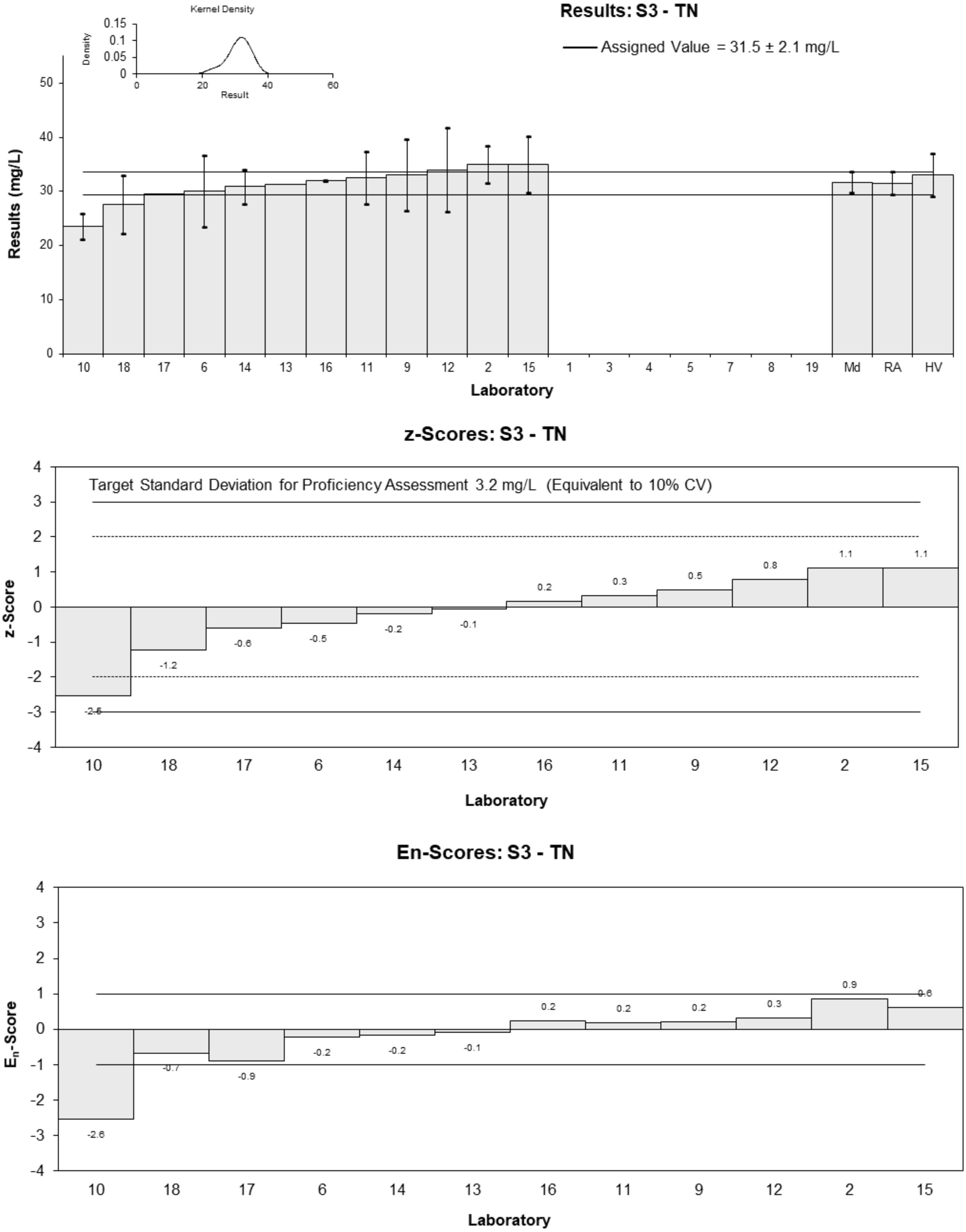

Results: S3 - TN
Assigned Value = 31.5 ± 2.1 mg/L
Kernel Density
Density
0.15
0.1
0.05
0
0
20
40
60
Result
Results (mg/L)
50
40
30
20
10
0
10
18
17
6
14
13
16
11
9
12
2
15
1
3
4
5
7
8
19
Md
RA
HV
Laboratory
z-Scores: S3 - TN
Target Standard Deviation for Proficiency Assessment 3.2 mg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.6
-1.2
-0.6
-0.5
-0.2
-0.1
0.2
0.3
0.5
0.8
1.1
1.1
10
18
17
6
14
13
16
11
9
12
2
15
Laboratory
En-Scores: S3 - TN
E_n-Score
4
3
2
1
0
-1
-2
-3
-4
-2.6
-0.7
-0.9
-0.2
-0.2
-0.1
0.2
0.2
0.2
0.3
0.9
0.6
10
18
17
6
14
13
16
11
9
12
2
15
Laboratory

Figure 27

Table 30

Sample Details

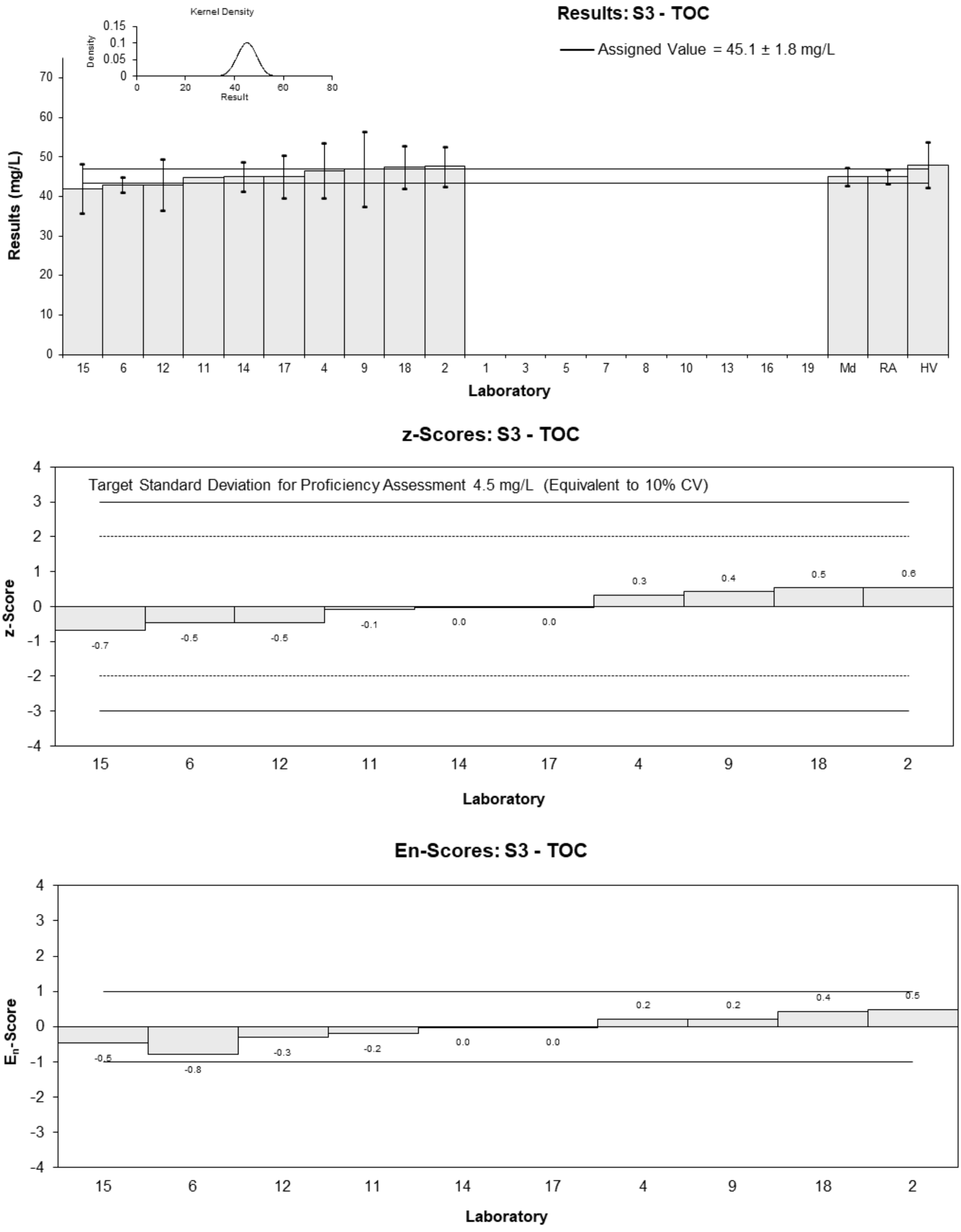
Sample No.	S3
Matrix	Wastewater
Analyte	TOC
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	47.6	5.0	0.55	0.47
3	NT	NT		
4	46.6	6.99	0.33	0.21
5	NT	NT		
6	43	2	-0.47	-0.78
7	NT	NT		
8	NT	NT		
9	47	9.4	0.42	0.20
10	NT	NT		
11	44.75	NR	-0.08	-0.19
12	43	6.5	-0.47	-0.31
13	NT	NT		
14	45	3.7	-0.02	-0.02
15	42	6.3	-0.69	-0.47
16	NR	NR		
17	45	5.4	-0.02	-0.02
18	47.48	5.40	0.53	0.42
19	NT	NT		

Statistics

Assigned Value	45.1	1.8
Homogeneity Value	48.0	5.8
Robust Average	45.1	1.8
Median	45.0	2.3
Mean	45.1	
N	10	
Max	47.6	
Min	42	
Robust SD	2.3	
Robust CV	5%	



Results: S3 - TOC
Assigned Value = 45.1 ± 1.8 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15 6 12 11 14 17 4 9 18 2 1 3 5 7 8 10 13 16 19 Md RA HV
z-Scores: S3 - TOC
Target Standard Deviation for Proficiency Assessment 4.5 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - TOC
En-Score
Laboratory

Figure 28

Table 31

Sample Details

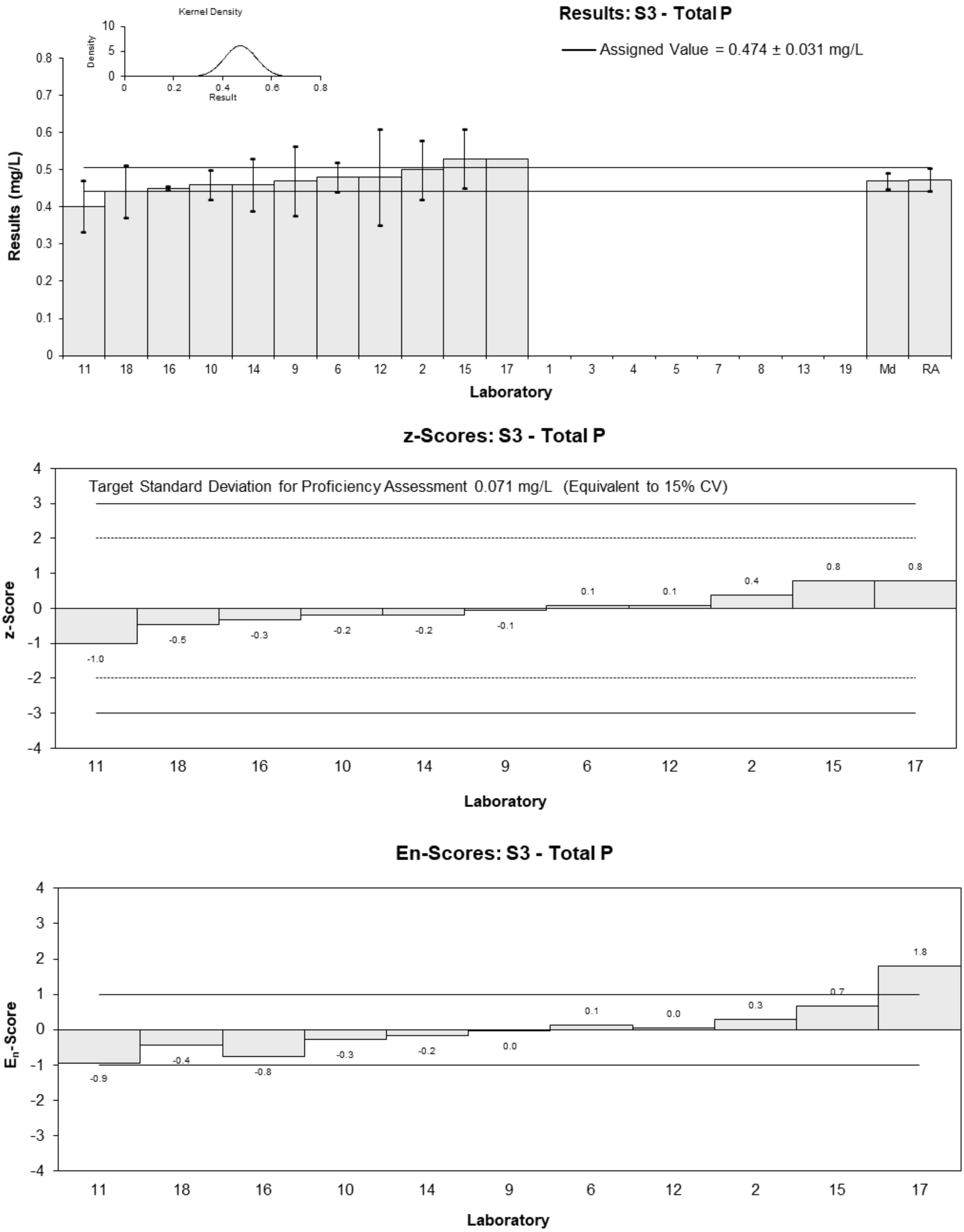
Sample No.	S3
Matrix	Wastewater
Analyte	Total P
Unit	mg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.50	0.08	0.37	0.30
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	0.48	0.04	0.08	0.12
7	NT	NT		
8	NT	NT		
9	0.47	0.094	-0.06	-0.04
10	0.46	0.04	-0.20	-0.28
11	0.402	0.070	-1.01	-0.94
12	0.48	0.13	0.08	0.04
13	<1.5	NR		
14	0.46	0.07	-0.20	-0.18
15	.530	0.0795	0.79	0.66
16	0.45	0.005	-0.34	-0.76
17	0.53	NR	0.79	1.81
18	0.4413	0.0702	-0.46	-0.43
19	NT	NT		

Statistics

Assigned Value	0.474	0.031
Robust Average	0.474	0.031
Median	0.470	0.022
Mean	0.473	
N	11	
Max	0.53	
Min	0.402	
Robust SD	0.04	
Robust CV	8.5%	



Results: S3 - Total P
Assigned Value = 0.474 ± 0.031 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
11 18 16 10 14 9 6 12 2 15 17 1 3 4 5 7 8 13 19 Md RA
z-Scores: S3 - Total P
Target Standard Deviation for Proficiency Assessment 0.071 mg/L (Equivalent to 15% CV)
z-Score
-1.0 -0.5 -0.3 -0.2 -0.2 -0.1 0.1 0.1 0.4 0.8 0.8
11 18 16 10 14 9 6 12 2 15 17
Laboratory
En-Scores: S3 - Total P
E_n-Score
-0.9 -0.4 -0.8 -0.3 -0.2 0.0 0.1 0.0 0.3 0.7 1.8
11 18 16 10 14 9 6 12 2 15 17
Laboratory

Figure 29

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Assigned Values were the robust average of participants' results. The robust averages and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons'. 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 for the robust average of Ammonia-N in Sample S1 and its associated uncertainty.

No assigned value was set for bromide in S1 and colour in S2 because the results were either too few or too variable. However, participants may still compare their reported results for these analytes with other participants' results and/or the homogeneity value. Descriptive statistics for these elements are presented in Chapter 5. No descriptive statistics were presented for sulphide in S1 due to only one result (0.028 mg/L) being reported.

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

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 356 numerical results, 338 (95%) were reported with an expanded measurement uncertainty, indicating that laboratories have addressed this requirement of ISO 17025.[8] The magnitude of these expanded uncertainties was within the range 0.013% to 180% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 2.

Approaches to estimating measurement uncertainty include standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[8 – 13]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded uncertainties are presented in the bar charts for each analyte (Figure 2 to 30). 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, 16 laboratories reported results for ammonia in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 16 laboratories' results is 1.7 mg/L (see equation 4, Appendix 2). If Laboratory 1 result is coming from one measurement, then they might have under-estimated their expanded measurement uncertainties reported for ammonia in S1 (0.28 mg/L) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 16 measurements. Alternatively, estimates of uncertainties for Na in S2 larger than 52 mg/L (the uncertainty of the assigned value, 8 mg/L plus the allowable variation from the assigned value, the target standard deviation of 22 mg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainty reported by laboratory 11 for Na in S2 (92 mg/L) might have been over-estimated.

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[9] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Laboratory 13 reported an estimate of expanded uncertainty for fluoride in S1 larger than the result itself.

Laboratories 8, 12 and 13 attached estimates of the expanded measurement uncertainty to results reported as being less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 2990 ± 228 mg/L, it is better to report 2990 ± 230 mg/L or instead of 4.60 ± 0.5 mg/L, it is better to report 4.6 ± 0.5 mg/L.[8]

6.3 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% to 15% PCV were used to calculate z-scores. A set target standard deviation enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 33.

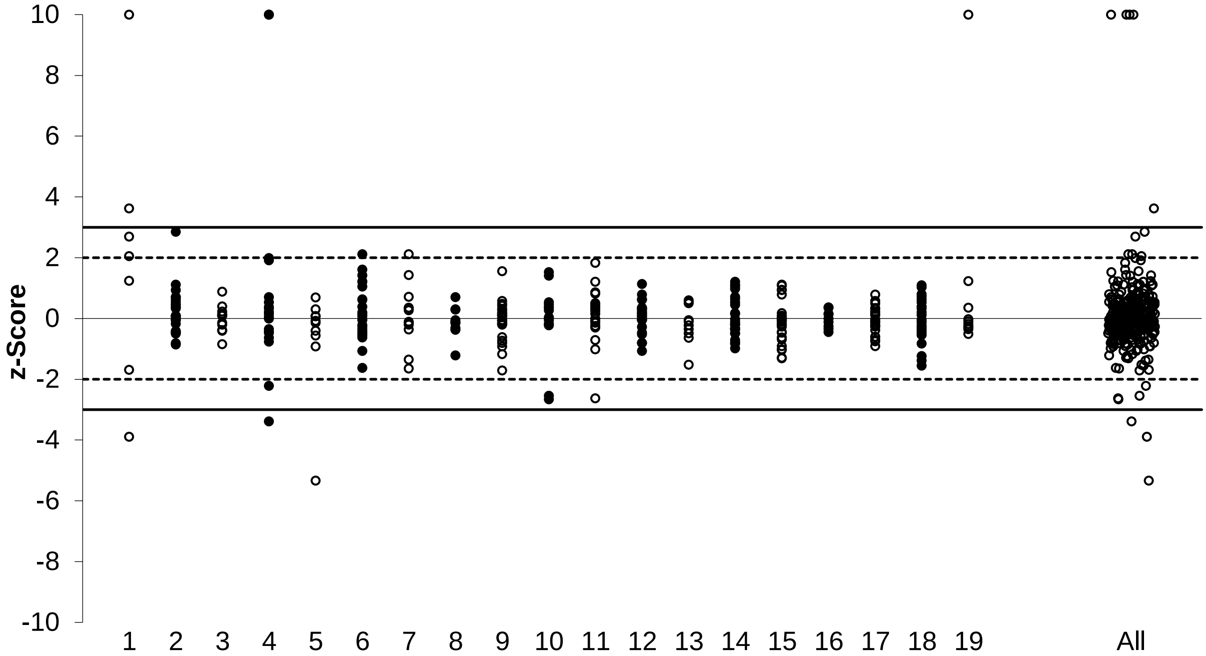
The dispersal of participants' z-scores is presented in Figure 30 (by laboratory code) and in Figure 32 (by analyte). Of 338 results for which z-scores were calculated, 321 (95%) returned a satisfactory score of $|z| \leq 2.0$ and 9 (3%) were questionable of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias (Figure 30).

Laboratory 6 reported results for all 26 tests for which a z-score was calculated and returned satisfactory z-scores for 25 of them.

Laboratories 9, 15, 18, 14 and 17 reported results for 25 tests each and retuned satisfactory z-scores for all of them.

All results reported by **laboratories 12** (23), **3** (11), **8** (11), **13** (11), and **16** (9) also returned satisfactory z scores.

A summary of participants' performance is presented in Figure 33**.**



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

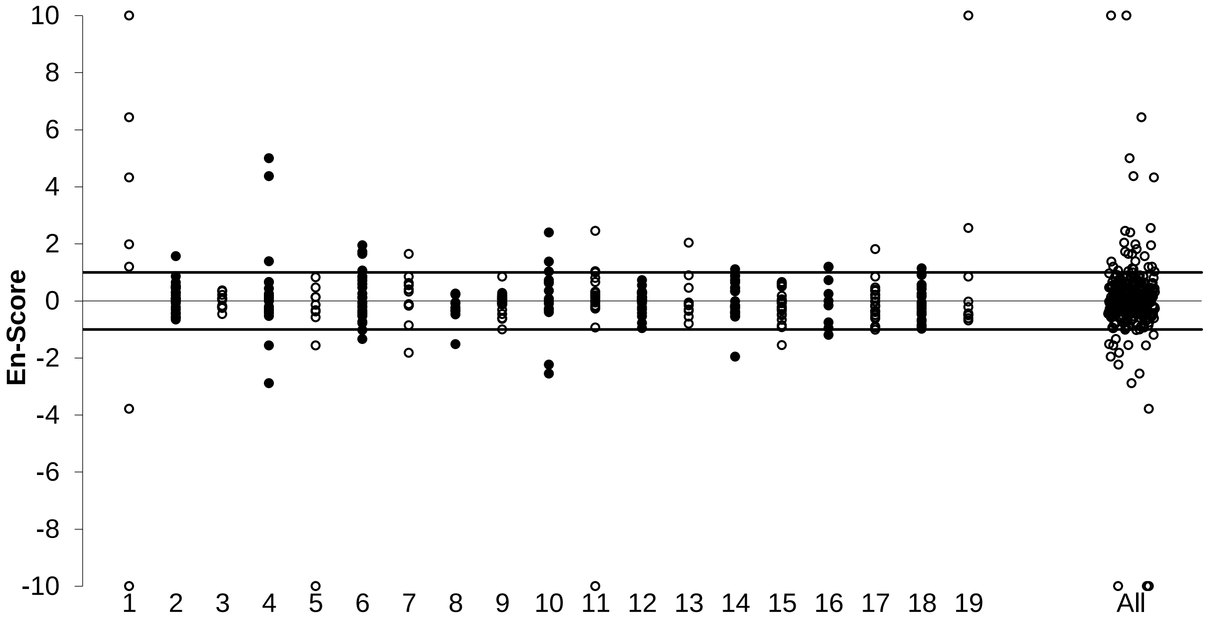
Figure 30 z-Score Dispersal by Laboratory

6.4 E_n-score

E_n-score can be interpreted in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value considering the respective uncertainties. An 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 31. 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 338 results for which E_n-scores were calculated, 294 (87%) 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 31 E_n-Score Dispersal by Laboratory

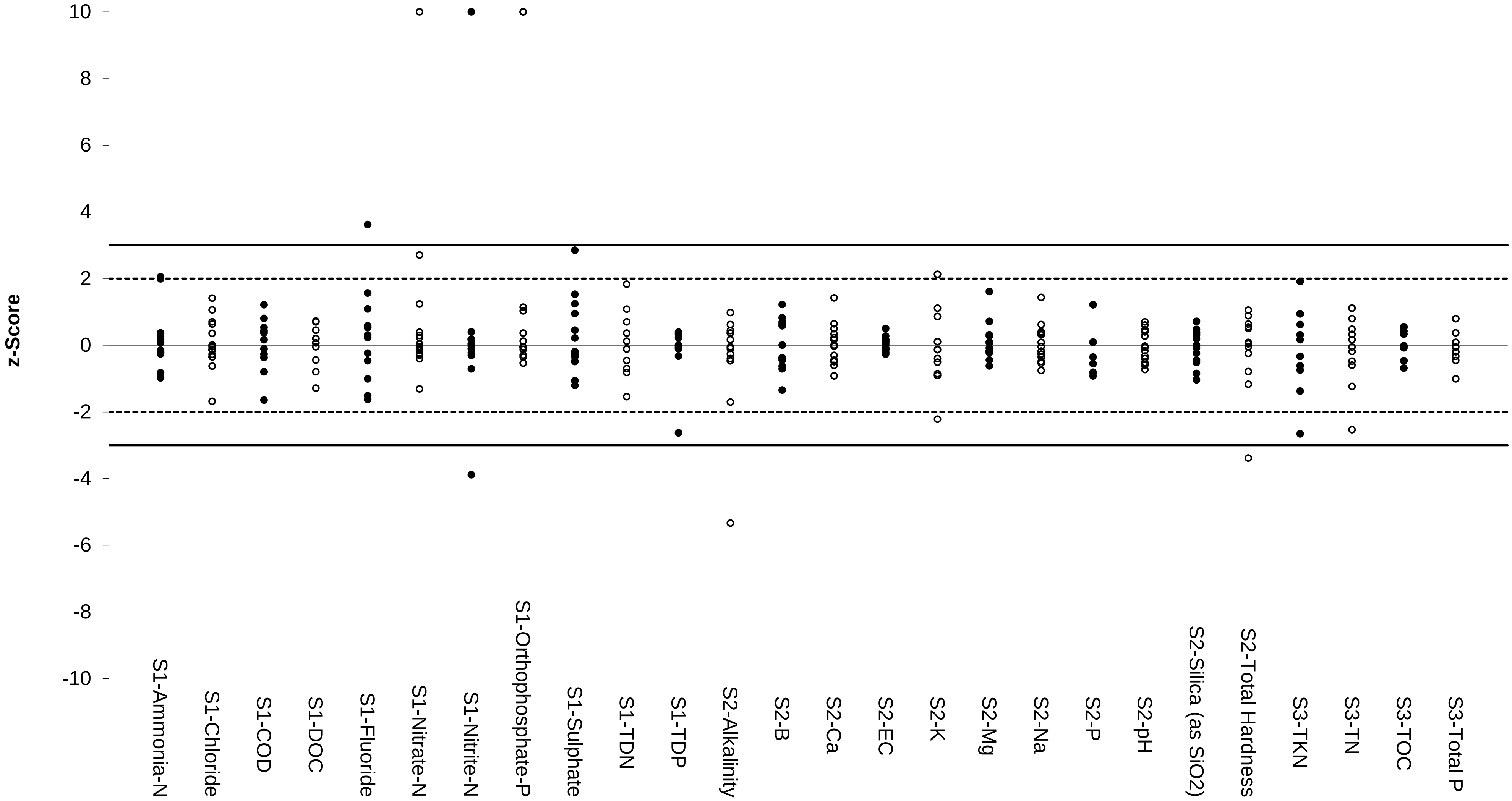
Laboratory 9 had the highest number of satisfactory E_n-scores (25 out of 25 reported).

All results reported by **Laboratories 12** (23), and **3** (11) also returned satisfactory E_n-scores.

Table 32 Between Laboratory 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	36.1	7.5%	9.3%	15%
S1	Bromide	Not Set	12%	NA	Not Set
S1	COD	125	12%	7.7%	15%
S1	Chloride	142	6.3%	7.6%	10%
S1	DOC	40.2	6.7%	9.2%	10%
S1	Fluoride	0.648	17%	17%	15%
S1	Nitrate-N	0.996	6.2%	16%	15%
S1	Nitrite-N	0.487	3.7%	18%	15%
S1	Orthophosphate-P	1.11	6.3%	16%	15%
S1	Sulphate	34.7	9.6%	9.4%	10%
S1	Sulphide	Not Set	NA	NA	Not Set
S1	TDN	41.5	9.9%	9.1%	10%
S1	TDP	1.20	4.6%	16%	15%
S2	B	0.624	8.6%	17%	10%
S2	Ca	63.9	5.6%	8.6%	10%
S2	K	19.8	12%	10%	10%
S2	Mg	22.4	4.1%	10%	10%
S2	Na	224	5.2%	7.1%	10%
S2	P	0.892	9.5%	16%	10%
S2	Alkalinity	193	5.6%	7.2%	10%
S2	Colour	Not Set	93%	NA	Not Set
S2	EC	1820 µS/cm	2.1%	5.2%	10%
S2	pH	8.62	1.9%	12%	3.5%
S2	Silica (as SiO2)	21.2	5.7%	10%	10%
S2	Total Hardness	239	8.8%	75	10%
S3	TKN	32.0	13%	9.5%	10%
S3	TN	31.5	9.4%	9.5%	10%
S3	TOC	45.1	5%	9%	10%
S3	Total P	0.474	8.5%	18%	15%

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



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

Figure 32 z-Score Dispersal by Analyte

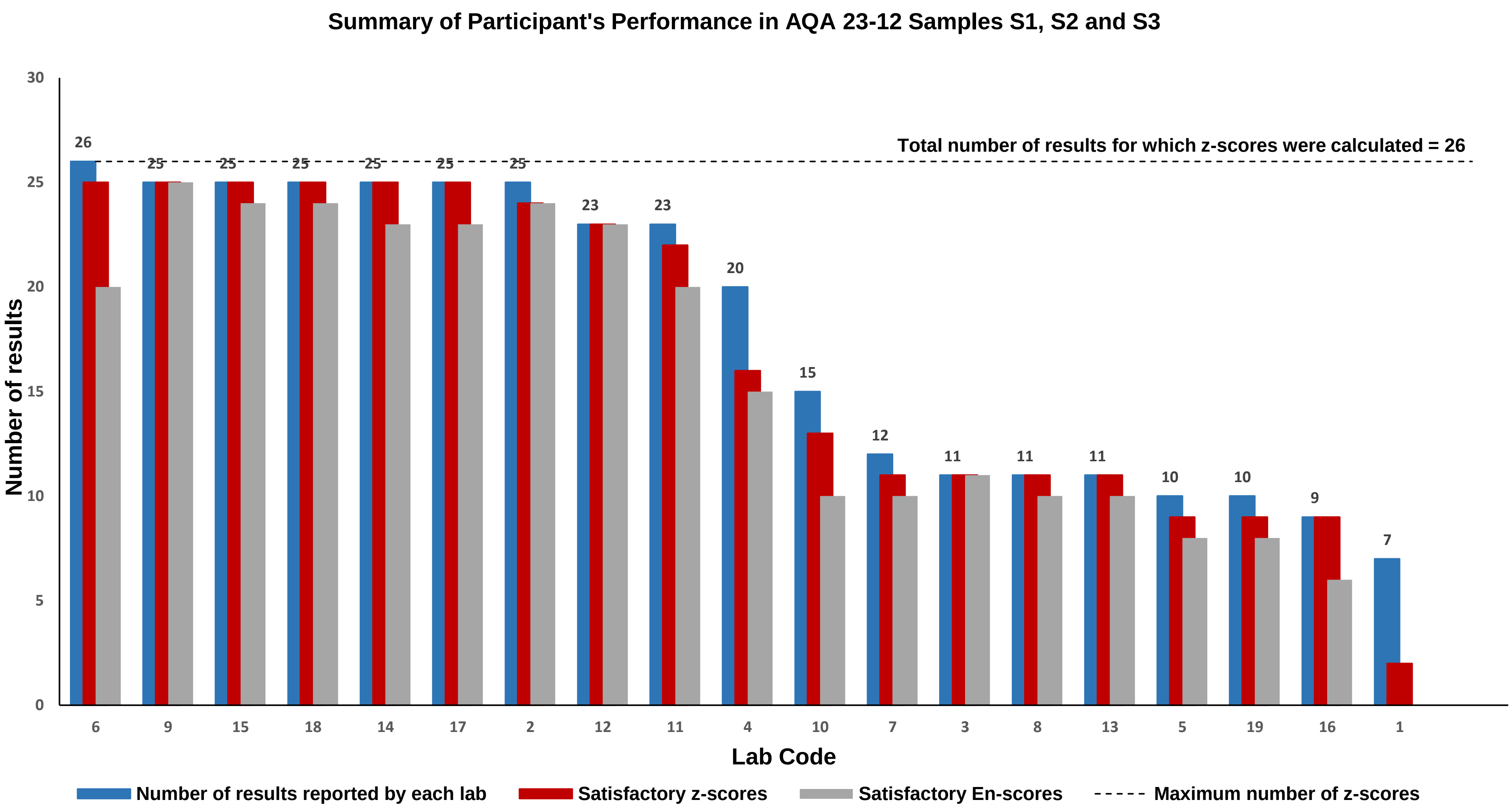


Figure 33 Summary of Participants' Performance

Table 33 Summary of Participants' Results and Performance for Sample S1

Lab Code	S1-Ammonia-N (mg/L)	S1-Bromide (mg/L)	S1-COD (mg/L)	S1-Chloride (mg/L)	S1-DOC (mg/L)	S1-Fluoride (mg/L)	S1-Nitrate-N (mg/L)	S1-Nitrite-N (mg/L)	S1-Orthophosphate-P (mg/L)	S1-Sulphate (mg/L)	S1-Sulphide (mg/L)	S1-TDN (mg/L)	S1-TDP (mg/L)
AV	36.1	Not Set	125	142	40.2	0.648	0.996	0.487	1.11	34.7	Not Set	41.5	1.20
HV	37.7	NA	110	140	43.0	NA	0.96	0.487	NA	30.0	NA	41.0	NA
1	47.18	NR	NR	118	NR	1.00	1.4	0.203	4.04	39	NR	NR	NR
2	36.5	<1	133	152	40.5	NT	0.934	0.485	1.10	44.6	NT	44.4	1.26
3	NR	0.15	NR	140	NR	0.67	NR	NR	NR	34.0	NR	NR	NR
4	46.9	NT	135	133	38.4	0.602	4.00	1.45	NT	33.5	<0.1	NT	NT
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	34.7	0.180	128	151	41	0.490	0.99	0.47	1.02	31	0.028	39.6	1.27
7	NT	NT	94	140	NT	NT	NT	NT	NT	34	NT	NT	NT
8	35.3	NT	118	137.1	43	0.677	1.04	0.464	1.089	30.5	<0.05	41.0	1.19
9	37	0.2	110	140	41	0.8	0.97	0.49	1.1	34	NR	42	NR
10	34.9	NT	132	162	NT	0.7	0.97	0.49	1.10	40	NT	NT	NT
11	37.5	NT	147.6	NT	NT	0.6249	1.055	0.435	1.06	36.2532	NT	49.1	0.726
12	38	<0.3	110	138	37	<0.15	1.0	0.5	1.3	31.0	<0.02	43	1.24
13	34.9	<0.2	NT	137	NT	0.5	0.985	NT	NT	33	NT	NT	NT
14	30.8	NR	NR	157	42	0.7	0.98	0.50	1.05	33	<0.1	38.1	1.14
15	35	0.19	120	142	35	0.55	0.8	0.5	1.1	38	<0.1	46	1.2
16	38.1	NR	NR	NR	NR	NR	0.957	0.497	1.170	NR	NR	41	1.2
17	36.7	0.182	123	147	40	0.704	1.03	0.480	1.13	33.9	<0.1	38.6	1.18
18	31.617	NT	140	141.36	43.08	0.754	0.95	0.5159	1.281	35.428	<0.1	35.07	1.185
19	34.7	NT	NT	137	NT	NT	1.18	0.48	3.36	33.7	NT	NT	NT

Shaded cells are results which returned a questionable or unsatisfactory z-score. AV = Assigned Value, HV = Homogeneity Value, NA = Not Available

Table 34 Summary of Participants' Results and Performance for Samples S2 and S3

Lab Code	S2-B (mg/L)	S2-Ca (mg/L)	S2-K (mg/L)	S2-Mg (mg/L)	S2-Na (mg/L)	S2-P (mg/L)	S2-Alkalinity (mg/L)	S2-Colour (Pt-Co units)
AV	0.624	63.9	19.8	22.4	224	0.892	193	Not Set
HV	0.631	66.3	19.8	22.8	215	0.86	180	NA
1	NT	NT	NT	NT	NT	NT	NT	NT
2	0.596	60.7	18.1	22.6	238	0.82	184	188
3	0.60	64.9	19.0	22.6	233	0.90	NR	NR
4	0.624	65.3	15.4	21.4	207	NT	196	50
5	0.667	58.029	19.532	22.562	225.776	0.842	90	NT
6	0.7	73	24	26	216	1	205	45
7	0.54	66	24	24	256	0.86	200	240
8	NT	NT	NT	NT	NT	NT	NT	NT
9	0.66	60	20	23	220	0.81	160	71
10	NT	NT	NT	NT	NT	NT	200	70
11	0.675	63.9	21.5	22.2	218	NT	201.3	453
12	NT	63.7	20.0	23.1	223	NT	192	226
13	0.585	NT	NT	NT	NT	NT	191	NT
14	0.58	68	22	22	213	1	212	40
15	NR	61	18	21	220	0.9	184	45
16	NR	NR	NR	NR	NR	NR	NR	NR
17	0.6	67	18	22	231	<1	188	45
18	0.663	61.916	19.537	21.880	211.8	<1	185.26	40
19	NT	63.8	18.8	22.0	232	NT	NT	NT

Shaded cells are results which returned a questionable or unsatisfactory z-score. AV = Assigned Value, HV = Homogeneity Value, NA = Not Available

Table 36 Summary of Participants' Results and Performance for Samples S2 and S3

Lab Code	S2-EC (µS/cm)	S2-pH	S2-Silica (mg/L)	S2-Total Hardness (mg/L)	S3-TKN (mg/L)	S3-TN (mg/L)	S3-TOC (mg/L)	S3-Total P (mg/L)
AV	1820	8.62	21.2	239	32.0	31.5	45.1	0.474
HV	NA	8.60	NA	246	NA	33.0	48.0	NA
1	NT	NT	NT	NT	NT	NT	NT	NT
2	1820	8.57	22.2	241	35.0	35.0	47.6	0.50
3	NR	NR	19.4	260	NT	NT	NT	NT
4	1830	8.83	22.0	158	38.1	NT	46.6	NT
5	1806	8.5	21.829	NT	NT	NT	NT	NT
6	1780	8.61	20.7	264	30.0	30.0	43	0.48
7	1800	8.7	NT	NT	NT	NT	NT	NT
8	NT	NT	NT	NT	NT	NT	NT	NT
9	1840	8.4	21	211	33	33	47	0.47
10	1870	8.76	21.2	NT	23.5	23.5	NT	0.46
11	1795.30	8.74	22.0347	250.9779	32.5	32.5	44.75	0.402
12	1850	8.7	20.1	254	34	34	43	0.48
13	1911	8.8	NT	252	NT	31.3	NT	<1.5
14	1850	8.52	22.7	220	30.9	30.9	45	0.46
15	1800	8.6	19	240	35	35	42	.530
16	NR	NR	20.24	NR	NR	32	NR	0.45
17	1770	8.44	21.6	233	29.6	29.6	45	0.53
18	1840	8.46	21.894	237.92	27.577	27.596	47.48	0.4413
19	NT	NT	NT	NT	NT	NT	NT	NT

Shaded cells are results which returned a questionable or unsatisfactory z-score. AV = Assigned Value, HV = Homogeneity Value, NA = Not Available

6.5 Participants' Results and Analytical Methods

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

Colour in S2 were the test that most most challenged participants' analytical techniques.

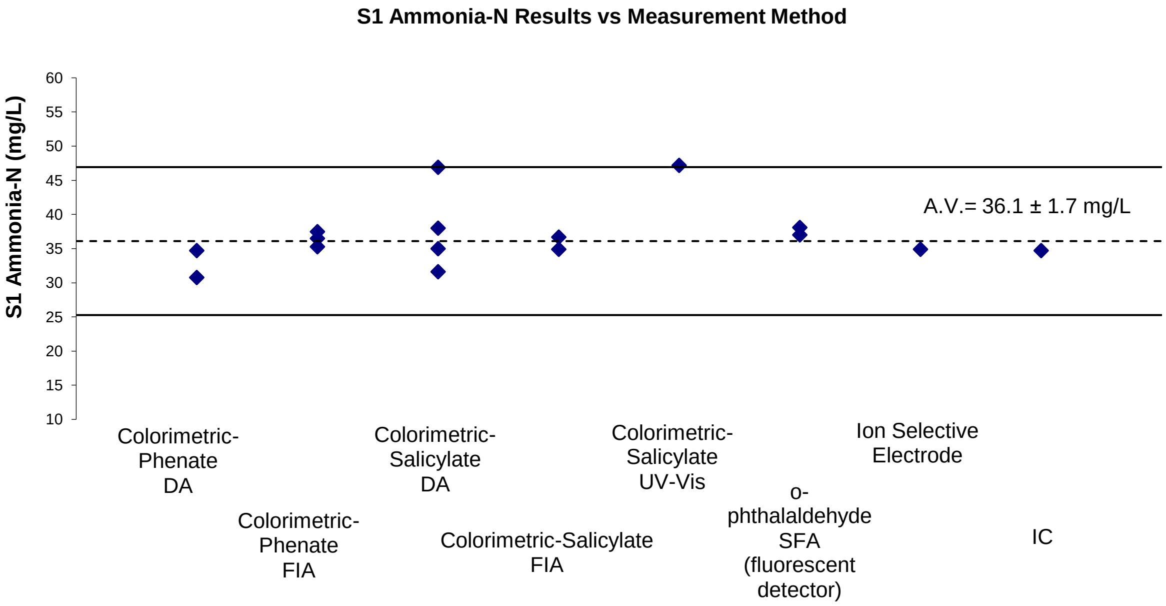
Individual Test Commentary

Alkalinity to pH 4.5 as ($CaCO_3$) Participants used auto-titration or manual titration to measure alkalinity in S2, and all but one performed satisfactorily. Electrodes close to the end of life, changes in titrant strength (due to variations in temperature or contamination), or contamination of solvents are typical causes of titration errors.

Ammonia-Nitrogen level in the wastewater sample was 36.1 mg/L. Participants used a wide variety of analytical techniques and all the results produced but one were compatible with each other and with the assigned value (Figure 34).

Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination.

Ammonia results in the wastewater sample S1 from *o*-phthalaldehyde method with SFA were in excellent agreement with each other and with the assigned value.



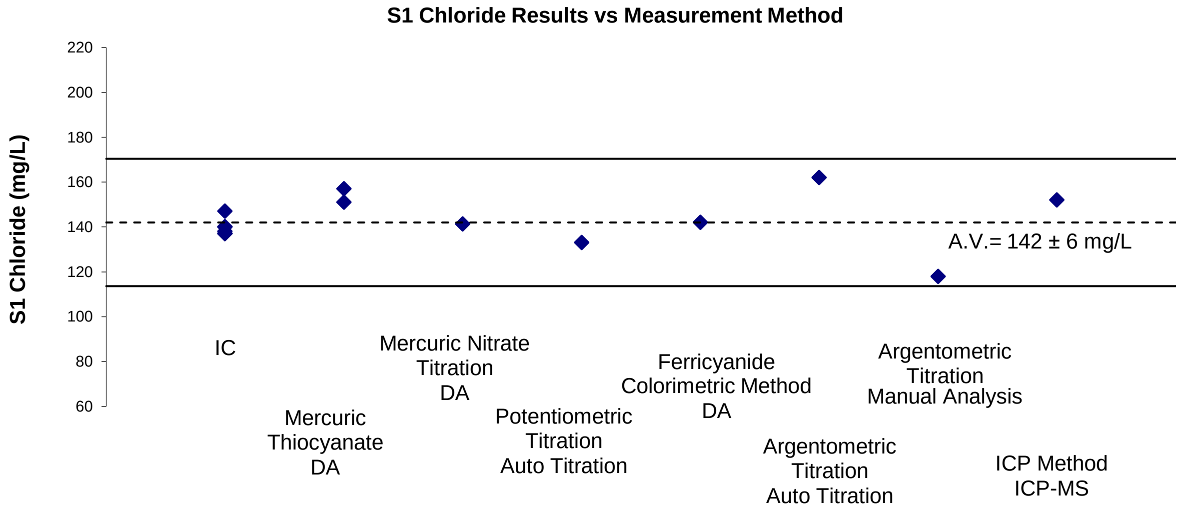
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 34 S1-NH_3-N Results vs. Measurement Method

Bromide One laboratory used ICP-MS for bromide measurement, while all the others used the Ion Chromatographic. All performed satisfactorily.

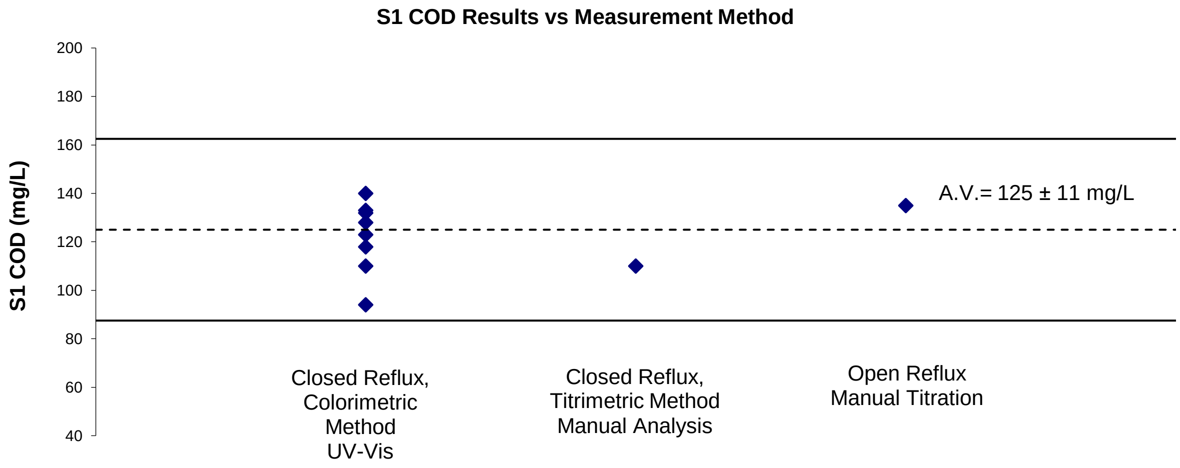
Chloride level in S1 was 142 mg/L Participants used a wide variety of methods; these are presented in Figure 35 versus participants' results.

Chemical Oxygen Demand Plots of participants results versus the measurement method used are presented in Figure 36. All reported results returned satisfactory z-scores.



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

Figure 35 S1-Chloride Results vs. Measurement Method



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

Figure 36 S1-COD Results vs. Measurement Method

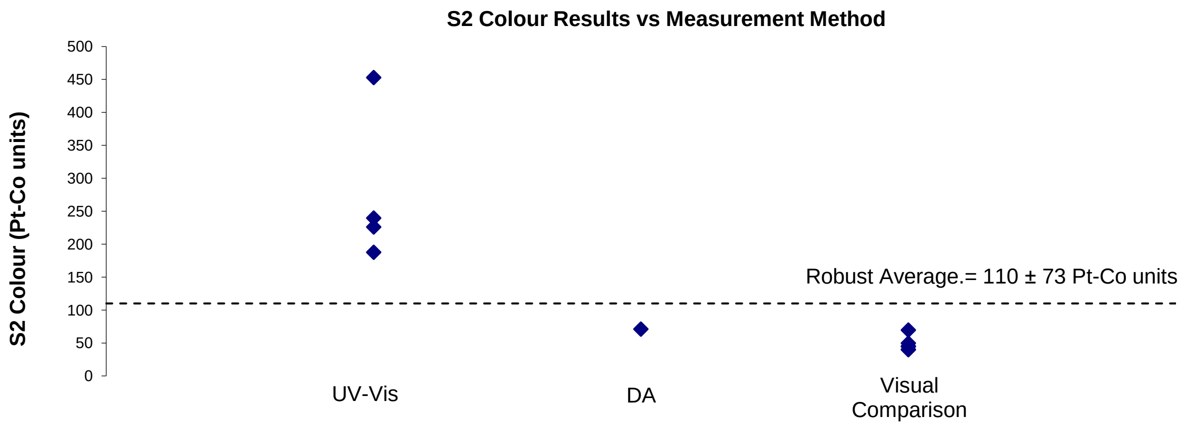
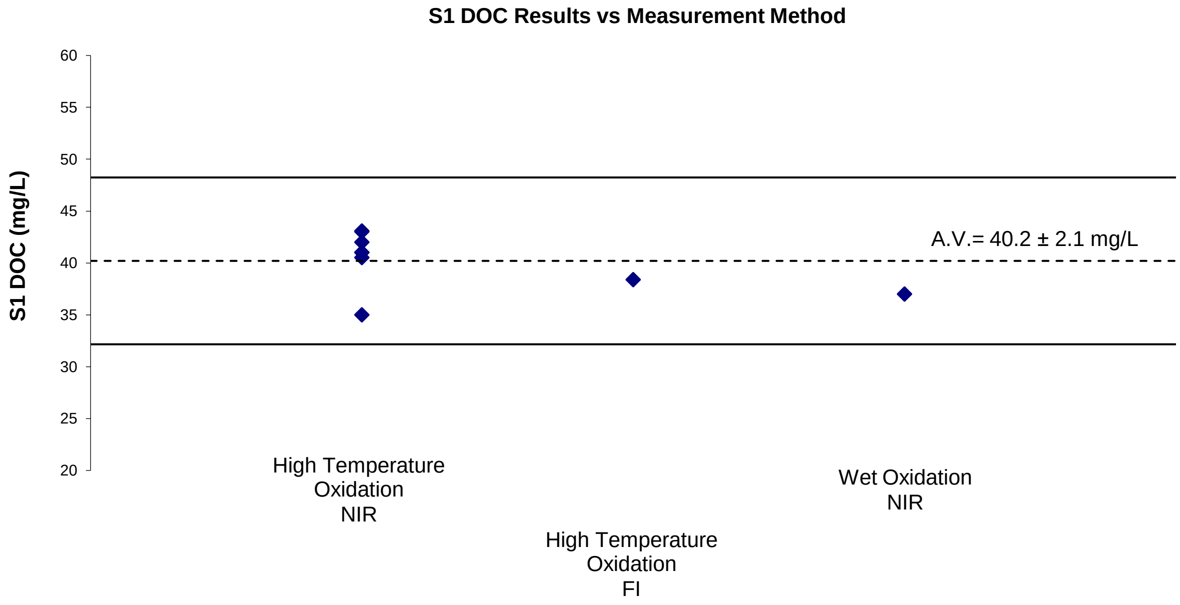


Figure 37 S2-Colour Results vs. Measurement Method

Colour measurements challenged participants' analytical methods; the reported results were not compatible with each other. For colour measurements laboratories primarily used the Spectrophotometric method or Visual Comparison method (Figure 37).

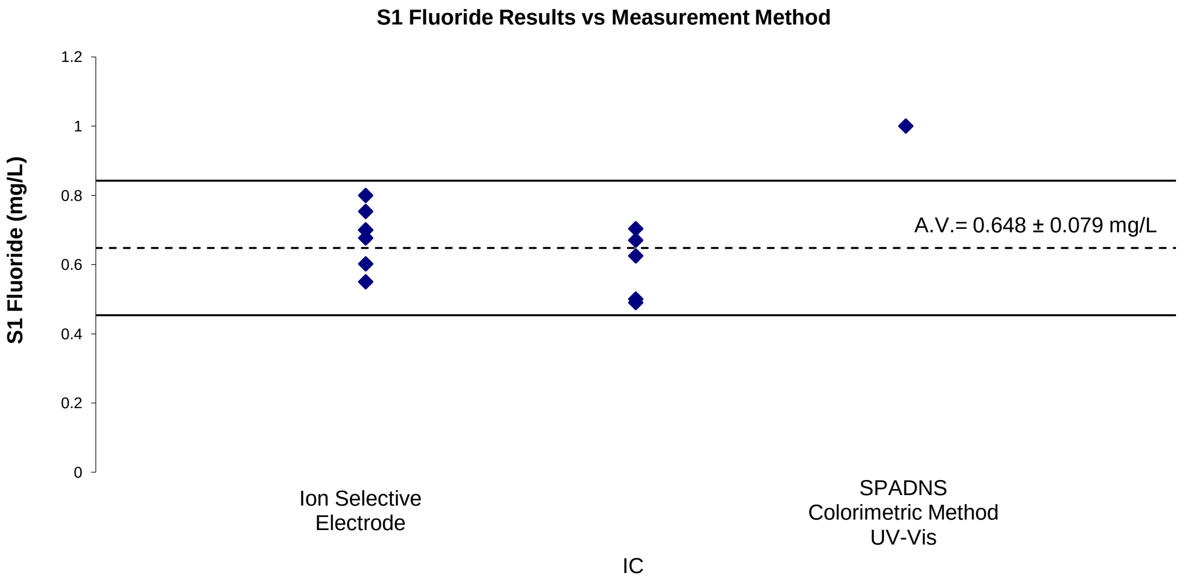
Dissolved Organic Carbon as dNPOC The measurements of DOC in the water Sample S1 did not challenge participants' analytical techniques (Figure 38).



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

Figure 38 S1-DOC Results vs. Measurement Method

Fluoride Of 13 results reported for fluoride in the wastewater sample S1, 12 returned satisfactory z-scores (Figure 39). Caution should be exercised when fluoride is measured by the colorimetric method as it suffers from interference from chlorides. [14]

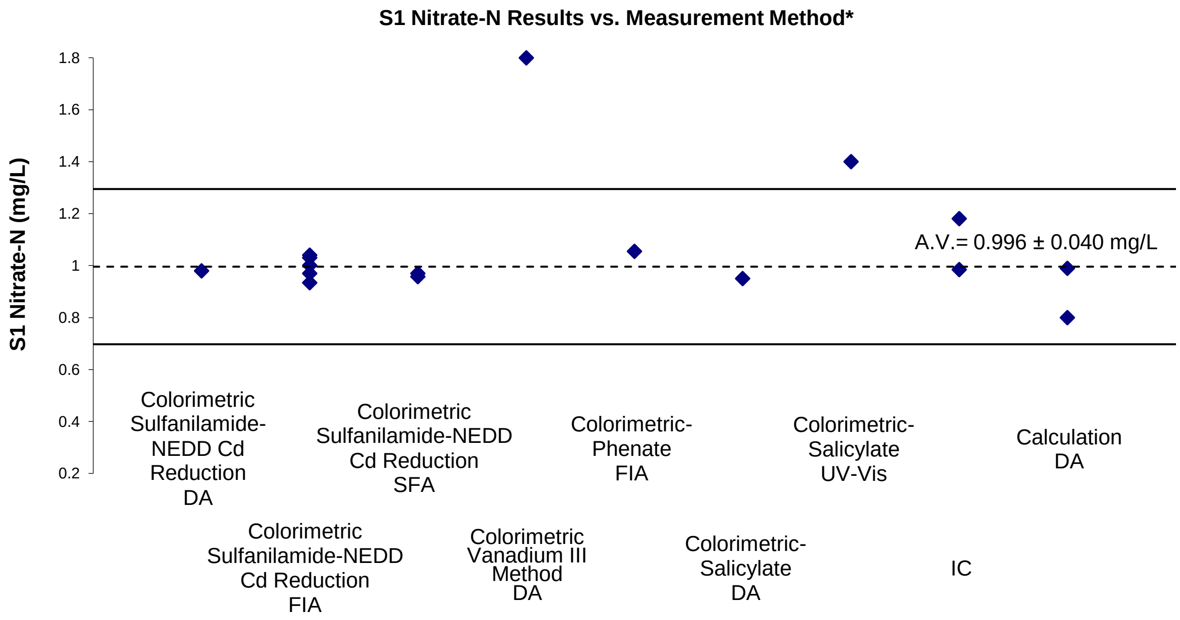


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 39 S1-Fluoride Results vs. Measurement Method

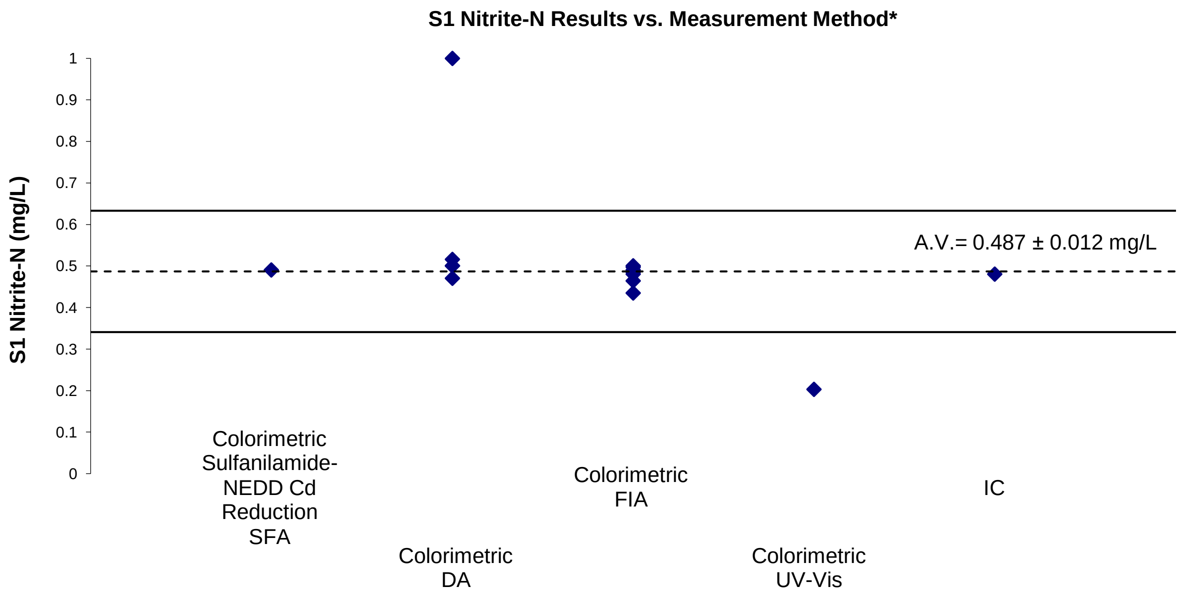
Nitrate-Nitrogen and **Nitrite-Nitrogen** Most laboratories used the colorimetric-sulfanilamide-NEDD Cd reduction method with FIA (Figures 40 and 41).

The reported results were in excellent agreement with each other, with a between-laboratory CV of 6.2% for NO_3-N and 3.7% for NO_2-N.



*Laboratory 4 results of 4 mg/L has been plotted as 1.8 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 40 S1-Nitrate-N vs. Measurement Method



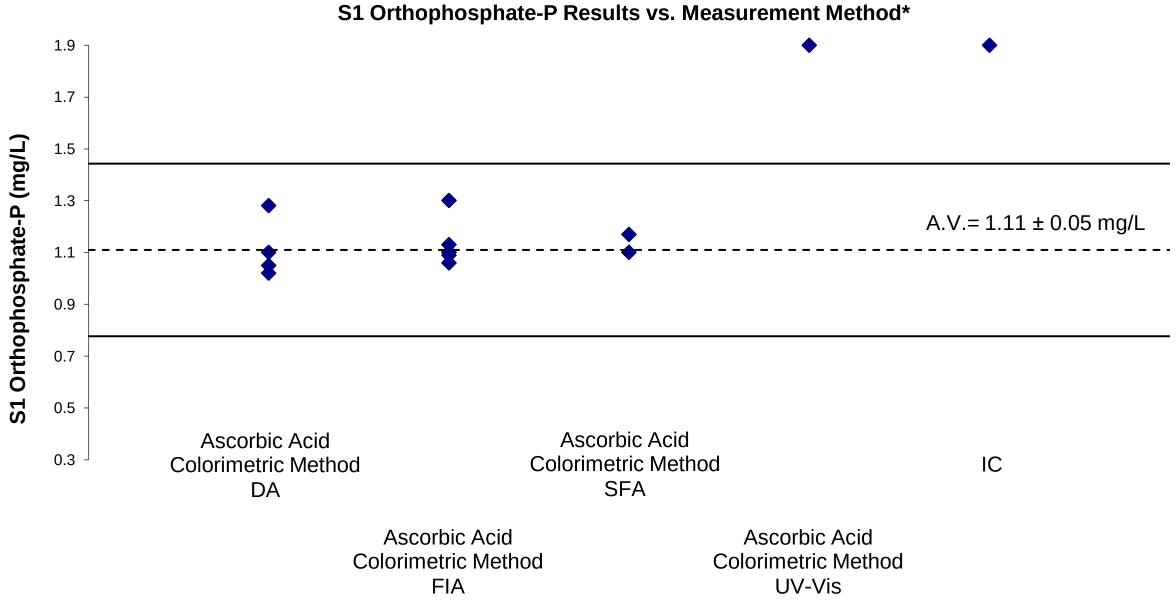
*Laboratory 4 results of 1.45 mg/L has been plotted as 1 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 41 S1-Nitrite-N vs. Measurement Method

Problems with calculation/dilution procedure might explain Laboratory 4 unsatisfactory results. The results reported by them for both tests, NO_3-N and NO_2-N, were higher than the assigned value by almost the same factor of 4.

Orthophosphate-P Ascorbic acid colorimetric method with FIA, DA or SFA determination was the preferred method of measurement (Figure 42). All results were in good agreement with each-other except for two.

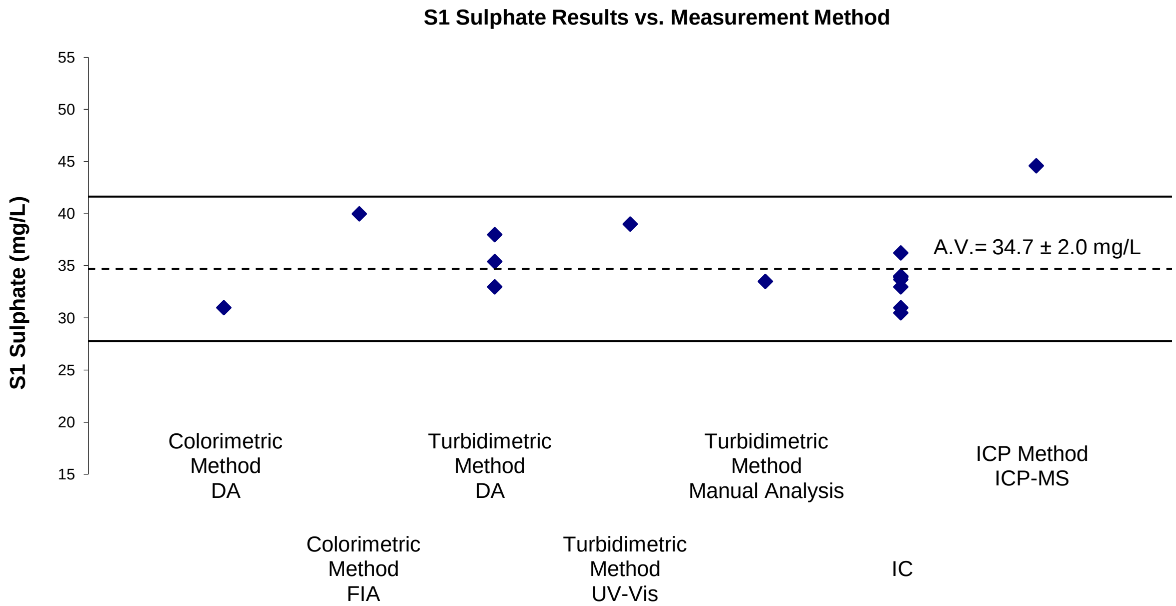
Laboratories 1 and 19 might have reported the orthophosphate -P as orthophosphate, the assigned value for orthophosphate-P converted to orthophosphate is 3.37 mg/L.



*Results larger than 1.9 mg/L have been plotted as 1.9 mg/L. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 42 S1-Orthophosphate-P Results vs. Measurement Method

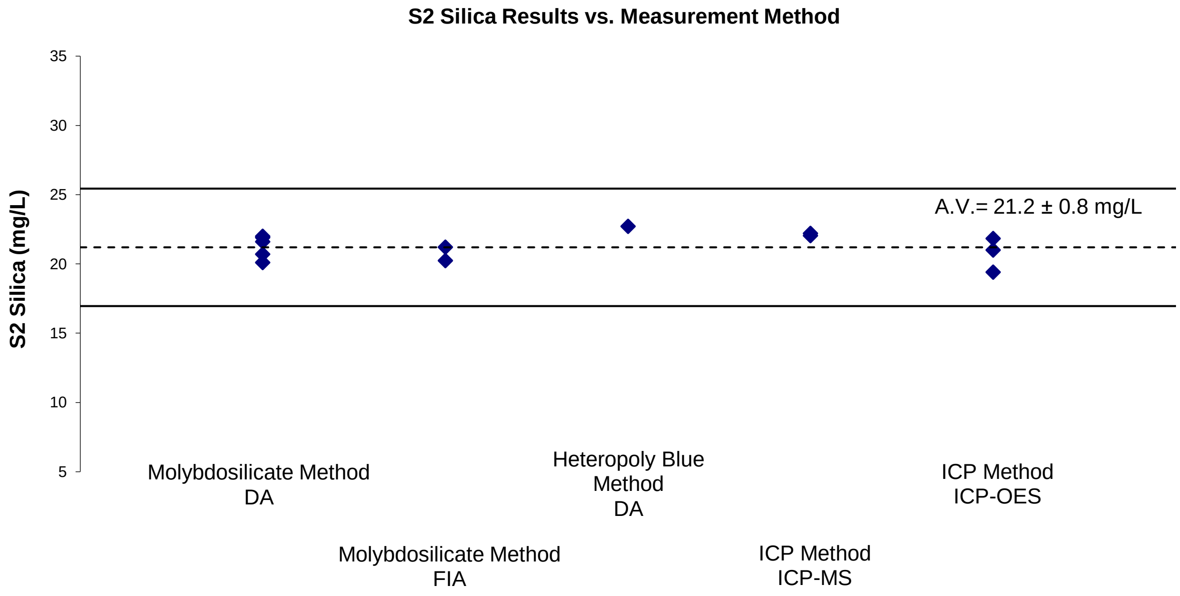
Sulphate One participant reported using ICP-MS for sulphate measurements. Caution should be exercised when using the ICP method because it measures total S and not just S from sulphate compounds (Figure 43).



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

Figure 43 S1-Sulphate Results vs. Measurement Method

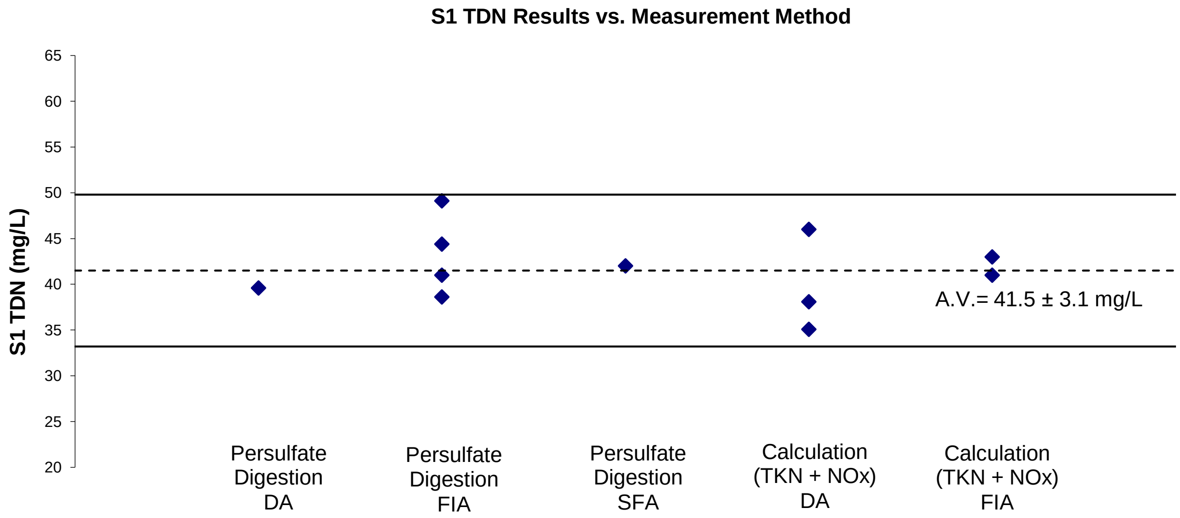
Silica (as SiO_2) Participants used a colorimetric or an ICP-method for silica measurements (Figure 44). All reported results returned satisfactory z-scores.



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

Figure 44 S2-Silica Results vs. Measurement Method

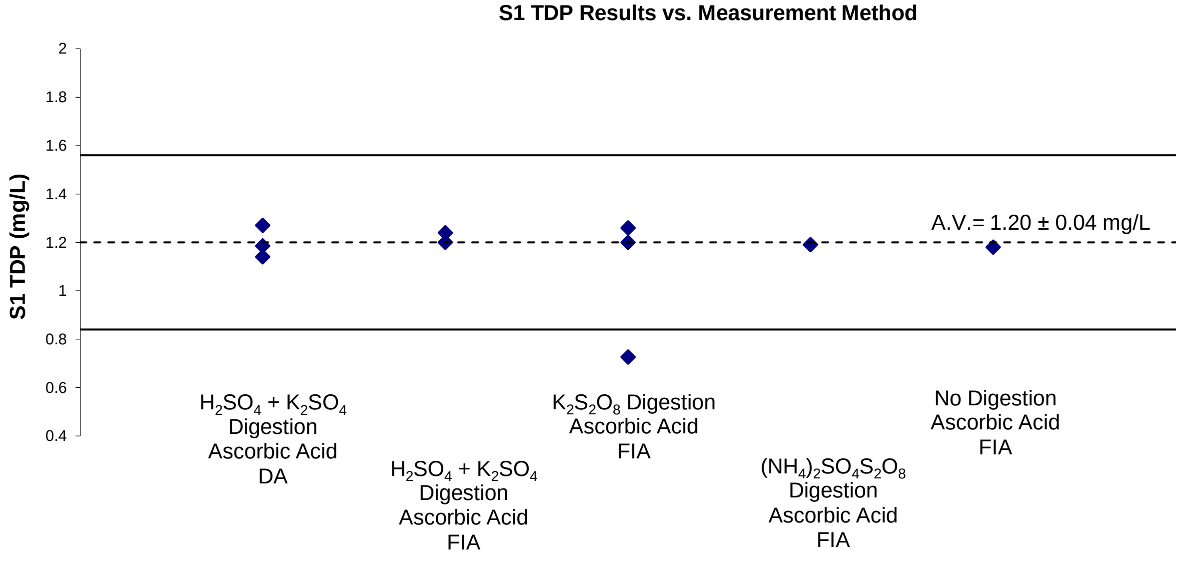
Total Dissolved Nitrogen All results reported for TDN in S1 returned satisfactory z-scores. Figure 45 presents the methods used by participating laboratories versus the results.



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

Figure 45 S1-TDN Results vs. Measurement Method and Instrumental Technique

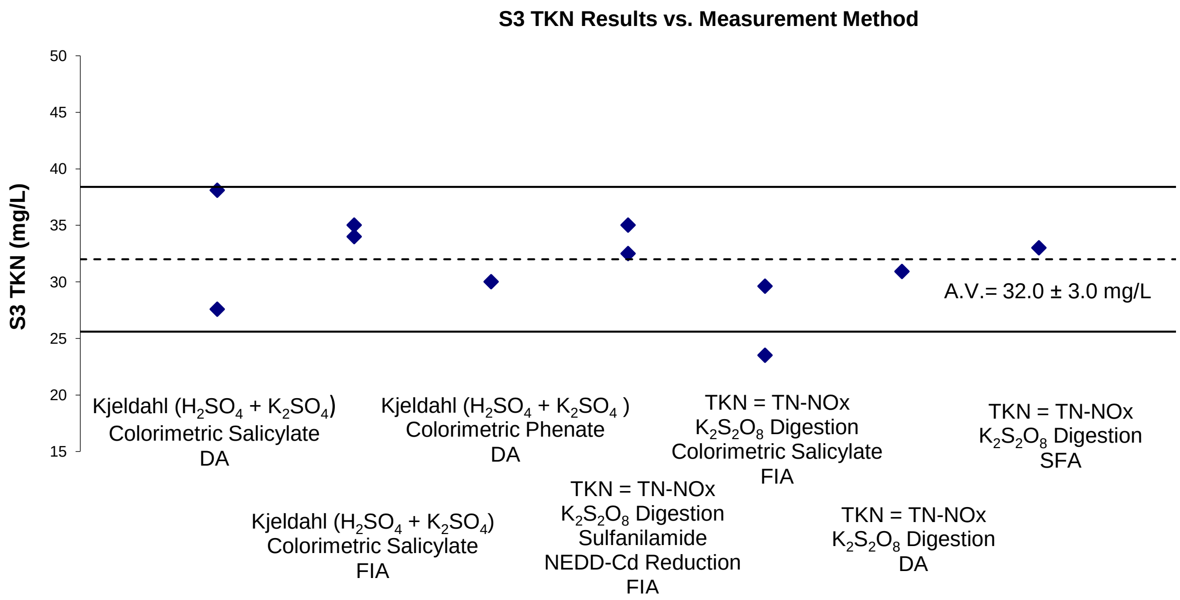
Total Dissolved Phosphorus level in the wastewater sample S1 was 1.20 mg/L. Of 19 participants, only 10 reported results, and all performed satisfactorily but one (Figure 46).



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

Figure 46 S1-TDP Results vs. Measurement Method and Instrumental Technique

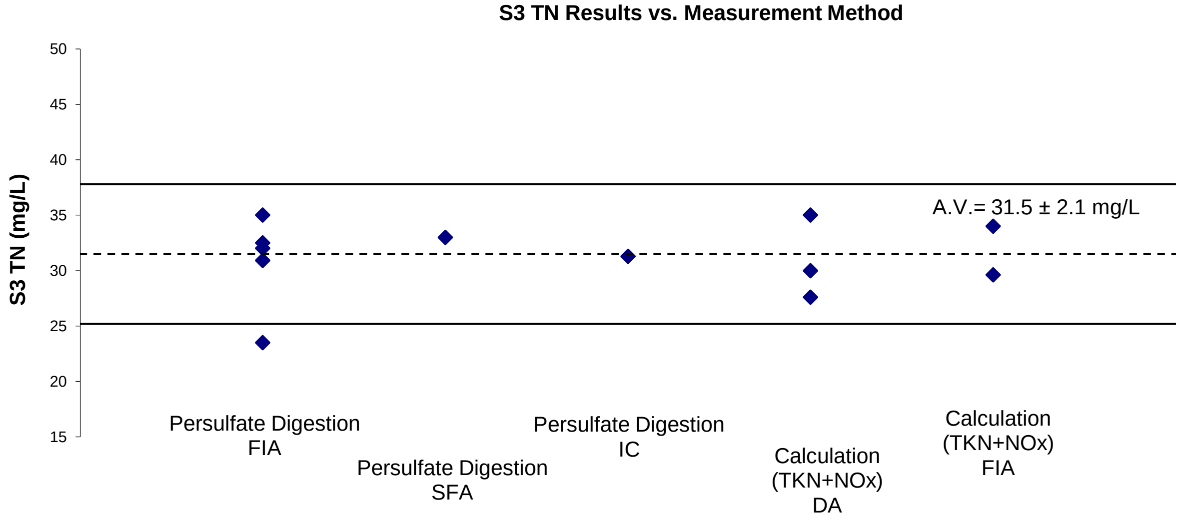
Total Kjeldahl Nitrogen Plots of participants results versus the measurement method used are presented in Figure 47. Five laboratories used Kjeldahl digestion followed by ammonia determination by DA or FIA. Six laboratories reported TKN as a calculated result (TN – NOx).



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

Figure 47 S3-TKN Results vs. Measurement Method

Total Nitrogen Of 12 reported results, one returned an unsatisfactory z-score (Figure 48). Problems with TKN measurements may explain Laboratory 10’s unsatisfactory result reported for TN S3.

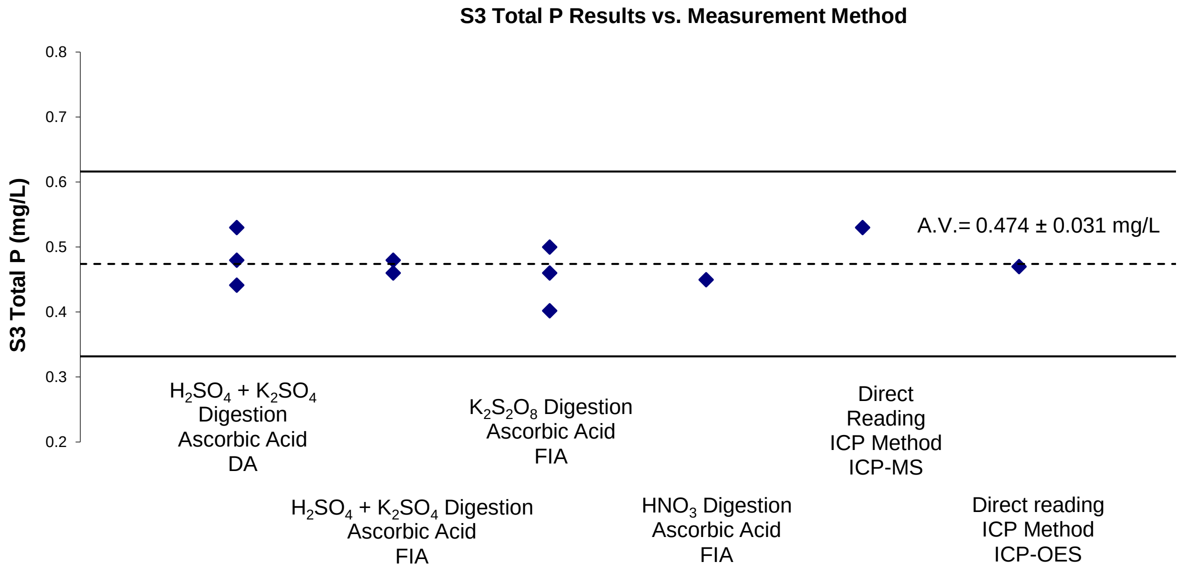


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 48 S3-TN Results vs. Measurement Method

Total Organic Carbon. All results reported for TOC in S3 produced by the High Temperature Oxidation Method or Wet Oxidation Method were compatible with each other and with the assigned value.

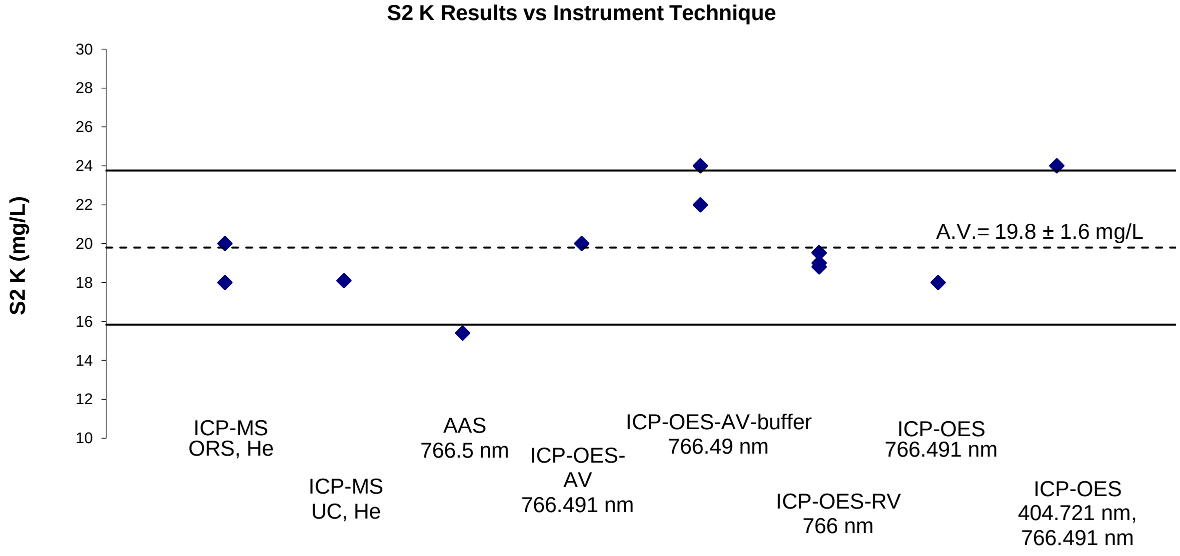
Total Phosphorus Measurements of total phosphorus in S3 challenged participants' analytical techniques. A small number of laboratories reported results; however, the reported results were in good agreement with each-other (Figure 49).



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

Figure 49 S3-TP Results vs. Measurement Method

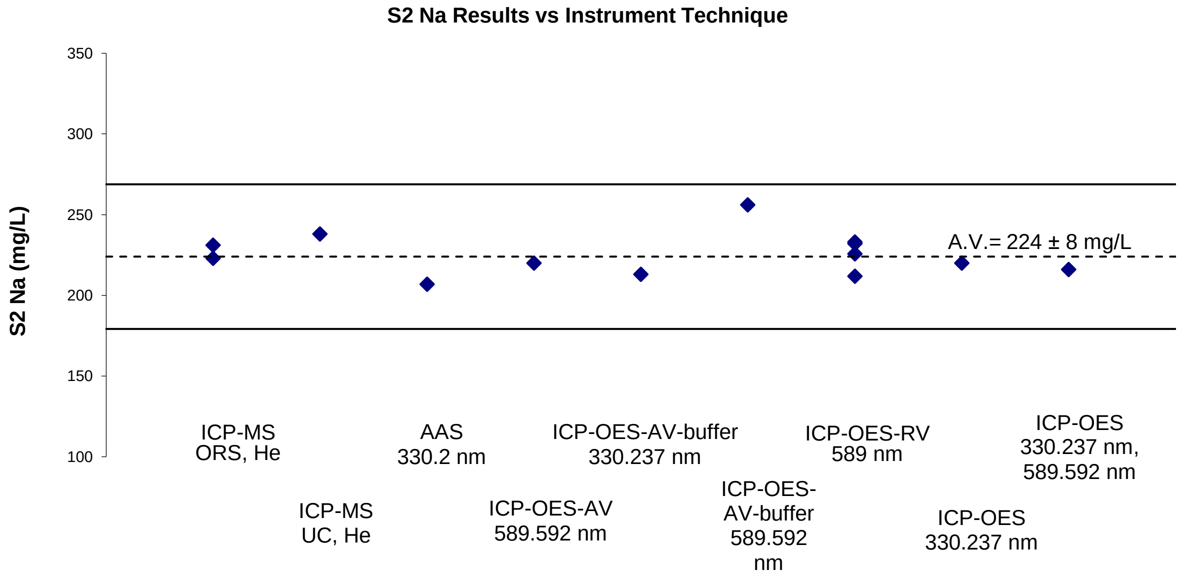
Potassium challenged some participants' analytical techniques. Of 14 reported results, 3 returned unsatisfactory z-scores. Ionization interference caused by other easily ionised elements might explain some of these poor performances. When K measurements are conducted using an ICP-OES with axially-viewed plasma, the emission signal of potassium (K 766.490 nm) is significantly enhanced in the presence of the other easily ionised elements such as: Na, Al and Mg. [15]



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

Figure 50 S2-K Results vs. Measurement Method

Sodium Participants used various instrumental techniques for Na measurement in S2, and all produced compatible results (Figure 51).



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

Figure 51 S2-Na Results vs. Measurement Method

6.6 Comparison with Previous NMI Proficiency Tests of Water Characteristics

AQA 23-12 is the 16th NMI proficiency study of nutrients, anions, and physical tests in water. Figure 52 presents participant performance over time. Despite different matrices and analytes' concentrations, on average, participants' performance has remained consistent over time.

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

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.

6.7 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 36).

Table 35 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CRM – Drinking Water Inorganics Quality Control Standard-HACH
2	CRM - CWW-TM-B and CWW-TM-C (metals) Minerals 1 and 2 (Salts)
4	SS
5	CRM - CRM-TMDW-500, CCV-1B, CCV-1A, GWS-5 (in-house standard)
6	CRM
7	CRM
8	RM
10	RM
11	CRM
12	CRM
13	CRM - WQC-ALK (HPS CRM) FOR ALKALINITY, NSI STANDARD FOR AMMONIA, PH EC ACCUSPEC CRM, QCI-155 TURBIDITY STANDARD (NSI)
16	AQA-22-18-S1, AQA-21-19-S2, AQA-21-19-S1
17	RM
18	CRM

Matrix matched control samples taken through all steps of the analytical process, are most valuable quality control tools for assessing the methods' performance.

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

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

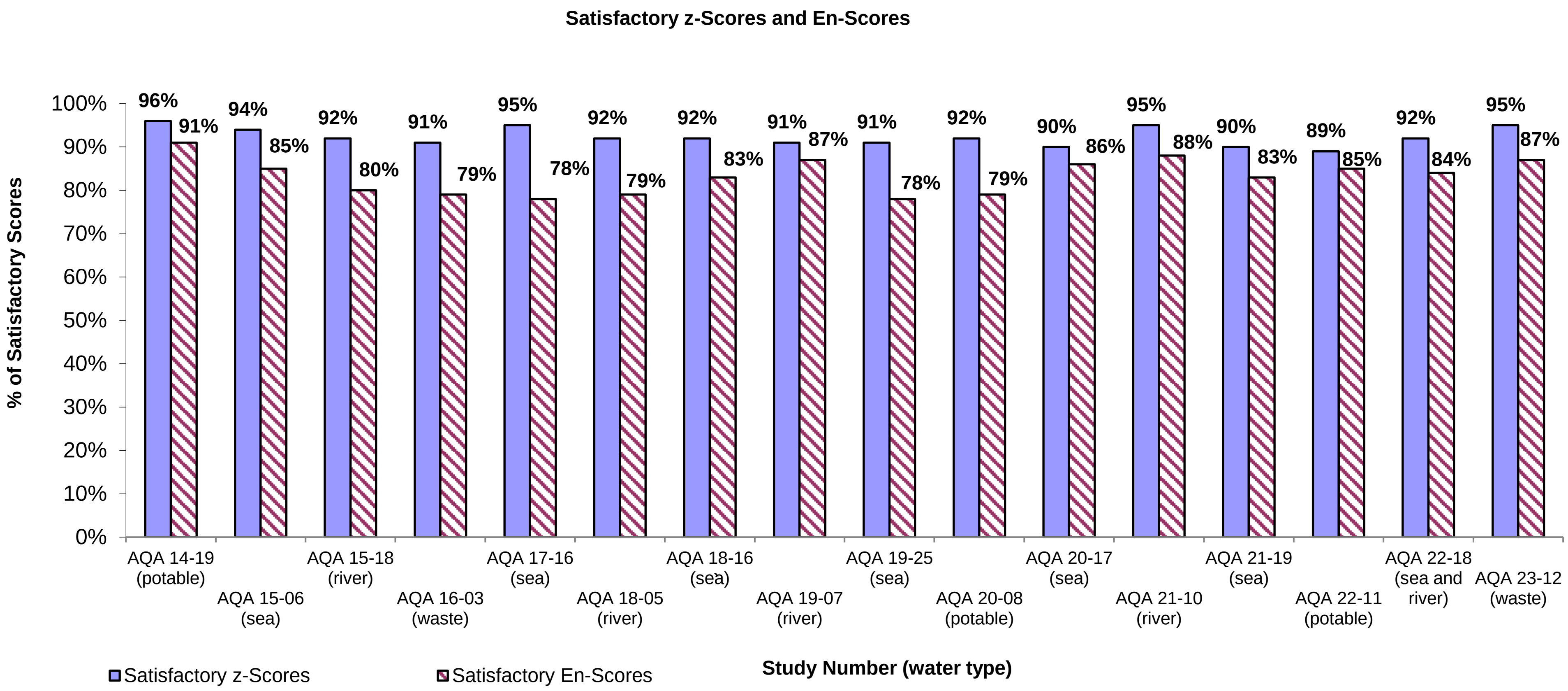


Figure 52 Participants' Performance in Nutrients, Anions and Physical Tests in Water PT Studies over Time

7 REFERENCES

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

[1] ISO17043:2010, Conformity assessment – *General requirements for the competence of proficiency testing providers.*

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[14] American Public Health Association, American Water Works Association, & Water Environmet Federation, *Standard Methods for the Examination of Water and Wastewater, 24th edition*

[15] Dubuisson, C. Poussel, E. (1997), *Comparison of axially viewed and radially viewed inductively coupled plasma atomic emission spectrometry in terms of signal-to background ratio and matrix effects* Journal of Analytical Atomic Spectrometry 12, 281-286.

[16] JCGM 200:2012, International vocabulary of metrology – Basic and General Concepts and Associated Terms (VIM), 3rd edition.

[17] NMI, *AQA 21-19 Nutrients, Anions and Physical Tests in Sea Water*, viewed October 2023, https://www.industry.gov.au/publications/proficiency-test-reports-2021.

APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was 400 mL of filtered and autoclaved wastewater.

Sample S2 was two identical bottles of 200 mL autoclaved wastewater.

Sample S3 was 400 mL of autoclaved and wastewater.

None of the study samples have been fortified with any of the analytes of interest.

Sample Analysis and Homogeneity Testing

Except for bromide, fluoride, orthophosphate-P, sulphide and TDP in S1, colour, EC and silica in S2, and TKN and total P in S3, a partial homogeneity test was conducted for all analytes of interest. Three bottles were analysed in duplicate, and the average of the results was reported as the homogeneity value.

Sample Analysis for Dissolved Elements

Measurements for total elements were made using a method for which NMI holds third party (NATA) accreditation for this method. 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.

Testing involved measurements using ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates and sample matrix spikes was carried through the same set of procedures and analysed simultaneously with the samples.

A summary of the instrument conditions used for each analyte is given in Table 42.

Table 36 Methodology for Dissolved Elements

Analyte	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength
B	ICP-OES-AV	Y	NA	NA	2.1	249 nm
Ca	ICP-OES	Y	NA	NA	2.1	422 nm
K	ICP-OES (matrix correction applied)	Y	NA	NA	2.1	766 nm
Mg	ICP-OES	Y	NA	NA	2.1	285 nm
Na	ICP-OES	Y	NA	NA	2.1	588 nm
P	ICP-OES	Y	NA	NA	2.1	177 nm

Methodology for Tests Other Than Dissolved Elements

Analyses for all the tests other than dissolved elements were conducted by NMI Inorganics section. A summary of the measurement methods and instrumental techniques is presented in Table 38.

Table 37 Methodology for Tests Other Than Dissolved Elements

Test	Measurement Method	Instrument
Alkalinity to pH 4.5 (as $CaCO_3$)	Titration	
Ammonia-N	Fluorometric Determination – OPA Method	SFA
Chloride	Turbidimetric Method	DA

COD	Closed Reflux, Titrimetric Method	
Dissolved Organic Carbon	High-Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	ISE
Nitrate-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Nitrite-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Sulphate	Ion Chromatographic Method	IC
TDN	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Hardness (as $CaCO_3$)	Calculation	ICP-OES
Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	SFA
Total Organic Carbon	High-Temperature Oxidation	NIR-detector

APPENDIX 2 - STABILITY STUDY

The samples were dispatched by courier on 3 July 2023. Samples S1 and S3 were frozen, while S2 was refrigerated.

Samples' condition on receipt and the date when the samples were received and analysed by participants are presented in Table 39. No relationship between participants' results, samples' condition on receipt, and days spent in transit were evident (Figures 53 and 56).

Table 38 Samples 'Condition on Receipt and the Date When the Samples were Received and Analysed

Lab Code	Received Date	S1		S2		S3	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	12/07/2023	Cold	17/07/2023	NA	NA	NA	NA
2	4/07/2023	Frozen	12/07/2023	Cold	11/07/2023	Frozen	12/07/2023
3	4/07/2023	Frozen	10/07/2023	Cold	10/07/2023	NA	NA
4	4/07/2023	Frozen	5/07/2023	Cold	5/07/2023	Frozen	5/07/2023
5	4/07/2023	NA	NA	Frozen	13/07/2023	NA	NA
6	5/07/2023	Frozen	12/07/2023	Cold	12/07/2023	Frozen	12/07/2023
7	4/07/2023	Cold	13/07/2023	Cold	4/07/2023	Frozen	NA
8	5/07/2023	Frozen	7/07/2023	NA	NA	Frozen	10/07/2023
9	4/07/2023	Frozen	11/07/2023	Cold	11/07/2023	Frozen	12/07/2023
10	4/07/2023	Frozen	4/07/2023	Cold	4/07/2023	Frozen	4/07/2023
11	5/07/2023	Partially thawed	21/07/2023	Cold	21/07/2023	Frozen	21/07/2023
12	4/07/2023	Frozen	Not Given	Cold	Not Given	Frozen	Not Given
13	5/07/2023	Cold	9/07/2023	Cold	8/07/2023	Cold	9/07/2023
14	4/07/2023	Cold	10/07/2023	Cold	10/07/2023	Cold	10/07/2023
15	10/07/2023	Frozen	12/07/2023	Cold	13/07/2023	Frozen	12/07/2023
16*	25/07/2023	Frozen	3/08/2023	Cold	2/08/2023	Frozen	26/07/2023
17	5/07/2023	Frozen	6/07/2023	Cold	6/07/2023	Frozen	6/07/2023
18	4/07/2023	Frozen	10/07/2023	Cold	10/07/2023	Frozen	10/07/2023
19	4/07/2023	Frozen	20/07/2023	Cold	20/07/2023	NA	NA

NA = Not Applicable. *Laboratory 16 samples were dispatched 24/07/2023.

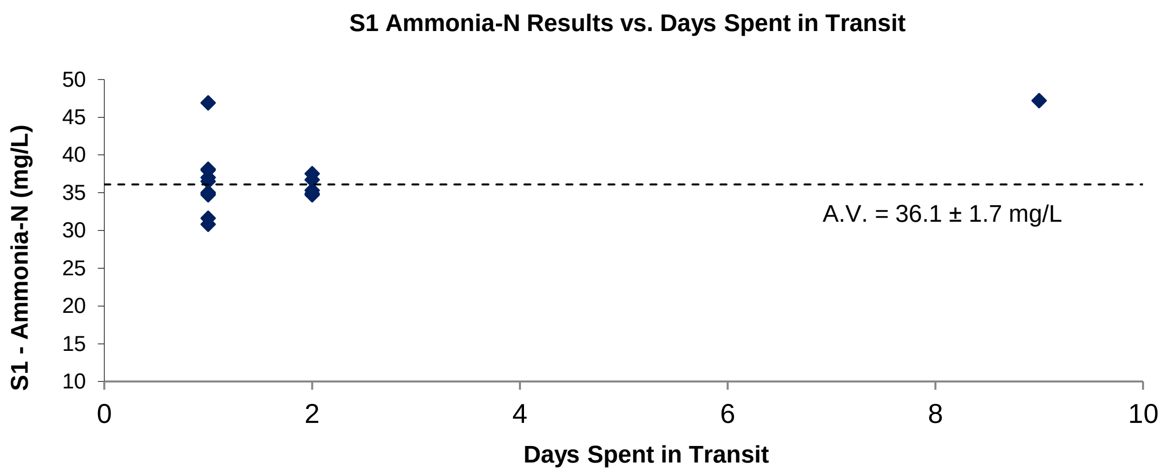


Figure 53 S1-NH_3-N Results vs Days Spent in Transit

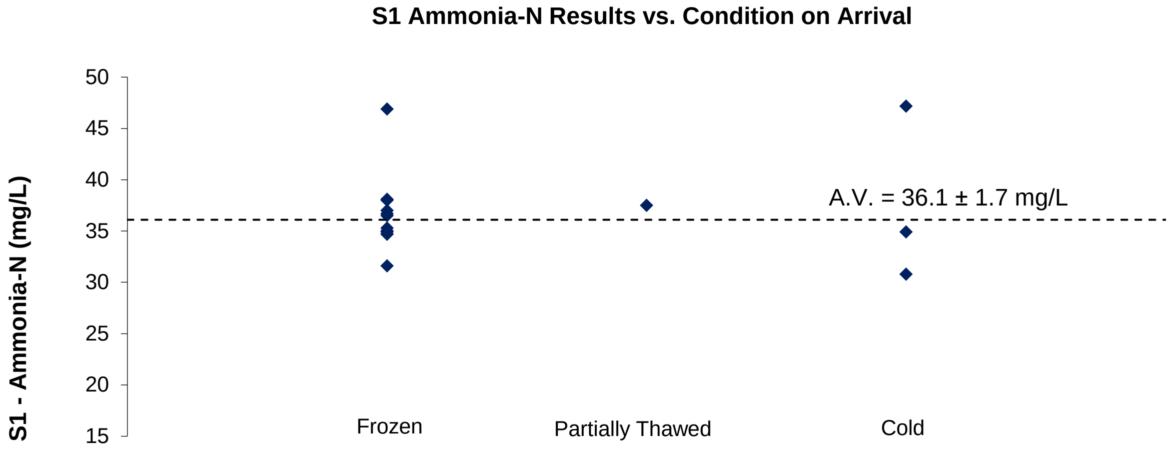


Figure 54 S1-NH_3-N Results vs Condition on Arrival

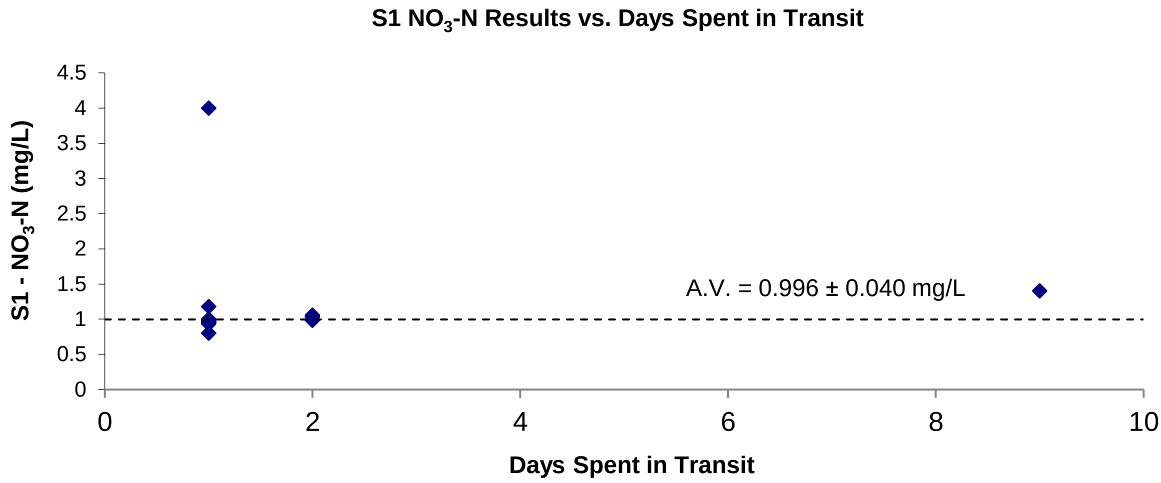


Figure 55 S1-NO_3-N Results vs Days Spent in Transit

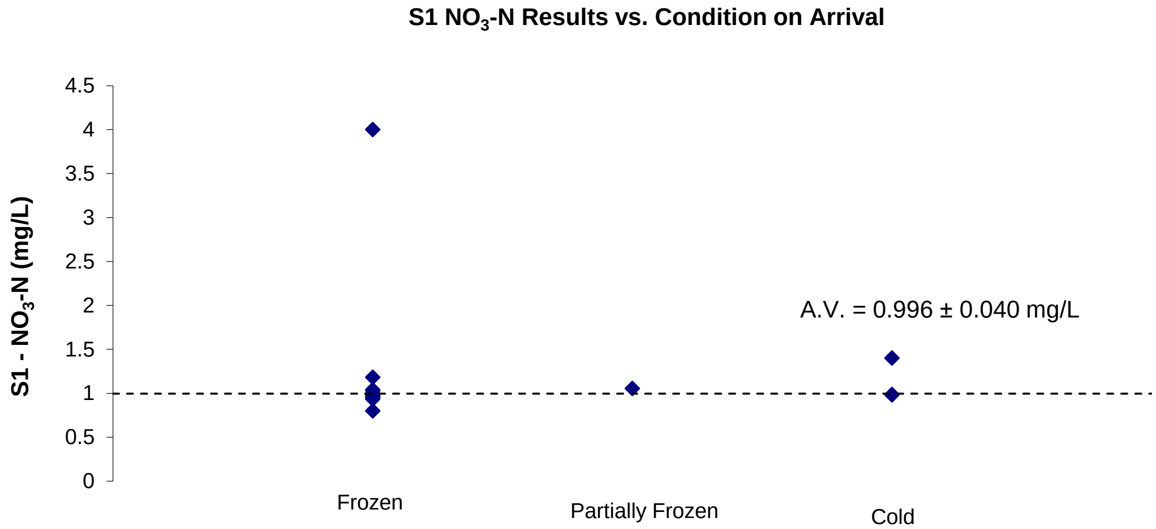


Figure 56 S1-NO_3-N Results vs Condition on Arrival

In a previous study of ammonia and NOx-N in water (AQA 21-19), one set of samples spent eight days in transit. To assess analytes' stability during transport, results from the "transport set of samples" with eight days in transit (T8) were compared with results from a set of samples sent to the same laboratory but with only two days in transit (T2). The results from this study are presented in Figure 57. The two sets of results were in good agreement with each other within their stated uncertainties. [17]

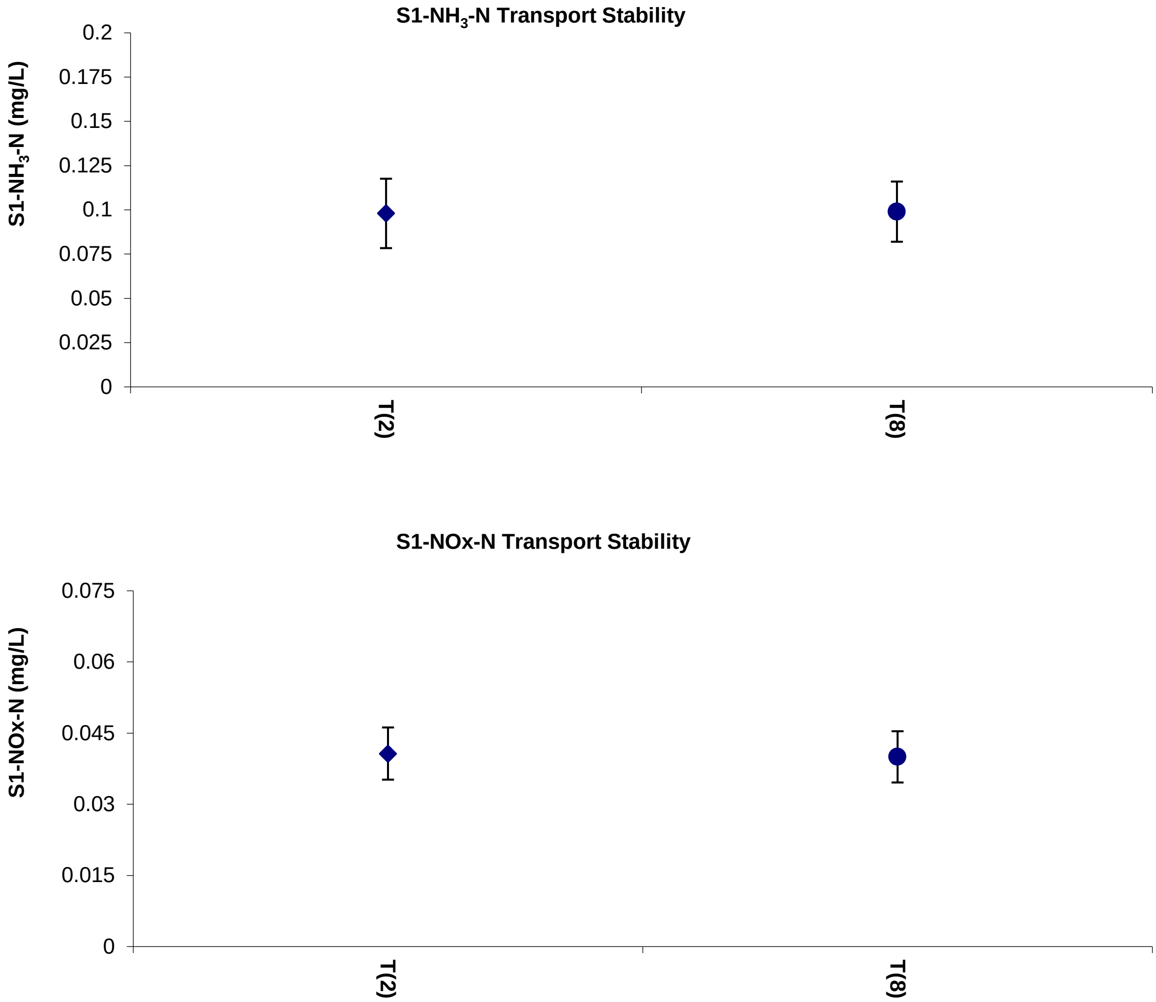


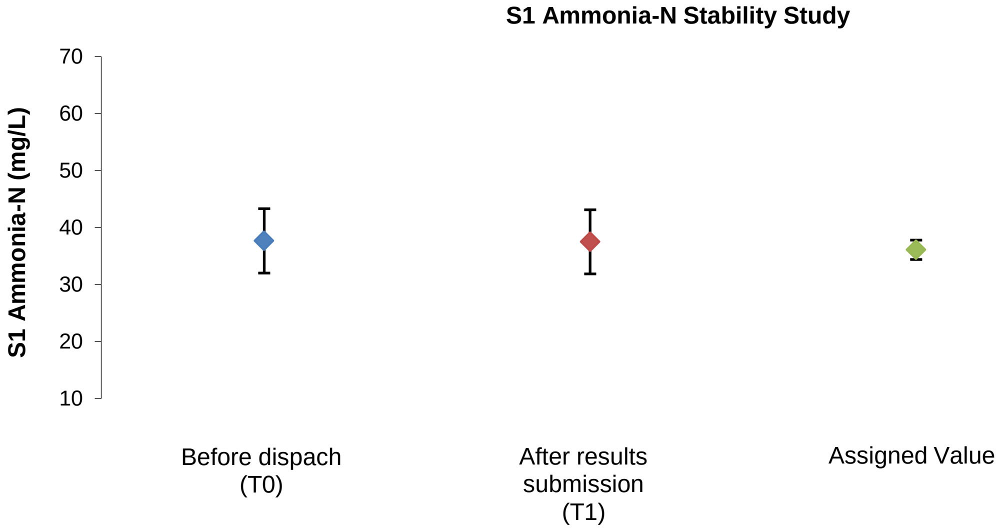
Figure 57 Transport Stability Results

Stability Study

In previous PT studies, stability studies conducted for nutrients and physical tests in water found no significant changes in any of the analytes' concentrations. A stability study was however, conducted in the present study for the less stabile analytes: NH_3-N and NO_3-N.

A comparison was conducted of the results from samples analysed before the samples' dispatch (T0) versus those analysed at the end of the study, after submission of results (T1). Each sample was analysed in duplicate together with a set of quality control samples consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes.

Results from both studies were in good agreement with each other and the assigned value were within their stated uncertainties (Figure 58).



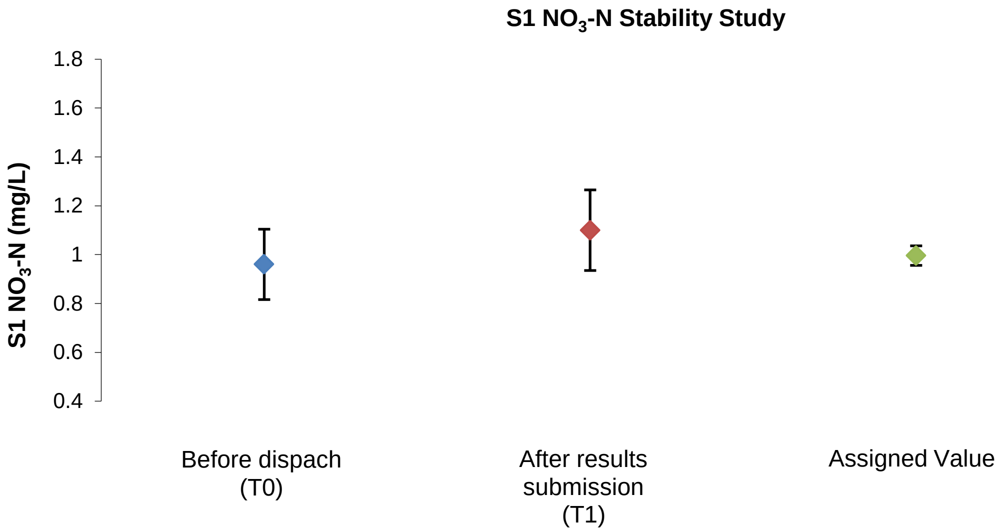


Figure 58 Stability Study Results

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 'ISO13528:2015, 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 39.

Table 39 Uncertainty of Assigned Value for Ammonia-N in Sample S1

No. results (p)	16
Robust Average	36.1 mg/L
$S_{rob\ av}$	2.7 mg/L
$u_{rob\ av}$	0.84 mg/L
k	2
$U_{rob\ av}$	1.7 mg/L

The assigned value for **Ammonia-N** in Sample S1 is **36.1 ± 1.7 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 9).

A worked example is set out below in Table 40.

Table 40 z-Score and E_n-score for Ammonia-N result reported by Laboratory 2 in S1

Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
36.5 ± 4.0	36.1 ± 1.7	15% as CV or 0.15 x 36.1= =5.4 mg/L	$z = \frac{(36.5 - 36.1)}{5.4}$ z = 0.07	$\text{En} = \frac{(36.5 - 36.1)}{\sqrt{4.0^2 + 1.7^2}}$ E_n= 0.09

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 also be used to estimate the uncertainty of their measurement results.[10, 12] An example is given in Table 41. Between 2014 and 2023, NMI carried out 16 proficiency tests for nutrients, anions and physical tests in water. These studies involved measurements of these analytes in potable, fresh (river), waste and seawater. Laboratory X participated and submitted satisfactory results for all studies with chloride in these PTs.

Table 41 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	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	16600 ± 1600	17300 ± 1600	13	13
AQA 19-07	River	57.0 ± 12	53.7 ± 2.0	4.7	10
AQA 19-25	Sea	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	9800 ± 980	10700 ± 400	4.9	10
AQA 21-10	River	81 ± 10	86.3 ± 2.7	5.7	20
AQA 21-19	Sea	19440 ± 1950	20100 ± 600	3.8	9
AQA 22-11	Potable	22.3 ± 5.0	25.5 ± 0.8	5.5	19
AQA 22-18	Sea	14073 ± 1400	13800 ± 500	5.3	14
AQA 22-18	River	60 ± 10	62.3 ± 1.5	4.1	19
AQA 23-12	Waste	152 ± 20	142 ± 6	6.3	16
Average				5.3**	

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

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 5.3%. Using a coverage factor of 2 gives a relative expanded uncertainty of 11%, at a level of confidence of approximately 95%. Table 42 sets out the expanded uncertainty for results of the measurement of Chloride in potable, fresh, waste or seawater over the range 20.0 – 20000 mg/L.

Table 42 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 MU estimates made using PT data is close to Laboratory X's own uncertainty estimates reported with their PT results. The estimate of 11% passes the test of being reasonable, and the analysis of the four different matrices over nine years can safely be assumed to include all the relevant uncertainty components (different operators, reagents, calibrants etc), and so complies with ISO 17025:2018.[8]

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
CV_{rob}	Robust Coefficient of Variation
DA	Discrete Analyser
dNPOC	Dissolved non-purgeable organic carbon
FIA	Flow Injection Analyser
GUM	Guide to the Expression of Uncertainty in Measurement
H.V.	Homogeneity Value
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view
ICP-OES-AV-buffer	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view with buffer
ICP-OES-RV	Inductively Coupled Plasma – Optical Emission Spectrometry- radial view
ISE	Ion Selective Electrode
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MU	Measurement Uncertainty
N	Number of Participants
NATA	National Association of Testing Authorities
NEDD	N-(1-naphthyl)-ethylenediamine dihhydrochloride (NED dihydrochloride)
NIR-Detector	Near-infrared Detector
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
OPA	o-Phthalaldehyde
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PFAS	Polyfluoroalkyl Substances
PT	Proficiency Test
R.A.	Robust Average
RM	Reference Material
SD_{rob}	Robust Standard Deviation
SFA	Segment Flow Analyser
SI	The International System of Units
SS	Spiked Sample
S.V.	Spiked or formulated concentration of a PT sample
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation (symbol: σ)
UV-Vis	Ultraviolet -visible spectroscopy

APPENDIX 6 - METHODOLOGY FOR S1

Table 43 Measurement Methods and Instrument Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - Salicylate Method	UV-Vis Spectrophotometer	HACH Method 10205 TNT Plus 831
2	Colorimetric - Phenate Method	FIA	APHA4500NH3-H
4	Colorimetric - Salicylate Method	DA	In-house method based onAPHA 23rd edition 4500 NH3 B
6	Colorimetric - Phenate Method	DA	APHA 4500-NH3
8	Colorimetric - Phenate Method	FIA	APHA4500-NH3
9	Fluorometric Determination - OPA Method	SFA	SFA
10	Colorimetric - Salicylate Method	FIA	APHA 4500-NH3 H (EN/EK055A)
12	Colorimetric - Salicylate Method	DA	In house
13	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-NH3 D
14	Colorimetric - Phenate Method	DA	APHA 4500-NH3
15	Colorimetric - Salicylate Method	DA	QWI-EN.WK055G16
16	Fluorometric determination	SFA	
17	Colorimetric - Salicylate Method	FIA	APHA
18	Colorimetric - Salicylate Method	DA	In house
19	if other please type	IC	In-house method

Table 44 Measurement Methods and Instrument Techniques for Bromide

Lab. Code	Measurement Method	Instrument	Method Reference
2	ICP Method	ICP-MS	W32
3	Ion Chromatographic Method	IC	Inhouse
6	Ion Chromatographic Method	IC	APHA 4110
9	Ion Chromatographic Method	IC	APHA
12	Ion Chromatographic Method	IC	In house
13	Ion Chromatographic Method	IC	APHA 411 B
15	Ion Chromatographic Method	IC	QWI-EN.WD013
17	Ion Chromatographic Method	IC	APHA

Table 45 Measurement Methods and Instrument Techniques for Chemical Oxygen Demand

Lab. Code	Measurement Method	Instrument	Method Reference
2	Closed Reflux, Colorimetric Method	HACH	
4	Open Reflux Method	Manual Titration	In house method based on APHA 5220 B
6	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	APHA 5220
7	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	APHA 5220 D
8	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	APHA 5220D
9	Closed Reflux, Titrimetric Method		APHA
10	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	APHA 5220D (EN/EP026SP.WN)
12	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	In house
15	Closed Reflux, Colorimetric Method		QWI-EN.WP026
17	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	APHA
18	Closed Reflux, Colorimetric Method	UV-Vis Spectrophotometer	In house

Table 46 Measurement Methods and Instrument Techniques for Chloride

Lab. Code	Measurement Method	Instrument	Method Reference
1	Argentometric Titration	Manual Analysis	HACH Method 8225 Buret Titration
2	ICP-Method	ICP-MS	W32
3	Ion Chromatographic Method	IC	In house
4	Potentiometric-Titration	Auto Titration	In-house method based on APHA 23rd edition 4500 Cl D
6	Mercuric Thiocyanate	DA	APHA 4500-Cl-
7	Ion Chromatographic Method	IC	APHA 4110 B
8	Ion Chromatographic Method	IC	APHA4110B(modified)
9	Ion Chromatographic Method	IC	APHA
10	Argentometric Titration	Auto Titration	APHA, 4500-Cl- B (EN/ED045)
12	Ion Chromatographic Method	IC	In house
13	Ion Chromatographic Method	IC	APHA 411 B
14	Mercuric Thiocyanate	DA	APHA 4500-Cl-
15	Ferricyanide Colorimetric Method	DA	QWI-EN.WD045G
17	Ion Chromatographic Method	IC	APHA
18	Mercurric Nitrate Titration	DA	In house
19	Ion Chromatographic Method	IC	In-house method

Table 47 Measurement Methods and Instrument Techniques for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
2	High-Temperature Oxidation	NIR-detector	APHA5310-B
4	High-Temperature Oxidation	FI-detector	In-house method based on APHA 23rd edition 5310-TOC B
6	High-Temperature Oxidation	NIR-detector	APHA 5310
8	High-Temperature Oxidation	NIR-detector	APHA5310C(modified)
9	High-Temperature Oxidation	NIR-detector	APHA
12	Wet-Oxidation	NIR-detector	In house
14	High-Temperature Oxidation	NIR-detector	APHA 5310
15	High-Temperature Oxidation	NIR-detector	QWI-EN.WP005SF002SF
18	High-Temperature Oxidation	NIR-detector	In house

Table 48 Measurement Methods and Instrument Techniques for Fluoride

Lab. Code	Measurement Method	Instrument	Method Reference
1	SPADNS Colorimetric Method	UV-Vis Spectrophotometer	HACH SPADNS Method
3	Ion Chromatographic Method	IC	In house
4	Ion Selective Electrode Method	Ion Selective Electrode	In-house method based on APHA 23rd edition 4500-F C
6	Ion Chromatographic Method	IC	APHA 4110
8	Ion Selective Electrode Method	Ion Selective Electrode	APHA4500-F-C
9	Ion Selective Electrode Method	Ion Selective Electrode	APHA
10	Ion Selective Electrode Method	Ion Selective Electrode	APHA, 4500-F- A,C (CEN/EK040&P)
12	Ion Chromatographic Method	IC	In house
13	Ion Chromatographic Method	IC	APHA 411 B
14	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F-
15	Ion Selective Electrode Method	Ion Selective Electrode	QWI-EN.WK040LL
17	Ion Selective Electrode Method	IC	APHA
18	Ion Selective Electrode Method	Auto Titration	In house

Table 49 Measurement Methods and Instrument Techniques for Nitrate N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric - salicylate method	UV-Vis Spectrophotometer	HACH Cadmium Reduction Method 8171
2	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO3-F
4	Colorimetric -vanadium III method	DA	In house method based on APHA 4500-NO2 B
6	Calculation	DA	NEMI 9171
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Calculation
9	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
10	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA, 4500- APHA 411 B - A,E,I (EN/EK058A)
12	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In house
13	Ion Chromatographic Method	IC	APHA 411 B
14	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	APHA 4500-NO3-
15	Calculation	NA	
16	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
18	Colorimetric - salicylate method	DA	In house
19	Ion Chromatographic Method	IC	In-house method

Table 50 Measurement Methods and Instrument Techniques for Nitrite N

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric Method	UV-Vis Spectrophotometer	HACH Diazotization Method 8507
2	Colorimetric Method	FIA	APHA4500NO3-F
4	Colorimetric Method	DA	In house method based on APHA 4500-NO2 B
6	Colorimetric Method	DA	APHA 4500-NO2-
8	Colorimetric Method	FIA	APHA4500-NO3(modified)
9	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	APHA
10	Colorimetric Method	FIA	APHA, 4500-NO2- (EN/EK057A)
12	Colorimetric Method	FIA	In house
14	Colorimetric Method	DA	APHA 4500-NO2-
15	Colorimetric Method	DA	QWI-EN.EK057G
16	Colorimetric Method	FIA	APHA
17	Colorimetric Method	FIA	APHA
18	Colorimetric Method	DA	In house
19	Ion Chromatographic Method	IC	In-house method

Table 51 Measurement Methods and Instrument Techniques for Orthophosphate-P

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer	HACH Ascorbic Acid Method 8048
2	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-G
6	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
8	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PG
9	Ascorbic Acid Colorimetric Method	SFA	APHA
10	Ascorbic Acid Colorimetric Method	FIA	APHA, 4500-P A,B,E (EN/EK071A)
12	Ascorbic Acid Colorimetric Method	FIA	In house
14	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
15	Ascorbic Acid Colorimetric Method	DA	QWI-EN.WK071G
16	Ascorbic Acid Colorimetric Method	SFA	
17	Ascorbic Acid Colorimetric Method	FIA	APHA
18	Ascorbic Acid Colorimetric Method	DA	In house
19	Ion Chromatographic Method	IC	In-house method

Table 52 Measurement Methods and Instrument Techniques for Sulphate

Lab. Code	Measurement Method	Instrument	Method Reference
1	Turbidimetric Method	UV-Vis Spectrophotometer	HACH SulfaVer Method 8051
2	ICP Method	ICP-MS	W32
3	Ion Chromatographic Method	IC	In house
4	Turbidimetric Method	Manual Analysis	In-house method based on USEPA method 9038, Sept 1986
6	Colorimetric Method	DA	APHA 4500-SO4
7	Ion Chromatographic Method	IC	APHA 4110 B
8	Ion Chromatographic Method	IC	APHA4110B(modified)
9	Ion Chromatographic Method	IC	APHA
10	Colorimetric Method	FIA	APHA, 4500-SO4 2- (EN/ED041A)
12	Ion Chromatographic Method	IC	In house
13	Ion Chromatographic Method	IC	APHA 411 B
14	Turbidimetric Method	DA	APHA 4500-SO4 2-
15	Turbidimetric Method	DA	QWI-EN.WD041G
17	Ion Chromatographic Method	IC	APHA
18	Turbidimetric Method	DA	In house
19	Ion Chromatographic Method	IC	In-house method

Table 53 Measurement Methods and Instrument Techniques for Sulphide

Lab. Code	Measurement Method	Instrument	Method Reference
4	Colorimetric Method	UV-Vis Spectrophotometer	In-house method based on APHA 23rd edition 4500-S2- D
6	Colorimetric Method	DA	APHA 4500-S2-
8	In-line Distillation and Colourimetric Method	SFA	APHA 4500-S2-E Modified
12	Colorimetric Method	UV-Vis Spectrophotometer	In house
14	Colorimetric Method	UV-Vis Spectrophotometer	APHA 4500 S2-
15	Colorimetric Method		QWI-EN.WK085
17	Colorimetric Method	UV-Vis Spectrophotometer	APHA
18	Colorimetric Method	UV-Vis Spectrophotometer	In house

Table 54 Measurement Methods and Instrument Techniques for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
2	Persulfate digestion	FIA	APHA4500P-J
6	Persulfate digestion	DA	APHA 4500 NORG
8	Calculation (TKN+NOx)		
9	Persulfate digestion	SFA	APHA
12	Calculation (TKN+NOx)	FIA	In house
14	Calculation (TKN+NOx)	DA	
15	Calculation (TKN+NOx)	NA	QWI-EN.WK062
16	Persulfate digestion	FIA	APHA
17	Persulfate digestion	FIA	APHA
18	Calculation (TKN+NOx)	DA	In house

Table 55 Measurement Methods and Instrument Techniques for Total Dissolved Phosphorus

Lab. Code	Measurement Method		Instrument	Method Reference
2	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
6	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500 NORG
8	(NH4)2SO4S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500-PH
12	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	In house
14	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA 4500-P
15	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	QWI-EN.WK061A
16	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
17		Ascorbic Acid Colorimetric Method	FIA	APHA
18	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	In house

APPENDIX 7 - METHODOLOGY FOR S2

Table 56 Measurement Methods and Instrument Techniques for Alkalinity

Lab. Code	Measurement Method	Instrument	Method Reference
2	Titration	Auto Titration	APHA2320B
4	Titration	Auto Titration	In-house method based on APHA 23rd edition 2320 B
5	Titration	Auto Titration	
6	Titration	Auto Titration	APHA 2320
7	Titration	Auto Titration	APHA 2320 B
9	Titration	Auto Titration	APHA
10	Titration	Auto Titration	APHA, 2320-Alkalinity A,B (EN/ED037)
12	Titration	Auto Titration	In house
13	Titration	Manual Analysis	APHA 2320-Alkalinity
14	Titration	Auto Titration	APHA 2320
15	Titration	Auto Titration	QWI-EN.WD037
17	Titration	Auto Titration	APHA
18	Titration	Auto Titration	APHA 2320

Table 57 Measurement Methods and Instrument Techniques for Colour, apparent

Lab. Code	Measurement Method	Instrument	Method Reference
2	Spectrophotometric Method	UV-Vis Spectrophotometer	In House - W1
4	Visual Comparison Method	Manual Analysis	In-house method based on APHA 23rd edition 2120B
6	Visual Comparison Method	Manual Analysis	APHA 2120
7	Spectrophotometric Method	UV-Vis Spectrophotometer	APHA 2120 C
9	Spectrophotometric Method	DA	APHA
10	Visual Comparison Method	Manual Analysis	APHA, 2120 A,B (EN/EA040)
12	Spectrophotometric Method	UV-Vis Spectrophotometer	In house
14	Visual Comparison Method		APHA 2120
15	Visual Comparison Method		QWI-EN.WA040
17	Visual Comparison Method		APHA
18	Visual Comparison Method	Manual Analysis	APHA 2120

Table 58 Measurement Methods and Instrument Techniques for Silica

Lab. Code	Measurement Method	Instrument	Method Reference
2	ICP-Method	ICP-MS	In House - W32
3	ICP Method by Calculation	ICP-OES	In House
4	Molybdosilicate Method	DA	In-house method based on APHA 23rd edition 4500-SiO2 E
5	ICP-Method	ICP-OES	
6	Molybdosilicate Method	DA	APHA 4500-SiO2
10	Molybdosilicate Method	FIA	APHA, 4500-SiO2 F (EN/EG052A)
12	Molybdosilicate Method	DA	In house
14	Heteropoly Blue Method	DA	APHA 4500-SiO2
16	Molybdosilicate Method	FIA	APHA
17	Molybdosilicate Method	DA	APHA
18	Molybdosilicate Method	DA	APHA 4500 SIO2-D

Table 59 Measurement Methods and Instrument Techniques for Total Hardness

Lab. Code	Measurement Method	Instrument	Method Reference
2	Titration	Manual Analysis	In House - W21
4	Calculation	Not Applicable	In-house method based on APHA 23rd edition 2340 B
6	Calculation	ICP-OES	APHA 2340
12	Calculation	Not Applicable	In house
13	Calculation	ICP-MS	APHA 2340 B-Hardness
14	Calculation	ICP-OES	APHA 2340
17	Calculation	Auto Titration	APHA
18	Calculation	ICP-OES	APHA 2340

Table 60 Instrument Techniques for Boron

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-MS	Sc	NA	NA	1	10
3	ICP-OES-AV	Lu			1.05	208.956
4	ICP-OES-AV	NA	NA	NA	Neat	208.956
5	ICP-OES-AV	Lu				208
6	ICP-OES	Eu & Cs	NA	NA	1	249.773
7	ICP-OES-AV-buffer	Y			1	208.957
9	ICP-OES-AV	Y	NA	NA	800	249.678
13	ICP-MS	Sc	NA		1	
14	ICP-MS	Sc	ORS			11
17	ICP-MS	SC,Rh,Ir		He	10	NA

Table 61 Instrument Techniques for Calcium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-MS	Sc	UC	He	1	44
3	ICP-OES-RV	Lu			1.05	422.673
4	AAS	NA	NA	NA	10	422.7
5	ICP-OES-RV	Lu				317
6	ICP-OES	Eu & Cs	NA	NA	1	315.887, 370.602nm
7	ICP-OES-AV-buffer	Y			1	315.887
9	ICP-OES-AV	Y	NA	NA	800	422.673
12	ICP-MS	Sc45	ORS	He	1	44
14	ICP-OES-AV-buffer	Eu				315.887nm
15	ICP-OES	Cs, Y			1	370.602
17	ICP-MS	SC,Rh,Ir		He	10	NA
18	ICP-OES-RV	Eu	NA	NA	NA	315.887

Table 62 Instrument Techniques for Potassium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-MS	Sc	UC	He	1	39
3	ICP-OES-RV	Lu			1.05	766.491
4	AAS	NA	NA	NA	10	766.5
5	ICP-OES-RV	Lu				766
6	ICP-OES	Eu & Cs	NA	NA	1	404.721nm, 766.491nm
7	ICP-OES-AV-buffer	Y			1	766.49
9	ICP-OES-AV	Y	NA	NA	800	766.491
12	ICP-MS	Sc45	ORS	He	1	39
14	ICP-OES-AV-buffer	Eu				766.491nm
15	ICP-OES	Cs, Y			1	766.491
17	ICP-MS	SC,Rh,Ir		He	10	NA
18	ICP-OES-RV	Eu	NA	NA	NA	766.491

Table 63 Instrument Techniques for Magnesium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-MS	Sc	UC	He	1	25
3	ICP-OES-RV	Lu			1.05	285.213
4	AAS	NA	NA	NA	10	285.5
5	ICP-OES-RV	Lu				277
6	ICP-OES	Eu & Cs	NA	NA	1	383.830 (nm)
7	ICP-OES-AV-buffer	Y			1	285.213
9	ICP-OES-AV	Y	NA	NA	800	279.078
12	ICP-MS	Sc45	ORS	He	1	24
14	ICP-OES-AV-buffer	Eu				383.829nm
15	ICP-OES	Cs, Y			1	285.213
17	ICP-MS	SC,Rh,Ir		He	10	NA
18	ICP-OES-RV	Eu	NA	NA	NA	383.829

Table 64 Instrument Techniques for Sodium

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-MS	Sc	UC	He	1	23
3	ICP-OES-RV	Lu			1.05	589.592
4	AAS	NA	NA	NA	10	330.2
5	ICP-OES-RV	Lu				589
6	ICP-OES	Eu & Cs	NA	NA	1	330.237, 589.592nm
7	ICP-OES-AV-buffer	Y			1	589.592
9	ICP-OES-AV	Y	NA	NA	800	589.592
12	ICP-MS	Sc45	ORS	He	1	23
14	ICP-OES-AV-buffer	Eu				330.237nm
15	ICP-OES	Cs, Y			1	330.237
17	ICP-MS	SC,Rh,Ir		He	10	NA
18	ICP-OES-RV	Eu	NA	NA	NA	589.592

Table 65 Instrument Techniques for Phosphorus

Lab. Code	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/ Absorbance (nm)
2	ICP-MS	Sc	UC	He	1	31
3	ICP-OES-RV	Lu			1.05	177.434
5	ICP-OES-RV	Lu				178
6	ICP-OES	Eu & Cs	NA	NA	1	185.827 (nm)
7	ICP-OES-AV-buffer	Y			1	178.221
9	ICP-OES-AV	Y	NA	NA	800	213.618
14	ICP-OES-AV-buffer	Eu				185.827nm
15	ICP-OES	Cs, Y			1	213.618
17	ICP-MS	SC,Rh,Ir		He	10	NA
18	ICP-OES-RV	Eu	NA	NA	NA	

APPENDIX 8 – METHODOLOGY FOR S3

Table 66 Measurement Methods and Instrument Techniques for Total Kjeldahl Nitrogen

Lab. Code	Measurement Method		Instrument	Method Reference
2	TKN=TN-NOx (K2S2O8 digestion)		FIA	
4	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	In-house method based on APHA 23rd edition 4500-Norg B
6	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - phenate method	DA	APHA 4500 NORG
9		Calculation from TN and NOX	SFA	APHA
10	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric - salicylate method	FIA	APHA, 4500-N Org A,D (EN/EK061)
12	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	In house
14	TKN=TN-NOx (K2S2O8 digestion)	Calculation	Not Applicable	
15	Kjeldahl (H2SO4+K2SO4 digestion)		FIA	QWI-EN.WK061A
17		Colorimetric - salicylate method	FIA	APHA
18	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	DA	APHA 4500 Norg-A

Table 67 Measurement Methods and Instrument Techniques for Total Nitrogen

Lab. Code	Measurement Method	Instrument	Method Reference
2	Persulfate digestion	FIA	
6	Calculation (TKN+NOx)	DA	APHA 4500 NORG
9	Persulfate digestion	SFA	APHA
10	Persulfate digestion	FIA	APHA, 4500-N C (EN/EK062A)
12	Calculation (TKN+NOx)	FIA	In house
13	Persulfate digestion	IC	ASTM D8001-16e1
14	Persulfate digestion	FIA	APHA 4500-N
15	Calculation (TKN+NOx)	NA	QWI-EN.WK062
16	Persulfate digestion	FIA	
17	Calculation (TKN+NOx)	FIA	APHA
18	Calculation (TKN+NOx)	DA	

Table 68 Measurement Methods and Instrument Techniques for Total Organic Carbon

Lab. Code	Measurement Method	Instrument	Method Reference
2	High-Temperature Oxidation	Shimadzu	
4	High-Temperature Oxidation	NIR-detector	In-house method based on APHA 23rd edition 5310 B
6	High-Temperature Oxidation	TOC Analyser	APHA 5310
9	High-Temperature Oxidation	NIR-detector	APHA
12	Wet-Oxidation	NIR-detector	In house
14	High-Temperature Oxidation	TOC analyser	APHA 5310
15	Persulfate-Ultraviolet Oxidation	FIA	
17	High-Temperature Oxidation		APHA
18	High-Temperature Oxidation	NIR-detector	APHA 5310

END OF REPORT