Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Proficiency Test Report AQA 19-07 River Water Characterisation

August 2019

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, conducting and reporting of the study is acknowledged.

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Dr Andrew Evans

Luke Viskovic

Hamish Lenton

Wei Huang

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1 SUMMARY

This report presents the results of the proficiency test AQA 19-07, River Water Characterisation. The study focused on the measurement of dissolved: Al, Ag, As, Be, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn and total: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, U and Zn. Bromide, chloride, dissolved organic carbon (as dNPOC), fluoride, ammonia-N, nitrate-N, total dissolved nitrogen, total dissolved phosphorus, orthophosphate-P, sulphate, alkalinity to pH 4.5 (as $CaCO_3$), colour (apparent), total hardness (as $CaCO_3$), pH at 25ºC, silica (as SiO_2), total solids at 103-105°C, turbidity (NTU), total Kjeldahl nitrogen, total nitrogen and total organic carbon (as NPOC) were also included in the program.

The sample set consisted of four water samples.

17 laboratories registered to participate and 16 submitted results.

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

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

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

Of 552 z-scores, 496 (90%) returned a satisfactory score of $|z| \leq 2$.
Of 552 E_n-scores, 485 (88%) returned a satisfactory score of $|E_n| \leq 1$

ii. evaluate the laboratories' methods used in determination of inorganic analytes in river water;

Low level boron was the test that presented the most analytical difficulty to participating laboratories.

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

On average participants' performance has 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 571 numerical results, 495 (87%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 4.

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

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

2 INTRODUCTION

2.1 NMI Proficiency Testing Program

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

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

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

AQA 19-07 is the 23rd NMI proficiency study of inorganic analytes in water.

2.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy in the performance of 61 tests in river water;
- evaluate the laboratories' methods used in determination of inorganic elements in river water;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

2.3 Study Conduct

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

NMI is accredited by National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes.[1]

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

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The sixty one tests were selected from those for which an investigation level is published in the Australian and New Zealand Guidelines for Sewerage Systems - Effluent Management[5] and are commonly measured by water testing laboratories.

3.2 Participation

17 laboratories participated and 16 submitted results.

The timetable of the study was:

Invitation issued:	15 April 2019	Results due:	14 June 2019
Samples dispatched:	13 May 2019	Interim report issued	20 June 2019

3.3 Test Material Specification

Three samples were provided for analysis:

Sample S1 was 100 mL of filtered river water preserved by adding 2% (v/w) HNO_3 and 0.01% (v/w) HCl;

Sample S2 was 100 mL of unfiltered river water preserved by adding 2% (v/w) HNO_3 and 0.01% (v/w) HCl;

Sample S3 was 200 mL of filtered, autoclaved and frozen river water; and

Sample S4 consisted of two bottles labelled A and B. The bottle A was 700 mL of unfiltered, chilled river water, while the container labelled B contained 200 mL of unfiltered, autoclaved and frozen river water.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

Partial homogeneity testing was conducted for the study samples except for TDP in S3 and total Ca, K, Mg, Na, Silica (as SiO_2) and Total Hardness in S4. The same validated sample preparation procedure was followed as in previous studies where the test samples were demonstrated to be sufficiently homogeneous for evaluation of participants' performance.[1, 6, 7]

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

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

No stability study was carried out for samples S1 and S2. Stability studies conducted for the previous similar proficiency studies of metals in water found no significant changes in any of the analytes' concentration. [6, 7]

For samples S3 and S4, to address issues with holding time and holding conditions a stability study was conducted for the less stable analytes. The stability study was conducted over the entire period of the PT study and was carried out to simulate the conditions encountered by the samples during storage. Details of the study and results are given in Appendix 2. The test samples were stable for the period of the proficiency test.

3.7 Sample Storage, Dispatch and Receipt

Samples labelled S1, S2 and S4A were refrigerated before dispatch, while samples labelled S3 and S4B were frozen.

The samples were dispatched by courier on 13 May 2019. A description of the test samples and instructions for participants, and a samples received form for participants to confirm the receipt of the test samples, were sent with the samples. An Excel spreadsheet for the electronic reporting of results was e-mailed to participants.

3.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- If analyses cannot be commenced on the day of receipt, please store the sample labelled S1, S2, S4A chilled and the samples S3 and S4B frozen.
- Prior to testing thaw samples S3 and S4B completely.
- The bottles labelled S4A and S4B are NOT to be composited. The samples should be tested for the analytes of interest as indicated in the table below.
- Participants are asked to report results in units of mg/L except for turbidity and colour. Report turbidity result in nephelometric turbidity units (NTU) and the result for colour in Pt-Co units

SAMPLE S1 filtered, acidified river water		SAMPLE S2 unfiltered, acidified river water		SAMPLE S3 filtered, autoclaved, frozen river water		SAMPLE S4 A unfiltered, autoclaved, chilled river water	
Test Dissolved	Approximate Conc. Range µg/L	Test Total	Approximate Conc. Range µg/L	Test	Approximate Conc. Range mg/L	Test	Approximate Conc. Range mg/L
Al	<75	Al	<500	Ammonia-N	<0.5	B (total)	<10
Ag	<10	As	<50	Nitrate-N	<0.5	Ca (total)	<50
As	<10	Ba	<500	Total Dissolved Nitrogen (TDN)	<0.5	K (total)	<50
Be	<10	Cd	<50	Orthophosphate-P (FRP)	<0.5	Mg (total)	<50
Cd	<10	Co	<50	TDP	<0.5	Na (total)	<100
Cr	<10	Cr	<50	Dissolved Organic Carbon (dNPOC)	<5	P (total)	<0.5
Cu	<10	Cu	<75	Bromide	<5	Alkalinity to pH 4.5 as $CaCO_3$	<100
Hg	<10	Fe	<1000	Chloride	<500	Chemical Oxygen Demand	
Mn	<10	Mn	<100	Fluoride	<5	Colour, apparent (Pt-Co units)	<50
Ni	<10	Mo	<50	Sulphate	<500	Total Hardness ($CaCO_3$)	<500
Pb	<10	Ni	<50			pH (at 25°C)	
Sb	<10	Pb	<50			Silica (as SiO_2)	<50
Se	<10	Sb	<50			Turbidity (NTU)	<5
Sn	<10	Se	<50			Total Solids at 103-105C	
Tl	<10	Sn	<50			SAMPLE S4 B unfiltered, autoclaved, frozen river water	
V	<10	U	<50			TKN	
Zn	<10	Zn	<100			Total Nitrogen	
						Total Organic Carbon (NPOC)	

- Report results as you would report to a client. Report the expanded measurement uncertainty associated with your analytical result.
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.

3.9 Interim Report

An interim report was emailed to participants on 20 June 2019.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for Total Elements

Summaries of test methods for total elements are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 6.

Table 1 Methodology for Total Elements (Part 1)

Lab Code	Method Reference
1	In House W32 - referencing APHA 3125
2	3051A
3	USEPA METHOD 3050B
5	Inhouse Methods referenced to USEPA6010, USEPA6020
6	APHA 3125
9	APHA 3120
10	In House
12	Digestion using USEPA. 1992 Method 3005A, Analysis USEPA 2001 Method 200.7, US EPA Method 200.8
14	Atomic Absorption- 600/4-79-020
15	In House
16	US EPA 200.8 APHA 3125B 22nd Edition 2012
17	APHA 3030E

Table 2 Methodology for Total Elements (Part 2)

Lab. Code	Sample Volume (mL)	Digestion Temp. (°C)	Digestion Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)	Additional Information
2	20	170	15	1	1	
3	50	85	120	1	1	
4		80	90	1.25	1.25	
5	10	95	90	0.2	0.3	
6	5	95	120	2	1	
8	30	95-100	90	2		
9	30	105	120	0.6		
10	10	95	120	0.2	0.5	
12	50	95	420	1	2.5	S1 and S2 were not digested
15	40	112.5	120	4	0	
16	10	100	60	0.5	0	
17	50	105	480	5		

4.2 Methodology for S3

Measurement methods and instrumental techniques used for the tests other than total elements in Samples S3 and S4 are presented in Appendix 7.

4.3 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 3).

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision*	Method Bias*	
1	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM Instrument calibration	Nordtest Report TR537
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM	NMI Uncertainty Course
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-SS Duplicate analyses	Recoveries of SS	Nata Technical Note 33
4	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples Duplicate analyses	CRM Instrument calibration	Nordtest Report TR537
5	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate analyses Instrument calibration	CRM Recoveries of SS Instrument calibration	Eurachem/CITAC Guide
6	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-CRM Duplicate analyses	CRM Laboratory bias from PT studies Standard Purity	Nata Technical Note 33
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM	Nata Technical Note 33
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples-RM Duplicate analysis	CRM Recoveries of SS	Nordtest Report TR537
9	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-RM Duplicate analysis	Recoveries of SS	Nata Technical Note 33
10	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples-CRM Duplicate analyses Instrument Calibration	CRM Recoveries of SS Laboratory bias from PT studies Instrument calibration	Nata Technical Note 33
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM Recoveries of SS	Nata Technical Note 33
14	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples Duplicate analyses Instrument Calibration	Laboratory bias from PT studies Instrument calibration Standard purity	IANZ Technical guide
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-CRM Duplicate analyses Instrument Calibration	CRM Instrument calibration Recoveries of SS	Nata Technical Note 33
16	Top Down - precision and estimates of the method and laboratory bias	Duplicate analyses		Eurachem/CITAC Guide
17	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate analyses	CRM Recoveries of SS	ISO/GUM

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

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

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Participants' comments are reproduced in Table 4.

Table 4 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
The preservation acid mixture for mercury in sample S1 is quite different to that recommended for techniques such as CV-AFS where bromine chloride is regularly used. For this reason we did not test for mercury.	This preservation procedure for Hg in fresh water: 2%HNO_3, 0.01%HCl in HDPE container is based on a peer reviewed paper published in Analytical Methods in 2012. This preservation procedure was validated through a series of previous trials, a full stability study and through previous PT studies using various techniques including CV-AFS,. In present study a good agreement was found between results from CV-AFS technique, robust average and spike value. Other participants are invited to comment.
The preservation acids listed on the label of Bottle 2 are different to that listed in the documentation accompanying the samples, i.e. paperwork is 2% (v/w) HNO3 and bottle label is 2% (v/w) HNO3 and 0.01% HCl	The sample was preserved in 2% HNO_3 and 0.01% HCL. We attempt to give our participants as much value as possible for their money. In this study we have included 61 tests: there is a lot of information included in our studies details. Although we have a review process in place some errors may still occur. We encourage our participants to contact us when they have questions/requests regarding the present study or any study. "Questions about the study may be included on the sample received form. Alternately please contact me by email." We will try our best to avoid these types of errors in the future. We apologise for the inconvenience caused.
For Free Reactive Phosphorus, I am assuming that the units in the box in Sample S3 are orthophosphate as P. These are the units on the documentation accompanying the samples.	Free reactive phosphorus is a measure of orthophosphate-P. In the sample out letter the request is orthophosphate-P (FRP) while in the results form the request is for free reactive phosphorus (FRP). Thank you for your feedback we will be more consistent with our terminology for laboratories that are not familiar with this terminology. Participants are encouraged to contact the study coordinator if they have questions.
Reactive Silica should be measured on Filtered sample. Measuring Si in the unfiltered sample can cause blockage in the FIA system and also the data may not be very useful.	Participants are advised to treat the PT samples as a normal sample. The sample was filtered through a coarse filter. This not only helps us with achieving sample homogeneity but also prevents particles from getting to the instrument. This preparation procedure was validated in previous trials and through previous PT studies. If you experienced blockages in FIA system these are more likely from the samples run in the same batch with the PT sample.
Don't call samples 4A and 4B, just call them sample 4. Calling them separate names can confuse staff into thinking that each sample is to be tested individually for all tests required for sample 4.	Clear instructions were provided in the dispatch letter. Different tests were requested to be performed in the two containers labelled S4A and S4B.
Thank You for making me part of this proficiency study. I was not able to conduct most of the heavy metal testing (Na, K, Mg, Ni, Cr) due to issues with our AAS with decreasing weave length. I'm interested in many more proficiency tests in future to validate our methods and hopefully get the lab ISO certified.	Our next study will be in seawater and it will be run in October.
Would be great to have separate analysis for TSS and TDS and not just TS; have sample for dissolved Ca, K, Na, Mg, have sample for EC analysis	Thank you for your feedback! It is our attempt to include samples in our PT that covers all laboratories' needs.
Sample would have been more useful to us with a minimum value of 100ug/L for all parameters.	

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 5 to 65 with resultant summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 62.

An example chart with interpretation guide is shown in Figure 1.

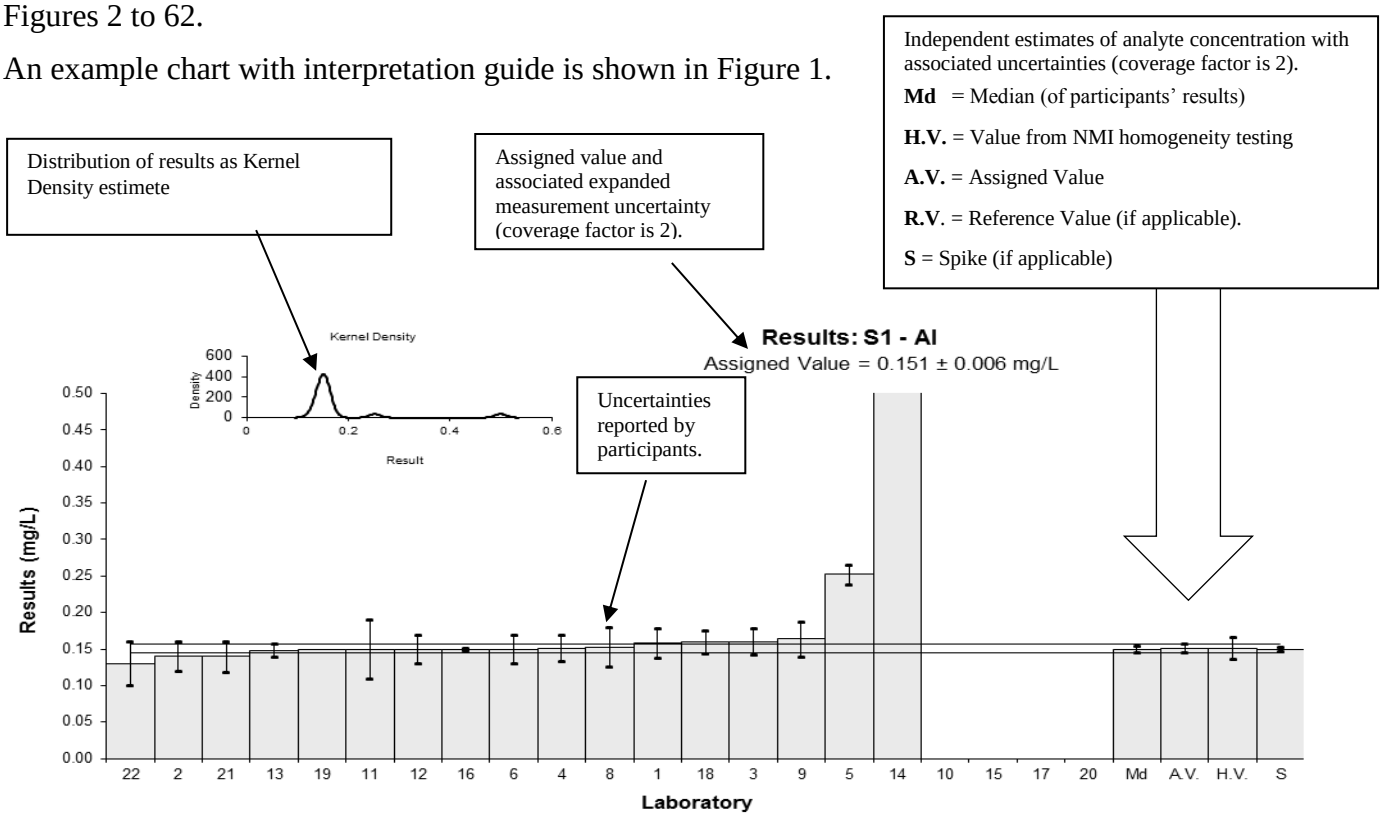


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

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

5.3 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'.[8]

5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2015(E).[8]

5.5 Target Standard Deviation

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

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

This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value. 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.[9] By setting a fixed and realistic value for PCV, the participant's performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 z-Score

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

For each participant's result a z-score is calculated according to Equation 2 below:

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

where:

- z is z-score
- χ is participant result
- X is the study assigned value
- σ is the target standard deviation from Equation 1

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

- $|z| \leq 2$ is satisfactory;
- $2 < |z| < 3$ is questionable;
- $|z| \geq 3$ is unsatisfactory.

5.7 E_n-Score

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

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

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

where:

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

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

- $|E_n| \leq 1$ is satisfactory;
- $|E_n| > 1$ is unsatisfactory.

5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[10] 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.[11]

6 TABLES AND FIGURES

Table 5

Sample Details

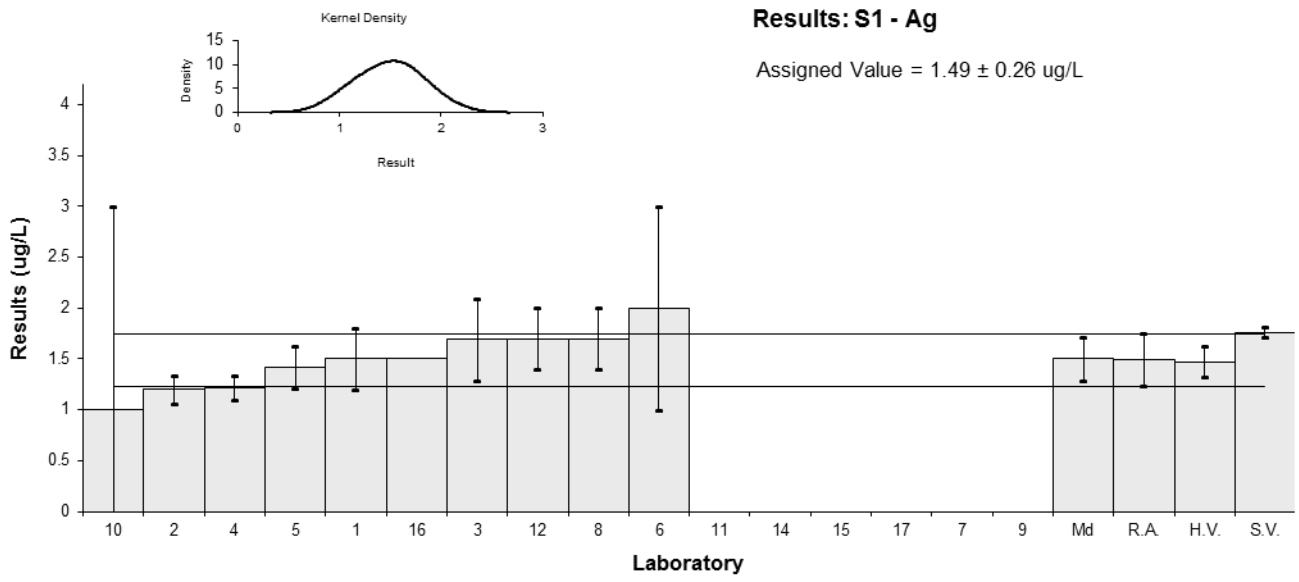
Sample No.	S1
Matrix.	River Water
Analyte.	Ag
Units	ug/L

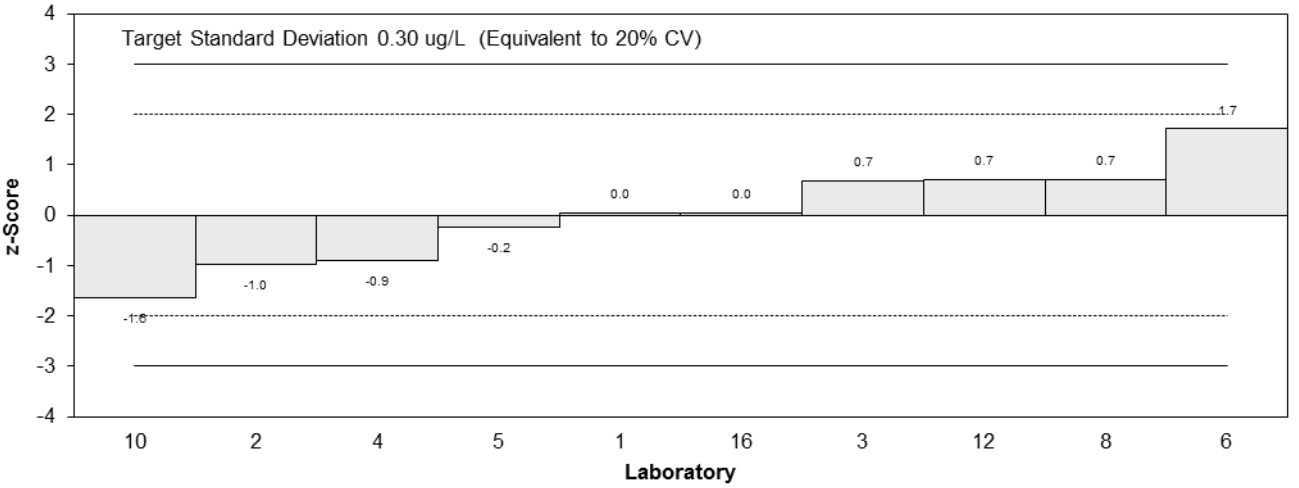
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.5	0.3	0.03	0.03
2	1.2	0.14	-0.97	-0.98
3	1.69	0.4	0.67	0.42
4	1.22	0.12	-0.91	-0.94
5	1.42	0.21	-0.23	-0.21
6	2	1	1.71	0.49
7	NT	NT		
8	1.7	0.3	0.70	0.53
9	NT	NT		
10	1	2	-1.64	-0.24
11	NT	NT		
12	1.7	0.3	0.70	0.53
14	NT	NT		
15	NT	NT		
16	1.5	NR	0.03	0.04
17	NT	NT		

Statistics

Assigned Value	1.49	0.26
Spike	1.76	0.05
Homogeneity Value	1.47	0.15
Robust Average	1.49	0.26
Median	1.50	0.21
Mean	1.49	
N	10	
Max.	2	
Min.	1	
Robust SD	0.33	
Robust CV	22%	


Kernel Density
Density
Result
Results: S1 - Ag
Assigned Value = 1.49 ± 0.26 ug/L
Results (ug/L)
10 2 4 5 1 16 3 12 8 6 11 14 15 17 7 9 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Ag
Target Standard Deviation 0.30 ug/L (Equivalent to 20% CV)
z-Score
-1.6 -1.0 -0.9 -0.2 0.0 0.0 0.7 0.7 0.7 1.7
10 2 4 5 1 16 3 12 8 6
Laboratory

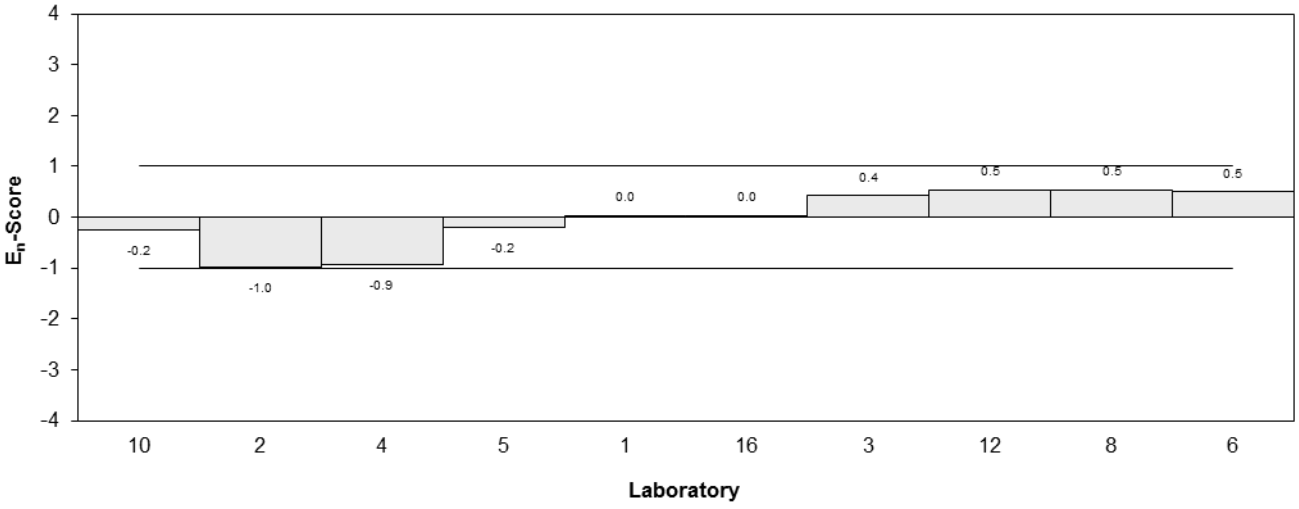

En-Scores: S1 - Ag
En-Score
-0.2 -1.0 -0.9 -0.2 0.0 0.0 0.4 0.5 0.5 0.5
10 2 4 5 1 16 3 12 8 6
Laboratory

Figure 2

Table 6

Sample Details

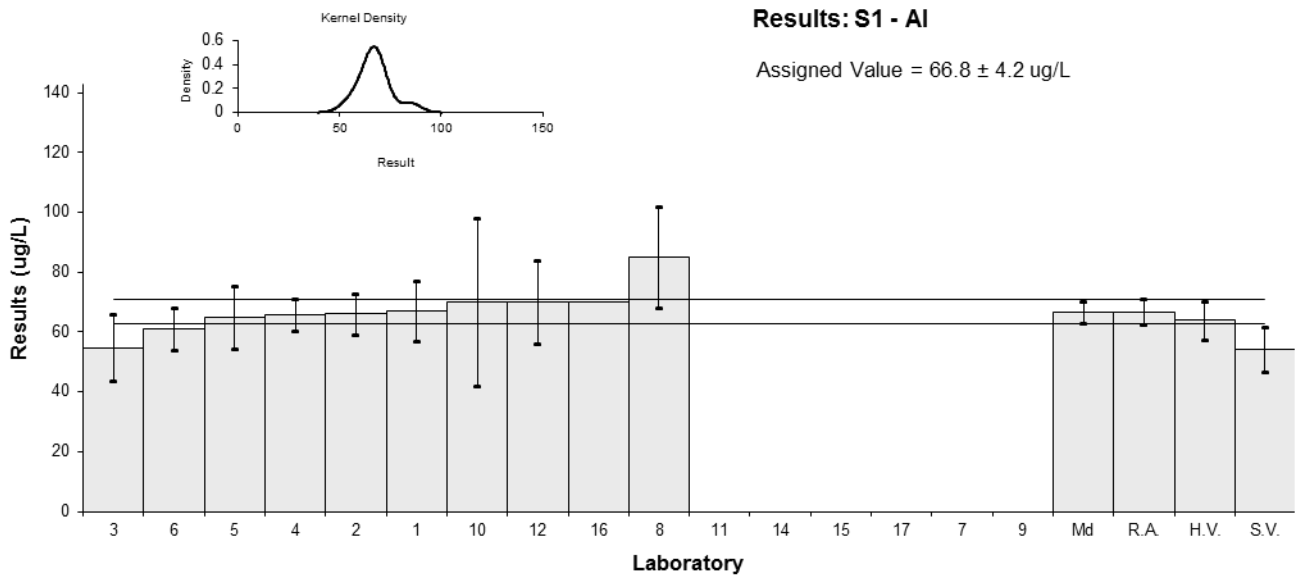
Sample No.	S1
Matrix.	River Water
Analyte.	Al
Units	ug/L

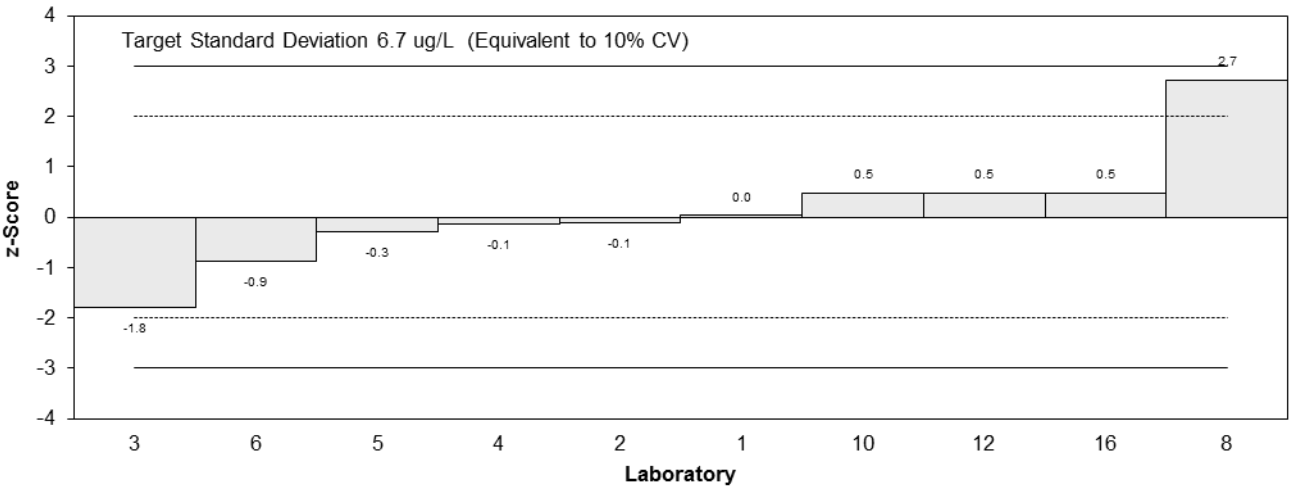
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	67	10	0.03	0.02
2	66	6.9	-0.12	-0.10
3	54.8	11	-1.80	-1.02
4	65.9	5.3	-0.13	-0.13
5	64.8	10.5	-0.30	-0.18
6	61	7	-0.87	-0.71
7	NT	NT		
8	85	17	2.72	1.04
9	NT	NT		
10	70	28	0.48	0.11
11	NT	NT		
12	70	14	0.48	0.22
14	NT	NT		
15	NT	NT		
16	70	NR	0.48	0.76
17	NT	NT		

Statistics

Assigned Value	66.8	4.2
Spike	54.3	7.4
Homogeneity Value	64.0	6.4
Robust Average	66.8	4.2
Median	66.5	3.7
Mean	67.5	
N	10	
Max.	85	
Min.	54.8	
Robust SD	5.3	
Robust CV	7.9%	


Kernel Density
Density
Result
Results: S1 - Al
Assigned Value = 66.8 ± 4.2 ug/L
Results (ug/L)
Laboratory
3 6 5 4 2 1 10 12 16 8 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Al
Target Standard Deviation 6.7 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
3 6 5 4 2 1 10 12 16 8
-1.8 -0.9 -0.3 -0.1 -0.1 0.0 0.5 0.5 0.5 2.7

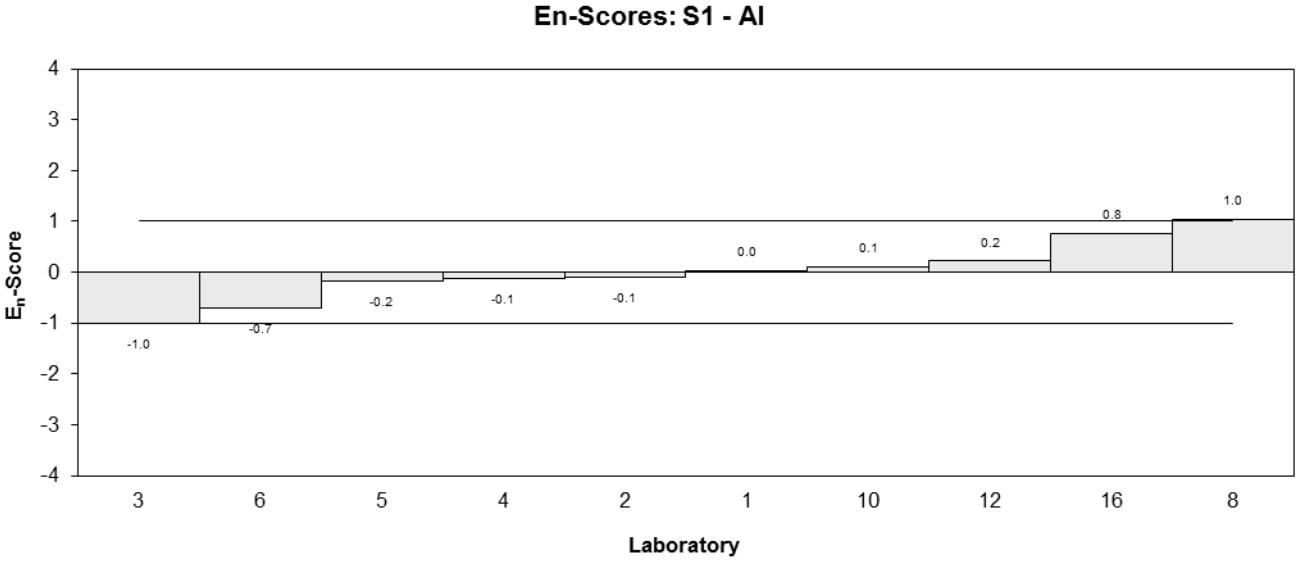

En-Scores: S1 - Al
En-Score
Laboratory
3 6 5 4 2 1 10 12 16 8
-1.0 -0.7 -0.2 -0.1 -0.1 0.0 0.1 0.2 0.8 1.0

Figure 3

Table 7

Sample Details

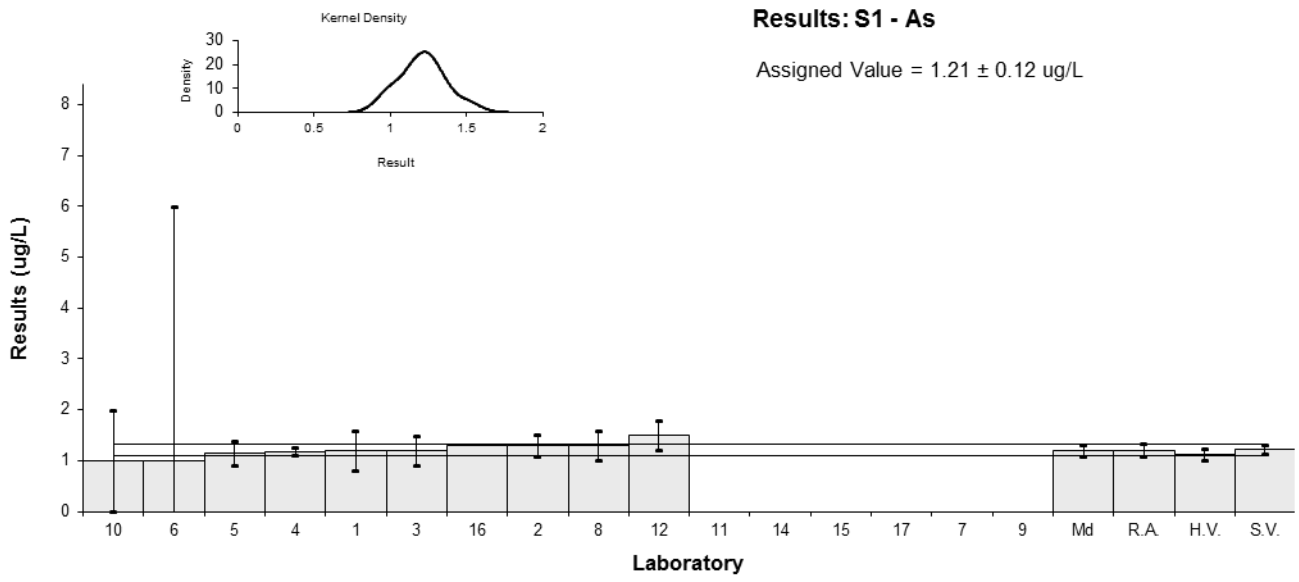
Sample No.	S1
Matrix.	River Water
Analyte.	As
Units	ug/L

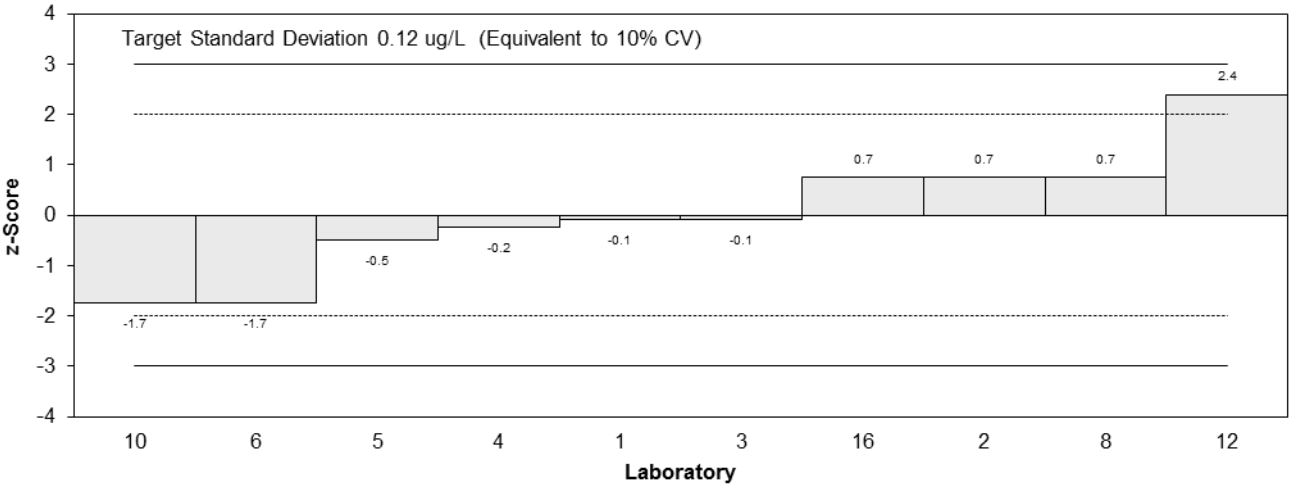
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.2	0.4	-0.08	-0.02
2	1.3	0.22	0.74	0.36
3	1.20	0.3	-0.08	-0.03
4	1.18	0.07	-0.25	-0.22
5	1.15	0.23	-0.50	-0.23
6	1	5	-1.74	-0.04
7	NT	NT		
8	1.3	0.3	0.74	0.28
9	NT	NT		
10	1	1	-1.74	-0.21
11	NT	NT		
12	1.5	0.3	2.40	0.90
14	NT	NT		
15	NT	NT		
16	1.3	NR	0.74	0.75
17	NT	NT		

Statistics

Assigned Value	1.21	0.12
Spike	1.22	0.09
Homogeneity Value	1.13	0.11
Robust Average	1.21	0.12
Median	1.20	0.11
Mean	1.21	
N	10	
Max.	1.5	
Min.	1	
Robust SD	0.16	
Robust CV	13%	


Kernel Density
Density
Result
Results: S1 - As
Assigned Value = 1.21 ± 0.12 ug/L
Results (ug/L)
Laboratory
10 6 5 4 1 3 16 2 8 12 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - As
Target Standard Deviation 0.12 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
10 6 5 4 1 3 16 2 8 12
-1.7 -1.7 -0.5 -0.2 -0.1 -0.1 0.7 0.7 0.7 2.4

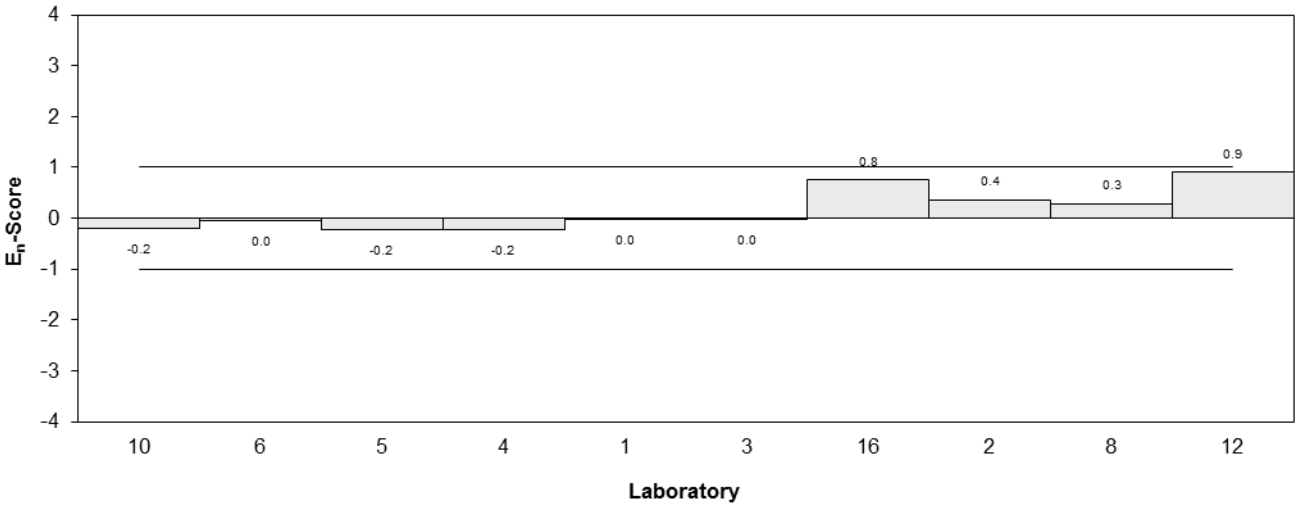

En-Scores: S1 - As
En-Score
Laboratory
10 6 5 4 1 3 16 2 8 12
-0.2 0.0 -0.2 -0.2 0.0 0.0 0.8 0.4 0.3 0.9

Figure 4

Table 8

Sample Details

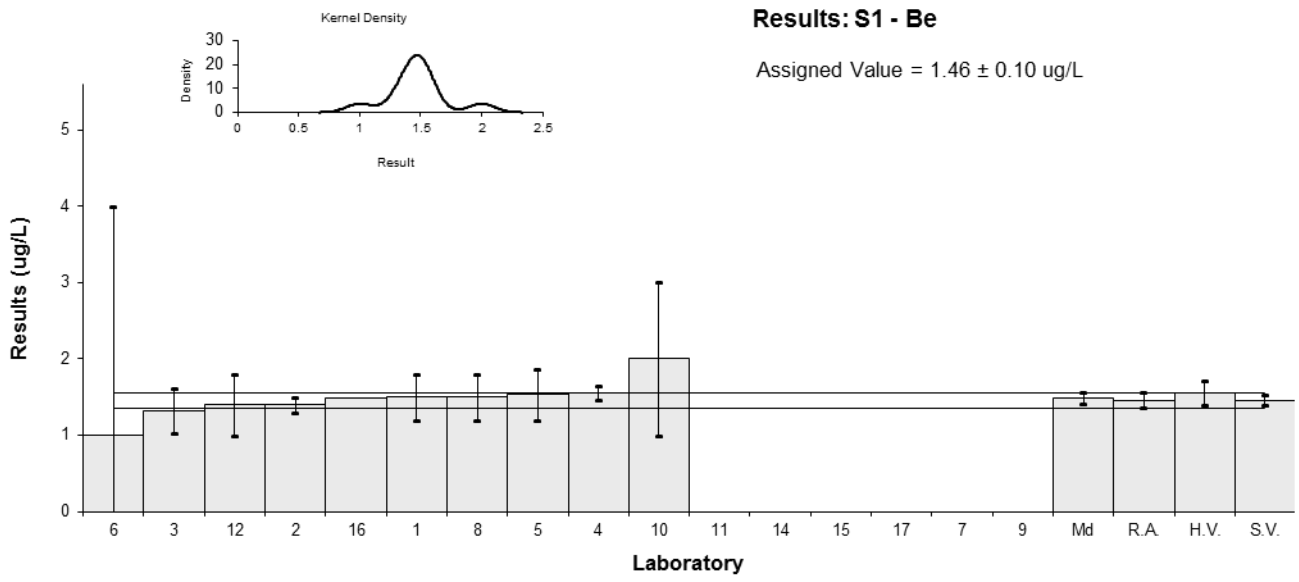
Sample No.	S1
Matrix.	River Water
Analyte.	Be
Units	ug/L

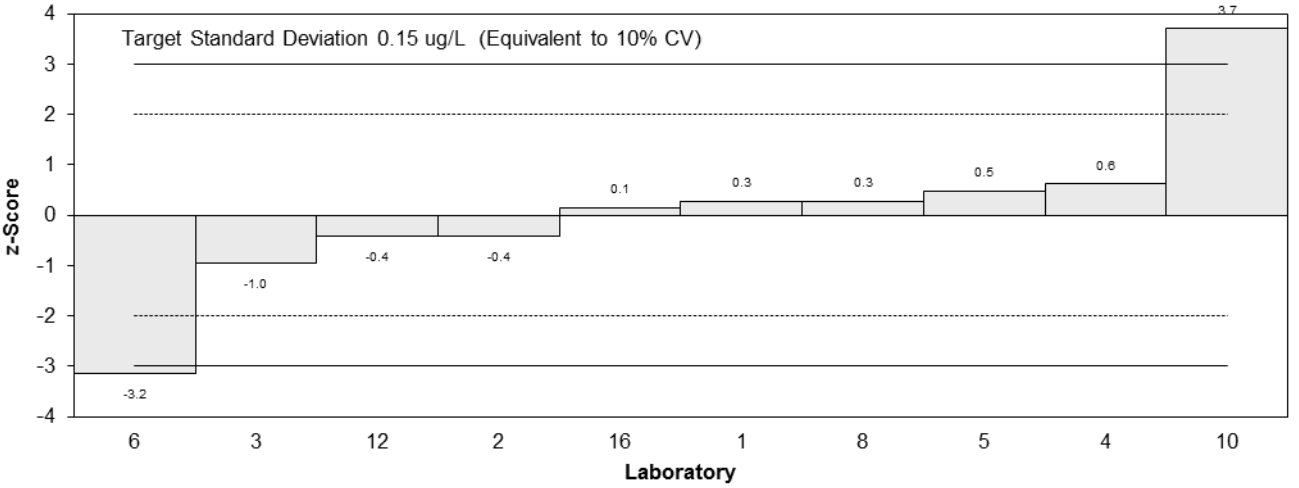
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.5	0.3	0.27	0.13
2	1.4	0.1	-0.41	-0.42
3	1.32	0.3	-0.96	-0.44
4	1.55	0.09	0.62	0.67
5	1.53	0.33	0.48	0.20
6	1	3	-3.15	-0.15
7	NT	NT		
8	1.5	0.3	0.27	0.13
9	NT	NT		
10	2	1	3.70	0.54
11	NT	NT		
12	1.4	0.4	-0.41	-0.15
14	NT	NT		
15	NT	NT		
16	1.48	NR	0.14	0.20
17	NT	NT		

Statistics

Assigned Value	1.46	0.10
Spike	1.46	0.07
Homogeneity Value	1.55	0.16
Robust Average	1.46	0.10
Median	1.49	0.08
Mean	1.47	
N	10	
Max.	2	
Min.	1	
Robust SD	0.13	
Robust CV	8.9%	


Kernel Density
Density
Result
Results: S1 - Be
Assigned Value = 1.46 ± 0.10 ug/L
Results (ug/L)
Laboratory
6 3 12 2 16 1 8 5 4 10 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Be
Target Standard Deviation 0.15 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
6 3 12 2 16 1 8 5 4 10
-3.2 -1.0 -0.4 -0.4 0.1 0.3 0.3 0.5 0.6 3.7

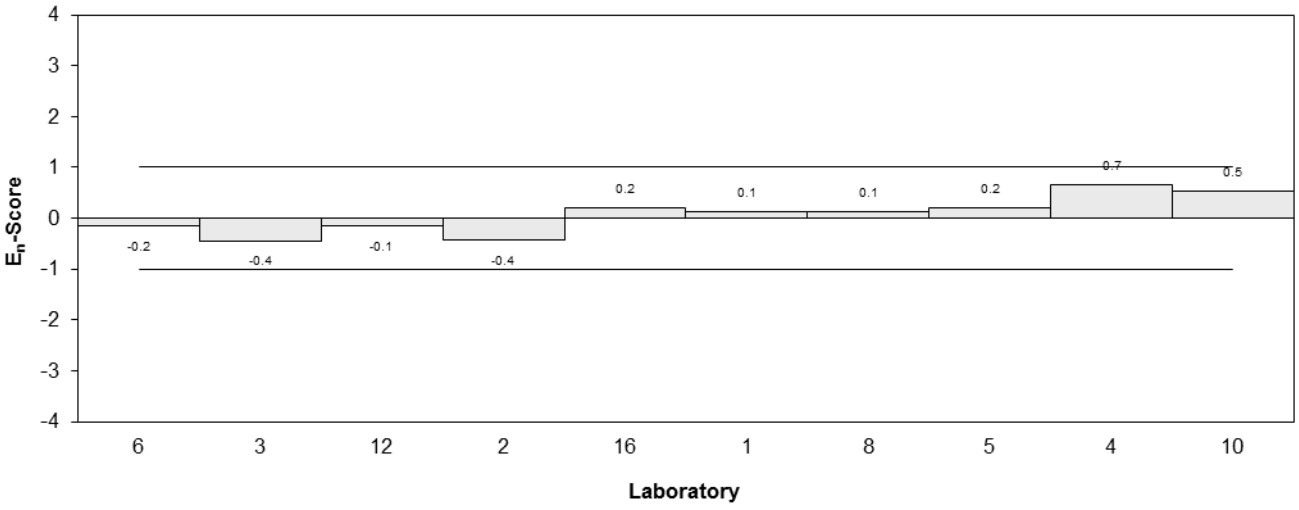

En-Scores: S1 - Be
En-Score
Laboratory
6 3 12 2 16 1 8 5 4 10
-0.2 -0.4 -0.1 -0.4 0.2 0.1 0.1 0.2 0.7 0.5

Figure 5

Table 9

Sample Details

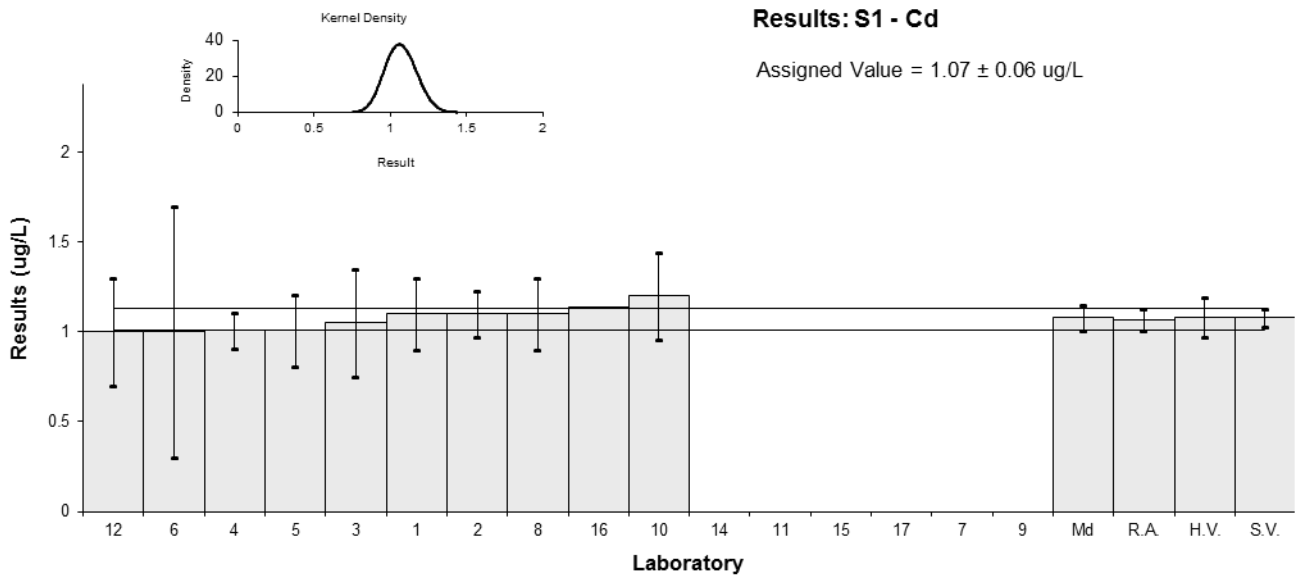
Sample No.	S1
Matrix.	River Water
Analyte.	Cd
Units	ug/L

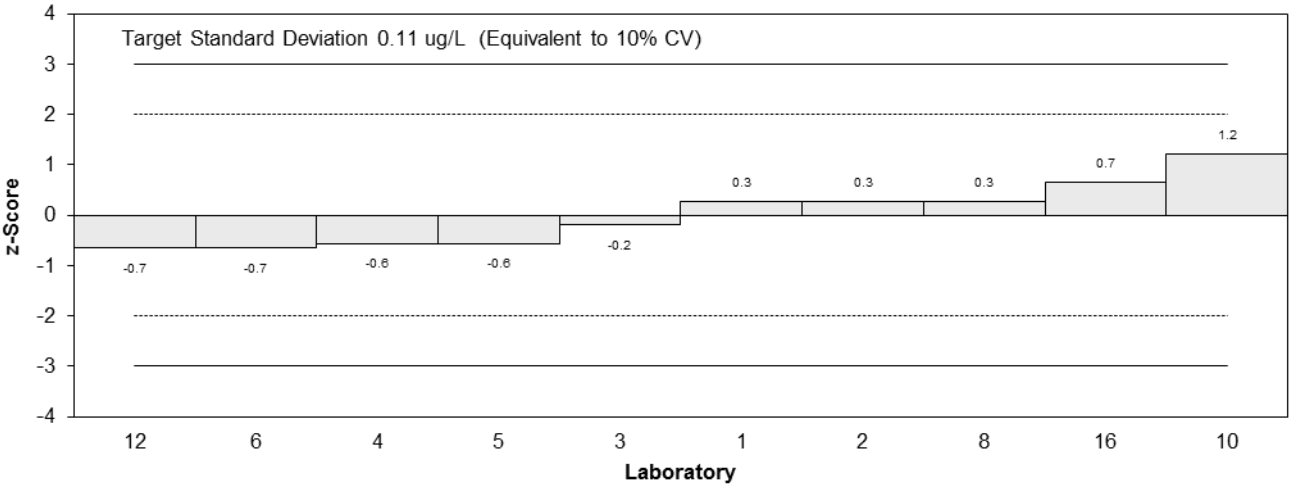
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.1	0.2	0.28	0.14
2	1.1	0.13	0.28	0.21
3	1.05	0.3	-0.19	-0.07
4	1.01	0.10	-0.56	-0.51
5	1.01	0.20	-0.56	-0.29
6	1	0.7	-0.65	-0.10
7	NT	NT		
8	1.1	0.2	0.28	0.14
9	NT	NT		
10	1.2	0.24	1.21	0.53
11	NT	NT		
12	1.0	0.3	-0.65	-0.23
14	<0.01	0.05		
15	NT	NT		
16	1.14	NR	0.65	1.17
17	NT	NT		

Statistics

Assigned Value	1.07	0.06
Spike	1.08	0.05
Homogeneity Value	1.08	0.11
Robust Average	1.07	0.06
Median	1.08	0.07
Mean	1.07	
N	10	
Max.	1.2	
Min.	1	
Robust SD	0.07	
Robust CV	6.5%	


Kernel Density
Density
Result
Results: S1 - Cd
Assigned Value = 1.07 ± 0.06 ug/L
Results (ug/L)
12 6 4 5 3 1 2 8 16 10 14 11 15 17 7 9 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Cd
Target Standard Deviation 0.11 ug/L (Equivalent to 10% CV)
z-Score
-0.7 -0.7 -0.6 -0.6 -0.2 0.3 0.3 0.3 0.7 1.2
12 6 4 5 3 1 2 8 16 10
Laboratory

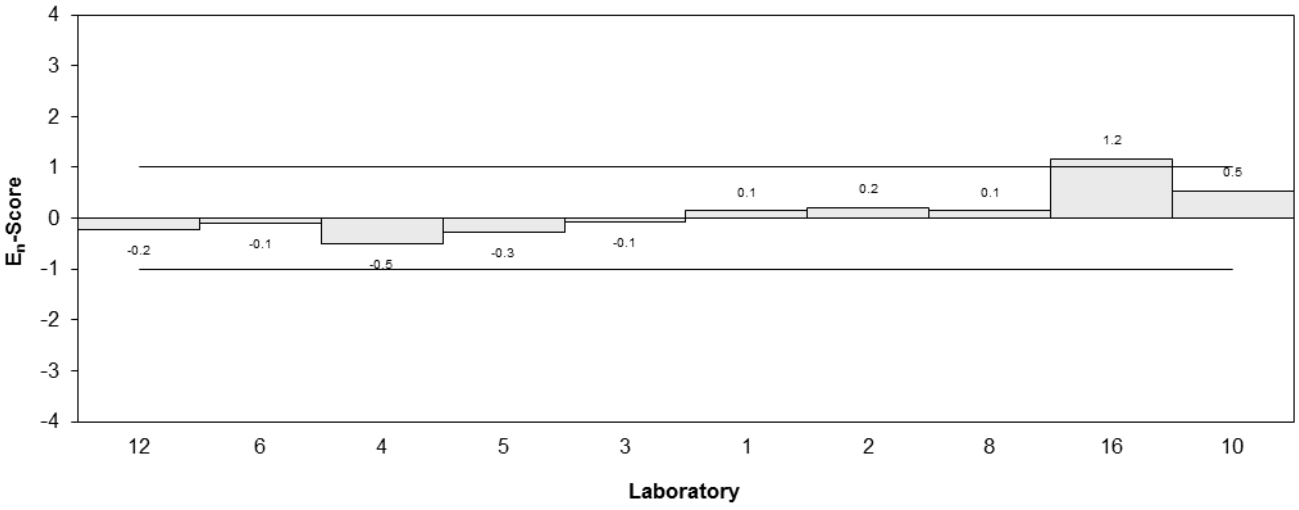

En-Scores: S1 - Cd
En-Score
-0.2 -0.1 -0.5 -0.3 -0.1 0.1 0.2 0.1 1.2 0.5
12 6 4 5 3 1 2 8 16 10
Laboratory

Figure 6

Table 10

Sample Details

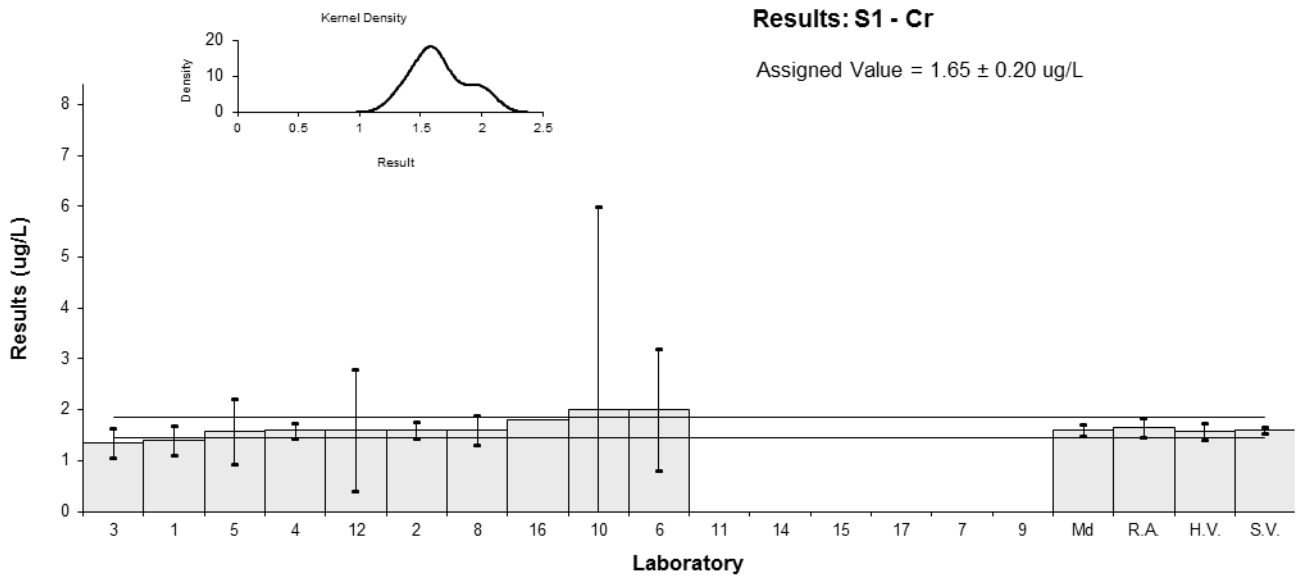
Sample No.	S1
Matrix.	River Water
Analyte.	Cr
Units	ug/L

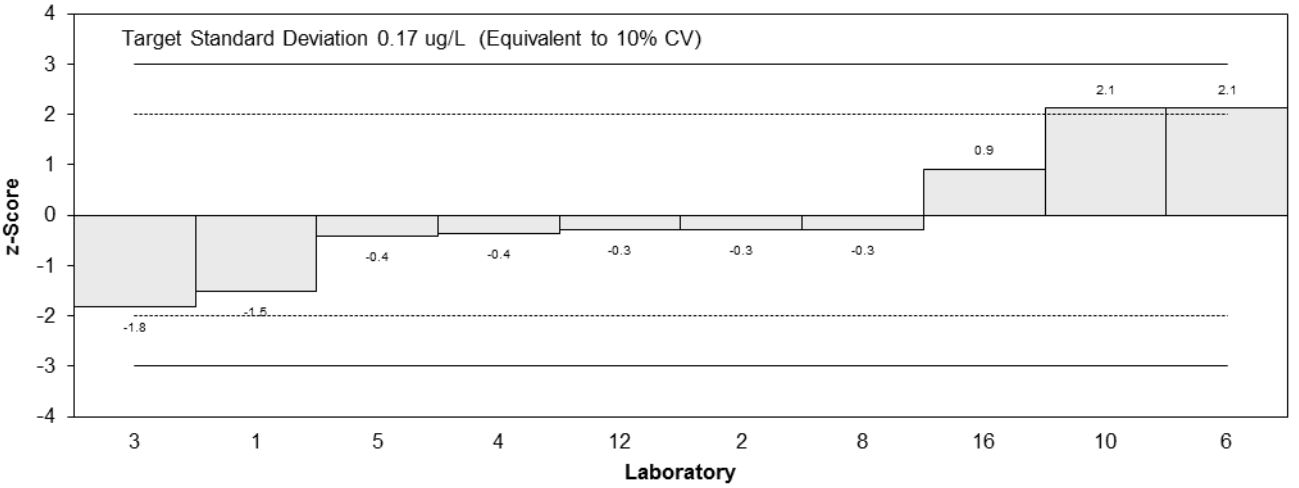
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.3	-1.52	-0.69
2	1.6	0.17	-0.30	-0.19
3	1.35	0.3	-1.82	-0.83
4	1.59	0.15	-0.36	-0.24
5	1.58	0.64	-0.42	-0.10
6	2	1.2	2.12	0.29
7	NT	NT		
8	1.6	0.3	-0.30	-0.14
9	NT	NT		
10	2	4	2.12	0.09
11	NT	NT		
12	1.6	1.2	-0.30	-0.04
14	NT	NT		
15	NT	NT		
16	1.8	NR	0.91	0.75
17	NT	NT		

Statistics

Assigned Value	1.65	0.20
Spike	1.60	0.07
Homogeneity Value	1.58	0.16
Robust Average	1.65	0.20
Median	1.60	0.12
Mean	1.65	
N	10	
Max.	2	
Min.	1.35	
Robust SD	0.25	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - Cr
Assigned Value = 1.65 ± 0.20 ug/L
Results (ug/L)
Laboratory
3 1 5 4 12 2 8 16 10 6 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Cr
Target Standard Deviation 0.17 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
3 1 5 4 12 2 8 16 10 6
-1.8 -1.5 -0.4 -0.4 -0.3 -0.3 -0.3 0.9 2.1 2.1

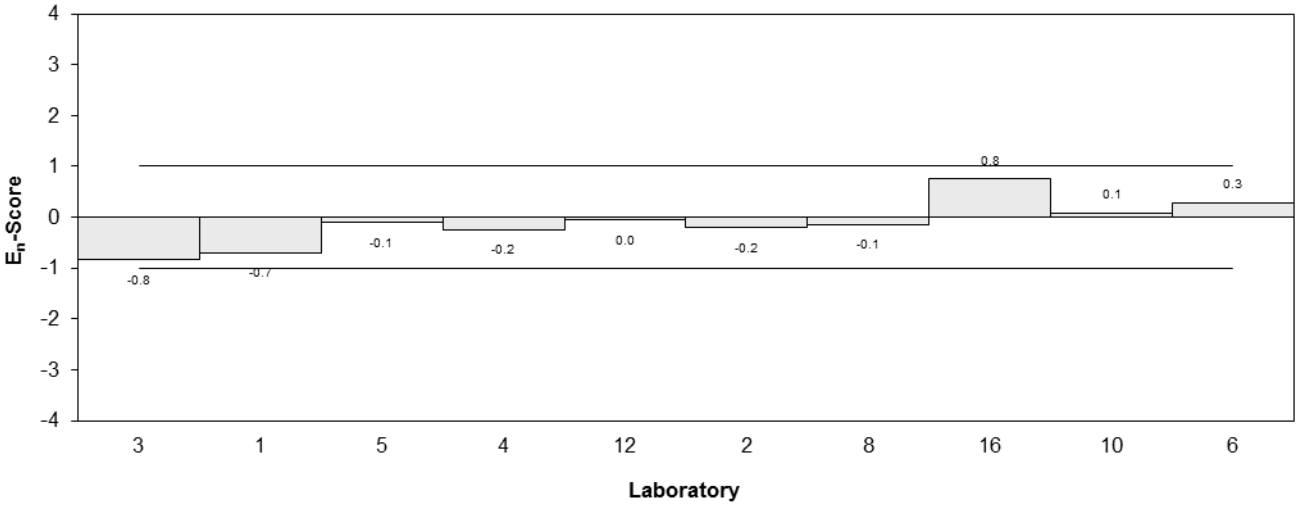

En-Scores: S1 - Cr
En-Score
Laboratory
3 1 5 4 12 2 8 16 10 6
-0.8 -0.7 -0.1 -0.2 0.0 -0.2 -0.1 0.8 0.1 0.3

Figure 7

Table 11

Sample Details

Sample No.	S1
Matrix.	River Water
Analyte.	Cu
Units	ug/L

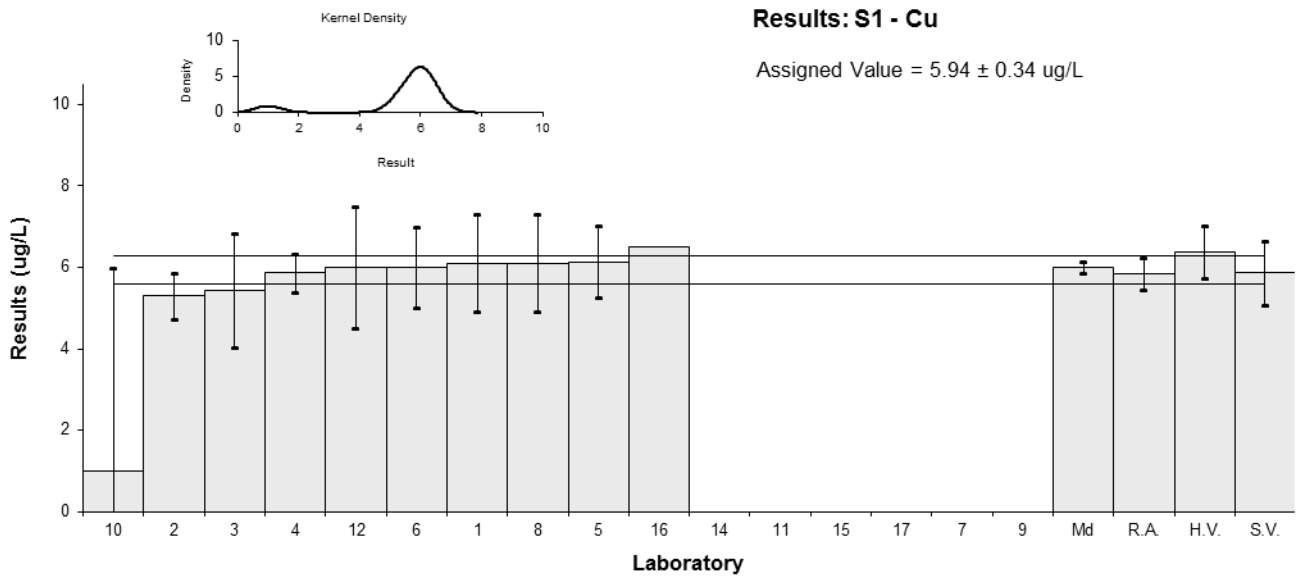
Participant Results

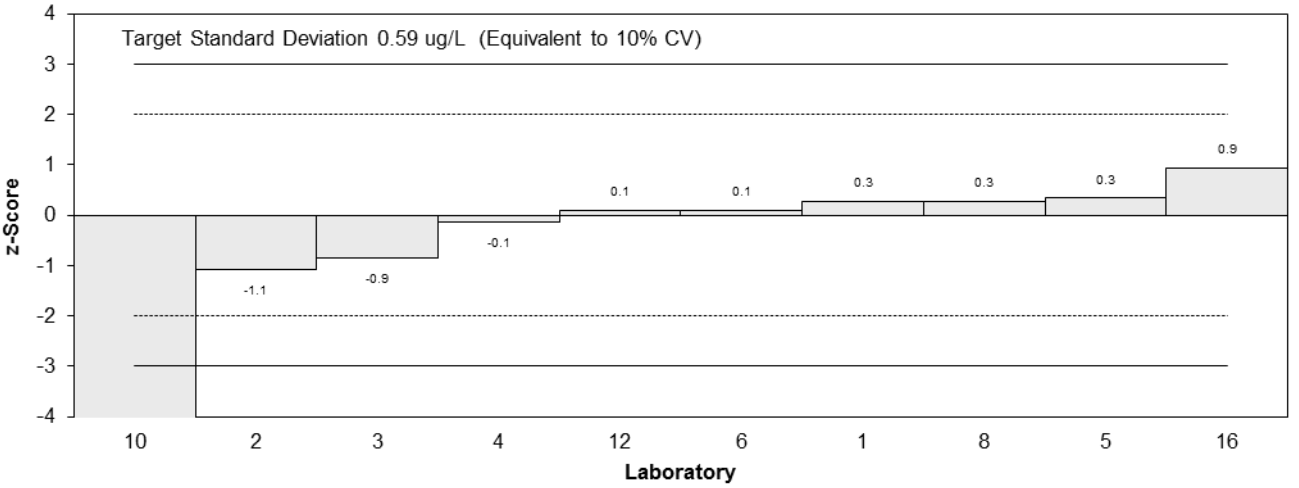
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	6.1	1.2	0.27	0.13
2	5.3	0.56	-1.08	-0.98
3	5.43	1.4	-0.86	-0.35
4	5.86	0.46	-0.13	-0.14
5	6.14	0.89	0.34	0.21
6	6	1	0.10	0.06
7	NT	NT		
8	6.1	1.2	0.27	0.13
9	NT	NT		
10	1	5	-8.32	-0.99
11	NT	NT		
12	6.0	1.5	0.10	0.04
14	<0.01	0.05		
15	NT	NT		
16	6.5	NR	0.94	1.65
17	NT	NT		

Statistics

Assigned Value*	5.94	0.34
Spike	5.86	0.78
Homogeneity Value	6.37	0.64
Robust Average	5.85	0.39
Median	6.00	0.15
Mean	5.44	
N	10	
Max.	6.5	
Min.	1	
Robust SD	0.41	
Robust CV	7%	

* Robust Average excluding Laboratory 10.


Kernel Density
Density
Result
Results: S1 - Cu
Assigned Value = 5.94 ± 0.34 ug/L
Results (ug/L)
Laboratory
10 2 3 4 12 6 1 8 5 16 14 11 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Cu
Target Standard Deviation 0.59 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
10 2 3 4 12 6 1 8 5 16
-1.1 -0.9 -0.1 0.1 0.1 0.3 0.3 0.3 0.9

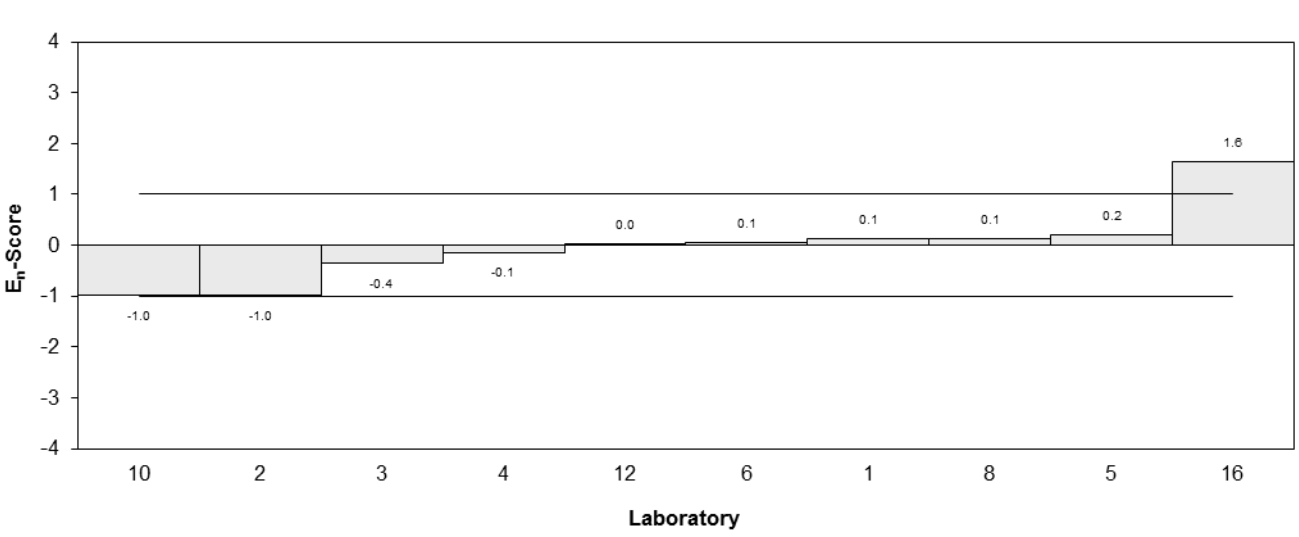

En-Scores: S1 - Cu
En-Score
Laboratory
10 2 3 4 12 6 1 8 5 16
-1.0 -1.0 -0.4 -0.1 0.0 0.1 0.1 0.1 0.2 1.6

Figure 8

Table 12

Sample Details

Sample No.	S1
Matrix.	River Water
Analyte.	Hg
Units	ug/L

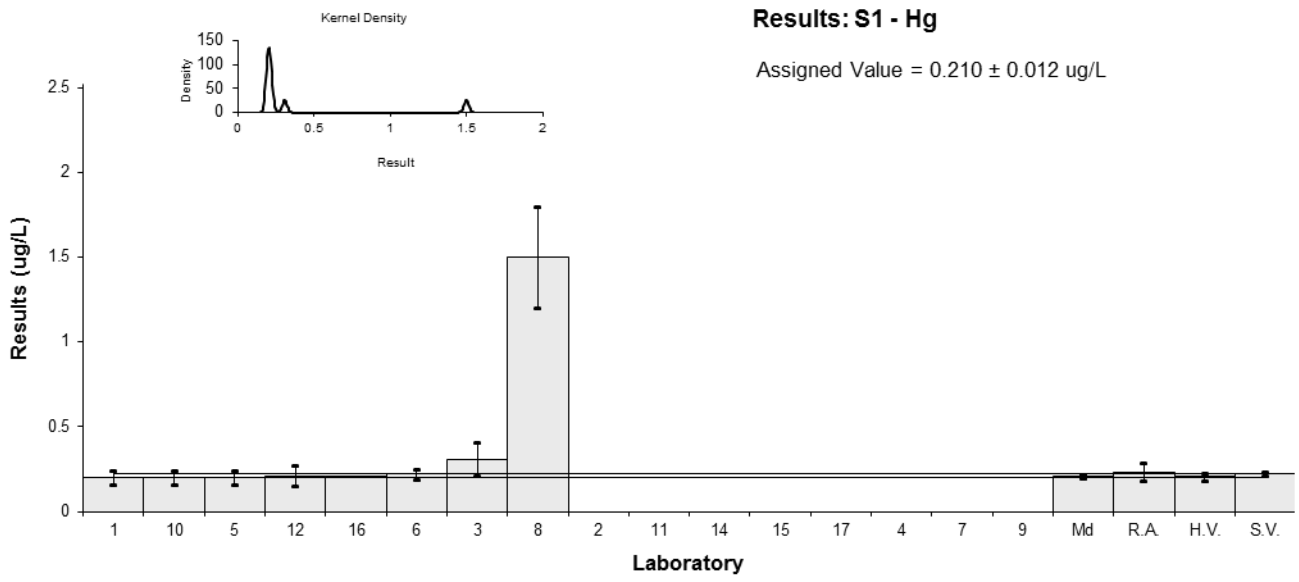
Participant Results

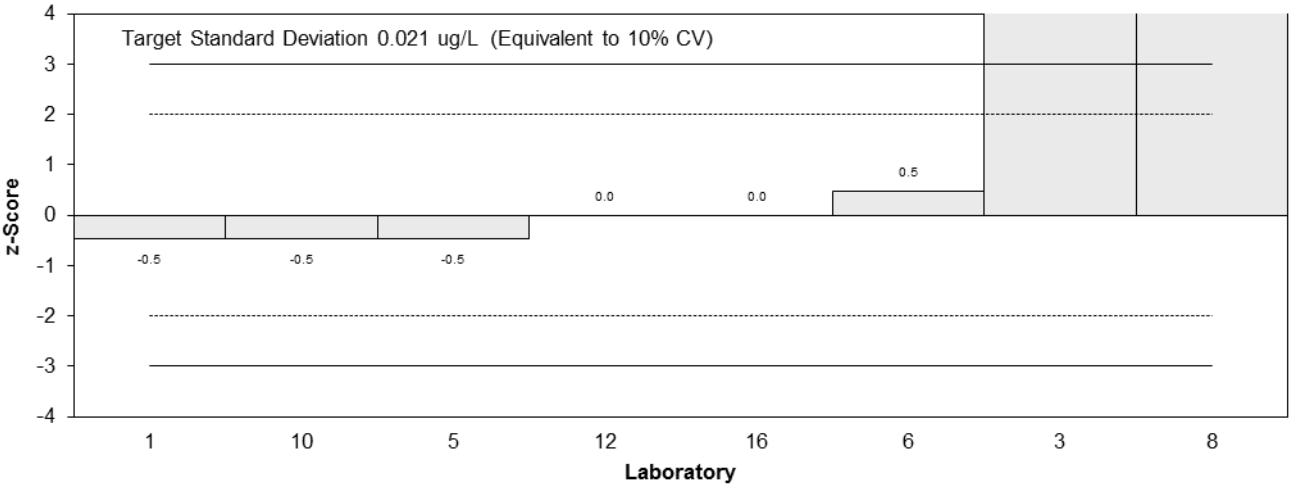
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.2	0.04	-0.48	-0.24
2	<0.1	NR		
3	0.31	0.1	4.76	0.99
4	NT	NT		
5	0.20	0.04	-0.48	-0.24
6	0.22	0.03	0.48	0.31
7	NT	NT		
8	1.5	0.3	61.43	4.30
9	NT	NT		
10	0.2	0.04	-0.48	-0.24
11	NT	NT		
12	0.21	0.06	0.00	0.00
14	NT	NT		
15	NT	NT		
16	0.21	NR	0.00	0.00
17	NT	NT		

Statistics

Assigned Value*	0.210	0.012
Spike	0.225	0.011
Homogeneity Value	0.205	0.021
Robust Average	0.234	0.051
Median	0.210	0.012
Mean	0.381	
N	8	
Max.	1.5	
Min.	0.2	
Robust SD	0.013	
Robust CV	5.6%	

* Robust Average excluding Laboratory 8.


Kernel Density
Density
Result
Results: S1 - Hg
Assigned Value = 0.210 ± 0.012 ug/L
Results (ug/L)
Laboratory
1 10 5 12 16 6 3 8 2 11 14 15 17 4 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Hg
Target Standard Deviation 0.021 ug/L (Equivalent to 10% CV)
z-Score
-0.5 -0.5 -0.5 0.0 0.0 0.5
Laboratory
1 10 5 12 16 6 3 8

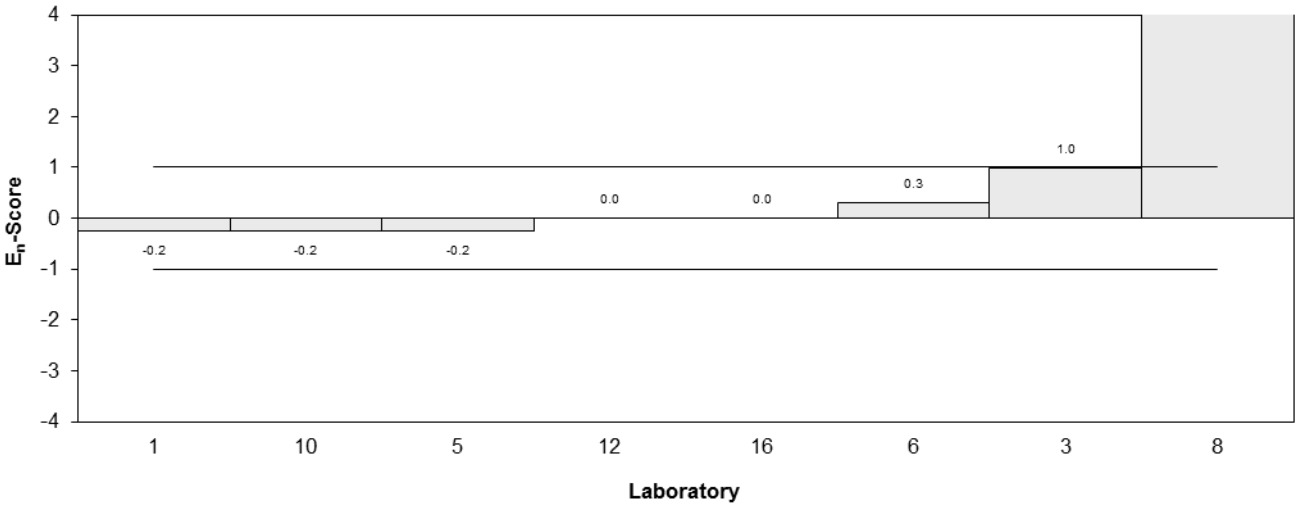

En-Scores: S1 - Hg
En-Score
-0.2 -0.2 -0.2 0.0 0.0 0.3 1.0
Laboratory
1 10 5 12 16 6 3 8

Figure 9

Table 13

Sample Details

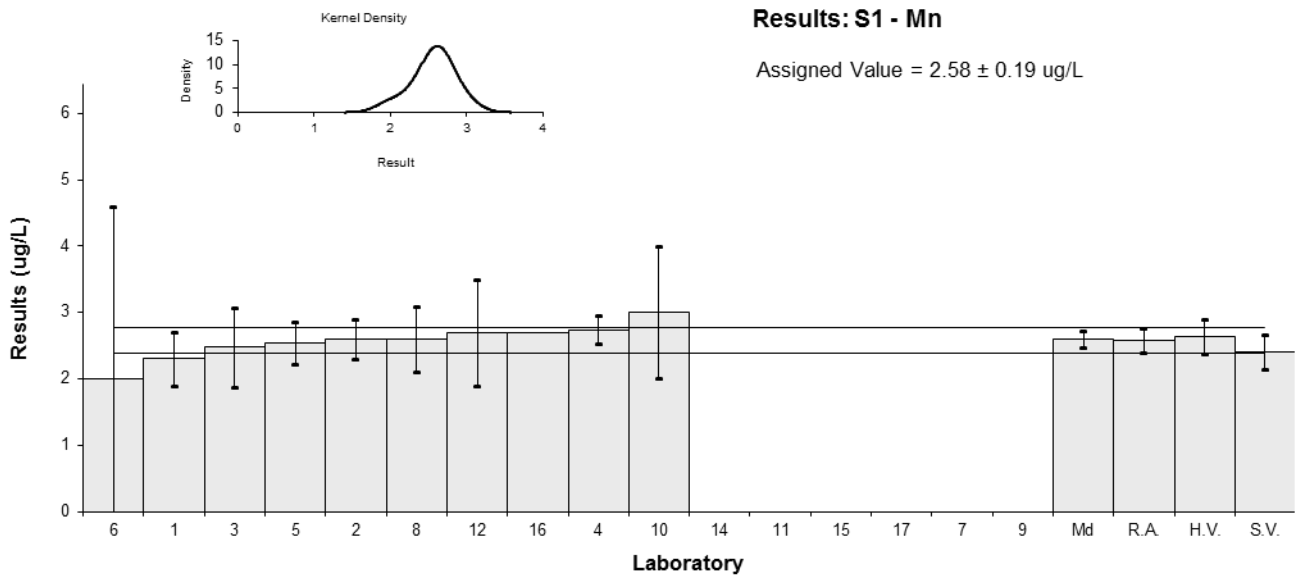
Sample No.	S1
Matrix.	River Water
Analyte.	Mn
Units	ug/L

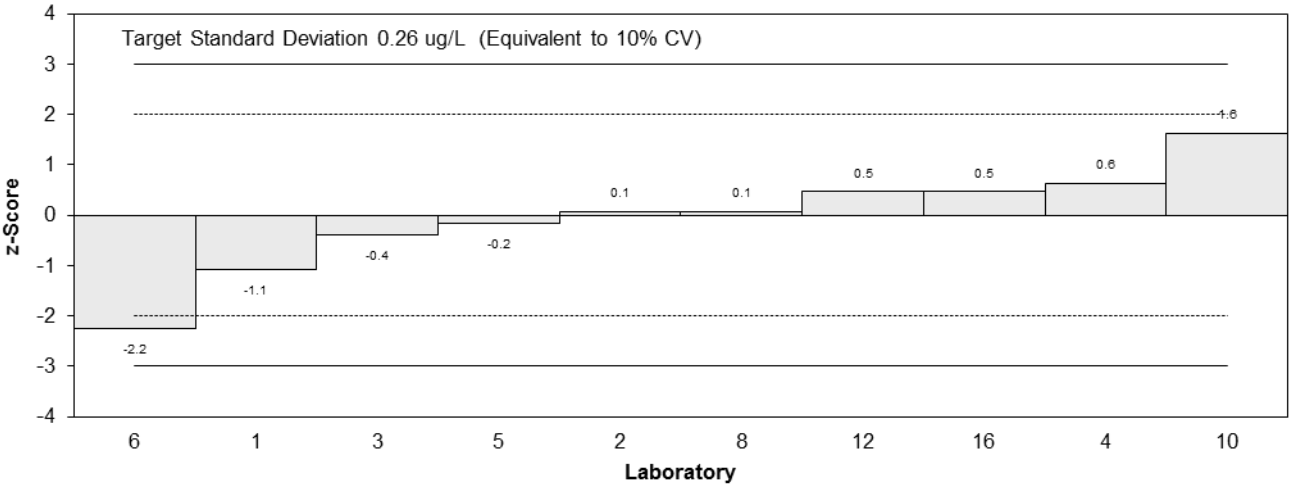
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.3	0.4	-1.09	-0.63
2	2.6	0.3	0.08	0.06
3	2.48	0.6	-0.39	-0.16
4	2.74	0.21	0.62	0.56
5	2.54	0.32	-0.16	-0.11
6	2	2.6	-2.25	-0.22
7	NT	NT		
8	2.6	0.5	0.08	0.04
9	NT	NT		
10	3	1	1.63	0.41
11	NT	NT		
12	2.7	0.8	0.47	0.15
14	<0.01	0.05		
15	NT	NT		
16	2.7	NR	0.47	0.63
17	NT	NT		

Statistics

Assigned Value	2.58	0.19
Spike	2.41	0.26
Homogeneity Value	2.63	0.26
Robust Average	2.58	0.19
Median	2.60	0.12
Mean	2.57	
N	10	
Max.	3	
Min.	2	
Robust SD	0.24	
Robust CV	9.3%	


Kernel Density
Density
Result
Results: S1 - Mn
Assigned Value = 2.58 ± 0.19 ug/L
Results (ug/L)
Laboratory
6 1 3 5 2 8 12 16 4 10 14 11 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Mn
Target Standard Deviation 0.26 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
6 1 3 5 2 8 12 16 4 10
-2.2 -1.1 -0.4 -0.2 0.1 0.1 0.5 0.5 0.6 1.6

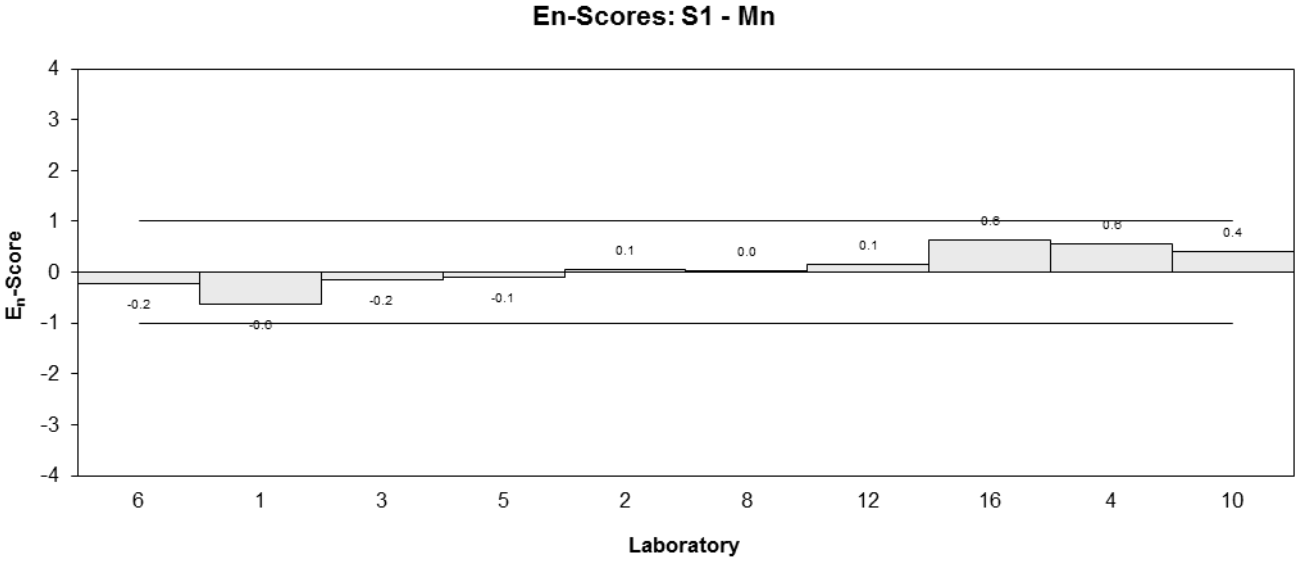

En-Scores: S1 - Mn
En-Score
Laboratory
6 1 3 5 2 8 12 16 4 10
-0.2 -0.6 -0.2 -0.1 0.1 0.0 0.1 0.6 0.6 0.4

Figure 10

Table 14

Sample Details

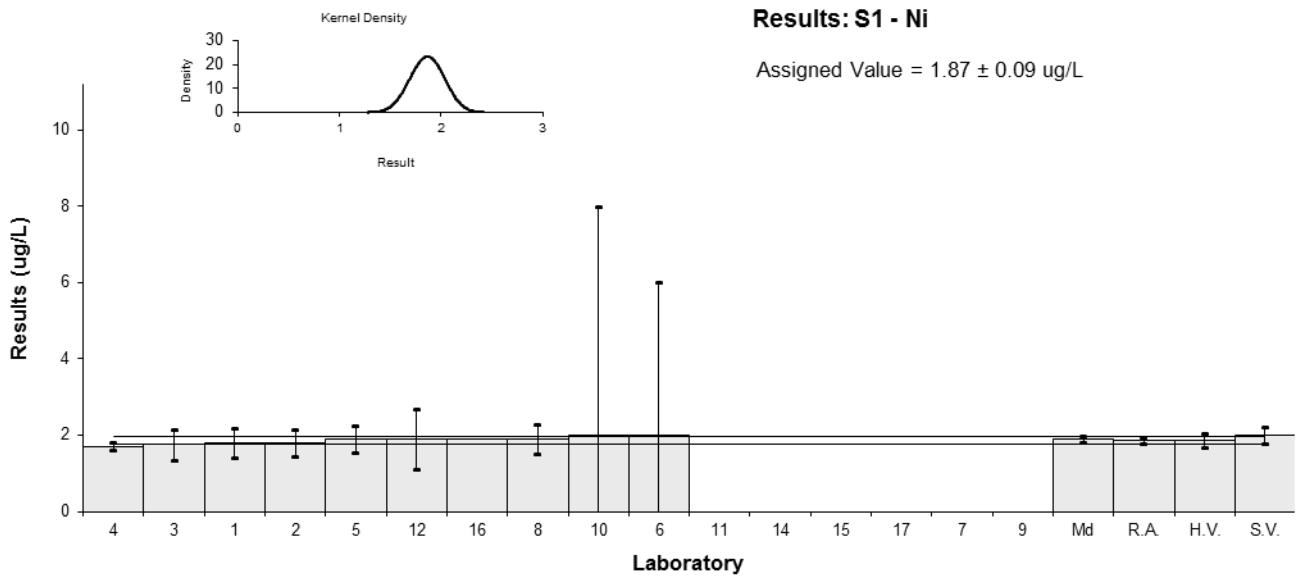
Sample No.	S1
Matrix.	River Water
Analyte.	Ni
Units	ug/L

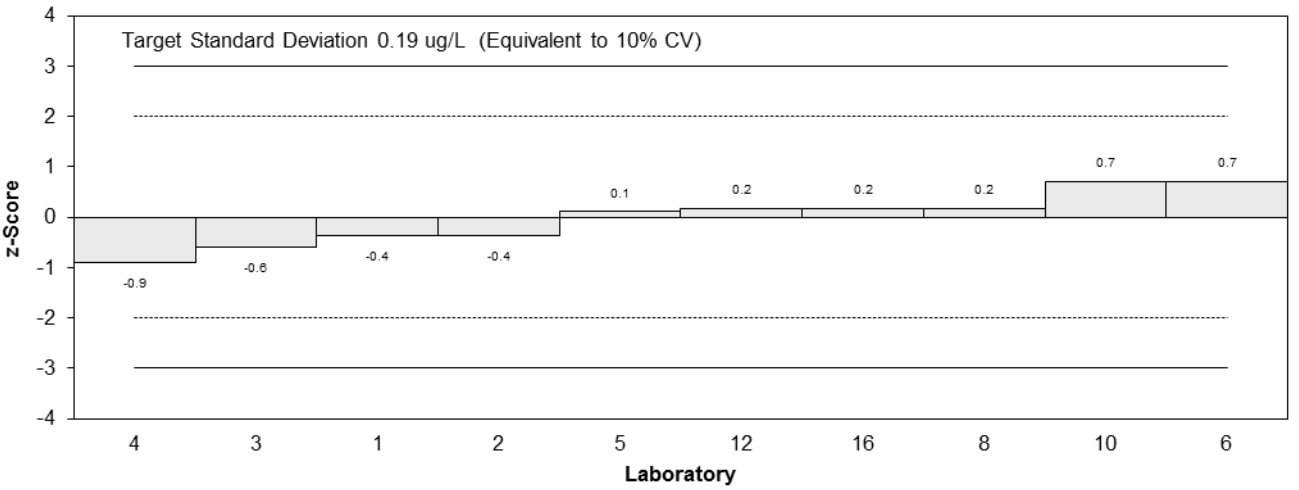
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.8	0.4	-0.37	-0.17
2	1.8	0.36	-0.37	-0.19
3	1.76	0.4	-0.59	-0.27
4	1.70	0.10	-0.91	-1.26
5	1.89	0.35	0.11	0.06
6	2	4	0.70	0.03
7	NT	NT		
8	1.9	0.4	0.16	0.07
9	NT	NT		
10	2	6	0.70	0.02
11	NT	NT		
12	1.9	0.8	0.16	0.04
14	NT	NT		
15	NT	NT		
16	1.9	NR	0.16	0.33
17	NT	NT		

Statistics

Assigned Value	1.87	0.09
Spike	2.01	0.22
Homogeneity Value	1.87	0.19
Robust Average	1.87	0.09
Median	1.90	0.10
Mean	1.87	
N	10	
Max.	2	
Min.	1.7	
Robust SD	0.1	
Robust CV	5.3%	


Kernel Density
Density
Result
Results: S1 - Ni
Assigned Value = 1.87 ± 0.09 ug/L
Results (ug/L)
Laboratory
4 3 1 2 5 12 16 8 10 6 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Ni
Target Standard Deviation 0.19 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.9 -0.6 -0.4 -0.4 0.1 0.2 0.2 0.2 0.7 0.7
4 3 1 2 5 12 16 8 10 6

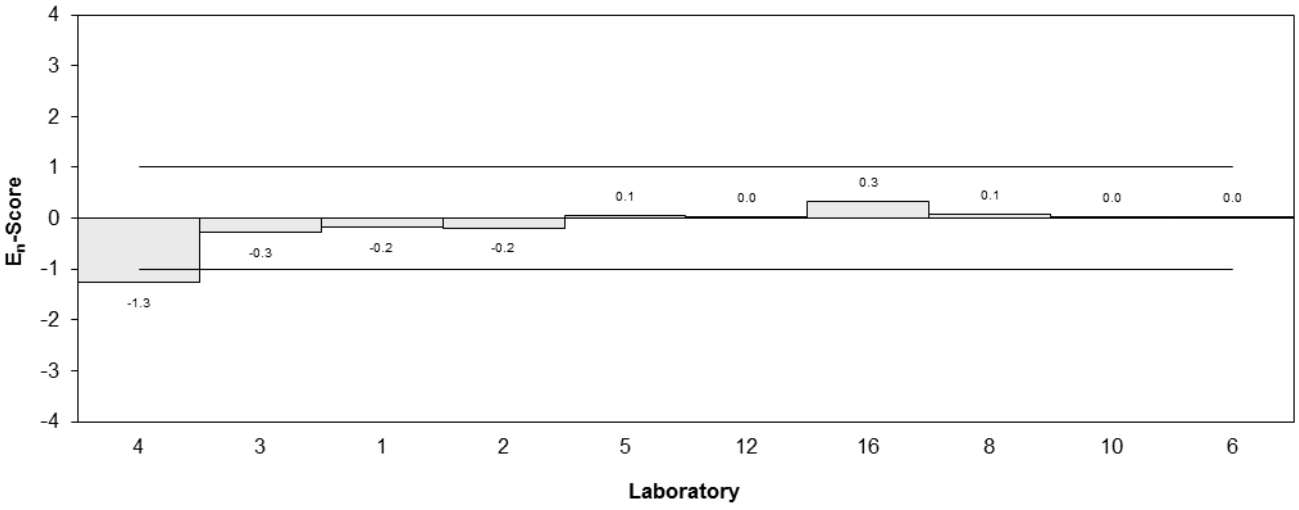

En-Scores: S1 - Ni
En-Score
Laboratory
-1.3 -0.3 -0.2 -0.2 0.1 0.0 0.3 0.1 0.0 0.0
4 3 1 2 5 12 16 8 10 6

Figure 11

Table 15

Sample Details

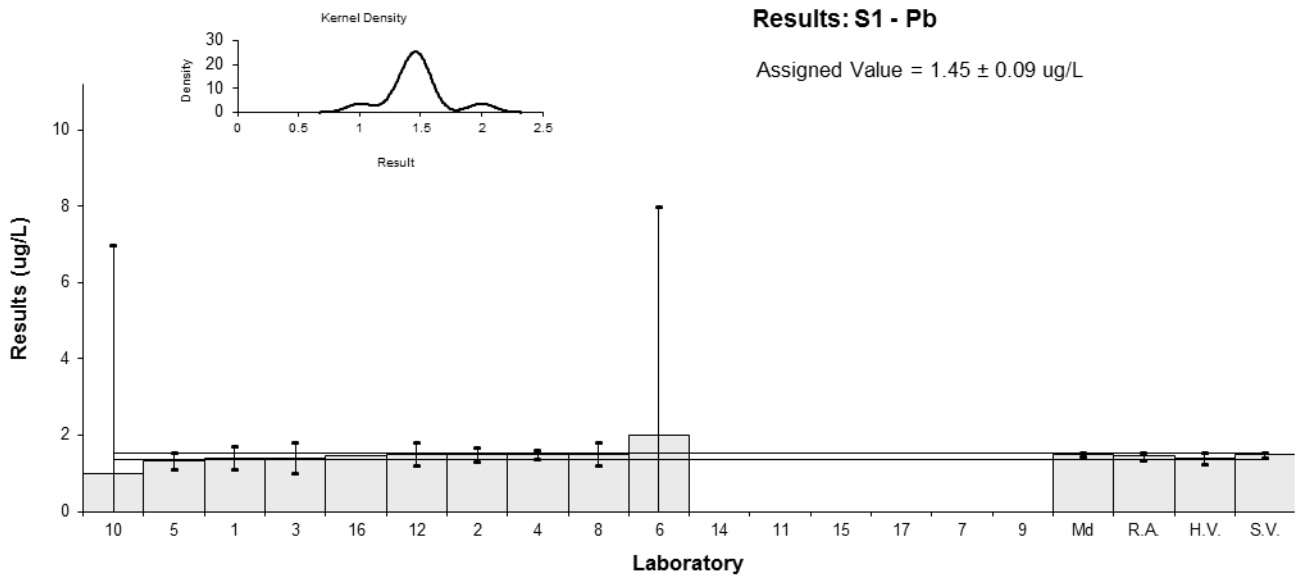
Sample No.	S1
Matrix.	River Water
Analyte.	Pb
Units	ug/L

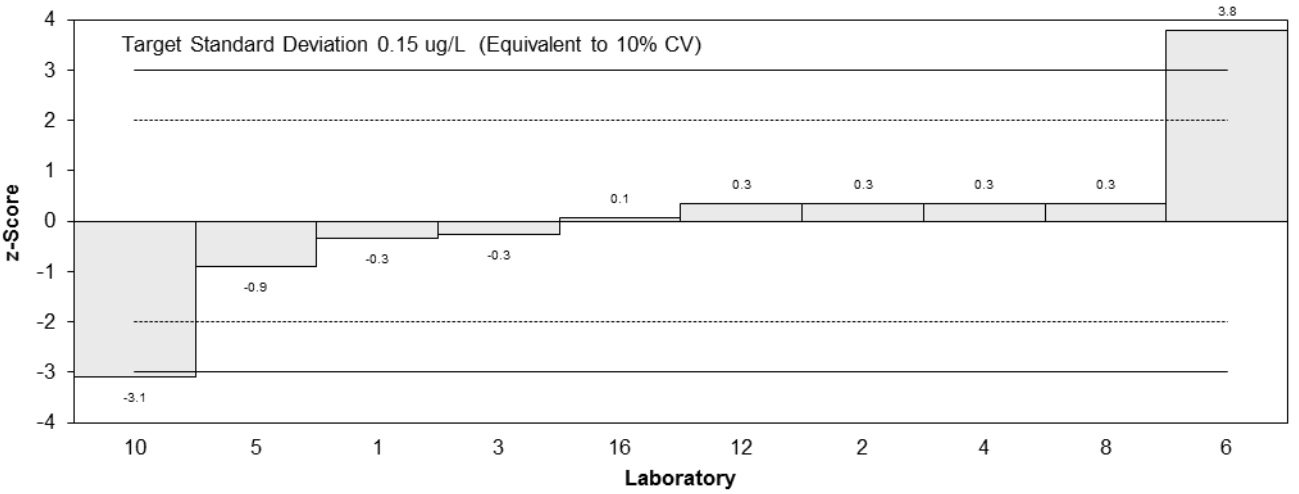
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.3	-0.34	-0.16
2	1.5	0.19	0.34	0.24
3	1.41	0.4	-0.28	-0.10
4	1.50	0.12	0.34	0.33
5	1.32	0.22	-0.90	-0.55
6	2	6	3.79	0.09
7	NT	NT		
8	1.5	0.3	0.34	0.16
9	NT	NT		
10	1	6	-3.10	-0.07
11	NT	NT		
12	1.5	0.3	0.34	0.16
14	<0.01	0.05		
15	NT	NT		
16	1.46	NR	0.07	0.11
17	NT	NT		

Statistics

Assigned Value	1.45	0.09
Spike	1.48	0.07
Homogeneity Value	1.40	0.14
Robust Average	1.45	0.09
Median	1.48	0.05
Mean	1.46	
N	10	
Max.	2	
Min.	1	
Robust SD	0.10	
Robust CV	6.9%	


Kernel Density
Density
Result
Results: S1 - Pb
Assigned Value = 1.45 ± 0.09 ug/L
Results (ug/L)
Laboratory
10 5 1 3 16 12 2 4 8 6 14 11 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Pb
Target Standard Deviation 0.15 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
10 5 1 3 16 12 2 4 8 6
-3.1 -0.9 -0.3 -0.3 0.1 0.3 0.3 0.3 0.3 3.8

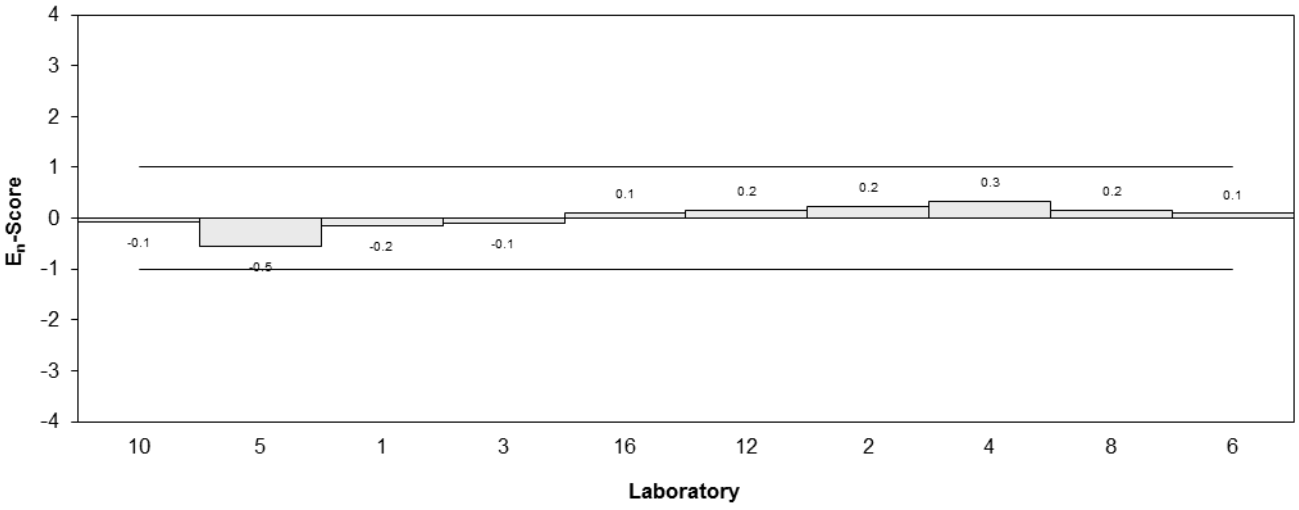

En-Scores: S1 - Pb
En-Score
Laboratory
10 5 1 3 16 12 2 4 8 6
-0.1 -0.5 -0.2 -0.1 0.1 0.2 0.2 0.3 0.2 0.1

Figure 12

Table 16

Sample Details

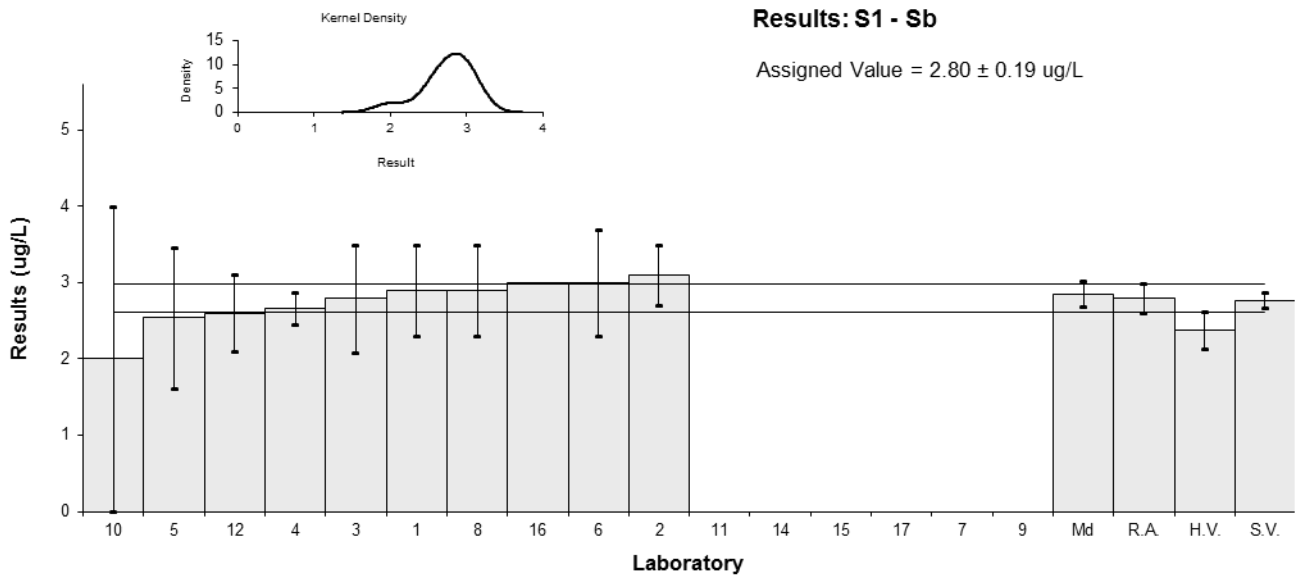
Sample No.	S1
Matrix.	River Water
Analyte.	Sb
Units	ug/L

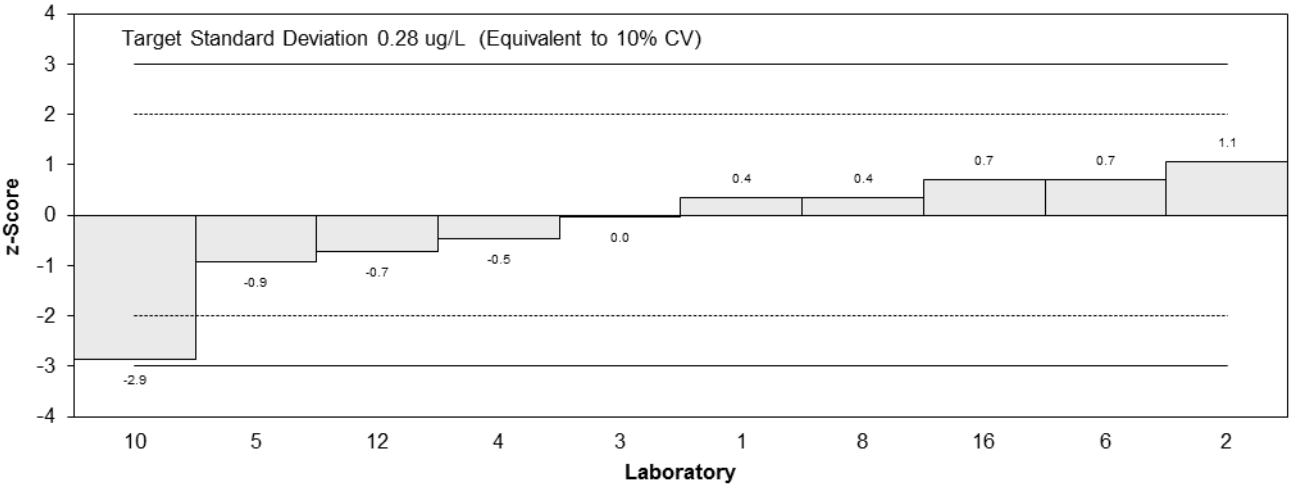
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.9	0.6	0.36	0.16
2	3.1	0.4	1.07	0.68
3	2.79	0.7	-0.04	-0.01
4	2.67	0.21	-0.46	-0.46
5	2.54	0.92	-0.93	-0.28
6	3	0.7	0.71	0.28
7	NT	NT		
8	2.9	0.6	0.36	0.16
9	NT	NT		
10	2	2	-2.86	-0.40
11	NT	NT		
12	2.6	0.5	-0.71	-0.37
14	NT	NT		
15	NT	NT		
16	3.0	NR	0.71	1.05
17	NT	NT		

Statistics

Assigned Value	2.80	0.19
Spike	2.77	0.10
Homogeneity Value	2.38	0.24
Robust Average	2.80	0.19
Median	2.85	0.17
Mean	2.75	
N	10	
Max.	3.1	
Min.	2	
Robust SD	0.24	
Robust CV	8.6%	


Kernel Density
Density
Result
Results: S1 - Sb
Assigned Value = 2.80 ± 0.19 ug/L
Results (ug/L)
10 5 12 4 3 1 8 16 6 2 11 14 15 17 7 9 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Sb
Target Standard Deviation 0.28 ug/L (Equivalent to 10% CV)
z-Score
-2.9 -0.9 -0.7 -0.5 0.0 0.4 0.4 0.7 0.7 1.1
10 5 12 4 3 1 8 16 6 2
Laboratory

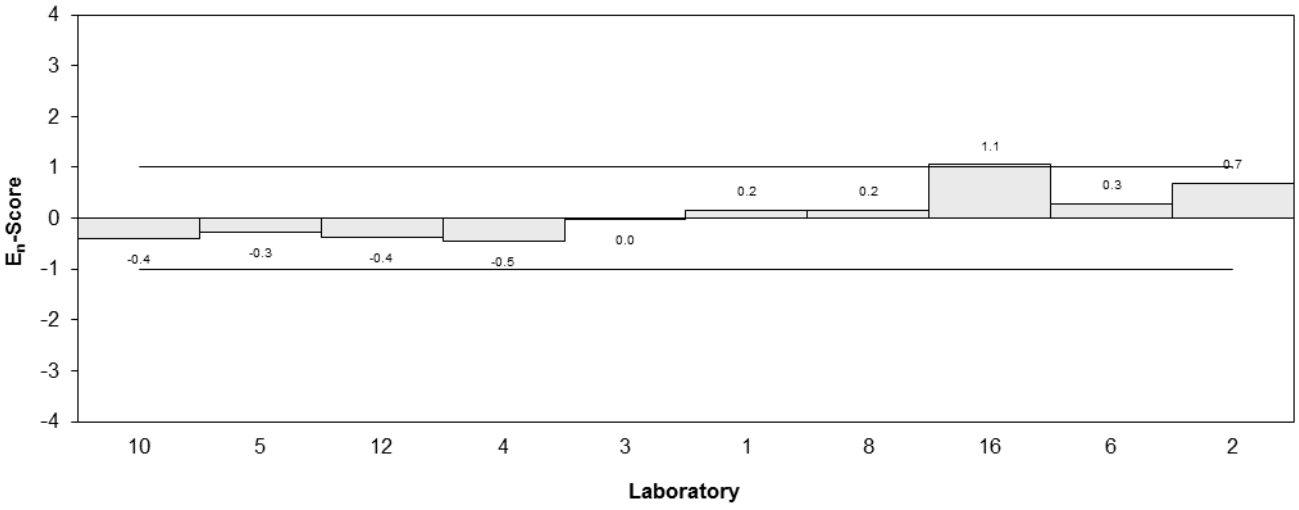

En-Scores: S1 - Sb
En-Score
-0.4 -0.3 -0.4 -0.5 0.0 0.2 0.2 1.1 0.3 0.7
10 5 12 4 3 1 8 16 6 2
Laboratory

Figure 13

Table 17

Sample Details

Sample No.	S1
Matrix.	River Water
Analyte.	Se
Units	ug/L

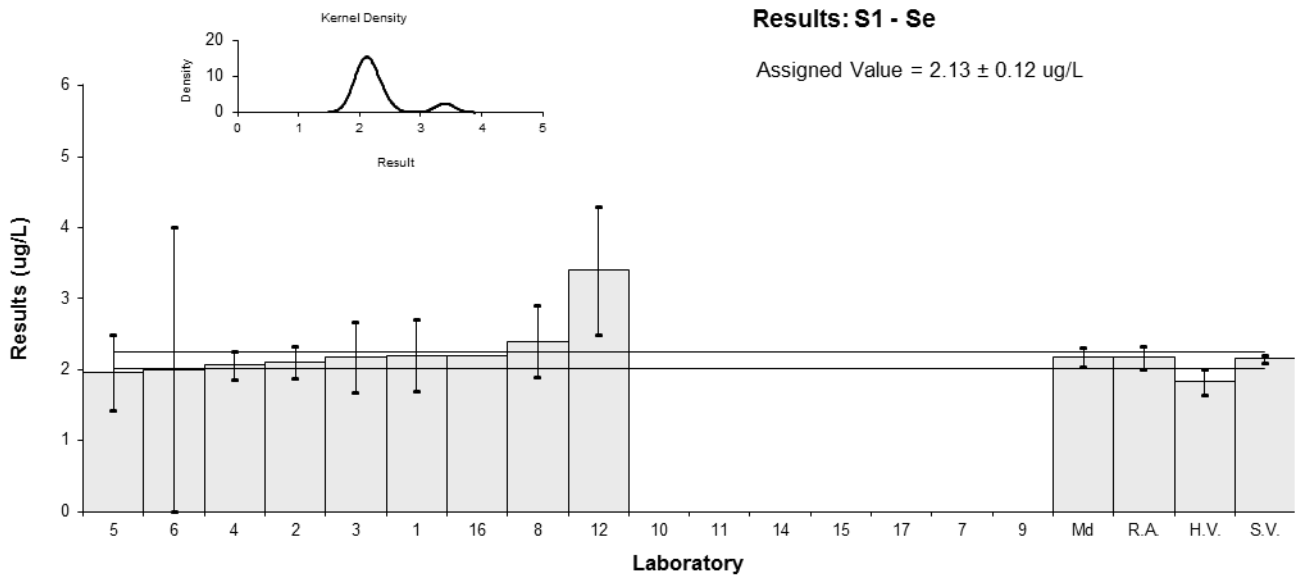
Participant Results

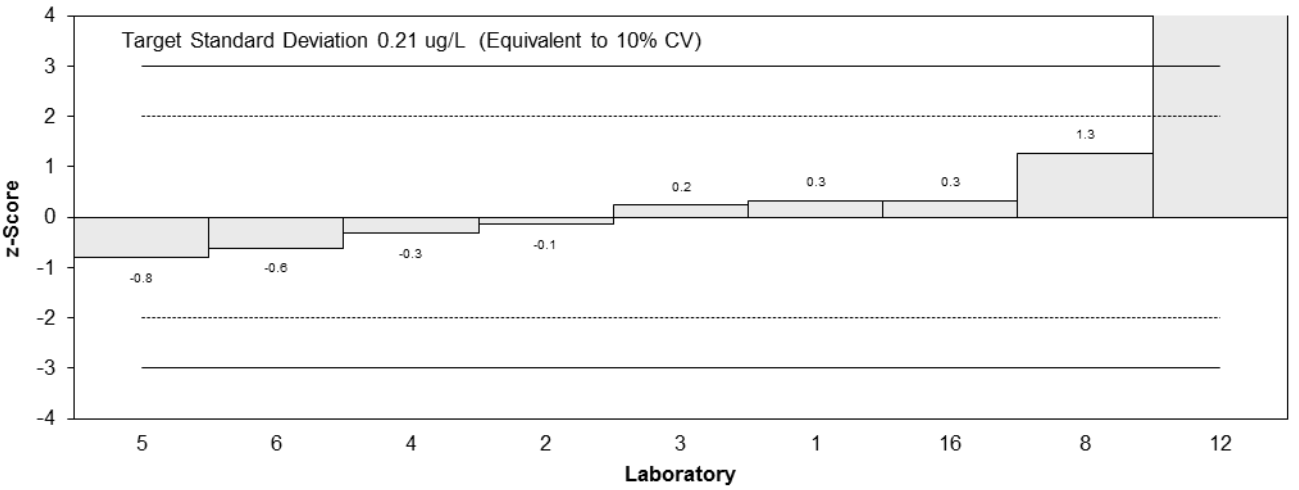
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.2	0.5	0.33	0.14
2	2.1	0.23	-0.14	-0.12
3	2.18	0.5	0.23	0.10
4	2.06	0.20	-0.33	-0.30
5	1.96	0.54	-0.80	-0.31
6	2	2	-0.61	-0.06
7	NT	NT		
8	2.4	0.5	1.27	0.53
9	NT	NT		
10	<10	10		
11	NT	NT		
12	3.4	0.9	5.96	1.40
14	NT	NT		
15	NT	NT		
16	2.2	NR	0.33	0.58
17	NT	NT		

Statistics

Assigned Value*	2.13	0.12
Spike	2.15	0.06
Homogeneity Value	1.83	0.18
Robust Average	2.17	0.16
Median	2.18	0.14
Mean	2.28	
N	9	
Max.	3.4	
Min.	1.96	
Robust SD	0.14	
Robust CV	6.5%	

* Robust Average excluding Laboratory 12.


Kernel Density
Density
Result
Results: S1 - Se
Assigned Value = 2.13 ± 0.12 ug/L
Results (ug/L)
Laboratory
5 6 4 2 3 1 16 8 12 10 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Se
Target Standard Deviation 0.21 ug/L (Equivalent to 10% CV)
z-Score
-0.8 -0.6 -0.3 -0.1 0.2 0.3 0.3 1.3
Laboratory
5 6 4 2 3 1 16 8 12

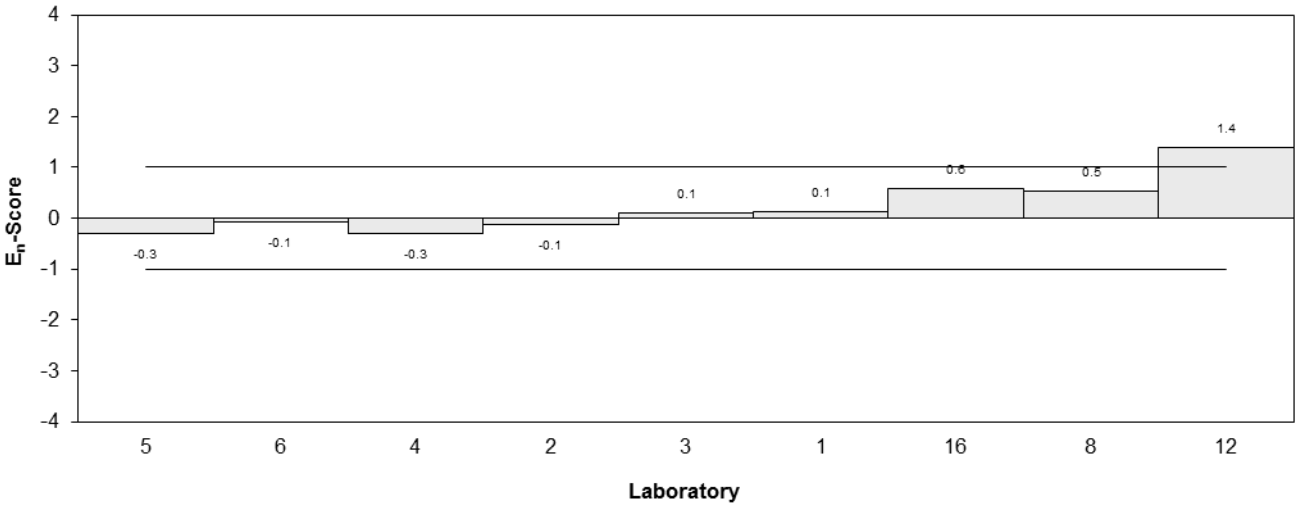

En-Scores: S1 - Se
En-Score
-0.3 -0.1 -0.3 -0.1 0.1 0.1 0.6 0.5 1.4
Laboratory
5 6 4 2 3 1 16 8 12

Figure 14

Table 18

Sample Details

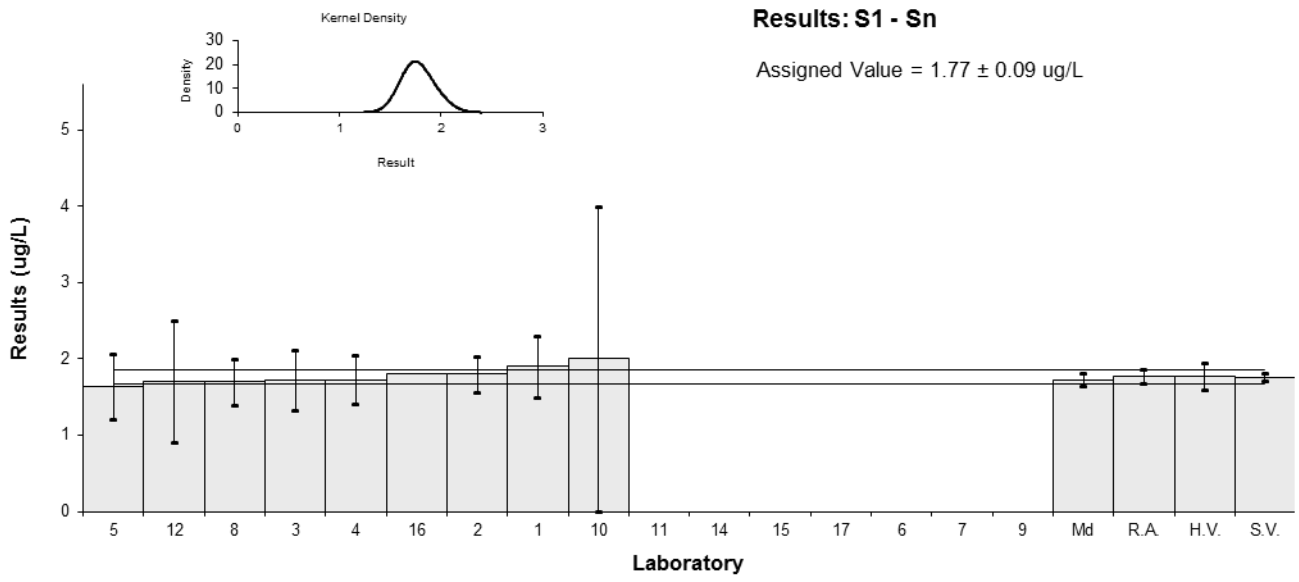
Sample No.	S1
Matrix.	River Water
Analyte.	Sn
Units	ug/L

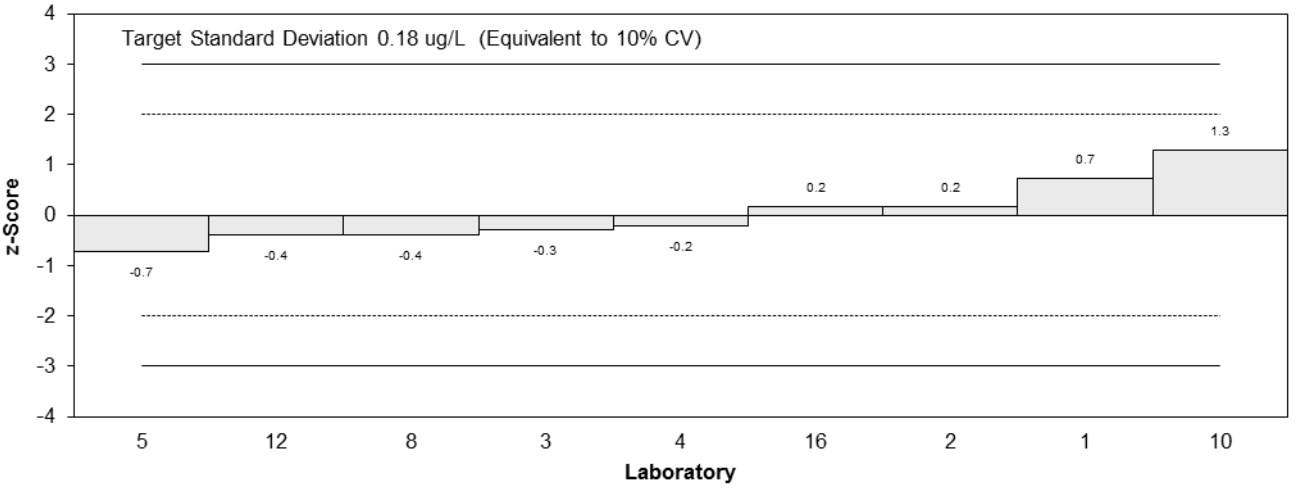
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.9	0.4	0.73	0.32
2	1.8	0.23	0.17	0.12
3	1.72	0.4	-0.28	-0.12
4	1.73	0.32	-0.23	-0.12
5	1.64	0.43	-0.73	-0.30
6	NT	NT		
7	NT	NT		
8	1.7	0.3	-0.40	-0.22
9	NT	NT		
10	2	2	1.30	0.11
11	NT	NT		
12	1.7	0.8	-0.40	-0.09
14	NT	NT		
15	NT	NT		
16	1.8	NR	0.17	0.33
17	NT	NT		

Statistics

Assigned Value	1.77	0.09
Spike	1.76	0.05
Homogeneity Value	1.77	0.18
Robust Average	1.77	0.09
Median	1.73	0.08
Mean	1.78	
N	9	
Max.	2	
Min.	1.64	
Robust SD	0.10	
Robust CV	5.6%	


Kernel Density
Density
Result
Results: S1 - Sn
Assigned Value = 1.77 ± 0.09 ug/L
Results (ug/L)
Laboratory
5 12 8 3 4 16 2 1 10 11 14 15 17 6 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Sn
Target Standard Deviation 0.18 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
5 12 8 3 4 16 2 1 10
-0.7 -0.4 -0.4 -0.3 -0.2 0.2 0.2 0.7 1.3

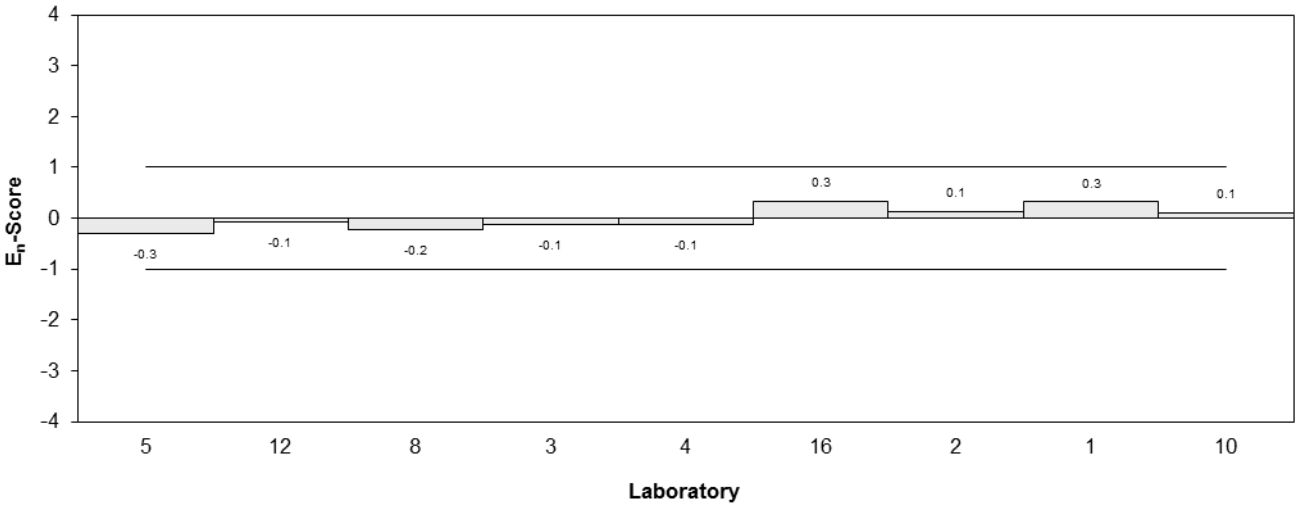

En-Scores: S1 - Sn
En-Score
Laboratory
5 12 8 3 4 16 2 1 10
-0.3 -0.1 -0.2 -0.1 -0.1 0.3 0.1 0.3 0.1

Figure 15

Table 19

Sample Details

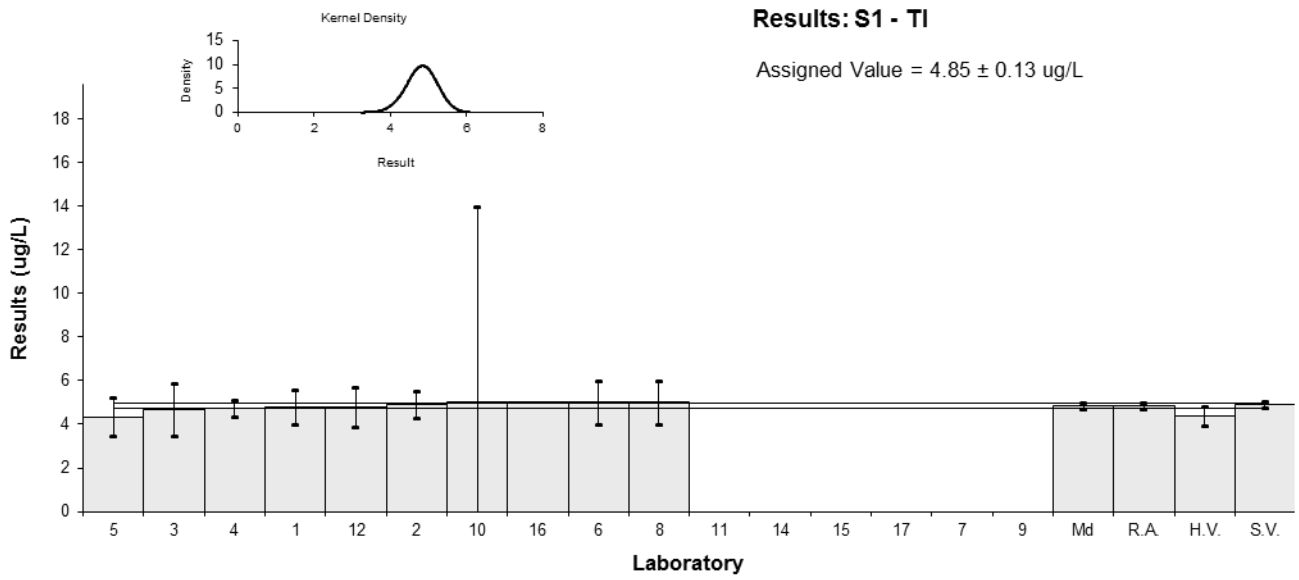
Sample No.	S1
Matrix.	River Water
Analyte.	Tl
Units	ug/L

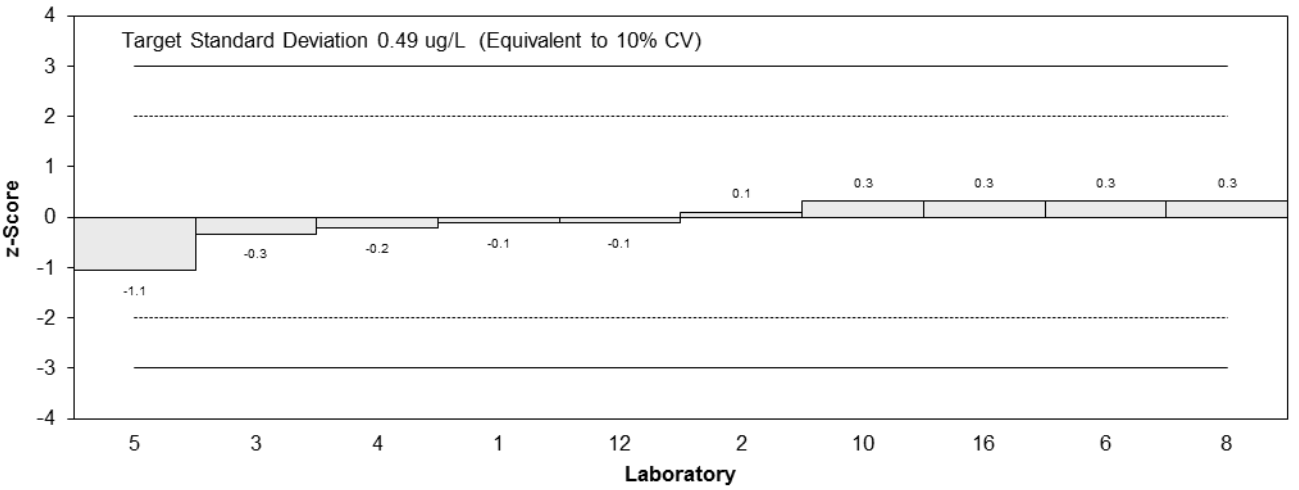
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.8	0.8	-0.10	-0.06
2	4.9	0.62	0.10	0.08
3	4.69	1.2	-0.33	-0.13
4	4.74	0.37	-0.23	-0.28
5	4.34	0.88	-1.05	-0.57
6	5	1	0.31	0.15
7	NT	NT		
8	5.0	1.0	0.31	0.15
9	NT	NT		
10	5	9	0.31	0.02
11	NT	NT		
12	4.8	0.9	-0.10	-0.05
14	NT	NT		
15	NT	NT		
16	5.0	NR	0.31	1.15
17	NT	NT		

Statistics

Assigned Value	4.85	0.13
Spike	4.90	0.14
Homogeneity Value	4.37	0.44
Robust Average	4.85	0.13
Median	4.85	0.16
Mean	4.83	
N	10	
Max.	5	
Min.	4.34	
Robust SD	0.17	
Robust CV	3.5%	


Kernel Density
Density
Result
Results: S1 - Tl
Assigned Value = 4.85 ± 0.13 ug/L
Results (ug/L)
Laboratory
5 3 4 1 12 2 10 16 6 8 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Tl
Target Standard Deviation 0.49 ug/L (Equivalent to 10% CV)
z-Score
-1.1 -0.3 -0.2 -0.1 -0.1 0.1 0.3 0.3 0.3 0.3
Laboratory
5 3 4 1 12 2 10 16 6 8

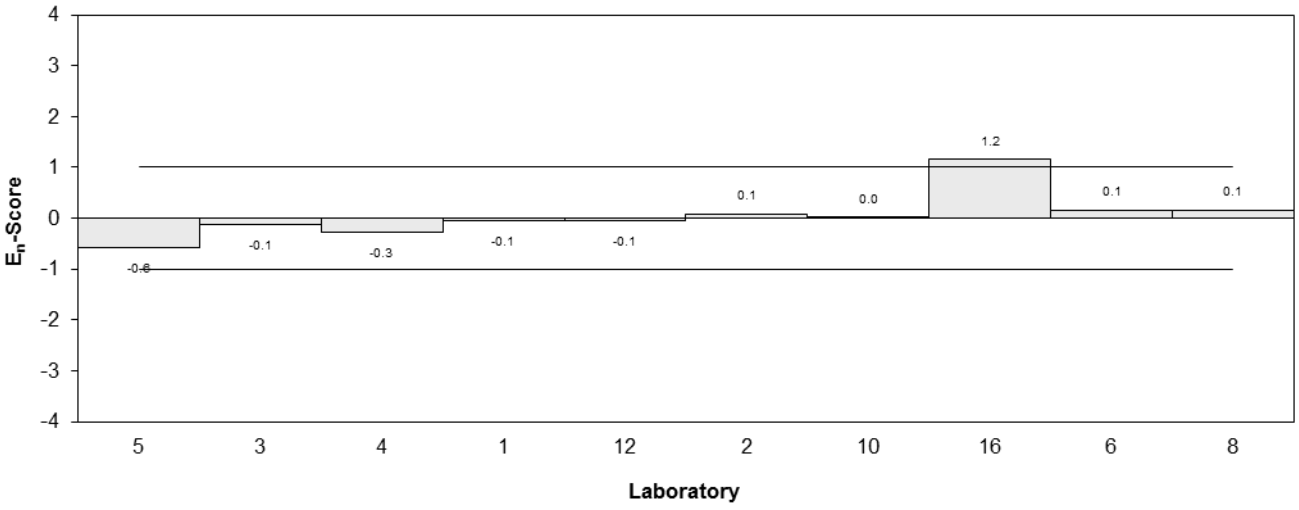

En-Scores: S1 - Tl
En-Score
-0.6 -0.1 -0.3 -0.1 -0.1 0.1 0.0 1.2 0.1 0.1
Laboratory
5 3 4 1 12 2 10 16 6 8

Figure 16

Table 20

Sample Details

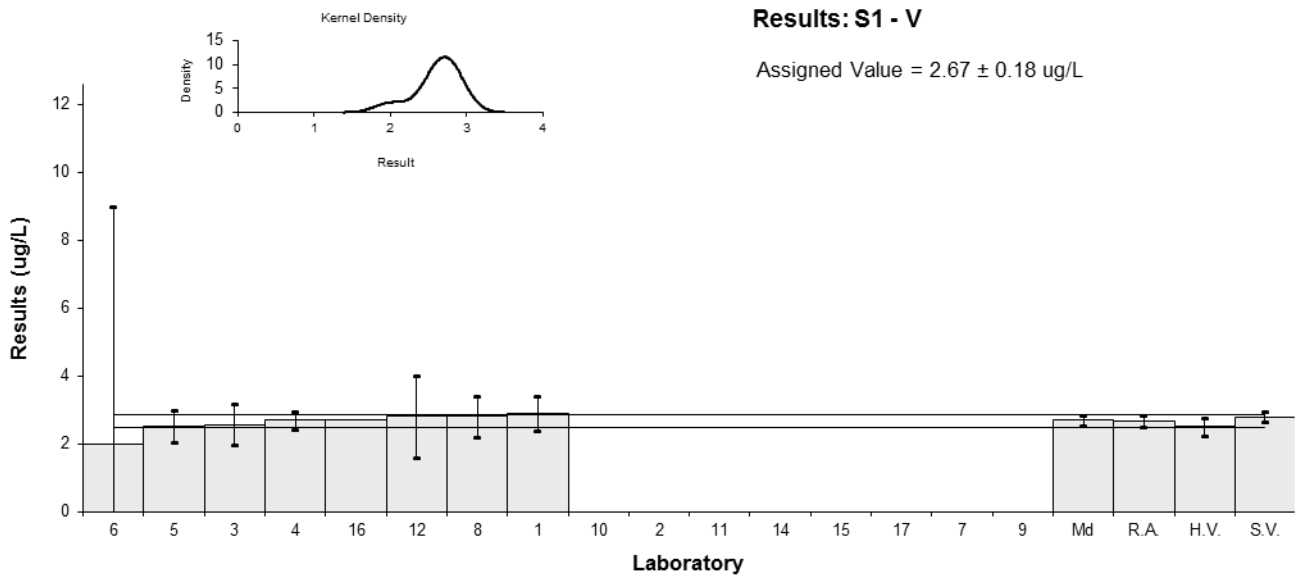
Sample No.	S1
Matrix.	River Water
Analyte.	V
Units	ug/L

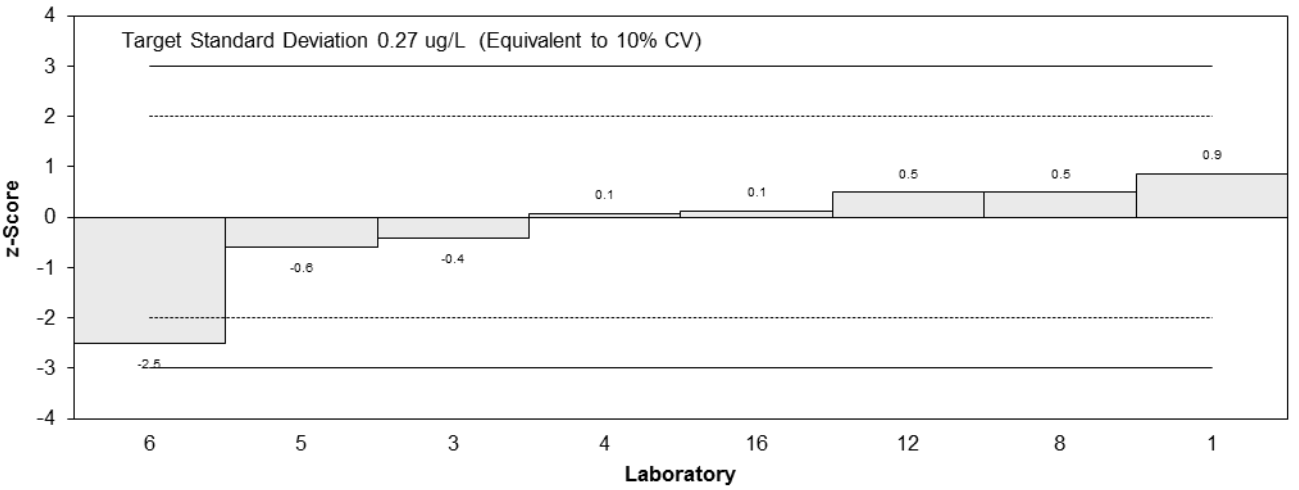
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.9	0.5	0.86	0.43
2	<5	NR		
3	2.56	0.6	-0.41	-0.18
4	2.69	0.26	0.07	0.06
5	2.51	0.48	-0.60	-0.31
6	2	7	-2.51	-0.10
7	NT	NT		
8	2.8	0.6	0.49	0.21
9	NT	NT		
10	<10	10		
11	NT	NT		
12	2.8	1.2	0.49	0.11
14	NT	NT		
15	NT	NT		
16	2.7	NR	0.11	0.17
17	NT	NT		

Statistics

Assigned Value	2.67	0.18
Spike	2.79	0.16
Homogeneity Value	2.50	0.25
Robust Average	2.67	0.18
Median	2.70	0.15
Mean	2.62	
N	8	
Max.	2.9	
Min.	2	
Robust SD	0.20	
Robust CV	7.5%	


Kernel Density
Density
Result
Results: S1 - V
Assigned Value = 2.67 ± 0.18 ug/L
Results (ug/L)
Laboratory
6 5 3 4 16 12 8 1 10 2 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - V
Target Standard Deviation 0.27 ug/L (Equivalent to 10% CV)
z-Score
-2.5
-0.6
-0.4
0.1
0.1
0.5
0.5
0.9
Laboratory
6 5 3 4 16 12 8 1

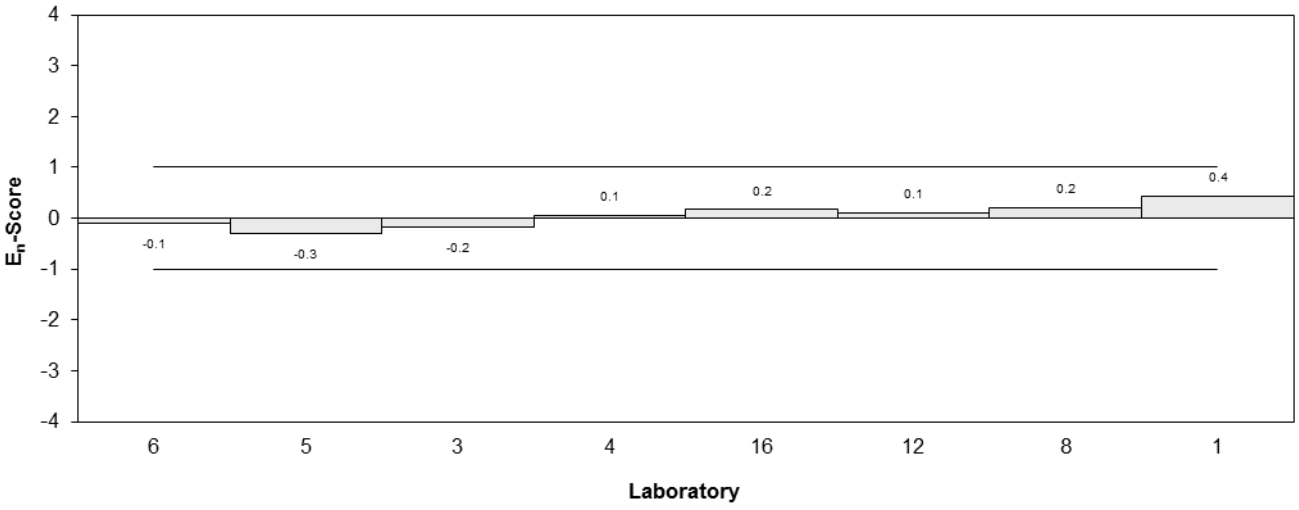

En-Scores: S1 - V
En-Score
-0.1
-0.3
-0.2
0.1
0.2
0.1
0.2
0.4
Laboratory
6 5 3 4 16 12 8 1

Figure 17

Table 21

Sample Details

Sample No.	S1
Matrix.	River Water
Analyte.	Zn
Units	ug/L

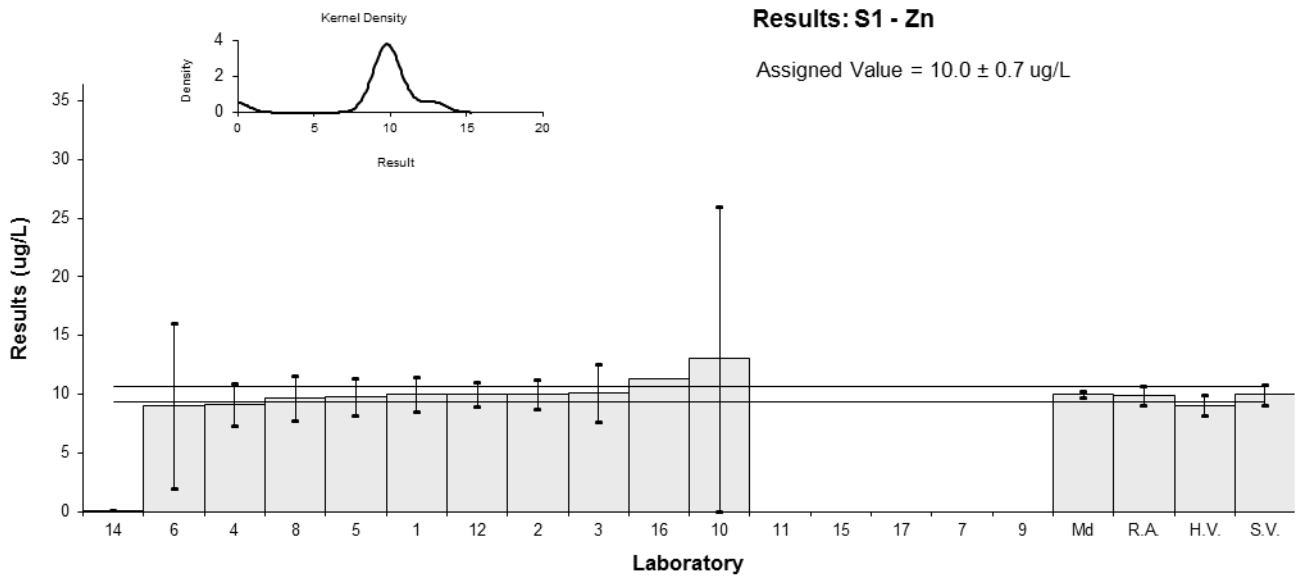
Participant Results

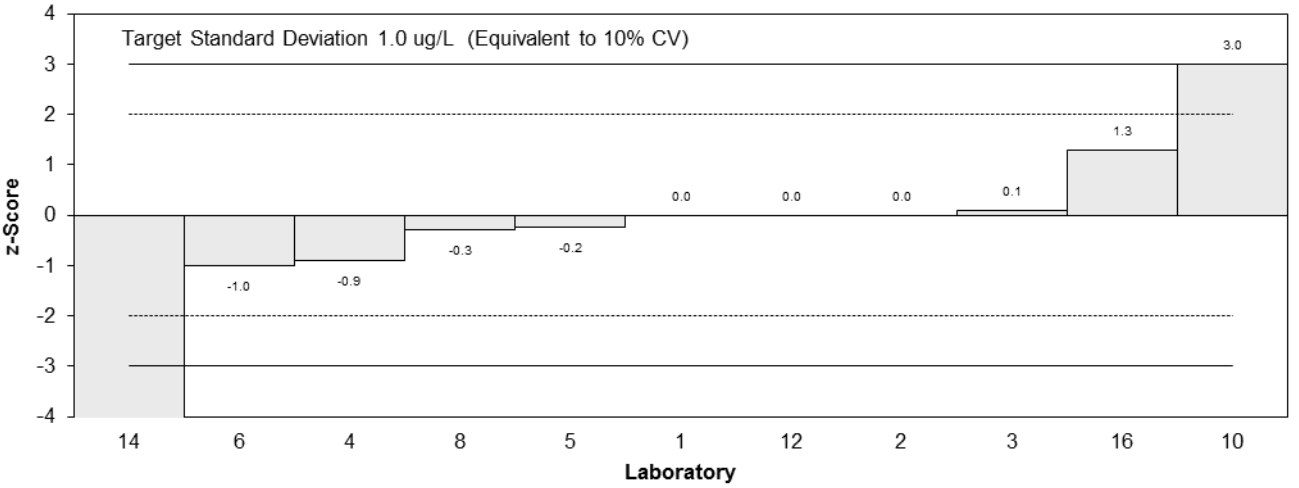
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	10	1.5	0.00	0.00
2	10	1.3	0.00	0.00
3	10.1	2.5	0.10	0.04
4	9.10	1.82	-0.90	-0.46
5	9.76	1.56	-0.24	-0.14
6	9	7	-1.00	-0.14
7	NT	NT		
8	9.7	1.9	-0.30	-0.15
9	NT	NT		
10	13	13	3.00	0.23
11	NT	NT		
12	10	1	0.00	0.00
14	0.012	0.05	-9.99	-14.23
15	NT	NT		
16	11.3	NR	1.30	1.86
17	NT	NT		

Statistics

Assigned Value*	10.0	0.7
Spike	9.96	0.84
Homogeneity Value	9.05	0.91
Robust Average	9.88	0.78
Median	10.0	0.3
Mean	9.27	
N	11	
Max.	13	
Min.	0.012	
Robust SD	0.89	
Robust CV	9%	

* Robust Average excluding Laboratory 14.


Kernel Density
Density
Result
Results: S1 - Zn
Assigned Value = 10.0 ± 0.7 ug/L
Results (ug/L)
Laboratory
14 6 4 8 5 1 12 2 3 16 10 11 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S1 - Zn
Target Standard Deviation 1.0 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
14 6 4 8 5 1 12 2 3 16 10
-1.0 -0.9 -0.3 -0.2 0.0 0.0 0.0 0.1 1.3 3.0

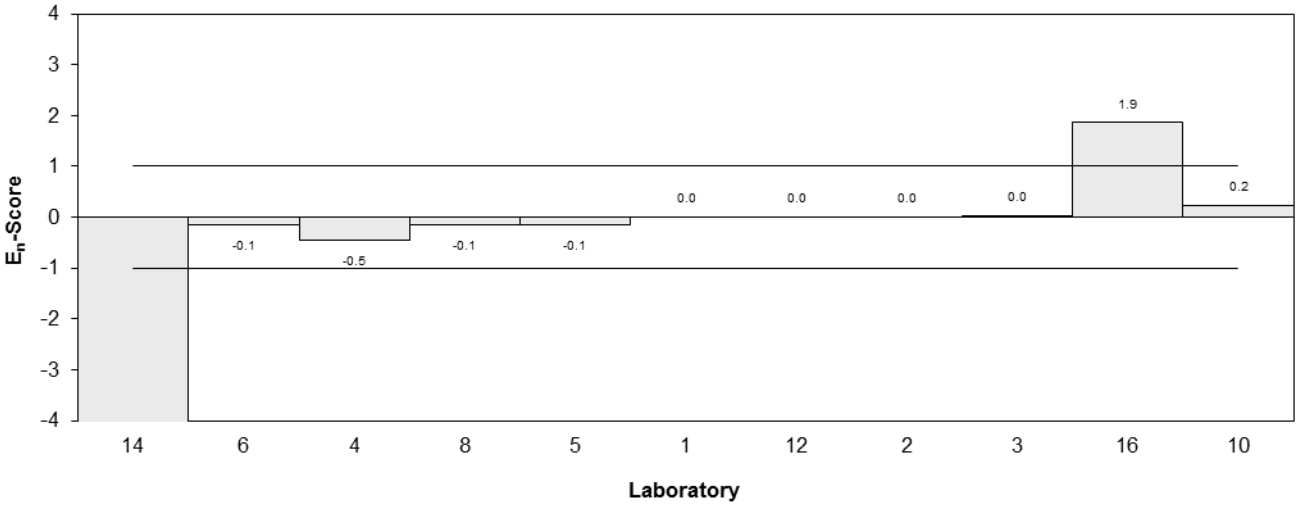

En-Scores: S1 - Zn
En-Score
Laboratory
14 6 4 8 5 1 12 2 3 16 10
-0.1 -0.5 -0.1 -0.1 0.0 0.0 0.0 0.0 1.9 0.2

Figure 18

Table 22

Sample Details

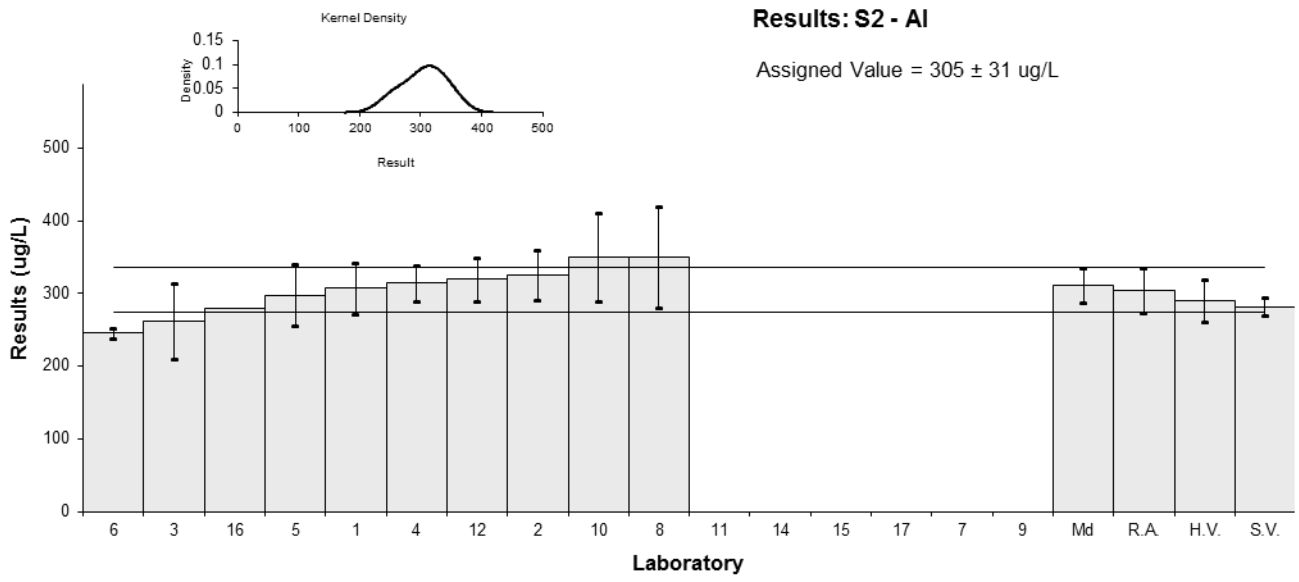
Sample No.	S2
Matrix.	River Water
Analyte.	Al
Units	ug/L

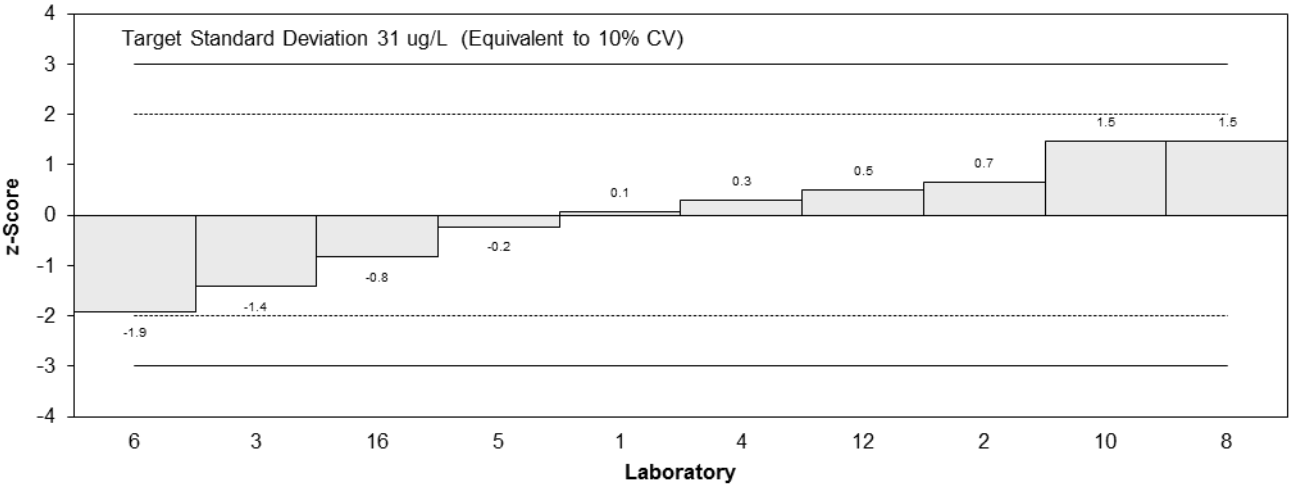
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	307	35	0.07	0.04
2	325	34	0.66	0.43
3	262	52	-1.41	-0.71
4	314	25	0.30	0.23
5	298	42	-0.23	-0.13
6	246	7	-1.93	-1.86
7	NT	NT		
8	350	70	1.48	0.59
9	NT	NT		
10	350	61	1.48	0.66
11	NT	NT		
12	320	30	0.49	0.35
14	NT	NT		
15	NT	NT		
16	280	NR	-0.82	-0.81
17	NT	NT		

Statistics

Assigned Value	305	31
Spike	282	13
Homogeneity Value	290	29
Robust Average	305	31
Median	311	24
Mean	305	
N	10	
Max.	350	
Min.	246	
Robust SD	39	
Robust CV	13%	


Kernel Density
Density
Result
Results: S2 - Al
Assigned Value = 305 ± 31 ug/L
Results (ug/L)
Laboratory
6 3 16 5 1 4 12 2 10 8 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Al
Target Standard Deviation 31 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
6 3 16 5 1 4 12 2 10 8
-1.9 -1.4 -0.8 -0.2 0.1 0.3 0.5 0.7 1.5 1.5

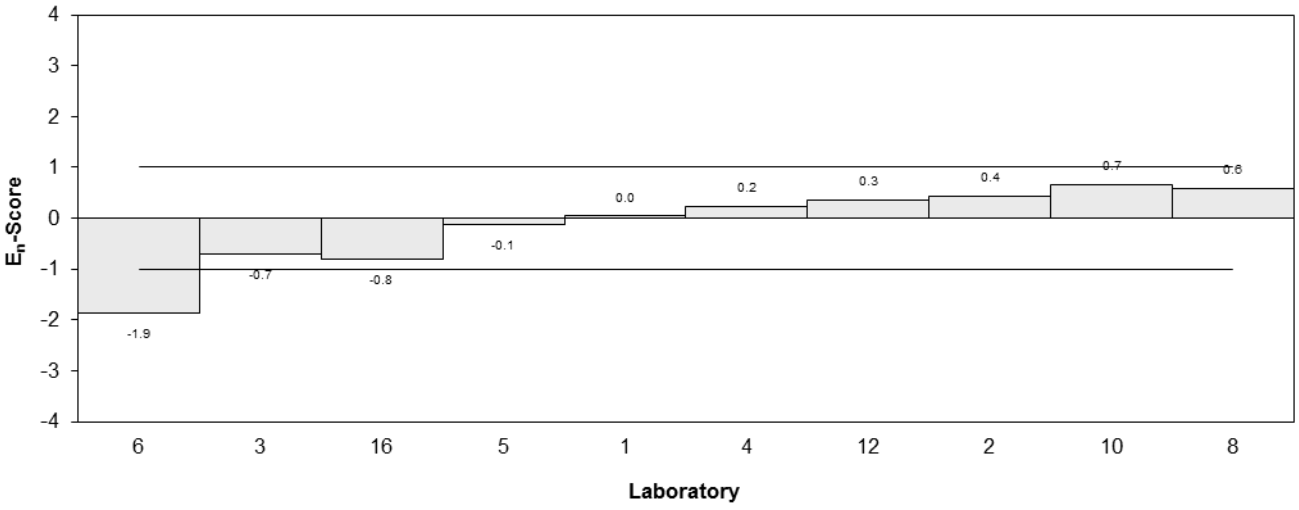

En-Scores: S2 - Al
En-Score
Laboratory
6 3 16 5 1 4 12 2 10 8
-1.9 -0.7 -0.8 -0.1 0.0 0.2 0.3 0.4 0.7 0.6

Figure 19

Table 23

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	As
Units	ug/L

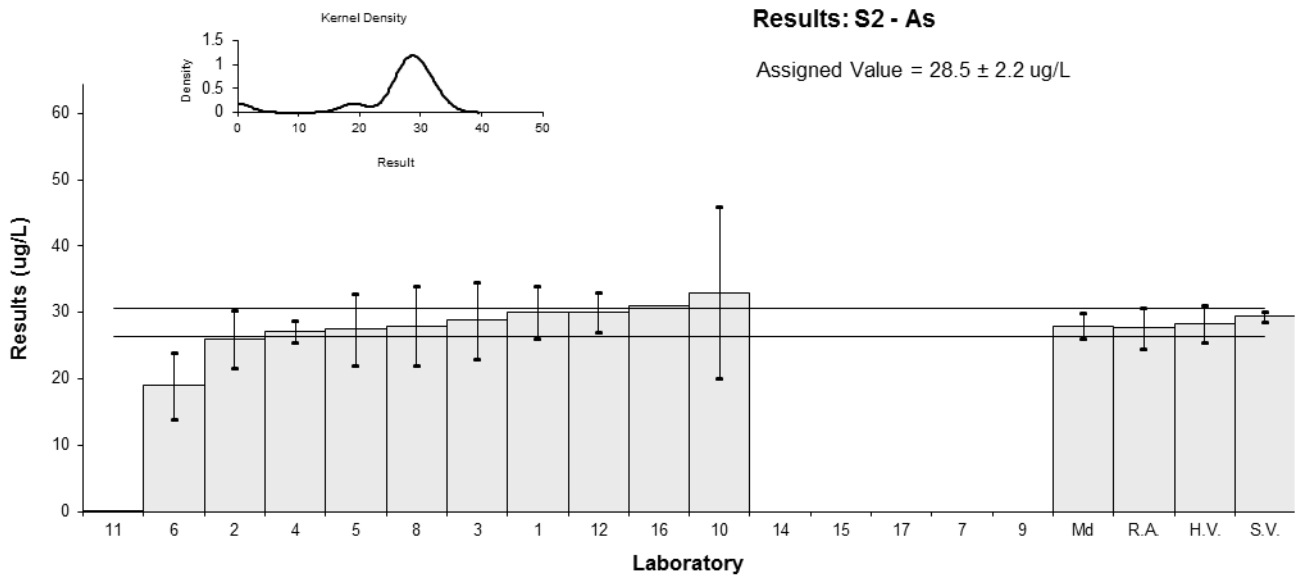
Participant Results

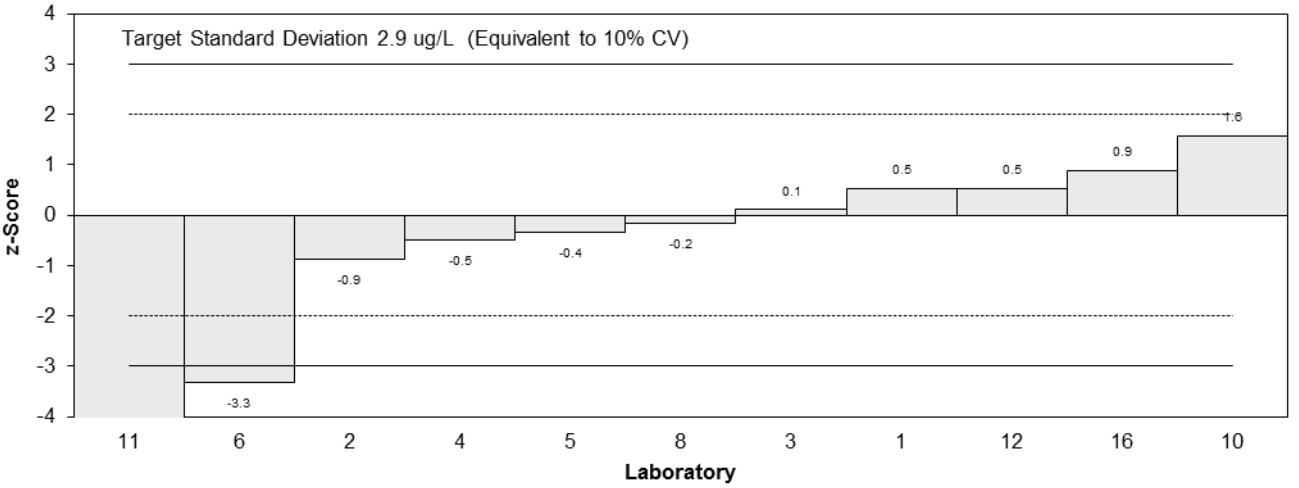
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	30	4.0	0.53	0.33
2	26	4.4	-0.88	-0.51
3	28.8	5.8	0.11	0.05
4	27.1	1.6	-0.49	-0.51
5	27.5	5.4	-0.35	-0.17
6	19	5	-3.33	-1.74
7	NT	NT		
8	28	6	-0.18	-0.08
9	NT	NT		
10	33	13	1.58	0.34
11	0.032	NR	-9.99	-12.94
12	30	3	0.53	0.40
14	NT	NT		
15	NT	NT		
16	31	NR	0.88	1.14
17	NT	NT		

Statistics

Assigned Value*	28.5	2.2
Spike	29.4	0.8
Homogeneity Value	28.3	2.8
Robust Average	27.7	3.1
Median	28.0	2.0
Mean	25.5	
N	11	
Max.	33	
Min.	0.032	
Robust SD	2.8	
Robust CV	10%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - As
Assigned Value = 28.5 ± 2.2 ug/L
Results (ug/L)
Laboratory
11 6 2 4 5 8 3 1 12 16 10 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - As
Target Standard Deviation 2.9 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 6 2 4 5 8 3 1 12 16 10
-3.3
-0.9
-0.5
-0.4
-0.2
0.1
0.5
0.5
0.9
1.6

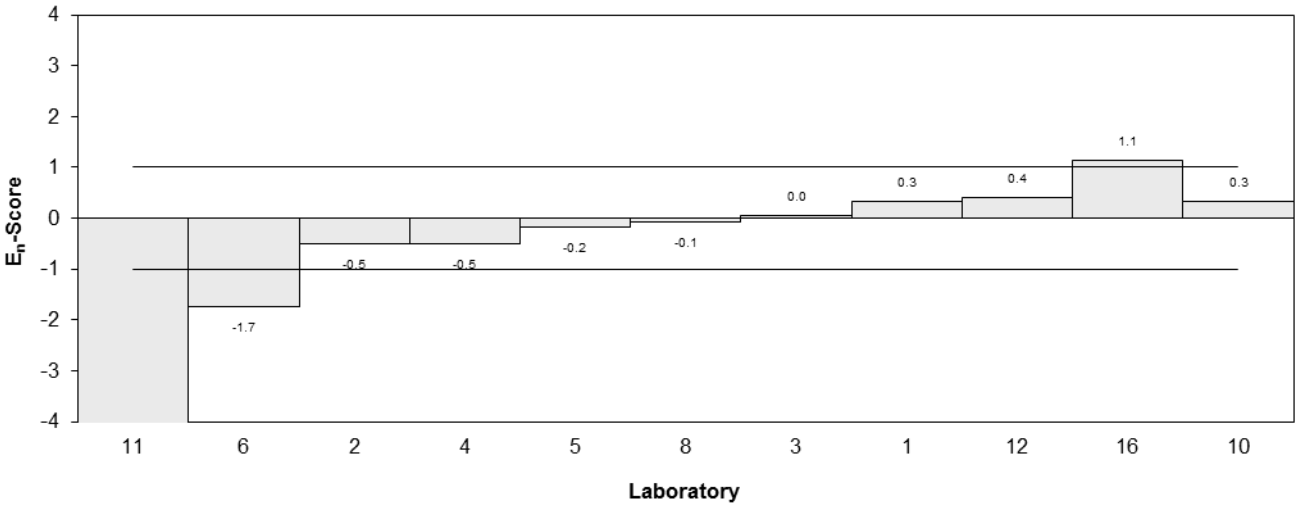

En-Scores: S2 - As
En-Score
Laboratory
11 6 2 4 5 8 3 1 12 16 10
-1.7
-0.5
-0.5
-0.2
-0.1
0.0
0.3
0.4
1.1
0.3

Figure 20

Table 24

Sample Details

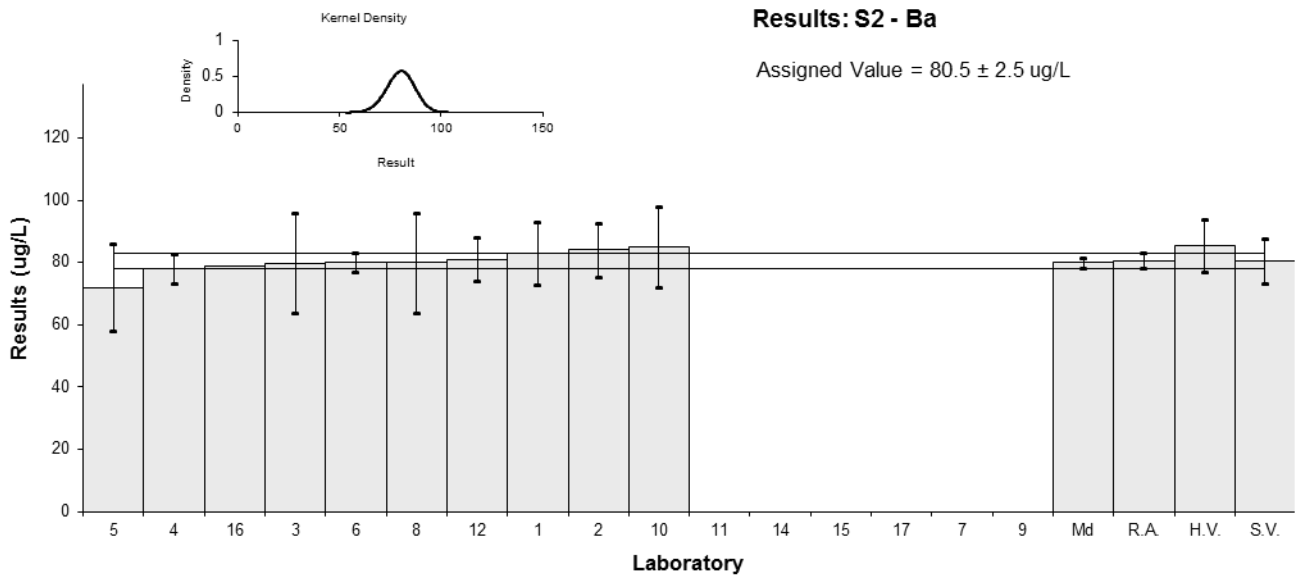
Sample No.	S2
Matrix.	River Water
Analyte.	Ba
Units	ug/L

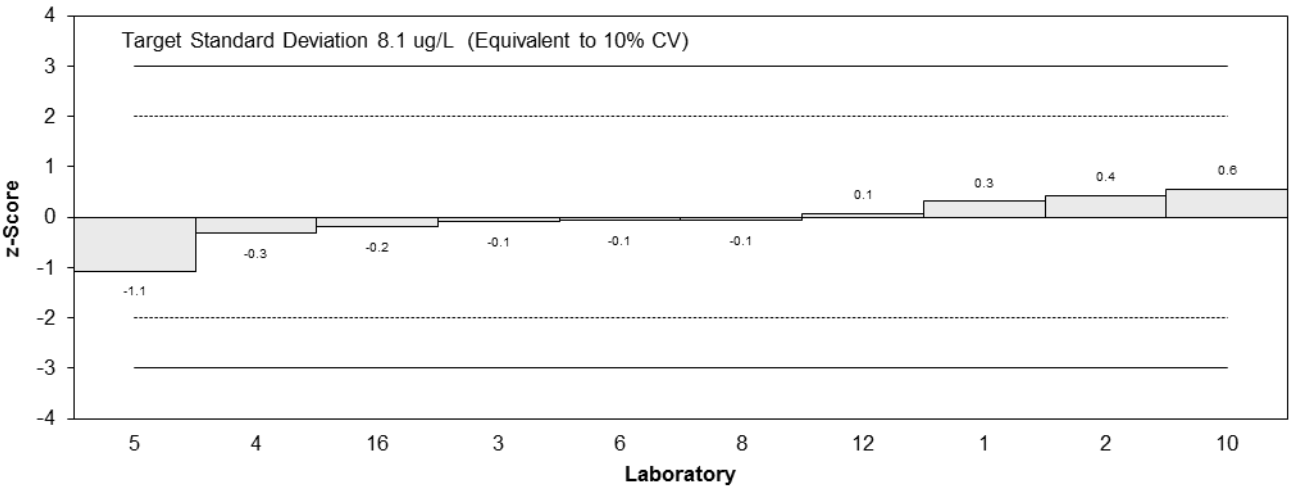
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	83	10	0.31	0.24
2	84	8.8	0.43	0.38
3	79.7	16	-0.10	-0.05
4	77.9	4.7	-0.32	-0.49
5	71.9	14.0	-1.07	-0.60
6	80	3	-0.06	-0.13
7	NT	NT		
8	80	16	-0.06	-0.03
9	NT	NT		
10	85	13	0.56	0.34
11	NT	NT		
12	81	7	0.06	0.07
14	NT	NT		
15	NT	NT		
16	79	NR	-0.19	-0.60
17	NT	NT		

Statistics

Assigned Value	80.5	2.5
Spike	80.4	7.1
Homogeneity Value	85.3	8.5
Robust Average	80.5	2.5
Median	80.0	1.6
Mean	80.2	
N	10	
Max.	85	
Min.	71.9	
Robust SD	3.2	
Robust CV	4%	


Kernel Density
Density
Result
Results: S2 - Ba
Assigned Value = 80.5 ± 2.5 ug/L
Results (ug/L)
Laboratory
5 4 16 3 6 8 12 1 2 10 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Ba
Target Standard Deviation 8.1 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
5 4 16 3 6 8 12 1 2 10
-1.1 -0.3 -0.2 -0.1 -0.1 -0.1 0.1 0.3 0.4 0.6

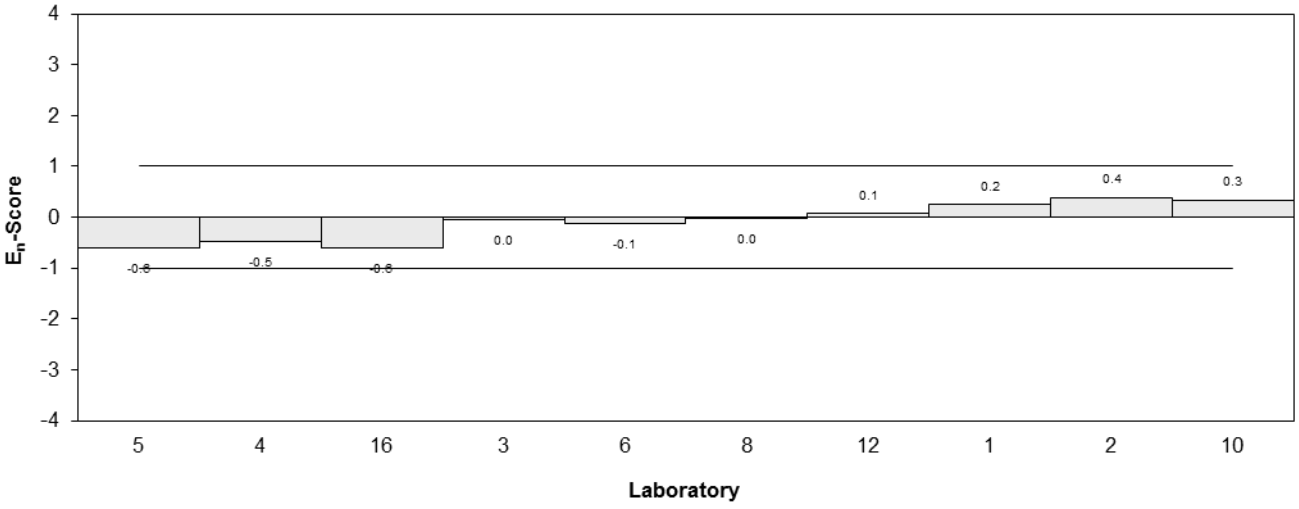

En-Scores: S2 - Ba
En-Score
Laboratory
5 4 16 3 6 8 12 1 2 10
-0.6 -0.5 -0.6 0.0 -0.1 0.0 0.1 0.2 0.4 0.3

Figure 21

Table 25

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Cd
Units	ug/L

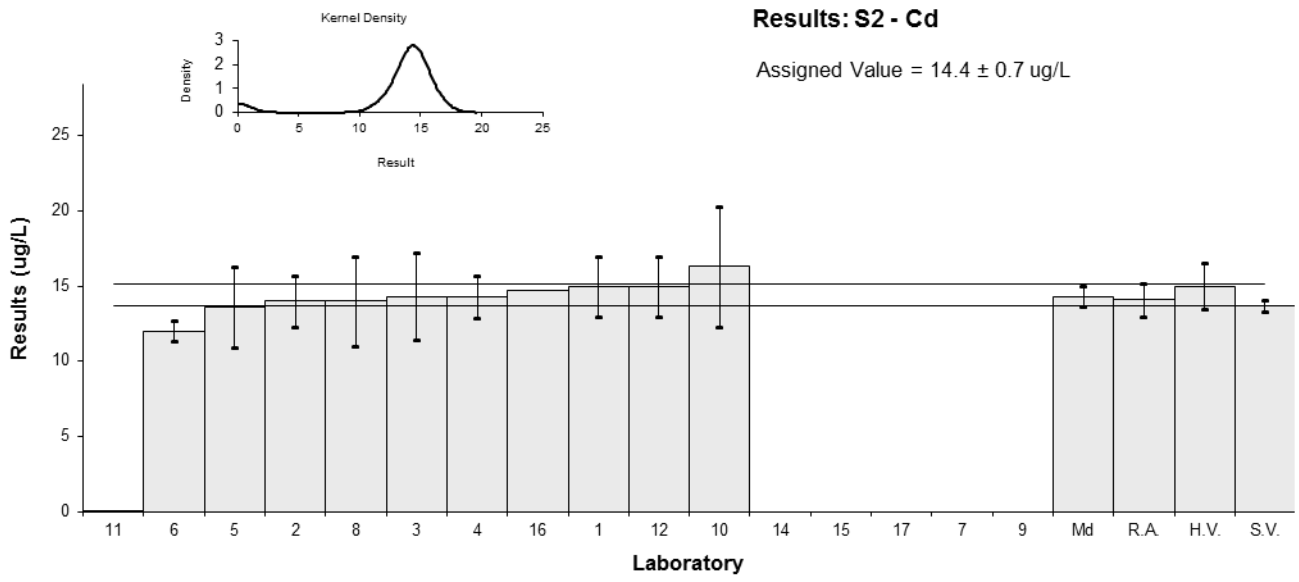
Participant Results

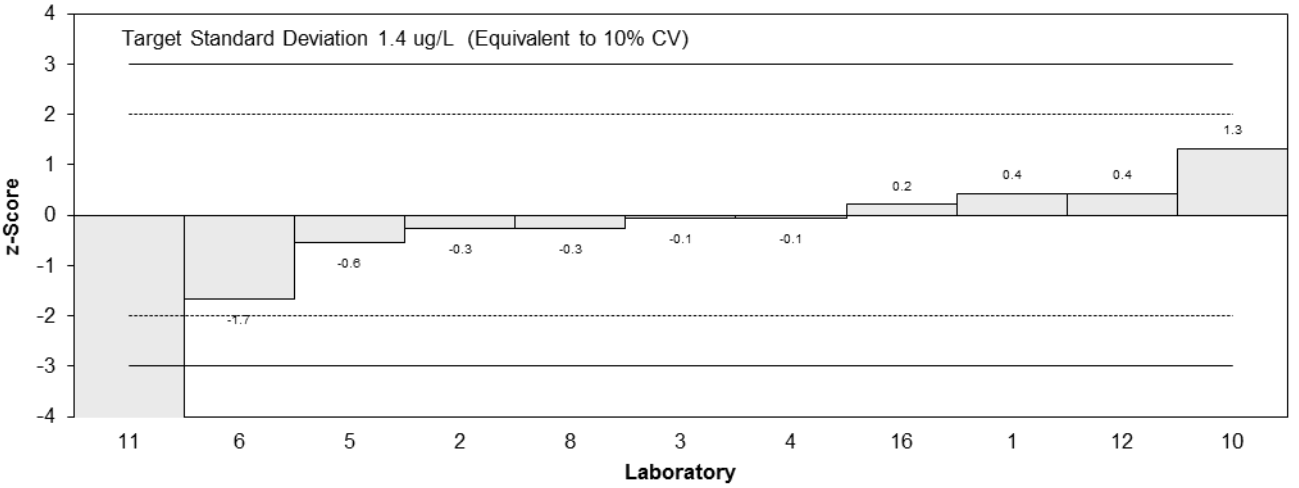
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	15	2.0	0.42	0.28
2	14	1.7	-0.28	-0.22
3	14.3	2.9	-0.07	-0.03
4	14.3	1.4	-0.07	-0.06
5	13.6	2.7	-0.56	-0.29
6	12	0.7	-1.67	-2.42
7	NT	NT		
8	14	3	-0.28	-0.13
9	NT	NT		
10	16.3	4	1.32	0.47
11	0.014	NR	-9.99	-20.55
12	15	2	0.42	0.28
14	<0.01	0.05		
15	NT	NT		
16	14.7	NR	0.21	0.43
17	NT	NT		

Statistics

Assigned Value*	14.4	0.7
Spike	13.7	0.4
Homogeneity Value	15.0	1.5
Robust Average	14.1	1.1
Median	14.3	0.7
Mean	13.0	
N	11	
Max.	16.3	
Min.	0.014	
Robust SD	0.84	
Robust CV	6%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Cd
Assigned Value = 14.4 ± 0.7 ug/L
Results (ug/L)
Laboratory
11 6 5 2 8 3 4 16 1 12 10 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Cd
Target Standard Deviation 1.4 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 6 5 2 8 3 4 16 1 12 10
-1.7 -0.6 -0.3 -0.3 -0.1 -0.1 0.2 0.4 0.4 1.3

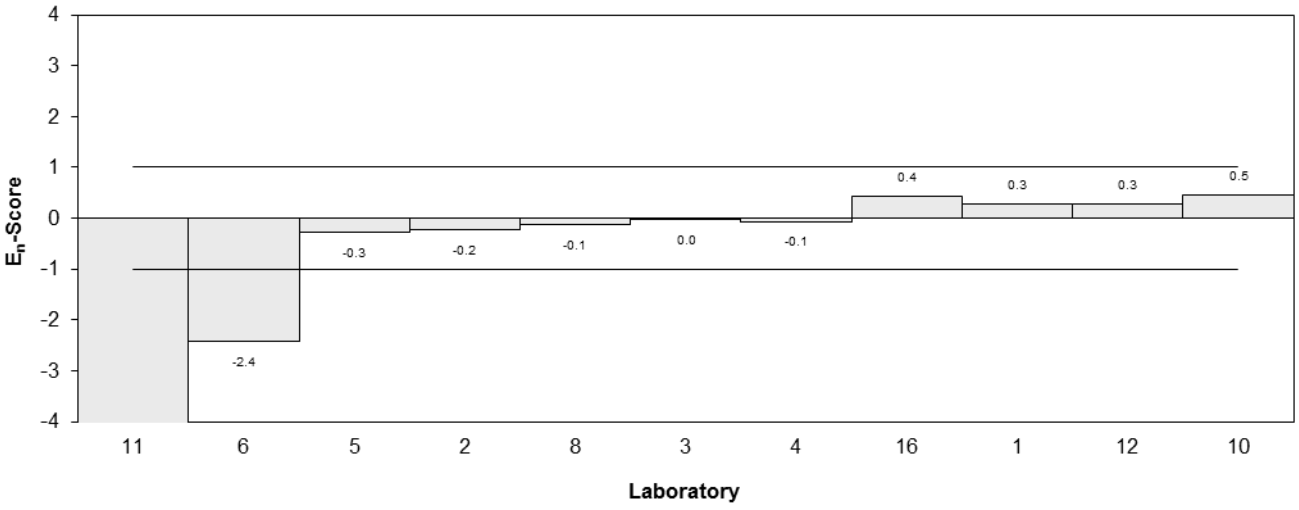

En-Scores: S2 - Cd
En-Score
Laboratory
11 6 5 2 8 3 4 16 1 12 10
-2.4 -0.3 -0.2 -0.1 0.0 -0.1 0.4 0.3 0.3 0.5

Figure 22

Table 26

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Co
Units	ug/L

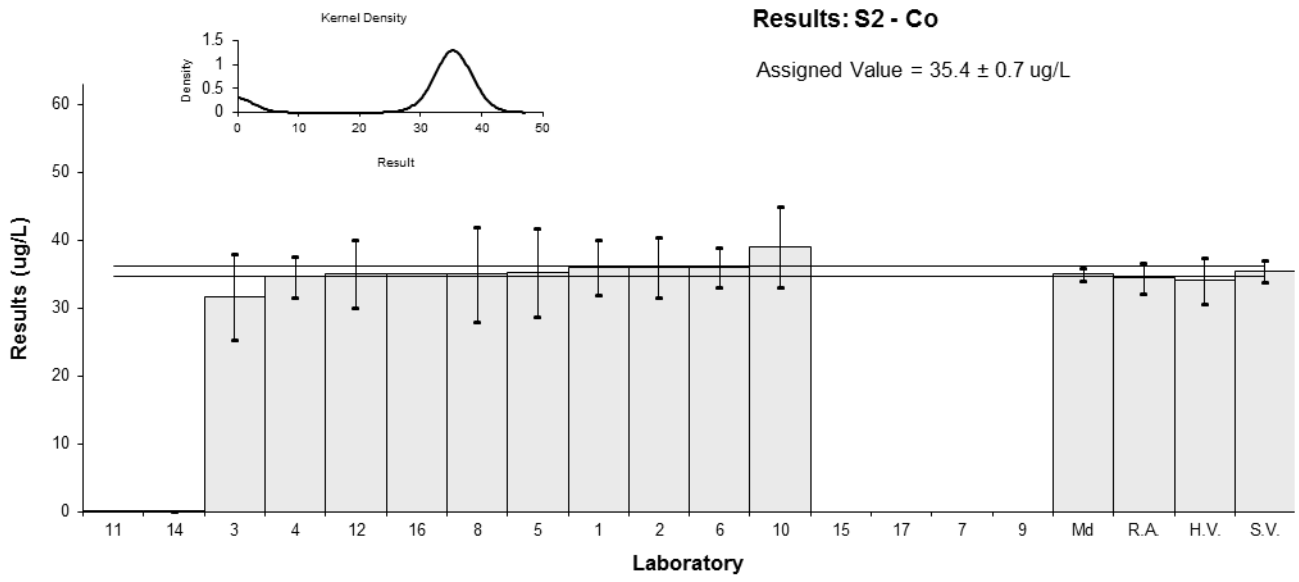
Participant Results

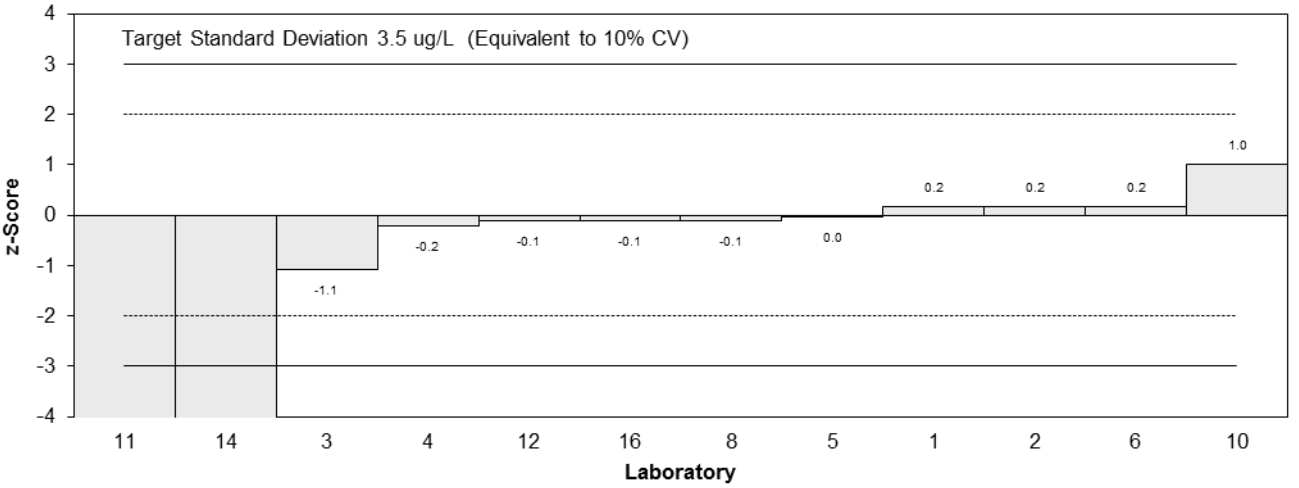
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	36	4.0	0.17	0.15
2	36	4.4	0.17	0.13
3	31.6	6.3	-1.07	-0.60
4	34.6	3.1	-0.23	-0.25
5	35.3	6.5	-0.03	-0.02
6	36	3	0.17	0.19
7	NT	NT		
8	35	7	-0.11	-0.06
9	NT	NT		
10	39	6	1.02	0.60
11	0.026	NR	-9.99	-50.53
12	35	5	-0.11	-0.08
14	0.037	0.05	-9.99	-50.39
15	NT	NT		
16	35	NR	-0.11	-0.57
17	NT	NT		

Statistics

Assigned Value*	35.4	0.7
Spike	35.5	1.6
Homogeneity Value	34.1	3.4
Robust Average	34.4	2.2
Median	35.0	0.9
Mean	29.5	
N	12	
Max.	39	
Min.	0.026	
Robust SD	0.94	
Robust CV	2.7%	

* Robust Average excluding Laboratories 11 and 14.


Kernel Density
Density
Result
Results: S2 - Co
Assigned Value = 35.4 ± 0.7 ug/L
Results (ug/L)
Laboratory
11 14 3 4 12 16 8 5 1 2 6 10 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Co
Target Standard Deviation 3.5 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 14 3 4 12 16 8 5 1 2 6 10
-1.1 -0.2 -0.1 -0.1 -0.1 0.0 0.2 0.2 0.2 1.0

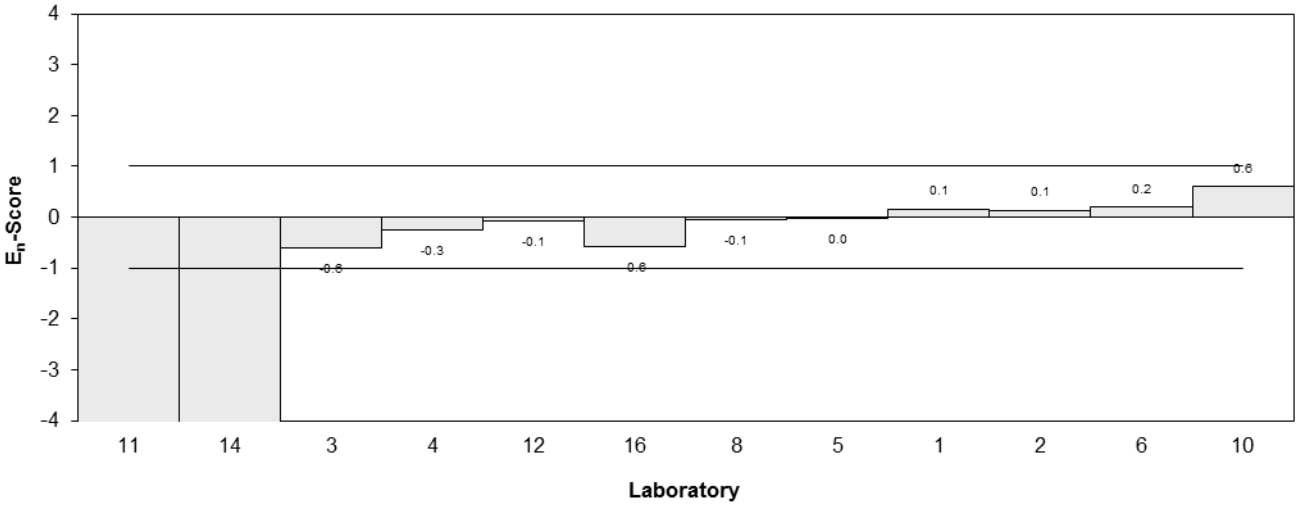

En-Scores: S2 - Co
En-Score
Laboratory
11 14 3 4 12 16 8 5 1 2 6 10
-0.6 -0.3 -0.1 -0.6 -0.1 0.0 0.1 0.1 0.2 0.6

Figure 23

Table 27

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Cr
Units	ug/L

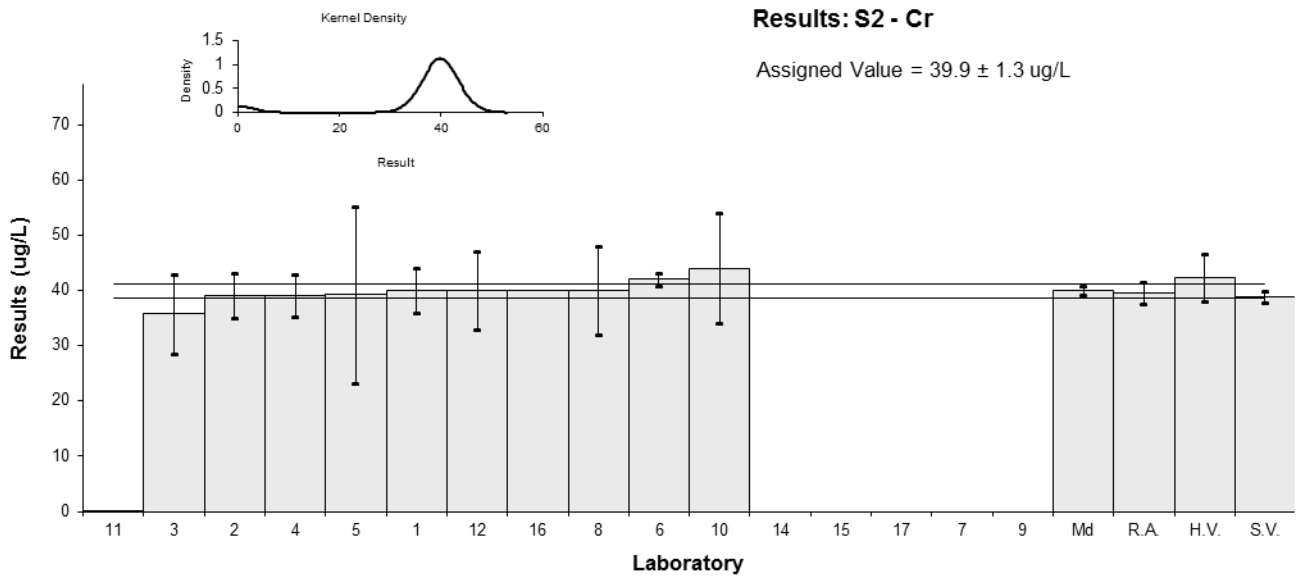
Participant Results

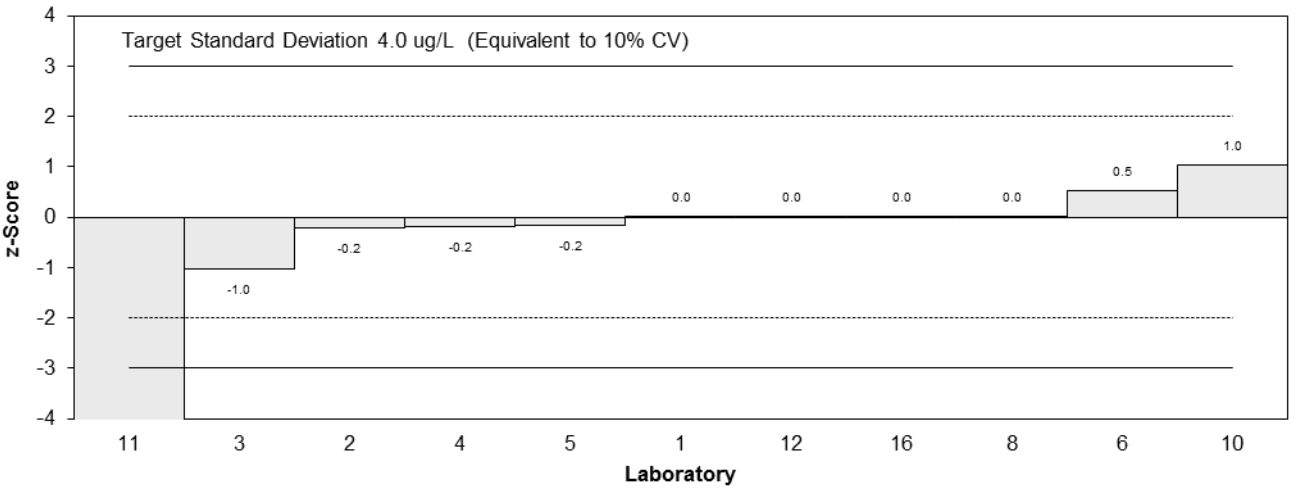
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	40	4.0	0.03	0.02
2	39	4.1	-0.23	-0.21
3	35.8	7.2	-1.03	-0.56
4	39.1	3.9	-0.20	-0.19
5	39.2	16.0	-0.18	-0.04
6	42	1.2	0.53	1.19
7	NT	NT		
8	40	8	0.03	0.01
9	NT	NT		
10	44	10	1.03	0.41
11	0.041	NR	-9.99	-30.66
12	40	7	0.03	0.01
14	NT	NT		
15	NT	NT		
16	40	NR	0.03	0.08
17	NT	NT		

Statistics

Assigned Value*	39.9	1.3
Spike	38.8	1.1
Homogeneity Value	42.3	4.2
Robust Average	39.5	1.9
Median	40.0	0.9
Mean	36.3	
N	11	
Max.	44	
Min.	0.041	
Robust SD	1.6	
Robust CV	4.1%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Cr
Assigned Value = 39.9 ± 1.3 ug/L
Results (ug/L)
Laboratory
11 3 2 4 5 1 12 16 8 6 10 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Cr
Target Standard Deviation 4.0 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 3 2 4 5 1 12 16 8 6 10
-1.0 -0.2 -0.2 -0.2 0.0 0.0 0.0 0.0 0.5 1.0

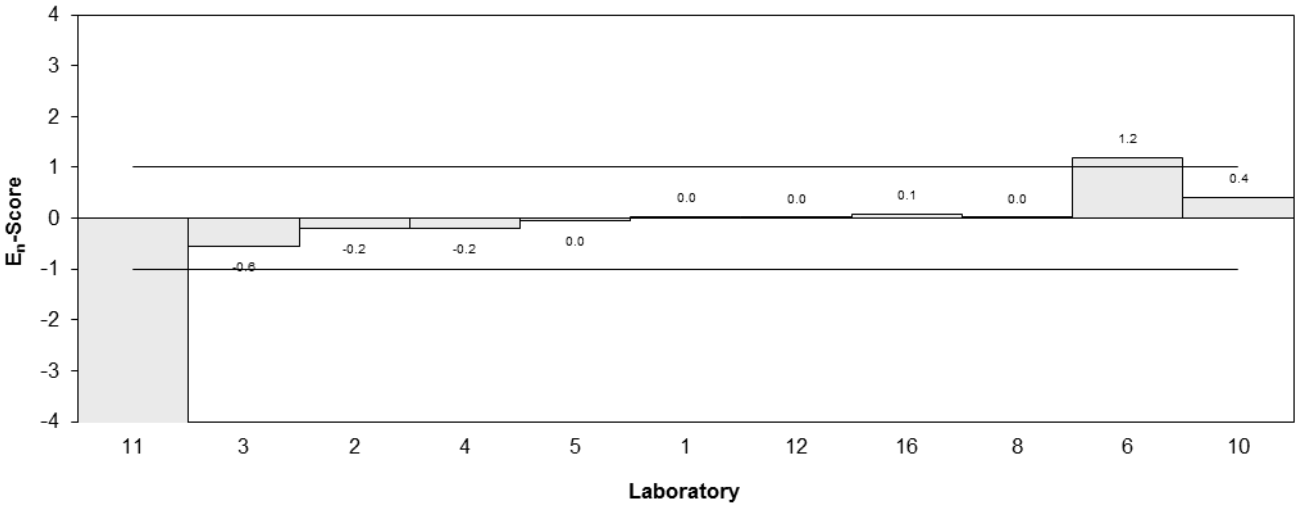

En-Scores: S2 - Cr
En-Score
Laboratory
11 3 2 4 5 1 12 16 8 6 10
-0.6 -0.2 -0.2 0.0 0.0 0.0 0.1 0.0 1.2 0.4

Figure 24

Table 28

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Cu
Units	ug/L

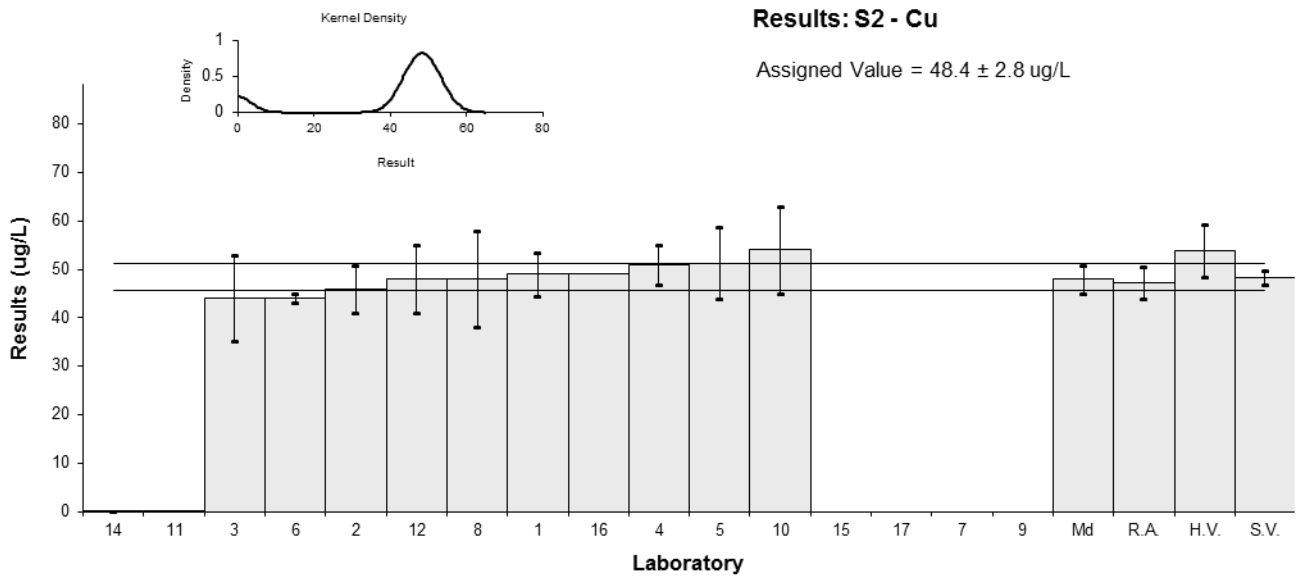
Participant Results

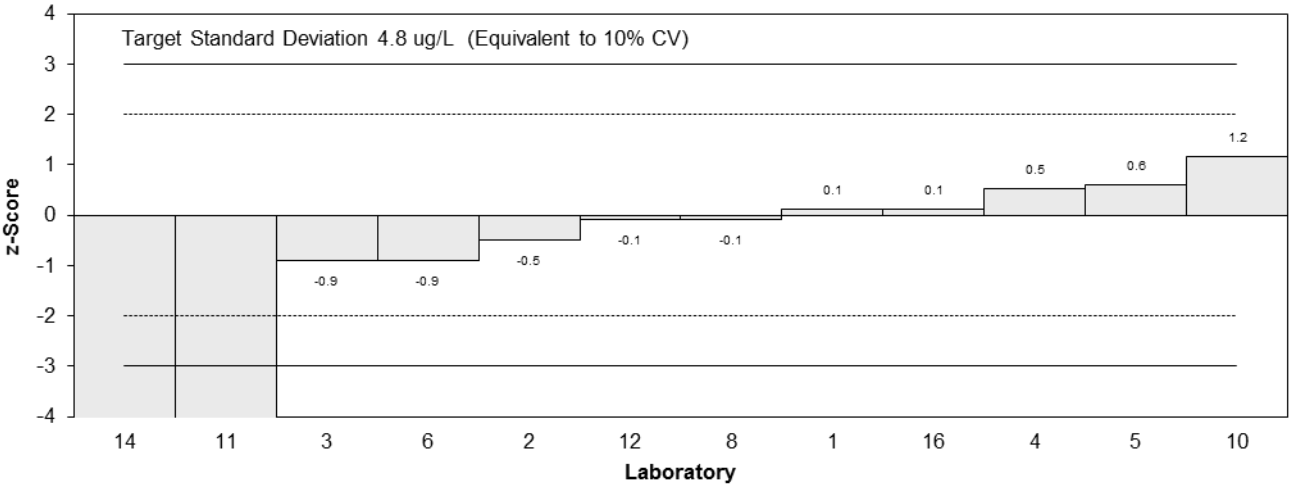
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	49	4.5	0.12	0.11
2	46	4.9	-0.50	-0.43
3	44.0	8.8	-0.91	-0.48
4	50.9	4.1	0.52	0.50
5	51.3	7.5	0.60	0.36
6	44	1	-0.91	-1.48
7	NT	NT		
8	48	10	-0.08	-0.04
9	NT	NT		
10	54	9	1.16	0.59
11	0.052	NR	-9.99	-17.27
12	48	7	-0.08	-0.05
14	0.036	0.05	-9.99	-17.27
15	NT	NT		
16	49	NR	0.12	0.21
17	NT	NT		

Statistics

Assigned Value*	48.4	2.8
Spike	48.2	1.5
Homogeneity Value	53.8	5.4
Robust Average	47.2	3.3
Median	48.0	2.9
Mean	40.4	
N	12	
Max.	54	
Min.	0.036	
Robust SD	3.6	
Robust CV	7.6%	

* Robust Average excluding Laboratories 11 and 14.


Kernel Density
Density
Result
Results: S2 - Cu
Assigned Value = 48.4 ± 2.8 ug/L
Results (ug/L)
Laboratory
14 11 3 6 2 12 8 1 16 4 5 10 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Cu
Target Standard Deviation 4.8 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
14 11 3 6 2 12 8 1 16 4 5 10
-0.9 -0.9 -0.5 -0.1 -0.1 0.1 0.1 0.5 0.6 1.2

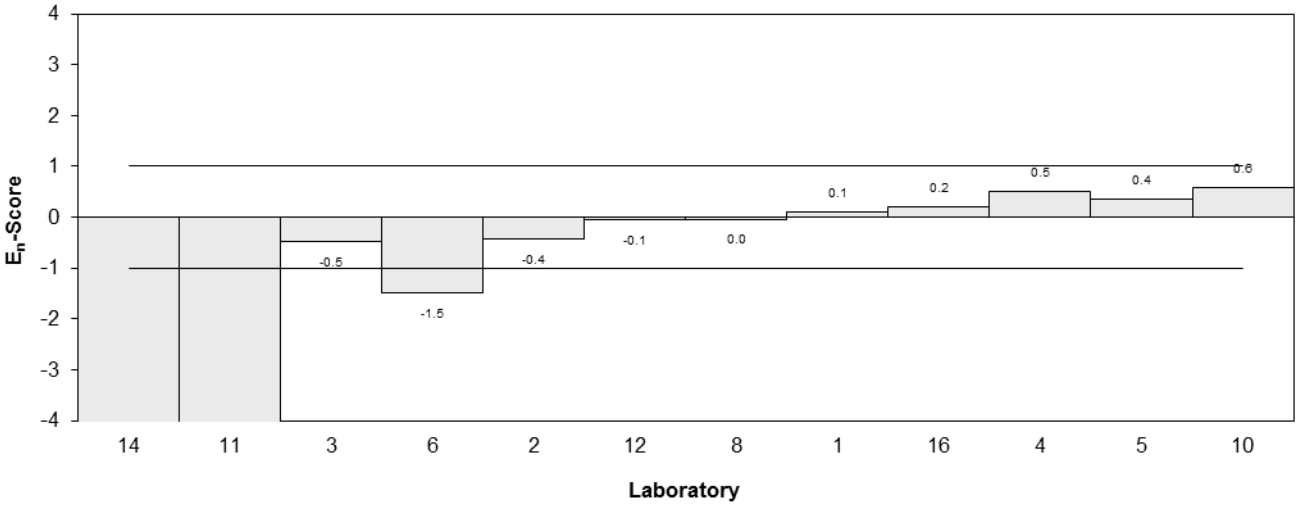

En-Scores: S2 - Cu
En-Score
Laboratory
14 11 3 6 2 12 8 1 16 4 5 10
-0.5 -1.5 -0.4 -0.1 0.0 0.1 0.2 0.5 0.4 0.6

Figure 25

Table 29

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Fe
Units	ug/L

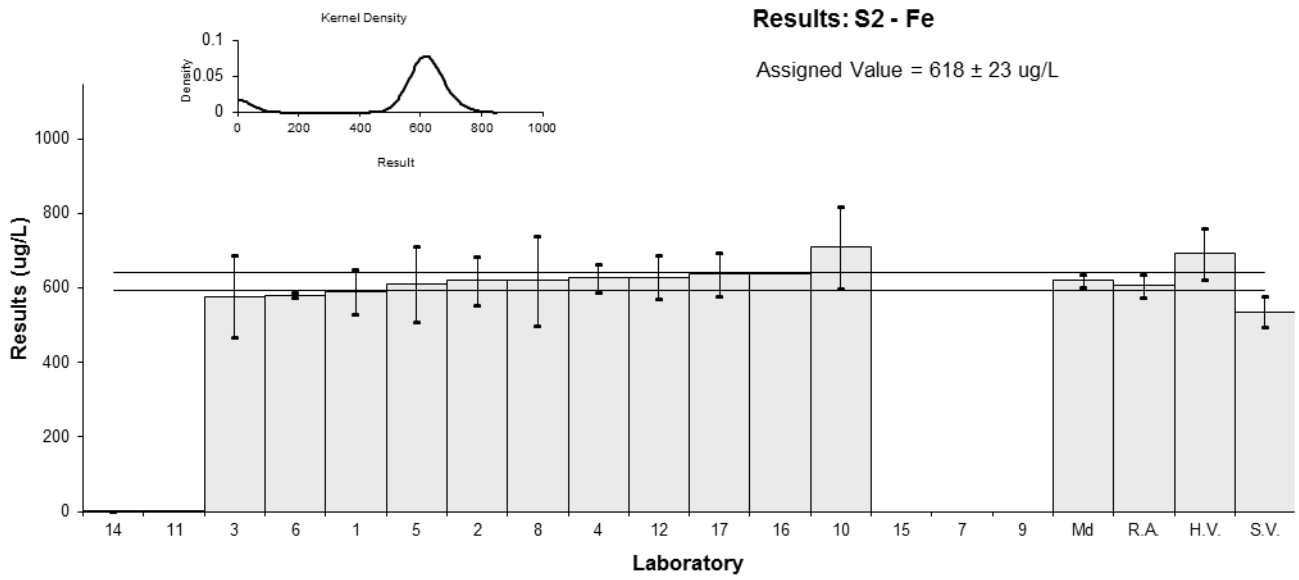
Participant Results

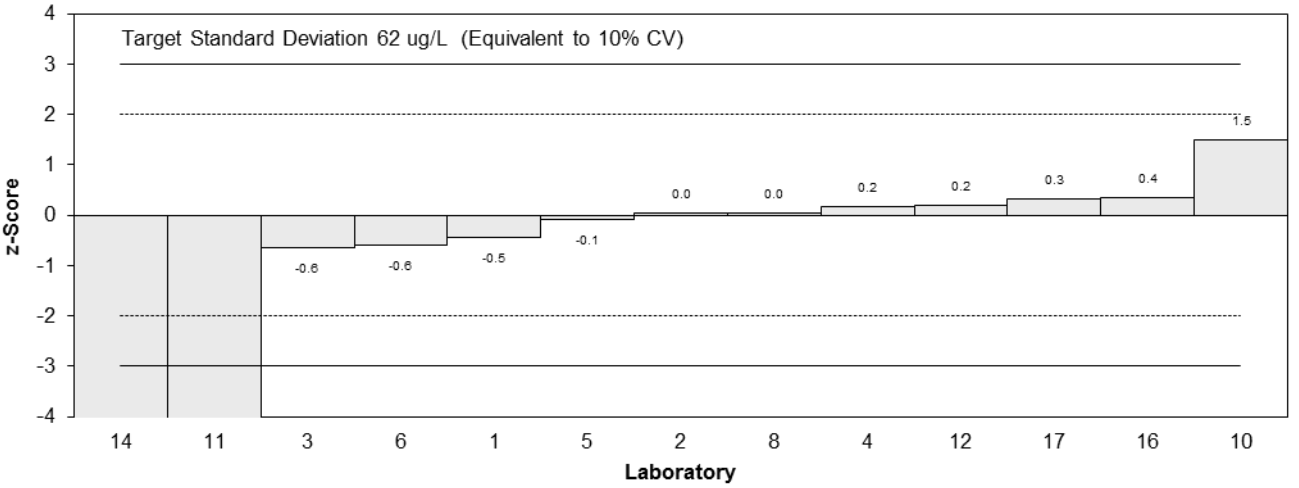
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	590	60	-0.45	-0.44
2	620	67	0.03	0.03
3	578	111	-0.65	-0.35
4	628	38	0.16	0.23
5	612	102	-0.10	-0.06
6	581	7	-0.60	-1.54
7	NT	NT		
8	620	120	0.03	0.02
9	NT	NT		
10	710	110	1.49	0.82
11	0.779	NR	-9.99	-26.84
12	630	60	0.19	0.19
14	0.042	0.05	-10.00	-26.87
15	NT	NT		
16	640	NR	0.36	0.96
17	638	58	0.32	0.32

Statistics

Assigned Value*	618	23
Spike	537	42
Homogeneity Value	693	69
Robust Average	607	31
Median	620	18
Mean	527	
N	13	
Max.	710	
Min.	0.042	
Robust SD	30	
Robust CV	4.9%	

* Robust Average excluding Laboratories 11 and 14.


Kernel Density
Density
Result
Results: S2 - Fe
Assigned Value = 618 ± 23 ug/L
Results (ug/L)
Laboratory
14 11 3 6 1 5 2 8 4 12 17 16 10 15 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Fe
Target Standard Deviation 62 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
14 11 3 6 1 5 2 8 4 12 17 16 10
-0.6 -0.6 -0.5 -0.1 0.0 0.0 0.2 0.2 0.3 0.4 1.5

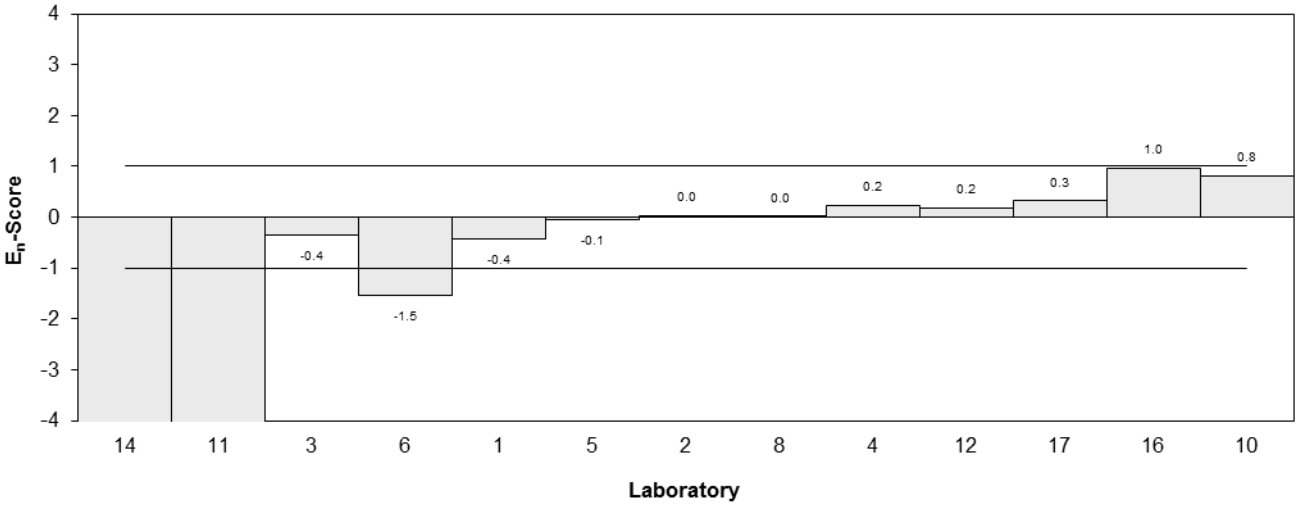

En-Scores: S2 - Fe
En-Score
Laboratory
14 11 3 6 1 5 2 8 4 12 17 16 10
-0.4 -1.5 -0.4 -0.1 0.0 0.0 0.2 0.2 0.3 1.0 0.8

Figure 26

Table 30

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Mn
Units	ug/L

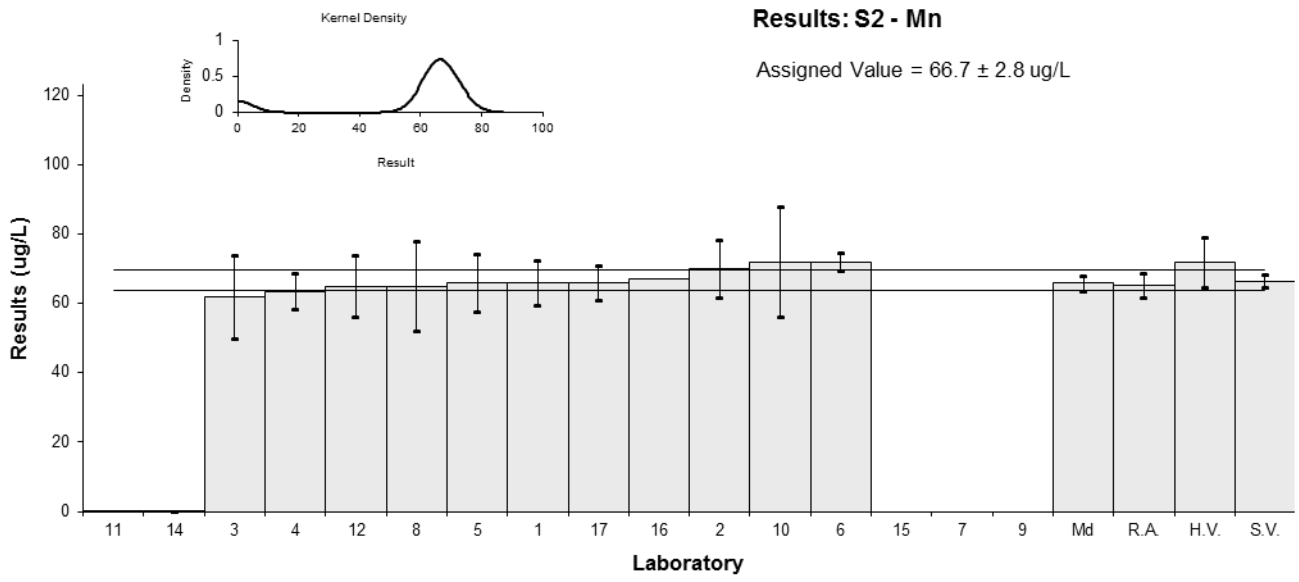
Participant Results

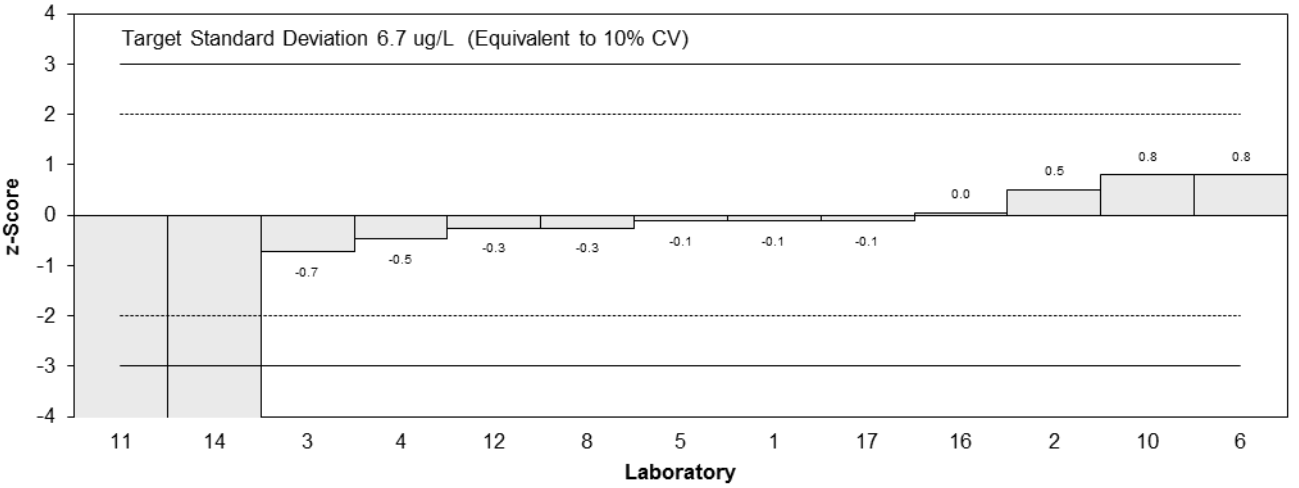
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	66	6.5	-0.10	-0.10
2	70	8.2	0.49	0.38
3	61.8	12	-0.73	-0.40
4	63.5	5.1	-0.48	-0.55
5	65.9	8.4	-0.12	-0.09
6	72	2.6	0.79	1.39
7	NT	NT		
8	65	13	-0.25	-0.13
9	NT	NT		
10	72	16	0.79	0.33
11	0.061	NR	-9.99	-23.80
12	65	9	-0.25	-0.18
14	0.069	0.05	-9.99	-23.79
15	NT	NT		
16	67	NR	0.04	0.11
17	66	5	-0.10	-0.12

Statistics

Assigned Value*	66.7	2.8
Spike	66.4	1.9
Homogeneity Value	71.8	7.2
Robust Average	65.3	3.6
Median	65.9	2.2
Mean	56.5	
N	13	
Max.	72	
Min.	0.061	
Robust SD	3.7	
Robust CV	5.7%	

* Robust Average excluding Laboratories 11 and 14.


Kernel Density
Density
Result
Results: S2 - Mn
Assigned Value = 66.7 ± 2.8 ug/L
Results (ug/L)
Laboratory
11 14 3 4 12 8 5 1 17 16 2 10 6 15 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Mn
Target Standard Deviation 6.7 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 14 3 4 12 8 5 1 17 16 2 10 6
-0.7 -0.5 -0.3 -0.3 -0.1 -0.1 -0.1 0.0 0.5 0.8 0.8

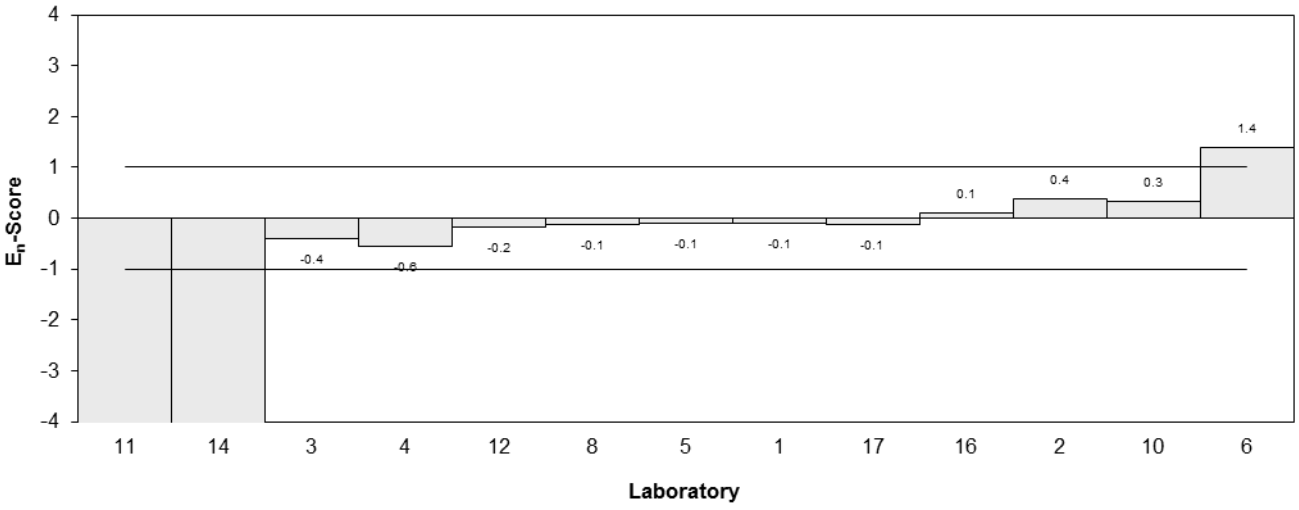

En-Scores: S2 - Mn
En-Score
Laboratory
11 14 3 4 12 8 5 1 17 16 2 10 6
-0.4 -0.6 -0.2 -0.1 -0.1 -0.1 -0.1 0.1 0.4 0.3 1.4

Figure 27

Table 31

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Mo
Units	ug/L

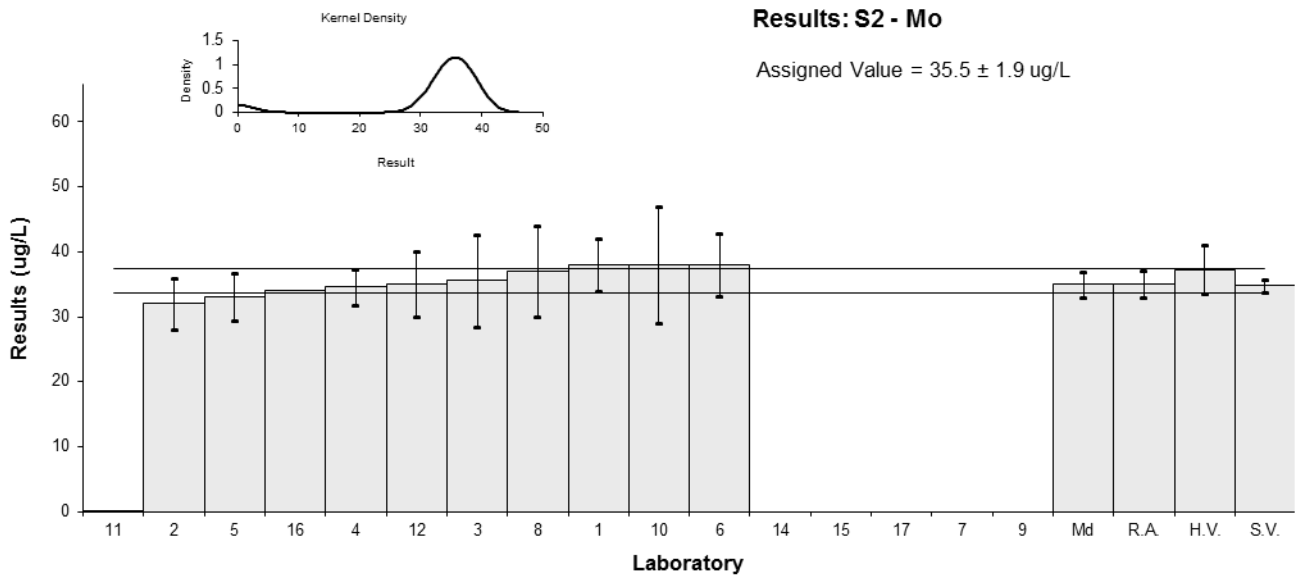
Participant Results

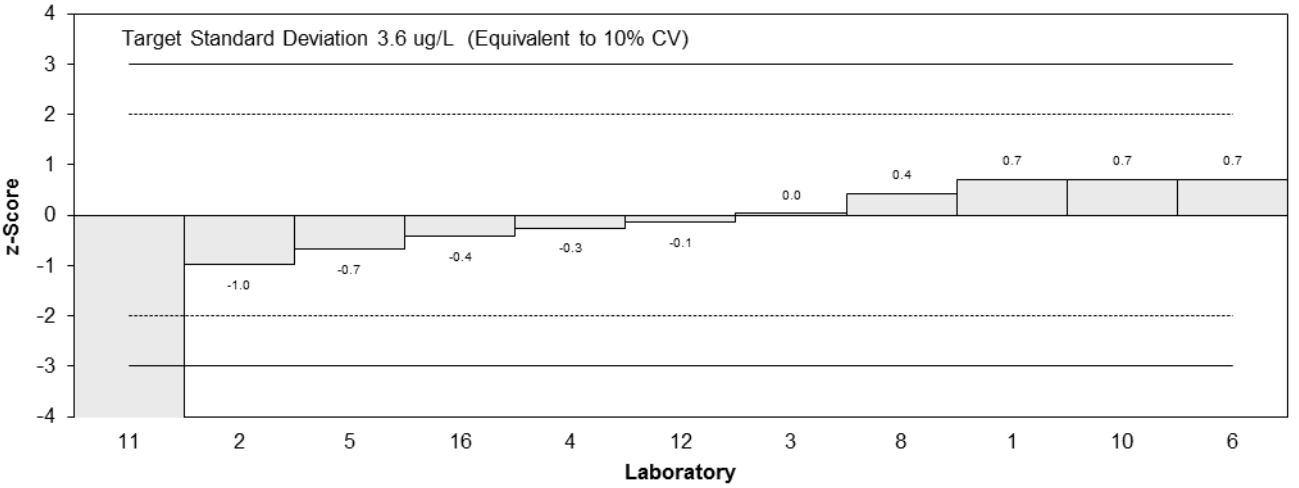
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	38	4.0	0.70	0.56
2	32	4.0	-0.99	-0.79
3	35.6	7.1	0.03	0.01
4	34.6	2.8	-0.25	-0.27
5	33.1	3.7	-0.68	-0.58
6	38	4.8	0.70	0.48
7	NT	NT		
8	37	7	0.42	0.21
9	NT	NT		
10	38	9	0.70	0.27
11	0.091	NR	-9.97	-18.64
12	35	5	-0.14	-0.09
14	NT	NT		
15	NT	NT		
16	34	NR	-0.42	-0.79
17	NT	NT		

Statistics

Assigned Value*	35.5	1.9
Spike	34.8	1.0
Homogeneity Value	37.3	3.7
Robust Average	35.1	2.1
Median	35.0	2.0
Mean	32.3	
N	11	
Max.	38	
Min.	0.091	
Robust SD	2.5	
Robust CV	7.1%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Mo
Assigned Value = 35.5 ± 1.9 ug/L
Results (ug/L)
Laboratory
11 2 5 16 4 12 3 8 1 10 6 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Mo
Target Standard Deviation 3.6 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 2 5 16 4 12 3 8 1 10 6
-1.0 -0.7 -0.4 -0.3 -0.1 0.0 0.4 0.7 0.7 0.7

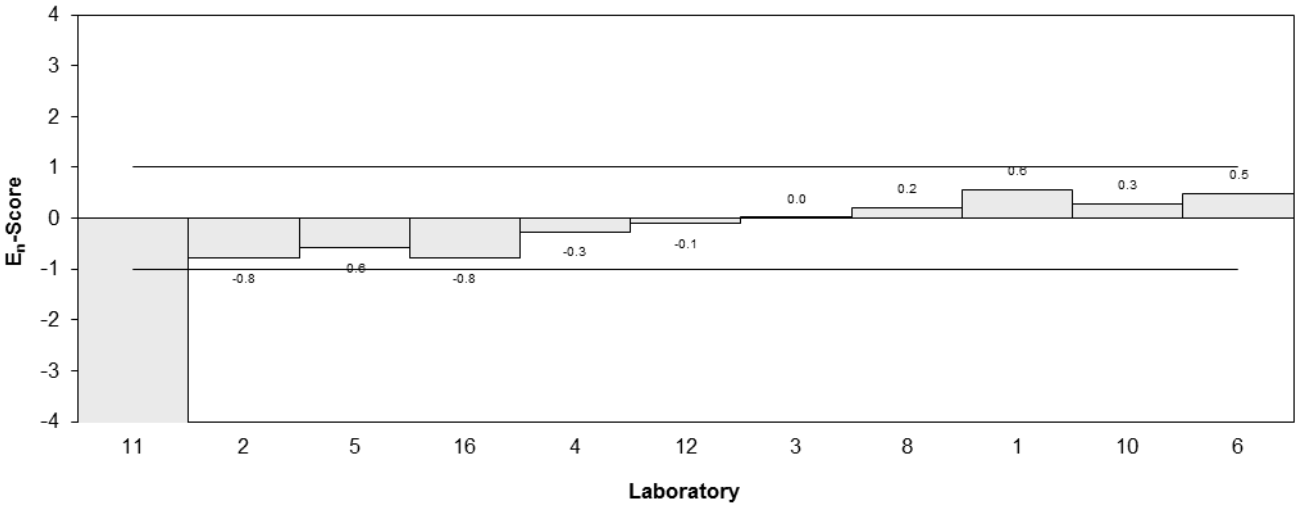

En-Scores: S2 - Mo
En-Score
Laboratory
11 2 5 16 4 12 3 8 1 10 6
-0.8 -0.6 -0.8 -0.3 -0.1 0.0 0.2 0.6 0.3 0.5

Figure 28

Table 32

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Ni
Units	ug/L

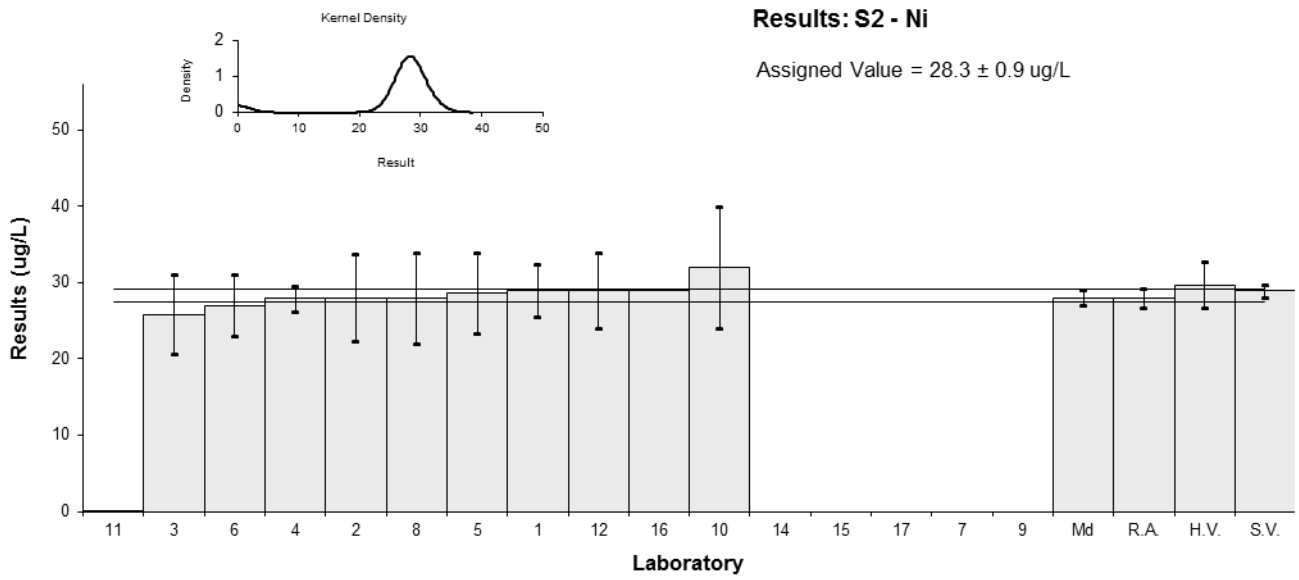
Participant Results

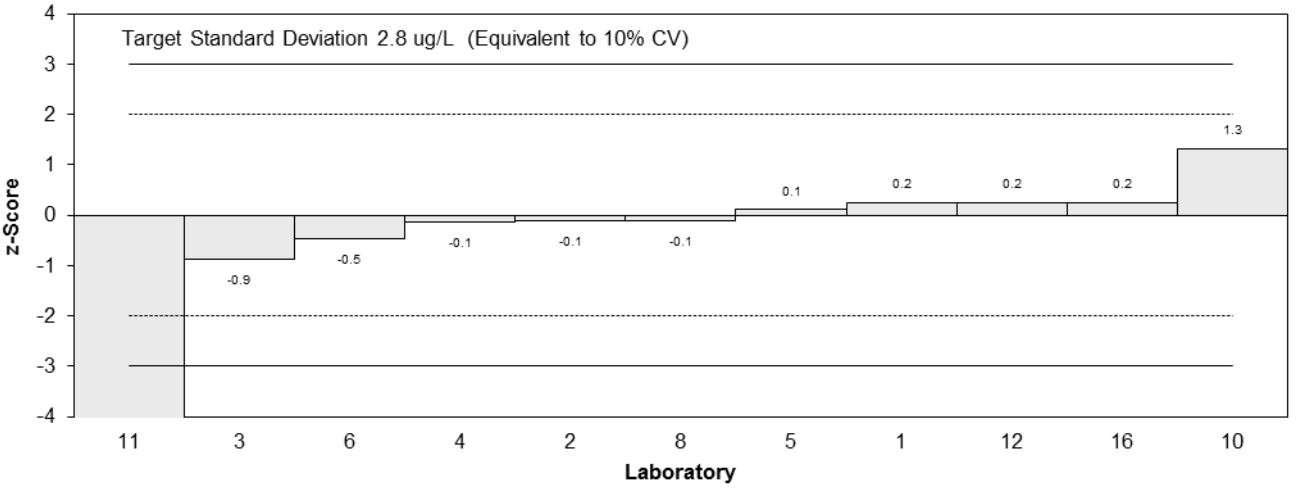
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	29	3.5	0.25	0.19
2	28	5.7	-0.11	-0.05
3	25.8	5.2	-0.88	-0.47
4	27.9	1.7	-0.14	-0.21
5	28.6	5.3	0.11	0.06
6	27	4	-0.46	-0.32
7	NT	NT		
8	28	6	-0.11	-0.05
9	NT	NT		
10	32	8	1.31	0.46
11	0.029	NR	-9.99	-31.41
12	29	5	0.25	0.14
14	NT	NT		
15	NT	NT		
16	29	NR	0.25	0.78
17	NT	NT		

Statistics

Assigned Value*	28.3	0.9
Spike	28.9	0.8
Homogeneity Value	29.7	3.0
Robust Average	28.0	1.3
Median	28.0	1.0
Mean	25.8	
N	11	
Max.	32	
Min.	0.029	
Robust SD	1.2	
Robust CV	4.3%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Ni
Assigned Value = 28.3 ± 0.9 ug/L
Results (ug/L)
Laboratory
11 3 6 4 2 8 5 1 12 16 10 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Ni
Target Standard Deviation 2.8 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 3 6 4 2 8 5 1 12 16 10
-0.9 -0.5 -0.1 -0.1 -0.1 0.1 0.2 0.2 0.2 1.3

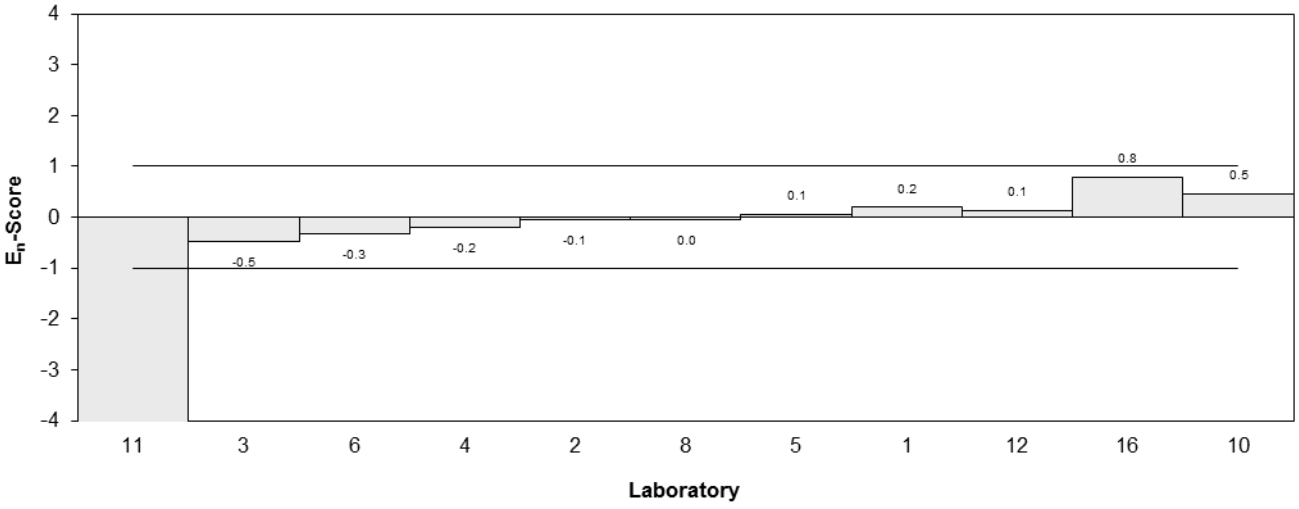

En-Scores: S2 - Ni
En-Score
Laboratory
11 3 6 4 2 8 5 1 12 16 10
-0.5 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.1 0.8 0.5

Figure 29

Table 33

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Pb
Units	ug/L

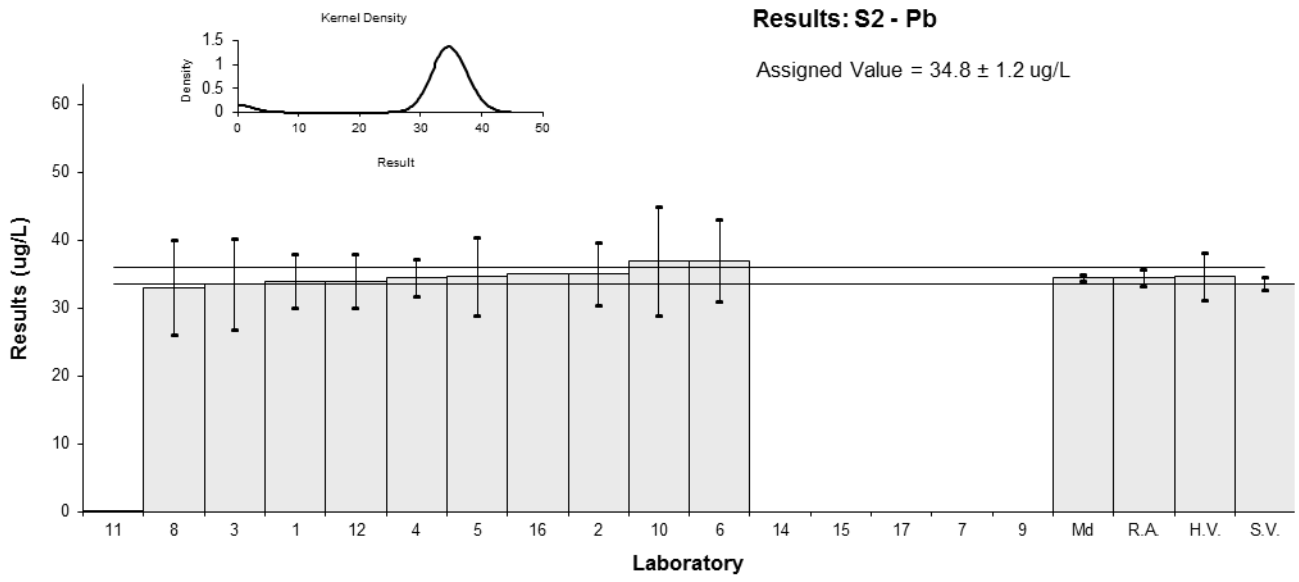
Participant Results

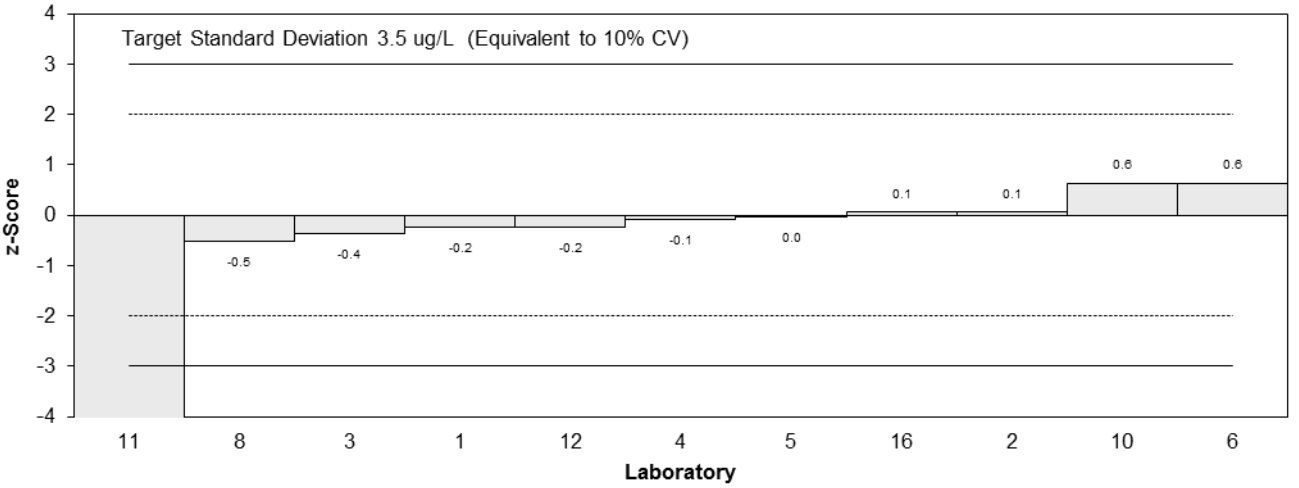
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	34	4.0	-0.23	-0.19
2	35	4.6	0.06	0.04
3	33.5	6.7	-0.37	-0.19
4	34.5	2.8	-0.09	-0.10
5	34.7	5.7	-0.03	-0.02
6	37	6	0.63	0.36
7	NT	NT		
8	33	7	-0.52	-0.25
9	NT	NT		
10	37	8	0.63	0.27
11	0.032	NR	-9.99	-28.97
12	34	4	-0.23	-0.19
14	<0.01	0.05		
15	NT	NT		
16	35	NR	0.06	0.17
17	NT	NT		

Statistics

Assigned Value*	34.8	1.2
Spike	33.6	0.9
Homogeneity Value	34.7	3.5
Robust Average	34.5	1.3
Median	34.5	0.5
Mean	31.6	
N	11	
Max.	37	
Min.	0.032	
Robust SD	1.5	
Robust CV	4.3%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Pb
Assigned Value = 34.8 ± 1.2 ug/L
Results (ug/L)
Laboratory
11 8 3 1 12 4 5 16 2 10 6 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Pb
Target Standard Deviation 3.5 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 8 3 1 12 4 5 16 2 10 6
-0.5 -0.4 -0.2 -0.2 -0.1 0.0 0.1 0.1 0.6 0.6

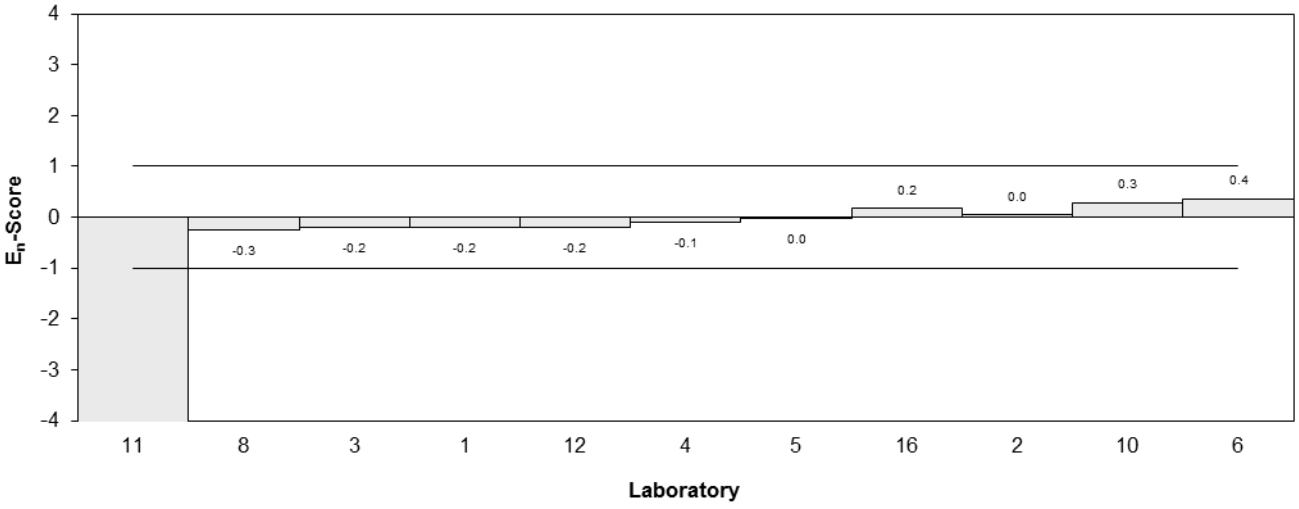

En-Scores: S2 - Pb
En-Score
Laboratory
11 8 3 1 12 4 5 16 2 10 6
-0.3 -0.2 -0.2 -0.2 -0.1 0.0 0.2 0.0 0.3 0.4

Figure 30

Table 34

Sample Details

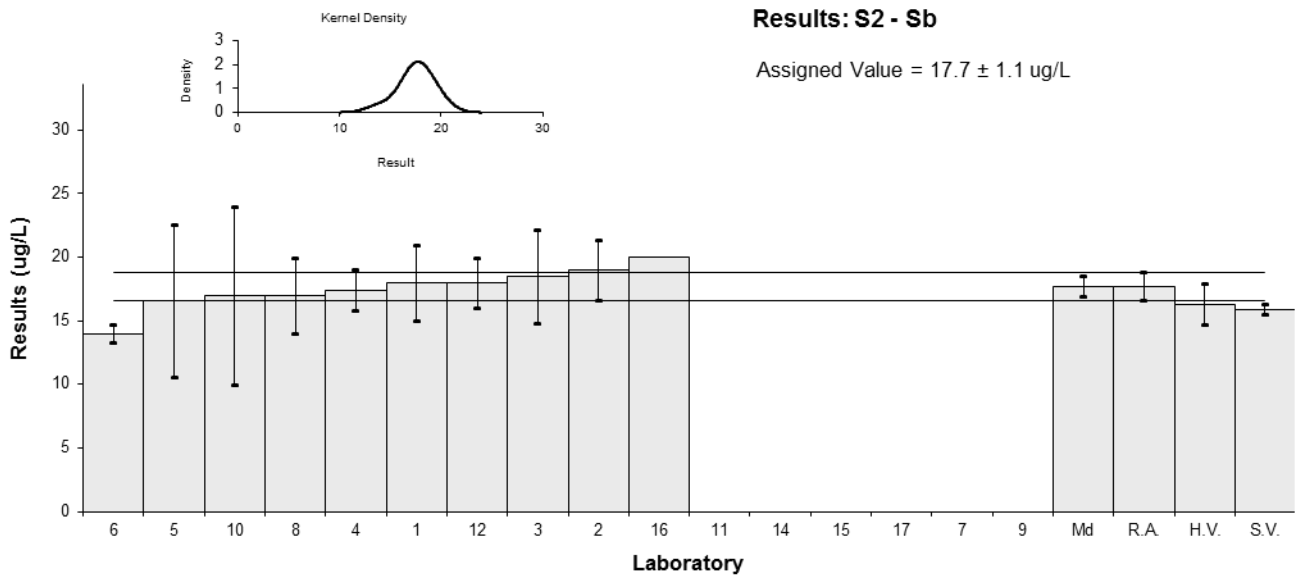
Sample No.	S2
Matrix.	River Water
Analyte.	Sb
Units	ug/L

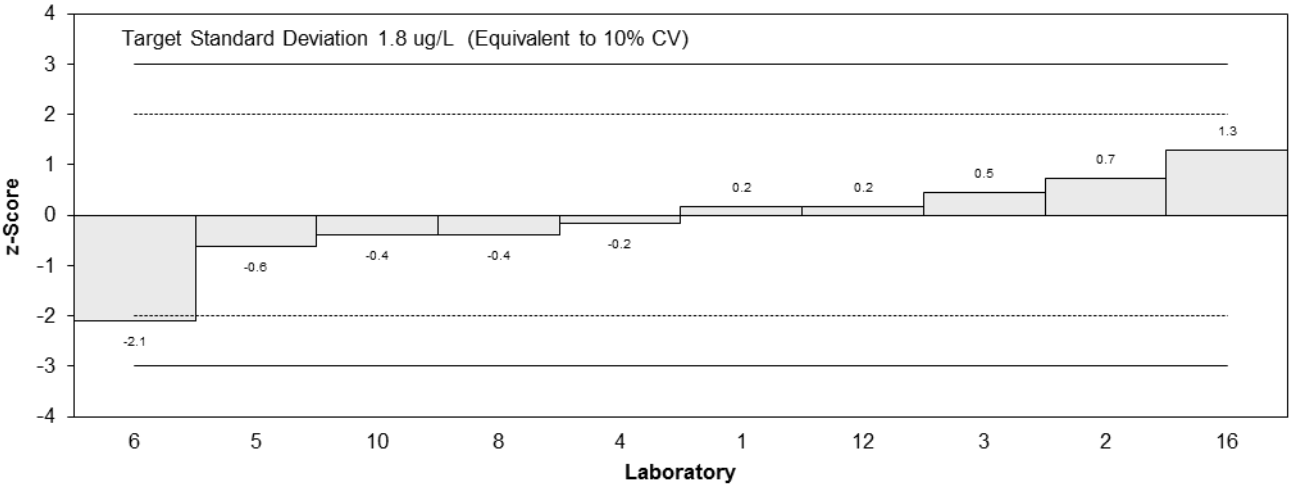
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	18	3.0	0.17	0.09
2	19	2.4	0.73	0.49
3	18.5	3.7	0.45	0.21
4	17.4	1.6	-0.17	-0.15
5	16.6	6.0	-0.62	-0.18
6	14	0.7	-2.09	-2.84
7	NT	NT		
8	17	3	-0.40	-0.22
9	NT	NT		
10	17	7	-0.40	-0.10
11	NT	NT		
12	18	2	0.17	0.13
14	NT	NT		
15	NT	NT		
16	20	NR	1.30	2.09
17	NT	NT		

Statistics

Assigned Value	17.7	1.1
Spike	15.9	0.4
Homogeneity Value	16.3	1.6
Robust Average	17.7	1.1
Median	17.7	0.8
Mean	17.6	
N	10	
Max.	20	
Min.	14	
Robust SD	1.4	
Robust CV	7.9%	


Kernel Density
Density
Result
Results: S2 - Sb
Assigned Value = 17.7 ± 1.1 ug/L
Results (ug/L)
Laboratory
6 5 10 8 4 1 12 3 2 16 11 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Sb
Target Standard Deviation 1.8 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
6 5 10 8 4 1 12 3 2 16
-2.1 -0.6 -0.4 -0.4 -0.2 0.2 0.2 0.5 0.7 1.3

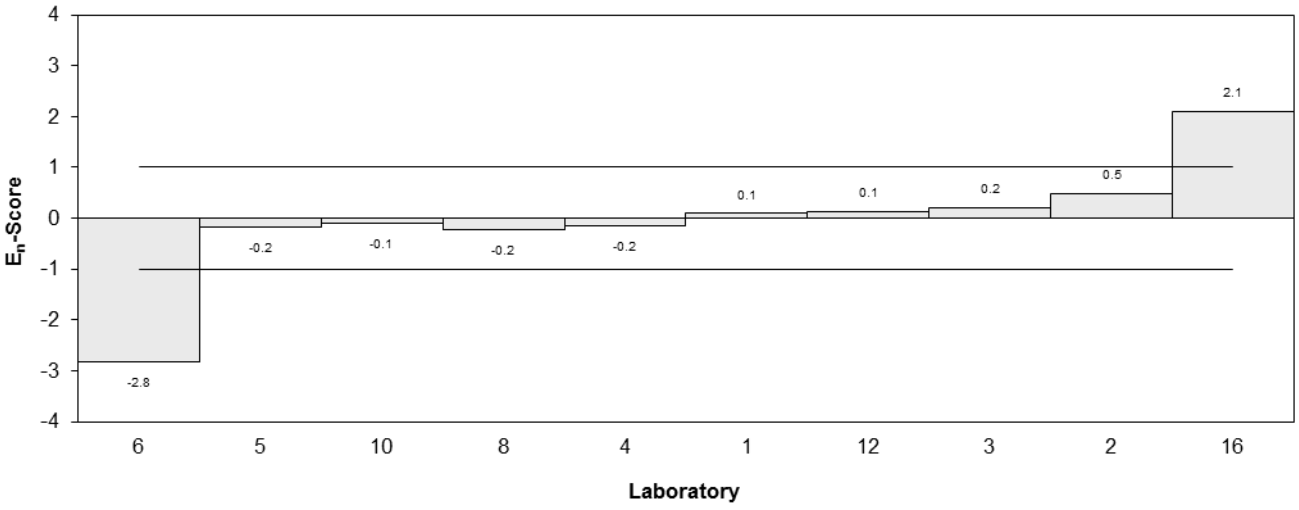

En-Scores: S2 - Sb
En-Score
Laboratory
6 5 10 8 4 1 12 3 2 16
-2.8 -0.2 -0.1 -0.2 -0.2 0.1 0.1 0.2 0.5 2.1

Figure 31

Table 35

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Se
Units	ug/L

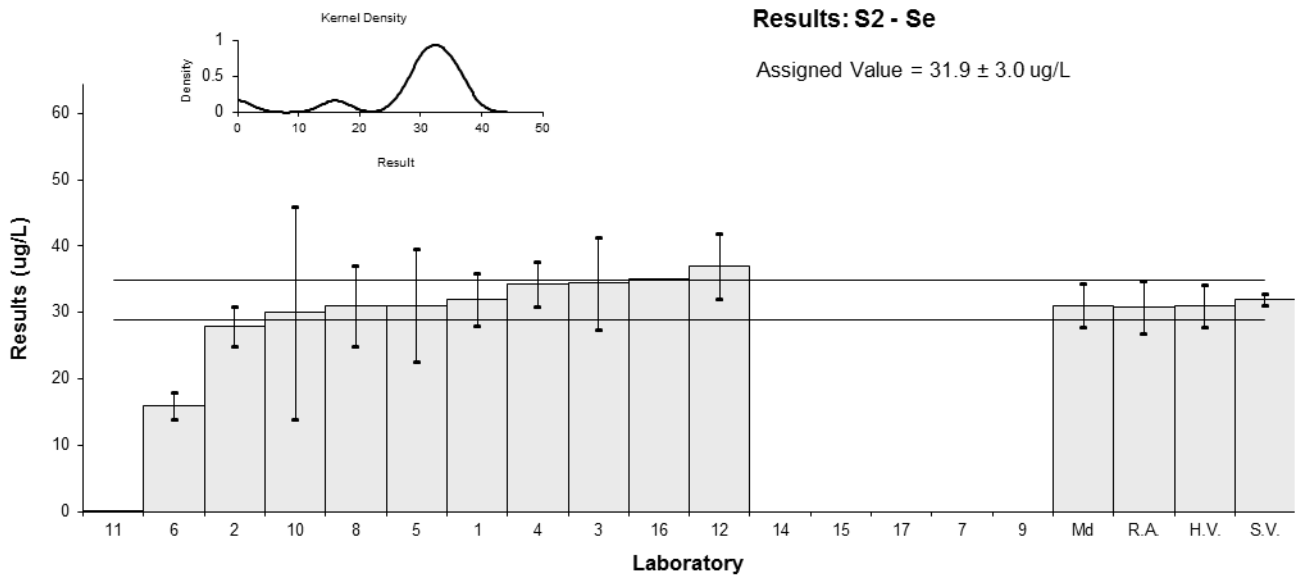
Participant Results

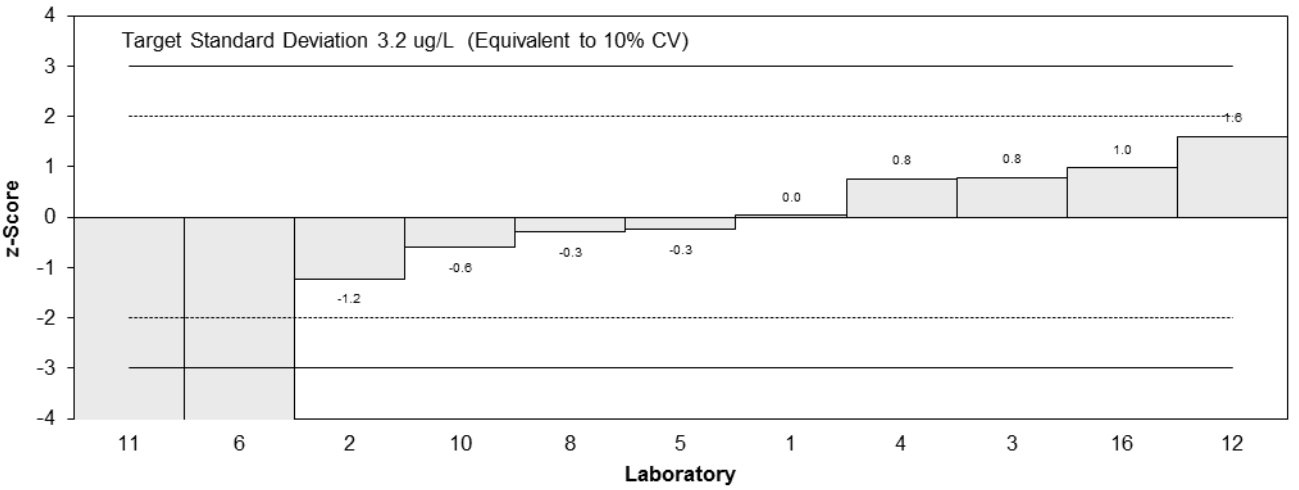
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	32	4.0	0.03	0.02
2	28	3.0	-1.22	-0.92
3	34.4	6.9	0.78	0.33
4	34.3	3.3	0.75	0.54
5	31.1	8.5	-0.25	-0.09
6	16	2	-4.98	-4.41
7	NT	NT		
8	31	6	-0.28	-0.13
9	NT	NT		
10	30	16	-0.60	-0.12
11	0.044	NR	-9.99	-10.62
12	37	5	1.60	0.87
14	NT	NT		
15	NT	NT		
16	35	NR	0.97	1.03
17	NT	NT		

Statistics

Assigned Value*	31.9	3.0
Spike	32.0	0.9
Homogeneity Value	31.0	3.1
Robust Average	30.8	4.0
Median	31.1	3.2
Mean	28.1	
N	11	
Max.	37	
Min.	0.044	
Robust SD	3.8	
Robust CV	12%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S2 - Se
Assigned Value = 31.9 ± 3.0 ug/L
Results (ug/L)
Laboratory
11 6 2 10 8 5 1 4 3 16 12 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Se
Target Standard Deviation 3.2 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
11 6 2 10 8 5 1 4 3 16 12
-1.2 -0.6 -0.3 -0.3 0.0 0.8 0.8 1.0 1.6

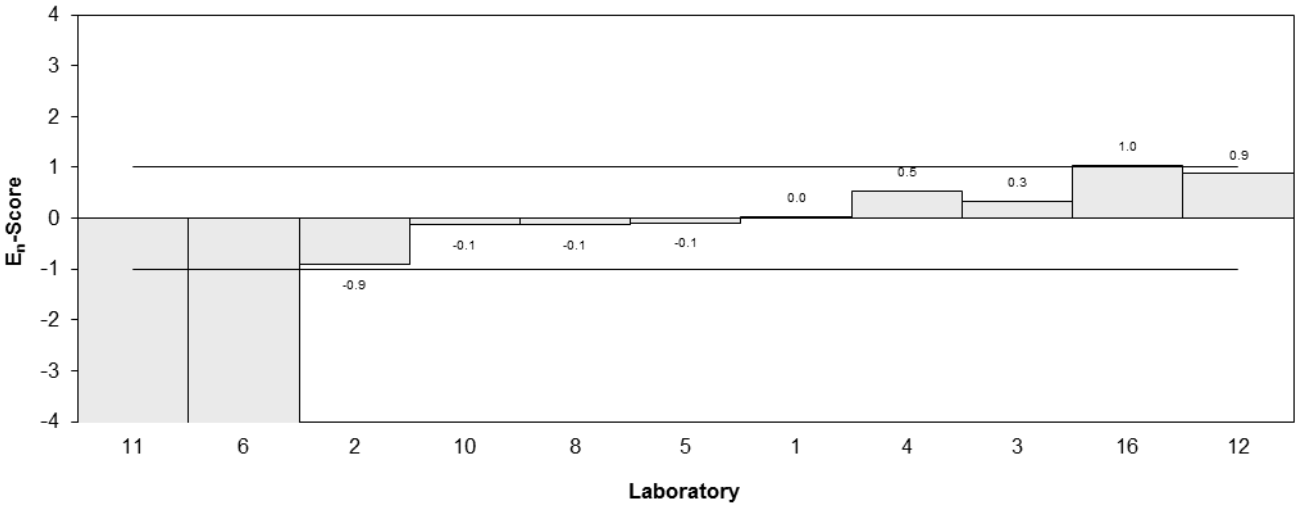

En-Scores: S2 - Se
En-Score
Laboratory
11 6 2 10 8 5 1 4 3 16 12
-0.9 -0.1 -0.1 -0.1 0.0 0.5 0.3 1.0 0.9

Figure 32

Table 36

Sample Details

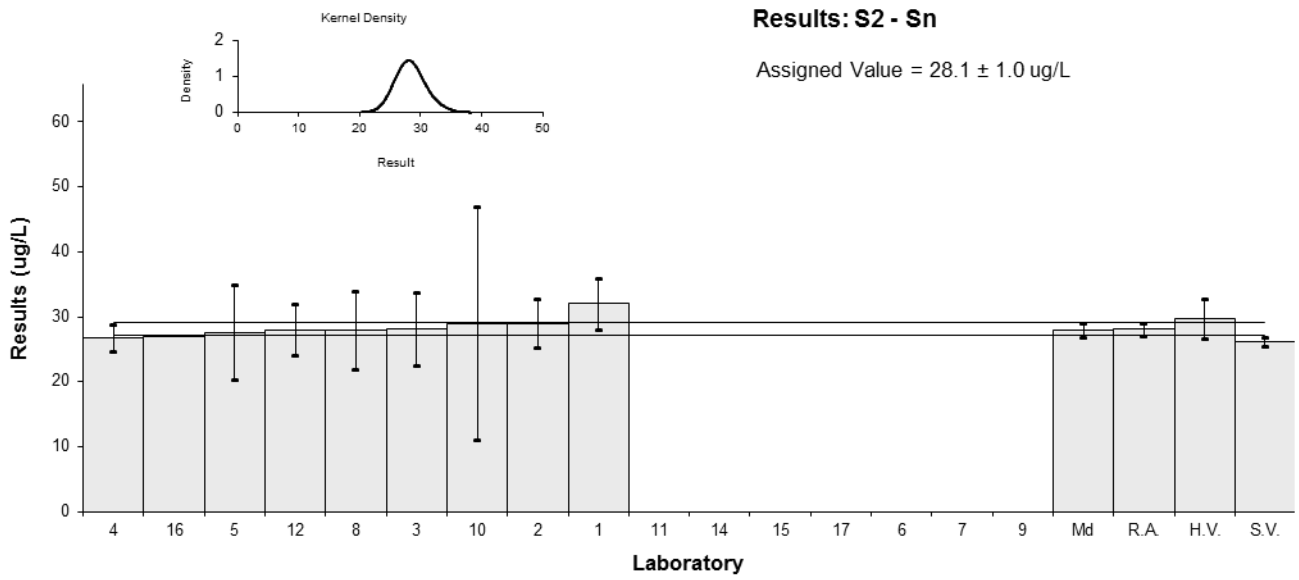
Sample No.	S2
Matrix.	River Water
Analyte.	Sn
Units	ug/L

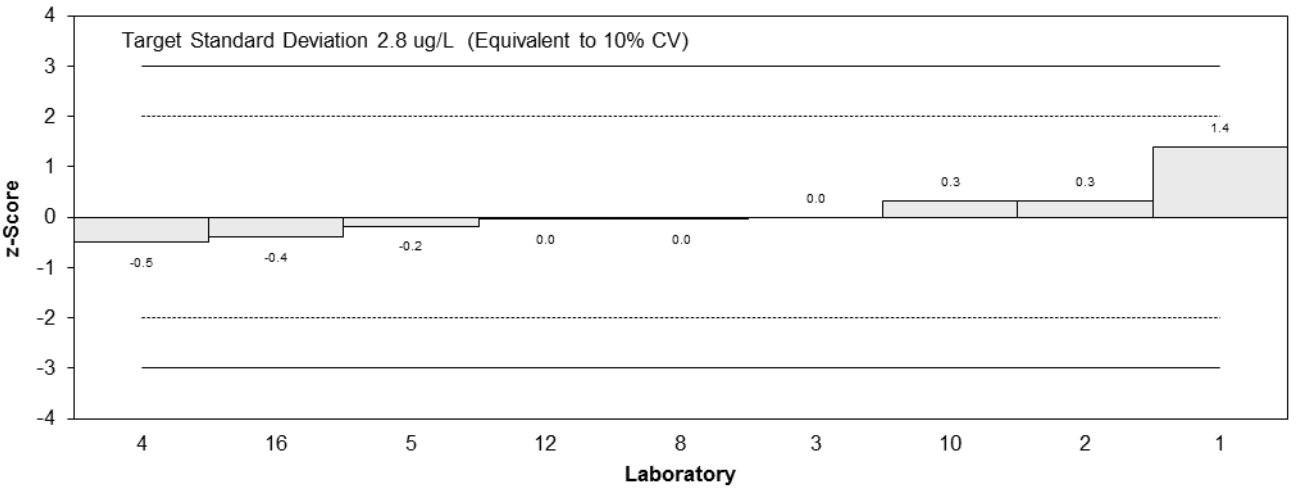
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	32	4.0	1.39	0.95
2	29	3.7	0.32	0.23
3	28.1	5.6	0.00	0.00
4	26.7	2.1	-0.50	-0.60
5	27.6	7.3	-0.18	-0.07
6	NT	NT		
7	NT	NT		
8	28	6	-0.04	-0.02
9	NT	NT		
10	29	18	0.32	0.05
11	NT	NT		
12	28	4	-0.04	-0.02
14	NT	NT		
15	NT	NT		
16	27	NR	-0.39	-1.10
17	NT	NT		

Statistics

Assigned Value	28.1	1.0
Spike	26.2	0.7
Homogeneity Value	29.7	3.0
Robust Average	28.1	1.0
Median	28.0	1.1
Mean	28.4	
N	9	
Max.	32	
Min.	26.7	
Robust SD	1	
Robust CV	3.6%	


Kernel Density
Density
Result
Results: S2 - Sn
Assigned Value = 28.1 ± 1.0 ug/L
Results (ug/L)
Laboratory
4 16 5 12 8 3 10 2 1 11 14 15 17 6 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Sn
Target Standard Deviation 2.8 ug/L (Equivalent to 10% CV)
z-Score
-0.5 -0.4 -0.2 0.0 0.0 0.0 0.3 0.3 1.4
Laboratory
4 16 5 12 8 3 10 2 1

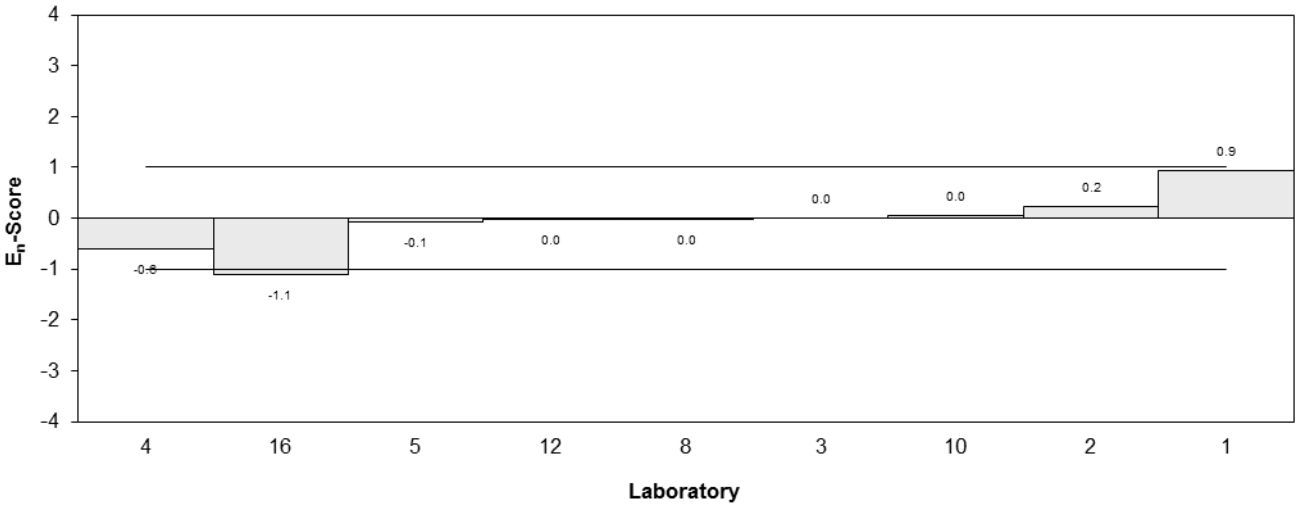

En-Scores: S2 - Sn
En-Score
-0.6 -1.1 -0.1 0.0 0.0 0.0 0.0 0.2 0.9
Laboratory
4 16 5 12 8 3 10 2 1

Figure 33

Table 37

Sample Details

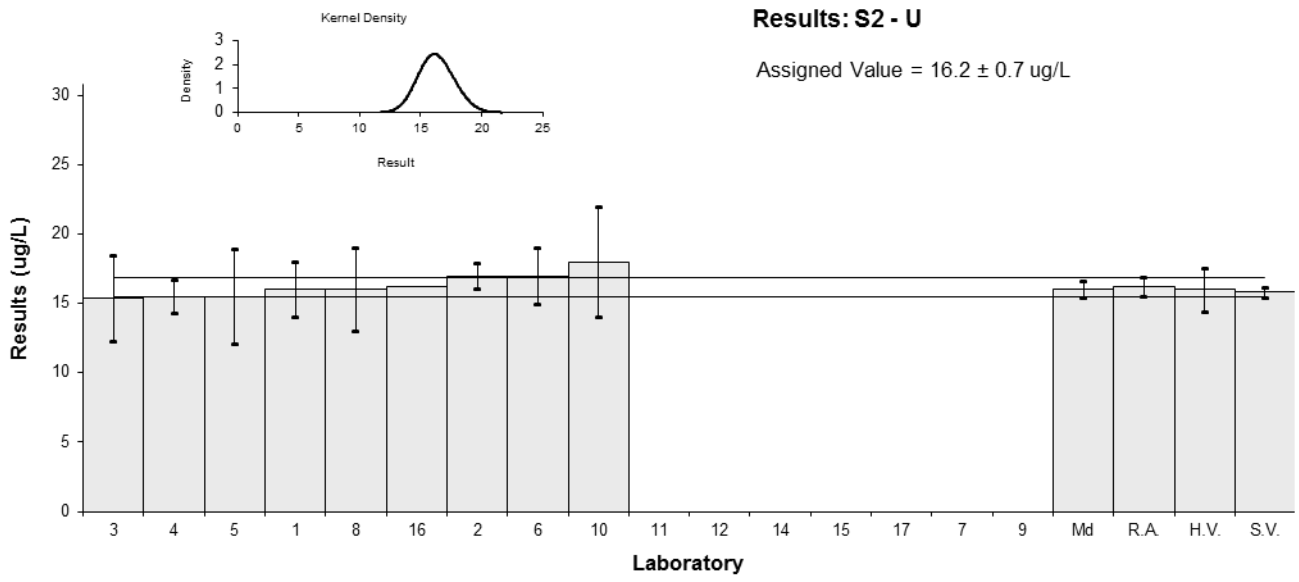
Sample No.	S2
Matrix.	River Water
Analyte.	U
Units	ug/L

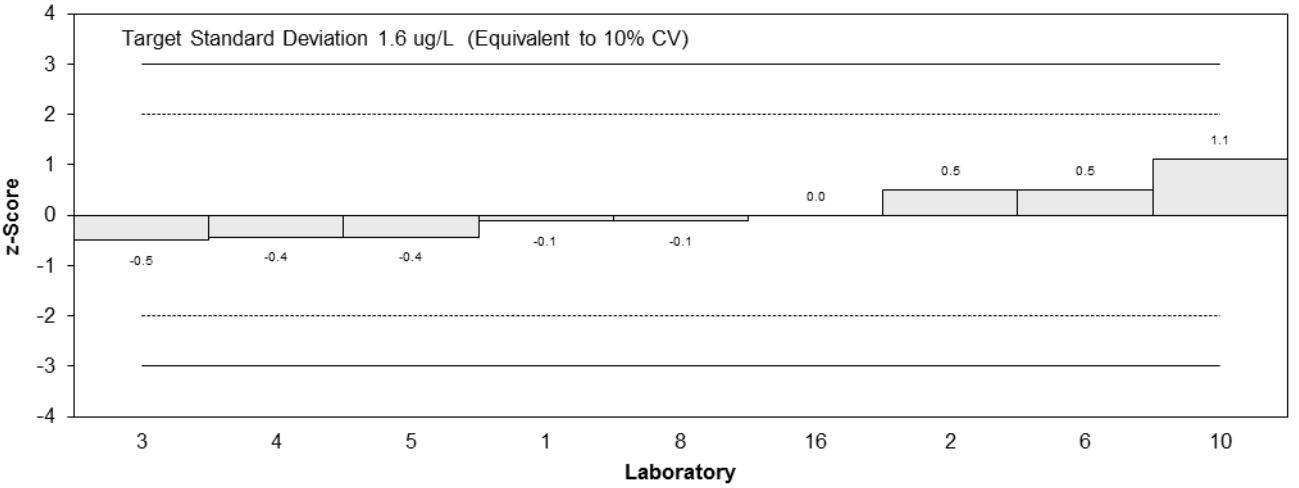
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	16	2.0	-0.12	-0.09
2	17	0.9	0.49	0.70
3	15.4	3.1	-0.49	-0.25
4	15.5	1.2	-0.43	-0.50
5	15.5	3.4	-0.43	-0.20
6	17	2	0.49	0.38
7	NT	NT		
8	16	3	-0.12	-0.06
9	NT	NT		
10	18	4	1.11	0.44
11	NT	NT		
12	NT	NT		
14	NT	NT		
15	NT	NT		
16	16.2	NR	0.00	0.00
17	NT	NT		

Statistics

Assigned Value	16.2	0.7
Spike	15.8	0.4
Homogeneity Value	16.0	1.6
Robust Average	16.2	0.7
Median	16.0	0.6
Mean	16.3	
N	9	
Max.	18	
Min.	15.4	
Robust SD	0.9	
Robust CV	5.6%	


Kernel Density
Density
Result
Results: S2 - U
Assigned Value = 16.2 ± 0.7 ug/L
Results (ug/L)
Laboratory
3 4 5 1 8 16 2 6 10 11 12 14 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - U
Target Standard Deviation 1.6 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
3 4 5 1 8 16 2 6 10
-0.5 -0.4 -0.4 -0.1 -0.1 0.0 0.5 0.5 1.1

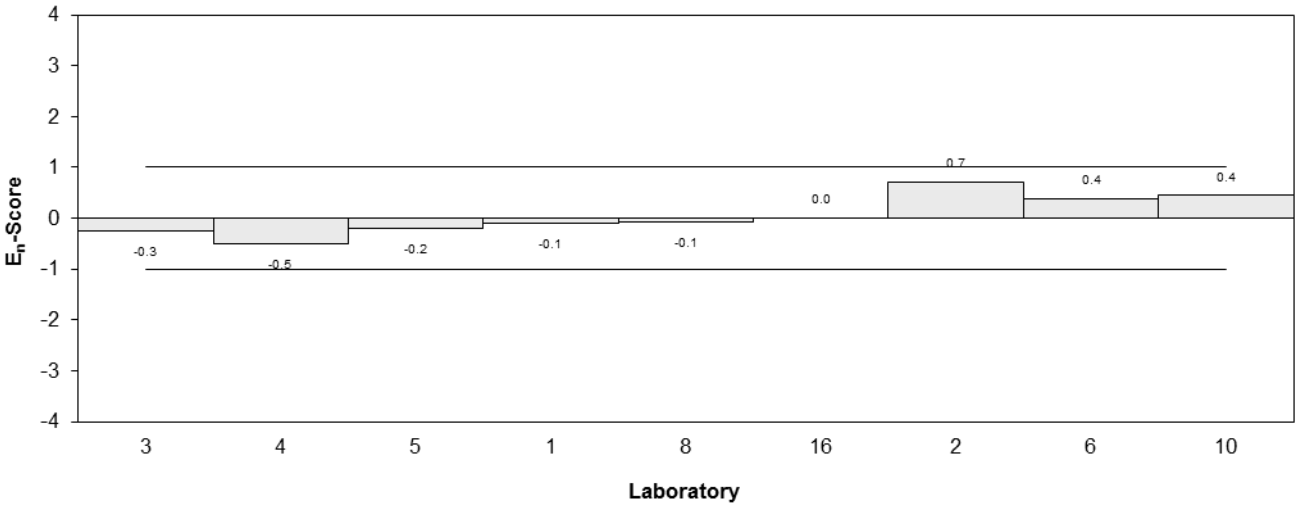

En-Scores: S2 - U
En-Score
Laboratory
3 4 5 1 8 16 2 6 10
-0.3 -0.5 -0.2 -0.1 -0.1 0.0 0.7 0.4 0.4

Figure 34

Table 38

Sample Details

Sample No.	S2
Matrix.	River Water
Analyte.	Zn
Units	ug/L

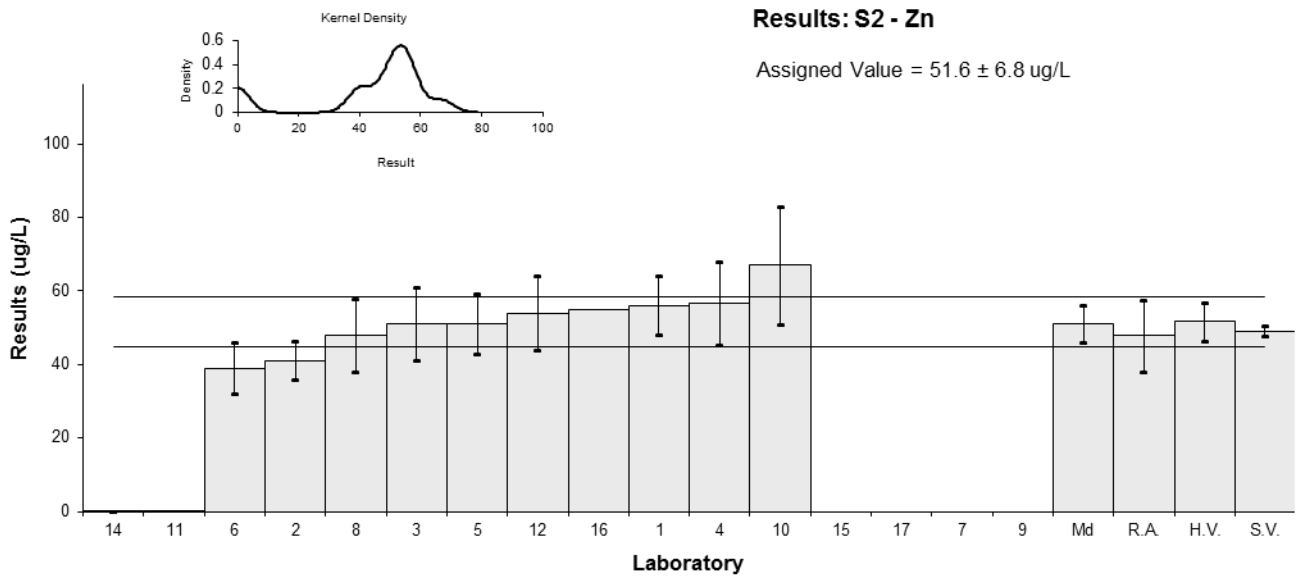
Participant Results

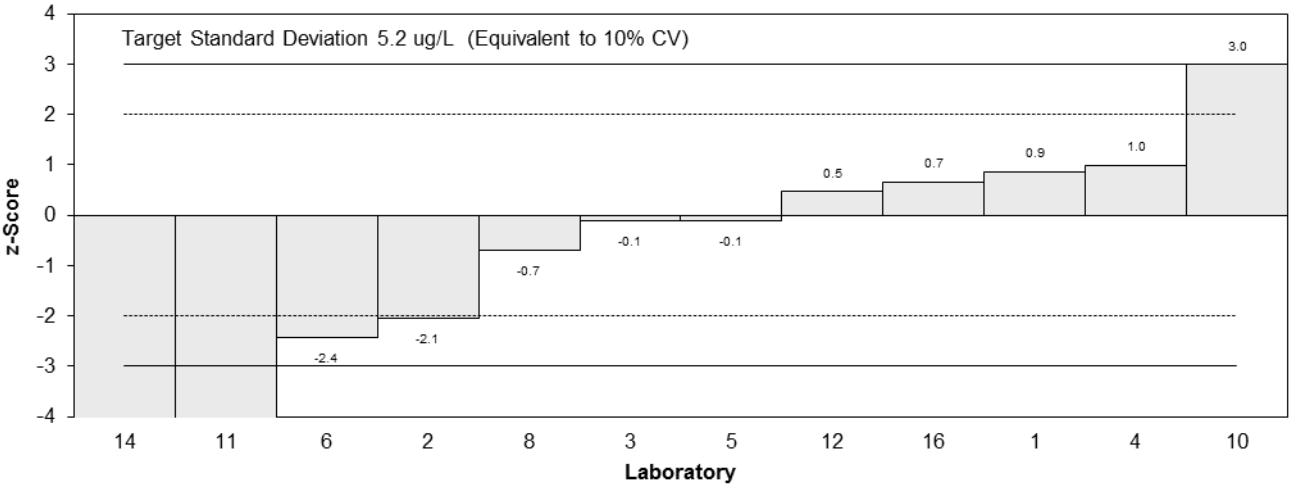
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	56	8.0	0.85	0.42
2	41	5.2	-2.05	-1.24
3	51.0	10	-0.12	-0.05
4	56.7	11.3	0.99	0.39
5	51.0	8.2	-0.12	-0.06
6	39	7	-2.44	-1.29
7	NT	NT		
8	48	10	-0.70	-0.30
9	NT	NT		
10	67	16	2.98	0.89
11	0.055	NR	-9.99	-7.58
12	54	10	0.47	0.20
14	0.054	0.05	-9.99	-7.58
15	NT	NT		
16	55	NR	0.66	0.50
17	NT	NT		

Statistics

Assigned Value*	51.6	6.8
Spike	49.1	1.5
Homogeneity Value	51.7	5.2
Robust Average	47.8	9.8
Median	51.0	5.0
Mean	43.2	
N	12	
Max.	67	
Min.	0.054	
Robust SD	8.6	
Robust CV	18%	

* Robust Average excluding Laboratories 11 and 14.


Kernel Density
Density
Result
Results: S2 - Zn
Assigned Value = 51.6 ± 6.8 ug/L
Results (ug/L)
Laboratory
14 11 6 2 8 3 5 12 16 1 4 10 15 17 7 9 Md R.A. H.V. S.V.


z-Scores: S2 - Zn
Target Standard Deviation 5.2 ug/L (Equivalent to 10% CV)
z-Score
Laboratory
14 11 6 2 8 3 5 12 16 1 4 10
-2.4
-2.1
-0.7
-0.1
-0.1
0.5
0.7
0.9
1.0
3.0

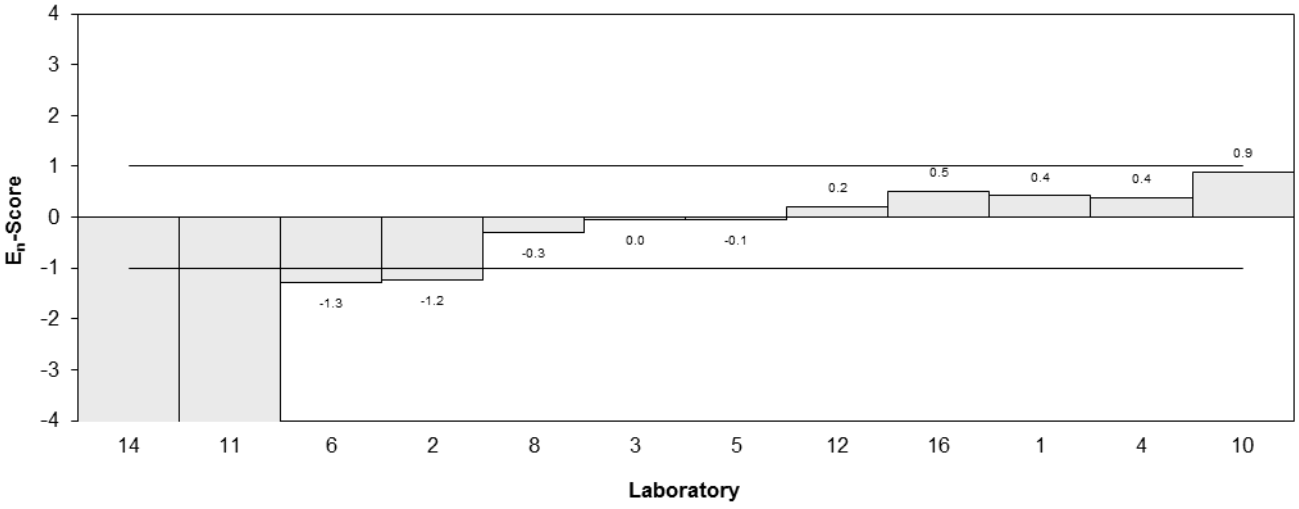

En-Scores: S2 - Zn
En-Score
Laboratory
14 11 6 2 8 3 5 12 16 1 4 10
-1.3
-1.2
-0.3
0.0
-0.1
0.2
0.5
0.4
0.4
0.9

Figure 35

Table 39

Sample Details

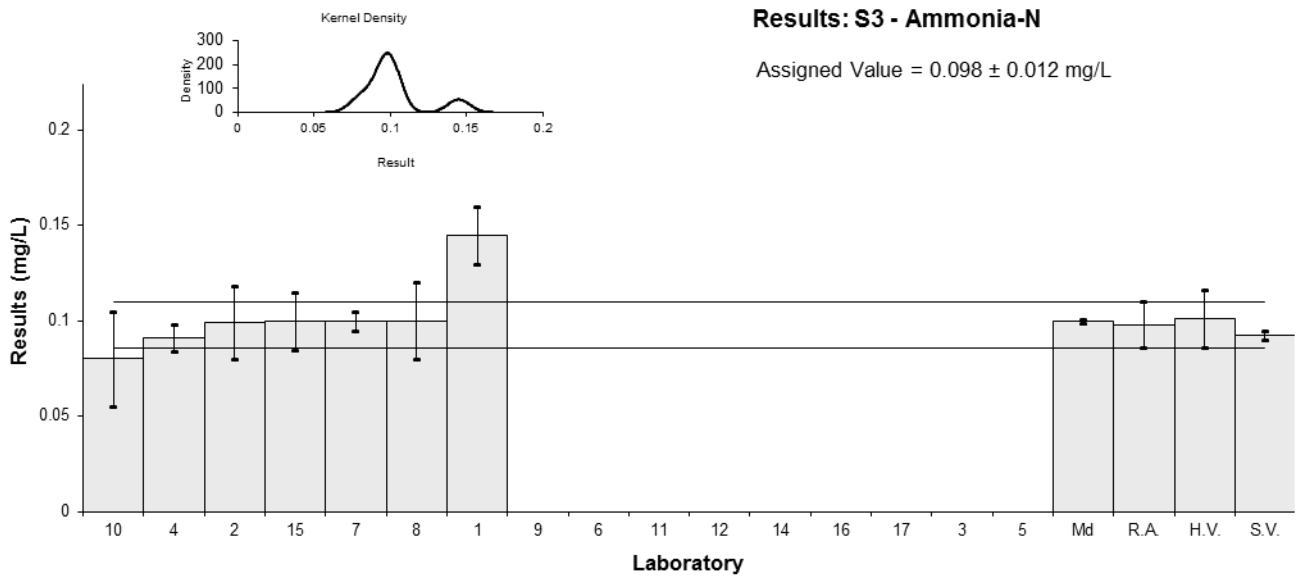
Sample No.	S3
Matrix.	River Water
Analyte.	Ammonia-N
Units	mg/L

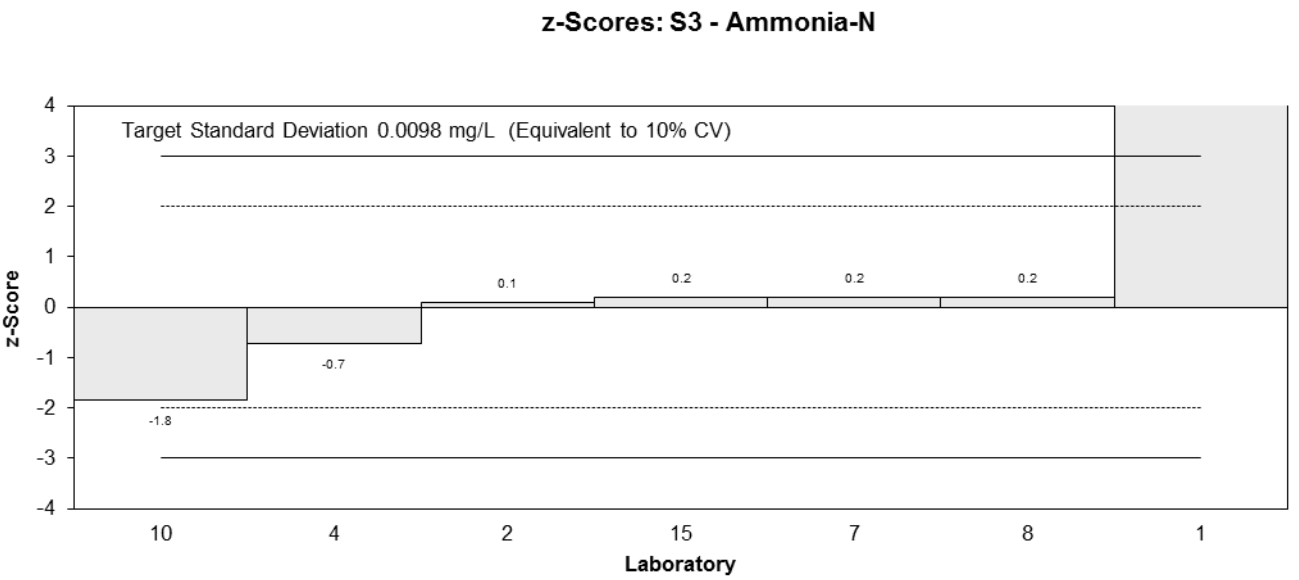
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.145	0.015	4.80	2.45
2	0.099	0.019	0.10	0.04
3	NT	NT		
4	0.091	0.007	-0.71	-0.50
5	NT	NT		
6	<0.2	0.11		
7	0.100	0.005	0.20	0.15
8	0.10	0.02	0.20	0.09
9	<0.1	0.1		
10	0.08	0.025	-1.84	-0.65
11	NT	NT		
12	NT	NT		
14	NT	NT		
15	0.10	0.015	0.20	0.10
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	0.098	0.012
Spike	0.092	0.002
Homogeneity Value	0.101	0.015
Robust Average	0.098	0.012
Median	0.100	0.001
Mean	0.102	
N	7	
Max.	0.145	
Min.	0.08	
Robust SD	0.013	
Robust CV	13%	


Results: S3 - Ammonia-N
Assigned Value = 0.098 ± 0.012 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
10 4 2 15 7 8 1 9 6 11 12 14 16 17 3 5 Md R.A. H.V. S.V.


z-Scores: S3 - Ammonia-N
Target Standard Deviation 0.0098 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
10 4 2 15 7 8 1

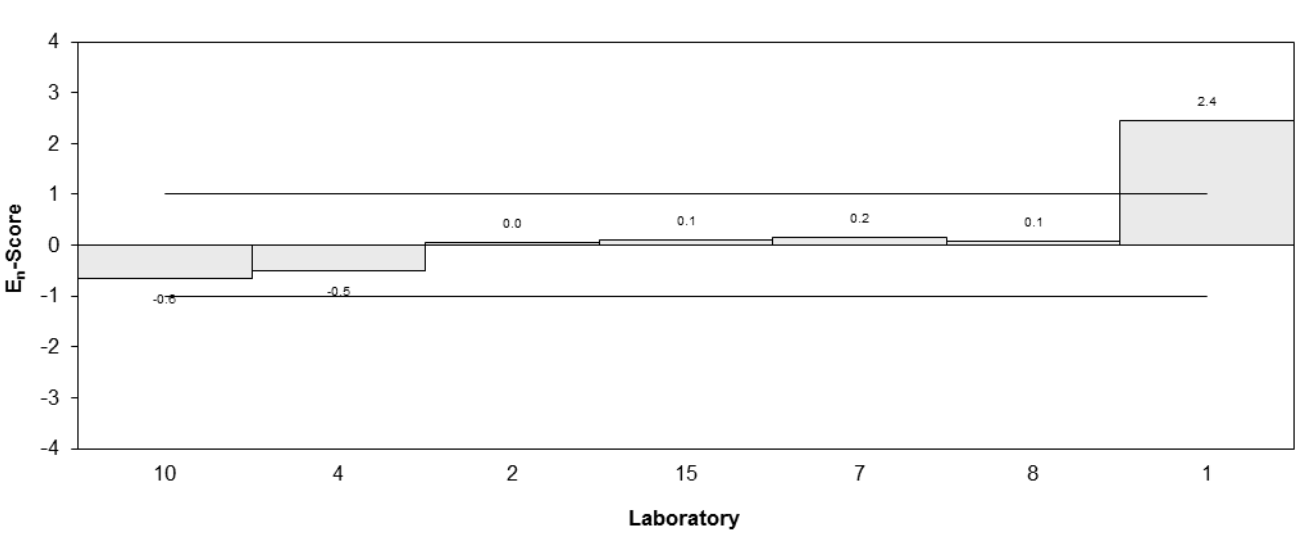

En-Scores: S3 - Ammonia-N
En-Score
Laboratory
10 4 2 15 7 8 1

Figure 36

Table 40

Sample Details

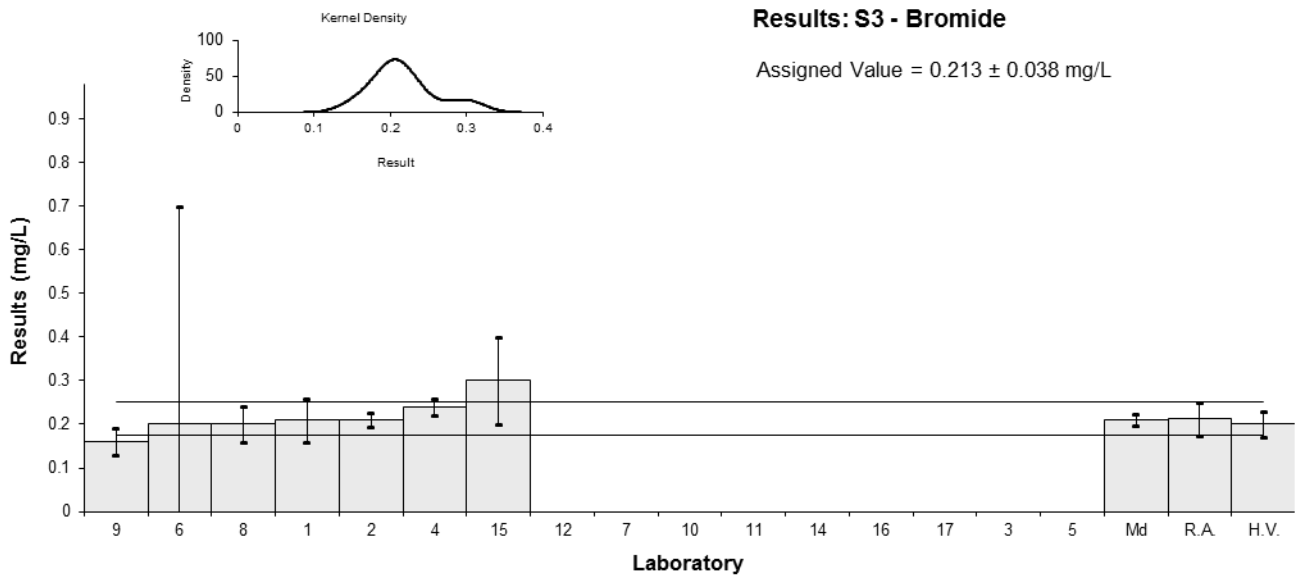
Sample No.	S3
Matrix.	River Water
Analyte.	Bromide
Units	mg/L

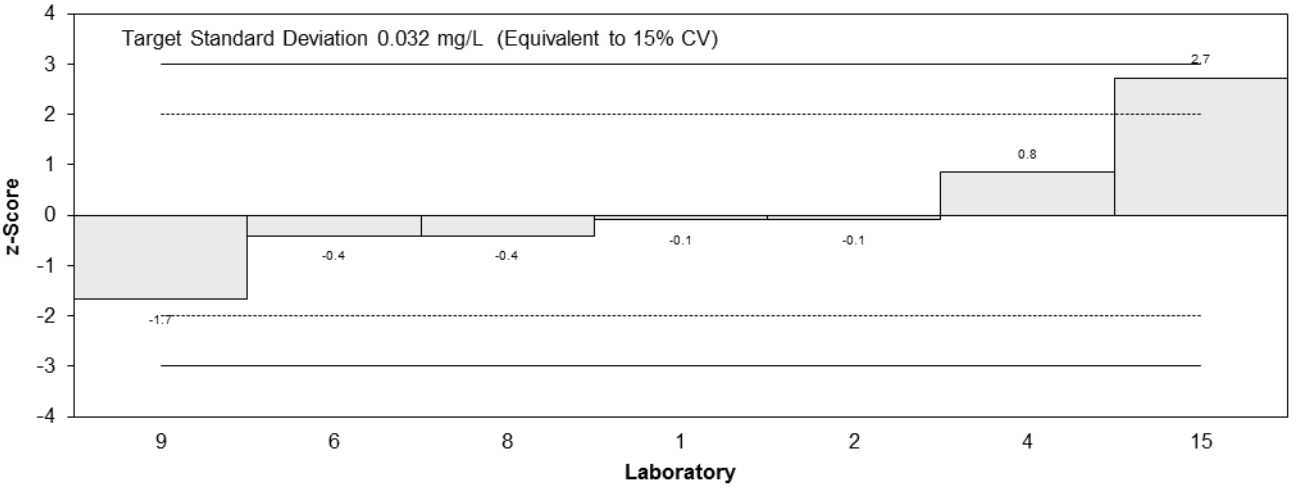
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.21	0.05	-0.09	-0.05
2	0.21	0.017	-0.09	-0.07
3	NT	NT		
4	0.24	0.02	0.85	0.63
5	NT	NT		
6	0.2	0.5	-0.41	-0.03
7	NR	NR		
8	0.2	0.04	-0.41	-0.24
9	0.16	0.03	-1.66	-1.09
10	NT	NT		
11	NT	NT		
12	<0.5	NR		
14	NT	NT		
15	0.3	0.1	2.72	0.81
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	0.213	0.038
Spike	Not Spiked	
Homogeneity Value	0.200	0.030
Robust Average	0.213	0.038
Median	0.210	0.014
Mean	0.217	
N	7	
Max.	0.3	
Min.	0.16	
Robust SD	0.04	
Robust CV	19%	


Results: S3 - Bromide
Assigned Value = 0.213 ± 0.038 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
9 6 8 1 2 4 15 12 7 10 11 14 16 17 3 5 Md R.A. H.V.


z-Scores: S3 - Bromide
Target Standard Deviation 0.032 mg/L (Equivalent to 15% CV)
z-Score
Laboratory
9 6 8 1 2 4 15
2.7
0.8
-0.4
-0.4
-0.1
-0.1
-1.7

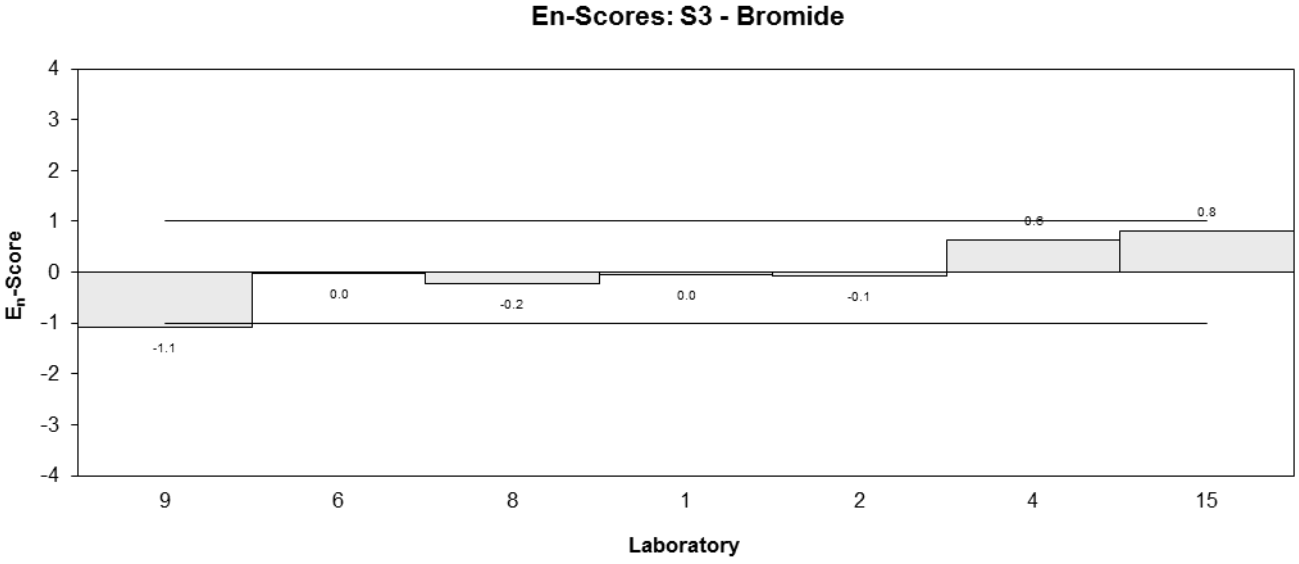

En-Scores: S3 - Bromide
En-Score
Laboratory
9 6 8 1 2 4 15
0.8
0.8
0.0
-0.2
0.0
-0.1
-1.1

Figure 37

Table 41

Sample Details

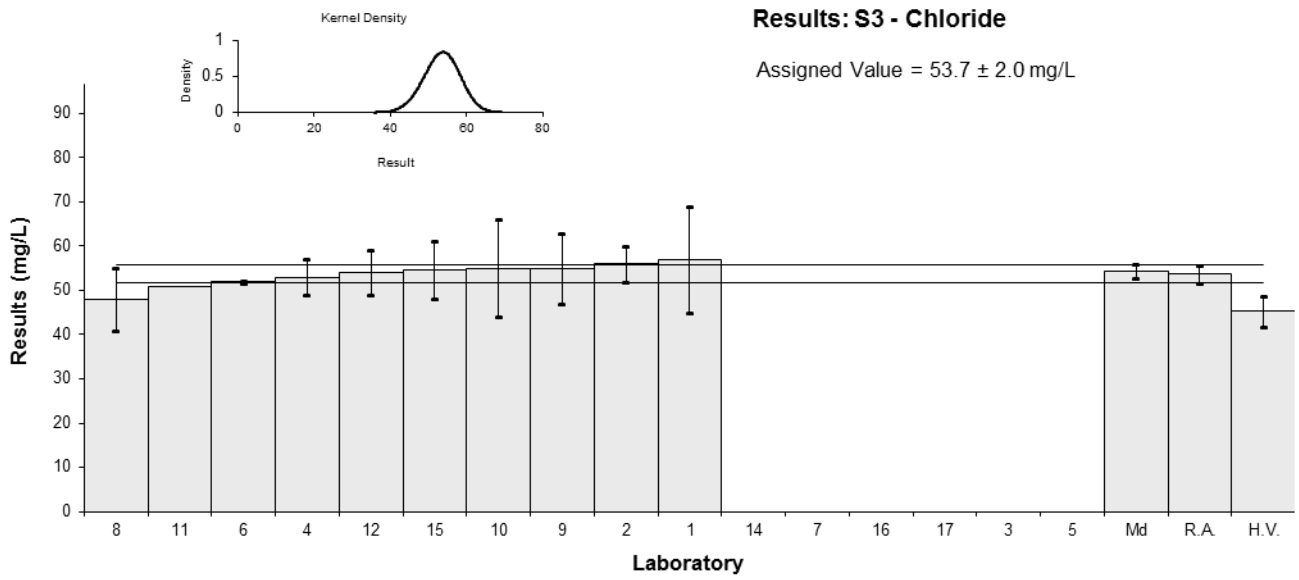
Sample No.	S3
Matrix.	River Water
Analyte.	Chloride
Units	mg/L

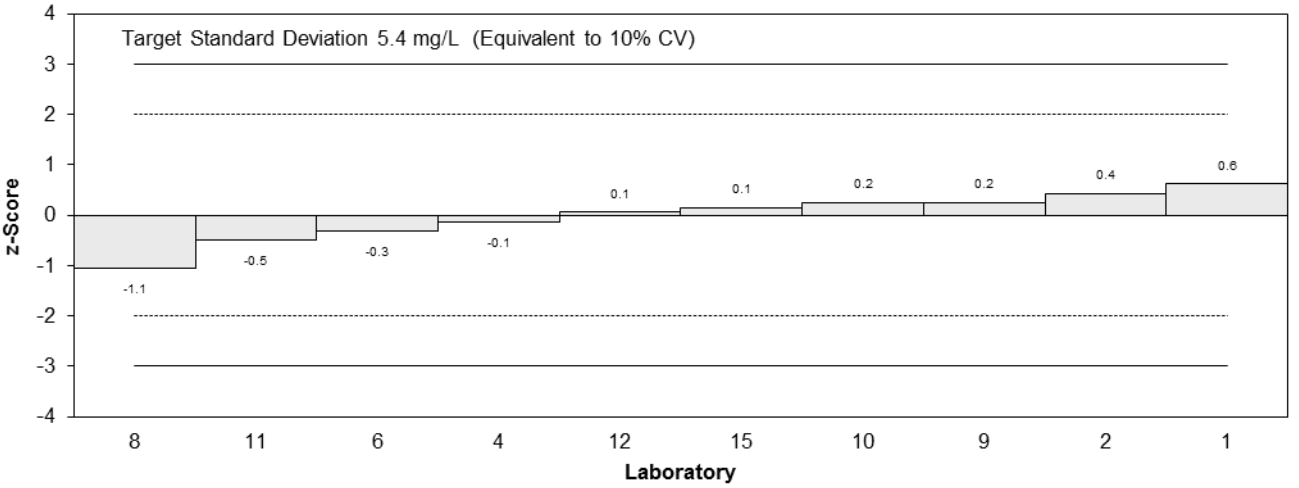
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	57.0	12	0.61	0.27
2	56	4.0	0.43	0.51
3	NT	NT		
4	53	4	-0.13	-0.16
5	NT	NT		
6	52	0.3	-0.32	-0.84
7	NR	NR		
8	48	7	-1.06	-0.78
9	55	8	0.24	0.16
10	55	11	0.24	0.12
11	51.0	NR	-0.50	-1.35
12	54	5	0.06	0.06
14	NR	NR		
15	54.5	6.5	0.15	0.12
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	53.7	2.0
Spike	Not Spiked	
Homogeneity Value	45.3	3.5
Robust Average	53.7	2.0
Median	54.3	1.6
Mean	53.6	
N	10	
Max.	57	
Min.	48	
Robust SD	2.5	
Robust CV	4.7%	


Kernel Density
Density
Result
Results: S3 - Chloride
Assigned Value = 53.7 ± 2.0 mg/L
Results (mg/L)
Laboratory
8 11 6 4 12 15 10 9 2 1 14 7 16 17 3 5 Md R.A. H.V.


z-Scores: S3 - Chloride
Target Standard Deviation 5.4 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
8 11 6 4 12 15 10 9 2 1
-1.1 -0.5 -0.3 -0.1 0.1 0.1 0.2 0.2 0.4 0.6

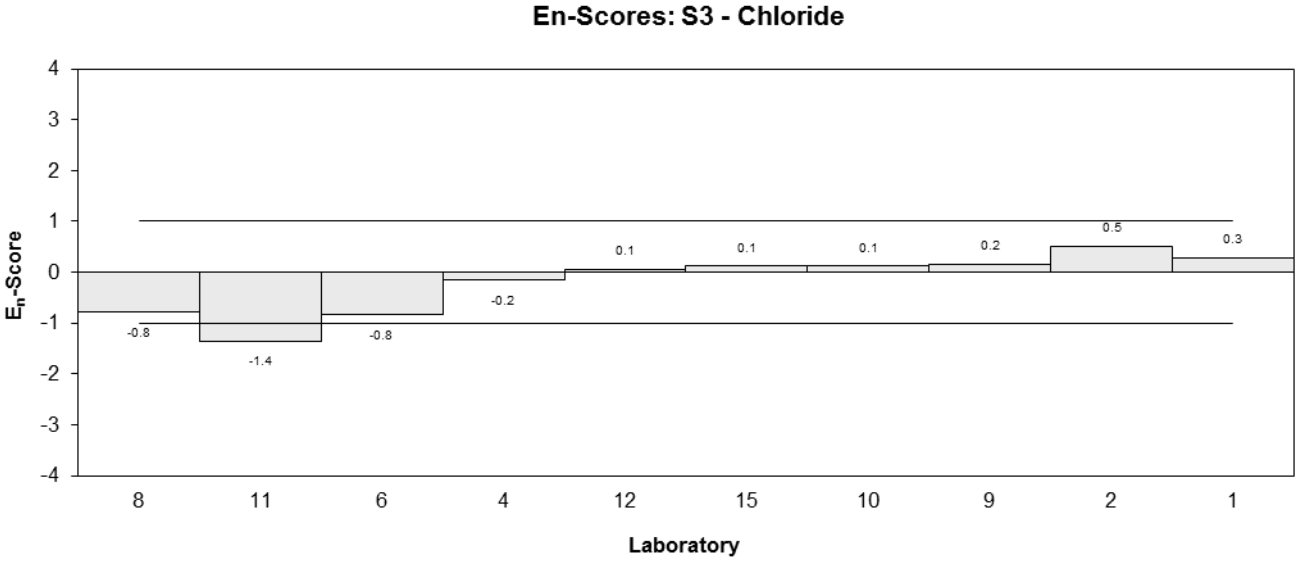

En-Scores: S3 - Chloride
En-Score
Laboratory
8 11 6 4 12 15 10 9 2 1
-0.8 -1.4 -0.8 -0.2 0.1 0.1 0.1 0.2 0.5 0.3

Figure 38

Table 42

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	7.32	0.75
2	6.0	0.6
3	NT	NT
4	5.55	0.55
5	NT	NT
6	NT	NT
7	NR	NR
8	6.3	1
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT
14	NT	NT
15	5.5	0.825
16	NT	NT
17	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	6.13	0.45
Robust Average	6.13	0.94
Median	6.00	0.83
Mean	6.13	
N	5	
Max.	7.32	
Min.	5.5	
Robust SD	0.84	
Robust CV	14%	

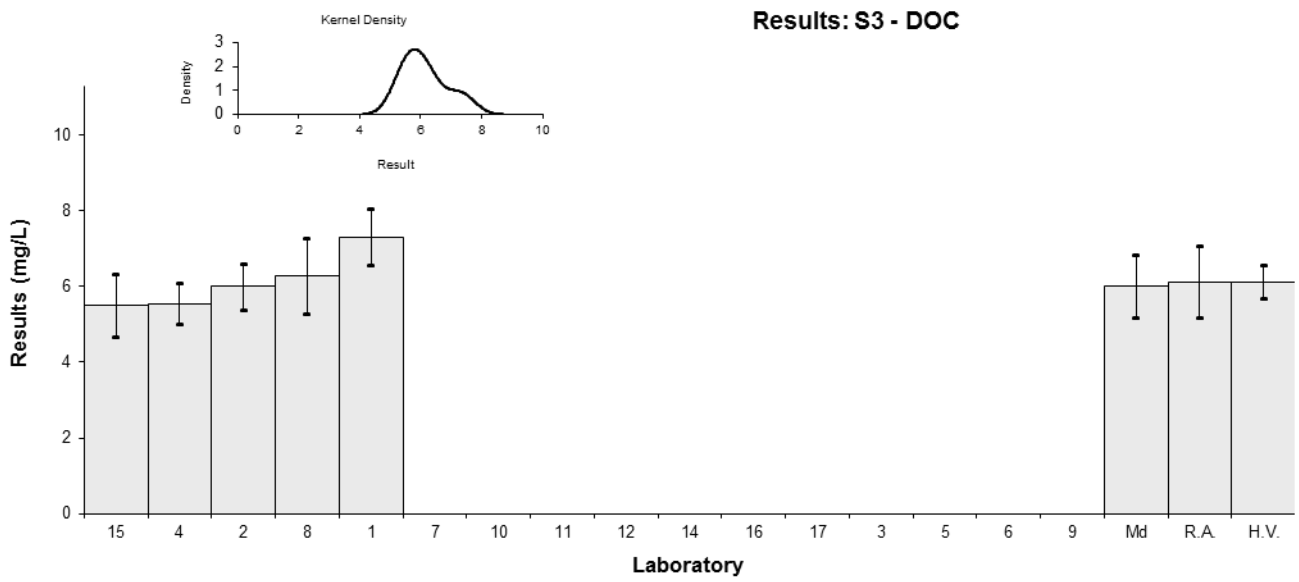

Results: S3 - DOC
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15
4
2
8
1
7
10
11
12
14
16
17
3
5
6
9
Md
R.A.
H.V.

Figure 39

Table 43

Sample Details

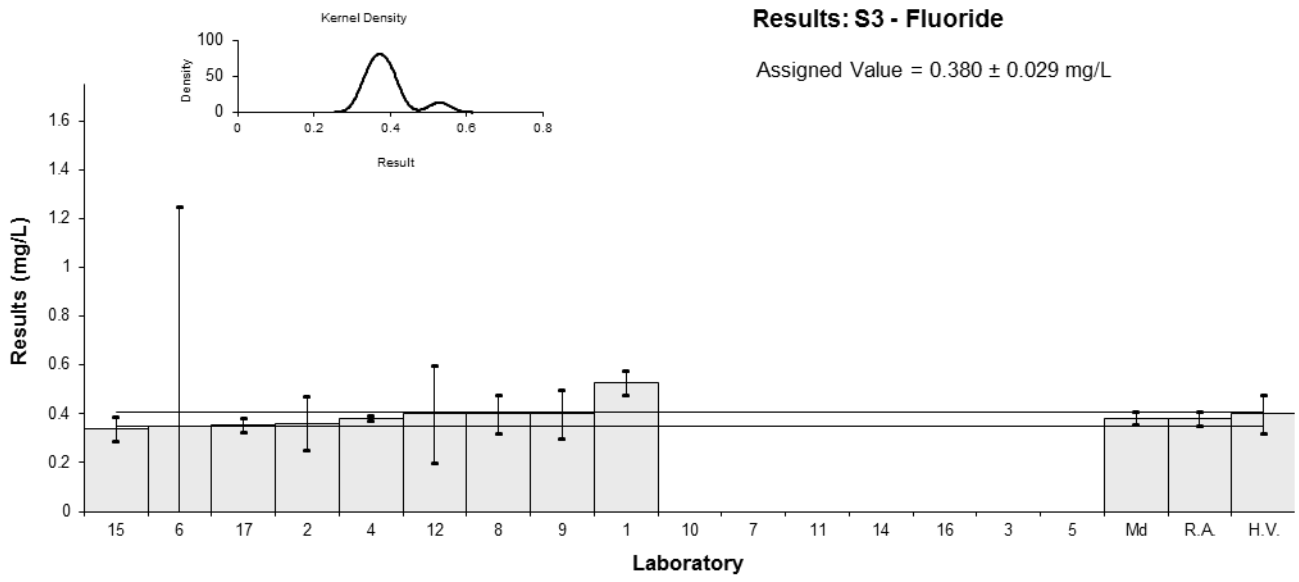
Sample No.	S3
Matrix.	River Water
Analyte.	Fluoride
Units	mg/L

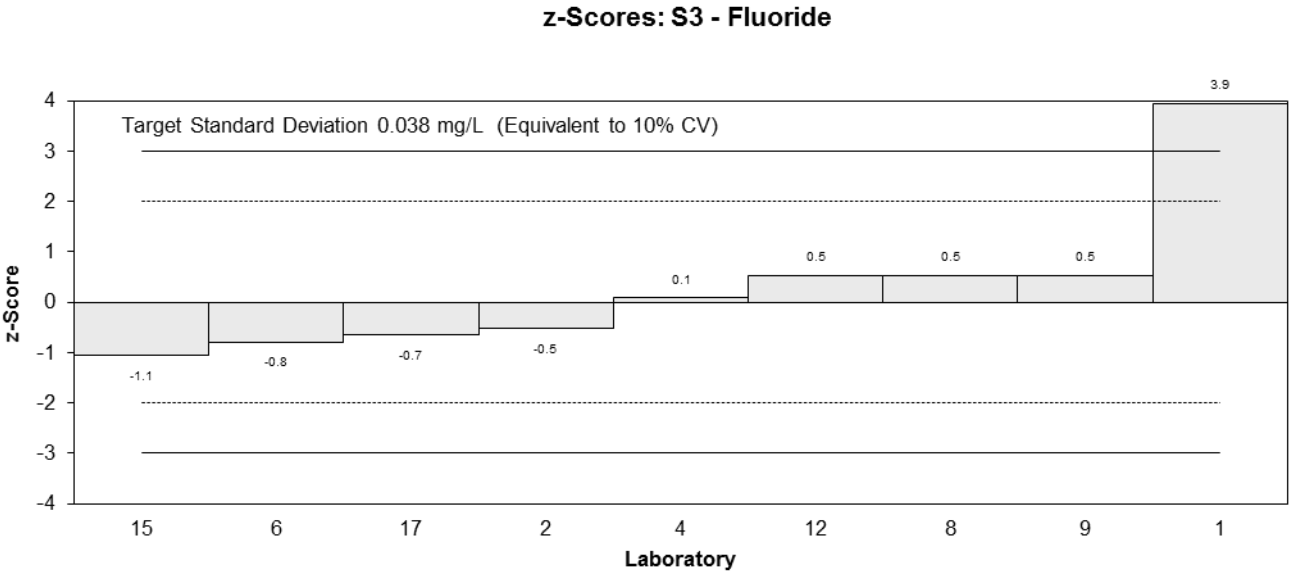
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.53	0.05	3.95	2.60
2	0.36	0.11	-0.53	-0.18
3	NT	NT		
4	0.383	0.01	0.08	0.10
5	NT	NT		
6	0.35	0.9	-0.79	-0.03
7	NR	NR		
8	0.4	0.08	0.53	0.24
9	0.4	0.1	0.53	0.19
10	<0.1	0.1		
11	NT	NT		
12	0.4	0.2	0.53	0.10
14	NT	NT		
15	0.34	0.05	-1.05	-0.69
16	NT	NT		
17	0.355	0.03	-0.66	-0.60

Statistics

Assigned Value	0.380	0.029
Spike	Not Spiked	
Homogeneity Value	0.400	0.080
Robust Average	0.380	0.029
Median	0.383	0.026
Mean	0.391	
N	9	
Max.	0.53	
Min.	0.34	
Robust SD	0.035	
Robust CV	9.2%	


Results: S3 - Fluoride
Assigned Value = 0.380 ± 0.029 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
15 6 17 2 4 12 8 9 1 10 7 11 14 16 3 5 Md R.A. H.V.


z-Scores: S3 - Fluoride
Target Standard Deviation 0.038 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
15 6 17 2 4 12 8 9 1
-1.1 -0.8 -0.7 -0.5 0.1 0.5 0.5 0.5 3.9

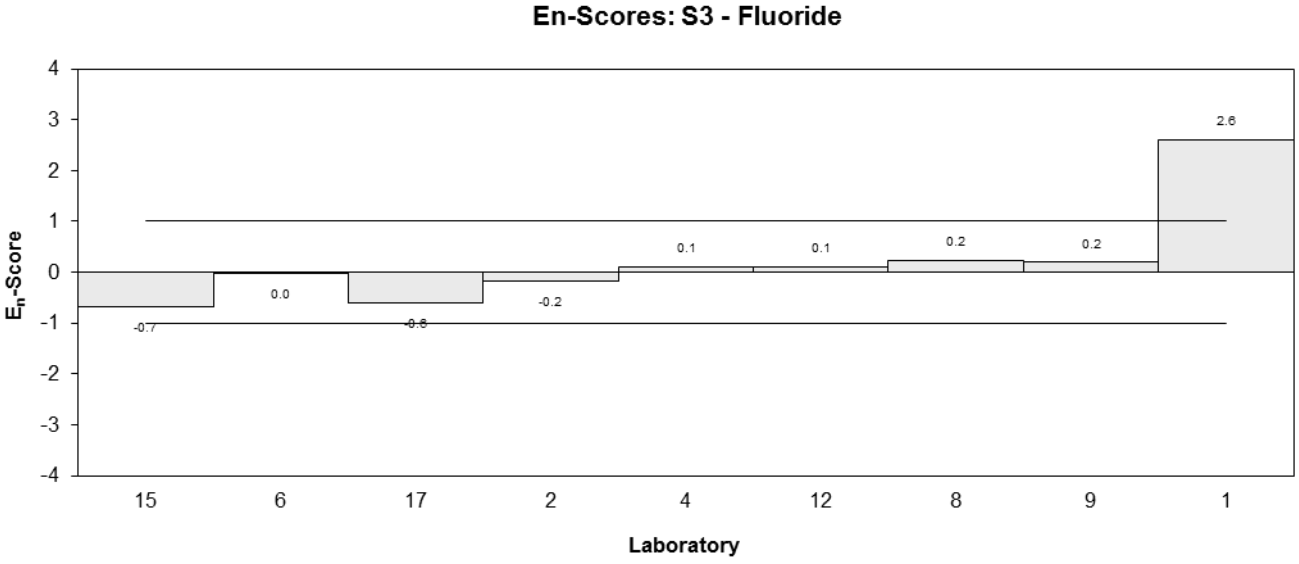

En-Scores: S3 - Fluoride
En-Score
Laboratory
15 6 17 2 4 12 8 9 1
-0.7 0.0 -0.6 -0.2 0.1 0.1 0.2 0.2 2.6

Figure 40

Table 44

Sample Details

Sample No.	S3
Matrix.	River Water
Analyte.	Nitrate-N
Units	mg/L

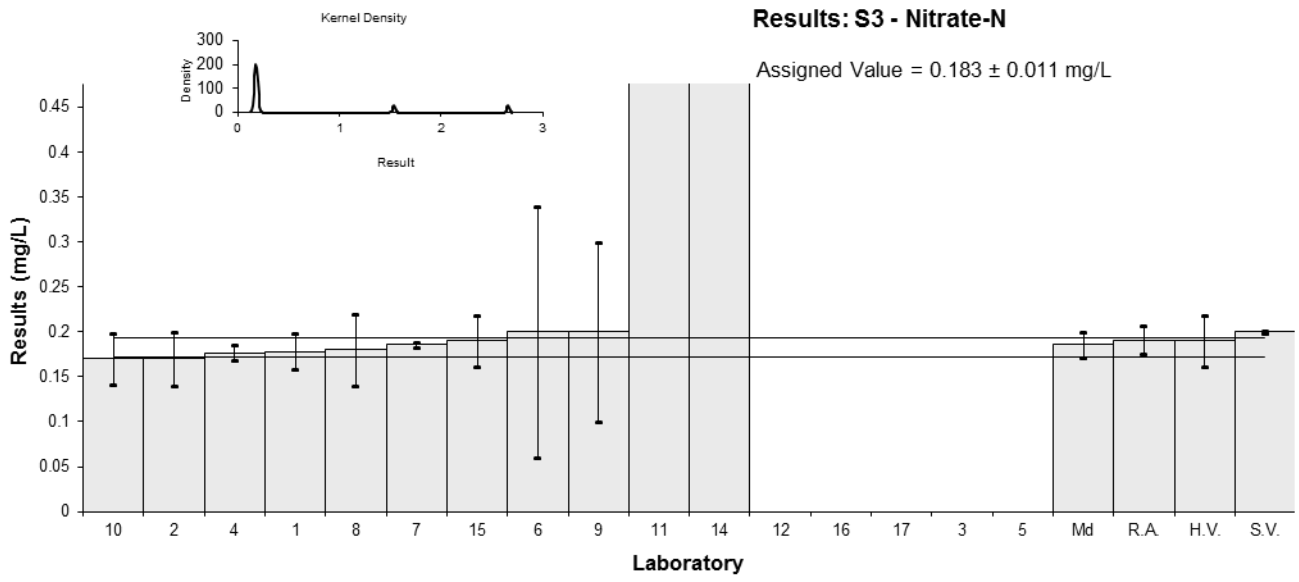
Participant Results

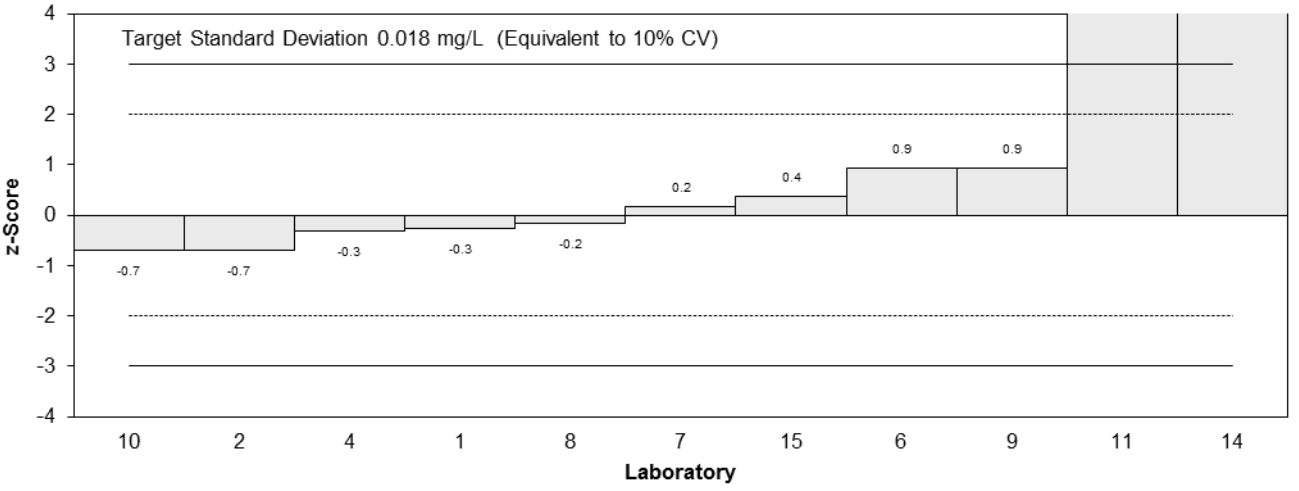
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.178	0.02	-0.27	-0.22
2	0.17	0.03	-0.71	-0.41
3	NT	NT		
4	0.177	0.009	-0.33	-0.42
5	NT	NT		
6	0.2	0.14	0.93	0.12
7	0.186	0.003	0.16	0.26
8	0.18	0.04	-0.16	-0.07
9	0.2	0.1	0.93	0.17
10	0.17	0.029	-0.71	-0.42
11	1.54	NR	74.15	123.36
12	NT	NT		
14	2.66	NR	135.36	225.18
15	0.19	0.029	0.38	0.23
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value*	0.183	0.011
Spike	0.200	0.002
Homogeneity Value	0.190	0.029
Robust Average	0.191	0.016
Median	0.186	0.014
Mean	0.532	
N	11	
Max.	2.66	
Min.	0.17	
Robust SD	0.013	
Robust CV	6.8%	

* Robust Average excluding Laboratories 11 and 14.


Kernel Density
Density
Result
Results: S3 - Nitrate-N
Assigned Value = 0.183 ± 0.011 mg/L
Results (mg/L)
Laboratory
10 2 4 1 8 7 15 6 9 11 14 12 16 17 3 5 Md R.A. H.V. S.V.


z-Scores: S3 - Nitrate-N
Target Standard Deviation 0.018 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
10 2 4 1 8 7 15 6 9 11 14

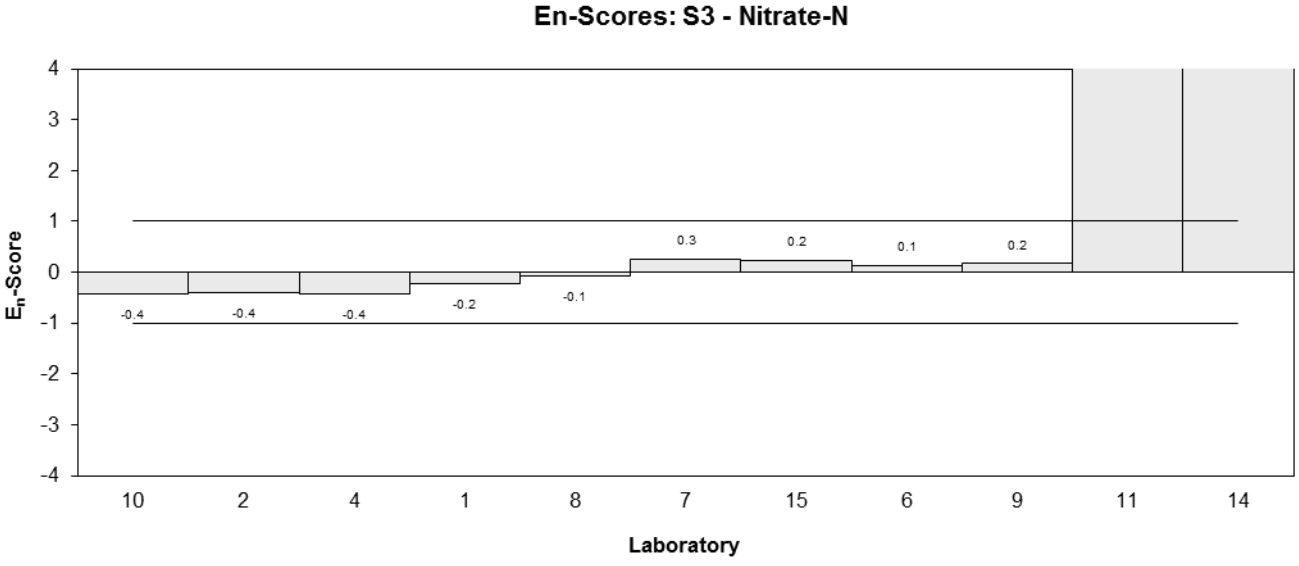

En-Scores: S3 - Nitrate-N
En-Score
Laboratory
10 2 4 1 8 7 15 6 9 11 14

Figure 41

Table 45

Sample Details

Sample No.	S3
Matrix.	River Water
Analyte.	Orthophosphate-P
Units	mg/L

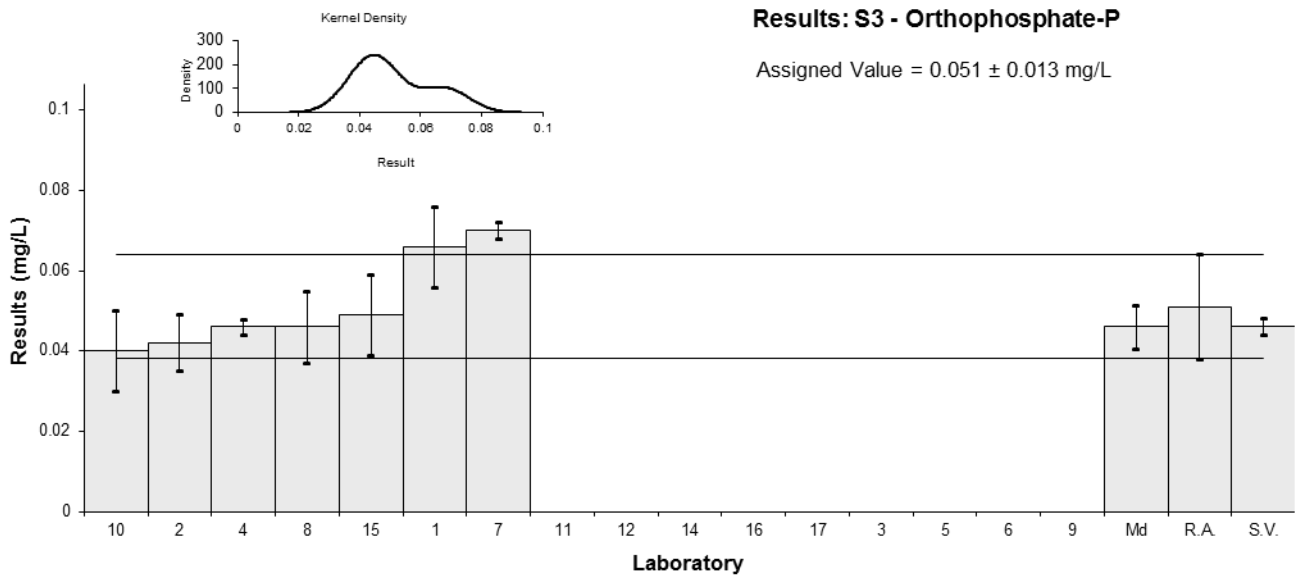
Participant Results

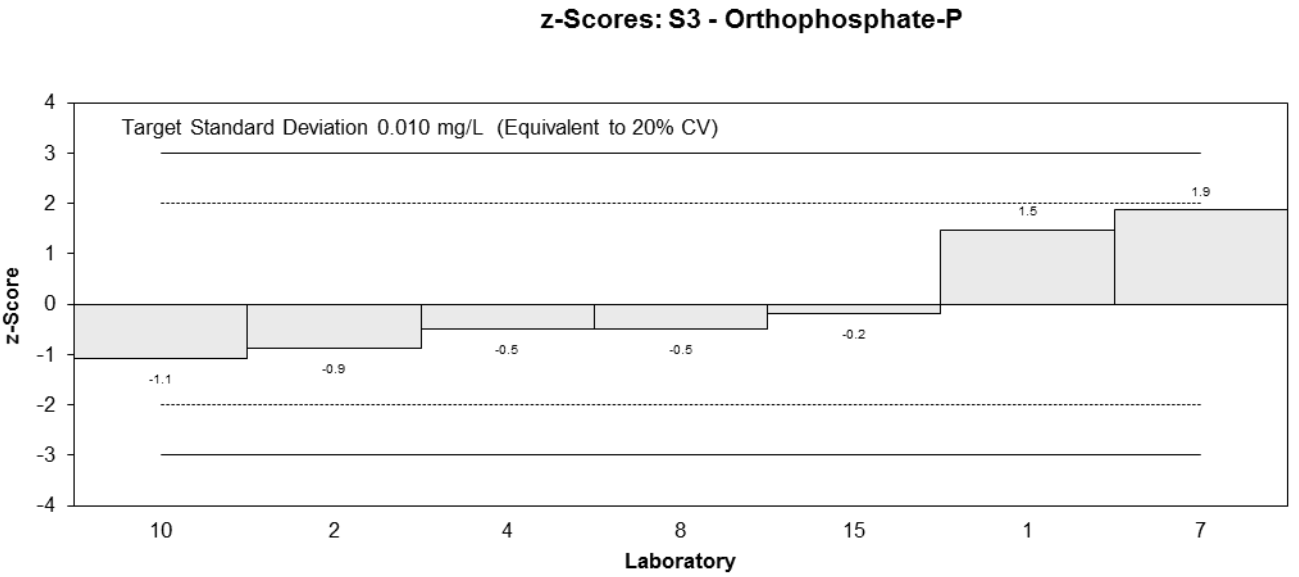
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.066	0.01	1.47	0.91
2	0.042	0.007	-0.88	-0.61
3	NT	NT		
4	0.046	0.002	-0.49	-0.38
5	NT	NT		
6	NT	NT		
7	0.070	0.002	1.86	1.44
8	0.046	0.009	-0.49	-0.32
9	NT	NT		
10	0.04	0.01	-1.08	-0.67
11	NT	NT		
12	NT	NT		
14	NT	NT		
15	0.049	0.01	-0.20	-0.12
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	0.051	0.013
Spike*	0.046	0.002
Robust Average	0.051	0.013
Median	0.046	0.006
Mean	0.051	
N	7	
Max.	0.07	
Min.	0.04	
Robust SD	0.013	
Robust CV	25%	

*Incurred value not included


Kernel Density
Density
Result
Results: S3 - Orthophosphate-P
Assigned Value = 0.051 ± 0.013 mg/L
Results (mg/L)
Laboratory
10 2 4 8 15 1 7 11 12 14 16 17 3 5 6 9 Md R.A. S.V.


z-Scores: S3 - Orthophosphate-P
Target Standard Deviation 0.010 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
10 2 4 8 15 1 7
-1.1 -0.9 -0.5 -0.5 -0.2 1.5 1.9

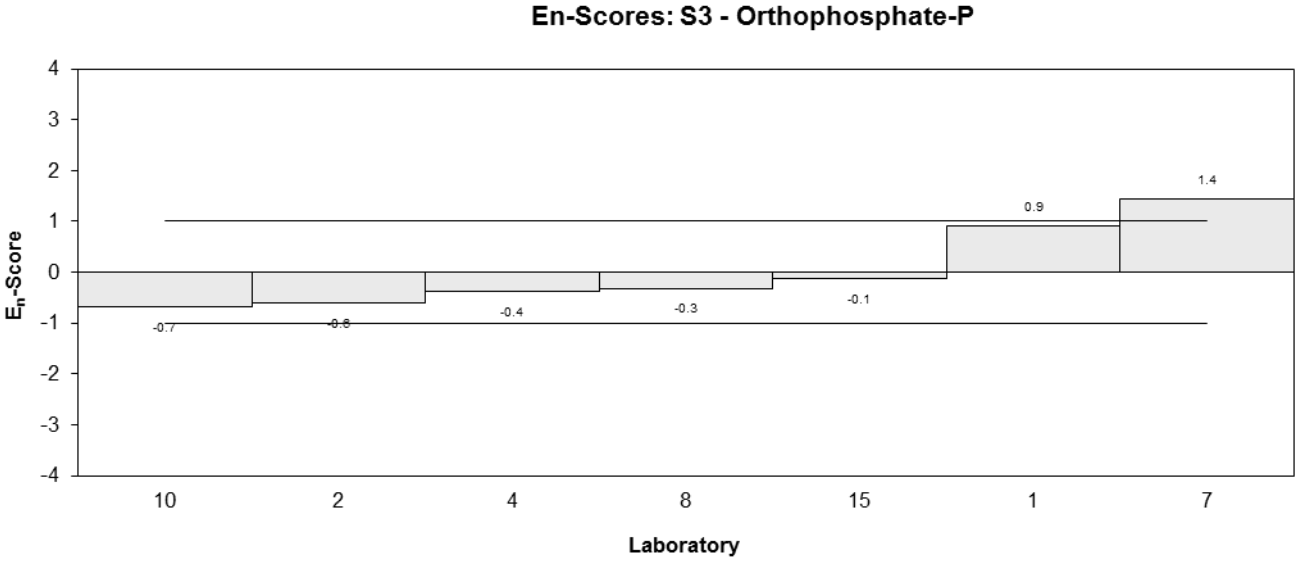

En-Scores: S3 - Orthophosphate-P
En-Score
Laboratory
10 2 4 8 15 1 7
-0.7 -0.6 -0.4 -0.3 -0.1 0.9 1.4

Figure 42

Table 46

Sample Details

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

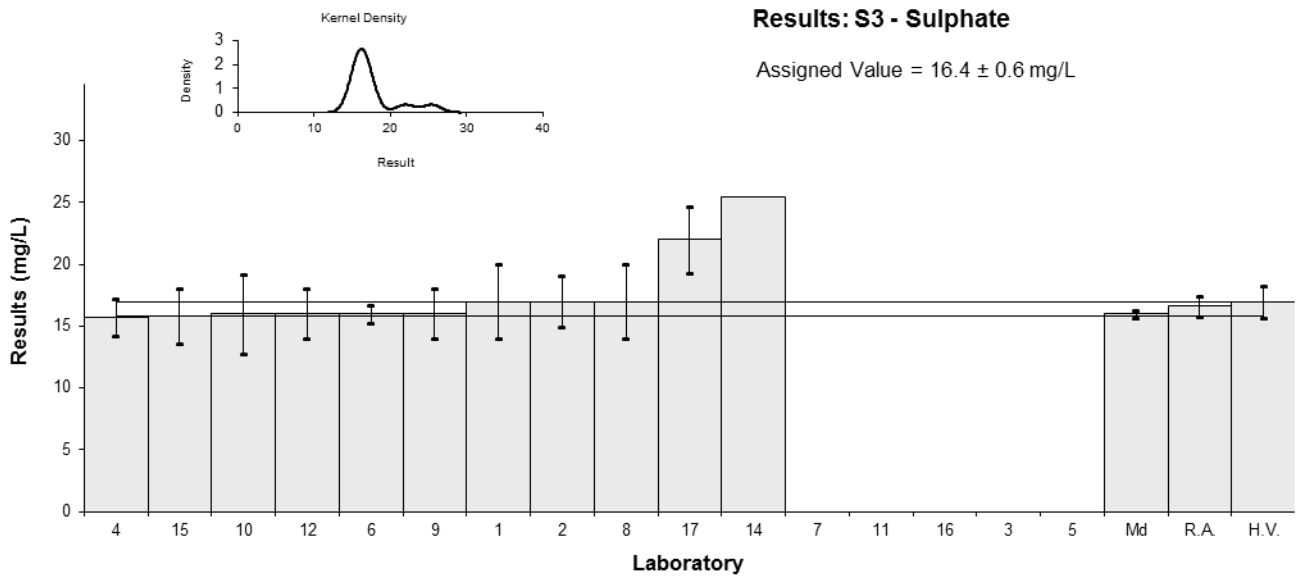
Participant Results

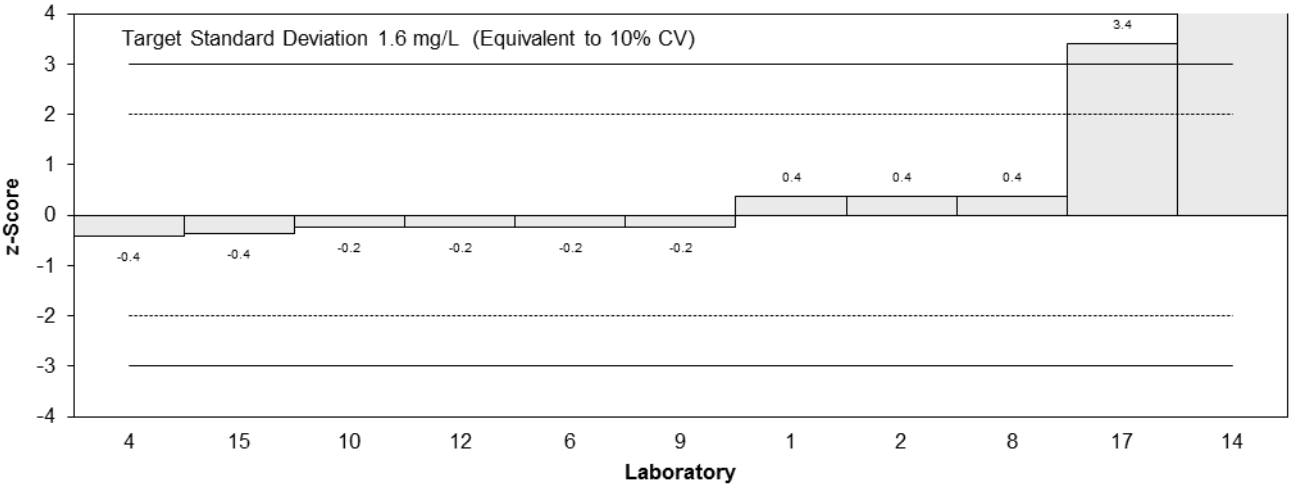
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	17.0	3.0	0.37	0.20
2	17	2.1	0.37	0.27
3	NT	NT		
4	15.7	1.5	-0.43	-0.43
5	NT	NT		
6	16	0.7	-0.24	-0.43
7	NR	NR		
8	17	3	0.37	0.20
9	16	2	-0.24	-0.19
10	16	3.2	-0.24	-0.12
11	NT	NT		
12	16	2	-0.24	-0.19
14	25.5	NR	5.55	15.17
15	15.8	2.2	-0.37	-0.26
16	NT	NT		
17	22	2.7	3.41	2.02

Statistics

Assigned Value*	16.4	0.6
Spike	Not Spiked	
Homogeneity Value	17.0	1.3
Robust Average	16.6	0.8
Median	16.0	0.3
Mean	17.6	
N	11	
Max.	25.5	
Min.	15.7	
Robust SD	0.7	
Robust CV	4.2%	

* Robust Average excluding Laboratory 14.


Kernel Density
Density
Result
Results: S3 - Sulphate
Assigned Value = 16.4 ± 0.6 mg/L
Results (mg/L)
Laboratory
4 15 10 12 6 9 1 2 8 17 14 7 11 16 3 5 Md R.A. H.V.


z-Scores: S3 - Sulphate
Target Standard Deviation 1.6 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
4 15 10 12 6 9 1 2 8 17 14
-0.4 -0.4 -0.2 -0.2 -0.2 -0.2 0.4 0.4 0.4 3.4

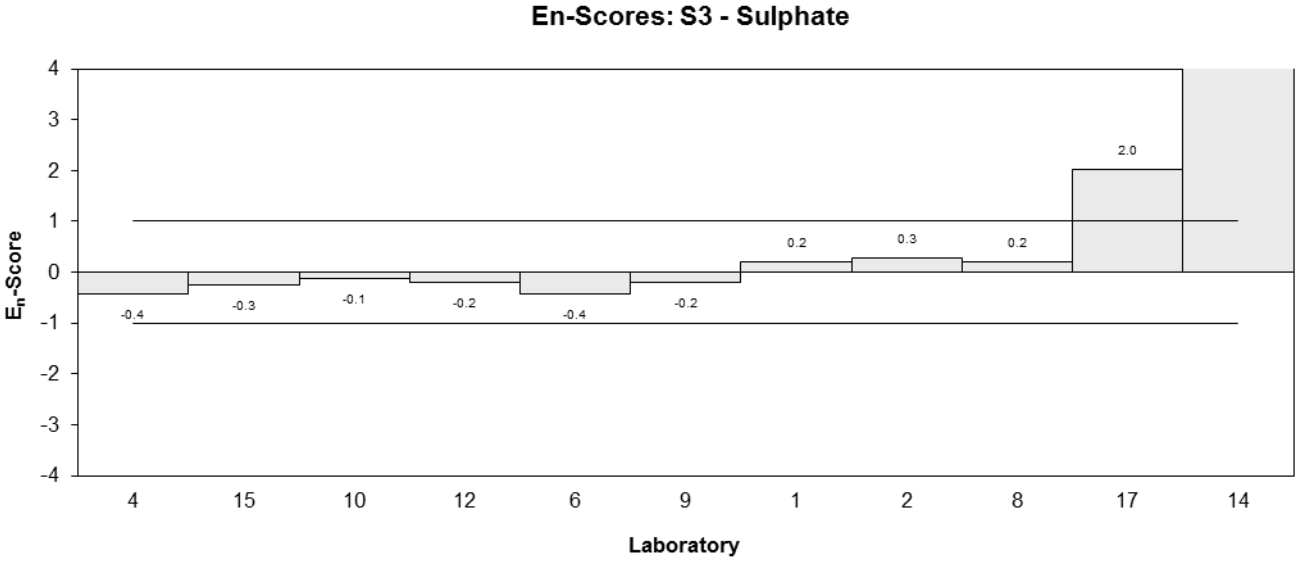

En-Scores: S3 - Sulphate
En-Score
Laboratory
4 15 10 12 6 9 1 2 8 17 14
-0.4 -0.3 -0.1 -0.2 -0.4 -0.2 0.2 0.3 0.2 2.0

Figure 43

Table 47

Sample Details

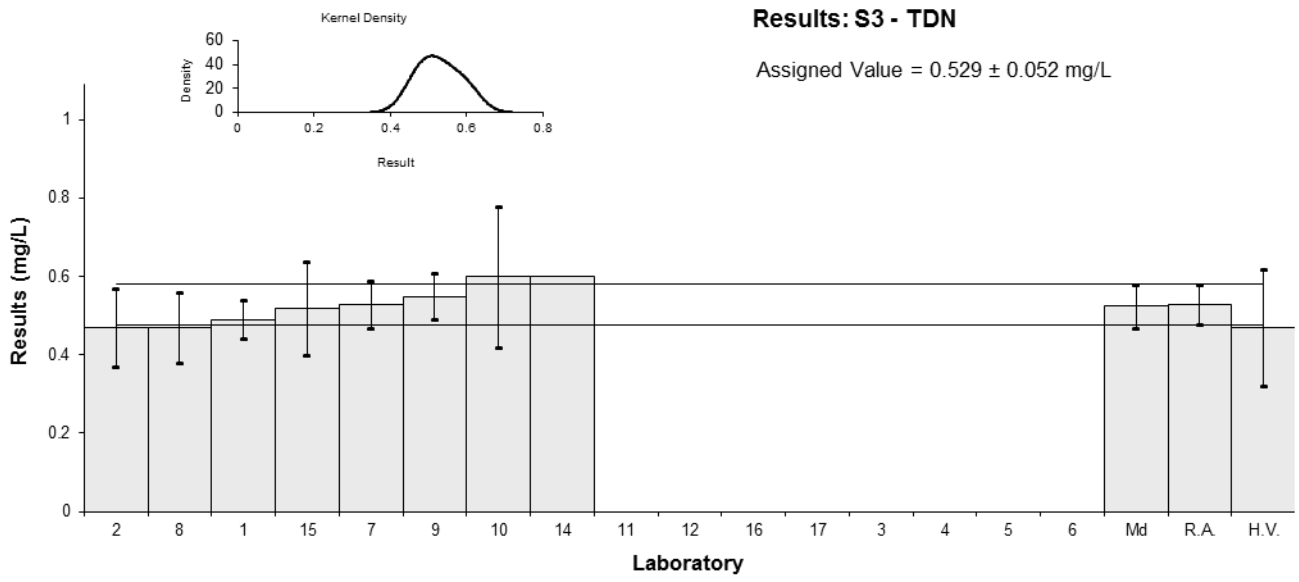
Sample No.	S3
Matrix.	River Water
Analyte.	TDN
Units	mg/L

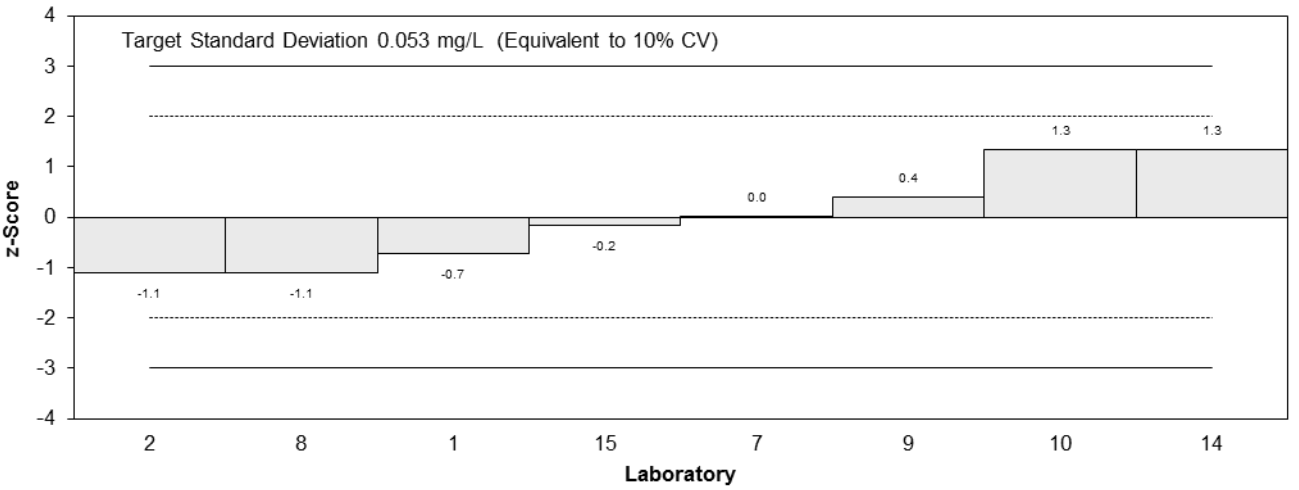
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.491	0.05	-0.72	-0.53
2	0.47	0.10	-1.12	-0.52
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	0.53	0.06	0.02	0.01
8	0.47	0.09	-1.12	-0.57
9	0.55	0.06	0.40	0.26
10	0.6	0.18	1.34	0.38
11	NT	NT		
12	NT	NT		
14	0.6	NR	1.34	1.37
15	0.52	0.12	-0.17	-0.07
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	0.529	0.052
Spike	Not Spiked	
Homogeneity Value	0.47	0.15
Robust Average	0.529	0.052
Median	0.525	0.055
Mean	0.529	
N	8	
Max.	0.6	
Min.	0.47	
Robust SD	0.059	
Robust CV	11%	


Kernel Density
Density
Result
Results: S3 - TDN
Assigned Value = 0.529 ± 0.052 mg/L
Results (mg/L)
Laboratory
2 8 1 15 7 9 10 14 11 12 16 17 3 4 5 6 Md R.A. H.V.


z-Scores: S3 - TDN
Target Standard Deviation 0.053 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
2 8 1 15 7 9 10 14
-1.1 -1.1 -0.7 -0.2 0.0 0.4 1.3 1.3

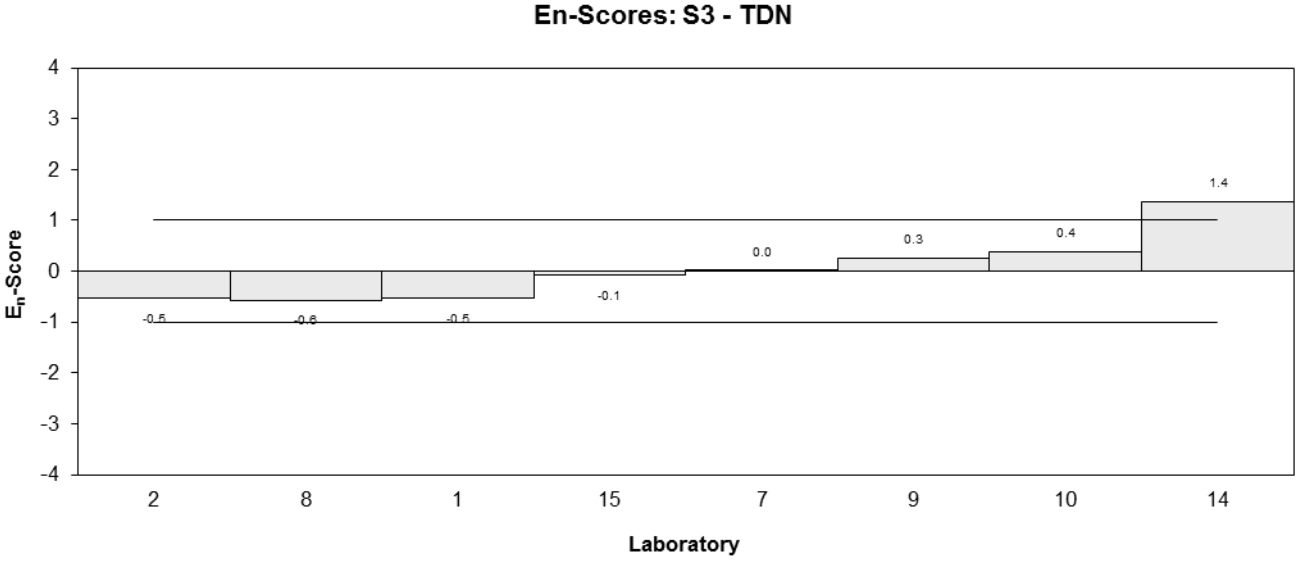

En-Scores: S3 - TDN
En-Score
Laboratory
2 8 1 15 7 9 10 14
-0.5 -0.6 -0.5 -0.1 0.0 0.3 0.4 1.4

Figure 44

Table 48

Sample Details

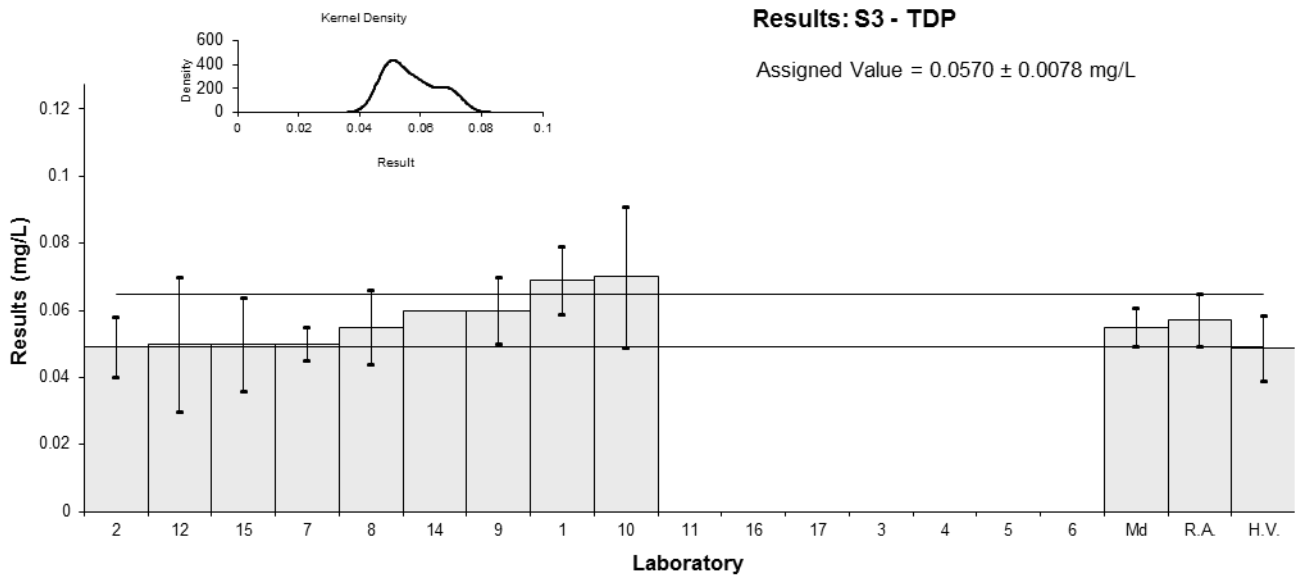
Sample No.	S3
Matrix.	River Water
Analyte.	TDP
Units	mg/L

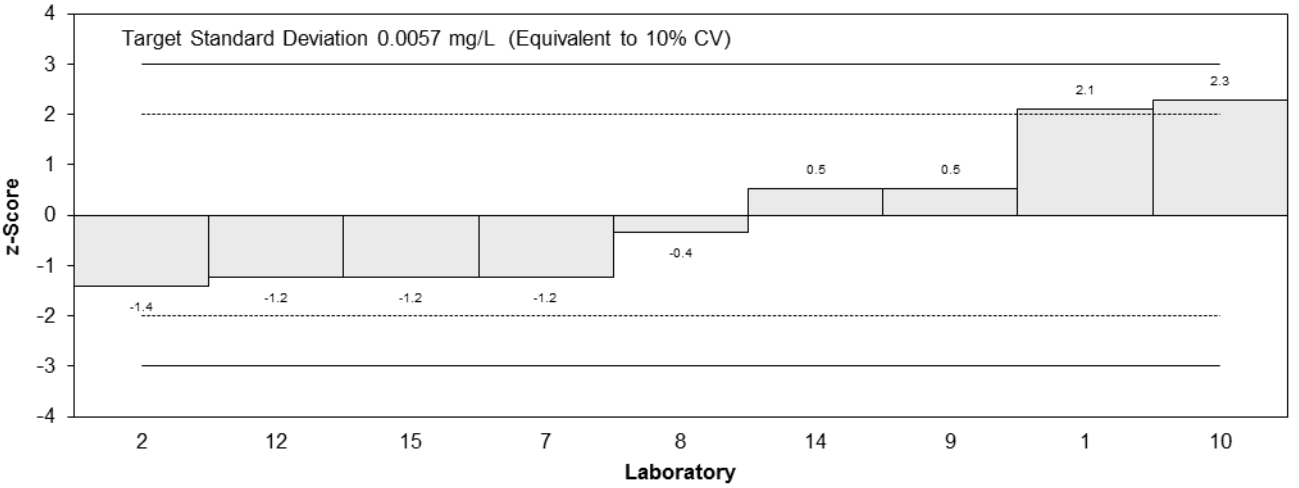
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.069	0.01	2.11	0.95
2	0.049	0.009	-1.40	-0.67
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	0.05	0.005	-1.23	-0.76
8	0.055	0.011	-0.35	-0.15
9	0.06	0.01	0.53	0.24
10	0.07	0.021	2.28	0.58
11	NT	NT		
12	0.05	0.02	-1.23	-0.33
14	0.06	NR	0.53	0.38
15	0.05	0.014	-1.23	-0.44
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	0.0570	0.0078
Spike	Not Spiked	
Homogeneity Value	0.0487	0.0097
Robust Average	0.0570	0.0078
Median	0.0550	0.0057
Mean	0.0570	
N	9	
Max.	0.07	
Min.	0.049	
Robust SD	0.0094	
Robust CV	16%	


Kernel Density
Density
Result
Results: S3 - TDP
Assigned Value = 0.0570 ± 0.0078 mg/L
Results (mg/L)
Laboratory
2 12 15 7 8 14 9 1 10 11 16 17 3 4 5 6 Md R.A. H.V.


z-Scores: S3 - TDP
Target Standard Deviation 0.0057 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
2 12 15 7 8 14 9 1 10
-1.4 -1.2 -1.2 -1.2 -0.4 0.5 0.5 2.1 2.3

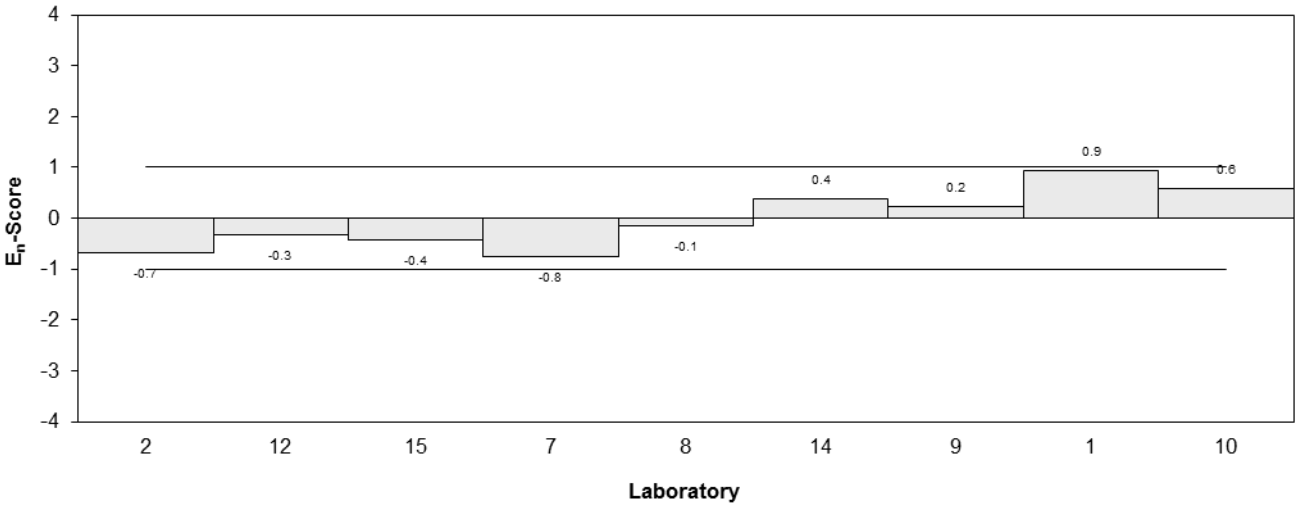

En-Scores: S3 - TDP
En-Score
Laboratory
2 12 15 7 8 14 9 1 10
-0.7 -0.3 -0.4 -0.8 -0.1 0.4 0.2 0.9 0.6

Figure 45

Table 49

Sample Details

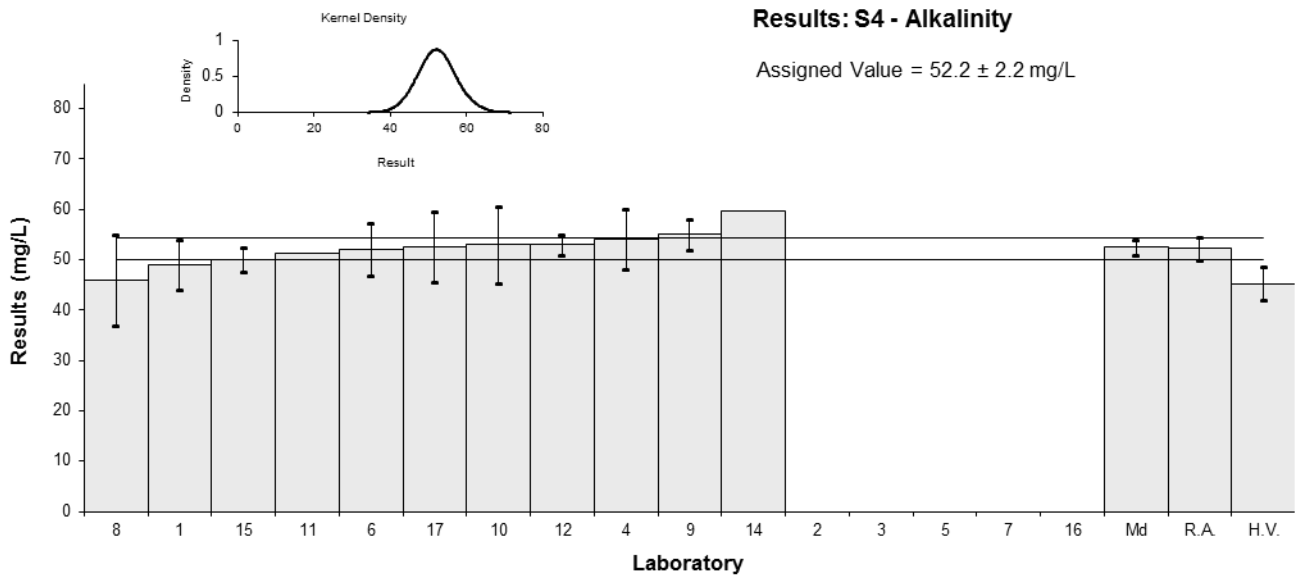
Sample No.	S4
Matrix.	River Water
Analyte.	Alkalinity
Units	mg/L

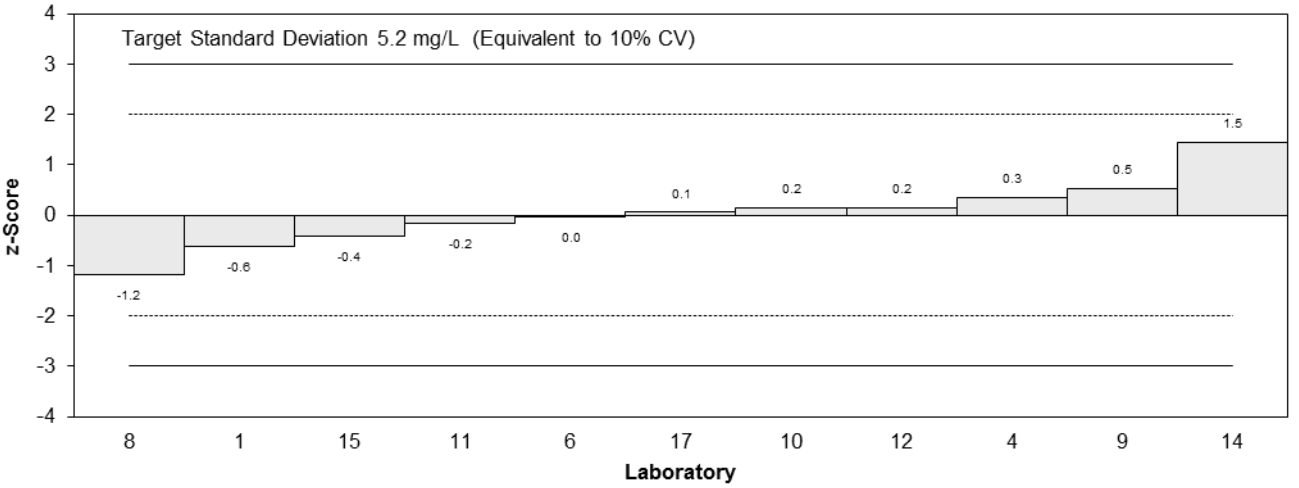
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	49	5	-0.61	-0.59
2	NR	NR		
3	NR	NR		
4	54	6	0.34	0.28
5	NR	NR		
6	52	5.2	-0.04	-0.04
7	NR	NR		
8	46	9	-1.19	-0.67
9	55	3	0.54	0.75
10	53	7.6	0.15	0.10
11	51.3	NR	-0.17	-0.41
12	53	2	0.15	0.27
14	59.78	NR	1.45	3.45
15	50	2.5	-0.42	-0.66
16	NT	NT		
17	52.5	7.0	0.06	0.04

Statistics

Assigned Value	52.2	2.2
Spike	Not Spiked	
Homogeneity Value	45.3	3.4
Robust Average	52.2	2.2
Median	52.5	1.5
Mean	52.3	
N	11	
Max.	59.78	
Min.	46	
Robust SD	2.9	
Robust CV	5.6%	


Kernel Density
Density
Result
Results: S4 - Alkalinity
Assigned Value = 52.2 ± 2.2 mg/L
Results (mg/L)
Laboratory
8 1 15 11 6 17 10 12 4 9 14 2 3 5 7 16 Md R.A. H.V.


z-Scores: S4 - Alkalinity
Target Standard Deviation 5.2 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
8 1 15 11 6 17 10 12 4 9 14
-1.2 -0.6 -0.4 -0.2 0.0 0.1 0.2 0.2 0.3 0.5 1.5

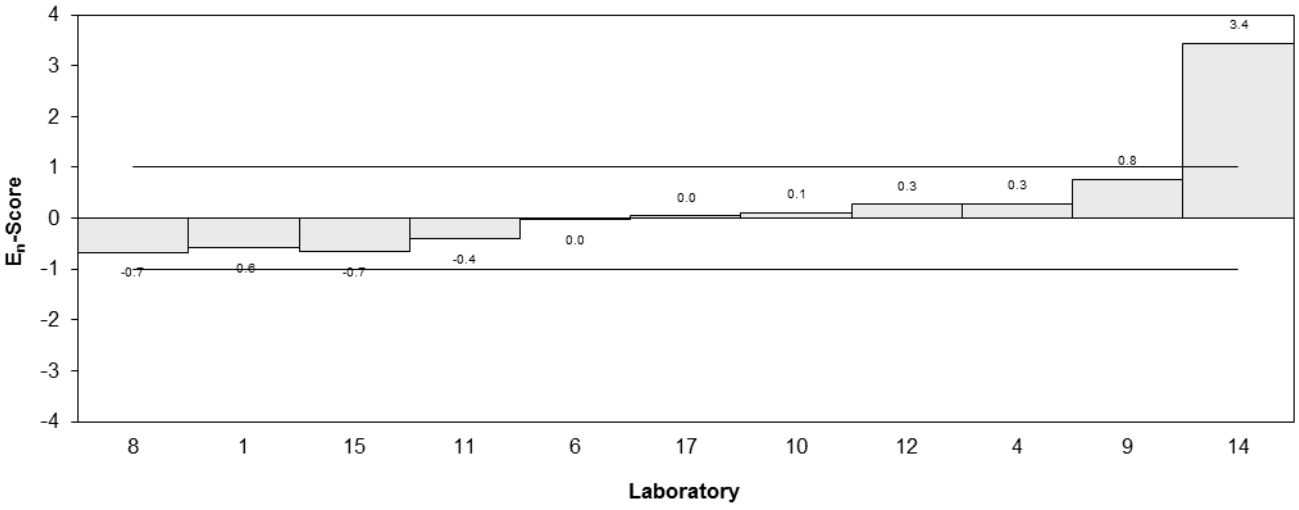

En-Scores: S4 - Alkalinity
En-Score
Laboratory
8 1 15 11 6 17 10 12 4 9 14
-0.7 -0.6 -0.7 -0.4 0.0 0.0 0.1 0.3 0.3 0.8 3.4

Figure 46

Table 50

Sample Details

Sample No.	S4
Matrix.	River Water
Analyte.	B
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	0.045	0.08
2	NR	NR
3	NR	NR
4	NT	NT
5	0.041	0.007
6	28	2
7	NR	NR
8	310	60
9	NT	NT
10	<0.05	0.05
11	0.051	NR
12	<0.1	NR
14	NT	NT
15	NT	NT
16	0.039	NR
17	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.043	0.007
Robust Average	12	23
Median	0.048	0.012
Mean	56	
N	6	
Max.	310	
Min.	0.039	
Robust SD	23	
Robust CV	183%	

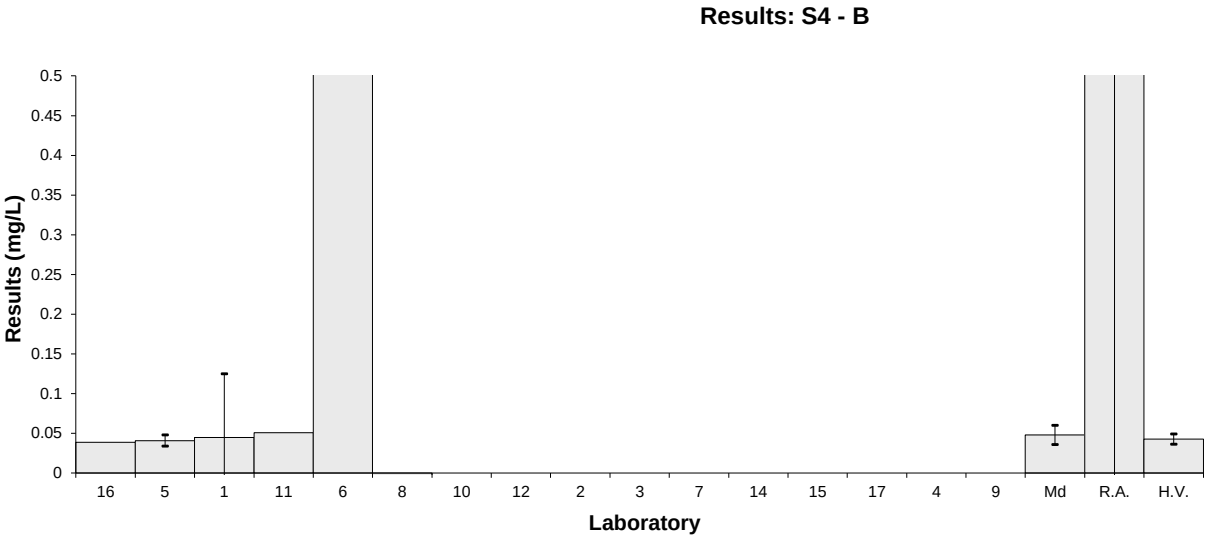

Results: S4 - B
Results (mg/L)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
16
5
1
11
6
8
10
12
2
3
7
14
15
17
4
9
Md
R.A.
H.V.
Laboratory

Figure 47

Table 51

Sample Details

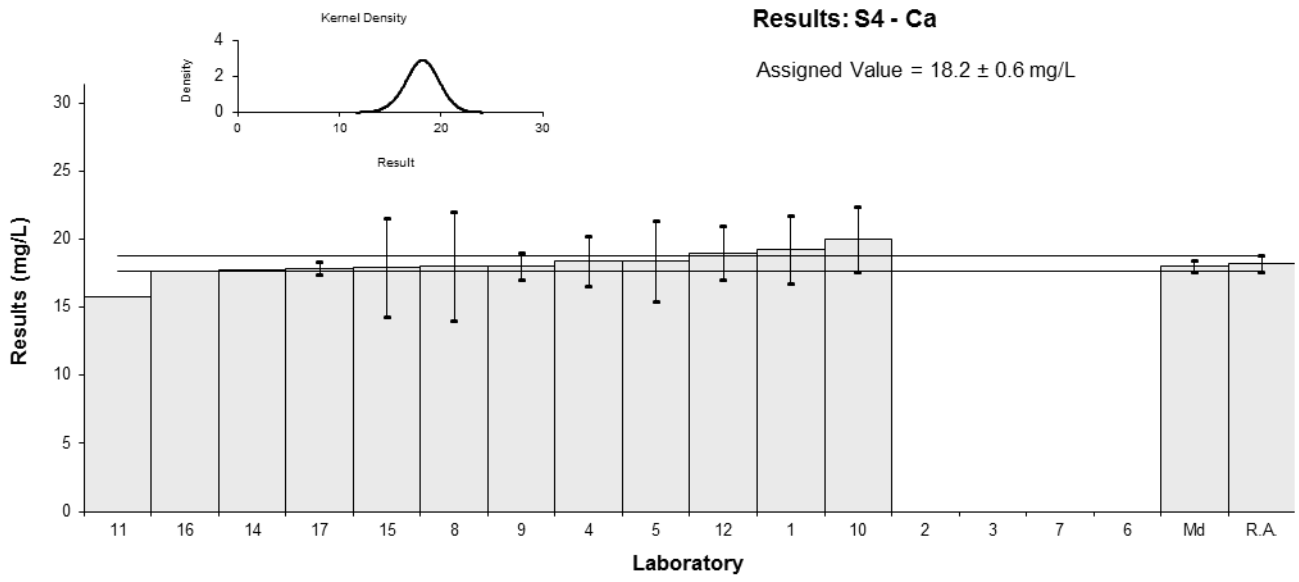
Sample No.	S4
Matrix.	River Water
Analyte.	Ca
Units	mg/L

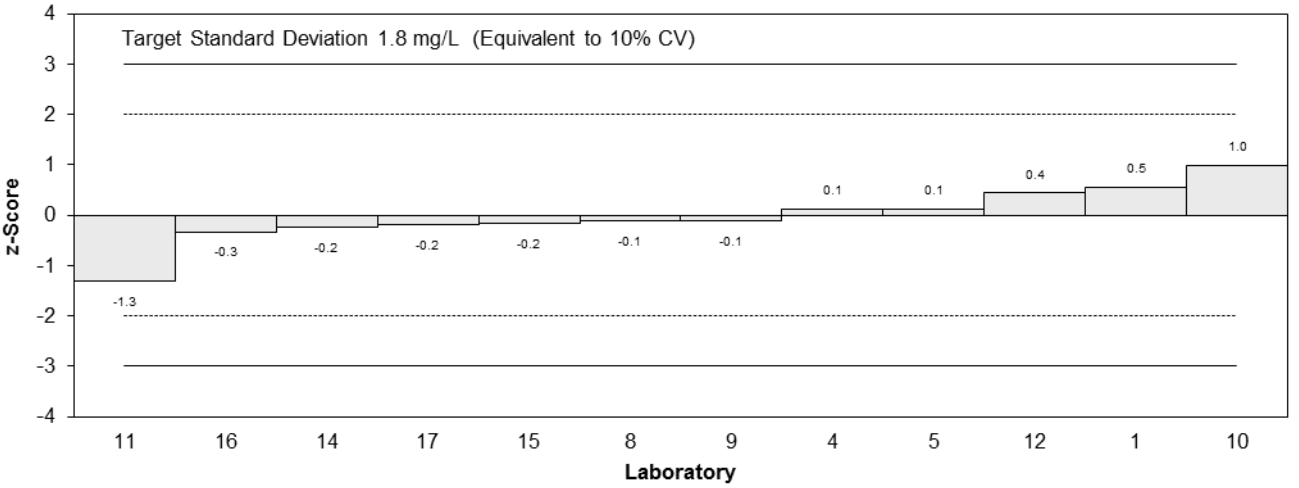
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	19.2	2.5	0.55	0.39
2	NR	NR		
3	NR	NR		
4	18.4	1.8	0.11	0.11
5	18.4	3.0	0.11	0.07
6	NT	NT		
7	NR	NR		
8	18	4	-0.11	-0.05
9	18	1	-0.11	-0.17
10	20	2.4	0.99	0.73
11	15.8	NR	-1.32	-4.00
12	19	2	0.44	0.38
14	17.77	NR	-0.24	-0.72
15	17.9	3.6	-0.16	-0.08
16	17.6	NR	-0.33	-1.00
17	17.85	0.48	-0.19	-0.46

Statistics

Assigned Value	18.2	0.6
Spike	Not Spiked	
Robust Average	18.2	0.6
Median	18.0	0.4
Mean	18.2	
N	12	
Max.	20	
Min.	15.8	
Robust SD	0.8	
Robust CV	4.4%	


Kernel Density
Density
Result
Results: S4 - Ca
Assigned Value = 18.2 ± 0.6 mg/L
Results (mg/L)
Laboratory
11 16 14 17 15 8 9 4 5 12 1 10 2 3 7 6 Md R.A.


z-Scores: S4 - Ca
Target Standard Deviation 1.8 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 16 14 17 15 8 9 4 5 12 1 10
-1.3 -0.3 -0.2 -0.2 -0.2 -0.1 -0.1 0.1 0.1 0.4 0.5 1.0

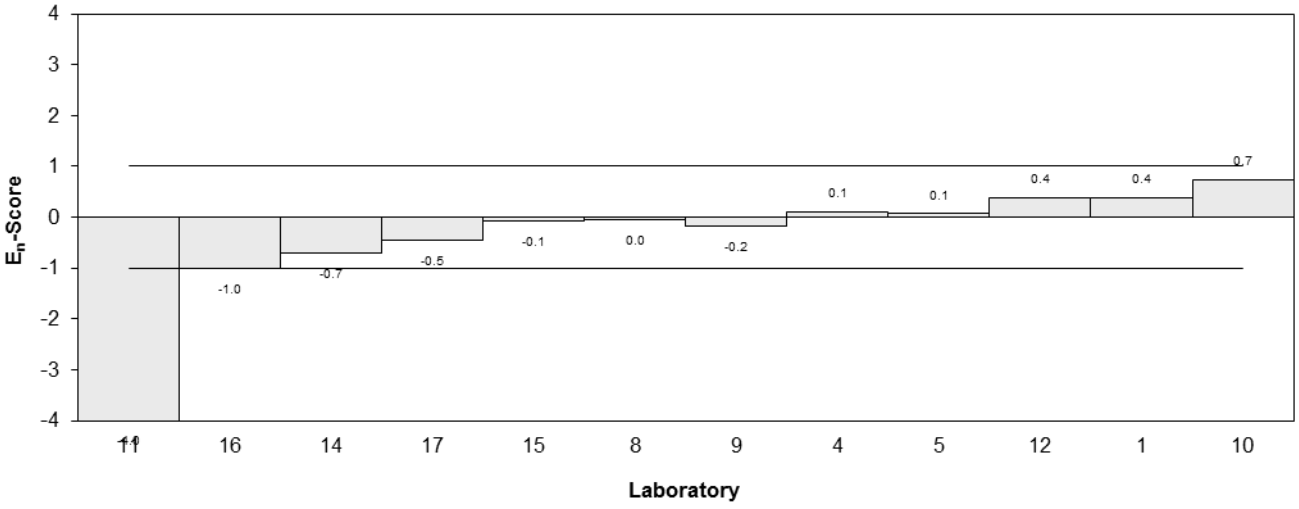

En-Scores: S4 - Ca
En-Score
Laboratory
11 16 14 17 15 8 9 4 5 12 1 10
-1.0 -0.7 -0.5 -0.1 0.0 -0.2 0.1 0.1 0.4 0.4 0.7

Figure 48

Table 52

Sample Details

Sample No.	S4
Matrix.	River Water
Analyte.	COD
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	16	2
2	NR	NR
3	NR	NR
4	NT	NT
5	NR	NR
6	NT	NT
7	NR	NR
8	17	3
9	18	2
10	NT	NT
11	NT	NT
12	<25	NR
14	NT	NT
15	<25	2.5
16	NT	NT
17	18	3.2

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	17.0	2.6
Robust Average	17.3	1.4
Median	17.5	1.2
Mean	17.3	
N	4	
Max.	18	
Min.	16	
Robust SD	1.1	
Robust CV	6.4%	

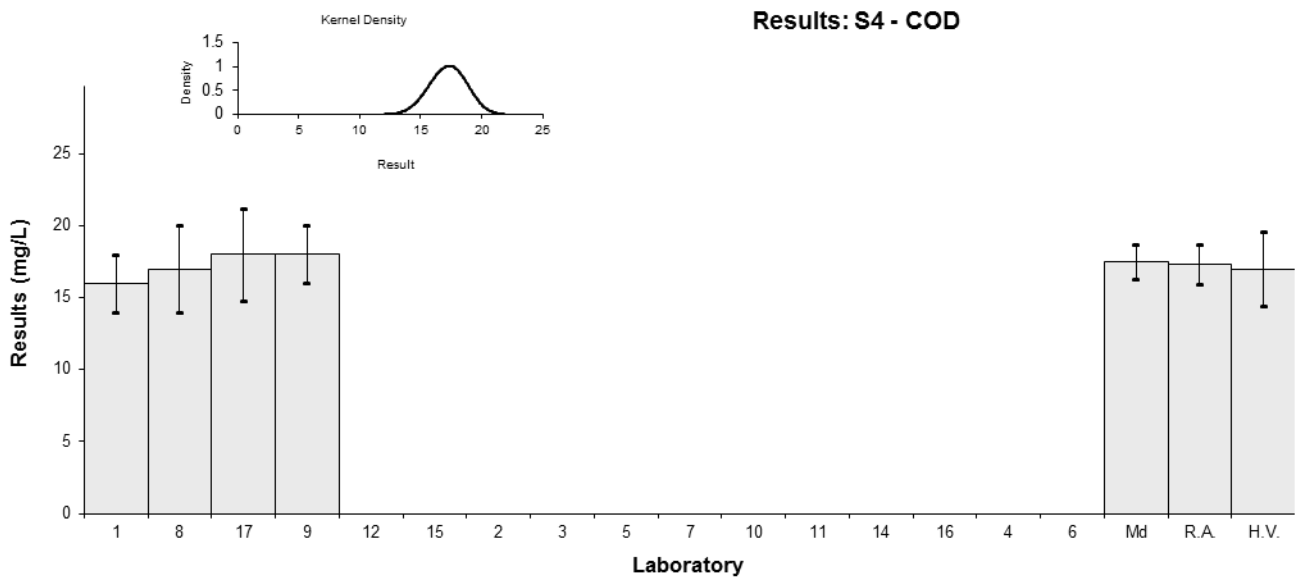

Results: S4 - COD
Kernel Density
Density
Result
Results (mg/L)
Laboratory
1
8
17
9
12
15
2
3
5
7
10
11
14
16
4
6
Md
R.A.
H.V.

Figure 49

Table 53

Sample Details

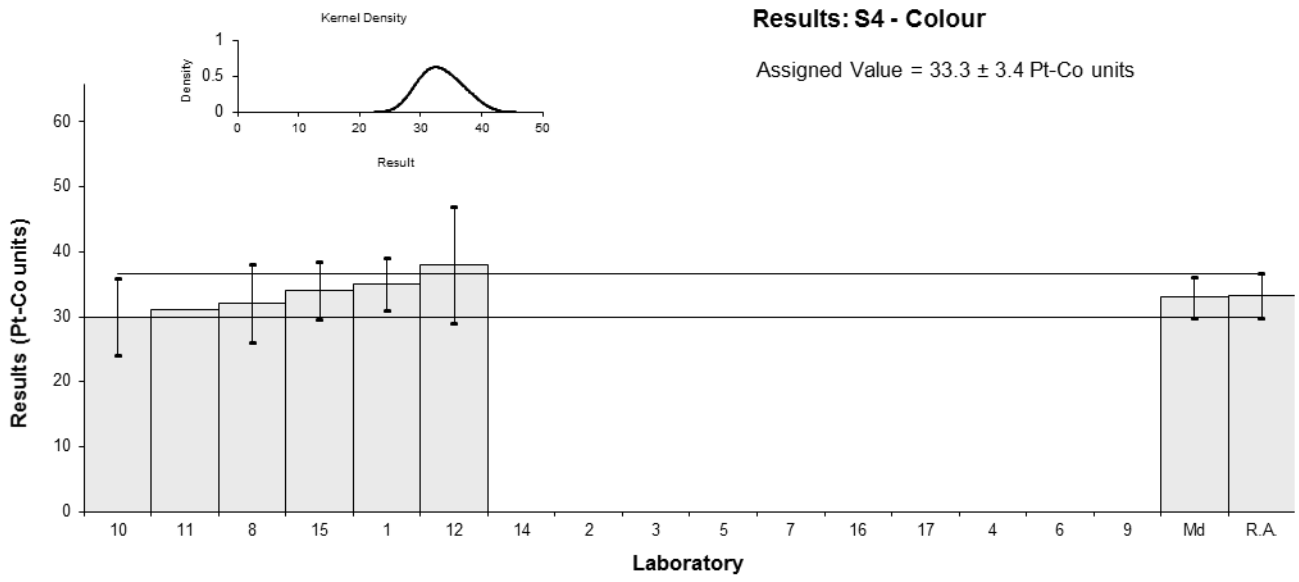
Sample No.	S4
Matrix.	River Water
Analyte.	Colour
Units	Pt-Co units

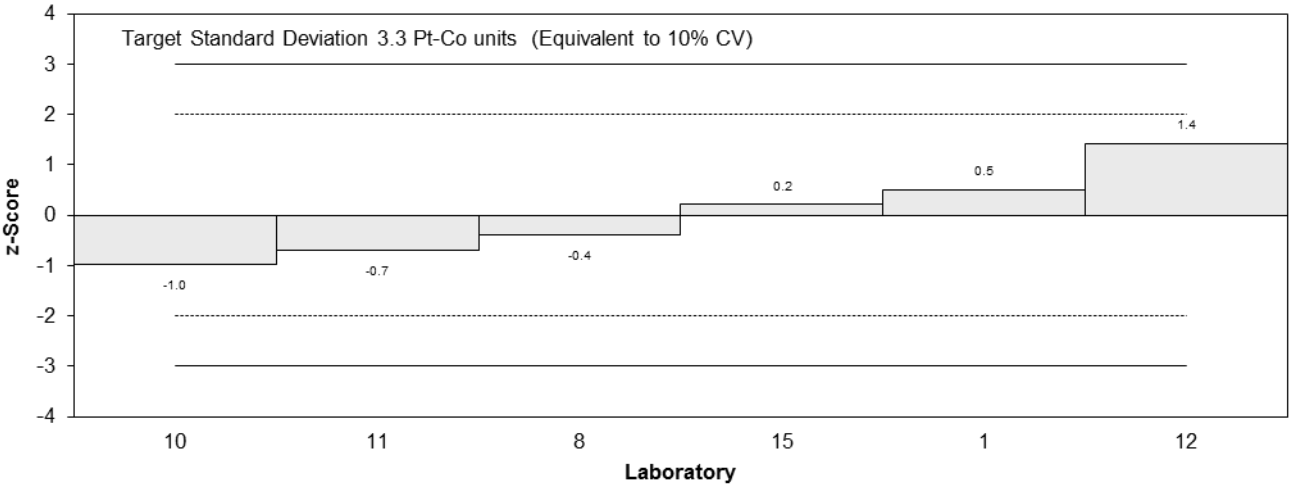
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	35	4	0.51	0.32
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	NT	NT		
7	NR	NR		
8	32	6	-0.39	-0.19
9	NT	NT		
10	30	6	-0.99	-0.48
11	31	NR	-0.69	-0.68
12	38	9	1.41	0.49
14	NR	NR		
15	34	4.4	0.21	0.13
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	33.3	3.4
Spike	Not Spiked	
Robust Average	33.3	3.4
Median	33.0	3.1
Mean	33.3	
N	6	
Max.	38	
Min.	30	
Robust SD	3.3	
Robust CV	9.9%	


Kernel Density
Density
Result
Results: S4 - Colour
Assigned Value = 33.3 ± 3.4 Pt-Co units
Results (Pt-Co units)
Laboratory
10 11 8 15 1 12 14 2 3 5 7 16 17 4 6 9 Md R.A.


z-Scores: S4 - Colour
Target Standard Deviation 3.3 Pt-Co units (Equivalent to 10% CV)
z-Score
-1.0
-0.7
-0.4
0.2
0.5
1.4
Laboratory
10 11 8 15 1 12

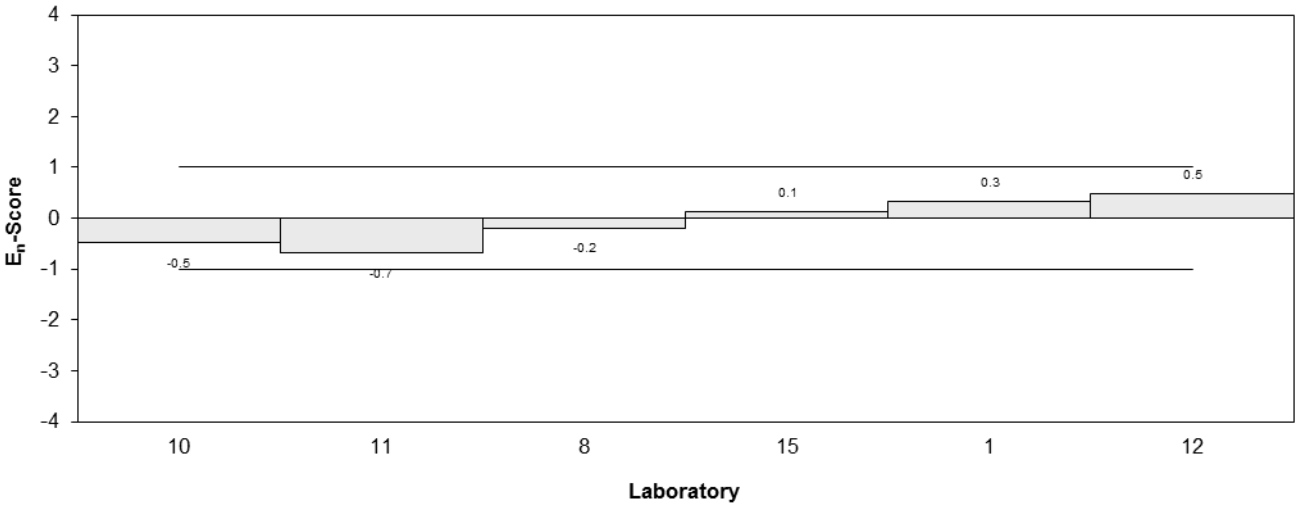

En-Scores: S4 - Colour
En-Score
-0.5
-0.7
-0.2
0.1
0.3
0.5
Laboratory
10 11 8 15 1 12

Figure 50

Table 54

Sample Details

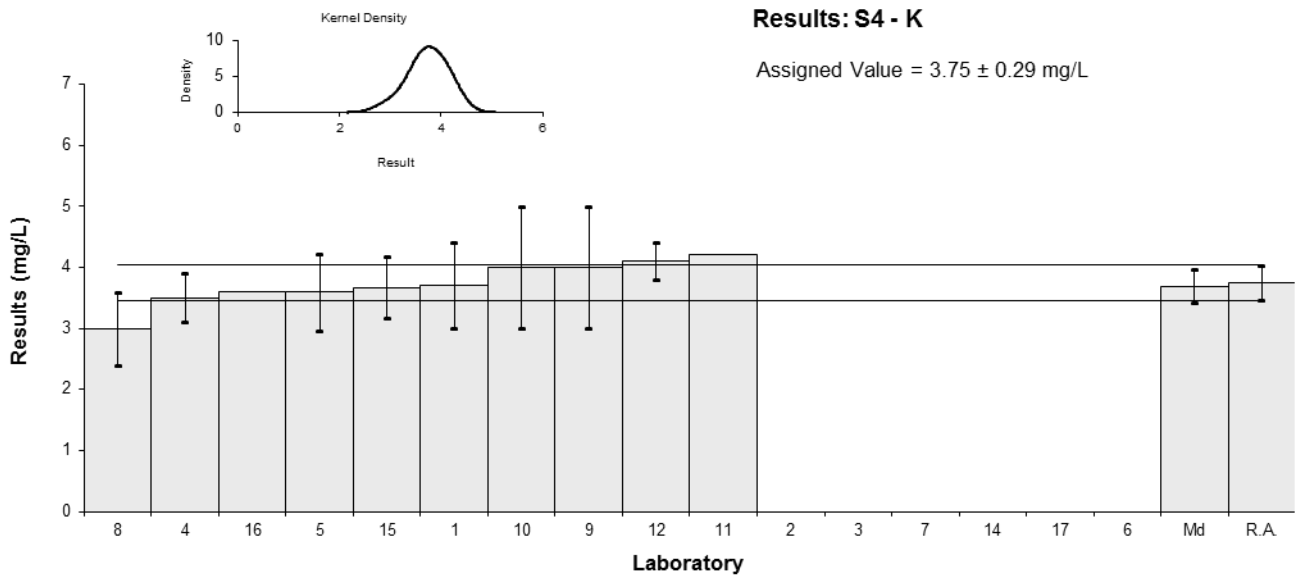
Sample No.	S4
Matrix.	River Water
Analyte.	K
Units	mg/L

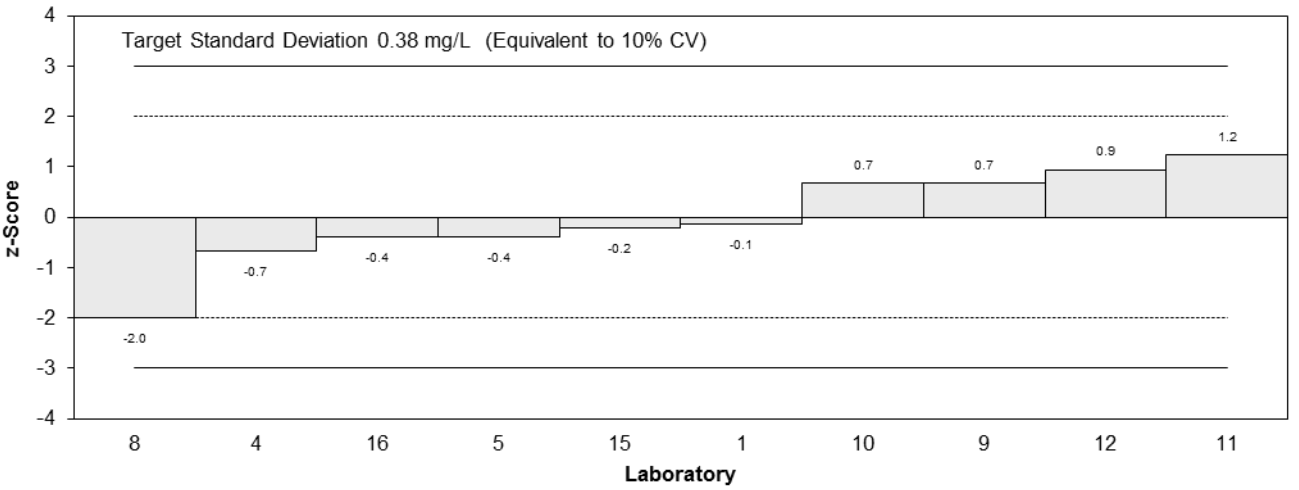
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.70	0.7	-0.13	-0.07
2	NR	NR		
3	NR	NR		
4	3.5	0.4	-0.67	-0.51
5	3.60	0.63	-0.40	-0.22
6	NT	NT		
7	NR	NR		
8	3.0	0.6	-2.00	-1.13
9	4	1	0.67	0.24
10	4	1	0.67	0.24
11	4.21	NR	1.23	1.59
12	4.1	0.3	0.93	0.84
14	NT	NT		
15	3.67	0.5	-0.21	-0.14
16	3.6	NR	-0.40	-0.52
17	NT	NT		

Statistics

Assigned Value	3.75	0.29
Spike	Not Spiked	
Robust Average	3.75	0.29
Median	3.69	0.27
Mean	3.74	
N	10	
Max.	4.21	
Min.	3	
Robust SD	0.37	
Robust CV	9.9%	


Results: S4 - K
Assigned Value = 3.75 ± 0.29 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
8 4 16 5 15 1 10 9 12 11 2 3 7 14 17 6 Md R.A.


z-Scores: S4 - K
Target Standard Deviation 0.38 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
8 4 16 5 15 1 10 9 12 11
-2.0 -0.7 -0.4 -0.4 -0.2 -0.1 0.7 0.7 0.9 1.2

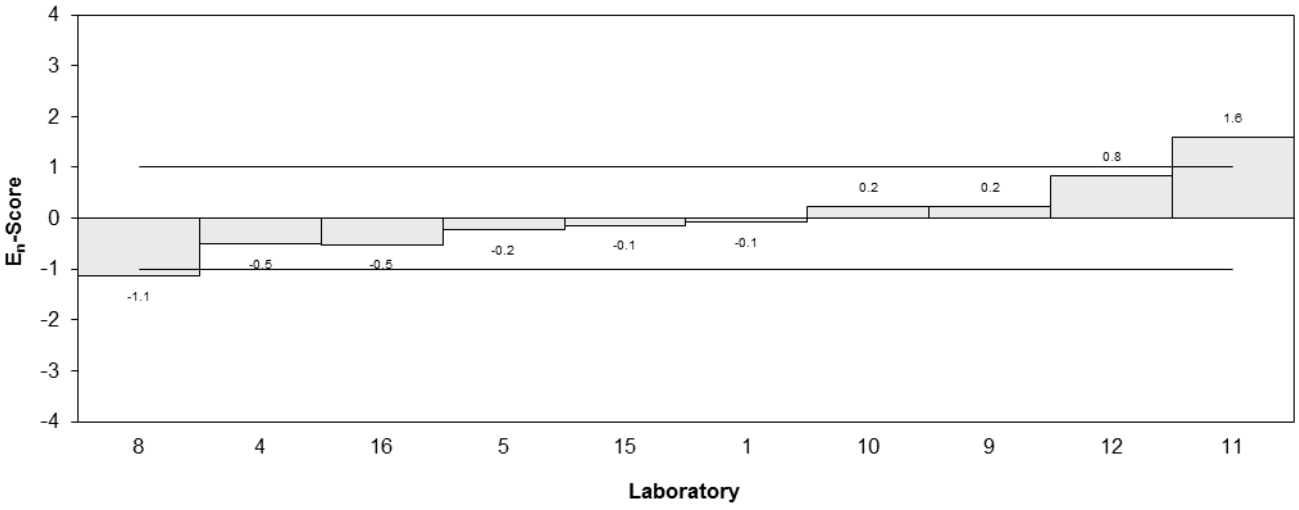

En-Scores: S4 - K
En-Score
Laboratory
8 4 16 5 15 1 10 9 12 11
-1.1 -0.5 -0.5 -0.2 -0.1 -0.1 0.2 0.2 0.8 1.6

Figure 51

Table 55

Sample Details

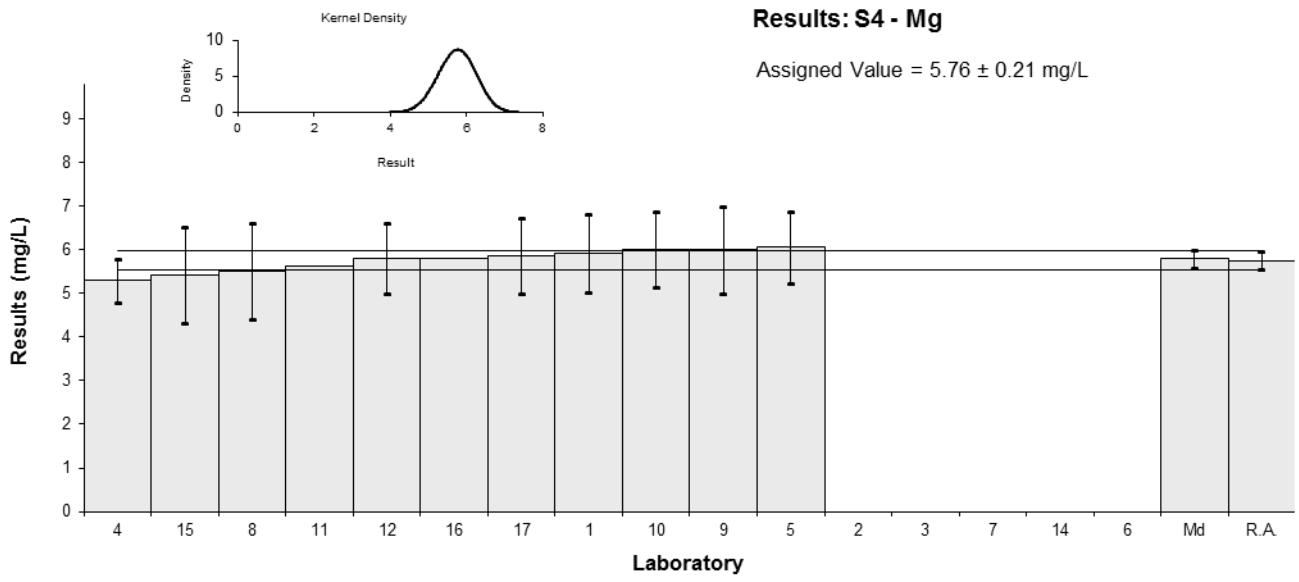
Sample No.	S4
Matrix.	River Water
Analyte.	Mg
Units	mg/L

Participant Results

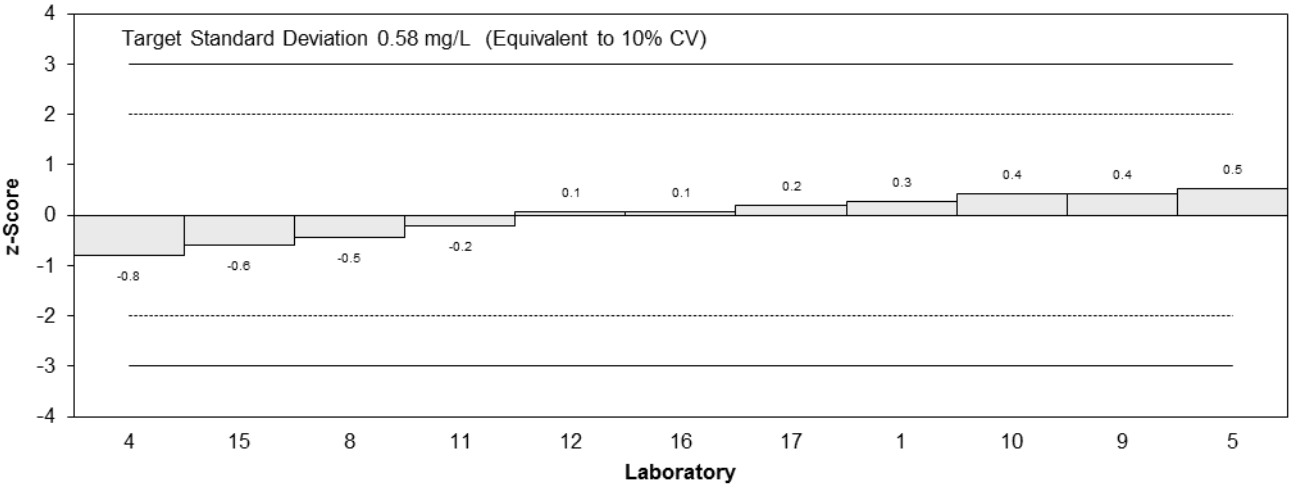
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5.92	0.9	0.28	0.17
2	NR	NR		
3	NR	NR		
4	5.3	0.5	-0.80	-0.85
5	6.06	0.82	0.52	0.35
6	NT	NT		
7	NR	NR		
8	5.5	1.1	-0.45	-0.23
9	6	1	0.42	0.23
10	6	0.87	0.42	0.27
11	5.63	NR	-0.23	-0.62
12	5.8	0.8	0.07	0.05
14	NT	NT		
15	5.42	1.1	-0.59	-0.30
16	5.8	NR	0.07	0.19
17	5.87	0.87	0.19	0.12

Statistics

Assigned Value	5.76	0.21
Spike	Not Spiked	
Robust Average	5.76	0.21
Median	5.80	0.20
Mean	5.75	
N	11	
Max.	6.06	
Min.	5.3	
Robust SD	0.28	
Robust CV	4.9%	



z-Scores: S4 - Mg



En-Scores: S4 - Mg

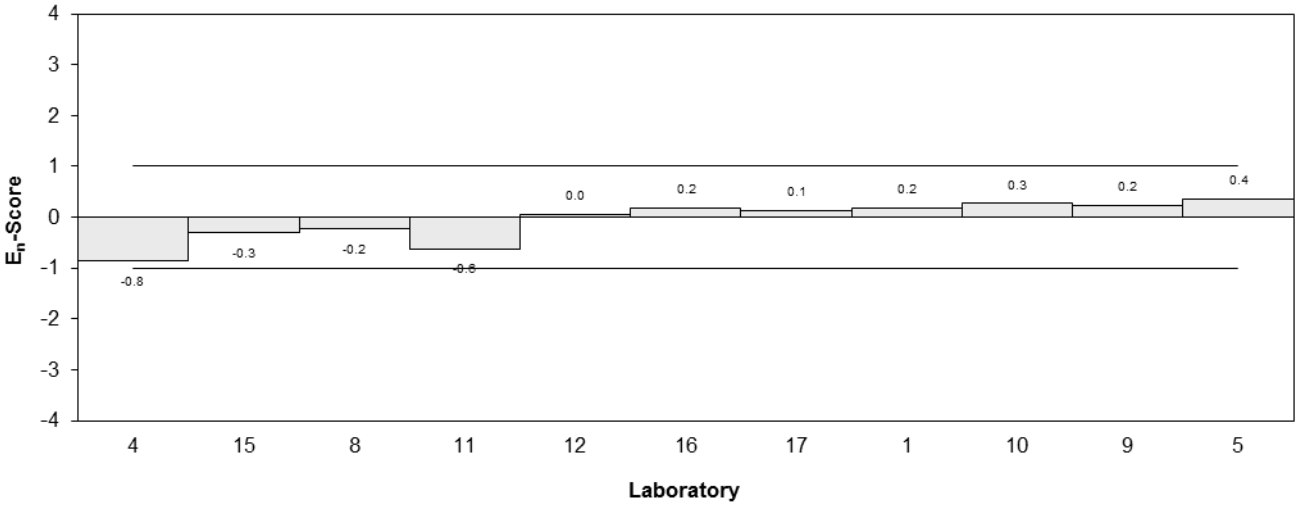


Figure 52

Table 56

Sample Details

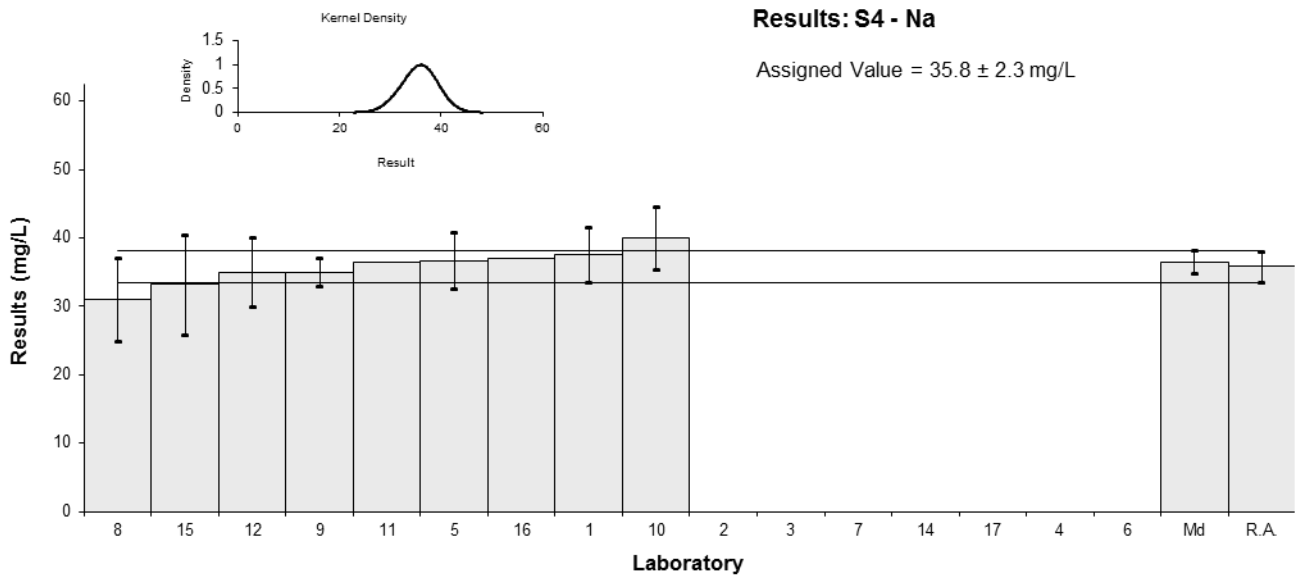
Sample No.	S4
Matrix.	River Water
Analyte.	Na
Units	mg/L

Participant Results

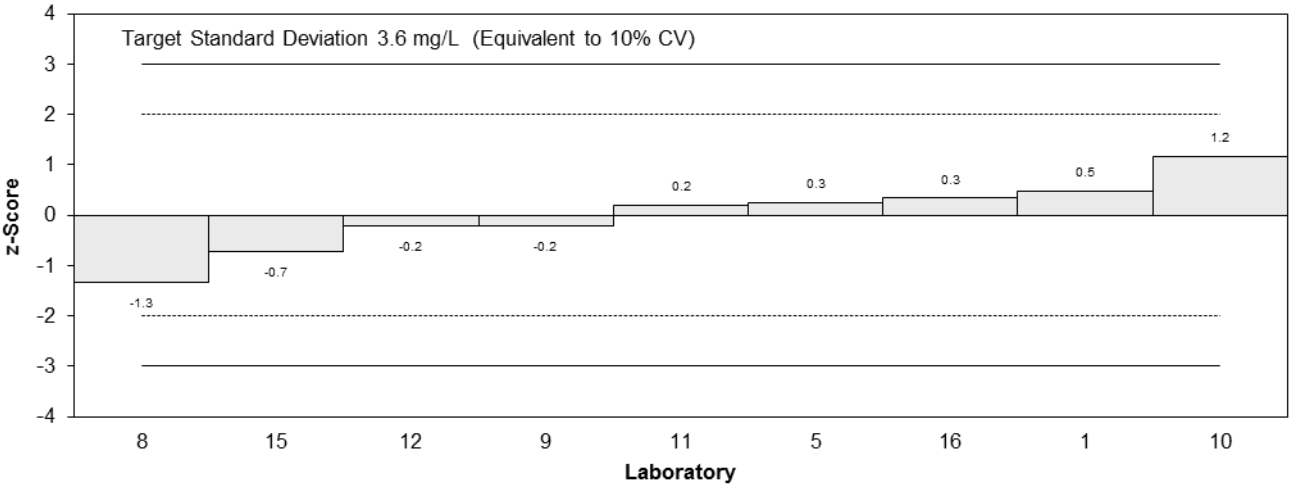
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	37.5	4.0	0.47	0.37
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	36.7	4.1	0.25	0.19
6	NT	NT		
7	NR	NR		
8	31	6	-1.34	-0.75
9	35	2	-0.22	-0.26
10	40	4.6	1.17	0.82
11	36.5	NR	0.20	0.30
12	35	5	-0.22	-0.15
14	NT	NT		
15	33.2	7.3	-0.73	-0.34
16	37	NR	0.34	0.52
17	NT	NT		

Statistics

Assigned Value	35.8	2.3
Spike	Not Spiked	
Robust Average	35.8	2.3
Median	36.5	1.7
Mean	35.8	
N	9	
Max.	40	
Min.	31	
Robust SD	2.8	
Robust CV	7.8%	



z-Scores: S4 - Na



En-Scores: S4 - Na

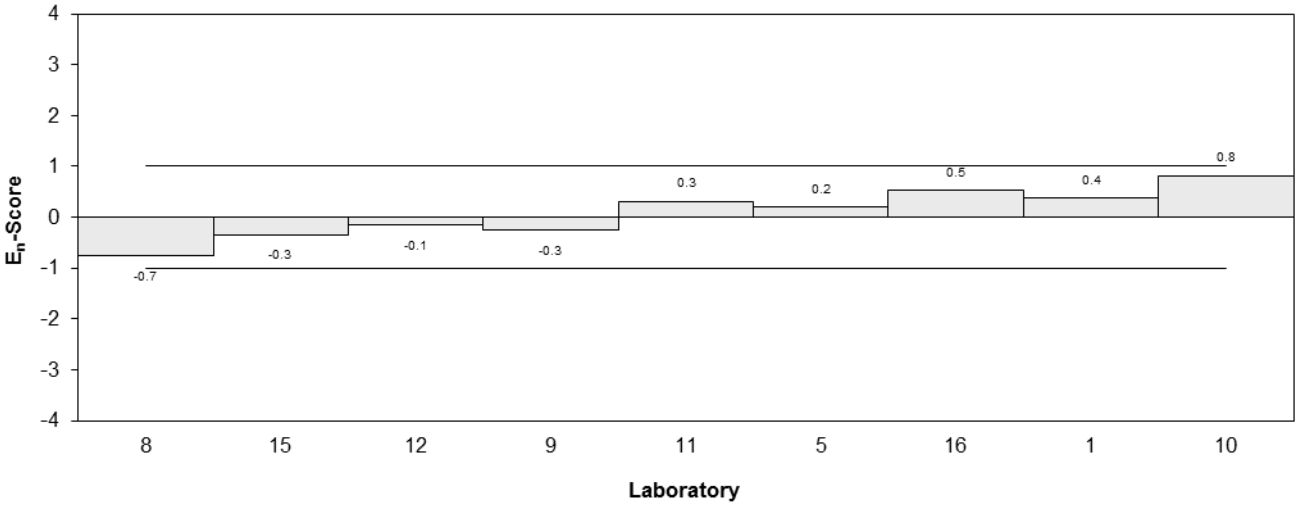


Figure 53

Table 57

Sample Details

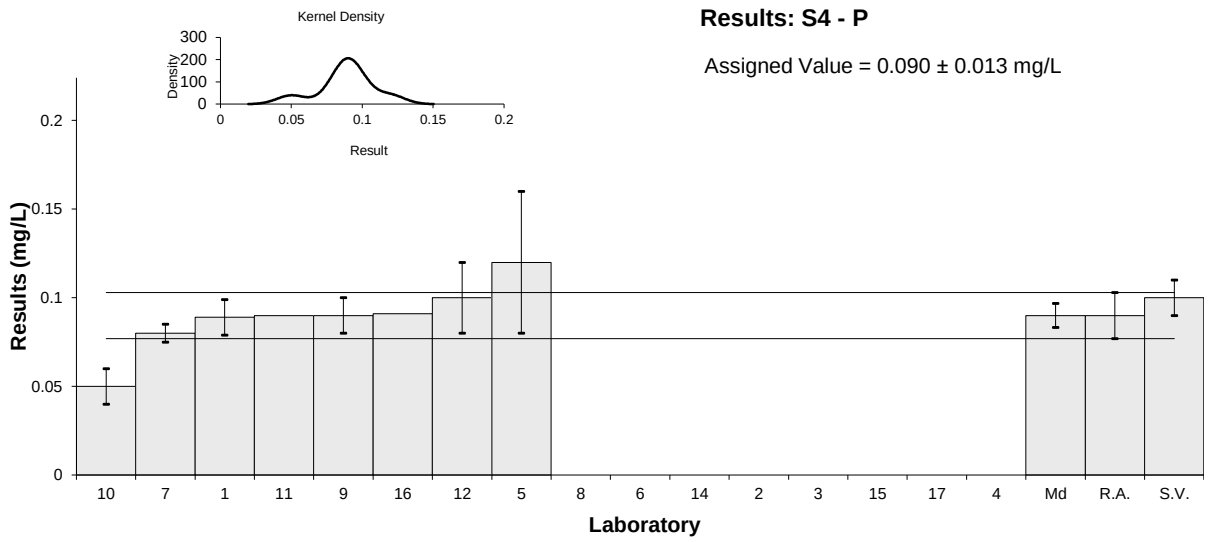
Sample No.	S4
Matrix.	River Water
Analyte.	P
Units	mg/L

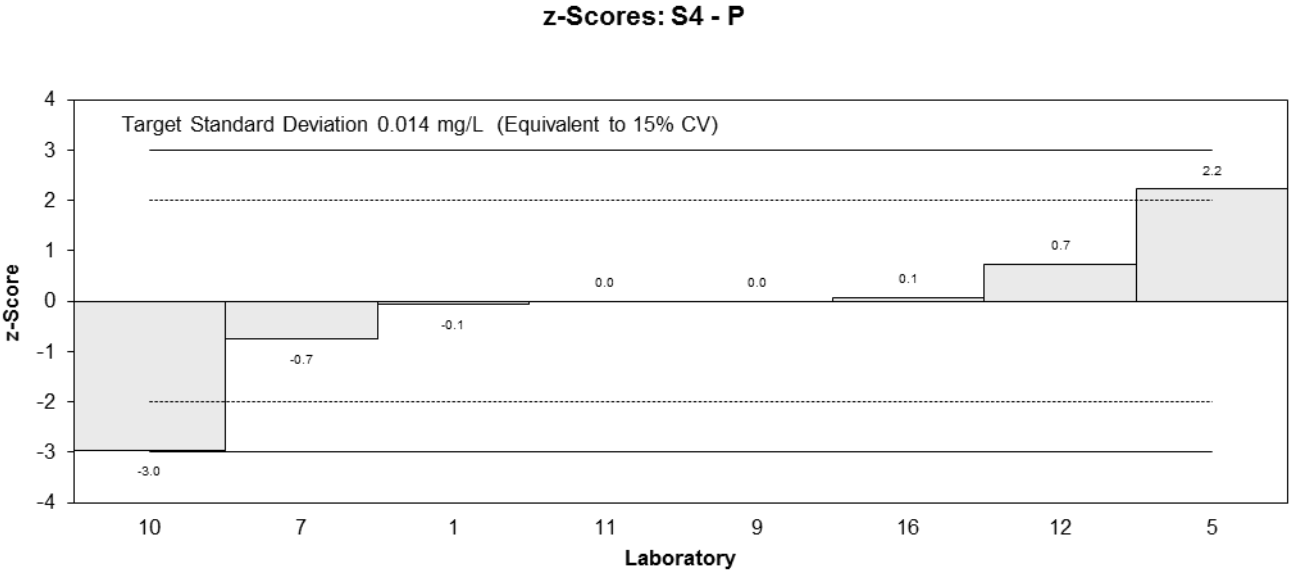
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.089	0.01	-0.07	-0.06
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	0.12	0.04	2.22	0.71
6	<1.5	1.8		
7	0.08	0.005	-0.74	-0.72
8	<0.05	NR		
9	0.09	0.01	0.00	0.00
10	0.05	0.01	-2.96	-2.44
11	0.09	NR	0.00	0.00
12	0.10	0.02	0.74	0.42
14	NR	NR		
15	NT	NT		
16	0.091	NR	0.07	0.08
17	NT	NT		

Statistics

Assigned Value	0.090	0.013
Spike	0.100	0.010
Robust Average	0.090	0.013
Median	0.090	0.007
Mean	0.089	
N	8	
Max.	0.12	
Min.	0.05	
Robust SD	0.014	
Robust CV	16%	


Kernel Density
Density
300
200
100
0
0
0.05
0.1
0.15
0.2
Result
Results: S4 - P
Assigned Value = 0.090 ± 0.013 mg/L
Results (mg/L)
0.2
0.15
0.1
0.05
0
10
7
1
11
9
16
12
5
8
6
14
2
3
15
17
4
Md
R.A.
S.V.
Laboratory


z-Scores: S4 - P
Target Standard Deviation 0.014 mg/L (Equivalent to 15% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-3.0
-0.7
-0.1
0.0
0.0
0.1
0.7
2.2
10
7
1
11
9
16
12
5
Laboratory

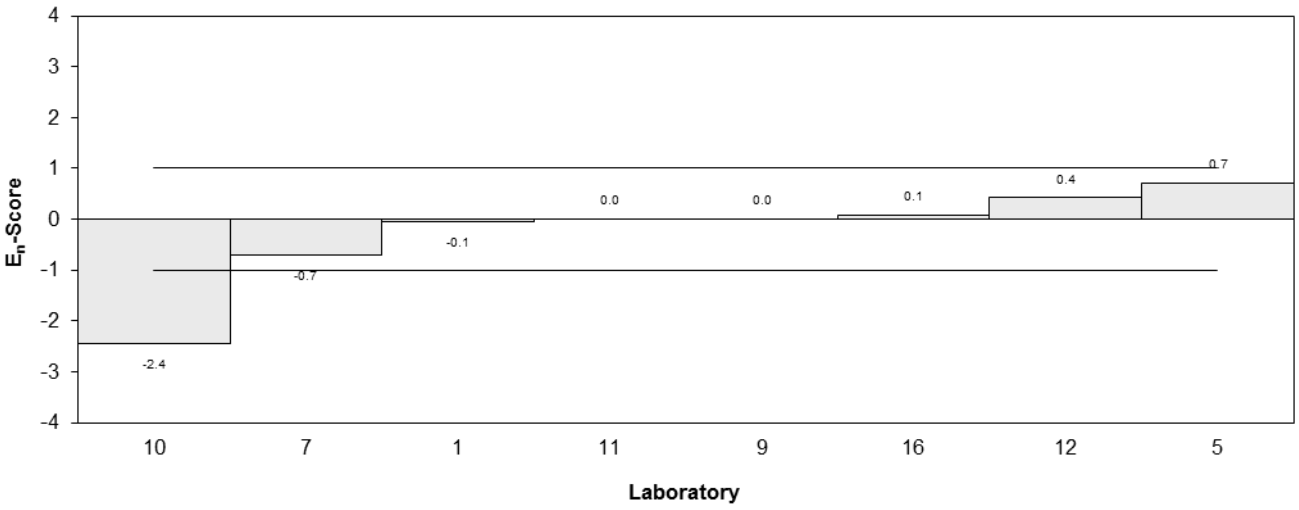

En-Scores: S4 - P
En-Score
4
3
2
1
0
-1
-2
-3
-4
-2.4
-0.7
-0.1
0.0
0.0
0.1
0.4
0.7
10
7
1
11
9
16
12
5
Laboratory

Figure 54

Table 58

Sample Details

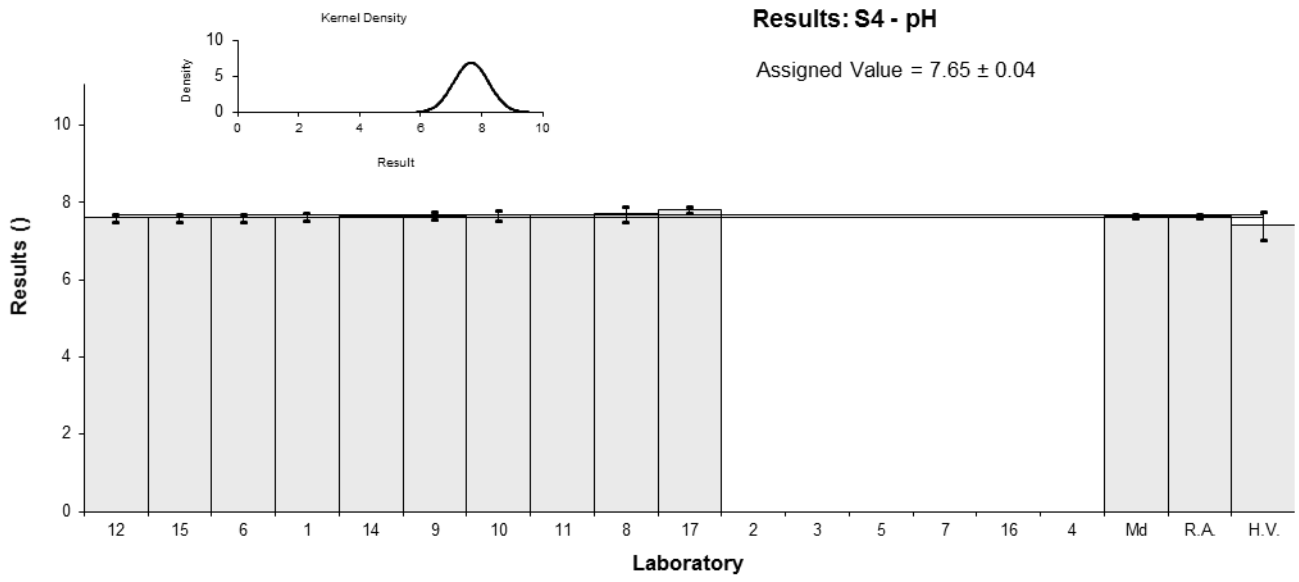
Sample No.	S4
Matrix.	River Water
Analyte.	pH

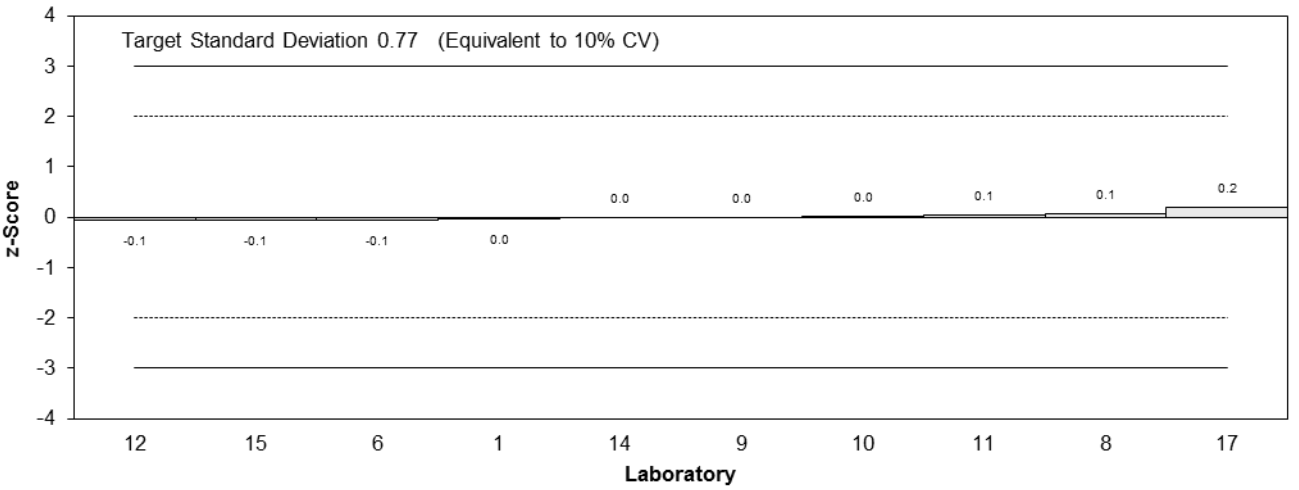
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.63	0.1	-0.03	-0.19
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	7.6	0.1	-0.07	-0.46
7	NR	NR		
8	7.7	0.2	0.07	0.25
9	7.65	0.1	0.00	0.00
10	7.67	0.13	0.03	0.15
11	7.69	NR	0.05	1.00
12	7.6	0.1	-0.07	-0.46
14	7.65	NR	0.00	0.00
15	7.6	0.1	-0.07	-0.46
16	NT	NT		
17	7.8	0.08	0.20	1.68

Statistics

Assigned Value	7.65	0.04
Spike	Not Spiked	
Homogeneity Value	7.40	0.37
Robust Average	7.65	0.04
Median	7.65	0.05
Mean	7.66	
N	10	
Max.	7.8	
Min.	7.6	
Robust SD	0.05	
Robust CV	0.7%	


Kernel Density
Density
Result
Results: S4 - pH
Assigned Value = 7.65 ± 0.04
Results ()
12 15 6 1 14 9 10 11 8 17 2 3 5 7 16 4 Md R.A. H.V.
Laboratory


z-Scores: S4 - pH
Target Standard Deviation 0.77 (Equivalent to 10% CV)
z-Score
-0.1 -0.1 -0.1 0.0 0.0 0.0 0.0 0.1 0.1 0.2
12 15 6 1 14 9 10 11 8 17
Laboratory

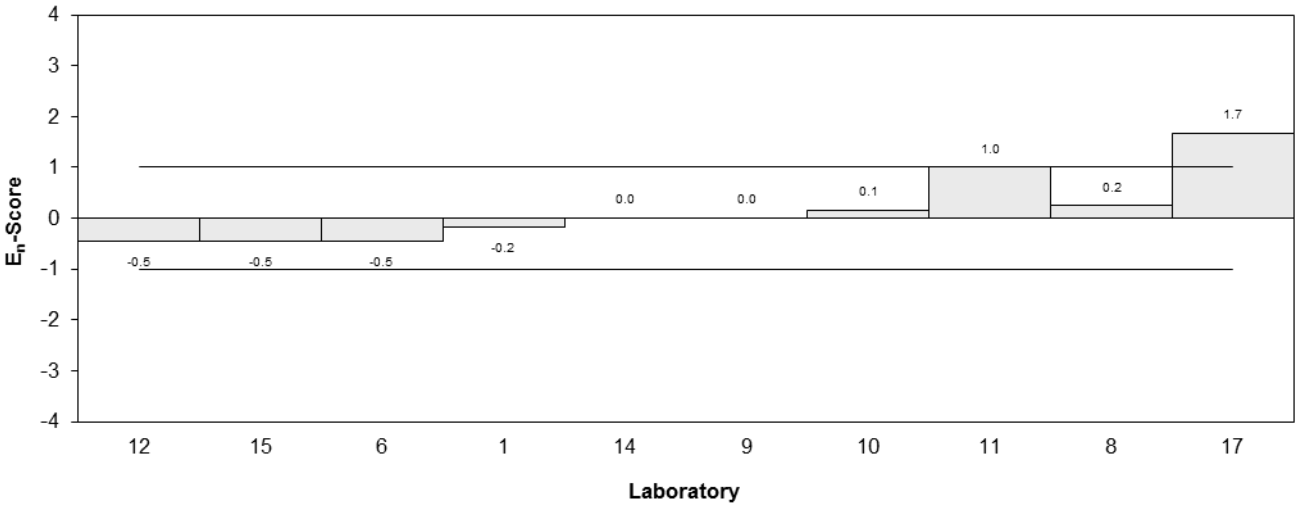

En-Scores: S4 - pH
En-Score
-0.5 -0.5 -0.5 -0.2 0.0 0.0 0.1 1.0 0.2 1.7
12 15 6 1 14 9 10 11 8 17
Laboratory

Figure 55

Table 59

Sample Details

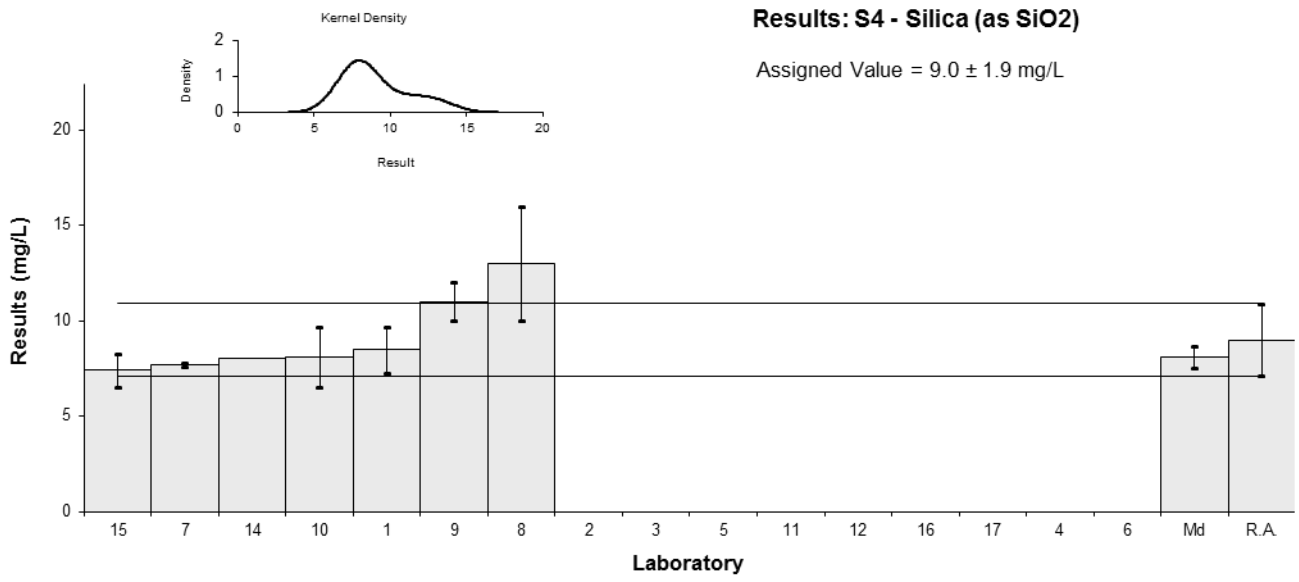
Sample No.	S4
Matrix.	River Water
Analyte.	Silica (as SiO2)
Units	mg/L

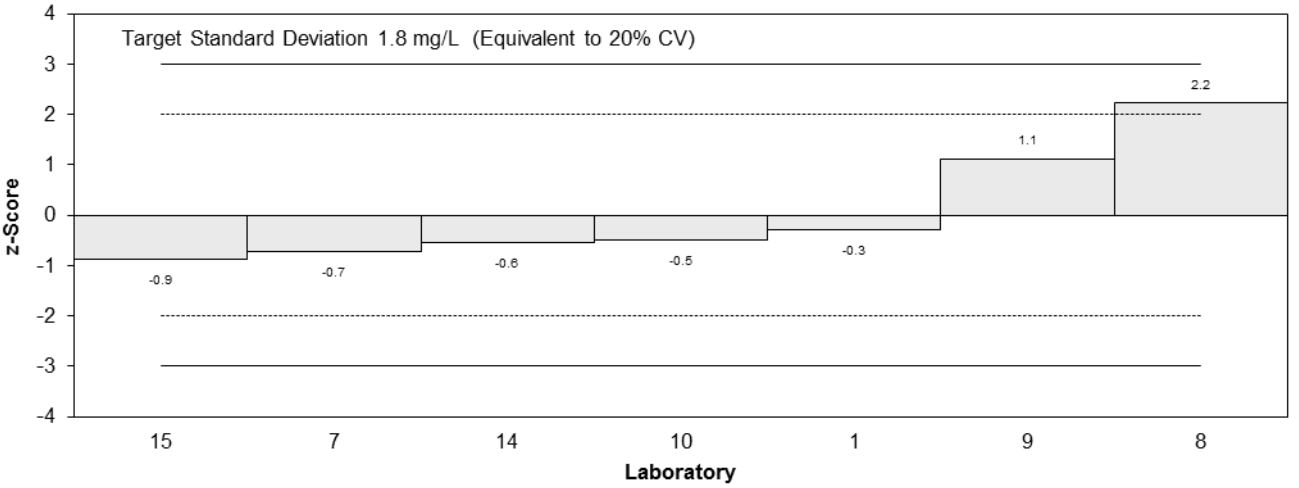
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	8.47	1.2	-0.29	-0.24
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	NT	NT		
7	7.69	0.10	-0.73	-0.69
8	13	3	2.22	1.13
9	11	1	1.11	0.93
10	8.1	1.6	-0.50	-0.36
11	NT	NT		
12	NT	NT		
14	8	NR	-0.56	-0.53
15	7.4	0.89	-0.89	-0.76
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value	9.0	1.9
Spike	Not Spiked	
Robust Average	9.0	1.9
Median	8.1	0.7
Mean	9.1	
N	7	
Max.	13	
Min.	7.4	
Robust SD	2.0	
Robust CV	22%	


Kernel Density
Density
Result
Results: S4 - Silica (as SiO2)
Assigned Value = 9.0 ± 1.9 mg/L
Results (mg/L)
Laboratory
15 7 14 10 1 9 8 2 3 5 11 12 16 17 4 6 Md R.A.


z-Scores: S4 - Silica (as SiO2)
Target Standard Deviation 1.8 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
15 7 14 10 1 9 8
-0.9 -0.7 -0.6 -0.5 -0.3 1.1 2.2

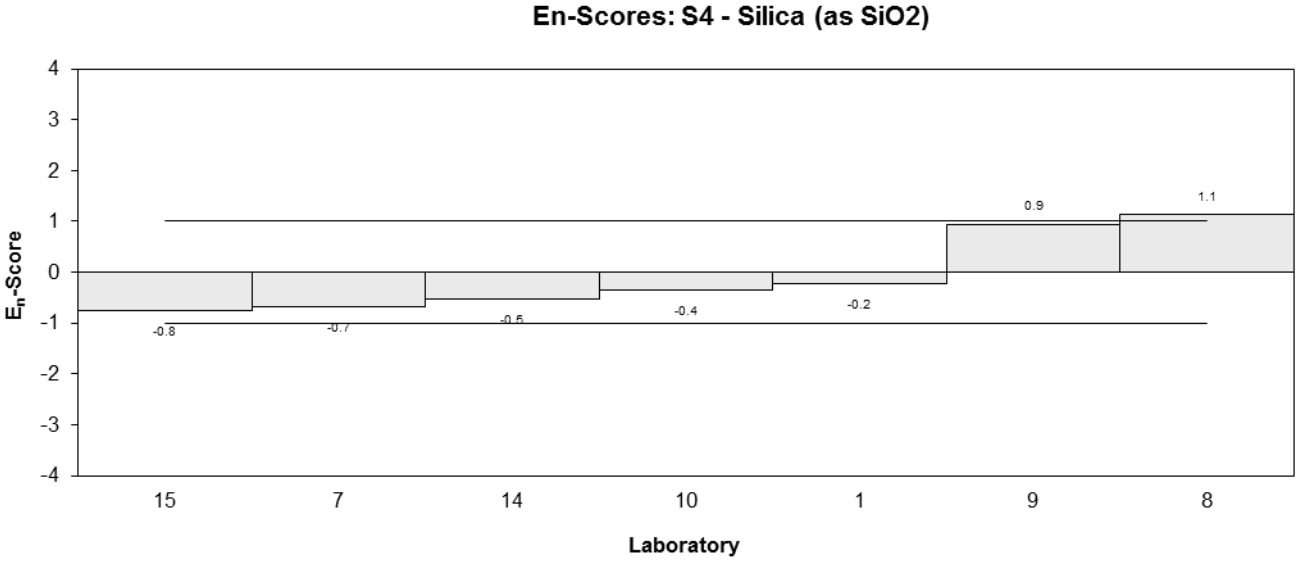

En-Scores: S4 - Silica (as SiO2)
En-Score
Laboratory
15 7 14 10 1 9 8
-0.8 -0.7 -0.5 -0.4 -0.2 0.9 1.1

Figure 56

Table 60

Sample Details

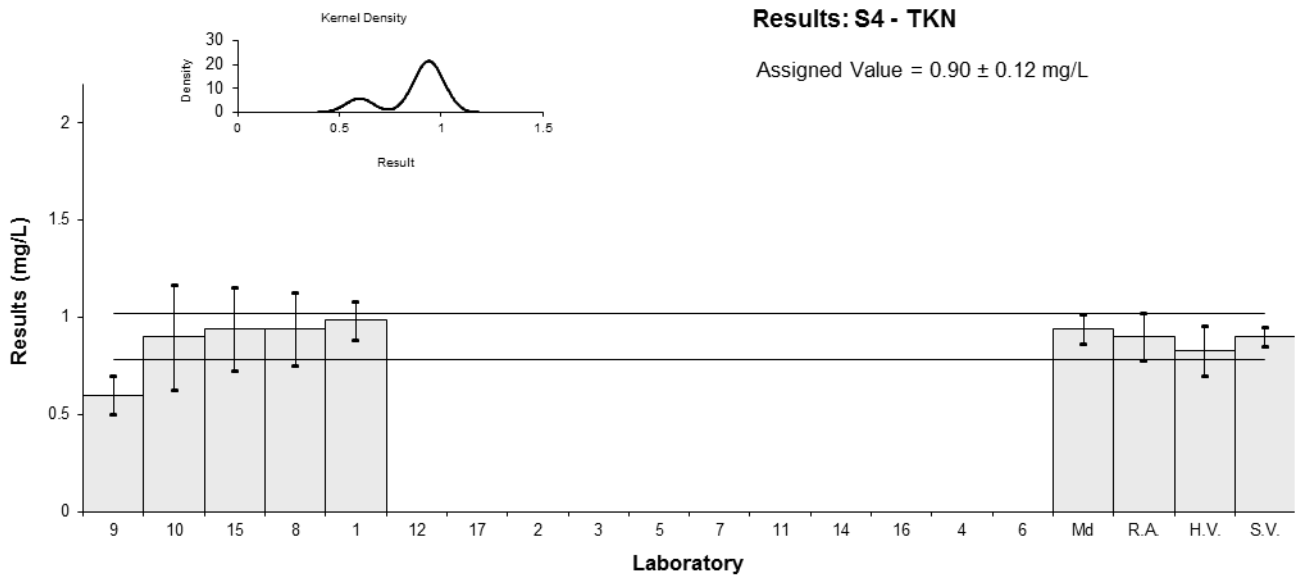
Sample No.	S4
Matrix.	River Water
Analyte.	TKN
Units	mg/L

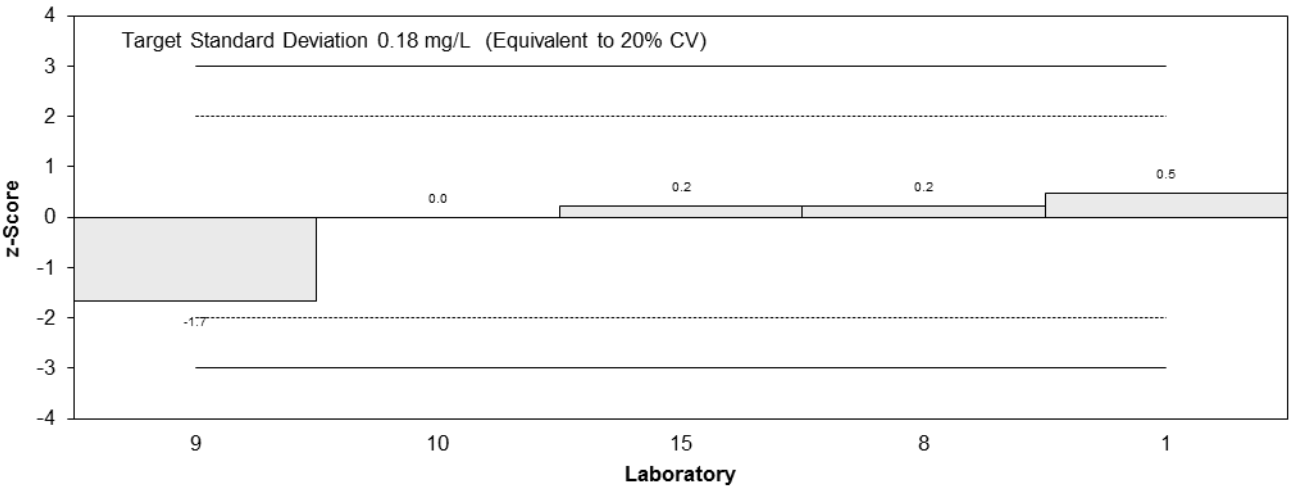
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.984	0.1	0.47	0.54
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	NT	NT		
7	NR	NR		
8	0.94	0.19	0.22	0.18
9	0.6	0.1	-1.67	-1.92
10	0.9	0.27	0	0
11	NT	NT		
12	NR	NR		
14	NT	NT		
15	0.94	0.216	0.22	0.16
16	NT	NT		
17	NR	NR		

Statistics

Assigned Value	0.90	0.12
Spike	0.90	0.05
Homogeneity Value	0.83	0.13
Robust Average	0.90	0.12
Median	0.94	0.07
Mean	0.87	
N	5	
Max.	0.984	
Min.	0.6	
Robust SD	0.1	
Robust CV	11%	


Kernel Density
Density
Result
Results: S4 - TKN
Assigned Value = 0.90 ± 0.12 mg/L
Results (mg/L)
Laboratory
9
10
15
8
1
12
17
2
3
5
7
11
14
16
4
6
Md
R.A.
H.V.
S.V.


z-Scores: S4 - TKN
Target Standard Deviation 0.18 mg/L (Equivalent to 20% CV)
z-Score
Laboratory
0.0
0.2
0.2
0.5
-1.7
9
10
15
8
1

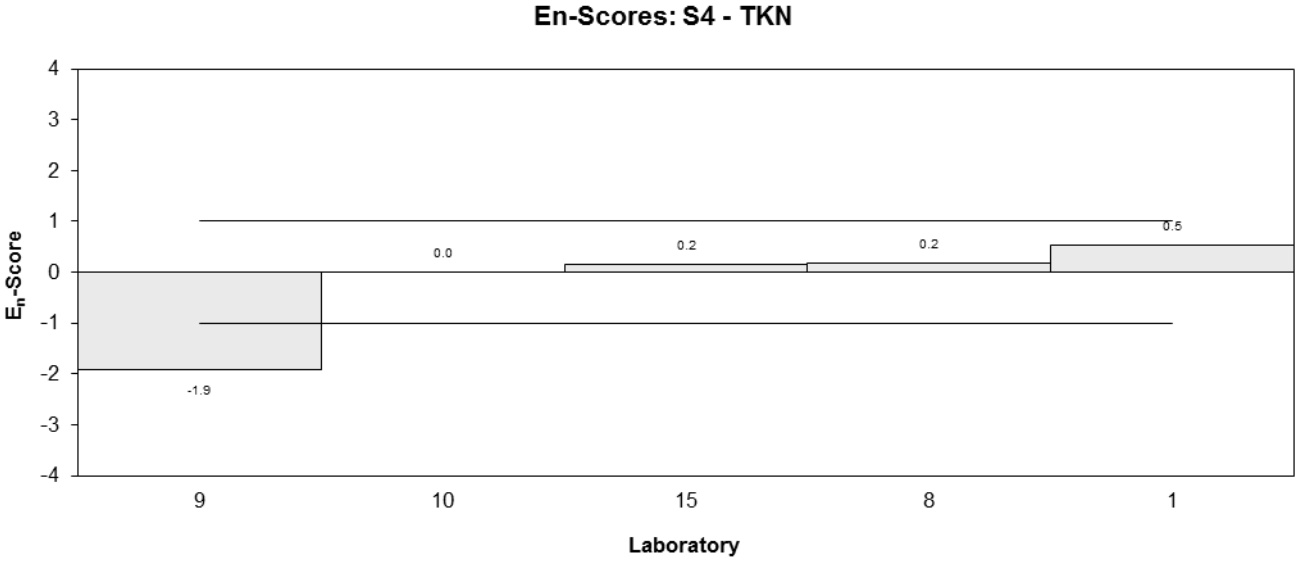

En-Scores: S4 - TKN
En-Score
Laboratory
0.0
0.2
0.2
0.5
-1.9
9
10
15
8
1

Figure 57

Table 61

Sample Details

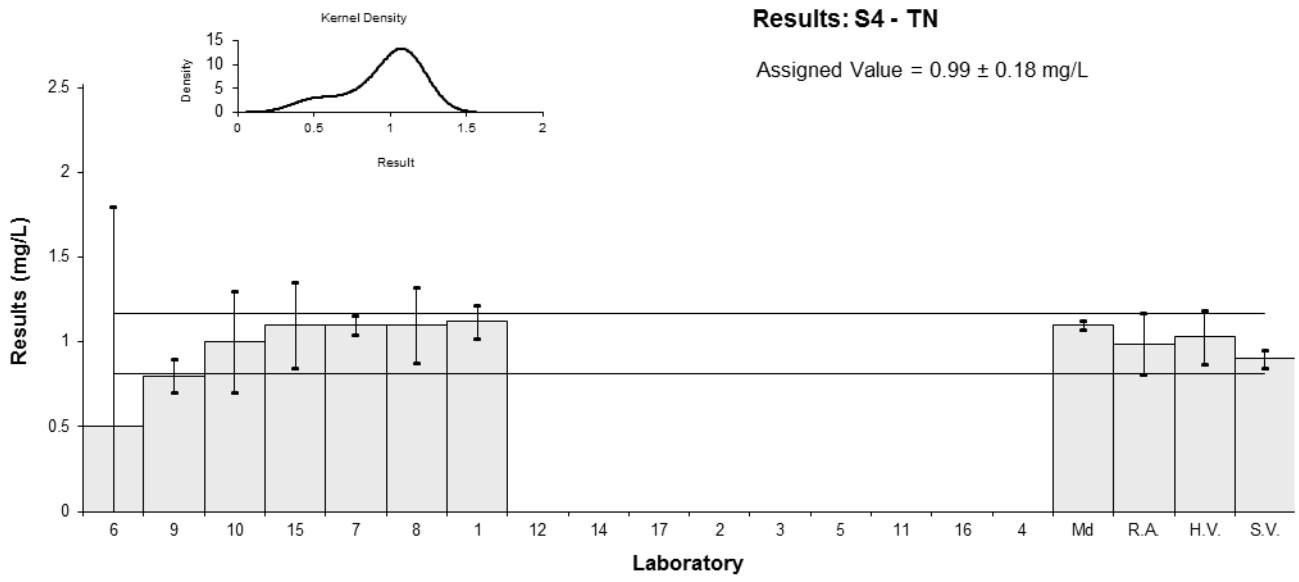
Sample No.	S4
Matrix.	River Water
Analyte.	TN
Units	mg/L

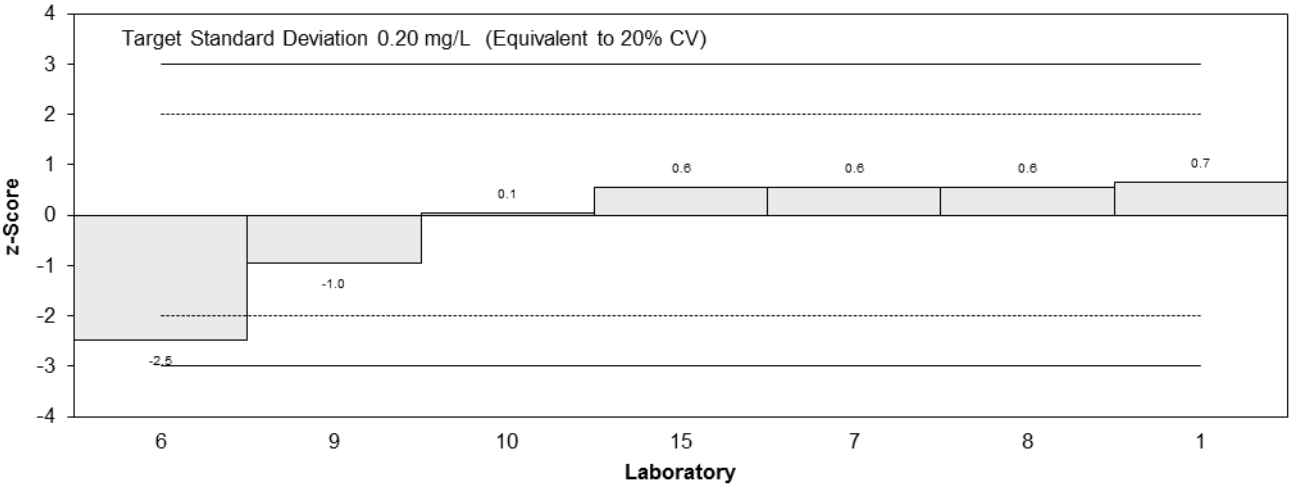
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.12	0.1	0.66	0.63
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	0.5	1.3	-2.47	-0.37
7	1.1	0.06	0.56	0.58
8	1.1	0.22	0.56	0.39
9	0.8	0.1	-0.96	-0.92
10	1.0	0.3	0.05	0.03
11	NT	NT		
12	NR	NR		
14	NR	NR		
15	1.1	0.253	0.56	0.35
16	NT	NT		
17	NR	NR		

Statistics

Assigned Value	0.99	0.18
Spike	0.90	0.05
Homogeneity Value	1.03	0.16
Robust Average	0.99	0.18
Median	1.10	0.03
Mean	0.96	
N	7	
Max.	1.12	
Min.	0.5	
Robust SD	0.19	
Robust CV	19%	


Kernel Density
Density
Result
Results: S4 - TN
Assigned Value = 0.99 ± 0.18 mg/L
Results (mg/L)
Laboratory
6 9 10 15 7 8 1 12 14 17 2 3 5 11 16 4 Md R.A. H.V. S.V.


z-Scores: S4 - TN
Target Standard Deviation 0.20 mg/L (Equivalent to 20% CV)
z-Score
-2.5
-1.0
0.1
0.6
0.6
0.6
0.7
Laboratory
6 9 10 15 7 8 1

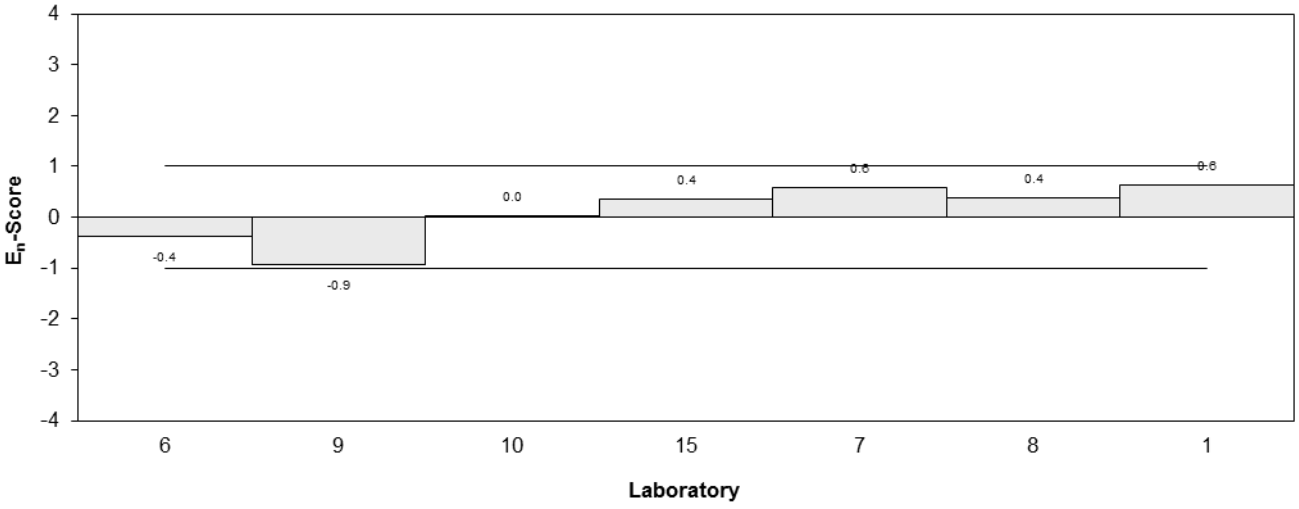

En-Scores: S4 - TN
En-Score
-0.4
-0.9
0.0
0.4
0.6
0.4
0.6
Laboratory
6 9 10 15 7 8 1

Figure 58

Table 62

Sample Details

Sample No.	S4
Matrix.	River Water
Analyte.	TOC
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	10.1	1
2	NR	NR
3	NR	NR
4	8.2	0.8
5	NR	NR
6	NT	NT
7	NR	NR
8	9.5	2
9	NT	NT
10	NT	NT
11	NT	NT
12	NR	NR
14	NT	NT
15	8.7	1.31
16	NT	NT
17	NR	NR

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	6.57	0.99
Robust Average	9.1	1.2
Median	9.1	1.5
Mean	9.1	
N	4	
Max.	10.1	
Min.	8.2	
Robust SD	0.95	
Robust CV	10%	

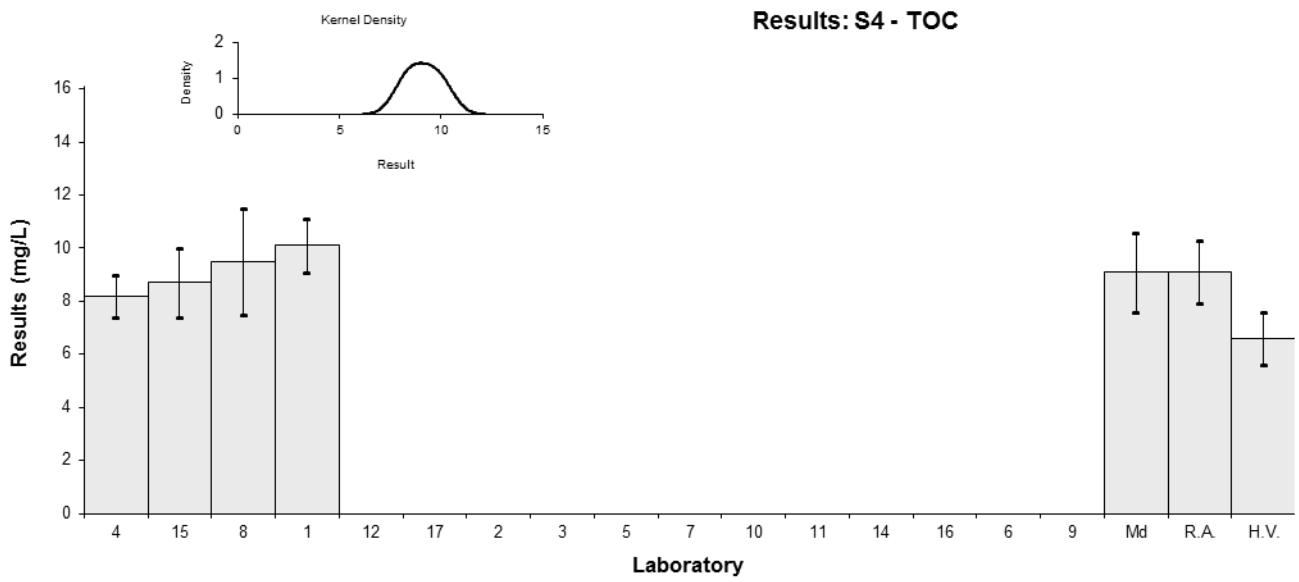

Results: S4 - TOC
Kernel Density
Density
Result
Results (mg/L)
Laboratory
4
15
8
1
12
17
2
3
5
7
10
11
14
16
6
9
Md
R.A.
H.V.

Figure 59

Table 63

Sample Details

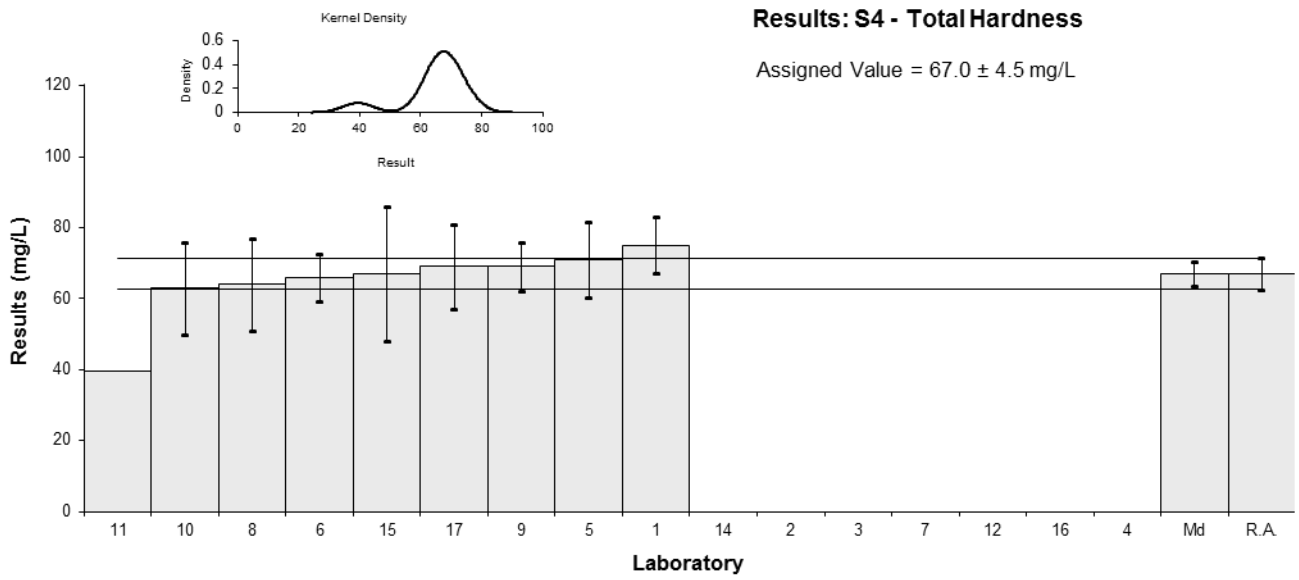
Sample No.	S4
Matrix.	River Water
Analyte.	Total Hardness
Units	mg/L

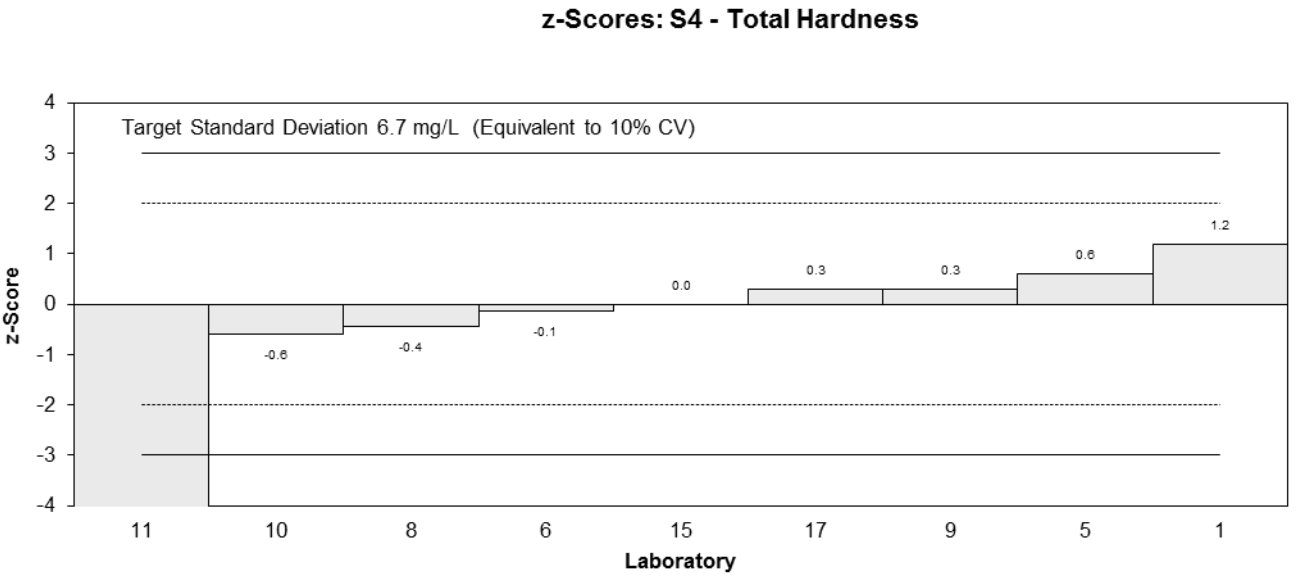
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	75	8	1.19	0.87
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	71.0	10.6	0.60	0.35
6	66	6.6	-0.15	-0.13
7	NR	NR		
8	64	13	-0.45	-0.22
9	69	7	0.30	0.24
10	63	13	-0.60	-0.29
11	39.5	NR	-4.10	-6.11
12	NT	NT		
14	NR	NR		
15	67	19	0.00	0.00
16	NT	NT		
17	69	11.9	0.30	0.16

Statistics

Assigned Value	67.0	4.5
Spike	Not Spiked	
Robust Average	67.0	4.5
Median	67.0	3.4
Mean	64.8	
N	9	
Max.	75	
Min.	39.5	
Robust SD	5.4	
Robust CV	8.1%	


Results: S4 - Total Hardness
Assigned Value = 67.0 ± 4.5 mg/L
Kernel Density
Density
Result
Results (mg/L)
Laboratory
11 10 8 6 15 17 9 5 1 14 2 3 7 12 16 4 Md R.A.


z-Scores: S4 - Total Hardness
Target Standard Deviation 6.7 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 10 8 6 15 17 9 5 1
-0.6 -0.4 -0.1 0.0 0.3 0.3 0.6 1.2

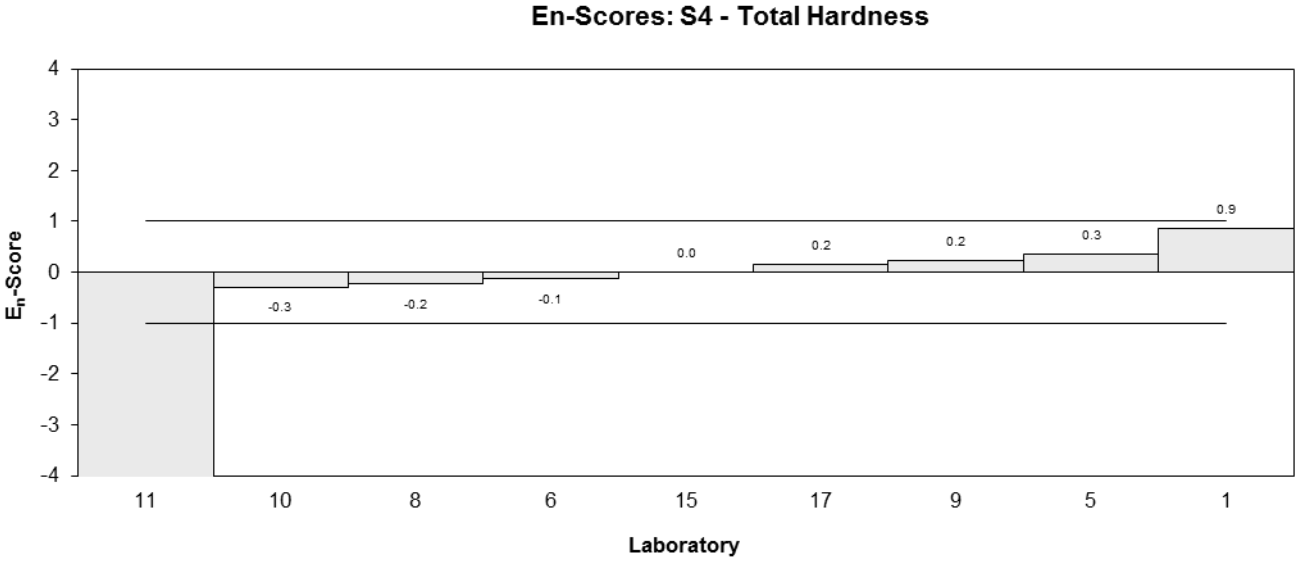

En-Scores: S4 - Total Hardness
En-Score
Laboratory
11 10 8 6 15 17 9 5 1
-0.3 -0.2 -0.1 0.0 0.2 0.2 0.3 0.9

Figure 60

Table 64

Sample Details

Sample No.	S4
Matrix.	River Water
Analyte.	TS
Units	mg/L

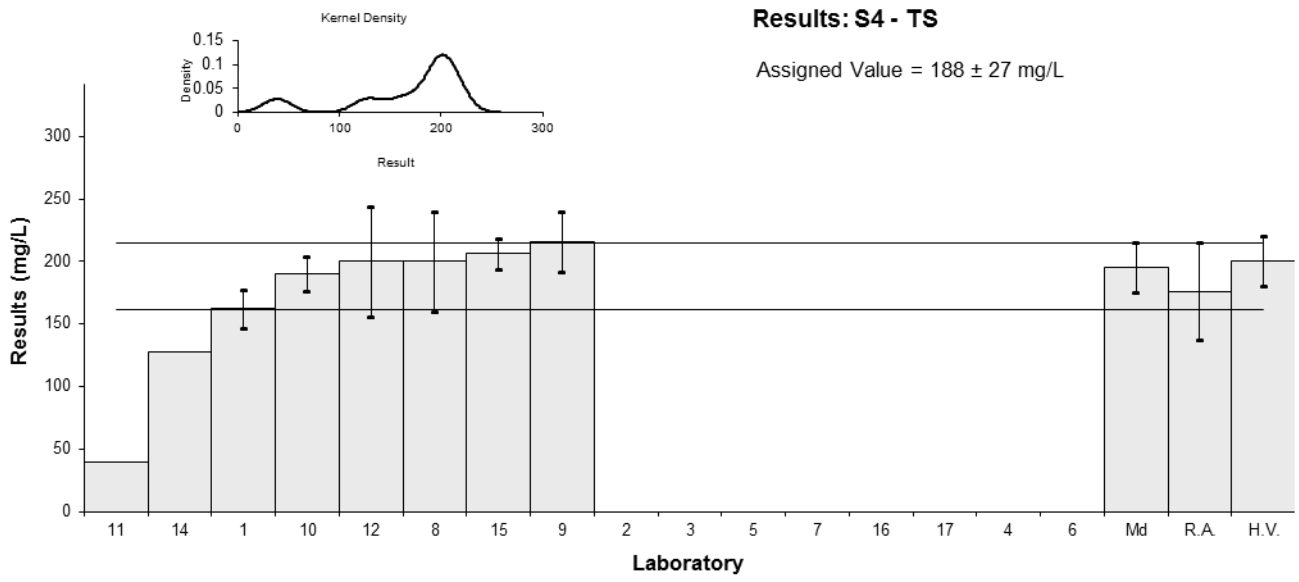
Participant Results

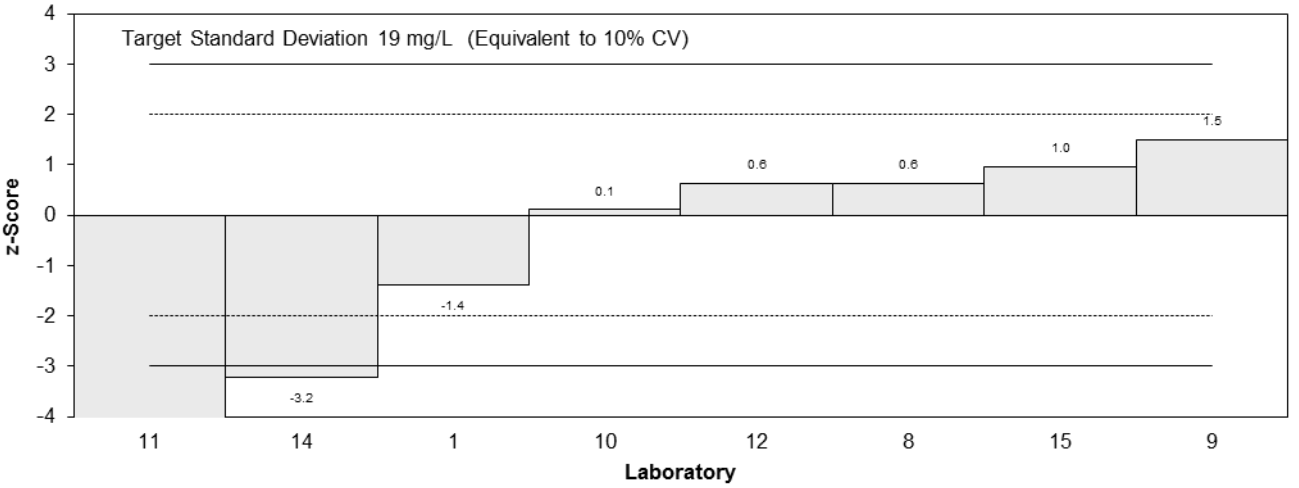
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	162	15	-1.38	-0.84
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	NT	NT		
7	NR	NR		
8	200	40	0.64	0.25
9	216	24	1.49	0.78
10	190	14	0.11	0.07
11	39	NR	-7.93	-5.52
12	200	44	0.64	0.23
14	127.6	NR	-3.21	-2.24
15	206	12.4	0.96	0.61
16	NT	NT		
17	NT	NT		

Statistics

Assigned Value*	188	27
Spike	Not Spiked	
Homogeneity Value	200	20
Robust Average	176	39
Median	195	20
Mean	168	
N	8	
Max.	216	
Min.	39	
Robust SD	29	
Robust CV	16%	

* Robust Average excluding Laboratory 11.


Kernel Density
Density
Result
Results: S4 - TS
Assigned Value = 188 ± 27 mg/L
Results (mg/L)
Laboratory
11 14 1 10 12 8 15 9 2 3 5 7 16 17 4 6 Md R.A. H.V.


z-Scores: S4 - TS
Target Standard Deviation 19 mg/L (Equivalent to 10% CV)
z-Score
Laboratory
11 14 1 10 12 8 15 9
-3.2
-1.4
0.1
0.6
0.6
1.0
1.5

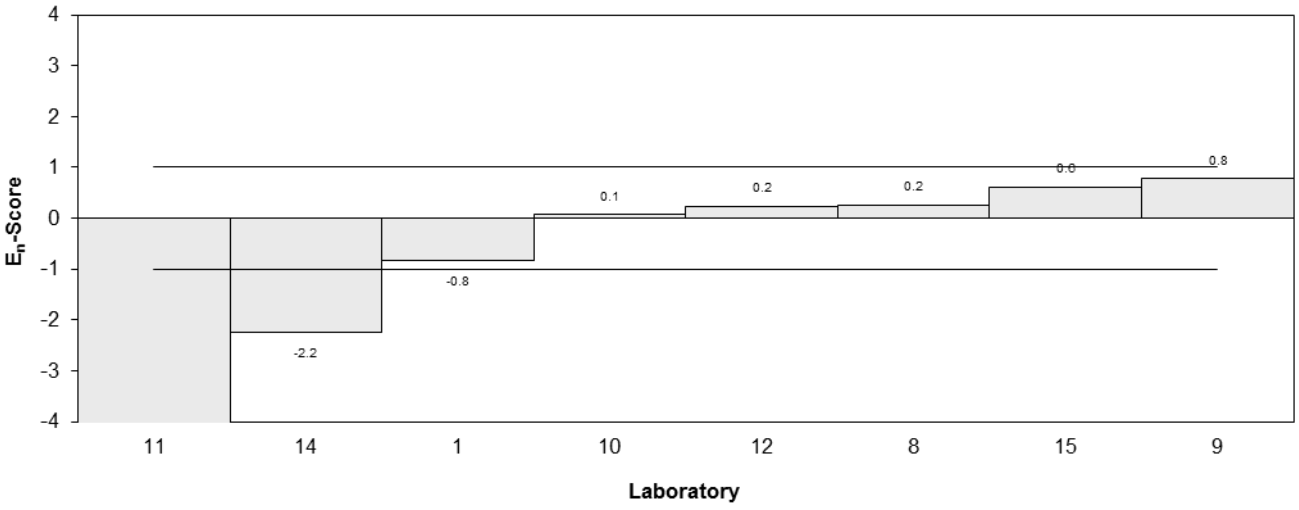

En-Scores: S4 - TS
En-Score
Laboratory
11 14 1 10 12 8 15 9
-2.2
-0.8
0.1
0.2
0.2
0.6
0.8

Figure 61

Table 65

Sample Details

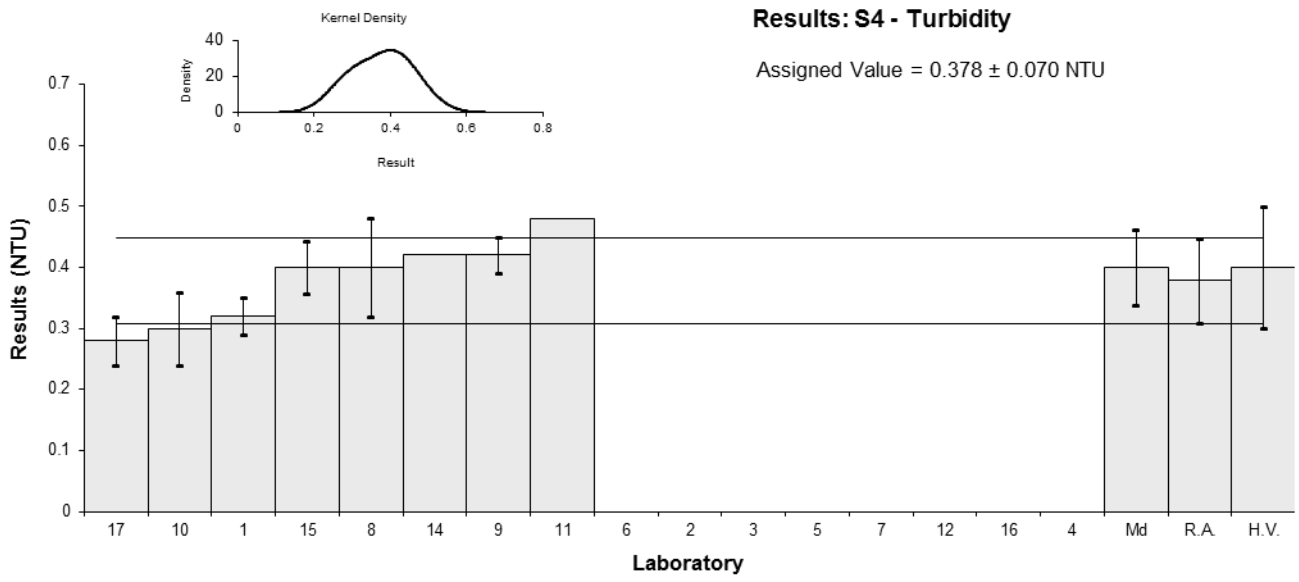
Sample No.	S4
Matrix.	River Water
Analyte.	Turbidity
Units	NTU

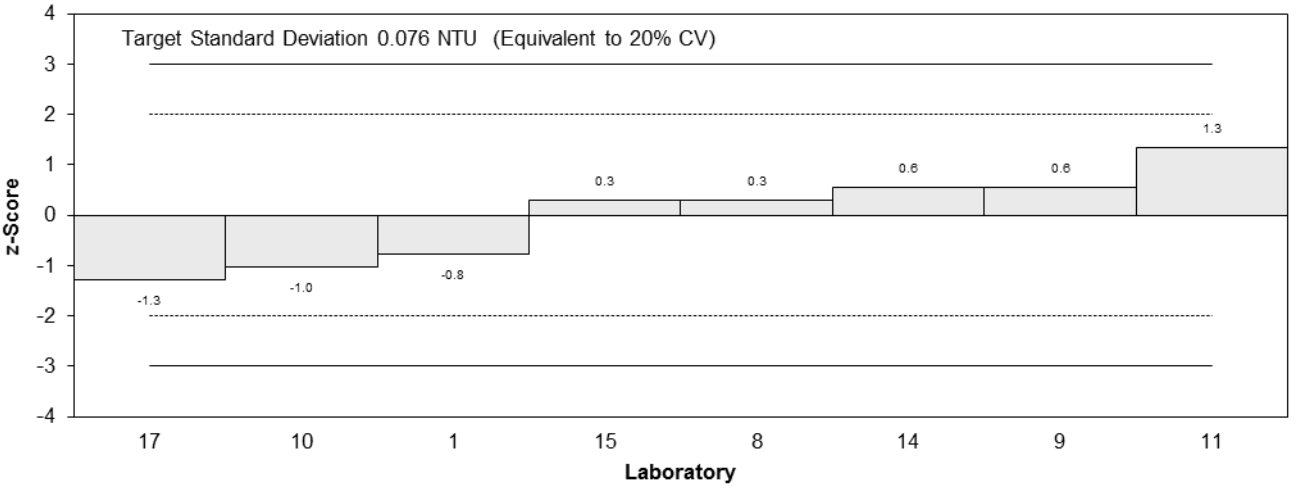
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.32	0.03	-0.77	-0.76
2	NR	NR		
3	NR	NR		
4	NT	NT		
5	NR	NR		
6	<1	1		
7	NR	NR		
8	0.4	0.08	0.29	0.21
9	0.42	0.03	0.56	0.55
10	0.3	0.06	-1.03	-0.85
11	0.48	NR	1.35	1.46
12	NT	NT		
14	0.42	NR	0.56	0.60
15	0.4	0.044	0.29	0.27
16	NT	NT		
17	0.28	0.04	-1.30	-1.22

Statistics

Assigned Value	0.378	0.070
Spike	Not Spiked	
Homogeneity Value	0.40	0.10
Robust Average	0.378	0.070
Median	0.400	0.062
Mean	0.378	
N	8	
Max.	0.48	
Min.	0.28	
Robust SD	0.079	
Robust CV	21%	


Kernel Density
Density
Result
Results: S4 - Turbidity
Assigned Value = 0.378 ± 0.070 NTU
Results (NTU)
Laboratory
17 10 1 15 8 14 9 11 6 2 3 5 7 12 16 4 Md R.A. H.V.


z-Scores: S4 - Turbidity
Target Standard Deviation 0.076 NTU (Equivalent to 20% CV)
z-Score
Laboratory
17 10 1 15 8 14 9 11
-1.3
-1.0
-0.8
0.3
0.3
0.6
0.6
1.3

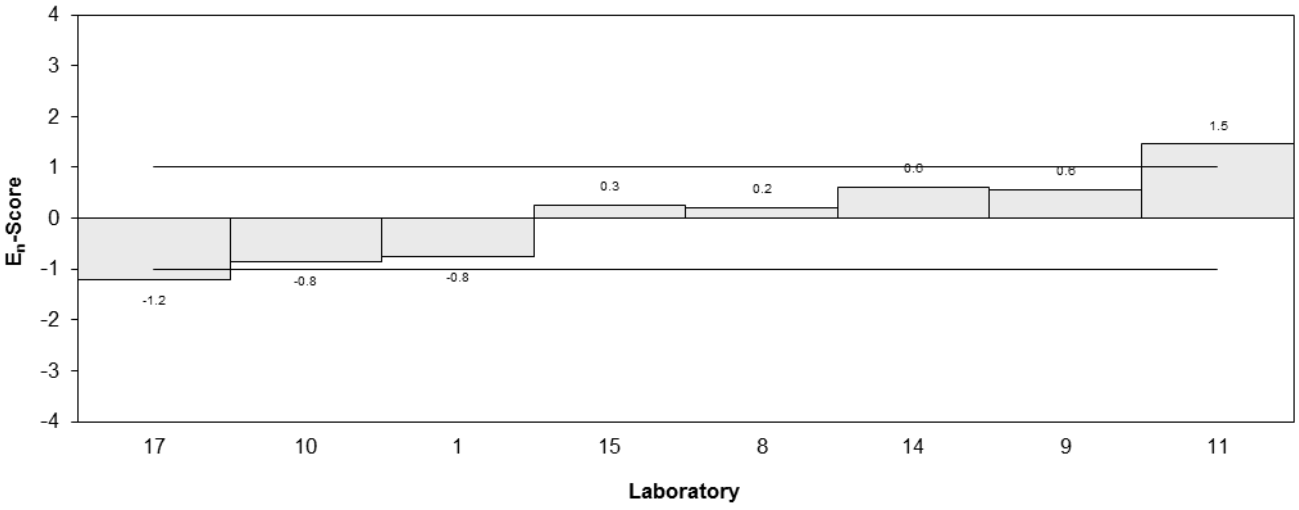

En-Scores: S4 - Turbidity
En-Score
Laboratory
17 10 1 15 8 14 9 11
-1.2
-0.8
-0.8
0.3
0.2
0.6
0.6
1.5

Figure 62

7 DISCUSSION OF RESULTS

7.1 Assigned Value

Sample S1 was 100 mL of filtered, river water. Participants were asked to report for this sample results for dissolved: Al, Ag, As, Be, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Zn. The sample was chilled before dispatch.

Sample S2 was 100 mL of unfiltered, river water. Participants were asked to report for this sample results for total: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, U and Zn. The sample was chilled before dispatch.

Sample S3 was 200 mL of frozen, filtered and autoclaved river water collected from Brown's Waterhole Turramurra on which analyses of ammonia-N (NH_3-N), bromide (Br^-), chloride (Cl^-), dissolved organic carbon (DOC as dNPOC), fluoride (F^-), orthophosphate-P (FRP), nitrate-N (NO_3-N), total dissolved nitrogen (TDN), total dissolved phosphorus (TDP) and sulphate (SO_4^{2-}) were to be performed.

Sample S4 consisted of two containers labelled A and B. Participants were instructed not to composite the contents of the two containers prior to analyses. The container labelled S4A contained 700 mL of unfiltered, unpreserved chilled river water to be analysed for total: B, Ca, K, Mg, Na and P and for alkalinity to pH 4.5 (as $CaCO_3$), apparent colour (units Pt/Co), pH (at 25ºC), silica (as SiO_2), total hardness (as $CaCO_3$), total solids (dried at 103-105ºC) and turbidity. The container labelled S4B consisted of 200 mL of frozen unfiltered and autoclaved river water to be analysed for total Kjeldahl nitrogen (TKN), total nitrogen (TN) and total organic carbon (TOC as NPOC). Sample S4A was chilled before dispatch while Sample S4B was frozen.

Assigned Value for the 57 tests were the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'. Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value.[8] No assigned value was set for DOC in S3 and B, COD and TOC in S4 because too few results were reported. Although only four participants reported results for TKN in S4 an assigned value was still set for this analyte because the reported results were in very good agreement with each other and with the spike value. Appendix 3 sets out the calculation of the robust average and assigned value for As in Sample S1 and its associated uncertainty.

Spike Values for each test of interest includes both the incurred value and the fortified value except for orthophosphate-P (FRP).

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

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 571 numerical results, 495 (87%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025. [10] The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, 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.[11 – 17]

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 62). In this study in some cases, the reported expanded measurement uncertainty has been over (e.g. Lab 10 for Al, Be in S1) or under-estimated (e.g. Lab 6 for Al, Cu in S2). As a simple rule of thumb, when the uncertainty estimate is smaller than the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be viewed as suspect.

For estimating the laboratory precision one participant used only the data from duplicate analyses. This gives an estimate of within-run precision (repeatability), the intermediate precision (reproducibility) should be considered too.

Double counting the precision uncertainty components and overestimation of the laboratory or method bias are the most common errors seen in the laboratories' estimated uncertainty budgets. According to General Accreditation Guidance, Estimating and reporting measurement uncertainty of chemical test results[14] and to NORDTEST TR 537 [12] the most common experimental data used for estimating the precision component for the measurement uncertainty calculation in the top down approach are from:

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

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

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[12, 14] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Some laboratories estimated uncertainties for measurement results are larger than the reported results themselves. Measurement uncertainty is the range estimated by laboratories that contain the true value. The reported result should be within the estimated range.

Two laboratories attached estimates of the expanded measurement uncertainty to results reported as less than their limit of detection. An estimate of uncertainty expressed as a numerical value cannot be attached to a result expressed as a range.[11]

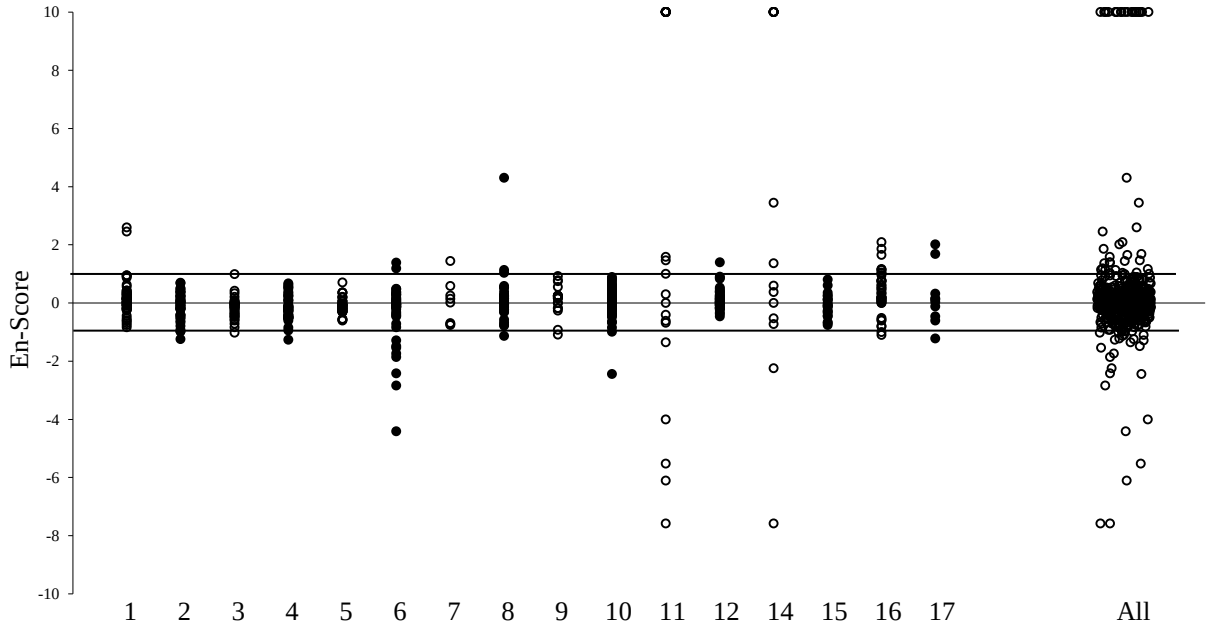
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 18.44 ± 3.4 mg/L, it is better to report 18.4 ± 3.4 mg/L or instead of 0.0023 ± 0.00048 mg/L, it is better to report 0.0023 ± 0.0005 mg/L.[11]

7.3 E_n-score

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

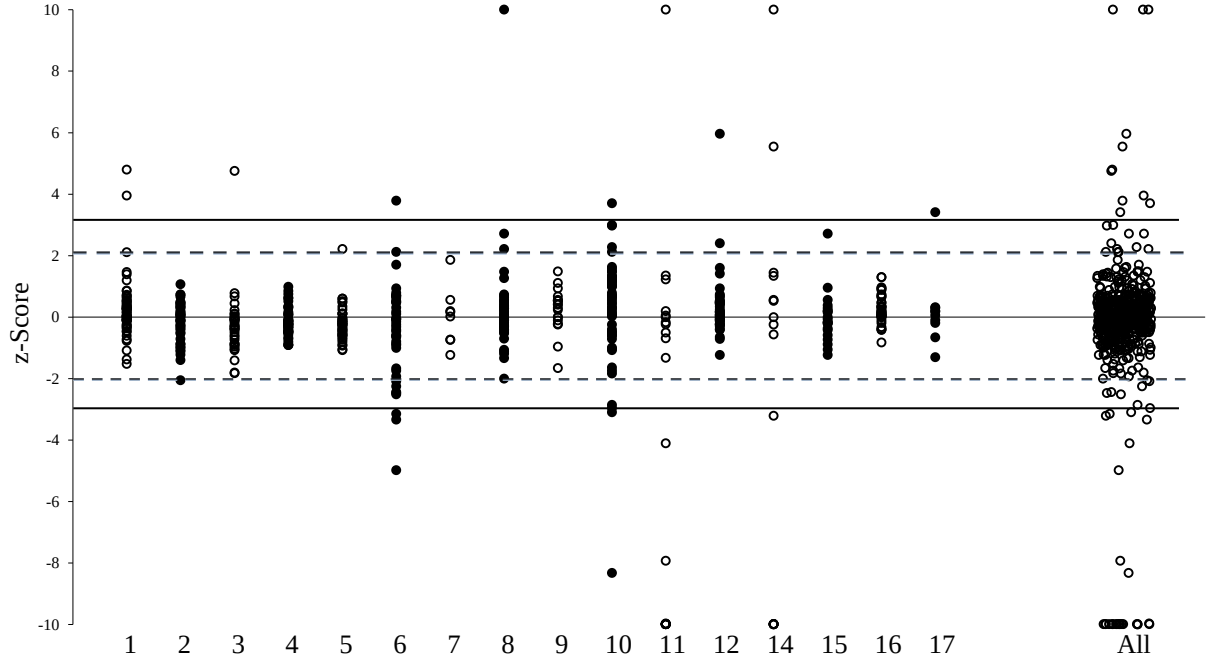
The dispersal of participants' E_n-scores is graphically presented in Figure 63. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 552 results for which E_n-scores were calculated, 485 (88%) returned a satisfactory score of $|E_n| \leq 1$ 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 63 E_n-Score Dispersal by Laboratory



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

Figure 64 z-Score Dispersal by Laboratory

7.4 z-Score

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

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 10%, 15% and 20% PCV were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation as a realistic set value, enables z-scores to be used as a fixed reference value point for assessment of laboratory performance, independent of group performance.

The between laboratories coefficient of variation predicted by the Thompson equation[9] and the between laboratories coefficient of variation resulted in this study are presented for comparison in Table 66.

The dispersal of participants' z-scores is presented in Figure 64 (by laboratory code) and in Figure 65 (by test). Of 552 results for which z-scores were calculated, 496 (90%) returned a satisfactory score of $|z| \leq 2$ and 19 (3%) were questionable with a score of $2 < |z| < 3$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

Laboratories **4, 7, 9** and **16** returned satisfactory z-scores for all inorganic analytes reported.

Table 66 Between Laboratories CV of this study, Thompson CV and Set Target CV

Sample	Analyte	Assigned Value	Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Al	66.8 µg/L	7.9%	22%	10%
S1	Ag	1.49 µg/L	22%	22%	20%
S1	As	1.21 µg/L	13%	22%	10%
S1	Be	1.46 µg/L	8.9%	22%	10%
S1	Cd	1.07 µg/L	6.5%	22%	10%
S1	Cr	1.65 µg/L	15%	22%	10%
S1	Cu	5.94 µg/L	7%	22%	10%
S1	Hg	0.21 µg/L	5.6%	22%	10%
S1	Mn	2.58 µg/L	9.3%	22%	10%
S1	Ni	1.87 µg/L	5.3%	22%	10%
S1	Pb	1.45 µg/L	6.9%	22%	10%
S1	Sb	2.8 µg/L	8.6%	22%	10%
S1	Se	2.13 µg/L	6.5%	22%	10%
S1	Sn	1.77 µg/L	5.6%	22%	10%
S1	Tl	4.85 µg/L	3.5%	22%	10%
S1	V	2.67 µg/L	7.5%	22%	10%
S1	Zn	10.0 µg/L	9%	22%	10%
S2	Al	305 µg/L	13%	19%	10%
S2	As	28.5 µg/L	10%	22%	10%
S2	Ba	80.5 µg/L	4%	22%	10%
S2	Cd	14.4 µg/L	6%	22%	10%
S2	Co	35.4 µg/L	2.7%	22%	10%
S2	Cr	39.9 µg/L	4%	22%	10%
S2	Cu	48.4 µg/L	7.6%	22%	10%
S2	Fe	618 µg/L	4.9%	18%	10%
S2	Mn	66.7 µg/L	5.7%	22%	10%
S2	Mo	35.5 µg/L	7.1%	22%	10%
S2	Ni	28.3 µg/L	4.3%	22%	10%
S2	Pb	34.8 µg/L	4.3%	22%	10%
S2	Sb	17.7 µg/L	7.9%	22%	10%

Table 66 Between Laboratories CV of this study, Thompson CV and Set Target CV (continued)

Sample	Analyte	Assigned Value	Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as CV)
S2	Se	31.9 µg/L	12%	22%	10%
S2	Sn	28.1 µg/L	3.6%	22%	10%
S2	U	16.2 µg/L	5.6%	22%	10%
S2	Zn	51.6 µg/L	18%	22%	10%
S3	Ammonia-N	0.098 mg/L	13%	22%	10%
S3	Bromide	0.213 mg/L	19%	20%	15%
S3	Chloride	53.7 mg/L	4.7%	9%	10%
S3	Dissolved Organic Carbon	Not set	14%	NA	Not set
S3	Fluoride	0.38 mg/L	9.2%	19%	10%
S3	Orthophosphate-P (FRP)	0.051 mg/L	25%	22%	20%
S3	Nitrate-N	0.183 mg/L	6.8%	21%	10%
S3	Sulphate	16.4 mg/L	4.2%	11%	10%
S3	Total Dissolved Nitrogen	0.529 mg/L	11%	18%	10%
S3	Total Dissolved Phosphorus	0.057 mg/L	16%	22%	10%
S4	Alkalinity to pH 4.5 (as CaCO3)	52.2 mg/L	5.6%	9%	10%
S4	B	Not set	183%	NA	Not set
S4	Ca	18.2 mg/L	4.4%	10%	10%
S4	Chemical Oxygen Demand	Not set	6.4%	NA	Not set
S4	Colour, apparent	33.3 (Pt-Co units)	9.9%	9%	10%
S4	K	3.75 mg/L	9.9%	13%	10%
S4	Mg	5.76 mg/L	4.9%	12%	10%
S4	Na	35.8 mg/L	7.8%	9%	10%
S4	P	0.09 mg/L	16%	22%	15%
S4	pH (at 25ºC)	7.65	0.7%	12%	10%
S4	Silica (as SiO2)	9 mg/L	22%	11%	20%
S4	Total Hardness (as CaCO3)	67 mg/L	8.1%	8%	10%
S4	Total Solids at 103-105°C	188 mg/L	16%	7%	10%
S4	Turbidity	0.378 NTU	21%	19%	20%
S4	Total Kjeldahl Nitrogen	0.90 mg/L	11%	16%	20%
S4	Total Nitrogen	0.99 mg/L	19%	16%	20%
S4	Total Organic Carbon	Not set	10%	NA	Not set

* NA=Not Available

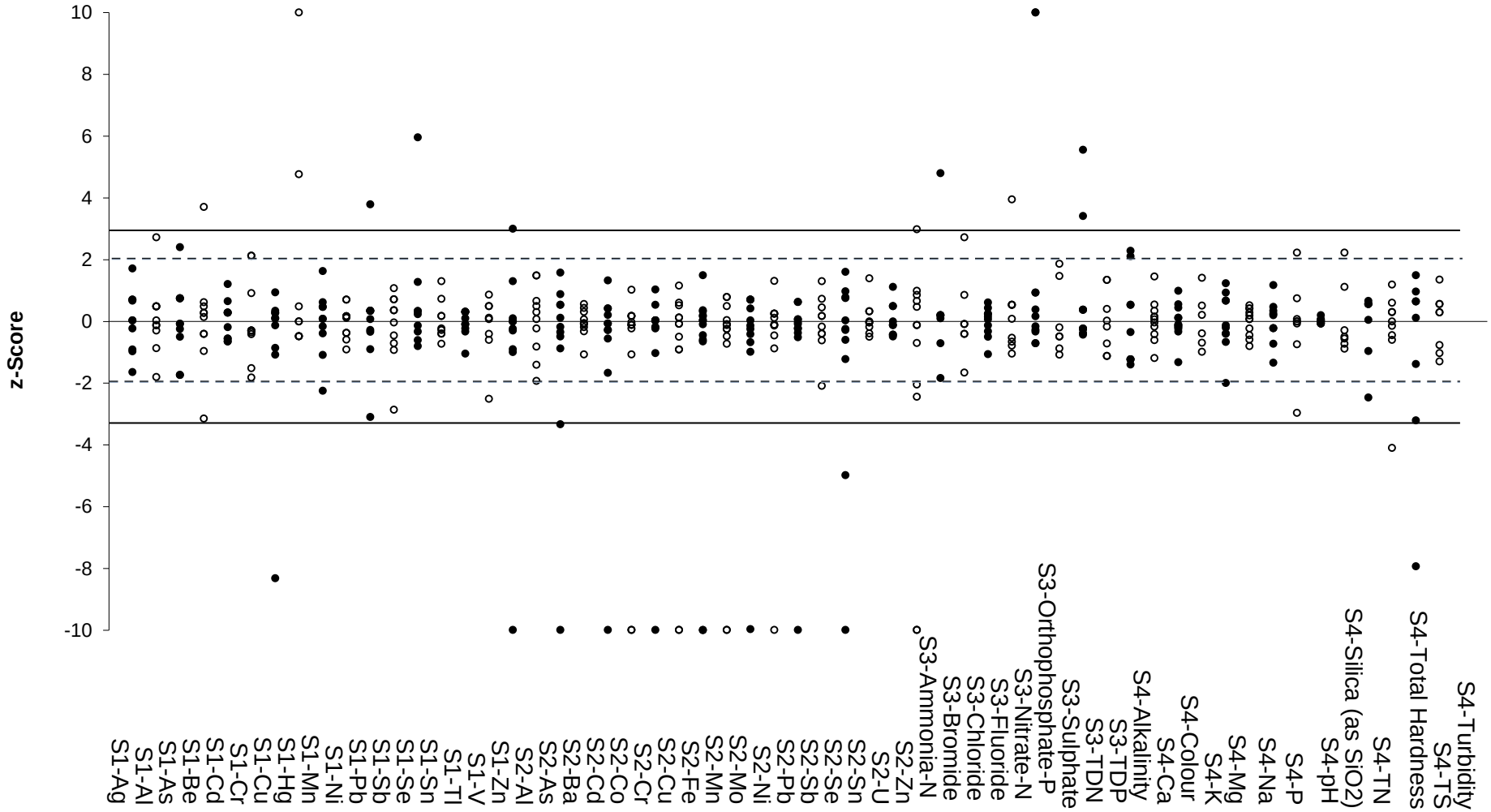


Figure 65 z-Score Dispersal by Test

Table 67 Summary of Participants' Results and Performance for S1 and S2

Lab Code	S1-Al ug/L	S2-Al ug/L	S1-Ag ug/L	S1-As ug/L	S2-As ug/L	S2-Ba ug/L	S1-Be ug/L	S1-Cd ug/L	S2-Cd ug/L	S2-Co ug/L	S1-Cr ug/L	S2-Cr ug/L	S1-Cu ug/L	S2-Cu ug/L	S2-Fe ug/L	S1-Hg ug/L	S1-Mn ug/L	S2-Mn ug/L
H.V.	64.0	290	1.47	1.13	28.3	85.3	1.55	1.08	15.0	34.1	1.58	42.3	6.37	53.8	693	0.205	2.63	71.8
A.V.	66.8	305	1.49	1.21	28.5	80.5	1.46	1.07	14.4	35.4	1.65	39.9	5.94	48.4	618	0.210	2.58	66.7
1	67	307	1.5	1.2	30	83	1.5	1.1	15	36	1.4	40	6.1	49	590	0.2	2.3	66
2	66	325	1.2	1.3	26	84	1.4	1.1	14	36	1.6	39	5.3	46	620	<0.1	2.6	70
3	54.8	262	1.69	1.2	28.8	79.7	1.32	1.05	14.3	31.6	1.35	35.8	5.43	44	578	0.31	2.48	61.8
4	65.9	314	1.22	1.18	27.1	77.9	1.55	1.01	14.3	34.6	1.59	39.1	5.86	50.9	628	NT	2.74	63.5
5	64.8	298	1.42	1.15	27.5	71.9	1.53	1.01	13.6	35.3	1.58	39.2	6.14	51.3	612	0.2	2.54	65.9
6	61	246	2	1	19	80	1	1	12	36	2	42	6	44	581	0.22	2	72
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	85	350	1.7	1.3	28	80	1.5	1.1	14	35	1.6	40	6.1	48	620	1.5	2.6	65
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	70	350	1	1	33	85	2	1.2	16.3	39	2	44	1	54	710	0.2	3	72
11	NT	NT	NT	NT	0.032	NT	NT	NT	0.014	0.026	NT	0.041	NT	0.052	0.779	NT	NT	0.061
12	70	320	1.7	1.5	30	81	1.4	1	15	35	1.6	40	6	48	630	0.21	2.7	65
14	NT	NT	NT	NT	NT	NT	NT	<0.01	<0.01	0.037	NT	NT	<0.01	0.036	0.042	NT	<0.01	0.069
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	70	280	1.5	1.3	31	79	1.48	1.14	14.7	35	1.8	40	6.5	49	640	0.21	2.7	67
17	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	638	NT	NT	66

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

Table 67 Summary of Participants' Results and Performance for S1 and S2 (continued)

Lab Code	S2-Mo ug/L	S1-Ni ug/L	S2-Ni ug/L	S1-Pb ug/L	S2-Pb ug/L	S1-Sb ug/L	S2-Sb ug/L	S1-Se ug/L	S2-Se ug/L	S1-Sn ug/L	S2-Sn ug/L	S1-Tl ug/L	S2-U ug/L	S1-V ug/L	S1-Zn ug/L	S2-Zn ug/L
H.V.	37.3	1.87	29.7	1.40	34.7	2.38	16.3	1.83	31.0	1.77	29.7	4.37	16.0	2.50	9.05	51.7
A.V.	35.5	1.87	28.3	1.45	34.8	2.80	17.7	2.13	31.9	1.77	28.1	4.85	16.2	2.67	10.0	51.6
1	38	1.8	29	1.4	34	2.9	18	2.2	32	1.9	32	4.8	16	2.9	10	56
2	32	1.8	28	1.5	35	3.1	19	2.1	28	1.8	29	4.9	17	<5	10	41
3	35.6	1.76	25.8	1.41	33.5	2.79	18.5	2.18	34.4	1.72	28.1	4.69	15.4	2.56	10.1	51
4	34.6	1.7	27.9	1.5	34.5	2.67	17.4	2.06	34.3	1.73	26.7	4.74	15.5	2.69	9.1	56.7
5	33.1	1.89	28.6	1.32	34.7	2.54	16.6	1.96	31.1	1.64	27.6	4.34	15.5	2.51	9.76	51
6	38	2	27	2	37	3	14	2	16	NT	NT	5	17	2	9	39
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	37	1.9	28	1.5	33	2.9	17	2.4	31	1.7	28	5	16	2.8	9.7	48
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	38	2	32	1	37	2	17	<10	30	2	29	5	18	<10	13	67
11	0.091	NT	0.029	NT	0.032	NT	NT	NT	0.044	NT	NT	NT	NT	NT	NT	0.055
12	35	1.9	29	1.5	34	2.6	18	3.4	37	1.7	28	4.8	NT	2.8	10	54
14	NT	NT	NT	<0.01	<0.01	NT	NT	NT	NT	NT	NT	NT	NT	NT	0.012	0.054
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	34	1.9	29	1.46	35	3	20	2.2	35	1.8	27	5	16.2	2.7	11.3	55
17	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

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

Table 68 Summary of Participants' Results and Performance for S3

Lab Code	S3-Ammonia-N mg/L	S3-Bromide mg/L	S3-Chloride mg/L	S3-Dissolved Organic Carbon mg/L	S3-Fluoride mg/L	S3-Orthophosphate-P (FRP) mg/L	S3-Nitrate-N mg/L	S3-Sulphate mg/L	S3-Total Dissolved Nitrogen mg/L	S3-Total Dissolved Phosphorus mg/L
H.V.	0.101	0.200	45.3	6.13	0.400	Not Set	0.190	17.0	0.47	0.0487
A.V.	0.098	0.213	53.7	Not Set	0.380	0.051	0.183	16.4	0.529	0.0570
1	0.145	0.21	57	7.32	0.53	0.066	0.178	17	0.491	0.069
2	0.099	0.21	56	6	0.36	0.042	0.17	17	0.47	0.049
3	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	0.091	0.24	53	5.55	0.383	0.046	0.177	15.7	NT	NT
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	<0.2	0.2	52	NT	0.35	NT	0.2	16	NT	NT
7	0.1	NR	NR	NR	NR	0.07	0.186	NR	0.53	0.05
8	0.1	0.2	48	6.3	0.4	0.046	0.18	17	0.47	0.055
9	<0.1	0.16	55	NT	0.4	NT	0.2	16	0.55	0.06
10	0.08	NT	55	NT	<0.1	0.04	0.17	16	0.6	0.07
11	NT	NT	51	NT	NT	NT	1.54	NT	NT	NT
12	NT	<0.5	54	NT	0.4	NT	NT	16	NT	0.05
14	NT	NT	NR	NT	NT	NT	2.66	25.5	0.6	0.06
15	0.1	0.3	54.5	5.5	0.34	0.049	0.19	15.8	0.52	0.05
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	NT	NT	NT	0.355	NT	NT	22	NT	NT

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

Table 69 Summary of Participants' Results and Performance for S4

Lab Code	S4-Alkalinity to pH 4.5 (as $CaCO_3$) mg/L	S4-B mg/L	S4-Ca mg/L	S4-Chemical Oxygen Demand mg/L	S4-Colour, apparent Pt-Co Units	S4-K mg/L	S4-Mg mg/L	S4-Na mg/L
H.V.	45.3	0.0430	NA	17.0	17.7	NA	NA	NA
A.V.	52.2	Not Set	18.2	Not Set	33.3	3.75	5.76	35.8
1	49	0.045	19.2	16	35	3.7	5.92	37.5
2	NR	NR	NR	NR	NR	NR	NR	NR
3	NR	NR	NR	NR	NR	NR	NR	NR
4	54	NT	18.4	NT	NT	3.5	5.3	NT
5	NR	0.041	18.4	NR	NR	3.6	6.06	36.7
6	52	28	NT	NT	NT	NT	NT	NT
7	NR	NR	NR	NR	NR	NR	NR	NR
8	46	310	18	17	32	3	5.5	31
9	55	NT	18	18	NT	4	6	35
10	53	<0.05	20	NT	30	4	6	40
11	51.3	0.051	15.8	NT	31	4.21	5.63	36.5
12	53	<0.1	19	<25	38	4.1	5.8	35
14	59.78	NT	17.77	NT	NR	NT	NT	NT
15	50	NT	17.9	<25	34	3.67	5.42	33.2
16	NT	0.039	17.6	NT	NT	3.6	5.8	37
17	52.5	NT	17.85	18	NT	NT	5.87	NT

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

Table 69 Summary of Participants' Results and Performance for S4 (continued)

Lab Code	S4-Total P mg/L	S4-pH (at 25ºC)	S4-Silica (as SiO_2) mg/L	S4-Total Hardness (as $CaCO_3$) mg/L	S4-Total Solids at 103-105°C mg/L	S4-Turbidity NTU	S4-TN mg/L	Total Kjeldahl Nitrogen mg/L	Total Organic Carbon mg/L
H.V.	NA	7.40	NA	NA	200	0.40	1.03	NA	NA
A.V.	0.090	7.65	9.0	67.0	188	0.378	0.99	0.90	Not Set
1	0.089	7.63	8.47	75	162	0.32	1.12	0.984	10.1
2	NR	NR	NR	NR	NR	NR	NR	NR	NR
3	NR	NR	NR	NR	NR	NR	NR	NR	NR
4	NT	NT	NT	NT	NT	NT	NT	NT	8.2
5	0.12	NR	NR	71	NR	NR	NR	NR	NR
6	<1.5	7.6	NT	66	NT	<1	0.5	NT	NT
7	0.08	NR	7.69	NR	NR	NR	1.1	NR	NR
8	<0.05	7.7	13	64	200	0.4	0.8	0.94	9.5
9	0.09	7.65	11	69	216	0.42	1.0	0.6	NT
10	0.05	7.67	8.1	63	190	0.3	NT	0.9	NT
11	0.09	7.69	NT	39.5	39	0.48	NR	NT	NT
12	0.1	7.6	NT	NT	200	NT	NR	NR	NR
14	NR	7.65	8	NR	127.6	0.42	NR	NT	NT
15	NT	7.6	7.4	67	206	0.4	1.1	0.94	8.7
16	0.091	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	7.8	NT	69	NT	0.28	NR	NR	NR

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

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

A summary of participants' results and performance is presented in Tables 67 to 69 and in Figures 64 and 65.

Reporting results in wrong units was one of the main causes of participants' poor performance. Except for Co, Mo and Se in S2 Laboratory 11 correctly measured all tested elements but reported results in different units (mg/L). Laboratory 14 correctly measured Zn in S1 and S2 and Mn and Co in S2 but reported results in units of mg/L and not in units of µg/L. The z-score results from these laboratories are not a reflection of their analytical performance and were not taken into consideration when assessing the effects of analyte on participants' performance.

Low level B was the test that presented the most analytical difficulty to participating laboratories.

Participants were requested to analyse the water samples S2 and S4 for total elements. The method descriptions provided by participants are presented in Tables 1 and 2 and the instrumental conditions are presented in Appendix 6.

No relationship was evident between the performance of participants and the digestion procedure used for total elements in samples S2 and S4. The instrumental measurement was one of the main factors that influenced the results. However, participants' performance does not reflect only the instrument performance, but also the performance of the analyst and of the analytical method used by the testing laboratory. Thus, these results should not be construed as an evaluation of a particular instrument.

Participants used a wide variety of instrumental techniques, collision/reaction cells and cell gases. Most laboratories reported using ICP-MS with a collision/reaction cell, some used ICP-OES and some only ICP-MS. One participant reported using ICP-MS in MS/MS mode. Plots of participants' results and performance versus instrumental techniques used are presented in Figure 66.

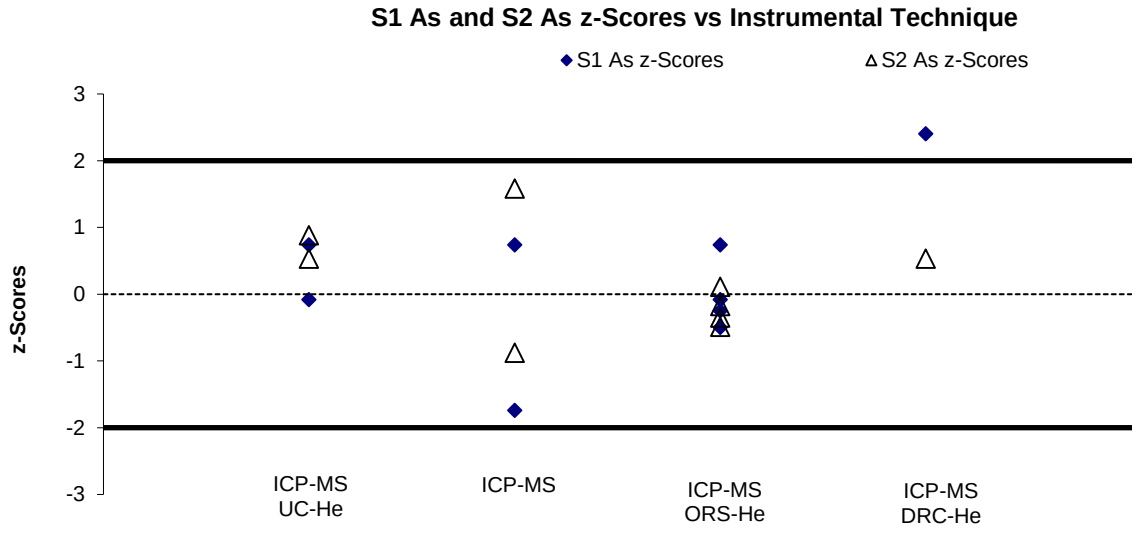
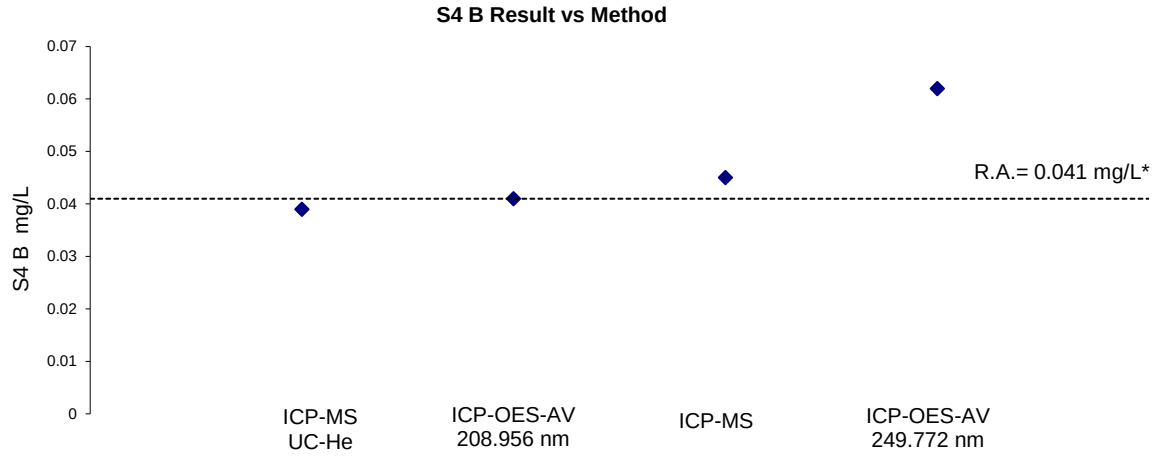
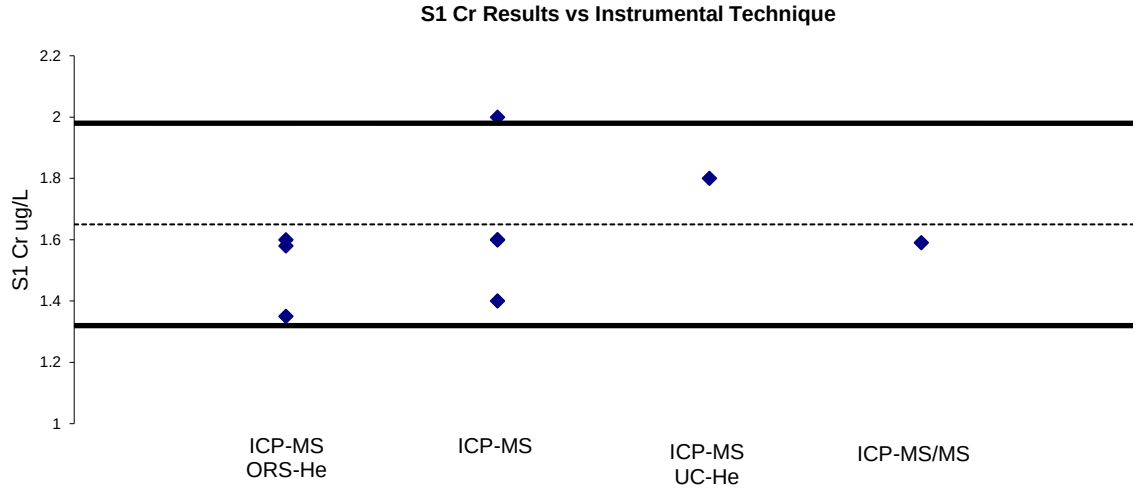
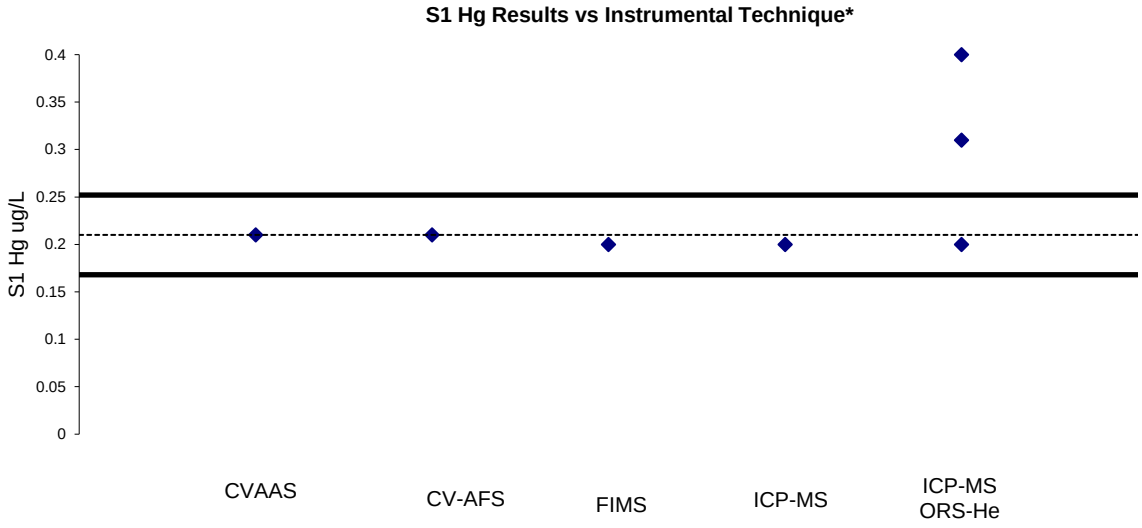


Figure 66 Participants' Results and Performance vs Instrumental Technique



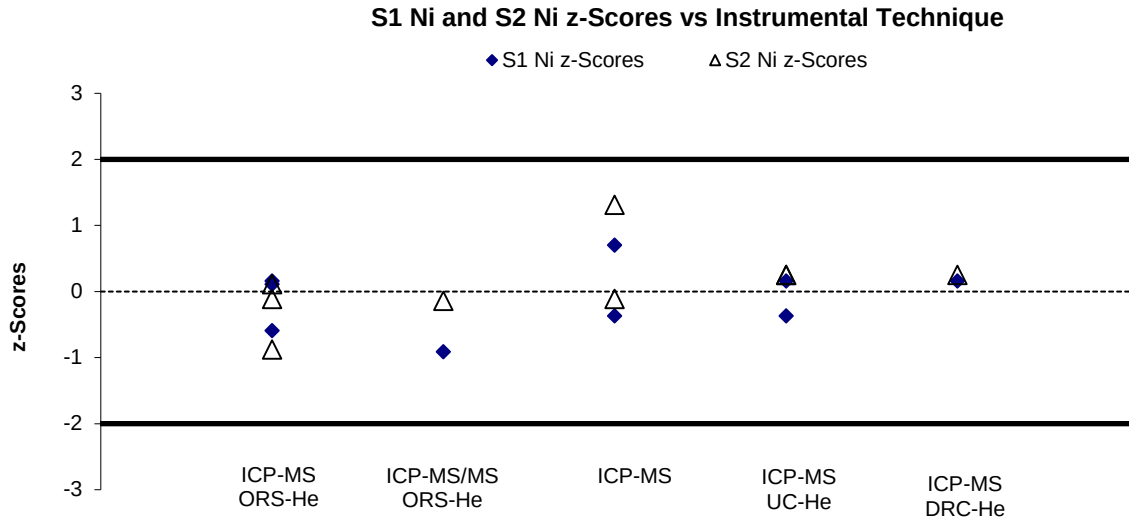
*R.A. = Robust Average excluding Laboratory 8.

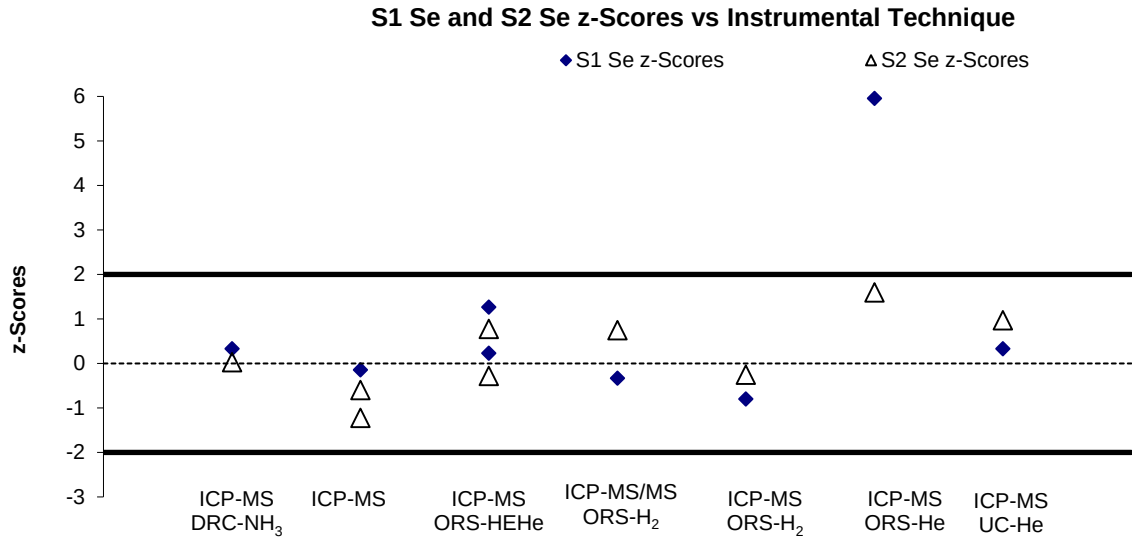


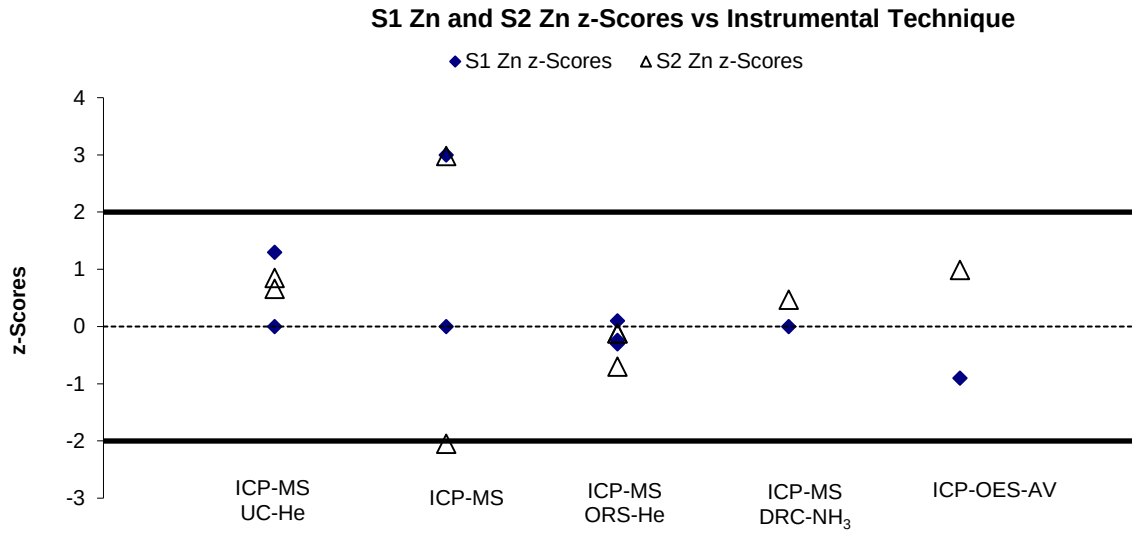


*Mercury result larger than 0.4 mg/L has been plotted as 0.4 mg/L. Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 66 Participants' Results and Performance vs Instrumental Technique (continued)

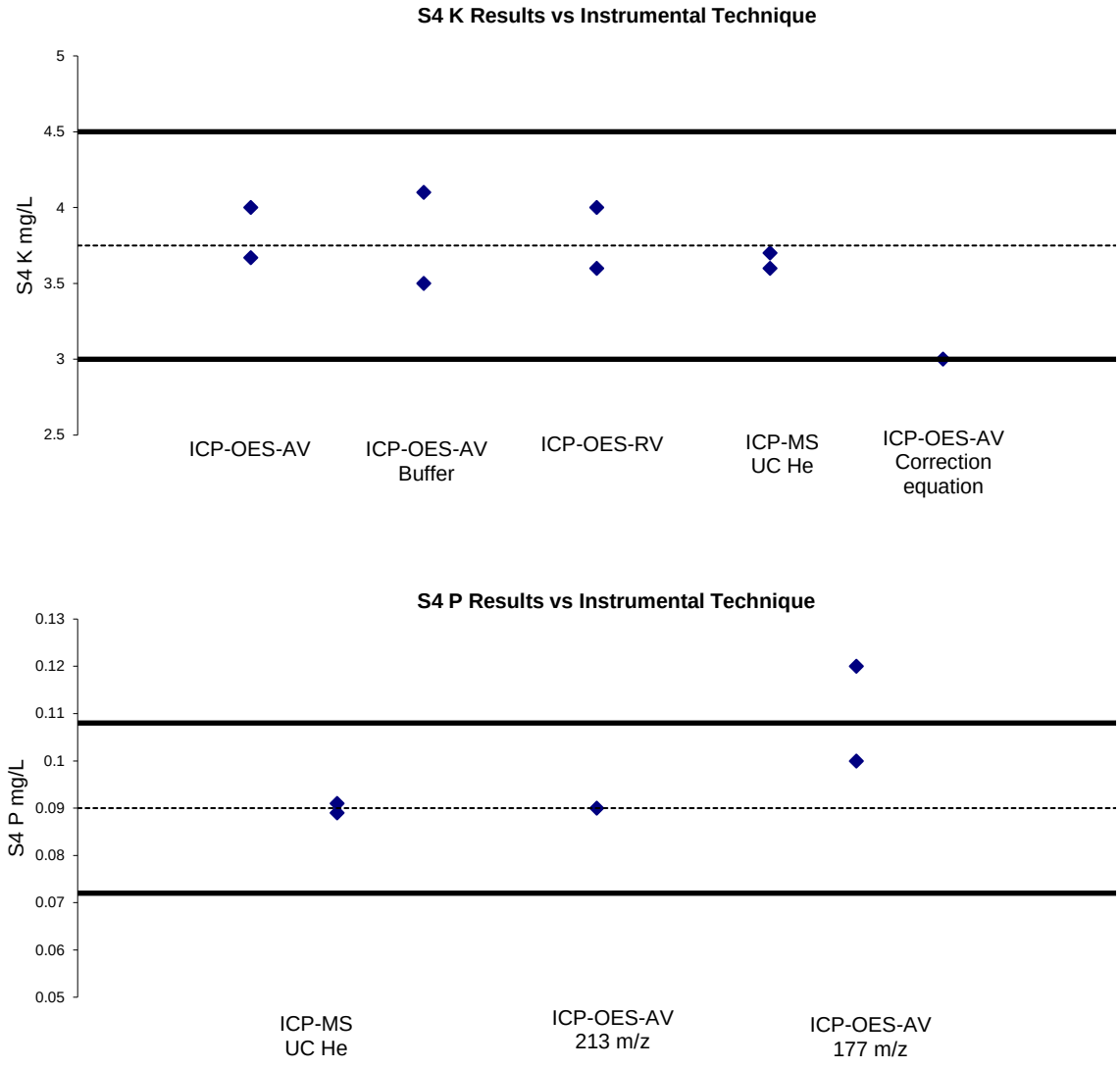






Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 66 Participants' Results and Performance vs Instrumental Technique (continued)



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

Figure 66 Participants' Results vs Instrumental Technique (continued)

Individual Element Commentary

Aluminium measurements at low level have not posed significant problems for laboratories. The between laboratories CV for Al in S1 was 7.9%.

Arsenic Participants used a wide variety of instrumental techniques for As measurements in S1. Unsolved interference problems might explain the high, unsatisfactory z-score in the low level Sample S1 (Figure 66).

Boron level in sample S4 was low (0.041 mg/L) and this might have presented difficulties to some laboratories. Laboratory 6 reported B in wrong units.

Boron measured at 249.7 nm can have significant interferences from Fe 249.771 nm if on-line inter-element correction is not used. Plots of participants' results versus instrumental technique used are presented in Figure 66.

Chromium Matrix effects and polyatomic spectral interferences from C when low level Cr is measured by ICP-MS in river water without the help of collision/reaction cell, may explain some high Cr results reported in the low test Sample S1 (Figure 66).

Mercury level in S1 (0.210 µg/L) has not presented a challenge for participants' analytical techniques. The between coefficient of variation was small, 6.1%. Use of expired standards or those not prepared fresh from standard stock solutions before measurement could be a cause of high Hg results (Figure 66).

Nickel Participants used a wide variety of methods for measurement of Ni in S1 and S2 and all produced satisfactory results (Figure 66).

Selenium Although Se level in S1 (2.13 µg/L) was lower than in S2 (31.9 µg/L) the between laboratories coefficient of variation in S2 was two times higher (12%). Participants reported using 7 different instrumental techniques: ICP-MS in collision, reaction or MS/MS mode and with various collision/reaction gases: He, NH_3, and H_2 (see Figure 66).

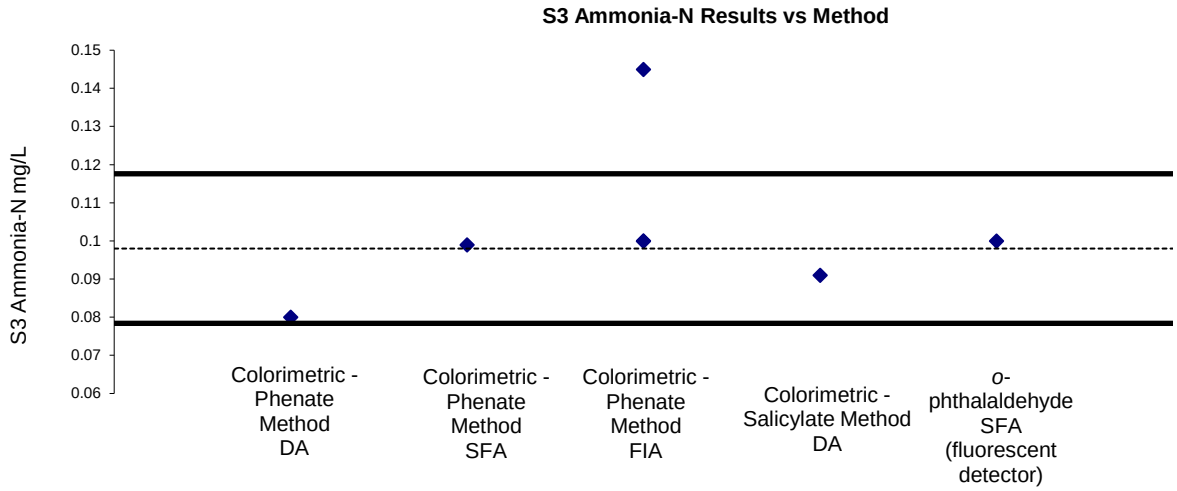
Zinc Laboratory 10 should revised the method used for Zn measurements. Both results reported by them for Zn in S1 and S2 returned high, unsatisfactory z-scores.

7.6 Participants' Results and Analytical Methods for Tests in Samples S3 and S4 Other than Total and Dissolved Elements

Participants were asked to analyse samples S3 and S4 using their normal test method. Stability studies were conducted and these samples were found to be sufficiently stable for evaluation of participants' performance (See Appendix 2). The measurement methods and instrumental techniques used for S2 and S3 analyses are presented in Appendix 2.

Sample S3-Individual Test Commentary

Ammonia-Nitrogen Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination. One laboratory reported using ion selective electrode method and one the *o*-phthalaldehyde method with SFA with fluorescent detector (Figure 67).

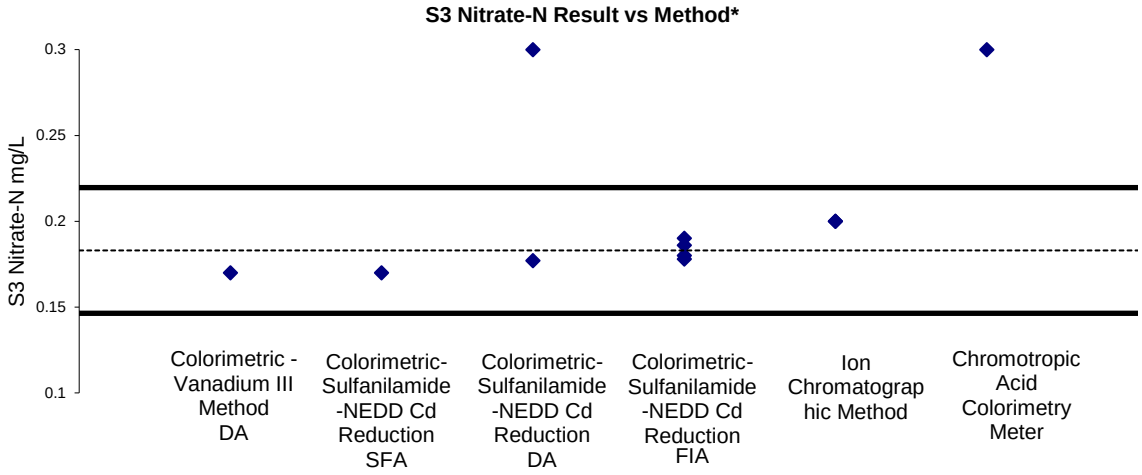


Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 67 S3-NH_3-N Results vs. Measurement Method

Nitrate-Nitrogen Six participants used colorimetric-sulfanilamide-NEDD Cd reduction and two used the ion chromatographic method. One laboratory reported using Vanadium III colorimetric method and one measured nitrate-n by colorimetry meter. Except for two, all the

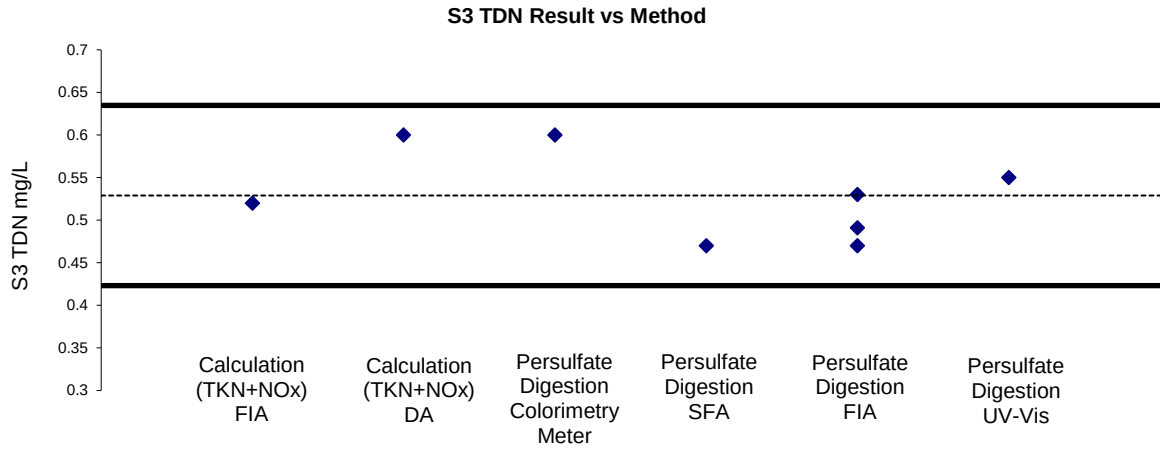
results reported for nitrate-N in S3 were in good agreement with each other and returned satisfactory z-scores**.** A plot of participants' results versus analytical method and instrumental technique used is presented in Figure 68.



Horizontal lines on charts are the results correspond to z-scores of 2 and -2. *Results larger than 0.3 mg/L have been plotted as 0.3 mg/L

Figure 68 S3-Nitrate-N Results vs. Measurement Method

Total Dissolved Nitrogen All reported results for TDN were in agreement with each other and with the robust average of 0.529 ± 0.052 mg/L. Figure 69 presents plots of participants' results vs the measurement method used for TDN determination in S3.



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

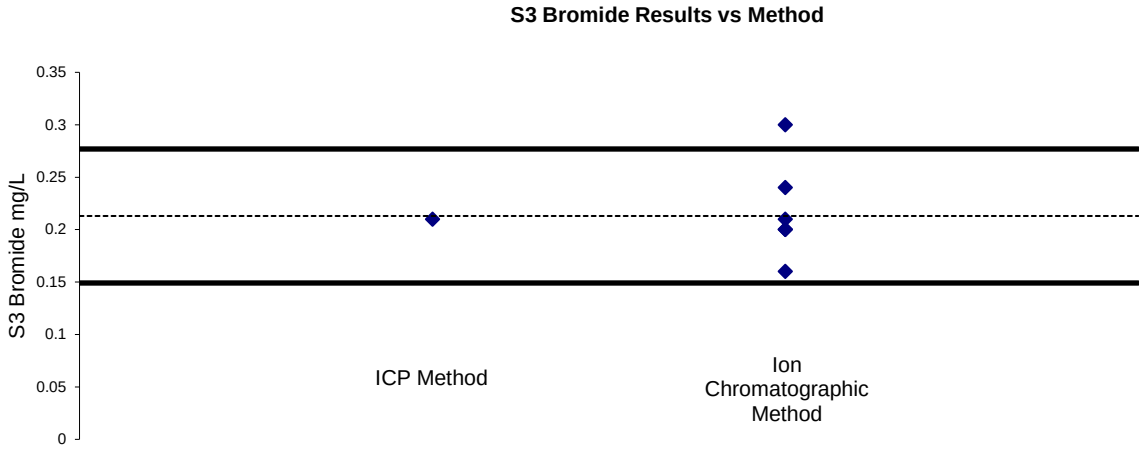
Figure 69 S3-TDN Results vs. Measurement Method

Bromide Ion chromatography was the method chosen by most laboratories for bromide measurements. One participant reported using ICP method for bromide measurements in S3 (Figure 70).

Chloride Participants used a wide variety of methods for chloride analysis in S3 and all produced comparable results (Figure 71).

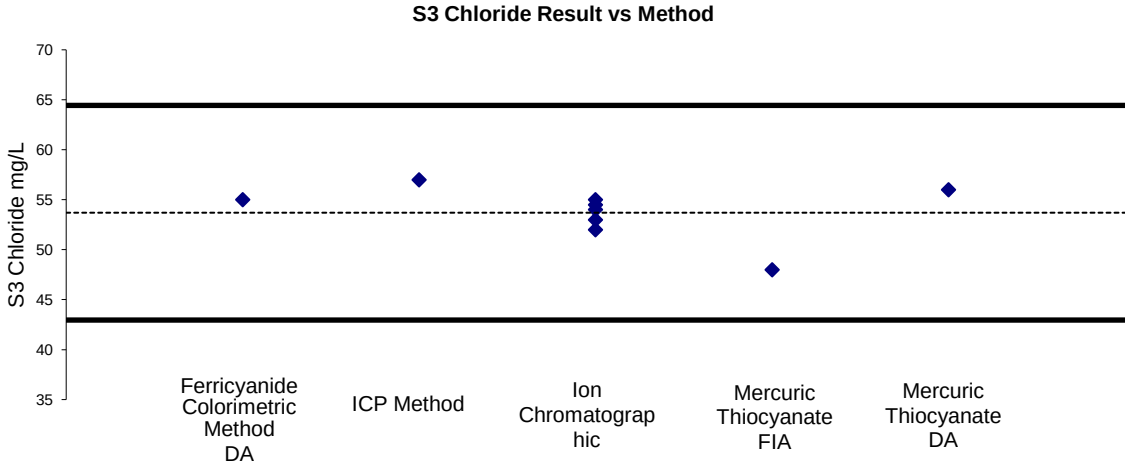
Fluoride Most participants used ion selective electrode method or ion chromatographic method. One laboratory used SPADNS colorimetric method with UV-Vis determination

(Figure 72). Fluoride by colorimetric method has interference from chlorides and SPANDS might not be the best choice for fluoride measurements at low levels in water.



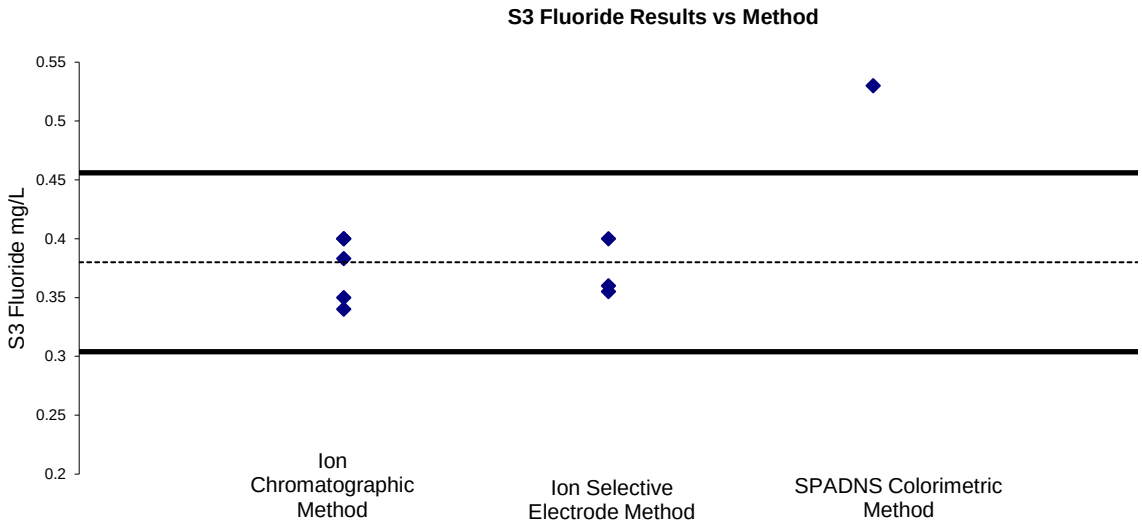
Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 70 S3-Bromide Results vs. Measurement Method



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

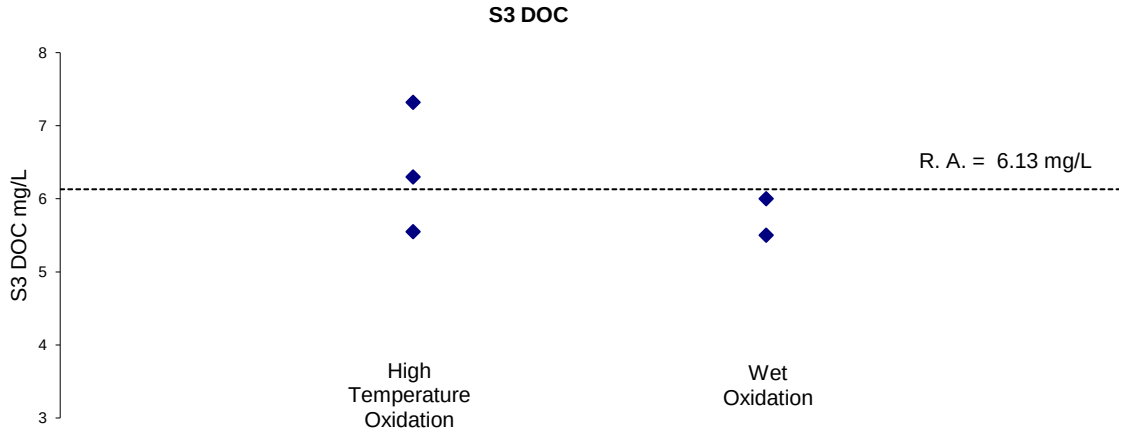
Figure 71 S3-Chloride Results vs. Measurement Method



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

Figure 72 S3-Fluoride Results vs. Measurement Method

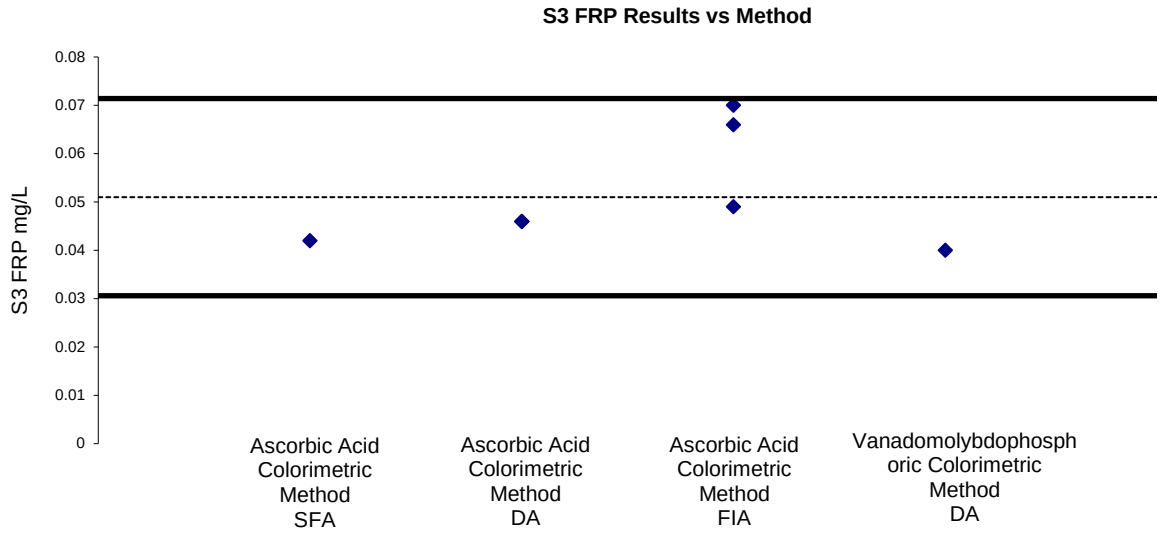
Dissolved Organic Carbon as dNPOC. Only 5 results were reported for DOC in S3 and all were in agreement with each other centred on 6.13 mg/L. Participants used high temperature oxidation or wet oxidation; no significant difference was noticed between DOC results produced by these two methods (Figure 73).



R.A. = Robust Average

Figure 73 S3-DOC vs. Measurement Method

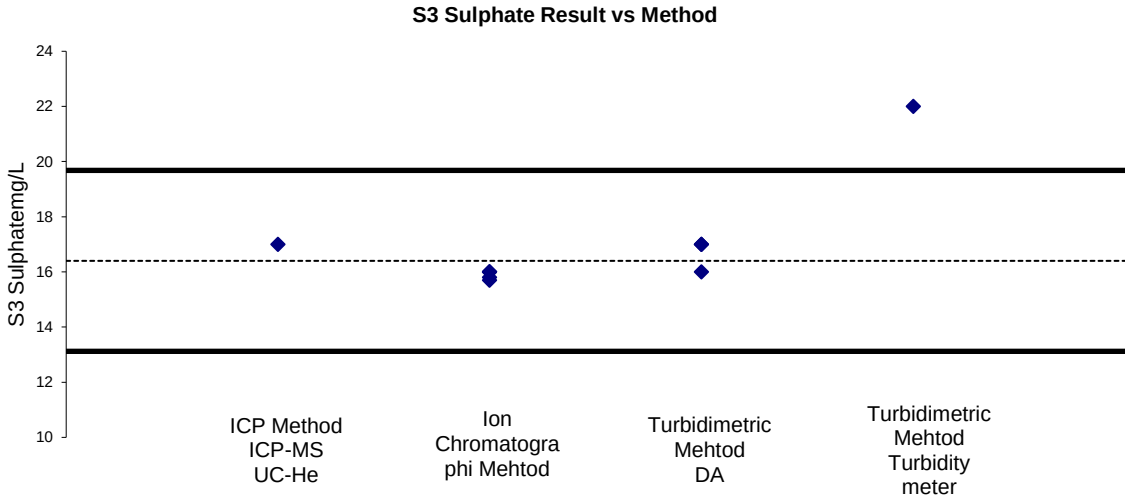
Orthophosphate-P One participant reported using a vanadomolybdophosphoric method for orthophosphate-P measurements in S3; all other participants used ascorbic acid colorimetric method with FIA, SFA or DA determination (Figure 74).



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

Figure 74 S3-Orthophosphate-P Results vs. Measurement

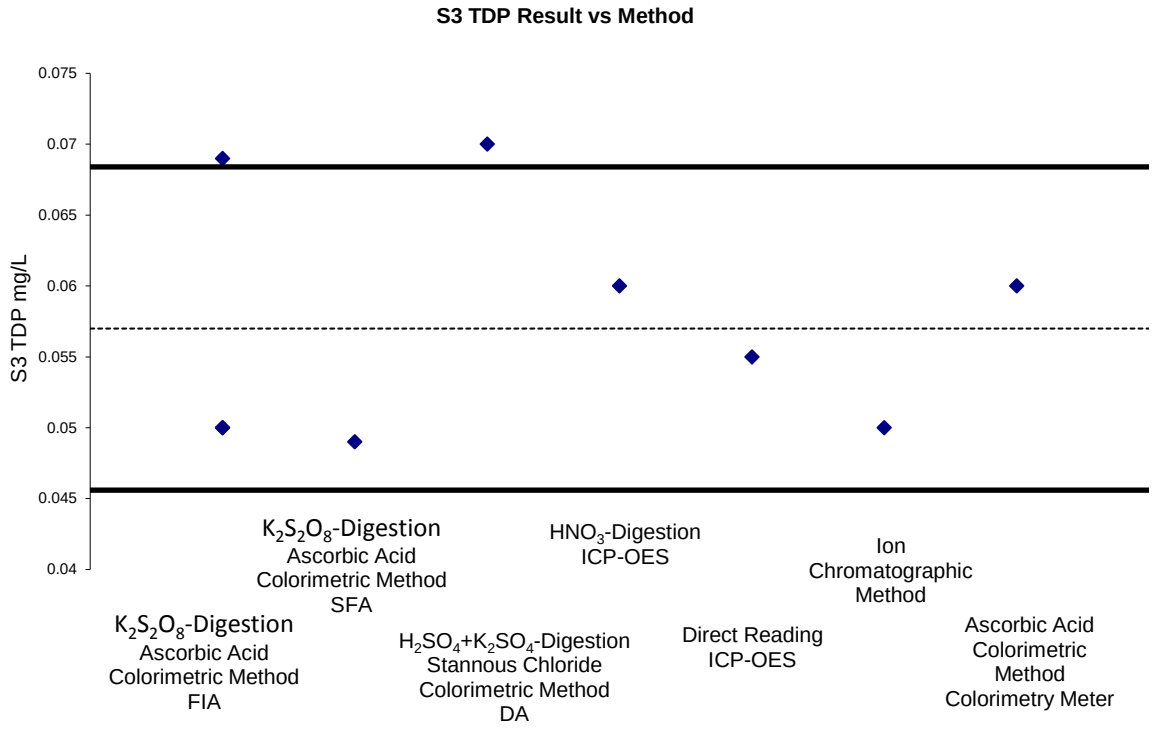
Sulphate One participant reported using ICP-MS for sulphate measurements in S3; caution should be exercised when the ICP method is used because it measures total S and not only S from sulphate compounds (Figure 75).



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

Figure 75 S3-Sulphate Results vs. Measurement Method

Total dissolved phosphorus level in S3 was low (0.057 mg/L) and this might have presented difficulties to some laboratories. The reported results were variable with a between laboratories coefficient of variation high (16%). Most laboratories used potassium persulphate for digestion and then measured the liberated orthophosphate colorimetrically by FIA or SFA. No digestion was performed by one participant they reported measuring TDP in the sample by ICP-OES (Figure 76).



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

Figure 76 S3-TDP Results vs. Measurement Method

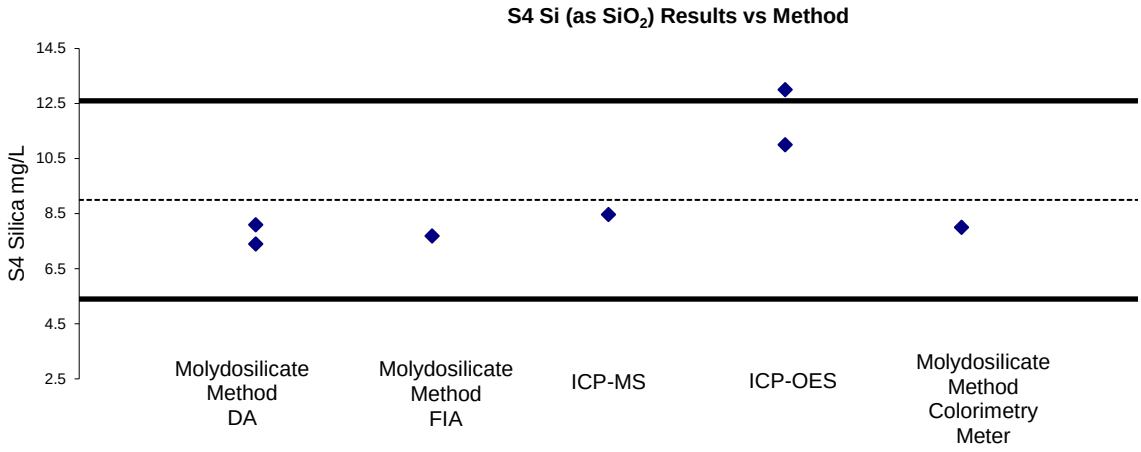
Sample S4-Individual Test Commentary

Alkalinity to pH 4.5 as ($CaCO_3$) did not present analytical difficulty to participants. All reported results returned satisfactory z-scores (Table 69).

Chemical Oxygen Demand Only 6 results were reported for COD in S4 and all were in agreement with each other centred on 17.3 mg/L. Except for one, all participants used closed reflux colorimetric methos with UV-Vis. One laboratory used titrimetric method for COD measurements in S4.

Colour Participating laboratories used both visual comparison method and spectrophotometric method and all performed satisfactorily.

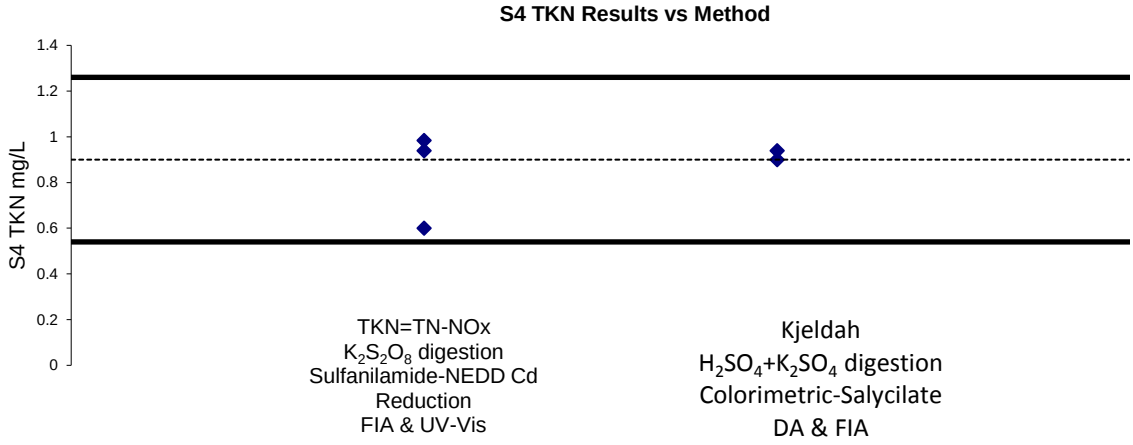
Silica (as SiO_2) Plots of participants' results versus measurement technique used are presented in Figure 77.



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

Figure 77 S3-Si (as SiO_2) Results vs. Measurement Method

Total Kjeldahl Nitrogen Although only five participants reported results for TKN in S4, an assigned value was still set for this analyte because the reported results were in very good agreement with each other and with the with the spike value. Plots of participants' results versus analytical method and measurement technique used are presented in Figure 78.



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

Figure 78 S4-TKN Results vs. Measurement Method

Total Nitrogen Five participants used persulphate digestion for TN measurements in S4 and 2 reported TN as TKN+NOx. Except for one all reported results returned satisfactory z-scores.

Total Hardness Of nine results reported for Total Hardness, eight returned satisfactory z-score.

Total Phosphorus A summary of participants' results and methods used for total P measurements in S4 are presented in Figure 79.

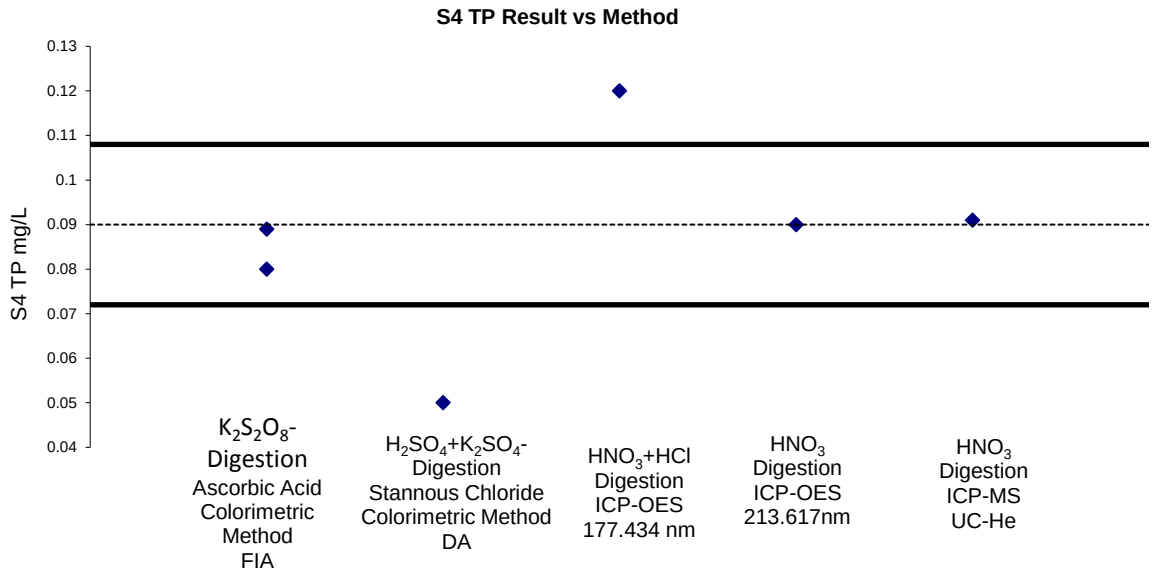


Figure 79 S4-TP Results vs. Measurement Method

7.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 19-07 is the twenty-third NMI proficiency test of metals in water. For most of the analytes the same fixed target standard deviation was used in the present study as in the previous studies of metals in water. This allowed a comparison of participants' performance (z-score) over time and provided a benchmark for progressive improvement.

Despite different matrices, analytes and analytes' concentrations, on average participants' performance has remained consistent with the percentage of satisfactory z-scores ranging from 71% to 97% and satisfactory E_n -scores from 55% to 89% (Figure 80).

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

Over time laboratories should expect at least 95% of its scores to lie within the range $|z| \leq 2$. Scores in the range $2 < |z| < 3$ occasionally can occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line are an indication of method or laboratory bias.

7.8 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 70).

Table 70 Control Samples Used by Participants

Lab. Code	RMs or CRMs identity
1	CWW-TM-A, B and C (metals)
4	Environment Canada
5	HPS CRMs
7	ENCT Round 22 Bot No1-8
12	CWWTMC; CWWTMA

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

> *'a reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'*[18]

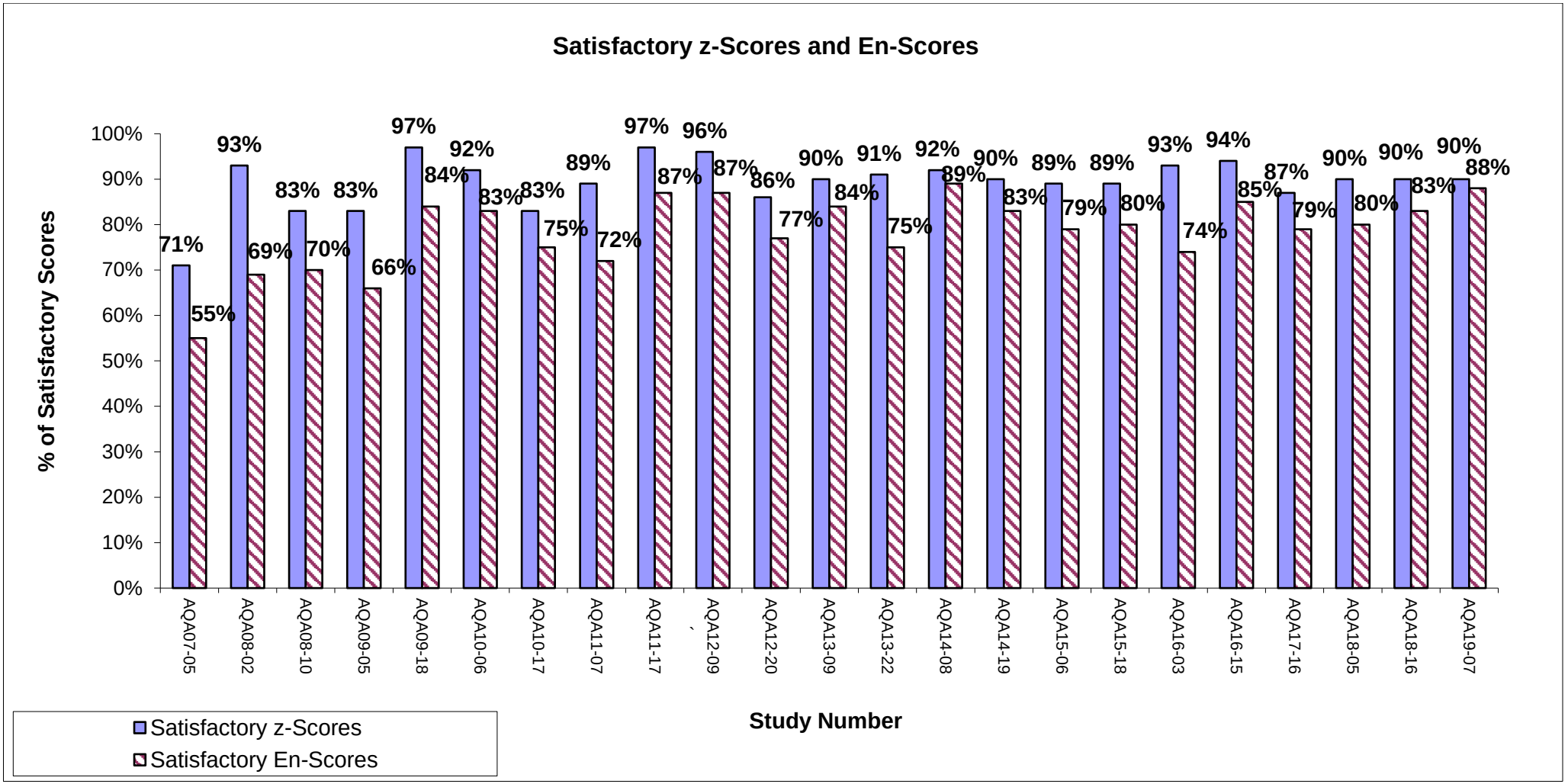


Figure 80 Participants' Performance over Time

8 REFERENCES

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

[2] NMI 2019, *NMI Chemical Proficiency Testing Study Protocol*, 2017, <http://www.measurement.gov.au>.

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Samples S1– was filtered and acidified (1% HNO_3, 0.01% HCl) river water collected from Brown's Waterhole Turramurra. The water was further fortified for the elements of interest.

Samples S2– was filtered and acidified (1% HNO3, 0.01% HCl) river water collected from Brown's Waterhole Turramurra. The water was further fortified for the elements of interest.

Samples S3– was prepared from river water collected from Brown's Waterhole Turramurra. Approximately 10 L of water were filtered through 0.45 µm pore size filter, autoclaved and further fortified for orthophosphate-P, ammonia-N and nitrate-N. The prepared material was dispensed in units of 200 mL each and stored frozen.

Sample S4 – consisted of two containers labelled S4A and S4B. The bottle S4A contained 700 mL of unfiltered, chilled, river water. Except for P the analytes' levels in this sample were the incurred level. The container labelled S4B consisted of 200 mL of unfiltered, autoclaved, frozen river water. This sample was spiked with glutamic acid. Participants were instructed not to composite the contents of the two containers prior to analyses.

Sample Analysis and Homogeneity Testing

Except for TDP in S3 and total Ca, K, Mg, Na, Silica (as SiO_2) and total hardness in S4, a partial homogeneity test was conducted for all the analytes of interest in Samples S1, S2 and S3 and S4.[1, 6, 7] Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Methodology for Total and Dissolved Elements

Measurements for total and dissolved elements were made using NMI Method for which NMI holds third party (NATA) accreditation for this method. For total elements in S2 and S4 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 acid on a hot block at 90±100ºC for 90 min.

Testing involved measurements using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, duplicates and sample matrix spikes, was carried through the same set of procedures and analysed at the same time as the samples. A summary of the ion/s and wavelength used for each analyte is given in Table 71.

Table 71 Instrumental Technique used for Total Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1 Final Dilution Factor	S2/S4 Final Dilution Factor	Ion/Wavelength
Ag	ICP-MS	Rh	ORS	He	1	NA	107 m/z
Al	ICP-MS	Rh	NA	NA	1	1.1	27 m/z
As	ICP-MS	Rh	ORS	He	1	1.1	75 m/z
B	ICP-OES	Y	NA	NA	NA	1.1	208.956 nm
Ba	ICP-MS	Rh	ORS	He	NA	1.1	137 m/z
Be	ICP-MS	Rh	NA	NA	1	NA	9 m/z
Cd	ICP-MS	Rh	ORS	He	1	1.1	111 m/z
Co	ICP-MS	Rh	ORS	He	NA	1.1	59 m/z
Cr	ICP-MS	Rh	ORS	He	1	1.1	52 m/z

Table 71 Instrumental Technique used for Total Elements (continued)

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1 Final Dilution Factor	S2/S4 Final Dilution Factor	Ion/Wavelength
Cu	ICP-MS	Rh	ORS	He	1	1.1	63 m/z
Fe	ICP-MS	Rh	ORS	He	NA	1.1	56 m/z
Hg	CVAFS	NA	NA	NA	1	NA	253.7 nm nm
Mn	ICP-MS	Rh	ORS	He	1	1.1	55 m/z
Mo	ICP-MS	Rh	ORS	He	NA	1.1	95 m/z
Ni	ICP-MS	Rh	ORS	He	1	1.1	60 m/z
Pb	ICP-MS	Ir	ORS	He	1	1.1	Average of 206, 207, 208 m/z
Sb	ICP-MS	Ir	ORS	He	1	NA	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	1	1.1	78 m/z
Sn	ICP-MS	Rh	ORS	He	1	1.1	118 m/z
Tl	ICP-MS	Rh	ORS	He	1	NA	205 m/z
U	ICP-MS	Ir	ORS	He	1	NA	238 m/z
V	ICP-MS	Rh	ORS	He	1	NA	51 m/z
Zn	ICP-MS	Rh	ORS	He	1	1.1	64 m/z

Methodology for Tests Other Than Total Elements in S3 and S4

A summary of the measurement methods and instrumental techniques is presented in Tables 72 and 73.

Table 72 Methodology for S3 and S4

Test	Measurement Method	Instrument
S3-Ammonia-N	Fluorometric Determination - OPA Method	SFA
S3-Bromide	Ion Chromatographic Method	IC
S3-Chloride	Ferricyanide Colorimetric Method	DA
S3-Fluoride	Ion Selective Electrode Method	ISE
S3-Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA
S3-Nitrate-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
S3-Sulphate	Turbidimetric Method	DA
S3-Total Dissolved Nitrogen	Persulfate digestion	FIA
S4-Alkalinity to pH 4.5 (as $CaCO_3$)	Titration	Titration
S4-Chemical Oxygen Demand	Closed Reflux, Titrimetric Method	
S4-Colour, apparent	Spectrophotometric method	DA
S4-Total Kjeldahl Nitrogen	TKN=TN-NOx, Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
S4-Total Phosphorus	Nitric Acid digestion, ICP Method	ICP-OES
S4-Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Organic Carbon	High-Temperature Oxidation	NIR

APPENDIX 2 - STABILITY STUDY

Samples S1 and S2 No stability study was carried out for elements in S1 and S2. Stability studies conducted for previous proficiency studies of metals in water found no significant changes in any of the analytes' concentration. [6, 7]

Samples S3 and S4 Participants were advised to store the Samples S3 and S4B frozen if analyses cannot be commenced on the day of receipt. Samples' condition on receipt and the date when the samples were received and analysed by the participants are presented in Table 73. No significant trends between participants' results and samples' condition on receipt were noticed.

Table 73 Samples S3 and S4B Condition on Receipt and the Date When the Samples were Received and Analysed

Lab Code	Received Date	S3		S4B	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	14/15/2019	Frozen	17/05/2019	Frozen	15/05/2019
2	14/05/2019	Frozen	26/05/2019	NA	NA
3	16/05/2019	NA	NA	NA	NA
4	14/05/2019	Frozen	19/05/2019	Frozen	22/05/2019
5	14/05/2019	NA	NA	NA	NA
6	16/05/2019	Frozen	23/05/2019	Frozen	16/05/2019
7	15/05/2019	Frozen	05/06/2019	Frozen	05/06/2019
8	13/05/2019	Frozen	15/05/2019	Frozen	15/05/2019
9	14/05/2019	Frozen	04/06/2019	Frozen	04/06/2019
10	14/05/2019	Cold	16/05/2019	Cold	16/05/2019
11	14/05/2019	Frozen	15/05/2019	Frozen	15/05/2019
12	14/05/2019	Frozen	23/05/2019	Frozen	15/05/2019
14	15/05/2019	Cold	29/05/2019	Cold	29/05/2019
15	15/05/2019	Frozen	21/05/2019	Frozen	24/05/2019
16	15/05/2019	NA	NA	NA	17/05/2019
17	14/05/2019	Frozen	15/05/2019	Frozen	14/05/2019

*The samples have been dispatched on 13/05/2019, NA = Not Applicable

Stability Study

Stability studies conducted for nutrients and physical tests in water in the previous studies found no significant changes in any of the analytes' concentration. [6, 7] A stability study was however conducted in the present study for the less stabile analytes: NH_3-N, and NO_3-N in S3 and for TN in S4.

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

To test for storage stability results from two sets of samples kept at -20°C (reference samples-RS) were compared with results from two samples left out on laboratory table for one week (Room). Theses samples were analysed in duplicate, in random order at the same time.

For short term stability testing results from samples analysed over the study period, before the samples' dispatch (T0) and the end of the study after results' submission (T1) were compared. Each sample was analysed in duplicate together with a set of quality control samples

consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes.

Results were in good agreement with each other and the assigned value within their stated uncertainties (Figure 81).

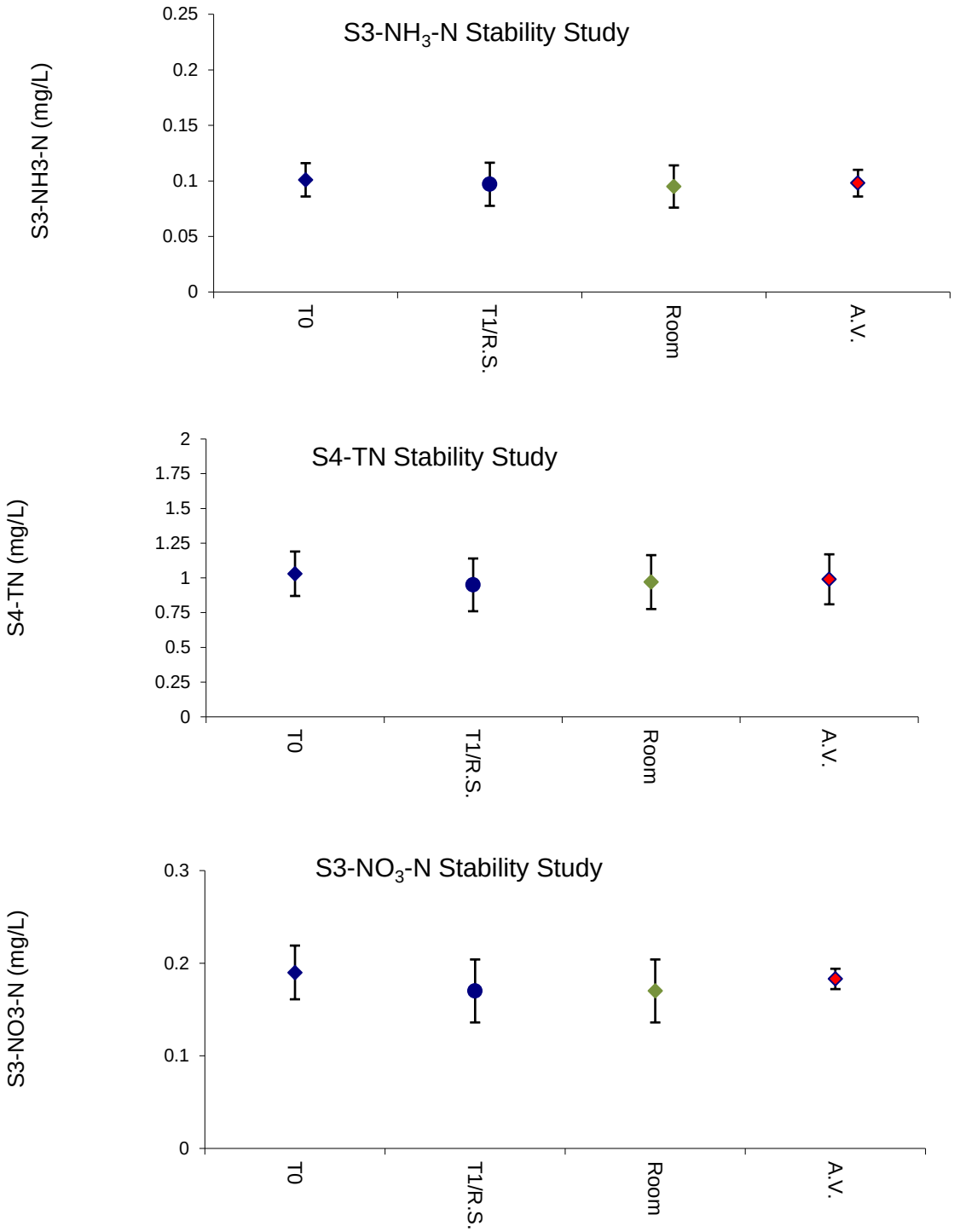

Figure 81 Stability Study Results

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

The assigned value was calculated as the robust average using the procedure described in ISO13258:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C[8] 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 74.

Table 74 Uncertainty of Assigned Value for As in Sample S1

No. results (p)	10
Robust Average	1.207 mg/L
$S_{rob\ av}$	0.156 mg/L
$u_{rob\ av}$	0.062 mg/L
k	2
$U_{rob\ av}$	0.12 mg/L

The assigned value for As in Sample S1 is **1.21 ± 0.12 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 1 and Equation 2 respectively (see page 13).

A worked example is set out below in Table 75.

Table 75 z-Score and E_n-score for As result reported by Laboratory 1 in S1

As Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E_n-Score
1.2±0.4	1.21±0.12	10% as CV or 0.10x1.21= =0.121 ug/L	$z = \frac{(1.2 - 1.21)}{0.121}$ z = -0.083	$En = \frac{(1.2 - 1.21)}{\sqrt{0.4^2 + 0.121^2}}$ E_n=-0.024

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can be used to estimate the uncertainty of their measurement results.[14, 12] An example is given below.

Between 2007 and 2014, NMI carried out fifteen proficiency tests of metals in water. These studies involved analyses of dissolved or acid-extractable metals at low and high levels in potable, fresh (river), saline water, ground water and waste water. Laboratory X participated and submitted satisfactory results in ten of these PTs.

Table 76 Ni Results for Laboratory X From Proficiency Testing Studies of Metals in Water.

Study No.	Sample	Laboratory result* µg/L	Assigned value µg/L	Robust CV of all results (%)	Number of Results
AQA 08-02	Fresh	51 ± 7.2	52.0 ± 3.1	9.9	18
AQA 08-10	Fresh	20 ± 3	18.9 ± 0.6	7.8	26
	Fresh	200 ± 20	191 ± 5	5.5	26
AQA 09-05	Saline	5.0 ± 1.2	5.5 ± 0.6	13.3	14
	Saline	43 ± 5	44.7 ± 3.3	10.8	18
AQA 09-18	Fresh	5.3 ± 0.5	5.04 ± 0.27	7.4	14
	Fresh	49 ± 4	48.9 ± 1.2	3.3	16
AQA 10-06	Potable	49 ± 4	50 ± 1	5.9	20
	Potable	48 ± 4	50 ± 1	3	20
AQA 11-17	Waste water	97 ± 9	99 ± 1	1.5	15
	Waste water	97 ± 9	98 ± 1	1.5	15
AQA 12-09	Fresh	43 ± 6	45 ± 2	6.6	19
	Fresh	51 ± 7	53 ± 2	7.5	19
AQA 12-20	Sea water	40 ± 4.4	38.4 ± 2.1	11	22
AQA 13-09	Fresh	4.3 ± 0.5	4.09 ± 0.17	8.5	15
	Fresh	36 ± 4	36.1 ± 1.0	4.5	16
AQA 14-08	Ground water	18.0 ± 2.0	19.1 ± 0.7	7.9	13
Average				6.8**	

* 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 6.8%. Using a coverage factor of 2 gives a relative expanded uncertainty of 14%, at a level of confidence of approximately 95%. Table 77 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the range 5 – 200 µg/L.

Table 77 Uncertainty of Ni results estimated using PT data.

Results µg/L	Uncertainty µg/L
5.0	0.7
20.0	2.8
50	7
200	28

The MU estimates made using PT data is close to Laboratory X's own uncertainty estimates reported with their PT results. The estimate of 14% passes the test of being reasonable, and the analysis of the six different matrices over three years can safely be assumed to include all the relevant uncertainty components (different operators, reagents, calibrants etc), and so complies with ISO 17025.[10]

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AFS	Atomic fluorescence spectroscopy
CRI	Collision Reaction Interface
CV	Coefficient of Variation
DA	Discreet Analyser
dNPOC	Dissolved non-purgeable organic carbon
DRC	Dynamic Reaction Cell
FIA	Flow Injection Analyser
HEHe	High energy He mode
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma - Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma - Optical Emission Spectrometry- radial view
ISE	Ion selective electrode
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
NEDD	N-(1-naphthyl)-ethylenediamine dihhydrochloride (NED dihydrochloride)
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NIR	Near-infrared
NT	Not Tested
ORS	Octopole Reaction System
PT	Proficiency Test
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
SFA	Segment Flow Analyser
SI	The International System of Units
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
SPANDS	2-(4-Sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalenedisulfonic Acid Trisodium Salt.
Target SD	Target standard deviation
σ	Target standard deviation
UC	Universal Cell
UV-Vis	Ultraviolet and Visible Spectroscopy
VGA	Vapour Generator Accessory

APPENDIX 6 - INSTRUMENT DETAILS FOR TOTAL AND DISSOLVED ELEMENTS

Table 78 Instrument Conditions Al

Lab Code	Instrument	Internal standard	Reaction /Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	1	1	27
2	ICP-OES-AV						
3	ICP-MS		ORS	He	1	10	
4	ICP-OES-AV				none	X12	167
5	ICP-MS	Ge	ORS	He	1.05	1.05	27
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	2	2	167.019
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			1	1	167.078
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	1	1	27
17					NA		

Table 79 Instrument Conditions Ag

Lab Code	Instrument	Internal standard	Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	NA	109
2	ICP-MS					NA	
3	ICP-MS		ORS	He	1	NA	
4	ICP-MS/MS					NA	107
5	ICP-MS	In	ORS	He	1.05	NA	107
6						NA	
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	NA	107
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh				NA	
11	ICP-OES-AV				NA	NA	
12	ICP-MS	In	NA	NA	1	NA	107
14						NA	
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Rh	UC	He	2	NA	109
17					NA	NA	

Table 80 Instrument Conditions As

Lab Code	Instrument	Internal standard	Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	He	1	1	75
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		ORS	He		X12	75
5	ICP-MS	Ge	ORS	He	1.05	1.05	75
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25		75
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ge	DRC	He	1	1	75
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Te	UC	He	1	1	75
17					NA		

Table 81 Instrument Conditions B

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	NA	NA	NA	1	10
2					NA	NA	
3					NA	NA	
4					NA		
5	ICP-OES-AV	Lu	NA	NA	NA	1.05	208.956
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	2	2	249.772
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh			NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	208.959
14					NA		
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	NA	1	10
17					NA		

Table 82 Instrument Conditions Ba

Lab Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	NA	1	138
2	ICP-MS				NA		
3	ICP-MS		ORS	He	NA	1	
4	ICP-MS/MS		ORS		NA		137
5	ICP-MS	Ir	ORS	He	NA	1.05	137
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	455.403
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh			NA		
11	ICP-OES-AV				NA		
12	ICP-MS	In	NA	NA	NA	1	137
14					NA		
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Tb	UC	He	NA	1	137
17					NA		

Table 83 Instrument Conditions Be

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	NA	NA	1	NA	9
2	ICP-MS					NA	
3	ICP-MS		ORS	NA	1	NA	
4	ICP-MS/MS		NA			NA	9
5	ICP-MS	Ge	ORS	He	1.05	NA	9
6						NA	
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Sc	ORS	NA	1.25	NA	9
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh				NA	
11	ICP-OES-AV				NA	NA	
12	ICP-MS	In	NA	NA	1	NA	9
14						NA	
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	**He**	**1**	NA	9
17					**NA**	NA	

Table 84 Instrument Conditions Ca

Lab Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	NA	1	44
2					NA	NA	
3					NA	NA	
4	ICP-OES-AV				NA	X12	315
5	ICP-OES-RV	Lu	NA	NA	NA	1.05	422.673
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	315.887
9	ICP-OES-RV	NA	NA	NA	NA	NA	317.933nm
10	ICP-OES-AV	Eu, Cs			NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	317.933
14					NA		
15	ICP-OES-AV	Y 371.029	NA	NA	NA	1	430.253
16	ICP-MS	Sc	UC	He	NA	1	43
17	CVAAS				NA		422.7

Table 85 Instrument Conditions Cd

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion (m/z)
1	ICP-MS	Rh	NA	NA	1	1	111
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		ORS			X12	111
5	ICP-MS	In	ORS	He	1.05	1.05	111
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	111
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	In	NA	NA	1	1	111
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm					228.80nm/ 0.6760nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Rh	UC	He	1	1	111
17					NA		

Table 86 Instrument Conditions Co

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	He	NA	1	59
2	ICP-MS				NA		
3	ICP-MS		ORS	He	NA	1	
4	ICP-MS/MS		ORS		NA	X12	59
5	ICP-MS	Ge	ORS	He	NA	1.05	59
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	NA	1.25	59
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh			NA		
11	ICP-OES-AV				NA		
12	ICP-MS	Ga	DRC	He	NA	1	59
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm			NA		240.73nm/ 0.1141nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Ga	UC	He	NA	1	59
17					NA		

Table 87 Instrument Conditions Cr

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	1	1	52
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		ORS			X12	52
5	ICP-MS	Ge	ORS	He	1.05	1.05	52
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	52
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ga	DRC	NH3	1	1	52
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	1	1	52
17					NA		

Table 88 Instrument Conditions Cu

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	He	1	1	63
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		ORS				
5	ICP-MS	Ge	ORS	He	1.05	1.05	63
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	63
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ga	DRC	He	1	1	63
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm					324.75nm/ 0.3693
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Ga	UC	He	1	1	63
17					NA		

Table 89 Instrument Conditions Fe

Lab Code	Instrument	Internal standard	Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	NA	1	56
2	ICP-OES-AV				NA		
3	ICP-MS		ORS	He	NA	10	
4	ICP-OES-AV				NA		
5	ICP-MS	Ge	ORS	He	NA	1.05	56
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	238.204
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh			NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	259.941
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm			NA		248.33nm/ 0.1164nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	NA	1	56
17	CVAAS				NA		248.3

Table 90 Instrument Conditions Hg

Lab Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	201
2	ICP-MS					NA	
3	ICP-MS		ORS	He	1	NA	
4						NA	
5	ICP-MS	Ir	ORS	He	1.05	NA	202
6						NA	
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Ir	ORS	He	1.25	NA	202
9	NA	NA	NA	NA	NA	NA	NA
10	FIMS					NA	
11	ICP-OES-AV				NA	NA	
12	CVAAS				2	NA	253.7
14						NA	
15	NA	NA	NA	NA	NA	NA	NA
16	CV-AFS	NA	NA	NA	5	NA	254 nm
17					NA	NA	

Table 91 Instrument Conditions K

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion (m/z)
1	ICP-MS	Sc	UC	He	NA	1	39
2					NA	NA	
3					NA	NA	
4	ICP-OES-AV-buffer				NA	X12	
5	ICP-OES-RV	Y	NA	NA	NA	1.05	766.491
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	766.491
9	ICP-OES-RV	NA	NA	NA	NA	NA	766.496nm
10	ICP-OES-AV	Eu, Cs			NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	769.896
14					NA		
15	ICP-OES-AV	Y 371.029	NA	NA	NA	1	769.897
16	ICP-MS	Sc	UC	He	NA	1	39
17					NA		

Table 92 Instrument Conditions Mg

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion (m/z)
1	ICP-MS	Sc	UC	He	NA	1	25
2					NA	NA	
3					NA	NA	
4	ICP-OES-AV-buffer				NA	X12	
5	ICP-OES-RV	Y	NA	NA	NA	1.05	285.213
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	279.8
9	ICP-OES-RV	NA	NA	NA	NA	NA	285.215nm
10	ICP-OES-AV	Eu, Cs			NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	285.213
14					NA		
15	ICP-OES-AV	Y 371.029	NA	NA	NA	1	277.983
16	ICP-MS	Sc	UC	He	NA	1	25
17	CVAAS				NA		

Table 93 Instrument Conditions Mn

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	1	1	55
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-OES-AV						
5	ICP-MS	Ge	ORS	He	1.05	1.05	55
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	55
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ga	DRC	He	1	1	55
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm					279.48nm/ 1.7508nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	1	1	55
17	CVAAS				NA		279.5

Table 94 Instrument Conditions Mo

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	NA	1	95
2	ICP-OES-AV				NA		
3	ICP-MS		ORS	He	NA	1	
4	ICP-MS/MS				NA	X12	98
5	ICP-MS	In	ORS	He	NA	1.05	95
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	NA	1.25	95
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh			NA		
11	ICP-OES-AV				NA		
12	ICP-MS	In	NA	NA	NA	1	95
14					NA		
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Rh	UC	He	NA	1	98
17					NA		

Table 95 Instrument Conditions Na

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion (m/z)
1	ICP-MS	Sc	UC	He	NA	1	23
2					NA	NA	
3					NA	NA	
4	ICP-OES-RV				NA		
5	ICP-OES-RV	Lu	NA	NA	NA	1.05	589.592
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	588.995
9	ICP-OES-RV	NA	NA	NA	NA	NA	589.591nm
10	ICP-OES-AV	Eu, Cs			NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	589.592
14					NA		
15	ICP-OES-AV	Y 371.029	NA	NA	NA	1	568.821
16	ICP-MS	Sc	UC	He	NA	1	23
17					NA		

Table 96 Instrument Conditions Ni

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	He	1	1	60
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		ORS			X12	60
5	ICP-MS	Ge	ORS	He	1.05	1.05	60
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	60
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ga	DRC	He	1	1	60
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Ga	UC	He	1	1	60
17					NA		

Table 97 Instrument Conditions P

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	NA	1	31
2					NA	NA	
3					NA	NA	
4					NA		
5	ICP-OES-AV	Lu	NA	NA	NA	1.05	177.434
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-OES-AV	Y	NA	NA	NA	2	213.618
9	ICP-OES-AV	NA	NA	NA	NA	NA	213.617nm
10					NA		
11	ICP-OES-AV				NA		
12	ICP-OES-AV-buffer	Yttrium			NA	1	177.495
14					NA		
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	NA	1	31
17					NA		

Table 98 Instrument Conditions Pb

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	1	206+207+208
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		NA			X12	208
5	ICP-MS	Ir	ORS	He	1.05	1.05	208
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Ir	ORS	He	1.25	1.25	207
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ir	NA	NA	1	1	208
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm					283.31nm/ 0.2263nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Tb	UC	He	1	1	206, 207, 208
17					NA		

Table 99 Instrument Conditions Sb

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	1	121
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		NA			X12	121
5	ICP-MS	In	ORS	He	1.05	1.05	121
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	121
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	In	NA	NA	1	1	121
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Rh	UC	He	1	1	121
17					NA		

Table 100 Instrument Conditions Se

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	DRC	NH3	1	1	82
2	ICP-MS						
3	ICP-MS		ORS	HEHe	1	1	
4	ICP-MS/MS		ORS	H2		X12	78
5	ICP-MS	Ge	ORS	H2	1.05	1.05	78
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	HEHe	1.25	1.25	78
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ge	DRC	He	1	1	78
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Te	UC	He	1	1	82
17					NA		

Table 101 Instrument Conditions Sn

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	1	118
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-MS/MS		NA			X12	118
5	ICP-MS	In	ORS	He	1.05	1.05	118
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	118
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	In	NA	NA	1	1	118
14							
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Rh	UC	He	1	1	120
17					NA		

Table 102 Instrument Conditions Tl

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	205
2	ICP-MS					NA	
3	ICP-MS		ORS	He	1	NA	
4	ICP-MS/MS		NA			NA	203
5	ICP-MS	Ir	ORS	He	1.05	NA	205
6						NA	
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Ir	ORS	He	1.25	NA	205
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh				NA	
11	ICP-OES-AV				NA	NA	
12	ICP-MS	Ir	NA	NA	1	NA	203
14						NA	
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Tb	UC	He	1	NA	205
17					NA	NA	

Table 103 Instrument Conditions U

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	NA	1	238
2	ICP-MS				NA		
3	ICP-MS		ORS	He	NA	1	
4	ICP-MS/MS		NA		NA	X12	238
5	ICP-MS	Ir	ORS	He	NA	1.05	238
6					NA		
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Ir	ORS	He	NA	1.25	238
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh			NA		
11	ICP-OES-AV				NA		
12					NA		
14					NA		
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Tb	UC	He	NA	1	238
17					NA		

Table 104 Instrument Conditions V

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	1	NA	51
2	ICP-OES-AV					NA	
3	ICP-MS		ORS	He	1	NA	
4	ICP-MS/MS		ORS	He		NA	51
5	ICP-MS	Ge	ORS	He	1.05	NA	51
6						NA	
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	NA	51
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh				NA	
11	ICP-OES-AV				NA	NA	
12	ICP-MS	Ga	DRC	He	1	NA	51
14						NA	
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Sc	UC	He	1	NA	51
17					NA	NA	

Table 105 Instrument Conditions Zn

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-MS	Ge	UC	He	1	1	66
2	ICP-MS						
3	ICP-MS		ORS	He	1	1	
4	ICP-OES-AV					X12	213
5	ICP-MS	Ge	ORS	He	1.05	1.05	66
6							
7	NA	NA	NA	NA	NA	NA	NA
8	ICP-MS	Rh	ORS	He	1.25	1.25	64
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir, Sc, Rh					
11	ICP-OES-AV				NA		
12	ICP-MS	Ga	DRC	NH3	1	1	66
14	Atomic Absorption	0.5ppm,1.5ppm,,2.0ppm Qc 1.0ppm					213.86nm/ 1.9536nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	Te	UC	He	1	1	66
17					NA		

APPENDIX 7 - METHODOLOGY FOR TESTS OTHER THAN TOTAL ELEMENTS IN S3 AND S4

Table 106 Measurement Methods and Instrumental Techniques for Dissolved Organic Carbon in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	APHA5310B
2	Persulfate-Heated Oxidation		
3	NA	NA	NA
4	High-Temperature Oxidation	NIR-detector	
5	NA	NA	NA
6			
7			
8	High-Temperature Oxidation	NIR-detector	APHA
9	NA	NA	NA
10			
11	NT		
12			
14			
15	Wet-Oxidation	NIR-detector	in house
16	NA	NA	NA
17			

Table 107 Measurement Methods and Instrumental Techniques for Fluoride in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	SPADNS Colorimetric Method	UV-Vis Spectrophotometer	W1
2	Ion Selective Electrode Method	Ion Selective Electrode	
3	NA	NA	NA
4	Ion Chromatographic Method	IC	
5	NA	NA	NA
6	Ion Chromatographic Method	IC	APHA 4110 B
7			
8	Ion Selective Electrode Method	Ion Selective Electrode	APHA
9	Ion Chromatographic Method	IC	APHA4110 B
10	Ion Selective Electrode Method	Ion Selective Electrode	In House
11	NT		
12	Ion Chromatographic Method	IC	APHA 4110B
14			
15	Ion Chromatographic Method	IC	in house
16	NA	NA	NA
17	Ion Selective Electrode Method	Ion Selective Electrode	APHA 4500-F-C

Table 108 Measurement Methods and Instrumental Techniques for Orthophosphate-P (FRP) in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-G
2	Ascorbic Acid Colorimetric Method	SFA	
3	NA	NA	NA
4	Ascorbic Acid Colorimetric Method	DA	
5	NA	NA	NA
6			
7	Ascorbic Acid Colorimetric Method	FIA	APHA
8	Ascorbic Acid Colorimetric Method	DA	APHA
9	NA	Not Applicable	NA
10	Vanadomolybdophosphoric Colorimetric Method	DA	In House
11	NT		
12			
14			
15	Ascorbic Acid Colorimetric Method	FIA	in house
16	NA	NA	NA
17			

Table 109 Measurement Methods and Instrumental Techniques for Nitrate-N in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500NO3-F
2	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	
3	NA	NA	NA
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	
5	NA	NA	NA
6	Ion Chromatographic Method	IC	APHA 4110 B
7	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
9	Ion Chromatographic Method	IC	APHA4110 B
10	Colorimetric -vanadium III method	DA	In House
11	DA		
12			
14	Colorimetric method	colorimetry meter-Aqua fast AQ3700	Thermo scientific colorimetry user guide
15	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	in house
16	NA	NA	NA
17			

Table 110 Measurement Methods and Instrumental Techniques for Sulphate in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	ICP Method	ICP-MS	W32
2	Turbidimetric Method	DA	
3	NA	NA	NA
4	Ion Chromatographic Method	IC	
5	NA	NA	NA
6	Ion Chromatographic Method	IC	APHA 4110 B
7			
8	Turbidimetric Method	DA	APHA
9	Ion Chromatographic Method	IC	APHA4110 B
10	Turbidimetric Method	DA	In House
11	NT		
12	Ion Chromatographic Method	IC	APHA 4110B
14	Colorimetric Method	colorimetry meter-Aqua fast AQ3700	Thermo scientific colorimetry meter user guide
15	Ion Chromatographic Method	IC	in house
16	NA	NA	NA
17	Turbidimetric Method	Turbidity Meter	APHA 4500-SO4 E

Table 111 Measurement Methods and Instrumental Techniques for Total Dissolved Nitrogen in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	APHA4500P-J
2	Persulfate digestion	SFA	
3	NA	NA	NA
4			
5	NA	NA	NA
6			
7	Persulfate digestion	FIA	APHA
8	Persulfate digestion	FIA	APHA
9	Persulfate digestion	UV-Vis Spectrophotometer	APHA4500 C
10	Calculation (TKN+NOx)	DA	In House
11	NT		
12			
14	Colorimetric Method	colorimetry meter-Aqua fast AQ3700	Thermo scientific colorimetry meter user guide
15	Calculation (TKN+NOx)	FIA	in house
16	NA	NA	NA
17			

Table 112 Measurement Methods and Instrumental Techniques for Total Dissolved Phosphorus in S3

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
2	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	SFA	
3	NA	NA	NA	NA
4				
5	NA	NA	NA	NA
6				
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
8		ICP Method	ICP-OES	
9	HNO3-Digestion	ICP Method	ICP-OES	APHA3120
10	H2SO4+K2SO4-Digestion	Stannous Chloride Colorimetric Method	DA	In House
11	NT			
12		Ion Chromatographic Method	IC	APHA 4110B
14		Colorimetric Method	colorimetry meter-Aqua fast AQ3700	Thermo scientific colorimetry meter user guide
15	Ascorbic Acid Colorimetric Method		FIA	in house
16	NA	NA	NA	NA
17				

Table 113 Measurement Methods and Instrumental Techniques for Alkalinity to pH4.5 as ($Ca\ CO_3$) in S4

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Auto Titration	APHA2320B
2	NA	NA	NA
3	NA	NA	NA
4	Titration	Manual Analysis	
5			
6	Titration	Manual Analysis	APHA-2320
7			
8	Titration	Auto Titration	APHA
9	Titration	Manual Analysis	APHA2320 B
10	Titration	Auto Titration	In House
11		Titrate	
12	Titration	Ion Selective Electrode	APHA 2320B
14	Titration	Manual Analysis	Lenore S. Clesceri, Arnold E. Greenberg, Andrew D. Eaton
15	Titration	Auto Titration	in house
16	NA	NA	NA
17	Titration	Auto Titration	APHA 2320 B

Table 114 Measurement Methods and Instrumental Techniques for Colour (Apparent) in S4

Lab. Code	Measurement Method	Instrument	Method Reference
1	Spectrophotometric Method	UV-Vis Spectrophotometer	W1
2	NA	NA	NA
3	NA	NA	NA
4			
5			
6			
7			
8	Spectrophotometric Method	DA	APHA
9	NA	Not Applicable	NA
10	Spectrophotometric Method	UV-Vis Spectrophotometer	In House
11		Meter	
12	Spectrophotometric Method	UV-Vis Spectrophotometer	APHA 2120C
14	Visual Comparison Method	Manual Analysis	Lenore S. Clesceri, Arnold E. Greenberg, Andrew D. Eaton
15	Spectrophotometric Method	UV-Vis Spectrophotometer	in house
16	NA	NA	NA
17			

Table 115 Measurement Methods and Instrumental Techniques Used for Silica (as SiO_2) in S4

Lab. Code	Measurement Method	Instrument	Method Reference
1	ICP-Method	ICP-MS	W32
2	NA	NA	NA
3	NA	NA	NA
4			
5			
6			
7	Molybdosilicate Method	FIA	
8	ICP-Method	ICP-OES	
9	ICP-Method	ICP-OES	APHA 3120
10	Molybdosilicate Method	DA	In House
11		NT	
12	ICP-Method	ICP-OES	USEPA 2001 Method 200.7
14	colorimeter	AQ3700	Thermo scientific colorimetry user guide
15	Molybdosilicate Method	DA	in house
16	NA	NA	NA
17			

Table 116 Measurement Methods and Instrumental Techniques Used for Total Hardness (as $CaCO_3$) in S4

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	Manual Analysis	W21
2	NA	NA	NA
3	NA	NA	NA
4			
5	Calculation	ICP-OES	APHA 2340B
6	Calculation	ICP-MS	APHA 3125
7			
8	Calculation	ICP-OES	APHA
9	Calculation	ICP-OES	APHA 3120
10	Calculation	Not Applicable	In House
11		Titrate	
12			
14			
15	Calculation	ICP-OES	in house
16	NA	NA	NA
17	Calculation	AAS	APHA 2340 B

Table 117 Measurement Methods and Instrumental Techniques Used for Total Kjeldahl Nitrogen in S4

Lab. Code	Measurement Method		Instrument	Method Reference
1	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	Calculation
2	NA	NA	NA	NA
3	NA	NA	NA	NA
4				
5				
6				
7				
8	TKN=TN-NOx (K2S2O8 digestion)	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA
9	TKN=TN-Nox	Calculation	IC and UV-Vis	APHA 2340
10	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric -vanadium III method	DA	In House
11			NT	
12				
14				Thermo scientific colorimetry user guide
15	Kjeldahl (H2SO4+K2SO4 digestion)	Colorimetric - salicylate method	FIA	in house
16	NA	NA	NA	NA
17				

Table 118 Measurement Methods and Instrumental Techniques Used for Total Phosphorus in S4

Lab. Code	Measurement Method		Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA4500P-J
2	NA	NA	NA	NA
3	NA	NA	NA	NA
4				
5	HNO3+HCl	ICP Method	ICP-OES	In house method referenced to USEPA 6010
6	K2S2O8-Digestion	Ion Chromatographic Method	IC	ASTM D8001-16E1
7	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	APHA
8		ICP Method	ICP-OES	
9	HNO3-Digestion	ICP Method	ICP-OES	APHA 3120
10	H2SO4+K2SO4-Digestion	Vanadomolybdophosphoric Colorimetric Method	DA	In House
11			ICP OES	
12				
14		colorimeter	AQ3700	Thermo scientific colorimetry user guide
15	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	FIA	in house
16	NA	NA	NA	NA
17				

Table 119 Measurement Methods and Instrumental Techniques Used for Total Nitrogen in S4

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	APHA4500P-J
2	NA	NA	NA
3	NA	NA	NA
4			
5			
6	Persulfate digestion	IC	ASTM D8001-16E1
7	Persulfate digestion	FIA	APHA
8	Persulfate digestion	FIA	APHA
9	Persulfate digestion	UV-Vis Spectrophotometer	APHA4500 C
10	Calculation (TKN+NOx)	Not Applicable	In House
11		NT	
12			
14	colorimetre	AQ3700	Thermo scientific colorimetry user guide
15	Calculation (TKN+NOx)	FIA	in house
16	NA	NA	NA
17			

Table 120 Measurement Methods and Instrumental Techniques Used for Total Organic Carbon in S4

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	APHA5310B
2	NA	NA	NA
3	NA	NA	NA
4	High-Temperature Oxidation	NIR-detector	
5			
6			
7			
8	High-Temperature Oxidation	NIR-detector	APHA
9	NA	NA	NA
10			
11		NT	
12			
14			
15	Wet-Oxidation	NIR-detector	in house
16	NA	NA	NA
17			

END OF STUDY