Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 23-18 Trace Elements in River and Sea Water

February 2024

ACKNOWLEDGMENTS

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

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

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

Luminita Antin

Andrew Evans

Hamish Lenton

Shobhna Chandra

Raluca Iavetz

Manager, Chemical Reference Values

Phone: 61-2-9449 0111
proficiency@measurement.gov.au

Accredited for compliance with ISO/IEC 17043

THIS PAGE IS INTENTIONALLY BLANK

TABLE OF CONTENTS

Summary

This report presents the results of the proficiency test AQA 23-18, Trace Elements in River and Sea Water. The study focused on the measurement of dissolved Ag, Al, As, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Sb, Se, Sn, Ti, Tl, U, V and Zn in sea water and of dissolved Ag, Al, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, U, V and Zn in river water.

The assigned values were the robust averages of participants' results. The associated uncertainties were estimated from the robust standard deviation of participants' results.

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

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

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

Of 379 scored results, 363 (96%) returned a satisfactory score of $|z| \leq 2.0$.

Of 379 scored results, 344 (91%) returned a satisfactory score of $|En| \leq 1.0$.

Laboratory 12 reported results for all 42 tests.

Laboratory 6 reported results for all 38 tests for which a z-score was calculated and returned satisfactory z-scores for all of them.

Laboratory 8 had the highest number of satisfactory E_n scores, 38 out of 38 reported.

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

The results reported for trace elements in the sea water sample (S1) were more variable and had more unsatisfactory results than those of freshwater sample (S2). Arsenic, Cr and Ni in sea water were the tests which challenged most participants analytical techniques when compared to the river water sample.

For As measurements in sea water participants reported using ICP-MS in collision mode with He or ICP-MS in reaction mode with O_2. For Ni and Cr measurements in sea water most participants reported using ICP-MS in collision mode.

A limited number of laboratories reported results for P, Sn and Ti.

Low level Be and Fe in sea water were the tests which presented the most analytical difficulty to participating laboratories with CVs of 27% and 28% respectively.

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

AQA 23-18 is the 33rd NMI proficiency study of metals in water. Over last 10 years, the average proportion of satisfactory scores was 91% for z-scores and 84% for E_n-scores.

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 392 numerical results, 390 (99%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 3.2% to 333% of the reported value. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 3.

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

Surplus test samples from the present study are available for sale. A certified reference material for metals in sea water (MX014) with reference values traceable to SI is also available for sale from NMI.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

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

AQA 23-18 is the 33rd NMI proficiency study of metals in water.

1.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories methods used in determination of inorganic analytes in river and sea 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.

1.3 Study Conduct

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

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

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The 42 tests were selected from those for which an investigation level is published in Australian and New Zealand Guidelines for Fresh and Marine Water Quality[5] and are commonly measured by water testing laboratories.

2.2 Participation

Thirteen laboratories participated and eleven submitted results.

The timetable of the study was:

Invitation issued:	16 October 2023
Samples dispatched:	13 November 2023
Results due:	15 December 2023
Interim report issued	18 December 2023
Preliminary report issued:	19 December 2023

2.3 Test Material Specification

Two samples were provided for analysis:

Sample S1 was 100 mL of filtered sea water preserved by adding 2% (v/w) nitric acid; and

Sample S2 was 100 mL of filtered river water preserved by adding 2% (v/w) nitric acid and 0.01% (v/w) hydrochloric acid.

2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.5 Sample Preparation, Analysis and Homogeneity Testing

A partial homogeneity test was conducted in this study. The same validated preparation procedure was followed as in previous studies.[2] Test samples from previous studies were demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. The results from the partial homogeneity test are reported in this study as the homogeneity values. No homogeneity testing was conducted for Al in S1.

The preparation and analysis are described in Appendix 1.

2.6 Stability of Analytes

No stability study was carried out for Samples S1 and S2. Stability studies conducted for similar previous studies of metals in river and sea water including the MX014 certification found no significant changes in any of the analytes' concentration.

2.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were refrigerated before dispatch.

The samples were dispatched by courier on 13 November 2023.

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

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

2.8 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 samples chilled.
- Participants are asked to report results in units of µg/L for:

SAMPLE S1 sea water		SAMPLE S2 river water	
Test DISSOLVED	**Estimated Value µg/L**	**Test DISSOLVED**	**Estimated Value µg/L**
Ag	0.5-20	Ag	0.5-20
Al	1-40	Al	50-2000
As	0.5-20	As	0.5-20
Be	0.5-20	Be	0.5-20
Cd	0.5-20	Cd	0.5-20
Cr	0.5-20	Co	0.5-20
Cu	1-400	Cr	0.5-20
Fe	10-400	Cu	2-80
Hg	0.025-1	Fe	20-800
Mn	0.5-20	Hg	0.05-2
Ni	0.5-20	Mn	2-80
P	10-400	Mo	1-40
Pb	0.5-20	Ni	0.5-20
Sb	0.5-20	Pb	0.5-20
Se	0.5-20	Sb	1-40
Sn	0.5-20	Se	0.5-20
Ti	0.5-20	Ti	1-40
Tl	0.5-20	Tl	0.5-20
U	0.5-20	U	0.5-20
V	0.5-20	V	0.5-20
Zn	1-40	Zn	2-80

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (e.g. 5.23 ± 0.51 µg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.
- Please return the completed results sheet by 1 December 2023.

The due date for results was extended to 15 December 2023 due to staffing issues with some participants.

2.9 Interim Report

An interim report was emailed to participants on 18 December 2023.

A preliminary report was issued on 19 December 2023. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants.

The following was changed from the preliminary report in the present final report: the uncertainty of the spike value for Cr in S1 was changed from 0.06 µg/L to 0.13 µg/L to incorporate the uncertainty of the incurred value too.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Methodology for Dissolved Elements

Summaries of test methods are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 5.

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	HNO_3 (mL)	HCl (mL)	Other (mL)
2*	EPA6020 and APHA3112	10	95	120	0.25		0.5 (H_2SO_4)
3*	USEPA SW846 6020B						
4	APHA 3125 B						
5	In House W32 (River water) In House W32a (Seawater) referencing APHA 3125						
6*	APHA 3125; USEPA SW846 - 6020	10	98	120	0.5		
10	APHA 3125, EPA 200.8	5	95	120	2	1	

*Additional Information in Table 2.

3.2 Additional Information

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

Table 2 Additional information

Lab Code	Additional Information
1	Sample S1and S2: Sample analysed 'as is'.
2	Methodology: 1.5 mL $KMnO_4$ and 1 mL $K_2S_2O_8$ were also added into digestion tube. Instrument Techniques: Collision/Reaction Cell with Kinetic Energy Discrimination.
3	Methodology: No digestion performed.
6	Sample S1and S2: Sample analysed as received.
13	Methodology: Direct analysis.

3.3 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[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
2	Professional judgment	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Inhouse Method
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
4	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis		Eurachem/CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	CRM Recoveries of SS	Eurachem/CITAC Guide
8	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis		
10	Other	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies	Eurachem/CITAC Guide
12		Control Samples Duplicate Analysis Instrument Calibration	CRM	
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537

[a] RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples.

3.4 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. Such feedback may be useful in improving future studies. Participants' comments are reproduced in Table 4.

Table 4 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
"If possible, Bi is included in the next study."	Thank you for your feedback, we will include Bi in our future studies.
For S1: "Good concentration range"	Thank you for your feedback.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 5 to 46 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 43. An example chart with an interpretation guide is shown in Figure 1.

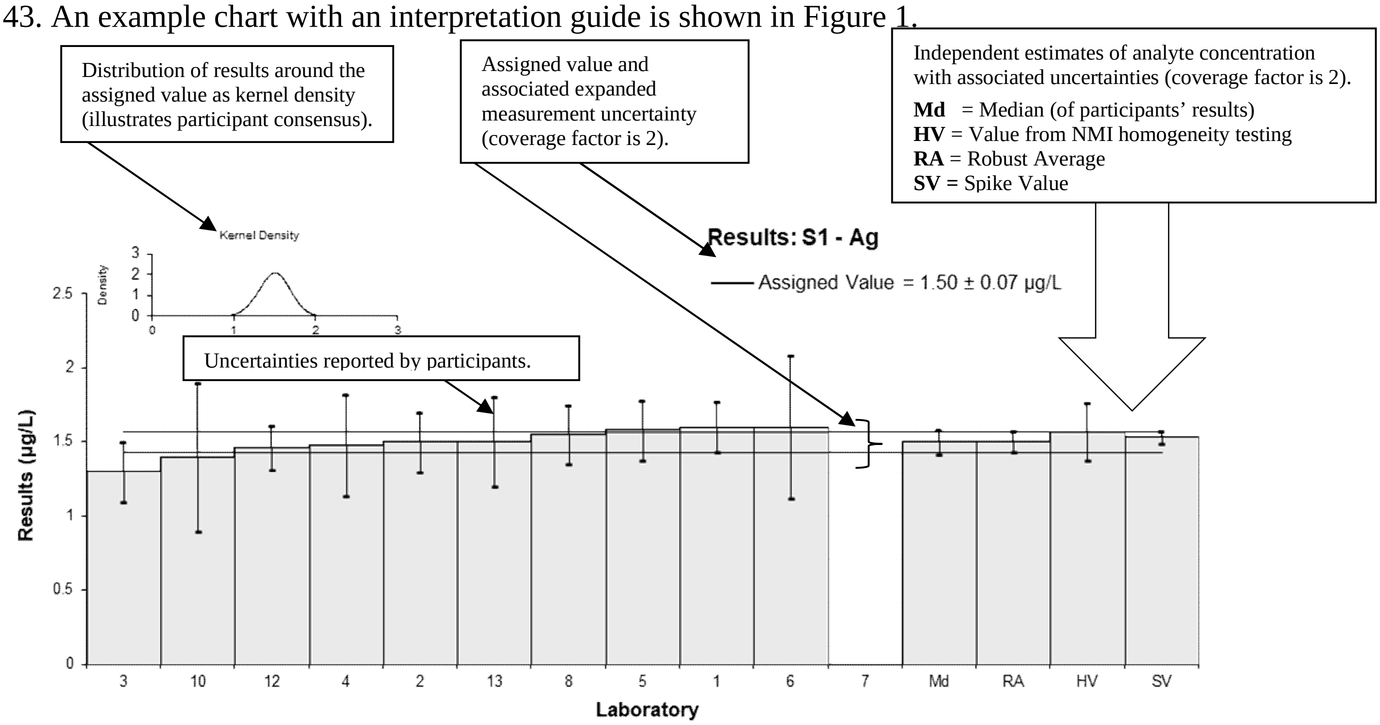


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

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

4.3 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 2. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'[1] In this study, the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, outliers removed; the expanded uncertainties were estimated from the associated robust standard deviations.[4, 6]

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by inter-laboratory comparisons, ISO13528'.[6] The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528.[6]

4.5 Target Standard Deviation for Proficiency Assessment

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

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

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

4.6 z-Score

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

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

where:

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

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

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

4.7 E_n-Score

An example of E_n-score calculation using data from the present study is given in Appendix 2. 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 participants' result;
- X is the assigned value;
- U_χ is the expanded uncertainty of the participants' result;
- U_X is the expanded uncertainty of the assigned value.

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

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

4.8 Traceability and Measurement Uncertainty

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

5 TABLES AND FIGURES

Table 5

Sample Details

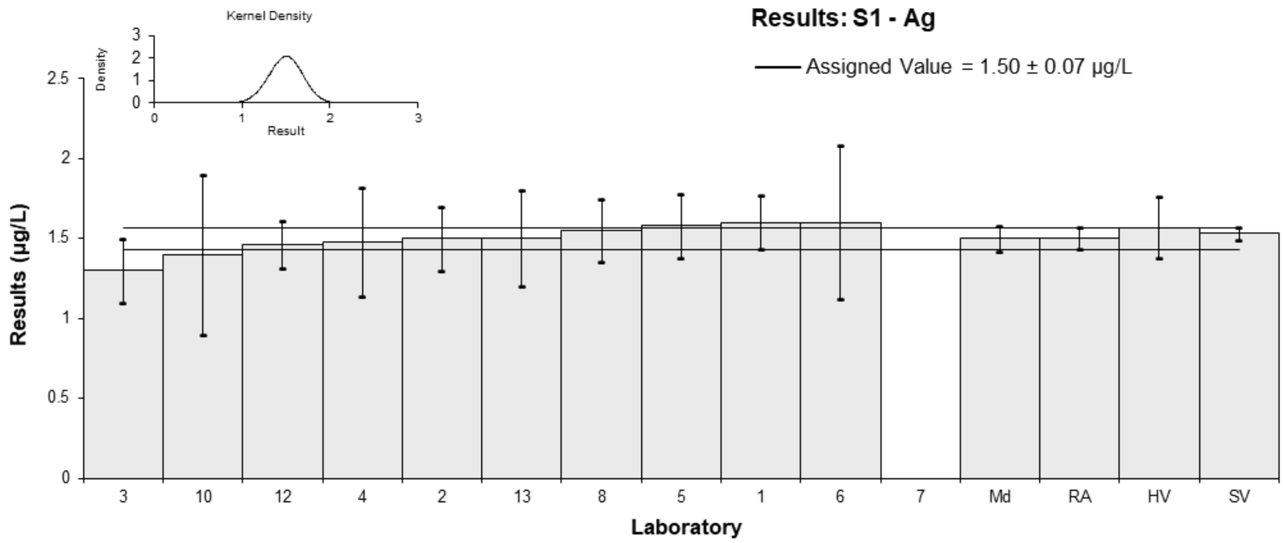
Sample No.	S1
Matrix	Sea Water
Analyte	Ag
Unit	µg/L

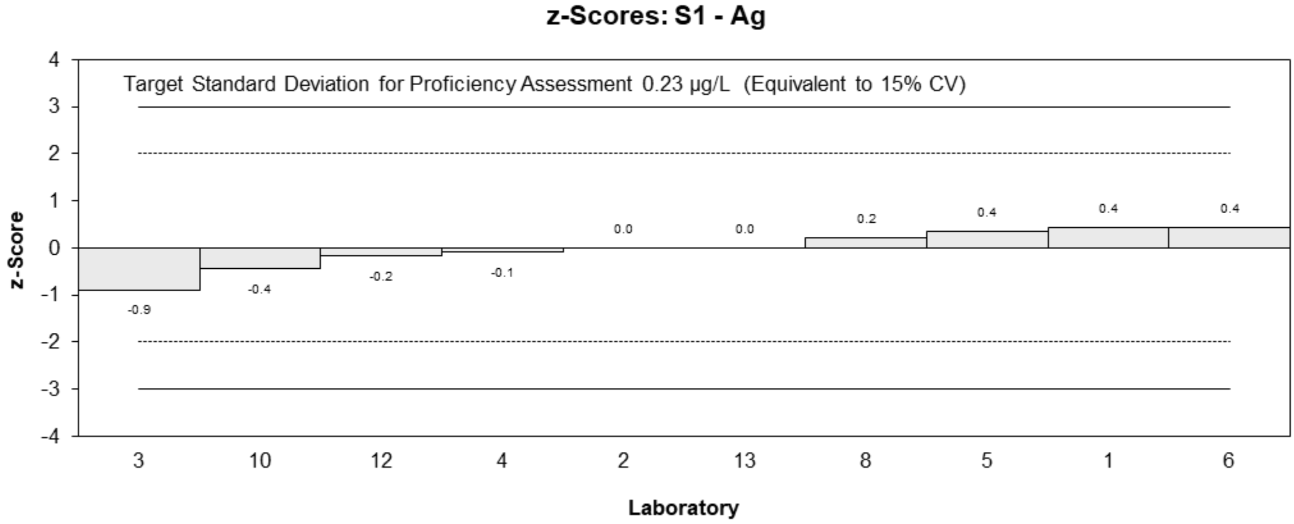
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.6	0.17	0.44	0.54
2	1.5	0.2	0.00	0.00
3	1.3	0.2	-0.89	-0.94
4	1.48	0.34	-0.09	-0.06
5	1.58	0.2	0.36	0.38
6	1.6	0.48	0.44	0.21
7	<5	NR		
8	1.55	0.20	0.22	0.24
10	1.4	0.5	-0.44	-0.20
12	1.46	0.15	-0.18	-0.24
13	1.5	0.3	0.00	0.00

Statistics

Assigned Value	1.50	0.07
Spike Value	1.53	0.04
Homogeneity Value	1.57	0.19
Robust Average	1.50	0.07
Median	1.50	0.08
Mean	1.50	
N	10	
Max	1.6	
Min	1.3	
Robust SD	0.092	
Robust CV	6.1%	


Results: S1 - Ag
Assigned Value = 1.50 ± 0.07 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3
10
12
4
2
13
8
5
1
6
7
Md
RA
HV
SV


z-Scores: S1 - Ag
Target Standard Deviation for Proficiency Assessment 0.23 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.9
-0.4
-0.2
-0.1
0.0
0.0
0.2
0.4
0.4
0.4

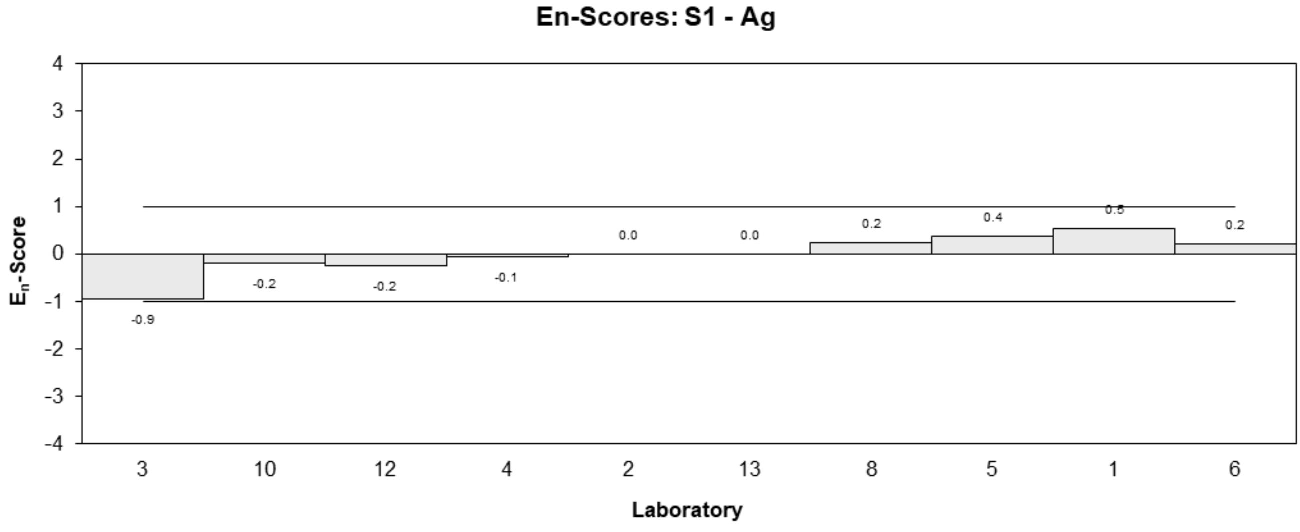

En-Scores: S1 - Ag
En-Score
Laboratory
-0.9
-0.2
-0.2
-0.1
0.0
0.0
0.2
0.4
0.5
0.2

Figure 2

Table 6

Sample Details

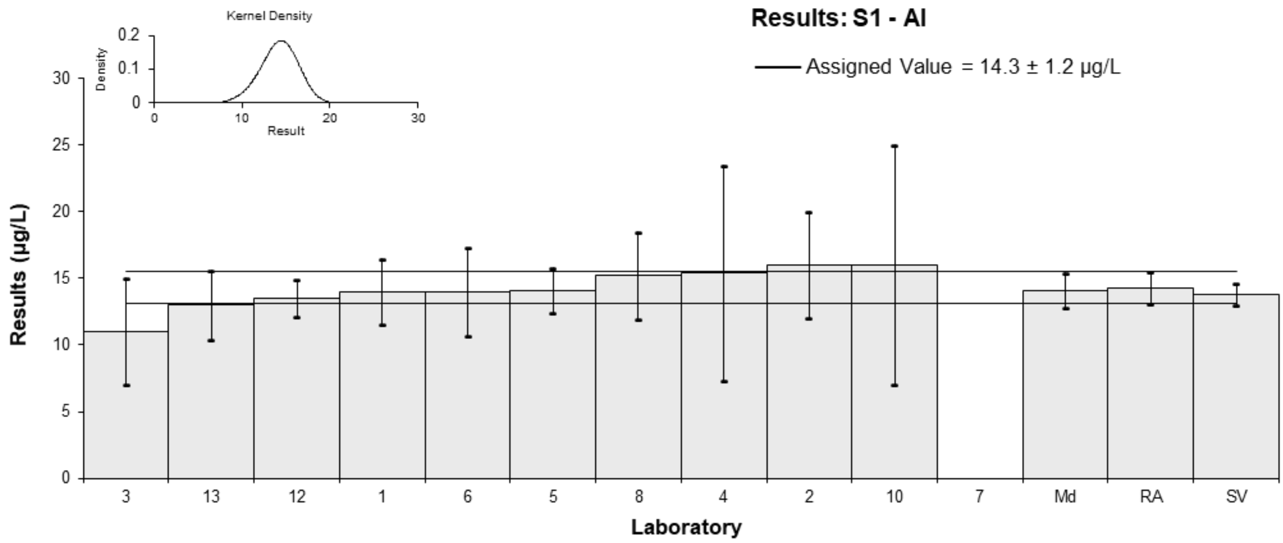
Sample No.	S1
Matrix	Sea Water
Analyte	Al
Unit	µg/L

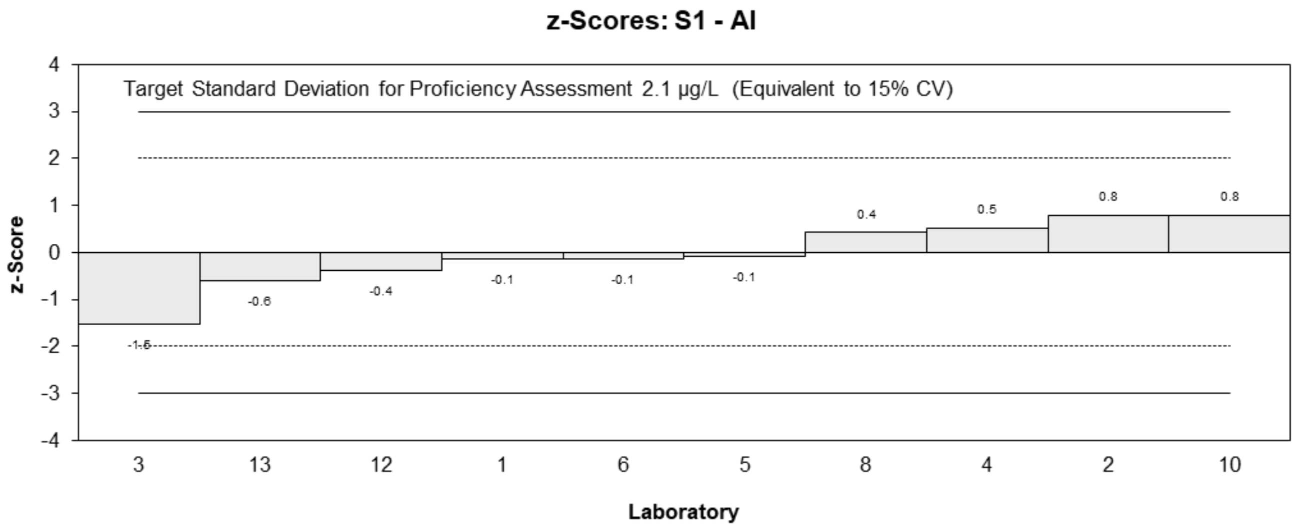
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	14	2.46	-0.14	-0.11
2	16	4	0.79	0.41
3	11	4	-1.54	-0.79
4	15.4	8.1	0.51	0.13
5	14.1	1.7	-0.09	-0.10
6	14	3.3	-0.14	-0.09
7	<50	NR		
8	15.2	3.3	0.42	0.26
10	16	9	0.79	0.19
12	13.48	1.4	-0.38	-0.44
13	13	2.6	-0.61	-0.45

Statistics

Assigned Value	14.3	1.2
Spike Value	13.8	0.8
Robust Average	14.3	1.2
Median	14.1	1.3
Mean	14.2	
N	10	
Max	16	
Min	11	
Robust SD	1.5	
Robust CV	10%	


Results: S1 - Al
Assigned Value = 14.3 ± 1.2 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3
13
12
1
6
5
8
4
2
10
7
Md
RA
SV


z-Scores: S1 - Al
Target Standard Deviation for Proficiency Assessment 2.1 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.5
-0.6
-0.4
-0.1
-0.1
-0.1
0.4
0.5
0.8
0.8
3
13
12
1
6
5
8
4
2
10

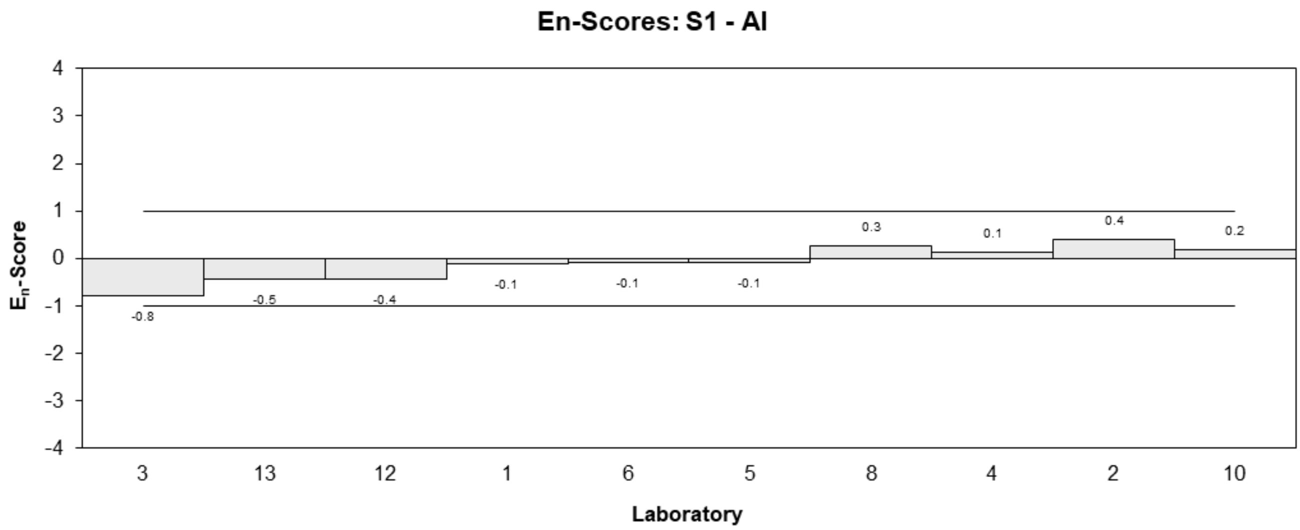

En-Scores: S1 - Al
En-Score
Laboratory
-0.8
-0.5
-0.4
-0.1
-0.1
-0.1
0.3
0.1
0.4
0.2
3
13
12
1
6
5
8
4
2
10

Figure 3

Table 7

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	As
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	5.0	0.73	0.18	0.15
2	4.5	1.1	-0.51	-0.31
3	4.3	0.3	-0.78	-1.07
4	5.2	2.8	0.45	0.12
5	4.18	0.5	-0.94	-1.04
6	5.5	0.77	0.86	0.71
7	5.157	0.3899	0.39	0.49
8	5.01	0.65	0.19	0.18
10	7.3	5	3.33	0.48
12	4.63	0.46	-0.33	-0.38
13	4.4	0.88	-0.64	-0.48

Statistics

Assigned Value	4.87	0.44
Spike Value	4.42	0.41
Homogeneity Value	4.52	0.54
Robust Average	4.87	0.44
Median	5.00	0.56
Mean	5.02	
N	11	
Max	7.3	
Min	4.18	
Robust SD	0.58	
Robust CV	12%	

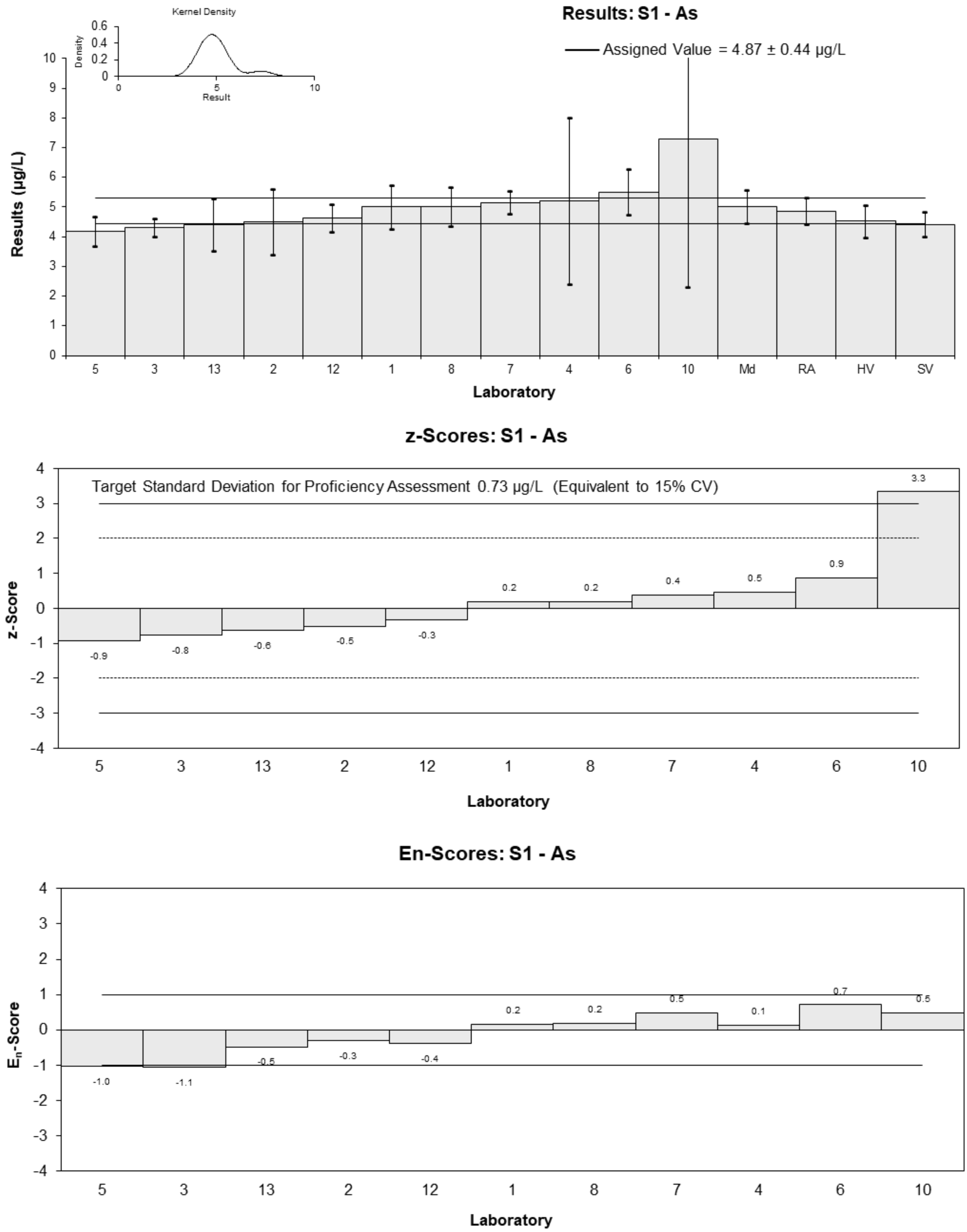

Results: S1 - As
Assigned Value = 4.87 ± 0.44 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5 3 13 2 12 1 8 7 4 6 10 Md RA HV SV
z-Scores: S1 - As
Target Standard Deviation for Proficiency Assessment 0.73 µg/L (Equivalent to 15% CV)
-0.9 -0.8 -0.6 -0.5 -0.3 0.2 0.2 0.4 0.5 0.9 3.3
z-Score
Laboratory
5 3 13 2 12 1 8 7 4 6 10
En-Scores: S1 - As
-1.0 -1.1 -0.5 -0.3 -0.4 0.2 0.2 0.5 0.1 0.7 0.5
En-Score
Laboratory
5 3 13 2 12 1 8 7 4 6 10

Figure 4

Table 8

Sample Details

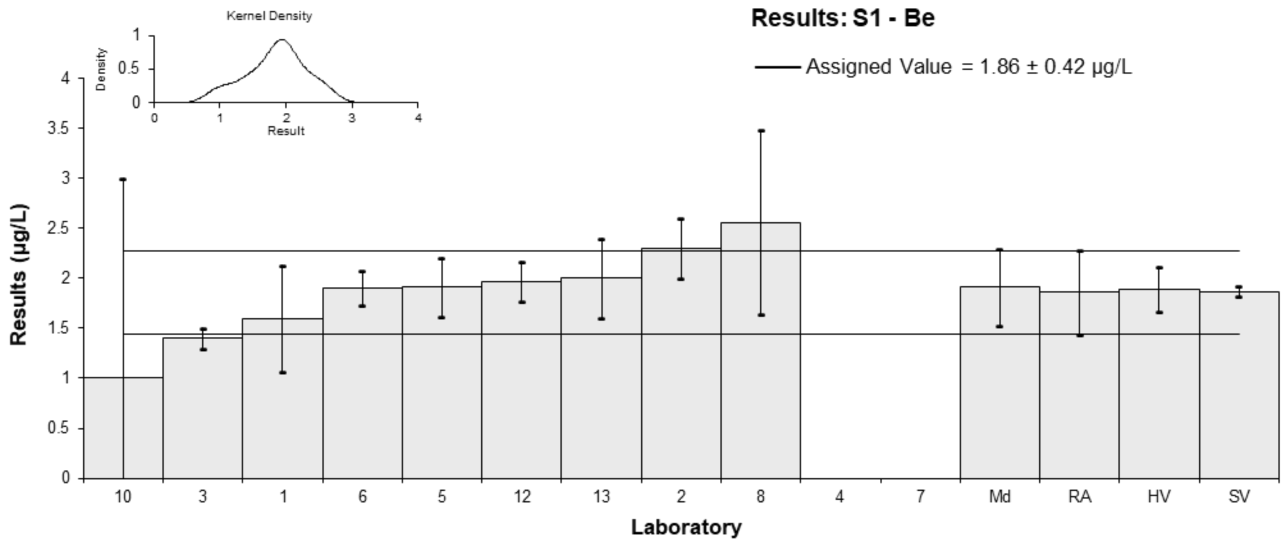
Sample No.	S1
Matrix	Sea Water
Analyte	Be
Unit	µg/L

Participant Results

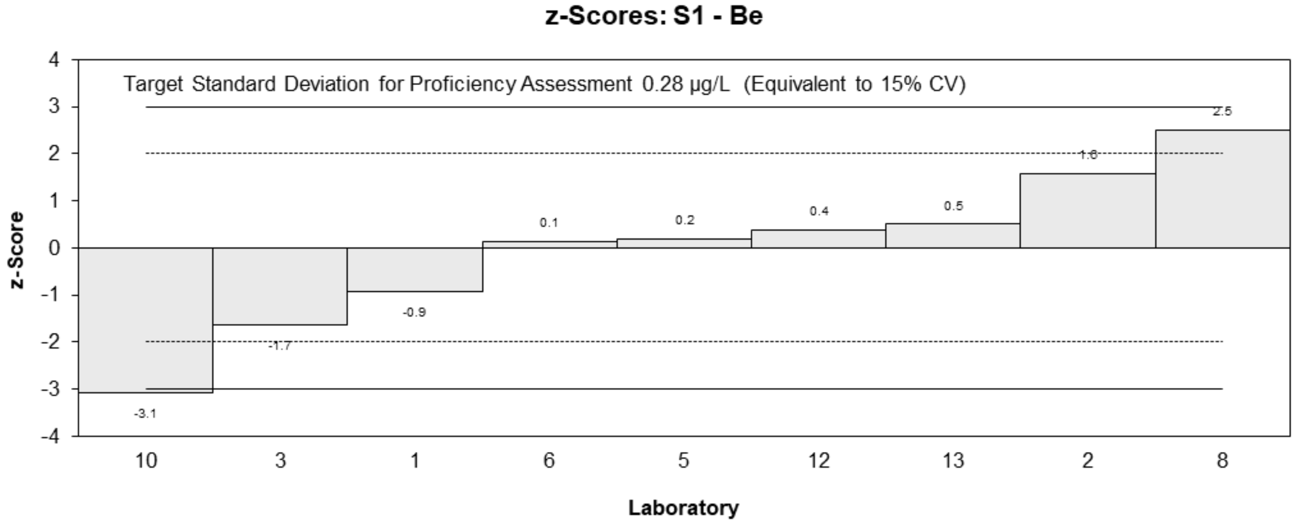
Lab. Code	Result	Uncertainty	z	E_n
1	1.6	0.53	-0.93	-0.38
2	2.3	0.3	1.58	0.85
3	1.4	0.1	-1.65	-1.07
4	NT	NT		
5	1.91	0.3	0.18	0.10
6	1.9	0.17	0.14	0.09
7	<5	NR		
8	2.56	0.92	2.51	0.69
10	1	2	-3.08	-0.42
12	1.97	0.2	0.39	0.24
13	2.0	0.4	0.50	0.24

Statistics

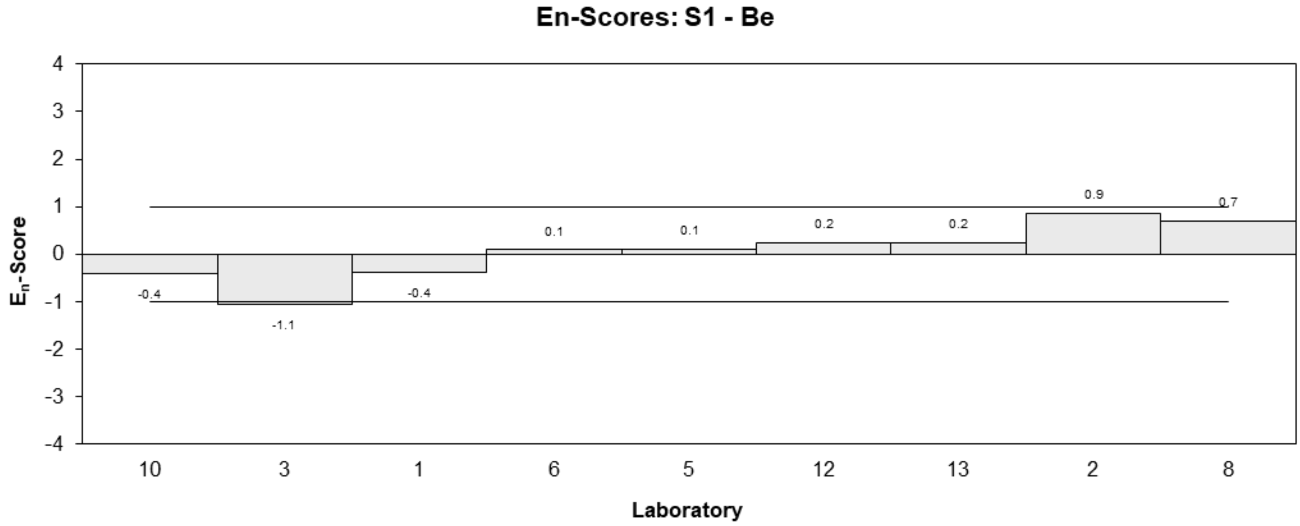
Assigned Value	1.86	0.42
Spike Value	1.87	0.05
Homogeneity Value	1.89	0.23
Robust Average	1.86	0.42
Median	1.91	0.38
Mean	1.85	
N	9	
Max	2.56	
Min	1	
Robust SD	0.50	
Robust CV	27%	



Results: S1 - Be
Assigned Value = 1.86 ± 0.42 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
10
3
1
6
5
12
13
2
8
4
7
Md
RA
HV
SV



z-Scores: S1 - Be
Target Standard Deviation for Proficiency Assessment 0.28 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-3.1
-1.7
-0.9
0.1
0.2
0.4
0.5
1.6
2.5



En-Scores: S1 - Be
En-Score
Laboratory
-0.4
-1.1
-0.4
0.1
0.1
0.2
0.2
0.9
0.7

Figure 5

Table 9

Sample Details

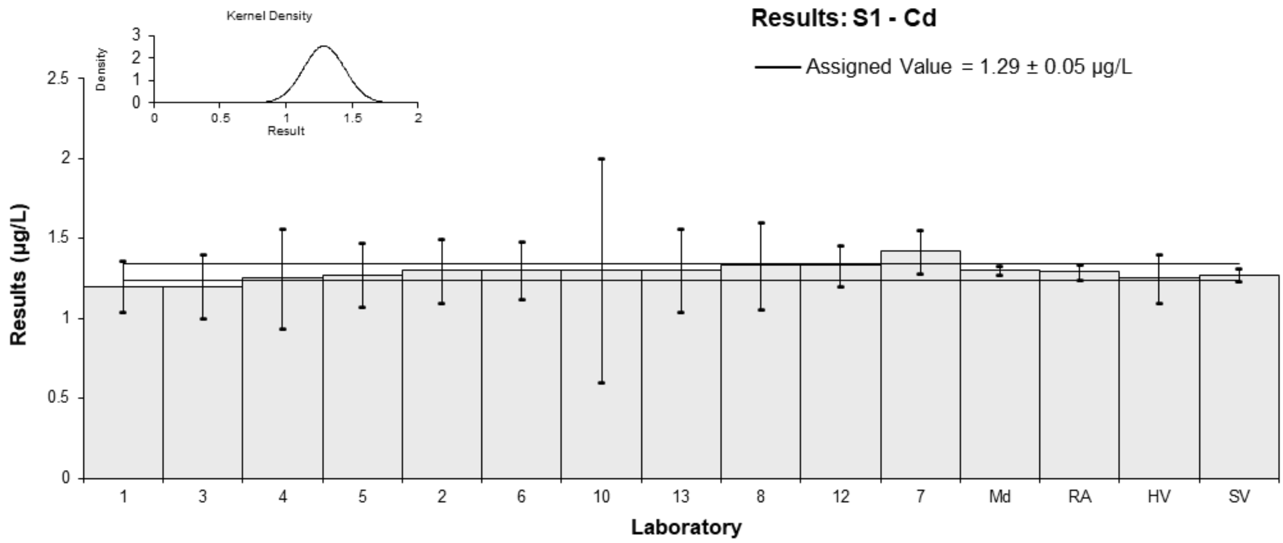
Sample No.	S1
Matrix	Sea Water
Analyte	Cd
Unit	µg/L

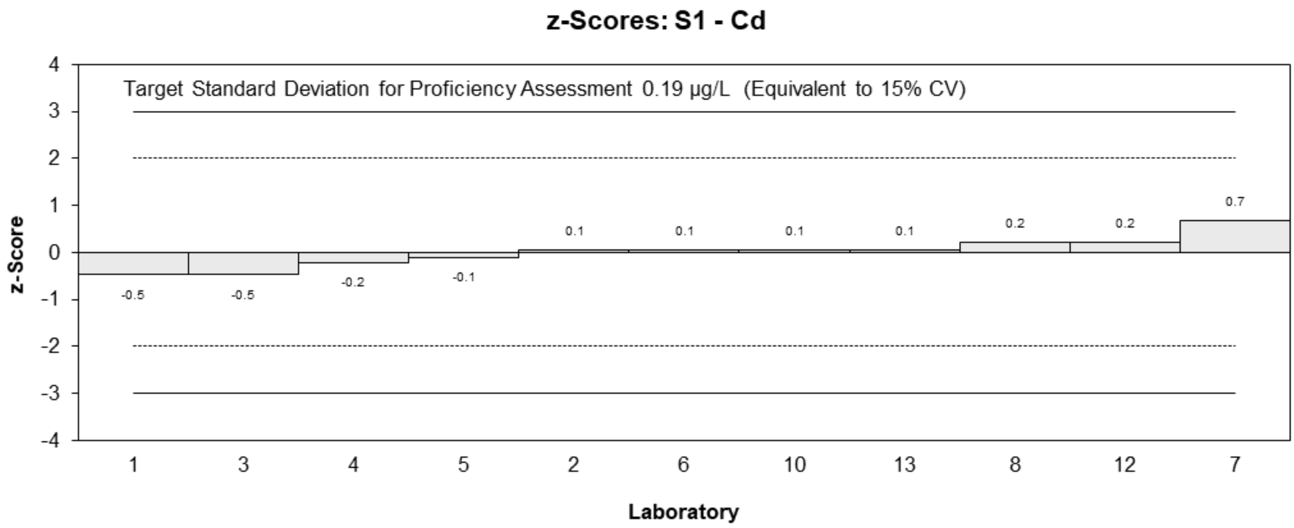
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.2	0.16	-0.47	-0.54
2	1.3	0.2	0.05	0.05
3	1.2	0.2	-0.47	-0.44
4	1.25	0.31	-0.21	-0.13
5	1.27	0.2	-0.10	-0.10
6	1.3	0.18	0.05	0.05
7	1.419	0.1362	0.67	0.89
8	1.33	0.27	0.21	0.15
10	1.3	0.7	0.05	0.01
12	1.33	0.13	0.21	0.29
13	1.3	0.26	0.05	0.04

Statistics

Assigned Value	1.29	0.05
Spike Value	1.27	0.04
Homogeneity Value	1.25	0.15
Robust Average	1.29	0.05
Median	1.30	0.03
Mean	1.29	
N	11	
Max	1.419	
Min	1.2	
Robust SD	0.062	
Robust CV	4.8%	


Results: S1 - Cd
Assigned Value = 1.29 ± 0.05 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1 3 4 5 2 6 10 13 8 12 7 Md RA HV SV


z-Scores: S1 - Cd
Target Standard Deviation for Proficiency Assessment 0.19 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
1 3 4 5 2 6 10 13 8 12 7
-0.5 -0.5 -0.2 -0.1 0.1 0.1 0.1 0.1 0.2 0.2 0.7

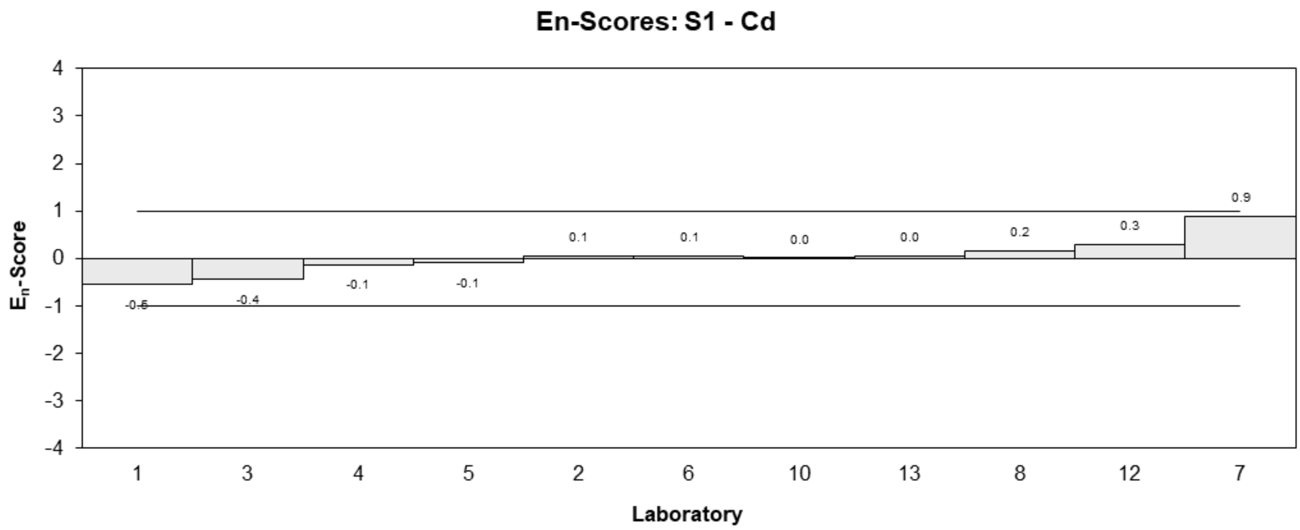

En-Scores: S1 - Cd
En-Score
Laboratory
1 3 4 5 2 6 10 13 8 12 7
-0.5 -0.4 -0.1 -0.1 0.1 0.1 0.0 0.0 0.2 0.3 0.9

Figure 6

Table 10

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Cr
Unit	µg/L

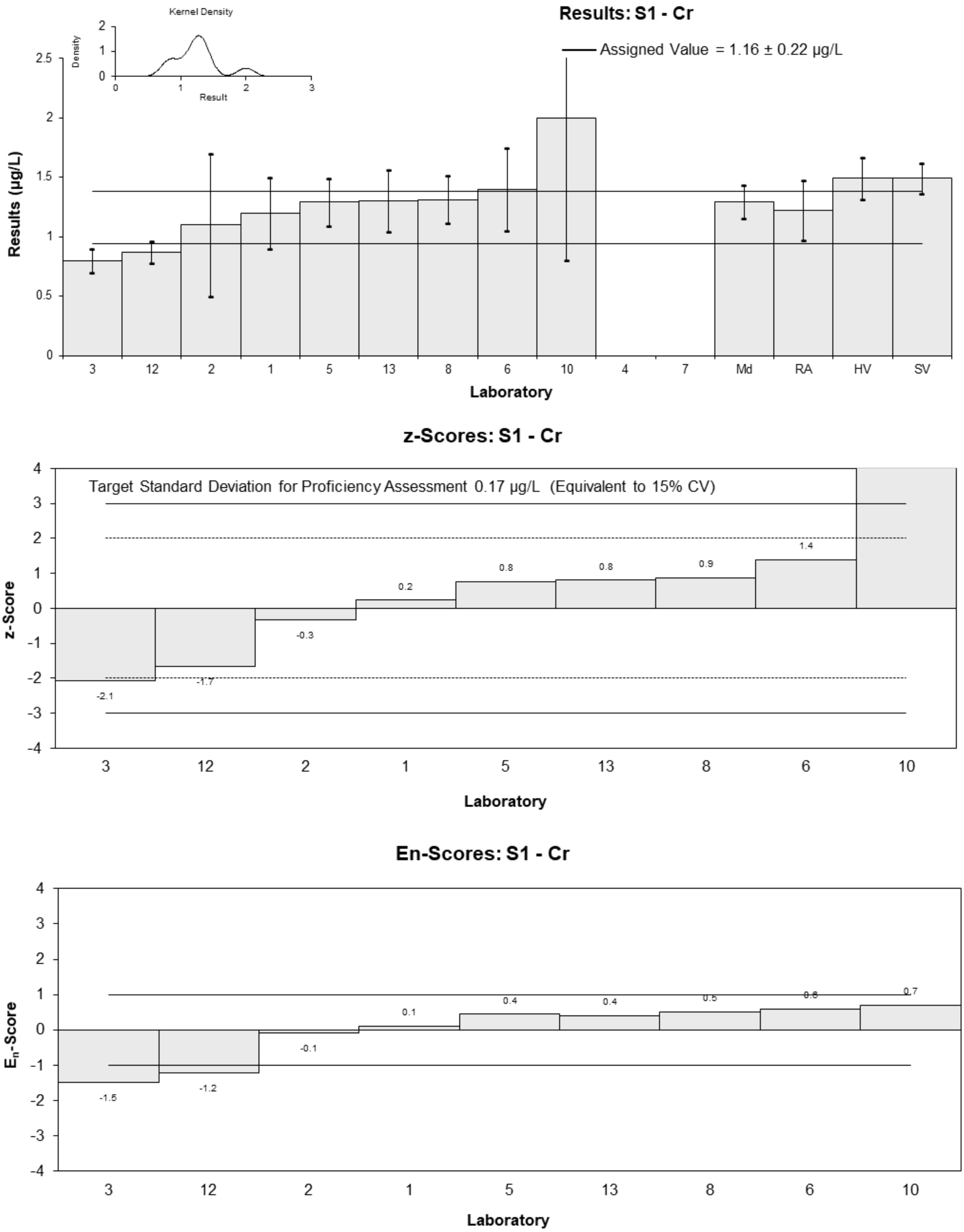
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.2	0.3	0.23	0.11
2	1.1	0.6	-0.34	-0.09
3	0.8	0.1	-2.07	-1.49
4	<2	0.74		
5	1.29	0.2	0.75	0.44
6	1.4	0.35	1.38	0.58
7	<5	NR		
8	1.31	0.20	0.86	0.50
10*	2	1.2	4.83	0.69
12	0.87	0.09	-1.67	-1.22
13	1.3	0.26	0.80	0.41

* Outlier, see Section 4.2

Statistics

Assigned Value	1.16	0.22
Spike Value	1.49	0.13
Homogeneity Value	1.49	0.18
Robust Average	1.22	0.25
Median	1.29	0.14
Mean	1.25	
N	9	
Max	2	
Min	0.8	
Robust SD	0.30	
Robust CV	25%	



Results: S1 - Cr
Assigned Value = 1.16 ± 0.22 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3 12 2 1 5 13 8 6 10 4 7 Md RA HV SV
z-Scores: S1 - Cr
Target Standard Deviation for Proficiency Assessment 0.17 µg/L (Equivalent to 15% CV)
z-Score
-2.1 -1.7 -0.3 0.2 0.8 0.8 0.9 1.4
Laboratory
3 12 2 1 5 13 8 6 10
En-Scores: S1 - Cr
En-Score
-1.5 -1.2 -0.1 0.1 0.4 0.4 0.5 0.6 0.7
Laboratory
3 12 2 1 5 13 8 6 10

Figure 7

Table 11

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Cu
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	9.0	1.37	-0.48	-0.48
2	9.7	1.2	0.00	0.00
3	10	1	0.21	0.27
4	8.8	2.2	-0.62	-0.40
5	9.35	1.0	-0.24	-0.32
6	11	1.6	0.89	0.78
7	10.017	0.7914	0.22	0.34
8	10.3	1.8	0.41	0.32
10	10	2	0.21	0.15
12	9.57	0.96	-0.09	-0.12
13	9.3	1.9	-0.27	-0.20

Statistics

Assigned Value	9.70	0.48
Spike Value	9.75	0.75
Homogeneity Value	9.7	1.2
Robust Average	9.70	0.48
Median	9.70	0.39
Mean	9.73	
N	11	
Max	11	
Min	8.8	
Robust SD	0.64	
Robust CV	6.6%	

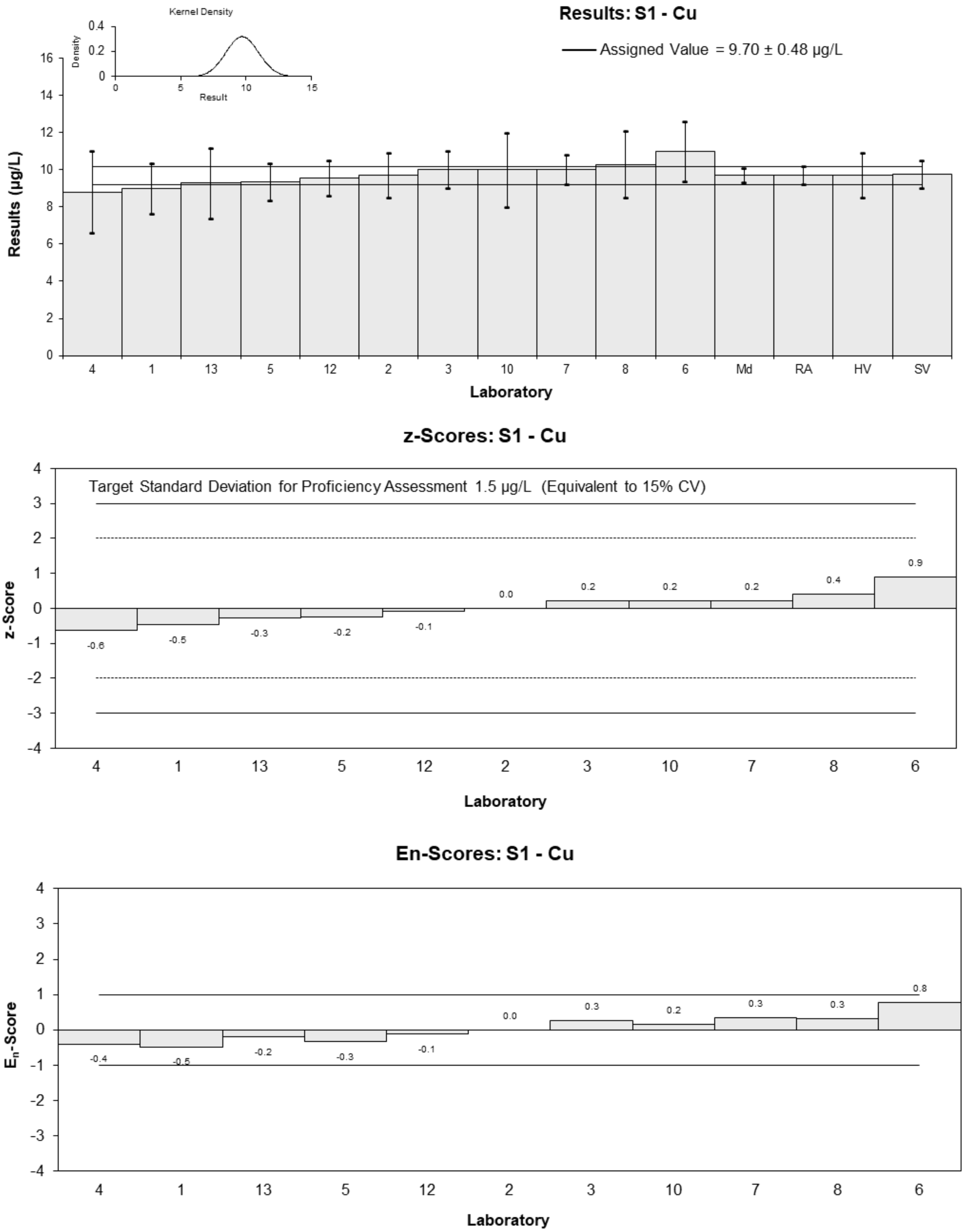

Results: S1 - Cu
Assigned Value = 9.70 ± 0.48 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
4 1 13 5 12 2 3 10 7 8 6 Md RA HV SV
z-Scores: S1 - Cu
Target Standard Deviation for Proficiency Assessment 1.5 µg/L (Equivalent to 15% CV)
z-Score
-0.6 -0.5 -0.3 -0.2 -0.1 0.0 0.2 0.2 0.2 0.4 0.9
4 1 13 5 12 2 3 10 7 8 6
Laboratory
En-Scores: S1 - Cu
E_n-Score
-0.4 -0.5 -0.2 -0.3 -0.1 0.0 0.3 0.2 0.3 0.3 0.8
4 1 13 5 12 2 3 10 7 8 6
Laboratory

Figure 8

Table 12

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Fe
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	16	0.8	-2.66	-1.78
2	33	8	1.60	0.64
3	25	7	-0.40	-0.17
4	25.9	4.1	-0.18	-0.10
5	34.2	4.0	1.90	1.07
6	22	NR	-1.15	-0.78
7	<250	NR		
8	21.0	2.9	-1.40	-0.85
10	32	7	1.35	0.59
12	22.08	2.2	-1.13	-0.72
13	35	7	2.11	0.92

Statistics

Assigned Value	26.6	5.9
Spike Value	24.6	1.0
Homogeneity Value	25.9	3.1
Robust Average	26.6	5.9
Median	25.5	6.4
Mean	26.6	
N	10	
Max	35	
Min	16	
Robust SD	7.4	
Robust CV	28%	

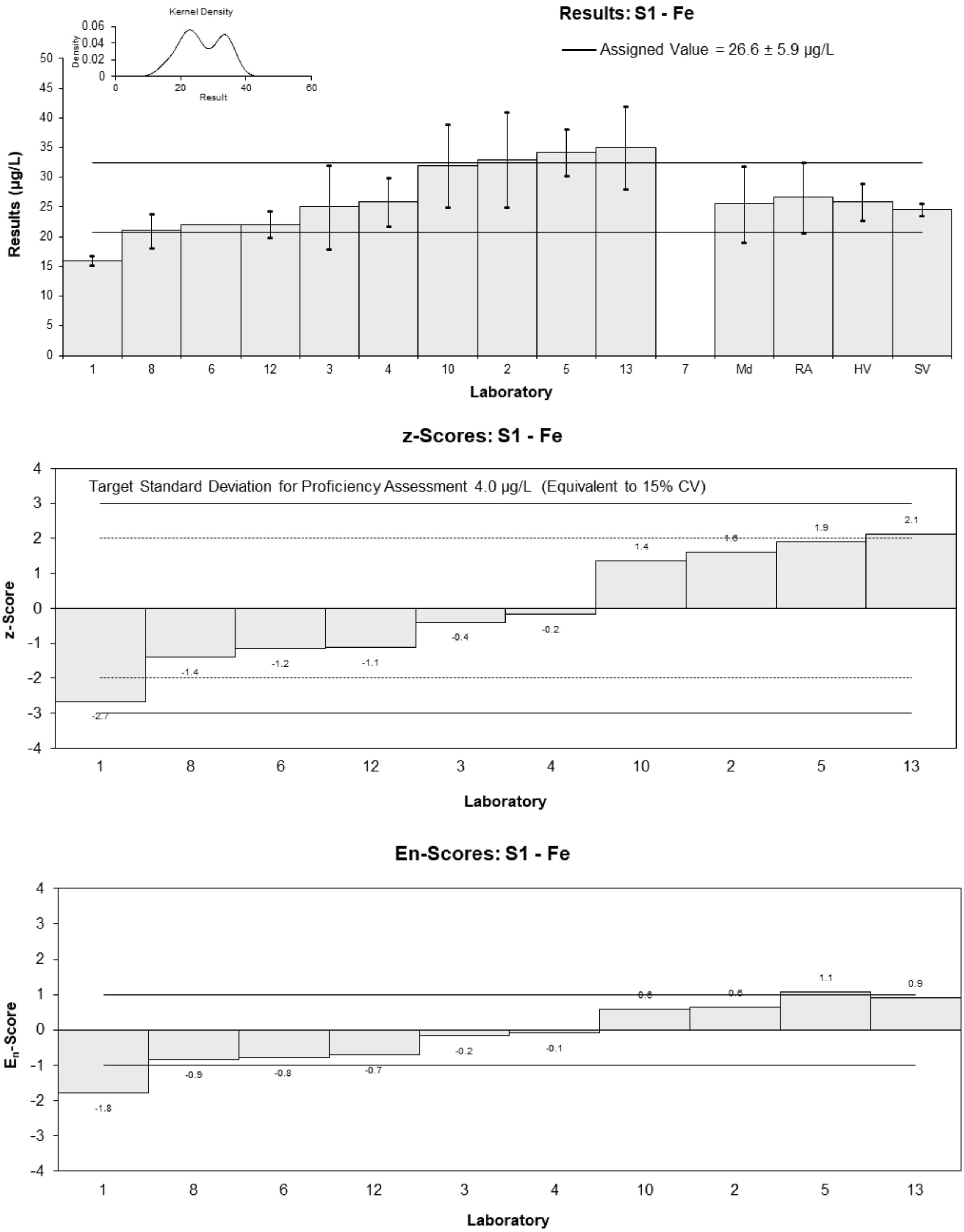

Kernel Density
Density
Result
Results: S1 - Fe
Assigned Value = 26.6 ± 5.9 µg/L
Results (µg/L)
1
8
6
12
3
4
10
2
5
13
7
Md
RA
HV
SV
Laboratory
z-Scores: S1 - Fe
Target Standard Deviation for Proficiency Assessment 4.0 µg/L (Equivalent to 15% CV)
z-Score
-2.7
-1.4
-1.2
-1.1
-0.4
-0.2
1.4
1.6
1.9
2.1
Laboratory
En-Scores: S1 - Fe
E_n-Score
-1.8
-0.9
-0.8
-0.7
-0.2
-0.1
0.6
0.6
1.1
0.9
Laboratory

Figure 9

Table 13

Sample Details

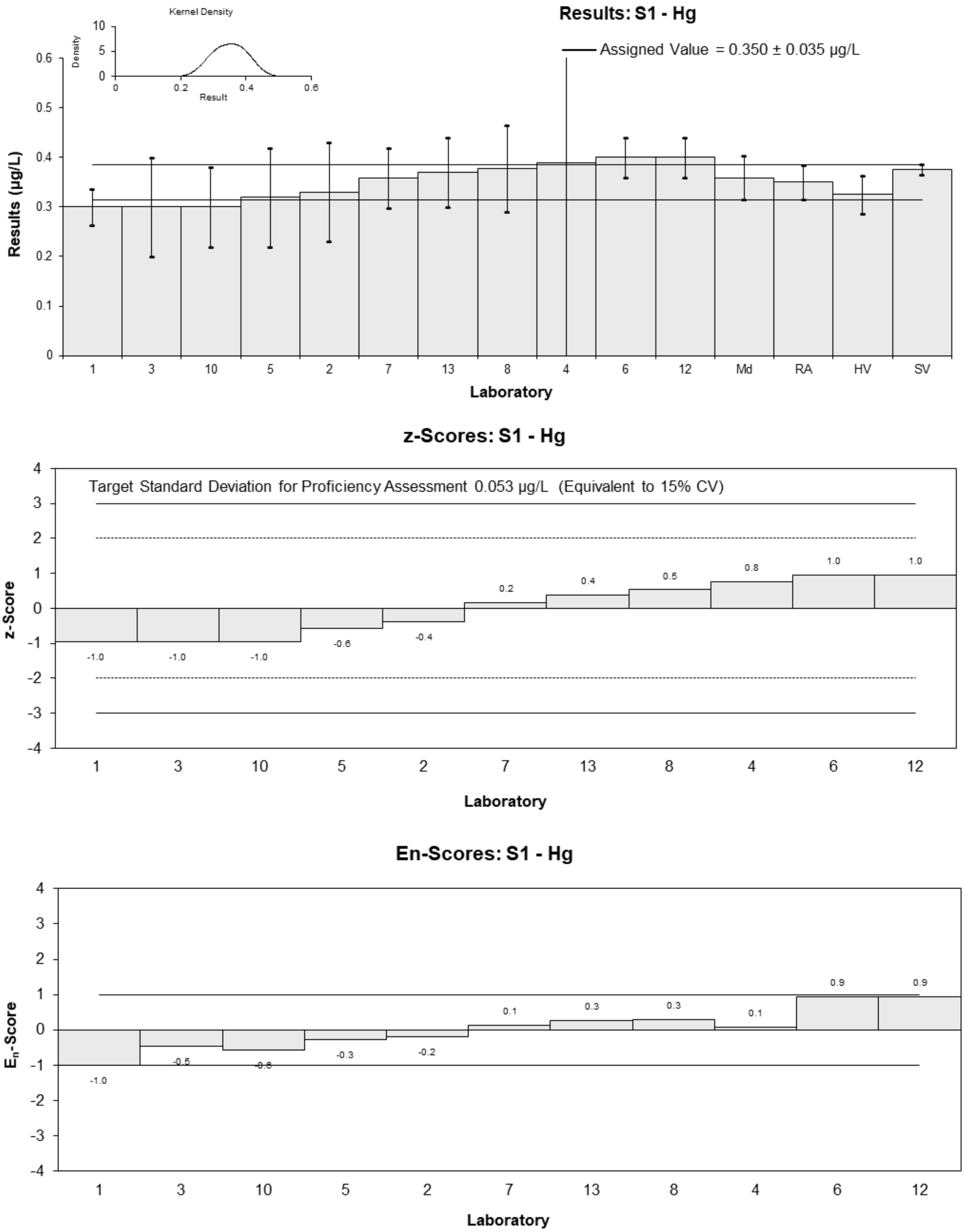
Sample No.	S1
Matrix	Sea Water
Analyte	Hg
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.3	0.036	-0.95	-1.00
2	0.33	0.1	-0.38	-0.19
3	0.3	0.1	-0.95	-0.47
4	0.39	0.53	0.76	0.08
5	0.32	0.1	-0.57	-0.28
6	0.4	0.04	0.95	0.94
7	0.359	0.061	0.17	0.13
8	0.378	0.087	0.53	0.30
10	0.3	0.08	-0.95	-0.57
12	0.4	0.04	0.95	0.94
13	0.37	0.07	0.38	0.26

Statistics

Assigned Value	0.350	0.035
Spike Value	0.376	0.011
Homogeneity Value	0.325	0.039
Robust Average	0.350	0.035
Median	0.359	0.044
Mean	0.350	
N	11	
Max	0.4	
Min	0.3	
Robust SD	0.046	
Robust CV	13%	



Results: S1 - Hg
Assigned Value = 0.350 ± 0.035 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1 3 10 5 2 7 13 8 4 6 12 Md RA HV SV
z-Scores: S1 - Hg
Target Standard Deviation for Proficiency Assessment 0.053 µg/L (Equivalent to 15% CV)
z-Score
-1.0 -1.0 -1.0 -0.6 -0.4 0.2 0.4 0.5 0.8 1.0 1.0
1 3 10 5 2 7 13 8 4 6 12
Laboratory
En-Scores: S1 - Hg
En-Score
-1.0 -0.5 -0.6 -0.3 -0.2 0.1 0.3 0.3 0.1 0.9 0.9
1 3 10 5 2 7 13 8 4 6 12
Laboratory

Figure 10

Table 14

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Mn
Unit	µg/L

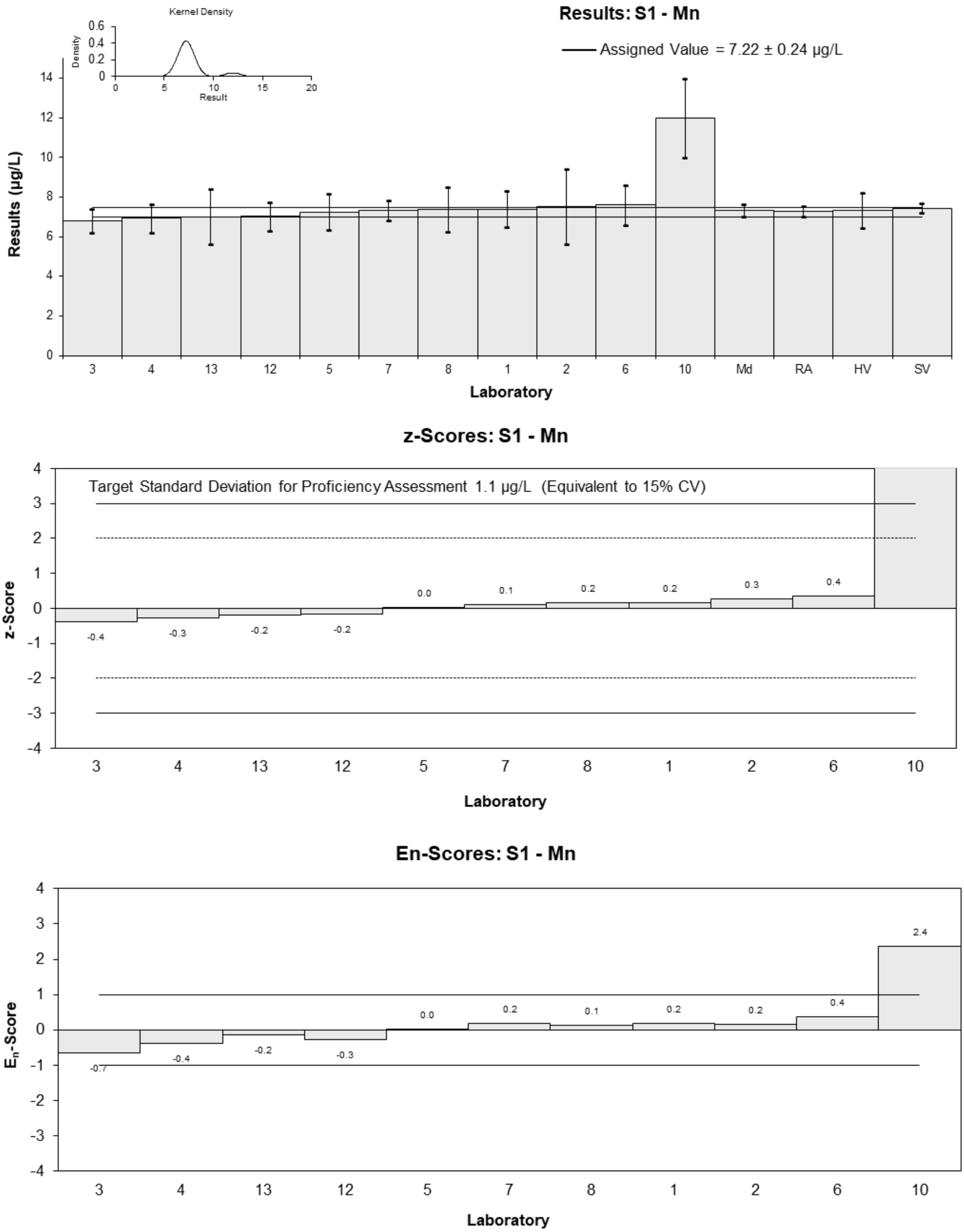
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	7.4	0.92	0.17	0.19
2	7.5	1.9	0.26	0.15
3	6.8	0.6	-0.39	-0.65
4	6.93	0.73	-0.27	-0.38
5	7.25	0.9	0.03	0.03
6	7.6	1.0	0.35	0.37
7	7.326	0.4996	0.10	0.19
8	7.38	1.11	0.15	0.14
10*	12	2	4.41	2.37
12	7.02	0.7	-0.18	-0.27
13	7.0	1.4	-0.20	-0.15

* Outlier, see Section 4.2

Statistics

Assigned Value	7.22	0.24
Spike Value	7.43	0.24
Homogeneity Value	7.34	0.88
Robust Average	7.27	0.26
Median	7.33	0.31
Mean	7.66	
N	11	
Max	12	
Min	6.8	
Robust SD	0.35	
Robust CV	4.8%	



Results: S1 - Mn
Assigned Value = 7.22 ± 0.24 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
3
4
13
12
5
7
8
1
2
6
10
Md
RA
HV
SV
z-Scores: S1 - Mn
Target Standard Deviation for Proficiency Assessment 1.1 μg/L (Equivalent to 15% CV)
z-Score
-0.4
-0.3
-0.2
-0.2
0.0
0.1
0.2
0.2
0.3
0.4
Laboratory
En-Scores: S1 - Mn
E_n-Score
-0.7
-0.4
-0.2
-0.3
0.0
0.2
0.1
0.2
0.2
0.4
2.4
Laboratory

Figure 11

Table 15

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Ni
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.2	0.44	-0.87	-0.54
2	1.8	0.9	-1.92	-0.74
3	2.2	0.4	-0.87	-0.57
4	<7	4.7		
5	2.36	0.3	-0.45	-0.33
6	3.2	0.7	1.77	0.82
7	<5	NR		
8	2.93	0.44	1.05	0.66
10	3	3	1.24	0.16
12	2.48	0.25	-0.13	-0.10
13	2.6	0.52	0.18	0.10

Statistics

Assigned Value	2.53	0.42
Spike Value	2.75	0.13
Homogeneity Value	2.74	0.33
Robust Average	2.53	0.42
Median	2.48	0.35
Mean	2.53	
N	9	
Max	3.2	
Min	1.8	
Robust SD	0.51	
Robust CV	20%	

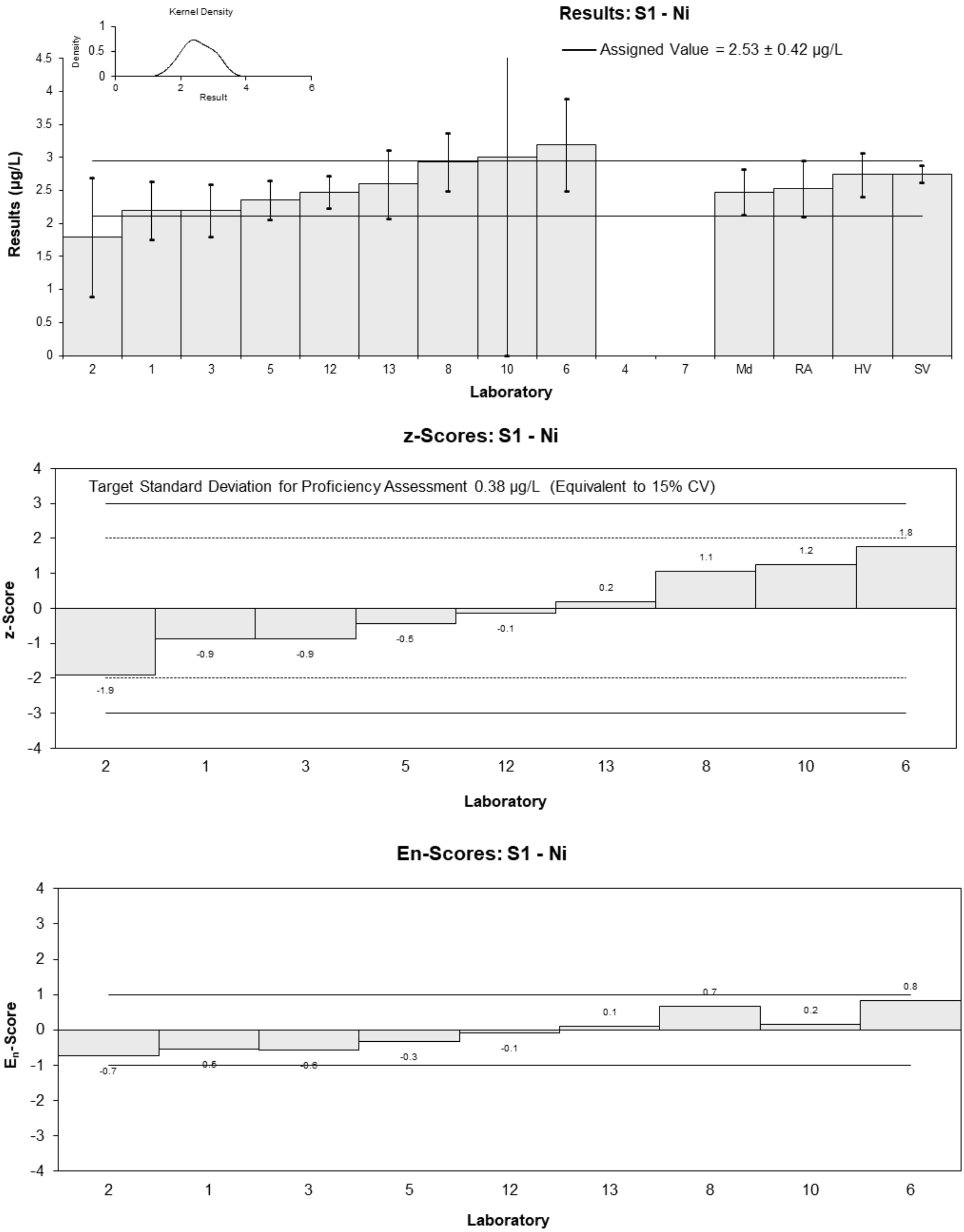

Results: S1 - Ni
Assigned Value = 2.53 ± 0.42 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
2 1 3 5 12 13 8 10 6 4 7 Md RA HV SV
z-Scores: S1 - Ni
Target Standard Deviation for Proficiency Assessment 0.38 µg/L (Equivalent to 15% CV)
z-Score
-1.9 -0.9 -0.9 -0.5 -0.1 0.2 1.1 1.2 1.8
2 1 3 5 12 13 8 10 6
Laboratory
En-Scores: S1 - Ni
E_n-Score
-0.7 -0.3 -0.1 0.1 0.7 0.2 0.8
2 1 3 5 12 13 8 10 6
Laboratory

Figure 12

Table 16

Sample Details

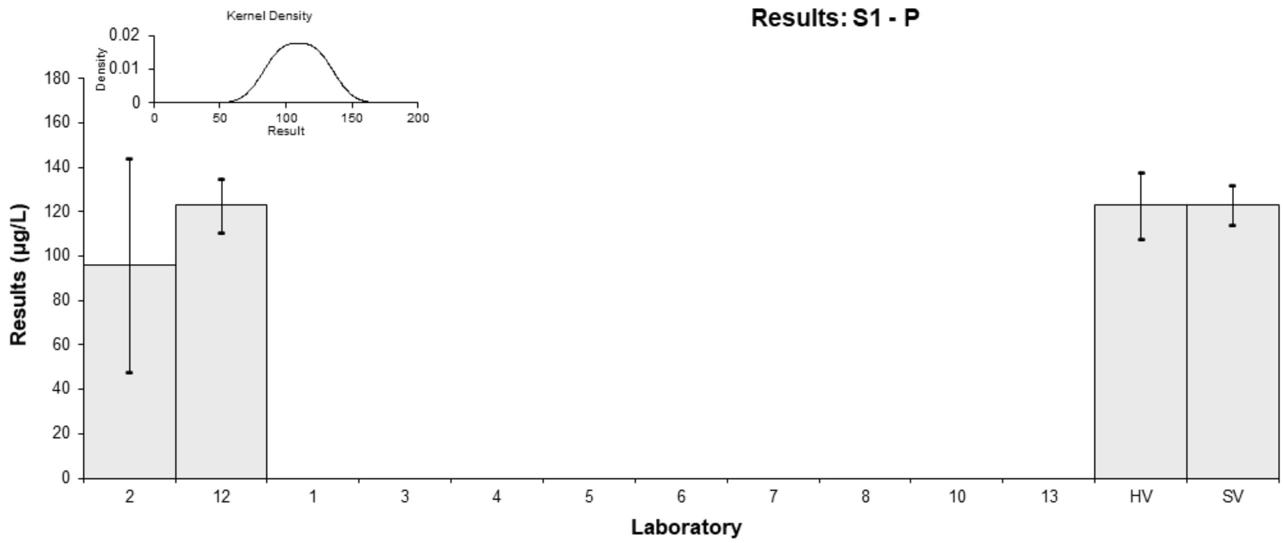
Sample No.	S1
Matrix	Sea Water
Analyte	P
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty
1	<5000	431
2	96	48
3	<1000	NR
4	NT	NT
5	NT	NT
6	<1000	NR
7	<1000	NR
8	NT	NT
10	NT	NT
12	123	12
13	NR	NR

Statistics

Assigned Value	Not Set	
Spike Value	123	9
Homogeneity Value	123	15
Mean	110	
N	2	



Results: S1 - P
Kernel Density
Density
Result
Results (µg/L)
Laboratory
2
12
1
3
4
5
6
7
8
10
13
HV
SV

Figure 13

Table 17

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Pb
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.6	0.25	0.08	0.08
2	1.7	0.9	0.51	0.13
3	1.4	0.1	-0.76	-1.34
4	1.52	0.73	-0.25	-0.08
5	1.51	0.2	-0.30	-0.32
6	1.6	0.22	0.08	0.08
7	<5	NR		
8	1.58	0.32	0.00	0.00
10	1.7	3	0.51	0.04
12	1.51	0.15	-0.30	-0.40
13	1.7	0.34	0.51	0.34

Statistics

Assigned Value	1.58	0.09
Spike Value	1.56	0.04
Homogeneity Value	1.46	0.18
Robust Average	1.58	0.09
Median	1.59	0.09
Mean	1.58	
N	10	
Max	1.7	
Min	1.4	
Robust SD	0.11	
Robust CV	6.9%	

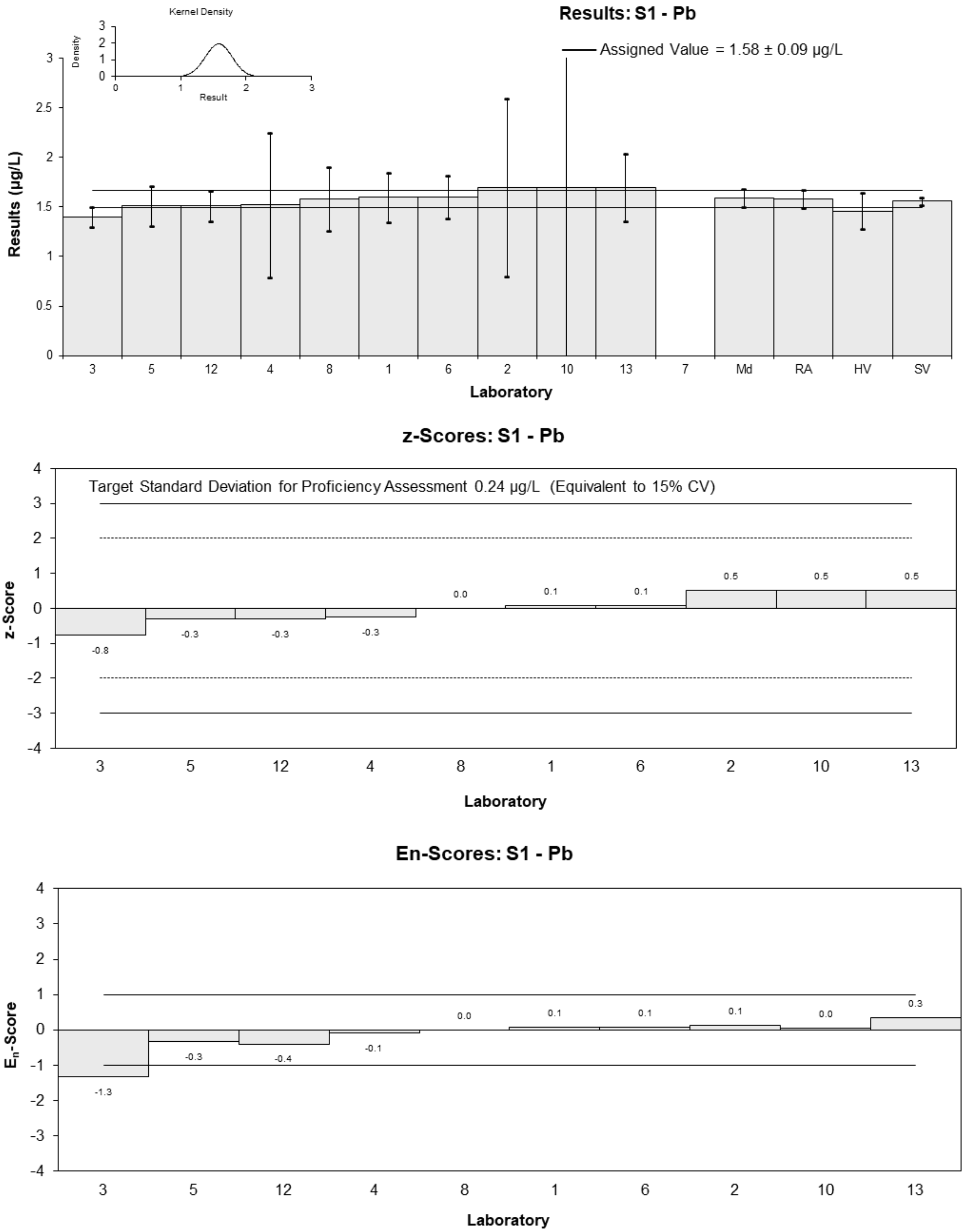

Results: S1 - Pb
Assigned Value = 1.58 ± 0.09 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3
5
12
4
8
1
6
2
10
13
7
Md
RA
HV
SV
z-Scores: S1 - Pb
Target Standard Deviation for Proficiency Assessment 0.24 µg/L (Equivalent to 15% CV)
z-Score
-0.8
-0.3
-0.3
-0.3
0.0
0.1
0.1
0.5
0.5
0.5
Laboratory
En-Scores: S1 - Pb
En-Score
-1.3
-0.3
-0.4
-0.1
0.0
0.1
0.1
0.1
0.0
0.3
Laboratory

Figure 14

Table 18

Sample Details

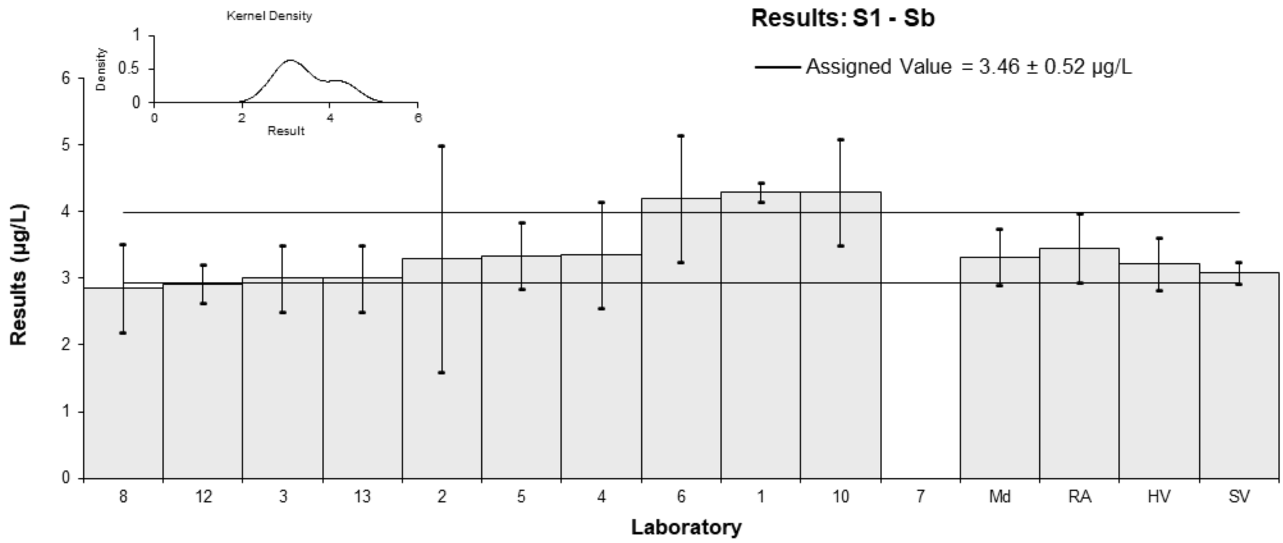
Sample No.	S1
Matrix	Sea Water
Analyte	Sb
Unit	µg/L

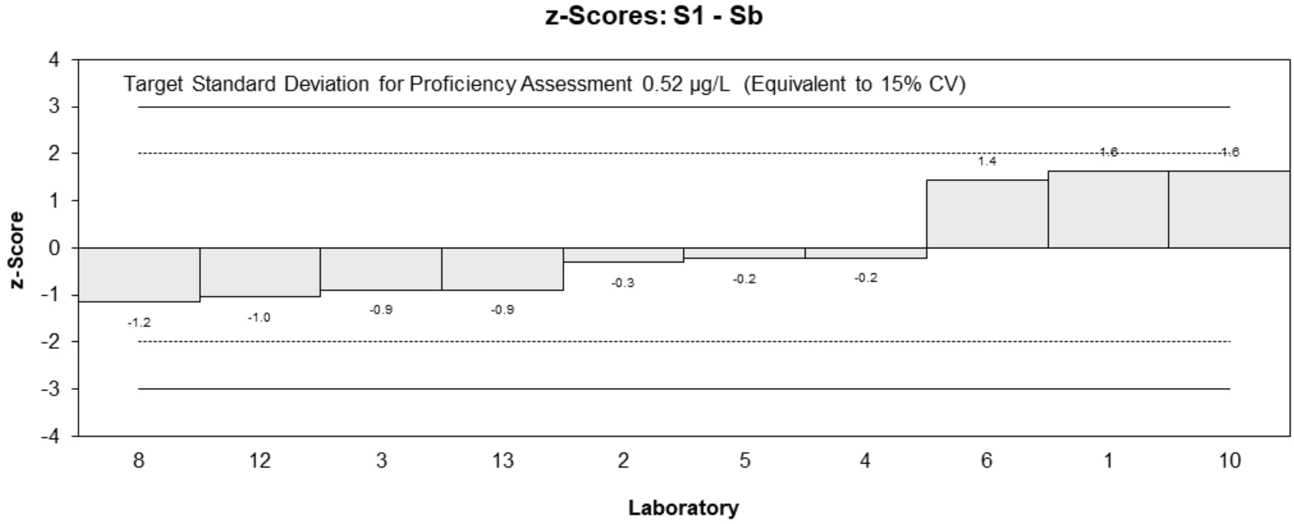
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.3	0.14	1.62	1.56
2	3.3	1.7	-0.31	-0.09
3	3.0	0.5	-0.89	-0.64
4	3.35	0.8	-0.21	-0.12
5	3.34	0.5	-0.23	-0.17
6	4.2	0.96	1.43	0.68
7	<5	NR		
8	2.86	0.66	-1.16	-0.71
10	4.3	0.8	1.62	0.88
12	2.92	0.29	-1.04	-0.91
13	3.0	0.5	-0.89	-0.64

Statistics

Assigned Value	3.46	0.52
Spike Value	3.08	0.16
Homogeneity Value	3.22	0.39
Robust Average	3.46	0.52
Median	3.32	0.42
Mean	3.46	
N	10	
Max	4.3	
Min	2.86	
Robust SD	0.66	
Robust CV	19%	


Results: S1 - Sb
Assigned Value = 3.46 ± 0.52 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
8
12
3
13
2
5
4
6
1
10
7
Md
RA
HV
SV


z-Scores: S1 - Sb
Target Standard Deviation for Proficiency Assessment 0.52 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.2
-1.0
-0.9
-0.9
-0.3
-0.2
-0.2
1.4
1.6
1.6
8
12
3
13
2
5
4
6
1
10

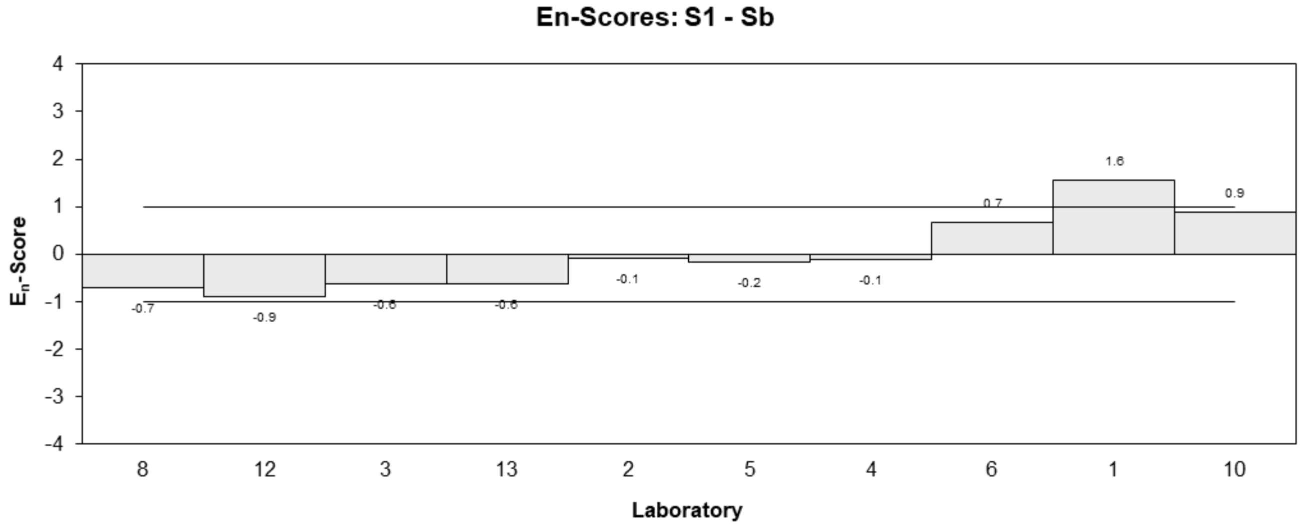

En-Scores: S1 - Sb
E_n-Score
Laboratory
-0.7
-0.9
-0.6
-0.6
-0.1
-0.2
-0.1
0.7
1.6
0.9
8
12
3
13
2
5
4
6
1
10

Figure 15

Table 19

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Se
Unit	µg/L

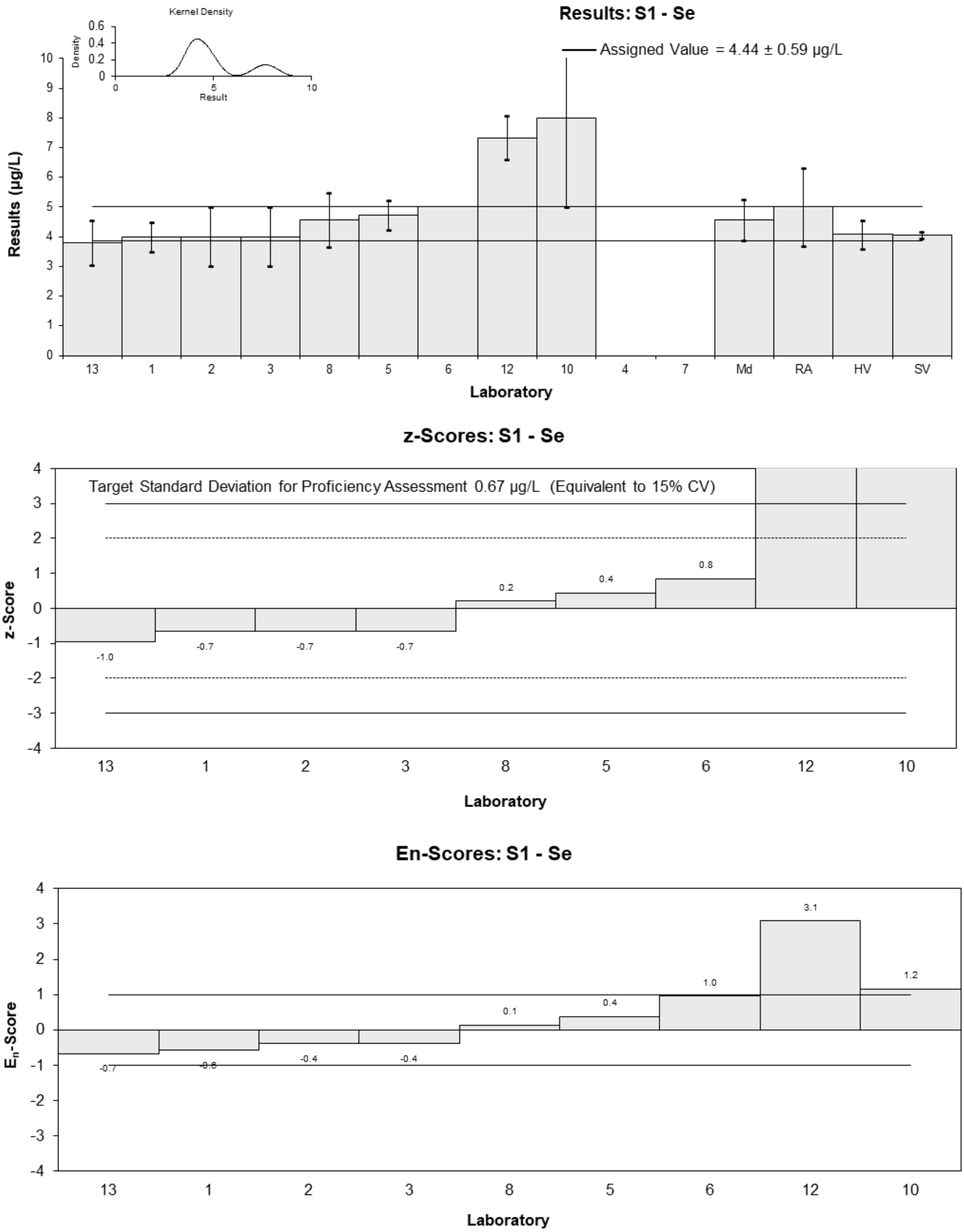
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.0	0.5	-0.66	-0.57
2	4.0	1	-0.66	-0.38
3	4	1	-0.66	-0.38
4	<4	2.7		
5	4.73	0.5	0.44	0.37
6	5	NR	0.84	0.95
7	<50	NR		
8	4.57	0.91	0.20	0.12
10*	8	3	5.35	1.16
12	7.33	0.73	4.34	3.08
13	3.8	0.76	-0.96	-0.67

* Outlier, see Section 4.2

Statistics

Assigned Value	4.44	0.59
Spike Value	4.06	0.12
Homogeneity Value	4.07	0.49
Robust Average	5.0	1.3
Median	4.57	0.70
Mean	5.0	
N	9	
Max	8	
Min	3.8	
Robust SD	1.6	
Robust CV	32%	



Kernel Density
Density
Result
Results: S1 - Se
Assigned Value = 4.44 ± 0.59 µg/L
Results (µg/L)
Laboratory
13
1
2
3
8
5
6
12
10
4
7
Md
RA
HV
SV
z-Scores: S1 - Se
Target Standard Deviation for Proficiency Assessment 0.67 µg/L (Equivalent to 15% CV)
z-Score
-1.0
-0.7
-0.7
-0.7
0.2
0.4
0.8
Laboratory
En-Scores: S1 - Se
En-Score
-0.7
-0.6
-0.4
-0.4
0.1
0.4
1.0
3.1
1.2
Laboratory

Figure 16

Table 20

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Sn
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty
1	<5	0.52
2	3.8	1
3	<5	NR
4	<5	3.4
5	NT	NT
6	<5	NR
7	<5	NR
8	4.10	0.86
10	NT	NT
12	3.75	0.38
13	4.1	0.82

Statistics

Assigned Value	Not Set	
Spike Value	3.76	0.11
Homogeneity Value	4.18	0.50
Median	3.95	0.28
Mean	3.94	
N	4	
Max	4.1	
Min	3.75	

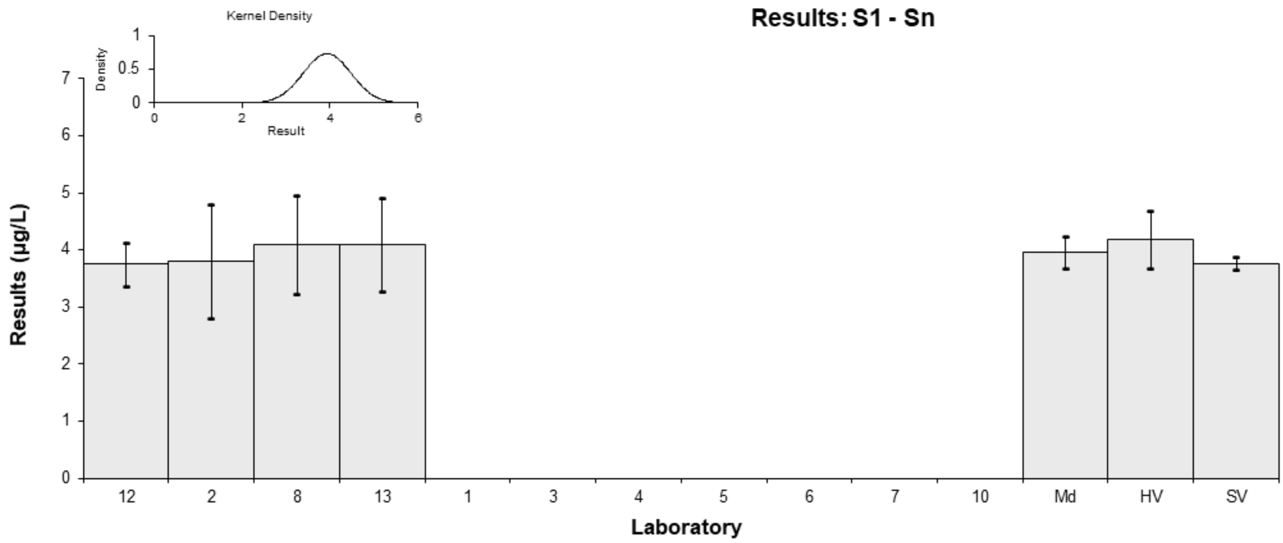

Results: S1 - Sn
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
2
8
13
1
3
4
5
6
7
10
Md
HV
SV

Figure 17

Table 21

Sample Details

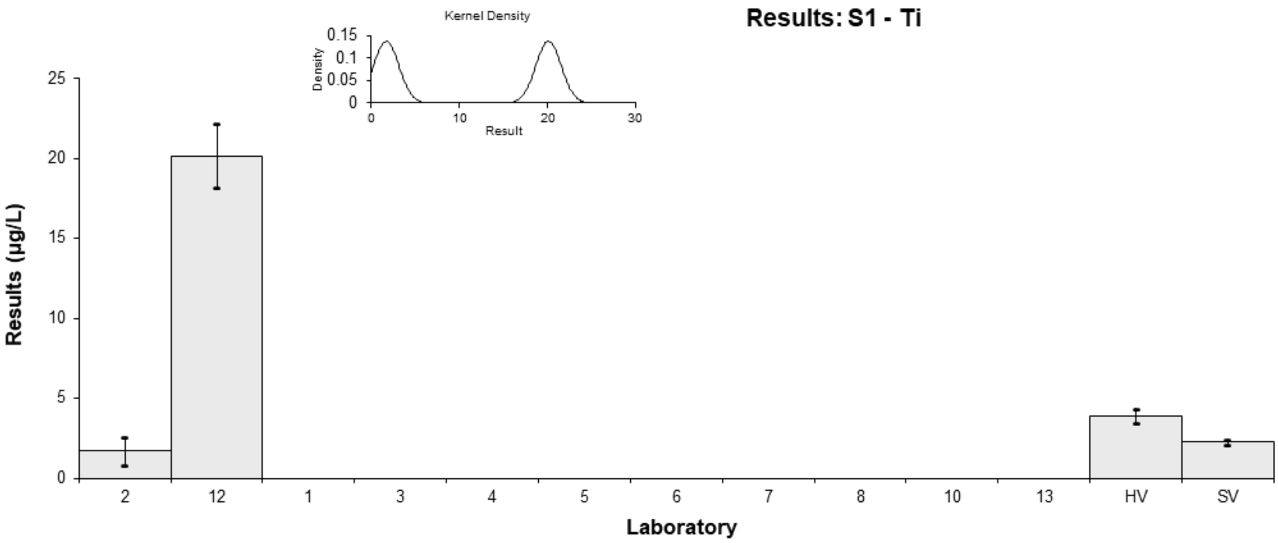
Sample No.	S1
Matrix	Sea Water
Analyte	Ti
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty
1	<5	1.02
2	1.7	0.9
3	<5	NR
4	<20	NR
5	NT	NT
6	<5	NR
7	<50	NR
8	NT	NT
10	NT	NT
12	20.15	2.0
13	<5	NR

Statistics

Assigned Value	Not Set	
Spike Value	2.27	0.16
Homogeneity Value	3.88	0.47
Mean	11	
N	2	



Results: S1 - Ti
Kernel Density
Density
0.15
0.1
0.05
0
0
10
20
30
Result
Results (µg/L)
25
20
15
10
5
0
2
12
1
3
4
5
6
7
8
10
13
HV
SV
Laboratory

Figure 18

Table 22

Sample Details

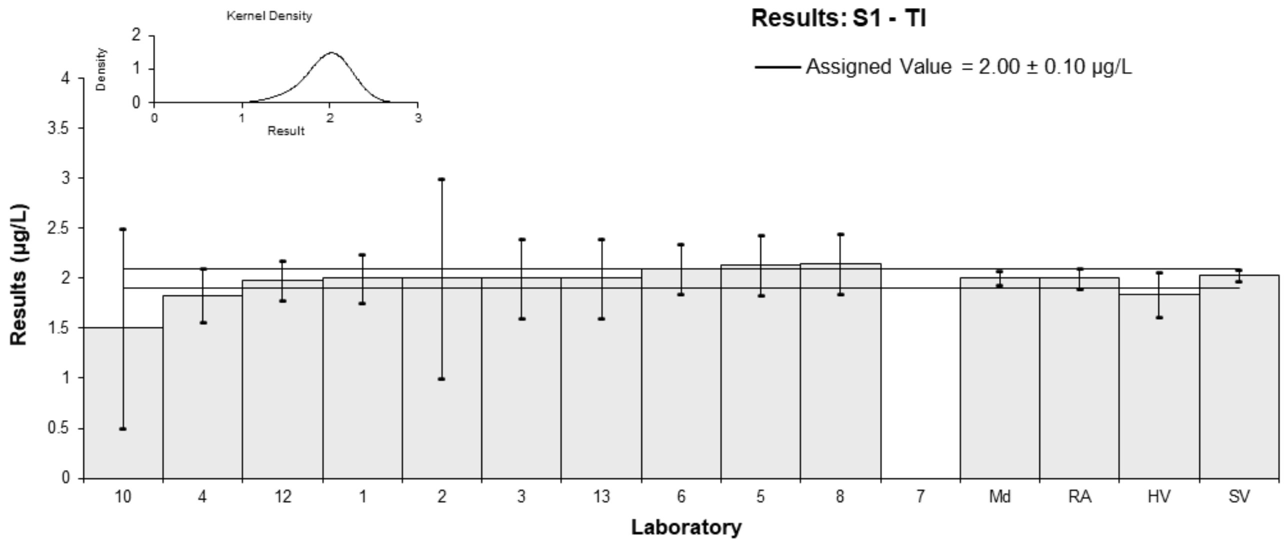
Sample No.	S1
Matrix	Sea Water
Analyte	Tl
Unit	μg/L

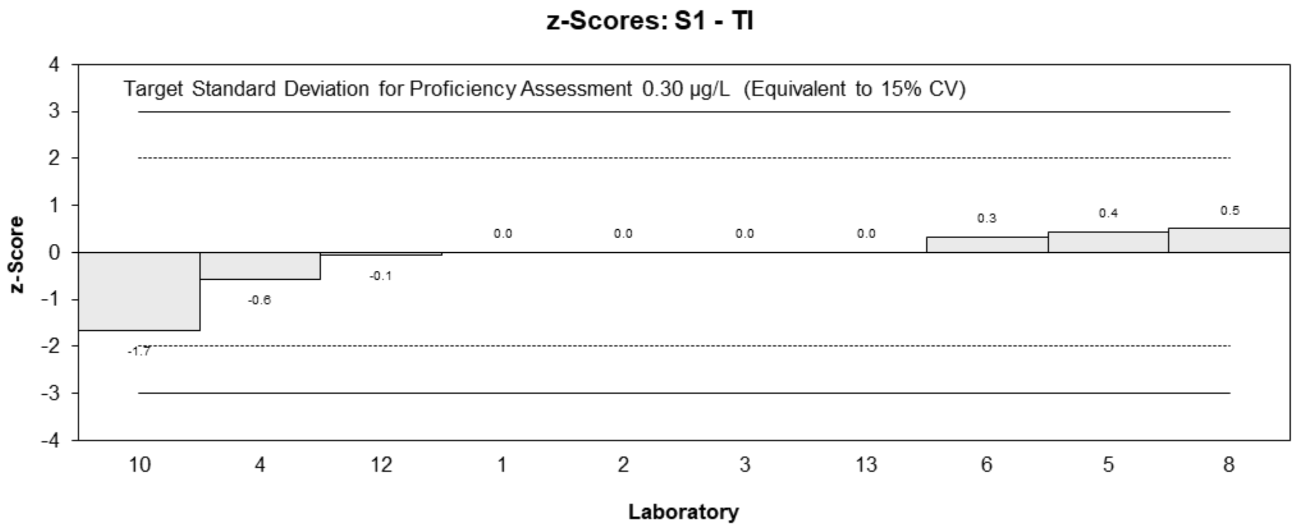
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.0	0.24	0.00	0.00
2	2.0	1	0.00	0.00
3	2.0	0.4	0.00	0.00
4	1.83	0.27	-0.57	-0.59
5	2.13	0.3	0.43	0.41
6	2.1	0.25	0.33	0.37
7	<5	NR		
8	2.15	0.30	0.50	0.47
10	1.5	1	-1.67	-0.50
12	1.98	0.2	-0.07	-0.09
13	2.0	0.4	0.00	0.00

Statistics

Assigned Value	2.00	0.10
Spike Value	2.03	0.06
Homogeneity Value	1.84	0.22
Robust Average	2.00	0.10
Median	2.00	0.07
Mean	1.97	
N	10	
Max	2.15	
Min	1.5	
Robust SD	0.13	
Robust CV	6.4%	


Results: S1 - Tl
Assigned Value = 2.00 ± 0.10 µg/L
Kernel Density
Density
Result
Results (µg/L)
10
4
12
1
2
3
13
6
5
8
7
Md
RA
HV
SV
Laboratory


z-Scores: S1 - Tl
Target Standard Deviation for Proficiency Assessment 0.30 µg/L (Equivalent to 15% CV)
z-Score
-1.7
-0.6
-0.1
0.0
0.0
0.0
0.0
0.3
0.4
0.5
10
4
12
1
2
3
13
6
5
8
Laboratory

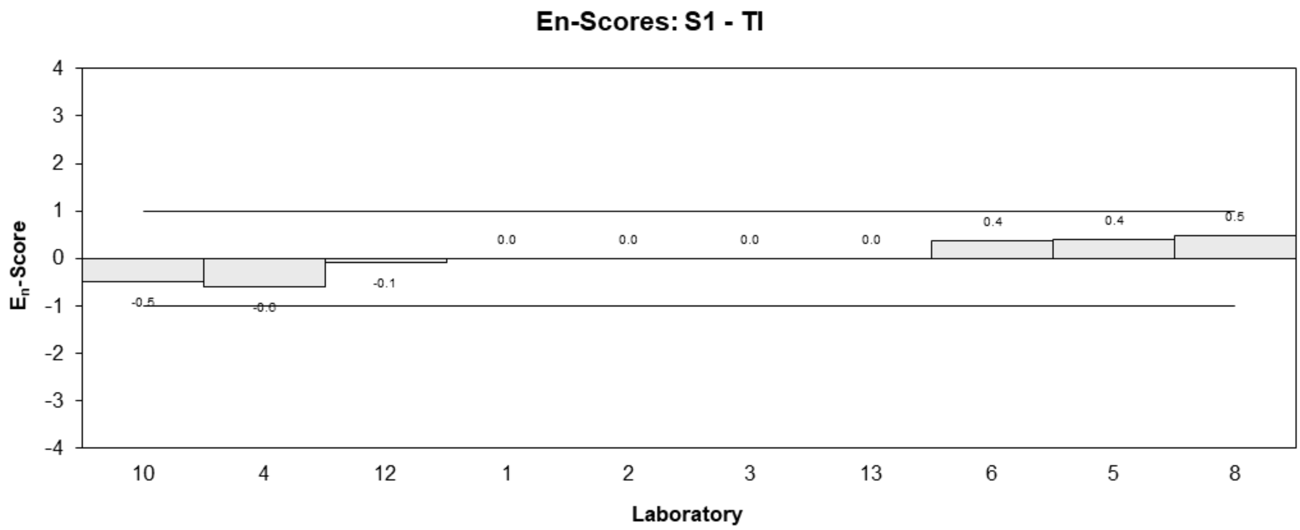

En-Scores: S1 - Tl
E_n-Score
-0.5
-0.6
-0.1
0.0
0.0
0.0
0.0
0.4
0.4
0.5
10
4
12
1
2
3
13
6
5
8
Laboratory

Figure 19

Table 23

Sample Details

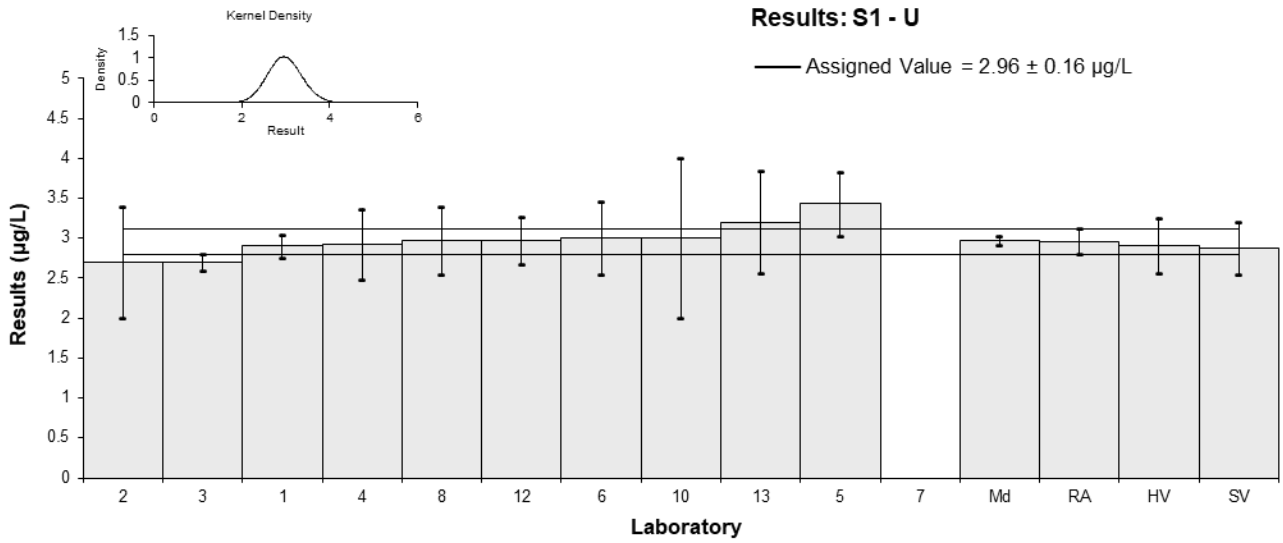
Sample No.	S1
Matrix	Sea Water
Analyte	U
Unit	µg/L

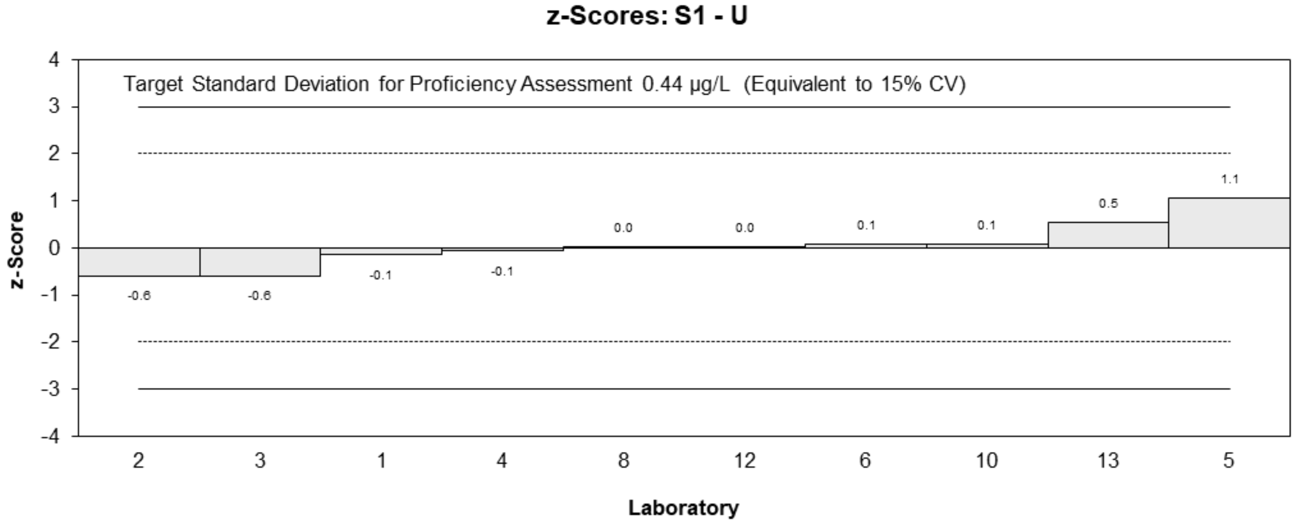
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.9	0.15	-0.14	-0.27
2	2.7	0.7	-0.59	-0.36
3	2.7	0.1	-0.59	-1.38
4	2.93	0.44	-0.07	-0.06
5	3.43	0.4	1.06	1.09
6	3	0.46	0.09	0.08
7	<5	NR		
8	2.97	0.42	0.02	0.02
10	3	1	0.09	0.04
12	2.97	0.3	0.02	0.03
13	3.2	0.64	0.54	0.36

Statistics

Assigned Value	2.96	0.16
Spike Value	2.87	0.33
Homogeneity Value	2.91	0.35
Robust Average	2.96	0.16
Median	2.97	0.06
Mean	2.98	
N	10	
Max	3.43	
Min	2.7	
Robust SD	0.21	
Robust CV	7%	


Kernel Density
Density
Result
Results: S1 - U
Assigned Value = 2.96 ± 0.16 μg/L
Results (μg/L)
Laboratory
2
3
1
4
8
12
6
10
13
5
7
Md
RA
HV
SV


z-Scores: S1 - U
Target Standard Deviation for Proficiency Assessment 0.44 μg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.6
-0.6
-0.1
-0.1
0.0
0.0
0.1
0.1
0.5
1.1

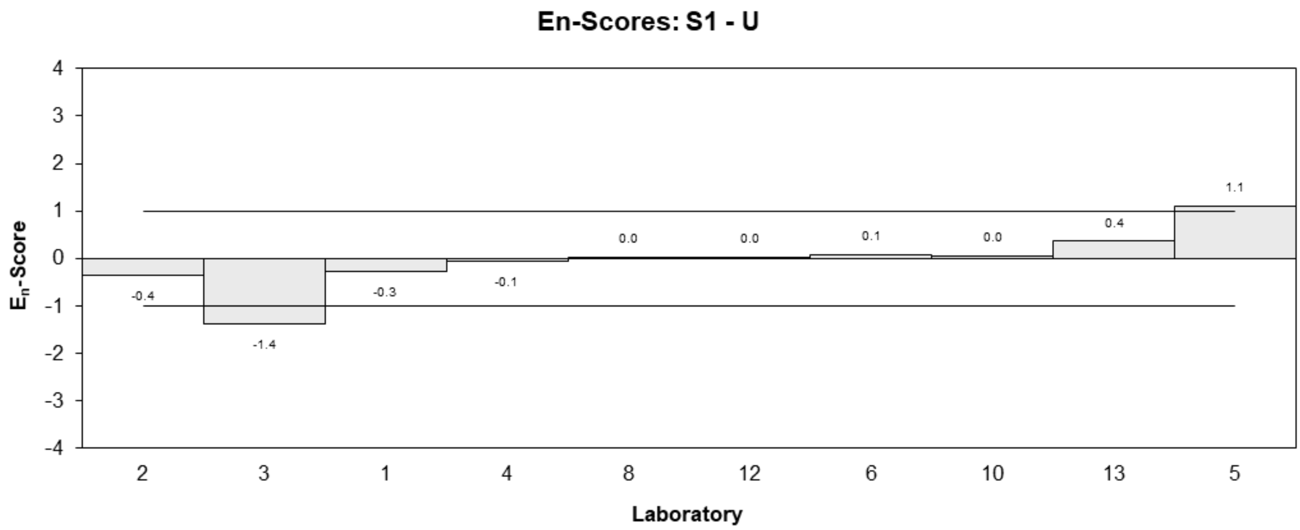

En-Scores: S1 - U
En-Score
Laboratory
-0.4
-1.4
-0.3
-0.1
0.0
0.0
0.1
0.0
0.4
1.1

Figure 20

Table 24

Sample Details

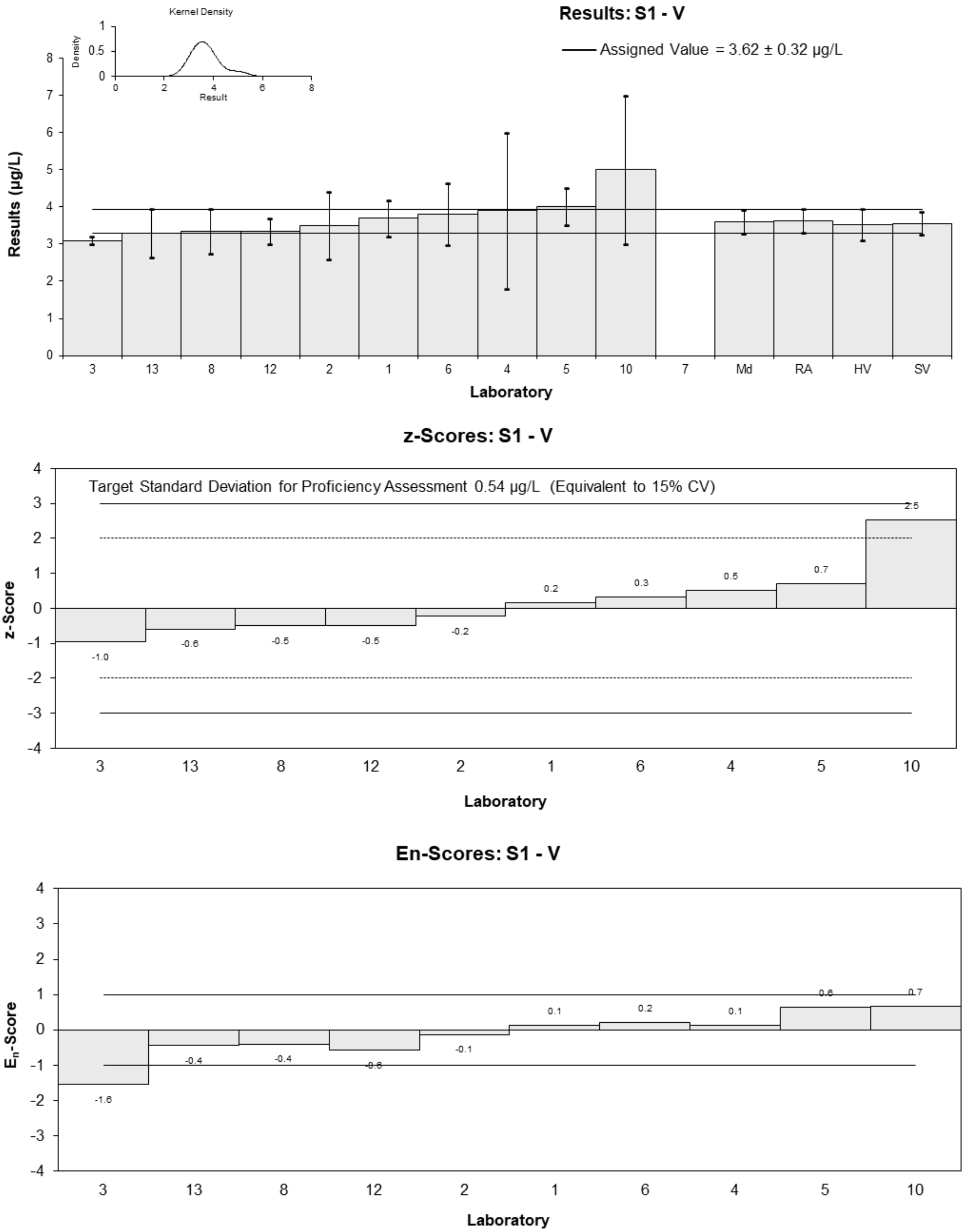
Sample No.	S1
Matrix	Sea Water
Analyte	V
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.7	0.49	0.15	0.14
2	3.5	0.9	-0.22	-0.13
3	3.1	0.1	-0.96	-1.55
4	3.9	2.1	0.52	0.13
5	4.00	0.5	0.70	0.64
6	3.8	0.83	0.33	0.20
7	<50	NR		
8	3.35	0.60	-0.50	-0.40
10	5	2	2.54	0.68
12	3.35	0.34	-0.50	-0.58
13	3.3	0.66	-0.59	-0.44

Statistics

Assigned Value	3.62	0.32
Spike Value	3.56	0.31
Homogeneity Value	3.52	0.42
Robust Average	3.62	0.32
Median	3.60	0.32
Mean	3.70	
N	10	
Max	5	
Min	3.1	
Robust SD	0.41	
Robust CV	11%	



Results: S1 - V
Assigned Value = 3.62 ± 0.32 µg/L
Kernel Density
Density
Result
Results (µg/L)
3
13
8
12
2
1
6
4
5
10
7
Md
RA
HV
SV
Laboratory
z-Scores: S1 - V
Target Standard Deviation for Proficiency Assessment 0.54 µg/L (Equivalent to 15% CV)
z-Score
-1.0
-0.6
-0.5
-0.5
-0.2
0.2
0.3
0.5
0.7
2.5
Laboratory
En-Scores: S1 - V
En-Score
-1.6
-0.4
-0.4
-0.6
-0.1
0.1
0.2
0.1
0.6
0.7
Laboratory

Figure 21

Table 25

Sample Details

Sample No.	S1
Matrix	Sea Water
Analyte	Zn
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	16	2.95	-0.99	-0.80
2	18	2	-0.28	-0.29
3	16	4	-0.99	-0.63
4	17.8	3.9	-0.35	-0.23
5	19.2	2.5	0.14	0.13
6	21	3.5	0.78	0.55
7	<25	NR		
8	18.6	3.9	-0.07	-0.05
10	21	5	0.78	0.41
12	24.39	2.4	1.98	1.83
13	18	3.6	-0.28	-0.20

Statistics

Assigned Value	18.8	1.9
Spike Value	18.3	0.8
Homogeneity Value	17.6	2.1
Robust Average	18.8	1.9
Median	18.3	1.9
Mean	19.0	
N	10	
Max	24.39	
Min	16	
Robust SD	2.4	
Robust CV	13%	

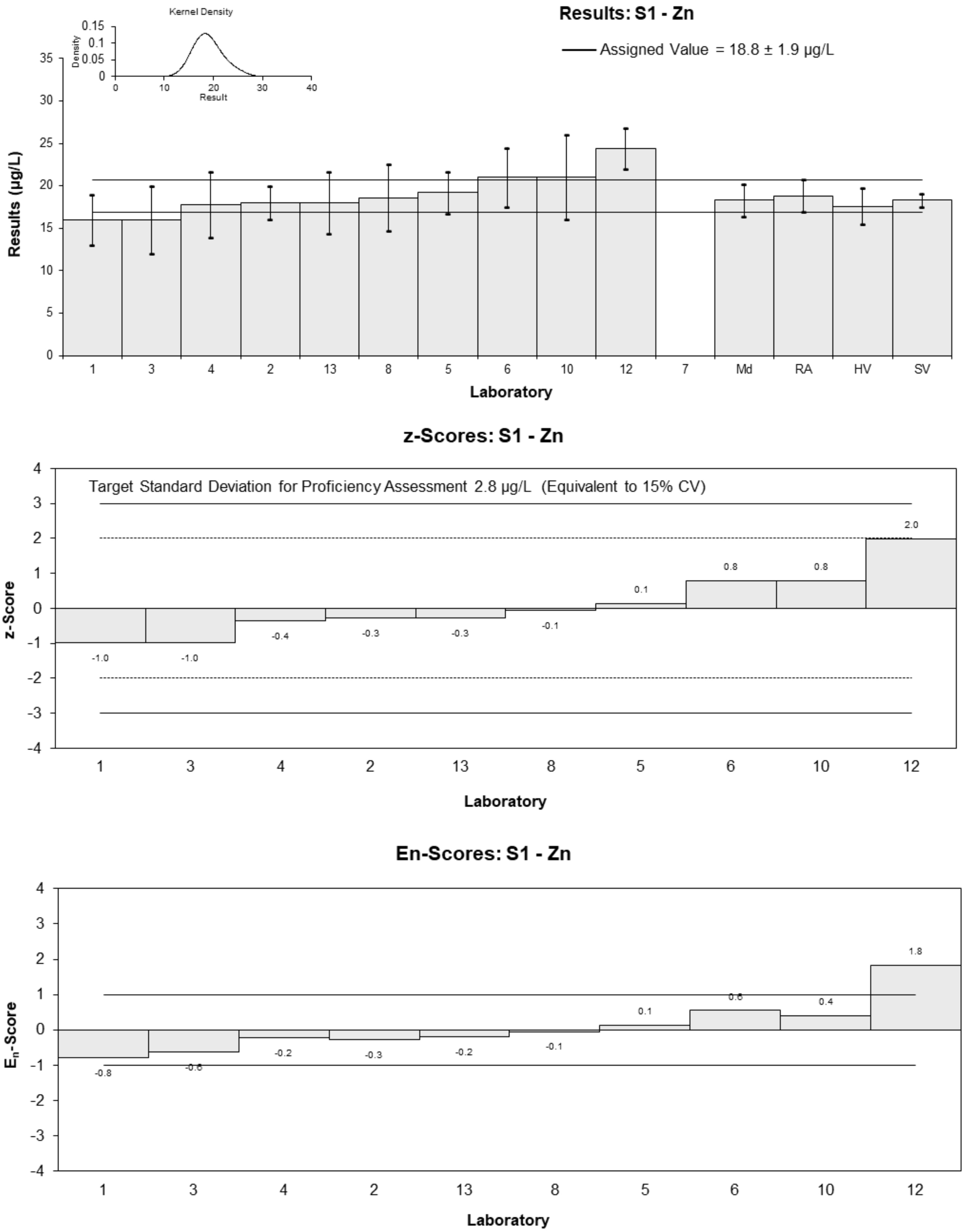

Kernel Density
Density
Result
Results: S1 - Zn
Assigned Value = 18.8 ± 1.9 µg/L
Results (µg/L)
Laboratory
1 3 4 2 13 8 5 6 10 12 7 Md RA HV SV
z-Scores: S1 - Zn
Target Standard Deviation for Proficiency Assessment 2.8 µg/L (Equivalent to 15% CV)
-1.0 -1.0 -0.4 -0.3 -0.3 -0.1 0.1 0.8 0.8 2.0
z-Score
Laboratory
1 3 4 2 13 8 5 6 10 12
En-Scores: S1 - Zn
-0.8 -0.6 -0.2 -0.3 -0.2 -0.1 0.1 0.6 0.4 1.8
En-Score
Laboratory
1 3 4 2 13 8 5 6 10 12

Figure 22

Table 26

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Ag
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.4	0.9	0.23	0.09
2	NT	NT		
3	1.8	0.2	-1.49	-1.62
4	2.6	1.7	0.80	0.16
5	1.62	0.3	-2.01	-1.79
6	2.6	0.45	0.80	0.54
7	2.226	0.319	-0.27	-0.23
8	2.56	0.31	0.69	0.60
10	2.4	0.5	0.23	0.14
12	2.43	0.12	0.32	0.40
13	2.3	0.46	-0.06	-0.04

Statistics

Assigned Value	2.32	0.25
Spike Value	2.50	0.07
Homogeneity Value	2.26	0.27
Robust Average	2.32	0.25
Median	2.40	0.20
Mean	2.29	
N	10	
Max	2.6	
Min	1.62	
Robust SD	0.31	
Robust CV	13%	

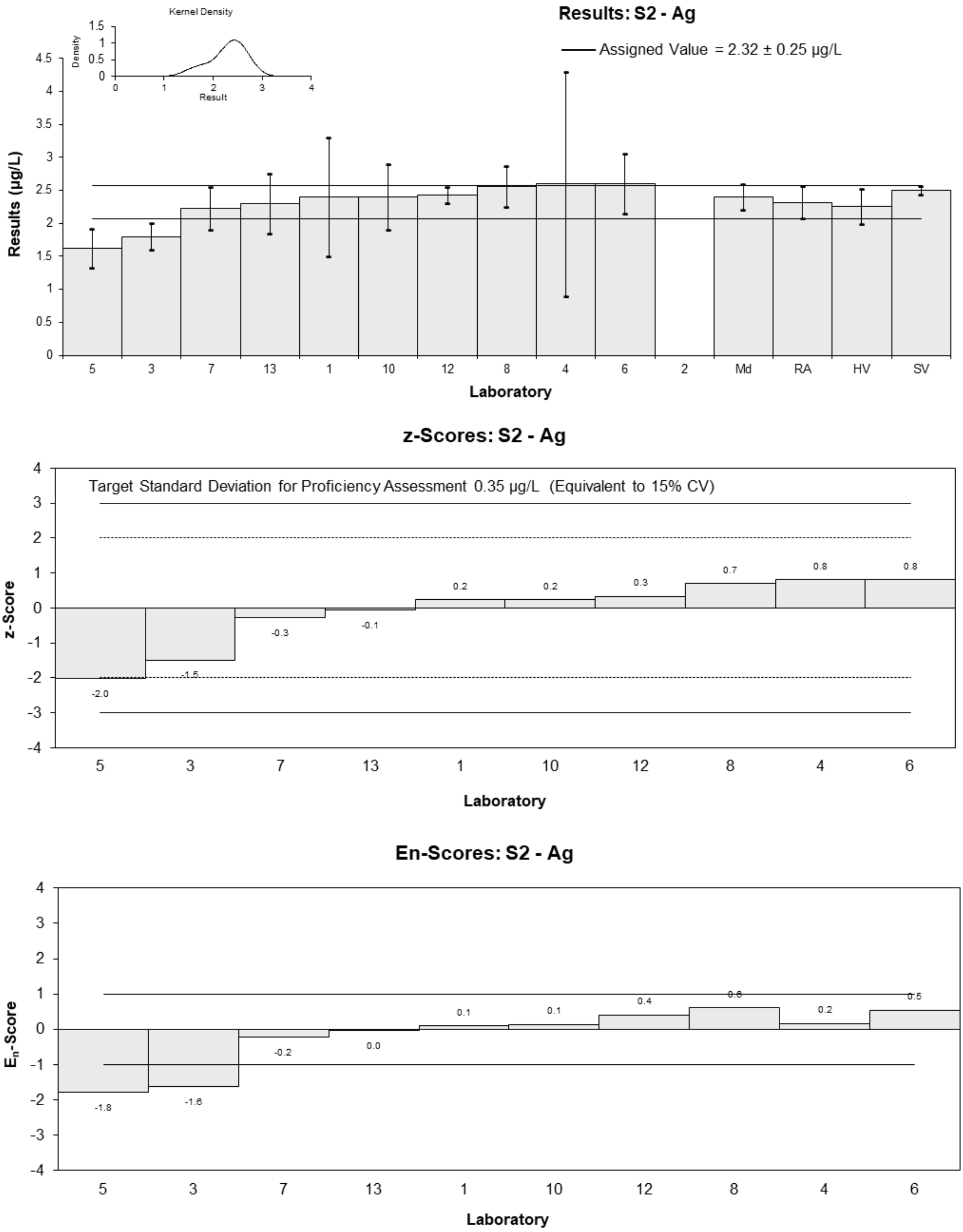

Results: S2 - Ag
Assigned Value = 2.32 ± 0.25 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5
3
7
13
1
10
12
8
4
6
2
Md
RA
HV
SV
z-Scores: S2 - Ag
Target Standard Deviation for Proficiency Assessment 0.35 µg/L (Equivalent to 15% CV)
z-Score
-2.0
-1.5
-0.3
-0.1
0.2
0.2
0.3
0.7
0.8
0.8
Laboratory
En-Scores: S2 - Ag
En-Score
-1.8
-1.6
-0.2
0.0
0.1
0.1
0.4
0.6
0.2
0.5
Laboratory

Figure 23

Table 27

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Al
Unit	µg/L

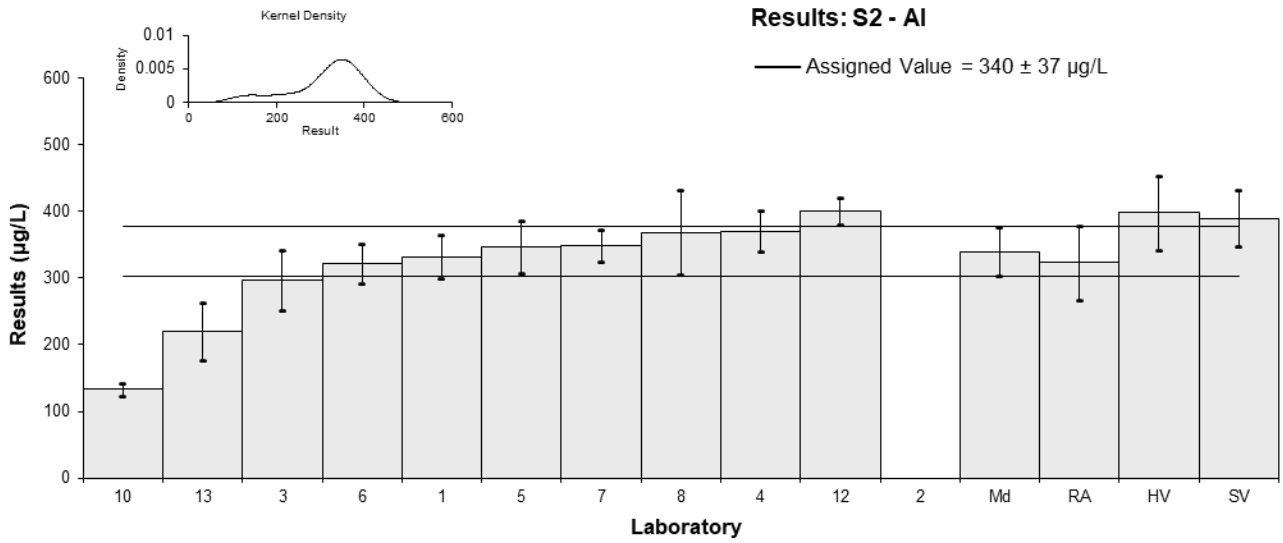
Participant Results

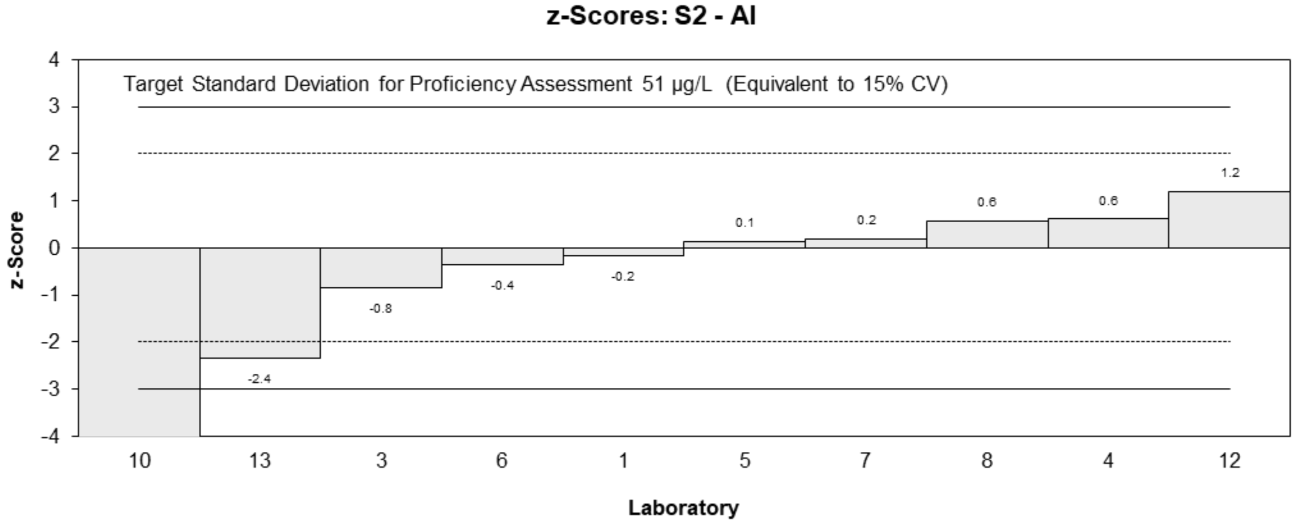
Lab. Code	Result	Uncertainty	z	E_n
1	332	32.76	-0.16	-0.16
2	NT	NT		
3	297	46	-0.84	-0.73
4	371	30	0.61	0.65
5	347	40	0.14	0.13
6	322	29.7	-0.35	-0.38
7	349.3	24.2	0.18	0.21
8	369	63	0.57	0.40
10*	133	9	-4.06	-5.44
12	401	20.05	1.20	1.45
13	220	44	-2.35	-2.09

* Outlier, see Section 4.2

Statistics

Assigned Value	340	37
Spike Value	390	42
Homogeneity Value	398	56
Robust Average	323	55
Median	340	36
Mean	314	
N	10	
Max	401	
Min	133	
Robust SD	70	
Robust CV	22%	


Results: S2 - Al
Assigned Value = 340 ± 37 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
10
13
3
6
1
5
7
8
4
12
2
Md
RA
HV
SV


z-Scores: S2 - Al
Target Standard Deviation for Proficiency Assessment 51 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.4
-0.8
-0.4
-0.2
0.1
0.2
0.6
0.6
1.2

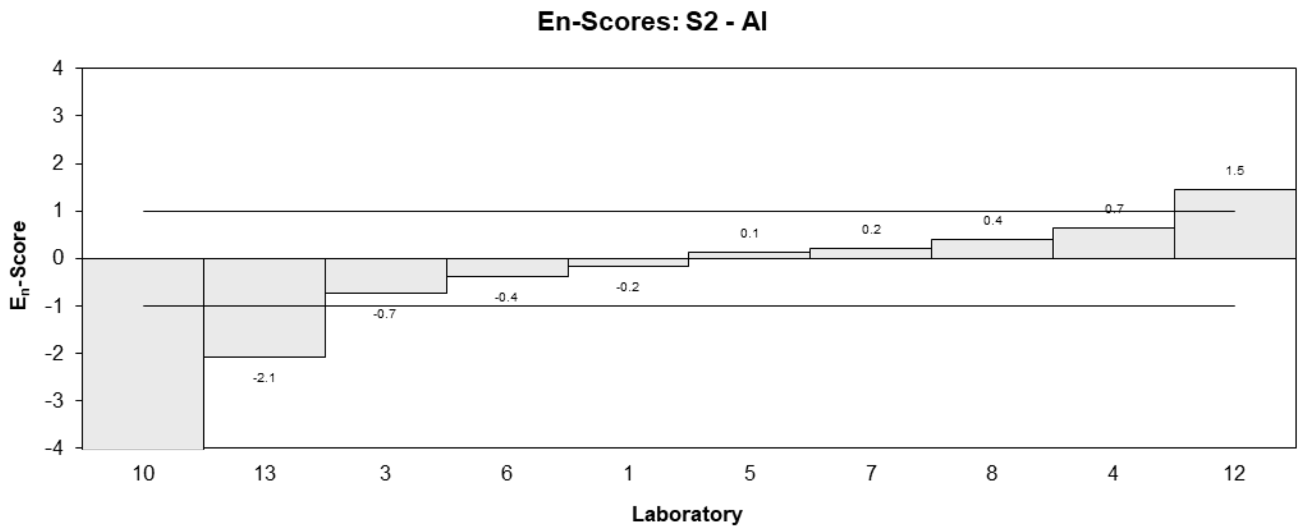

En-Scores: S2 - Al
En-Score
Laboratory
-2.1
-0.7
-0.4
-0.2
0.1
0.2
0.4
0.7
1.5

Figure 24

Table 28

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	As
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.5	0.15	0.09	0.12
2	NT	NT		
3	1.5	0.2	0.09	0.09
4	1.4	0.67	-0.36	-0.12
5	1.43	0.3	-0.23	-0.16
6	1.4	0.19	-0.36	-0.40
7	1.374	0.104	-0.48	-0.85
8	1.57	0.25	0.41	0.35
10	1.5	5	0.09	0.00
12	1.61	0.08	0.59	1.22
13	1.5	0.30	0.09	0.06

Statistics

Assigned Value	1.48	0.07
Spike Value	1.51	0.05
Homogeneity Value	1.60	0.19
Robust Average	1.48	0.07
Median	1.50	0.08
Mean	1.48	
N	10	
Max	1.61	
Min	1.374	
Robust SD	0.087	
Robust CV	5.9%	

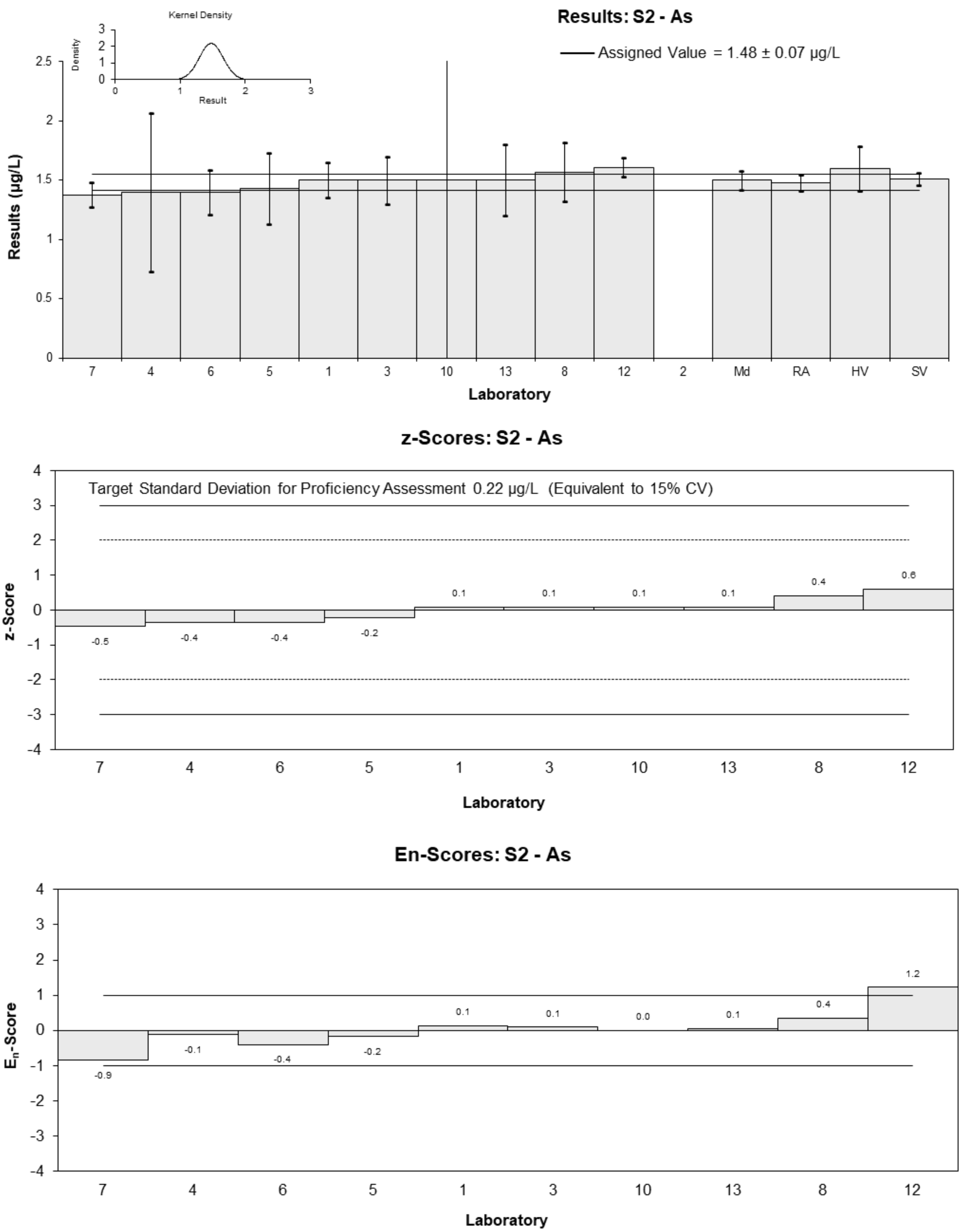

Results: S2 - As
Assigned Value = 1.48 ± 0.07 µg/L
Kernel Density
Density
Result
Results (µg/L)
7 4 6 5 1 3 10 13 8 12 2 Md RA HV SV
Laboratory
z-Scores: S2 - As
Target Standard Deviation for Proficiency Assessment 0.22 µg/L (Equivalent to 15% CV)
z-Score
-0.5 -0.4 -0.4 -0.2 0.1 0.1 0.1 0.1 0.4 0.6
7 4 6 5 1 3 10 13 8 12
Laboratory
En-Scores: S2 - As
En-Score
-0.9 -0.1 -0.4 -0.2 0.1 0.1 0.0 0.1 0.4 1.2
7 4 6 5 1 3 10 13 8 12
Laboratory

Figure 25

Table 29

Sample Details

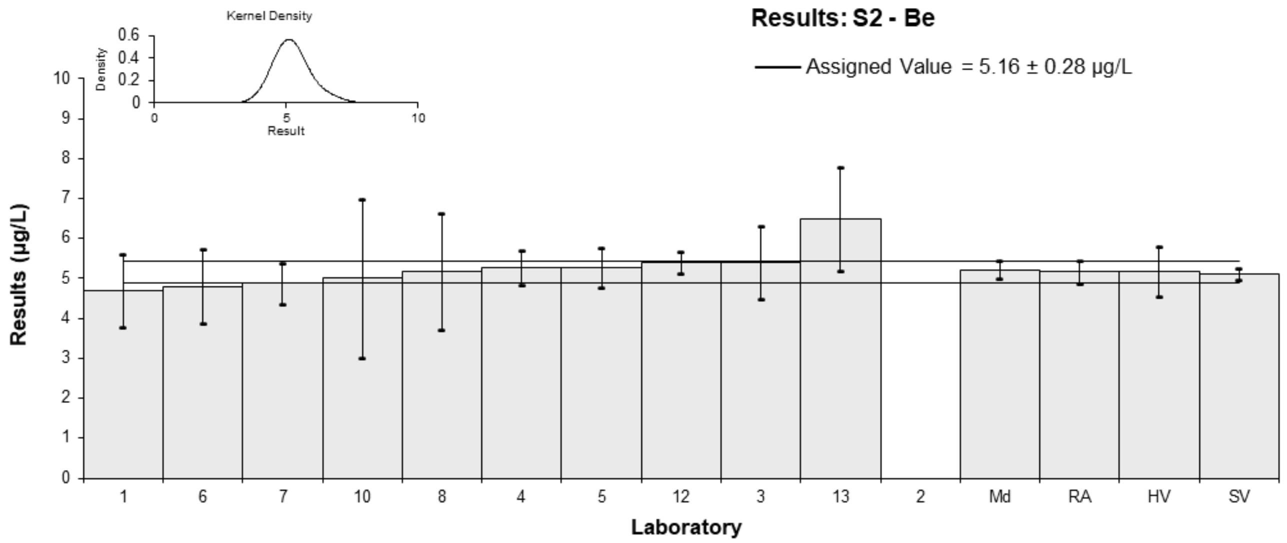
Sample No.	S2
Matrix	River Water
Analyte	Be
Unit	µg/L

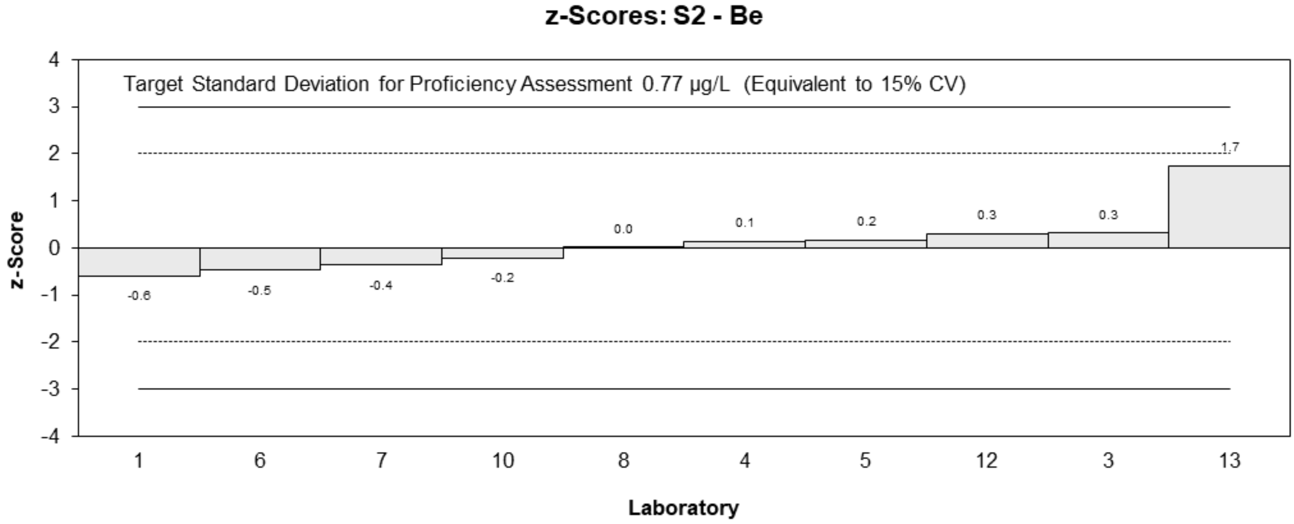
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.7	0.92	-0.59	-0.48
2	NT	NT		
3	5.4	0.9	0.31	0.25
4	5.27	0.43	0.14	0.21
5	5.28	0.5	0.16	0.21
6	4.8	0.92	-0.47	-0.37
7	4.874	0.519	-0.37	-0.48
8	5.17	1.45	0.01	0.01
10	5	2	-0.21	-0.08
12	5.39	0.27	0.30	0.59
13	6.5	1.3	1.73	1.01

Statistics

Assigned Value	5.16	0.28
Spike Value	5.10	0.14
Homogeneity Value	5.18	0.62
Robust Average	5.16	0.28
Median	5.22	0.23
Mean	5.24	
N	10	
Max	6.5	
Min	4.7	
Robust SD	0.35	
Robust CV	6.8%	


Results: S2 - Be
Assigned Value = 5.16 ± 0.28 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1
6
7
10
8
4
5
12
3
13
2
Md
RA
HV
SV


z-Scores: S2 - Be
Target Standard Deviation for Proficiency Assessment 0.77 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.6
-0.5
-0.4
-0.2
0.0
0.1
0.2
0.3
0.3
1.7
1
6
7
10
8
4
5
12
3
13

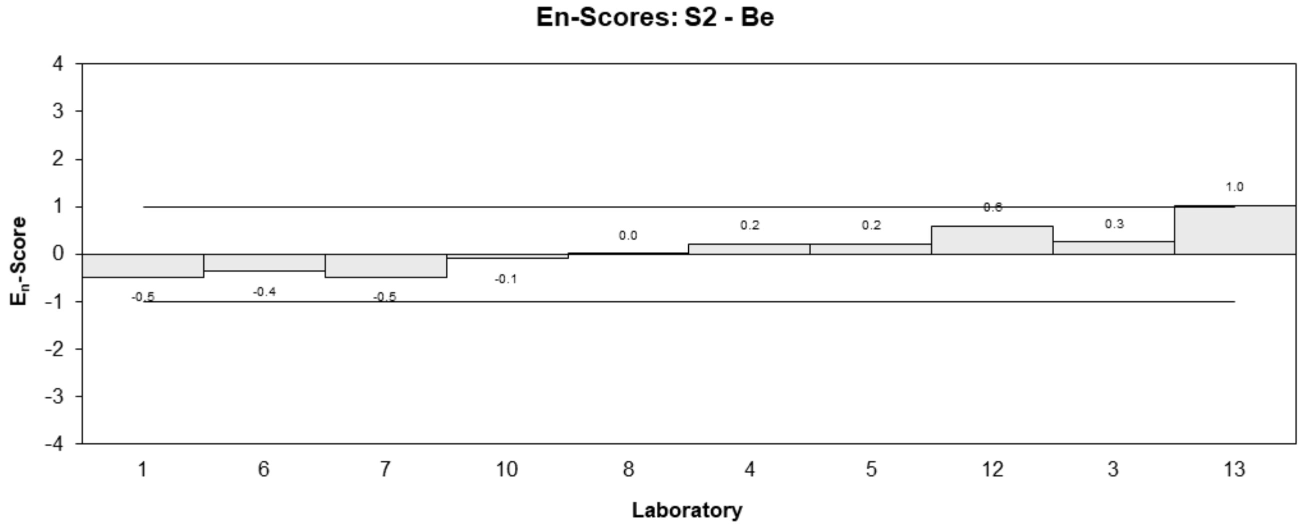

En-Scores: S2 - Be
En-Score
Laboratory
-0.5
-0.4
-0.5
-0.1
0.0
0.2
0.2
0.6
0.3
1.0
1
6
7
10
8
4
5
12
3
13

Figure 26

Table 30

Sample Details

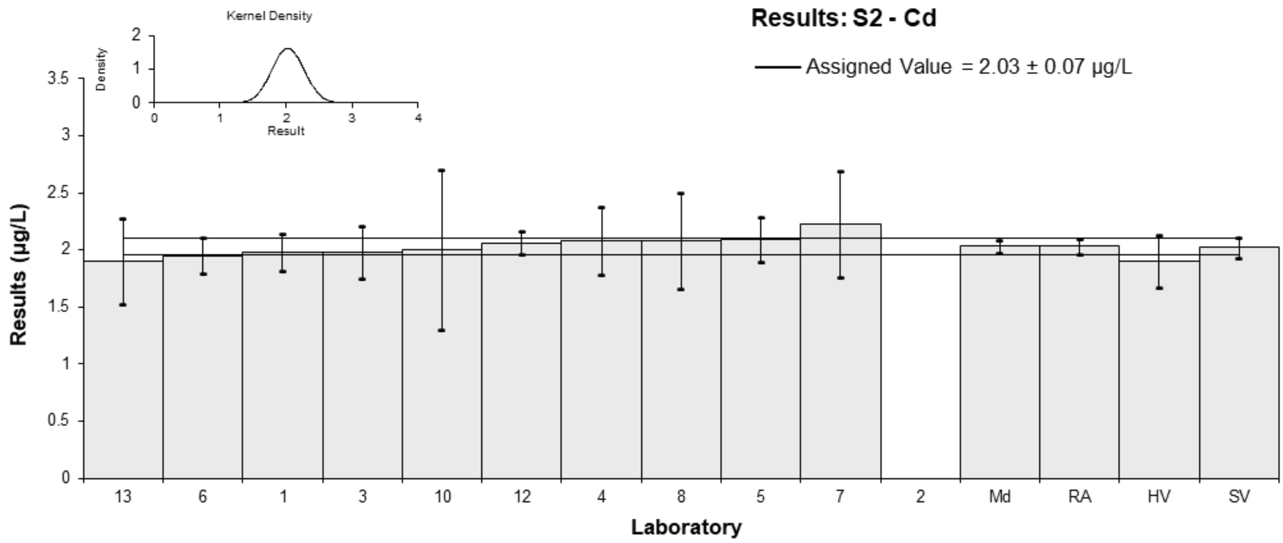
Sample No.	S2
Matrix	River Water
Analyte	Cd
Unit	µg/L

Participant Results

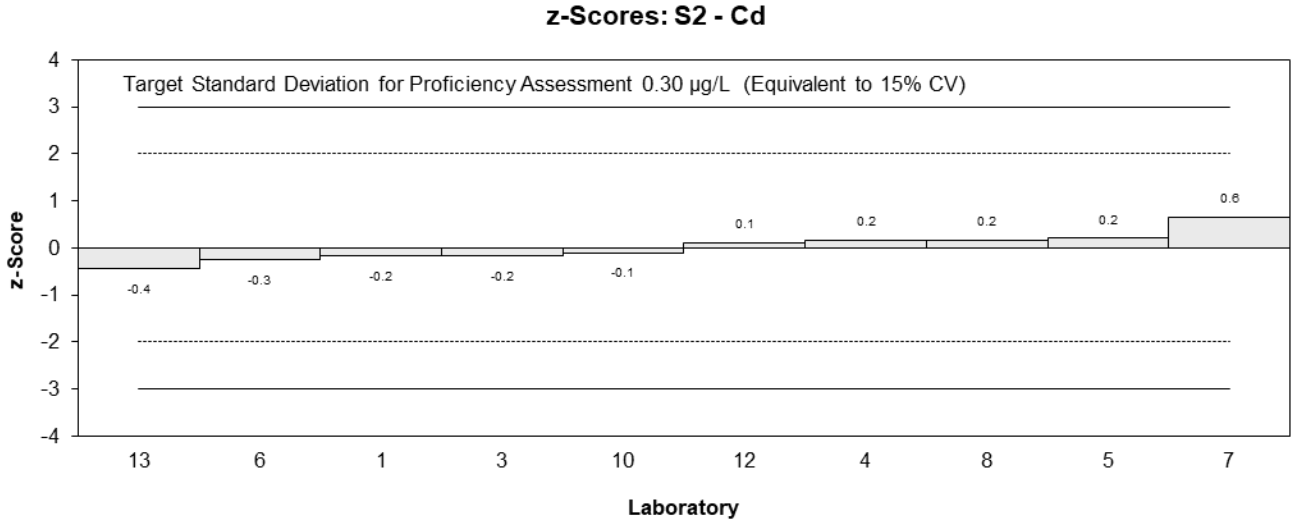
Lab. Code	Result	Uncertainty	z	E_n
1	1.98	0.16	-0.16	-0.29
2	NT	NT		
3	1.98	0.23	-0.16	-0.21
4	2.08	0.3	0.16	0.16
5	2.09	0.2	0.20	0.28
6	1.95	0.16	-0.26	-0.46
7	2.225	0.465	0.64	0.41
8	2.08	0.42	0.16	0.12
10	2	0.7	-0.10	-0.04
12	2.06	0.10	0.10	0.25
13	1.9	0.38	-0.43	-0.34

Statistics

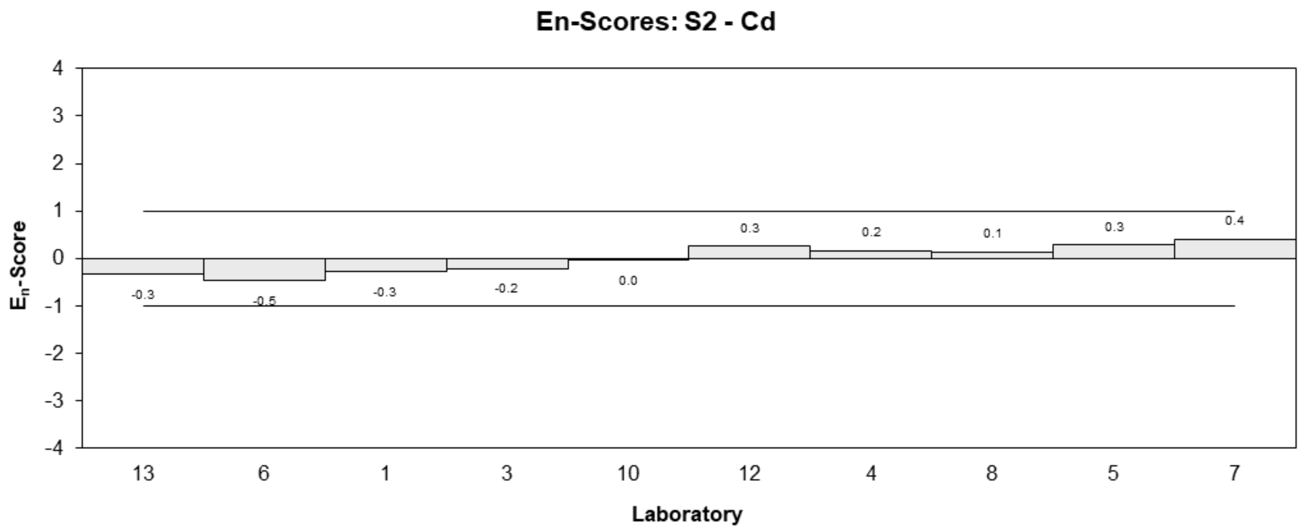
Assigned Value	2.03	0.07
Spike Value	2.02	0.09
Homogeneity Value	1.90	0.23
Robust Average	2.03	0.07
Median	2.03	0.06
Mean	2.03	
N	10	
Max	2.225	
Min	1.9	
Robust SD	0.090	
Robust CV	4.4%	



Results: S2 - Cd
Assigned Value = 2.03 ± 0.07 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
13
6
1
3
10
12
4
8
5
7
2
Md
RA
HV
SV



z-Scores: S2 - Cd
Target Standard Deviation for Proficiency Assessment 0.30 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.4
-0.3
-0.2
-0.2
-0.1
0.1
0.2
0.2
0.2
0.6
13
6
1
3
10
12
4
8
5
7



En-Scores: S2 - Cd
En-Score
Laboratory
-0.3
-0.5
-0.3
-0.2
0.0
0.3
0.2
0.1
0.3
0.4
13
6
1
3
10
12
4
8
5
7

Figure 27

Table 31

Sample Details

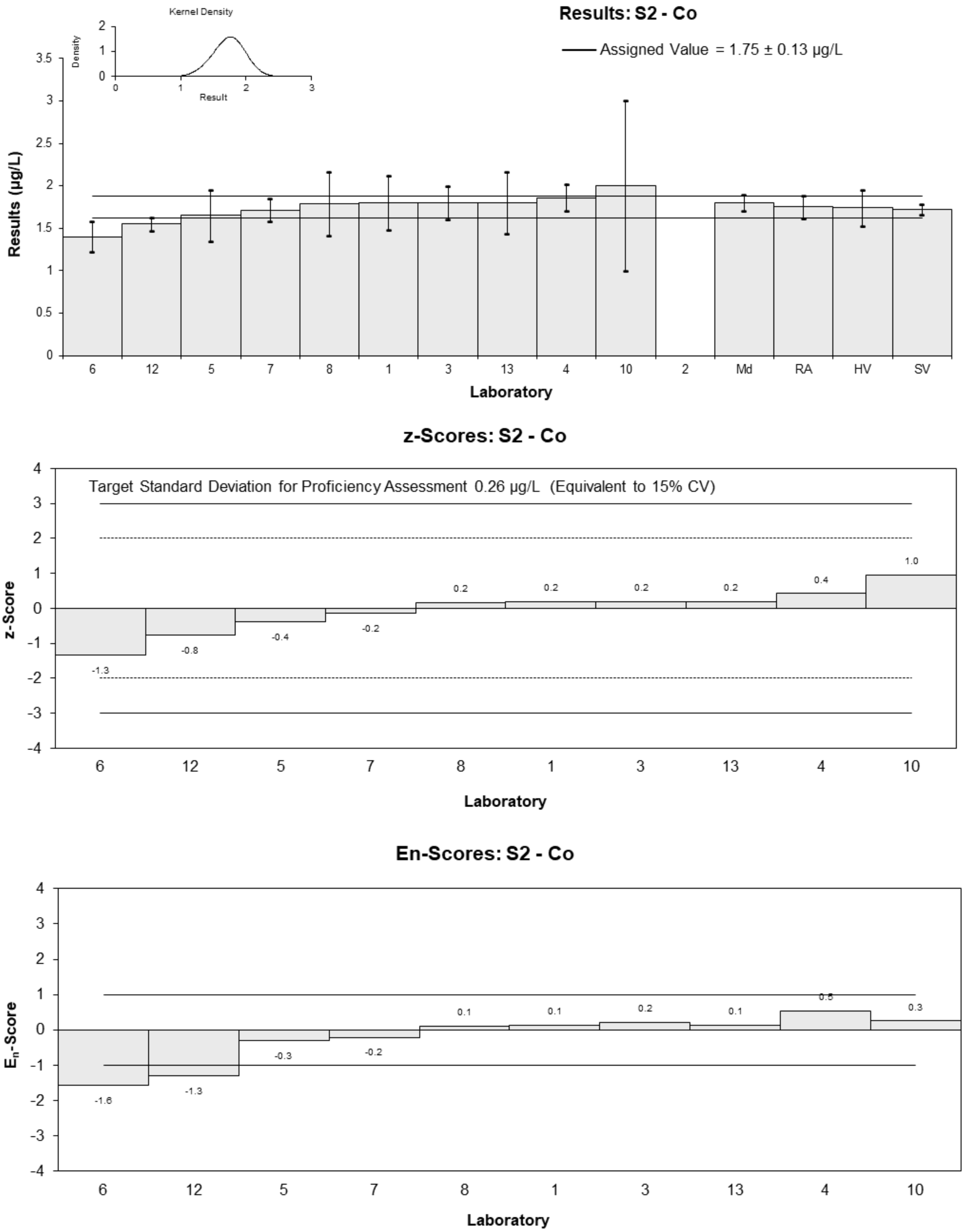
Sample No.	S2
Matrix	River Water
Analyte	Co
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.8	0.32	0.19	0.14
2	NT	NT		
3	1.8	0.2	0.19	0.21
4	1.86	0.16	0.42	0.53
5	1.65	0.3	-0.38	-0.31
6	1.4	0.18	-1.33	-1.58
7	1.711	0.135	-0.15	-0.21
8	1.79	0.38	0.15	0.10
10	2	1	0.95	0.25
12	1.55	0.08	-0.76	-1.31
13	1.8	0.36	0.19	0.13

Statistics

Assigned Value	1.75	0.13
Spike Value	1.72	0.06
Homogeneity Value	1.74	0.21
Robust Average	1.75	0.13
Median	1.80	0.09
Mean	1.74	
N	10	
Max	2	
Min	1.4	
Robust SD	0.17	
Robust CV	9.7%	



Kernel Density
Density
Result
Results: S2 - Co
Assigned Value = 1.75 ± 0.13 µg/L
Results (µg/L)
6
12
5
7
8
1
3
13
4
10
2
Md
RA
HV
SV
Laboratory
z-Scores: S2 - Co
Target Standard Deviation for Proficiency Assessment 0.26 µg/L (Equivalent to 15% CV)
z-Score
-1.3
-0.8
-0.4
-0.2
0.2
0.2
0.2
0.2
0.4
1.0
Laboratory
En-Scores: S2 - Co
En-Score
-1.6
-1.3
-0.3
-0.2
0.1
0.1
0.2
0.1
0.5
0.3
Laboratory

Figure 28

Table 32

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Cr
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.5	0.25	-0.13	-0.11
2	NT	NT		
3	1.6	0.4	0.31	0.17
4	1.66	0.36	0.57	0.35
5	1.53	0.3	0.00	0.00
6	1.6	0.20	0.31	0.32
7	1.386	0.108	-0.63	-1.02
8	1.56	0.23	0.13	0.12
10	1.4	1.2	-0.57	-0.11
12*	0.64	0.03	-3.88	-9.38
13	1.5	0.30	-0.13	-0.10

* Outlier, see Section 4.2

Statistics

Assigned Value	1.53	0.09
Spike Value	1.71	0.10
Homogeneity Value	1.70	0.20
Robust Average	1.51	0.10
Median	1.52	0.10
Mean	1.44	
N	10	
Max	1.66	
Min	0.64	
Robust SD	0.12	
Robust CV	8.1%	

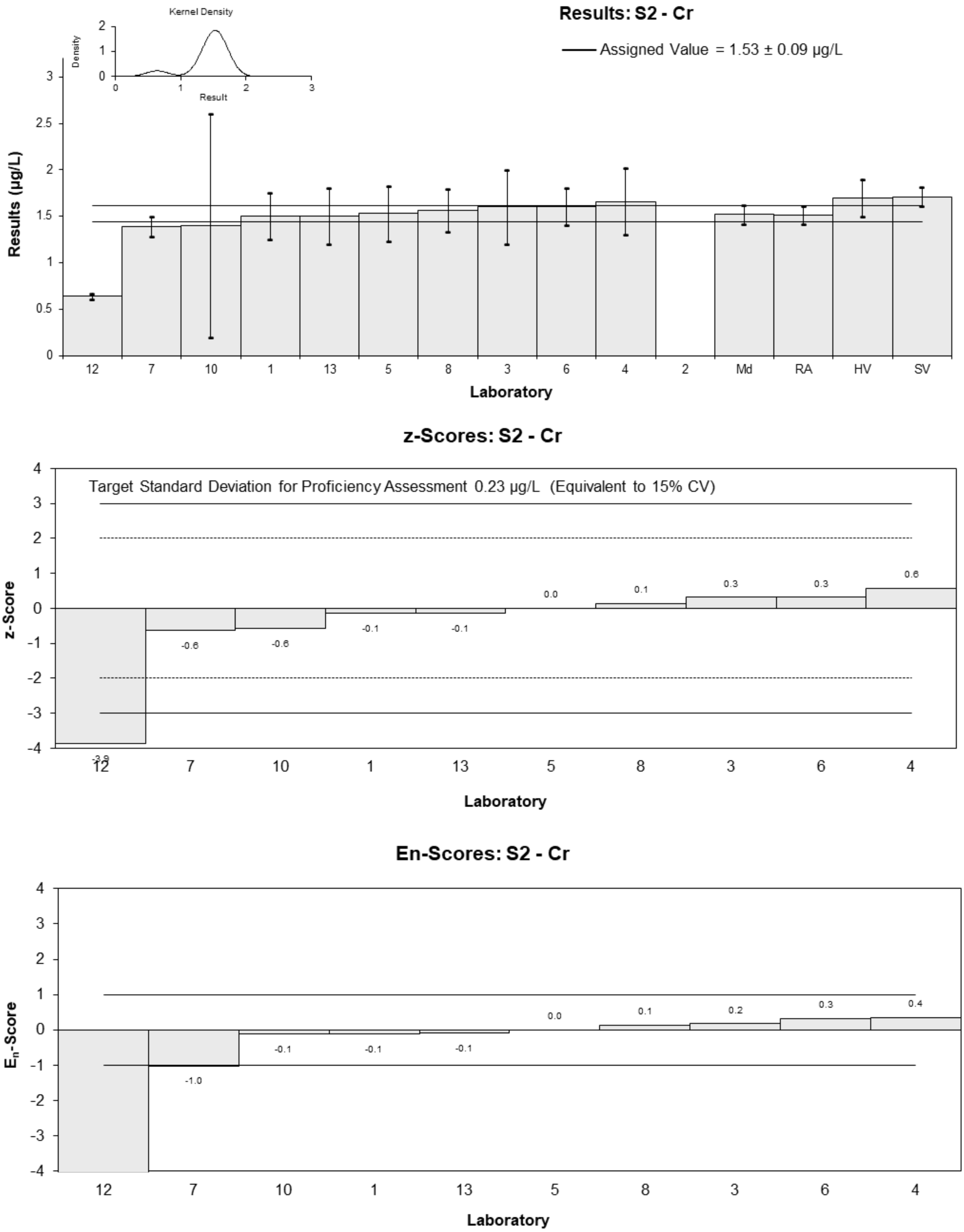

Results: S2 - Cr
Assigned Value = 1.53 ± 0.09 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
7
10
1
13
5
8
3
6
4
2
Md
RA
HV
SV
z-Scores: S2 - Cr
Target Standard Deviation for Proficiency Assessment 0.23 µg/L (Equivalent to 15% CV)
z-Score
-3.9
-0.6
-0.6
-0.1
-0.1
0.0
0.1
0.3
0.3
0.6
En-Scores: S2 - Cr
En-Score
-1.0
-0.1
-0.1
-0.1
0.0
0.1
0.2
0.3
0.4

Figure 29

Table 33

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Cu
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	19.1	3.5	-0.07	-0.06
2	NT	NT		
3	20.0	2.9	0.24	0.24
4	19.9	1.9	0.21	0.30
5	18.2	2.0	-0.38	-0.53
6	18.5	2.3	-0.28	-0.34
7	19.3	1.52	0.00	0.00
8	20.9	3.6	0.55	0.44
10	19	2	-0.10	-0.14
12	19.45	0.97	0.05	0.13
13	19	3.8	-0.10	-0.08

Statistics

Assigned Value	19.3	0.6
Spike Value	19.2	0.6
Homogeneity Value	20.0	2.4
Robust Average	19.3	0.6
Median	19.2	0.6
Mean	19.3	
N	10	
Max	20.9	
Min	18.2	
Robust SD	0.78	
Robust CV	4.1%	

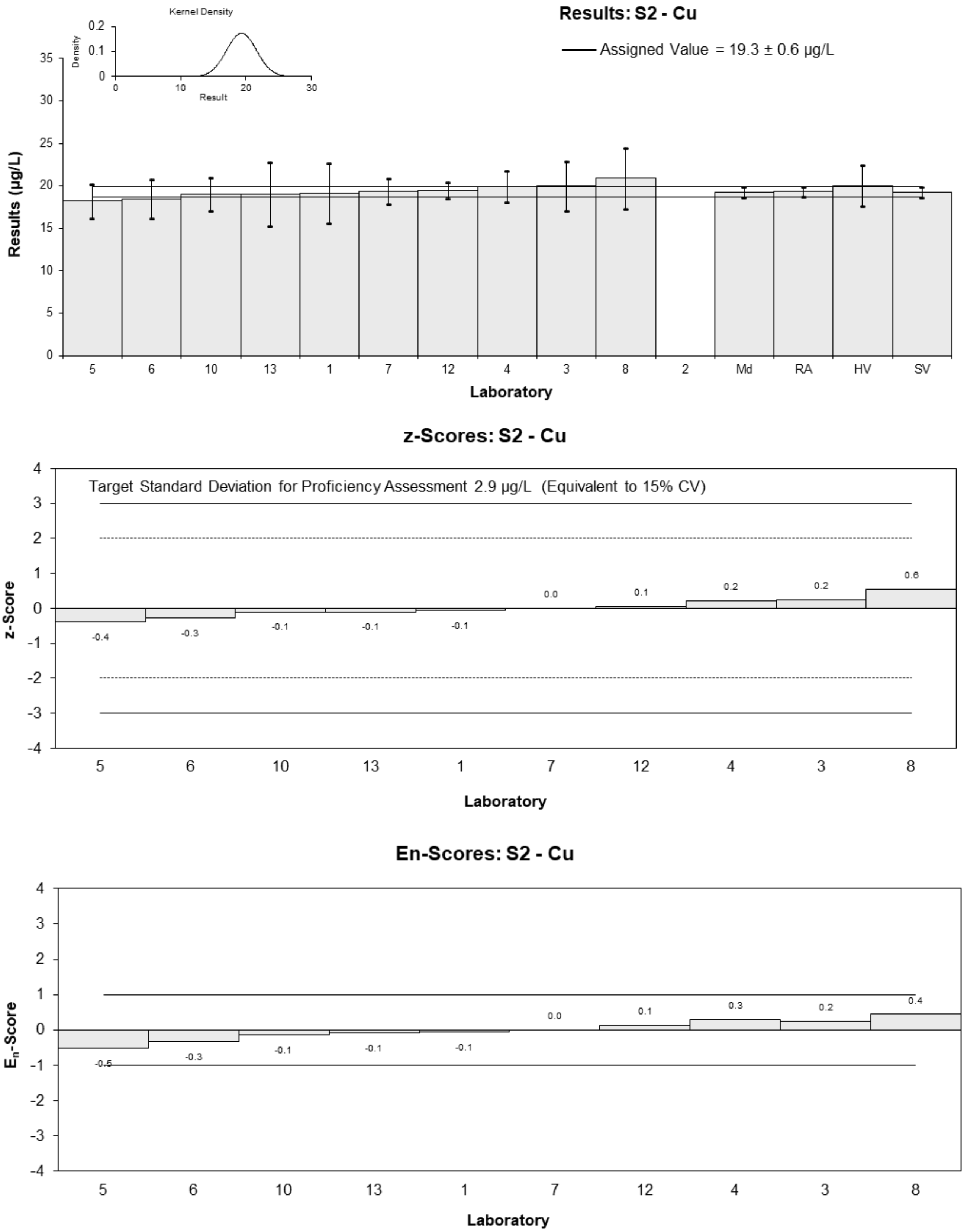

Kernel Density
Density
Result
Results: S2 - Cu
Assigned Value = 19.3 ± 0.6 µg/L
Results (µg/L)
Laboratory
5
6
10
13
1
7
12
4
3
8
2
Md
RA
HV
SV
z-Scores: S2 - Cu
Target Standard Deviation for Proficiency Assessment 2.9 µg/L (Equivalent to 15% CV)
z-Score
-0.4
-0.3
-0.1
-0.1
-0.1
0.0
0.1
0.2
0.2
0.6
Laboratory
En-Scores: S2 - Cu
E_n-Score
-0.5
-0.3
-0.1
-0.1
-0.1
0.0
0.1
0.3
0.2
0.4
Laboratory

Figure 30

Table 34

Sample Details

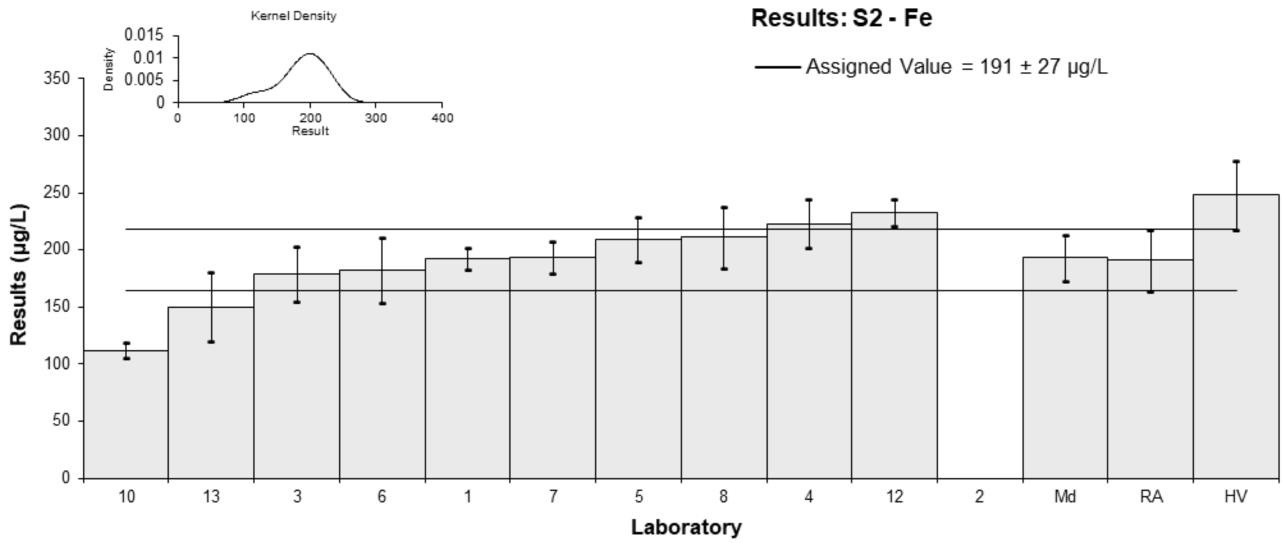
Sample No.	S2
Matrix	River Water
Analyte	Fe
Unit	µg/L

Participant Results

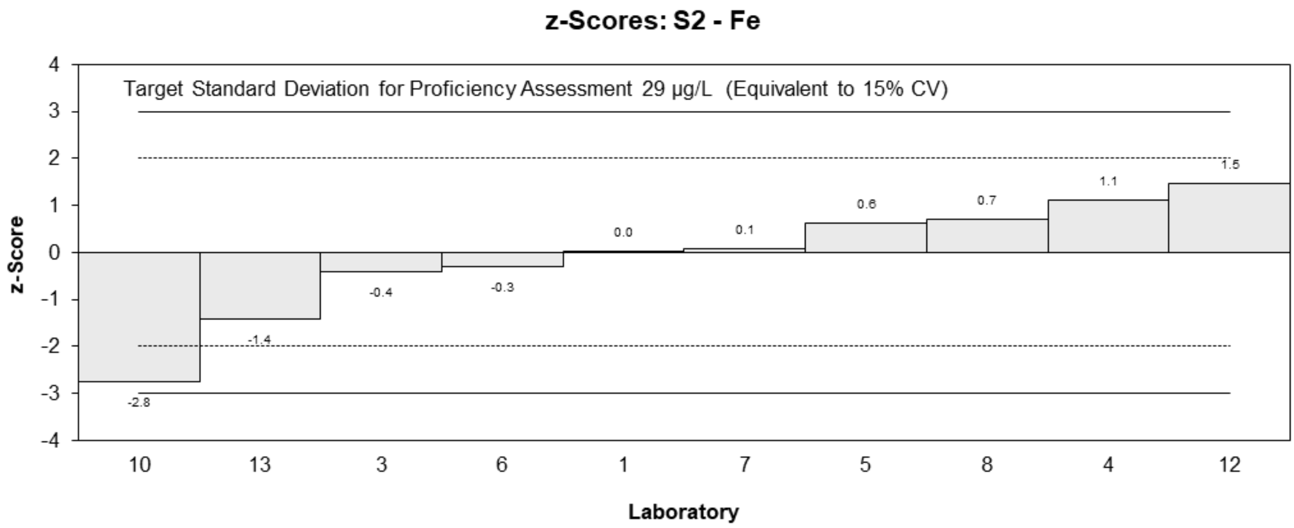
Lab. Code	Result	Uncertainty	z	E_n
1	192	9.6	0.03	0.03
2	NT	NT		
3	179	24	-0.42	-0.33
4	223	21	1.12	0.94
5	209	20	0.63	0.54
6	182	28.7	-0.31	-0.23
7	193.398	13.654	0.08	0.08
8	211	27	0.70	0.52
10	112	7	-2.76	-2.83
12	233	11.65	1.47	1.43
13	150	30	-1.43	-1.02

Statistics

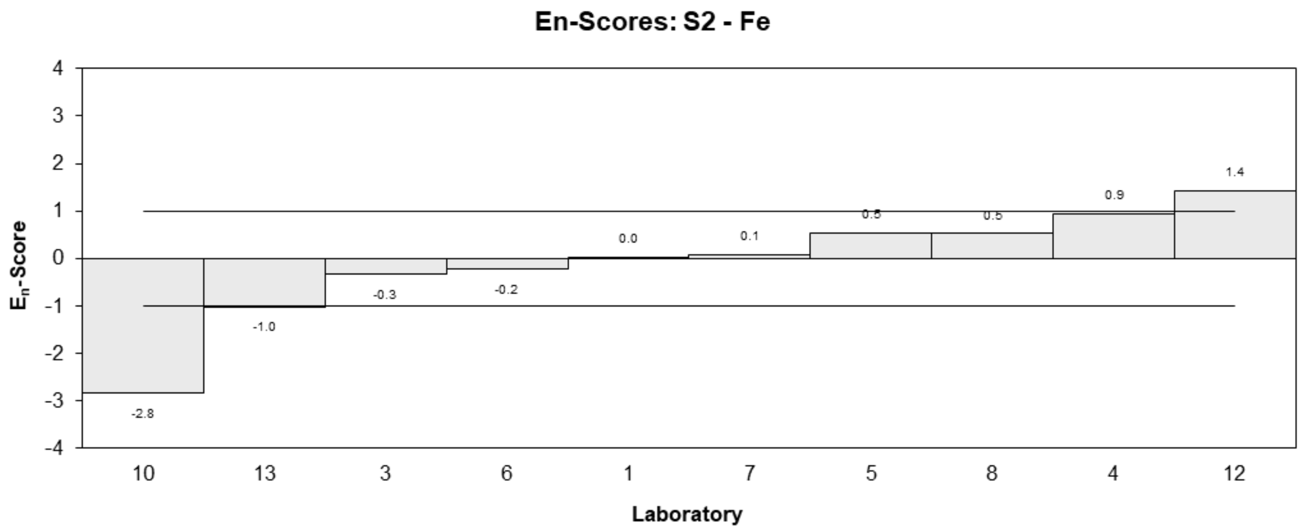
Assigned Value	191	27
Spike Value	Not Spiked	
Homogeneity Value	248	30
Robust Average	191	27
Median	193	20
Mean	188	
N	10	
Max	233	
Min	112	
Robust SD	34	
Robust CV	18%	



Kernel Density
Density
Result
Results: S2 - Fe
Assigned Value = 191 ± 27 µg/L
Results (µg/L)
Laboratory
10
13
3
6
1
7
5
8
4
12
2
Md
RA
HV



z-Scores: S2 - Fe
Target Standard Deviation for Proficiency Assessment 29 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.8
-1.4
-0.4
-0.3
0.0
0.1
0.6
0.7
1.1
1.5



En-Scores: S2 - Fe
En-Score
Laboratory
-2.8
-1.0
-0.3
-0.2
0.0
0.1
0.5
0.5
0.9
1.4

Figure 31

Table 35

Sample Details

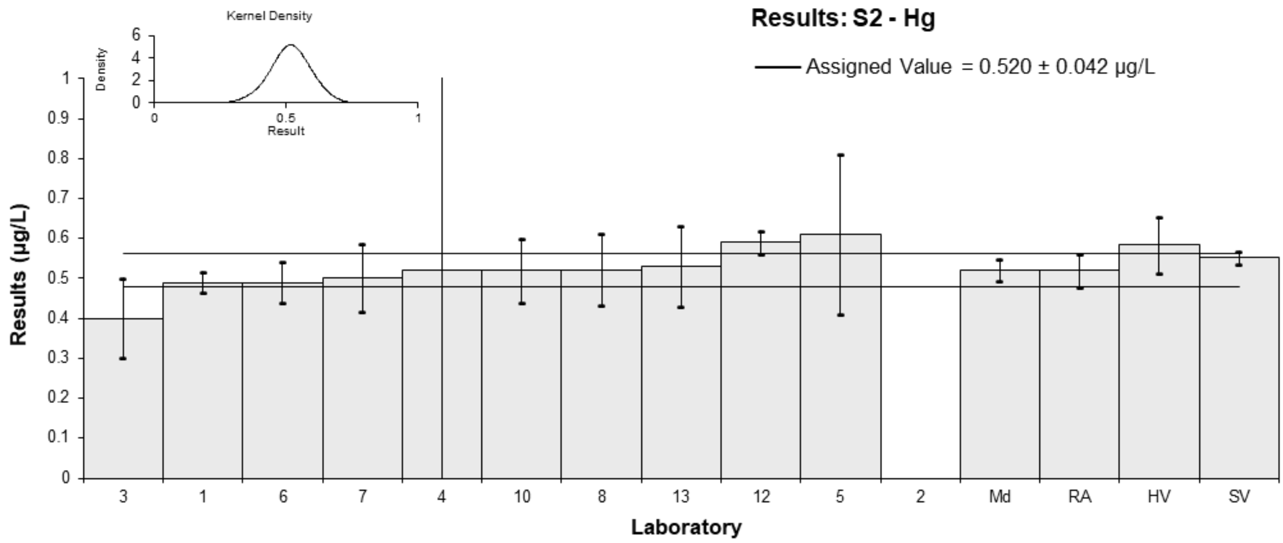
Sample No.	S2
Matrix	River Water
Analyte	Hg
Unit	µg/L

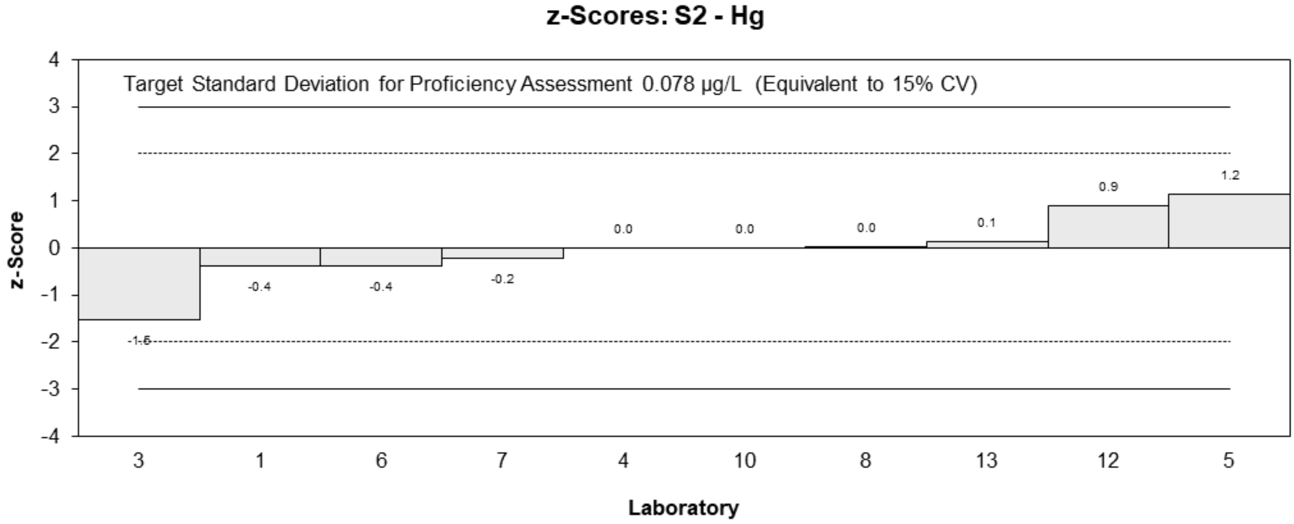
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.49	0.026	-0.38	-0.61
2	NT	NT		
3	0.4	0.1	-1.54	-1.11
4	0.52	0.53	0.00	0.00
5	0.61	0.2	1.15	0.44
6	0.49	0.05	-0.38	-0.46
7	0.502	0.085	-0.23	-0.19
8	0.522	0.089	0.03	0.02
10	0.52	0.08	0.00	0.00
12	0.59	0.03	0.90	1.36
13	0.53	0.10	0.13	0.09

Statistics

Assigned Value	0.520	0.042
Spike Value	0.552	0.016
Homogeneity Value	0.584	0.070
Robust Average	0.520	0.042
Median	0.520	0.028
Mean	0.517	
N	10	
Max	0.61	
Min	0.4	
Robust SD	0.053	
Robust CV	10%	


Results: S2 - Hg
Assigned Value = 0.520 ± 0.042 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
3
1
6
7
4
10
8
13
12
5
2
Md
RA
HV
SV


z-Scores: S2 - Hg
Target Standard Deviation for Proficiency Assessment 0.078 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.5
-0.4
-0.4
-0.2
0.0
0.0
0.0
0.1
0.9
1.2
3
1
6
7
4
10
8
13
12
5

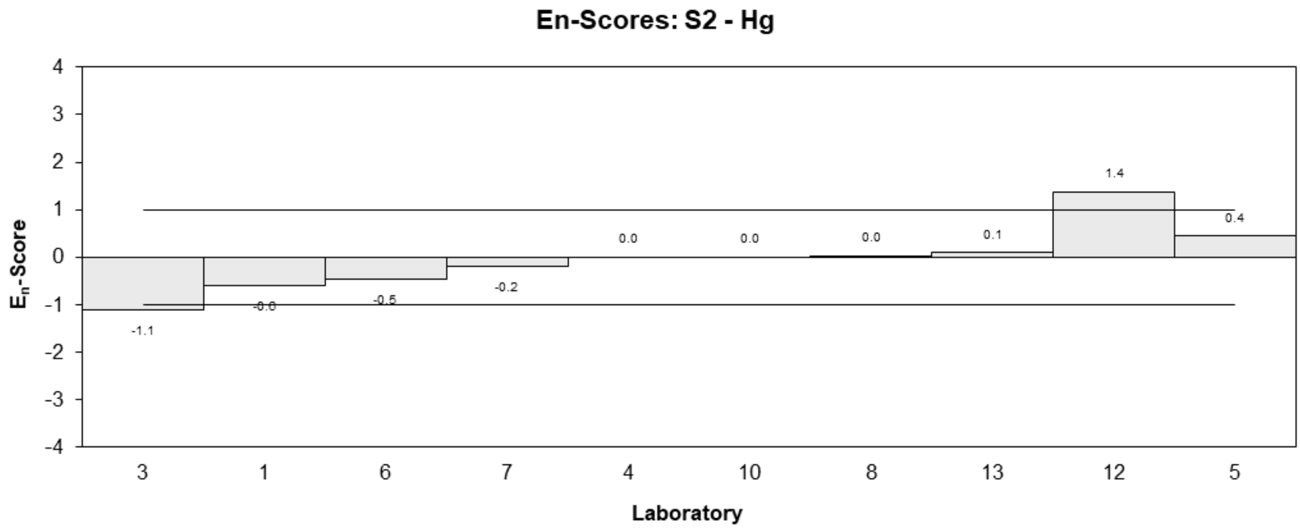

En-Scores: S2 - Hg
En-Score
Laboratory
-1.1
-0.6
-0.5
-0.2
0.0
0.0
0.0
0.1
1.4
0.4
3
1
6
7
4
10
8
13
12
5

Figure 32

Table 36

Sample Details

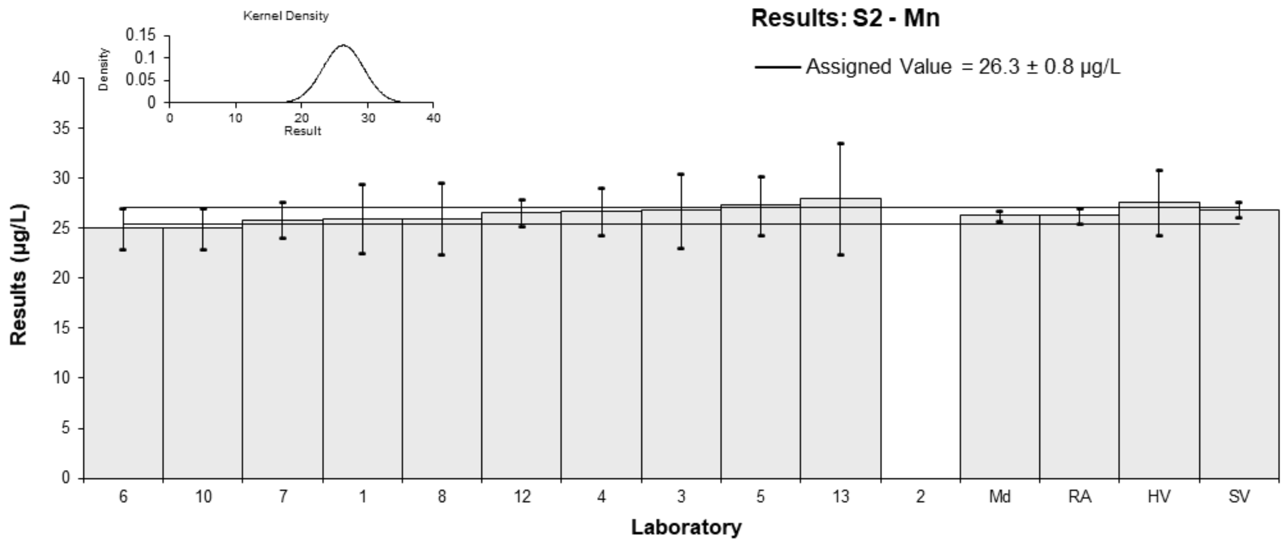
Sample No.	S2
Matrix	River Water
Analyte	Mn
Unit	µg/L

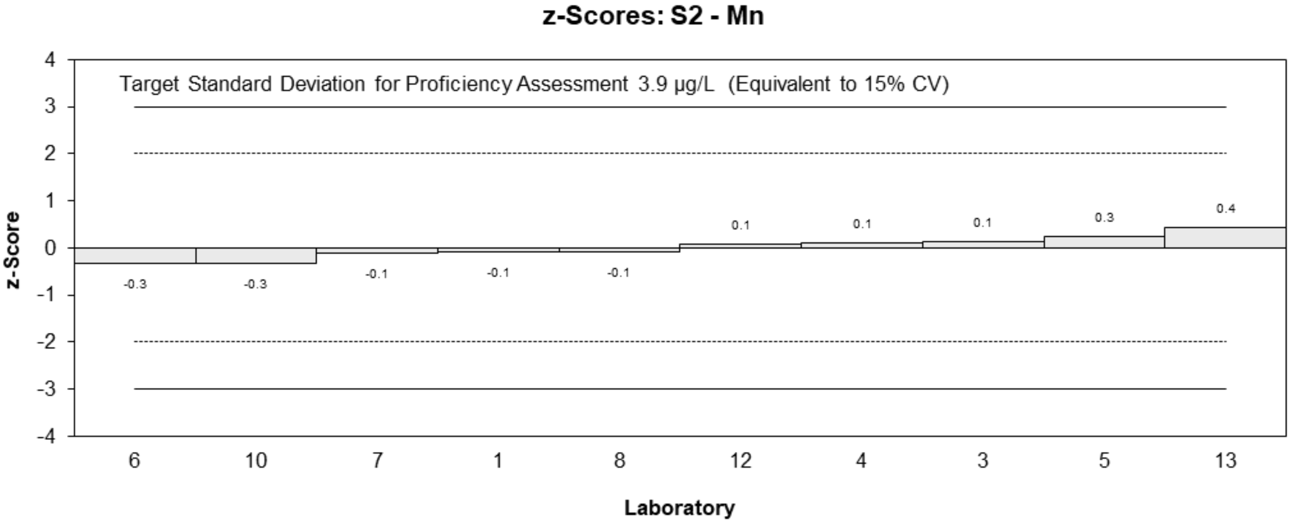
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	26	3.43	-0.08	-0.09
2	NT	NT		
3	26.8	3.7	0.13	0.13
4	26.7	2.4	0.10	0.16
5	27.3	3.0	0.25	0.32
6	25	2.0	-0.33	-0.60
7	25.872	1.764	-0.11	-0.22
8	26.0	3.6	-0.08	-0.08
10	25	2	-0.33	-0.60
12	26.57	1.33	0.07	0.17
13	28	5.6	0.43	0.30

Statistics

Assigned Value	26.3	0.8
Spike Value	26.9	0.8
Homogeneity Value	27.6	3.3
Robust Average	26.3	0.8
Median	26.3	0.5
Mean	26.3	
N	10	
Max	28	
Min	25	
Robust SD	1.1	
Robust CV	4%	


Kernel Density
Density
Result
Results: S2 - Mn
Assigned Value = 26.3 ± 0.8 µg/L
Results (µg/L)
6
10
7
1
8
12
4
3
5
13
2
Md
RA
HV
SV
Laboratory


z-Scores: S2 - Mn
Target Standard Deviation for Proficiency Assessment 3.9 µg/L (Equivalent to 15% CV)
z-Score
-0.3
-0.3
-0.1
-0.1
-0.1
0.1
0.1
0.1
0.3
0.4
6
10
7
1
8
12
4
3
5
13
Laboratory

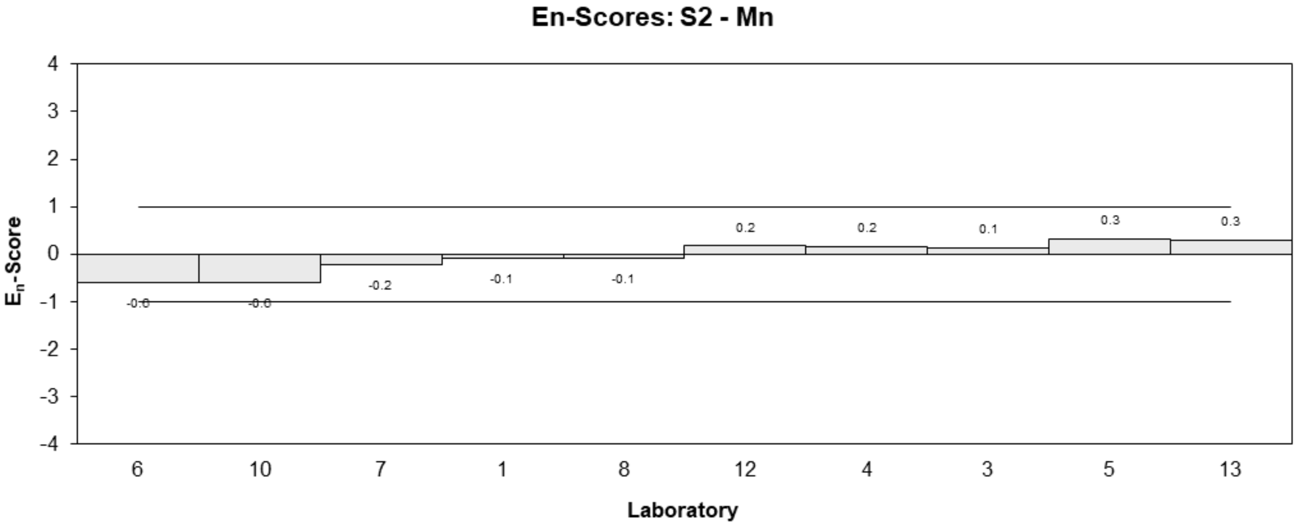

En-Scores: S2 - Mn
En-Score
-0.2
-0.1
-0.1
0.2
0.2
0.1
0.3
0.3
6
10
7
1
8
12
4
3
5
13
Laboratory

Figure 33

Table 37

Sample Details

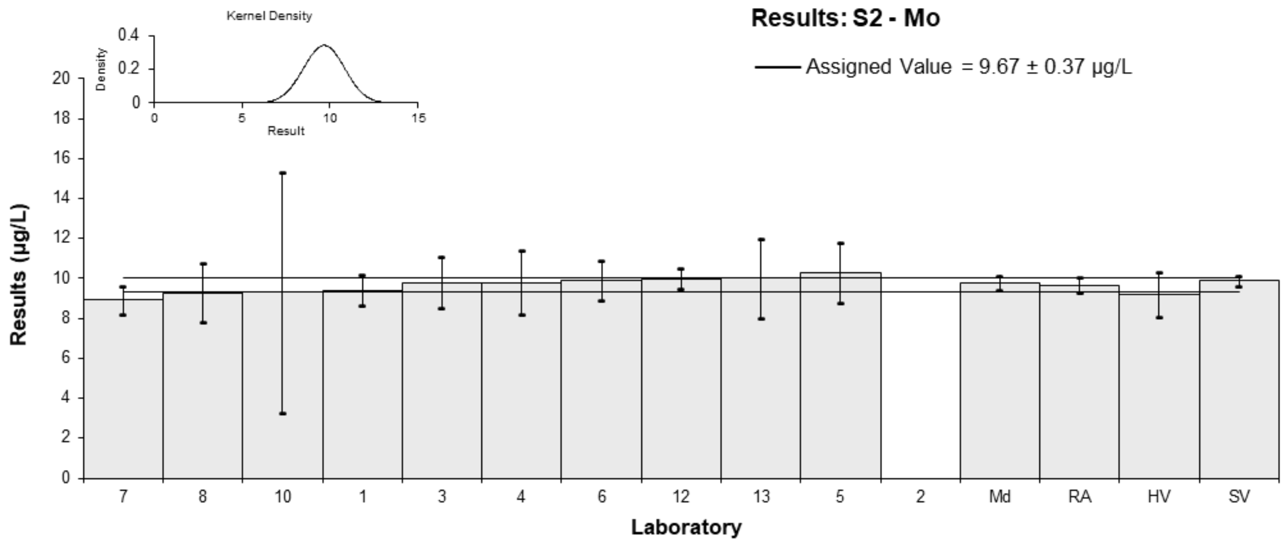
Sample No.	S2
Matrix	River Water
Analyte	Mo
Unit	µg/L

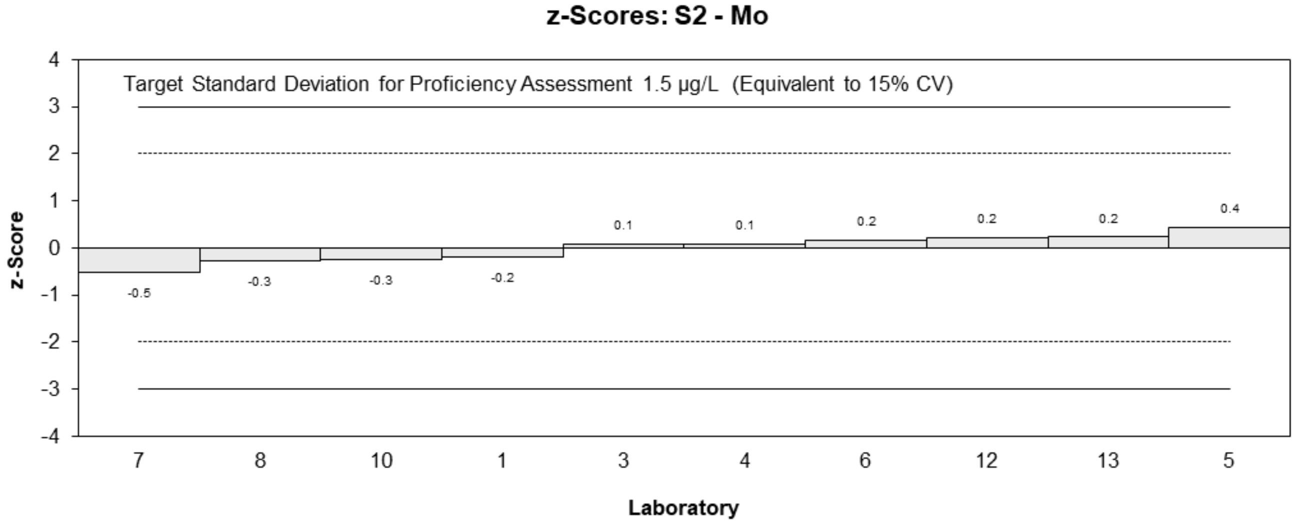
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	9.4	0.78	-0.19	-0.31
2	NT	NT		
3	9.8	1.3	0.09	0.10
4	9.8	1.6	0.09	0.08
5	10.3	1.5	0.43	0.41
6	9.9	0.99	0.16	0.22
7	8.922	0.687	-0.52	-0.96
8	9.28	1.48	-0.27	-0.26
10	9.3	6	-0.26	-0.06
12	9.98	0.50	0.21	0.50
13	10	2.0	0.23	0.16

Statistics

Assigned Value	9.67	0.37
Spike Value	9.87	0.28
Homogeneity Value	9.2	1.1
Robust Average	9.67	0.37
Median	9.80	0.35
Mean	9.67	
N	10	
Max	10.3	
Min	8.922	
Robust SD	0.47	
Robust CV	4.9%	


Results: S2 - Mo
Assigned Value = 9.67 ± 0.37 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
8
10
1
3
4
6
12
13
5
2
Md
RA
HV
SV


z-Scores: S2 - Mo
Target Standard Deviation for Proficiency Assessment 1.5 µg/L (Equivalent to 15% CV)
z-Score
-0.5
-0.3
-0.3
-0.2
0.1
0.1
0.2
0.2
0.2
0.4
Laboratory
7
8
10
1
3
4
6
12
13
5

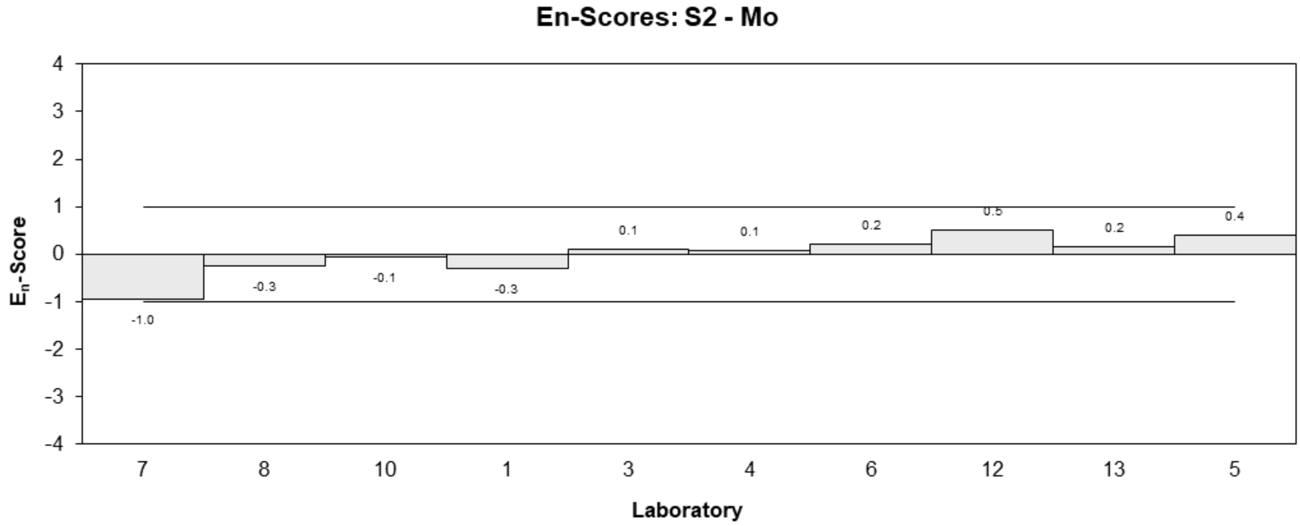

En-Scores: S2 - Mo
E_n-Score
-1.0
-0.3
-0.1
-0.3
0.1
0.1
0.2
0.5
0.2
0.4
Laboratory
7
8
10
1
3
4
6
12
13
5

Figure 34

Table 38

Sample Details

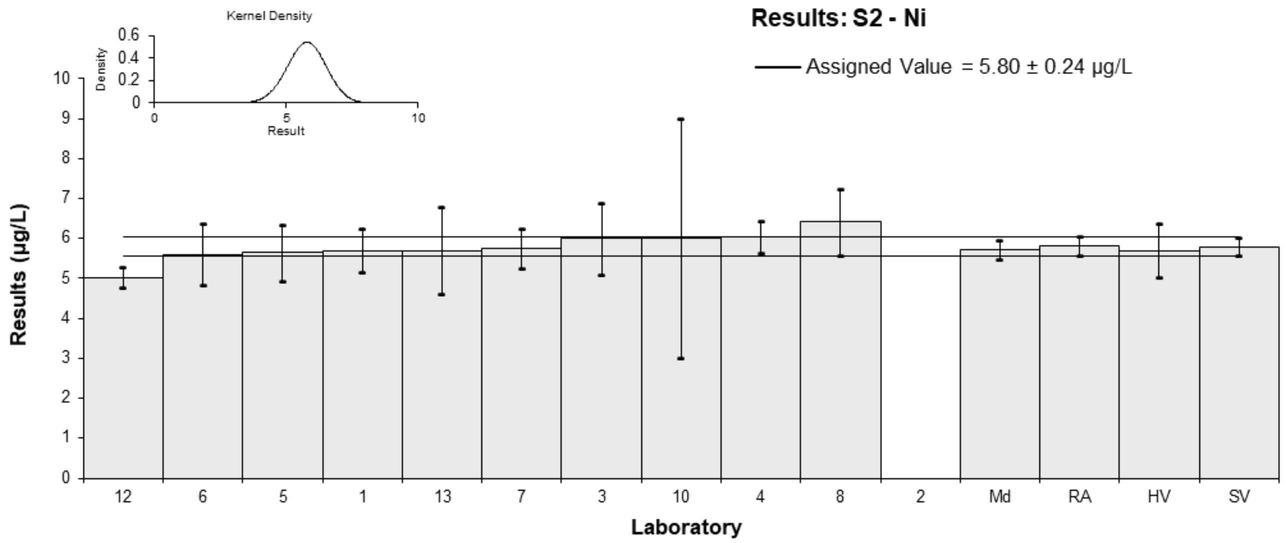
Sample No.	S2
Matrix	River Water
Analyte	Ni
Unit	µg/L

Participant Results

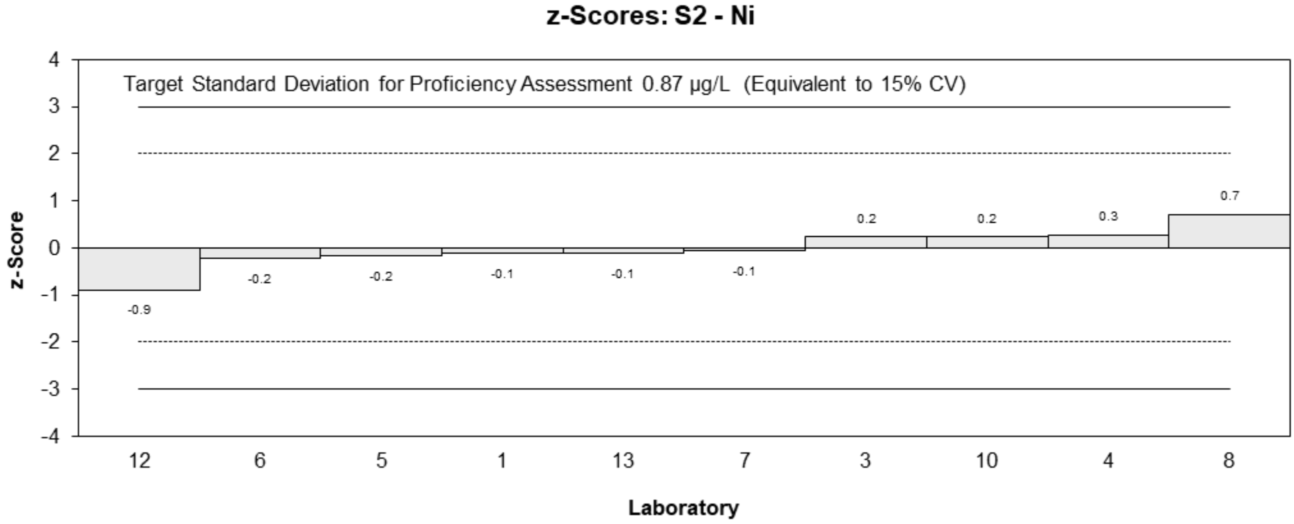
Lab. Code	Result	Uncertainty	z	E_n
1	5.7	0.55	-0.11	-0.17
2	NT	NT		
3	6.0	0.9	0.23	0.21
4	6.04	0.4	0.28	0.51
5	5.65	0.7	-0.17	-0.20
6	5.6	0.77	-0.23	-0.25
7	5.745	0.495	-0.06	-0.10
8	6.41	0.83	0.70	0.71
10	6	3	0.23	0.07
12	5.03	0.25	-0.89	-2.22
13	5.7	1.1	-0.11	-0.09

Statistics

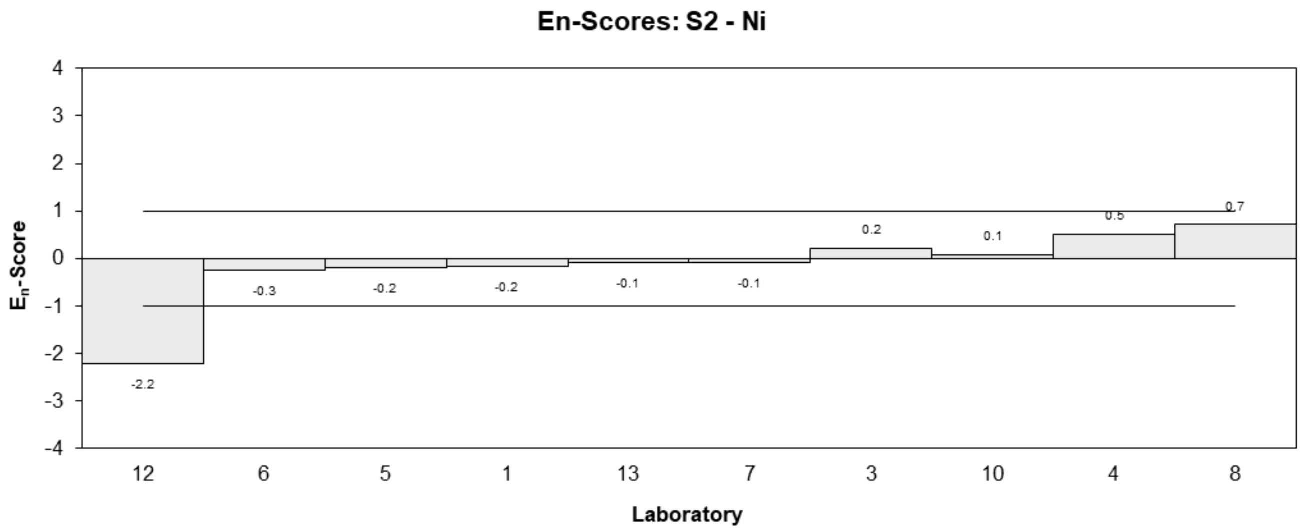
Assigned Value	5.80	0.24
Spike Value	5.79	0.22
Homogeneity Value	5.70	0.68
Robust Average	5.80	0.24
Median	5.72	0.23
Mean	5.79	
N	10	
Max	6.41	
Min	5.03	
Robust SD	0.30	
Robust CV	5.2%	



Results: S2 - Ni
Assigned Value = 5.80 ± 0.24 µg/L
Kernel Density
Density
Result
Results (µg/L)
12
6
5
1
13
7
3
10
4
8
2
Md
RA
HV
SV
Laboratory



z-Scores: S2 - Ni
Target Standard Deviation for Proficiency Assessment 0.87 µg/L (Equivalent to 15% CV)
z-Score
-0.9
-0.2
-0.2
-0.1
-0.1
-0.1
0.2
0.2
0.3
0.7
12
6
5
1
13
7
3
10
4
8
Laboratory



En-Scores: S2 - Ni
En-Score
-2.2
-0.3
-0.2
-0.2
-0.1
-0.1
0.2
0.1
0.5
0.7
12
6
5
1
13
7
3
10
4
8
Laboratory

Figure 35

Table 39

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Pb
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.9	0.93	-0.34	-0.28
2	NT	NT		
3	5.1	0.5	-0.08	-0.11
4	5.36	0.38	0.26	0.48
5	5.06	0.7	-0.13	-0.14
6	5	0.48	-0.21	-0.31
7	5.26	0.392	0.13	0.23
8	5.45	0.93	0.37	0.31
10	4.9	3	-0.34	-0.09
12	5.22	0.26	0.08	0.19
13	5.3	1.1	0.18	0.13

Statistics

Assigned Value	5.16	0.17
Spike Value	5.22	0.15
Homogeneity Value	4.78	0.57
Robust Average	5.16	0.17
Median	5.16	0.18
Mean	5.16	
N	10	
Max	5.45	
Min	4.9	
Robust SD	0.22	
Robust CV	4.2%	

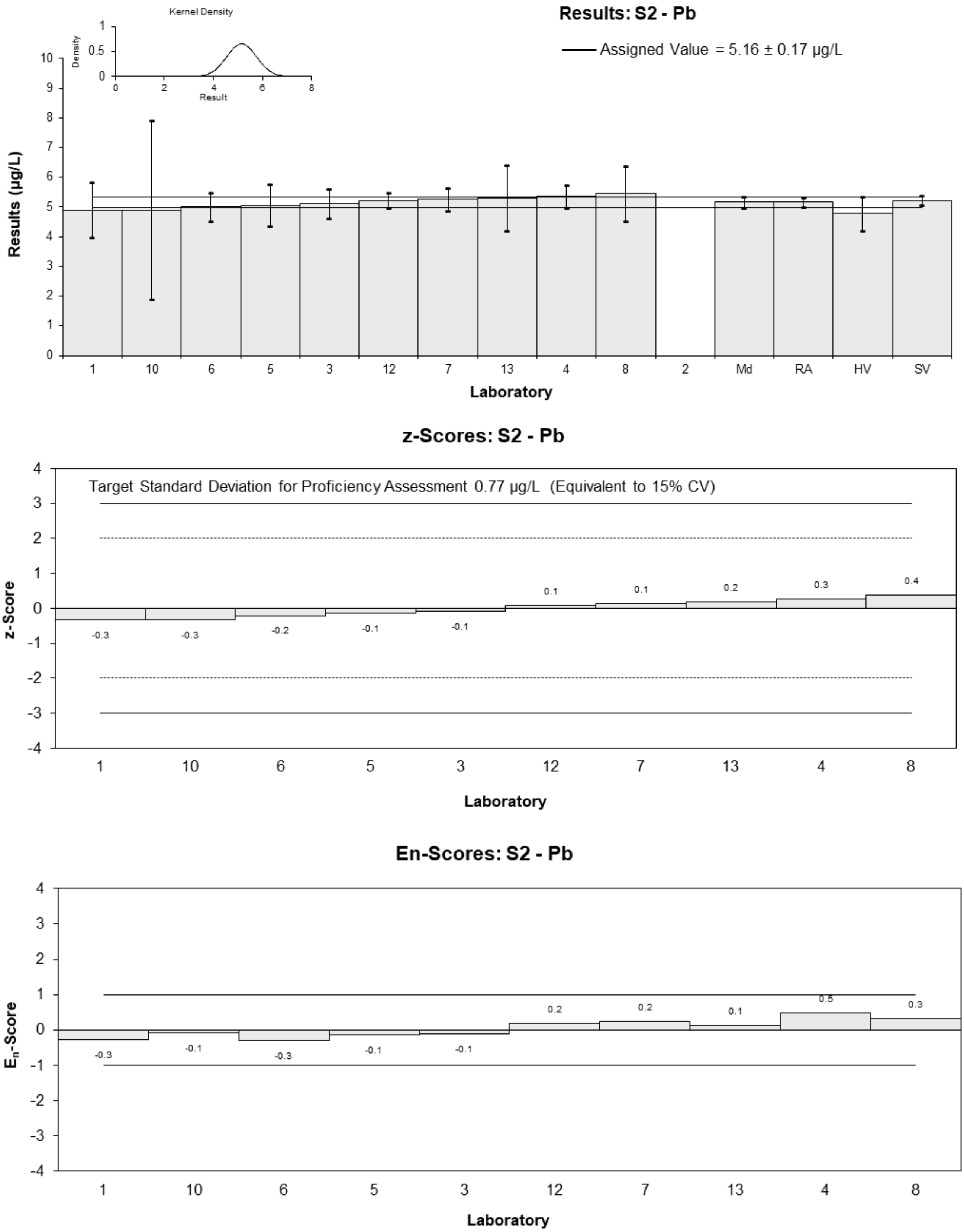

Kernel Density
Density
Result
Results: S2 - Pb
Assigned Value = 5.16 ± 0.17 µg/L
Results (µg/L)
1 10 6 5 3 12 7 13 4 8 2 Md RA HV SV
Laboratory
z-Scores: S2 - Pb
Target Standard Deviation for Proficiency Assessment 0.77 µg/L (Equivalent to 15% CV)
z-Score
-0.3 -0.3 -0.2 -0.1 -0.1 0.1 0.1 0.2 0.3 0.4
1 10 6 5 3 12 7 13 4 8
Laboratory
En-Scores: S2 - Pb
En-Score
-0.3 -0.1 -0.3 -0.1 -0.1 0.2 0.2 0.1 0.5 0.3
1 10 6 5 3 12 7 13 4 8
Laboratory

Figure 36

Table 40

Sample Details

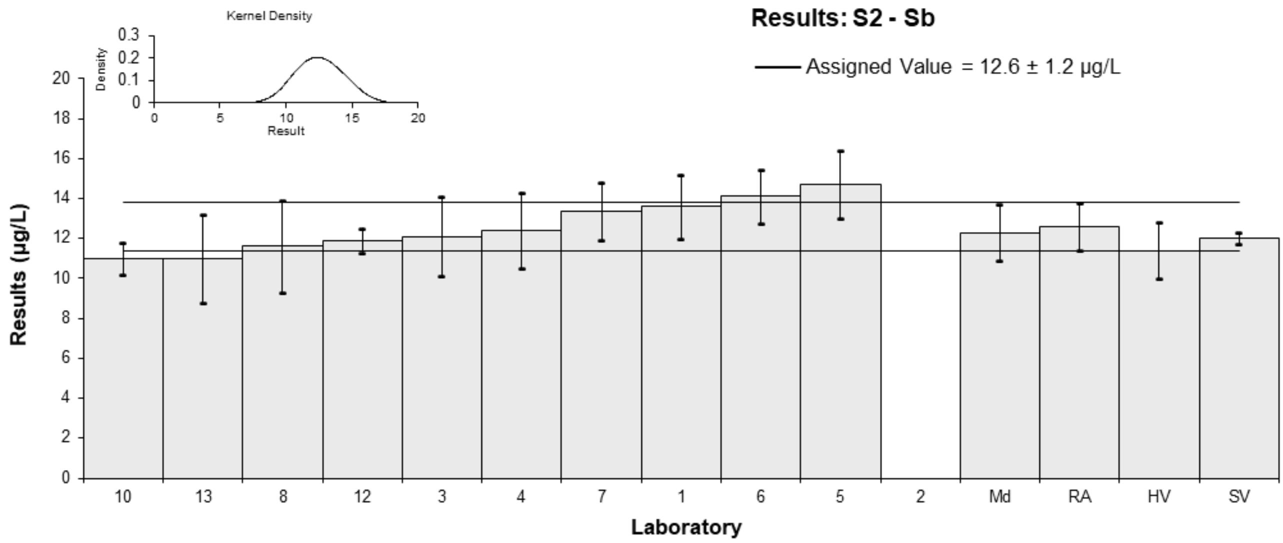
Sample No.	S2
Matrix	River Water
Analyte	Sb
Unit	µg/L

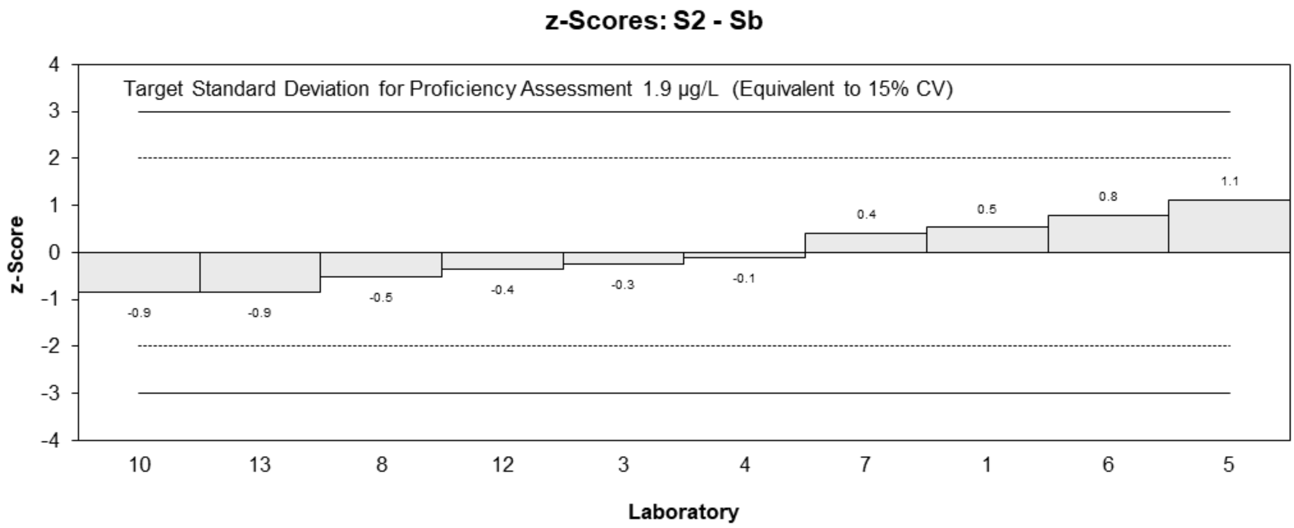
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	13.6	1.6	0.53	0.50
2	NT	NT		
3	12.1	2.0	-0.26	-0.21
4	12.4	1.9	-0.11	-0.09
5	14.7	1.7	1.11	1.01
6	14.1	1.33	0.79	0.84
7	13.354	1.459	0.40	0.40
8	11.6	2.3	-0.53	-0.39
10	11	0.8	-0.85	-1.11
12	11.90	0.60	-0.37	-0.52
13	11	2.2	-0.85	-0.64

Statistics

Assigned Value	12.6	1.2
Spike Value	12.0	0.3
Homogeneity Value	11.4	1.4
Robust Average	12.6	1.2
Median	12.3	1.4
Mean	12.6	
N	10	
Max	14.7	
Min	11	
Robust SD	1.5	
Robust CV	12%	


Results: S2 - Sb
Assigned Value = 12.6 ± 1.2 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
10
13
8
12
3
4
7
1
6
5
2
Md
RA
HV
SV


z-Scores: S2 - Sb
Target Standard Deviation for Proficiency Assessment 1.9 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.9
-0.9
-0.5
-0.4
-0.3
-0.1
0.4
0.5
0.8
1.1
10
13
8
12
3
4
7
1
6
5

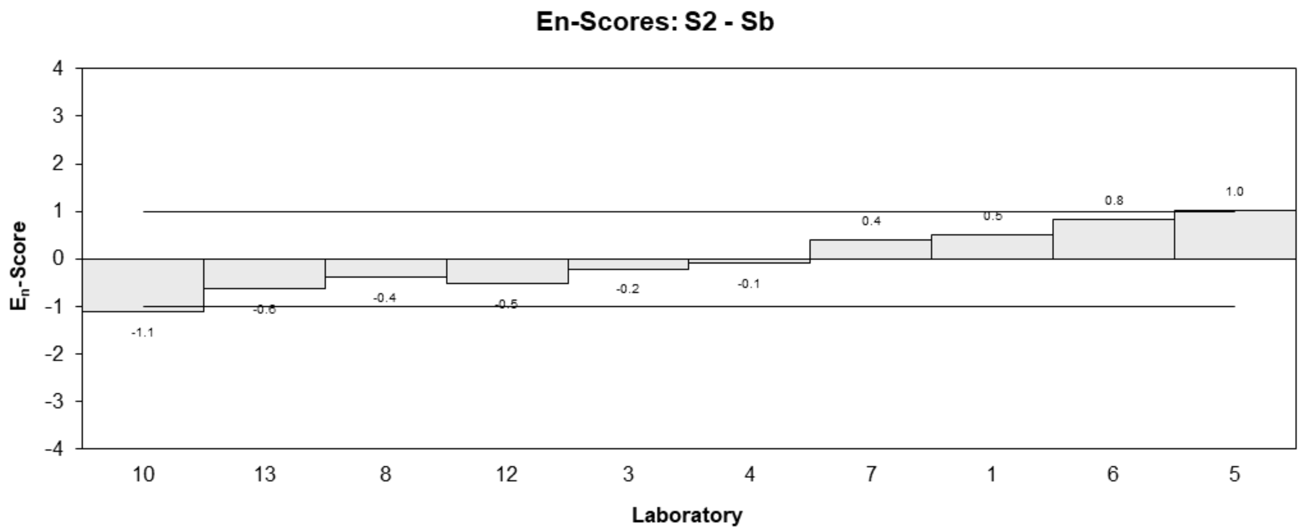

En-Scores: S2 - Sb
En-Score
Laboratory
-1.1
-0.6
-0.4
-0.5
-0.2
-0.1
0.4
0.5
0.8
1.0
10
13
8
12
3
4
7
1
6
5

Figure 37

Table 41

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Se
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.9	0.095	-0.36	-0.68
2	NT	NT		
3	2.0	0.4	-0.03	-0.02
4	2.0	0.69	-0.03	-0.01
5	2.18	0.3	0.56	0.52
6	1.8	0.27	-0.70	-0.70
7	<10	NR		
8	2.25	0.50	0.80	0.46
10	2	3	-0.03	0.00
12	2.09	0.10	0.27	0.49
13	1.9	0.38	-0.36	-0.27

Statistics

Assigned Value	2.01	0.13
Spike Value	2.04	0.06
Homogeneity Value	2.10	0.25
Robust Average	2.01	0.13
Median	2.00	0.12
Mean	2.01	
N	9	
Max	2.25	
Min	1.8	
Robust SD	0.16	
Robust CV	8%	

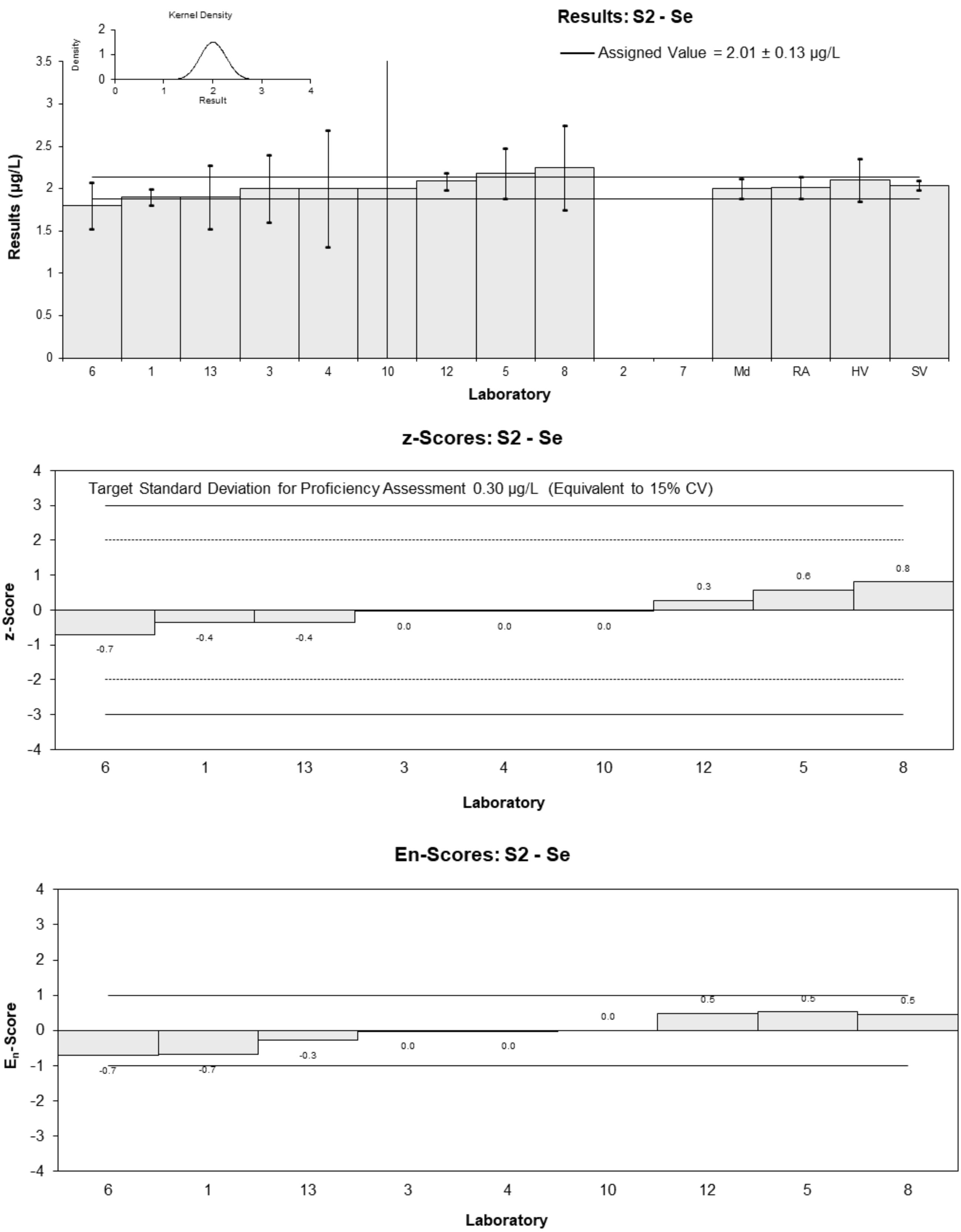

Results: S2 - Se
Assigned Value = 2.01 ± 0.13 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
1
13
3
4
10
12
5
8
2
7
Md
RA
HV
SV
z-Scores: S2 - Se
Target Standard Deviation for Proficiency Assessment 0.30 µg/L (Equivalent to 15% CV)
z-Score
-0.7
-0.4
-0.4
0.0
0.0
0.0
0.3
0.6
0.8
Laboratory
En-Scores: S2 - Se
En-Score
-0.7
-0.7
-0.3
0.0
0.0
0.0
0.5
0.5
0.5
Laboratory

Figure 38

Table 42

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Ti
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty
1	8.0	0.66
2	NT	NT
3	7	1
4	<20	NR
5	NT	NT
6	6	0.56
7	<10	NR
8	NT	NT
10	NT	NT
12	6.32	0.32
13	6.5	1.3

Statistics

Assigned Value	Not Set	
Spike Value	6.56	0.71
Homogeneity Value	5.4	1.4
Median	6.50	0.83
Mean	6.76	
N	5	
Max	8	
Min	6	

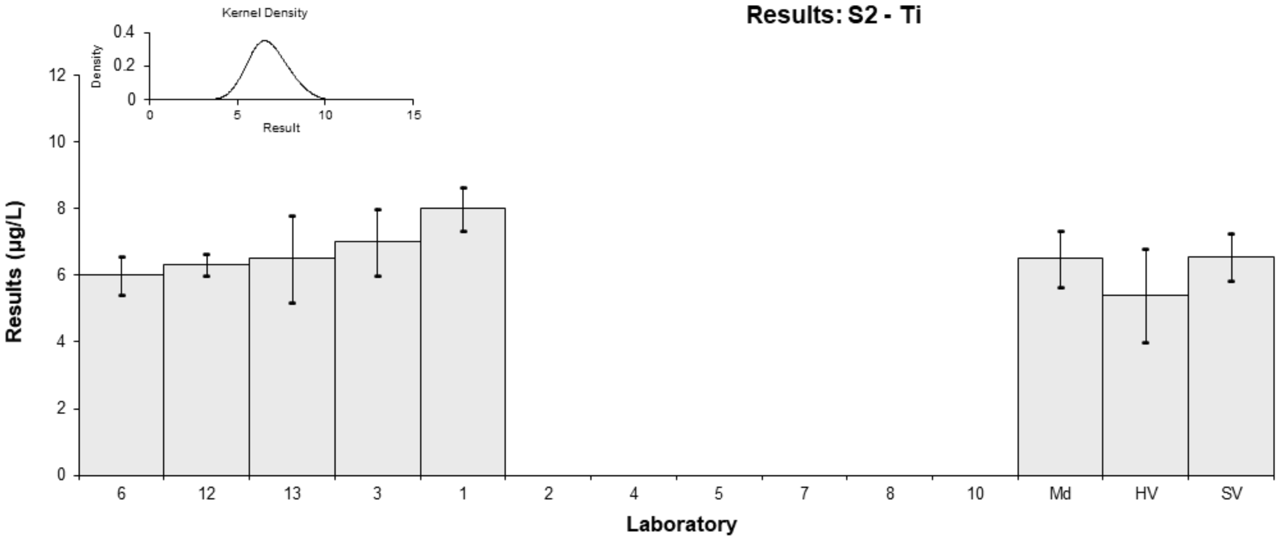

Results: S2 - Ti
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
12
13
3
1
2
4
5
7
8
10
Md
HV
SV

Figure 39

Table 43

Sample Details

Sample No.	S2
Matrix	River Water
Analyte	Tl
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.94	0.99	-0.13	-0.08
2	NT	NT		
3	3.88	0.44	-0.23	-0.30
4	4.24	0.19	0.36	0.93
5	4.13	0.4	0.18	0.26
6	3.76	0.53	-0.43	-0.47
7	4.02	0.303	0.00	0.00
8	4.25	0.59	0.38	0.38
10	4	1	-0.03	-0.02
12	4.12	0.21	0.17	0.40
13	3.9	0.78	-0.20	-0.15

Statistics

Assigned Value	4.02	0.14
Spike Value	4.04	0.11
Homogeneity Value	3.96	0.43
Robust Average	4.02	0.14
Median	4.01	0.13
Mean	4.02	
N	10	
Max	4.25	
Min	3.76	
Robust SD	0.18	
Robust CV	4.5%	

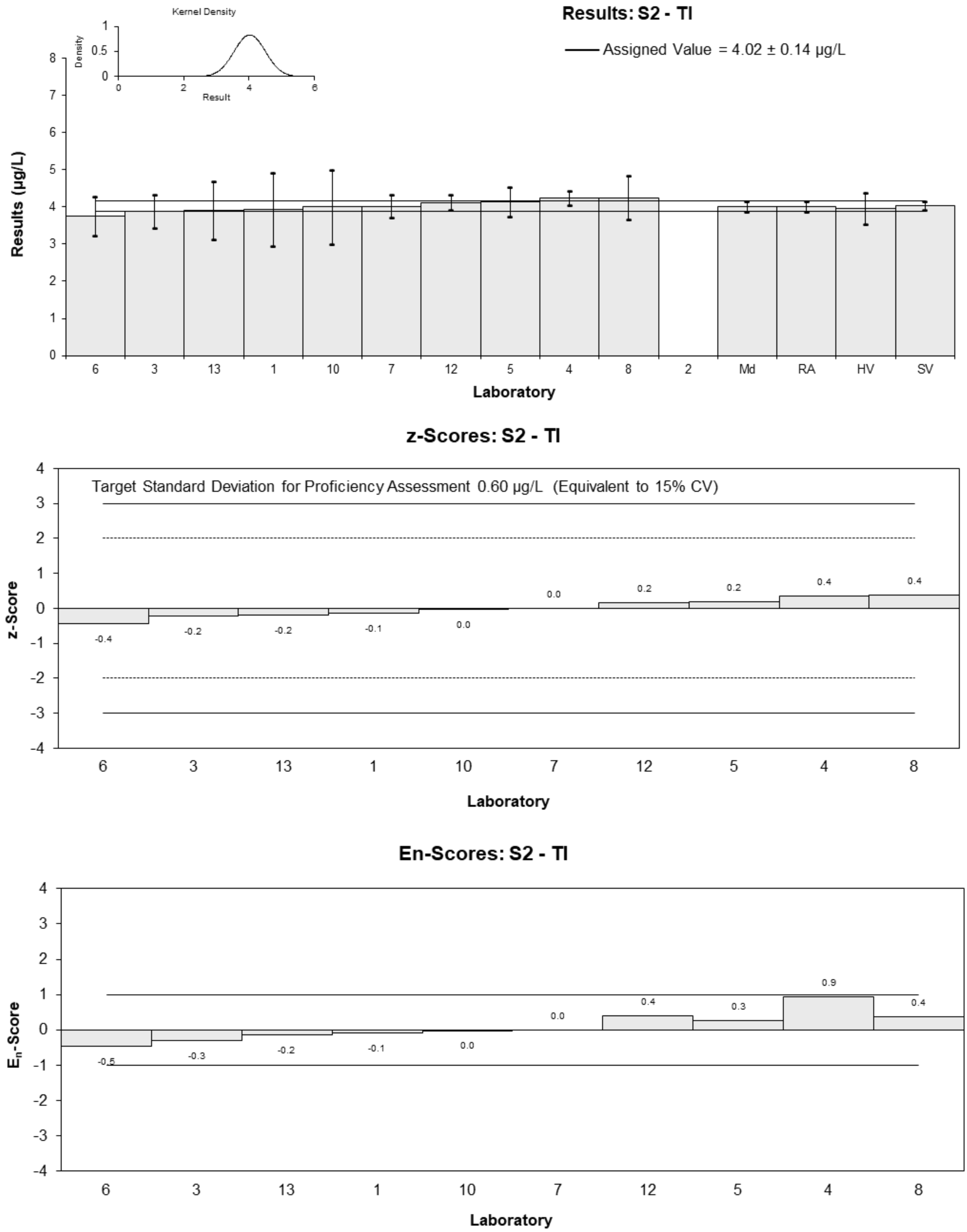

Results: S2 - Tl
Assigned Value = 4.02 ± 0.14 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
3
13
1
10
7
12
5
4
8
2
Md
RA
HV
SV
z-Scores: S2 - Tl
Target Standard Deviation for Proficiency Assessment 0.60 µg/L (Equivalent to 15% CV)
z-Score
-0.4
-0.2
-0.2
-0.1
0.0
0.0
0.2
0.2
0.4
0.4
En-Scores: S2 - Tl
En-Score
-0.5
-0.3
-0.2
-0.1
0.0
0.0
0.4
0.3
0.9
0.4

Figure 40

Table 44

Sample Details

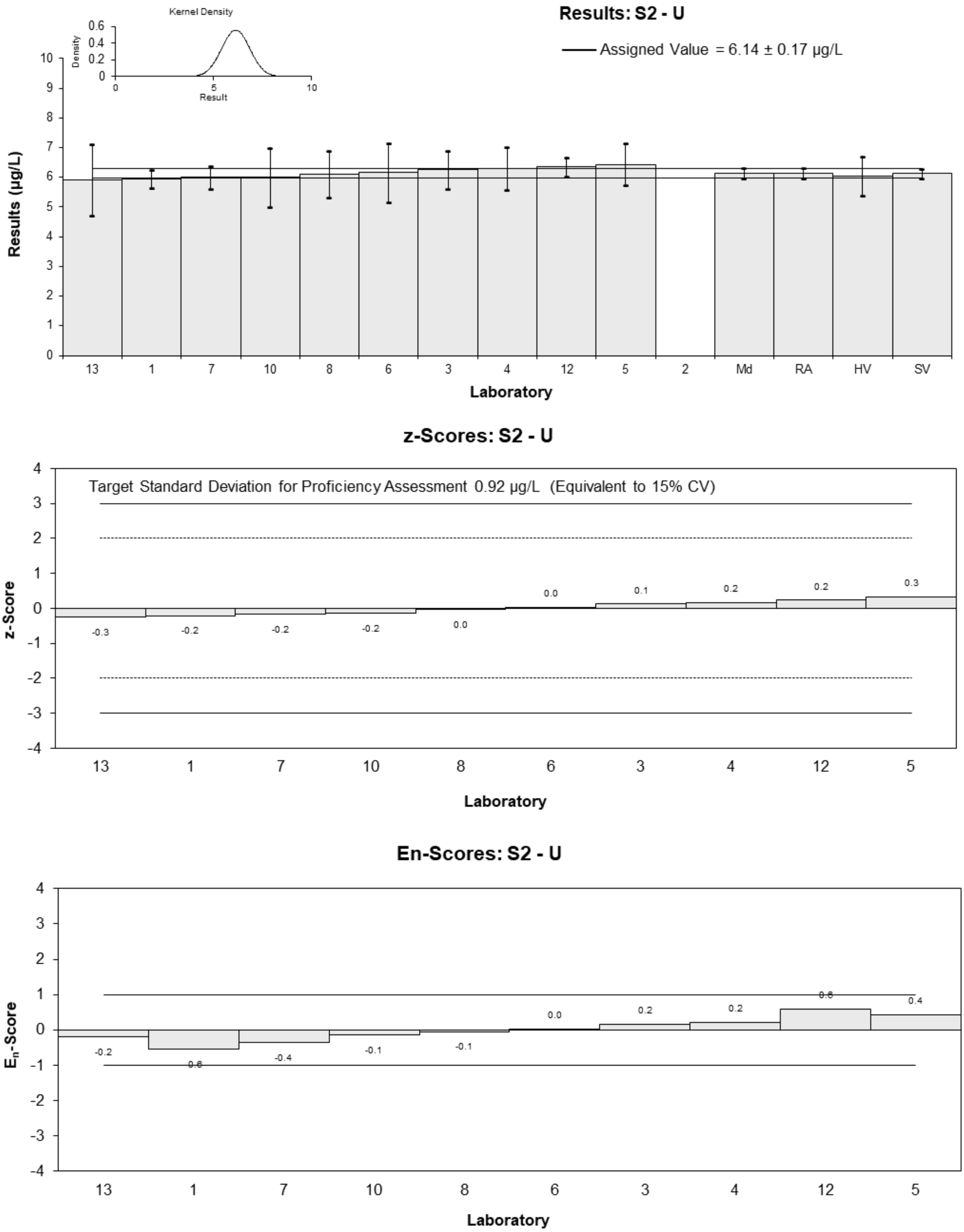
Sample No.	S2
Matrix	River Water
Analyte	U
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	5.95	0.3	-0.21	-0.55
2	NT	NT		
3	6.25	0.65	0.12	0.16
4	6.3	0.71	0.17	0.22
5	6.44	0.7	0.33	0.42
6	6.16	0.99	0.02	0.02
7	5.993	0.378	-0.16	-0.35
8	6.10	0.79	-0.04	-0.05
10	6	1	-0.15	-0.14
12	6.35	0.32	0.23	0.58
13	5.9	1.2	-0.26	-0.20

Statistics

Assigned Value	6.14	0.17
Spike Value	6.12	0.17
Homogeneity Value	6.04	0.67
Robust Average	6.14	0.17
Median	6.13	0.18
Mean	6.14	
N	10	
Max	6.44	
Min	5.9	
Robust SD	0.21	
Robust CV	3.4%	



Results: S2 - U
Assigned Value = 6.14 ± 0.17 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
13 1 7 10 8 6 3 4 12 5 2 Md RA HV SV
z-Scores: S2 - U
Target Standard Deviation for Proficiency Assessment 0.92 µg/L (Equivalent to 15% CV)
z-Score
-0.3 -0.2 -0.2 -0.2 0.0 0.0 0.1 0.2 0.2 0.3
13 1 7 10 8 6 3 4 12 5
Laboratory
En-Scores: S2 - U
E_n-Score
-0.2 -0.6 -0.4 -0.1 -0.1 0.0 0.2 0.2 0.6 0.4
13 1 7 10 8 6 3 4 12 5
Laboratory

Figure 41

Table 45

Sample Details

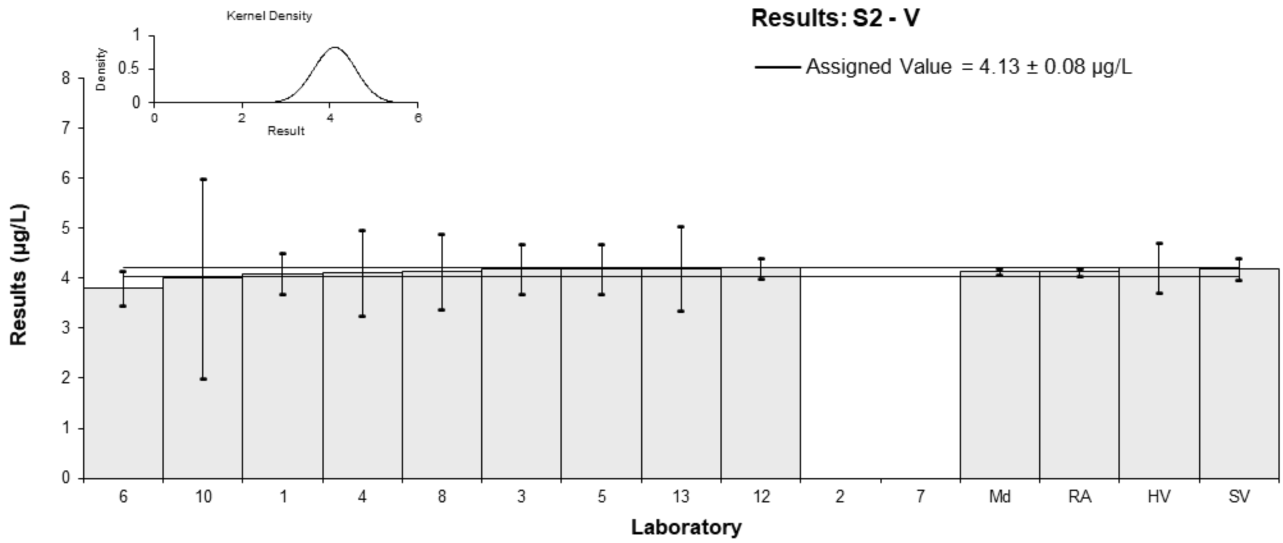
Sample No.	S2
Matrix	River Water
Analyte	V
Unit	µg/L

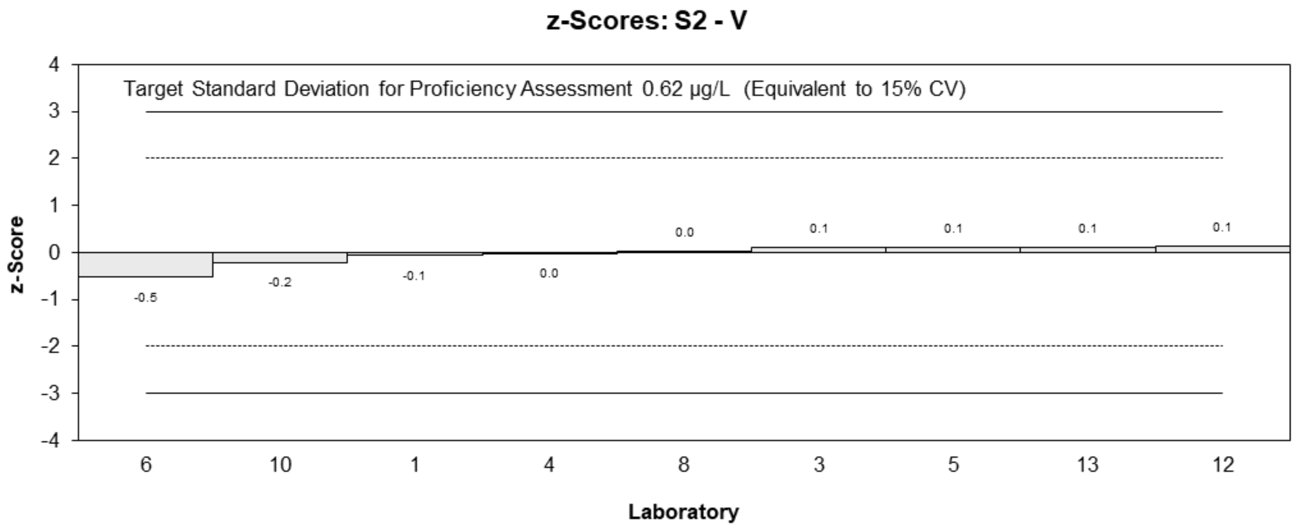
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.1	0.42	-0.05	-0.07
2	NT	NT		
3	4.2	0.5	0.11	0.14
4	4.12	0.86	-0.02	-0.01
5	4.20	0.5	0.11	0.14
6	3.8	0.34	-0.53	-0.94
7	<10	NR		
8	4.14	0.75	0.02	0.01
10	4	2	-0.21	-0.06
12	4.21	0.21	0.13	0.36
13	4.2	0.84	0.11	0.08

Statistics

Assigned Value	4.13	0.08
Spike Value	4.19	0.22
Homogeneity Value	4.21	0.50
Robust Average	4.13	0.08
Median	4.14	0.07
Mean	4.11	
N	9	
Max	4.21	
Min	3.8	
Robust SD	0.10	
Robust CV	2.4%	


Results: S2 - V
Assigned Value = 4.13 ± 0.08 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
10
1
4
8
3
5
13
12
2
7
Md
RA
HV
SV


z-Scores: S2 - V
Target Standard Deviation for Proficiency Assessment 0.62 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.5
-0.2
-0.1
0.0
0.0
0.1
0.1
0.1
0.1
6
10
1
4
8
3
5
13
12

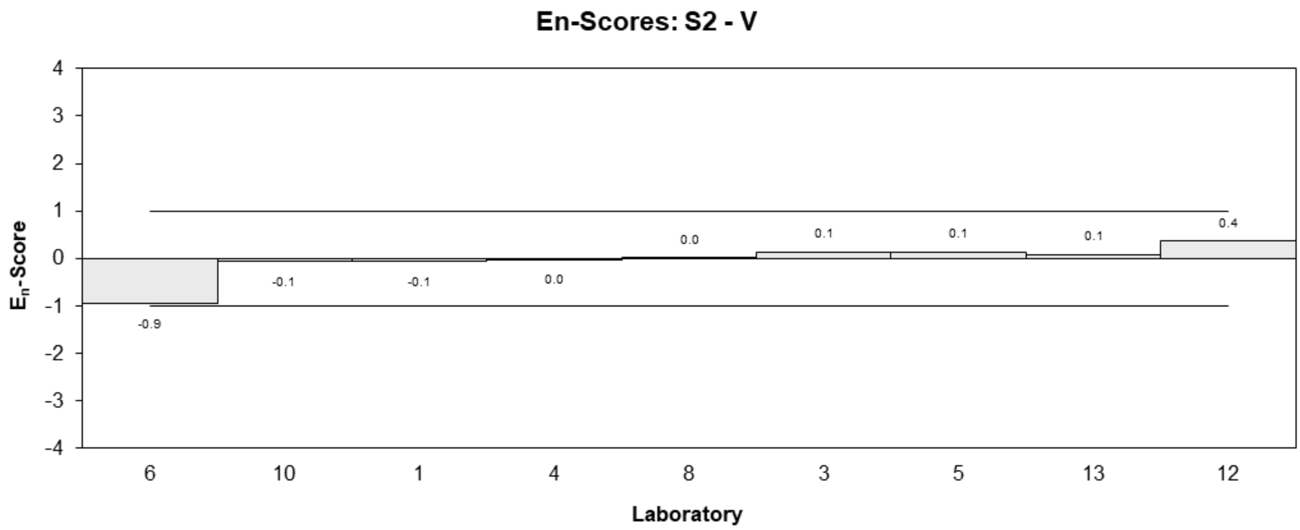

En-Scores: S2 - V
En-Score
Laboratory
-0.9
-0.1
-0.1
0.0
0.0
0.1
0.1
0.1
0.4
6
10
1
4
8
3
5
13
12

Figure 42

Table 46

Sample Details

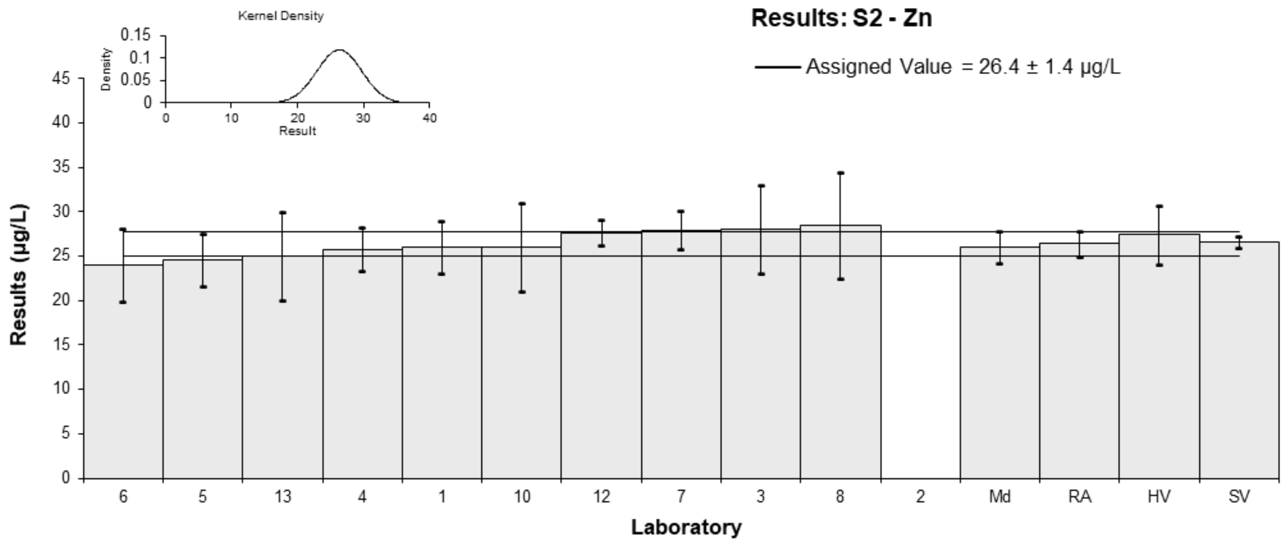
Sample No.	S2
Matrix	River Water
Analyte	Zn
Unit	µg/L

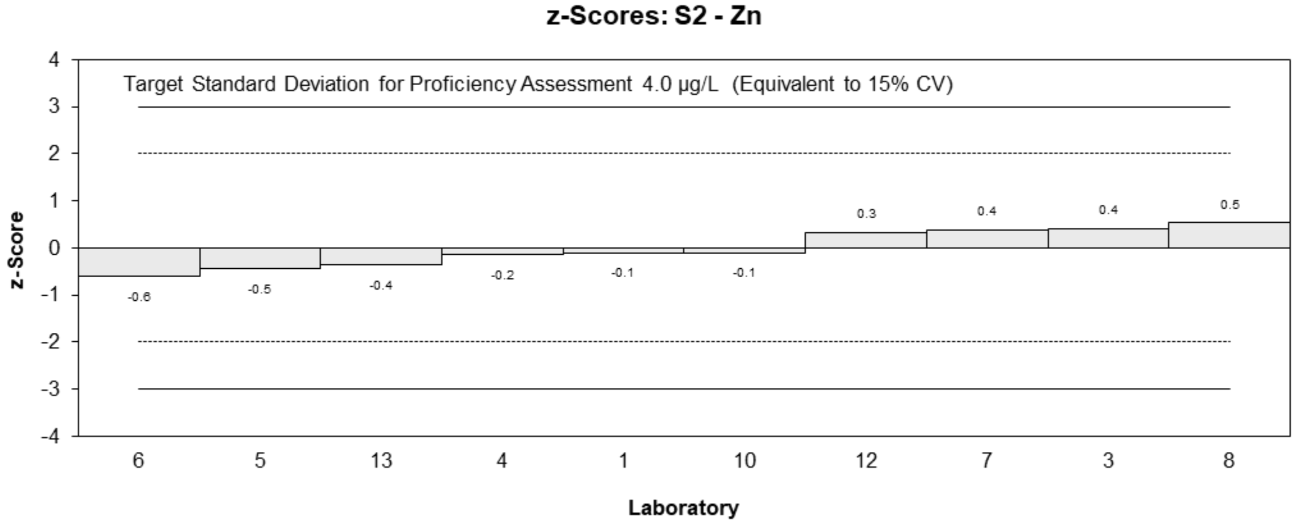
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	26	2.92	-0.10	-0.12
2	NT	NT		
3	28	5	0.40	0.31
4	25.8	2.5	-0.15	-0.21
5	24.6	3.0	-0.45	-0.54
6	24	4.06	-0.61	-0.56
7	27.955	2.158	0.39	0.60
8	28.5	6.0	0.53	0.34
10	26	5	-0.10	-0.08
12	27.68	1.38	0.32	0.65
13	25	5	-0.35	-0.27

Statistics

Assigned Value	26.4	1.4
Spike Value	26.6	0.7
Homogeneity Value	27.4	3.3
Robust Average	26.4	1.4
Median	26.0	1.8
Mean	26.4	
N	10	
Max	28.5	
Min	24	
Robust SD	1.8	
Robust CV	6.8%	


Results: S2 - Zn
Assigned Value = 26.4 ± 1.4 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
6
5
13
4
1
10
12
7
3
8
2
Md
RA
HV
SV


z-Scores: S2 - Zn
Target Standard Deviation for Proficiency Assessment 4.0 μg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.6
-0.5
-0.4
-0.2
-0.1
-0.1
0.3
0.4
0.4
0.5
6
5
13
4
1
10
12
7
3
8

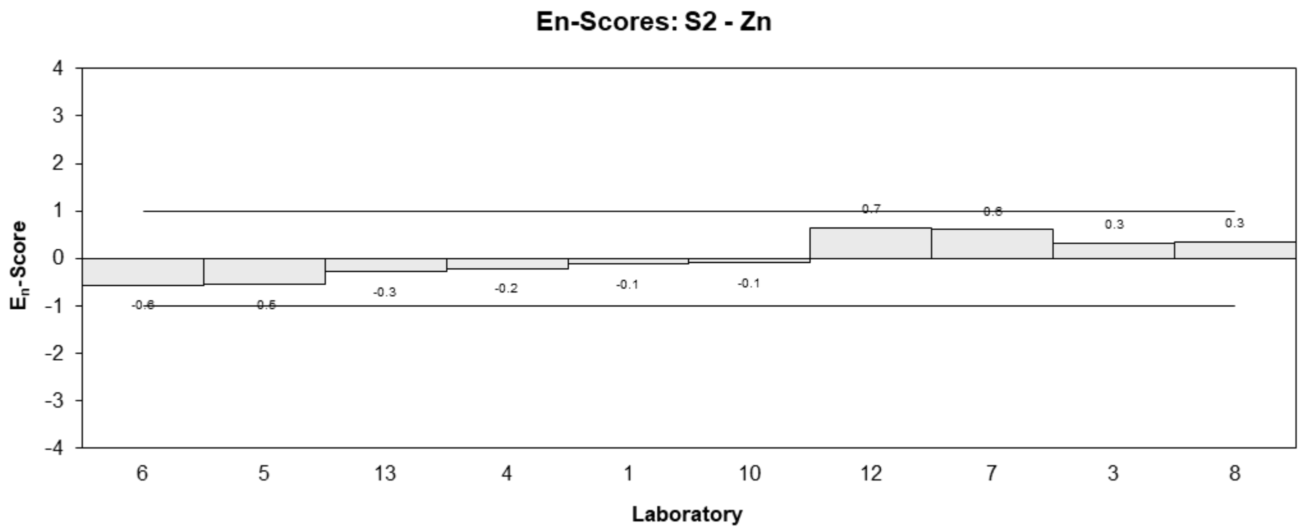

En-Scores: S2 - Zn
En-Score
Laboratory
-0.6
-0.5
-0.3
-0.2
-0.1
-0.1
0.7
0.6
0.3
0.3
6
5
13
4
1
10
12
7
3
8

Figure 43

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Sample S1 was filtered sea water while **Sample S2** was filtered river water. A known amount of single element standard solutions was added to both.

Assigned Values were the robust average of participants' results. The robust averages and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2022. Results less than 50% and more than 150% of the robust average were excluded prior to the calculation of each assigned value.[7] Appendix 2 sets out the calculation for the robust average of Ag in Sample S1 and its associated uncertainty.

No assigned value was set for P, Sn, Ti in S1 and Ti in S2 because too few results were reported. However, participants may still compare their reported results for these analytes against other participants' results the spike value and the homogeneity value. Descriptive statistics for these elements are presented in Chapter 5.

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

The assigned values, spike values and homogeneity values were in agreement with each other within their estimates of uncertainty for all elements of interest.

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

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 392 numerical results, 390 (99%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 3.2% to 333% of the reported value. 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, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[9 – 14]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded uncertainties are presented in the bar charts for each analyte (Figure 2 to 43). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 10 laboratories reported results for V in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 10 laboratories' results is 0.32 µg/L (8.8% of the assigned value). If Laboratory 3's result is coming from one measurement, then they might have under-estimated its expanded measurement uncertainties reported for V in S1 (0.10 µg/L or 3.2%) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 10 measurements. Alternatively, estimates of uncertainties for Al in S1 larger than 5.49 µg/L (the uncertainty of the assigned value, 1.2 µg/L plus the allowable variation from the assigned value, the target standard deviation of 2.15 µg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainty reported by laboratory 10 for Al in S1 (9 µg/L) might have been over-estimated.

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[10] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 3.

Laboratory 12 should review their procedure for estimating measurement uncertainty as most of their uncertainties were low.

Laboratory 10 should also review their procedure for estimating measurement uncertainty. Most of their reported uncertainties were over-estimated. They also reported an estimate of expanded uncertainty for some measurement results which was equal to or larger than the result itself.

Laboratory 1, 4 and 6 attached estimates of the expanded measurement uncertainty to results reported as being less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 106.7 ± 21.3 µg/L, it is better to report 107 ± 21 µg/L or instead of 2.102 ± 0.21 µg/L, it is better to report 2.10 ± 0.21 µg/L.[9]

6.3 z-Score

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

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

The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 47.

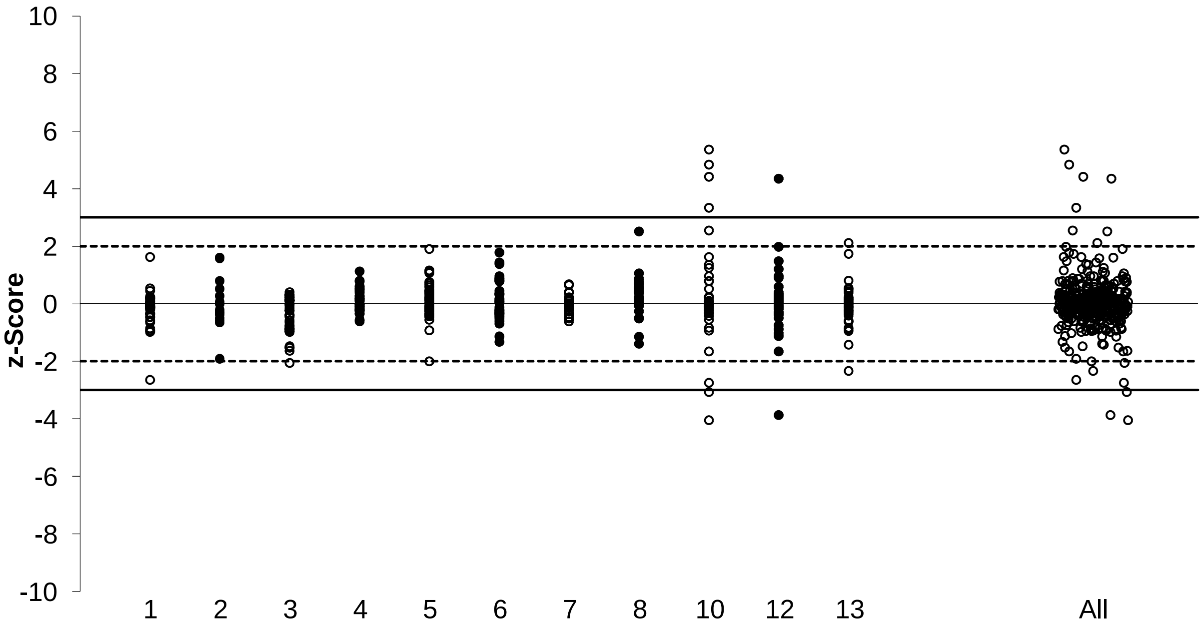
Table 47 Between Laboratory CV of this Study, Thompson CV and Set Target CV

Sample	Test	Assigned value (µg/L)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as CV)
S1	Ag	1.50	6.1%	22%	15%
S1	Al	14.3	10%	22%	15%
S1	As	4.87	12%	22%	15%
S1	Be	1.86	27%	22%	15%
S1	Cd	1.29	4.8%	22%	15%
S1	Cr	1.16	21%	22%	15%
S1	Cu	9.70	6.6%	22%	15%
S1	Fe	26.6	28%	22%	15%
S1	Hg	0.350	13%	22%	15%
S1	Mn	7.22	4.2%	22%	15%
S1	Ni	2.53	20%	22%	15%
S1	Pb	1.58	6.9%	22%	15%
S1	Sb	3.46	19%	22%	15%
S1	Se	4.44	15%	22%	20%
S1	U	2.96	7.0%	22%	15%
S1	V	3.62	11%	22%	15%

Sample	Test	Assigned value (µg/L)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as CV)
S1	Zn	18.8	13%	22%	15%
S2	Ag	2.32	13%	22%	15%
S2	Al	340	13%	19%	15%
S2	As	1.48	5.9%	22%	20%
S2	Be	5.16	6.8%	22%	15%
S2	Cd	2.03	4.4%	22%	10%
S2	Co	1.75	9.7%	22%	15%
S2	Cr	1.53	6.8%	22%	15%
S2	Cu	19.3	4.1%	22%	10%
S2	Fe	191	18%	21%	10%
S2	Hg	0.520	10%	22%	15%
S2	Mn	26.3	4%	22%	10%
S2	Mo	9.67	4.9%	22%	10%
S2	Ni	5.80	5.2%	22%	15%
S2	Pb	5.16	4.2%	22%	15%
S2	Sb	12.6	12%	22%	15%
S2	Se	2.01	8.0%	22%	20%
S2	Tl	4.02	4.5%	22%	15%
S2	U	6.14	3.4%	22%	15%
S2	V	4.13	2.4%	22%	15%
S2	Zn	26.4	6.8%	22%	15%

*Robust between Laboratories CV with outliers removed.

The dispersal of participants' z-scores is presented in Figure 44 (by laboratory code) and in Figure 46 (by analyte). Of 379 results for which z-scores were calculated, 363 (96%) returned a satisfactory score of |z| ≤ 2.0 and 8 (2%) were questionable of 2.0 < |z| < 3.0. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.



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

Figure 44: z-Score Dispersal by Laboratory

A summary of participants' performance is presented in Figure 47**.**

Laboratory **6** reported results for all 38 tests for which a z-score was calculated and returned satisfactory z-scores for all of them.

Laboratory **12** reported numeric results for all 42 tests and returned satisfactory z-scores for 36 of the 38 analytes for which z-scores were calculated.

Laboratories **1, 3, 5,** and **8** reported results for all 38 tests for which z-scores were calculated and returned satisfactory z-scores for 37 of them.

All results reported by Laboratories **4** (34), **7** (23), and **2** (18) returned satisfactory z-scores.

6.4 E_n-score

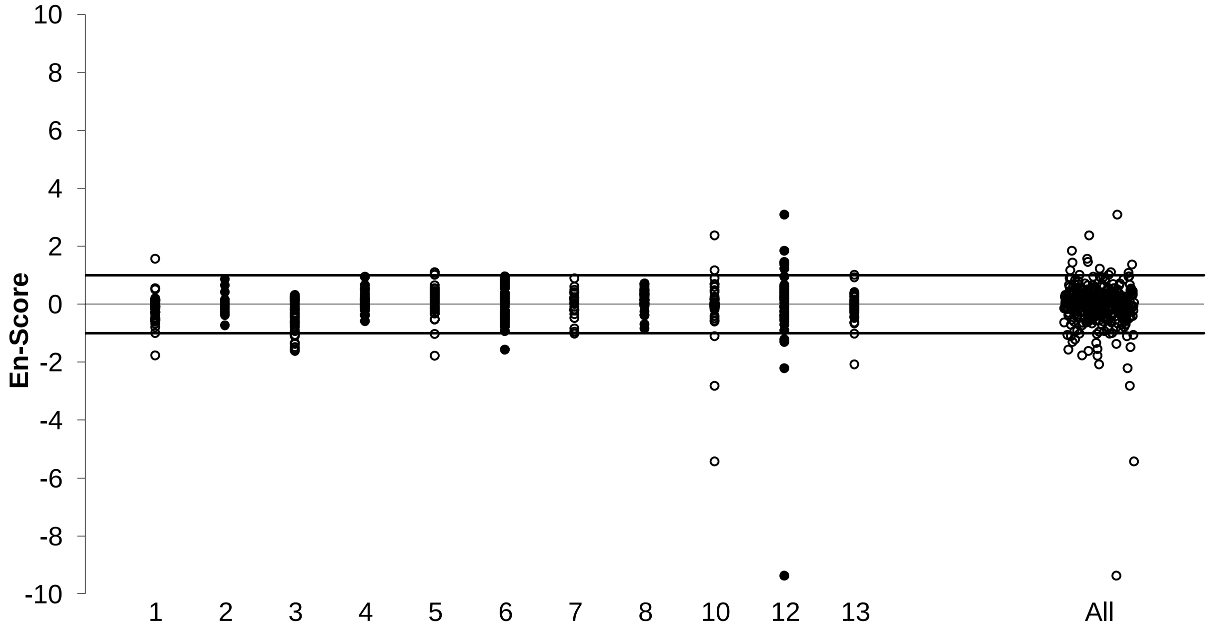
E_n-score can be interpreted only in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value taking into account the respective uncertainties. An unsatisfactory E_n score for an analyte can either be caused by an inappropriate measurement, an inappropriate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

The dispersal of participants' E_n-scores is graphically presented in Figure 45. 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 379 results for which E_n-scores were calculated, 344 (91%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

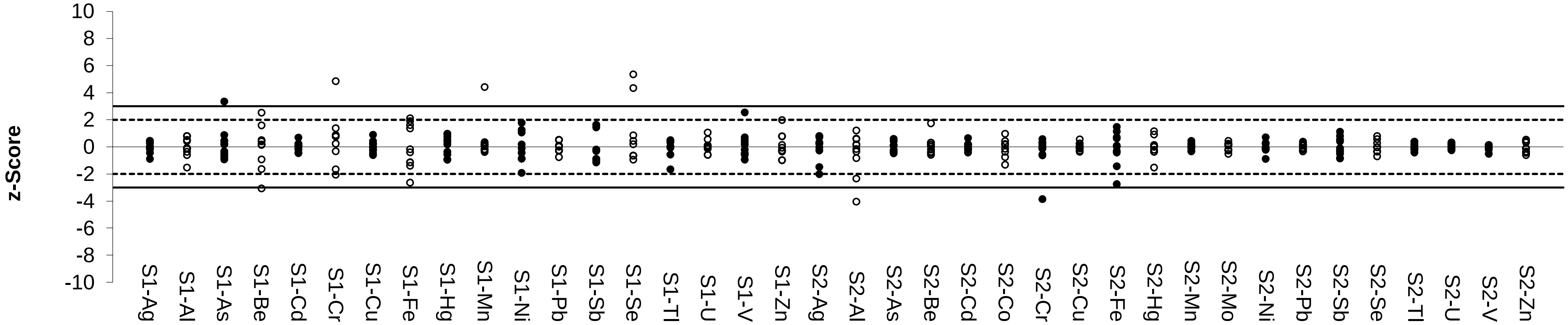
Laboratory **8** had the highest number of satisfactory E_n scores, 38 out of 38 reported.

All results reported by laboratories **4** (34), and **2** (18) returned satisfactory E_n-scores.



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

Figure 45 E_n-Score Dispersal by Laboratory



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

Figure 46 z-Score Dispersal by Analyte

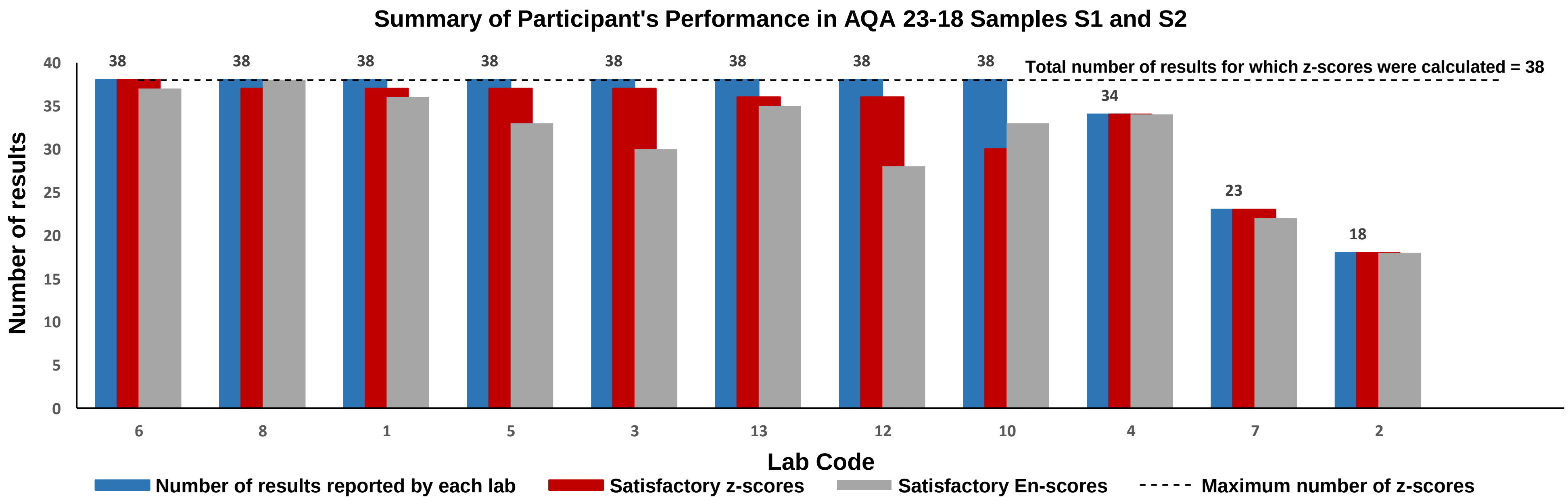


Figure 47: Summary of Participants Performance in AQA 23-18

Table 48 Summary of Participants' Results and Performance for Sample S1

Lab	Ag µg/L	Al µg/L	As µg/L	Be µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Fe µg/L	Hg µg/L	Mn µg/L
AV	1.50	14.3	4.87	1.86	1.29	1.16	9.70	26.6	0.350	7.22
HV	1.57	NA	4.52	1.89	1.25	1.49	9.7	25.9	0.325	7.34
1	1.6	14	5.0	1.6	1.2	1.2	9.0	16	0.3	7.4
2	1.5	16	4.5	2.3	1.3	1.1	9.7	33	0.33	7.5
3	1.3	11	4.3	1.4	1.2	0.8	10	25	0.3	6.8
4	1.48	15.4	5.2	NT	1.25	<2	8.8	25.9	0.39	6.93
5	1.58	14.1	4.18	1.91	1.27	1.29	9.35	34.2	0.32	7.25
6	1.6	14	5.5	1.9	1.3	1.4	11	22	0.4	7.6
7	<5	<50	5.157	<5	1.419	<5	10.017	<250	0.359	7.326
8	1.55	15.2	5.01	2.56	1.33	1.31	10.3	21.0	0.378	7.38
10	1.4	16	7.3	1	1.3	2	10	32	0.3	12
12	1.46	13.48	4.63	1.97	1.33	0.87	9.57	22.08	0.4	7.02
13	1.5	13	4.4	2.0	1.3	1.3	9.3	35	0.37	7.0

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

Table 48 Summary of Participants' Results and Performance for Sample S1 (continued)

Lab	Ni (µg/L)	P (µg/L)	Pb (µg/L)	Sb (µg/L)	Se (µg/L)	Sn (µg/L)	Ti (µg/L)	Tl (µg/L)	U (µg/L)	V (µg/L)	Zn (µg/L)
AV	2.53	Not Set	1.58	3.46	4.44	Not Set	Not Set	2.00	2.96	3.62	18.8
HV	2.74	123	1.46	3.22	4.07	4.18	3.88	1.84	2.91	3.52	17.6
1	2.2	<5000	1.6	4.3	4.0	<5	<5	2.0	2.9	3.7	16
2	1.8	96	1.7	3.3	4.0	3.8	1.7	2.0	2.7	3.5	18
3	2.2	<1000	1.4	3.0	4	<5	<5	2.0	2.7	3.1	16
4	<7	NT	1.52	3.35	<4	<5	<20	1.83	2.93	3.9	17.8
5	2.36	NT	1.51	3.34	4.73	NT	NT	2.13	3.43	4.00	19.2
6	3.2	<1000	1.6	4.2	5	<5	<5	2.1	3	3.8	21
7	<5	<1000	<5	<5	<50	<5	<50	<5	<5	<50	<25
8	2.93	NT	1.58	2.86	4.57	4.10	NT	2.15	2.97	3.35	18.6
10	3	NT	1.7	4.3	8	NT	NT	1.5	3	5	21
12	2.48	123	1.51	2.92	7.33	3.75	20.15	1.98	2.97	3.35	24.39
13	2.6	NR	1.7	3.0	3.8	4.1	<5	2.0	3.2	3.3	18

Shaded cells are results which returned a questionable or unsatisfactory z-score. AV = Assigned Value, HV = Homogeneity Value

Table 49 Summary of Participants’ Results and Performance for Sample S2

Lab	Ag µg/L	Al µg/L	As µg/L	Be µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Fe µg/L	Hg µg/L
AV	2.32	340	1.48	5.16	2.03	1.75	1.53	19.3	191	0.520
HV	2.26	398	1.60	5.18	1.90	1.74	1.70	20.0	248	0.584
1	2.4	332	1.5	4.7	1.98	1.8	1.5	19.1	192	0.49
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	1.8	297	1.5	5.4	1.98	1.8	1.6	20.0	179	0.4
4	2.6	371	1.4	5.27	2.08	1.86	1.66	19.9	223	0.52
5	1.62	347	1.43	5.28	2.09	1.65	1.53	18.2	209	0.61
6	2.6	322	1.4	4.8	1.95	1.4	1.6	18.5	182	0.49
7	2.226	349.3	1.374	4.874	2.225	1.711	1.386	19.3	193.398	0.502
8	2.56	369	1.57	5.17	2.08	1.79	1.56	20.9	211	0.522
10	2.4	133	1.5	5	2	2	1.4	19	112	0.52
12	2.43	401	1.61	5.39	2.06	1.55	0.64	19.45	233	0.59
13	2.3	220	1.5	6.5	1.9	1.8	1.5	19	150	0.53

Shaded cells are results which returned a questionable or unsatisfactory z-score. AV = Assigned Value, HV = Homogeneity Value

Table 49 Summary of Participants' Results and Performance for Sample S2 (continued)

Lab	Mn µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Sb µg/L	Se µg/L	Ti µg/L	Tl µg/L	U µg/L	V µg/L	Zn µg/L
AV	26.3	9.67	5.80	5.16	12.6	2.01	Not Set	4.02	6.14	4.13	26.4
HV	27.6	9.2	5.70	4.78	11.4	2.10	5.4	3.96	6.04	4.21	27.4
1	26	9.4	5.7	4.9	13.6	1.9	8.0	3.94	5.95	4.1	26
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	26.8	9.8	6.0	5.1	12.1	2.0	7	3.88	6.25	4.2	28
4	26.7	9.8	6.04	5.36	12.4	2.0	<20	4.24	6.3	4.12	25.8
5	27.3	10.3	5.65	5.06	14.7	2.18	NT	4.13	6.44	4.20	24.6
6	25	9.9	5.6	5	14.1	1.8	6	3.76	6.16	3.8	24
7	25.872	8.922	5.745	5.26	13.354	<10	<10	4.02	5.993	<10	27.955
8	26.0	9.28	6.41	5.45	11.6	2.25	NT	4.25	6.10	4.14	28.5
10	25	9.3	6	4.9	11	2	NT	4	6	4	26
12	26.57	9.98	5.03	5.22	11.90	2.09	6.32	4.12	6.35	4.21	27.68
13	28	10	5.7	5.3	11	1.9	6.5	3.9	5.9	4.2	25

Shaded cells are results which returned a questionable or unsatisfactory z-score. AV = Assigned Value, HV = Homogeneity Value

6.5 Participants' Results and Analytical Methods for Dissolved Elements

Sample S1 was filtered sea water and **Sample S2** was filtered river water. Silver Cd, Cr, Hg, V and Zn had similar concentrations in S1 and S2. This study design was aimed at helping laboratories to investigate the effect of sample matrix on their performance.

Sea water contains significant quantities of dissolved salts, especially sodium chloride and sulphates. Molecular ions originated from dissolved salts can frequently cause severe interference in ICP-MS measurements because these molecular ions have similar mass to the isotopes used in elemental determination. As a result, false positives, and concentrations much higher than the true values are frequently obtained by conventional quadrupole ICP-MS which does not have the resolution required to separate molecular ions from the isotope of interest. The isotopes most frequently affected in saltwater analysis are ^{52}Cr, ^{58}Ni, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{64}Zn, ^{66}Zn, ^{75}As, ^{78}Se, ^{82}Se. Overall, the between-laboratory CVs of the river water Sample S2 were lower than those of the sea water sample S1.

Arsenic, Cr and Ni in sea water were the tests which challenged most participants analytical techniques when compared to the river water sample. The between-laboratory CVs for these tests were 2 to 4 times higher than in S2.

Titanium in S1 and S2 followed by P and Sn in S1 were the tests that most challenged participants' analytical techniques. A limited number of participants reported results for these tests.

Low level Be and Fe in S1 also presented analytical difficulty to participating laboratories with CVs of 27% and 28% respectively.

A summary of participants' results and performance in the two study samples is presented in Tables 48 and 49 and in Figures 44 to 47.

Individual Element Commentary

Participants were requested to analyse the two water samples for dissolved elements using their normal test methods and to report a single result as they would normally report to a client. The method descriptions provided by participants are presented in Tables 1 and 3 and instrumental conditions are presented in Appendix 5.

No significant difference was observed between the performances of participants who performed digestion and the ones who did not conduct a digestion procedure on the test samples. Instrumental measurement was one of the main factors that influenced results in the two water samples. However, participants' performance does not reflect instrumental performance alone, 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.

Most laboratories reported using ICP-MS with a collision/reaction cell; some used ICP-OES and some ICP-MS in standard mode. Most laboratories used Sc, Y or Rh as internal standard.

Aluminium level in S1 was low at 14.3 µg/L and did not challenge participants' analytical techniques. The between-laboratory CV was 10% compared to the CV predicted by the Thompson equation of 22%. Plots of instrumental techniques versus results are presented in Figure 48.

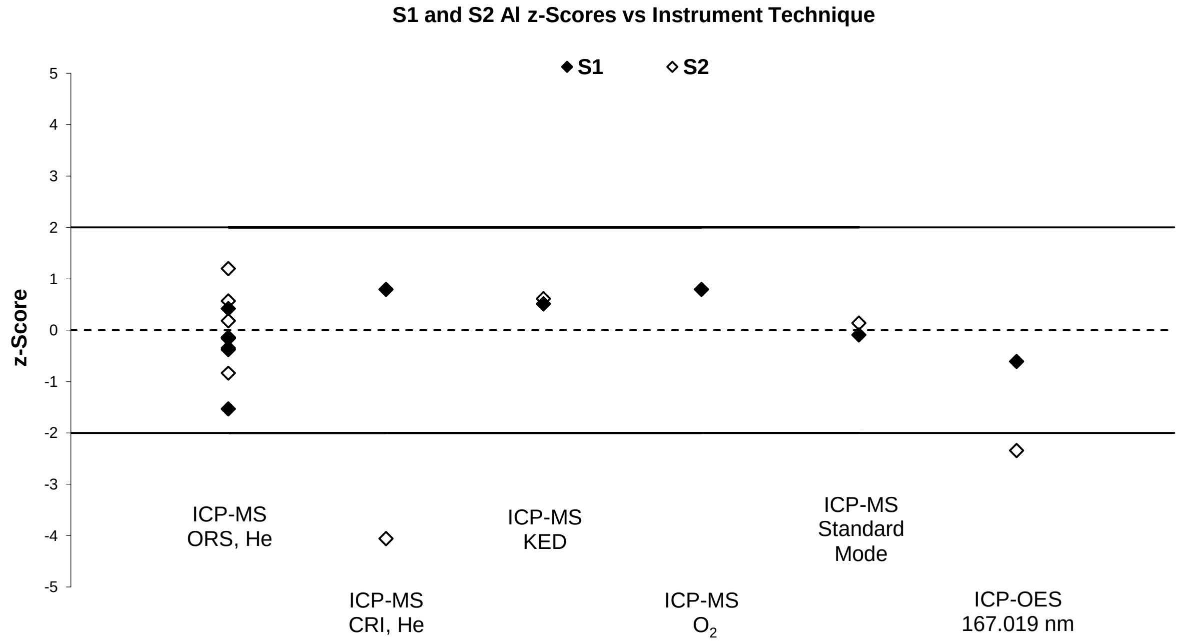


Figure 48 S1-Al Results vs Instrumental Technique

Aluminium level in the river water sample S2 was 24 times higher than in S1. The results reported by Laboratories 10 and 13 returned satisfactory z-scores for Al in S1 but their reported results for S2 were unsatisfactory (Figure 49). Laboratory 13 should check for method bias as both of their results reported for Al in S1 and S2 were lower than the assigned value.

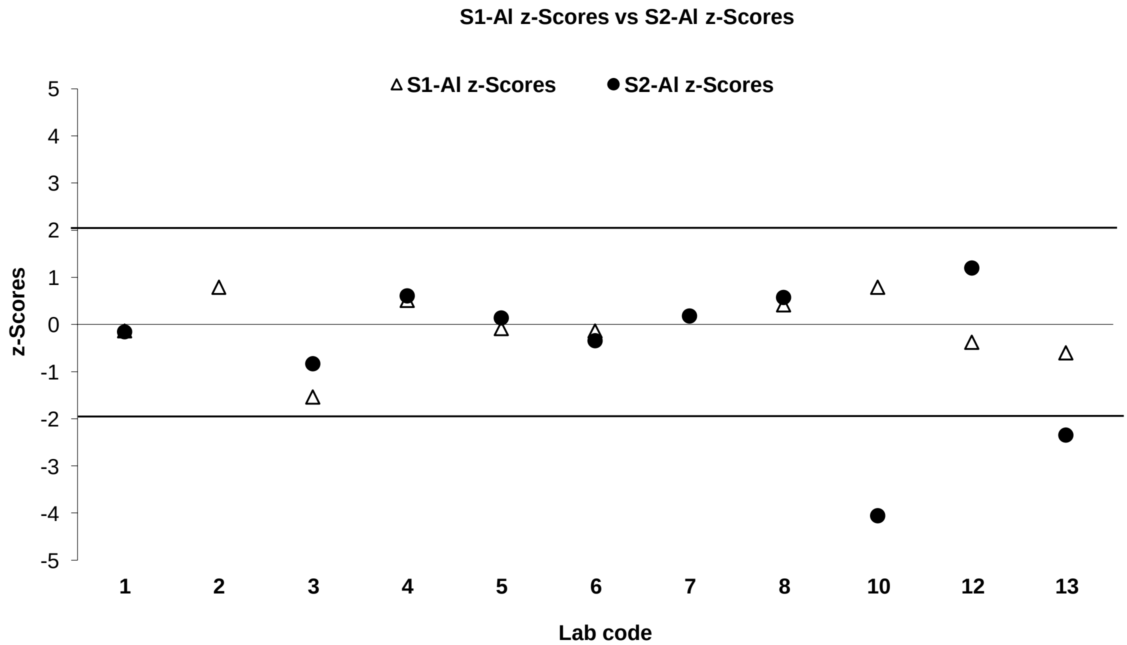


Figure 49 S1 and S2 Al z-Scores vs Laboratory Code

Antimony level in S1 was 3.46 µg/L and in S2 was 12.6 µg/L. All results reported for Sb in the two study samples returned satisfactory z-scores (Figure 50).

ICP-MS in collision mode was the preferred instrumental technique (Figure 51).

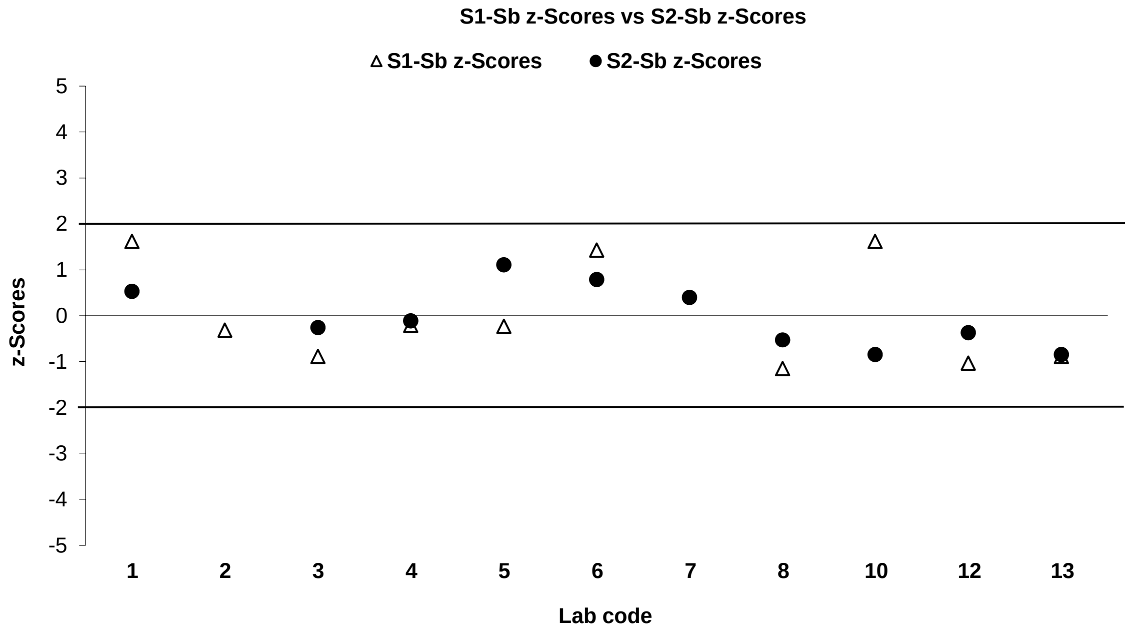


Figure 50 S1 and S2 Sb z-Scores vs Laboratory Code

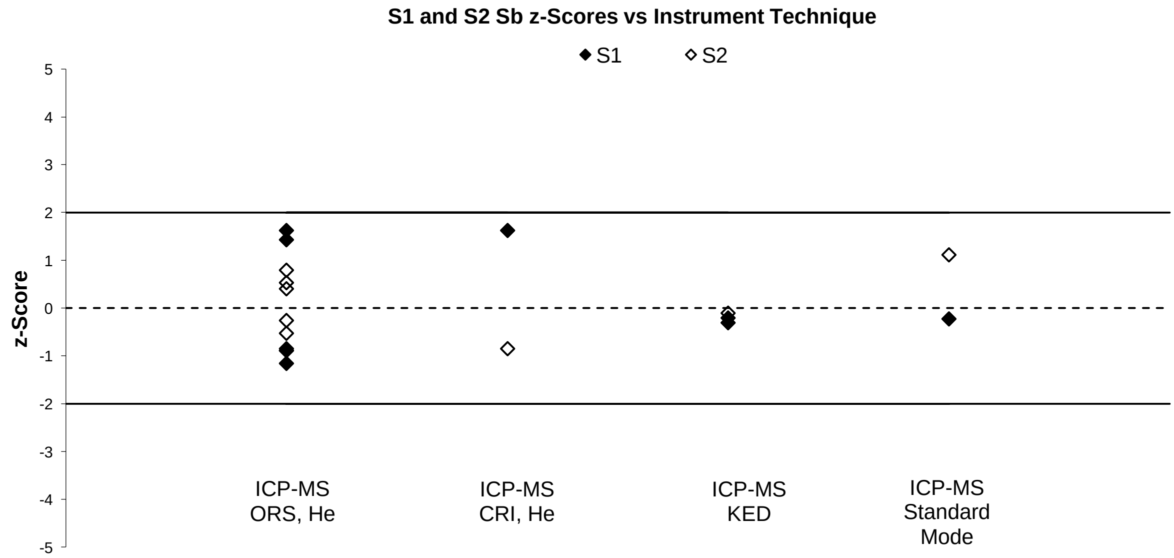


Figure 51 S1 and S2 Sb z-Scores vs Instrumental Technique

Arsenic level in S1 was 4.87 µg/L and in S2 was 1.48 µg/L. Although all but one of the participants that reported results for As in S1 and S2 returned satisfactory z-scores, the reported results for the sea water sample were more variable than in river water; the between-laboratory CV in S1 was 12% while in S2 it was half of this, at 5.9% (Table 44 and Figure 52). Unsolved interference problem may explain the high unsatisfactory As result.

For As measurements participants reported using ICP-MS in collision or reaction mode with He or O_2 as collision/reaction gas (Figure 53).

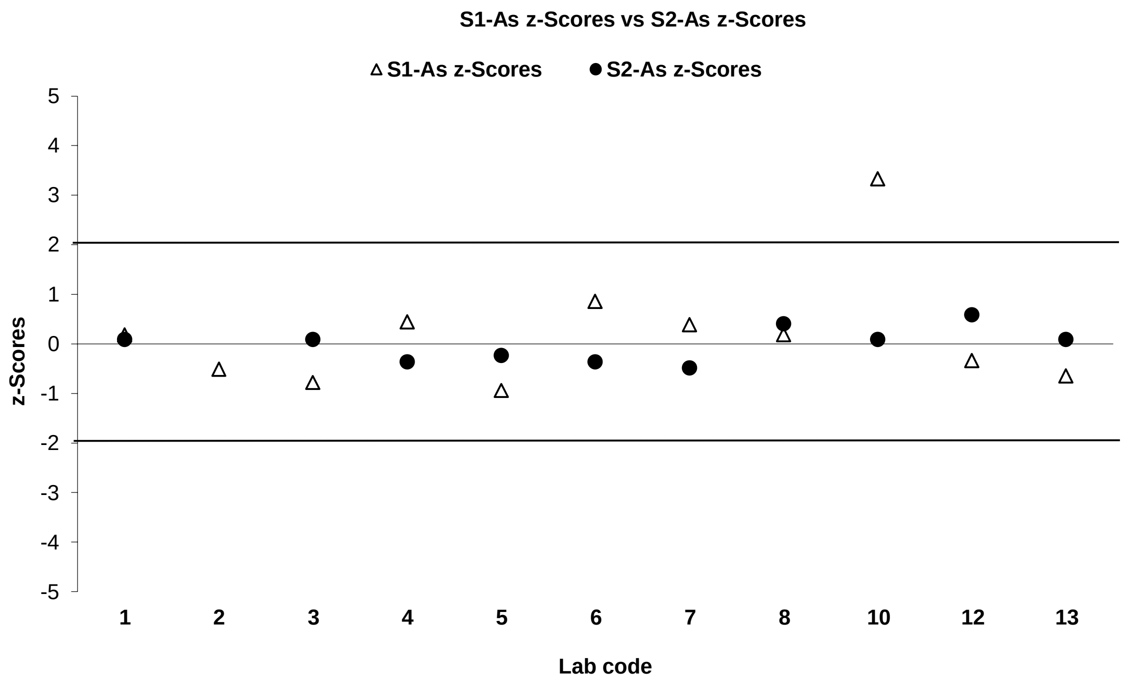


Figure 52 S1 and S2 As z-Scores vs Laboratory Code

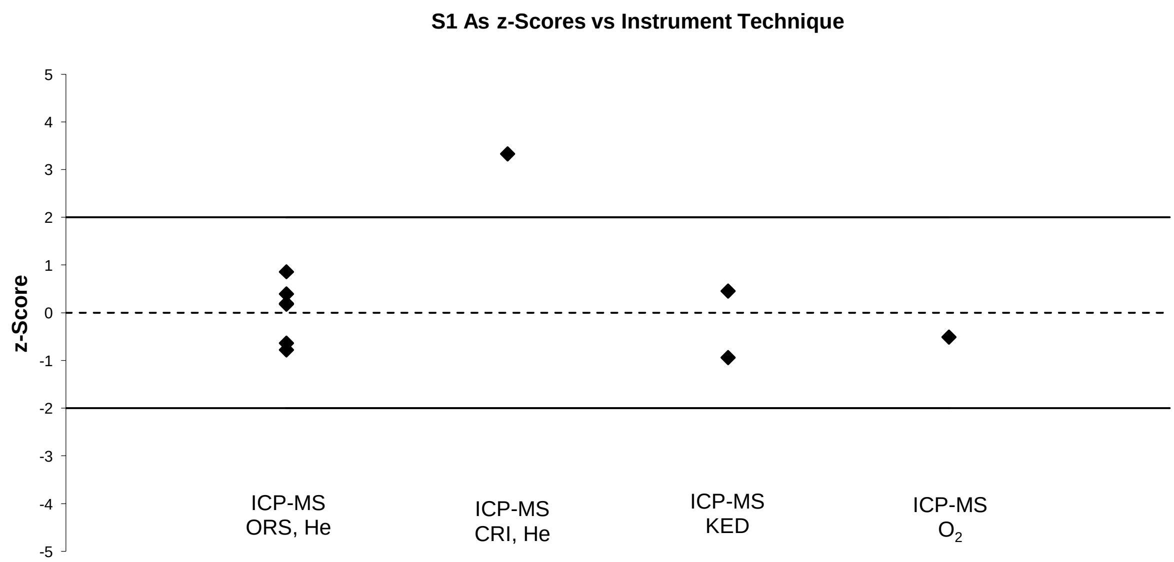


Figure 53 S1 and S2 As z-Scores vs Instrumental Technique

Beryllium in sea water was one of the tests that challenged most laboratories' analytical techniques. The between-laboratory CV was high, at 27%, much higher than in the river water sample (6.8%).

Plots of participants' performance in the sea water sample versus instrumental technique used are presented in Figure 54. The ICP-OES technique may not be sensitive enough for the measurement of Be in sea water at the level of parts per billion.

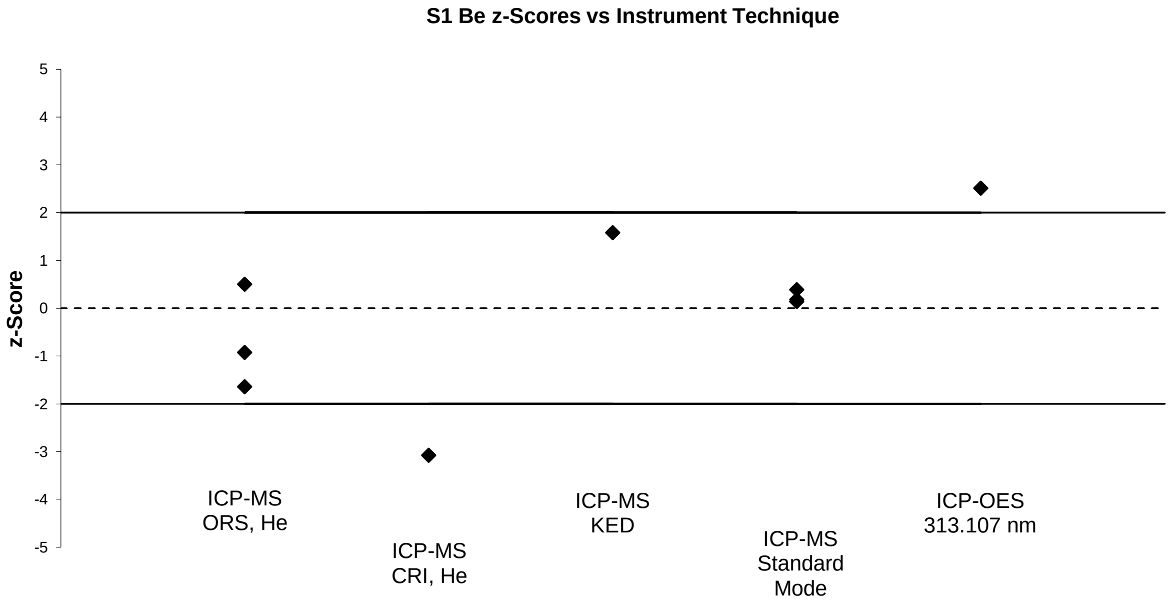
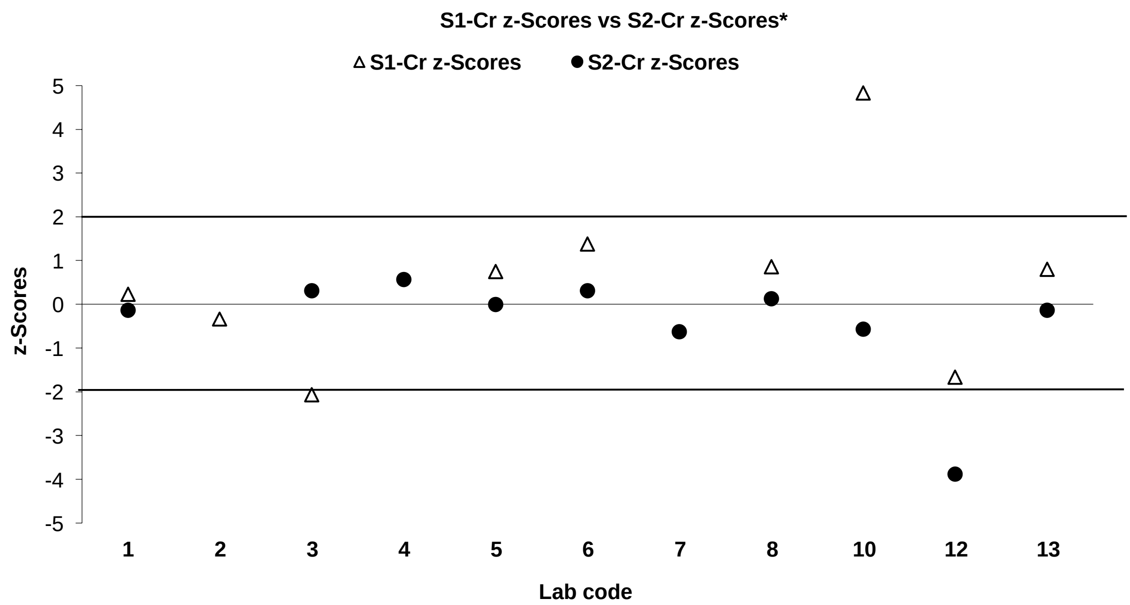


Figure 54 S1 Be z-Scores vs Instrumental Technique

Chromium was at similar level in both the sea water and river water samples at 1.16 µg/L and 1.53µg/L respectively. Results in the sea water sample were more variable than those in river water. The between-laboratory CV in S1 was 21% while in S2 it was 3 times lower, at 6.8%.

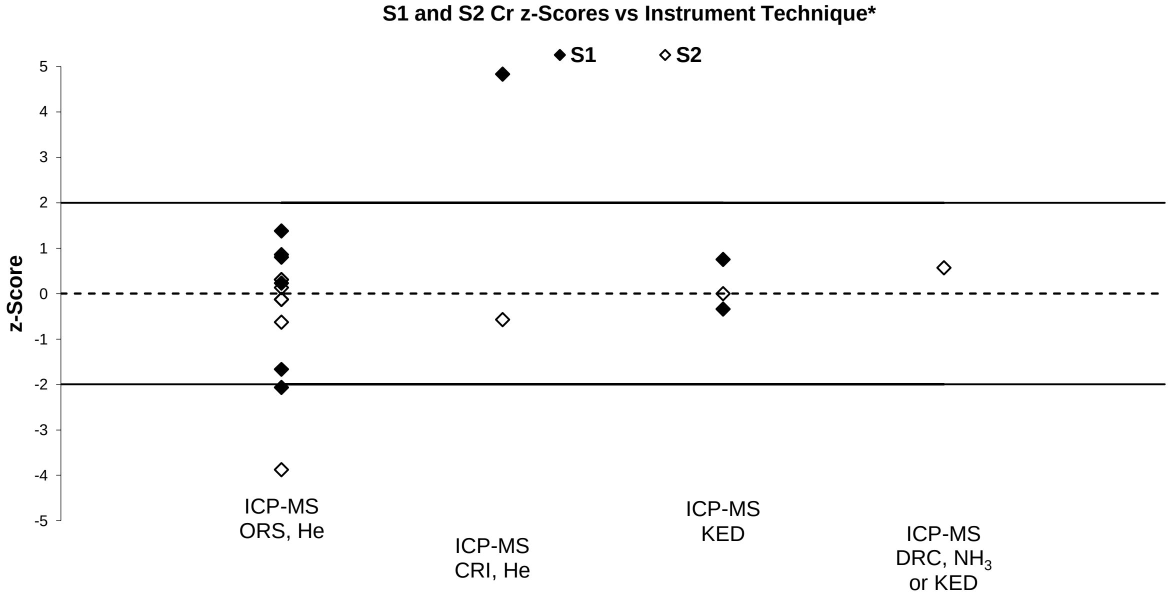
Participants' performance in the two water samples are presented in Figure 55. Laboratory 12 should check for method bias as the results reported by them were low.

Plots of participants' performance in the two water samples versus instrumental technique used are presented in Figure 56. ^{52}Cr has significant interferences from polyatomic species such as $^{35}Cl^{16}O^{1}H^{+}$ or $^{35}Cl^{14}N^{1}H^{+}$. Unsolved interference problem may explain the high unsatisfactory Cr result.



*The z-Score >5 has been plotted as 5.

Figure 55 S1 and S2 Cr z-Scores vs Laboratory Code



*The z-Score >5 has been plotted as 5.

Figure 56 S1 and S2 Cr z-Scores vs Instrumental Technique

Iron measurements in the sea water sample challenged participants' analytical techniques, and the between-laboratory CV was large at 28%. A relatively large variation of 18% was also noticed between results reported for Fe in the river water sample (Figure 57). Iron is known to be ubiquitous in the environment; hence, special precautions are necessary in order to avoid contamination.

For Fe measurements in the two water samples participants used a wide variety of instrumental techniques: ICP-MS in collision mode with He or HEHe, ICP-MS in reaction mode with NH_3 or ICP-OES with wavelength 238 nm. Plots of participants' performance in the two water samples versus instrumental technique used are presented in Figure 58.

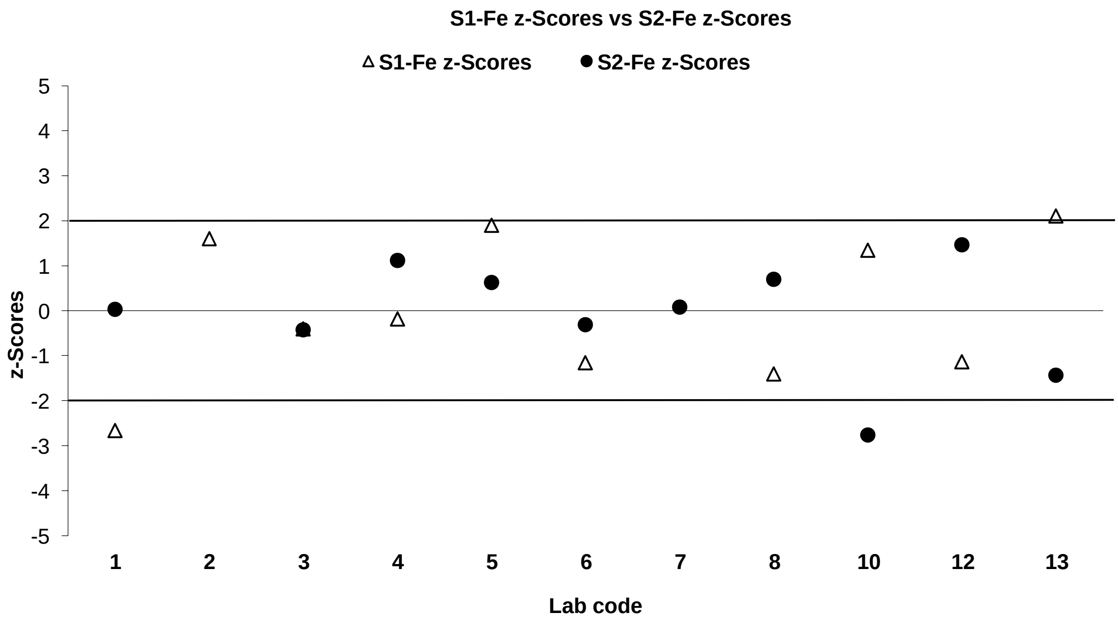


Figure 57 S1 and S2 Fe z-Scores vs Laboratory Code

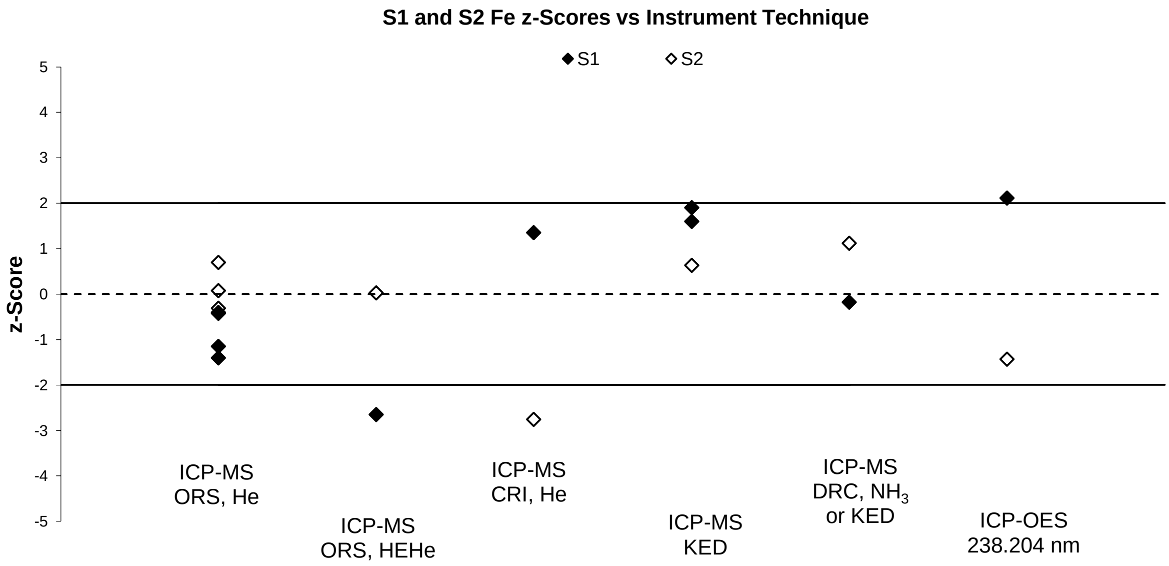


Figure 58 S1 and S2 Fe z-Scores vs Instrumental Technique

Mercury level in S1 was 0.350 µg/L and in S2 was 0.520 µg/L. Participants used a wide variety of instrumental techniques for Hg measurements in the two water samples and all produced compatible results (Figure 59). CV-AAS was the most popular instrumental technique. One participant used ICP-OES with hydride generation accessory and a wavelength of 194.164 nm.

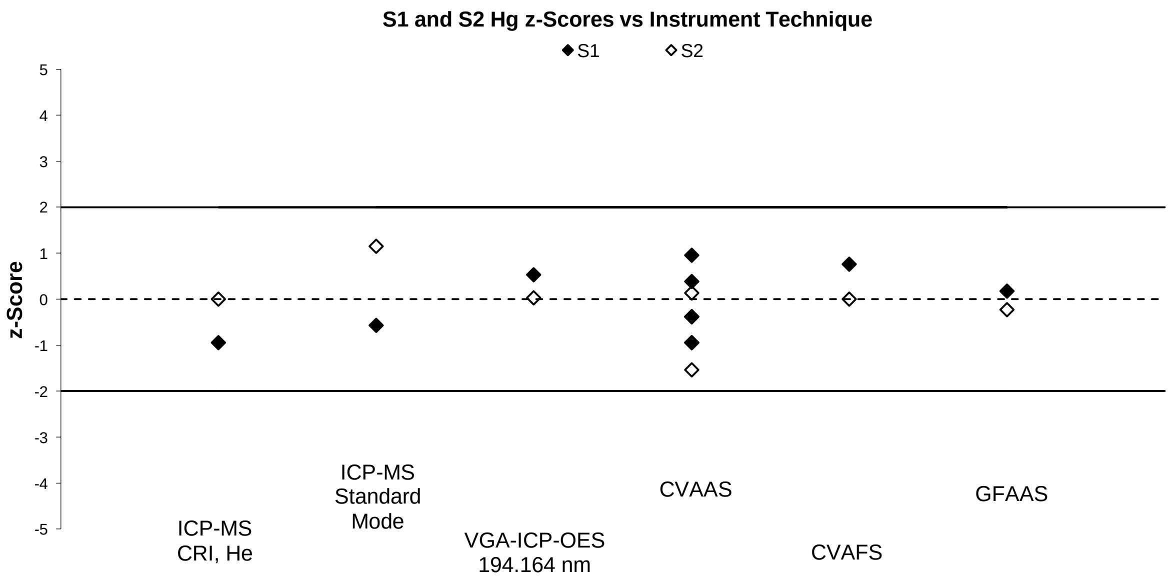


Figure 59 S1 and S2 Hg z-Scores vs Instrumental Technique

Nickel level in S1 was 2.53 µg/L and in S2 was 5.80 µg/L. The between-laboratory CV for this test in S1 was 20% and in S2 was 4 time lower at 5.2%. All reported results returned satisfactory z-scores (Figure 60).

Plots of participants' performance in the two water samples versus instrumental technique used are presented in Figure 61. All participants measured Ni by ICP-MS in collision mode.

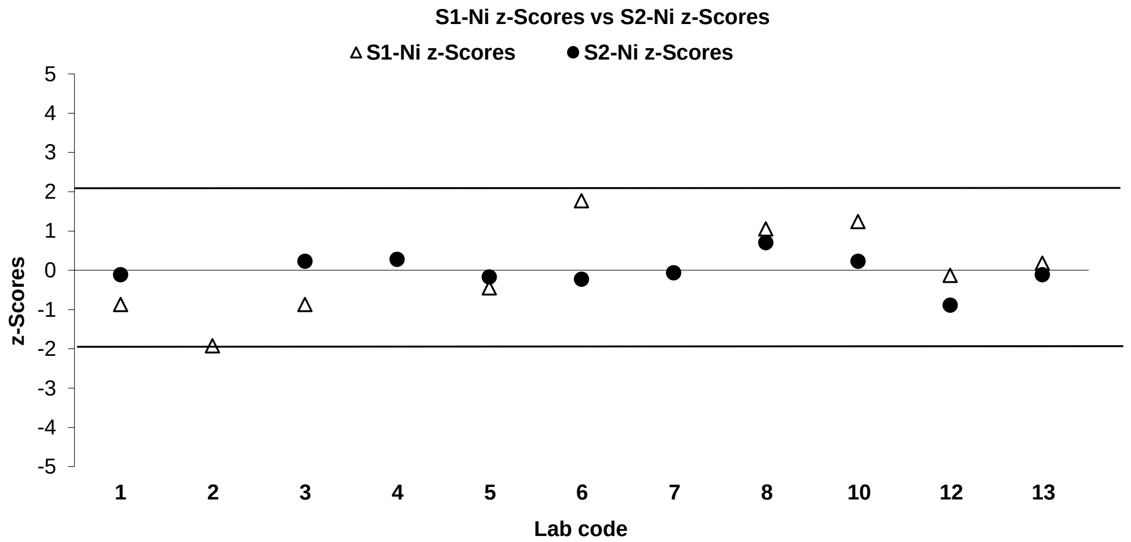


Figure 60 S1 and S2 Ni z-Scores vs Laboratory Code

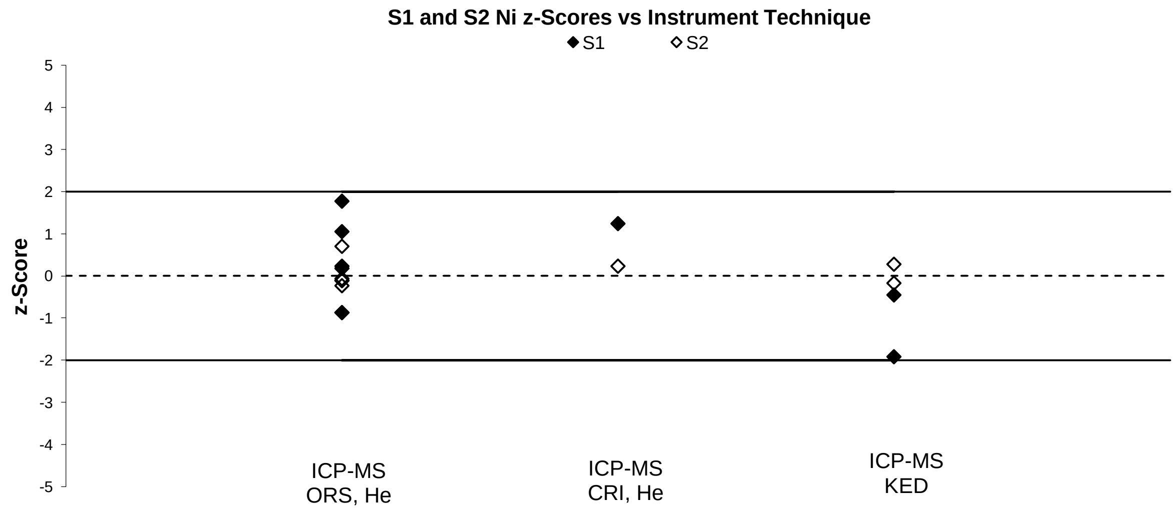


Figure 61 S1 and S2 Ni Results vs Instrumental Technique

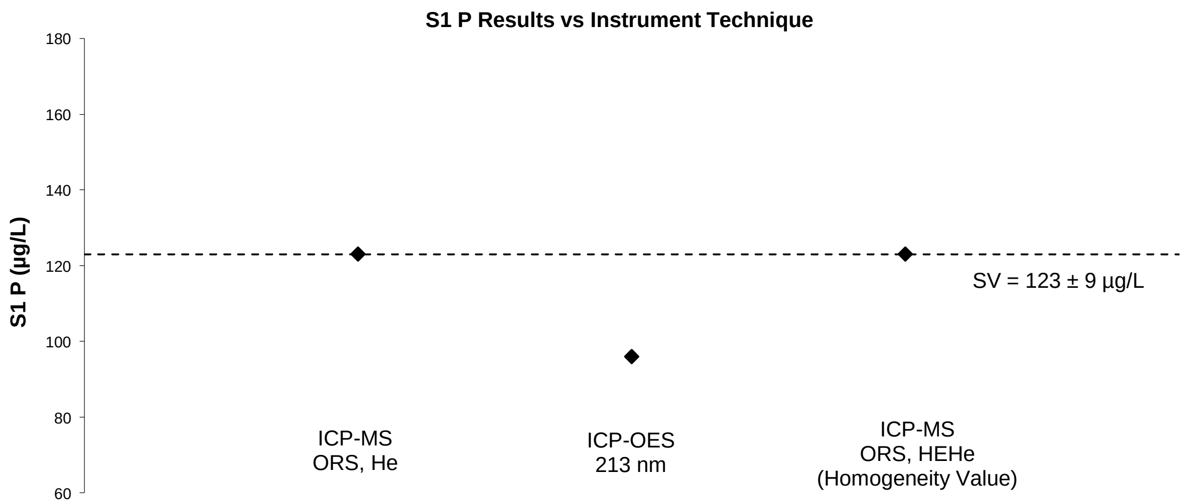


Figure 62 S1 P Results vs Instrumental Technique

Phosphorus spike level in the sea water sample was 123 µg/L A limited number of laboratories had the capability to measure P in sea water at this level. Only two participants reported results for this test and both results were in relatively good agreement with each other, with the homogeneity value, and with the spike value (Figure 62).

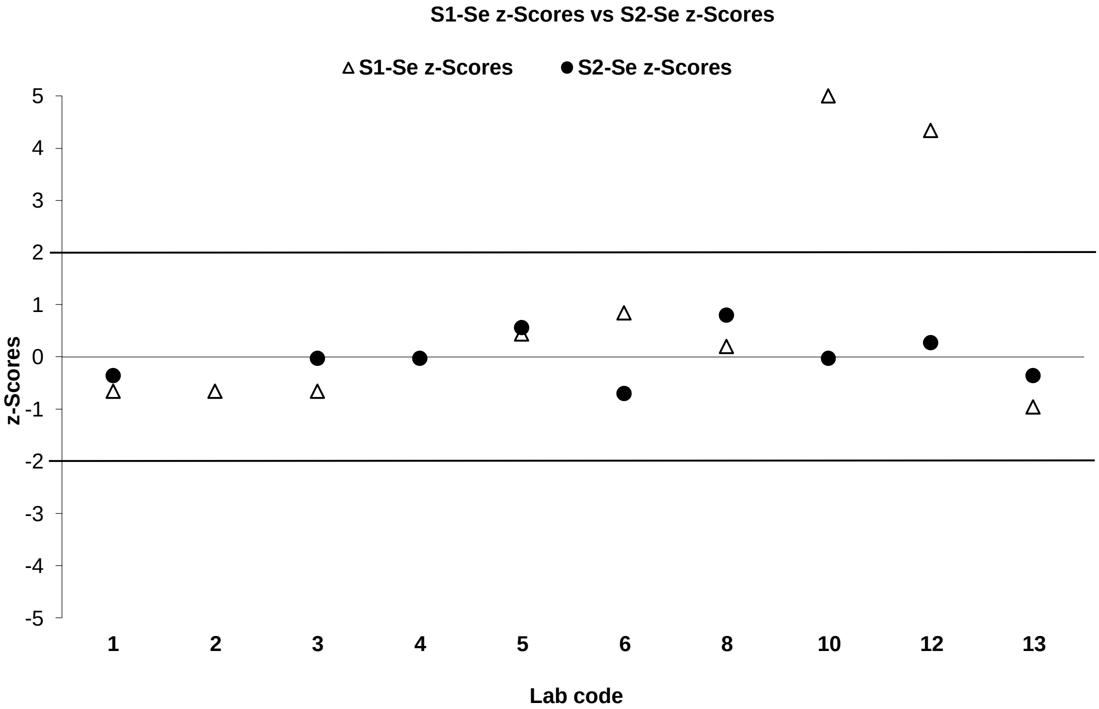


Figure 63 S1 and S2 Se z-Scores vs Laboratory Code

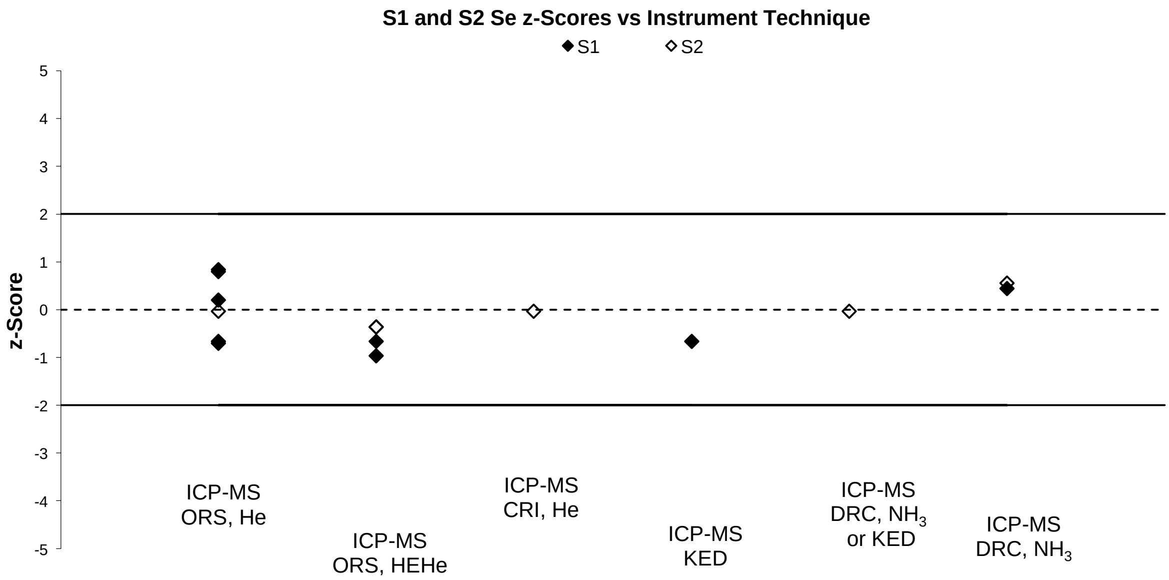


Figure 64 S1 and S2 Se z-Scores vs Instrumental Technique

Selenium analysis in sea water is challenging due to there being multiple sources of significant interference. This is especially problematic at low levels where any unresolved interference can have a more significant effect on results. While all reported results in the river water sample returned satisfactory z-scores, only 7 were satisfactory in the sea water sample. Participants who reported satisfactory Se results in S2 but reported high unsatisfactory results in S1 may not have overcome the interference problem in the sea water sample (Figure 63).

Plots of participants' performance for Se in S1 and S2 versus instrumental technique used are presented in Figure 64.

Silver in the river and sea water sample was at similar levels. Participants' performance in the two study samples are presented in Figure 65. All participants used ICP-MS.

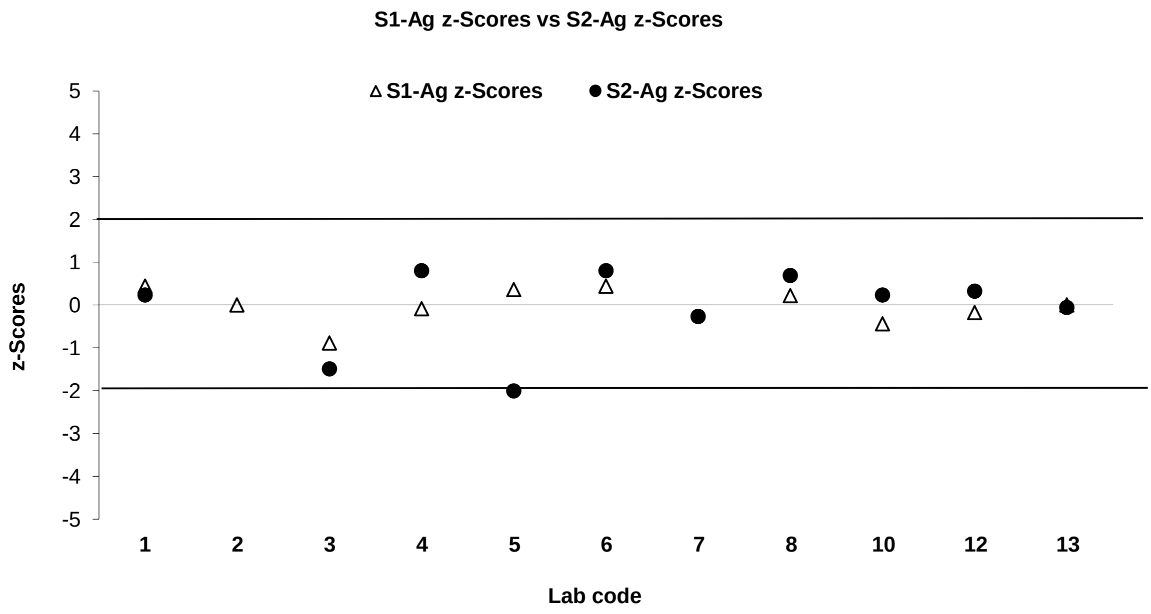


Figure 65 S1 and S2 Ag z-Scores vs Laboratory Code

Titanium Like for P, a limited number of participants reported results for Ti in the two study samples. Five laboratories reported results for this test in S2 and all 5 results were in good agreement with each other with the homogeneity value and with spike value (Figure 66).

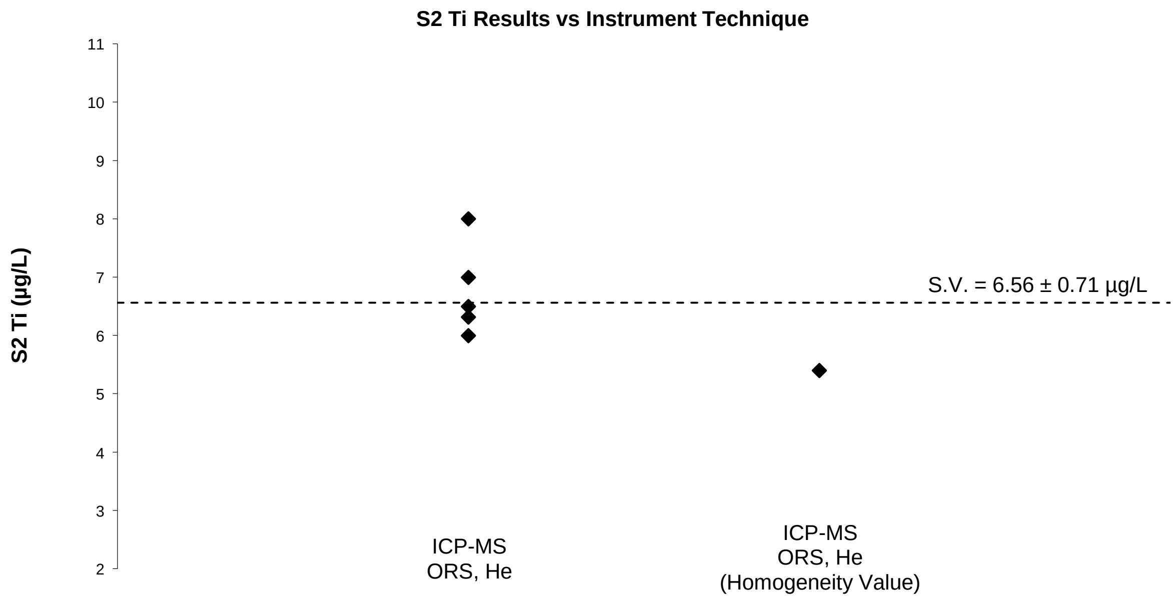


Figure 66 S2 Ti Results vs Laboratory Code

Vanadium All laboratories who reported results for V in S1 and S2 performed satisfactorily but one. Laboratory who reported a satisfactory V result in S2 but high unsatisfactory result in S1 may not have overcome the interference problem in the sea water sample for this test (Figure 67). ^{51}V has significant interferences from polyatomic species such as $^{35}Cl^{16}O^{+}$ or $^{34}S^{16}O^{1}H^{+}$. Plots of participants performance in the two samples versus the instrumental technique used are presented in Figure 68.

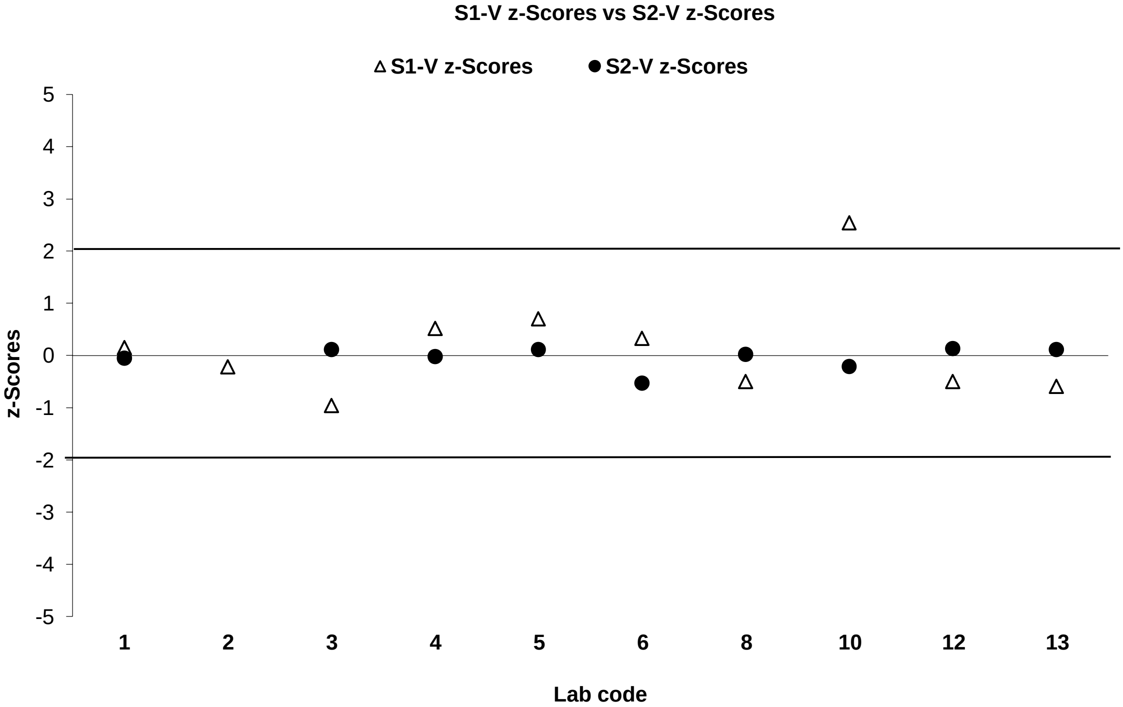


Figure 67 S1 and S2 V z-Scores vs Laboratory Code

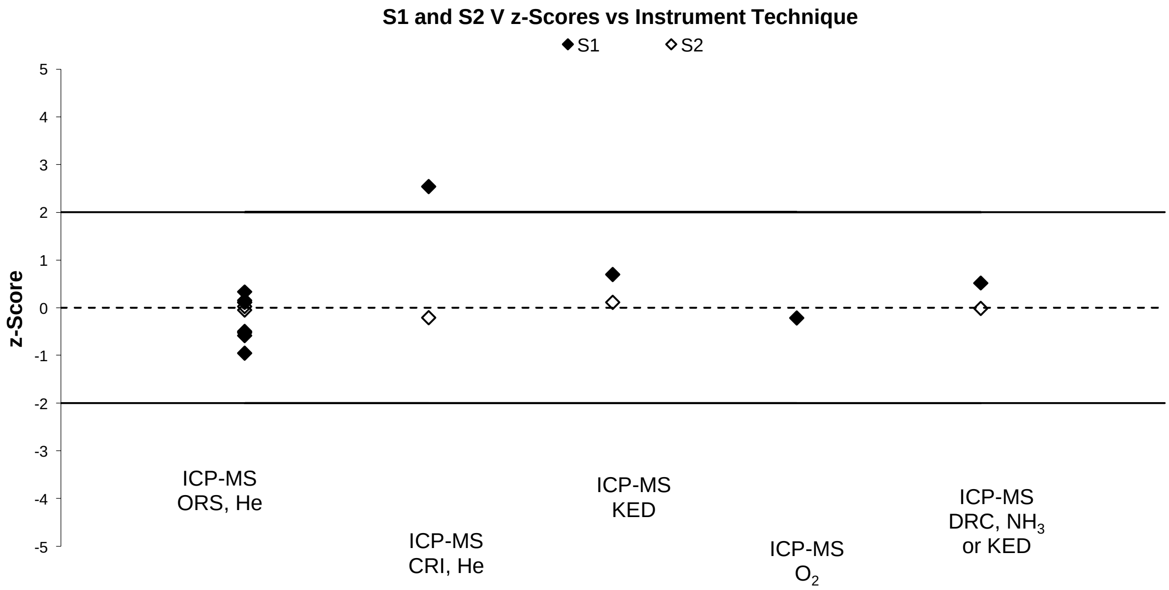
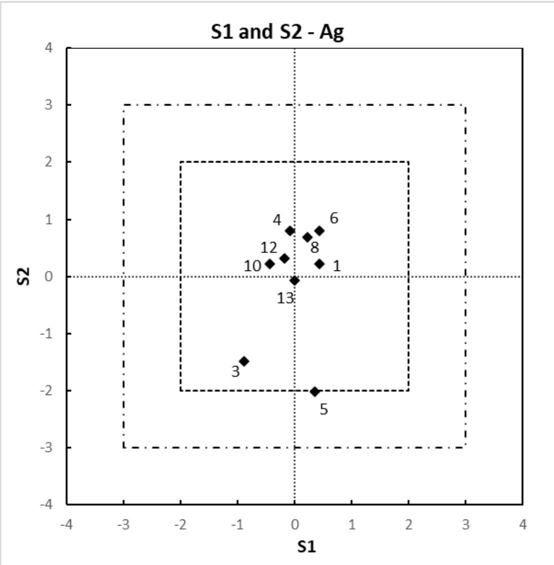
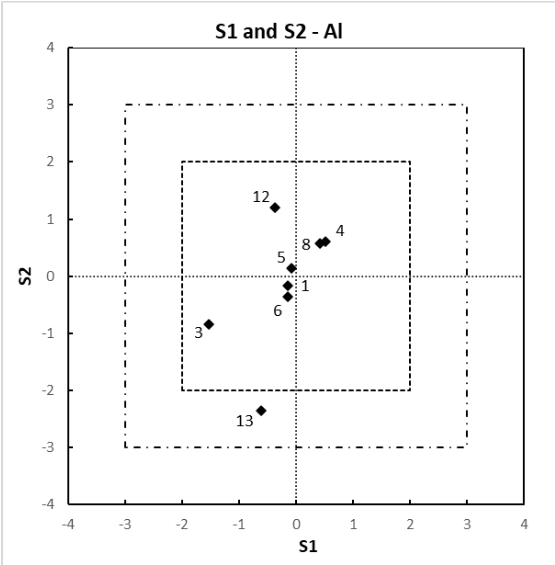


Figure 68 S1 and S2-V z-Scores vs Instrumental Technique

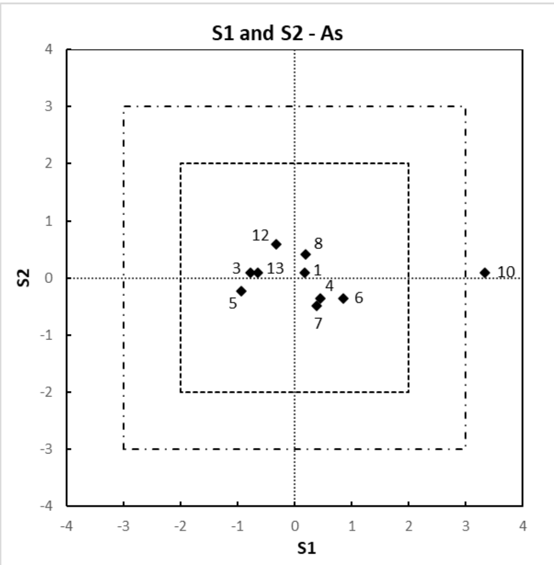
6.6 z-Score Scatter plots

Scatter plots of z-scores for all analytes present in both study samples at a similar level are presented in Figure 69. Scores are predominantly in the upper right and lower left quadrants, indicating that laboratory bias is the major contributor to the variability of results. Points close to the diagonal axis demonstrate excellent repeatability, while points close to the zero demonstrate excellent repeatability and accuracy.





Laboratory 10 is off scale.



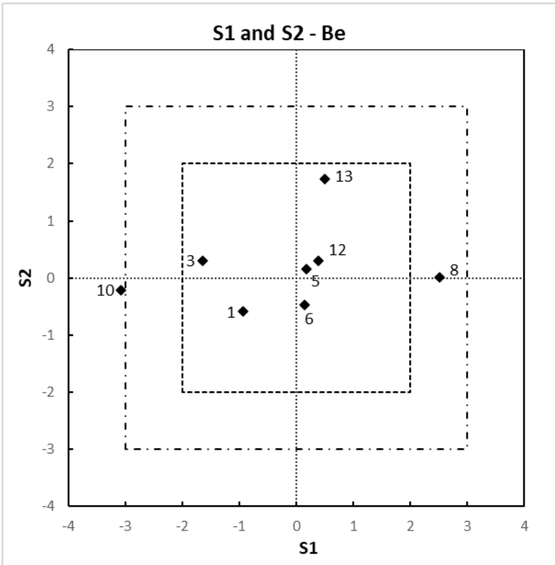
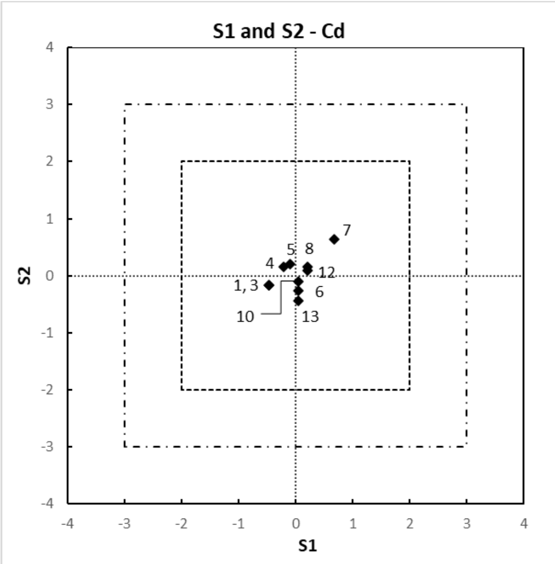
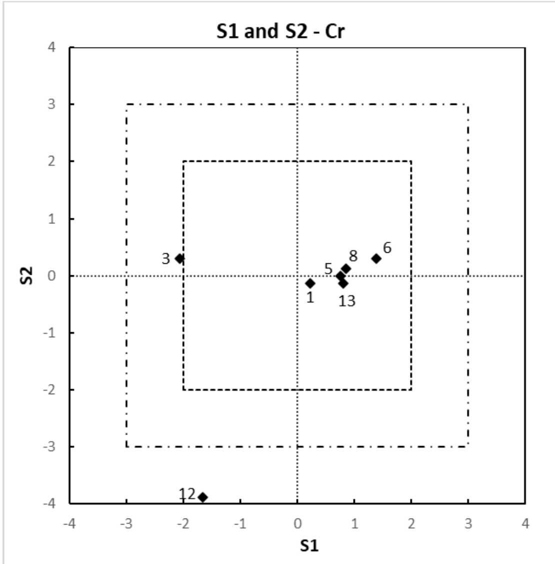
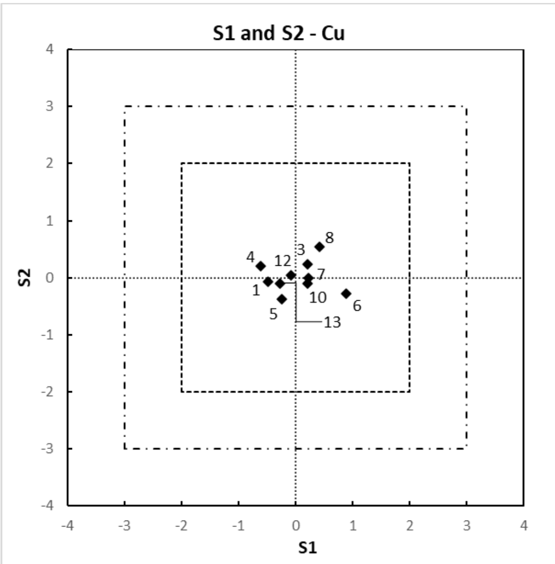


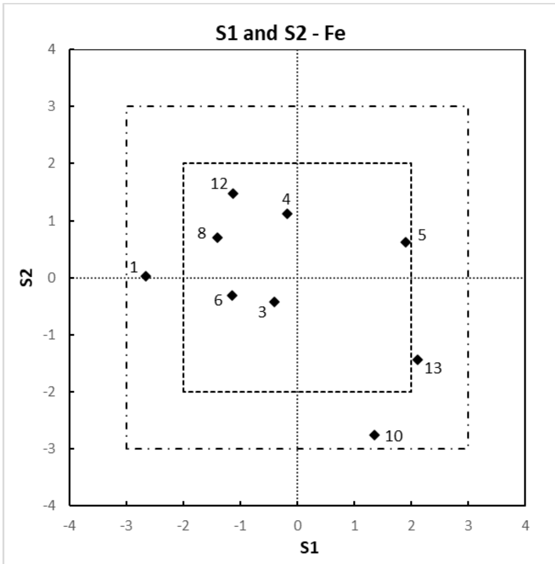
Figure 69 Scatter Plots of z-Scores for S1 and S2

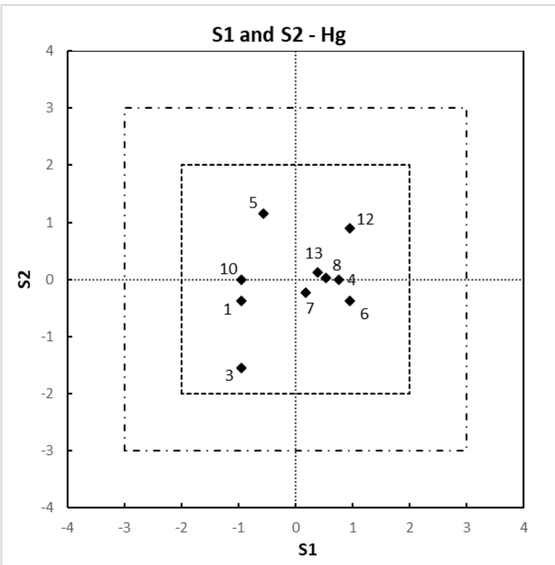


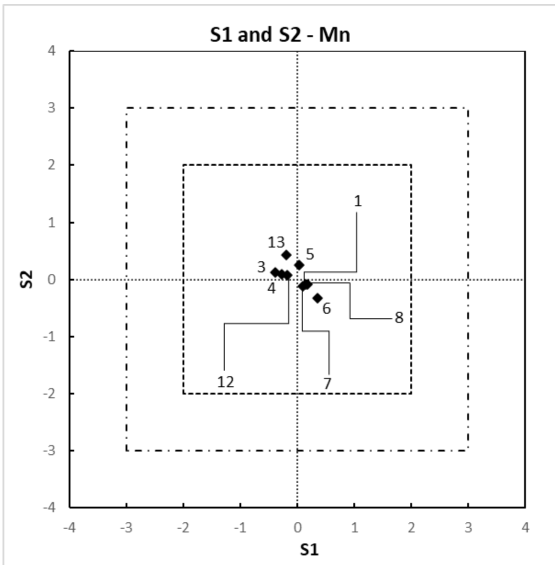


Laboratory 10 is off scale.



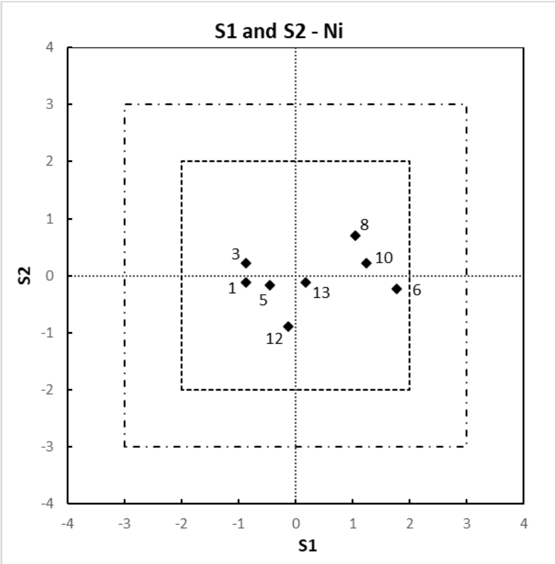


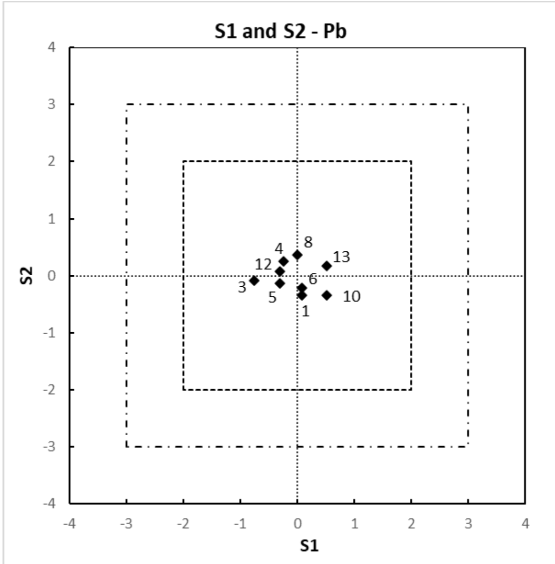


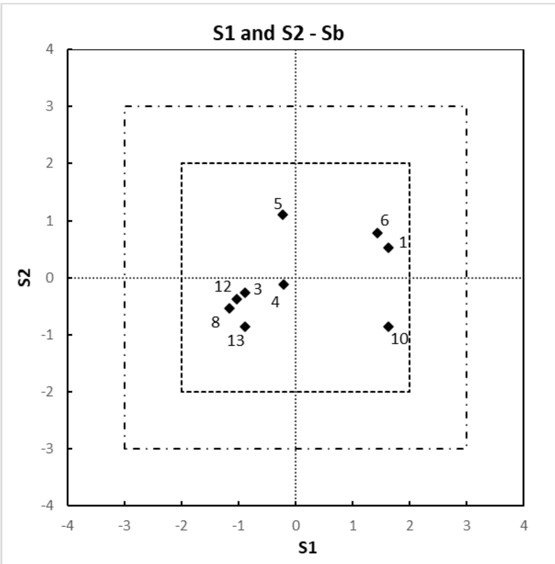


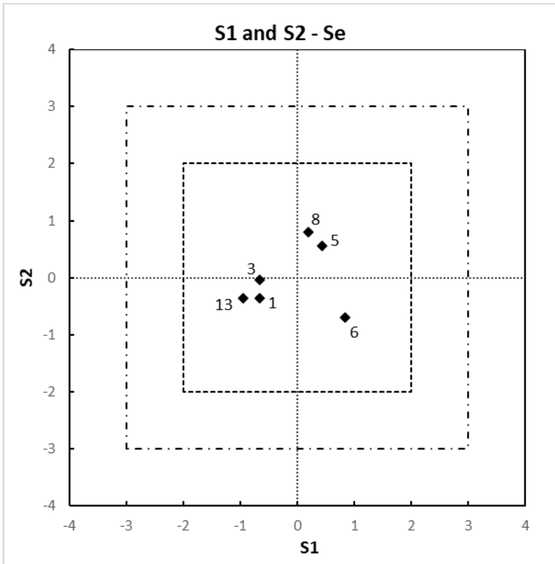
Laboratory 10 is off scale.

Figure 69: Scatter Plots of z-Scores for S1 and S2 (continued)

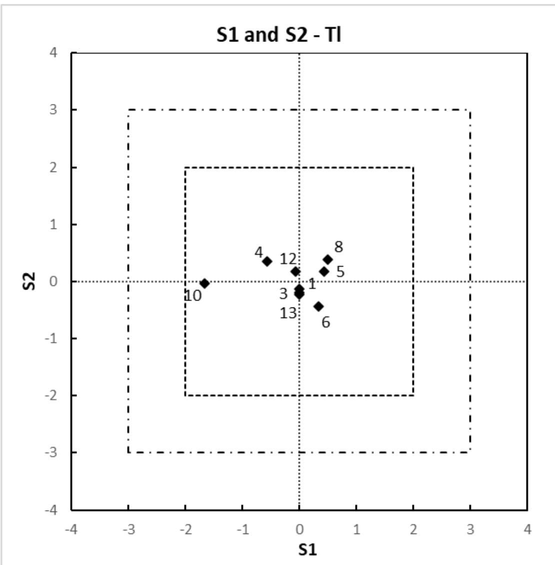








Laboratories 10 and 12 are off scale.



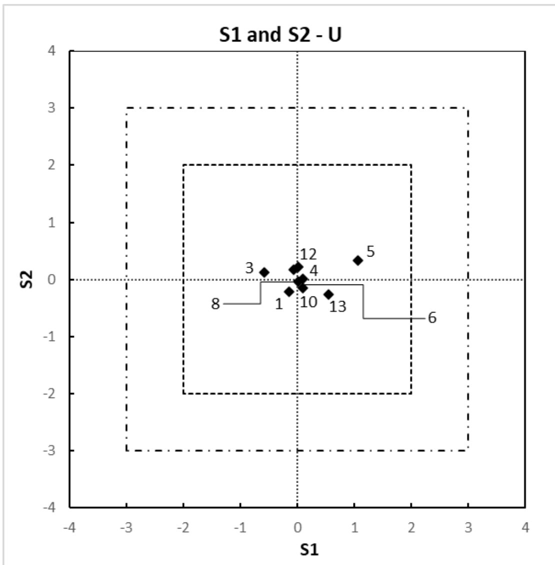
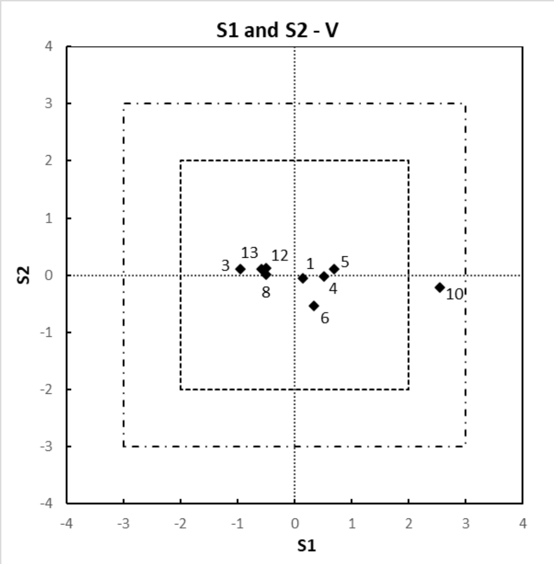


Figure 69: Scatter Plots of z-Score for S1 and S2 (continued)



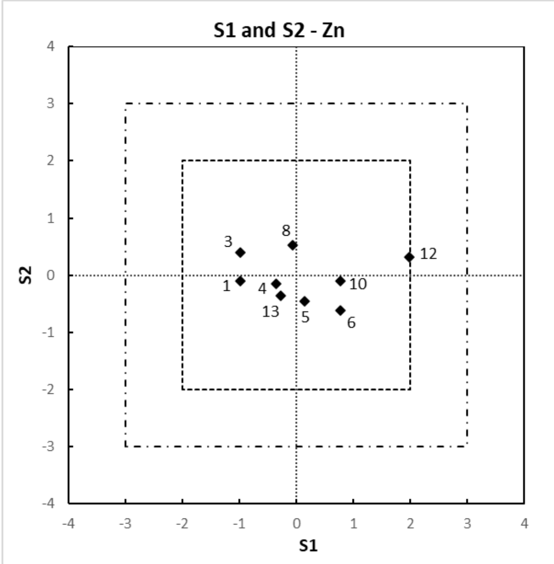


Figure 69: Scatter Plots of z-Score for S1 and S2 (continued)

6.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 23-18 is the 33rd NMI proficiency study of metals in water. Participants' performance in the measurement of trace elements in water (river water, seawater, wastewater and potable water) over the last ten years is presented in Figure 70. Over this period, the average proportion of satisfactory scores was 91% for z-scores and 84% for E_n-scores.

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

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

6.8 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 50).

Table 50 Control Samples Used by Participants

Lab. Code	Description of Control Samples
2	CRM – High Purity Standards-Multi Components Standards
3	CRM – Choice Analytical High Purity CRMs
4	SS
5	CRM - CWW-TM-B and CWW-TM-C (river water) NASS 7, CASS 6 and NMI MX014 (seawater)
6	RM
7	SS
8	SS
10	CRM – TMDW LOT 2308120
13	CRM

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

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

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

A certified reference material for trace elements in sea water (MX014) is available from NMI.

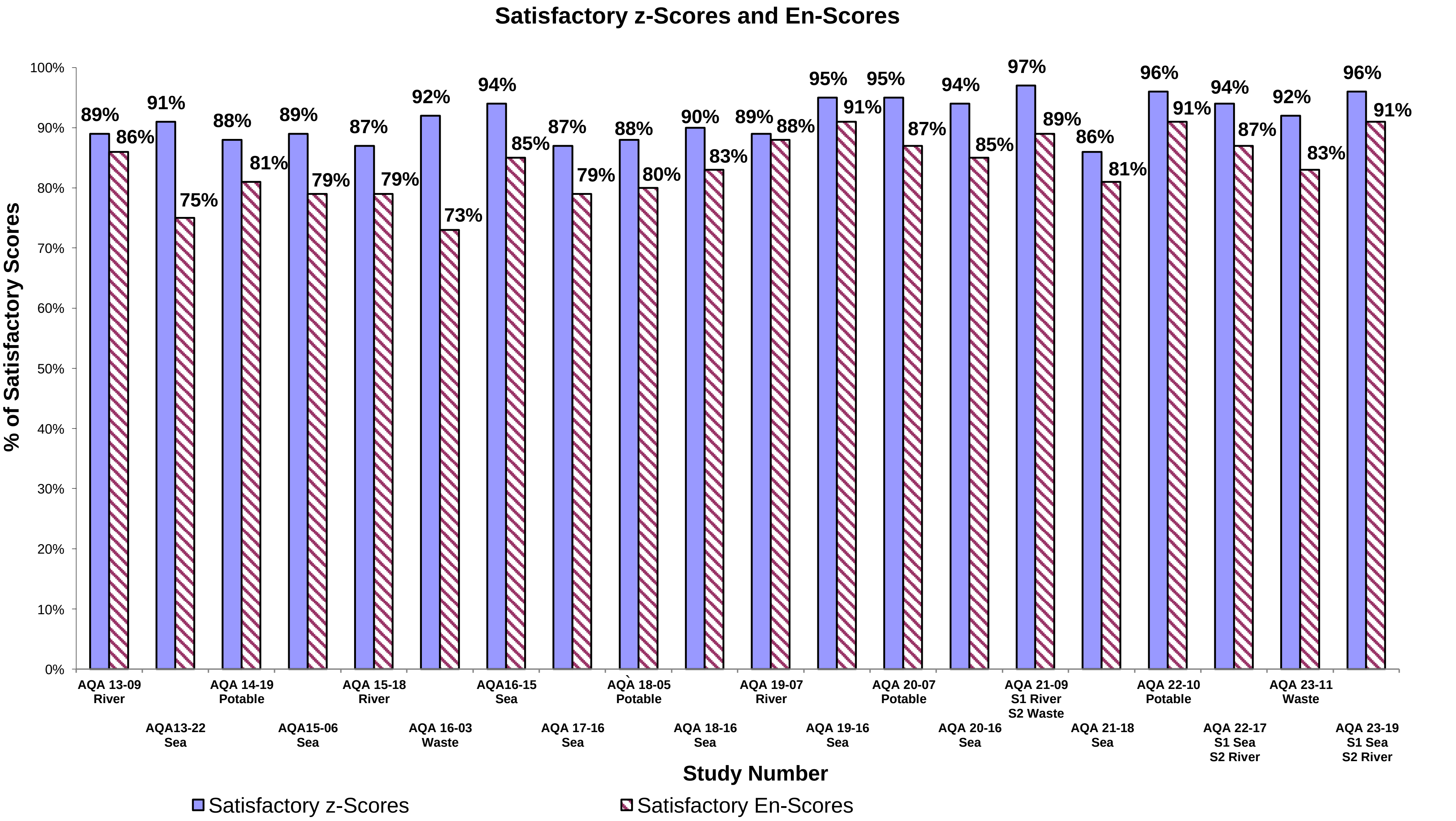


Figure 70 Participants' Performance in Metals in Water PT Studies over Last Ten Years

7 REFERENCES

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

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

[2] NMI, *Study Protocol for Proficiency Testing*, viewed January 2024, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf >.

[3] NMI, *Chemical Proficiency Testing Statistical Manual*, viewed January 2024, <https://www.industry.gov.au/sites/default/files/2019-07/cpt_statistical_manual.pdf>.

[4] Thompson, M, Ellison, S & Wood, R 2006, 'The international harmonized protocol for proficiency testing of (chemical) analytical laboratories', *Pure Appl. Chem*, vol 78, pp 145-196.

[5] National Environmental Protection Council, Schedule B1 Guidelines on the Investigation Levels for Soil and Groundwater, viewed January 2024, <https://www.legislation.gov.au/Details/F2013C00288/Html/Volume_2>.

[6] ISO13528, *Statistical methods for use in proficiency testing by inter laboratory comparisons.*

[7] Thompson, M, 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst,* vol 125, pp 385-386.

[8] AS ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

[9] Eurachem/CITAC Guide CG4, QUAM 2012, *Quantifying Uncertainty in Analytical Measurement*, 3rd ed., viewed January 2024, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[10] Bertil, M, 2004, *Nordtest Report Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories TR 537,* 4th Edition, Nordest Tekniikantie, Finland, Esopo.

[11] Hibbert, B 2007, *Quality Assurance for the Analytical Chemistry Laboratory*, Oxford University Press.

[12] ISO (2008), *Guide to the Expression of Uncertainty in Measurement (GUM)*, Geneva, Switzerland.

[13] Eurolab 2002, Technical Report No 1/2002 - Measurement Uncertainty in Testing.

[14] NMI, *Estimating Measurement Uncertainty for Chemists* – viewed January 2024, <https://www.industry.gov.au/client-services/training-and-assessment>.

[15] Jackson, B & Liba, A 2015, 'Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods' *J. Anal. At. Spectrometry,* vol. 30, pp1179-1183.

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

[17] National Measurement Institute, Method Number NT2.47: Determination of Total Acid Extractable Metals and Dissolved Elements in Water using Inductively Coupled

Plasma Mass Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry.

APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared from sea water. Approximately 10 L of sea water was filtered through a 0.45 µm pore size filter, stabilised by adding 2% (v/w) nitric acid and further fortified for 21 elements.

Sample S2 was prepared by filtering 5 L of river water through a 0.2 µm pore size filter and then stabilised by adding 2% (v/w) nitric acid and 0.01% (v/w) HCl. The acidified and filtered river water was then further fortified for 20 elements.

Sample Analysis and Homogeneity Testing

With the exception of Al in S1, a partial homogeneity test was conducted for all analytes of interest. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Sample Analysis for Dissolved Elements

For analyses of dissolved elements in Sample S1, a test portion of 1 mL was transferred to a 14 mL graduated polypropylene centrifuge tube and diluted to 10 mL with 2% HNO_3.[17]

For analyses of dissolved elements in Sample S2, a test portion of 8 mL was transferred to a 14 mL graduated polypropylene centrifuge tube and diluted to 10 mL with 2% HNO_3.[17]

Testing involved measurements using ICP-MS. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates, sample matrix spikes and control samples (MX014, AQA 20-16 S1, AQA 21-18 S1, AQA 22-17 S1, and AQA 22-17 S2) was carried through the same set of procedures and analysed simultaneously with the samples. A summary of the ion/wavelength and instrument conditions used for each analyte is presented in Table 51 for S1 and in Table 52 for S2.

Table 51 Instrumental Techniques used for Dissolved Elements in S1

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	Final Dilution Factor	Ion / Wavelength
Ag	ICP-MS	Rh	ORS	He	10	107 m/z
As	ICP-MS	Rh	ORS	He	10	75 m/z
Be	ICP-MS	Rh	ORS	He	10	9 m/z
Cd	ICP-MS	Rh	ORS	He	10	114 m/z
Cr	ICP-MS	Rh	ORS	He	10	52 m/z
Cu	ICP-MS	Rh	ORS	He	10	65 m/z
Fe	ICP-MS	Rh	ORS	He	10	56 m/z
Hg	ICP-MS	Ir	ORS	He	10	202 m/z
Mn	ICP-MS	Rh	ORS	He	10	55 m/z
Ni	ICP-MS	Rh	ORS	He	10	60 m/z
P	ICP-MS	Rh	ORS	HEHe	10	31 m/z
Pb	ICP-MS	Ir	ORS	He	10	208 m/z
Sb	ICP-MS	Rh	ORS	He	10	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	10	78 m/z
Sn	ICP-MS	Rh	ORS	He	10	118 m/z
Ti	ICP-MS	Rh	ORS	He	10	49 m/z
Tl	ICP-MS	Rh	ORS	He	10	205 m/z
U	ICP-MS	Ir	ORS	He	10	238 m/z
V	ICP-MS	Rh	ORS	He	10	51 m/z
Zn	ICP-MS	Rh	ORS	He	10	66 m/z

Table 52 Instrumental Techniques used for Dissolved Elements in S2

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	Final Dilution Factor	Ion / Wavelength
Ag	ICP-MS	Rh	ORS	He	1.25	107 m/z
Al	ICP-MS	Rh	ORS	He	1.25	27 m/z
As	ICP-MS	Rh	ORS	He	1.25	75 m/z
Be	ICP-MS	Rh	ORS	He	1.25	9 m/z
Cd	ICP-MS	Rh	ORS	He	1.25	114 m/z
Co	ICP-MS	Rh	ORS	He	1.25	59 m/z
Cr	ICP-MS	Rh	ORS	He	1.25	52 m/z
Cu	ICP-MS	Rh	ORS	He	1.25	65 m/z
Fe	ICP-MS	Rh	ORS	He	1.25	56 m/z
Hg	ICP-MS	Ir	ORS	He	1.25	202 m/z
Mn	ICP-MS	Rh	ORS	He	1.25	55 m/z
Mo	ICP-MS	Rh	ORS	He	1.25	95 m/z
Ni	ICP-MS	Rh	ORS	He	1.25	60 m/z
Pb	ICP-MS	Ir	ORS	He	1.25	208 m/z
Sb	ICP-MS	Rh	ORS	He	1.25	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	1.25	78 m/z
Ti	ICP-MS	Rh	ORS	He	1.25	49 m/z
Tl	ICP-MS	Rh	ORS	He	1.25	205 m/z
U	ICP-MS	Ir	ORS	He	1.25	238 m/z
V	ICP-MS	Rh	ORS	He	1.25	51 m/z
Zn	ICP-MS	Rh	ORS	He	1.25	66 m/z

APPENDIX 2 – ASSIGNED VALUE, Z-SCORE AND E_N SCORE CALCULATION

The assigned value was calculated as the robust average using the procedure described in 'ISO13528, Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] The uncertainty was estimated as:

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

where:

$u_{rob\ av}$ robust average standard uncertainty
$S_{rob\ av}$ robust average standard deviation
p number of results

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

A worked example is set out below in Table 53.

Table 53 Uncertainty of Assigned Value for Ag in Sample S1

No. results (p)	10
Robust Average	1.50 µg/L
$S_{rob\ av}$	0.092 µg/L
$u_{rob\ av}$	0.036 µg/L
k	2
$U_{rob\ av}$	0.07 µg/L

The assigned value for **Ag** in Sample S1 is **1.50 ± 0.07 µg/L.**

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 2 and Equation 3 respectively (see page 7).

A worked example is set out below in Table 54.

Table 54 z-Score and E_n-score for Ag result reported by Laboratory 4 in S1

Ag Result µg/L	Assigned Value µg/L	Set Target Standard Deviation	z-Score	E_n-Score
1.48 ± 0.34	1.50 ± 0.07	15% as CV or 0.15 x 1.50 = = 0.23 µg/L	$z = \frac{(1.48 - 1.50)}{0.23}$ z = -0.09	$En = \frac{(1.48 - 1.50)}{\sqrt{0.34^2 + 0.07^2}}$ E_n = -0.06

APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10, 12] Between 2007 and 2024, NMI carried out 33 proficiency tests for metals in water. These studies involved analyses of dissolved or total elements at low and high levels in potable, fresh (river), saline water, ground water and waste water. Laboratory X participated and submitted satisfactory results in 25 of these PTs. This data can be separated into two ranges of results: 0.0005 to 0.01 mg/L and 0.01 to 0.10 mg/L. Results are presented in Tables 55 and 56.

Table 55 Laboratory X Reported Results for Ni at 0.0005 to 0.01 mg/L Level

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 11-07	Fresh	0.0015 ± 0.0003	0.00100 ± 0.00001	24	15
	Fresh	0.0039 ± 0.00078	0.00306 ± 0.00016	18	19
	Fresh	0.0039 ± 0.00078	0.00306 ± 0.00016	9.6	19
AQA 12-20	Saline	0.0039 ± 0.0008	0.00370 ± 0.00028	13	19
AQA 13-09	Fresh	0.0044 ± 0.0009	0.00409 ± 0.00017	7.9	15
AQA 13-22	Saline	0.00170 ± 0.00034	0.00165 ± 0.00014	13	14
	Saline	0.00384 ± 0.00077	0.00378 ± 0.00012	13	14
AQA 15-06	Sea	0.00180 ±0.0004	0.00177 ± 0.00021	28	12
	Sea	0.00172 ± 0.0004	0.00177 ± 0.00021	28	11
AQA 15-18	Surface	0.002 ± 0.0003	0.00196 ± 0.00013	7.8	10
AQA 16-03	Waste	0.0041 ± 0.0008	0.00398 ± 0.00031	8.6	9
AQA 16-15	Sea	0.0070 ± 0.0010	0.00652 ± 0.00038	9.4	16
AQA 17-16	Sea	0.0015 ± 0.0003	0.00143 ± 0.00029	22	10
AQA 18-16	Sea	0.0022 ± 0.0005	0.00206 ± 0.00015	11	14
AQA 19-07	Fresh	0.0018 ± 0.0004	0.00187 ± 0.00009	5.3	10
AQA 19-16	Sea	0.0021 ± 0.0004	0.00168 ± 0.00037	25	8
AQA 20-16	Sea	0.0013 ± 0.0003	0.00178 ± 0.00034	24	10
AQA 21-09	River	0.0007 ± 0.0002	0.000756 ± 0.000059	8.9	8
AQA 21-18	Saline	0.0029 ± 0.0006	0.00298 ± 0.00031	13	6
AQA 22-10	Potable	0.007 ± 0.0011	0.00845 ± 0.00036	6.1	13
AQA 22-17	Sea	0.0028 ± 0.00056	0.00286 ± 0.00027	12	15
AQA 22-17	River	0.0035 ± 0.00027	0.00364 ± 0.00026	10	13
AQA 23-11	Waste	0.0085 ± 0.0009	0.00825 ± 0.0052	9.2	13
AQA 23-18	Sea	0.00236 ± 0.0003	0.00253 ± 0.00042	20	9
	River	0.00565 ± 0.0007	0.00580 ± 0.00024	5.2	10
Average				14**	

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

Table 56 Laboratory X Reported Results for Ni at 0.01 to 0.10 mg/L Level

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 11-17	Waste	0.10 ± 0.009	0.099 ± 0.001	2	15
	Waste	0.10 ± 0.009	0.098 ± 0.001	2	15
AQA 12-09	Potable	0.047 ± 0.007	0.045 ± 0.002	6.7	19
	Potable	0.055 ± 0.008	0.053 ± 0.002	7.4	19
AQA 12-20	Saline	0.0415 ± 0.0083	0.0384 ± 0.0021	11	22
AQA 13-09	Fresh	0.0393 ± 0.0040	0.0361 ± 0.0010	4.8	16

Table 56 Laboratory X Reported Results for Ni at 0.01 to 0.10 mg/L Level (continued)

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Robust CV of all results (%)	Number of Results
AQA 13-09	Fresh	0.0258 ± 0.0030	0.0272 ± 0.0025	15	15
AQA 14-08	Ground	0.019 ± 0.004	0.0191 ± 0.0007	7.9	13
AQA 14-19	Potable	0.019 ± 0.004	0.0183 ± 0.0013	11	14
AQA 15-18	Surface	0.036 ± 0.0035	0.0336 ± 0.0013	5.1	13
AQA 16-03	Waste	0.042 ± 0.0045	0.0352 ± 0.0050	19	11
AQA 16-15	Sea	0.0456 ± 0.0060	0.0409 ± 0.0029	12	17
AQA 17-16	Sea	0.0116 ± 0.0012	0.0101 ± 0.0023	27	9
AQA 18-05	Potable	0.017 ± 0.002	0.0172 ± 0.0010	8.7	16
AQA 18-16	Sea	0.015 ± 0.0030	0.0138 ± 0.0014	15	15
AQA 19-07	Fresh	0.029 ± 0.0035	0.0283 ± 0.0009	4.3	11
AQA 20-07	Potable	0.010 ± 0.002	0.0106 ± 0.0004	6	16
AQA 21-09	Waste	0.014 ± 0.0021	0.0143 ± 0.0006	8.1	21
Average				9.6**	

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

Taking the average of the robust CVs over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 14% and 9.6% respectively. Using a coverage factor of two gives relative expanded uncertainties of 28% and 20% respectively, at a level of confidence of 95% level.

Table 57 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the ranges 0.0005 – 0.01 mg/L and 0.01 – 0.10 mg/L.

Table 57 Uncertainty of Ni results estimated using PT data

Results mg/L	Uncertainty mg/L
0.00050	0.00014
0.00100	0.00028
0.0100	0.0020
0.100	0.020
0.150	0.030

The estimates of 28% and 20% relative passes the test of being reasonable, and the analysis of the thirty-three different PT samples over ten years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrators etc.), and so complies with ISO 17025.[8]

APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
CV_{rob}	Robust Coefficient of Variation
CVAAS	Cold Vapour Atomic Absorption Spectrometry
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
DRC	Dynamic Reaction Cell
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GUM	Guide to the Expression of Uncertainty in Measurement
HEHe	High energy He mode
H.V.	Homogeneity Value
HR-ICP-MS	High Resolution Inductively Coupled Plasma – Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-MS/MS	Inductively Coupled Plasma – Tandem Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
IUPAC	International Union of Pure and Applied Chemists
KED	Kinetic Energy Discrimination
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MU	Measurement Uncertainty
N	Number of Participants
NIST	National Institute of Standards and Technology
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PT	Proficiency Test
RM	Reference Material
SA-ICP-MS	Standard Addition Inductively Coupled Plasma – Mass Spectrometry
SD_{rob}	Robust Standard Deviation
SI	The International System of Units
SS	Spiked sample
S.V.	Spiked or formulated concentration of a PT sample
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation (symbol: σ)
UC	Universal Cell
VGA-ICP-OES	Vapour Generation Accessory – Inductively Coupled Plasma – Optical Emission Spectrometry

APPENDIX 5 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 58 Instrument Conditions Ag

Laboratory 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	ORS	He	NA	NA	107
2	ICP-MS	Y			10	NA	107
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	328.069nm
4	ICP-MS	Rh	KED	He	20	1	109
5	ICP-MS	Rh	NA	NA	1	1	109
6	ICP-MS	Rh	ORS	He			107
7	ICP-MS	Sc, Ir, Rh	ORS	He			107
8	ICP-MS	103	ORS	He	1	1	107
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	NA	107

Table 59 Instrument Conditions Al

Laboratory 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	ORS	He	NA	NA	27
2	ICP-MS	Li6		O2	10	NA	27
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	27 (m/z)
4	ICP-MS	Sc	KED	He	20	1	27
5	ICP-MS	Sc	NA	NA	1	1	27
6	ICP-MS	Sc	ORS	He			27
7	ICP-MS	Sc, Ir, Rh	ORS	He			27
8	ICP-MS	45	ORS	He	1	1	27
10	ICP-MS	Sc	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-OES-AV	Y	NA	NA	NA	2	167.019

Table 60 Instrument Conditions As

Laboratory 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	ORS	He	NA	NA	75
2	ICP-MS	Y		O2	10	NA	75
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	75 (m/z)
4	ICP-MS	Te	KED	He	20	1	75
5	ICP-MS	Rh	KED	He	1	1	75
6	ICP-MS	Sc	ORS	He			75
7	ICP-MS	Sc, Ir, Rh	ORS	He			75
8	ICP-MS	72	ORS	He	1	1	75
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	75

Table 61 Instrument Conditions Be

Laboratory 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	NA	He	NA	NA	9
2	ICP-MS	Li6			10	NA	9
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	9 (m/z)
4	ICP-MS	Sc	KED	He	NA	1	9
5	ICP-MS	Sc	NA	NA	1	1	9
6	ICP-MS	Sc	NA				8
7	ICP-MS	Sc, Ir, Rh	ORS	NA			9
8	ICP-OES-AV-buffer	Lu			1	1	313.107
10	ICP-MS	Sc	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	NA	9

Table 62 Instrument Conditions Cd

Laboratory 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	ORS	He	NA	NA	111
2	ICP-MS	In			10	NA	111
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	111 (m/z)
4	ICP-MS	Rh	KED	He	20	1	111
5	ICP-MS	Rh	NA	NA	1	1	111
6	ICP-MS	Rh	ORS	He			111
7	ICP-MS	Sc, Ir, Rh	ORS	He			111
8	ICP-MS	103	ORS	He	1	1	114
10	ICP-MS	Ir	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	111

Table 63 Instrument Conditions Co

Laboratory 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	ORS	He	NA	NA	59
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Ir, Rh & Sc	ORS	He	NA	1	59 (m/z)
4	ICP-MS	Ga	KED	He	NA	1	59
5	ICP-MS	Rh	KED	He	NA	1	59
6	ICP-MS	Sc	ORS	He	NA		59
7	ICP-MS	Sc, Ir, Rh	ORS	He	NA		59
8	ICP-MS	103	ORS	He	1	1	59
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh			NA		
13	ICP-MS	Rh	ORS	He	NA	10	59

Table 64 Instrument Conditions Cr

Laboratory 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	ORS	He	NA	NA	52
2	ICP-MS	Sc			10	NA	52
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	52 (m/z)
4	ICP-MS	Ga/Sc	DRC/KED	NH3/He	20	1	52
5	ICP-MS	Sc	KED	He	1	1	52
6	ICP-MS	Sc	ORS	He			52
7	ICP-MS	Sc, Ir, Rh	ORS	He			52
8	ICP-MS	72	ORS	He	1	1	52
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	52

Table 65 Instrument Conditions Cu

Laboratory 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	ORS	He	NA	NA	65
2	ICP-MS	Sc			10	NA	63
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	63 (m/z)
4	ICP-MS	Ga	KED	He	20	1	63
5	ICP-MS	Rh	KED	He	1	1	65
6	ICP-MS	Sc	ORS	He			63
7	ICP-MS	Sc, Ir, Rh	ORS	He			63
8	ICP-MS	103	ORS	He	1	1	65
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	63

Table 66 Instrument Conditions Fe

Laboratory 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	ORS	HEHe	NA	NA	56
2	ICP-MS	Sc			10	NA	56
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	56 (m/z)
4	ICP-MS	Sc/Ga	DRC/KED	NH3/He	20	1	54/56
5	ICP-MS	Sc	KED	He	1	1	56
6	ICP-MS	Sc	ORS	He			56
7	ICP-MS	Sc, Ir, Rh	ORS	He			56
8	ICP-MS	72	ORS	He	1	1	56
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-OES-AV	Y	NA	NA	2	2	238.204

Table 67 Instrument Conditions Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	CVAAS	NA	NA	NA	NA	NA	253.7
2	CVAAS	SnCl2			15	NA	
3	CETAC	NA	NA	NA	1	1	253 nm
4	CVAFS	NA	NA	NA	5	5	253.7
5	ICP-MS	Ir	NA	NA	1	1	201
6	CVAAS		NA				253.7
7	GFAAS	NA	NA	NA			253.7
8	VGA-ICP-OES				1	1	194.164
10	ICP-MS	Ir	CRI	He	1	1	
12	ICP-MS	Rh					
13	CVAAS					2	

Table 68 Instrument Conditions Mn

Laboratory 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	ORS	He	NA	NA	55
2	ICP-MS	Sc			10	NA	55
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	55 (m/z)
4	ICP-MS	Sc	KED	He	20	1	55
5	ICP-MS	Sc	KED	He	1	1	55
6	ICP-MS	Sc	ORS	He			55
7	ICP-MS	Sc, Ir, Rh	ORS	He			55
8	ICP-MS	72	ORS	He	1	1	55
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	55

Table 69 Instrument Conditions Mo

Laboratory 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	ORS	He	NA	NA	95
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Ir, Rh & Sc	ORS	He	NA	1	95 (m/z)
4	ICP-MS	Rh	KED	He	NA	1	98
5	ICP-MS	Rh	NA	NA	NA	1	95
6	ICP-MS	Rh	ORS	He	NA		95
7	ICP-MS	Sc, Ir, Rh	ORS	He	NA		95
8	ICP-MS	72	ORS	He	1	1	98
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh			NA		
13	ICP-MS	Rh	ORS	He	NA	10	95

Table 70 Instrument Conditions Ni

Laboratory 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	ORS	He	NA	NA	60
2	ICP-MS	Sc			10	NA	60
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	60 (m/z)
4	ICP-MS	Ga	KED	He	20	1	60
5	ICP-MS	Rh	KED	He	1	1	60
6	ICP-MS	Sc	ORS	He			60
7	ICP-MS	Sc, Ir, Rh	ORS	He			60
8	ICP-MS	103	ORS	He	1	1	60
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	60

Table 71 Instrument Conditions P

Laboratory 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-OES-AV-buffer	Eu	NA	NA	NA	NA	185.827
2	ICP-OES-AV	Yb			10	NA	213nm
3	ICP-OES	Eu & Cs	NA	NA	1	NA	185.827 (nm)
4	NA	NA	NA	NA	NA	NA	NA
5						NA	
6	ICP-OES-AV	Eu	NA			NA	185.8
7	ICP-OES-AV	Eu	NA	NA		NA	185.827
8							
10	NA						
12	ICP-MS	Rh				NA	
13	ICP-OES-AV	Y	NA	NA	2	NA	213.618

Table 72 Instrument Conditions Pb

Laboratory 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	ORS	He	NA	NA	208
2	ICP-MS	Ir			10	NA	206
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	208 (m/z)
4	ICP-MS	Tb	KED	He	20	1	206+207+208
5	ICP-MS	Ir	NA	NA	1	1	206+207+208
6	ICP-MS	Ir	ORS	He			208
7	ICP-MS	Sc, Ir, Rh	ORS	He			208
8	ICP-MS	193	ORS	He	1	1	208
10	ICP-MS	Ir	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Ir	ORS	He	10	10	208

Table 73 Instrument Conditions Sb

Laboratory 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	ORS	He	NA	NA	121
2	ICP-MS	In			10	NA	121
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	121 (m/z)
4	ICP-MS	Rh	KED	He	20	1	121
5	ICP-MS	Rh	NA	NA	1	1	121
6	ICP-MS	Rh	ORS	He			121
7	ICP-MS	Sc, Ir, Rh	ORS	He			121
8	ICP-MS	72	ORS	He	1	1	121
10	ICP-MS	Ir	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	NA	10	121

Table 74 Instrument Conditions Se

Laboratory 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	ORS	HEHe	NA	NA	78
2	ICP-MS	Y			10	NA	78
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	78 (m/z)
4	ICP-MS	Te	DRC/KED	NH3/He	20	1	82
5	ICP-MS	Rh	DRC	NH3	1	1	82
6	ICP-MS	Sc	ORS	He			78
7	ICP-MS	Sc, Ir, Rh	ORS	HEHe			78
8	ICP-MS	103	ORS	He	1	1	78
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	HEHe	10	10	77

Table 75 Instrument Conditions Sn

Laboratory 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	ORS	He	NA	NA	118
2	ICP-MS	In			10	NA	118
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	NA	188 (m/z)
4	ICP-MS	Rh	KED	He	20	NA	120
5						NA	
6	ICP-MS	Rh	ORS	He		NA	118
7	ICP-MS	Sc, Ir, Rh	ORS	He		NA	118
8	ICP-MS	115	ORS	He	1	1	118
10	NA						
12	ICP-MS	Rh				NA	
13	ICP-MS	Rh	ORS	He	10	10	118

Table 76 Instrument Conditions Ti

Laboratory 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	ORS	He	NA	NA	47
2	ICP-MS	Sc			10	NA	48
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	47 (m/z)
4	ICP-OES-RV	NA	NA	NA	1	1	338
5							
6	ICP-MS	Sc	ORS	He			47
7	ICP-MS	Sc, Ir, Rh	ORS	He			47
8							
10	NA						
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	47

Table 74 Instrument Conditions Tl

Laboratory 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	ORS	He	NA	NA	205
2	ICP-MS	Ir			10	NA	205
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	205 (m/z)
4	ICP-MS	Tb	KED	He	20	1	205
5	ICP-MS	Ir	NA	NA	1	1	205
6	ICP-MS	Ir	ORS	He			205
7	ICP-MS	Sc, Ir, Rh	ORS	He			205
8	ICP-MS	193	ORS	He	1	1	205
10	ICP-MS	Ir	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Ir	ORS	He	10	NA	205

Table 75 Instrument Conditions U

Laboratory 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	ORS	He	NA	NA	238
2	ICP-MS	Ir		O2	10	NA	238
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	238 (m/z)
4	ICP-MS	Tb	KED	He	20	1	238
5	ICP-MS	Ir	NA	NA	1	1	238
6	ICP-MS	Ir	ORS	He			238
7	ICP-MS	Sc, Ir, Rh	ORS	He			238
8	ICP-MS	193	ORS	He	1	1	238
10	ICP-MS	Ir	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	238

Table 76 Instrument Conditions V

Laboratory 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	ORS	He	NA	NA	51
2	ICP-MS	Sc		O2	10	NA	51
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	51 (m/z)
4	ICP-MS	Ga/Sc	DRC/KED	NH3/He	20	1	51
5	ICP-MS	Sc	KED	He	1	1	51
6	ICP-MS	Sc	ORS	He			51
7	ICP-MS	Sc, Ir, Rh	ORS	He			51
8	ICP-MS	45	ORS	He	1	1	51
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	51

Table 77 Instrument Conditions Zn

Laboratory 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	ORS	He	NA	NA	68
2	ICP-MS	Y			10	NA	66
3	ICP-MS	Ir, Rh & Sc	ORS	He	1	1	64 (m/z)
4	ICP-MS	Te	KED	He	20	1	66
5	ICP-MS	Rh	KED	He	1	1	66
6	ICP-MS	Sc	ORS	He			66
7	ICP-MS	Sc, Ir, Rh	ORS	He			66
8	ICP-MS	115	ORS	He	1	1	66
10	ICP-MS	Rh	CRI	He	1	1	
12	ICP-MS	Rh					
13	ICP-MS	Rh	ORS	He	10	10	64

END OF REPORT