Australian Government
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National Measurement Institute

Proficiency Test Final Report AQA 21-18 Trace Elements in Sea Water

July 2022

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.

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1 SUMMARY

This report presents the results of the proficiency test AQA 21-18, Trace Elements in Sea Water. The study focused on the measurement of dissolved: Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Tl, U, V and Zn.

The assigned values were the robust averages of participants' results, with the exception of As, Fe, Hg, Ni, P, Pb, Se and Zn in S1 and of Hg, Ni and Se in S2. The associated uncertainties were estimated from the robust standard deviation of participants' results. The assigned values for As, Fe, P, Pb, and Zn in S1 were reference values measured using standard addition mass spectrometry. For Hg, Ni and Se in S1 and S2 the assigned values were the reference values measured using isotope dilution mass spectrometry (IDMS).

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

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

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

Of 263 scored results, 226 (86%) returned a satisfactory score of $|z| \leq 2.0$.

Of 263 scored results, 214 (81%) returned a satisfactory score of $|E_n| \leq 1.0$.

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

Measurement of low level elements in the sea water samples presented difficulty to participants. A limited number of laboratories reported results for some elements, and in other cases, the reported results were too variable for an assigned value to be set.

Low level Fe, Cr, P, Pb and Zn in S1 were the tests which presented the most analytical difficulty to participating laboratories.

Selenium challenged participants' analytical techniques regardless of its level in the test sample or the sample's salinity.

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

AQA 21-18 is the 11th NMI proficiency test of metals in sea water. Measurements of low level elements in sea water continues to challenge participants' analytical techniques.

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 284 numerical results, 274 (96%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 4.

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

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

A certified reference material for metals in sea water (MX014) with reference values traceable to SI is also available for sale from NMI.

2 INTRODUCTION

2.1 NMI Proficiency Testing Program

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

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

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

AQA 21-18 is the 29th NMI proficiency study of metals in water.

2.2 Study Aims

The aims of the study were to:

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

2.3 Study Conduct

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

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

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

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The 38 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.

3.2 Participation

Eleven laboratories participated and ten submitted results.

The timetable of the study was:

Invitation issued:	8 November 2021
Samples dispatched:	29 November 2021
Results due:	24 January 2022
Interim report issued:	24 January 2022

The final report of this study was delayed in order to incorporate reference values for 11 analytes to support laboratories to assess and develop their methods for measurement of low level analytes in saline matrices.

3.3 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 low salinity sea water preserved by adding 2% (v/w) nitric acid and 0.01% (v/w) hydrochloric acid.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 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 Li and Sn in S1, nor for Al in S2.

Homogeneity values of As, Fe, Hg, Ni, P, Pb, Se and Zn in S1 and of Hg, Ni and Se in S2 were the reference value

The preparation and analysis are described in Appendices 1 and 3.

3.6 Stability of Analytes

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

3.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were refrigerated before dispatch.

The samples were dispatched by courier on 29 November 2021.

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

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

3.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.

- Participants are asked to report results in units of µg/L for:

SAMPLE S1 low level sea water		SAMPLE S2 low salinity sea water	
Test DISSOLVED	**Approximate Conc. Range µg/L**	**Test DISSOLVED**	**Approximate Conc. Range µg/L**
Ag	<5	Al	<50
As	<5	As	<10
Be	<5	B	<5000
Cd	<5	Ba	<50
Cr	<5	Cd	<10
Cu	<5	Co	<10
Fe	<25	Cr	<10
Hg	<5	Fe	<50
Li	NA	Cu	<50
Mn	<5	Hg	<10
Ni	<5	Mn	<10
P	<150	Mo	<10
Pb	<5	Ni	<10
Se	<5	Pb	<10
Sn	<5	Sb	<10
Tl	<5	Se	<10
U	<5	Sn	<10
V	<5	V	<10
Zn	<5	Zn	<50

NA = Not Available

- 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.

3.9 Interim Report

An interim report was emailed to participants on 24 January 2022.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for Total and Dissolved Elements

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

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Volume (mL)	Temp. (°C)	Time (min)	HNO_3 (mL)	HCl (mL)	HNO_3 (1:1) (mL)	.HCl (1:1) (mL)	H_2O_2 (mL)
2	APHA3120B								
4	APHA 3125 B								
5		50	100	120	1				
6*	Samples analysed as received (no digestion).								
7	USEPA 200.7 and 200.8								
9*	USEPA 200.8 & 245, APHA 3125								
10	In House W32a – referencing APHA 3125								
11*	Standard Methods for the Examination and Testing of Water and Waste Water, APHA, Edn 23	10	170	20	0.75	0.375			

*Additional Information in Table 2.

4.2 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
6	Methodology: Samples diluted in 2% v/v nitric acid/0.5%. Instrumental Techniques: Samples diluted offline. A further 2X dilution was done via the internal standard which was added inline 50/50 (sample/internal std.). Calibration via Standard Additions.
9	Methodology: Not digested.
11	Sample S1: Uncertainty Derived from validation spreadsheet at appropriate level. Sample S2: Uncertainty derived from validation spreadsheet. Methodology: Samples are digested and then made up to a prep volume and diluted. Total dilution on samples in x15.

4.3 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis		
2	Professional judgement	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
5	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration	ISO/GUM
6	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis	CRM Recoveries of SS	ISO/GUM
7	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	Instrument Calibration	Nordtest Report TR537
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - SS Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537
11	Uncertainty derived from validation spreadsheet where % uncertainty is calculated at various concentrations. Uncertainty selected closest to that of sample concentration per analyte.	Control Samples	CRM Instrument Calibration	

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

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

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

There were no participants' comments reported in this study.

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 4 to 49 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 47. An example chart with an interpretation guide is shown in Figure 1.

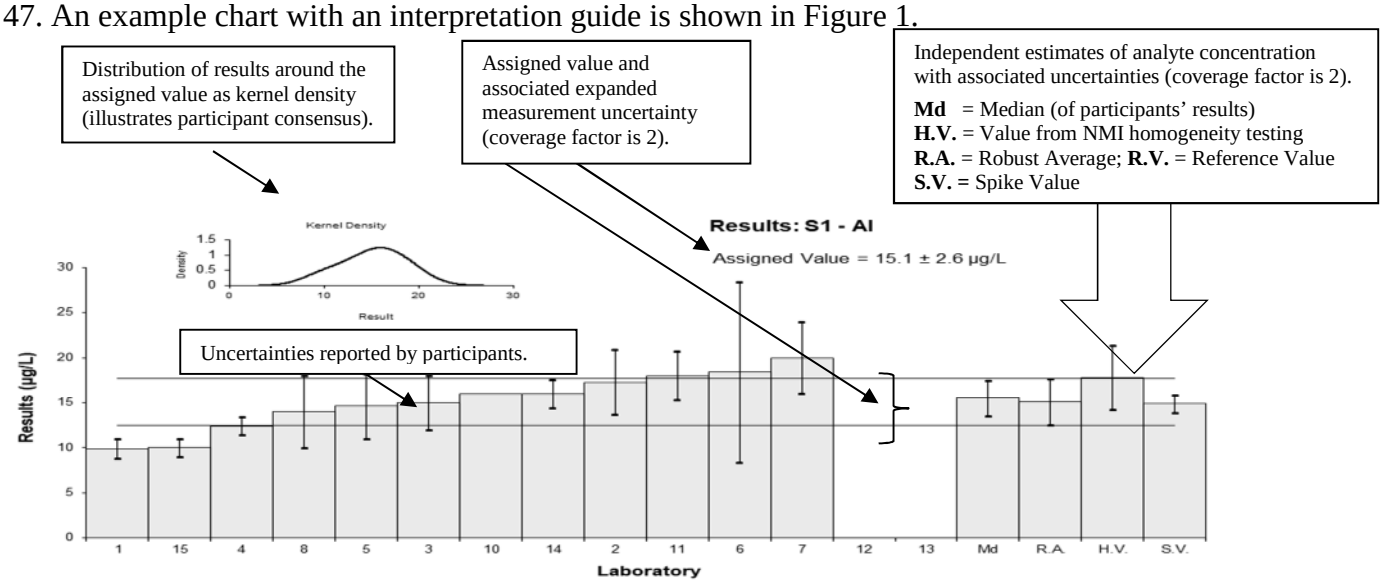


Figure 1 Guide to Presentation of Results

5.2 Outliers and Extreme Outliers

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

5.3 Assigned Value

The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'[1] In this study, the property is the mass concentration of analyte. For As, Fe, P, Pb, and Zn in S1, the assigned values were reference values measured using standard addition mass spectrometry. For Hg, Ni and Se in S1 and S2, the assigned values were reference values measured using isotope dilution mass spectrometry. For all other analytes the assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.[4, 6] An example of an assigned value calculation using data from the present study is given in Appendix 2.

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

5.5 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.

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

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

5.6 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:

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

where:

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

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

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

5.7 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:

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

5.8 Traceability and Measurement Uncertainty

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

6 TABLES AND FIGURES

Table 4

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Ag
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty
1	0.76	0.11
2	0.46	0.1
4	0.7	NR
5	NT	NT
6	0.79	0.045
7	NT	NT
8	<1	NR
9	0.6	0.3
10	<1	NR
11	NT	NT

Statistics

Assigned Value	Not Set	
Spike	0.77	0.02
Homogeneity Value	0.73	0.11
Median	0.70	0.17
Mean	0.66	
N	5	
Max.	0.79	
Min.	0.46	

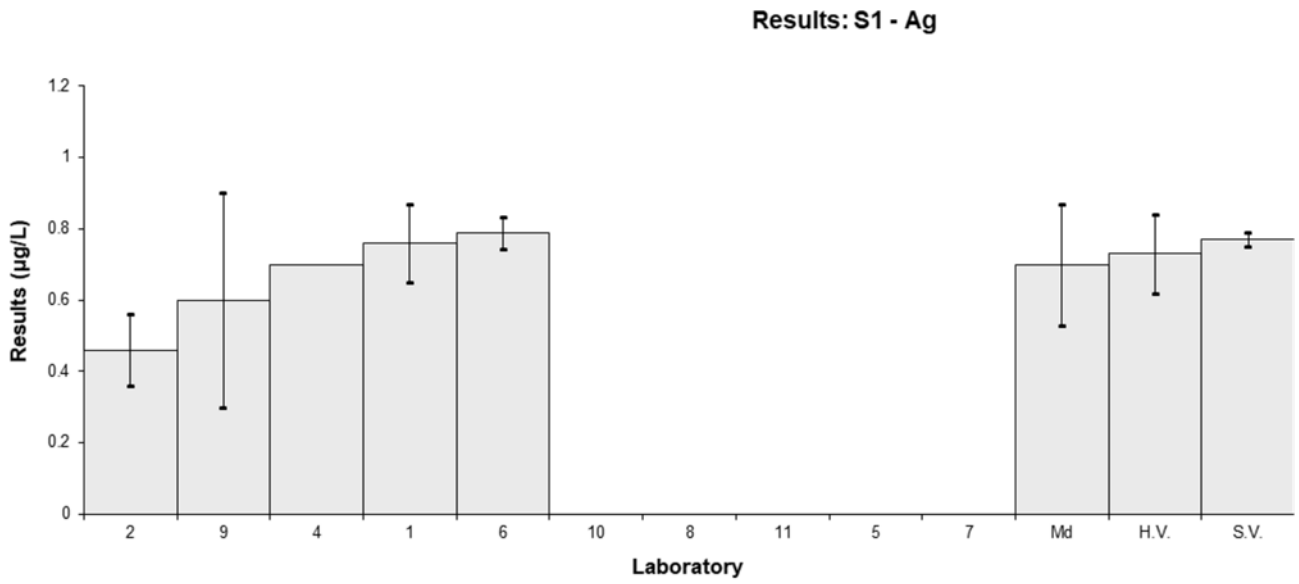

Results: S1 - Ag
Results (µg/L)
1.2
1
0.8
0.6
0.4
0.2
0
2
9
4
1
6
10
8
11
5
7
Md
H.V.
S.V.
Laboratory

Figure 2

Table 5

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	As
Units	µg/L

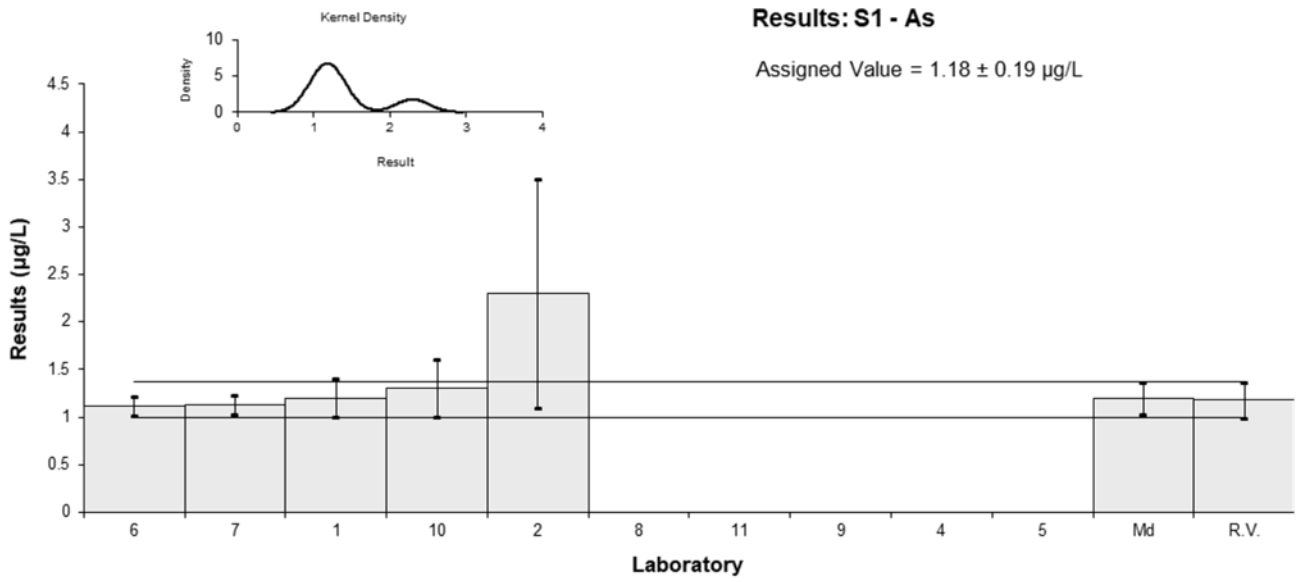
Participant Results

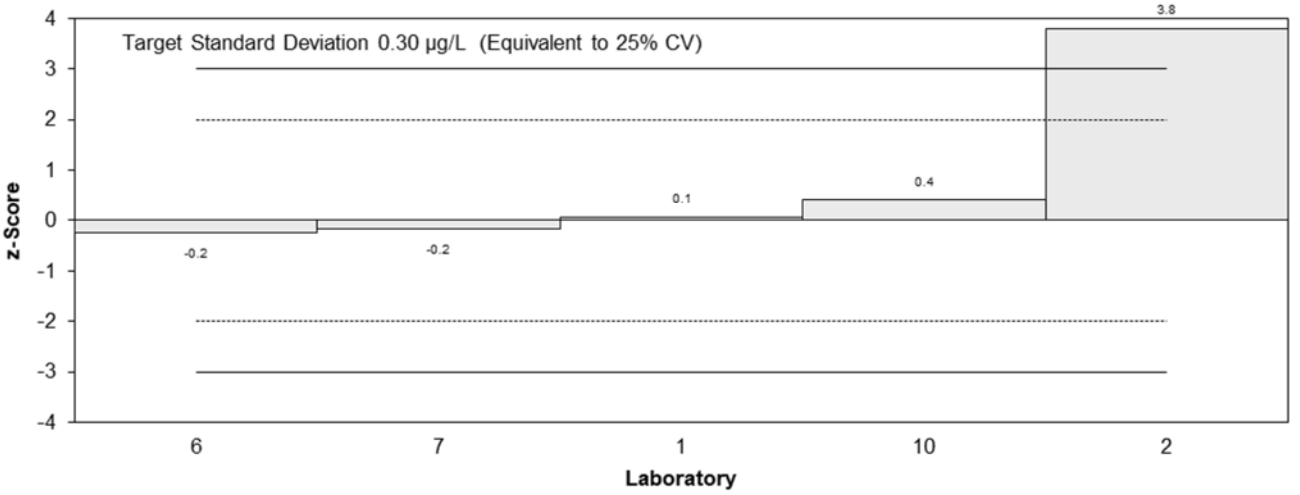
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.20	0.20	0.07	0.07
2	2.3	1.2	3.80	0.92
4	<4	2.7		
5	NT	NT		
6	1.11	0.10	-0.24	-0.33
7	1.13	0.1	-0.17	-0.23
8	<1	NR		
9	<3	NR		
10	1.3	0.3	0.41	0.34
11	<1.5	NR		

Statistics

Assigned Value*	1.18	0.19
Spike	Not Spiked	
Reference Value*	1.18	0.19
Median	1.20	0.17
Mean	1.41	
N	5	
Max.	2.3	
Min.	1.11	

*Reference Value by SA-ICP-MS


Kernel Density
Density
Result
Results: S1 - As
Assigned Value = 1.18 ± 0.19 µg/L
Results (µg/L)
Laboratory
6
7
1
10
2
8
11
9
4
5
Md
R.V.


z-Scores: S1 - As
Target Standard Deviation 0.30 µg/L (Equivalent to 25% CV)
z-Score
Laboratory
-0.2
-0.2
0.1
0.4
3.8
6
7
1
10
2

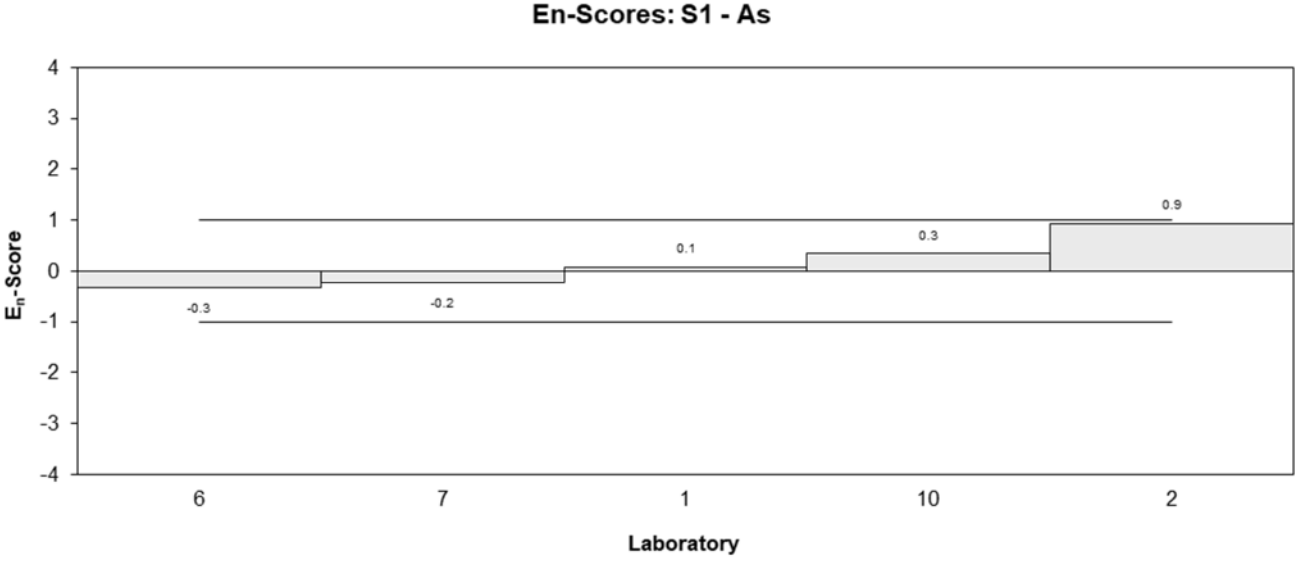

En-Scores: S1 - As
En-Score
Laboratory
-0.3
-0.2
0.1
0.3
0.9
6
7
1
10
2

Figure 3

Table 6

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Be
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty
1	<1	NR
2	0.66	1
4	NT	NT
5	NT	NT
6	0.69	0.083
7	0.615	0.030
8	<1	NR
9	0.5	0.5
10	0.76	0.2
11	NT	NT

Statistics

Assigned Value	Not Set	
Spike	0.63	0.02
Homogeneity Value	0.68	0.10
Median	0.660	0.083
Mean	0.645	
N	5	
Max.	0.76	
Min.	0.5	

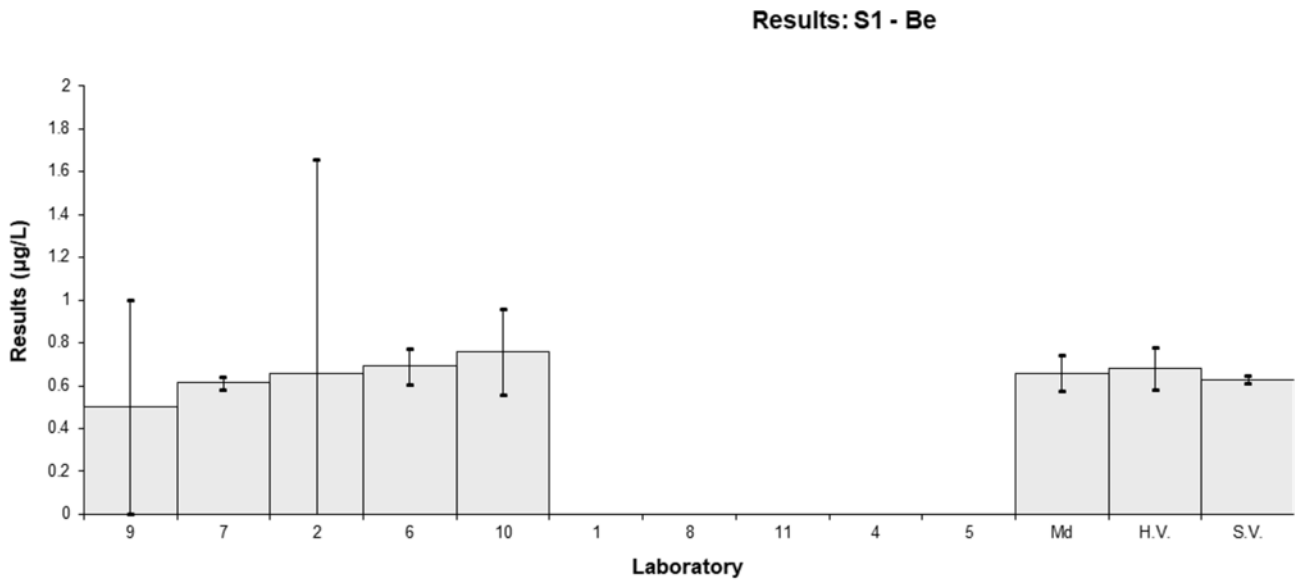

Results: S1 - Be
Results (µg/L)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
9
7
2
6
10
1
8
11
4
5
Md
H.V.
S.V.
Laboratory

Figure 4

Table 7

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Cd
Units	µg/L

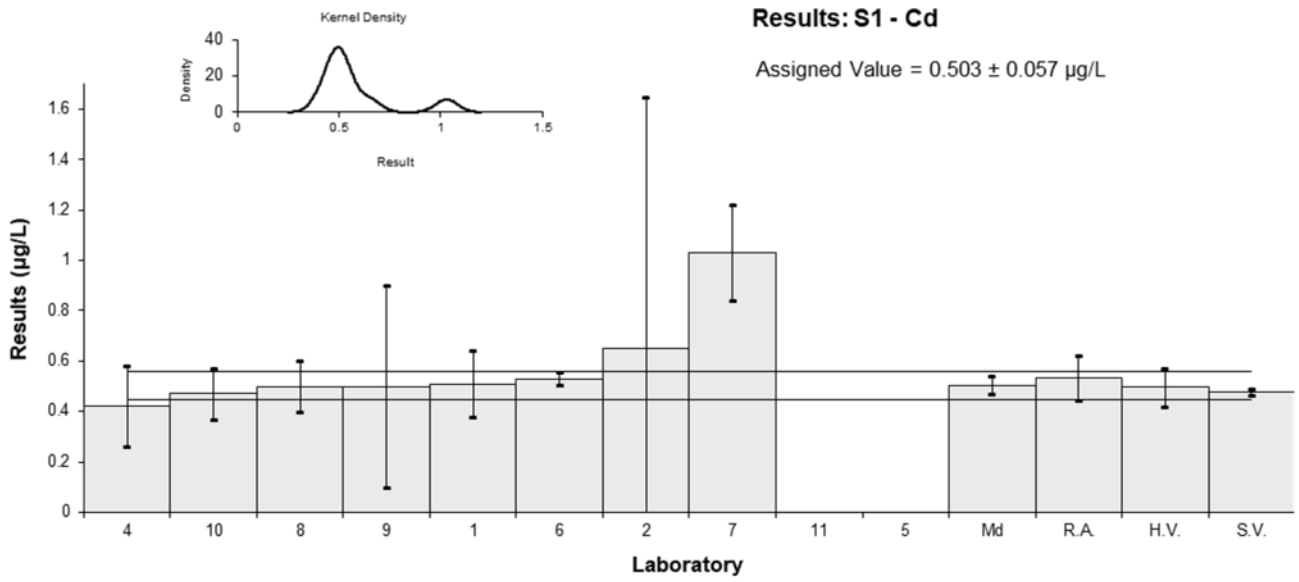
Participant Results

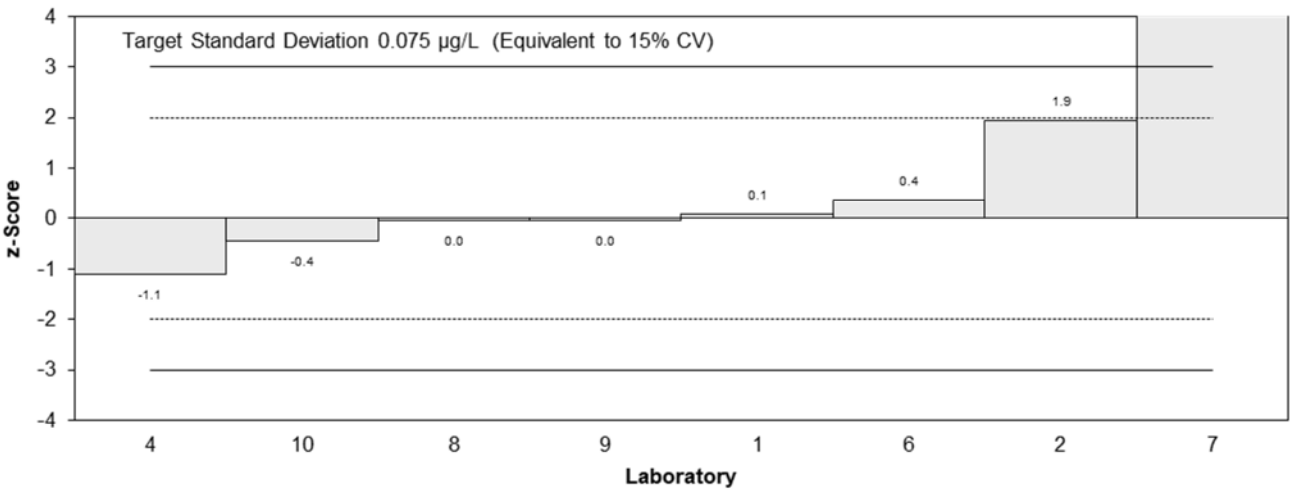
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.51	0.13	0.09	0.05
2	0.65	1	1.95	0.15
4	0.42	0.16	-1.10	-0.49
5	NT	NT		
6	0.53	0.026	0.36	0.43
7	1.03	0.19	6.98	2.66
8	0.50	0.10	-0.04	-0.03
9	0.5	0.4	-0.04	-0.01
10	0.47	0.1	-0.44	-0.29
11	<1.5	NR		

Statistics

Assigned Value*	0.503	0.057
Spike	0.477	0.014
Homogeneity Value	0.495	0.074
Robust Average	0.533	0.090
Median	0.505	0.037
Mean	0.576	
N	8	
Max.	1.03	
Min.	0.42	
Robust SD	0.1	
Robust CV	19%	

*Robust Average excluding laboratory 7.


Kernel Density
Density
Result
Results: S1 - Cd
Assigned Value = 0.503 ± 0.057 µg/L
Results (µg/L)
Laboratory
4
10
8
9
1
6
2
7
11
5
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Cd
Target Standard Deviation 0.075 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.1
-0.4
0.0
0.0
0.1
0.4
1.9

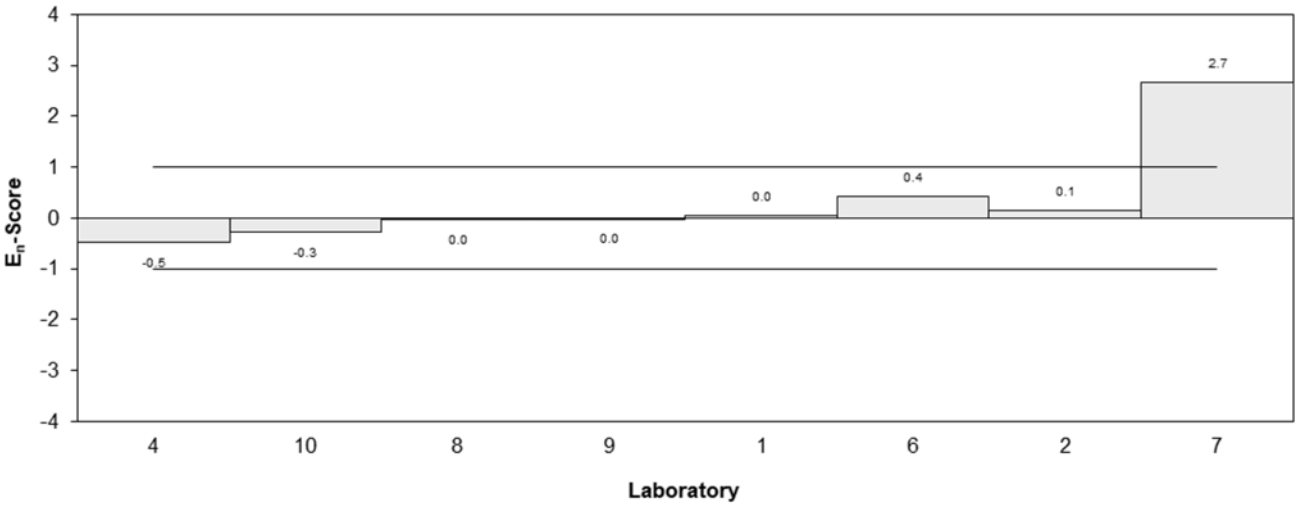

En-Scores: S1 - Cd
En-Score
Laboratory
-0.5
-0.3
0.0
0.0
0.0
0.4
0.1
2.7

Figure 5

Table 8

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Cr
Units	µg/L

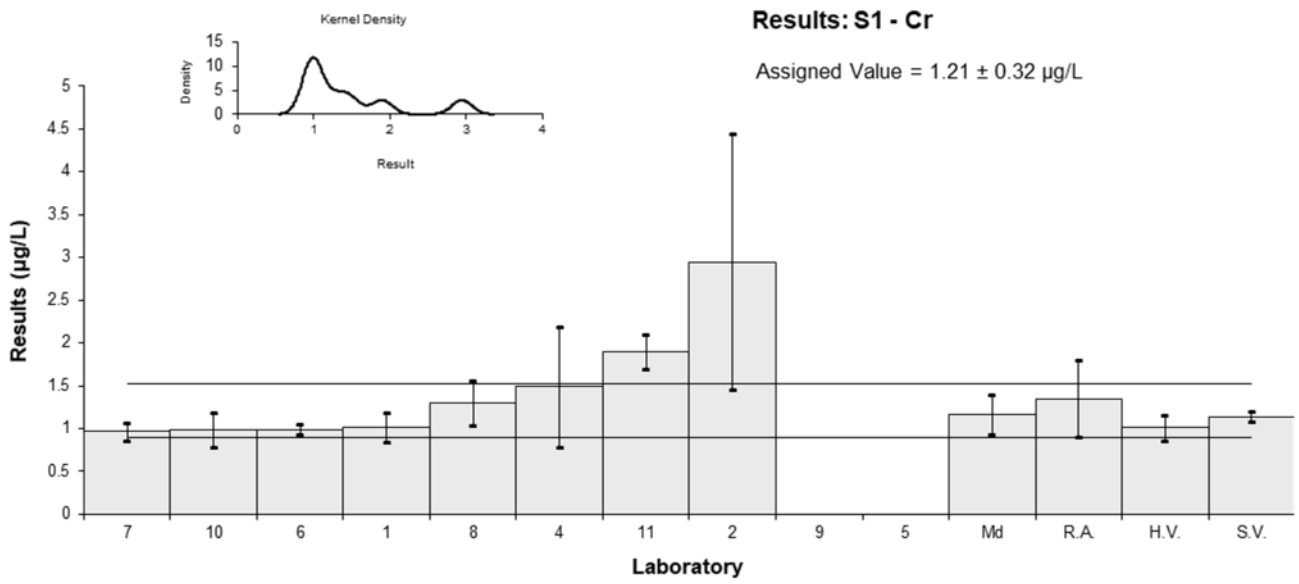
Participant Results

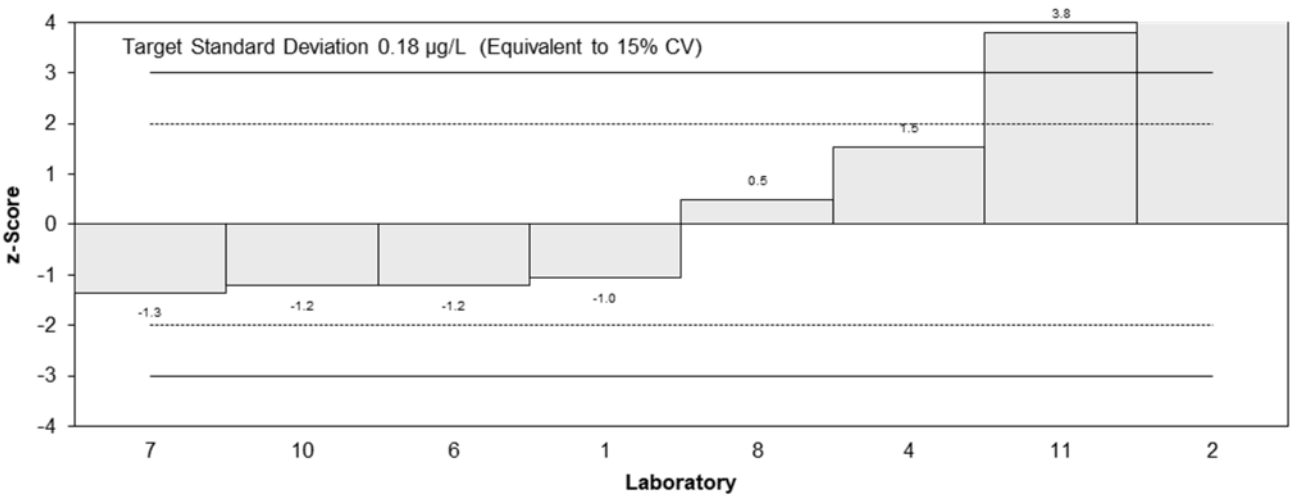
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.02	0.17	-1.05	-0.52
2	2.95	1.5	9.59	1.13
4	1.49	0.70	1.54	0.36
5	NT	NT		
6	0.99	0.055	-1.21	-0.68
7	0.965	0.10	-1.35	-0.73
8	1.3	0.26	0.50	0.22
9	<1	NR		
10	0.99	0.2	-1.21	-0.58
11	1.9	0.2	3.80	1.83

Statistics

Assigned Value*	1.21	0.32
Spike	1.14	0.06
Homogeneity Value	1.01	0.15
Robust Average	1.35	0.45
Median	1.16	0.23
Mean	1.45	
N	8	
Max.	2.95	
Min.	0.965	
Robust SD	0.51	
Robust CV	38%	

*Robust Average excluding laboratory 2.


Kernel Density
Density
Result
Results: S1 - Cr
Assigned Value = 1.21 ± 0.32 µg/L
Results (µg/L)
Laboratory
7
10
6
1
8
4
11
2
9
5
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Cr
Target Standard Deviation 0.18 µg/L (Equivalent to 15% CV)
z-Score
-1.3
-1.2
-1.2
-1.0
0.5
1.5
3.8
Laboratory
7
10
6
1
8
4
11
2

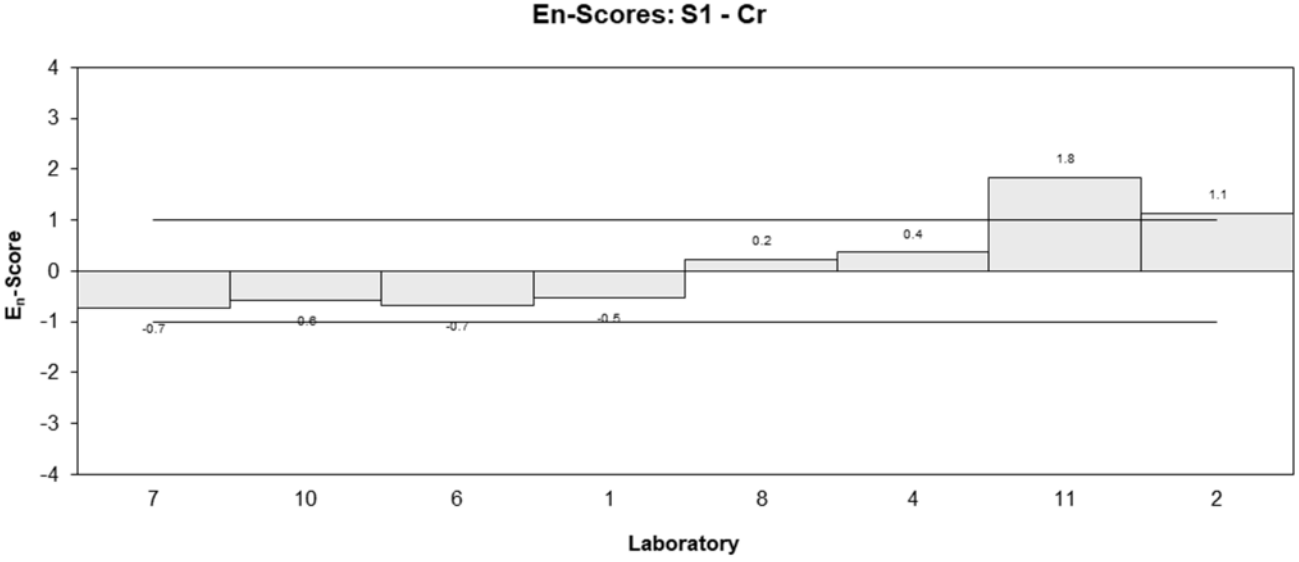

En-Scores: S1 - Cr
En-Score
-0.7
-0.6
-0.7
-0.5
0.2
0.4
1.8
1.1
Laboratory
7
10
6
1
8
4
11
2

Figure 6

Table 9

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Cu
Units	µg/L

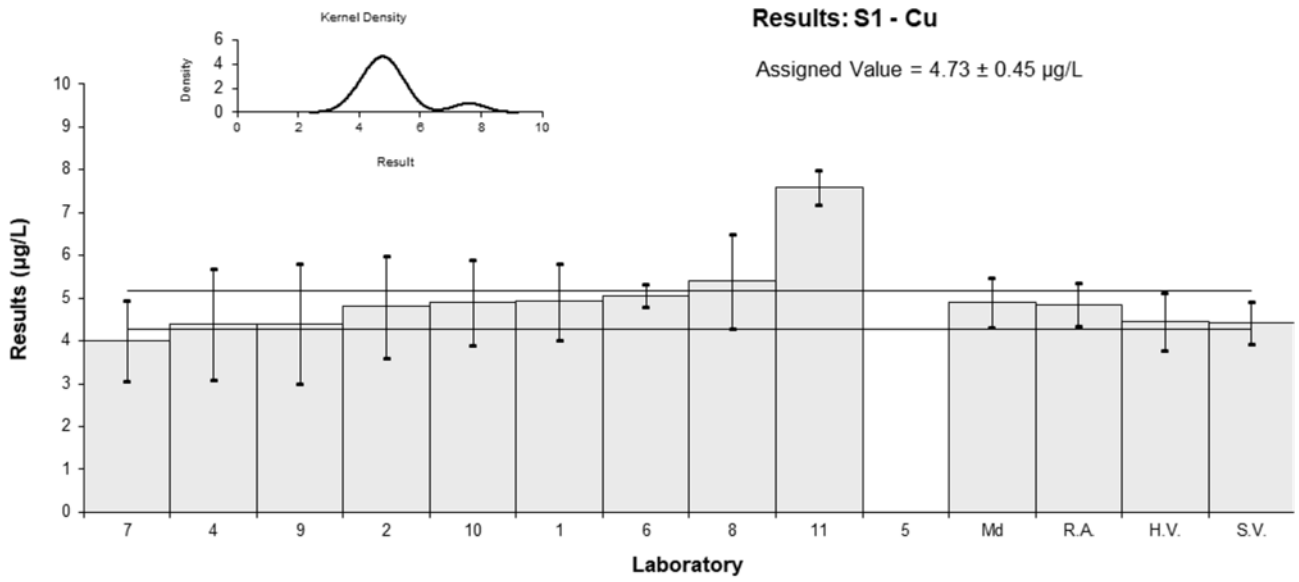
Participant Results

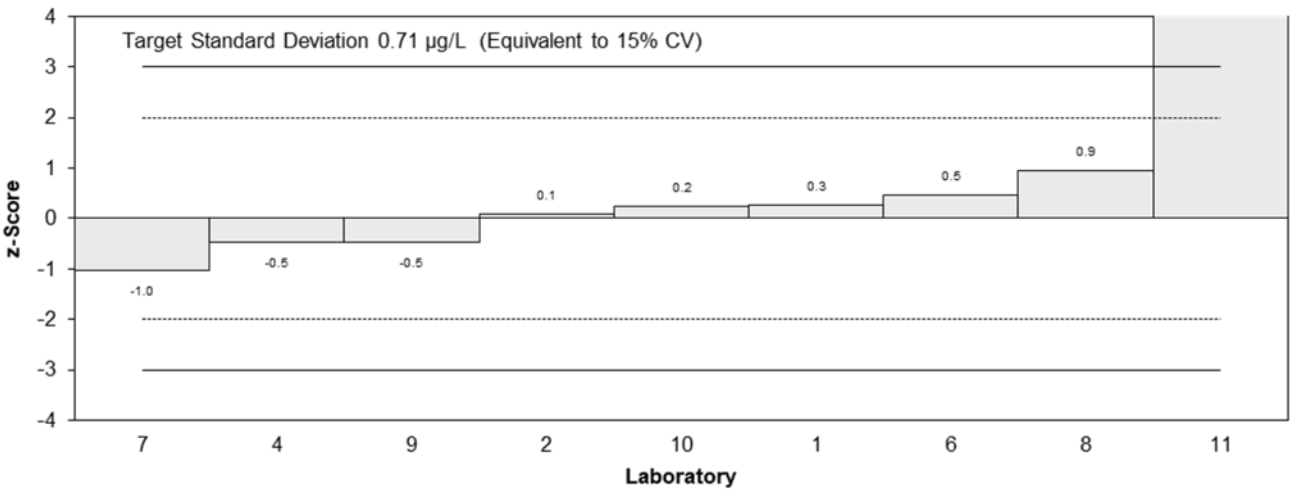
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.92	0.89	0.27	0.19
2	4.8	1.2	0.10	0.05
4	4.4	1.3	-0.47	-0.24
5	NT	NT		
6	5.06	0.26	0.47	0.63
7	3.99	0.94	-1.04	-0.71
8	5.4	1.1	0.94	0.56
9	4.4	1.4	-0.47	-0.22
10	4.9	1.0	0.24	0.16
11	7.6	0.4	4.05	4.77

Statistics

Assigned Value*	4.73	0.45
Spike	4.42	0.50
Homogeneity Value	4.46	0.67
Robust Average	4.85	0.51
Median	4.90	0.57
Mean	5.05	
N	9	
Max.	7.6	
Min.	3.99	
Robust SD	0.61	
Robust CV	13%	

*Robust Average excluding laboratory 11.


Kernel Density
Density
Result
Results: S1 - Cu
Assigned Value = 4.73 ± 0.45 µg/L
Results (µg/L)
7 4 9 2 10 1 6 8 11 5 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Cu
Target Standard Deviation 0.71 µg/L (Equivalent to 15% CV)
z-Score
-1.0 -0.5 -0.5 0.1 0.2 0.3 0.5 0.9
7 4 9 2 10 1 6 8 11
Laboratory

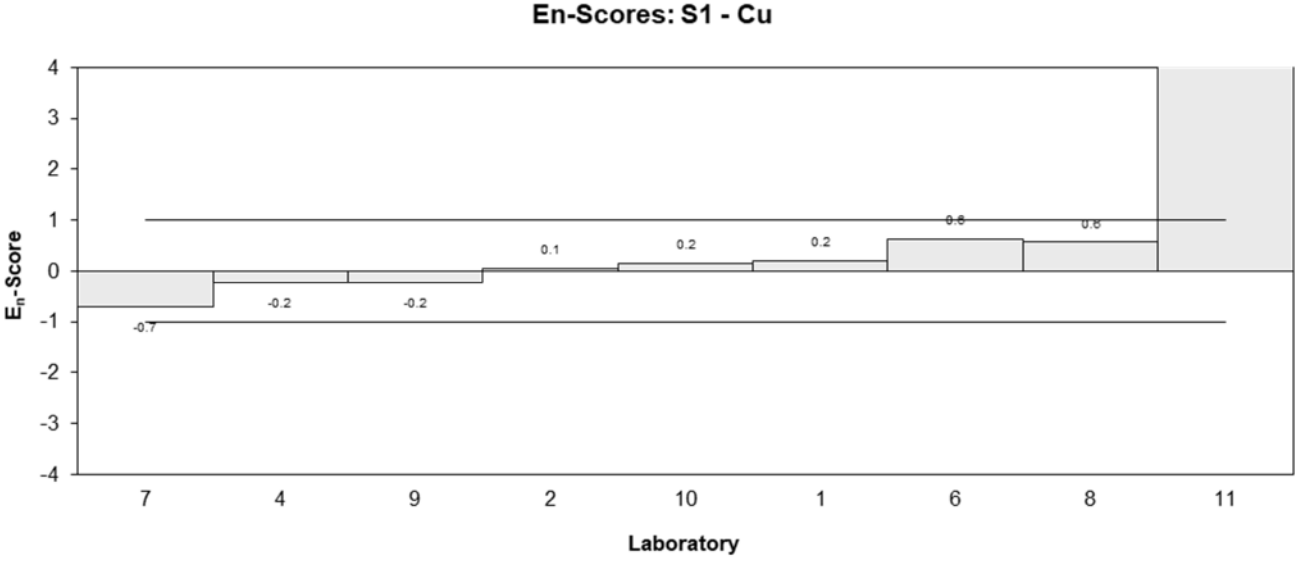

En-Scores: S1 - Cu
En-Score
-0.7 -0.2 -0.2 0.1 0.2 0.2 0.6 0.6
7 4 9 2 10 1 6 8 11
Laboratory

Figure 7

Table 10

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	Fe
Units	µg/L

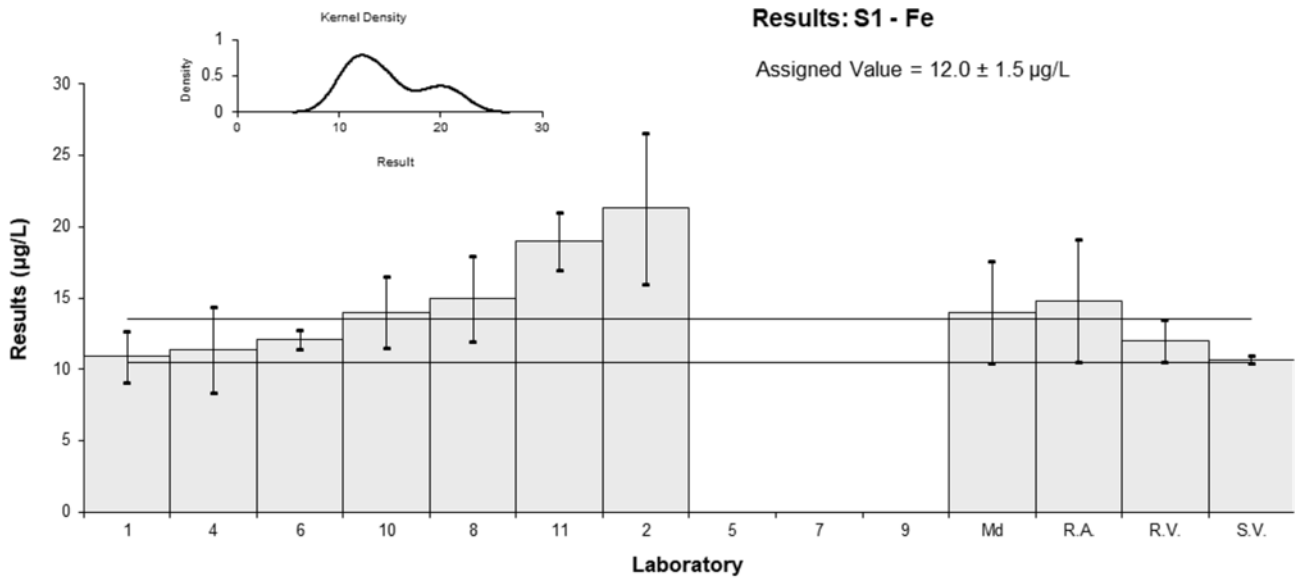
Participant Results

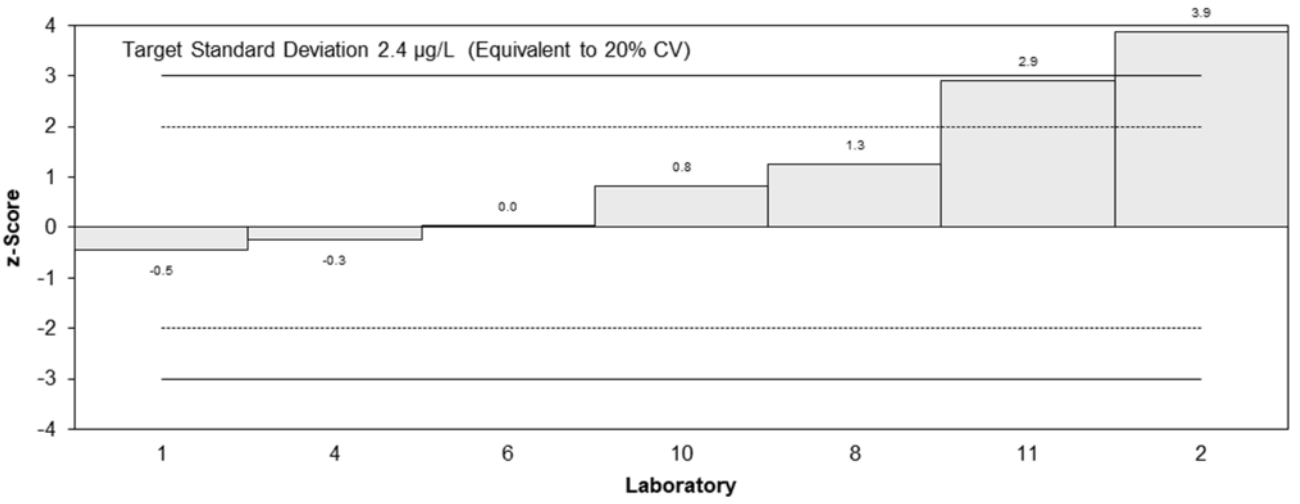
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	10.9	1.8	-0.46	-0.47
2	21.3	5.3	3.87	1.69
4	11.4	3.0	-0.25	-0.18
5	NT	NT		
6	12.1	0.65	0.04	0.06
7	NT	NT		
8	15	3	1.25	0.89
9	NT	NT		
10	14	2.5	0.83	0.69
11	19	2	2.92	2.80

Statistics

Assigned Value*	12.0	1.5
Spike	10.7	0.3
Reference Value*	12.0	1.5
Robust Average	14.8	4.3
Median	14.0	3.6
Mean	14.8	
N	7	
Max.	21.3	
Min.	10.9	
Robust SD	4.5	
Robust CV	30%	

*Reference Value by SA-ICP-MS


Kernel Density
Density
Result
Results: S1 - Fe
Assigned Value = 12.0 ± 1.5 µg/L
Results (µg/L)
Laboratory
1
4
6
10
8
11
2
5
7
9
Md
R.A.
R.V.
S.V.


z-Scores: S1 - Fe
Target Standard Deviation 2.4 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-0.5
-0.3
0.0
0.8
1.3
2.9
3.9

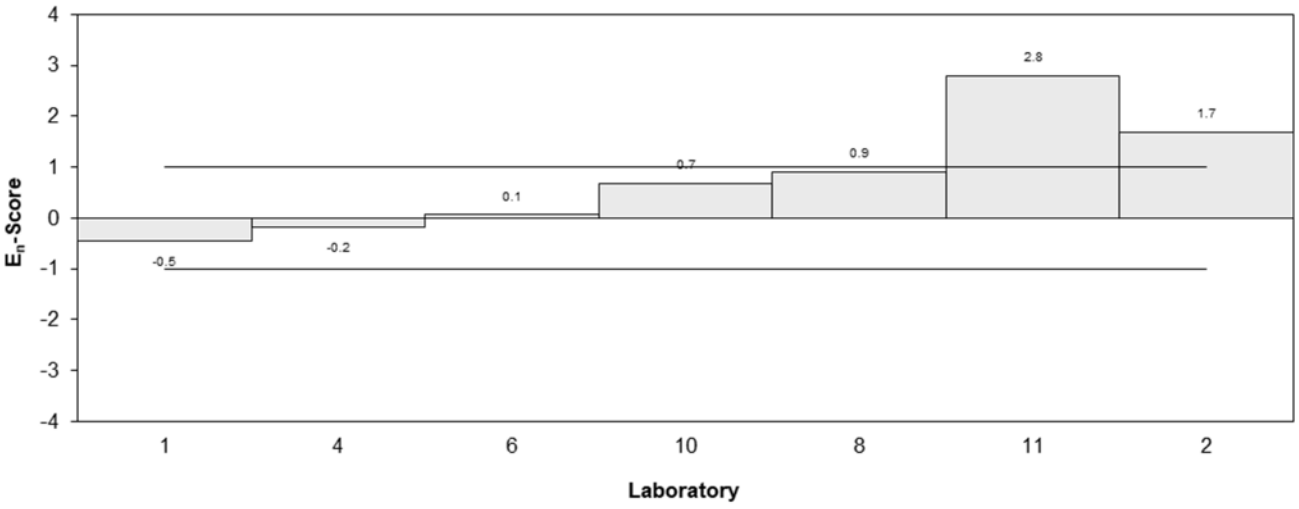

En-Scores: S1 - Fe
En-Score
Laboratory
-0.5
-0.2
0.1
0.7
0.9
2.8
1.7

Figure 8

Table 11

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	Hg
Units	µg/L

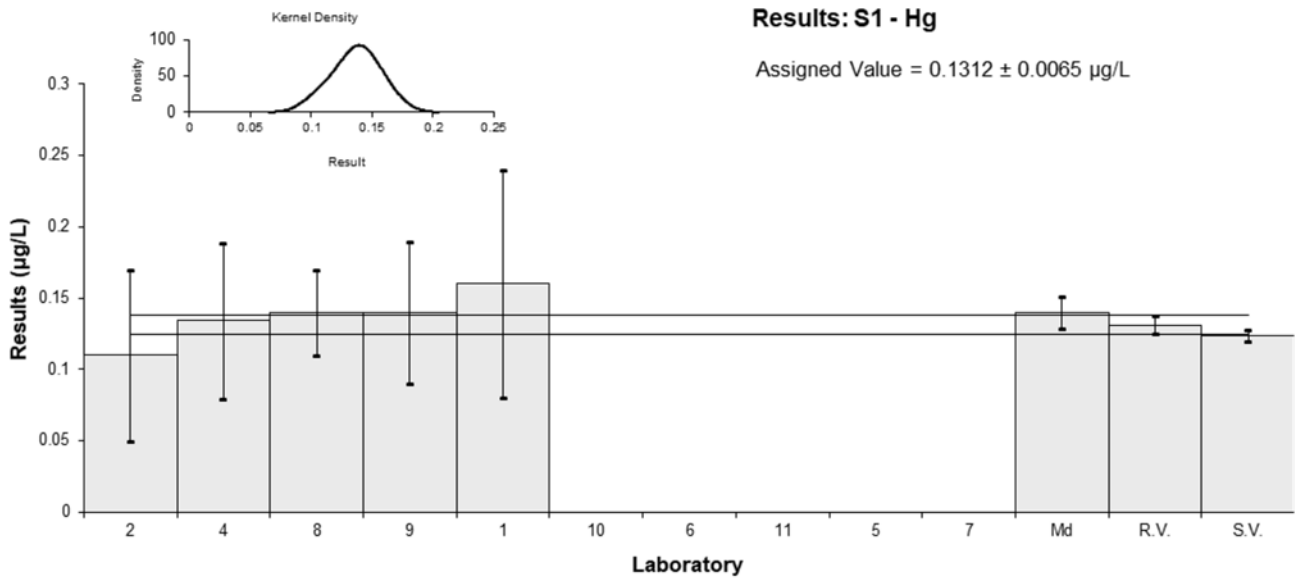
Participant Results

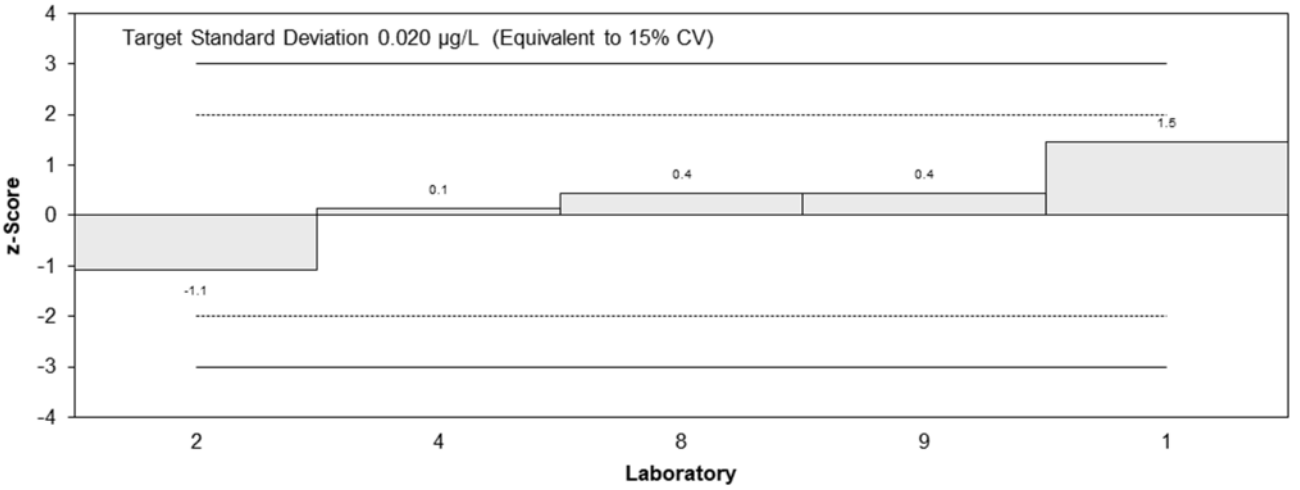
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.16	0.080	1.46	0.36
2	0.11	0.06	-1.08	-0.35
4	0.134	0.055	0.14	0.05
5	NT	NT		
6	NR	NR		
7	NT	NT		
8	0.14	0.03	0.45	0.29
9	0.14	0.05	0.45	0.17
10	<0.5	NR		
11	NT	NT		

Statistics

Assigned Value*	0.131	0.007
Spike	0.124	0.004
Reference Value*	0.1312	0.0065
Median	0.140	0.011
Mean	0.137	
N	5	
Max.	0.16	
Min.	0.11	

*Reference Value by dIDMS


Kernel Density
Density
Result
Results: S1 - Hg
Assigned Value = 0.1312 ± 0.0065 µg/L
Results (µg/L)
Laboratory
2
4
8
9
1
10
6
11
5
7
Md
R.V.
S.V.


z-Scores: S1 - Hg
Target Standard Deviation 0.020 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.1
0.1
0.4
0.4
1.5
2
4
8
9
1

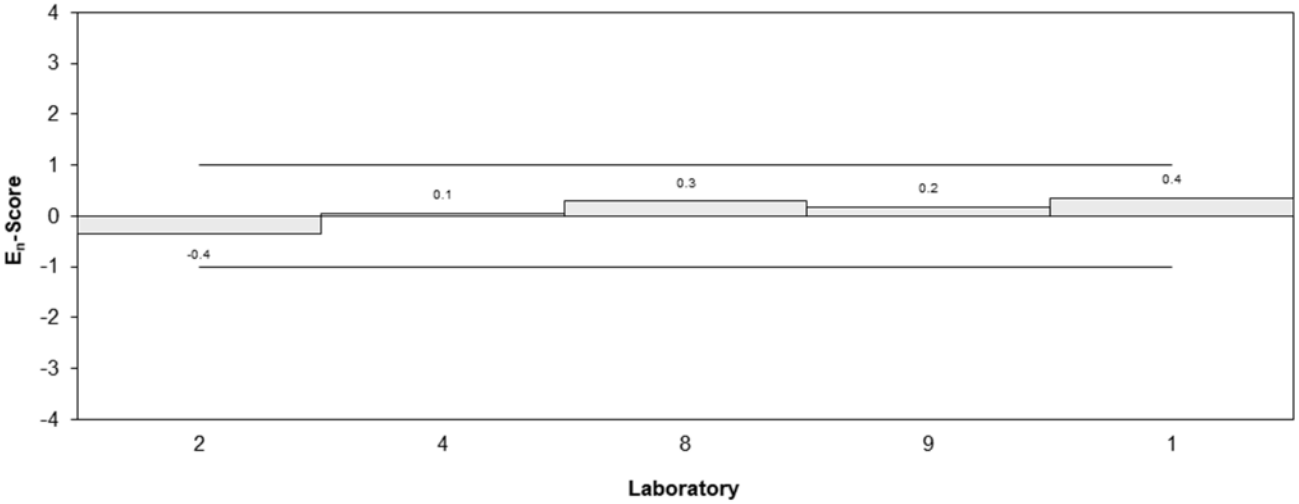

En-Scores: S1 - Hg
En-Score
Laboratory
-0.4
0.1
0.3
0.2
0.4
2
4
8
9
1

Figure 9

Table 12

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Li
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty
1	160	50
2	NT	NT
4	165	NR
5	NT	NT
6	175	5.2
7	0.192	0.039
8	170	34
9	NT	NT
10	175	25
11	NT	NT

Statistics*

Assigned Value	Not Set	
Spike	Not Spiked	
Median	170	9
Mean	169	
N	5	
Max.	175	
Min.	160	

*Laboratory 7 was excluded from statistical calculation (extreme outlier).

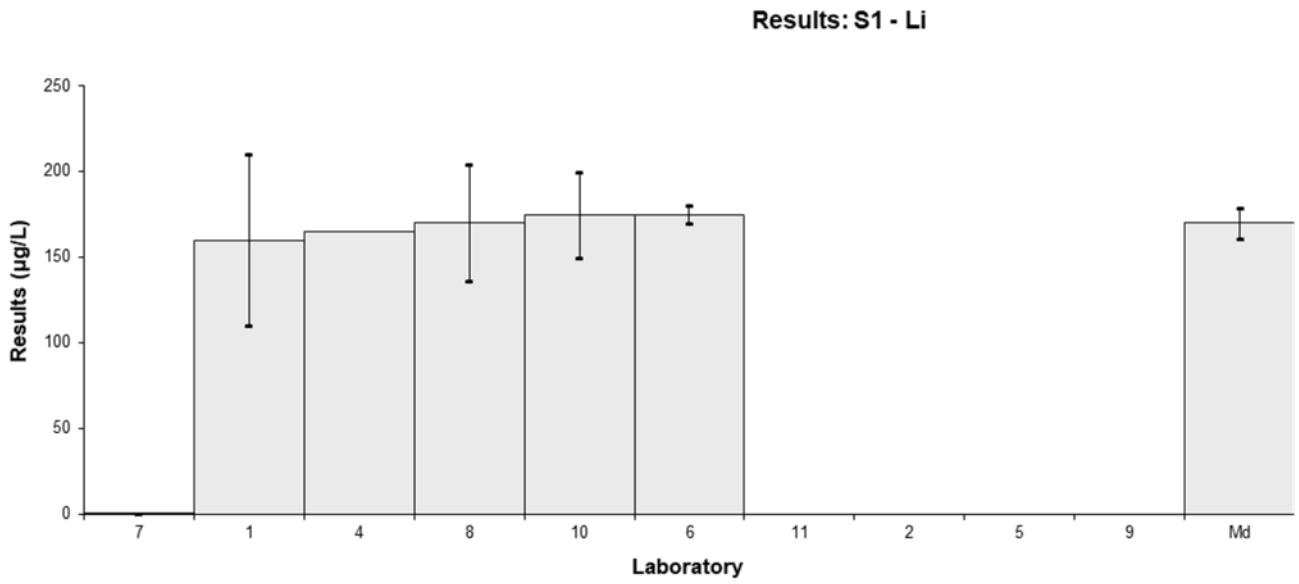

Results: S1 - Li
Results (µg/L)
250
200
150
100
50
0
7
1
4
8
10
6
11
2
5
9
Md
Laboratory

Figure 10

Table 13

Sample Details

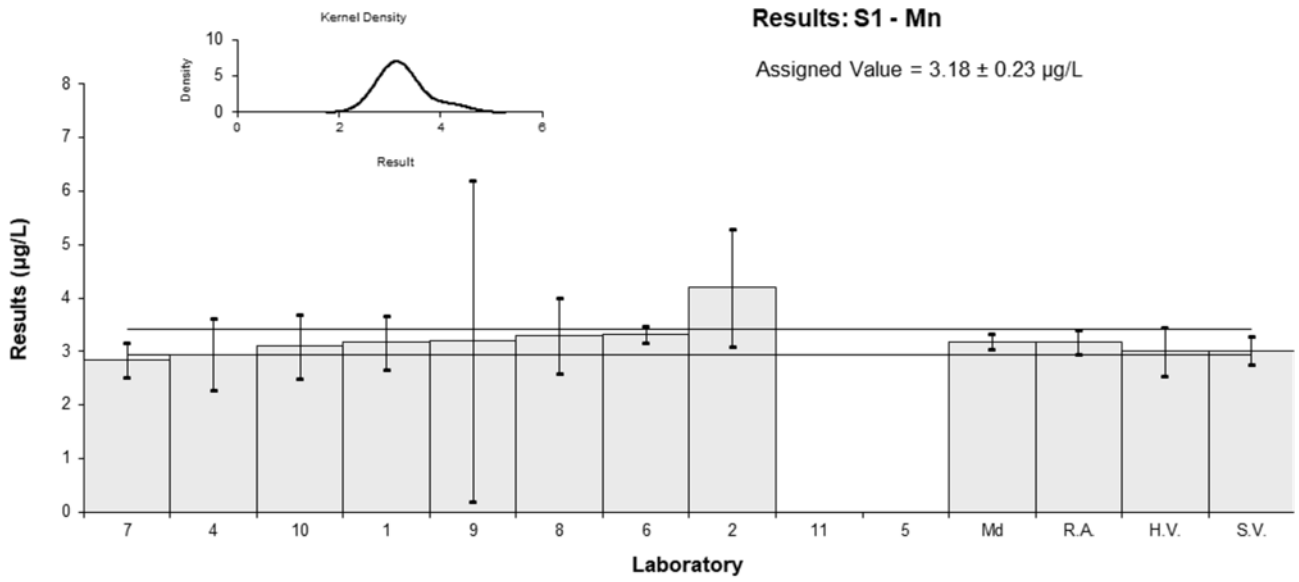
Sample No.	S1
Matrix.	Sea water
Analyte.	Mn
Units	µg/L

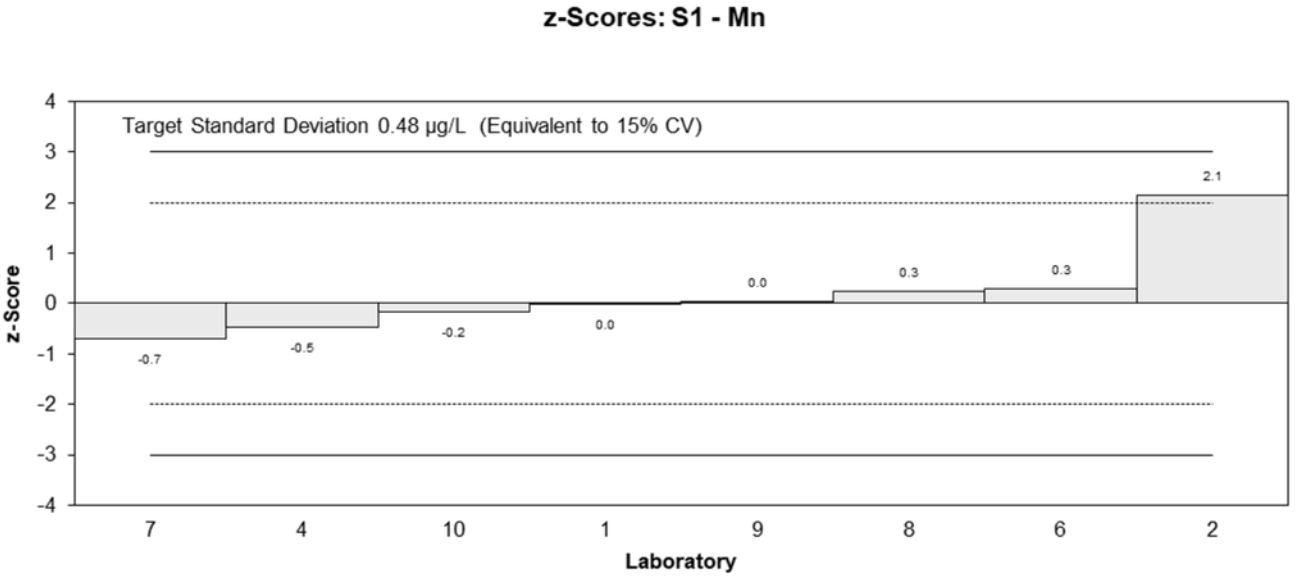
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.17	0.51	-0.02	-0.02
2	4.2	1.1	2.14	0.91
4	2.95	0.68	-0.48	-0.32
5	NT	NT		
6	3.32	0.15	0.29	0.51
7	2.84	0.33	-0.71	-0.85
8	3.3	0.7	0.25	0.16
9	3.2	3.0	0.04	0.01
10	3.1	0.6	-0.17	-0.12
11	NT	NT		

Statistics

Assigned Value	3.18	0.23
Spike	3.02	0.26
Homogeneity Value	3.00	0.45
Robust Average	3.18	0.23
Median	3.19	0.15
Mean	3.26	
N	8	
Max.	4.2	
Min.	2.84	
Robust SD	0.26	
Robust CV	8.1%	


Results: S1 - Mn
Assigned Value = 3.18 ± 0.23 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
4
10
1
9
8
6
2
11
5
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Mn
Target Standard Deviation 0.48 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.7
-0.5
-0.2
0.0
0.0
0.3
0.3
2.1

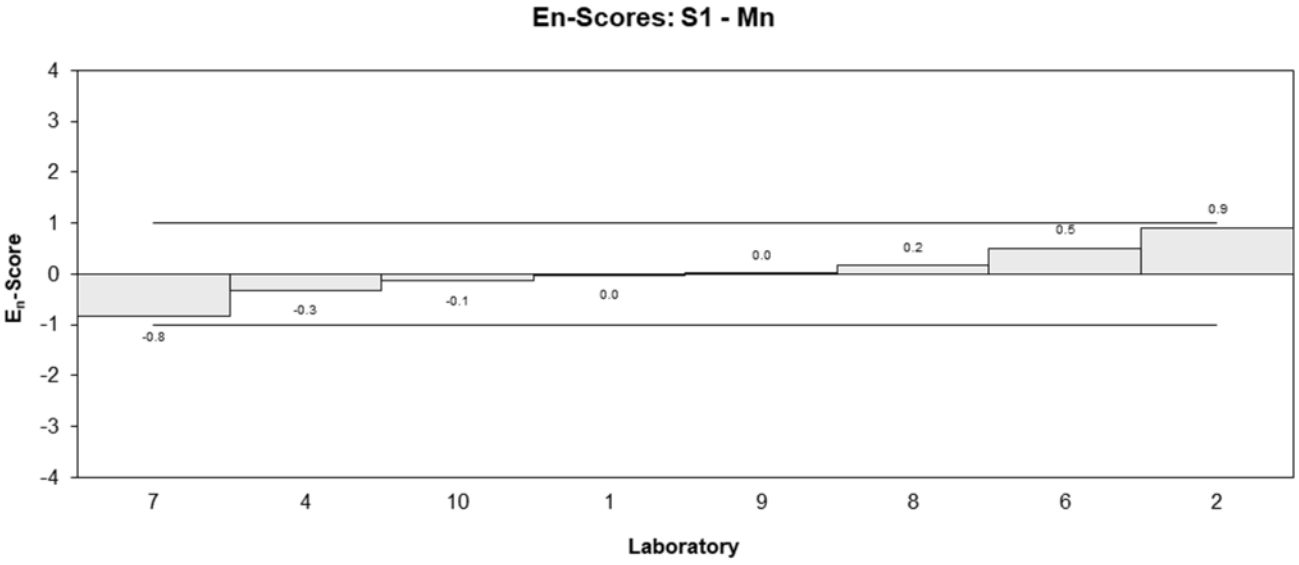

En-Scores: S1 - Mn
En-Score
Laboratory
-0.8
-0.3
-0.1
0.0
0.0
0.2
0.5
0.9

Figure 11

Table 14

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	Ni
Units	µg/L

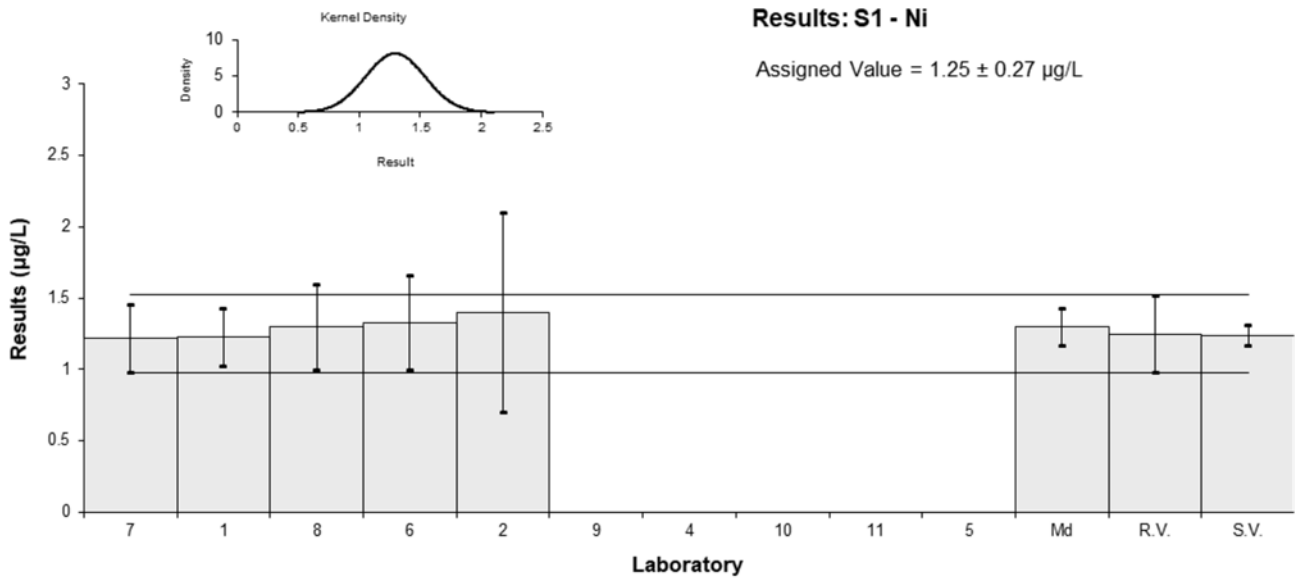
Participant Results

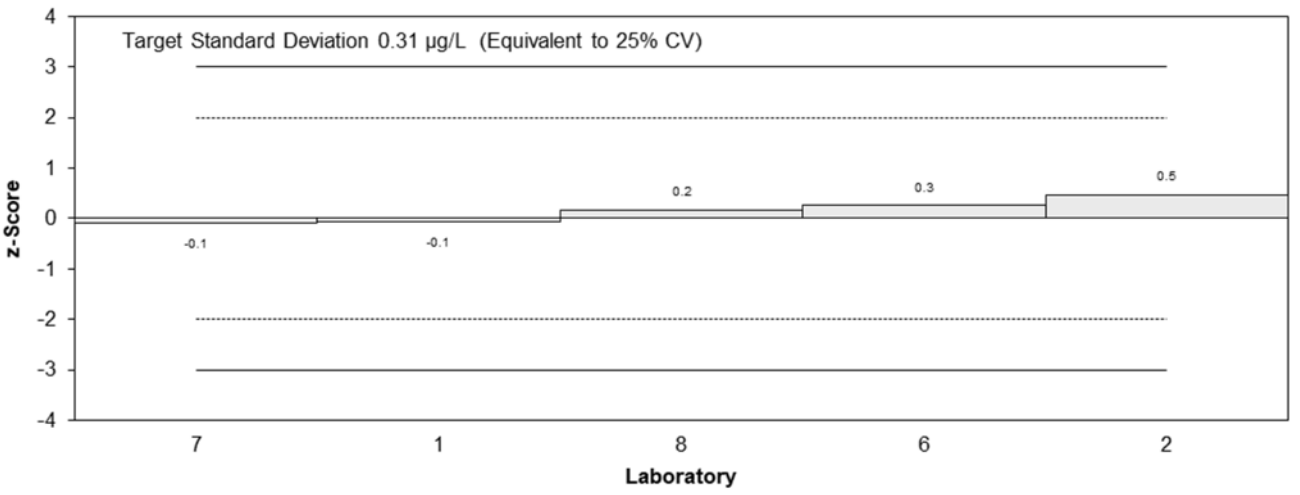
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.23	0.20	-0.06	-0.06
2	1.4	0.7	0.48	0.20
4	<7	NR		
5	NT	NT		
6	1.33	0.33	0.26	0.19
7	1.22	0.24	-0.10	-0.08
8	1.3	0.3	0.16	0.12
9	<1	NR		
10	NT	NT		
11	NT	NT		

Statistics

Assigned Value*	1.25	0.27
Spike	1.24	0.07
Reference Value*	1.25	0.27
Median	1.30	0.13
Mean	1.30	
N	5	
Max.	1.4	
Min.	1.22	

*Reference Value by dIDMS


Kernel Density
Density
Result
Results: S1 - Ni
Assigned Value = 1.25 ± 0.27 µg/L
Results (µg/L)
Laboratory
7
1
8
6
2
9
4
10
11
5
Md
R.V.
S.V.


z-Scores: S1 - Ni
Target Standard Deviation 0.31 µg/L (Equivalent to 25% CV)
z-Score
Laboratory
-0.1
-0.1
0.2
0.3
0.5
7
1
8
6
2

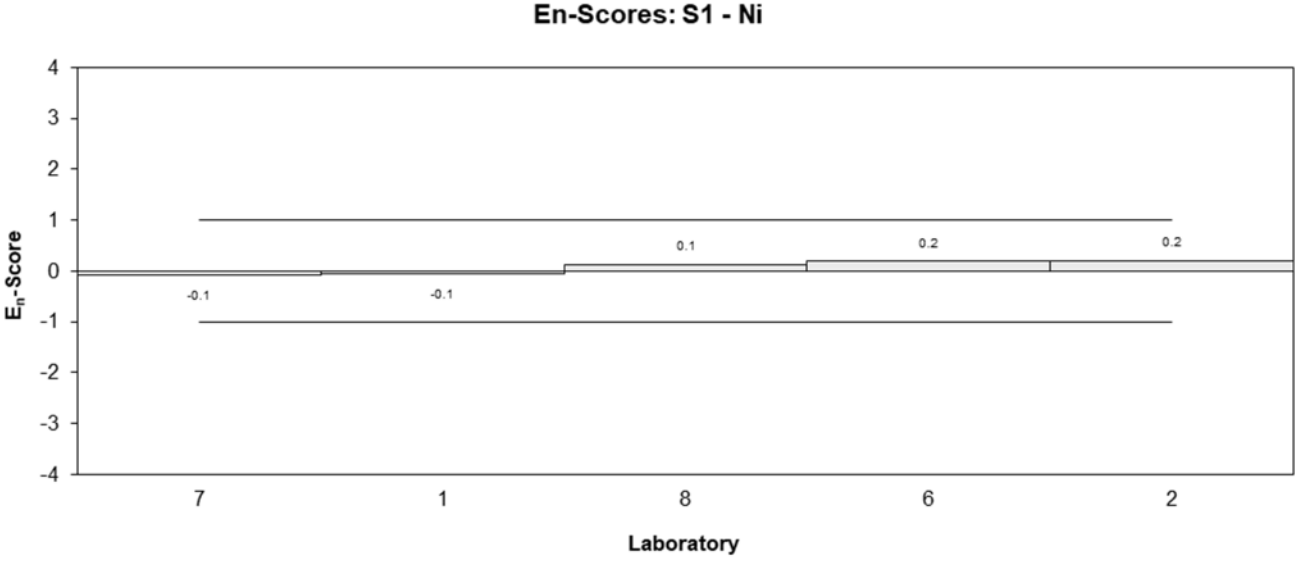

En-Scores: S1 - Ni
En-Score
Laboratory
-0.1
-0.1
0.1
0.2
0.2
7
1
8
6
2

Figure 12

Table 15

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	P
Units	µg/L

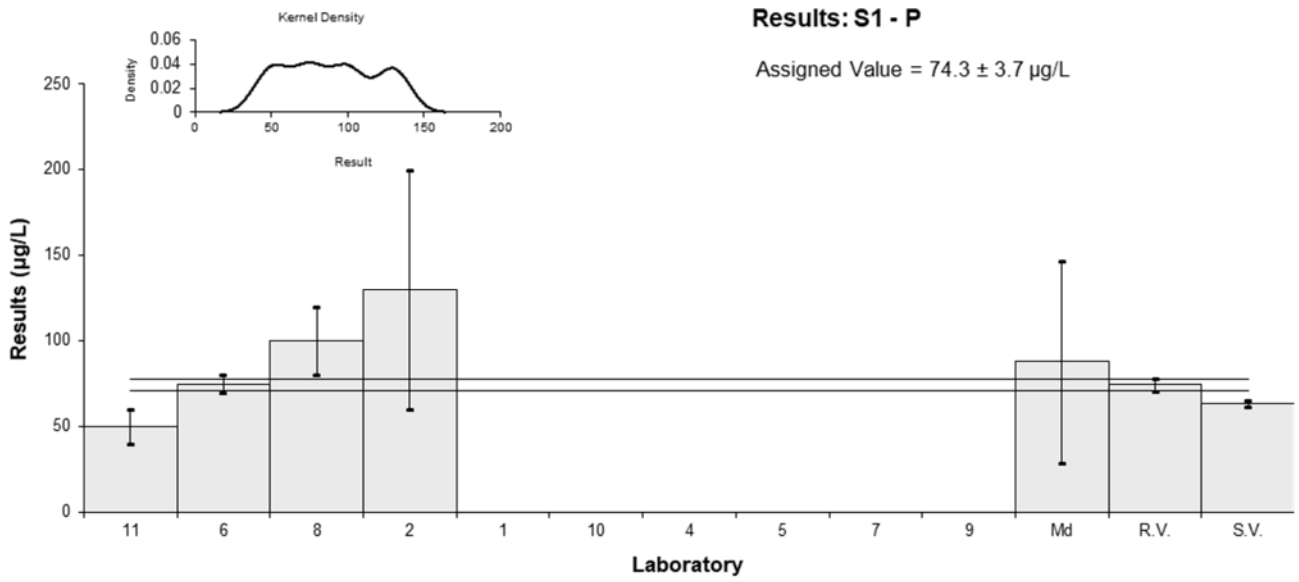
Participant Results

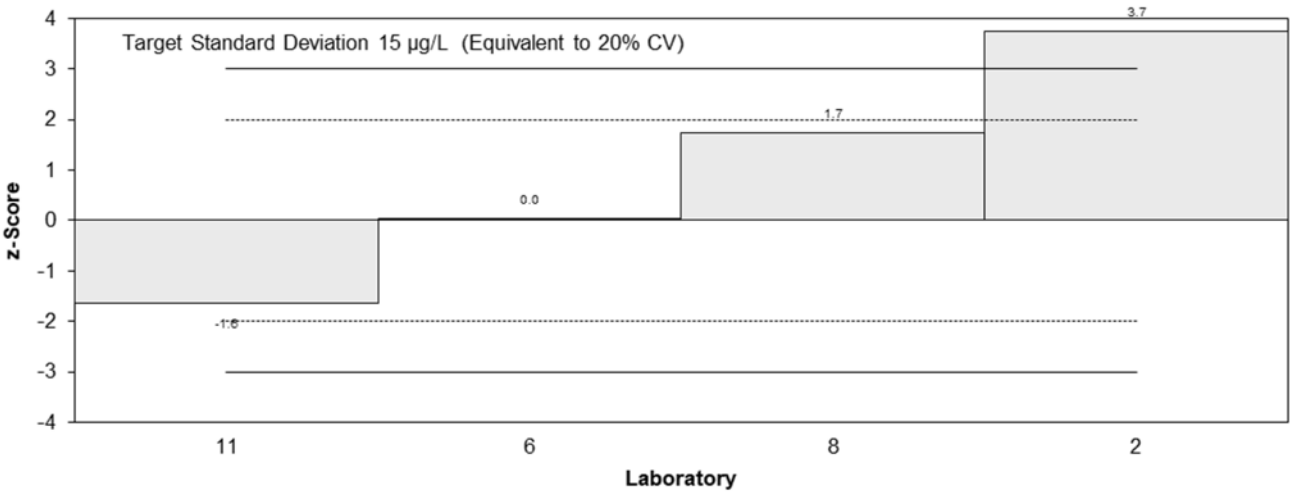
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	130	70	3.75	0.79
4	NT	NT		
5	NT	NT		
6	75.0	5.0	0.05	0.11
7	NT	NT		
8	100	20	1.73	1.26
9	NT	NT		
10	NT	NT		
11	50	10	-1.64	-2.28

Statistics

Assigned Value*	74.3	3.7
Spike**	63.2	1.8
Reference Value*	74.3	3.7
Median	88	59
Mean	89	
N	4	
Max.	130	
Min.	50	

*Reference Value by SA-ICP-MS, **Incurred value not included


Kernel Density
Density
0.06
0.04
0.02
0
0
50
100
150
200
Result
Results: S1 - P
Assigned Value = 74.3 ± 3.7 µg/L
Results (µg/L)
250
200
150
100
50
0
11
6
8
2
1
10
4
5
7
9
Md
R.V.
S.V.
Laboratory


z-Scores: S1 - P
Target Standard Deviation 15 µg/L (Equivalent to 20% CV)
3.7
1.7
0.0
-1.6
z-Score
4
3
2
1
0
-1
-2
-3
-4
11
6
8
2
Laboratory

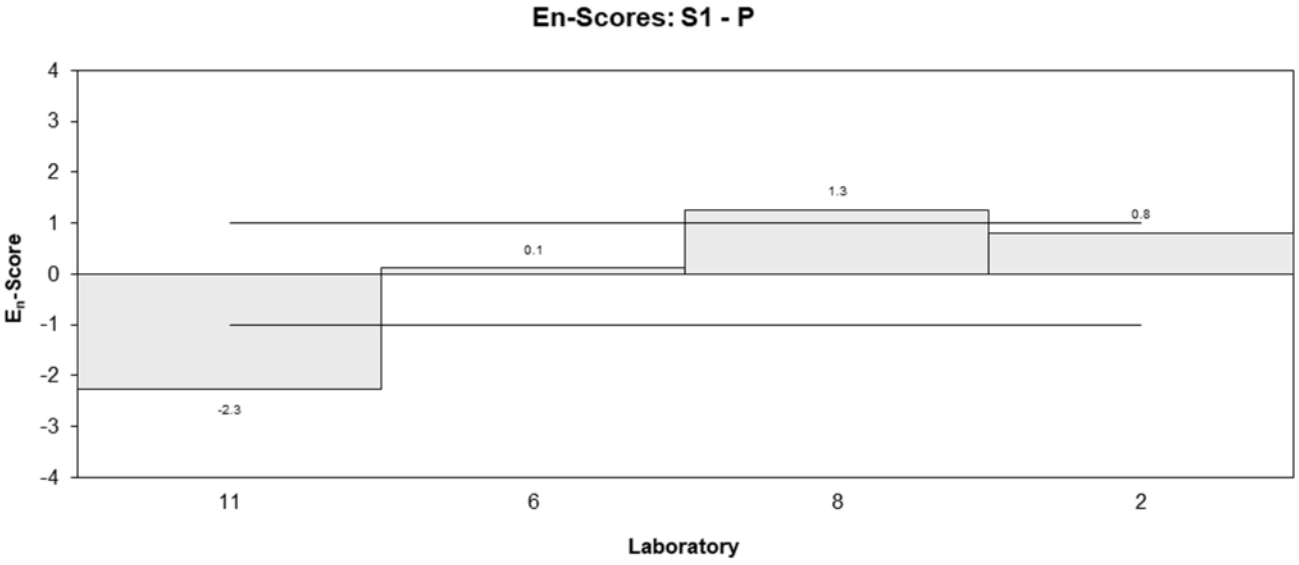

En-Scores: S1 - P
1.3
0.8
0.1
-2.3
En-Score
4
3
2
1
0
-1
-2
-3
-4
11
6
8
2
Laboratory

Figure 13

Table 16

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	Pb
Units	µg/L

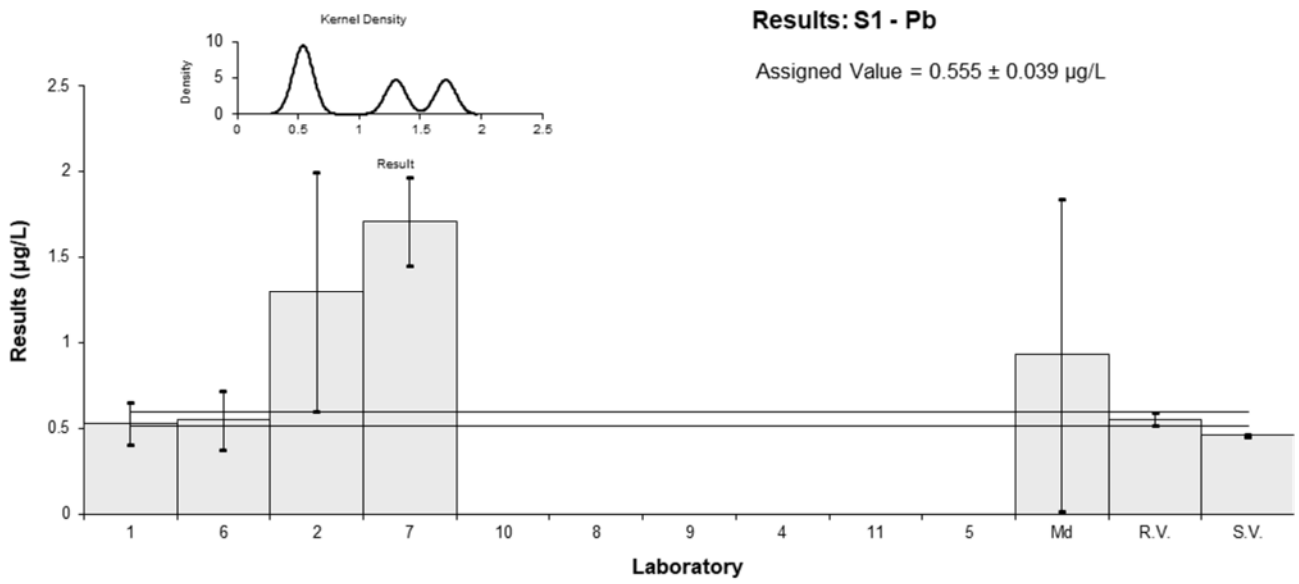
Participant Results

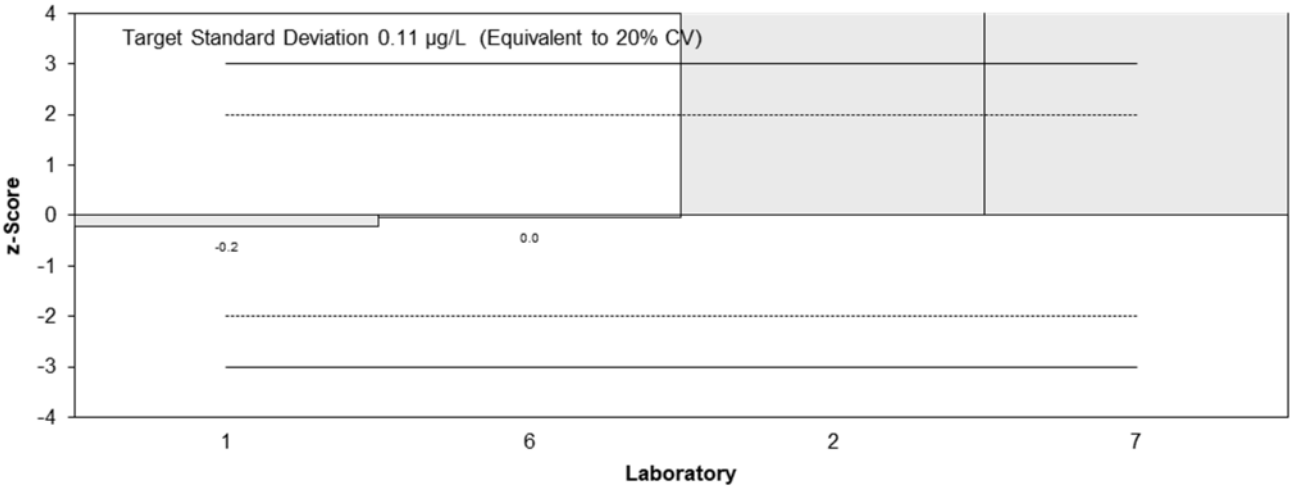
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.53	0.12	-0.23	-0.20
2	1.3	0.7	6.71	1.06
4	<1.0	0.67		
5	NT	NT		
6	0.55	0.17	-0.05	-0.03
7	1.71	0.26	10.41	4.39
8	<1	NR		
9	<1	NR		
10	<1	NR		
11	<1.5	NR		

Statistics

Assigned Value*	0.555	0.039
Spike**	0.460	0.010
Reference Value*	0.555	0.039
Median	0.93	0.91
Mean	1.0	
N	4	
Max.	1.71	
Min.	0.53	

*Reference Value by SA-ICP-MS, **Incurred value not included


Results: S1 - Pb
Assigned Value = 0.555 ± 0.039 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1
6
2
7
10
8
9
4
11
5
Md
R.V.
S.V.


z-Scores: S1 - Pb
Target Standard Deviation 0.11 µg/L (Equivalent to 20% CV)
z-Score
-0.2
0.0
Laboratory
1
6
2
7

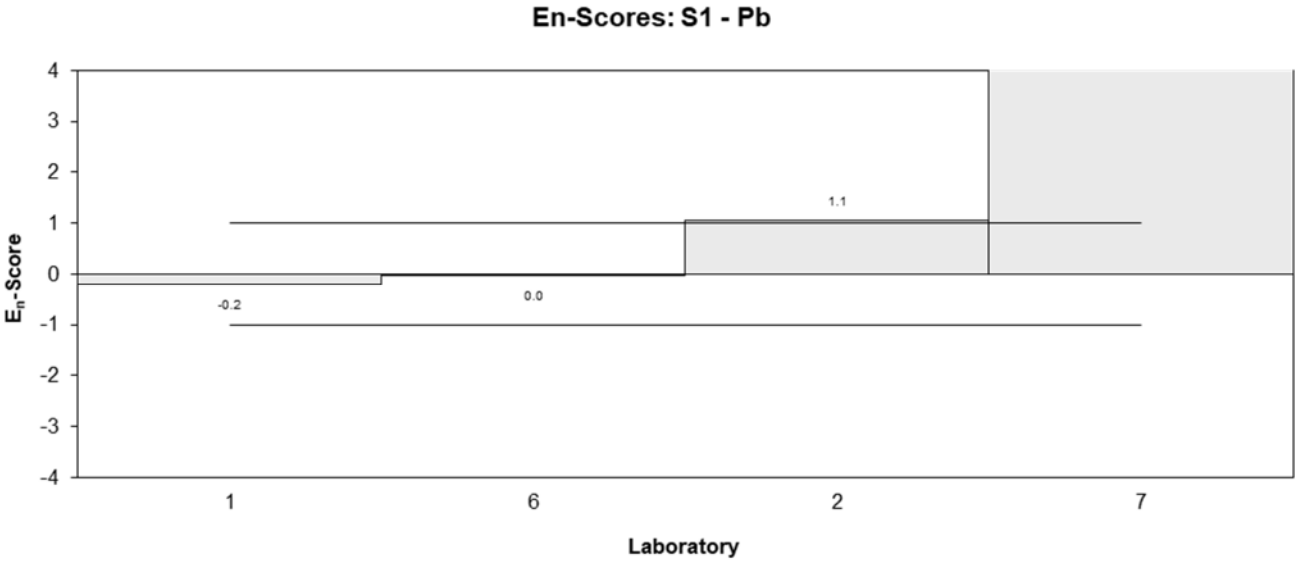

En-Scores: S1 - Pb
En-Score
1.1
-0.2
0.0
Laboratory
1
6
2
7

Figure 14

Table 17

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	Se
Units	µg/L

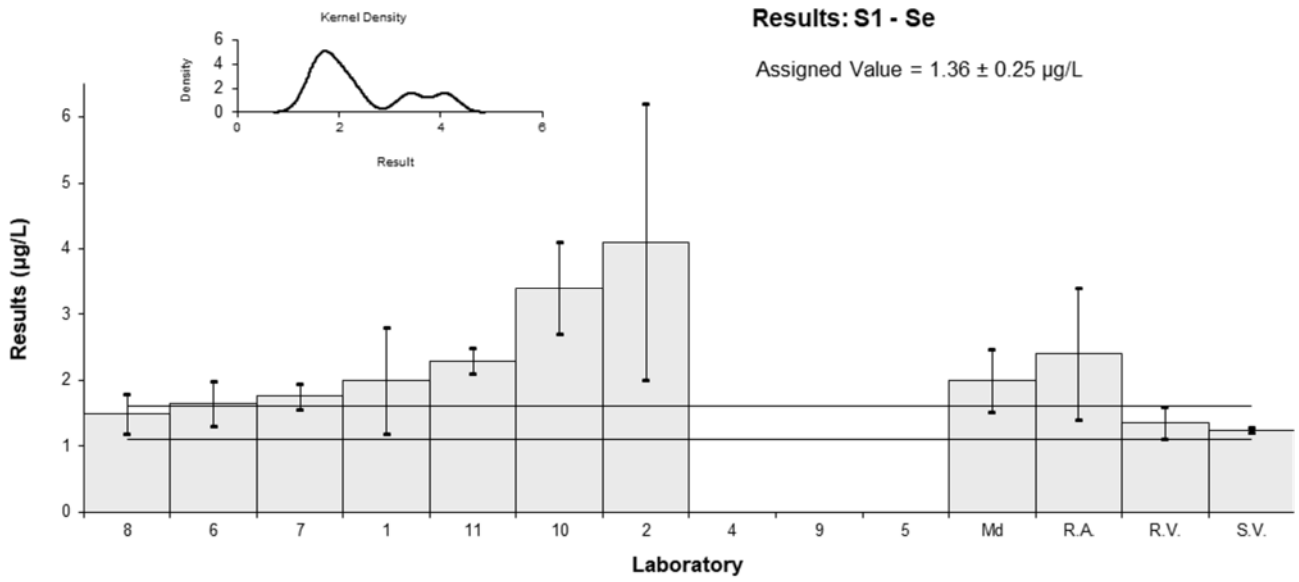
Participant Results

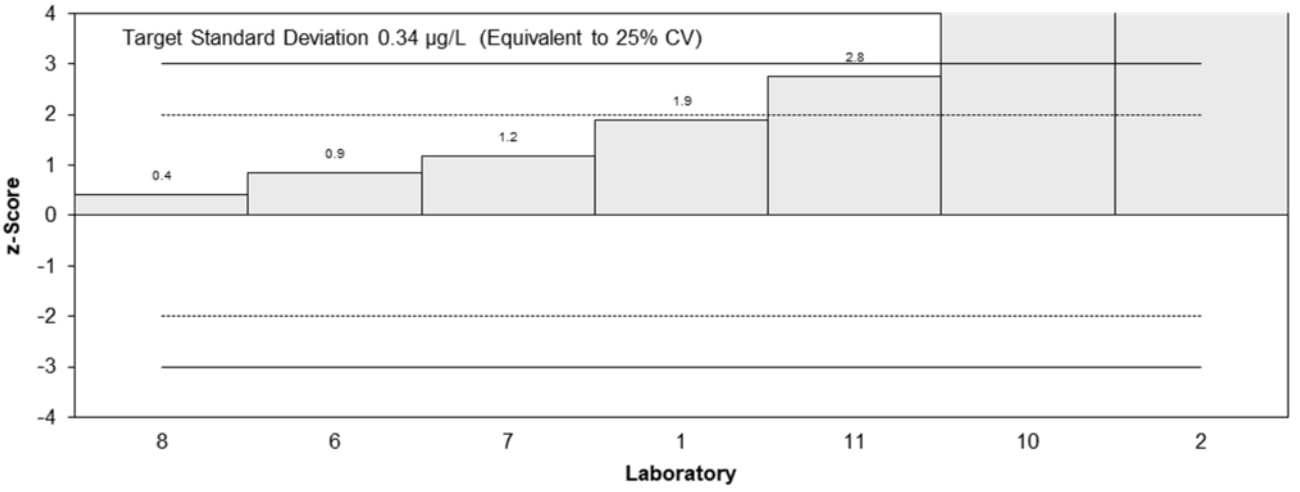
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.0	0.8	1.88	0.76
2	4.1	2.1	8.06	1.30
4	<4	2.7		
5	NT	NT		
6	1.65	0.34	0.85	0.69
7	1.76	0.2	1.18	1.25
8	1.5	0.3	0.41	0.36
9	<5	NR		
10	3.4	0.7	6.00	2.74
11	2.3	0.2	2.76	2.94

Statistics

Assigned Value*	1.36	0.25
Spike**	1.25	0.04
Reference Value*	1.36	0.25
Robust Average	2.4	1.0
Median	2.00	0.48
Mean	2.39	
N	7	
Max.	4.1	
Min.	1.5	
Robust SD	1.1	
Robust CV	46%	

*Reference Value by dIDMS, **Incurred value not included


Kernel Density
Density
Result
Results: S1 - Se
Assigned Value = 1.36 ± 0.25 µg/L
Results (µg/L)
Laboratory
8
6
7
1
11
10
2
4
9
5
Md
R.A.
R.V.
S.V.


z-Scores: S1 - Se
Target Standard Deviation 0.34 µg/L (Equivalent to 25% CV)
z-Score
0.4
0.9
1.2
1.9
2.8
Laboratory
8
6
7
1
11
10
2

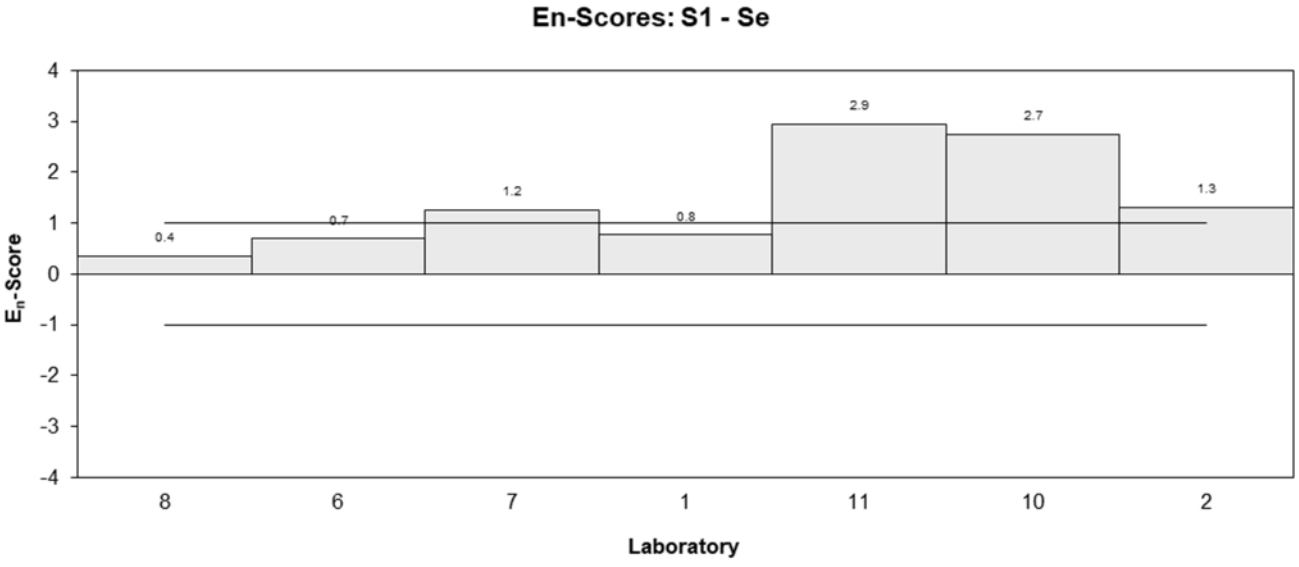

En-Scores: S1 - Se
En-Score
0.4
0.7
1.2
0.8
2.9
2.7
1.3
Laboratory
8
6
7
1
11
10
2

Figure 15

Table 18

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	Sn
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty
1	<1	NR
2	2.3	1.2
4	<5.0	NR
5	NT	NT
6	0.81	0.08
7	1.01	0.23
8	1.1	0.2
9	<1	NR
10	NT	NT
11	1.1	0.1

Statistics

Assigned Value	Not Set	
Spike	0.78	0.02
Median	1.10	0.17
Mean	1.26	
N	5	
Max.	2.3	
Min.	0.81	

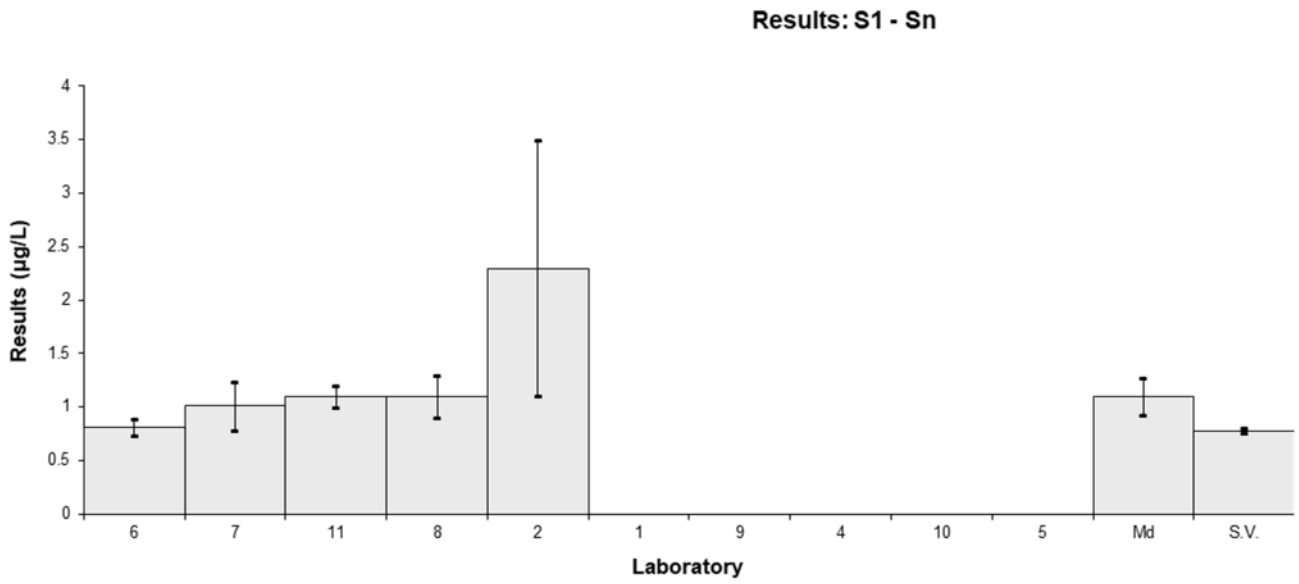

Results: S1 - Sn
Results (µg/L)
4
3.5
3
2.5
2
1.5
1
0.5
0
6
7
11
8
2
1
9
4
10
5
Md
S.V.
Laboratory

Figure 16

Table 19

Sample Details

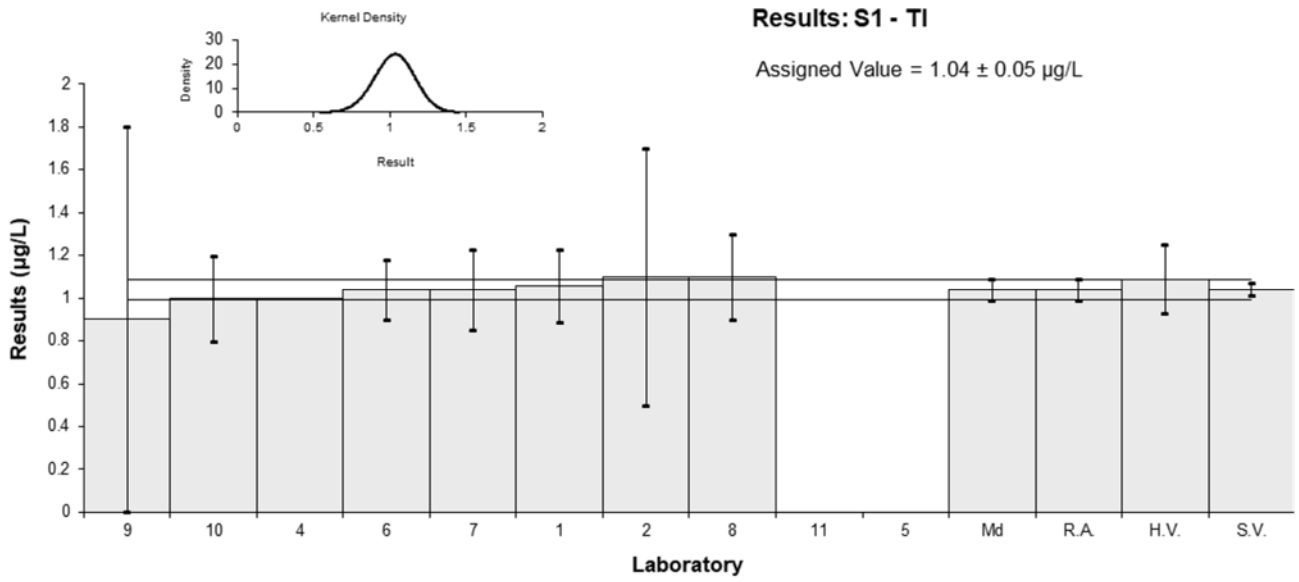
Sample No.	S1
Matrix.	Sea water
Analyte.	Tl
Units	µg/L

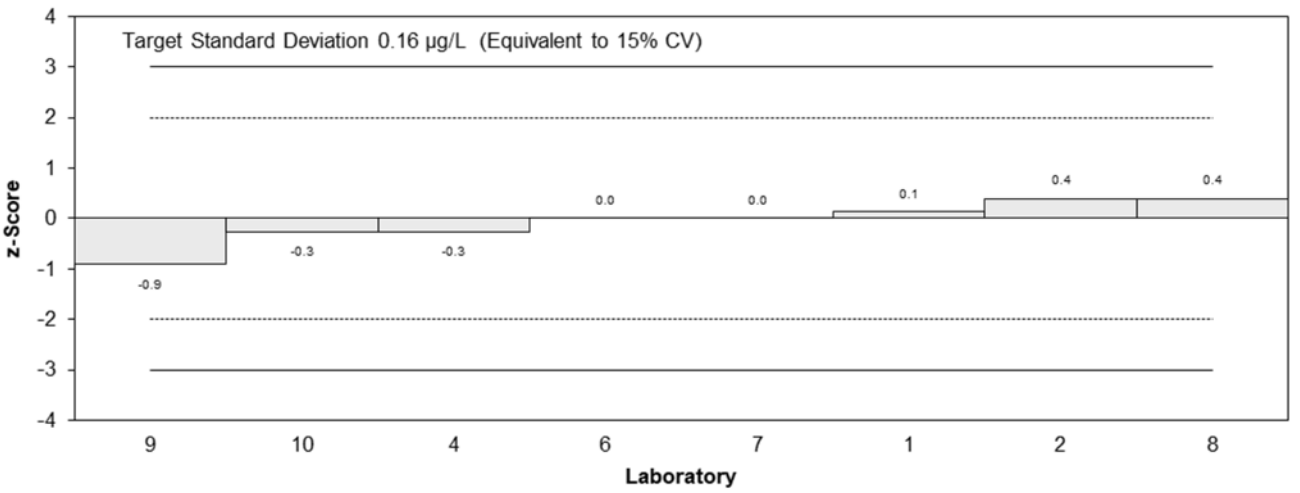
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.06	0.17	0.13	0.11
2	1.1	0.6	0.38	0.10
4	1.0	NR	-0.26	-0.80
5	NT	NT		
6	1.04	0.14	0.00	0.00
7	1.04	0.19	0.00	0.00
8	1.1	0.2	0.38	0.29
9	0.9	0.9	-0.90	-0.16
10	1.0	0.2	-0.26	-0.19
11	NT	NT		

Statistics

Assigned Value	1.04	0.05
Spike	1.04	0.03
Homogeneity Value	1.09	0.16
Robust Average	1.04	0.05
Median	1.04	0.05
Mean	1.03	
N	8	
Max.	1.1	
Min.	0.9	
Robust SD	0.06	
Robust CV	5.8%	


Results: S1 - Tl
Assigned Value = 1.04 ± 0.05 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
9
10
4
6
7
1
2
8
11
5
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Tl
Target Standard Deviation 0.16 µg/L (Equivalent to 15% CV)
z-Score
-0.9
-0.3
-0.3
0.0
0.0
0.1
0.4
0.4
Laboratory
9
10
4
6
7
1
2
8

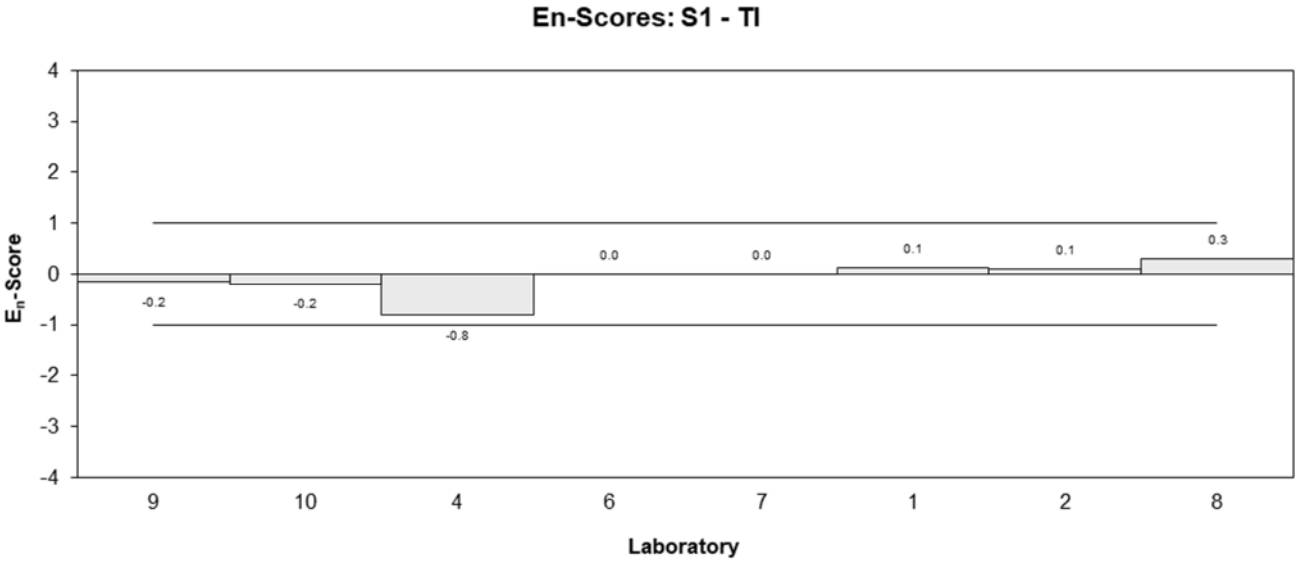

En-Scores: S1 - Tl
En-Score
-0.2
-0.2
-0.8
0.0
0.0
0.1
0.1
0.3
Laboratory
9
10
4
6
7
1
2
8

Figure 17

Table 20

Sample Details

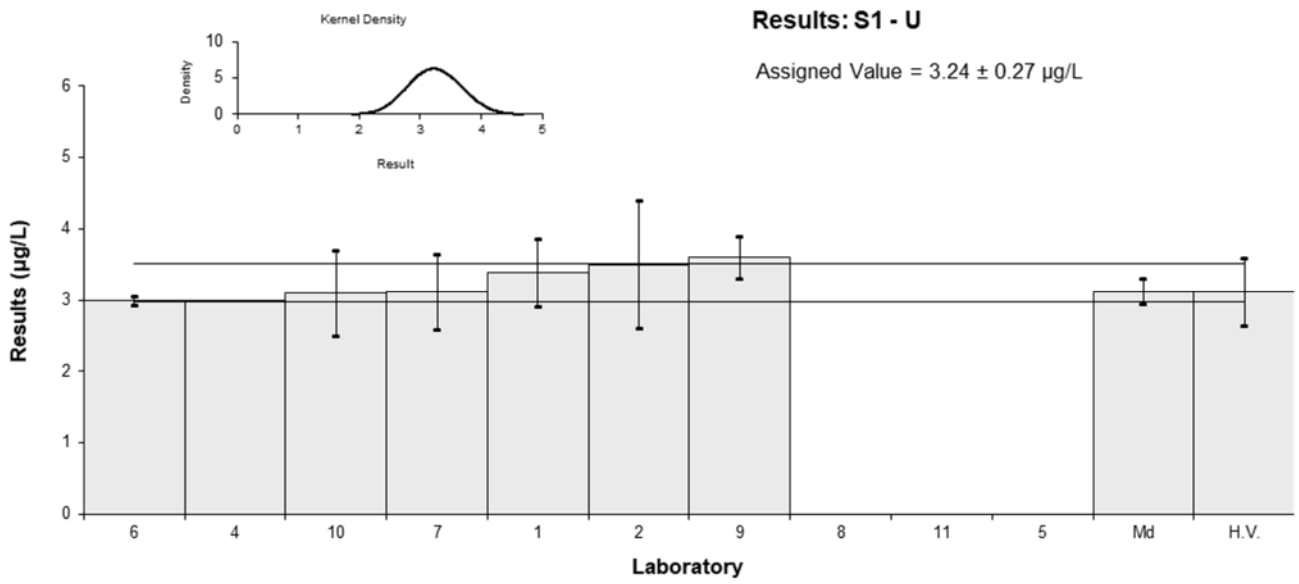
Sample No.	S1
Matrix.	Sea water
Analyte.	U
Units	µg/L

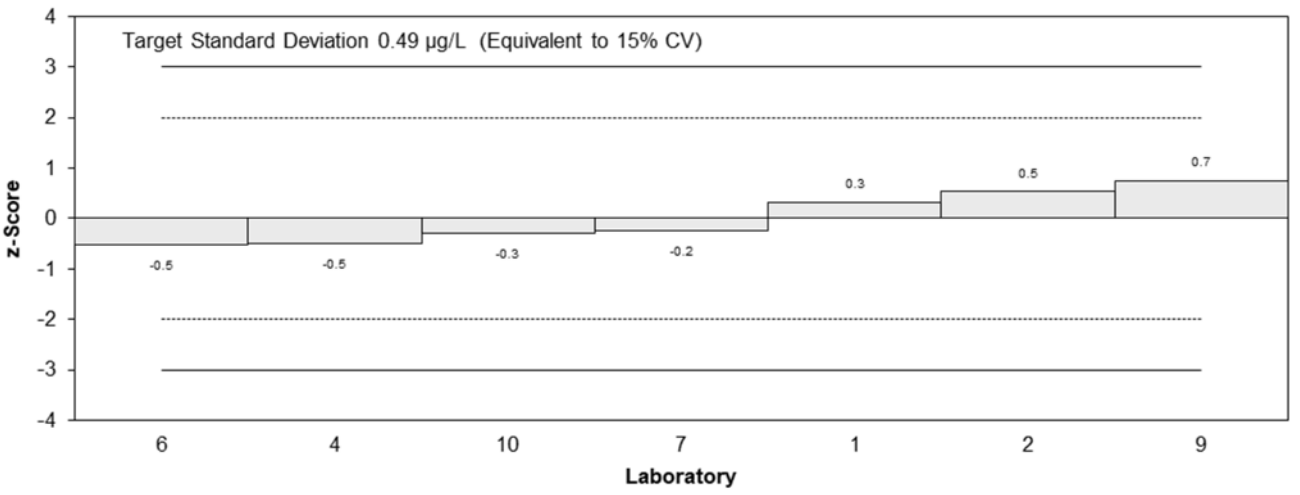
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.39	0.47	0.31	0.28
2	3.5	0.9	0.53	0.28
4	3.0	NR	-0.49	-0.89
5	NT	NT		
6	2.99	0.06	-0.51	-0.90
7	3.12	0.53	-0.25	-0.20
8	NR	NR		
9	3.6	0.3	0.74	0.89
10	3.1	0.6	-0.29	-0.21
11	NT	NT		

Statistics

Assigned Value	3.24	0.27
Spike	Not Spiked	
Homogeneity Value	3.12	0.47
Robust Average	3.24	0.27
Median	3.12	0.18
Mean	3.24	
N	7	
Max.	3.6	
Min.	2.99	
Robust SD	0.28	
Robust CV	8.7%	


Kernel Density
Density
Result
Results: S1 - U
Assigned Value = 3.24 ± 0.27 µg/L
Results (µg/L)
Laboratory
6
4
10
7
1
2
9
8
11
5
Md
H.V.


z-Scores: S1 - U
Target Standard Deviation 0.49 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.5
-0.5
-0.3
-0.2
0.3
0.5
0.7

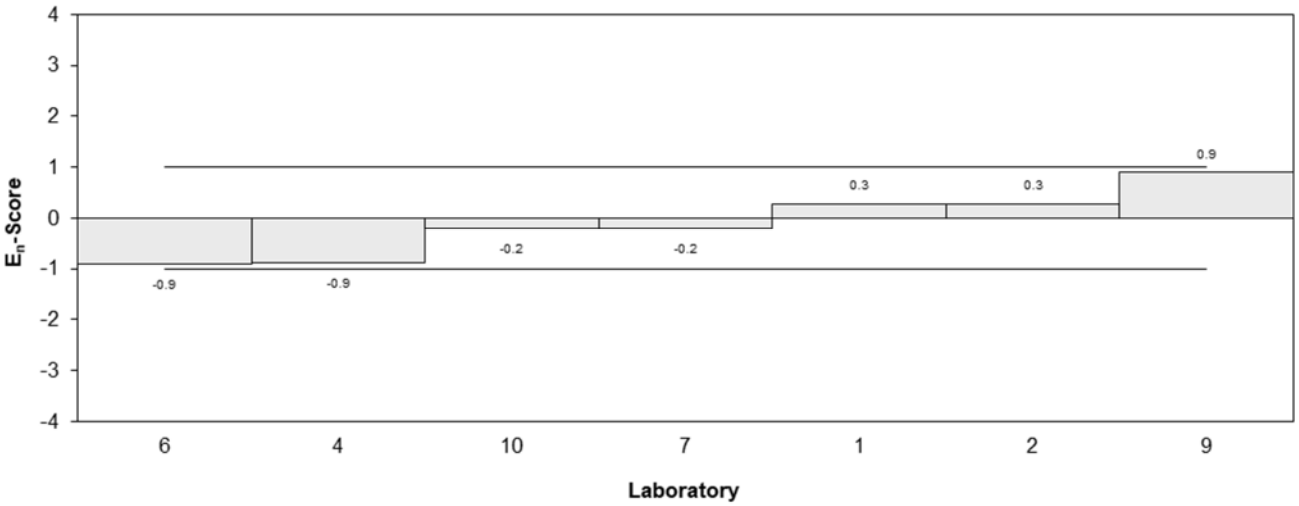

En-Scores: S1 - U
En-Score
Laboratory
-0.9
-0.9
-0.2
-0.2
0.3
0.3
0.9

Figure 18

Table 21

Sample Details

Sample No.	S1
Matrix.	Sea water
Analyte.	V
Units	µg/L

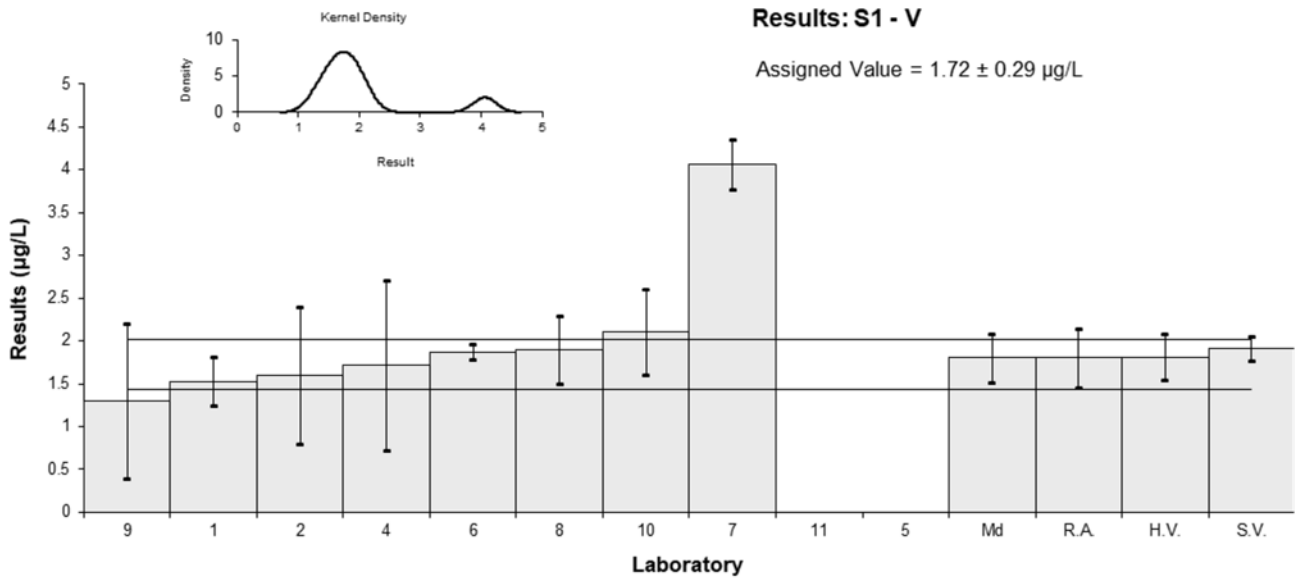
Participant Results

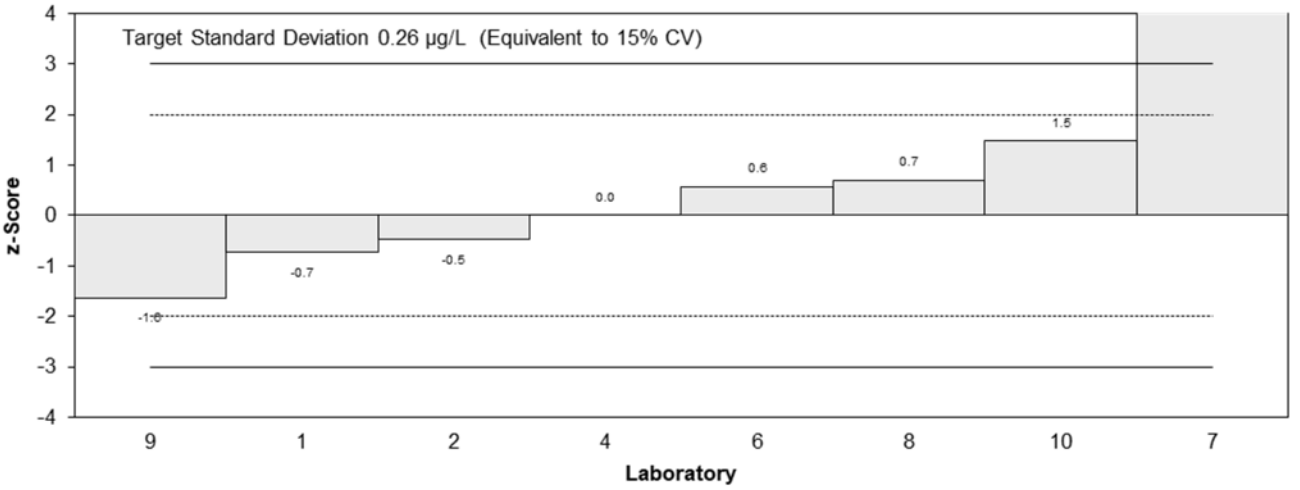
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.53	0.29	-0.74	-0.46
2	1.6	0.8	-0.47	-0.14
4	1.72	0.99	0.00	0.00
5	NT	NT		
6	1.87	0.09	0.58	0.49
7	4.06	0.29	9.07	5.71
8	1.9	0.4	0.70	0.36
9	1.3	0.9	-1.63	-0.44
10	2.1	0.5	1.47	0.66
11	NT	NT		

Statistics

Assigned Value*	1.72	0.29
Spike	1.91	0.14
Homogeneity Value	1.81	0.27
Robust Average	1.80	0.34
Median	1.80	0.29
Mean	2.01	
N	8	
Max.	4.06	
Min.	1.3	
Robust SD	0.38	
Robust CV	21%	

*Robust Average excluding laboratory 7.


Kernel Density
Density
Result
Results: S1 - V
Assigned Value = 1.72 ± 0.29 µg/L
Results (µg/L)
Laboratory
9
1
2
4
6
8
10
7
11
5
Md
R.A.
H.V.
S.V.


z-Scores: S1 - V
Target Standard Deviation 0.26 µg/L (Equivalent to 15% CV)
z-Score
-1.6
-0.7
-0.5
0.0
0.6
0.7
1.5
Laboratory

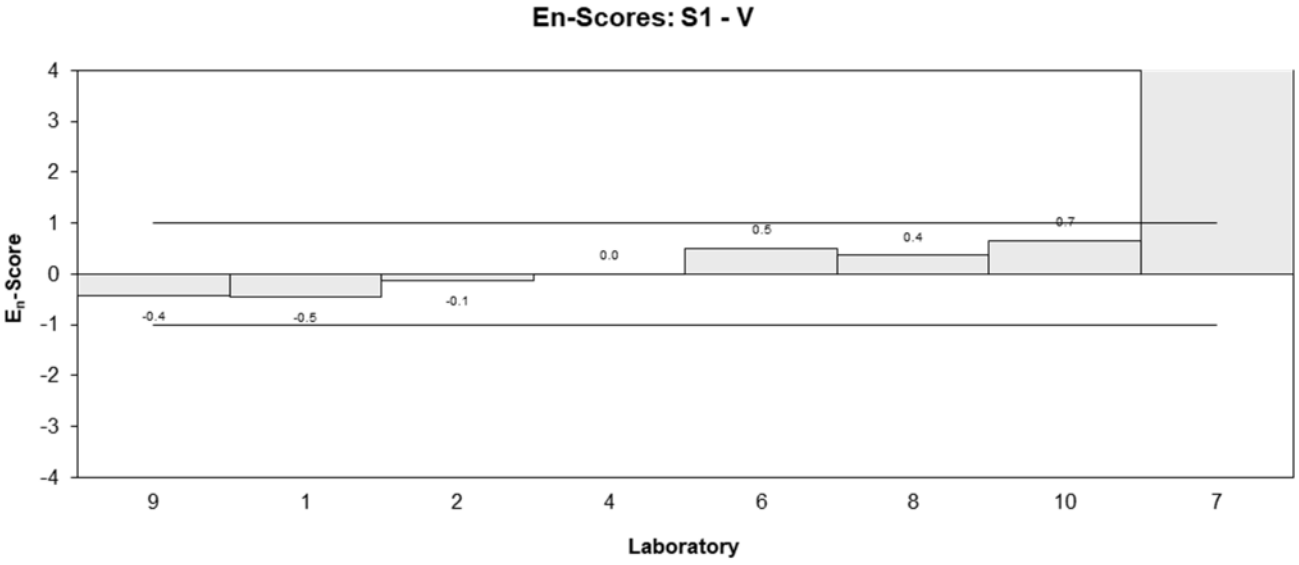

En-Scores: S1 - V
En-Score
-0.4
-0.5
-0.1
0.0
0.5
0.4
0.7
Laboratory

Figure 19

Table 22

Sample Details

Sample No.	S1
Matrix.	Seawater
Analyte.	Zn
Units	µg/L

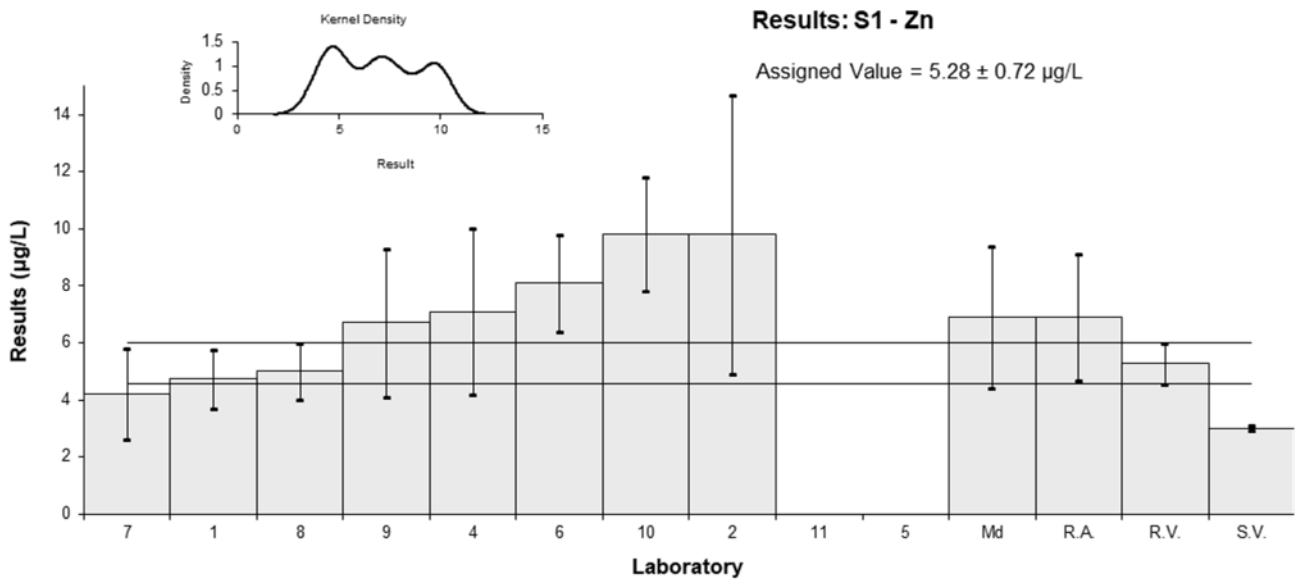
Participant Results

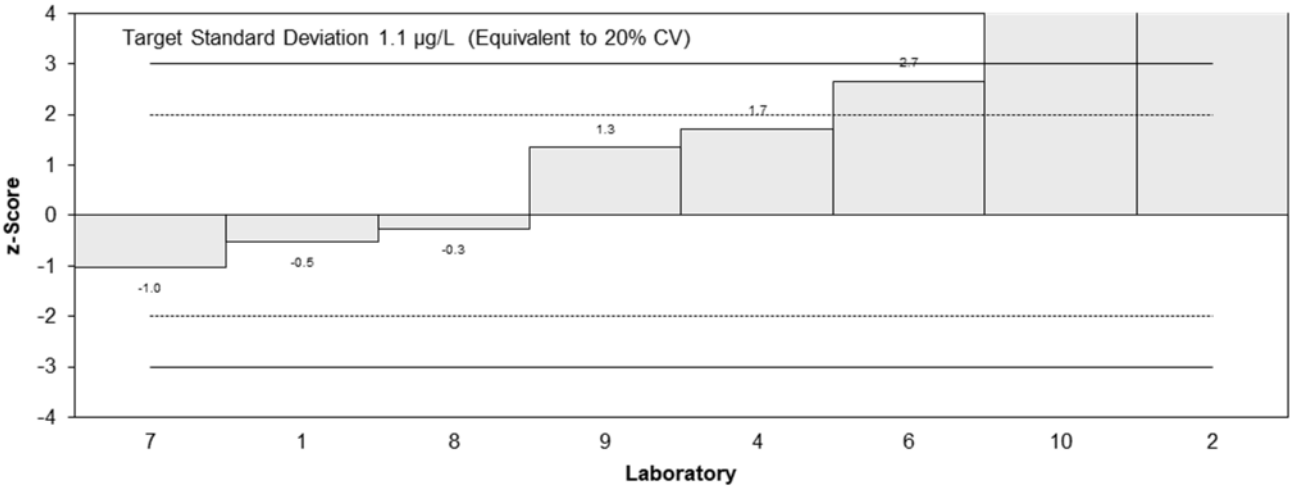
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.73	1.04	-0.52	-0.43
2	9.8	4.9	4.28	0.91
4	7.1	2.9	1.72	0.61
5	NT	NT		
6	8.09	1.7	2.66	1.52
7	4.20	1.59	-1.02	-0.62
8	5.0	1.0	-0.27	-0.23
9	6.7	2.6	1.34	0.53
10	9.8	2.0	4.28	2.13
11	<45	NR		

Statistics

Assigned Value*	5.28	0.72
Spike**	3.01	0.09
Reference Value*	5.28	0.72
Robust Average	6.9	2.2
Median	6.9	2.5
Mean	6.9	
N	8	
Max.	9.8	
Min.	4.2	
Robust SD	2.5	
Robust CV	36%	

*Reference Value by SA-ICP-MS, **Spike value not included


Kernel Density
Density
Result
Results: S1 - Zn
Assigned Value = 5.28 ± 0.72 µg/L
Results (µg/L)
Laboratory
7
1
8
9
4
6
10
2
11
5
Md
R.A.
R.V.
S.V.


z-Scores: S1 - Zn
Target Standard Deviation 1.1 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.0
-0.5
-0.3
1.3
1.7
2.7

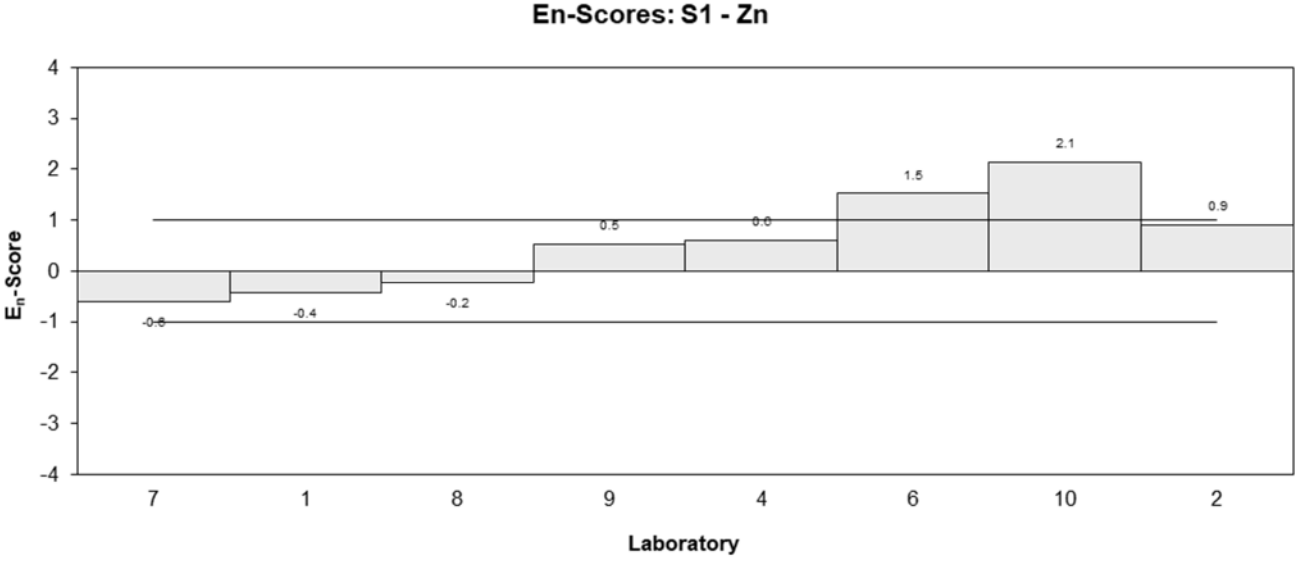

En-Scores: S1 - Zn
En-Score
Laboratory
-0.6
-0.4
-0.2
0.5
0.6
1.5
2.1
0.9

Figure 20

Table 23

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	Al
Units	µg/L

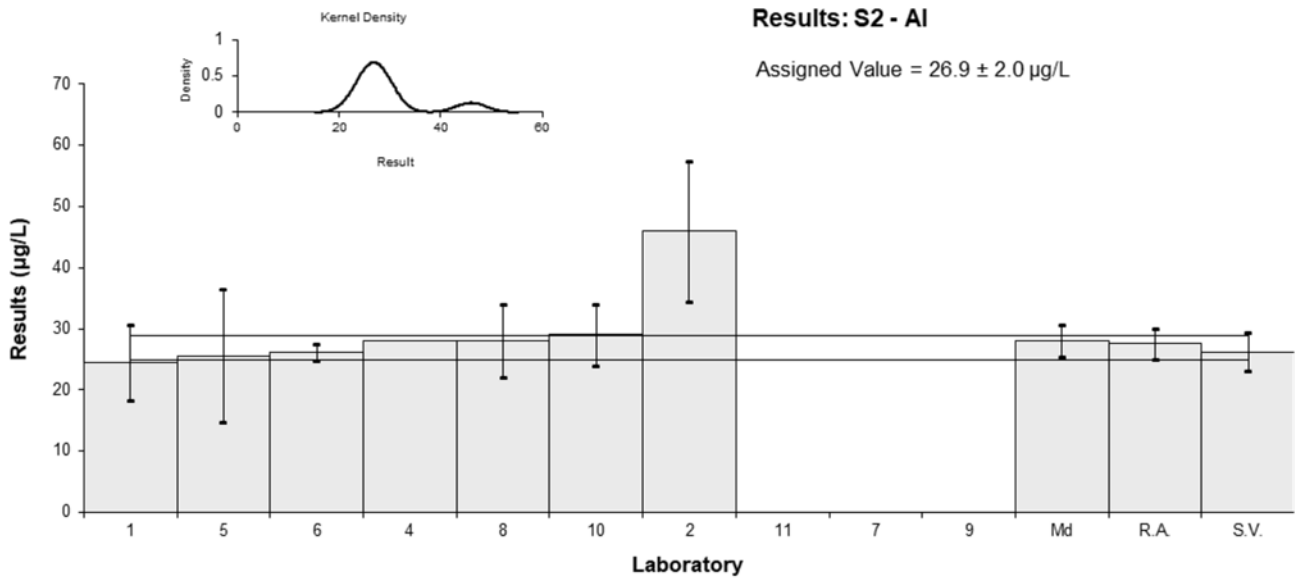
Participant Results

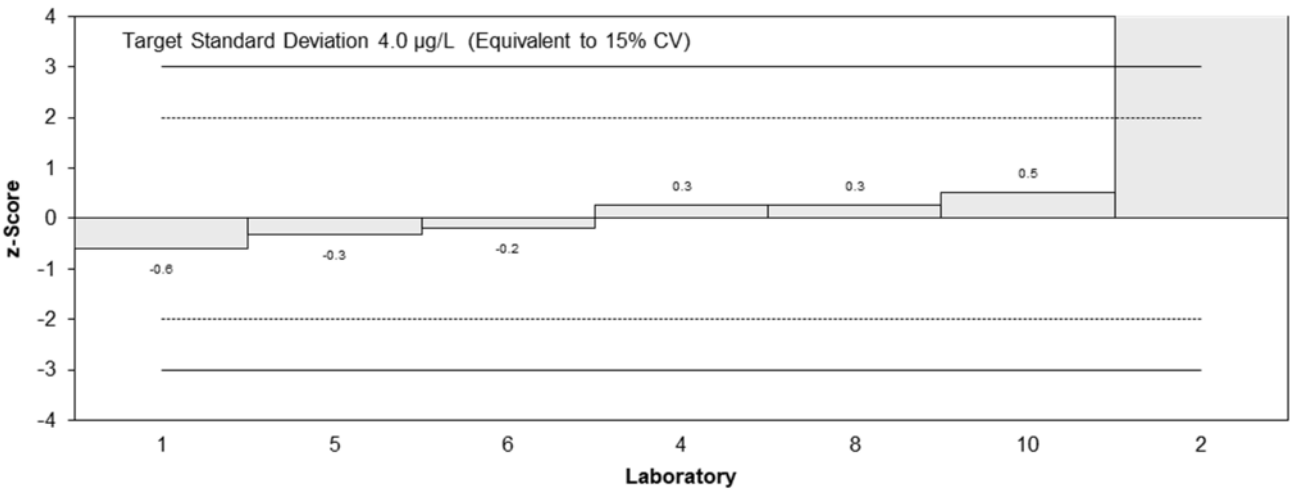
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	24.5	6.2	-0.59	-0.37
2	46	11.5	4.73	1.64
4	28	NR	0.27	0.55
5	25.6	10.8	-0.32	-0.12
6	26.1	1.4	-0.20	-0.33
7	NT	NT		
8	28	6	0.27	0.17
9	NT	NT		
10	29	5.0	0.52	0.39
11	NT	NT		

Statistics

Assigned Value*	26.9	2.0
Spike	26.2	3.1
Robust Average	27.5	2.6
Median	28.0	2.6
Mean	29.6	
N	7	
Max.	46	
Min.	24.5	
Robust SD	2.7	
Robust CV	9.8%	

*Robust Average excluding laboratory 2.


Kernel Density
Density
Result
Results: S2 - Al
Assigned Value = 26.9 ± 2.0 µg/L
Results (µg/L)
Laboratory
1
5
6
4
8
10
2
11
7
9
Md
R.A.
S.V.


z-Scores: S2 - Al
Target Standard Deviation 4.0 µg/L (Equivalent to 15% CV)
z-Score
-0.6
-0.3
-0.2
0.3
0.3
0.5
Laboratory

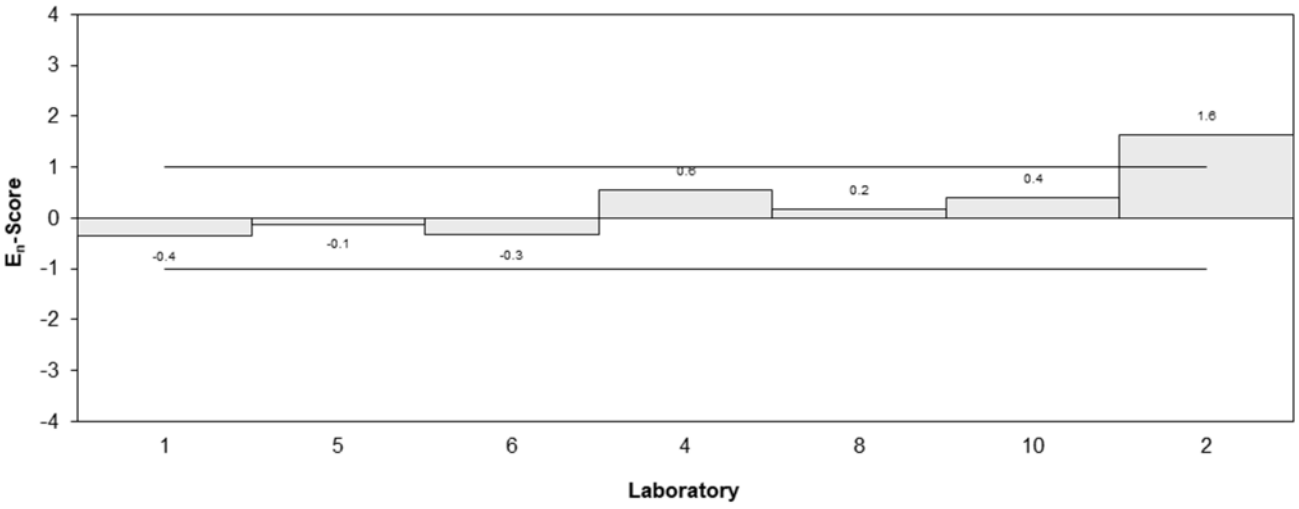

En-Scores: S2 - Al
En-Score
-0.4
-0.1
-0.3
0.6
0.2
0.4
1.6
Laboratory

Figure 21

Table 24

Sample Details

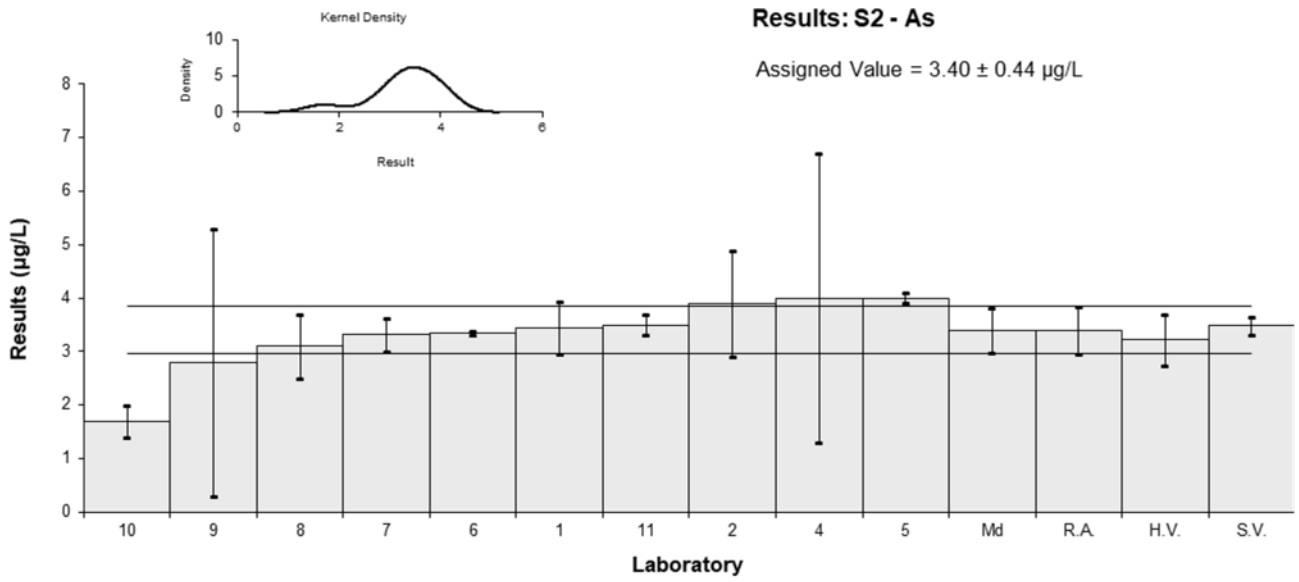
Sample No.	S2
Matrix.	Sea water
Analyte.	As
Units	µg/L

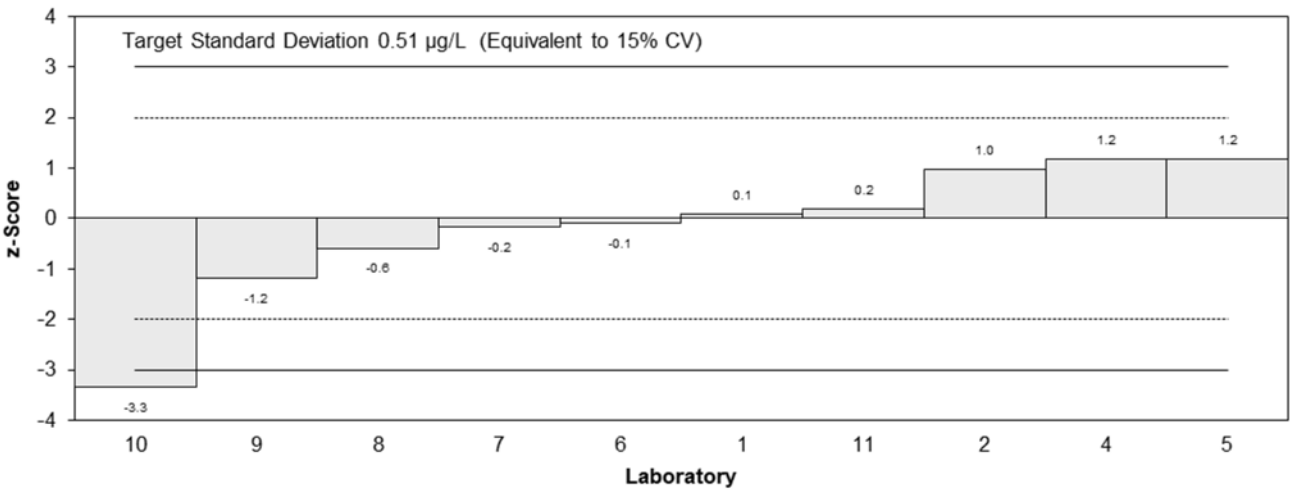
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.45	0.49	0.10	0.08
2	3.9	0.99	0.98	0.46
4	4.0	2.7	1.18	0.22
5	4	0.1	1.18	1.33
6	3.35	0.04	-0.10	-0.11
7	3.31	0.3	-0.18	-0.17
8	3.1	0.6	-0.59	-0.40
9	2.8	2.5	-1.18	-0.24
10	1.7	0.3	-3.33	-3.19
11	3.5	0.2	0.20	0.21

Statistics

Assigned Value	3.40	0.44
Spike	3.48	0.16
Homogeneity Value	3.22	0.48
Robust Average	3.40	0.44
Median	3.40	0.42
Mean	3.31	
N	10	
Max.	4	
Min.	1.7	
Robust SD	0.55	
Robust CV	16%	


Kernel Density
Density
Result
Results: S2 - As
Assigned Value = 3.40 ± 0.44 µg/L
Results (µg/L)
Laboratory
10
9
8
7
6
1
11
2
4
5
Md
R.A.
H.V.
S.V.


z-Scores: S2 - As
Target Standard Deviation 0.51 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-3.3
-1.2
-0.6
-0.2
-0.1
0.1
0.2
1.0
1.2
1.2

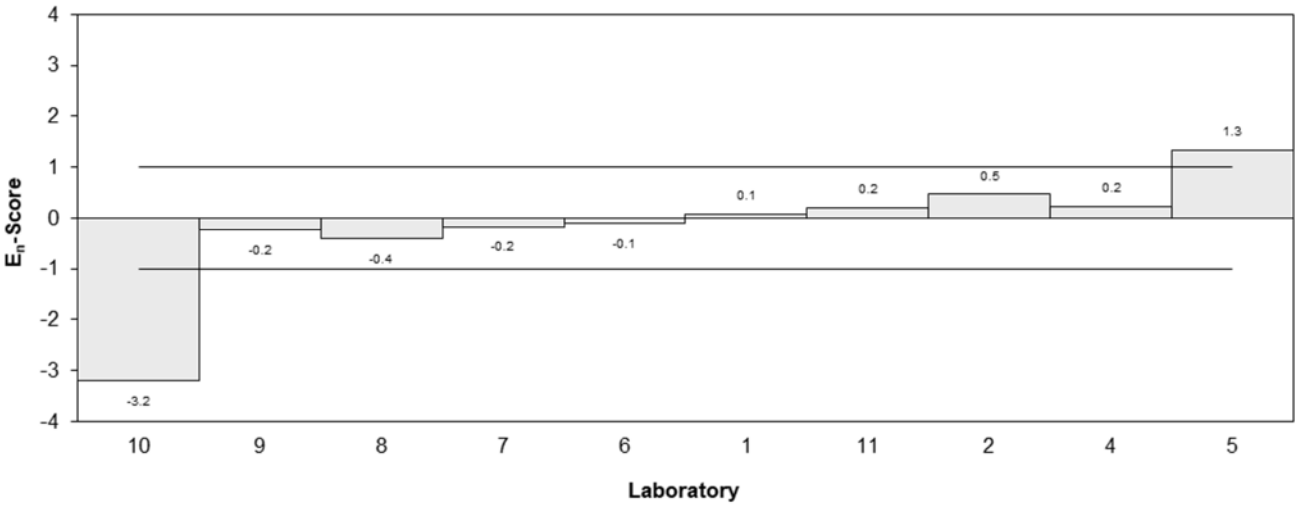

En-Scores: S2 - As
En-Score
Laboratory
-3.2
-0.2
-0.4
-0.2
-0.1
0.1
0.2
0.5
0.2
1.3

Figure 22

Table 25

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	B
Units	µg/L

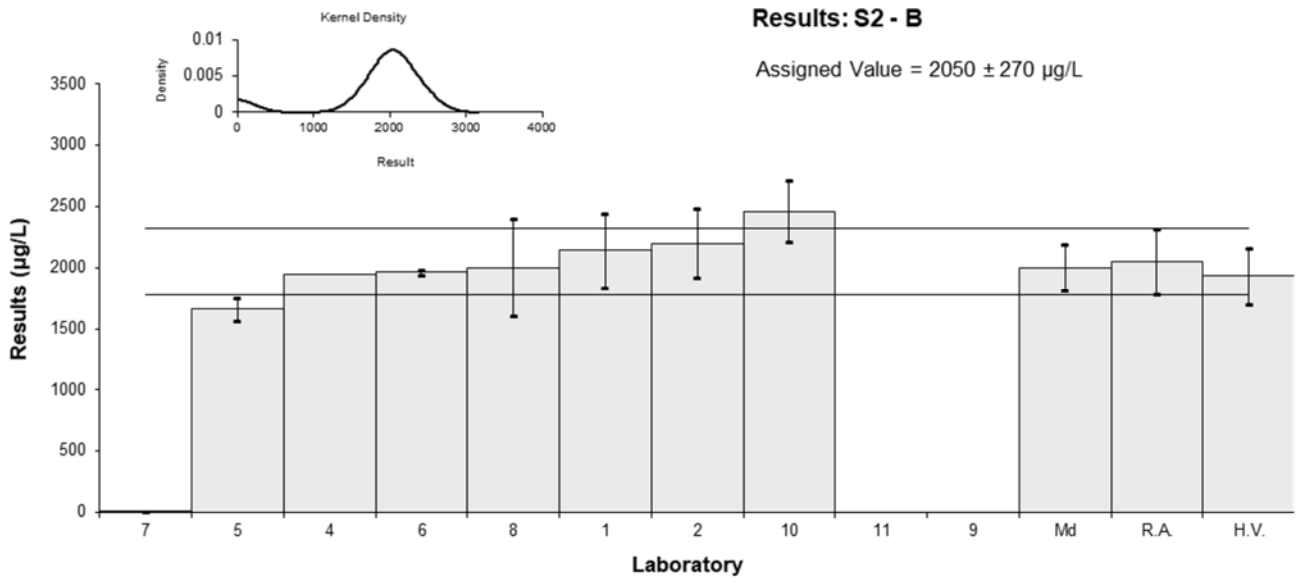
Participant Results

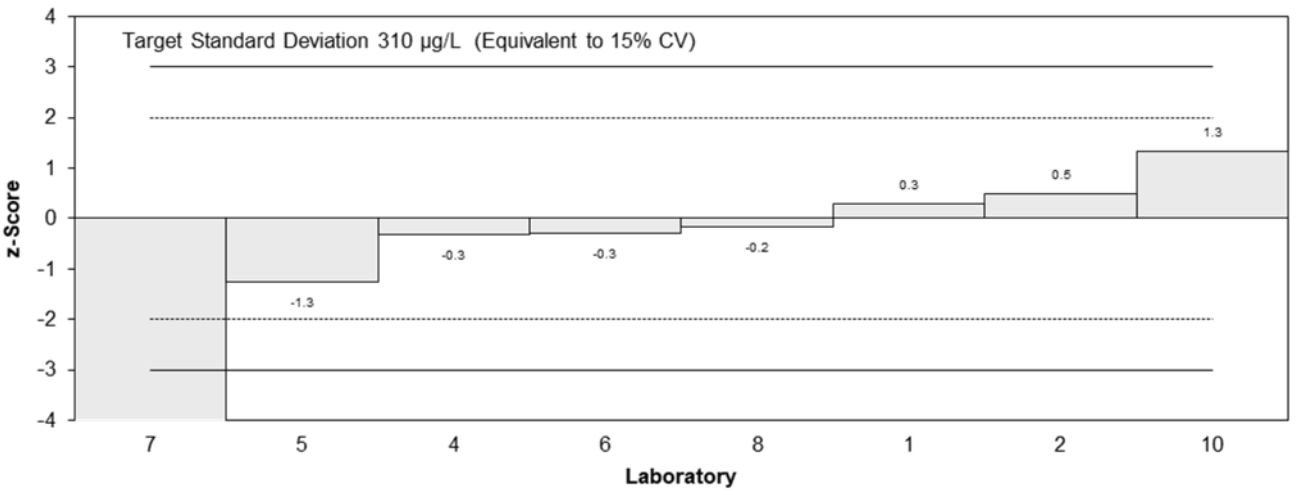
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2140	300	0.29	0.22
2	2200	280	0.49	0.39
4	1950	NR	-0.33	-0.37
5	1659	96	-1.27	-1.36
6	1961	22	-0.29	-0.33
7	2.70	0.20	-6.66	-7.58
8	2000	400	-0.16	-0.10
9	NT	NT		
10	2460	250	1.33	1.11
11	NT	NT		

Statistics*

Assigned Value	2050	270
Spike	Not Spiked	
Homogeneity Value	1930	230
Robust Average	2050	270
Median	2000	190
Mean	2050	
N	7	
Max.	2460	
Min.	1659	
Robust SD	280	
Robust CV	14%	

*Laboratory 7 was excluded from statistical calculation (extreme outlier).


Kernel Density
Density
Result
Results: S2 - B
Assigned Value = 2050 ± 270 µg/L
Results (µg/L)
Laboratory
7
5
4
6
8
1
2
10
11
9
Md
R.A.
H.V.


z-Scores: S2 - B
Target Standard Deviation 310 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.3
-0.3
-0.3
-0.2
0.3
0.5
1.3

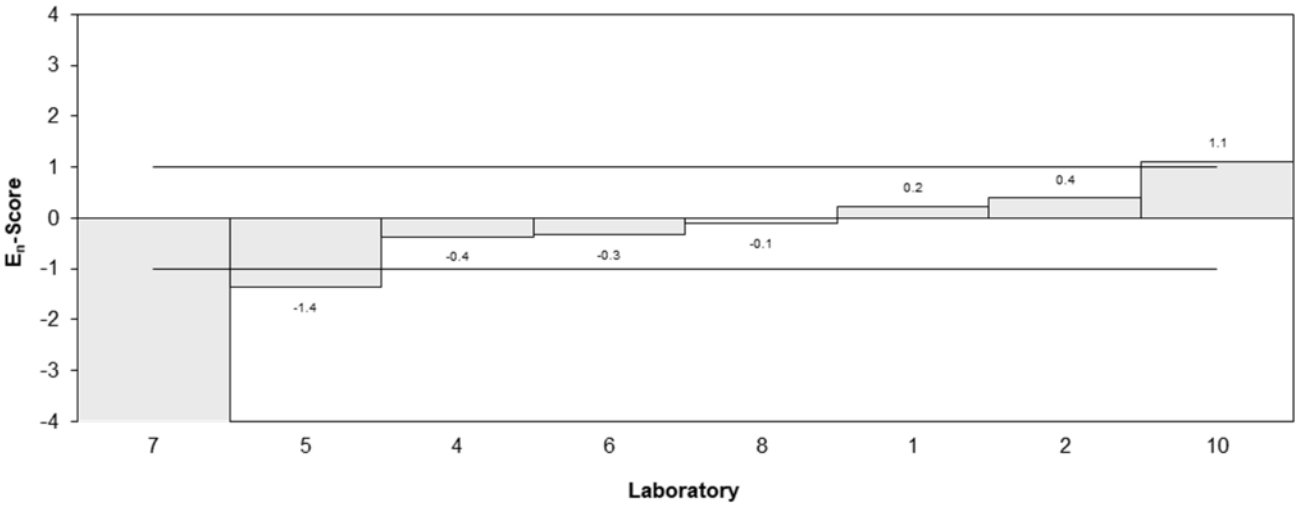

En-Scores: S2 - B
En-Score
Laboratory
-1.4
-0.4
-0.3
-0.1
0.2
0.4
1.1

Figure 23

Table 26

Sample Details

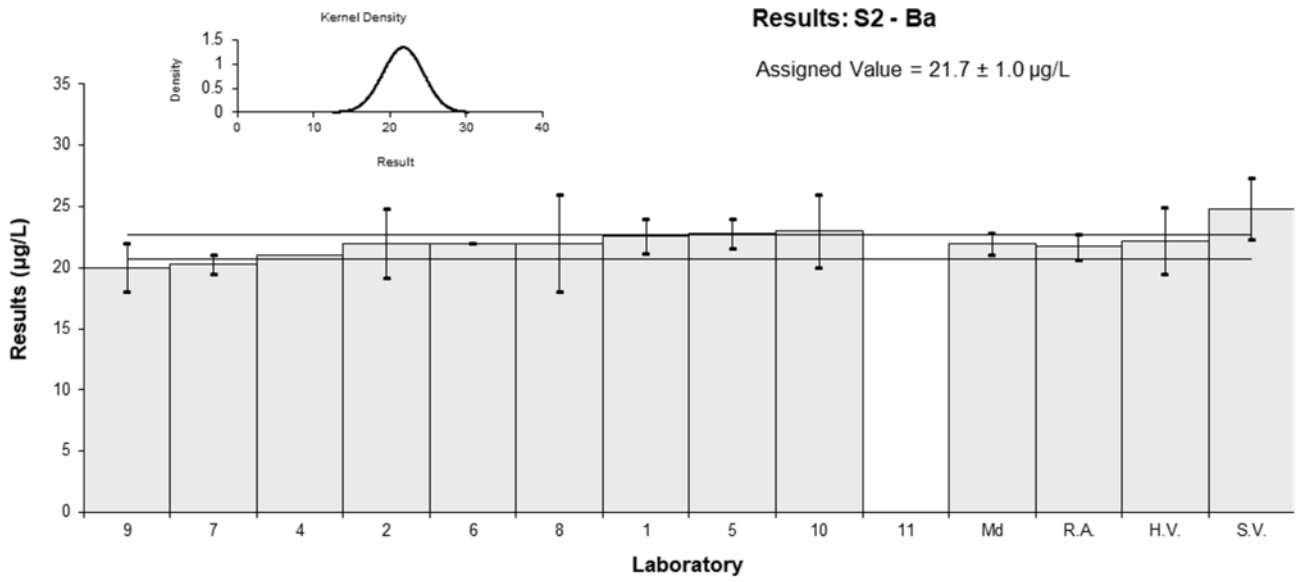
Sample No.	S2
Matrix.	Sea water
Analyte.	Ba
Units	µg/L

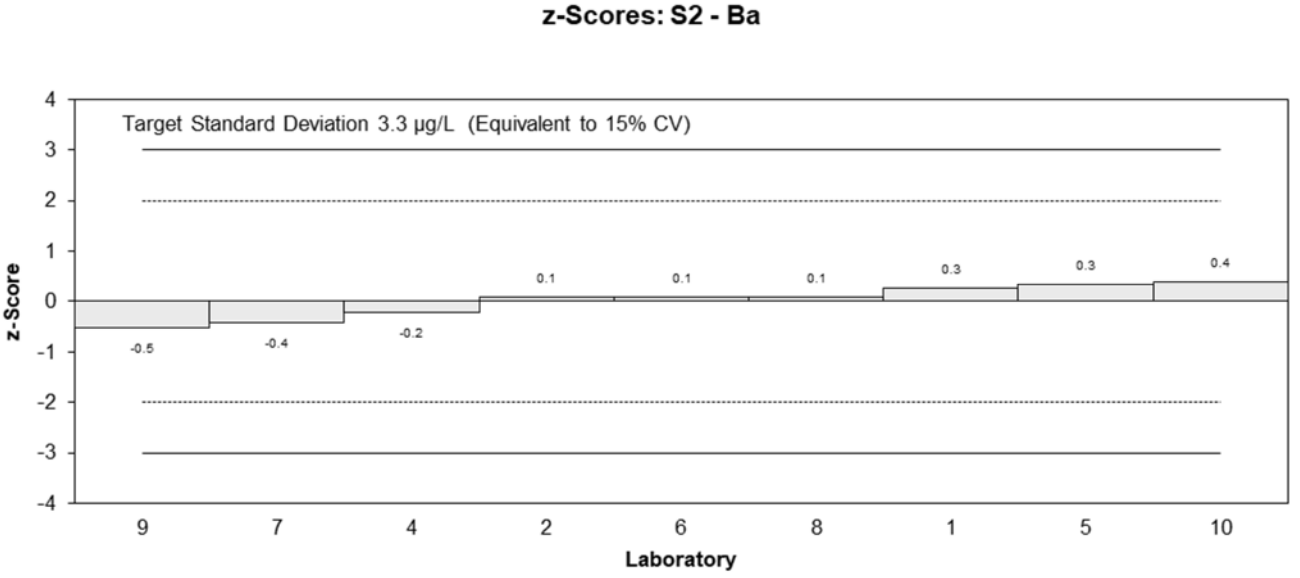
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	22.6	1.4	0.28	0.52
2	22	2.8	0.09	0.10
4	21	NR	-0.22	-0.70
5	22.8	1.2	0.34	0.70
6	22.0	0.03	0.09	0.30
7	20.3	0.8	-0.43	-1.09
8	22	4	0.09	0.07
9	20	2.0	-0.52	-0.76
10	23	3.0	0.40	0.41
11	NT	NT		

Statistics

Assigned Value	21.7	1.0
Spike	24.8	2.5
Homogeneity Value	22.2	2.7
Robust Average	21.7	1.0
Median	22.0	0.9
Mean	21.7	
N	9	
Max.	23	
Min.	20	
Robust SD	1.2	
Robust CV	5.6%	


Kernel Density
Density
Result
Results: S2 - Ba
Assigned Value = 21.7 ± 1.0 µg/L
Results (µg/L)
Laboratory
9
7
4
2
6
8
1
5
10
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Ba
Target Standard Deviation 3.3 µg/L (Equivalent to 15% CV)
z-Score
-0.5
-0.4
-0.2
0.1
0.1
0.1
0.3
0.3
0.4
Laboratory
9
7
4
2
6
8
1
5
10

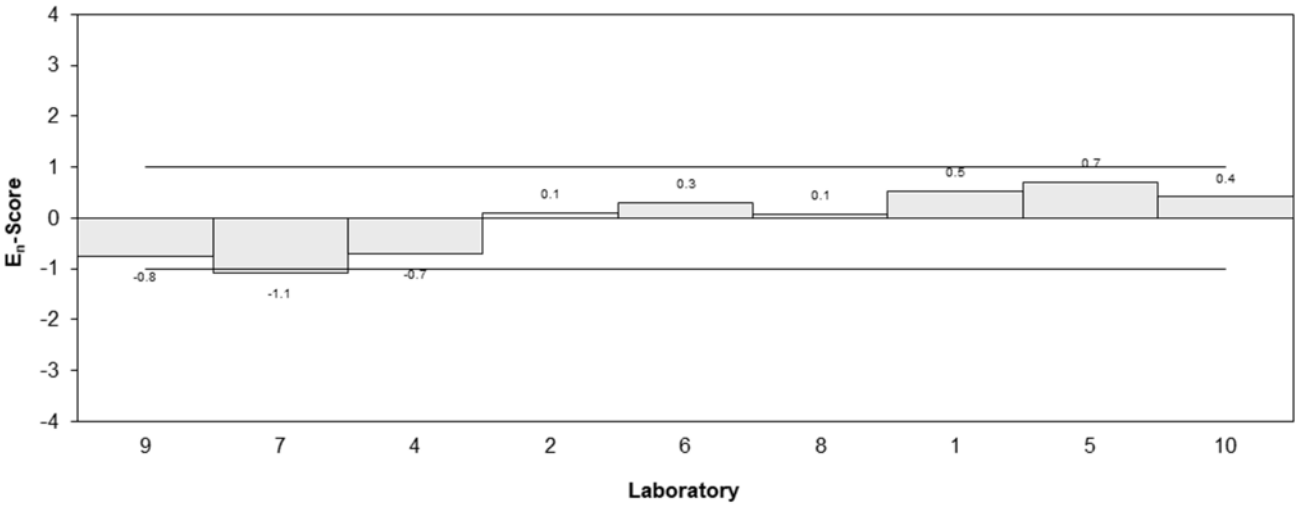

En-Scores: S2 - Ba
En-Score
-0.8
-1.1
-0.7
0.1
0.3
0.1
0.5
0.7
0.4
Laboratory
9
7
4
2
6
8
1
5
10

Figure 24

Table 27

Sample Details

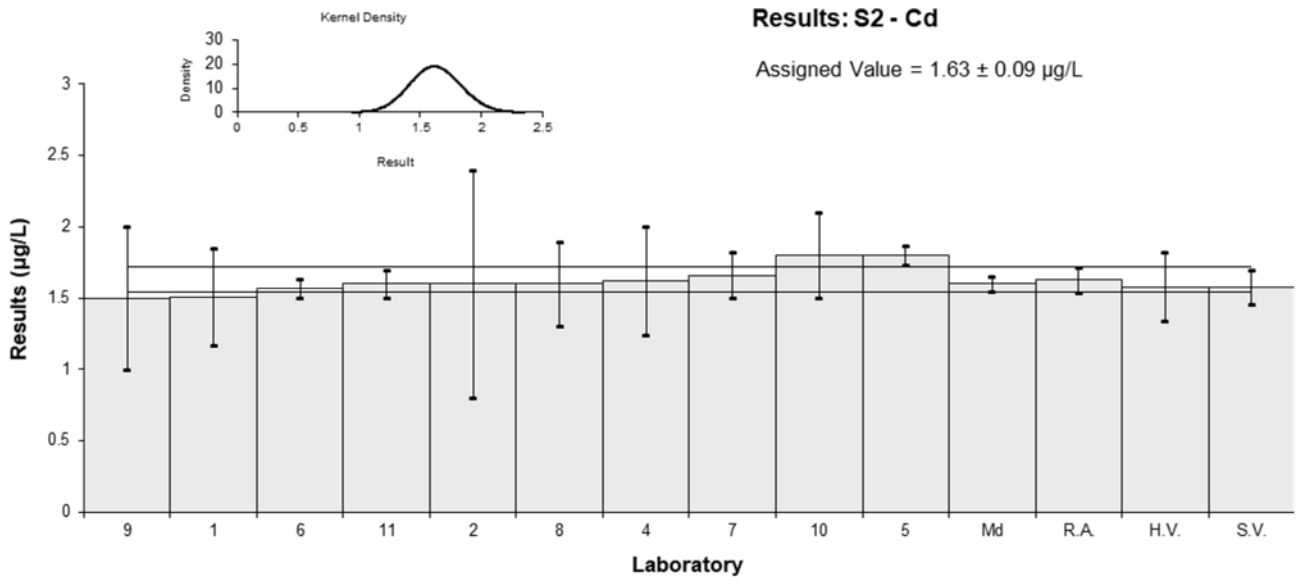
Sample No.	S2
Matrix.	Sea water
Analyte.	Cd
Units	µg/L

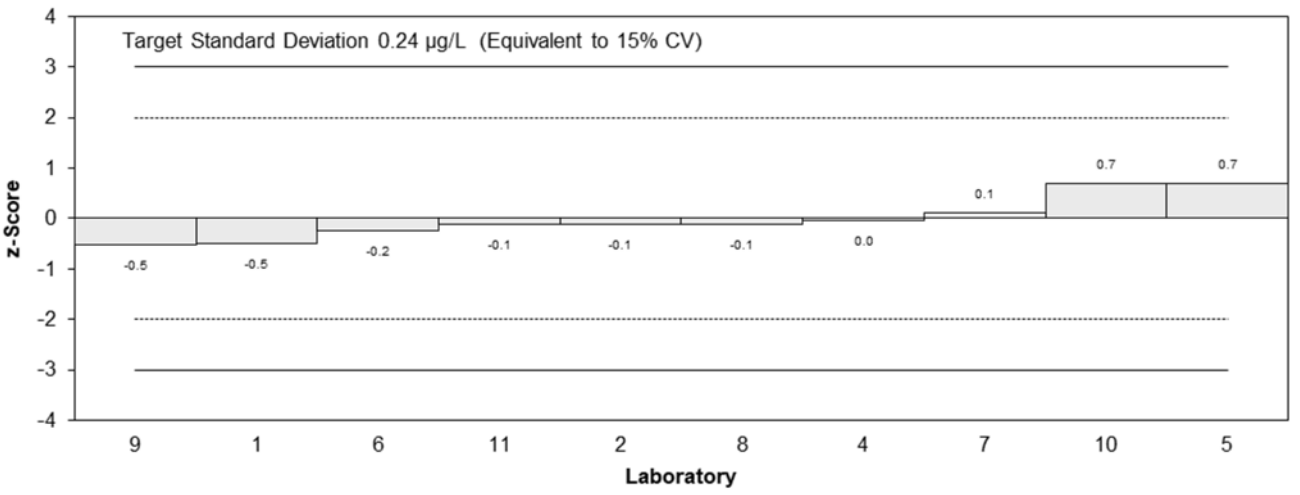
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.51	0.34	-0.49	-0.34
2	1.6	0.8	-0.12	-0.04
4	1.62	0.38	-0.04	-0.03
5	1.8	0.07	0.70	1.49
6	1.57	0.066	-0.25	-0.54
7	1.66	0.16	0.12	0.16
8	1.6	0.3	-0.12	-0.10
9	1.5	0.5	-0.53	-0.26
10	1.8	0.3	0.70	0.54
11	1.6	0.1	-0.12	-0.22

Statistics

Assigned Value	1.63	0.09
Spike	1.58	0.12
Homogeneity Value	1.58	0.24
Robust Average	1.63	0.09
Median	1.60	0.05
Mean	1.63	
N	10	
Max.	1.8	
Min.	1.5	
Robust SD	0.12	
Robust CV	7.2%	


Kernel Density
Density
Result
Results: S2 - Cd
Assigned Value = 1.63 ± 0.09 µg/L
Results (µg/L)
Laboratory
9
1
6
11
2
8
4
7
10
5
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cd
Target Standard Deviation 0.24 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.5
-0.5
-0.2
-0.1
-0.1
-0.1
0.0
0.1
0.7
0.7

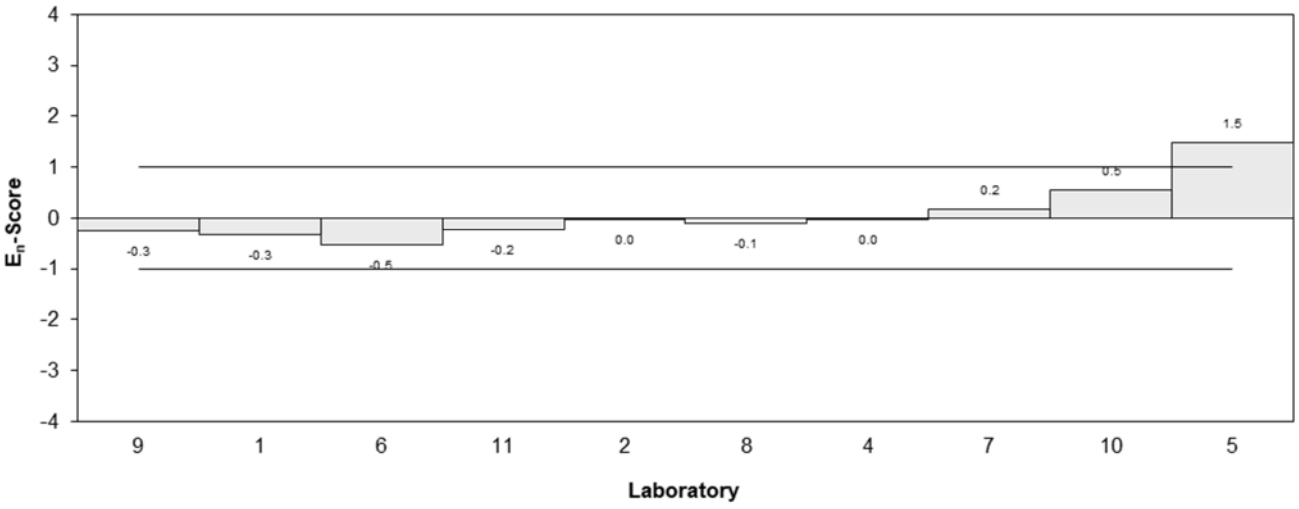

En-Scores: S2 - Cd
En-Score
Laboratory
-0.3
-0.3
-0.5
-0.2
0.0
-0.1
0.0
0.2
0.5
1.5

Figure 25

Table 28

Sample Details

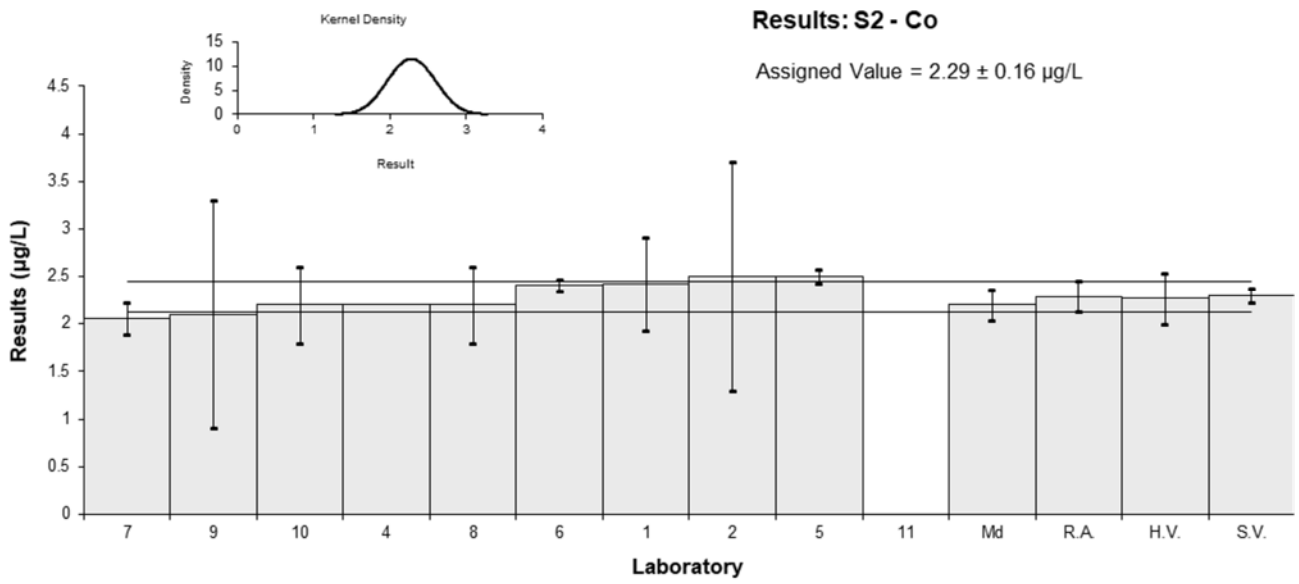
Sample No.	S2
Matrix.	Sea water
Analyte.	Co
Units	µg/L

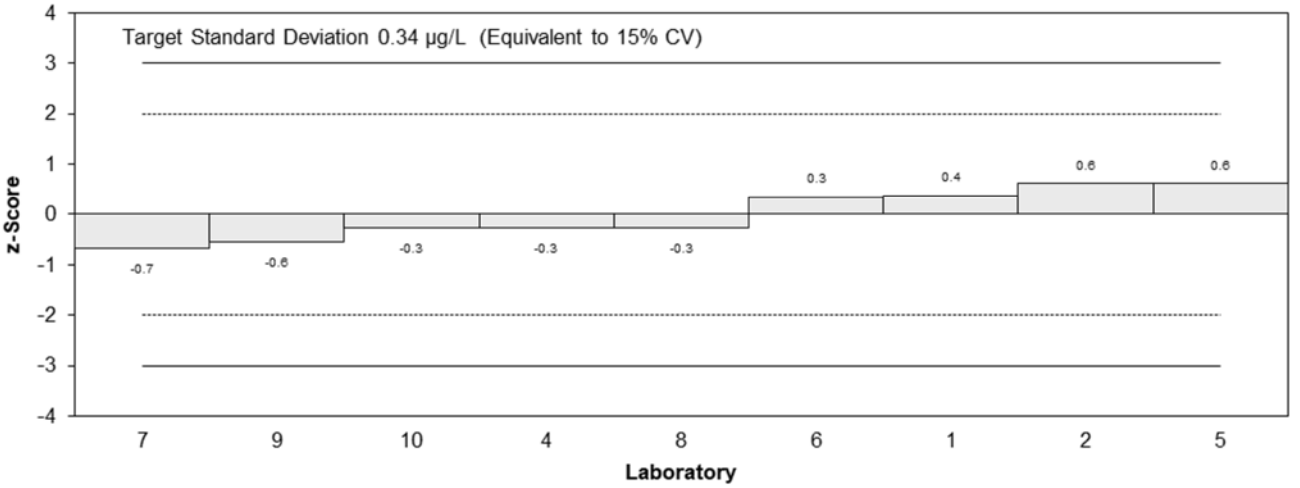
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.42	0.49	0.38	0.25
2	2.5	1.2	0.61	0.17
4	2.2	NR	-0.26	-0.56
5	2.5	0.08	0.61	1.17
6	2.41	0.058	0.35	0.71
7	2.06	0.17	-0.67	-0.99
8	2.2	0.4	-0.26	-0.21
9	2.1	1.2	-0.55	-0.16
10	2.2	0.4	-0.26	-0.21
11	NT	NT		

Statistics

Assigned Value	2.29	0.16
Spike	2.30	0.07
Homogeneity Value	2.27	0.27
Robust Average	2.29	0.16
Median	2.20	0.16
Mean	2.29	
N	9	
Max.	2.5	
Min.	2.06	
Robust SD	0.19	
Robust CV	8.5%	


Kernel Density
Density
Result
Results: S2 - Co
Assigned Value = 2.29 ± 0.16 µg/L
Results (µg/L)
Laboratory
7
9
10
4
8
6
1
2
5
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Co
Target Standard Deviation 0.34 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.7
-0.6
-0.3
-0.3
-0.3
0.3
0.4
0.6
0.6

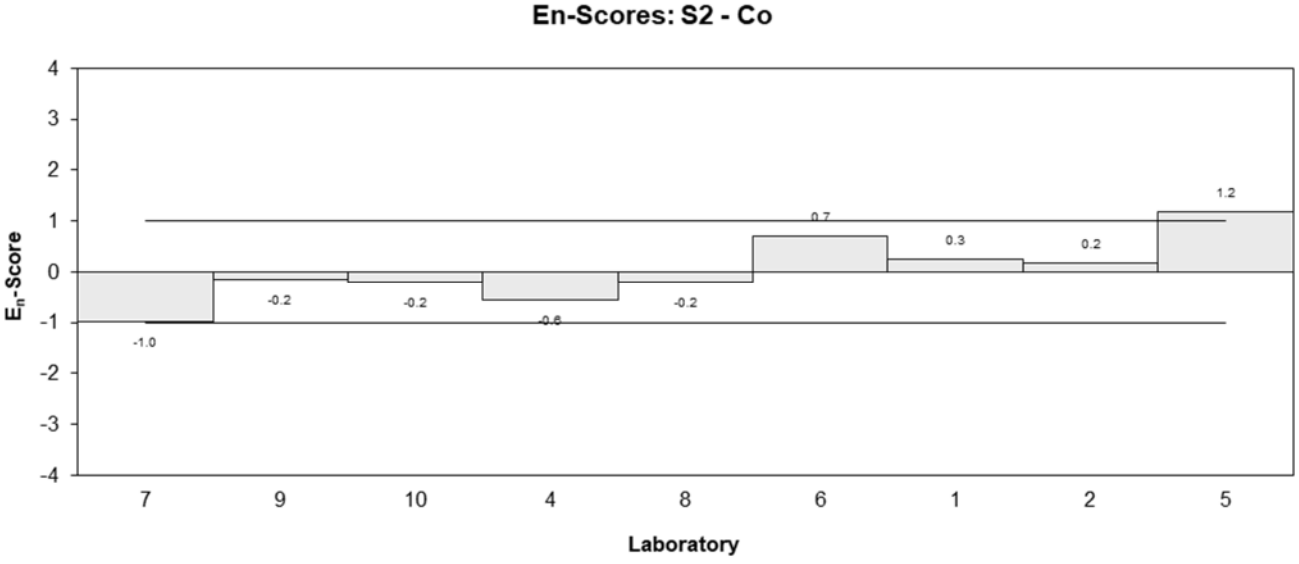

En-Scores: S2 - Co
En-Score
Laboratory
-1.0
-0.2
-0.2
-0.6
-0.2
0.7
0.3
0.2
1.2

Figure 26

Table 29

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	Cr
Units	µg/L

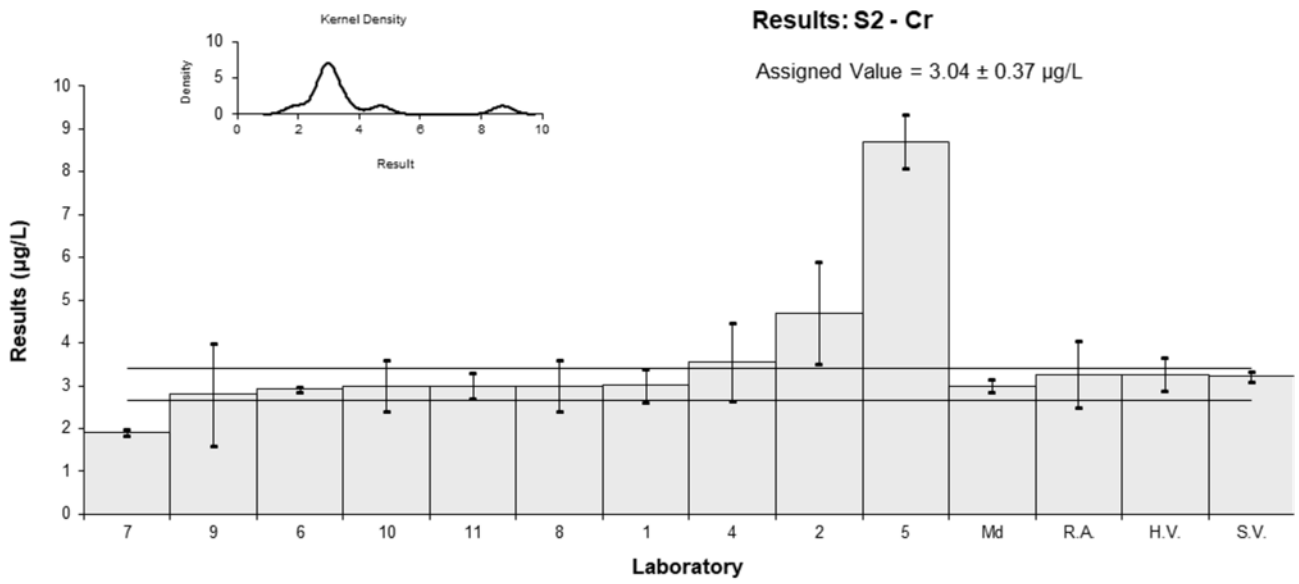
Participant Results

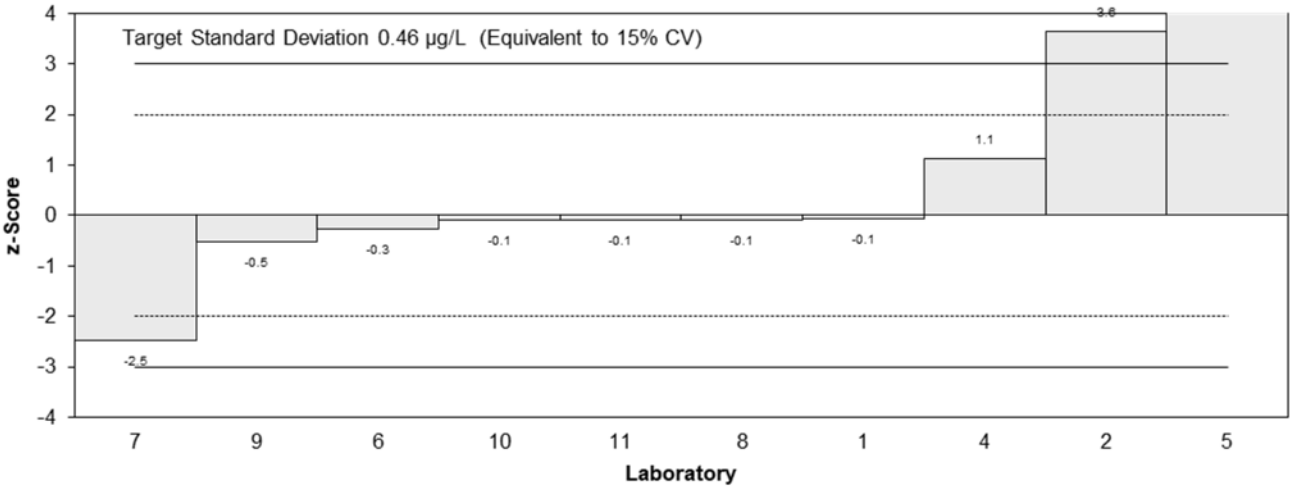
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.01	0.39	-0.07	-0.06
2	4.7	1.2	3.64	1.32
4	3.56	0.91	1.14	0.53
5	8.7	0.63	12.41	7.75
6	2.92	0.062	-0.26	-0.32
7	1.91	0.07	-2.48	-3.00
8	3.0	0.6	-0.09	-0.06
9	2.8	1.2	-0.53	-0.19
10	3.0	0.6	-0.09	-0.06
11	3.0	0.3	-0.09	-0.08

Statistics

Assigned Value*	3.04	0.37
Spike	3.22	0.12
Homogeneity Value	3.26	0.39
Robust Average	3.26	0.78
Median	3.00	0.15
Mean	3.66	
N	10	
Max.	8.7	
Min.	1.91	
Robust SD	0.98	
Robust CV	30%	

*Robust Average excluding laboratory 5.


Kernel Density
Density
Result
Results: S2 - Cr
Assigned Value = 3.04 ± 0.37 µg/L
Results (µg/L)
Laboratory
7
9
6
10
11
8
1
4
2
5
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cr
Target Standard Deviation 0.46 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.5
-0.5
-0.3
-0.1
-0.1
-0.1
-0.1
1.1
3.6

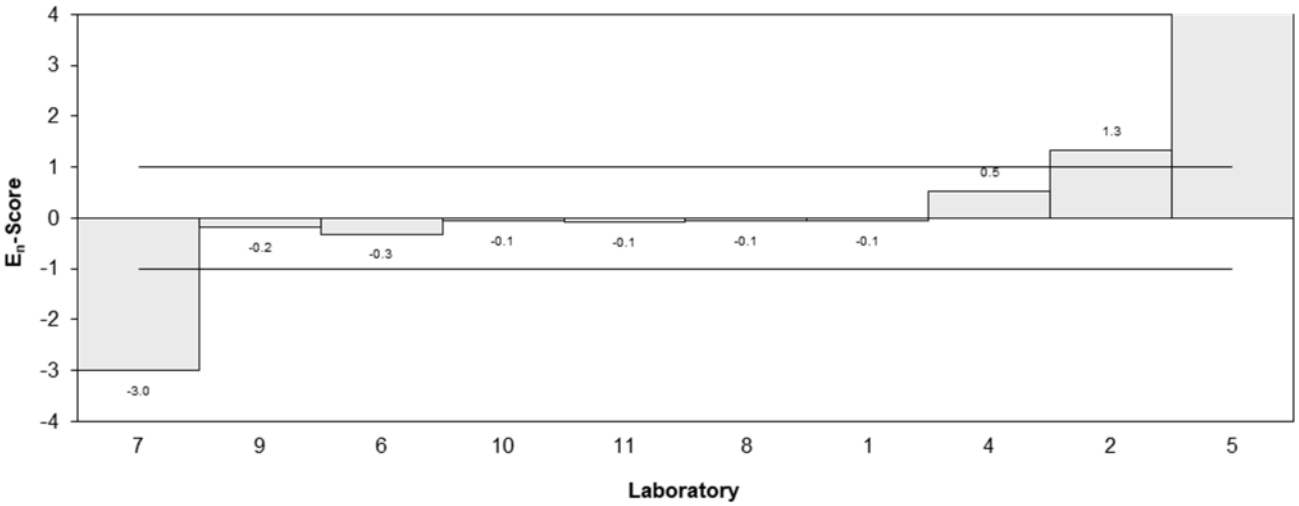

En-Scores: S2 - Cr
En-Score
Laboratory
-3.0
-0.2
-0.3
-0.1
-0.1
-0.1
-0.1
0.5
1.3

Figure 27

Table 30

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	Cu
Units	µg/L

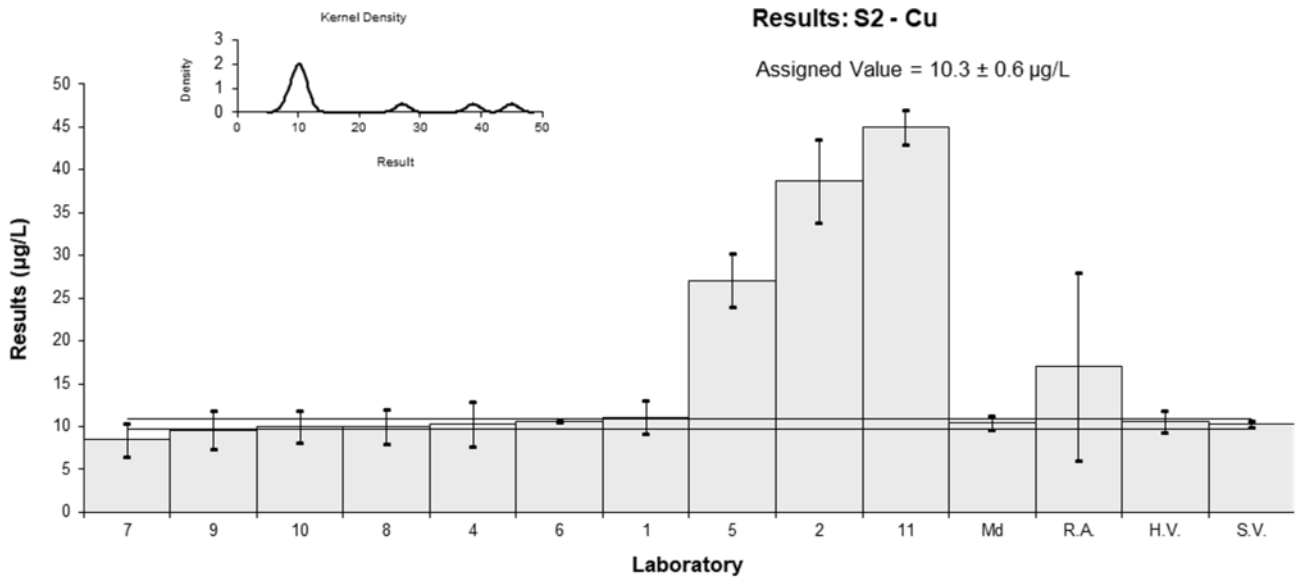
Participant Results

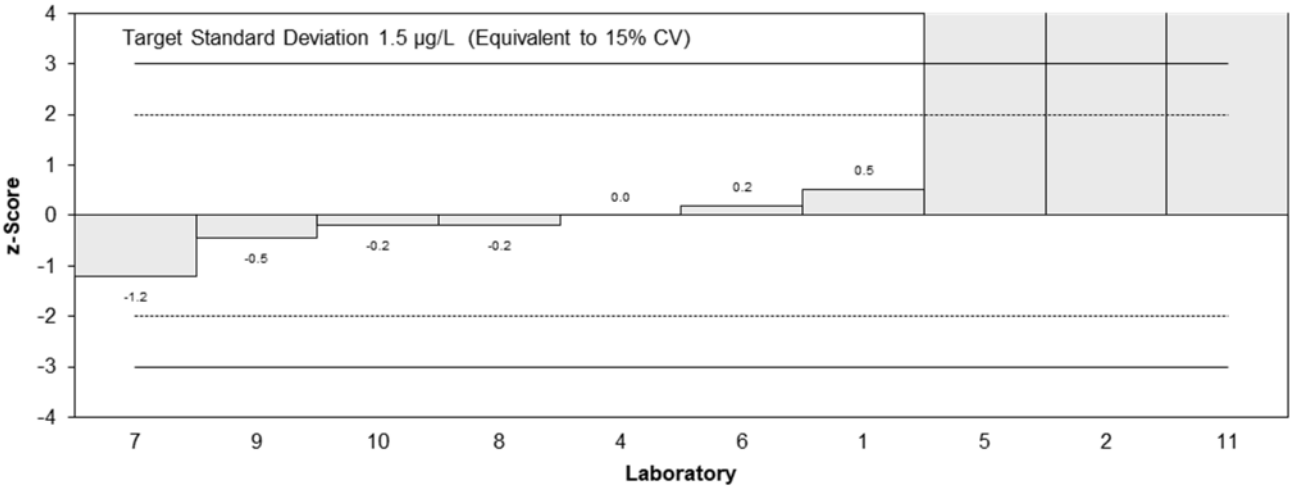
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	11.1	1.9	0.52	0.40
2	38.7	4.8	18.38	5.87
4	10.3	2.6	0.00	0.00
5	27.1	3.1	10.87	5.32
6	10.6	0.08	0.19	0.50
7	8.44	1.95	-1.20	-0.91
8	10	2	-0.19	-0.14
9	9.6	2.2	-0.45	-0.31
10	10	1.8	-0.19	-0.16
11	45	2	22.46	16.62

Statistics

Assigned Value*	10.3	0.6
Spike	10.3	0.4
Homogeneity Value	10.6	1.3
Robust Average	17	11
Median	10.5	0.8
Mean	18.1	
N	10	
Max.	45	
Min.	8.44	
Robust SD	13	
Robust CV	79%	

*Robust Average excluding laboratories 2, 5, 7 and 11.


Kernel Density
Density
Result
Results: S2 - Cu
Assigned Value = 10.3 ± 0.6 µg/L
Results (µg/L)
Laboratory
7
9
10
8
4
6
1
5
2
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cu
Target Standard Deviation 1.5 µg/L (Equivalent to 15% CV)
z-Score
-1.2
-0.5
-0.2
-0.2
0.0
0.2
0.5
Laboratory
7
9
10
8
4
6
1
5
2
11

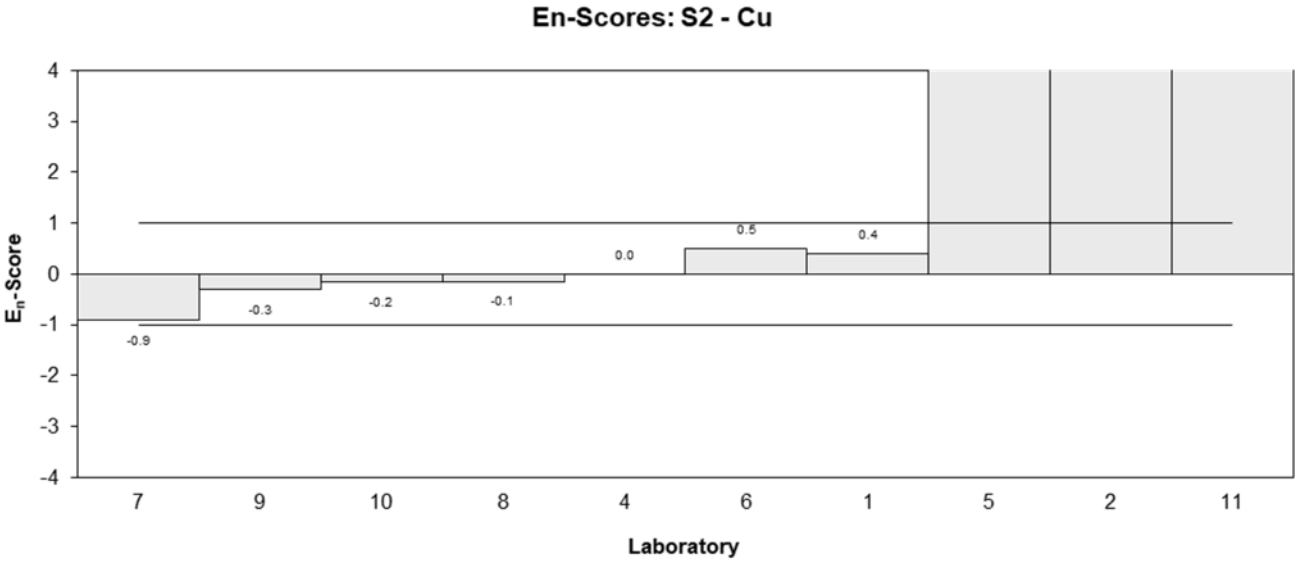

En-Scores: S2 - Cu
En-Score
-0.9
-0.3
-0.2
-0.1
0.0
0.5
0.4
Laboratory
7
9
10
8
4
6
1
5
2
11

Figure 28

Table 31

Sample Details

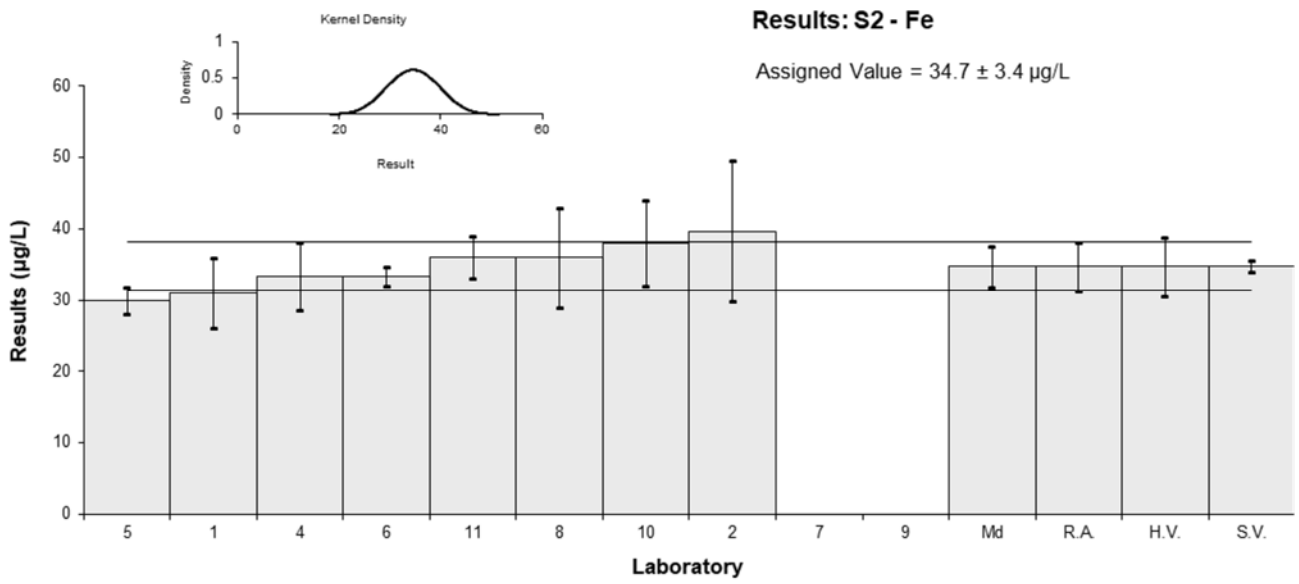
Sample No.	S2
Matrix.	Sea water
Analyte.	Fe
Units	µg/L

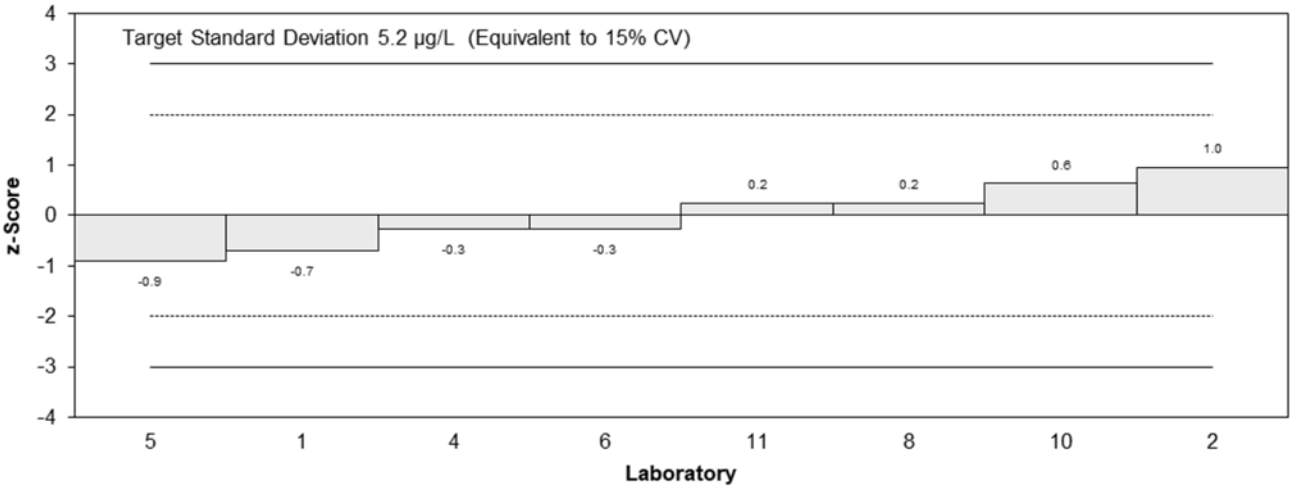
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	31.0	5.0	-0.71	-0.61
2	39.7	9.9	0.96	0.48
4	33.3	4.8	-0.27	-0.24
5	30	1.9	-0.90	-1.21
6	33.3	1.3	-0.27	-0.38
7	NT	NT		
8	36	7	0.25	0.17
9	NT	NT		
10	38	6.0	0.63	0.48
11	36	3	0.25	0.29

Statistics

Assigned Value	34.7	3.4
Spike	34.7	0.8
Homogeneity Value	34.7	4.2
Robust Average	34.7	3.4
Median	34.7	2.9
Mean	34.7	
N	8	
Max.	39.7	
Min.	30	
Robust SD	3.8	
Robust CV	11%	


Kernel Density
Density
Result
Results: S2 - Fe
Assigned Value = 34.7 ± 3.4 µg/L
Results (µg/L)
Laboratory
5
1
4
6
11
8
10
2
7
9
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Fe
Target Standard Deviation 5.2 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.9
-0.7
-0.3
-0.3
0.2
0.2
0.6
1.0

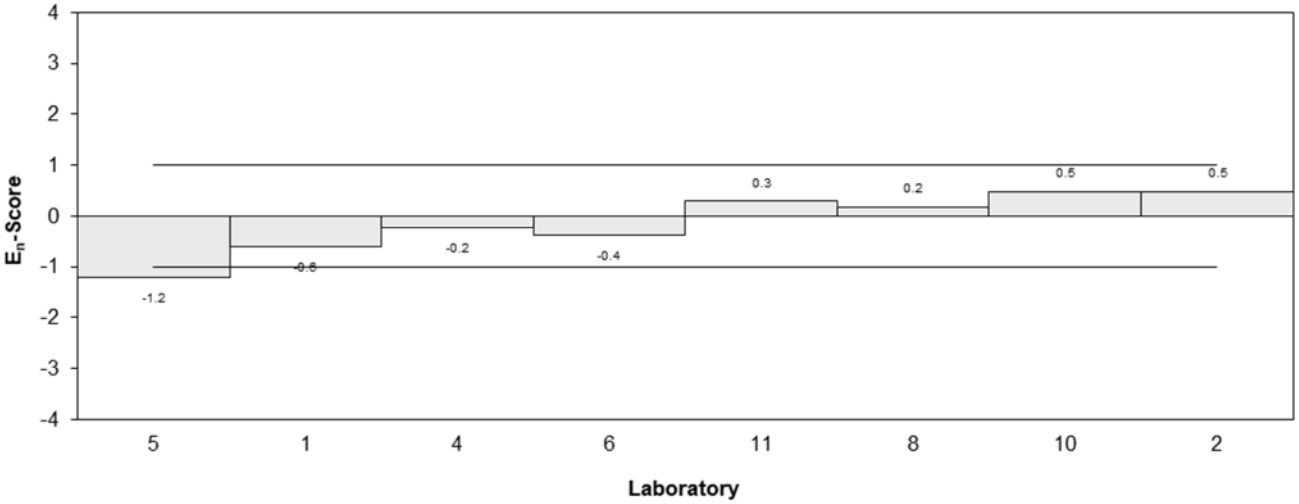

En-Scores: S2 - Fe
En-Score
Laboratory
-1.2
-0.6
-0.2
-0.4
0.3
0.2
0.5
0.5

Figure 29

Table 32

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	Hg
Units	µg/L

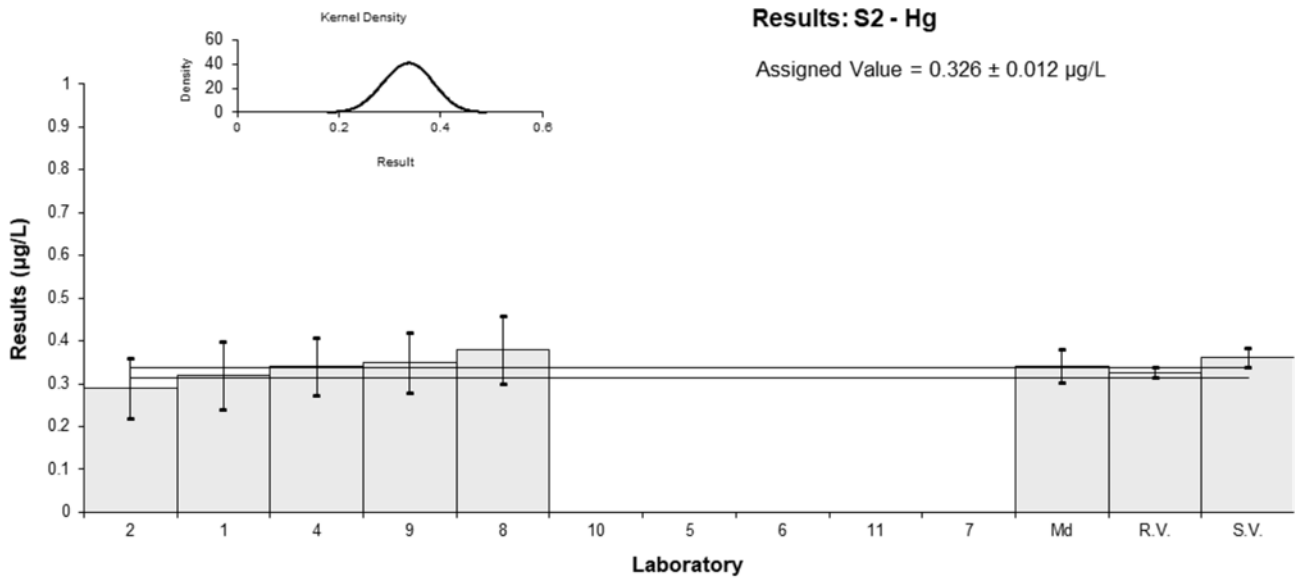
Participant Results

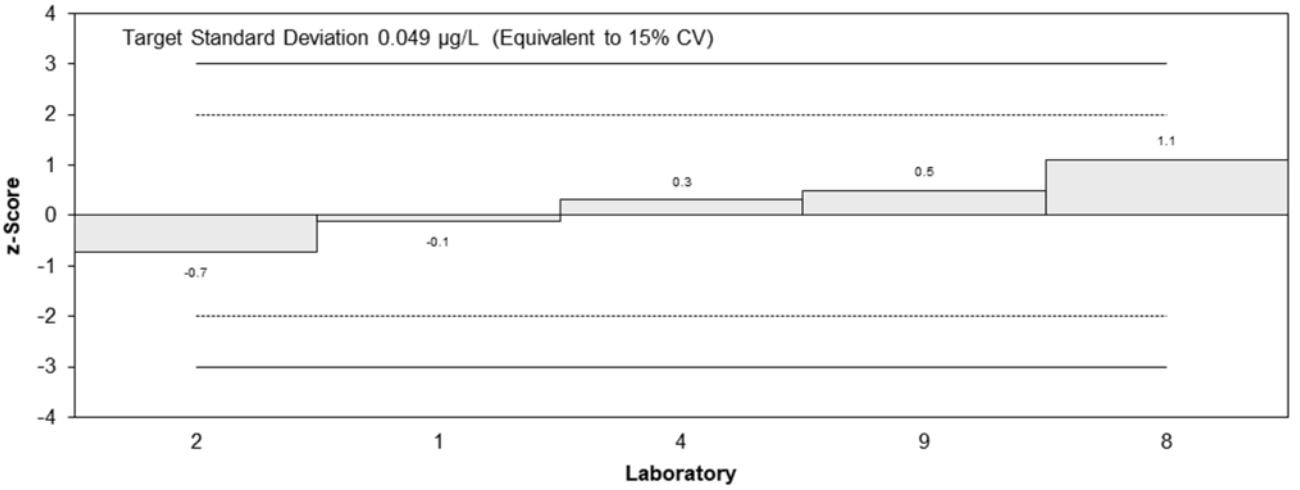
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.32	0.08	-0.12	-0.07
2	0.29	0.07	-0.74	-0.51
4	0.341	0.067	0.31	0.22
5	NR	NR		
6	NR	NR		
7	NT	NT		
8	0.38	0.08	1.10	0.67
9	0.35	0.07	0.49	0.34
10	<0.5	NR		
11	NT	NT		

Statistics

Assigned Value*	0.326	0.012
Spike	0.362	0.022
Reference Value*	0.326	0.012
Median	0.341	0.039
Mean	0.336	
N	5	
Max.	0.38	
Min.	0.29	

*Reference Value by dIDMS


Kernel Density
Density
Result
Results: S2 - Hg
Assigned Value = 0.326 ± 0.012 µg/L
Results (µg/L)
Laboratory
2
1
4
9
8
10
5
6
11
7
Md
R.V.
S.V.


z-Scores: S2 - Hg
Target Standard Deviation 0.049 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.7
-0.1
0.3
0.5
1.1
2
1
4
9
8

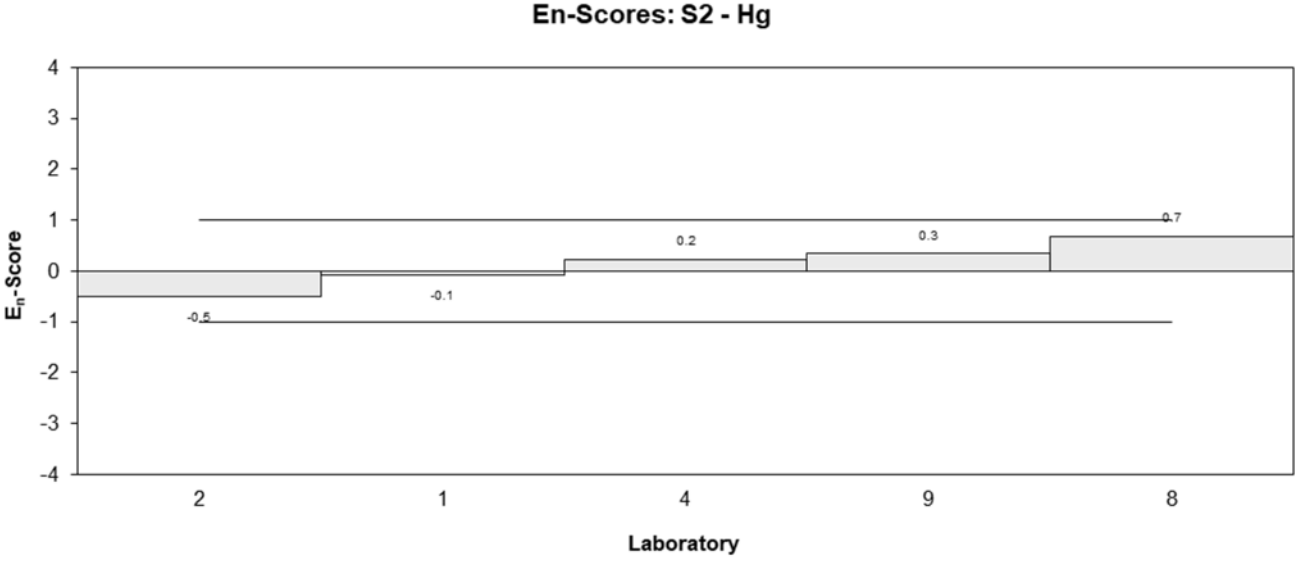

En-Scores: S2 - Hg
En-Score
Laboratory
-0.5
-0.1
0.2
0.3
0.7
2
1
4
9
8

Figure 30

Table 33

Sample Details

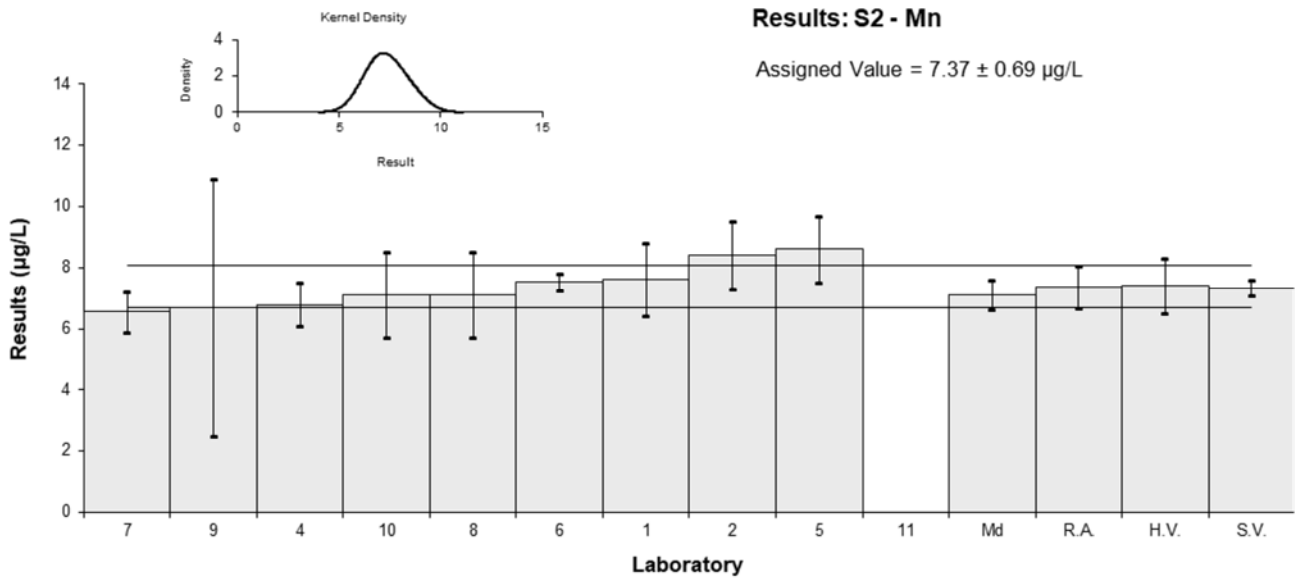
Sample No.	S2
Matrix.	Sea water
Analyte.	Mn
Units	µg/L

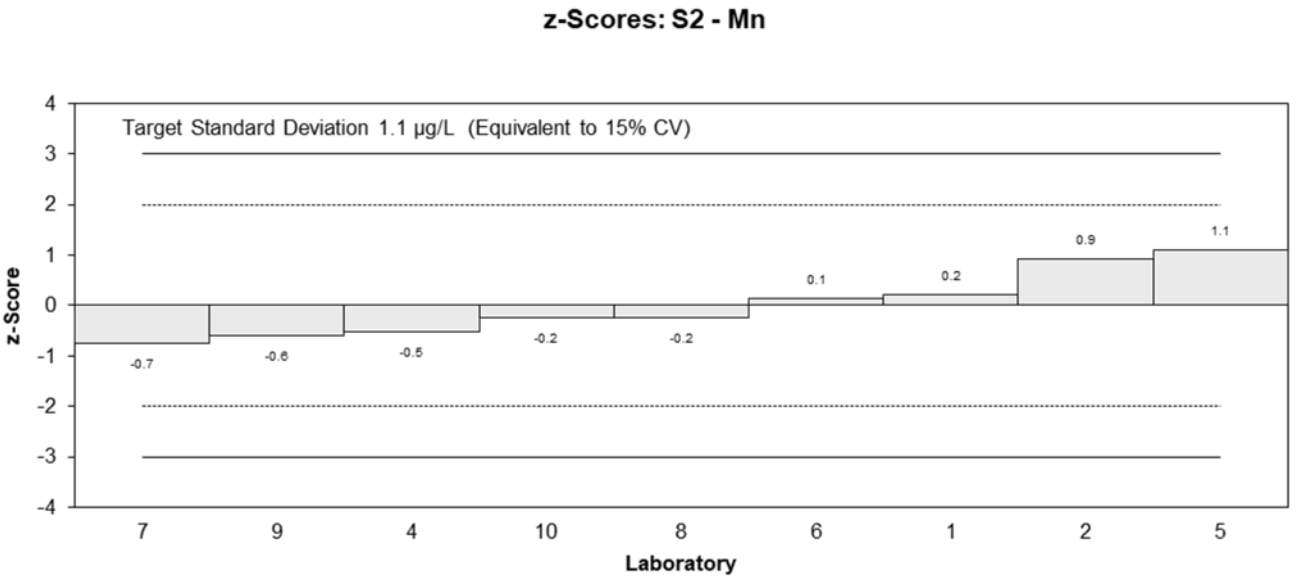
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.6	1.2	0.21	0.17
2	8.4	1.1	0.93	0.79
4	6.79	0.72	-0.52	-0.58
5	8.6	1.1	1.11	0.95
6	7.53	0.28	0.14	0.21
7	6.55	0.67	-0.74	-0.85
8	7.1	1.4	-0.24	-0.17
9	6.7	4.2	-0.61	-0.16
10	7.1	1.4	-0.24	-0.17
11	NT	NT		

Statistics

Assigned Value	7.37	0.69
Spike	7.34	0.25
Homogeneity Value	7.40	0.89
Robust Average	7.37	0.69
Median	7.10	0.49
Mean	7.37	
N	9	
Max.	8.6	
Min.	6.55	
Robust SD	0.83	
Robust CV	11%	


Results: S2 - Mn
Assigned Value = 7.37 ± 0.69 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
9
4
10
8
6
1
2
5
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Mn
Target Standard Deviation 1.1 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.7
-0.6
-0.5
-0.2
-0.2
0.1
0.2
0.9
1.1

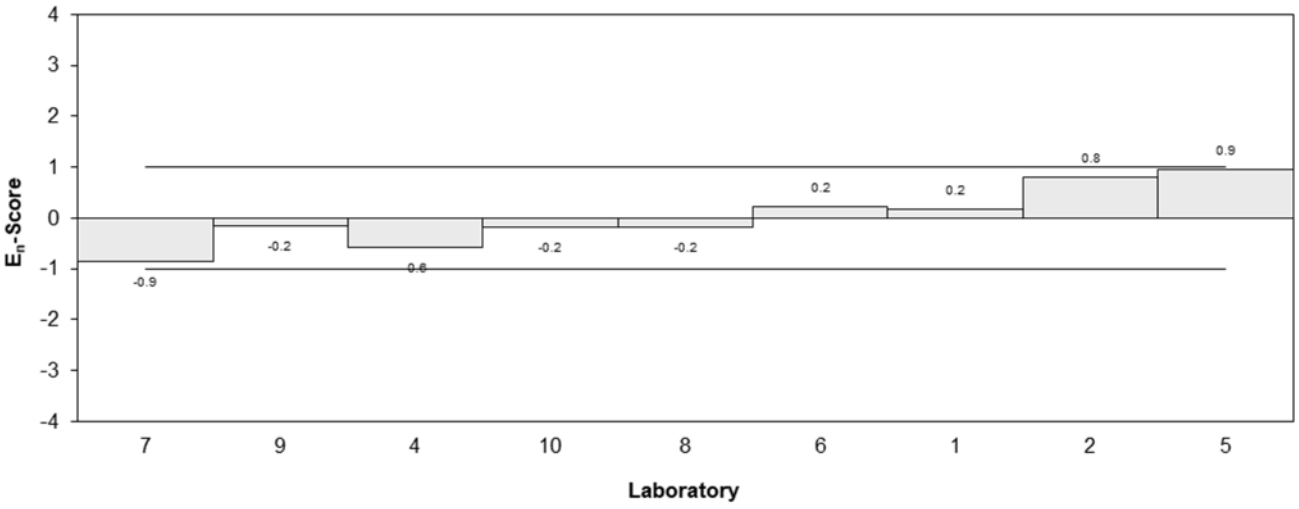

En-Scores: S2 - Mn
En-Score
Laboratory
-0.9
-0.2
-0.6
-0.2
-0.2
0.2
0.2
0.8
0.9

Figure 31

Table 34

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	Mo
Units	µg/L

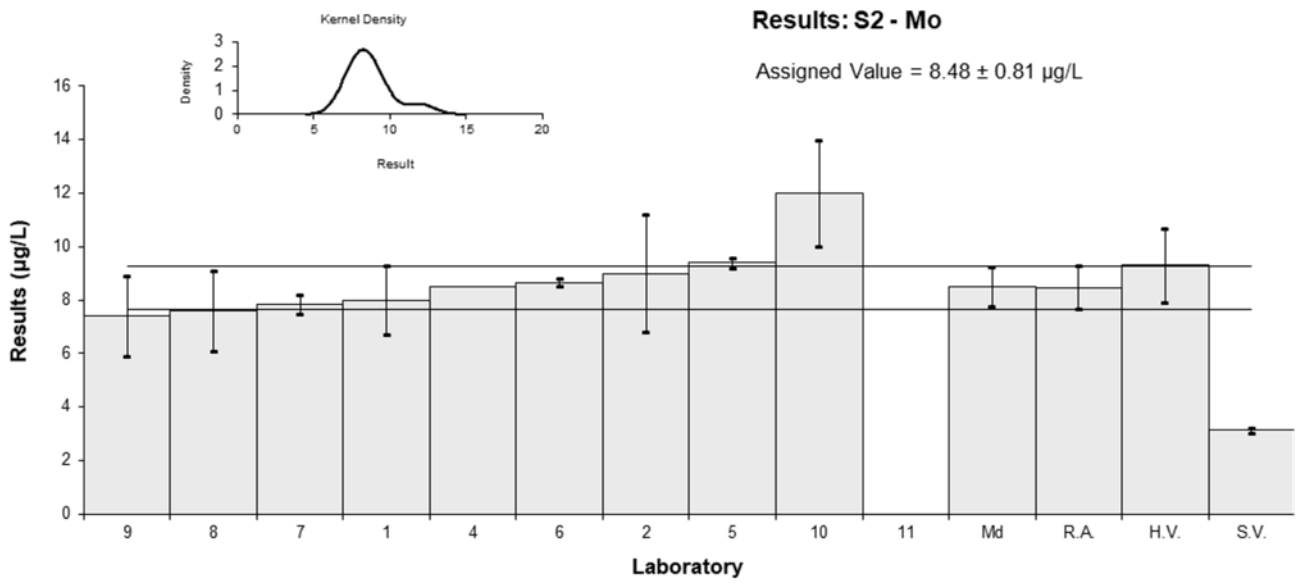
Participant Results

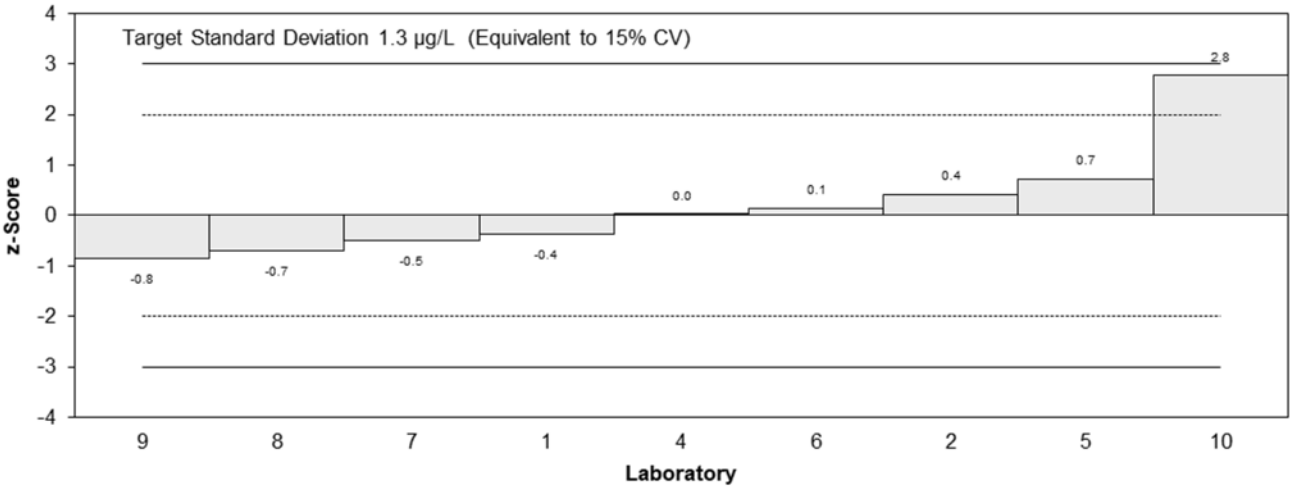
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	8.0	1.3	-0.38	-0.31
2	9.0	2.2	0.41	0.22
4	8.5	NR	0.02	0.02
5	9.4	0.2	0.72	1.10
6	8.67	0.13	0.15	0.23
7	7.85	0.37	-0.50	-0.71
8	7.6	1.5	-0.69	-0.52
9	7.4	1.5	-0.85	-0.63
10	12	2.0	2.77	1.63
11	NT	NT		

Statistics

Assigned Value	8.48	0.81
Spike*	3.13	0.09
Homogeneity Value	9.3	1.4
Robust Average	8.48	0.81
Median	8.50	0.74
Mean	8.71	
N	9	
Max.	12	
Min.	7.4	
Robust SD	0.97	
Robust CV	11%	

*Incurred value not included


Kernel Density
Density
Result
Results: S2 - Mo
Assigned Value = 8.48 ± 0.81 µg/L
Results (µg/L)
Laboratory
9
8
7
1
4
6
2
5
10
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Mo
Target Standard Deviation 1.3 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.8
-0.7
-0.5
-0.4
0.0
0.1
0.4
0.7
2.8

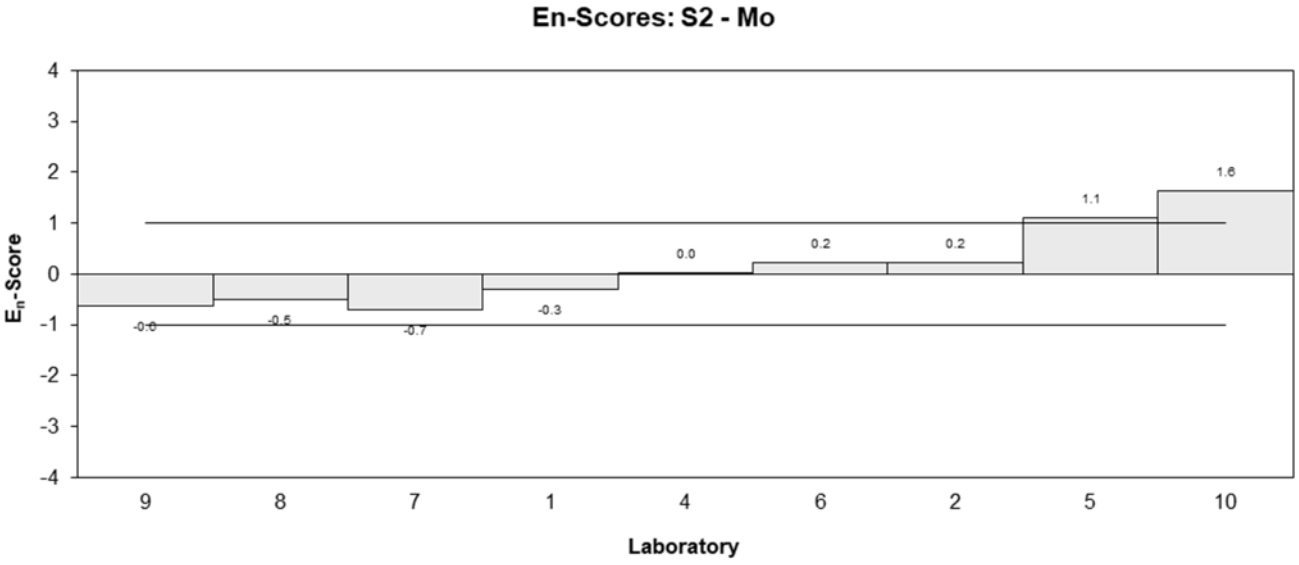

En-Scores: S2 - Mo
En-Score
Laboratory
-0.6
-0.5
-0.7
-0.3
0.0
0.2
0.2
1.1
1.6

Figure 32

Table 35

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	Ni
Units	µg/L

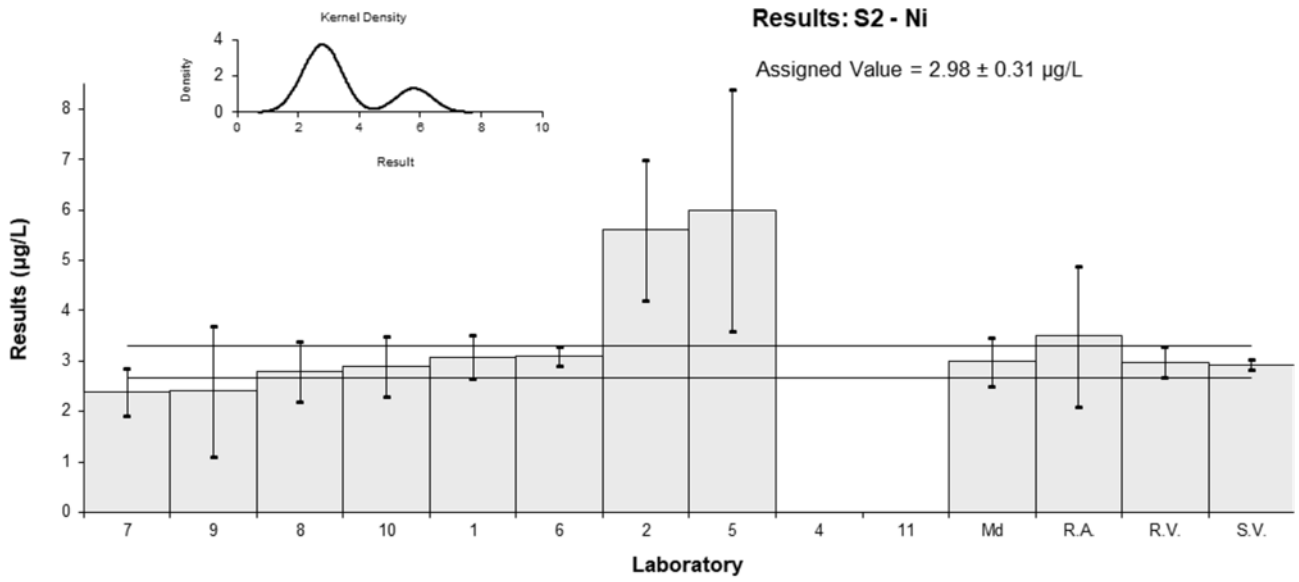
Participant Results

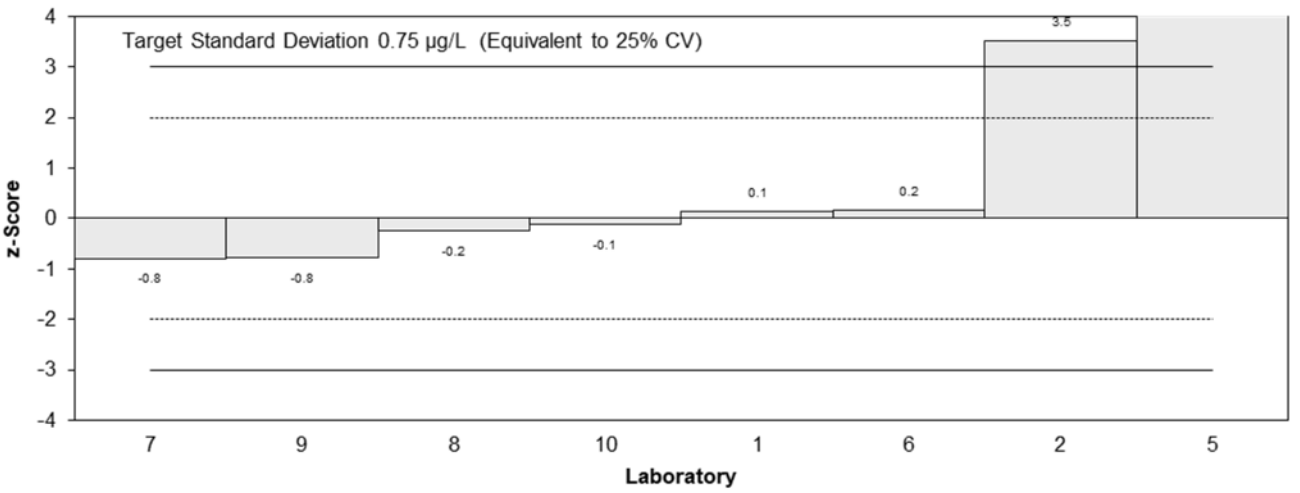
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.08	0.43	0.13	0.19
2	5.6	1.4	3.52	1.83
4	<7	NR		
5	6.0	2.4	4.05	1.25
6	3.10	0.19	0.16	0.33
7	2.39	0.47	-0.79	-1.05
8	2.8	0.6	-0.24	-0.27
9	2.4	1.3	-0.78	-0.43
10	2.9	0.6	-0.11	-0.12
11	NT	NT		

Statistics

Assigned Value*	2.98	0.31
Spike	2.93	0.10
Reference Value*	2.98	0.31
Robust Average	3.5	1.4
Median	2.99	0.48
Mean	3.53	
N	8	
Max.	6	
Min.	2.39	
Robust SD	1.6	
Robust CV	45%	

*Reference Value by dIDMS


Results: S2 - Ni
Assigned Value = 2.98 ± 0.31 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
9
8
10
1
6
2
5
4
11
Md
R.A.
R.V.
S.V.


z-Scores: S2 - Ni
Target Standard Deviation 0.75 µg/L (Equivalent to 25% CV)
z-Score
-0.8
-0.8
-0.2
-0.1
0.1
0.2
3.5
Laboratory
7
9
8
10
1
6
2
5

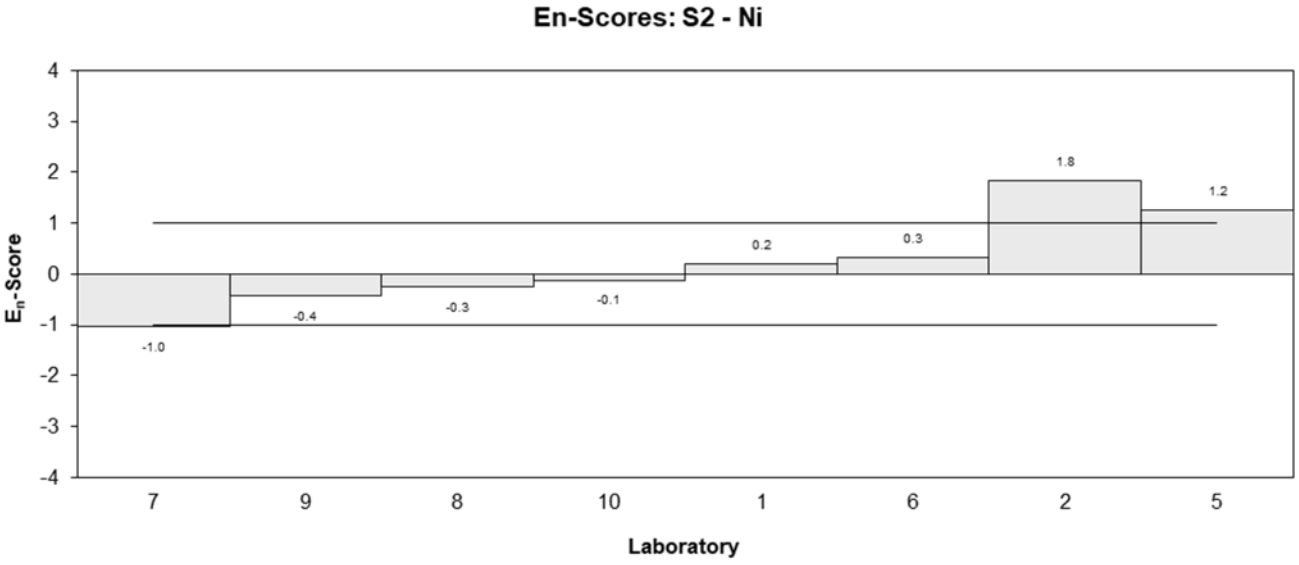

En-Scores: S2 - Ni
En-Score
-1.0
-0.4
-0.3
-0.1
0.2
0.3
1.8
1.2
Laboratory
7
9
8
10
1
6
2
5

Figure 33

Table 36

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	Pb
Units	µg/L

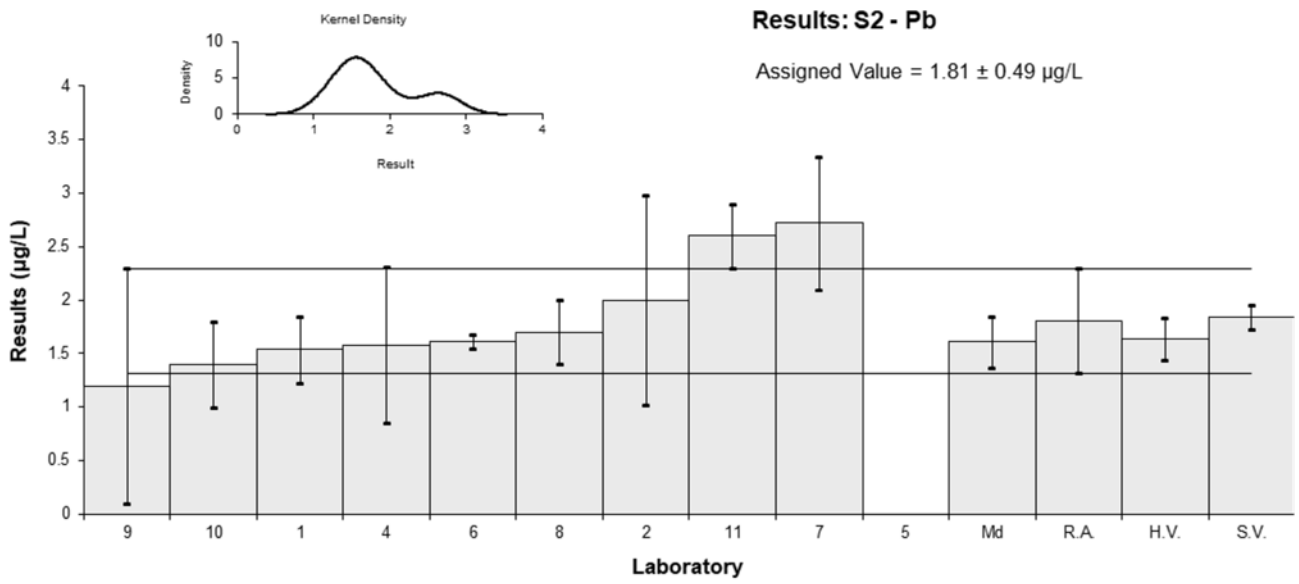
Participant Results

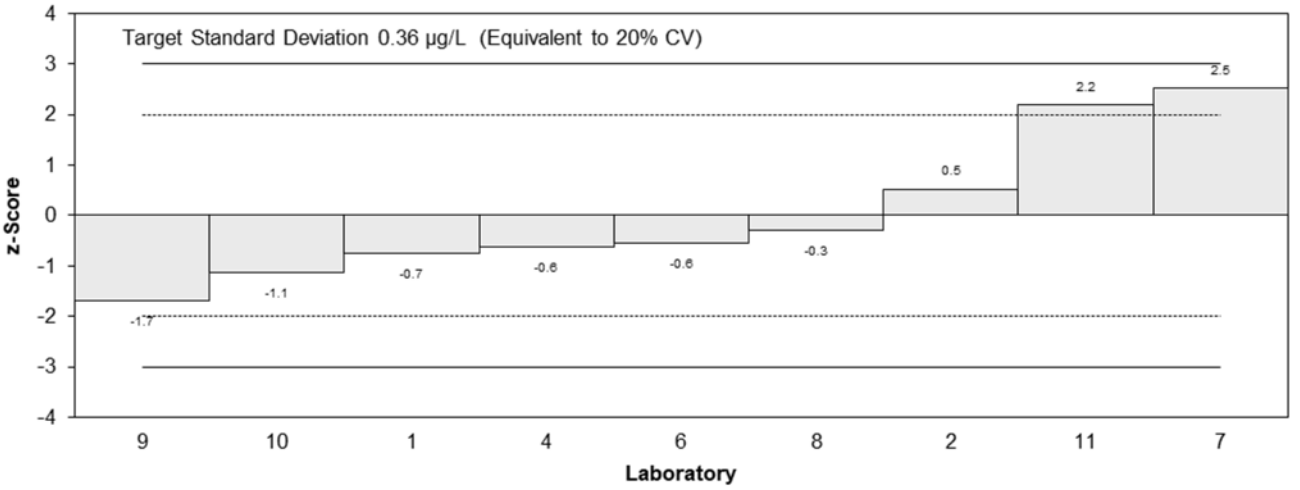
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.54	0.31	-0.75	-0.47
2	2	0.98	0.52	0.17
4	1.58	0.73	-0.64	-0.26
5	NR	NR		
6	1.61	0.063	-0.55	-0.40
7	2.72	0.62	2.51	1.15
8	1.7	0.3	-0.30	-0.19
9	1.2	1.1	-1.69	-0.51
10	1.4	0.4	-1.13	-0.65
11	2.6	0.3	2.18	1.38

Statistics

Assigned Value	1.81	0.49
Spike*	1.84	0.11
Homogeneity Value	1.64	0.20
Robust Average	1.81	0.49
Median	1.61	0.24
Mean	1.82	
N	9	
Max.	2.72	
Min.	1.2	
Robust SD	0.59	
Robust CV	33%	

*Incurred value not included


Kernel Density
Density
Result
Results: S2 - Pb
Assigned Value = 1.81 ± 0.49 µg/L
Results (µg/L)
Laboratory
9
10
1
4
6
8
2
11
7
5
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Pb
Target Standard Deviation 0.36 µg/L (Equivalent to 20% CV)
z-Score
Laboratory
-1.7
-1.1
-0.7
-0.6
-0.6
-0.3
0.5
2.2
2.5

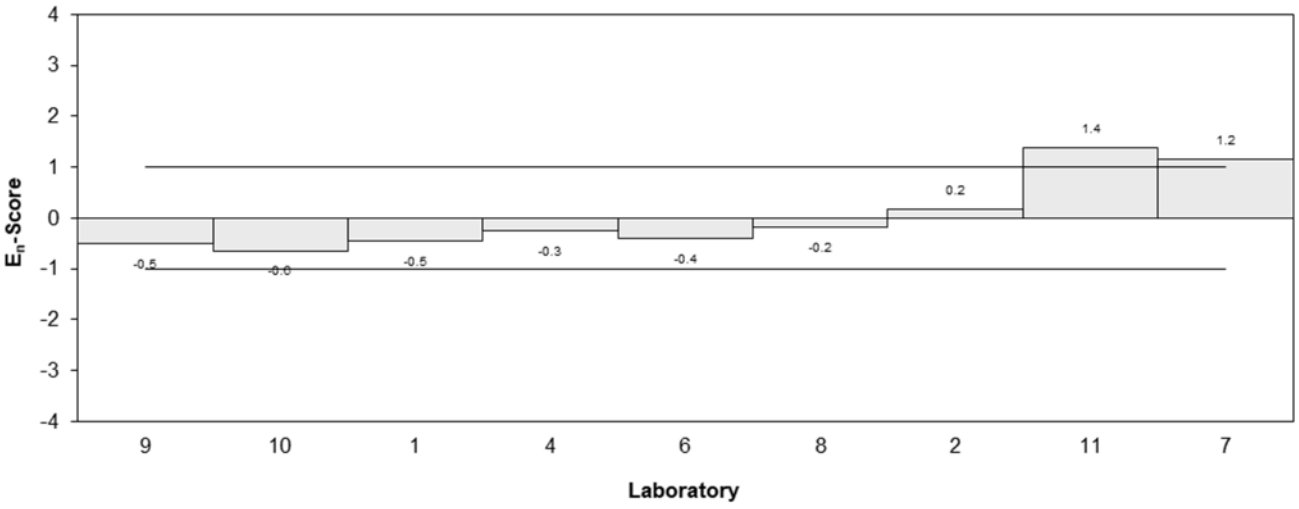

En-Scores: S2 - Pb
En-Score
Laboratory
-0.5
-0.6
-0.5
-0.3
-0.4
-0.2
0.2
1.4
1.2

Figure 34

Table 37

Sample Details

Sample No.	S2
Matrix.	Sea water
Analyte.	Sb
Units	µg/L

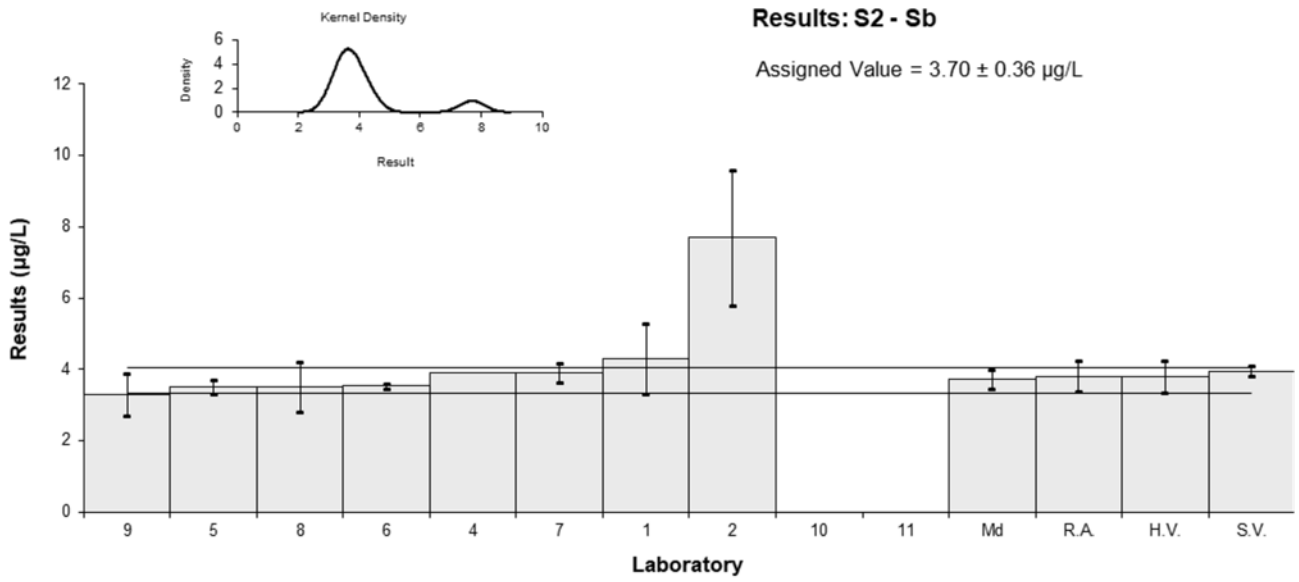
Participant Results

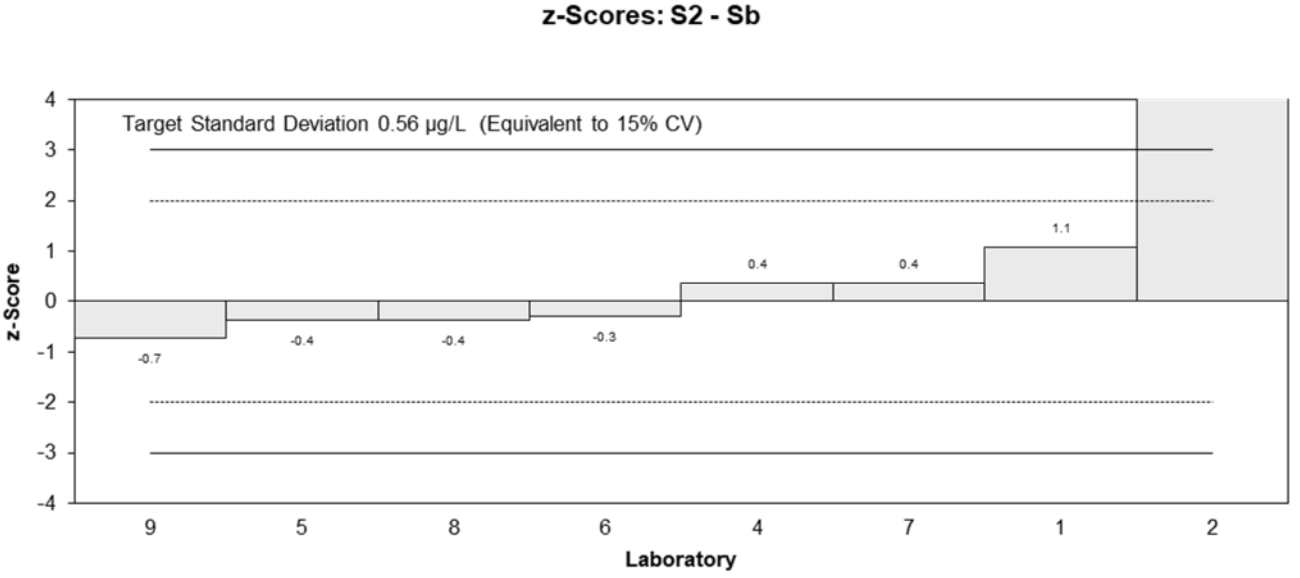
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.3	1.0	1.08	0.56
2	7.7	1.9	7.21	2.07
4	3.9	NR	0.36	0.56
5	3.5	0.2	-0.36	-0.49
6	3.53	0.067	-0.31	-0.46
7	3.90	0.26	0.36	0.45
8	3.5	0.7	-0.36	-0.25
9	3.3	0.6	-0.72	-0.57
10	NT	NT		
11	NT	NT		

Statistics

Assigned Value*	3.70	0.36
Spike	3.96	0.13
Homogeneity Value	3.79	0.45
Robust Average	3.81	0.44
Median	3.72	0.27
Mean	4.20	
N	8	
Max.	7.7	
Min.	3.3	
Robust SD	0.5	
Robust CV	13%	

*Robust Average excluding laboratory 2.


Kernel Density
Density
Result
Results: S2 - Sb
Assigned Value = 3.70 ± 0.36 µg/L
Results (µg/L)
Laboratory
9
5
8
6
4
7
1
2
10
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Sb
Target Standard Deviation 0.56 µg/L (Equivalent to 15% CV)
z-Score
-0.7
-0.4
-0.4
-0.3
0.4
0.4
1.1
Laboratory
9
5
8
6
4
7
1
2

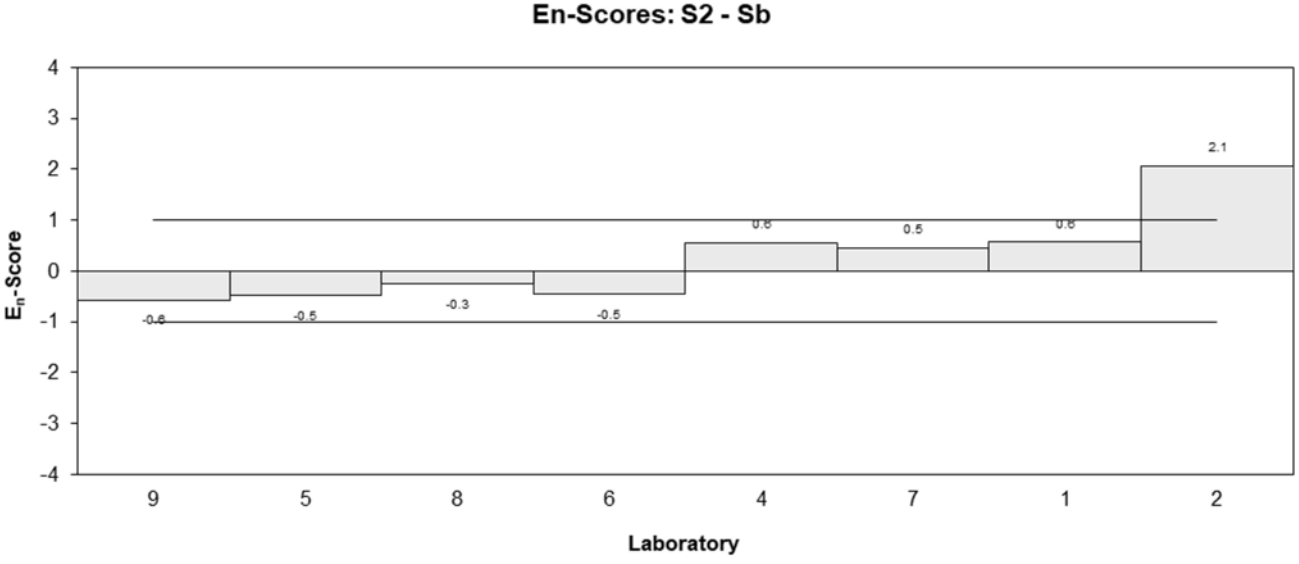

En-Scores: S2 - Sb
En-Score
-0.6
-0.5
-0.3
-0.5
0.6
0.5
0.6
2.1
Laboratory
9
5
8
6
4
7
1
2

Figure 35

Table 38

Sample Details

Sample No.	S2
Matrix.	Seawater
Analyte.	Se
Units	µg/L

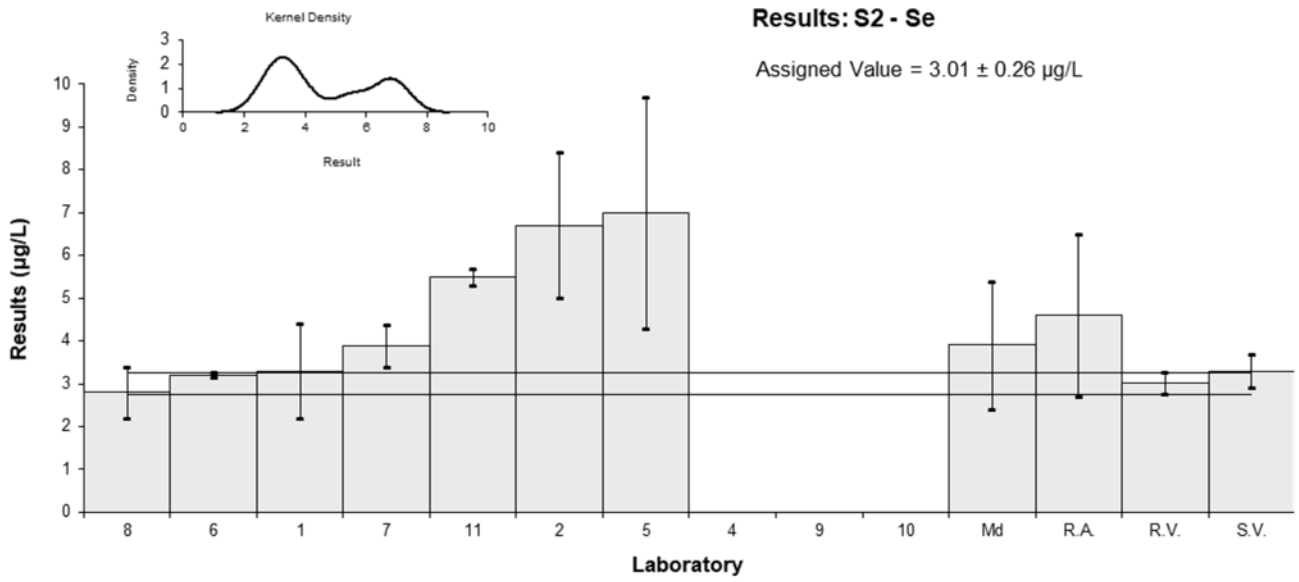
Participant Results

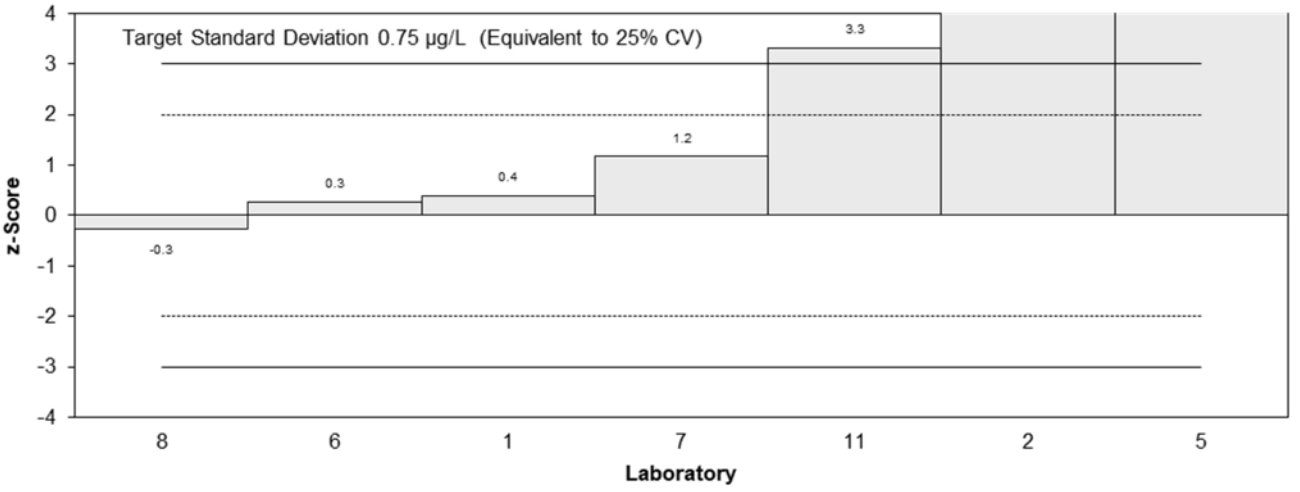
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.3	1.1	0.39	0.26
2	6.7	1.7	4.90	2.15
4	<4	2.7		
5	7	2.7	5.30	1.47
6	3.21	0.066	0.27	0.75
7	3.89	0.5	1.17	1.56
8	2.8	0.6	-0.28	-0.32
9	<5	NR		
10	NT	NT		
11	5.5	0.2	3.31	7.59

Statistics

Assigned Value*	3.01	0.26
Spike**	3.30	0.40
Reference Value*	3.01	0.26
Robust Average	4.6	1.9
Median	3.9	1.5
Mean	4.6	
N	7	
Max.	7	
Min.	2.8	
Robust SD	2	
Robust CV	43%	

*Reference Value by IDMS, **Incurred value not included


Kernel Density
Density
Result
Results: S2 - Se
Assigned Value = 3.01 ± 0.26 µg/L
Results (µg/L)
Laboratory
8
6
1
7
11
2
5
4
9
10
Md
R.A.
R.V.
S.V.


z-Scores: S2 - Se
Target Standard Deviation 0.75 µg/L (Equivalent to 25% CV)
z-Score
-0.3
0.3
0.4
1.2
3.3
Laboratory
8
6
1
7
11
2
5

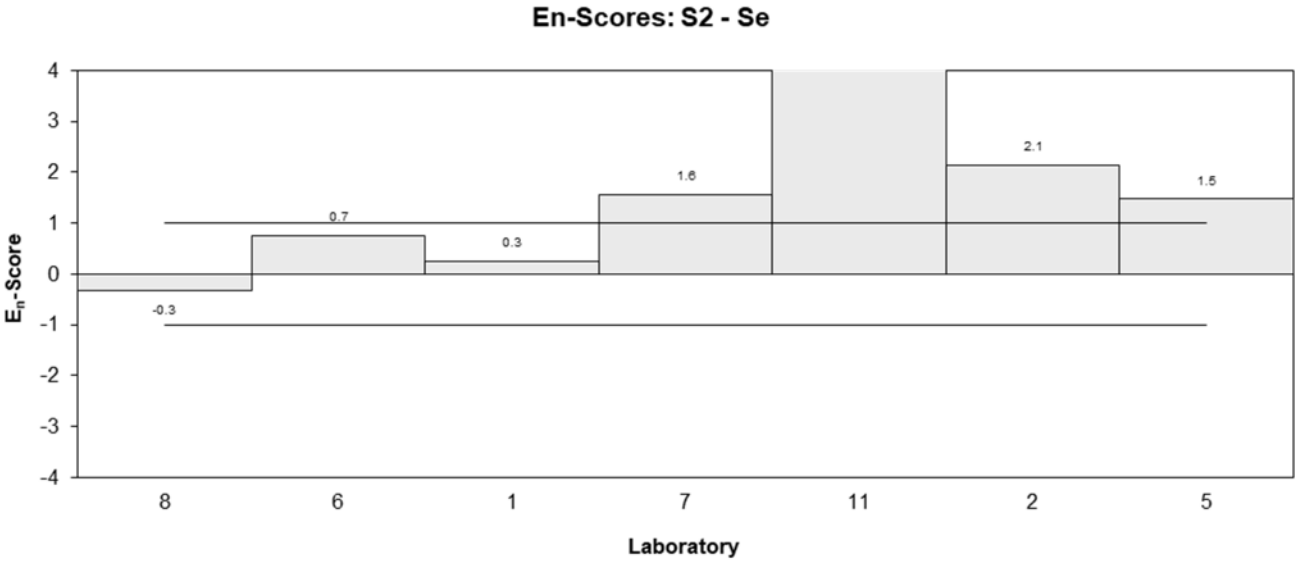

En-Scores: S2 - Se
En-Score
-0.3
0.7
0.3
1.6
2.1
1.5
Laboratory
8
6
1
7
11
2
5

Figure 36

Table 39

Sample Details

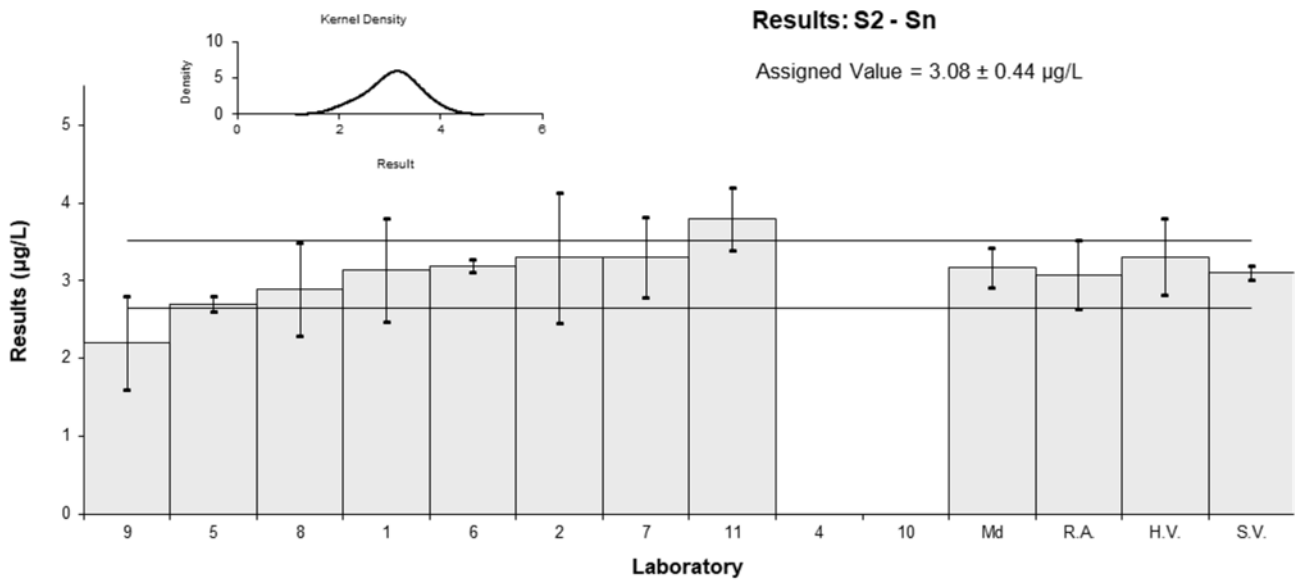
Sample No.	S2
Matrix.	Sea water
Analyte.	Sn
Units	µg/L

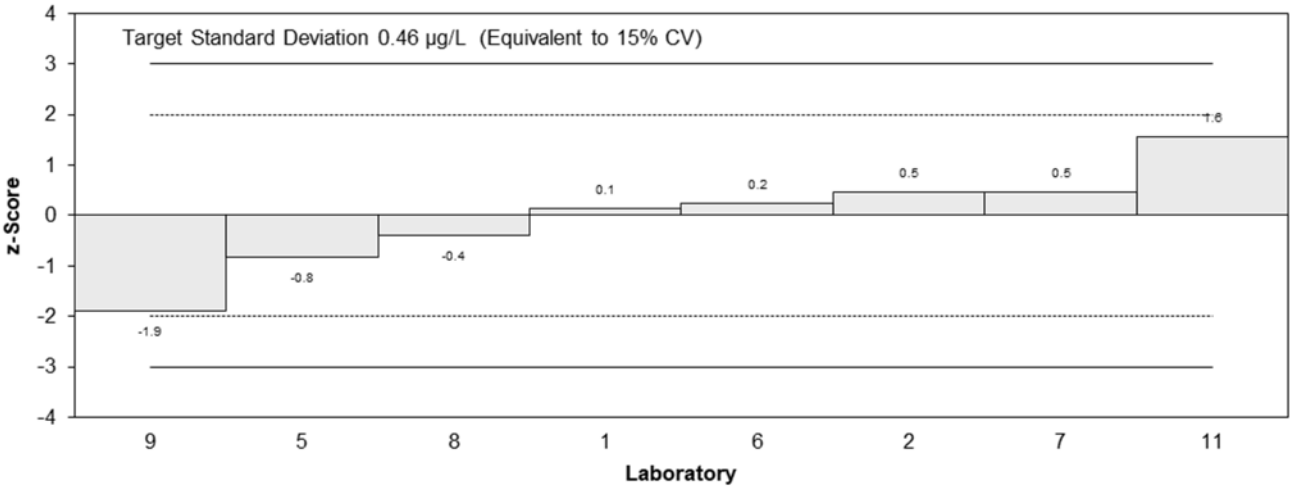
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.14	0.66	0.13	0.08
2	3.3	0.84	0.48	0.23
4	<5	NR		
5	2.7	0.1	-0.82	-0.84
6	3.19	0.08	0.24	0.25
7	3.30	0.52	0.48	0.32
8	2.9	0.6	-0.39	-0.24
9	2.2	0.6	-1.90	-1.18
10	NT	NT		
11	3.8	0.4	1.56	1.21

Statistics

Assigned Value	3.08	0.44
Spike	3.11	0.09
Homogeneity Value	3.31	0.50
Robust Average	3.08	0.44
Median	3.17	0.25
Mean	3.07	
N	8	
Max.	3.8	
Min.	2.2	
Robust SD	0.5	
Robust CV	16%	


Kernel Density
Density
Result
Results: S2 - Sn
Assigned Value = 3.08 ± 0.44 µg/L
Results (µg/L)
9
5
8
1
6
2
7
11
4
10
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - Sn
Target Standard Deviation 0.46 µg/L (Equivalent to 15% CV)
z-Score
-1.9
-0.8
-0.4
0.1
0.2
0.5
0.5
1.6
Laboratory

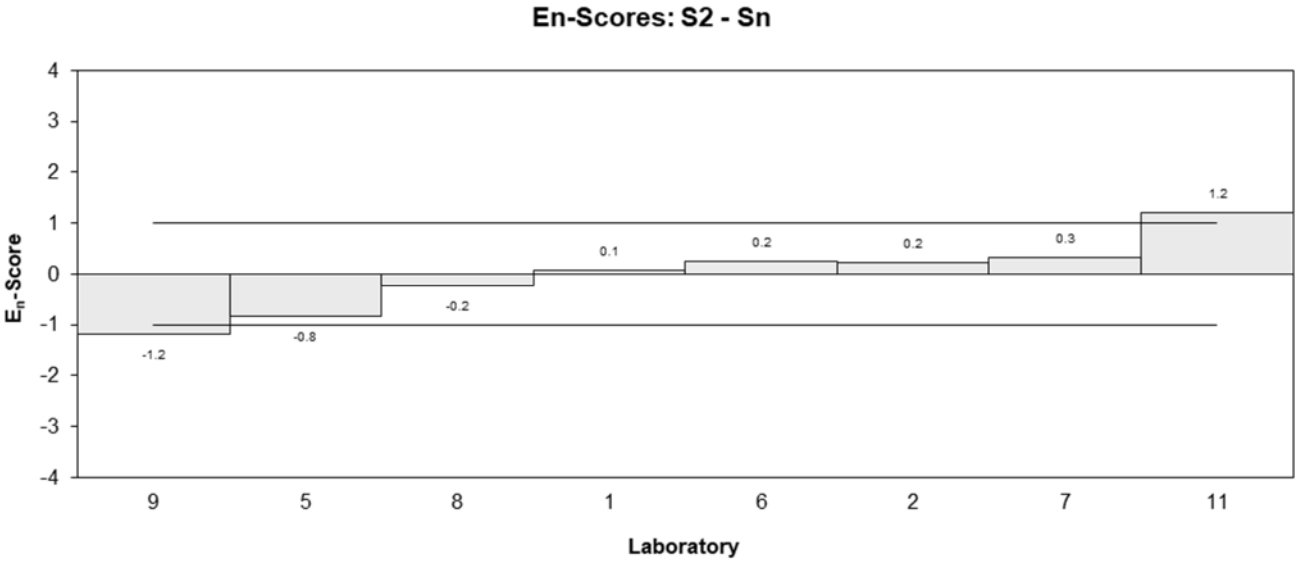

En-Scores: S2 - Sn
En-Score
-1.2
-0.8
-0.2
0.1
0.2
0.2
0.3
1.2
Laboratory

Figure 37

Table 40

Sample Details

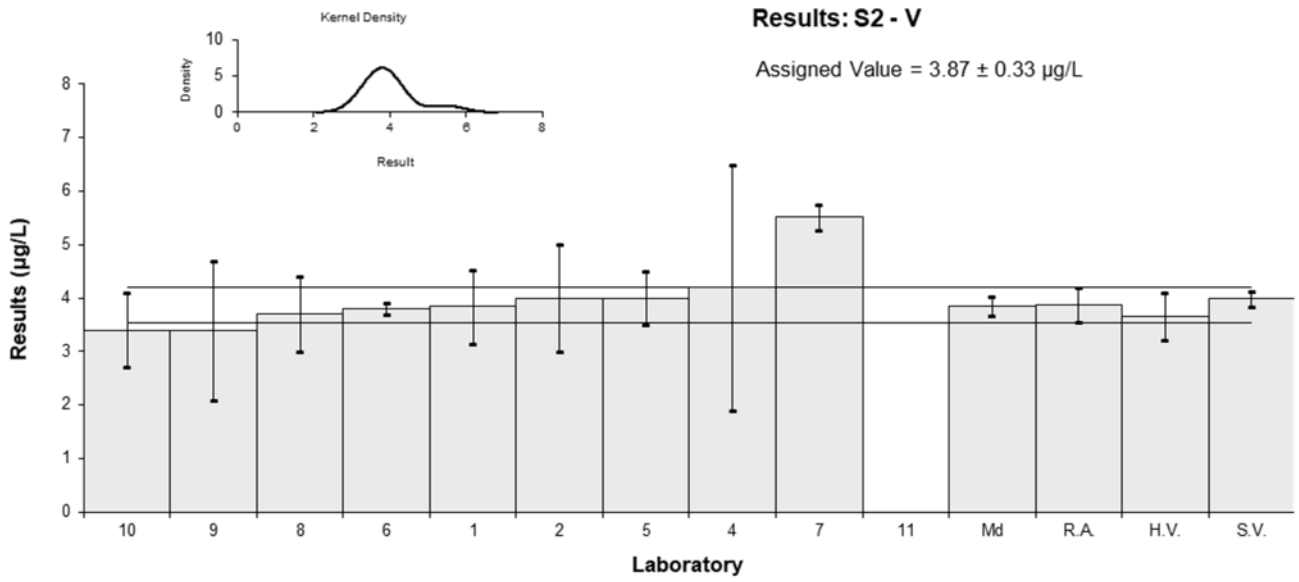
Sample No.	S2
Matrix.	Sea water
Analyte.	V
Units	µg/L

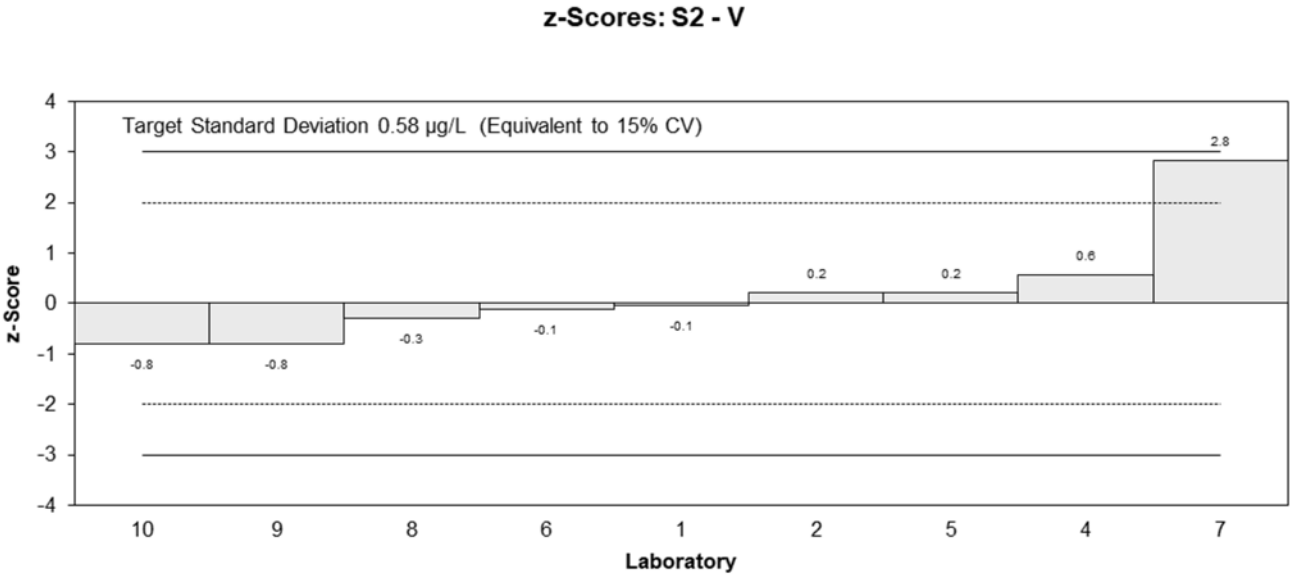
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.84	0.70	-0.05	-0.04
2	4	1	0.22	0.12
4	4.2	2.3	0.57	0.14
5	4	0.5	0.22	0.22
6	3.80	0.10	-0.12	-0.20
7	5.51	0.25	2.83	3.96
8	3.7	0.7	-0.29	-0.22
9	3.4	1.3	-0.81	-0.35
10	3.4	0.7	-0.81	-0.61
11	NT	NT		

Statistics

Assigned Value	3.87	0.33
Spike	3.98	0.14
Homogeneity Value	3.66	0.44
Robust Average	3.87	0.33
Median	3.84	0.18
Mean	3.98	
N	9	
Max.	5.51	
Min.	3.4	
Robust SD	0.39	
Robust CV	10%	


Kernel Density
Density
Result
Results: S2 - V
Assigned Value = 3.87 ± 0.33 µg/L
Results (µg/L)
10 9 8 6 1 2 5 4 7 11 Md R.A. H.V. S.V.
Laboratory


z-Scores: S2 - V
Target Standard Deviation 0.58 µg/L (Equivalent to 15% CV)
z-Score
-0.8 -0.8 -0.3 -0.1 -0.1 0.2 0.2 0.6 2.8
10 9 8 6 1 2 5 4 7
Laboratory

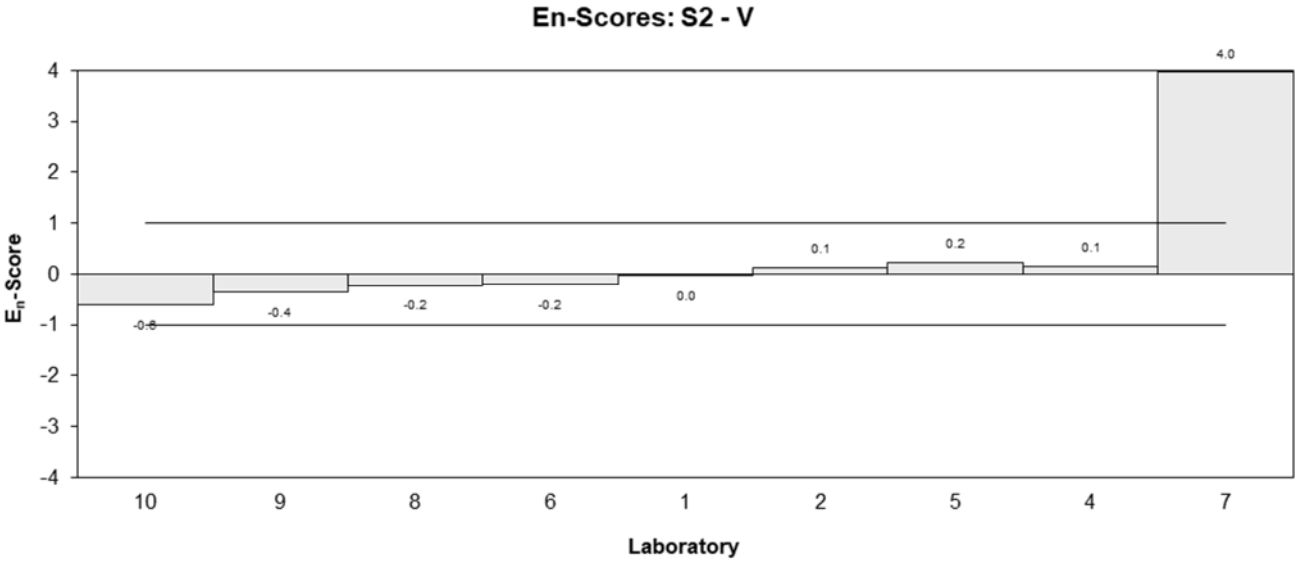

En-Scores: S2 - V
En-Score
-0.6 -0.4 -0.2 -0.2 0.0 0.1 0.2 0.1 4.0
10 9 8 6 1 2 5 4 7
Laboratory

Figure 38

Table 41

Sample Details

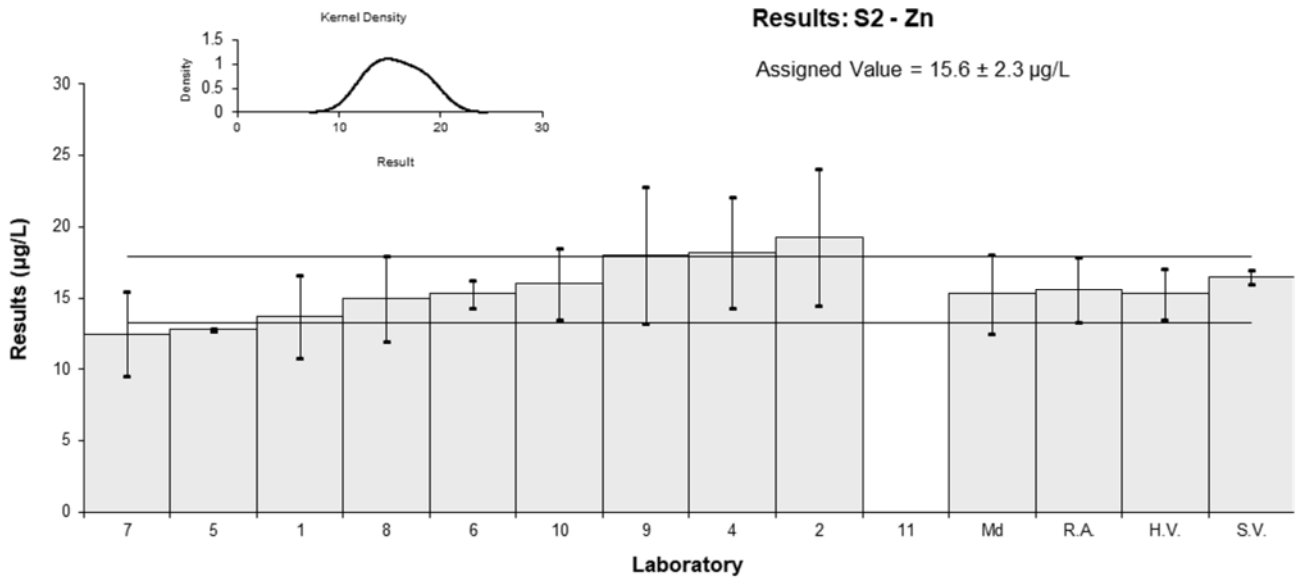
Sample No.	S2
Matrix.	Sea water
Analyte.	Zn
Units	µg/L

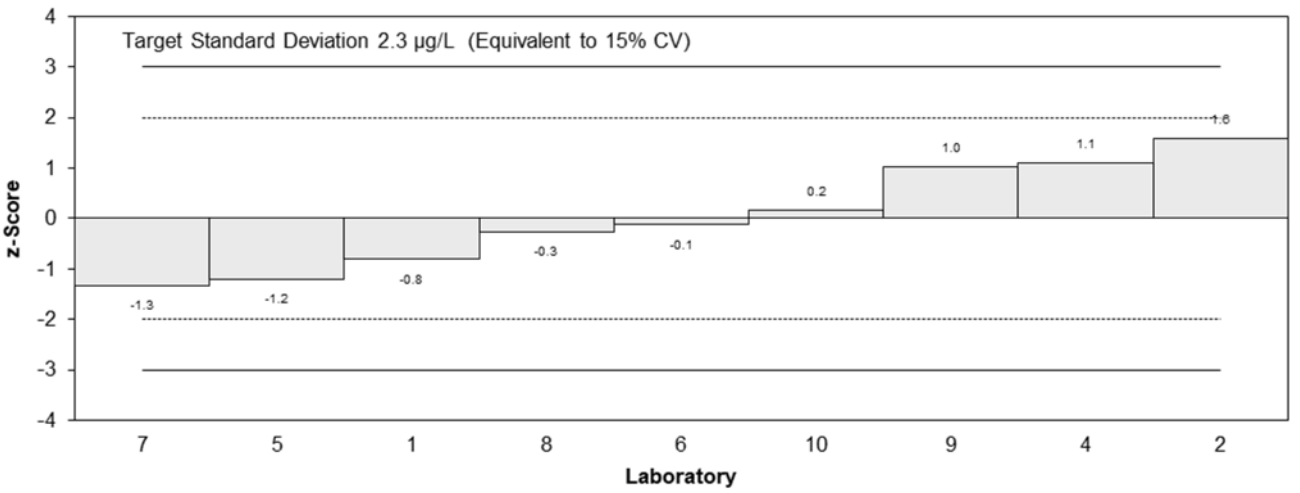
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	13.7	2.9	-0.81	-0.51
2	19.3	4.8	1.58	0.70
4	18.2	3.9	1.11	0.57
5	12.8	0.1	-1.20	-1.22
6	15.3	0.97	-0.13	-0.12
7	12.5	3.0	-1.32	-0.82
8	15	3	-0.26	-0.16
9	18	4.8	1.03	0.45
10	16	2.5	0.17	0.12
11	<45	NR		

Statistics

Assigned Value	15.6	2.3
Spike	16.5	0.5
Homogeneity Value	15.3	1.8
Robust Average	15.6	2.3
Median	15.3	2.8
Mean	15.6	
N	9	
Max.	19.3	
Min.	12.5	
Robust SD	2.8	
Robust CV	18%	


Kernel Density
Density
Result
Results: S2 - Zn
Assigned Value = 15.6 ± 2.3 µg/L
Results (µg/L)
Laboratory
7
5
1
8
6
10
9
4
2
11
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Zn
Target Standard Deviation 2.3 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.3
-1.2
-0.8
-0.3
-0.1
0.2
1.0
1.1
1.6

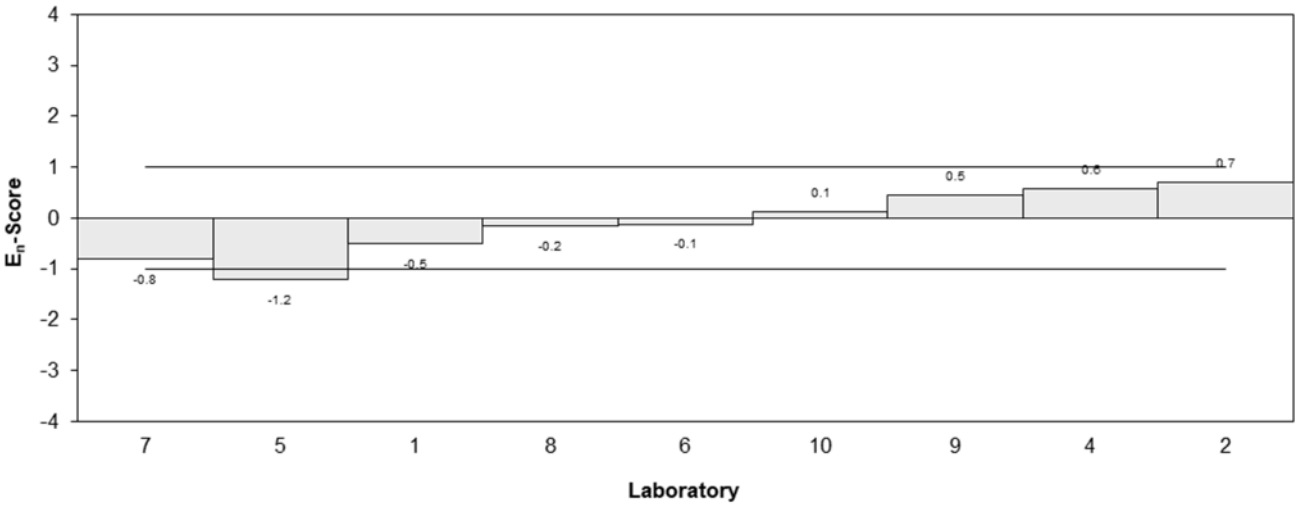

En-Scores: S2 - Zn
En-Score
Laboratory
-0.8
-1.2
-0.5
-0.2
-0.1
0.1
0.5
0.6
0.7

Figure 39

7 DISCUSSION OF RESULTS

7.1 Assigned Value

Sample S1 was filtered sea water, to which a known amount of single element standard solutions was added. **Sample S2** was filtered sea water to which a known amount of ultrapure water and single element standard solutions was added.

Assigned Values were the robust average of participants' results, with the exception of As, Fe, Hg, Ni, P, Pb, Se and Zn in S1 and of Hg, Ni and Se in S2. The robust averages and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'. 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 Mn in Sample S1 and its associated uncertainty.

Assigned values for As, P, Pb and Zn were reference values from measurements made using standard addition ICP-MS. Assigned values for Hg, Ni and Se in S1 and S2 were reference values measured using IDMS (Appendix 3).

No assigned values were calculated for Ag, Be, Li and Sn in S1 because the reported results were too few or too variable. However, participants may still compare their reported results for these elements with the median of participants' results and/or the homogeneity value. Descriptive statistics for these elements are presented in Section 6.

Traceability of the reference values for As, Fe, Hg, Ni, P, Pb, Se and Zn in S1 Hg, Ni and Se in S2 and rely on gravimetric sample preparation and elemental quantification by ICP-MS. Gravimetric measurements were calibrated using Australian standards for mass and are traceable to the SI unit for mass (kg). ICP-MS measurements calibrated with standard addition and isotope dilution are traceable to the SI units for mass (kg) through the primary calibration standard certified by NIST (USA) and the SI unit for amount of substance (mol) through data for isotopic composition and relative atomic mass. Isotopic compositions are traceable to IUPAC published data with the exception of Pb which is traceable to the certified isotopic composition of an isotopically certified material from NIST (USA).

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.

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 284 numerical results, 274 (96%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.136% to 154% 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 MU are presented in the bar charts for each analyte (Figure 2 to 39). 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 As in S2. The uncertainty of the assigned value estimated from the robust standard deviation of the 10 laboratories' results is 0.44 mg/kg (see equation 4, Appendix 2). **Laboratory 5** might have under-estimated its expanded measurement uncertainties reported for As in S2 (0.1 mg/kg). Alternatively, estimates of uncertainties for Cd in S1 larger than 0.207 mg/kg (the uncertainty of the assigned value, 0.057 mg/kg plus the allowable variation from the assigned value, the target standard deviation of 0.075 mg/kg, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainties reported by **laboratory 9** for Cd in S1 (0.4 mg/kg) 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 4.

Laboratories 2, 6 and **9** should review their procedure for estimating measurement uncertainty as most of the uncertainties estimated by laboratory 2 were likely under-estimated while most of the uncertainties estimated by laboratories 6 and 9 were likely over-estimated.

Laboratory 4 attached estimates of the expanded measurement uncertainty to results reported as 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]

Laboratories 2 and **9** reported an estimate of expanded uncertainty for some measurement results equal or larger than the results themselves.

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]

7.3 E_n-score

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

The dispersal of participants' E_n-scores is graphically presented in Figure 40. 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 263 results for which E_n-scores were calculated, 214 (81%) 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.

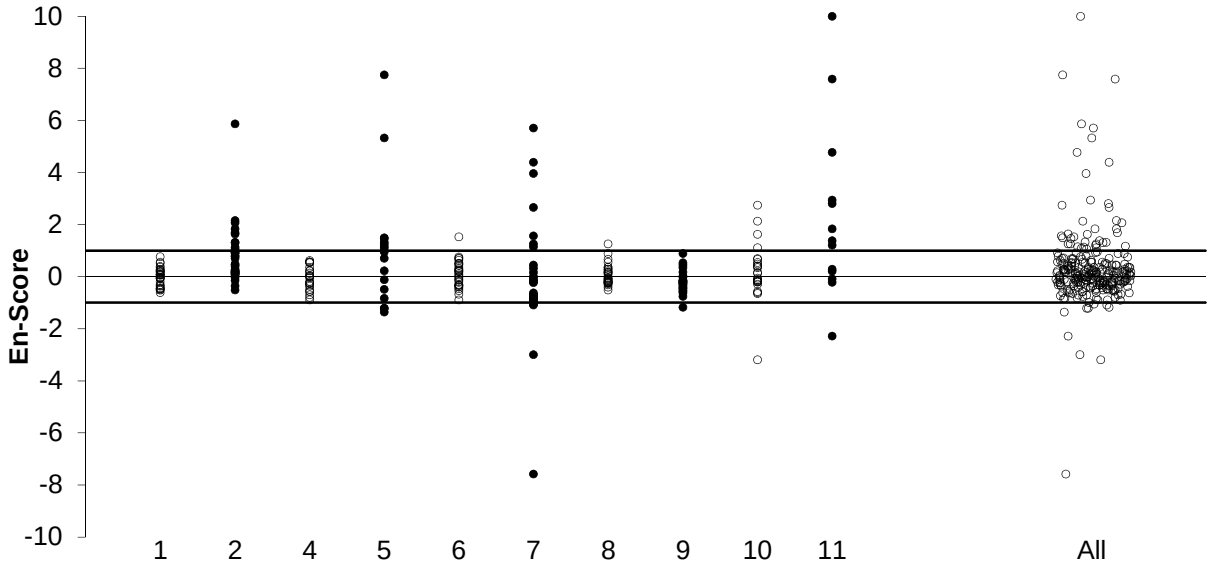
7.4 z-Score

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

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 15% to 25% 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.

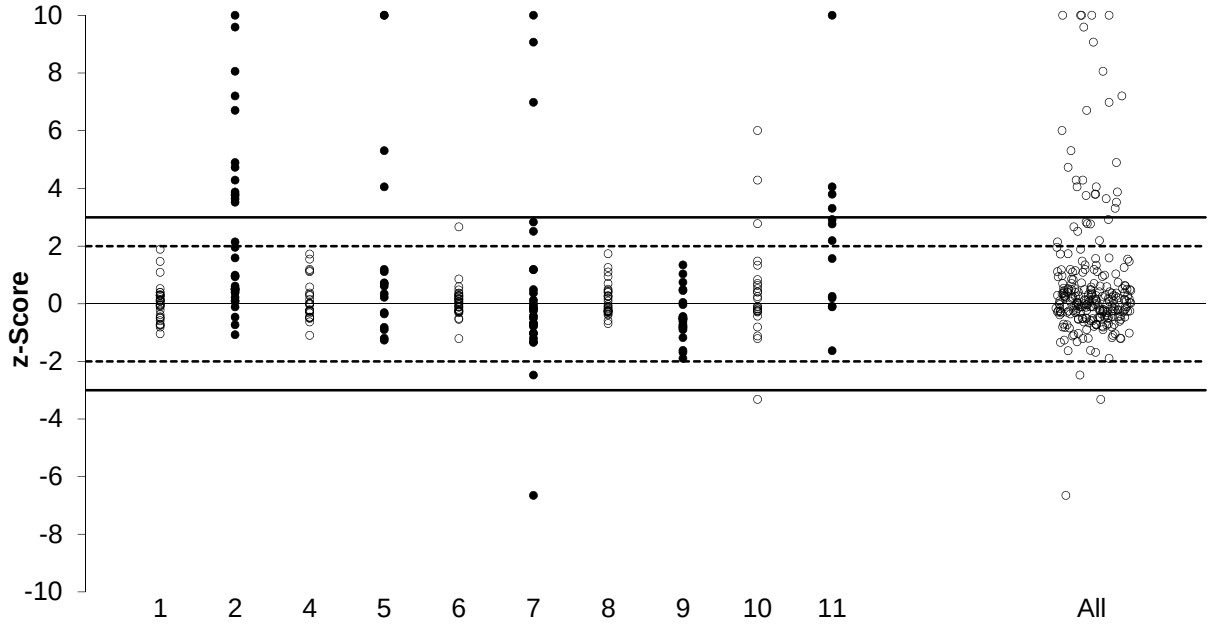
The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 42.

The dispersal of participants' z-scores is presented in Figure 41 (by laboratory code) and in Figure 42 (by test). Of 263 results for which z-scores were calculated, 226 (86%) returned a satisfactory score of $|z| \leq 2.0$ and 9 (3%) were questionable of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.



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

Figure 40 E_n-Score Dispersal by Laboratory



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

Figure 41: z-Score Dispersal by Laboratory

A summary of participants' performance is presented in Figure 43**. Laboratory 2** reported results for all 34 tests for which a z-score was calculated.

Laboratory 1 returned the highest number of satisfactory z-scores and the highest number of satisfactory E_n-scores (33 out of a total of 33 reported).

Laboratory **6** returned satisfactory results for 31 tests out of a total of 32 reported.

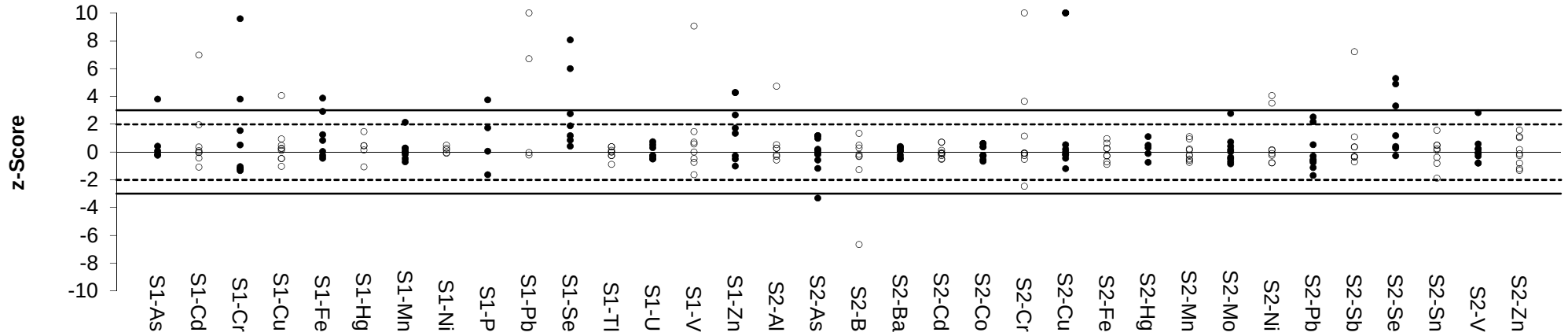
All results reported by **laboratories 8** (31), **4** (26) and **9** (23) returned satisfactory z-scores.

All results reported by **laboratory 4** (26) returned satisfactory E_n scores.

Table 42 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	Not Set	23%	NA	Not Set
S1	As	1.18	8.2%	22%	25%
S1	Be	Not Set	17%	NA	Not Set
S1	Cd	0.503	12%	22%	15%
S1	Cr	1.21	28%	22%	15%
S1	Cu	4.73	11%	22%	15%
S1	Fe	12.0	30%	22%	20%
S1	Hg	0.1312	15%	22%	15%
S1	Li	Not Set	4.4%	NA	Not Set
S1	Mn	3.18	8.1%	22%	15%
S1	Ni	1.25	6.5%	22%	25%
S1	P	74.3	44%	22%	20%
S1	Pb	0.555	63%	22%	20%
S1	Se	1.36	29%	22%	25%
S1	Sn	Not Set	15%	NA	Not Set
S1	Tl	1.04	5.8%	22%	15%
S1	U	3.24	8.7%	22%	15%
S1	V	1.72	18%	22%	15%
S1	Zn	5.28	36%	22%	20%
S2	Al	26.9	7.3%	22%	15%
S2	As	3.40	16%	22%	15%
S2	B	2050	14%	14%	15%
S2	Ba	21.7	5.6%	22%	15%
S2	Cd	1.63	7.2%	22%	15%
S2	Co	2.29	8.5%	22%	15%
S2	Cr	3.04	15%	22%	15%
S2	Cu	10.3	5.8%	22%	15%
S2	Fe	34.7	11%	22%	15%
S2	Hg	0.326	11%	22%	15%
S2	Mn	7.37	11%	22%	15%
S2	Mo	8.48	11%	22%	15%
S2	Ni	2.98	13%	22%	25%
S2	Pb	1.81	33%	22%	20%
S2	Sb	3.70	10%	22%	15%
S2	Se	3.01	41%	22%	25%
S2	Sn	3.08	16%	22%	15%
S2	V	3.87	10%	22%	15%
S2	Zn	15.6	18%	22%	15%

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



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

Figure 42 z-Score Dispersal by Analyte

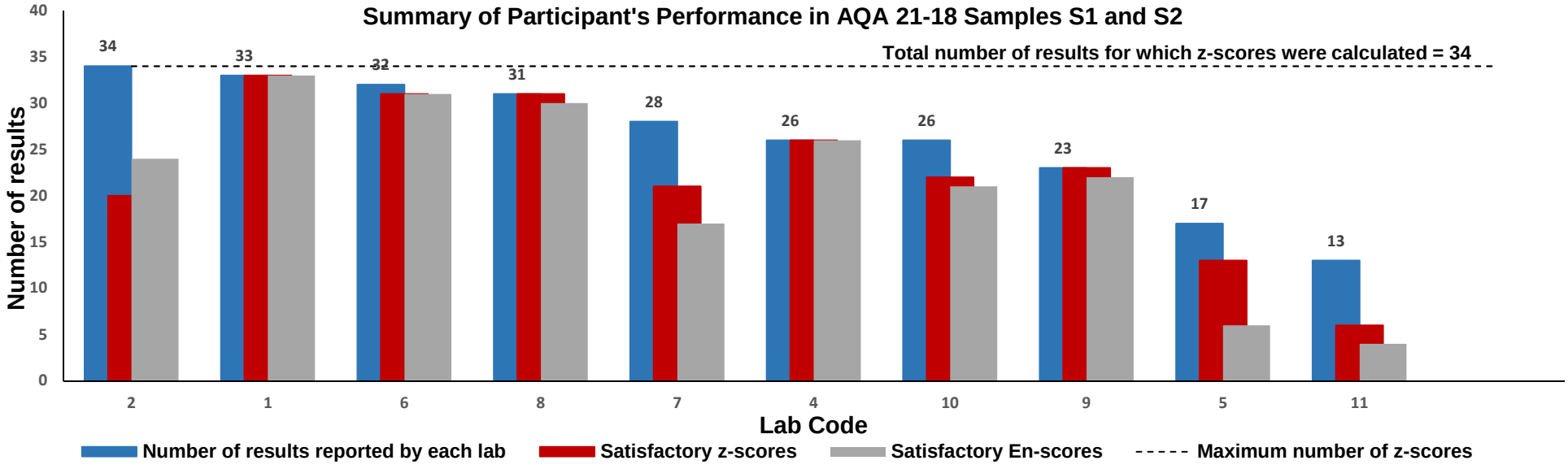


Figure 43: Summary of Participants Performance in AQA 21-18

Table 43 Summary of Participants' Results and Performance for Sample S1

Lab Code	Ag (µg/L)	As (µg/L)	Be (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Li (µg/L)	Mn (µg/L)
A.V.	Not Set	1.18	Not Set	0.503	1.21	4.73	12.0	0.1312	Not Set	3.18
H.V./R.V.	0.73	1.18	0.68	0.495	1.01	4.46	12.0	0.1312	NA	3.00
1	0.76	1.20	<1	0.51	1.02	4.92	10.9	0.16	160	3.17
2	0.46	2.3	0.66	0.65	2.95	4.8	21.3	0.11	NT	4.2
4	0.7	<4	NT	0.42	1.49	4.4	11.4	0.134	165	2.95
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	0.79	1.11	0.69	0.53	0.99	5.06	12.1	NR	175	3.32
7	NT	1.13	0.615	1.03	0.965	3.99	NT	NT	0.192	2.84
8	<1	<1	<1	0.50	1.3	5.4	15	0.14	170	3.3
9	0.6	<3	0.5	0.5	<1	4.4	NT	0.14	NT	3.2
10	<1	1.3	0.76	0.47	0.99	4.9	14	<0.5	175	3.1
11	NT	<1.5	NT	<1.5	1.9	7.6	19	NT	NT	NT

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

Table 43 Summary of Participants' Results and Performance for Sample S1 (continued)

Lab Code	Ni (µg/L)	P (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Tl (µg/L)	U (µg/L)	V (µg/L)	Zn (µg/L)
A.V.	1.25	74.3	0.555	1.36	Not Set	1.04	3.24	1.72	5.28
H.V./R.V.	1.25	74.3	0.555	1.36	NA	1.09	3.12	1.81	5.28
1	1.23	NR	0.53	2.0	<1	1.06	3.39	1.53	4.73
2	1.4	130	1.3	4.1	2.3	1.1	3.5	1.6	9.8
4	<7	NT	<1.0	<4	<5.0	1.0	3.0	1.72	7.1
5	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	1.33	75.0	0.55	1.65	0.81	1.04	2.99	1.87	8.09
7	1.22	NT	1.71	1.76	1.01	1.04	3.12	4.06	4.20
8	1.3	100	<1	1.5	1.1	1.1	NR	1.9	5.0
9	<1	NT	<1	<5	<1	0.9	3.6	1.3	6.7
10	NT	NT	<1	3.4	NT	1.0	3.1	2.1	9.8
11	NT	50	<1.5	2.3	1.1	NT	NT	NT	<45

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

Table 44 Summary of Participants' Results and Performance for Sample S2

Lab Code	Al (µg/L)	As (µg/L)	B (µg/L)	Ba (µg/L)	Cd (µg/L)	Co (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)
A.V.	26.9	3.40	2050	21.7	1.63	2.29	3.04	10.3	34.7	0.326
H.V./R.V.	NA	3.22	1930	22.2	1.58	2.27	3.26	10.6	34.7	0.326
1	24.5	3.45	2140	22.6	1.51	2.42	3.01	11.1	31.0	0.32
2	46	3.9	2200	22	1.6	2.5	4.7	38.7	39.7	0.29
4	28	4.0	1950	21	1.62	2.2	3.56	10.3	33.3	0.341
5	25.6	4	1659	22.8	1.8	2.5	8.7	27.1	30	NR
6	26.1	3.35	1961	22.0	1.57	2.41	2.92	10.6	33.3	NR
7	NT	3.31	2.70	20.3	1.66	2.06	1.91	8.44	NT	NT
8	28	3.1	2000	22	1.6	2.2	3.0	10	36	0.38
9	NT	2.8	NT	20	1.5	2.1	2.8	9.6	NT	0.35
10	29	1.7	2460	23	1.8	2.2	3.0	10	38	<0.5
11	NT	3.5	NT	NT	1.6	NT	3.0	45	36	NT

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

Table 44 Summary of Participants' Results and Performance for Sample S2 (continued)

Lab Code	Mn (µg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)	Sb (µg/L)	Se (µg/L)	Sn (µg/L)	V (µg/L)	Zn (µg/L)
A.V.	7.37	8.48	2.98	1.81	3.70	3.01	3.08	3.87	15.6
H.V./R.V.	7.40	9.3	2.98	1.64	3.79	3.01	3.31	3.66	15.3
1	7.6	8.0	3.08	1.54	4.3	3.3	3.14	3.84	13.7
2	8.4	9.0	5.6	2	7.7	6.7	3.3	4	19.3
4	6.79	8.5	<7	1.58	3.9	<4	<5	4.2	18.2
5	8.6	9.4	6.0	NR	3.5	7	2.7	4	12.8
6	7.53	8.67	3.10	1.61	3.53	3.21	3.19	3.80	15.3
7	6.55	7.85	2.39	2.72	3.90	3.89	3.30	5.51	12.5
8	7.1	7.6	2.8	1.7	3.5	2.8	2.9	3.7	15
9	6.7	7.4	2.4	1.2	3.3	<5	2.2	3.4	18
10	7.1	12	2.9	1.4	NT	NT	NT	3.4	16
11	NT	NT	NT	2.6	NT	5.5	3.8	NT	<45

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

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

Sample S1 was filtered sea water and **sample S2** was low salinity sea water. The concentration of analytes in S1 ranged from 0.131 µg/L to 74.3 µg/L, whereas concentration in S2 was 2 to 30 times higher than in S1. Overall, between-laboratory CVs of the low salinity sea water sample S2 were lower than those of the sea water sample S1.

Low level Cr, Fe, P Pb and Zn in S1 were the tests which had the highest coefficient of variation, ranging from 30% to 63%.

Selenium challenged participants' analytical techniques, regardless of its level in the test sample or the sample's salinity. The between-laboratory CV of Se was 29% in S1 and 41% in S2.

A summary of participants' results and performance in the two study samples is presented in Tables 43 and 44 and in Figures 40 to 43.

Measurements of low level elements in the sea water samples challenged participating laboratories. A limited number of participants reported results for some elements and for others, the reported results were too variable for an assigned value to be set. In order to be able to assess participants and support them to develop methods for the measurement of low level trace elements in saline water, reference values traceable to SI were produced in this study by NMI for eight tests in S1 and three in S2. The production of reference values involves using methods which have high accuracy and precision, thoroughly demonstrated, with numerous confirmations and targeted investigations of interference and other systematic errors. The provision of a reference value requires a well-defined measurement uncertainty and the establishment of the traceability of the measurement result to stated high-level internationally recognised standards.

To provide reference values in this study, IDMS or standard addition ICP-MS calibration approached were undertaken with various instrumental techniques, instrumental conditions and measured isotopes ratios. These included: HR-ICP-MS in low, medium or high resolutions, ICP-MS/MS in reaction mode with O_2, ICP-MS/MS in reaction mode with H_2, ICP-MS/MS in collision mode with He. For standard addition measurements multiple internal standards were also used, these were ^{55}Mn, ^{72}Ge, ^{89}Y, ^{115}In and ^{193}Ir. Each of the reference values was calculated from 3 experiments conducted for each of these instrumental techniques, instrumental conditions and measured isotope ratios.

Individual Element Commentary

Participants were requested to analyse the samples using their normal test methods and to report a single result as they would normally report to a client.

As the study demand was for dissolved elements, instrumental measurement was one of the main factors that influenced results in the sea 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.

Participants used a wide variety of instrumental techniques, collision/reaction cells and cell gases. Most laboratories reported using ICP-MS with a collision/reaction cell; some used ICP-OES and GFAAS, and some ICP-MS in standard mode. Three participants reported using ICP-MS/MS in standard, collision, or reaction mode with He, O_2 or N_2O. Plots of participants' results and performance versus instrumental techniques used are presented in Figures 44 to 60.

Silver Only five results were reported for Ag in S1, and all were in good agreement with each other and with the median (0.70 µg/L). One laboratory measured Ag using GFAAS with a wavelength of 328.1 nm (Figure 44).

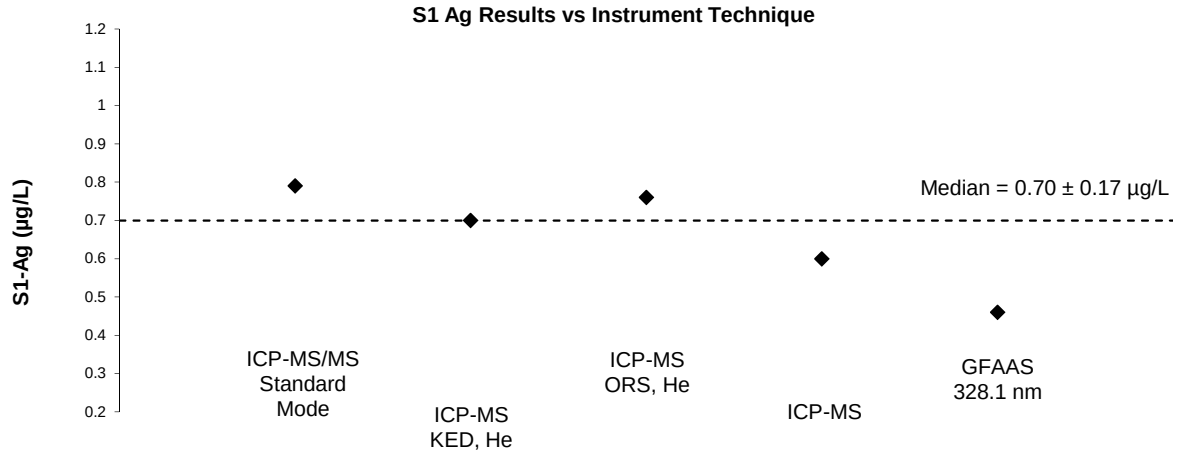
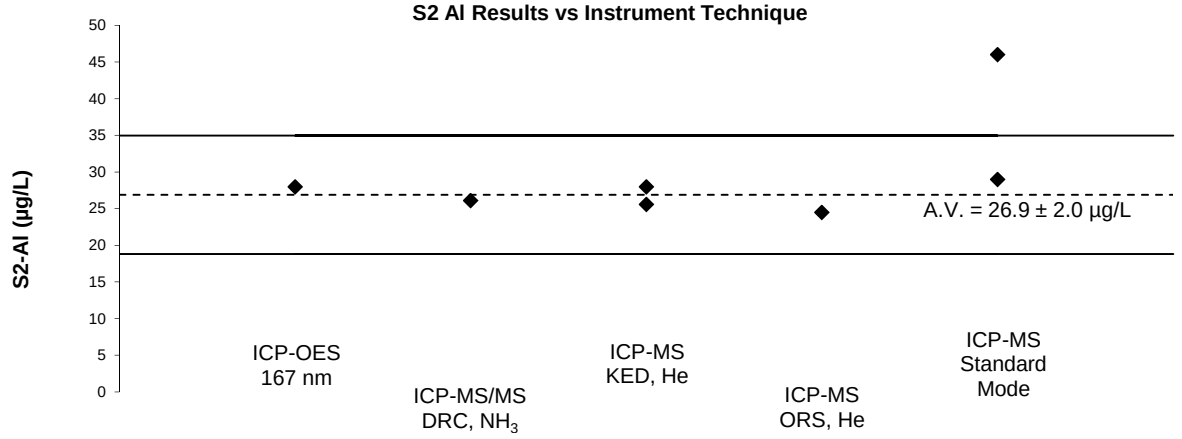


Figure 44 S1-Ag Results vs Instrumental Technique

Aluminium level in S2 was 26.9 µg/L and was among the most challenging tests for participating laboratories, with a between-laboratory CV of only 7.3%. Plots of instrumental techniques versus results are presented in Figure 44.



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

Figure 45 S2-Al Results vs Instrumental Technique

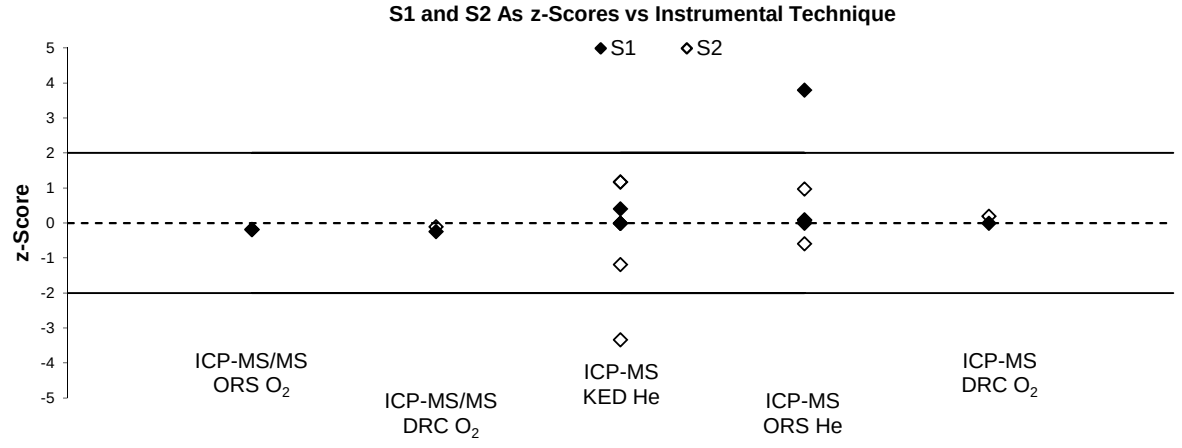
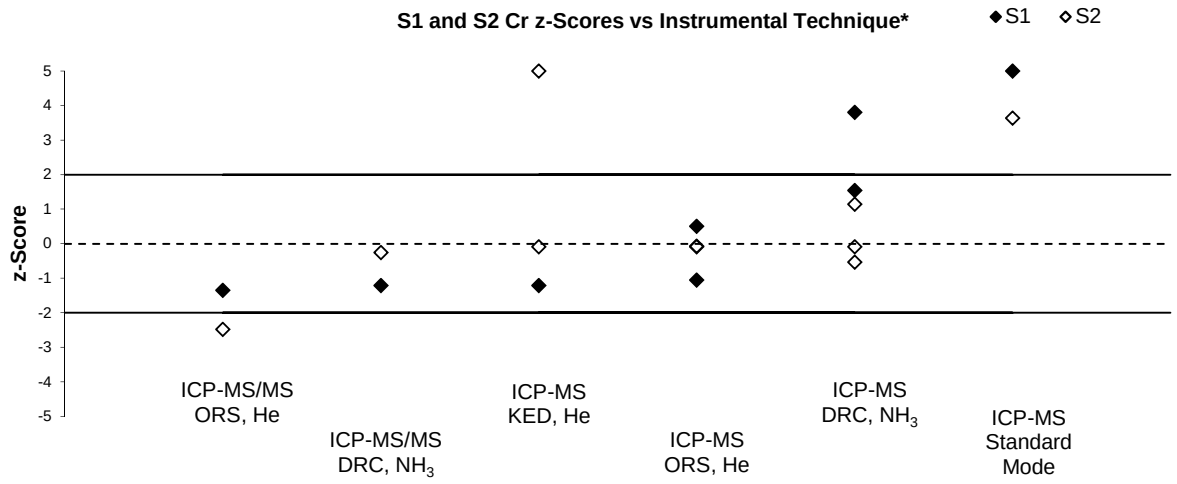


Figure 46 S1 and S2 As z-Scores vs Instrumental Technique

Arsenic level in S1 was the natural level of 1.18 µg/L. Only five results were reported for As in S1; all returned satisfactory z-scores but one. Participants used ICP-MS in collision or reaction mode with He or O_2 as collision/reaction gases (Figure 46).

The results from ICP-MS in collision mode were variable, indicating that this technique might struggle with overcoming the $^{40}Ar^{35}Cl^{+}$ interferences on $^{75}As^{+}$ and hence may not produce accurate results for this analyte at a low level in saline matrices.

Chromium level in S1 was 1.21 µg/L and in S2 was 3.04 µg/L. Participants used a wide variety of instrumental techniques to overcome interference problems with Cr in the sea water sample (Figure 47).



*Laboratory 2 z-score of 9.59 and laboratory 5 z-score of 12.41 were plotted as 5

Figure 47 S1 and S2 Cr z-Scores vs Instrumental Technique

The high unsatisfactory z-score is likely an indication of unsolved interference problems.

Iron level in S1 was 12.0 µg/L and in S2 was 34.7 µg/L. Measurements of low-level Fe in S1 challenged participants, with the seven reported results being incompatible with each other (Figure 48). The NMI reference value was used as assigned value for this test.

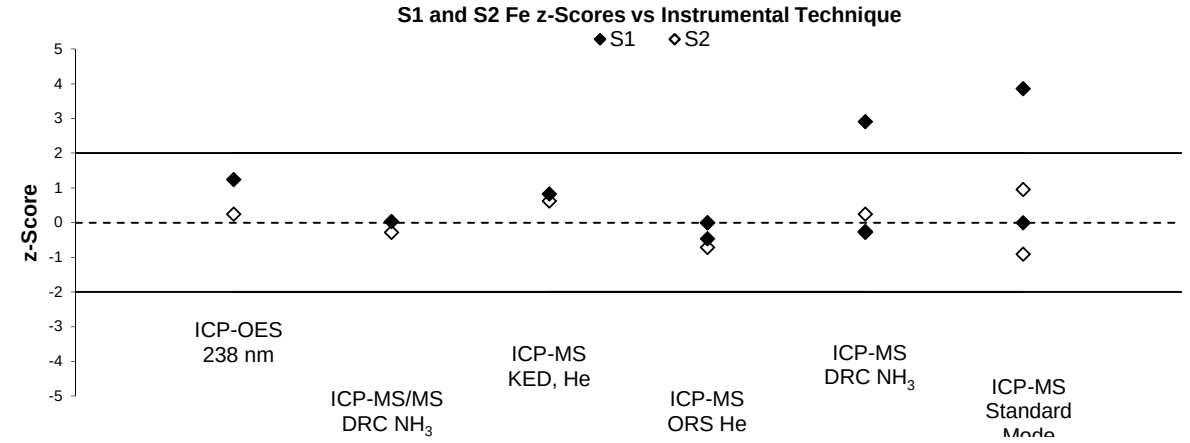


Figure 48 S1 and S2 Fe z-Scores vs Instrumental Technique

Mercury Only 5 participants reported results for Hg in S1 in S2 and all reported results were in agreement with each other and with the assigned values. Plots of participants' performance versus instrumental techniques used are presented in Figure 49. The assigned values for Hg in the two test samples were reference values by IDMS.

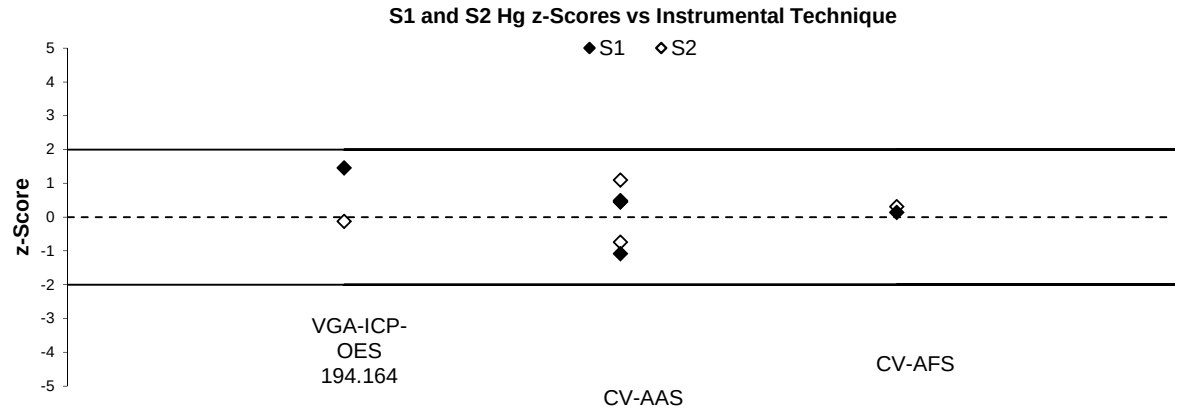
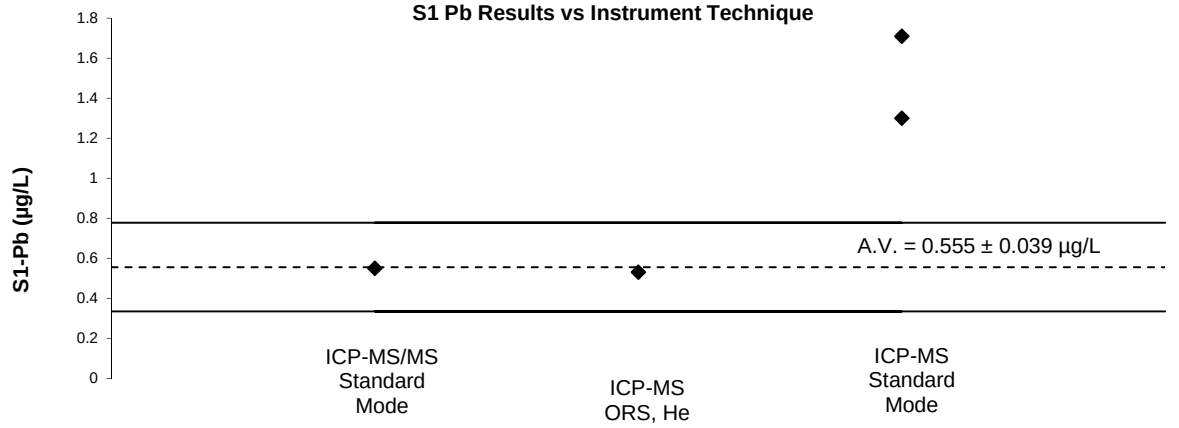


Figure 49 S1 and S2 Hg z-Scores vs Instrumental Technique

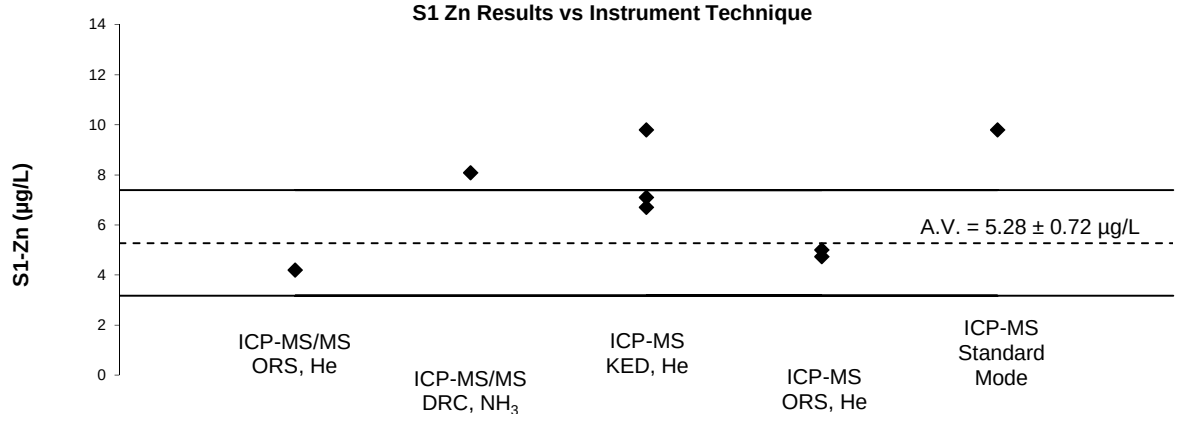
CV-AAS was the popular instrumental technique used for the measurement of low level Hg in sea water. One participant used ICP-OES with hydride generation accessory and a wavelength of 14.164 nm.

Lead and zinc are known to be ubiquitous in the environment; hence, special precautions (e.g. special gloves) are necessary in order to avoid contamination. Plots of participants' results reported for Pb and Zn in S1 versus measurement technique used are presented in Figures 50 and 51.



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

Figure 50 S1-Pb Results vs Instrumental Technique



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

Figure 51S1-Zn Results vs Instrumental Technique

Lithium Two participants measured Li in S1 using ICP-OES. Laboratory 7 may have reported results in the wrong units, with their result being below the median value by a factor of 1,000. All laboratories reported using Sc as internal standard, with the exception of one; Laboratory 8 used Rh (Figure 52).

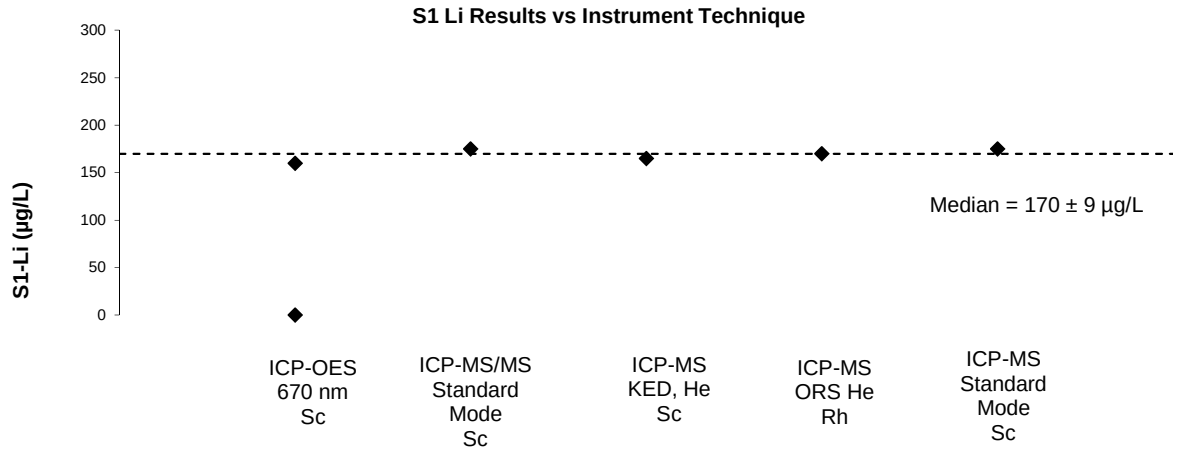


Figure 52 S1 Li Results vs Instrumental Technique

Manganese was one of the least challenging analyte in this study. All reported results returned satisfactory z-scores except for one. Figure 53 presents plots of participants' performance versus the instrumental technique used.

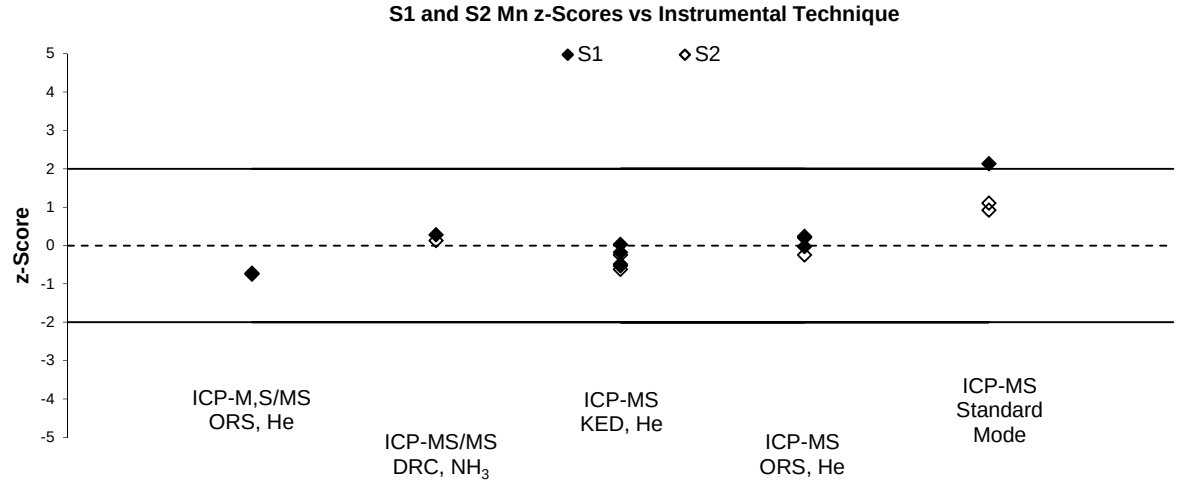
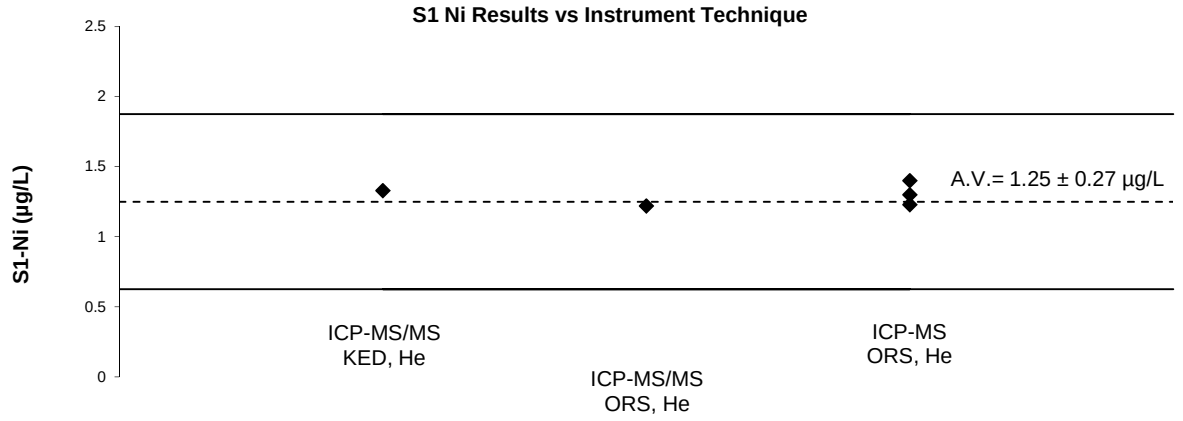


Figure 53 S1 and S2 Mn z-Scores vs Instrumental Technique

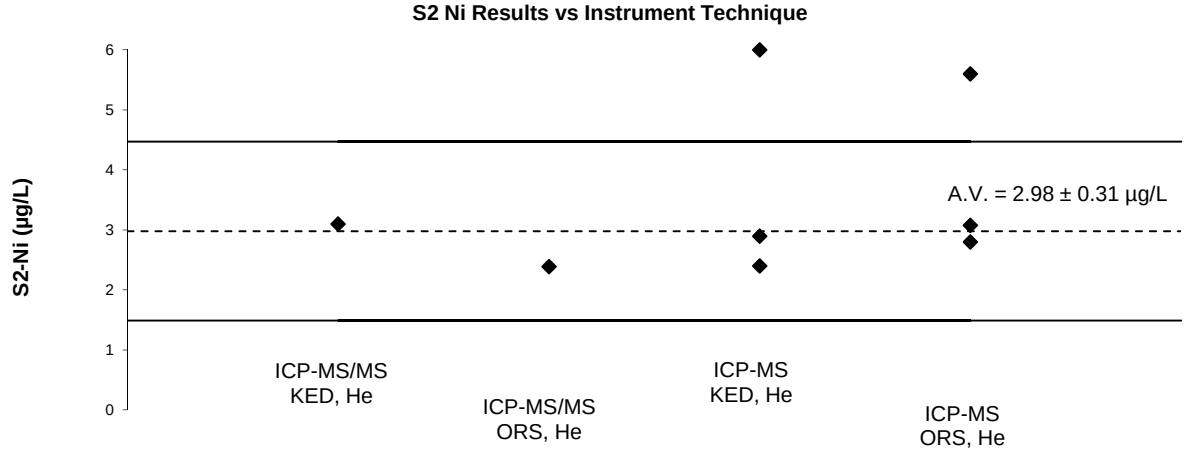
Nickel was one of the analytes which presented the most analytical difficulty to participants. Ni level in S1 was 1.25 µg/L and only five participants reported results. In S2, Ni level was almost 2.5 times higher, and of eight participants, six performed satisfactorily.

All laboratories reported measuring Ni using ICP-MS or ICP-MS/MS in reaction mode (Figures 54 and 55).



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

Figure 54 S1 Ni Results vs Instrumental Technique

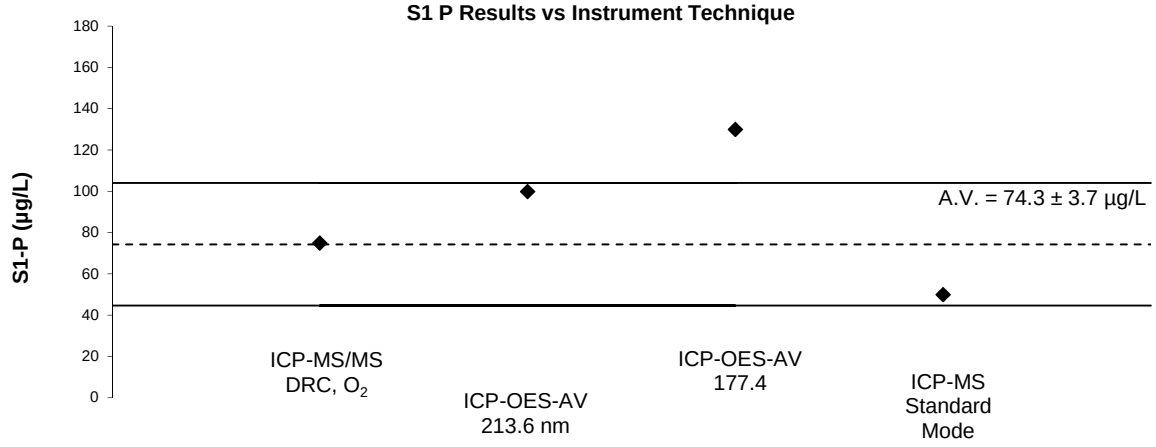


Horizontal lines on chart are the results corresponding to z-scores of 2 and -2

Figure 55 S2 Ni Results vs Instrumental Technique

Phosphorus reference value in S1 was 74.3 µg/L. A limited number of laboratories had the capability to measure P in sea water at this level. Only four participants reported results for this test and all but one were compatible with each other and with the assigned value (Figure 56).

The P result produced by ICP-MS/MS in reaction mode and O_2 as reaction gas (75 µg/L) was in excellent agreement with the reference value (74.3 µg/L).

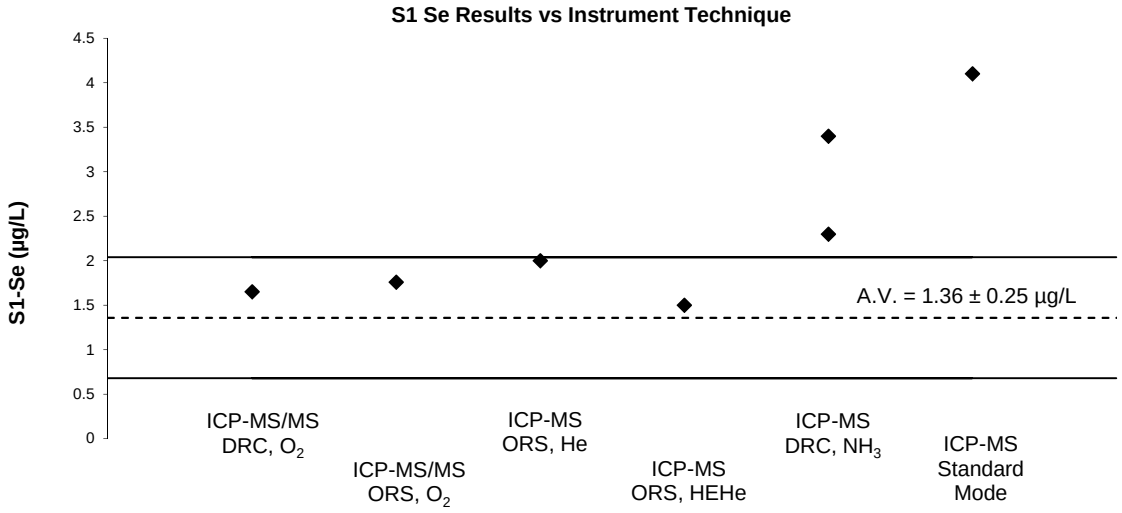


Horizontal lines on chart are the results corresponding to z-scores of 2 and -2

Figure 56 S1 P Results vs Instrumental Technique

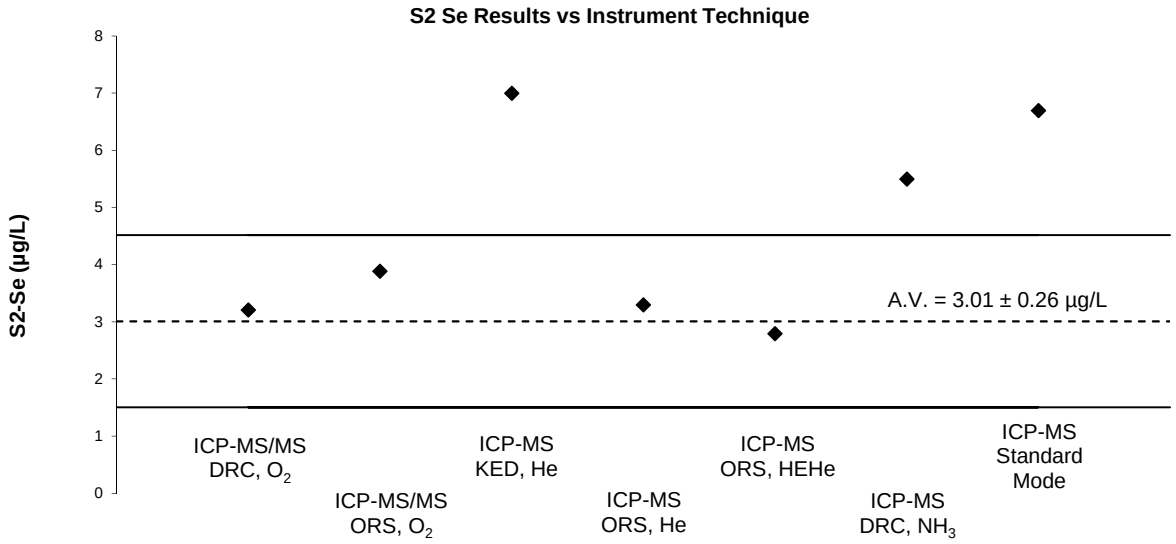
Selenium analysis in sea water is challenging due to there being multiple sources of significant interference. This is especially problematic at low levels where any unresolved interference can have a more significant effect on results.

Plots of participants' performance for Se in S1 and S2 versus instrumental technique used are presented in Figures 57 and 58. Participants reported using seven different instrumental techniques in the present study. High unsatisfactory results are an indication that some participants may have not overcome the interference problem.[15]



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

Figure 57 S1 Se Results vs Instrumental Technique



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

Figure 58 S2 Se Results vs Instrumental Technique

Tin Only 5 participants reported results for this analyte in S1 and all but one were compatible with each other and with the median value of 1.10 µg/L. ICP-MS in standard mode was the preferred instrumental technique (Figure 59).

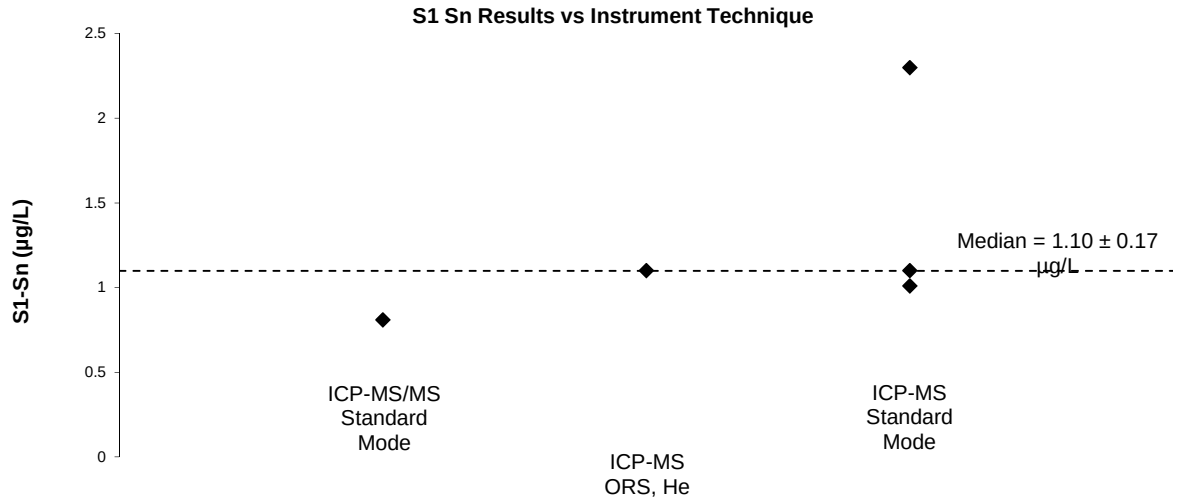
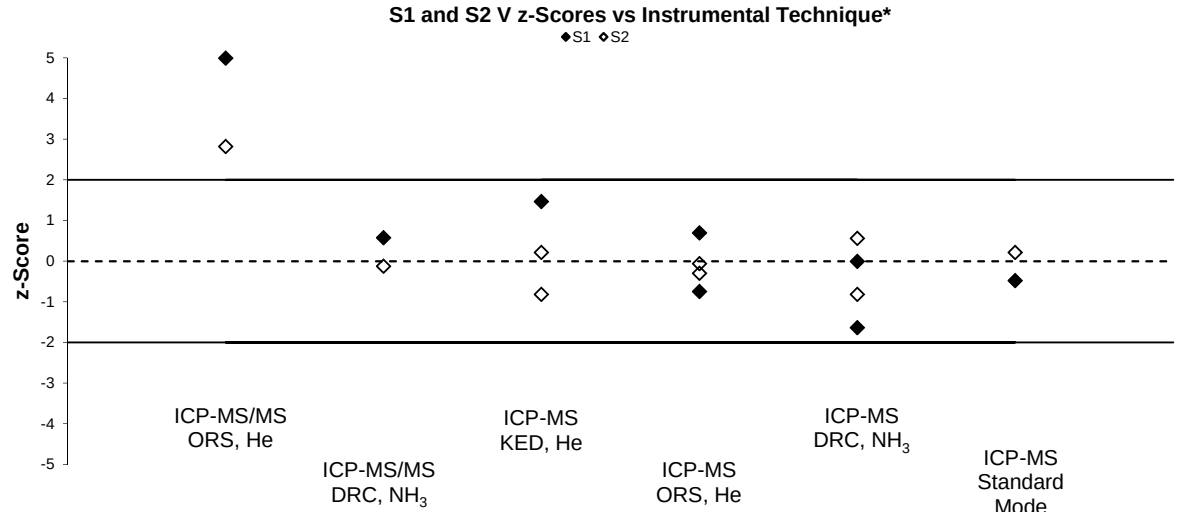


Figure 59 S2 Sn Results vs Instrumental Technique

Vanadium level was 1.72 µg/L in S1 and 3.01 µg/L in S2. Eight laboratories reported results for V in S1 and nine in S2. All laboratories performed satisfactorily but one, which reported unsatisfactory results for V in both study samples (Figure 60).

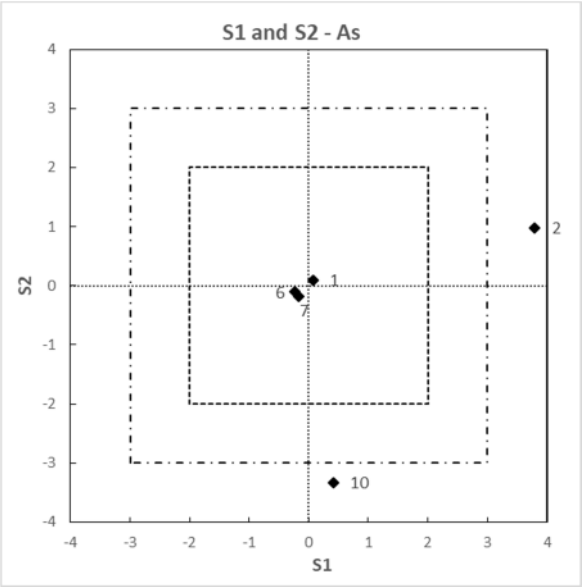


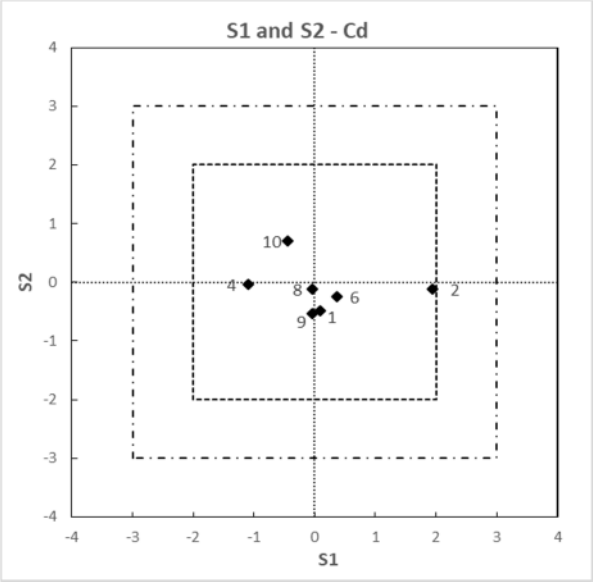
*Laboratory 7 z-score of 9.07 has been plotted as 5.

Figure 60 S1 and S2-V Results vs Instrumental Technique

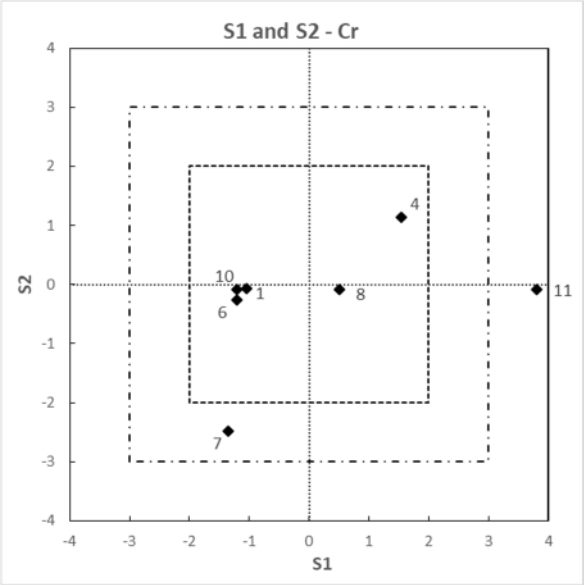
7.6 z-Score Scatter plots

Scatter plots of z-scores for all analytes present in both study samples are presented in Figure 61. Points close to the diagonal axis represent excellent reproducibility and points close to zero represent excellent reproducibility and accuracy**.**

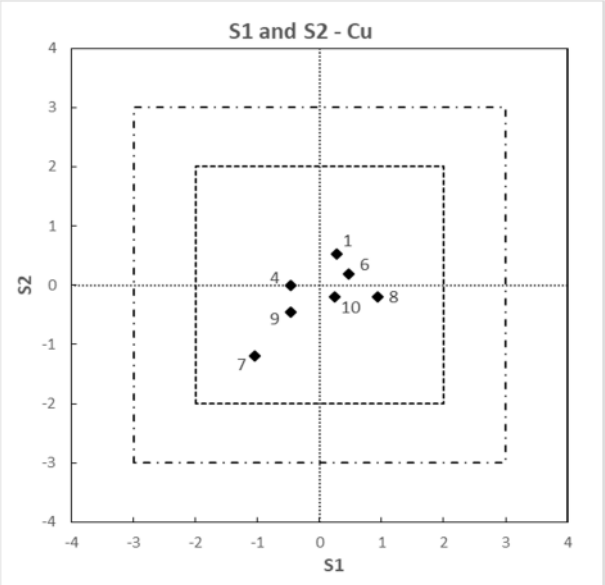




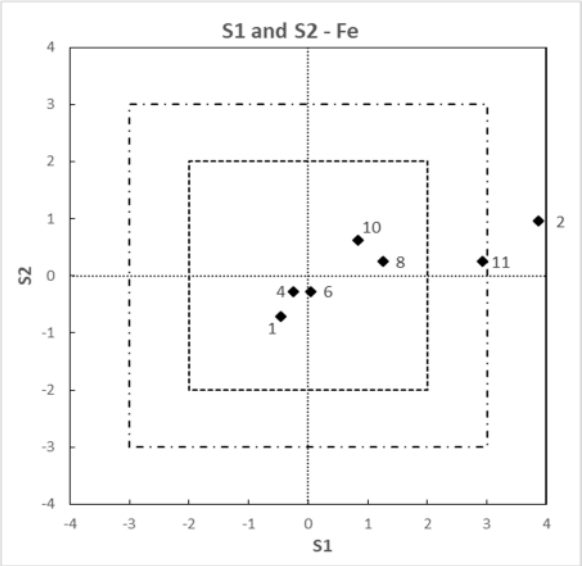
Laboratory 7 is off scale



Laboratory 2 is off scale



Laboratories 2 and 11 are off scale



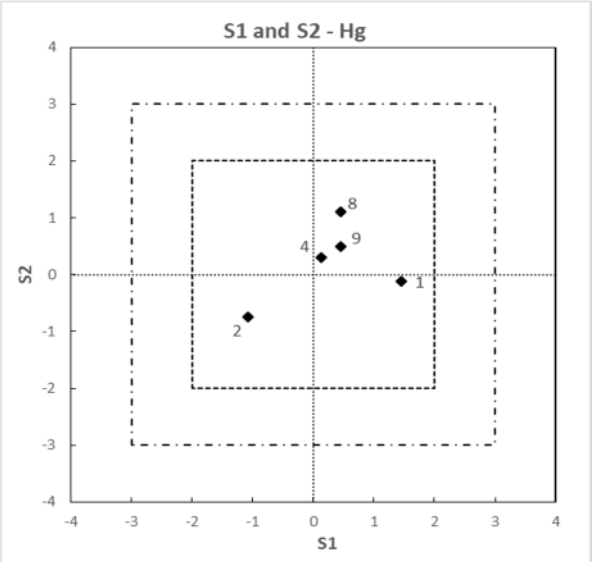
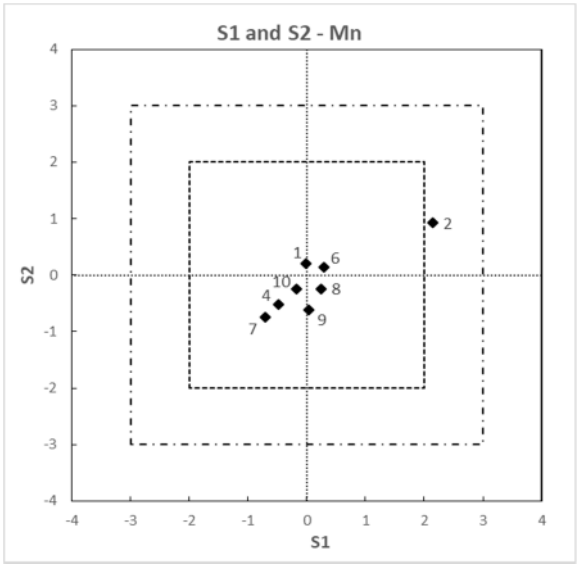
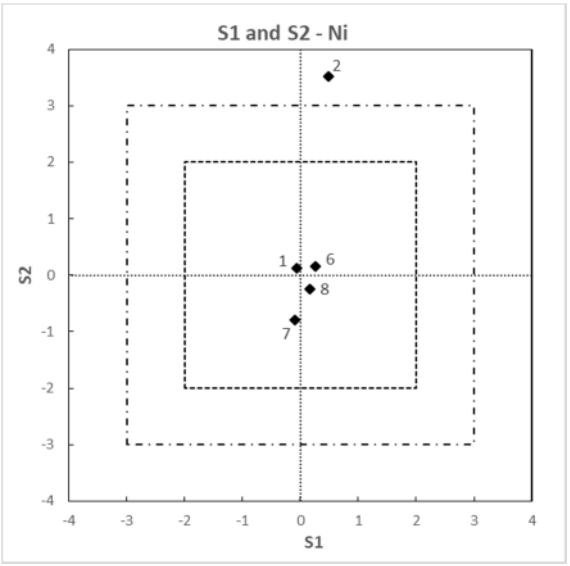
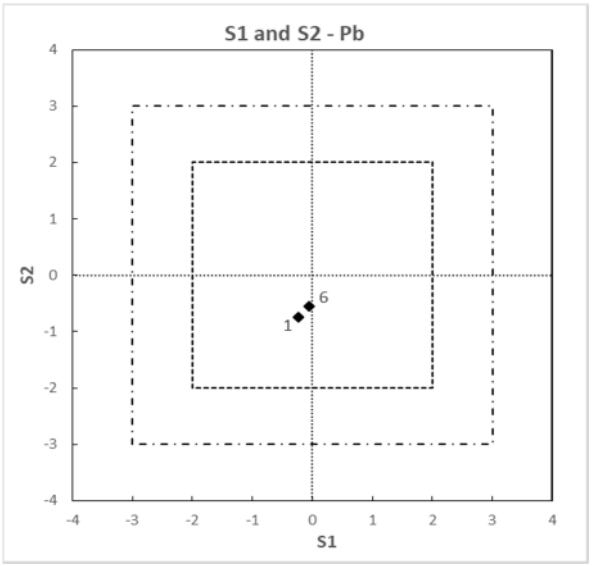


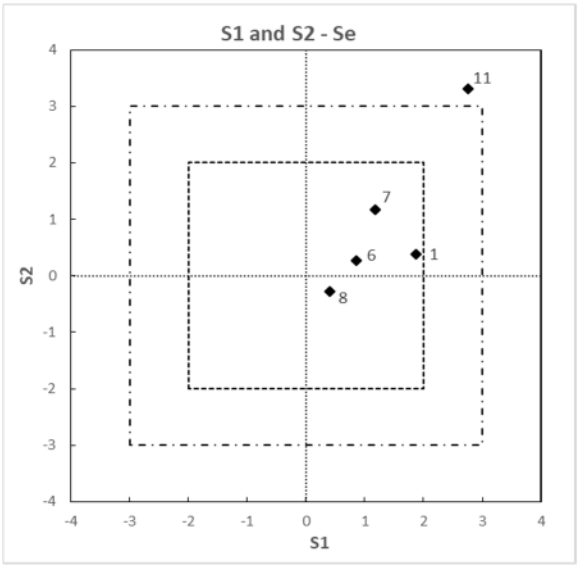
Figure 61 Scatter Plots of: z-Score for S1 and S2



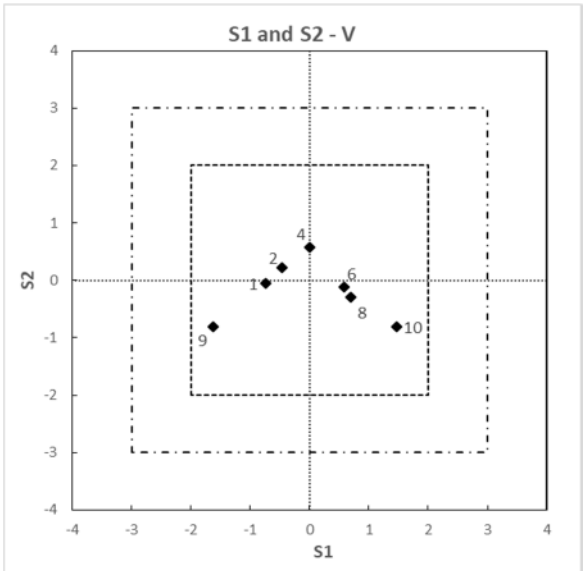




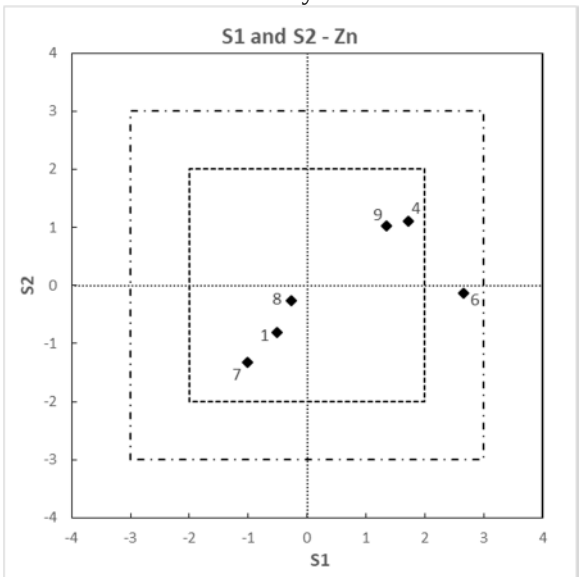
Laboratories 2 and 7 are off scale



Laboratory 2 is off scale



Laboratory 7 is off scale



Laboratories 2 and 10 are off scale

Figure 61: Scatter Plots of: z-Score for S1 and S2 (continued)

7.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 21-18 is the 11th NMI proficiency test of metals in sea water. Measurements of low level elements in sea water continues to challenge participants' analytical techniques.

Participants' performance in measurement of metals in sea water over last eleven years is presented in Figure 62.

Individual performance history reports are emailed to each participant at the end of the study; the consideration of z-scores for an analyte over time provides much more useful information than a single z-score. Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \leq 2.0$. Scores in the range $2.0 < |z| < 3.0$ can occasionally occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line is an indication of method or laboratory bias.

7.8 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 45).

Table 45 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	SS
2	CRM
4	SS
5	CRM
6	MX014 and ERM-CA403
8	CRM
9	SS
10	CRM – NASS 7, CASS 6 and NMI MX014
11	

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.

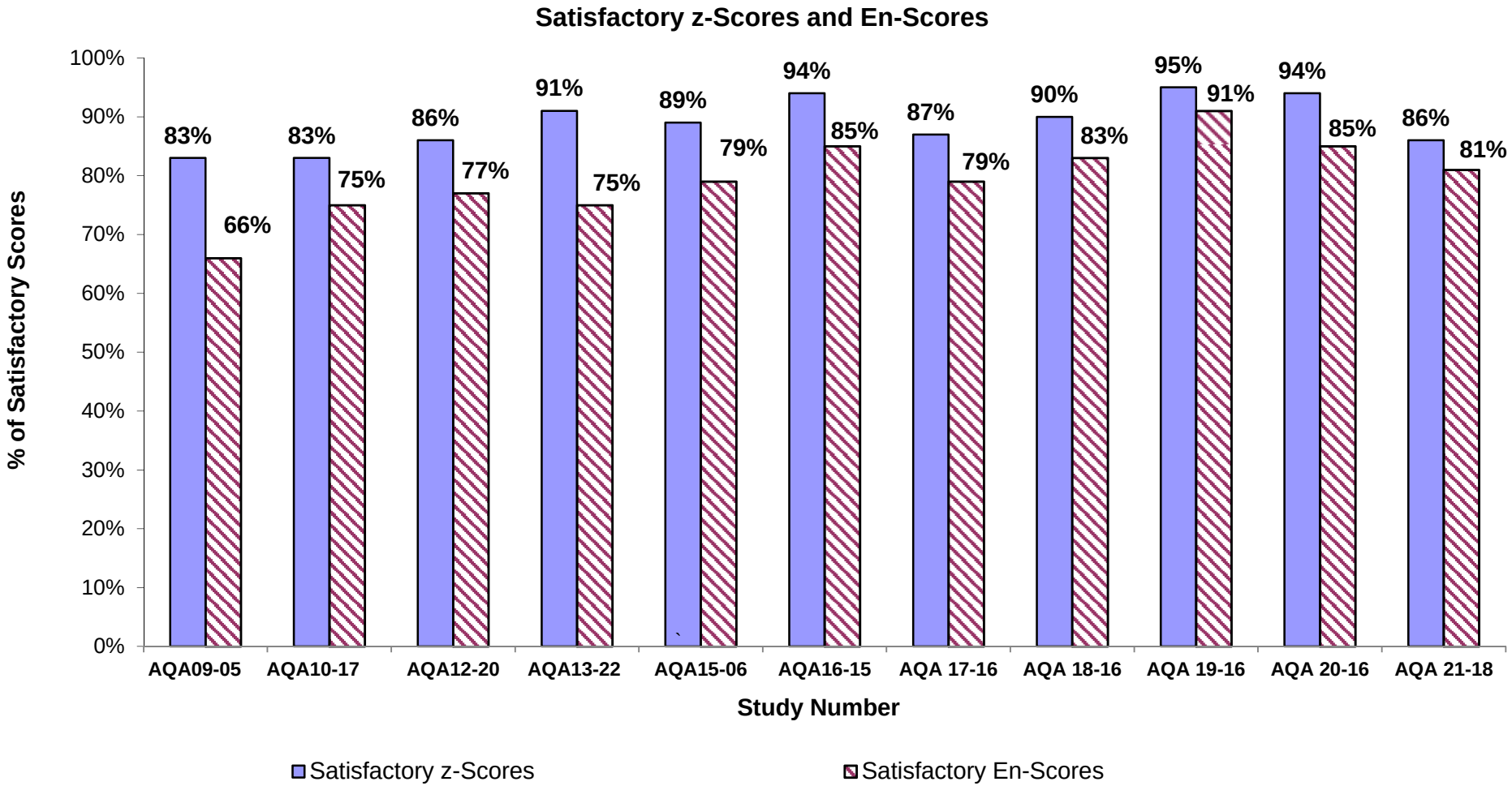


Figure 62 Participants' Performance in Metals in Sea water PT Studies over Last Twelve Years

8 REFERENCES

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared from sea water. Approximately 6.5 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 16 elements.

Sample S2 was prepared by mixing 2 L of Sample S1 with 2 L milli-Q water to create low-salinity sea water. The prepared water was stabilised by adding 2% (v/w) nitric acid and 0.01% (v/w) HCl and was further fortified with 19 elements.

Sample Analysis and Homogeneity Testing

With the exception of Li and Sn in S1 and of Al in S2, 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.

Homogeneity values for As, Fe, Hg, Ni, P, Pb, Se and Zn in S1 and of Hg, Ni and Se in S2 were set as the reference values.

Sample Analysis for Dissolved Elements

For analyses of dissolved elements in Samples S1 and S2, a test portion of 1 mL was transferred to a 14 mL graduated polypropylene centrifuge tube and diluted to 10 mL with milli-Q water.

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 a former PT sample (AQA 20-16 S1) 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 given in Table 46.

Table 46 Instrumental Techniques used for Dissolved Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Ion / Wavelength
Ag	ICP-MS	Rh	ORS	He	10	NA	107 m/z
S2: As	ICP-MS	Rh	ORS	He	10	10	75 m/z
B	ICP-MS	Rh	ORS	He	NA	10	11 m/z
Ba	ICP-MS	Rh	ORS	He	NA	10	137 m/z
Be	ICP-MS	Rh	NA	NA	10	NA	9 m/z
Cd	ICP-MS	Rh	ORS	He	10	10	111 m/z
Co	ICP-MS	Rh	ORS	He	NA	10	59 m/z
Cr	ICP-MS	Rh	ORS	He	10	10	52 m/z
Cu	ICP-MS	Rh	ORS	He	10	10	65 m/z
S2: Fe	ICP-MS	Rh	ORS	He	NA	10	56 m/z
Mn	ICP-MS	Rh	ORS	He	10	10	55 m/z
Mo	ICP-MS	Rh	ORS	He	NA	10	95 m/z
S2: Pb	ICP-MS	Ir	ORS	He	10	10	208 m/z
Sb	ICP-MS	Rh	ORS	He	NA	10	121 m/z
Tl	ICP-MS	Rh	ORS	He	10	NA	205 m/z
U	ICP-MS	Ir	ORS	He	10	NA	238 m/z
V	ICP-MS	Rh	ORS	He	10	10	51 m/z
S2: Zn	ICP-MS	Rh	ORS	He	10	10	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 'ISO13258:2015, Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] The uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 47.

Table 47 Uncertainty of Assigned Value for Mn in Sample S1

No. results (p)	8
Robust Average	3.18 µg/L
$S_{rob\ av}$	0.26 µg/L
$u_{rob\ av}$	0.11 µg/L
k	2
$U_{rob\ av}$	0.23 µg/L

The assigned value for **Mn** in Sample S1 is **3.18 ± 0.23 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 10).

A worked example is set out below in Table 48.

Table 48 z-Score and E_n-score for Mn result reported by Laboratory 6 in S1

Ag Result µg/L	Assigned Value µg/L	Set Target Standard Deviation	z-Score	E_n-Score
3.32 ± 0.15	3.18 ± 0.23	15% as CV or 0.15 x 3.18 = = 0.48 µg/L	$z = \frac{(3.32 - 3.18)}{0.48}$ z = 0.29	$En = \frac{(3.32 - 3.18)}{\sqrt{0.15^2 + 0.23^2}}$ $E_n = 0.51$

APPENDIX 3 – REFERENCE VALUES

A.3.1 Description of Method of Analysis

All analytes were quantified by either double isotope dilution ICP-MS (Hg, Ni, Se) or standard addition ICP-MS (As, Fe, P, Pb, Zn). NIST 3100 series primary calibration materials were used, see table below for details, and these were diluted gravimetrically to working concentrations.

Analyte	Standard Name	Lot No.
As	NIST 3103a	100818
Fe	NIST 3126a	140812
Hg	NIST 3133	160921
Ni	NIST 3136	120619
P	NIST 3139a	060717
Pb	NIST 3128	101026
Se	NIST 3149	100901
Zn	NIST 3168a	120629

Isotope dilution was performed by spiking calibration standards and samples with isotopically enriched ^{201}Hg (Oakridge), ^{61}Ni (Oakridge) and ^{74}Se (Cambridge Isotope Laboratories) standards. For each sample analysis approximately 16 g of the sample was weighed along with an appropriate masses of the aforementioned isotopic internal standards. Calibration solutions were prepared to approximately match the sample solution mass fraction and isotope ratio. Samples and calibration were then thoroughly mixed before instrumental analysis. A further 1/10 dilution using UHP water was performed for all solutions analysed on HR-ICP-MS.

Standard addition for each sample analysis used approximately 16 g of the sample, this sample was weighed and then spiked with a mixed internal standard solution containing Ge, Y, Mn, In and Ir. These solutions were then thoroughly mixed before being gravimetrically separated into a ‘spiked’ and an ‘unspiked’ solutions with gravimetric additions of standards to the ‘spiked’ solutions. These solutions were then thoroughly mixed before instrumental analysis. A further 1/10 dilution using UHP water was performed for all solutions analysed on HR-ICP-MS. For both isotope dilution and standard addition each experimental batch contained CRMs and/or QC materials and method blanks prepared using the same procedures.

Reference values were calculated from isotope ratios measured by HR-ICP-MS using low resolution (Hg, Pb), medium resolution (Fe, Ni, P) and high resolution (Se), and by ICP-MS/MS using He gas at 3 mL/min (Zn). Where possible confirmation analysis was performed using different isotope ratios and different instruments

All isotope dilution measurements for all samples were measured bracketed on either side by the calibration solutions. All standard addition measurements for all samples were measured with the spiked solution bracketed on either side by the paired unspiked solution.

A.3.2 Reference Values

The reference values and associated measurement uncertainty estimates for AQA 21-18 samples S1 and S2 are presented below. The reference values come from the analysis of 4 bottles with 4 subsamples taken from each. Measurement uncertainty is given as a 95% level of confidence. The reference values were determined as mass fractions then converted to mass

concentrations using the density of the sample. The density measurement is valid for 15°C to 25°C and atmospheric pressure.

Sample	Analyte	Reference Value (µg/L)	Expanded Uncertainty (95%) (µg/L)	Relative Expanded Uncertainty	Coverage Factor (95%)
AQA 21-18 S1	As	1.18	0.19	16%	2.78
	Fe	12.0	1.5	13%	2.20
	Hg	0.1312	0.0065	5.0%	2.16
	Ni	1.25	0.27	22%	2.04
	P	74.3	3.7	5.0%	2.04
	Pb	0.555	0.39	7.0%	2.78
	Se	1.36	0.25	18%	2.02
	Zn	5.28	0.72	14%	2.00
AQA 21-18 S2	Hg	0.326	0.012	3.7%	2.31
	Ni	2.98	0.31	10%	2.04
	Se	3.01	0.26	8.6%	1.97

A.3.3 Homogeneity Assessment

Homogeneity was assessed on the data set used for the provision of the reference value. This data set was assessed using ANOVAs for both between batch variation and inhomogeneity. To avoid double counting of uncertainty components only the batch to batch uncertainty and associated method precision or the homogeneity uncertainty and associated method precision was included in the overall measurement uncertainty. This choice was made such that if either factor was significant the uncertainty contribution from that factor would be used while if neither or both were significant the most conservative estimates were used. During these assessments the methods used were found to be precise enough to reveal inhomogeneity for Fe in S1 and Ni in S2 at nominally 95% confidence†. In both cases, as indicated above the uncertainty of the reference value was calculated using an estimate of uncertainty related potential inhomogeneity between sample bottles.

A.3.4 Stability Assessment

Stability was not assessed.

A.3.5 Statement of Traceability

The reference values given in this report rely on gravimetric sample preparation and elemental quantification by ICP-MS. Gravimetric measurements were calibrated using Australian standards for mass and are traceable to the SI unit for mass (kg). ICP-MS measurements were calibrated with isotope dilution and standard addition and are traceable to (i) the SI unit for mass (kg) through the primary calibration standard certified by NIST (USA) and (ii) the SI unit for amount of substance (mol) through data for isotopic composition and relative atomic mass. Isotopic composition is traceable to IUPAC published data. Density measurement was calibrated using ultra high purity water and is traceable to the NMI determination of the density of water (see www.measurement.gov.au/publications/pages/determinations.aspx).

†It is noted that due to the multiple comparisons performed the exact significance of these results is less than the nominal 95% tested. However as an uncertainty term containing this variance will be included in either respect this has not been calculated further.

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10, 12] Between 2007 and 2020, NMI carried out 29 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 21 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 49 and 50.

Table 49 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 Water	0.0029 ± 0.0006	0.00298 ± 0.00031	13	6
Average				15**	

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

Table 50 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 50 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
	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 15% and 9.6% respectively. Using a coverage factor of two gives relative expanded uncertainties of 30% and 20% respectively, at a level of confidence of 95% level.

Table 51 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 51 Uncertainty of Ni results estimated using PT data

Results mg/L	Uncertainty mg/L
0.00050	0.00015
0.00100	0.00030
0.0100	0.0020
0.100	0.020
0.150	0.030

The estimates of 32% 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 5 - 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 6 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 52 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	103	ORS	He	1	NA	107
2	GFAAS				10	NA	328.1
4	ICP-MS	Rh	KED	He	20	NA	109
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS/MS	Rh103	NA	standard mode	10	NA	107
7						NA	
8	ICP-MS	Rh	ORS	He	10	NA	107
9	ICP-MS	In			10	NA	107
10	ICP-MS	Rh	NA	NA	1	NA	109
11	NA	NA	NA	NA	NA	NA	NA

Table 53 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	45	ORS	He	NA	1	27
2	ICP-MS	Li6	ORS		NA	10	
4	ICP-MS	Sc	KED	He	NA	20	27
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Sc45	DRC	NH3	NA	5	27
7					NA		
8	ICP-OES-AV	Y	NA	NA	NA	2	167.019
9					NA		
10	ICP-MS	Sc	NA	NA	NA	1	27
11	NA	NA	NA	NA	NA	NA	NA

Table 54 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	72	ORS	He	1	1	75
2	ICP-MS	Y	ORS	He	10	10	75
4	ICP-MS	Te	KED	He	20	20	75
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	DRC	O2	10	5	91
7	ICP-MS/MS	Re187	ORS	O2	10	10	91
8	ICP-MS	Rh	ORS	He	10	10	75
9	ICP-MS	Ga	KED	He	10	10	75
10	ICP-MS	Rh	KED	He	1	1	75
11	ICP-MS	Ga	DRC	O2	15	15	91

Table 55 Instrument Conditions B

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	Lu			NA	5	249.678
2	ICP-OES-AV	Yb			NA	10	249.772
4	ICP-MS	Sc	KED	He	NA	20	10
5	ICP-MS	Y	NA		NA		
6	ICP-MS/MS	Sc45	NA	standard mode	NA	5	10
7	ICP-OES-AV	Rh			NA	10	249.773
8	ICP-OES-AV	Y	NA	NA	NA	2	249.678
9					NA		
10	ICP-MS	Sc	NA	NA	NA	1	10
11	NA	NA	NA	NA	NA	NA	NA

Table 56 Instrument Conditions Ba

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	175	ORS	He	NA	1	138
2	ICP-MS	Tb	ORS		NA	10	135
4	ICP-MS	Tb	KED	He	NA	20	137
5	ICP-MS	Y	NA		NA		
6	ICP-MS/MS	Rh103	NA	standard mode	NA	5	138
7	ICP-MS	In115			NA	10	137
8	ICP-OES-AV	Y	NA	NA	NA	2	233.527
9	ICP-MS	In			NA	10	137
10	ICP-MS	Rh	NA	NA	NA	1	138
11	NA	NA	NA	NA	NA	NA	NA

Table 57 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	45	ORS	He	5	NA	9
2	ICP-MS	Li6	ORS		10	NA	9
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS/MS	Sc45	NA	standard mode	10	NA	9
7	ICP-MS	Y89			1	NA	9
8	ICP-MS	Rh	ORS	He	10	NA	9
9	ICP-MS	Sc			10	NA	9
10	ICP-MS	Sc	NA	NA	1	NA	9
11	NA	NA	NA	NA	NA	NA	NA

Table 58 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	103	ORS	He	1	1	114
2	ICP-MS	In	ORS		10	10	111
4	ICP-MS	Rh	KED	He	20	20	111
5	ICP-MS	Y	NA		NA		
6	ICP-MS/MS	Rh103	DRC	O2	10	5	111
7	ICP-MS	In115			10	10	111
8	ICP-MS	Rh	ORS	He	10	10	111
9	ICP-MS	In			10	10	111
10	ICP-MS	Rh	NA	NA	1	1	111
11	ICP-MS	Rh	Nil	standard mode	15	15	111

Table 59 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	103	ORS	He	NA	1	59
2	ICP-MS	Sc	ORS		NA	10	59
4	ICP-MS	Ga	KED	He	NA	20	59
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	KED	He	NA	5	59
7	ICP-MS/MS	Sc45	ORS	He	NA	10	59
8	ICP-MS	Rh	ORS	He	NA	10	59
9	ICP-MS	Ga	KED	He	NA	10	59
10	ICP-MS	Rh	KED	He	NA	1	59
11	NA	NA	NA	NA	NA	NA	NA

Table 60 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	72	ORS	He	1	1	52
2	ICP-MS	Sc	ORS		10	10	52
4	ICP-MS	Ga	DRC	NH3	20	20	52
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Sc45	DRC	NH3	10	5	52
7	ICP-MS/MS	Sc45		He	1	1	52
8	ICP-MS	Rh	ORS	He	10	10	52
9	ICP-MS	Ga	DRC	NH3	10	10	52
10	ICP-MS	Sc	KED	He	1	1	52
11	ICP-MS	Ga	DRC	NH3	15	15	52

Table 61 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	103	ORS	He	1	1	65
2	ICP-MS	Y	ORS		10	10	65
4	ICP-MS	Ga	KED	He	20	20	63
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	KED	He	10	5	63
7	ICP-MS/MS	Sc45		He	10	10	63
8	ICP-MS	Rh	ORS	He	10	10	63
9	ICP-MS	Ga	KED	He	10	10	63
10	ICP-MS	Rh	KED	He	1	1	65
11	ICP-MS	Ga	KED	He	15	15	63

Table 62 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	72	ORS	He	1	1	56
2	ICP-MS	Sc	ORS		10	10	56
4	ICP-MS	Ga	DRC	NH3	20	20	54
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	DRC	NH3	10	5	54
7							
8	ICP-OES-AV	Y	NA	NA	2	2	238.204
9							
10	ICP-MS	Sc	KED	He	1	1	56
11	ICP-MS	Ga	KED	NH3	15	15	57

Table 63 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	VGA-ICP-OES				1	1	194.164
2	CVAAS	SnCl2			NA	NA	3470
4	CVAFS	NA	NA	NA	5	5	NA
5					NA		
6	ICP-MS/MS	Rh103	NA	NA	NA	NA	NA
7							
8	CVAAS					2	
9	CVAAS				2	2	253.7
10	ICP-MS	Ir	NA	NA	1	1	201
11	NA	NA	NA	NA	NA	NA	NA

Table 64 Instrument Conditions Li

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				5	NA	670.783
2	NA	NA	NA	NA	NA	NA	NA
4	ICP-MS	Sc	KED	He	20	NA	7
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS/MS	Sc45	NA	standard mode	10	NA	7
7	ICP-OES-AV	In			10	NA	670.784
8	ICP-MS	Rh	ORS	He	10	NA	7
9	ICP-MS	Sc			10	NA	7
10	ICP-MS	Sc	NA	NA	1	NA	7
11	NA	NA	NA	NA	NA	NA	NA

Table 65 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	72	ORS	He	1	1	55
2	ICP-MS	Sc	ORS		10	10	55
4	ICP-MS	Ga	KED	He	20	20	55
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	DRC	NH3	10	5	55
7	ICP-MS/MS	Sc45	ORS	He	10	10	55
8	ICP-MS	Rh	ORS	He	10	10	55
9	ICP-MS	Sc	KED	He	10	10	55
10	ICP-MS	Sc	KED	He	1	1	55
11	NA	NA	NA	NA	NA	NA	NA

Table 66 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	72	ORS	He	NA	1	98
2	ICP-MS	In	ORS		NA	10	97
4	ICP-MS	Rh	KED	He	NA	20	98
5	ICP-MS	Y			NA		
6	ICP-MS/MS	Rh103	NA	standard mode	NA	5	95
7	ICP-MS	Y89			NA	10	95
8	ICP-MS	Rh	ORS	He	NA	10	95
9	ICP-MS	In			NA	10	95
10	ICP-MS	Rh	NA	NA	NA	1	95
11	NA	NA	NA	NA	NA	NA	NA

Table 67 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	103	ORS	He	1	1	60
2	ICP-MS	Sc	ORS	He	10	10	60
4	ICP-MS	Ga	KED	He	20	20	60
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	KED	He	10	5	60
7	ICP-MS/MS	Sc45	ORS	He	10	10	60
8	ICP-MS	Rh	ORS	He	10	10	60
9	ICP-MS	Ga	KED	He	10	10	60
10	ICP-MS	Rh	KED	He		1	60
11	NA	NA	NA	NA	NA	NA	NA

Table 68 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					1	NA	
2	ICP-OES-AV					NA	177.43
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS/MS	Sc61	DRC	O2	10	NA	47
7						NA	
8	ICP-OES-AV	Y	NA	NA	2	NA	213.618
9						NA	
10						NA	
11	ICP-MS	Be	Nil	standard mode	15	NA	31

Table 69 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	193	ORS	He	1	1	208
2	ICP-MS	Ir	ORS		10	10	206
4	ICP-MS	Tb	KED	He	20	20	206+207+208
5	ICP-MS	Y	NA		NA		
6	ICP-MS/MS	Ir193	NA	standard mode	10	5	208
7	ICP-MS	Ir193			1	1	sum (204, 206, 207, 208)
8	ICP-MS	Ir	ORS	He	10	10	208
9	ICP-MS	Ir			10	10	208
10	ICP-MS	Ir	NA	NA	1	1	206+207+208
11	ICP-MS	Lu	Nil	standard mode	15	15	208

Table 70 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	72	ORS	He	NA	1	121
2	ICP-MS	In	ORS		NA	10	123
4	ICP-MS	Rh	KED	He	NA	20	121
5	ICP-MS	Y	NA		NA		
6	ICP-MS/MS	Rh103	NA	standard mode	NA	5	121
7	ICP-MS	In115			NA	10	121
8	ICP-MS	Rh	ORS	He	NA	10	121
9	ICP-MS	In			NA	10	121
10					NA		
11	NA	NA	NA	NA	NA	NA	NA

Table 71 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	103	ORS	He	1	1	78
2	ICP-MS	Y	ORS		10	10	78
4	ICP-MS	Te	DRC	NH3	20	20	82
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	DRC	O2	10	5	96
7	ICP-MS/MS	Re187	ORS	O2	10	10	94
8	ICP-MS	Rh	ORS	HEHe	10	10	77
9	ICP-MS	Ge	DRC	NH3	10	10	82
10	ICP-MS	Rh	DRC	NH3	1		82
11	ICP-MS	Ga	DRC	NH3	15	15	82

Table 72 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	115	ORS	He	1	1	118
2	ICP-MS	In	ORS		10	10	118
4	ICP-MS	Rh	KED	He	20	20	120
5	ICP-MS	Y	NA		NA		
6	ICP-MS/MS	Rh103	NA	standard mode	10	5	118
7	ICP-MS	In115			10	10	118
8	ICP-MS	Rh	ORS	He	10	10	118
9	ICP-MS	In			10	10	118
10							
11	ICP-MS	Rh	Nil	standard mode	15	15	118

Table 73 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	193	ORS	He	1	NA	205
2	ICP-MS	Ir	ORS		10	NA	205
4	ICP-MS	Tb	KED	He	20	NA	205
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS/MS	Rh103	NA	standard mode	10	NA	205
7	ICP-MS	Ir193			1	NA	205
8	ICP-MS	Ir	ORS	He	10	NA	205
9	ICP-MS	Ir			10	NA	203
10	ICP-MS	Ir	NA	NA	1	NA	205
11	NA	NA	NA	NA	NA	NA	NA

Table 74 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	193	ORS	He	1	NA	238
2	ICP-MS	Ir	ORS		10	NA	238
4	ICP-MS	Tb	KED	He	20	NA	238
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS/MS	Rh103	NA	standard mode	10	NA	238
7	ICP-MS	Ir193			10	NA	238
8							
9	ICP-MS	Ir			10	NA	238
10	ICP-MS	Ir	NA	NA	1	NA	238
11	NA	NA	NA	NA	NA	NA	NA

Table 75 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	45	ORS	He	1	1	51
2	ICP-MS	Sc	ORS		10	10	51
4	ICP-MS	Ga	DRC	NH3	20	20	51
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Sc45	DRC	NH3	10	5	51
7	ICP-MS/MS	Sc45	ORS	He	1	1	51
8	ICP-MS	Rh	ORS	He	10	10	51
9	ICP-MS	Ga	DRC	NH3	10	10	51
10	ICP-MS	Sc	KED	He	1	1	51
11	NA	NA	NA	NA	NA	NA	NA

Table 76 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	115	ORS	He	1	1	66
2	ICP-MS	Y	ORS		10	10	66
4	ICP-MS	Te	KED	He	20	20	66
5	ICP-MS	Y	KED		NA		
6	ICP-MS/MS	Rh103	DRC	NH3	10	5	66
7	ICP-MS/MS	Sc45	ORS	He	1	1	66
8	ICP-MS	Rh	ORS	He	10	10	66
9	ICP-MS	Ga	KED	He	10	10	66
10	ICP-MS	Rh	KED	He	1	1	66
11	ICP-MS	Ga	KED	He	15	15	66

END OF REPORT