Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Final Report AQA 20-16 Trace Elements in Sea Water

February 2021

ACKNOWLEDGMENTS

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

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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Accredited for compliance with ISO/IEC 17043

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1 SUMMARY

This report presents the results of the proficiency test AQA 20-16, Trace Elements in Sea Water. The study focused on the measurement of dissolved: Ag, Al, As, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, La, Li, Mn, Ni, P, Pb, Se, Sn, Th, Tl, U, V and Zn and total: Ag, Al, As, B, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, Tl, U, V and Zn.

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

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

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

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

Of 450 scored results, 425 (94%) returned a satisfactory score of $|z| \leq 2.0$.

Of 450 scored results, 382 (85%) returned a satisfactory score of $|E_n| \leq 1.0$.

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

Aluminium and nickel at low levels in seawater were the analytes which presented the most analytical difficulty to participating laboratories.

A limited number of laboratories have the capability to measure P in seawater at low level.

iii. *evaluate within-laboratory reproducibility;*

Sample S2 was previously distributed as S2 of AQA 19-16. In some cases, the reported results and the expanded measurement uncertainty in the two study samples are significantly different.

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

Despite differences in the analytes' concentrations, on average participants' performance has improved over last ten years.

v. *develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates;*

Of 454 numerical results, 446 (98%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 3.

vi. *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 20-16 is the 27th 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;
- evaluate within-laboratory reproducibility;
- 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 46 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

Fifteen laboratories participated and fourteen submitted results.

The timetable of the study was:

Invitation issued:	12 October 2020
Samples dispatched:	9 November 2020
Results due:	8 December 2020
Interim report issued:	9 December 2020

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 unfiltered sea water preserved by adding 2% (v/w) nitric acid, previously distributed as Sample S2 of proficiency testing AQA 19-16.[6]

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

A partial homogeneity testing was conducted in this study. The same validated preparation procedure was followed as in previous studies.[2] The test samples from the previous studies were demonstrated to be sufficiently homogeneous for evaluation of participants' performance. The results from the partial homogeneity testing are reported in this study as homogeneity values. No homogeneity testing was conducted for Bi, Li and Sn in S1 and B and Sr S2.

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

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

No stability study was carried out for samples S1 and S2. Stability studies conducted for similar previous studies of metals in seawater 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 9 November 2020.

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 filtered, sea water		SAMPLE S2 unfiltered, sea water	
Test DISSOLVED	**Approximate Conc. Range µg/L**	**Test TOTAL**	**Approximate Conc. Range µg/L**
Al	3-60	Ag	20-250
Ag	0.2-5	Al	200-2500
As	0.2-5	As	20-250
Be	0.2-5	B	500-10000
Bi	0.2-5	Ba	200-2500
Cd	0.2-5	Cd	20-250
Co	0.2-5	Cr	20-250
Cr	0.2-5	Cu	40-500
Cu	1-25	Fe	200-2500
Fe	5-200	Mn	200-2500
Hg	0.1-2.5	Mo	20-250
La	0.2-5	Ni	20-250
Li	10-400	P	200-2500
Mn	0.2-5	Pb	20-250
Ni	0.2-5	Sb	40-500
P	25-200	Se	20-250
Pb	0.2-5	Sn	20-250
Se	0.2-5	Sr	NA
Sn	0.5-7.5	Tl	20-250
Th	0.2-5	U	20-250
Tl	0.2-5	V	20-250
U	0.2-5	Zn	40-500
V	0.2-5		
Zn	1-25		

- 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 9 December 2020.

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 5.

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	HNO_3 (mL)	HCl (mL)	HNO_3 (1:1) (mL)	.HCl (1:1) (mL)	H_2O_2 (mL)
1*	3051A	20	170	15	1	1			
2	USEPA6010, USEPA6020	10	95	90	2	3			
6	APHA 3030E	10	105	120	0.5	0	0	0	0
7		30	95-100	90	2				
11	APHA, USEPA 6020B and USEPA 200.8	40	95	120	5.0	2.5			
12*	200.7-8								
13		10	170	40	1.25	0.63			
15	USEPA 200.7 and 200.8	20	180	15	1	0.2			

*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
1	Total Elements: Microwave digestion
12	Sample S1: S1 tested by ICPMS Sample S2: S2 tested by ICPOES Total Elements: Samples were not digested
14	Instrumental Techniques: Triple Quad was utilised for measurements

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	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis		NMI Uncertainty Course
2	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples	CRM Instrument Calibration	Eurachem/CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM	Nordtest Report TR537
5	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	Instrument Calibration	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
6	Professional judgment	Control Samples - RM	Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples	CRM	
10	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
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Top Down Approach
13	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Instrument Calibration	CRM Recoveries of SS	
14		Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	
15	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	Instrument Calibration	Nordtest Report TR537

[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.

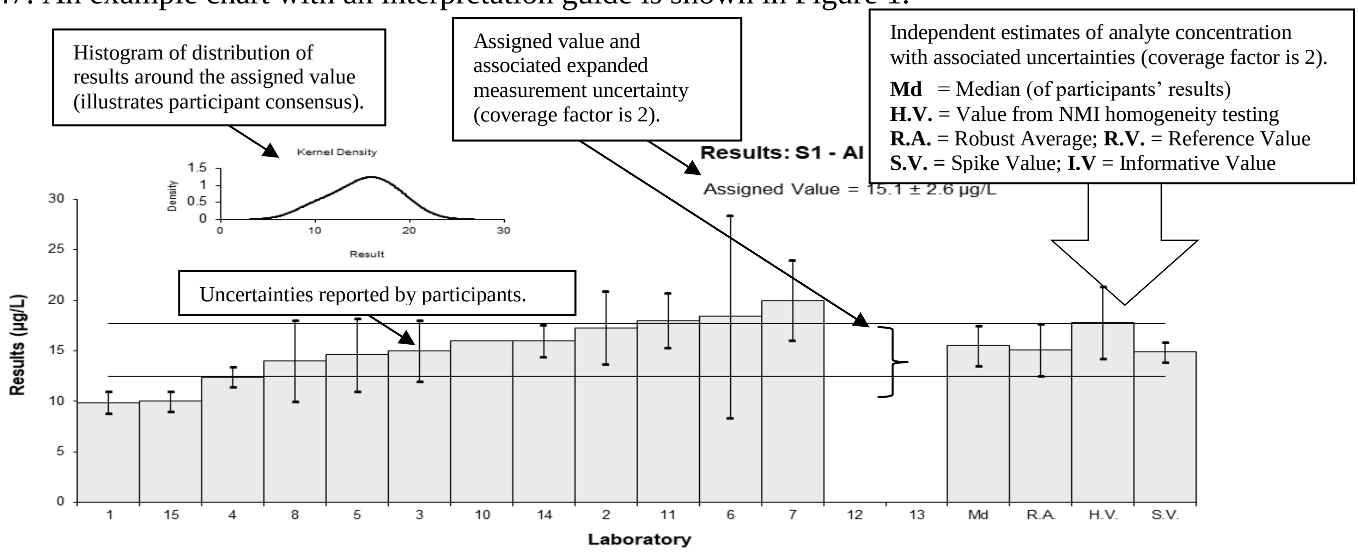


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

An example of an assigned value calculation using data from the present study is given in Appendix 2. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'[1] In this study, the property is the mass concentration of analyte. Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations (results less than 50% and greater than 150% of the robust average were removed before the calculation of the assigned value).[3,4]

5.3 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by inter-laboratory comparisons, ISO13528:2015(E)'.[7]

5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2015(E).[7]

5.5 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study coordinator would be expected from participants. It is important to note that is not the coefficient of variation of participant 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.[8] By setting a fixed and realistic value for the PCV, the participant's performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 Target Standard Deviation

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

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

5.7 z-Score

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

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

where:

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

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

- |z| ≤ 2.0 is satisfactory;
- 2.0 < |z| < 3.0 is questionable;
- |z| ≥ 3.0 is unsatisfactory.

5.8 E_n-Score

An example of E_n-score calculation using data from the present study is given in Appendix 2. The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

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

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

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

5.9 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2018[9] 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.[10]

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	z-Score	E_n-Score
1	1.2	0.13	0.81	0.76
2	1.10	0.26	0.19	0.11
3	<1	NR		
4	1.12	0.13	0.31	0.29
5	0.821	0.082	-1.55	-1.81
6	<2	2		
7	1.2	0.24	0.81	0.49
8	1.2	0.2	0.81	0.57
10	1.1	NR	0.19	0.27
11	1.0	0.15	-0.44	-0.38
12	1.0	0.4	-0.44	-0.17
13	NT	NT		
14	1.17	0.12	0.62	0.61
15	0.82	0.16	-1.56	-1.29

Statistics

Assigned Value	1.07	0.11
Spike	1.13	0.03
Homogeneity Value	1.18	0.18
Robust Average	1.07	0.11
Median	1.10	0.10
Mean	1.07	
N	11	
Max.	1.2	
Min.	0.82	
Robust SD	0.15	
Robust CV	14%	

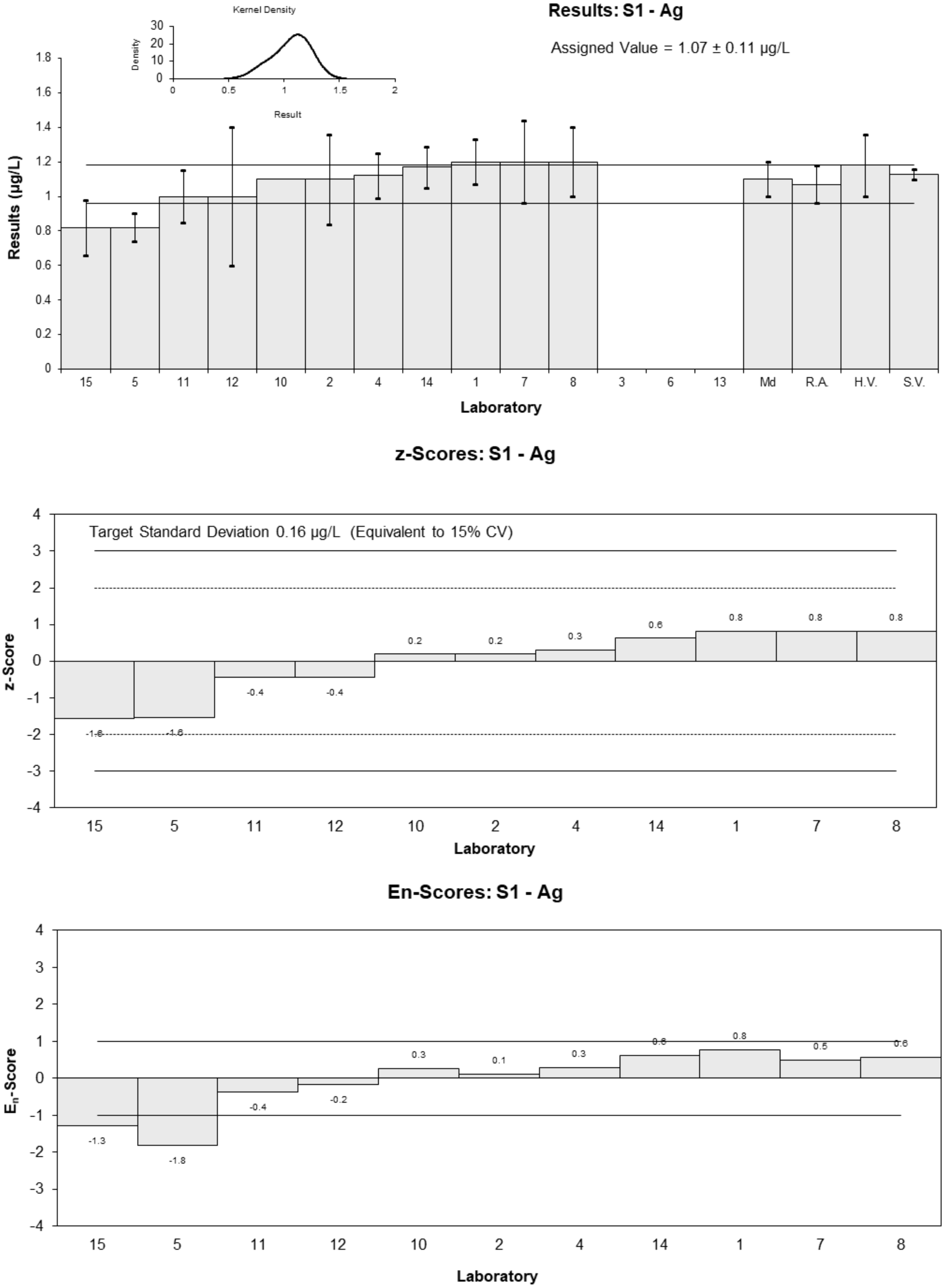

Results: S1 - Ag
Assigned Value = 1.07 ± 0.11 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15 5 11 12 10 2 4 14 1 7 8 3 6 13 Md R.A. H.V. S.V.
z-Scores: S1 - Ag
Target Standard Deviation 0.16 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
15 5 11 12 10 2 4 14 1 7 8
En-Scores: S1 - Ag
E_n-Score
Laboratory
15 5 11 12 10 2 4 14 1 7 8

Figure 2

Table 5

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	9.9	1.04	-1.72	-1.86
2	17.3	3.6	0.73	0.50
3	15	3.0	-0.03	-0.03
4	12.4	1.0	-0.89	-0.97
5	14.60	3.65	-0.17	-0.11
6	18.4	10	1.09	0.32
7	20	4.0	1.62	1.03
8	14	4	-0.36	-0.23
10	16	NR	0.30	0.35
11	18	2.7	0.96	0.77
12	NT	NT		
13	NT	NT		
14	16	1.6	0.30	0.29
15	10	1	-1.69	-1.83

Statistics

Assigned Value	15.1	2.6
Spike*	9.88	0.28
Homogeneity Value	17.8	3.6
Robust Average	15.1	2.6
Median	15.5	2.0
Mean	15.1	
N	12	
Max.	20	
Min.	9.9	
Robust SD	3.6	
Robust CV	24%	

*Incurred value not included.

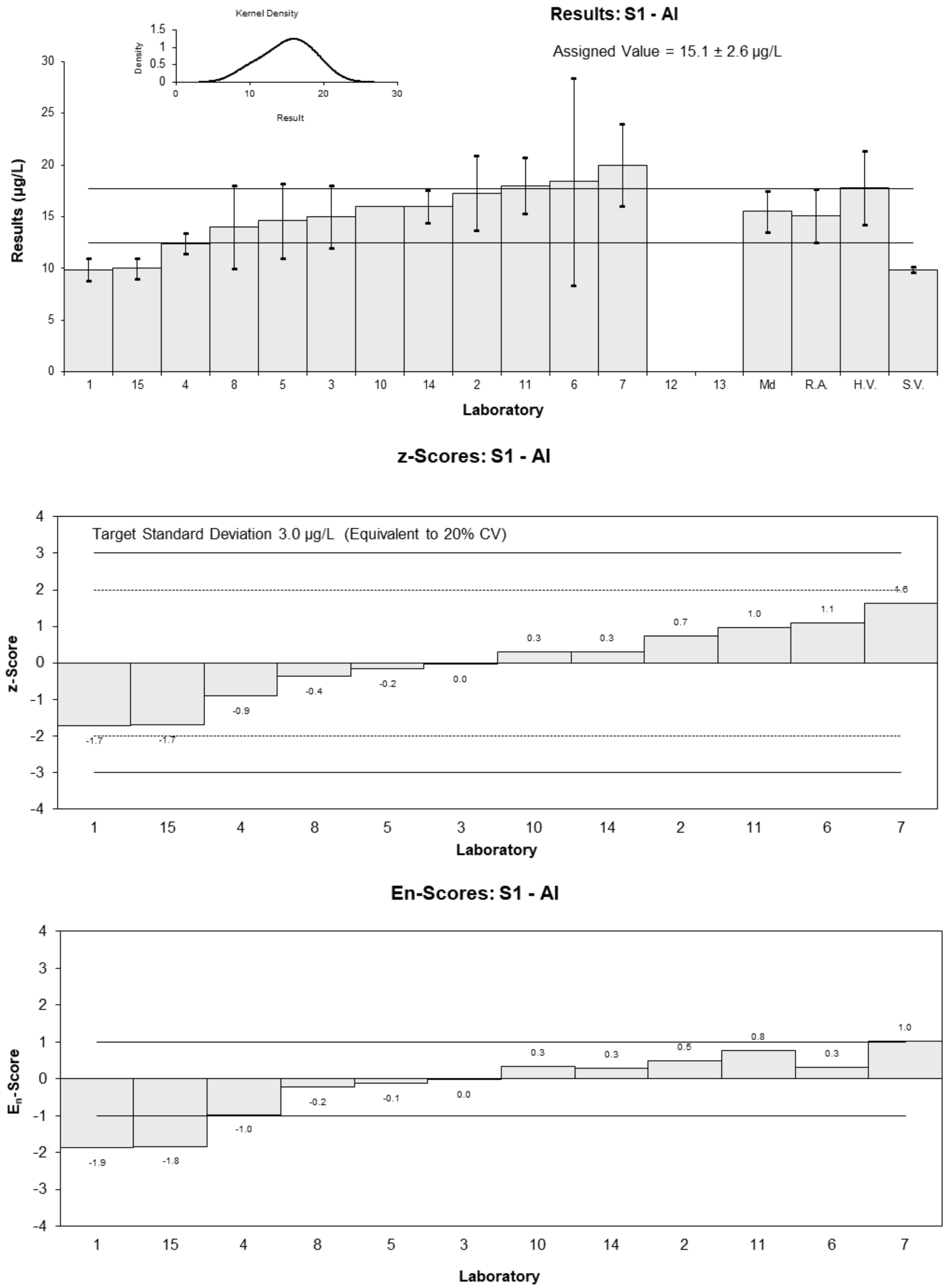

Results: S1 - Al
Assigned Value = 15.1 ± 2.6 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1 15 4 8 5 3 10 14 2 11 6 7 12 13 Md R.A. H.V. S.V.
z-Scores: S1 - Al
Target Standard Deviation 3.0 µg/L (Equivalent to 20% CV)
z-Score
-1.7 -1.7 -0.9 -0.4 -0.2 0.0 0.3 0.3 0.7 1.0 1.1 1.6
Laboratory
En-Scores: S1 - Al
E_n-Score
-1.9 -1.8 -1.0 -0.2 -0.1 0.0 0.3 0.3 0.5 0.8 0.3 1.0
Laboratory

Figure 3

Table 6

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<10	10		
2	1.24	0.28	-0.26	-0.17
3	1.3	0.3	0.05	0.03
4	1.26	0.20	-0.16	-0.14
5	1.151	0.115	-0.72	-0.95
6	1.45	1	0.83	0.16
7	1.4	0.28	0.57	0.37
8	1.4	0.3	0.57	0.35
10	<4	2.7		
11	1.4	0.21	0.57	0.48
12	< 3	NR		
13	1.3	0.1	0.05	0.07
14	1.2	0.12	-0.47	-0.60
15	1.12	0.31	-0.88	-0.53

Statistics

Assigned Value	1.29	0.09
Spike	Not Spiked	
Homogeneity Value	1.35	0.20
Robust Average	1.29	0.09
Median	1.30	0.10
Mean	1.29	
N	11	
Max.	1.45	
Min.	1.12	
Robust SD	0.13	
Robust CV	10%	

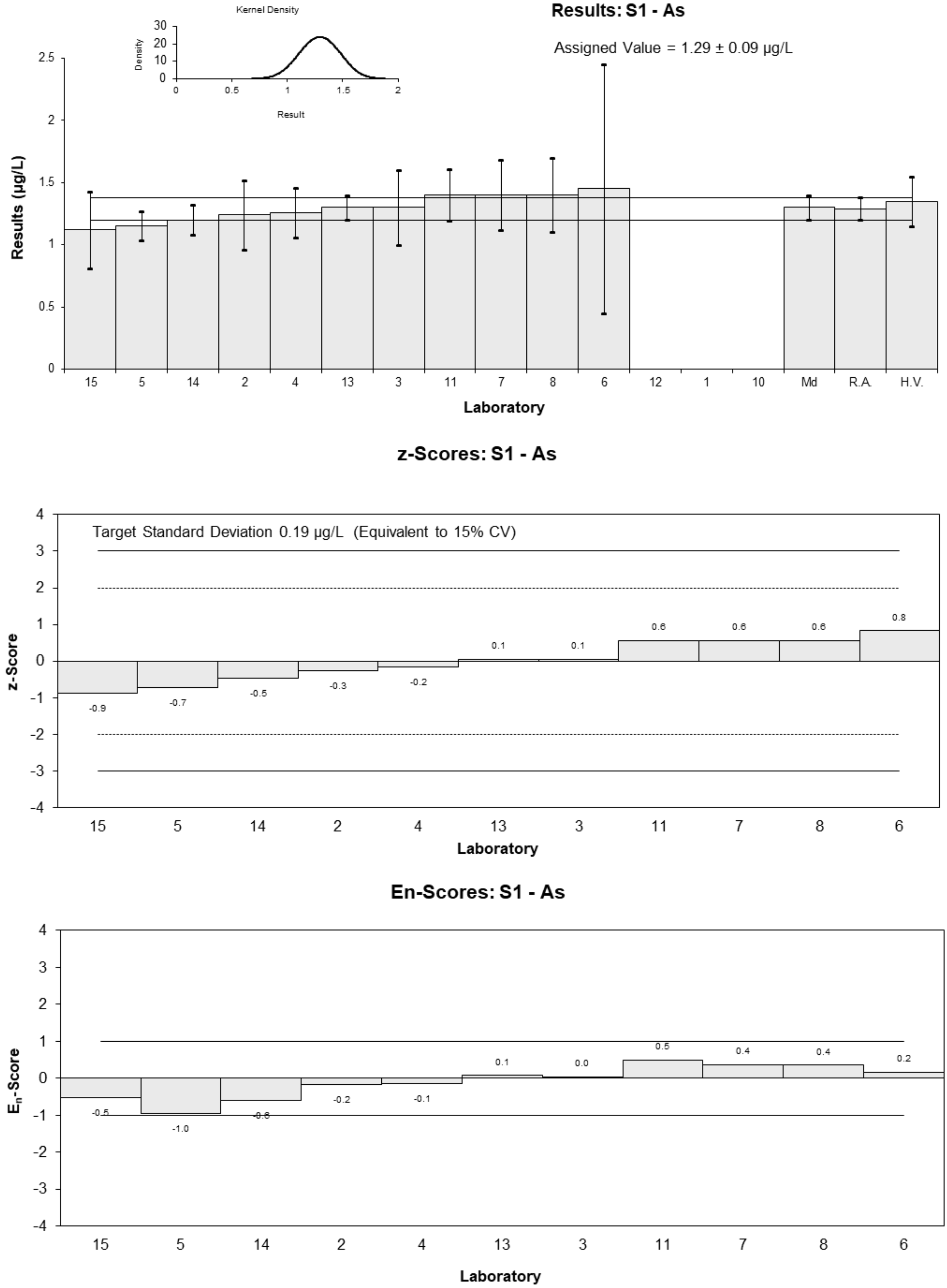

Results: S1 - As
Assigned Value = 1.29 ± 0.09 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15 5 14 2 4 13 3 11 7 8 6 12 1 10 Md R.A. H.V.
z-Scores: S1 - As
Target Standard Deviation 0.19 µg/L (Equivalent to 15% CV)
z-Score
-0.9 -0.7 -0.5 -0.3 -0.2 0.1 0.1 0.6 0.6 0.6 0.8
15 5 14 2 4 13 3 11 7 8 6
Laboratory
En-Scores: S1 - As
En-Score
-0.5 -1.0 -0.6 -0.2 -0.1 0.1 0.0 0.5 0.4 0.4 0.2
15 5 14 2 4 13 3 11 7 8 6
Laboratory

Figure 4

Table 7

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.5	0.1	1.03	1.22
2	1.16	0.36	-0.72	-0.37
3	1.3	0.3	0.00	0.00
4	1.22	0.12	-0.41	-0.45
5	1.323	0.132	0.12	0.12
6	1.36	1	0.31	0.06
7	1.2	0.24	-0.51	-0.37
8	1.5	0.8	1.03	0.25
10	NT	NT		
11	1.5	0.22	1.03	0.78
12	1.1	0.8	-1.03	-0.25
13	NT	NT		
14	1.42	0.14	0.62	0.63
15	1.01	0.12	-1.49	-1.64

Statistics

Assigned Value	1.30	0.13
Spike	1.21	0.03
Homogeneity Value	1.46	0.22
Robust Average	1.30	0.13
Median	1.31	0.12
Mean	1.30	
N	12	
Max.	1.5	
Min.	1.01	
Robust SD	0.18	
Robust CV	14%	

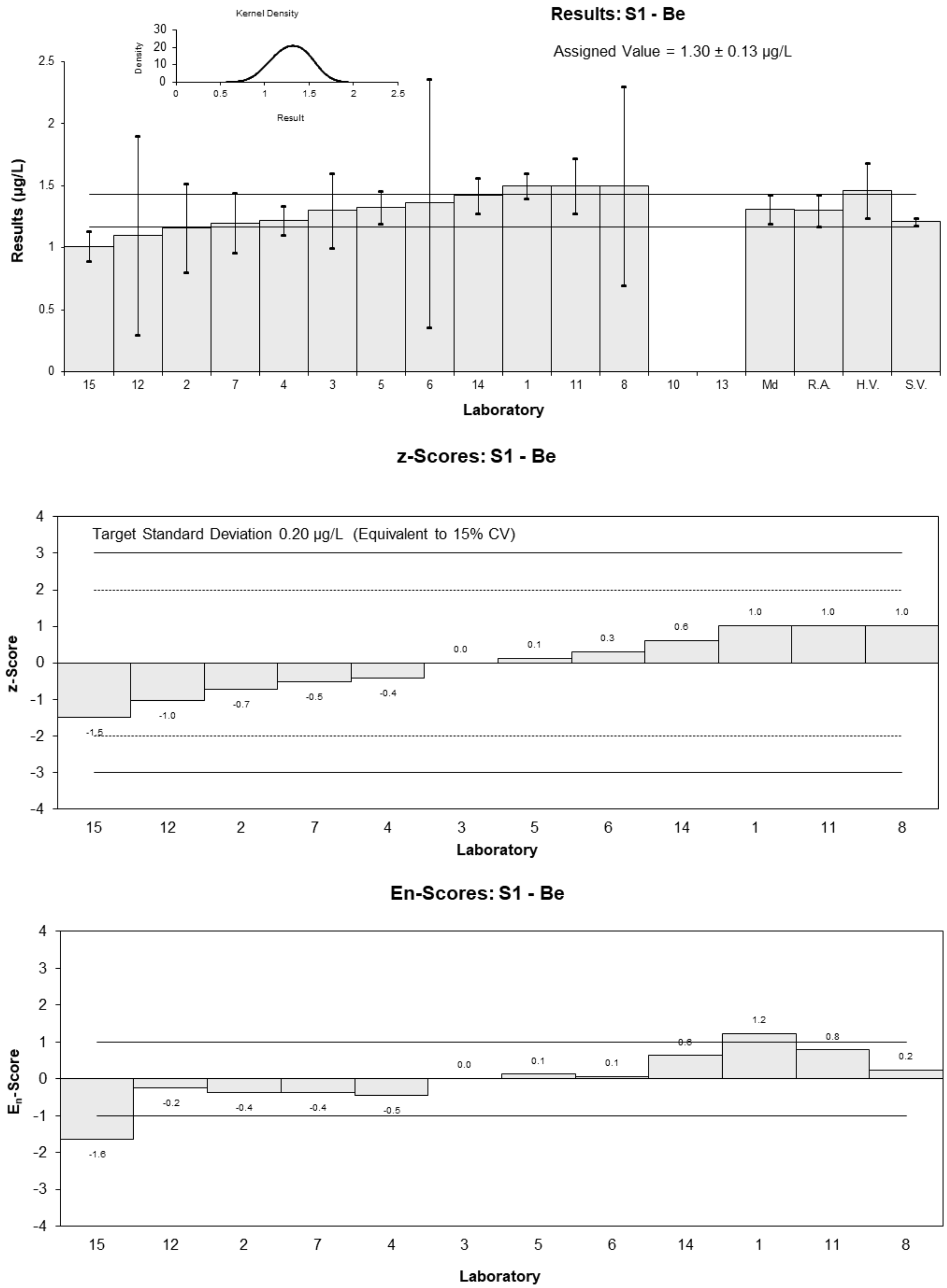

Results: S1 - Be
Assigned Value = 1.30 ± 0.13 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15 12 2 7 4 3 5 6 14 1 11 8 10 13 Md R.A. H.V. S.V.
z-Scores: S1 - Be
Target Standard Deviation 0.20 µg/L (Equivalent to 15% CV)
z-Score
-1.5 -1.0 -0.7 -0.5 -0.4 0.0 0.1 0.3 0.6 1.0 1.0 1.0
Laboratory
15 12 2 7 4 3 5 6 14 1 11 8
En-Scores: S1 - Be
En-Score
-1.6 -0.2 -0.4 -0.4 -0.5 0.0 0.1 0.1 0.6 1.2 0.8 0.2
Laboratory
15 12 2 7 4 3 5 6 14 1 11 8

Figure 5

Table 8

Sample Details

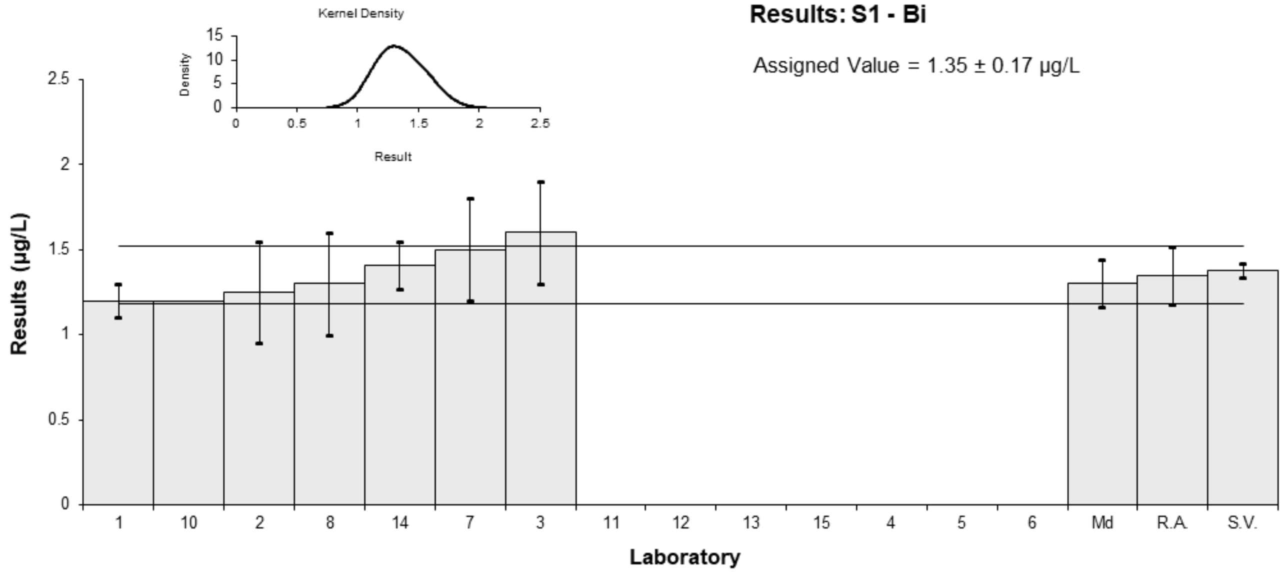
Sample No.	S1
Matrix.	Sea Water
Analyte.	Bi
Units	µg/L

Participant Results

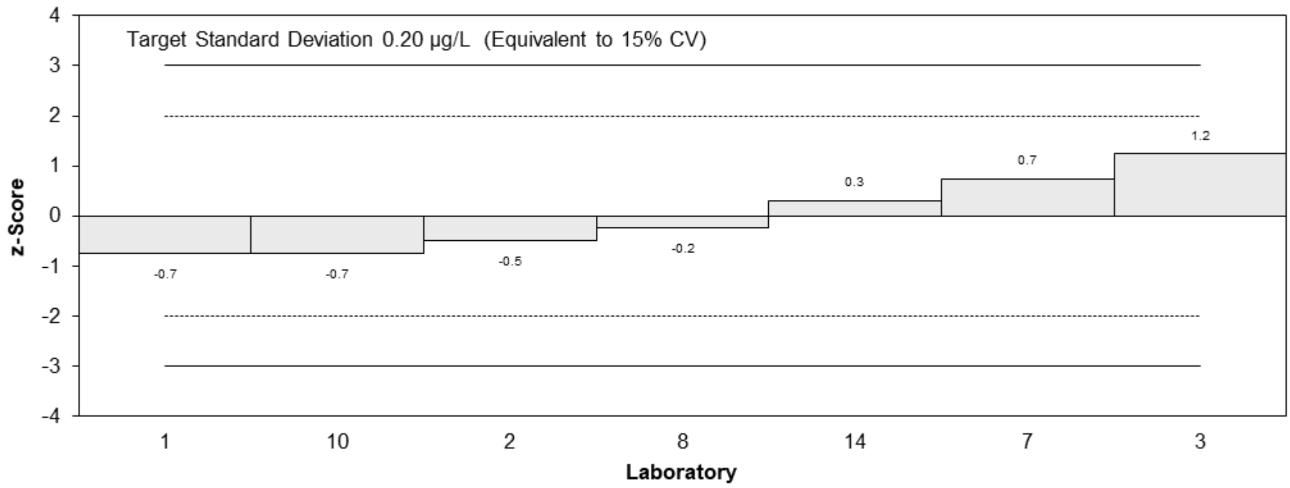
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.2	0.1	-0.74	-0.76
2	1.25	0.30	-0.49	-0.29
3	1.6	0.3	1.23	0.73
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	1.5	0.30	0.74	0.44
8	1.3	0.3	-0.25	-0.15
10	1.2	NR	-0.74	-0.88
11	NR	NR		
12	NT	NT		
13	NT	NT		
14	1.41	0.14	0.30	0.27
15	NT	NT		

Statistics

Assigned Value	1.35	0.17
Spike	1.38	0.04
Robust Average	1.35	0.17
Median	1.30	0.14
Mean	1.35	
N	7	
Max.	1.6	
Min.	1.2	
Robust SD	0.18	
Robust CV	13%	



z-Scores: S1 - Bi



En-Scores: S1 - Bi

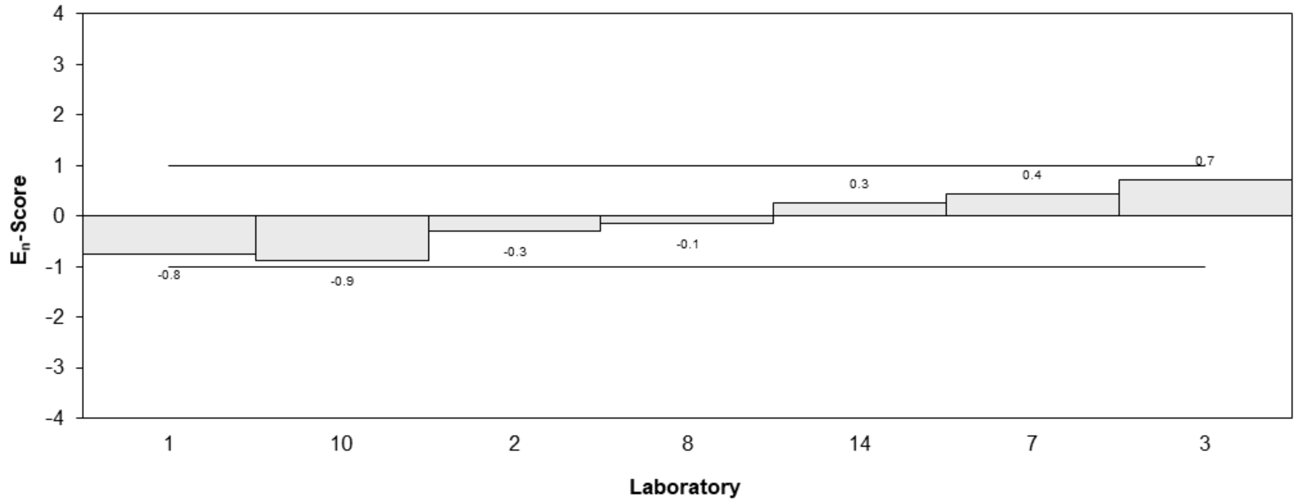


Figure 6

Table 9

Sample Details

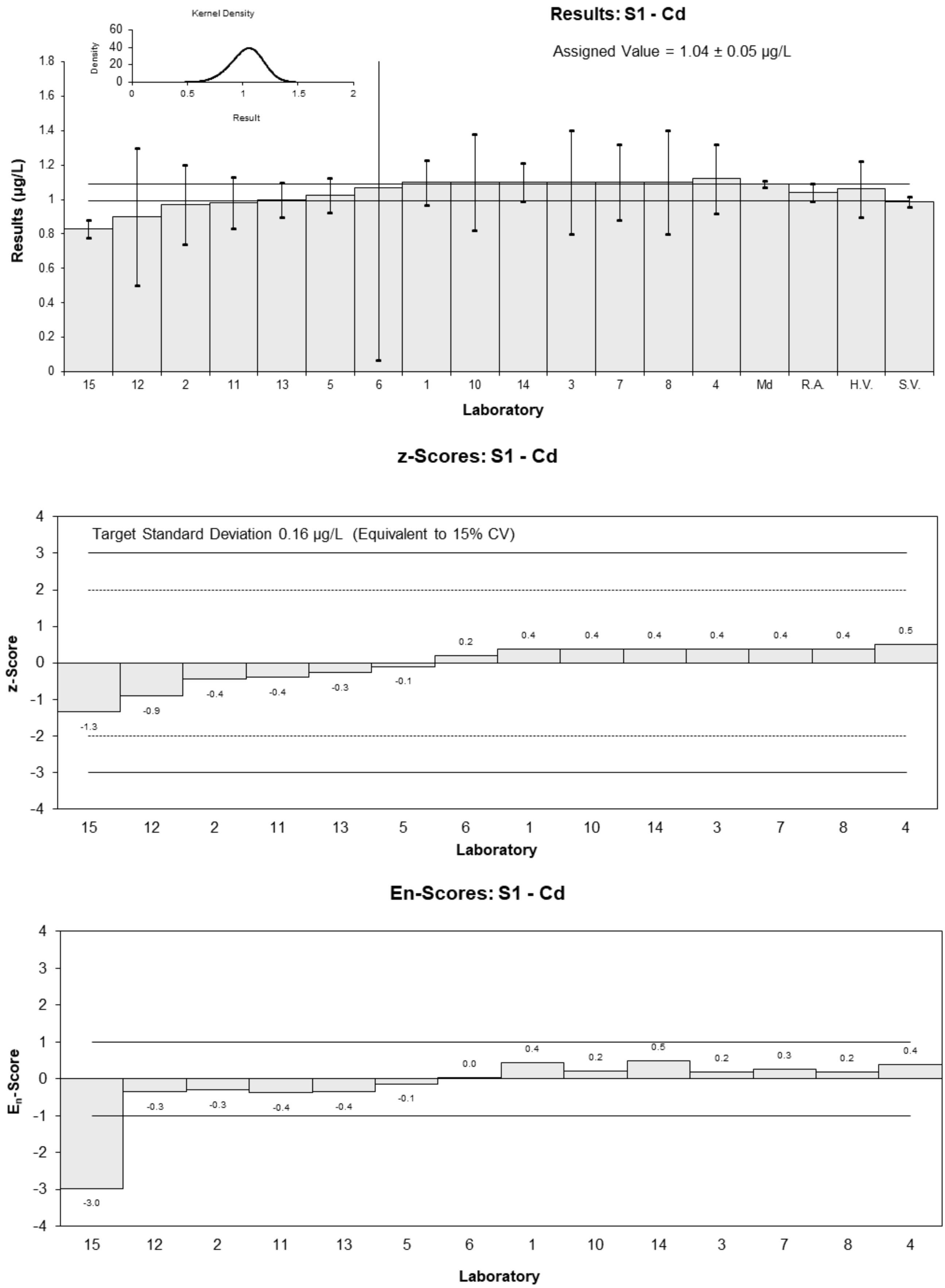
Sample No.	S1
Matrix.	Sea Water
Analyte.	Cd
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.1	0.13	0.38	0.43
2	0.97	0.23	-0.45	-0.30
3	1.1	0.3	0.38	0.20
4	1.12	0.20	0.51	0.39
5	1.025	0.102	-0.10	-0.13
6	1.07	1	0.19	0.03
7	1.1	0.22	0.38	0.27
8	1.1	0.3	0.38	0.20
10	1.10	0.28	0.38	0.21
11	0.98	0.15	-0.38	-0.38
12	0.9	0.4	-0.90	-0.35
13	1.0	0.1	-0.26	-0.36
14	1.10	0.11	0.38	0.50
15	0.83	0.05	-1.35	-2.97

Statistics

Assigned Value	1.04	0.05
Spike	0.987	0.028
Homogeneity Value	1.06	0.16
Robust Average	1.04	0.05
Median	1.09	0.02
Mean	1.04	
N	14	
Max.	1.12	
Min.	0.83	
Robust SD	0.08	
Robust CV	7.7%	



Results: S1 - Cd
Assigned Value = 1.04 ± 0.05 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15 12 2 11 13 5 6 1 10 14 3 7 8 4 Md R.A. H.V. S.V.
z-Scores: S1 - Cd
Target Standard Deviation 0.16 µg/L (Equivalent to 15% CV)
z-Score
-1.3 -0.9 -0.4 -0.4 -0.3 -0.1 0.2 0.4 0.4 0.4 0.4 0.4 0.4 0.5
Laboratory
15 12 2 11 13 5 6 1 10 14 3 7 8 4
En-Scores: S1 - Cd
En-Score
-3.0 -0.3 -0.3 -0.4 -0.4 -0.1 0.0 0.4 0.2 0.5 0.2 0.3 0.2 0.4
Laboratory
15 12 2 11 13 5 6 1 10 14 3 7 8 4

Figure 7

Table 10

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Co
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.17	1.31	1.28
2	1.09	0.27	-0.46	-0.29
3	1.1	0.3	-0.40	-0.23
4	1.21	0.10	0.23	0.34
5	1.093	0.109	-0.44	-0.62
6	1.19	1	0.11	0.02
7	1.2	0.24	0.17	0.12
8	1.2	0.3	0.17	0.10
10	1.2	NR	0.17	0.50
11	1.2	0.18	0.17	0.16
12	1	1	-0.97	-0.17
13	NT	NT		
14	1.09	0.11	-0.46	-0.64
15	1.28	0.09	0.63	1.02

Statistics

Assigned Value	1.17	0.06
Spike	1.10	0.03
Homogeneity Value	1.21	0.18
Robust Average	1.17	0.06
Median	1.20	0.07
Mean	1.17	
N	13	
Max.	1.4	
Min.	1	
Robust SD	0.093	
Robust CV	7.9%	

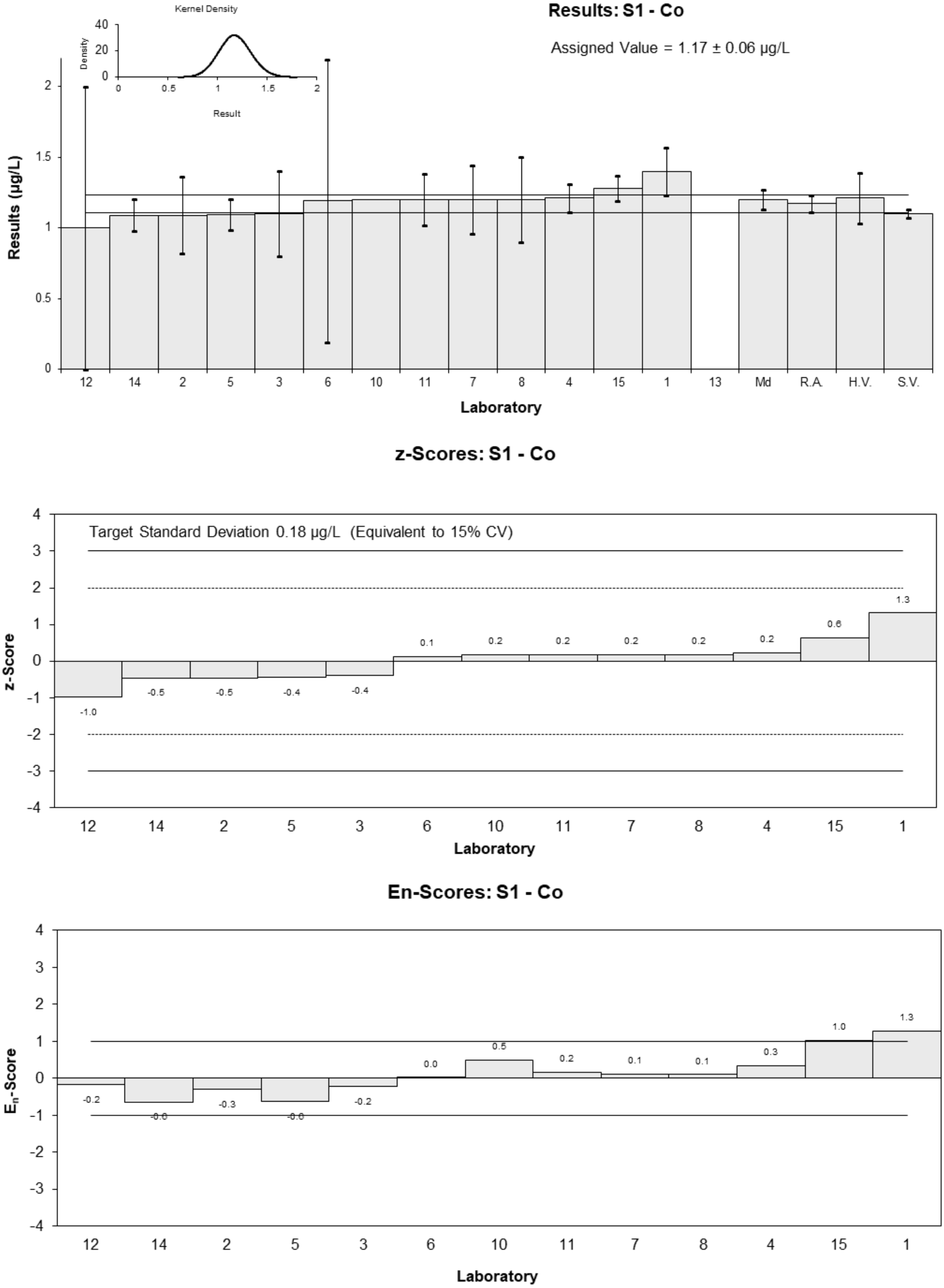

Results: S1 - Co
Assigned Value = 1.17 ± 0.06 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12 14 2 5 3 6 10 11 7 8 4 15 1 13 Md R.A. H.V. S.V.
z-Scores: S1 - Co
Target Standard Deviation 0.18 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
12 14 2 5 3 6 10 11 7 8 4 15 1
-1.0 -0.5 -0.5 -0.4 -0.4 0.1 0.2 0.2 0.2 0.2 0.2 0.6 1.3
En-Scores: S1 - Co
E_n-Score
Laboratory
12 14 2 5 3 6 10 11 7 8 4 15 1
-0.2 -0.6 -0.3 -0.6 -0.2 0.0 0.5 0.2 0.1 0.1 0.3 1.0 1.3

Figure 8

Table 11

Sample Details

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

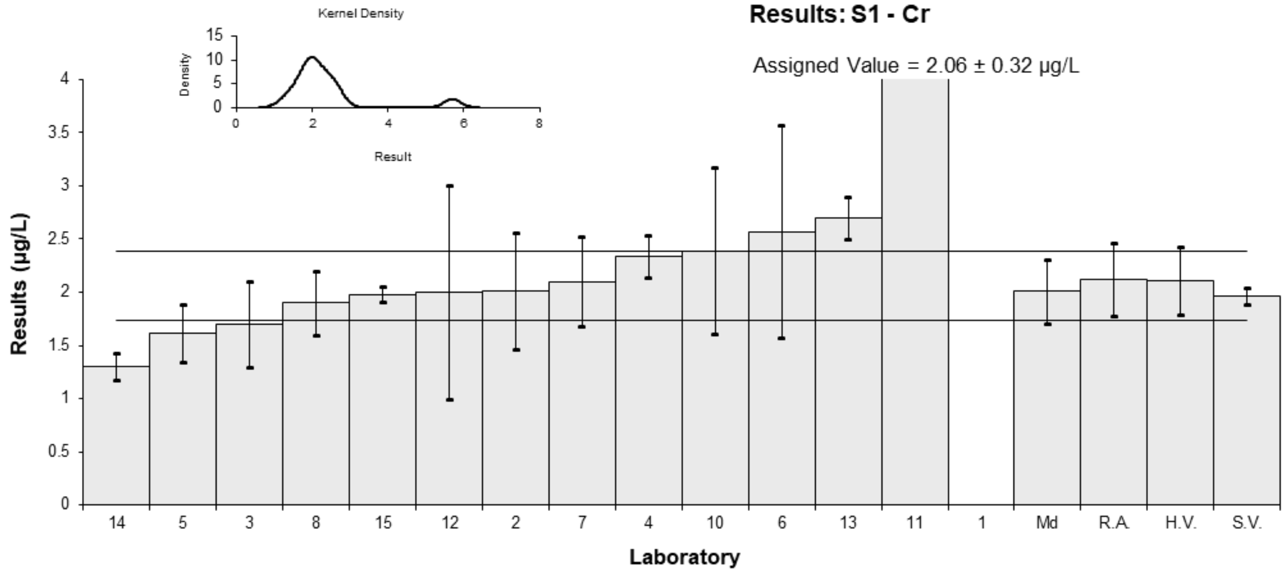
Participant Results

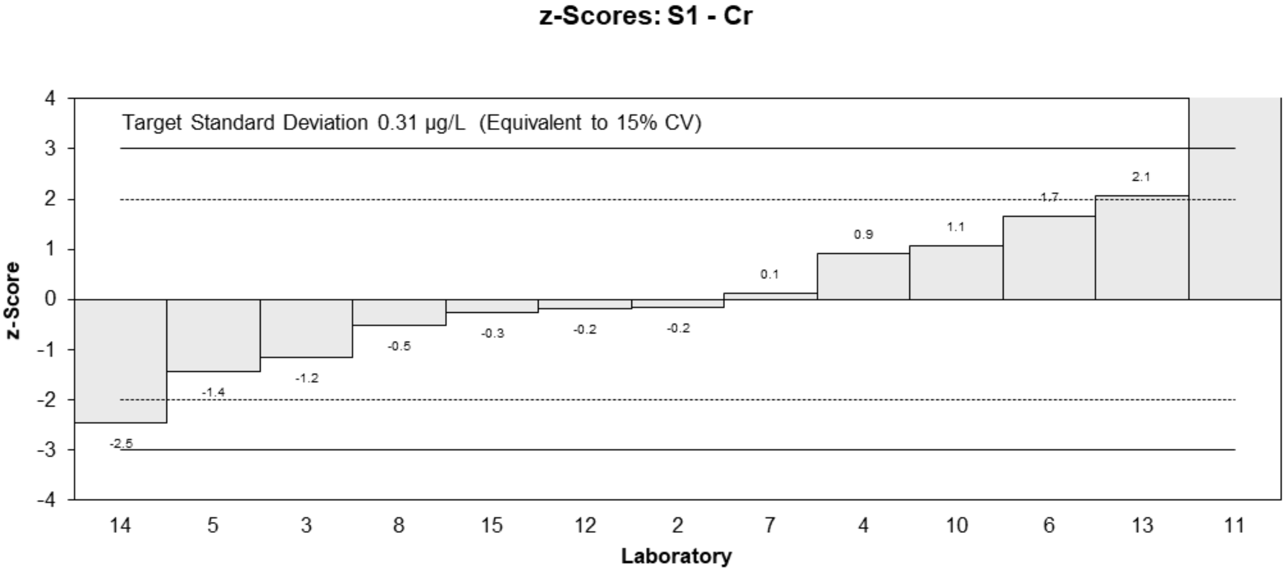
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<5	5		
2	2.01	0.55	-0.16	-0.08
3	1.7	0.4	-1.17	-0.70
4	2.34	0.20	0.91	0.74
5	1.617	0.274	-1.43	-1.05
6	2.57	1	1.65	0.49
7	2.1	0.42	0.13	0.08
8	1.9	0.3	-0.52	-0.36
10	2.39	0.78	1.07	0.39
11	5.7	0.86	11.78	3.97
12	2	1	-0.19	-0.06
13	2.7	0.2	2.07	1.70
14	1.3	0.13	-2.46	-2.20
15	1.98	0.07	-0.26	-0.24

Statistics

Assigned Value*	2.06	0.32
Spike	1.96	0.08
Homogeneity Value	2.11	0.32
Robust Average	2.12	0.34
Median	2.01	0.30
Mean	2.33	
N	13	
Max.	5.7	
Min.	1.3	
Robust SD	0.49	
Robust CV	23%	

*Robust Average excluding Laboratory 11.


Results: S1 - Cr
Assigned Value = 2.06 ± 0.32 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
14 5 3 8 15 12 2 7 4 10 6 13 11 1 Md R.A. H.V. S.V.


z-Scores: S1 - Cr
Target Standard Deviation 0.31 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
14 5 3 8 15 12 2 7 4 10 6 13 11
-2.5 -1.4 -1.2 -0.5 -0.3 -0.2 -0.2 0.1 0.9 1.1 1.7 2.1

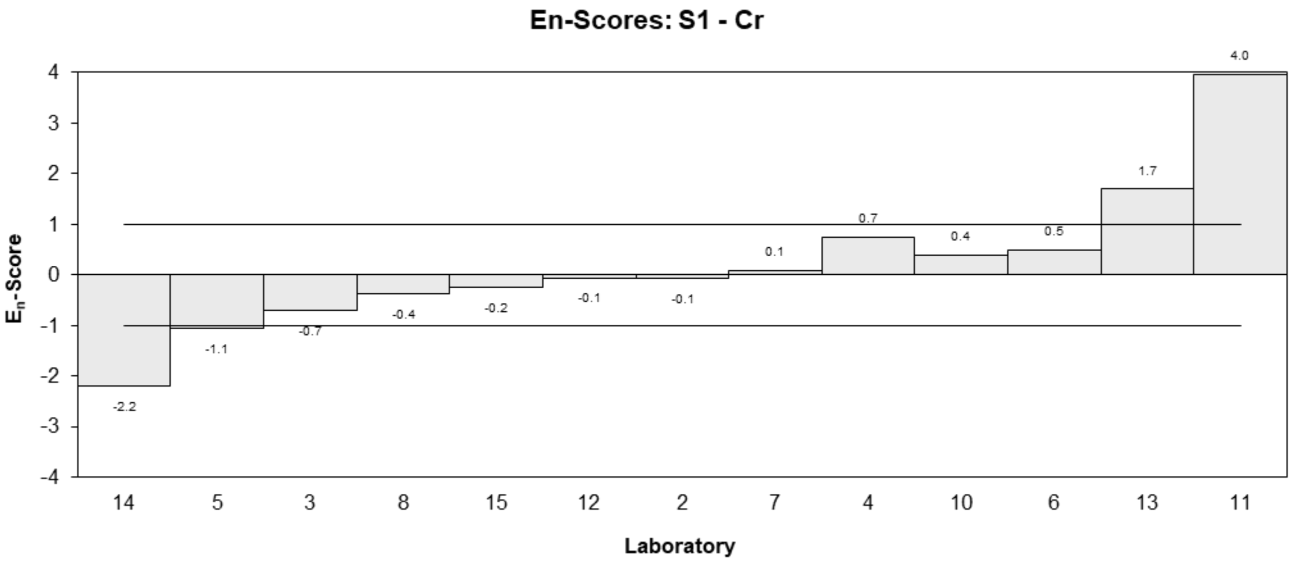

En-Scores: S1 - Cr
En-Score
Laboratory
14 5 3 8 15 12 2 7 4 10 6 13 11
-2.2 -1.1 -0.7 -0.4 -0.2 -0.1 -0.1 0.1 0.7 0.4 0.5 1.7 4.0

Figure 9

Table 12

Sample Details

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

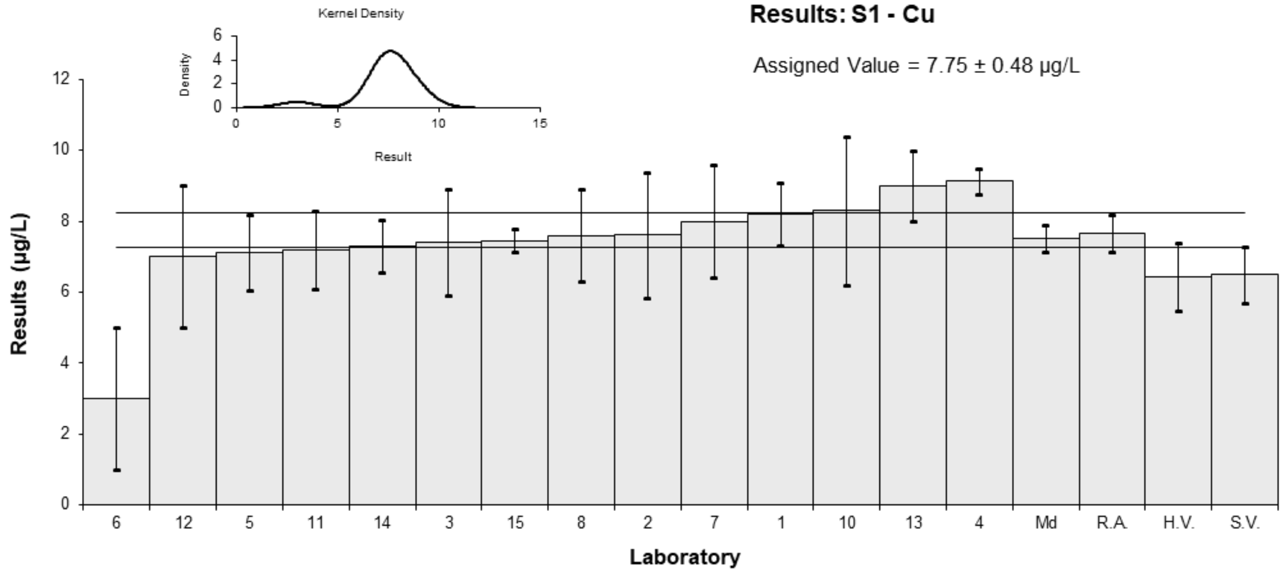
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	8.2	0.87	0.39	0.45
2	7.61	1.77	-0.12	-0.08
3	7.4	1.5	-0.30	-0.22
4	9.13	0.36	1.19	2.30
5	7.123	1.068	-0.54	-0.54
6	2.99	2	-4.09	-2.31
7	8.0	1.6	0.22	0.15
8	7.6	1.3	-0.13	-0.11
10	8.3	2.1	0.47	0.26
11	7.2	1.1	-0.47	-0.46
12	7	2	-0.65	-0.36
13	9	1	1.08	1.13
14	7.3	0.73	-0.39	-0.52
15	7.45	0.32	-0.26	-0.52

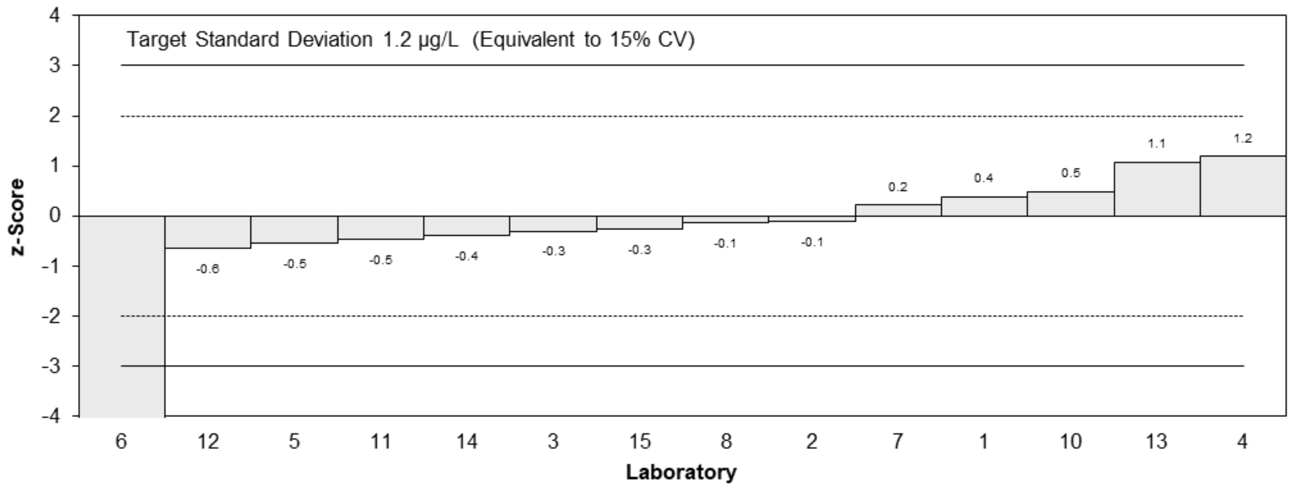
Statistics

Assigned Value*	7.75	0.48
Spike	6.49	0.80
Homogeneity Value	6.43	0.96
Robust Average	7.67	0.52
Median	7.53	0.38
Mean	7.45	
N	14	
Max.	9.13	
Min.	2.99	
Robust SD	0.77	
Robust CV	10%	

*Robust Average excluding Laboratory 6.



z-Scores: S1 - Cu



En-Scores: S1 - Cu

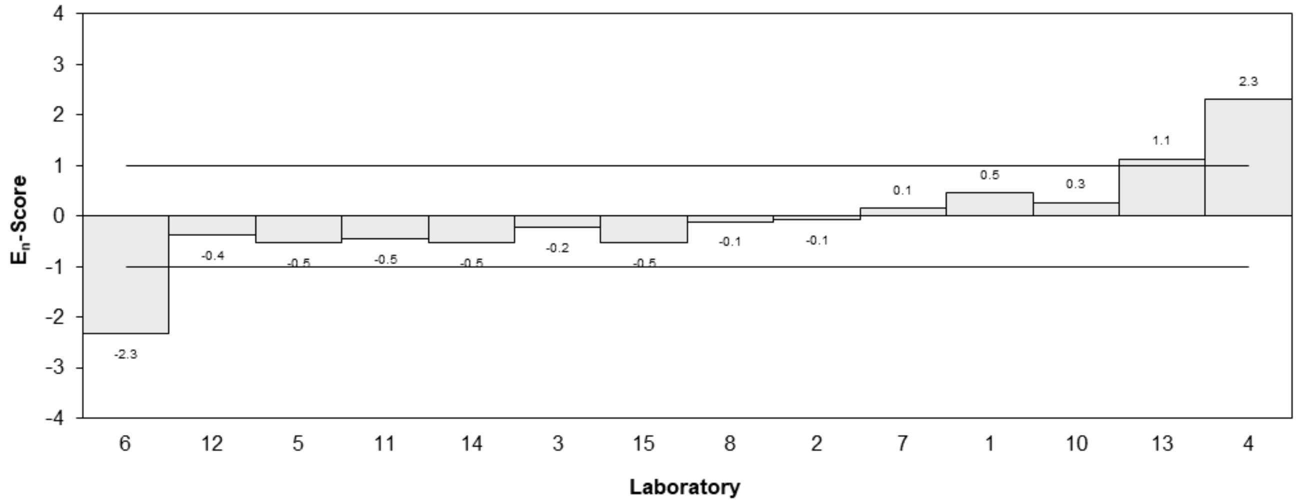


Figure 10

Table 13

Sample Details

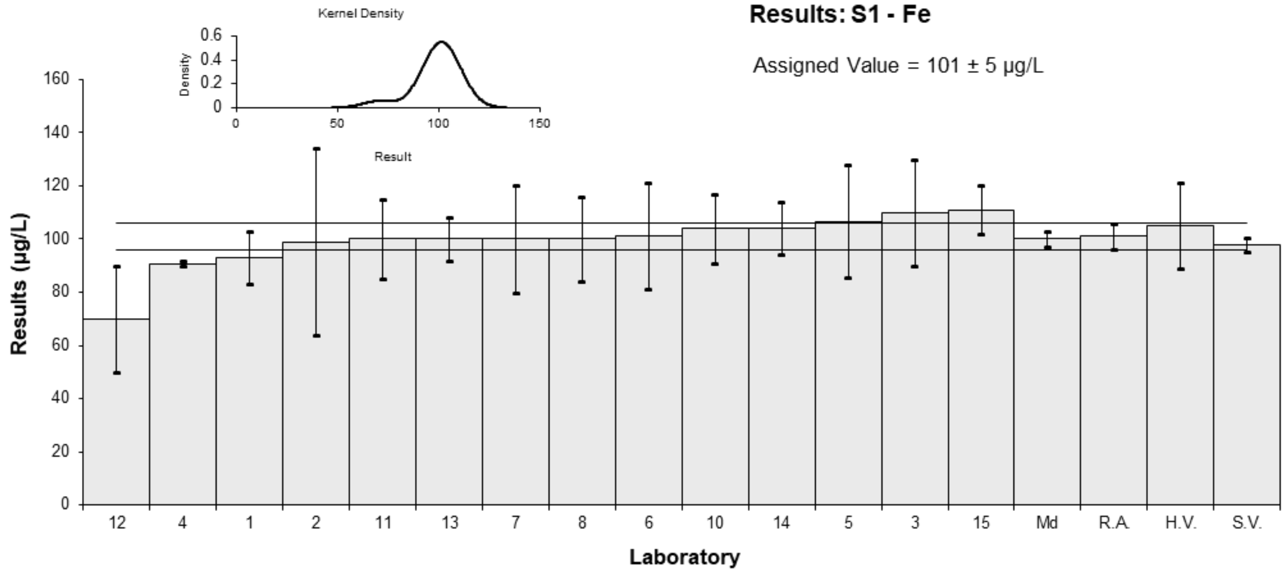
Sample No.	S1
Matrix.	Sea Water
Analyte.	Fe
Units	µg/L

Participant Results

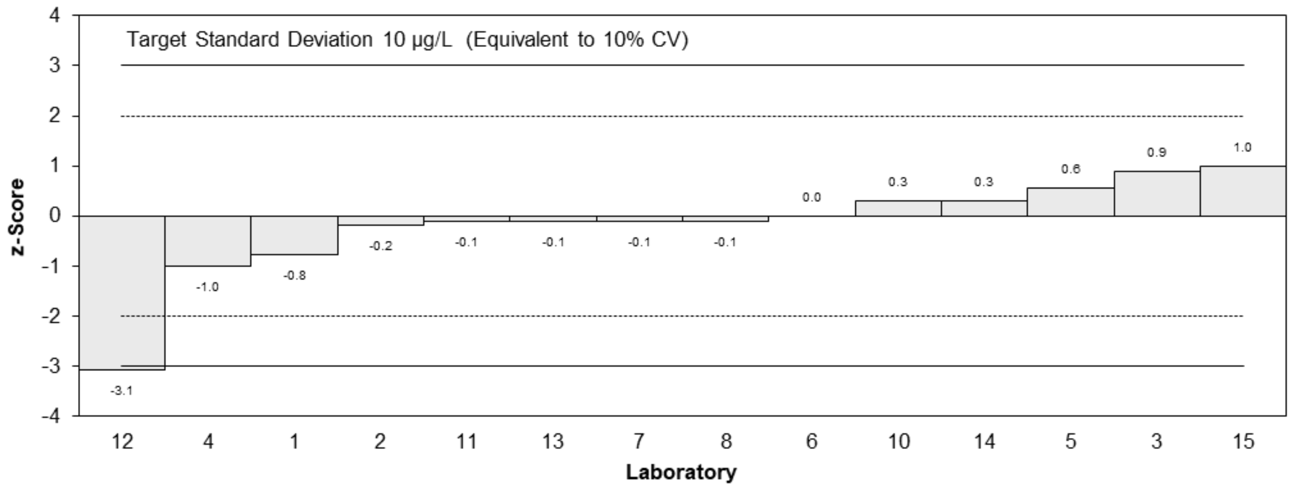
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	93.1	9.96	-0.78	-0.71
2	99	35	-0.20	-0.06
3	110	20	0.89	0.44
4	90.8	1.0	-1.01	-2.00
5	106.7	21.3	0.56	0.26
6	101	20	0.00	0.00
7	100	20	-0.10	-0.05
8	100	16	-0.10	-0.06
10	104	13	0.30	0.22
11	100	15	-0.10	-0.06
12	70	20	-3.07	-1.50
13	100	8	-0.10	-0.11
14	104	10	0.30	0.27
15	111	9	0.99	0.97

Statistics

Assigned Value	101	5
Spike	97.9	2.8
Homogeneity Value	105	16
Robust Average	101	5
Median	100	3
Mean	99	
N	14	
Max.	111	
Min.	70	
Robust SD	7.2	
Robust CV	7.1%	



z-Scores: S1 - Fe



En-Scores: S1 - Fe

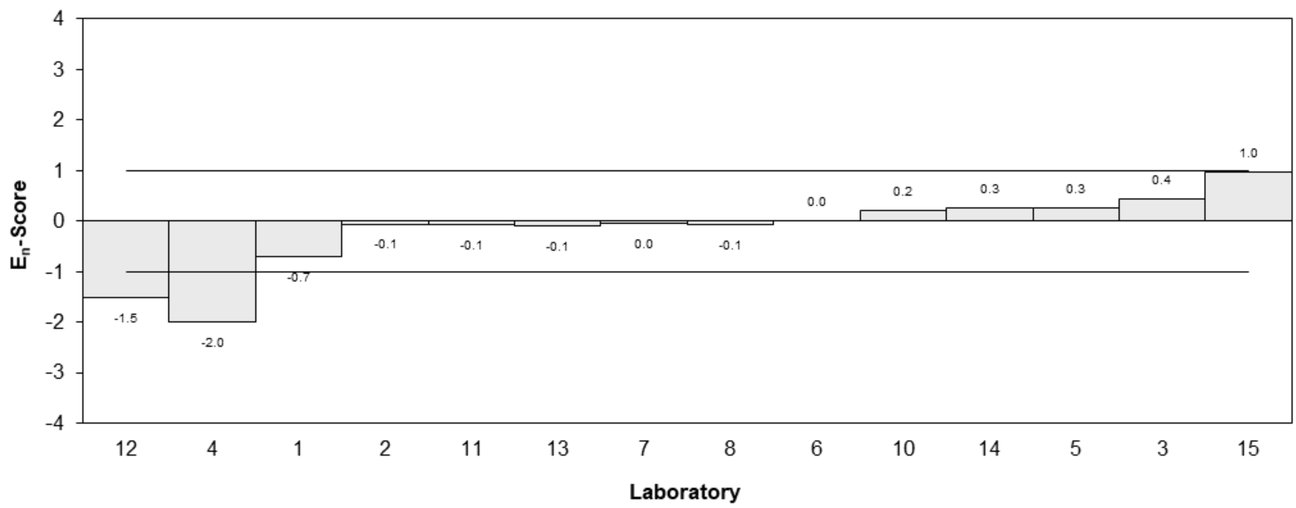


Figure 11

Table 14

Sample Details

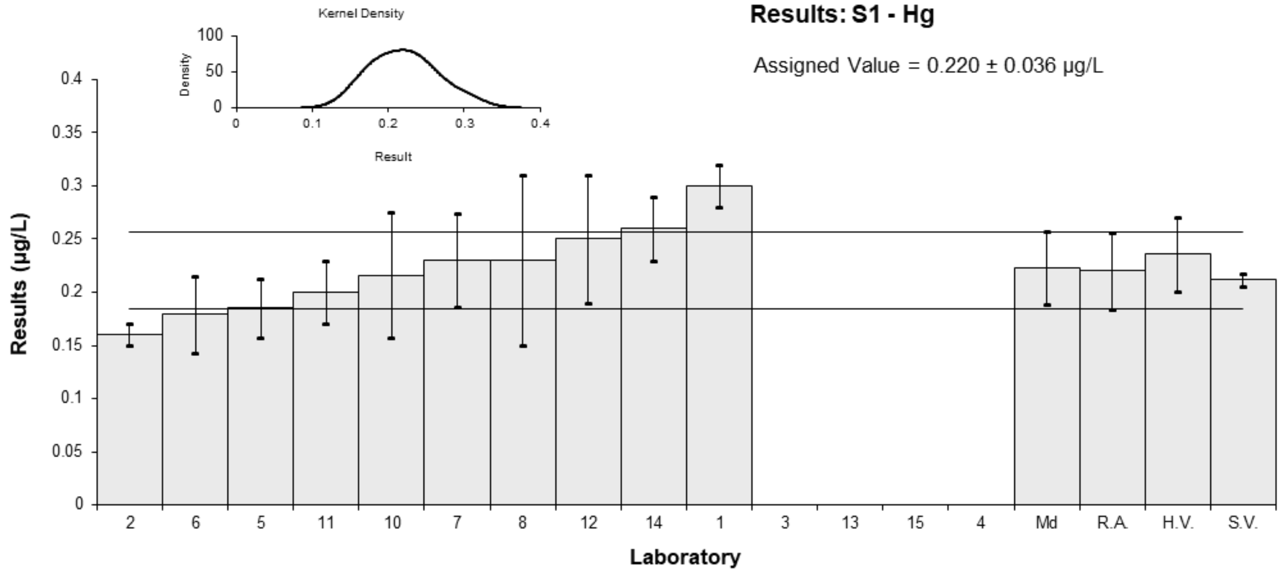
Sample No.	S1
Matrix.	Sea Water
Analyte.	Hg
Units	µg/L

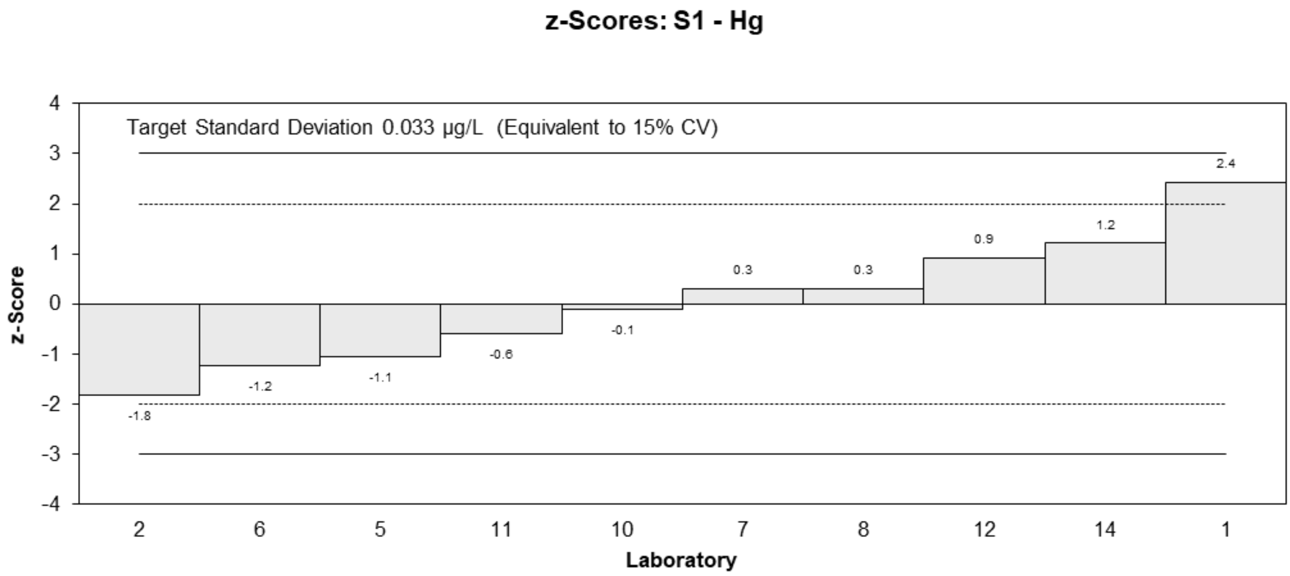
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.3	0.02	2.42	1.94
2	0.16	0.01	-1.82	-1.61
3	<0.5	NR		
4	NT	NT		
5	0.185	0.028	-1.06	-0.77
6	0.179	0.036	-1.24	-0.81
7	0.23	0.044	0.30	0.18
8	0.23	0.08	0.30	0.11
10	0.216	0.059	-0.12	-0.06
11	0.2	0.03	-0.61	-0.43
12	0.25	0.06	0.91	0.43
13	NT	NT		
14	0.26	0.03	1.21	0.85
15	NT	NT		

Statistics

Assigned Value	0.220	0.036
Spike	0.212	0.006
Homogeneity Value	0.236	0.035
Robust Average	0.220	0.036
Median	0.223	0.034
Mean	0.221	
N	10	
Max.	0.3	
Min.	0.16	
Robust SD	0.045	
Robust CV	20%	


Results: S1 - Hg
Assigned Value = 0.220 ± 0.036 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
2
6
5
11
10
7
8
12
14
1
3
13
15
4
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Hg
Target Standard Deviation 0.033 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.8
-1.2
-1.1
-0.6
-0.1
0.3
0.3
0.9
1.2
2.4
2
6
5
11
10
7
8
12
14
1

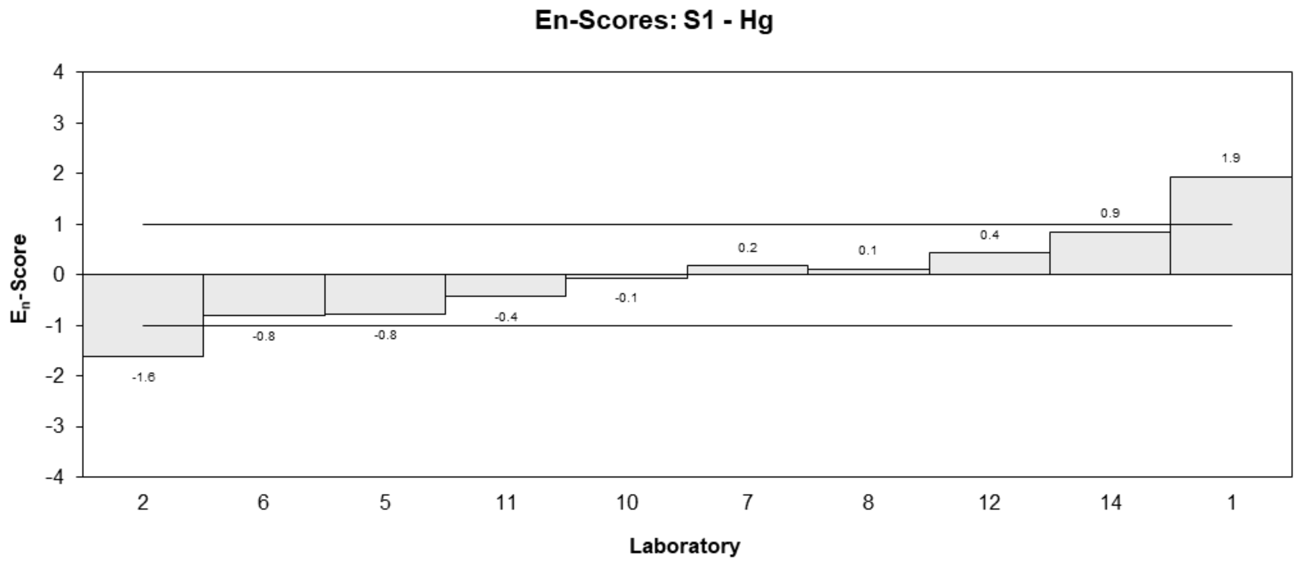

En-Scores: S1 - Hg
E_n-Score
Laboratory
-1.6
-0.8
-0.8
-0.4
-0.1
0.2
0.1
0.4
0.9
1.9
2
6
5
11
10
7
8
12
14
1

Figure 12

Table 15

Sample Details

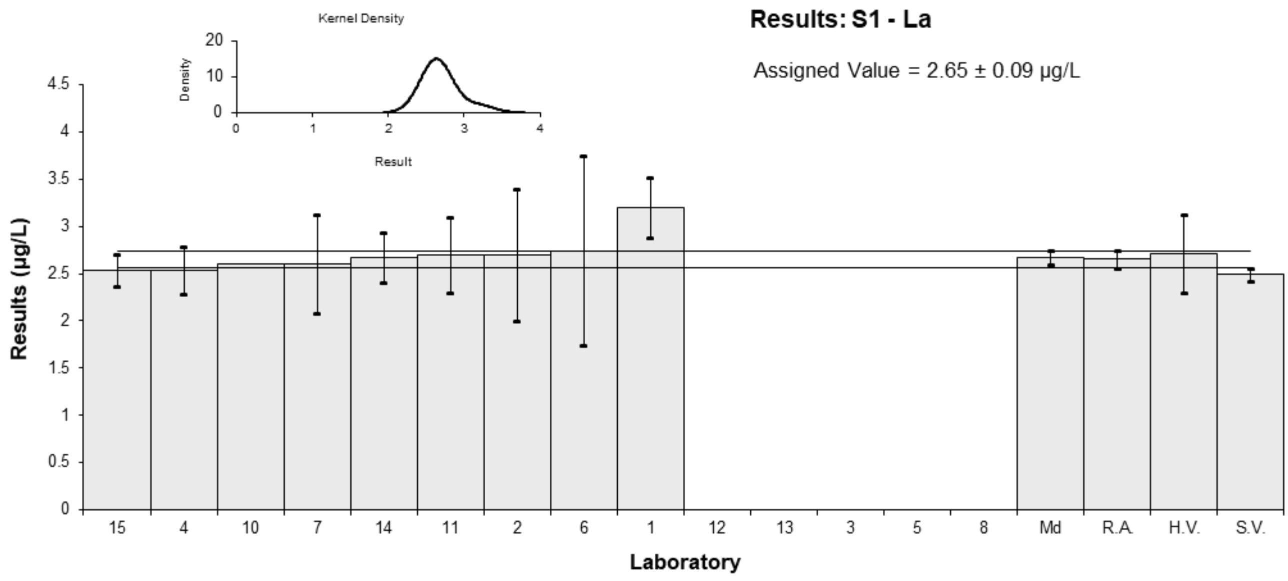
Sample No.	S1
Matrix.	Sea Water
Analyte.	La
Units	µg/L

Participant Results

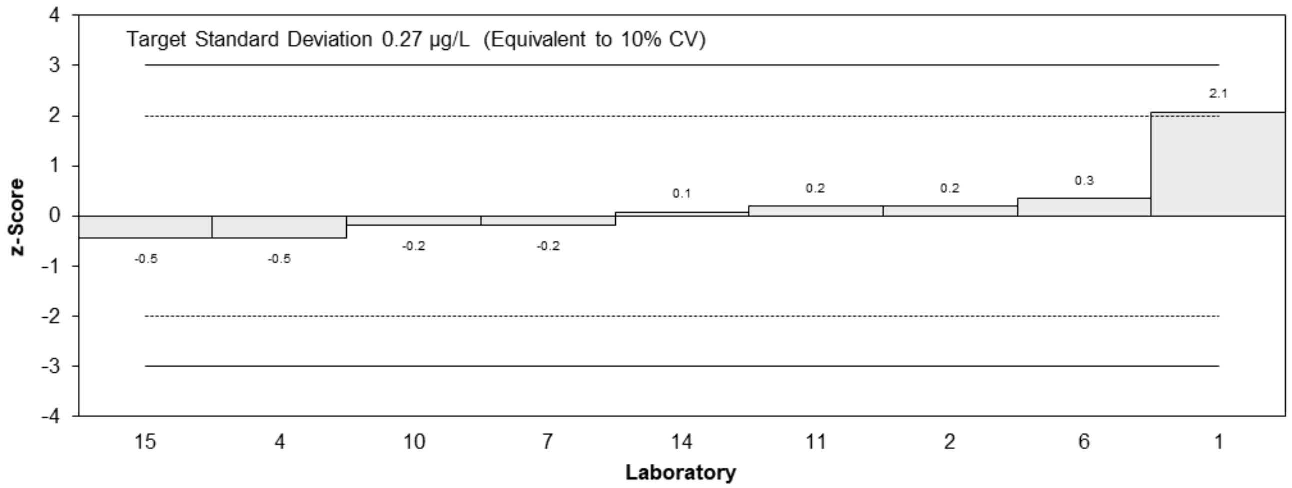
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.2	0.32	2.08	1.65
2	2.70	0.70	0.19	0.07
3	NT	NT		
4	2.53	0.25	-0.45	-0.45
5	NT	NT		
6	2.74	1	0.34	0.09
7	2.6	0.52	-0.19	-0.09
8	NT	NT		
10	2.6	NR	-0.19	-0.56
11	2.7	0.40	0.19	0.12
12	NT	NT		
13	NT	NT		
14	2.67	0.27	0.08	0.07
15	2.53	0.17	-0.45	-0.62

Statistics

Assigned Value	2.65	0.09
Spike	2.49	0.07
Homogeneity Value	2.71	0.41
Robust Average	2.65	0.09
Median	2.67	0.08
Mean	2.70	
N	9	
Max.	3.2	
Min.	2.53	
Robust SD	0.11	
Robust CV	4.2%	



z-Scores: S1 - La



En-Scores: S1 - La

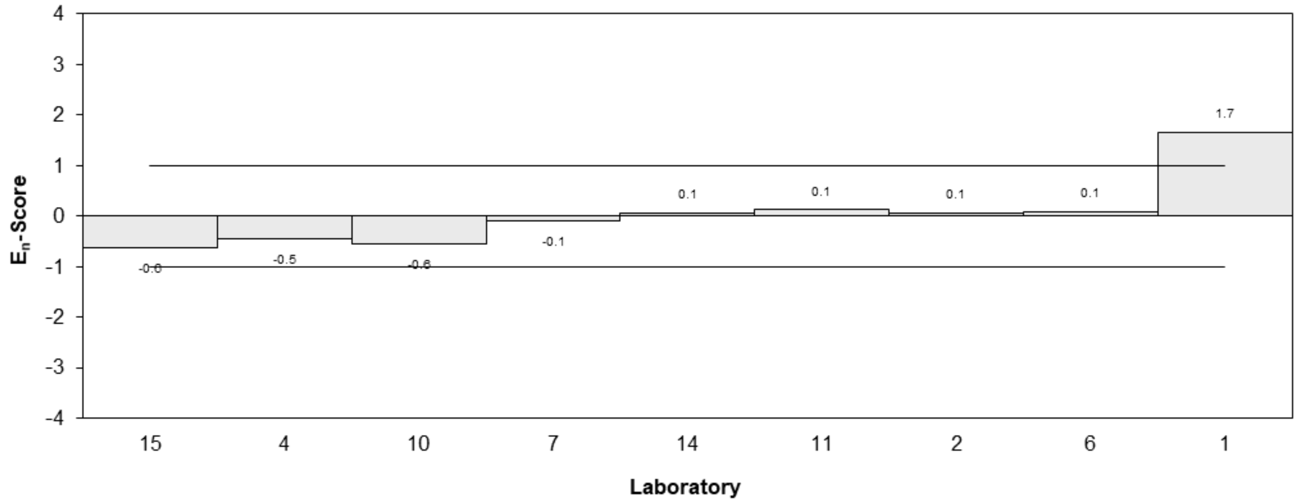


Figure 13

Table 16

Sample Details

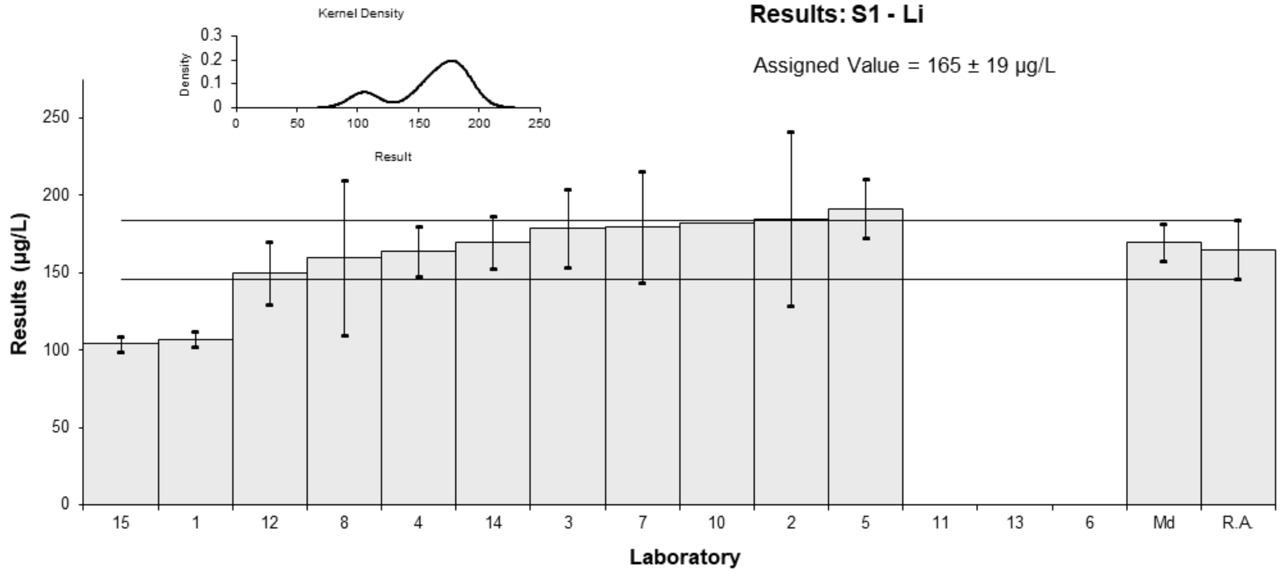
Sample No.	S1
Matrix.	Sea Water
Analyte.	Li
Units	µg/L

Participant Results

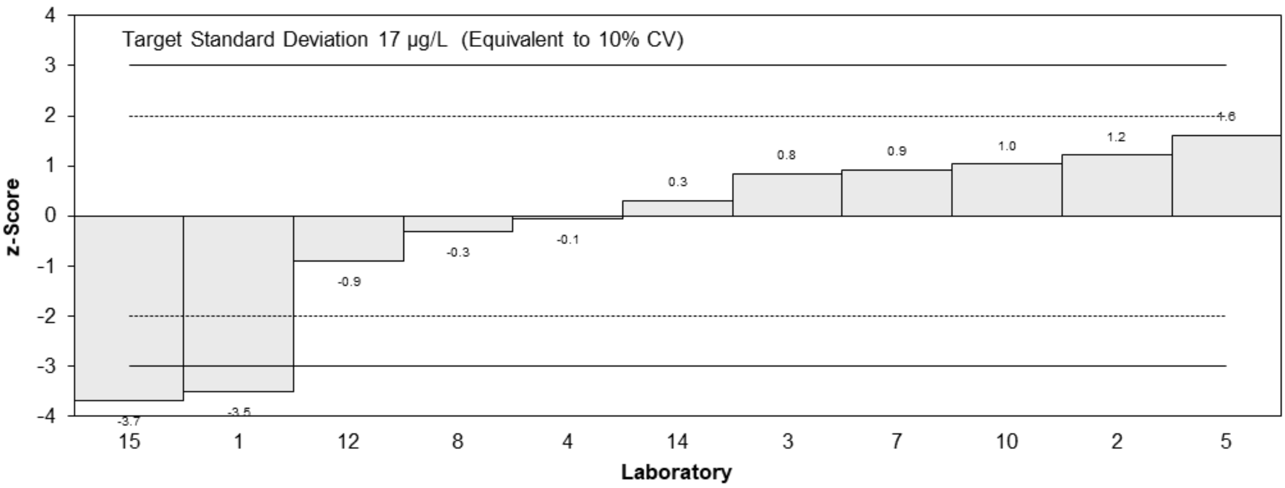
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	107	5	-3.52	-2.95
2	185	56	1.21	0.34
3	179	25	0.85	0.45
4	164	16	-0.06	-0.04
5	191.6	19.2	1.61	0.98
6	NT	NT		
7	180	36	0.91	0.37
8	160	50	-0.30	-0.09
10	182	NR	1.03	0.89
11	NR	NR		
12	150	20	-0.91	-0.54
13	NT	NT		
14	170	17	0.30	0.20
15	104	5	-3.70	-3.10

Statistics

Assigned Value	165	19
Spike	Not Spiked	
Robust Average	165	19
Median	170	12
Mean	161	
N	11	
Max.	191.6	
Min.	104	
Robust SD	25	
Robust CV	15%	



z-Scores: S1 - Li



En-Scores: S1 - Li

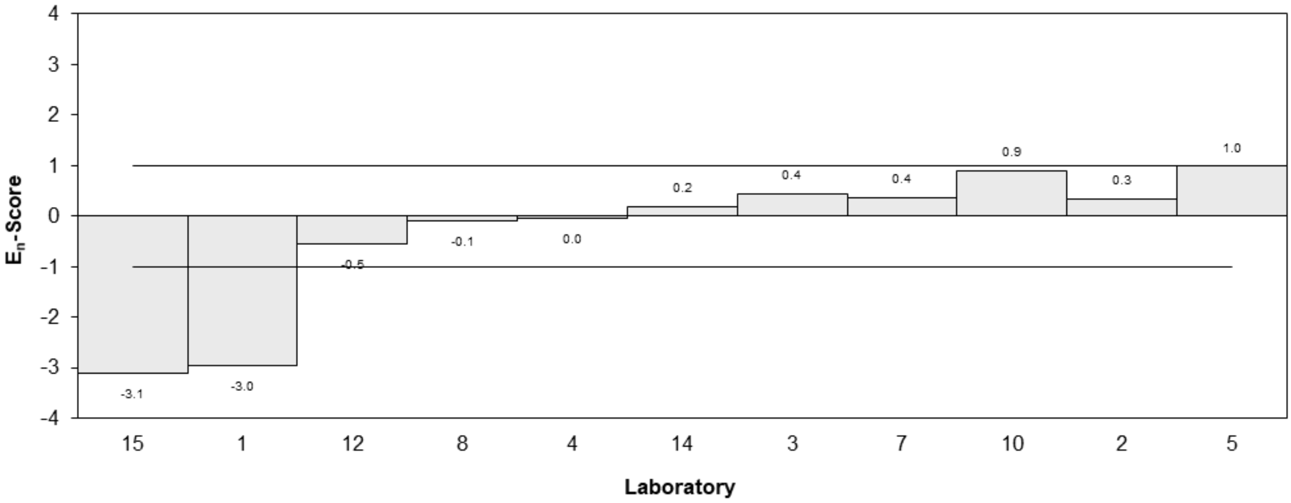


Figure 14

Table 17

Sample Details

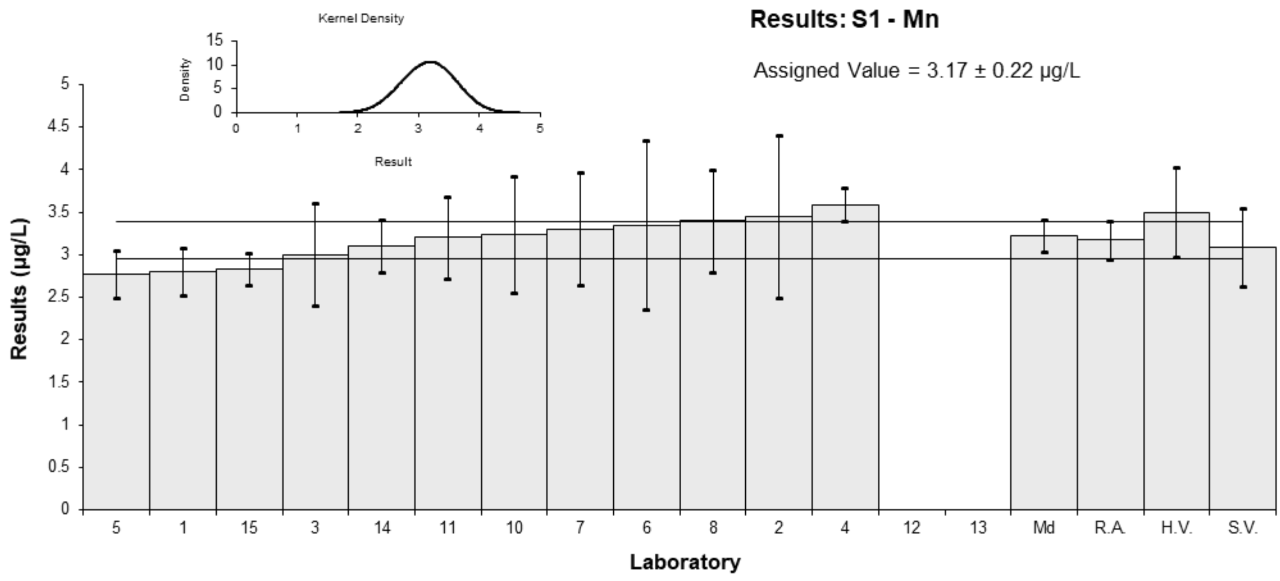
Sample No.	S1
Matrix.	Sea Water
Analyte.	Mn
Units	µg/L

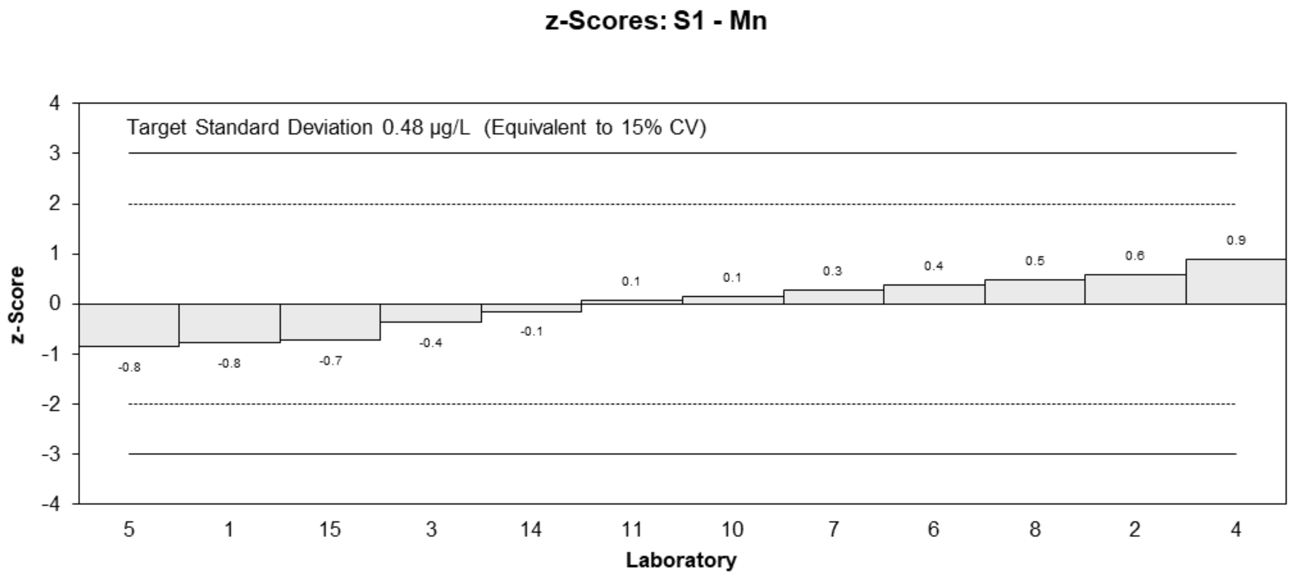
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.8	0.28	-0.78	-1.04
2	3.45	0.95	0.59	0.29
3	3.0	0.6	-0.36	-0.27
4	3.59	0.20	0.88	1.41
5	2.77	0.277	-0.84	-1.13
6	3.35	1	0.38	0.18
7	3.3	0.66	0.27	0.19
8	3.4	0.6	0.48	0.36
10	3.24	0.68	0.15	0.10
11	3.2	0.48	0.06	0.06
12	< 3	NR		
13	NT	NT		
14	3.1	0.31	-0.15	-0.18
15	2.83	0.19	-0.72	-1.17

Statistics

Assigned Value	3.17	0.22
Spike	3.09	0.46
Homogeneity Value	3.50	0.52
Robust Average	3.17	0.22
Median	3.22	0.19
Mean	3.17	
N	12	
Max.	3.59	
Min.	2.77	
Robust SD	0.31	
Robust CV	9.8%	


Results: S1 - Mn
Assigned Value = 3.17 ± 0.22 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5
1
15
3
14
11
10
7
6
8
2
4
12
13
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
-0.8
-0.8
-0.7
-0.4
-0.1
0.1
0.1
0.3
0.4
0.5
0.6
0.9
5
1
15
3
14
11
10
7
6
8
2
4

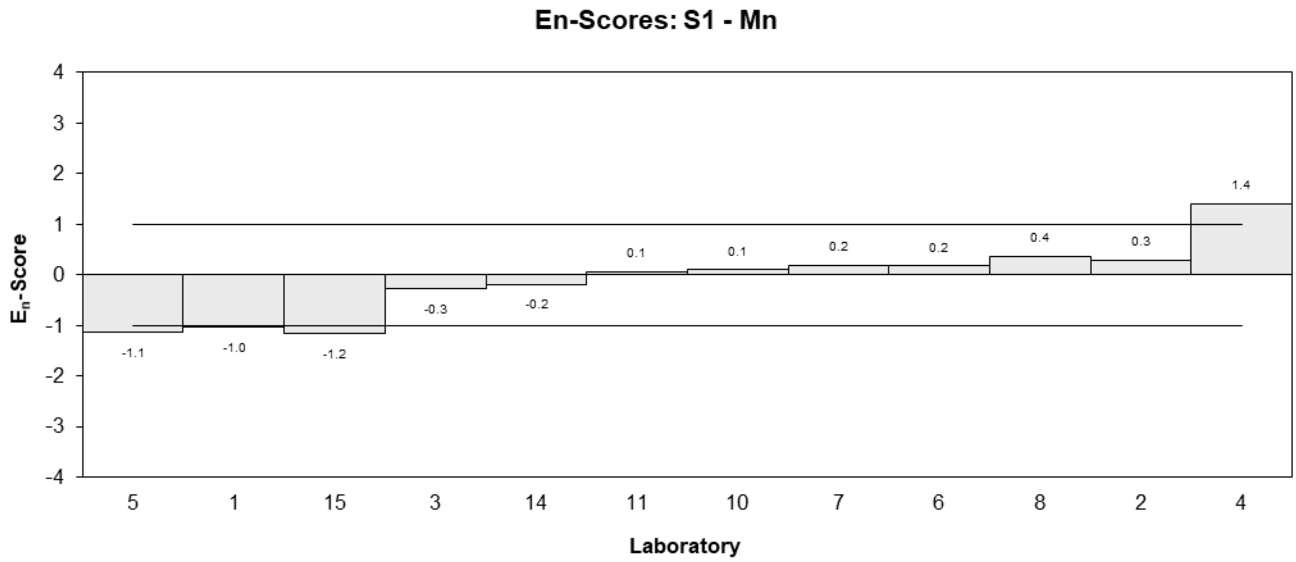

En-Scores: S1 - Mn
E_n-Score
Laboratory
-1.1
-1.0
-1.2
-0.3
-0.2
0.1
0.1
0.2
0.2
0.4
0.3
1.4
5
1
15
3
14
11
10
7
6
8
2
4

Figure 15

Table 18

Sample Details

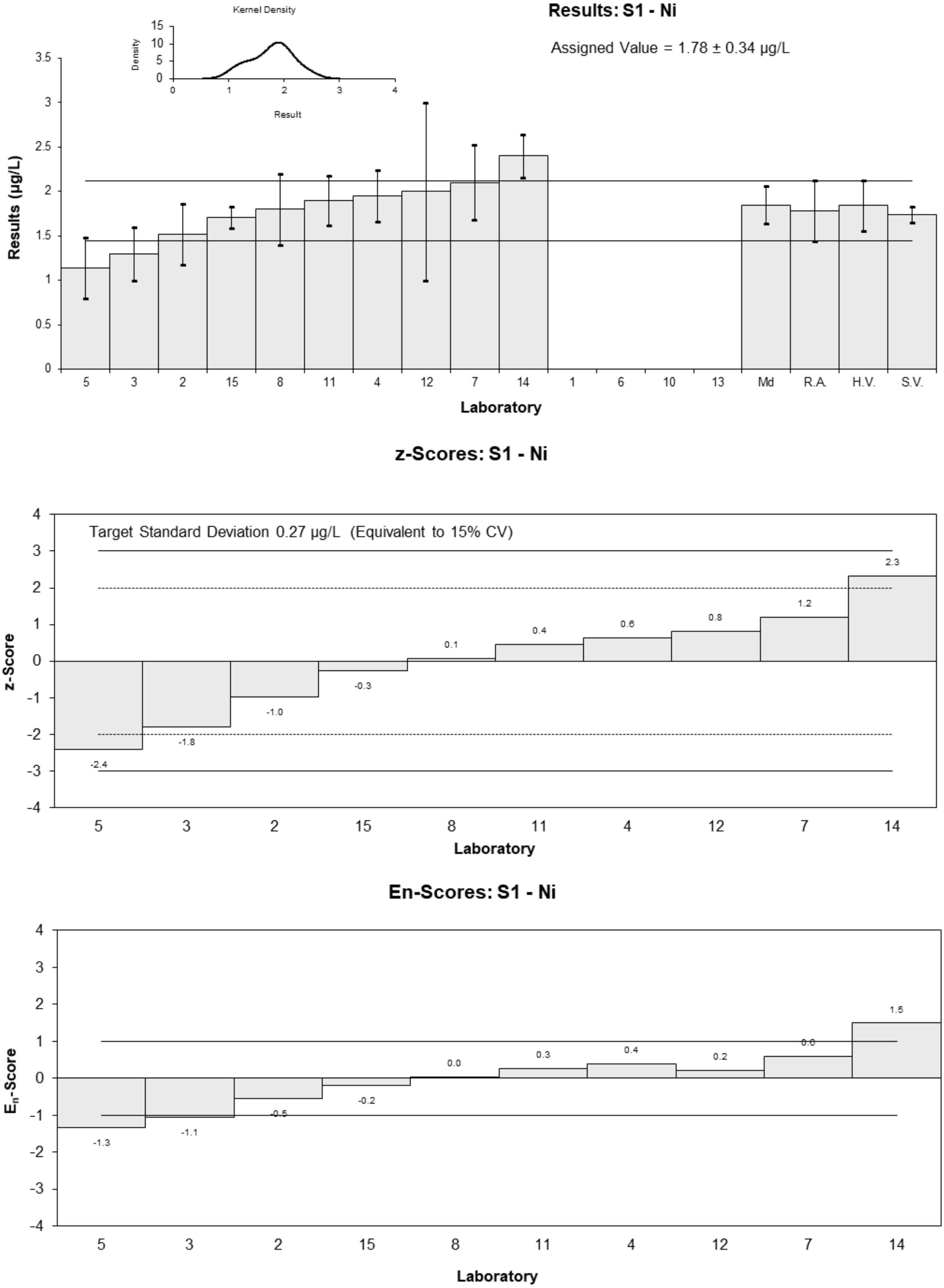
Sample No.	S1
Matrix.	Sea Water
Analyte.	Ni
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<10	10		
2	1.52	0.34	-0.97	-0.54
3	1.3	0.3	-1.80	-1.06
4	1.95	0.29	0.64	0.38
5	1.137	0.341	-2.41	-1.34
6	<2	2		
7	2.1	0.42	1.20	0.59
8	1.8	0.4	0.07	0.04
10	<7	NR		
11	1.9	0.28	0.45	0.27
12	2	1	0.82	0.21
13	NT	NT		
14	2.4	0.24	2.32	1.49
15	1.71	0.12	-0.26	-0.19

Statistics

Assigned Value	1.78	0.34
Spike	1.74	0.09
Homogeneity Value	1.84	0.28
Robust Average	1.78	0.34
Median	1.85	0.21
Mean	1.78	
N	10	
Max.	2.4	
Min.	1.137	
Robust SD	0.43	
Robust CV	24%	



Results: S1 - Ni
Assigned Value = 1.78 ± 0.34 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5
3
2
15
8
11
4
12
7
14
1
6
10
13
Md
R.A.
H.V.
S.V.
z-Scores: S1 - Ni
Target Standard Deviation 0.27 µg/L (Equivalent to 15% CV)
z-Score
-2.4
-1.8
-1.0
-0.3
0.1
0.4
0.6
0.8
1.2
2.3
En-Scores: S1 - Ni
En-Score
-1.3
-1.1
-0.5
-0.2
0.0
0.3
0.4
0.2
0.6
1.5

Figure 16

Table 19

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	<100	100
2	NR	NR
3	NT	NT
4	NT	NT
5	NT	NT
6	NT	NT
7	110	20
8	NT	NT
10	NT	NT
11	NR	NR
12	< 40	NR
13	156	18
14	100	10
15	135	10

Statistics

Assigned Value	Not Set	
Spike	120	7
Homogeneity Value	98	15
Median	123	41
Mean	125	
N	4	
Max.	156	
Min.	100	
Robust SD	28	
Robust CV	35%	

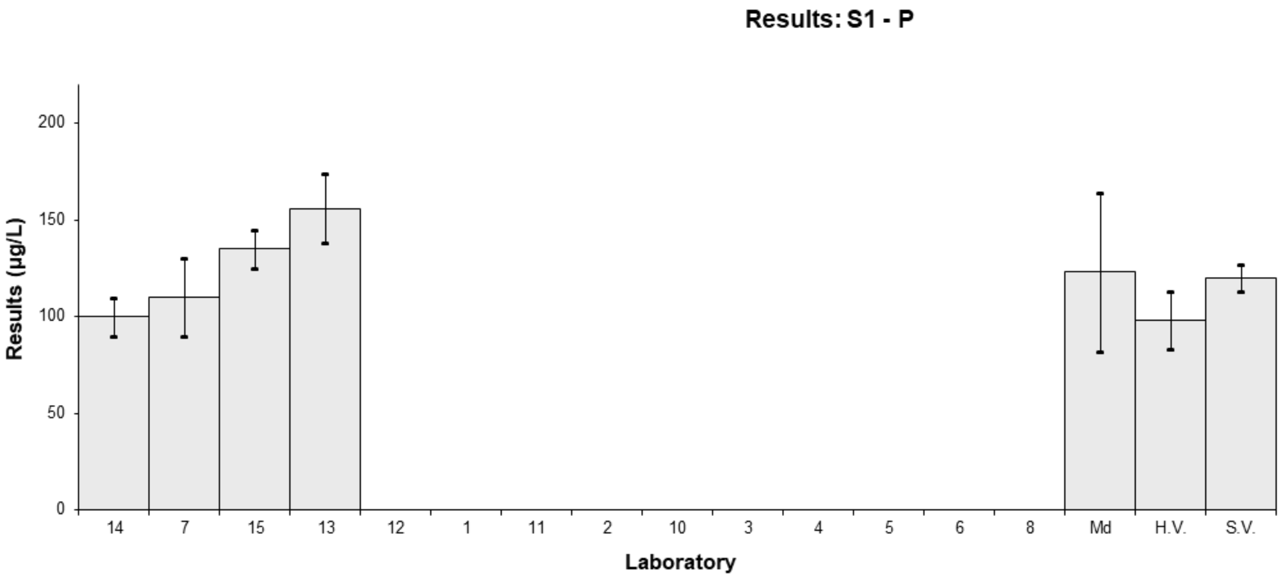

Results: S1 - P
Results (µg/L)
200
150
100
50
0
14
7
15
13
12
1
11
2
10
3
4
5
6
8
Md
H.V.
S.V.
Laboratory

Figure 17

Table 20

Sample Details

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

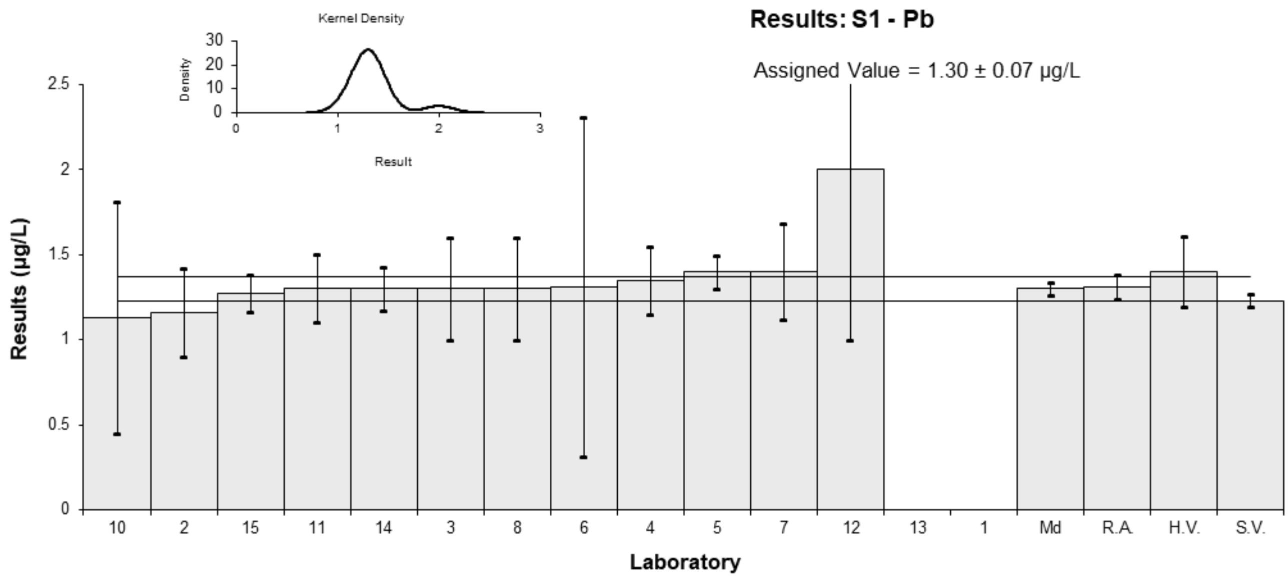
Participant Results

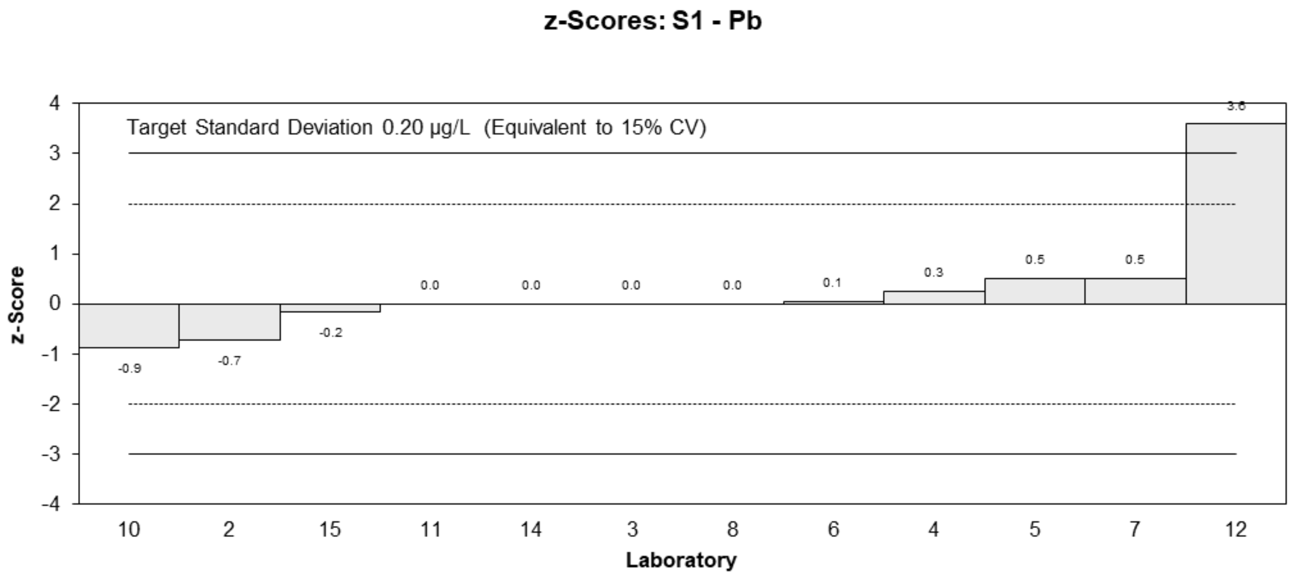
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<10	10		
2	1.16	0.26	-0.72	-0.52
3	1.3	0.3	0.00	0.00
4	1.35	0.20	0.26	0.24
5	1.397	0.098	0.50	0.81
6	1.31	1	0.05	0.01
7	1.4	0.28	0.51	0.35
8	1.3	0.3	0.00	0.00
10	1.13	0.68	-0.87	-0.25
11	1.3	0.20	0.00	0.00
12	2	1	3.59	0.70
13	<1	NR		
14	1.3	0.13	0.00	0.00
15	1.27	0.11	-0.15	-0.23

Statistics

Assigned Value*	1.30	0.07
Spike	1.23	0.04
Homogeneity Value	1.40	0.21
Robust Average	1.31	0.07
Median	1.30	0.04
Mean	1.35	
N	12	
Max.	2	
Min.	1.13	
Robust SD	0.10	
Robust CV	7.6%	

*Robust Average excluding Laboratory 12.


Results: S1 - Pb
Assigned Value = 1.30 ± 0.07 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
10
2
15
11
14
3
8
6
4
5
7
12
13
1
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Pb
Target Standard Deviation 0.20 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.9
-0.7
-0.2
0.0
0.0
0.0
0.0
0.1
0.3
0.5
0.5
3.6

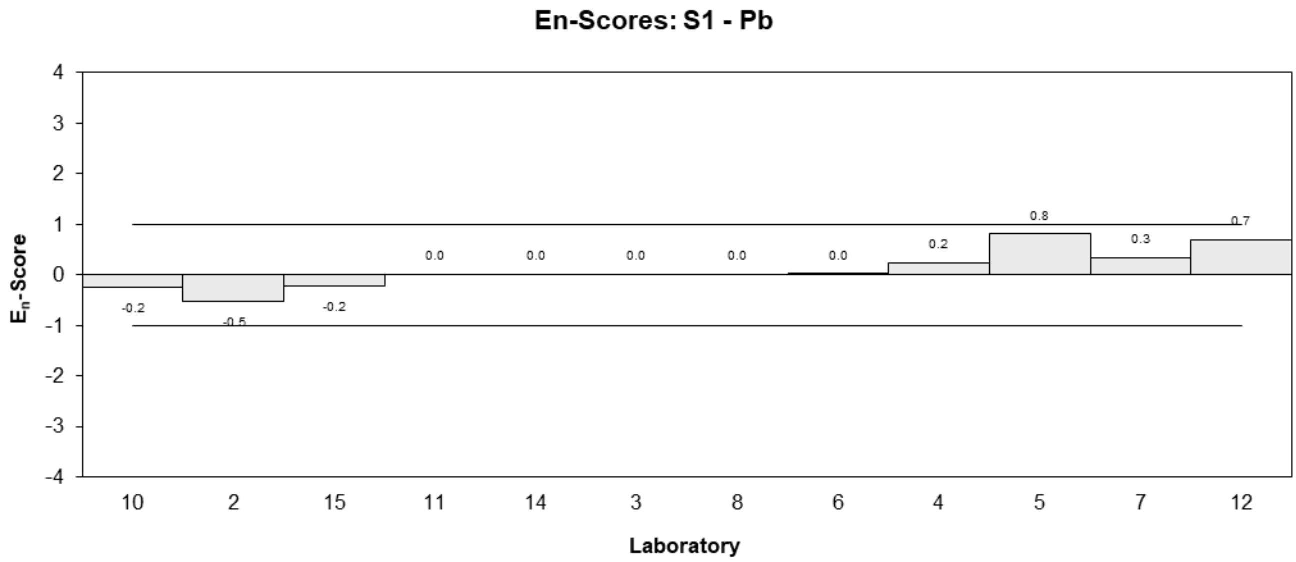

En-Scores: S1 - Pb
En-Score
Laboratory
-0.2
-0.5
-0.2
0.0
0.0
0.0
0.0
0.0
0.2
0.8
0.3
0.7

Figure 18

Table 21

Sample Details

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

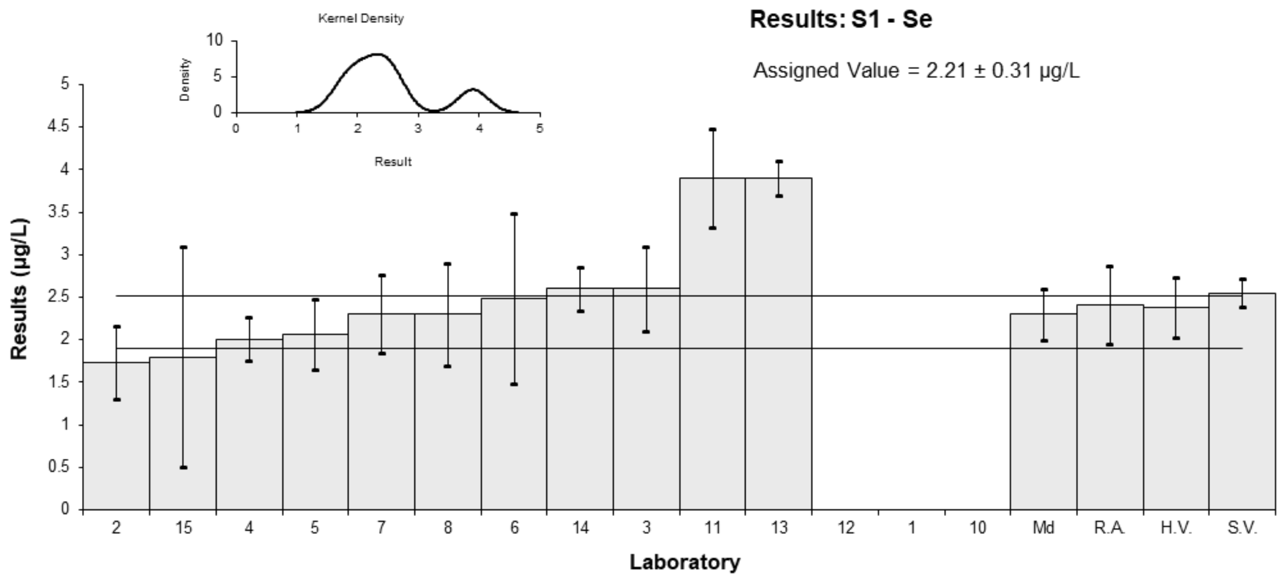
Participant Results

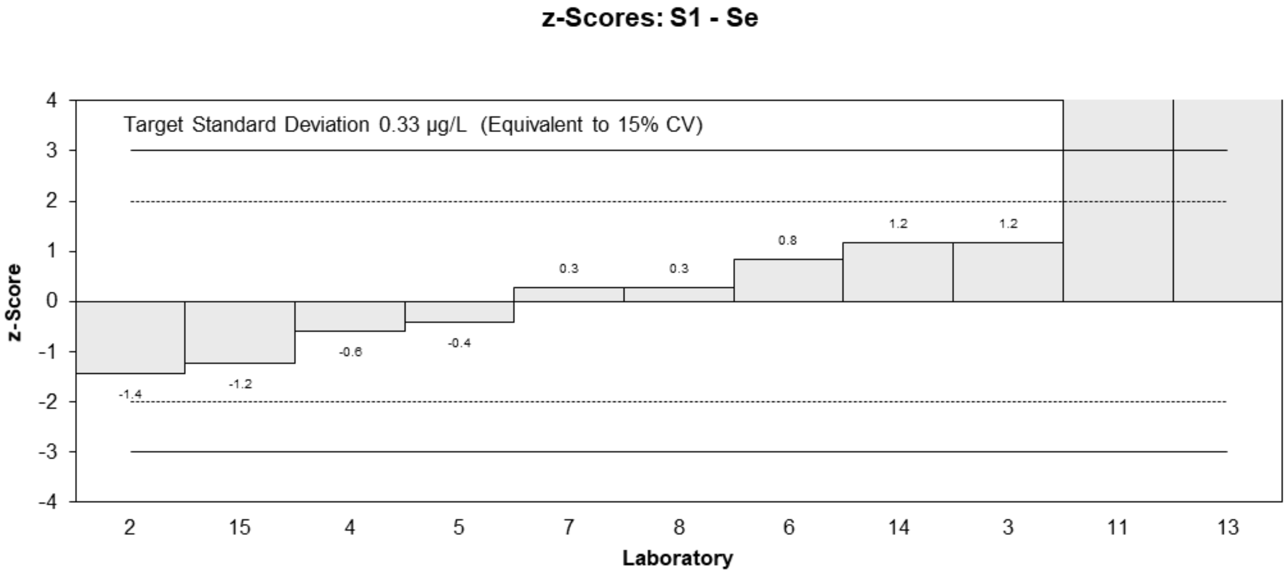
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<10	10		
2	1.73	0.43	-1.45	-0.91
3	2.6	0.5	1.18	0.66
4	2.01	0.25	-0.60	-0.50
5	2.069	0.414	-0.43	-0.27
6	2.49	1	0.84	0.27
7	2.3	0.46	0.27	0.16
8	2.3	0.6	0.27	0.13
10	<4	2.7		
11	3.9	0.58	5.10	2.57
12	< 5	NR		
13	3.9	0.2	5.10	4.58
14	2.6	0.26	1.18	0.96
15	1.8	1.3	-1.24	-0.31

Statistics

Assigned Value*	2.21	0.31
Spike	2.55	0.17
Homogeneity Value	2.38	0.36
Robust Average	2.41	0.46
Median	2.30	0.30
Mean	2.52	
N	11	
Max.	3.9	
Min.	1.73	
Robust SD	0.61	
Robust CV	25%	

*Robust Average excluding Laboratories 11 and 13.


Results: S1 - Se
Assigned Value = 2.21 ± 0.31 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
2
15
4
5
7
8
6
14
3
11
13
12
1
10
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Se
Target Standard Deviation 0.33 μg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.4
-1.2
-0.6
-0.4
0.3
0.3
0.8
1.2
1.2
2
15
4
5
7
8
6
14
3
11
13

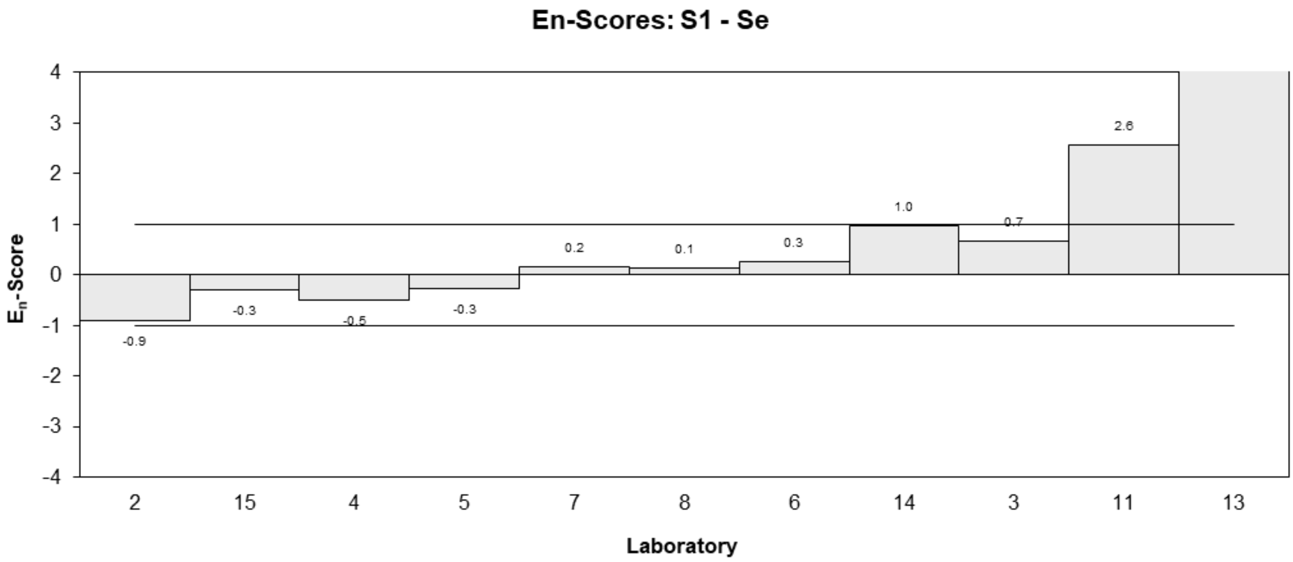

En-Scores: S1 - Se
En-Score
Laboratory
-0.9
-0.3
-0.5
-0.3
0.2
0.1
0.3
1.0
0.7
2.6
2
15
4
5
7
8
6
14
3
11
13

Figure 19

Table 22

Sample Details

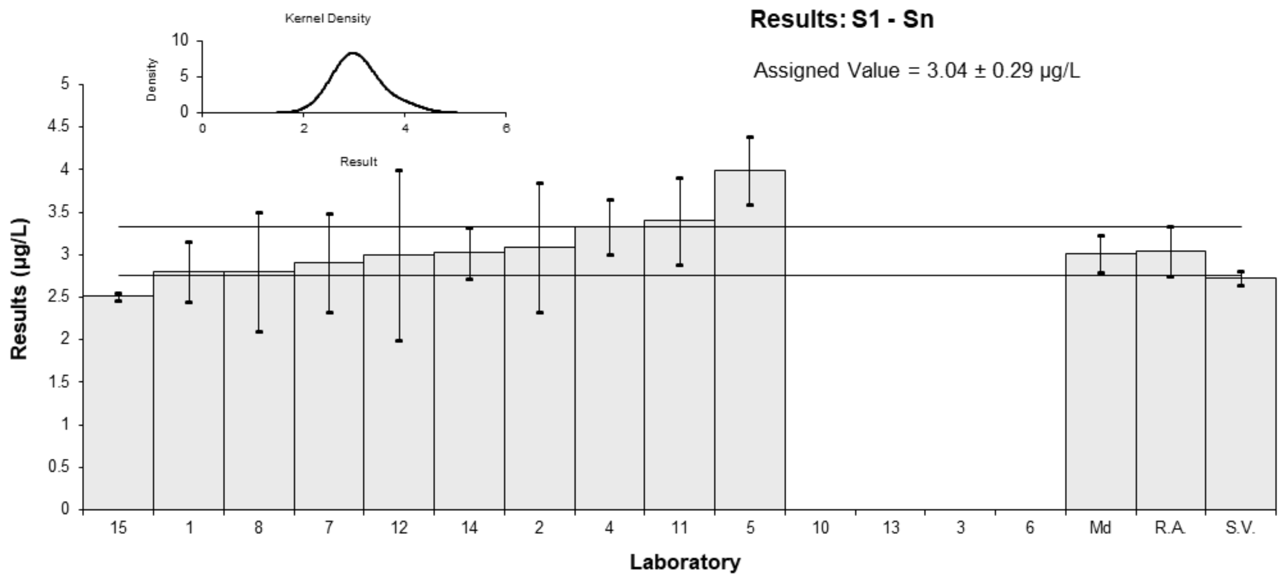
Sample No.	S1
Matrix.	Sea Water
Analyte.	Sn
Units	µg/L

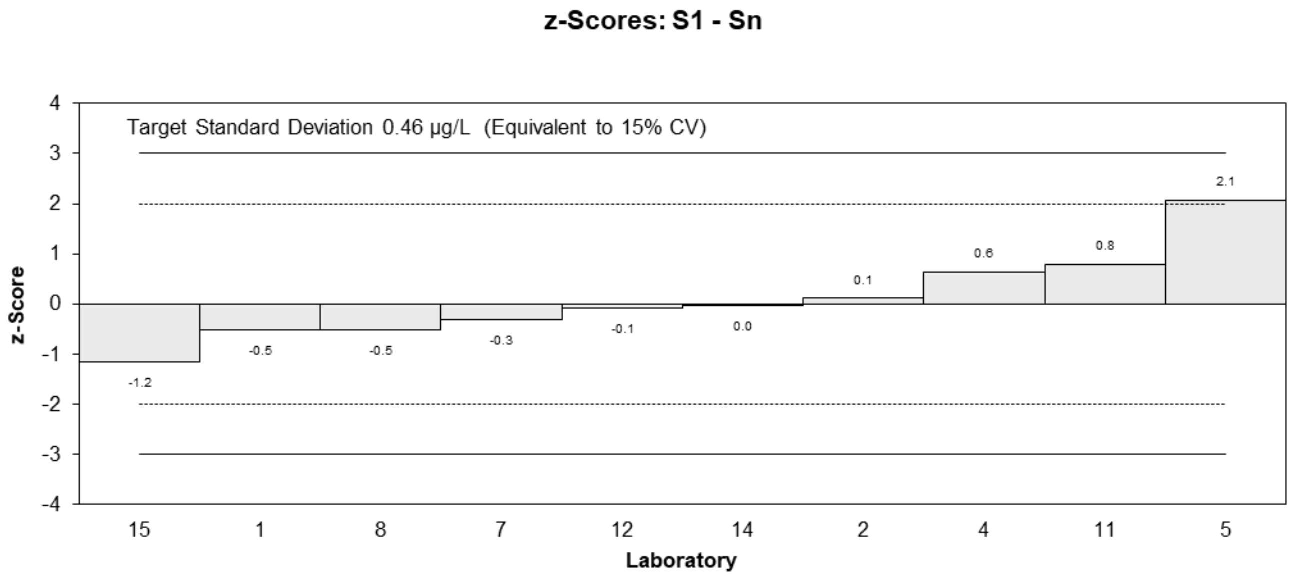
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.8	0.35	-0.53	-0.53
2	3.09	0.76	0.11	0.06
3	NT	NT		
4	3.33	0.32	0.64	0.67
5	3.987	0.399	2.08	1.92
6	NT	NT		
7	2.9	0.58	-0.31	-0.22
8	2.8	0.7	-0.53	-0.32
10	<5.0	NR		
11	3.4	0.51	0.79	0.61
12	3	1	-0.09	-0.04
13	NT	NT		
14	3.02	0.30	-0.04	-0.05
15	2.51	0.05	-1.16	-1.80

Statistics

Assigned Value	3.04	0.29
Spike	2.73	0.08
Robust Average	3.04	0.29
Median	3.01	0.22
Mean	3.08	
N	10	
Max.	3.987	
Min.	2.51	
Robust SD	0.37	
Robust CV	12%	


Results: S1 - Sn
Assigned Value = 3.04 ± 0.29 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15
1
8
7
12
14
2
4
11
5
10
13
3
6
Md
R.A.
S.V.


z-Scores: S1 - Sn
Target Standard Deviation 0.46 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.2
-0.5
-0.5
-0.3
-0.1
0.0
0.1
0.6
0.8
2.1
15
1
8
7
12
14
2
4
11
5

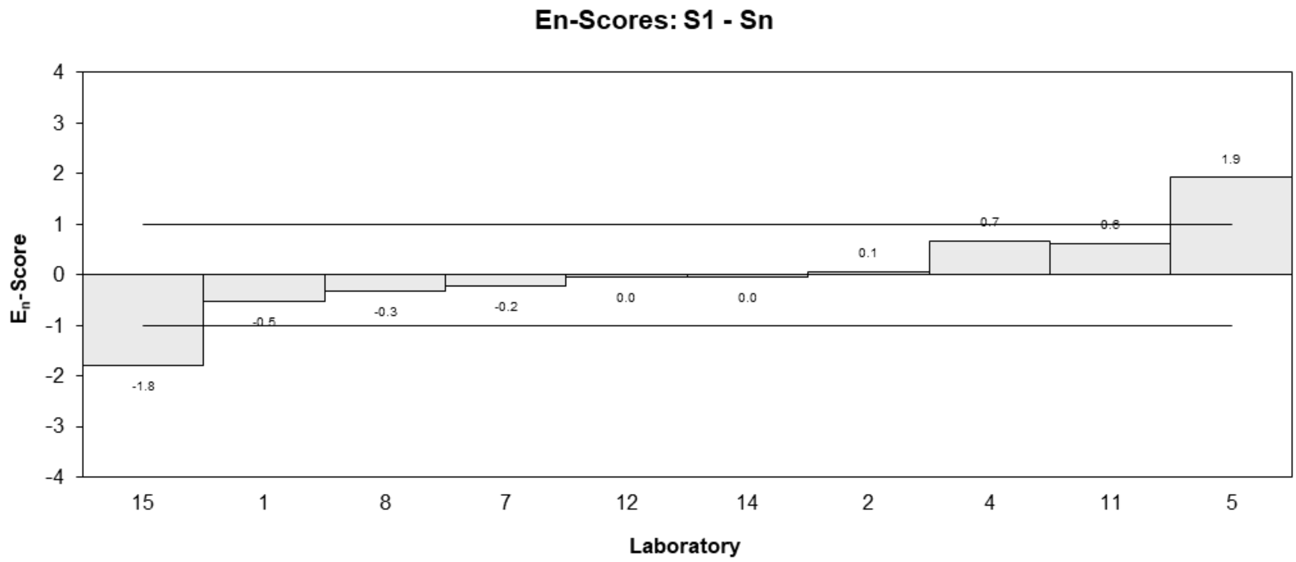

En-Scores: S1 - Sn
En-Score
Laboratory
-1.8
-0.5
-0.3
-0.2
0.0
0.0
0.1
0.7
0.6
1.9
15
1
8
7
12
14
2
4
11
5

Figure 20

Table 23

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Th
Units	µg/L

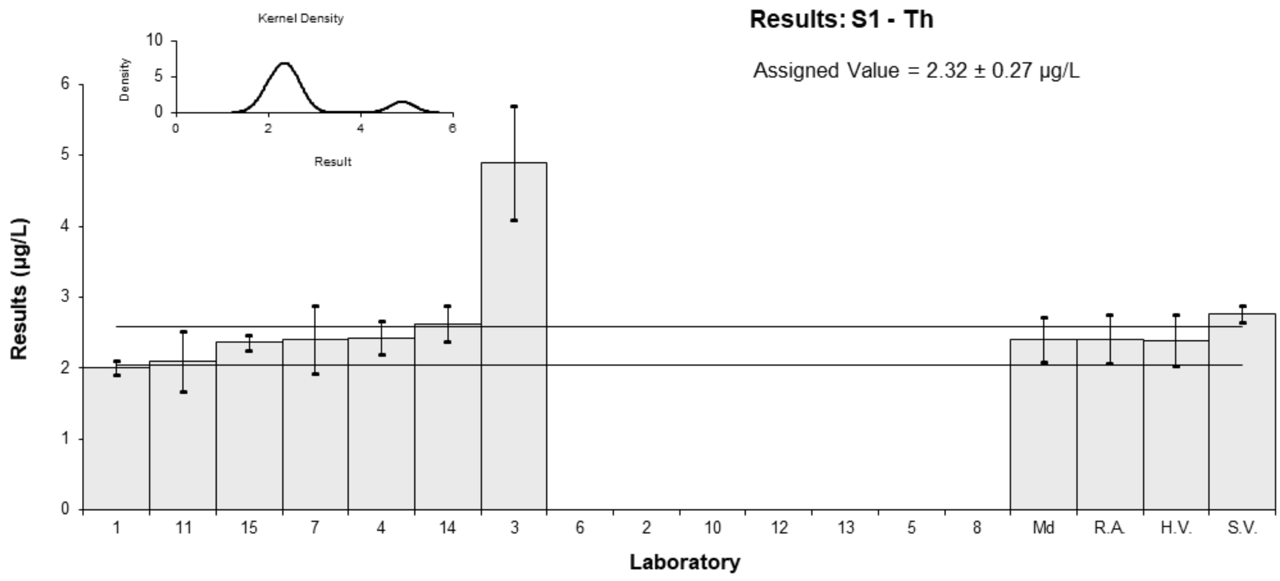
Participant Results

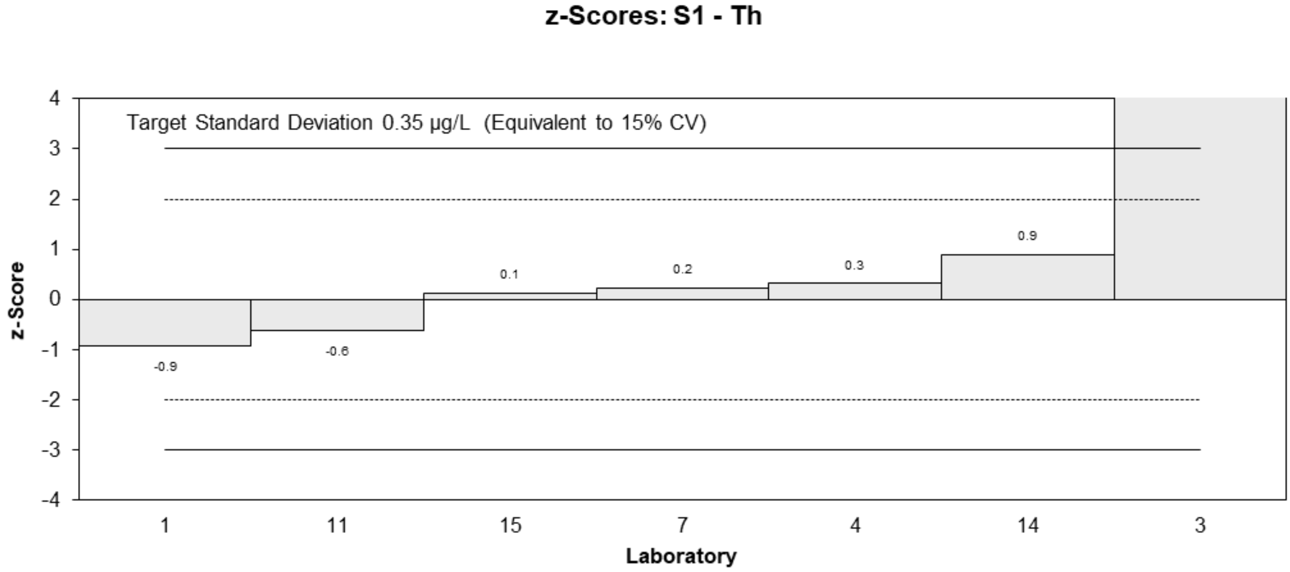
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2	0.1	-0.92	-1.11
2	NR	NR		
3	4.9	0.8	7.41	3.06
4	2.43	0.24	0.32	0.30
5	NT	NT		
6	<2	2		
7	2.4	0.48	0.23	0.15
8	NT	NT		
10	NT	NT		
11	2.1	0.42	-0.63	-0.44
12	NT	NT		
13	NT	NT		
14	2.63	0.26	0.89	0.83
15	2.36	0.10	0.11	0.14

Statistics

Assigned Value*	2.32	0.27
Spike	2.77	0.12
Homogeneity Value	2.39	0.36
Robust Average	2.41	0.34
Median	2.40	0.32
Mean	2.69	
N	7	
Max.	4.9	
Min.	2	
Robust SD	0.36	
Robust CV	15%	

*Robust Average excluding Laboratory 3.


Results: S1 - Th
Assigned Value = 2.32 ± 0.27 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1
11
15
7
4
14
3
6
2
10
12
13
5
8
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Th
Target Standard Deviation 0.35 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.9
-0.6
0.1
0.2
0.3
0.9
1
11
15
7
4
14
3

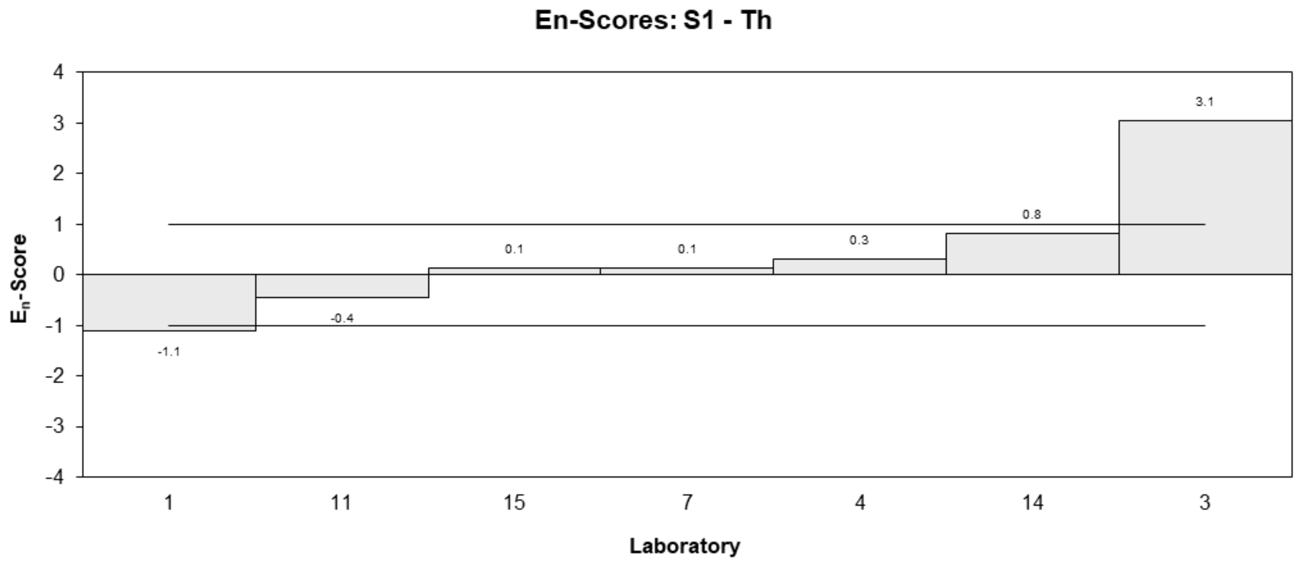

En-Scores: S1 - Th
E_n-Score
Laboratory
-1.1
-0.4
0.1
0.1
0.3
0.8
3.1
1
11
15
7
4
14
3

Figure 21

Table 24

Sample Details

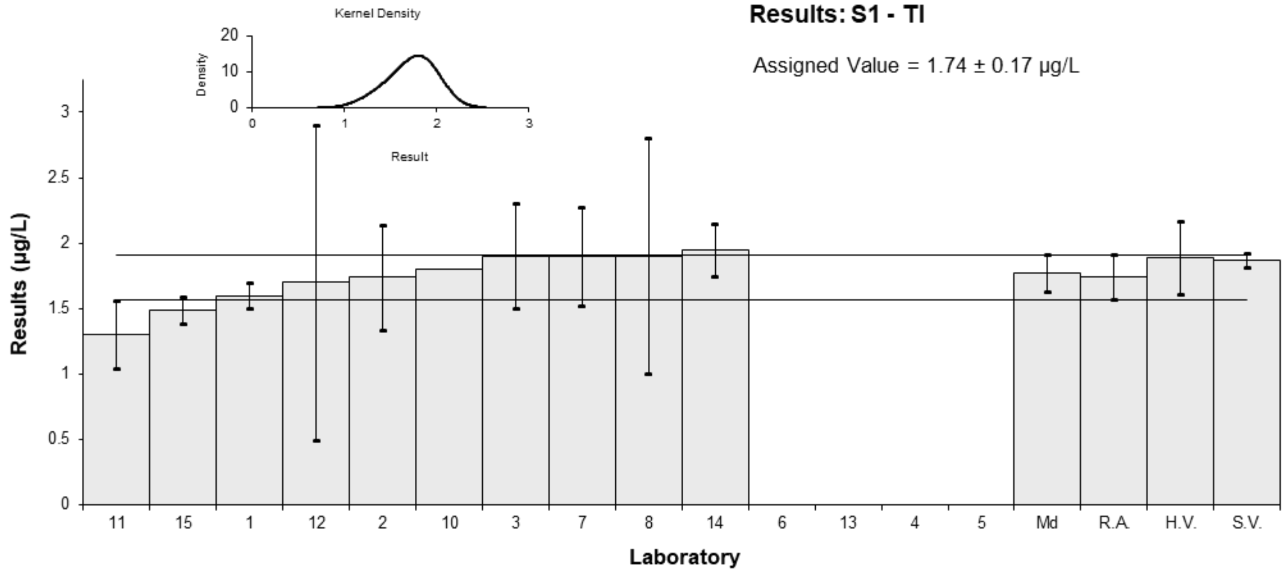
Sample No.	S1
Matrix.	Sea Water
Analyte.	Tl
Units	µg/L

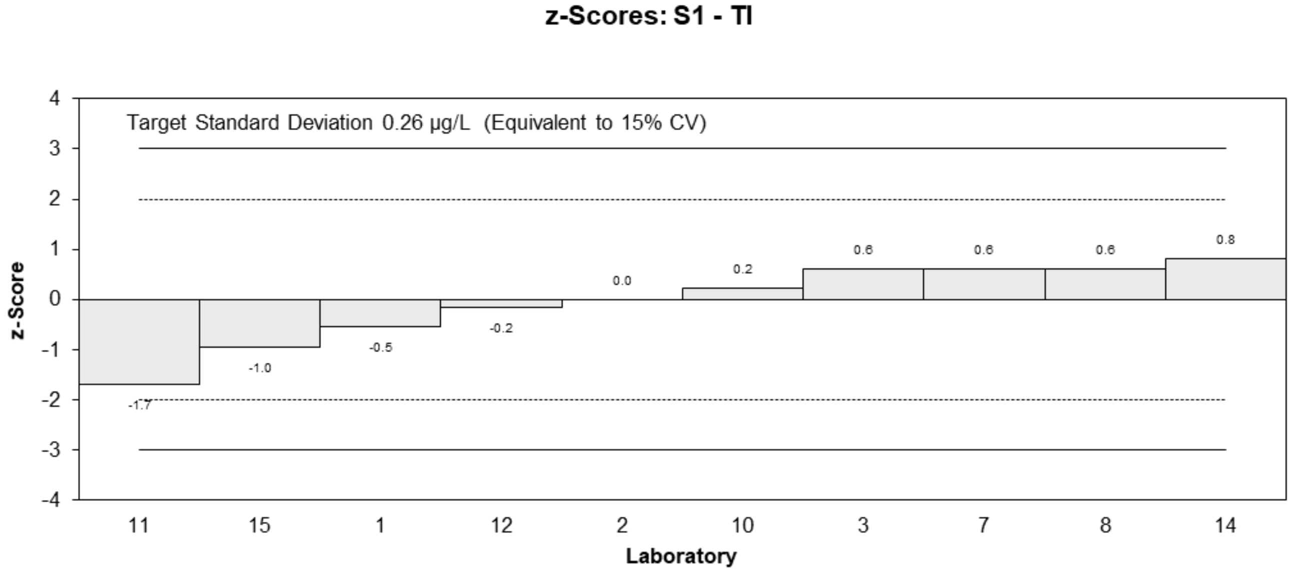
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.6	0.1	-0.54	-0.71
2	1.74	0.40	0.00	0.00
3	1.9	0.4	0.61	0.37
4	NT	NT		
5	NT	NT		
6	<1	1		
7	1.9	0.38	0.61	0.38
8	1.9	0.9	0.61	0.17
10	1.8	NR	0.23	0.35
11	1.3	0.26	-1.69	-1.42
12	1.7	1.2	-0.15	-0.03
13	NT	NT		
14	1.95	0.20	0.80	0.80
15	1.49	0.10	-0.96	-1.27

Statistics

Assigned Value	1.74	0.17
Spike	1.87	0.05
Homogeneity Value	1.89	0.28
Robust Average	1.74	0.17
Median	1.77	0.14
Mean	1.73	
N	10	
Max.	1.95	
Min.	1.3	
Robust SD	0.21	
Robust CV	12%	


Kernel Density
Density
Result
Results: S1 - Tl
Assigned Value = 1.74 ± 0.17 μg/L
Results (μg/L)
Laboratory
11 15 1 12 2 10 3 7 8 14 6 13 4 5 Md R.A. H.V. S.V.


z-Scores: S1 - Tl
Target Standard Deviation 0.26 μg/L (Equivalent to 15% CV)
z-Score
Laboratory
11 15 1 12 2 10 3 7 8 14
-1.7 -1.0 -0.5 -0.2 0.0 0.2 0.6 0.6 0.6 0.8

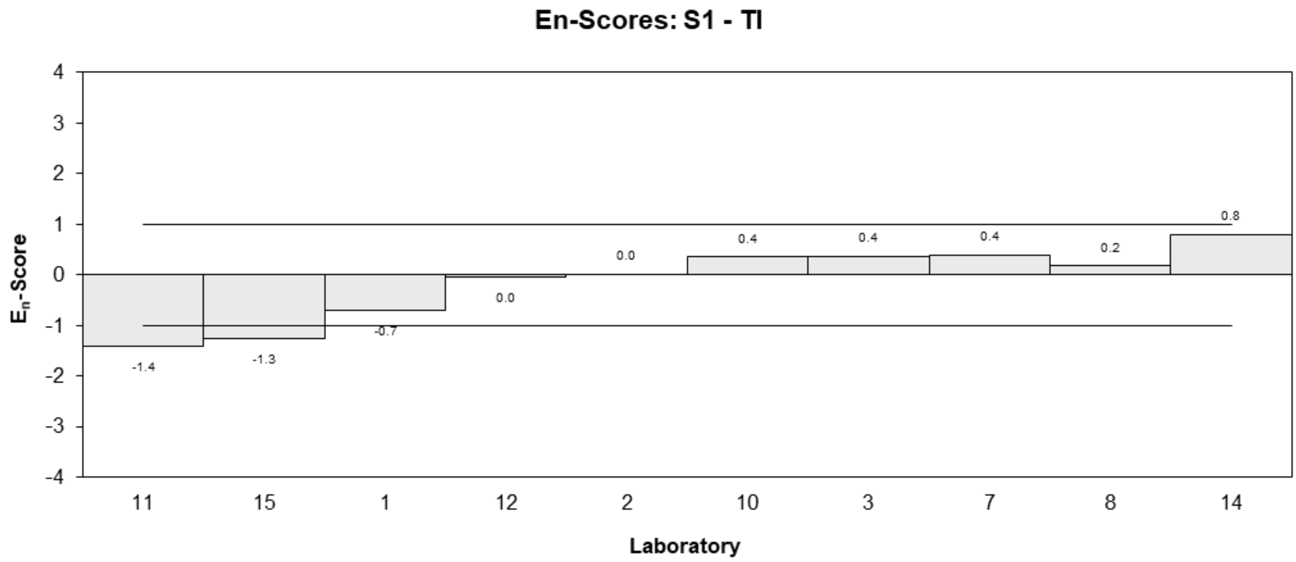

En-Scores: S1 - Tl
En-Score
Laboratory
11 15 1 12 2 10 3 7 8 14
-1.4 -1.3 -0.7 0.0 0.0 0.4 0.4 0.4 0.2 0.8

Figure 22

Table 25

Sample Details

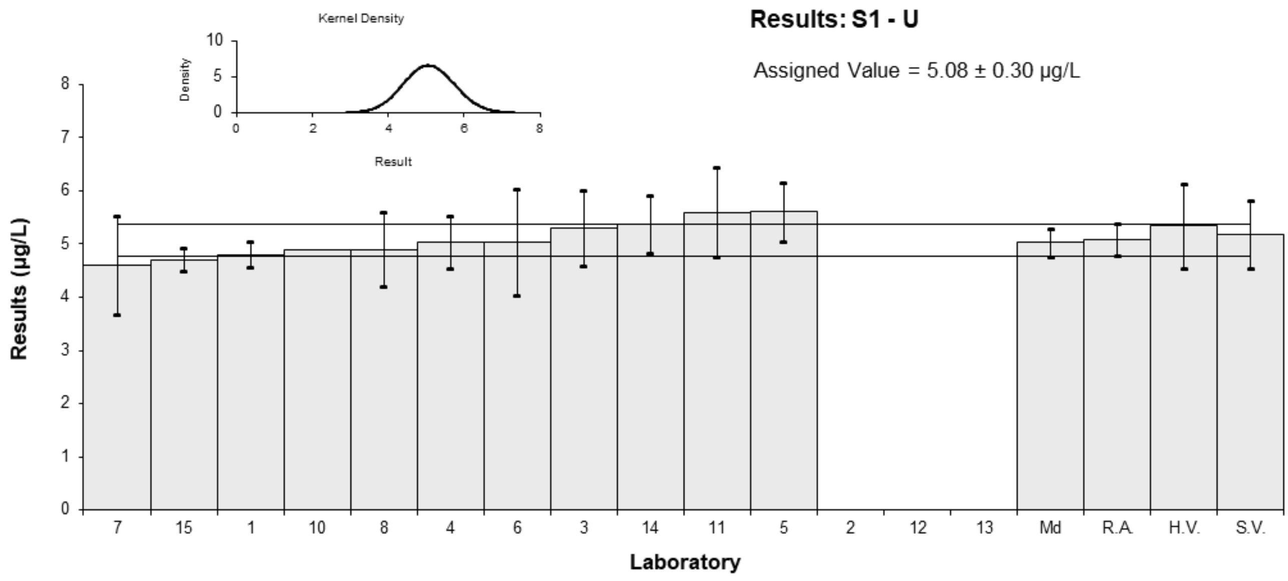
Sample No.	S1
Matrix.	Sea Water
Analyte.	U
Units	µg/L

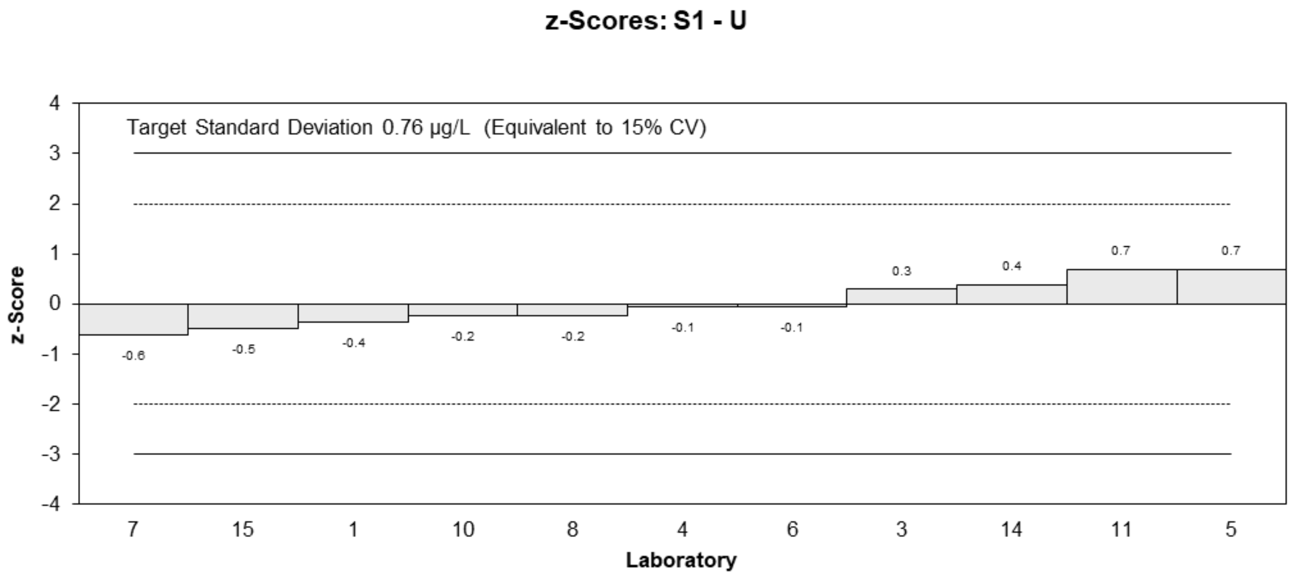
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	4.8	0.24	-0.37	-0.73
2	NR	NR		
3	5.3	0.7	0.29	0.29
4	5.03	0.50	-0.07	-0.09
5	5.604	0.560	0.69	0.82
6	5.04	1	-0.05	-0.04
7	4.6	0.92	-0.63	-0.50
8	4.9	0.7	-0.24	-0.24
10	4.9	NR	-0.24	-0.60
11	5.6	0.84	0.68	0.58
12	NT	NT		
13	NT	NT		
14	5.37	0.54	0.38	0.47
15	4.71	0.21	-0.49	-1.01

Statistics

Assigned Value	5.08	0.30
Spike	5.17	0.64
Homogeneity Value	5.34	0.80
Robust Average	5.08	0.30
Median	5.03	0.27
Mean	5.08	
N	11	
Max.	5.604	
Min.	4.6	
Robust SD	0.39	
Robust CV	7.7%	


Results: S1 - U
Assigned Value = 5.08 ± 0.30 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
15
1
10
8
4
6
3
14
11
5
2
12
13
Md
R.A.
H.V.
S.V.


z-Scores: S1 - U
Target Standard Deviation 0.76 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.6
-0.5
-0.4
-0.2
-0.2
-0.1
-0.1
0.3
0.4
0.7
0.7

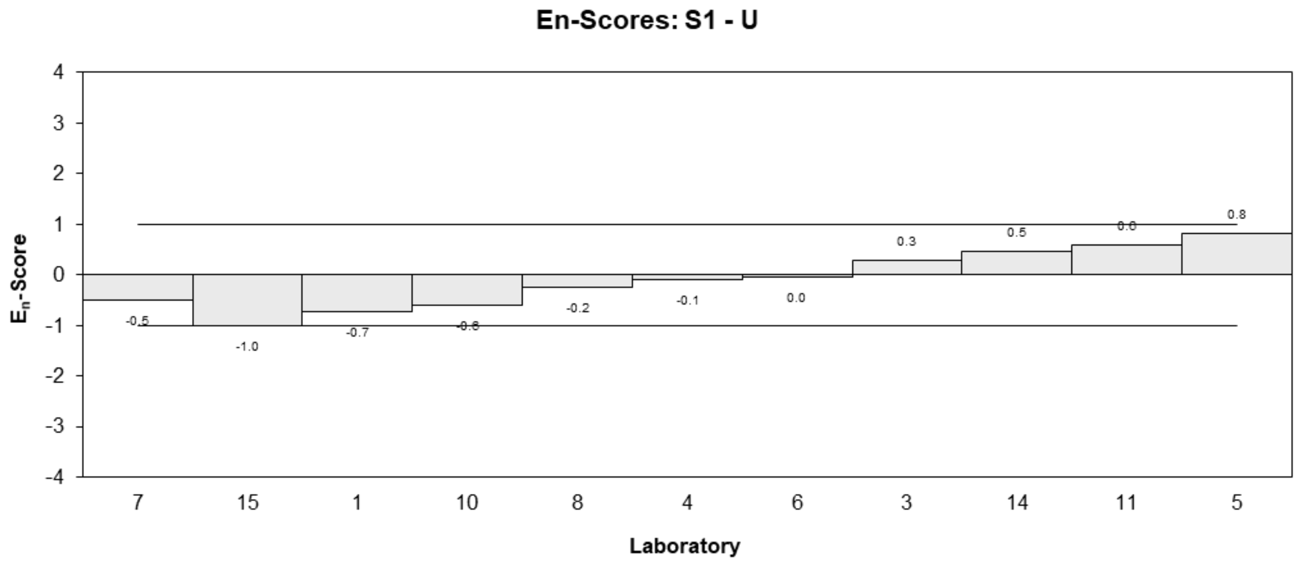

En-Scores: S1 - U
En-Score
Laboratory
-0.5
-1.0
-0.7
-0.6
-0.2
-0.1
0.0
0.3
0.5
0.6
0.8

Figure 23

Table 26

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	<5	5		
2	1.86	0.53	-1.23	-0.66
3	2.5	0.5	0.64	0.36
4	2.08	0.10	-0.58	-0.54
5	2.102	0.210	-0.52	-0.43
6	2.99	1	2.08	0.67
7	2.6	0.52	0.94	0.51
8	1.8	0.4	-1.40	-0.89
10	2.3	1.3	0.06	0.01
11	2.9	0.44	1.81	1.09
12	1.8	1.0	-1.40	-0.45
13	NT	NT		
14	2.18	0.22	-0.29	-0.24
15	3.56	0.23	3.74	3.00

Statistics

Assigned Value*	2.28	0.36
Spike	2.13	0.27
Homogeneity Value	2.42	0.36
Robust Average	2.36	0.39
Median	2.24	0.35
Mean	2.39	
N	12	
Max.	3.56	
Min.	1.8	
Robust SD	0.54	
Robust CV	23%	

*Robust Average excluding Laboratory 15.

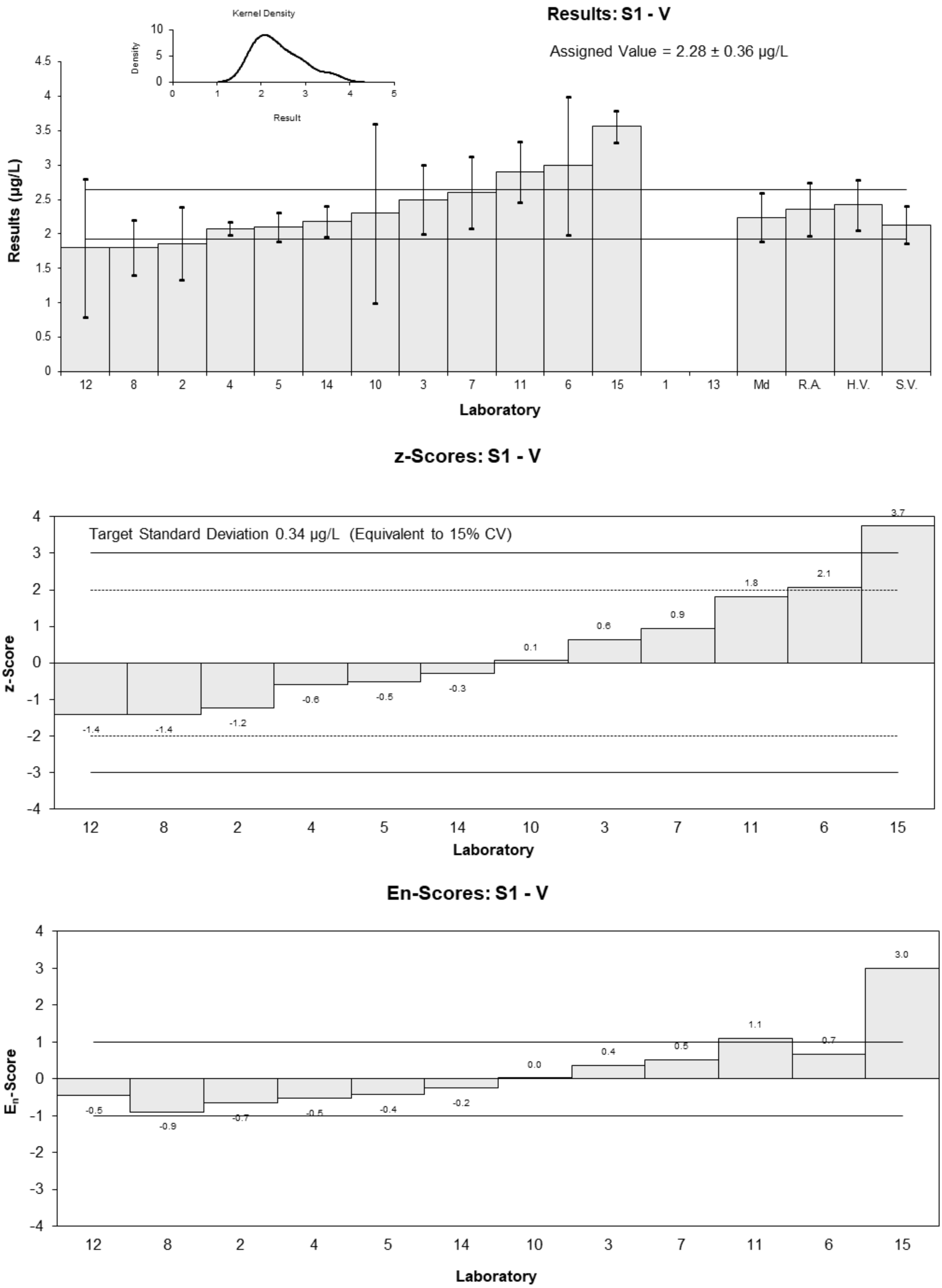

Results: S1 - V
Assigned Value = 2.28 ± 0.36 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
8
2
4
5
14
10
3
7
11
6
15
1
13
Md
R.A.
H.V.
S.V.
z-Scores: S1 - V
Target Standard Deviation 0.34 µg/L (Equivalent to 15% CV)
z-Score
En-Scores: S1 - V
En-Score

Figure 24

Table 27

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	9.4	1.19	2.01	1.46
2	7.17	1.74	-0.05	-0.03
3	7.6	1.5	0.35	0.22
4	9.04	0.64	1.68	1.65
5	7.598	1.5196	0.35	0.21
6	<10	10		
7	7.4	1.5	0.17	0.10
8	6.5	1.5	-0.66	-0.41
10	7.5	2.9	0.26	0.09
11	5.2	0.78	-1.87	-1.70
12	7	3	-0.20	-0.07
13	15	2	7.18	3.55
14	6.2	0.62	-0.94	-0.93
15	6.22	0.93	-0.92	-0.77

Statistics

Assigned Value*	7.22	0.90
Spike	6.99	0.46
Homogeneity Value	8.5	1.3
Robust Average	7.4	1.0
Median	7.40	0.81
Mean	7.83	
N	13	
Max.	15	
Min.	5.2	
Robust SD	1.5	
Robust CV	20%	

*Robust Average excluding Laboratory 13.

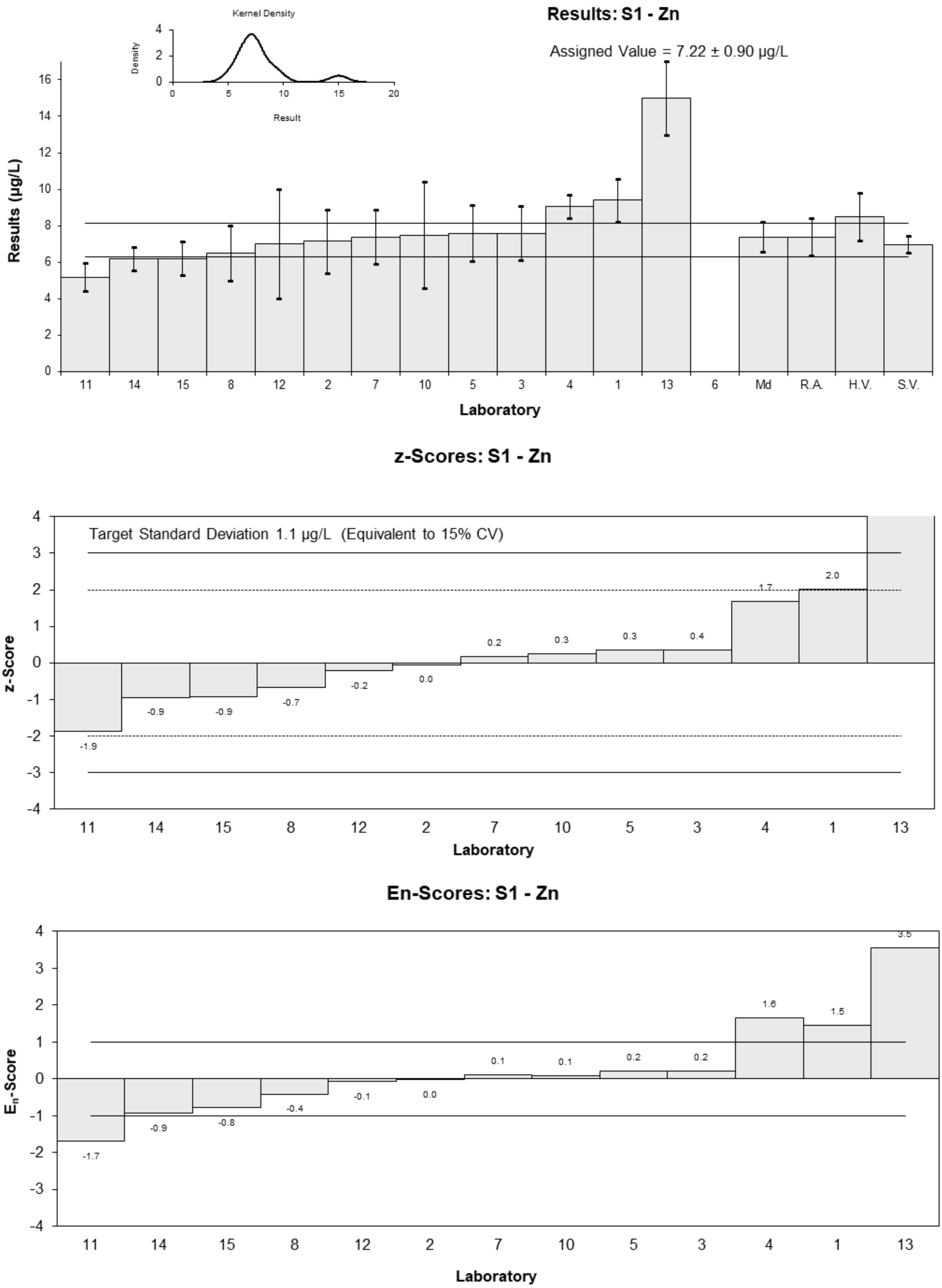

Results: S1 - Zn
Assigned Value = 7.22 ± 0.90 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
11 14 15 8 12 2 7 10 5 3 4 1 13 6 Md R.A. H.V. S.V.
z-Scores: S1 - Zn
Target Standard Deviation 1.1 µg/L (Equivalent to 15% CV)
z-Score
-1.9 -0.9 -0.9 -0.7 -0.2 0.0 0.2 0.3 0.3 0.4 1.7 2.0
Laboratory
11 14 15 8 12 2 7 10 5 3 4 1 13
En-Scores: S1 - Zn
En-Score
-1.7 -0.9 -0.8 -0.4 -0.1 0.0 0.1 0.1 0.2 0.2 1.6 1.5 3.5
Laboratory
11 14 15 8 12 2 7 10 5 3 4 1 13

Figure 25

Table 28

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	Ag
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	114	12.5	0.75	0.56
2	97	23	-0.85	-0.37
3	NT	NT		
4	108	4	0.19	0.25
5	91.304	9.134	-1.39	-1.28
6	104	31	-0.19	-0.06
7	110	20	0.38	0.19
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	110	11	0.38	0.31
13	NT	NT		
14	115	12	0.85	0.65
15	99.5	11.3	-0.61	-0.49

Statistics

Assigned Value	106	7
Spike	122	3
Homogeneity Value	113	17
Robust Average	106	7
Median	108	7
Mean	105	
N	9	
Max.	115	
Min.	91.304	
Robust SD	9.0	
Robust CV	8.5%	

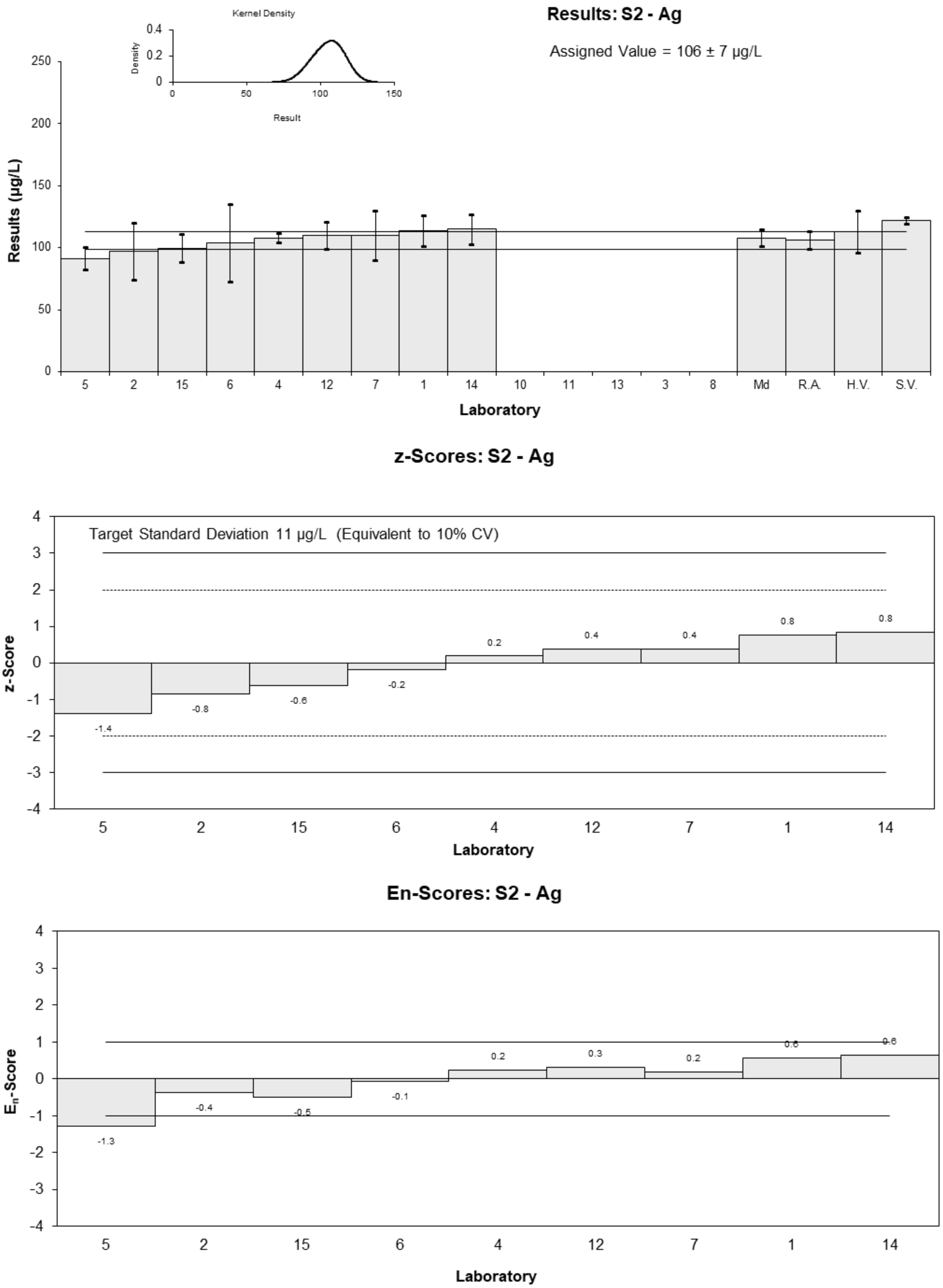

Results: S2 - Ag
Assigned Value = 106 ± 7 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5 2 15 6 4 12 7 1 14 10 11 13 3 8 Md R.A. H.V. S.V.
z-Scores: S2 - Ag
Target Standard Deviation 11 µg/L (Equivalent to 10% CV)
z-Score
-1.4 -0.8 -0.6 -0.2 0.2 0.4 0.4 0.8 0.8
Laboratory
5 2 15 6 4 12 7 1 14
En-Scores: S2 - Ag
E_n-Score
-1.3 -0.4 -0.5 -0.1 0.2 0.3 0.2 0.6 0.6
Laboratory
5 2 15 6 4 12 7 1 14

Figure 26

Table 29

Sample Details

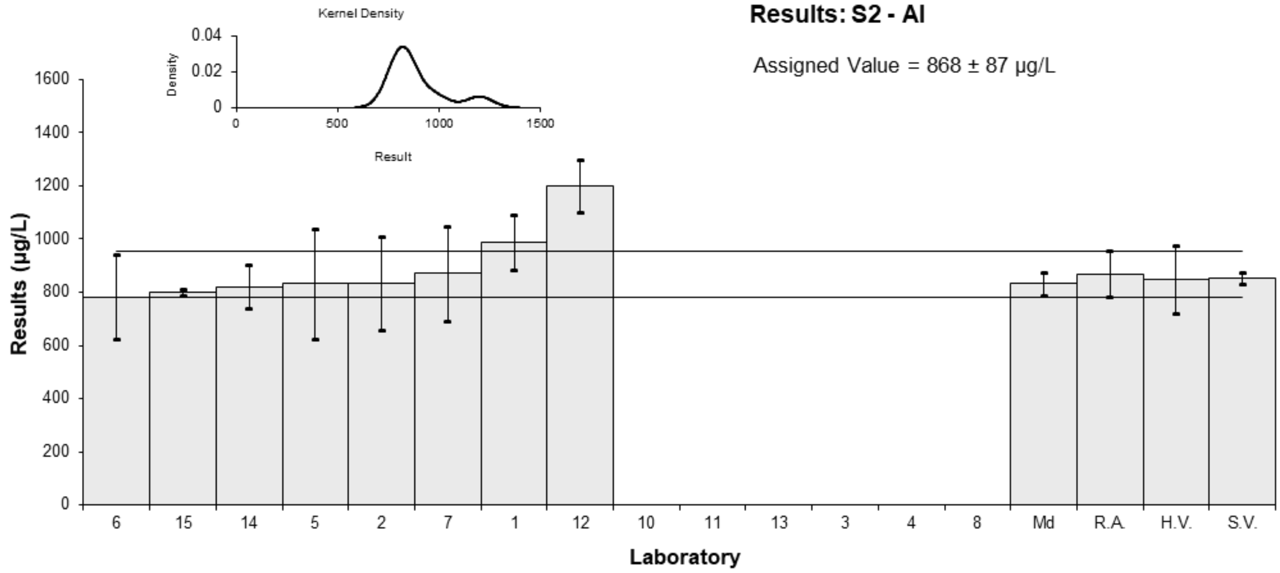
Sample No.	S2
Matrix.	Sea Water
Analyte.	Al
Units	µg/L

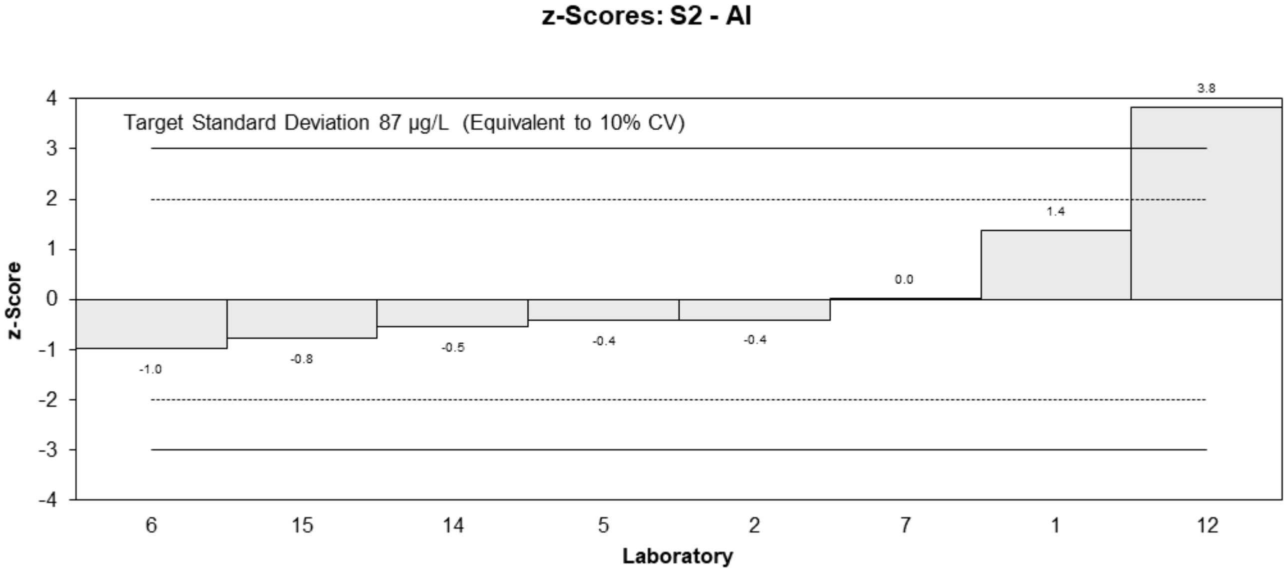
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	988	104	1.38	0.89
2	833	175	-0.40	-0.18
3	NT	NT		
4	NT	NT		
5	832.0	208	-0.41	-0.16
6	783	160	-0.98	-0.47
7	870	180	0.02	0.01
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	1200	100	3.82	2.50
13	NT	NT		
14	821	82	-0.54	-0.39
15	800	14	-0.78	-0.77

Statistics

Assigned Value	868	87
Spike	853	24
Homogeneity Value	848	127
Robust Average	868	87
Median	833	43
Mean	891	
N	8	
Max.	1200	
Min.	783	
Robust SD	98	
Robust CV	11%	


Results: S2 - Al
Assigned Value = 868 ± 87 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
15
14
5
2
7
1
12
10
11
13
3
4
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Al
Target Standard Deviation 87 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.0
-0.8
-0.5
-0.4
-0.4
0.0
1.4
3.8

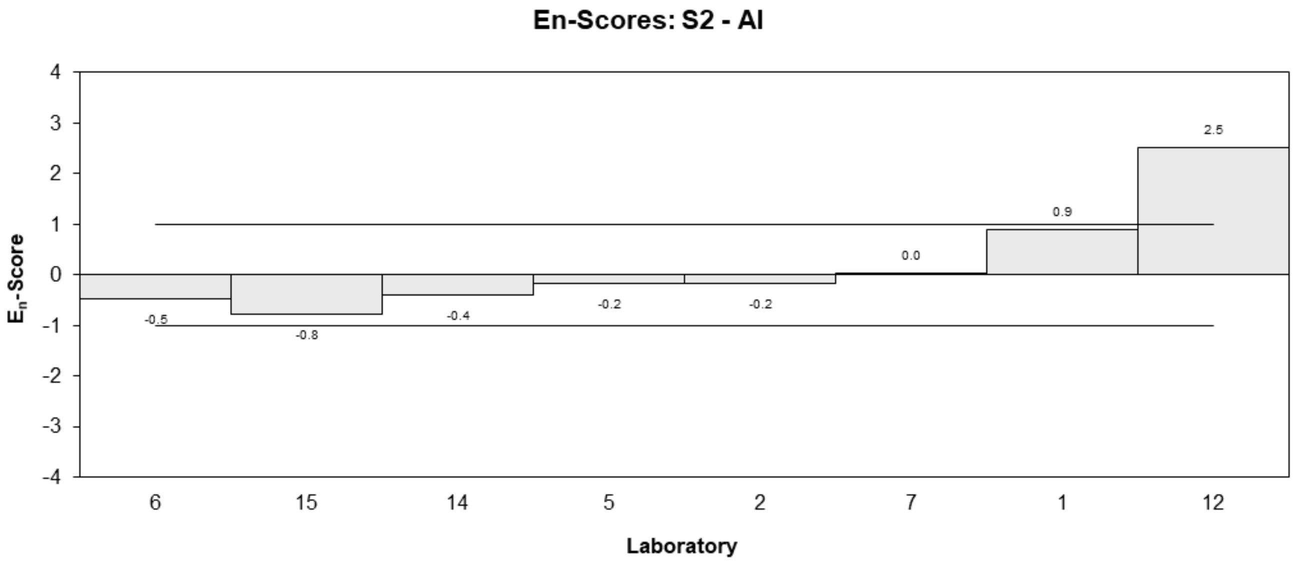

En-Scores: S2 - Al
En-Score
Laboratory
-0.5
-0.8
-0.4
-0.2
-0.2
0.0
0.9
2.5

Figure 27

Table 30

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	280	104	2.07	0.46
2	230	51	-0.09	-0.04
3	NT	NT		
4	222	5	-0.43	-0.77
5	239.9	23.99	0.34	0.29
6	246	49	0.60	0.28
7	230	45	-0.09	-0.04
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	220	53	-0.52	-0.22
13	240	20	0.34	0.34
14	228	23	-0.17	-0.15
15	211	34	-0.91	-0.58

Statistics

Assigned Value	232	12
Spike	257	7
Homogeneity Value	255	35
Robust Average	232	12
Median	230	11
Mean	235	
N	10	
Max.	280	
Min.	211	
Robust SD	15	
Robust CV	6.5%	

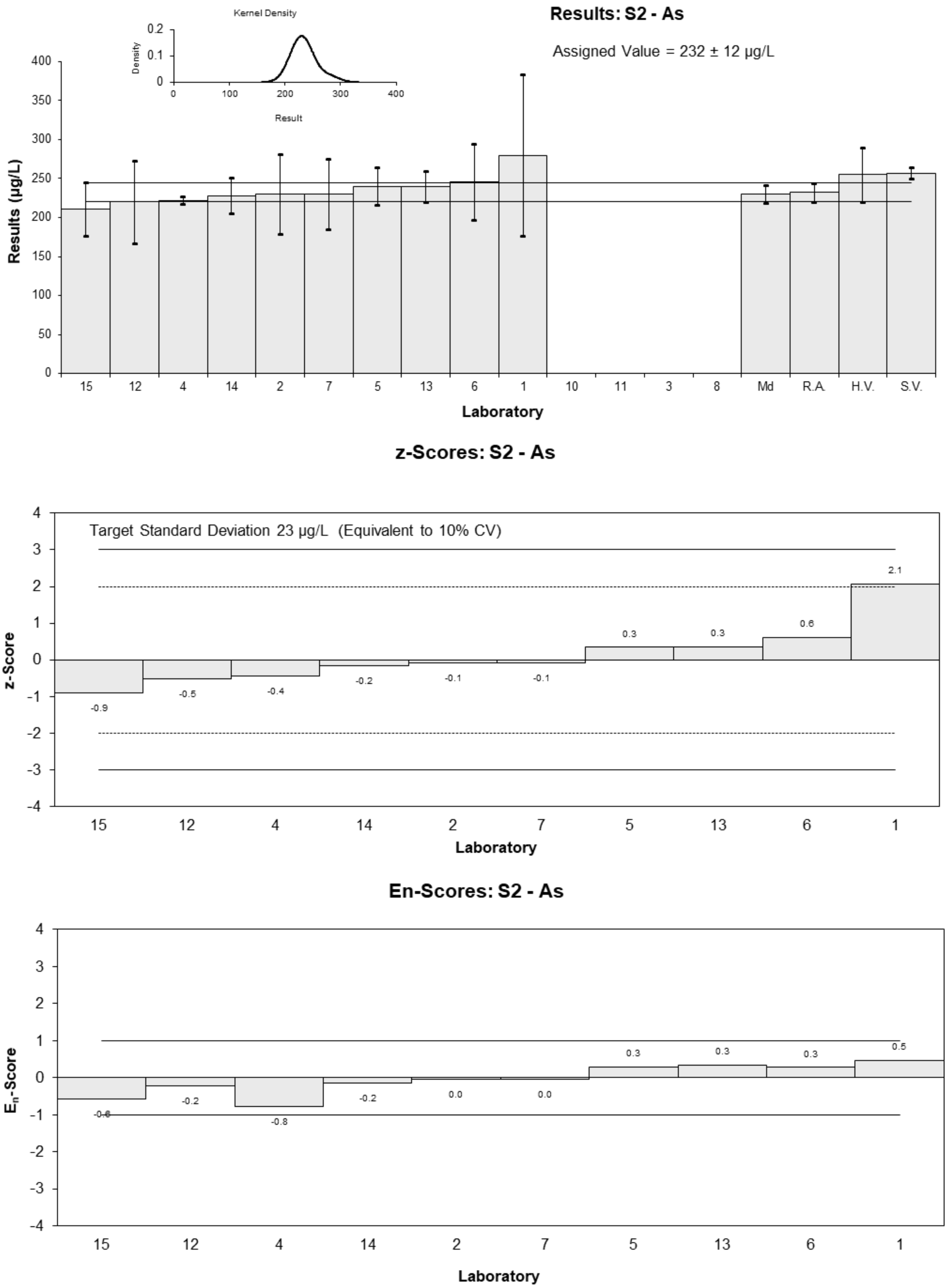

Results: S2 - As
Assigned Value = 232 ± 12 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15
12
4
14
2
7
5
13
6
1
10
11
3
8
Md
R.A.
H.V.
S.V.
z-Scores: S2 - As
Target Standard Deviation 23 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.9
-0.5
-0.4
-0.2
-0.1
-0.1
0.3
0.3
0.6
2.1
En-Scores: S2 - As
E_n-Score
Laboratory
-0.6
-0.2
-0.8
-0.2
0.0
0.0
0.3
0.3
0.3
0.5

Figure 28

Table 31

Sample Details

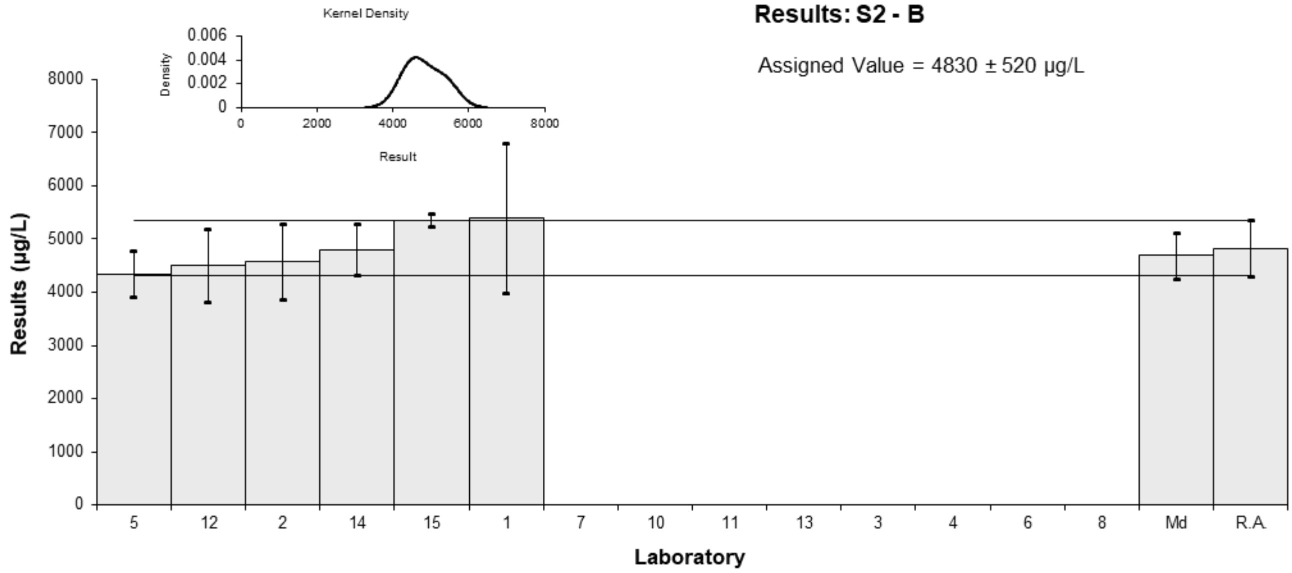
Sample No.	S2
Matrix.	Sea Water
Analyte.	B
Units	µg/L

Participant Results

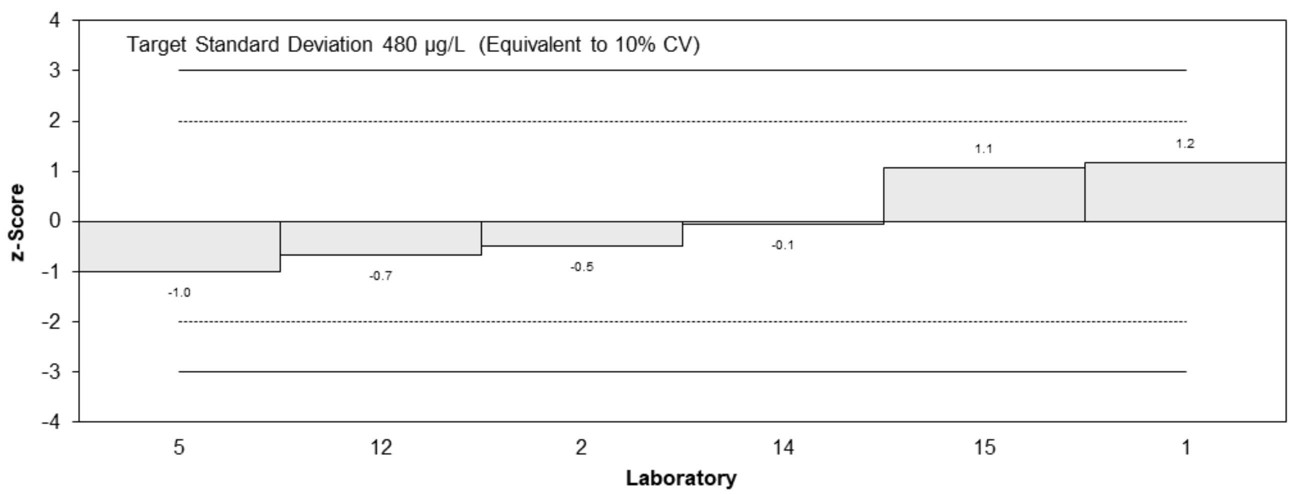
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5397	1403	1.17	0.38
2	4589	710	-0.50	-0.27
3	NT	NT		
4	NT	NT		
5	4341	434	-1.01	-0.72
6	NT	NT		
7	NR	NR		
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	4500	680	-0.68	-0.39
13	NT	NT		
14	4800	480	-0.06	-0.04
15	5350	120	1.08	0.97

Statistics

Assigned Value	4830	520
Spike	Not Spiked	
Robust Average	4830	520
Median	4690	430
Mean	4830	
N	6	
Max.	5397	
Min.	4341	
Robust SD	510	
Robust CV	11%	



z-Scores: S2 - B



En-Scores: S2 - B

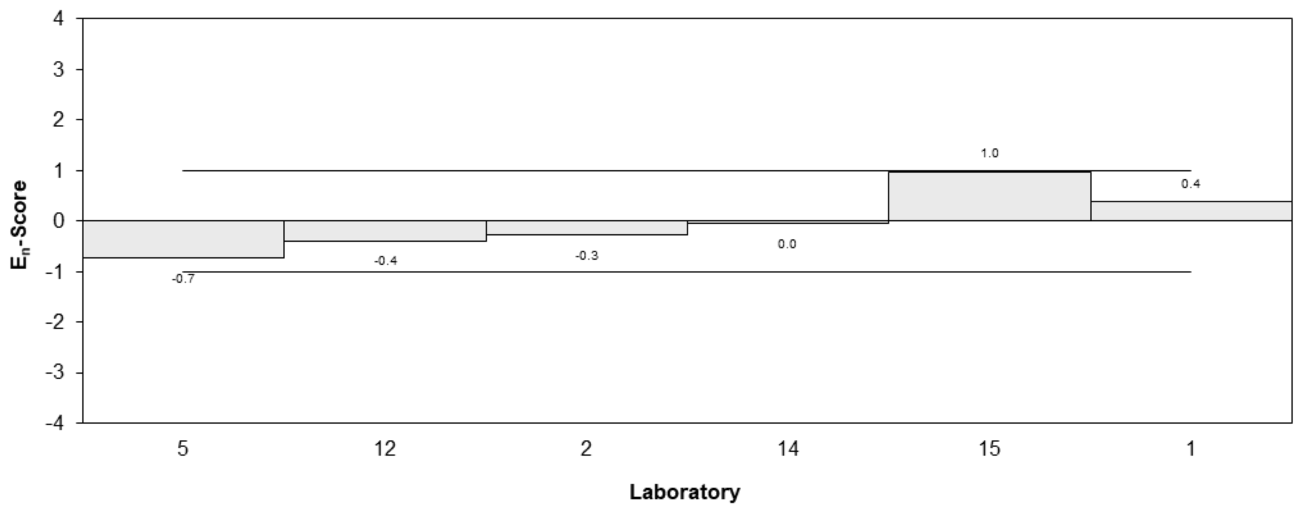


Figure 29

Table 32

Sample Details

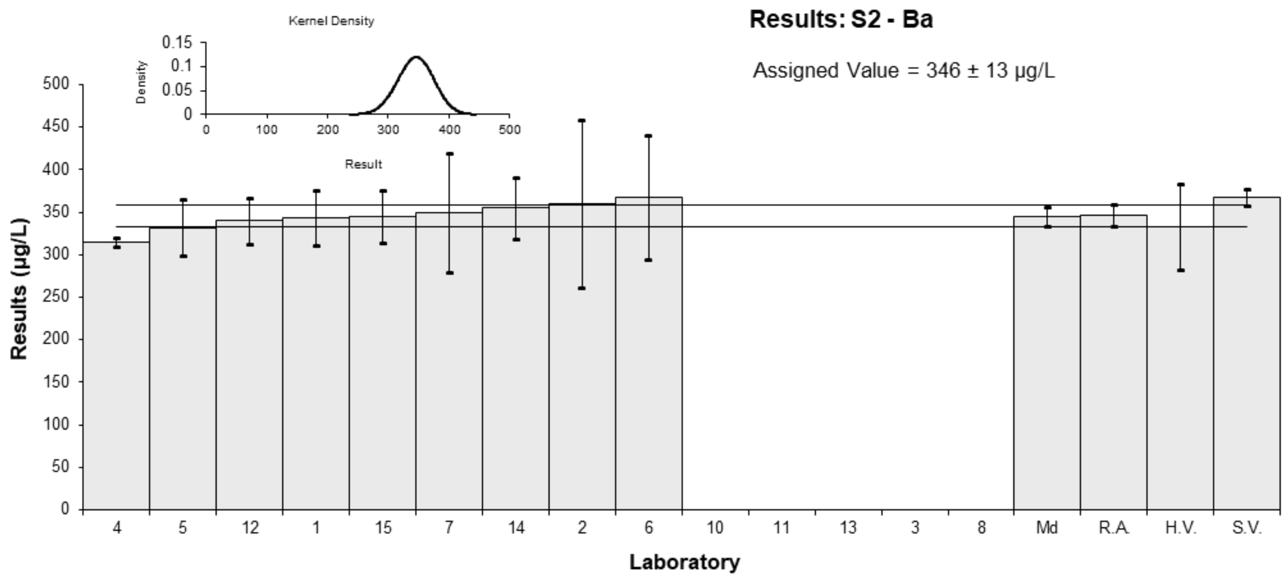
Sample No.	S2
Matrix.	Sea Water
Analyte.	Ba
Units	µg/L

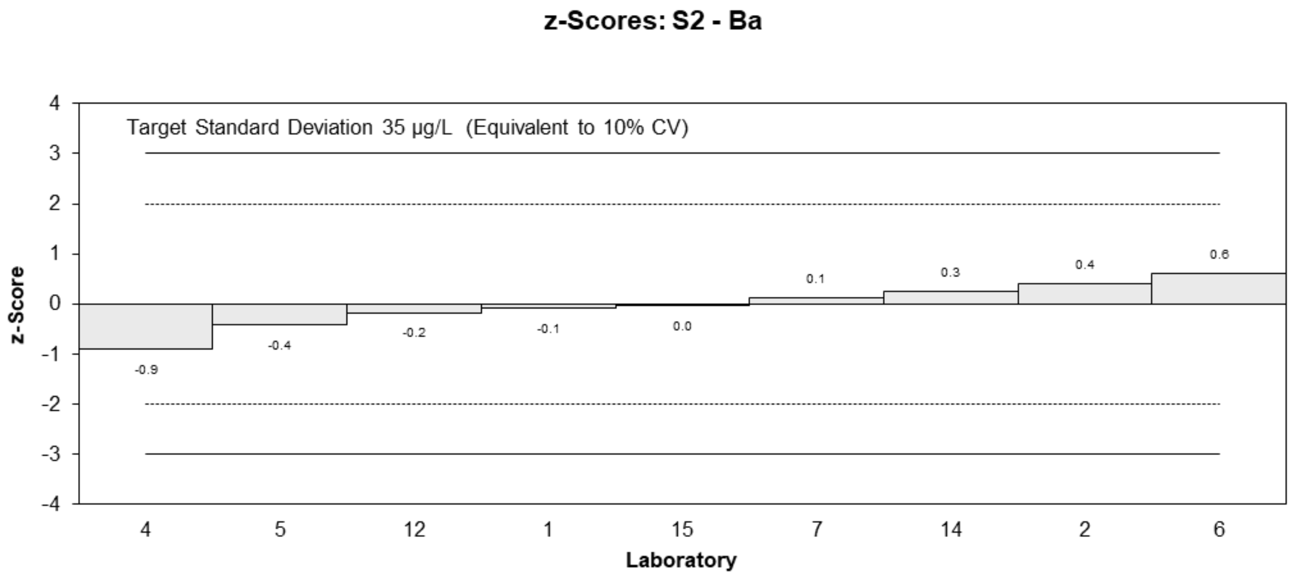
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	343	32	-0.09	-0.09
2	360	99	0.40	0.14
3	NT	NT		
4	315	5	-0.90	-2.23
5	331.9	33.19	-0.41	-0.40
6	367	73	0.61	0.28
7	350	70	0.12	0.06
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	340	27	-0.17	-0.20
13	NT	NT		
14	355	36	0.26	0.24
15	345	31	-0.03	-0.03

Statistics

Assigned Value	346	13
Spike	367	10
Homogeneity Value	333	50
Robust Average	346	13
Median	345	11
Mean	345	
N	9	
Max.	367	
Min.	315	
Robust SD	16	
Robust CV	4.6%	


Results: S2 - Ba
Assigned Value = 346 ± 13 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
4
5
12
1
15
7
14
2
6
10
11
13
3
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Ba
Target Standard Deviation 35 µg/L (Equivalent to 10% CV)
z-Score
-0.9
-0.4
-0.2
-0.1
0.0
0.1
0.3
0.4
0.6
4
5
12
1
15
7
14
2
6
Laboratory

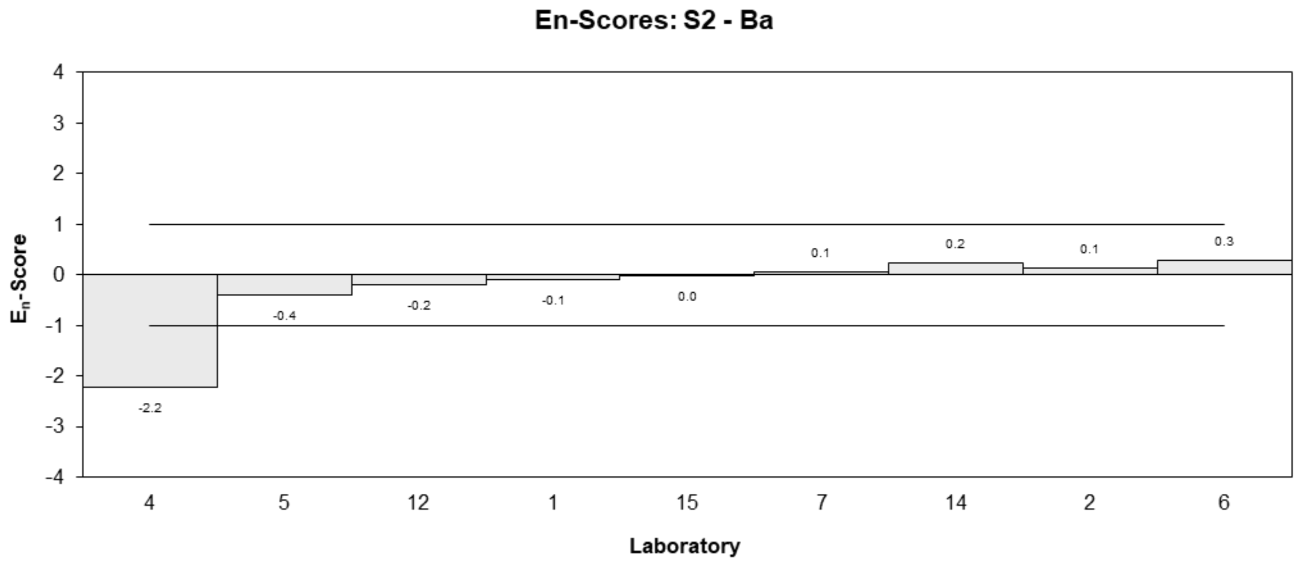

En-Scores: S2 - Ba
E_n-Score
-2.2
-0.4
-0.2
-0.1
0.0
0.1
0.2
0.1
0.3
4
5
12
1
15
7
14
2
6
Laboratory

Figure 30

Table 33

Sample Details

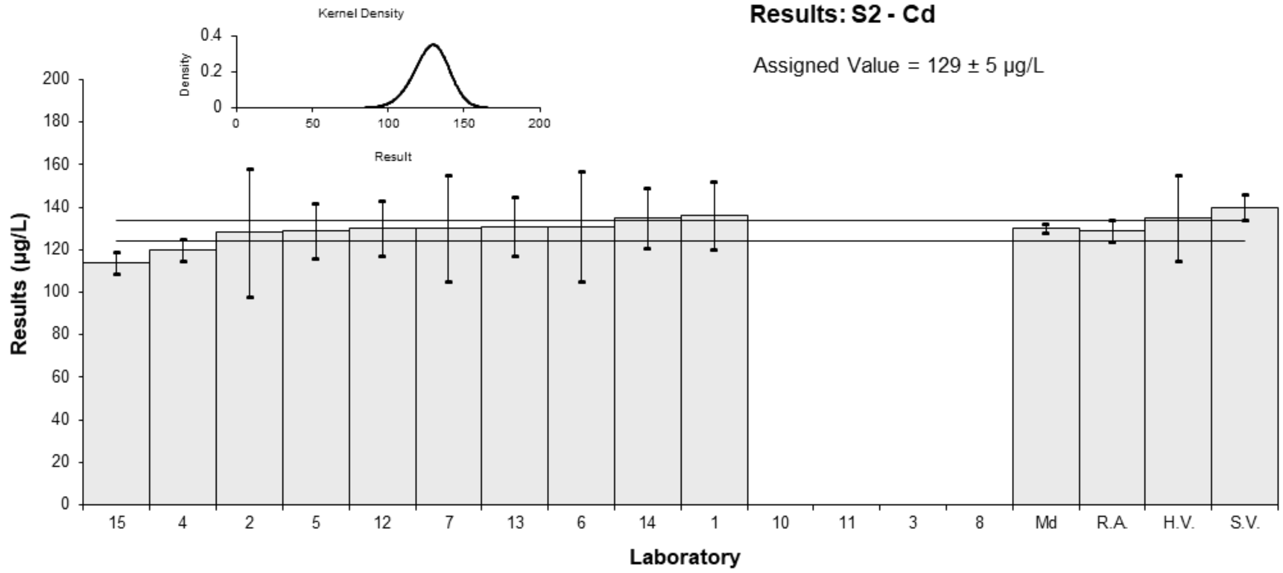
Sample No.	S2
Matrix.	Sea Water
Analyte.	Cd
Units	µg/L

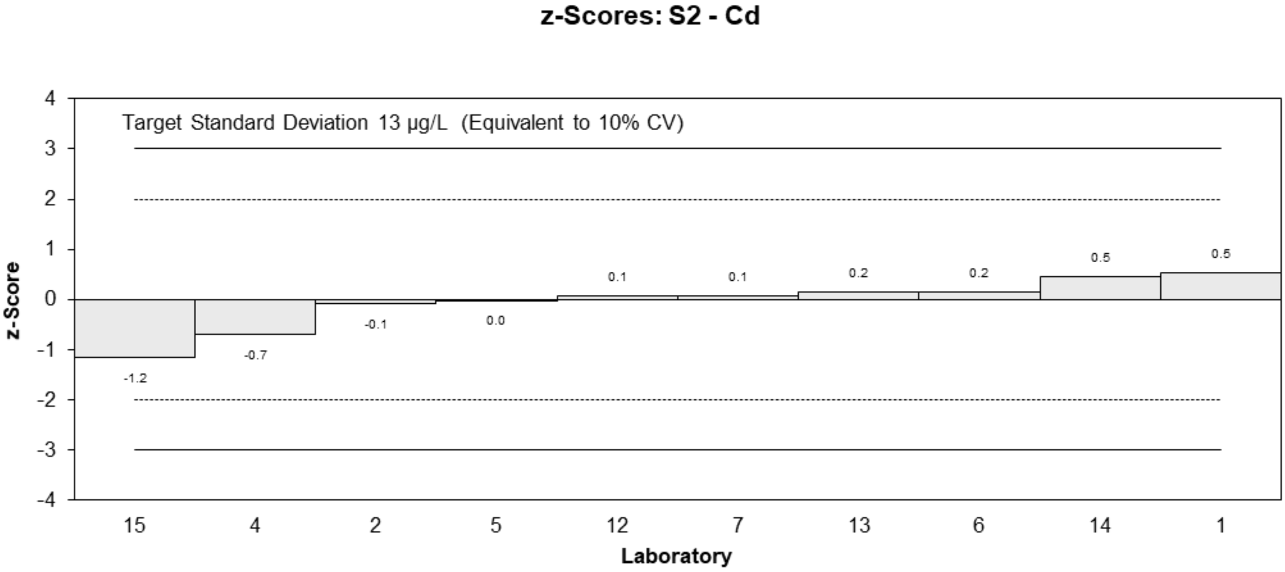
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	136	16	0.54	0.42
2	128	30	-0.08	-0.03
3	NT	NT		
4	120	5	-0.70	-1.27
5	128.9	12.89	-0.01	-0.01
6	131	26	0.16	0.08
7	130	25	0.08	0.04
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	130	13	0.08	0.07
13	131	14	0.16	0.13
14	135	14	0.47	0.40
15	114	5	-1.16	-2.12

Statistics

Assigned Value	129	5
Spike	140	6
Homogeneity Value	135	20
Robust Average	129	5
Median	130	2
Mean	128	
N	10	
Max.	136	
Min.	114	
Robust SD	6.1	
Robust CV	4.7%	


Results: S2 - Cd
Assigned Value = 129 ± 5 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15
4
2
5
12
7
13
6
14
1
10
11
3
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cd
Target Standard Deviation 13 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.2
-0.7
-0.1
0.0
0.1
0.1
0.2
0.2
0.5
0.5
15
4
2
5
12
7
13
6
14
1

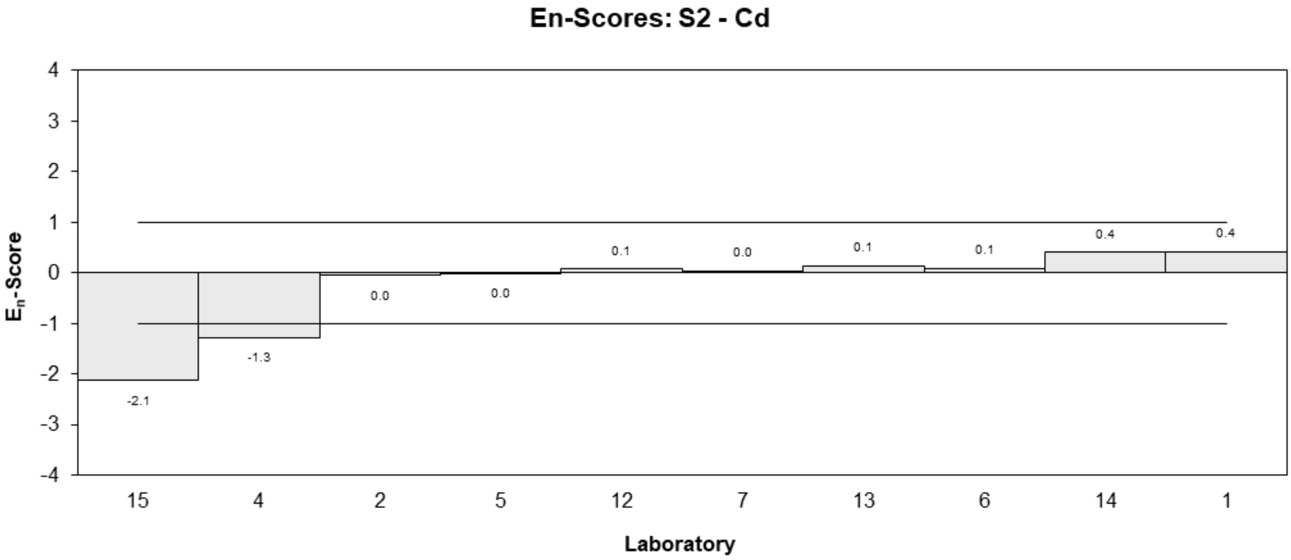

En-Scores: S2 - Cd
E_n-Score
Laboratory
-2.1
-1.3
0.0
0.0
0.1
0.0
0.1
0.1
0.4
0.4
15
4
2
5
12
7
13
6
14
1

Figure 31

Table 34

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	161	17	-0.80	-0.75
2	188	51	0.74	0.25
3	NT	NT		
4	163	4	-0.69	-1.34
5	174.3	34.86	-0.04	-0.02
6	177	35	0.11	0.06
7	180	35	0.29	0.14
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	170	26	-0.29	-0.18
13	172	11	-0.17	-0.22
14	173	17	-0.11	-0.11
15	189	5	0.80	1.48

Statistics

Assigned Value	175	8
Spike	186	5
Homogeneity Value	184	28
Robust Average	175	8
Median	174	5
Mean	175	
N	10	
Max.	189	
Min.	161	
Robust SD	11	
Robust CV	6.3%	

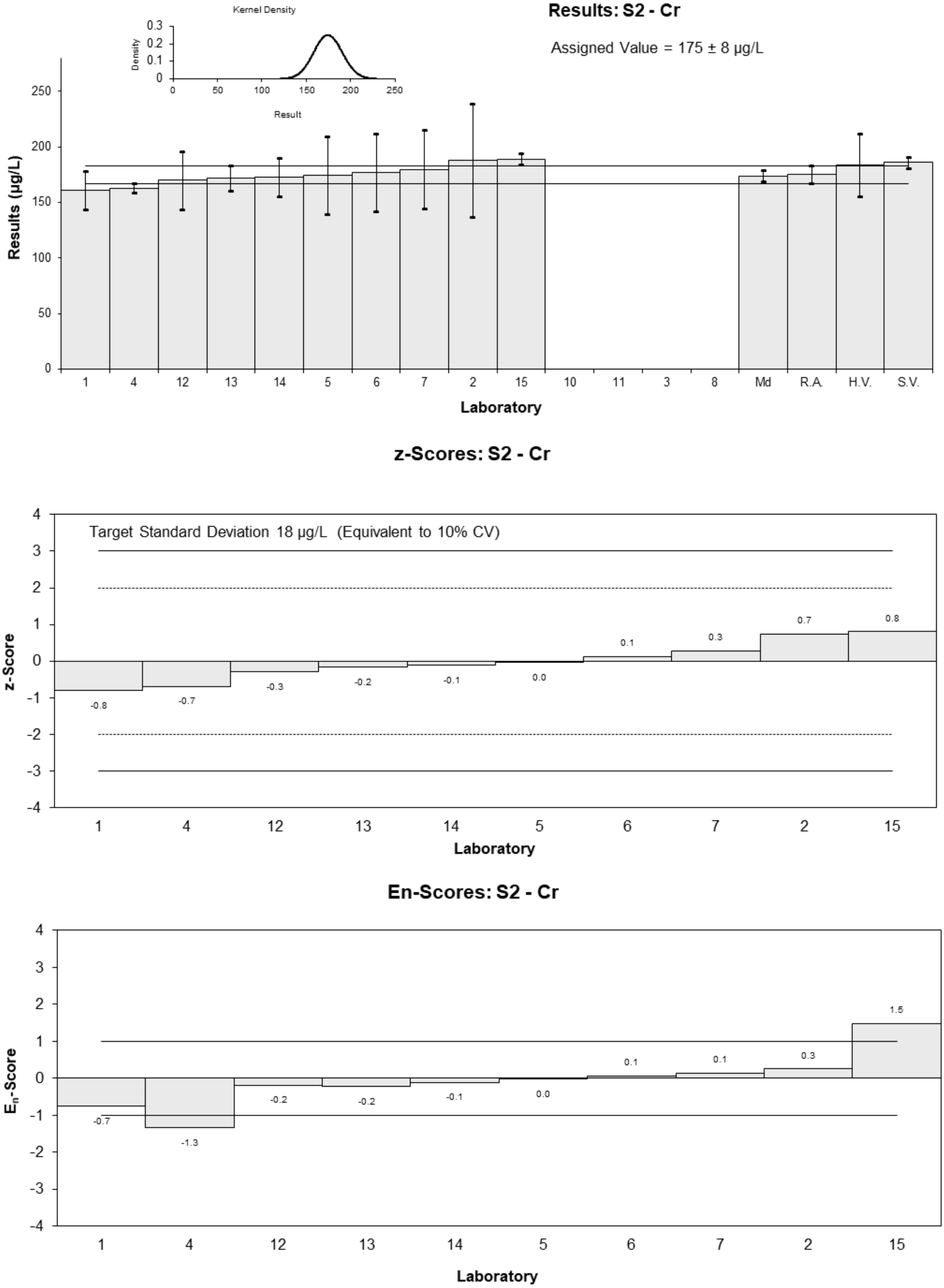

Results: S2 - Cr
Assigned Value = 175 ± 8 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
1 4 12 13 14 5 6 7 2 15 10 11 3 8 Md R.A. H.V. S.V.
z-Scores: S2 - Cr
Target Standard Deviation 18 μg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.7 -0.3 -0.2 -0.1 0.0 0.1 0.3 0.7 0.8
Laboratory
1 4 12 13 14 5 6 7 2 15
En-Scores: S2 - Cr
En-Score
-0.7 -1.3 -0.2 -0.2 -0.1 0.0 0.1 0.1 0.3 1.5
Laboratory
1 4 12 13 14 5 6 7 2 15

Figure 32

Table 35

Sample Details

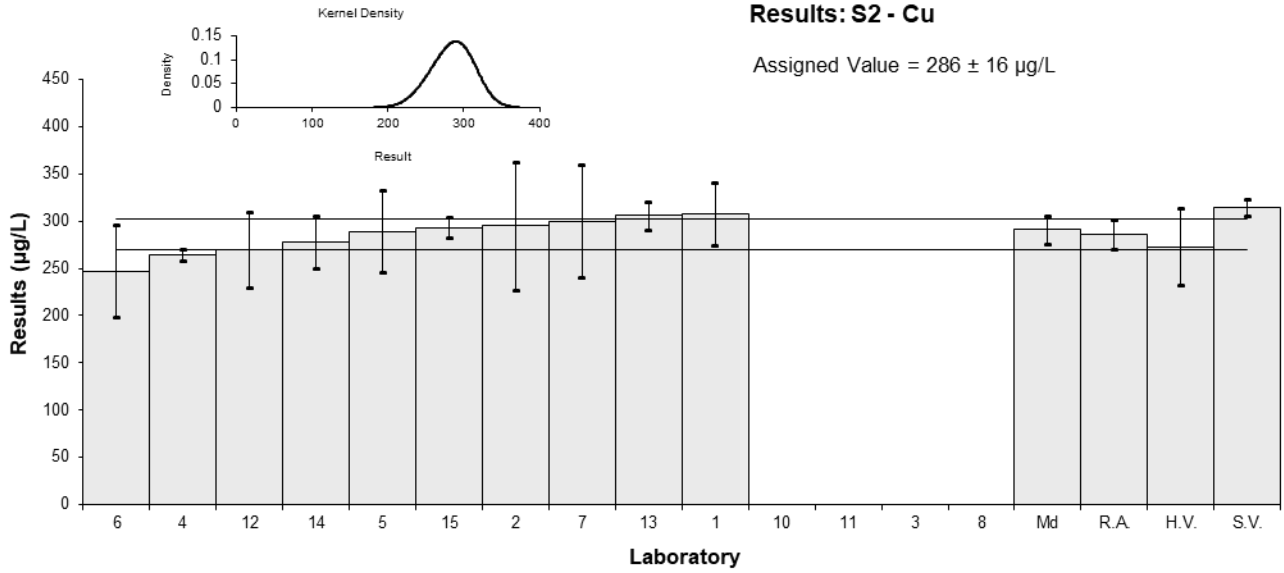
Sample No.	S2
Matrix.	Sea Water
Analyte.	Cu
Units	µg/L

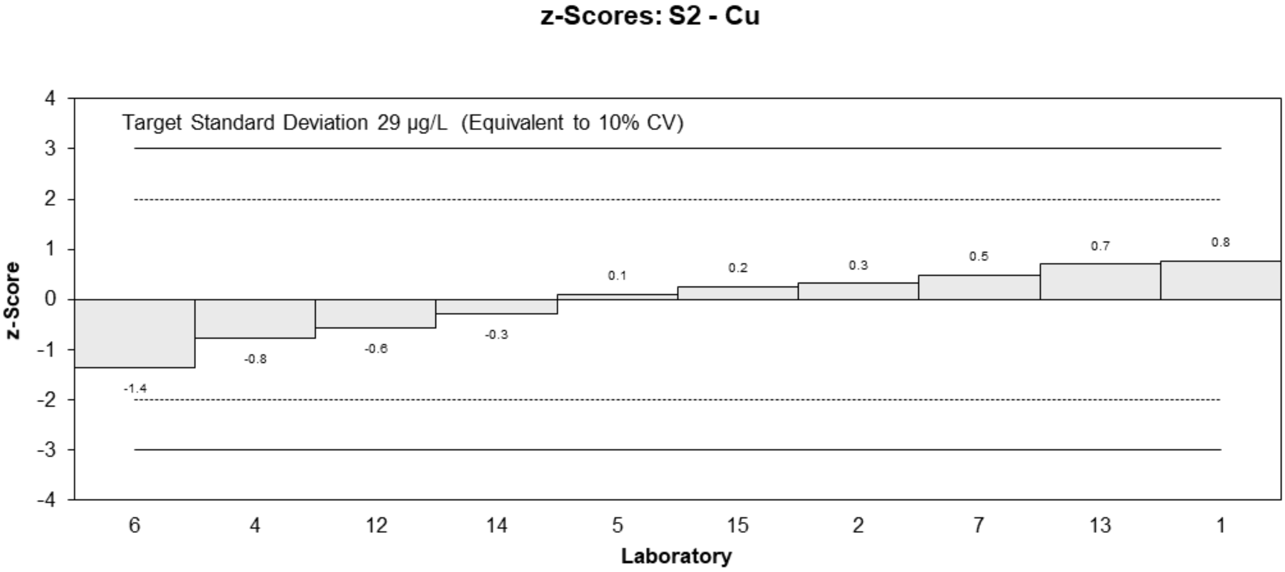
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	308	33	0.77	0.60
2	295	68	0.31	0.13
3	NT	NT		
4	264	6	-0.77	-1.29
5	289.0	43.35	0.10	0.06
6	247	49	-1.36	-0.76
7	300	60	0.49	0.23
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	270	40	-0.56	-0.37
13	306	15	0.70	0.91
14	278	28	-0.28	-0.25
15	293	11	0.24	0.36

Statistics

Assigned Value	286	16
Spike	314	9
Homogeneity Value	273	41
Robust Average	286	16
Median	291	15
Mean	285	
N	10	
Max.	308	
Min.	247	
Robust SD	21	
Robust CV	7.3%	


Results: S2 - Cu
Assigned Value = 286 ± 16 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6
4
12
14
5
15
2
7
13
1
10
11
3
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cu
Target Standard Deviation 29 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.4
-0.8
-0.6
-0.3
0.1
0.2
0.3
0.5
0.7
0.8

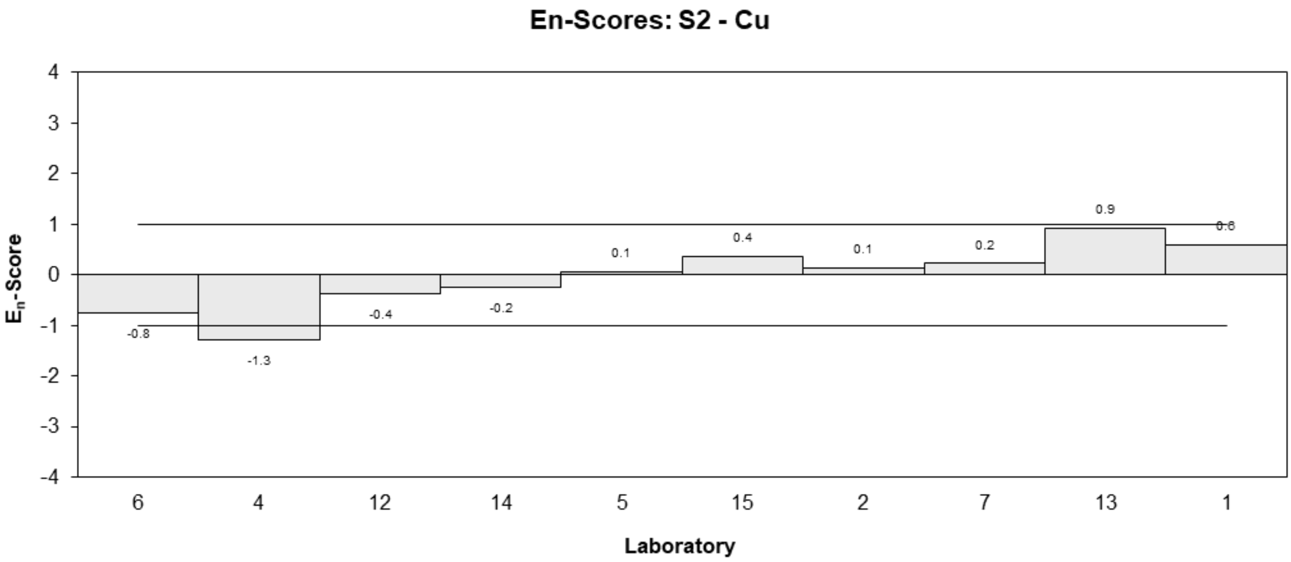

En-Scores: S2 - Cu
En-Score
Laboratory
-0.8
-1.3
-0.4
-0.2
0.1
0.4
0.1
0.2
0.9
0.6

Figure 33

Table 36

Sample Details

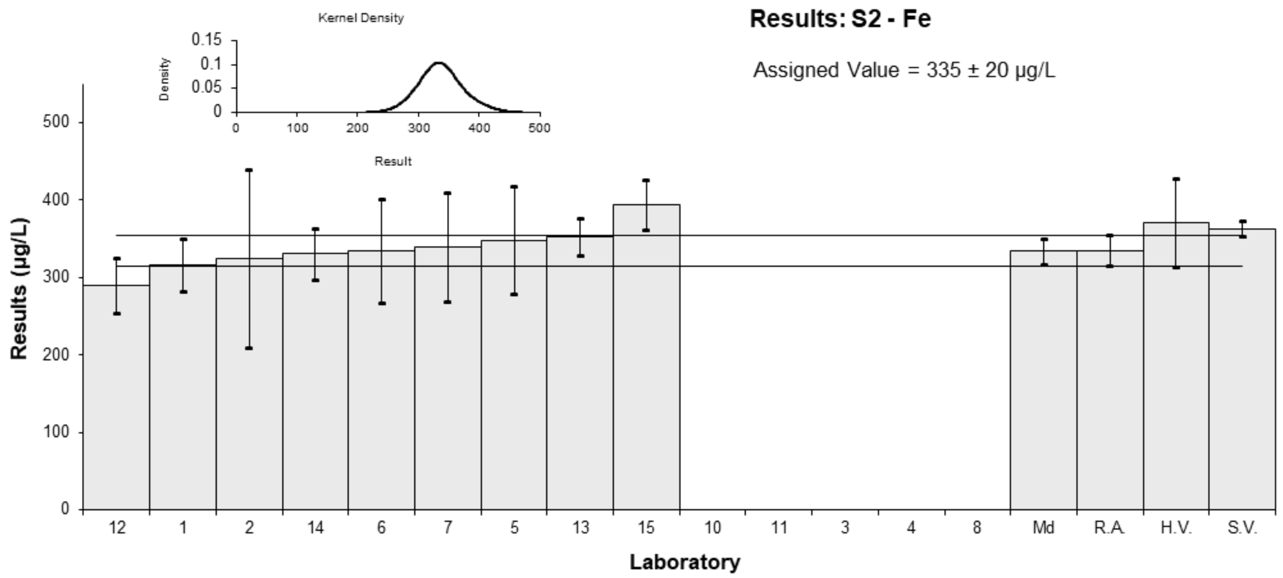
Sample No.	S2
Matrix.	Sea Water
Analyte.	Fe
Units	µg/L

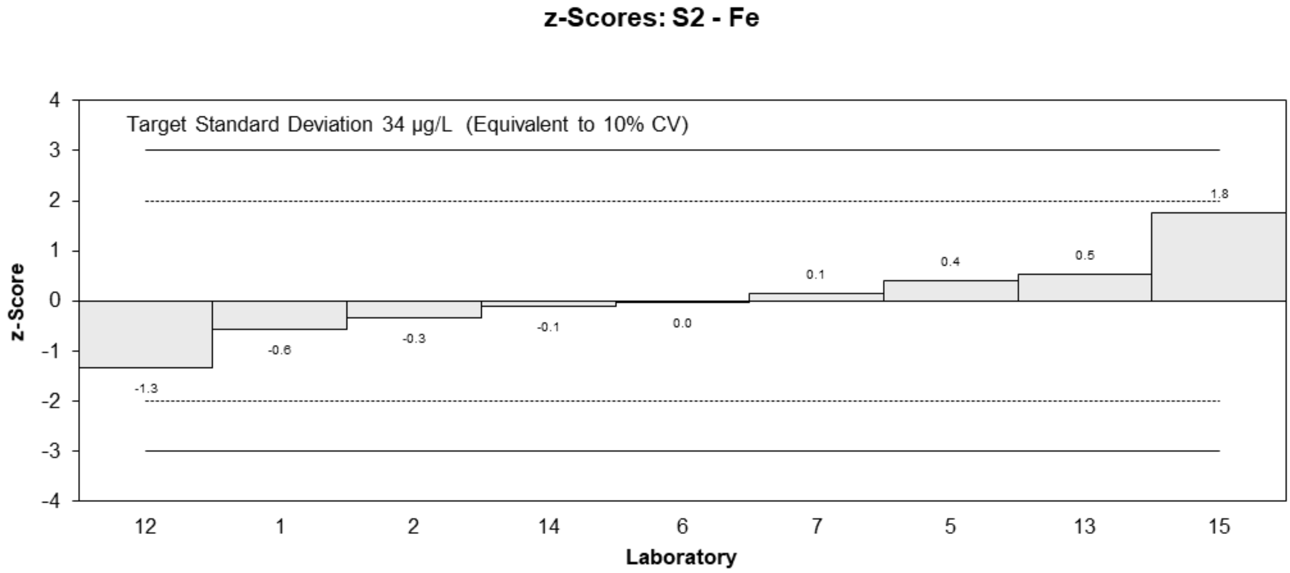
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	316	34	-0.57	-0.48
2	324	115	-0.33	-0.09
3	NT	NT		
4	NT	NT		
5	348.5	69.7	0.40	0.19
6	334	67	-0.03	-0.01
7	340	70	0.15	0.07
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	290	35	-1.34	-1.12
13	353	24	0.54	0.58
14	331	33	-0.12	-0.10
15	394	32	1.76	1.56

Statistics

Assigned Value	335	20
Spike	363	10
Homogeneity Value	371	57
Robust Average	335	20
Median	334	17
Mean	337	
N	9	
Max.	394	
Min.	290	
Robust SD	24	
Robust CV	7.2%	


Results: S2 - Fe
Assigned Value = 335 ± 20 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
12
1
2
14
6
7
5
13
15
10
11
3
4
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Fe
Target Standard Deviation 34 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.3
-0.6
-0.3
-0.1
0.0
0.1
0.4
0.5
1.8

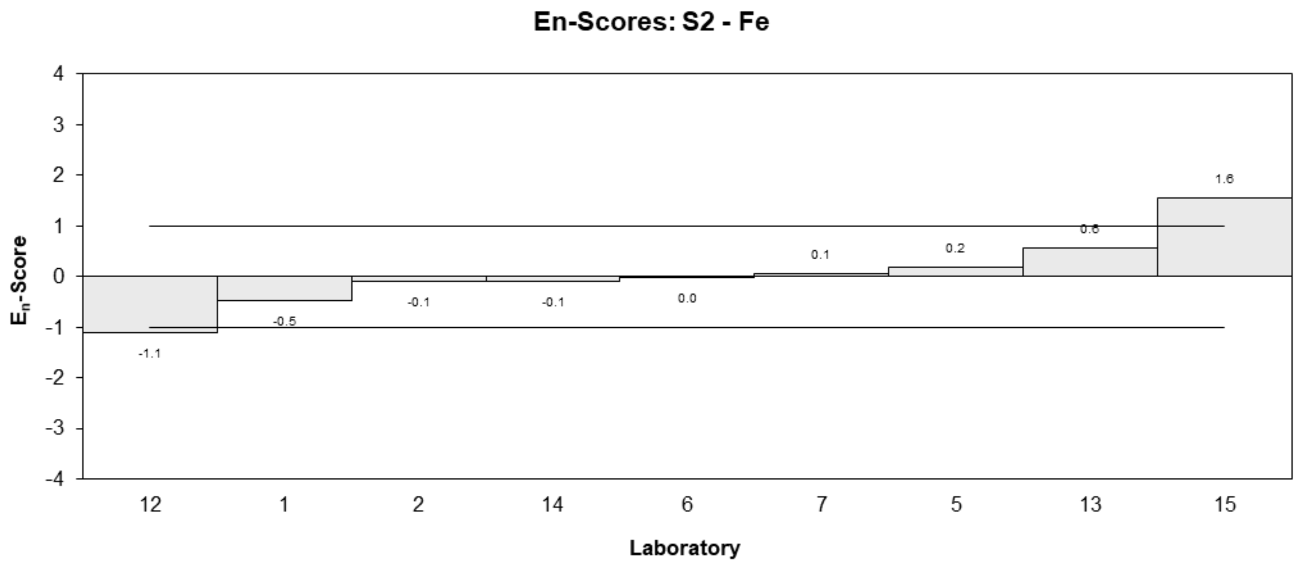

En-Scores: S2 - Fe
En-Score
Laboratory
-1.1
-0.5
-0.1
-0.1
0.0
0.1
0.2
0.6
1.6

Figure 34

Table 37

Sample Details

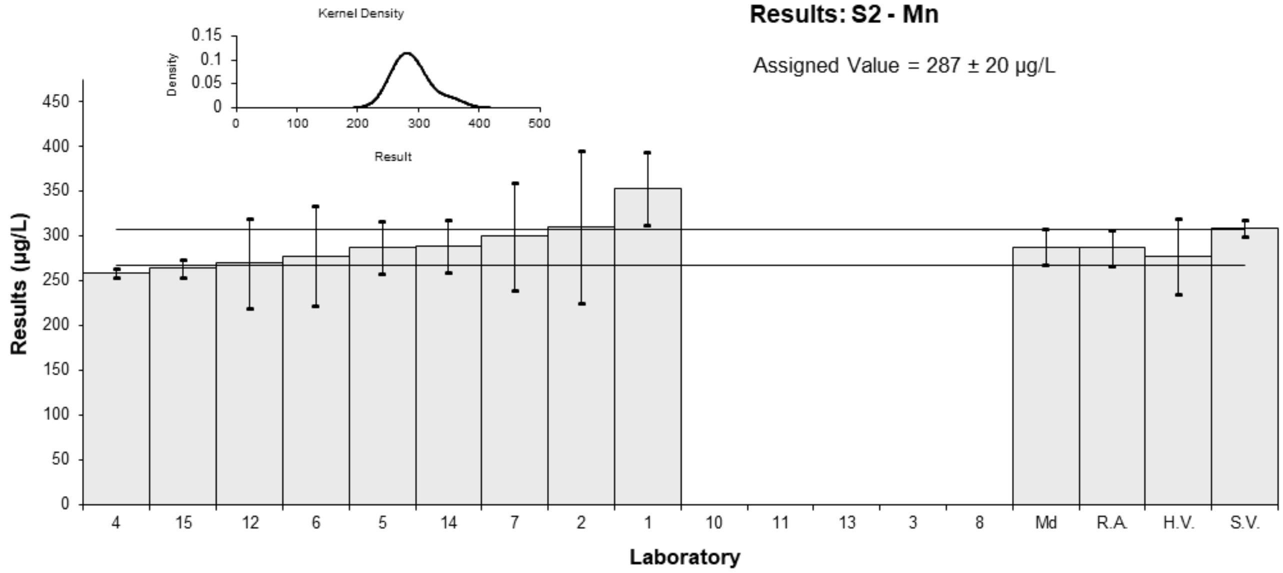
Sample No.	S2
Matrix.	Sea Water
Analyte.	Mn
Units	µg/L

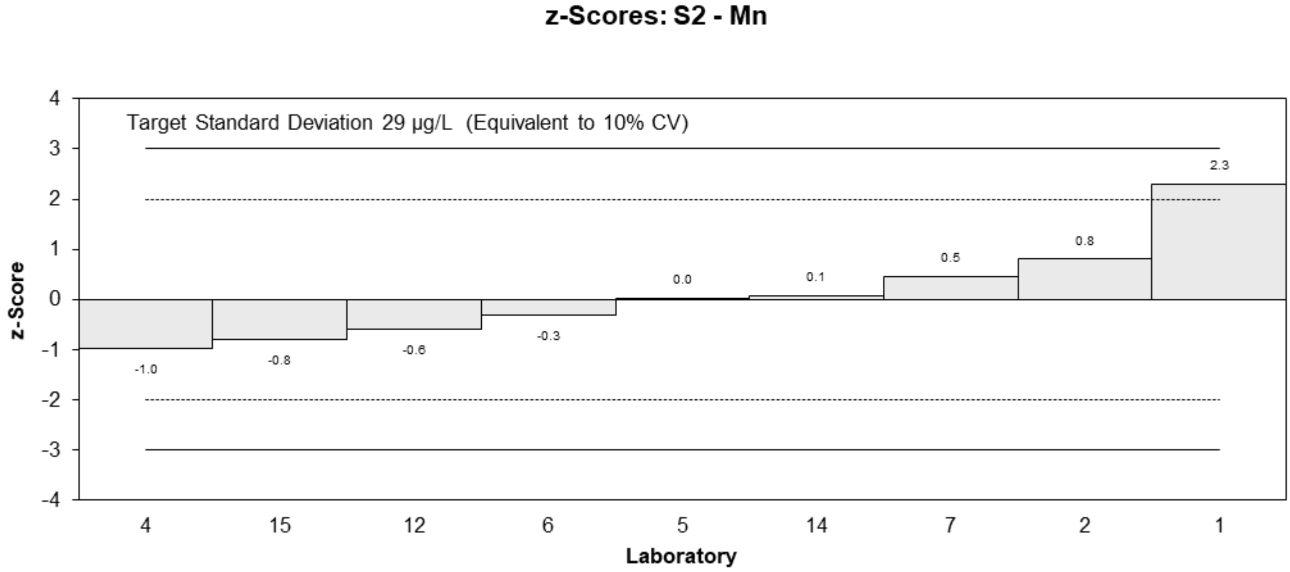
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	353	41	2.30	1.45
2	310	85	0.80	0.26
3	NT	NT		
4	259	5	-0.98	-1.36
5	287.5	28.75	0.02	0.01
6	278	56	-0.31	-0.15
7	300	60	0.45	0.21
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	270	50	-0.59	-0.32
13	NT	NT		
14	289	29	0.07	0.06
15	264	10	-0.80	-1.03

Statistics

Assigned Value	287	20
Spike	309	9
Homogeneity Value	278	42
Robust Average	287	20
Median	288	20
Mean	290	
N	9	
Max.	353	
Min.	259	
Robust SD	24	
Robust CV	8.4%	


Results: S2 - Mn
Assigned Value = 287 ± 20 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
4
15
12
6
5
14
7
2
1
10
11
13
3
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Mn
Target Standard Deviation 29 μg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.0
-0.8
-0.6
-0.3
0.0
0.1
0.5
0.8
2.3
4
15
12
6
5
14
7
2
1

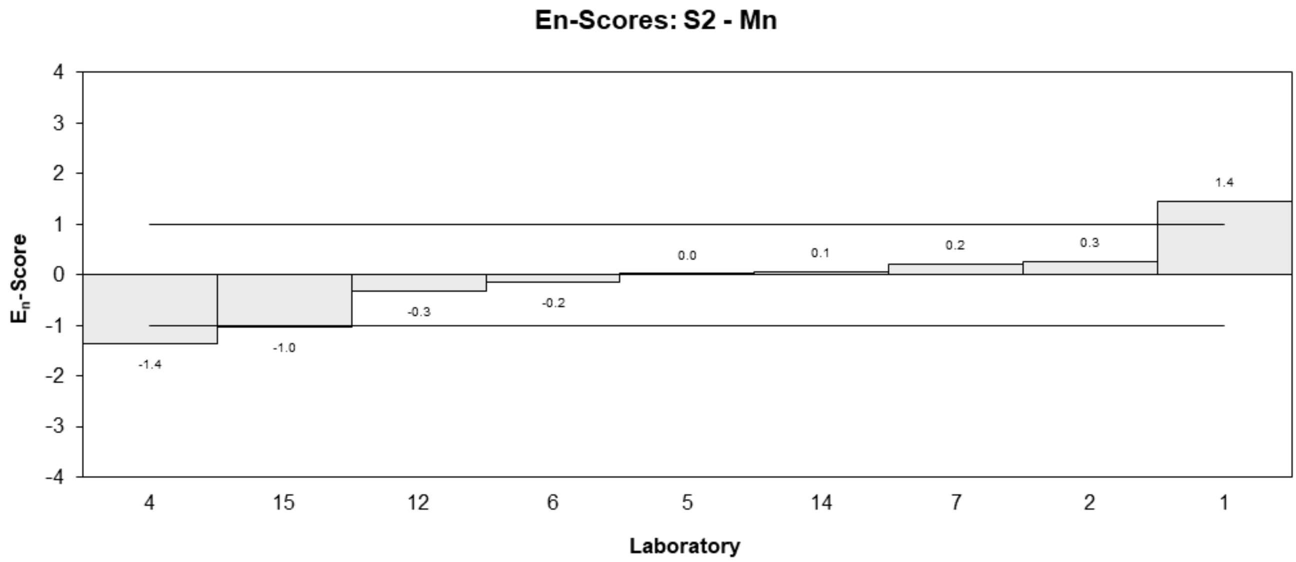

En-Scores: S2 - Mn
En-Score
Laboratory
-1.4
-1.0
-0.3
-0.2
0.0
0.1
0.2
0.3
1.4
4
15
12
6
5
14
7
2
1

Figure 35

Table 38

Sample Details

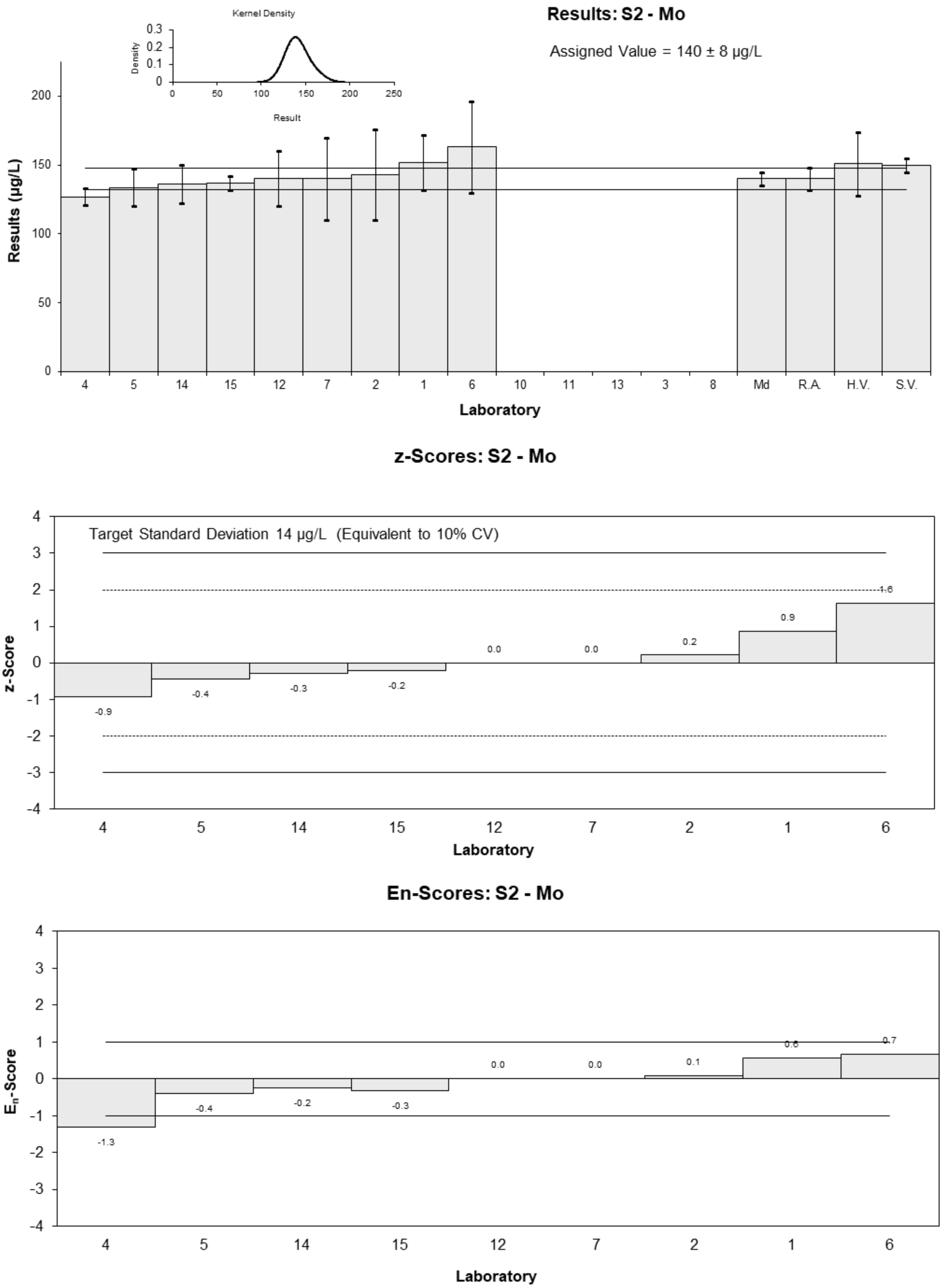
Sample No.	S2
Matrix.	Sea Water
Analyte.	Mo
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	152	20	0.86	0.56
2	143	33	0.21	0.09
3	NT	NT		
4	127	6	-0.93	-1.30
5	133.8	13.38	-0.44	-0.40
6	163	33	1.64	0.68
7	140	30	0.00	0.00
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	140	20	0.00	0.00
13	NT	NT		
14	136	14	-0.29	-0.25
15	137	5	-0.21	-0.32

Statistics

Assigned Value	140	8
Spike	150	5
Homogeneity Value	151	23
Robust Average	140	8
Median	140	5
Mean	141	
N	9	
Max.	163	
Min.	127	
Robust SD	10	
Robust CV	7.1%	



Results: S2 - Mo
Assigned Value = 140 ± 8 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
4 5 14 15 12 7 2 1 6 10 11 13 3 8 Md R.A. H.V. S.V.
z-Scores: S2 - Mo
Target Standard Deviation 14 µg/L (Equivalent to 10% CV)
z-Score
-0.9 -0.4 -0.3 -0.2 0.0 0.0 0.2 0.9 1.6
En-Scores: S2 - Mo
En-Score
-1.3 -0.4 -0.2 -0.3 0.0 0.0 0.1 0.6 0.7

Figure 36

Table 39

Sample Details

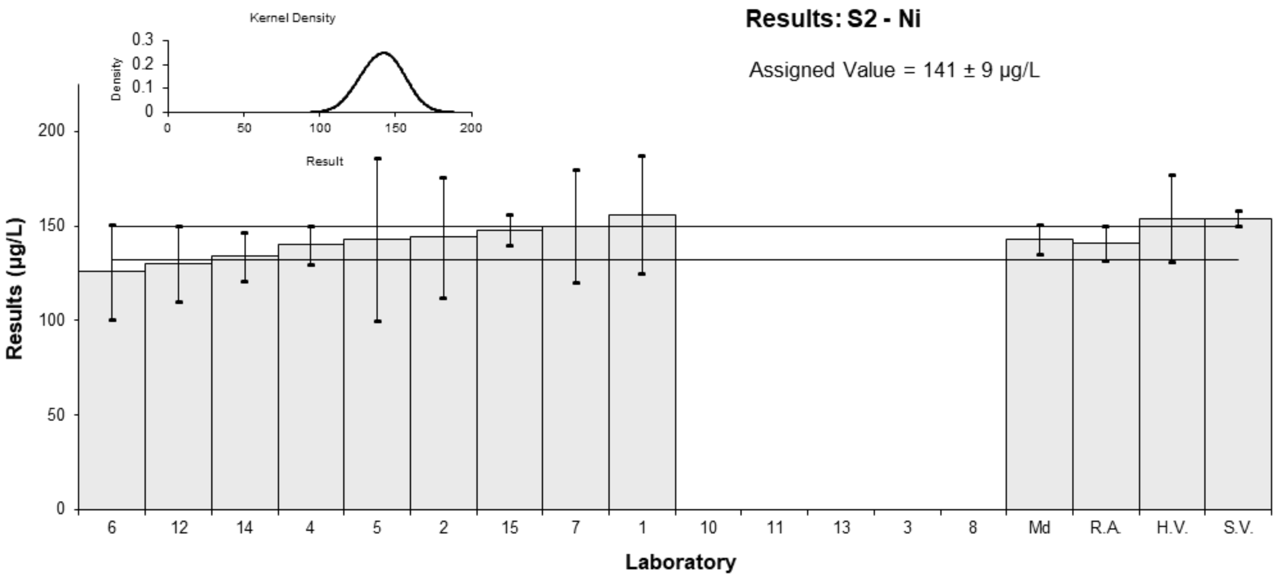
Sample No.	S2
Matrix.	Sea Water
Analyte.	Ni
Units	µg/L

Participant Results

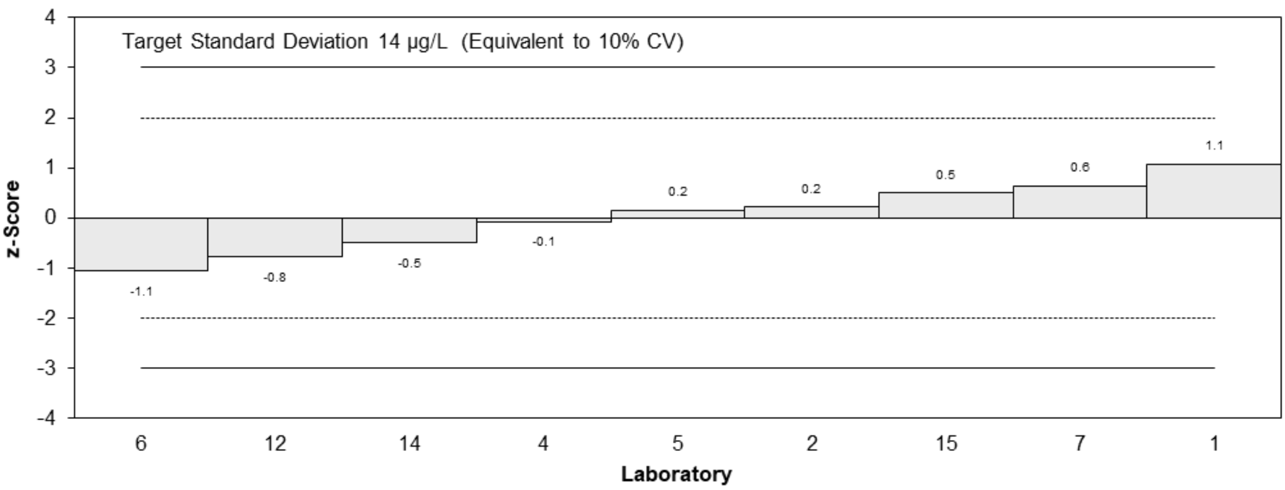
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	156	31	1.06	0.46
2	144	32	0.21	0.09
3	NT	NT		
4	140	10	-0.07	-0.07
5	143.2	42.96	0.16	0.05
6	126	25	-1.06	-0.56
7	150	30	0.64	0.29
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	130	20	-0.78	-0.50
13	NT	NT		
14	134	13	-0.50	-0.44
15	148	8	0.50	0.58

Statistics

Assigned Value	141	9
Spike	154	4
Homogeneity Value	154	23
Robust Average	141	9
Median	143	8
Mean	141	
N	9	
Max.	156	
Min.	126	
Robust SD	11	
Robust CV	7.8%	



z-Scores: S2 - Ni



En-Scores: S2 - Ni

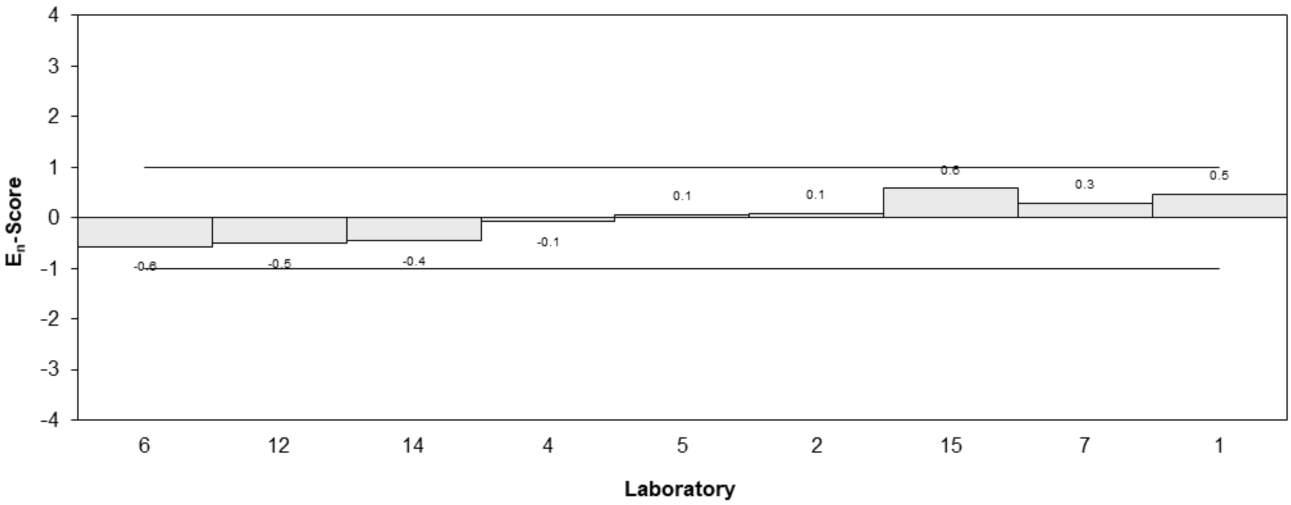


Figure 37

Table 40

Sample Details

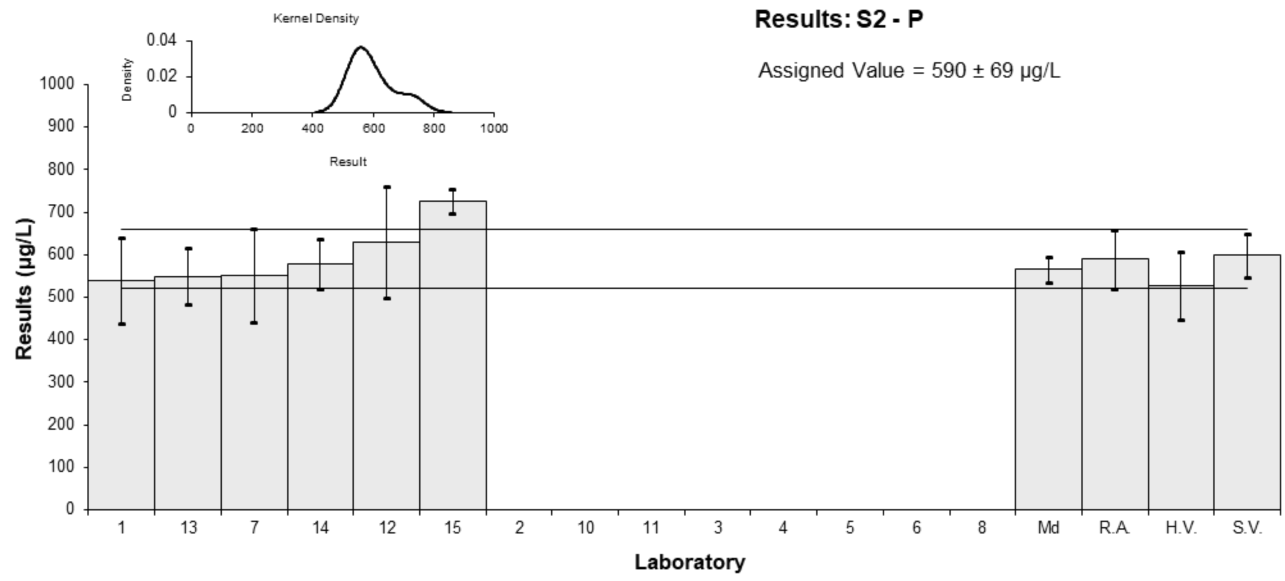
Sample No.	S2
Matrix.	Sea Water
Analyte.	P
Units	µg/L

Participant Results

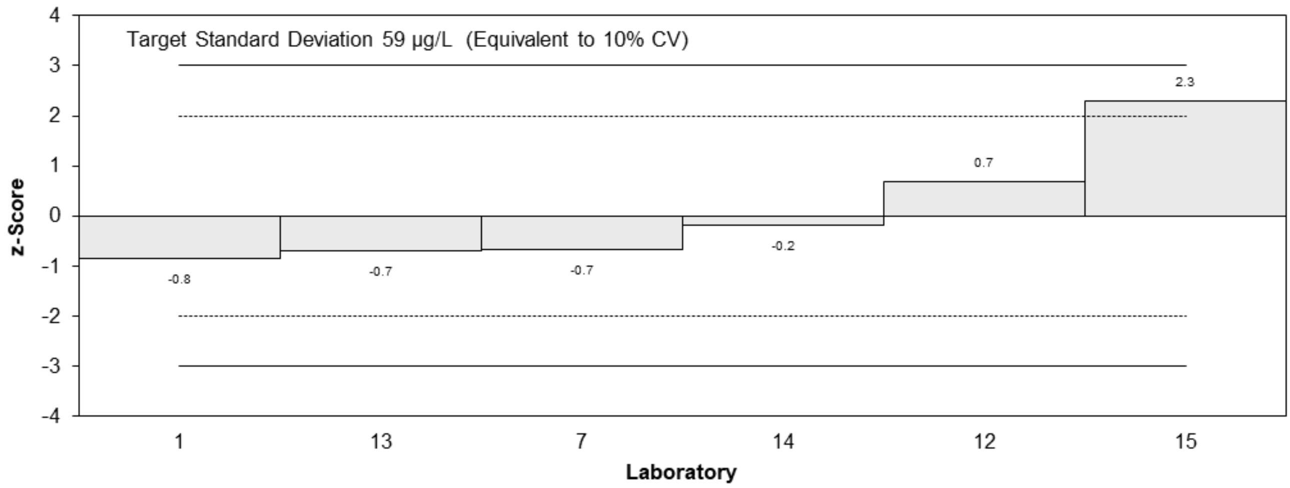
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	540	101	-0.85	-0.41
2	NR	NR		
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	550	110	-0.68	-0.31
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	630	130	0.68	0.27
13	549	66	-0.69	-0.43
14	579	58	-0.19	-0.12
15	725	29	2.29	1.80

Statistics

Assigned Value	590	69
Spike	598	50
Homogeneity Value	527	79
Robust Average	590	69
Median	565	31
Mean	596	
N	6	
Max.	725	
Min.	540	
Robust SD	67	
Robust CV	11%	



z-Scores: S2 - P



En-Scores: S2 - P

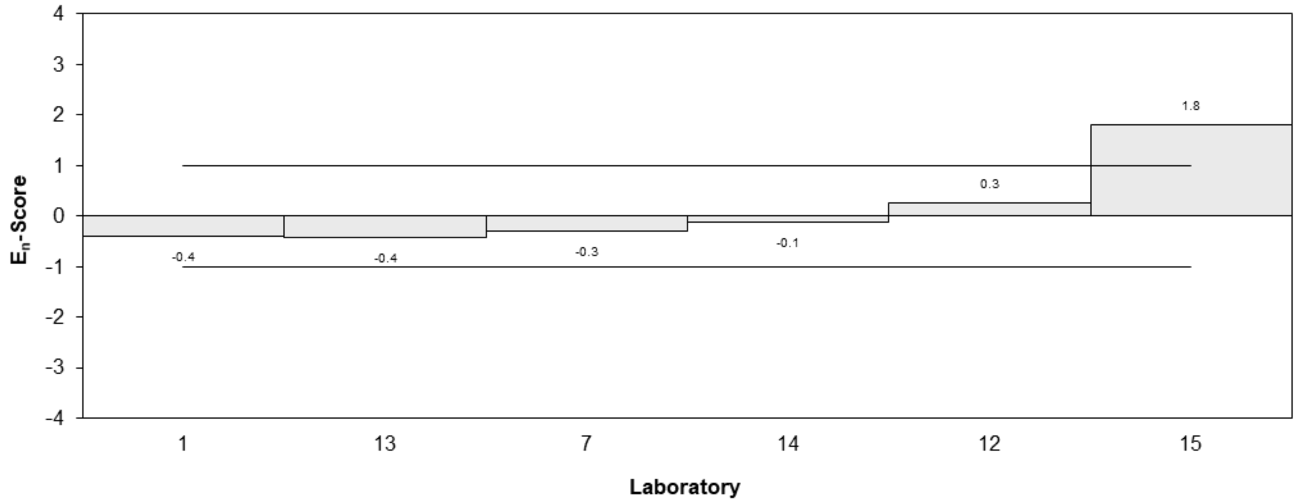


Figure 38

Table 41

Sample Details

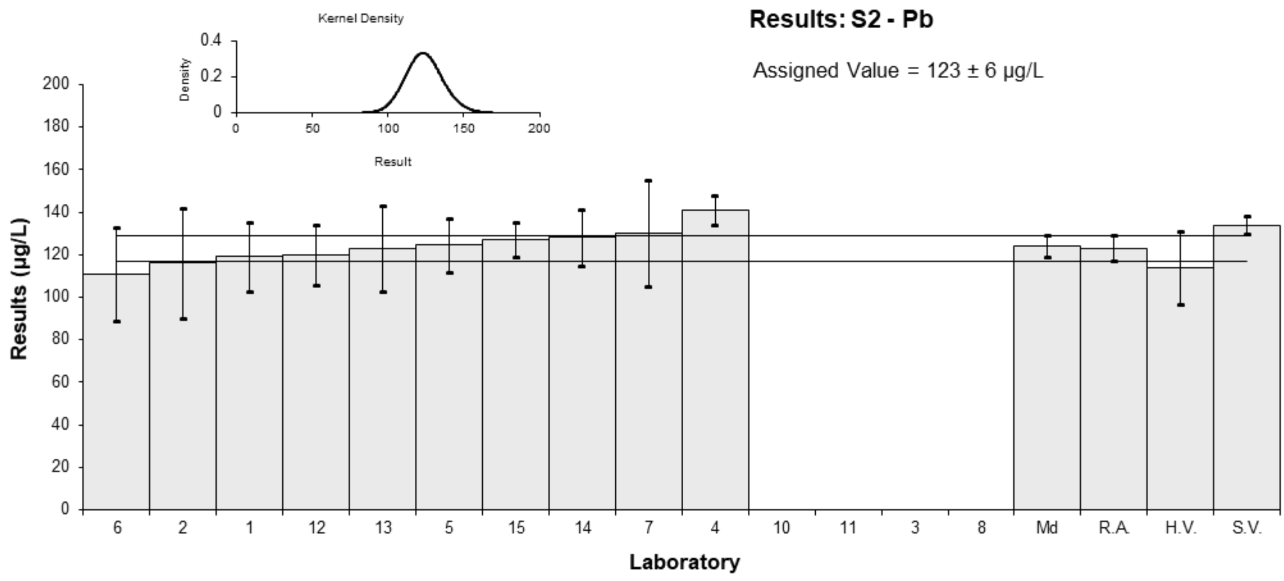
Sample No.	S2
Matrix.	Sea Water
Analyte.	Pb
Units	µg/L

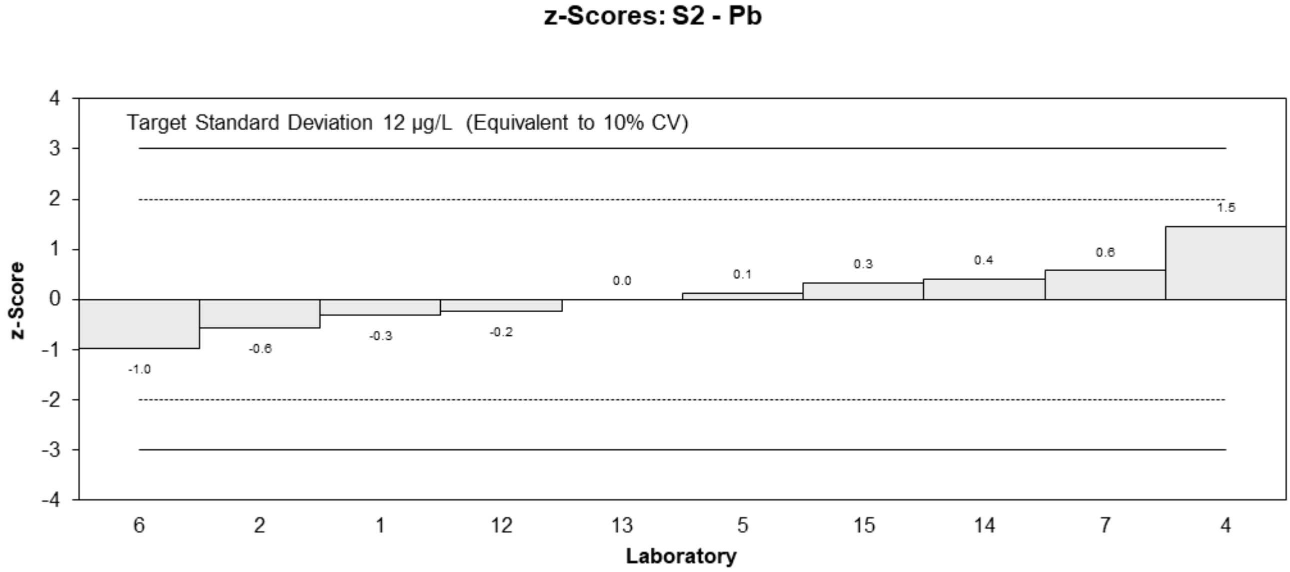
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	119	16	-0.33	-0.23
2	116	26	-0.57	-0.26
3	NT	NT		
4	141	7	1.46	1.95
5	124.4	12.44	0.11	0.10
6	111	22	-0.98	-0.53
7	130	25	0.57	0.27
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	120	14	-0.24	-0.20
13	123	20	0.00	0.00
14	128	13	0.41	0.35
15	127	8	0.33	0.40

Statistics

Assigned Value	123	6
Spike	134	4
Homogeneity Value	114	17
Robust Average	123	6
Median	124	5
Mean	124	
N	10	
Max.	141	
Min.	111	
Robust SD	8.1	
Robust CV	6.6%	


Results: S2 - Pb
Assigned Value = 123 ± 6 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
6
2
1
12
13
5
15
14
7
4
10
11
3
8
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Pb
Target Standard Deviation 12 μg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.0
-0.6
-0.3
-0.2
0.0
0.1
0.3
0.4
0.6
1.5

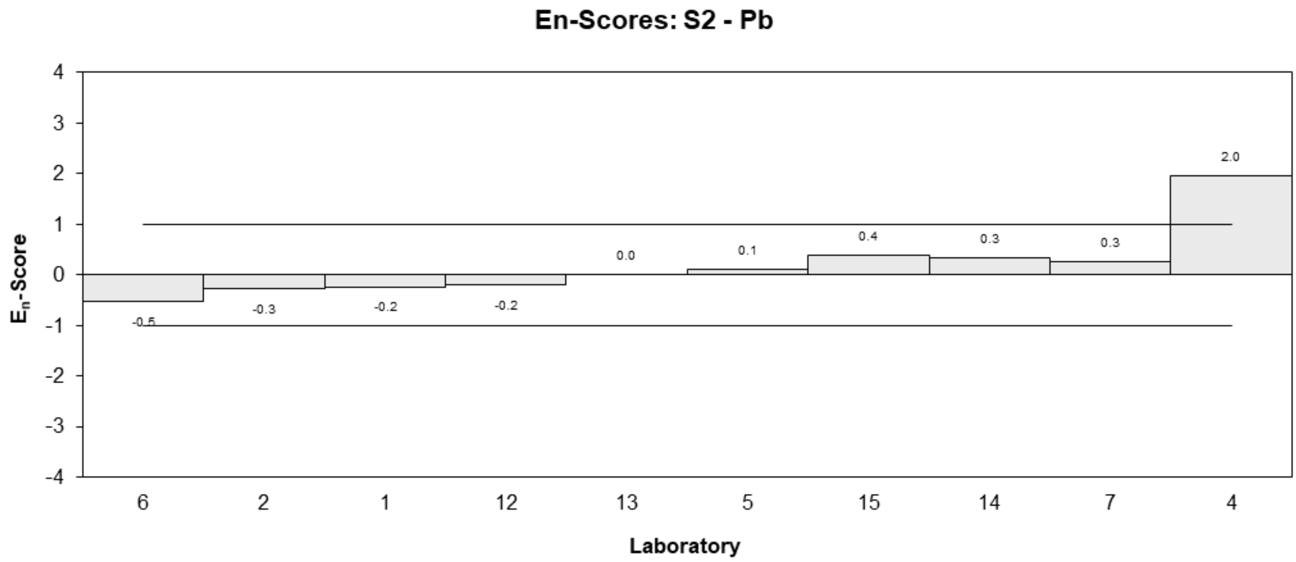

En-Scores: S2 - Pb
En-Score
Laboratory
-0.5
-0.3
-0.2
-0.2
0.0
0.1
0.4
0.3
0.3
2.0

Figure 39

Table 42

Sample Details

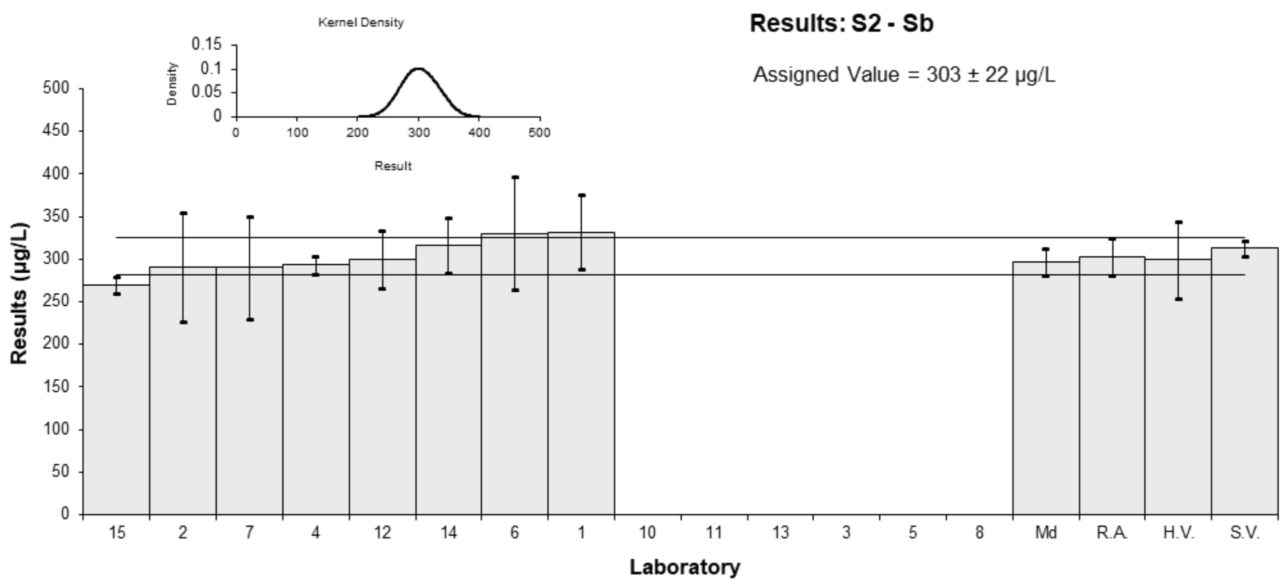
Sample No.	S2
Matrix.	Sea Water
Analyte.	Sb
Units	µg/L

Participant Results

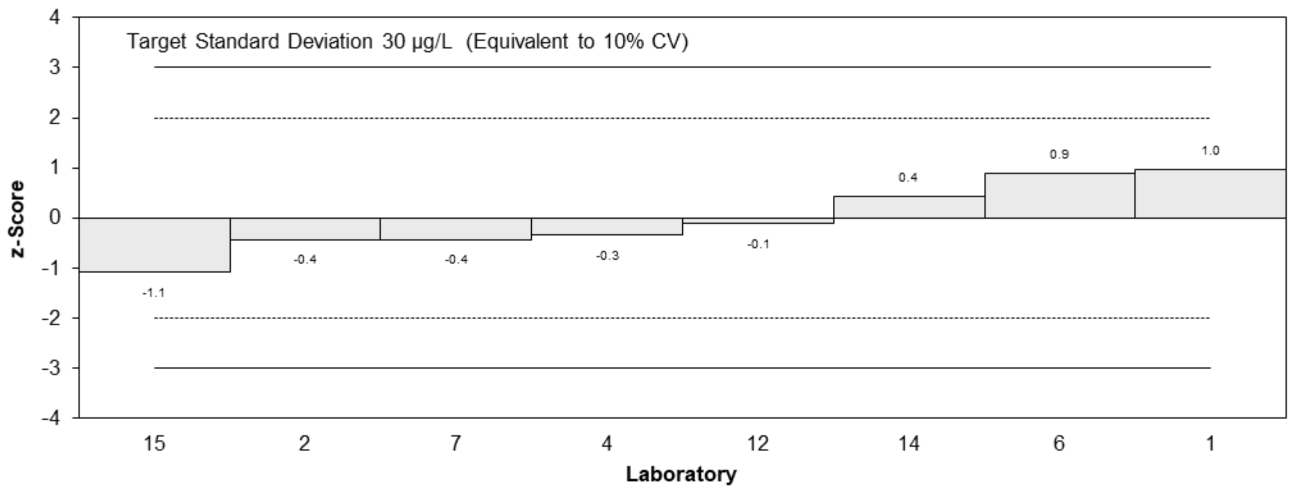
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	332	43	0.96	0.60
2	290	64	-0.43	-0.19
3	NT	NT		
4	293	11	-0.33	-0.41
5	NT	NT		
6	330	66	0.89	0.39
7	290	60	-0.43	-0.20
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	300	34	-0.10	-0.07
13	NT	NT		
14	316	32	0.43	0.33
15	270	10	-1.09	-1.37

Statistics

Assigned Value	303	22
Spike	313	9
Homogeneity Value	299	45
Robust Average	303	22
Median	297	16
Mean	303	
N	8	
Max.	332	
Min.	270	
Robust SD	25	
Robust CV	8.3%	



z-Scores: S2 - Sb



En-Scores: S2 - Sb

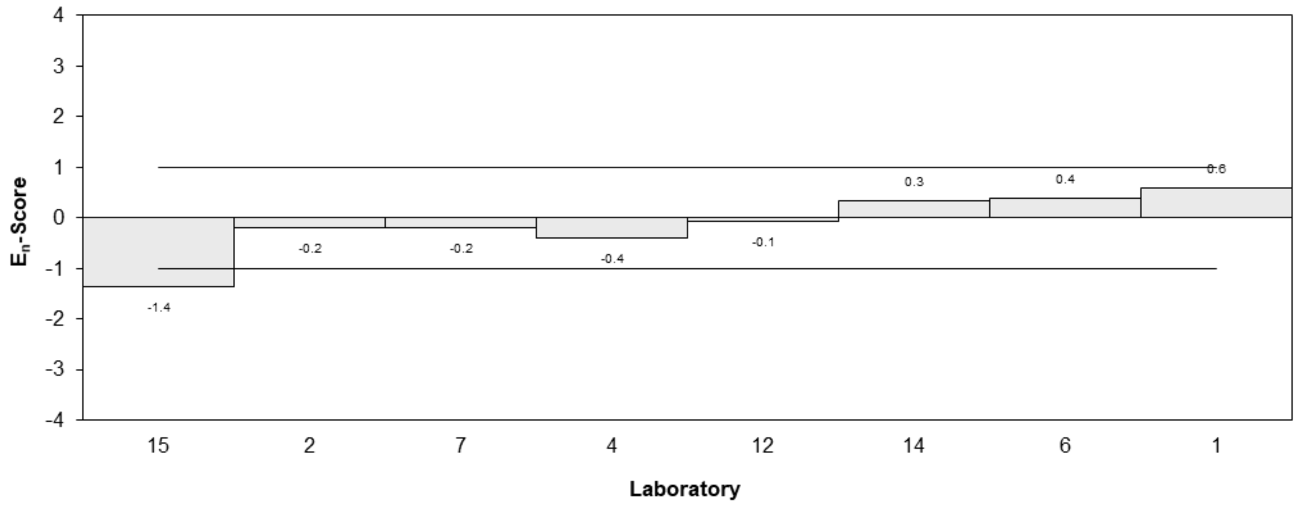


Figure 40

Table 43

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	Se
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	137	15	-0.35	-0.29
2	145	36	0.21	0.08
3	NT	NT		
4	143	6	0.07	0.10
5	138.0	13.8	-0.28	-0.25
6	137	27	-0.35	-0.18
7	140	30	-0.14	-0.06
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	140	20	-0.14	-0.09
13	154	10	0.85	0.94
14	165	17	1.62	1.22
15	115	23	-1.90	-1.11

Statistics

Assigned Value	142	8
Spike	153	4
Homogeneity Value	146	22
Robust Average	142	8
Median	140	3
Mean	141	
N	10	
Max.	165	
Min.	115	
Robust SD	9.5	
Robust CV	6.7%	

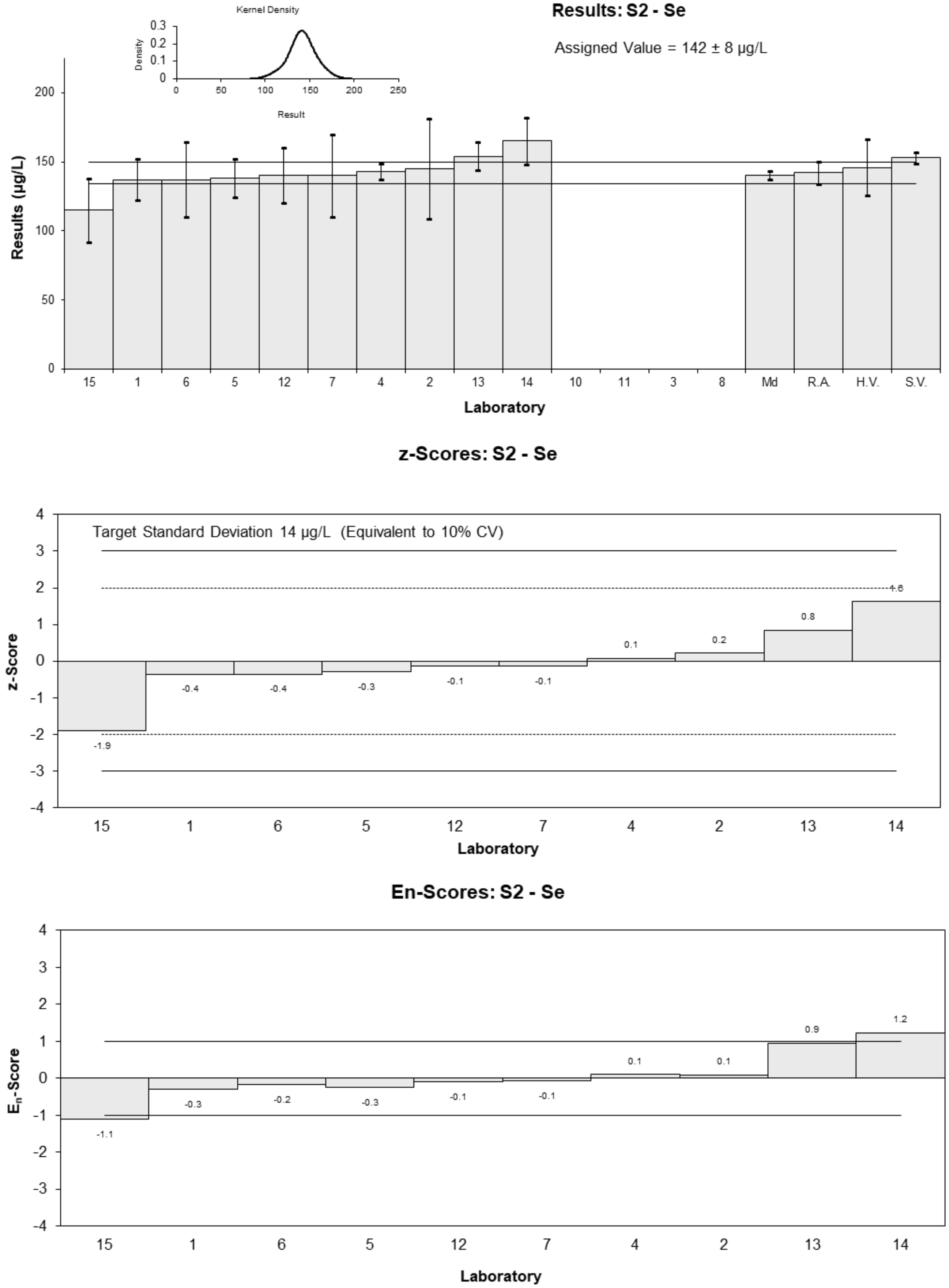

Results: S2 - Se
Assigned Value = 142 ± 8 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
15
1
6
5
12
7
4
2
13
14
10
11
3
8
Md
R.A.
H.V.
S.V.
z-Scores: S2 - Se
Target Standard Deviation 14 µg/L (Equivalent to 10% CV)
z-Score
-1.9
-0.4
-0.4
-0.3
-0.1
-0.1
0.1
0.2
0.8
1.6
En-Scores: S2 - Se
En-Score
-1.1
-0.3
-0.2
-0.3
-0.1
-0.1
0.1
0.1
0.9
1.2

Figure 41

Table 44

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	124	16	0.78	0.50
2	126	30	0.96	0.35
3	NT	NT		
4	110	11	-0.43	-0.37
5	104.1	10.41	-0.95	-0.83
6	NT	NT		
7	120	25	0.43	0.19
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	110	15	-0.43	-0.29
13	111	7	-0.35	-0.38
14	122	12	0.61	0.49
15	105	4	-0.87	-1.12

Statistics

Assigned Value	115	8
Spike	121	3
Homogeneity Value	99	15
Robust Average	115	8
Median	111	8
Mean	115	
N	9	
Max.	126	
Min.	104.1	
Robust SD	9.5	
Robust CV	8.3%	

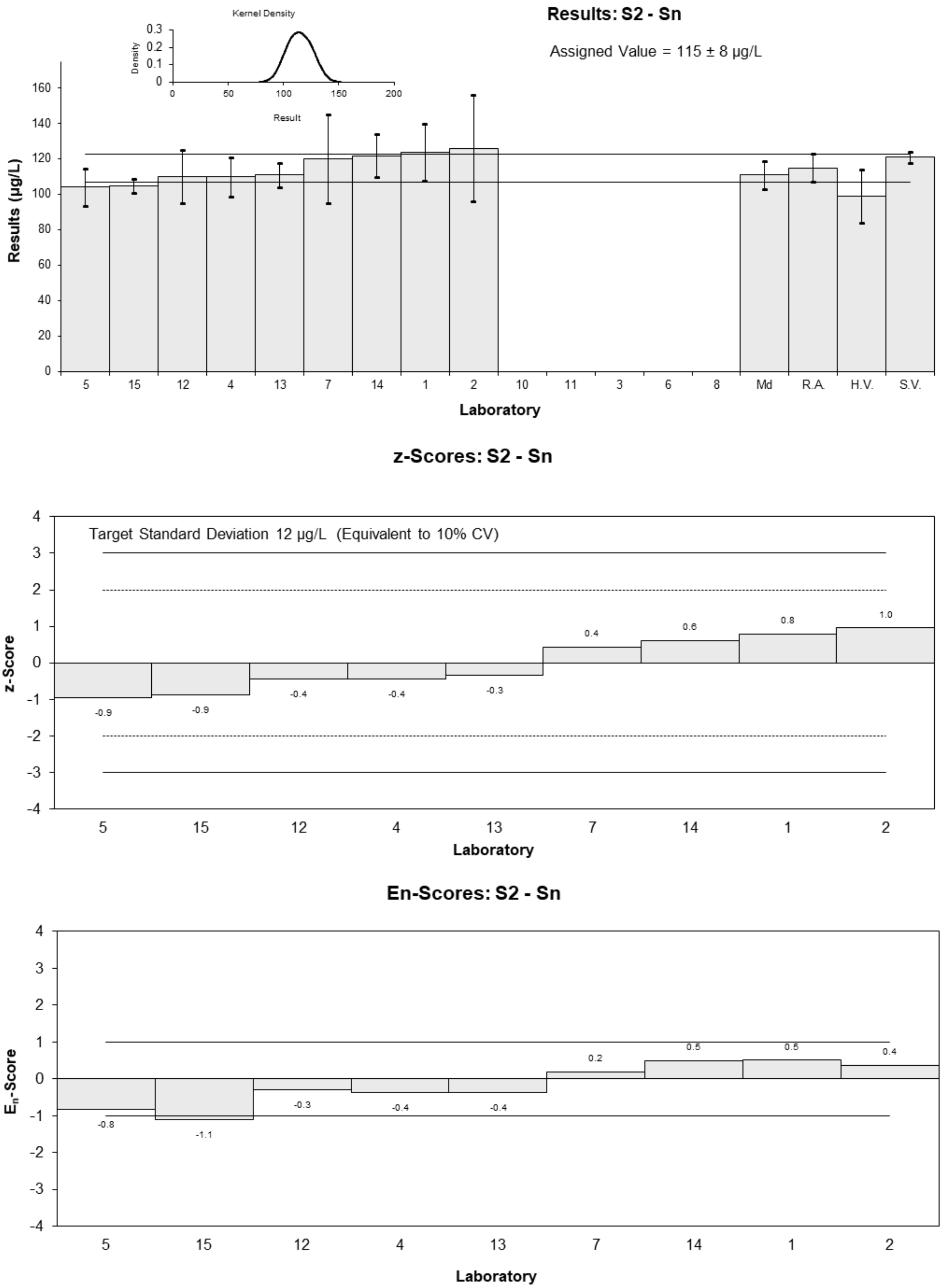

Results: S2 - Sn
Assigned Value = 115 ± 8 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
5
15
12
4
13
7
14
1
2
10
11
3
6
8
Md
R.A.
H.V.
S.V.
z-Scores: S2 - Sn
Target Standard Deviation 12 µg/L (Equivalent to 10% CV)
z-Score
-0.9
-0.9
-0.4
-0.4
-0.3
0.4
0.6
0.8
1.0
En-Scores: S2 - Sn
En-Score
-0.8
-1.1
-0.3
-0.4
-0.4
0.2
0.5
0.5
0.4

Figure 42

Table 45

Sample Details

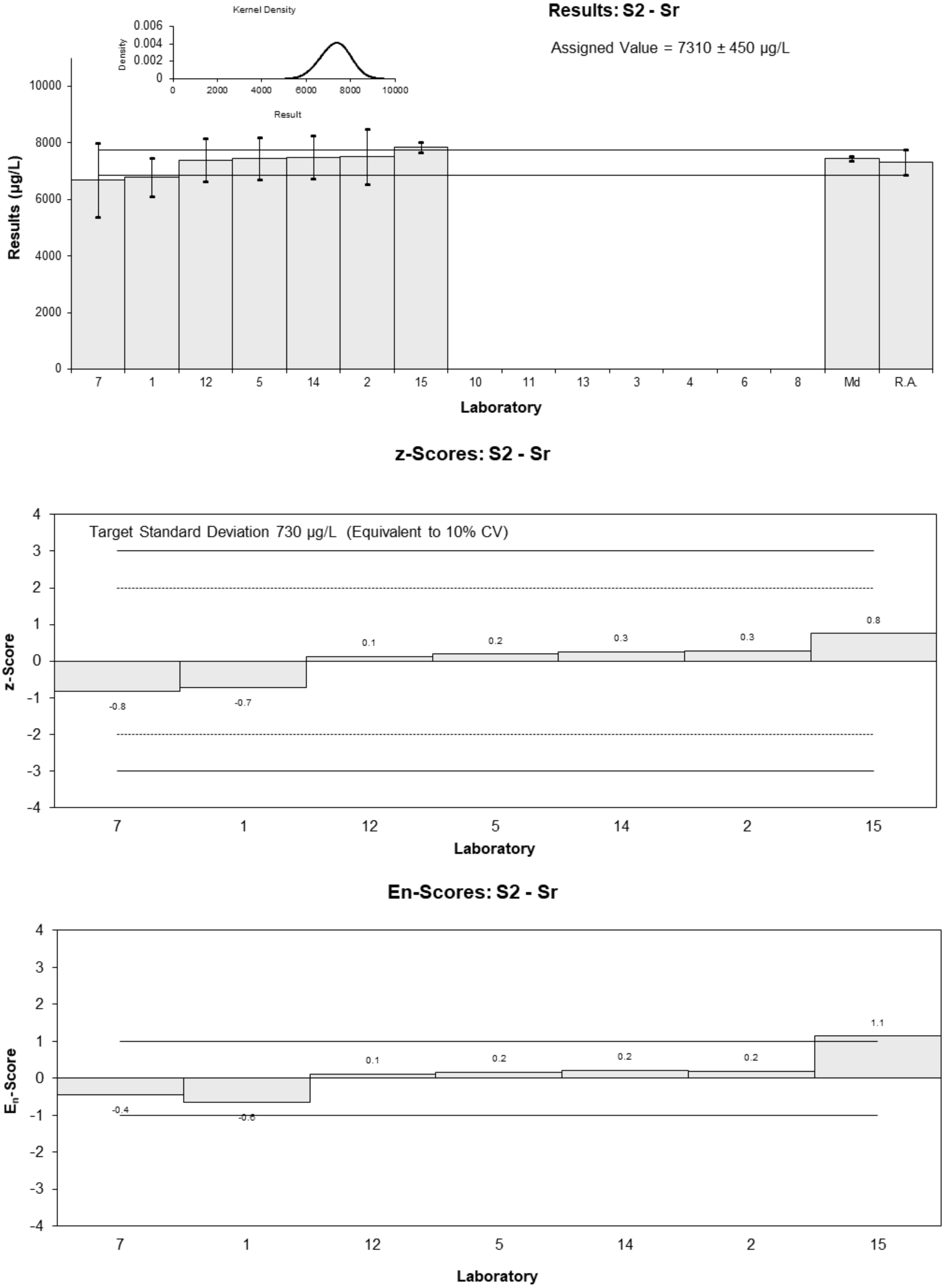
Sample No.	S2
Matrix.	Sea Water
Analyte.	Sr
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	6788	679	-0.71	-0.64
2	7510	970	0.27	0.19
3	NT	NT		
4	NT	NT		
5	7446	744	0.19	0.16
6	NT	NT		
7	6700	1300	-0.83	-0.44
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	7400	770	0.12	0.10
13	NT	NT		
14	7500	750	0.26	0.22
15	7860	180	0.75	1.13

Statistics

Assigned Value	7310	450
Spike	Not Spiked	
Robust Average	7310	450
Median	7450	90
Mean	7310	
N	7	
Max.	7860	
Min.	6700	
Robust SD	470	
Robust CV	6.4%	



Results: S2 - Sr
Assigned Value = 7310 ± 450 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
7
1
12
5
14
2
15
10
11
13
3
4
6
8
Md
R.A.
z-Scores: S2 - Sr
Target Standard Deviation 730 µg/L (Equivalent to 10% CV)
z-Score
-0.8
-0.7
0.1
0.2
0.3
0.3
0.8
Laboratory
En-Scores: S2 - Sr
E_n-Score
-0.4
-0.6
0.1
0.2
0.2
0.2
1.1
Laboratory

Figure 43

Table 46

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	Tl
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	75	4	-2.72	-1.70
2	110	26	0.68	0.23
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	85.9	17	-1.66	-0.73
7	110	20	0.68	0.27
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	110	15	0.68	0.32
13	NT	NT		
14	114	11	1.07	0.57
15	116	4	1.26	0.79

Statistics

Assigned Value	103	16
Spike	121	3
Homogeneity Value	106	16
Robust Average	103	16
Median	110	5
Mean	103	
N	7	
Max.	116	
Min.	75	
Robust SD	17	
Robust CV	17%	

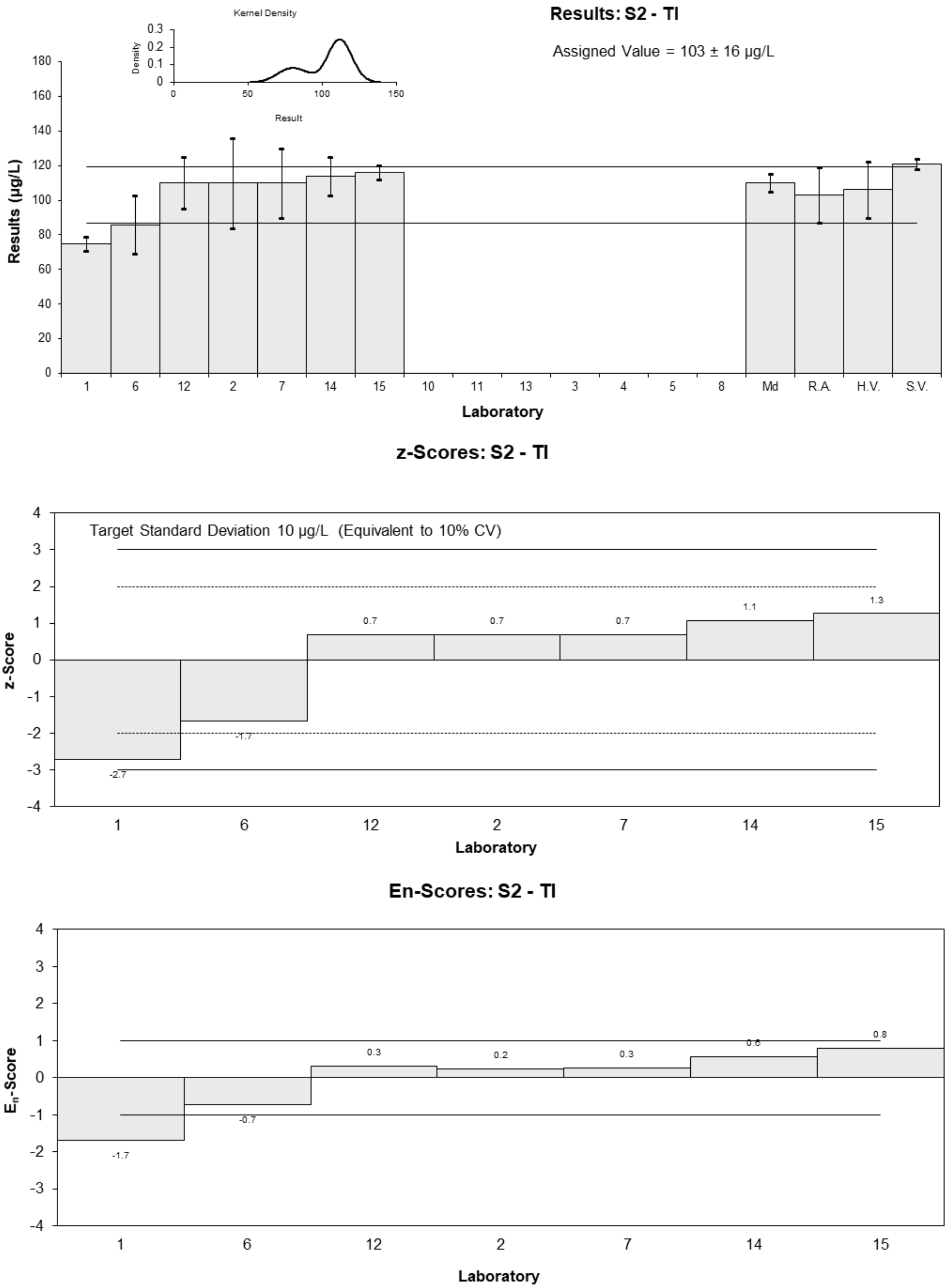

Results: S2 - Tl
Assigned Value = 103 ± 16 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
1 6 12 2 7 14 15 10 11 13 3 4 5 8 Md R.A. H.V. S.V.
z-Scores: S2 - Tl
Target Standard Deviation 10 µg/L (Equivalent to 10% CV)
-2.7 -1.7 0.7 0.7 0.7 1.1 1.3
z-Score
Laboratory
1 6 12 2 7 14 15
En-Scores: S2 - Tl
-1.7 -0.7 0.3 0.2 0.3 0.6 0.8
E_n-Score
Laboratory
1 6 12 2 7 14 15

Figure 44

Table 47

Sample Details

Sample No.	S2
Matrix.	Sea Water
Analyte.	U
Units	µg/L

Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	130	7	0.00	0.00
2	NR	NR		
3	NT	NT		
4	136	14	0.46	0.37
5	122.4	12.24	-0.58	-0.52
6	127	25	-0.23	-0.11
7	120	25	-0.77	-0.38
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	139	14	0.69	0.56
15	138	5	0.62	0.85

Statistics

Assigned Value	130	8
Spike	138	4
Homogeneity Value	124	19
Robust Average	130	8
Median	130	10
Mean	130	
N	7	
Max.	139	
Min.	120	
Robust SD	8.6	
Robust CV	6.6%	

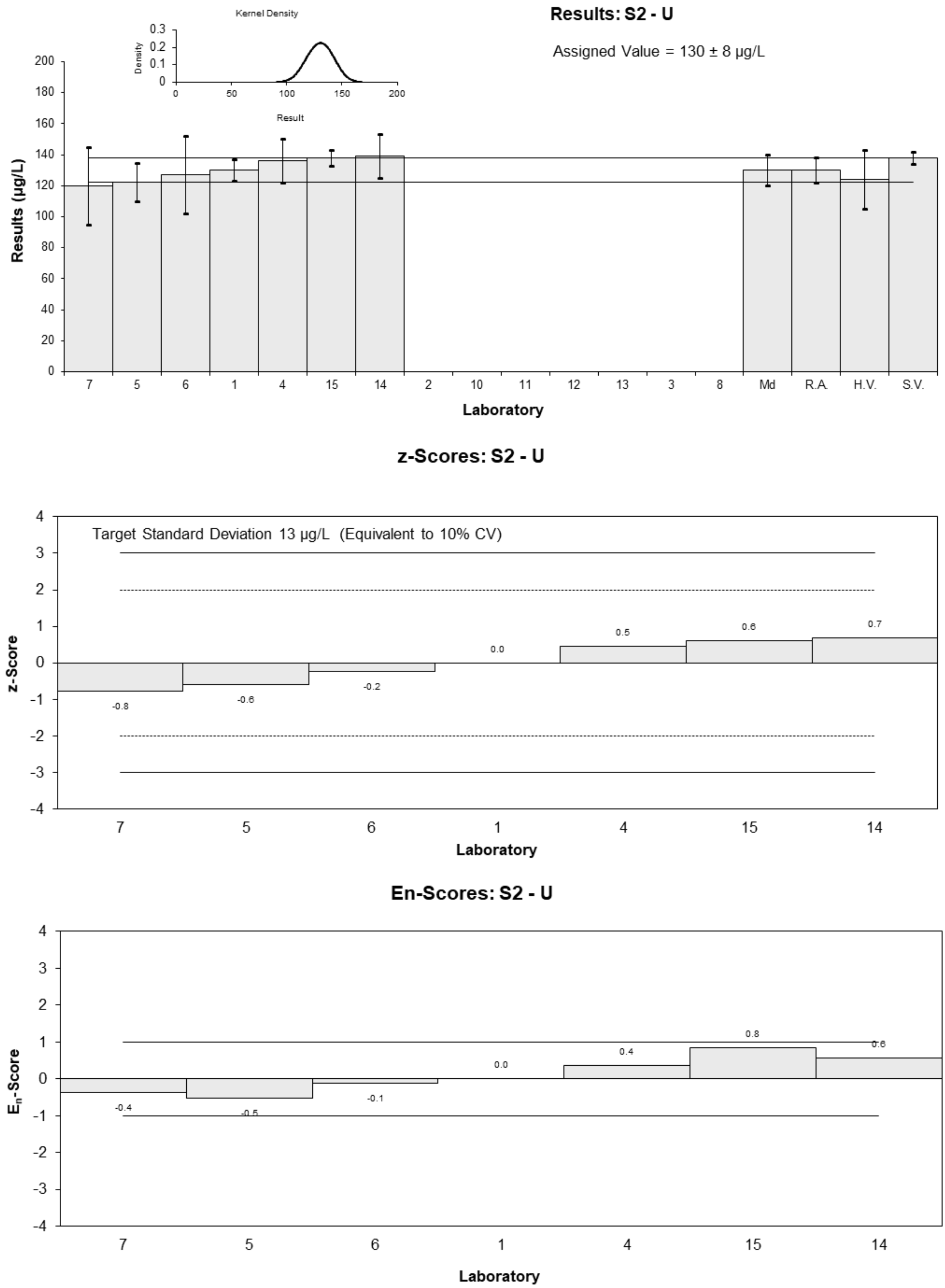

Results: S2 - U
Assigned Value = 130 ± 8 µg/L
Kernel Density
Density
Result
Results (µg/L)
7 5 6 1 4 15 14 2 10 11 12 13 3 8 Md R.A. H.V. S.V.
Laboratory
z-Scores: S2 - U
Target Standard Deviation 13 µg/L (Equivalent to 10% CV)
z-Score
-0.8 -0.6 -0.2 0.0 0.5 0.6 0.7
7 5 6 1 4 15 14
Laboratory
En-Scores: S2 - U
E_n-Score
-0.4 -0.5 -0.1 0.0 0.4 0.8 0.6
7 5 6 1 4 15 14
Laboratory

Figure 45

Table 48

Sample Details

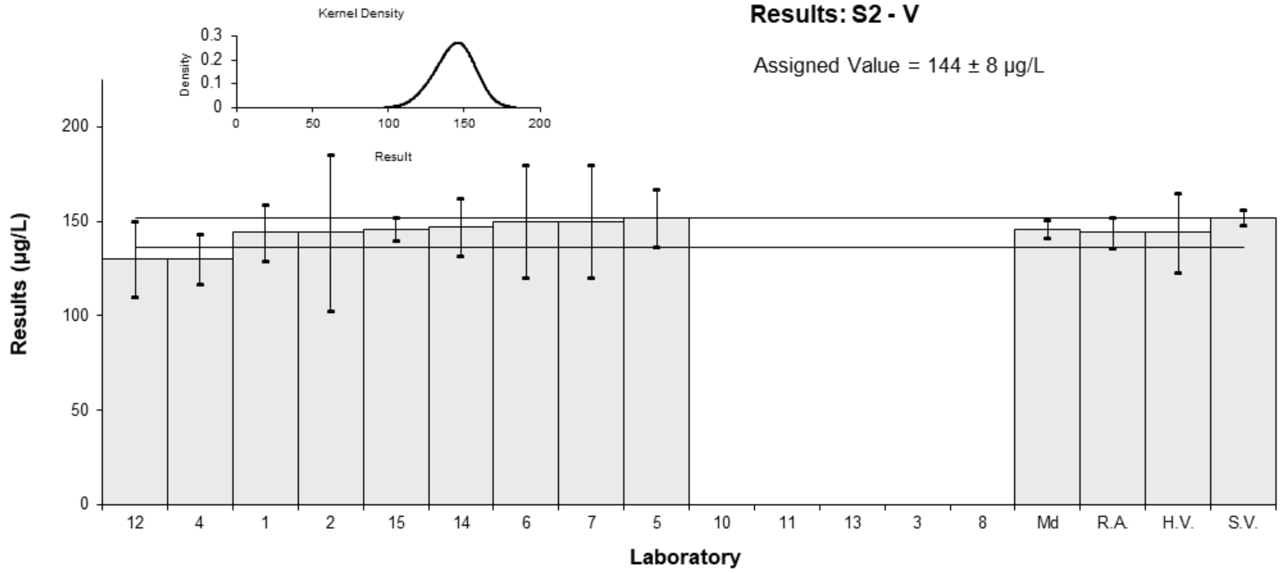
Sample No.	S2
Matrix.	Sea Water
Analyte.	V
Units	µg/L

Participant Results

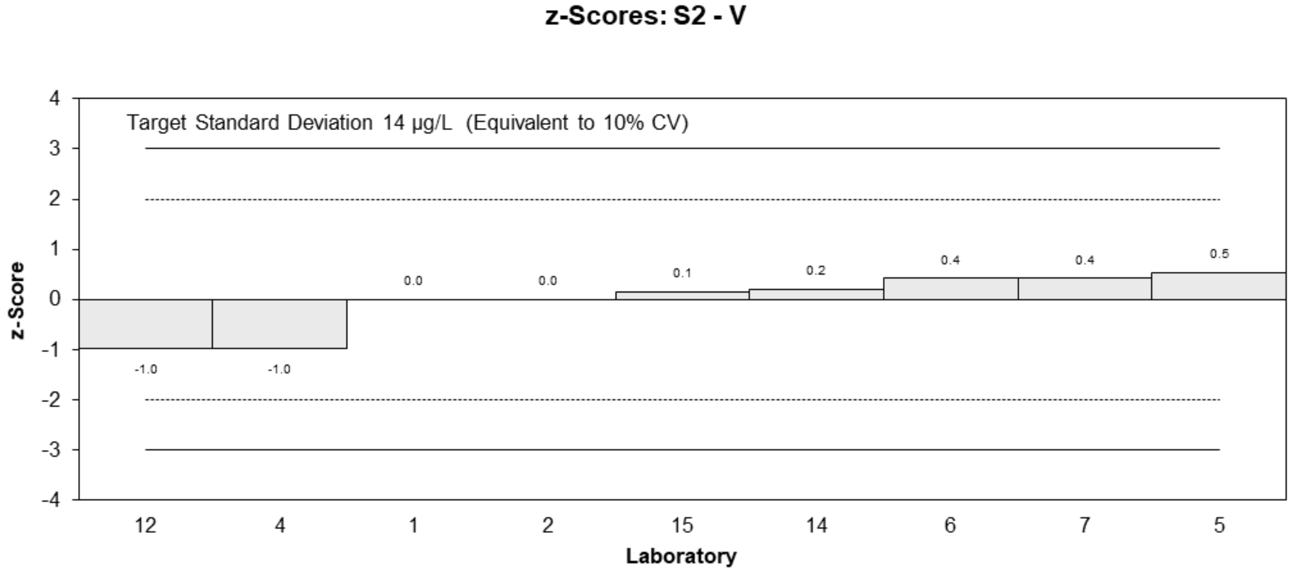
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	144	15	0.00	0.00
2	144	41	0.00	0.00
3	NT	NT		
4	130	13	-0.97	-0.92
5	151.7	15.17	0.53	0.45
6	150	30	0.42	0.19
7	150	30	0.42	0.19
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	130	20	-0.97	-0.65
13	NT	NT		
14	147	15	0.21	0.18
15	146	6	0.14	0.20

Statistics

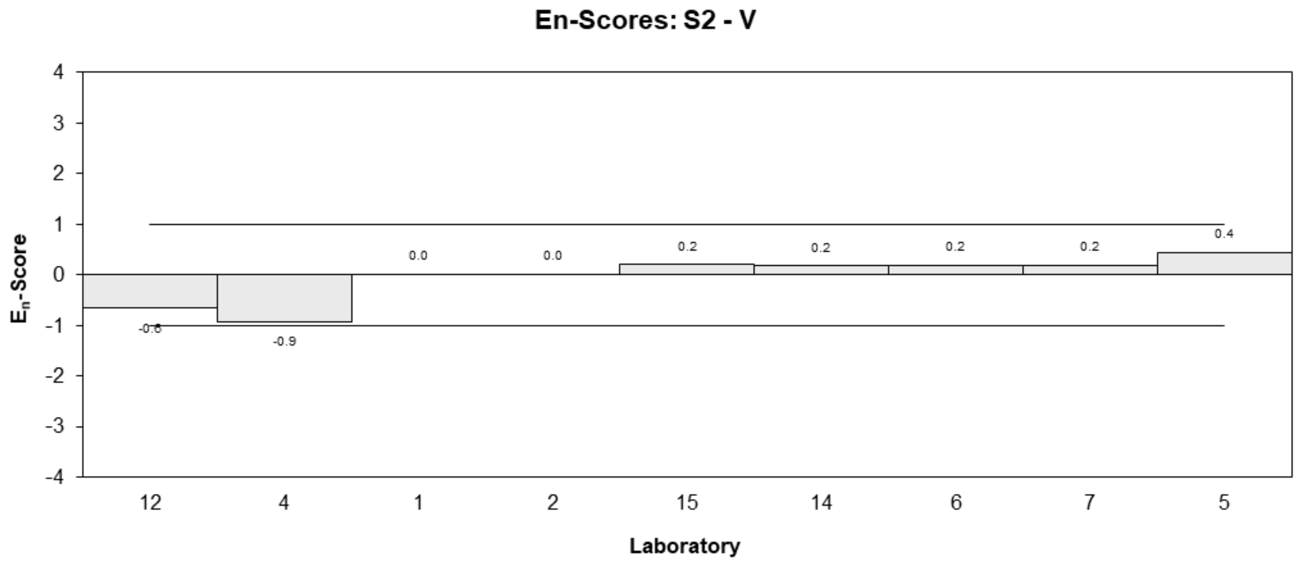
Assigned Value	144	8
Spike	152	4
Homogeneity Value	144	21
Robust Average	144	8
Median	146	5
Mean	144	
N	9	
Max.	151.7	
Min.	130	
Robust SD	9.3	
Robust CV	6.5%	



Results: S2 - V
Assigned Value = 144 ± 8 μg/L
Kernel Density
Density
Result
Results (μg/L)
Laboratory
12
4
1
2
15
14
6
7
5
10
11
13
3
8
Md
R.A.
H.V.
S.V.



z-Scores: S2 - V
Target Standard Deviation 14 μg/L (Equivalent to 10% CV)
z-Score
-1.0
-1.0
0.0
0.0
0.1
0.2
0.4
0.4
0.5
12
4
1
2
15
14
6
7
5
Laboratory



En-Scores: S2 - V
E_n-Score
-0.6
-0.9
0.0
0.0
0.2
0.2
0.2
0.2
0.4
12
4
1
2
15
14
6
7
5
Laboratory

Figure 46

Table 49

Sample Details

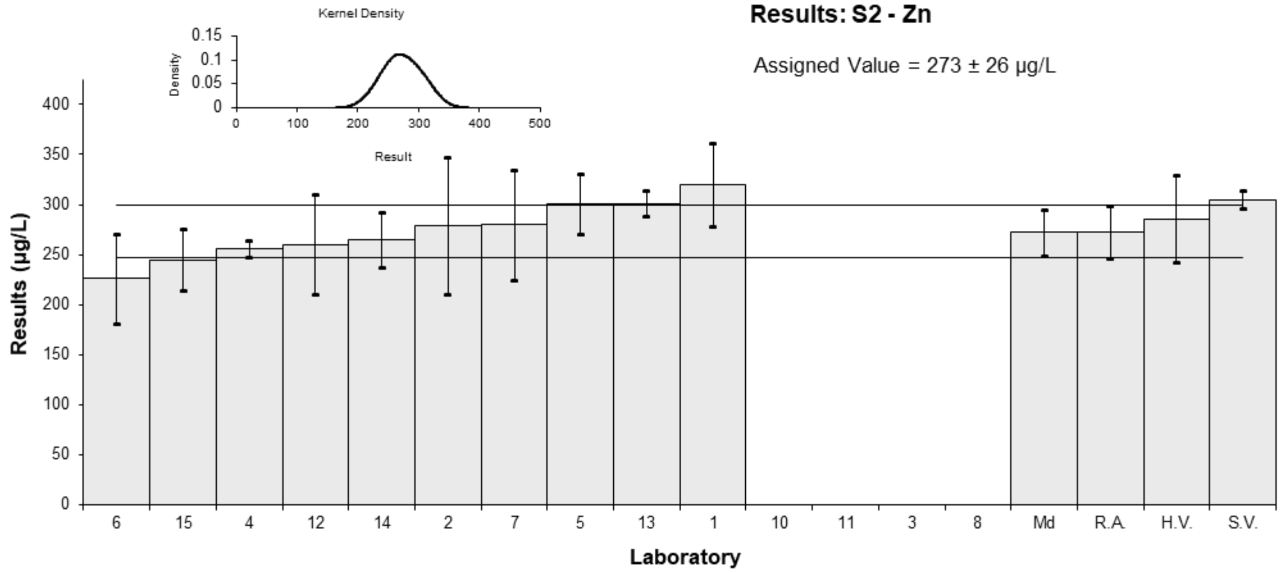
Sample No.	S2
Matrix.	Sea Water
Analyte.	Zn
Units	µg/L

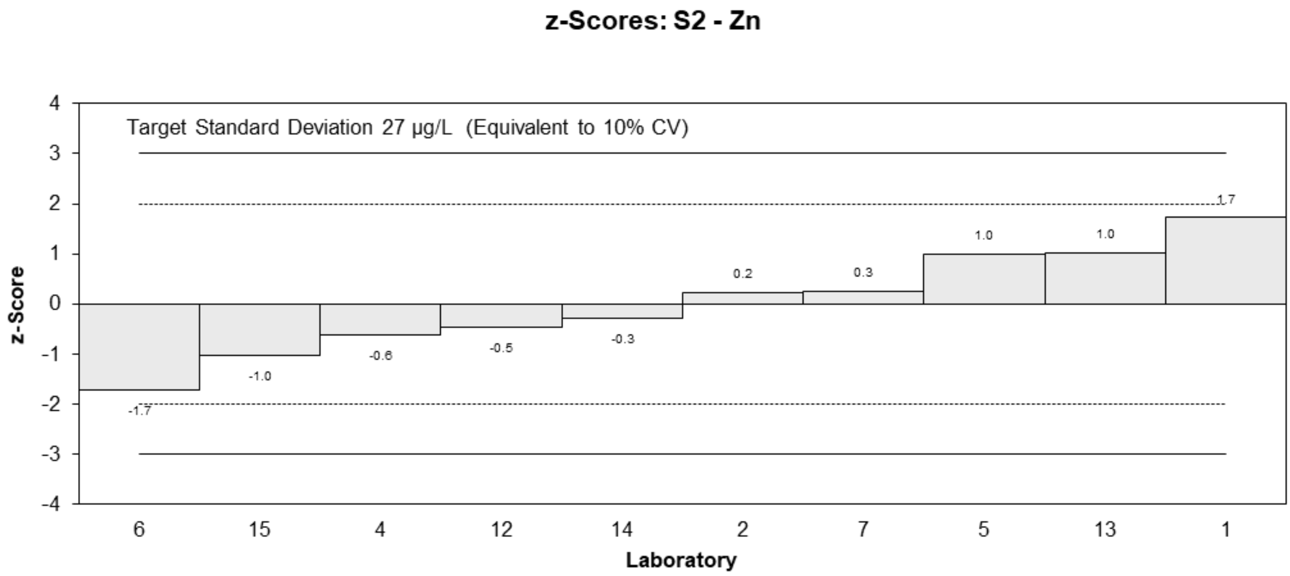
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	320	41	1.72	0.97
2	279	68	0.22	0.08
3	NT	NT		
4	256	8	-0.62	-0.62
5	300.2	30.02	1.00	0.68
6	226	45	-1.72	-0.90
7	280	55	0.26	0.12
8	NT	NT		
10	NT	NT		
11	NT	NT		
12	260	50	-0.48	-0.23
13	301	13	1.03	0.96
14	265	27	-0.29	-0.21
15	245	31	-1.03	-0.69

Statistics

Assigned Value	273	26
Spike	305	9
Homogeneity Value	286	43
Robust Average	273	26
Median	272	23
Mean	273	
N	10	
Max.	320	
Min.	226	
Robust SD	32	
Robust CV	12%	


Results: S2 - Zn
Assigned Value = 273 ± 26 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
6 15 4 12 14 2 7 5 13 1 10 11 3 8 Md R.A. H.V. S.V.


z-Scores: S2 - Zn
Target Standard Deviation 27 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.7 -1.0 -0.6 -0.5 -0.3 0.2 0.3 1.0 1.0 1.7
6 15 4 12 14 2 7 5 13 1

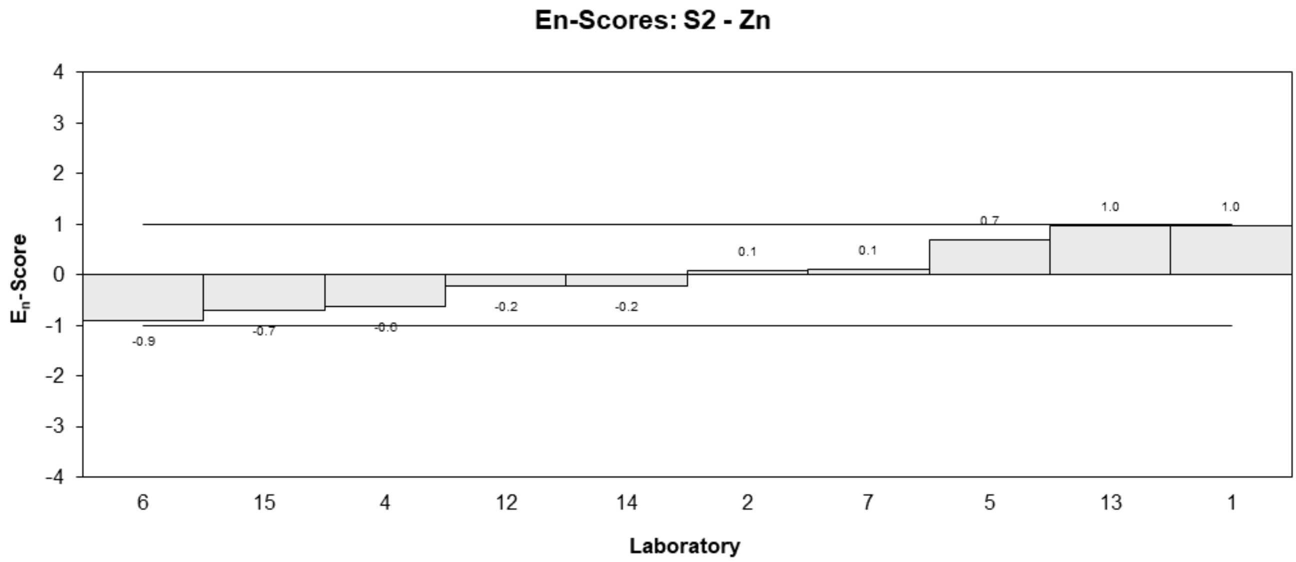

En-Scores: S2 - Zn
E_n-Score
Laboratory
-0.9 -0.7 -0.6 -0.2 -0.2 0.1 0.1 0.7 1.0 1.0
6 15 4 12 14 2 7 5 13 1

Figure 47

7 DISCUSSION OF RESULTS

7.1 Assigned Value

Sample S1 was filtered seawater to which a known amount of single element standard solutions was added. **Sample S2** was unfiltered sea water sample previously distributed as Sample S2 of proficiency testing study AQA 19-16.[6] The stability of Sample S2 over one year was assumed to be in line with that of MX014 certification data as the same preparation/preservation procedure was used in both cases.

Assigned Values were the robust average of participants' results. For S2 the assigned values were the robust average of participants' results from present study only. 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 removed before calculation of each assigned value.[7] Appendix 2 sets out the calculation for the robust average of Ag in Sample S1 and its associated uncertainty.

No assigned value was set for P in S1 because too few results were reported for this test.

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

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 454 numerical results, 446 (98%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1.1% to 100% of the reported value. 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, 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 comparisons studies.[10 – 16]

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 41). In this study, the reported expanded measurement uncertainty has been over-estimated in some cases (e.g. Labs 6, 8 and 12 for Be in S1, Lab 6 for Al, As and Co in S1 or Lab 12 for Ni in S1) or under-estimated (e.g. Lab 4 for Fe in S1). As a simple rule of thumb, when the uncertainty estimate is either smaller than the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be reviewed as suspect.

Overestimation of the precision and/or laboratory or method bias is the most common error seen in the laboratories' estimated uncertainty budgets. According to NATA General Accreditation Guidance, Estimating and reporting measurement uncertainty of chemical test results[12] and to NORDTEST TR 537,[10] the most common sources used to estimate the precision component are from:

- Stable control samples that cover the whole analytical process (including extraction) and **have a matrix similar** to the samples; or
- Stable control samples **and** duplicate analyses if control samples do not cover whole analytical process (e.g. the control sample is a synthetic sample- we have to take into consideration uncertainties arising from different matrices); **or**

- When control samples are not stable, from analysis of natural duplicates (gives within-day variation for sampling and measurement) and long-term uncertainty component from the variation in the instrument calibration; **or**
- Replicate analyses performed on the same sample at different times to obtain estimates of intermediate precision; within-batch replication provides estimates of repeatability only.

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

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[11, 13] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 3.

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

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.[10]

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 48. 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 450 results for which E_n-scores were calculated, 382 (85%) 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.

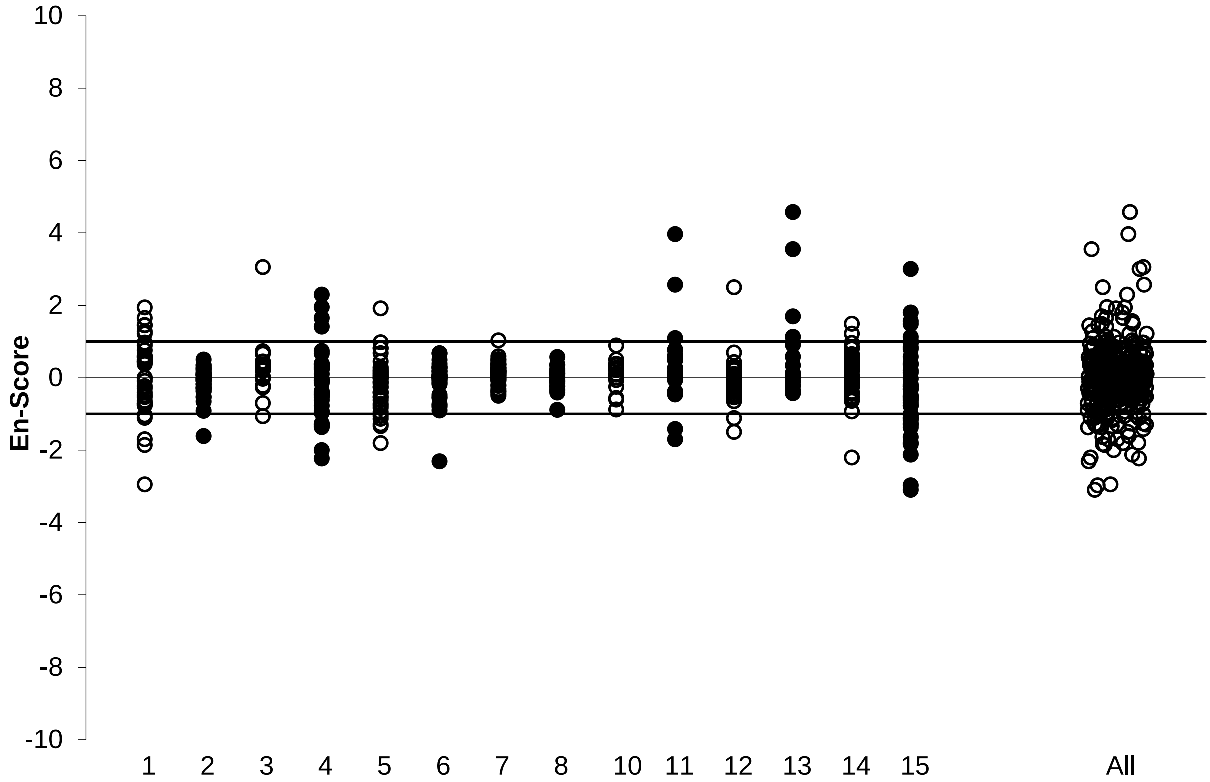
7.4 z-Score

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

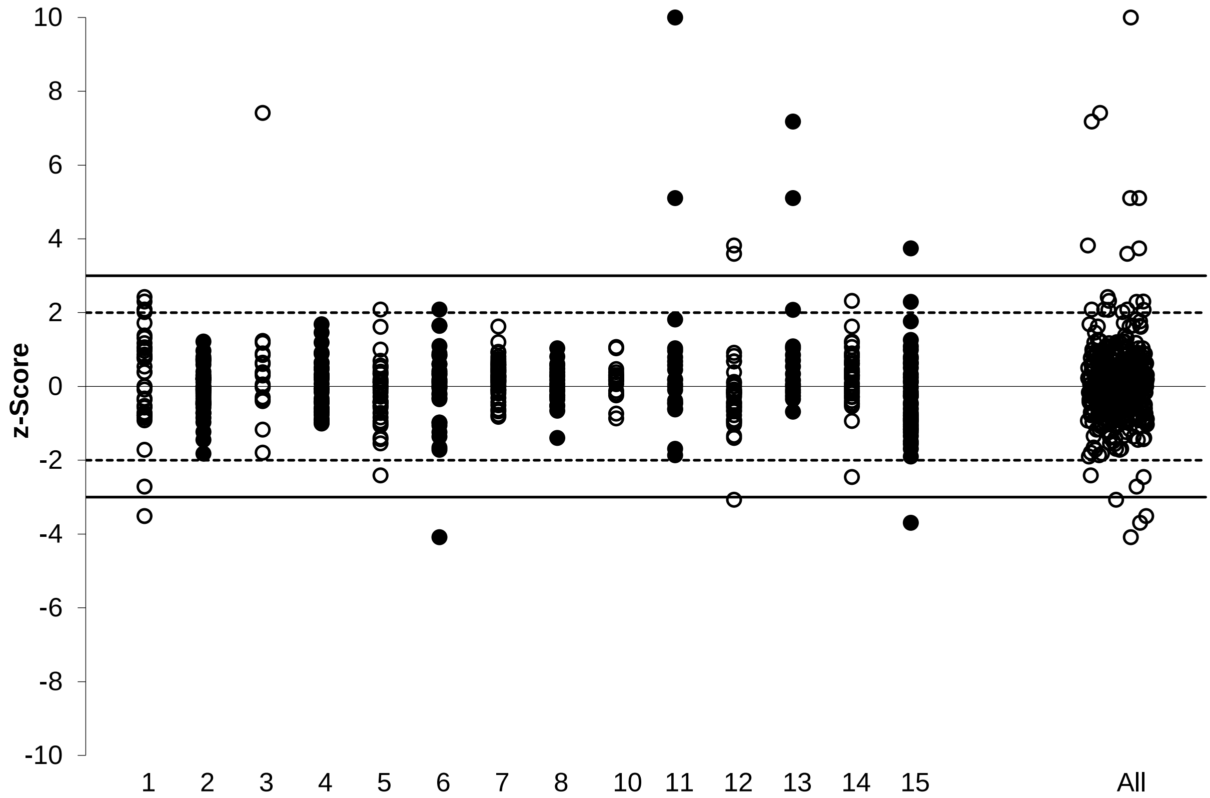
The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 50.

The dispersal of participants' z-scores is presented in Figure 49 (by laboratory code) and in Figure 50 (by test). Of 450 results for which z-scores were calculated, 425 (95%) returned a satisfactory score of |z| ≤ 2.0 and 13 (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 48 E_n-Score Dispersal by Laboratory



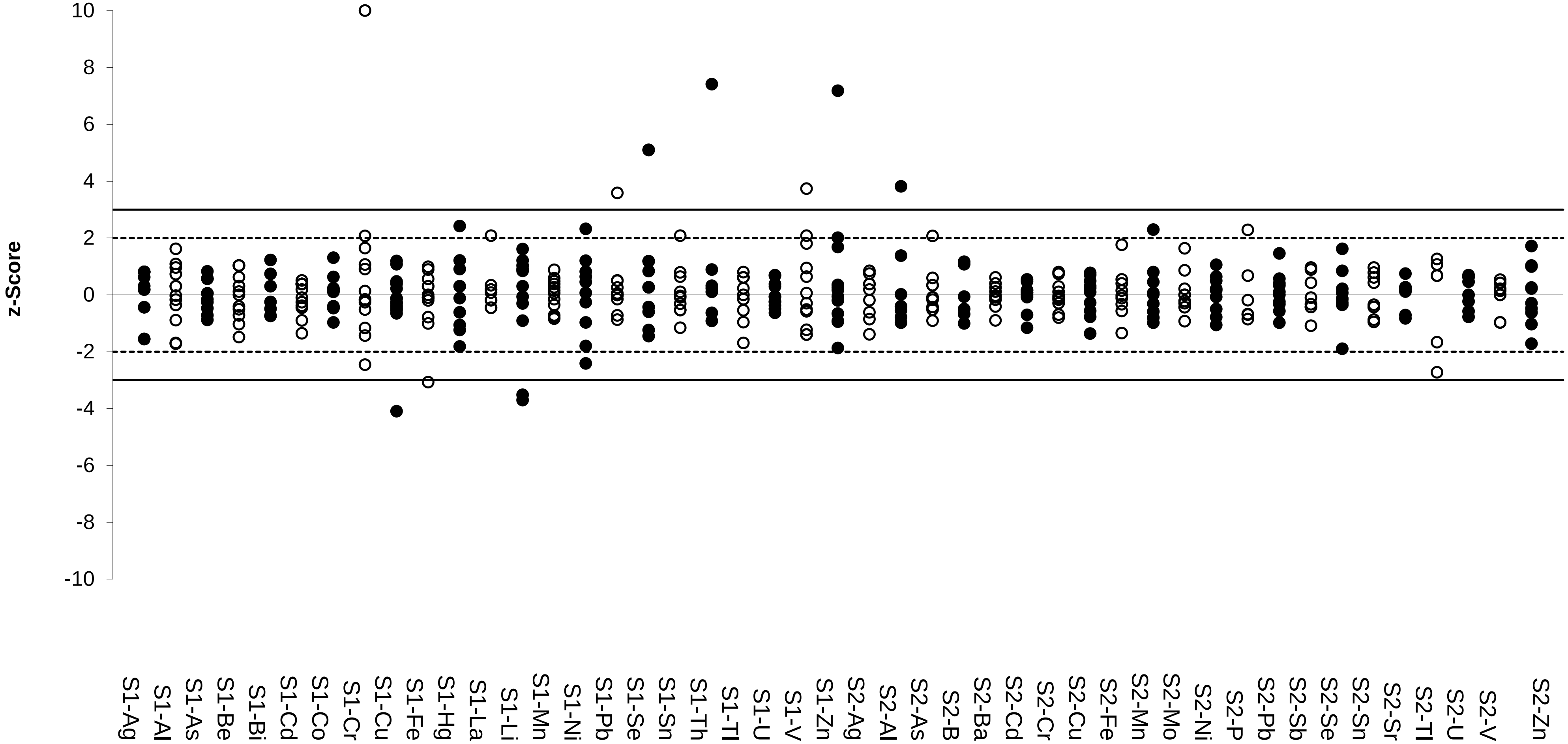
Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 49 z-Score Dispersal by Laboratory

Table 50 Between Laboratory CV of this Study, Thompson CV and Set Target CV

Sample	Test	Assigned value (µg/L)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as CV)
S1	Ag	1.07	14%	22%	15%
S1	Al	15.1	24%	22%	20%
S1	As	1.29	10%	22%	15%
S1	Be	1.30	14%	22%	15%
S1	Bi	1.35	13%	22%	15%
S1	Cd	1.04	7.7%	22%	15%
S1	Co	1.17	7.9%	22%	15%
S1	Cr	2.06	21%	22%	15%
S1	Cu	7.75	8.7%	22%	15%
S1	Fe	101	7.1%	22%	10%
S1	Hg	0.220	20%	22%	15%
S1	La	2.65	4.2%	22%	10%
S1	Li	165	15%	21%	10%
S1	Mn	3.17	9.8%	22%	15%
S1	Ni	1.78	24%	22%	15%
S1	P	120**	35%	22%	Not Set
S1	Pb	1.30	6.7%	22%	15%
S1	Se	2.21	17%	22%	15%
S1	Sn	3.04	12%	22%	15%
S1	Th	2.32	11%	22%	15%
S1	Tl	1.74	12%	22%	15%
S1	U	5.08	7.7%	22%	15%
S1	V	2.28	21%	22%	15%
S1	Zn	7.22	17%	22%	15%
S2	Ag	106	8.5%	22%	10%
S2	Al	868	11%	16%	10%
S2	As	232	6.5%	20%	10%
S2	B	4830	11%	13%	10%
S2	Ba	346	4.6%	19%	10%
S2	Cd	129	4.7%	22%	10%
S2	Cr	175	6.3%	21%	10%
S2	Cu	286	7.3%	19%	10%
S2	Fe	335	7.2%	19%	10%
S2	Mn	287	8.4%	19%	10%
S2	Mo	140	7.1%	22%	10%
S2	Ni	141	7.8%	21%	10%
S2	P	590	11%	17%	10%
S2	Pb	123	6.6%	22%	10%
S2	Sb	303	8.3%	19%	10%
S2	Se	142	6.7%	21%	10%
S2	Sn	115	8.3%	22%	10%
S2	Sr	7310	6.4%	12%	10%
S2	Tl	103	17%	22%	10%
S2	U	130	6.6%	22%	10%
S2	V	144	6.5%	21%	10%
S2	Zn	273	12%	19%	10%

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



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

Figure 50 z-Score Dispersal by Analyte

Table 51 Summary of Participants' Results and Performance for Sample S1

Lab Code	Ag (μg/L)	Al (μg/L)	As (μg/L)	Be (μg/L)	Bi (μg/L)	Cd (μg/L)	Co (μg/L)	Cr (μg/L)	Cu (μg/L)	Fe (μg/L)	Hg (μg/L)	La (μg/L)
A.V.	1.07	15.1	1.29	1.30	1.35	1.04	1.17	2.06	7.75	101	0.220	2.65
H.V.	1.18	17.8	1.35	1.46	2.04	1.06	1.21	2.11	5.91	105	0.236	2.71
S.V.	1.13	9.88	Not Spiked	1.21	1.38	0.987	1.10	1.96	6.39	97.9	0.212	2.49
1	1.2	9.9	<10	1.5	1.2	1.1	1.4	<5	8.2	93.1	0.3	3.2
2	1.10	17.3	1.24	1.16	1.25	0.97	1.09	2.01	7.61	99	0.16	2.70
3	<1	15	1.3	1.3	1.6	1.1	1.1	1.7	7.4	110	<0.5	NT
4	1.12	12.4	1.26	1.22	NT	1.12	1.21	2.34	9.13	90.8	NT	2.53
5	0.821	14.60	1.151	1.323	NT	1.025	1.093	1.617	7.123	106.7	0.185	NT
6	<2	18.4	1.45	1.36	NT	1.07	1.19	2.57	2.99	101	0.179	2.74
7	1.2	20	1.4	1.2	1.5	1.1	1.2	2.1	8.0	100	0.23	2.6
8	1.2	14	1.4	1.5	1.3	1.1	1.2	1.9	7.6	100	0.23	NT
10	1.1	16	<4	NT	1.2	1.10	1.2	2.39	8.3	104	0.216	2.6
11	1.0	18	1.4	1.5	NR	0.98	1.2	5.7	7.2	100	0.2	2.7
12	1.0	NT	< 3	1.1	NT	0.9	1	2	7	70	0.25	NT
13	NT	NT	1.3	NT	NT	1.0	NT	2.7	9	100	NT	NT
14	1.17	16	1.2	1.42	1.41	1.10	1.09	1.3	7.3	104	0.26	2.67
15	0.82	10	1.12	1.01	NT	0.83	1.28	1.98	7.45	111	NT	2.53

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

Table 51 Summary of Participants' Results and Performance for Sample S1 (continued)

Lab Code	Li (µg/L)	Mn (µg/L)	Ni (µg/L)	P (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Th (µg/L)	Tl (µg/L)	U (µg/L)	V (µg/L)	Zn (µg/L)
A.V.	165	3.17	1.78	Not Set	1.30	2.21	3.04	2.32	1.74	5.08	2.28	7.22
H.V.	223	3.50	1.84	98	1.40	2.38	NA	2.39	1.89	5.34	2.42	8.5
S.V.	Not Spiked	3.09	1.74	120	1.23	2.55	2.73	2.77	1.87	5.17	2.13	6.99
1	107	2.8	<10	<100	<10	<10	2.8	2	1.6	4.8	<5	9.4
2	185	3.45	1.52	NR	1.16	1.73	3.09	NR	1.74	NR	1.86	7.17
3	179	3.0	1.3	NT	1.3	2.6	NT	4.9	1.9	5.3	2.5	7.6
4	164	3.59	1.95	NT	1.35	2.01	3.33	2.43	NT	5.03	2.08	9.04
5	191.6	2.77	1.137	NT	1.397	2.069	3.987	NT	NT	5.604	2.102	7.598
6	NT	3.35	<2	NT	1.31	2.49	NT	<2	<1	5.04	2.99	<10
7	180	3.3	2.1	110	1.4	2.3	2.9	2.4	1.9	4.6	2.6	7.4
8	160	3.4	1.8	NT	1.3	2.3	2.8	NT	1.9	4.9	1.8	6.5
10	182	3.24	<7	NT	1.13	<4	<5.0	NT	1.8	4.9	2.3	7.5
11	NR	3.2	1.9	NR	1.3	3.9	3.4	2.1	1.3	5.6	2.9	5.2
12	150	< 3	2	< 40	2	< 5	3	NT	1.7	NT	1.8	7
13	NT	NT	NT	156	<1	3.9	NT	NT	NT	NT	NT	15
14	170	3.1	2.4	100	1.3	2.6	3.02	2.63	1.95	5.37	2.18	6.2
15	104	2.83	1.71	135	1.27	1.8	2.51	2.36	1.49	4.71	3.56	6.22

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

Table 52 Summary of Participants' Results and Performance for Sample S2

Lab Code	Ag (µg/L)	Al (µg/L)	As (µg/L)	B (µg/L)	Ba (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Mo (µg/L)
A.V.	106	868	232	4830	346	129	175	286	335	287	140
H.V.	113	848	255	NA	333	135	184	273	371	278	151
S.V.	122	853	257	Not Spiked	367	140	186	314	363	309	150
1	114	988	280	5397	343	136	161	308	316	353	152
2	97	833	230	4589	360	128	188	295	324	310	143
3	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	108	NT	222	NT	315	120	163	264	NT	259	127
5	91.304	832.0	239.9	4341	331.9	128.9	174.3	289.0	348.5	287.5	133.8
6	104	783	246	NT	367	131	177	247	334	278	163
7	110	870	230	NR	350	130	180	300	340	300	140
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	110	1200	220	4500	340	130	170	270	290	270	140
13	NT	NT	240	NT	NT	131	172	306	353	NT	NT
14	115	821	228	4800	355	135	173	278	331	289	136
15	99.5	800	211	5350	345	114	189	293	394	264	137

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

Table 52 Summary of Participants' Results and Performance for Sample S2 (continued)

Lab Code	Ni (µg/L)	P (µg/L)	Pb (µg/L)	Sb (µg/L)	Se (µg/L)	Sn (µg/L)	Sr (µg/L)	Tl (µg/L)	U (µg/L)	V (µg/L)	Zn (µg/L)
A.V.	141	590	123	303	142	115	7310	103	130	144	273
H.V.	154	527	114	299	146	99	NA	106	124	144	286
S.V.	154	598	134	313	153	121	Not Spiked	121	138	152	305
1	156	540	119	332	137	124	6788	75	130	144	320
2	144	NR	116	290	145	126	7510	110	NR	144	279
3	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	140	NT	141	293	143	110	NT	NT	136	130	256
5	143.2	NT	124.4	NT	138.0	104.1	7446	NT	122.4	151.7	300.2
6	126	NT	111	330	137	NT	NT	85.9	127	150	226
7	150	550	130	290	140	120	6700	110	120	150	280
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	130	630	120	300	140	110	7400	110	NT	130	260
13	NT	549	123	NT	154	111	NT	NT	NT	NT	301
14	134	579	128	316	165	122	7500	114	139	147	265
15	148	725	127	270	115	105	7860	116	138	146	245

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

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

Sample S1 was filtered seawater. The analytes' concentration in this sample ranged from 0.220 to 1654 µg/L. **Sample S2** was unfiltered seawater and participants were asked to report results for total elements. Analytes' concentration in this sample was 3 to 180 times higher than in Sample S1. A summary of participants' results and performance in the two study samples is presented in Tables 51 and 52 and in Figures 48 to 50.

Low level Al, Ni and P were the test which had the highest coefficient of variation, ranging from 24% to 35%.

Individual Element Commentary

Participants were requested to analyse the samples using their normal test method and to report a single result as they would normally report to a client. With the exception of 4 participants, all who reported results for total elements in S2 performed digestion. Most used a digestion temperature of 85°C to 100°C and three digested their samples at 170°C or 180°C. Six laboratories used nitric acid and hydrochloric acid for extraction and one used only nitric acid. No relationship was evident between the results reported for total elements in S2 and the digestion method employed.

Instrumental measurement was one of the main factors that influenced the results for total and dissolved elements in the seawater samples. However, participants' performance does not reflect only instrumental performance, but also the performance of the analyst and of the analytical method used by the testing laboratory. Thus, these results should not be construed as an evaluation of a particular instrument.

Participants used a wide variety of instrumental techniques, collision/reaction cells and cell gases. Most laboratories reported using ICP-MS with a collision/reaction cell; some used ICP-OES, and some only ICP-MS. 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 Figure 51.

Silver measurements did not present analytical difficulty to participating laboratories. Silver level in seawater samples S1 and S2 was 1.07 µg/L and 106 µg/L respectively. All reported results returned satisfactory z-scores.

Aluminium Low level Al in S1 (15.1 µg/L) challenged participants' instrumental techniques. The between laboratory CV for Al in S1 was 24%.

Arsenic level in S1 was the natural level 1.29 µg/L. Measurements of As at low level in sea water posed no significant problems for laboratories. The between-laboratory CV for As in S1 was 10%. Participants used various instrumental techniques, ICP-MS in collision or reaction mode with He, O_2 or N_2O as collision/reaction gases, and all produced satisfactory results.

Chromium The results reported for Cr in S1 were variable, the between coefficient of variation was large, 21%.

Participants used a wide variety of instrumental techniques to overcome the interference problems with Cr in the seawater sample (Figure 51).

Iron level in S1 was 101 µg/L and in S2 was 335 µg/L. The largest variation was noticed between the results coming from ICP-OES measurements. Measurements of low level Fe in S1 by ICP-OES may have presented difficulties to laboratories.

Mercury High mercury results may be caused by expired standards or those not prepared fresh from standard stock solutions.

Nickel was one of the analytes which presented most analytical difficulty to participants. Ni level in S1 was 1.78 µg/L and the between laboratory coefficient of variation was 24%. Except for one, all participants used for Ni measurement ICP-MS with collision/reaction cell and He as the collision gas. One participant reported using ICP-MS/MS and N_2O as reaction gas.

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

Phosphorus spike value in S1 was 120 µg/L. A limited number of laboratories had the capability to measure P in seawater at this level. Only 4 participants reported results for this analyte and all were compatible with each other centred on 125 µg/L

For P measurements in S1, 2 laboratories used ICP-OES with wavelength 213.618 nm or 187.284 nm one laboratory used ICP-MS and one laboratory used ICP-MS/MS in collision mode.

Selenium analysis in sea water is challenging due to multiple sources of significant interferences, this is especially problematic at low levels were any unresolved interference can have a more significant effect on the results. Participants reported using 8 different instrumental techniques in the present study. Plots of participants' performance for Se in S1 versus instrumental technique used are presented in Figure 51. Some participants may have not overcome the interference problem.[17]

Vanadium level in S1 was low at 2.28 µg/L. Of 12 results reported 10 returned satisfactory z-scores.

Zinc All unsatisfactory results reported for Zn in S1 were high. This element is known to be ubiquitous in the environment (e.g. often contained within nitrile gloves) and controlling Zn contamination is a challenge for laboratories. No relationship between the results reported for these elements and the instrumental technique used was evident.

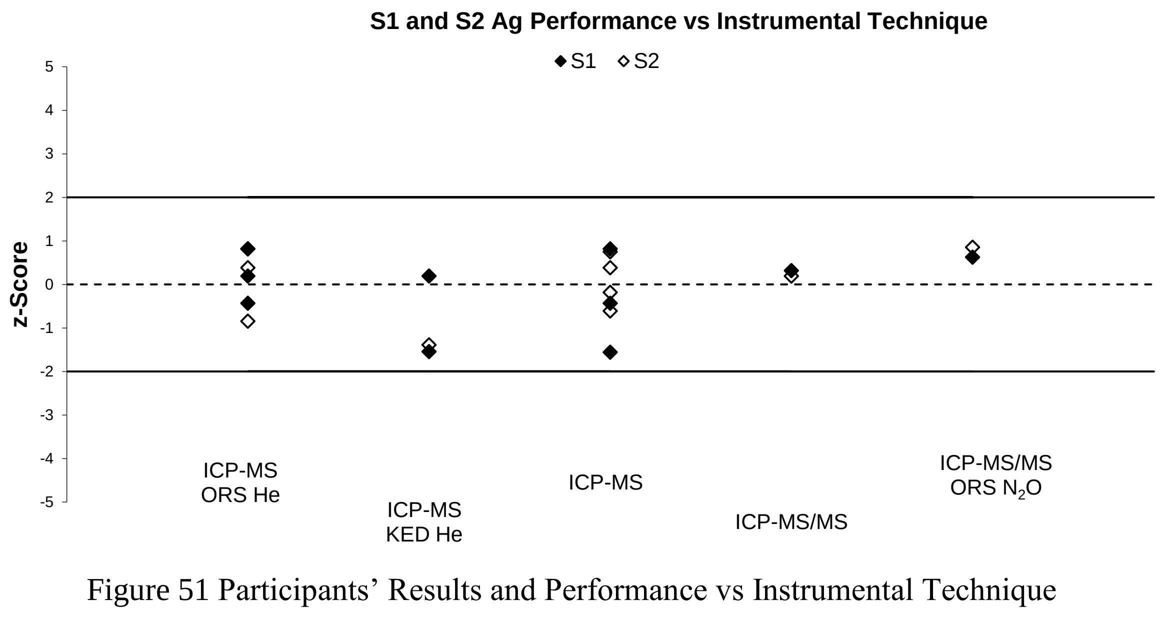
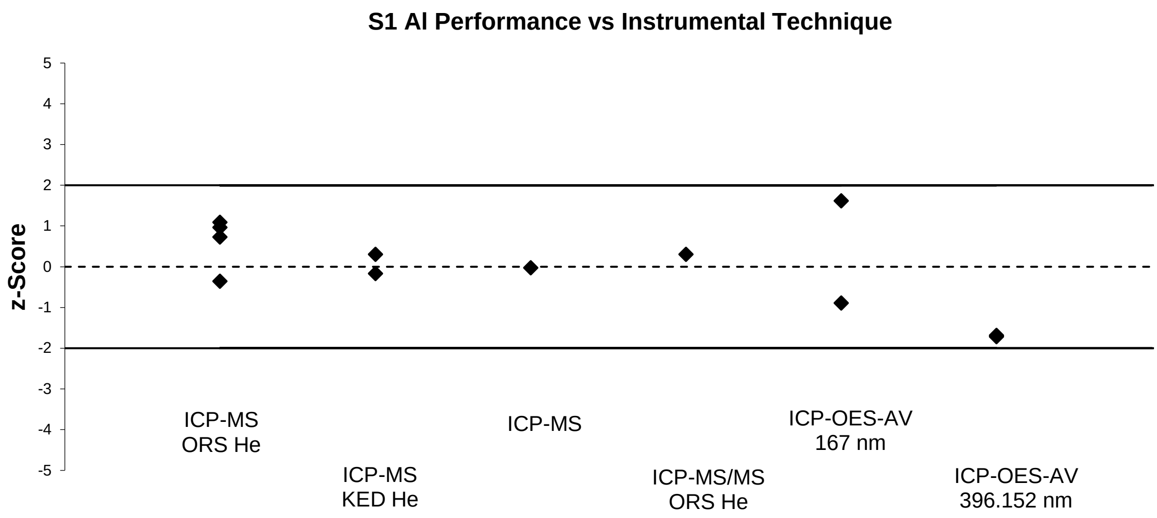
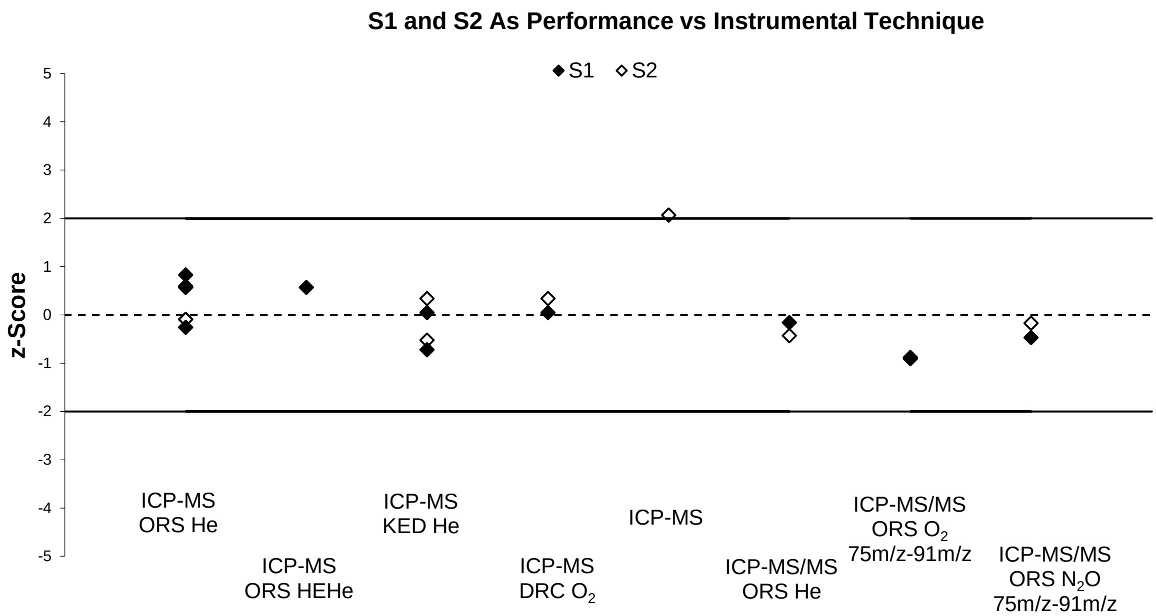
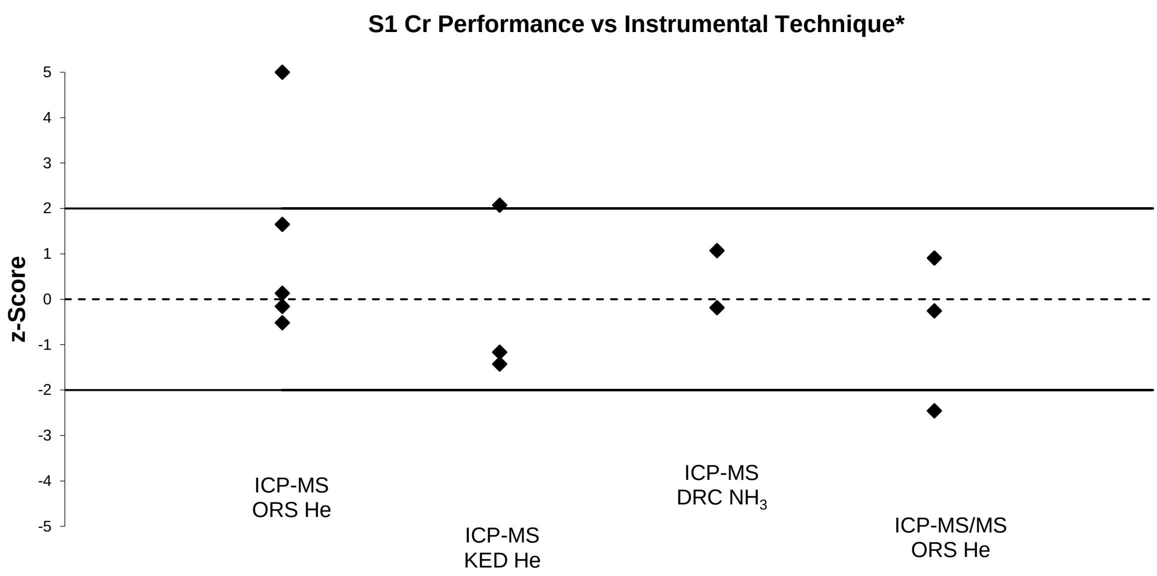


Figure 51 Participants' Results and Performance vs Instrumental Technique

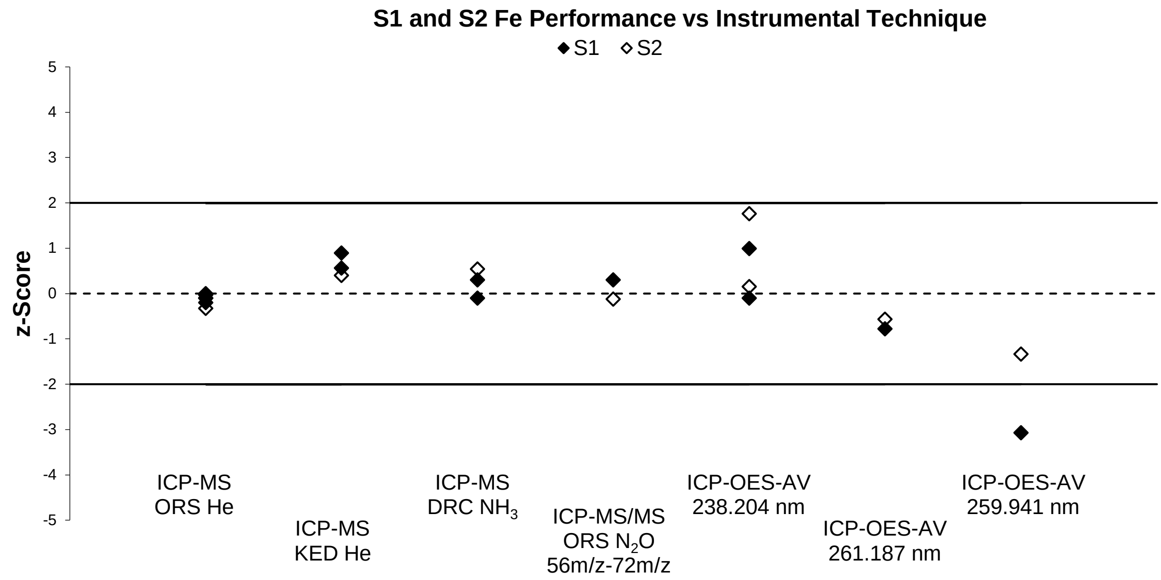


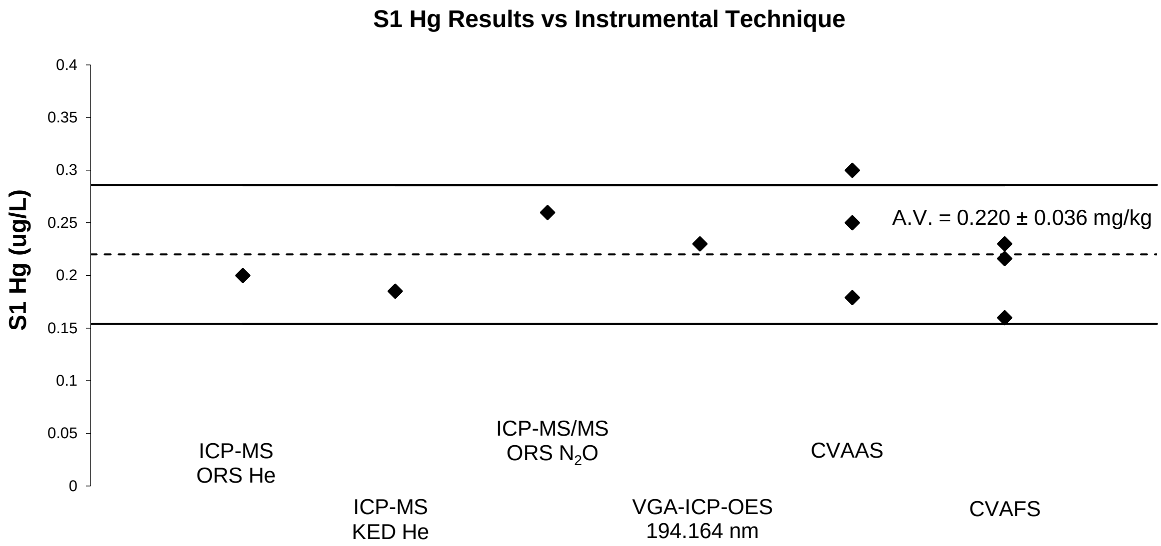




*Score of >5 has been plotted as 5

Figure 51 Participants' Results and Performance vs Instrumental Technique (continued)





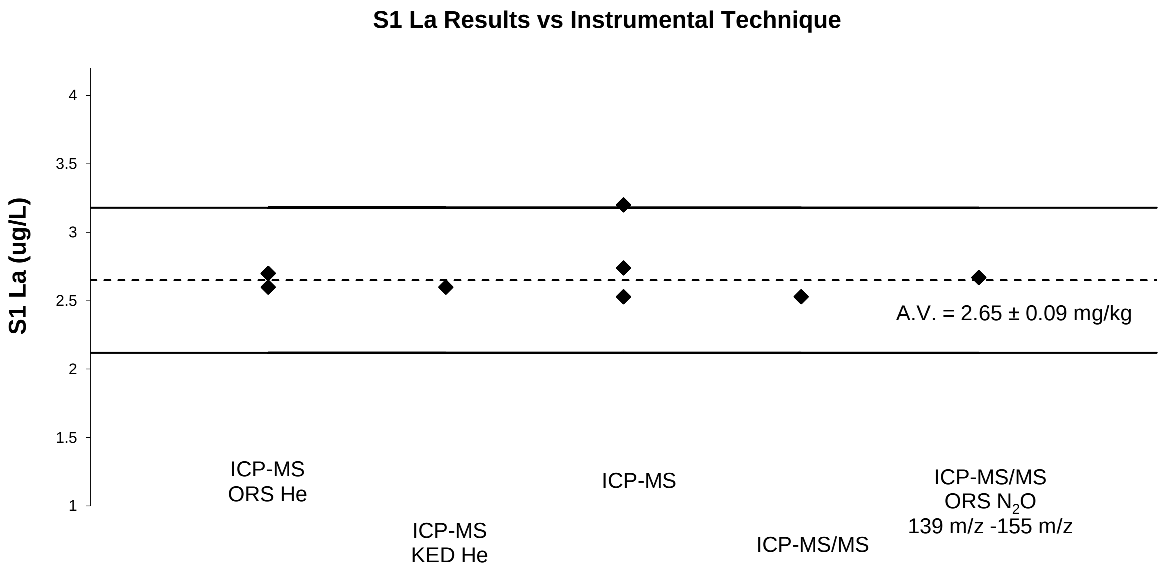
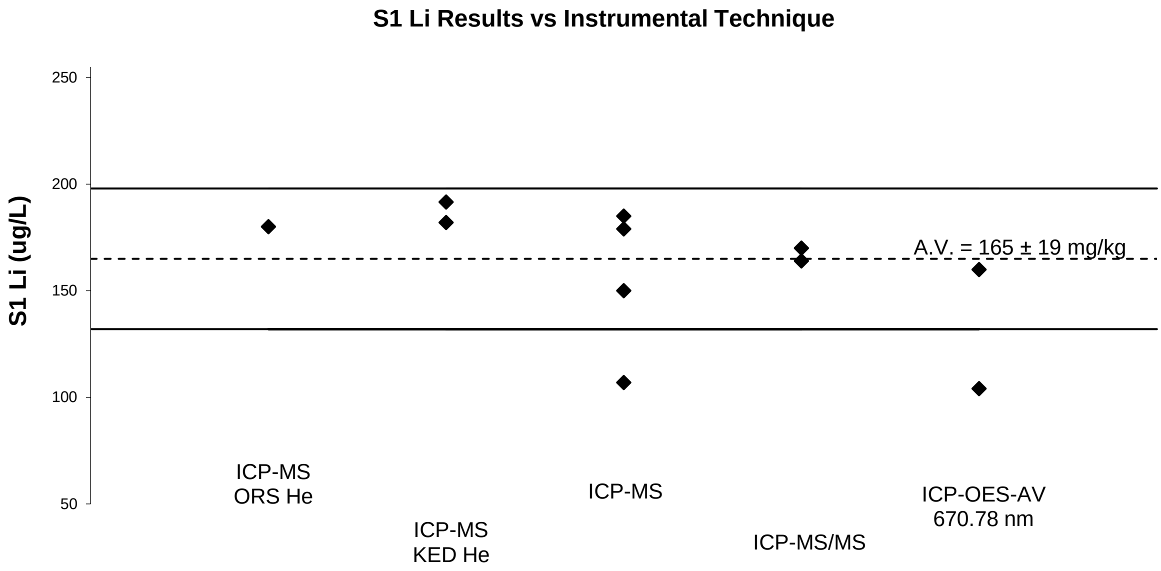
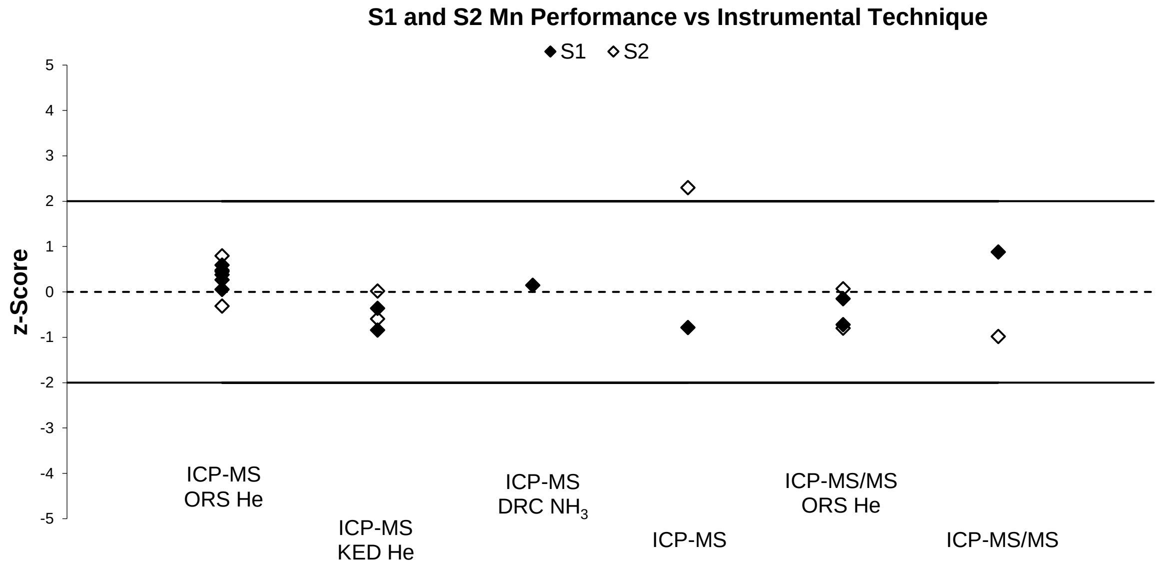


Figure 51 Participants' Results and Performance vs Instrumental Technique (continued)





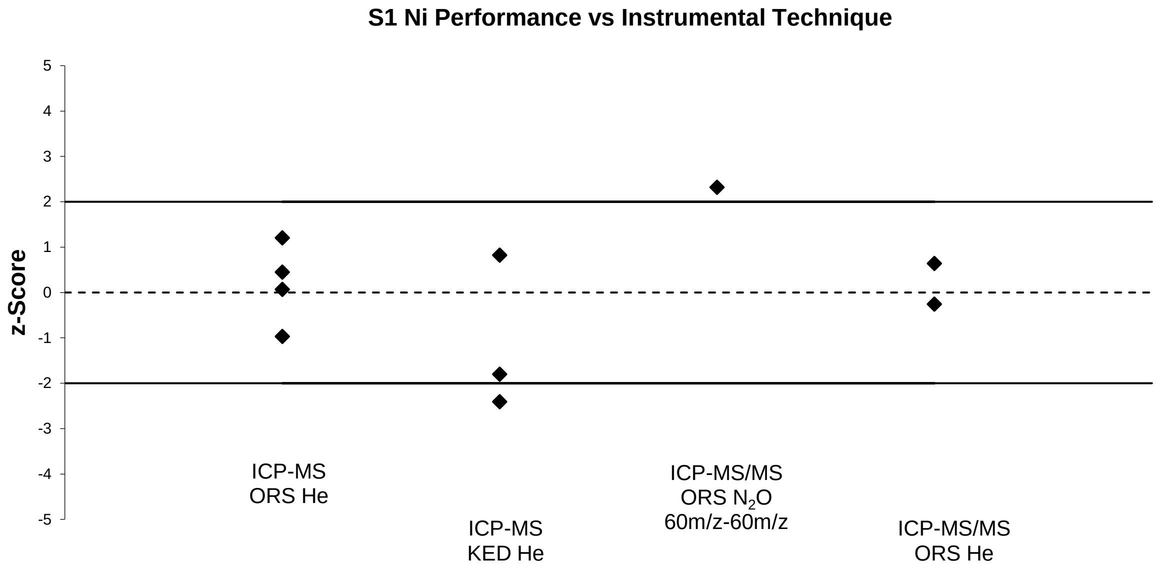
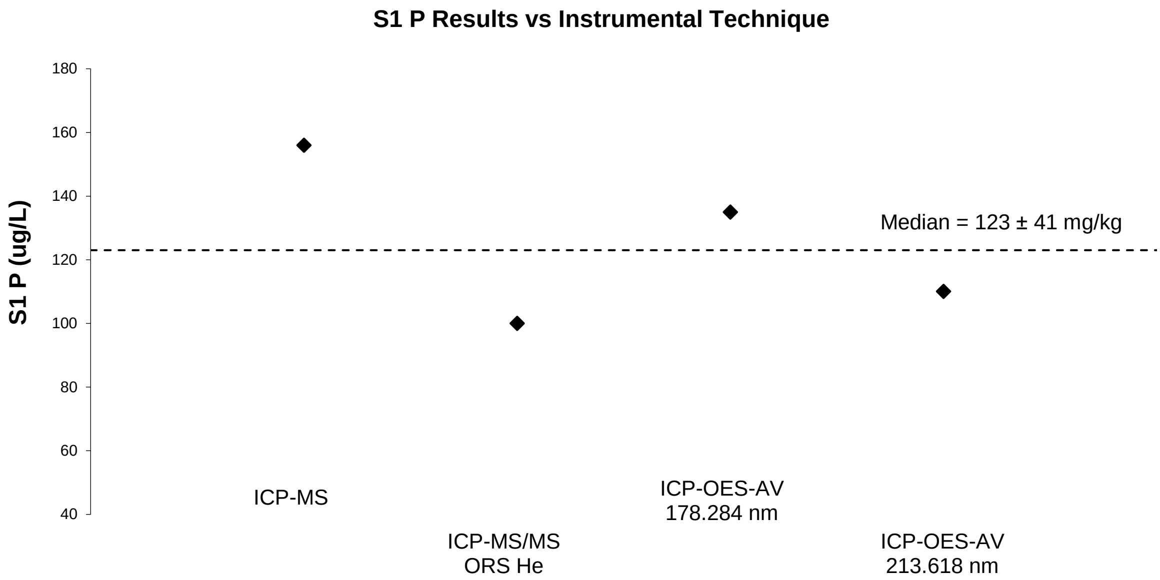
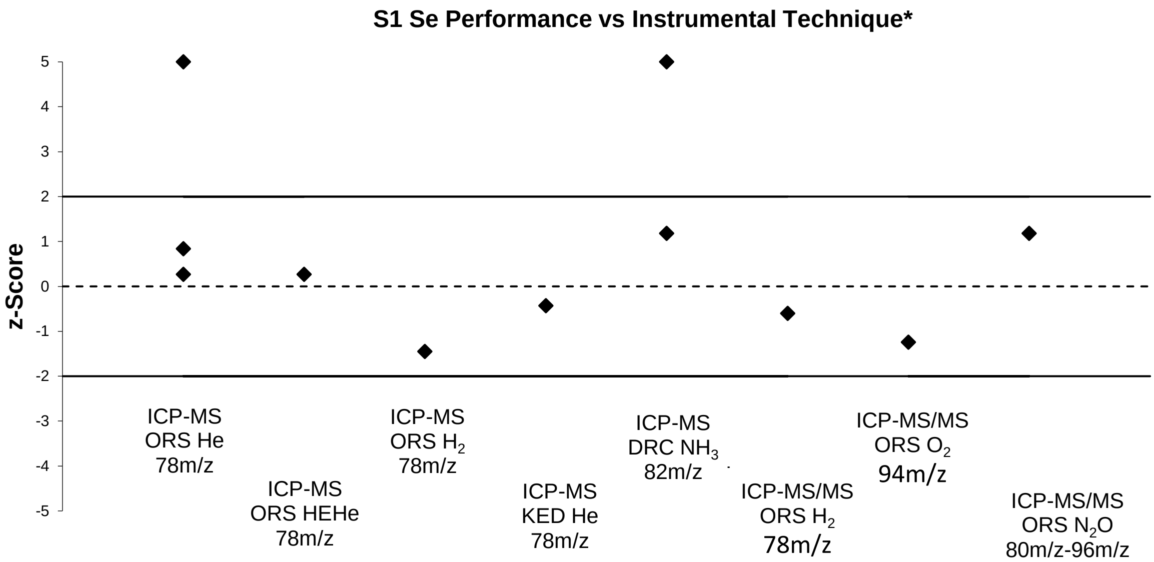


Figure 51 Participants' Results and Performance vs Instrumental Technique (continued)





*Scores of >5 have been plotted as 5

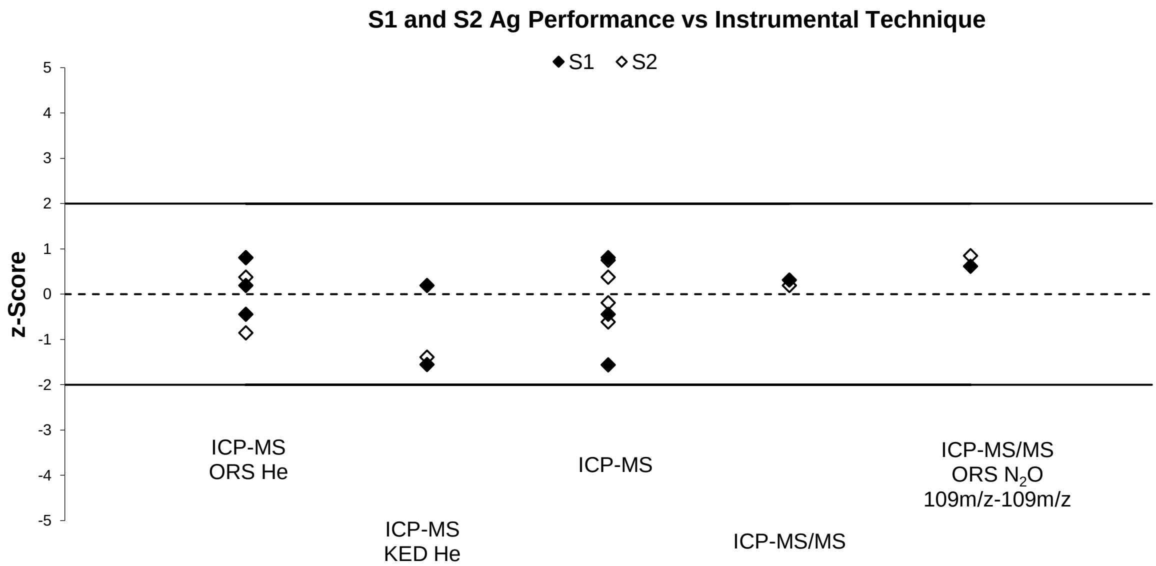
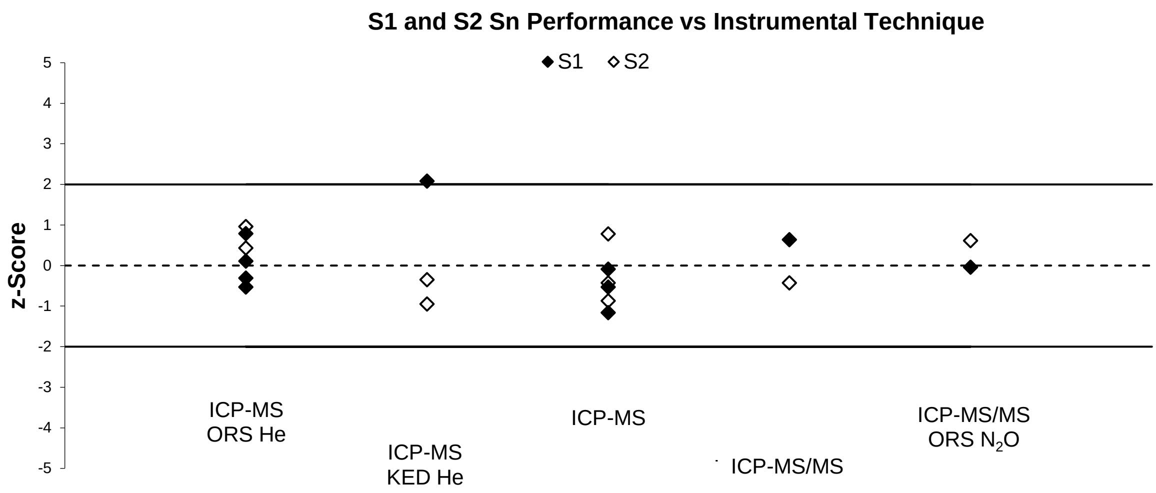
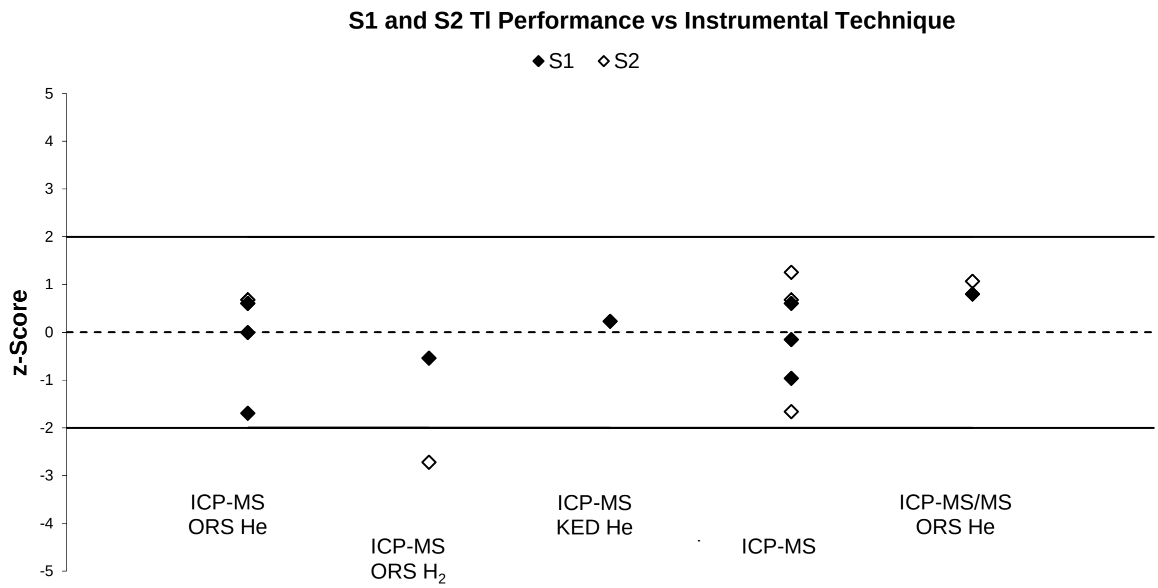


Figure 51 Participants' Results and Performance vs Instrumental Technique (continued)





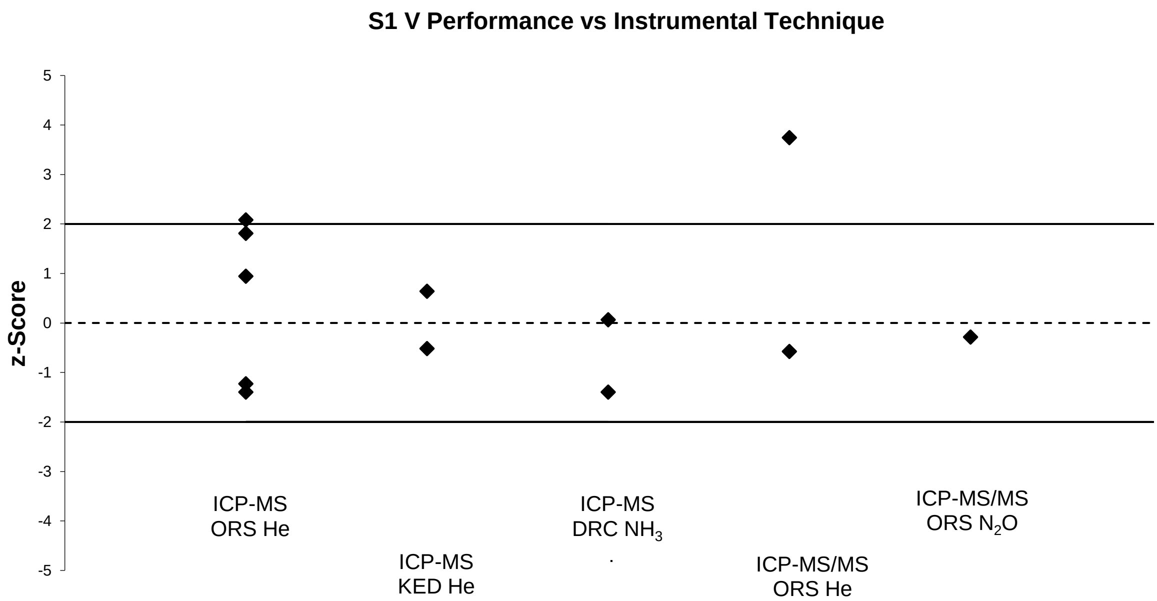
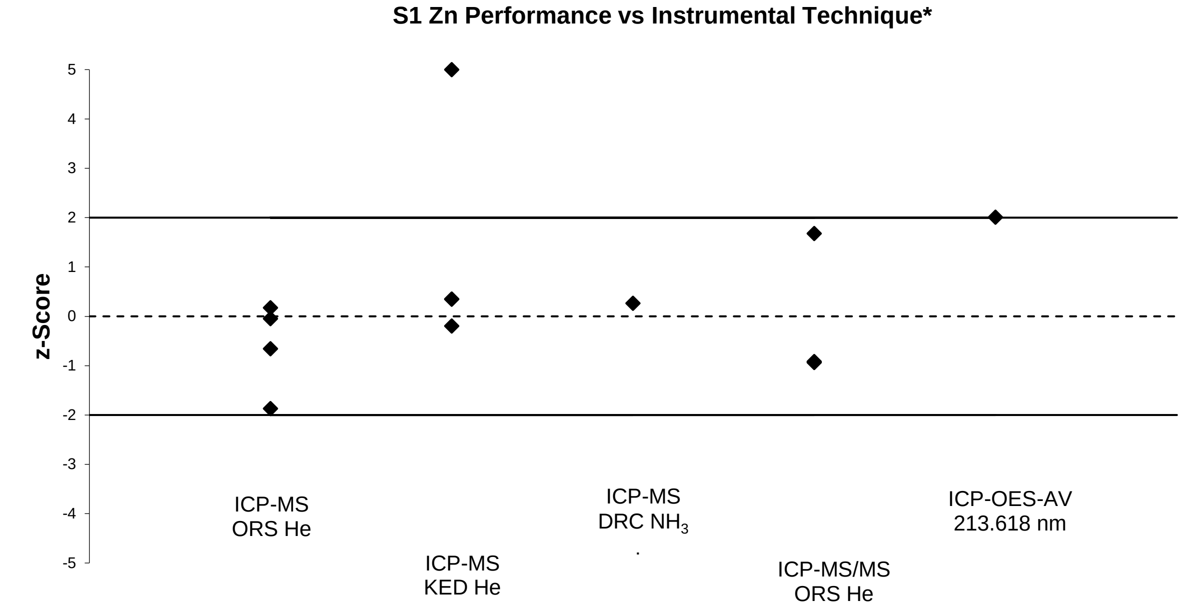


Figure 51 Participants' Results and Performance vs Instrumental Technique (continued)



*Scores of >5 has been plotted as 5

Figure 51 Participants' Results and Performance vs Instrumental Technique (continued)

7.6 Participants' Within-Laboratory Reproducibility

Sample S2 was an unfiltered sea water sample previously distributed as S2 of AQA 19-16. [6] Of 10 laboratories who reported results in the present study for S2, 5 also reported results for S2 of AQA 19-16 (Laboratories 1, 2, 7, 12 and 13).

Results from the two studies reported by participants along with the associated uncertainties, are presented in Figure 52. In some cases, the reported results and the expanded measurement uncertainty in the two study samples are significantly different.

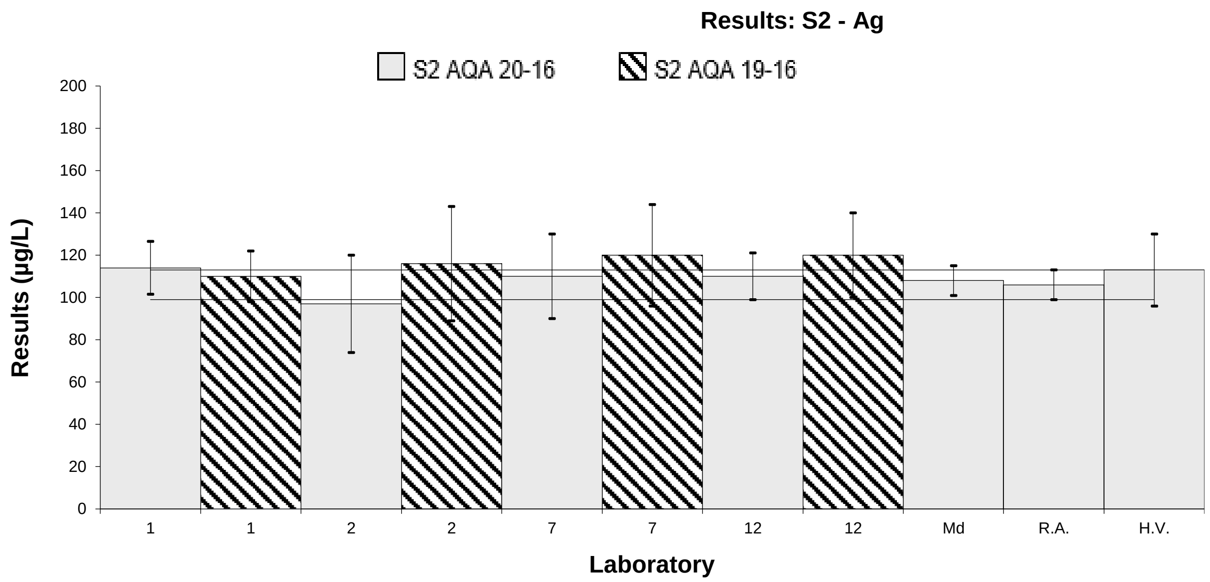
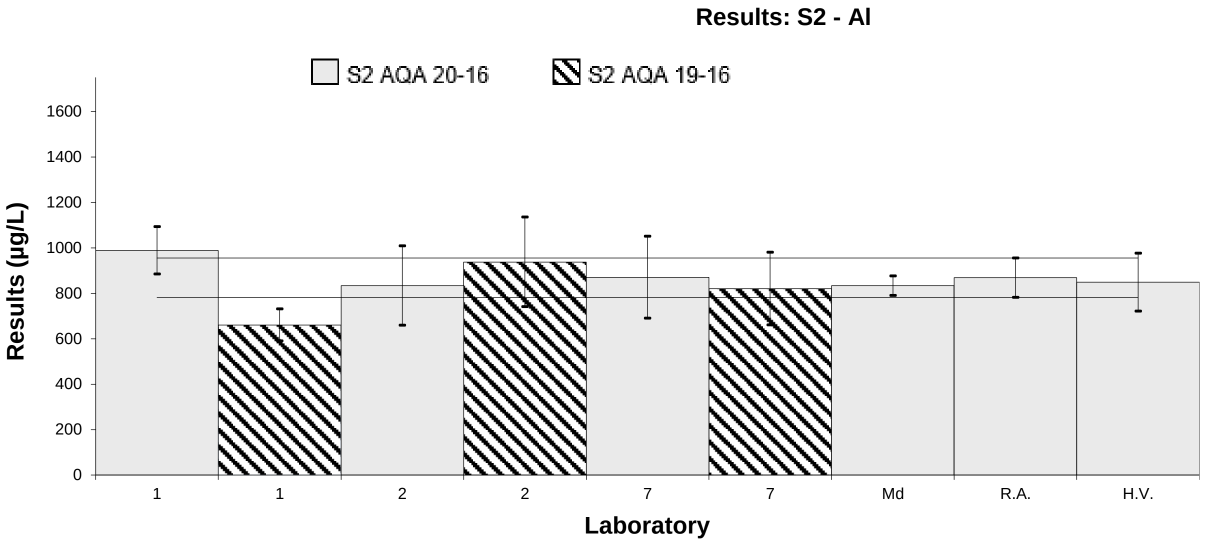
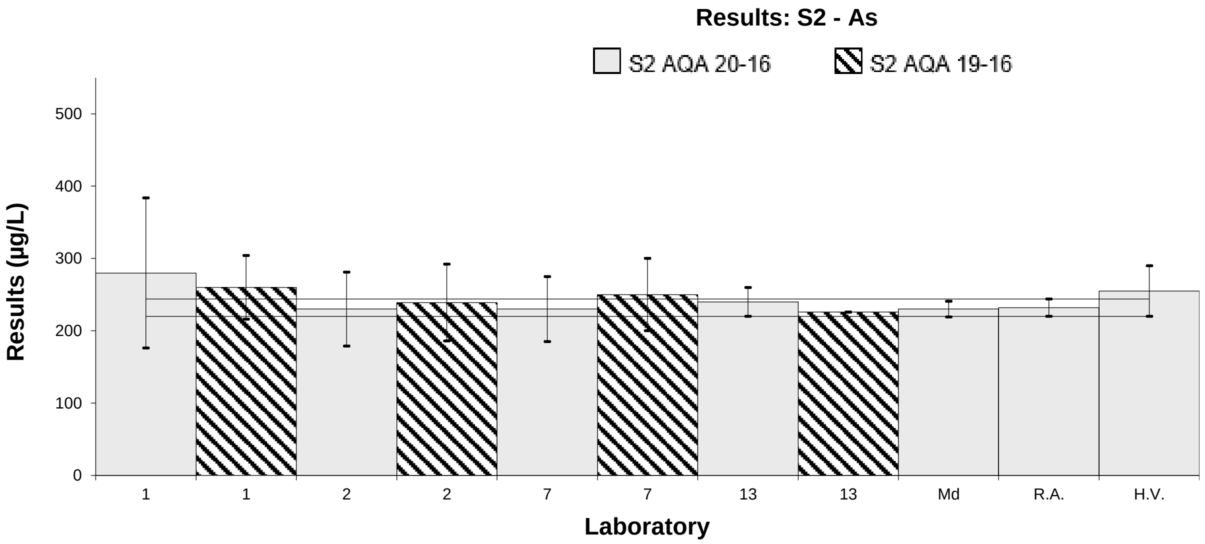


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16





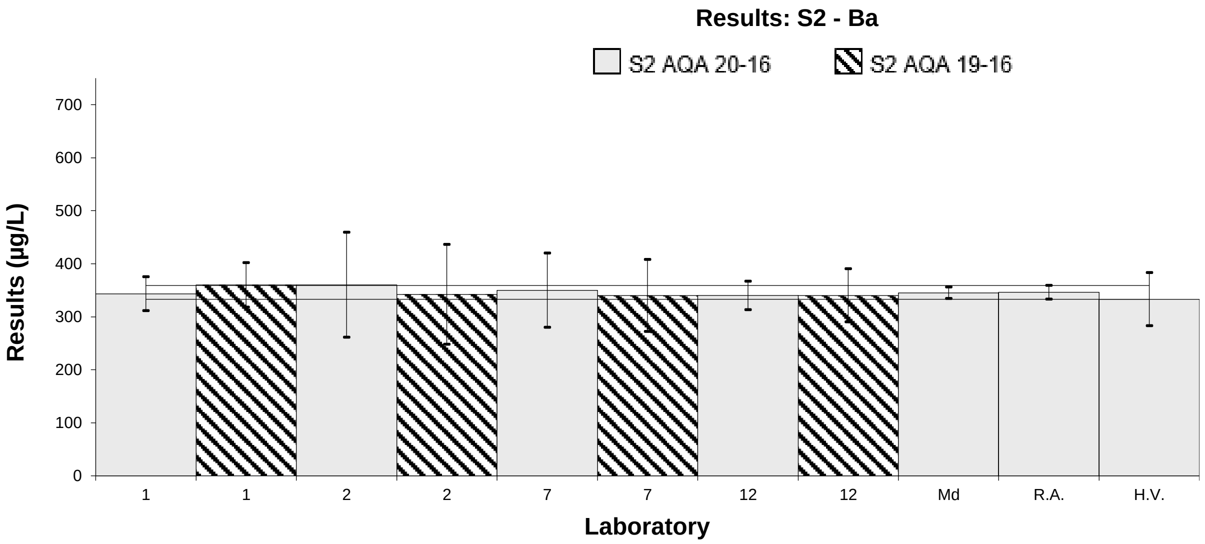
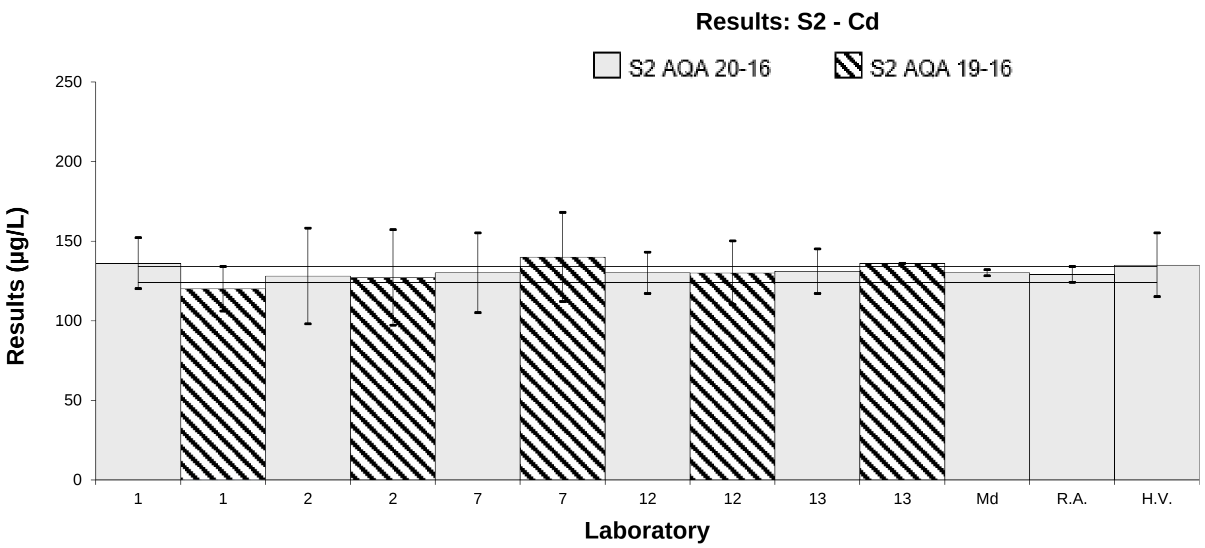
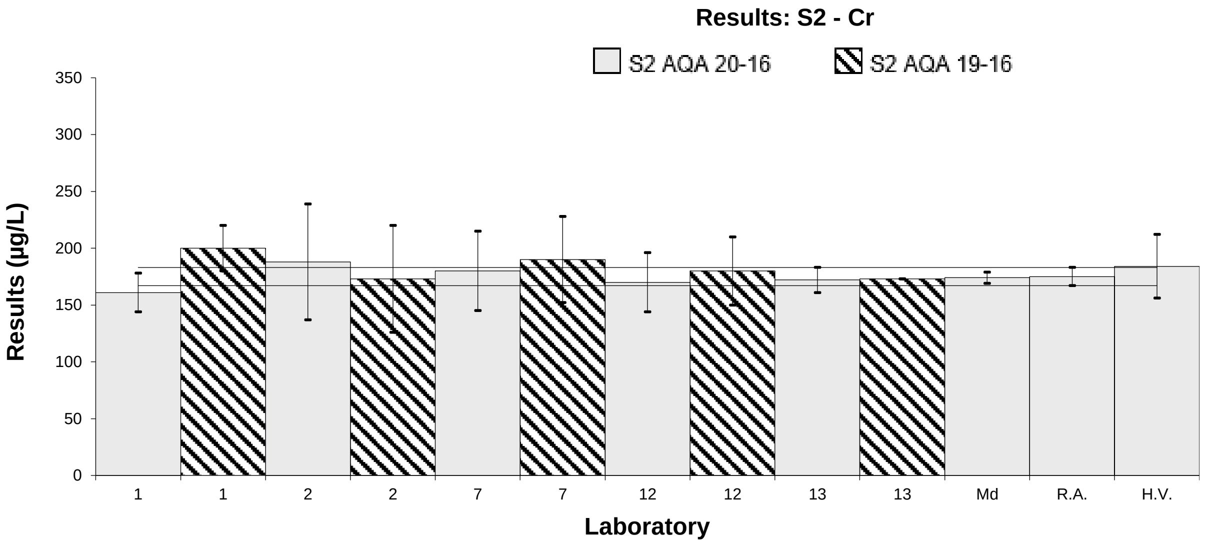


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)





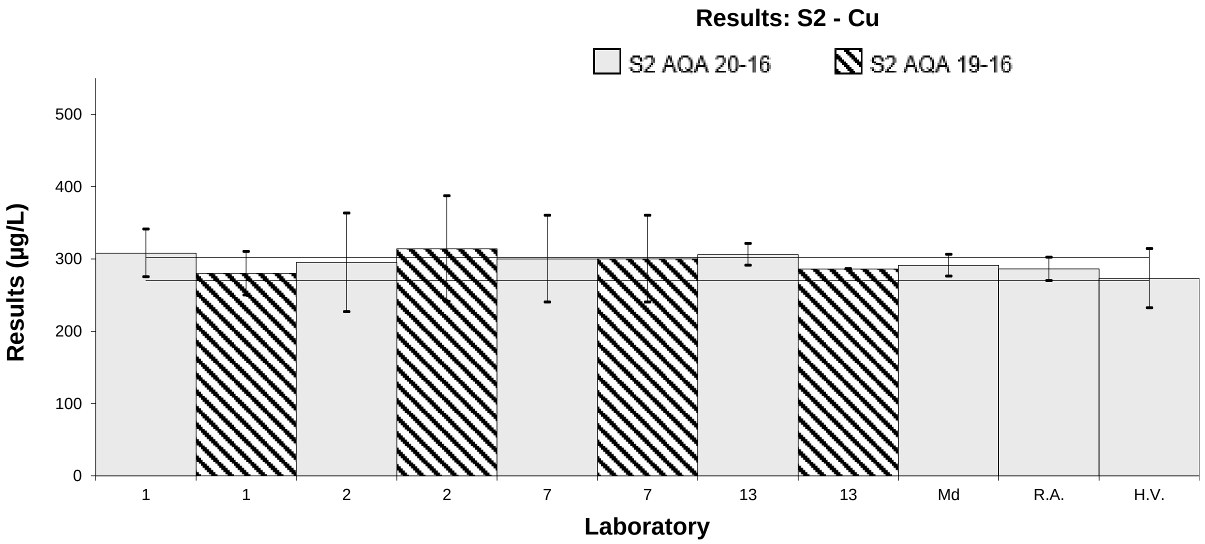
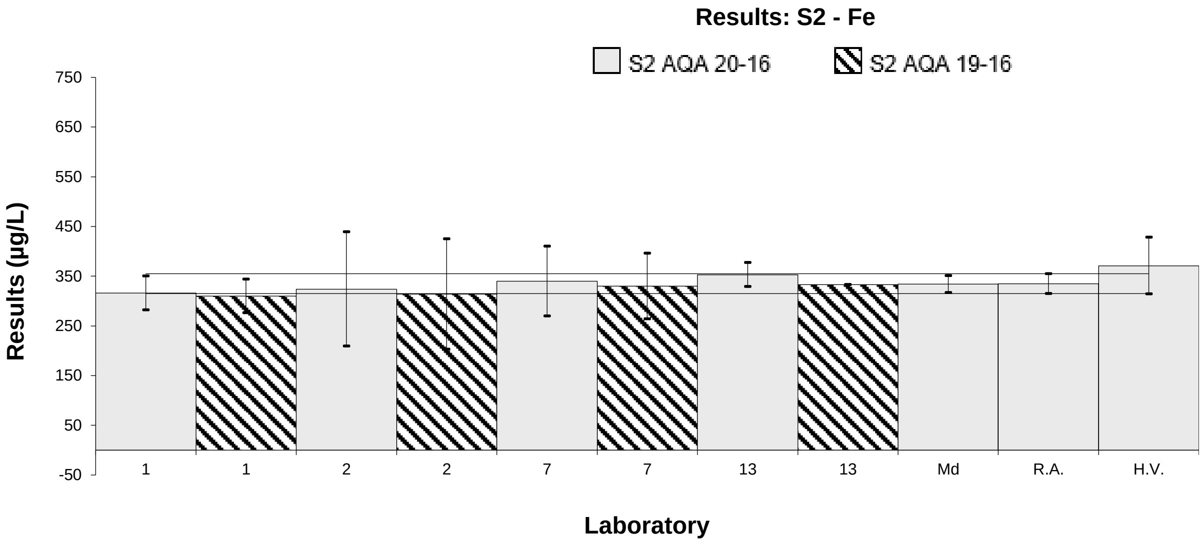
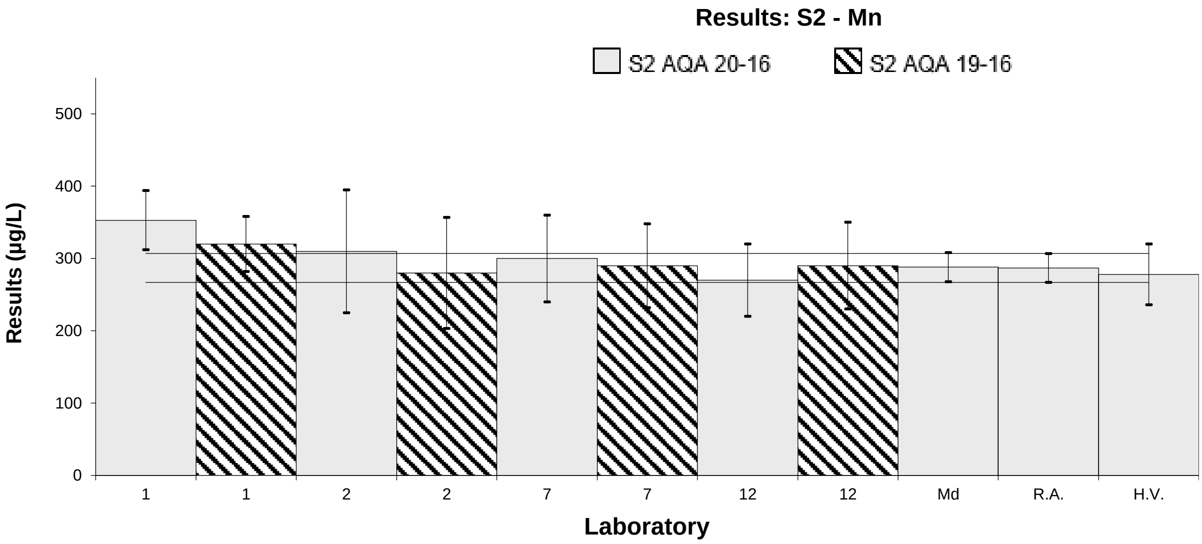


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)





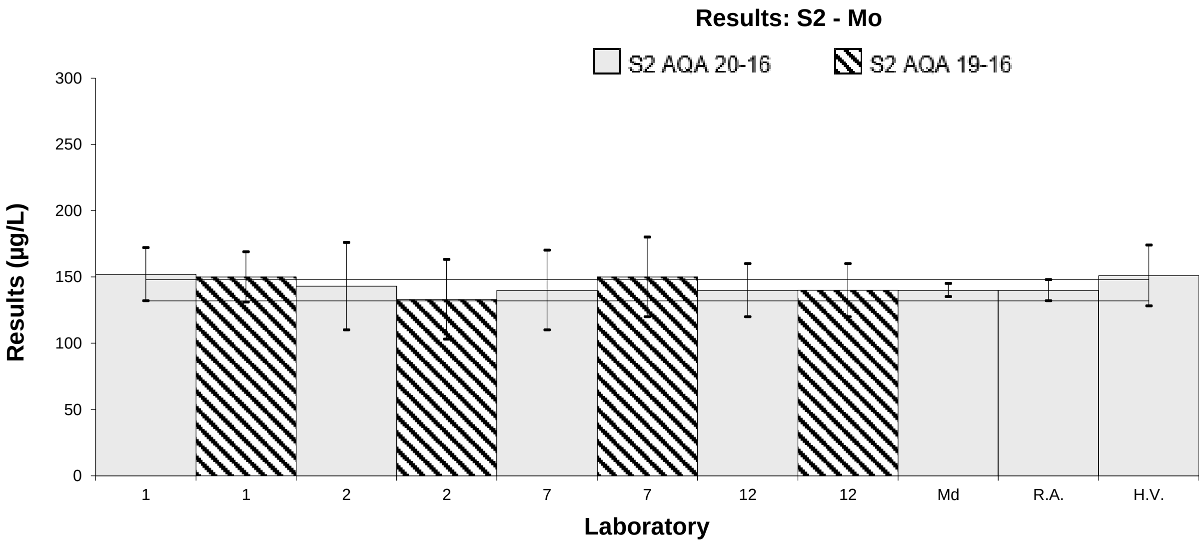
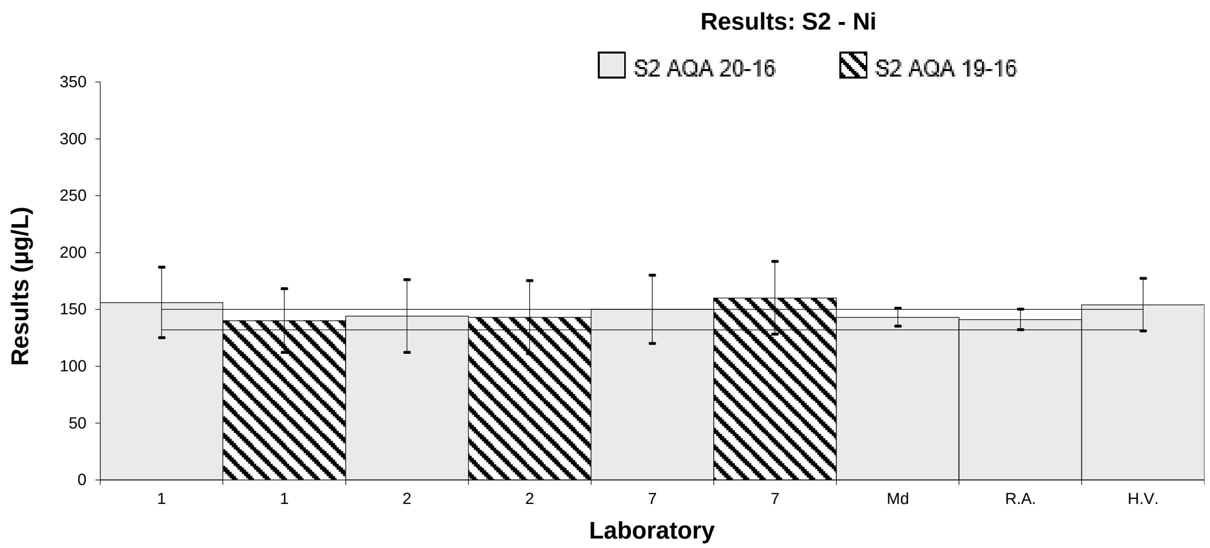
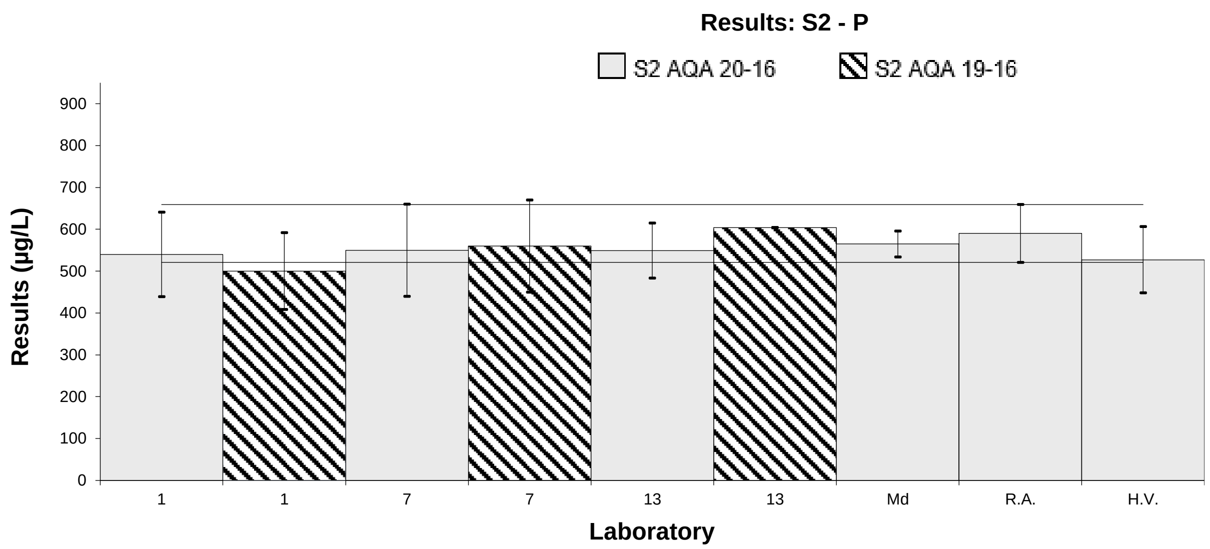


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)





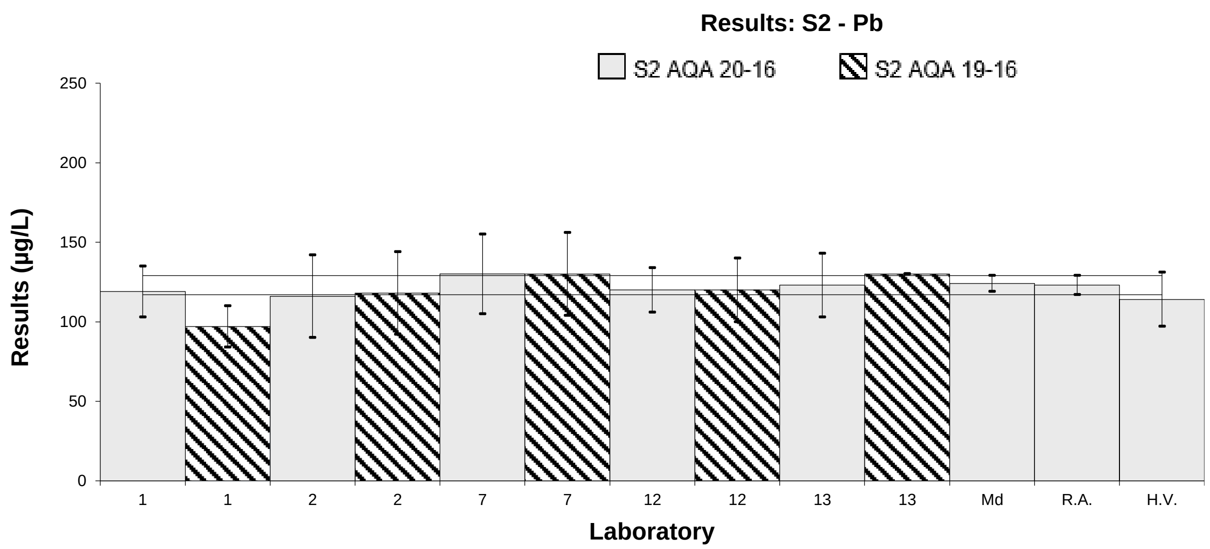
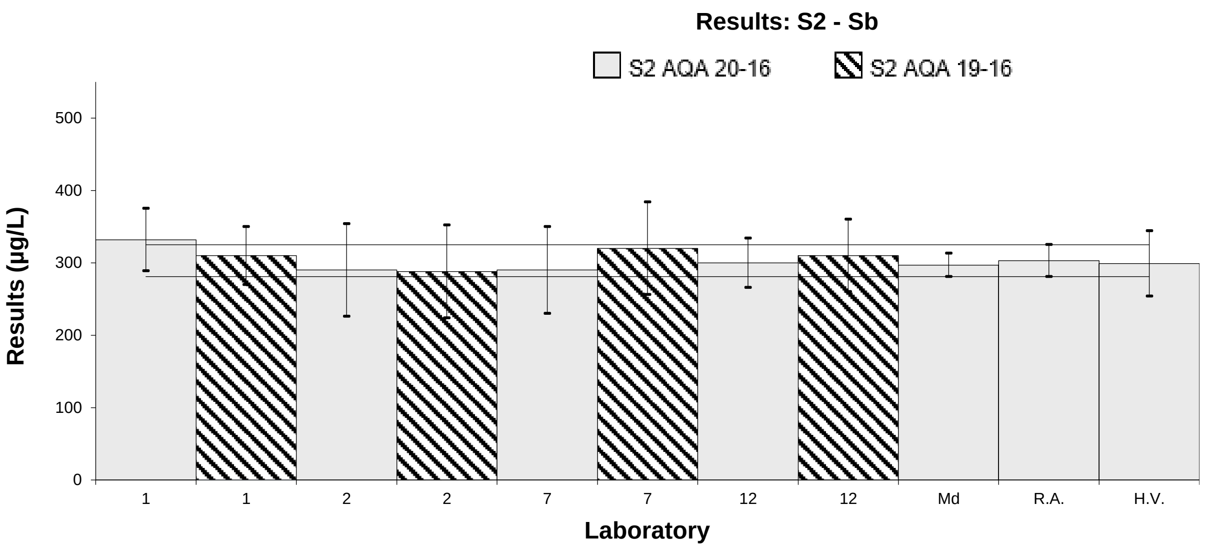
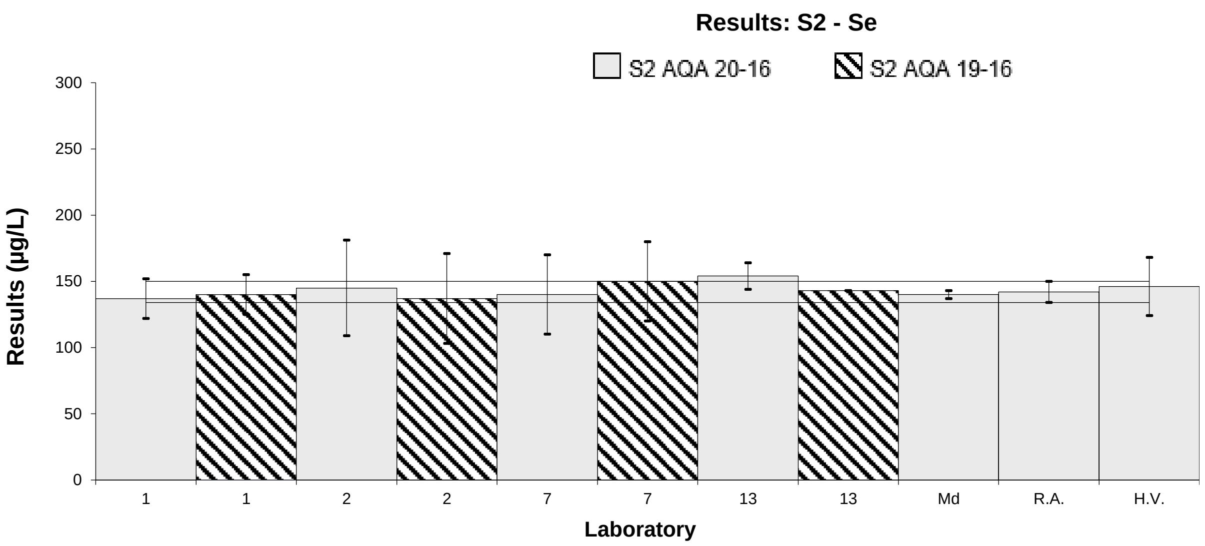


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)





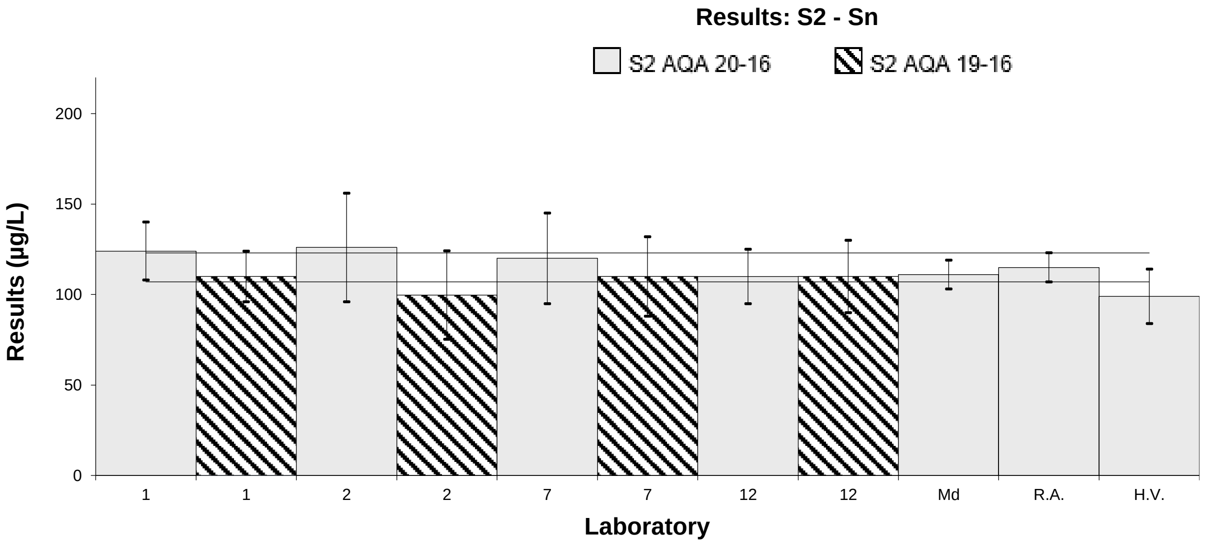
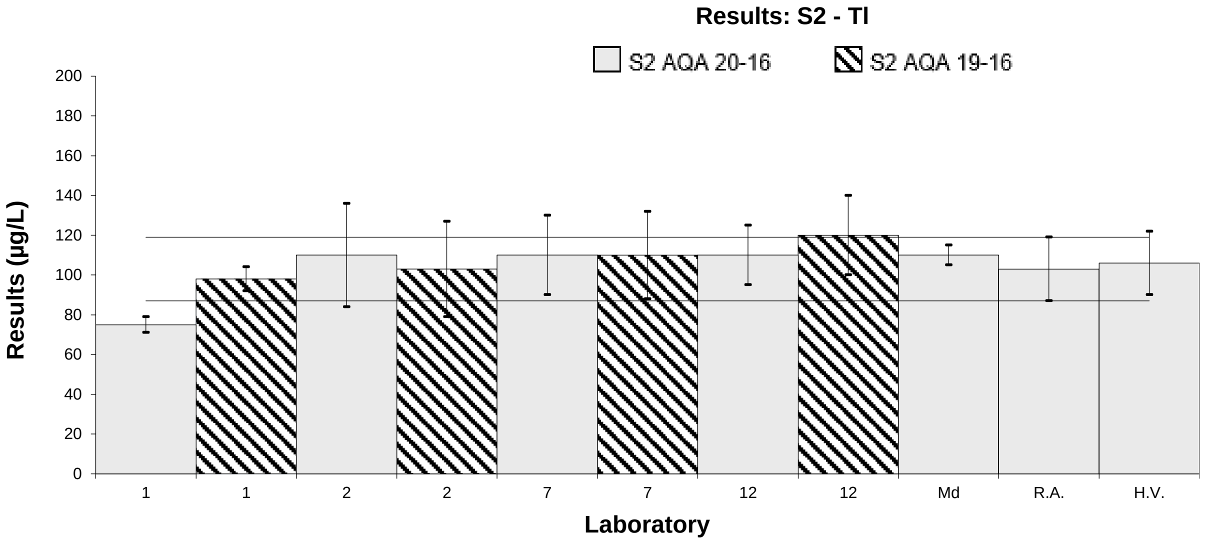
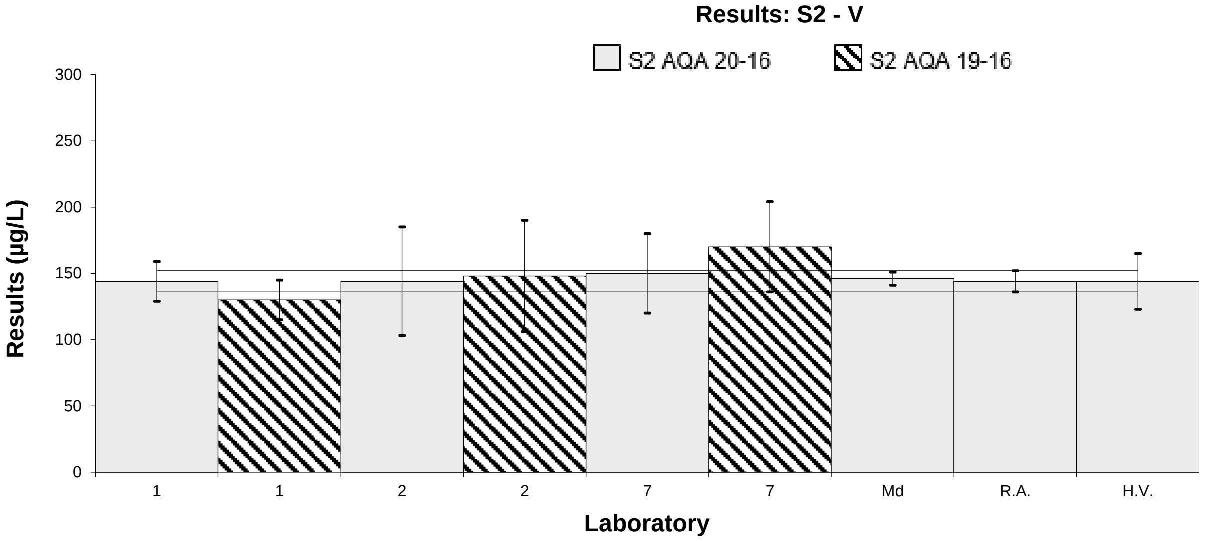


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)





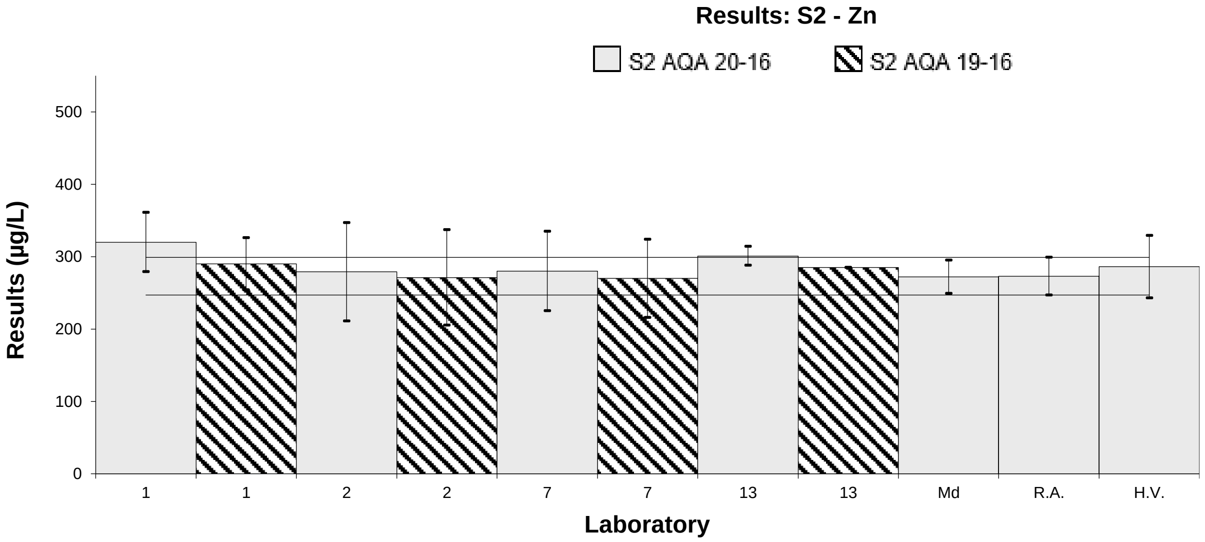


Figure 52 Bar charts of Results in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)

The same target standard deviation was used to calculate z-scores for analytes in both samples. This allowed evaluation of the within laboratory reproducibility of participants.

Scatter plots of z-scores in Sample S2 of AQA 20-16 and S2 of AQA 19-16 are presented in Figure53. Points close to the diagonal axis represent excellent reproducibility and points close to zero represent excellent reproducibility and accuracy.

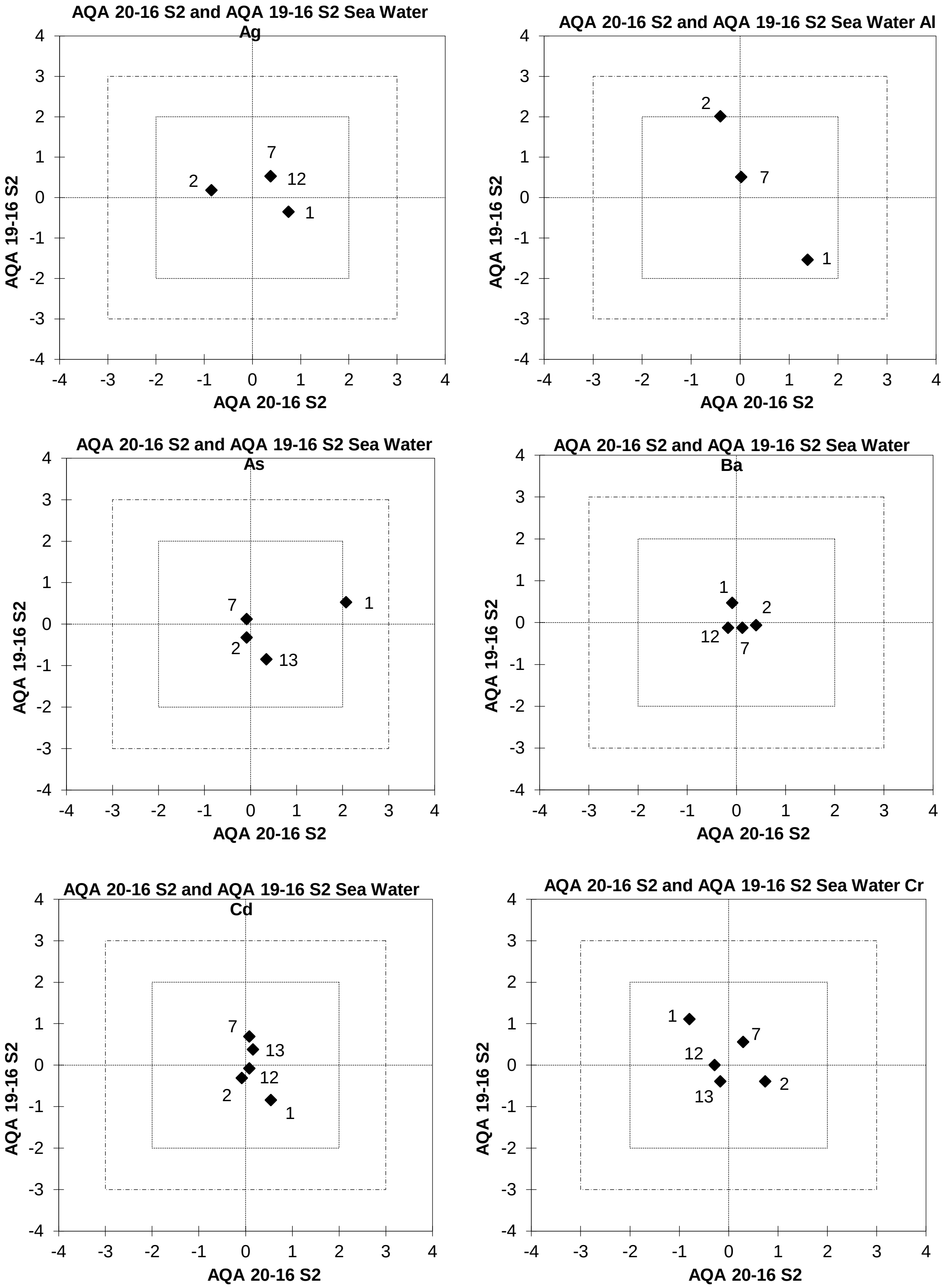


Figure 53 Scatter Plots of: z-Score in S2 of AQA 20-16 and S2 of AQA 19-16

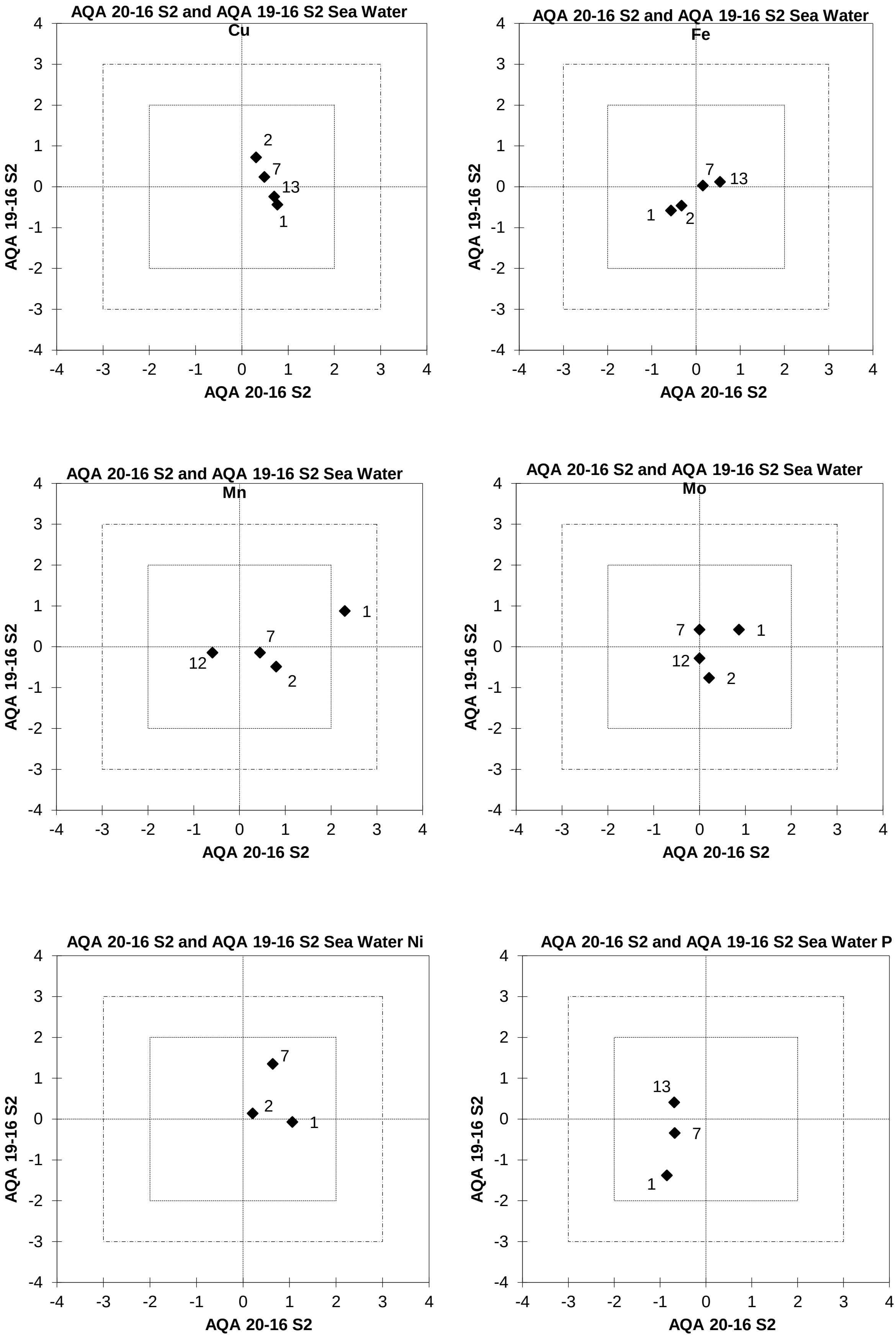


Figure 53 Scatter Plots of: z-Score in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)

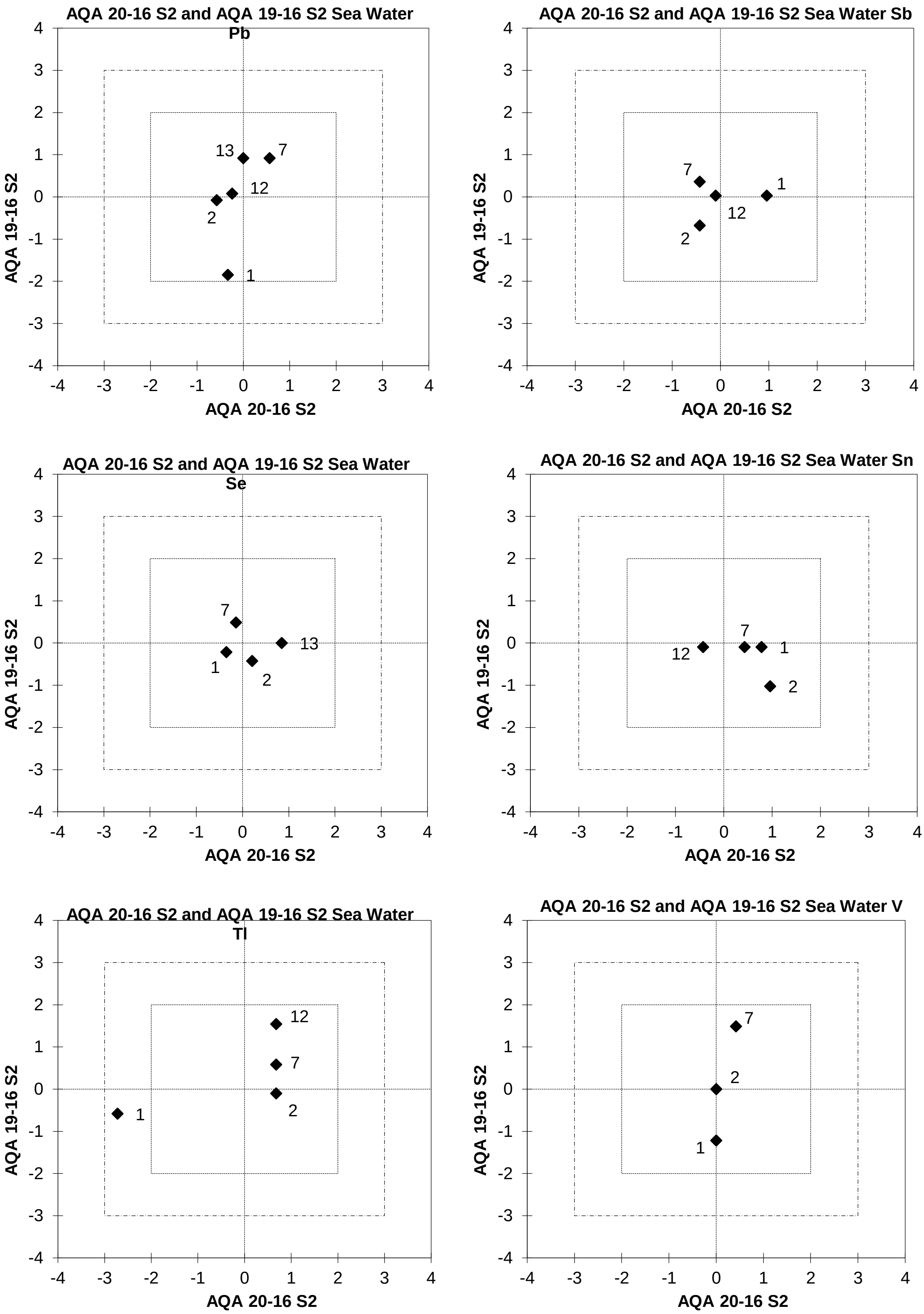


Figure 53 Scatter Plots of: z-Score in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)

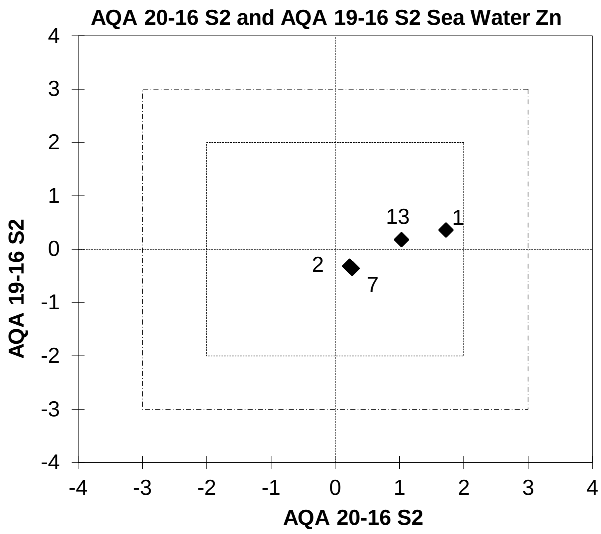


Figure 53 Scatter Plots of: z-Score in S2 of AQA 20-16 and S2 of AQA 19-16 (continued)

7.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 20-16 is the 19th NMI proficiency test of metals in seawater.

Participants' performance in measurement of metals in seawater over last ten years is presented in Figure 54. While each sample has different analytes at different concentration on average participants' performance has improved over time.

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 53).

Table 53 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CRM
2	CASS6, CRM Seawater
3	CRM – NASS 7, CASS 6 and NMI MX014
4	CASS-6
6	RM
7	CRM
10	Spiked Sample
11	RM
12	CRM – CWWTMA, CWWTMC
13	CPA Chem RM032448L25

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'*[18]

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

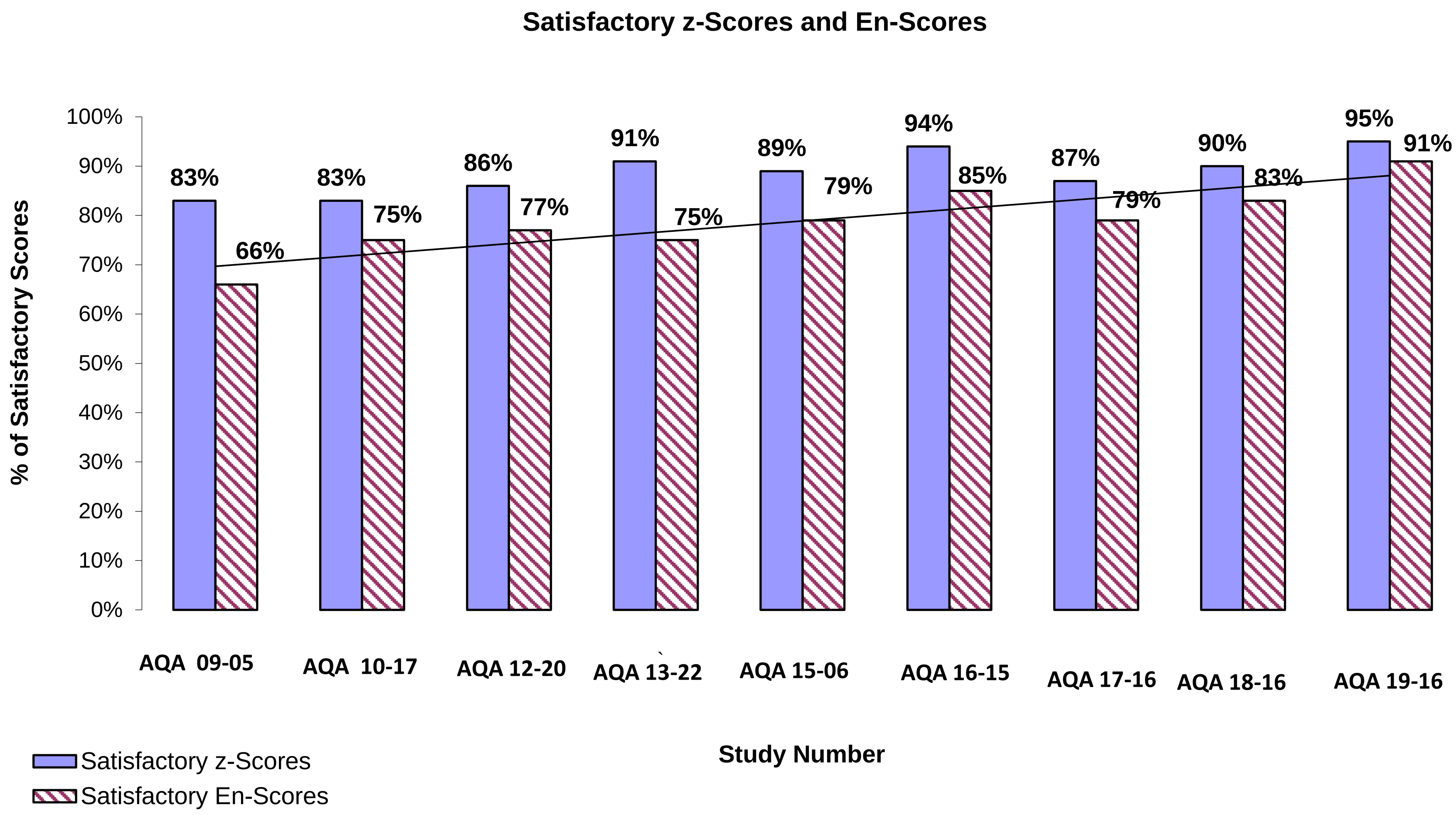


Figure 54 Participants' Performance in Metals in Seawater PT Studies over Last Ten Years

8 REFERENCES

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared from seawater. Approximately 10 L of seawater from Sydney harbour was filtered through a 0.45 µm pore size filter, stabilised by adding 2% (v/w) nitric acid and further fortified with 23 elements.

Sample S2 was an unfiltered sea water sample previously distributed as S2 of AQA 19-16. The procedures for preparation and analysis of this material were provided in the report of AQA 19-16.[6]

Sample Analysis and Homogeneity Testing

With the exception of Bi, Li and Sn in S1 and of B and Sr 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.

Sample Analysis for Dissolved and Total Elements

For analyses of total elements in Sample S2, a test portion of 30 mL was transferred to a 50 mL graduated polypropylene centrifuge tube. The samples were digested using 2 mL of nitric acid and 1 mL of hydrochloric acid on a hot block at 95±5ºC for 120 min.

Testing involved measurements using ICP-MS or ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates, sample matrix spikes and a certified reference material (MX014) 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 54.

Table 54 Instrumental Technique 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	20	107 m/z
Al	ICP-OES	Y	NA	NA	10	20	167.019 nm
As	ICP-MS	Rh	ORS	He	10	20	75 m/z
Ba	ICP-MS	Rh	ORS	He	NA	20	137 m/z
Be	ICP-MS	Rh	ORS	He	10	NA	9 m/z
Cd	ICP-MS	Rh	ORS	He	10	20	111 m/z
Co	ICP-MS	Rh	ORS	He	10	NA	59 m/z
Cr	ICP-MS	Rh	ORS	He	10	20	52 m/z
Cu	ICP-MS	Rh	ORS	He	10	20	65 m/z
Fe	ICP-OES	Y	NA	NA	10	20	259.940 nm
Hg	ICP-MS	Rh	ORS	He	10	NA	202 m/z
La	ICP-MS	Rh	ORS	He	10	NA	139 m/z
Mn	ICP-MS	Rh	ORS	He	10	20	55 m/z
Mo	ICP-MS	Rh	ORS	He	NA	20	95 m/z
Ni	ICP-MS	Rh	ORS	He	10	20	60 m/z
P	ICP-MS	Rh	ORS	HEHe	10	20	31 m/z
Pb	ICP-MS	Ir	ORS	He	10	20	208 m/z
Sb	ICP-MS	Rh	ORS	He	NA	20	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	10	20	78 m/z
Sn	ICP-MS	Rh	ORS	He	NA	20	118 m/z
Th	ICP-MS	Ir	ORS	He	10	NA	232 m/z
Tl	ICP-MS	Rh	ORS	He	10	20	205 m/z
U	ICP-MS	Ir	ORS	He	10	20	238 m/z

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Ion / Wavelength
V	ICP-MS	Rh	ORS	He	10	20	51 m/z
Zn	ICP-MS	Rh	ORS	He	10	20	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 55.

Table 55 Uncertainty of Assigned Value for Ag in Sample S1

No. results (p)	11
Robust Average	1.07 µg/L
$S_{rob\ av}$	0.15 µg/L
$u_{rob\ av}$	0.056 µg/L
k	2
$U_{rob\ av}$	0.11 µg/L

The assigned value for **Ag** in Sample S1 is **1.07 ± 0.11 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 11).

A worked example is set out below in Table 56.

Table 56 z-Score and E_n-score for Ag result reported by Laboratory 2 in S1

Ag Result µg/L	Assigned Value µg/L	Set Target Standard Deviation	z-Score	E_n-Score
1.10 ± 0.26	1.07 ± 0.11	15% as CV or 0.15 x 1.07 = = 0.1605 µg/L	$z = \frac{(1.10 - 1.07)}{0.1605}$ z = 0.19	$En = \frac{(1.10 - 1.07)}{\sqrt{0.26^2 + 0.11^2}}$ E_n = 0.11

APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10, 12] Between 2007 and 2020, NMI carried out 27 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 19 of these PTs. This data can be separated into two ranges of results: 0.001 to 0.01 mg/L and 0.01 to 0.10 mg/L. Results are presented in Tables 57 and 58.

Table 57 Laboratory X Reported Results for Ni at 0.001 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
Average				16**	

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

Table 58 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
	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
Average				9.7**	

*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 16% and 9.7% respectively. Using a coverage factor of two gives relative expanded uncertainties of 32% and 20% respectively, at a level of confidence of 95% level.

Table 59 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the ranges 0.001 – 0.01 mg/L and 0.01 – 0.10 mg/L.

Table 59 Uncertainty of Ni results estimated using PT data

Results mg/L	Uncertainty mg/L
0.00050	0.00016
0.00100	0.00032
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 4 - ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
CV_{rob}	Robust Coefficient of Variation
CVAAS	Cold Vapour Atomic Absorption Spectrometry
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
DRC	Dynamic Reaction Cell
GUM	Guide to the Expression of Uncertainty in Measurement
HEHe	High energy He mode
H.V.	Homogeneity Value
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-MS/MS	Inductively Coupled Plasma – Tandem Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view
ICP-OES-AV-buffer	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view with buffer
ICP-OES-RV	Inductively Coupled Plasma – Optical Emission Spectrometry- radial view
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
NATA	National Association of Testing Authorities
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
PFAS	Polyfluoroalkyl Substances
PT	Proficiency Test
RM	Reference Material
SD_{rob}	Robust Standard Deviation
SI	The International System of Units
SS	Spiked sample
S.V.	Spiked or formulated concentration of a PT sample
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation (symbol: σ)
UC	Universal Cell
VGA-ICP-OES	Vapour Generation Accessory – Inductively Coupled Plasma – Optical Emission Spectrometry

APPENDIX 5 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 60 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						
2	ICP-MS	Rh	ORS	He	1.05	10	107
3	ICP-MS	Rh	NA	NA	1	NA	109
4	ICP-MS/MS				10	10	107
5	ICP-MS	Y 89	KED	He	1	10	107
6	ICP-MS	Rh	ORS	NA	10	10	107
7	ICP-MS	Rh	ORS	He	10	10	107
8	ICP-MS	103	ORS	He	1	NA	107
10	ICP-MS	Rh	KED	He	20	NA	109
11	ICP-MS	Yes	ORS	He	10	NA	107
12	ICP-MS	In		standard mode	10	10	107
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Y	ORS	N2O	2	2	109/109
15	ICP-MS	In			1	1	107

Table 61 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-OES-AV						
2	ICP-MS	Ge	ORS	He	1.05	10	27
3	ICP-MS	Sc	NA	NA	1	NA	27
4	ICP-OES-AV				10	10	167
5	ICP-MS	Sc-2 45	KED	He	1	10	27
6	ICP-MS	Sc	ORS	He	10	10	27
7	ICP-OES-AV	Y	NA	NA	2	2	167.019
8	ICP-MS	45	ORS	He	1	NA	27
10	ICP-MS	Sc	KED	He	20	NA	27
11	ICP-MS	Yes	ORS	He	10	NA	27
12	ICP-OES-AV-buffer	Y	NA	NA	1	1	308.215
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Sc	ORS	He	2	2	271
15	ICP-OES-AV	In			1	1	396.152

Table 62 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						
2	ICP-MS	Ge	ORS	He	1.05	10	75
3	ICP-MS	Rh	KED	He	1	NA	75
4	ICP-MS/MS		ORS	He	10	10	75
5	ICP-MS	Ge-1 72	KED	He	1	10	75
6	ICP-MS	Rh	ORS	He	10	10	75
7	ICP-MS	Rh	ORS	He	10	10	75
8	ICP-MS	72	ORS	HEHe	1	NA	75
10	ICP-MS	Te	DRC	NH3	20	NA	75
11	ICP-MS	Yes	ORS	He	10	NA	75
12	ICP-MS	Ge	KED	He	10	10	75
13	ICP-MS	Ga	DRC	O2	25	25	90.9165
14	ICP-MS/MS	Y	ORS	N2O	2	2	75/92
15	ICP-MS/MS	Rh	ORS	O2	5	5	91

Table 63 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				NA		
2	ICP-OES-AV	Lu			NA	10	208.957
3	NA	NA	NA	NA	NA	NA	NA
4					NA	10	
5	ICP-MS	Sc-2 45	KED	He	NA	100	11
6	NT	NT	NT	NT	NT	NT	NT
7	ICP-OES-AV	Y	NA	NA	NA	NA	NA
8	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV-buffer	Y	NA	NA	NA	1	208.954
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Sc	ORS	NA	NA	2	11
15	ICP-OES-AV	Rh			NA	1	249.773

Table 64 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				NA		
2	ICP-MS	Ir	ORS	He	NA	10	137
3	NA	NA	NA	NA	NA	NA	NA
4	ICP-OES-AV				NA	10	137
5	ICP-MS	In-1 115	KED	He	NA	10	138
6	ICP-MS	Tb	ORS	NA	NA	10	135
7	ICP-MS	Rh	ORS	He	NA	10	134
8	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	In		standard mode	NA	10	137
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Rh	ORS	He	NA	2	137
15	ICP-MS	In			NA	1	137

Table 65 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					NA	
2	ICP-MS	Li6		standard mode	1.05	NA	9
3	ICP-MS	Sc	NA	NA	1	NA	9
4	ICP-MS/MS		ORS		10	NA	9
5	ICP-MS	Sc-2 45	KED	He	1	NA	9
6	ICP-MS	6Li	ORS	NA	10	NA	9
7	ICP-MS	Sc	ORS	He	10	NA	9
8	ICP-MS	45	ORS	He	1	NA	9
10	NA	NA	NA	NA	NA	NA	NA
11	ICP-MS	Yes	ORS	He	10	NA	9
12	ICP-MS	Sc		standard mode	10	NA	9
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Sc	ORS	NA	2	NA	9
15	ICP-MS	Li			10	NA	9

Table 66 Instrument Conditions Bi

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					NA	
2	ICP-MS	Ir	ORS	He	1.05	NA	209
3	ICP-MS	Ir	NA	NA	1	NA	209
4						NA	
5						NA	
6	NT	NT	NT	NT	NT	NT	NT
7	ICP-MS	Ir	ORS	He	10	NA	209
8	ICP-MS	193	ORS	He	1	NA	209
10	ICP-MS	Tb	KED	He	20	NA	209
11	ICP-MS	Yes	ORS	He	10	NA	NA
12	NA					NA	
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ir	ORS	He	2	NA	209
15	NA				1	NA	

Table 67 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						
2	ICP-MS	In	ORS	He	1.05	10	111
3	ICP-MS	Rh	NA	NA	1	NA	111
4	ICP-MS/MS		ORS	ORS	10	10	111
5	ICP-MS	In-1 115	KED	He	1	10	111
6	ICP-MS	Rh	ORS	NA	10	10	111
7	ICP-MS	Rh	ORS	He	10	10	111
8	ICP-MS	103	ORS	He	1	NA	114
10	ICP-MS	Rh	KED	He	20	NA	111
11	ICP-MS	Yes	ORS	He	10	NA	111
12	ICP-MS	In	NA	standard mode	10	10	111
13	ICP-MS	Rh	NA	standard mode	25	NA	110.904
14	ICP-MS/MS	Rh	ORS	N2O	2	2	111/111
15	ICP-MS	In			1	1	111

Table 68 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					NA	
2	ICP-MS	Ge	ORS	He	1.05	NA	59
3	ICP-MS	Rh	KED	He	1	NA	59
4	ICP-MS/MS		ORS	ORS		NA	59
5	ICP-MS	Sc 45	KED	He	1	NA	7
6	ICP-MS	Sc	ORS	He	10	NA	59
7	ICP-MS	Rh	ORS	He	10	NA	59
8	ICP-MS	115	ORS	He	1	NA	59
10	ICP-MS	Ga	KED	He	20	NA	59
11	ICP-MS	Yes	ORS	He	10	NA	59
12	ICP-MS	Sc	KED	He	10	NA	59
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Y	ORS	He	2	NA	59
15	ICP-MS/MS	Rh	ORS	He	1	NA	59

Table 69 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						
2	ICP-MS	Ge	ORS	He	1.05	1.05	52
3	ICP-MS	Sc	KED	He	1	NA	52
4	ICP-MS/MS		ORS	ORS	10	10	52
5	ICP-MS	Sc 45	KED	He	1	10	52
6	ICP-MS	Sc	ORS	He	10	10	52
7	ICP-MS	Rh	ORS	He	10	10	52
8	ICP-MS	72	ORS	He	1	NA	52
10	ICP-MS	Ga	DRC	NH3	20	NA	52
11	ICP-MS	Yes	ORS	He	10	NA	52
12	ICP-MS	Ga	DRC	NH3	10	10	52
13	ICP-MS	Ga	KED	He	25	25	51.9405
14	ICP-MS/MS	Sc	ORS	He	2	2	52
15	ICP-MS/MS	Rh	ORS	He	1	1	52

Table 70 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						
2	ICP-MS	Ge	ORS	He	1.05	1.05	63
3	ICP-MS	Rh	KED	He	1	NA	65
4	ICP-MS/MS		ORS	ORS	10	10	63
5	ICP-MS	Sc 45	KED	He	1	10	63
6	ICP-MS	Sc	ORS	He	10	10	63
7	ICP-MS	Rh	ORS	He	10	10	63
8	ICP-MS	103	ORS	He	1	NA	65
10	ICP-MS	Rh	KED	He	20	NA	63
11	ICP-MS	Yes	ORS	He	10	NA	63
12	ICP-MS	Sc	KED	He	10	10	63
13	ICP-MS	Ga	KED	He	25	25	62.9298
14	ICP-MS/MS	Y	ORS	He	2	2	65
15	ICP-MS/MS	Rh	ORS	He	1	1	63

Table 71 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-OES-AV						
2	ICP-MS	Ge	ORS	He	1.05	1.05	56
3	ICP-MS	Sc	KED	He	1	NA	56
4							
5	ICP-MS	Sc 45	KED	He	10	10	56
6	ICP-MS	Sc	ORS	He	10	10	56
7	ICP-MS	Y	NA	NA	2	2	238.204
8	ICP-MS	72	ORS	He	1	NA	56
10	ICP-MS	Ga	DRC	NH3	20	NA	54
11	ICP-MS	Yes	ORS	He	10	NA	56
12	ICP-OES-AV-buffer	Y	NA	NA	1	1	259.941
13	ICP-MS	Ga	DRC	NH3	25	25	53.9396
14	ICP-MS/MS	Sc	ORS	N2O	2	2	56/72
15	ICP-OES-AV	Rh			1	1	238.204

Table 72 Instrument Conditions Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	CVAAS					NA	
2	CVAFS				10	NA	253.7
3	ICP-MS	Ir	NA	NA	1	NA	201
4						NA	
5	ICP-MS	Ir 193	KED	He	1	NA	202
6	CVAAS	NA	NA	NA	10	NA	253 nm
7	CVAFS	NA	NA	NA	2	NA	NA
8	VGA-ICP-OES				1	NA	194.164
10	CVAFS	NA	NA	NA	5	NA	NA
11	ICP-MS	Yes	ORS	He	10	NA	201
12	CVAAS	NA	NA	NA	1	NA	253.7
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ir	ORS	N2O	2	NA	201/201
15	NA				1	NA	

Table 73 Instrument Conditions La

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					NA	
2	ICP-MS	Ir	ORS	He	1.05	NA	139
3	NA	NA	NA	NA	NA	NA	NA
4						NA	
5						NA	
6	ICP-MS	Tb	ORS	NA	10	NA	139
7	ICP-MS	Rh	ORS	He	10	NA	139
8						NA	
10	ICP-MS	Tb	KED	He	20	NA	139
11	ICP-MS	Yes	ORS	He	10	NA	139
12	NA					NA	
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ir	ORS	N2O	2	NA	139/155
15	ICP-MS	In			1	NA	139

Table 74 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-MS					NA	
2	ICP-MS	Li6		standard mode	1.05	NA	7
3	ICP-MS	Sc	NA	NA	1	NA	7
4	ICP-MS/MS				10	NA	7
5	ICP-MS	Sc-2 45	KED	He	10	NA	7
6	NT	NT	NT	NT	NT	NT	NT
7	ICP-MS	Sc	ORS	He	10	NA	7
8	ICP-OES-AV	Lu			5	NA	670.783
10	ICP-MS	Sc	KED	He	20	NA	7
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc		standard mode	10	NA	7
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Sc	ORS	NA	2	NA	7
15	ICP-OES-AV	In			1	NA	670.784

Table 75 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						
2	ICP-MS	Ge	ORS	He	1.05	1.05	55
3	ICP-MS	Sc	KED	He	1	NA	55
4	ICP-MS/MS		ORS	ORS	10	10	55
5	ICP-MS	Sc-2 45	KED	He	1	10	55
6	ICP-MS	Sc	ORS	He	10	10	55
7	ICP-MS	Rh	ORS	He	10	10	55
8	ICP-MS	72	ORS	He	1	NT	55
10	ICP-MS	Ga	DRC	NH3	20	NA	55
11	ICP-MS	Yes	ORS	He	10	NA	55
12	ICP-MS	Sc	KED	He	10	10	55
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Sc	ORS	He	2	2	55
15	ICP-MS/MS	Rh	ORS	He	5	5	55

Table 76 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				NA		
2	ICP-MS	Ge	ORS	He	NA	10	95
3	NA	NA	NA	NA	NA	NA	NA
4	ICP-MS/MS		ORS	ORS	NA	10	95
5	ICP-MS	Y 89	KED	He	NA	10	98
6	ICP-MS	Rh	ORS	He	NA	10	95
7	ICP-MS	Rh	ORS	He	NA	10	35
8	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV-buffer	Y	NA	NA	NA	1	202.095
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Y	ORS	He	NA	2	95
15	ICP-MS	Y			NA	1	95

Table 77 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						
2	ICP-MS	Ge	ORS	He	1.05	1.05	60
3	ICP-MS	Rh	KED	He	1	NA	60
4	ICP-MS/MS		ORS	ORS	10	10	60
5	ICP-MS	Sc 45	KED	He	1	10	60
6	ICP-MS	Sc	ORS	He	10	10	60
7	ICP-MS	Rh	ORS	He	10	10	60
8	ICP-MS	103	ORS	He	1	NT	60
10	ICP-MS	Ga	KED	He	20	NA	60
11	ICP-MS	Yes	ORS	He	10	NA	60
12	ICP-MS	Sc	KED	He	10	10	60
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Y	ORS	N2O	2	2	60/60
15	ICP-MS/MS	Rh	ORS	He	1	1	60

Table 78 Instrument Conditions P

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV						
2							
3	NA	NA	NA	NA	NA	NA	NA
4							
5							
6	NT	NT	NT	NT	NT	NT	NT
7	ICP-OES-AV	Y	NA	NA	2	2	213.618
8						NA	
10	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV-buffer	Y	NA	NA	1	1	177.495
13	ICP-MS	Be	NA	standard mode	25	25	30.9938
14	ICP-MS/MS	Sc	ORS	He	2	2	31
15	ICP-OES-AV	Rh			1	1	178.284

Table 79 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						
2	ICP-MS	Ir	ORS	He	1.05	1.05	208
3	ICP-MS	Ir	NA	NA	1	NA	206+207+208
4	ICP-MS/MS		ORS		10	10	
5	ICP-MS	Ir 193	KED	He	1	10	208
6	ICP-MS	Ir	ORS	NA	10	10	208
7	ICP-MS	Ir	ORS	He	10	10	208
8	ICP-MS	103	ORS	He	1	NT	208
10	ICP-MS	Tb	KED	He	20	NA	206+207+208
11	ICP-MS	Yes	ORS	He	10	NA	208
12	ICP-MS	Ir		standard mode	10	10	208
13	ICP-MS	Lu	NA	standard mode	25	25	207.977
14	ICP-MS/MS	Ir	ORS	He	2	2	208
15	ICP-MS	Bi			1	1	sum(204,206,207,208)

Table 80 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				NA		
2	ICP-MS	In	ORS	He	NA	10	120
3	NA	NA	NA	NA	NA	NA	NA
4					NA	10	
5					NA		
6	ICP-MS	Rh	ORS	NA	NA	10	121
7	ICP-MS	Rh	ORS	He	NA	10	121
8	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	In		standard mode	NA	10	121
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Rh	ORS	N2O	NA	2	121/121
15	ICP-MS	In			1	1	121

Table 81 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						
2	ICP-MS	Ge	ORS	H2	1.05	10	78
3	ICP-MS	Rh	DRC	NH3	1	NA	82
4	ICP-MS/MS		ORS	H2	10	10	78
5	ICP-MS	Ge-1 72	KED	He	1	10	78
6	ICP-MS	Rh	ORS	He	10	10	78
7	ICP-MS	Rh	ORS	He	10	10	78
8	ICP-MS	103	ORS	HEHe	1	NT	78
10	ICP-MS	Te	DRC	NH3	20	NA	82
11	ICP-MS	Yes	ORS	He	10	NA	78
12	ICP-MS	Ge	DRC	NH3	10	10	82
13	ICP-MS	Ga	DRC	NH3	25	25	81.9167
14	ICP-MS/MS	Y	ORS	N2O	2	2	80/96
15	ICP-MS/MS	Rh	ORS	O2	5	5	94

Table 82 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						
2	ICP-MS	In	ORS	He	1.05	10	118
3	NA	NA	NA	NA	NA	NA	NA
4	ICP-MS/MS				10	10	118
5	ICP-MS	In-1 115	KED	He	1	10	118
6	NT	NT	NT	NT	NT	NT	NT
7	ICP-MS	Rh	ORS	He	10	10	118
8	ICP-MS	115	ORS	He	1	NT	118
10	ICP-MS	Rh	KED	He	20	NA	120
11	ICP-MS	Yes	ORS	He	10	NA	118
12	ICP-MS	In		standard mode	10	10	118
13	ICP-MS	Rh	KED	He	25	25	117.902
14	ICP-MS/MS	Rh	ORS	N2O	2	2	118
15	ICP-MS	In			1	1	118

Table 83 Instrument Conditions Sr

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				NA		
2	ICP-OES-AV	Lu			NA	10	421.552
3	NA	NA	NA	NA	NA	NA	NA
4					NA		
5	ICP-MS	Y 89	KED	He	NA	100	88
6	NT	NT	NT	NT	NT	NT	NT
7	ICP-OES-AV	Y	NA	NA	NA	2	421.552
8	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV-buffer	Y	NA	NA	NA	1	407.771
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Y	ORS	He	NA	2	88
15	ICP-OES-AV	In			NA	10	407.771

Table 84 Instrument Conditions Th

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					NA	
2						NA	
3	ICP-MS	Ir	NA	NA	1	NA	232
4						NA	
5						NA	
6	ICP-MS	Ir	ORS	NA	10	NA	232
7	ICP-MS	Ir	ORS	He	10	NA	232
8						NA	
10	NA	NA	NA	NA	NA	NA	NA
11	ICP-MS	Yes	ORS	He	10	NA	232
12	NA					NA	
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ir	ORS	He	2	NA	232
15	ICP-MS	Bi			1	NA	232

Table 85 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						
2	ICP-MS	Ir	ORS	He	1.05	10	205
3	ICP-MS	Ir	NA	NA	1	NA	205
4							
5							
6	ICP-MS	Ir	ORS	NA	10	10	205
7	ICP-MS	Ir	ORS	He	10	10	205
8	ICP-MS	193	ORS	He	1	NA	205
10	ICP-MS	Tb	KED	He	20	NA	205
11	ICP-MS	Yes	ORS	He	10	NA	205
12	ICP-MS	Ir		standard mode	10	10	203
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ir	ORS	He	2	2	205
15	ICP-MS	Bi			1	1	205

Table 86 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						
2							
3	ICP-MS	Ir	NA	NA	1	NA	238
4	ICP-MS/MS						238
5	ICP-MS	Ir 193	KED	He	1	10	238
6	ICP-MS	Ir	ORS	NA	10	10	238
7	ICP-MS	Ir	ORS	He	10	10	238
8	ICP-MS	103	ORS	He	1	NA	238
10	ICP-MS	Tb	KED	He	20	NA	238
11	ICP-MS	Yes	ORS	He	10	NA	238
12	NA						
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ir	ORS	He	2	2	238
15	ICP-MS	Bi			1	1	238

Table 87 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-OES-AV						
2	ICP-MS	Ge	ORS	He	1.05	10	51
3	ICP-MS	Sc	KED	He	1	NA	51
4	ICP-MS/MS		ORS	He	10	10	51
5	ICP-MS	Sc 45	KED	He	1	10	51
6	ICP-MS	Sc	ORS	He	10	10	51
7	ICP-MS	Rh	ORS	He	10	10	51
8	ICP-MS	45	ORS	He	1	NT	51
10	ICP-MS	Ga	DRC	NH3	20	NA	51
11	ICP-MS	Yes	ORS	He	10	NA	51
12	ICP-MS	Ga	DRC	NH3	10	10	51
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Sc	ORS	N2O	2	2	51/67
15	ICP-MS/MS	Rh	ORS	He	5	5	51

Table 88 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-OES-AV						
2	ICP-MS	Ge	ORS	He	1.05	1.05	68
3	ICP-MS	Rh	KED	He	1	NA	66
4	ICP-MS/MS			He	10	10	66
5	ICP-MS	Sc 45	KED	He	1	10	66
6	ICP-MS	Sc	ORS	He	10	10	66
7	ICP-MS	Rh	ORS	He	10	10	64
8	ICP-MS	103	ORS	He	1	NT	66
10	ICP-MS	Te	DRC	NH3	20	NA	66
11	ICP-MS	Yes	ORS	He	10	NA	66
12	ICP-MS	Sc	KED	He	10	10	66
13	ICP-MS	Ga	KED	He	25	25	65.926
14	ICP-MS/MS	Y	ORS	He	2	2	66
15	ICP-MS/MS	Rh	ORS	He	1	1	66

END OF REPORT