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Department of Industry,
Science and Resources

National
Measurement
Institute

Proficiency Test Final Report AQA 24-17 Trace Elements in River and Sea Water

February 2025

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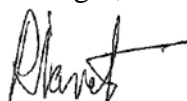
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Summary

This report presents the results of the proficiency test AQA 24-17, Trace Elements in River and Sea Water. The study focused on the measurement of dissolved Ag, Al, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, U, V and Zn in river water and of dissolved Ag, Al, As, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Sb, Se, Sn, Tl, U, V and Zn in sea water.

The assigned values were the robust averages of participants' results for all samples except for P in S2. The associated uncertainties were estimated from the robust standard deviation of participants' results. The assigned value for P in S2 was a reference value measured using standard addition inductively couple plasma mass spectrometry (SA-ICP-MS).

Laboratory 8 requested Sample S2 only, but they entered results against Sample S1 on the results' sheet. For this reason, all results from this laboratory have been marked as extreme outliers; they were excluded from the robust average calculation and from the calculation of all summary statistics

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

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

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

Of 669 scored results, 622 (93%) returned an acceptable score of $|z| \leq 2.0$.

Of 669 scored results, 588 (88%) returned an acceptable score of $|En| < 1.0$.

Laboratory 20 reported results for all 40 tests in the two study samples and returned acceptable z-scores for 39 of the tests.

Laboratory 20 also had the highest number of acceptable En-scores, 39 out of 40 reported.

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

Overall, the between-laboratory CVs of the sea water Sample S2 were higher than those of the river water sample S1.

Pb, Se, Cr and Zn in sea water were the tests which most challenged participants' analytical techniques when compared to the river water sample.

Cr in sea water was the test which challenged most participants' analytical techniques.

As in previous studies a limited number of laboratories reported numerical results for P in S2 highlighting the difficulties in analysis.

Reporting results with an insufficient number of significant figures may explain some of the unacceptable z-scores.

For Se measurements, most participants used ICP-MS in reaction mode with H₂ or NH₃. One laboratory reported using ICP-MS/MS in reaction mode with O₂ as reaction gas. The unacceptable results reported for Se in sea water were from ICP-MS or ICP-MS/MS in collision mode.

- iii. *evaluate within-laboratory precision reproducibility*

AQA 24-17 S2 was the same as the previously prepared sample, AQA 23-18 S1.

In some cases, the results reported for these tests in the two study samples were significantly different.

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

AQA 24-17 is the 35th NMI proficiency study of metals in water. Over last 10 years, the average proportion of acceptable scores was 92% for z-scores and 84% for E_n-scores.

This is the first study when the results reported for P in sea water at a level close to 100 µg/L have been in good agreement with each other and with the spike value.

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

All 669 numerical results were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.47% to 625% of the reported value.

An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 4.

- 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.

A certified reference material for metals in sea water (MX014) with reference values traceable to SI is also available for sale from NMI (<https://www.industry.gov.au/national-measurement-institute/nmi-services/chemical-and-biological-measurement-services/chemical-reference-materials/matrix-reference-materials>).

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

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

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

AQA 24-17 is the 35th NMI proficiency study of metals in water.

1.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories methods used in determination of inorganic analytes in river and sea water;
- evaluate within-laboratory precision reproducibility;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.² The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.³ These documents have been prepared with reference to ISO Standard 17043¹ 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 17043:2023 as a provider of proficiency testing schemes. This proficiency test is within the scope of NMI's accreditation.

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The 40 tests in two water samples were selected from those for which an investigation level is published in Australian and New Zealand Guidelines for Fresh and Marine Water Quality⁵ and are commonly measured by water testing laboratories.

2.2 Participation

Twenty-three laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued:	23 September 2024
Samples dispatched:	21 October 2024
Results due:	15 November 2024
Interim report issued	22 November 2024
Preliminary report issued:	25 November 2024

2.3 Test Material Specification

Two samples were provided for analysis:

Sample S1 was 100 mL of filtered and fortified river water preserved by adding acid; and

Sample S2 was 100 mL of filtered and fortified sea water preserved by adding acid, previously distributed as Sample S1 of proficiency testing study AQA 23-18.⁶

2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.5 Sample Preparation, Analysis and Homogeneity Testing

The same validated preparation procedure was followed as in previous studies.² Test samples from previous studies were demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. However a partial homogeneity test was conducted for all tests in Sample S1 with the exception of Al. The results of the partial homogeneity test are reported in this study as the homogeneity values.

No homogeneity test was conducted for Sample S2. Homogeneity of this sample has been previously demonstrated in AQA 23-18.⁶

The preparation and analysis are described in Appendix 1.

2.6 Stability of Analytes

No stability study was carried out for Samples S1 and S2. Stability studies conducted for similar previous studies of metals in river and sea water found no significant changes. NMI also produced a Certified Reference Material MX014 for metals in sea water for which long term stability (over 10 years) has been demonstrated.

2.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were refrigerated before dispatch.

The samples were dispatched by courier on 21 October 2024.

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

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

2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.

- If analyses cannot be commenced on the day of receipt, please store the samples chilled.
- Participants are asked to report results in units of µg/L for:

SAMPLE S1 river water		SAMPLE S2 sea water	
Test DISSOLVED	Estimated Value µg/L	Test DISSOLVED	Estimated Value µg/L
Ag	0.5-20	Ag	0.5-20
Al	Not Available	Al	0.5-20
As	0.5-20	As	0.5-20
Be	0.5-20	Be	0.5-20
Cd	0.5-20	Cd	0.5-20
Co	0.5-20	Cr	0.5-20
Cr	0.5-20	Cu	0.5-20
Cu	0.5-20	Fe	5-200
Fe	50-1000	Hg	0.05-2
Hg	0.25-10	Mn	0.5-20
Mn	5-200	Ni	0.5-20
Mo	0.5-20	P	5-200
Ni	0.5-20	Pb	0.5-20
Pb	0.5-20	Sb	0.5-20
Sb	0.5-20	Se	0.5-20
Se	0.5-20	Sn	0.5-20
Tl	0.5-20	Tl	0.5-20
U	0.5-20	U	0.5-20
V	0.5-20	V	0.5-20
Zn	5-200	Zn	5-200

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (e.g. 5.23 ± 0.51 µg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.
- Please return the completed results sheet by 15 November 2024.

2.9 Interim Report and Preliminary Report

An interim report was emailed to participants on 22 November 2024.

A preliminary report was issued on 25 November 2024. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants.

The following was changed from the preliminary report in the present final report, the participants performance for P in S2 was assessed using a reference value as the assigned value. The reference value was produced by NMI Australia using standard addition inductively couple plasma mass spectrometry.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Methodology for Dissolved Elements

Summaries of test methods are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 6. The information received from participants has been adjusted to remove identifying data.

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	HNO ₃ (mL)	HCl (mL)	Other (mL)
1	In House, US EPA 6020B						
3	In House Method						
4	APHA 3120B						
5	In house; APHA 3125						
7	USEPA Method 6020 - Determination of Trace Metals by ICP-MS						
8	EPA6020 and APHA3112	10	95	120	0.25		0.5 (H ₂ SO ₄) 1.5 (KMnO ₄) 1 (K ₂ S ₂ O ₈)
9	Inhouse Method	14	95	60	0.28	0.42	
10	APHA 3125 B and US EPA Method 245.7						
11	USEPA method 3010	20	100	60	0.5	0.5	
12*	USEPA 200.8 & 245, APHA 3125						
14	EPA3005A						
15*	US EPA METHOD 3010						
17	USEPA 1638 and APHA 3125B	100	95	240	1		
19	APHA 3125, EPA 200.8	5	90	120	2	1	
20	USEPA 6010, 6020, 200.7, 200.8, 200.2 APHA 3010 and 3030						
22	USEPA Method 6020 - Determination of Trace Metals by ICP-MS						
23	USEPA Method 6020 - Determination of Trace Metals by ICP-MS	30	90-98	90	1.5	1.5	
24	APHA3125	50	105	120	2		

*Additional Information in Table 2.

3.2 Additional Information

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

Table 2 Additional information

Lab Code	Additional Information
12	Not digested
15	Sample not digested but acidified with four drops of both HNO ₃ and HCl

3.3 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation ^a		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - SS	Recoveries of SS	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - SS Duplicate Analysis	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
4	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NMI Uncertainty Course
5	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537
6	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Standard deviation from PT studies only		ISO/GUM
7	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - SS	Recoveries of SS	ISO/GUM
8	Professional judgment Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS Standard Purity	Inhouse Method
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
10	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - SS Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
11	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	Instrument Calibration	ISO/GUM
12	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram) k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
13	Coverage factor not reported	Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	
14	Professional judgment Coverage factor not reported			
15	Control chart Coverage factor not reported	Control Samples - CRM Instrument Calibration	CRM	ASTM E2554-13
16	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - SS Duplicate Analysis		

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation ^a		Guide Document for Estimating MU
		Precision	Method Bias	
17	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
19	Coverage factor not reported	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies	Eurachem/CITAC Guide
20	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
21	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	
22	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - SS	Recoveries of SS	ISO/GUM
23	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples	Recoveries of SS	NATA Technical Note 33
24	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	ISO/GUM

^aRM = Reference Material, CRM = Certified Reference Material, SS = Spiked samples.

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

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

In this study, no participants made any comments.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 4 to 43 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD) and robust coefficient of variation (CV). Bar charts of results and performance scores are presented in Figures 2 to 41. An example chart with an interpretation guide is shown in Figure 2 to 41.

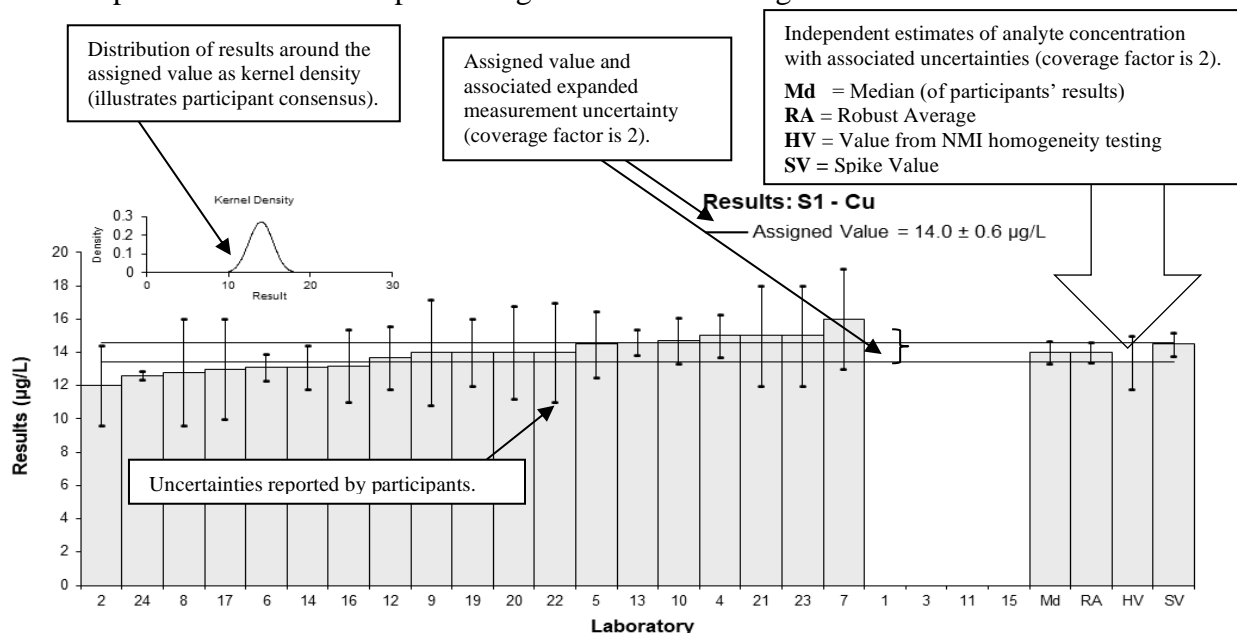


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

Outliers were results less than 50% and greater than 150% of the robust average and were removed before assigned value calculation. Extreme outliers (gross errors) were obvious blunders, such as those with incorrect units, decimal errors, or results from a different proficiency test item and were removed for calculation of summary statistics.^{3,4,7}

4.3 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 3. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'¹ In this study, the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, outliers removed except for P in S2; the expanded uncertainties were estimated from the associated robust standard deviations.^{4,7} The assigned value for P in S2 was a reference value measured using SA-ICP-MS.

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

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

4.5 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value (X) and the performance coefficient of variation (PCV). This value is used for

calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

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

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.⁸

4.6 z-Score

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

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

where:

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

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

- $|z| \leq 2.0$ is acceptable;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ is unacceptable.

4.7 E_n-Score

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

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

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 ($|E_n|$):

- $|E_n| < 1.0$ is acceptable;
- $|E_n| \geq 1.0$ is unacceptable.

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to AS ISO/IEC Standard 17025:2018⁹ 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

5 TABLES AND FIGURES

Table 4

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	NT	NT		
2	1.7	0.34	-1.63	-1.30
3	NT	NT		
4	2.4	0.3	0.44	0.38
5	2.27	0.5	0.06	0.04
6	2.63	0.12	1.13	1.37
7	3	1	2.22	0.73
8**	2.1	0.3	-0.44	-0.38
9	NT	NT		
10	2.4	1.6	0.44	0.09
11	NT	NT		
12	2.3	0.1	0.15	0.19
13	2.42	0.15	0.50	0.58
14	1.39	0.2	-2.55	-2.69
15	NT	NT		
16	2.40	0.29	0.44	0.39
17	1.6	0.4	-1.93	-1.38
19	2.4	0.5	0.44	0.27
20	2.5	0.5	0.74	0.45
21	2.4	0.6	0.44	0.23
22	2	1	-0.74	-0.24
23	2	1	-0.74	-0.24
24	NT	NT		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.25	0.25
Spike Value	2.58	0.13
Homogeneity Value	2.50	0.30
Robust Average	2.25	0.25
Median	2.40	0.11
Mean	2.24	
N	16	
Max	3	
Min	1.39	
Robust SD	0.40	
Robust CV	18%	

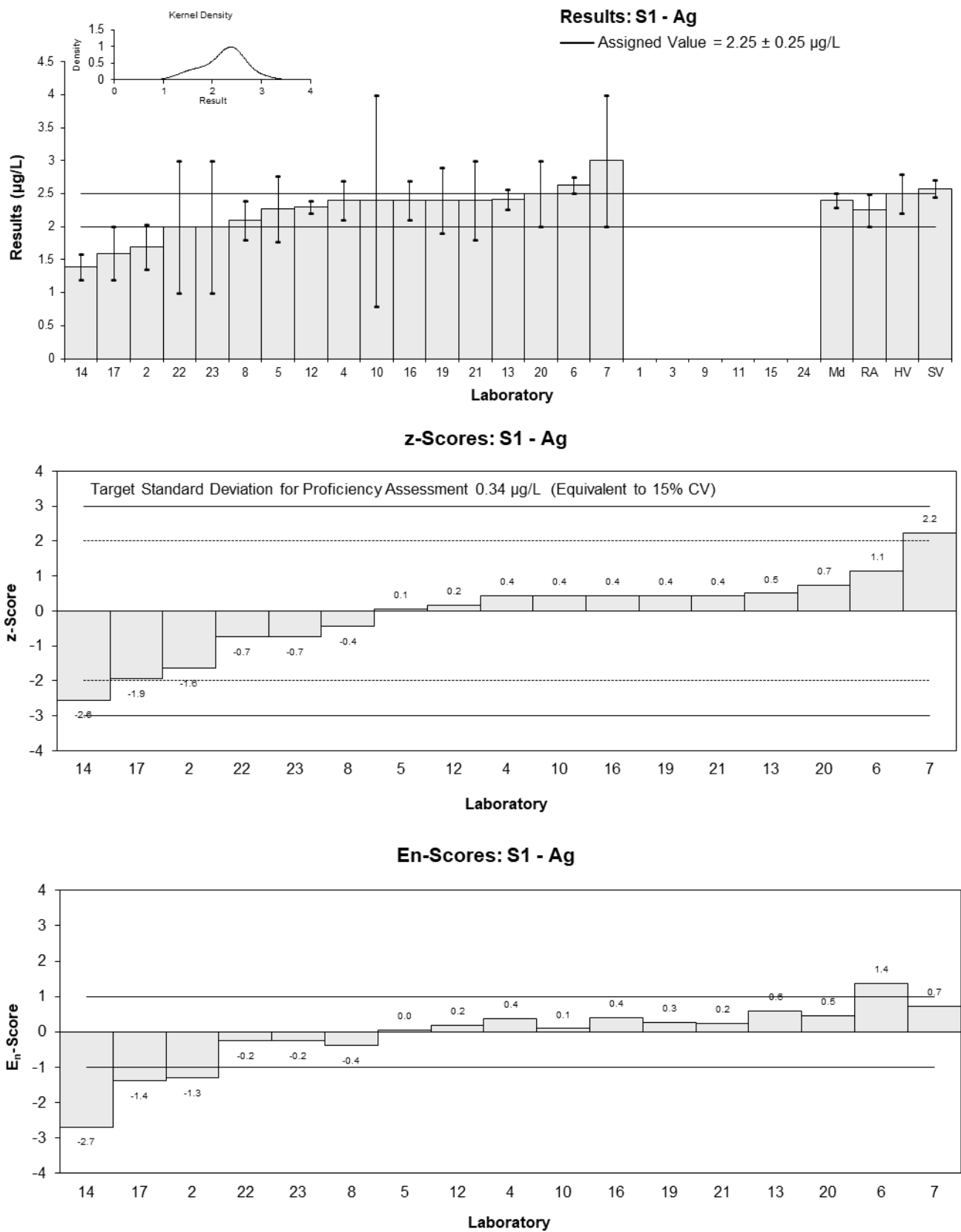


Figure 2

Table 5

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	7.7	1.54	-0.23	-0.16
3	NT	NT		
4	9	5	0.86	0.20
5	7.79	0.9	-0.15	-0.16
6**	0.30	0.12	-6.42	-11.27
7	<10	NR		
8**	17	4.2	7.55	2.12
9	10.2	2.1	1.87	1.01
10	7.9	2.1	-0.06	-0.03
11	NT	NT		
12	7	2	-0.81	-0.46
13	8.34	0.40	0.31	0.47
14	7.65	0.77	-0.27	-0.31
15	NT	NT		
16	8.22	2.38	0.21	0.10
17	5.5	1.2	-2.07	-1.80
19	7	9	-0.81	-0.11
20	9.05	1.81	0.90	0.56
21	8	1	0.03	0.02
22	<10	NR		
23	<10	NR		
24	NT	NT		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	7.97	0.67
Spike Value	Not Spiked	
Robust Average	7.97	0.67
Median	7.90	0.45
Mean	7.95	
N	13	
Max	10.2	
Min	5.5	
Robust SD	0.97	
Robust CV	12%	

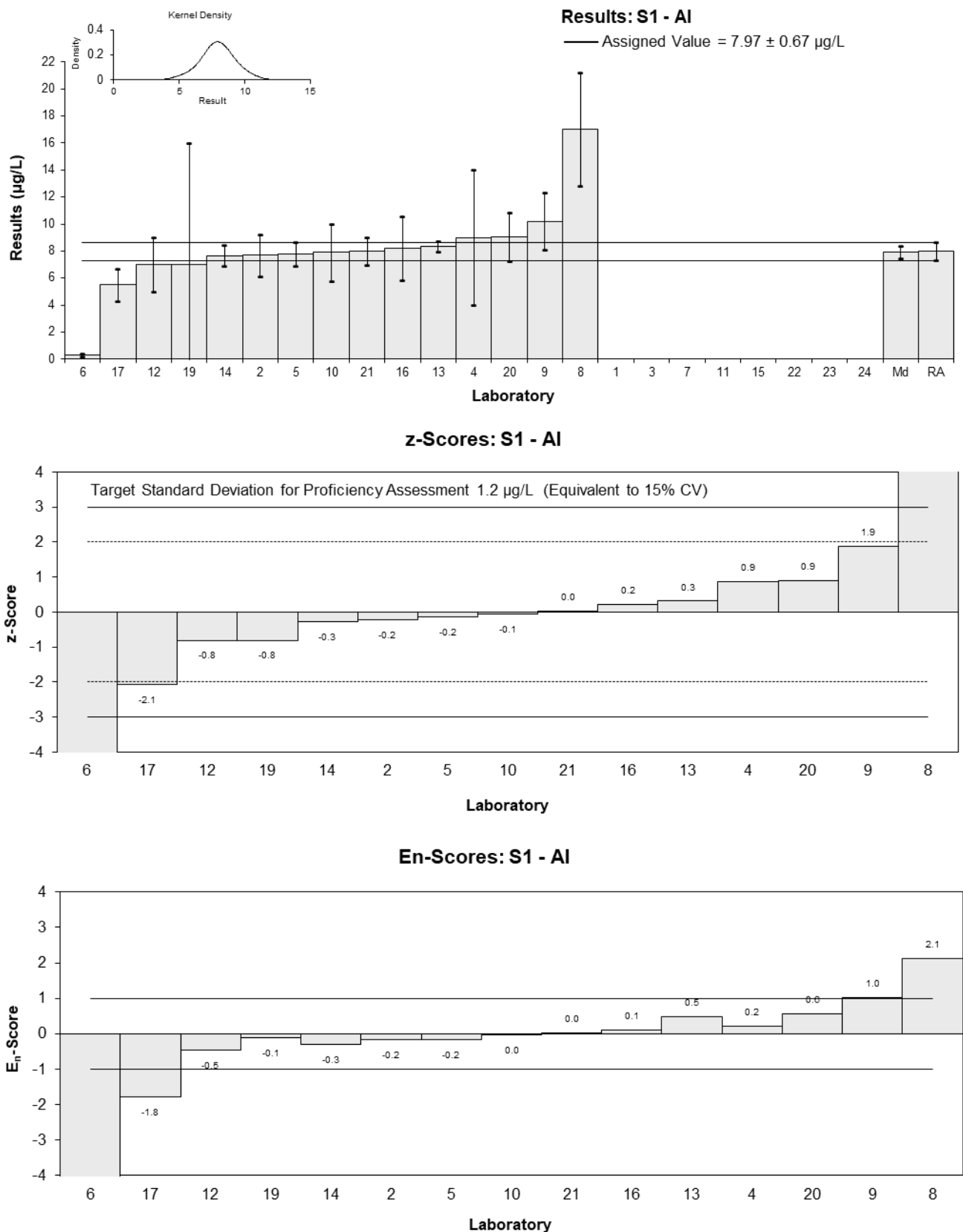


Figure 3

Table 6

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.89	0.178	-1.32	-1.17
3	NT	NT		
4	1.2	1	0.54	0.09
5	1.07	0.2	-0.24	-0.19
6	1.25	0.10	0.84	1.20
7	1	1	-0.66	-0.11
8**	4.2	1.04	18.56	2.97
9	1.05	0.23	-0.36	-0.25
10	1.16	0.25	0.30	0.19
11	NT	NT		
12	1.22	0.29	0.66	0.37
13	1.12	0.05	0.06	0.13
14	1.12	0.2	0.06	0.05
15	NT	NT		
16	1.15	0.18	0.24	0.21
17	1.1	0.2	-0.06	-0.05
19	1.2	5	0.54	0.02
20	1.1	0.22	-0.06	-0.04
21	1	0.1	-0.66	-0.94
22	1	1	-0.66	-0.11
23	1	1	-0.66	-0.11
24	1.2	0.024	0.54	1.39

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.11	0.06
Spike Value	1.13	0.05
Homogeneity Value	1.02	0.12
Robust Average	1.11	0.06
Median	1.11	0.08
Mean	1.10	
N	18	
Max	1.25	
Min	0.89	
Robust SD	0.10	
Robust CV	9.3%	

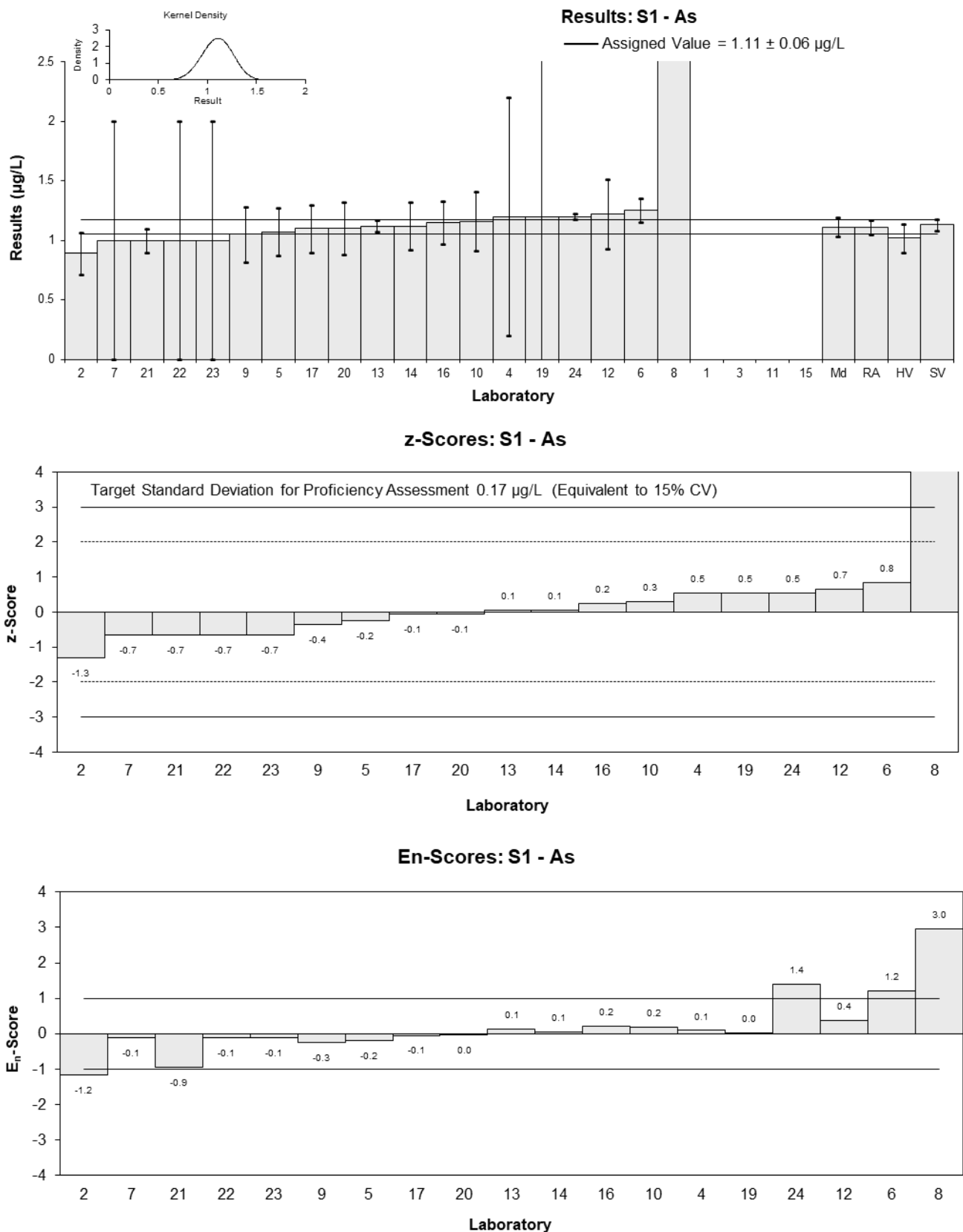


Figure 4

Table 7

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	1.8	0.36	-0.43	-0.22
3	NT	NT		
4	1.9	0.2	0.11	0.10
5	1.99	0.3	0.59	0.36
6	1.81	0.10	-0.37	-0.60
7	2	2	0.64	0.06
8**	2.3	0.29	2.23	1.42
9	1.68	0.53	-1.06	-0.37
10	1.9	0.17	0.11	0.11
11	NT	NT		
12	1.9	0.2	0.11	0.10
13	1.82	0.10	-0.32	-0.51
14	1.79	0.2	-0.48	-0.43
15	NT	NT		
16	NT	NT		
17	1.9	0.4	0.11	0.05
19	2	2	0.64	0.06
20	1.85	0.37	-0.16	-0.08
21	1.8	1	-0.43	-0.08
22	2	0.6	0.64	0.20
23	2	1	0.64	0.12
24	1.8	0.036	-0.43	-1.14

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.88	0.06
Spike Value	1.90	0.10
Homogeneity Value	1.87	0.22
Robust Average	1.88	0.06
Median	1.90	0.09
Mean	1.88	
N	17	
Max	2	
Min	1.68	
Robust SD	0.10	
Robust CV	5.5%	

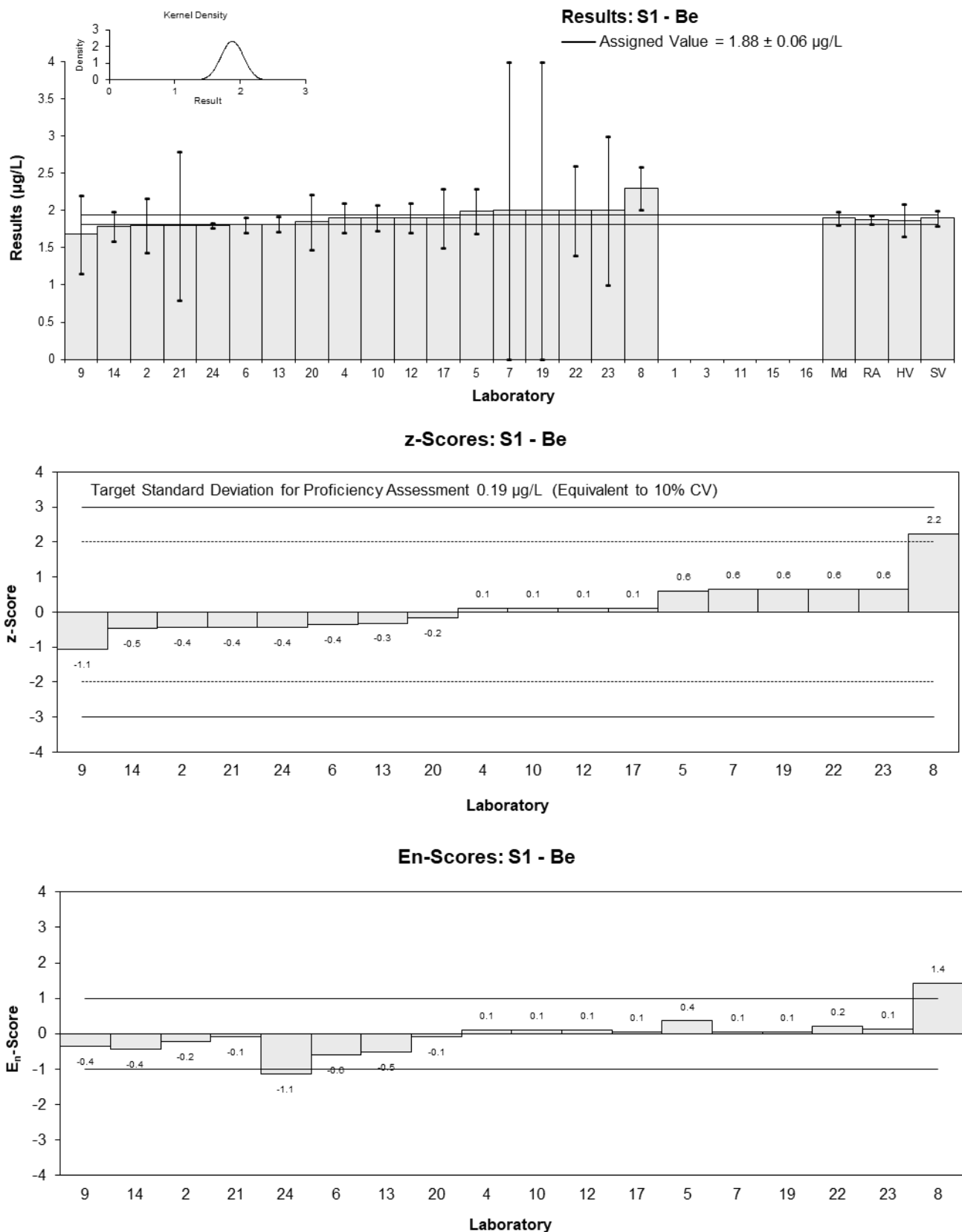


Figure 5

Table 8

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	1.4	0.28	0.69	0.32
3	NT	NT		
4	1.3	0.2	-0.08	-0.05
5	1.38	0.3	0.53	0.23
6	1.28	0.10	-0.23	-0.28
7	1.4	0.4	0.69	0.22
8**	1.1	0.13	-1.60	-1.54
9	1.30	0.30	-0.08	-0.03
10	1.29	0.19	-0.15	-0.10
11	NT	NT		
12	1.3	0.1	-0.08	-0.09
13	1.30	0.065	-0.08	-0.13
14	1.30	0.2	-0.08	-0.05
15	NT	NT		
16	1.28	0.27	-0.23	-0.11
17	1.1	0.2	-1.60	-1.03
19	1.3	0.7	-0.08	-0.01
20	1.3	0.26	-0.08	-0.04
21	1.3	0.1	-0.08	-0.09
22	1.2	0.4	-0.84	-0.27
23	1.5	0.3	1.45	0.63
24	1.3	0.026	-0.08	-0.21

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.31	0.04
Spike Value	1.32	0.07
Homogeneity Value	1.23	0.15
Robust Average	1.31	0.04
Median	1.30	0.004
Mean	1.31	
N	18	
Max	1.5	
Min	1.1	
Robust SD	0.061	
Robust CV	4.7%	

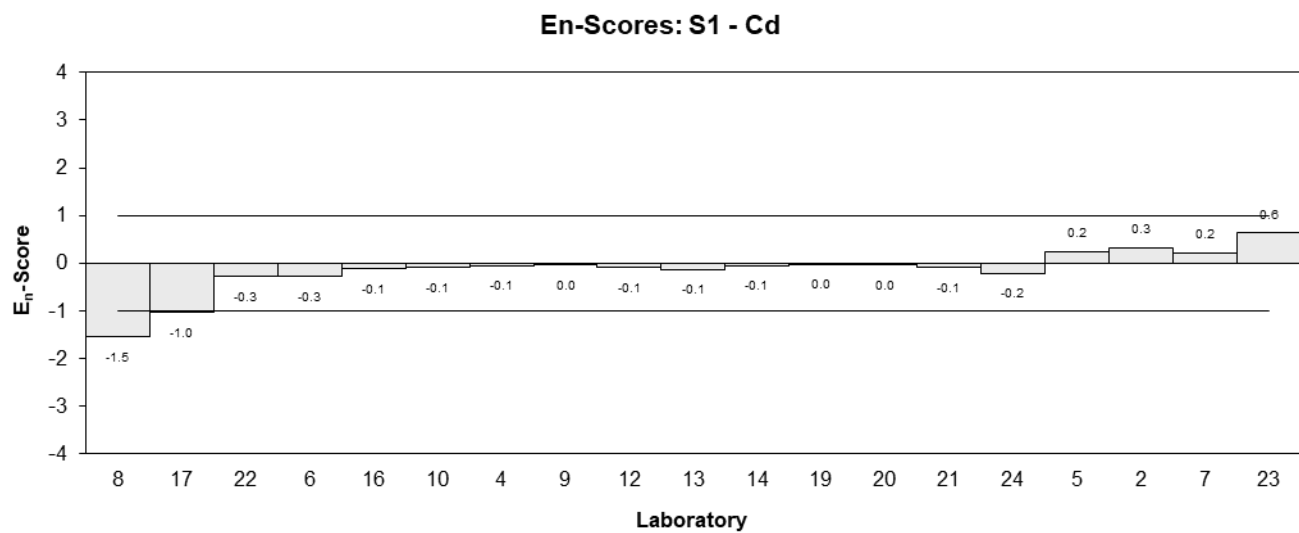
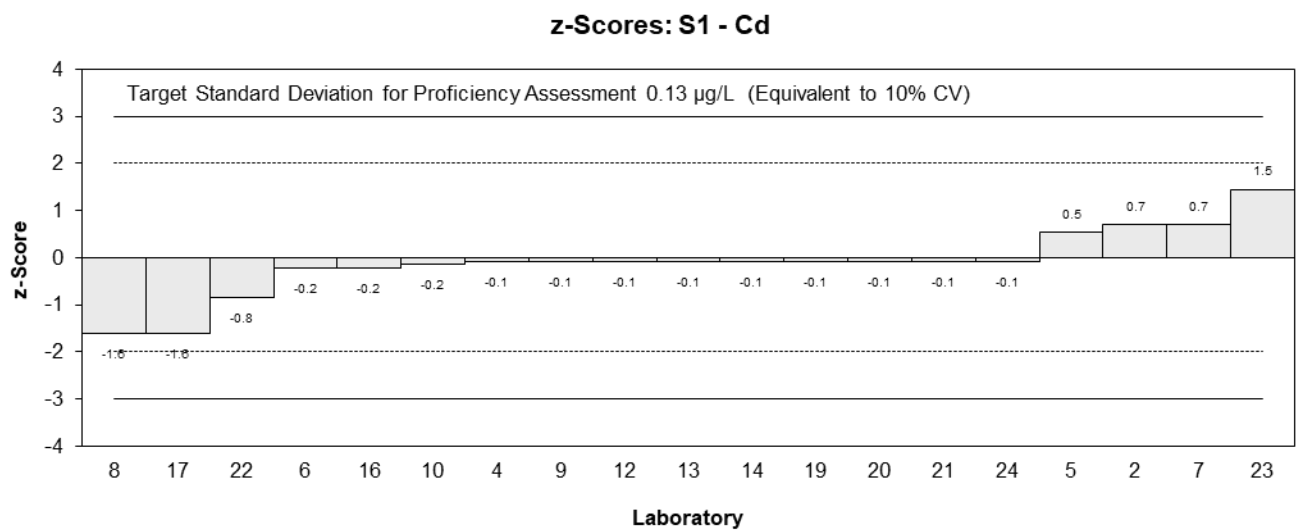
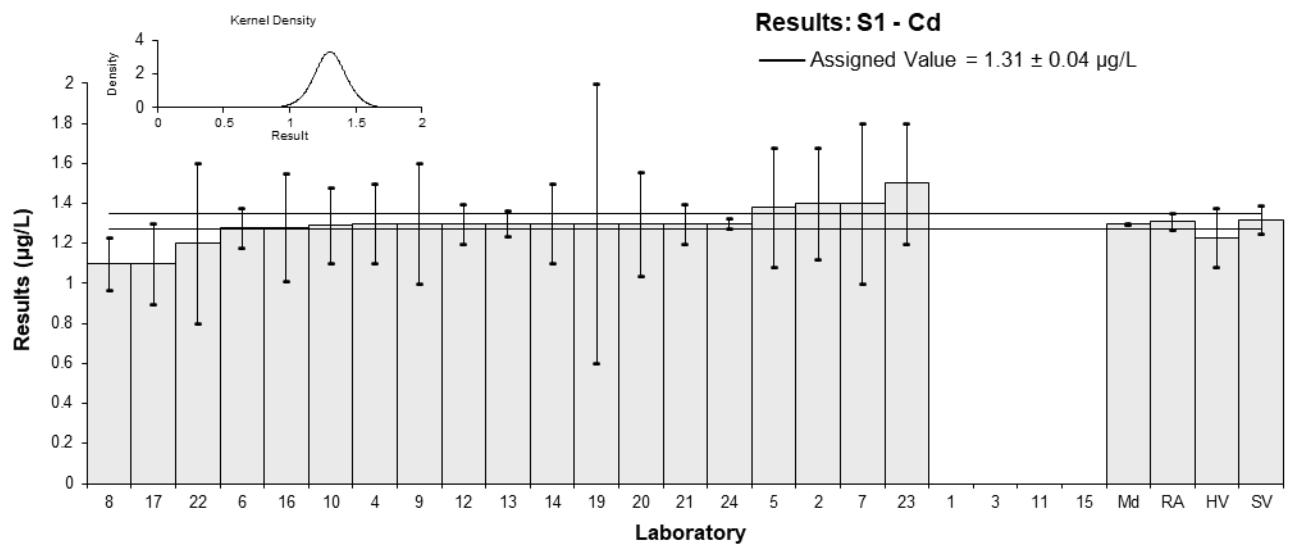


Figure 6

Table 9

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	Co
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	2.2	0.44	-0.09	-0.07
3	NT	NT		
4	2.4	0.3	0.51	0.52
5	2.42	0.5	0.57	0.37
6	1.27	0.14	-2.87	-5.02
7	2	1	-0.69	-0.23
8**	1.8	0.9	-1.29	-0.47
9	2.45	0.60	0.66	0.36
10	2.53	0.17	0.90	1.40
11	NT	NT		
12	2.26	0.50	0.09	0.06
13	2.31	0.15	0.24	0.40
14	2.25	0.22	0.06	0.08
15	NT	NT		
16	2.08	0.42	-0.45	-0.34
17	2.2	0.4	-0.09	-0.07
19	2	1	-0.69	-0.23
20	2	0.4	-0.69	-0.55
21	2.2	0.3	-0.09	-0.09
22	2	1	-0.69	-0.23
23	3	1	2.30	0.76
24	2.3	0.046	0.21	0.51

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.23	0.13
Spike Value	2.36	0.12
Homogeneity Value	2.22	0.27
Robust Average	2.23	0.13
Median	2.23	0.16
Mean	2.22	
N	18	
Max	3	
Min	1.27	
Robust SD	0.23	
Robust CV	10%	

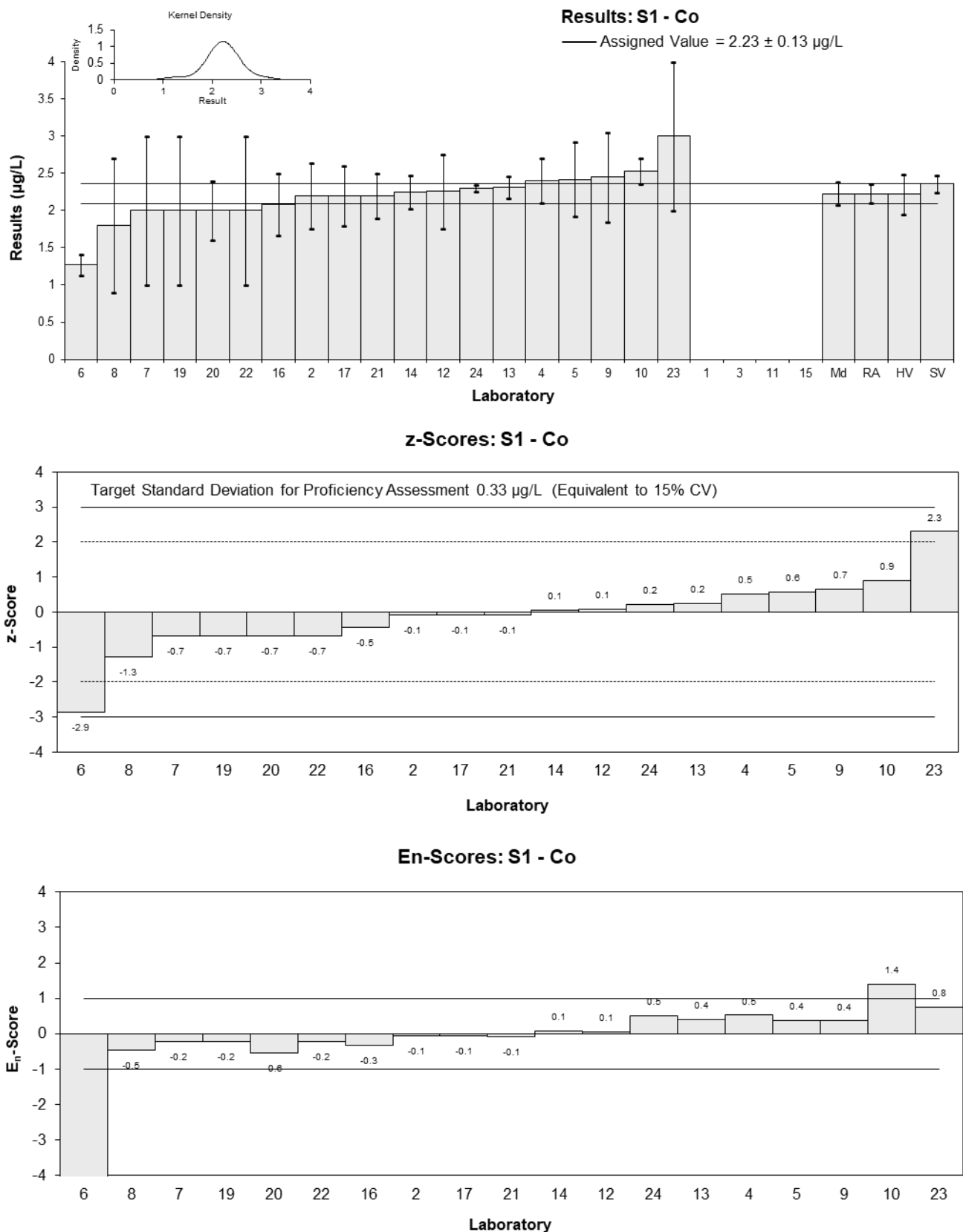


Figure 7

Table 10

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2*	0.39	0.078	-3.56	-4.51
3	NT	NT		
4	0.9	0.5	0.50	0.13
5	<1	NR		
6	0.67	0.10	-1.33	-1.43
7	<1	NR		
8**	7.3	1.8	51.48	3.59
9	0.90	0.24	0.50	0.25
10	0.78	0.34	-0.45	-0.17
11	NT	NT		
12	0.84	0.15	0.02	0.02
13	0.850	0.05	0.10	0.16
14	0.810	0.2	-0.22	-0.13
15	NT	NT		
16	0.732	0.124	-0.84	-0.76
17	<1	NR		
19	0.8	1.2	-0.29	-0.03
20	0.854	0.191	0.14	0.08
21	<1	NR		
22	<1	NR		
23	1	1	1.30	0.16
24	0.9	0.018	0.50	0.99

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.837	0.061
Spike Value	0.839	0.039
Homogeneity Value	0.808	0.097
Robust Average	0.821	0.073
Median	0.840	0.062
Mean	0.802	
N	13	
Max	1	
Min	0.39	
Robust SD	0.11	
Robust CV	13%	

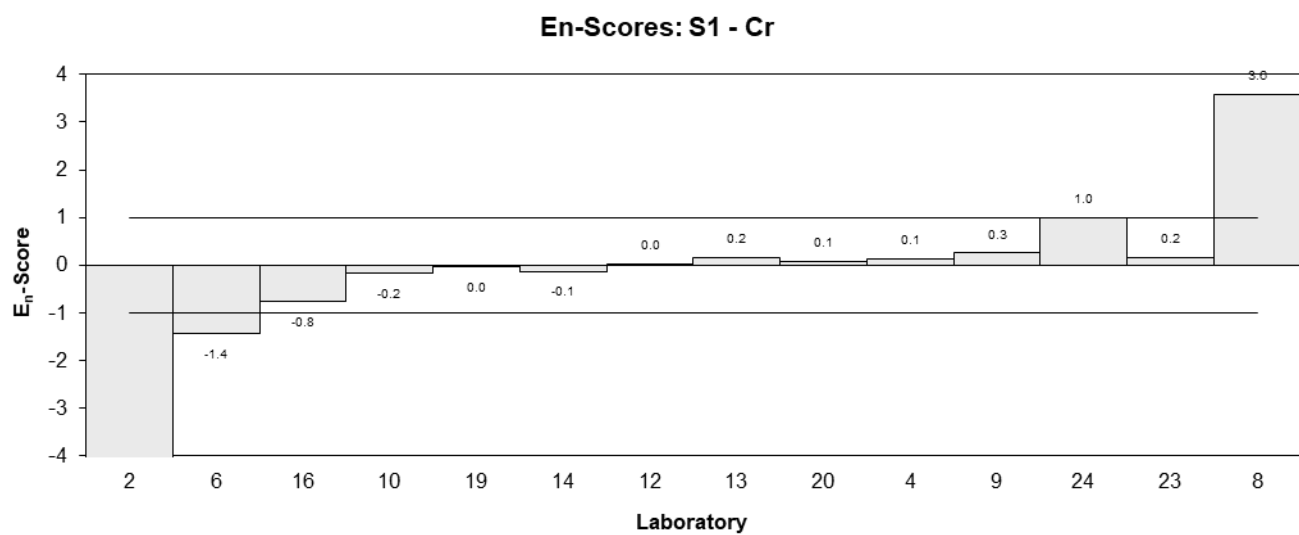
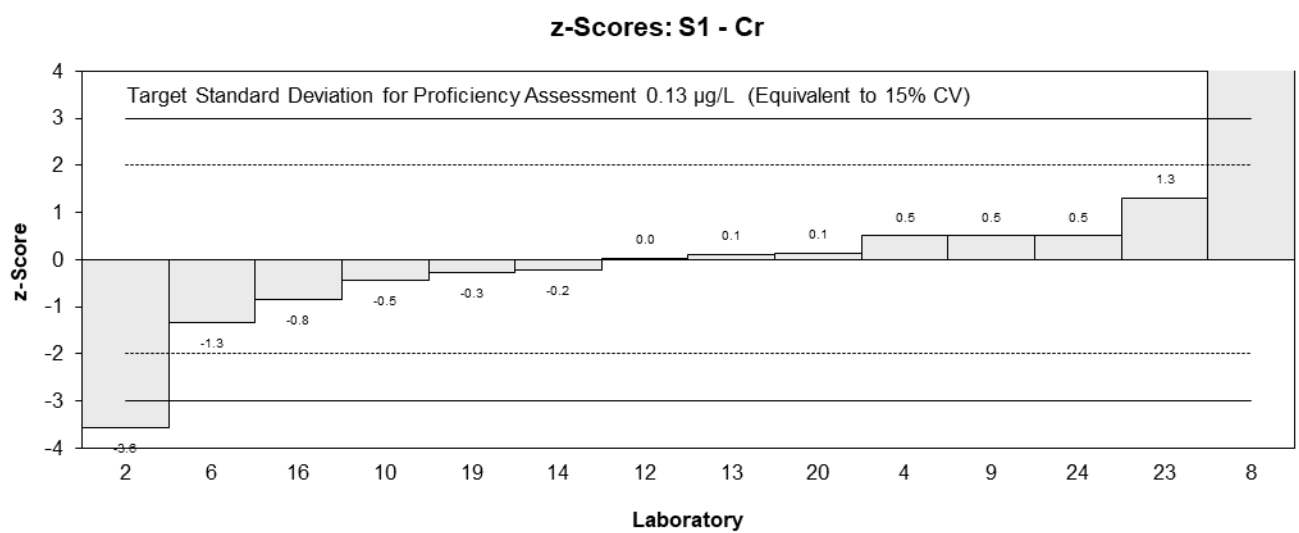
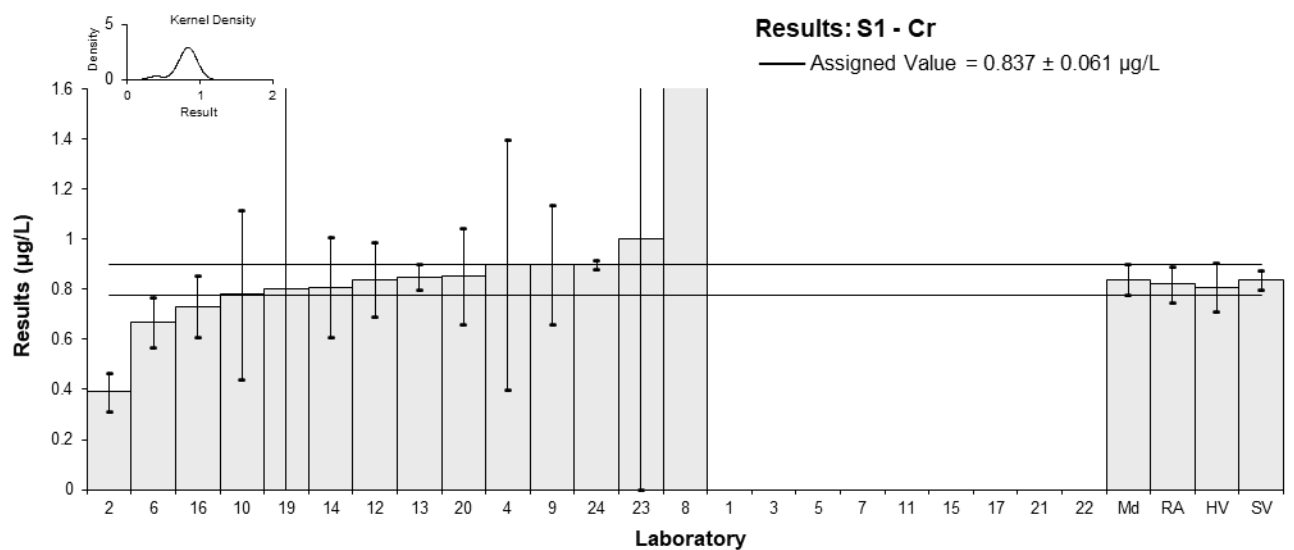


Figure 8

Table 11

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	NT	NT		
2	12	2.4	-1.43	-0.81
3	NT	NT		
4	15	1.3	0.71	0.70
5	14.5	2.0	0.36	0.24
6	13.09	0.8	-0.65	-0.91
7	16	3	1.43	0.65
8**	12.8	3.2	-0.86	-0.37
9	14.0	3.2	0.00	0.00
10	14.7	1.4	0.50	0.46
11	NT	NT		
12	13.7	1.9	-0.21	-0.15
13	14.6	0.75	0.43	0.62
14	13.1	1.3	-0.64	-0.63
15	NT	NT		
16	13.2	2.2	-0.57	-0.35
17	13	3	-0.71	-0.33
19	14	2	0.00	0.00
20	14	2.8	0.00	0.00
21	15	3	0.71	0.33
22	14	3	0.00	0.00
23	15	3	0.71	0.33
24	12.6	0.252	-1.00	-2.15

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	14.0	0.6
Spike Value	14.5	0.7
Homogeneity Value	13.4	1.6
Robust Average	14.0	0.6
Median	14.0	0.7
Mean	14.0	
N	18	
Max	16	
Min	12	
Robust SD	1.0	
Robust CV	7.4%	

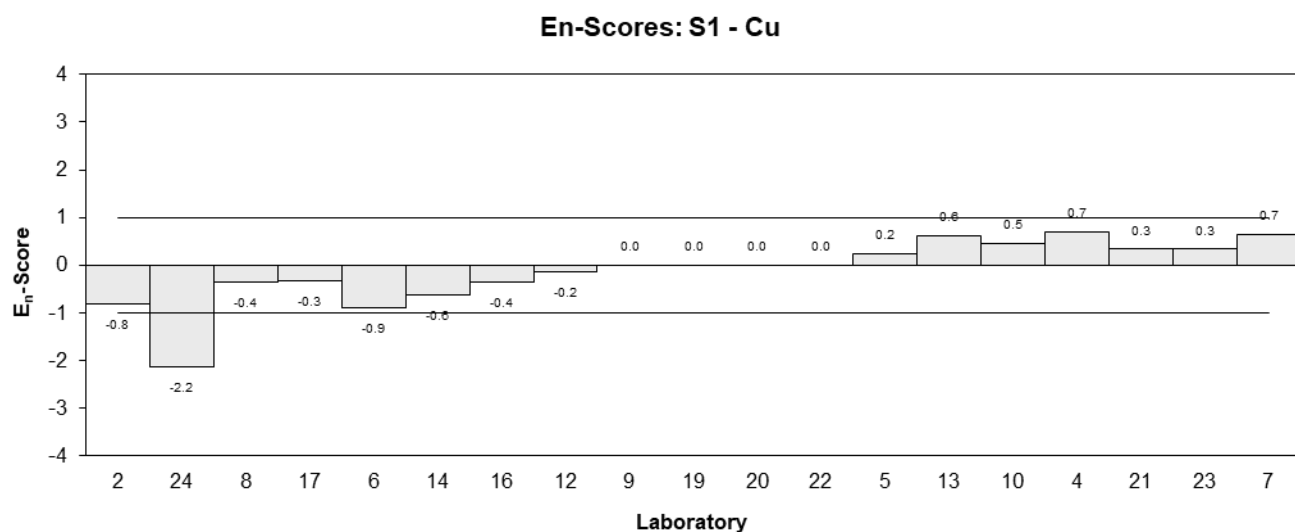
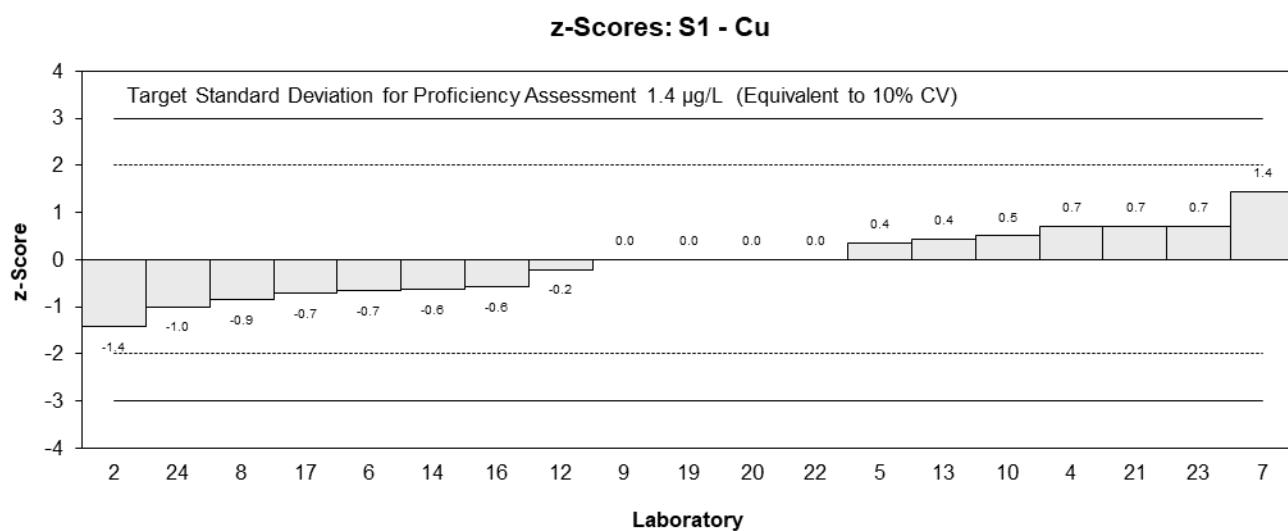
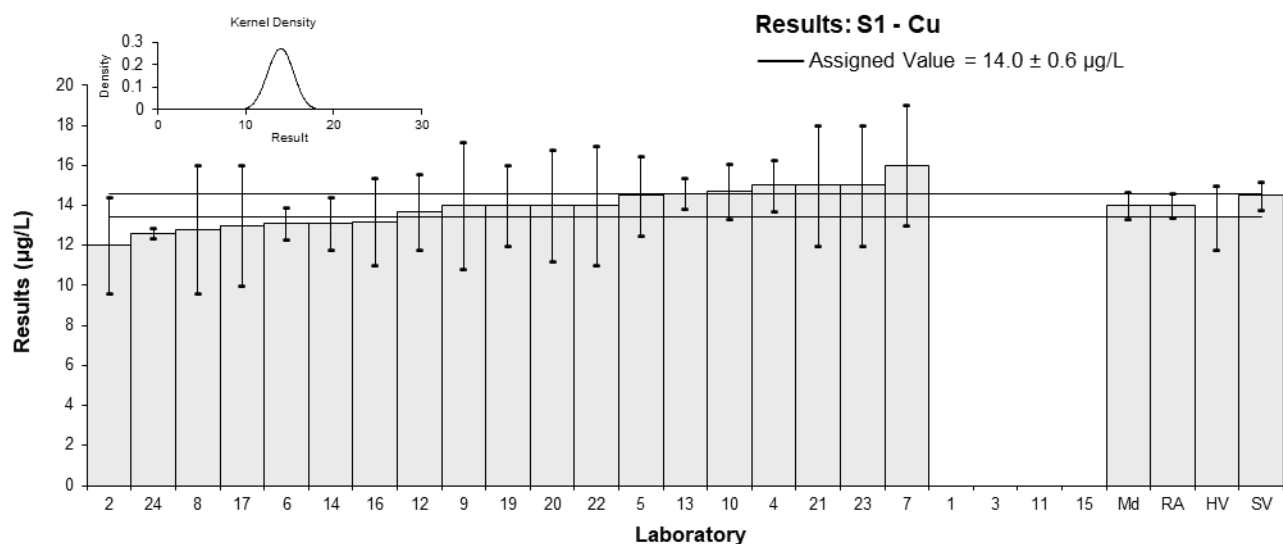


Figure 9

Table 12

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	450	90	-0.47	-0.24
3	NT	NT		
4	490	100	0.38	0.18
5	486	50	0.30	0.27
6	461.79	101	-0.22	-0.10
7	500	100	0.59	0.28
8**	79	20	-8.33	-14.97
9	494	170	0.47	0.13
10	485	36	0.28	0.33
11	NT	NT		
12	545	51	1.55	1.36
13	473	25	0.02	0.03
14	476	48	0.08	0.08
15	NT	NT		
16	437	66	-0.74	-0.51
17	430	95	-0.89	-0.44
19	441	44.1	-0.66	-0.66
20	486	97.2	0.30	0.14
21	452	80	-0.42	-0.24
22	470	100	-0.04	-0.02
23	500	100	0.59	0.28
24	444.6	8.892	-0.58	-1.43

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	472	17
Spike Value	Not Spiked	
Homogeneity Value	500	60
Robust Average	472	17
Median	475	18
Mean	473	
N	18	
Max	545	
Min	430	
Robust SD	28	
Robust CV	5.9%	

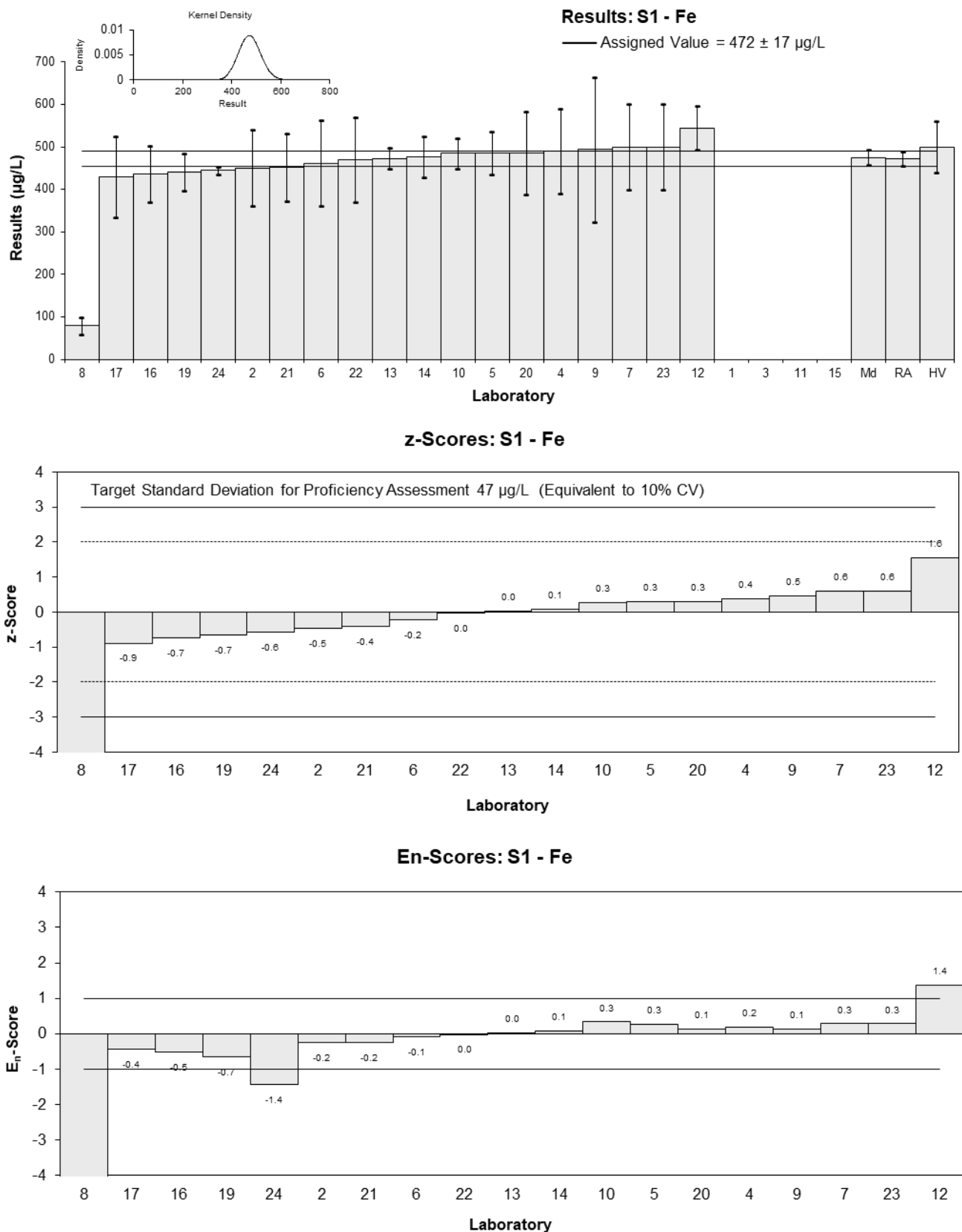


Figure 10

Table 13

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.48	0.096	0.27	0.18
3	NT	NT		
4	0.44	0.05	-0.30	-0.31
5	<0.5	NR		
6	0.43	0.002	-0.45	-0.67
7	0.4	0.1	-0.88	-0.55
8**	0.38	0.095	-1.17	-0.77
9	0.50	0.04	0.56	0.64
10	0.44	0.53	-0.30	-0.04
11	NT	NT		
12	0.481	0.031	0.29	0.36
13	NT	NT		
14	0.590	0.1	1.87	1.17
15	NT	NT		
16	0.402	0.080	-0.85	-0.64
17	0.37	0.07	-1.32	-1.09
19	0.42	0.08	-0.59	-0.44
20	0.48	0.096	0.27	0.18
21	0.42	0.1	-0.59	-0.37
22	0.4	0.08	-0.88	-0.66
23	0.57	0.1	1.58	0.99
24	0.6	0.012	2.01	2.92

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.461	0.046
Spike Value	0.452	0.023
Homogeneity Value	0.438	0.053
Robust Average	0.461	0.046
Median	0.440	0.037
Mean	0.464	
N	16	
Max	0.6	
Min	0.37	
Robust SD	0.074	
Robust CV	16%	

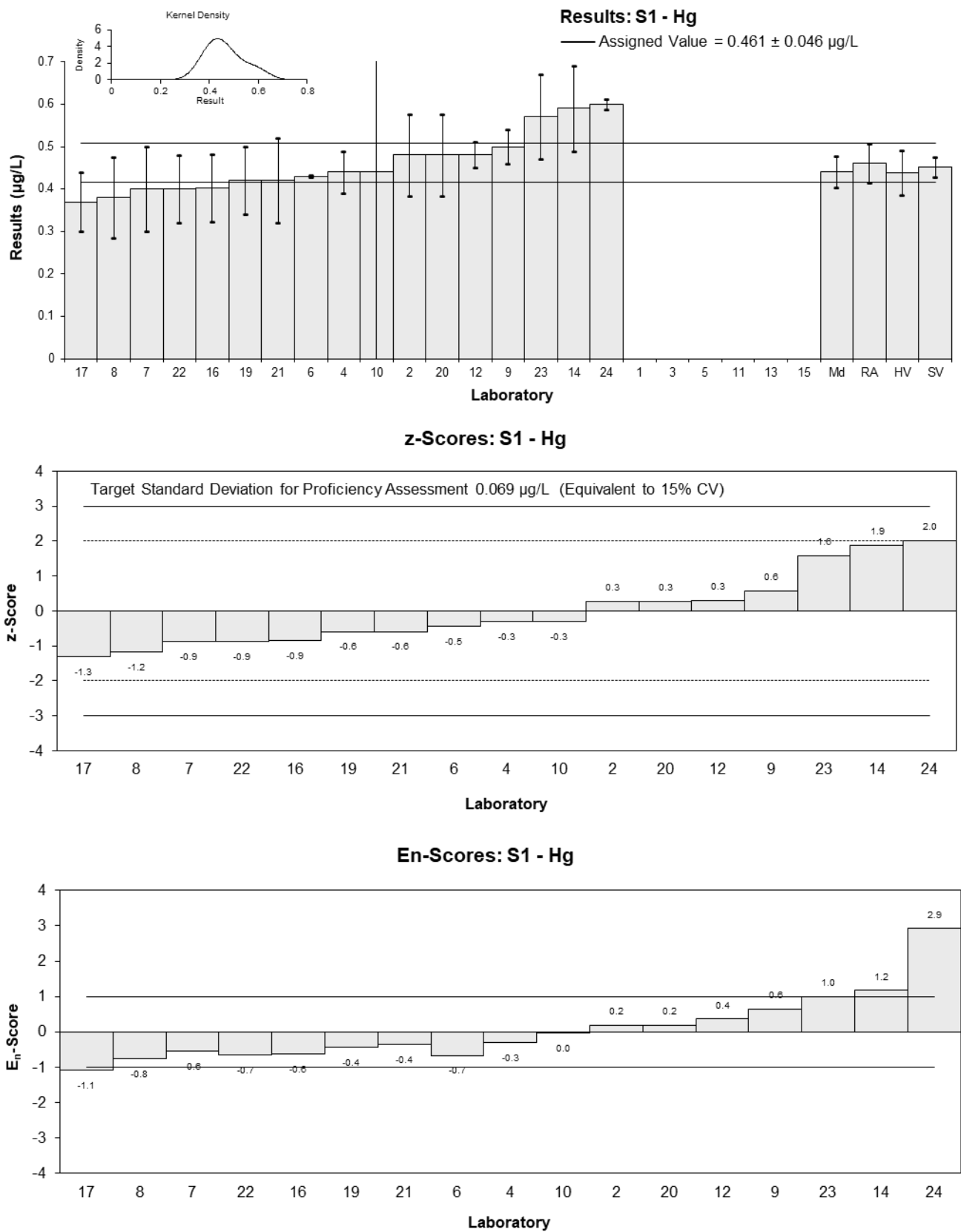


Figure 11

Table 14

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	24	4.8	-0.36	-0.18
3	NT	NT		
4	26	3.4	0.44	0.31
5	25.5	3.0	0.24	0.19
6	25.66	2.8	0.31	0.26
7	24	6	-0.36	-0.15
8**	7.6	1.9	-6.95	-8.23
9	26.2	7.2	0.52	0.18
10	25.6	2.3	0.28	0.28
11	NT	NT		
12	24.7	6.8	-0.08	-0.03
13	25.0	1.25	0.04	0.06
14	24.8	2.48	-0.04	-0.04
15	NT	NT		
16	22.7	3.2	-0.88	-0.66
17	23	5	-0.76	-0.37
19	23	2	-0.76	-0.87
20	25.4	5.08	0.20	0.10
21	24	4	-0.36	-0.22
22	27	6	0.84	0.35
23	27	8	0.84	0.26
24	25.4	0.508	0.20	0.48

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	24.9	0.9
Spike Value	24.7	1.5
Homogeneity Value	23.2	2.8
Robust Average	24.9	0.9
Median	25.2	0.8
Mean	24.9	
N	18	
Max	27	
Min	22.7	
Robust SD	1.5	
Robust CV	5.8%	

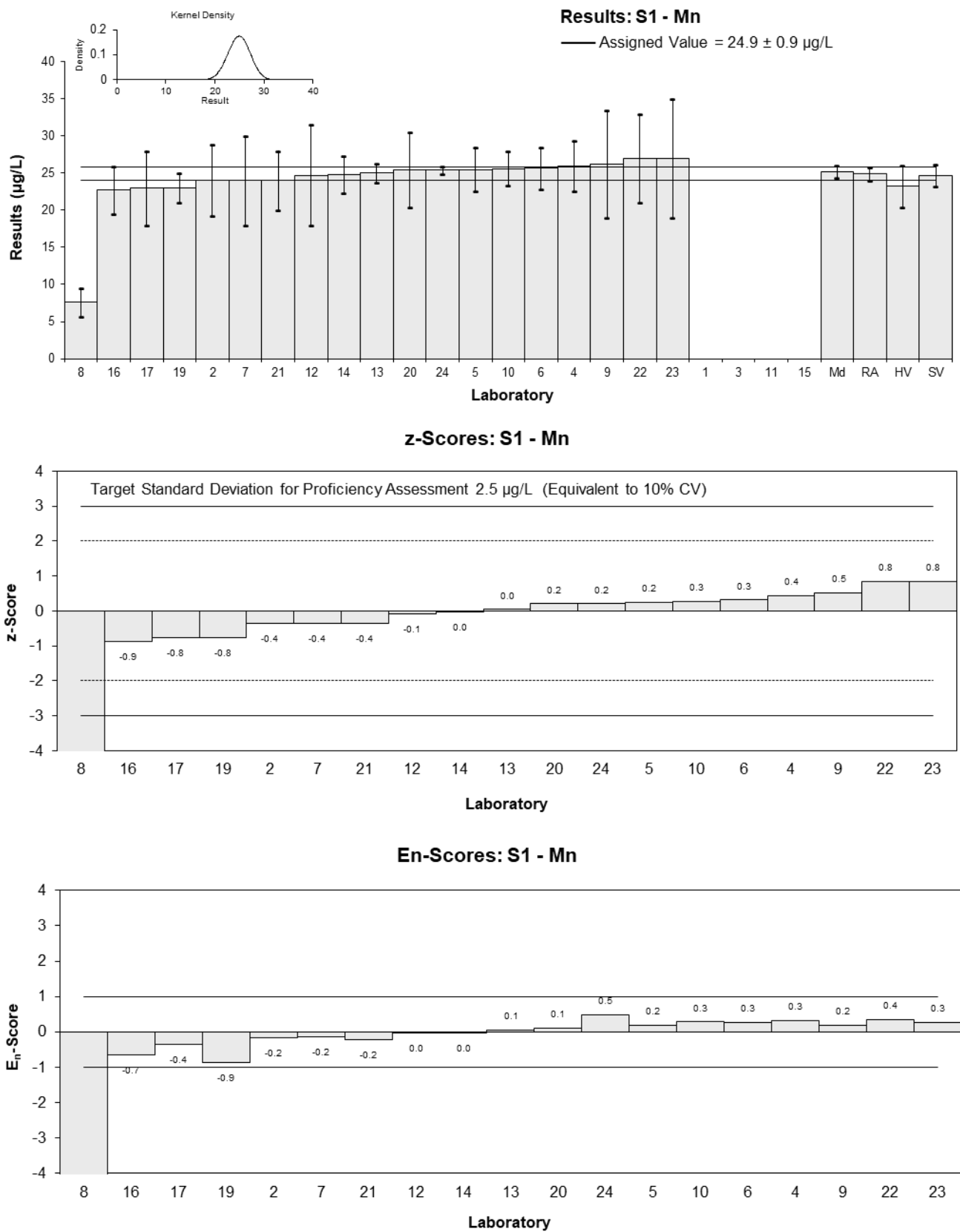


Figure 12

Table 15

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	Mo
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	6.9	1.38	-0.44	-0.22
3	NT	NT		
4	7.5	1	0.39	0.26
5	7.68	0.9	0.64	0.48
6	7.87	0.8	0.90	0.74
7	8	2	1.08	0.38
8**	9.02	2.3	2.49	0.77
9	6.85	1.57	-0.51	-0.23
10	7.5	1.3	0.39	0.21
11	NT	NT		
12	7.5	0.9	0.39	0.29
13	7.0	0.35	-0.30	-0.44
14	7.49	0.75	0.37	0.33
15	NT	NT		
16	6.50	1.04	-1.00	-0.66
17	5.9	1.5	-1.83	-0.86
19	6.6	6	-0.86	-0.10
20	7.3	1.46	0.11	0.05
21	6.9	1	-0.44	-0.30
22	7	2	-0.30	-0.11
23	9	2	2.47	0.88
24	6.9	0.138	-0.44	-0.85

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	7.22	0.35
Spike Value	7.19	0.35
Homogeneity Value	6.66	0.80
Robust Average	7.22	0.35
Median	7.15	0.31
Mean	7.24	
N	18	
Max	9	
Min	5.9	
Robust SD	0.59	
Robust CV	8.1%	

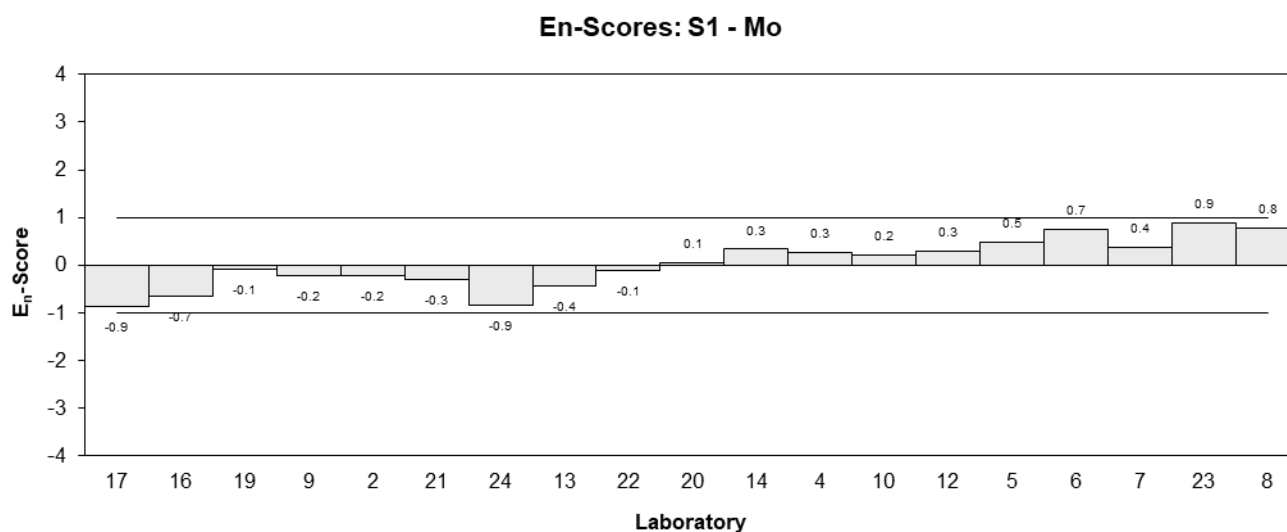
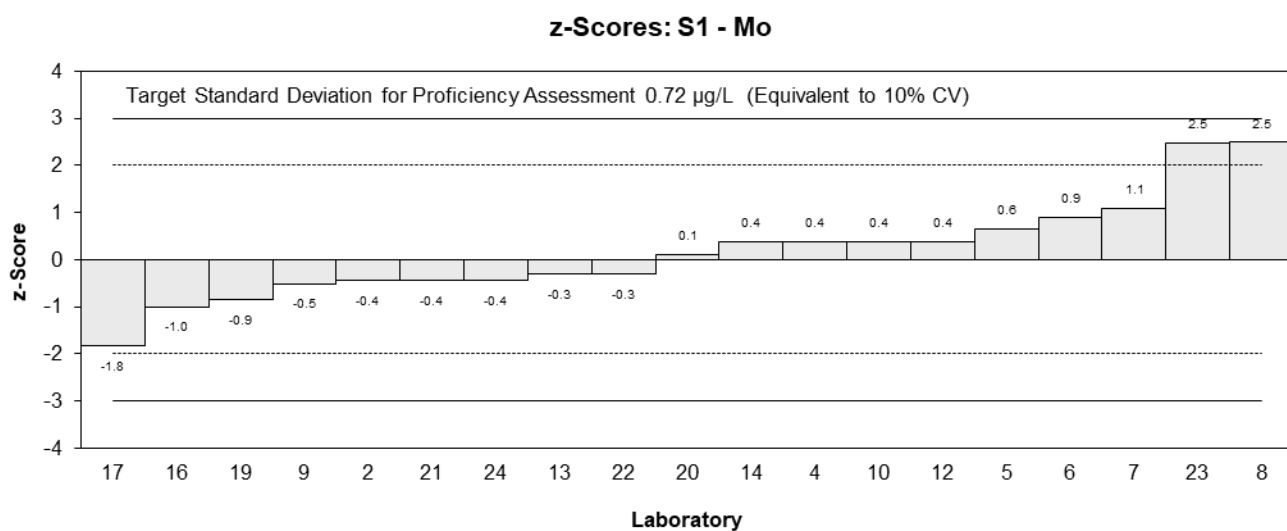
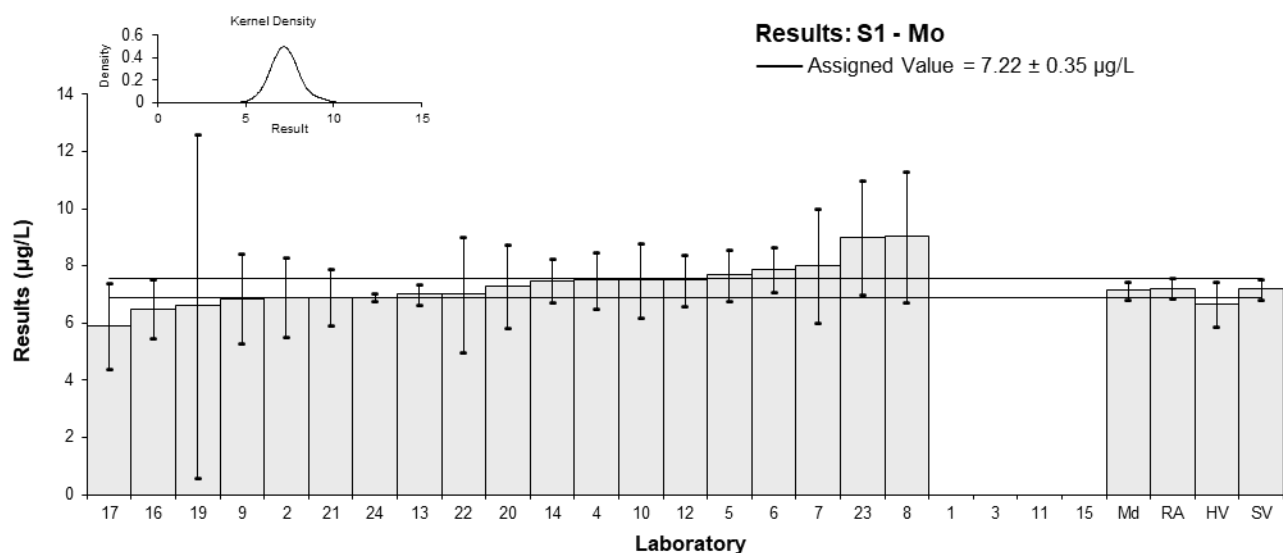


Figure 13

Table 16

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	2.2	0.44	-0.50	-0.38
3	NT	NT		
4	2.4	1	0.06	0.02
5	2.66	0.4	0.78	0.65
6	2.40	0.12	0.06	0.10
7	3	1	1.74	0.61
8**	4.3	1.1	5.38	1.73
9	2.45	0.55	0.20	0.12
10	2.65	0.35	0.76	0.70
11	NT	NT		
12	2.32	0.29	-0.17	-0.18
13	2.25	0.15	-0.36	-0.59
14	2.21	0.22	-0.48	-0.62
15	NT	NT		
16	2.24	0.34	-0.39	-0.37
17	2.1	0.4	-0.78	-0.65
19	2	3	-1.06	-0.13
20	2.4	0.48	0.06	0.04
21	2.5	0.4	0.34	0.28
22	2	1	-1.06	-0.38
23	3	1	1.74	0.61
24	2.5	0.05	0.34	0.72

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.38	0.16
Spike Value	2.41	0.12
Homogeneity Value	2.28	0.27
Robust Average	2.38	0.16
Median	2.40	0.15
Mean	2.40	
N	18	
Max	3	
Min	2	
Robust SD	0.27	
Robust CV	12%	

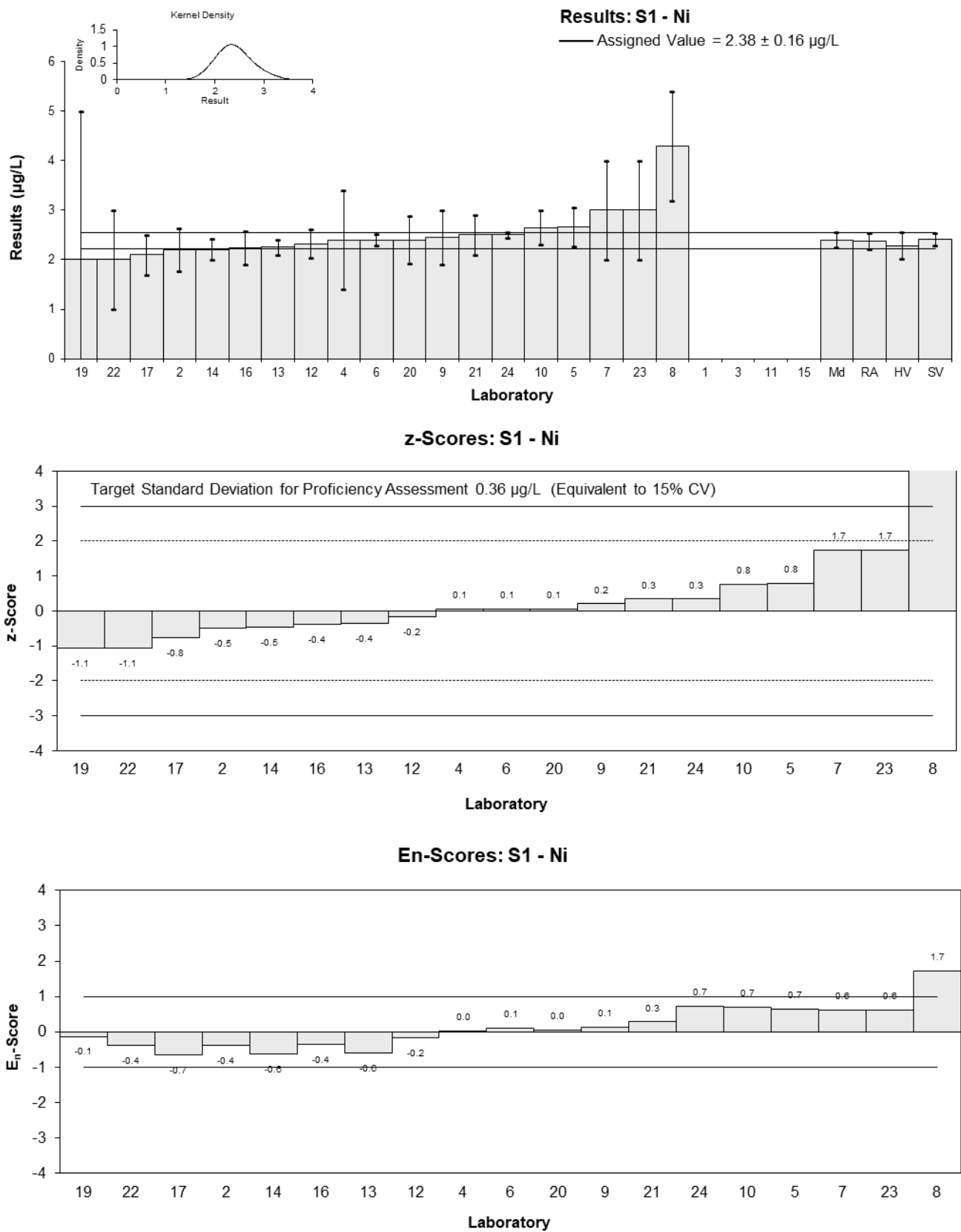


Figure 14

Table 17

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	4.1	0.82	0.41	0.19
3	NT	NT		
4	3.9	0.6	-0.10	-0.07
5	4.06	0.7	0.30	0.17
6	3.58	0.8	-0.91	-0.45
7	4	1	0.15	0.06
8**	2.1	1.1	-4.67	-1.67
9	4.27	0.95	0.84	0.35
10	4.03	0.29	0.23	0.29
11	NT	NT		
12	3.9	0.42	-0.10	-0.09
13	3.97	0.20	0.08	0.13
14	3.88	0.39	-0.15	-0.15
15	NT	NT		
16	3.96	0.67	0.05	0.03
17	3.5	0.7	-1.12	-0.62
19	3.8	3	-0.36	-0.05
20	4	0.8	0.15	0.07
21	4.1	0.6	0.41	0.26
22	4	1	0.15	0.06
23	4	1	0.15	0.06
24	3.5	0.07	-1.12	-3.60

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	3.94	0.10
Spike Value	4.09	0.20
Homogeneity Value	3.82	0.46
Robust Average	3.94	0.10
Median	3.99	0.07
Mean	3.92	
N	18	
Max	4.27	
Min	3.5	
Robust SD	0.16	
Robust CV	4.1%	

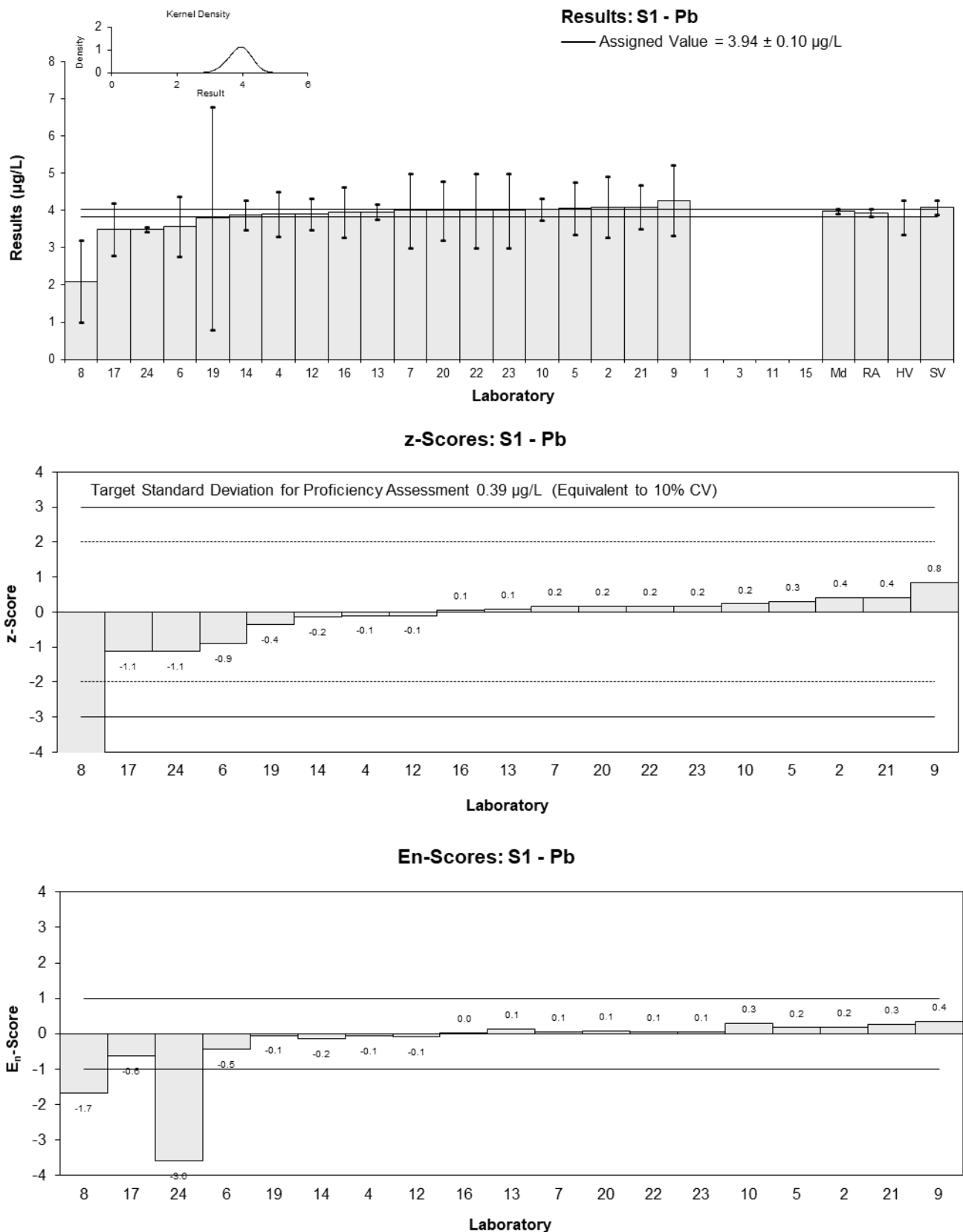


Figure 15

Table 18

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	3.8	0.76	-0.78	-0.64
3	NT	NT		
4	4.4	0.4	0.16	0.23
5	4.40	0.7	0.16	0.14
6	4.43	0.6	0.20	0.21
7	5	1	1.09	0.69
8**	3.7	1.8	-0.93	-0.33
9	4.10	0.91	-0.31	-0.22
10	4.38	0.66	0.12	0.12
11	NT	NT		
12	4.5	0.40	0.31	0.46
13	4.18	0.20	-0.19	-0.47
14	4.43	0.44	0.20	0.28
15	NT	NT		
16	4.25	0.93	-0.08	-0.05
17	4	1	-0.47	-0.30
19	4.1	0.8	-0.31	-0.25
20	4.15	0.83	-0.23	-0.18
21	4.2	0.6	-0.16	-0.16
22	4	1	-0.47	-0.30
23	5	1	1.09	0.69
24	4.6	0.092	0.47	1.63

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	4.30	0.16
Spike Value	4.26	0.20
Homogeneity Value	4.25	0.51
Robust Average	4.30	0.16
Median	4.32	0.15
Mean	4.33	
N	18	
Max	5	
Min	3.8	
Robust SD	0.28	
Robust CV	6.5%	

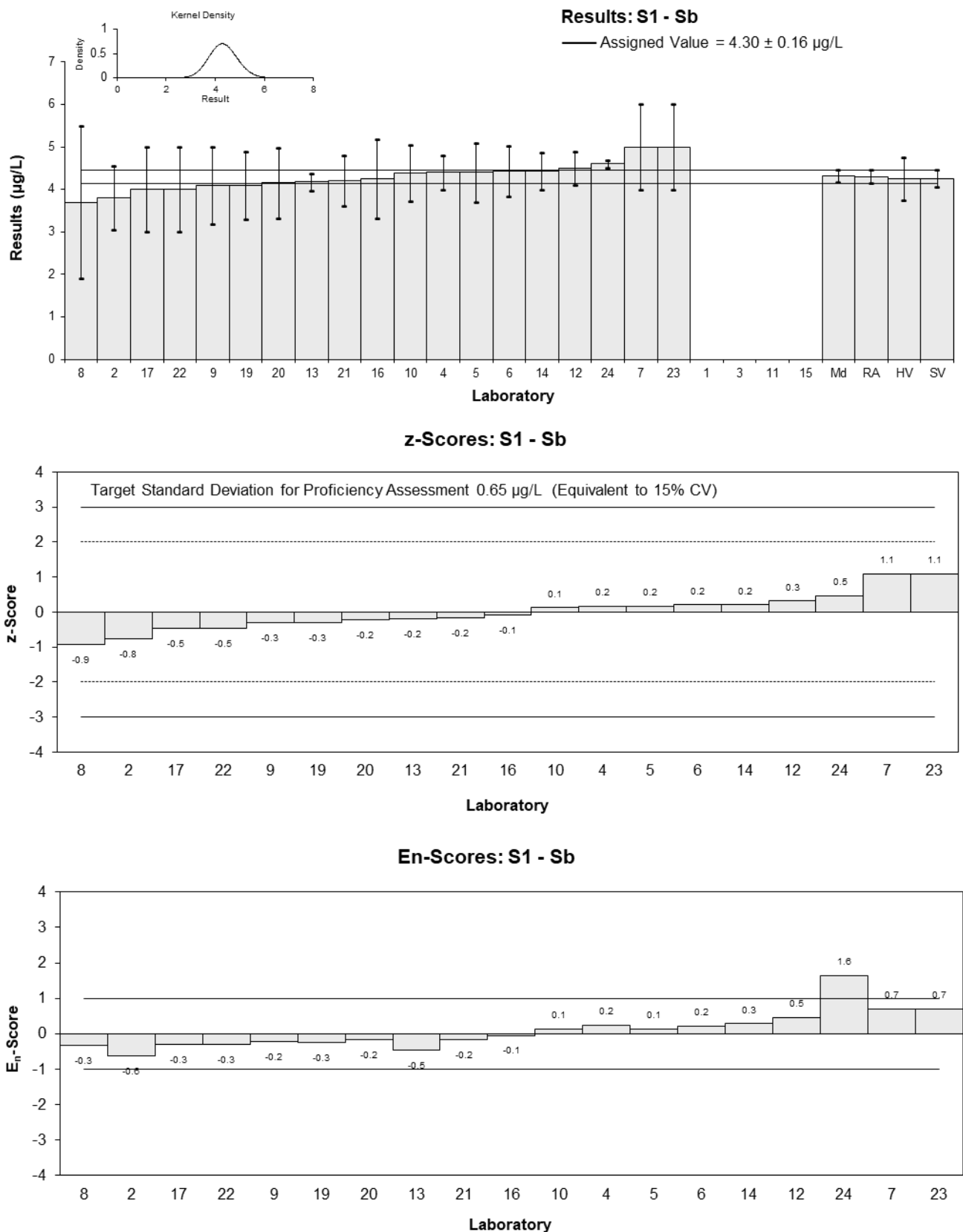


Figure 16

Table 19

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	2.2	0.44	0.56	0.38
3	NT	NT		
4	2.2	1	0.56	0.17
5	1.35	0.3	-2.23	-2.19
6	2.43	0.10	1.31	3.12
7	2	1	-0.10	-0.03
8**	5.1	1.3	10.08	2.36
9	2.09	0.52	0.20	0.11
10	2.01	0.69	-0.07	-0.03
11	NT	NT		
12	2.1	0.8	0.23	0.09
13	1.94	0.10	-0.30	-0.70
14	2.09	0.21	0.20	0.27
15	NT	NT		
16	2.09	0.46	0.20	0.13
17	2	0.3	-0.10	-0.10
19	2	3	-0.10	-0.01
20	1.8	0.36	-0.76	-0.62
21	<2	NR		
22	2	1	-0.10	-0.03
23	2	1	-0.10	-0.03
24	1.9	0.038	-0.43	-1.47

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.03	0.08
Spike Value	2.01	0.10
Homogeneity Value	1.72	0.21
Robust Average	2.03	0.08
Median	2.00	0.08
Mean	2.01	
N	17	
Max	2.43	
Min	1.35	
Robust SD	0.14	
Robust CV	6.7%	

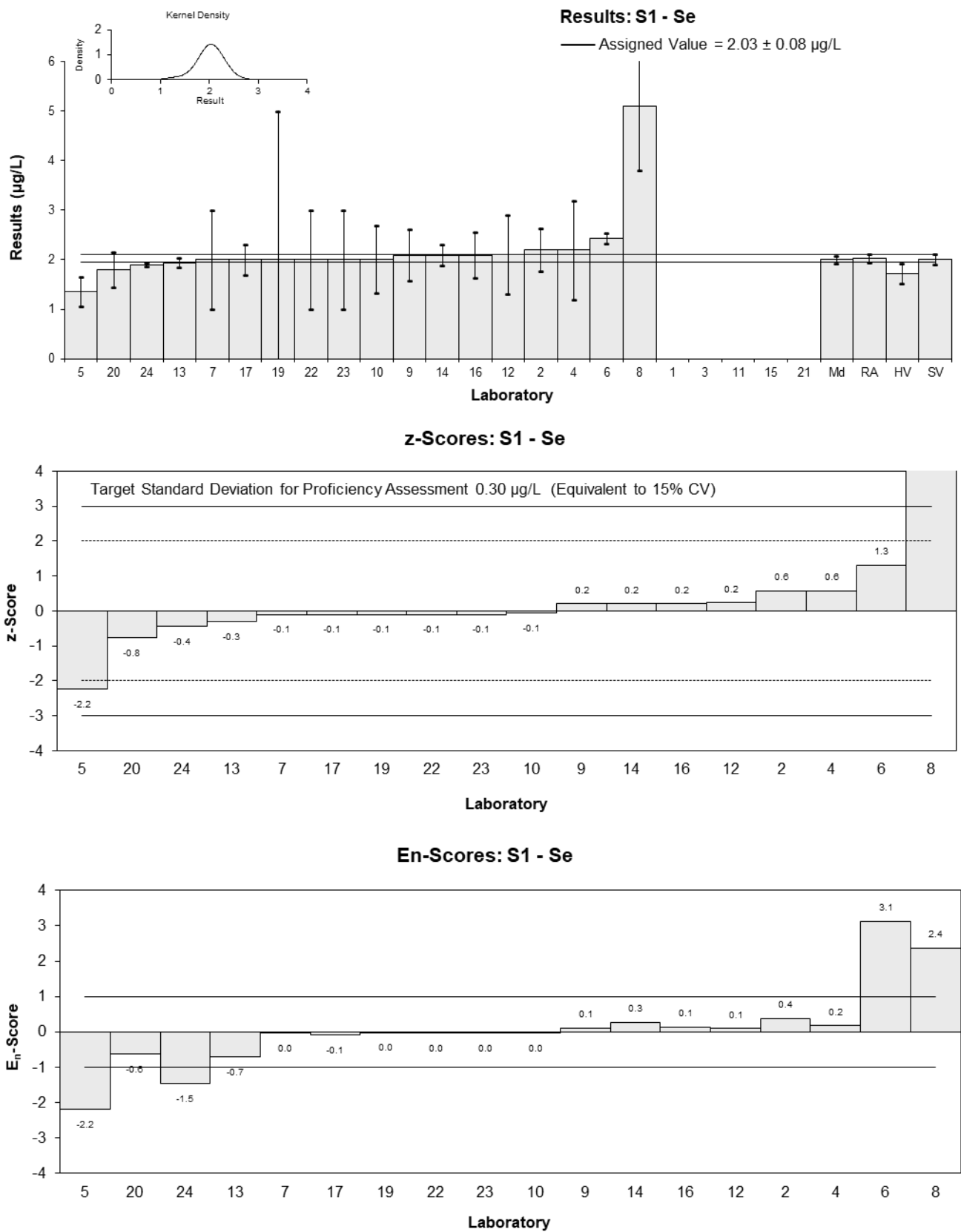


Figure 17

Table 20

Sample Details

Sample No.	S1
Matrix	River Water
Analyte	TI
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	1.4	0.28	-0.23	-0.17
3	NT	NT		
4	1.5	0.2	0.23	0.24
5	1.55	0.3	0.46	0.32
6	1.43	0.6	-0.09	-0.03
7	1	1	-2.07	-0.45
8**	2	1	2.53	0.55
9	1.52	0.35	0.32	0.20
10	1.517	0.075	0.31	0.65
11	NT	NT		
12	1.5	0.2	0.23	0.24
13	1.47	0.08	0.09	0.19
14	1.50	0.2	0.23	0.24
15	NT	NT		
16	1.45	0.23	0.00	0.00
17	NT	NT		
19	1.5	1	0.23	0.05
20	1.5	0.3	0.23	0.16
21	1.3	0.2	-0.69	-0.71
22	1	1	-2.07	-0.45
23	2	1	2.53	0.55
24	1.3	0.026	-0.69	-2.01

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.45	0.07
Spike Value	1.53	0.08
Homogeneity Value	1.42	0.17
Robust Average	1.45	0.07
Median	1.50	0.04
Mean	1.44	
N	17	
Max	2	
Min	1	
Robust SD	0.12	
Robust CV	8.2%	

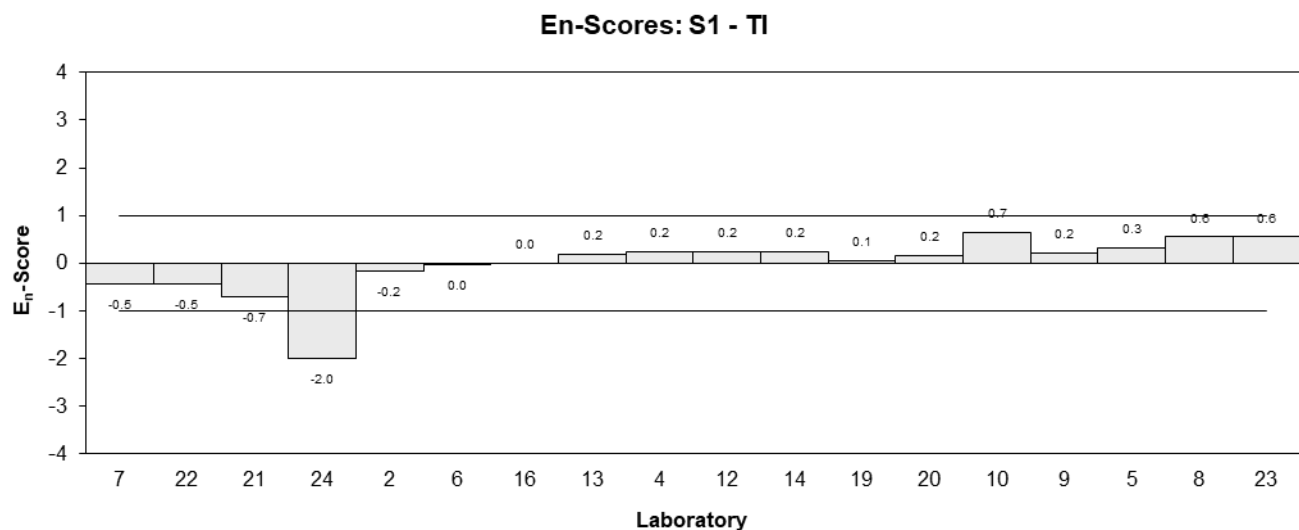
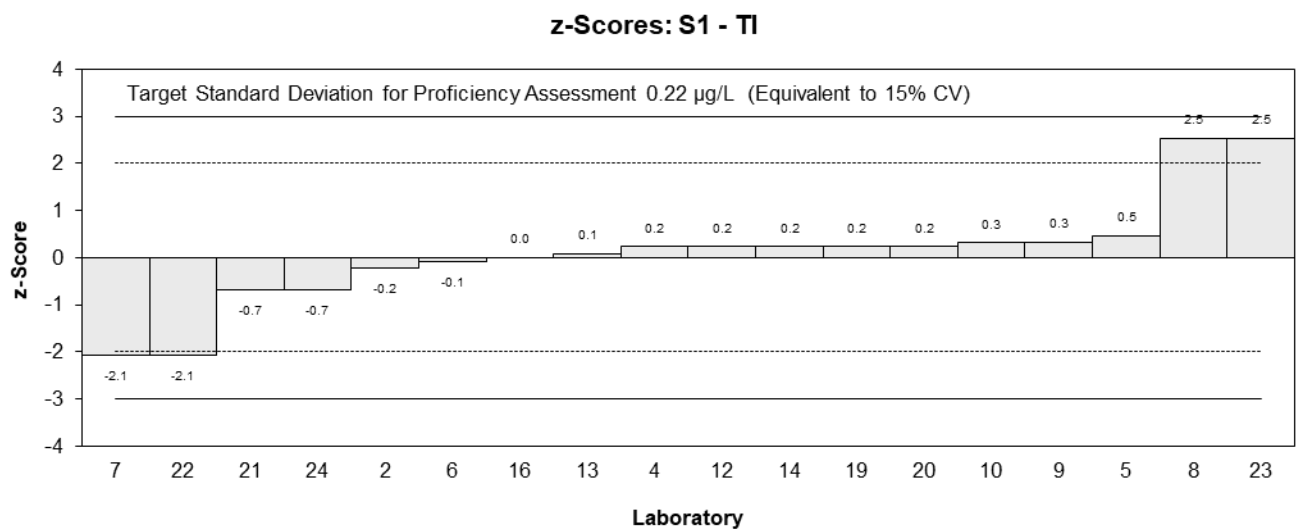
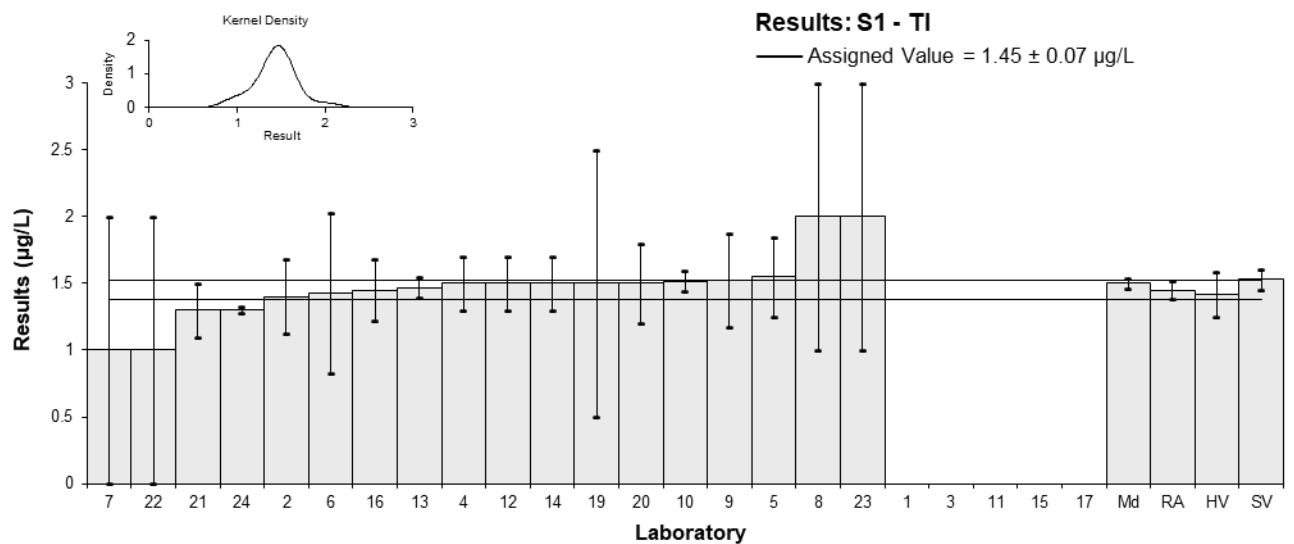


Figure 18

Table 21

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	3	0.6	0.03	0.02
3	NT	NT		
4	2.9	0.4	-0.30	-0.22
5	3.19	0.5	0.67	0.39
6	NT	NT		
7	3	1	0.03	0.01
8**	2.9	0.72	-0.30	-0.12
9	2.98	0.67	-0.03	-0.01
10	3.03	0.34	0.13	0.11
11	NT	NT		
12	3.1	0.2	0.37	0.51
13	2.97	0.15	-0.07	-0.12
14	3.02	0.30	0.10	0.10
15	NT	NT		
16	3.32	0.46	1.10	0.71
17	2.4	0.5	-1.97	-1.17
19	3	1	0.03	0.01
20	3.1	0.62	0.37	0.18
21	2.8	0.5	-0.64	-0.38
22	3	1	0.03	0.01
23	3	1	0.03	0.01
24	2.7	0.054	-0.97	-3.00

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	2.99	0.08
Spike Value	3.04	0.15
Homogeneity Value	2.93	0.35
Robust Average	2.99	0.08
Median	3.00	0.03
Mean	2.97	
N	17	
Max	3.32	
Min	2.4	
Robust SD	0.14	
Robust CV	4.7%	

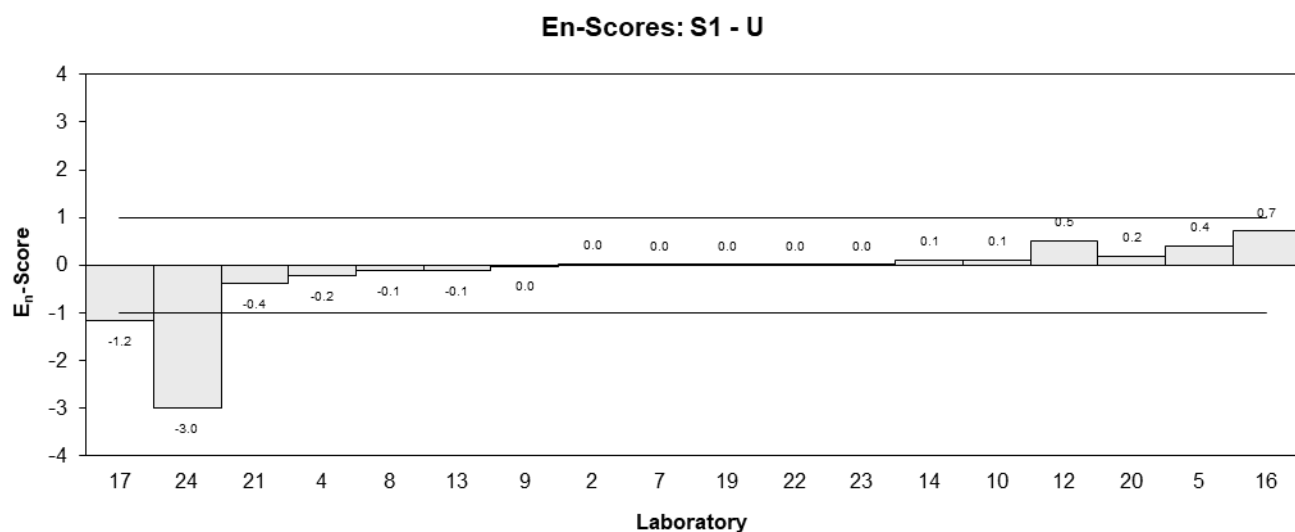
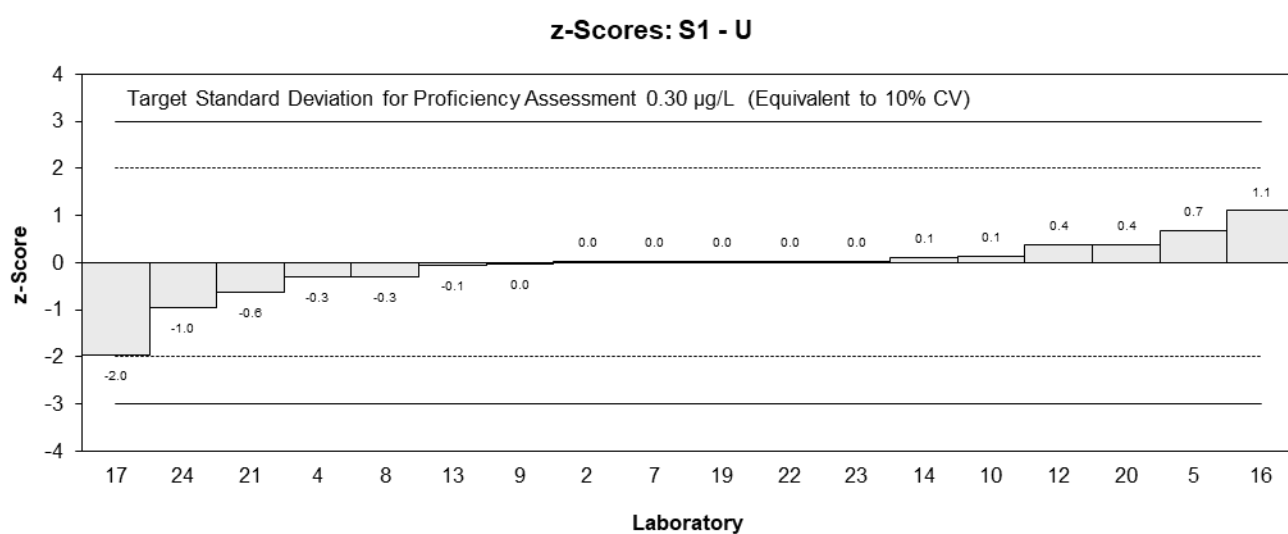
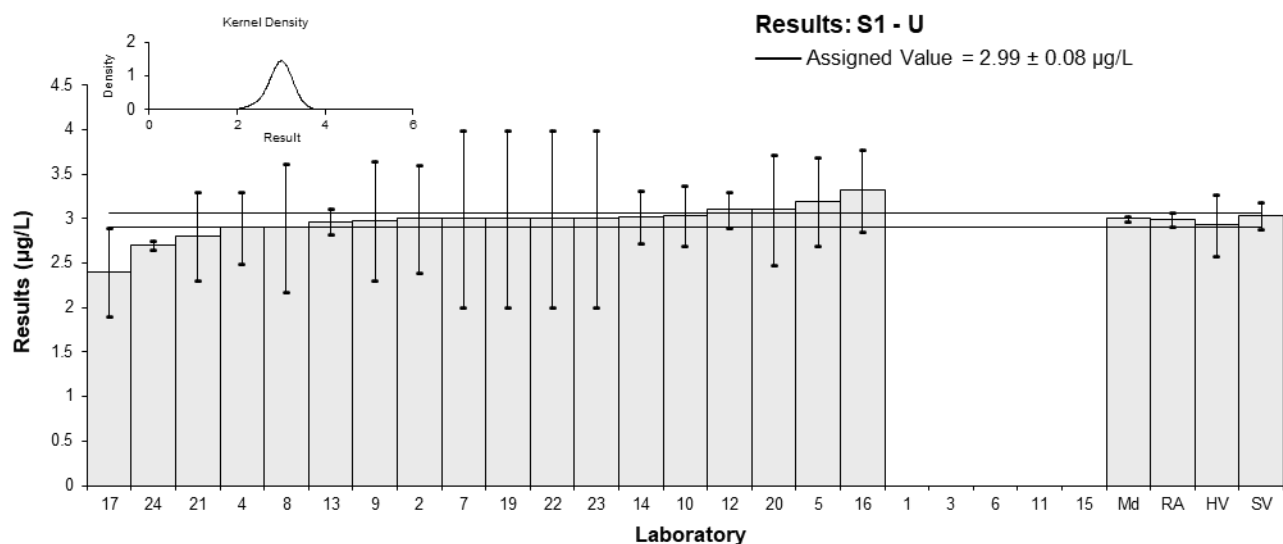


Figure 19

Table 22

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	0.7	0.14	-2.39	-2.19
3	NT	NT		
4	1.2	0.2	0.67	0.48
5	1.37	0.3	1.71	0.88
6	1.03	0.8	-0.37	-0.07
7	<1	NR		
8**	3.6	0.9	15.35	2.77
9	0.84	0.24	-1.53	-0.95
10	1.1	0.67	0.06	0.01
11	NT	NT		
12	1.2	0.2	0.67	0.48
13	1.13	0.06	0.24	0.32
14	1.10	0.2	0.06	0.04
15	NT	NT		
16	1.31	0.25	1.35	0.81
17	1	0.2	-0.55	-0.39
19	<1	2		
20	1.2	0.24	0.67	0.42
21	1	0.2	-0.55	-0.39
22	<1	NR		
23	1	1	-0.55	-0.09
24	1.1	0.022	0.06	0.09

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.09	0.11
Spike Value	1.11	0.05
Homogeneity Value	1.06	0.13
Robust Average	1.09	0.11
Median	1.10	0.10
Mean	1.09	
N	15	
Max	1.37	
Min	0.7	
Robust SD	0.16	
Robust CV	15%	

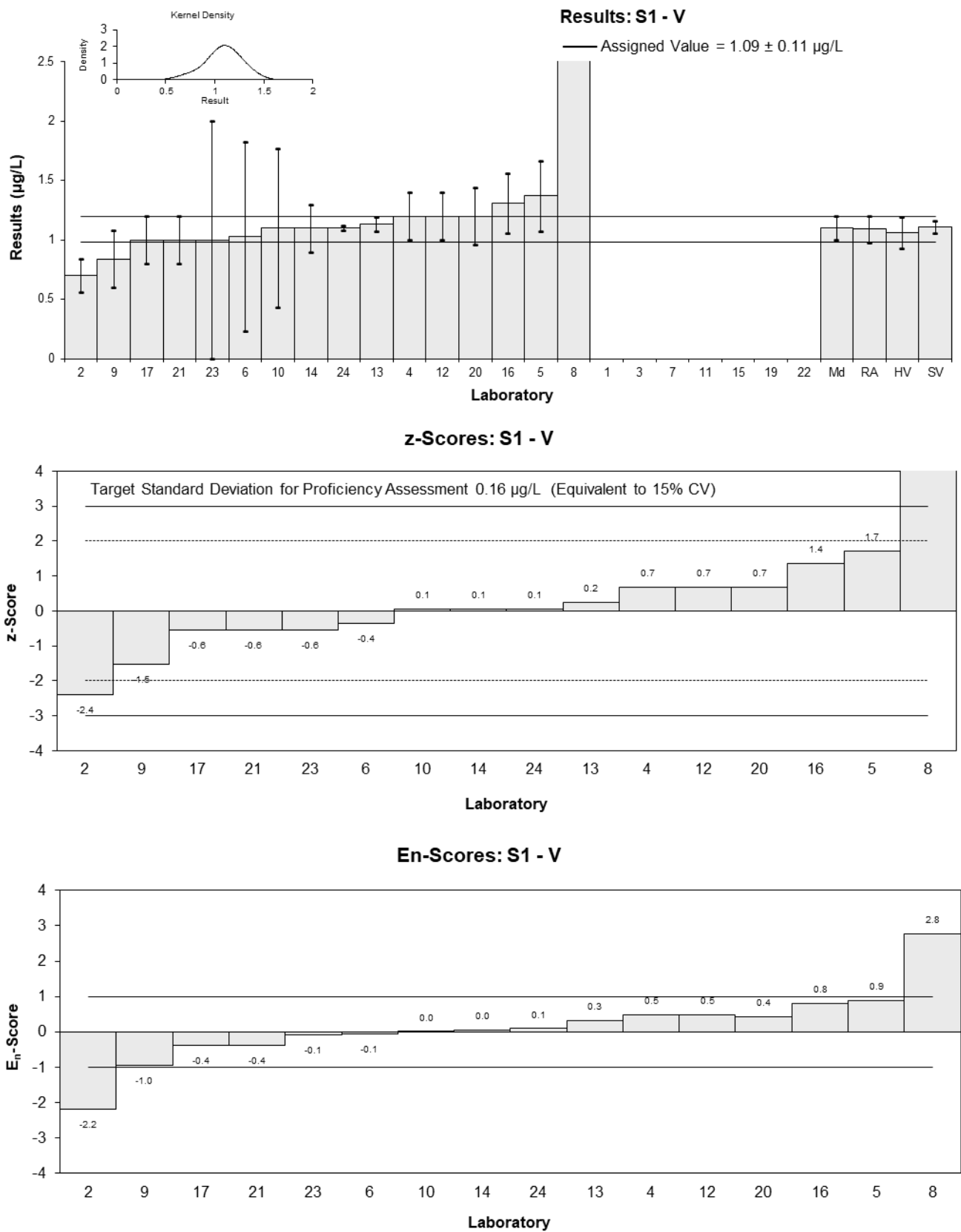


Figure 20

Table 23

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	30	6	1.00	0.63
3	NT	NT		
4	28	4.2	0.49	0.43
5	26.9	3.0	0.20	0.24
6	23.89	2.1	-0.56	-0.88
7	32	6	1.51	0.96
8**	18.8	2.4	-1.86	-2.63
9	26.7	6.5	0.15	0.09
10	26.5	1.7	0.10	0.18
11	NT	NT		
12	25.9	3.8	-0.05	-0.05
13	25.6	1.25	-0.13	-0.27
14	24.9	2.5	-0.31	-0.42
15	NT	NT		
16	23.0	4.8	-0.79	-0.62
17	23	4	-0.79	-0.73
19	25	5	-0.28	-0.21
20	23	4.6	-0.79	-0.64
21	25	5	-0.28	-0.21
22	28	6	0.49	0.31
23	28	6	0.49	0.31
24	26.8	0.536	0.18	0.47

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	26.1	1.4
Spike Value	26.0	1.2
Homogeneity Value	22.4	2.7
Robust Average	26.1	1.4
Median	26.2	1.4
Mean	26.2	
N	18	
Max	32	
Min	23	
Robust SD	2.4	
Robust CV	9.2%	

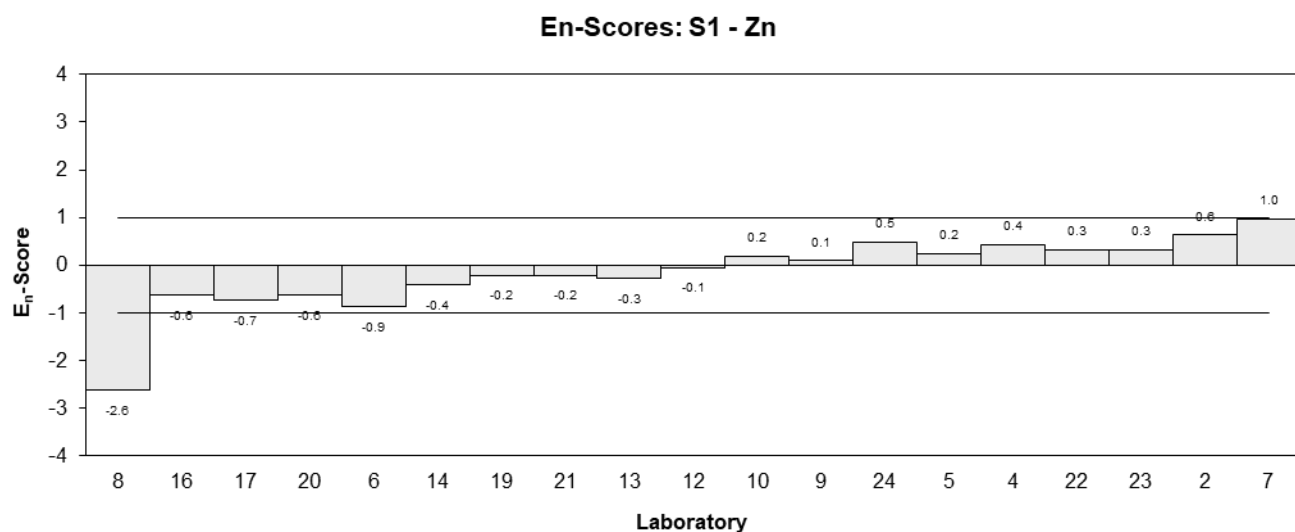
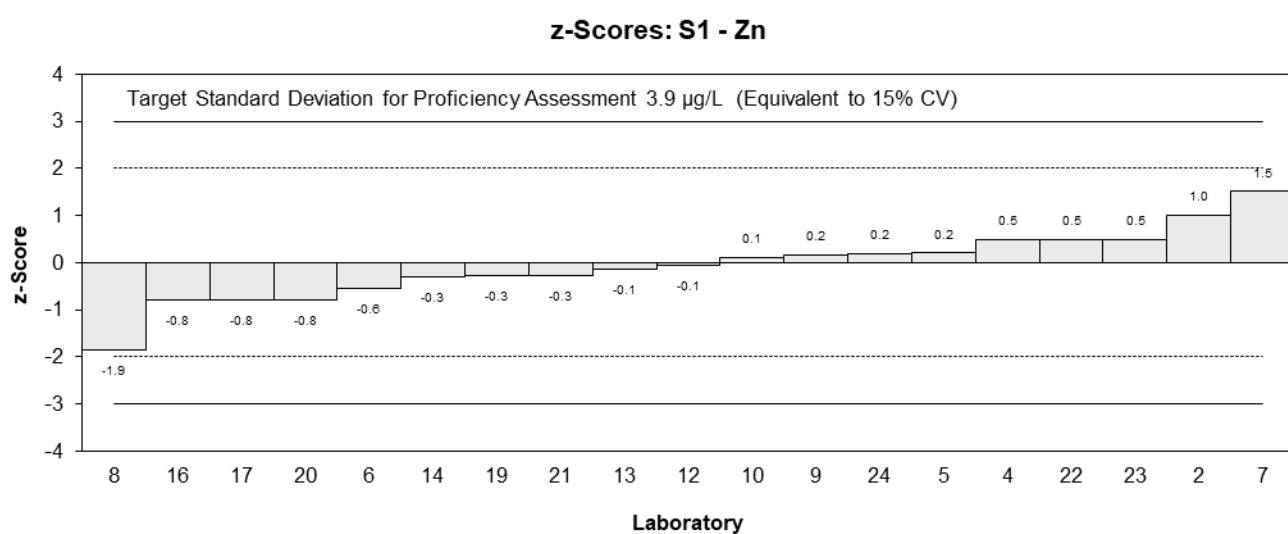
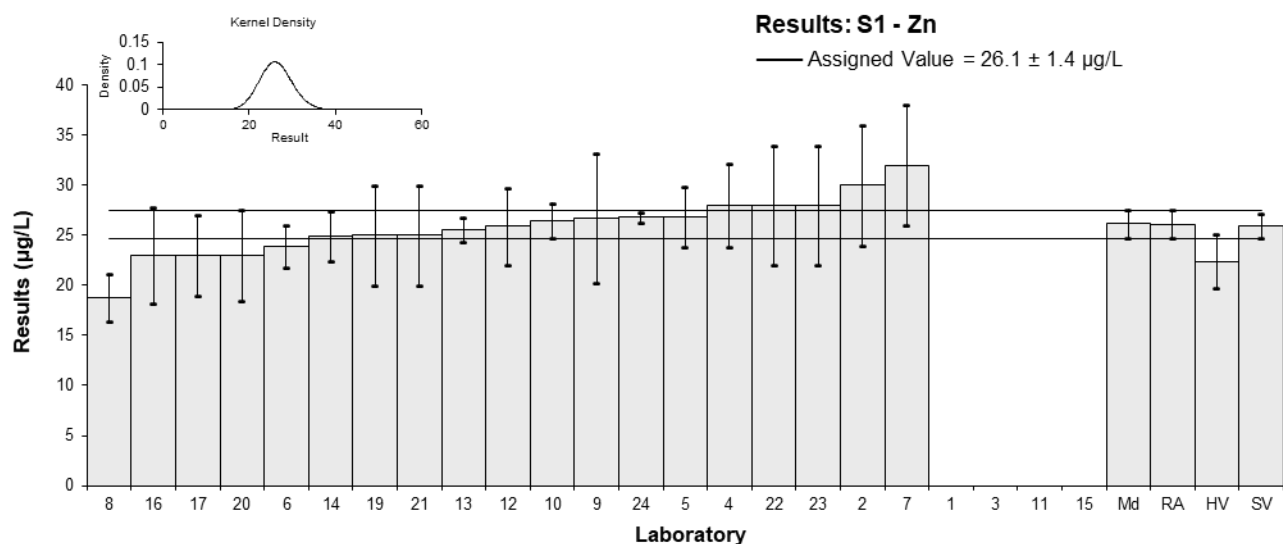


Figure 21

Table 24

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	<5	NR		
2	1.6	0.32	0.59	0.37
3	< 50	NR		
4	1.5	0.2	0.14	0.12
5	1.48	0.2	0.05	0.04
6	NT	NT		
7	2	1	2.40	0.52
8	NT	NT		
9	1.03	0.24	-2.00	-1.58
10	1.4	0.34	-0.32	-0.19
11	1.3	2	-0.77	-0.08
12	1.5	0.5	0.14	0.06
13	NT	NT		
14	1.54	1	0.32	0.07
15	1.32	0.17	-0.68	-0.68
16	1.42	0.17	-0.23	-0.23
17	NT	NT		
19	1.5	0.5	0.14	0.06
20	1.56	0.312	0.41	0.26
21	NT	NT		
22	2	1	2.40	0.52
23	1	1	-2.13	-0.47
24	NT	NT		

Statistics

Assigned Value	1.47	0.14
Spike Value	1.53	0.04
Robust Average	1.47	0.14
Median	1.50	0.10
Mean	1.48	
N	15	
Max	2	
Min	1	
Robust SD	0.22	
Robust CV	15%	

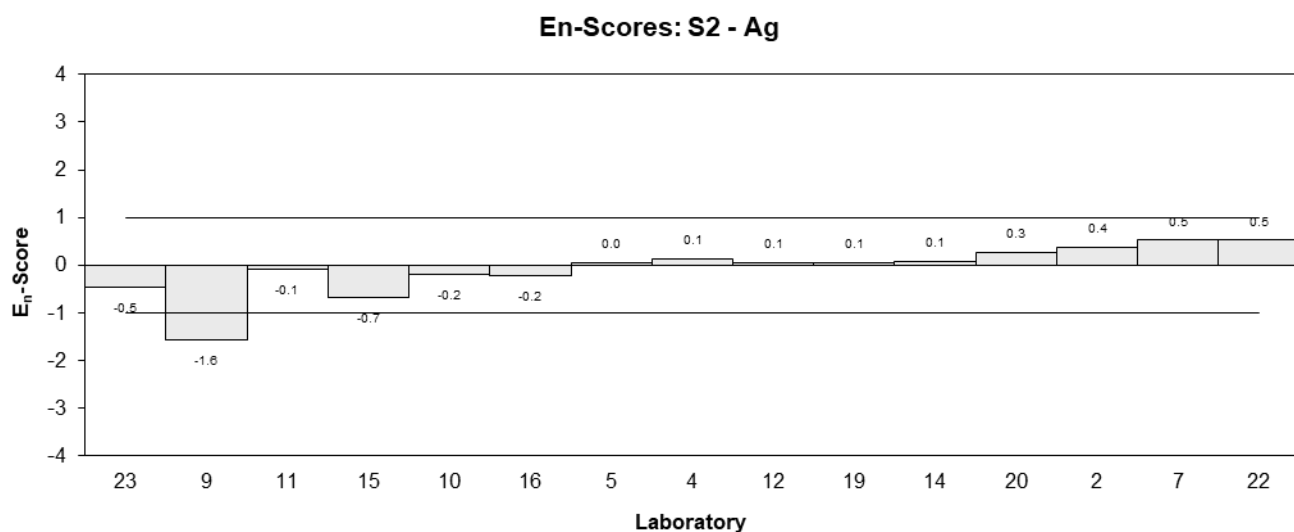
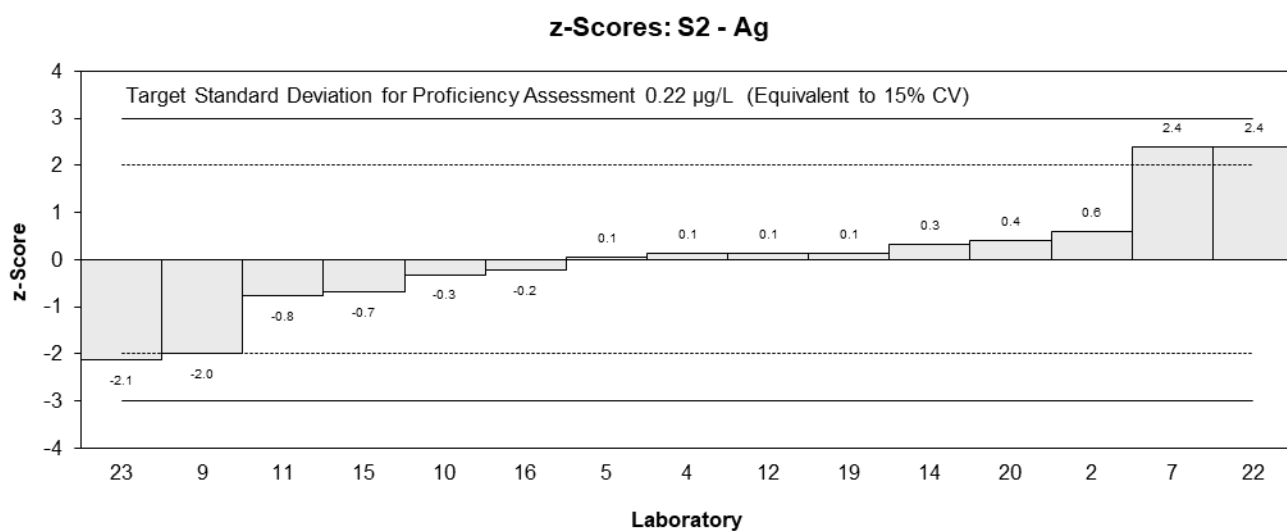
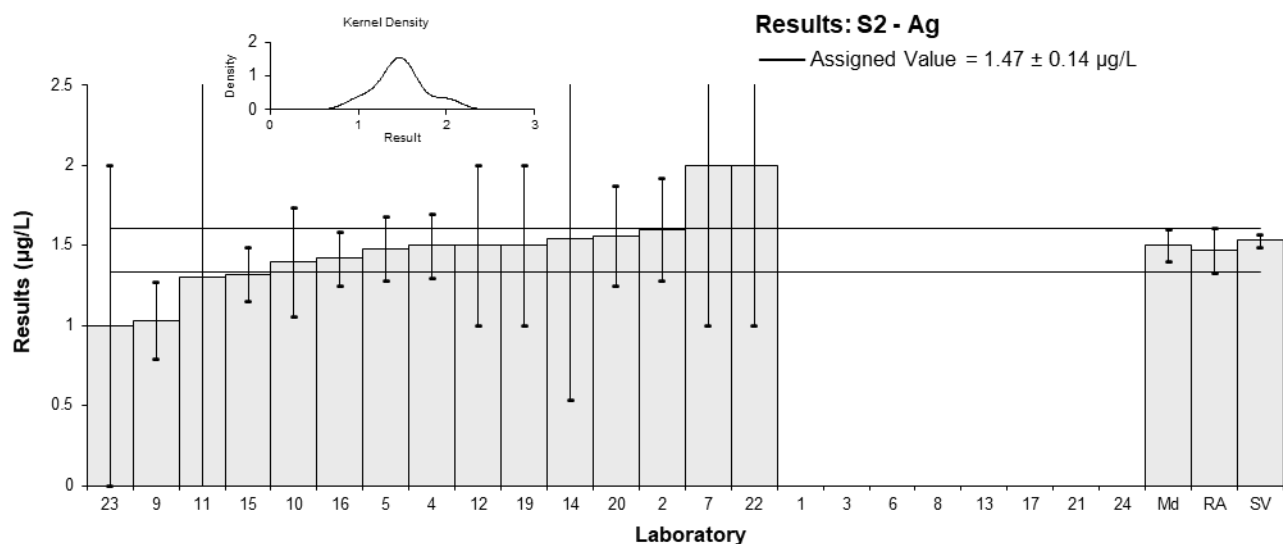


Figure 22

Table 25

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<50	NR		
2	<50	NR		
3	< 50	NR		
4	18	5	1.08	0.47
5	13.6	2.0	-0.82	-0.72
6	NT	NT		
7	14	10	-0.65	-0.15
8	NT	NT		
9	17.3	3.6	0.77	0.45
10	<40	8.5		
11	14	3	-0.65	-0.44
12	13	3	-1.08	-0.73
13	NT	NT		
14	20.0	2	1.94	1.71
15	< 50	NR		
16	15.0	3.3	-0.22	-0.13
17	NT	NT		
19	13	9	-1.08	-0.27
20	16.2	3.24	0.30	0.19
21	<20	NR		
22	17	10	0.65	0.15
23	16	10	0.22	0.05
24*	35.8	0.716	8.73	11.00

* Outlier, see Section 4.2

Statistics

Assigned Value	15.5	1.7
Spike Value	13.8	0.8
Robust Average	15.9	1.9
Median	16.0	2.1
Mean	17.1	
N	13	
Max	35.8	
Min	13	
Robust SD	2.8	
Robust CV	17%	

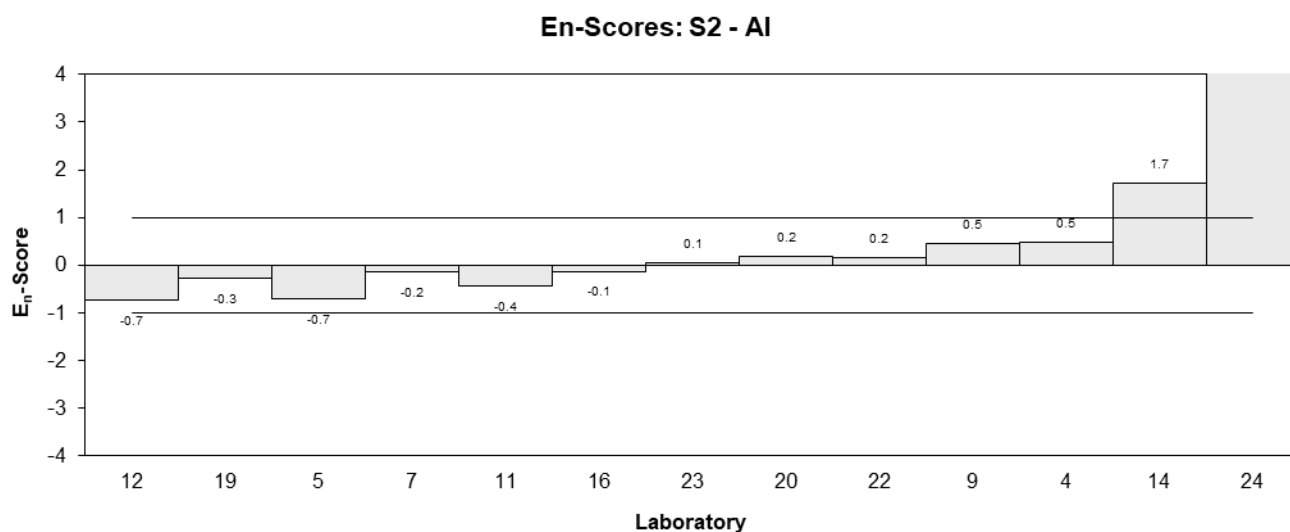
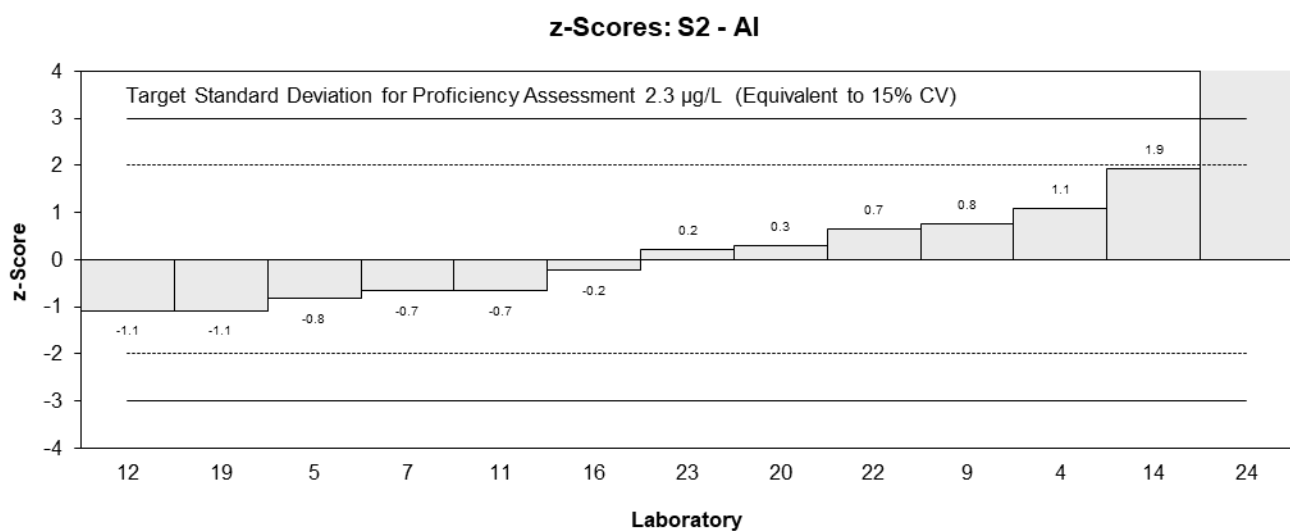
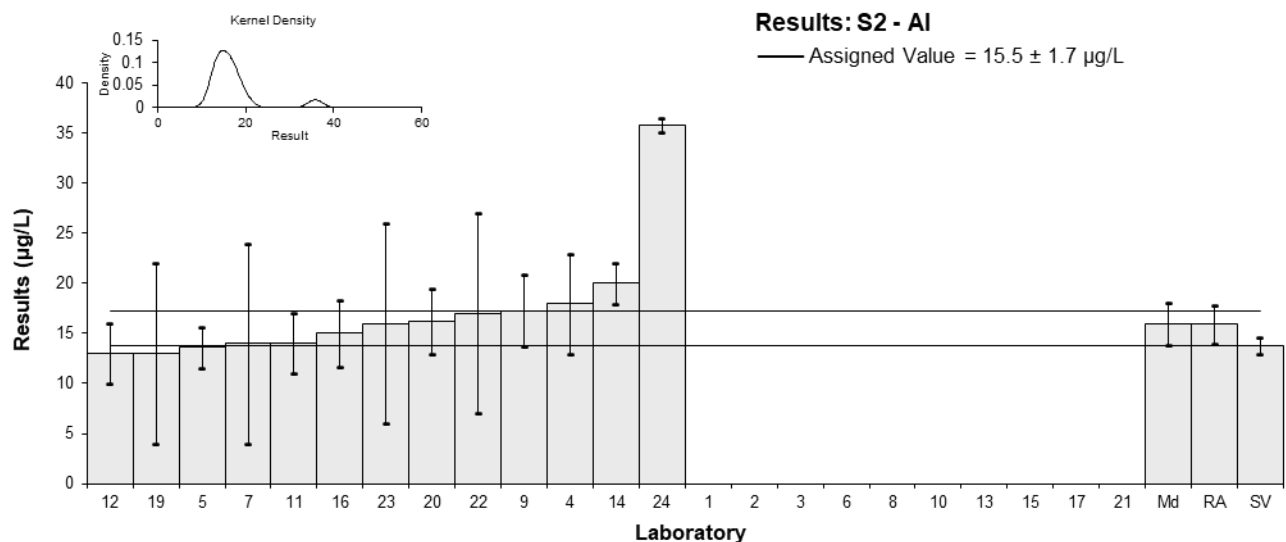


Figure 23

Table 26

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	6.18	1.24	1.40	0.83
2	4.8	0.96	-0.40	-0.30
3	5.11	0.50	0.00	0.00
4	5.3	1	0.25	0.18
5	5.14	0.7	0.04	0.04
6	NT	NT		
7	5	1	-0.14	-0.10
8	NT	NT		
9	4.57	1.02	-0.70	-0.50
10	5.6	2.8	0.64	0.17
11	7.3	2	2.86	1.08
12	5	3	-0.14	-0.04
13	NT	NT		
14	4.87	1	-0.31	-0.22
15	5.40	0.72	0.38	0.36
16	4.24	0.59	-1.14	-1.24
17	NT	NT		
19	6.4	5	1.68	0.26
20	4.4	0.88	-0.93	-0.74
21	<20	NR		
22	5	1	-0.14	-0.10
23	5	1	-0.14	-0.10
24	4.4	0.088	-0.93	-1.82

Statistics

Assigned Value	5.11	0.38
Spike Value	4.42	0.41
Robust Average	5.11	0.38
Median	5.00	0.31
Mean	5.21	
N	18	
Max	7.3	
Min	4.24	
Robust SD	0.64	
Robust CV	12%	

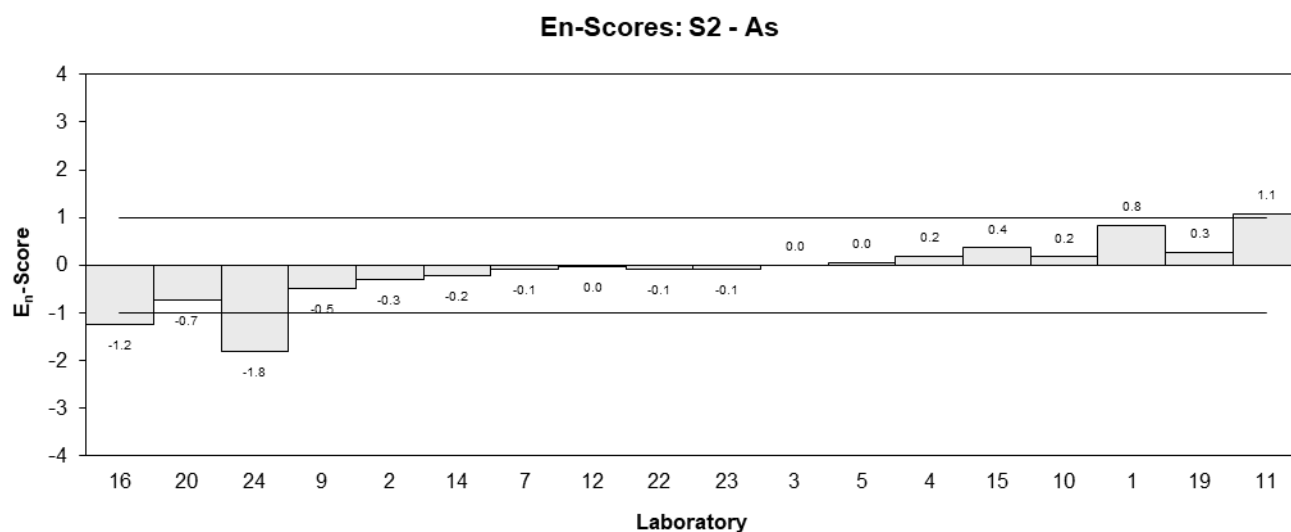
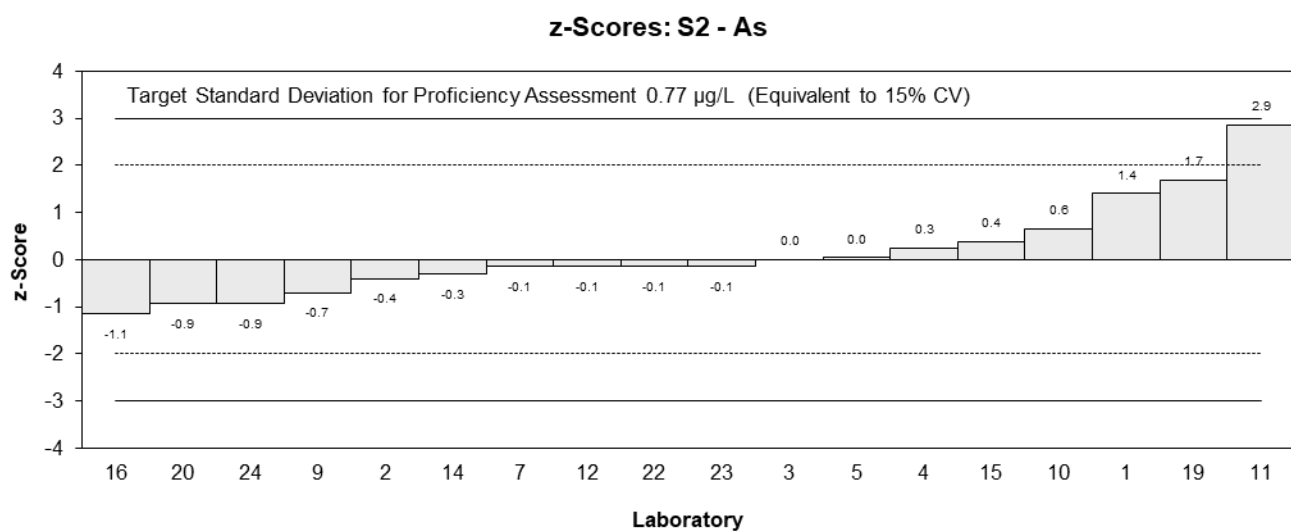
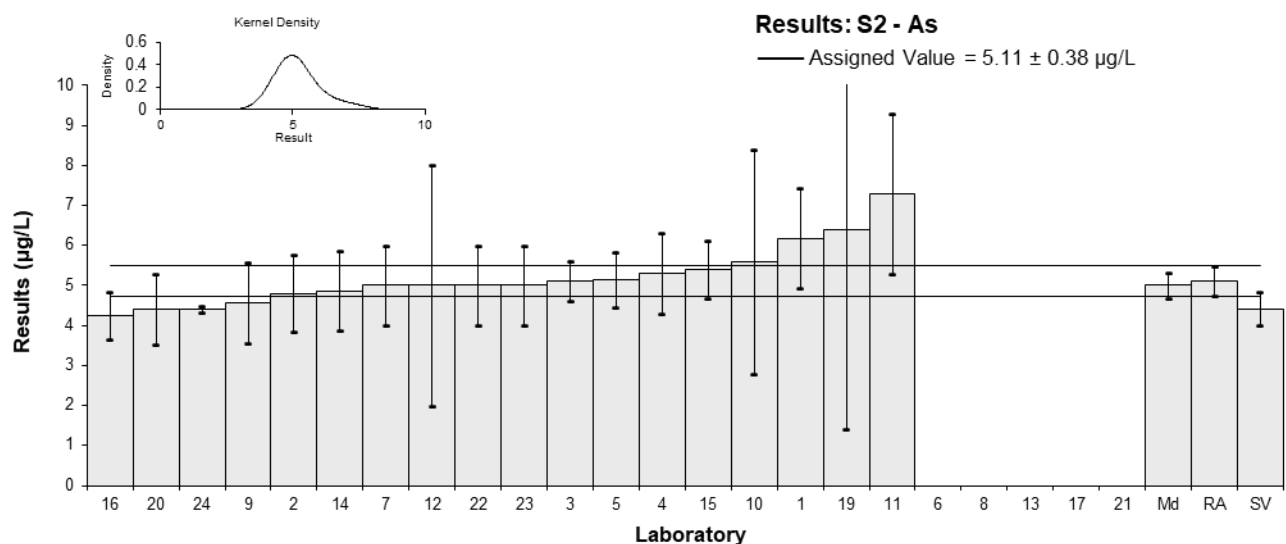


Figure 24

Table 27

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E _n
1	1.91	0.382	0.22	0.15
2	1.5	0.3	-1.26	-1.11
3	1.87	0.26	0.07	0.07
4	1.9	0.2	0.18	0.22
5	1.77	0.2	-0.29	-0.36
6	NT	NT		
7	2	0.6	0.54	0.25
8	NT	NT		
9	1.69	0.53	-0.58	-0.30
10	NT	NT		
11	1.8	2	-0.18	-0.02
12	1.91	1.06	0.22	0.06
13	NT	NT		
14	1.81	1	-0.14	-0.04
15	1.79	0.26	-0.22	-0.22
16	NT	NT		
17	NT	NT		
19	1	2	-3.06	-0.42
20	2.16	0.432	1.12	0.70
21	2	1	0.54	0.15
22	2	0.6	0.54	0.25
23	2	0.5	0.54	0.29
24	1.7	0.034	-0.54	-1.42

Statistics

Assigned Value	1.85	0.10
Spike Value	1.87	0.05
Robust Average	1.85	0.10
Median	1.87	0.12
Mean	1.81	
N	17	
Max	2.16	
Min	1	
Robust SD	0.17	
Robust CV	9.2%	

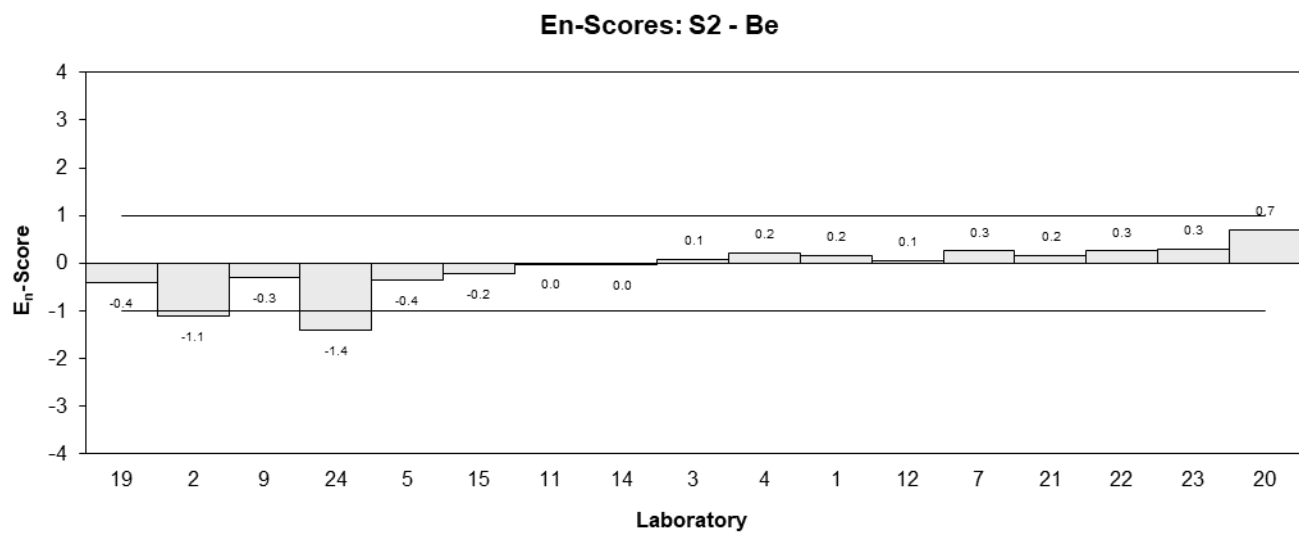
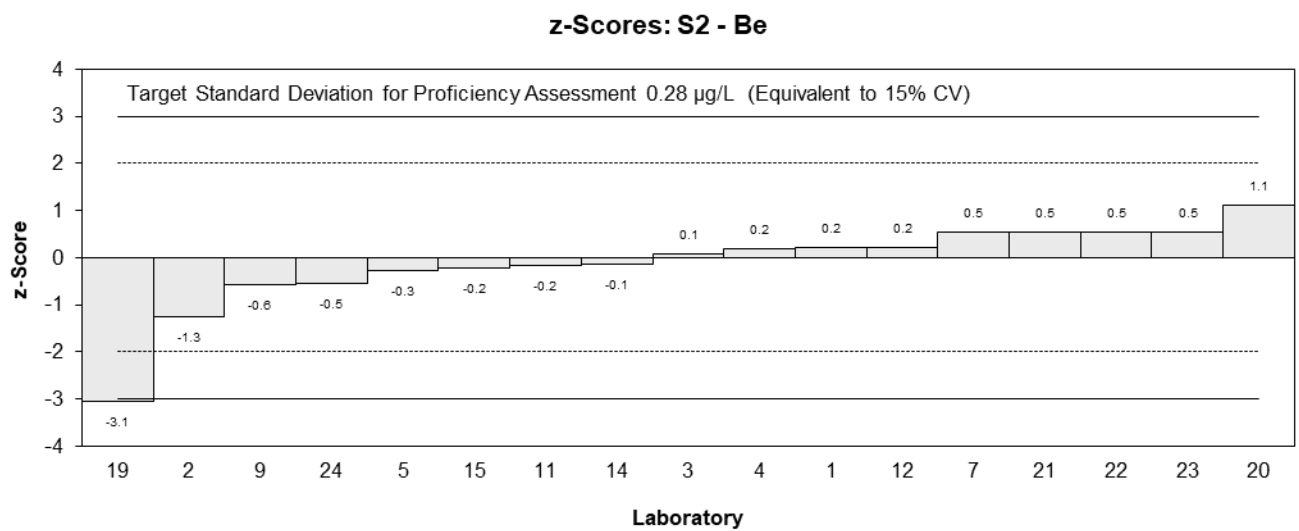
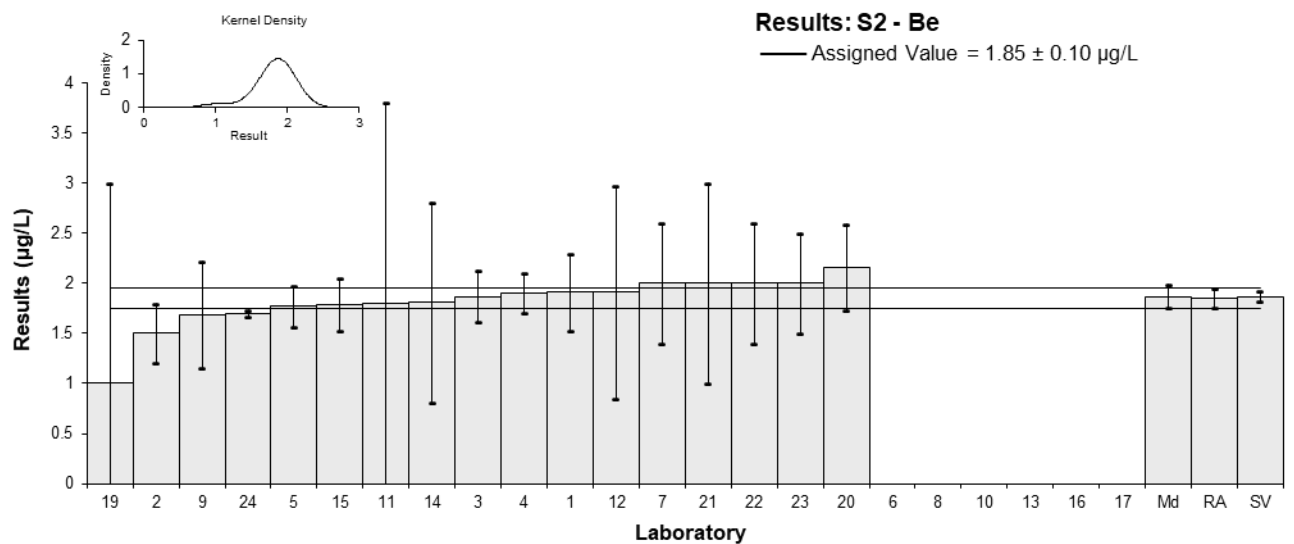


Figure 25

Table 28

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.36	0.272	0.47	0.32
2	1.2	0.24	-0.37	-0.28
3	< 2	NR		
4	1.3	0.2	0.16	0.14
5	1.16	0.2	-0.58	-0.53
6	NT	NT		
7	1.4	0.5	0.68	0.26
8	NT	NT		
9	1.16	0.27	-0.58	-0.40
10	1.26	0.31	-0.05	-0.03
11	1.3	0.2	0.16	0.14
12	1.6	0.5	1.73	0.66
13	NT	NT		
14	1.36	1	0.47	0.09
15	1.23	0.13	-0.21	-0.28
16	1.20	0.25	-0.37	-0.27
17	NT	NT		
19	1.2	0.7	-0.37	-0.10
20	1.3	0.26	0.16	0.11
21	<1	NR		
22	1.2	0.5	-0.37	-0.14
23	1.2	0.3	-0.37	-0.23
24	1.3	0.026	0.16	0.46

Statistics

Assigned Value	1.27	0.06
Spike Value	1.27	0.04
Robust Average	1.27	0.06
Median	1.26	0.05
Mean	1.28	
N	17	
Max	1.6	
Min	1.16	
Robust SD	0.092	
Robust CV	7.3%	

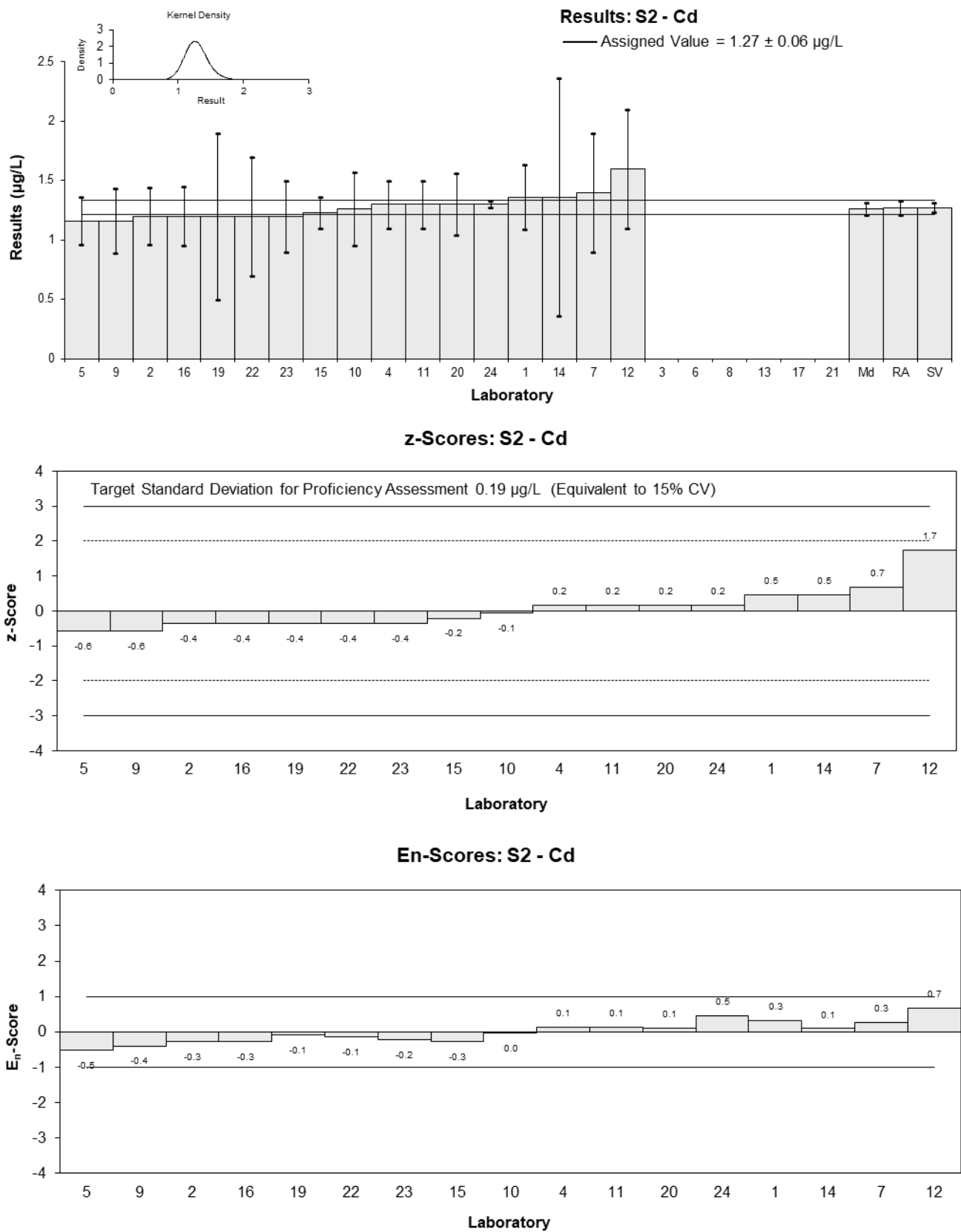


Figure 26

Table 29

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.15	0.231	-1.72	-1.20
2	<0.5	NR		
3	< 10	NR		
4	1.6	0.5	0.22	0.09
5	1.33	0.2	-0.95	-0.70
6	NT	NT		
7	2	1	1.94	0.44
8	NT	NT		
9	1.70	0.46	0.65	0.29
10	<2	0.74		
11	< 1	NR		
12	1.4	1.0	-0.65	-0.15
13	NT	NT		
14	1.47	1	-0.34	-0.08
15	1.16	0.12	-1.68	-1.45
16	1.21	0.18	-1.46	-1.13
17	NT	NT		
19	1.8	1.2	1.08	0.20
20	1.66	0.332	0.47	0.27
21	<1	NR		
22	2	1	1.94	0.44
23	2	1	1.94	0.44
24	1.2	0.024	-1.51	-1.45

Statistics

Assigned Value	1.55	0.24
Spike Value	1.49	0.13
Robust Average	1.55	0.24
Median	1.54	0.29
Mean	1.55	
N	14	
Max	2	
Min	1.15	
Robust SD	0.36	
Robust CV	23%	

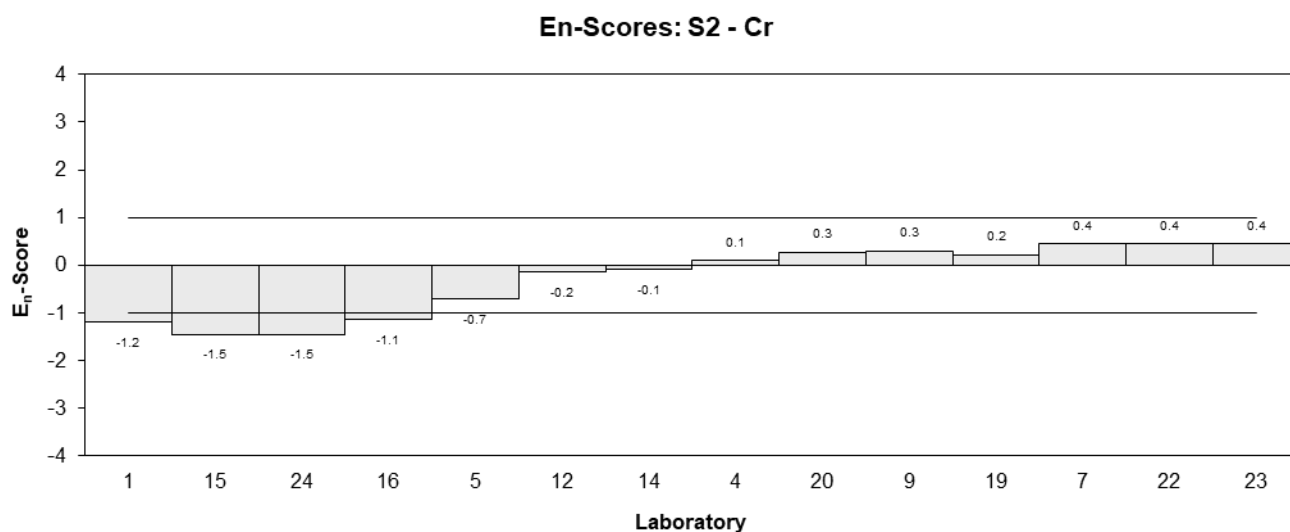
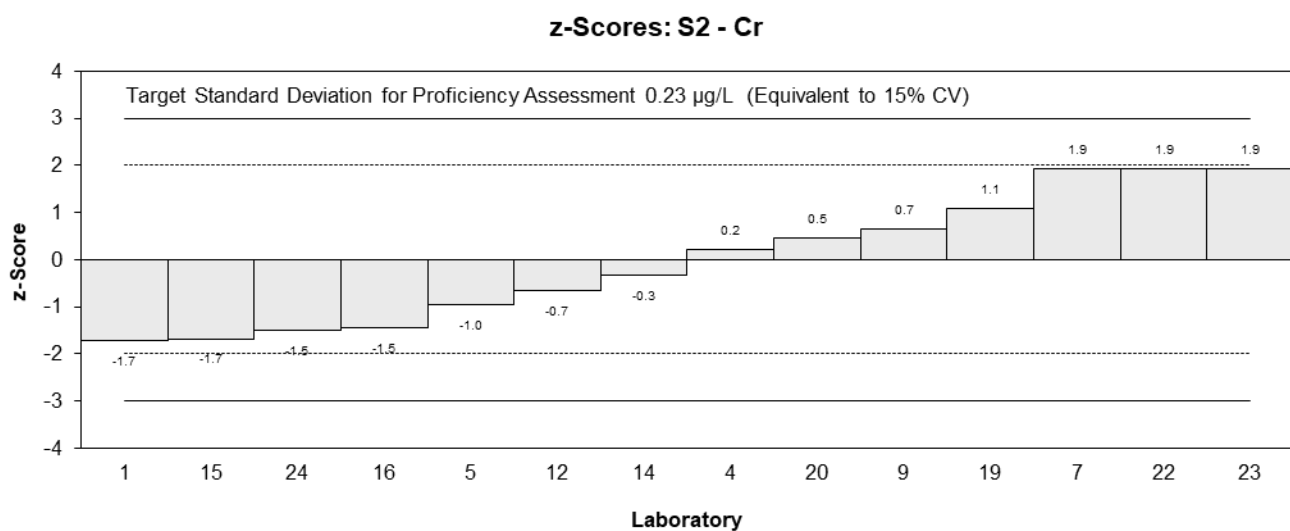
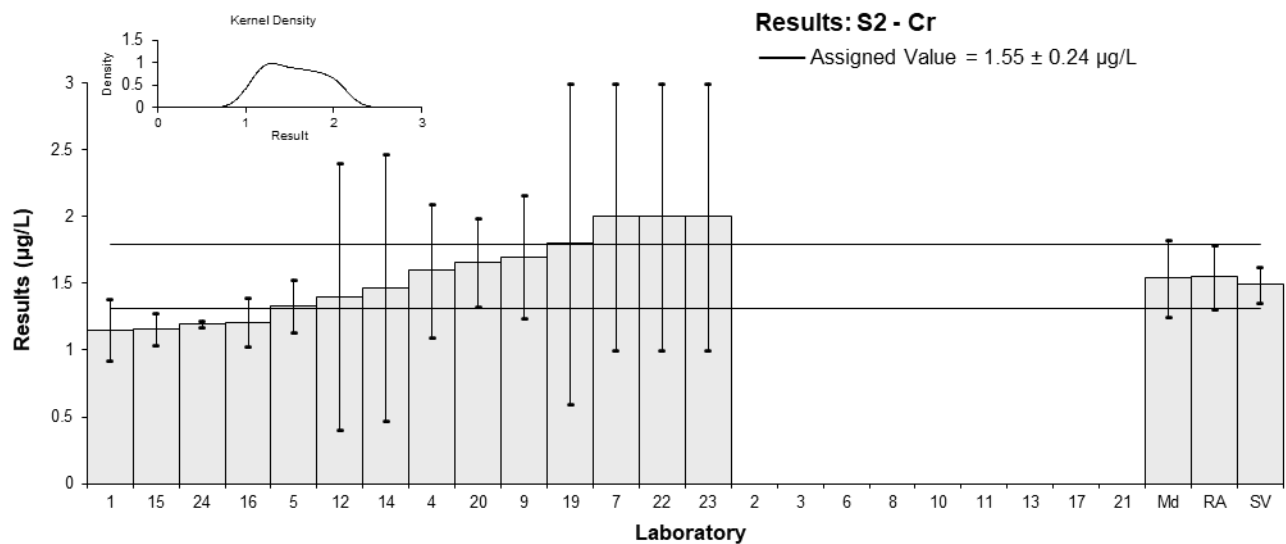


Figure 27

Table 30

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	6.98	1.396	-1.54	-1.31
2	7.9	1.58	-0.87	-0.67
3	< 10	NR		
4	9.8	1	0.53	0.57
5	9.29	1.0	0.15	0.17
6	NT	NT		
7	10	4	0.68	0.23
8	NT	NT		
9	8.44	1.96	-0.47	-0.30
10	9.7	2.5	0.46	0.24
11	5.9	2	-2.33	-1.48
12	10	2	0.68	0.43
13	NT	NT		
14	8.62	1	-0.34	-0.36
15	7.05	0.73	-1.49	-1.90
16	8.65	1.47	-0.32	-0.26
17	NT	NT		
19	10	2	0.68	0.43
20	9.62	1.924	0.40	0.26
21	10	2	0.68	0.43
22	11	4	1.41	0.47
23	10	2	0.68	0.43
24	9.1	0.182	0.01	0.02

Statistics

Assigned Value	9.08	0.78
Spike Value	9.75	0.75
Robust Average	9.08	0.78
Median	9.46	0.48
Mean	9.00	
N	18	
Max	11	
Min	5.9	
Robust SD	1.3	
Robust CV	15%	

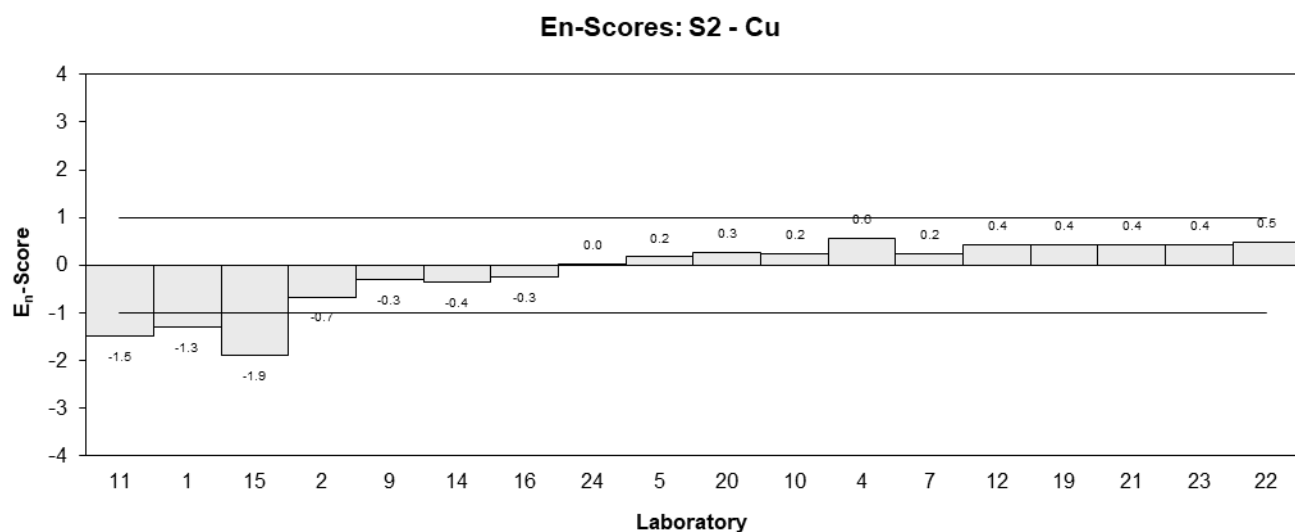
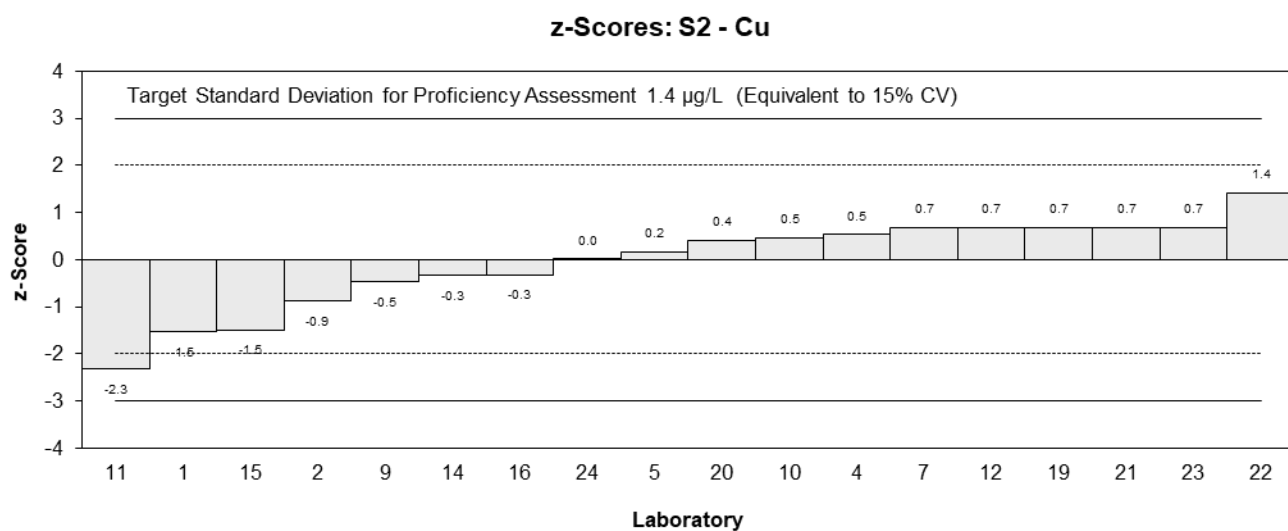
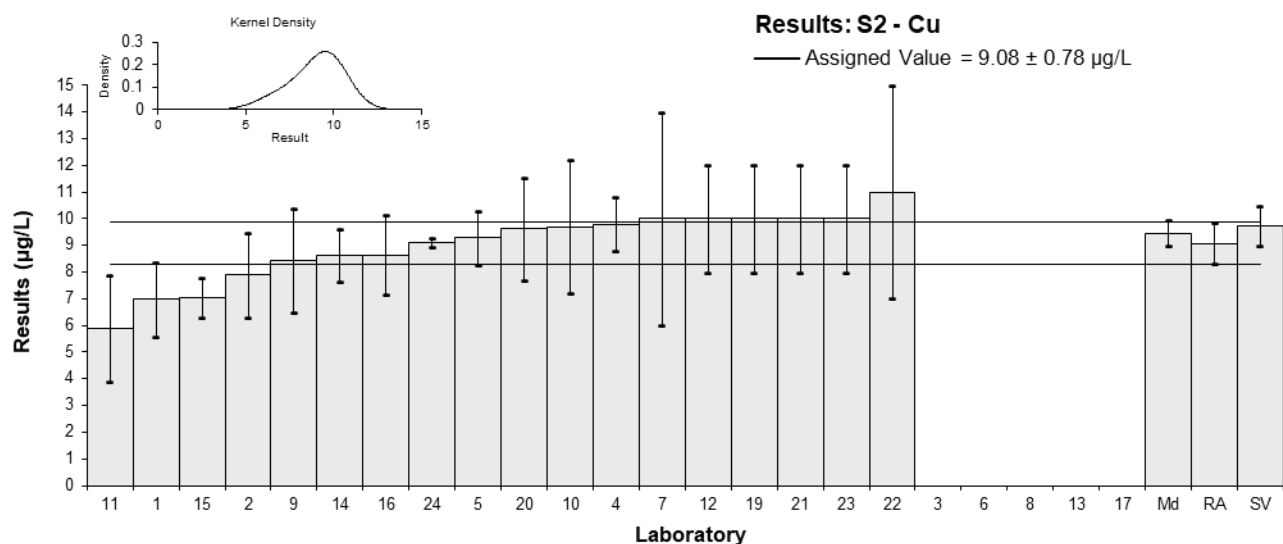


Figure 28

Table 31

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	17.5	3.50	-1.41	-1.12
2	21	4.2	-0.36	-0.25
3	< 50	NR		
4	26	5.5	1.14	0.64
5	21.7	2.5	-0.15	-0.15
6	NT	NT		
7	18	10	-1.26	-0.41
8	NT	NT		
9	24.2	8.6	0.60	0.22
10	24.1	4	0.57	0.41
11	17	20	-1.56	-0.26
12	<100	NR		
13	NT	NT		
14	23.6	2.3	0.42	0.43
15	< 50	NR		
16	19.5	3.1	-0.81	-0.70
17	NT	NT		
19	24	7	0.54	0.24
20	32.2	6.44	3.00	1.46
21	<20	NR		
22	23	10	0.24	0.08
23	25	10	0.84	0.27
24	21.2	0.424	-0.30	-0.43

Statistics

Assigned Value	22.2	2.3
Spike Value	24.6	1.0
Robust Average	22.2	2.3
Median	23.0	1.9
Mean	22.5	
N	15	
Max	32.2	
Min	17	
Robust SD	3.6	
Robust CV	16%	

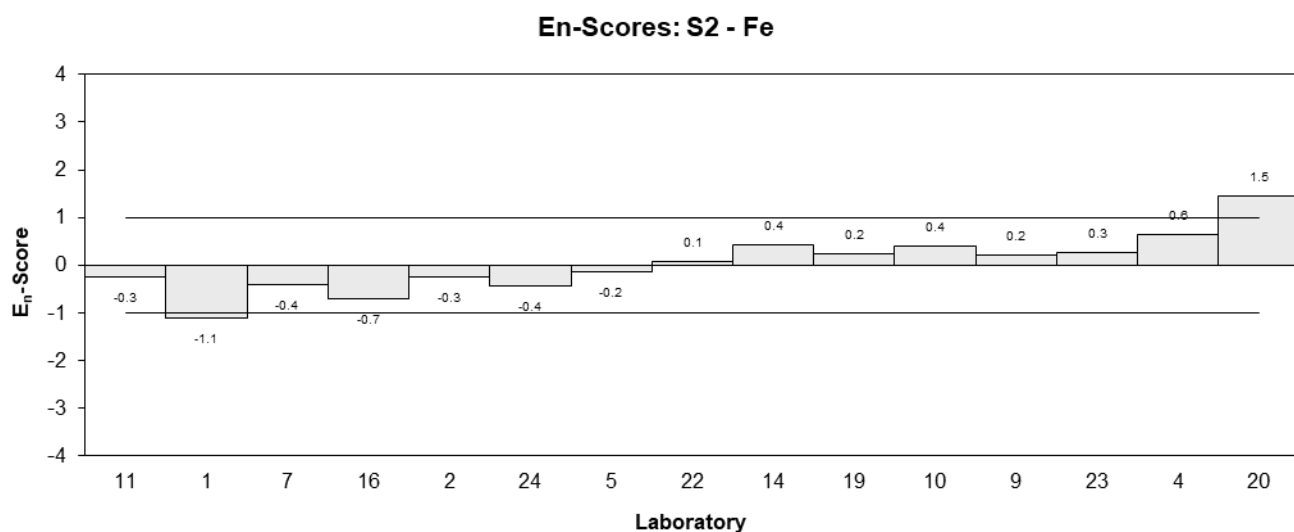
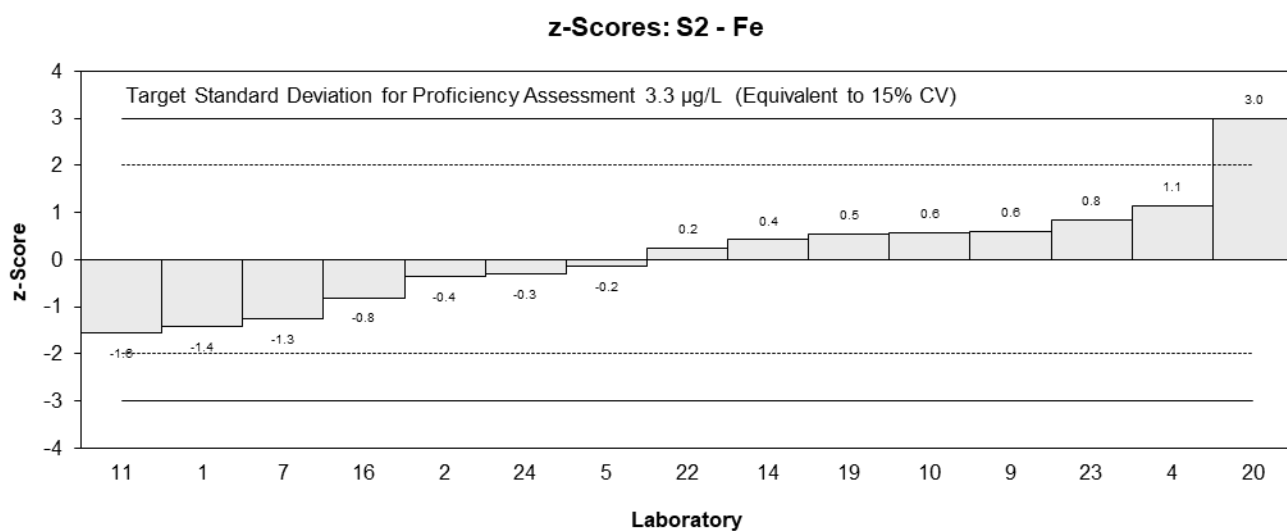
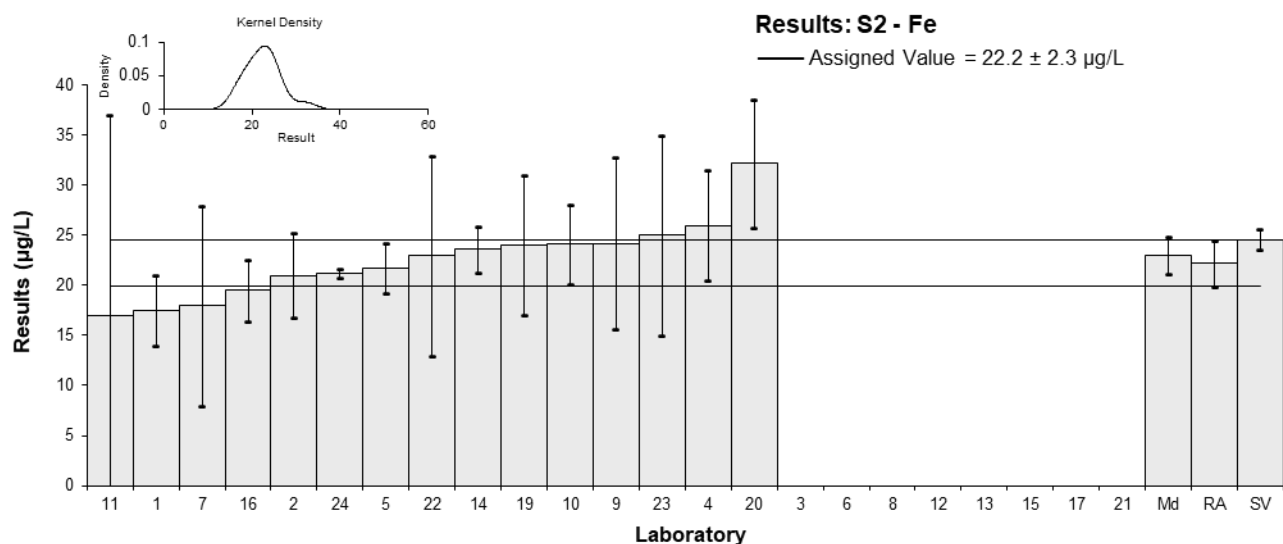


Figure 29

Table 32

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.313	0.0625	-0.95	-0.75
2	0.38	0.076	0.27	0.18
3	< 0.5	NR		
4	0.37	0.05	0.09	0.08
5	<0.5	NR		
6	NT	NT		
7	0.4	0.1	0.64	0.33
8	NT	NT		
9	0.42	0.03	1.00	1.27
10	0.38	0.53	0.27	0.03
11	0.31	0.2	-1.00	-0.27
12	0.406	0.052	0.75	0.68
13	NT	NT		
14	<1	1		
15	0.31	0.04	-1.00	-1.09
16	0.341	0.078	-0.44	-0.29
17	0.32	0.06	-0.82	-0.67
19	0.32	0.08	-0.82	-0.52
20	0.398	0.0796	0.60	0.39
21	0.34	0.1	-0.46	-0.24
22	0.4	0.08	0.64	0.41
23	0.51	0.1	2.65	1.38
24	NT	NT		

Statistics

Assigned Value	0.365	0.031
Spike Value	0.376	0.011
Robust Average	0.365	0.031
Median	0.375	0.032
Mean	0.370	
N	16	
Max	0.51	
Min	0.31	
Robust SD	0.049	
Robust CV	13%	

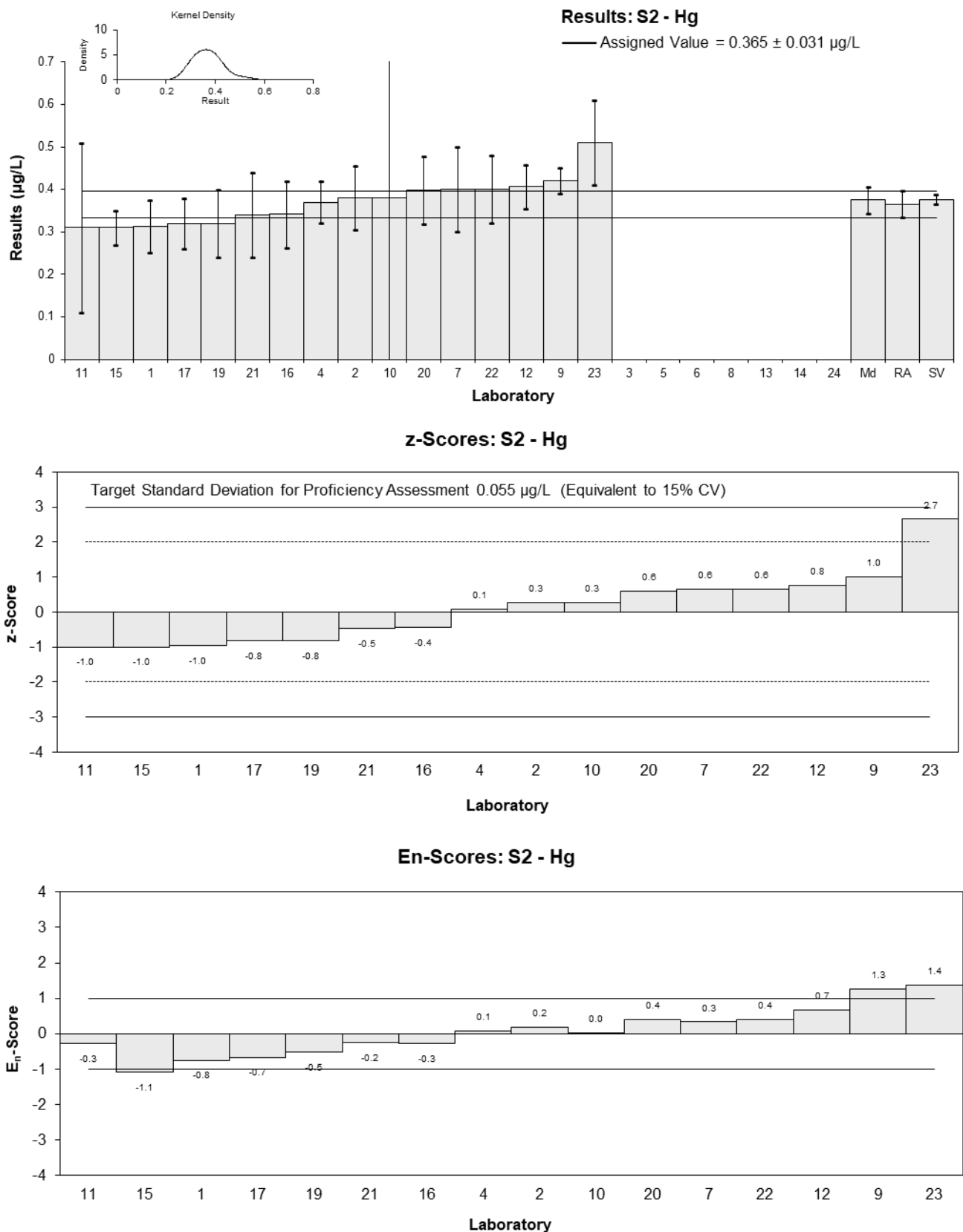


Figure 30

Table 33

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	6.93	1.04	-0.35	-0.35
2	6.7	1.34	-0.56	-0.44
3	6.97	0.68	-0.31	-0.44
4	8.8	1.8	1.36	0.81
5	7.03	0.8	-0.26	-0.32
6	NT	NT		
7	7	5	-0.28	-0.06
8	NT	NT		
9	7.83	2.15	0.47	0.24
10	7.32	0.73	0.01	0.01
11	6.5	10	-0.74	-0.08
12	7.3	4.3	-0.01	0.00
13	NT	NT		
14	7.32	1	0.01	0.01
15	6.70	0.65	-0.56	-0.83
16	6.85	1.03	-0.42	-0.42
17	NT	NT		
19	8.8	2	1.36	0.73
20	7.62	1.524	0.28	0.20
21	7	2	-0.28	-0.15
22	8	5	0.63	0.14
23	8	3	0.63	0.23
24	7.4	0.148	0.08	0.24

Statistics

Assigned Value	7.31	0.35
Spike Value	7.43	0.24
Robust Average	7.31	0.35
Median	7.30	0.31
Mean	7.37	
N	19	
Max	8.8	
Min	6.5	
Robust SD	0.60	
Robust CV	8.3%	

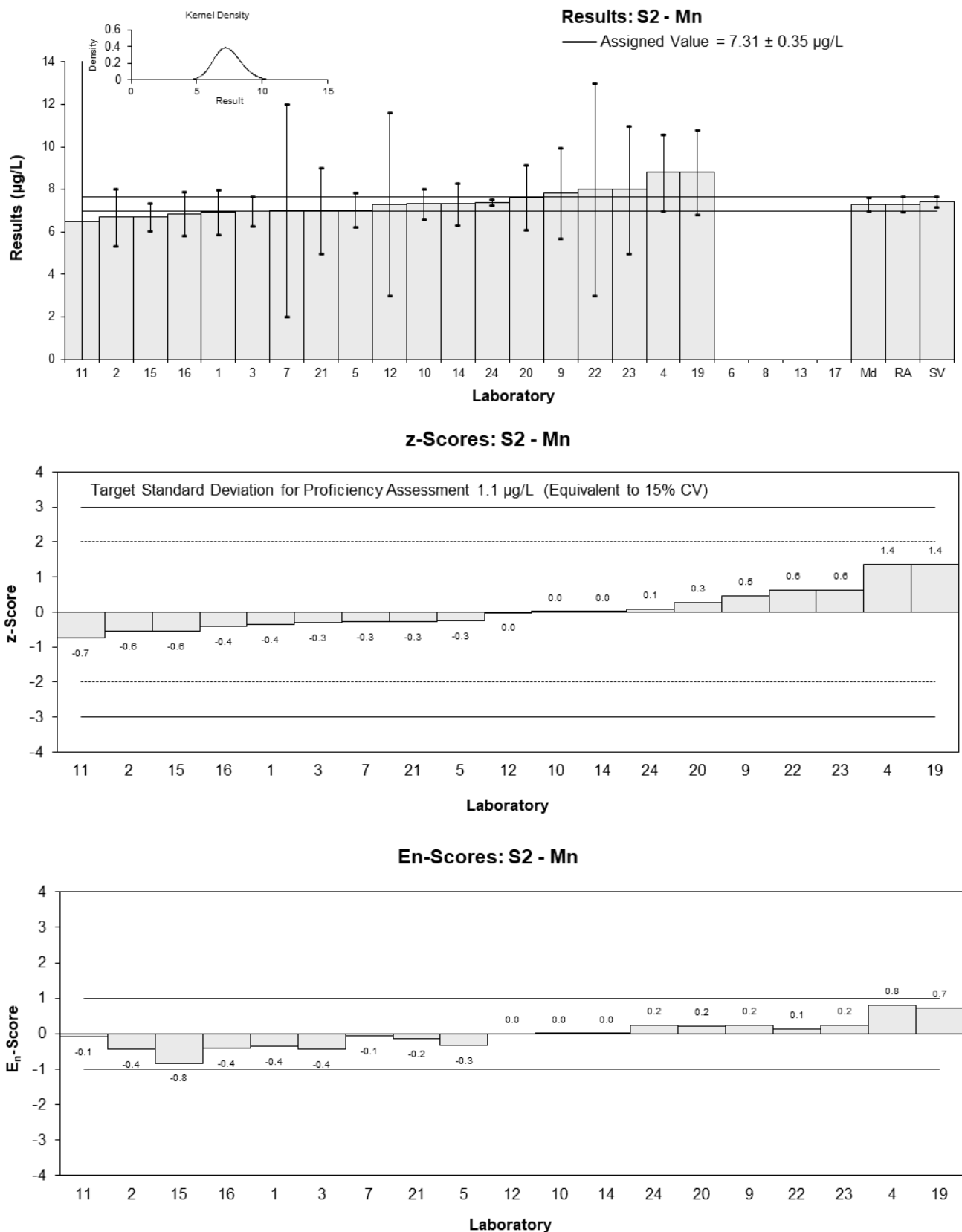


Figure 31

Table 34

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.69	0.338	-2.11	-1.65
2	2.2	0.44	-0.73	-0.49
3	< 10	NR		
4	2.8	1	0.89	0.31
5	2.32	0.3	-0.40	-0.34
6	NT	NT		
7	3	1	1.43	0.50
8	NT	NT		
9	2.37	0.53	-0.27	-0.16
10	<7	4.7		
11	1.6	2	-2.35	-0.43
12	2.8	1.3	0.89	0.25
13	NT	NT		
14	2.20	1	-0.73	-0.26
15	1.80	0.18	-1.81	-1.78
16	2.51	0.38	0.11	0.08
17	NT	NT		
19	3	3	1.43	0.18
20	2.68	0.536	0.57	0.33
21	<5	NR		
22	3	1	1.43	0.50
23	3	1	1.43	0.50
24	2.5	0.05	0.08	0.09

Statistics

Assigned Value	2.47	0.33
Spike Value	2.75	0.13
Robust Average	2.47	0.33
Median	2.51	0.28
Mean	2.47	
N	16	
Max	3	
Min	1.6	
Robust SD	0.53	
Robust CV	21%	

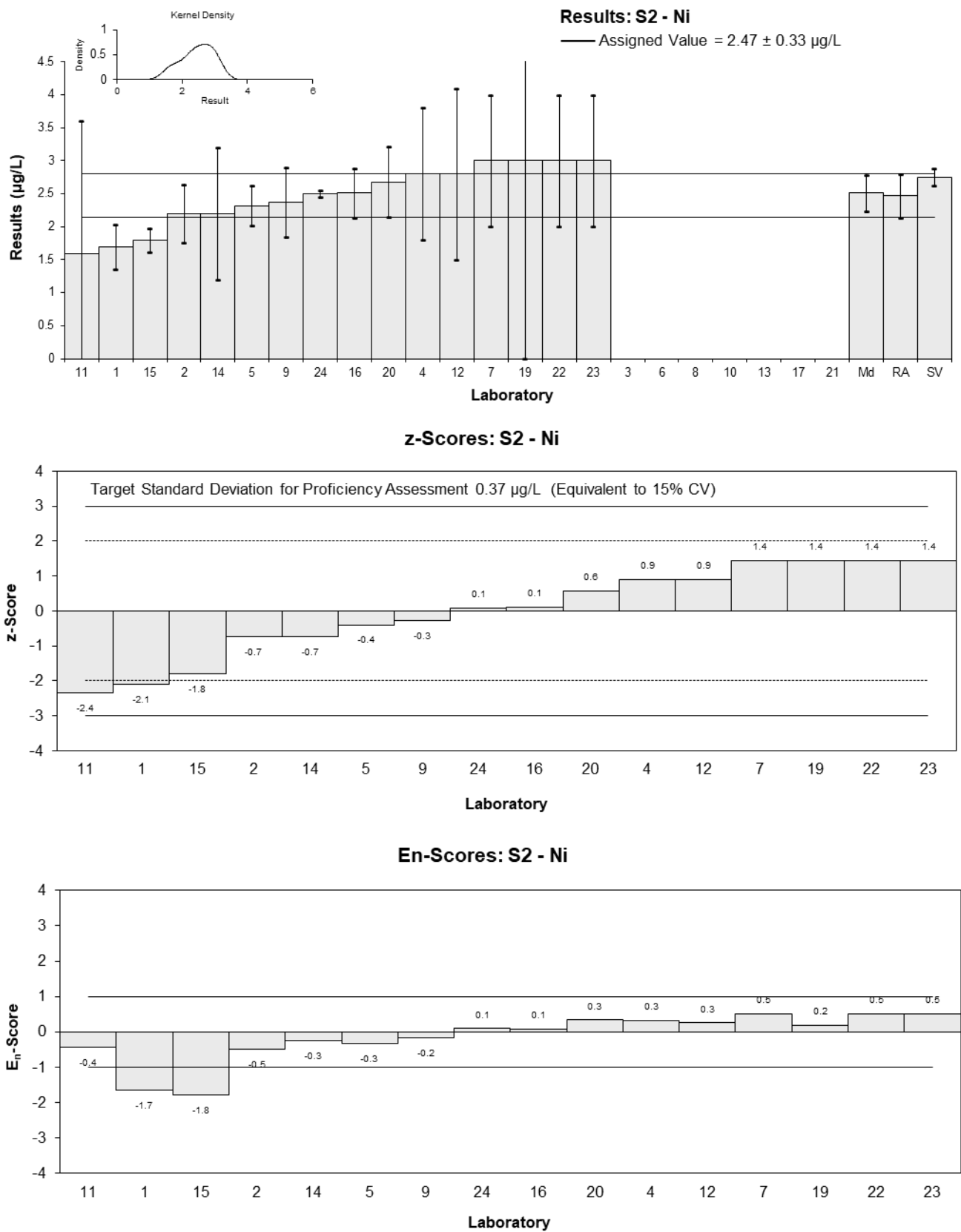


Figure 32

Table 35

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	139	27.8	1.06	0.68
2	<1000	NR		
3	< 5000	NR		
4	<200	200		
5	NT	NT		
6	NT	NT		
7	<100	100		
8	NT	NT		
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	129	43	0.51	0.21
13	NT	NT		
14	132	15	0.67	0.79
15	< 500	NR		
16	NT	NT		
17	NT	NT		
19	NT	NT		
20	126	25.2	0.34	0.24
21	106	20	-0.77	-0.69
22	140	100	1.12	0.20
23	110	100	-0.55	-0.10
24	NT	NT		

Statistics

Assigned Value*	119.9	3.0
Spike Value	123	9
Reference Value*	119.9	3.0
Robust Average	126	14
Median	129	14
Mean	126	
N	7	
Max	140	
Min	106	
Robust SD	15	
Robust CV	12%	

* Reference Value by SA-ICP-MS.

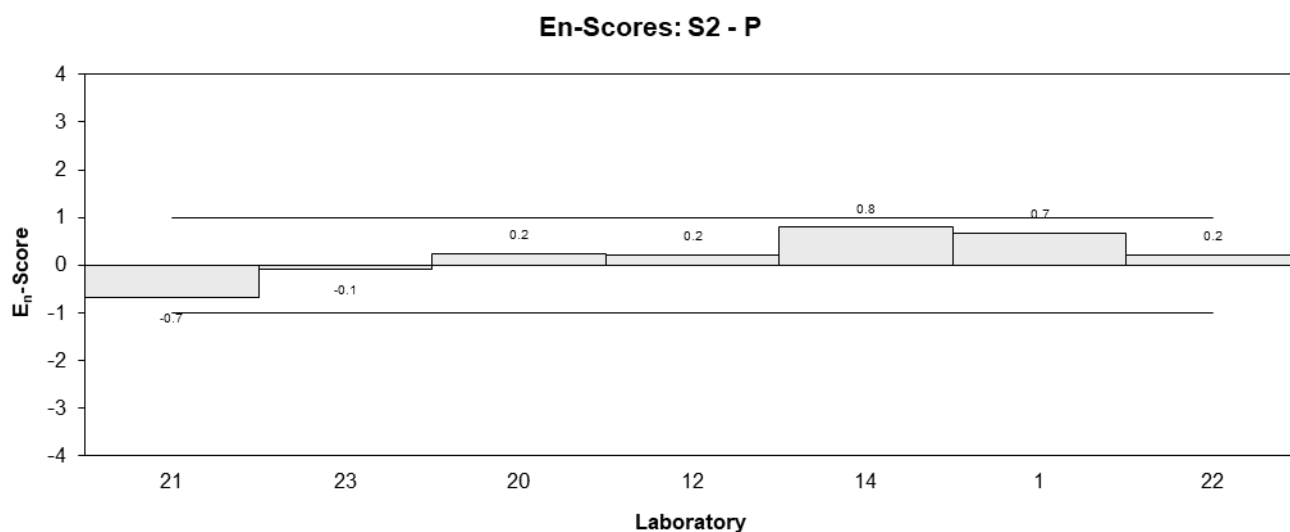
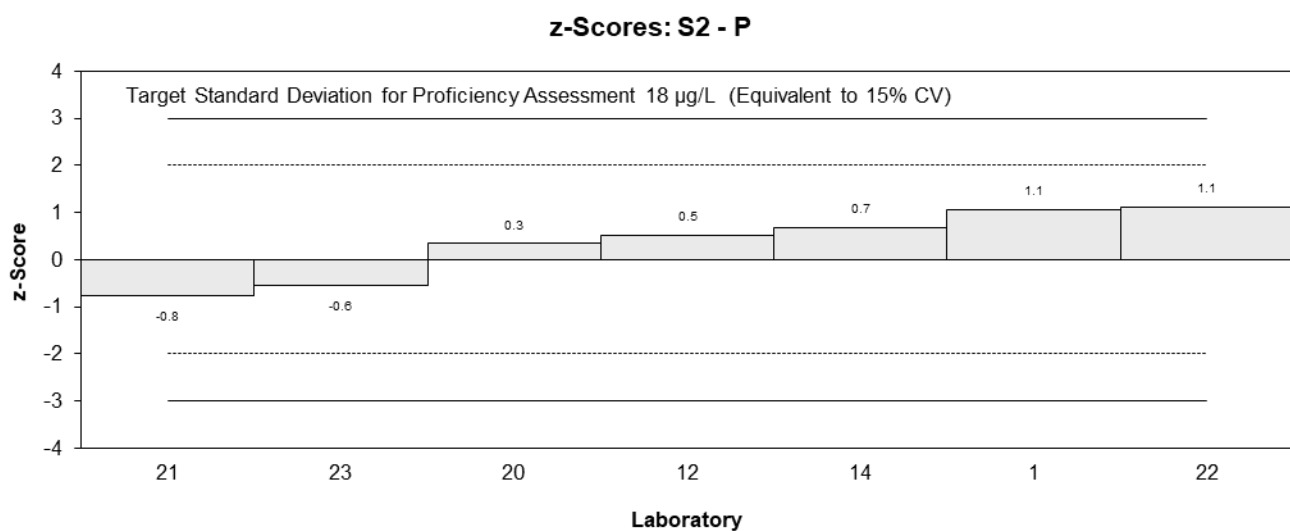
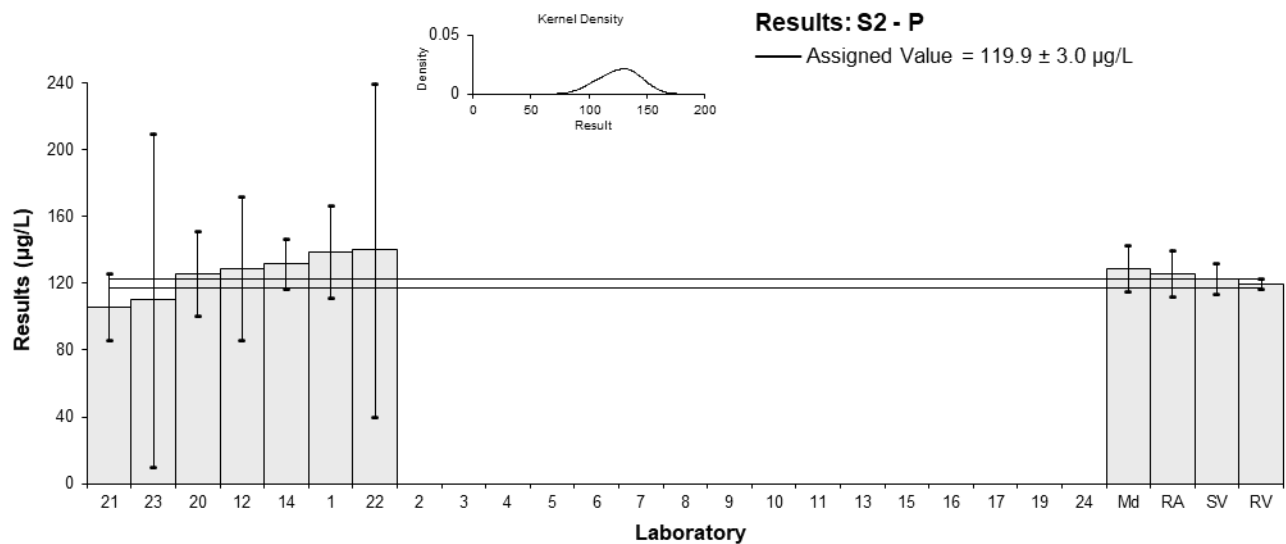


Figure 33

Table 36

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.40	0.280	-0.65	-0.44
2	1.8	0.36	1.08	0.61
3	< 10	NR		
4	1.5	0.2	-0.22	-0.18
5	1.58	0.2	0.13	0.11
6	NT	NT		
7	2	1	1.94	0.44
8	NT	NT		
9	2.20	0.49	2.80	1.24
10	1.6	0.74	0.22	0.07
11	1.3	2	-1.08	-0.12
12	1.6	1.3	0.22	0.04
13	NT	NT		
14	1.40	1	-0.65	-0.15
15	1.32	0.17	-0.99	-0.90
16	1.59	0.32	0.17	0.11
17	NT	NT		
19	1.9	3	1.51	0.12
20	1.56	0.312	0.04	0.03
21	<10	NR		
22	1	1	-2.37	-0.54
23	1	1	-2.37	-0.54
24	1.6	0.032	0.22	0.26

Statistics

Assigned Value	1.55	0.19
Spike Value	1.56	0.04
Robust Average	1.55	0.19
Median	1.58	0.16
Mean	1.55	
N	17	
Max	2.2	
Min	1	
Robust SD	0.31	
Robust CV	20%	

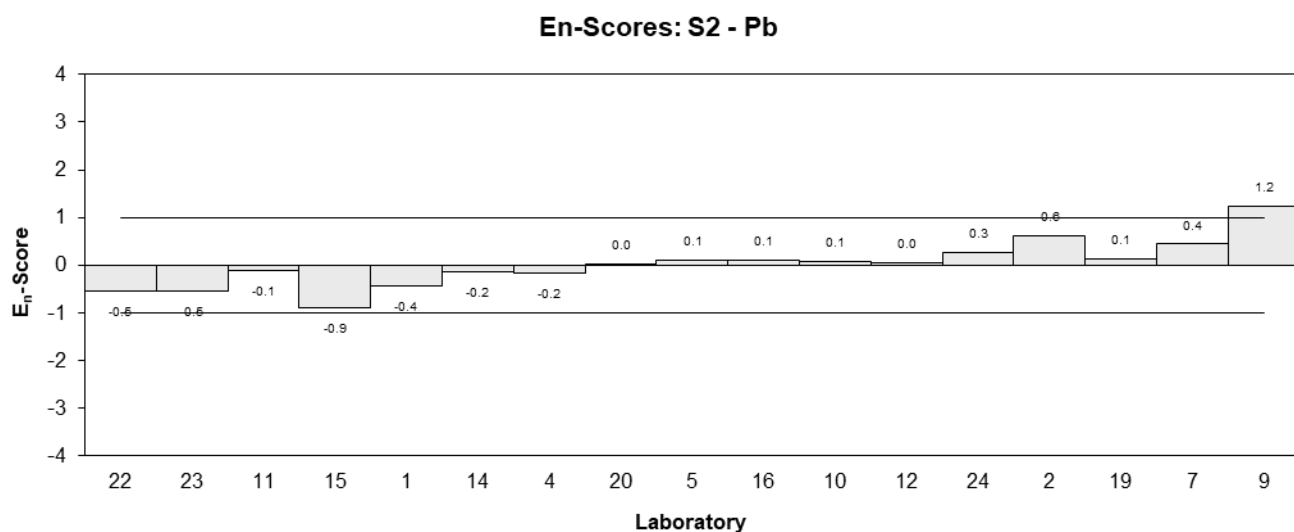
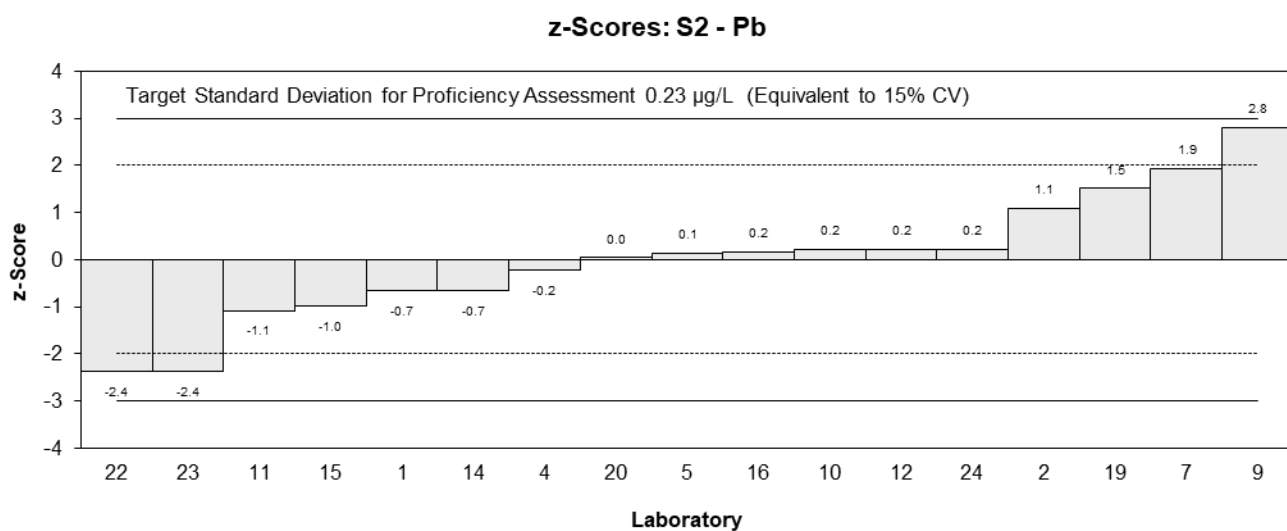
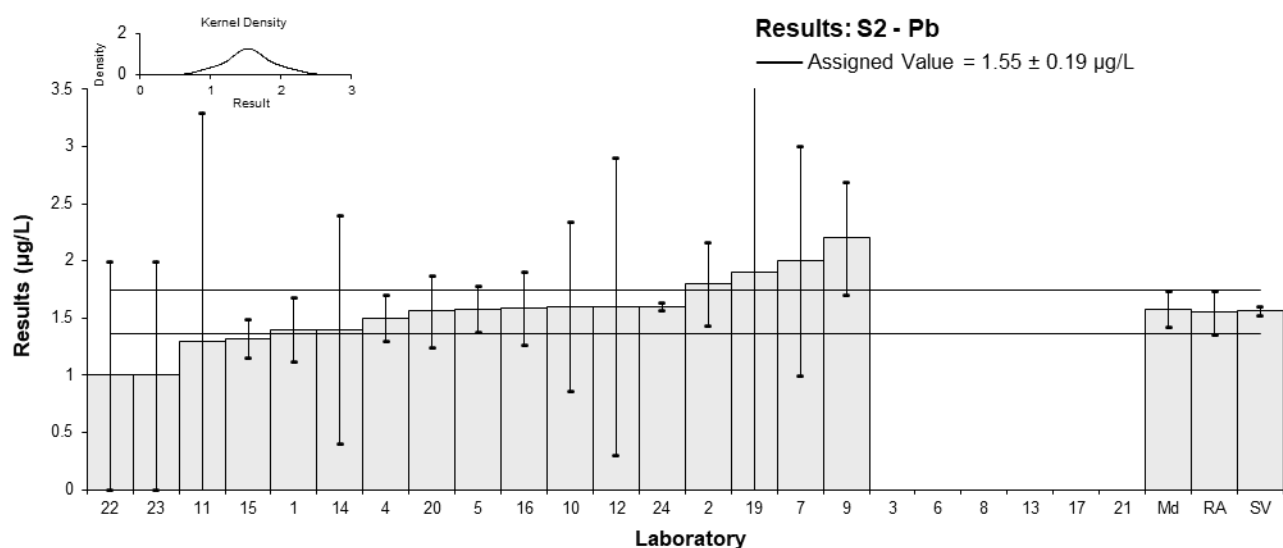


Figure 34

Table 37

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<5	NR		
2	2.7	0.54	-0.97	-0.82
3	< 5	NR		
4	3.2	0.3	0.08	0.12
5	3.06	0.5	-0.21	-0.19
6	NT	NT		
7*	5	2	3.88	0.92
8	NT	NT		
9	2.91	0.64	-0.53	-0.38
10	3.4	0.8	0.51	0.29
11	3.3	2	0.30	0.07
12	3.3	0.6	0.30	0.23
13	NT	NT		
14	3.38	1	0.46	0.22
15	< 5	NR		
16	3.17	0.70	0.02	0.01
17	NT	NT		
19	3.2	0.8	0.08	0.05
20	3.06	0.612	-0.21	-0.16
21	<20	NR		
22	3	2	-0.34	-0.08
23	4	1	1.77	0.83
24	2.9	0.058	-0.55	-1.53

* Outlier, see Section 4.2

Statistics

Assigned Value	3.16	0.16
Spike Value	3.08	0.16
Robust Average	3.19	0.18
Median	3.20	0.17
Mean	3.31	
N	15	
Max	5	
Min	2.7	
Robust SD	0.29	
Robust CV	8.9%	

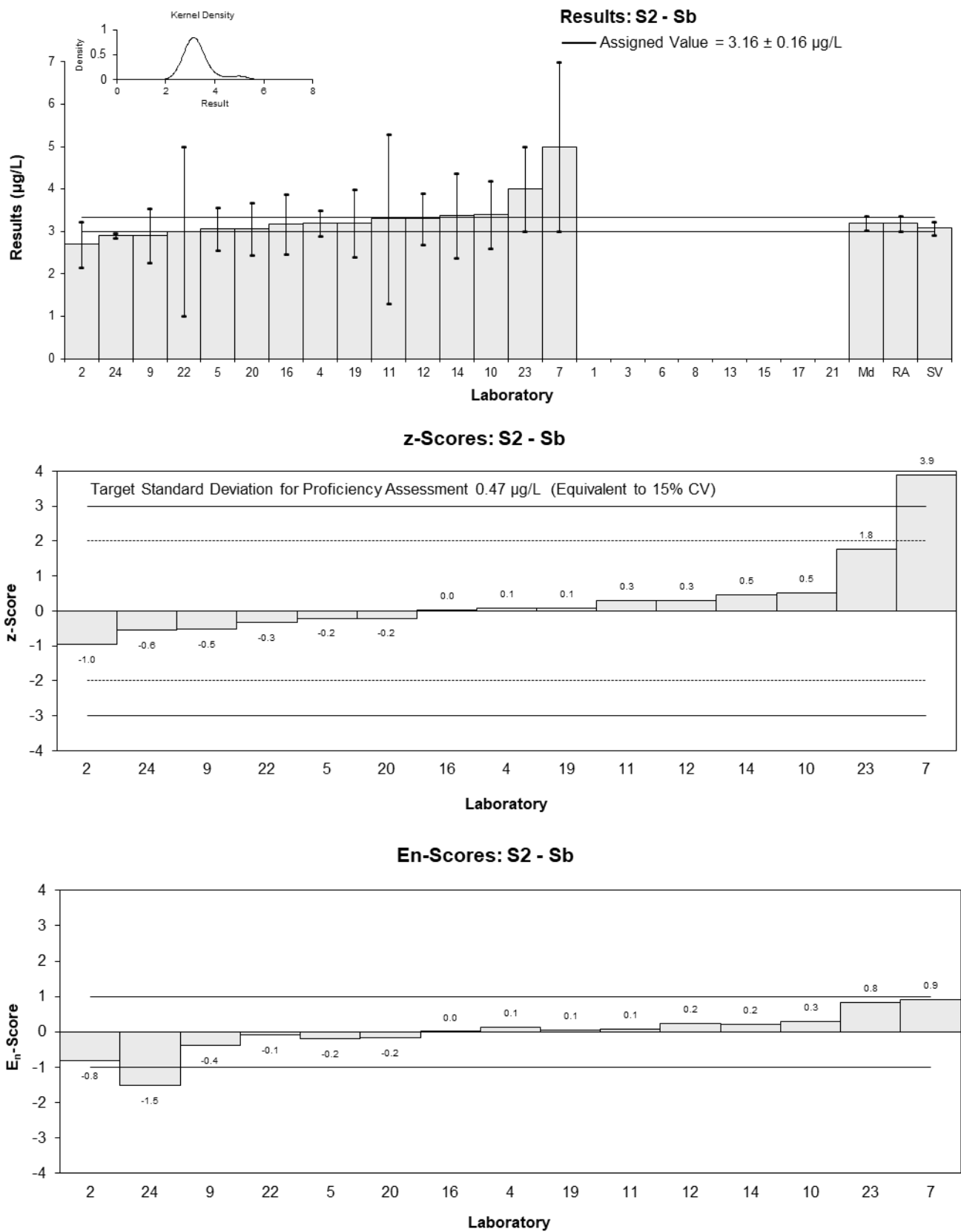


Figure 35

Table 38

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.95	0.592	-0.49	-0.51
2	5.7	1.14	1.51	1.02
3	< 10	NR		
4	4.1	0.3	-0.32	-0.42
5	2.95	0.5	-1.63	-1.83
6	NT	NT		
7	5	1	0.71	0.53
8	NT	NT		
9	3.93	0.97	-0.51	-0.39
10	5	3	0.71	0.20
11	5.2	2	0.94	0.39
12*	7	2	2.99	1.25
13	NT	NT		
14	4.82	1	0.50	0.38
15	3.91	0.35	-0.54	-0.68
16	3.43	0.69	-1.08	-1.04
17	NT	NT		
19	6	3	1.85	0.53
20	3.86	0.772	-0.59	-0.53
21	<20	NR		
22	4	1	-0.43	-0.33
23	4	1	-0.43	-0.33
24*	10.5	0.21	6.99	9.63

* Outlier, see Section 4.2

Statistics

Assigned Value	4.38	0.60
Spike Value	4.06	0.12
Robust Average	4.62	0.71
Median	4.10	0.65
Mean	4.90	
N	17	
Max	10.5	
Min	2.95	
Robust SD	1.2	
Robust CV	25%	

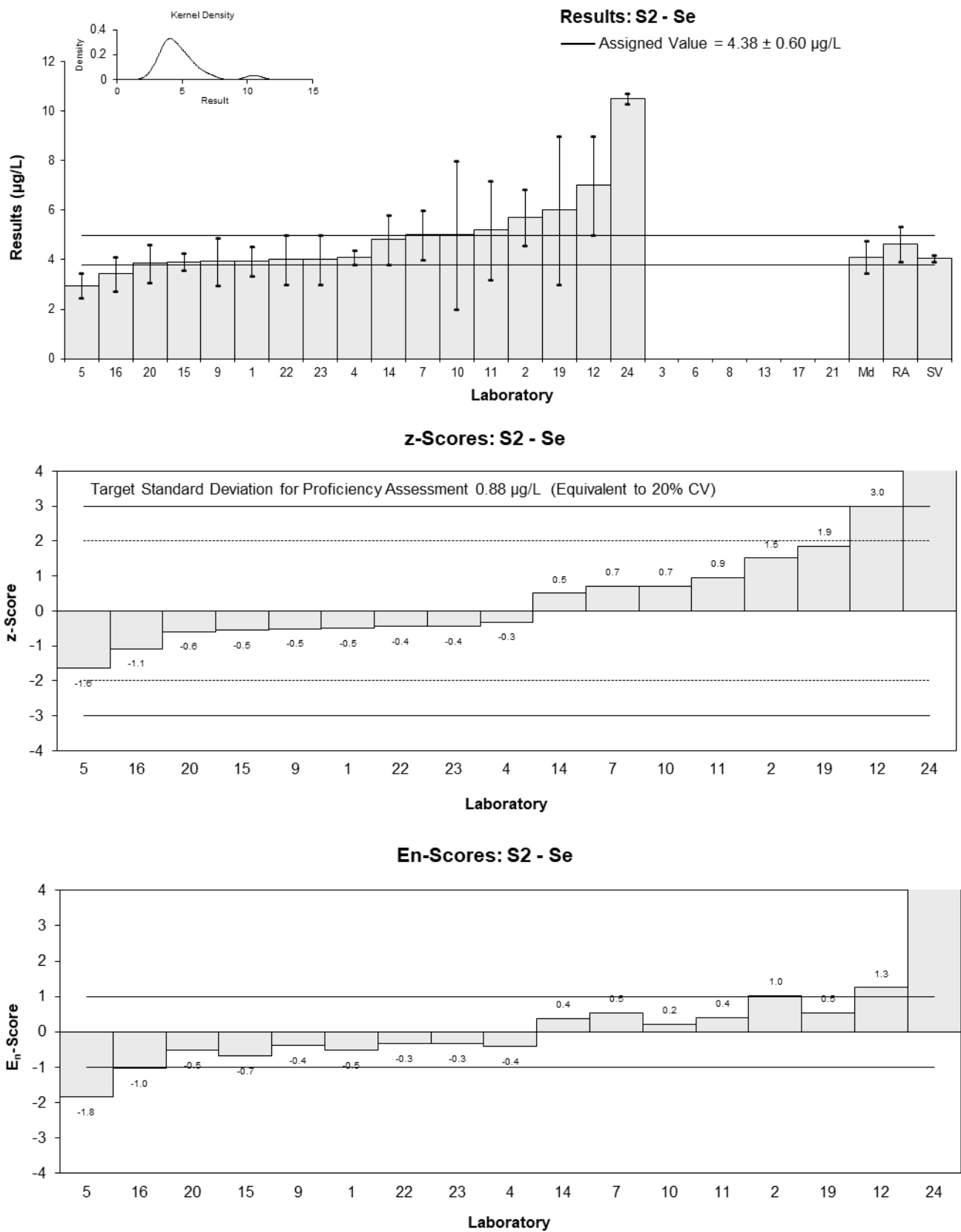


Figure 36

Table 39

Sample Details

Sample No.	S2
Matrix	Sea Water
Analyte	Sn
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<5	NR		
2	4	0.8	0.10	0.07
3	< 5	NR		
4	3.9	0.5	-0.07	-0.07
5	NT	NT		
6	NT	NT		
7*	6	1	3.49	2.02
8	NT	NT		
9	3.56	0.88	-0.64	-0.42
10	<5	3.4		
11	4.0	2	0.10	0.03
12	3.6	0.6	-0.58	-0.54
13	NT	NT		
14	4.16	1	0.37	0.22
15	< 5	NR		
16	3.96	0.83	0.03	0.02
17	NT	NT		
19	NT	NT		
20	4.38	0.876	0.74	0.49
21	<20	NR		
22	4	1	0.10	0.06
23	4	1	0.10	0.06
24	3.8	0.076	-0.24	-0.68

* Outlier, see Section 4.2

Statistics

Assigned Value	3.94	0.19
Spike Value	3.76	0.11
Robust Average	3.98	0.21
Median	4.00	0.14
Mean	4.11	
N	12	
Max	6	
Min	3.56	
Robust SD	0.30	
Robust CV	7.5%	

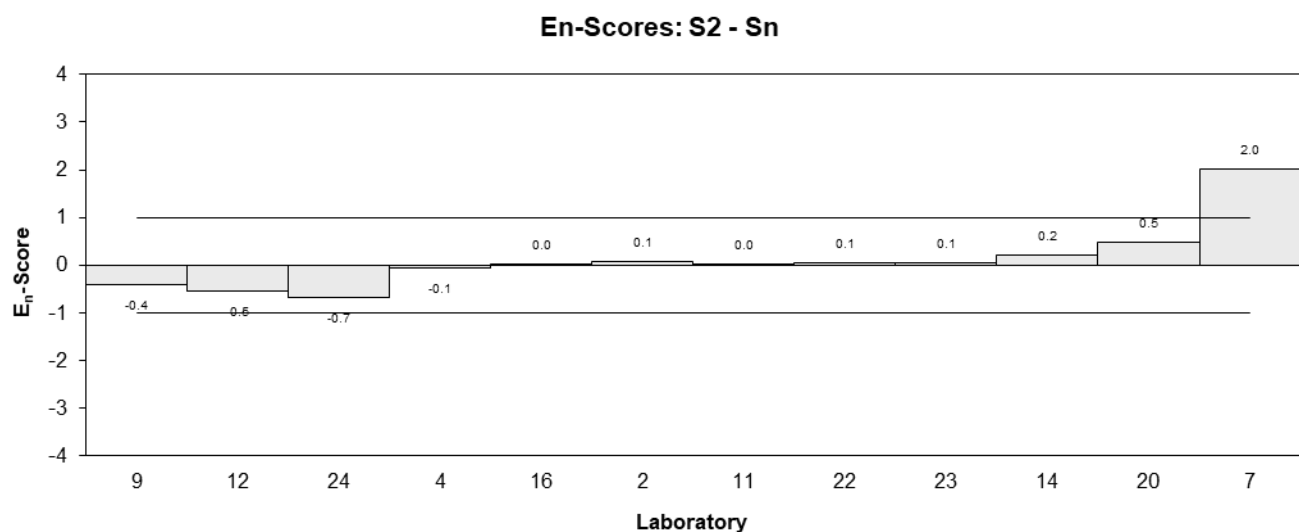
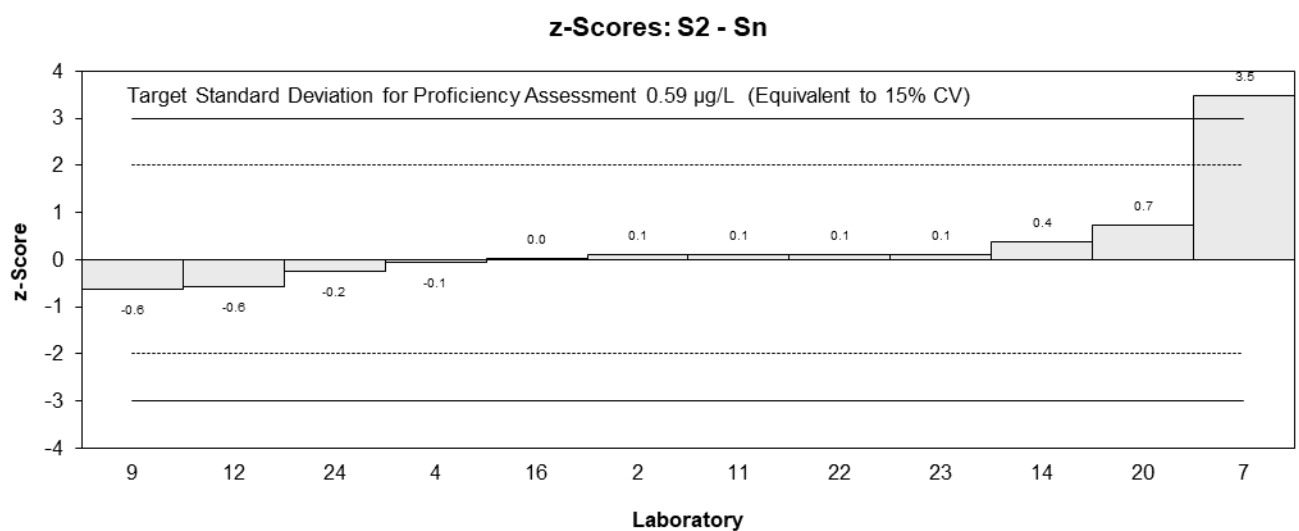
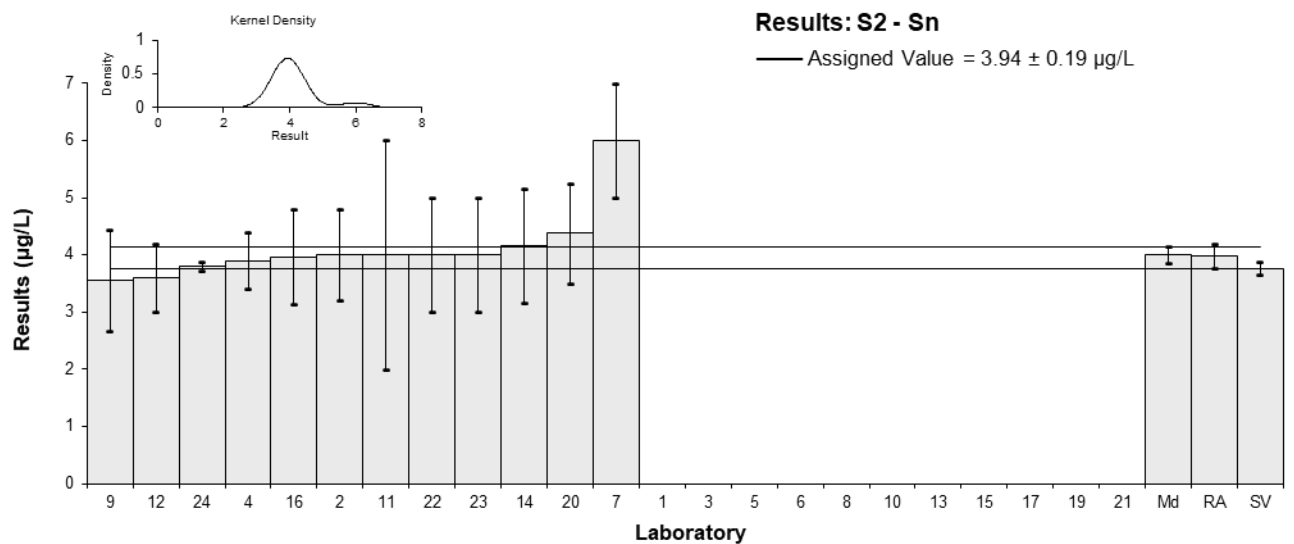


Figure 37

Table 40

Sample Details

Sample No.	S2
Matrix	Sea Water
Analyte	TI
Unit	µg/L

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<5	NR		
2	1.8	0.36	-0.64	-0.52
3	< 10	NR		
4	1.9	0.2	-0.30	-0.44
5	2.05	0.2	0.20	0.29
6	NT	NT		
7	2	1	0.03	0.01
8	NT	NT		
9	2.44	0.57	1.51	0.79
10	1.94	0.28	-0.17	-0.18
11	1.6	10	-1.31	-0.04
12	2.0	1.2	0.03	0.01
13	NT	NT		
14	2.02	1	0.10	0.03
15	< 5	NR		
16	2.03	0.28	0.13	0.14
17	NT	NT		
19	2	1	0.03	0.01
20	2.04	0.408	0.17	0.12
21	<50	NR		
22	2	1	0.03	0.01
23	2	1	0.03	0.01
24	2	0.04	0.03	0.18

Statistics

Assigned Value	1.99	0.04
Spike Value	2.03	0.06
Robust Average	1.99	0.04
Median	2.00	0.03
Mean	1.99	
N	15	
Max	2.44	
Min	1.6	
Robust SD	0.069	
Robust CV	3.5%	

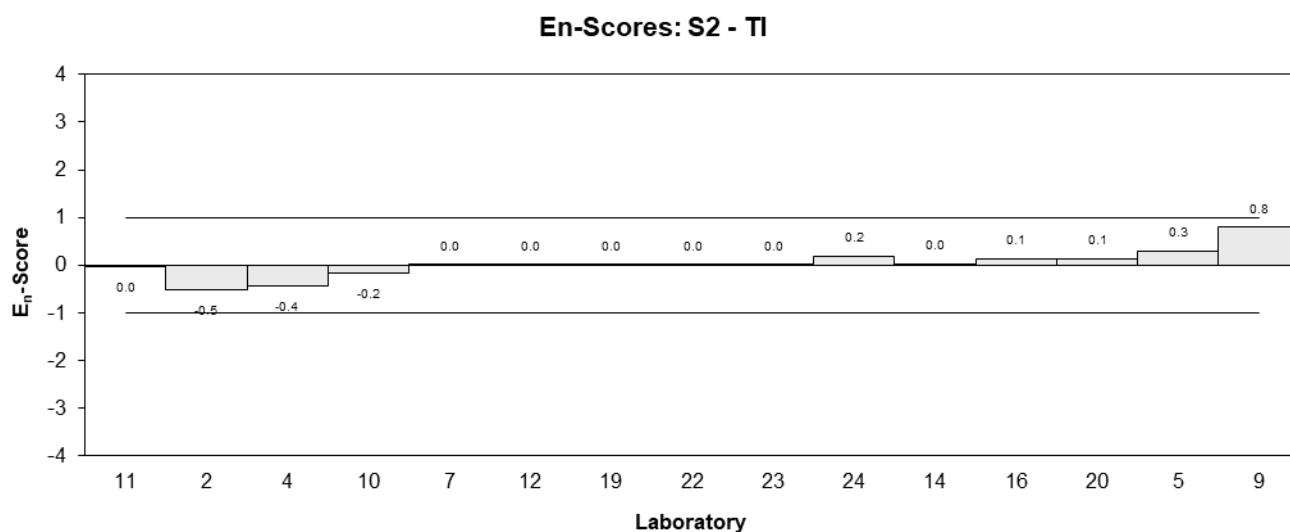
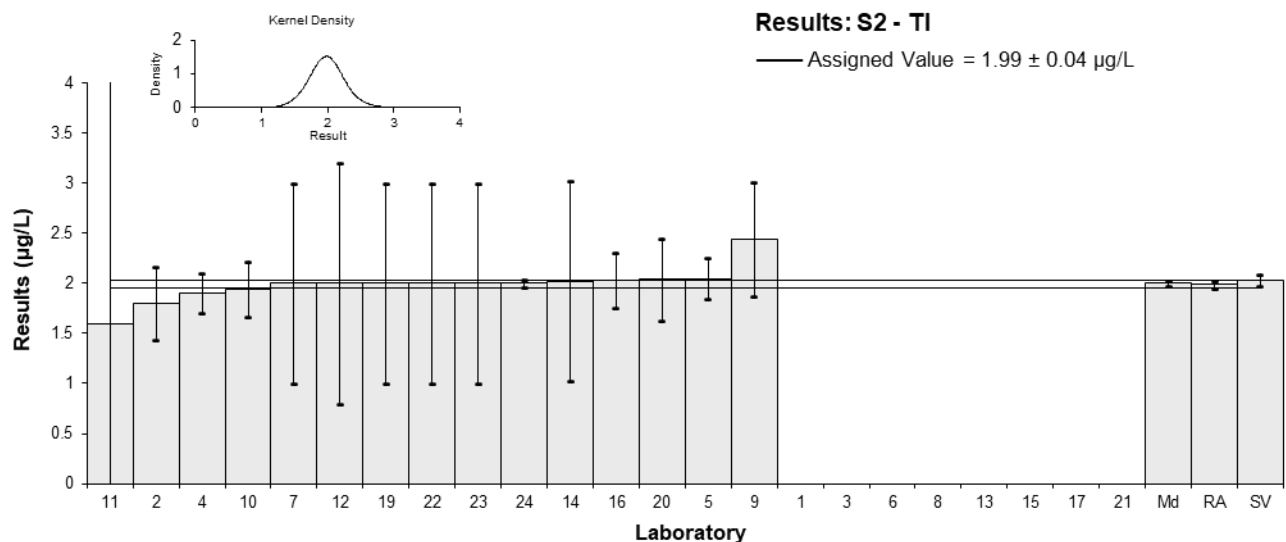


Figure 38

Table 41

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<5	NR		
2	2.8	0.56	-0.23	-0.18
3	< 5	NR		
4	2.5	0.3	-0.92	-1.25
5	2.96	0.3	0.14	0.19
6	NT	NT		
7	3	1	0.23	0.10
8	NT	NT		
9	2.96	0.67	0.14	0.09
10	2.9	0.44	0.00	0.00
11	2.3	2	-1.38	-0.30
12	2.7	1.6	-0.46	-0.12
13	NT	NT		
14	2.91	1	0.02	0.01
15	< 5	NR		
16	3.43	0.48	1.22	1.08
17	NT	NT		
19	3	1	0.23	0.10
20	3.04	0.608	0.32	0.23
21	NT	NT		
22	3	1	0.23	0.10
23	3	1	0.23	0.10
24	2.8	0.056	-0.23	-0.81

Statistics

Assigned Value	2.90	0.11
Spike Value	2.87	0.33
Robust Average	2.90	0.11
Median	2.96	0.06
Mean	2.89	
N	15	
Max	3.43	
Min	2.3	
Robust SD	0.17	
Robust CV	6%	

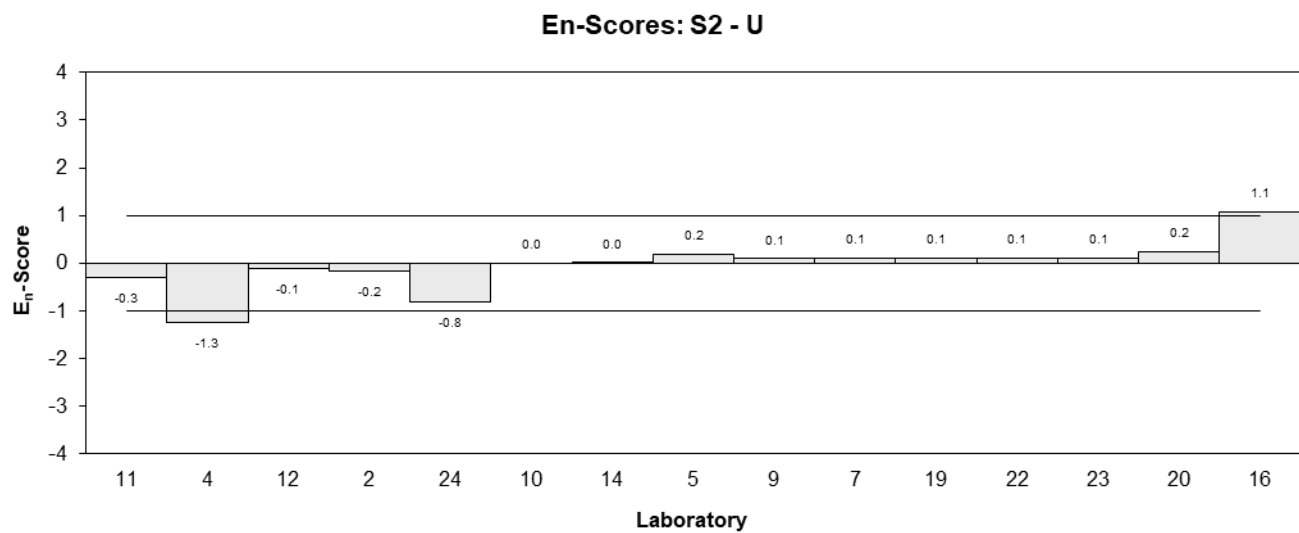
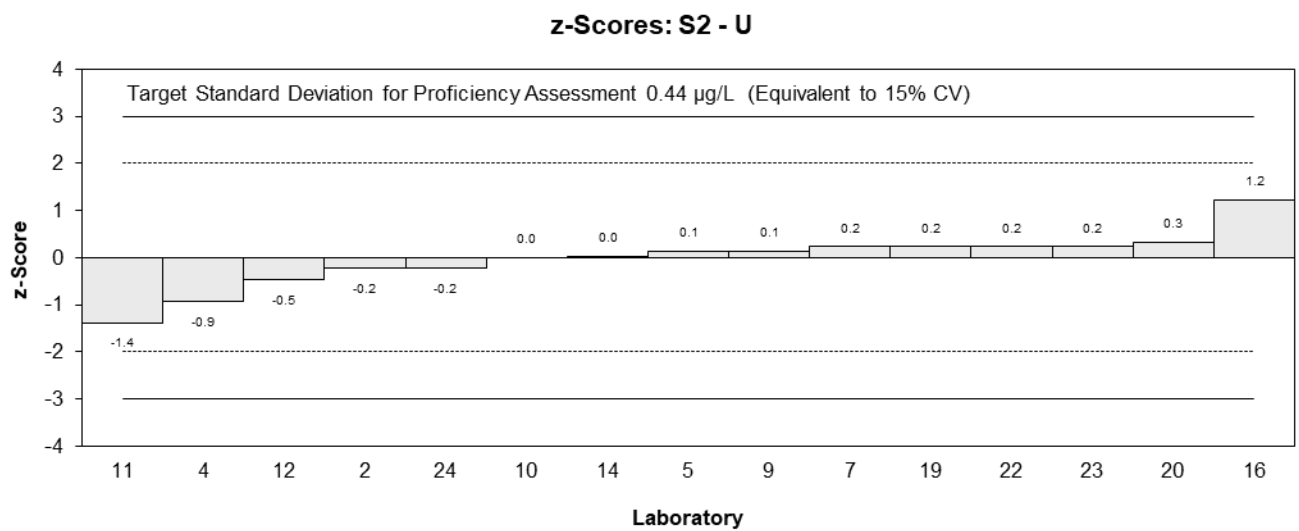
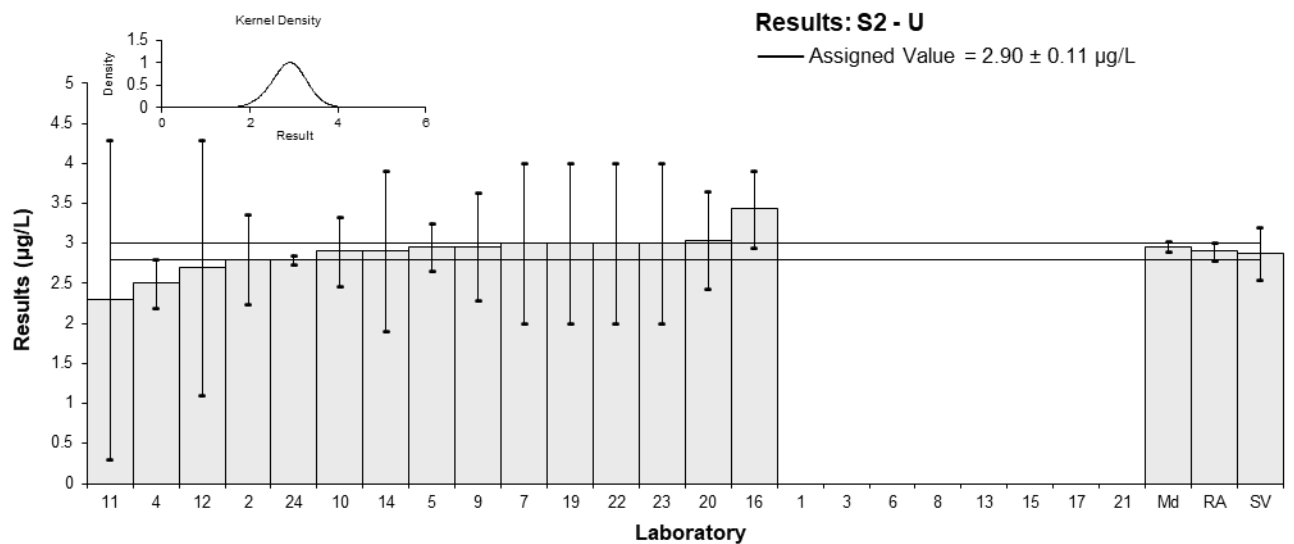


Figure 39

Table 42

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<5	NR		
2*	1.6	0.32	-3.64	-4.20
3	< 25	NR		
4	4.1	0.5	1.08	0.95
5	3.14	0.35	-0.74	-0.81
6	NT	NT		
7	3	1	-1.00	-0.50
8	NT	NT		
9	3.05	0.87	-0.91	-0.52
10	3.7	2	0.32	0.08
11	3.8	10	0.51	0.03
12	4.1	1.4	1.08	0.40
13	NT	NT		
14	3.53	1	0.00	0.00
15	< 5	NR		
16	3.14	0.56	-0.74	-0.60
17	NT	NT		
19	4	2	0.89	0.23
20	3.38	0.676	-0.28	-0.20
21	3	1	-1.00	-0.50
22	4	1	0.89	0.45
23	4	1	0.89	0.45
24	3	0.06	-1.00	-1.58

* Outlier, see Section 4.2

Statistics

Assigned Value	3.53	0.33
Spike Value	3.56	0.31
Robust Average	3.47	0.34
Median	3.46	0.42
Mean	3.41	
N	16	
Max	4.1	
Min	1.6	
Robust SD	0.55	
Robust CV	16%	

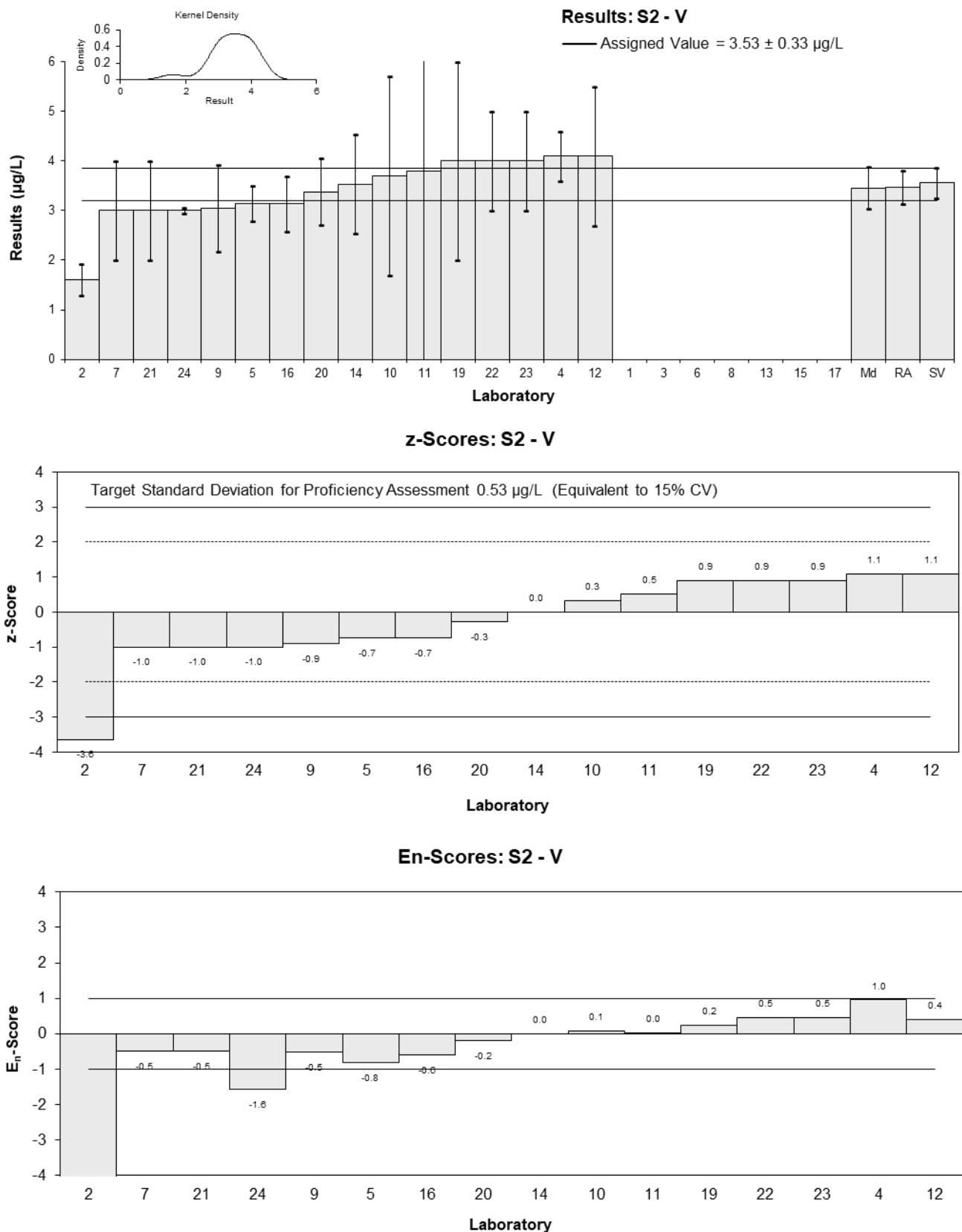


Figure 40

Table 43

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	13.4	2.67	-1.38	-0.99
2*	2.4	0.48	-5.72	-6.17
3	< 50	NR		
4	NR	NR		
5	12.5	1.5	-1.74	-1.60
6	NT	NT		
7	21	6	1.62	0.64
8	NT	NT		
9	14.4	3.5	-0.99	-0.60
10	20.1	4.2	1.26	0.67
11	13	10	-1.54	-0.38
12	20	5	1.22	0.56
13	NT	NT		
14	17.7	2	0.32	0.26
15	13.6	1.5	-1.30	-1.20
16	13.5	2.8	-1.34	-0.94
17	NT	NT		
19	18	5	0.43	0.20
20	16.6	3.32	-0.12	-0.07
21	17	4	0.04	0.02
22	23	6	2.41	0.95
23	17	5	0.04	0.02
24	19.8	0.396	1.14	1.24

* Outlier, see Section 4.2

Statistics

Assigned Value	16.9	2.3
Spike Value	18.3	0.8
Robust Average	16.5	2.4
Median	17.0	2.8
Mean	16.1	
N	17	
Max	23	
Min	2.4	
Robust SD	3.9	
Robust CV	24%	

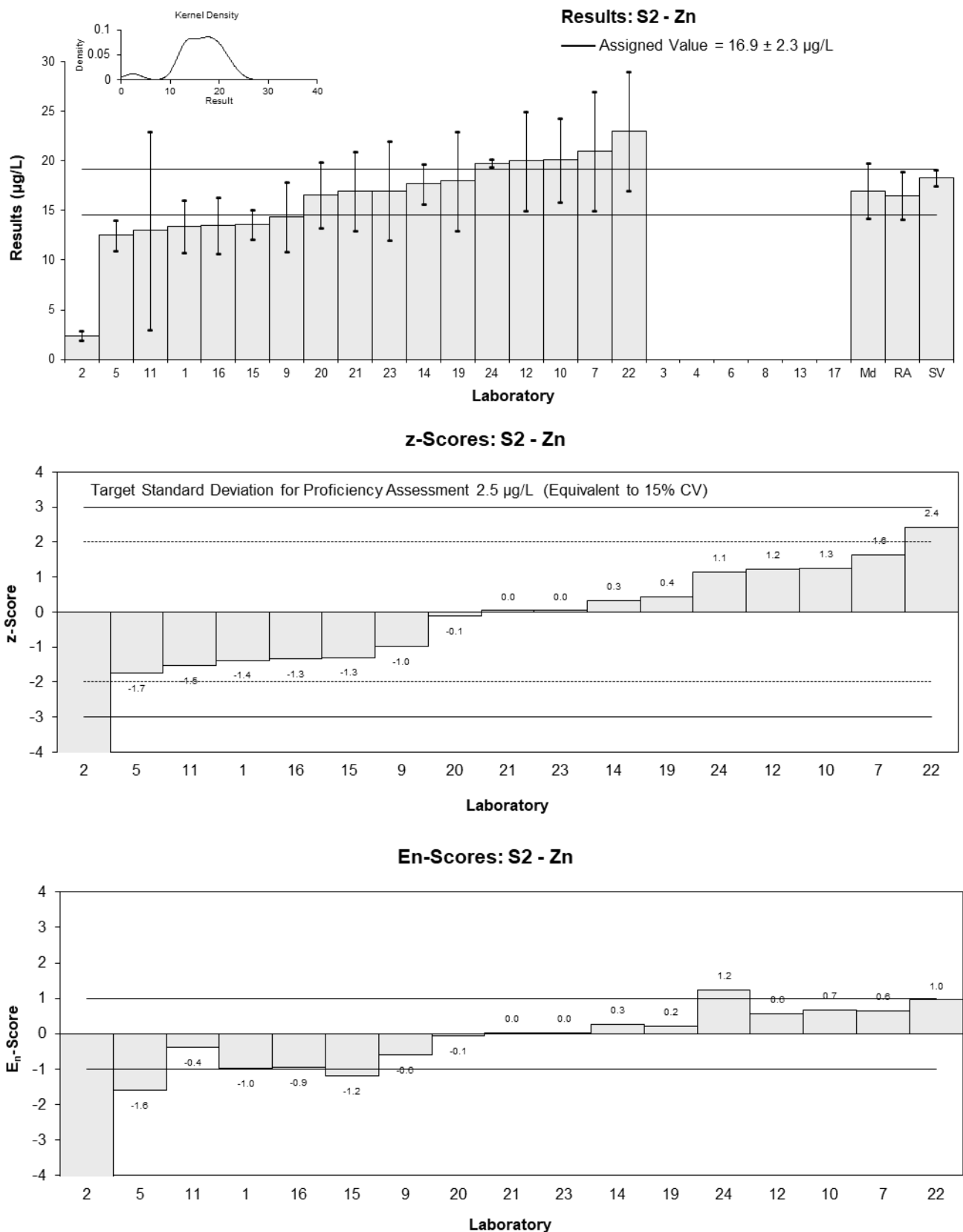


Figure 41

6 DISCUSSION OF RESULTS

6.1 Assigned Value

Sample S1 was filtered, acidified and fortified river water while **Sample S2** was a filtered, acidified and fortified sea water, previously distributed as Sample S1 of AQA 23-18.⁶

Assigned Values were the robust average of participants' results except for P in S2. The robust averages and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528. Results less than 50% and more than 150% of the robust average were excluded prior to the calculation of each assigned value.⁷ Appendix 3 sets out the calculation for the robust average of Hg in Sample S2 and its associated uncertainty.

The assigned value for P in S2 was a reference value measured using standard addition inductively couple plasma mass spectrometry.

Laboratory 8 enrolled with Sample S2 only, however they reported their Sample S2 results as Sample S1. To avoid bias in the calculation of the assigned value and unfair scoring, these results were excluded from the robust average calculation; they were also excluded from the calculation of all summary statistics.

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

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

Traceability of the reference value of P in S2 is established by gravimetric sample preparation and elemental quantification by ICP-MS. Gravimetric measurements were calibrated using Australian standards for mass and are traceable to the SI unit for mass (kg). ICP-MS measurements were calibrated with standard addition and are traceable to (i) the SI unit for mass (kg) through the primary calibration standard certified by KRISS (Korea) and (ii) the SI unit for amount of substance (mol) through data for isotopic composition and relative atomic mass. Isotopic composition is traceable to IUPAC published data.

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

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. All 669 numerical results were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.47% to 625% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty which are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.^{10 – 15}

Participation in proficiency testing programs allows laboratories to check how reasonable their estimates of uncertainty are. Results and the expanded uncertainties are presented in the bar charts for each analyte (Figure 2 to 41). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 17 laboratories reported results for Hg in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 17 laboratories' results is 0.046 µg/L (10% of the assigned value). If Laboratory 6's result is coming from one

measurement, then they might have under-estimated the expanded measurement uncertainty reported for Hg in S1 (0.002 µg/L or 0.47%) as an uncertainty estimated from one measurement is unlikely to be smaller than the uncertainty estimated from 17 measurements. Alternatively, estimates of uncertainty for Cd in S2 larger than 0.44 µg/L (the uncertainty of the assigned value, 0.06 µg/L plus the allowable variation from the assigned value, the target standard deviation of 0.19 µg/L, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainty reported by Laboratory 14 for Cd in S2 (1 µg/L) might have been over-estimated.

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.¹¹ An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Laboratory 24 may need to review their procedure for estimating measurement uncertainty as most of their reported uncertainties were low.

Laboratories 7, 10, 11, 19, 22, and 23 should also review their procedure for estimating measurement uncertainty. They reported an estimate of expanded uncertainty for some measurement results which was equal to or larger than the result itself.

Laboratories 4, 7, 10, 14, and 19 attached estimates of the expanded measurement uncertainty to results reported as being less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.¹⁰

In some cases, the results were reported with an inappropriate number of significant figures. The recommended format is to write the 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 6.98 ± 1.396 µg/L, it is better to report 7.0 ± 1.4 µg/L or, instead of 23.89 ± 2.1 µg/L, it is better to report 23.9 ± 2.1 µg/L.¹⁰

6.3 z-Score

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

The target standard deviation defines acceptable 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-laboratory 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.

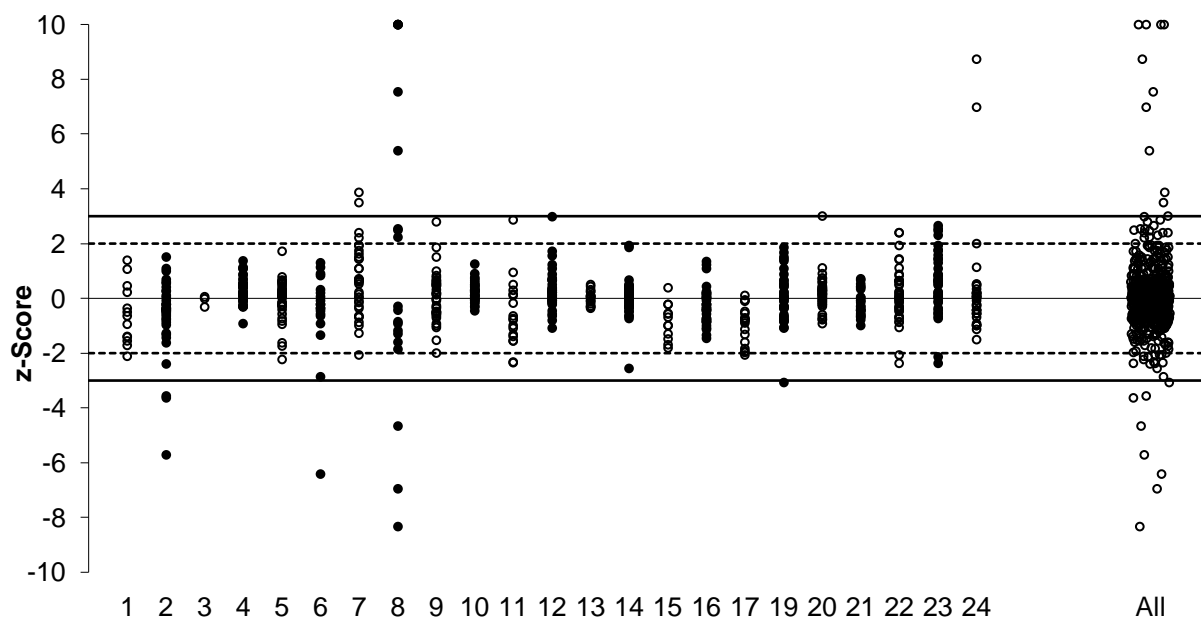
The between laboratory coefficient of variation predicted by the Thompson equation⁸ and the participants' coefficient of variation in this study are presented for comparison in Table 44.

Table 44 Between Laboratory CV of this Study, Thompson CV and Set Target SD

Sample	Test	Assigned value (µg/L)	Between Laboratory CV*	Thompson/Horwitz CV	Target SD (as CV)
S1	Ag	2.25	18%	22%	15%
S1	Al	7.97	12%	22%	15%
S1	As	1.11	9.3%	22%	15%
S1	Be	1.88	5.5%	22%	10%
S1	Cd	1.31	4.7%	22%	10%
S1	Co	2.23	10%	22%	15%
S1	Cr	0.837	10%	22%	15%
S1	Cu	14.0	7.4%	22%	10%
S1	Fe	472	5.9%	18%	10%
S1	Hg	0.461	16%	22%	15%

Sample	Test	Assigned value (µg/L)	Between Laboratory CV*	Thompson/ Horwitz CV	Target SD (as CV)
S1	Mn	24.9	5.8%	22%	10%
S1	Mo	7.22	8.1%	22%	10%
S1	Ni	2.38	12%	22%	15%
S1	Pb	3.94	4.1%	22%	10%
S1	Sb	4.30	6.5%	22%	15%
S1	Se	2.03	6.7%	22%	15%
S1	Tl	1.45	8.2%	22%	15%
S1	U	2.99	4.7%	22%	10%
S1	V	1.09	15%	22%	15%
S1	Zn	26.1	9.2%	22%	15%
S2	Ag	1.47	15%	22%	15%
S2	Al	15.5	15%	22%	15%
S2	As	5.11	12%	22%	15%
S2	Be	1.85	9.2%	22%	15%
S2	Cd	1.27	7.3%	22%	15%
S2	Cr	1.55	23%	22%	15%
S2	Cu	9.08	15%	22%	15%
S2	Fe	22.2	16%	22%	15%
S2	Hg	0.365	13%	22%	15%
S2	Mn	7.31	8.3%	22%	15%
S2	Ni	2.47	21%	22%	15%
S2	P	119.9**	12%	22%	15%
S2	Pb	1.55	20%	22%	15%
S2	Sb	3.16	7.6%	22%	15%
S2	Se	4.38	21%	22%	20%
S2	Sn	3.94	6.3%	22%	15%
S2	Tl	1.99	3.5%	22%	15%
S2	U	2.90	6.0%	22%	15%
S2	V	3.53	14%	22%	15%
S2	Zn	16.9	21%	22%	15%

*Robust between-laboratory CV outliers removed. Shaded cells represent between-laboratory CVs higher than both the target SD and the Thompson-Horwitz CV. ** Reference Value was used for the Assigned Value.



Scores greater than 10 have been plotted as 10.

Figure 42 z-Score Dispersion by Laboratory

The dispersal of participants' z-scores is presented in Figure 42 (by laboratory code) and in Figure 44 (by analyte). Of 669 results for which z-scores were calculated, 622 (93%) returned an acceptable score of $|z| \leq 2.0$ and 28 (4%) were questionable where $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

A summary of participants' performance is presented in Figure 45.

Laboratory **20** reported results for all 40 tests for which a z-score was calculated and returned acceptable z-scores for 39 of them, the highest of all participants.

All results reported by Laboratories **4** (38), **16** (37), **10** (34), **21** (25), **13** (19), **15** (12), and **3** (3) returned acceptable z-scores.

6.4 E_n -score

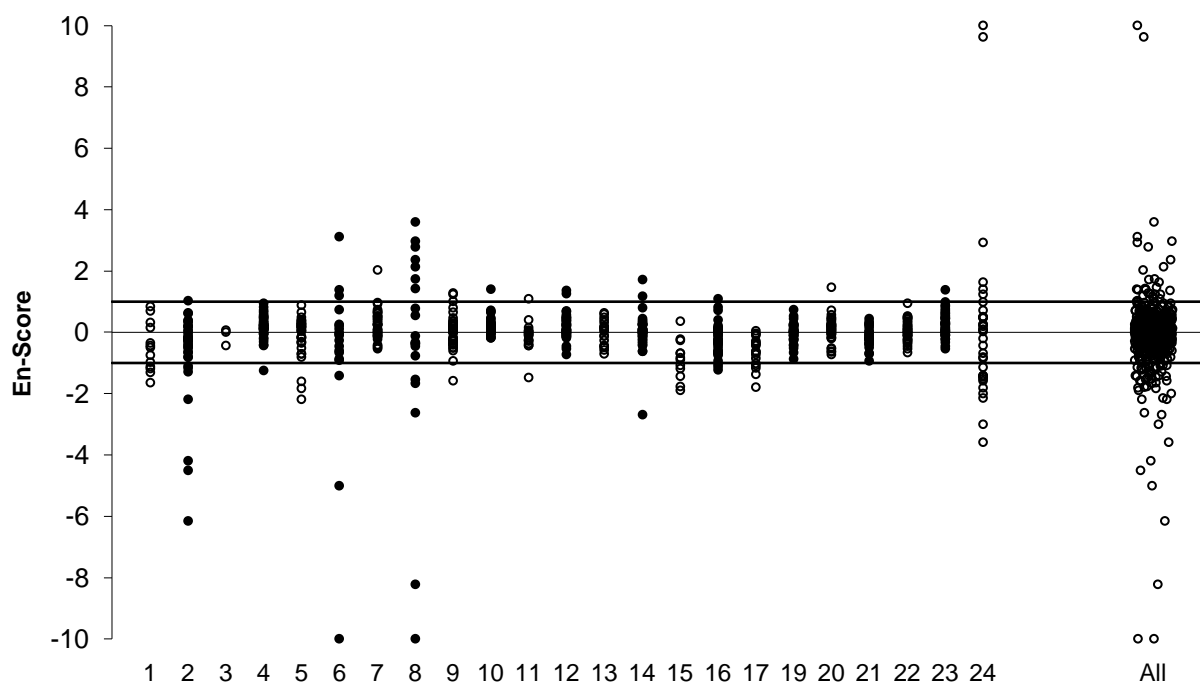
E_n -score can be interpreted only in conjunction with z-scores. The E_n -score indicates how closely a result agrees with the assigned value considering their respective uncertainties. An unacceptable E_n score for an analyte can either be caused by an inappropriate measurement, an inappropriate estimation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

The dispersal of participants' E_n -scores is graphically presented in Figure 43. 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 669 results for which E_n -scores were calculated, 588 (88%) returned an acceptable score of $|E_n| < 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

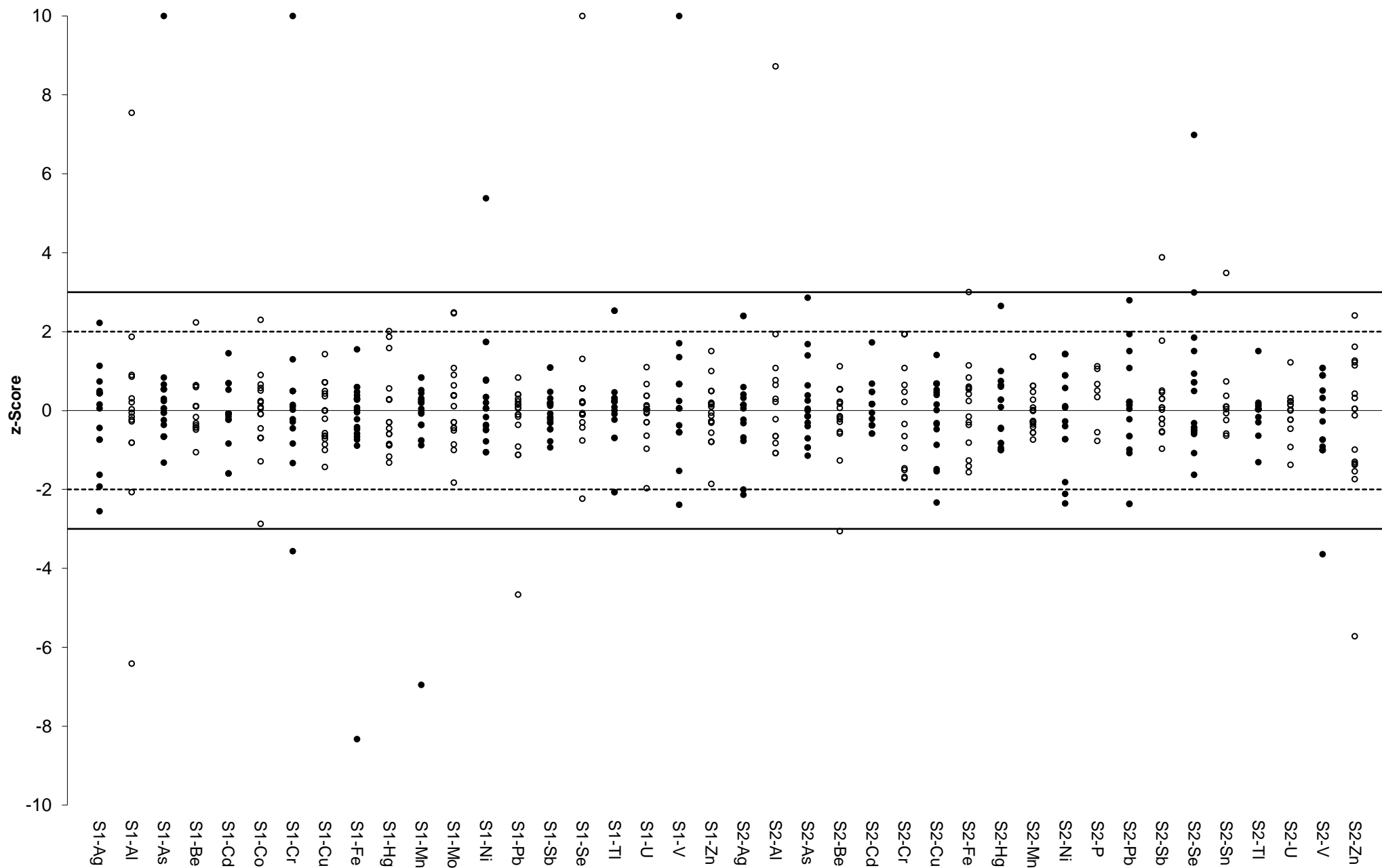
Laboratory **20** had the highest number of acceptable E_n scores, 39 out of 40 reported.

All results reported by Laboratories **19** (37), **22** (37), **21** (25), **13** (19), **3** (3) returned acceptable E_n -scores.



Scores greater than 10 or less than -10 have been plotted as 10 or -10 respectively.

Figure 43 E_n -Score Dispersal by Laboratory



Scores greater than 10 have been plotted as 10.

Figure 44 z-Score Dispersal by Analyte
AQA 24-17 Trace Elements in River and Sea Water

Summary of Participant's Performance in AQA 24-17 Samples S1 and S2

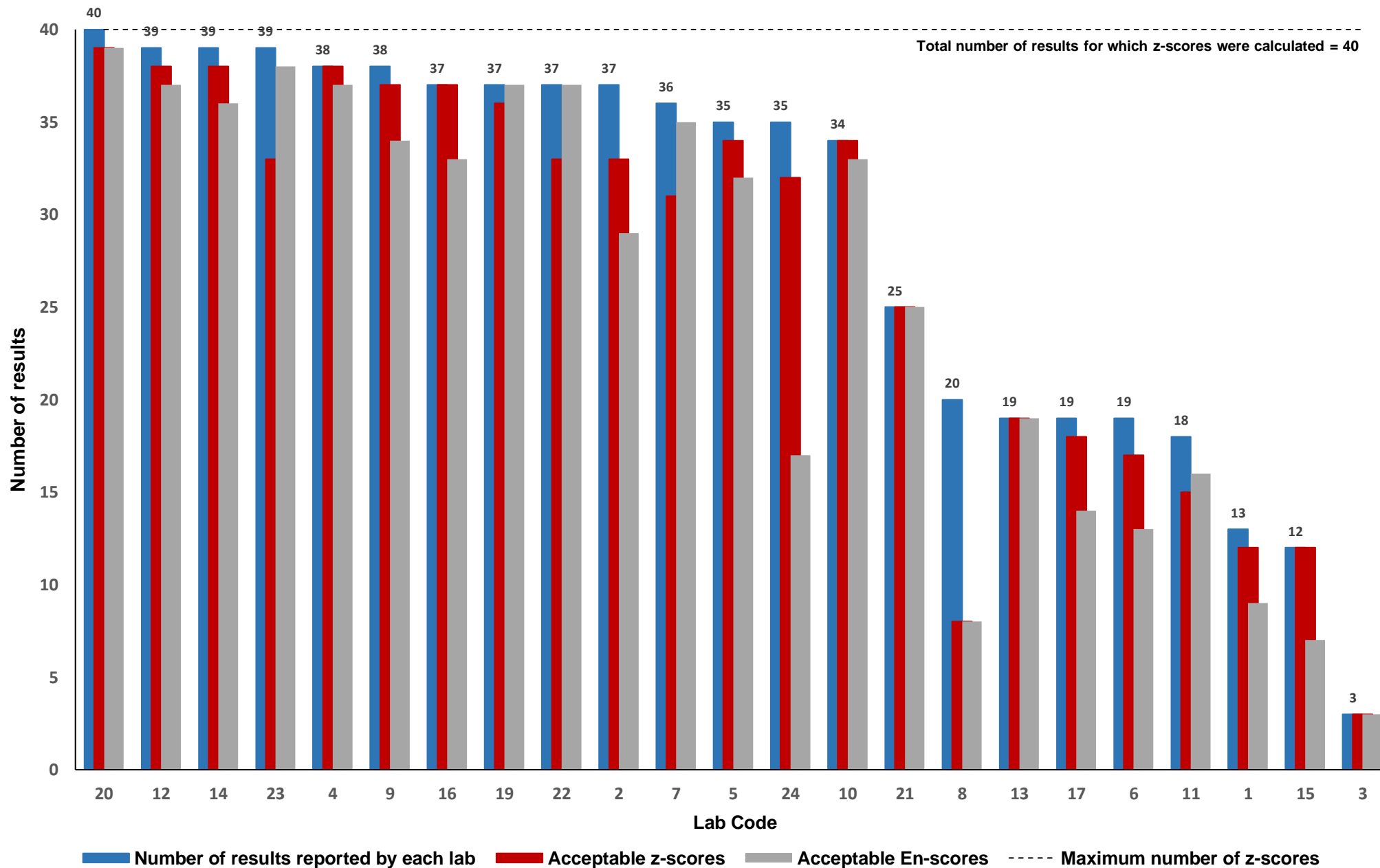


Figure 45 Summary of Participants Performance in AQA 24-17

AQA 24-17 Trace Elements in River and Sea Water

Table 45 Summary of Participants' Results and Performance for Sample S1

Lab	Ag µg/L	Al µg/L	As µg/L	Be µg/L	Cd µg/L	Co µg/L	Cr µg/L	Cu µg/L	Fe µg/L	Hg µg/L
AV	2.25	7.97	1.11	1.88	1.31	2.23	0.837	14.0	472	0.461
HV	2.50	-	1.02	1.87	1.23	2.22	0.808	13.4	500	0.438
SV	2.58	-	1.13	1.90	1.32	2.36	0.839	14.5	-	0.452
1	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
2	1.7	7.7	0.89	1.8	1.4	2.2	0.39	12	450	0.48
3	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	2.4	9	1.2	1.9	1.3	2.4	0.9	15	490	0.44
5	2.27	7.79	1.07	1.99	1.38	2.42	<1	14.5	486	<0.5
6	2.63	0.30	1.25	1.81	1.28	1.27	0.67	13.09	461.79	0.43
7	3	<10	1	2	1.4	2	<1	16	500	0.4
8	2.1	17	4.2	2.3	1.1	1.8	7.3	12.8	79	0.38
9	NT	10.2	1.05	1.68	1.30	2.45	0.90	14.0	494	0.50
10	2.4	7.9	1.16	1.9	1.29	2.53	0.78	14.7	485	0.44
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	2.3	7	1.22	1.9	1.3	2.26	0.84	13.7	545	0.481
13	2.42	8.34	1.12	1.82	1.30	2.31	0.850	14.6	473	NT
14	1.39	7.65	1.12	1.79	1.30	2.25	0.810	13.1	476	0.590
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	2.40	8.22	1.15	NT	1.28	2.08	0.732	13.2	437	0.402
17	1.6	5.5	1.1	1.9	1.1	2.2	<1	13	430	0.37
19	2.4	7	1.2	2	1.3	2	0.8	14	441	0.42
20	2.5	9.05	1.1	1.85	1.3	2	0.854	14	486	0.48
21	2.4	8	1	1.8	1.3	2.2	<1	15	452	0.42
22	2	<10	1	2	1.2	2	<1	14	470	0.4
23	2	<10	1	2	1.5	3	1	15	500	0.57
24	NT	NT	1.2	1.8	1.3	2.3	0.9	12.6	444.6	0.6

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, SV = Spike Value, NT = Not Tested.

Table 45 Summary of Participants' Results and Performance for Sample S1 (continued)

Lab	Mn µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Sb µg/L	Se µg/L	Tl µg/L	U µg/L	V µg/L	Zn µg/L
AV	24.9	7.22	2.38	3.94	4.30	2.03	1.45	2.99	1.09	26.1
HV	23.2	6.66	2.28	3.82	4.25	1.72	1.42	2.93	1.06	22.4
SV	24.7	7.19	2.41	4.09	4.26	2.01	1.53	3.04	1.11	26.0
1	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
2	24	6.9	2.2	4.1	3.8	2.2	1.4	3	0.7	30
3	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	26	7.5	2.4	3.9	4.4	2.2	1.5	2.9	1.2	28
5	25.5	7.68	2.66	4.06	4.40	1.35	1.55	3.19	1.37	26.9
6	25.66	7.87	2.40	3.58	4.43	2.43	1.43	NT	1.03	23.89
7	24	8	3	4	5	2	1	3	<1	32
8	7.6	9.02	4.3	2.1	3.7	5.1	2	2.9	3.6	18.8
9	26.2	6.85	2.45	4.27	4.10	2.09	1.52	2.98	0.84	26.7
10	25.6	7.5	2.65	4.03	4.38	2.01	1.517	3.03	1.1	26.5
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	24.7	7.5	2.32	3.9	4.5	2.1	1.5	3.1	1.2	25.9
13	25.0	7.0	2.25	3.97	4.18	1.94	1.47	2.97	1.13	25.6
14	24.8	7.49	2.21	3.88	4.43	2.09	1.50	3.02	1.10	24.9
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	22.7	6.50	2.24	3.96	4.25	2.09	1.45	3.32	1.31	23.0
17	23	5.9	2.1	3.5	4	2	NT	2.4	1	23
19	23	6.6	2	3.8	4.1	2	1.5	3	<1	25
20	25.4	7.3	2.4	4	4.15	1.8	1.5	3.1	1.2	23
21	24	6.9	2.5	4.1	4.2	<2	1.3	2.8	1	25
22	27	7	2	4	4	2	1	3	<1	28
23	27	9	3	4	5	2	2	3	1	28
24	25.4	6.9	2.5	3.5	4.6	1.9	1.3	2.7	1.1	26.8

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, SV = Spike Value, NT = Not Tested.

Table 46 Summary of Participants' Results and Performance for Sample S2

Lab	Ag µg/L	Al µg/L	As µg/L	Be µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Fe µg/L	Hg µg/L	Mn µg/L
AV	1.47	15.5	5.11	1.85	1.27	1.55	9.08	22.2	0.365	7.31
SV	1.53	13.8	4.42	1.87	1.27	1.49	9.75	24.6	0.376	7.43
1	<5	<50	6.18	1.91	1.36	1.15	6.98	17.5	0.313	6.93
2	1.6	<50	4.8	1.5	1.2	<0.5	7.9	21	0.38	6.7
3	< 50	< 50	5.11	1.87	< 2	< 10	< 10	< 50	< 0.5	6.97
4	1.5	18	5.3	1.9	1.3	1.6	9.8	26	0.37	8.8
5	1.48	13.6	5.14	1.77	1.16	1.33	9.29	21.7	<0.5	7.03
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	2	14	5	2	1.4	2	10	18	0.4	7
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
9	1.03	17.3	4.57	1.69	1.16	1.70	8.44	24.2	0.42	7.83
10	1.4	<40	5.6	NT	1.26	<2	9.7	24.1	0.38	7.32
11	1.3	14	7.3	1.8	1.3	< 1	5.9	17	0.31	6.5
12	1.5	13	5	1.91	1.6	1.4	10	<100	0.406	7.3
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	1.54	20.0	4.87	1.81	1.36	1.47	8.62	23.6	<1	7.32
15	1.32	< 50	5.40	1.79	1.23	1.16	7.05	< 50	0.31	6.70
16	1.42	15.0	4.24	NT	1.20	1.21	8.65	19.5	0.341	6.85
17	NT	NT	NT	NT	NT	NT	NT	NT	0.32	NT
19	1.5	13	6.4	1	1.2	1.8	10	24	0.32	8.8
20	1.56	16.2	4.4	2.16	1.3	1.66	9.62	32.2	0.398	7.62
21	NT	<20	<20	2	<1	<1	10	<20	0.34	7
22	2	17	5	2	1.2	2	11	23	0.4	8
23	1	16	5	2	1.2	2	10	25	0.51	8
24	NT	35.8	4.4	1.7	1.3	1.2	9.1	21.2	NT	7.4

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, RV = Reference Value, SV = Spike Value, NT = Not Tested.

Table 46 Summary of Participants' Results and Performance for Sample S2 (continued)

Lab	Ni µg/L	P µg/L	Pb µg/L	Sb µg/L	Se µg/L	Sn µg/L	Tl µg/L	U µg/L	V µg/L	Zn µg/L
AV	2.47	119.9	1.55	3.16	4.38	3.94	1.99	2.90	3.53	16.9
SV	2.75	123	1.56	3.08	4.06	3.76	2.03	2.87	3.56	18.3
1	1.69	139	1.40	<5	3.95	<5	<5	<5	<5	13.4
2	2.2	<1000	1.8	2.7	5.7	4	1.8	2.8	1.6	2.4
3	< 10	< 5000	< 10	< 5	< 10	< 5	< 10	< 5	< 25	< 50
4	2.8	<200	1.5	3.2	4.1	3.9	1.9	2.5	4.1	NR
5	2.32	NT	1.58	3.06	2.95	NT	2.05	2.96	3.14	12.5
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	3	<100	2	5	5	6	2	3	3	21
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
9	2.37	NT	2.20	2.91	3.93	3.56	2.44	2.96	3.05	14.4
10	<7	NT	1.6	3.4	5	<5	1.94	2.9	3.7	20.1
11	1.6	NT	1.3	3.3	5.2	4.0	1.6	2.3	3.8	13
12	2.8	129	1.6	3.3	7	3.6	2.0	2.7	4.1	20
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	2.20	132	1.40	3.38	4.82	4.16	2.02	2.91	3.53	17.7
15	1.80	< 500	1.32	< 5	3.91	< 5	< 5	< 5	< 5	13.6
16	2.51	NT	1.59	3.17	3.43	3.96	2.03	3.43	3.14	13.5
17	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
19	3	NT	1.9	3.2	6	NT	2	3	4	18
20	2.68	126	1.56	3.06	3.86	4.38	2.04	3.04	3.38	16.6
21	<5	106	<10	<20	<20	<20	<50	NT	3	17
22	3	140	1	3	4	4	2	3	4	23
23	3	110	1	4	4	4	2	3	4	17
24	2.5	NT	1.6	2.9	10.5	3.8	2	2.8	3	19.8

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, RV = Reference Value, SV = Spike Value, NT = Not Tested.

6.5 Participants' Results and Analytical Methods for Dissolved Elements

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

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

Pb, Se, Cr and Zn in sea water were the tests which most challenged participants' analytical techniques when compared to the river water sample. The between-laboratory CVs for these tests in S2 were 2 to 5 times higher than in S1.

Laboratory 8 reported their Sample S2 results as Sample S1. These results were not included in the analysis of the methods employed by participants.

A summary of participants' results and performance in the two study samples are presented in Tables 45 and 46 and in Figures 42 to 45.

Individual Element Commentary

Participants were requested to analyse the two water samples for dissolved elements using their normal test methods and to report a single result as they would normally report to a client. The method descriptions provided by participants are presented in Tables 1 and 2 and instrumental conditions are presented in Appendix 6.

No significant difference was observed between the performances of participants who performed digestion and those who did not conduct a digestion procedure on the test samples. Instrumental measurement was one of the main factors that influenced results in the two water samples. However, participants' performance does not reflect instrumental performance alone, but also the performance of the analyst and of the analytical method used by the testing laboratory. Thus, these results should not be construed as an evaluation of a particular instrument.

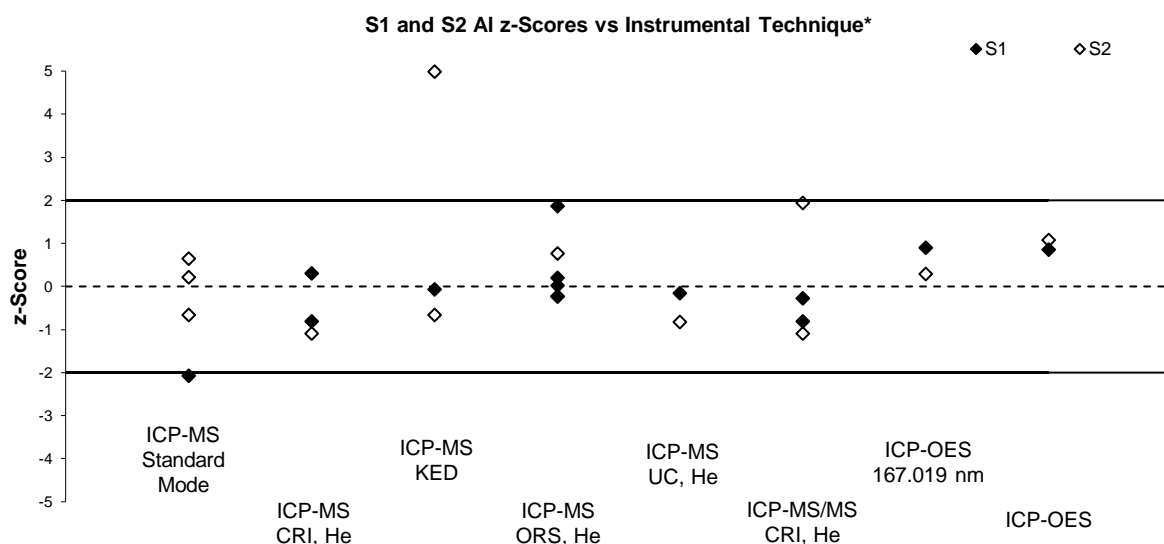
Most laboratories reported using ICP-MS or ICP-MS/MS with a collision/reaction cell.

Aluminium level in the two water samples S1 and S2 was low at 7.97 µg/L and 15.5 µg/L respectively. Sample or blank contamination may explain some of the unacceptable results. Plots of instrumental techniques versus z-scores are presented in Figure 46.

Arsenic Most participants used ICP-MS in collision mode for As measurement in the two study samples (Figure 47). Unresolved interferences may explain the high questionable result reported by Laboratory 11 in the sea water sample S2.

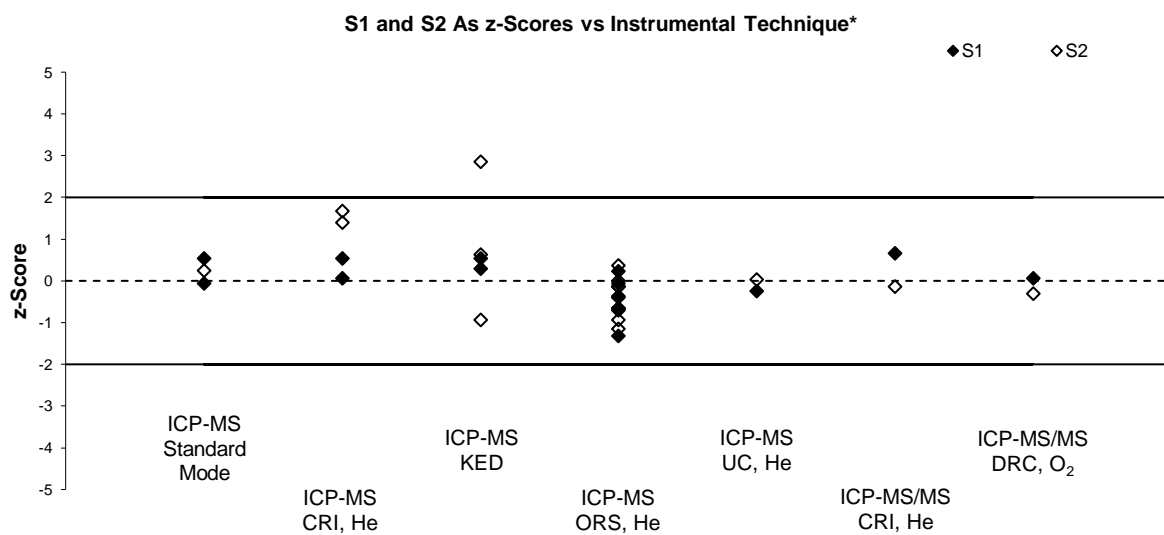
Beryllium measurements in the two water samples did not challenge participants' analytical techniques. All but one reported results returned acceptable z-scores.

Plots of participants' performance in both water samples versus instrumental technique used are presented in Figure 48 while plots of participants' performance by laboratory code number are presented in Figure 49.



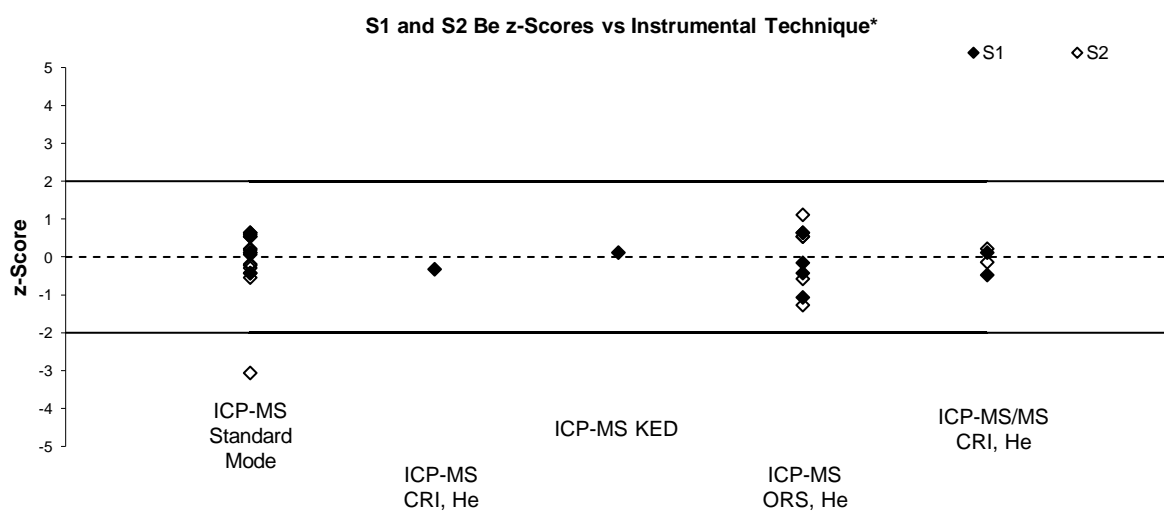
*The z-Score >5 has been plotted as 5. Laboratory 8 z-score excluded.

Figure 46 S1 and S2 Al z-scores vs Instrumental Technique



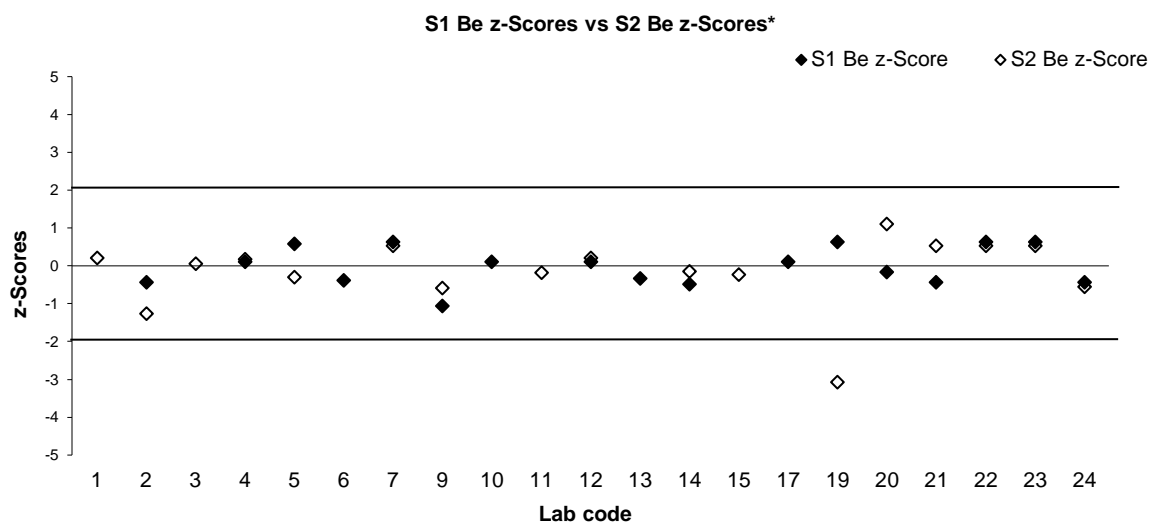
* Laboratory 8 z-score excluded.

Figure 47 S1 and S2 As z-scores vs Instrumental Technique



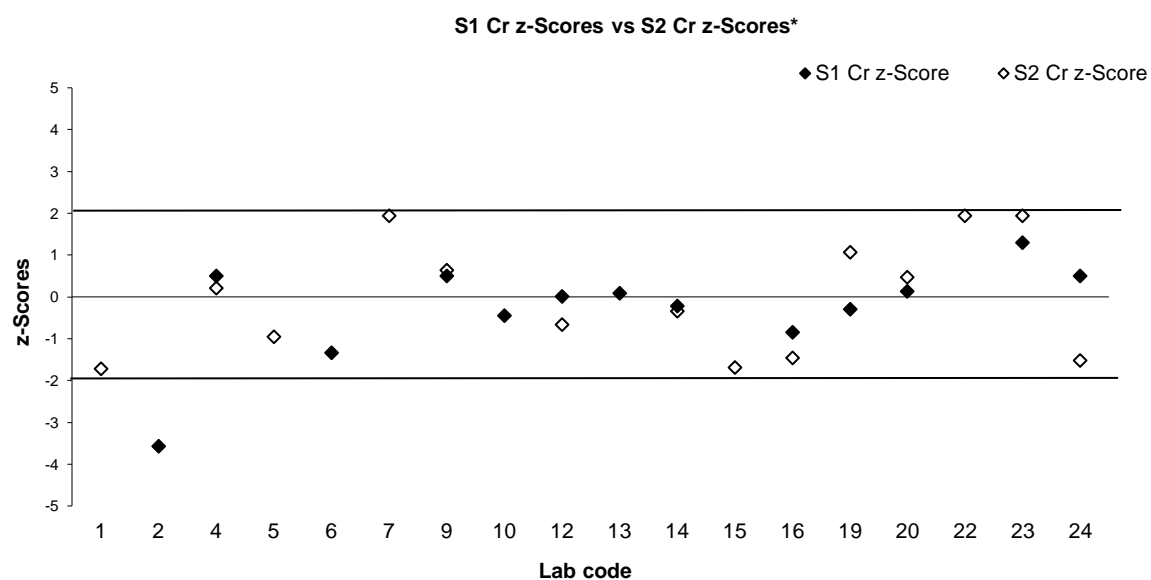
*Laboratory 8 z-score excluded.

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



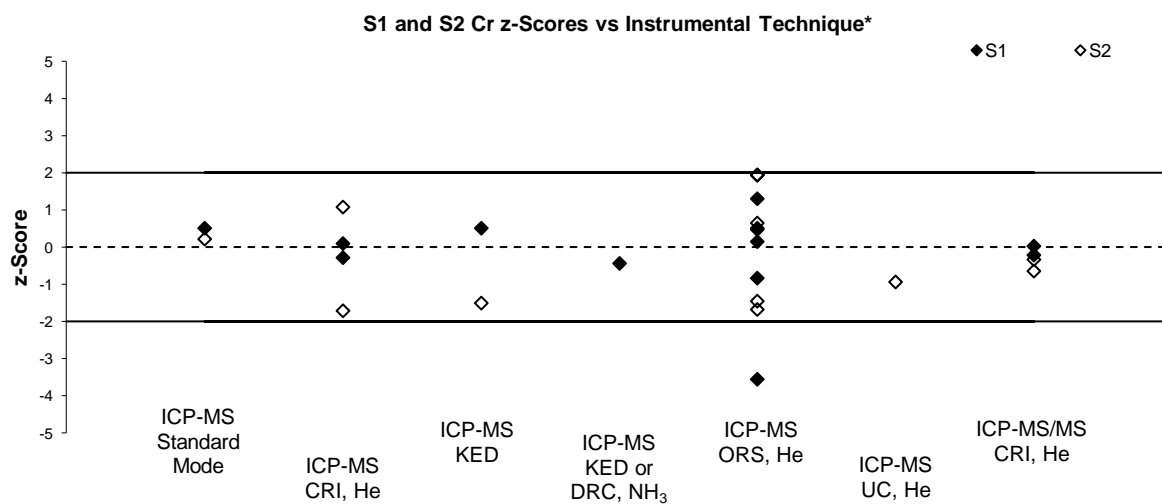
* Laboratory 8 z-score excluded.

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



* Laboratory 8 z-score excluded.

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



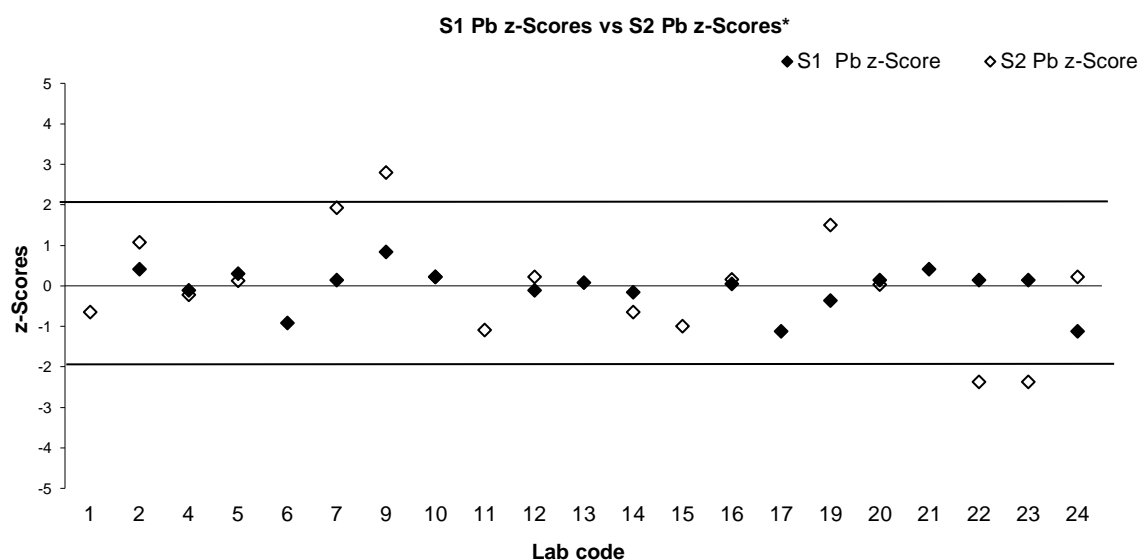
* Laboratory 8 z-score excluded.

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

Chromium in sea water was the test which challenged most participants' analytical techniques. The between laboratory CV was 23%, larger than the CV predicted by Thompson and Horwitz of 22%.

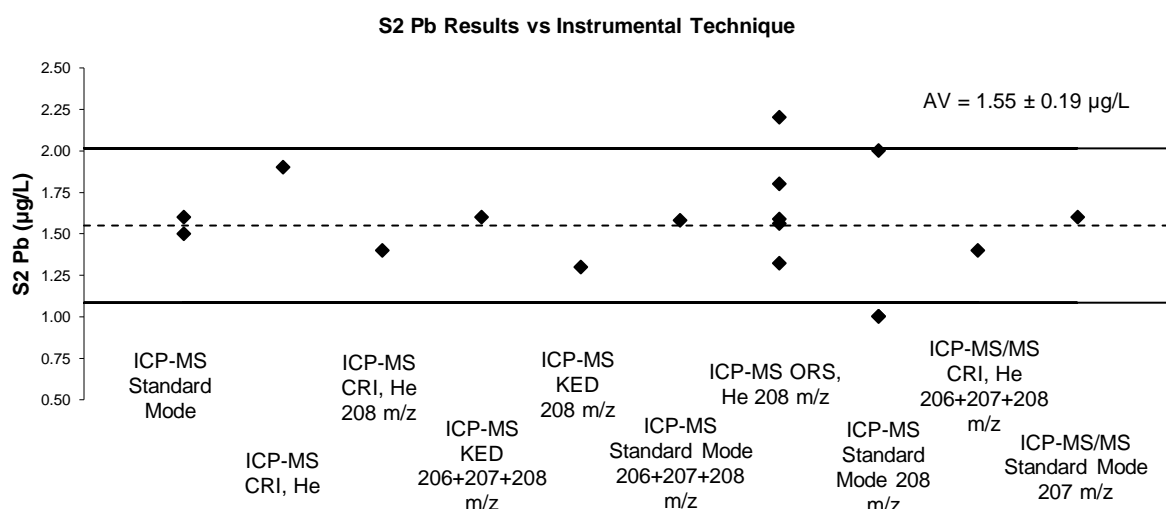
Although the Cr level in the two water samples was similar, the results in the sea water were more variable indicating that overcoming the matrix effects challenged some participants' analytical techniques. Plots of laboratories' performance in both water samples versus laboratory code number are presented in Figure 50, and versus instrumental technique in Figure 51.

Lead Eighteen laboratories reported results for Pb in S1 and all had an acceptable performance. Of 17 laboratories who reported results for Pb in S2, 14 returned acceptable z-scores. Reporting results with an insufficient number of significant figures may explain some of the unacceptable z-scores. Laboratory 9 reported a high, questionable result for this element in S2, they may need to review their practice and to check for contamination. The result reported by them in S1 although acceptable, was also higher than the assigned value (Figure 52). Figure 53 presents plots of participants performance for Pb in S2 samples versus instrumental techniques.



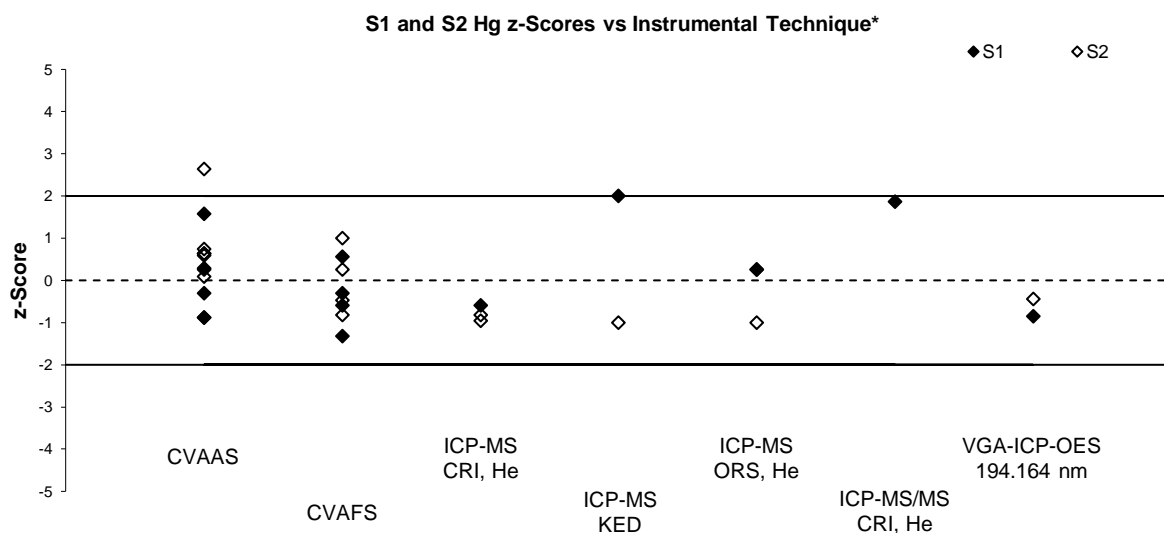
* Laboratory 8 z-score excluded.

Figure 52 S1 and S2 Pb z-scores vs Laboratory Code



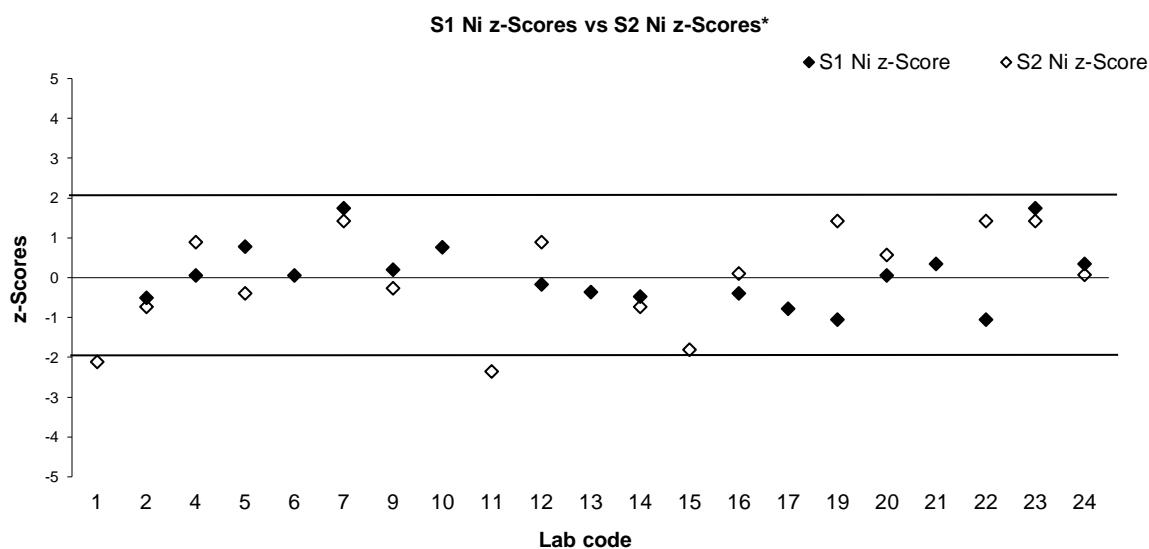
* Laboratory 8 result excluded. Horizontal lines correspond to z-scores of 2 and -2.

Figure 53 S2 Pb Results vs Instrumental Technique



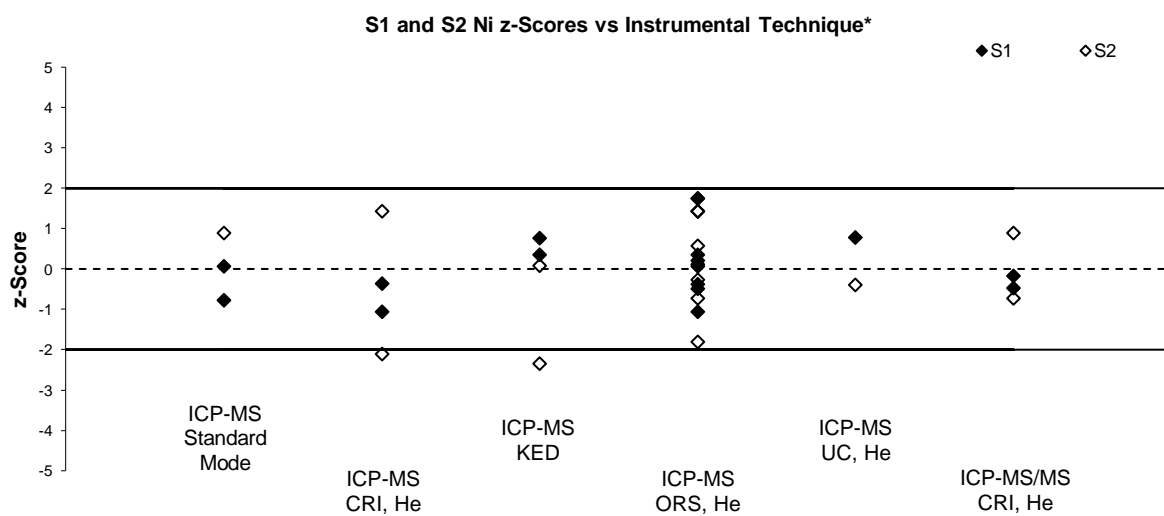
* Laboratory 8 z-score excluded.

Figure 54 S1 and S2 Hg z-Scores vs Instrumental Technique



*Laboratory 8 z-score excluded.

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



* Laboratory 8 z-score excluded.

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

Mercury Participants used a wide variety of instrumental techniques for Hg measurements in the two water samples and all produced compatible results but two (Figure 54).

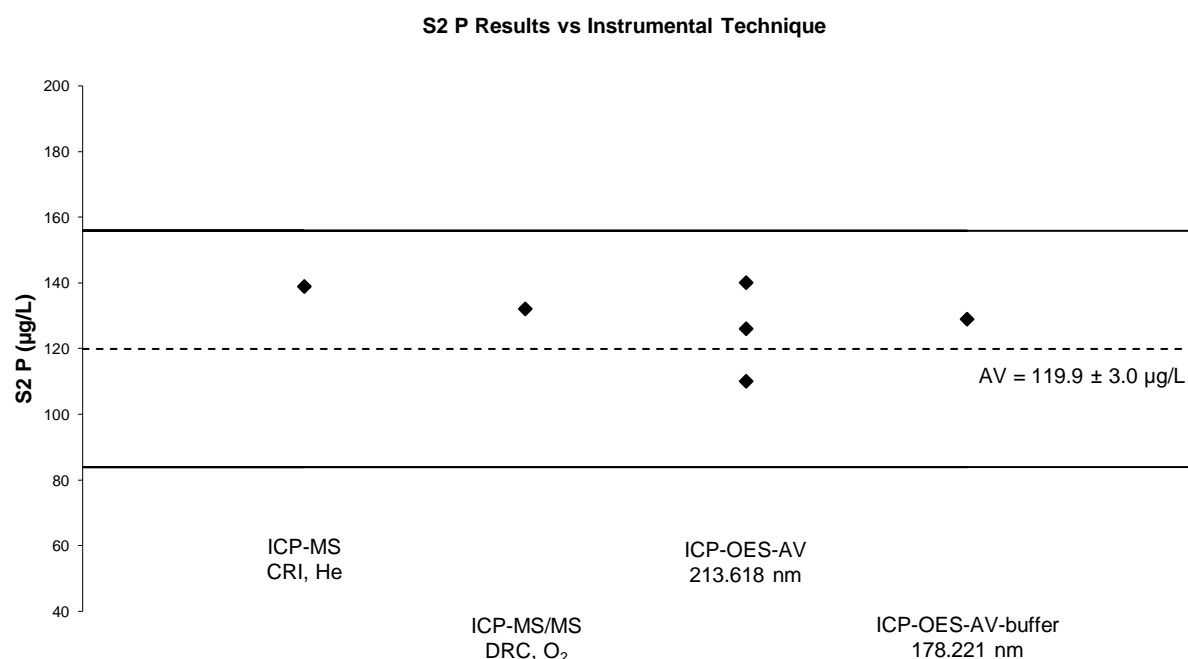
Expired standards, when not prepared fresh before measurements, is the most common cause for high Hg results.

Nickel was at a similar level in the two study samples: 2.38 µg/L in S1 and 2.47 µg/L in S2. The between-laboratory CV for this test in S1 was 12% and in S2 was 21%.

Plots of participants' performance in the two water samples versus laboratory code number are presented in Figure 55 and versus instrumental technique used are presented in Figure 56. All unacceptable results were lower than the assigned value and were produced using ICP-MS in collision mode.

Phosphorus spike level in the sea water sample S2 was 123 µg/L. As in previous studies, the measurement of P in seawater at a level close to 100 µg/L presents difficulties to laboratories. Only seven participants reported numerical results for this test.

This is the first study when the reported results were in relatively good agreement with each other and the spiked value (Figure 57). A reference value by SA-ICP-MS was produced for this analyte and used as the assigned value in order to give a feedback to participating laboratories on their performance.



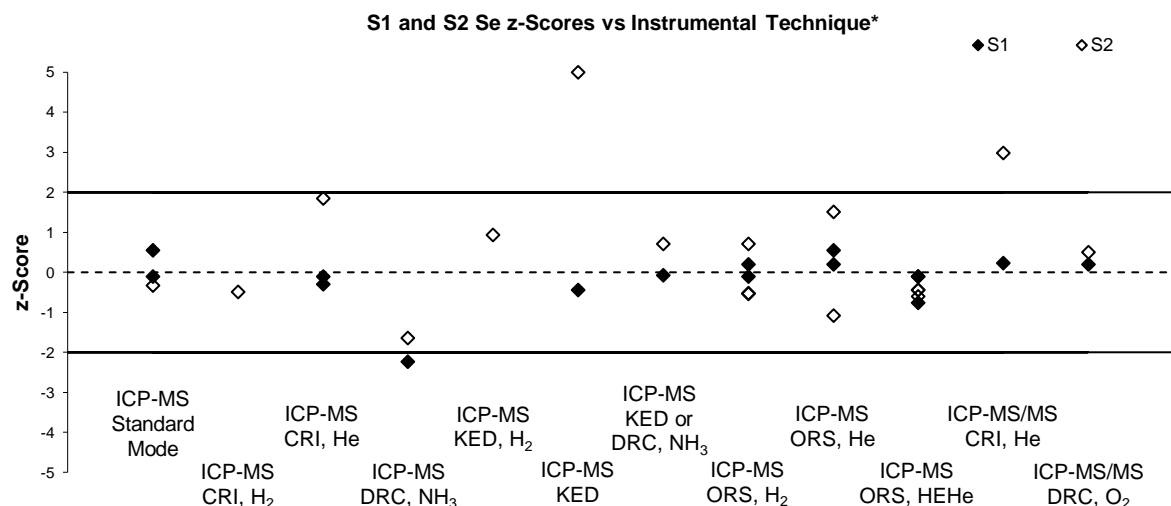
Horizontal lines correspond to z-scores of 2 and -2.

Figure 57 S2 P Results vs Instrumental Technique

Selenium Sea water contains significant quantities of dissolved salts, especially sodium chloride and sulphates. Molecular ions originated from dissolved salts with a mass similar to the Se isotope used in elemental determination can cause severe interference. As a result, false positives and concentrations much higher than the true values are frequently obtained when Se is measured by ICP-MS without the help of collision/reaction cell.

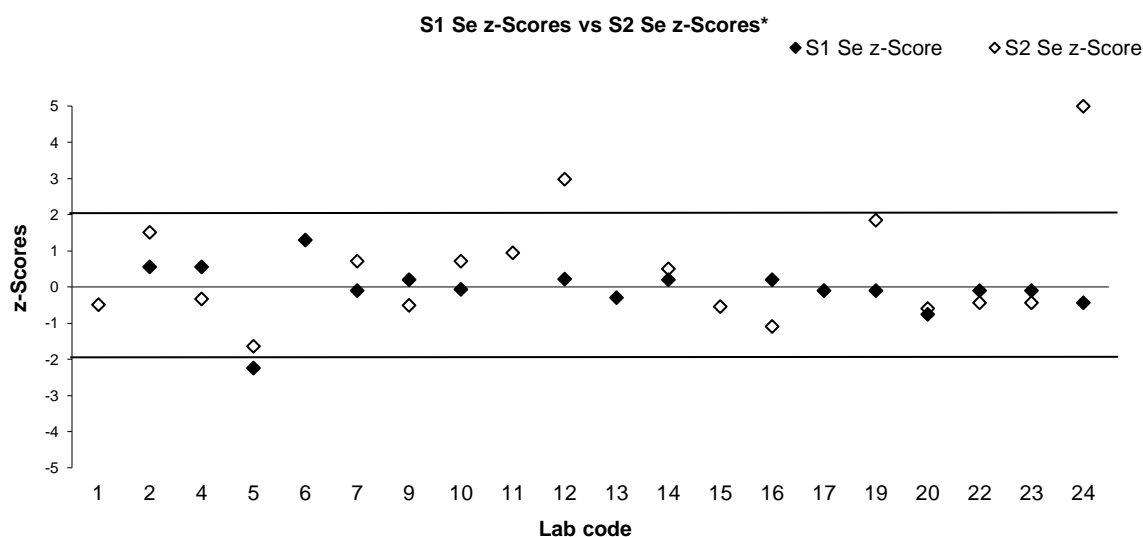
A plot of participants' performance for Se in S1 and S2 versus instrumental technique used is presented in Figure 58.

Laboratories who reported an acceptable Se result in S1 and unacceptable result in S2 may had an interference problem (Figure 59).



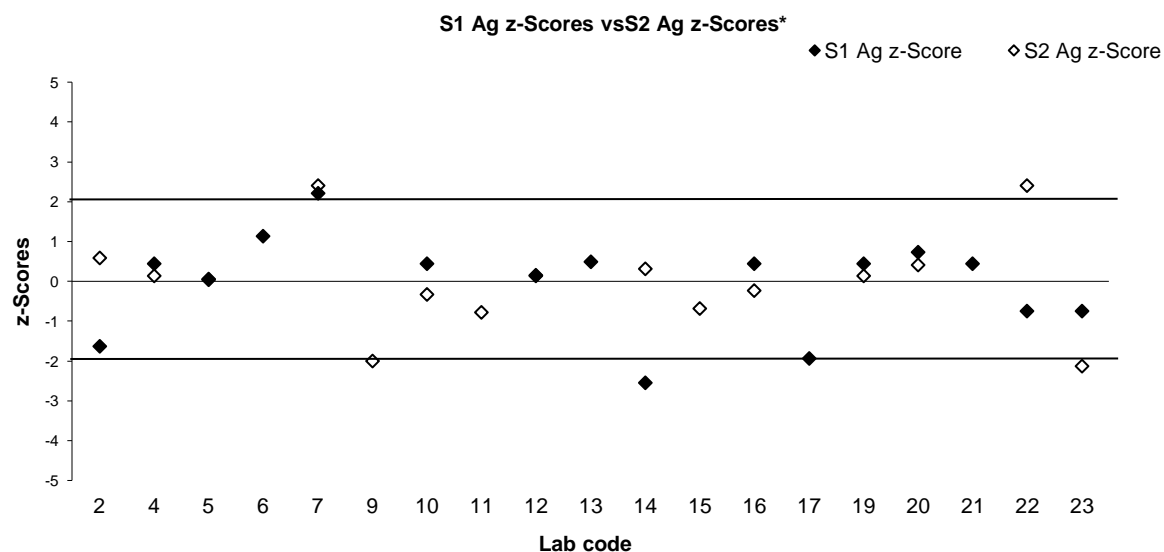
* Laboratory 8 z-score excluded. z-Score >5 has been plotted as 5.

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



* Laboratory 8 z-score excluded. z-Score >5 has been plotted as 5.

Figure 59 S1 and S2 Se z-Scores vs Laboratory Code



* Laboratory 8 z-score excluded.

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

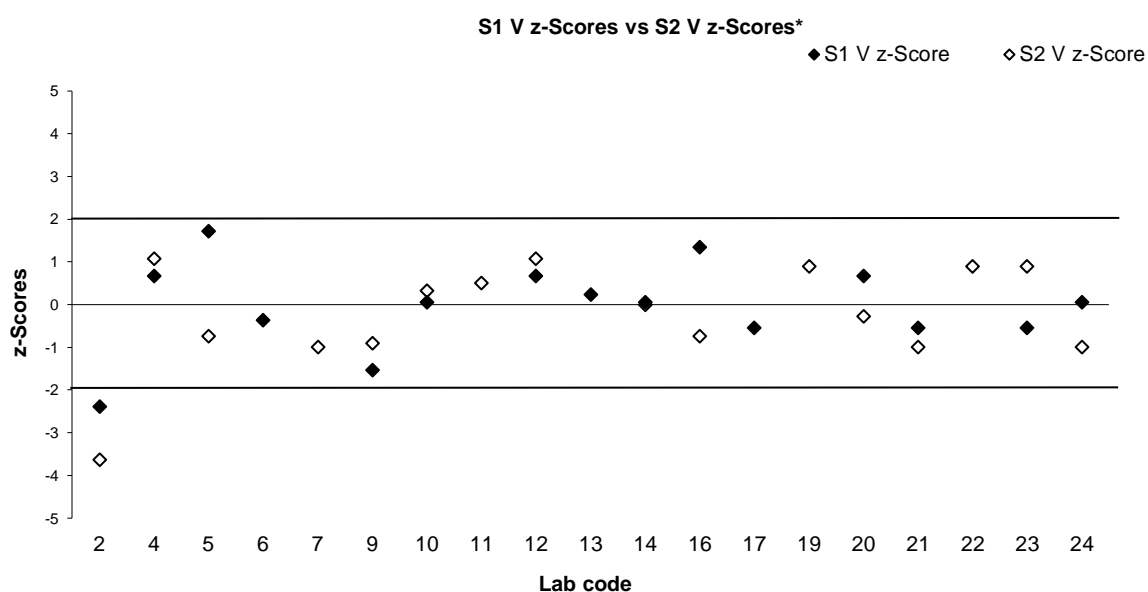
Silver in the river and sea water sample was low at 2.25 µg/L and 1.53 µg/L respectively. Participants' performance in the two samples are presented in Figure 60.

Laboratory 7 should check for method or laboratory bias as their Ag results reported in both samples are biased high and have questionable z-scores. High Ag results may be an indication of expired standards.

Thallium Reporting results with an insufficient number of significant figures may explain some of the questionable results reported for Tl in S1.

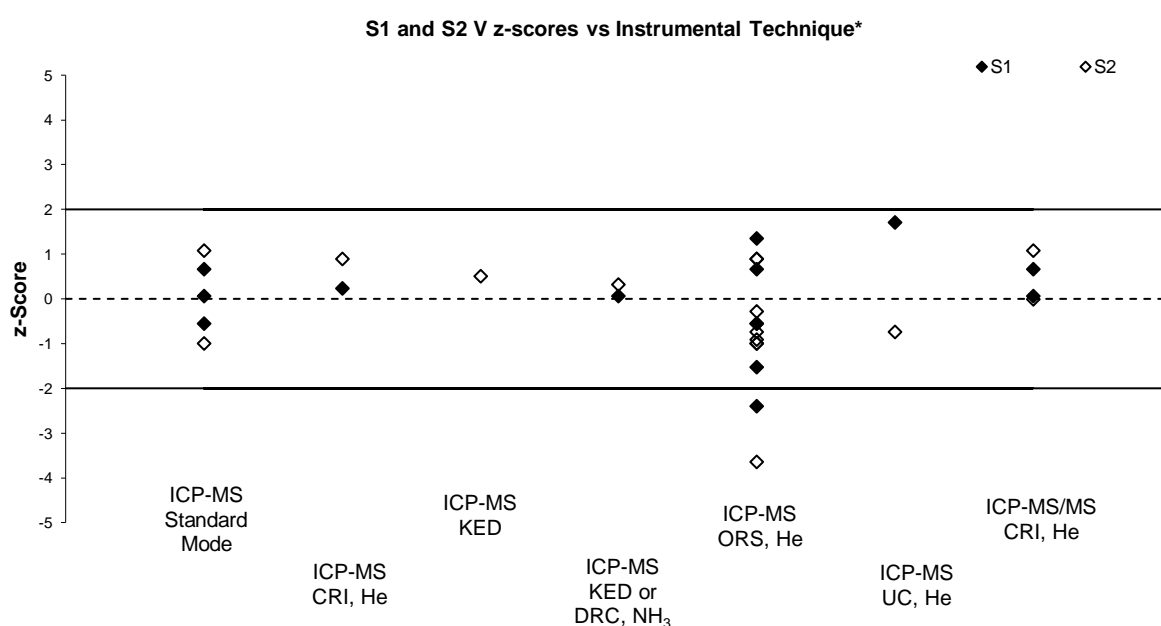
Vanadium Laboratory 2 should check for method bias as the results reported by them in both study samples are biased low (Figure 61).

Plots of participants performance in the two samples versus instrumental technique used are presented in Figure 62.



* Laboratory 8 z-score excluded.

Figure 61 S1 and S2 V z-Scores vs Laboratory Code



* Laboratory 8 z-score excluded.

Figure 62 S1 and S2-V z-Scores vs Instrumental Technique

6.6 Participants' Within-Laboratory Precision Reproducibility

Sample S2 was a sea water sample previously distributed as sample S1 of AQA 23-18. This study design was aimed at helping laboratories to assess their within-laboratory precision reproducibility in sea water.

Of 20 laboratories who reported results in AQA 24-17 S2, only five also reported results in AQA 23-18 S1: Laboratories **5, 10, 16, 19, and 20**. Results and the expanded MU reported by these laboratories in both study samples are presented in the bar charts in Figure 63.

In some cases, the results reported for these tests in the two study samples were significantly different.

Figure 64 presents scatter plots of z-scores in Sample S2 of AQA 24-17 and S1 of AQA 23-18. Points close to the diagonal axis represent excellent reproducibility and points close to zero represent excellent reproducibility and accuracy.

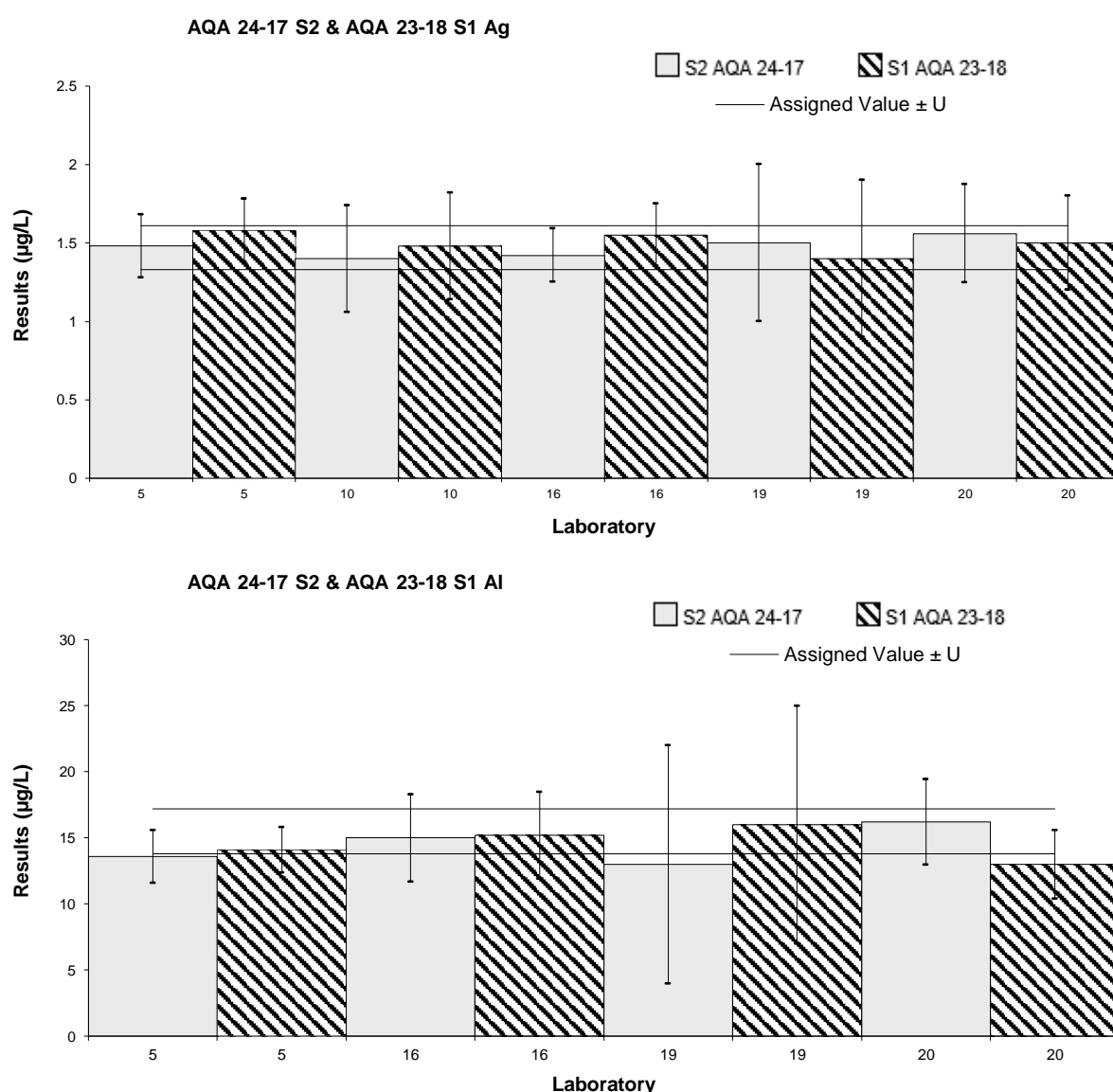


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18

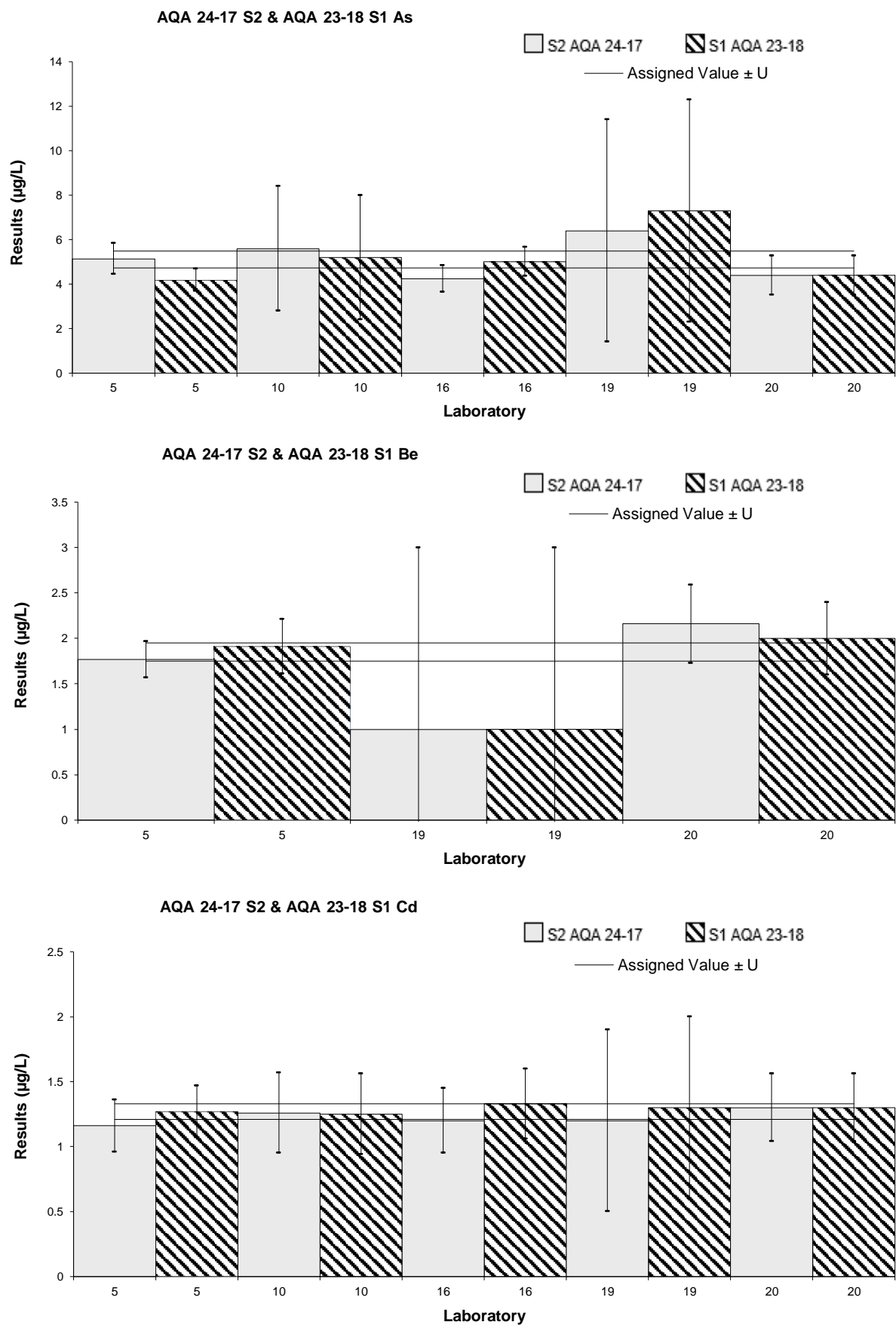


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

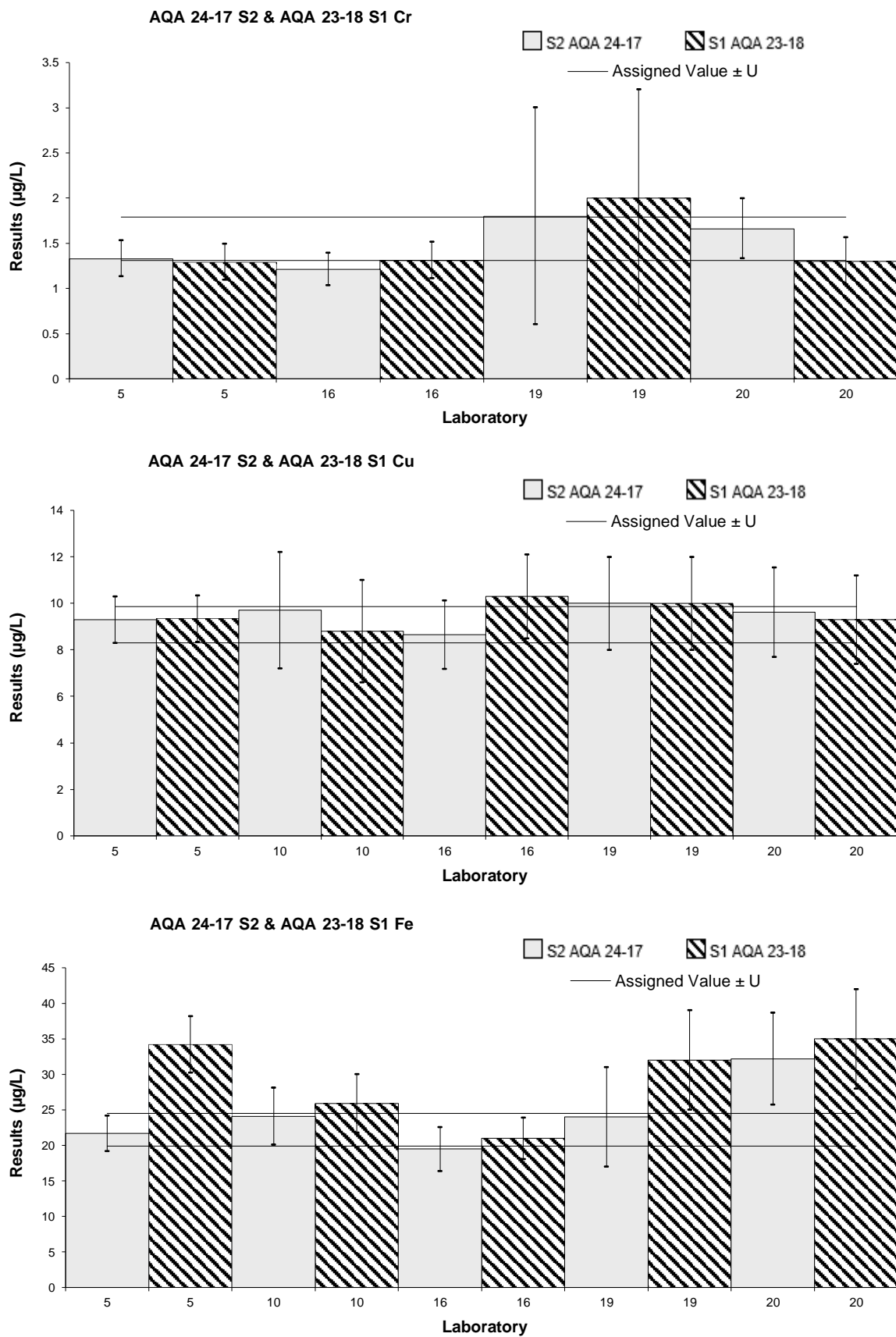


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

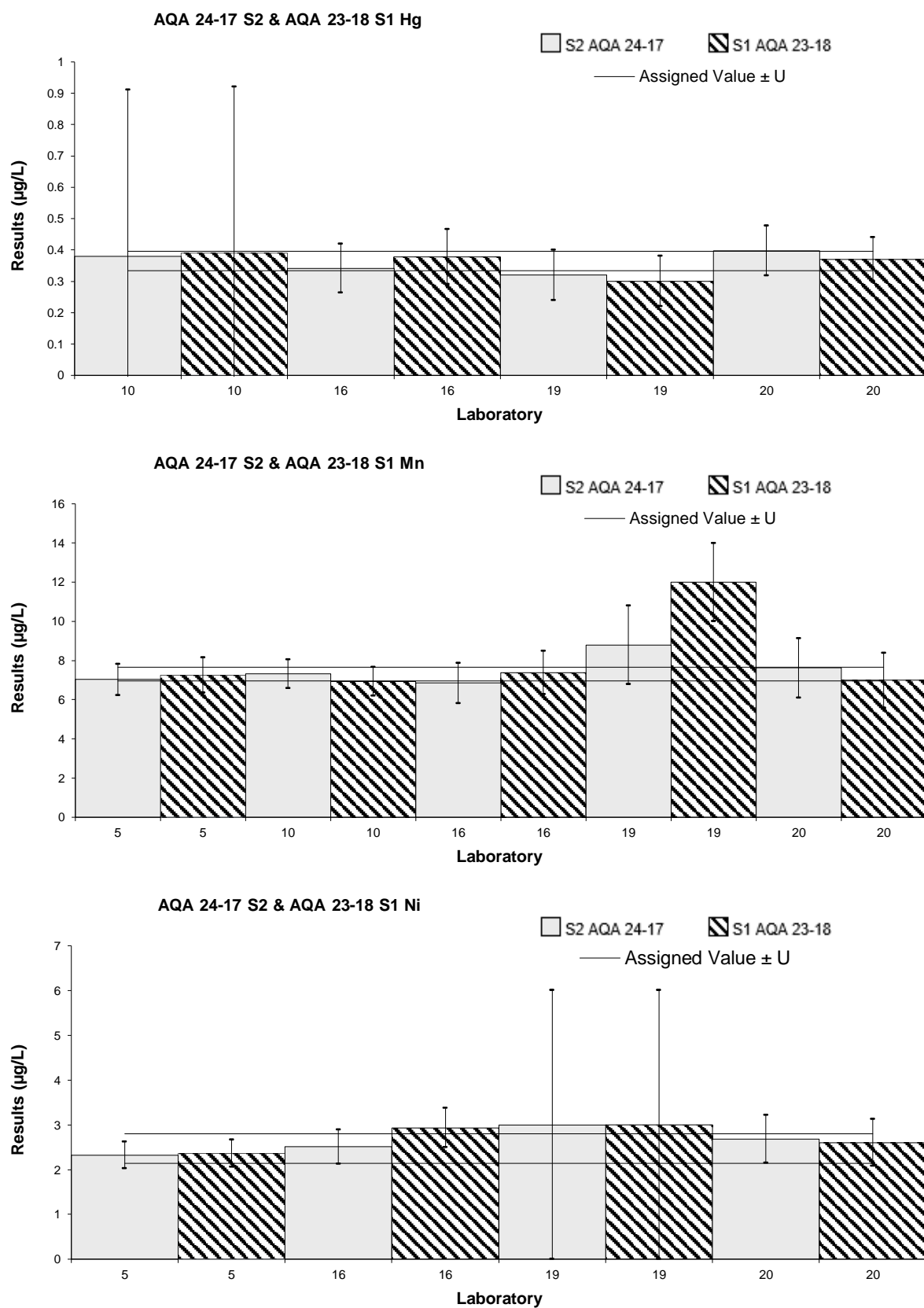


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

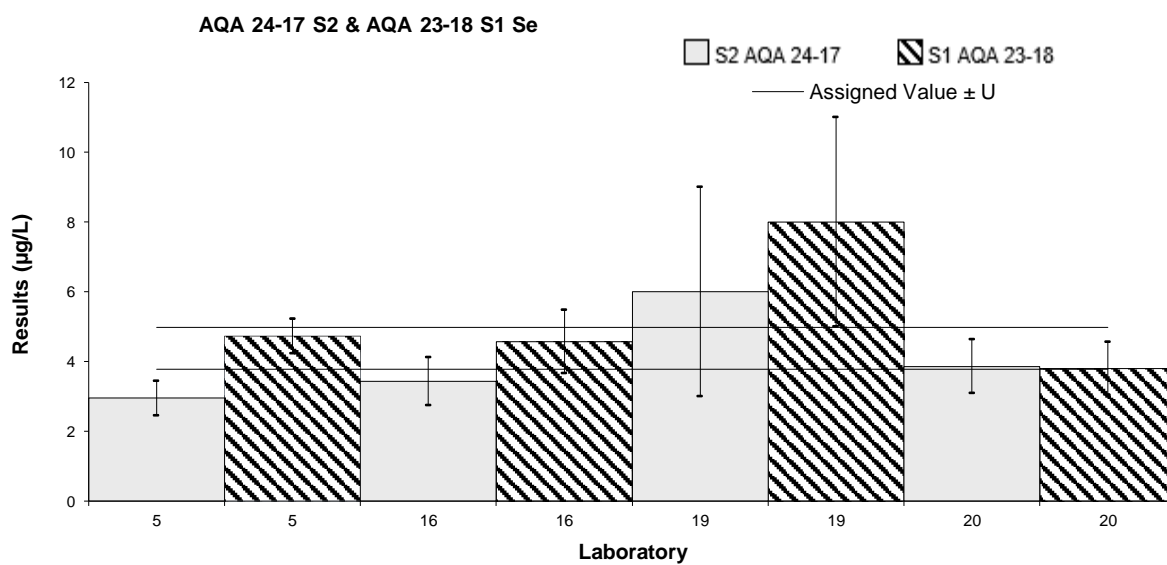
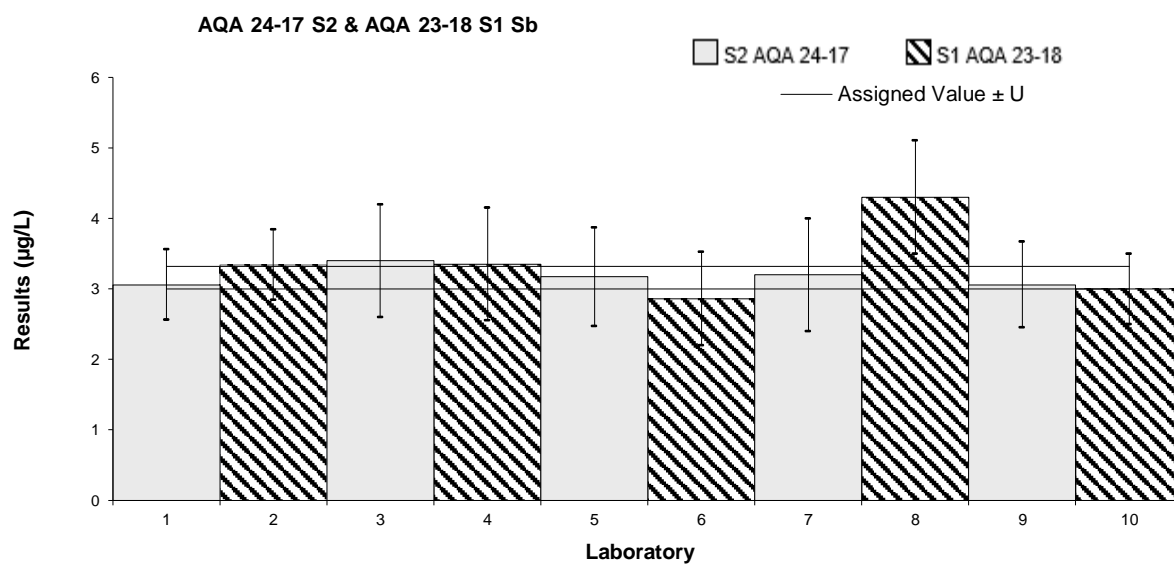
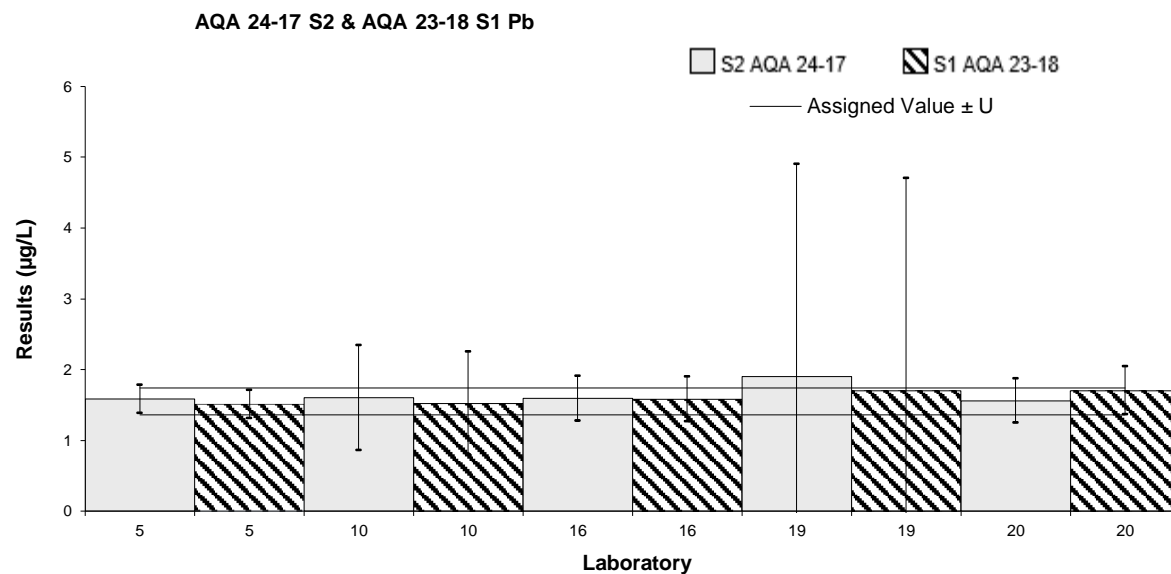


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

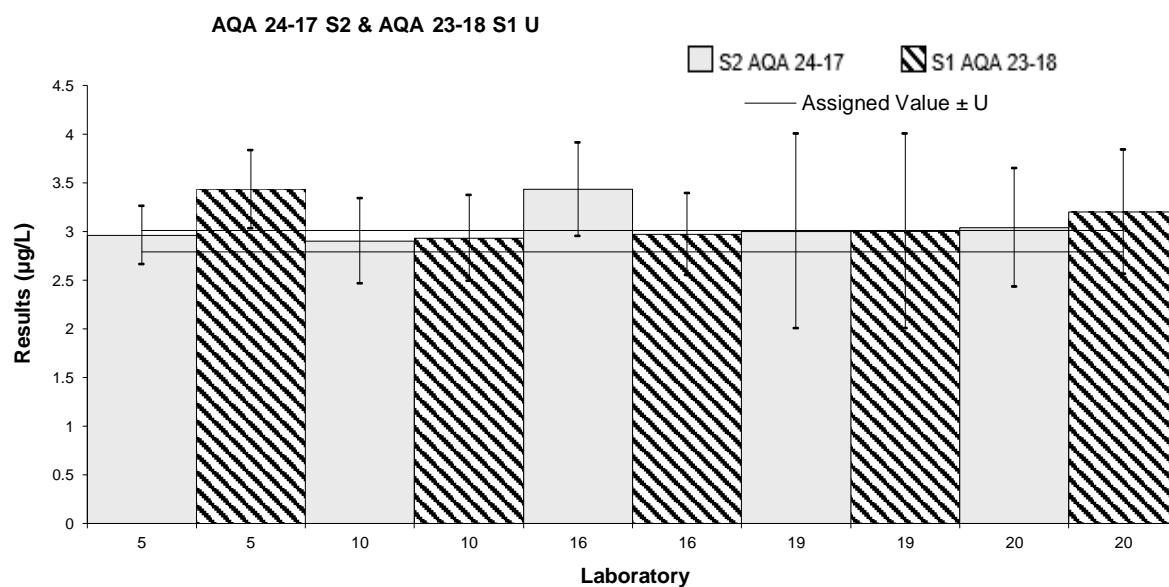
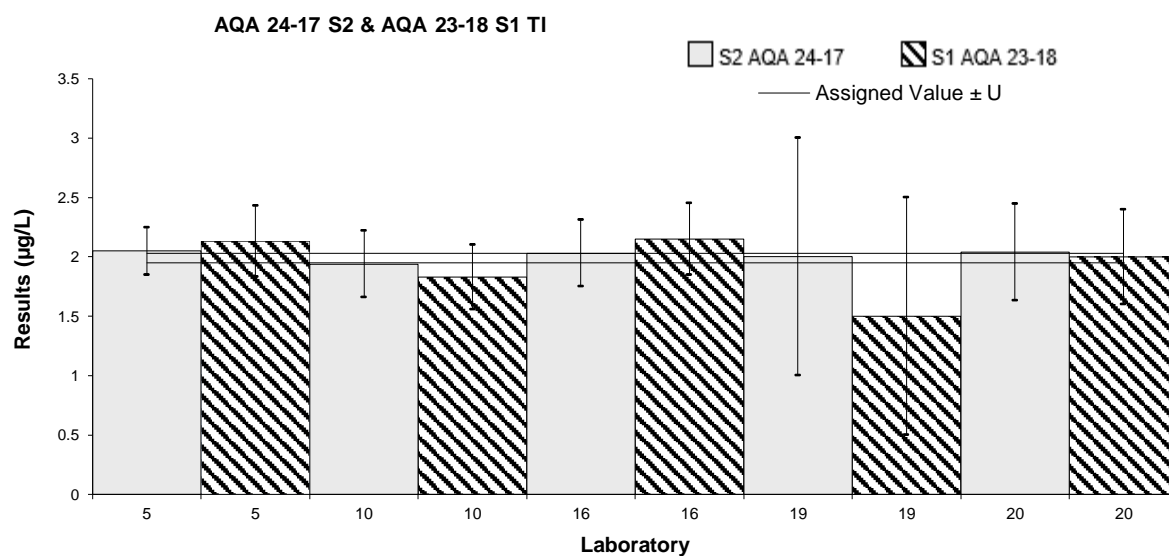
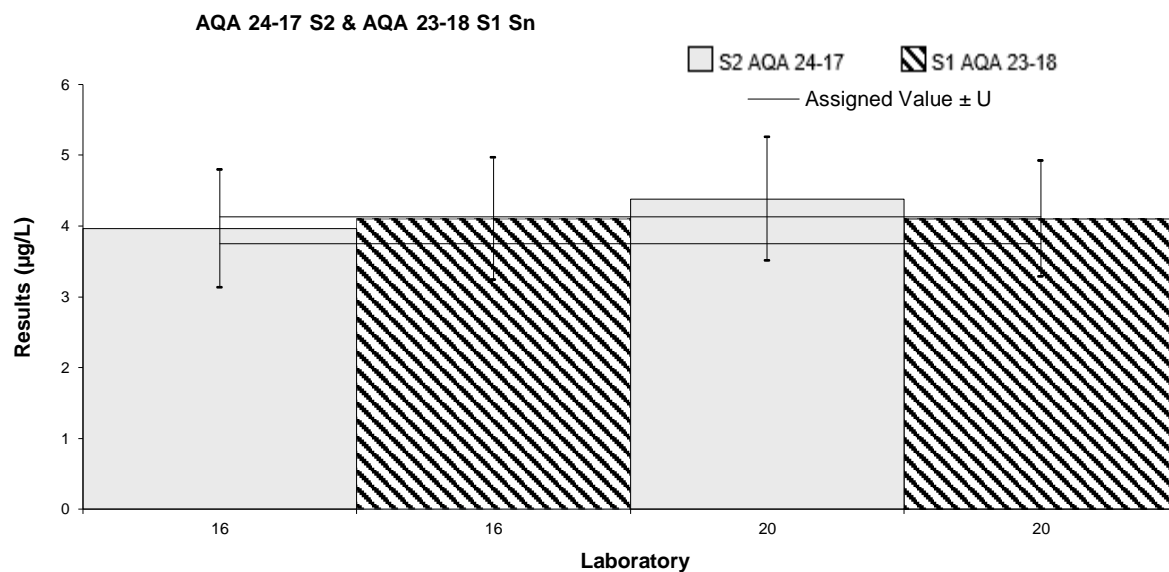


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

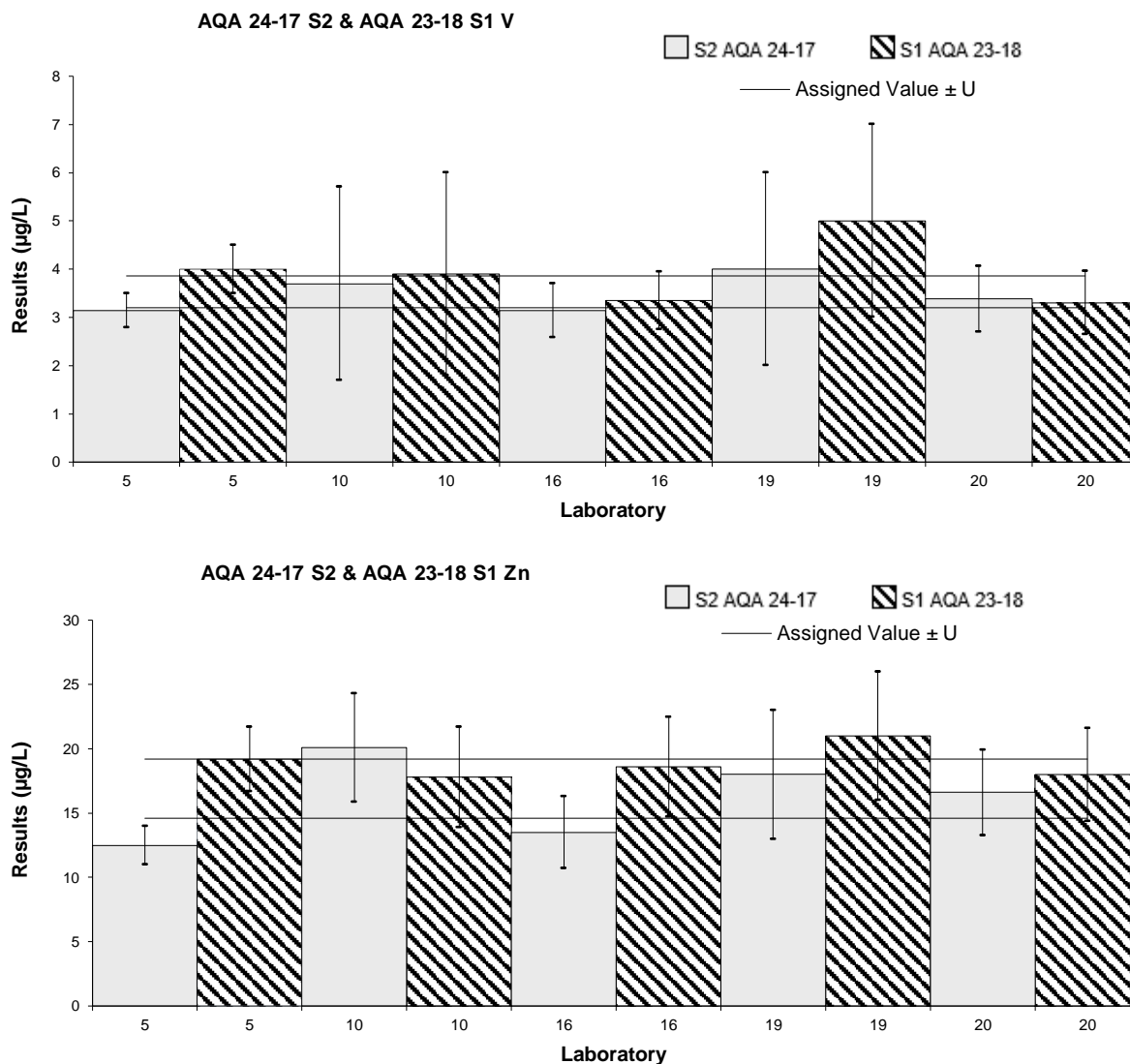


Figure 63 Bar chart of results in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

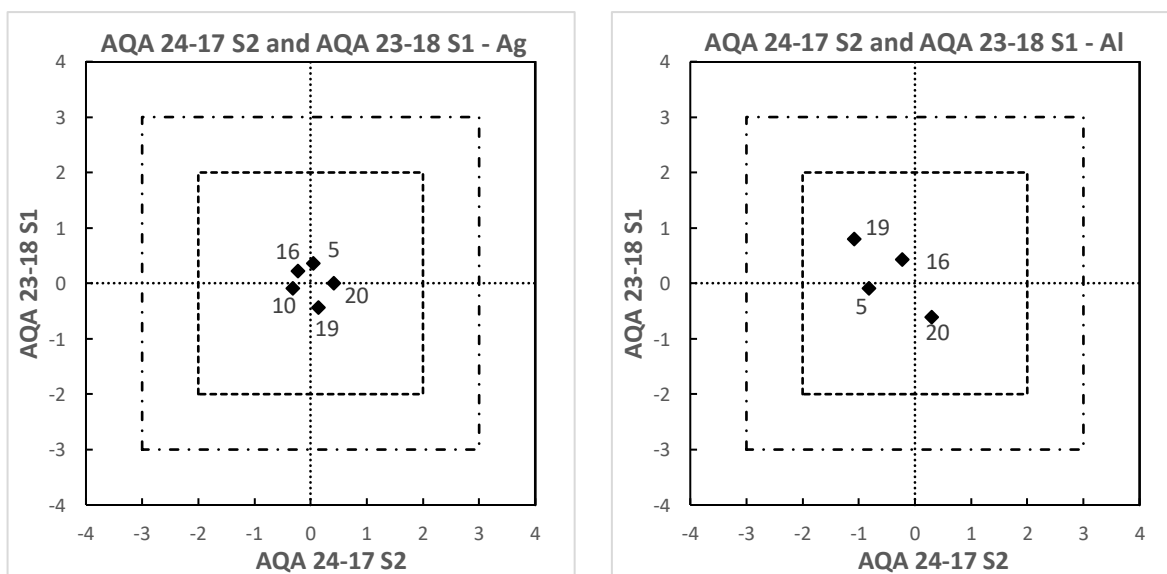


Figure 64 Scatter Plots of z-Score in S2 of AQA 24-17 and S1 of AQA 23-18

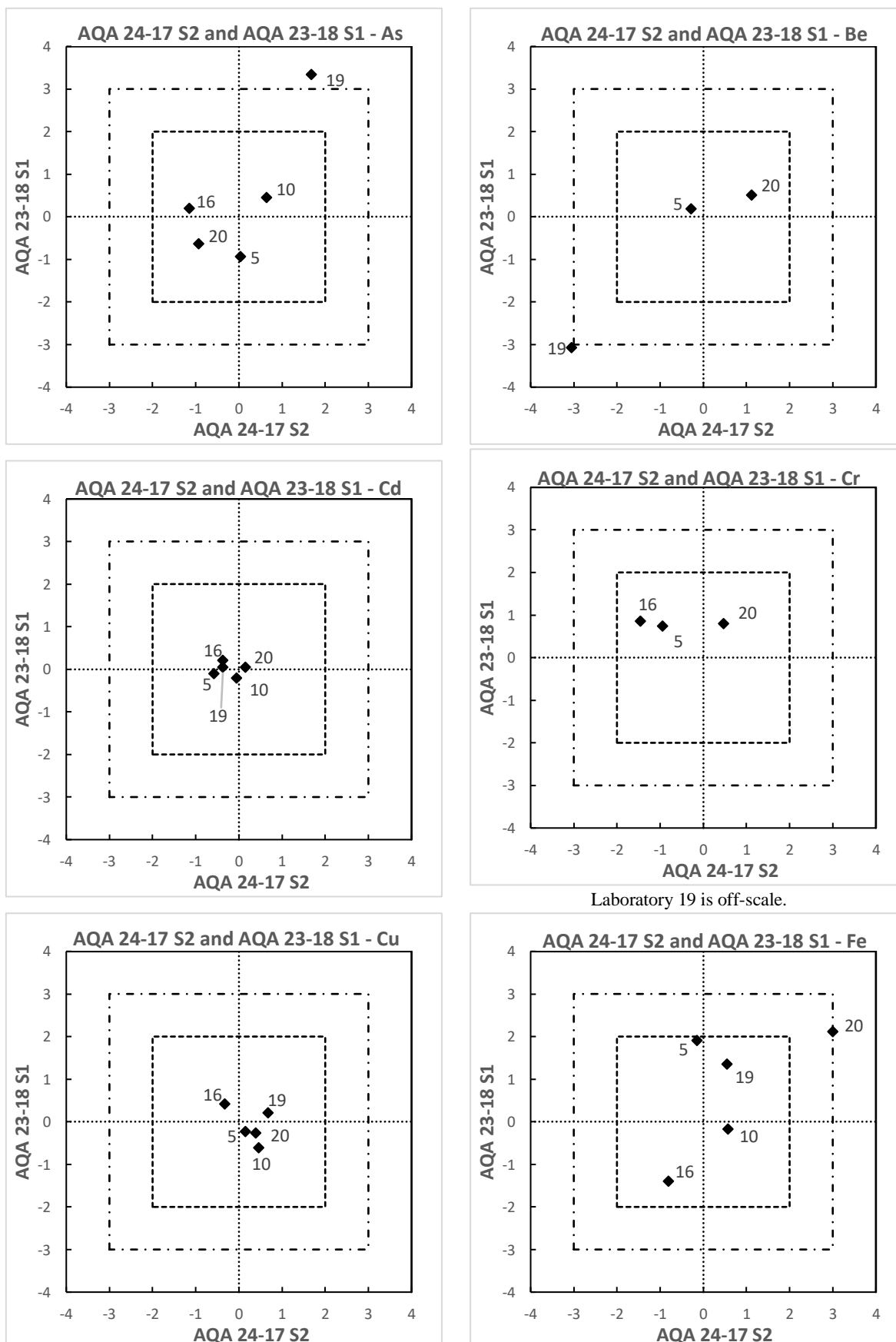
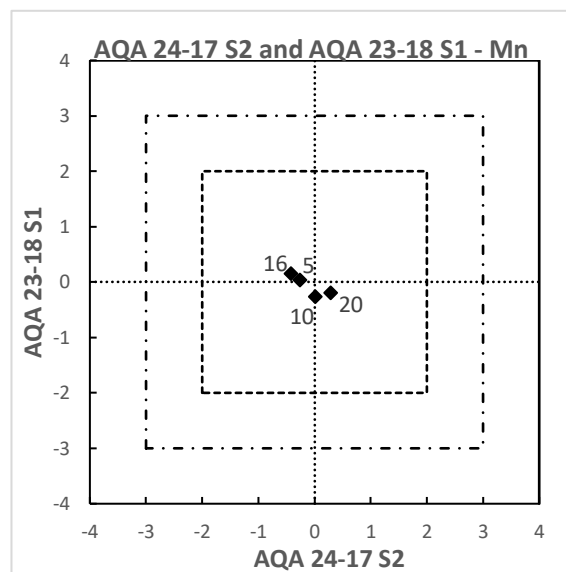
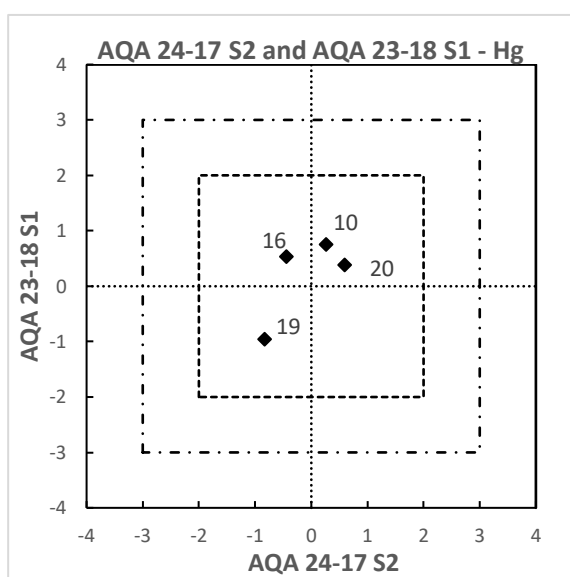
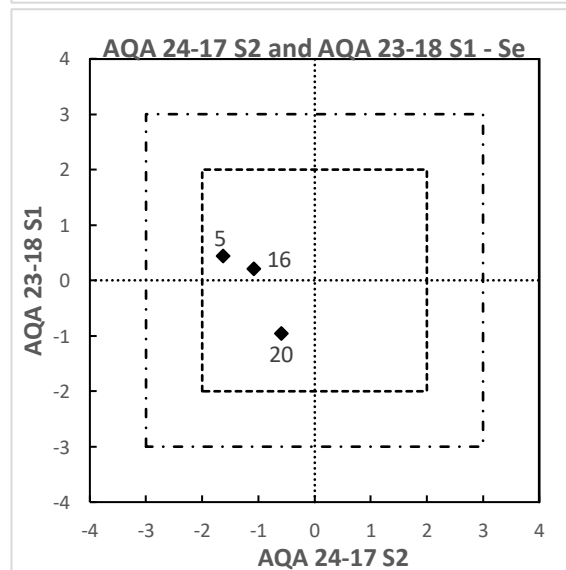
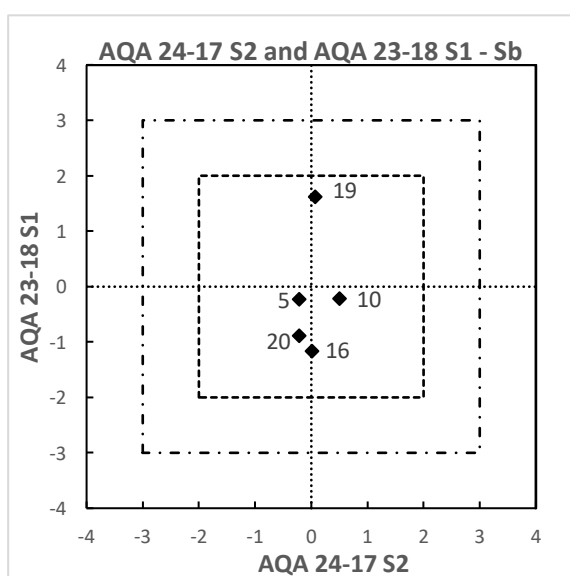
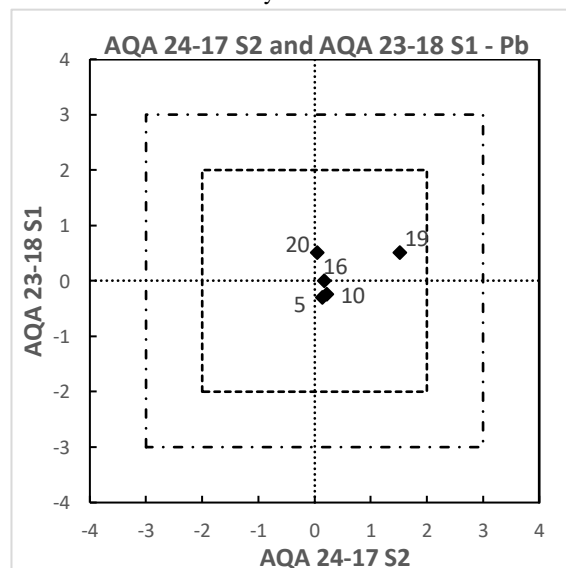
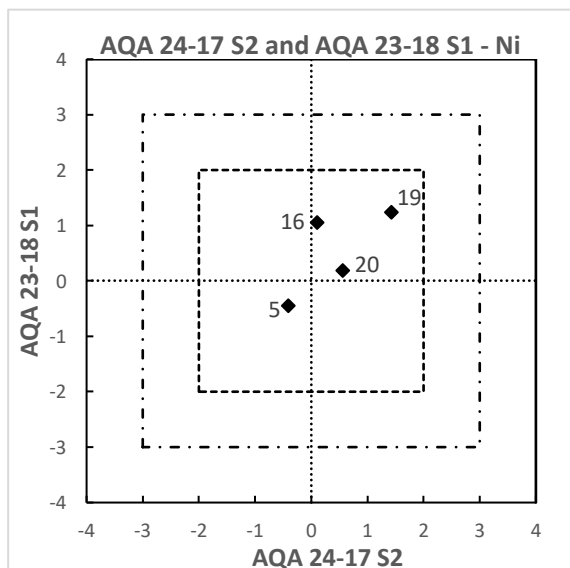


Figure 64 Scatter Plots of z-Score in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)



Laboratory 19 is off-scale.



Laboratory 19 is off-scale.

Figure 64 Scatter Plots of z-Score in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

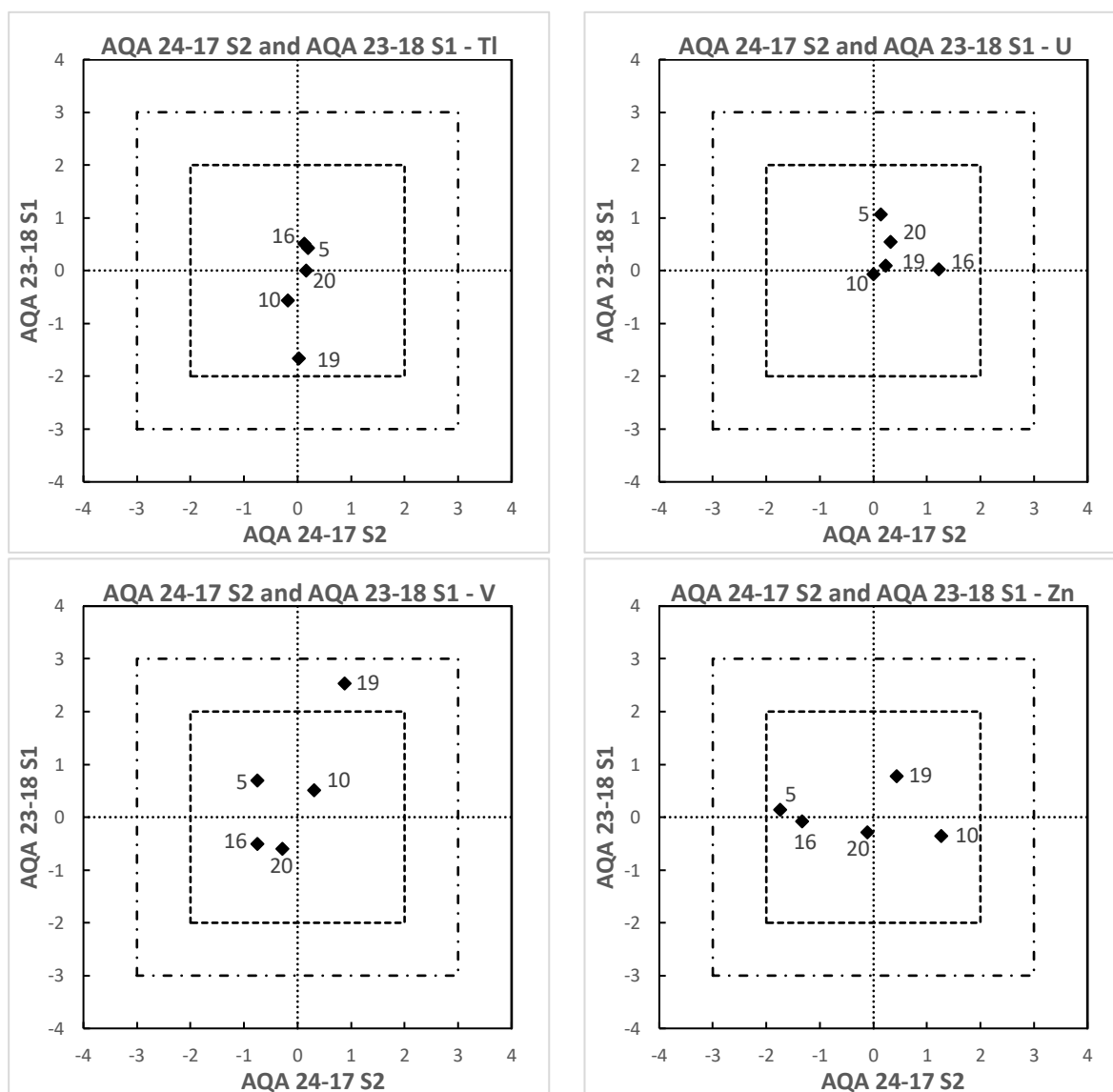


Figure 64 Scatter Plots of z-Score in S2 of AQA 24-17 and S1 of AQA 23-18 (continued)

6.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 24-17 is the 35th NMI proficiency study of metals in water. Participants' performance in the measurement of trace elements in water (river water, seawater, wastewater and potable water) over the last ten years is presented in Figure 65. Over this period, the average proportion of acceptable scores was 92% for z-scores and 84% for E_n -scores.

This is the first study when the results reported for P in sea water at a level close to 100 µg/L have been in good agreement with each other and the spike value.

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

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

6.8 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 47).

Table 47 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	SS
2	SS
3	CRM - RM010644L5
4	CRM
5	CRM - NASS 7, CASS 6 and NMI MX014 (Seawater) CWW-TM-B and CWW-TM-C (River water)
7	SS
8	CRM - High Purity Standards- Multi Components Standards
9	SS
10	SS
11	CRM
12	CRM - CWW-TMA, CWW-TMC
13	CRM – CRM-TMDW
15	CRM - Trace Metals in Drinking Water Standard - 29 Components CPA Chem; QCS-01-05 ICP Quality Control Standard #1; High Purity Standards CCV-1 Solution A; High Purity Standards CCV-1 Solution B; NMI AGAL-12 Biosoil; Australian Chemical Reagents Multi Element Standard; Australian Chemical Reagents Mixed Anion Standard; ERA Mercury WasteWatR
16	SS
17	CRM
19	CRM - CRM TMDW LOT 2401112
20	CRM
21	RM
22	SS
23	SS
24	CRM

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

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

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

A certified reference material for trace elements in sea water (MX014) is available from NMI. (<https://www.industry.gov.au/national-measurement-institute/nmi-services/chemical-and-biological-measurement-services/chemical-reference-materials/matrix-reference-materials>)

Acceptable z-Scores and En-Scores

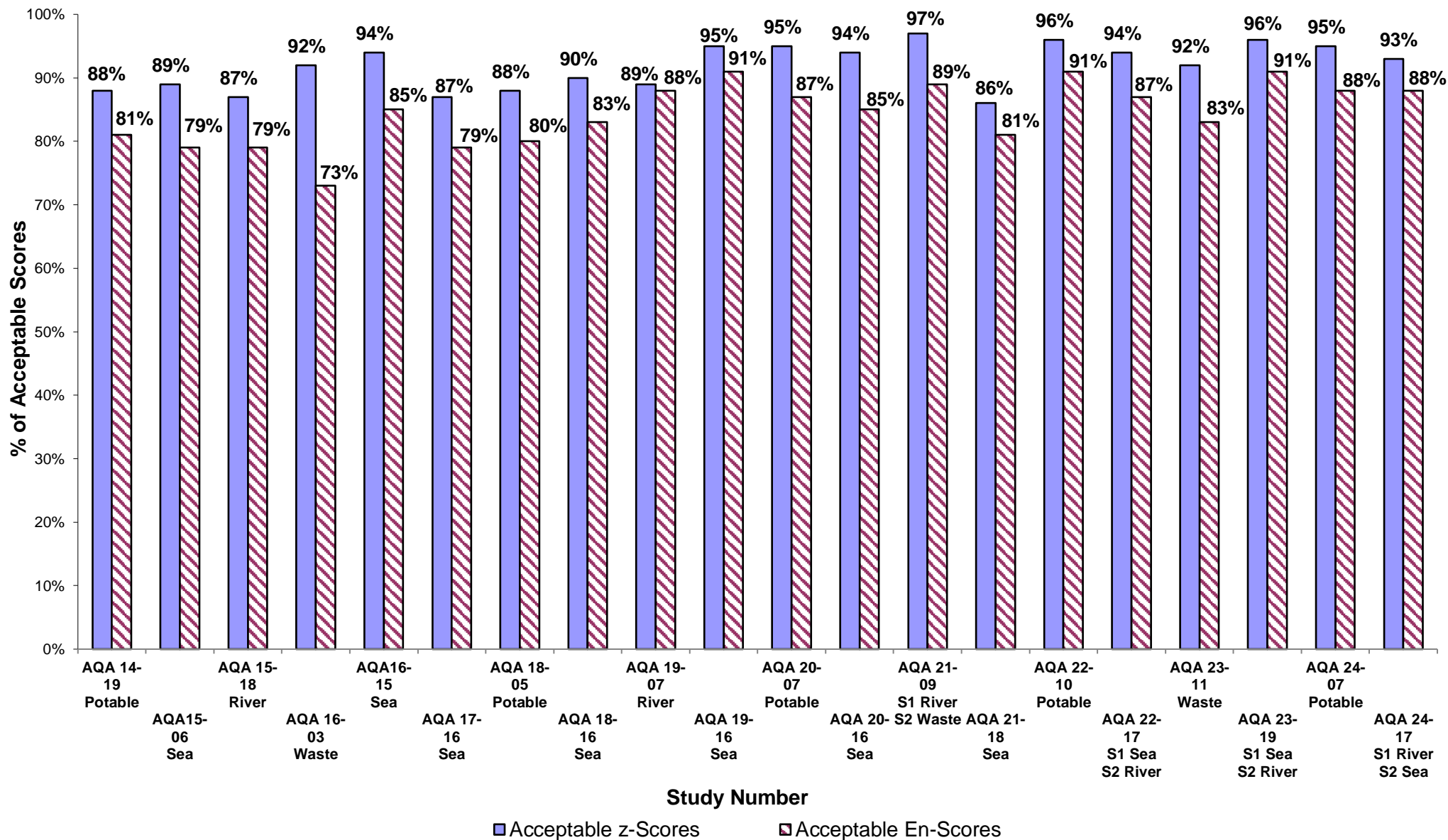


Figure 65 Participants' Performance in Metals in Water PT Studies over Last Ten Years

7 REFERENCES

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

- [1] ISO17043, Conformity assessment – *General requirements for proficiency testing*.
- [2] NMI, *Study Protocol for Proficiency Testing*, viewed January 2025, <https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.
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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared from river water. Approximately 6 L of river water was filtered, stabilised by adding acid and further fortified for 18 elements.

Sample S2 was a filtered and acidified sea water sample previously distributed as S1 of AQA 23-18. The procedures for preparation and analysis of this material were provided in the report of AQA 23-18.⁶

Sample Analysis and Homogeneity Testing

A partial homogeneity test was conducted for all tests except for Al in S1 as homogeneity had already been proven for S2 in AQA 23-18.⁶

Three bottles were analysed in duplicate, and the average of the results was reported as the homogeneity value.

Sample Analysis for Dissolved Elements

The analysis for partial homogeneity were conducted by CRV section of NMI as per method NT2.47.¹⁷ A test portion of 8 mL was diluted to 10 mL with 2% HNO₃.¹⁷ The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates, sample matrix spikes and control samples (MX014, AQA 20-16 S1, AQA 21-18 S1, AQA 22-17 S1, and AQA 22-17 S2) was carried through the same set of procedures and analysed simultaneously with the samples. A summary of the ion/wavelength and instrument conditions used for each analyte is presented in Table 48 for S1.

Table 48 Instrumental Techniques used for Dissolved Elements in S1

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	Final Dilution Factor	Ion / Wavelength
Ag	ICP-MS	Rh	ORS	He	1.25	107 m/z
As	ICP-MS	Rh	ORS	He	1.25	75 m/z
Be	ICP-MS	Rh	ORS	He	1.25	9 m/z
Cd	ICP-MS	Rh	ORS	He	1.25	111 m/z
Co	ICP-MS	Rh	ORS	He	1.25	59 m/z
Cr	ICP-MS	Rh	ORS	He	1.25	52 m/z
Cu	ICP-MS	Rh	ORS	He	1.25	63 m/z
Fe	ICP-MS	Rh	ORS	He	1.25	56 m/z
Hg	ICP-MS	Ir	ORS	He	1.25	202 m/z
Mn	ICP-MS	Rh	ORS	He	1.25	55 m/z
Mo	ICP-MS	Rh	ORS	He	1.25	95 m/z
Ni	ICP-MS	Rh	ORS	He	1.25	60 m/z
Pb	ICP-MS	Ir	ORS	He	1.25	206 m/z
Sb	ICP-MS	Rh	ORS	He	1.25	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	1.25	78 m/z
Tl	ICP-MS	Rh	ORS	He	1.25	205 m/z
U	ICP-MS	Ir	ORS	He	1.25	238 m/z
V	ICP-MS	Rh	ORS	He	1.25	51 m/z
Zn	ICP-MS	Rh	ORS	He	1.25	64 m/z

APPENDIX 2 – REFERENCE VALUE

The reference value and associated measurement uncertainty estimate for AQA 24-17 sample S2 are presented in Table 49.

The reference value for P in S2 comes from the analysis of 7 bottles with 3 subsamples taken from each bottle. Measurement uncertainty is given as a 95% level of confidence. The density measurement is valid for 15°C to 25°C and atmospheric pressure.

Table 49 Reference Value and the Associated Expanded Uncertainty for P in S2

Sample	Analyte	Reference Value (ug/L)	Expanded Uncertainty (95%) (ug/L)	Relative Expanded Uncertainty	Coverage Factor (95%)
AQA 24-17 S2	P	119.9	3.0	2.5%	2.01

Description of Method of Analysis

Phosphorus was quantified by standard addition ICP-MS. A KRISS primary calibration materials was used, see Table 50 for details, and this was diluted gravimetrically to working concentrations.

Table 50: Details of KRISS Reference Standard Material

Analyte	Standard Name	Serial No.
P	1205-02-022	160512-115

Standard addition for each sample analysis used approximately 20 g of the sample, this sample was weighed and then spiked with a mixed internal standard solution containing Mg, Sc, Co, As and Y. These solutions were then thoroughly mixed before being gravimetrically separated into a 'spiked' and an 'unspiked' solutions with gravimetric additions of standards to the 'spiked' solutions. These solutions were then thoroughly mixed before instrumental analysis. A further 1/10 dilution using UHP water was performed for all solutions analysed on the ICP-SF-MS.

Reference values were calculated from isotope ratios measured by ICP-SF-MS using medium resolution. Confirmation analysis was performed using a ICP-MS-MS with oxygen mass shift.

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

Homogeneity Assessment

Homogeneity was assessed on the data set used for the provision of the reference value. This data set was assessed using ANOVA for both between batch variation and inhomogeneity. To avoid double counting of uncertainty components the homogeneity uncertainty and associated method precision was included in the overall measurement uncertainty. This choice was made such that if either factor was significant the uncertainty contribution from that factor would be used while if neither or both were significant the most conservative estimates were used.

Reference Value Measurement Uncertainty

The measurement uncertainty associated with the reference value takes into account all factors that can reasonably be expected to affect the measurement result. Briefly, these include the primary calibration material, gravimetric sample preparation, homogeneity, density, method

trueness and method precision. Measurement uncertainty is reported as a 95% level of confidence.

Statement of Traceability

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

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

The assigned value was calculated as the robust average using the procedure described in ‘ISO13528, Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C’.⁷ The uncertainty was estimated as:

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

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 51.

Table 51 Uncertainty of Assigned Value for Hg in Sample S2

No. results (p)	19
Robust Average	7.31 µg/L
$S_{rob\ av}$	0.60 µg/L
$u_{rob\ av}$	0.17 µg/L
k	2
$U_{rob\ av}$	0.35 µg/L

The assigned value for **Hg** in Sample S2 is **7.31 ± 0.35 µg/L**.

z-Score and E_N-score

For each participant’s result a z-score and E_N-score are calculated according to Equation 2 and Equation 3 respectively (see page 10).

A worked example is set out below in Table 52.

Table 52 z-Score and E_N-score for Hg result reported by Laboratory **12** in S1

Hg Result µg/L	Assigned Value µg/L	Set Target Standard Deviation	z-Score	E _N -Score
7.3 ± 4.3	7.31 ± 0.35	15% as CV or 0.15 x 7.3 = = 1.095 µg/L	$z = \frac{(7.31 - 7.3)}{1.095}$ z = 0.01	$En = \frac{(7.31 - 7.3)}{\sqrt{4.3^2 + 0.35^2}}$ E _N = 0.00

APPENDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.^{11, 13} Between 2011 and 2024, NMI carried out 46 proficiency tests for metals in water. These involved analyses of dissolved or total elements at low and high levels in potable, fresh (river), sea, ground and waste water. Laboratory X participated and submitted acceptable results for Ni in all of these PTs. This data can be separated into two ranges of results: 0.0005 to 0.01 mg/L and 0.01 to 0.10 mg/L. Results are presented in Tables 53 and 54.

Table 53 Laboratory X Reported Results for Ni at 0.0005 to 0.01 mg/L Level

Study No.	Sample	Laboratory result* mg/L	Assigned value mg/L	Number of Results	Robust CV of all results (%)
AQA 11-07	Fresh	0.0015 ± 0.0003	0.00100 ± 0.00001	15	24
	Fresh	0.0039 ± 0.00078	0.00306 ± 0.00016	19	18
	Fresh	0.0039 ± 0.00078	0.00306 ± 0.00016	19	9.6
AQA 12-20	Saline	0.0039 ± 0.0008	0.00370 ± 0.00028	19	13
AQA 13-09	Fresh	0.0044 ± 0.0009	0.00409 ± 0.00017	15	7.9
AQA 13-22	Saline	0.00170 ± 0.00034	0.00165 ± 0.00014	14	13
	Saline	0.00384 ± 0.00077	0.00378 ± 0.00012	14	13
AQA 15-06	Sea	0.00180 ± 0.0004	0.00177 ± 0.00021	12	28
	Sea	0.00172 ± 0.0004	0.00177 ± 0.00021	11	28
AQA 15-18	Surface	0.002 ± 0.0003	0.00196 ± 0.00013	10	7.8
AQA 16-03	Waste	0.0041 ± 0.0008	0.00398 ± 0.00031	9	8.6
AQA 16-15	Sea	0.0070 ± 0.0010	0.00652 ± 0.00038	16	9.4
AQA 17-16	Sea	0.0015 ± 0.0003	0.00143 ± 0.00029	10	22
AQA 18-16	Sea	0.0022 ± 0.0005	0.00206 ± 0.00015	14	11
AQA 19-07	Fresh	0.0018 ± 0.0004	0.00187 ± 0.00009	10	5.3
AQA 19-16	Sea	0.0021 ± 0.0004	0.00168 ± 0.00037	8	25
AQA 20-16	Sea	0.0013 ± 0.0003	0.00178 ± 0.00034	10	24
AQA 21-09	River	0.0007 ± 0.0002	0.000756 ± 0.000059	8	8.9
AQA 21-18	Saline	0.0029 ± 0.0006	0.00298 ± 0.00031	6	13
AQA 22-10	Potable	0.007 ± 0.0011	0.00845 ± 0.00036	13	6.1
AQA 22-17	Sea	0.0028 ± 0.00056	0.00286 ± 0.00027	15	12
AQA 22-17	River	0.0035 ± 0.00027	0.00364 ± 0.00026	13	10
AQA 23-11	Waste	0.0085 ± 0.0009	0.00825 ± 0.00052	13	9.2
AQA 23-18	Sea	0.00236 ± 0.0003	0.00253 ± 0.00042	9	20
	River	0.00565 ± 0.0007	0.00580 ± 0.00024	10	5.2
AQA 24-07	Potable	0.0073 ± 0.0009	0.00772 ± 0.00020	14	3.8
AQA 24-17	River	0.00266 ± 0.0004	0.00238 ± 0.00016	18	12
	Sea	0.00232 ± 0.0003	0.00247 ± 0.00033	16	21
Average					14%**
$pooled\ s\% = \sqrt{\frac{(15-1) \times 24^2 + (19-1) \times 18^2 + \dots + (16-1) \times 21^2}{360-28}}$					15%

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

Table 54 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	Number of Results	Robust CV of all results (%)
AQA 11-17	Waste	0.10 ± 0.009	0.099 ± 0.001	15	2
	Waste	0.10 ± 0.009	0.098 ± 0.001	15	2
AQA 12-09	Potable	0.047 ± 0.007	0.045 ± 0.002	19	6.7
	Potable	0.055 ± 0.008	0.053 ± 0.002	19	7.4
AQA 12-20	Saline	0.0415 ± 0.0083	0.0384 ± 0.0021	22	11
AQA 13-09	Fresh	0.0393 ± 0.0040	0.0361 ± 0.0010	16	4.8
	Fresh	0.0258 ± 0.0030	0.0272 ± 0.0025	15	15
AQA 14-08	Ground	0.019 ± 0.004	0.0191 ± 0.0007	13	7.9
AQA 14-19	Potable	0.019 ± 0.004	0.0183 ± 0.0013	14	11
AQA 15-18	Surface	0.036 ± 0.0035	0.0336 ± 0.0013	13	5.1
AQA 16-03	Waste	0.042 ± 0.0045	0.0352 ± 0.0050	11	19
AQA 16-15	Sea	0.0456 ± 0.0060	0.0409 ± 0.0029	17	12
AQA 17-16	Sea	0.0116 ± 0.0012	0.0101 ± 0.0023	9	27
AQA 18-05	Potable	0.017 ± 0.002	0.0172 ± 0.0010	16	8.7
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	11	4.3
AQA 20-07	Potable	0.010 ± 0.002	0.0106 ± 0.0004	16	6
AQA 21-09	Waste	0.014 ± 0.0021	0.0143 ± 0.0006	21	8.1
Average					9.6**
$pooled\ s\% = \sqrt{\frac{(15-1) \times 2^2 + (15-1) \times 2^2 + \dots + (21-1) \times 8.1^2}{277-18}}$					11%

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

The pooled standard deviation of the robust CV over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 15% and 11% respectively. Using a coverage factor of two gives relative expanded uncertainties of 31% and 21% respectively, at a level of confidence of approximately 95%.

Table 55 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the ranges 0.0005 – 0.01 mg/L and 0.01 – 0.10 mg/L.

Table 55 Uncertainty of Ni results estimated using PT data

Results mg/L	Uncertainty mg/L
0.00050	0.00016
0.00100	0.00031
0.0100	0.0031
0.100	0.021
0.150	0.032

The estimates of 31% and 21% relative passes the test of being reasonable, and the analysis of the 46 different PT samples over 14 years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrators etc.), and so complies with ISO 17025.⁹

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
CV _{rob}	Robust Coefficient of Variation
CVAAS	Cold Vapour Atomic Absorption Spectrometry
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
DRC	Dynamic Reaction Cell
EPA	Environmental Protection Agency
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	Inductively Coupled Plasma – Optical Emission Spectrometry
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry – Axial View
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
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
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PT	Proficiency Test
R.V.	Reference Value
RM	Reference Material
SA-ICP-MS	Standard Addition – Inductively Coupled Plasma – Mass Spectrometry
SD _{rob}	Robust Standard Deviation
SI	The International System of Units
SS	Spiked sample
S.V.	Spiked or formulated concentration of a PT sample
s _a /σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation (symbol: σ)
UC	Universal Cell
VGA-ICP-OES	Vapour Generation Accessory – Inductively Coupled Plasma – Optical Emission Spectrometry

APPENDIX 6 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 56 Instrument Conditions Ag

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	NA	1	107
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	107
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 107
4	ICP-MS						
5	ICP-MS	Ir	NA	standard mode	1	1	109
6						NA	
7	ICP-MS	Indium	ORS	He	1	10	m/z 107
8	ICP-MS	Y	KED		10	NA	107
9	ICP-MS	103Rh	ORS	He	1.05	1.05	107
10	ICP-MS	Rh	KED	He	1	20	109
11	ICP-MS	Rh		He	NA		107
12	ICP-MS/MS	In	NA	standard mode	1	10	107
13	ICP-MS	Rh	CRI	He		NA	109
14	ICP-MS/MS	Rh	CRI	He	1	5	107
15	ICP-MS	Rh	ORS	He	NA	1	107 (m/z)
16	ICP-MS	103	ORS	He	1	1	107
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	107
22	ICP-MS	Indium	ORS	He	1	10	m/z 107

Table 57 Instrument Conditions Al

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	He	NA	1	27
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	27
3	ICP-MS	45 Sc	ORS	He	NA	1	m/z 27
4	ICP-OES-AV						
5	ICP-MS	Sc	UC	He	1	1	27
6						NA	
7	ICP-MS	Scandium	ORS	No Gas	1	10	m/z 27
8	ICP-MS	Li6	KED	O2	10	NA	27
9	ICP-MS	Li6	ORS	He	1.05	1.05	27
10	ICP-MS	Sc	KED	He	1	20	27
11	ICP-MS	Sc		He	NA		27
12	ICP-MS/MS	Sc	CRI	He	1	10	27
13	ICP-MS	Rh	CRI	He		NA	27
14	ICP-MS/MS	Ge	CRI	He	1	5	27
15	ICP-MS	Sc	ORS	He	NA	1	27 (m/z)
16	ICP-MS	45	ORS	He	1	1	27
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-OES-AV	Y	NA	NA	2	2	167.019
22	ICP-MS	Scandium	ORS	No Gas	1	10	m/z 27

Table 58 Instrument Conditions As

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	NA	1	75
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	75
3	ICP-MS	89 Y	ORS	He	NA	1	m/z 75
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	75
6						NA	
7	ICP-MS	Germanium	ORS	He	1	10	m/z 75
8	ICP-MS	Y	KED	O2	10	NA	75
9	ICP-MS	72Ge	ORS	He	1.05	1.05	75
10	ICP-MS	Te	KED	He	1	20	75
11	ICP-MS	Rh		He	NA		75
12	ICP-MS/MS	Ga	CRI	He	1	10	75
13	ICP-MS	Rh	CRI	He		NA	75
14	ICP-MS/MS	Ge	DRC	O2	1	5	75-91
15	ICP-MS	Rh	ORS	He	NA	1	75 (m/z)
16	ICP-MS	72	ORS	He	1	1	75
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	75
22	ICP-MS	Germanium	ORS	He	1	10	m/z 75

Table 59 Instrument Conditions Be

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	NA	NA	1	9
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	9
3	ICP-MS	45 Sc	ORS	No gas	NA	1	m/z 9
4	ICP-MS						
5	ICP-MS	Sc	NA	standard mode	1	1	9
6						NA	
7	ICP-MS	Lithium	ORS	He	1	10	m/z 9
8	ICP-MS	Li6	KED		10	NA	9
9	ICP-MS	Li6	ORS	He	1.05	1.05	9
10	ICP-MS	Sc	KED	He	1	NA	9
11	ICP-MS	Sc			NA		9
12	ICP-MS/MS	Sc	CRI	He	1	10	9
13	ICP-MS	Rh	CRI	He		NA	9
14	ICP-MS/MS	Ge	CRI	He	1	5	9
15	ICP-MS	Sc	NA	standard mode	NA	1	9 (m/z)
17	ICP-MS						
19	ICP-MS	Sc	CRI	Standard Mode	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	9
22	ICP-MS	Lithium	ORS	He	1	10	m/z 9

Table 60 Instrument Conditions Cd

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	NA	1	111
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	111
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 111
4	ICP-MS						
5	ICP-MS	Ir	NA	standard mode	1	1	111
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 111
8	ICP-MS	In	KED		10	NA	111
9	ICP-MS	193Ir	ORS	He	1.05	1.05	114
10	ICP-MS	Rh	KED	He	1	20	111
11	ICP-MS	Rh		He	NA		111
12	ICP-MS/MS	In	CRI	He	1	10	111
13	ICP-MS	Rh	CRI	He		NA	114
14	ICP-MS/MS	Rh	CRI	He	1	5	111
15	ICP-MS	Rh	ORS	He	NA	1	111 (m/z)
16	ICP-MS	103	ORS	He	1	1	114
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	111
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 111

Table 61 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	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	NA	59
3	NA	NA	NA	NA	NA	NA	NA
4	ICP-MS					NA	
5	ICP-MS	Sc	UC	He	1	NA	59
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	NA	m/z 59
8	NA	NA	NA	NA	NA	NA	NA
9	ICP-MS	72Ge	ORS	He	1.05	NA	59
10	ICP-MS	Ga	KED	He	1	NA	59
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS/MS	Ga	CRI	He	1	NA	59
13	ICP-MS	Rh	CRI	He		NA	59
14	ICP-MS/MS	Ge	CRI	He	1	NA	59
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	115	ORS	He	1	1	59
17	ICP-MS					NA	
19	ICP-MS	Rh	CRI	He	1	NA	
20	ICP-MS	Rh	ORS	He	1.25	10	59
21						NA	
22	ICP-MS	Rhodium	ORS	He	1	NA	m/z 59

Table 62 Instrument Conditions Cr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	He	NA	1	52
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	52
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 52
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	52
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 52
8	ICP-MS	Sc	KED		10	NA	52
9	ICP-MS	72Ge	ORS	He	1.05	1.05	52
10	ICP-MS	Sc/Ga	KED/DRC	He/NH3	1	20	52
11	ICP-MS	Sc		He	NA		52
12	ICP-MS/MS	Ga	CRI	He	1	10	52
13	ICP-MS	Rh	CRI	He		NA	52
14	ICP-MS/MS	Ge	CRI	He	1	5	52
15	ICP-MS	Sc	ORS	He	NA	1	52 (m/z)
16	ICP-MS	72	ORS	He	1	1	52
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	52
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 52

Table 63 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	Sc	CRI	He	NA	1	63
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	63
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 63
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	65
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 63
8	ICP-MS	Sc	KED		10	NA	63
9	ICP-MS	72Ge	ORS	He	1.05	1.05	63
10	ICP-MS	Ga	KED	He	1	20	63
11	ICP-MS	Sc		He	NA		63
12	ICP-MS/MS	Ga	CRI	He	1	10	63
13	ICP-MS	Rh	CRI	He		NA	63
14	ICP-MS/MS	Ge	CRI	He	1	5	63
15	ICP-MS	Sc	ORS	He	NA	1	63 (m/z)
16	ICP-MS	103	ORS	He	1	1	65
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	63
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 63

Table 64 Instrument Conditions Fe

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	He	NA	1	56
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	56
3	ICP-MS	45 Sc	ORS	He	NA	1	m/z 56
4	ICP-OES-AV						
5	ICP-MS	Sc	UC	He	1	1	56
6						NA	
7	ICP-MS	Rhodium	ORS	H2	1	10	m/z 56
8	ICP-MS	Sc	KED		10	NA	56
9	ICP-MS	72Ge	ORS	He	1.05	1.05	56
10	ICP-MS	Sc/Ga	KED/DRC	He/NH3	1	20	56/54
11	ICP-MS	Sc		He	NA		56
12	ICP-OES-AV-buffer	Y	NA		1	1	259.939
13	ICP-MS	Rh	CRI	He		NA	57
14	ICP-MS/MS	Ge	CRI	He	1	5	56
15	ICP-MS	Sc	ORS	He	NA	1	56 (m/z)
16	ICP-MS	72	ORS	He	1	1	56
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-OES-AV	Y	NA	NA	2	2	238.204
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 56

Table 65 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	ICP-MS	Lu	CRI	He	NA	1	202
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	201
3	ICP-MS	175 Lu	ORS	He	NA	5	m/z 201
4	CVAAS						
5	ICP-MS	Ir	NA	standard mode	1	1	201
6						NA	
7	CVAAS	NA	ORS	NA	1	10	253.7nm
8	CVAAS	SnCl2	KED			NA	
9	CVAFS				2	2	253.7
10	CVAFS	NA	DRC	NA	5	5	253.7
11	ICP-MS	Lu		He	NA		202
12	CVAAS		NA		2	2	253.7
13	NA	NA	NA	NA		NA	NA
14	ICP-MS/MS	Ir	CRI	He	1	5	202
15	ICP-MS	Lu	ORS	He	NA	1	202 (m/z)
16	VGA-ICP-OES				1	1	194.164
17	CVAFS						
19	ICP-MS	Ir	CRI	He	1	1	
20	CVAAS	NA	NA	NA	2	2	253.7
22	CVAAS	NA	ORS	NA	1	10	253.7nm

Table 66 Instrument Conditions Mn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	He	NA	1	55
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	55
3	ICP-MS	103 Rh	ORS	He	NA	10	m/z 55
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	55
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 55
8	ICP-MS	Sc	KED		10	NA	55
9	ICP-MS	72Ge	ORS	He	1.05	1.05	55
10	ICP-MS	Sc	KED	He	1	20	55
11	ICP-MS	Sc		He	NA		55
12	ICP-MS/MS	Ga	CRI	He	1	10	55
13	ICP-MS	Rh	CRI	He		NA	55
14	ICP-MS/MS	Ge	CRI	He	1	5	55
15	ICP-MS	Sc	ORS	He	NA	1	55 (m/z)
16	ICP-MS	72	ORS	He	1	1	55
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-OES-AV	Y	NA	NA	2	2	257.61
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 55

Table 67 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	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	NA	95
3	NA	NA	NA	NA	NA	NA	NA
4	ICP-MS					NA	
5	ICP-MS	Ir	NA	standard mode	1	NA	95
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	NA	m/z 95
8	NA	NA	NA	NA	NA	NA	NA
9	ICP-MS	103Rh	ORS	He	1.05	NA	95
10	ICP-MS	Rh	KED	He	1	NA	98
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS/MS	In	NA	standard mode	1	NA	95
13	ICP-MS	Rh	CRI	He		NA	98
14	ICP-MS/MS	Ge	CRI	He	1	NA	95
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-MS	72	ORS	He	1	1	98
17	ICP-MS					NA	
19	ICP-MS	Rh	CRI	He	1	NA	
20	ICP-MS	Rh	ORS	He	1.25	10	95
21						NA	
22	ICP-MS	Rhodium	ORS	He	1	NA	m/z 95

Table 68 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	Sc	CRI	He	NA	1	60
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	60
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 60
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	60
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 60
8	ICP-MS	Sc	KED		10	NA	60
9	ICP-MS	72Ge	ORS	He	1.05	1.05	60
10	ICP-MS	Ga	KED	He	1	20	60
11	ICP-MS	Sc		He	NA		60
12	ICP-MS/MS	Ga	CRI	He	1	10	60
13	ICP-MS	Rh	CRI	He		NA	60
14	ICP-MS/MS	Ge	CRI	He	1	5	60
15	ICP-MS	Sc	ORS	He	NA	1	60 (m/z)
16	ICP-MS	103	ORS	He	1	1	60
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	60
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 60

Table 69 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-MS	Sc	CRI	He	NA	1	31
2	ICP-OES	Cs,Y	NA	NA	NA	10	213.618
3	ICP-MS	72 Ge	ORS	He	NA	10	m/z 31
4	ICP-OES-AV				NA		
5					NA		
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	Lutetium	NA	NA	NA	10	213.618nm
8	ICP-OES-AV	Yb	KED		50	NA	213nm
9	ICP-MS	Li6	ORS	He	NA	1.05	31
10	N/A	NA	NA	NA	NA	NA	NA
11	NT				NA		
12	ICP-OES-AV-buffer	Y	NA		NA	1	178.221
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ge	DRC	O2	NA	5	31-47
15	ICP-MS	Sc	ORS	He	NA	1	31 (m/z)
17					NA		
19	NA				NA		
20	ICP-OES-AV	Y	NA	NA	2	2	213.618
21					NA		
22	ICP-OES-AV	Lutetium	NA	NA	NA	10	213.618nm

Table 70 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	Lu	CRI	He	NA	1	208
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	208
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 208
4	ICP-MS						
5	ICP-MS	Ir	NA	standard mode	1	1	206+207+208
6						NA	
7	ICP-MS	Lutetium	ORS	No Gas	1	10	m/z 208
8	ICP-MS	Ir	KED		10	NA	206
9	ICP-MS	193Ir	ORS	He	1.05	1.05	208
10	ICP-MS	Tb	KED	He	1	20	206+207+208
11	ICP-MS	Lu		He	NA		208
12	ICP-MS/MS	Ir	NA	standard mode	1	10	207
13	ICP-MS	Rh	CRI	He		NA	208
14	ICP-MS/MS	Ir	CRI	He	1	5	207+208+209
15	ICP-MS	Lu	ORS	He	NA	1	208 (m/z)
16	ICP-MS	193	ORS	He	1	1	208
17	ICP-MS						
19	ICP-MS	Ir	CRI	He	1	1	
20	ICP-MS	Ir	ORS	He	1.25	10	208
22	ICP-MS	Lutetium	ORS	No Gas	1	10	m/z 208

Table 71 Instrument Conditions Sb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	NA	1	123
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	121
3	ICP-MS	89 Y	ORS	He	NA	1	m/z 121
4	ICP-MS						
5	ICP-MS	Ir	NA	standard mode	1	1	121
6						NA	
7	ICP-MS	Indium	ORS	No Gas	1	10	m/z 121
8	ICP-MS	In	KED		10	NA	121
9	ICP-MS	115In	ORS	He	1.05	1.05	121
10	ICP-MS	Rh	KED	He	1	20	121
11	ICP-MS	Rh		He	NA		121
12	ICP-MS/MS	In	NA	standard mode	1	10	121
13	ICP-MS	Rh	CRI	He		NA	121
14	ICP-MS/MS	Rh	CRI	He	1	5	121
15	ICP-MS	Rh	ORS	He	NA	1	123 (m/z)
16	ICP-MS	72	ORS	He	1	1	121
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	121
22	ICP-MS	Indium	ORS	No Gas	1	10	m/z 121

Table 72 Instrument Conditions Se

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	H2	NA	1	78
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	78
3	ICP-MS	45 Sc	ORS	H2	NA	10	m/z 78
4	ICP-MS						
5	ICP-MS	Rh	DRC	NH3	1	1	82
6						NA	
7	ICP-MS	Germanium	ORS	H2	1	10	m/z 78
8	ICP-MS	Y	KED		10	NA	78
9	ICP-MS	72Ge	ORS	H2	1.05	1.05	78
10	ICP-MS	Te	KED/DRC	He/NH3	1	20	82
11	ICP-MS	Rh		H2	NA		78
12	ICP-MS/MS	Ga	CRI	He	1	10	78
13	ICP-MS	Rh	CRI	He		NA	80
14	ICP-MS/MS	Ge	DRC	O2	1	5	80-96
15	ICP-MS	Rh	ORS	H2	NA	1	78 (m/z)
16	ICP-MS	72	ORS	He	1	1	78
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	HEHe	1.25	10	78
22	ICP-MS	Germanium	ORS	HEHe	1	10	m/z 78

Table 73 Instrument Conditions Sn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	NA	1	118
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	NA	10	118
3	ICP-MS	175 Lu	ORS	He	NA	1	m/z 118
4	ICP-MS				NA		
5					NA		
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-MS	Indium	ORS	He	NA	10	m/z 118
8	ICP-MS	In	KED		10	NA	118
9	ICP-MS	115In	ORS	He	NA	1.05	118
10	ICP-MS	Rh	KED	He	NA	20	120
11	ICP-MS	Rh		He	NA		118
12	ICP-MS/MS	In	NA	standard mode	NA	10	118
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS/MS	Ge	CRI	He	NA	5	118
15	ICP-MS	Rh	ORS	He	NA	1	118 (m/z)
16	ICP-MS	45	ORS	He	1	1	118
17	ICP-MS				NA		
19	NA				NA		
20	ICP-MS	Rh	ORS	He	1.25	10	118
21					NA		
22	ICP-MS	Indium	ORS	He	NA	10	m/z 118

Table 74 Instrument Conditions TI

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Lu	CRI	He	NA	1	205
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	205
3	ICP-MS	175 Lu	ORS	He	NA	10	m/z 205
4	ICP-MS						
5	ICP-MS	Ir	NA	standard mode	1	1	205
6						NA	
7	ICP-MS	Lutetium	ORS	No Gas	1	10	m/z 205
8	ICP-MS	Ir	KED		10	NA	205
9	ICP-MS	193Ir	ORS	He	1.05	1.05	205
10	ICP-MS	Tb	KED	He	1	20	205
11	ICP-MS	Lu		He	NA		205
12	ICP-MS/MS	Ir	NA	standard mode	1	10	203
13	ICP-MS	Rh	CRI	He		NA	205
14	ICP-MS/MS	Rh	CRI	He	1	5	205
15	ICP-MS	Lu	ORS	He	NA	1	205 (m/z)
16	ICP-MS	193	ORS	He	1	1	205
19	ICP-MS	Ir	CRI	He	1	1	
20	ICP-MS	Ir	ORS	He	1.25	10	205
22	ICP-MS	Lutetium	ORS	No Gas	1	10	m/z 205

Table 75 Instrument Conditions U

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Lu	CRI	He	NA	1	238
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	238
3	ICP-MS	175 Lu	ORS	He	NA	1	m/z 238
4	ICP-MS						
5	ICP-MS	Ir	NA	standard mode	1	1	238
6						NA	
7	ICP-MS	Lutetium	ORS	No Gas	1	10	m/z 238
8	ICP-MS	Ir	KED	O2	10	NA	238
9	ICP-MS	193Ir	ORS	He	1.05	1.05	238
10	ICP-MS	Tb	KED	He	1	20	238
11	ICP-MS	Lu		He	NA		238
12	ICP-MS/MS	Ir	NA	standard mode	1	10	238
13	ICP-MS	Rh	CRI	He		NA	238
14	ICP-MS/MS	Ir	CRI	He	1	5	238
15	ICP-MS	Lu	ORS	He	NA	1	238 (m/z)
16	ICP-MS	103	ORS	He	1	1	238
17	ICP-MS						
19	ICP-MS	Ir	CRI	He	1	1	
20	ICP-MS	Ir	ORS	He	1.25	10	238
22	ICP-MS	Lutetium	ORS	No Gas	1	10	m/z 238

Table 76 Instrument Conditions V

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	He	NA	1	51
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	51
3	ICP-MS	45 Sc	ORS	He	NA	5	m/z 51
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	51
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 51
8	ICP-MS	Sc	KED	O2	10	NA	51
9	ICP-MS	72Ge	ORS	He	1.05	1.05	51
10	ICP-MS	Sc/Ga	KED/DRC	He/NH3	1	20	51
11	ICP-MS	Sc		He	NA		51
12	ICP-MS/MS	Ga	CRI	He	1	10	51
13	ICP-MS	Rh	CRI	He		NA	50
14	ICP-MS/MS	Ge	CRI	He	1	5	51
15	ICP-MS	Sc	ORS	He	NA	1	51 (m/z)
16	ICP-MS	45	ORS	He	1	1	51
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	51
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 51

Table 77 Instrument Conditions Zn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc	CRI	He	NA	1	66
2	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	1	10	66
3	ICP-MS	89 Y	ORS	He	NA	10	m/z 66
4	ICP-MS						
5	ICP-MS	Sc	UC	He	1	1	66
6						NA	
7	ICP-MS	Rhodium	ORS	He	1	10	m/z 66
8	ICP-MS	Y	KED		10	NA	66
9	ICP-MS	72Ge	ORS	He	1.05	1.05	66
10	ICP-MS	Te	KED	He	1	20	66
11	ICP-MS	Sc		He	NA		66
12	ICP-MS/MS	Ga	CRI	He	1	10	66
13	ICP-MS	Rh	CRI	He		NA	62
14	ICP-MS/MS	Ge	CRI	He	1	5	66
15	ICP-MS	Sc	ORS	He	NA	1	66 (m/z)
16	ICP-MS	115	ORS	He	1	1	66
17	ICP-MS						
19	ICP-MS	Rh	CRI	He	1	1	
20	ICP-MS	Rh	ORS	He	1.25	10	64
22	ICP-MS	Rhodium	ORS	He	1	10	m/z 66

END OF REPORT