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**National  
Measurement  
Institute**

# **Proficiency Test Report AQA 18-16 Seawater Characteristics**

February 2019



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

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Luminita Antin

Andrew Evans

Jeffrey Merrick

Ian White

Ping Di

Wei Huang

Alexander Sadler

Paul Armishaw

Manager, Chemical Proficiency Testing

Phone: 61-2-9449 0149

[proficiency@measurement.gov.au](mailto:proficiency@measurement.gov.au)



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## 1 SUMMARY

This report presents the results of the proficiency test AQA 18-16, Seawater Characteristics. The study focused on the measurement of dissolved: Al, Ag, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Se, Sn, V and Zn and total: Al, Ag, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, V and Zn. Measurement of pH at 25°C, electrical conductivity at 25°C, alkalinity to pH 4.5 (as  $\text{CaCO}_3$ ) and of ammonia-N, chloride, dissolved organic carbon (as dNPOC), fluoride, filterable reactive phosphorus, sulfate, total hardness (as  $\text{CaCO}_3$ ), nitrate-N, total dissolved nitrogen, total dissolved phosphorus, total Kjeldahl nitrogen, total nitrogen and total organic carbon (as NPOC) were also included in the program.

Twenty-one laboratories registered to participate and twenty submitted results.

The assigned values were the robust average of participants' results, excepting P in S1 and S2. The associated uncertainties were estimated from the robust standard deviation of the participants' results. For P in S1 and S2, the assigned value was a reference value measured using standard addition mass spectrometry.

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

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

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

Of 734 results, 662 (90%) returned a satisfactory score of  $|z| \leq 2$ .

Of 734 results, 611 (83%) returned a satisfactory score of  $|E_n| \leq 1$ .

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

A limited number of participants had the capability to measure phosphorus at a 124.9  $\mu\text{g/L}$  level in seawater.

Arsenic, iron and selenium at low levels in seawater were the analytes which presented the most analytical difficulty to participating laboratories.

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

Despite differences in analytes' concentrations, on average participants' performance in time remained fairly consistent.

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

Of 734 numerical results, 721 (98%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 5.

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

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

## **2 INTRODUCTION**

### **2.1 NMI Proficiency Testing Program**

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

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

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

AQA 18-16 is the 23<sup>rd</sup> NMI proficiency study of metals in water.

### **2.2 Study Aims**

The aims of the study were to:

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

### **2.3 Study Conduct**

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

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

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

## **3 STUDY INFORMATION**

### **3.1 Selection of Matrices and Inorganic Analytes**

The 57 tests were selected from those for which an investigation level is published in Australian and New Zealand Guidelines for Fresh and Marine Water Quality<sup>5</sup> and are commonly measured by water testing laboratories.

### **3.2 Participation**

Twenty-one laboratories participated and twenty submitted results.

The timetable of the study was:

Invitation issued: 02 October 2018  
Samples dispatched: 29 October 2018  
Results due: 26 November 2018  
Interim report issued: 29 November 2018

### **3.3 Test Material Specification**

Four samples were provided for analysis:

**Sample S1** was 100 mL of filtered seawater preserved by adding 2% (v/w) nitric acid;  
**Sample S2** was 100 mL of unfiltered seawater preserved by adding 2% (v/w) nitric acid;  
**Sample S3** was 200 mL of filtered, frozen sea water; and  
**Sample S4** was 400 mL of unfiltered, frozen sea water.

### **3.4 Laboratory Code**

All participant laboratories were assigned a confidential code number.

### **3.5 Sample Preparation, Analysis and Homogeneity Testing**

Partial homogeneity testing was conducted for the study samples except for Co in S1 and K in S4. The same validated sample preparation procedure was followed as in previous studies where the test samples were demonstrated to be sufficiently homogeneous for evaluation of participants' performance.<sup>6, 7</sup>.

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

The preparation and analysis are described in Appendix 1.

### **3.6 Stability of Analytes**

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

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

### **3.7 Sample Storage, Dispatch and Receipt**

Samples S1 and S2 were refrigerated before dispatch while Samples S3 and S4 were frozen.

The samples were dispatched by courier on 29 October 2018.

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

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

### **3.8 Instructions to Participants**

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- If analyses cannot be commenced on the day of receipt, please store the samples labelled S3 and S4 frozen.
- Prior to testing, thaw samples S3 and S4 completely.

- Participants are asked to report results in units of  $\mu\text{g/L}$  for S1 and S2 and in units of  $\text{mg/L}$  for S3 and S4 except for pH and EC. Report EC results in  $\mu\text{S}/\text{cm}$  units.

SAMPLE S1 filtered, acidified sea water		SAMPLE S2 unfiltered, acidified sea water		SAMPLE S3 filtered, frozen sea water		SAMPLE S4 unfiltered, frozen sea water	
Test Dissolved	Approximate Conc. Range $\mu\text{g/L}$	Test Total	Approximate Conc. Range $\mu\text{g/L}$	Test	Approximate Conc. Range $\text{mg/L}$	Test	Approximate Conc. Range $\text{mg/L}$
Al	<50	Al	<100	Ammonia-N	<0.5	B (total)	<5
Ag	<10	Ag	<50	Chloride	<25000	Ca (total)	<500
As	<10	As	<50	Dissolved Organic Carbon (dNPOC)	<5	K (total)	<500
Be	<10	Ba	<50	Fluoride	<5	Mg (total)	<1000
Cd	<10	Cd	<50	Nitrate-N	<0.5	Total Kjeldahl Nitrogen	<5
Co	<10	Cr	<50	Orthophosphate-P (FRP)	<0.5	Total Nitrogen	<5
Cr	<10	Cu	<50	Total Dissolved Nitrogen (TDN)	<0.5	Total Organic Carbon (as NPOC)	<50
Cu	<10	Fe	<100	Total Dissolved Phosphorus	<0.5	Alkalinity to pH 4.5 as $\text{CaCO}_3$	<500
Fe	<50	Mn	<50	Sulfate	<5000	Total Hardness ( $\text{CaCO}_3$ )	<5000
Hg	<10	Mo	<50			pH (at 25°C)	>2.5
Mn	<10	Ni	<50			EC (at 25°C)	<50000
Ni	<10	P	<50				
P	<100	Pb	<500				
Pb	<10	Sb	<50				
Se	<10	Se	<50				
Sn	<10	Sn	<50				
V	<10	V	<50				
Zn	<50	Zn	<50				

- 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  $\pm 0.51 \mu\text{g/L}$ ).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.
- Return the completed results sheet by e-mail ([proficiency@measurement.gov.au](mailto:proficiency@measurement.gov.au)) by 26 November 2018. Late results cannot be included in the report.

### 3.9 Interim Report

An interim report was emailed to participants on 29 November 2018.

## 4 PARTICIPANT LABORATORY INFORMATION

### 4.1 Methodology for Total and Dissolved Elements

Summaries of test methods are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 7.

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Volume (mL)	Digestion Temp. (°C)	Digestion Time (min)	Vol. HNO <sub>3</sub> (mL)	Vol. HCl (mL)
3	In house	40	112.5	120	4	
4	3051A	20	170	15	1	1
6	USEPA 6020	9.5	105	120	0.5	
7	EPA 200.7 and 200.8	1	200	120	1.5	4.5
8	USEPA Method 200.2, Revision 2.8	30	105	120	2	
9	"In-house referenced to US EPA 200.8 In-house referenced to APHA 3120B"	30	105	120	3	0.6
10	200.8 and 6020B	40	90-95	60	1	1
11	USEPA METHOD 3010 / 6020B	40	90-95	60	1	1
12	In House W32a - referencing APHA 3125					
14	Reference to USEPA 6010 and 6020	10	95	90	2	3
15	USEPA 200.2	10	95±5	120	0.5	
16	USEPA METHOD 3010 / 6020B	40	90-95	60	1	1
18	"APHA 3030 E 22nd ed. 2012 (modified), APHA 3030 F 22nd ed. 2012 (modified), US EPA Method 245.7, Feb 2005	10	100	60	0.5	0.1 (Ag only)
20*	USEPA200.7-6					
21		40	100	480	2	

\* Additional Information in Table 2.

### 4.2 Additional Information

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

Table 2 Additional information

Lab. Code	Additional Information
20	Sample not digested before analysis

### 4.3 Methodology for S3 and S4

Measurement methods and instrumental techniques used for the tests in Samples S3 and S4 are presented in Appendix 8.

### 4.4 Basis of Participants' Measurement Uncertainty Estimates

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

**Table 3 Basis of Uncertainty Estimate**

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision <sup>a</sup>	Method Bias <sup>a</sup>	
1	Top Down - precision and estimates of the method and laboratory bias	Control Sample Duplicate Analysis	CRM Recoveries of SS	
2	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Sample-CRM Duplicate Analysis Instrumental calibration	CRM Recoveries of SS	Eurachem/CITAC Guide
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Sample-RM Duplicate Analysis Instrumental calibration	CRM Recoveries of SS Instrument calibration	NATA Technical Note 33
4	Top Down - precision and estimates of the method and laboratory bias	Control Sample-CRM Duplicate Analysis	CRM	NMI Uncertainty Course
5		Duplicate Analysis		
6	Top Down - precision and estimates of the method and laboratory bias			NATA Technical Note 33
7	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples-CRM	CRM	Eurolab Technical Report No1/2007
8	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrumental calibration	Recoveries of SS Instrument calibration	Nordtest Report TR537
9	Top Down - precision and estimates of the method and laboratory bias	Control Sample Duplicate analysis	CRM Recoveries of SS	NATA Technical Note 33
10		Control Sample-CRM	CRM Laboratory bias from PT studies Recoveries of SS Instrument calibration	ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Technique
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples-SS Duplicate analysis	CRM Recoveries of SS Instrument calibration	NATA Technical Note 33 ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Technique
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analysis	CRM Instrument calibration	Nordtest Report TR537
13	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis	CRM	Nordtest Report TR537
14	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis Instrumental calibration	Recoveries of SS Instrument calibration	Eurachem/CITAC Guide
15	Top Down - precision and estimates of the method and laboratory bias	Control Sample-RM Duplicate Analysis Instrumental calibration	CRM Laboratory bias from PT studies Instrument calibration	NATA Technical Note 33

Table 3 Basis of Uncertainty Estimate (continued)

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision <sup>a</sup>	Method Bias <sup>a</sup>	
16	Top Down - precision and estimates of the method and laboratory bias	Control Sample-CRM Duplicate Analysis	CRM Laboratory bias from PT studies	NATA Technical Note 33 ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Technique
17	Calculated from Standard deviation and concentration of long term in house QC samples)	Control Samples-CRM Duplicate Analysis Instrumental calibration	CRM Laboratory bias from PT studies Recoveries of SS Instrument calibration Standard purity	NATA Technical Note 33
18	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-CRM Duplicate Analysis	CRM	Eurachem/CITAC Guide
19	Top Down - precision and estimates of the method and laboratory bias	Control Sample-RM Duplicate Analysis Instrumental calibration	CRM	NATA Technical Note 33
20	Top Down - precision and estimates of the method and laboratory bias	Control Sample Duplicate Analysis Instrumental calibration	CRM Instrument calibration	NATA Technical Note 33
21	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-CRM Duplicate Analysis	CRM Recoveries of SS Instrument calibration	ISO/GUM

<sup>a</sup>RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples.

#### 4.5 Participant Comments on this PT Study or Suggestions for Future Studies

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

Table 4 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
We would like to participate in new PT rounds with more elements such as U, Th, and Zr. In addition, it is preferred to contain greater contents so as to be reported by the ICP-OES radial-view.	Thank you for your suggestions, these tests will be included in our future studies. The analytes level in S2 is aimed to be above ICP-OES level of detection.

## 5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 5.1 Results Summary

Participant results are listed in Tables 5 to 60 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation ( $SD_{rob}$ ) and robust coefficient of variation ( $CV_{rob}$ ). Bar charts of results and performance scores are presented in Figures 2 to 57.

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

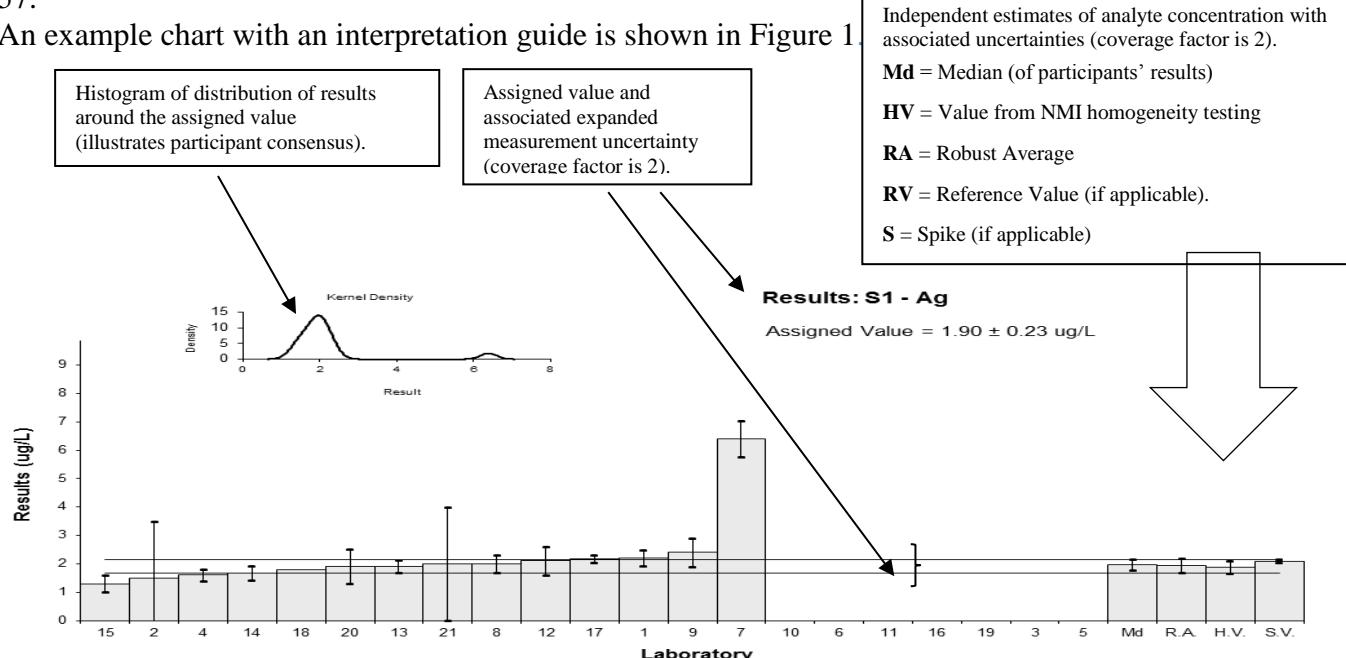


Figure 1 Guide to Presentation of Results

### 5.2 Assigned Value

An example of an assigned value calculation using data from the present study is given in Appendix 3. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'<sup>1</sup> In this study, the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, except for P; the expanded uncertainties were estimated from the associated robust standard deviations. For P in S1 and S2, the assigned values were reference values measured using standard addition ICP-MS.

### 5.3 Robust Average

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

### 5.4 Robust Between-Laboratory Coefficient of Variation

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

### 5.5 Target Standard Deviation

The target standard deviation ( $\sigma$ ) is the product of the assigned value ( $X$ ) and the performance coefficient of variation (PCV) as presented in Equation 1. 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.<sup>9</sup> By setting a fixed and realistic value for the PCV, the participants' performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

### **z-Score**

An example of z-score calculation using data from the present study is given in Appendix 4. For each participant's result a z-score is calculated according to Equation 1 below:

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

where:

- $z$  is z-score
- $\chi$  is participants' result
- $X$  is the study assigned value
- $\sigma$  is the target standard deviation

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

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

### **$E_n$ -Score**

An example of  $E_n$ -score calculation using data from the present study is given in Appendix 4. 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 2 below:

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

where:

- $E_n$  is  $E_n$ -score
- $\chi$  is a participants' result
- $X$  is the assigned value
- $U_\chi$  is the expanded uncertainty of the participants' result
- $U_X$  is the expanded uncertainty of the assigned value

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

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

### **5.7 Traceability and Measurement Uncertainty**

Laboratories accredited to ISO/IEC Standard 17025:2017<sup>10</sup> 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.<sup>11</sup>

## 6 TABLES AND FIGURES

Table 5

### Sample Details

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ag
<b>Units</b>	ug/L

### Participant Results

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2.20	0.27	1.05	0.85
2	1.48	2	-1.47	-0.21
3	NT	NT		
4	1.6	0.2	-1.05	-0.98
5	NT	NT		
6	<2	2		
7	6.40	0.64	15.79	6.62
8	2.0	0.3	0.35	0.26
9	2.4	0.5	1.75	0.91
10	<5	1		
11	<5	0.5		
12	2.1	0.5	0.70	0.36
13	1.92	0.22	0.07	0.06
14	1.68	0.25	-0.77	-0.65
15	1.3	0.308	-2.11	-1.56
16	<5	1		
17	2.17	0.13	0.95	1.02
18	1.8	NR	-0.35	-0.43
19	NT	NT		
20	1.9	0.6	0.00	0.00
21	2	2	0.35	0.05

### Statistics

<b>Assigned Value*</b>	1.90	0.23
<b>Spike</b>	2.09	0.06
<b>Homogeneity Value</b>	1.89	0.22
<b>Robust Average</b>	1.94	0.25
<b>Median</b>	1.96	0.19
<b>Mean</b>	2.21	
<b>N</b>	14	
<b>Max.</b>	6.4	
<b>Min.</b>	1.3	
<b>Robust SD</b>	0.34	
<b>Robust CV</b>	18%	

\*Robust Average excluding Laboratory 7.

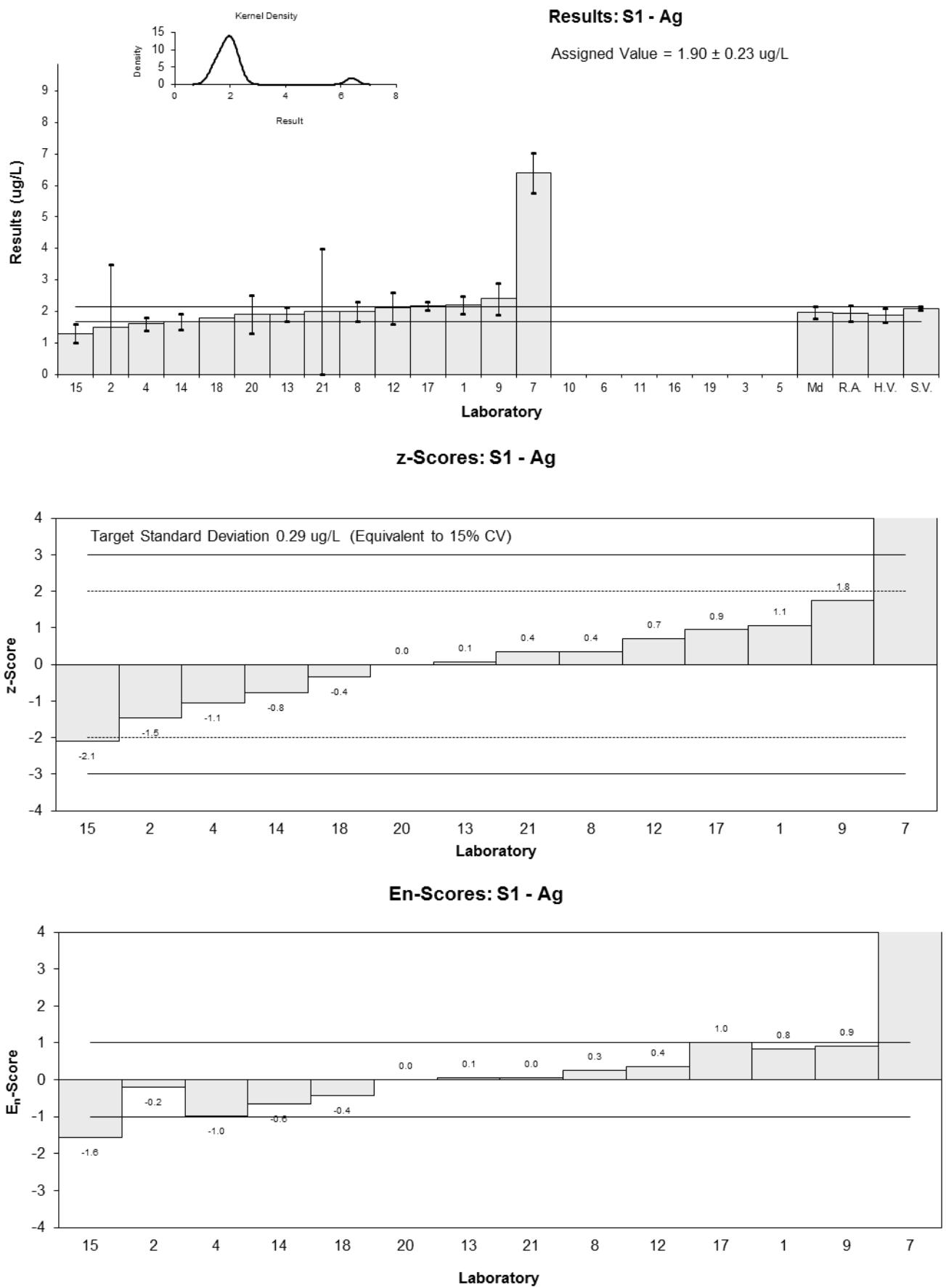


Figure 2

Table 6

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Al
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	17.9	3.8	-0.18	-0.12
2	20	20	0.58	0.08
3	<20	NR		
4	12.1	1.3	-2.28	-3.06
5	NT	NT		
6	20.8	10	0.87	0.24
7	<500	NT		
8	45	4.5	9.64	5.57
9	21	5	0.94	0.50
10	< 50	10		
11	<50	5		
12	20	5.0	0.58	0.30
13	17.8	0.28	-0.22	-0.37
14	19.3	3.1	0.33	0.26
15	14.0	1.744	-1.59	-1.86
16	<50	10		
17	18.4	1.7	0.00	0.00
18	17.00	NR	-0.51	-0.87
19	NT	NT		
20	<40	NR		
21	19	5	0.22	0.11

**Statistics**

<b>Assigned Value*</b>	18.4	1.6
<b>Spike</b>	18.3	1.1
<b>Homogeneity Value</b>	20.8	3.1
<b>Robust Average</b>	18.7	1.8
<b>Median</b>	19.0	1.1
<b>Mean</b>	20.2	
<b>N</b>	13	
<b>Max.</b>	45	
<b>Min.</b>	12.1	
<b>Robust SD</b>	2.3	
<b>Robust CV</b>	12%	

\*Robust Average excluding Laboratory 8.

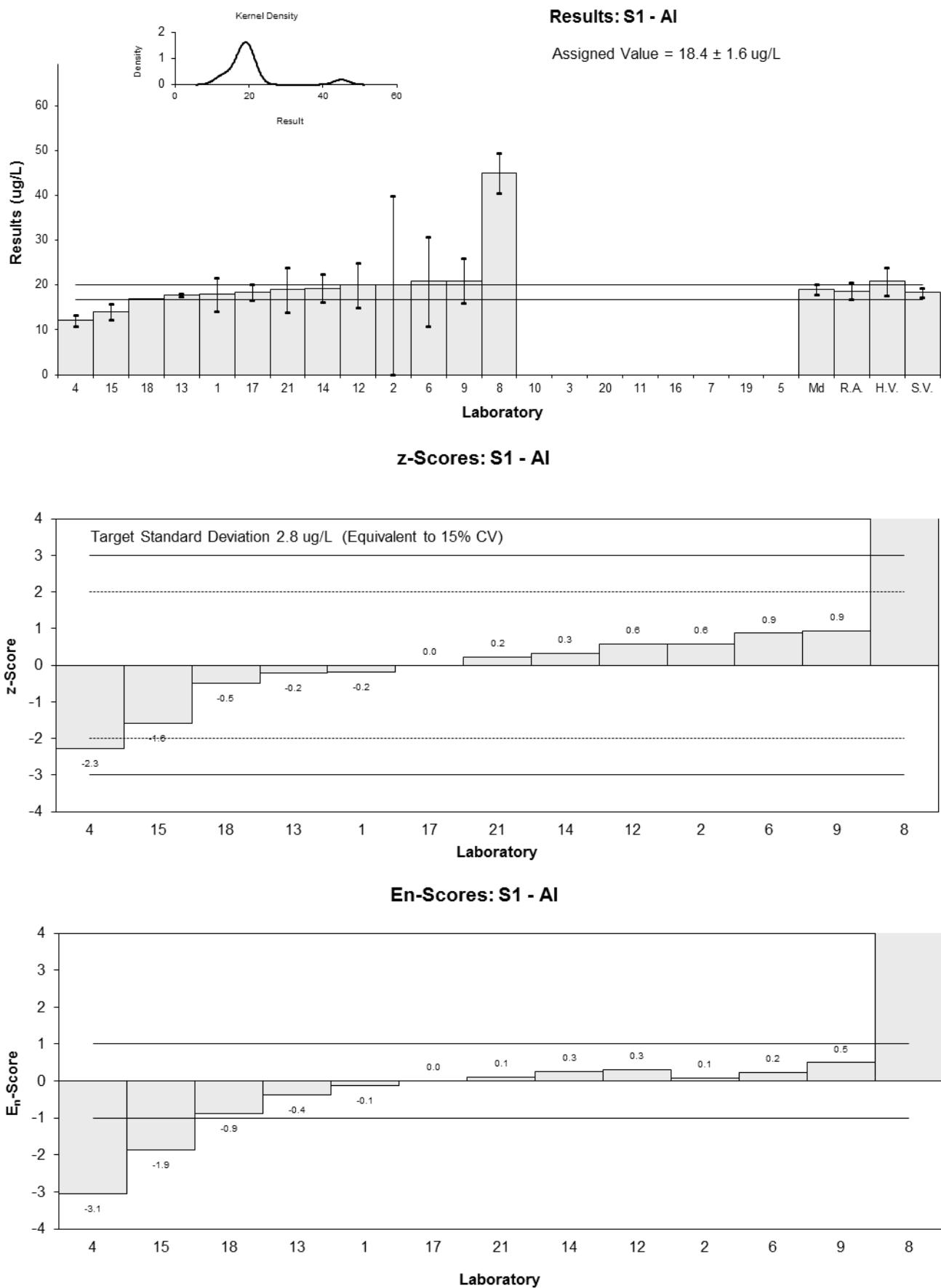


Figure 3

Table 7

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	As
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.32	0.22	-1.20	-0.85
2	1.69	2	0.33	0.04
3	<10	NR		
4	<10	NR		
5	NT	NT		
6	1.63	1	0.08	0.02
7	NT	NT		
8	2.5	0.5	3.69	1.58
9	1.7	0.2	0.37	0.27
10	1.55	0.31	-0.25	-0.15
11	2.1	0.21	2.03	1.47
12	1.1	0.4	-2.11	-1.07
13	1.20	0.40	-1.70	-0.86
14	3.27	0.64	6.87	2.40
15	1.5	0.167	-0.46	-0.36
16	2.00	0.27	1.61	1.04
17	1.49	0.19	-0.50	-0.37
18	<4	2.7		
19	NT	NT		
20	NT	NT		
21	1.5	1.0	-0.46	-0.11

**Statistics**

<b>Assigned Value</b>	1.61	0.26
<b>Spike</b>	1.57	0.19
<b>Homogeneity Value</b>	1.63	0.24
<b>Robust Average</b>	1.67	0.29
<b>Median</b>	1.59	0.16
<b>Mean</b>	1.75	
<b>N</b>	14	
<b>Max.</b>	3.27	
<b>Min.</b>	1.1	
<b>Robust SD</b>	0.37	
<b>Robust CV</b>	22%	

\*Robust Average excluding Laboratory 14.

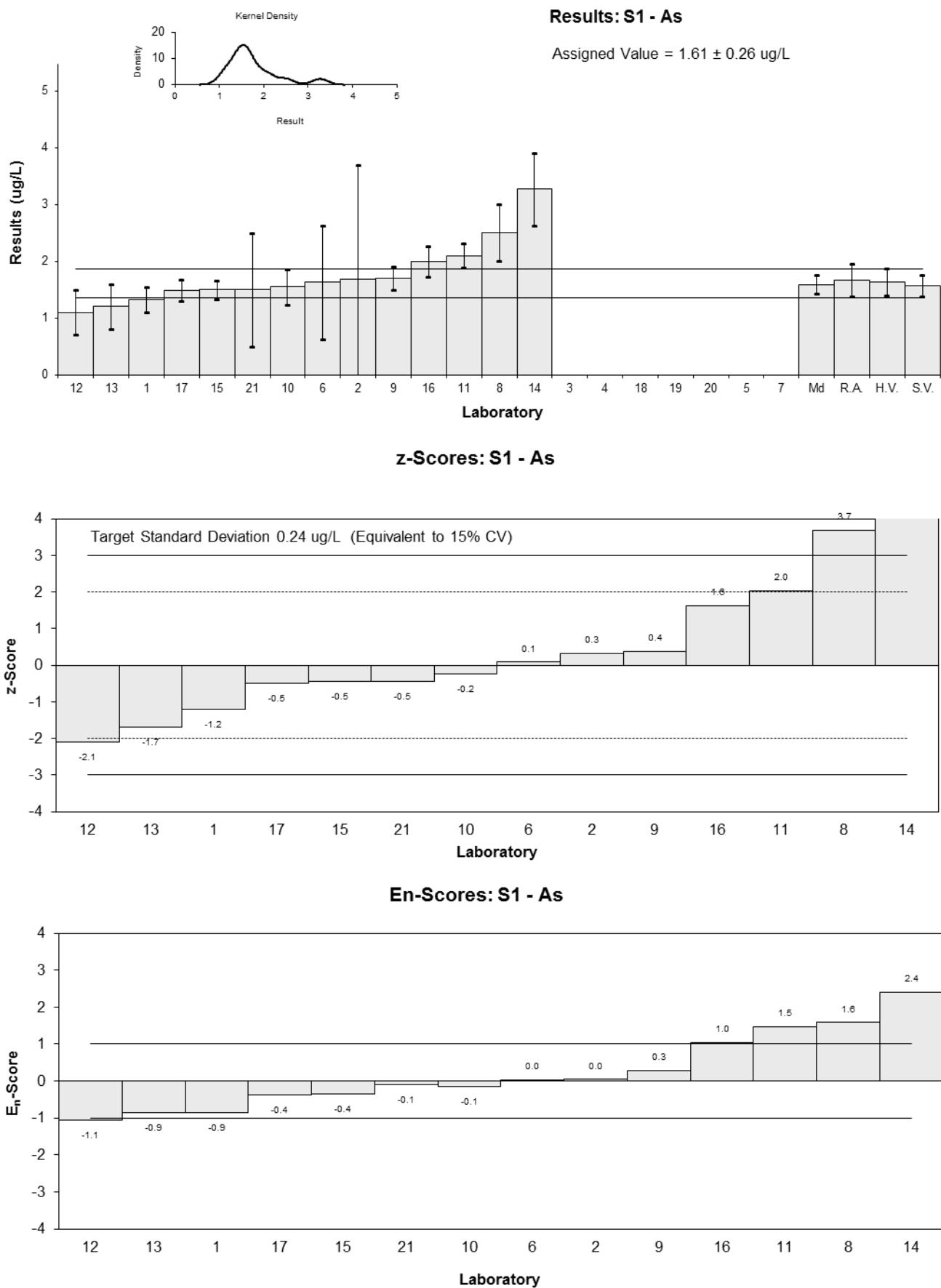


Figure 4

Table 8

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Be
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.13	0.57	0.31	0.09
2	1.21	2	0.80	0.06
3	<1	NR		
4	<1	NR		
5	NT	NT		
6	<1	1		
7	NT	NT		
8	<1	NR		
9	<3	1		
10	< 1	0.2		
11	<1	0.1		
12	1.1	0.4	0.12	0.05
13	1.00	0.17	-0.49	-0.42
14	1.18	0.25	0.62	0.38
15	1.0	0.118	-0.49	-0.54
16	<1	0.2		
17	1.0	0.19	-0.49	-0.38
18	NT	NT		
19	NT	NT		
20	1	1	-0.49	-0.08
21	<2	2		

**Statistics**

<b>Assigned Value</b>	1.08	0.09
<b>Spike</b>	1.00	0.05
<b>Homogeneity Value</b>	1.06	0.13
<b>Robust Average</b>	1.08	0.09
<b>Median</b>	1.05	0.06
<b>Mean</b>	1.08	
<b>N</b>	8	
<b>Max.</b>	1.21	
<b>Min.</b>	1	
<b>Robust SD</b>	0.10	
<b>Robust CV</b>	9.3%	

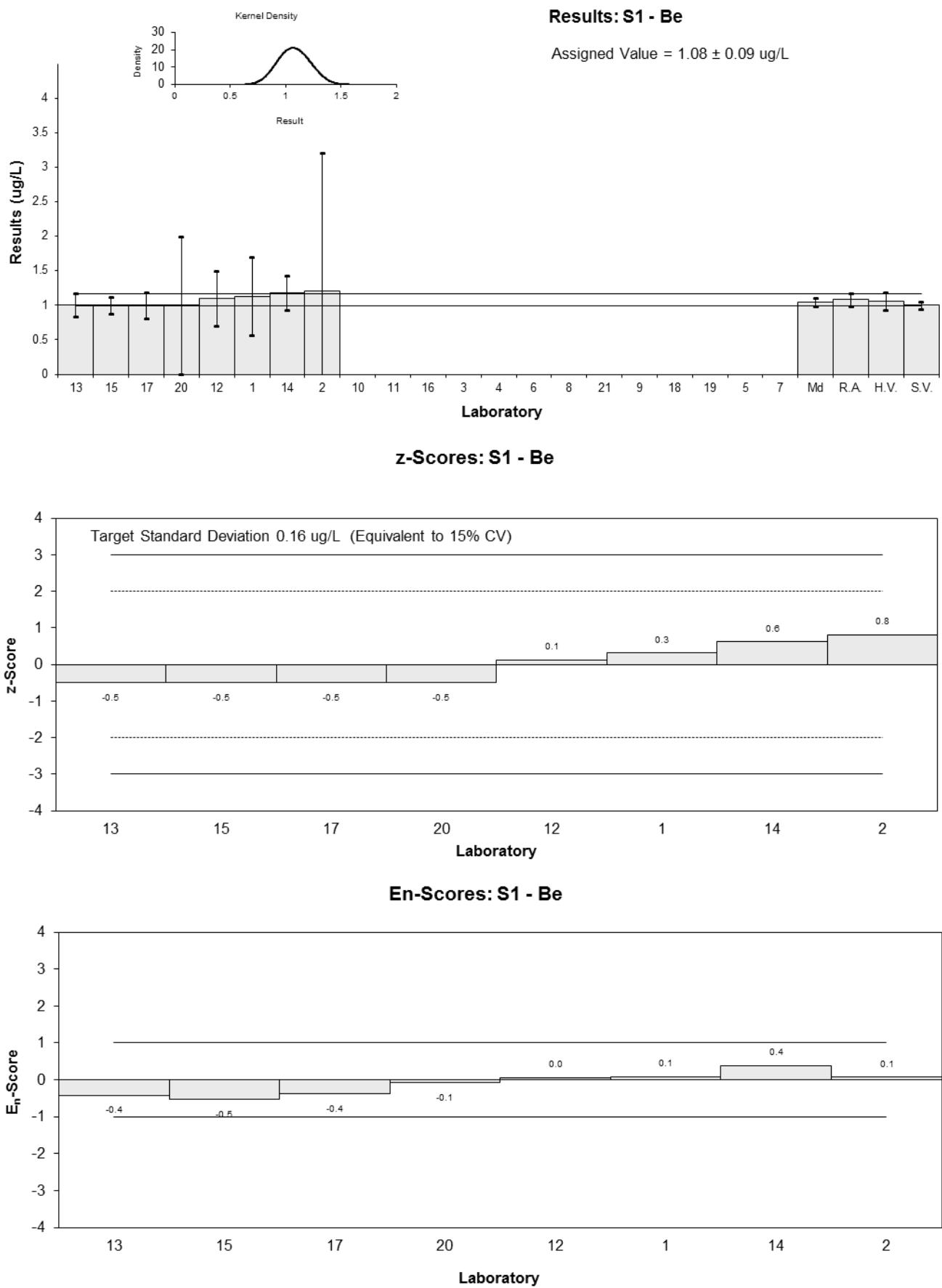


Figure 5

Table 9

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Cd
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.14	0.25	0.24	0.15
2	1.10	0.3	0.00	0.00
3	<1	NR		
4	1.6	0.2	3.03	2.19
5	NT	NT		
6	1.1	1	0.00	0.00
7	3.9	0.39	16.97	6.91
8	1.2	0.12	0.61	0.61
9	1.5	0.4	2.42	0.96
10	0.83	0.17	-1.64	-1.33
11	1.05	0.105	-0.30	-0.33
12	1.4	0.4	1.82	0.72
13	0.94	0.03	-0.97	-1.40
14	1.02	0.20	-0.48	-0.35
15	1.1	0.098	0.00	0.00
16	1.08	0.12	-0.12	-0.12
17	1.09	0.09	-0.06	-0.07
18	0.86	0.23	-1.45	-0.94
19	NT	NT		
20	1.1	0.5	0.00	0.00
21	1.0	0.3	-0.61	-0.31

**Statistics**

<b>Assigned Value*</b>	1.10	0.11
<b>Spike</b>	1.12	0.05
<b>Homogeneity Value</b>	1.12	0.13
<b>Robust Average</b>	1.13	0.13
<b>Median</b>	1.10	0.07
<b>Mean</b>	1.28	
<b>N</b>	18	
<b>Max.</b>	3.9	
<b>Min.</b>	0.83	
<b>Robust SD</b>	0.18	
<b>Robust CV</b>	16%	

\*Robust Average excluding Laboratory 7.

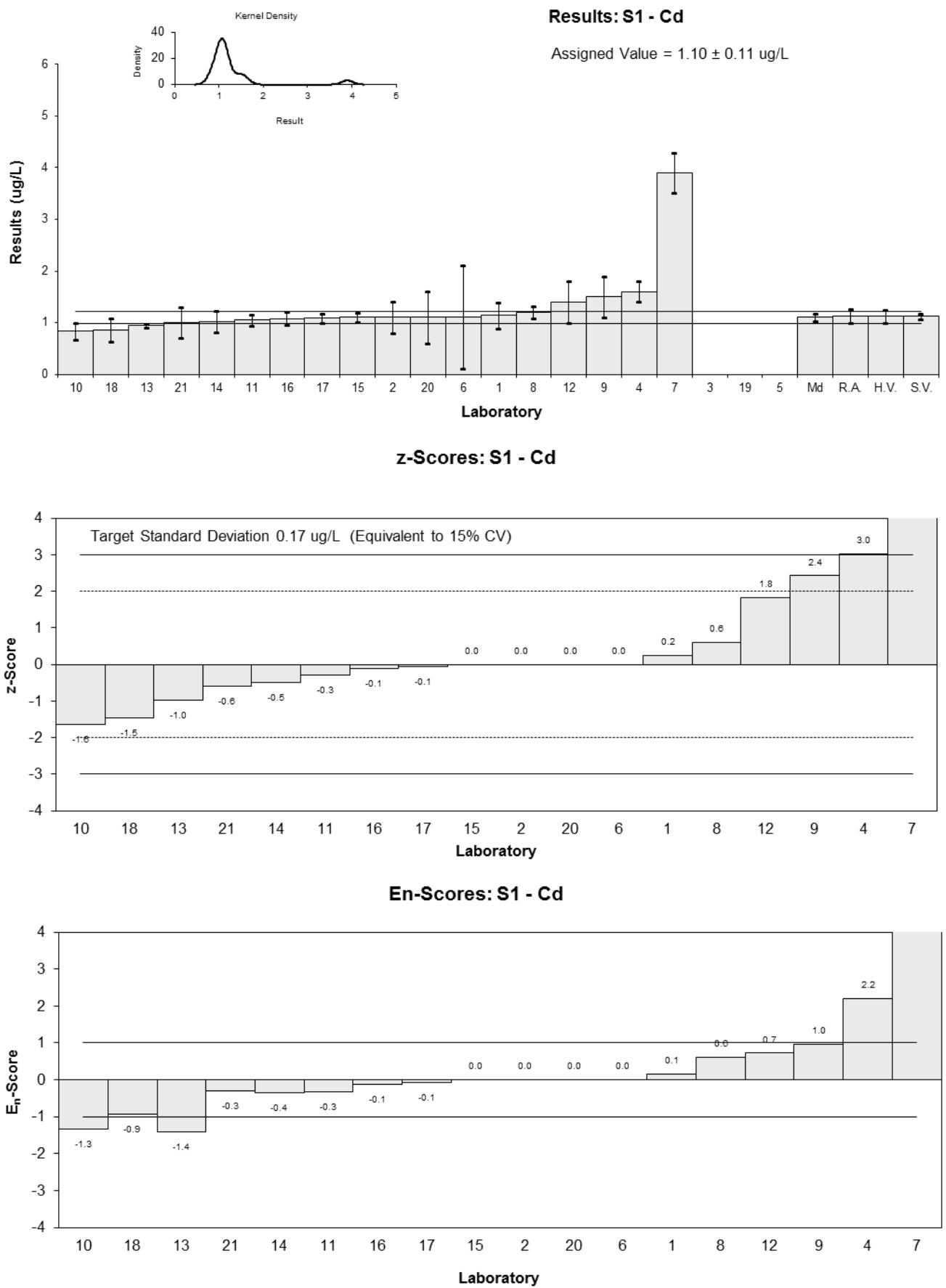


Figure 6

Table 10

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Co
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.42	0.30	0.29	0.18
2	3.15	2	8.77	0.89
3	<3	NR		
4	1.3	0.2	-0.29	-0.25
5	NT	NT		
6	1.24	1	-0.59	-0.12
7	8.9	0.89	36.96	8.38
8	1.4	0.22	0.20	0.16
9	1.9	0.3	2.65	1.65
10	1.15	0.23	-1.03	-0.79
11	<1	0.1		
12	1.6	0.4	1.18	0.57
13	1.35	0.07	-0.05	-0.07
14	1.33	0.25	-0.15	-0.11
15	1.2	0.117	-0.78	-0.91
16	1.31	0.16	-0.25	-0.24
17	1.38	0.08	0.10	0.13
18	2.1	NR	3.63	5.69
19	NT	NT		
20	1	1	-1.76	-0.36
21	1.4	0.3	0.20	0.12

**Statistics**

<b>Assigned Value*</b>	1.36	0.13
<b>Spike</b>	1.33	0.04
<b>Robust Average</b>	1.47	0.22
<b>Median</b>	1.38	0.11
<b>Mean</b>	1.95	
<b>N</b>	17	
<b>Max.</b>	8.9	
<b>Min.</b>	1	
<b>Robust SD</b>	0.19	
<b>Robust CV</b>	13%	

\*Robust Average excluding Laboratories 2 and 7.

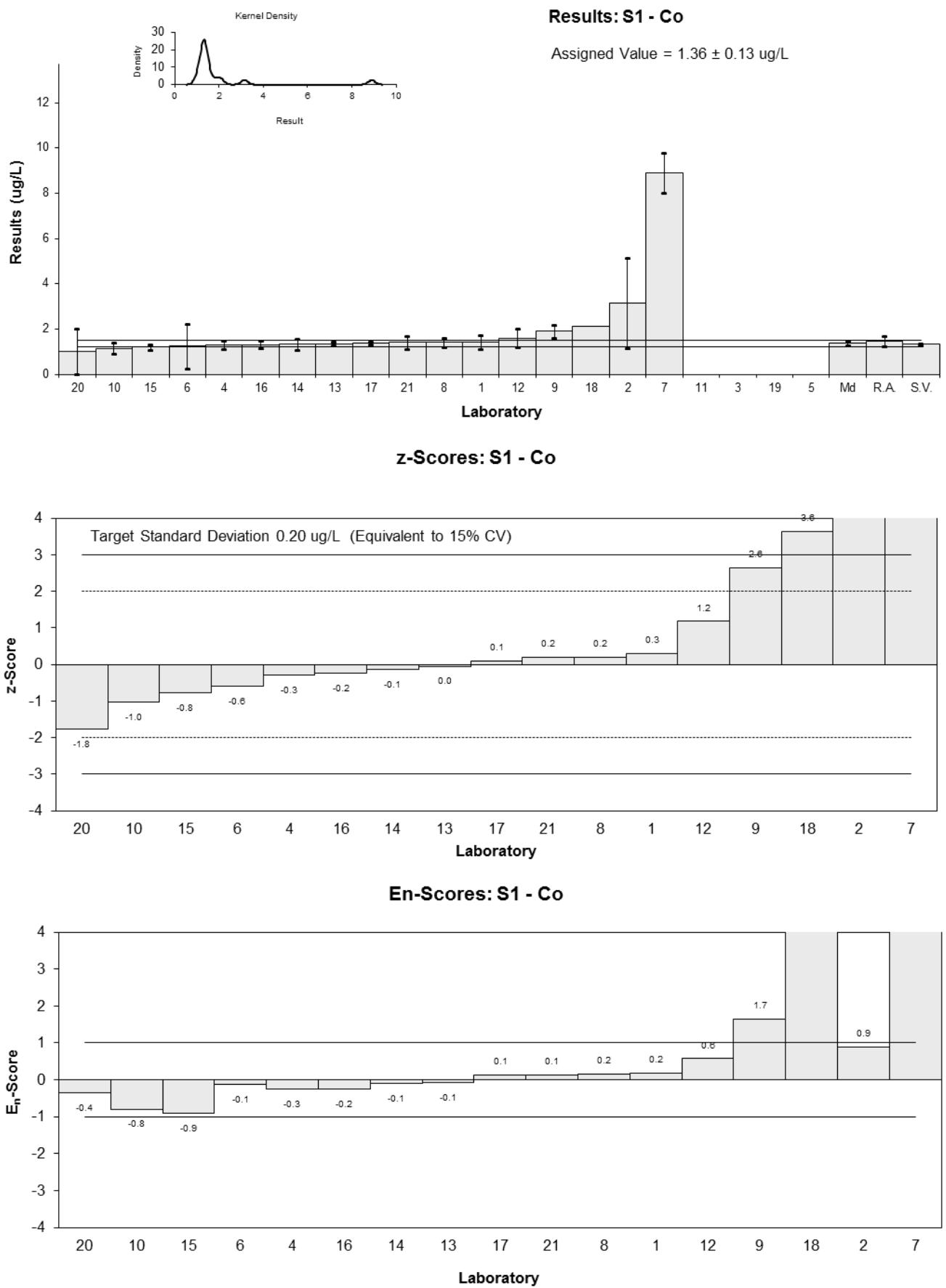


Figure 7

Table 11

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Cr
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.73	0.26	-1.01	-0.95
2	2.51	2	1.54	0.23
3	2	1	-0.13	-0.04
4	<5	NR		
5	NT	NT		
6	2.21	1	0.56	0.17
7	<50	NT		
8	2.1	0.32	0.20	0.16
9	3.3	0.7	4.12	1.73
10	1.37	0.27	-2.19	-1.99
11	1.71	0.171	-1.08	-1.25
12	2.1	0.5	0.20	0.11
13	2.26	0.11	0.72	0.96
14	3.34	1.36	4.25	0.95
15	1.8	0.192	-0.78	-0.87
16	1.91	0.22	-0.42	-0.44
17	2.16	0.19	0.39	0.43
18	2.74	0.81	2.29	0.84
19	NT	NT		
20	2	1	-0.13	-0.04
21	2.0	1.0	-0.13	-0.04

**Statistics**

<b>Assigned Value*</b>	2.04	0.20
<b>Spike</b>	1.94	0.06
<b>Homogeneity Value</b>	2.14	0.26
<b>Robust Average</b>	2.13	0.27
<b>Median</b>	2.10	0.14
<b>Mean</b>	2.19	
<b>N</b>	17	
<b>Max.</b>	3.34	
<b>Min.</b>	1.37	
<b>Robust SD</b>	0.30	
<b>Robust CV</b>	14%	

\*Robust Average excluding Laboratories 9 and 14.

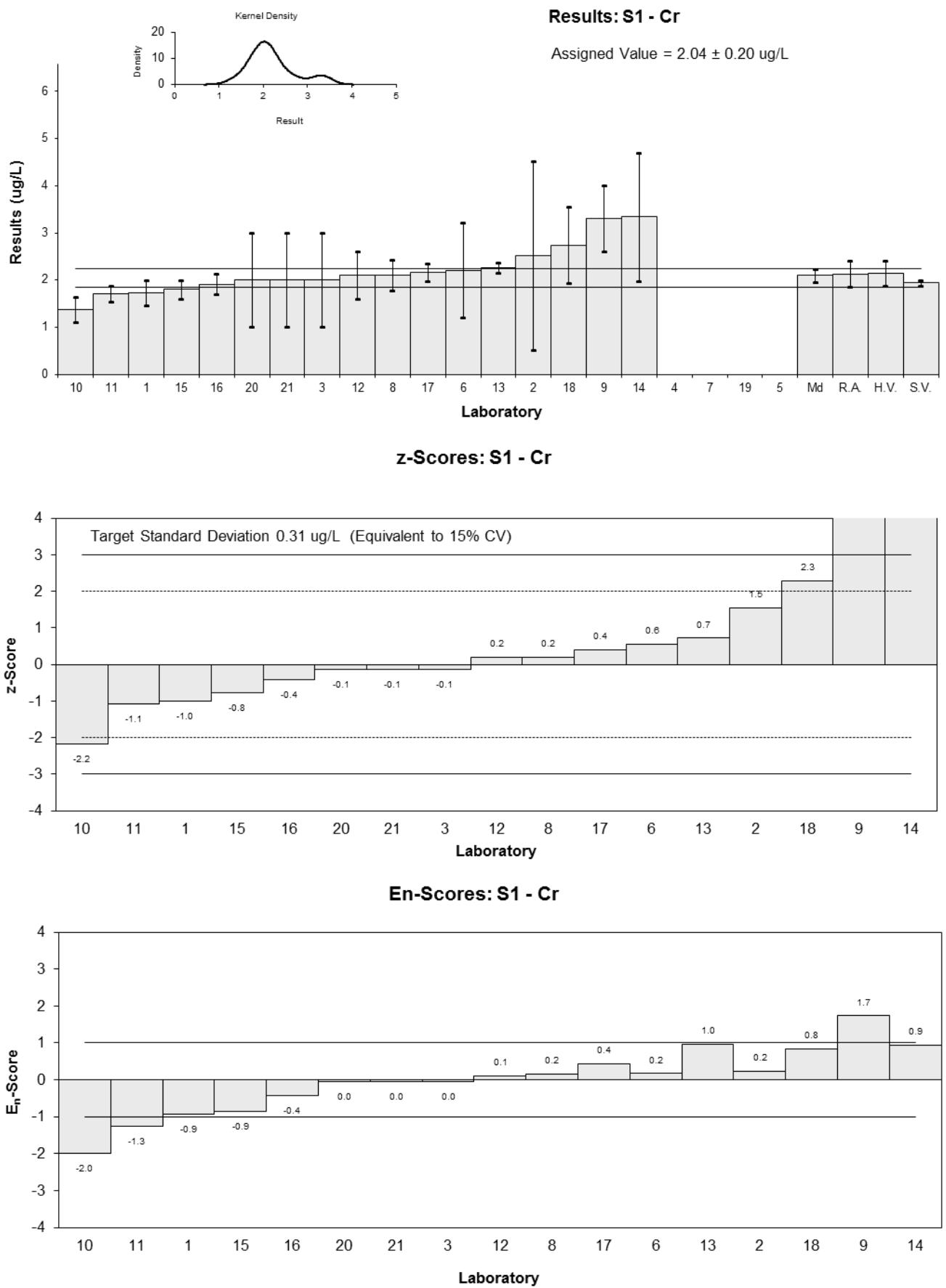


Figure 8

Table 12

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Cu
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	6.25	1.07	0.79	0.58
2	5.11	2	-0.57	-0.24
3	6	1	0.49	0.38
4	2.3	0.3	-3.92	-6.58
5	NT	NT		
6	5.61	2	0.02	0.01
7	<119	NT		
8	5.6	0.62	0.01	0.01
9	6.6	1	1.20	0.94
10	4.56	0.91	-1.23	-1.04
11	3.88	0.388	-2.04	-3.07
12	6.5	0.8	1.09	1.02
13	5.64	0.14	0.06	0.12
14	5.49	0.80	-0.12	-0.11
15	6.0	0.678	0.49	0.52
16	5.05	0.65	-0.64	-0.71
17	5.83	0.58	0.29	0.34
18	5.6	1.5	0.01	0.01
19	NT	NT		
20	5	2	-0.70	-0.29
21	5.6	0.4	0.01	0.02

**Statistics**

<b>Assigned Value</b>	5.59	0.40
<b>Spike</b>	5.16	0.57
<b>Homogeneity Value</b>	5.51	0.66
<b>Robust Average</b>	5.51	0.44
<b>Median</b>	5.60	0.33
<b>Mean</b>	5.37	
<b>N</b>	18	
<b>Max.</b>	6.6	
<b>Min.</b>	2.3	
<b>Robust SD</b>	0.67	
<b>Robust CV</b>	12%	

\*Robust Average excluding Laboratory 4.

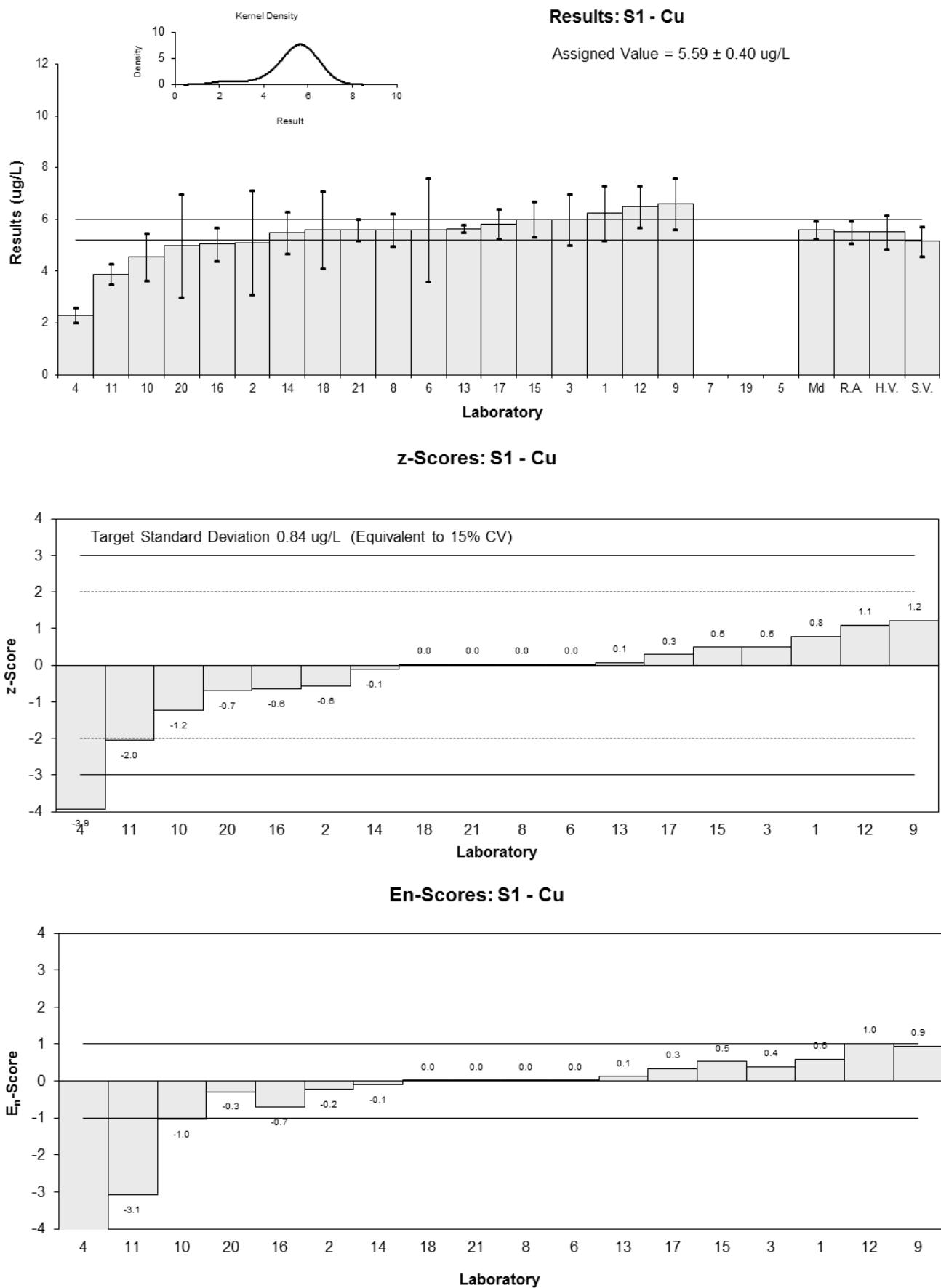


Figure 9

Table 13

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Fe
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	16.3	2.7	-1.38	-1.22
2	30	20	1.67	0.37
3	21	10	-0.33	-0.14
4	19.0	2.0	-0.78	-0.74
5	NT	NT		
6	19.8	10	-0.60	-0.25
7	NT	NT		
8	46	4.6	5.22	3.73
9	31	8	1.89	0.94
10	< 50	10		
11	<50	5		
12	22	6.0	-0.11	-0.07
13	20.7	1.20	-0.40	-0.40
14	25.6	5.96	0.69	0.42
15	<100	NR		
16	<50	10		
17	26.5	0.8	0.89	0.91
18	24.2	4.0	0.38	0.29
19	NT	NT		
20	<40	NR		
21	12	4	-2.33	-1.79

**Statistics**

<b>Assigned Value*</b>	22.5	4.3
<b>Spike</b>	22.6	0.8
<b>Homogeneity Value</b>	24.2	2.9
<b>Robust Average</b>	23.3	4.6
<b>Median</b>	22.0	3.2
<b>Mean</b>	24.2	
<b>N</b>	13	
<b>Max.</b>	46	
<b>Min.</b>	12	
<b>Robust SD</b>	5.9	
<b>Robust CV</b>	25%	

\*Robust Average excluding Laboratory 8.

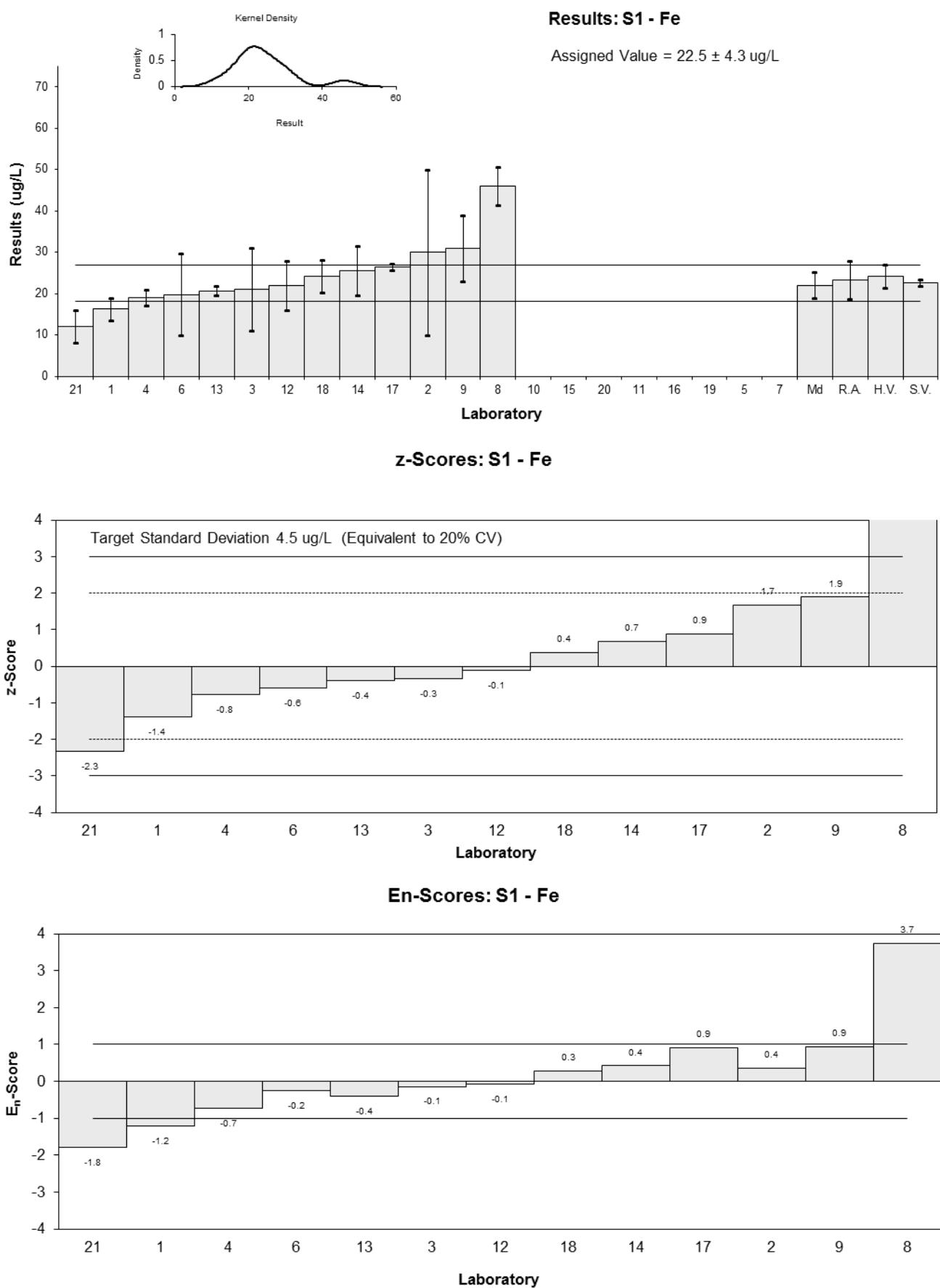


Figure 10

Table 14

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Hg
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.30	0.08	1.27	0.56
2	0.28	0.2	0.74	0.14
3	0.17	0.03	-2.17	-1.87
4	<1	NR		
5	NT	NT		
6	0.227	0.1	-0.66	-0.24
7	NT	NT		
8	0.3	0.05	1.27	0.81
9	0.25	0.06	-0.05	-0.03
10	0.21	0.04	-1.11	-0.82
11	0.206	0.0206	-1.22	-1.21
12	<0.5	NR		
13	0.284	0.003	0.85	1.00
14	0.37	0.03	3.12	2.69
15	0.2	0.023	-1.38	-1.32
16	0.282	0.046	0.79	0.54
17	0.27	0.02	0.48	0.48
18	0.243	0.061	-0.24	-0.13
19	NT	NT		
20	0.23	0.08	-0.58	-0.26
21	<0.5	0.5		

**Statistics**

<b>Assigned Value</b>	0.252	0.032
<b>Spike</b>	0.266	0.008
<b>Homogeneity Value</b>	0.213	0.026
<b>Robust Average</b>	0.252	0.032
<b>Median</b>	0.250	0.028
<b>Mean</b>	0.255	
<b>N</b>	15	
<b>Max.</b>	0.37	
<b>Min.</b>	0.17	
<b>Robust SD</b>	0.049	
<b>Robust CV</b>	19%	

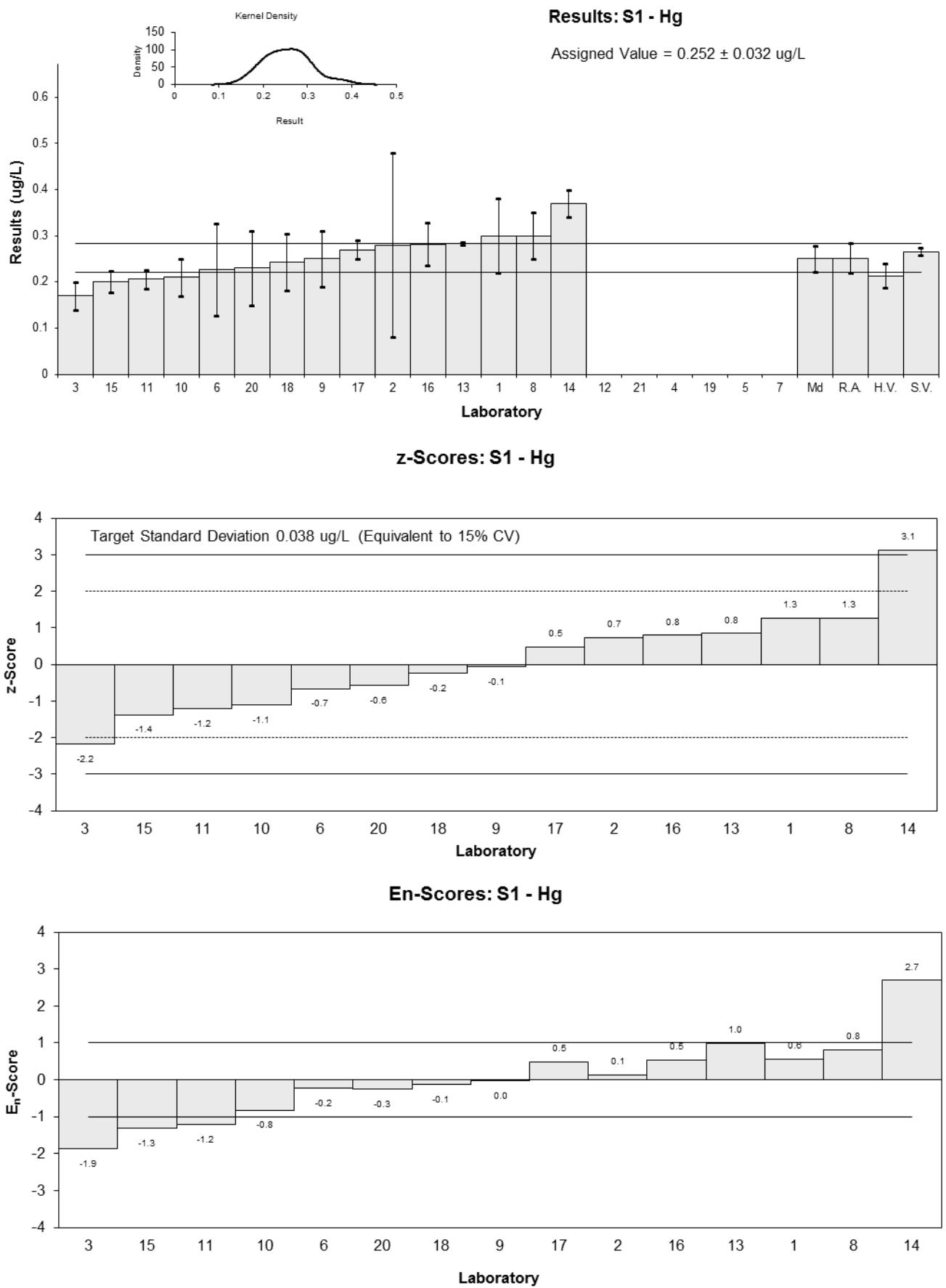


Figure 11

Table 15

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Mn
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	5.27	0.80	-1.15	-1.20
2	8.75	2	2.49	1.16
3	5	1	-1.43	-1.25
4	6.8	0.8	0.45	0.47
5	NT	NT		
6	6.00	1.5	-0.39	-0.24
7	NT	NT		
8	6.4	0.77	0.03	0.03
9	8	1.3	1.71	1.19
10	6.06	1.21	-0.32	-0.24
11	5.43	0.543	-0.98	-1.34
12	6.6	1.0	0.24	0.21
13	6.33	0.10	-0.04	-0.09
14	6.28	0.8	-0.09	-0.10
15	10.9	1.096	4.74	3.84
16	6.50	0.70	0.14	0.16
17	6.36	0.38	-0.01	-0.02
18	6.40	0.72	0.03	0.04
19	NT	NT		
20	7	4	0.66	0.16
21	6.6	1.0	0.24	0.21

**Statistics**

<b>Assigned Value*</b>	6.37	0.44
<b>Spike</b>	6.06	0.53
<b>Homogeneity Value</b>	6.41	0.77
<b>Robust Average</b>	6.48	0.53
<b>Median</b>	6.40	0.27
<b>Mean</b>	6.70	
<b>N</b>	18	
<b>Max.</b>	10.9	
<b>Min.</b>	5	
<b>Robust SD</b>	0.73	
<b>Robust CV</b>	11%	

\*Robust Average excluding Laboratory 15.

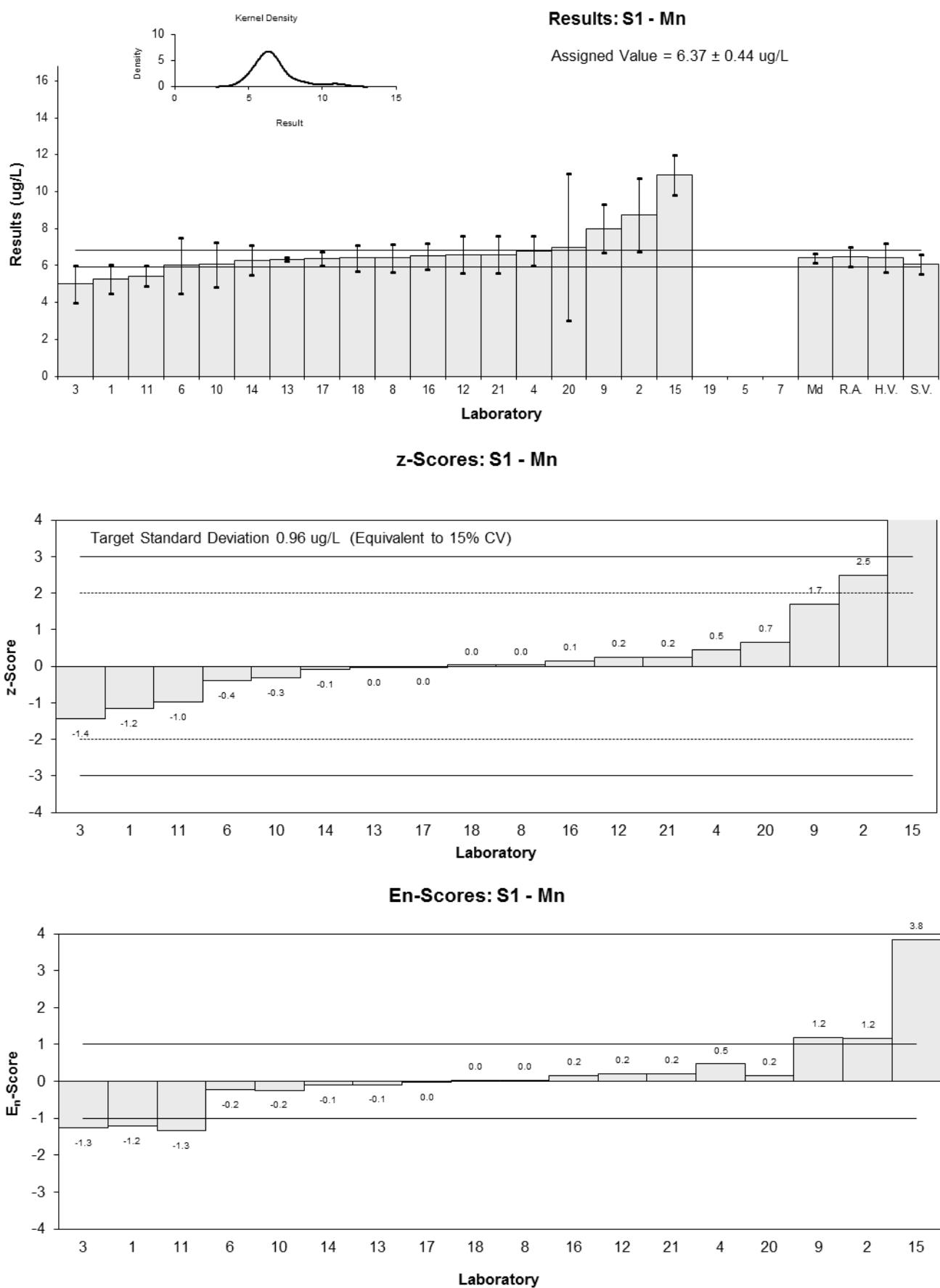


Figure 12

Table 16

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ni
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2.13	0.32	0.23	0.20
2	2.47	2	1.33	0.20
3	<5	NR		
4	2.0	0.4	-0.19	-0.14
5	NT	NT		
6	2.11	2	0.16	0.02
7	<89	NT		
8	2.0	0.28	-0.19	-0.19
9	2.2	0.4	0.45	0.33
10	1.49	0.3	-1.84	-1.70
11	<5	0.5		
12	2.2	0.5	0.45	0.27
13	1.89	0.25	-0.55	-0.58
14	2.23	0.36	0.55	0.44
15	16.2	1.701	45.76	8.28
16	<5	1		
17	2.13	0.3	0.23	0.21
18	<7	4.1		
19	NT	NT		
20	2	1	-0.19	-0.06
21	1.5	1.0	-1.81	-0.55

**Statistics**

<b>Assigned Value*</b>	2.06	0.15
<b>Spike</b>	2.05	0.08
<b>Homogeneity Value</b>	2.02	0.24
<b>Robust Average</b>	2.09	0.18
<b>Median</b>	2.12	0.10
<b>Mean</b>	3.04	
<b>N</b>	14	
<b>Max.</b>	16.2	
<b>Min.</b>	1.49	
<b>Robust SD</b>	0.22	
<b>Robust CV</b>	11%	

\*Robust Average excluding Laboratory 15.

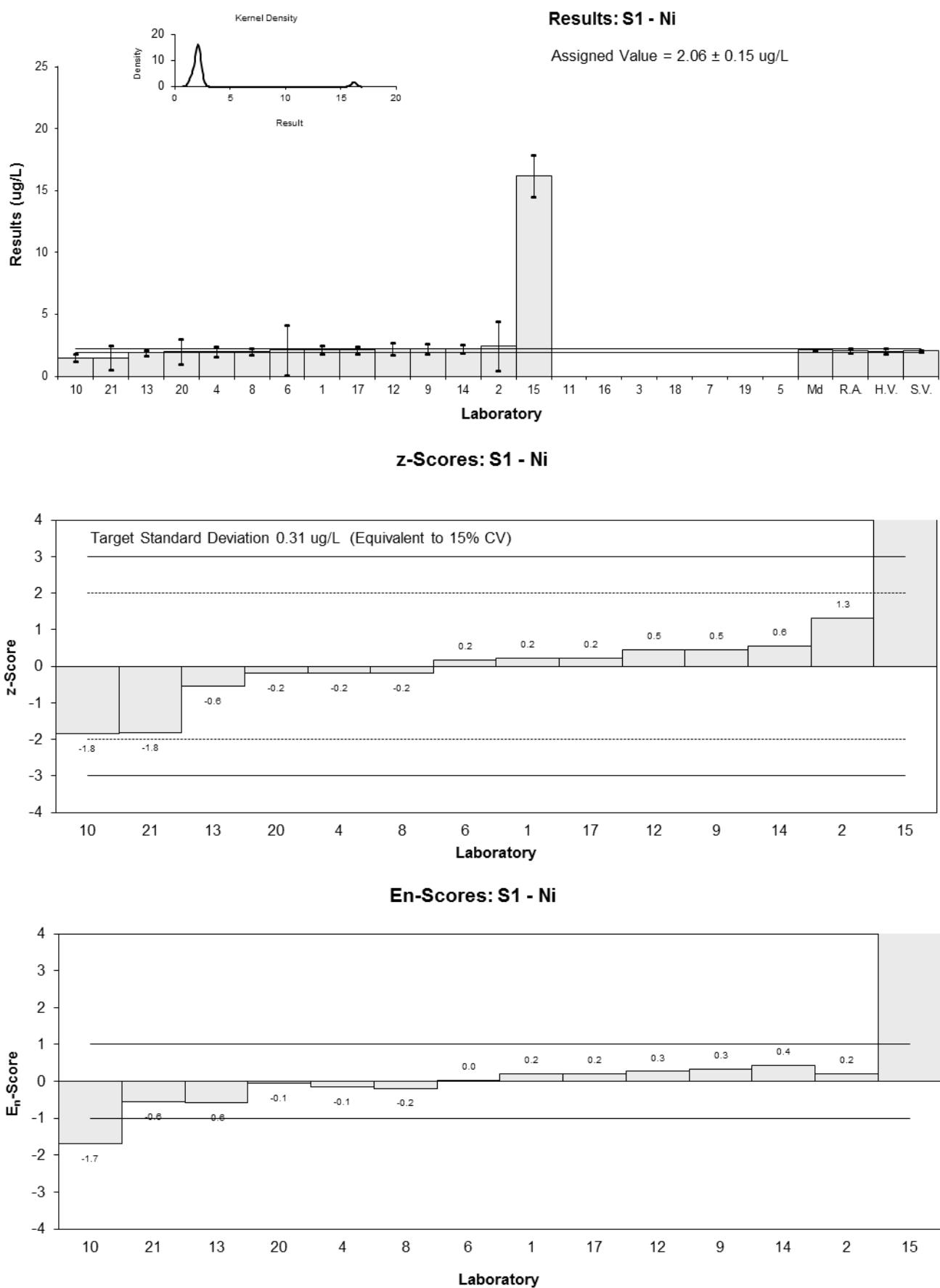


Figure 13

Table 17

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	P
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	112	22	-0.52	-0.58
4	130	25	0.20	0.20
5	NT	NT		
6	NT	NT		
7	<85	NT		
8	140	24	0.60	0.62
9	179	48	2.17	1.12
10	< 5000	1000		
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	207	60	3.29	1.37
15	<10	NR		
16	<500	100		
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	150	50	1.00	0.50
21	240	100	4.61	1.15

**Statistics**

<b>Reference Value*</b>	124.9	3.7
<b>Spike</b>	121	5
<b>Homogeneity Value</b>	124.9	3.7
<b>Robust Average</b>	165	49
<b>Median</b>	150	40
<b>Mean</b>	165	
<b>N</b>	7	
<b>Max.</b>	240	
<b>Min.</b>	112	
<b>Robust SD</b>	52	
<b>Robust CV</b>	32%	

\*Reference Value by standard addition ICP-MS.

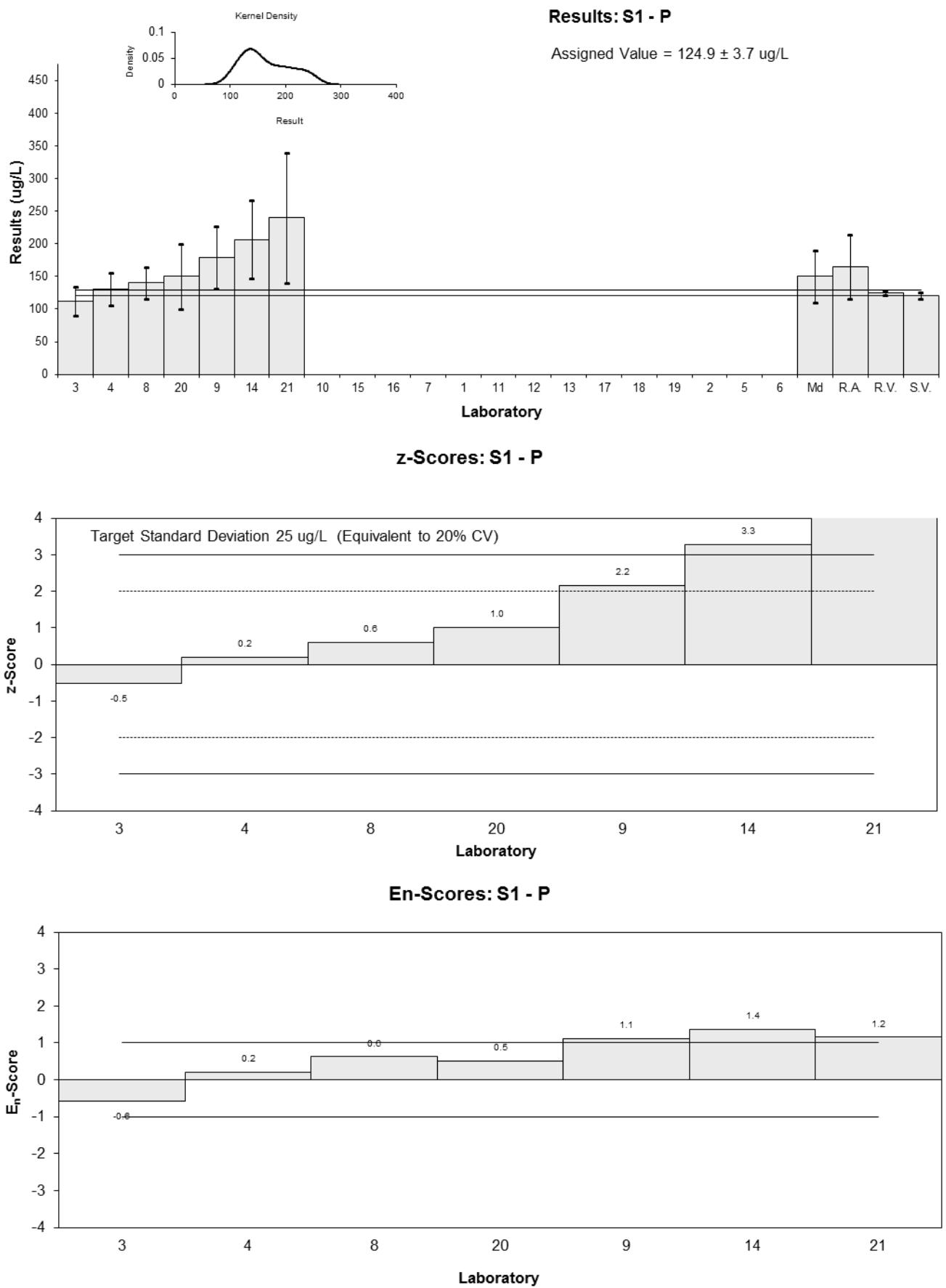


Figure 14

Table 18

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Pb
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.53	0.25	0.32	0.25
2	1.55	2	0.41	0.04
3	<10	NR		
4	1.4	0.2	-0.27	-0.25
5	NT	NT		
6	1.71	1	1.14	0.25
7	NT	NT		
8	1.6	0.37	0.64	0.36
9	2.1	0.4	2.92	1.52
10	1.20	0.24	-1.19	-0.95
11	1.26	0.126	-0.91	-1.10
12	1.7	0.5	1.10	0.46
13	1.27	0.16	-0.87	-0.92
14	1.59	0.23	0.59	0.49
15	1.4	0.131	-0.27	-0.33
16	1.47	0.19	0.05	0.04
17	1.56	0.09	0.46	0.63
18	1.28	0.70	-0.82	-0.25
19	NT	NT		
20	1	1	-2.10	-0.46
21	1.4	0.3	-0.27	-0.18

**Statistics**

<b>Assigned Value</b>	1.46	0.13
<b>Spike</b>	1.54	0.04
<b>Homogeneity Value</b>	1.60	0.19
<b>Robust Average</b>	1.46	0.13
<b>Median</b>	1.47	0.10
<b>Mean</b>	1.47	
<b>N</b>	17	
<b>Max.</b>	2.1	
<b>Min.</b>	1	
<b>Robust SD</b>	0.21	
<b>Robust CV</b>	14%	

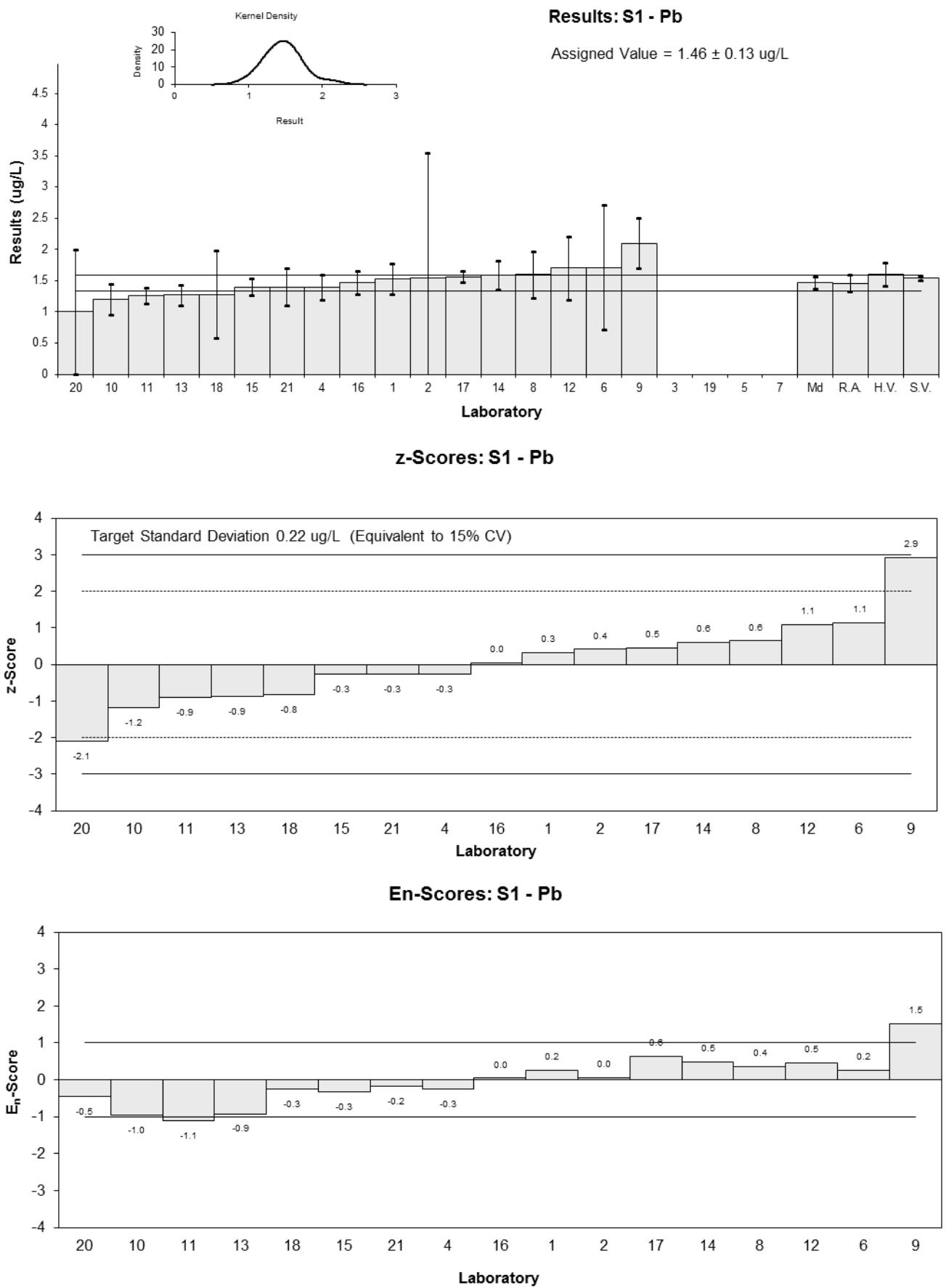


Figure 15

Table 19

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Se
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	4.26	0.86	0.37	0.26
2	2.95	2	-1.28	-0.48
3	<20	NR		
4	<10	NR		
5	NT	NT		
6	5.04	2	1.35	0.50
7	NT	NT		
8	4.8	0.91	1.05	0.72
9	5.5	0.9	1.93	1.33
10	3.17	0.63	-1.01	-0.84
11	3.45	0.345	-0.65	-0.65
12	4.0	1.0	0.04	0.02
13	2.66	0.13	-1.65	-1.79
14	3.25	0.89	-0.91	-0.63
15	<100	NR		
16	3.34	0.67	-0.79	-0.64
17	4.17	0.54	0.25	0.22
18	<4	2.7		
19	NT	NT		
20	<5	NR		
21	5	2	1.30	0.48

**Statistics**

<b>Assigned Value</b>	3.97	0.72
<b>Spike</b>	3.64	0.11
<b>Homogeneity Value</b>	4.38	0.53
<b>Robust Average</b>	3.97	0.72
<b>Median</b>	4.00	0.72
<b>Mean</b>	3.97	
<b>N</b>	13	
<b>Max.</b>	5.5	
<b>Min.</b>	2.66	
<b>Robust SD</b>	1	
<b>Robust CV</b>	25%	

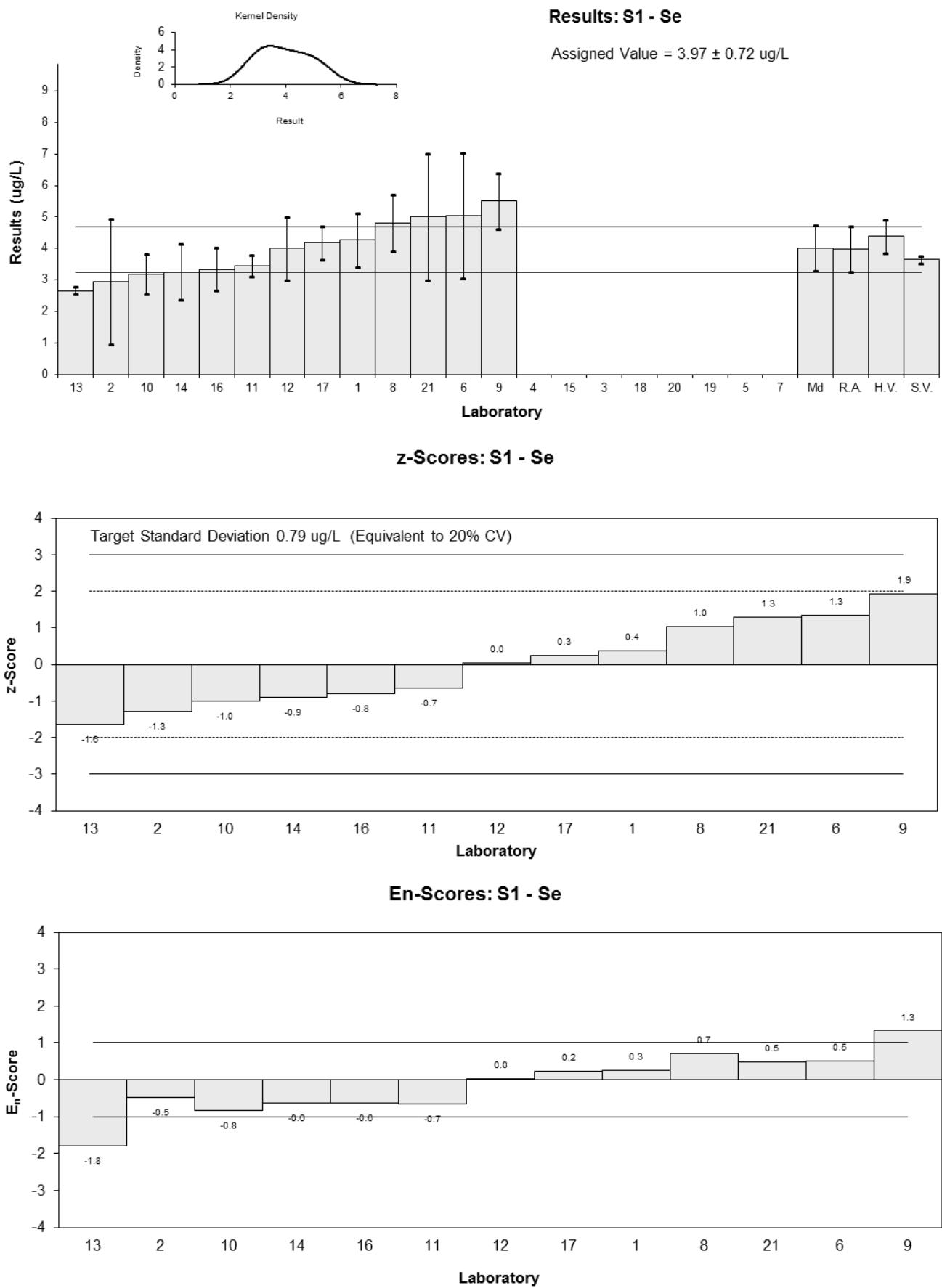


Figure 16

Table 20

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Sn
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.79	0.80	0.09	0.05
2	4.85	2	1.98	0.54
3	NT	NT		
4	2.9	0.4	-1.50	-1.36
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	3.8	0.61	0.11	0.08
9	4.2	0.6	0.82	0.60
10	< 5	1		
11	<5	0.5		
12	NT	NT		
13	3.41	0.48	-0.59	-0.49
14	3.35	0.89	-0.70	-0.39
15	<5.0	NR		
16	<5	1		
17	3.64	0.25	-0.18	-0.19
18	<5	NR		
19	NT	NT		
20	4	3	0.46	0.09
21	<5	5		

**Statistics**

<b>Assigned Value</b>	3.74	0.47
<b>Spike</b>	3.61	0.10
<b>Homogeneity Value</b>	3.63	0.44
<b>Robust Average</b>	3.74	0.47
<b>Median</b>	3.79	0.43
<b>Mean</b>	3.77	
<b>N</b>	9	
<b>Max.</b>	4.85	
<b>Min.</b>	2.9	
<b>Robust SD</b>	0.56	
<b>Robust CV</b>	15%	

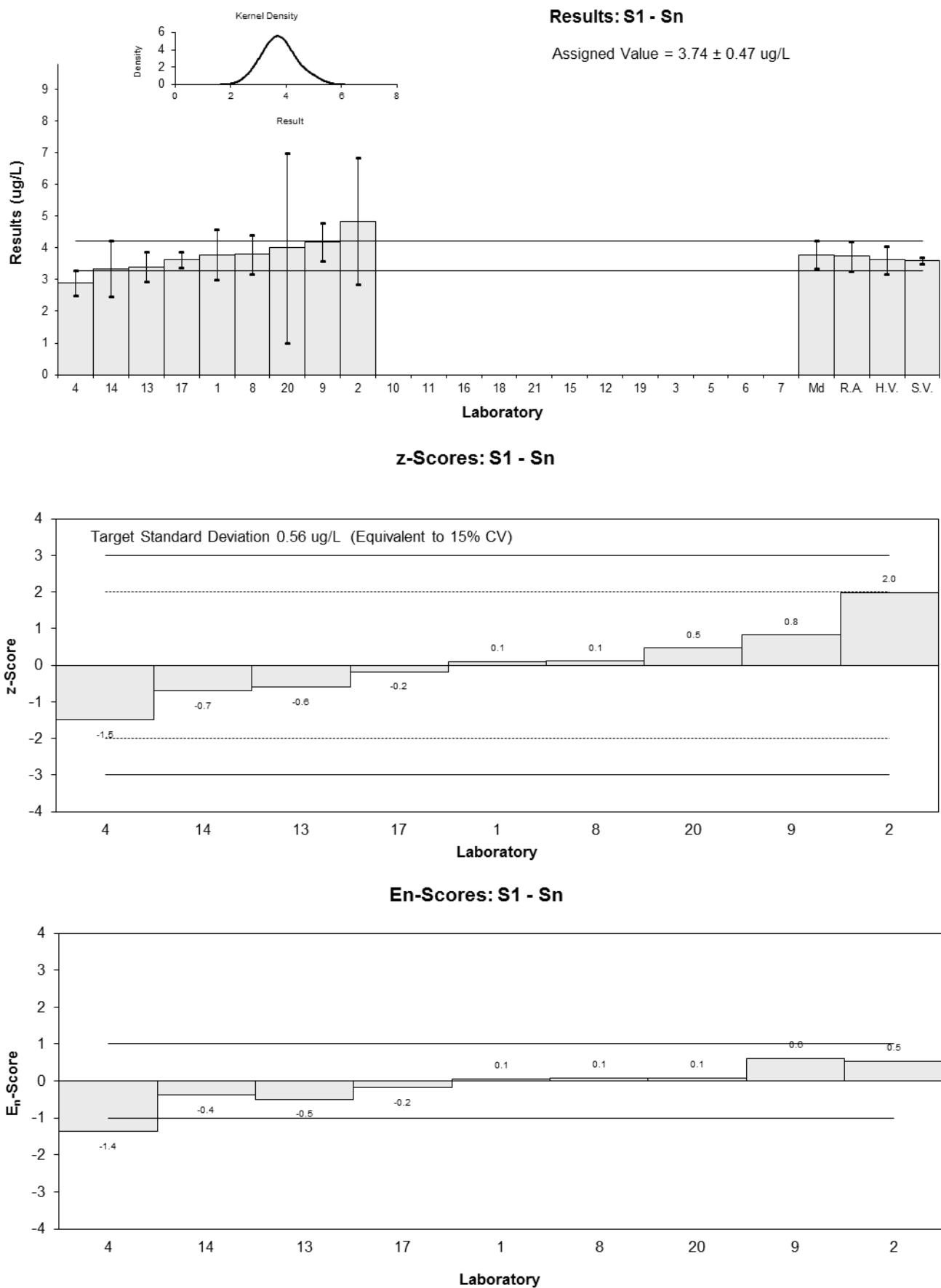


Figure 17

Table 21

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	V
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2.50	0.48	-0.65	-0.52
2	1.31	2	-3.51	-0.73
3	NT	NT		
4	2.4	0.3	-0.89	-1.03
5	NT	NT		
6	3.05	1	0.67	0.27
7	<52	NT		
8	2.6	0.42	-0.41	-0.37
9	3.3	0.6	1.28	0.84
10	< 5	1		
11	<5	0.5		
12	3.0	0.6	0.55	0.36
13	2.76	0.33	-0.02	-0.03
14	5.82	0.42	7.34	6.56
15	2.7	0.255	-0.17	-0.22
16	<5	1		
17	2.56	0.23	-0.51	-0.69
18	2.7	1.5	-0.17	-0.05
19	NT	NT		
20	2.8	1.2	0.07	0.02
21	3.0	1.0	0.55	0.23

**Statistics**

<b>Assigned Value*</b>	2.77	0.20
<b>Spike</b>	2.82	0.26
<b>Homogeneity Value</b>	3.09	0.37
<b>Robust Average</b>	2.78	0.25
<b>Median</b>	2.73	0.21
<b>Mean</b>	2.89	
<b>N</b>	14	
<b>Max.</b>	5.82	
<b>Min.</b>	1.31	
<b>Robust SD</b>	0.28	
<b>Robust CV</b>	10%	

\*Robust Average excluding Laboratories 2 and 14.

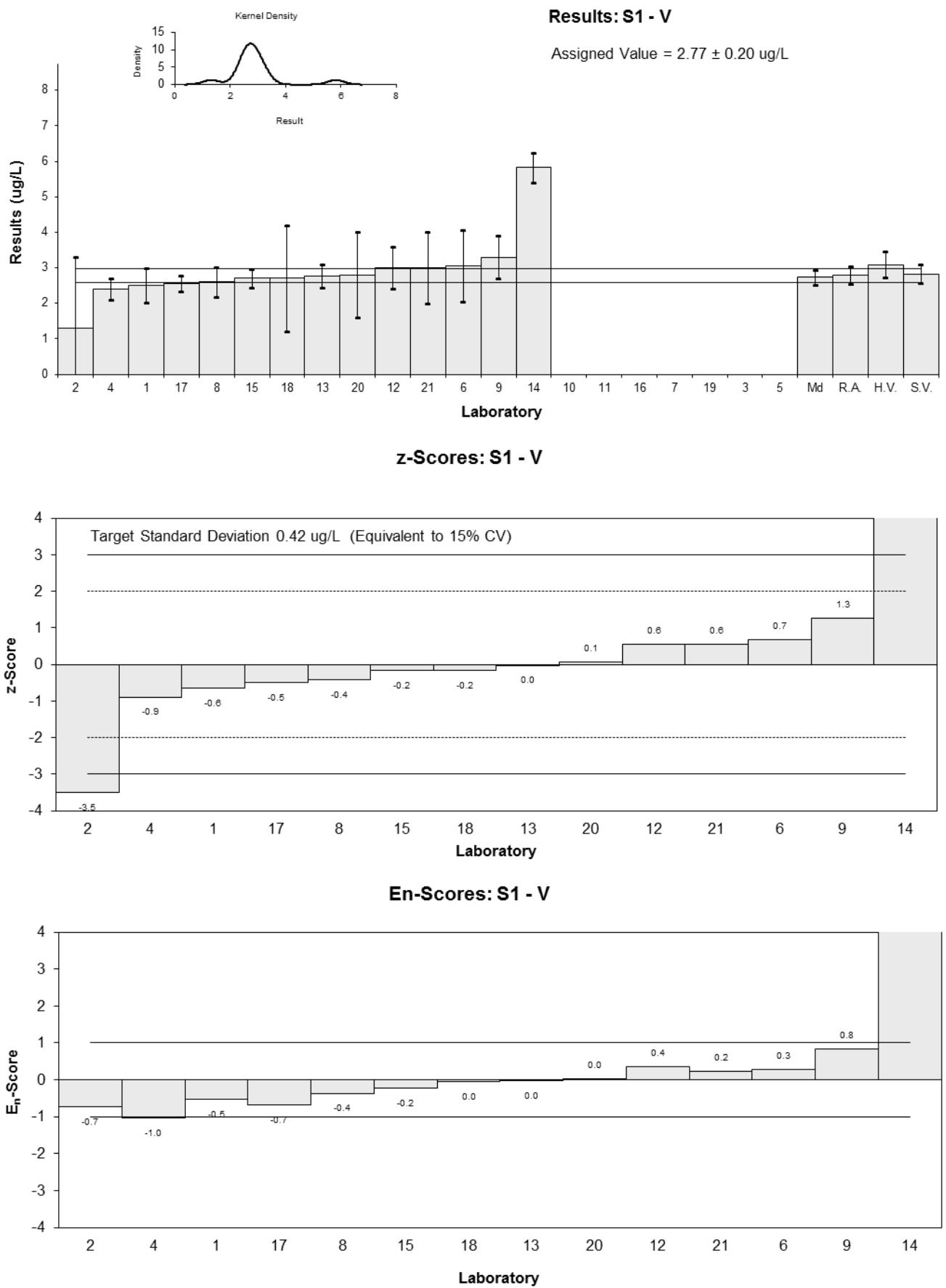


Figure 18

Table 22

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Zn
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	11.8	2.5	0.11	0.07
2	17	5	3.10	1.06
3	11	3	-0.34	-0.19
4	12.8	1.6	0.69	0.64
5	NT	NT		
6	11.4	10	-0.11	-0.02
7	<50	NT		
8	12	2.3	0.23	0.16
9	13	1.7	0.80	0.71
10	9.30	1.86	-1.32	-1.09
11	<5	0.5		
12	12	2.5	0.23	0.15
13	9.74	0.40	-1.07	-1.73
14	11.7	1.57	0.06	0.05
15	12	1.495	0.23	0.22
16	9.08	1.08	-1.45	-1.71
17	12.1	0.97	0.29	0.36
18	10.30	3.1	-0.75	-0.40
19	NT	NT		
20	15	4	1.95	0.82
21	11	3	-0.34	-0.19

**Statistics**

<b>Assigned Value</b>	11.6	1.0
<b>Spike</b>	11.7	0.8
<b>Homogeneity Value</b>	10.7	1.3
<b>Robust Average</b>	11.6	1.0
<b>Median</b>	11.8	0.6
<b>Mean</b>	11.8	
<b>N</b>	17	
<b>Max.</b>	17	
<b>Min.</b>	9.08	
<b>Robust SD</b>	2.0	
<b>Robust CV</b>	17%	

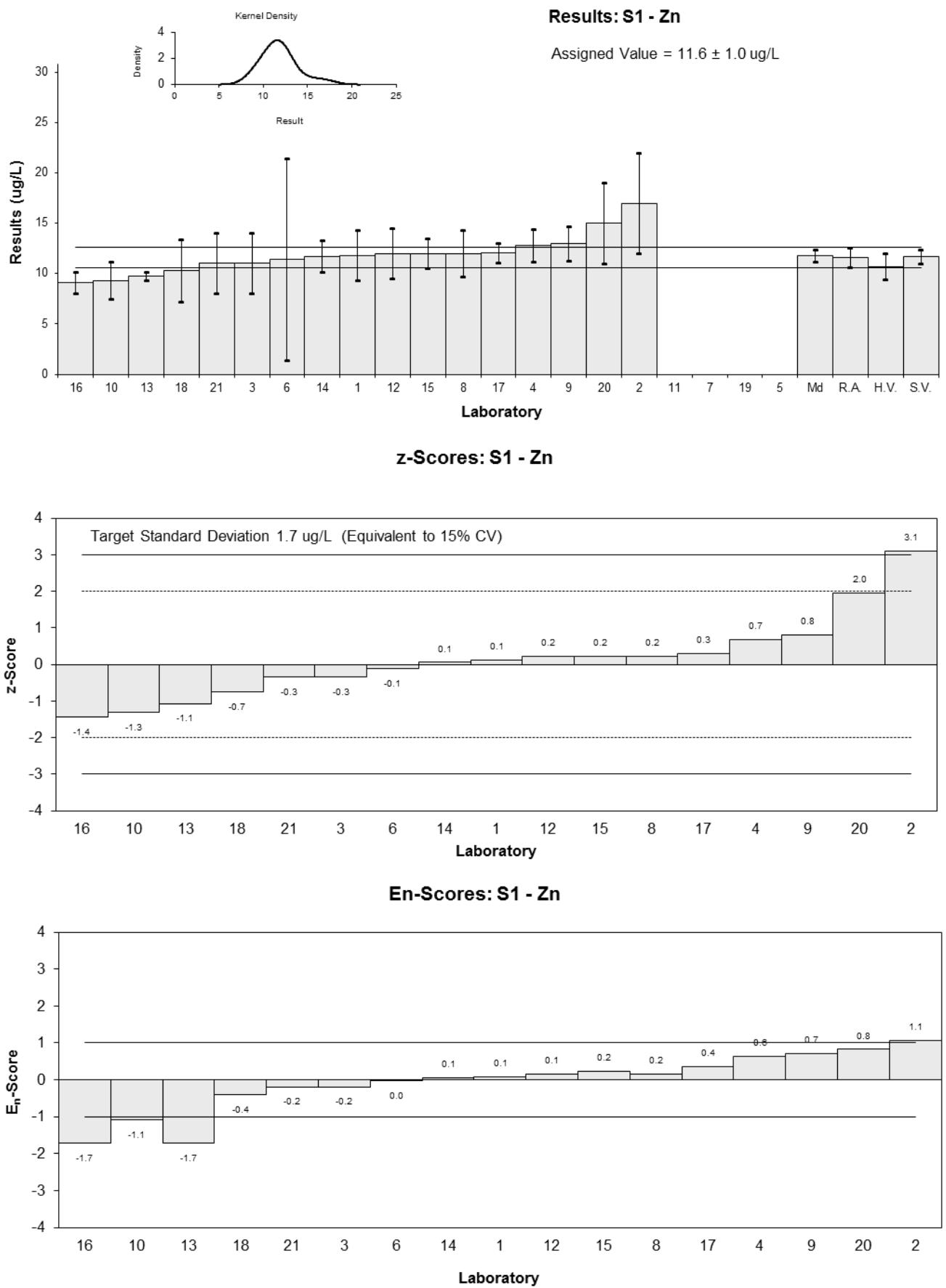


Figure 19

Table 23

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ag
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	9.5	1.0	-1.88	-1.56
5	NT	NT		
6	10.5	4	-1.03	-0.29
7	16.2	1.62	3.85	2.36
8	12	2.3	0.26	0.12
9	14	2.8	1.97	0.77
10	8.86	1.77	-2.43	-1.40
11	10.7	1.07	-0.85	-0.68
12	13	2.5	1.11	0.48
13	11.0	0.3	-0.60	-0.67
14	11.5	1.7	-0.17	-0.10
15	11.5	2.836	-0.17	-0.07
16	11.8	1.15	0.09	0.07
17	NT	NT		
18	12.2	5.4	0.43	0.09
19	NT	NT		
20	12	2	0.26	0.13
21	12.8	3	0.94	0.35

**Statistics**

<b>Assigned Value</b>	11.7	1.0
<b>Spike</b>	12.2	0.4
<b>Homogeneity Value</b>	11.1	1.3
<b>Robust Average</b>	11.7	1.0
<b>Median</b>	11.8	0.8
<b>Mean</b>	11.8	
<b>N</b>	15	
<b>Max.</b>	16.2	
<b>Min.</b>	8.86	
<b>Robust SD</b>	1.6	
<b>Robust CV</b>	14%	

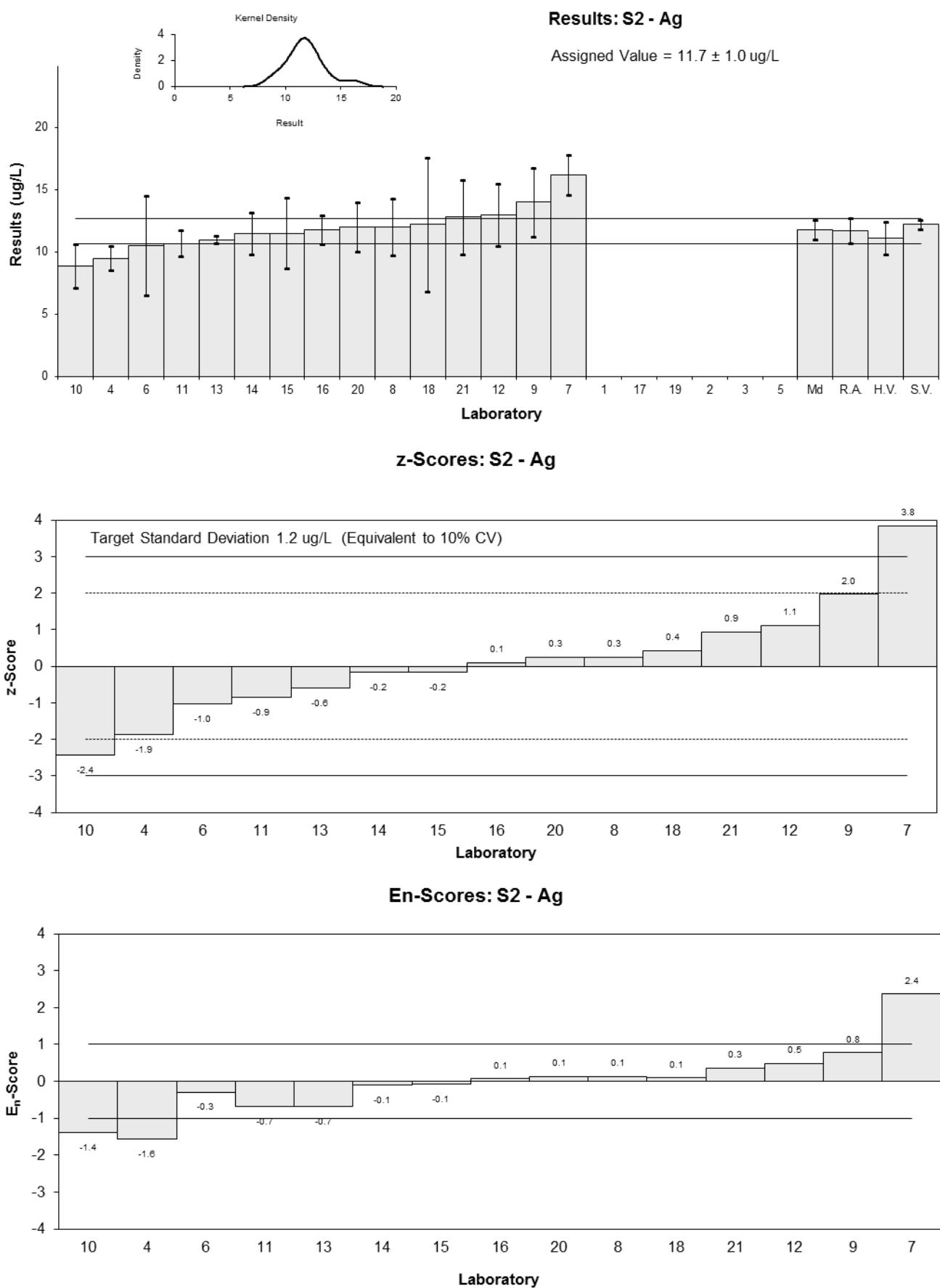


Figure 20

Table 24

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	AI
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	55	10	-0.33	-0.18
4	48.2	5.1	-1.53	-1.34
5	NT	NT		
6	63.7	10	1.20	0.63
7	<500	NT		
8	44	4.4	-2.27	-2.17
9	65	14	1.42	0.56
10	50.1	10.0	-1.20	-0.63
11	57.7	5.77	0.14	0.11
12	63	10	1.07	0.57
13	54.3	1.1	-0.46	-0.63
14	54.4	8.8	-0.44	-0.26
15	57.0	7.982	0.02	0.01
16	55.0	7.15	-0.33	-0.23
17	NT	NT		
18	60	15	0.54	0.20
19	NT	NT		
20	60	10	0.54	0.29
21	62	10	0.90	0.47

**Statistics**

<b>Assigned Value</b>	56.9	4.0
<b>Spike</b>	55.1	1.8
<b>Homogeneity Value</b>	54.3	6.5
<b>Robust Average</b>	56.9	4.0
<b>Median</b>	57.0	2.5
<b>Mean</b>	56.6	
<b>N</b>	15	
<b>Max.</b>	65	
<b>Min.</b>	44	
<b>Robust SD</b>	6.3	
<b>Robust CV</b>	11%	

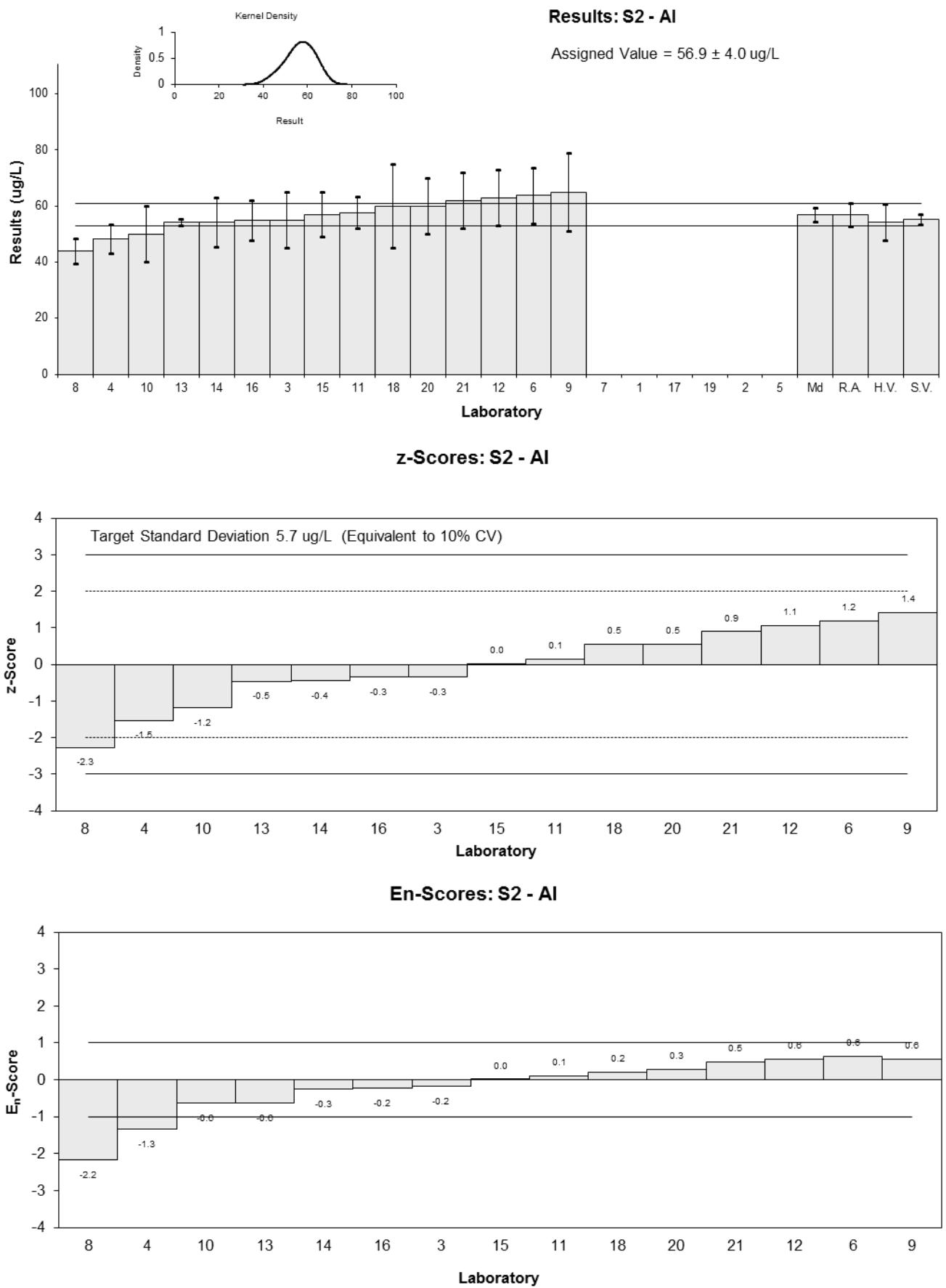


Figure 21

Table 25

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	As
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	16	5	0.26	0.08
4	16.6	2.8	0.64	0.32
5	NT	NT		
6	14.9	2	-0.45	-0.29
7	NT	NT		
8	14	2.8	-1.03	-0.52
9	18	2.2	1.54	0.94
10	14.3	2.9	-0.83	-0.41
11	15.9	1.59	0.19	0.15
12	13	3.0	-1.67	-0.80
13	13.3	2.7	-1.47	-0.77
14	15.9	3.1	0.19	0.09
15	14.6	1.557	-0.64	-0.49
16	17.6	2.34	1.28	0.75
17	NT	NT		
18	19.1	5.0	2.24	0.68
19	NT	NT		
20	NT	NT		
21	15.8	3	0.13	0.06

**Statistics**

<b>Assigned Value</b>	15.6	1.3
<b>Spike</b>	15.3	0.5
<b>Homogeneity Value</b>	14.8	1.8
<b>Robust Average</b>	15.6	1.3
<b>Median</b>	15.9	1.2
<b>Mean</b>	15.6	
<b>N</b>	14	
<b>Max.</b>	19.1	
<b>Min.</b>	13	
<b>Robust SD</b>	1.9	
<b>Robust CV</b>	12%	

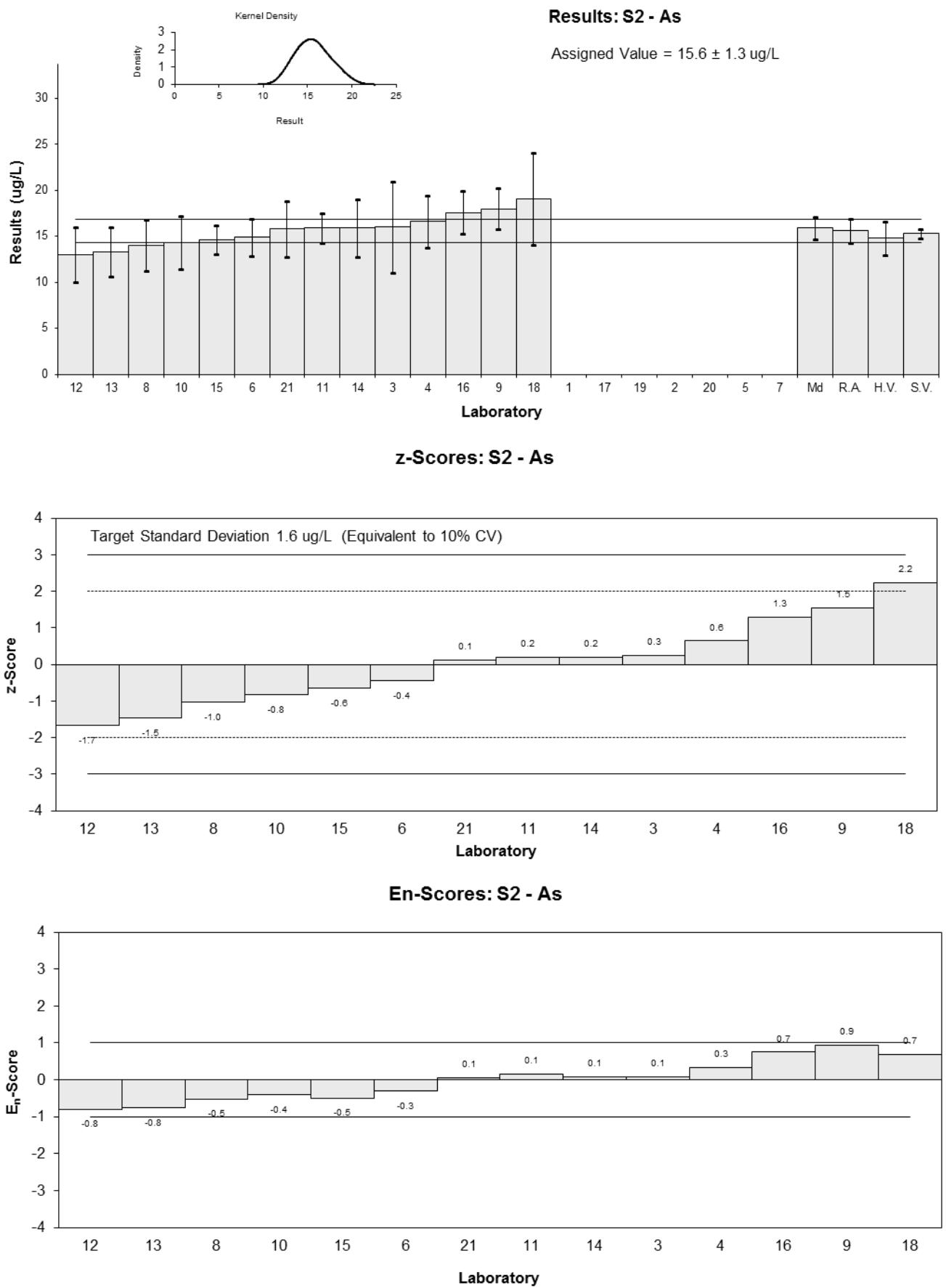


Figure 22

Table 26

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ba
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	34.9	4.0	0.33	0.26
5	NT	NT		
6	34.8	8	0.30	0.12
7	<50	NT		
8	30	6.3	-1.12	-0.59
9	42	8.9	2.43	0.91
10	33.6	6.7	-0.06	-0.03
11	33.2	3.32	-0.18	-0.16
12	35	7.0	0.36	0.17
13	33.0	0.6	-0.24	-0.50
14	36.6	4.0	0.83	0.66
15	32.0	2.875	-0.53	-0.56
16	35.5	7.1	0.50	0.23
17	NT	NT		
18	32.3	4.6	-0.44	-0.31
19	NT	NT		
20	33	3	-0.24	-0.24
21	31.5	5	-0.68	-0.44

**Statistics**

<b>Assigned Value</b>	33.8	1.5
<b>Spike</b>	32.8	1.8
<b>Homogeneity Value</b>	32.4	3.9
<b>Robust Average</b>	33.8	1.5
<b>Median</b>	33.4	1.2
<b>Mean</b>	34.1	
<b>N</b>	14	
<b>Max.</b>	42	
<b>Min.</b>	30	
<b>Robust SD</b>	2.2	
<b>Robust CV</b>	6.5%	

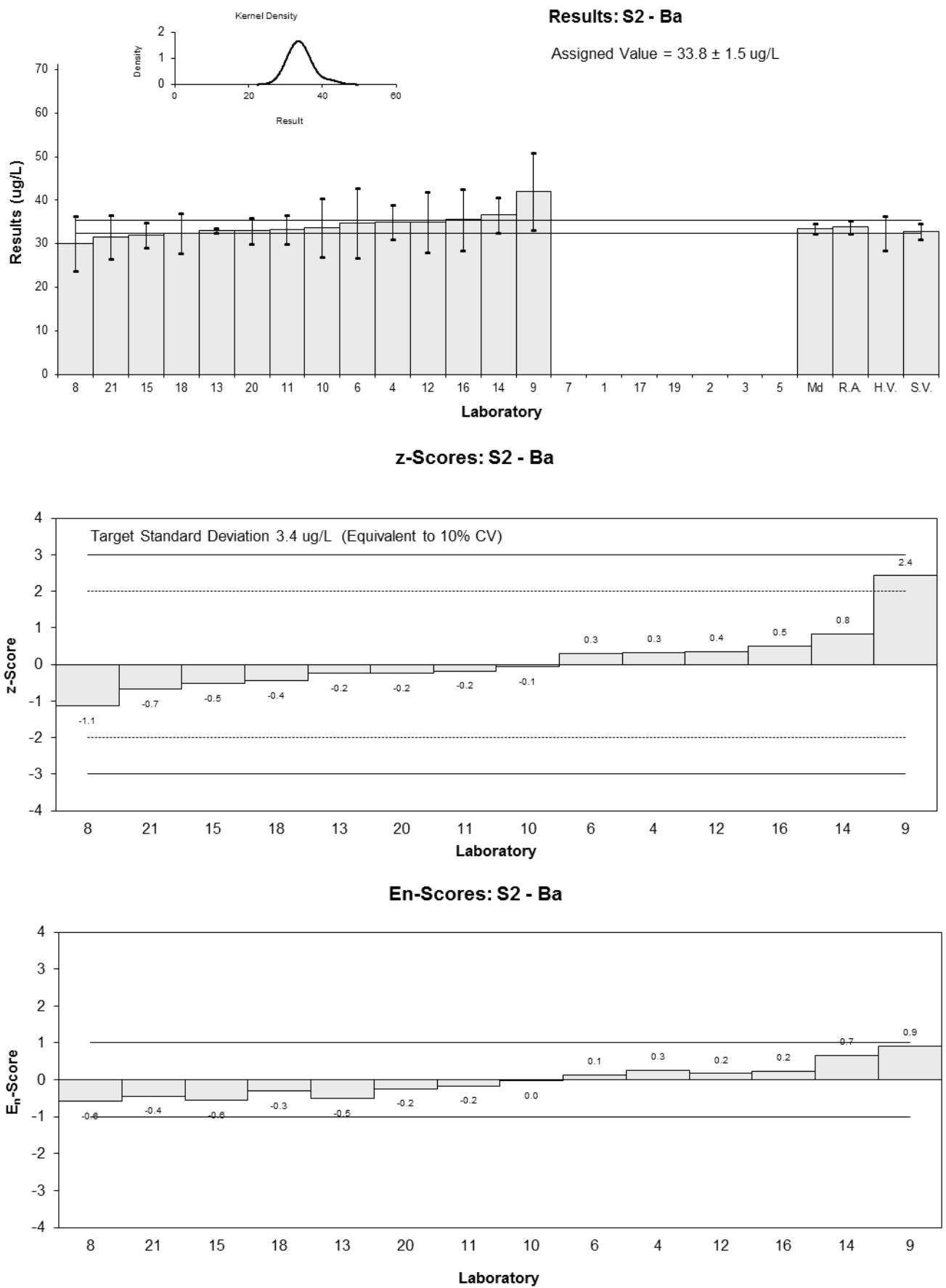


Figure 23

Table 27

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Cd
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	5	1	-0.42	-0.20
4	4.7	0.6	-1.00	-0.69
5	NT	NT		
6	4.83	1	-0.75	-0.35
7	7.65	0.77	4.66	2.71
8	5.3	0.58	0.15	0.11
9	7	1.7	3.41	1.01
10	3.85	0.77	-2.62	-1.53
11	4.56	0.456	-1.26	-1.02
12	6.2	1.0	1.88	0.89
13	4.54	0.19	-1.30	-1.37
14	5.29	1.04	0.13	0.06
15	5.4	0.603	0.34	0.24
16	5.32	0.58	0.19	0.14
17	NT	NT		
18	5.0	1.2	-0.42	-0.17
19	NT	NT		
20	5.6	1	0.73	0.35
21	5.0	0.8	-0.42	-0.24

**Statistics**

<b>Assigned Value</b>	5.22	0.46
<b>Spike</b>	5.18	0.23
<b>Homogeneity Value</b>	4.96	0.60
<b>Robust Average</b>	5.22	0.46
<b>Median</b>	5.15	0.30
<b>Mean</b>	5.33	
<b>N</b>	16	
<b>Max.</b>	7.65	
<b>Min.</b>	3.85	
<b>Robust SD</b>	0.73	
<b>Robust CV</b>	14%	

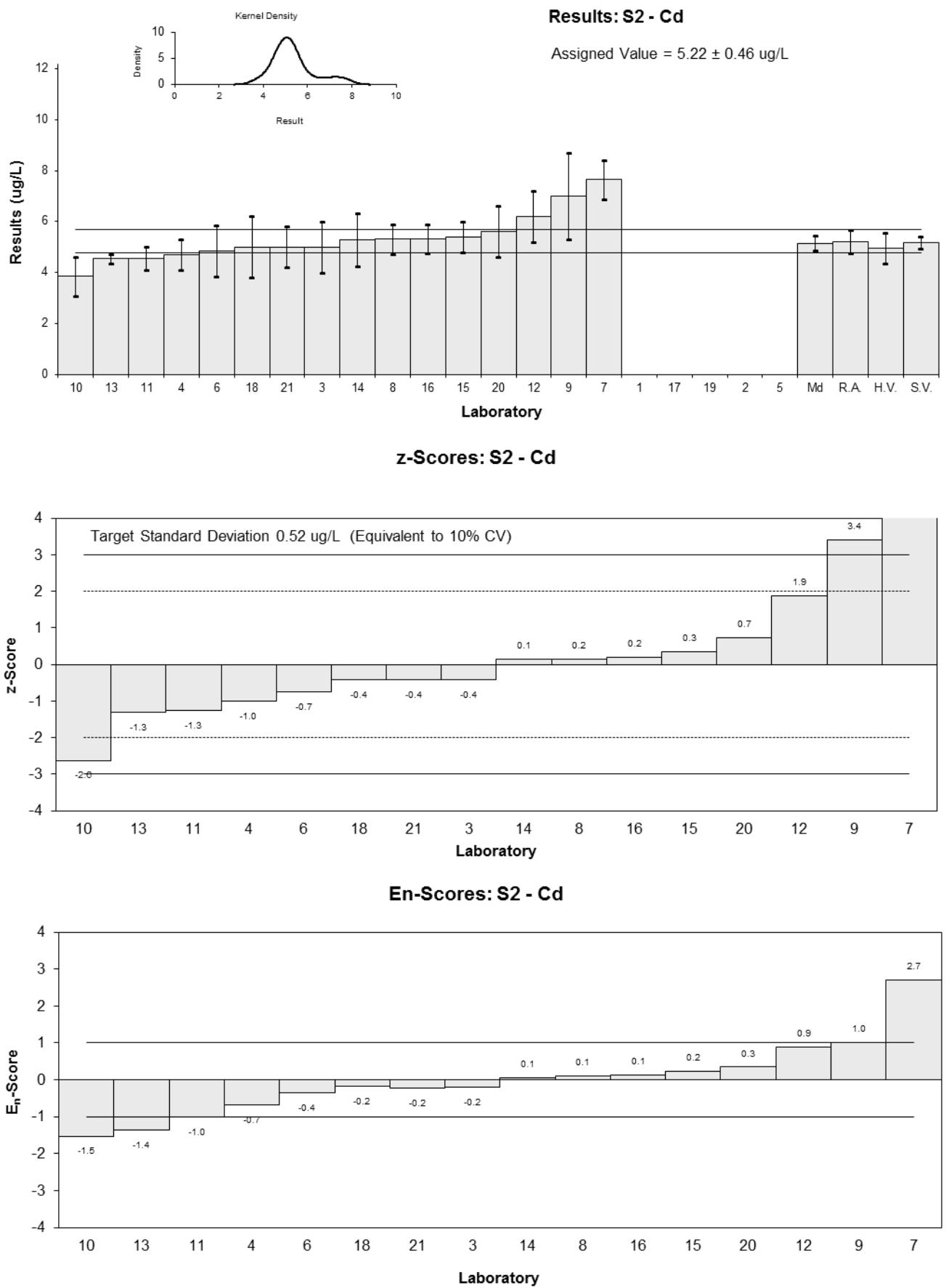


Figure 24

Table 28

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Cr
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	11	3	-1.06	-0.41
4	11.5	1.2	-0.65	-0.51
5	NT	NT		
6	11.5	2	-0.65	-0.36
7	<50	NT		
8	11	1.7	-1.06	-0.66
9	18	3.5	4.63	1.57
10	10.4	2.1	-1.54	-0.82
11	10.3	1.03	-1.63	-1.39
12	13	2.5	0.57	0.26
13	11.8	1.3	-0.41	-0.30
14	14.1	5.7	1.46	0.31
15	12.4	1.286	0.08	0.06
16	11.7	1.36	-0.49	-0.36
17	NT	NT		
18	13.1	2.5	0.65	0.30
19	NT	NT		
20	14	3	1.38	0.54
21	13.8	2.5	1.22	0.56

**Statistics**

<b>Assigned Value</b>	12.3	1.0
<b>Spike</b>	12.3	0.4
<b>Homogeneity Value</b>	12.2	1.5
<b>Robust Average</b>	12.3	1.0
<b>Median</b>	11.8	1.0
<b>Mean</b>	12.5	
<b>N</b>	15	
<b>Max.</b>	18	
<b>Min.</b>	10.3	
<b>Robust SD</b>	1.6	
<b>Robust CV</b>	13%	

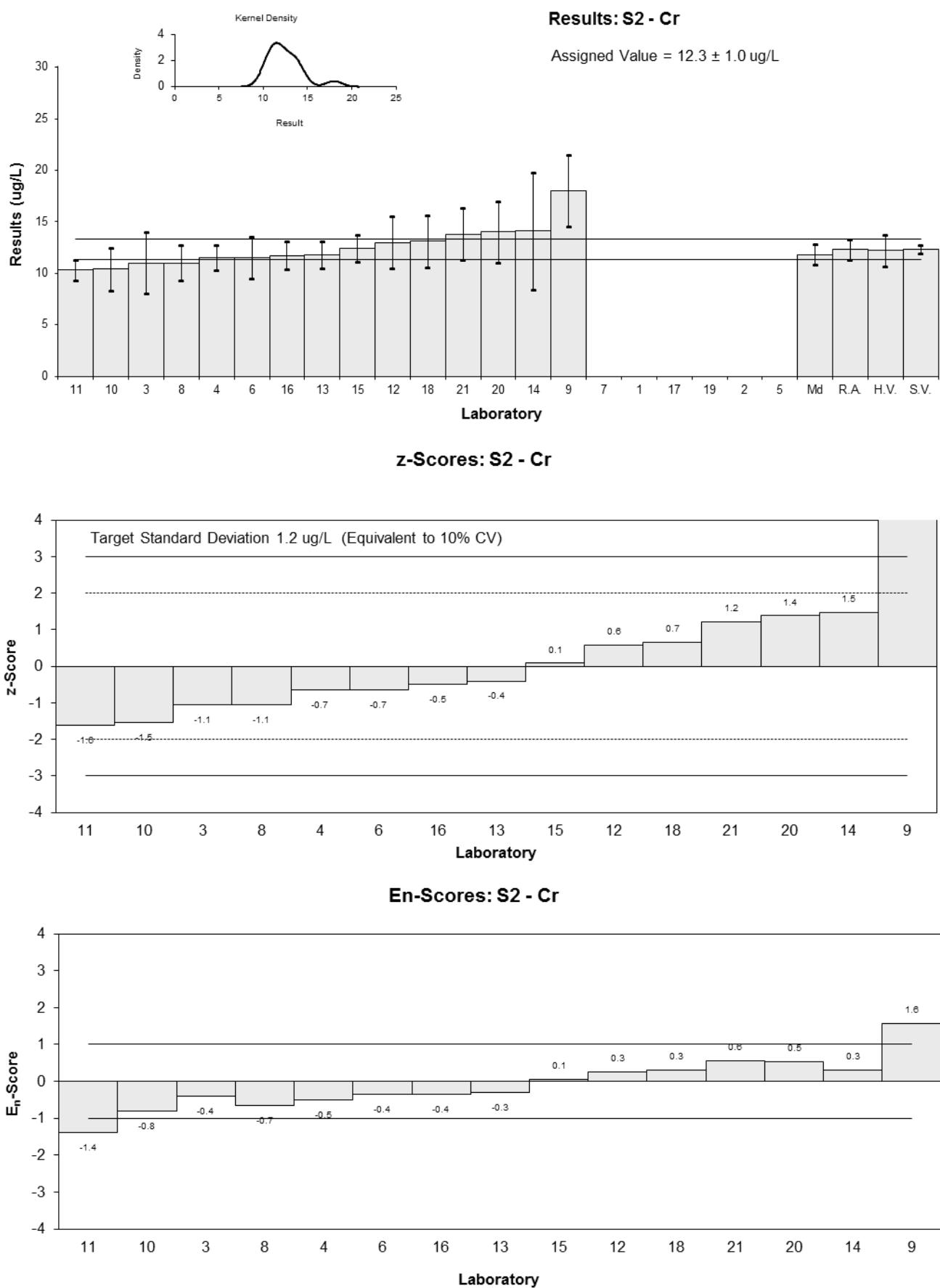


Figure 25

Table 29

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Cu
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	18	3	0.07	0.06
4	13.9	1.5	-1.46	-1.72
5	NT	NT		
6	17.5	3	-0.11	-0.09
7	<119	NT		
8	18	2	0.07	0.08
9	22	3.1	1.57	1.19
10	14.7	2.9	-1.16	-0.92
11	13.1	1.31	-1.76	-2.19
12	22	4.0	1.57	0.97
13	18.0	0.21	0.07	0.12
14	17.5	2.5	-0.11	-0.10
15	18.0	2.105	0.07	0.07
16	16.8	2.15	-0.37	-0.36
17	NT	NT		
18	18.7	4.6	0.34	0.18
19	NT	NT		
20	19	4	0.45	0.28
21	19.0	4	0.45	0.28

**Statistics**

<b>Assigned Value</b>	17.8	1.7
<b>Spike</b>	17.3	0.6
<b>Homogeneity Value</b>	17.9	2.2
<b>Robust Average</b>	17.8	1.7
<b>Median</b>	18.0	0.8
<b>Mean</b>	17.7	
<b>N</b>	15	
<b>Max.</b>	22	
<b>Min.</b>	13.1	
<b>Robust SD</b>	2.7	
<b>Robust CV</b>	15%	

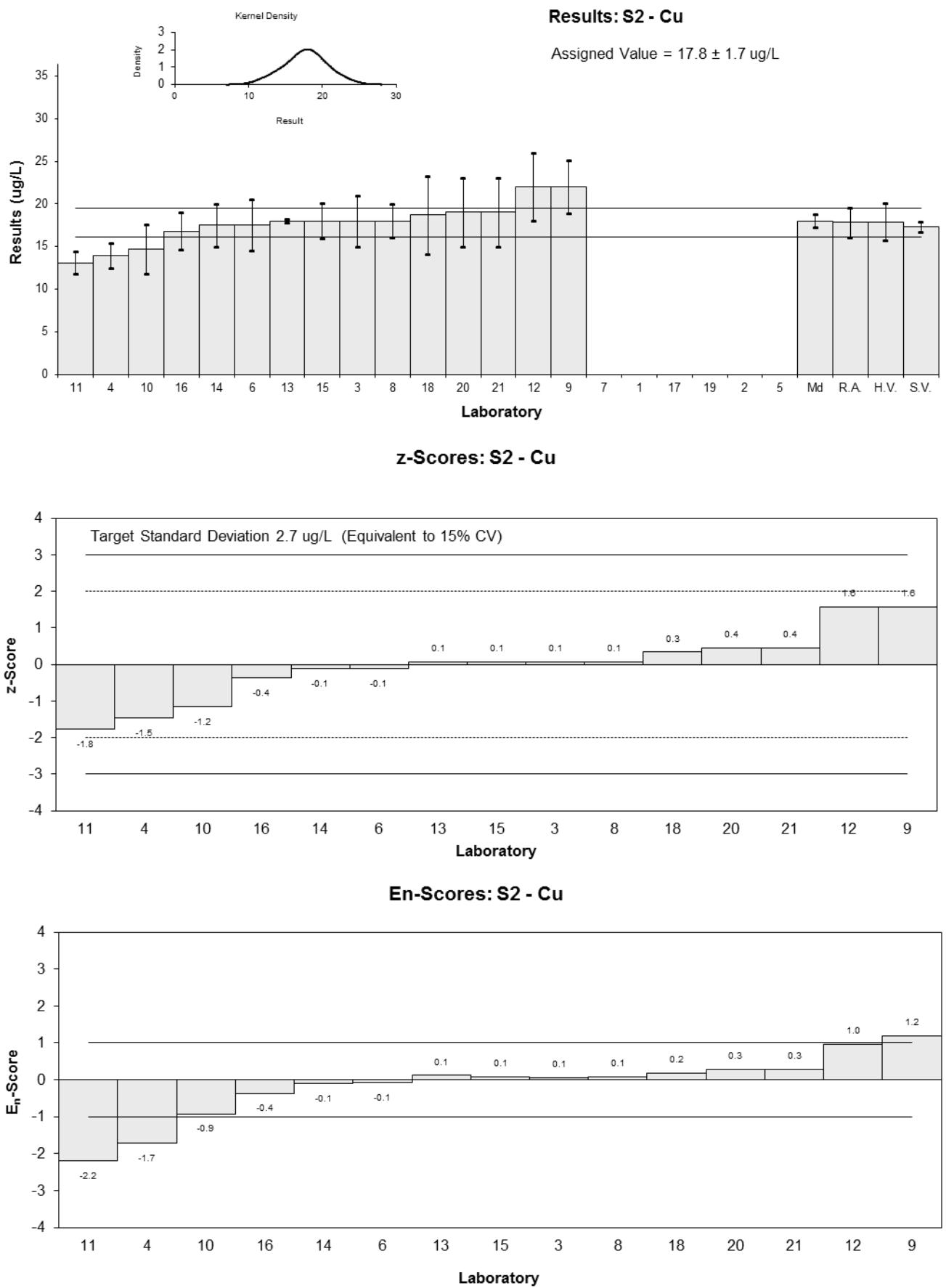


Figure 26

Table 30

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Fe
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	46	11	-1.32	-0.57
4	46.7	5.0	-1.19	-0.86
5	NT	NT		
6	52.0	10	-0.19	-0.09
7	NT	NT		
8	60	6	1.32	0.87
9	82	20	5.47	1.40
10	< 50	10		
11	<50	5		
12	52	10	-0.19	-0.09
13	51.3	0.1	-0.32	-0.32
14	58.9	13.7	1.11	0.40
15	62.0	7.685	1.70	0.96
16	<50	10		
17	NT	NT		
18	55.2	7.2	0.42	0.25
19	NT	NT		
20	<40	NR		
21	46	8	-1.32	-0.73

**Statistics**

<b>Assigned Value</b>	53.0	5.3
<b>Spike</b>	52.2	1.5
<b>Homogeneity Value</b>	54.3	6.5
<b>Robust Average</b>	54.2	5.8
<b>Median</b>	52.0	6.0
<b>Mean</b>	55.6	
<b>N</b>	11	
<b>Max.</b>	82	
<b>Min.</b>	46	
<b>Robust SD</b>	6.7	
<b>Robust CV</b>	12 %	

\*Robust Average excluding Laboratory 9.

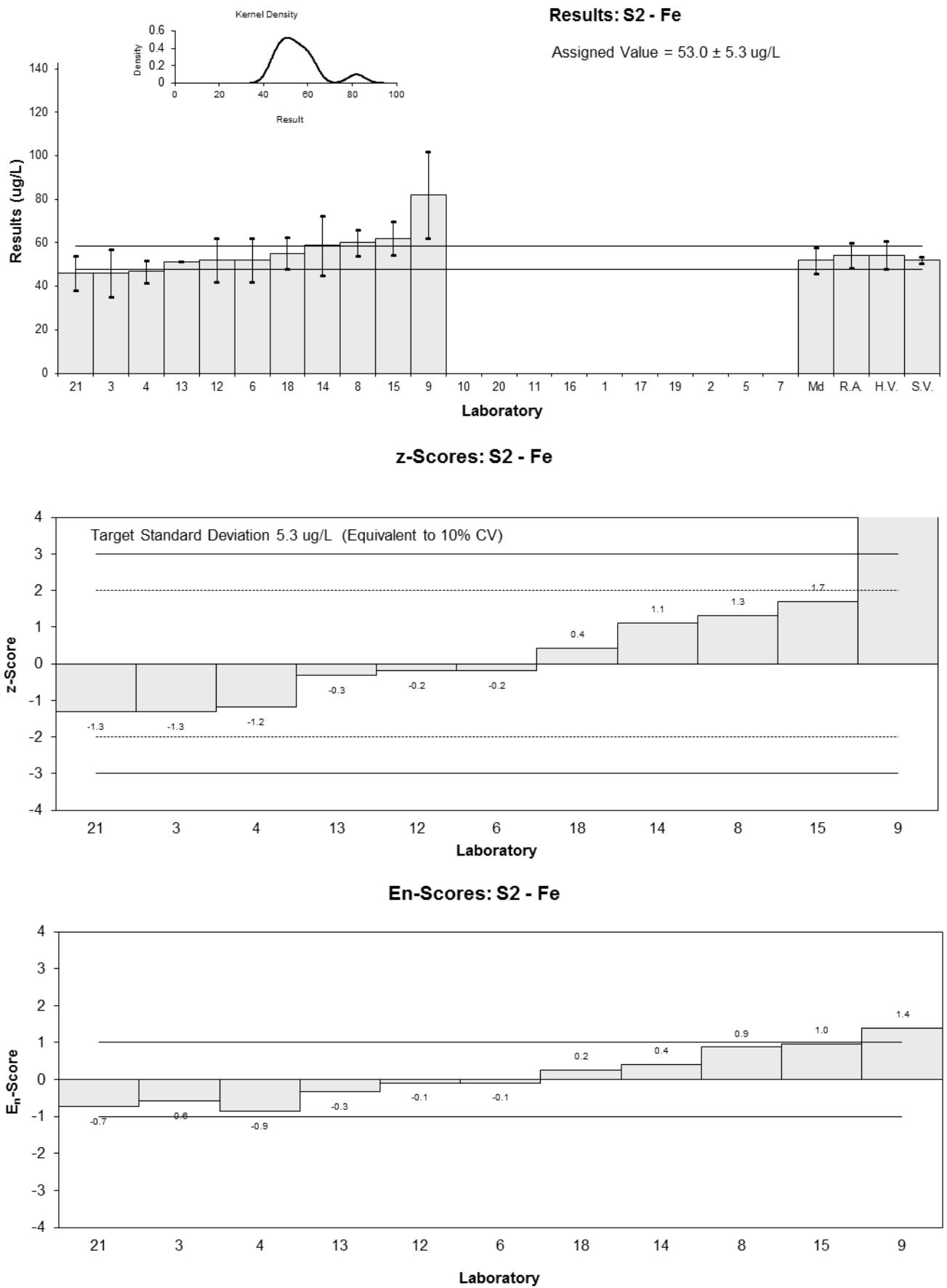


Figure 27

Table 31

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Mn
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	9	2	-1.26	-0.61
4	9.8	1.1	-0.49	-0.38
5	NT	NT		
6	9.97	2	-0.32	-0.16
7	48.5	3.39	37.09	11.04
8	8.9	1.1	-1.36	-1.07
9	12.4	2	2.04	0.99
10	10.3	2.1	0.00	0.00
11	8.36	0.836	-1.88	-1.78
12	11	2.0	0.68	0.33
13	10.2	0.16	-0.10	-0.14
14	10.6	1.4	0.29	0.19
15	10.9	1.109	0.58	0.46
16	11.0	1.19	0.68	0.51
17	NT	NT		
18	10.75	0.85	0.44	0.41
19	NT	NT		
20	11	5	0.68	0.14
21	11.0	2	0.68	0.33

**Statistics**

<b>Assigned Value</b>	10.3	0.7
<b>Spike</b>	10.5	0.7
<b>Homogeneity Value</b>	10.4	1.2
<b>Robust Average</b>	10.5	0.7
<b>Median</b>	10.7	0.3
<b>Mean</b>	12.7	
<b>N</b>	16	
<b>Max.</b>	48.5	
<b>Min.</b>	8.36	
<b>Robust SD</b>	1.0	
<b>Robust CV</b>	9.5%	

\*Robust Average excluding Laboratory 7.

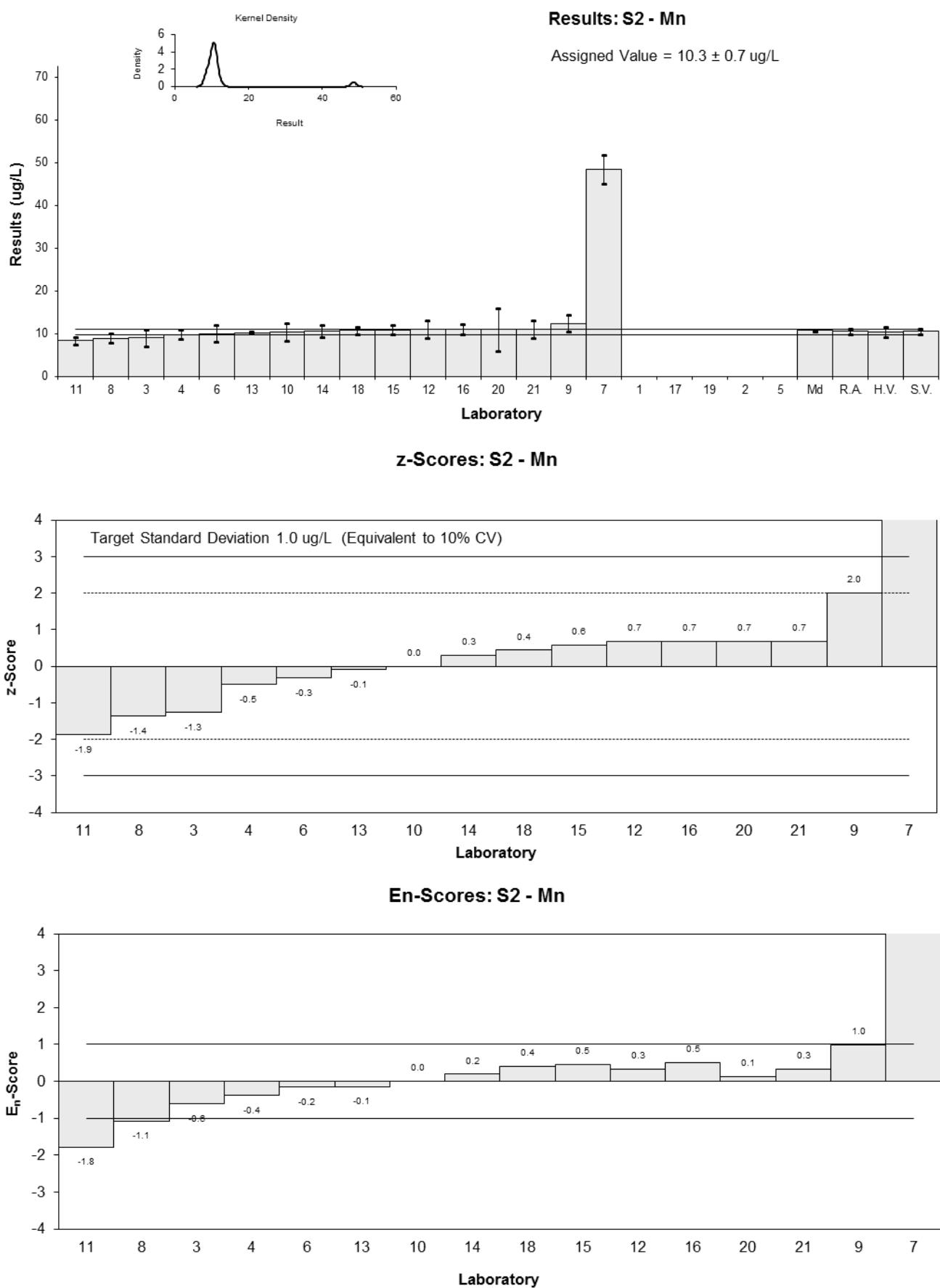


Figure 28

Table 32

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Mo
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	22	4	-2.03	-1.24
4	27.5	3.4	-0.04	-0.03
5	NT	NT		
6	30.4	8	1.01	0.34
7	24.6	1.72	-1.09	-1.11
8	25	3.3	-0.94	-0.66
9	35.5	5.7	2.86	1.30
10	21.8	4.4	-2.10	-1.19
11	29.7	2.97	0.76	0.58
12	32	7.0	1.59	0.60
13	28.2	0.6	0.22	0.27
14	26.7	3.0	-0.33	-0.25
15	26.8	2.672	-0.29	-0.24
16	29.4	4.17	0.65	0.39
17	NT	NT		
18	28.1	7.4	0.18	0.07
19	NT	NT		
20	28	4	0.14	0.09
21	27.0	4	-0.22	-0.13

**Statistics**

<b>Assigned Value</b>	27.6	2.1
<b>Spike</b>	27.6	2.5
<b>Homogeneity Value</b>	28.3	3.4
<b>Robust Average</b>	27.6	2.1
<b>Median</b>	27.8	1.4
<b>Mean</b>	27.7	
<b>N</b>	16	
<b>Max.</b>	35.5	
<b>Min.</b>	21.8	
<b>Robust SD</b>	3.3	
<b>Robust CV</b>	12%	

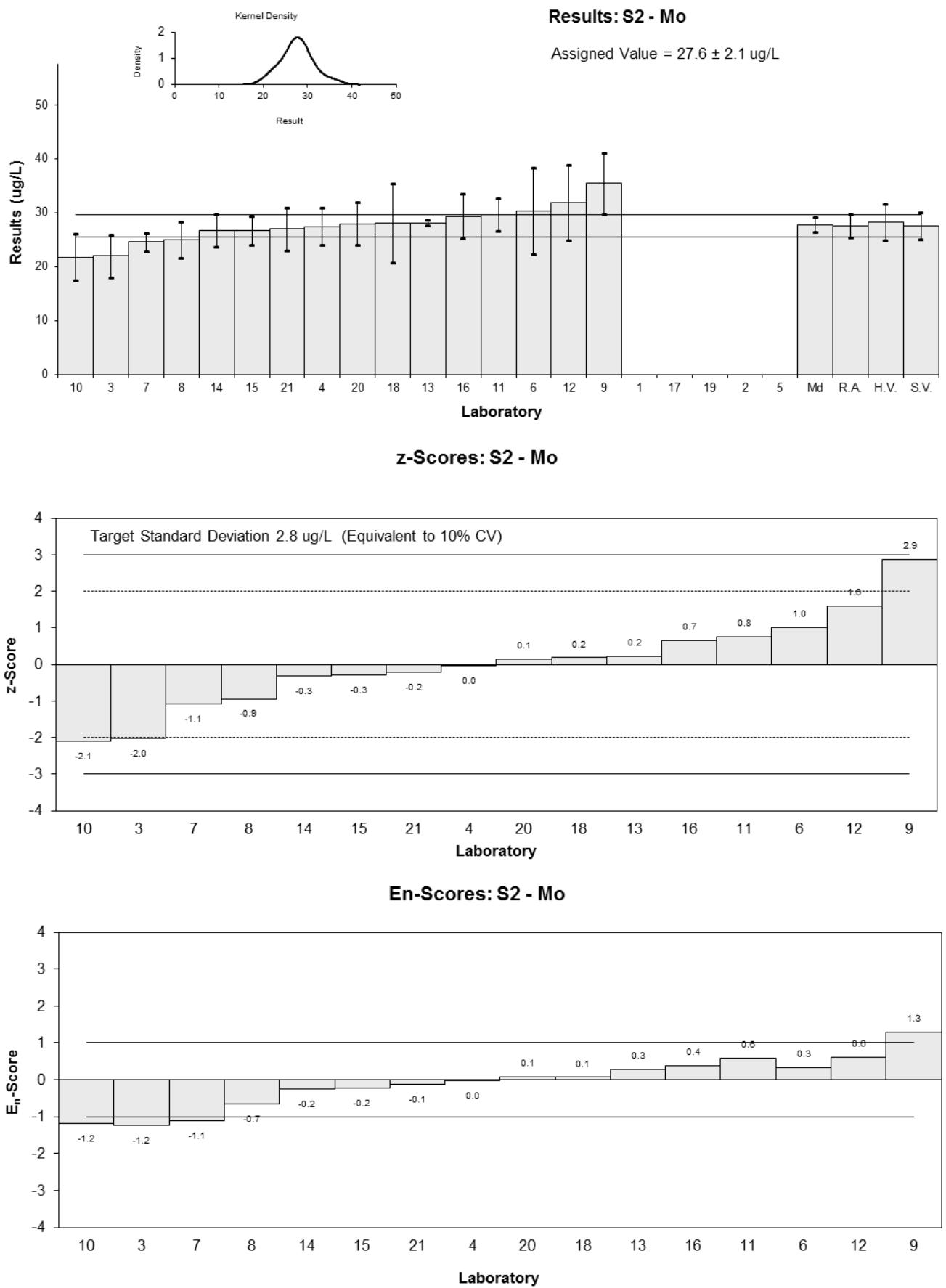


Figure 29

Table 33

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ni
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	10	3	-1.84	-1.15
4	12.3	2.5	-0.72	-0.52
5	NT	NT		
6	14.9	3	0.53	0.33
7	<89	NT		
8	14	2	0.10	0.08
9	17.5	2.5	1.79	1.29
10	12.4	2.5	-0.68	-0.49
11	10.9	1.09	-1.40	-1.63
12	15	3.0	0.58	0.36
13	14.9	0.7	0.53	0.70
14	14.5	2.7	0.34	0.23
15	16.2	1.862	1.16	1.03
16	12.7	1.56	-0.53	-0.52
17	NT	NT		
18	14.7	4.6	0.43	0.19
19	NT	NT		
20	12	3	-0.87	-0.54
21	14.9	3	0.53	0.33

**Statistics**

<b>Assigned Value</b>	13.8	1.4
<b>Spike</b>	14.5	0.4
<b>Homogeneity Value</b>	13.7	1.6
<b>Robust Average</b>	13.8	1.4
<b>Median</b>	14.5	1.4
<b>Mean</b>	13.8	
<b>N</b>	15	
<b>Max.</b>	17.5	
<b>Min.</b>	10	
<b>Robust SD</b>	2.1	
<b>Robust CV</b>	15%	

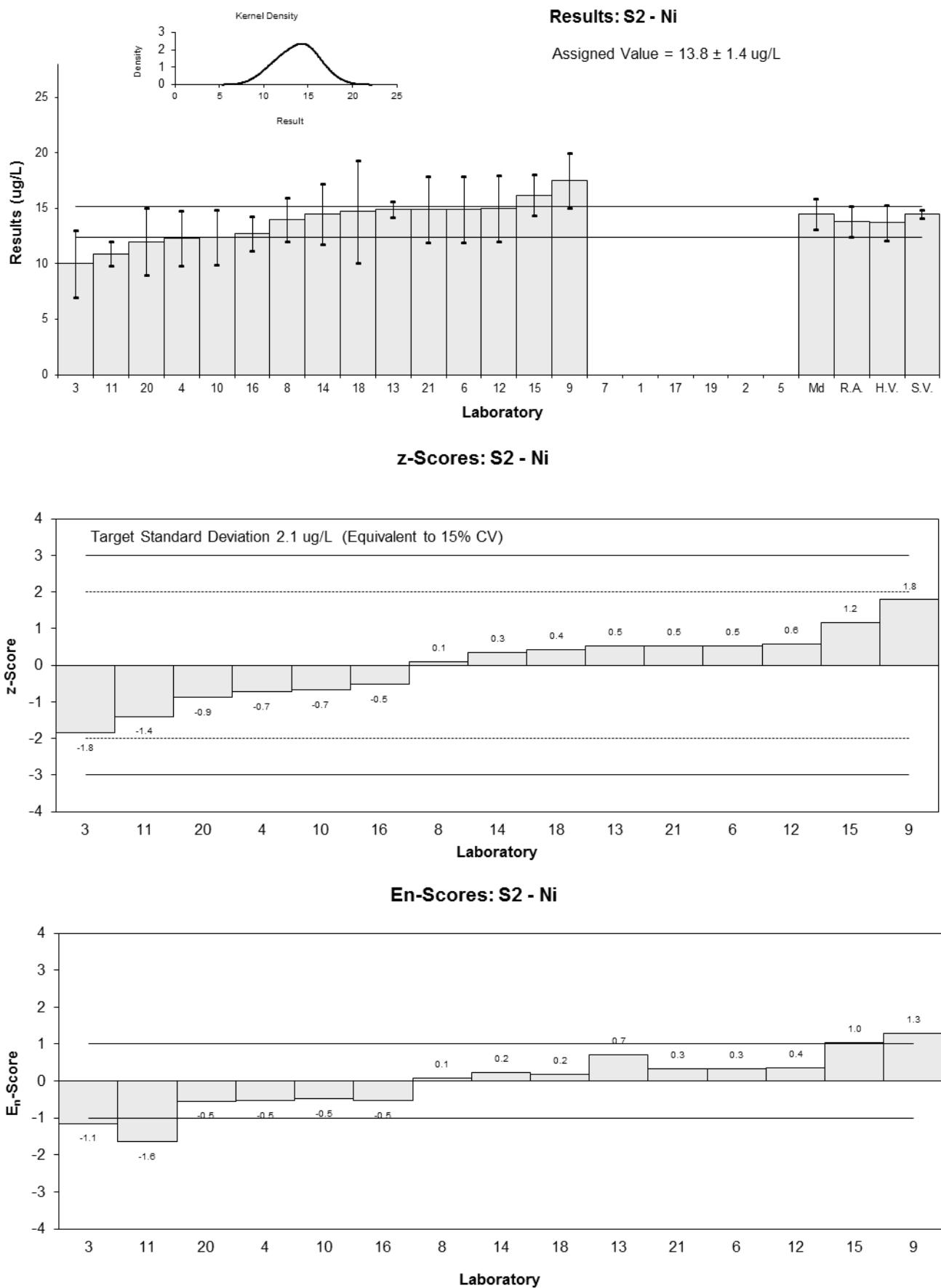


Figure 30

Table 34

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	P
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	250	50	-0.63	-0.71
4	266	49	-0.35	-0.40
5	NT	NT		
6	NT	NT		
7	<85	NT		
8	290	49	0.07	0.08
9	395	107	1.91	1.01
10	< 5000	1000		
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	385	120	1.73	0.82
15	<1000	NR		
16	328	65.6	0.73	0.63
17	NT	NT		
18	<420	NR		
19	NT	NT		
20	350	80	1.12	0.79
21	340	100	0.94	0.54

**Statistics**

<b>Assigned Value*</b>	286	10
<b>Spike</b>	272	8
<b>Homogeneity Value</b>	286	10
<b>Robust Average</b>	326	53
<b>Median</b>	334	59
<b>Mean</b>	326	
<b>N</b>	8	
<b>Max.</b>	395	
<b>Min.</b>	250	
<b>Robust SD</b>	60	
<b>Robust CV</b>	18%	

\*Reference Value by standard addition ICP-MS.

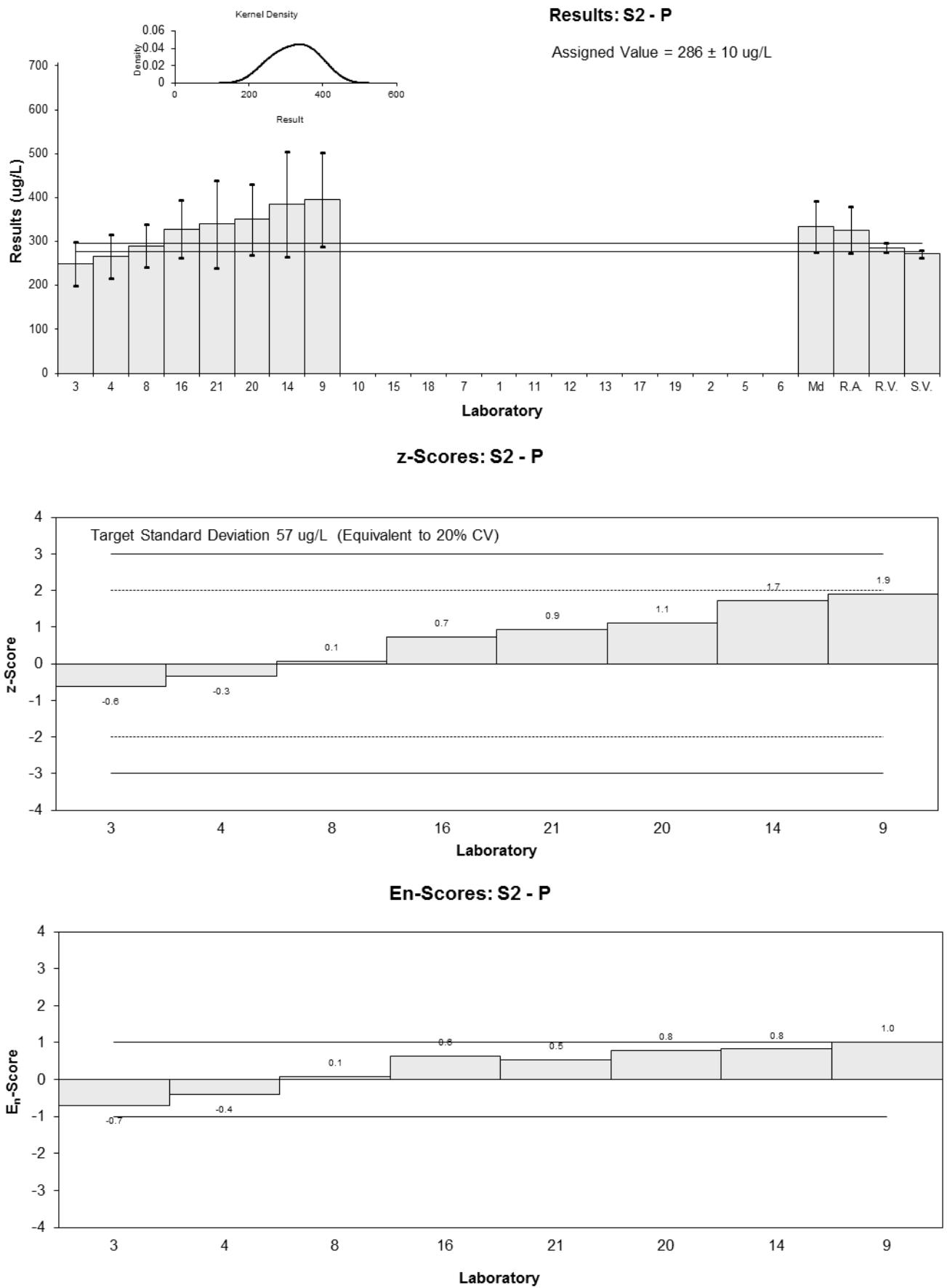


Figure 31

Table 35

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Pb
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NT	NT		
2	NT	NT		
3	<10	NR		
4	4.6	0.6	-0.98	-0.70
5	NT	NT		
6	5.29	1	0.37	0.18
7	NT	NT		
8	5.3	1.2	0.39	0.16
9	7	1.4	3.73	1.31
10	4.18	0.84	-1.80	-1.00
11	4.26	0.426	-1.65	-1.47
12	5.8	1.0	1.37	0.65
13	5.39	0.06	0.57	0.75
14	5.29	0.87	0.37	0.20
15	4.9	0.488	-0.39	-0.32
16	5.34	0.70	0.47	0.30
17	NT	NT		
18	5.1	1.4	0.00	0.00
19	NT	NT		
20	5	2	-0.20	-0.05
21	4.9	1	-0.39	-0.19

**Statistics**

<b>Assigned Value</b>	5.10	0.38
<b>Spike</b>	5.22	0.15
<b>Homogeneity Value</b>	5.51	0.66
<b>Robust Average</b>	5.10	0.38
<b>Median</b>	5.20	0.21
<b>Mean</b>	5.17	
<b>N</b>	14	
<b>Max.</b>	7	
<b>Min.</b>	4.18	
<b>Robust SD</b>	0.56	
<b>Robust CV</b>	11%	

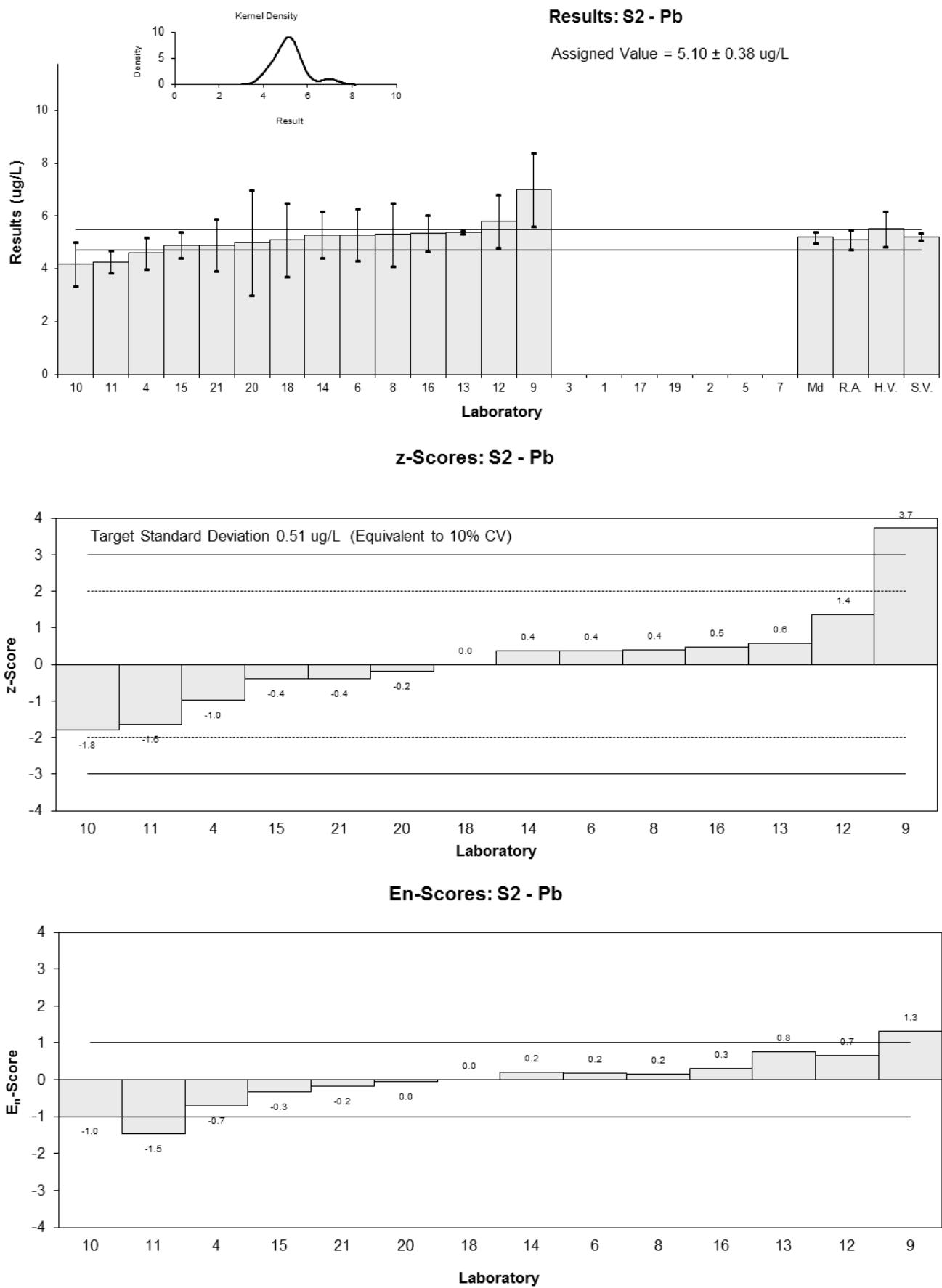


Figure 32

Table 36

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Sb
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	18.0	2.3	0.29	0.19
5	NT	NT		
6	17.7	4	0.11	0.05
7	NT	NT		
8	16	2.6	-0.86	-0.52
9	20.6	2.9	1.77	0.98
10	15.0	3.0	-1.43	-0.76
11	15.8	1.58	-0.97	-0.83
12	19	4.0	0.86	0.36
13	NT	NT		
14	15.6	5.6	-1.09	-0.33
15	18.2	0.100	0.40	0.54
16	19.2	3.84	0.97	0.42
17	NT	NT		
18	18.5	8.9	0.57	0.11
19	NT	NT		
20	16	2	-0.86	-0.63
21	18	3	0.29	0.15

**Statistics**

<b>Assigned Value</b>	17.5	1.3
<b>Spike</b>	15.7	0.4
<b>Homogeneity Value</b>	18.1	2.2
<b>Robust Average</b>	17.5	1.3
<b>Median</b>	18.0	1.1
<b>Mean</b>	17.5	
<b>N</b>	13	
<b>Max.</b>	20.6	
<b>Min.</b>	15	
<b>Robust SD</b>	1.9	
<b>Robust CV</b>	11%	

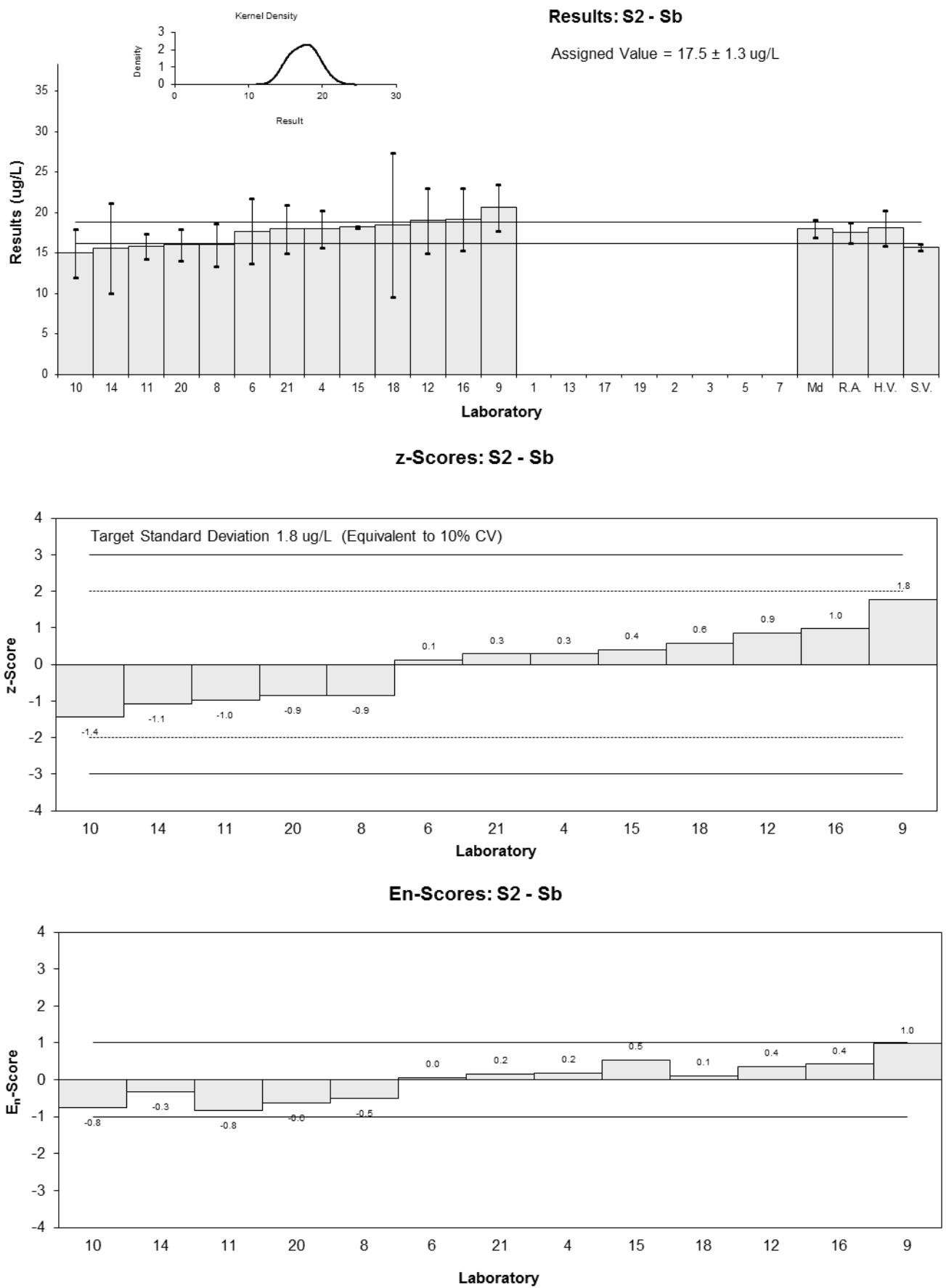


Figure 33

Table 37

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Se
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	<20	NR		
4	11.2	1.2	-0.39	-0.38
5	NT	NT		
6	13.3	3	0.78	0.42
7	NT	NT		
8	13	2.5	0.62	0.38
9	16	2.4	2.30	1.48
10	10.0	2.0	-1.06	-0.78
11	9.47	0.947	-1.36	-1.44
12	12	2.5	0.06	0.03
13	9.07	0.33	-1.59	-1.97
14	11.5	3.2	-0.22	-0.11
15	13.0	1.657	0.62	0.51
16	10.2	2.04	-0.95	-0.69
17	NT	NT		
18	12.6	6.2	0.39	0.11
19	NT	NT		
20	11	2	-0.50	-0.37
21	14.8	3	1.62	0.88

**Statistics**

<b>Assigned Value</b>	11.9	1.4
<b>Spike</b>	12.0	0.3
<b>Homogeneity Value</b>	13.2	1.6
<b>Robust Average</b>	11.9	1.4
<b>Median</b>	11.8	1.2
<b>Mean</b>	11.9	
<b>N</b>	14	
<b>Max.</b>	16	
<b>Min.</b>	9.07	
<b>Robust SD</b>	2.1	
<b>Robust CV</b>	18%	

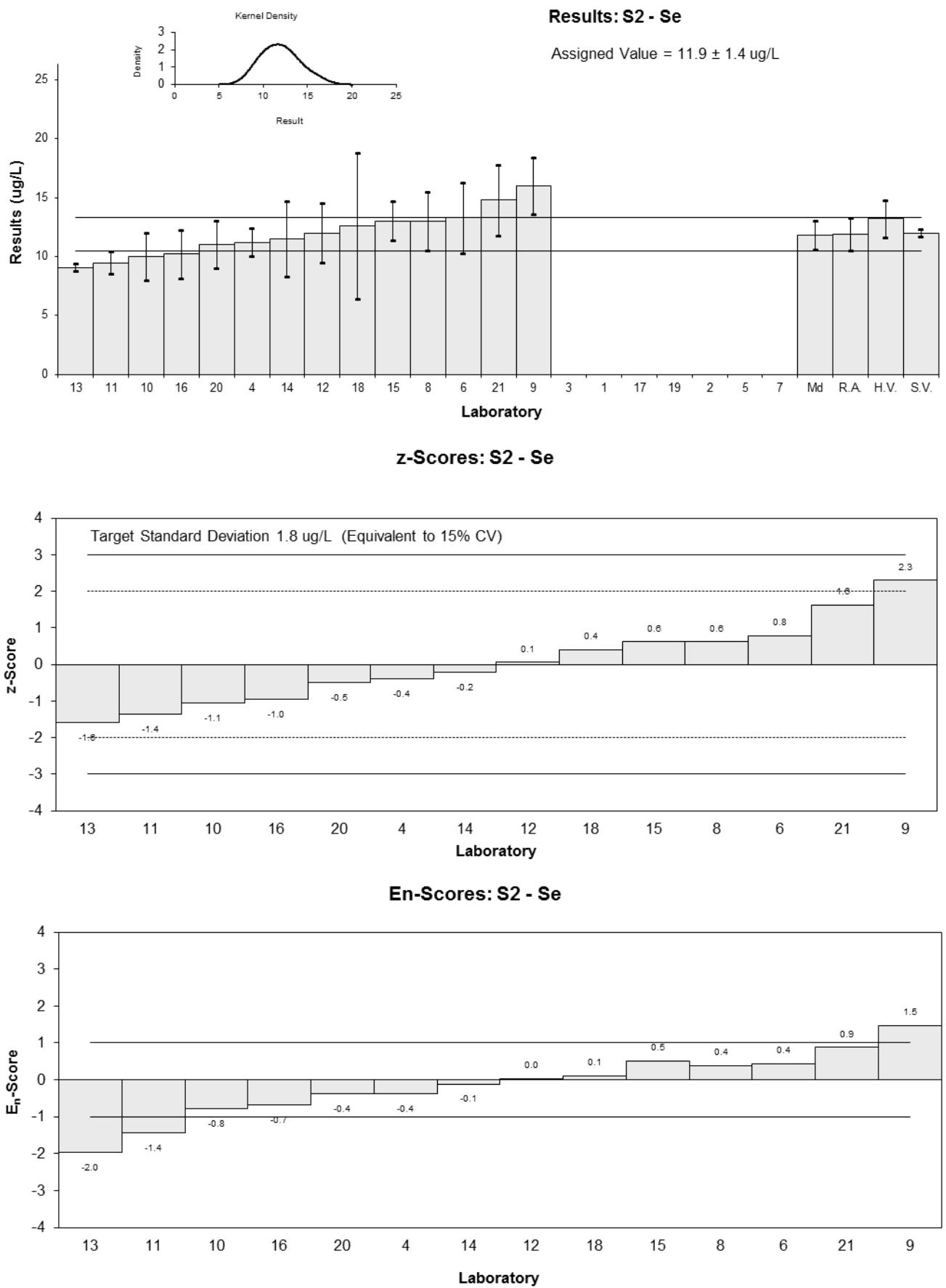


Figure 34

Table 38

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Sn
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	<10	NR		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	7.2	1.2	0.06	0.03
9	8.1	1.2	1.31	0.74
10	6.89	1.38	-0.38	-0.19
11	7.6	0.76	0.61	0.50
12	NT	NT		
13	6.77	0.01	-0.54	-0.91
14	6.62	1.75	-0.75	-0.30
15	8.0	0.810	1.17	0.92
16	6.62	1.32	-0.75	-0.39
17	NT	NT		
18	7.1	2.4	-0.08	-0.02
19	NT	NT		
20	7	4	-0.22	-0.04
21	7	5	-0.22	-0.03

**Statistics**

<b>Assigned Value</b>	7.16	0.43
<b>Spike</b>	7.40	0.21
<b>Homogeneity Value</b>	7.46	0.90
<b>Robust Average</b>	7.16	0.43
<b>Median</b>	7.00	0.23
<b>Mean</b>	7.17	
<b>N</b>	11	
<b>Max.</b>	8.1	
<b>Min.</b>	6.62	
<b>Robust SD</b>	0.57	
<b>Robust CV</b>	8%	

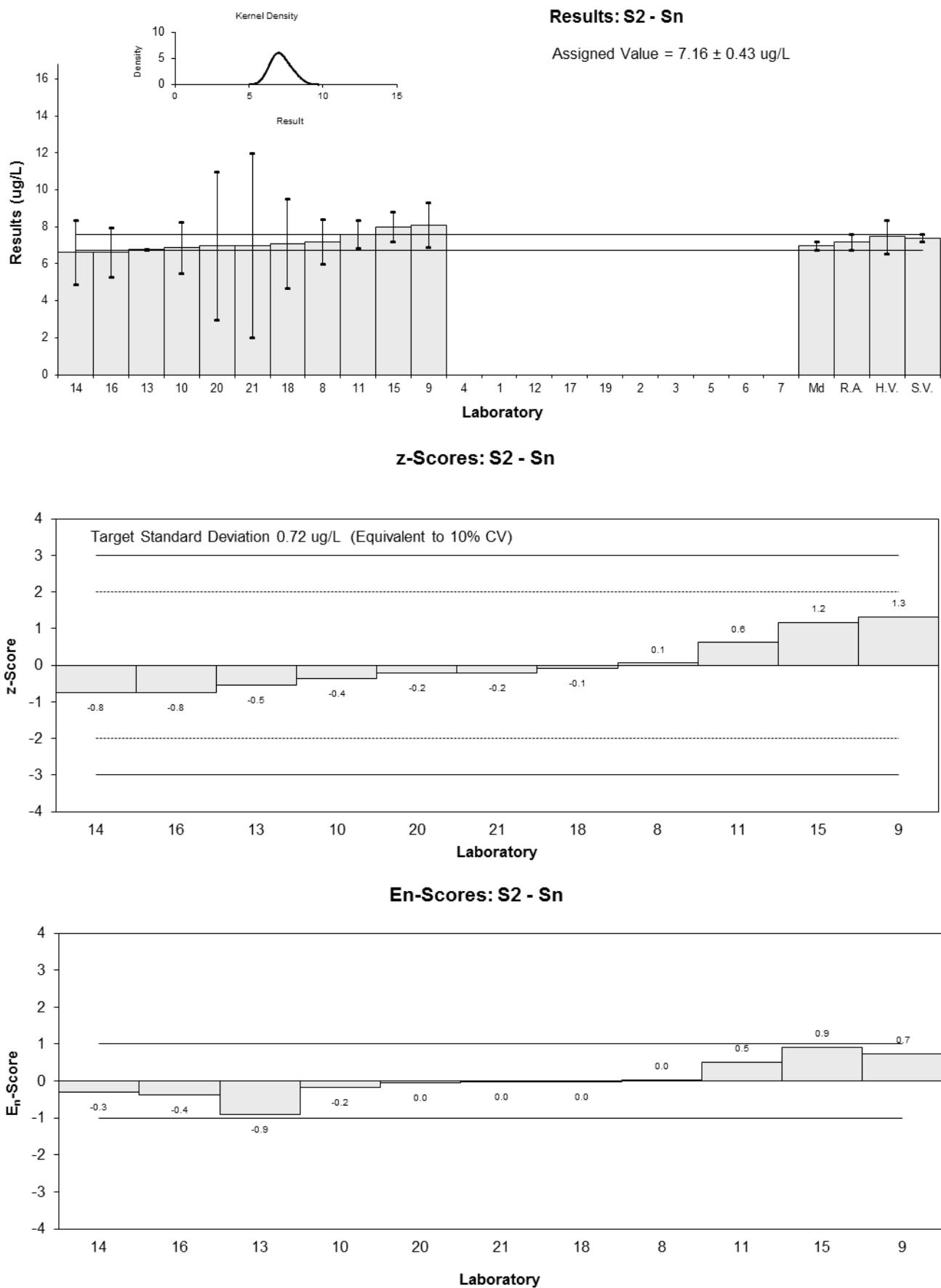


Figure 35

Table 39

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	V
<b>Units</b>	ug/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	NT	NT		
4	15.1	1.7	-0.07	-0.05
5	NT	NT		
6	14.7	3	-0.33	-0.15
7	<52	NT		
8	14	2.2	-0.79	-0.48
9	20.1	3.5	3.22	1.32
10	12.9	2.6	-1.51	-0.80
11	12.9	1.29	-1.51	-1.31
12	17	3.0	1.18	0.56
13	14.8	1.8	-0.26	-0.18
14	17.1	2.6	1.25	0.66
15	16.3	1.454	0.72	0.58
16	13.9	1.67	-0.86	-0.63
17	NT	NT		
18	14.6	7.7	-0.39	-0.08
19	NT	NT		
20	16	3	0.53	0.25
21	16	3.5	0.53	0.22

**Statistics**

<b>Assigned Value</b>	15.2	1.2
<b>Spike</b>	15.2	0.6
<b>Homogeneity Value</b>	15.5	1.9
<b>Robust Average</b>	15.2	1.2
<b>Median</b>	15.0	0.9
<b>Mean</b>	15.4	
<b>N</b>	14	
<b>Max.</b>	20.1	
<b>Min.</b>	12.9	
<b>Robust SD</b>	1.7	
<b>Robust CV</b>	11%	

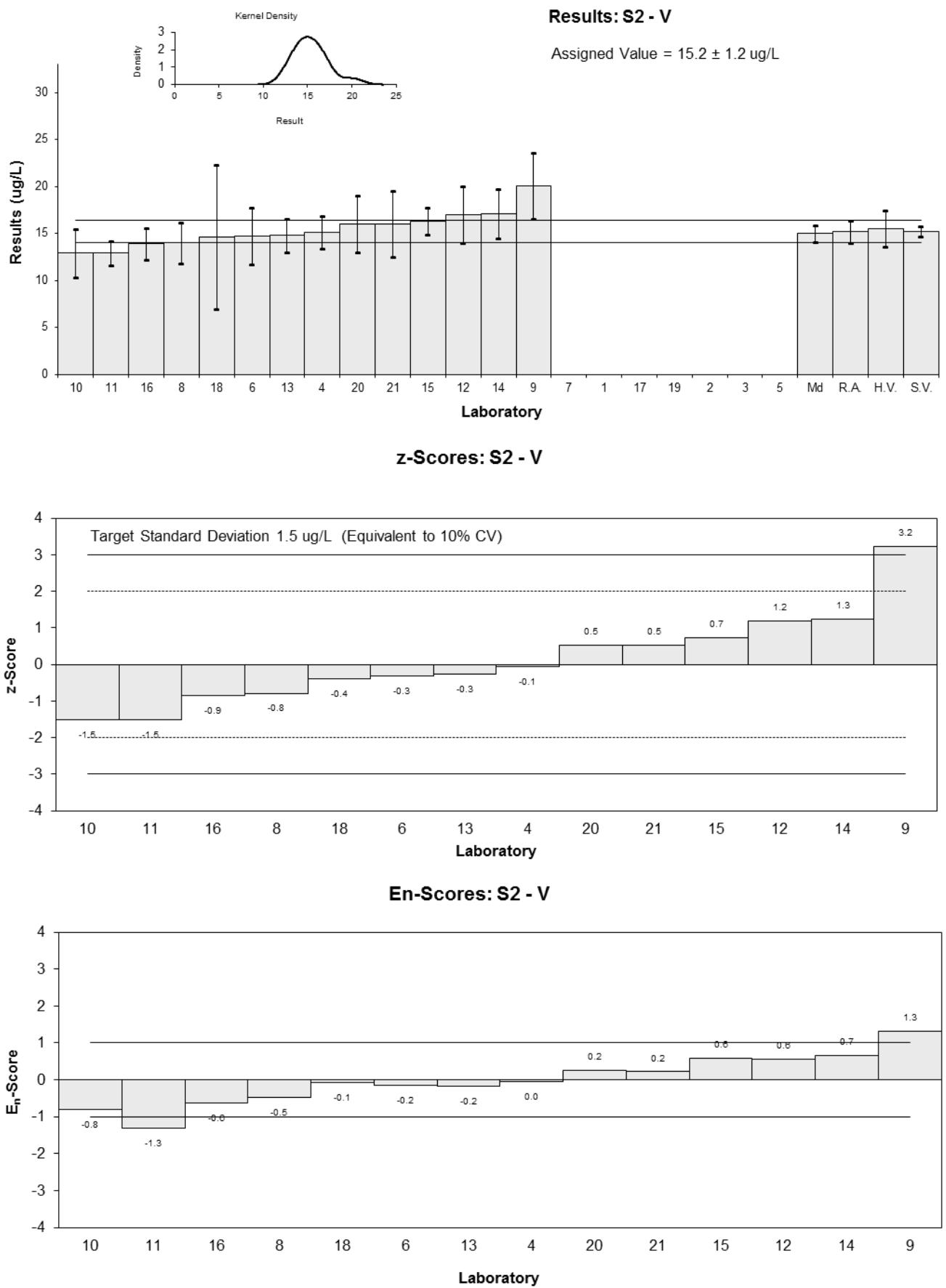


Figure 36

Table 40

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Zn
<b>Units</b>	ug/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NT	NT		
2	NT	NT		
3	30	8	-1.55	-0.64
4	36.6	4.6	0.31	0.20
5	NT	NT		
6	36.9	10	0.39	0.13
7	<50	NT		
8	34	6.5	-0.42	-0.21
9	44	5.8	2.39	1.28
10	29.4	5.9	-1.72	-0.91
11	16.6	1.66	-5.32	-5.24
12	35	7.0	-0.14	-0.06
13	33.6	2.2	-0.54	-0.49
14	38.6	5.7	0.87	0.47
15	37.0	4.247	0.42	0.28
16	28.3	3.38	-2.03	-1.55
17	NT	NT		
18	40.6	7.1	1.44	0.65
19	NT	NT		
20	39	9	0.99	0.37
21	35	6	-0.14	-0.07

**Statistics**

<b>Assigned Value*</b>	35.5	3.2
<b>Spike</b>	34.8	1.0
<b>Homogeneity Value</b>	34.2	4.1
<b>Robust Average</b>	34.9	3.4
<b>Median</b>	35.0	3.0
<b>Mean</b>	34.3	
<b>N</b>	15	
<b>Max.</b>	44	
<b>Min.</b>	16.6	
<b>Robust SD</b>	4.800	
<b>Robust CV</b>	13.8%	

\*Robust Average excluding Laboratory 11.

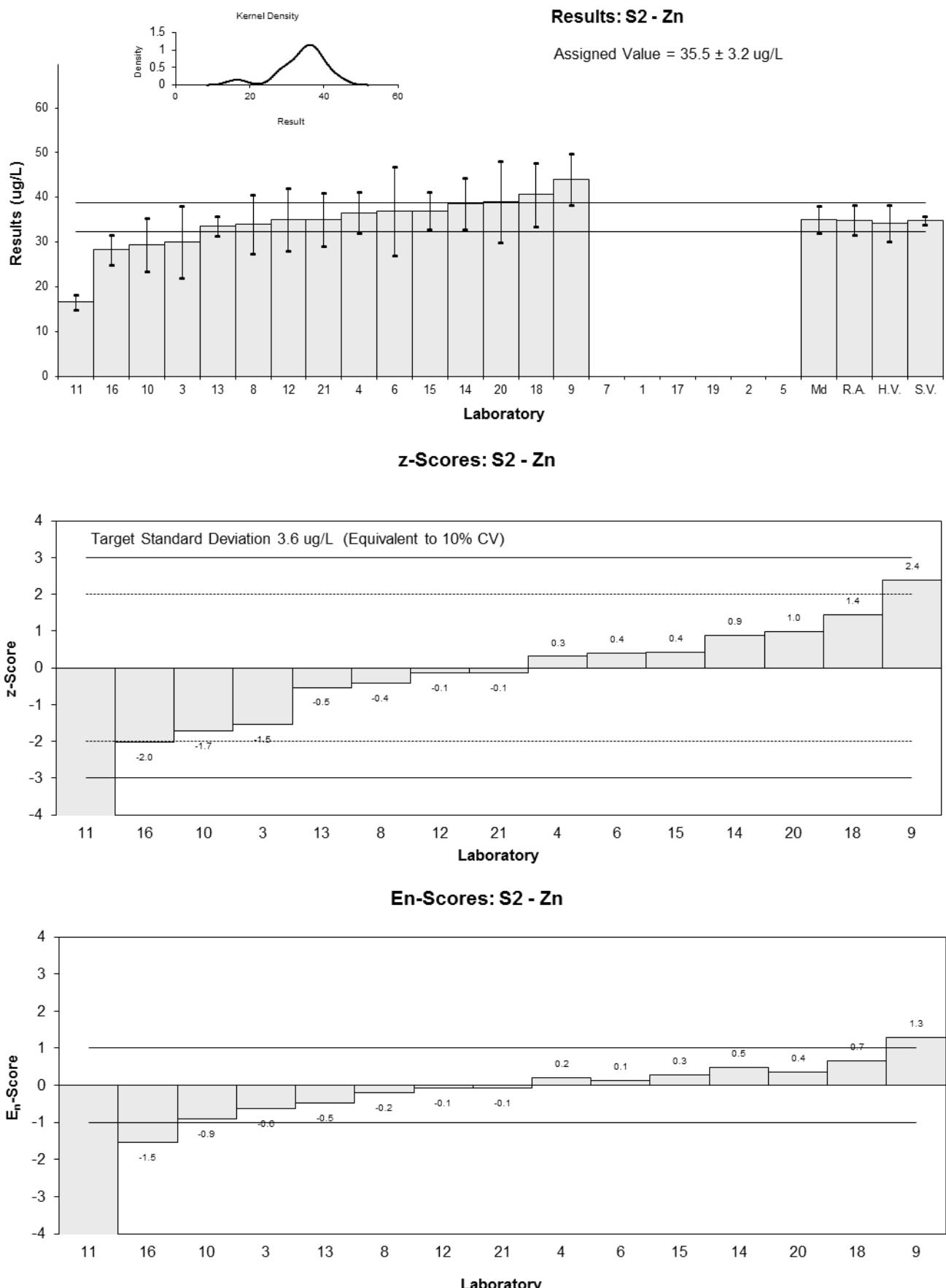


Figure 37

Table 41

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ammonia-N
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.109	0.015	0.14	0.16
2	0.13	0.05	1.13	0.47
3	0.099	0.015	-0.33	-0.38
4	0.10	0.02	-0.28	-0.26
5	0.26	NR	7.26	14.00
6	NT	NT		
7	NT	NT		
8	0.096	0.02	-0.47	-0.44
9	0.119	0.030	0.61	0.41
10	0.0884	0.01	-0.83	-1.18
11	NT	NT		
12	0.108	0.01	0.09	0.13
13	NT	NT		
14	NT	NT		
15	0.063	0.0248	-2.03	-1.58
16	0.108	0.0123	0.09	0.12
17	0.102	0.006	-0.19	-0.32
18	NT	NT		
19	0.105	0.005	-0.05	-0.08
20	NT	NT		
21	0.139	0.01	1.56	2.22

**Statistics**

<b>Assigned Value*</b>	0.106	0.011
<b>Spike**</b>	0.079	0.003
<b>Homogeneity Value</b>	0.094	0.019
<b>Robust Average</b>	0.109	0.013
<b>Median</b>	0.107	0.008
<b>Mean</b>	0.116	
<b>N</b>	14	
<b>Max.</b>	0.26	
<b>Min.</b>	0.063	
<b>Robust SD</b>	0.016	
<b>Robust CV</b>	15%	

\*Robust Average excluding Laboratory 5. \*\*Incurred value not included.

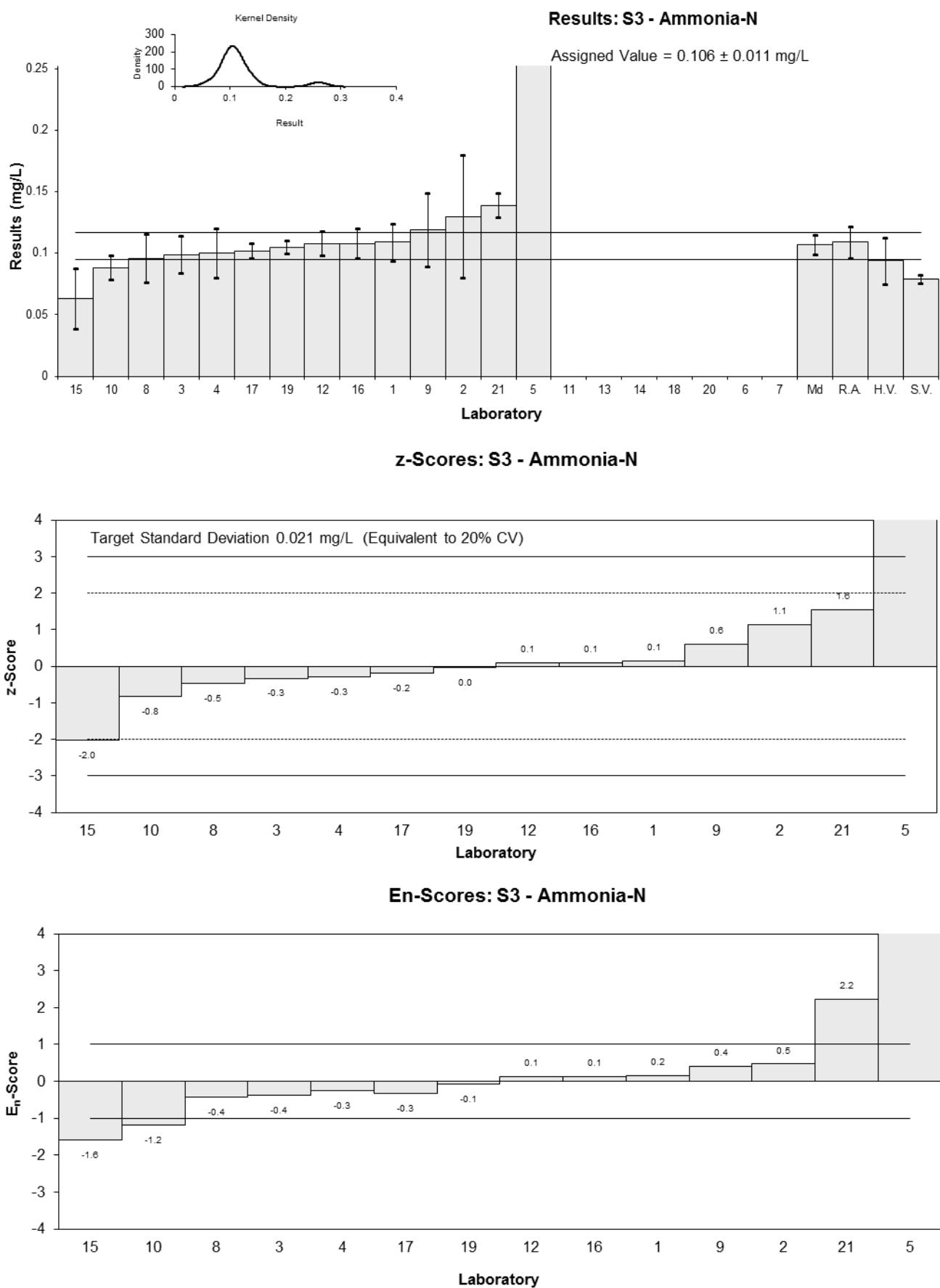


Figure 38

Table 42

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Chloride
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	17500	2100	0.12	0.08
2	17001	2800	-0.17	-0.09
3	NT	NT		
4	15800	1100	-0.87	-0.77
5	17250	NR	-0.03	-0.03
6	NT	NT		
7	NT	NT		
8	20000	3000	1.56	0.79
9	13900	2085	-1.97	-1.29
10	18550	2838	0.72	0.38
11	NT	NT		
12	16600	1600	-0.40	-0.31
13	NT	NT		
14	NT	NT		
15	20100	2912.7	1.62	0.84
16	19300	1130	1.16	1.02
17	17100	700	-0.12	-0.11
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	14600	1500	-1.56	-1.23

**Statistics**

<b>Assigned Value</b>	17300	1600
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	17000	900
<b>Robust Average</b>	17300	1600
<b>Median</b>	17200	1300
<b>Mean</b>	17300	
<b>N</b>	12	
<b>Max.</b>	20100	
<b>Min.</b>	13900	
<b>Robust SD</b>	2200	
<b>Robust CV</b>	13%	

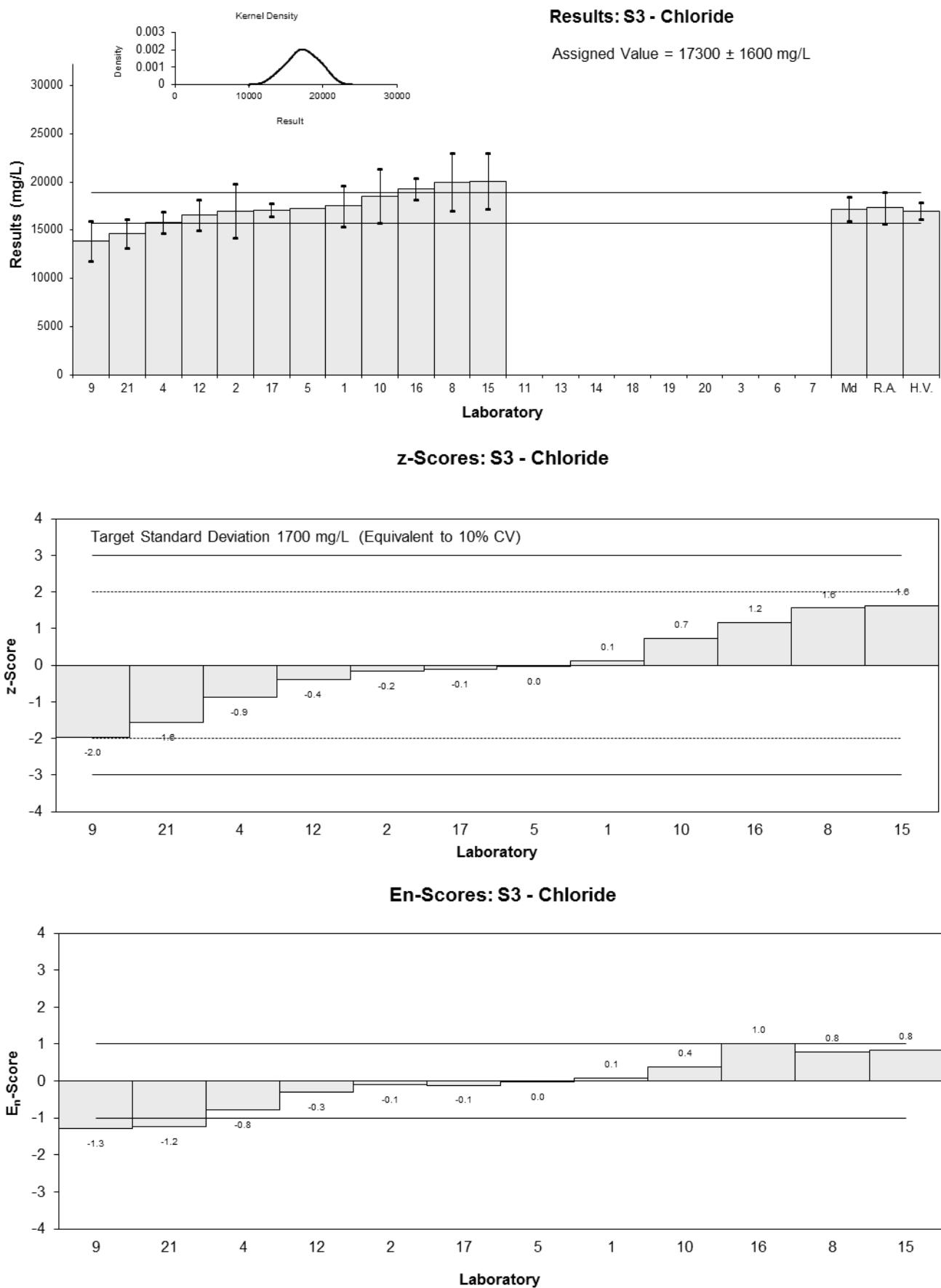


Figure 39

Table 43

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	DOC
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	4.01	0.61	-0.05	-0.03
2	NT	NT		
3	3.3	0.5	-1.81	-1.42
4	4.1	0.41	0.17	0.16
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	4.2	0.8	0.42	0.21
9	NT	NT		
10	< 5	0.7		
11	NT	NT		
12	6.67	0.7	6.55	3.72
13	NT	NT		
14	NT	NT		
15	4.0	1.6	-0.07	-0.02
16	NT	NT		
17	4.07	0.3	0.10	0.12
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	4.0	1	-0.07	-0.03

**Statistics**

<b>Assigned Value*</b>	4.03	0.12
<b>Spike**</b>	2.78	0.12
<b>Homogeneity Value</b>	4.22	0.32
<b>Robust Average</b>	4.06	0.16
<b>Median</b>	4.04	0.06
<b>Mean</b>	4.29	
<b>N</b>	8	
<b>Max.</b>	6.67	
<b>Min.</b>	3.3	
<b>Robust SD</b>	0.12	
<b>Robust CV</b>	3%	

\*Robust Average excluding Laboratory 12. \*\*Incurred value not included.

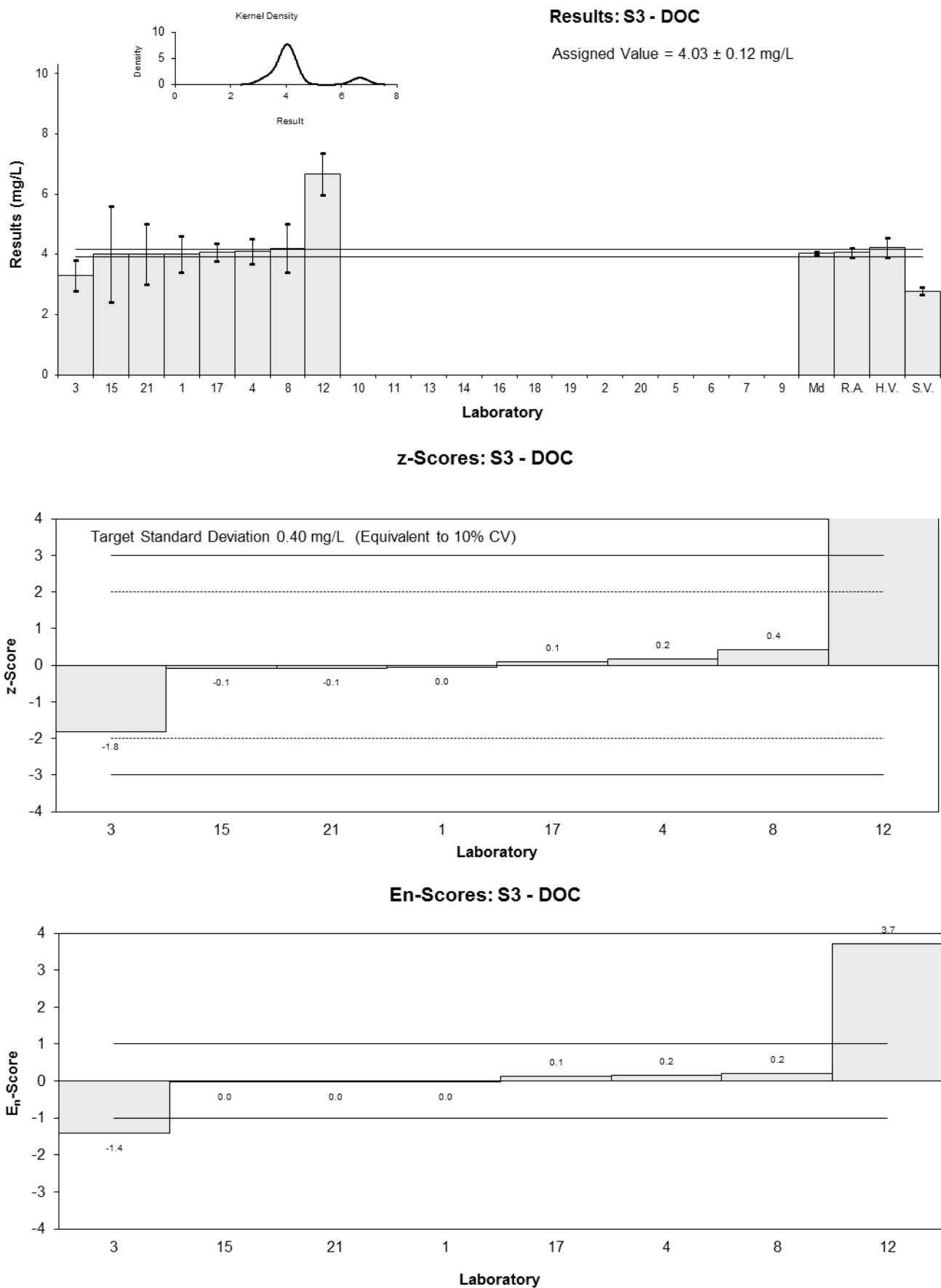


Figure 40

Table 44

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Fluoride
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.11	0.18	-0.49	-0.39
2	NT	NT		
3	NT	NT		
4	1.31	0.40	0.33	0.17
5	1.55	NR	1.30	1.28
6	NT	NT		
7	NT	NT		
8	1.2	0.2	-0.12	-0.09
9	0.82	0.09	-1.67	-1.54
10	0.88	0.15	-1.42	-1.20
11	NT	NT		
12	1.73	0.2	2.03	1.56
13	NT	NT		
14	NT	NT		
15	1.1	0.27	-0.53	-0.35
16	NT	NT		
17	1.46	0.07	0.93	0.89
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	1.2	0.1	-0.12	-0.11

**Statistics**

<b>Assigned Value</b>	1.23	0.25
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1.22	0.24
<b>Robust Average</b>	1.23	0.25
<b>Median</b>	1.20	0.20
<b>Mean</b>	1.24	
<b>N</b>	10	
<b>Max.</b>	1.73	
<b>Min.</b>	0.82	
<b>Robust SD</b>	0.32	
<b>Robust CV</b>	26%	

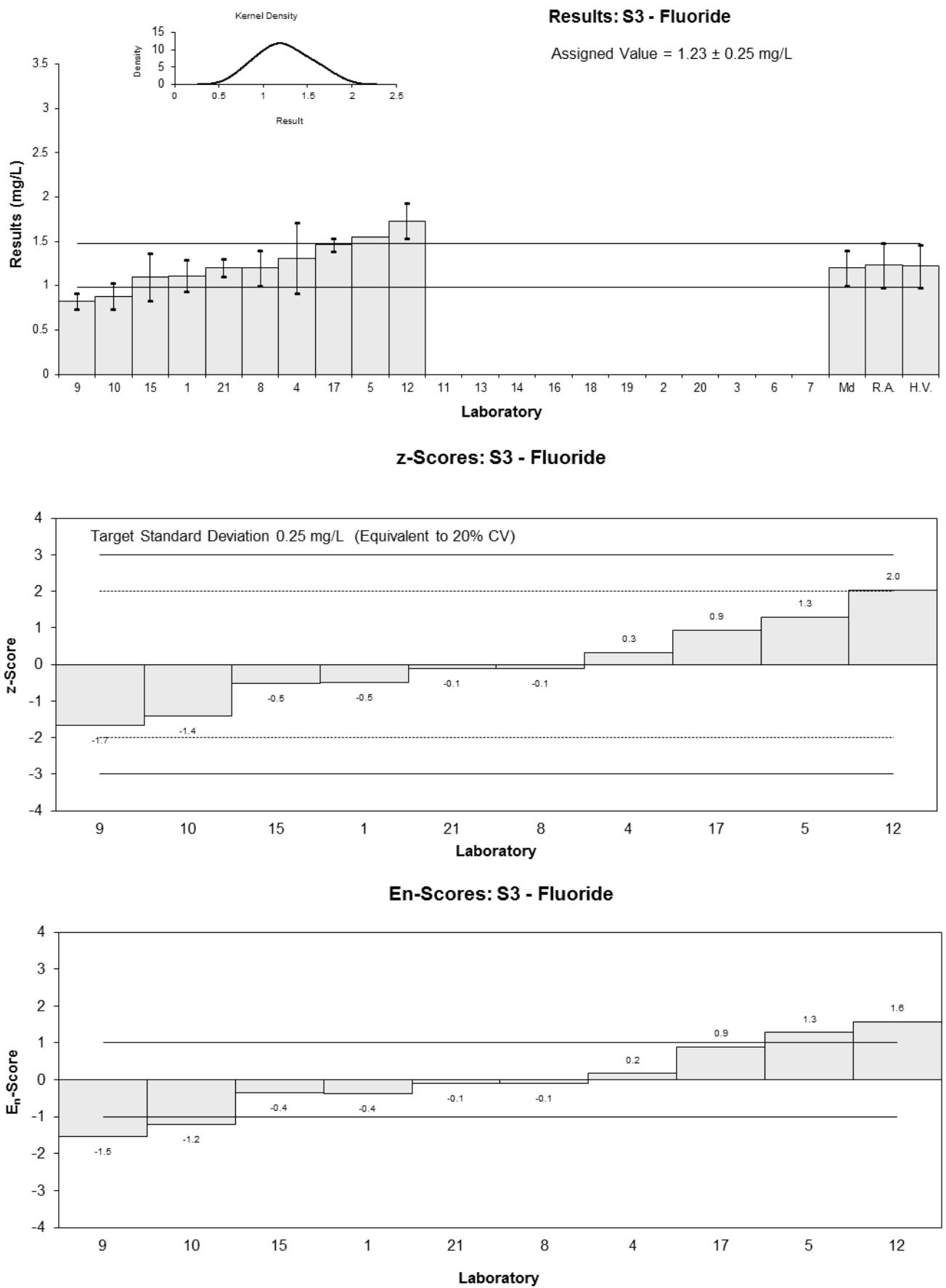


Figure 41

Table 45

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Nitrate-N
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.0476	0.0096	0.89	0.70
2	0.034	0.02	-0.79	-0.31
3	0.0415	0.006	0.14	0.16
4	0.040	0.007	-0.05	-0.05
5	4.43	NR	543.27	1219.33
6	NT	NT		
7	NT	NT		
8	0.039	0.008	-0.17	-0.16
9	0.034	0.008	-0.79	-0.73
10	0.0608	0.010	2.52	1.92
11	NT	NT		
12	0.038	0.005	-0.30	-0.39
13	NT	NT		
14	NT	NT		
15	0.038	NR	-0.30	-0.67
16	NT	NT		
17	0.0396	0.004	-0.10	-0.15
18	NT	NT		
19	0.043	0.003	0.32	0.55
20	NT	NT		
21	0.042	0.01	0.20	0.15

**Statistics**

<b>Assigned Value*</b>	0.0404	0.0036
<b>Spike**</b>	0.0317	0.0014
<b>Homogeneity Value</b>	0.0440	0.0090
<b>Robust Average</b>	0.0414	0.0043
<b>Median</b>	0.0400	0.0018
<b>Mean</b>	0.379	
<b>N</b>	13	
<b>Max.</b>	4.43	
<b>Min.</b>	0.034	
<b>Robust SD</b>	0.005	
<b>Robust CV</b>	12%	

\*Robust Average excluding Laboratory 5. \*\*Incurred value not included.

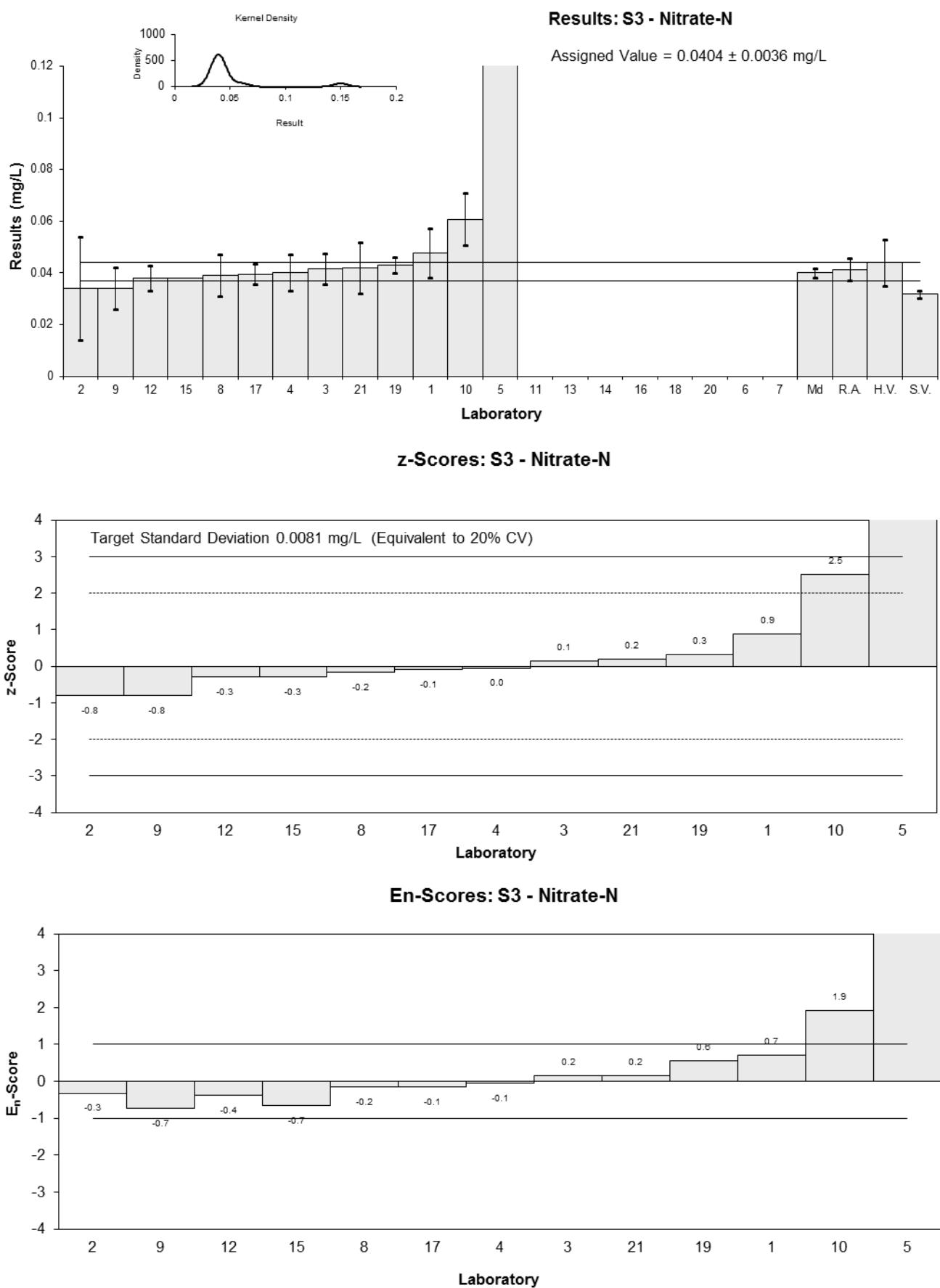


Figure 42

Table 46

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Orthophosphate-P
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.0747	0.0142	0.58	0.37
2	0.06	0.02	-0.84	-0.40
3	0.076	0.015	0.71	0.43
4	0.056	0.010	-1.23	-0.99
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	0.071	0.014	0.22	0.14
9	0.079	0.021	1.00	0.46
10	0.046	0.007	-2.20	-2.14
11	NT	NT		
12	0.079	0.008	1.00	0.91
13	NT	NT		
14	NT	NT		
15	0.074	0.0069	0.51	0.50
16	0.04	0.004	-2.79	-3.21
17	0.0705	0.005	0.17	0.19
18	NT	NT		
19	0.075	0.002	0.61	0.76
20	NT	NT		
21	0.075	0.01	0.61	0.49

**Statistics**

<b>Assigned Value</b>	0.0687	0.0080
<b>Spike*</b>	0.0586	0.0025
<b>Homogeneity Value</b>	0.1080	0.0220
<b>Robust Average</b>	0.0687	0.0080
<b>Median</b>	0.0740	0.0031
<b>Mean</b>	0.0670	
<b>N</b>	13	
<b>Max.</b>	0.079	
<b>Min.</b>	0.04	
<b>Robust SD</b>	0.012	
<b>Robust CV</b>	18%	

\*Incurred value not included.

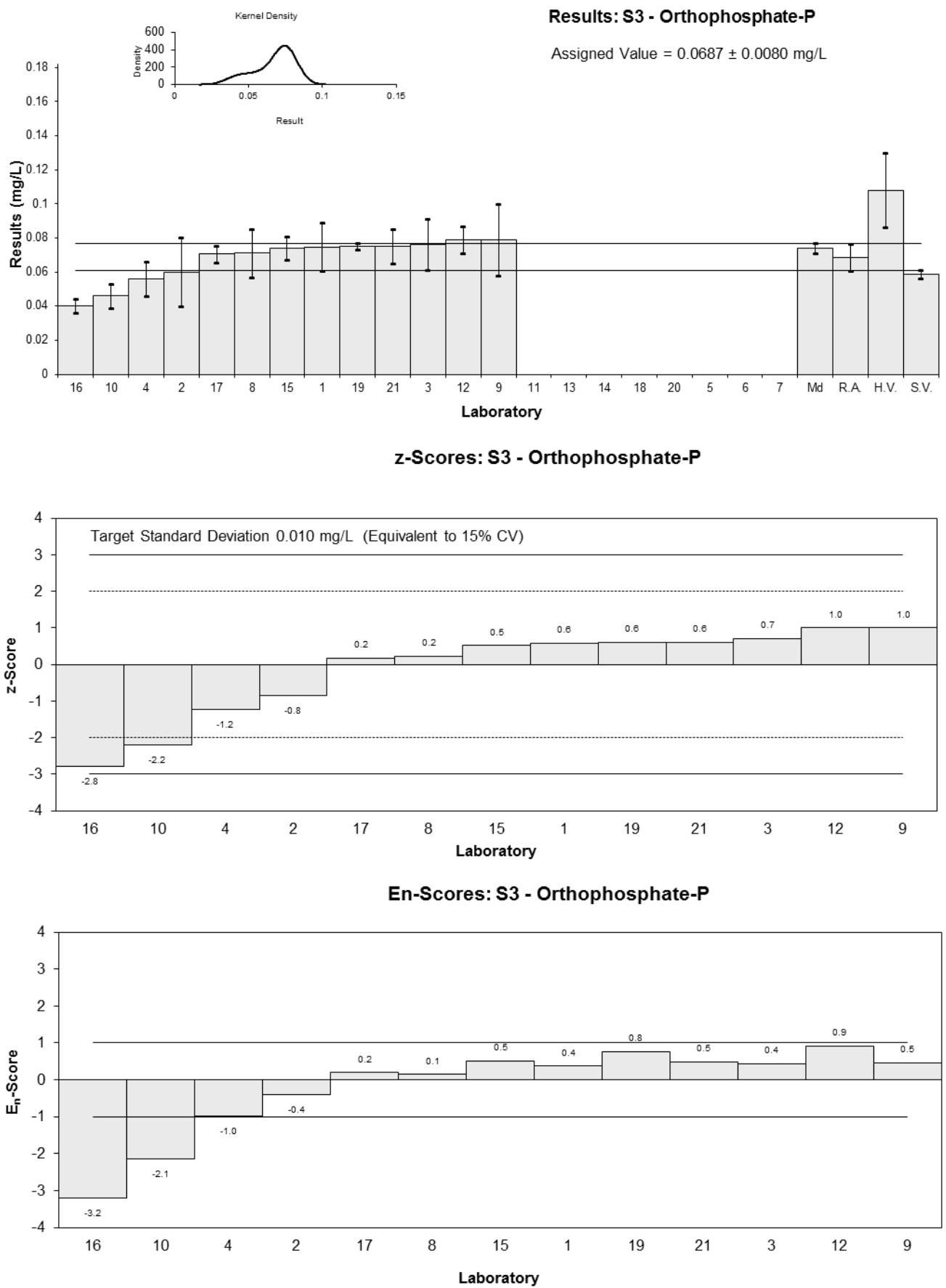


Figure 43

Table 47

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Sulfate
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2340	400	-0.25	-0.15
2	2614	270	0.89	0.74
3	NT	NT		
4	2150	258	-1.04	-0.90
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	2600	500	0.83	0.39
9	2360	614	-0.17	-0.06
10	2313.5	231	-0.36	-0.34
11	NT	NT		
12	2450	240	0.21	0.19
13	NT	NT		
14	NT	NT		
15	2410	NR	0.04	0.10
16	2345	127.24	-0.23	-0.34
17	2400	100	0.00	0.00
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	2410	240	0.04	0.04

**Statistics**

<b>Assigned Value</b>	2400	100
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2530	190
<b>Robust Average</b>	2400	100
<b>Median</b>	2400.	50
<b>Mean</b>	2400	
<b>N</b>	11	
<b>Max.</b>	2614	
<b>Min.</b>	2150	
<b>Robust SD</b>	130	
<b>Robust CV</b>	5.4%	

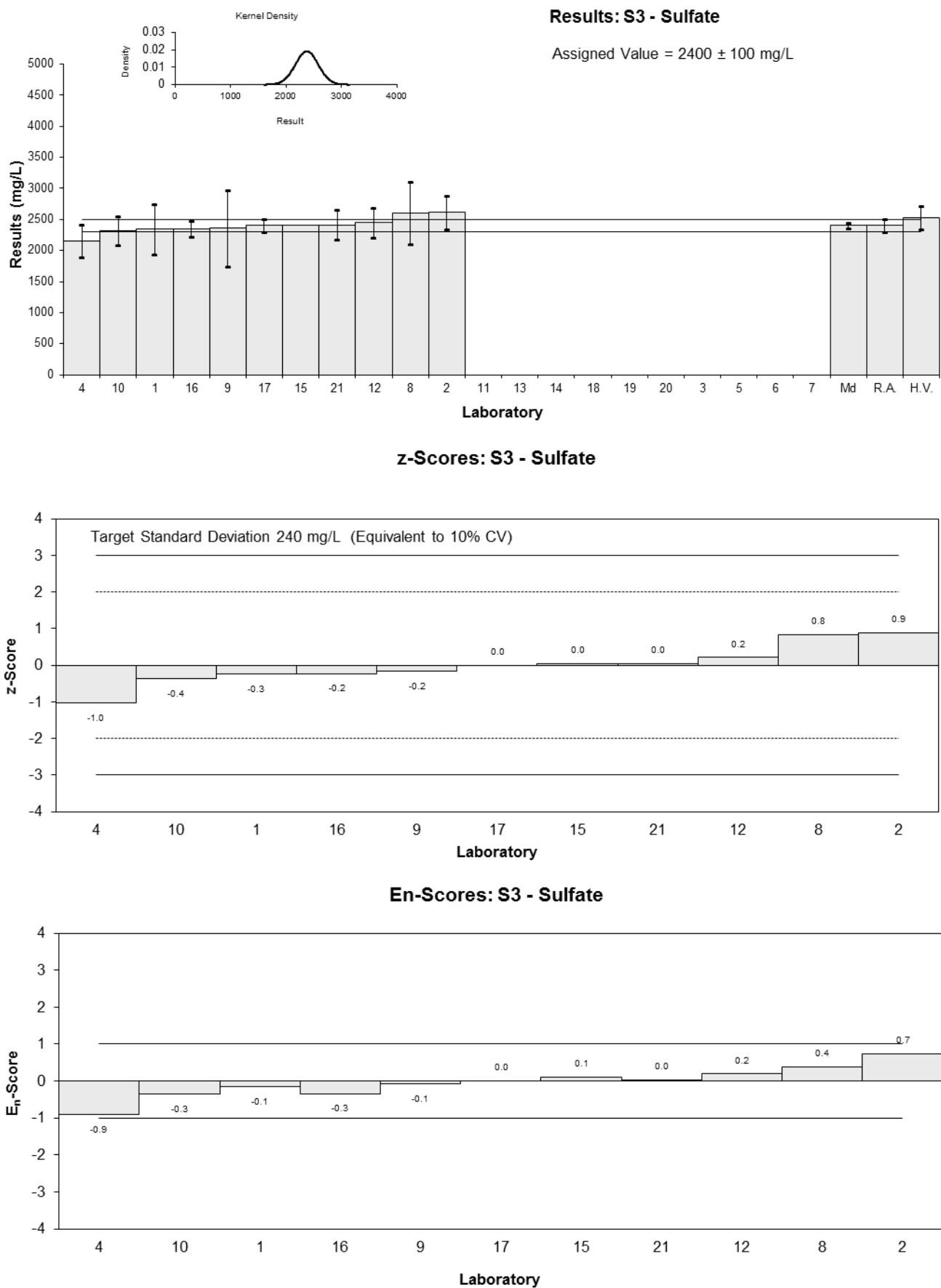


Figure 44

Table 48

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	TDN
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.260	0.055	0.08	0.04
2	0.47	0.2	5.53	1.04
3	0.334	0.077	2.00	0.87
4	0.21	0.05	-1.22	-0.71
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	0.20	0.04	-1.48	-0.96
9	0.45	0.10	5.01	1.77
10	0.294	0.07	0.96	0.45
11	NT	NT		
12	0.21	0.02	-1.22	-0.97
13	NT	NT		
14	NT	NT		
15	0.236	0.033	-0.54	-0.38
16	NT	NT		
17	0.272	0.04	0.39	0.25
18	NT	NT		
19	0.294	0.06	0.96	0.50
20	NT	NT		
21	NT	NT		

**Statistics**

<b>Assigned Value*</b>	0.257	0.044
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.235	0.047
<b>Robust Average</b>	0.285	0.065
<b>Median</b>	0.272	0.062
<b>Mean</b>	0.294	
<b>N</b>	11	
<b>Max.</b>	0.47	
<b>Min.</b>	0.2	
<b>Robust SD</b>	0.052	
<b>Robust CV</b>	18%	

\*Robust Average excluding Laboratories 2 and 9.

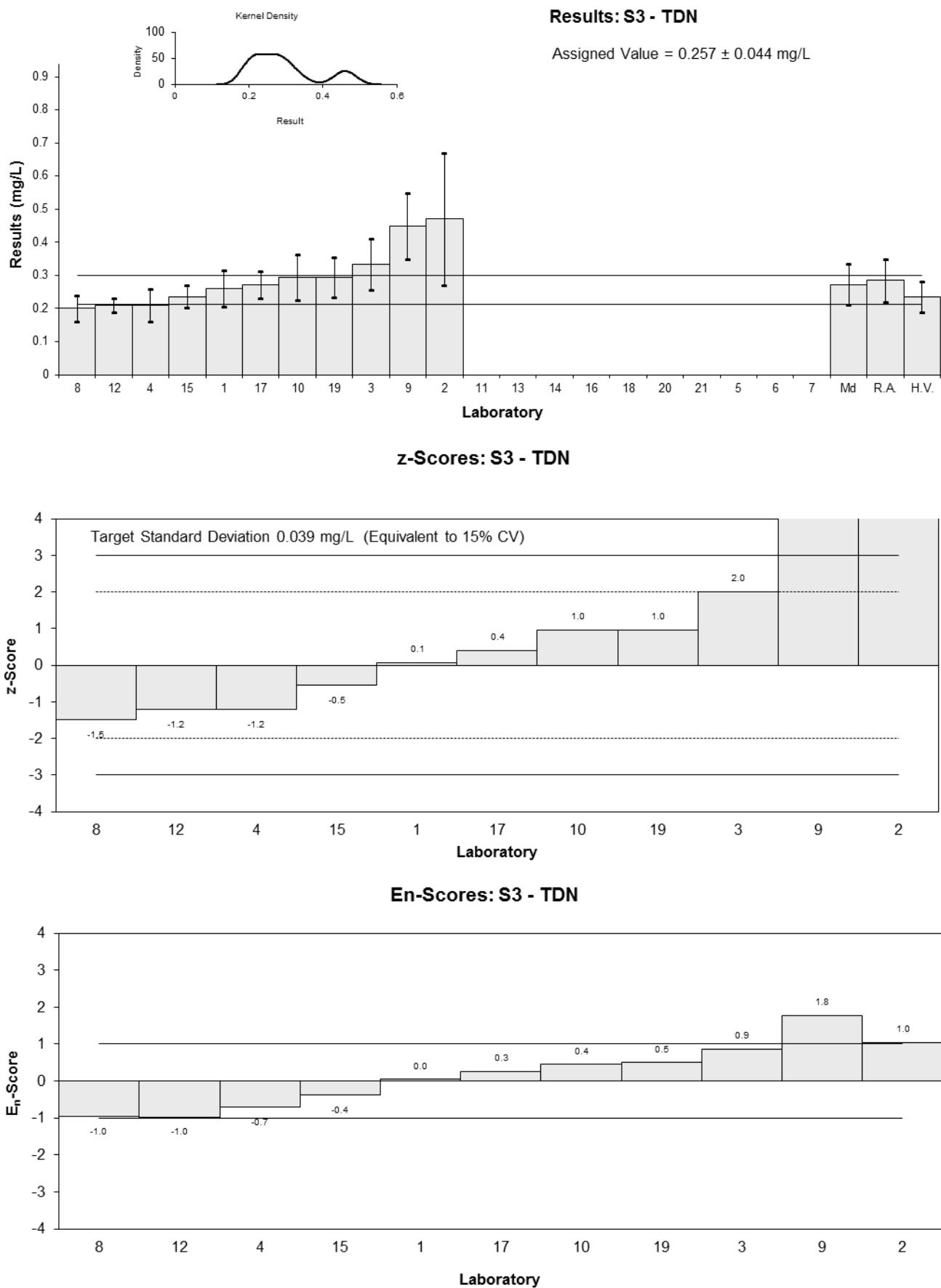


Figure 45

Table 49

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	TDP
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.0866	0.0130	0.22	0.19
2	0.074	0.03	-0.54	-0.27
3	0.116	0.032	1.99	0.94
4	0.056	0.010	-1.63	-1.57
5	3.60	NR	211.87	251.21
6	NT	NT		
7	NT	NT		
8	<0.05	NR		
9	0.081	0.024	-0.12	-0.07
10	0.0931	0.015	0.61	0.49
11	NT	NT		
12	0.09	0.01	0.42	0.41
13	NT	NT		
14	NT	NT		
15	0.074	0.0095	-0.54	-0.53
16	NT	NT		
17	0.069	0.005	-0.84	-0.94
18	NT	NT		
19	0.099	0.005	0.96	1.08
20	NT	NT		
21	NT	NT		

**Statistics**

<b>Assigned Value*</b>	0.083	0.014
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.108	0.022
<b>Robust Average</b>	0.087	0.017
<b>Median</b>	0.087	0.013
<b>Mean</b>	0.404	
<b>N</b>	11	
<b>Max.</b>	3.6	
<b>Min.</b>	0.056	
<b>Robust SD</b>	0.018	
<b>Robust CV</b>	21%	

\*Robust Average excluding Laboratory 5.

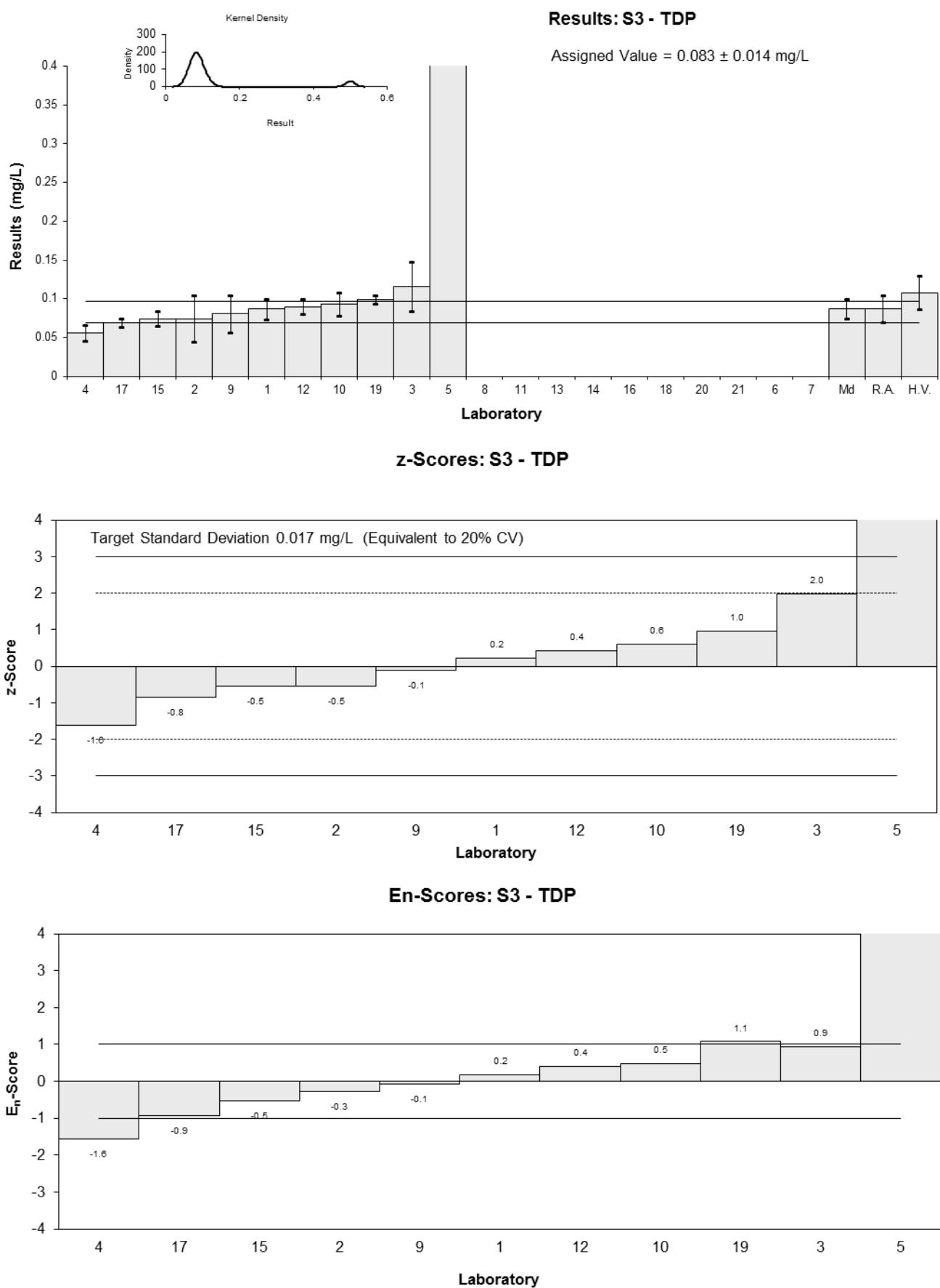


Figure 46

Table 50

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Alkalinity
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	98.2	6.5	-0.09	-0.13
2	NT	NT		
3	98	5	-0.11	-0.20
4	97	8	-0.21	-0.25
5	NT	NT		
6	NT	NT		
7	<700	NT		
8	95	19	-0.41	-0.21
9	98	11	-0.11	-0.10
10	106.35	13.2	0.73	0.54
11	NT	NT		
12	100	10	0.09	0.09
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	101	5.0	0.19	0.35
18	NT	NT		
19	NT	NT		
20	100	4	0.09	0.20
21	101	10	0.19	0.19

**Statistics**

<b>Assigned Value</b>	99.1	2.0
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	95.2	7.1
<b>Robust Average</b>	99.1	2.0
<b>Median</b>	99.1	1.6
<b>Mean</b>	99.5	
<b>N</b>	10	
<b>Max.</b>	106.35	
<b>Min.</b>	95	
<b>Robust SD</b>	2.6	
<b>Robust CV</b>	2.6%	

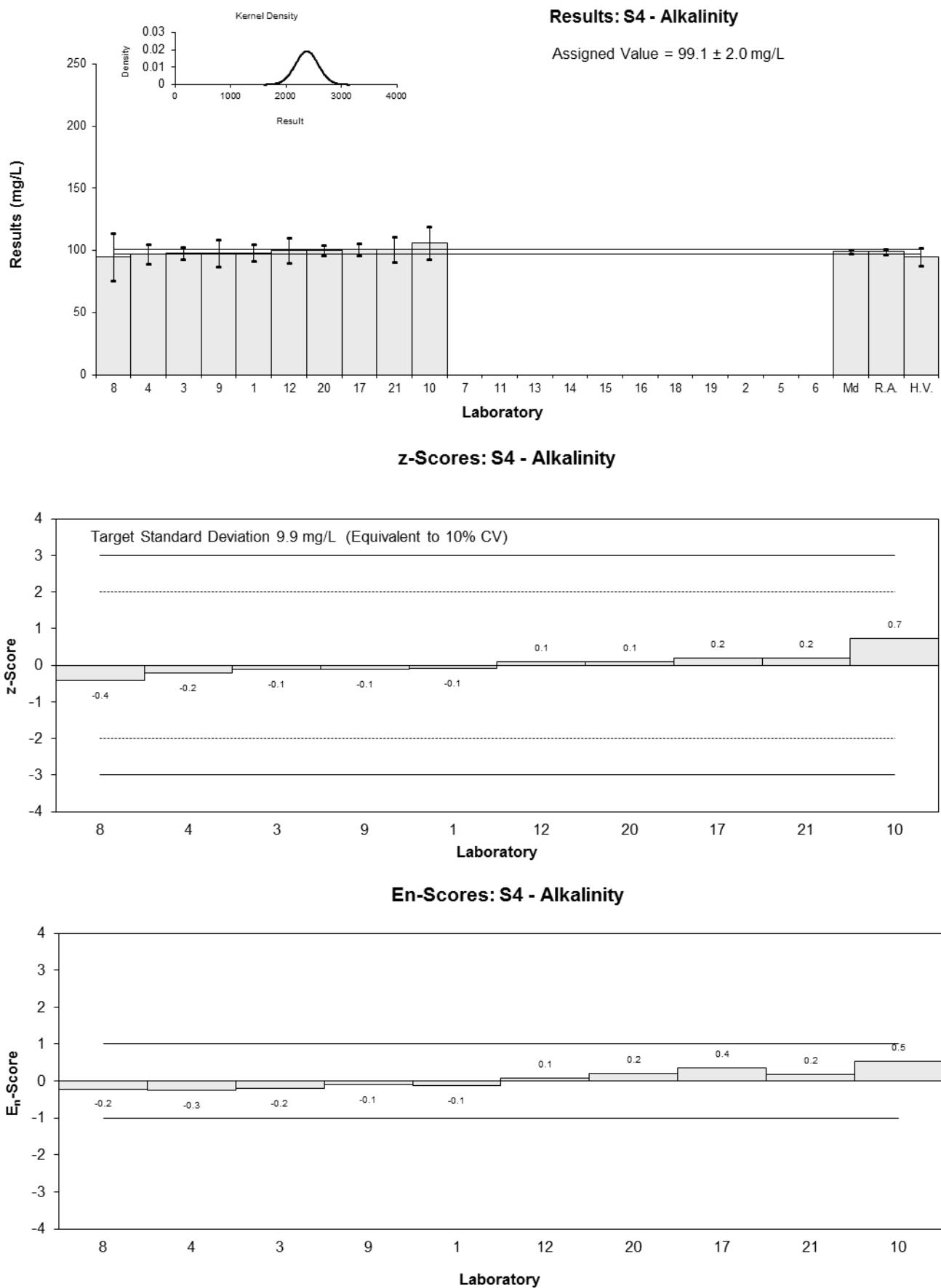


Figure 47

Table 51

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	B
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	4.00	0.56	0.34	0.21
2	NT	NT		
3	3.47	0.69	-1.03	-0.55
4	4.4	0.5	1.37	0.96
5	NT	NT		
6	NT	NT		
7	4.21	0.42	0.88	0.70
8	3.9	0.7	0.08	0.04
9	3.45	1	-1.09	-0.41
10	4.31	0.86	1.14	0.49
11	NT	NT		
12	3.49	0.35	-0.98	-0.90
13	NT	NT		
14	3.77	0.58	-0.26	-0.16
15	NT	NT		
16	4.15	0.83	0.72	0.32
17	3.97	0.20	0.26	0.32
18	3.60	0.51	-0.70	-0.48
19	NT	NT		
20	3.9	0.6	0.08	0.05
21	3.6	0.5	-0.70	-0.49

**Statistics**

<b>Assigned Value</b>	3.87	0.24
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	4.65	0.47
<b>Robust Average</b>	3.87	0.24
<b>Median</b>	3.90	0.26
<b>Mean</b>	3.87	
<b>N</b>	14	
<b>Max.</b>	4.4	
<b>Min.</b>	3.45	
<b>Robust SD</b>	0.36	
<b>Robust CV</b>	9.3%	

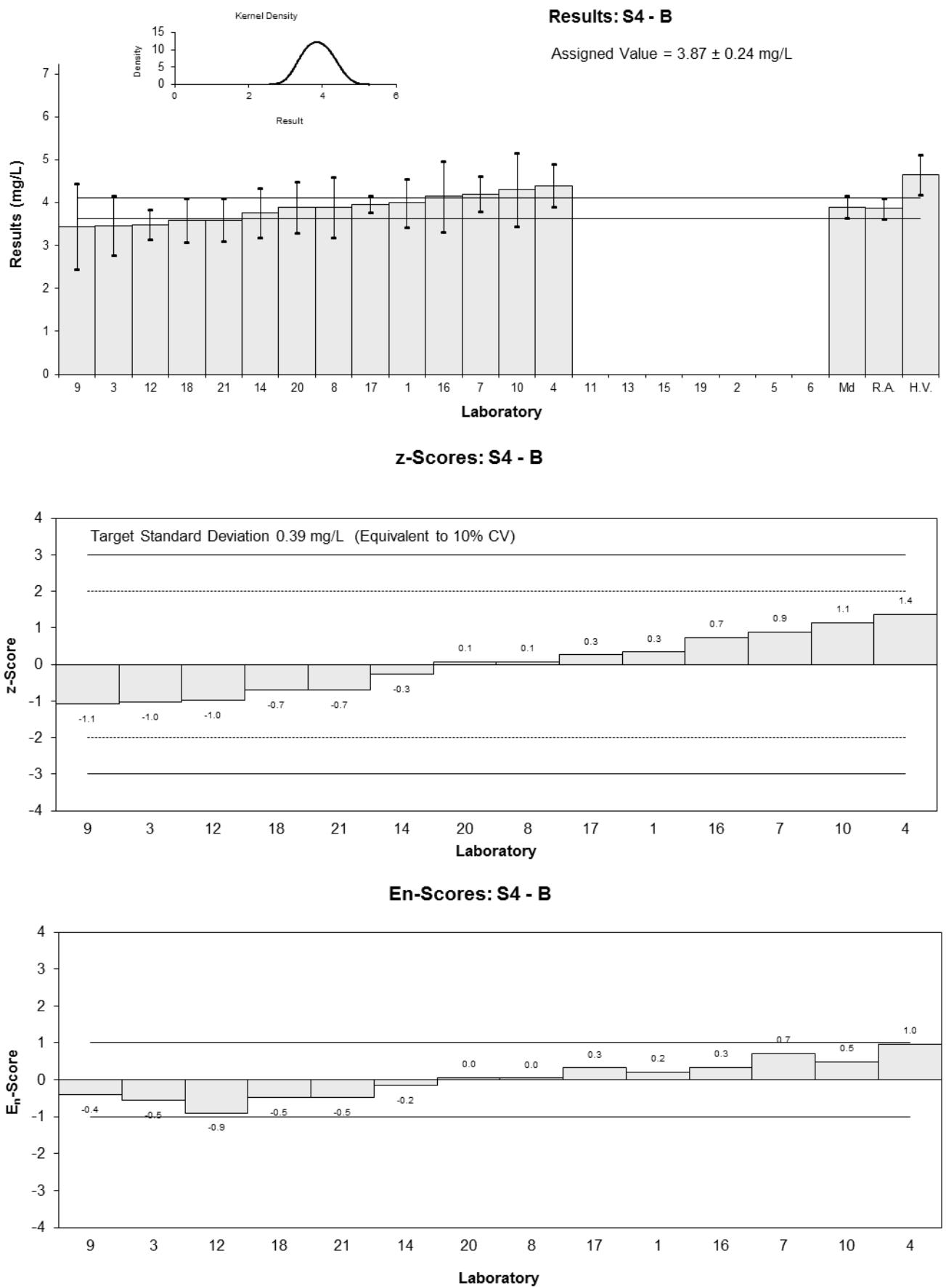


Figure 48

Table 52

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Ca
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	374	53	0.56	0.35
2	NT	NT		
3	389	117	0.99	0.29
4	329	38	-0.71	-0.58
5	NT	NT		
6	NT	NT		
7	311.1	45.11	-1.21	-0.87
8	340	54	-0.40	-0.24
9	318	79	-1.02	-0.44
10	340	43	-0.40	-0.30
11	NT	NT		
12	387	40	0.93	0.74
13	NT	NT		
14	365	60	0.31	0.17
15	NT	NT		
16	395	79	1.16	0.50
17	354	18	0.00	0.00
18	349	14	-0.14	-0.20
19	NT	NT		
20	360	30	0.17	0.17
21	340	34	-0.40	-0.35

**Statistics**

<b>Assigned Value</b>	354	20
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	303	30
<b>Robust Average</b>	354	20
<b>Median</b>	352	15
<b>Mean</b>	354	
<b>N</b>	14	
<b>Max.</b>	395	
<b>Min.</b>	311.1	
<b>Robust SD</b>	30	
<b>Robust CV</b>	8.5%	

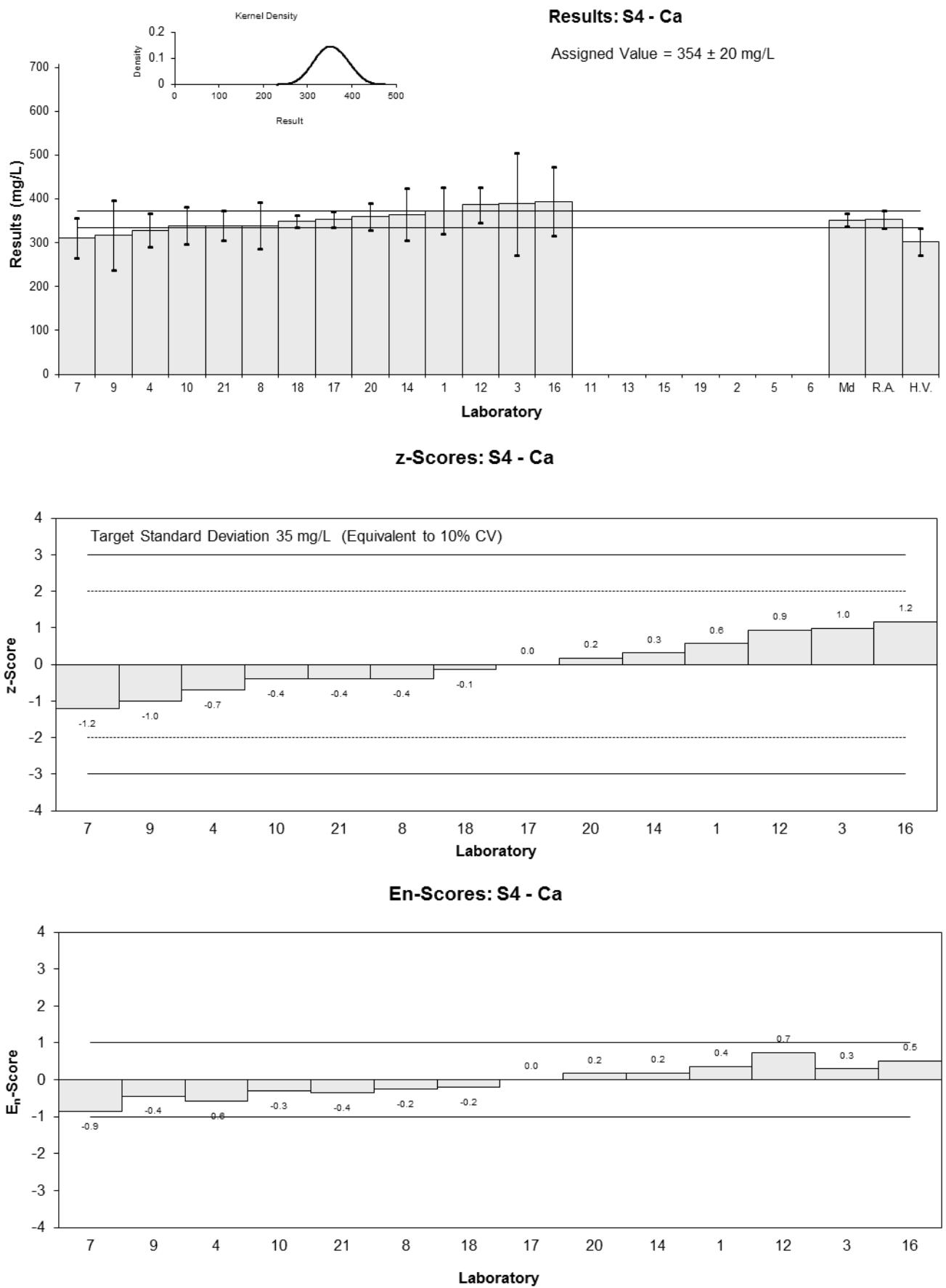


Figure 49

Table 53

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	EC
<b>Units</b>	uS/cm

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	45300	2270	0.41	0.49
2	NT	NT		
3	43200	2160	-0.07	-0.08
4	44000	880	0.11	0.16
5	46400	NR	0.67	1.00
6	NT	NT		
7	NT	NT		
8	38000	3800	-1.26	-1.15
9	44900	4939	0.32	0.24
10	38800	7100	-1.08	-0.61
11	NT	NT		
12	46820	4500	0.76	0.62
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	46800	5359.572	0.76	0.54
17	4390	200	-8.99	-13.45
18	NT	NT		
19	NT	NT		
20	46000	600	0.57	0.84
21	38800	4000	-1.08	-0.95

**Statistics**

<b>Assigned Value*</b>	43500	2900
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	35800	4800
<b>Robust Average</b>	43000	3200
<b>Median</b>	44500	2000
<b>Mean</b>	40300	
<b>N</b>	12	
<b>Max.</b>	46820	
<b>Min.</b>	4390	
<b>Robust SD</b>	3900	
<b>Robust CV</b>	9.1%	

\*Robust Average excluding Laboratory 17.

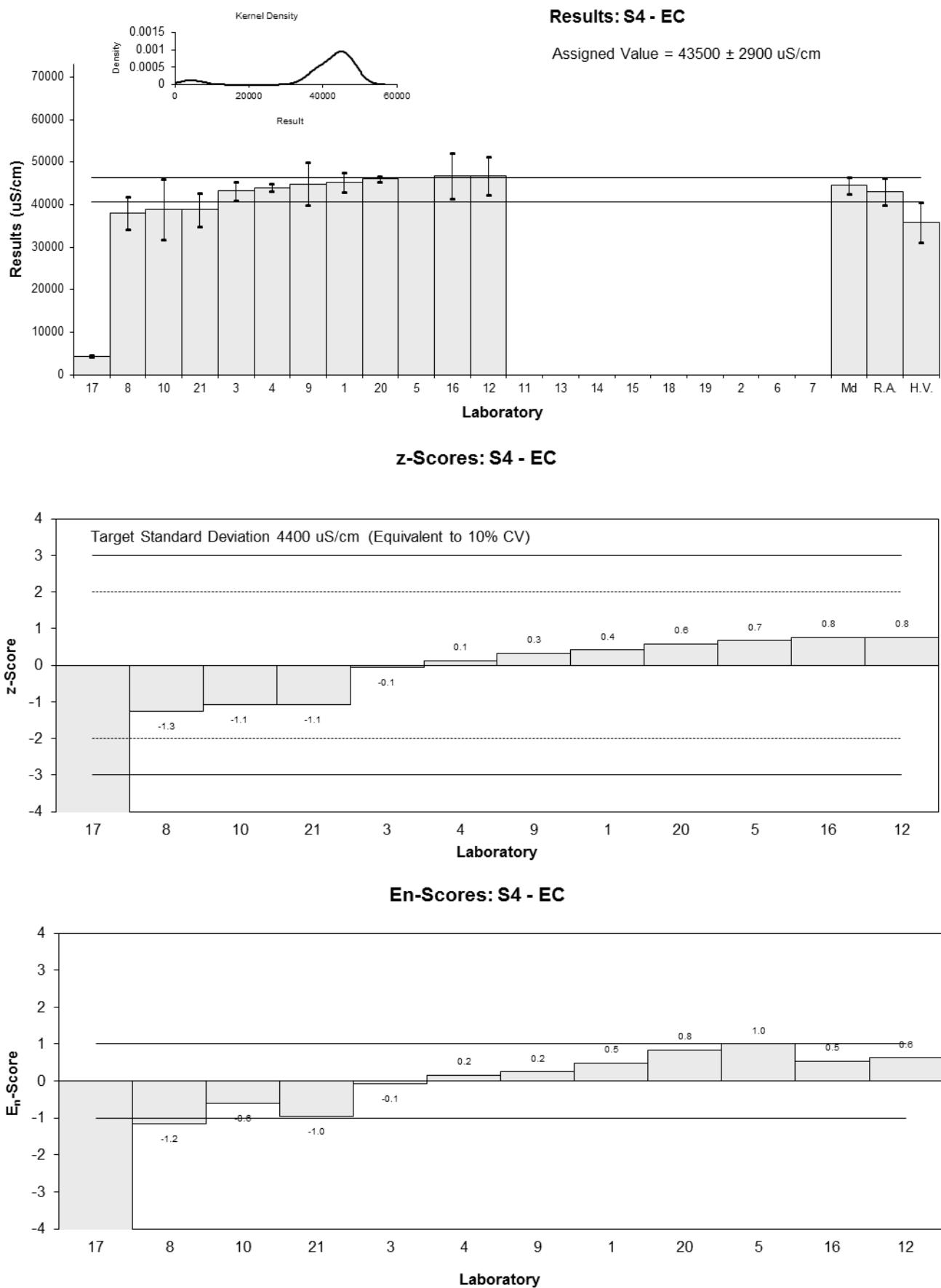


Figure 50

Table 54

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	K
<b>Units</b>	mg/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	397	111	1.34	0.41
4	346	36	-0.11	-0.09
5	NT	NT		
6	NT	NT		
7	323.8	30.15	-0.75	-0.66
8	260	44	-2.57	-1.76
9	320	86	-0.86	-0.33
10	348	35	-0.06	-0.05
11	NT	NT		
12	396	40	1.31	0.96
13	NT	NT		
14	343	60	-0.20	-0.11
15	NT	NT		
16	369	73.8	0.54	0.24
17	340	17	-0.29	-0.32
18	339	14	-0.31	-0.37
19	NT	NT		
20	460	30	3.14	2.77
21	333	35	-0.49	-0.39

**Statistics**

<b>Assigned Value</b>	350	26
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	350	26
<b>Median</b>	343	17
<b>Mean</b>	352	
<b>N</b>	13	
<b>Max.</b>	460	
<b>Min.</b>	260	
<b>Robust SD</b>	38	
<b>Robust CV</b>	11%	

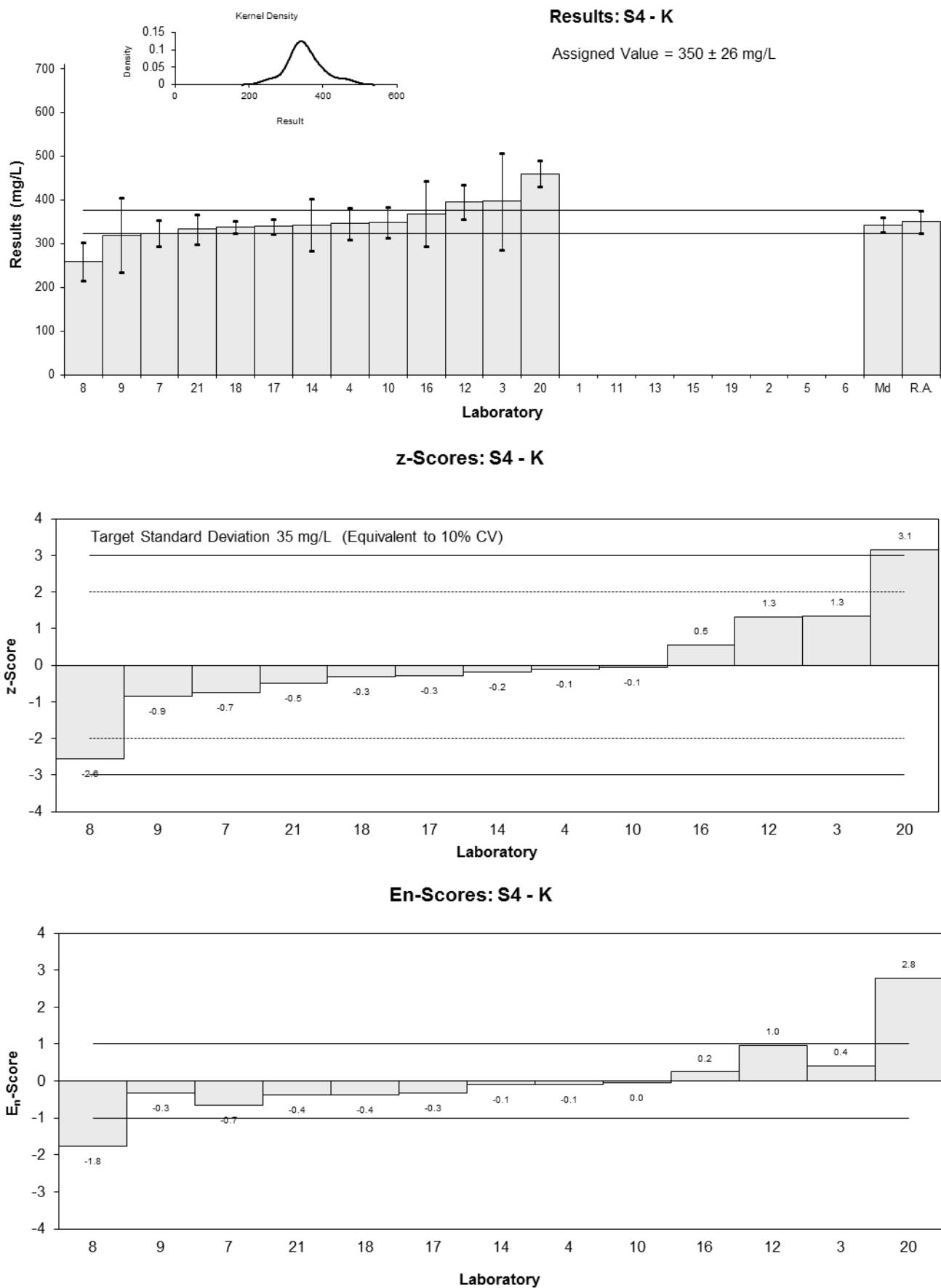


Figure 51

Table 55

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Mg
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1150	170	0.36	0.23
2	NT	NT		
3	1100	260	-0.09	-0.04
4	1100	181	-0.09	-0.05
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	1130	147	0.18	0.13
9	1110	277	0.00	0.00
10	1080	190	-0.27	-0.16
11	NT	NT		
12	1110	110	0.00	0.00
13	NT	NT		
14	1152	157	0.38	0.27
15	NT	NT		
16	1119	223	0.08	0.04
17	1100	60	-0.09	-0.16
18	1010	110	-0.90	-0.89
19	NT	NT		
20	1100	150	-0.09	-0.07
21	1080	110	-0.27	-0.27

**Statistics**

<b>Assigned Value</b>	1110	20
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1040	100
<b>Robust Average</b>	1110	20
<b>Median</b>	1100	20
<b>Mean</b>	1100	
<b>N</b>	13	
<b>Max.</b>	1152	
<b>Min.</b>	1010	
<b>Robust SD</b>	30	
<b>Robust CV</b>	2.7%	

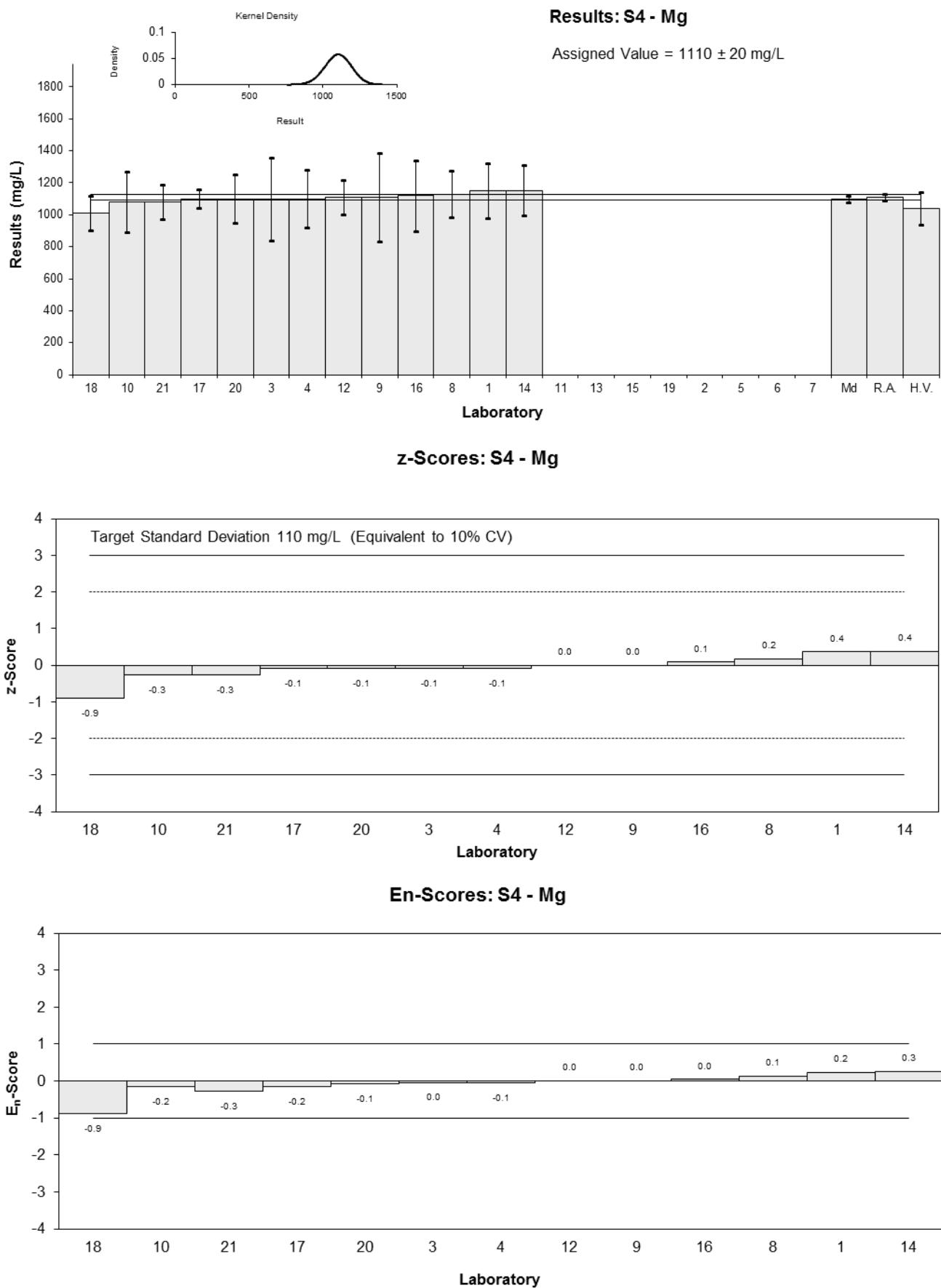


Figure 52

Table 56

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	pH

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	8.0	0.1	0.11	0.77
2	NT	NT		
3	8	0.1	0.11	0.77
4	7.96	0.24	0.06	0.20
5	7.82	NR	-0.11	-1.50
6	NT	NT		
7	NT	NT		
8	7.9	0.2	-0.01	-0.05
9	7.9	0.2	-0.01	-0.05
10	7.93	0.1	0.03	0.17
11	NT	NT		
12	7.82	0.2	-0.11	-0.43
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	7.67	0.06	-0.30	-2.83
17	8.03	0.3	0.15	0.39
18	NT	NT		
19	NT	NT		
20	7.9	0.1	-0.01	-0.09
21	7.9	0.2	-0.01	-0.05

**Statistics**

<b>Assigned Value</b>	7.91	0.06
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	7.90	0.40
<b>Robust Average</b>	7.91	0.06
<b>Median</b>	7.90	0.07
<b>Mean</b>	7.90	
<b>N</b>	12	
<b>Max.</b>	8.03	
<b>Min.</b>	7.67	
<b>Robust SD</b>	0.09	
<b>Robust CV</b>	1.1%	

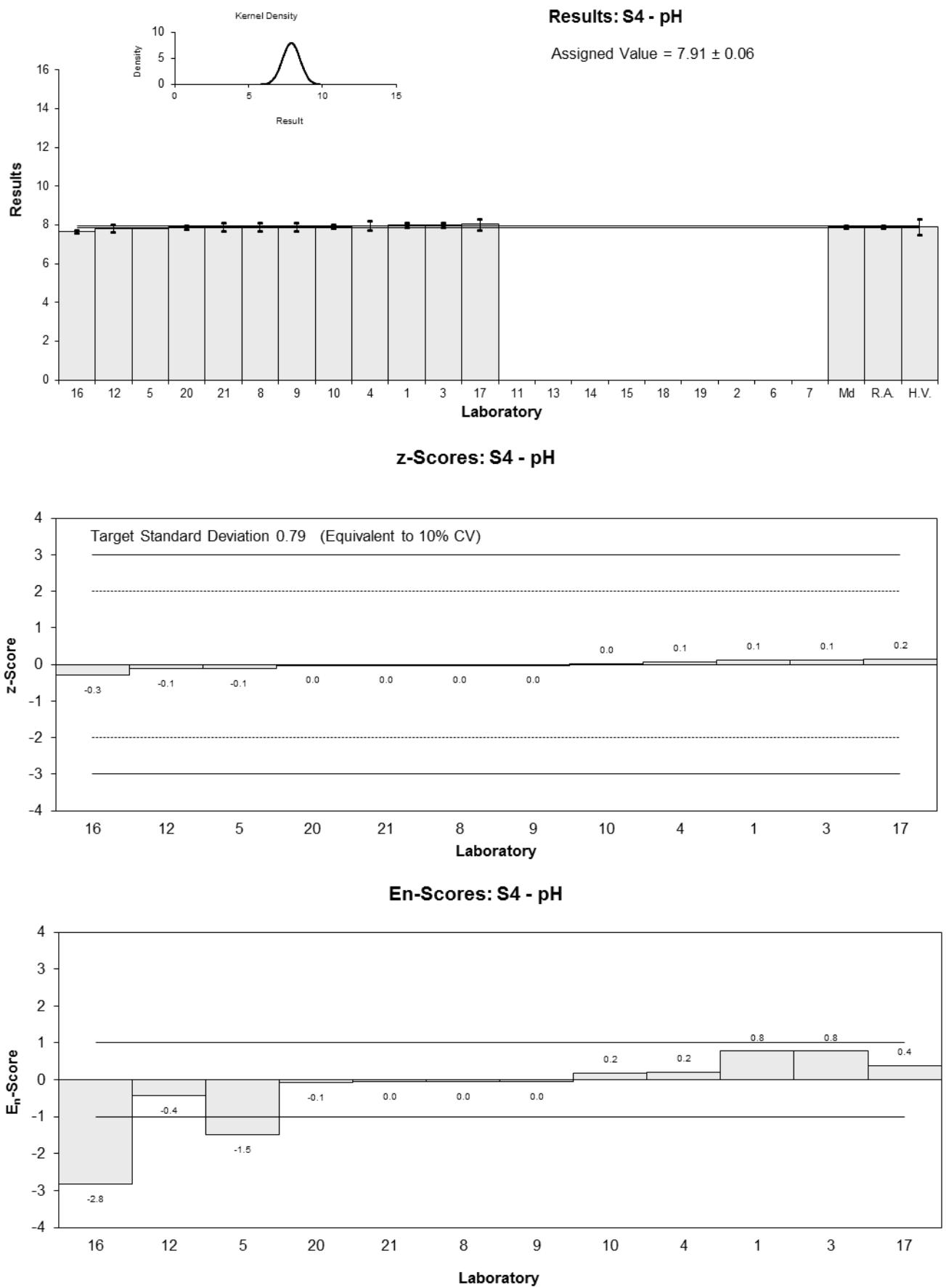


Figure 53

Table 57

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	TKN
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NT	NT		
2	NT	NT		
3	0.634	0.15	0.60	0.31
4	0.56	0.12	-0.25	-0.15
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	0.52	0.10	-0.71	-0.48
9	0.55	0.07	-0.37	-0.30
10	0.73	0.20	1.70	0.69
11	NT	NT		
12	0.49	0.05	-1.05	-0.98
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	0.611	0.1	0.33	0.23
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.582	0.080
<b>Spike*</b>	0.467	0.020
<b>Homogeneity Value</b>	0.461	0.092
<b>Robust Average</b>	0.582	0.080
<b>Median</b>	0.560	0.070
<b>Mean</b>	0.585	
<b>N</b>	7	
<b>Max.</b>	0.73	
<b>Min.</b>	0.49	
<b>Robust SD</b>	0.085	
<b>Robust CV</b>	15%	

\*Incurred value not included.

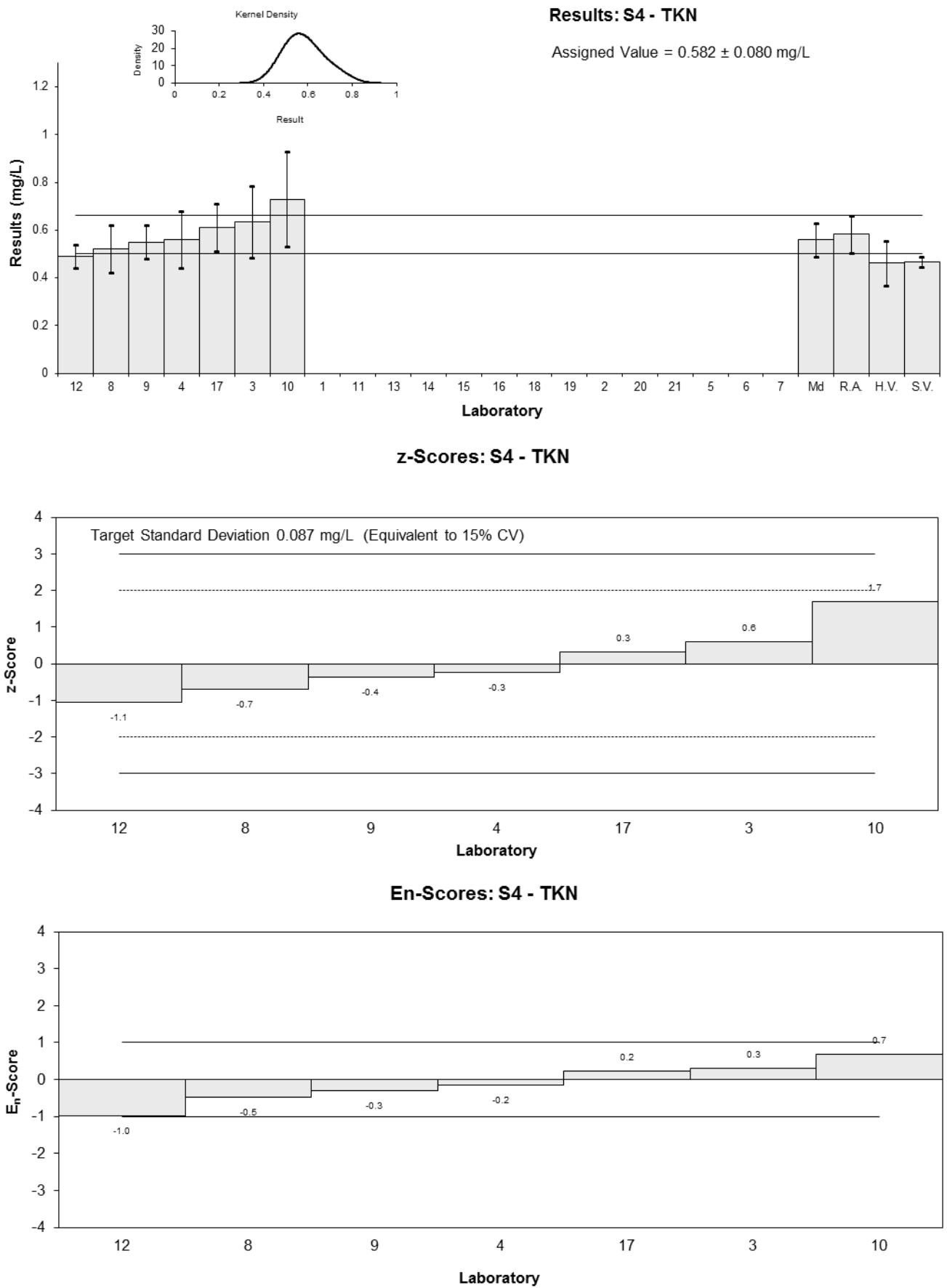


Figure 54

Table 58

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	TN
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.611	0.123	-0.02	-0.01
2	NT	NT		
3	0.638	0.15	0.27	0.15
4	0.56	0.12	-0.58	-0.39
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	0.56	0.11	-0.58	-0.41
9	0.56	0.08	-0.58	-0.51
10	0.73	0.20	1.27	0.56
11	NT	NT		
12	0.51	0.05	-1.12	-1.24
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	0.678	0.05	0.71	0.79
18	NT	NT		
19	0.712	0.06	1.08	1.11
20	NT	NT		
21	0.57	0.10	-0.47	-0.36

**Statistics**

<b>Assigned Value</b>	0.613	0.066
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.502	0.100
<b>Robust Average</b>	0.613	0.066
<b>Median</b>	0.591	0.041
<b>Mean</b>	0.613	
<b>N</b>	10	
<b>Max.</b>	0.73	
<b>Min.</b>	0.51	
<b>Robust SD</b>	0.084	
<b>Robust CV</b>	14%	

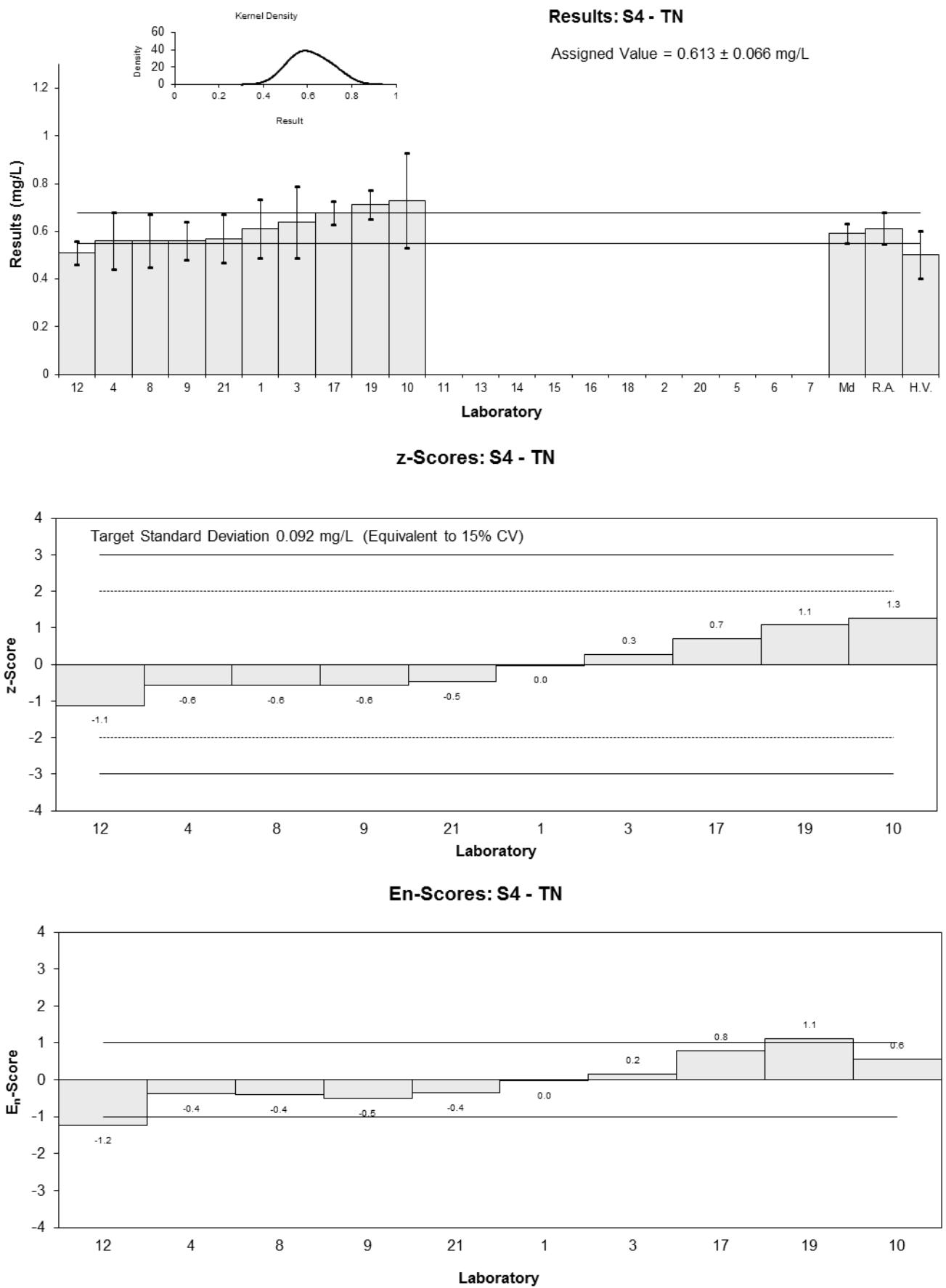


Figure 55

Table 59

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	TOC
<b>Units</b>	mg/L

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	5.12	0.72	0.71	0.34
2	NT	NT		
3	3.9	0.6	-1.84	-0.97
4	4.7	0.5	-0.17	-0.09
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	5.3	1.1	1.09	0.40
9	4.397	0.44	-0.80	-0.47
10	< 5	0.7		
11	NT	NT		
12	6.94	0.7	4.52	2.21
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	4.85	0.3	0.15	0.09
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	4.0	1	-1.63	-0.65

**Statistics**

<b>Assigned Value</b>	4.78	0.68
<b>Spike*</b>	1.98	0.08
<b>Homogeneity Value</b>	5.30	0.80
<b>Robust Average</b>	4.78	0.68
<b>Median</b>	4.78	0.56
<b>Mean</b>	4.90	
<b>N</b>	8	
<b>Max.</b>	6.94	
<b>Min.</b>	3.9	
<b>Robust SD</b>	0.77	
<b>Robust CV</b>	16%	

\*Incurred value not included.

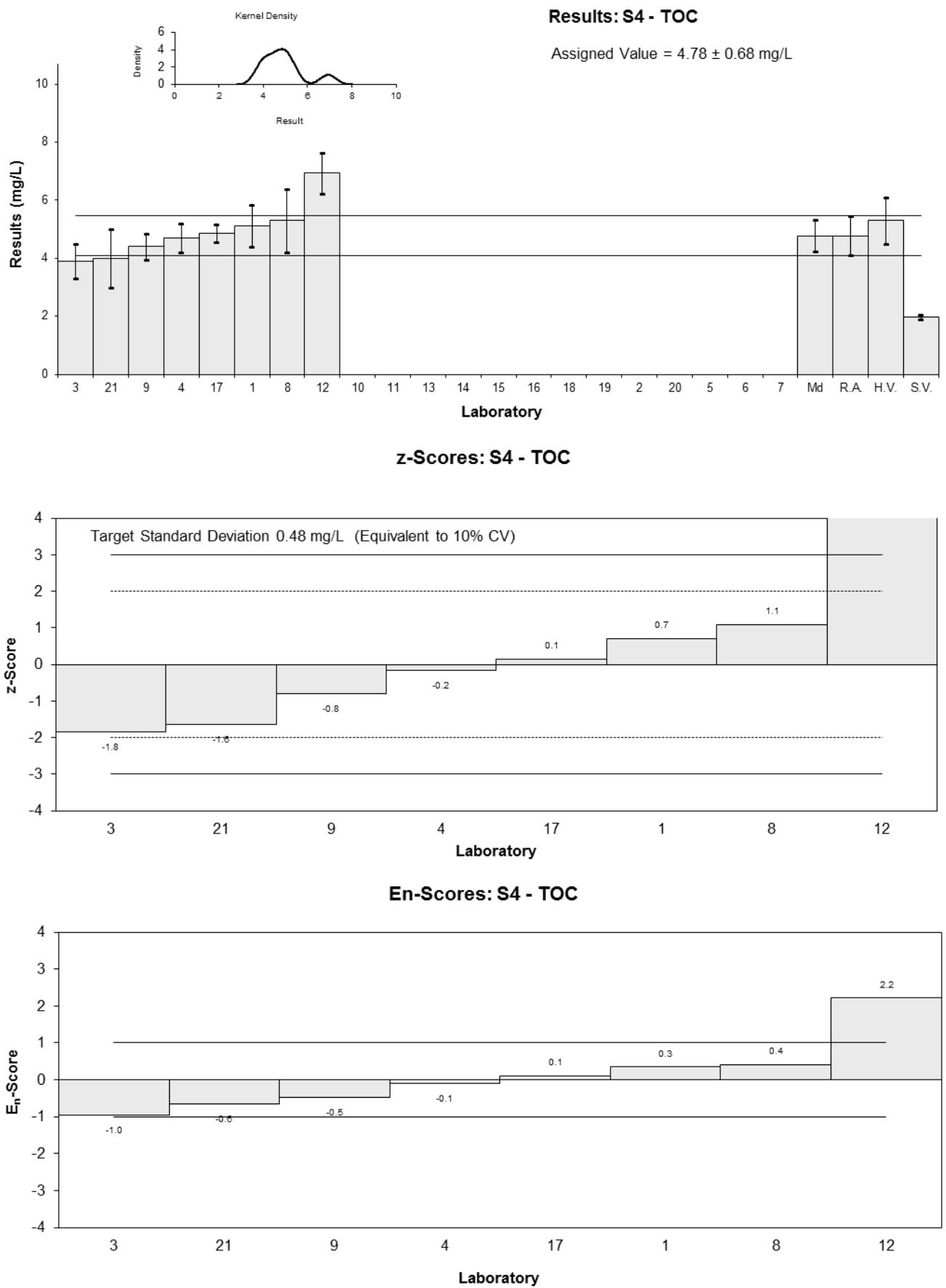


Figure 56

Table 60

**Sample Details**

<b>Sample No.</b>	S4
<b>Matrix.</b>	Seawater
<b>Analyte.</b>	Total Hardness
<b>Units</b>	mg/L

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NT	NT		
2	NT	NT		
3	5480	1370	0.09	0.04
4	5360	620	-0.13	-0.11
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	5600	1100	0.31	0.15
9	5360	1340	-0.13	-0.05
10	5290	1060	-0.26	-0.13
11	NT	NT		
12	5500	500	0.13	0.14
13	NT	NT		
14	5600	1180	0.31	0.14
15	NT	NT		
16	5592	1118.4	0.30	0.14
17	5410	200	-0.04	-0.09
18	NT	NT		
19	NT	NT		
20	5300	NR	-0.24	-1.18
21	5290	530	-0.26	-0.26

**Statistics**

<b>Assigned Value</b>	5430	110
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	4640	230
<b>Robust Average</b>	5430	110
<b>Median</b>	5410	110
<b>Mean</b>	5435	
<b>N</b>	11	
<b>Max.</b>	5600	
<b>Min.</b>	5290	
<b>Robust SD</b>	140	
<b>Robust CV</b>	2.6%	

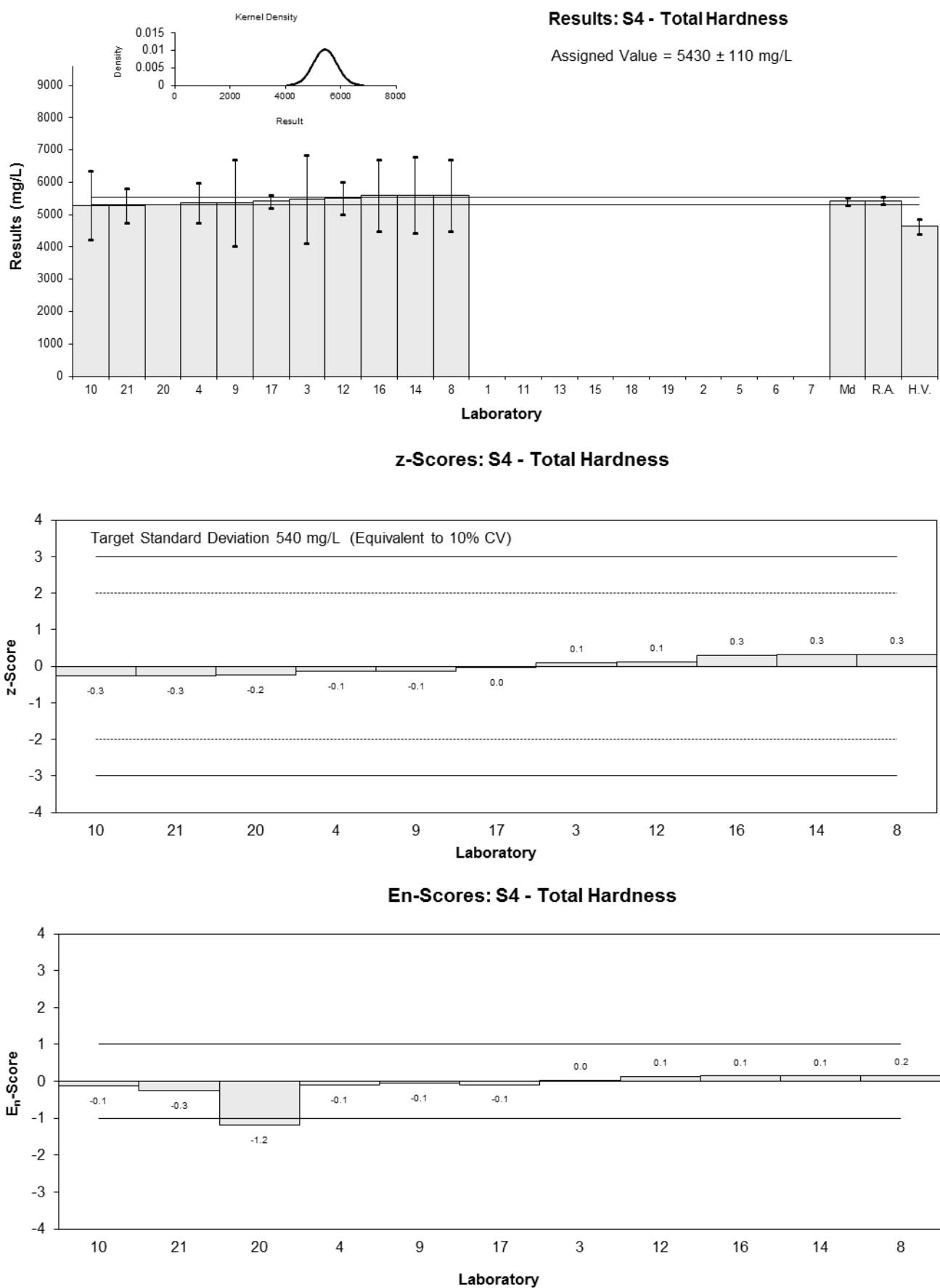


Figure 57

## 7 DISCUSSION OF RESULTS

### 7.1 Assigned Value

**Sample S1** was filtered seawater while **Sample S2** was the same seawater unfiltered. A known amount of single element standard solutions were added to the two study samples.

**Samples S3** was filtered seawater fortified with ammonia-N, dissolved organic carbon, nitrate-N and orthophosphate-P.

**Samples S4** was unfiltered seawater fortified with total Kjeldahl nitrogen and total organic carbon.

**Assigned Values** for P in S1 and S2 were reference values measured using standard addition inductively coupled plasma mass spectrometry (see Appendix 3). For the other analytes the assigned value was the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'. Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value.<sup>8</sup> Appendix 4 sets out the calculation for the robust average of Zn in Sample S1 and its associated uncertainty.

**Traceability** of the reference values for P in S1 and S2 rely on gravimetric sample preparation, elemental quantification by ICP-MS and density measurement. 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 the SI unit for mass (kg) - through the primary calibration standard certified by NIST (USA) and to the SI unit for amount of substance (mol) - through data for isotopic composition and relative atomic mass. Density measurement was calibrated using ultra high purity water and is traceable to the NMI determination of the density of water.

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

### 7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 734 numerical results, 721 (98%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.<sup>10</sup> The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparisons studies.<sup>11 – 17</sup>

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 57). In this study, the reported expanded measurement uncertainty has been over-estimated in some cases (e.g. Lab 2 for Al in S1, Lab 6 for Cd in S1 or Lab 20 for Mn in S1) or under-estimated (e.g. Lab 17 for Ag and in S1 or Lab 13 for Al in S1). As a simple rule of thumb, when the uncertainty estimate is smaller than the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be viewed as suspect.

Overestimation of the precision and/or laboratory or method bias is the most common error seen in the laboratories' estimated uncertainty budgets. According to NATA Technical Note 33<sup>14</sup> and to NORDTEST TR 537,<sup>12</sup> the most common experimental data used for estimating

the precision component for the measurement uncertainty calculation in the top down approach are from:

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

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

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.<sup>12,14</sup> An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 5.

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

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of  $16.2 \pm 1.701 \mu\text{g/L}$ , it is better to report  $16.2 \pm 1.7 \mu\text{g/L}$  or instead of  $10.75 \pm 1.20 \mu\text{g/L}$ , it is better to report  $10.8 \pm 1.2 \mu\text{g/L}$ .<sup>11</sup>

### 7.3 E<sub>n</sub>-score

E<sub>n</sub>-score should be interpreted only in conjunction with z-scores. The E<sub>n</sub>-score indicates how closely a result agrees with the assigned value taking into account the respective uncertainties. An unsatisfactory E<sub>n</sub> 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<sub>n</sub>-scores is graphically presented in Figure 58. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E<sub>n</sub>-score.

Of 734 results for which E<sub>n</sub>-scores were calculated, 611 (83%) returned a satisfactory score of  $|E_n| \leq 1$  indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

### 7.4 z-Score

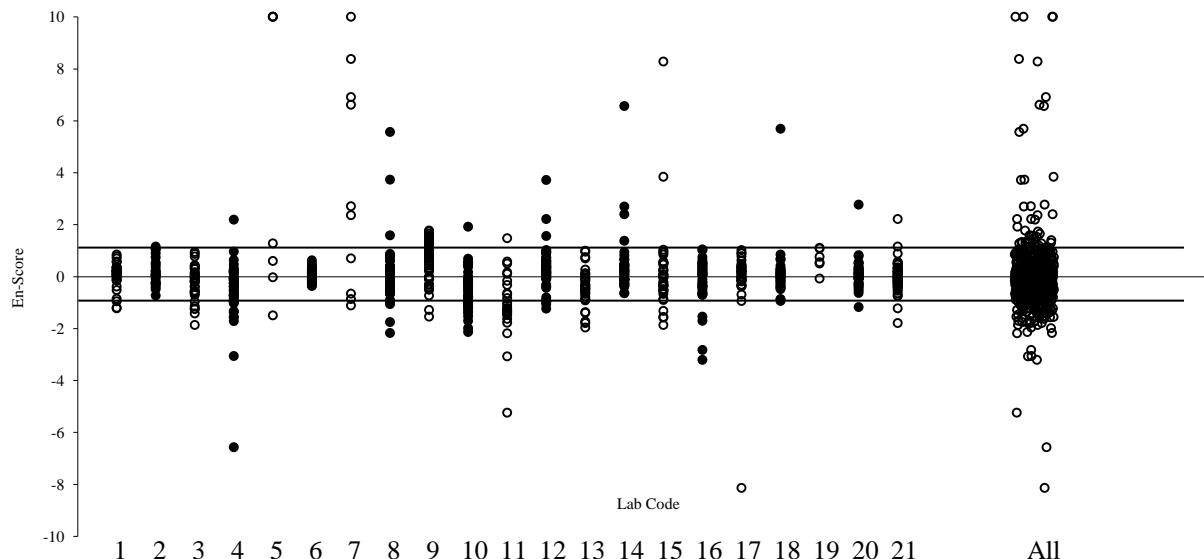
The z-score compares the participant's deviation from the assigned value with the target standard deviation set for proficiency assessment.

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

The between laboratory coefficient of variation predicted by the Thompson equation<sup>8</sup> and the participants' coefficient of variation resulted in this study are presented for comparison in Table 61.

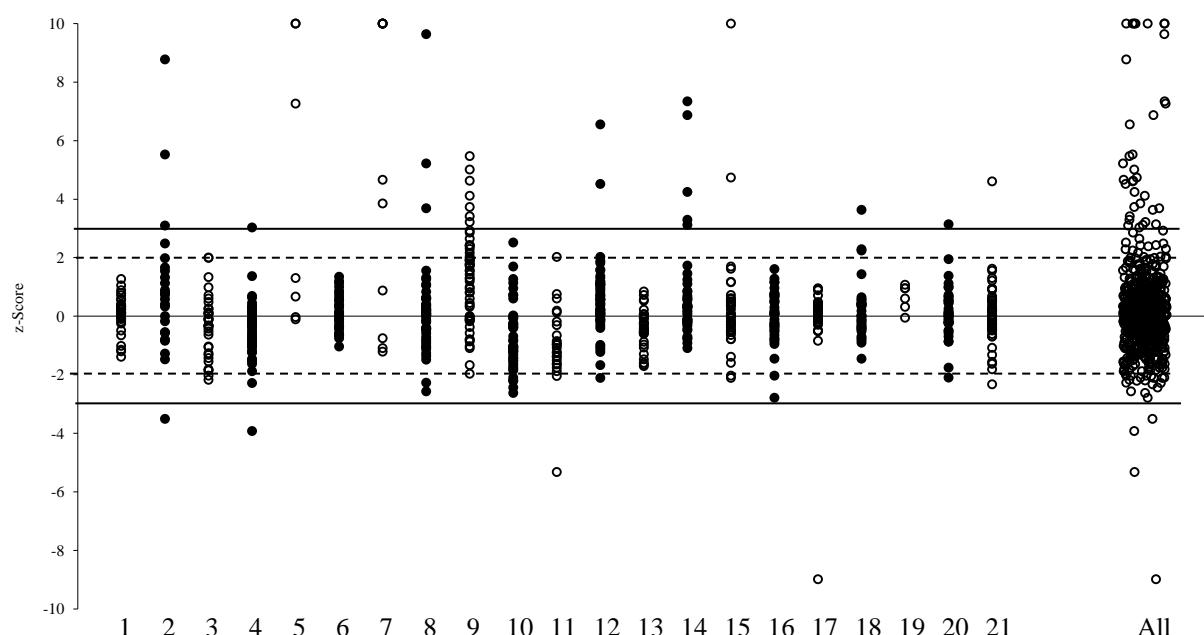
The dispersal of participants' z-scores is presented in Figure 59 (by laboratory code) and in Figure 60 (by test). Of 734 results for which z-scores were calculated, 662 (90%) returned a satisfactory score of  $|z| \leq 2$  and 33 (4%) were questionable of  $2 < |z| \leq 3$ . Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

**Laboratories 1, 6, 13, and 19** returned satisfactory z-scores for all analytes reported.



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

Figure 58 En-Score Dispersal by Laboratory



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

Figure 59 z-Score Dispersal by Laboratory

Table 61 Between Laboratory CV of this study, Thompson CV and Set Target CV

Sample	Analyte	Assigned value	Between Laboratory CV	Thompson/Horwitz CV	Target SD (as CV)
S1	Ag	1.9 µg/L	18%	22%	15%
S1	Al	18.4 µg/L	12%	22%	15%
S1	As	1.61 µg/L	22%	22%	15%
S1	Be	1.08 µg/L	9.3%	22%	15%
S1	Cd	1.1 µg/L	16%	22%	15%
S1	Co	1.36 µg/L	13%	22%	15%
S1	Cr	2.04 µg/L	14%	22%	15%
S1	Cu	5.59 µg/L	12%	22%	15%
S1	Fe	22.5 µg/L	25%	22%	20%
S1	Hg	0.252 µg/L	19%	22%	15%
S1	Mn	6.37 µg/L	11%	22%	15%
S1	Ni	2.06 µg/L	11%	22%	15%
S1	P	124.9 µg/L	32%	22%	20%
S1	Pb	1.46 µg/L	14%	22%	15%
S1	Se	3.97 µg/L	25%	22%	20%
S1	Sn	3.74 µg/L	15%	22%	15%
S1	V	2.77 µg/L	10%	22%	15%
S1	Zn	11.6 µg/L	17%	22%	15%
S2	Ag	11.7 µg/L	14%	22%	10%
S2	Al	56.9 µg/L	11%	22%	10%
S2	As	15.6 µg/L	12%	22%	10%
S2	Ba	33.8 µg/L	6.5%	22%	10%
S2	Cd	5.22 µg/L	14%	22%	10%
S2	Cr	12.3 µg/L	13%	22%	10%
S2	Cu	17.8 µg/L	15%	22%	15%
S2	Fe	53 µg/L	12%	22%	10%
S2	Mn	10.3 µg/L	9.5%	22%	10%
S2	Mo	27.6 µg/L	12%	22%	10%
S2	Ni	13.8 µg/L	15%	22%	15%
S2	P	286 µg/L	18%	20%	20%
S2	Pb	5.1 µg/L	11%	22%	10%
S2	Sb	17.5 µg/L	11%	22%	10%
S2	Se	11.9 µg/L	18%	22%	15%
S2	Sn	7.16 µg/L	8%	22%	10%
S2	V	15.2 µg/L	11%	22%	10%
S2	Zn	35.5 µg/L	14%	22%	10%
S3	Ammonia-N	0.106 mg/L	15%	22%	20%
S3	Chloride	17300 mg/L	13%	3.7%	10%
S3	DOC	4.03 mg/L	3%	16%	10%
S3	Fluoride	1.23 mg/L	26%	3%	20%
S3	Nitrate-N	0.0404 mg/L	12%	22%	20%
S3	Orthophosphate-P	0.0687 mg/L	18%	22%	15%
S3	Sulfate	2400 mg/L	5.4%	5%	10%
S3	TDN	0.257 mg/L	18%	20%	15%
S3	TDP	0.083 mg/L	21%	22%	20%
S4	Alkalinity	99.1 mg/L	2.6%	8%	10%
S4	B	3.87 mg/L	9.3%	13%	10%
S4	Ca	354 mg/L	8.5%	6.6%	10%
S4	EC	43500 µS/cm	9.1%	3.2%	10%
S4	K	350 mg/L	11%	6.6%	10%
S4	Mg	1110 mg/L	2.7%	5.6%	10%
S4	pH	7.91	1.1%	12%	10%

S4	TKN	0.582 mg/L	15%	17%	15%
S4	TN	0.613 mg/L	14%	17%	15%
S4	TOC	4.78 mg/L	16%	13%	10%
S4	Total Hardness	5430 mg/L	2.6%	4.4%	10%

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

**Sample S1** was filtered seawater. The analytes' concentration in this sample ranged from 0.252 to 124.9 µg/L. **Sample S2** was unfiltered seawater and participants were asked to report results for total elements. Analytes' concentration in this sample was 2 to 7 times higher than in Sample S1. A summary of participants' results and performance in the two study samples is presented in Table 60 and in Figures 59 and 60.

Low level P, Se, Fe and As in S1 were the tests that had the highest coefficient of variation, between 18% and 32%.

All unsatisfactory results reported by Laboratories 7 and 9 were greater than the assigned value. This is an indication of method or laboratory bias. The z-score results from these laboratories were not taken into consideration when assessing the effects of analyte on participants' performance

### Individual Element Commentary

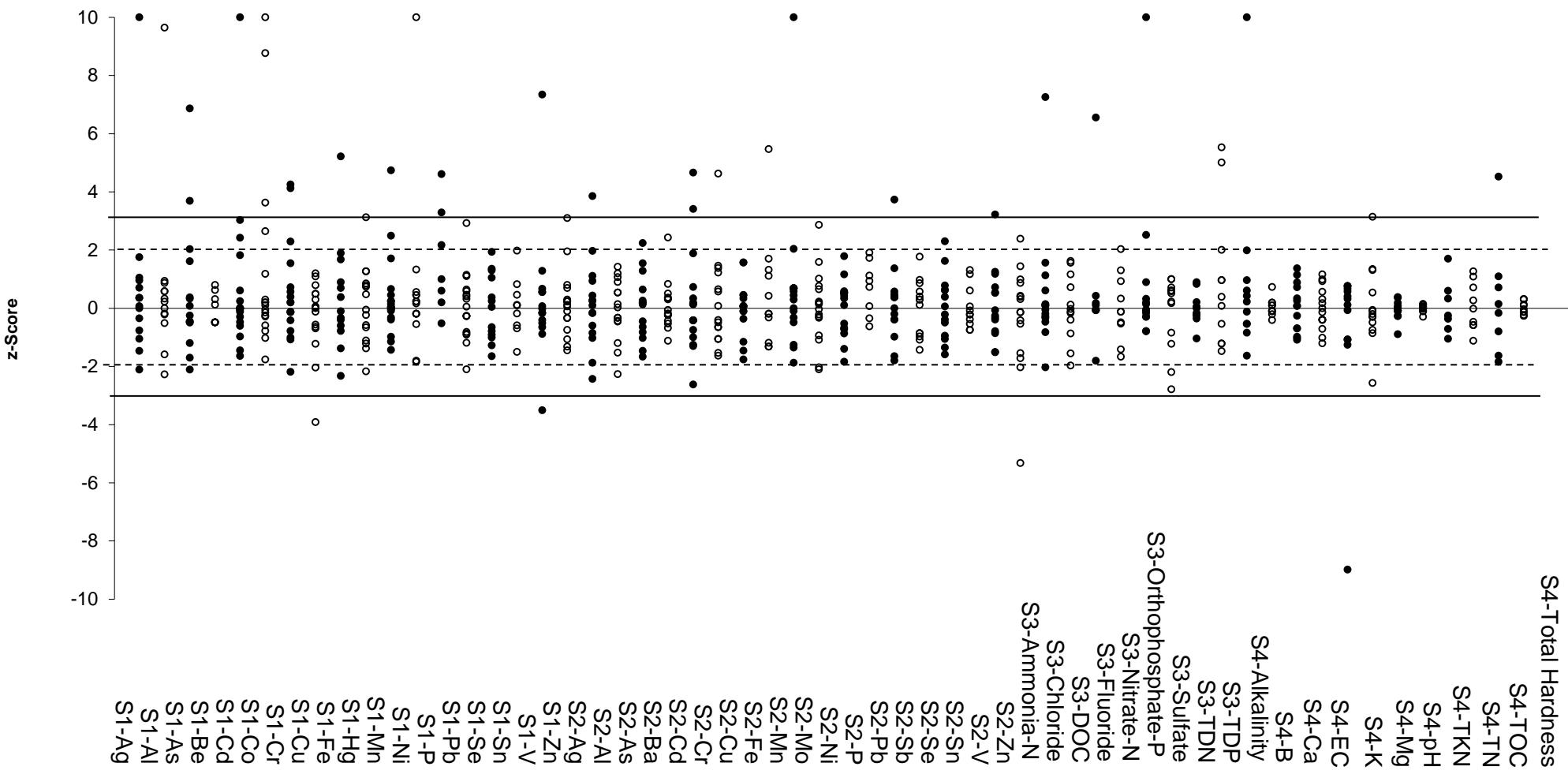
Participants were requested to analyse the samples using their normal test method and to report a single result as they would normally report to a client. Excepting one, all participants who reported results for total elements in S2 performed digestion. Most used a digestion temperature of 85°C to 120°C; one digested its samples at 170°C and one at 200°C. Seven laboratories used nitric acid and hydrochloric acid for extraction and five used only nitric acid. Laboratory 15 reported using only hydrochloric acid for Ag extraction. No relationship between the results reported for total elements in S2 and the digestion method employed was evident.

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

Participants used a wide variety of instrumental techniques, collision/reaction cells and cell gases. Most laboratories reported using ICP-MS with a collision/reaction cell, some used ICP-OES and some only ICP-MS. One participant used ICP-MS measurements with a preconcentration and matrix separation step (seaFAST-ICP-MS) and one reported using a spectrophotometer. Plots of participants' results and performance versus instrumental techniques used are presented in Figure 61.

**Arsenic** measurements at low levels posed significant problems for laboratories. The between-laboratories CV for As in S1 was 22%. Most of the unsatisfactory z-scores were high, indicating unsolved interference problems (Figure 61).

Ammonia as reaction gas is not effective in removing  $^{40}\text{Ar}^{35}\text{Cl}^+$  interferences on As. ICP-MS with H<sub>2</sub> or O<sub>2</sub> as reaction gases might be a better option. When testing As in seawater, the largest and most common interference to overcome in analysis by ICP-MS is  $^{40}\text{Ar}^{35}\text{Cl}^+$ . Hydrogen as reaction gas has been proven to reduce Ar-based interferences while the mass shifting of  $^{75}\text{As}^+$  to m/z 91 as  $^{75}\text{AsO}^{16+}$ , by O<sub>2</sub> is also considered an effective solution for overcoming As interferences in seawater.<sup>18</sup>



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

Figure 60 z-Score Dispersal by Analyte

Table 62 Summary of Participants' Results and Performance for Total and Dissolved Elements

Lab. code	S1-Al µg/L	S2-Al µg/L	S1-Ag µg/L	S2-Ag µg/L	S1-As µg/L	S2-As µg/L	S4-B mg/L	S2-Ba µg/L	S1-Be µg/L	S4-Ca mg/L	S1-Cd µg/L	S2-Cd µg/L	S1-Co µg/L	S1-Cr µg/L	S2-Cr µg/L	S1-Cu µg/L	S2-Cu µg/L
H.V.	20.8	54.3	1.89	11.1	1.63	14.8	4.65	32.4	1.06	303	1.12	4.96	NA	2.14	12.2	5.51	17.9
A.V.	18.4	56.9	1.9	11.7	1.61	15.6	3.87	33.8	1.08	354	1.1	5.22	1.36	2.04	12.3	5.59	17.8
1	17.9	NT	2.2	NT	1.32	NT	4	NT	1.13	374	1.14	NT	1.42	1.73	NT	6.25	NT
2	20	NT	1.48	NT	1.69	NT	NT	NT	1.21	NT	1.1	NT	3.15	2.51	NT	5.11	NT
3	<20	55	NT	NT	<10	16	3.47	NT	<1	389	<1	5	<3	2	11	6	18
4	12.1	48.2	1.6	9.5	<10	16.6	4.4	34.9	<1	329	1.6	4.7	1.3	<5	11.5	2.3	13.9
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	20.8	63.7	<2	10.5	1.63	14.9	NT	34.8	<1	NT	1.1	4.83	1.24	2.21	11.5	5.61	17.5
7	<500	<500	6.4	16.2	NT	NT	4.21	<50	NT	311.1	3.9	7.65	8.9	<50	<50	<119	<119
8	45	44	2	12	2.5	14	3.9	30	<1	340	1.2	5.3	1.4	2.1	11	5.6	18
9	21	65	2.4	14	1.7	18	3.45	42	<3	318	1.5	7	1.9	3.3	18	6.6	22
10	<50	50.1	<5	8.86	1.55	14.3	4.31	33.6	<1	340	0.83	3.85	1.15	1.37	10.4	4.56	14.7
11	<50	57.7	<5	10.7	2.1	15.9	NT	33.2	<1	NT	1.05	4.56	<1	1.71	10.3	3.88	13.1
12	20	63	2.1	13	1.1	13	3.49	35	1.1	387	1.4	6.2	1.6	2.1	13	6.5	22
13	17.8	54.3	1.92	11	1.2	13.3	NT	33	1	NT	0.94	4.54	1.35	2.26	11.8	5.64	18
14	19.3	54.4	1.68	11.5	3.27	15.9	3.77	36.6	1.18	365	1.02	5.29	1.33	3.34	14.1	5.49	17.5
15	14	57	1.3	11.5	1.5	14.6	NT	32	1	NT	1.1	5.4	1.2	1.8	12.4	6	18
16	<50	55	<5	11.8	2	17.6	4.15	35.5	<1	395	1.08	5.32	1.31	1.91	11.7	5.05	16.8
17	18.4	NT	2.17	NT	1.49	NT	3.97	NT	1	354	1.09	NT	1.38	2.16	NT	5.83	NT
18	17	60	1.8	12.2	<4	19.1	3.6	32.3	NT	349	0.86	5	2.1	2.74	13.1	5.6	18.7
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	<40	60	1.9	12	NT	NT	3.9	33	1	360	1.1	5.6	1	2	14	5	19
21	19	62	2	12.8	1.5	15.8	3.6	31.5	<2	340	1	5	1.4	2	13.8	5.6	19

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

Table 60 Summary of Participants' Results and Performance for Total and Dissolved Elements (continued)

Lab. code	S1-Fe µg/L	S2-Fe µg/L	S1-Hg µg/L	S4-K mg/L	S4-Mg mg/L	S1-Mn µg/L	S2-Mn µg/L	S2-Mo µg/L	S1-Ni µg/L	S2-Ni µg/L	S1-P µg/L	S2-P µg/L
H.V.	24.2	54.3	0.213	NA	1040	6.41	10.4	28.3	2.02	13.7	124.9	286
A.V.	22.5	53	0.252	350	1110	6.37	10.3	27.6	2.06	13.8	124.9	286
1	16.3	NT	0.3	NT	1150	5.27	NT	NT	2.13	NT	NT	NT
2	30	NT	0.28	NT	NT	8.75	NT	NT	2.47	NT	NT	NT
3	21	46	0.17	397	1100	5	9	22	<5	10	112	250
4	19	46.7	<1	346	1100	6.8	9.8	27.5	2	12.3	130	266
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	19.8	52	0.227	NT	NT	6	9.97	30.4	2.11	14.9	NT	NT
7	NT	NT	NT	323.8	NT	NT	48.5	24.6	<89	<89	<85	<85
8	46	60	0.3	260	1130	6.4	8.9	25	2	14	140	290
9	31	82	0.25	320	1110	8	12.4	35.5	2.2	17.5	179	395
10	<50	<50	0.21	348	1080	6.06	10.3	21.8	1.49	12.4	<5000	<5000
11	<50	<50	0.206	NT	NT	5.43	8.36	29.7	<5	10.9	NT	NT
12	22	52	<0.5	396	1110	6.6	11	32	2.2	15	NT	NT
13	20.7	51.3	0.284	NT	NT	6.33	10.2	28.2	1.89	14.9	NT	NT
14	25.6	58.9	0.37	343	1152	6.28	10.6	26.7	2.23	14.5	207	385
15	<100	62	0.2	NT	NT	10.9	10.9	26.8	16.2	16.2	<10	<1000
16	<50	<50	0.282	369	1119	6.5	11	29.4	<5	12.7	<500	328
17	26.5	NT	0.27	340	1100	6.36	NT	NT	2.13	NT	NT	NT
18	24.2	55.2	0.243	339	1010	6.4	10.75	28.1	<7	14.7	NT	<420
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	<40	<40	0.23	460	1100	7	11	28	2	12	150	350
21	12	46	<0.5	333	1080	6.6	11	27	1.5	14.9	240	340

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

Table 60 Summary of Participants' Results and Performance for Total and Dissolved Elements (continued)

Lab. code	S1-Pb µg/L	S2-Pb µg/L	S2-Sb µg/L	S1-Se µg/L	S2-Se µg/L	S1-Sn µg/L	S2-Sn µg/L	S1-V µg/L	S2-V µg/L	S1-Zn µg/L	S2-Zn µg/L
H.V.	1.6	5.51	18.1	4.38	13.2	3.63	7.46	3.09	15.5	10.7	34.2
A.V.	1.46	5.1	17.5	3.97	11.9	3.74	7.16	2.77	15.2	11.6	35.5
1	1.53	NT	NT	4.26	NT	3.79	NT	2.5	NT	11.8	NT
2	1.55	NT	NT	2.95	NT	4.85	NT	1.31	NT	17	NT
3	<10	<10	NT	<20	<20	NT	NT	NT	NT	11	30
4	1.4	4.6	18	<10	11.2	2.9	<10	2.4	15.1	12.8	36.6
5	NT	NT	NT	NT	NT						
6	1.71	5.29	17.7	5.04	13.3	NT	NT	3.05	14.7	11.4	36.9
7	NT	<52	<52	<50	<50						
8	1.6	5.3	16	4.8	13	3.8	7.2	2.6	14	12	34
9	2.1	7	20.6	5.5	16	4.2	8.1	3.3	20.1	13	44
10	1.2	4.18	15	3.17	10	<5	6.89	<5	12.9	9.3	29.4
11	1.26	4.26	15.8	3.45	9.47	<5	7.6	<5	12.9	<5	16.6
12	1.7	5.8	19	4	12	NT	NT	3	17	12	35
13	1.27	5.39	NT	2.66	9.07	3.41	6.77	2.76	14.8	9.74	33.6
14	1.59	5.29	15.6	3.25	11.5	3.35	6.62	5.82	17.1	11.7	38.6
15	1.4	4.9	18.2	<100	13	<5.0	8	2.7	16.3	12	37
16	1.47	5.34	19.2	3.34	10.2	<5	6.62	<5	13.9	9.08	28.3
17	1.56	NT	NT	4.17	NT	3.64	NT	2.56	NT	12.1	NT
18	1.28	5.1	18.5	<4	12.6	<5	7.1	2.7	14.6	10.3	40.6
19	NT	NT	NT	NT	NT						
20	1	5	16	<5	11	4	7	2.8	16	15	39
21	1.4	4.9	18	5	14.8	<5	7	3	16	11	35

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

Table 63 Summary of Participants' Results and Performance in S3

Lab. code	S3-NH <sub>3</sub> -N mg/L	S3-Cl <sup>-</sup> mg/L	S3-DOC mg/L	S3-F <sup>-</sup> mg/L	S3-PO <sub>4</sub> -P mg/L	S3-NO <sub>3</sub> -N mg/L	S3-SO <sub>4</sub> <sup>2-</sup> mg/L	S3-TDN mg/L	S3-TDP mg/L
H.V.	0.094	17000	4.22	1.22	0.108	0.044	2530	0.235	0.108
A.V.	0.106	17300	4.03	1.23	0.0687	0.0404	2400	0.257	0.083
1	0.109	17500	4.01	1.11	0.0747	0.0476	2340	0.26	0.0866
2	0.13	17001	NT	NT	0.06	0.034	2614	0.47	0.074
3	0.099	NT	3.3	NT	0.076	0.0415	NT	0.334	0.116
4	0.1	15800	4.1	1.31	0.056	0.04	2150	0.21	0.056
5	0.26	17250	NT	1.55	NT	4.43	NT	NT	3.6
6	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	0.096	20000	4.2	1.2	0.071	0.039	2600	0.2	<0.05
9	0.119	13900	NT	0.82	0.079	0.034	2360	0.45	0.081
10	0.0884	18550	< 5	0.88	0.046	0.0608	2313.5	0.294	0.0931
11	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	0.108	16600	6.67	1.73	0.079	0.038	2450	0.21	0.09
13	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	NT	NT	NT	NT	NT	NT	NT	NT	NT
15	0.063	20100	4	1.1	0.074	0.038	2410	0.236	0.074
16	0.108	19300	NT	NT	0.04	NT	2345	NT	NT
17	0.102	17100	4.07	1.46	0.0705	0.0396	2400	0.272	0.069
18	NT	NT	NT	NT	NT	NT	NT	NT	NT
19	0.105	NT	NT	NT	0.075	0.043	NT	0.294	0.099
20	NT	NT	NT	NT	NT	NT	NT	NT	NT
21	0.139	14600	4	1.2	0.075	0.042	2410	NT	NT

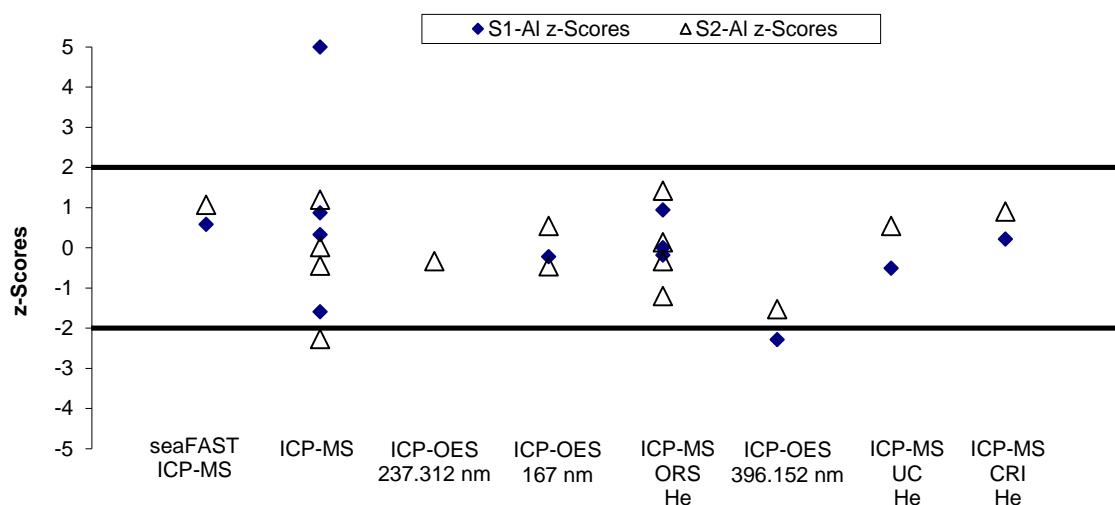
Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, NA= Not Available

Table 64 Summary of Participants' Results and Performance in S4

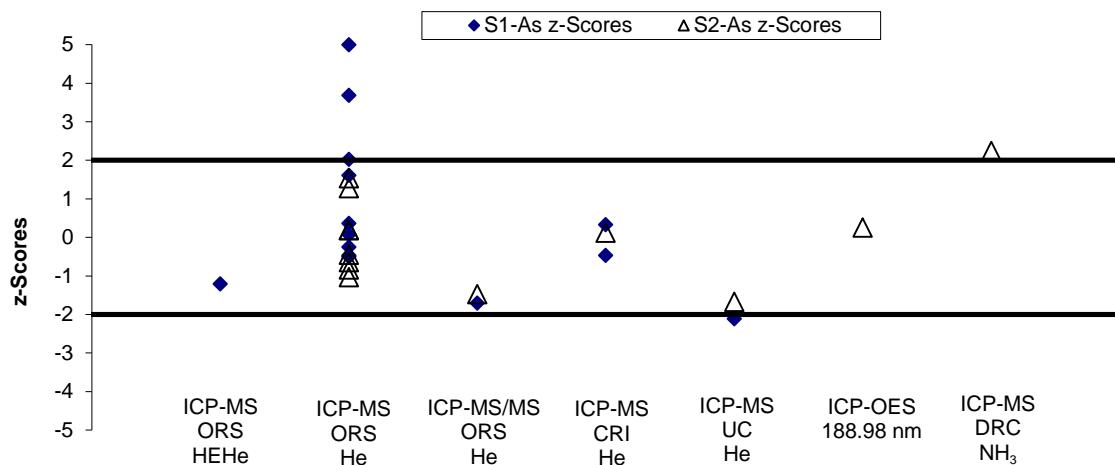
Lab. code	S4-Alkalinity mg/L	S4-EC µS/cm	S4-pH	S4-Hardness mg/L	S4-TKN mg/L	S4-TN mg/L	S4-TOC mg/L
H.V.	95.2	35800	7.9	4640	0.461	0.502	5.3
A.V.	99.1	43500	7.91	5430	0.582	0.613	4.78
1	98.2	45300	8	NT	NT	0.611	5.12
2	NT	NT	NT	NT	NT	NT	NT
3	98	43200	8	5480	0.634	0.638	3.9
4	97	44000	7.96	5360	0.56	0.56	4.7
5	NT	46400	7.82	NT	NT	NT	NT
6	NT	NT	NT	NT	NT	NT	NT
7	<700	NT	NT	NT	NT	NT	NT
8	95	38000	7.9	5600	0.52	0.56	5.3
9	98	44900	7.9	5360	0.55	0.56	4.397
10	106.35	38800	7.93	5290	0.73	0.73	< 5
11	NT	NT	NT	NT	NT	NT	NT
12	100	46820	7.82	5500	0.49	0.51	6.94
13	NT	NT	NT	NT	NT	NT	NT
14	NT	NT	NT	5600	NT	NT	NT
15	NT	NT	NT	NT	NT	NT	NT
16	NT	46800	7.67	5592	NT	NT	NT
17	101	4390	8.03	5410	0.611	0.678	4.85
18	NT	NT	NT	NT	NT	NT	NT
19	NT	NT	NT	NT	NT	0.712	NT
20	100	46000	7.9	5300	NT	NT	NT
21	101	38800	7.9	5290	NT	0.57	4

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

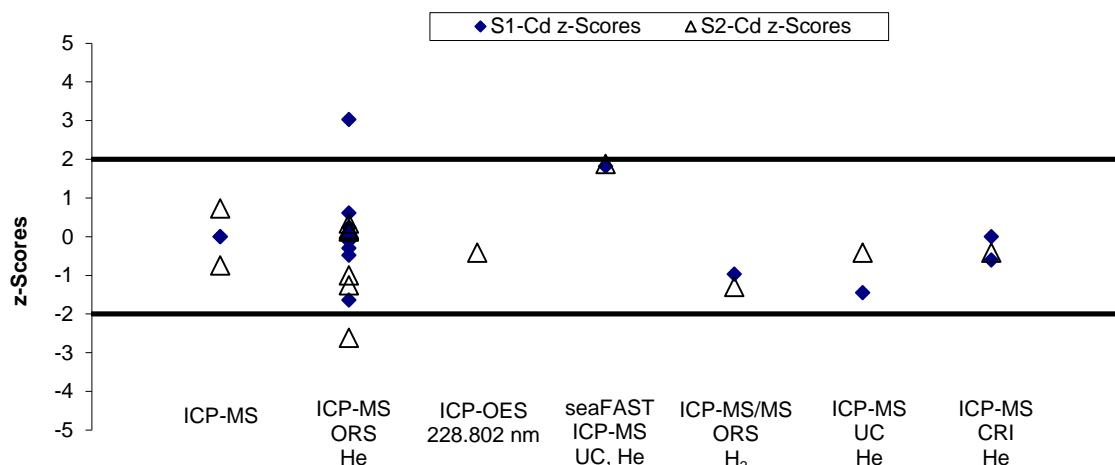
### S1 Al and S2 Al z-Scores vs Instrumental Technique



### S1 As and S2 As z-Scores vs Instrumental Technique

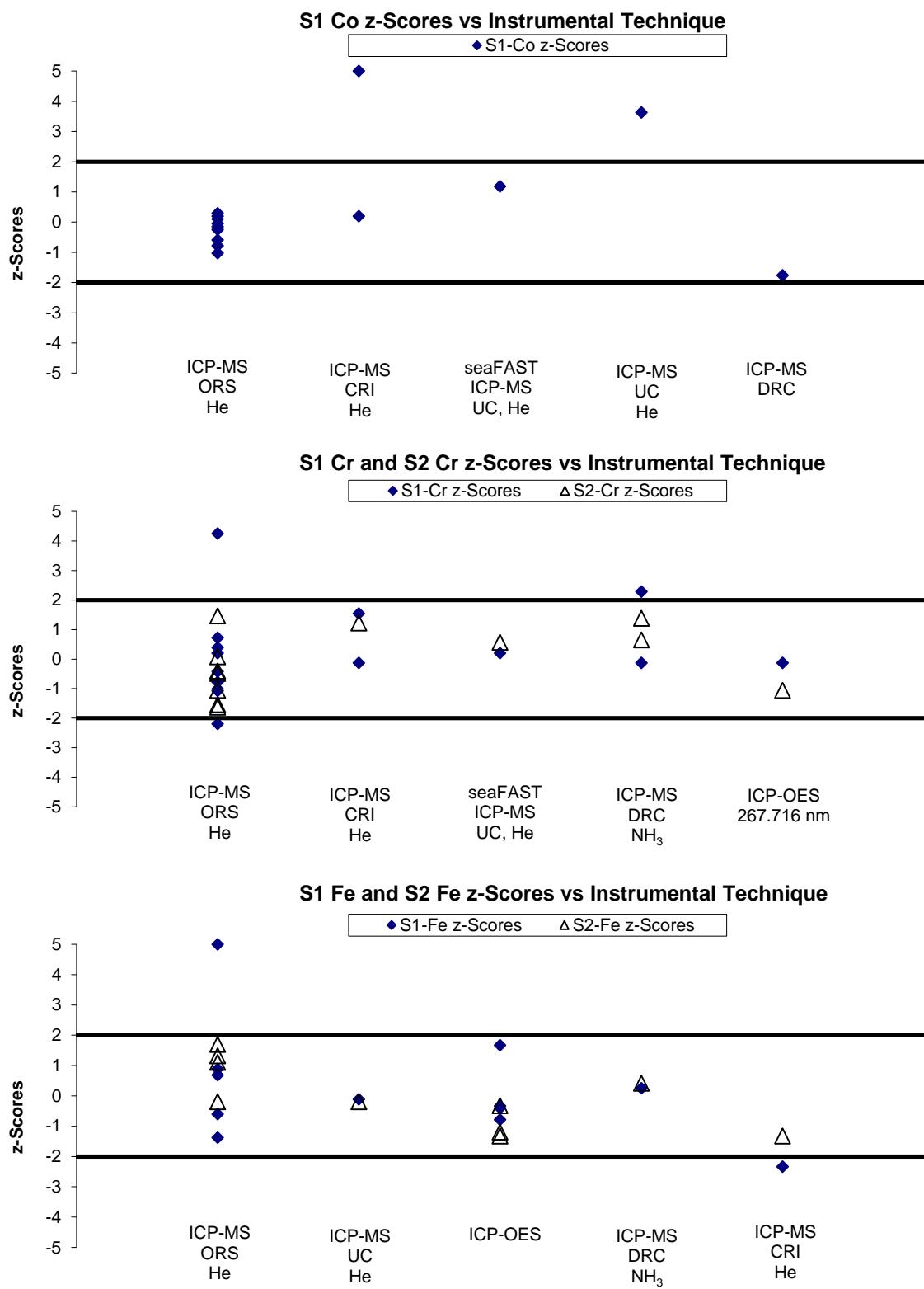


### S1 Cd and S2 Cd z-Scores vs Instrumental Technique



Scores of >5 or <-5 have been plotted as 5 or -5.

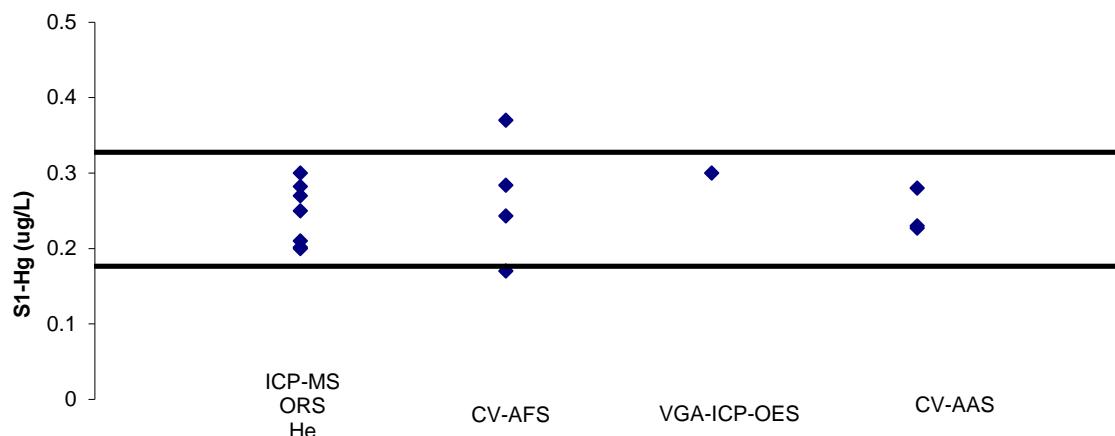
Figure 61 Participants' Results and Performance vs Instrumental Technique



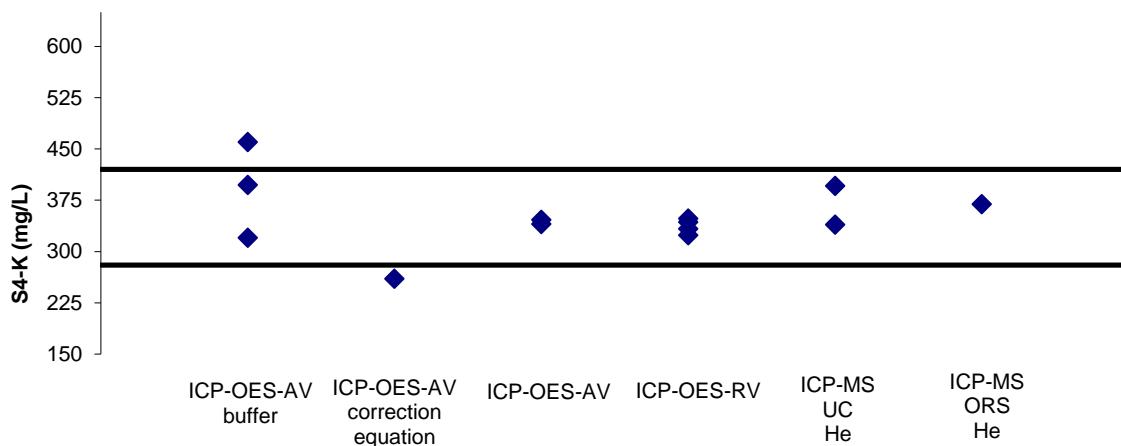
Scores of >5 or <-5 have been plotted as 5 or -5.

Figure 61 Participants' Results and Performance vs Instrumental Technique (continued)

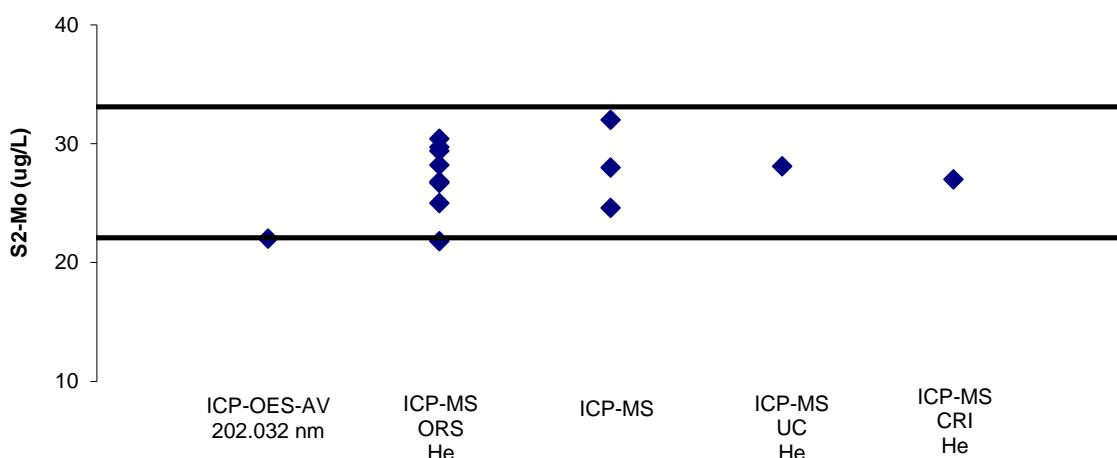
### S1 Hg Results vs Instrumental Technique



### S4 K Results vs Instrumental Technique



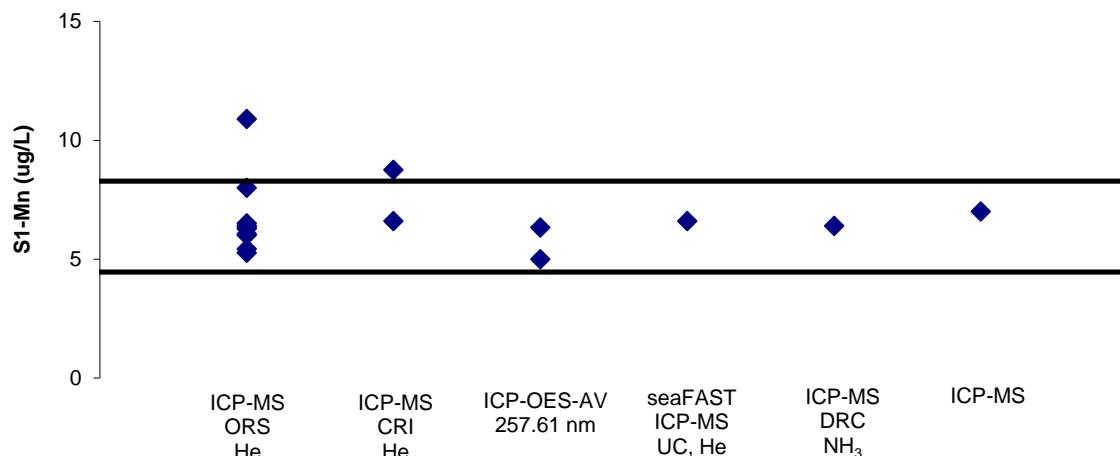
### S2 Mo Results vs Instrumental Technique



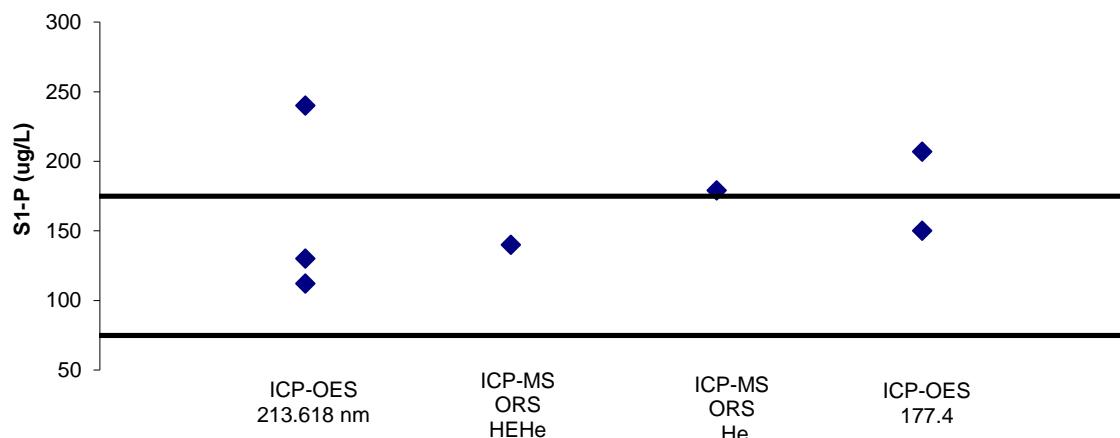
Scores of >5 or <-5 have been plotted as 5 or -5. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 61 Participants' Results and Performance vs Instrumental Technique (continued)

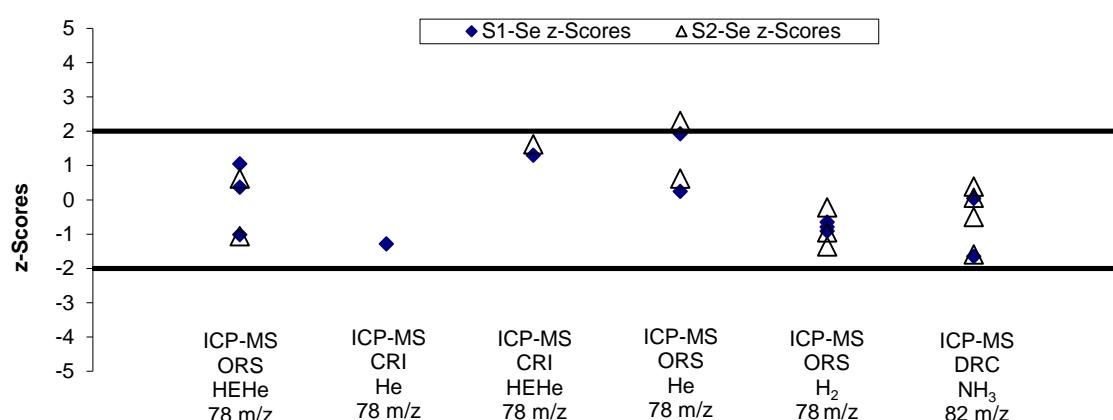
### S1 Mn Results vs Instrumental Technique



### S1 P Results vs Instrumental Technique

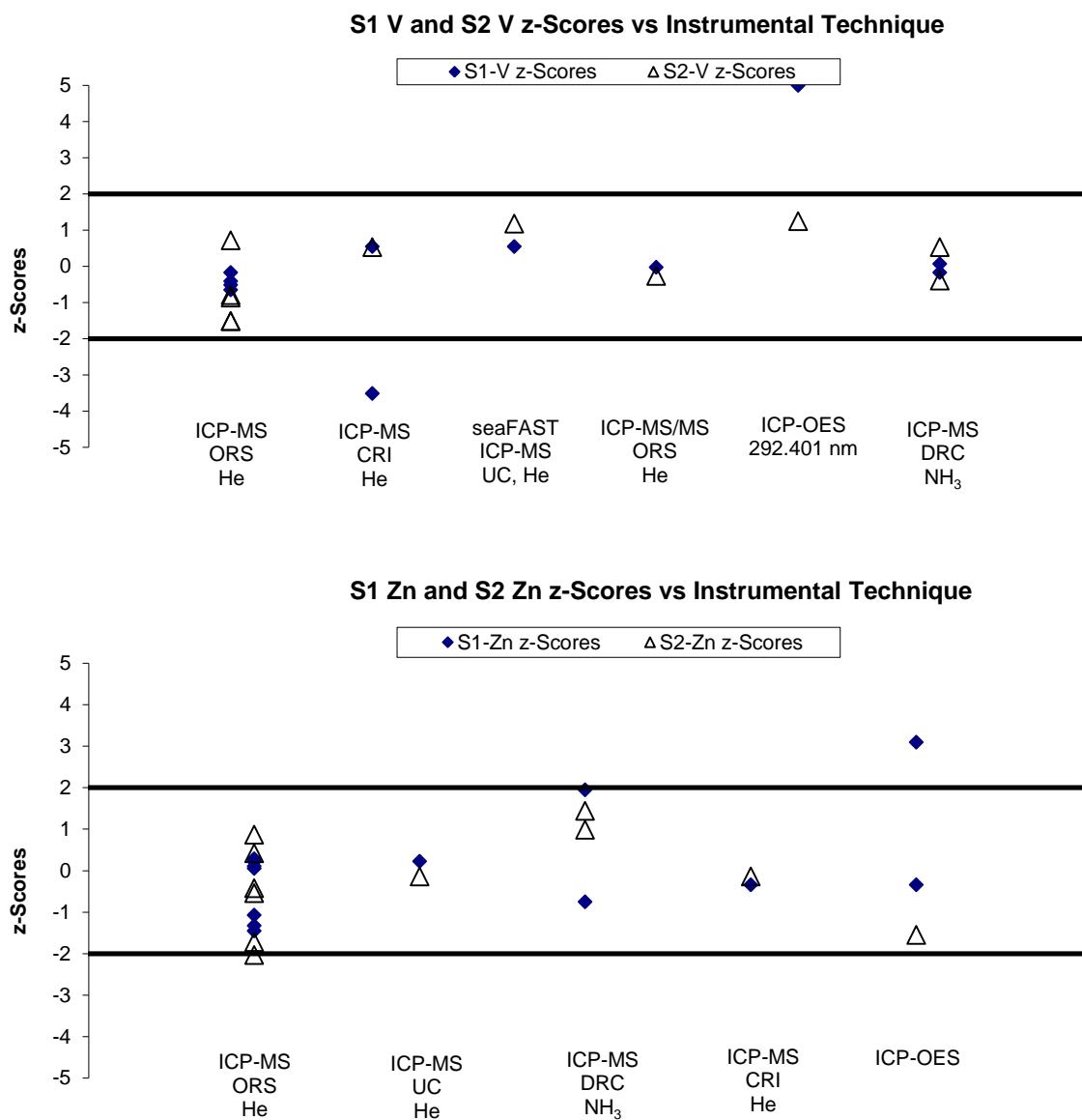


### S1 Se and S2 Se z-Scores vs Instrumental Technique



Scores of  $>5$  or  $<-5$  have been plotted as 5 or -5. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 61 Participants' Results and Performance vs Instrumental Technique (continued)



Scores of >5 or <-5 have been plotted as 5 or -5.

Figure 61 Participants' Results and Performance vs Instrumental Technique (continued)

**Cobalt** challenged participants' analytical techniques. Of the 17 reported results, 13 returned satisfactory z-scores.

Unsolved interference problems might explain participants' poor performance. The most common interferences for <sup>59</sup>Co in seawater are from <sup>43</sup>Ca<sup>16</sup>O<sup>+</sup>, <sup>42</sup>Ca<sup>16</sup>O<sup>1</sup>H<sup>+</sup>, <sup>24</sup>Mg<sup>35</sup>Cl<sup>+</sup>, <sup>36</sup>Ar<sup>23</sup>Na<sup>+</sup> and <sup>40</sup>Ar<sup>18</sup>O<sup>1</sup>H<sup>+</sup>. Conventional quadrupole ICP-MS does not have the resolution required to separate molecular ions from the isotope of interest and false positives and concentrations much higher than the true values are obtained when this is used.

**Chromium** Participants used a wide variety of instrumental techniques to overcome the interference problems with Cr in the seawater sample; these are presented in Figure 61.

**Iron and Zinc** The coefficient of variation in S1 for Fe and Zn was high, between 16% and 25%. These elements are known to be ubiquitous in the environment and controlling Fe or Zn contamination is a challenge for laboratories. No relationship between the results reported for these elements and the instrumental technique used was evident.

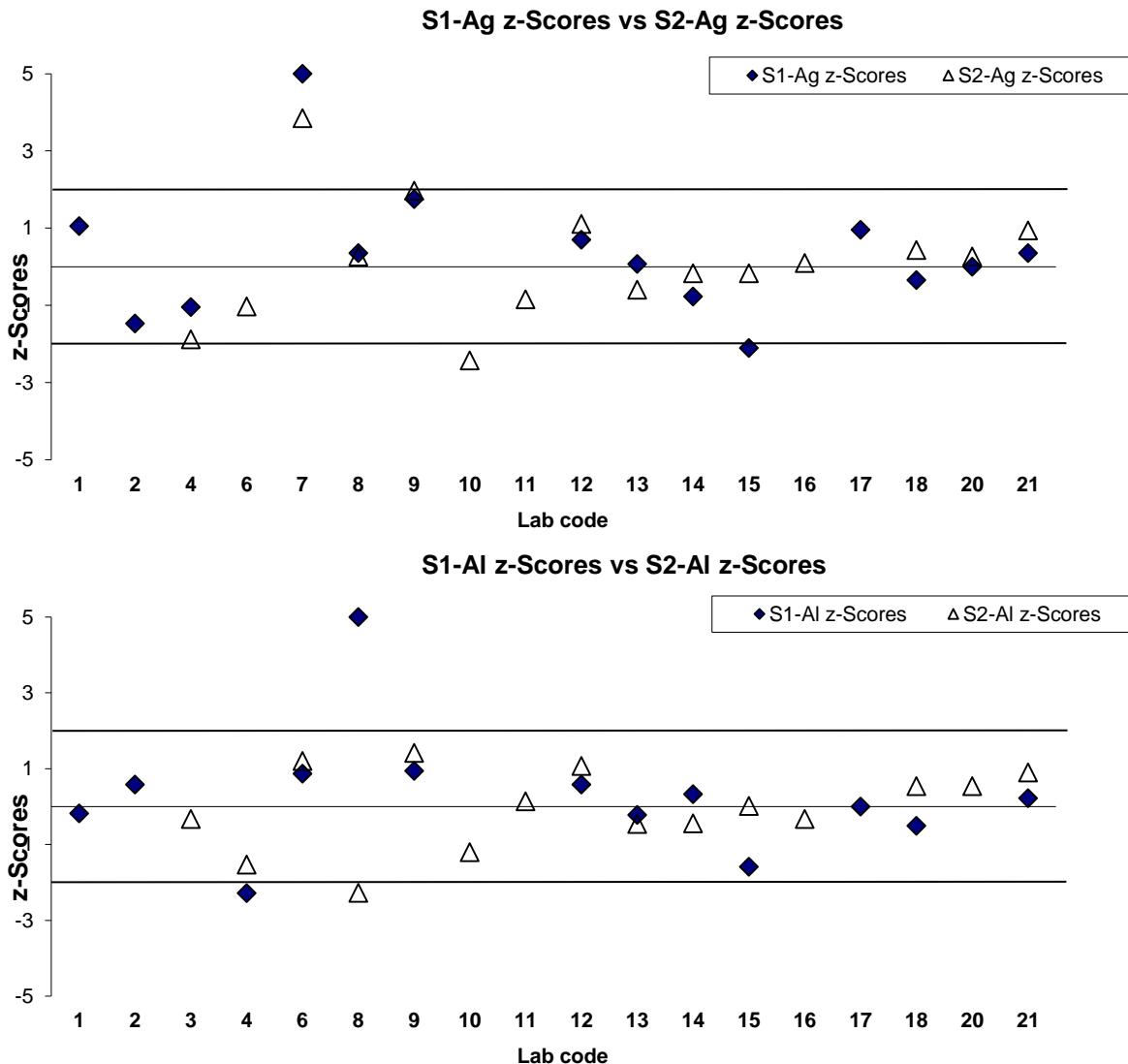
**Phosphorus** reference value in S1 was 124.9 µg/L. A limited number of laboratories had the capability to measure P in seawater at this level. Only 7 participants reported results for this analyte. Most laboratories used ICP-OES with wavelength 213.618 nm or 177.4 nm for P measurements in S1. One laboratory reported a satisfactory P result from ICP-MS measurements with high energy He.

**Selenium** presented analytical difficulty to participants. The Se level in S1 was 3.97 µg/L and in S2, 11.9 µg/L. The coefficient of variation for Se in S1 was 25% and 18% in S2. Most participants reported using ICP-MS with various collision cells and He or high energy He as collision gas, and some reported using ICP-MS in reaction mode with H<sub>2</sub> or NH<sub>3</sub>. Plots of participants' results versus instrumental technique used are presented in Figure 61.

### Comparisons of Participants' Performance in Samples S1 and S2

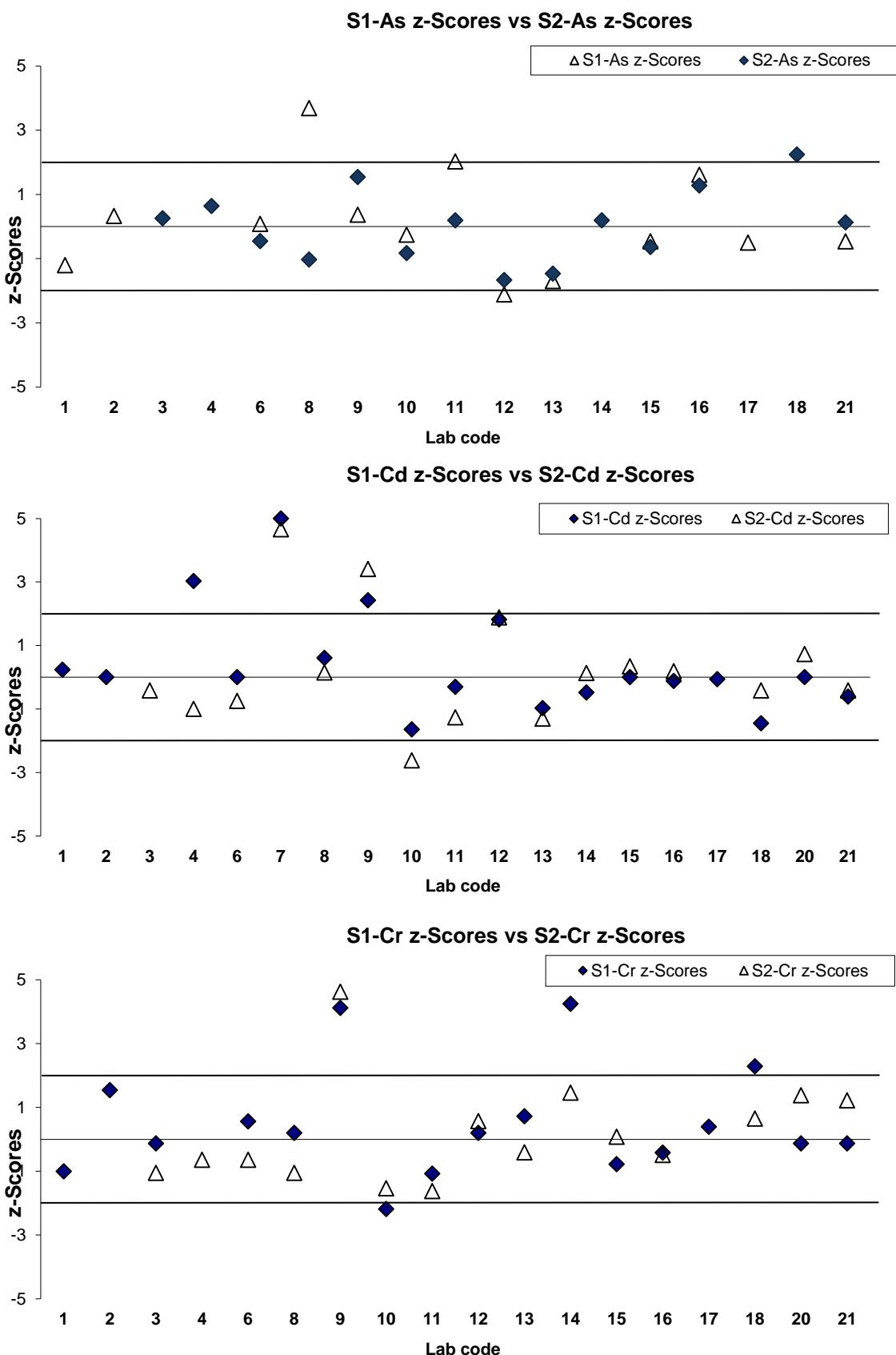
Plots of participants' performance in Samples S1 and S2 are presented in Figure 62. Plots of z-scores that are close to the zero axes are an indication of excellent accuracy.

Laboratories whose z-scores for an element in both samples S1 and S2 lie on the same side of the centre line may need to monitor its procedure as this can be an indication of method bias.



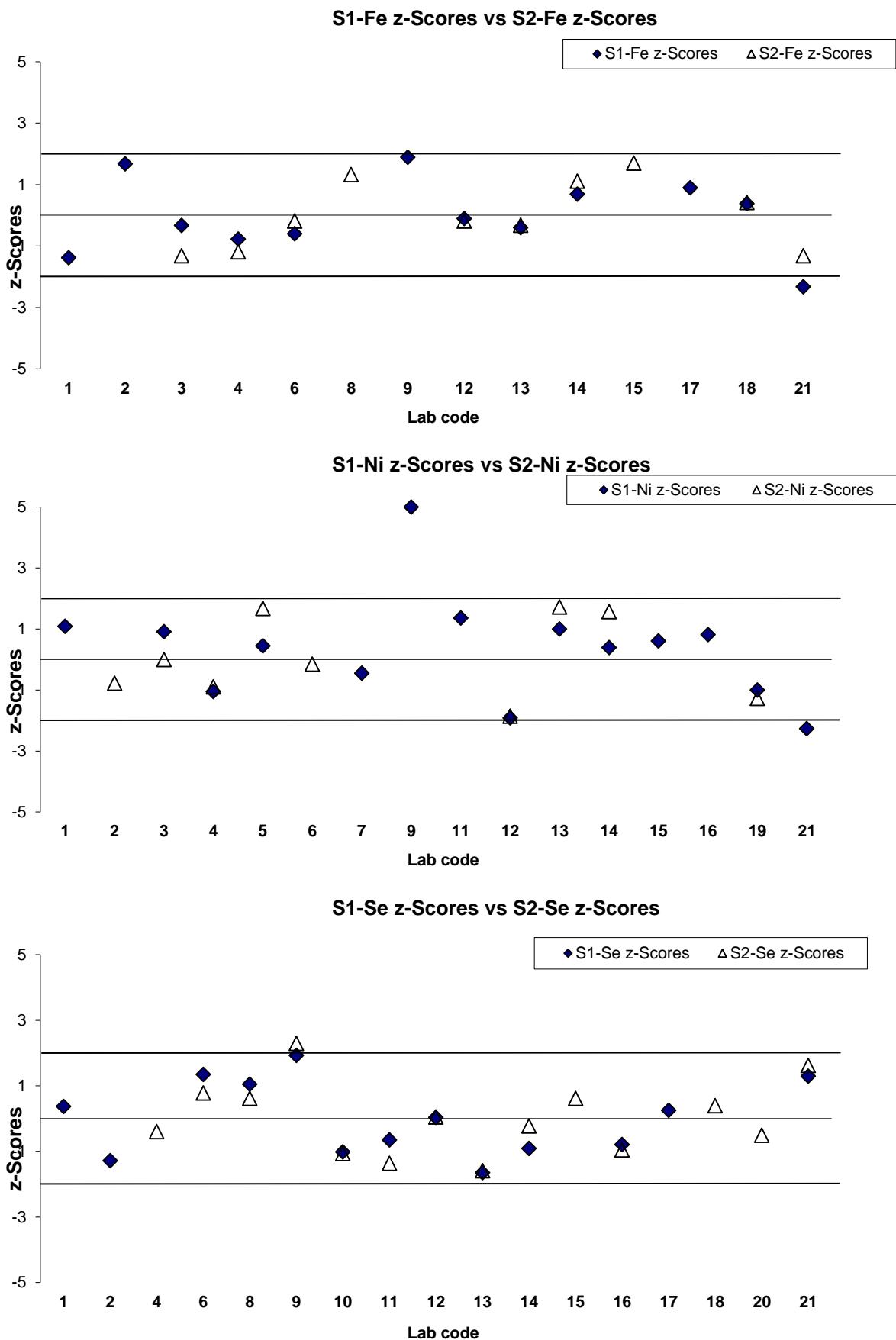
Scores of >5 or <-5 have been plotted as 5 or -5.

Figure 62 Comparisons of Participants' Performance in S1 and S2



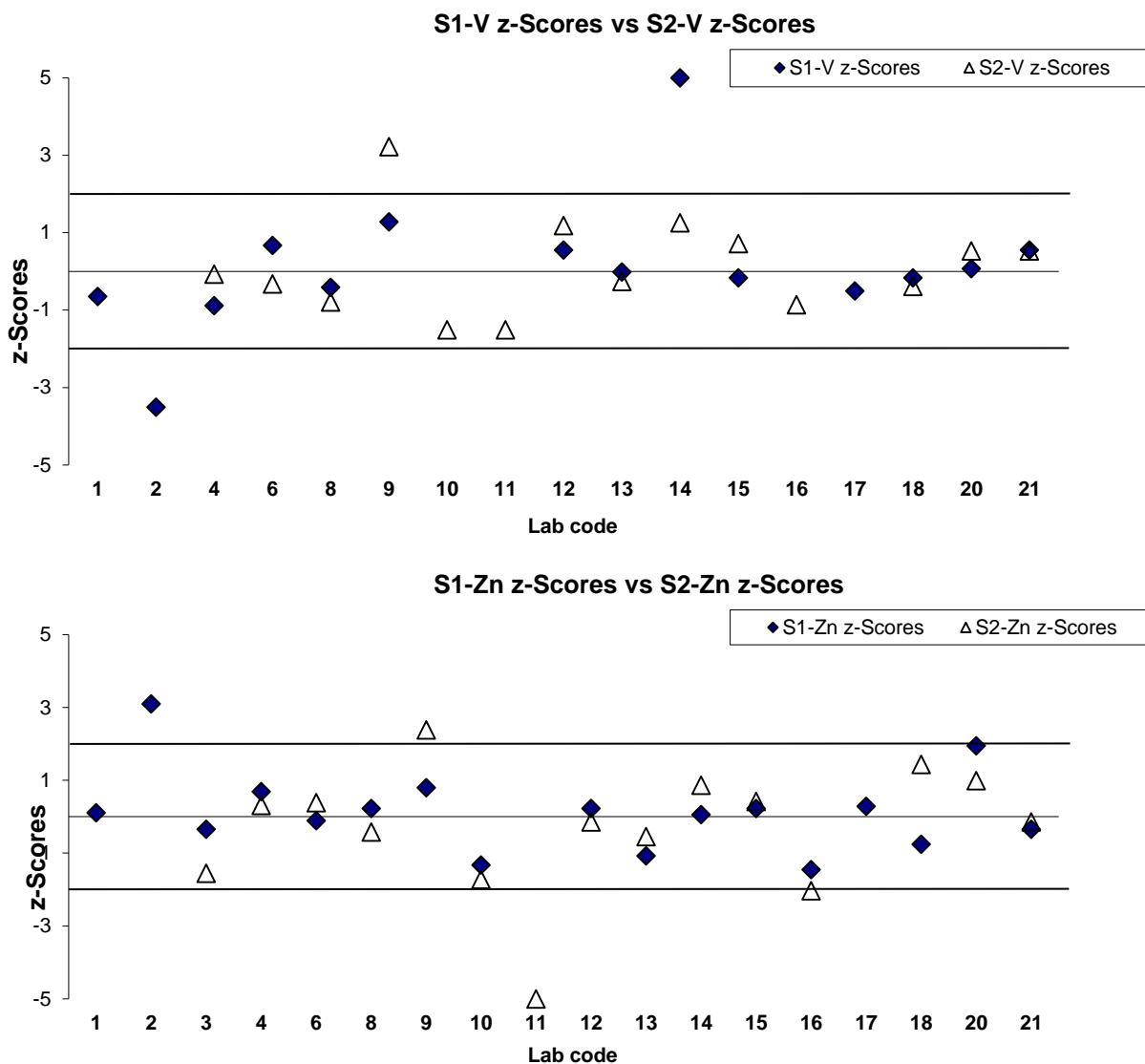
Scores of >5 or <-5 have been plotted as 5 or -5.

Figure 62 Comparisons of Participants' Performance in S1 and S2 (continued)



Scores of  $>5$  or  $<-5$  have been plotted as 5 or -5.

Figure 62 Comparisons of Participants' Performance in S1 and S2 (continued)



Scores of >5 or <-5 have been plotted as 5 or -5.

Figure 62 Comparisons of Participants' Performance in S1 and S2 (continued)

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

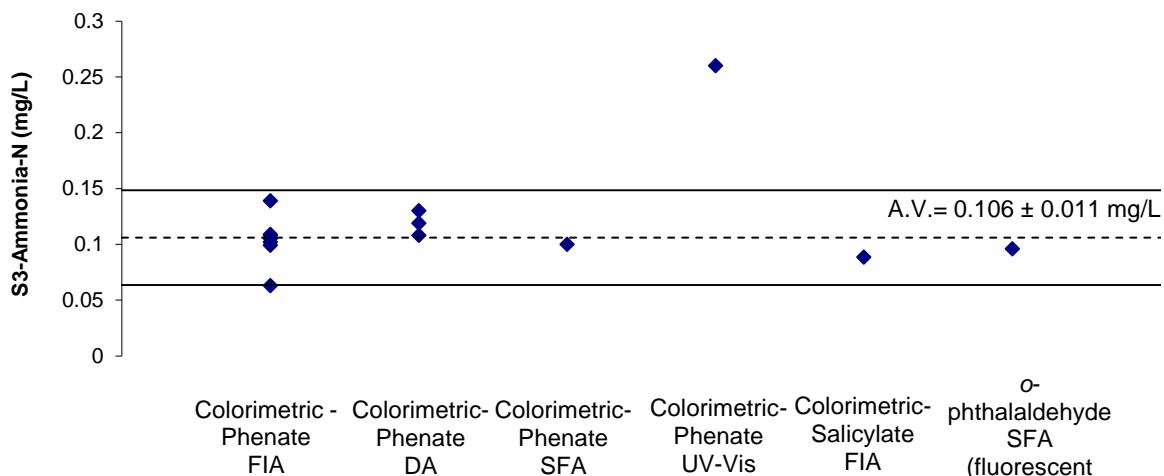
Participants were asked to analyse samples S3 and S4 using their normal test method. Stability studies were conducted and these samples were found to be sufficiently stable for evaluation of participants' performance (See Appendix 2). The measurement methods and instrumental techniques used for S3 and S4 analyses are presented in Appendix 8.

### Sample S3-Individual Test Commentary

**Ammonia-Nitrogen** Excepting two, all results reported for NH<sub>3</sub>-N returned satisfactory z-scores. Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination. One laboratory reported using the *o*-phthalaldehyde method with SFA with fluorescent detector (Figure 63).

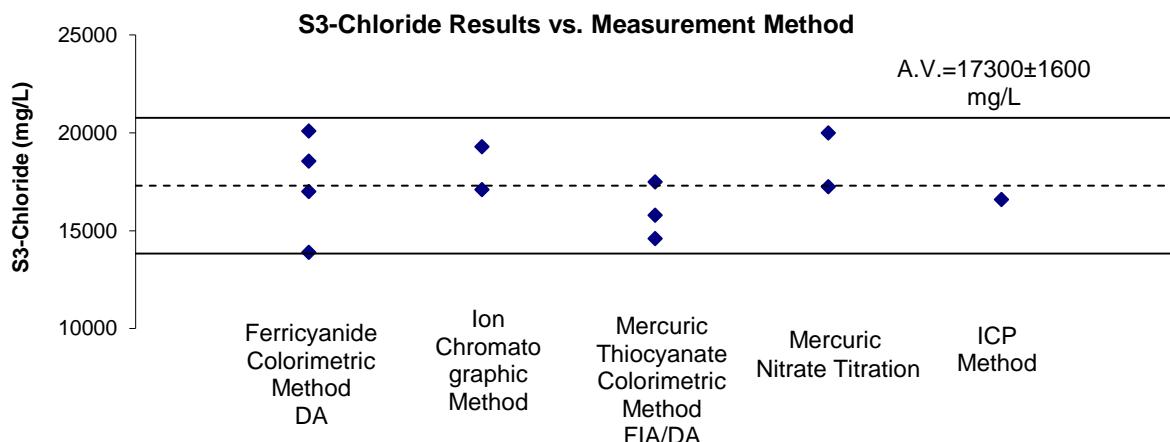
**Chloride** level in S3 was 17300 mg/L. Participants used a wide variety of methods for chloride analysis in S3; all produced comparable results (Figure 64).

### S3-Ammonia-N Results vs. Measurement Method



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

Figure 63 S3-NH<sub>3</sub>-N Results vs. Measurement Method



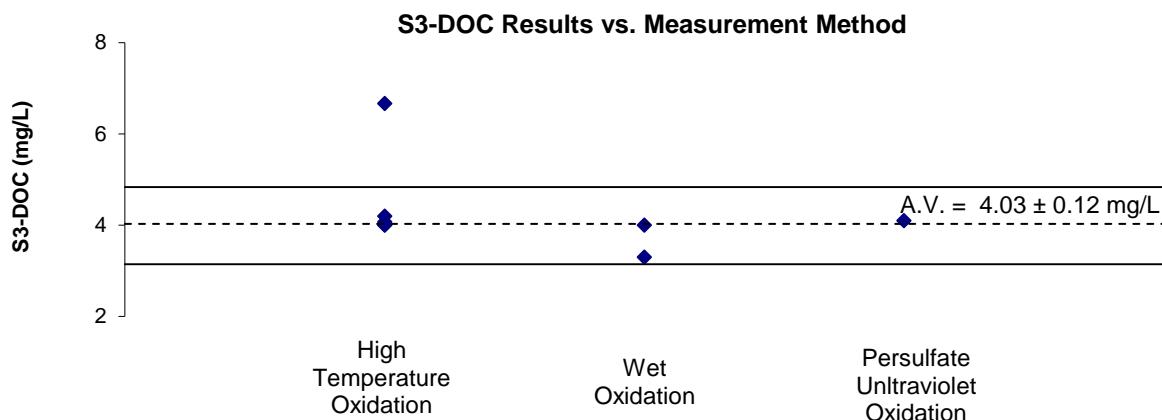
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 64 S3-Chloride Results vs. Measurement Method

**Dissolved Organic Carbon as dNPOC** Participants used high temperature oxidation, wet oxidation or persulfate-ultraviolet oxidation; no significant difference was noticed between DOC results produced by all these methods (Figure 65).

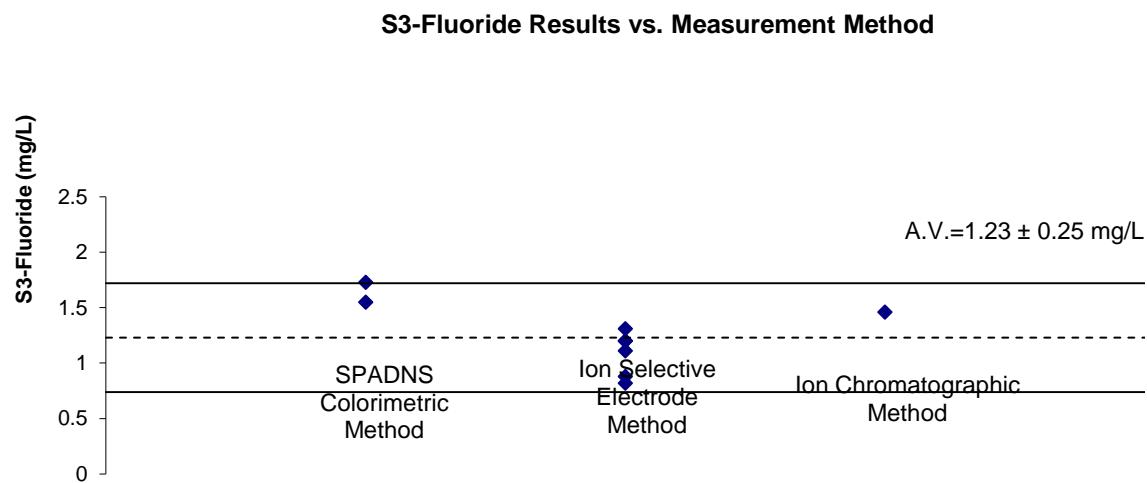
**Fluoride** Two participants used SPANDS colorimetric methods; the results they reported were higher than the robust average of participants' results (Figure 66). Fluoride by colorimetric method has interference from chlorides and SPANDS might not be the best choice for fluoride measurements at low level in seawater.

**Orthophosphate-P** All participants used the ascorbic acid colorimetric method for orthophosphate-P measurements in S3 with DA, FIA or SFA as instrumental technique (Figure 67).



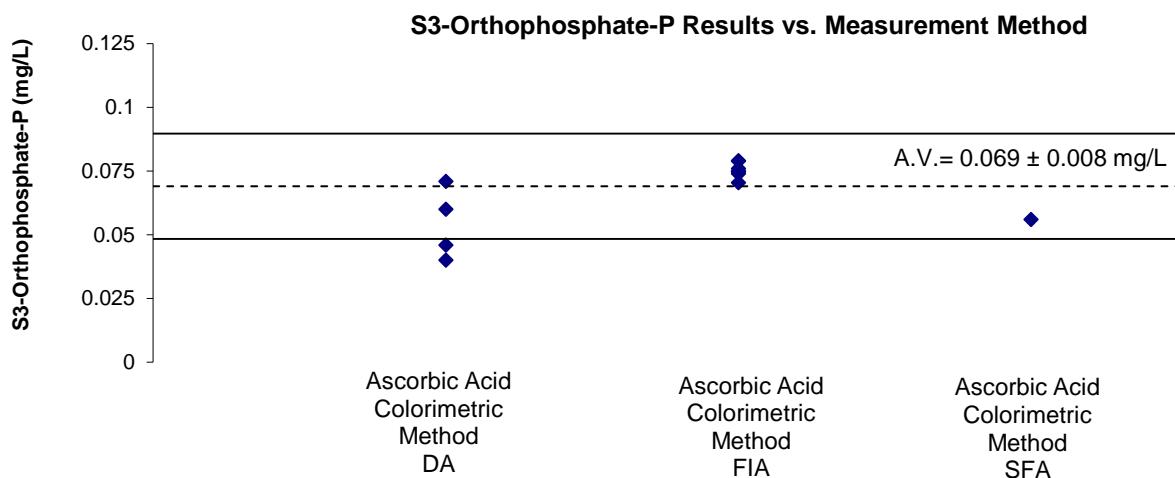
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 65 S3-DOC vs. Measurement Method



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

Figure 66 S3-Fluoride Results vs. Measurement Method

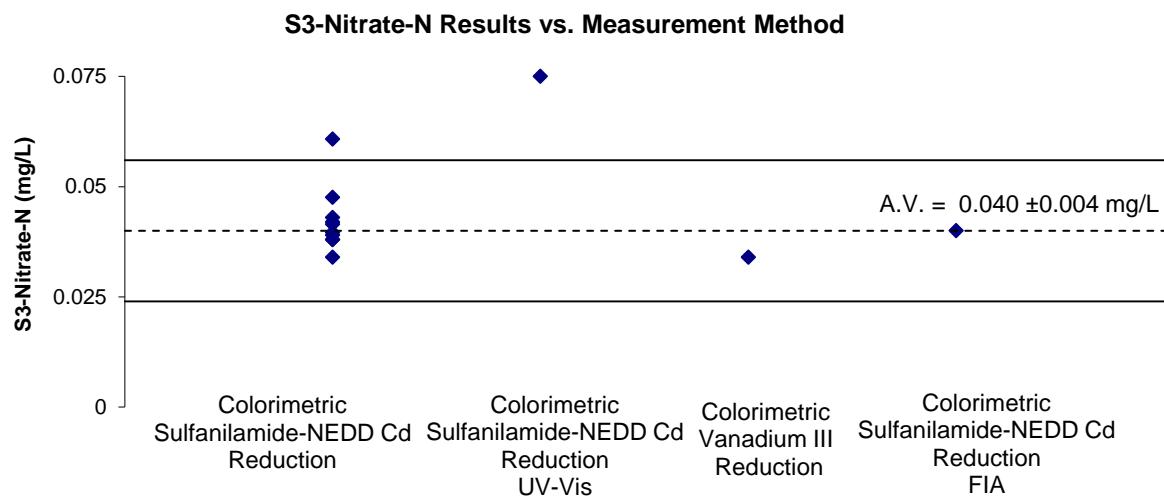


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 67 S3-Orthophosphate-P Results vs. Measurement Method

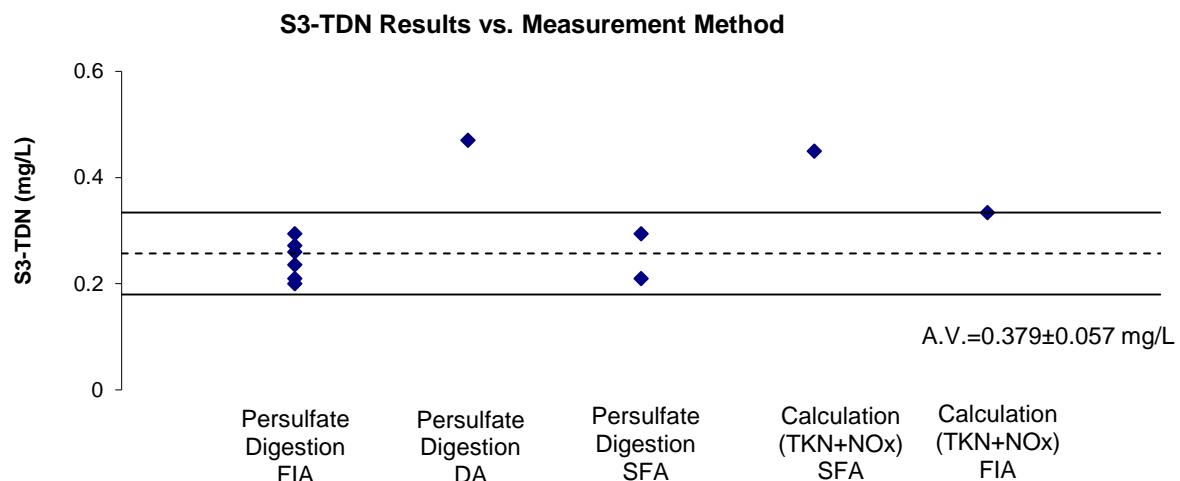
**Nitrate-Nitrogen** Twelve participants used colorimetric-sulfanilamide-NEDD Cd reduction and one used the colorimetric-vanadium III method. Excepting two, all results reported for nitrate-N in S3 were in good agreement with each other and returned satisfactory z-scores.

A plot of participants' results versus analytical method and instrumental technique used is presented in Figure 68.



Horizontal lines on charts are the results corresponding to z-scores of 2 and -2. Result >0.075 mg/L has been plotted as 0.075 mg/L.

Figure 68 S3-Nitrate-N Results vs. Measurement Method and Instrumental Technique

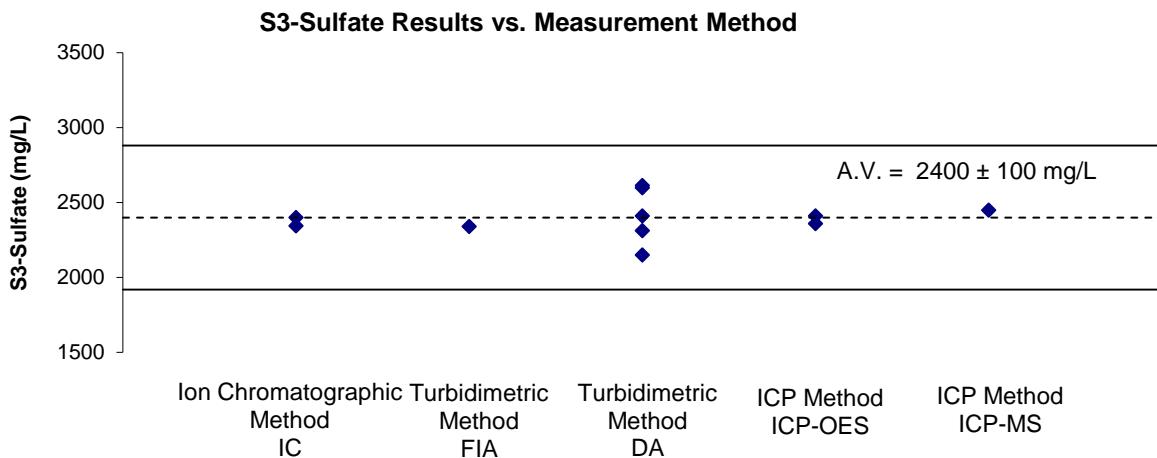


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 69 S3-TDN Results vs. Measurement Method and Instrumental Technique

**Total Dissolved Nitrogen** Excepting two, all participants determined total nitrogen by oxidation of all nitrogenous compounds to nitrate (Figure 69).

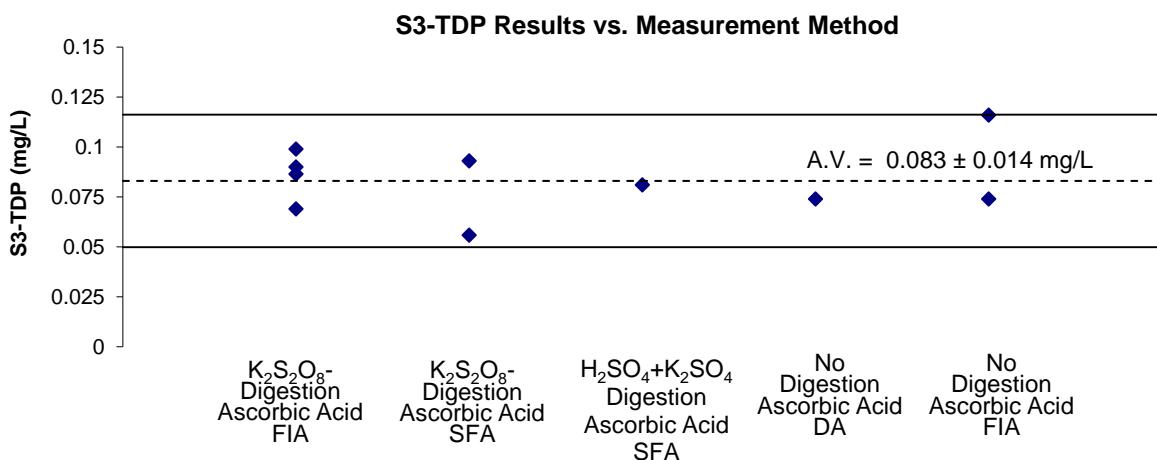
**Sulfate** One participant reported using ICP-MS for sulfate measurements and two measured sulfate by ICP-OES. Six participants used the turbidimetric method by DA or FIA for sulfate analyses and two used the ion chromatographic method (Figure 70). All reported results were in good agreement with each other and returned a satisfactory z-score.



Horizontal lines on chart are the upper and lower 95% confidence interval of the assigned value

Figure 70 S3-Sulfate Results vs. Measurement Method

**Total dissolved phosphorus** level in S3 was low (0.083 mg/L) and this might have presented difficulties to some laboratories. The reported results were variable with a high between-laboratories coefficient of variation high of 21%. Eight laboratories used potassium persulfate for digestion and one used sulfuric acid and potassium sulfate; these participants further measured the liberated orthophosphate colorimetrically by FIA or SFA. No digestion was performed by three participants who reported measuring TDP in the sample by DA or FIA (Figure 71). Excepting one, all results reported for TDP in S3 were satisfactory.



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

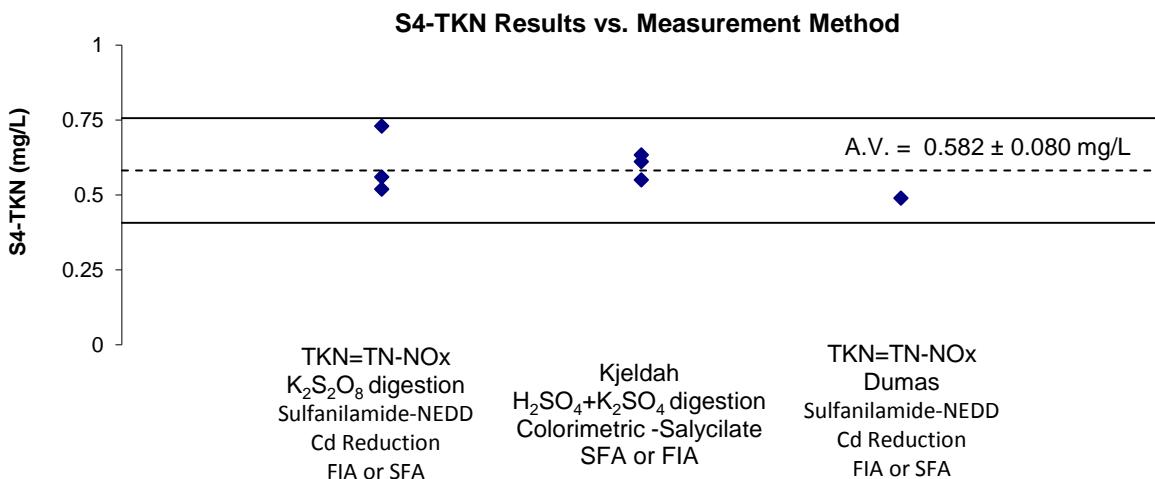
Figure 71 S3-TDP Results vs. Measurement Method

#### Sample S4-Individual Test Commentary

**Alkalinity to pH 4.5 as (CaCO<sub>3</sub>)** Participants used auto titration for alkalinity determination in S4 and all performed satisfactorily.

**EC** The unsatisfactory result reported by Laboratory 17 in S4 is not a reflection of their ability to perform this test, but of a transcription error.

**Total Kjeldahl Nitrogen** Measurements of TKN in S4 did not present any difficulty to laboratories; all performed satisfactorily. Plots of participants' results versus analytical method and measurement technique used are presented in Figure 72.



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

Figure 72 S4-TKN Results vs. Measurement Method

**Total Nitrogen** Eight participants used persulfate digestion for TN measurements in S4 and 2 reported TN as TKN+NOx; all performed satisfactorily.

### 7.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 18-16 is the twenty-third NMI proficiency test of metals in water and the seventh study in seawater.

Participants' performance in measurement of metals in seawater over time is presented in Figure 73. Despite differences in the analytes' concentrations, on average participants' performance remained fairly consistent.

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

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

### 7.8 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 65).

Table 65 Control Samples Used by Participants

Lab. Code	RMs or CRMs identity
7	NIST SRM 1640a
8	Previous PT samples
9	TM-25.5, TM-26.3, TMDA-52.4, TMAD-52.3, CASS-6
10	M/MET/P18/0115

11	B/Metals/P18/0017 Multi CRM (26 compounds)
12	NASS 7, CASS 6, NMI MX014 (Metals)
14	HPS CRM-SW
16	CPA Chem Certified Reference Material (26 elements), High Purity Standards CCV-1 Solution A, QCS-01-05 ICP Quality Control Standard #1
18	Cass 6, Nass 7
19	ENCT Round 22 No1-8

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

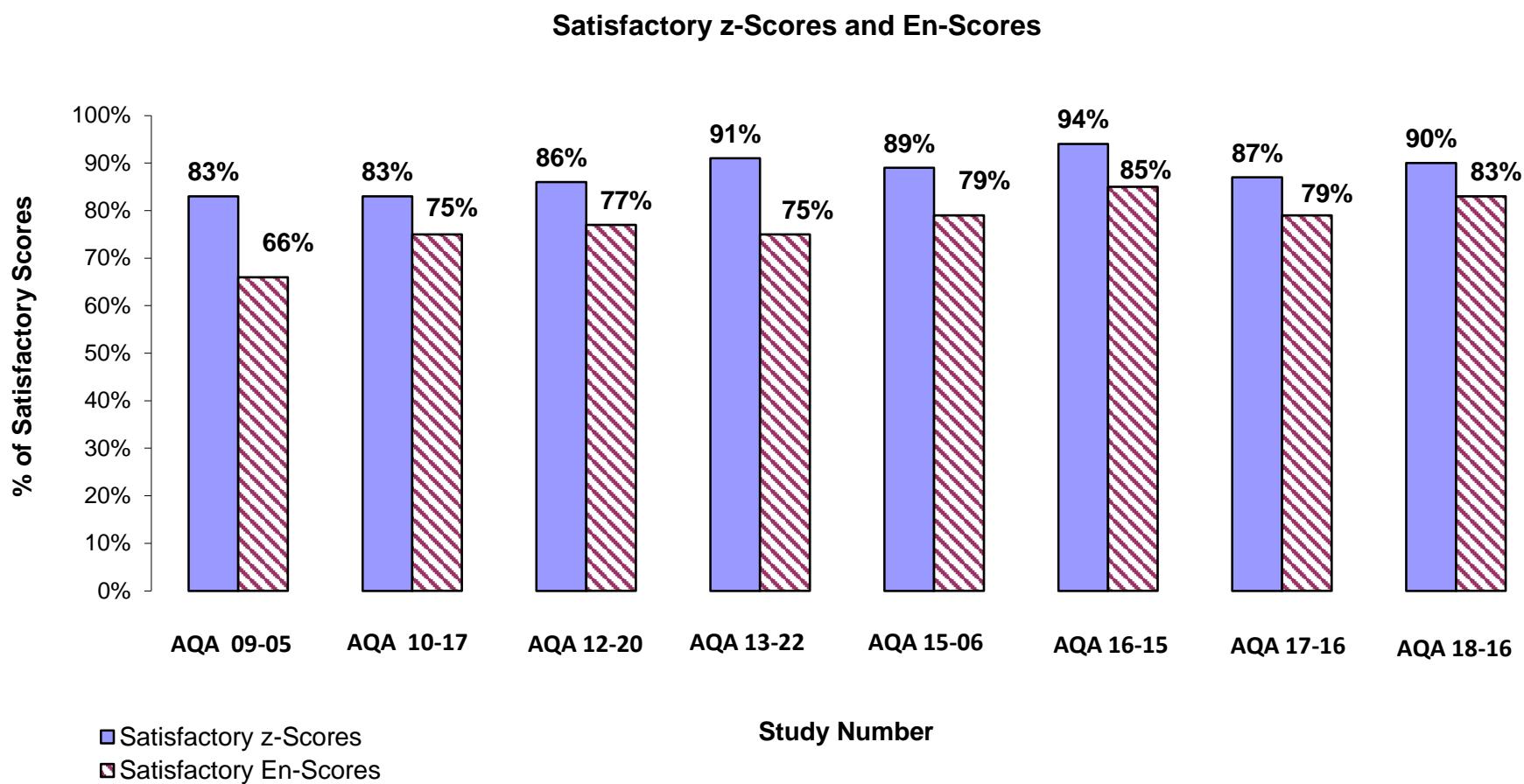


Figure 73 Participants' Performance in Metals in Seawater PT Studies over Time

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*Determination of Inorganic Anions*

## APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

### Sample Preparation

**Sample S1** was prepared from seawater. Approximately 10 L of seawater from Sydney harbour was filtered through a 0.45 µm pore size filter, stabilised by adding 2% (v/w) nitric acid and further fortified with 18 elements.

**Sample S2** was unfiltered seawater stabilised by adding 2% (v/w) nitric acid and further fortified for 18 elements.

**Sample S3** was 200 mL of filtered, frozen seawater fortified with ammonia-N, dissolved organic carbon, nitrate-N and orthophosphate-P.

**Sample S4** was 400 mL of unfiltered frozen seawater fortified with total Kjeldahl nitrogen and total organic carbon.

### Sample Analysis and Homogeneity Testing

Excepting Co in S1 and K in S4 a partial homogeneity test was conducted for all the analytes of interest in Samples S1, S2, S3 and S4.<sup>1, 6, 7</sup> Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

### Sample Analysis for Dissolved and Total Elements

Measurements for dissolved and total elements were made using NMI Method NT2.47.<sup>19</sup> NMI holds third party (NATA) accreditation for this method. For analyses of total elements in Sample S2, a test portion of 30 mL was transferred to a 50 mL graduated polypropylene centrifuge tube. The samples were digested using 2 mL of nitric acid and 1 mL of hydrochloric acid on a hot block at 95±5°C for 120 min.

Testing using NMI Method NT2.47 involved measurements using ICP-MS or ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates, sample matrix spikes and a certified reference material (MX014) was carried through the same set of procedures and analysed at the same time as the samples. A summary of the ion/wavelength and instrument conditions used for each analyte is given in Table 66.

Table 66 Instrumental Technique used for Dissolved Elements

Analyte	Instrument	Internal Standard	Reaction/Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1 Final Dilution Factor	S2/S4 Final Dilution Factor	Ion/Wavelength
Ag	ICP-MS	Rh	ORS	He	10	10	107 m/z
Al	ICP-MS	Rh	NA	NA	10	10	27 m/z
As	ICP-MS	Rh	ORS	He	10	10	75 m/z
B	ICP-OES	Y	NA	NA	NA	2	208.956 nm
Ba	ICP-MS	Rh	ORS	He	NA	10	134 m/z
Be	ICP-MS	Rh	NA	NA	10	NA	9 m/z
Ca	ICP-OES	Y	NA	NA	NA	2	422.491 nm
Cd	ICP-MS	Rh	ORS	He	10	10	111 m/z
Cr	ICP-MS	Rh	ORS	He	10	10	52 m/z
Cu	ICP-MS	Rh	ORS	He	10	10	63 m/z
Fe	ICP-MS	Rh	ORS	He	10	10	56 m/z
Hg	ICP-MS	Rh	ORS	He	10	NA	201 m/z
Mg	ICP-OES	Y	NA	NA	NA	2	279.8 nm
Mn	ICP-MS	Rh	ORS	He	10	10	55 m/z
Mo	ICP-MS	Rh	ORS	He	NA	10	60 m/z

Table 66 Instrumental Technique used for Dissolved Elements (continued)

Analyte	Instrument	Internal Standard	Reaction/Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1Final Dilution Factor	S2/S4 Final Dilution Factor	Ion/Wavelength
Ni	ICP-MS	Rh	ORS	He	10	10	60 m/z
Pb	ICP-MS	Ir	NA	NA	10	10	Average of 206, 207, 208 m/z
Sb	ICP-MS	Rh	ORS	He	NA	10	78 m/z
Se	ICP-MS	Rh	ORS	HEHe	10	10	78 m/z
Sn	ICP-MS	Rh	NA	NA	10	10	118 m/z
V	ICP-MS	Rh	ORS	He	10	10	51 m/z
Zn	ICP-MS	Rh	ORS	He	10	10	66 m/z

### Methodology for Tests Other Than Total Elements in S2 and S3

Measurements were made using NMI Methods: NW\_B1, NW\_D4, NW\_B23\_B19, NW\_S15, NW\_B10, NW\_B11, NW\_S11, NW\_B14, NW\_D3\_B14, NW\_D17, NW\_S15, NW\_B23, NW\_D9, NW\_D10\_B14, NW\_B3\_B14 and NW\_B19. NMI holds third party (NATA) accreditation for these methods. A summary of the measurement methods and instrumental techniques is presented in Tables 67 and 68.

Table 67 Methodology for S3

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination – OPA Method	SFA
Dissolved Organic Carbon	High-Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	Ion Selective Electrode
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA
Nitrate-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Sulfate	Turbidimetric Method	DA
Total Dissolved Nitrogen	Persulfate digestion	FIA
Total Dissolved Phosphorus	ICP-Method	ICP-OES

Table 68 Methodology for S4

Test	Measurement Method	Instrument
Alkalinity to pH 4.5 (as CaCO <sub>3</sub> )	Titration	Auto Titration
Total Hardness (as CaCO <sub>3</sub> )	Calculation	ICP-OES
Total Kjeldahl Nitrogen	TKN=TN-NOx, Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Organic Carbon	High-Temperature Oxidation	NIR-detector

## APPENDIX 2 - STABILITY STUDY

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

**Samples S3 and S4** Participants were advised to store the Samples S3 and S4 frozen if analyses cannot be commenced on the day of receipt. Samples' condition on receipt and the date when the samples were received and analysed by the participants are presented in Table 69. No significant trends between participants' results, samples' condition on receipt and date of analysis were noticed.

Table 69 Sample S3 and S4 Condition on Receipt and the Date When the Sample was Received and Analysed

Lab Code	Received Date	S3		S4	
		Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis
1	30.10.2018	Partially thawed	various	Partially thawed	various
2	30.10.2018	frozen	15.11.2018	NA	NA
3	30.10.2018	frozen	09.11.2018	frozen	09.11.2019
4	30.10.2018	frozen	07.11.2018	frozen	05.11.2018
5	31.10.2018	cold	31.10.2018	cold	02.11.2018
7	31.10.2018	NA	NA	frozen	22.11.2018
8	29.10.2018	frozen	05.11.2018	frozen	05.11.2018
9	31.10.2018	frozen	07.11.2018	frozen	07.11.2018
10	30.10.2018	semi frozen	05.11.2018	semi frozen	05.11.2018
12	30.10.2018	frozen	02.11.2018	frozen	02.11.2018
14	30.10.2018	NA	NA	frozen	13.11.2018
15	30.10.2018	frozen	31.10.2018	NA	NA
16	30.10.2018	frozen	08.11.2018	frozen	09.11.2018
17	30.10.2018	frozen	07.11.2018	frozen	07.11.2018
18	30.10.2018	NA	NA	Not recorded	
19	30.10.2018	frozen	08.11.2018	frozen	08.11.2018
20	30.10.2018	NA	NA	frozen	30.10.2018
21	30.10.2018	cold	27.11.2018	cold	27.11.2018

NA = Not Applicable

### Stability Study

Stability studies conducted for nutrients and physical tests in water in the previous studies found no significant changes in any of the analytes' concentration.<sup>6,7</sup> A stability study was however conducted in the present study for the less stable analytes: NH<sub>3</sub>-N, NO<sub>3</sub>-N and DOC in S3 and for turbidity, TN and TOC in S4.

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

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

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

Results were in good agreement with each other and the assigned value within their stated uncertainties (Figure 74).

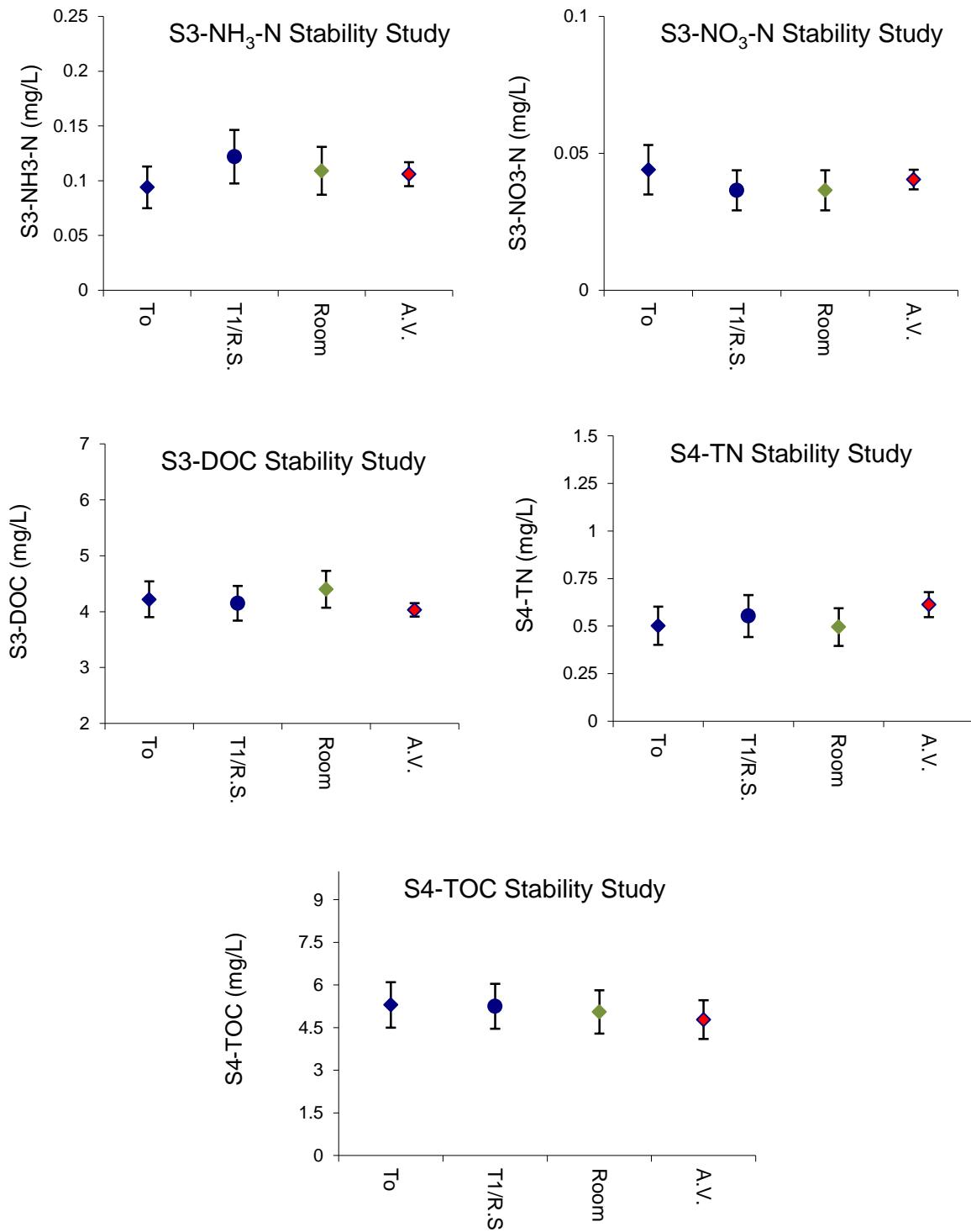


Figure 74 Stability Study Results

## APPENDIX 3 – REFERENCE VALUES

### A.3.1 Description of Method of Analysis

P quantification was performed by single point standard addition. NIST SRM 3139a (lot #060717) was used as the primary calibration material and diluted gravimetrically to working concentrations. Single point standard addition was performed gravimetrically by diluting a 4 g subsample to 40 g with ultra-high purity water before dividing the sample into unspiked and spiked portions. Spiked portions were fortified to approximately 10 times the expected sample mass fraction. No further sample treatment was performed. Experiments also contained internally prepared QC materials and method blanks prepared using the same procedures. Four incurred isotopes were measured for internal standardisation, those being  $^{43}\text{Ca}$ ,  $^{59}\text{Co}$ ,  $^{34}\text{S}$  and  $^{88}\text{Sr}$ . Measurements were made by HR-ICP-MS using medium resolution and HMI-ICP-MS-ORS-MS using both  $\text{H}_2$  and  $\text{O}_2$  to mass shift the  $^{31}\text{P}$  signal to  $^{31}\text{P}^1\text{H}$  and  $^{31}\text{P}^{16}\text{O}$  respectively. For all spiked solution ICP-MS measurements, solutions were bracketed by the unspiked solutions. Mass fraction reference values were converted to mass concentration using the density of the samples measured with an oscillating u-tube density meter (Anton Paar DMA 35N). The measured density of AQA 18-16 Sample S1 was  $1.0342 \text{ kg/L} \pm 0.0017 \text{ kg/L}$  and S2 was  $1.0342 \text{ kg/L} \pm 0.0017 \text{ kg/L}$ . The measurement uncertainty associated with density measurement has been determined such that the mass concentration reference values are valid for a temperature range of 15–25 °C at atmospheric pressure.

### A.3.2 Reference Values

The reference values and associated measurement uncertainty estimates for AQA 18-16 Samples S1 and S2 are presented below. The reference values come from the analysis of three bottles in duplicate. Measurement uncertainty is given as a 95% level of confidence.

Sample	Analyte	Reference Value	Units	Expanded Uncertainty (95%)	Relative Expanded Uncertainty	Coverage Factor (95%)
AQA 18-16 S1	P	120.8	$\mu\text{g/kg}$	3.7	3.1 %	2.03
		124.9	$\mu\text{g/L}$	3.7	3.0 %	2.03
AQA 18-16 S2	P	276	$\mu\text{g/kg}$	10	3.7 %	2.04
		286	$\mu\text{g/L}$	10	3.5 %	2.04

The reference values were determined as mass fractions then converted to mass concentrations using the density of the sample. The density measurement is valid for 15°C to 25°C and atmospheric pressure.

### A.3.4 Measurement Uncertainty

The measurement uncertainty associated with the reference values takes into account all factors that can reasonably be expected to affect the measurement result. Briefly, these include the accuracy of the primary calibration material, gravimetric preparation, method precision and method trueness. Measurement uncertainty is reported as a 95% level of confidence using the coverage factors given.

### A.3.5 Statement of Traceability

The reference values given in this report rely on gravimetric sample preparation, elemental quantification by ICP-MS and density measurement. 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 NIST (USA) and (ii) the SI unit for amount of substance (mol) through data for isotopic composition and relative atomic mass. 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](http://www.measurement.gov.au/publications/pages/determinations.aspx)).

#### APPENDIX 4 – ASSIGNED VALUE, Z-SCORE AND E<sub>n</sub> SCORE CALCULATION

The assigned value was calculated as the robust average using the procedure described in ‘ISO13258:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C<sup>8</sup>’ 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

$S_{rob\ mean}$  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 71.

Table 70 Uncertainty of Assigned Value for Zn in Sample S1

No. results (p)	17
Robust Average	11.6 µg/L
$S_{rob\ av}$	1.64 µg/L
$u_{rob\ av}$	0.50 µg/L
$k$	2
$U_{rob\ av}$	1.0 µg/L

The assigned value for Zn in Sample S1 is **11.6 ± 1.0 µg/L**.

#### z-Score and E<sub>n</sub>-score

For each participant’s result a z-score and E<sub>n</sub>-score are calculated according to Equation 2 and Equation 4 respectively (see page 13).

A worked example is set out below in Table 72.

Table 71 z-Score and E<sub>n</sub>-score for Zn result reported by Laboratory 1 in S1

Zn Result µg/L	Assigned Value µg/L	Set Target Standard Deviation	z-Score	E <sub>n</sub> -Score
11.8±2.5	11.6±1.0	15% as CV or 0.15x11.6= =1.7 µg/L	$z = \frac{(11.8 - 11.6)}{1.7}$ $z = 0.12$	$E_n = \frac{(11.8 - 11.6)}{\sqrt{2.5^2 + 1^2}}$ $E_n = 0.07$

## APPENDIX 5 - 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.<sup>12, 14</sup> An example is given below.

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

Table 72 Ni Results for Laboratory X From Proficiency Testing Studies of Metals in Water

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

\* Expanded uncertainty at approximately 95% confidence. \*\* The mean value of Robust CV was used. The pooled standard deviation could also be used. In this case the pooled standard deviation is 7.5%. Using a coverage factor of 2 gives an estimate of 15%.

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 6.8%. Using a coverage factor of 2 gives a relative expanded uncertainty of 14%, at a level of confidence of approximately 95%. Table 73 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the range 5 – 200 µg/L.

Table 73 Uncertainty of Ni results estimated using PT data

Results µg/L	Uncertainty µg/L
5.0	0.7
20	2.8
50	7
200	28

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

## APPENDIX 6 - ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
CRI	Collision Reaction Interface
CV	Coefficient of Variation
AFS	Atomic fluorescence spectroscopy
DRC	Dynamic Reaction Cell
FIA	Flow Injection Analyser
FSE	Fluoride Selective Electrode
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HEHe	High energy He mode
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma – Optical Emission Spectrometry- radial view
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PT	Proficiency Test
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
seaFAST-ICP-MS	Automated inductively coupled plasma spectrometry preconcentration system for undiluted seawater
SFA	Segment Flow Analyser
SI	The International System of Units
$s_{\text{sam}}^2$	Sampling variance
$s_a/\sigma$	Analytical standard deviation divided by the target standard deviation
SPANDS	2-(4-Sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalenedisulfonic Acid Trisodium Salt.
SRM	Standard Reference Material (Trademark of NIST)
Target SD	Target standard deviation
$\sigma$	Target standard deviation
UC	Universal Cell
VGA	Vapour Generator Accessory

## APPENDIX 7 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 74 Instrument Conditions Al

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	45	ORS	He	1	NT	27
2	ICP-OES-AV		NA		10	NT	
3	ICP-OES-AV	No			1	1	237.312
4	ICP-OES-AV						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	27
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Al_394.4
8	ICP-MS	Sc Rh Ir	NA	NA	10	10	27
9	ICP-MS	Scandium	ORS	He	10	10	27
10	ICP-MS	Sc	ORS	He	5	5	27
11	ICP-MS	Sc	ORS	He	1	1	27
12	seaFAST-ICP-MS	Sc	NA	NA	1	1	27
13	ICP-OES-AV	None			None		167.502
14	ICP-MS	Ge	NA	NA	1.05	1.05	27
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	27
17	ICP-MS	Sc 45	ORS	He	2	NT	27 m/z
18	ICP-MS	Sc	UC	He	20	20	27
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-OES-AV-buffer	Y			1	1	167.078
21	ICP-MS		CRI	He		NA	27

Table 75 Instrument Conditions Ag

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	He	1	NT	107
2	ICP-MS		CRI		10	NT	
3							NA
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			NA	10	10	107
7	ICP-MS	Rh and Bi	NA	NA	1000	1000	Ag_107
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	107
9	ICP-MS	Indium	ORS	He	10	10	107
10	ICP-MS	Y	ORS	He	5	5	107
11	ICP-MS	Rh	ORS	He	1	1	107
12	ICP-MS	Rh	NA	NA	1	1	109
13	ICP-MS/MS	In					107
14	ICP-MS	In	ORS	He	1.05	1.05	107
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Rh	ORS	He	1	1	107

17	ICP-MS	Rh 103	ORS	He	2	NT	107 m/z
18	ICP-MS	Rh	UC	He	20	20	109
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	In			1	1	107
21	ICP-MS			He			109

Table 76 Instrument Conditions As

Lab. Code	Instrument	Internal standard	Reaction/Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	72	ORS	HEHe	1	NT	75
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	188.98
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	75
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	75
9	ICP-MS	Germanium	ORS	He	10	10	75
10	ICP-MS	Y	ORS	He	5	5	75
11	ICP-MS	Rh	ORS	He	1	1	75
12	ICP-MS	Rh	UC	He	1	1	75
13	ICP-MS/MS	In	ORS	He			75
14	ICP-MS	Ge	ORS	He	1.05	1.05	75
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Rh	ORS	He	1	1	75
17	ICP-MS	Rh 103	ORS	He	2	NT	75 m/z
18	ICP-MS	Te	DRC	NH3	20	20	75
19	NT	NT	NT	NT	NT	NT	NT
20							
21	ICP-MS		CRI	He		NA	75

Table 77 Instrument Conditions B

Lab. Code	Instrument	Internal standard	Reaction/Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-OES-AV-buffer	Lu			NA	10	249.678
2	ICP-OES-AV				NA	NT	
3	ICP-OES-AV-buffer	Yes			NA	5	208.889
4	ICP-OES-AV				NA		
5							
6					NA	NT	
7	ICP-MS	Rh and Bi	NA	NA	1000	1000	B_10
8	ICP-MS	Sc Rh Ir	NA	NA	NA	10	11
9	ICP-MS	Scandium	ORS	He	10	10	11
10	ICP-MS	Sc	ORS	NA	NA	50	11
11	ICP-MS	Sc	ORS	He	NA	NT	11

12	ICP-MS	Sc	NA	NA	NA	10	10
13					NA	NT	
14	ICP-OES-AV	Lu			NA	1.05	208.956
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Sc	ORS	He	NA	1	11
17	ICP-OES-AV	Eu 271.700	NA	NA	NA	20	B 249.678
18	ICP-MS	Sc	UC	He	NA	20	10
19							
20	ICP-OES-AV-buffer	Y			NA	1	208.959
21	ICP-MS		CRI	He	NA		11

Table 78 Instrument Conditions Ba

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NT	NT	NA	NA	NA	NT	NT
2	NT	NT	NA	NA	NA	NT	NT
3					NA		NA
4	ICP-MS				NA		
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			NA	NA	10	135
7	ICP-OES-RV	Rh and Bi	NA	NA	NA	NA	Ba_230.4
8	ICP-MS	Sc Rh Ir	ORS	He	NA	10	134
9	ICP-MS	Indium	ORS	He	10	10	137
10	ICP-MS	Lu	ORS	He	NA	5	137
11	ICP-MS	Rh	ORS	He	NA	1	135
12	ICP-MS	Rh	NA	NA	NA	1	138
13	ICP-OES-AV	In			NA		455.403
14	ICP-OES-RV	Lu			NA	1.05	455.403
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Lu	ORS	He	NA	1	135
17	NT	NT	NA	NA	NA	NT	NT
18	ICP-MS	Lu	UC	He	NA	20	137
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	In			NA	1	137
21	ICP-MS		CRI	He		NA	137

Table 79 Instrument Conditions Be

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	45	ORS	He	1	NT	9
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	NA	234.861
4	ICP-MS					NA	
5	NT	NT	NT	NT	NT	NA	NT
6	ICP-MS			NA	10	NA	9

7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	NA	NA	10	NA	9
9	ICP-MS	Scandium	ORS	He	10	10	9
10	ICP-MS	Sc	ORS	NA	5	NA	9
11	ICP-MS	Sc	ORS	He	1	NA	9
12	seaFAST-ICP-MS	Sc	NA	NA	1	NA	9
13	ICP-MS/MS	In				NA	9
14	ICP-MS	Ge	ORS	He	1.05	NA	9
15	ICP-MS	Sc,Rh,Ir		He	10	NA	NA
16	ICP-MS	Sc	ORS	He	1	NA	9
17	ICP-MS	Sc 45	ORS	He	2	NT	9 m/z
18	ICP-MS	Sc	UC	He	NA	NA	9
19	NT	NT	NT	NT	NT	NA	NT
20	ICP-MS	Sc			1	NA	9
21	ICP-MS		CRI	He		NA	9

Table 80 Instrument Conditions Ca

Lab. Code	Instrument	Internal standard	Reaction/Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-OES-AV-buffer	Lu			NA	10	430.253
2					NA	NT	
3	ICP-OES-AV-buffer	Yes			NA	10	430.253
4	ICP-OES-AV				NA		
5							
6					NA	NT	
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Ca_422.6
8	ICP-OES-AV	Y	NA	NA	NA	50	315.887
9	ICP-OES-AV-buffer	Scandium			10	10	
10	ICP-OES-RV	Lu	NA	NA	NA	10	317.941
11	ICP-MS		ORS	He	NA	NT	40
12	ICP-MS	Sc	UC	He	NA	10	44
13					NA	NT	
14	ICP-OES-RV	Lu			NA	1.05	422.673
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Sc	ORS	He	NA	1	40
17	ICP-OES-AV	Eu 290.667	NA	NA	NA	20	Ca 370.602
18	ICP-MS	Sc	UC	He	NA	20	43
19							
20	ICP-OES-AV-buffer	Y			NA	1	317.933
21	ICP-OES-RV				NA		315.8

**Table 81 Instrument Conditions Cd**

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	He	1	NT	114
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	228.802
4	ICP-MS		ors	he			
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			NA	10	10	111
7	ICP-MS	Rh and Bi	NA	NA	1000	1000	Cd_111
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	111
9	ICP-MS	Gold	ORS	He	10	10	111
10	ICP-MS	Y	ORS	He	5	5	111
11	ICP-MS	Rh	ORS	He	1	1	111
12	seaFAST-ICP-MS	NA	UC	He	1	1	111
13	ICP-MS/MS	Rh	ORS	H2			111
14	ICP-MS	Ir	ORS	He	1.05	1.05	114
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Rh	ORS	He	1	1	111
17	ICP-MS	Rh 103	ORS	He	2	NT	111 m/z
18	ICP-MS	Rh	UC	He	20	20	111
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	In			1	1	111
21	ICP-MS		CRI	He		NA	114

**Table 82 Instrument Conditions Co**

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	115	ORS	He	1	NT	59
2	ICP-MS		CRI	He	10	NT	
3	ICP-OES-AV	No			1	NA	230.786
4	ICP-MS					NA	
5	NT	NT	NT	NT	NT	NA	NT
6	ICP-MS			He	10	NA	59
7	ICP-MS	Rh and Bi	NA	NA	1000	1000	Co_59
8	ICP-MS	Sc Rh Ir	ORS	He	10	NA	59
9	ICP-MS	Germanium	ORS	He	10	10	59
10	ICP-MS	Y	ORS	He	5	NA	59
11	ICP-MS	Sc	ORS	He	1	NA	59
12	seaFAST-ICP-MS	NA	UC	He	1	NA	59
13	ICP-MS/MS	In	ORS	He		NA	59
14	ICP-MS	Ge	ORS	He	1.05	NA	59
15	ICP-MS	Sc,Rh,Ir		He	10	NA	NA
16	ICP-MS	Sc	ORS	He	1	NA	59
17	ICP-MS	Rh 103	ORS	He	2	NT	59 m/z
18	ICP-MS	Ga	UC	He	20	NA	59
19	NT	NT	NT	NT	NT	NA	NT

20	ICP-MS	In	DRC	He	1	NA	59
21	ICP-MS		CRI	He		NA	59

Table 83 Instrument Conditions Cr

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	72	ORS	He	1	NT	52
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	267.716
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	52
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Cr_267.7
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	52
9	ICP-MS	Germanium	ORS	He	10	10	52
10	ICP-MS	Sc	ORS	He	5	5	52
11	ICP-MS	Sc	ORS	He	1	1	52
12	seaFAST-ICP-MS	Ge	UC	He	1	1	52
13	ICP-MS/MS	In	ORS	He			52
14	ICP-MS	Ge	ORS	He	1.05	1.05	52
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	52
17	ICP-MS	Sc 45	ORS	He	2	NT	52 m/z
18	ICP-MS	Ga	DRC	NH3	20	20	52
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Sc	DRC	NH3	1	1	52
21	ICP-MS		CRI	He		NA	52

Table 84 Instrument Conditions Cu

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	He	1	NT	65
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	327.395
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	63
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Cu_324.7
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	65
9	ICP-MS	Germanium	ORS	He	10	10	65
10	ICP-MS	Y	ORS	He	5	5	63
11	ICP-MS	Sc	ORS	He	1	1	63
12	seaFAST-ICP-MS	NA	UC	He	1	1	65
13	ICP-MS/MS	In	ORS	He			63
14	ICP-MS	Ge	ORS	He	1.05	1.05	63

15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	63
17	ICP-MS	Rh 103	ORS	He	2	NT	63 m/z
18	ICP-MS	Ga	UC	He	20	20	63
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Sc	DRC	He	1	1	63
21	ICP-MS		CRI	He		NA	63

Table 85 Instrument Conditions Fe

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	72	ORS	He	1	NT	56
2	ICP-OES-AV				10	NT	
3	ICP-OES-AV	No			1	1	238.204
4	ICP-OES-AV						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	56
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	56
9	ICP-MS	Germanium	ORS	HEHe	10	10	56
10	ICP-MS	Y	ORS	He	5	5	56
11	ICP-MS	Sc	ORS	He	1	1	56
12	ICP-MS	Sc	UC	He	1	1	56
13	ICP-OES-AV	None			None		238.204
14	ICP-MS	Ge	ORS	He	1.05	1.05	56
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	56
17	ICP-MS	Rh 103	ORS	He	2	NT	56 m/z
18	ICP-MS	Ga	DRC	NH3	20	20	54
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-OES-AV-buffer	Y			1	1	259.941
21	ICP-MS		CRI	He		NA	56

Table 86 Instrument Conditions Hg

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	VGA-ICP-OES				1	NT	194.164
2	CVAAS				1	NT	
3	CV-AFS				1	NA	
4	ICP-MS					NA	
5	NT	NT	NT	NT	NT	NA	NT
6	CVAAS			NA	2	NA	253.7nm
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	ORS	He	10	NA	201
9	ICP-MS	Gold	ORS	He	10	10	202
10	ICP-MS	Lu	ORS	He	5	NA	202

11	ICP-MS	Lu	ORS	He	1	NA	202
12	ICP-MS	Ir	NA	NA	1	NA	201
13	CVAFS	None			None	NA	
14	CVAFS	NA	NA	NA	6	NA	253.7
15	ICP-MS	Sc,Rh,Ir		He	10	NA	NA
16	ICP-MS	Lu	ORS	He	1	NA	202
17	ICP-MS	Ir 193	ORS	He	2	NT	202 m/z
18	Fluorescence	N/A	N/A	N/A	5	NA	254
19	NT	NT	NT	NT	NT	NA	NT
20	CVAAS				2	NA	253.7
21	ICP-MS		CRI	He		NA	202

Table 87 Instrument Conditions K

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1					NA		
2					NA	NT	
3	ICP-OES-AV-buffer	Yes			NA	10	769.897
4	ICP-OES-AV				NA		
5							
6					NA	NT	
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	K_769.8
8	ICP-OES-AV	Y	NA	NA	NA	50	766.491
9	ICP-OES-AV-buffer	Scandium			10	10	
10	ICP-OES-RV	Lu	NA	NA	NA	10	766.502
11	ICP-MS		ORS	He	NA	NT	39
12	ICP-MS	Sc	UC	He	NA	10	39
13					NA	NT	
14	ICP-OES-RV	Lu			NA	1.05	766.491
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Sc	ORS	He	NA	1	39
17	ICP-OES-AV	Cs 697.327	NA	NA	NA	20	K 766.491
18	ICP-MS	Sc	UC	He	NA	20	39
19							
20	ICP-OES-AV-buffer	Y			NA	1	769.896
21	ICP-OES-RV				NA		766.4

Table 88 Instrument Conditions Mg

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-OES-AV	Lu			NA	100	279.078
2					NA	NT	
3	ICP-OES-AV-buffer	Yes			NA	10	277.983
4	ICP-OES-AV				NA		
5							
6					NA	NT	

7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Mg_285.2
8	ICP-OES-AV	Y	NA	NA	NA	50	279.8
9	ICP-OES-AV-buffer	Scandium			10	10	
10	ICP-OES-RV	Lu	NA	NA	NA	10	285.217
11	ICP-MS		ORS	He	NA	NT	24
12	ICP-MS	Sc	UC	He	NA	10	25
13					NA	NT	
14	ICP-OES-RV	Lu			NA	1.05	285.213
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Sc	ORS	He	NA	1	24
17	ICP-OES-AV	Eu 390.711	NA	NA	NA	20	Mg 383.829
18	ICP-MS	Sc	UC	He	NA	20	25
19							
20	ICP-OES-AV-buffer	Y			NA	1	285.213
21	ICP-OES-RV				NA		279.8

Table 89 Instrument Conditions Mn

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	72	ORS	He	1	NT	55
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	257.61
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	55
7	ICP-MS	Rh and Bi	NA	NA	1000	1000	Mn_55
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	55
9	ICP-MS	Scandium	ORS	He	10	10	55
10	ICP-MS	Y	ORS	He	5	5	55
11	ICP-MS	Sc	ORS	He	1	1	55
12	seaFAST-ICP-MS	NA	UC	He	1	1	55
13	ICP-OES-AV	None			None		257.61
14	ICP-MS	Ge	ORS	He	1.05	1.05	55
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	55
17	ICP-MS	Rh 103	ORS	He	2	NT	55 m/z
18	ICP-MS	Ga	DRC	NH3	20	20	55
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Ga			1	1	55
21	ICP-MS		CRI	He		NA	55

Table 90 Instrument Conditions Mo

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NT	NT	NA	NA	NA	NT	NT
2	NT	NT	NA	NA	NA	NT	NT

3	ICP-OES-AV	No			NA	1	202.032
4	ICP-MS				NA		
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	NA	10	95
7	ICP-MS	Rh and Bi	NA	NA	1000	1000	Mo_94
8	ICP-MS	Sc Rh Ir	ORS	He	NA	10	95
9	ICP-MS	Indium	ORS	He	10	10	98
10	ICP-MS	Y	ORS	He	NA	10	95
11	ICP-MS	Rh	ORS	He	NA	1	95
12	ICP-MS	Rh	NA	NA	NA	1	95
13	ICP-MS/MS	In	ORS	He	NA		98
14	ICP-MS	In	ORS	He	NA	1.05	95
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Rh	ORS	He	NA	1	95
17	NT	NT	NA	NA	NA	NT	NT
18	ICP-MS	Rh	UC	He	NA	20	98
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	In			NA	1	95
21	ICP-MS		CRI	He		NA	95

Table 91 Instrument Conditions Ni

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	He	1	NT	60
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	231.604
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	60
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Ni_231.6
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	0
9	ICP-MS	Germanium	ORS	He	10	10	60
10	ICP-MS	Y	ORS	He	5	5	60
11	ICP-MS	Sc	ORS	He	1	1	60
12	ICP-MS	Rh	UC	He	1	1	60
13	ICP-MS/MS	In	ORS	He			60
14	ICP-MS	Ge	ORS	He	1.05	1.05	60
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	60
17	ICP-MS	Rh 103	ORS	He	2	NT	60 m/z
18	ICP-MS	Rh	UC	He	7	7	60
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Sc	DRC	He	1	1	60
21	ICP-MS		CRI	He		NA	60

**Table 92 Instrument Conditions P**

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1						NT	
2						NT	
3	ICP-OES-AV	No			1	1	213.618
4	ICP-OES-AV						
5	NT	NT	NT	NT	NT	NT	NT
6							
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	P_178.2
8	ICP-MS	In	ORS	HeHe	10	10	31
9	ICP-MS	Germanium	ORS	He	10	10	31
10	ICP-OES-RV	Lu	NA	NA	5	5	178.221
11	ICP-MS		ORS	He	NT	NT	31
12							
13							
14	ICP-OES-AV	Lu			1.05	1.05	177.434
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	31
17	NT	NT	NT	NT	NT	NT	NT
18	ICP-MS	Sc	UC	He	NA	20	31
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-OES-AV-buffer	Y			1	1	177.495
21	ICP-OES-RV				NA		213.6

**Table 93 Instrument Conditions Pb**

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	He	1	NT	208
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	220.353
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			NA	10	10	208
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	207
9	ICP-MS	Gold	ORS	He	10	10	208
10	ICP-MS	Lu	ORS	He	5	5	208
11	ICP-MS	Lu	ORS	He	1	1	208
12	ICP-MS	Ir	NA	NA	1	1	206+207+208
13	ICP-MS/MS	Lu					208
14	ICP-MS	Ir	ORS	He	1.05	1.05	208
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Lu	ORS	He	1	1	208
17	ICP-MS	Ir 193	ORS	He	2	NT	208 m/z
18	ICP-MS	Lu	UC	He	20	20	206+207+208

19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Ir			1	1	208
21	ICP-MS		CRI	He		NA	SUM ISOTOPES

Table 94 Instrument Conditions Sb

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NT	NT	NA	NA	NA	NT	NT
2	NT	NT	NA	NA	NA	NT	NT
3					NA		NA
4	ICP-MS				NA		
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			NA	NA	10	121
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	ORS	He	NA	10	121
9	ICP-MS	Indium	ORS	He	10	10	121
10	ICP-MS	Lu	ORS	He	NA	10	121
11	ICP-MS	Rh	ORS	He	NA	1	123
12	ICP-MS	Rh	NA	NA	NA	1	121
13					NA		
14	ICP-MS	In	ORS	He	NA	1.05	123
15	ICP-MS	Sc,Rh,Ir		He	NA	10	NA
16	ICP-MS	Rh	ORS	He	NA	1	123
17	NT	NT	NA	NA	NA	NT	NT
18	ICP-MS	Rh	UC	He	NA	20	121
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	In			NA	1	121
21	ICP-MS		CRI	He		NA	121

Table 95 Instrument Conditions Se

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	HEHe	1	NT	78
2	ICP-MS		CRI		10	NT	
3	ICP-OES-AV	No			1	1	196.026
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS				10	10	
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS/MS	Y	ORS	HEHe	10	10	78
9	ICP-MS	Tellurium	ORS	He	10	10	78
10	ICP-MS	Y	ORS	HEHe	5	5	78
11	ICP-MS	Rh	ORS	H2	1	1	78
12	ICP-MS	Rh	DRC	NH3	1	1	82
13	ICP-MS/MS	Rh	ORS	H2			78

14	ICP-MS	Ge	ORS	H2	1.05	1.05	78
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Rh	ORS	H2	1	1	78
17	ICP-MS	Rh 103	ORS	He	2	NT	78 m/z
18	ICP-MS	Te	DRC	NH3	20	20	82
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Ge	DRC	NH3	1	1	82
21	ICP-MS		CRI	HEHe		NA	78

Table 96 Instrument Conditions Sn

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	115	ORS	He	1	NT	118
2	ICP-MS		CRI		10	NT	
3							NA
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6							
7	NT	NT	NA	NA	NA	NA	NT
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	118
9	ICP-MS	Indium	ORS	He	10	10	118
10	ICP-MS	Lu	ORS	He	5	5	118
11	ICP-MS	Rh	ORS	He	1	1	118
12							
13	ICP-MS/MS	In					118
14	ICP-MS	In	ORS	He	1.05	1.05	118
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Rh	ORS	He	1	1	118
17	ICP-MS	Ir 193	ORS	He	2	NT	118 m/z
18	ICP-MS	Rh	UC	He	20	20	120
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	In			1	1	118
21	ICP-MS		CRI	He		NA	118

Table 97 Instrument Conditions V

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	45	ORS	He	1	NT	51
2	ICP-MS		CRI		10	NT	
3							NA
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	51
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	V_310.2
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	51
9	ICP-MS	Scandium	ORS	HEHe	10	10	51

10	ICP-MS	Sc	ORS	He	5	5	51
11	ICP-MS	Sc	ORS	He	1	1	51
12	seaFAST-ICP-MS	NA	UC	He	1	1	51
13	ICP-MS/MS	In	ORS	He			51
14	ICP-OES-AV	Lu			1.05	1.05	292.401
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	51
17	ICP-MS	Sc 45	ORS	He	2	NT	51 m/z
18	ICP-MS	Ga	DRC	NH3	20	20	51
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Ga	DRC	NH3	1	1	51
21	ICP-MS		CRI	He		NA	51

Table 98 Instrument Conditions Zn

Lab. Code	Instrument	Internal standard	Reaction/Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	103	ORS	He	1	NT	66
2	ICP-OES-AV				1	NT	
3	ICP-OES-AV	No			1	1	213.857
4	ICP-MS						
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS			He	10	10	66
7	ICP-OES-RV	Rh and Bi	NA	NA	10	10	Zn_2062
8	ICP-MS	Sc Rh Ir	ORS	He	10	10	66
9	ICP-MS	Tellurium	ORS	He	10	10	66
10	ICP-MS	Y	ORS	He	5	5	66
11	ICP-MS	Sc	ORS	He	1	1	66
12	ICP-MS	Rh	UC	He	1	1	66
13	ICP-MS	Rh	ORS	He			64
14	ICP-MS	Ge	ORS	He	1.05	1.05	68
15	ICP-MS	Sc,Rh,Ir		He	10	10	NA
16	ICP-MS	Sc	ORS	He	1	1	66
17	ICP-MS	Rh 103	ORS	He	2	NT	66 m/z
18	ICP-MS	Te	DRC	NH3	20	20	66
19	NT	NT	NT	NT	NT	NT	NT
20	ICP-MS	Ga	DRC	NH3	1	1	66
21	ICP-MS		CRI	He		NA	66

## APPENDIX 8 - METHODOLOGY FOR S3 AND S4

Table 99 Measurement Methods and Instrumental Techniques for Ammonia-N

Lab. Code	Measurement Method	Instrument
1	Colorimetric - Phenate Method	FIA
2	Colorimetric - Phenate Method	DA
3	Colorimetric - Phenate Method	FIA
4	Colorimetric - Phenate Method	SFA
5	Indophenol Method	UV-Vis Spectrophotometer
6	NT	NT
7	NT	NT
8	Fluorometric Determination - OPA Method	SFA
9	Colorimetric - Phenate Method	DA
10	Colorimetric - Salicylate Method	FIA
11	NT	NT
12	Colorimetric - Phenate Method	FIA
13	NT	NT
14	NT	NT
15	Colorimetric - Phenate Method	FIA
16	Colorimetric - Phenate Method	DA
17	Colorimetric - Phenate Method	FIA
18	NT	NT
19	Colorimetric - Phenate Method	FIA
20	NT	NT
21	Colorimetric - Phenate Method	FIA

Table 100 Measurement Methods and Instrumental Techniques Used for Nitrate-N

Lab. Code	Measurement Method	Instrument
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
2	Colorimetric -vanadium III method	DA
3	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA
5	Cadmium reduction Method	UV-Vis Spectrophotometer
6	NT	NT
7	NT	NT
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
9	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
10	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
11	NT	NT
12	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
13	NT	NT
14	NT	NT
15	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
16		
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
18	NT	NT

19	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
20	NT	NT
21	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA

Table 101 Measurement Methods and Instrumental Techniques Used for Total Dissolved Phosphorus

Lab. Code	Measurement Method	Instrument
1	Ascorbic Acid Colorimetric Method	FIA
2	Ascorbic Acid Colorimetric Method	DA
3	Ascorbic Acid Colorimetric Method	FIA
4	Ascorbic Acid Colorimetric Method	SFA
5		
6	NT	NT
7	NT	NT
8	ICP Method	ICP-MS
9	Ascorbic Acid Colorimetric Method	SFA
10	Ascorbic Acid Colorimetric Method	SFA
11	NT	NT
12	Ascorbic Acid Colorimetric Method	FIA
13	NT	NT
14	NT	NT
15	Ascorbic Acid Colorimetric Method	FIA
16	ICP Method	ICP-MS
17	Ascorbic Acid Colorimetric Method	FIA
18	NT	NT
19	Ascorbic Acid Colorimetric Method	FIA
20	NT	NT
21	Ascorbic Acid Colorimetric Method	FIA

Table 102 Measurement Methods and Instrumental Techniques Used for Total Dissolved Nitrogen

Lab. Code	Measurement Method	Instrument
1	Persulfate digestion	FIA
2	Persulfate digestion	DA
3	Calculation (TKN+NOx)	FIA
4	Persulfate digestion	SFA
5		
6	NT	NT
7	NT	NT
8	Persulfate digestion	FIA
9	Calculation (TKN+NOx)	SFA
10	Persulfate digestion	SFA
11	NT	NT
12	Persulfate digestion	FIA
13	NT	NT
14	NT	NT

15	Persulfate digestion	FIA
16		
17	Persulfate digestion	FIA
18	NT	NT
19	Persulfate digestion	FIA
20	NT	NT
21	Persulfate digestion	DA

Table 103 Measurement Methods and Instrumental Techniques Used for Chloride

Lab. Code	Measurement Method	Instrument
1	Mercuric Thiocyanate	FIA
2	Ferricyanide Colorimetric Method	DA
3		
4	Mercuric Thiocyanate	DA
5	Mercuric Nitrate Titration	
6	NT	NT
7	NT	NT
8	Mercuric Nitrate Titration	DA
9	Ferricyanide Colorimetric Method	DA
10	Ferricyanide Colorimetric Method	DB
11	NT	NT
12	ICP-Method	ICP-MS
13	NT	NT
14	NT	NT
15	Ferricyanide Colorimetric Method	DA
16	Ion Chromatographic Method	IC
17	Ion Chromatographic Method	IC
18	NT	NT
19		
20	NT	NT
21	Mercuric Thiocyanate	FIA

Table 104 Measurement Methods and Instrumental Techniques Used for Fluoride

Lab. Code	Measurement Method	Instrument
1	Ion Selective Electrode Method	Ion Selective Electrode
2		
3		
4	Ion Selective Electrode Method	Ion Selective Electrode
5	SPADNS Colorimetric Method	UV-Vis Spectrophotometer
6	NT	NT
7	NT	NT
8	Ion Selective Electrode Method	Ion Selective Electrode
9	Ion Selective Electrode Method	Ion Selective Electrode
10	Ion Selective Electrode Method	Ion Selective Electrode
11	NT	NT
12	SPADNS Colorimetric Method	UV-Vis Spectrophotometer

13	NT	NT
14	NT	NT
15	Ion Selective Electrode Method	Auto Titration
16		
17	Ion Chromatographic Method	IC
18	NT	NT
19		
20	NT	NT
21	Ion Selective Electrode Method	Ion Selective Electrode

Table 105 Measurement Methods and Instrumental Techniques Used for Orthophosphate-P

Lab. Code	Measurement Method	Instrument
1	Ascorbic Acid Colorimetric Method	FIA
2	Ascorbic Acid Colorimetric Method	DA
3	Ascorbic Acid Colorimetric Method	FIA
4	Ascorbic Acid Colorimetric Method	SFA
5		
6	NT	NT
7	NT	NT
8	Ascorbic Acid Colorimetric Method	DA
9	Ascorbic Acid Colorimetric Method	FIA
10	Ascorbic Acid Colorimetric Method	DB
11	NT	NT
12	Ascorbic Acid Colorimetric Method	FIA
13	NT	NT
14	NT	NT
15	Ascorbic Acid Colorimetric Method	FIA
16	Ascorbic Acid Colorimetric Method	DA
17	Ascorbic Acid Colorimetric Method	FIA
18	NT	NT
19	Ascorbic Acid Colorimetric Method	FIA
20	NT	NT
21	Ascorbic Acid Colorimetric Method	FIA

Table 106 Measurement Methods and Instrumental Techniques Used for Sulfate

Lab. Code	Measurement Method	Instrument
1	Turbidimetric Method	FIA
2	Turbidimetric Method	DA
3		
4	Turbidimetric Method	DA
5		
6	NT	NT
7	NT	NT
8	Turbidimetric Method	DA
9	ICP Method	ICP-OES
10	Turbidimetric Method	DB

11	NT	NT
12	ICP Method	ICP-MS
13	NT	NT
14	NT	NT
15	Turbidimetric Method	DA
16	Ion Chromatographic Method	IC
17	Ion Chromatographic Method	IC
18	NT	NT
19		
20	NT	NT
21	ICP Method	ICP-OES

Table 107 Measurement Methods and Instrumental Techniques Used for Alkalinity to pH 4.5 (as Ca CO<sub>3</sub>)

Lab. Code	Measurement Method	Instrument
1	Titration	Manual Analysis
2	NT	NT
3	Titration	Auto Titration
4	Titration	Auto Titration
5		
6	NT	NT
7	Titration	Ion Selective Electrode
8	Titration	Auto Titration
9	Titration	Auto Titration
10	Titration	Auto Titration
11	NT	NT
12	Titration	N/A
13	NT	NT
14		
15		
16		
17	Titration	
18	NT	NT
19		
20	Titration	Ion Selective Electrode
21	Titration	Auto Titration

Table 108 Measurement Methods and Instrumental Techniques Used for Total Hardness (as Ca CO<sub>3</sub>)

Lab. Code	Measurement Method	Instrument
1		
2	NT	NT
3	Calculation	ICP-OES
4	Calculation	ICP-OES
5		

6	NT	NT
7	NT	NT
8	Calculation	ICP AES
9	Calculation	ICP-OES
10	Calculation	ICP-OES
11	NT	NT
12	Titration	N/A
13	NT	NT
14	Calculation	ICP-OES
15		
16	Calculation	ICP-MS
17	Calculation	ICP-OES
18	NT	NT
19		
20	Calculation	ICP-OES
21	Calculation	ICP-OES

Table 109 Measurement Methods and Instrumental Techniques Used for Dissolved Organic Carbon

Lab. Code	Measurement Method	Instrument
1	High-Temperature Oxidation	NIR-detector
2		
3	Wet-Oxidation	NIR-detector
4	Persulfate-Ultraviolet Oxidation	NIR-detector
5		
6	NT	NT
7	NT	NT
8	High-Temperature Oxidation	NIR-detector
9		
10	High-Temperature Oxidation	NIR-detector
11	NT	NT
12	High-Temperature Oxidation	NIR-detector
13	NT	NT
14	NT	NT
15	High-Temperature Oxidation	DOC
16		
17	High-Temperature Oxidation	NIR-detector
18	NT	NT
19		
20	NT	NT
21	Wet-Oxidation	NIR-detector

Table 110 Measurement Methods and Instrumental Techniques Used for Total Kjeldahl Nitrogen

Lab. Code	Measurement Method	Instrument
1		
2	NT	NT
3	Colorimetric - salicylate method	FIA
4	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA
5		
6	NT	NT
7	NT	NT
8	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
9	Colorimetric - salicylate method	SFA
10		SFA
11	NT	NT
12	TKN = TN-NOx (Dumas)	FIA
13	NT	NT
14		
15		
16		
17	Colorimetric - salicylate method	SFA
18	NT	NT
19		
20	NT	
21		

Table 111 Measurement Methods and Instrumental Techniques Used for Total Nitrogen

Lab. Code	Measurement Method	Instrument
1	Persulfate digestion	FIA
2	NT	NT
3	Calculation (TKN+NOx)	FIA
4	Persulfate digestion	SFA
5		
6	NT	NT
7	NT	NT
8	Persulfate digestion	FIA
9	Calculation (TKN+NOx)	SFA
10	Persulfate digestion	SFA
11	NT	NT
12	Persulfate digestion	FIA
13	NT	NT
14		
15		
16		
17	Persulfate digestion	FIA
18	NT	NT

19	Persulfate digestion	FIA
20	NT	
21	Persulfate digestion	DA

Table 112 Measurement Methods and Instrumental Techniques Used for Total Organic Carbon

Lab. Code	Measurement Method	Instrument
1	High-Temperature Oxidation	NIR-detector
2	NT	NT
3	Wet-Oxidation	NIR-detector
4	Persulfate-Ultraviolet Oxidation	NIR-detector
5		
6	NT	NT
7	NT	NT
8	High-Temperature Oxidation	NIR-detector
9	Wet-Oxidation	NDIR-detector
10	High-Temperature Oxidation	NIR-detector
11	NT	NT
12	High-Temperature Oxidation	NIR-detector
13	NT	NT
14		
15		
16		
17	High-Temperature Oxidation	NIR-detector
18	NT	NT
19		
20	NT	
21	Wet-Oxidation	NIR-detector

**END OF REPORT**