



Australian Government  
Department of Industry,  
Science and Resources

National  
Measurement  
Institute

# **Proficiency Test Final Report AQA 22-15 Metals, Nutrients and Anions in Soil**

December 2022



## ACKNOWLEDGMENTS

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

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

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

Luminita Antin  
Andrew Evans  
Hamish Lenton  
Wei Huang  
Isaac Schipp

Raluca Iavetz  
Manager, Chemical Proficiency Testing



Phone: 61-2-9449 0111  
[proficiency@measurement.gov.au](mailto:proficiency@measurement.gov.au)



Accredited for compliance with ISO/IEC 17043

This page is intentionally blank

## TABLE OF CONTENTS

SUMMARY	1
1 INTRODUCTION	2
1.1 NMI Proficiency Testing Program	2
1.2 Study Aims	2
1.3 Study Conduct	2
2 STUDY INFORMATION	2
2.1 Selection of Matrices and Inorganic Analytes	2
2.2 Participation	2
2.3 Test Material Specification	3
2.4 Laboratory Code	3
2.5 Sample Preparation, Analysis and Homogeneity Testing	3
2.6 Stability of Analytes	3
2.7 Sample Storage, Dispatch and Receipt	3
2.8 Instructions to Participants	3
2.9 Interim Report	4
3 PARTICIPANT LABORATORY INFORMATION	5
3.1 Test Method Summaries	5
3.2 Instruments Used for Measurements	10
3.3 Additional Information	10
3.4 Basis of Participants' Measurement Uncertainty Estimates	10
3.5 Participant Comments on this PT Study or Suggestions for Future Studies	12
4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS	13
4.1 Results Summary	13
4.5 Target Standard Deviation for Proficiency Assessment	13
5 TABLES AND FIGURES	15
6 DISCUSSION OF RESULTS	103
6.1 Assigned Value and Traceability	103
6.2 Measurement Uncertainty Reported by Participants	103
6.3 $E_n$ -score	104
6.4 z-Score	104
6.5 Participants' Results and Analytical Methods for Acid Extractable Elements	113
6.6 Participants' Results and Analytical Methods for 2M KCl Extractable Ammonium-N and Nitrate-N	120
6.8 Participants' Results and Analytical Methods for Water Soluble Anions	122
6.9 Comparison with Previous NMI Proficiency Tests Studies of Metals in Soil	125
6.10 Reference Materials and Certified Reference Materials	125
7 REFERENCES	128
APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING	130
APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND $E_N$ SCORE CALCULATION	132
APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION	133



## SUMMARY

This report presents the results of the proficiency test AQA 22-15 Metals, Nutrients and Anions in Soil. The study covers the measurement of acid extractable elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Th, V and Zn. Measurement of pH, electrical conductivity (EC), water soluble chloride (Cl<sup>-</sup>), orthophosphate-P (PO<sub>4</sub><sup>3-</sup>-P), and sulphate (SO<sub>4</sub><sup>2-</sup>) and of total Kjeldahl nitrogen (TKN), 2M KCl extractable ammonium nitrogen (NH<sub>4</sub><sup>+</sup>-N) and 2M KCl extractable nitrate nitrogen (NO<sub>3</sub><sup>-</sup>-N) were also included in the program.

The sample set consisted of one dried sediment sample, one dried clay sample, and one dried agricultural soil sample.

Twenty-eight laboratories registered to participate and all submitted results.

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

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

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

Laboratory performance was assessed using both z-scores and E<sub>n</sub>-scores.

Of 669 z-scores, 602 (90%) were satisfactory with  $|z| \leq 2.0$ .

Of 669 E<sub>n</sub>-scores, 508 (76%) were satisfactory with  $|E_n| \leq 1.0$ .

No laboratories reported results for all analytes for which a z-score was calculated (36).

**Laboratory 27** returned the highest number of satisfactory z scores (34 out of 34 reported).

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

Chloride and sulphate levels in the study sample S3 were low and challenged participants' analytical techniques. The reported results for these tests were variable. The automated colour correction performed by DA may not overcome the problems caused by colour and turbidity.

As the ratio of extraction solution to dried sample size had to be 5 to 1, laboratories should use a determination method which is sensitive enough to accurately measure these tests close to the ppb level in the extraction solution, or otherwise increase their reporting level.

Alternatively, ICP-OES might not be the right instrumental technique for sulphate measurement in soil; false positive results can be produced because this technique measures total S and not just S from sulphate compounds.

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

Over the last 22 studies of inorganic analytes in soil, the average proportion of satisfactory scores was 90% for z-scores and 80% for E<sub>n</sub>-scores.

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

Of 789 numerical results, 738 (94%) were reported with an expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 0.00007% to 377% of the reported value. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 3.

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

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

## **1 INTRODUCTION**

### **1.1 NMI Proficiency Testing Program**

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

Proficiency testing (PT) "is evaluation of participant performance against pre-established criteria by means of inter-laboratory comparison."<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;
- controlled drug assay; and
- folic acid in flour.

AQA 22-15 is the 31<sup>st</sup> NMI proficiency study of inorganic analytes in soil.

### **1.2 Study Aims**

The aims of the study were to:

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

### **1.3 Study Conduct**

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.<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. This proficiency test is within the scope of NMI's accreditation.

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

## **2 STUDY INFORMATION**

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

The 44 tests were selected from those for which an investigation level is published in the Guideline on the Investigation Levels for Soil and Groundwater, promulgated by the National Environmental Protection Council (NEPC)<sup>5</sup> and from analytes commonly measured in soil.

### **2.2 Participation**

Twenty-eight laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued: 5 August 2022



Samples dispatched: 29 August 2022  
Results due: 30 September 2022  
Interim report issued: 6 October 2022

### 2.3 Test Material Specification

Three samples were provided for analysis:

**Sample S1** was 30 g of dried sediment;

**Sample S2** was 30 g of dried clay; and

**Sample S3** was 75 g of dried agricultural soil.

### 2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

### 2.5 Sample Preparation, Analysis and Homogeneity Testing

Test samples from previous studies have been demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. Therefore, only a partial homogeneity test was conducted for all analytes with the exception of Ga in S2 and TKN and 2M KCl extractable ammonium-N and nitrate-N in S3. The results from the partial homogeneity test for these samples are reported in the present study as the homogeneity value.

A full homogeneity test was conducted for water soluble chloride, sulphate and orthophosphate-P and pH, EC in S3.

The preparation, analysis and homogeneity testing of the study samples are described in Appendix 1.

### 2.6 Stability of Analytes

No stability study was carried out in the present study. Stability studies conducted for the previous proficiency tests of inorganic analytes in soil found no significant changes in any of the analytes' concentration.

### 2.7 Sample Storage, Dispatch and Receipt

The samples were dispatched by courier on 29 August 2022.

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

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

### 2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- For *Sample S3* for 2M KCl Extractable ( $\text{NO}_3^-$ -N) and ( $\text{NH}_4^+$ -N), participants are asked to follow the extraction procedure described below:

“Prepare a 1:10 w/v soil/2M KCl extracting solution. For example, weigh 5 g of soil into a suitable bottle or jar and add 50 mL of 2M KCl extracting solution.

Mechanically shake (end-over-end preferred), at room temperature for 1 h. Allow around 20-30 min for soil to settle and clarify and then take a known aliquot for the measurement technique employed. Further dilution of the aliquot may be required.”

Measure the analytes using a colorimetric method; and report results of 1:10 soil/2M KCl extracting solution on as received basis in units of mg/kg for: 2M KCl extractable ammonium-N ( $\text{NH}_4^+\text{-N}$ ) and 2M KCl extractable nitrate-N ( $\text{NO}_3^-\text{-N}$ ).

- Report on as received basis in units of mg/kg except for EC and pH. EC results are to be reported in units of  $\mu\text{S}/\text{cm}$ .

SAMPLE S1 Dried Sediment		SAMPLE S2 Dried Clay		SAMPLE S3 Dried Agricultural Soil	
Test acid extractable	Approximate Conc. Range mg/kg	Test acid extractable	Approximate Conc. Range mg/kg	Test	Approximate Conc. Range mg/kg
Ag	0.5-20	Al	2000-80000	Ca (acid extractable)	2000-80000
As	5-200	As	0.5-20	Fe (acid extractable)	2000-80000
Cd	0.5-20	B	0.5-20	K (acid extractable)	25-1000
Cr	5-200	Ba	25-1000	Mg (acid extractable)	2000-80000
Cu	5-200	Be	0.5-20	Na (acid extractable)	25-1000
Hg	0.5-20	Co	0.5-20	P(acid extractable)	25-1000
La	NA	Ga	0.5-20	S (acid extractable)	5-200
Mn	25-1000	Li	0.5-20	Sr (acid extractable)	0.5-20
Mo	0.25-10	Mn	25-1000	Water Soluble Chloride ( $\text{Cl}^-$ ) - 1:5 soil/water extract	0.5-20
Ni	5-200	Rb	5-200	Water Soluble Sulphate; ( $\text{SO}_4^{2-}$ ) - 1:5 soil/water extract	0.5-20
Pb	5-200	Sn	0.5-20	Water Soluble Orthophosphate-P; ( $\text{PO}_4^{3-}\text{-P}$ ) - 1:5 soil/water extract	0.5-20
Sb	0.5-20	Th	0.5-20	pH of 1:5 soil/water suspension	NA
Se	0.25-10	V	5-200	EC of 1:5 soil/water extract	NA
Zn	25-1000	Zn	5-200	Kjeldahl nitrogen, total (TKN)	50-2000
				2M KCl Extractable (Nitrate-N)	NA
				2M KCl Extractable (Ammonium-N)	NA

NA = Not Available

- Report results using the electronic results sheet emailed to you:
- Report results as you would report to a client. For each analyte, report the expanded measurement uncertainty.
- Please send the requested details regarding the test method and the basis of your uncertainty estimate.

## 2.9 Interim Report

An interim report was emailed participants on 6 October 2022.

### 3 PARTICIPANT LABORATORY INFORMATION

#### 3.1 Test Method Summaries

Summaries of test methods are transcribed in Tables 1 to 7.

Table 1 Methodology for Acid Extractable Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO <sub>3</sub> (mL)	Vol. HCl (mL)	Vol. HNO <sub>3</sub> (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H <sub>2</sub> O <sub>2</sub> (mL)	Other (mL)
1	SCP Science DigiPrep apparatus digestion block	1	90	240	4	1				
2		1	100	120	3	3				
3	3051A		180	15						5 (aqua regia)
4	USEPA Method 6010c, USEPA Methods 7471B, 7470A, 7471B	2.5	90 - 98	90	3	3				
5	US EPA Method 200.2		98	60	3	3				
6	AOAC 990.08	0.25	85	240	5	5				
7	In house reverse aqua regia digestion	1	110	60	3.5	1.5				
8	200.2 Revision 2.8	1	95 ± 5	60	2	10			2	
9	In House Method	0.1	100-120-140	180	2.5				2.5	
10	In House, US EPA 6020B	2	90-95	60	4	12				
11	In House Method	1	112.5	120	2.5	7.5				
12	USEPA Method 6010c, USEPA Methods 7471B, 7470A, 7471B	2.5	90 - 98	90	3	3				
13	USEPA 200.2	1	95	60			2		2	10 mL HCl (1:4)
14	In House S6 - Referencing APHA 3125	0.4	120	60	2.5	7.5				
15*	NA	1	98	70	2	4				2 mL H <sub>2</sub> O
16*	USEPA 3050B									
17	US-EPA Method 200.2	1	95	50	2	2				10 mL H <sub>2</sub> O
18	USEPA 3010	2	95-105	60	12	6				
19	USEPA Method 6010c, USEPA Methods 7471B, 7470A, 7471B	2.5	90 - 98	90	3	3				
20	EPA Method 3050B Acid Digestion of Sediments, Sludges and Soils	0.5	85	240	3	3				
21*	USEPA METHOD 3010 / 6020B	2	90-95	60	4	12				4 mL H <sub>2</sub> O
22	USEPA 200.2	1	95	60			2			10 mL HCl (1:4)
23	EPA 6010	3	95	115	15	5			6	
24	US EPA No. 3050	2	95-105	60	8	24				8 mL H <sub>2</sub> O
25	USEPA-6010C (Except Mercury by USEPA-7471B)	ICP=1g, FIMS=0.5g	95		5	5		3		

\*Additional information in Table 8

Table 1 Methodology for Acid Extractable Elements (continued)

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO <sub>3</sub> (mL)	Vol. HCl (mL)	Vol. HNO <sub>3</sub> (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H <sub>2</sub> O <sub>2</sub> (mL)	Other (mL)
26	US EPA 3050B	1	98	150	5	5				
27	USEPA method 200.2 Revision 2.8	1	95	60			2	10	2	
28	USEPA Method 200.7	1	95	45	2.5	2.5				10 mL H <sub>2</sub> O

\*Additional information in Table 8

Table 2 Methodology for Total Kjeldahl Nitrogen

Lab. Code	Method Reference	Digestion	Distillation	Measurement Method	Instrument
4	APHA 4500	Yes	No	Colorimetric - salicylate method	DA
6	AOAC 997.09	No	No	TKN = TN-NO <sub>x</sub> (Dumas)	LECO
8	APHA 22nd edition 4500 Norg A & D with Jirka Modification-Jirka et al. (1976) and the appropriate Discrete Analyser method.	Yes	No	Colorimetric - phenate method	DA
9	According to EN 13342 and DIN ISO 11261, modified by BUCHI (BUCHI 2013)	Yes	Yes	Titrimetric method	
11	Soil Chem Methods Australasia (Rayment and Lyons) and USEPA Methods 351.2 and 365.3	Yes		Colorimetric - phenate method	DA
12	APHA 4500	Yes	No	Colorimetric - salicylate method	DA
13	APHA 4500	Yes		Colorimetric - phenate method	DA
14*				TKN = TN-NO <sub>x</sub> (Dumas)	
18	APHA4500-Norg-B,C,D.(4-123)(TKN)	Yes		Colorimetric - phenate method	DA
19	APHA 4500	Yes	No	Colorimetric - salicylate method	DA
20	European Standard - Determination of Kjeldahl Nitrogen in soil, biowaste and sewage sludge 2005-08.	Yes	Yes	Titrimetric method	Buchi
22	APHA 4500 Norg A & D with Jirka modification - Jirka et al. (1976)	Yes	No	Colorimetric - salicylate method	DA
23	APHA	Yes		Colorimetric - salicylate method	DA
24	APHA 2500 B	Yes		Colorimetric - salicylate method	FIA
26	Method 7A5: Rayment, G.E. and David J. Lyons			TKN = TN-NO <sub>x</sub> (Dumas)	LECO
27	APHA 4500 - Norg. A & D.	Yes	No	Colorimetric - salicylate method	DA

\*Additional information in Table 8

Table 3 Methodology for 2M KCl Extractable Ammonium-N and Nitrate-N

Lab. Code	Method Reference		Sample Mass (g)	Extraction Solution 2M KCl Volume (mL)	Shake time (hours)	Measurement Method		Measurement Instrument	
	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N				NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N
1							Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	SFA
4	APHA	APHA	4.98	25	1.5	Colorimetric - Phenate method	Colorimetric - vanadium III method	DA	DA
9	HACH Method 10205 TNT Plus 831	HACH Method 8039	5	50	1	Colorimetric - Salicylate method	Colorimetric - salicylate method	Manual Analysis	Manual Analysis
11	In house	In house	1.5	15	1	Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA
12	APHA		5	25	1.5	Colorimetric - Phenate method	Colorimetric - vanadium III method	DA	DA
14	In House S37	In House S37	2	20	1	Colorimetric - Salicylate method	Colorimetric - vanadium III method	FIA	FIA
18	APHA	APHA	5	50	1	Colorimetric - Phenate method	Colorimetric - vanadium III method	DA	DA
19	APHA		5	25	1.5	Colorimetric - Phenate method	Colorimetric - vanadium III method	DA	DA
21	LTM-INO-4200	NA	5	50	1	Colorimetric - Phenate method		DA	
23	APHA4500	APHA4500				Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA
24	APHA 4500 NH3	APHA 4500 NOX	10	50	1	Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA
26	R&L 7C2b	R&L 7C2b	2	20	1			DA	DA

\*Additional information in Table 8

Table 4 Methodology for Water Soluble Chloride

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2					Ion Chromatographic Method	IC
4	USEPA	10.04	50	1.5	Ion Chromatographic Method	IC
5		5	25		Ion Chromatographic Method	IC
8	APHA 4500 - Cl	10	50	1	Ferricyanide Colorimetric Method	DA
9	Standard Method 4500 Cl- B	10	50	1	Argentometric Titration	Manual Analysis
11	In house	8	40	1	Ion Chromatographic Method	IC
12	USEPA	10	50	1.5	Ion Chromatographic Method	IC
13	APHA 4110	10	50	1	Ion Chromatographic Method	IC
14	In House S22	2	10	1	Mercuric Thiocyanate	Microplate reader
15	4500-Cl- C.	20	100	1	Ferricyanide Colorimetric Method	UV-Vis Spectrophotometer
19	USEPA	10	50	1.5	Ion Chromatographic Method	IC
20		10	50	1	Ion Chromatographic Method	IC
21	LTM-INO-4270	10	50	1	Ion Chromatographic Method	IC
22	APHA 4500-Cl-	10	50	1	Mercuric Thiocyanate	DA
23	APHA4500					DA
24	LTM-INO-4090	10	50	1	Mercuric Thiocyanate	DA
26		10	50	1		DA
27	APAH 4500-Cl	10	50	1	Ferricyanide Colorimetric Method	DA

Table 5 Methodology for Water Soluble Orthophosphate-P

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2					Ascorbic Acid Colorimetric Method	DA
4	APHA	10.04	50	1.5	Ascorbic Acid Colorimetric Method	DA
5		5	25		Ion Chromatographic Method	IC
8	APHA 4500 - P	10	50	1	Ascorbic Acid Colorimetric Method	DA
9	HACH Method 8048	10	50	1	Ascorbic Acid Colorimetric Method	Manual Analysis
11		8	40	1		
12	APHA	10	50	1.5	Ascorbic Acid Colorimetric Method	DA
13	APHA 4110	10	50	1.5	Ion Chromatographic Method	FIA
14		2	10	1	Vanadomolybdophosphoric Colorimetric Method	FIA
15	4500-P E.	20	100	1	Ascorbic Acid Colorimetric Method	UV-Vis Spectrophotometer
18	APHA	5	50	1	Ascorbic Acid Colorimetric Method	DA

Table 5 Methodology for Water Soluble Orthophosphate-P (continued)

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
19	APHA	10	50	1.5	Ascorbic Acid Colorimetric Method	DA
20		10	50	1	Vanadomolybdophosphoric Colorimetric Method	FIA
21	E052.2	10	50	1	Ascorbic Acid Colorimetric Method	DA
22	APHA 4500 - P	10	50	1	Ascorbic Acid Colorimetric Method	DA
23						DA
24	APHA 4500-P E	10	50	1	Ascorbic Acid Colorimetric Method	DA
26		10	50	1		DA
27	APHA 4500-P	10	50	1	Vanadomolybdophosphoric Colorimetric Method	DA

Table 6 Methodology for Water Soluble SO<sub>4</sub><sup>2-</sup>

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2					Ion Chromatographic Method	IC
4	USEPA	10.04	50	1.5	Ion Chromatographic Method	IC
5		5	25		Ion Chromatographic Method	IC
8	USEPA 200.2	10	50	1	ICP-Method	ICP-OES
9	HACH Method 8051	10	50	1	Turbidimetric Method	Manual Analysis
11	In house	8	40	1	Ion Chromatographic Method	IC
12	USEPA	10	50	1.5	Ion Chromatographic Method	IC
13	APHA 4110	10	50	1.5	Ion Chromatographic Method	IC
14		2	10	1	ICP-Method	ICP-OES
15*	ICP_W003	20	100	1	ICP-Method	ICP-OES
19	USEPA	10	50	1.5	Ion Chromatographic Method	IC
20		10	50	1	Ion Chromatographic Method	IC
21	LTM-INO-4270	10	50	1	Ion Chromatographic Method	IC
22	APHA 4500-SO <sub>4</sub> 2-	10	50	1	Turbidimetric Method	DA
23	APHA4500				Turbidimetric Method	DA
24	LTM-INO-4110	10	50	1	Turbidimetric Method	DA
26		10	50	1		ICP-OES
27	In house	10	50	1	ICP-Method	ICP-OES

\*Additional information in Table 8

### 3.2 Instruments Used for Measurements

The instruments and settings used by participants for acid extractable elements are presented in Appendix 4.

### 3.3 Additional Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 7.

Table 7 Additional information

Lab Code	Additional Information
1	Sample S1: Silver result not reported
3	Instrumental Techniques for Acid Extractable Elements: We use KED mode
7	Instrumental Techniques for Acid Extractable Elements: Cell Gas: Standard mode (Nogas)
14	TKN - TN done by LECO, NOx by FIA
15	Sample S3: Chloride, Sulphate and Orthophosphate-P values were multiplied by 5 to account for the 1:5 soil/water ratio Methodology for Acid Extractable Elements: 1g of sample was weighed in a polypropylene tube, then 2mL of water, 2mL of HNO <sub>3</sub> and 4mL of HCl were added. The samples were mixed and heated in a water bath at 98°C for 70 mins. 2mL of Yb (250ppm) or Ru (7.5ppm) solution was added before ICP analyses. Methodology for Water Soluble Sulphate: an internal method.
16	Sample S1 & S2: Microwave digestion Methodology for Acid Extractable Elements: Microwave digestion (Not hot block)
21	Methodology for Acid Extractable Elements: USEPA METHOD 200.8

### 3.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Tables 8 and 9).

Table 8 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation <sup>a</sup>		Guide Document for Estimating MU
		Precision	Method Bias	
1*	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	CRM	NATA General Accreditation, Guidance, Estimating and Reporting MU
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis	CRM	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	Recoveries of SS	Eurachem/CITAC Guide
5		Control Samples - CRM Duplicate Analysis	CRM	



Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation <sup>a</sup>		Guide Document for Estimating MU
		Precision	Method Bias	
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	
7	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	CRM Laboratory Bias from PT Studies Recoveries of SS	Eurachem/CITAC Guide
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
9	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	other please type
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	Recoveries of SS	ISO/GUM
11	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	Recoveries of SS	Eurachem/CITAC Guide
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration		Eurachem/CITAC Guide
14	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	Instrument Calibration Standard Purity	Nordtest Report TR537
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
16	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	NMI Uncertainty Course
17	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Laboratory Bias from PT Studies	Eurachem/CITAC Guide

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation <sup>a</sup>		Guide Document for Estimating MU
		Precision	Method Bias	
18	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
19	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	Recoveries of SS	Eurachem/CITAC Guide
20	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	Laboratory Bias from PT Studies	ISO/GUM
21	Standard deviation of laboratory control sample trends	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
22	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
24	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	ISO/GUM
25	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	NMI Uncertainty Course
26	Top Down - reproducibility (standard deviation) from PT studies used directly	Standard deviation from PT studies only		Eurolab Technical Report No1/2007
		Control samples - CRM	CRM	
27	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM Recoveries of SS	Eurachem/CITAC Guide
28	Professional judgment	Control Samples Duplicate Analysis Instrument Calibration	Standard Purity	Eurachem/CITAC Guide

<sup>a</sup>Additional information in Table 10. <sup>a</sup>RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples

Table 9 Additional Information for Basis of Uncertainty Estimate

Lab Code	Additional Information
1	Currently updating using NMI proficiency results

### 3.5 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.

There were no comments from participants on this study.

## 4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 4.1 Results Summary

Participant results are listed in Tables 10 to 53 with resultant 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 45. An example chart with interpretation guide is shown in Figure 1.

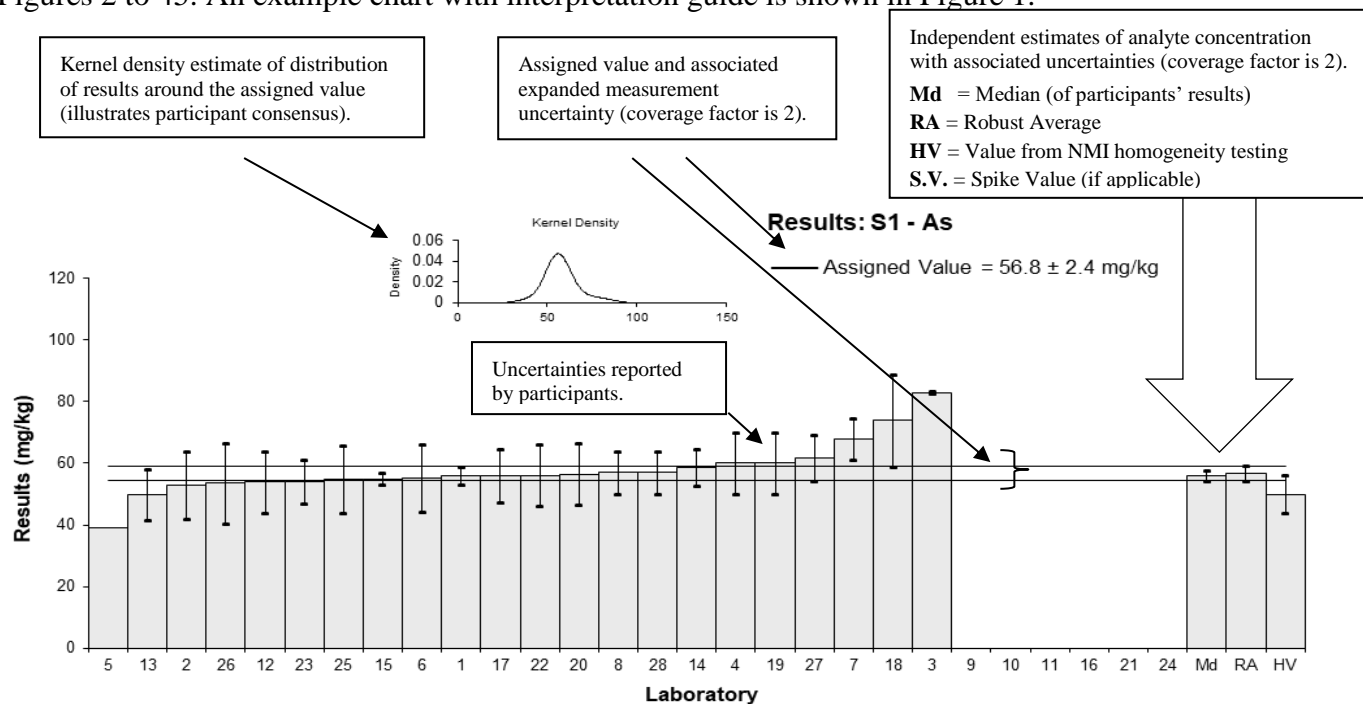


Figure 1 Guide to Presentation of Results

### 4.2 Outliers and Extreme Outliers

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

### 4.3 Assigned Value

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

### 4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'.<sup>6</sup> 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>6</sup>

### 4.5 Target Standard Deviation for Proficiency Assessment

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

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

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

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

#### 4.6 z-Score

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

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

Where:

- $z$  is z-score;
- $\chi$  is participant's result;
- $X$  is the study assigned value;
- $\sigma$  is the target standard deviation.

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

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

#### 4.7 E<sub>n</sub>-Score

An example of E<sub>n</sub>-score calculation using data from the present study is given in Appendix 2. The E<sub>n</sub>-score is complementary to the z-score in assessment of laboratory performance.

E<sub>n</sub>-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

- $E_n$  is E<sub>n</sub>-score;
- $\chi$  is a participant's result;
- $X$  is the study assigned value;
- $U_\chi$  is the expanded uncertainty of the participant's result;
- $U_X$  is the expanded uncertainty of the assigned value.

An E<sub>n</sub>-score with absolute value ( $|E_n|$ ):

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

#### 4.8 Traceability and Measurement Uncertainty

Laboratories accredited to AS ISO/IEC Standard 17025:2018<sup>8</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>9</sup>

## 5 TABLES AND FIGURES

Table 10

### Sample Details

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Ag
<b>Unit</b>	mg/kg

### Participant Results

Lab. Code	Result	Uncertainty
1	NR	NR
2	1.5	0.3
3	1.0	0.142
4	2	1
5	0.94	NR
6	1.006	0.2012
7	1.12	0.11
8	<2	NR
9	NT	NT
10	NT	NT
11	NT	NT
12	2	1
13	2.9	0.4
14	1.59	0.2
15	1.91	0.06
16	NT	NT
17	1.63	0.44
18	2.4	0.5
19	2	1
20	1.67	0.4
21	NT	NT
22	<2	0.2
23	1	0.181
24	NT	NT
25	NT	NT
26	<1	NR
27	0.948	0.14
28	2	1

### Statistics

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	1.57	0.19
<b>Robust Average</b>	1.60	0.36
<b>Median</b>	1.63	0.33
<b>Mean</b>	1.62	
<b>N</b>	17	
<b>Max</b>	2.9	
<b>Min</b>	0.94	
<b>Robust SD</b>	0.59	
<b>Robust CV</b>	37%	

Results: S1 - Ag

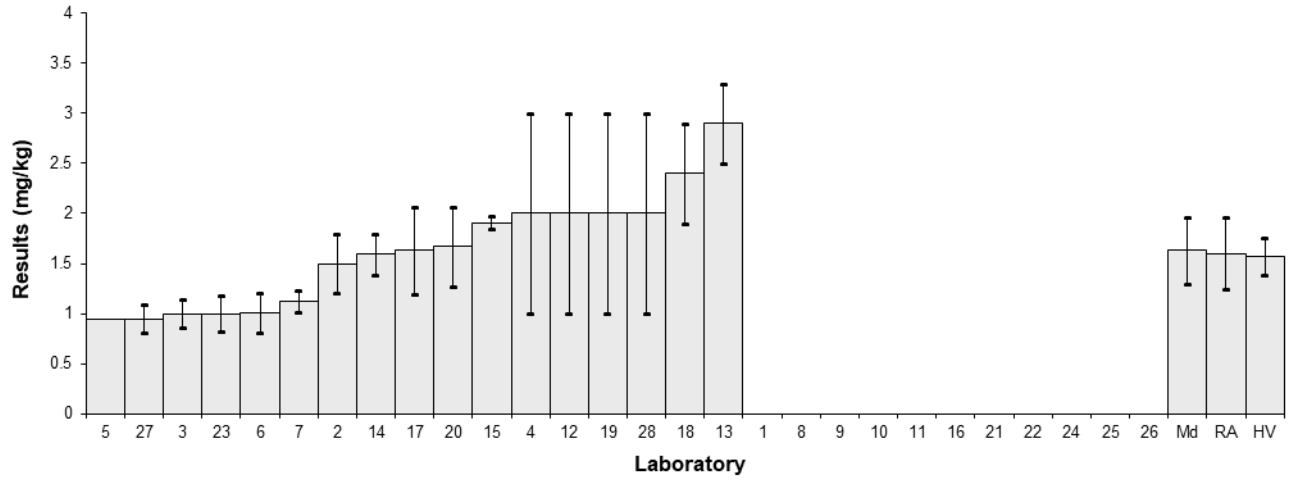


Figure 2

Table 11

**Sample Details**

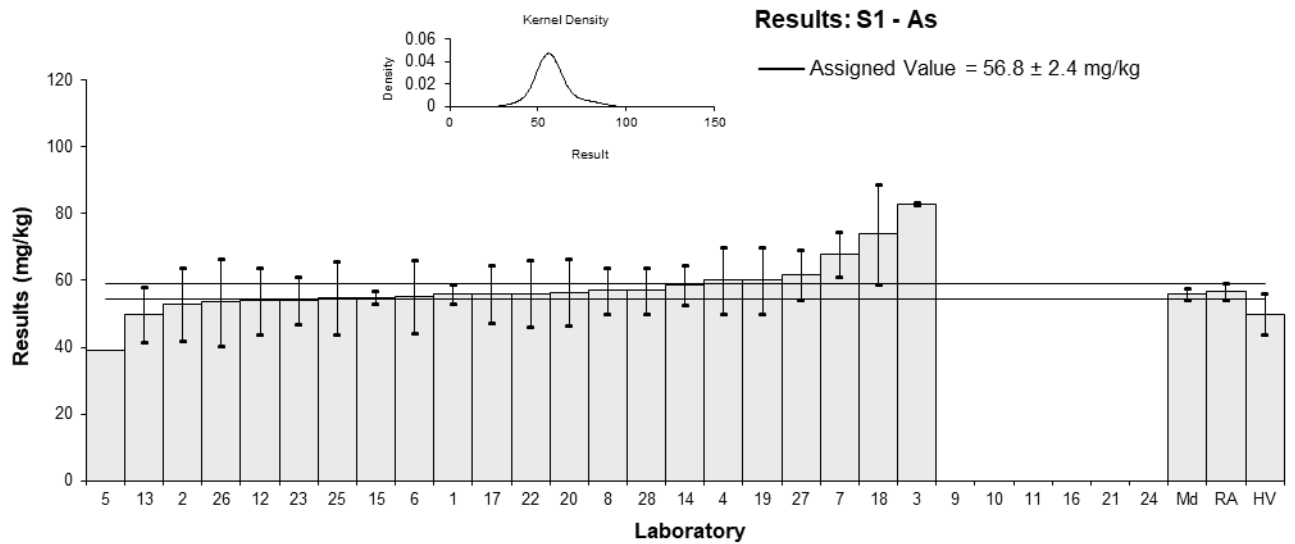
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	As
<b>Unit</b>	mg/kg

**Participant Results**

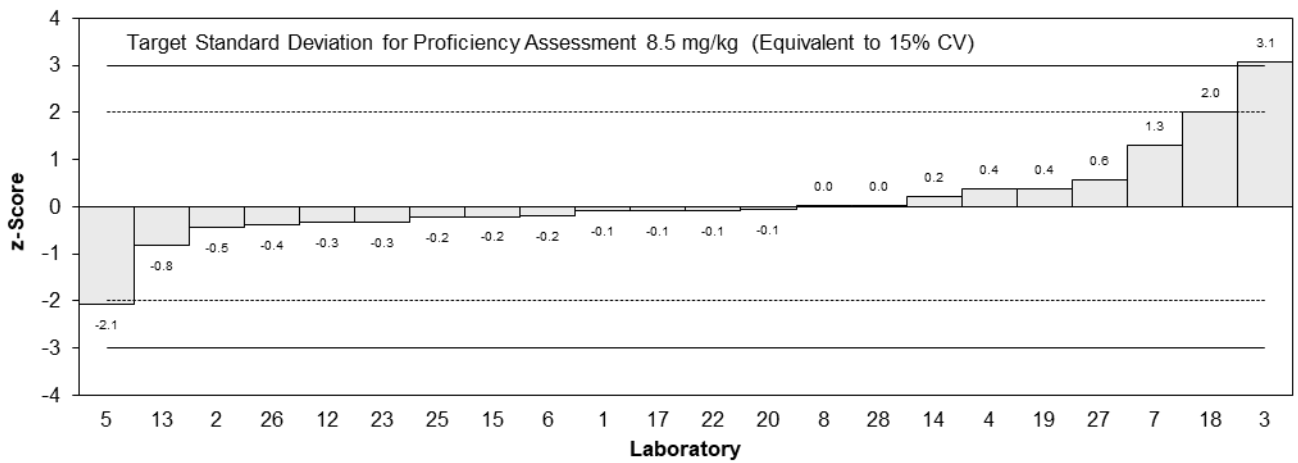
<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z</b>	<b>E<sub>n</sub></b>
1	56	2.8	-0.09	-0.22
2	53	11	-0.45	-0.34
3	83.0	0.288	3.08	10.84
4	60	10	0.38	0.31
5	39.1	NR	-2.08	-7.37
6	55.18	11.036	-0.19	-0.14
7	67.9	6.8	1.30	1.54
8	57	7	0.02	0.03
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	54	10	-0.33	-0.27
13	49.8	8.1	-0.82	-0.83
14	58.6	6.0	0.21	0.28
15	55.0	2.1	-0.21	-0.56
16	NT	NT		
17	56.0	8.5	-0.09	-0.09
18	74	15	2.02	1.13
19	60	10	0.38	0.31
20	56.4	10	-0.05	-0.04
21	NT	NT		
22	56	10	-0.09	-0.08
23	54	7.182	-0.33	-0.37
24	NT	NT		
25	54.802	11.014	-0.23	-0.18
26	53.5	13	-0.39	-0.25
27	61.78	7.54	0.58	0.63
28	57	7	0.02	0.03

**Statistics**

<b>Assigned Value</b>	56.8	2.4
<b>Homogeneity Value</b>	50.0	6.0
<b>Robust Average</b>	56.8	2.4
<b>Median</b>	56.0	1.8
<b>Mean</b>	57.8	
<b>N</b>	22	
<b>Max</b>	83	
<b>Min</b>	39.1	
<b>Robust SD</b>	4.4	
<b>Robust CV</b>	7.8%	



**z-Scores: S1 - As**



**En-Scores: S1 - As**

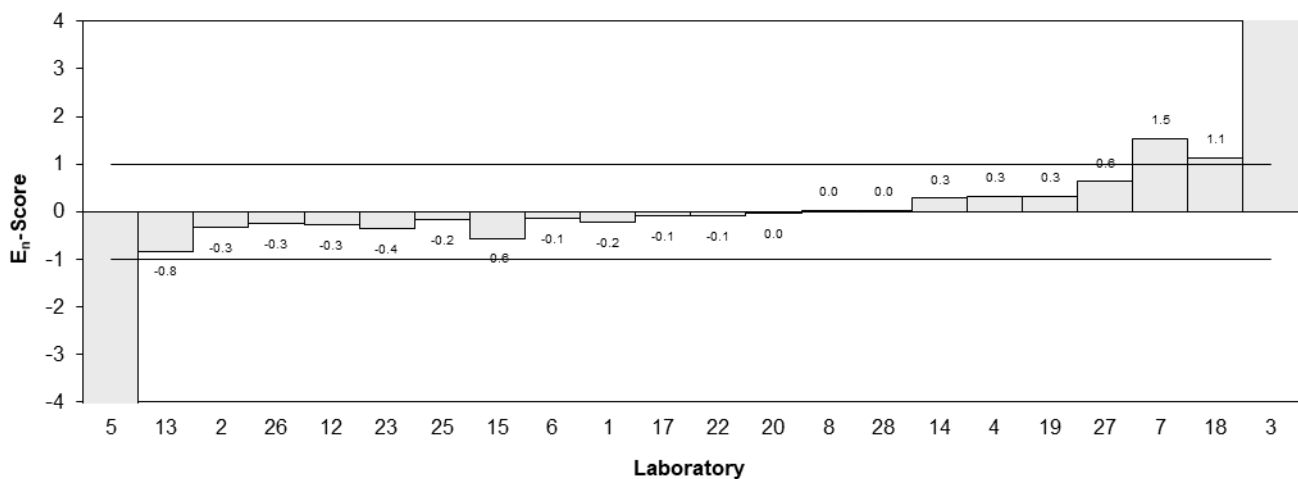


Figure 3



Table 12

**Sample Details**

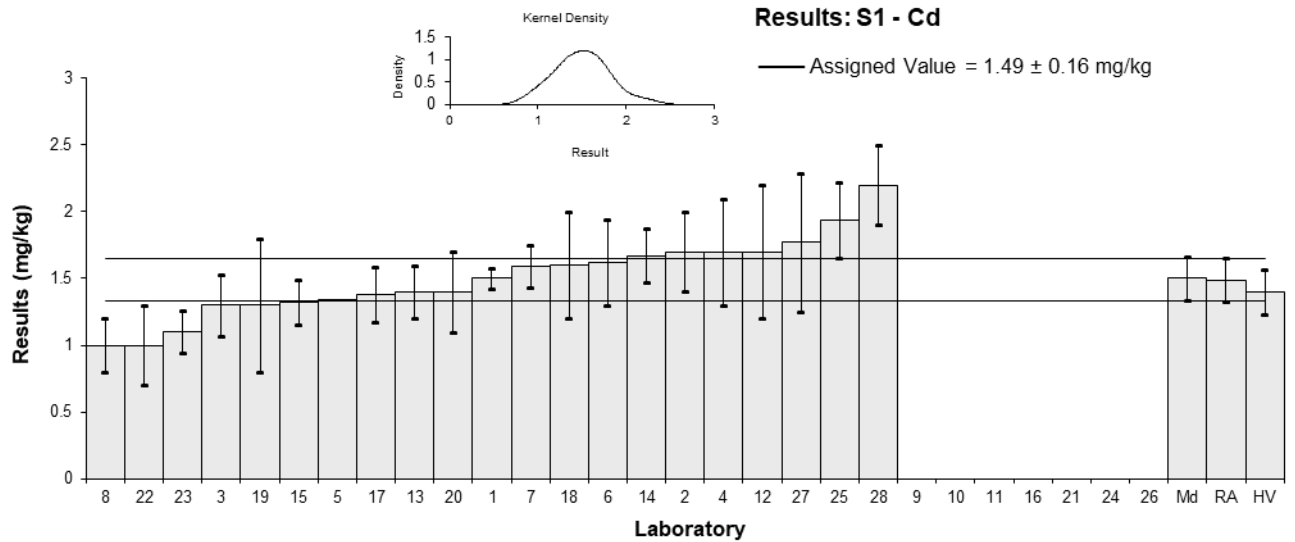
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Cd
<b>Unit</b>	mg/kg

**Participant Results**

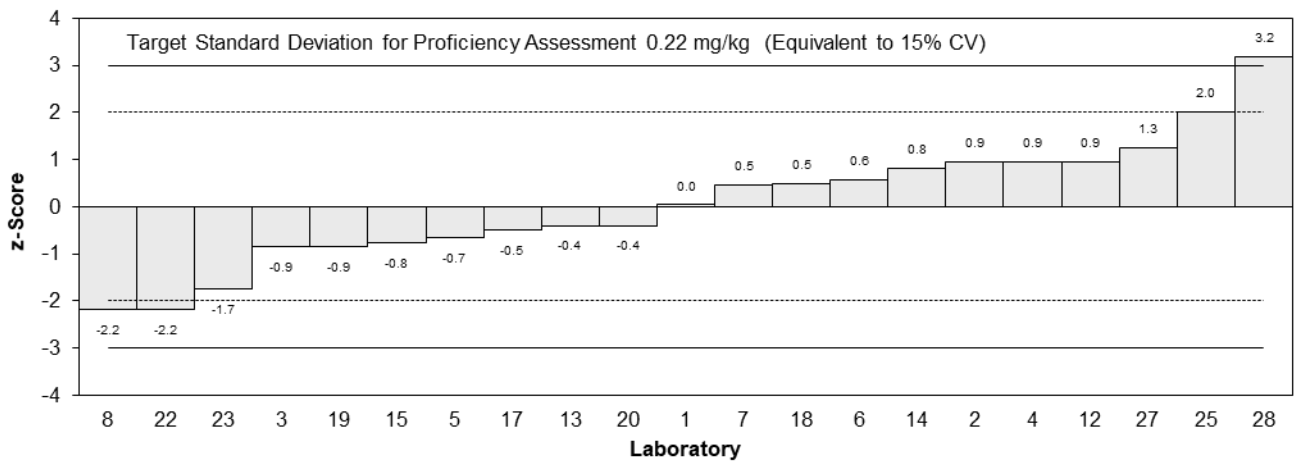
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	1.5	0.08	0.04	0.06
2	1.7	0.3	0.94	0.62
3	1.3	0.232	-0.85	-0.67
4	1.7	0.4	0.94	0.49
5	1.34	NR	-0.67	-0.94
6	1.620	0.324	0.58	0.36
7	1.59	0.16	0.45	0.44
8	1	0.2	-2.19	-1.91
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	1.7	0.5	0.94	0.40
13	1.4	0.2	-0.40	-0.35
14	1.67	0.2	0.81	0.70
15	1.32	0.17	-0.76	-0.73
16	NT	NT		
17	1.38	0.21	-0.49	-0.42
18	1.6	0.4	0.49	0.26
19	1.3	0.5	-0.85	-0.36
20	1.4	0.3	-0.40	-0.26
21	NT	NT		
22	1	0.3	-2.19	-1.44
23	1.1	0.1617	-1.74	-1.71
24	NT	NT		
25	1.9382	0.287	2.01	1.36
26	<1	NR		
27	1.77	0.52	1.25	0.51
28	2.2	0.3	3.18	2.09

**Statistics**

<b>Assigned Value</b>	1.49	0.16
<b>Homogeneity Value</b>	1.40	0.17
<b>Robust Average</b>	1.49	0.16
<b>Median</b>	1.50	0.16
<b>Mean</b>	1.50	
<b>N</b>	21	
<b>Max</b>	2.2	
<b>Min</b>	1	
<b>Robust SD</b>	0.30	
<b>Robust CV</b>	20%	



**z-Scores: S1 - Cd**



**En-Scores: S1 - Cd**

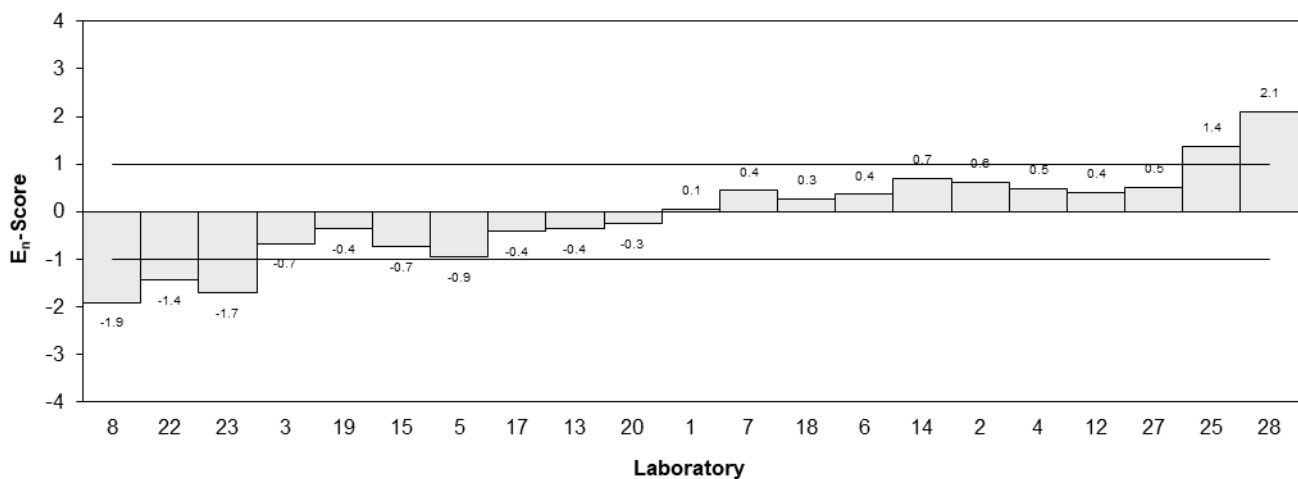


Figure 4

Table 13

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Cr
<b>Unit</b>	mg/kg

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	37	2.2	0.40	0.59
2	35	7	0.02	0.01
3	37.5	0.027	0.50	0.93
4	36	7	0.21	0.15
5	29.1	NR	-1.11	-2.07
6	33.67	6.734	-0.23	-0.17
7	33.0	3.3	-0.36	-0.44
8	25	4	-1.89	-2.03
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	33	10	-0.36	-0.18
13	27.6	7.7	-1.39	-0.89
14	36.5	4.0	0.31	0.33
15	40.0	4.2	0.97	1.01
16	NT	NT		
17	34.4	5.5	-0.10	-0.08
18	43.1	9	1.57	0.87
19	39	10	0.78	0.39
20	40.8	8	1.13	0.70
21	NT	NT		
22	28	5	-1.32	-1.20
23	30	3.57	-0.94	-1.08
24	NT	NT		
25	34.7018	5.107	-0.04	-0.03
26	50.5	15	2.98	1.02
27	33.24	7.08	-0.32	-0.22
28	36	4.5	0.21	0.21

**Statistics**

<b>Assigned Value</b>	34.9	2.8
<b>Homogeneity Value</b>	34.7	4.2
<b>Robust Average</b>	34.9	2.8
<b>Median</b>	34.9	1.9
<b>Mean</b>	35.1	
<b>N</b>	22	
<b>Max</b>	50.5	
<b>Min</b>	25	
<b>Robust SD</b>	5.2	
<b>Robust CV</b>	15%	

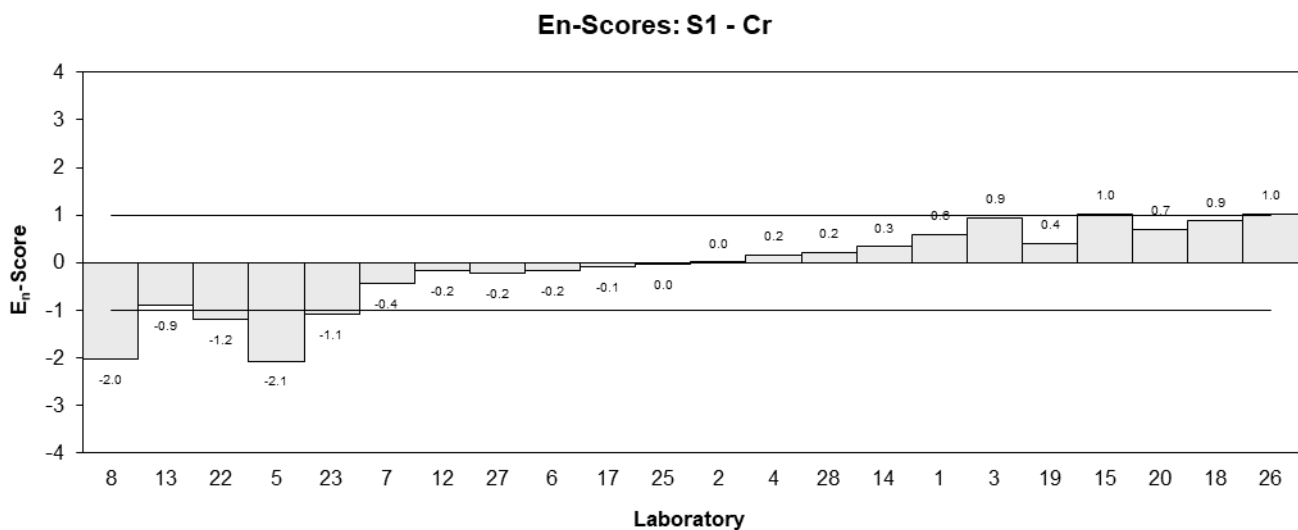
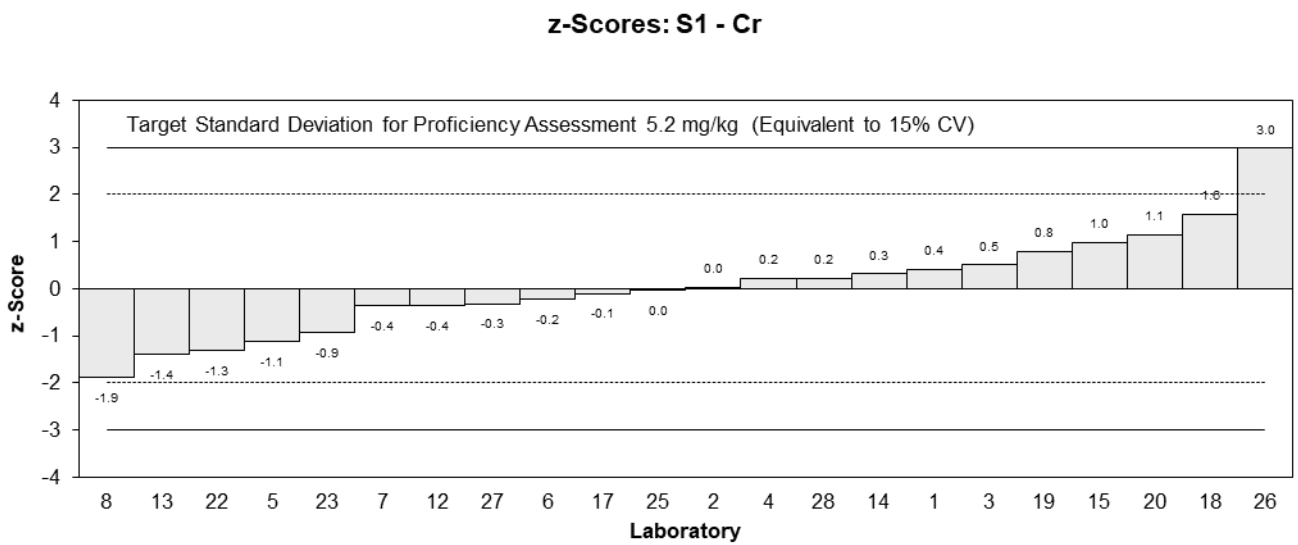
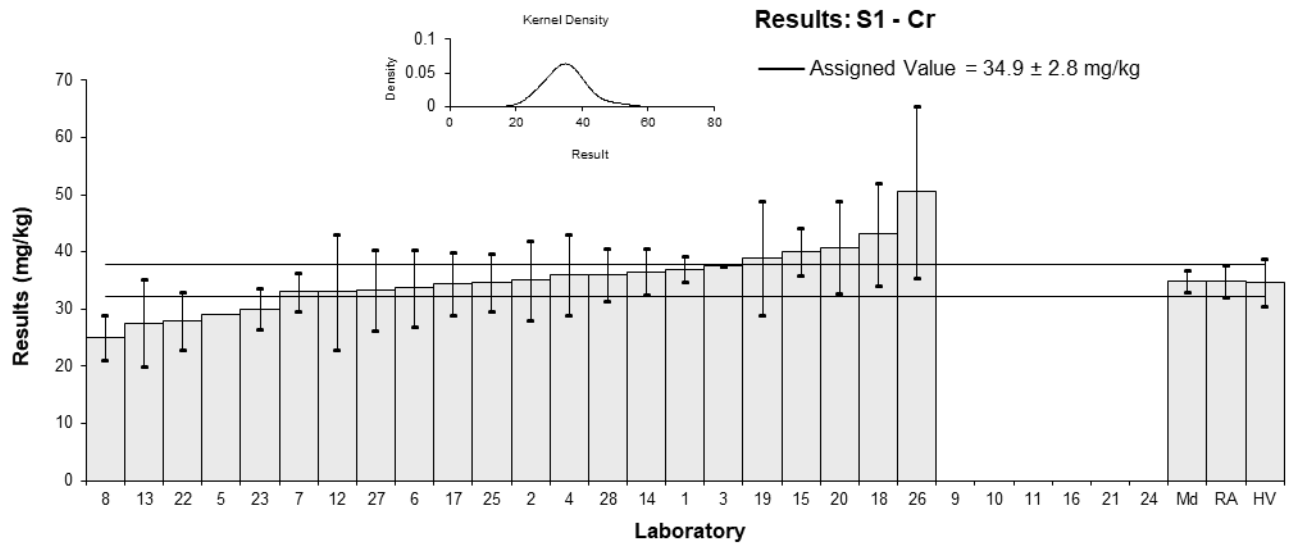


Figure 5

Table 14

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Cu
<b>Unit</b>	mg/kg

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	37	2.2	1.01	1.09
2	33	7	-0.18	-0.08
3	35.3	0.133	0.51	0.77
4	32	7	-0.48	-0.22
5	31.6	NR	-0.60	-0.91
6	27.93	5.586	-1.69	-0.94
7	31.7	3.2	-0.57	-0.49
8	28	3	-1.67	-1.51
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	35	10	0.42	0.14
13	25.8	4.3	-2.32	-1.61
14	35.9	4.0	0.68	0.50
15*	68.7	2.2	10.45	11.28
16	NT	NT		
17	32.2	4.6	-0.42	-0.27
18	39.6	8	1.79	0.72
19	37	10	1.01	0.33
20	35.4	7	0.54	0.25
21	NT	NT		
22	30.8	7	-0.83	-0.38
23	35	4.375	0.42	0.29
24	NT	NT		
25	29.50495	3.699	-1.22	-0.95
26	36.0	11	0.71	0.21
27	37.43	5.50	1.14	0.65
28	38	4.8	1.31	0.83

\* Outlier

**Statistics**

<b>Assigned Value</b>	33.6	2.2
<b>Homogeneity Value</b>	32.8	3.9
<b>Robust Average</b>	33.9	2.3
<b>Median</b>	35.0	2.3
<b>Mean</b>	35.1	
<b>N</b>	22	
<b>Max</b>	68.7	
<b>Min</b>	25.8	
<b>Robust SD</b>	4.2	
<b>Robust CV</b>	13%	

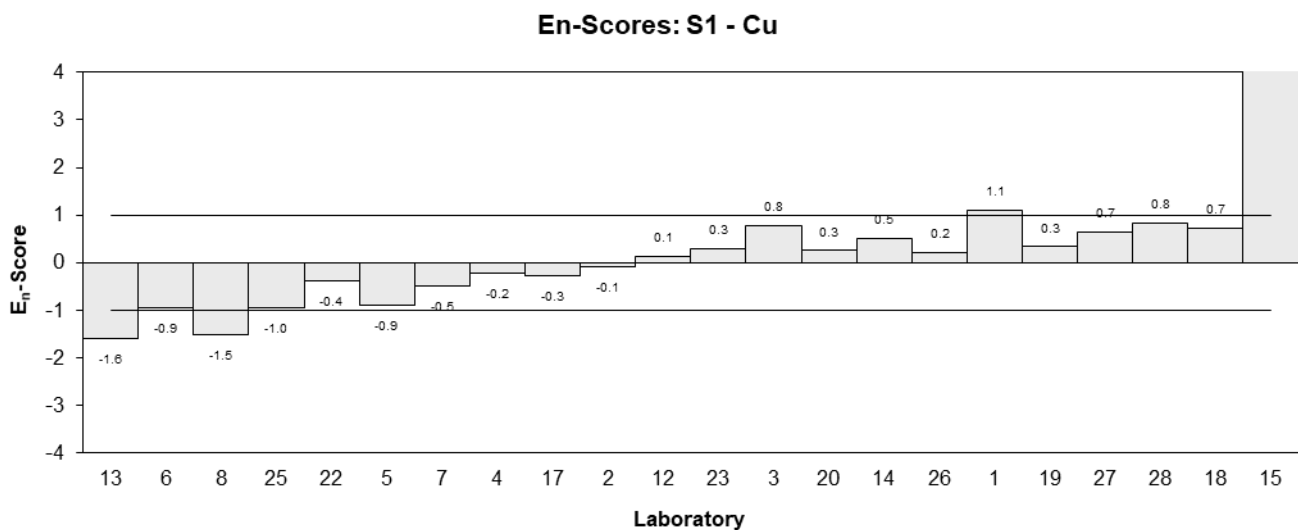
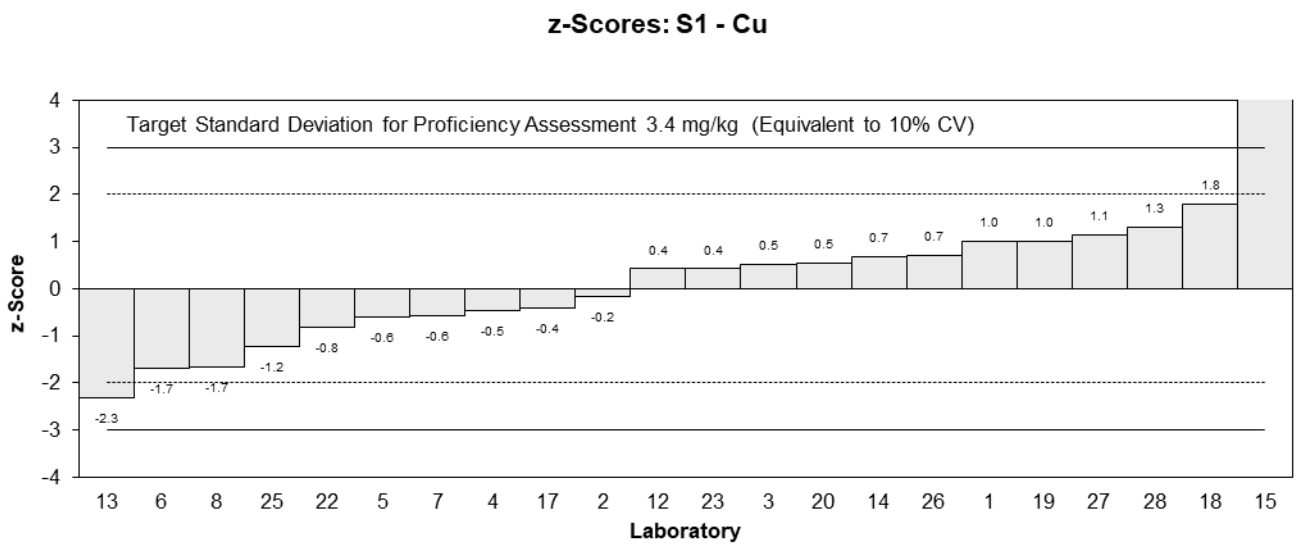
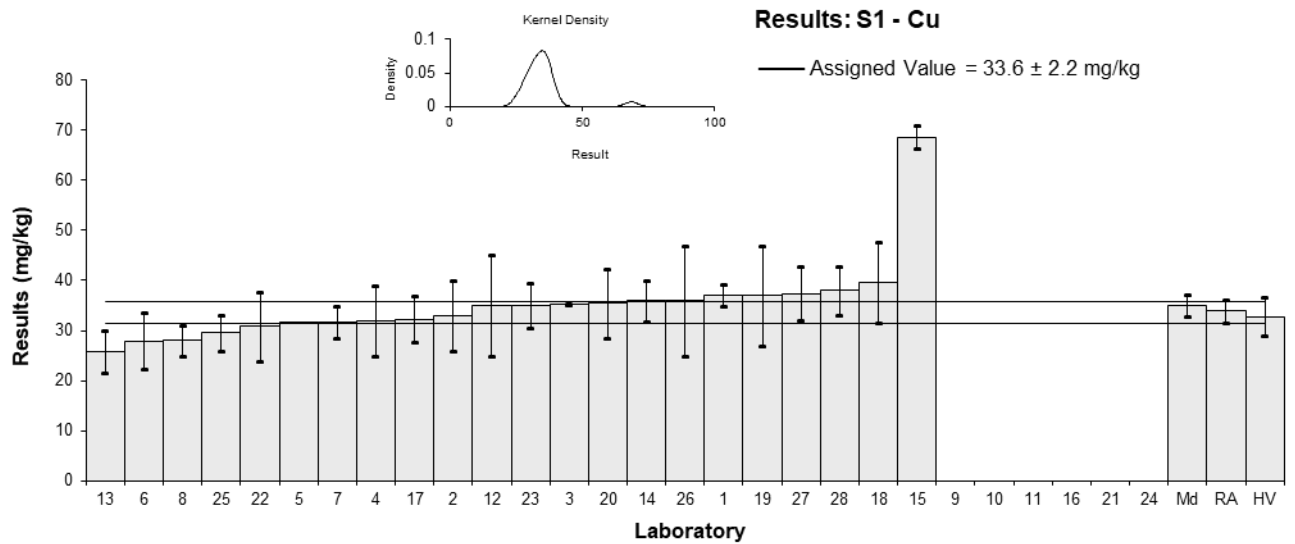


Figure 6

Table 15

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Hg
<b>Unit</b>	mg/kg

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	2.4	0.12	-0.11	-0.23
2	2.5	0.5	0.16	0.12
3	NT	NT		
4	2.8	0.8	0.98	0.44
5	2.15	NR	-0.79	-2.23
6	2.377	0.4754	-0.17	-0.13
7	2.31	0.23	-0.36	-0.49
8	2.6	0.6	0.44	0.26
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	2.7	0.5	0.71	0.50
13	2.4	0.5	-0.11	-0.08
14	2.27	0.4	-0.46	-0.40
15	2.20	0.15	-0.66	-1.21
16	2.19	0.1	-0.68	-1.52
17	2.61	0.42	0.46	0.39
18	3.34	0.75	2.46	1.18
19	2.5	0.5	0.16	0.12
20	2.04	0.4	-1.09	-0.95
21	NT	NT		
22	2.3	0.65	-0.38	-0.21
23	2.6	0.4368	0.44	0.35
24	NT	NT		
25	NT	NT		
26	2.65	0.8	0.57	0.26
27	2.57	0.38	0.36	0.32
28	2.3	0.3	-0.38	-0.43

**Statistics**

<b>Assigned Value</b>	2.44	0.13
<b>Homogeneity Value</b>	2.17	0.26
<b>Robust Average</b>	2.44	0.13
<b>Median</b>	2.40	0.16
<b>Mean</b>	2.47	
<b>N</b>	21	
<b>Max</b>	3.34	
<b>Min</b>	2.04	
<b>Robust SD</b>	0.24	
<b>Robust CV</b>	9.9%	

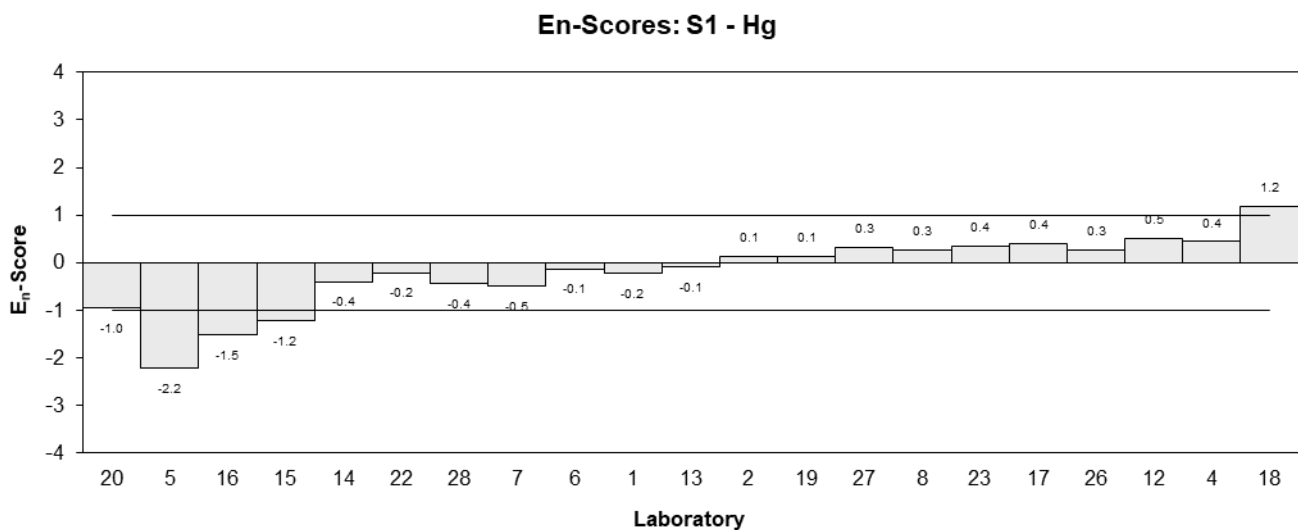
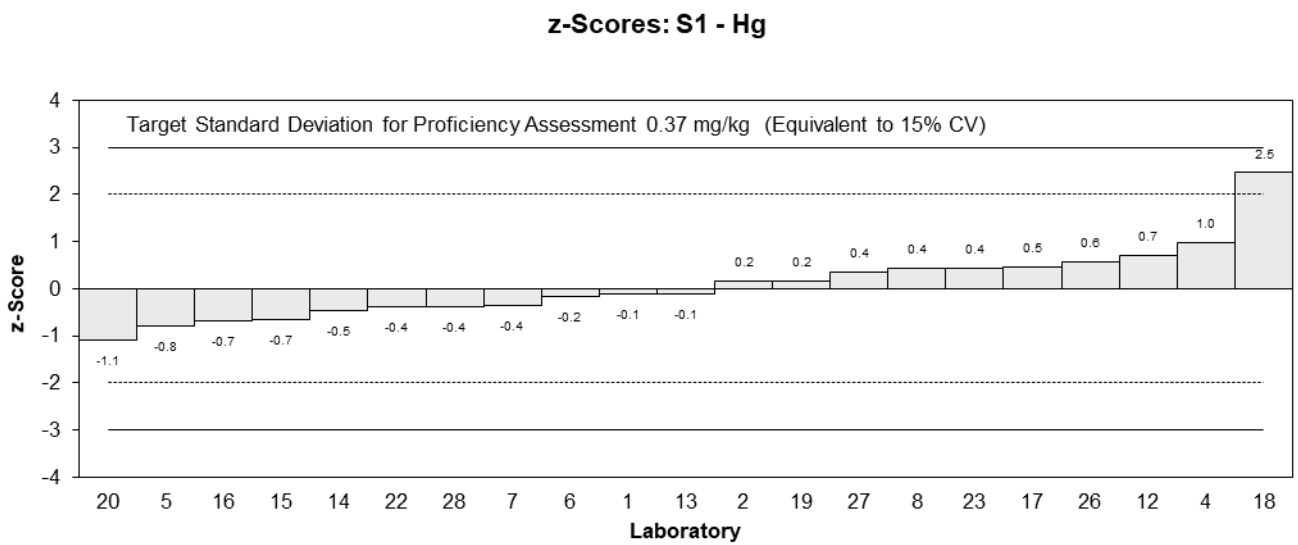
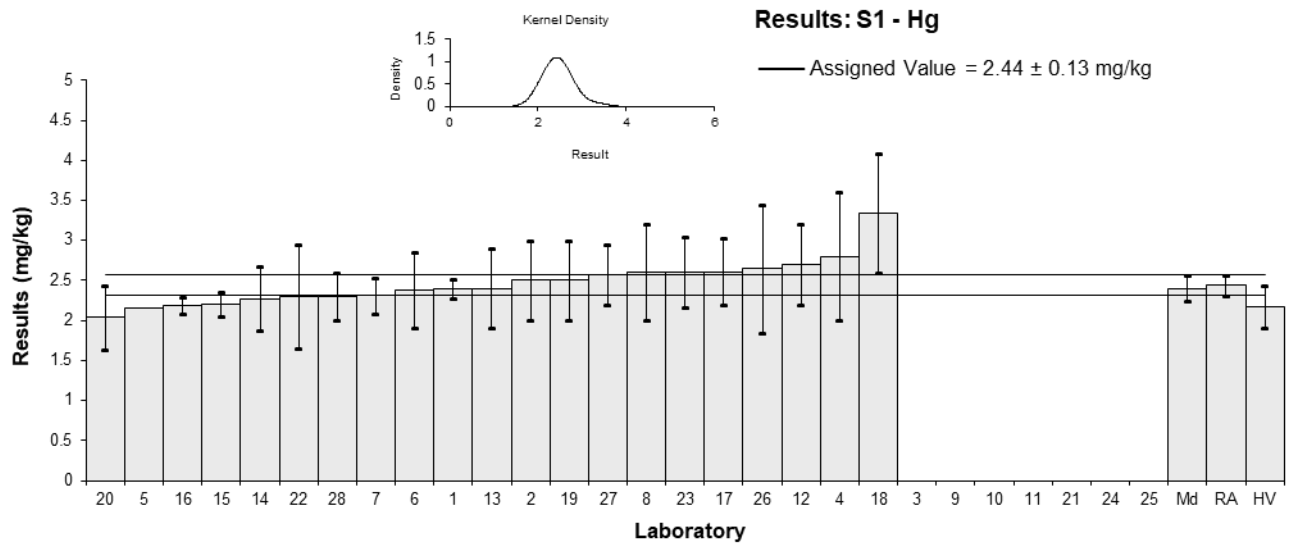


Figure 7



Table 16

**Sample Details**

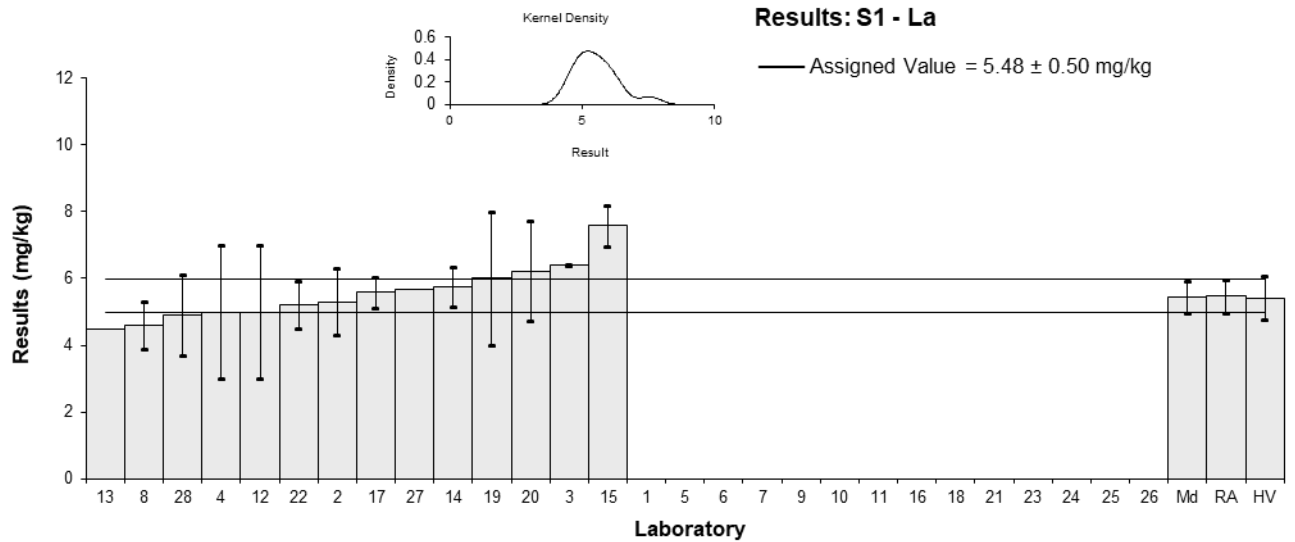
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	La
<b>Unit</b>	mg/kg

**Participant Results**

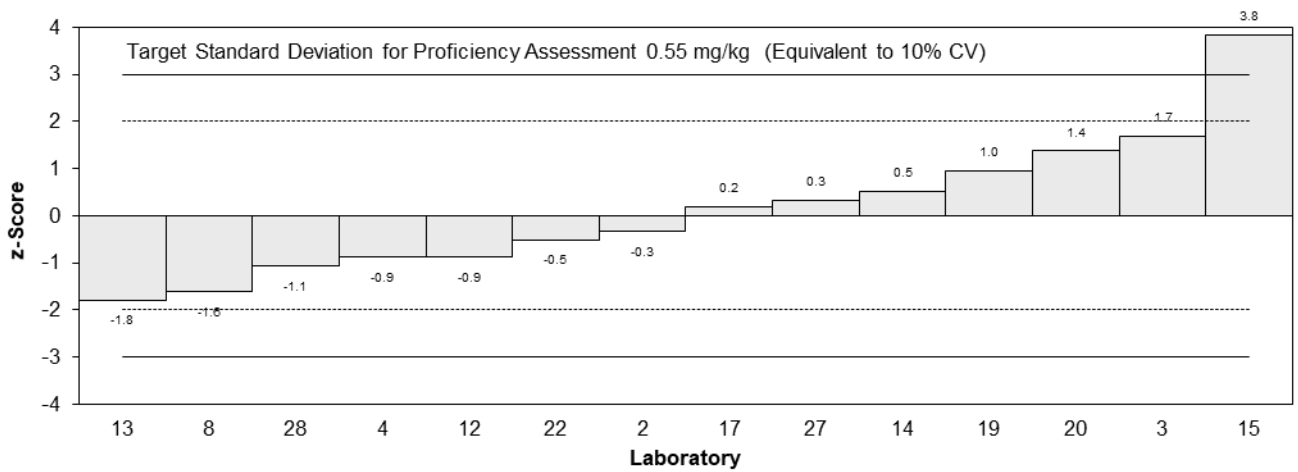
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	5.3	1	-0.33	-0.16
3	6.4	0.008	1.68	1.84
4	5	2	-0.88	-0.23
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	4.6	0.7	-1.61	-1.02
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	5	2	-0.88	-0.23
13	4.5	NR	-1.79	-1.96
14	5.76	0.6	0.51	0.36
15	7.58	0.62	3.83	2.64
16	NT	NT		
17	5.58	0.47	0.18	0.15
18	NT	NT		
19	6	2	0.95	0.25
20	6.23	1.5	1.37	0.47
21	NT	NT		
22	5.2	0.71	-0.51	-0.32
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	NT	NT		
27	5.662	NR	0.33	0.36
28	4.9	1.2	-1.06	-0.45

**Statistics**

<b>Assigned Value</b>	5.48	0.50
<b>Homogeneity Value</b>	5.42	0.65
<b>Robust Average</b>	5.48	0.50
<b>Median</b>	5.44	0.49
<b>Mean</b>	5.55	
<b>N</b>	14	
<b>Max</b>	7.58	
<b>Min</b>	4.5	
<b>Robust SD</b>	0.75	
<b>Robust CV</b>	14%	



**z-Scores: S1 - La**



**En-Scores: S1 - La**

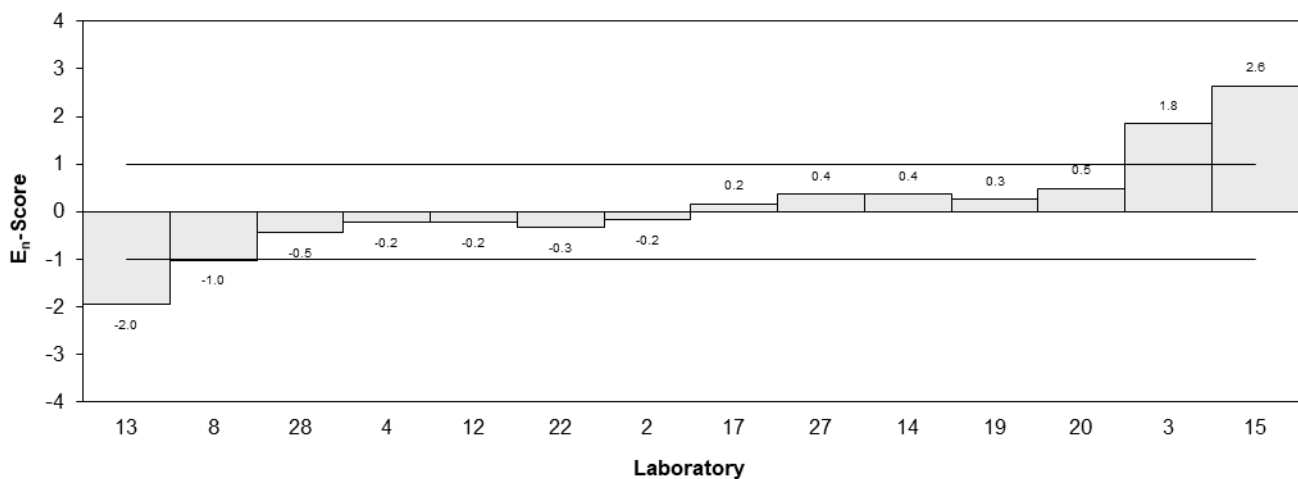


Figure 8

Table 17

**Sample Details**

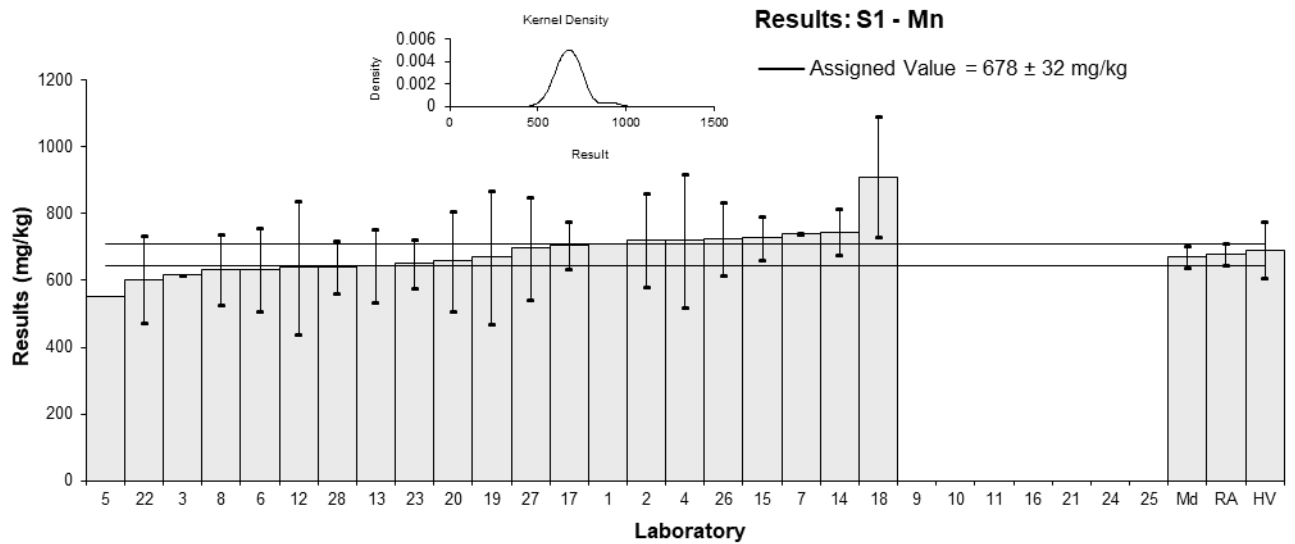
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Mn
<b>Unit</b>	mg/kg

**Participant Results**

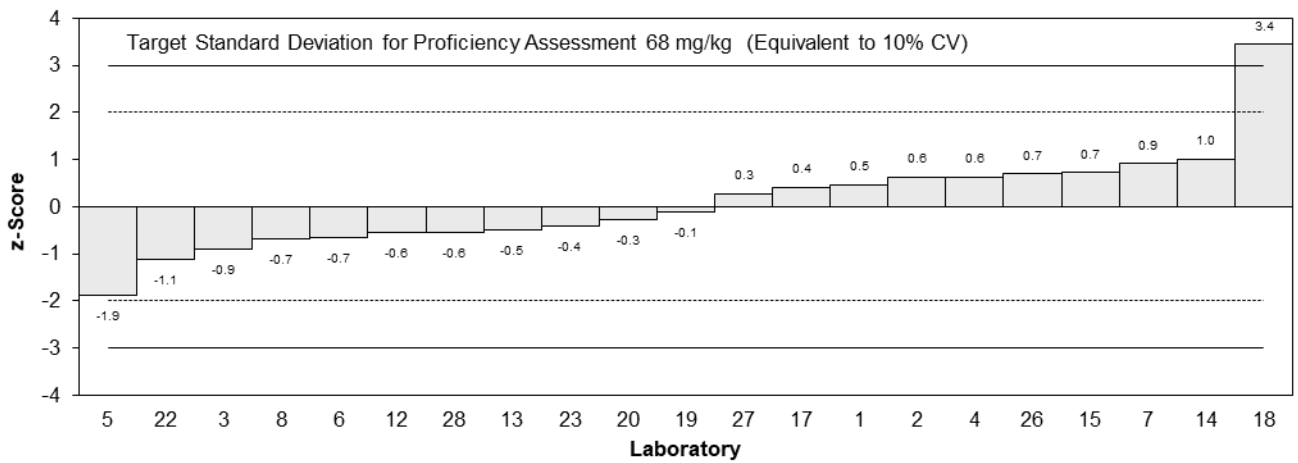
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	710	NR	0.47	1.00
2	720	140	0.62	0.29
3	617	0.003	-0.90	-1.91
4	720	200	0.62	0.21
5	550.5	NR	-1.88	-3.98
6	632.9	126.58	-0.67	-0.35
7	740	0.74	0.91	1.94
8	632	106	-0.68	-0.42
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	640	200	-0.56	-0.19
13	644	108	-0.50	-0.30
14	746	70	1.00	0.88
15	727	65	0.72	0.68
16	NT	NT		
17	705	71	0.40	0.35
18	911	180	3.44	1.27
19	670	200	-0.12	-0.04
20	659	150	-0.28	-0.12
21	NT	NT		
22	603	130	-1.11	-0.56
23	650	72.8	-0.41	-0.35
24	NT	NT		
25	NT	NT		
26	724.5	110	0.69	0.41
27	696.55	154.67	0.27	0.12
28	640	80	-0.56	-0.44

**Statistics**

<b>Assigned Value</b>	678	32
<b>Homogeneity Value</b>	692	83
<b>Robust Average</b>	678	32
<b>Median</b>	670	32
<b>Mean</b>	683	
<b>N</b>	21	
<b>Max</b>	911	
<b>Min</b>	550.5	
<b>Robust SD</b>	58	
<b>Robust CV</b>	8.6%	



**z-Scores: S1 - Mn**



**En-Scores: S1 - Mn**

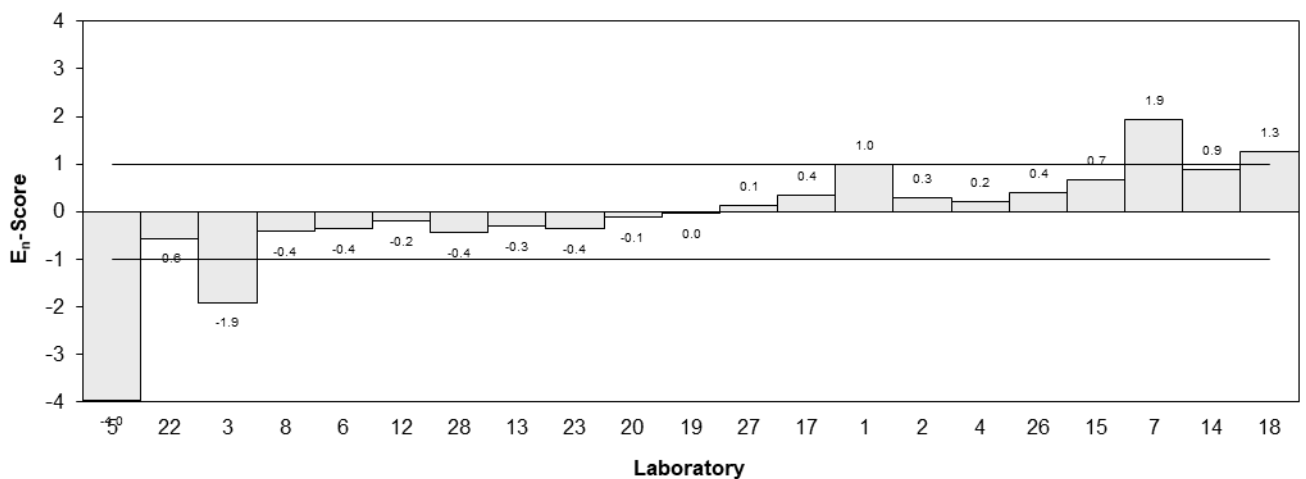


Figure 9

Table 18

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Mo
<b>Unit</b>	mg/kg

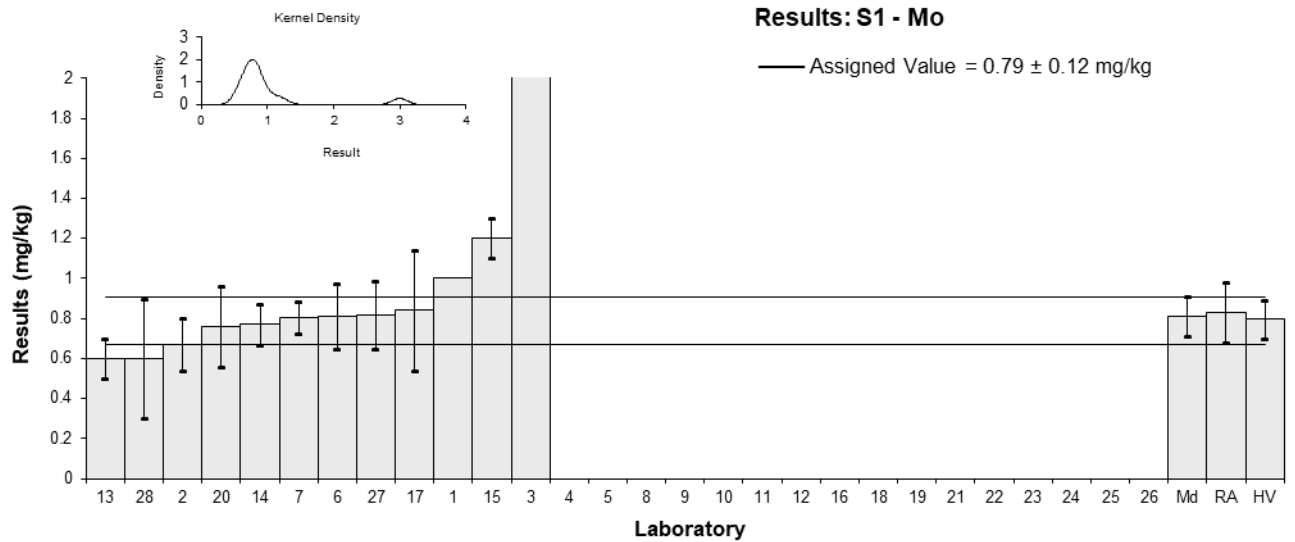
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	1.0	NR	1.33	1.75
2	0.67	0.13	-0.76	-0.68
3*	3.0	0.009	13.99	18.37
4	<1	NR		
5	NR	NR		
6	0.8125	0.1625	0.14	0.11
7	0.805	0.08	0.09	0.10
8	<2	NR		
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	<1	NR		
13	0.6	0.1	-1.20	-1.22
14	0.77	0.1	-0.13	-0.13
15	1.20	0.10	2.59	2.62
16	NT	NT		
17	0.84	0.30	0.32	0.15
18	< 2	NR		
19	<1	NR		
20	0.761	0.2	-0.18	-0.12
21	NT	NT		
22	<2	1		
23	<1	12.9		
24	NT	NT		
25	<2	NR		
26	<5	NR		
27	0.82	0.17	0.19	0.14
28	0.6	0.3	-1.20	-0.59

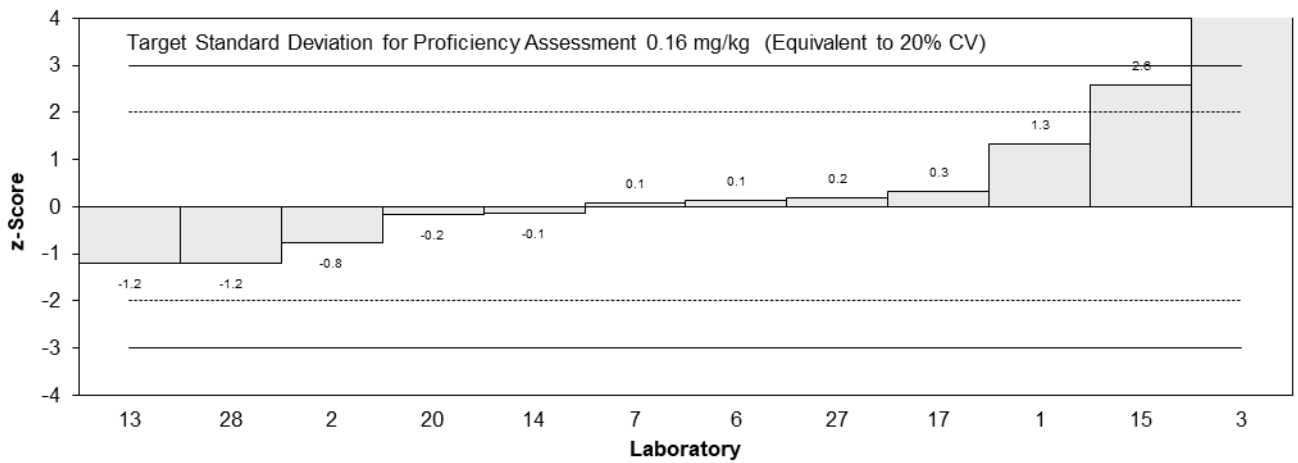
\* Outlier

**Statistics**

<b>Assigned Value</b>	0.79	0.12
<b>Homogeneity Value</b>	0.798	0.096
<b>Robust Average</b>	0.83	0.15
<b>Median</b>	0.809	0.100
<b>Mean</b>	0.99	
<b>N</b>	12	
<b>Max</b>	3	
<b>Min</b>	0.6	
<b>Robust SD</b>	0.20	
<b>Robust CV</b>	25%	



**z-Scores: S1 - Mo**



**En-Scores: S1 - Mo**

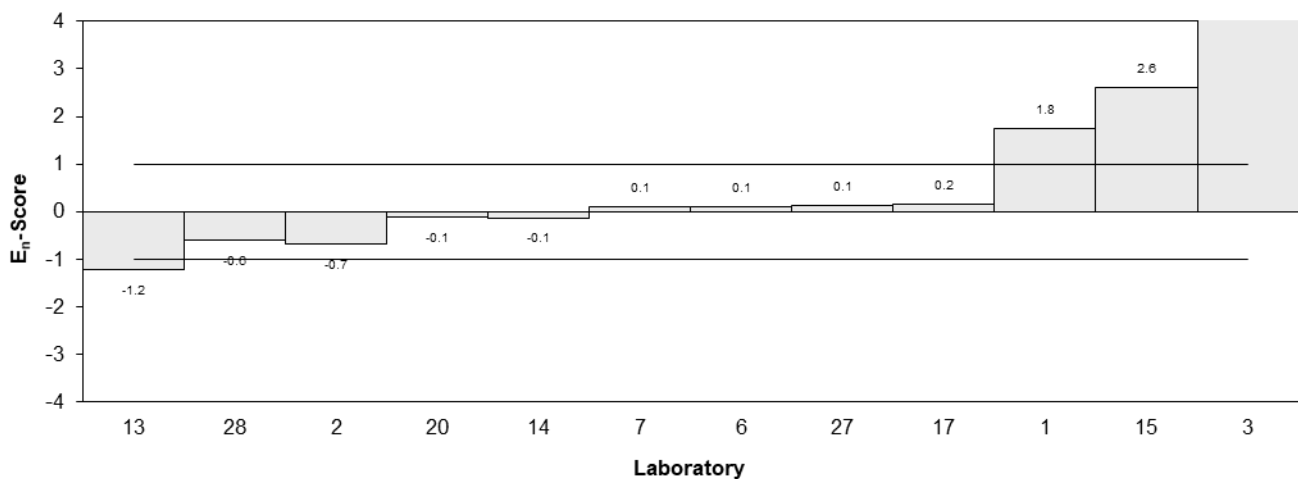


Figure 10

Table 19

**Sample Details**

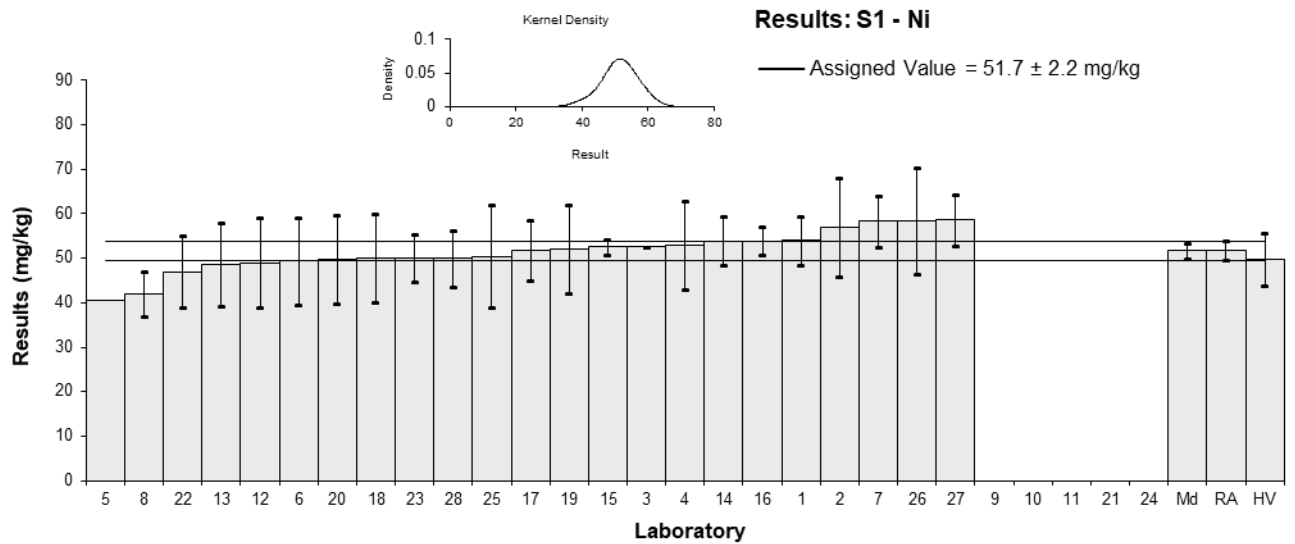
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Ni
<b>Unit</b>	mg/kg

**Participant Results**

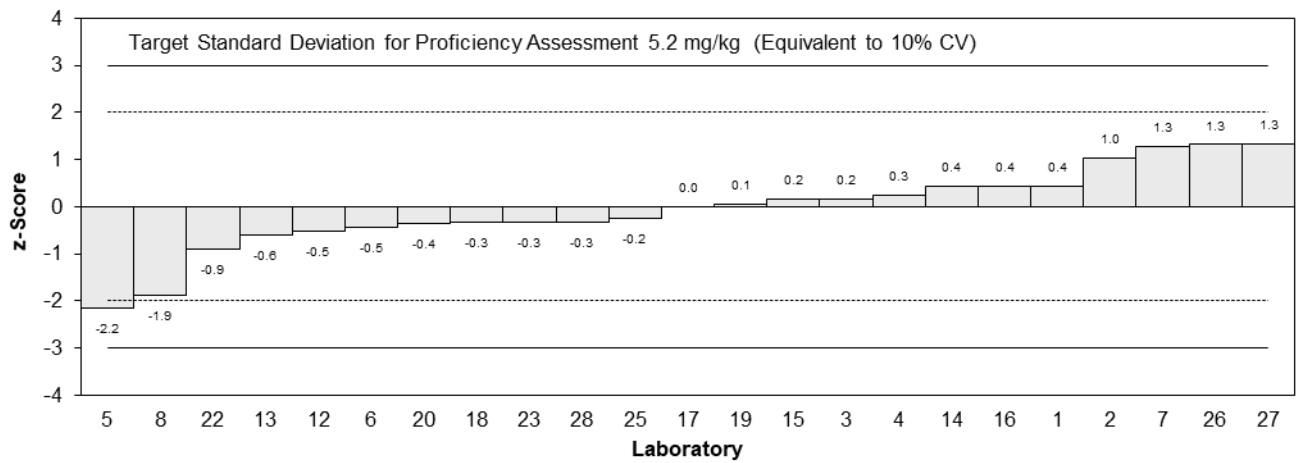
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	54.0	5.4	0.44	0.39
2	57	11	1.03	0.47
3	52.6	0.034	0.17	0.41
4	53	10	0.25	0.13
5	40.6	NR	-2.15	-5.05
6	49.39	9.878	-0.45	-0.23
7	58.3	5.8	1.28	1.06
8	42	5	-1.88	-1.78
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	49	10	-0.52	-0.26
13	48.6	9.5	-0.60	-0.32
14	53.9	5.5	0.43	0.37
15	52.5	1.8	0.15	0.28
16	53.9	3.2	0.43	0.57
17	51.7	6.8	0.00	0.00
18	50	10	-0.33	-0.17
19	52	10	0.06	0.03
20	49.8	10	-0.37	-0.19
21	NT	NT		
22	47	8	-0.91	-0.57
23	50	5.4	-0.33	-0.29
24	NT	NT		
25	50.4642	11.661	-0.24	-0.10
26	58.5	12	1.32	0.56
27	58.61	5.75	1.34	1.12
28	50	6.3	-0.33	-0.25

**Statistics**

<b>Assigned Value</b>	51.7	2.2
<b>Homogeneity Value</b>	49.8	6.0
<b>Robust Average</b>	51.7	2.2
<b>Median</b>	51.7	1.7
<b>Mean</b>	51.4	
<b>N</b>	23	
<b>Max</b>	58.61	
<b>Min</b>	40.6	
<b>Robust SD</b>	4.2	
<b>Robust CV</b>	8.2%	



**z-Scores: S1 - Ni**



**En-Scores: S1 - Ni**

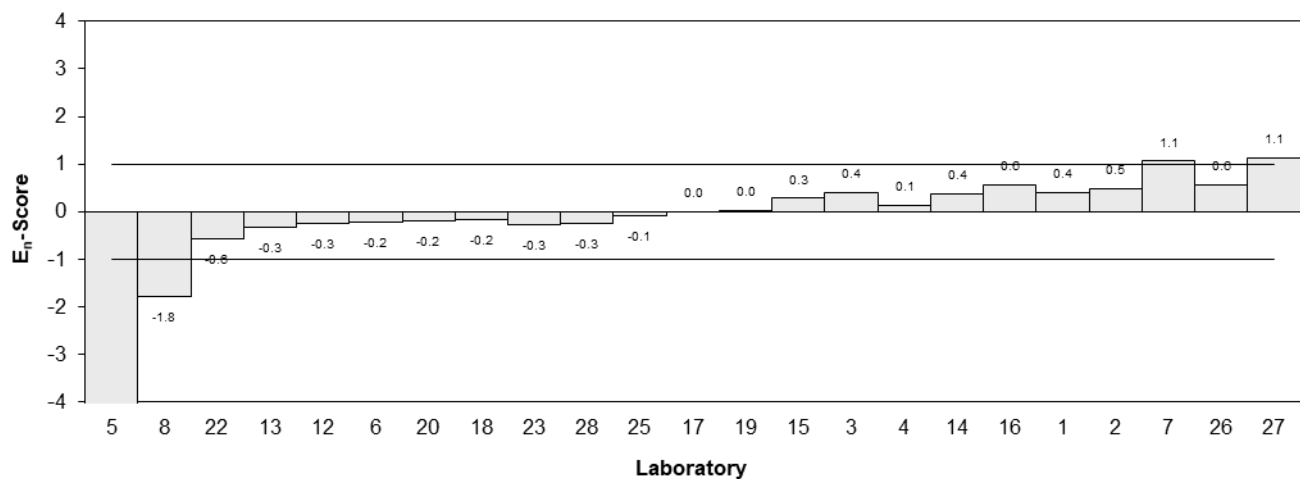


Figure 11



Table 20

**Sample Details**

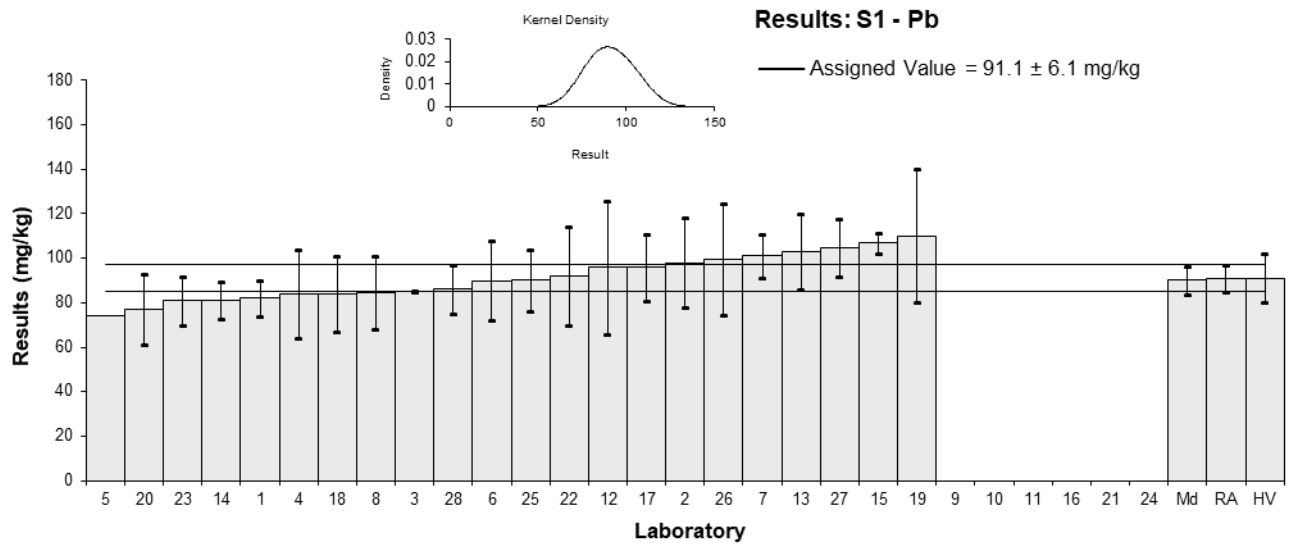
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Pb
<b>Unit</b>	mg/kg

**Participant Results**

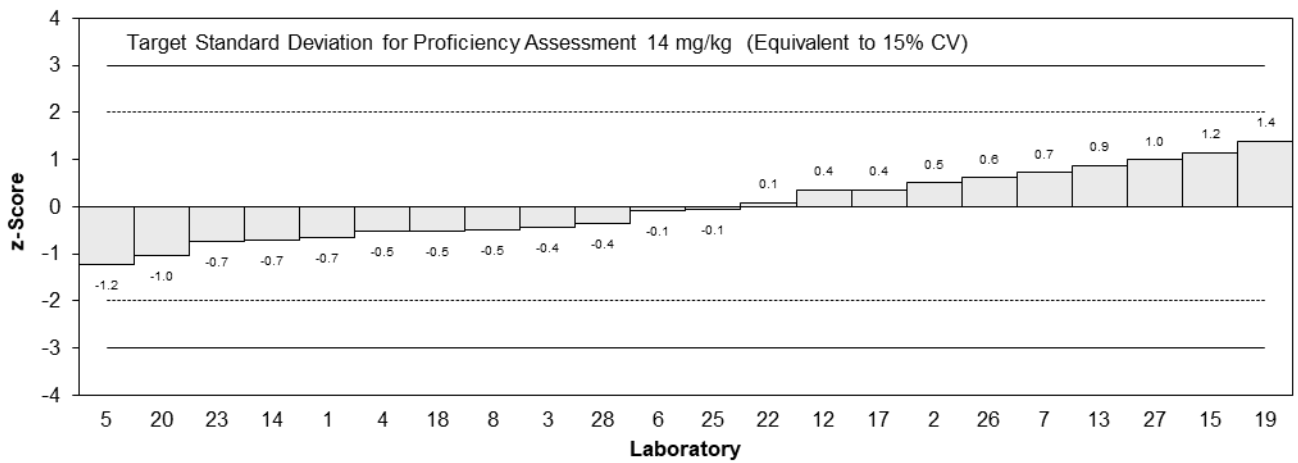
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	82	8.2	-0.67	-0.89
2	98	20	0.50	0.33
3	85.2	0.256	-0.43	-0.97
4	84	20	-0.52	-0.34
5	74.1	NR	-1.24	-2.79
6	89.92	17.984	-0.09	-0.06
7	101	10	0.72	0.85
8	84.4	16.3	-0.49	-0.38
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	96	30	0.36	0.16
13	103	17.1	0.87	0.66
14	81.2	8.5	-0.72	-0.95
15	106.8	4.7	1.15	2.04
16	NT	NT		
17	96	15	0.36	0.30
18	84	17	-0.52	-0.39
19	110	30	1.38	0.62
20	77	16	-1.03	-0.82
21	NT	NT		
22	92	22	0.07	0.04
23	81	11.016	-0.74	-0.80
24	NT	NT		
25	90.1296	13.957	-0.07	-0.06
26	99.5	25	0.61	0.33
27	104.67	13.19	0.99	0.93
28	86	11	-0.37	-0.41

**Statistics**

<b>Assigned Value</b>	91.1	6.1
<b>Homogeneity Value</b>	91	11
<b>Robust Average</b>	91.1	6.1
<b>Median</b>	90.0	6.3
<b>Mean</b>	91.2	
<b>N</b>	22	
<b>Max</b>	110	
<b>Min</b>	74.1	
<b>Robust SD</b>	11	
<b>Robust CV</b>	12%	



**z-Scores: S1 - Pb**



**En-Scores: S1 - Pb**

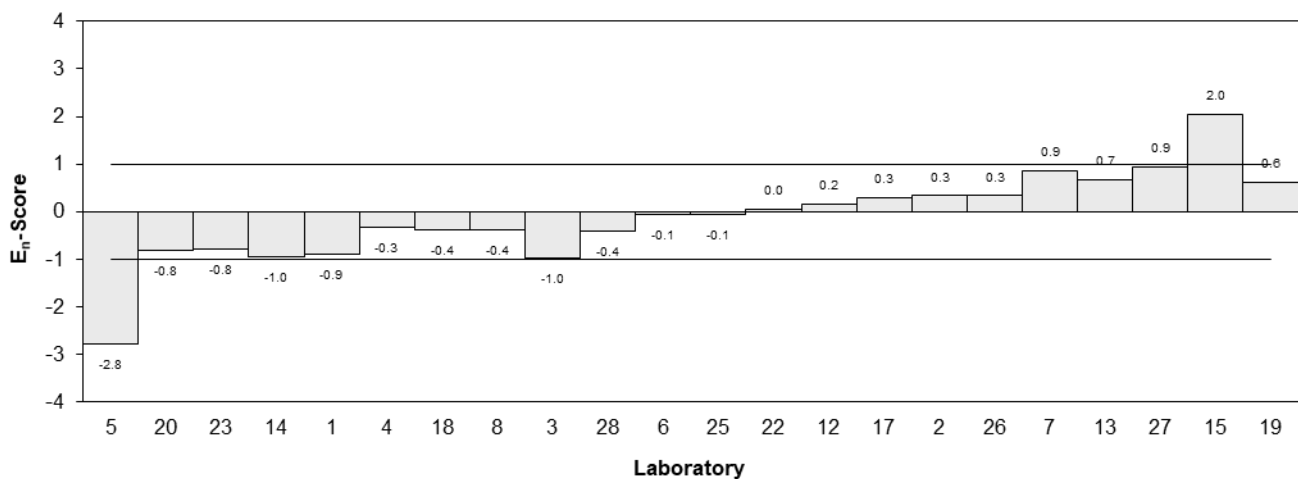


Figure 12

Table 21

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Sb
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NT	NT
2	0.59	0.12
3	0.7	0.447
4	<7	NR
5	NR	NR
6	1.109	0.2218
7	0.596	0.06
8	<5	NR
9	NT	NT
10	NT	NT
11	NT	NT
12	<7	NR
13	0.3	0.1
14	1.26	0.2
15	1.37	0.12
16	NT	NT
17	0.62	0.28
18	< 2	NR
19	<7	NR
20	NT	NT
21	NT	NT
22	<5	2
23	<3	23.8
24	NT	NT
25	<5	NR
26	NT	NT
27	0.655	0.21
28	2.8	3

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	0.88	0.11
<b>Robust Average</b>	0.88	0.38
<b>Median</b>	0.68	0.27
<b>Mean</b>	1.00	
<b>N</b>	10	
<b>Max</b>	2.8	
<b>Min</b>	0.3	
<b>Robust SD</b>	0.48	
<b>Robust CV</b>	54%	

Results: S1 - Sb

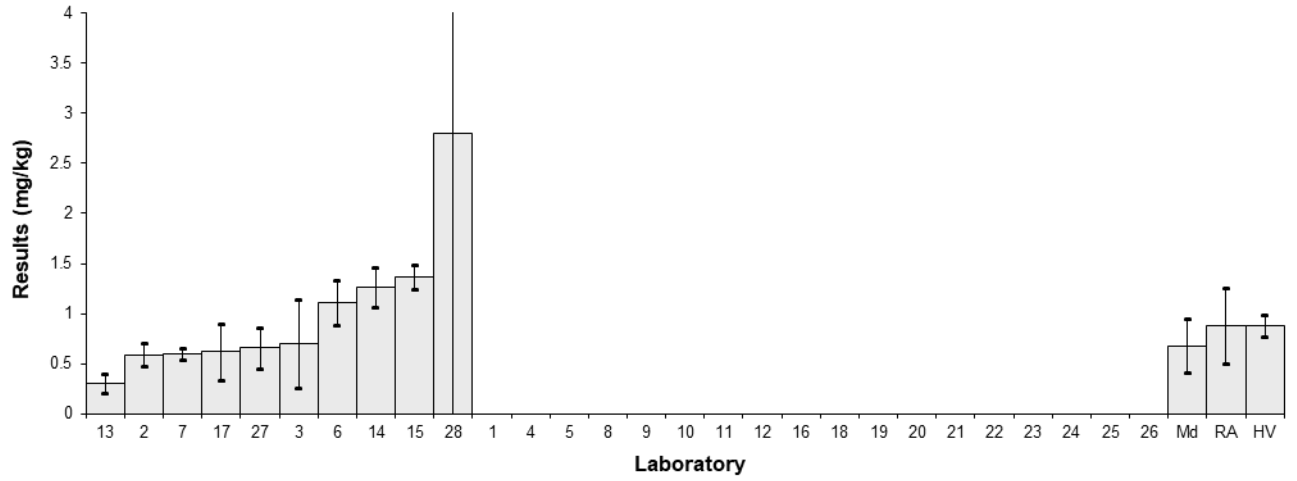


Figure 13

Table 22

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Se
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	1.3	0.06
2	0.69	0.14
3	1.3	0.078
4	<2	NR
5	NR	NR
6	0.732	0.1464
7	NR	NR
8	<5	NR
9	NT	NT
10	NT	NT
11	NT	NT
12	<2	NR
13	1.0	NR
14	0.45	0.1
15	0	0.03
16	NT	NT
17	< 20	14
18	3.98	0.9
19	<2	NR
20	0.637	0.2
21	NT	NT
22	<5	1
23	4	0.964
24	NT	NT
25	NT	NT
26	NT	NT
27	0.809	0.039
28	0.53	2

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	0.782	0.094
<b>Robust Average</b>	0.94	0.48
<b>Median</b>	0.77	0.30
<b>Mean</b>	1.29	
<b>N</b>	12	
<b>Max</b>	4	
<b>Min</b>	0	
<b>Robust SD</b>	0.66	
<b>Robust CV</b>	70%	

Results: S1 - Se

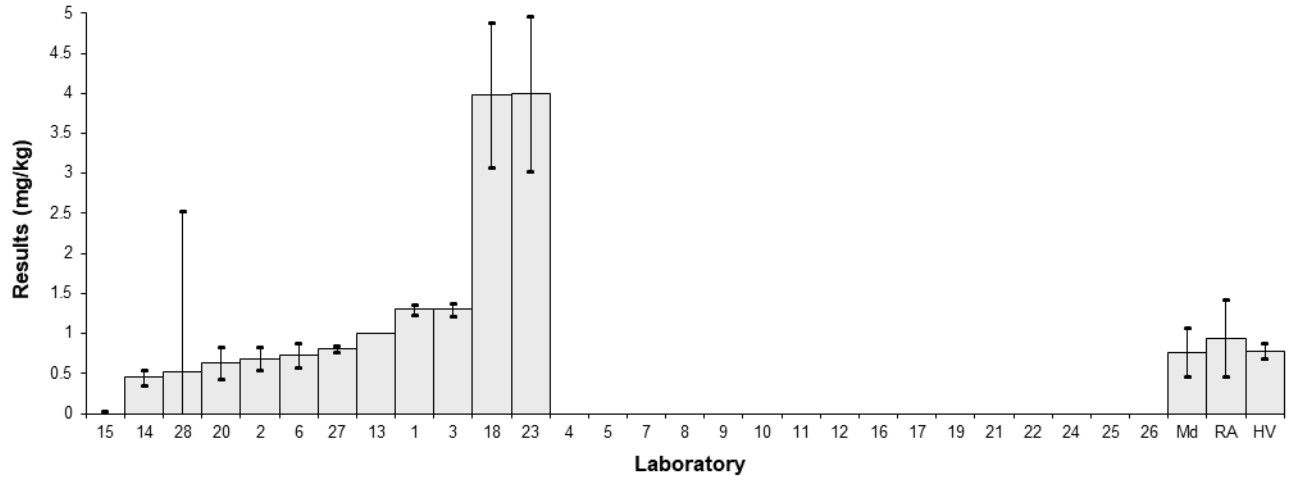


Figure 14

Table 23

**Sample Details**

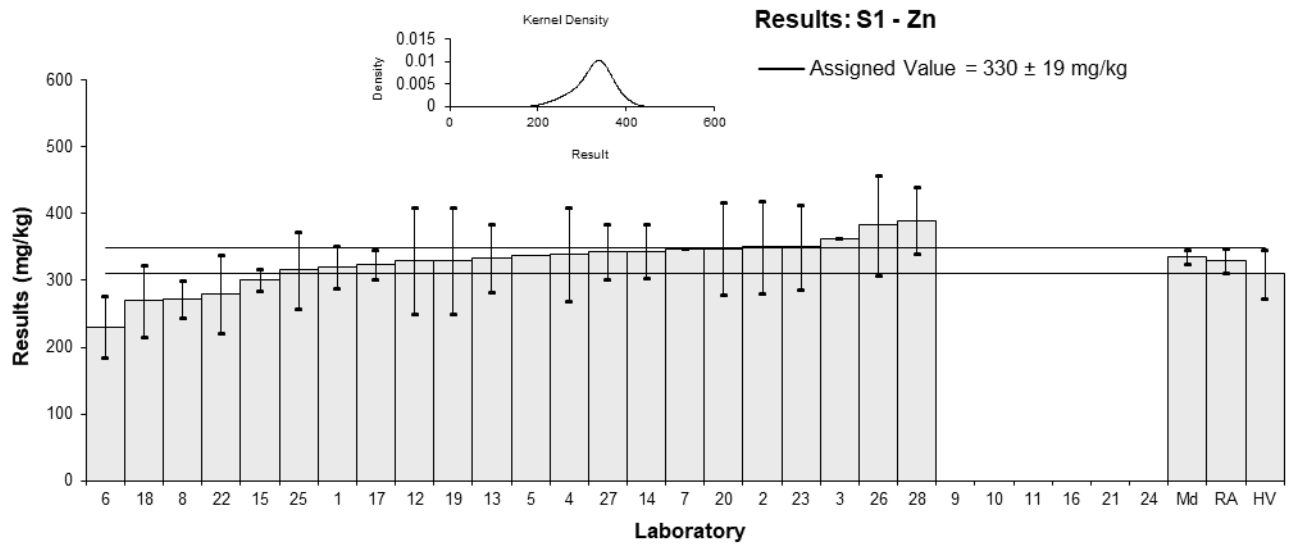
<b>Sample No.</b>	S1
<b>Matrix</b>	Sediment
<b>Analyte</b>	Zn
<b>Unit</b>	mg/kg

**Participant Results**

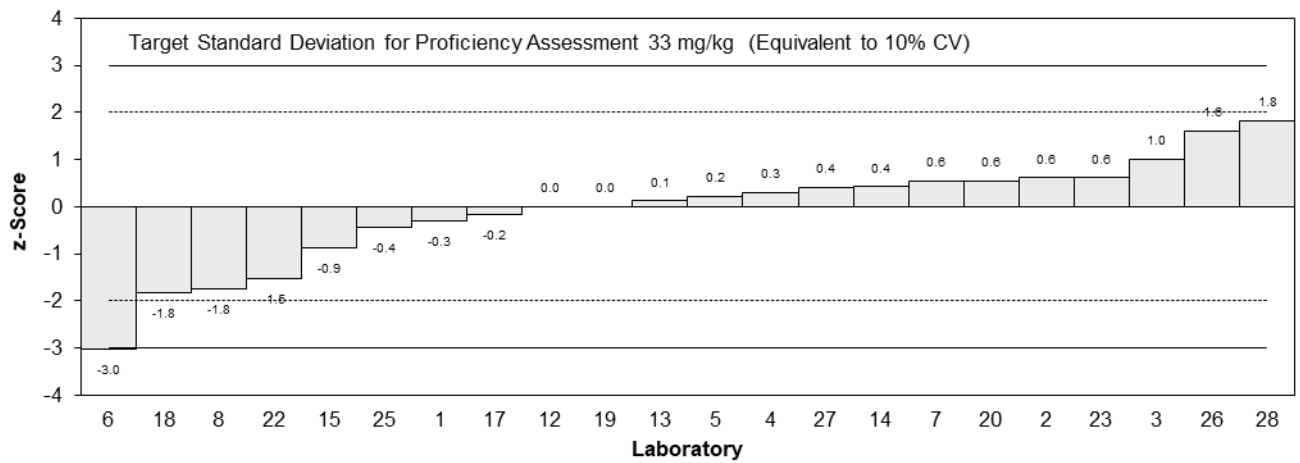
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	320	32	-0.30	-0.27
2	350	70	0.61	0.28
3	363	0.218	1.00	1.74
4	340	70	0.30	0.14
5	337.0	NR	0.21	0.37
6	230.1	46.02	-3.03	-2.01
7	348	0.35	0.55	0.95
8	272	28	-1.76	-1.71
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	330	80	0.00	0.00
13	334	51	0.12	0.07
14	344	40	0.42	0.32
15	301	17	-0.88	-1.14
16	NT	NT		
17	324	23	-0.18	-0.20
18	270	54	-1.82	-1.05
19	330	80	0.00	0.00
20	348	70	0.55	0.25
21	NT	NT		
22	280	59	-1.52	-0.81
23	350	63	0.61	0.30
24	NT	NT		
25	315.64055	57.689	-0.44	-0.24
26	383	75	1.61	0.69
27	343.35	41.82	0.40	0.29
28	390	50	1.82	1.12

**Statistics**

<b>Assigned Value</b>	330	19
<b>Homogeneity Value</b>	310	37
<b>Robust Average</b>	330	19
<b>Median</b>	336	11
<b>Mean</b>	327	
<b>N</b>	22	
<b>Max</b>	390	
<b>Min</b>	230.1	
<b>Robust SD</b>	36	
<b>Robust CV</b>	11%	



**z-Scores: S1 - Zn**



**En-Scores: S1 - Zn**

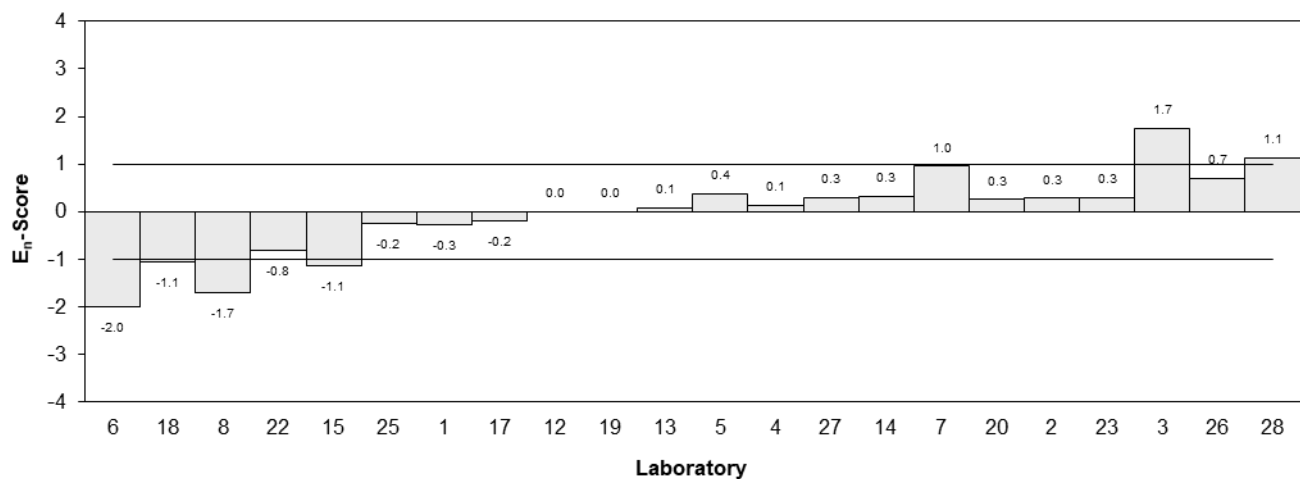


Figure 15



Table 24

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Al
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	18400	1840
2	19000	3800
3	23100	0.017
4	18000	5000
5	25000	NR
6	18330	3666
7	14900	1500
8	10500	1210
9	NT	NT
10	27600	4140
11	NT	NT
12	17000	4000
13	19600	3840
14	24166	2500
15	28368	4050
16	NT	NT
17	20600	2500
18	NT	NT
19	18000	4000
20	26500	5000
21	15039	2662
22	12800	2266
23	13000	2197
24	NT	NT
25	15177.2519	794.629
26	20800	3100
27	16022	2006
28	20000	2500

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	24700	3700
<b>Robust Average</b>	19200	2700
<b>Median</b>	18400	2500
<b>Mean</b>	19200	
<b>N</b>	23	
<b>Max</b>	28368	
<b>Min</b>	10500	
<b>Robust SD</b>	5200	
<b>Robust CV</b>	27%	

Results: S2 - Al

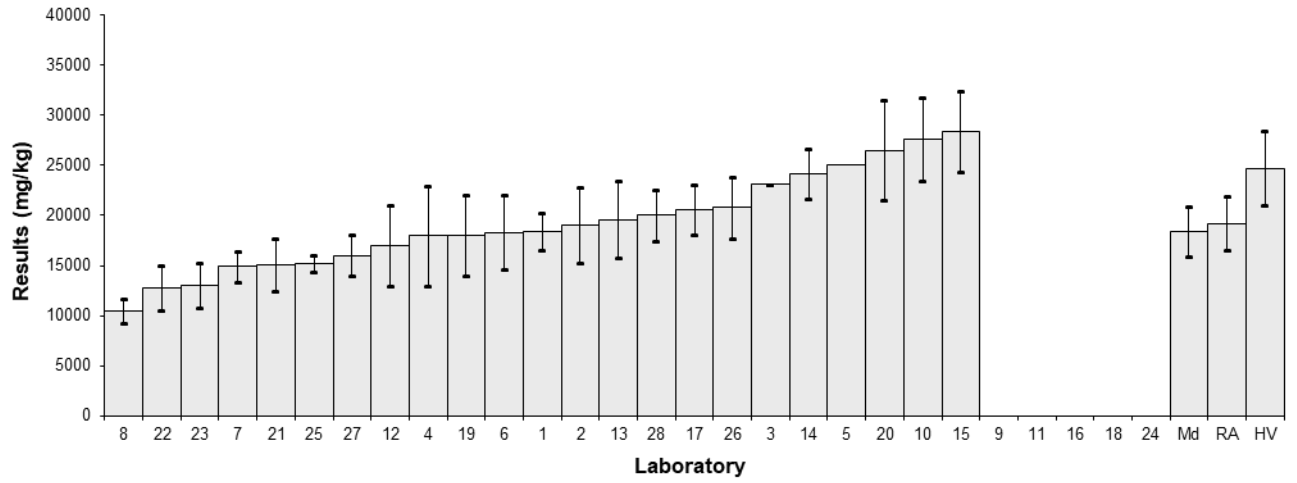


Figure 16

Table 25

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	As
<b>Unit</b>	mg/kg

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	5.0	0.25	2.52	3.13
2	3.5	0.7	-0.24	-0.17
3*	5.7	0.064	3.80	5.66
4	4	4	0.68	0.09
5	NR	NR		
6	3.586	0.7172	-0.08	-0.05
7	2.97	0.3	-1.21	-1.41
8*	6	1	4.35	2.23
9	NT	NT		
10	3.94	0.591	0.57	0.45
11	NT	NT		
12	3	2	-1.16	-0.31
13	2.8	0.4	-1.52	-1.54
14	4.29	0.5	1.21	1.07
15	4.0	0.2	0.68	0.90
16	NT	NT		
17	3.1	1.4	-0.97	-0.37
18	NT	NT		
19	4	2	0.68	0.18
20	3.64	0.7	0.02	0.01
21	4.32	0.72	1.27	0.86
22	<5	2		
23	3	0.399	-1.16	-1.17
24	NT	NT		
25	<3	NR		
26	<25	NR		
27	3.5	0.44	-0.24	-0.23
28	3.6	0.9	-0.06	-0.03

\* Outlier

**Statistics**

<b>Assigned Value</b>	3.63	0.36
<b>Homogeneity Value</b>	3.88	0.47
<b>Robust Average</b>	3.80	0.45
<b>Median</b>	3.64	0.46
<b>Mean</b>	3.89	
<b>N</b>	19	
<b>Max</b>	6	
<b>Min</b>	2.8	
<b>Robust SD</b>	0.78	
<b>Robust CV</b>	20%	

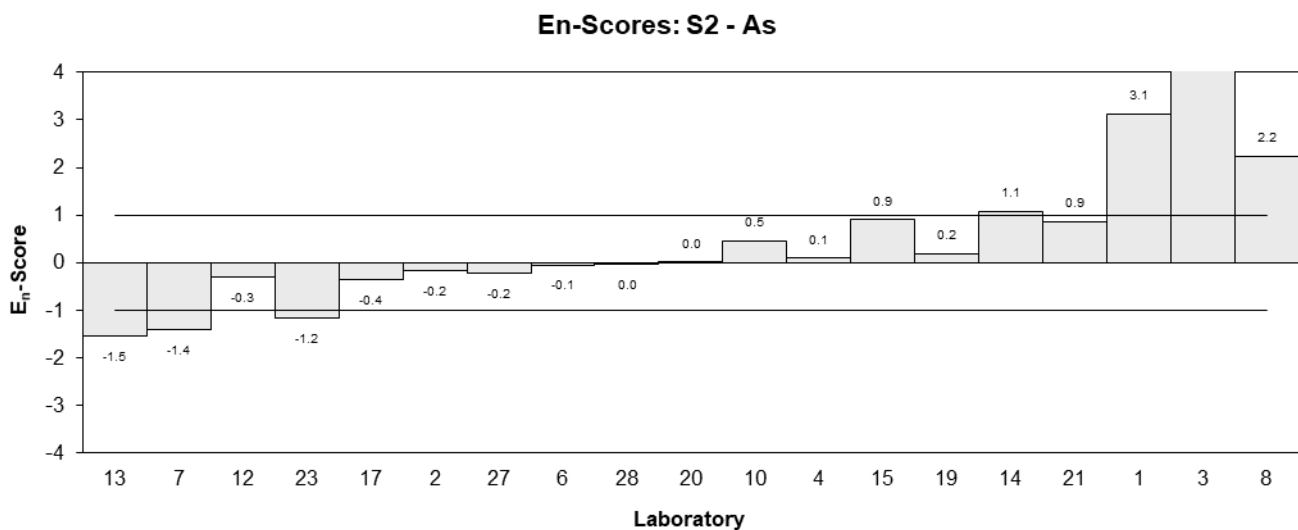
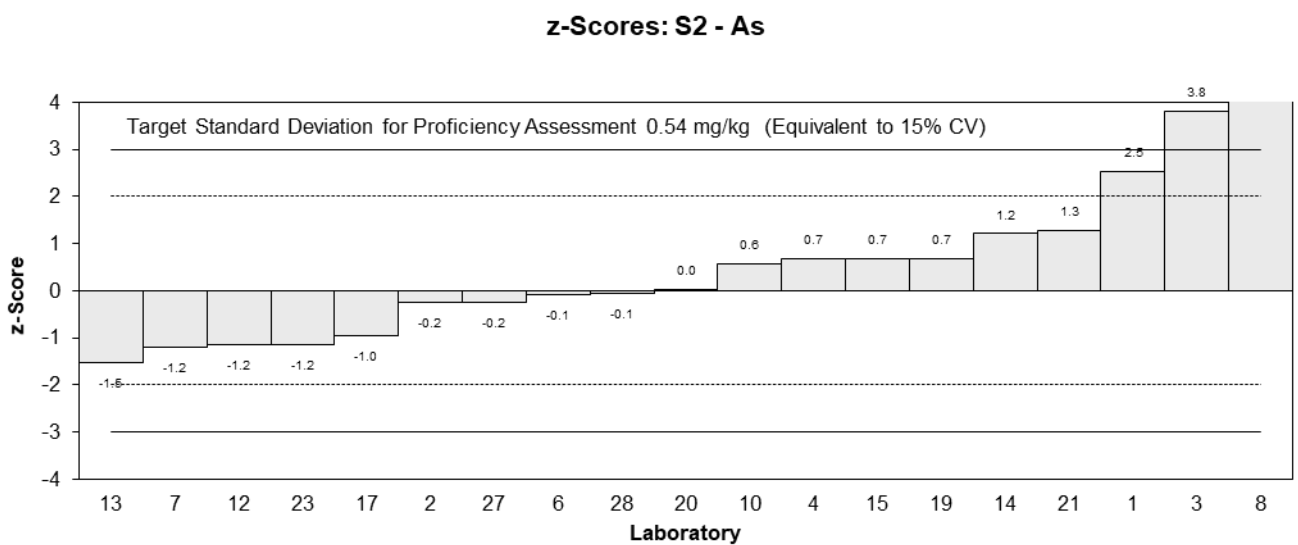
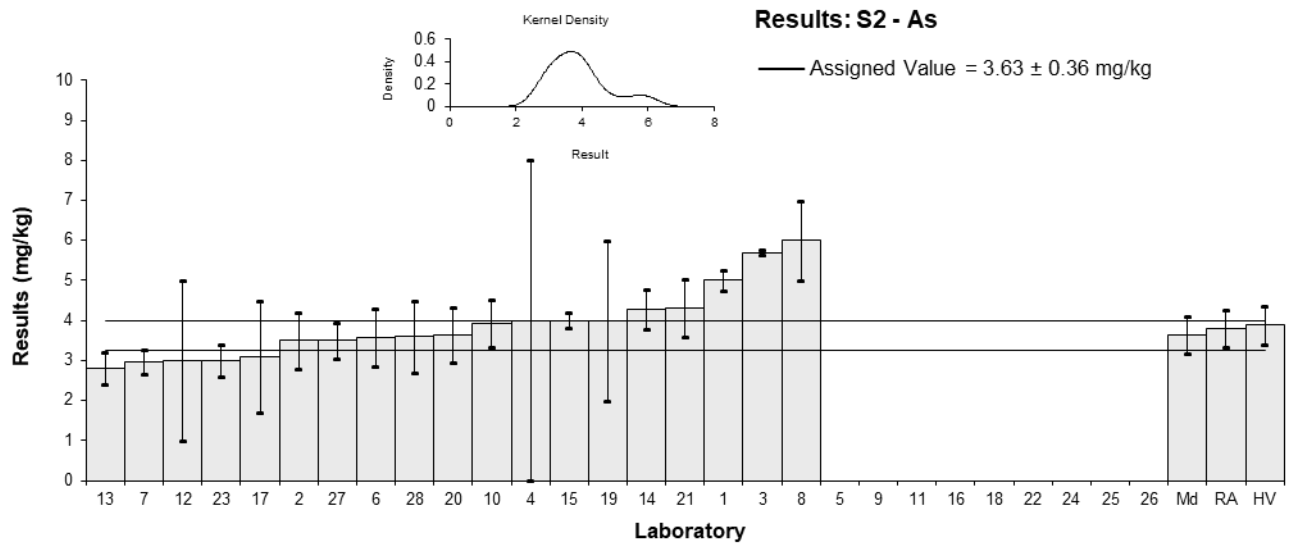


Figure 17

Table 26

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	B
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	5.2	NR
2	NR	NR
3	15.2	0.184
4	8	4
5	NR	NR
6	5.716	1.1432
7	NR	NR
8	<50	NR
9	NT	NT
10	12.2	1.83
11	NT	NT
12	7	5
13	NR	NR
14	15.3	2.0
15	9.0	5.3
16	NT	NT
17	< 20	3.6
18	NT	NT
19	6	5
20	9.74	1
21	< 10	NR
22	<50	5
23	<5	21.4
24	NT	NT
25	4.6017	1.861
26	<5	NR
27	8.68	1.47
28	19	2.4

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	12.2	1.5
<b>Robust Average</b>	9.5	3.2
<b>Median</b>	8.7	3.0
<b>Mean</b>	9.7	
<b>N</b>	13	
<b>Max</b>	19	
<b>Min</b>	4.6017	
<b>Robust SD</b>	4.6	
<b>Robust CV</b>	49%	

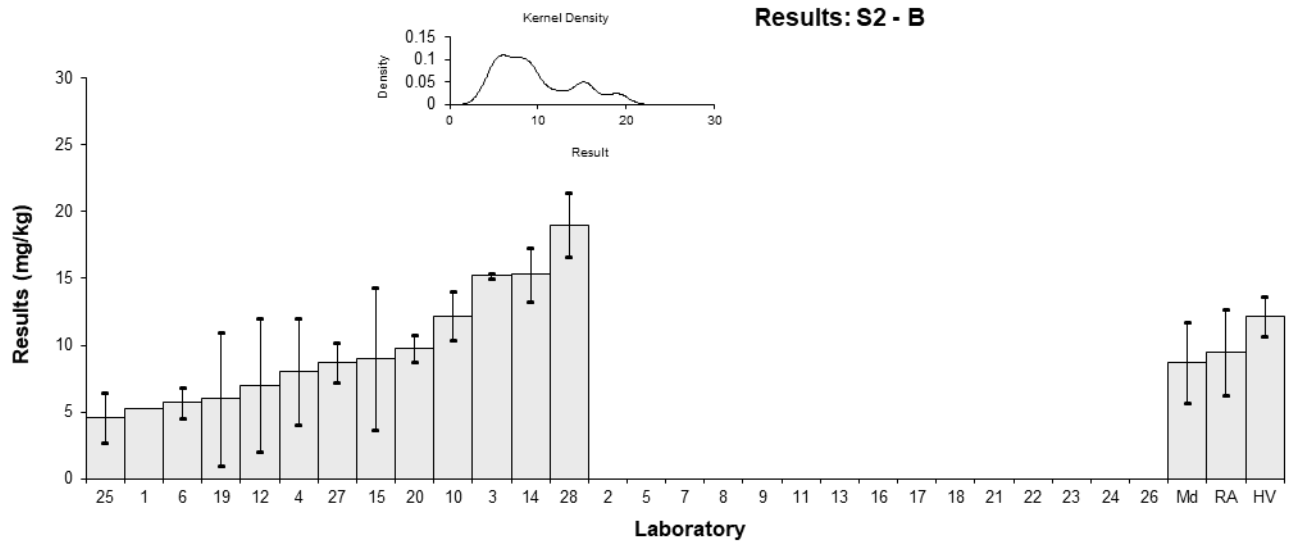


Figure 18

Table 27

**Sample Details**

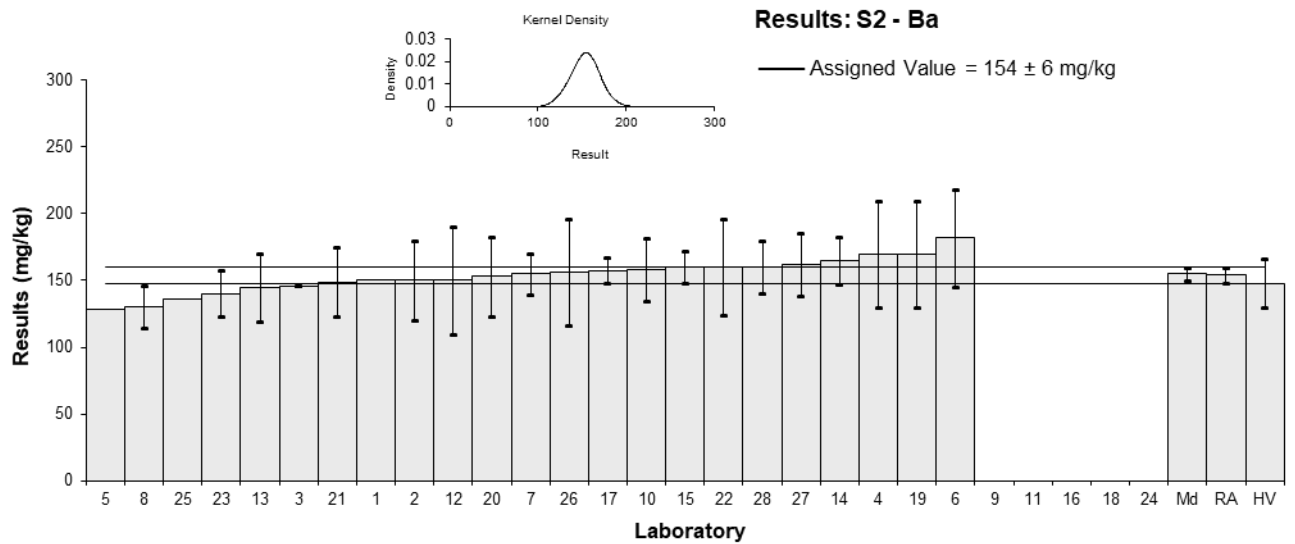
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Ba
<b>Unit</b>	mg/kg

**Participant Results**

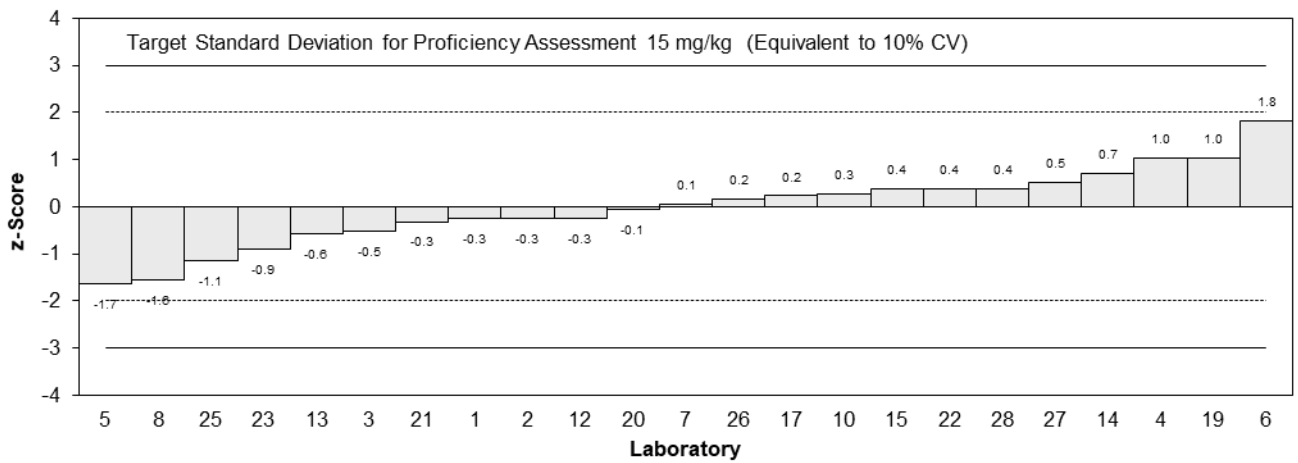
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	150	NR	-0.26	-0.67
2	150	30	-0.26	-0.13
3	146	0.021	-0.52	-1.33
4	170	40	1.04	0.40
5	128.6	NR	-1.65	-4.23
6	182.0	36.4	1.82	0.76
7	155	15.5	0.06	0.06
8	130	16	-1.56	-1.40
9	NT	NT		
10	158	23.7	0.26	0.16
11	NT	NT		
12	150	40	-0.26	-0.10
13	145	25.6	-0.58	-0.34
14	165	18	0.71	0.58
15	160	12	0.39	0.45
16	NT	NT		
17	157.5	9.5	0.23	0.31
18	NT	NT		
19	170	40	1.04	0.40
20	153	30	-0.06	-0.03
21	149	25.7	-0.32	-0.19
22	160	36	0.39	0.16
23	140	17.22	-0.91	-0.77
24	NT	NT		
25	136.38895	NR	-1.14	-2.94
26	156.5	40	0.16	0.06
27	161.95	23.62	0.52	0.33
28	160	20	0.39	0.29

**Statistics**

<b>Assigned Value</b>	154	6
<b>Homogeneity Value</b>	148	18
<b>Robust Average</b>	154	6
<b>Median</b>	155	5
<b>Mean</b>	154	
<b>N</b>	23	
<b>Max</b>	182	
<b>Min</b>	128.6	
<b>Robust SD</b>	12	
<b>Robust CV</b>	8%	



**z-Scores: S2 - Ba**



**En-Scores: S2 - Ba**

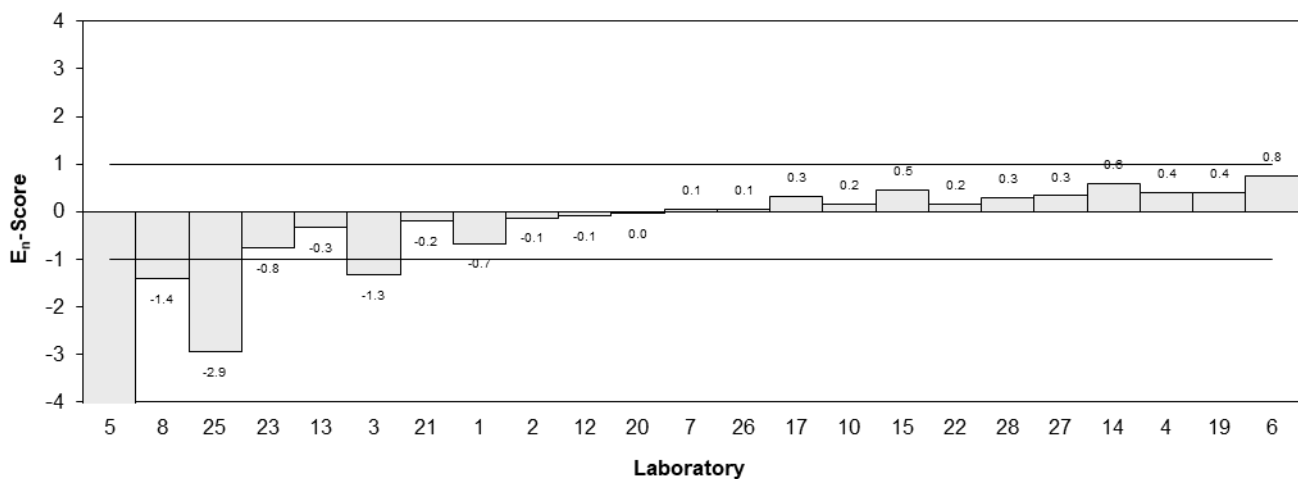


Figure 19



Table 28

## Sample Details

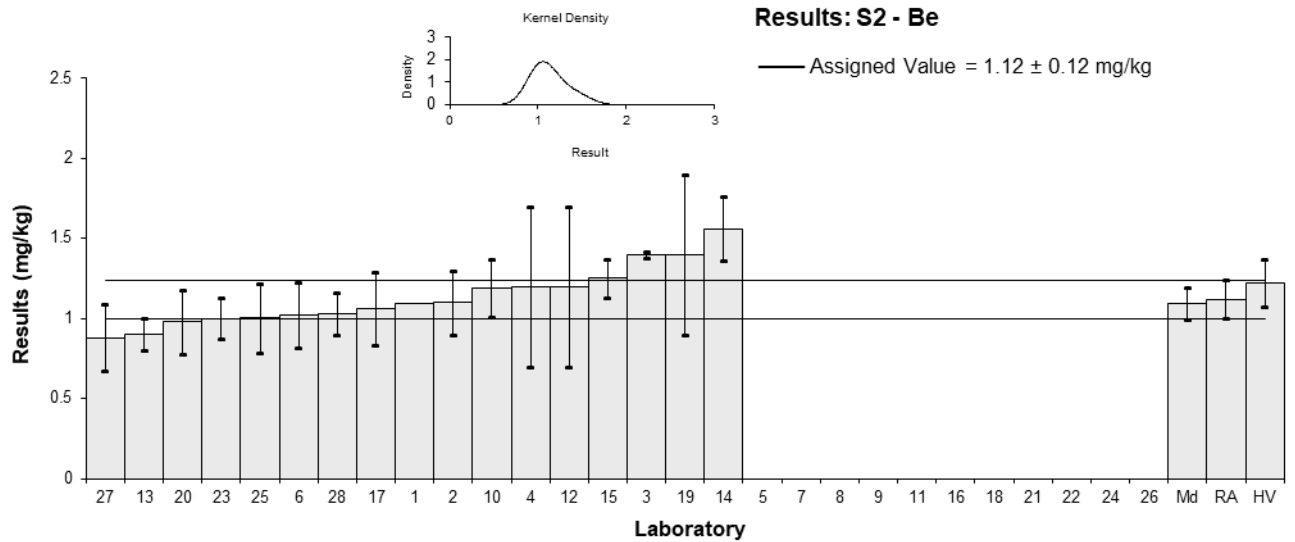
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Be
<b>Unit</b>	mg/kg

## Participant Results

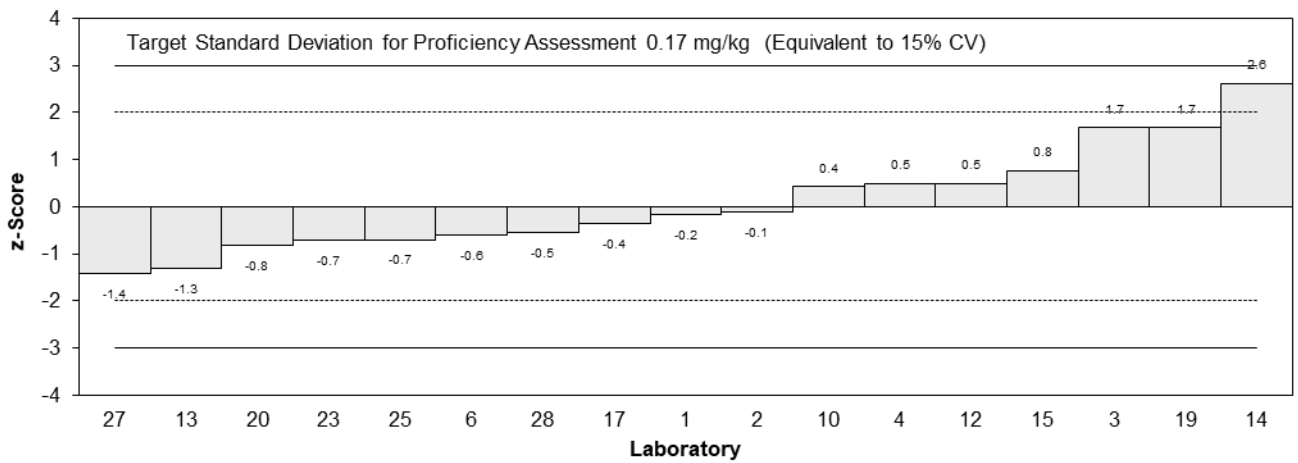
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	1.09	NR	-0.18	-0.25
2	1.1	0.2	-0.12	-0.09
3	1.4	0.022	1.67	2.30
4	1.2	0.5	0.48	0.16
5	NT	NT		
6	1.019	0.2038	-0.60	-0.43
7	NR	NR		
8	<1	NR		
9	NT	NT		
10	1.19	0.179	0.42	0.32
11	NT	NT		
12	1.2	0.5	0.48	0.16
13	0.9	0.1	-1.31	-1.41
14	1.56	0.2	2.62	1.89
15	1.25	0.12	0.77	0.77
16	NT	NT		
17	1.06	0.23	-0.36	-0.23
18	NT	NT		
19	1.4	0.5	1.67	0.54
20	0.98	0.2	-0.83	-0.60
21	< 2	NR		
22	<1	0.2		
23	1	0.13	-0.71	-0.68
24	NT	NT		
25	1.00215	0.214	-0.70	-0.48
26	<1	NR		
27	0.88	0.21	-1.43	-0.99
28	1.03	0.13	-0.54	-0.51

## Statistics

<b>Assigned Value</b>	1.12	0.12
<b>Homogeneity Value</b>	1.22	0.15
<b>Robust Average</b>	1.12	0.12
<b>Median</b>	1.09	0.10
<b>Mean</b>	1.13	
<b>N</b>	17	
<b>Max</b>	1.56	
<b>Min</b>	0.88	
<b>Robust SD</b>	0.19	
<b>Robust CV</b>	17%	



**z-Scores: S2 - Be**



**En-Scores: S2 - Be**

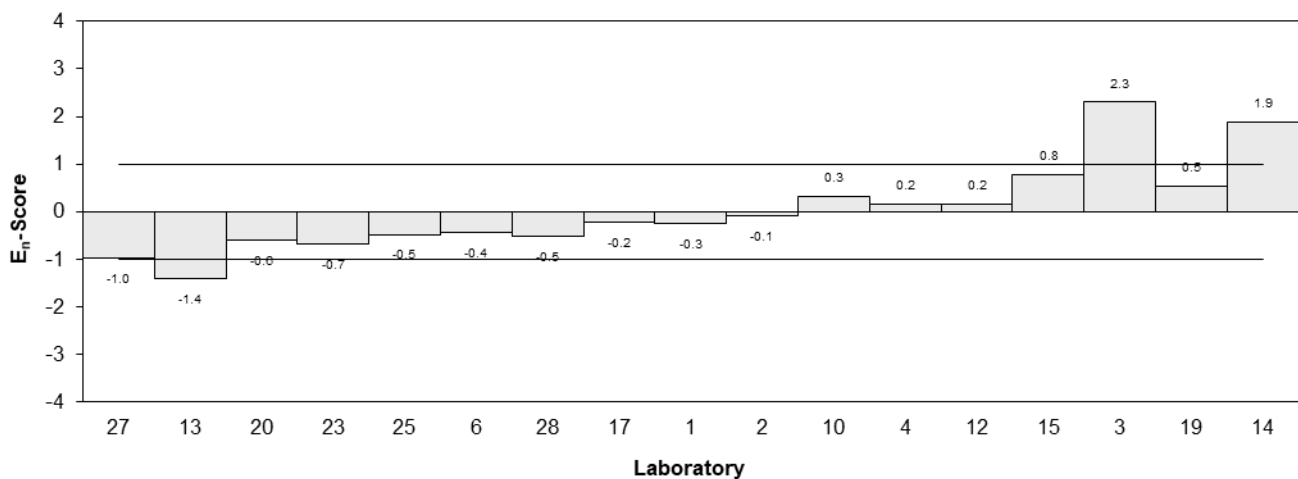


Figure 20

Table 29

## Sample Details

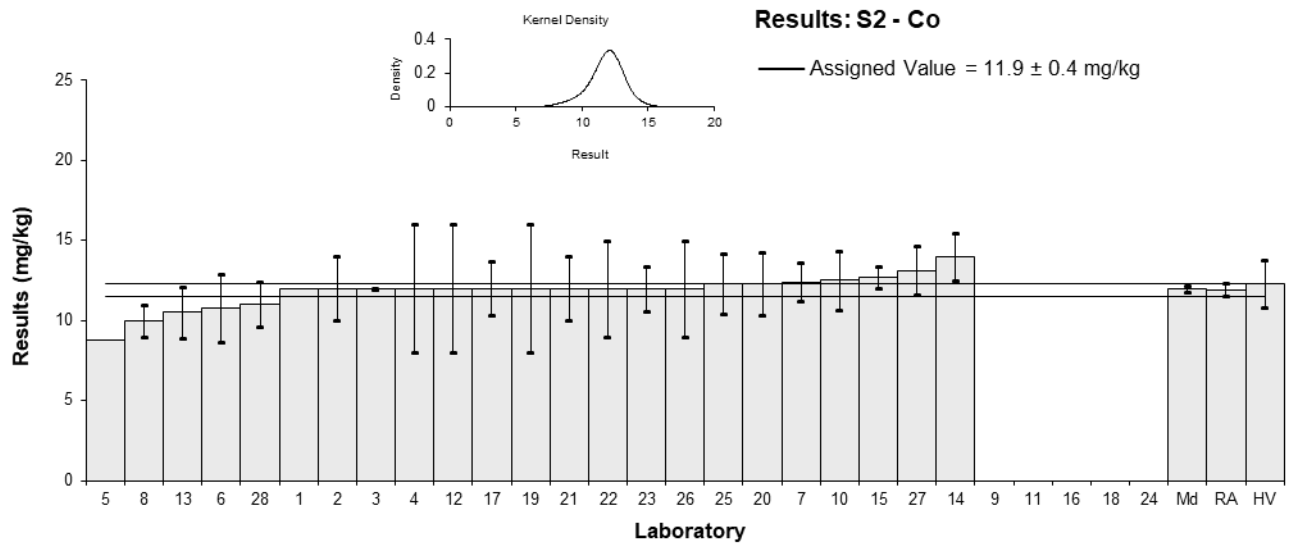
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Co
<b>Unit</b>	mg/kg

## Participant Results

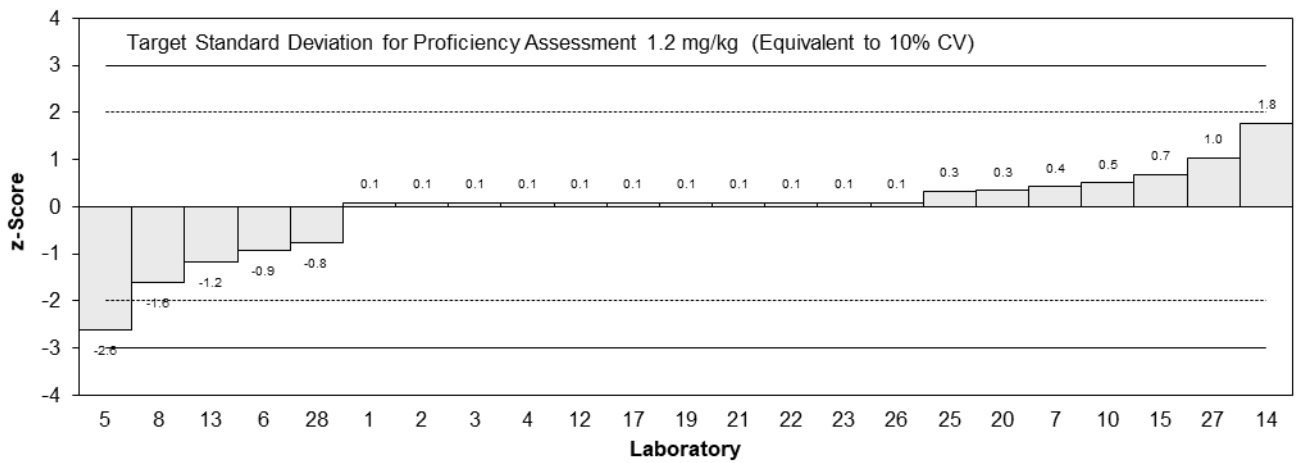
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	12	NR	0.08	0.25
2	12	2	0.08	0.05
3	12.0	0.028	0.08	0.25
4	12	4	0.08	0.02
5	8.8	NR	-2.61	-7.75
6	10.78	2.156	-0.94	-0.51
7	12.4	1.2	0.42	0.40
8	10	1	-1.60	-1.76
9	NT	NT		
10	12.5	1.88	0.50	0.31
11	NT	NT		
12	12	4	0.08	0.02
13	10.5	1.6	-1.18	-0.85
14	14.0	1.5	1.76	1.35
15	12.70	0.70	0.67	0.99
16	NT	NT		
17	12.0	1.7	0.08	0.06
18	NT	NT		
19	12	4	0.08	0.02
20	12.3	2	0.34	0.20
21	12.0	2.0	0.08	0.05
22	12	3	0.08	0.03
23	12	1.416	0.08	0.07
24	NT	NT		
25	12.28975	1.898	0.33	0.20
26	12	3	0.08	0.03
27	13.12	1.51	1.03	0.78
28	11	1.4	-0.76	-0.62

## Statistics

<b>Assigned Value</b>	11.9	0.4
<b>Homogeneity Value</b>	12.3	1.5
<b>Robust Average</b>	11.9	0.4
<b>Median</b>	12.0	0.2
<b>Mean</b>	11.8	
<b>N</b>	23	
<b>Max</b>	14	
<b>Min</b>	8.8	
<b>Robust SD</b>	0.79	
<b>Robust CV</b>	6.6%	



**z-Scores: S2 - Co**



**En-Scores: S2 - Co**

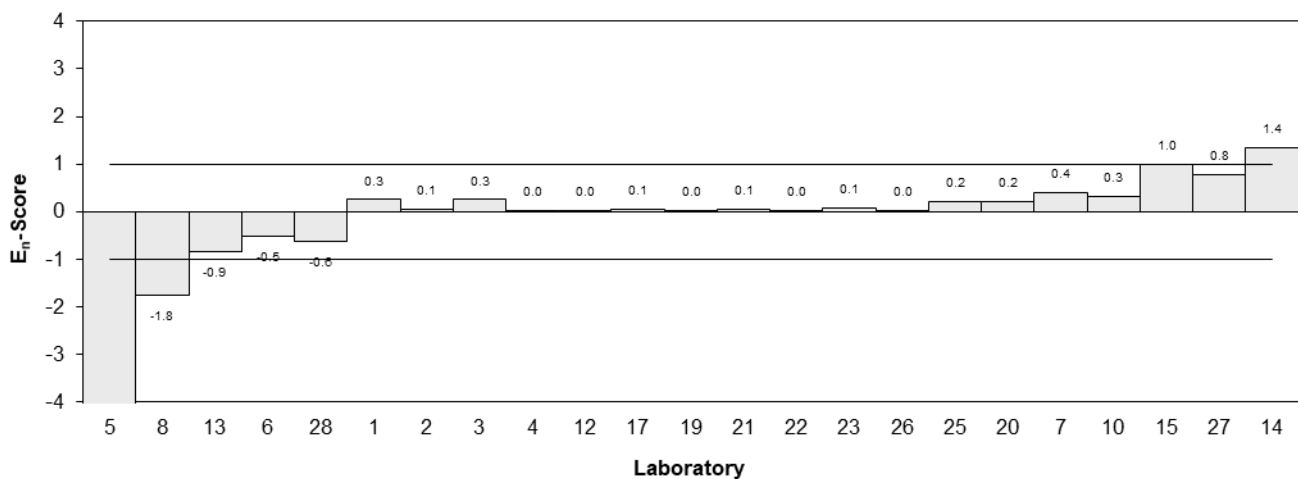


Figure 21

Table 30

## Sample Details

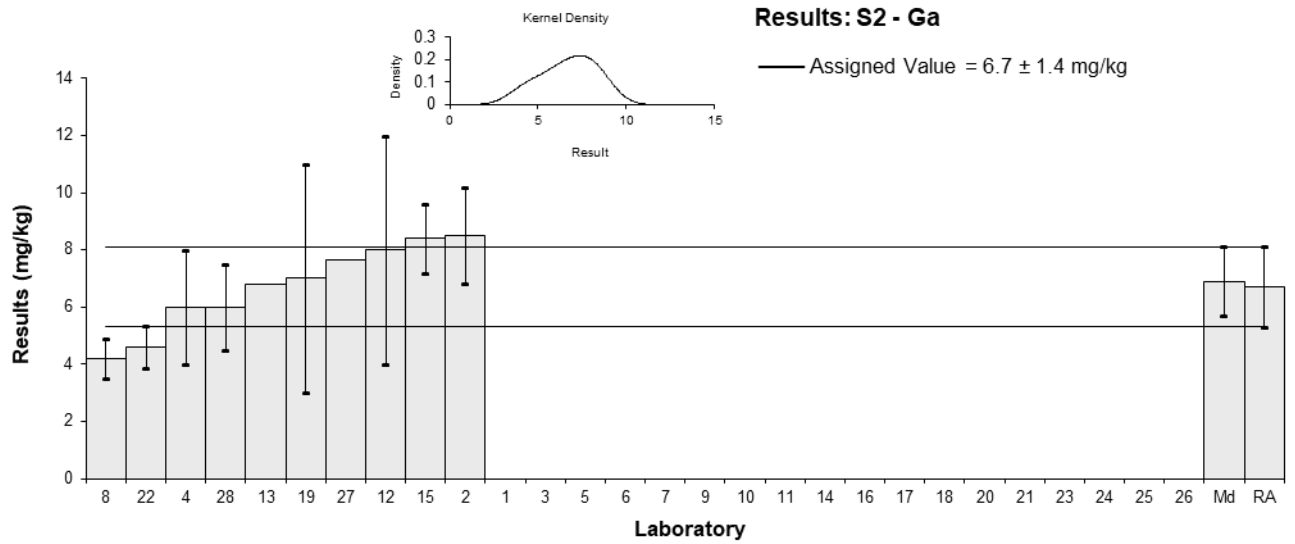
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Ga
<b>Unit</b>	mg/kg

## Participant Results

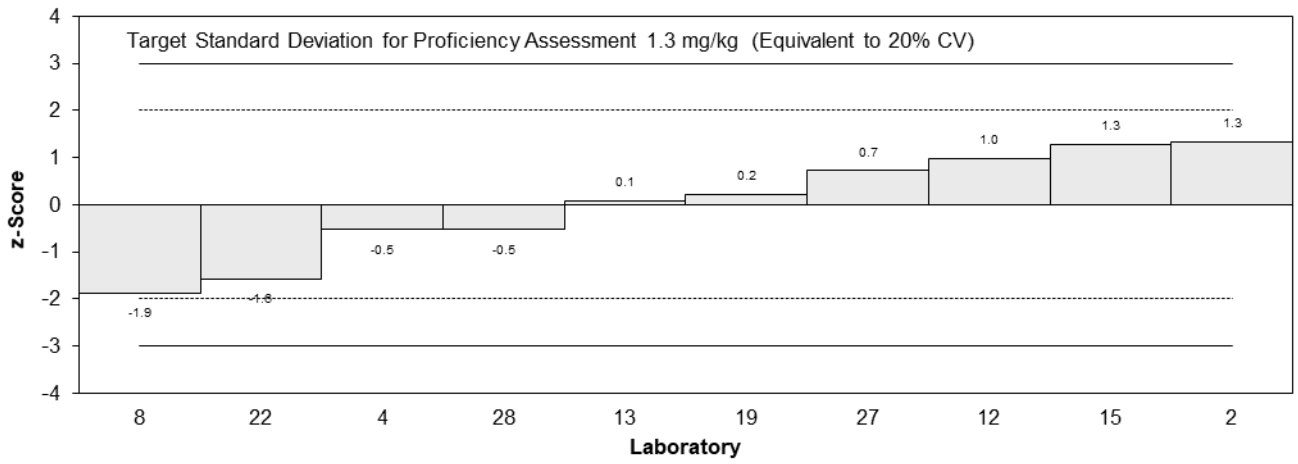
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	8.5	1.7	1.34	0.82
3	NT	NT		
4	6	2	-0.52	-0.29
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	4.2	0.7	-1.87	-1.60
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	8	4	0.97	0.31
13	6.8	NR	0.07	0.07
14	NT	NT		
15	8.4	1.2	1.27	0.92
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	7	4	0.22	0.07
20	NT	NT		
21	NT	NT		
22	4.6	0.72	-1.57	-1.33
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	NT	NT		
27	7.66	NR	0.72	0.69
28	6	1.5	-0.52	-0.34

## Statistics

<b>Assigned Value</b>	6.7	1.4
<b>Robust Average</b>	6.7	1.4
<b>Median</b>	6.9	1.2
<b>Mean</b>	6.72	
<b>N</b>	10	
<b>Max</b>	8.5	
<b>Min</b>	4.2	
<b>Robust SD</b>	1.7	
<b>Robust CV</b>	25%	



**z-Scores: S2 - Ga**



**En-Scores: S2 - Ga**

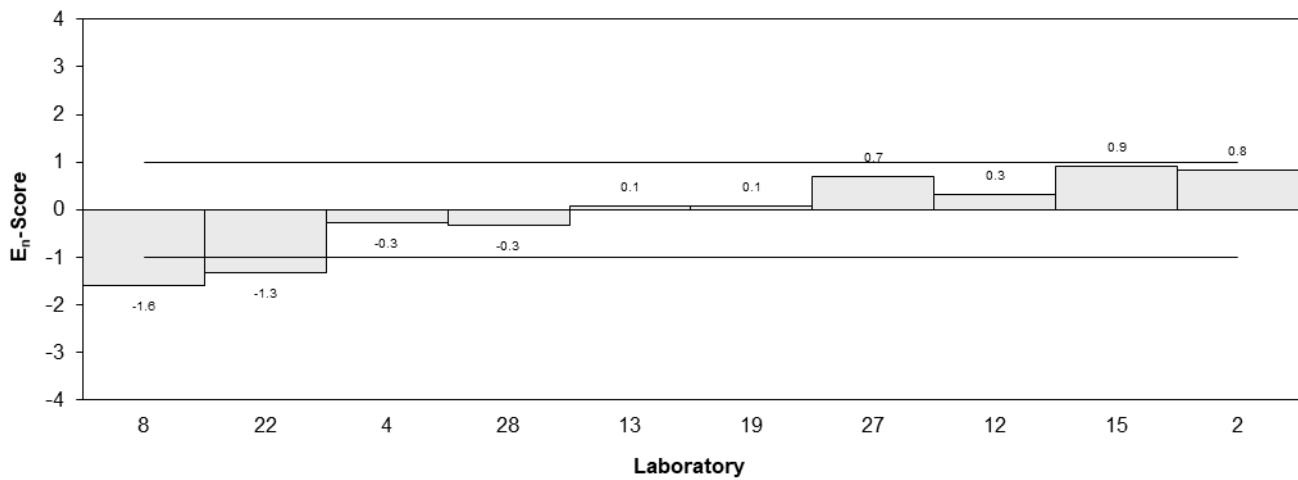


Figure 22

Table 31

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Li
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NT	NT
2	11	2.2
3	16.7	0.07
4	9	3
5	12.7	NR
6	7.313	1.4626
7	6.70	0.67
8	4.4	1.0
9	NT	NT
10	13.0	1.95
11	NT	NT
12	8	4
13	8.0	NR
14	12.7	1.5
15	14.0	1.7
16	18	1
17	9.4	1.2
18	NT	NT
19	11	4
20	12	2
21	7.13	1.47
22	5.9	0.91
23	NT	NT
24	NT	NT
25	NT	NT
26	12	5
27	7.56	1.81
28	13	1.6

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	11.5	1.4
<b>Robust Average</b>	10.3	2.0
<b>Median</b>	11.0	2.4
<b>Mean</b>	10.5	
<b>N</b>	21	
<b>Max</b>	18	
<b>Min</b>	4.4	
<b>Robust SD</b>	3.7	
<b>Robust CV</b>	36%	

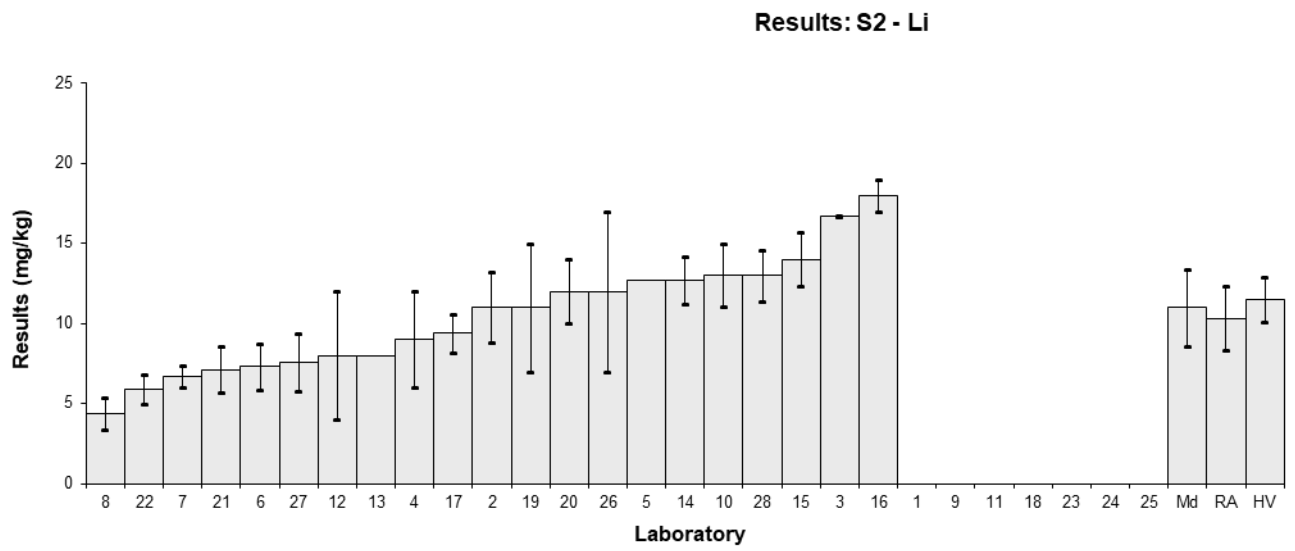


Figure 23



Table 32

## Sample Details

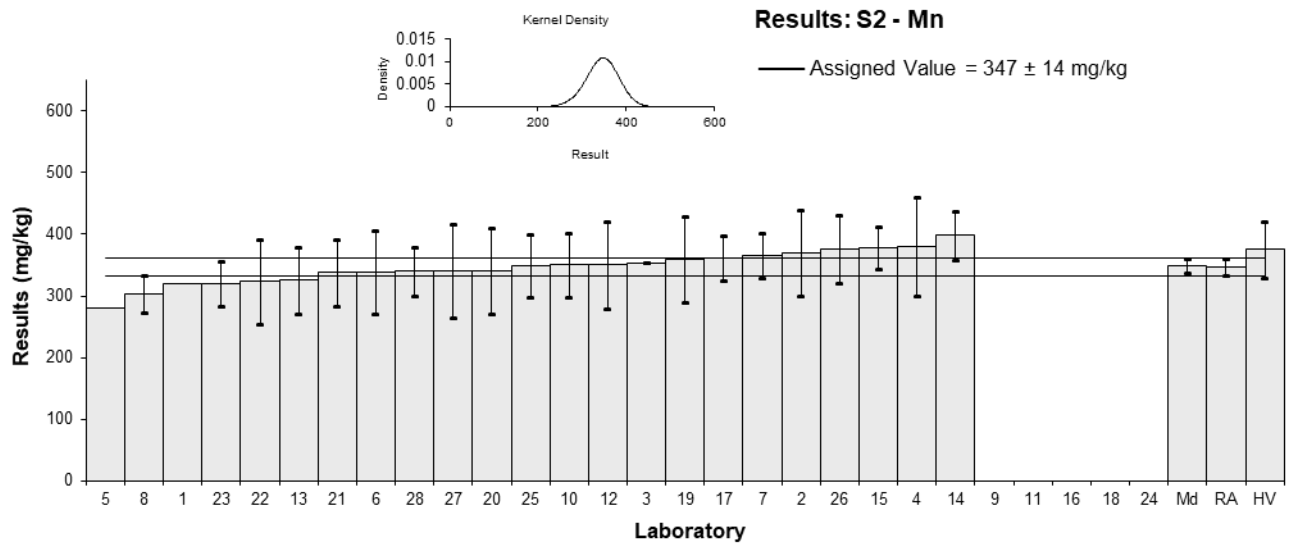
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Mn
<b>Unit</b>	mg/kg

## Participant Results

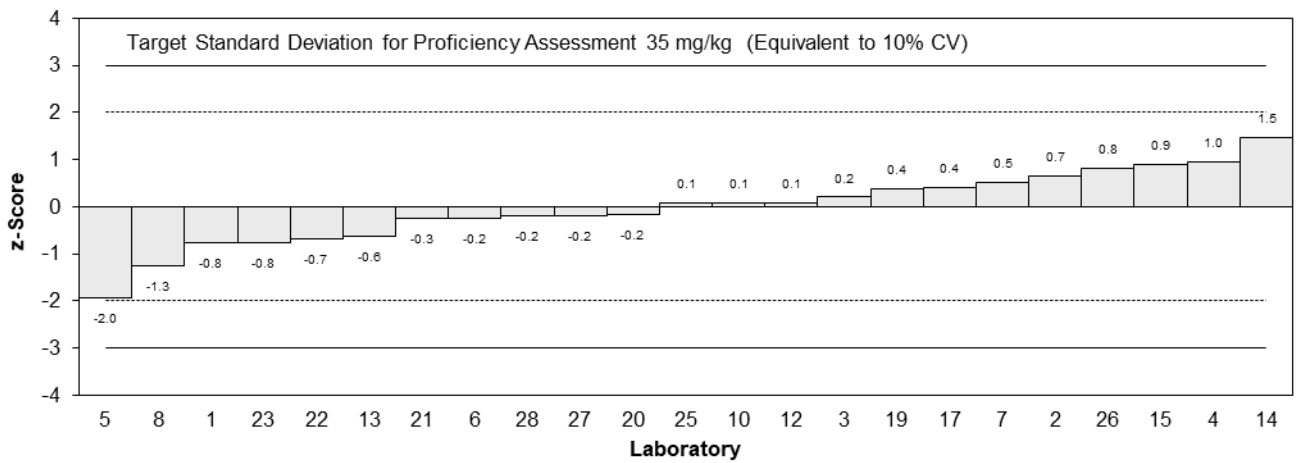
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	320	NR	-0.78	-1.93
2	370	70	0.66	0.32
3	354	0.004	0.20	0.50
4	380	80	0.95	0.41
5	279.4	NR	-1.95	-4.83
6	338.5	67.7	-0.24	-0.12
7	365	36.5	0.52	0.46
8	303	31	-1.27	-1.29
9	NT	NT		
10	350	52.5	0.09	0.06
11	NT	NT		
12	350	70	0.09	0.04
13	325	54	-0.63	-0.39
14	398	40	1.47	1.20
15	378	34	0.89	0.84
16	NT	NT		
17	361	37	0.40	0.35
18	NT	NT		
19	360	70	0.37	0.18
20	341	70	-0.17	-0.08
21	338	54	-0.26	-0.16
22	323	69	-0.69	-0.34
23	320	35.84	-0.78	-0.70
24	NT	NT		
25	349.40065	51.16	0.07	0.05
26	375.5	55	0.82	0.50
27	340.11	75.54	-0.20	-0.09
28	340	40	-0.20	-0.17

## Statistics

<b>Assigned Value</b>	347	14
<b>Homogeneity Value</b>	375	45
<b>Robust Average</b>	347	14
<b>Median</b>	349	12
<b>Mean</b>	346	
<b>N</b>	23	
<b>Max</b>	398	
<b>Min</b>	279.4	
<b>Robust SD</b>	26	
<b>Robust CV</b>	7.5%	



**z-Scores: S2 - Mn**



**En-Scores: S2 - Mn**

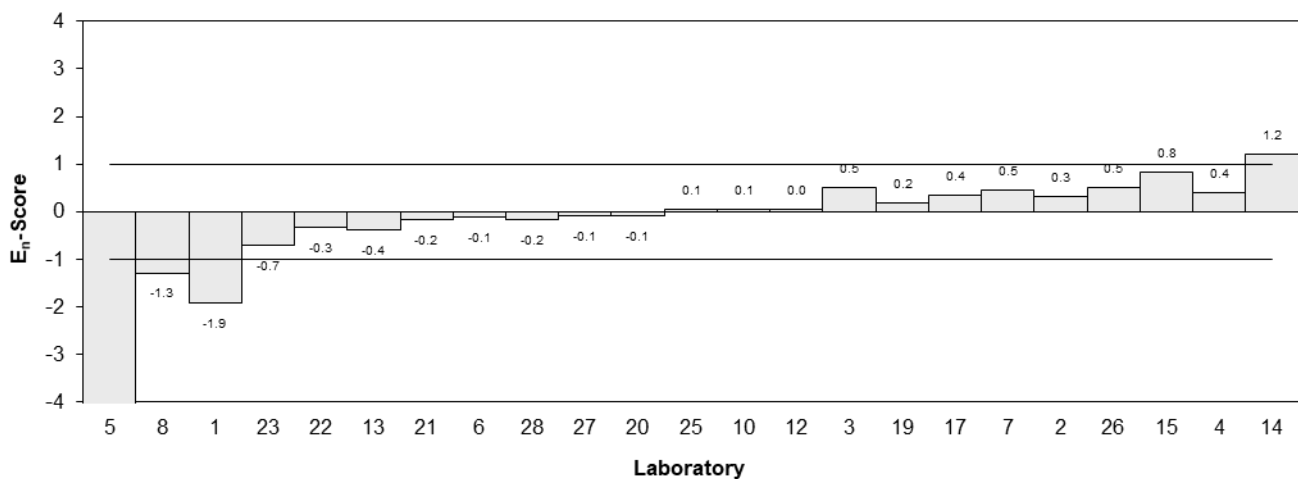


Figure 24

Table 33

## Sample Details

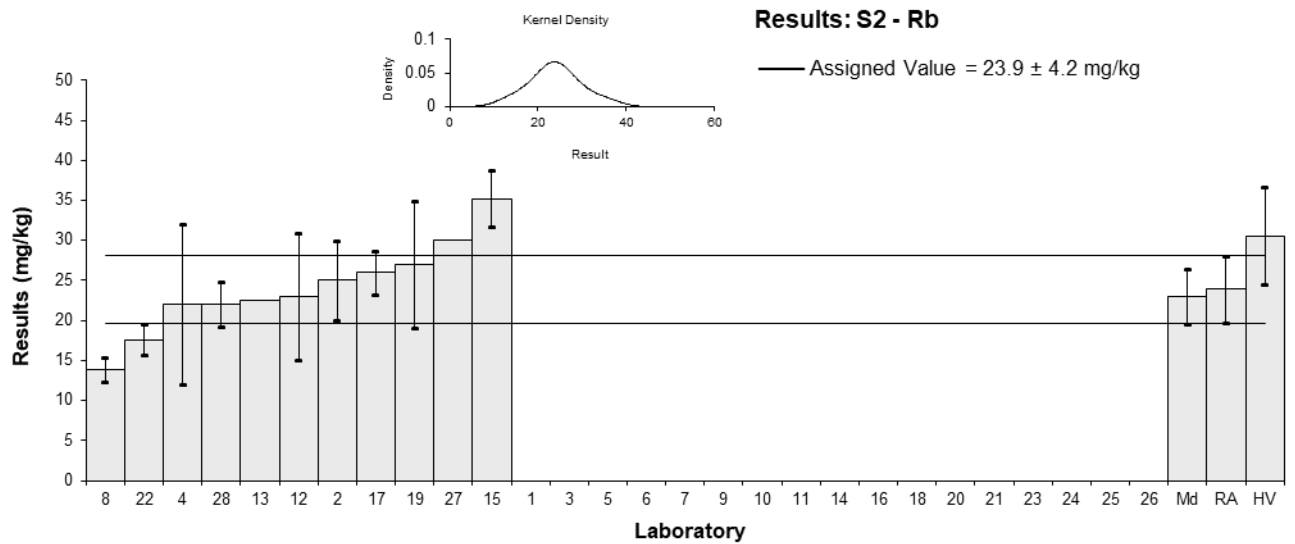
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Rb
<b>Unit</b>	mg/kg

## Participant Results

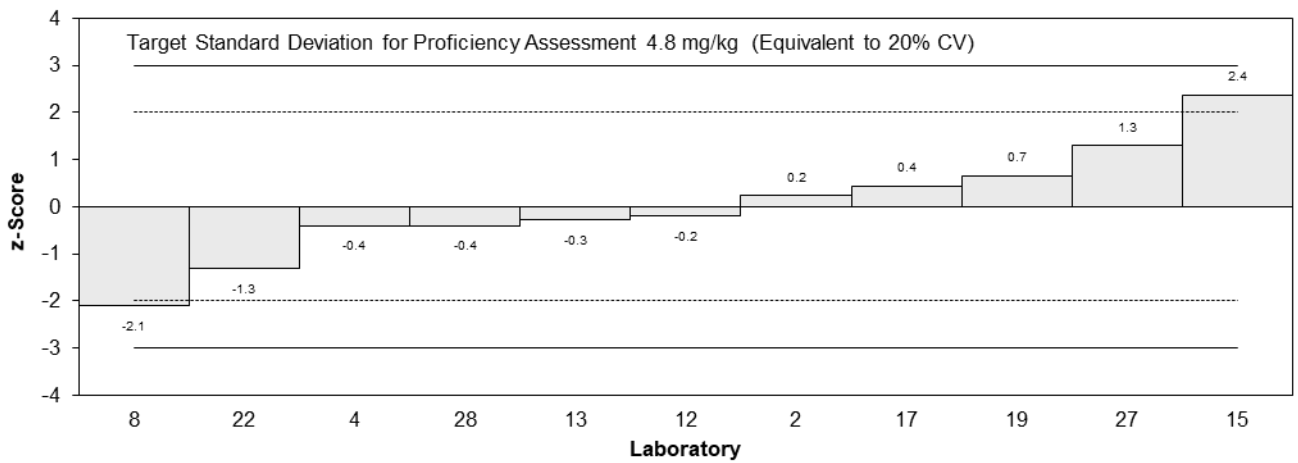
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	25	5	0.23	0.17
3	NT	NT		
4	22	10	-0.40	-0.18
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	13.9	1.5	-2.09	-2.24
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	23	8	-0.19	-0.10
13	22.5	NR	-0.29	-0.33
14	NT	NT		
15	35.2	3.5	2.36	2.07
16	NT	NT		
17	26.0	2.7	0.44	0.42
18	NT	NT		
19	27	8	0.65	0.34
20	NT	NT		
21	NT	NT		
22	17.6	1.89	-1.32	-1.37
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	NT	NT		
27	30.09	NR	1.29	1.47
28	22	2.8	-0.40	-0.38

## Statistics

<b>Assigned Value</b>	23.9	4.2
<b>Homogeneity Value</b>	30.6	6.1
<b>Robust Average</b>	23.9	4.2
<b>Median</b>	23.0	3.4
<b>Mean</b>	24.0	
<b>N</b>	11	
<b>Max</b>	35.2	
<b>Min</b>	13.9	
<b>Robust SD</b>	5.6	
<b>Robust CV</b>	23%	



**z-Scores: S2 - Rb**



**En-Scores: S2 - Rb**

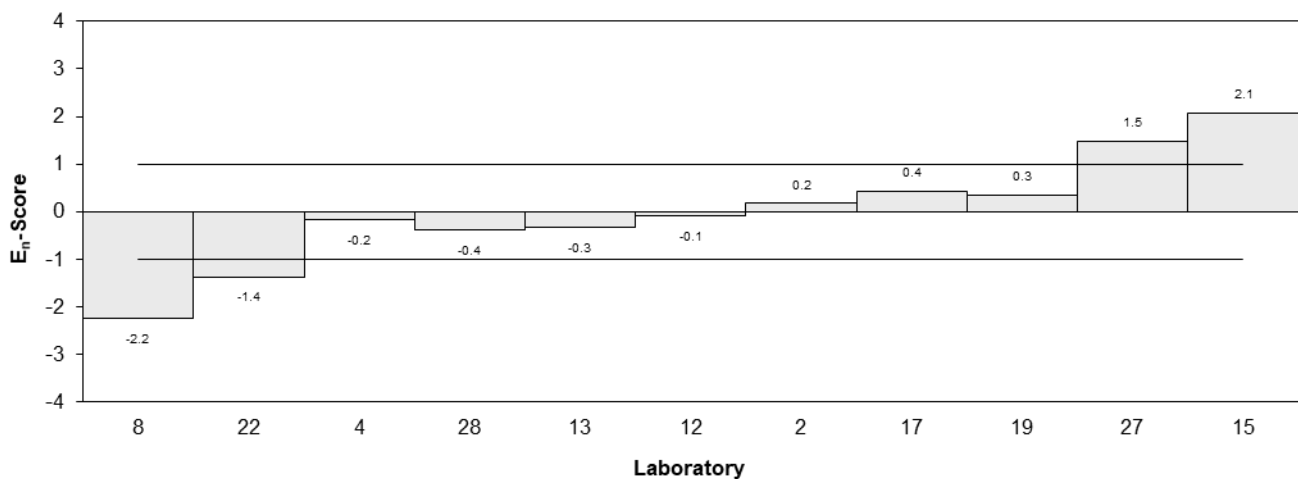


Figure 25

Table 34

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Sn
<b>Unit</b>	mg/kg

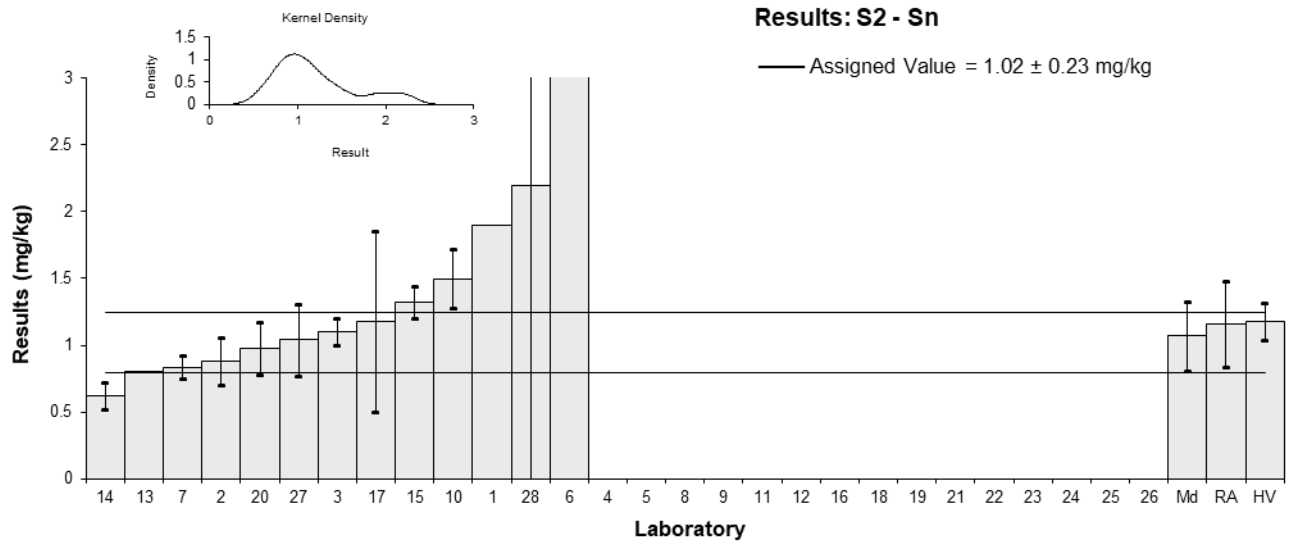
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1*	1.9	NR	4.31	3.83
2	0.88	0.18	-0.69	-0.48
3	1.1	0.100	0.39	0.32
4	<1	NR		
5	NT	NT		
6**	36.06	7.212	171.76	4.86
7	0.836	0.084	-0.90	-0.75
8	<5	NR		
9	NT	NT		
10	1.50	0.225	2.35	1.49
11	NT	NT		
12	<1	NR		
13	0.8	NR	-1.08	-0.96
14	0.62	0.1	-1.96	-1.59
15	1.32	0.12	1.47	1.16
16	NT	NT		
17	1.18	0.68	0.78	0.22
18	NT	NT		
19	<1	NR		
20	0.978	0.2	-0.21	-0.14
21	< 10	NR		
22	<5	1		
23	<3	17.3		
24	NT	NT		
25	<5	NR		
26	<50	NR		
27	1.04	0.27	0.10	0.06
28*	2.2	3	5.78	0.39

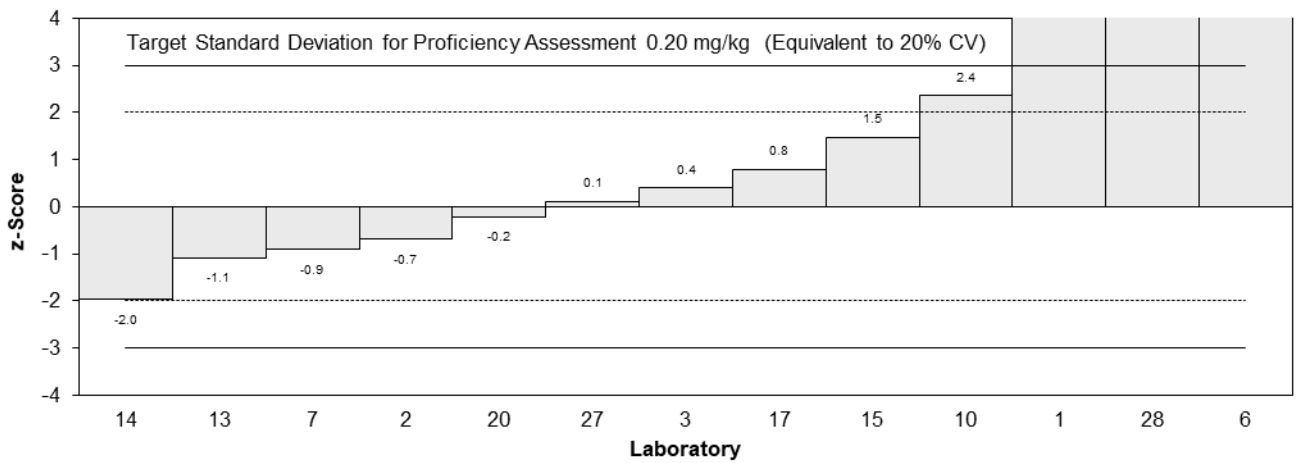
\* Outlier, \*\* Gross Error

**Statistics**

<b>Assigned Value</b>	1.02	0.23
<b>Homogeneity Value</b>	1.18	0.14
<b>Robust Average</b>	1.16	0.32
<b>Median</b>	1.07	0.26
<b>Mean</b>	1.20	
<b>N</b>	12	
<b>Max</b>	2.2	
<b>Min</b>	0.62	
<b>Robust SD</b>	0.44	
<b>Robust CV</b>	38%	



**z-Scores: S2 - Sn**



**En-Scores: S2 - Sn**

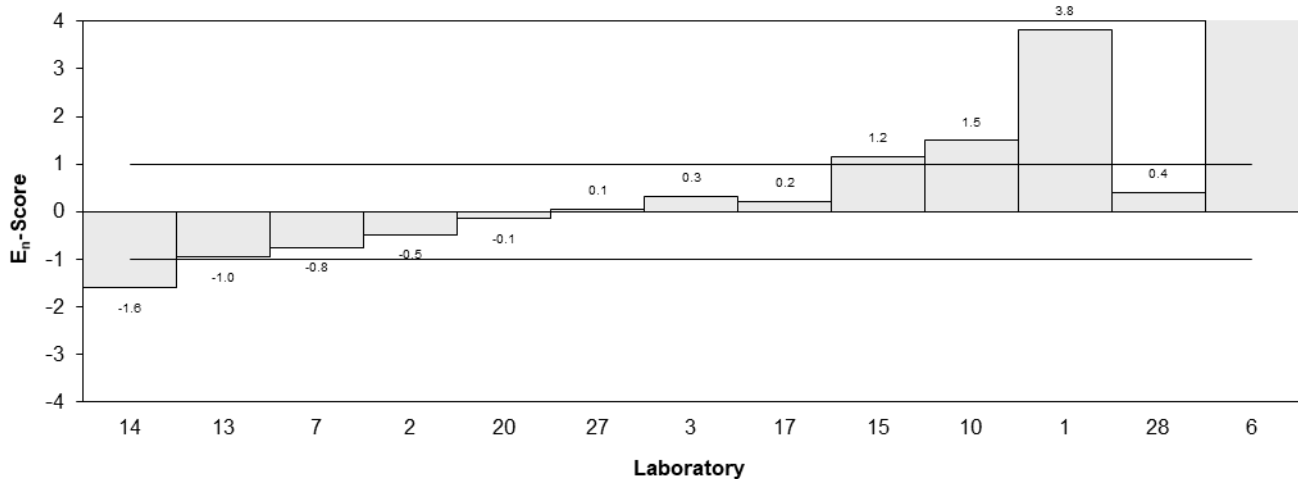


Figure 26

Table 35

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Th
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z</b>	<b>E<sub>n</sub></b>
1	NT	NT		
2	7.3	1.5	0.07	0.05
3	9.0	0.025	1.25	1.64
4	7	3	-0.14	-0.06
5	NT	NT		
6	7.922	1.5844	0.50	0.37
7	NT	NT		
8	5.3	1.3	-1.32	-1.12
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	7	3	-0.14	-0.06
13	6.17	NR	-0.72	-0.94
14	5.67	0.8	-1.06	-1.12
15	7.93	0.49	0.51	0.61
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	4	3	-2.22	-1.00
20	9.1	2	1.32	0.83
21	NT	NT		
22	8.4	0.86	0.83	0.86
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	NT	NT		
27	6.63	1.20	-0.40	-0.35
28	9.3	1.2	1.46	1.29

**Statistics**

<b>Assigned Value</b>	7.2	1.1
<b>Homogeneity Value</b>	7.82	0.94
<b>Robust Average</b>	7.2	1.1
<b>Median</b>	7.15	1.1
<b>Mean</b>	7.19	
<b>N</b>	14	
<b>Max</b>	9.3	
<b>Min</b>	4	
<b>Robust SD</b>	1.7	
<b>Robust CV</b>	23%	

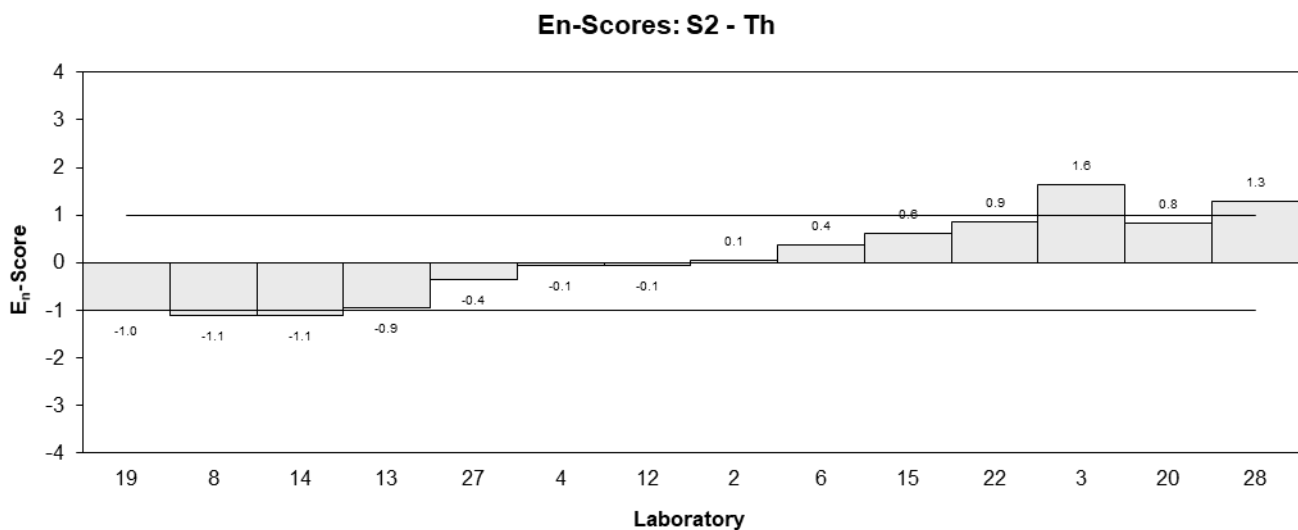
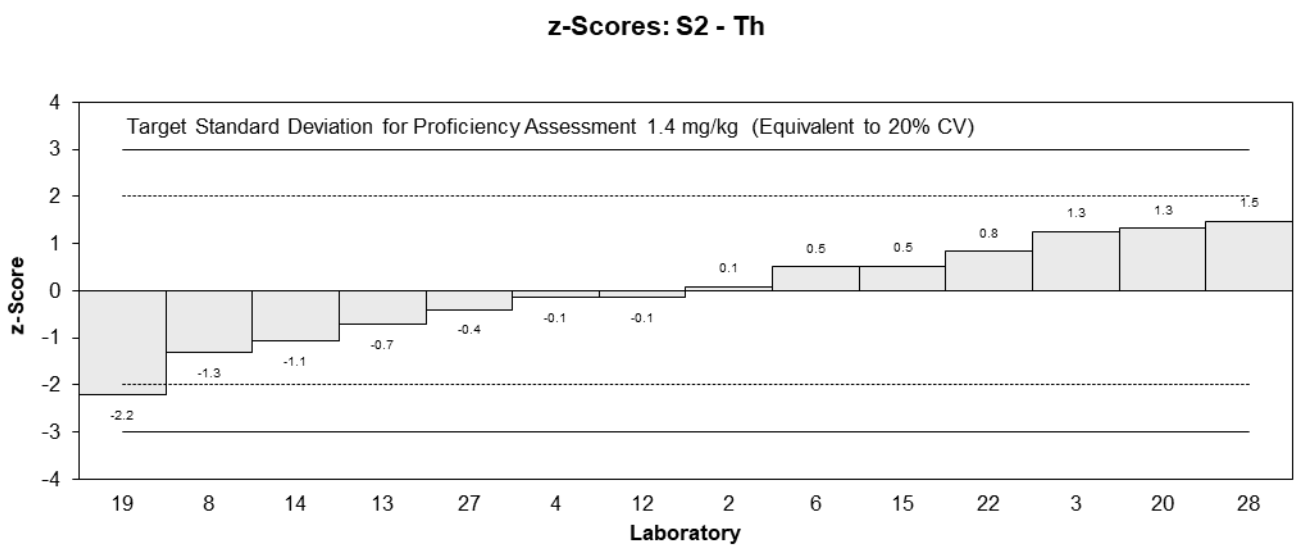
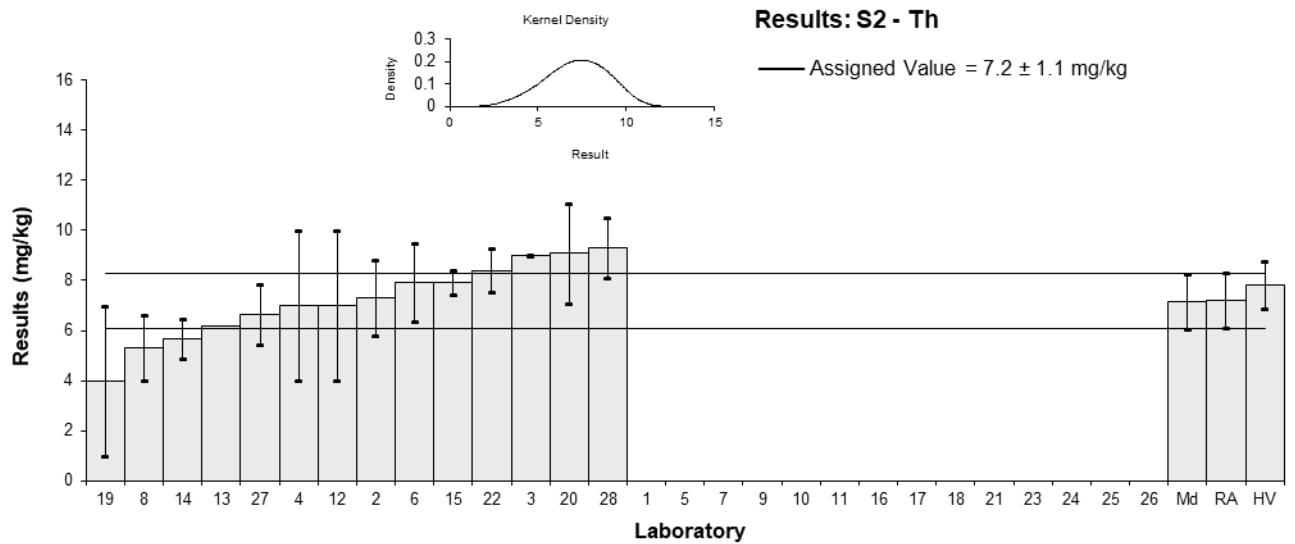


Figure 27



Table 36

**Sample Details**

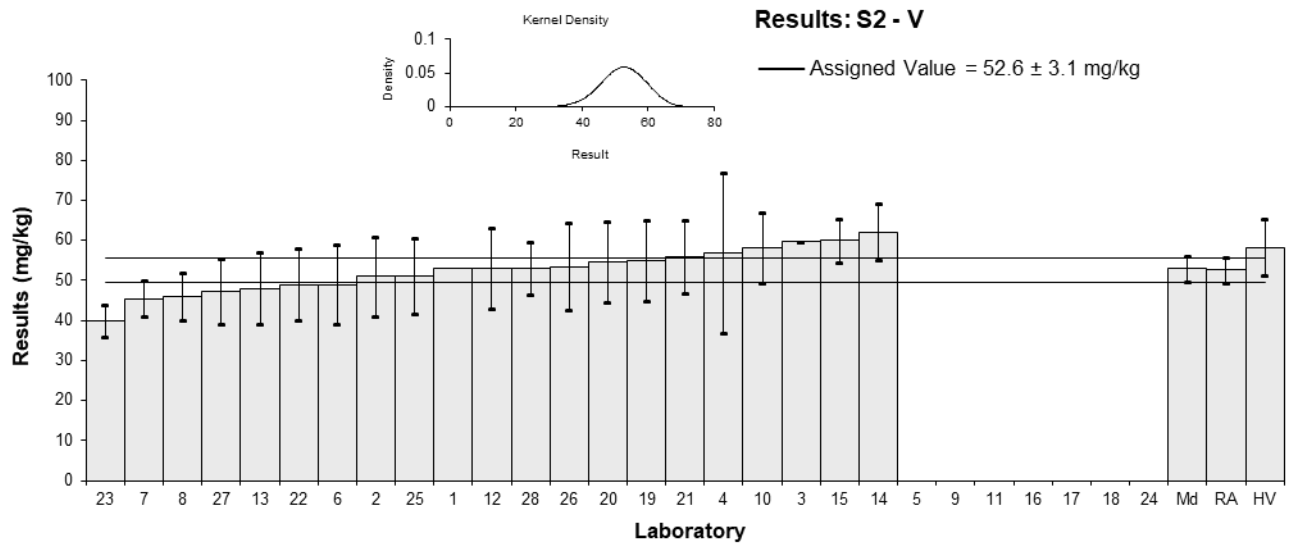
<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	V
<b>Unit</b>	mg/kg

**Participant Results**

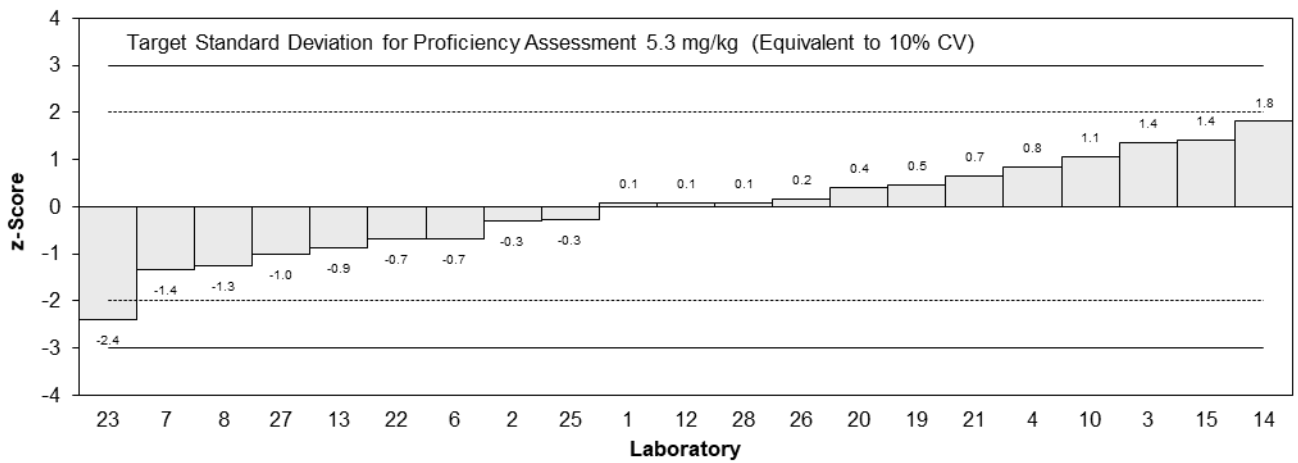
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	53	NR	0.08	0.13
2	51	10	-0.30	-0.15
3	59.7	0.044	1.35	2.29
4	57	20	0.84	0.22
5	NT	NT		
6	49.03	9.806	-0.68	-0.35
7	45.5	4.6	-1.35	-1.28
8	46	6	-1.25	-0.98
9	NT	NT		
10	58.1	8.72	1.05	0.59
11	NT	NT		
12	53	10	0.08	0.04
13	48	8.9	-0.87	-0.49
14	62.1	7.0	1.81	1.24
15	60.0	5.4	1.41	1.19
16	NT	NT		
17	< 100	67		
18	NT	NT		
19	55	10	0.46	0.23
20	54.7	10	0.40	0.20
21	56.0	9.1	0.65	0.35
22	49	9	-0.68	-0.38
23	40	4	-2.40	-2.49
24	NT	NT		
25	51.11685	9.543	-0.28	-0.15
26	53.5	11	0.17	0.08
27	47.23	8.16	-1.02	-0.62
28	53	6.6	0.08	0.05

**Statistics**

<b>Assigned Value</b>	52.6	3.1
<b>Homogeneity Value</b>	58.3	7.0
<b>Robust Average</b>	52.6	3.1
<b>Median</b>	53.0	3.2
<b>Mean</b>	52.5	
<b>N</b>	21	
<b>Max</b>	62.1	
<b>Min</b>	40	
<b>Robust SD</b>	5.6	
<b>Robust CV</b>	11%	



**z-Scores: S2 - V**



**En-Scores: S2 - V**

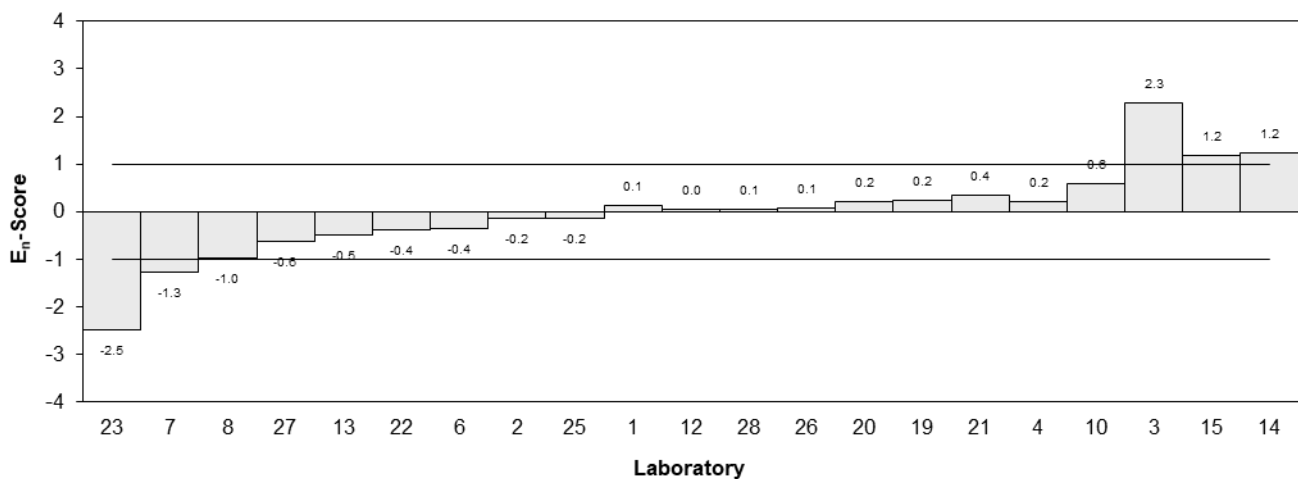


Figure 28

Table 37

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix</b>	Clay
<b>Analyte</b>	Zn
<b>Unit</b>	mg/kg

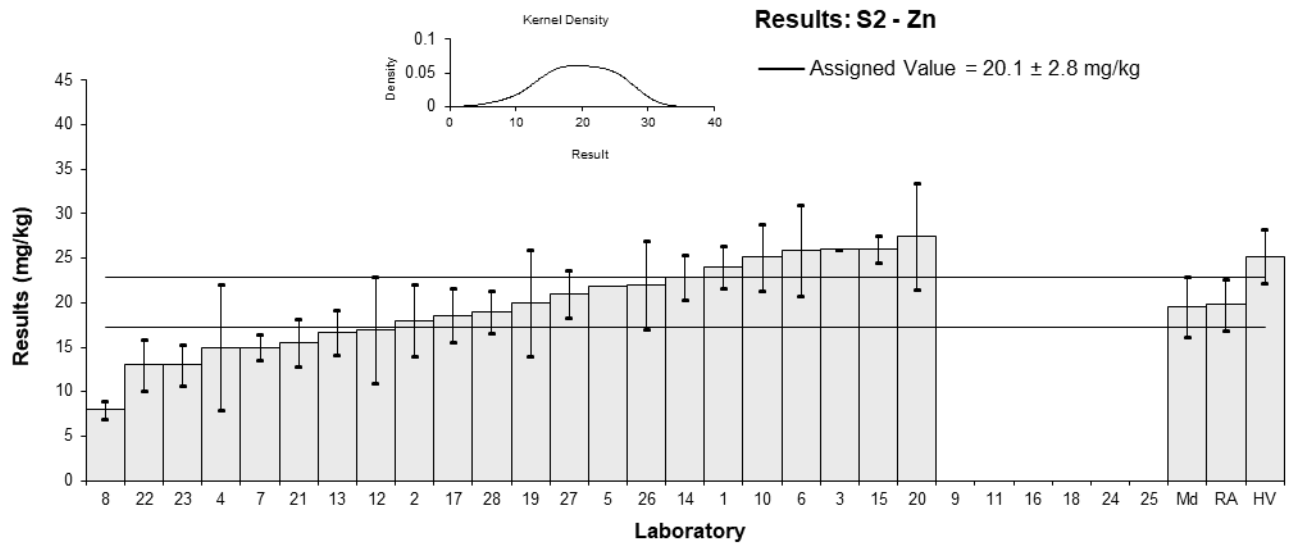
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	24	2.4	0.97	1.06
2	18	4	-0.52	-0.43
3	26.0	0.031	1.47	2.11
4	15	7	-1.27	-0.68
5	21.8	NR	0.42	0.61
6	25.89	5.178	1.44	0.98
7	15.0	1.5	-1.27	-1.61
8*	8	1	-3.01	-4.07
9	NT	NT		
10	25.1	3.77	1.24	1.06
11	NT	NT		
12	17	6	-0.77	-0.47
13	16.7	2.5	-0.85	-0.91
14	22.9	2.5	0.70	0.75
15	26.0	1.5	1.47	1.86
16	NT	NT		
17	18.6	3.0	-0.37	-0.37
18	NT	NT		
19	20	6	-0.02	-0.02
20	27.5	6	1.84	1.12
21	15.5	2.7	-1.14	-1.18
22	13	2.9	-1.77	-1.76
23	13	2.34	-1.77	-1.95
24	NT	NT		
25	NT	NT		
26	22	5	0.47	0.33
27	20.97	2.69	0.22	0.22
28	19	2.4	-0.27	-0.30

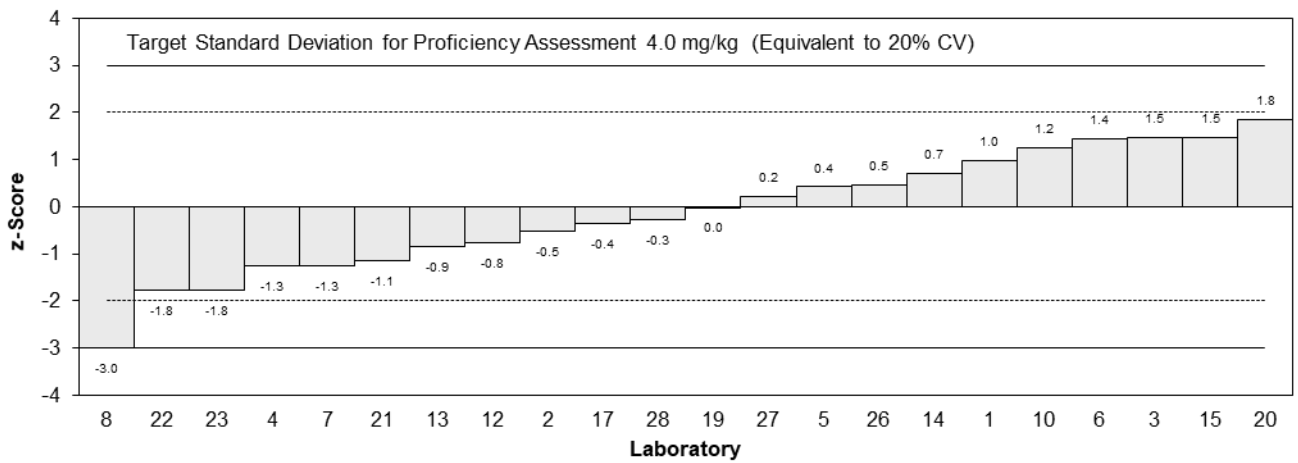
\* Outlier

**Statistics**

<b>Assigned Value</b>	20.1	2.8
<b>Homogeneity Value</b>	25.2	3.0
<b>Robust Average</b>	19.8	2.9
<b>Median</b>	19.5	3.4
<b>Mean</b>	19.6	
<b>N</b>	22	
<b>Max</b>	27.5	
<b>Min</b>	8	
<b>Robust SD</b>	5.5	
<b>Robust CV</b>	28%	



**z-Scores: S2 - Zn**



**En-Scores: S2 - Zn**

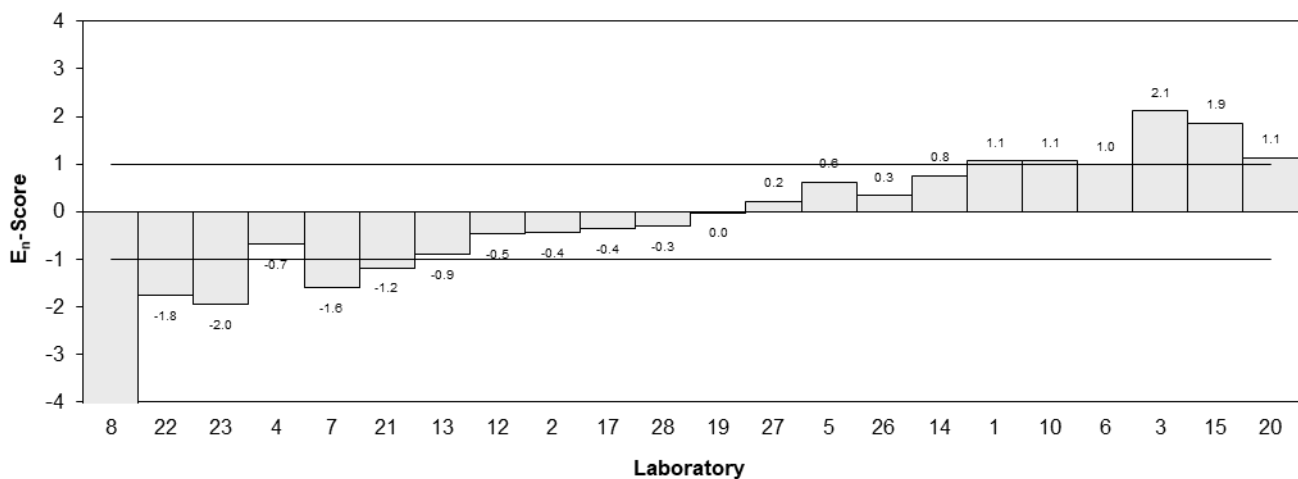


Figure 29

Table 38

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Ammonium-N
<b>Unit</b>	mg/kg

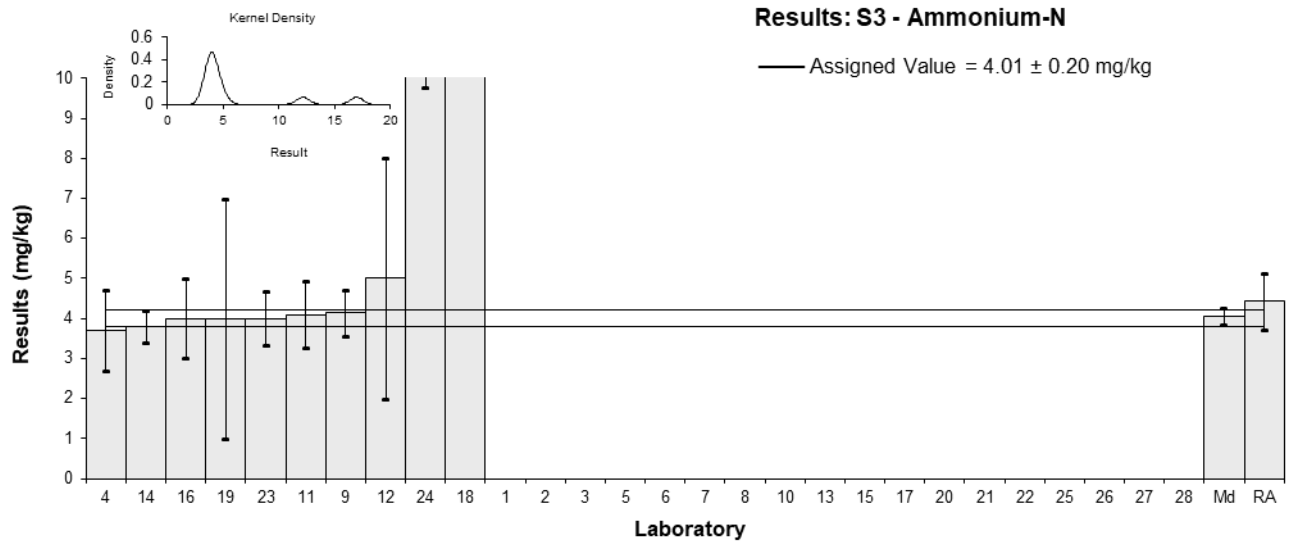
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	<30	5		
3	NT	NT		
4	3.7	1	-0.39	-0.30
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	4.14	0.58	0.16	0.21
10	NT	NT		
11	4.1	0.82	0.11	0.11
12	5	3	1.23	0.33
13	NT	NT		
14	3.8	0.4	-0.26	-0.47
15	NT	NT		
16	4	1	-0.01	-0.01
17	NT	NT		
18*	17	3.4	16.20	3.81
19	4	3	-0.01	0.00
20	NT	NT		
21	< 5	0.5		
22	NR	NR		
23	4	0.668	-0.01	-0.01
24*	12.18	2.4	10.19	3.39
25	NT	NT		
26	<5	NR		
27	NT	NT		
28	NT	NT		

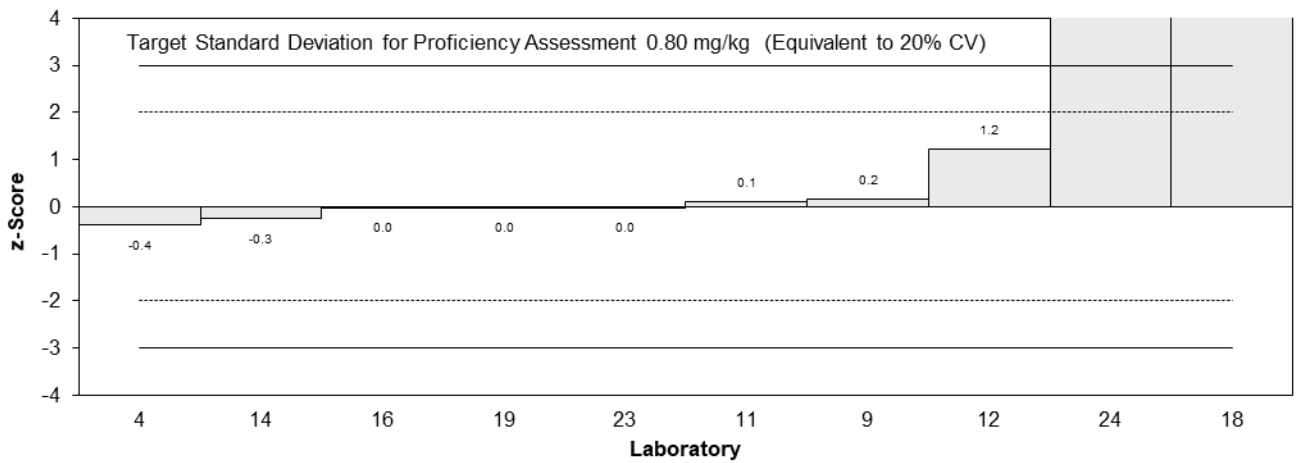
\* Outlier

**Statistics**

<b>Assigned Value</b>	4.01	0.20
<b>Robust Average</b>	4.43	0.70
<b>Median</b>	4.05	0.20
<b>Mean</b>	6.2	
<b>N</b>	10	
<b>Max</b>	17	
<b>Min</b>	3.7	
<b>Robust SD</b>	0.89	
<b>Robust CV</b>	20%	



**z-Scores: S3 - Ammonium-N**



**En-Scores: S3 - Ammonium-N**

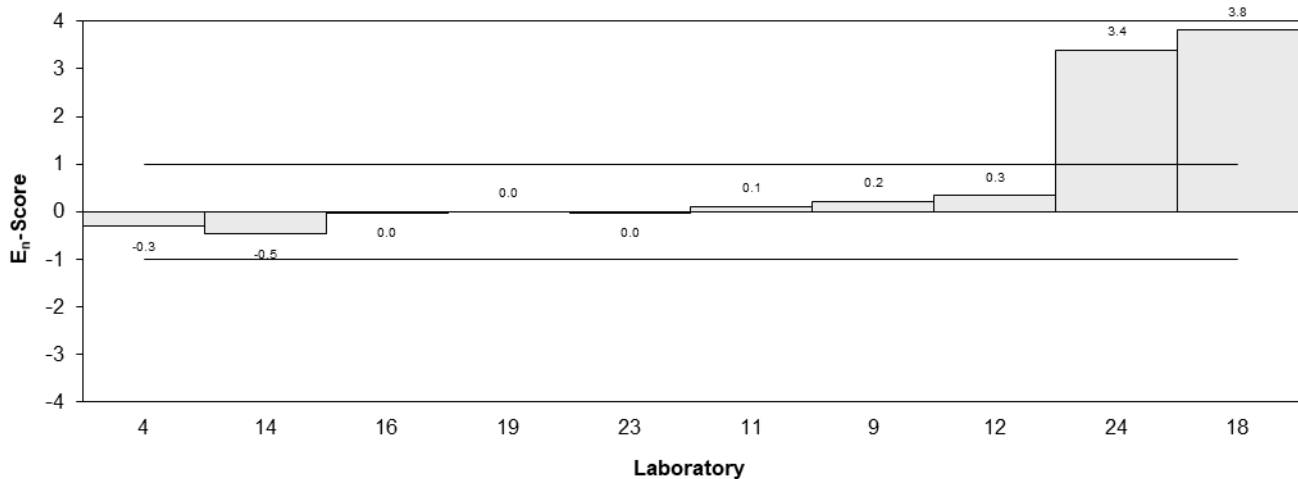


Figure 30

Table 39

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Ca
<b>Unit</b>	mg/kg

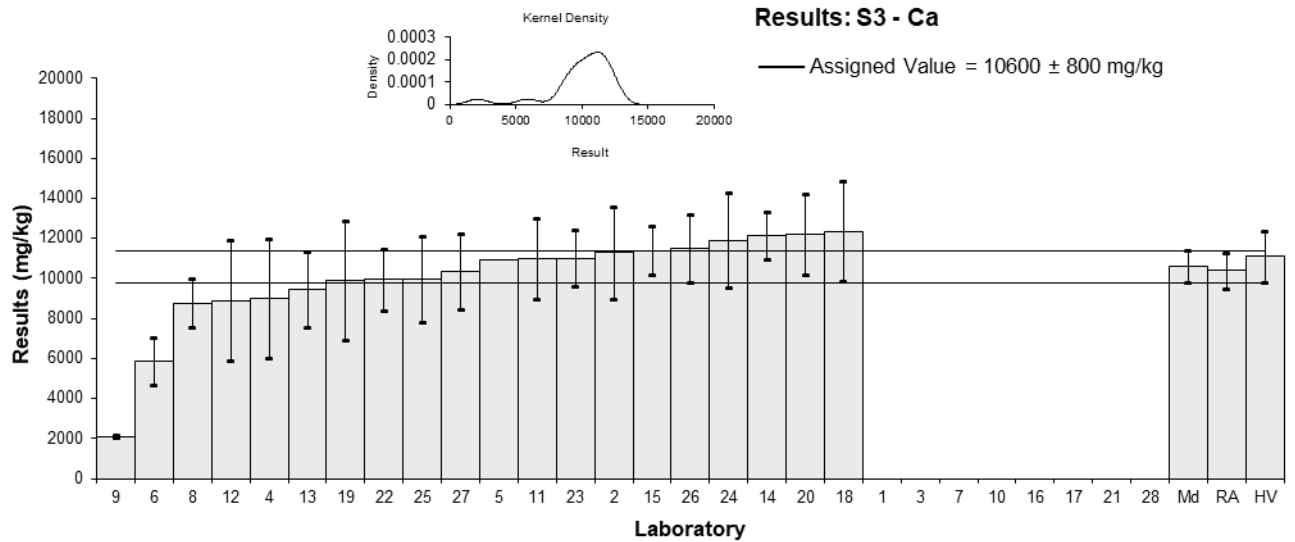
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	11300	2300	0.66	0.29
3	NT	NT		
4	9000	3000	-1.51	-0.52
5	10950	NR	0.33	0.44
6	5870	1174	-4.46	-3.33
7	NT	NT		
8	8780	1220	-1.72	-1.25
9*	2110.5	68.0	-8.01	-10.57
10	NT	NT		
11	11000	2000	0.38	0.19
12	8900	3000	-1.60	-0.55
13	9460	1890	-1.08	-0.56
14	12134	1200	1.45	1.06
15	11400	1225	0.75	0.55
16	NT	NT		
17	NT	NT		
18	12340	2500	1.64	0.66
19	9900	3000	-0.66	-0.23
20	12200	2000	1.51	0.74
21	NT	NT		
22	9960	1537	-0.60	-0.37
23	11000	1408	0.38	0.25
24	11900	2380	1.23	0.52
25	9960.5887	2152.629	-0.60	-0.28
26	11500	1700	0.85	0.48
27	10348	1876	-0.24	-0.12
28	NT	NT		

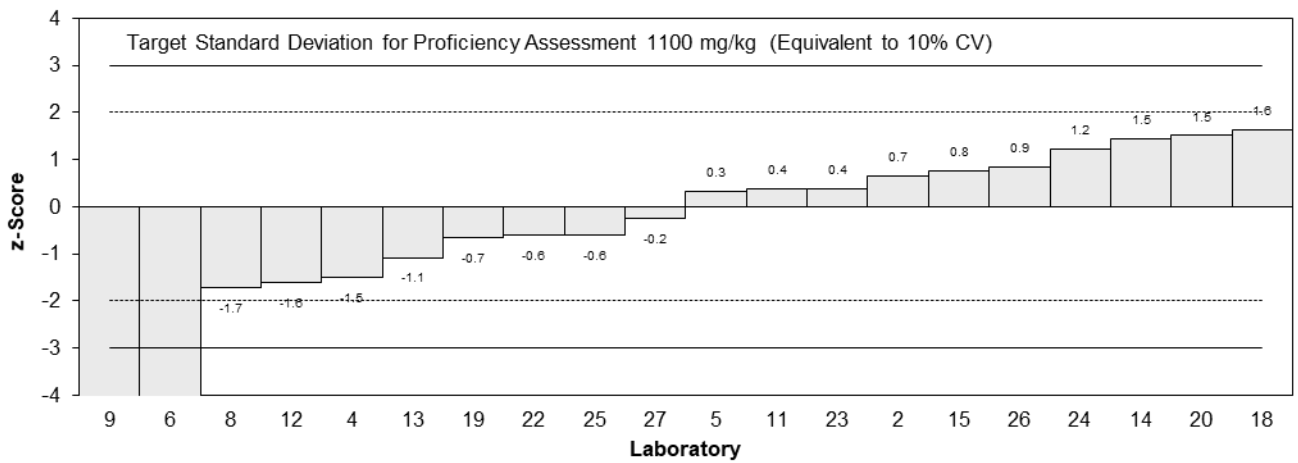
\* Outlier

**Statistics**

<b>Assigned Value</b>	10600	800
<b>Homogeneity Value</b>	11100	1300
<b>Robust Average</b>	10400	900
<b>Median</b>	10600	800
<b>Mean</b>	10000	
<b>N</b>	20	
<b>Max</b>	12340	
<b>Min</b>	2110.5	
<b>Robust SD</b>	1500	
<b>Robust CV</b>	15%	



**z-Scores: S3 - Ca**



**En-Scores: S3 - Ca**

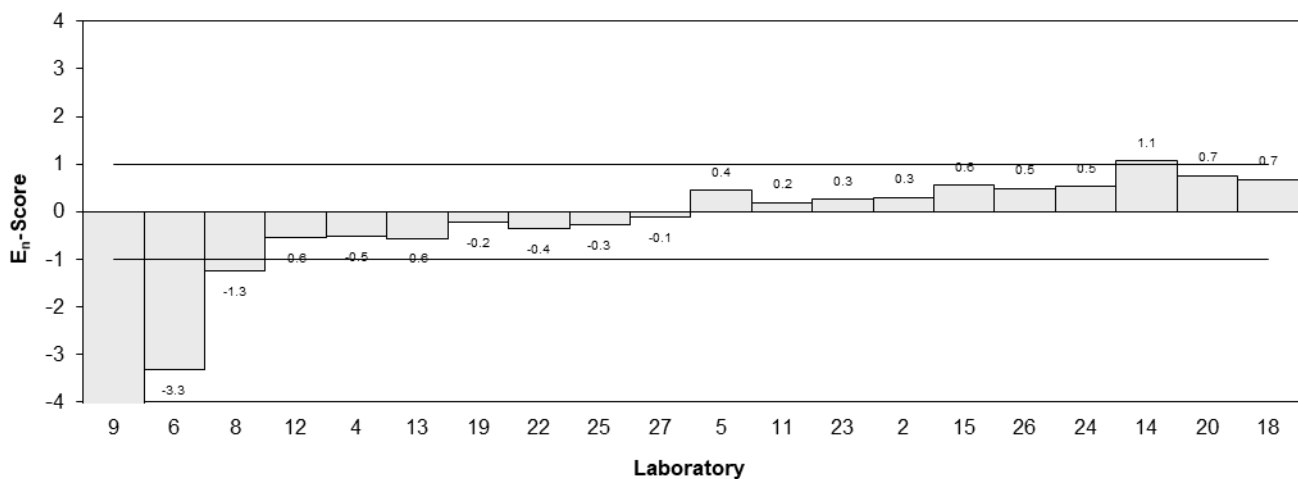


Figure 31



Table 40

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Chloride
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NT	NT
2	3.4	0.5
3	NT	NT
4	<10	NR
5	5.1	NR
6	NT	NT
7	NT	NT
8	<10	NR
9	1.30	NR
10	NT	NT
11	4	1
12	<10	NR
13	4.6	0.5
14	20	2.0
15	10	4
16	7	5
17	NT	NT
18	NT	NT
19	<10	NR
20	5.92	1
21	< 5	1
22	<10	2.46
23	8	0.576
24	< 5	1
25	NT	NT
26	10.4	4
27	8.92	2.00
28	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	4.00	0.48
<b>Robust Average</b>	6.7	2.6
<b>Median</b>	6.5	2.6
<b>Mean</b>	7.4	
<b>N</b>	12	
<b>Max</b>	20	
<b>Min</b>	1.3	
<b>Robust SD</b>	3.6	
<b>Robust CV</b>	54%	

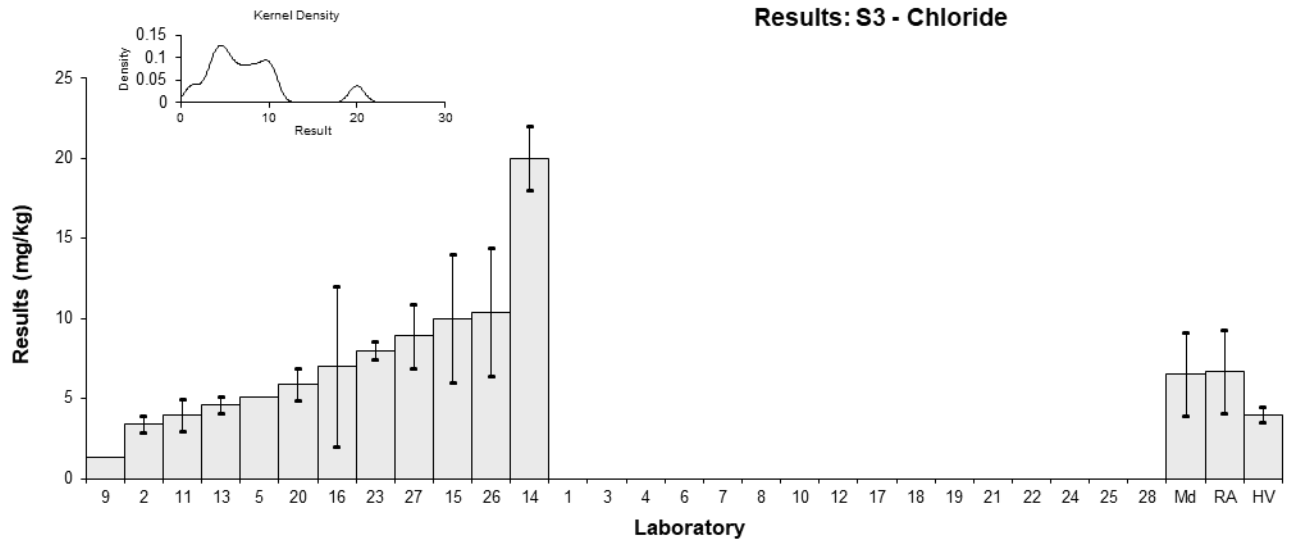


Figure 32

Table 41

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	EC
<b>Unit</b>	µS/cm

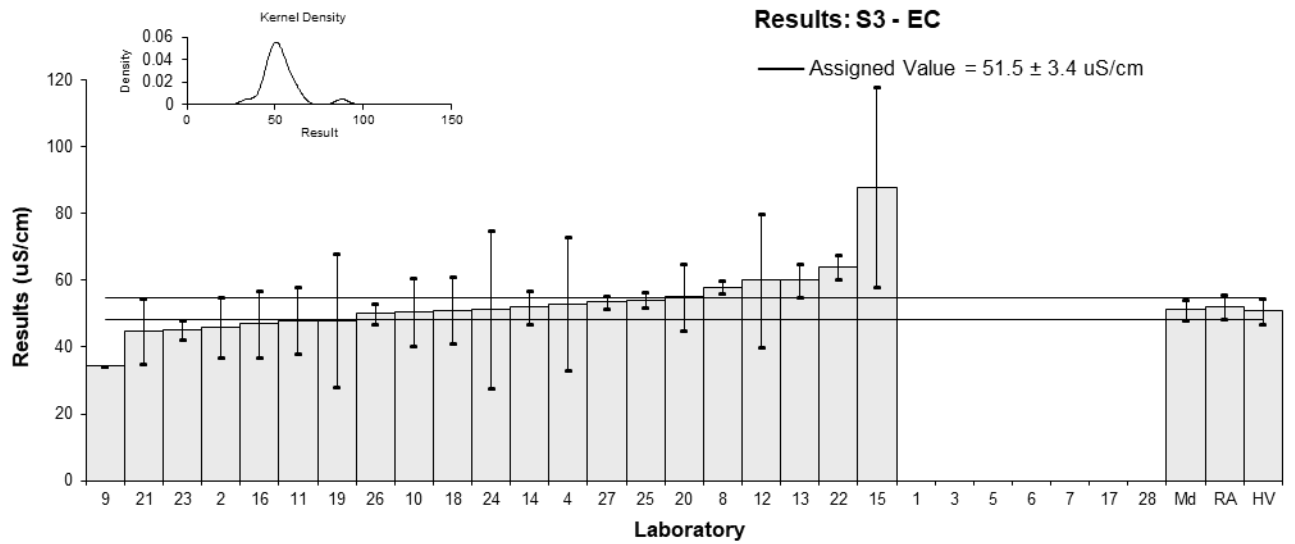
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	46	9	-1.07	-0.57
3	NT	NT		
4	53	20	0.29	0.07
5	NR	NR		
6	NT	NT		
7	NT	NT		
8	58	2	1.26	1.65
9	34.3	0.1	-3.34	-5.06
10	50.6	10.12	-0.17	-0.08
11	48	10	-0.68	-0.33
12	60	20	1.65	0.42
13	60	5	1.65	1.41
14	52	5.0	0.10	0.08
15*	88	30	7.09	1.21
16	47	10	-0.87	-0.43
17	NT	NT		
18	51	10	-0.10	-0.05
19	48	20	-0.68	-0.17
20	55	10	0.68	0.33
21	44.9	9.8	-1.28	-0.64
22	64	3.63	2.43	2.51
23	45	2.88	-1.26	-1.46
24	51.2	23.7	-0.06	-0.01
25	54.2	2.226	0.52	0.66
26	50	3	-0.29	-0.33
27	53.5	1.9	0.39	0.51
28	NT	NT		

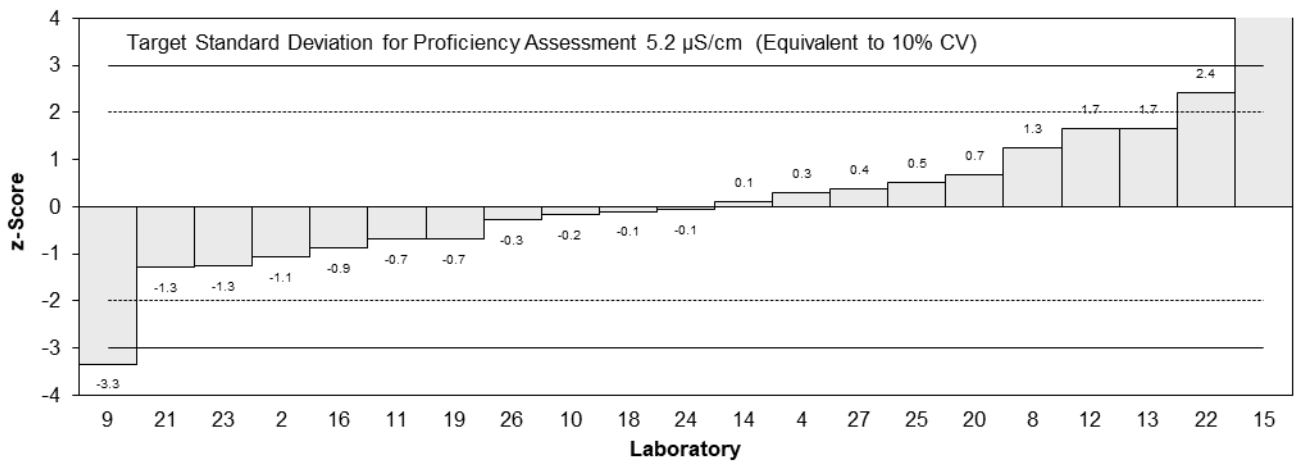
\* Outlier

**Statistics**

<b>Assigned Value</b>	51.5	3.4
<b>Homogeneity Value</b>	50.8	3.8
<b>Robust Average</b>	52.1	3.6
<b>Median</b>	51.2	3.1
<b>Mean</b>	53.0	
<b>N</b>	21	
<b>Max</b>	88	
<b>Min</b>	34.3	
<b>Robust SD</b>	6.6	
<b>Robust CV</b>	13%	



**z-Scores: S3 - EC**



**En-Scores: S3 - EC**

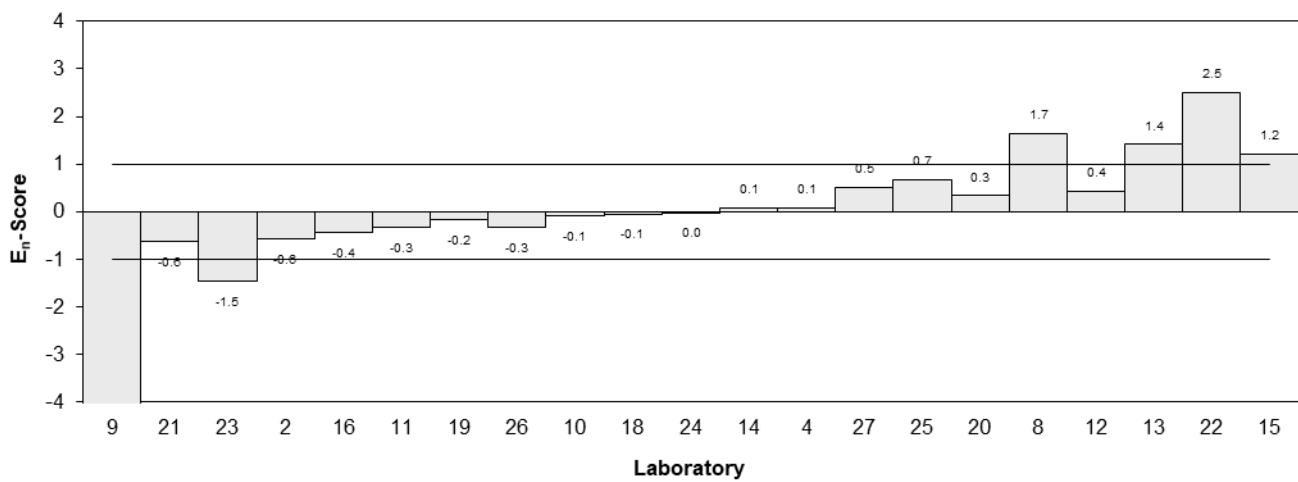


Figure 33

Table 42

## Sample Details

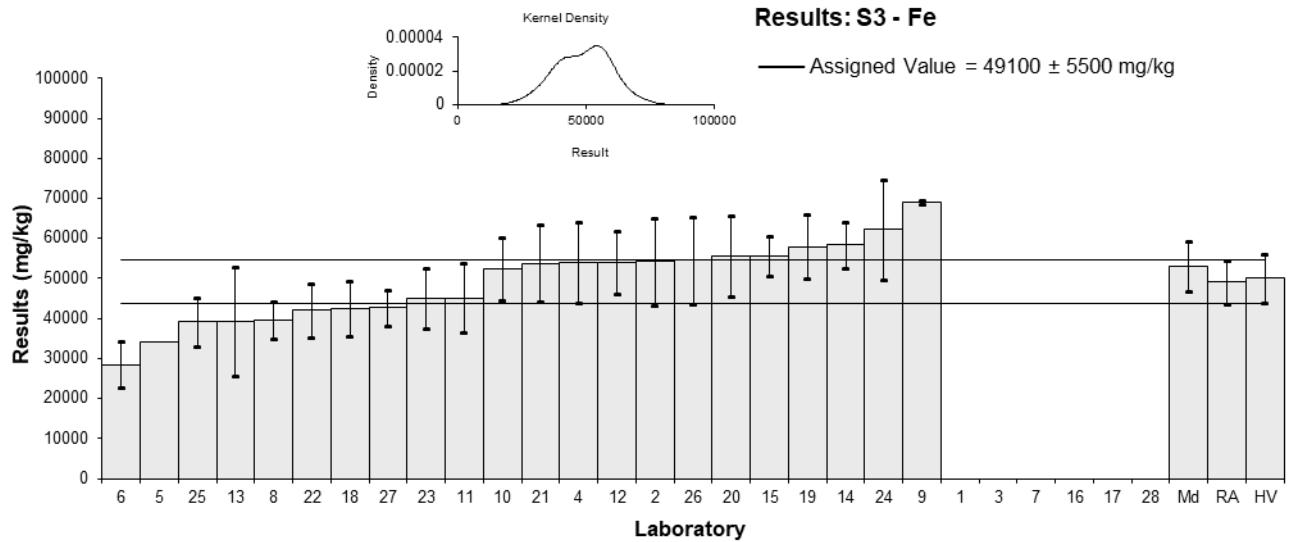
<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Fe
<b>Unit</b>	mg/kg

## Participant Results

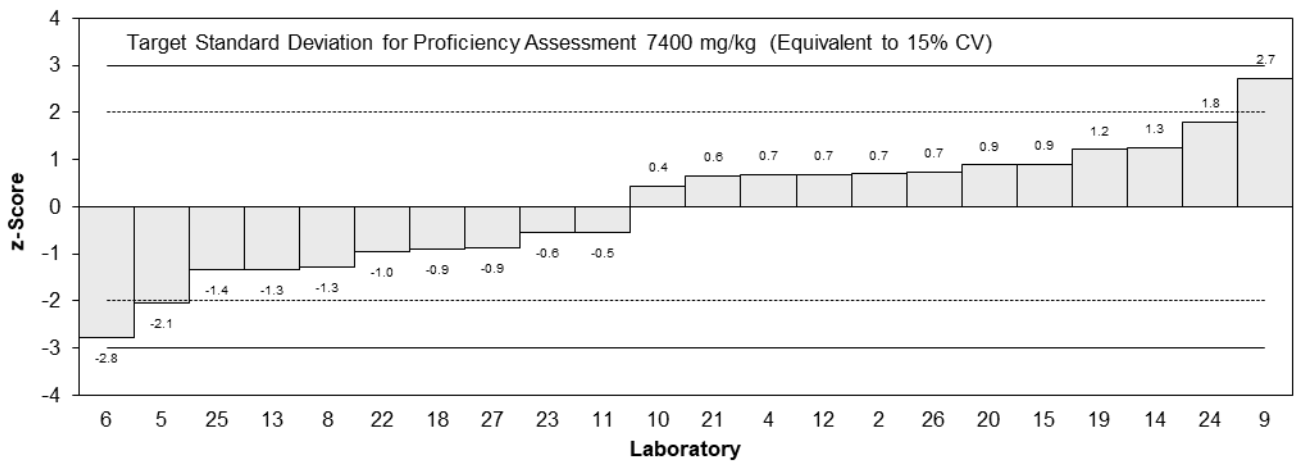
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	54200	10800	0.69	0.42
3	NT	NT		
4	54000	10000	0.67	0.43
5	34000	NR	-2.05	-2.75
6	28520	5704	-2.79	-2.60
7	NT	NT		
8	39600	4520	-1.29	-1.33
9	69063.5	508.4	2.71	3.61
10	52300	7850	0.43	0.33
11	45100	8600	-0.54	-0.39
12	54000	8000	0.67	0.50
13	39200	13600	-1.34	-0.67
14	58349	5800	1.26	1.16
15	55700	4900	0.90	0.90
16	NT	NT		
17	NT	NT		
18	42440	6800	-0.90	-0.76
19	58000	8000	1.21	0.92
20	55600	10000	0.88	0.57
21	53840	9691	0.64	0.43
22	42000	6875	-0.96	-0.81
23	45000	7425	-0.56	-0.44
24	62300	12500	1.79	0.97
25	39127.93265	5990.231	-1.35	-1.23
26	54500	11000	0.73	0.44
27	42693	4551	-0.87	-0.90
28	NT	NT		

## Statistics

<b>Assigned Value</b>	49100	5500
<b>Homogeneity Value</b>	50000	6000
<b>Robust Average</b>	49100	5500
<b>Median</b>	53100	6300
<b>Mean</b>	49100	
<b>N</b>	22	
<b>Max</b>	69063.5	
<b>Min</b>	28520	
<b>Robust SD</b>	10000	
<b>Robust CV</b>	21%	



**z-Scores: S3 - Fe**



**En-Scores: S3 - Fe**

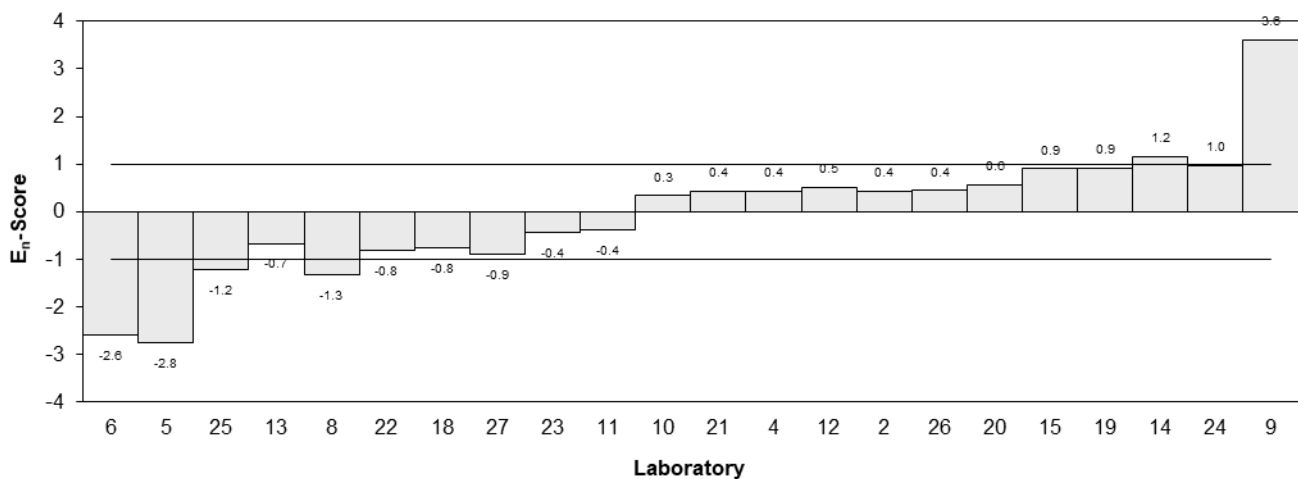


Figure 34

Table 43

**Sample Details**

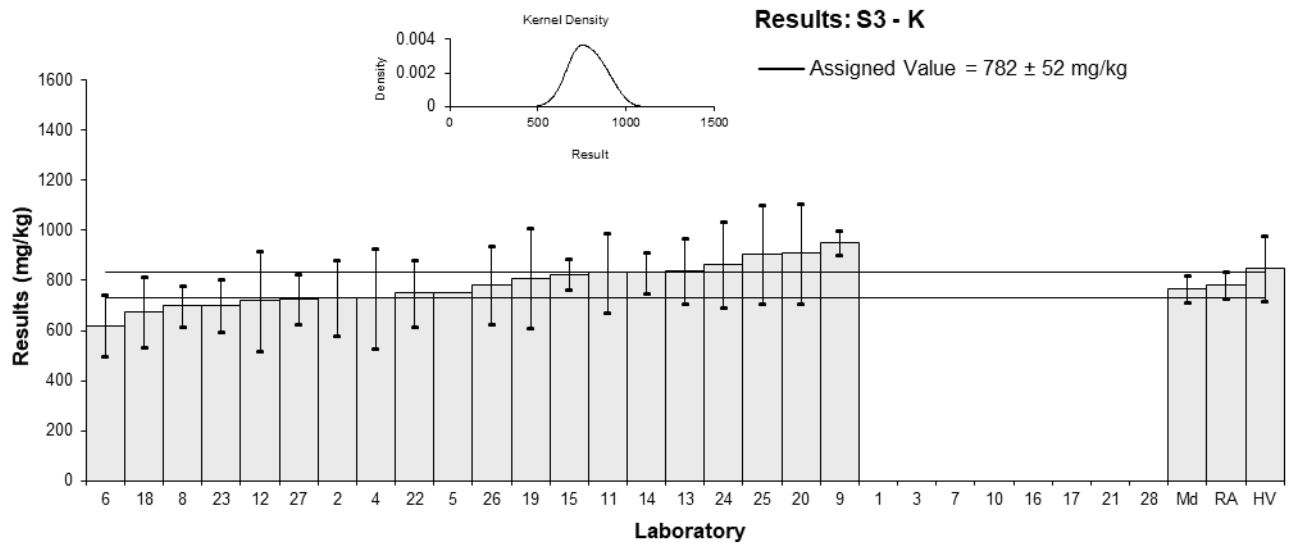
<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	K
<b>Unit</b>	mg/kg

**Participant Results**

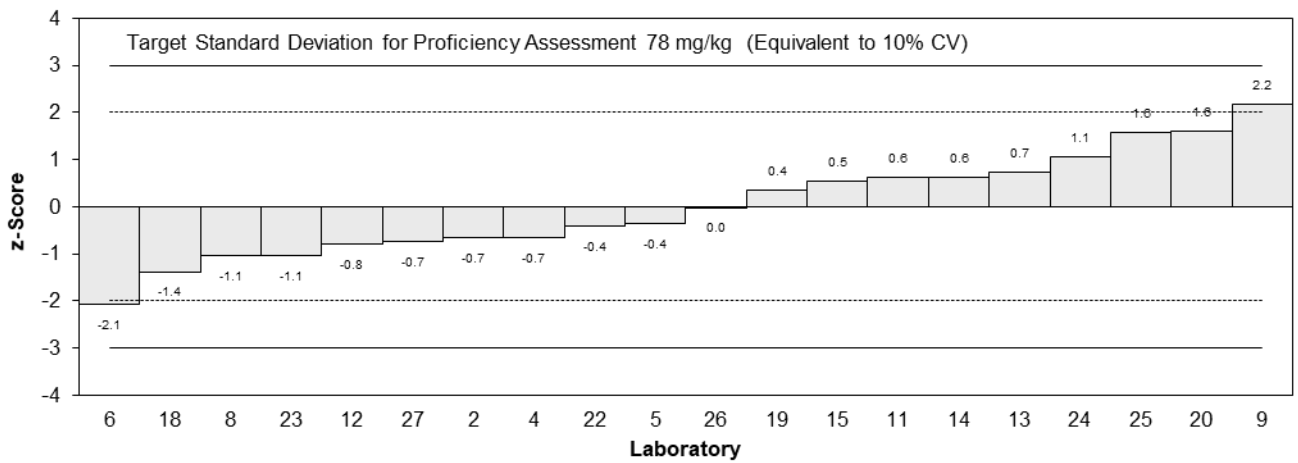
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	730	150	-0.66	-0.33
3	NT	NT		
4	730	200	-0.66	-0.25
5	753.2	NR	-0.37	-0.55
6	620.1	124.02	-2.07	-1.20
7	NT	NT		
8	700	82	-1.05	-0.84
9	951.7	47.6	2.17	2.41
10	NT	NT		
11	831	158	0.63	0.29
12	720	200	-0.79	-0.30
13	840	130	0.74	0.41
14	831	83	0.63	0.50
15	824	62	0.54	0.52
16	NT	NT		
17	NT	NT		
18	674	140	-1.38	-0.72
19	810	200	0.36	0.14
20	908	200	1.61	0.61
21	NT	NT		
22	750	134	-0.41	-0.22
23	700	106.4	-1.05	-0.69
24	865	173	1.06	0.46
25	905.27755	199.445	1.58	0.60
26	781	156	-0.01	-0.01
27	724.7	99.15	-0.73	-0.51
28	NT	NT		

**Statistics**

<b>Assigned Value</b>	782	52
<b>Homogeneity Value</b>	850	130
<b>Robust Average</b>	782	52
<b>Median</b>	767	53
<b>Mean</b>	782	
<b>N</b>	20	
<b>Max</b>	951.7	
<b>Min</b>	620.1	
<b>Robust SD</b>	93	
<b>Robust CV</b>	12%	



**z-Scores: S3 - K**



**En-Scores: S3 - K**

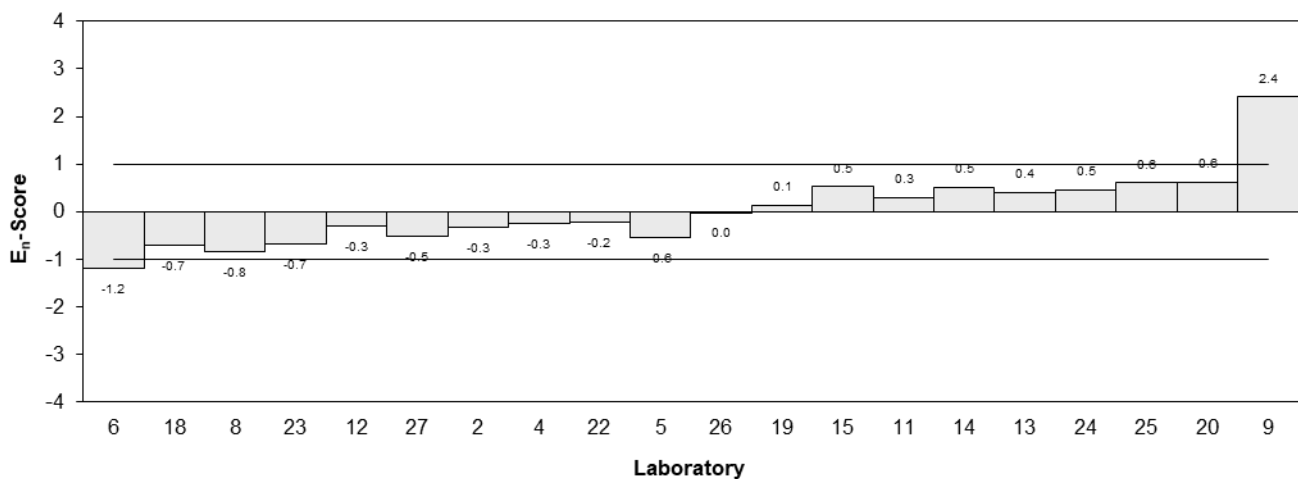


Figure 35



Table 44

## Sample Details

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Mg
<b>Unit</b>	mg/kg

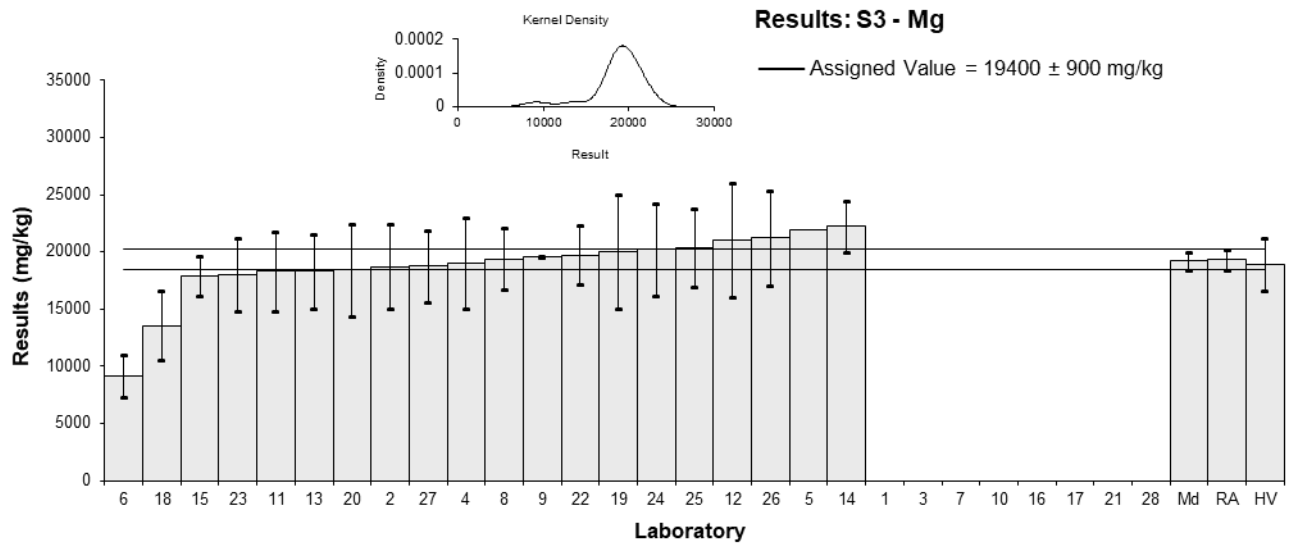
## Participant Results

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	18700	3700	-0.36	-0.18
3	NT	NT		
4	19000	4000	-0.21	-0.10
5	21940	NR	1.31	2.82
6*	9162	1832.4	-5.28	-5.01
7	NT	NT		
8	19400	2700	0.00	0.00
9	19535.5	41.0	0.07	0.15
10	NT	NT		
11	18300	3500	-0.57	-0.30
12	21000	5000	0.82	0.31
13	18300	3290	-0.57	-0.32
14	22246	2250	1.47	1.17
15	17900	1760	-0.77	-0.76
16	NT	NT		
17	NT	NT		
18	13560	3000	-3.01	-1.86
19	20000	5000	0.31	0.12
20	18400	4000	-0.52	-0.24
21	NT	NT		
22	19700	2576	0.15	0.11
23	18000	3222	-0.72	-0.42
24	20200	4040	0.41	0.19
25	20368.88415	3380.373	0.50	0.28
26	21200	4200	0.93	0.42
27	18770	3125	-0.32	-0.19
28	NT	NT		

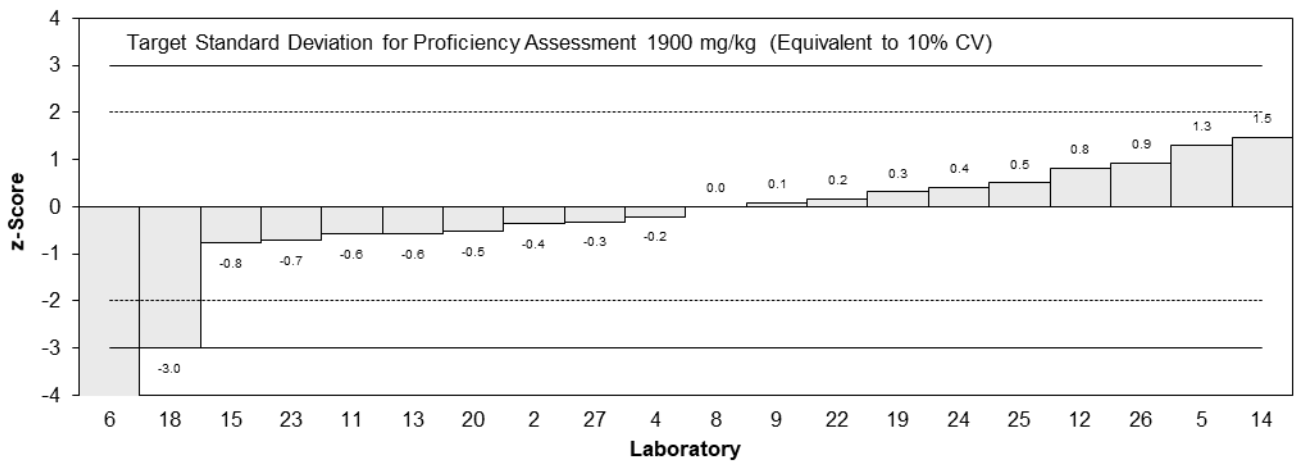
\* Outlier

## Statistics

<b>Assigned Value</b>	19400	900
<b>Homogeneity Value</b>	18900	2300
<b>Robust Average</b>	19300	900
<b>Median</b>	19200	800
<b>Mean</b>	18800	
<b>N</b>	20	
<b>Max</b>	22246	
<b>Min</b>	9162	
<b>Robust SD</b>	1700	
<b>Robust CV</b>	8.7%	



**z-Scores: S3 - Mg**



**En-Scores: S3 - Mg**

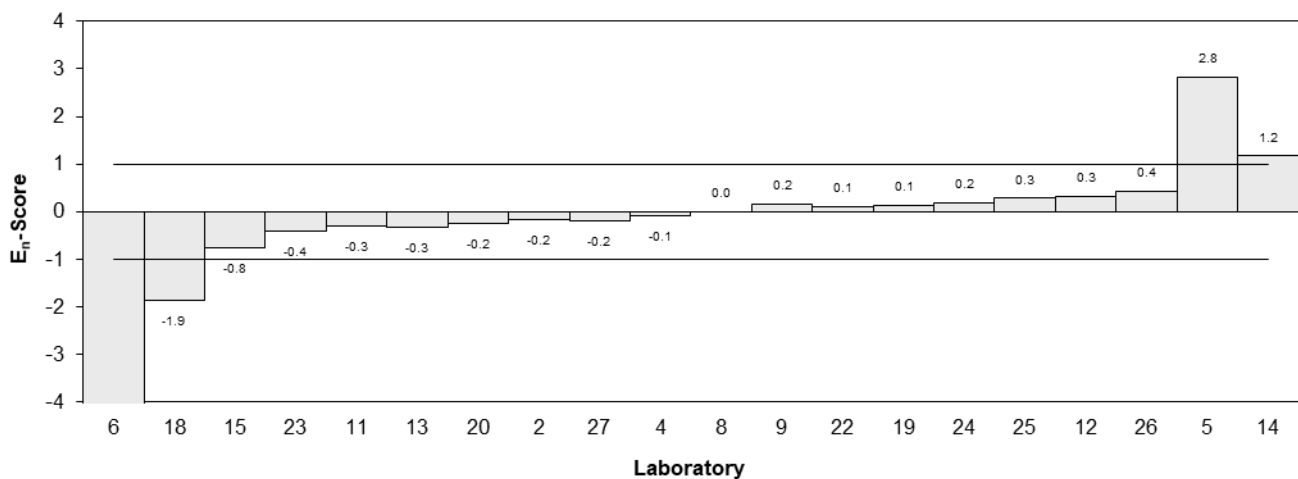


Figure 36

Table 45

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Na
<b>Unit</b>	mg/kg

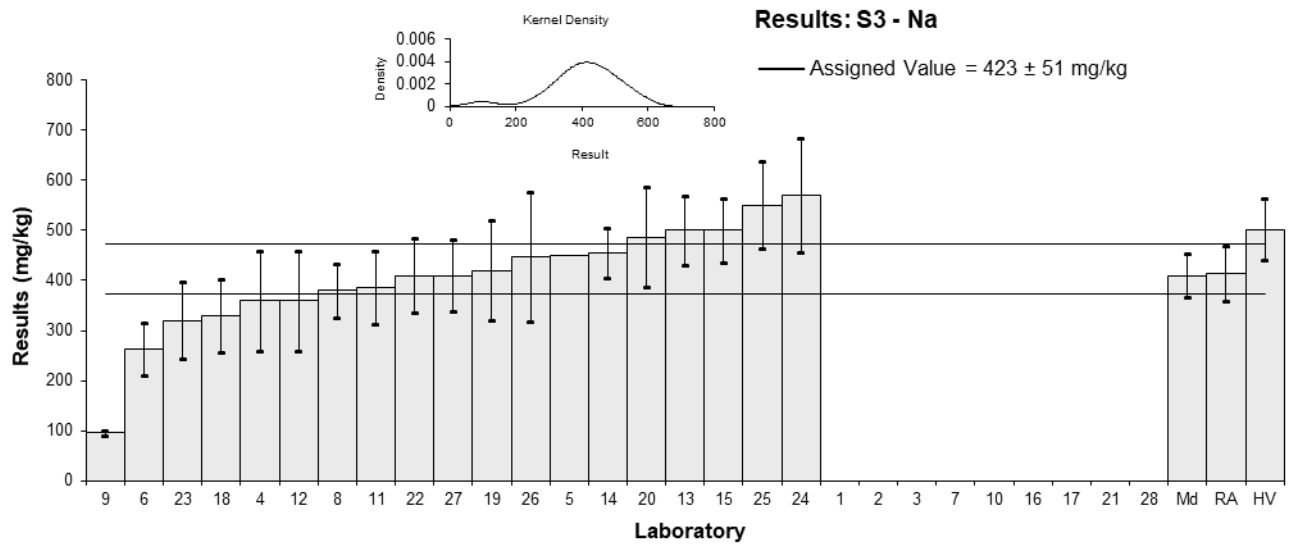
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	NR	NR		
3	NT	NT		
4	360	100	-0.99	-0.56
5	450.1	NR	0.43	0.53
6	262.3	52.46	-2.53	-2.20
7	NT	NT		
8	380	54	-0.68	-0.58
9*	96.02	5.07	-5.15	-6.38
10	NT	NT		
11	386	74	-0.58	-0.41
12	360	100	-0.99	-0.56
13	500	70	1.21	0.89
14	455	50	0.50	0.45
15	500	63	1.21	0.95
16	NT	NT		
17	NT	NT		
18	329	73	-1.48	-1.06
19	420	100	-0.05	-0.03
20	486	100	0.99	0.56
21	NT	NT		
22	410	75	-0.20	-0.14
23	320	76.8	-1.62	-1.12
24	570	114	2.32	1.18
25	550.4352	87.276	2.01	1.26
26	447	130	0.38	0.17
27	410.0	70.94	-0.20	-0.15
28	NT	NT		

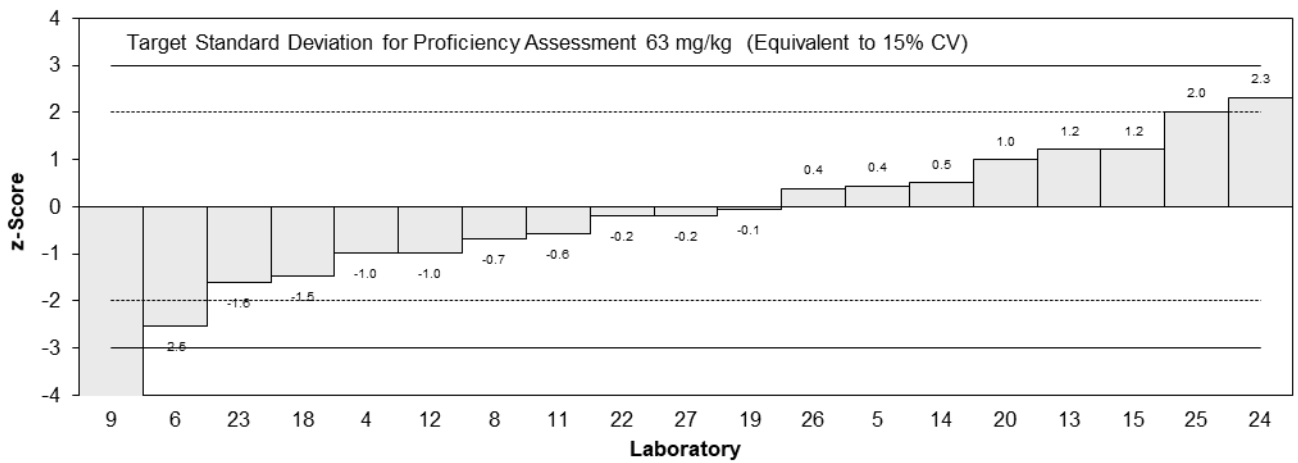
\* Outlier

**Statistics**

<b>Assigned Value</b>	423	51
<b>Homogeneity Value</b>	502	61
<b>Robust Average</b>	414	55
<b>Median</b>	410	43
<b>Mean</b>	405	
<b>N</b>	19	
<b>Max</b>	570	
<b>Min</b>	96.02	
<b>Robust SD</b>	96	
<b>Robust CV</b>	23%	



**z-Scores: S3 - Na**



**En-Scores: S3 - Na**

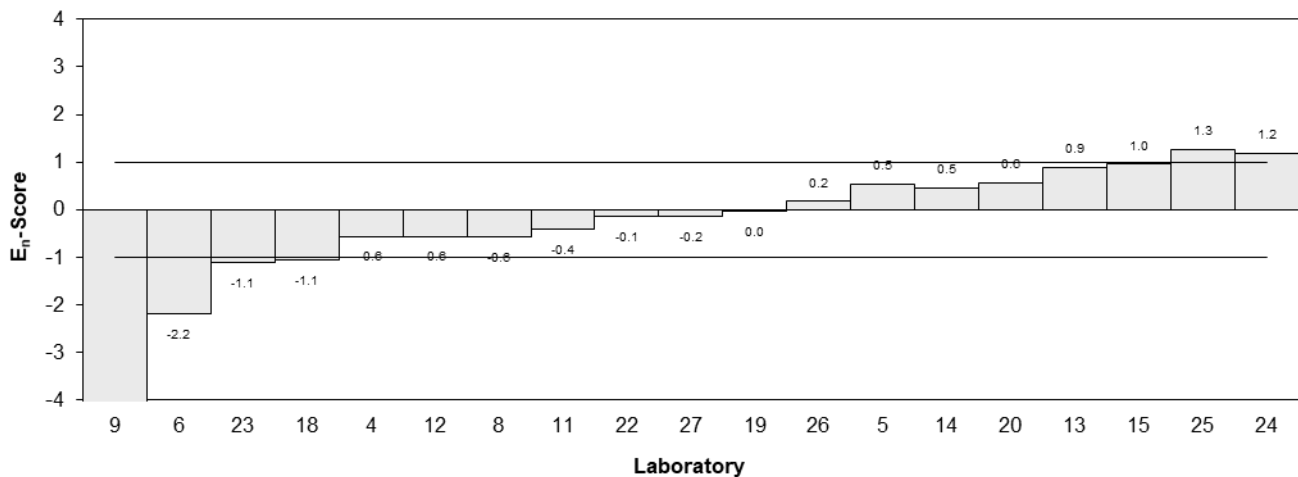


Figure 37

Table 46

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Nitrate-N
<b>Unit</b>	mg/kg

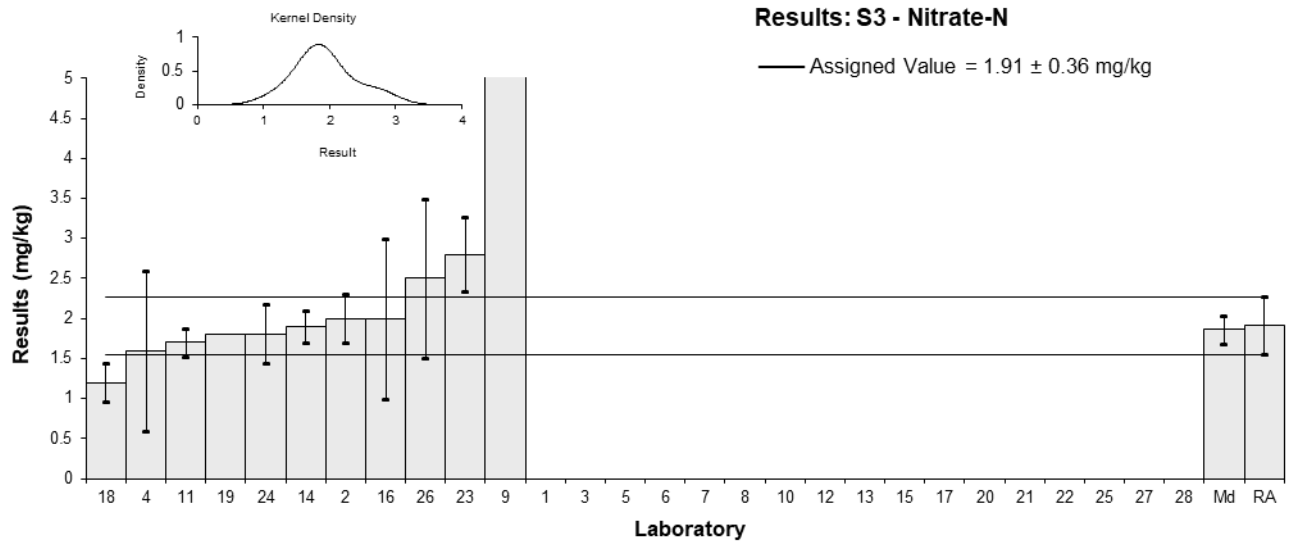
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	2.0	0.3	0.24	0.19
3	NT	NT		
4	1.6	1	-0.81	-0.29
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9**	16.68	0.45	38.66	25.63
10	NT	NT		
11	1.7	0.17	-0.55	-0.53
12	NT	NT		
13	NT	NT		
14	1.9	0.2	-0.03	-0.02
15	NT	NT		
16	2	1	0.24	0.08
17	NT	NT		
18	1.2	0.24	-1.86	-1.64
19	1.8	NT	-0.29	-0.31
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	2.8	0.462	2.33	1.52
24	1.81	0.362	-0.26	-0.20
25	NT	NT		
26	2.5	1	1.54	0.56
27	NT	NT		
28	NT	NT		

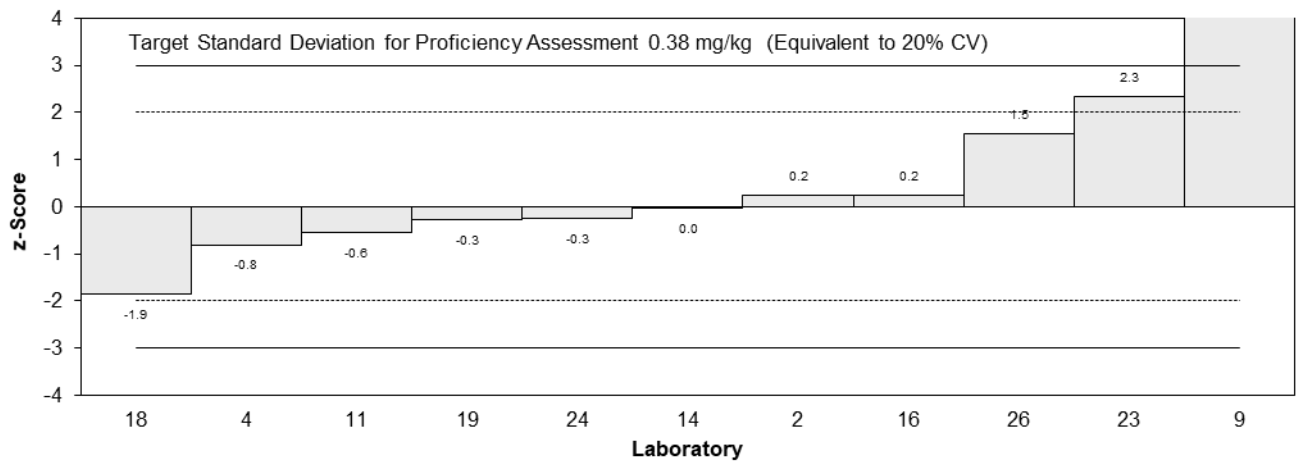
\*\* Gross Error

**Statistics**

<b>Assigned Value</b>	1.91	0.36
<b>Robust Average</b>	1.91	0.36
<b>Median</b>	1.86	0.18
<b>Mean</b>	1.93	
<b>N</b>	10	
<b>Max</b>	2.8	
<b>Min</b>	1.2	
<b>Robust SD</b>	0.46	
<b>Robust CV</b>	24%	



**z-Scores: S3 - Nitrate-N**



**En-Scores: S3 - Nitrate-N**

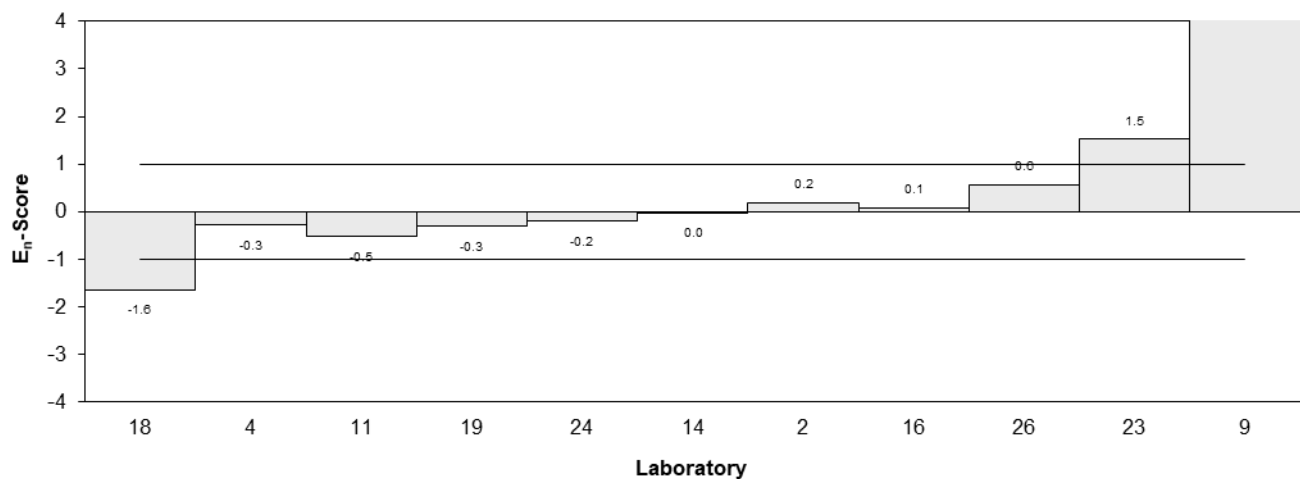


Figure 38

Table 47

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Orthophosphate-P
<b>Unit</b>	mg/kg

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2*	2.5	0.5	3.14	1.92
3	NT	NT		
4	<2	NR		
5	1.74	NR	0.97	1.21
6	NT	NT		
7	NT	NT		
8	1.1	0.1	-0.86	-1.01
9	1.81	0.24	1.17	1.11
10	NT	NT		
11	NT	NT		
12	2	2	1.71	0.30
13	1.2	0.1	-0.57	-0.67
14	1.8	0.2	1.14	1.16
15	1.21	0.10	-0.54	-0.64
16	NT	NT		
17	NT	NT		
18	1.7	0.34	0.86	0.68
19	1.2	2	-0.57	-0.10
20	0.92	0.2	-1.37	-1.39
21	< 10	1		
22	1.2	0.2	-0.57	-0.58
23	1.3	0.1846	-0.29	-0.30
24	< 5	1		
25	NT	NT		
26*	5.55	1.7	11.86	2.41
27	1.02	0.2	-1.09	-1.10
28	NT	NT		

\* Outlier

**Statistics**

<b>Assigned Value</b>	1.40	0.28
<b>Homogeneity Value</b>	1.15	0.14
<b>Robust Average</b>	1.52	0.33
<b>Median</b>	1.30	0.36
<b>Mean</b>	1.75	
<b>N</b>	15	
<b>Max</b>	5.55	
<b>Min</b>	0.92	
<b>Robust SD</b>	0.52	
<b>Robust CV</b>	34%	

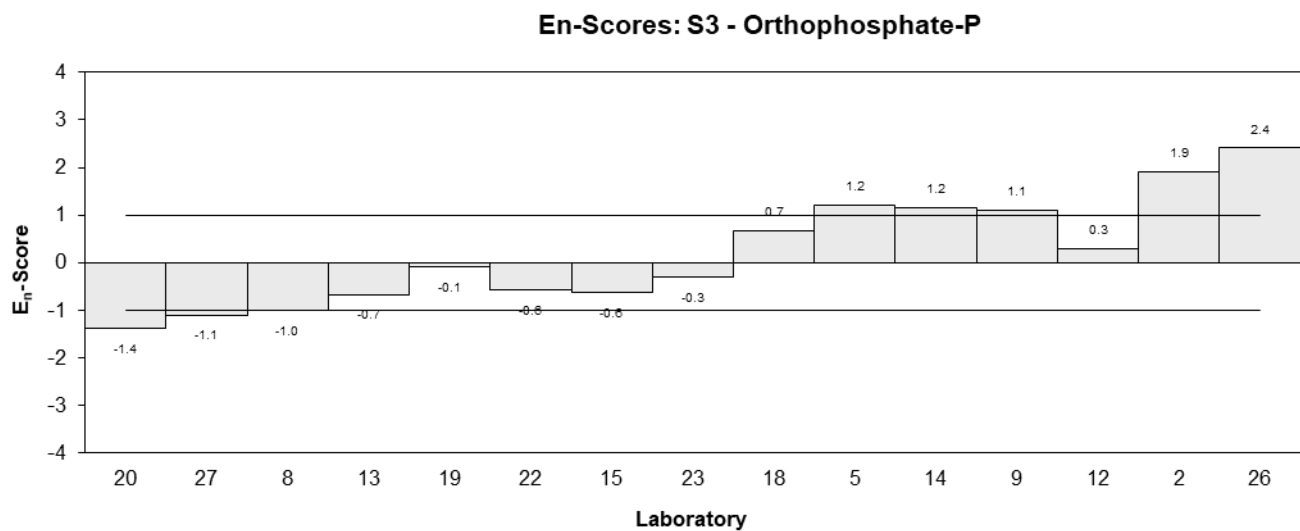
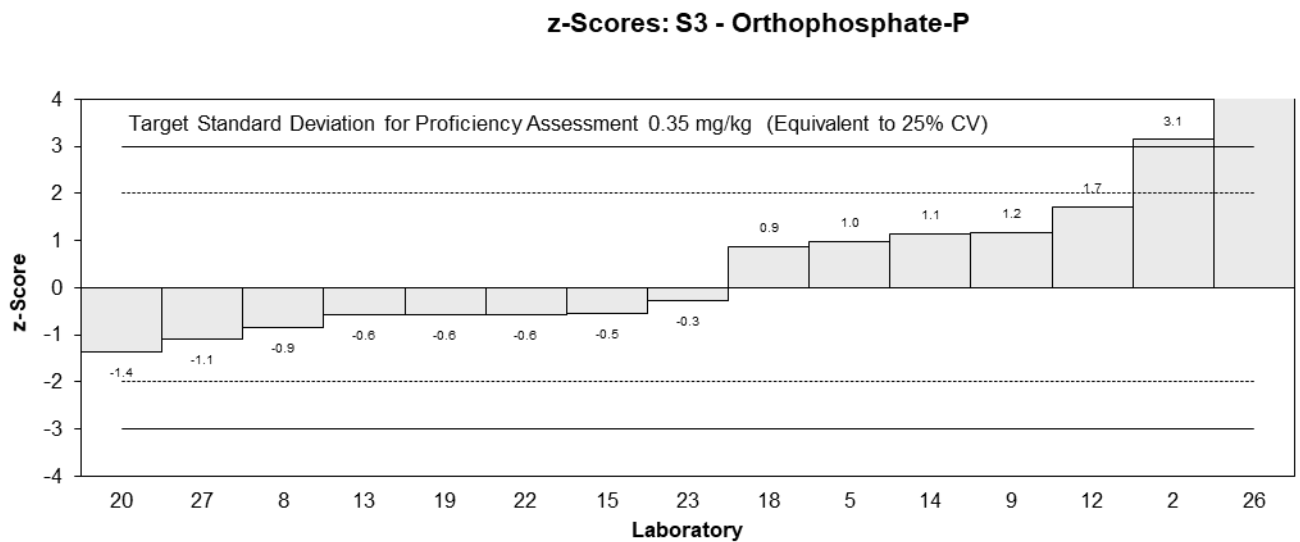
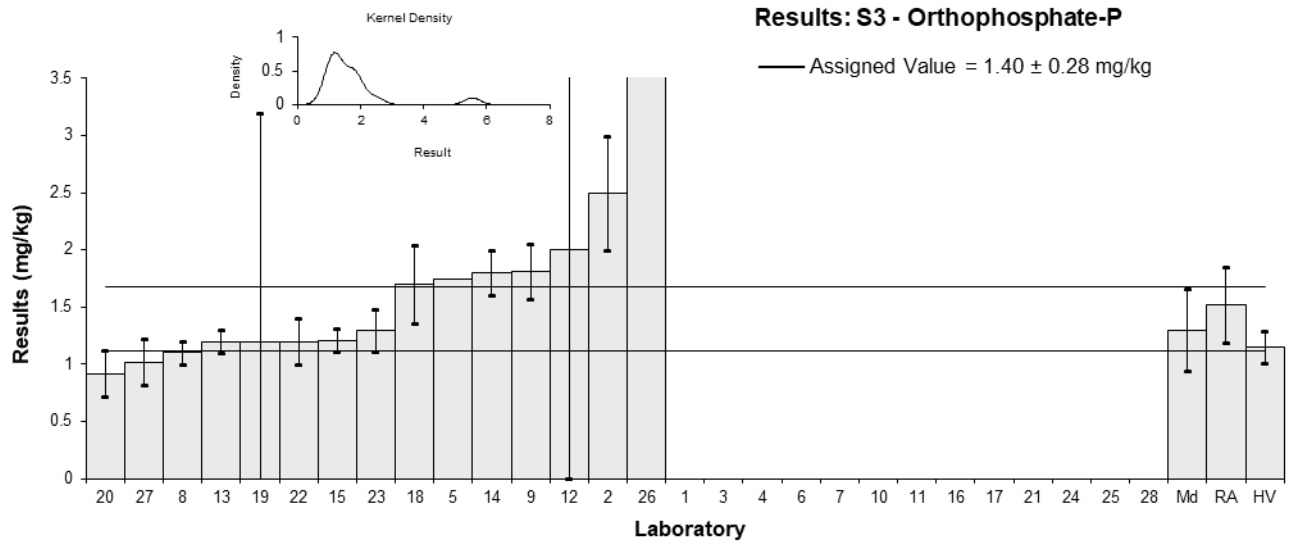


Figure 39



Table 48

## Sample Details

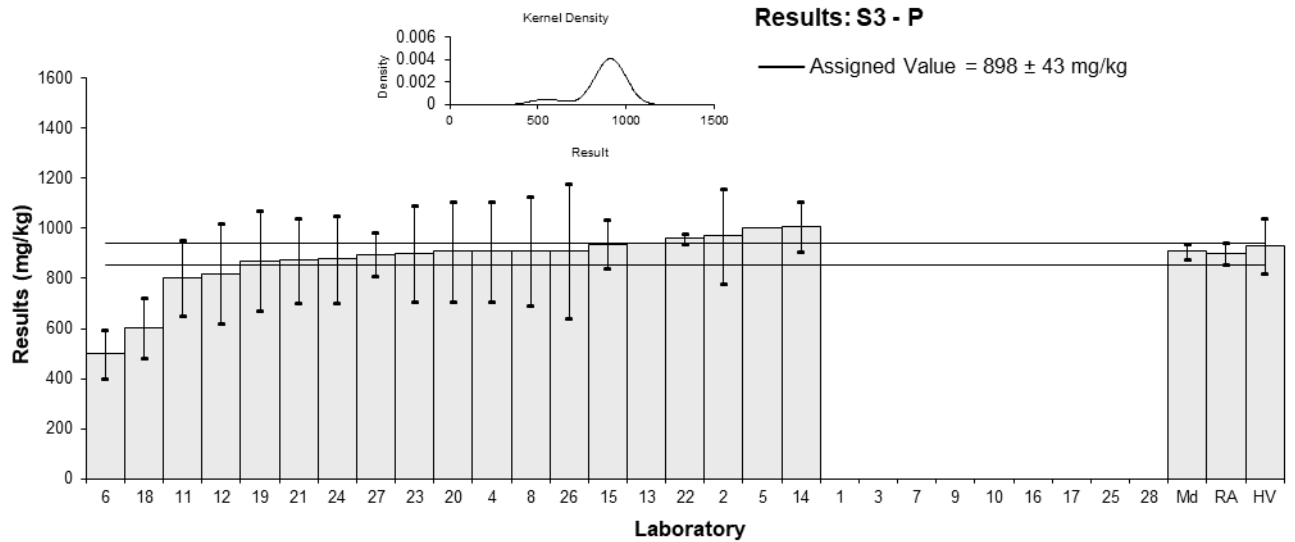
<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	P
<b>Unit</b>	mg/kg

## Participant Results

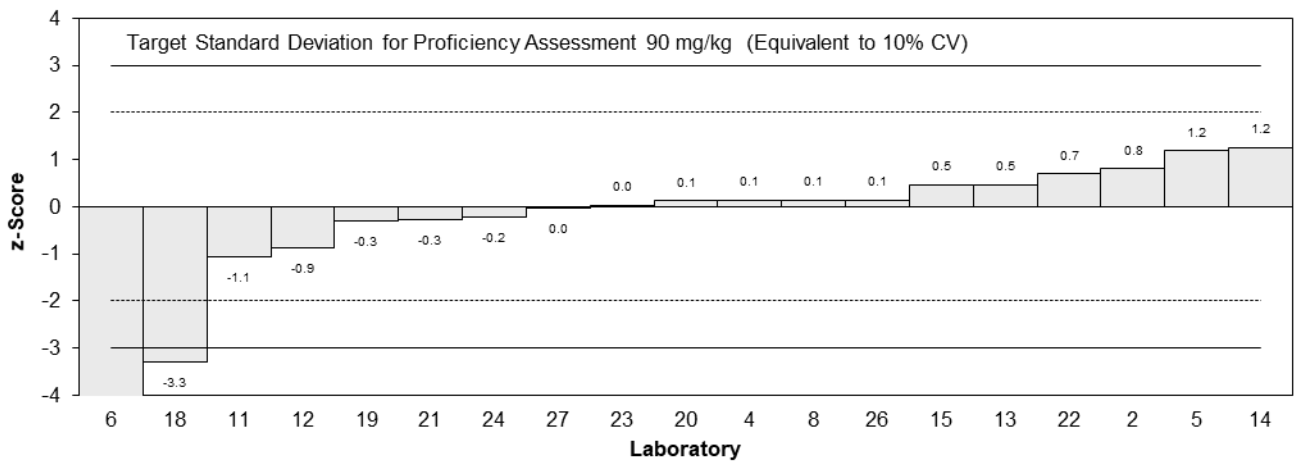
Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	970	190	0.80	0.37
3	NT	NT		
4	910	200	0.13	0.06
5	1004	NR	1.18	2.47
6	497.8	99.56	-4.46	-3.69
7	NT	NT		
8	910	216	0.13	0.05
9	NR	NR		
10	NT	NT		
11	802	153	-1.07	-0.60
12	820	200	-0.87	-0.38
13	940	NR	0.47	0.98
14	1009	100	1.24	1.02
15	938	96	0.45	0.38
16	NT	NT		
17	NT	NT		
18	603	120	-3.29	-2.31
19	870	200	-0.31	-0.14
20	909	200	0.12	0.05
21	873	170	-0.28	-0.14
22	960	19.2	0.69	1.32
23	900	193.5	0.02	0.01
24	877	175	-0.23	-0.12
25	NT	NT		
26	911	270	0.14	0.05
27	895.2	87.0	-0.03	-0.03
28	NT	NT		

## Statistics

<b>Assigned Value</b>	898	43
<b>Homogeneity Value</b>	930	110
<b>Robust Average</b>	898	43
<b>Median</b>	909	31
<b>Mean</b>	874	
<b>N</b>	19	
<b>Max</b>	1009	
<b>Min</b>	497.8	
<b>Robust SD</b>	75	
<b>Robust CV</b>	8.4%	



**z-Scores: S3 - P**



**En-Scores: S3 - P**

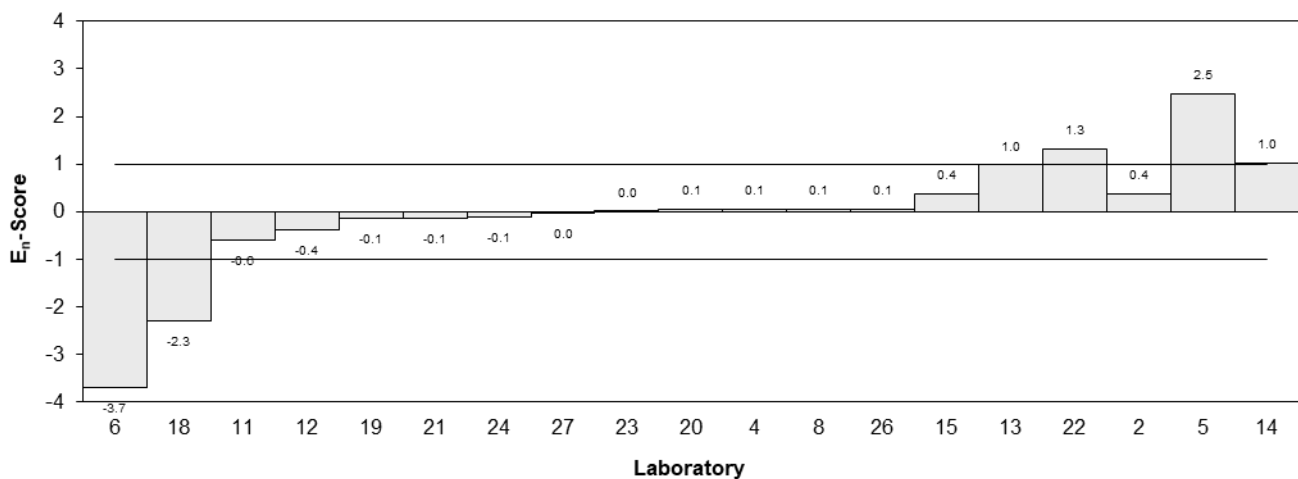


Figure 40

Table 49

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	pH

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	7.3	0.1	-0.58	-0.96
3	NT	NT		
4	7.3	0.2	-0.58	-0.64
5	7.4	NR	-0.19	-0.42
6	NT	NT		
7	NT	NT		
8	7.4	0.1	-0.19	-0.32
9	7.74	0.03	1.11	2.34
10	7.47	0.3735	0.08	0.05
11	7.5	0.1	0.19	0.32
12	7.5	0.2	0.19	0.21
13	7.5	0.2	0.19	0.21
14	7.41	0.2	-0.15	-0.17
15	6.9	0.3	-2.11	-1.70
16	7.6	0.2	0.58	0.64
17	NT	NT		
18	7.6	0.76	0.58	0.19
19	7.5	0.2	0.19	0.21
20	6.51	0.2	-3.60	-4.03
21	7.54	0.15	0.35	0.47
22	7.2	0.16	-0.96	-1.25
23	7.6	0.2	0.58	0.64
24	7.46	0.2	0.04	0.04
25	7.875	0.108	1.63	2.63
26	6.2	0.3	-4.79	-3.87
27	7.72	0.1	1.04	1.73
28	NT	NT		

**Statistics**

<b>Assigned Value</b>	7.45	0.12
<b>Homogeneity Value</b>	7.35	0.88
<b>Robust Average</b>	7.45	0.12
<b>Median</b>	7.49	0.09
<b>Mean</b>	7.37	
<b>N</b>	22	
<b>Max</b>	7.875	
<b>Min</b>	6.2	
<b>Robust SD</b>	0.22	
<b>Robust CV</b>	3%	

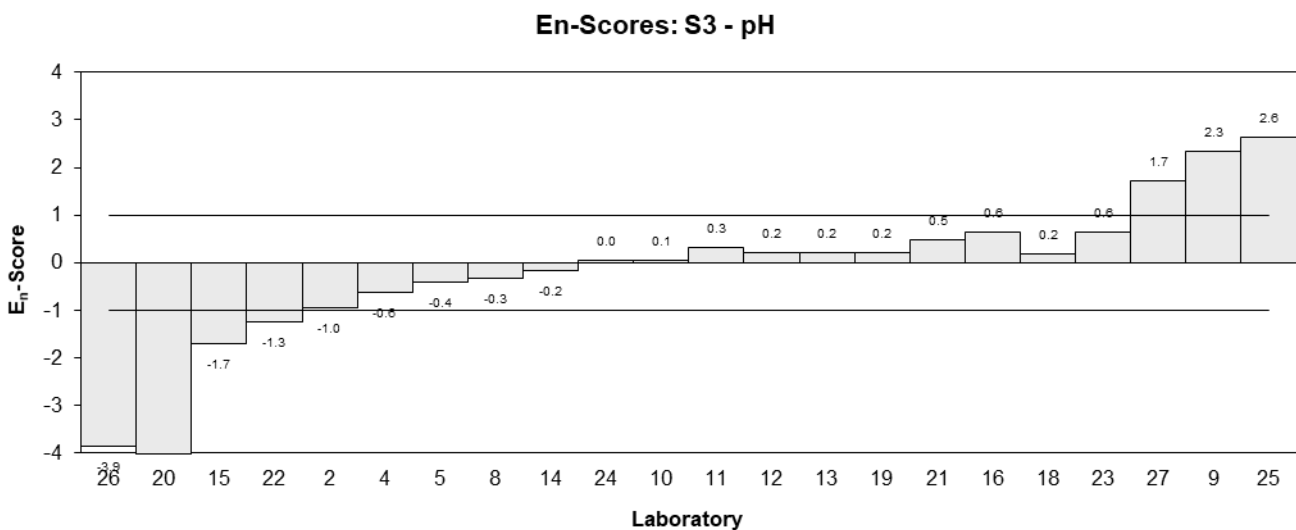
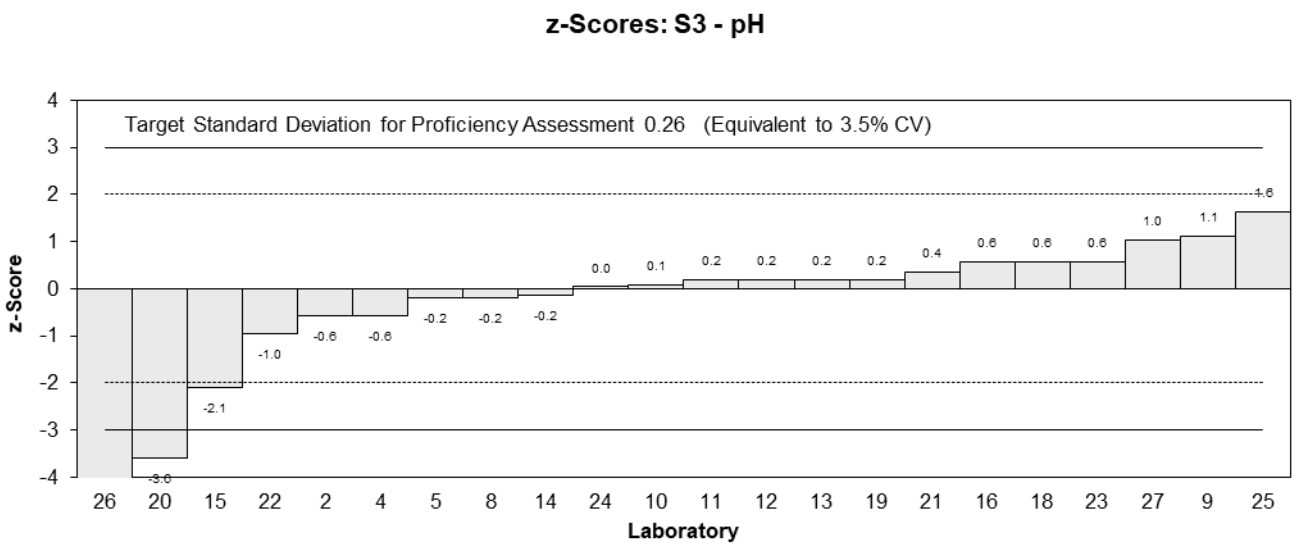
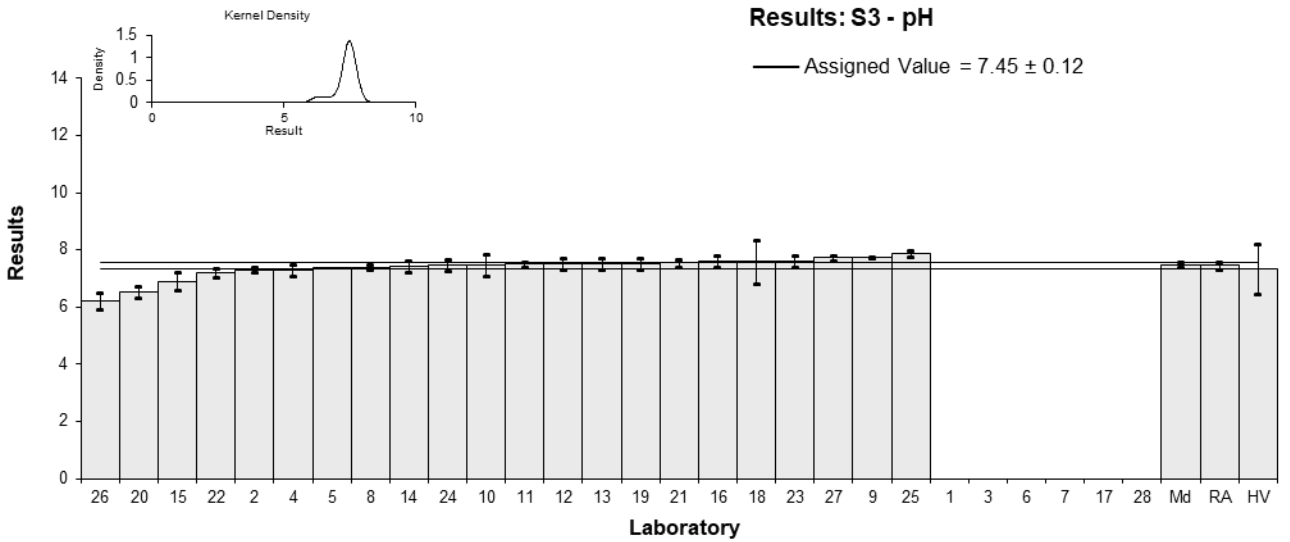


Figure 41

Table 50

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	S
<b>Unit</b>	mg/kg

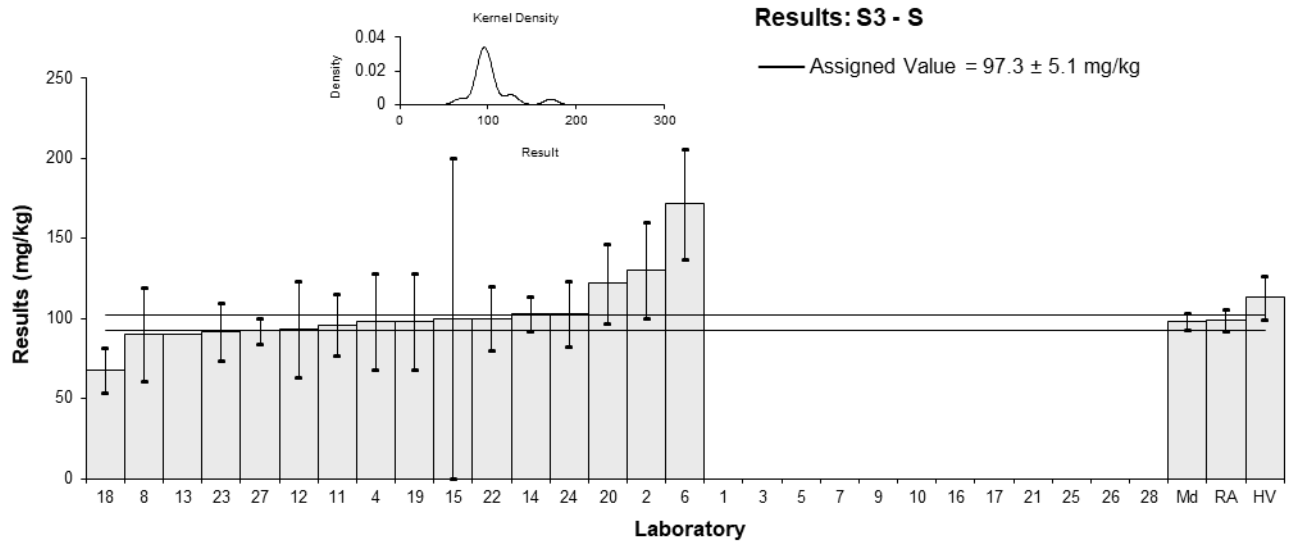
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	130	30	3.36	1.07
3	NT	NT		
4	98	30	0.07	0.02
5	NT	NT		
6*	171.5	34.3	7.63	2.14
7	NT	NT		
8	90	29	-0.75	-0.25
9	NT	NT		
10	NT	NT		
11	96	19	-0.13	-0.07
12	93	30	-0.44	-0.14
13	90	NR	-0.75	-1.43
14	103	11	0.59	0.47
15	100	100	0.28	0.03
16	NT	NT		
17	NT	NT		
18	68.0	14	-3.01	-1.97
19	98	30	0.07	0.02
20	122	25	2.54	0.97
21	NT	NT		
22	100	20	0.28	0.13
23	92	17.94	-0.54	-0.28
24	103	20.6	0.59	0.27
25	NT	NT		
26	<100	NR		
27	92.3	7.9	-0.51	-0.53
28	NT	NT		

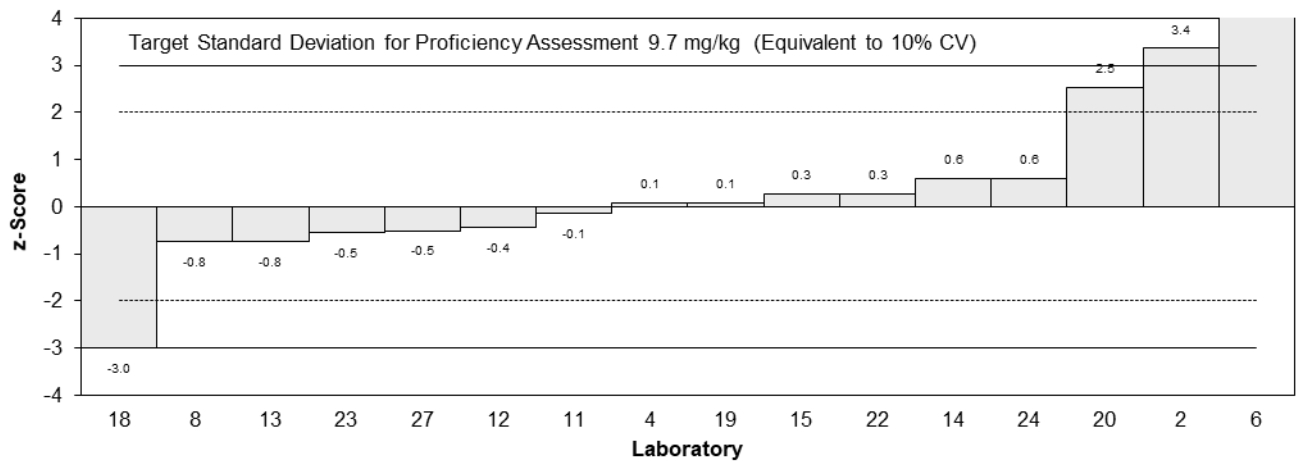
\* Outlier

**Statistics**

<b>Assigned Value</b>	97.3	5.1
<b>Homogeneity Value</b>	113	14
<b>Robust Average</b>	99.0	6.9
<b>Median</b>	98.0	5.0
<b>Mean</b>	103	
<b>N</b>	16	
<b>Max</b>	171.5	
<b>Min</b>	68	
<b>Robust SD</b>	11	
<b>Robust CV</b>	11%	



**z-Scores: S3 - S**



**En-Scores: S3 - S**

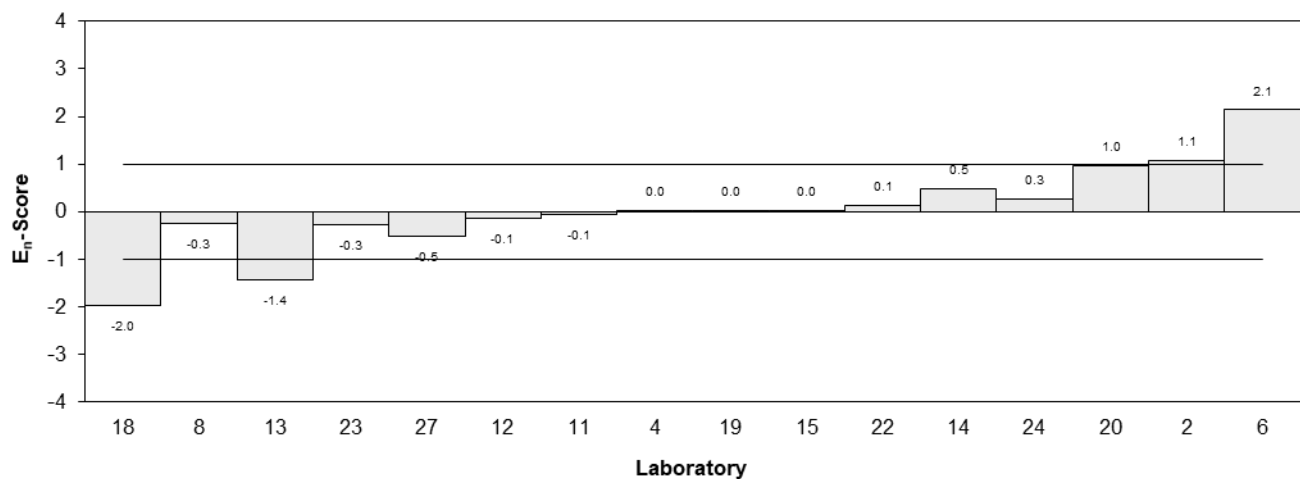


Figure 42

Table 51

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Sr
<b>Unit</b>	mg/kg

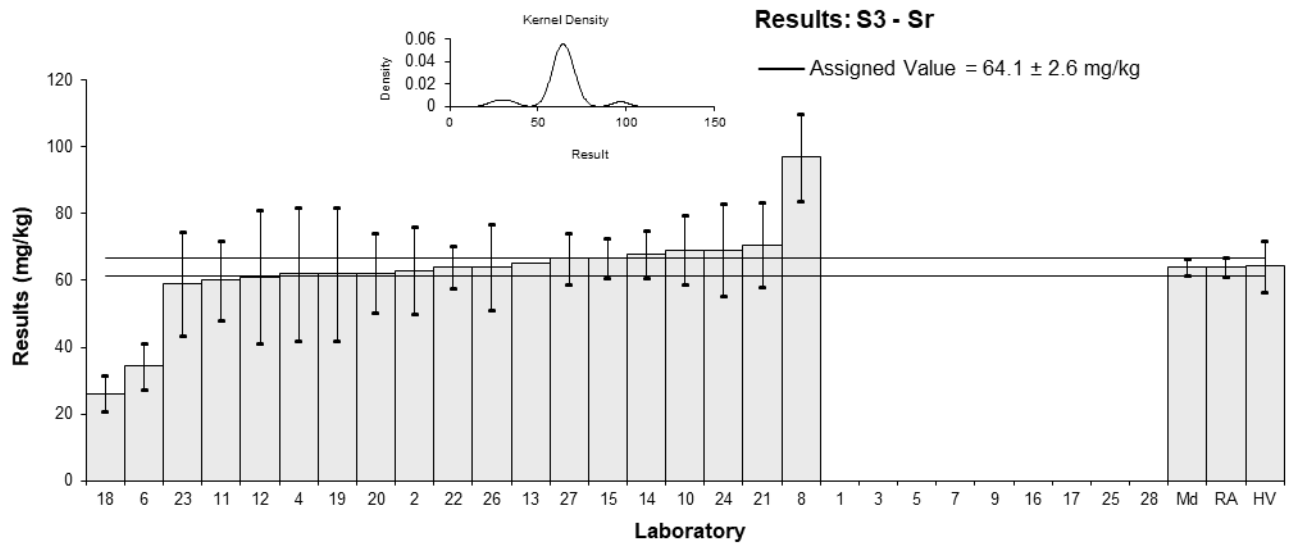
**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	63	13	-0.17	-0.08
3	NT	NT		
4	62	20	-0.33	-0.10
5	NT	NT		
6	34.25	6.85	-4.66	-4.07
7	NT	NT		
8*	97	13	5.13	2.48
9	NT	NT		
10	69.1	10.4	0.78	0.47
11	60	12	-0.64	-0.33
12	61	20	-0.48	-0.15
13	65.1	NR	0.16	0.38
14	67.9	7.0	0.59	0.51
15	66.63	6	0.39	0.39
16	NT	NT		
17	NT	NT		
18*	26.1	5.3	-5.93	-6.44
19	62	20	-0.33	-0.10
20	62.2	12	-0.30	-0.15
21	70.7	12.7	1.03	0.51
22	64	6.25	-0.02	-0.01
23	59	15.458	-0.80	-0.33
24	69.1	13.8	0.78	0.36
25	NT	NT		
26	64	13	-0.02	-0.01
27	66.58	7.6	0.39	0.31
28	NT	NT		

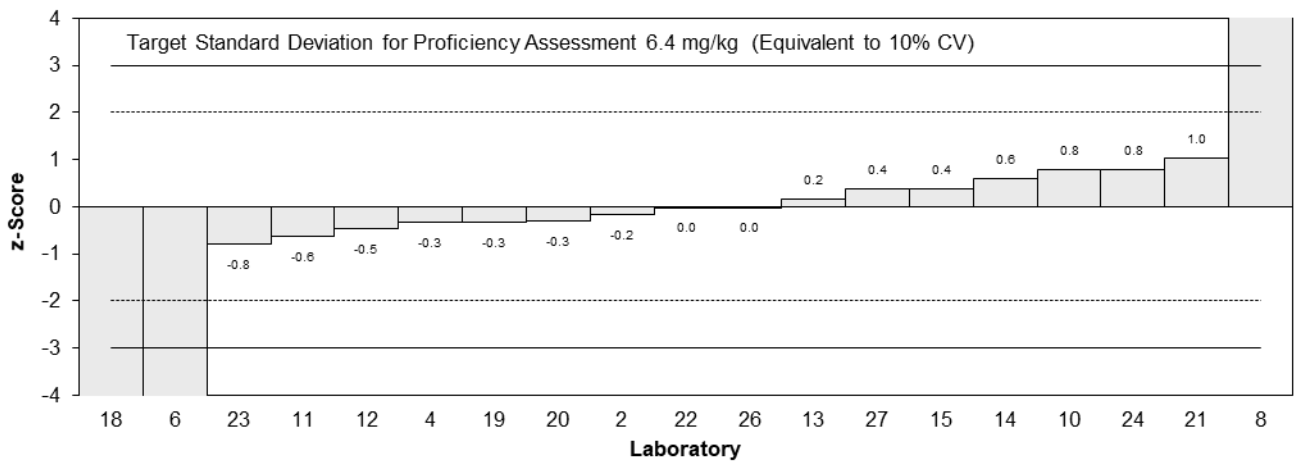
\* Outlier

**Statistics**

<b>Assigned Value</b>	64.1	2.6
<b>Homogeneity Value</b>	64.3	7.7
<b>Robust Average</b>	64.0	2.9
<b>Median</b>	64.0	2.6
<b>Mean</b>	62.6	
<b>N</b>	19	
<b>Max</b>	97	
<b>Min</b>	26.1	
<b>Robust SD</b>	5.1	
<b>Robust CV</b>	8%	



**z-Scores: S3 - Sr**



**En-Scores: S3 - Sr**

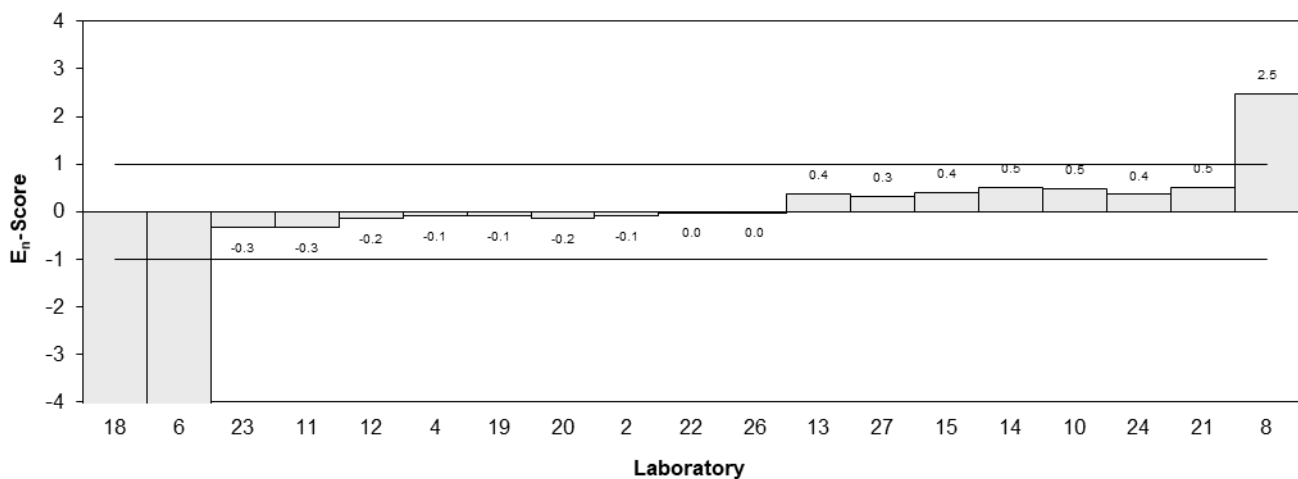


Figure 43



Table 52

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	Sulphate
<b>Unit</b>	mg/kg

**Participant Results**

<b>Lab. Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NT	NT
2	4.9	0.7
3	NT	NT
4	<10	NR
5	4.7	NR
6	NT	NT
7	NT	NT
8	10	1
9	10.0	2.5
10	NT	NT
11	3	1
12	<10	NR
13	3.7	0.6
14	32	4.5
15	10.1	0.6
16	NT	NT
17	NT	NT
18	NT	NT
19	<10	NR
20	7.15	1.5
21	< 10	3
22	10	4.79
23	13	1.248
24	< 25	1
25	NT	NT
26	<20	NR
27	12.0	1.1
28	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Robust Average</b>	8.7	3.2
<b>Median</b>	10.0	3.1
<b>Mean</b>	10.0	
<b>N</b>	12	
<b>Max</b>	32	
<b>Min</b>	3	
<b>Robust SD</b>	4.5	
<b>Robust CV</b>	52%	

Results: S3 - Sulphate

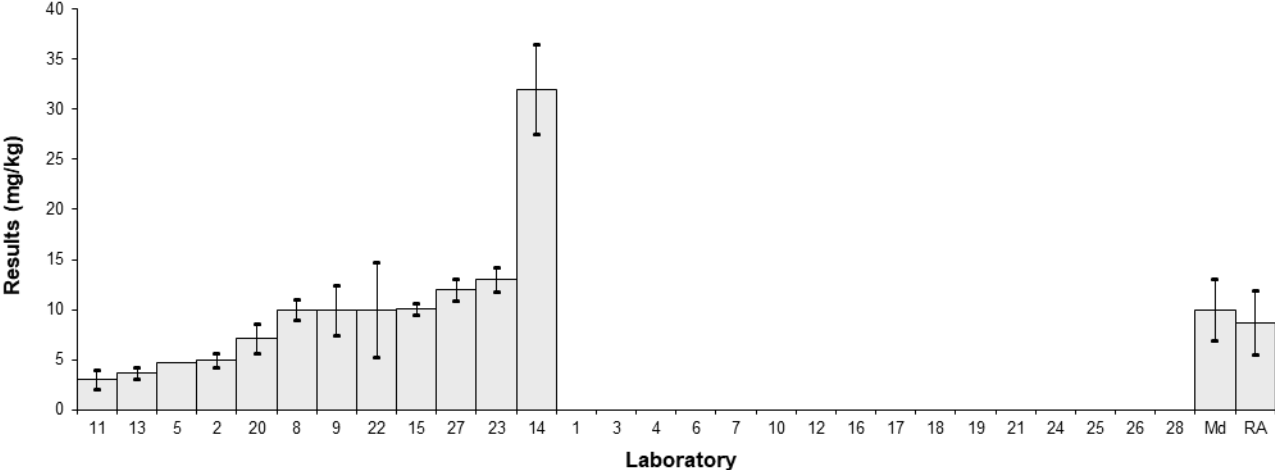


Figure 44

Table 53

**Sample Details**

<b>Sample No.</b>	S3
<b>Matrix</b>	Soil
<b>Analyte</b>	TKN
<b>Unit</b>	mg/kg

**Participant Results**

Lab. Code	Result	Uncertainty	z	E <sub>n</sub>
1	NT	NT		
2	1300	200	2.13	1.81
3	NT	NT		
4	720	300	-1.05	-0.62
5	NT	NT		
6**	0.642	0.0642	-5.00	-11.99
7	NT	NT		
8	860	154	-0.29	-0.30
9	704.2	42.4	-1.14	-2.39
10	NT	NT		
11	800	120	-0.61	-0.79
12	970	300	0.32	0.19
13	890	170	-0.12	-0.12
14	978	98	0.36	0.53
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	990	198	0.43	0.37
19	830	300	-0.45	-0.26
20	1060	200	0.81	0.69
21	NT	NT		
22	900	170	-0.07	-0.06
23	980	142.1	0.37	0.42
24	858.88	171.8	-0.29	-0.28
25	NT	NT		
26	1000	100	0.48	0.70
27	917.96	231.9	0.03	0.02
28	NT	NT		

\*\* Gross Error

**Statistics**

<b>Assigned Value</b>	912	76
<b>Robust Average</b>	912	76
<b>Median</b>	909	70
<b>Mean</b>	922	
<b>N</b>	16	
<b>Max</b>	1300	
<b>Min</b>	704.2	
<b>Robust SD</b>	120	
<b>Robust CV</b>	13%	

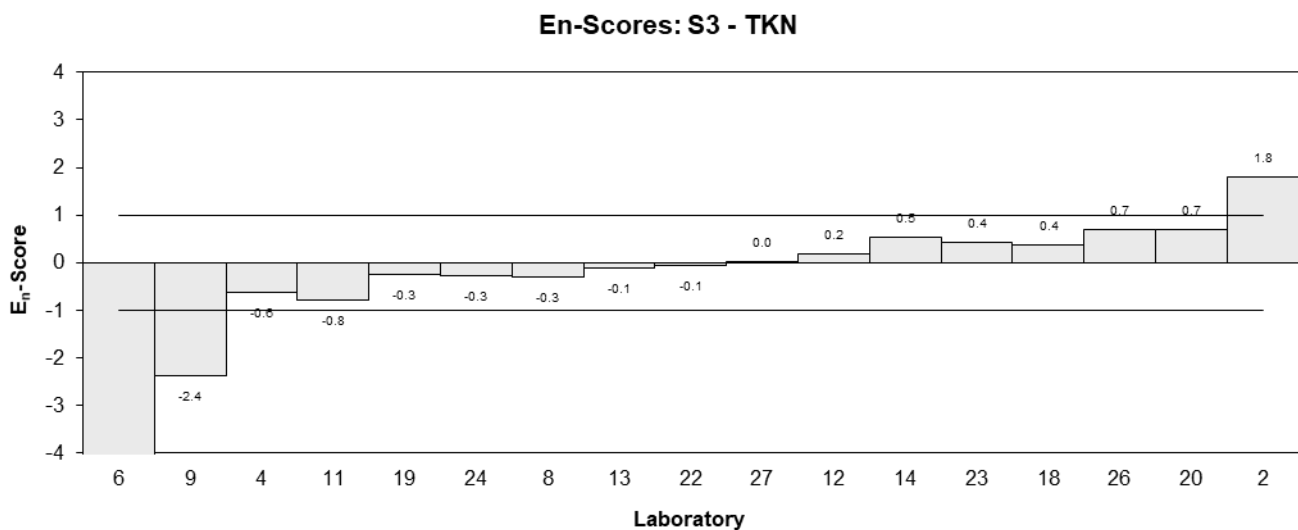
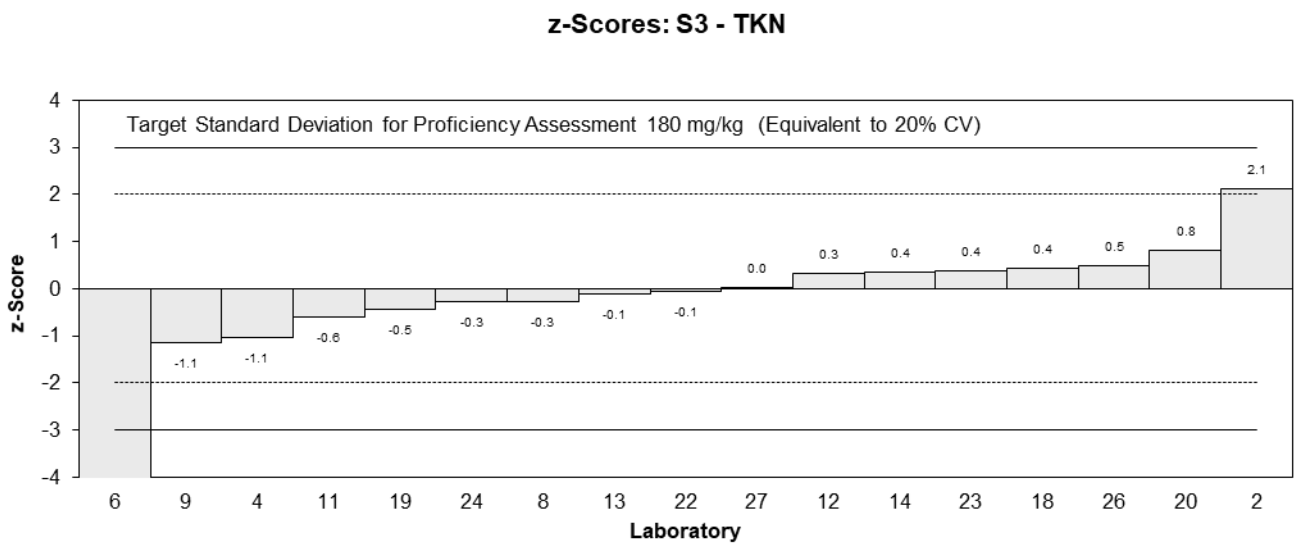
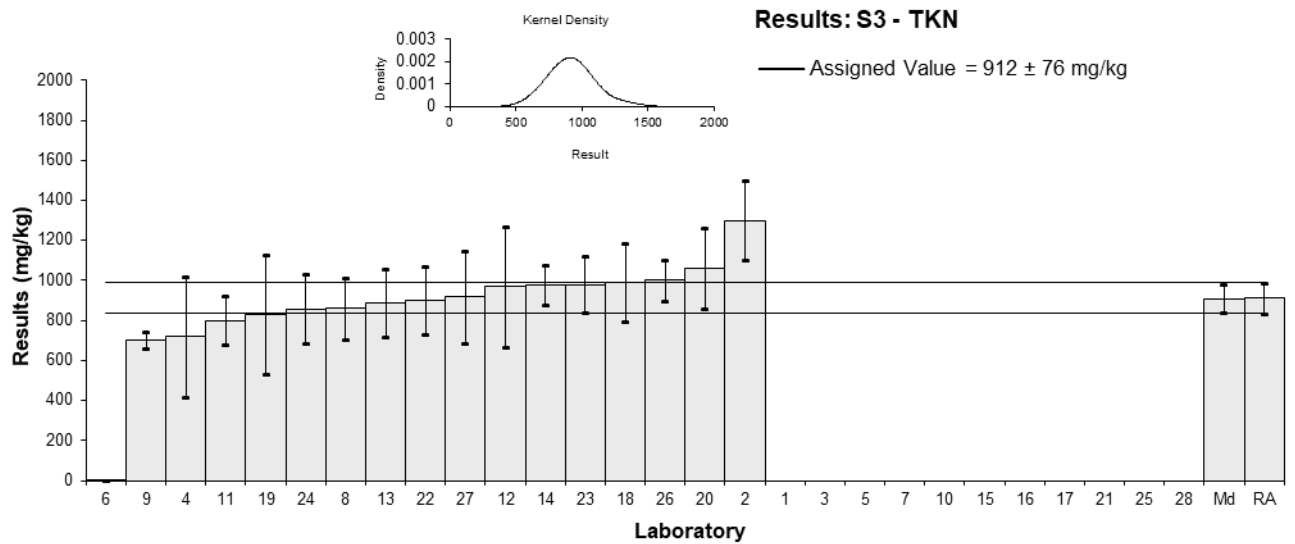


Figure 45

## 6 DISCUSSION OF RESULTS

### 6.1 Assigned Value and Traceability

**Assigned Values** were 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 investigated and then removed before calculation of the assigned value.<sup>6</sup> Appendix 2 sets out the calculation of the robust average of As in Sample S1 and its associated uncertainty.

No assigned value was set for Ag, Sb and Se in S1, Al, B and Li in S2 and chloride and sulphate in S3 because the reported results were too variable.

**Traceability** The assigned value is not traceable to any external reference; it is traceable to the consensus of participants' results deriving from a variety of measurement methods and (presumably) a variety of calibrators. So although expressed in SI units, the metrological traceability of the assigned values has not been established.

### 6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 789 numerical results, 738 (94%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.00007% to 377% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Tables 9 and 10.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.<sup>9 - 14</sup>

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 45). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 21 laboratories reported results for Mn in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 21 laboratories' results is 32 mg/kg (see equation 4, Appendix 2). If Laboratory 7 result is coming from one measurement then they might have under-estimated its expanded measurement uncertainties reported for Mn in S1 (0.74 mg/kg) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 21 measurements. Alternatively, estimates of uncertainties for As in S2 larger than 1.42 mg/kg (the uncertainty of the assigned value, 0.36 mg/kg plus the allowable variation from the assigned value, the target standard deviation of 0.54 mg/kg, multiplied by 2, the coverage factor for a confidence interval of 95%), should also be viewed as suspect. For example, the expanded measurement uncertainties reported by laboratory 12 for As in S2 (2 mg/kg) might have been over-estimated.

Laboratory 3 should review their calculation procedure for estimating measurement uncertainty as most of their uncertainties were very low.

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>10</sup> An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 3.

Laboratories 2, 17, 21, 22, 23 and 24 attached estimates of the expanded measurement uncertainty to results reported as “less than”. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.<sup>9</sup>

Laboratories 4, 12, 15, 19 and 28 reported estimates of expanded uncertainty for some of their measurement results equal or larger than the results themselves.

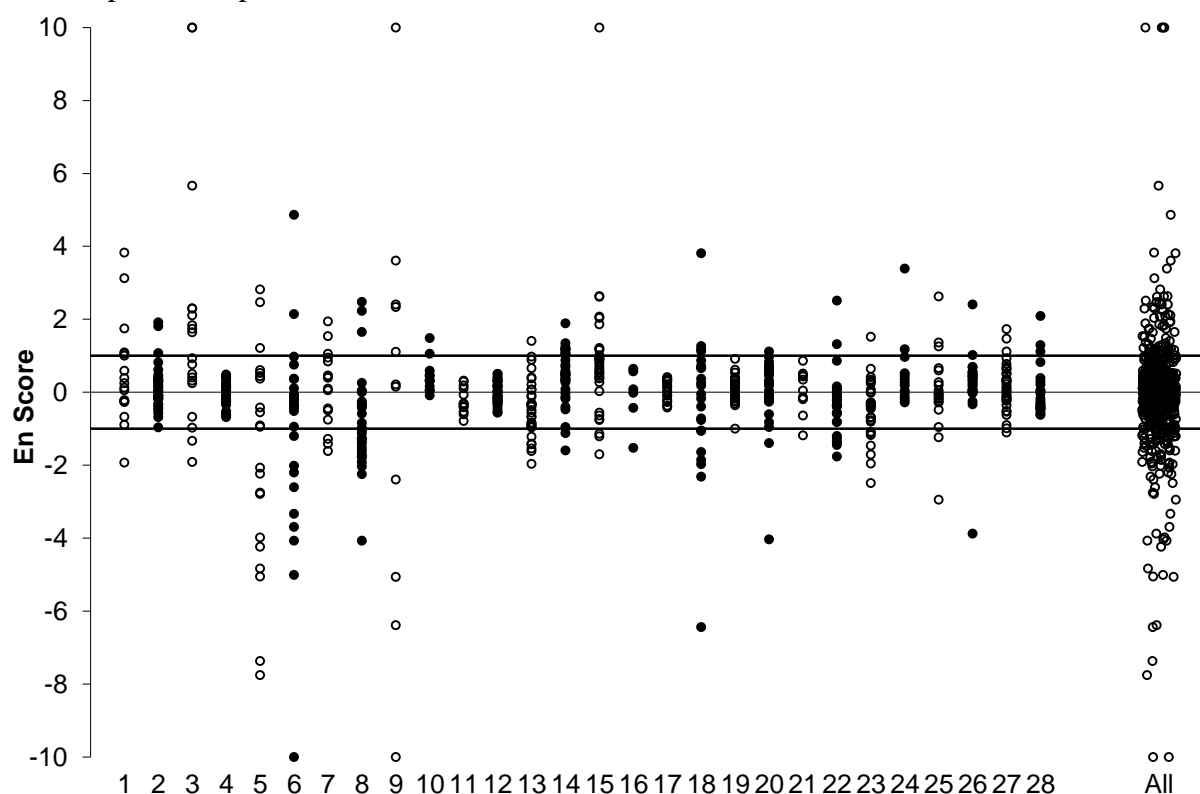
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of  $2495.52 \pm 374.33$  mg/kg, it is better to report  $2500 \pm 370$  mg/kg or instead of  $9910 \pm 1486.50$  mg/kg, it is better to report  $9910 \pm 1500$  mg/kg.<sup>9</sup>

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

E<sub>n</sub>-score can be interpreted 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 46. 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 669 results for which E<sub>n</sub>-scores were calculated, 508 (76%) returned a satisfactory score of  $|E_n| \leq 1.0$  indicating agreement of the participants’ results with the assigned values within their respective expanded measurement uncertainties.



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

Figure 46 E<sub>n</sub>-Score Dispersal by Laboratory

### 6.4 z-Score

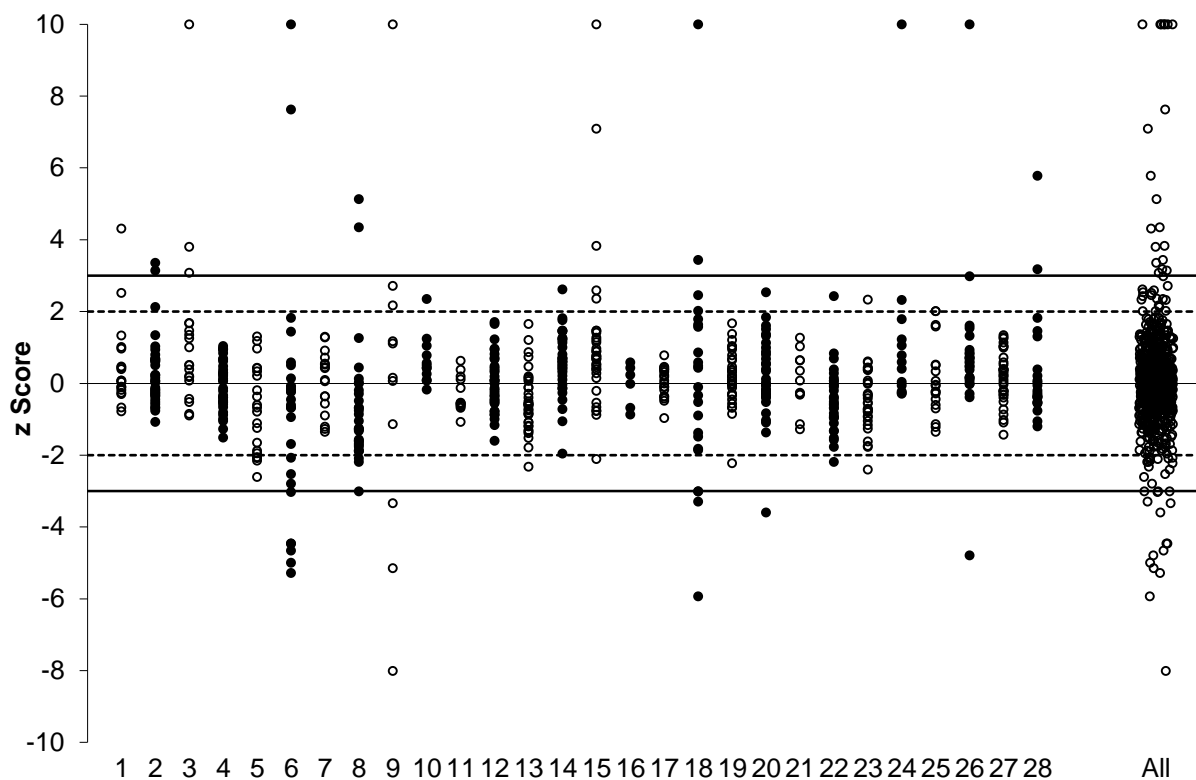
The z-score compares the participant’s deviation from the assigned value with the target standard deviation set for proficiency assessment.

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 3.5% to 25% PCV were used to calculate z-scores. Unlike

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

The between laboratory coefficient of variation predicted by the Thompson equation<sup>7</sup> and the participants' coefficient of variation resulted in this study are presented for comparison in Table 54.

The dispersal of participants' z-scores is presented in Figure 47 (by laboratory code) and in Figure 48 (by test). Of 669 results for which z-scores were calculated, 602 (90%) returned satisfactory score of  $|z| \leq 2.0$  and 31 (5%) were questionable of  $2.0 < |z| < 3.0$ . Participants with multiple z-scores larger than 2.0 or smaller than -2.0 should check for laboratory bias.



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

Figure 47 z-Score Dispersal by Laboratory

Summary of participants' reported results and performance is presented in Figure 49.

No Laboratories reported results for all analytes for which a z-score was calculated (36).

**Laboratory 27** returned the highest number of satisfactory z scores (34 out of 34 reported). All results reported by **laboratories 4, 12 (33), 17 (19), 7 (17), 11 (13), 21 (11) and 16 (6)** also returned satisfactory z scores.

All results reported by **laboratories 19 (34), 4 (33), 12 (33), 17 (19) and 11 (13)** returned satisfactory En scores.

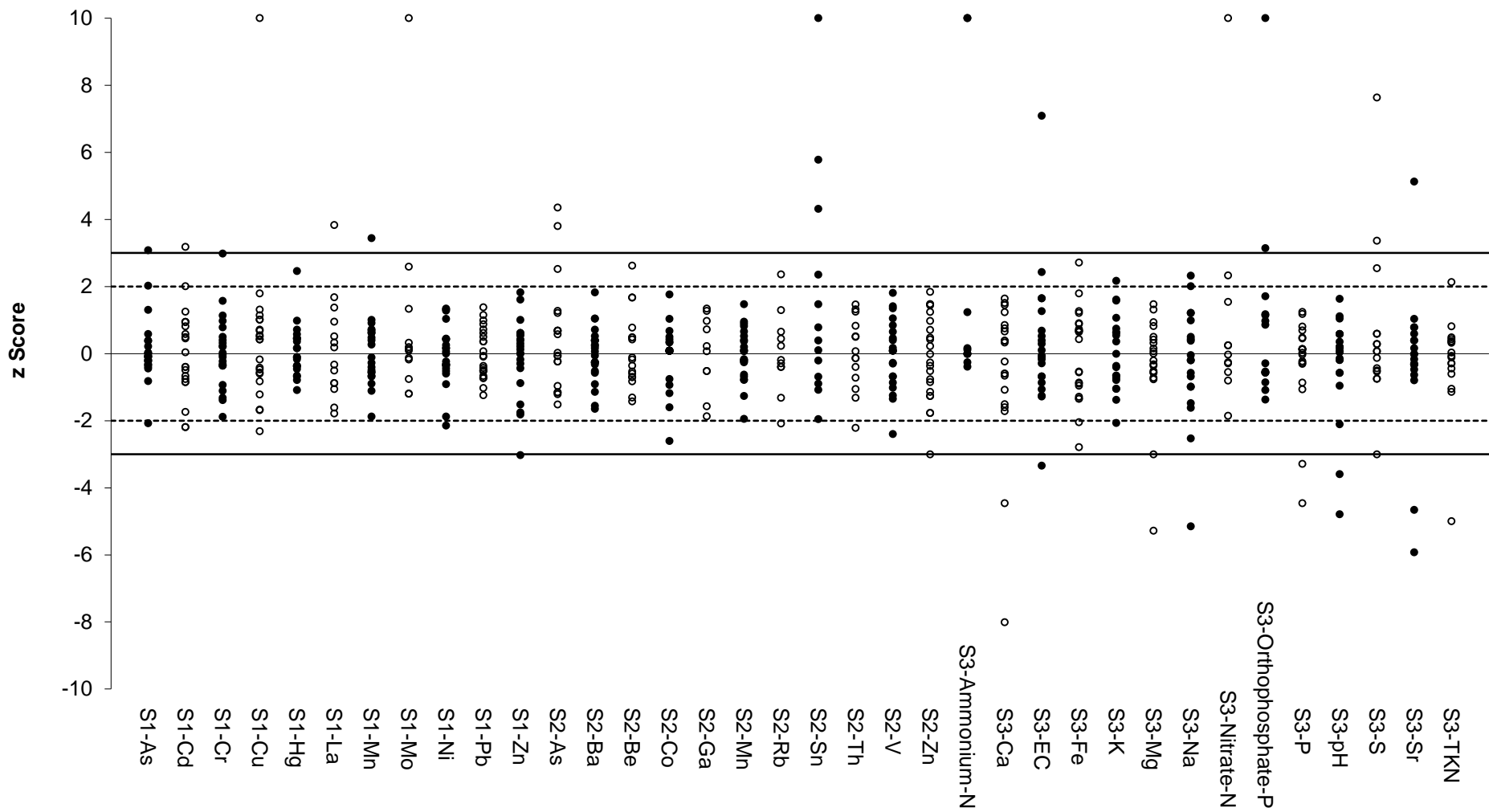
Table 54 Between Laboratory CV of this Study, Thompson CV and Set Target SD

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV*	Thompson/Horwitz CV	Target SD (as PCV)
S1	Ag	Not Set	37%	NA	Not Set
S1	As	56.8	7.8%	8.7%	15%
S1	Cd	1.49	20%	15%	15%
S1	Cr	34.9	15%	9.4%	15%
S1	Cu	33.6	12%	9.4%	10%
S1	Hg	2.44	9.9%	14%	15%
S1	La	5.48	14%	12%	10%

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Mn	678	8.6%	6%	10%
S1	Mo	0.79	20%	17%	20%
S1	Ni	51.7	8.2%	8.8%	10%
S1	Pb	91.1	13%	8.1%	15%
S1	Sb	Not Set	54%	NA	Not Set
S1	Se	Not Set	70%	NA	Not Set
S1	Zn	330	11%	6.7%	10%
S2	Al	Not Set	27%	NA	Not Set
S2	As	3.63	17%	13%	15%
S2	B	Not Set	49%	NA	Not Set
S2	Ba	154	8%	7.5%	10%
S2	Be	1.12	17%	16%	15%
S2	Co	11.9	6.6%	11%	10%
S2	Ga	6.7	26%	12%	20%
S2	Li	Not Set	36%	NA	Not Set
S2	Mn	347	7.5%	6.6%	10%
S2	Rb	23.9	24%	9.9%	20%
S2	Sn	1.02	28%	16%	20%
S2	Th	7.2	23%	12%	20%
S2	V	52.6	11%	8.8%	10%
S2	Zn	20.1	26%	10%	20%
S3	Ammonium-N	4.01	5.7%	13%	20%
S3	Ca	10600	13%	4%	10%
S3	Chloride	Not Set	54%	NA	Not Set
S3	EC	51.5 µS/cm	12%	8.8%	10%
S3	Fe	49100	21%	3.1%	15%
S3	K	782	12%	5.9%	10%
S3	Mg	19400	7.8%	3.6%	10%
S3	Na	423	21%	6.4%	15%
S3	Nitrate-N	1.91	24%	15%	20%
S3	Orthophosphate-P	1.40	29%	15%	25%
S3	P	898	8.4%	5.7%	10%
S3	pH	7.45	3%	12%	3.5%
S3	S	97.3	8.1%	8%	10%
S3	Sr	64.1	6.6%	8.6%	10%
S3	Sulphate	Not Set	52%	NA	Not Set
S3	TKN	912	13%	5.7%	20%

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





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

Figure 48 z-Score Dispersal by Test

### Summary of Participant's Performance in AQA 22-15 Samples S1, S2 and S3

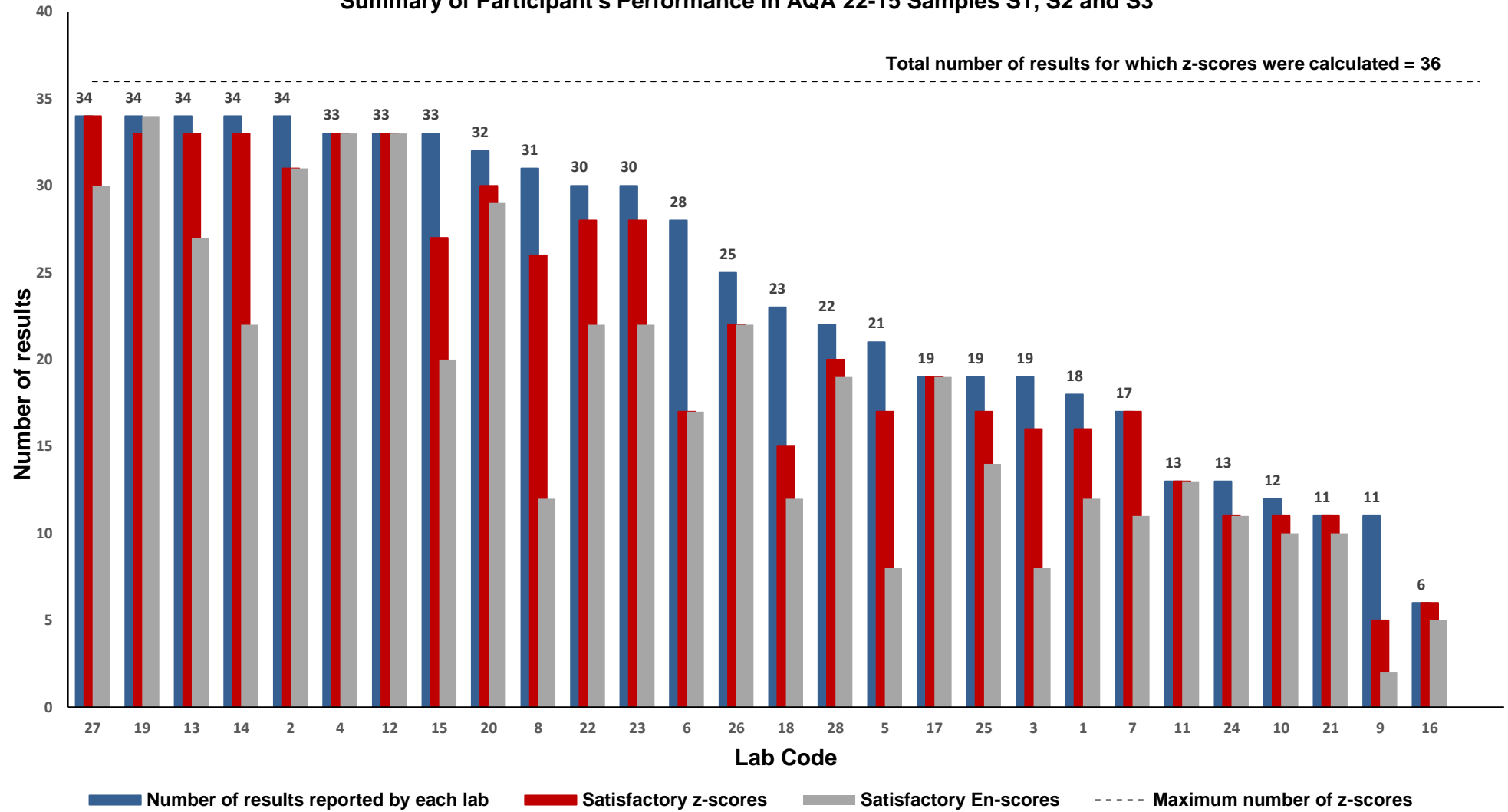


Figure 49 Summary of Participants' Performance

Table 55 Summary of Participants' Results and Performance in Sample S1

Lab Code	Ag (mg/kg)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	La (mg/kg)	Mn (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Se (mg/kg)	Zn (mg/kg)
A.V.	Not Set	56.8	1.49	34.9	33.6	2.44	5.48	678	0.79	51.7	91.1	Not Set	Not Set	330
H.V.	1.57	50.0	1.40	34.7	32.8	2.17	5.42	692	0.798	49.8	91	0.88	0.782	310
1	NR	56	1.5	37	37	2.4	NT	710	1.0	54.0	82	NT	1.3	320
2	1.5	53	1.7	35	33	2.5	5.3	720	0.67	57	98	0.59	0.69	350
3	1.0	83.0	1.3	37.5	35.3	NT	6.4	617	3.0	52.6	85.2	0.7	1.3	363
4	2	60	1.7	36	32	2.8	5	720	<1	53	84	<7	<2	340
5	0.94	39.1	1.34	29.1	31.6	2.15	NT	550.5	NR	40.6	74.1	NR	NR	337.0
6	1.006	55.18	1.620	33.67	27.93	2.377	NT	632.9	0.8125	49.39	89.92	1.109	0.732	230.1
7	1.12	67.9	1.59	33.0	31.7	2.31	NT	740	0.805	58.3	101	0.596	NR	348
8	<2	57	1	25	28	2.6	4.6	632	<2	42	84.4	<5	<5	272
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	2	54	1.7	33	35	2.7	5	640	<1	49	96	<7	<2	330
13	2.9	49.8	1.4	27.6	25.8	2.4	4.5	644	0.6	48.6	103	0.3	1.0	334
14	1.59	58.6	1.67	36.5	35.9	2.27	5.76	746	0.77	53.9	81.2	1.26	0.45	344
15	1.91	55.0	1.32	40.0	68.7	2.20	7.58	727	1.20	52.5	106.8	1.37	0	301
16	NT	NT	NT	NT	NT	2.19	NT	NT	NT	53.9	NT	NT	NT	NT
17	1.63	56.0	1.38	34.4	32.2	2.61	5.58	705	0.84	51.7	96	0.62	< 20	324
18	2.4	74	1.6	43.1	39.6	3.34	NT	911	< 2	50	84	< 2	3.98	270
19	2	60	1.3	39	37	2.5	6	670	<1	52	110	<7	<2	330
20	1.67	56.4	1.4	40.8	35.4	2.04	6.23	659	0.761	49.8	77	NT	0.637	348
21	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
22	<2	56	1	28	30.8	2.3	5.2	603	<2	47	92	<5	<5	280
23	1	54	1.1	30	35	2.6	NT	650	<1	50	81	<3	4	350
24	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
25	NT	54.802	1.9382	34.7018	29.50495	NT	NT	NT	<2	50.4642	90.1296	<5	NT	315.64055
26	<1	53.5	<1	50.5	36.0	2.65	NT	724.5	<5	58.5	99.5	NT	NT	383
27	0.948	61.78	1.77	33.24	37.43	2.57	5.662	696.55	0.82	58.61	104.67	0.655	0.809	343.35
28	2	57	2.2	36	38	2.3	4.9	640	0.6	50	86	2.8	0.53	390

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

Table 56 Summary of Participants' Results and Performance in Sample S2

Lab Code	Al (mg/kg)	As (mg/kg)	B (mg/kg)	Ba (mg/kg)	Be (mg/kg)	Co (mg/kg)	Ga (mg/kg)	Li (mg/kg)	Mn (mg/kg)	Rb (mg/kg)	Sn (mg/kg)	Th (mg/kg)	V (mg/kg)	Zn (mg/kg)
A.V.	Not Set	3.63	Not Set	154	1.12	11.9	6.7	Not Set	347	23.9	1.02	7.2	52.6	20.1
H.V.	24700	3.88	12.2	148	1.22	12.3	NA	11.5	375	30.6	1.18	7.82	58.3	25.2
1	18400	5.0	5.2	150	1.09	12	NT	NT	320	NT	1.9	NT	53	24
2	19000	3.5	NR	150	1.1	12	8.5	11	370	25	0.88	7.3	51	18
3	23100	5.7	15.2	146	1.4	12.0	NT	16.7	354	NT	1.1	9.0	59.7	26.0
4	18000	4	8	170	1.2	12	6	9	380	22	<1	7	57	15
5	25000	NR	NR	128.6	NT	8.8	NT	12.7	279.4	NT	NT	NT	NT	21.8
6	18330	3.586	5.716	182.0	1.019	10.78	NT	7.313	338.5	NT	36.06	7.922	49.03	25.89
7	14900	2.97	NR	155	NR	12.4	NT	6.70	365	NT	0.836	NT	45.5	15.0
8	10500	6	<50	130	<1	10	4.2	4.4	303	13.9	<5	5.3	46	8
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	27600	3.94	12.2	158	1.19	12.5	NT	13.0	350	NT	1.50	NT	58.1	25.1
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	17000	3	7	150	1.2	12	8	8	350	23	<1	7	53	17
13	19600	2.8	NR	145	0.9	10.5	6.8	8.0	325	22.5	0.8	6.17	48	16.7
14	24166	4.29	15.3	165	1.56	14.0	NT	12.7	398	NT	0.62	5.67	62.1	22.9
15	28368	4.0	9.0	160	1.25	12.70	8.4	14.0	378	35.2	1.32	7.93	60.0	26.0
16	NT	NT	NT	NT	NT	NT	NT	18	NT	NT	NT	NT	NT	NT
17	20600	3.1	< 20	157.5	1.06	12.0	NT	9.4	361	26.0	1.18	NT	< 100	18.6
18	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
19	18000	4	6	170	1.4	12	7	11	360	27	<1	4	55	20
20	26500	3.64	9.74	153	0.98	12.3	NT	12	341	NT	0.978	9.1	54.7	27.5
21	15039	4.32	< 10	149	< 2	12.0	NT	7.13	338	NT	< 10	NT	56.0	15.5
22	12800	<5	<50	160	<1	12	4.6	5.9	323	17.6	<5	8.4	49	13
23	13000	3	<5	140	1	12	NT	NT	320	NT	<3	NT	40	13
24	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
25	15177.2519	<3	4.6017	136.38895	1.00215	12.28975	NT	NT	349.40065	NT	<5	NT	51.11685	NT
26	20800	<25	<5	156.5	<1	12	NT	12	375.5	NT	<50	NT	53.5	22
27	16022	3.5	8.68	161.95	0.88	13.12	7.66	7.56	340.11	30.09	1.04	6.63	47.23	20.97
28	20000	3.6	19	160	1.03	11	6	13	340	22	2.2	9.3	53	19

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

Table 57 Summary of Participants' Results and Performance for Sample S3

Lab Code	Ca (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)	P (mg/kg)	S (mg/kg)	Sr (mg/kg)
A.V.	10600	49100	782	19400	423	898	97.3	64.1
H.V.	11100	50000	850	18900	502	930	113	64.3
1	NT	NT	NT	NT	NT	NT	NT	NT
2	11300	54200	730	18700	NR	970	130	63
3	NT	NT	NT	NT	NT	NT	NT	NT
4	9000	54000	730	19000	360	910	98	62
5	10950	34000	753.2	21940	450.1	1004	NT	NT
6	5870	28520	620.1	9162	262.3	497.8	171.5	34.25
7	NT	NT	NT	NT	NT	NT	NT	NT
8	8780	39600	700	19400	380	910	90	97
9	2110.5	69063.5	951.7	19535.5	96.02	NR	NT	NT
10	NT	52300	NT	NT	NT	NT	NT	69.1
11	11000	45100	831	18300	386	802	96	60
12	8900	54000	720	21000	360	820	93	61
13	9460	39200	840	18300	500	940	90	65.1
14	12134	58349	831	22246	455	1009	103	67.9
15	11400	55700	824	17900	500	938	100	66.63
16	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	NT	NT	NT	NT	NT	NT	NT
18	12340	42440	674	13560	329	603	68.0	26.1
19	9900	58000	810	20000	420	870	98	62
20	12200	55600	908	18400	486	909	122	62.2
21	NT	53840	NT	NT	NT	873	NT	70.7
22	9960	42000	750	19700	410	960	100	64
23	11000	45000	700	18000	320	900	92	59
24	11900	62300	865	20200	570	877	103	69.1
25	9960.5887	39127.93265	905.27755	20368.88415	550.4352	NT	NT	NT
26	11500	54500	781	21200	447	911	<100	64
27	10348	42693	724.7	18770	410.0	895.2	92.3	66.58
28	NT	NT	NT	NT	NT	NT	NT	NT

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

Table 58 Summary of Participants' Results and Performance for Sample S3 (continued)

Lab Code	Chloride (mg/kg)	Sulphate (mg/kg)	Orthophosphate-P (mg/kg)	pH	EC (µS/cm)	TKN (mg/kg)	Nitrate-N (mg/kg)	Ammonium-N (mg/kg)
A.V.	Not Set	Not Set	1.40	7.45	51.5	912	1.91	4.01
H.V.	4	3.78	1.15	7.35	50.8	NA	NA	NA
1	NT	NT	NT	NT	NT	NT	NT	NT
2	3.4	4.9	2.5	7.3	46	1300	2.0	<30
3	NT	NT	NT	NT	NT	NT	NT	NT
4	<10	<10	<2	7.3	53	720	1.6	3.7
5	5.1	4.7	1.74	7.4	NR	NT	NT	NT
6	NT	NT	NT	NT	NT	0.642	NT	NT
7	NT	NT	NT	NT	NT	NT	NT	NT
8	<10	10	1.1	7.4	58	860	NT	NT
9	1.30	10.0	1.81	7.74	34.3	704.2	16.68	4.14
10	NT	NT	NT	7.47	50.6	NT	NT	NT
11	4	3	NT	7.5	48	800	1.7	4.1
12	<10	<10	2	7.5	60	970	NT	5
13	4.6	3.7	1.2	7.5	60	890	NT	NT
14	20	32	1.8	7.41	52	978	1.9	3.8
15	10	10.1	1.21	6.9	88	NT	NT	NT
16	7	NT	NT	7.6	47	NT	2	4
17	NT	NT	NT	NT	NT	NT	NT	NT
18	NT	NT	1.7	7.6	51	990	1.2	17
19	<10	<10	1.2	7.5	48	830	1.8	4
20	5.92	7.15	0.92	6.51	55	1060	NT	NT
21	< 5	< 10	< 10	7.54	44.9	NT	NT	< 5
22	<10	10	1.2	7.2	64	900	NR	NR
23	8	13	1.3	7.6	45	980	2.8	4
24	< 5	< 25	< 5	7.46	51.2	858.88	1.81	12.18
25	NT	NT	NT	7.875	54.2	NT	NT	NT
26	10.4	<20	5.55	6.2	50	1000	2.5	<5
27	8.92	12.0	1.02	7.72	53.5	917.96	NT	NT
28	NT	NT	NT	NT	NT	NT	NT	NT

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

## 6.5 Participants' Results and Analytical Methods for Acid Extractable Elements

A summary of participants' results and performance is presented in Tables 55 to 58 and in Figures 46 to 49.

Low level Ag, Sb and Se in S1 and Al, B and Li in S2 were the analytes which presented most analytical difficulty to participating laboratories. No agreement was found between the results reported for these tests, with the between laboratory CVs varying from 27% to 70%.

Cobalt in S2 was the test which presented the least analytical difficulty to participating laboratories, with a between laboratory CV of 6.6 %.

All unsatisfactory results reported by Laboratory 6 in S3 for acid extractable elements were either lower or higher than the assigned value by the same factor of approximately 0.5 and 2 respectively. This laboratory should check their dilution and/or standard preparation procedure. The results reported by this laboratory were not included in the analyses of extraction methods and of instrumental techniques employed by participants for acid extractable elements in S3.

The method descriptions provided by participants for acid extractable elements are presented in Tables 1 and 7 and instrumental conditions are presented in Appendix 4.

### Extraction Methods

The request was for acid extractable elements; NMI PT studies of metals in soil focus on 'pseudo-total' analyses of elements in soil rather than on true total metal content because when an assessment of the anthropogenic impact of the metal content in a soil sample is made, aggressive digestion regimes (HF, high digestion temperature) can lead to misleading conclusions – since metals can be extracted from the fraction naturally present in the soil matrix.<sup>5, 15-18</sup> While an aggressive digestion regime can produce high, misleading results, weak digestion regimes (low digestion temperature, reduced digestion time, diluted acids and/or a low ratio of acid to sample size) may extract just a fraction of the contaminants from the soil. There is no standardisation of methods for acid extractable elements. In general methods are conventionally defined by procedures involving extractions: with aqua regia or with various amounts of HNO<sub>3</sub>, HCl, in combination or alone and most of these methods produce comparable results.<sup>19-21</sup>

In the present study, laboratories used various digestion regimes. Laboratory 8 extracted their sample at 85°C for 60 min while Laboratory 3 used a digestion temperature of 180°C for 15 min.

Some laboratories used a small sample size (0.1 g). Caution should be exercised when a small sample size is used for analysis as this might not be representative of the whole sample.

Laboratory 24 used an extraction regime involving diluted HNO<sub>3</sub> and HCl, and no hydrogen peroxide. The weak acid extraction method they employed might have facilitated extraction only of a fraction of the contaminants from the study samples. Most of the results reported by this laboratory for acid extractable elements were lower than the assigned values. According to Eurachem/CITAC Guide CG4, laboratories should consider using matrix matched control samples to assess their digestion regime (the bias of their analytical methods). Bias can be expressed as recovery and should be corrected for or included in the uncertainty estimate.<sup>9</sup>

### Individual Element Commentary

**Aluminium** is an element which is strongly dependent on digestion regime. The wide variety of extraction regimes employed by participants may explain the large variation in reported results. The between-laboratory CV was high at 27% and hence no assigned value could be set. There was no evident relationship between results and instrumental technique used (Figure 50).

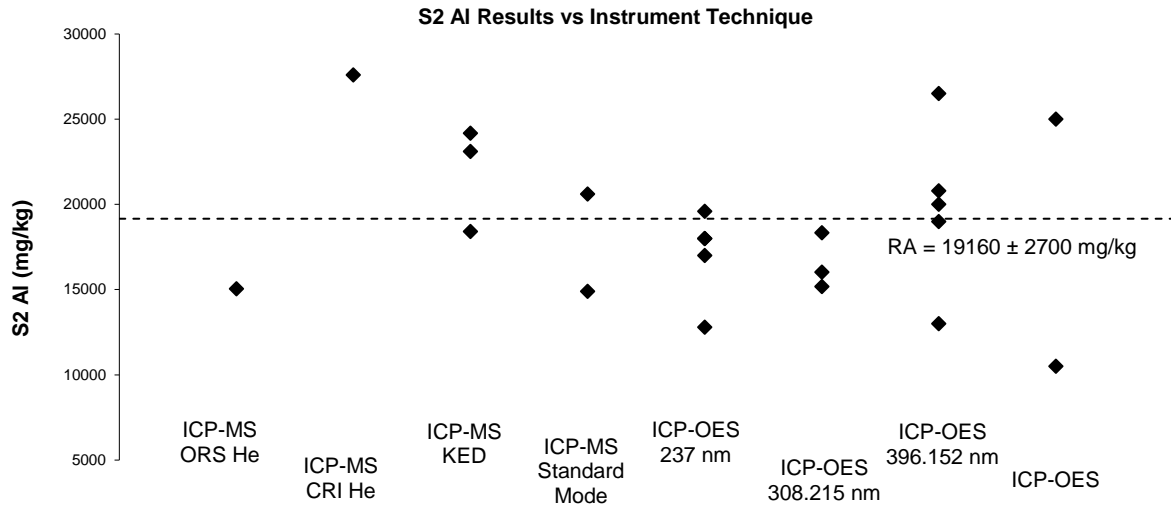


Figure 50 S1-Al z-Results vs. Instrumental Technique

\*RA=Robust average

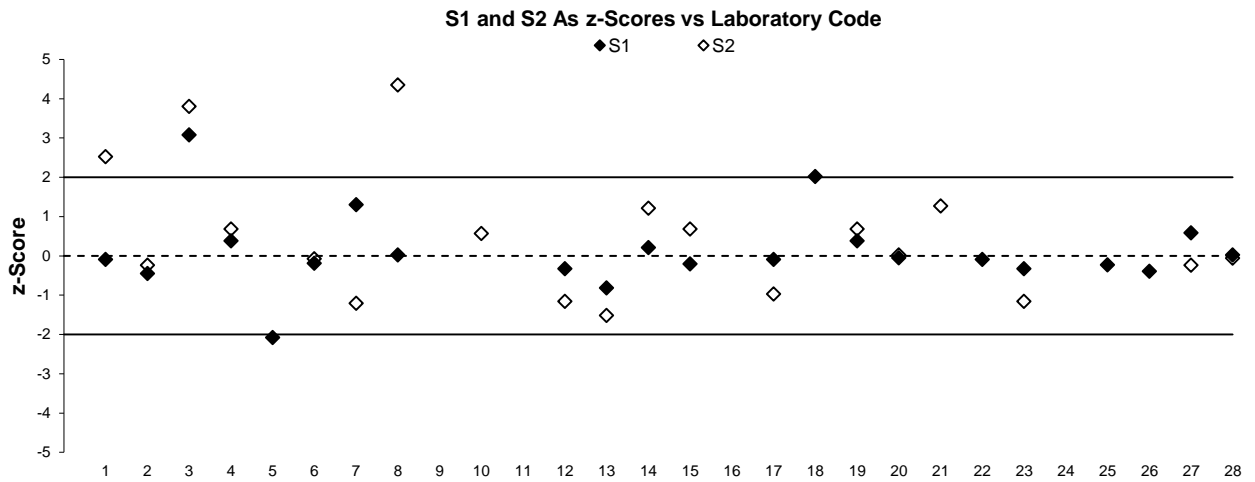


Figure 51 S1 and S2 As z-Scores vs. Laboratory Code

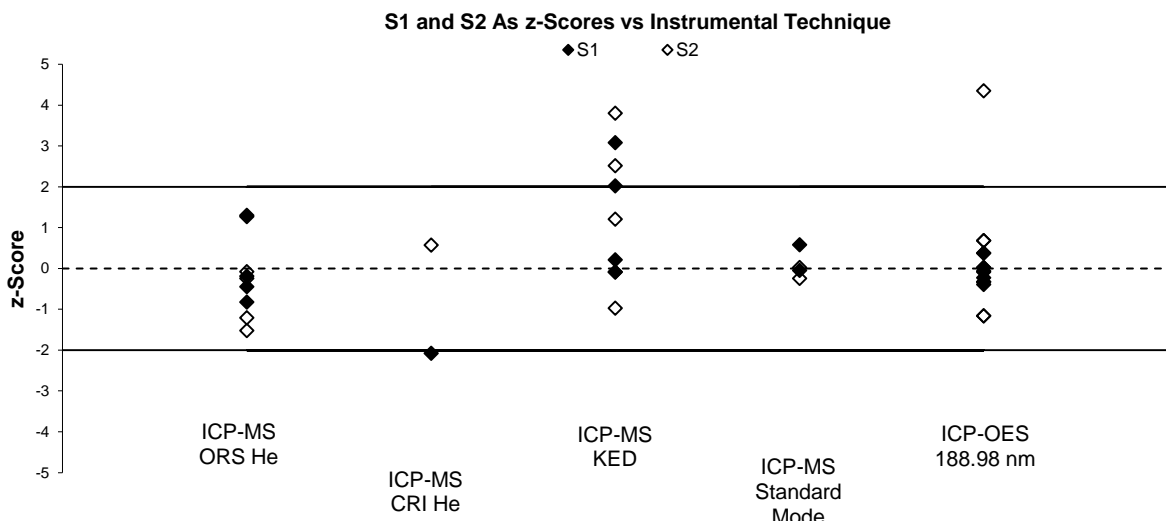


Figure 52 S1 and S2 As z-Scores vs. Instrumental Technique

**Arsenic** level in S1 was 56.8 mg/kg and in S2 was 3.63 mg/Kg. Laboratory 3 should review their procedure used for As measurement in soil as the results they reported returned high unsatisfactory z-scores in both study samples (Figure 51).



Plots of participants' performance versus instrumental techniques used for As measurements in S1 and S2 are presented in Figure 52. Most participants used ICP-MS in collision mode.

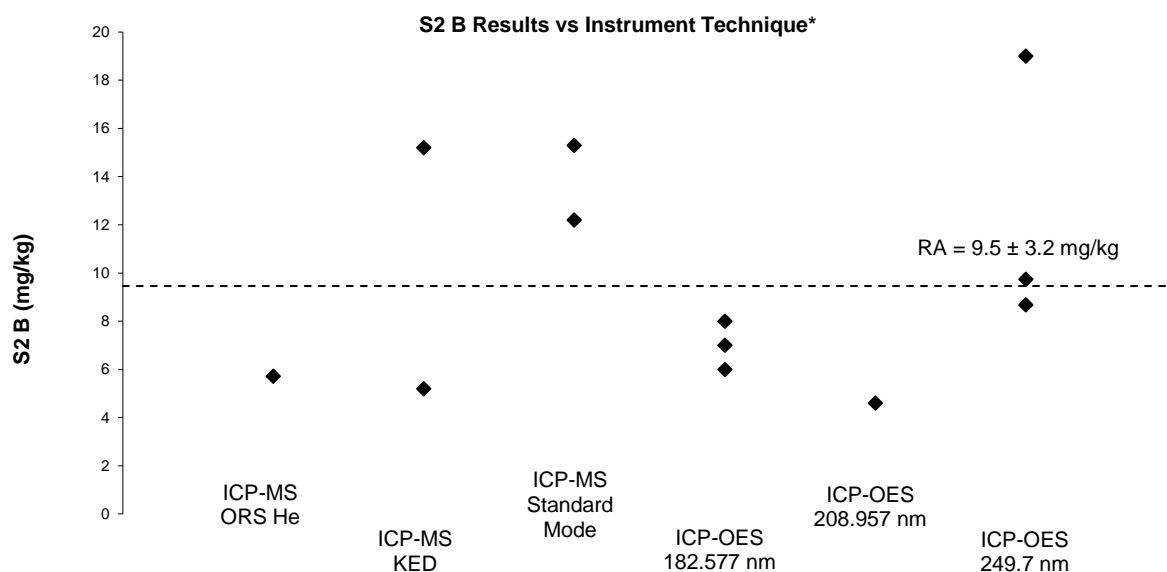
**Antimony** level in the soil sample S1 was low, close to 1 mg/kg. This may have contributed to the variability of participants' results, with the between-laboratory CV being 54%.

Antimony is an element whose recovery strongly depends on the acids employed for digestion. It is known that in nitric acid only, Sb is transformed in a mixture of insoluble oxides ( $Sb_2O_3$ ,  $Sb_2O_5$ ,  $Sb_4O_4(OH)_2(NO_3)_2$ ) but when hydrochloric acid is also involved it changes into chloro-complexes ( $SbCl_6^-$ ). In aqueous solution, sufficient hydrogen ion concentration must be maintained in order to prevent  $SbCl_6^-$  hydrolysis.<sup>22-24</sup> Laboratories should consider using matrix matched control samples to assess their digestion regime and increase their estimates of uncertainty for Sb measurements in soil.

All participants but one reported using ICP-MS for Sb measurement. Laboratory 28 used ICP-OES with a wavelength of 206.834 nm. ICP-OES might not be the right instrumental technique for low-level Sb measurement in soil.

**Boron** level in Sample S2 was low, which may have presented difficulty to some laboratories. The between-laboratory coefficient of variation was high (49%) and hence no assigned value could be set for this element. Boron is an element prone to contamination; the sampling system should be cleaned prior to determination of low-level B.

Caution should be exercised when ICP-OES with wavelength 249.7 nm is used for B measurement without correction equation. Iron line 249.771 nm has direct overlap interference on B line 249.7 nm. Plots of participants' results versus instrumental technique used are presented in Figure 53.



\*RA=Robust average

Figure 53 B Results vs. Instrumental Technique

**Cadmium** results from ICP-OES measurements were variable. Cadmium level in S1 may be too low for accurate determination by ICP-OES.

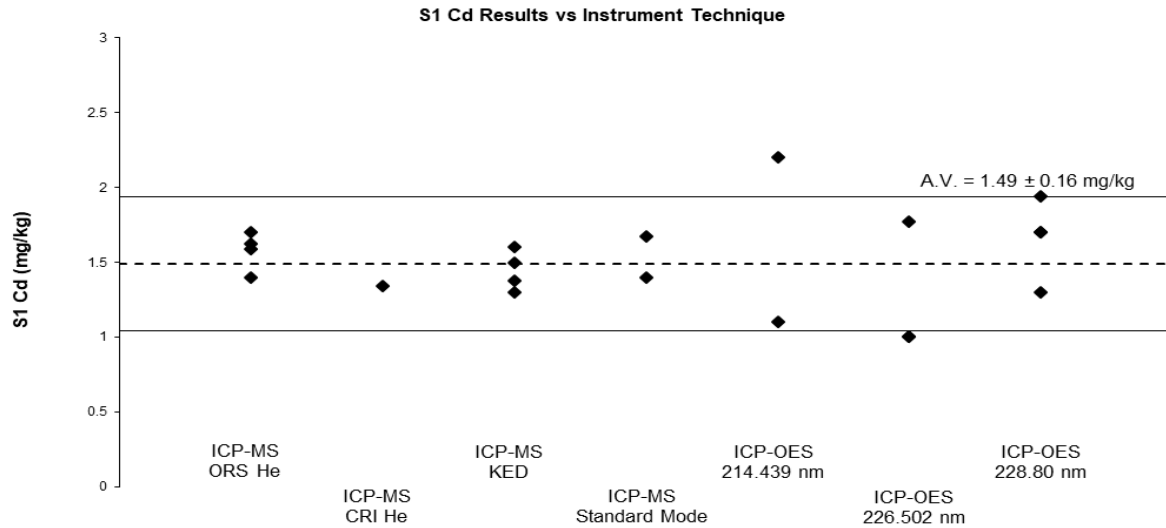


Figure 54 Cd Results vs. Instrumental Technique

**Mercury** Participants used a wide variety of instrumental techniques for Hg measurement in S1, however the results produced were in an excellent agreement with each other. CVAAS was the most popular instrumental technique used (Figure 55).

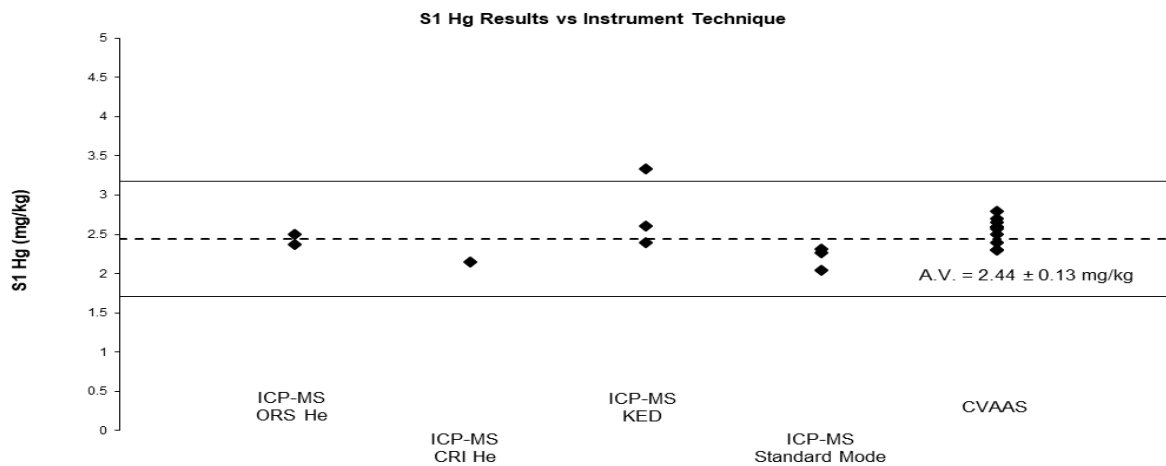
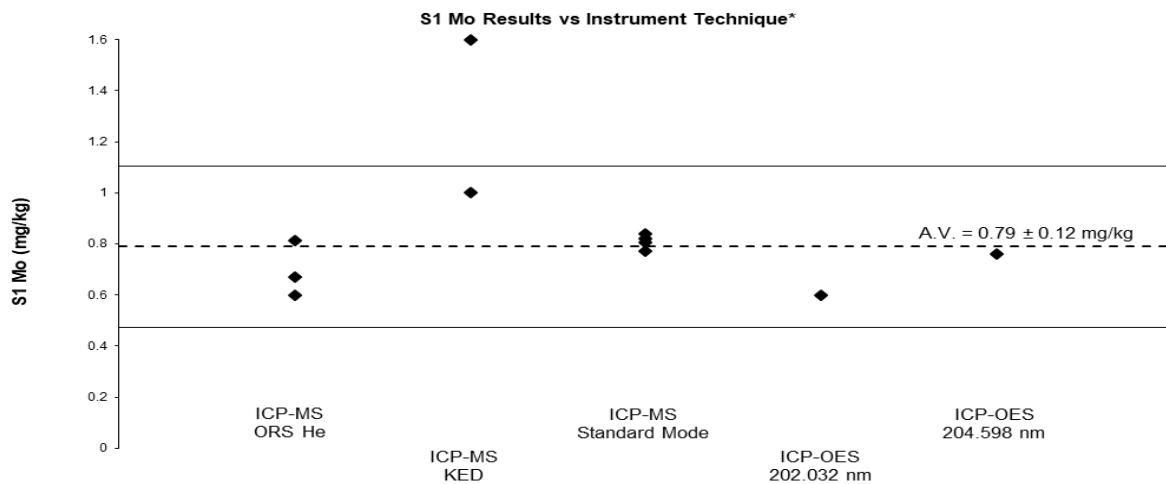


Figure 55 S1 Hg Results vs. Instrumental Technique



\*Laboratory 3 result of 3 mg/kg has been plotted as 1.6 mg/kg.

Figure 56 S1 Mo Results vs. Instrumental Technique

**Molybdenum** level in S1 was low at 0.79 mg/kg. Nine participants reported results from ICP-MS measurements and two from ICP-OES measurements. All reported results returned satisfactory z-scores, except for two.

**Iron and Sodium** Plots of Fe and Na results versus instrumental technique are presented in Figures 57 and 58. ICP-OES was the preferred analytical technique.

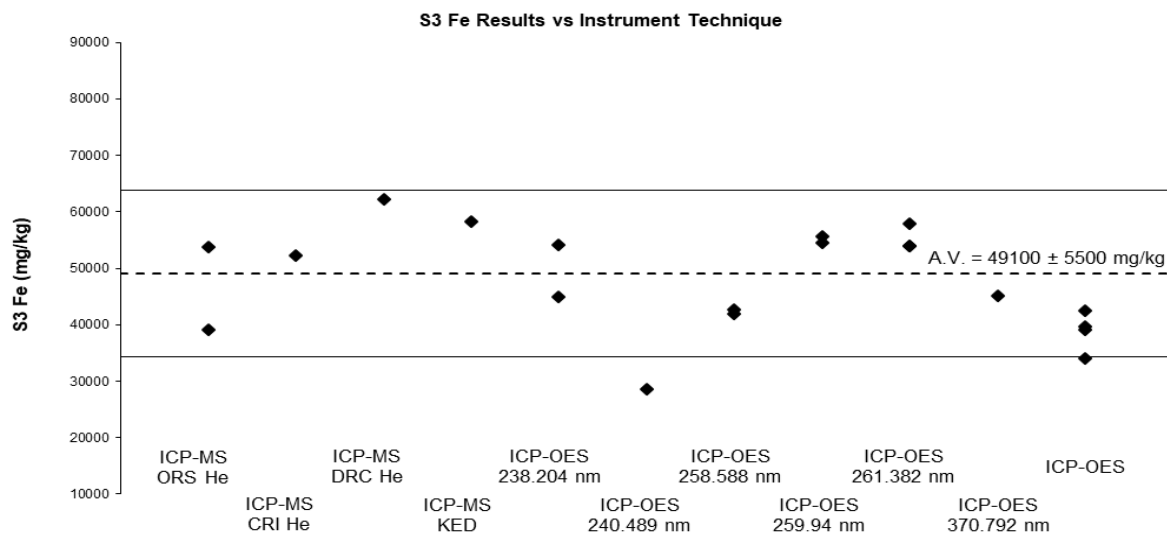


Figure 57 S3 Fe Results vs. Instrumental Technique

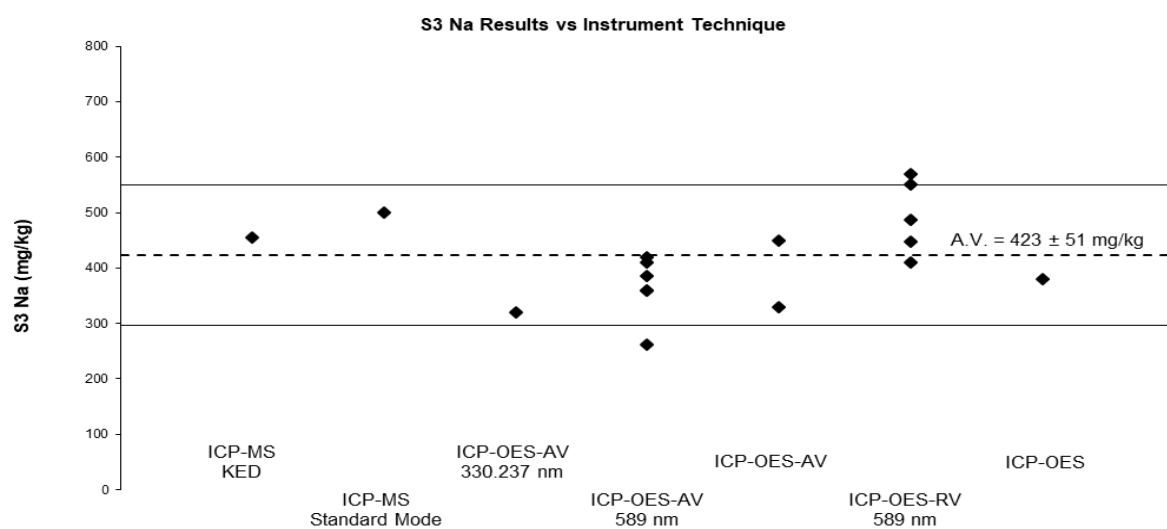
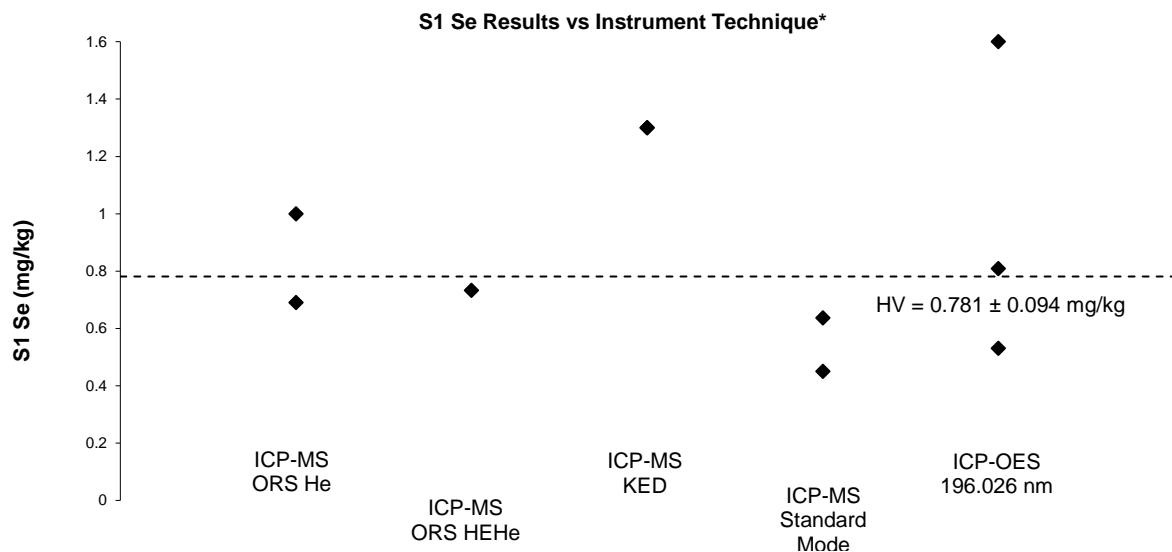


Figure 58 S3 Na Results vs. Instrumental Technique

**Lithium** The between-laboratory CV for this element was large at 36%. ICP-MS has low sensitivity for light elements due to space-charge effects. An internal standard with similar behaviour may overcome this problem.

**Selenium** level in S1 was low and challenged participants' instrumental techniques, returning a between-laboratory CV of 70%.

Plots of participants' results versus instrumental techniques used are presented in Figure 59

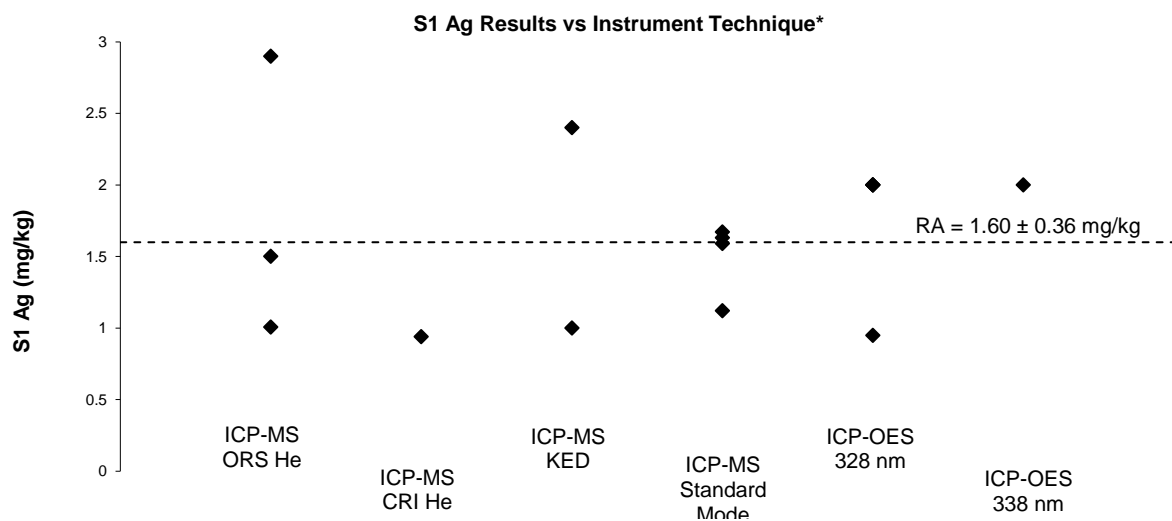


\*HV= Homogeneity value

Figure 59 S1 Se Results vs. Instrumental Technique

**Silver** level in S1 was low; the robust average was 1.60 mg/kg and homogeneity value was 1.57 mg/kg, which challenged participants' analytical techniques. The results reported by participants were not compatible with each other, with a CV of 37%, and no assigned value was set.

Plots of participants' results versus instrumental techniques used are presented in Figure 60.

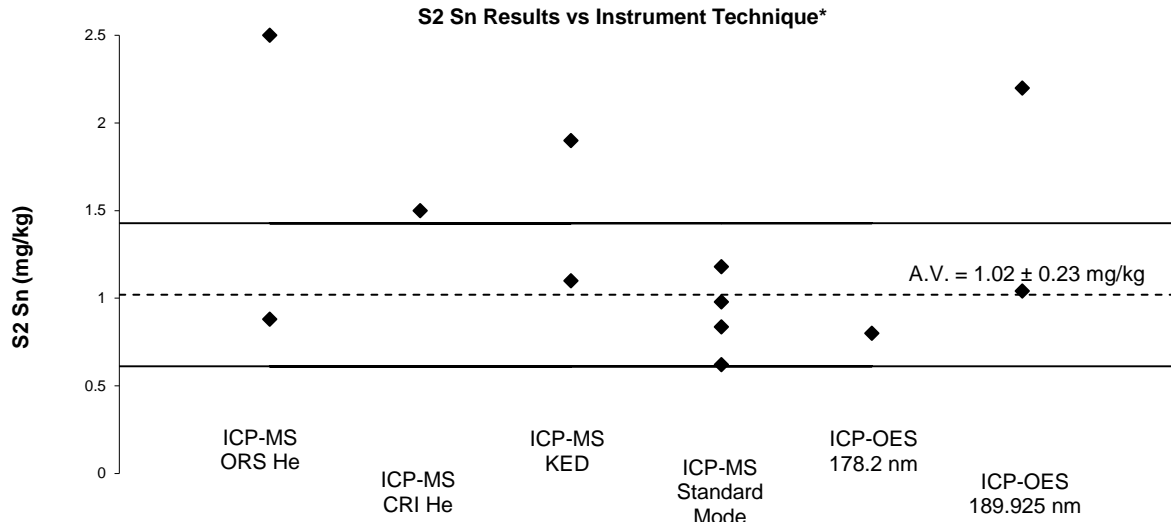


\*RA= robust average.

Figure 60 S1 Ag Results vs. Instrumental Technique

**Tin** Figure 61 presents Sn results versus instrumental techniques used. Most participants used ICP-MS in standard mode.

**Zinc** z-scores versus laboratory code are presented in Figure 62, and z-scores versus instrumental technique are presented in Figure 63. Most participants in the two study samples used ICP-OES with wavelength 206.2 nm for Zn measurement.



\*Laboratory 6 result of 36.06 mg/kg was plotted as 2.5 mg/kg.

Figure 61 S2 Sn Results vs. Instrumental Technique

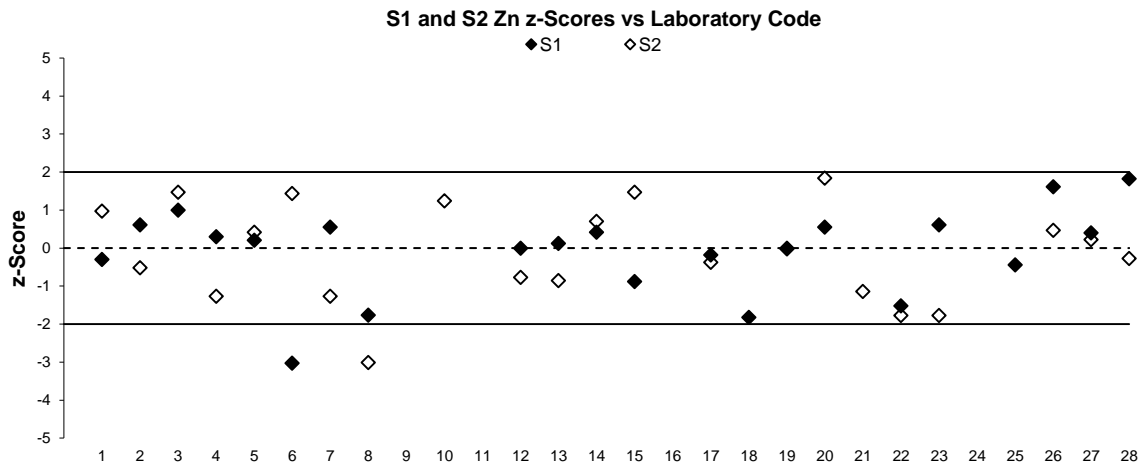


Figure 62 S1 and S2 Zn z-Scores vs Laboratory Code

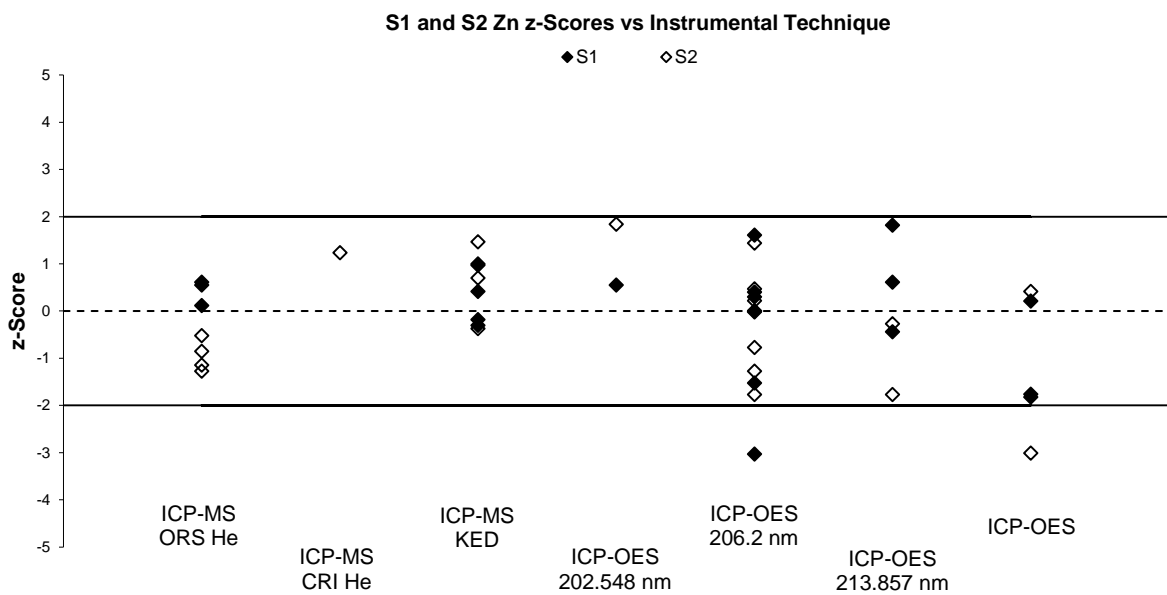


Figure 63 S1 and S2 Zn z-Scores vs Instrumental Technique

## 6.6 Participants' Results and Analytical Methods for 2M KCl Extractable Ammonium-N and Nitrate-N

Mineral nitrogen components, ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ), are of particular interest when soil fertility is assessed. While water can extract  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N from a majority of soils,  $\text{NH}_4^+$ -N has to be displaced by another cation when the surface soil colloids are negatively charged.<sup>25</sup>

The participating laboratories were asked to analyse the sample using their normal measurement technique, but to follow the preparation procedure for the soil extract which involved: a soil/2M KCl ratio of 1:10 and a mixing time of one hour.

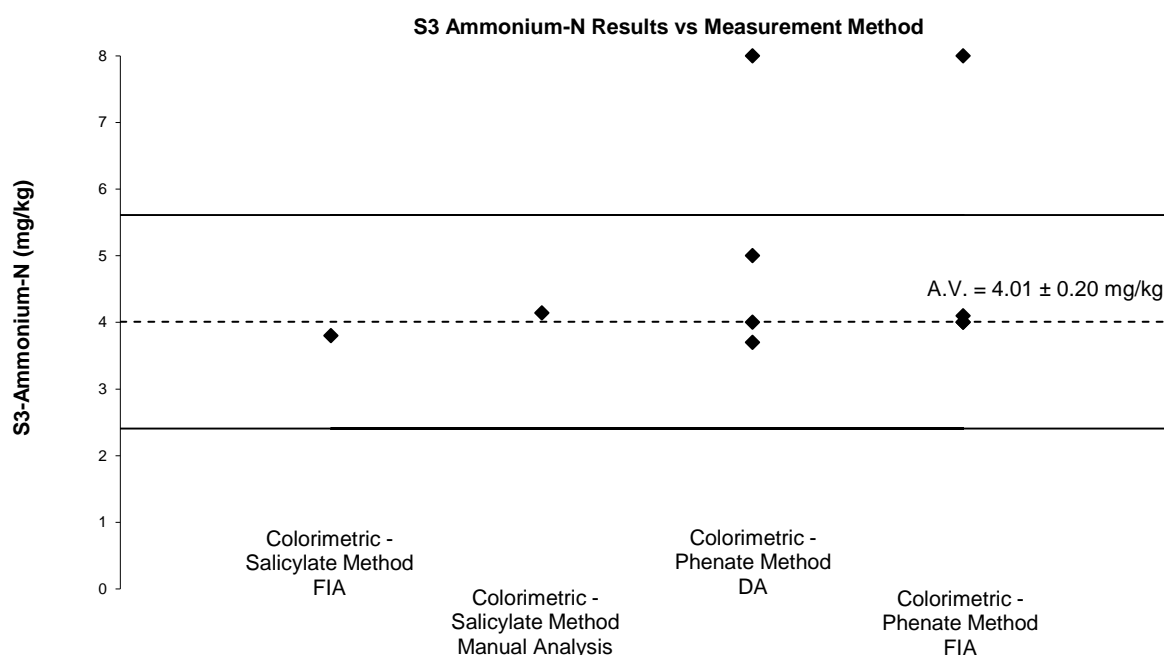
The method descriptions provided by participants are presented in Table 3. All but 4 participants used a soil/2M KCl ratio of 1:10.

**2M KCl Extractable Ammonium-Nitrogen** Plots of participants' results versus the analytical methods and instrumental technique used are presented in Figure 64.

Incorrect dilution factors may explain some of the unsatisfactory ammonium-N results.

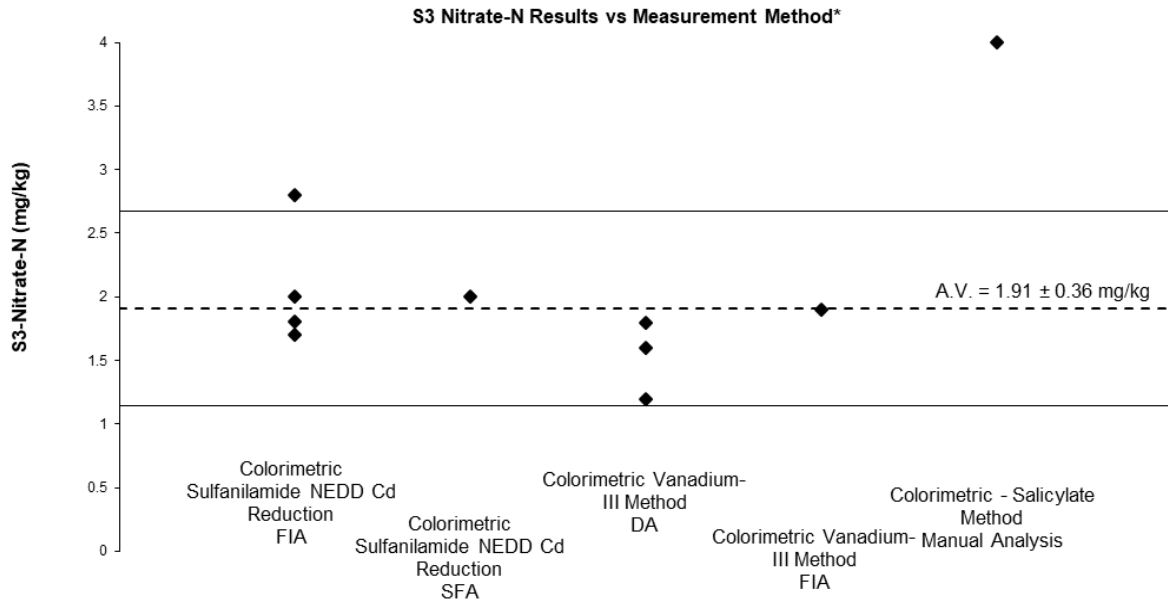
**2M KCl Extractable Nitrate-Nitrogen** The measurement method used by most laboratories involved  $\text{NO}_3^-$ -N reduction to  $\text{NO}_2^-$ -N by passage of the clarified soil extract through a Cd-Cu reduction column followed by  $\text{NO}_x$  (the reduced  $\text{NO}_2^-$ -N plus original  $\text{NO}_2^-$ -N) measurements.  $\text{NO}_x$  was determined colorimetrically based on Griess-Ilosvay reaction and  $\text{NO}_3^-$ -N calculated by subtracting  $\text{NO}_2^-$ -N value (obtained by analysis without passing the sample through the Cd-Cu reduction column), from the  $\text{NO}_x$  value.

Four laboratories used trivalent V for  $\text{NO}_3^-$ -N reduction to  $\text{NO}_2^-$ -N (Figure 65).



\*Laboratories 18 and 24 results of 17 mg/kg and 12.18 mg/kg have been plotted as 8 mg/kg.

Figure 64 S3- $\text{NH}_4^+$ -N Results vs. Analytical Method and Measurement Technique



\*Laboratory 9 result of 16.68 has been plotted as 4 mg/kg.

Figure 65: S3-NO<sub>3</sub><sup>-</sup>-N Results vs. Measurement Technique

### 6.7 Participants' Results and Analytical Methods for Total Kjeldahl Nitrogen

TKN assigned value was 912 mg/kg. Of 17 results reported for TKN in S3, only two returned an unsatisfactory z-score. Plots of participants' results versus analytical method and measurement technique used are presented in Figure 66.

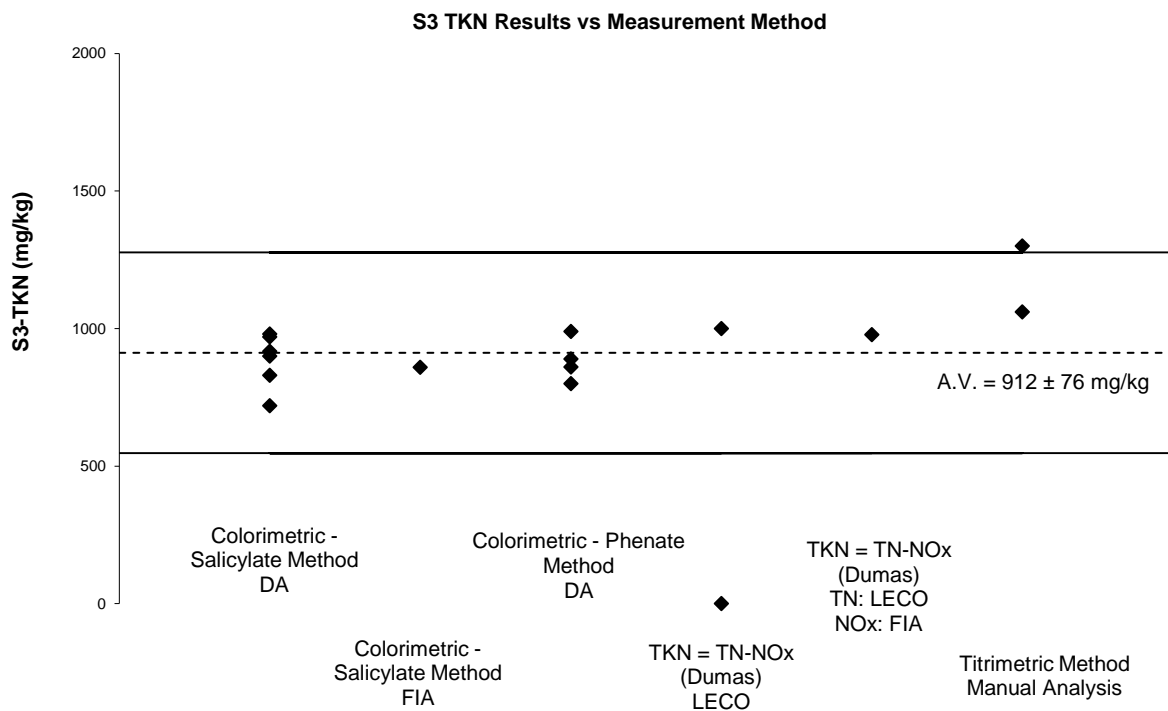


Figure 66 S3-TKN Results vs. Measurement Technique

## 6.8 Participants' Results and Analytical Methods for Water Soluble Anions

Measurement of water soluble anions in soil is an empirical procedure – where the method of extraction defines the measurand.<sup>25,26</sup> With testing laboratories using different methods, each could be considered to be measuring a different measurand that is their version of 'water soluble anions in soil'. This lack of uniformity in the procedures can make the comparison of participants' results difficult.

In the previous study of metals and anions in soil AQA 11-12, NMI conducted a study on water soluble anions content in soil using the same instrumental technique on two extraction procedures: one involved a soil/water ratio of 1: 5 and the other a soil/water ratio of 1:10. The fluoride, orthophosphate and sulphate results were found to change in direct proportion with the amount of water used in the extraction procedure.

In the present study participating laboratories were asked to analyse the sample using their normal measurement technique but to follow the same preparation procedure for the soil extract which involved: a soil/water ratio of 1:5 and a mixing time of one hour.

The method descriptions and instrumental techniques provided by participants are presented in Tables 5 to 7. All participating laboratories used a soil/water ratio of 1:5.

### Individual Water Soluble Anion Commentary

**Chloride** level in S3 was low, close to the reporting level of many participants, which may have challenged their analytical techniques. No assigned value was set for this test in S3 because the reported results were not compatible with each other (Figure 67).

All high chloride results were produced either using colorimetric or mercuric thiocyanate analyses. The colour in the 1:5 soil/water extract and the method used to remove the particulate matter from this solution may in part be the cause of the variability in results. Spectrophotometry has low specificity and is liable to interference from coloured species.

Table 59 presents Chloride results from two measurement techniques in an experiment conducted by NMI in 2017. Two sets of aqueous solutions, both from the same soil extract (sample S3 of AQA 17-11), were analysed: one filtered through 0.45 µm pore size filters, and one centrifuged. DA and IC were used as measurement techniques. No further dilutions were performed on the two aqueous solutions; the DA used performed automatic blank correction.

Table 59 Chloride Results in NMI Study

	Chloride by DA* (mg/kg)	Chloride by IC (mg/kg)
Aqueous solution - centrifuged.	90	NA
Aqueous solution - filtered through 0.45µm pore size filtered	50	32.5

NA- Not Applicable; DA analyser performed automatically blank correction.

The automated colour correction performed by DA may have not overcome problems caused by colour and turbidity.

Caution should be also exercised when the argentometric method is used. This method is suitable for use in clear aqueous solutions where the end point can be easily detected; Fe present in the extraction solution may also interfere by masking the end point.



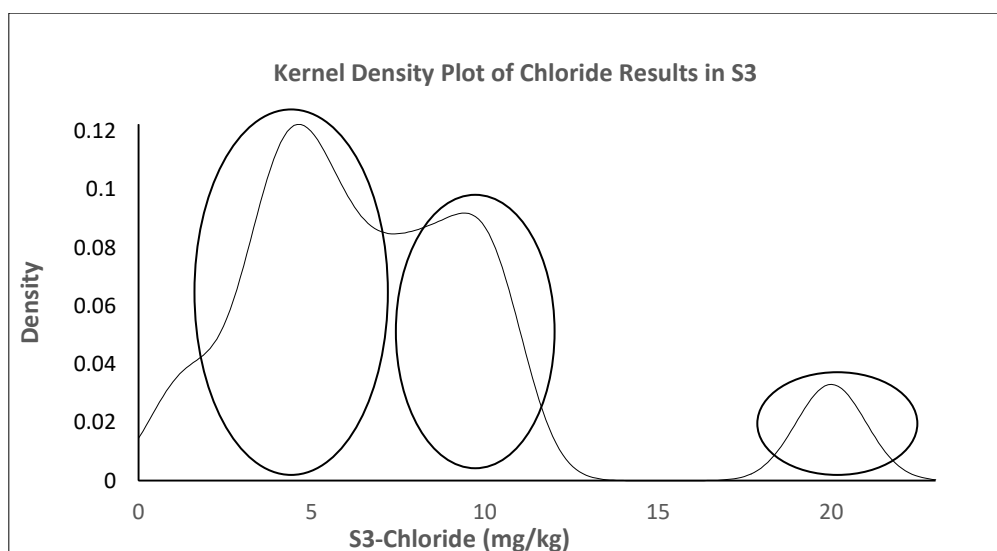


Figure 67 Kernel Density Plots of Chloride Results in S3

Lab code	Chloride Results mg/kg	Measurement Method	Measurement Instrument
9	1.3	Argentometric Titration	Manual Analysis
2	3.4	Ion Chromatographic Method	IC
11	4	Ion Chromatographic Method	IC
13	4.6	Ion Chromatographic Method	IC
5	5.1	Ion Chromatographic Method	IC
20	5.92	Ion Chromatographic Method	IC
23	8	Colorimetric Method	DA
27	8.92	Ferricyanide Colorimetric Method	DA
15	10	Ferricyanide Colorimetric Method	UV-Vis
26	10.4	Colorimetric Method	DA
14	12	Mercuric Thiocyanate	Microplate reader

Chloride level in the study sample was low. As the ratio of extracting solution to dried sample size had to be at 5:1, laboratories should use a determination method sensitive enough to accurately measure chloride at ppb level in the extracting solution or otherwise increase their reporting level.

**Sulphate** No assigned value was set for sulphate in S3 because the results reported were not compatible with each other. A distribution of participants' results with the analytical method used is presented in Figure 68.

All high sulphate results were produced using turbidimetric method or ICP measurement. Sulphate level in S3 is low, close to ppb level, when a ratio water/sample size of 5:1 is used. The turbidimetric method by DA might not be able to accurately measure sulphate close to the ppb level in coloured soil extraction solution. Alternatively, false positive results can be produced when sulphate is measured by ICP-OES: this technique measures total S and not only S from sulphate compounds.

Some participants might need to reassess their methods used for sulphate measurement at a low level as well as their level of reporting.

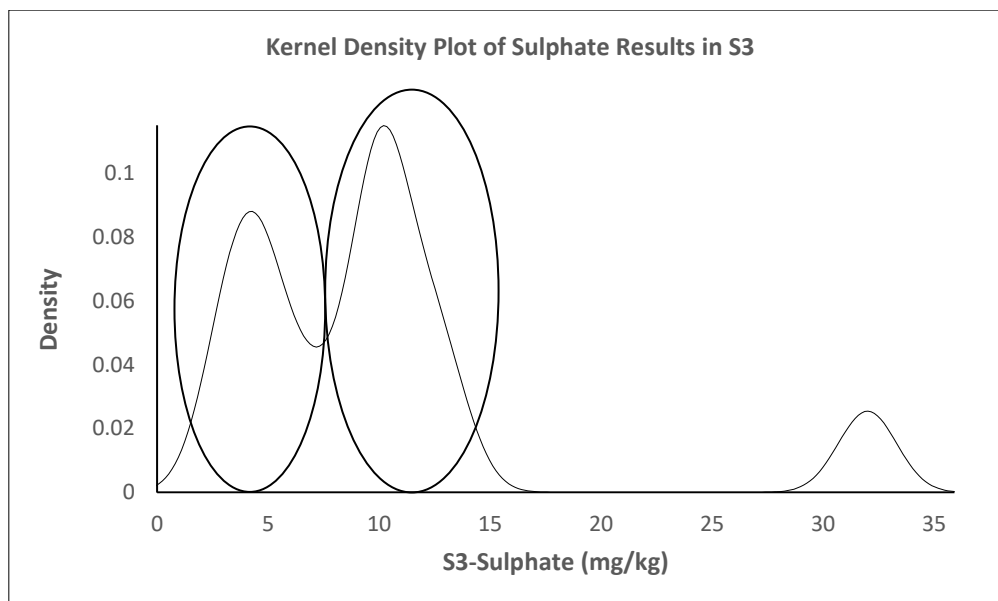


Figure 68 Kernel Density Plots of Sulphate Results in S3

Lab code	Sulphate Results mg/kg	Measurement Method	Measurement Instrument
11	3	Ion Chromatographic Method	IC
13	3.7	Ion Chromatographic Method	IC
5	4.7	Ion Chromatographic Method	IC
2	4.9	Ion Chromatographic Method	IC
20	7.15	Ion Chromatographic Method	IC
8	10	ICP-Method	ICP-OES
9	10	Turbidimetric Method	Manual Analysis
22	10	Turbidimetric Method	DA
15	10.1	ICP-Method	ICP-OES
27	12	ICP-Method	ICP-OES
23	13	Turbidimetric Method	DA
14	32	ICP-Method	ICP-OES

**Orthophosphate-P** level in S3 was low, which may explain the variability in participants' results. Participants used a wide variety of measurement methods and instrumental techniques (Figure 69). Ascorbic acid colorimetric method was the most popular method used by participants for the measurement of orthophosphate-P.

In some cases the automated colour correction performed by DA may have not overcome the problems caused by colour and turbidity.

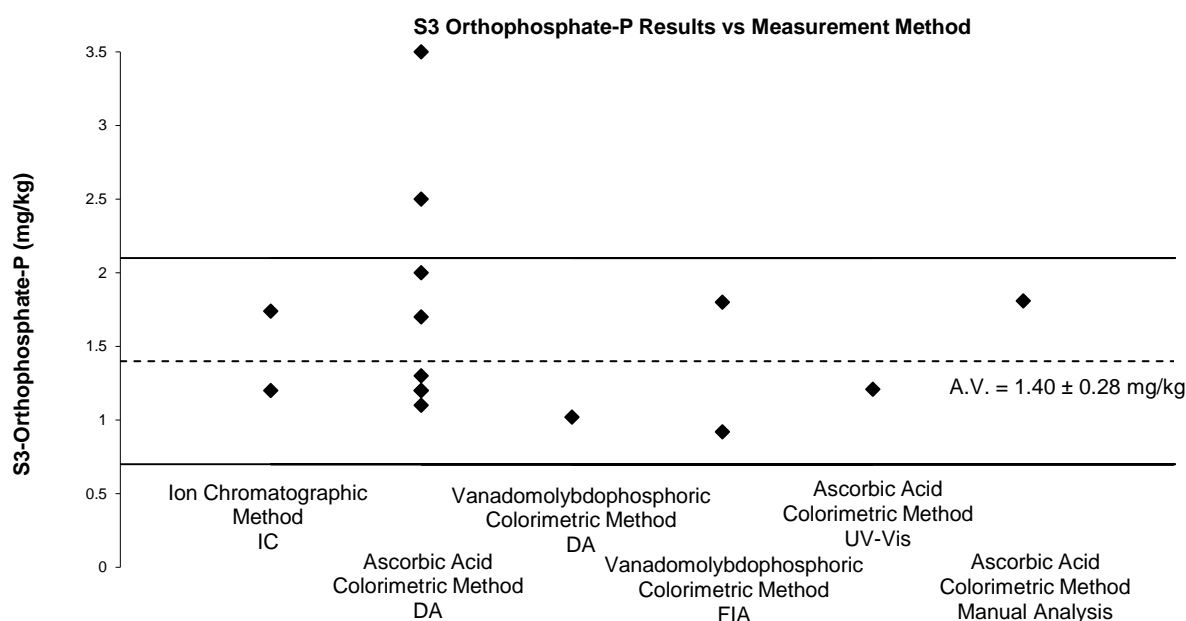


Figure 69 S3-Orthophosphate-P Results vs. Method

## 6.9 Comparison with Previous NMI Proficiency Tests Studies of Metals in Soil

AQA 22-15 is the 31<sup>st</sup> NMI proficiency study of inorganic analytes in soil. A summary of participants' performance over the last 22 studies (2012 to 2022) is presented in Figure 70. Over this period, the average proportion of satisfactory scores was 90% for z-scores and 80% for  $E_n$ -scores.

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

## 6.10 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 60).

Table 60 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	RM – VHGS-SL1-50g LOT#711217475
3	CRM – NIST SRM 2711a (Montana soil)
4	SS
5	CRM
6	CRM
7	NIST SRM 2711a (Montana soil)
8	CRM
9	Clean Sandy Loam, San Joaquin Soil
10	SS

Lab. Code	Description of Control Samples
11	CRM
12	SS
13	RM
14	RM – AGAL 12 (metals) In house AG reference
15	SS – OREAS258, GWS-4 (In-house reference)
16	CRM – PACS3
17	CRM – Agal-12 Biosoil
18	CRM
19	SS
21	06-664-260 pH CRM; 59755 Ammonium CRM; 38364 Phosphate CRM; COND2060 EC CRM; COND147 EC CRM; QC1364 Anions CRM
22	CRM
24	CRM
25	CRM – AGAL-10
26	CRM - AGAL12, LOAM B
27	CRM
28	AGAL 12

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

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

*' a reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures '<sup>27</sup>*

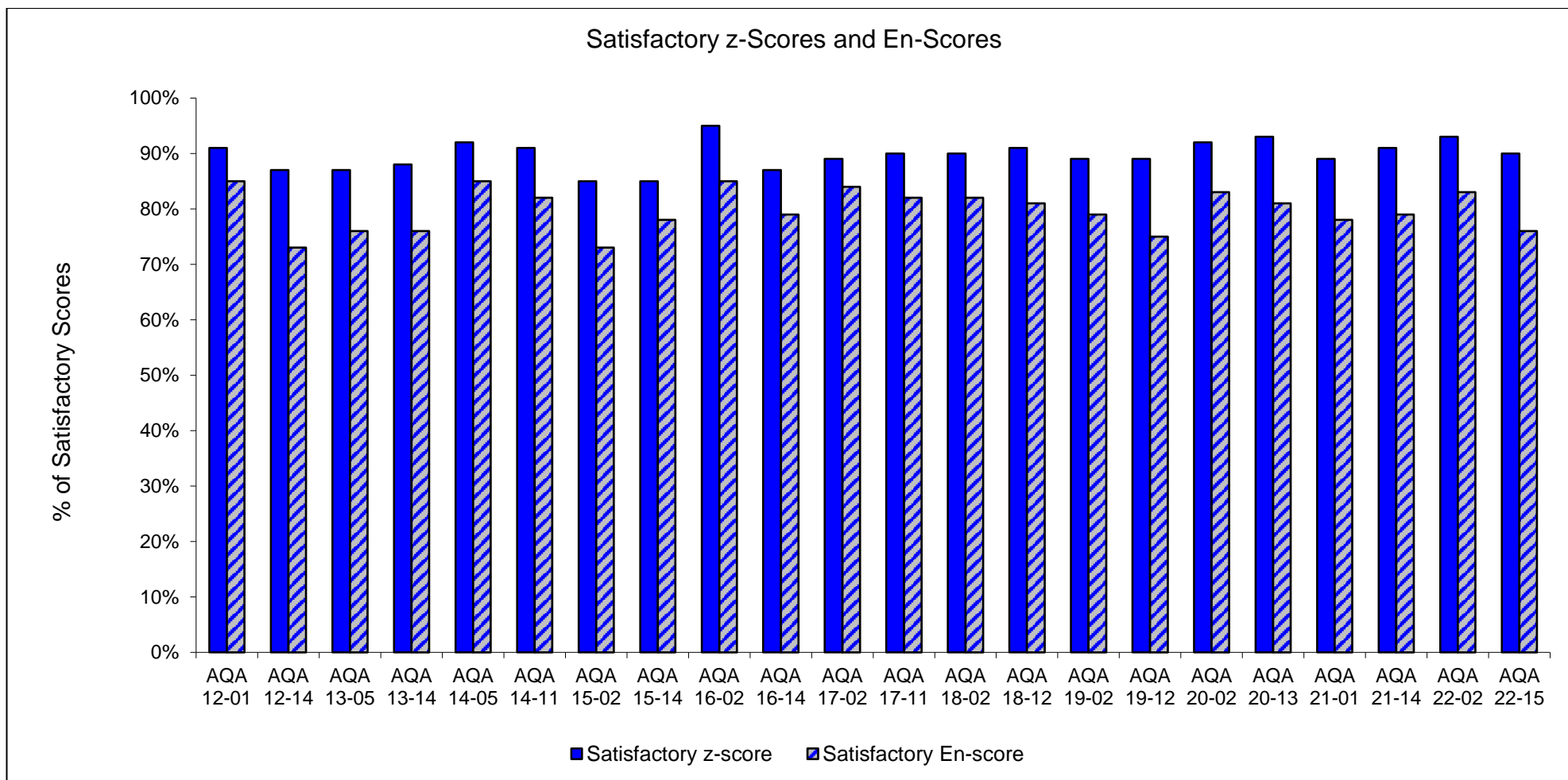


Figure 70 Participants' Performance over Time

## 7 REFERENCES

- [1] ISO17043:2010, Conformity assessment – *General requirements for proficiency testing*.
- [2] NMI Chemical Proficiency Testing Study Protocol, viewed 28 November 2022, <<https://www.industry.gov.au>>.
- [3] NMI Chemical Proficiency Testing Statistical Manual, viewed 28 November 2022, <<https://www.industry.gov.au>>.
- [4] Thompson, M, Ellison, S.L.R & Wood, R 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem*, vol 78, pp 145-196.
- [5] National Environmental Protection Council, NEPM Schedule B1 Guideline on Investigation Levels for Soil and Groundwater, viewed 10 November 2022, <[https://www.legislation.gov.au/Details/F2013C00288/Html/Volume\\_2](https://www.legislation.gov.au/Details/F2013C00288/Html/Volume_2)>.
- [6] ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons.
- [7] Thompson, M 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst*, vol 125, pp 385-386.
- [8] AS ISO/IEC 17025:2018, General requirements for the competence of testing and calibration laboratories
- [9] Eurachem/CITAC 2012, Quantifying uncertainty in Analytical Measurement, 3rd edition, viewed 10 November 2022, <<http://www.eurachem.org>>.
- [10] Bertil, M, Näykki, T, Hovind, H & Krysell, M 2012, Nordtest Report Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories TR 537, 4th Edition, Nordest Tekniikantie, Finland, Esopo.
- [11] Hibbert, B 2007, Quality Assurance for the Analytical Chemistry Laboratory, Oxford University Press.
- [12] ISO (2008), Guide to the Expression of Uncertainty in Measurement (GUM), Geneva, Switzerland.
- [13] Eurolab 2002, Technical Report No 1/2002 - Measurement Uncertainty in Testing.
- [14] NMI, Estimating Measurement Uncertainty for Chemists – viewed 19 September 2022, <<https://www.industry.gov.au/client-services/training-and-assessment>>.
- [15] Australian Health Commission 1995, Contaminated Sites Monograph No4: Trace Element Concentrations in Soils from Rural and Urban Areas of Australia
- [16] European Commission, DG Research, Brussels Belgium 2002, Methodologies for Soil and Sediment Fraction Studies.
- [17] Gaudino, S, Galas, C 2007, 'The role of different soil sample digestion methods on trace element analysis: a comparison of ICP-MS and INAA measurement results', *Accred Qual Assur* vol 12, pp 84-93.
- [18] Chen, M, Ma, L 2001, 'Comparison of Three Aqua Regia Digestion Methods for Twenty Florida Soil', *Soil Sci. Soc. Am J*, vol 65, pp 491-499.
- [19] Charun, Y 2006, 'A comparative study of acid-extractable and total digestion methods for the determination of inorganic elements in peat material by inductively coupled plasma-optical emission spectrometry', *Analytica Chmica Acta*, vol 557, pp 296-303.
- [20] Roje, V 2010, 'Multi-elemental analysis of marine sediment reference material MESS-3: one-step microwave digestion and determination by high resolution inductively

coupled plasma-mass spectrometry (HR-ICP-MS)', Chemical papers vol 64 (4), pp.409-414.

[21] Cotton, F. A., Wilkinson, G., (1998) Advanced Inorganic Chemistry, ( 4th ed, p394-401). NY, USA

[22] Wiley Lee, J.D., (1996) Concise Inorganic Chemistry (p 510), London, UK Chapman & Hill

[23] Bailar, J.C., et. al (1973) Comprehensive Inorganic Chemistry, (1st ed. p558-680) Pergamon Press Ltd., Headington Hill Hall, Oxford

[24] Rayment, G. E.& Lyons, D. J 2011 Soil Chemical Methods – Australasia, CSIRO Publishing, Collingwood VIC Australia

[25] Afzal M., Yasin M, (2002), Effect of soil to water ratios on chemical properties of saline-sodic and normal soil Pakistan J. agric. Res. 17, 379-386.

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

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

### Sample Preparation

**Samples S1** was unspiked dried sediment while **Sample S2** was unspiked dried clay. The analytes level in these sample was the incurred level. The sediment and clay materials were dried, ground, and passed through a 350  $\mu\text{m}$  sieve before being further mixed and divided into portions of 30 g each.

**Sample S3** was an agricultural soil material dried, ground, passed through a 350  $\mu\text{m}$  sieve before being further mixed and divided into portions of 75 g each.

### Sample Analysis and Homogeneity Testing

The same preparation procedure as in previous NMI PT studies for inorganic analytes in soil was followed for Samples S1, S2 and S3. Partial homogeneity testing was conducted for the elements of interest with the exception of exception of Ga in S2 and TKN and 2M KCl extractable ammonium-N and nitrate-N in S3. Three bottles were analysed in duplicate and the average of these results was reported as the homogeneity value. Measurements were made under repeatability conditions in random order.

A full homogeneity test was conducted for water soluble chloride, sulphate and orthophosphate-P and pH, EC in S3. Homogeneity testing was based on that described in the International Protocol. Six sample bottles were selected at random. Duplicate test-portions were taken from each bottle and the concentration of all targeted analytes measured. Measurements were made under repeatability conditions in random order. Table 61 sets out an example for the testing of the homogeneity of chloride in Sample S3.

Table 61 Homogeneity Testing of chloride in Sample S3

BOTTLE	A Chloride (mg/kg)	B Chloride (mg/kg)
2	3.8	3.9
11	4.1	4.2
15	3.8	4.2
20	3.9	4.1
31	3.9	3.9
40	4	3.9

	Value	Critical	Result
Cochran	0.40	0.78	Pass
$S_{an}/\sigma$	0.17	0.5	Pass
$S^2_{sam}$	0.001	0.16	Pass

### Sample Analysis for Acid Extractable Elements

A test portion of approximately 0.5 g of soil was weighed into a 50 mL graduated polypropylene centrifuge tube. The sample was digested using 3 mL of concentrated nitric acid and 3 mL of concentrated hydrochloric acid on a hot block at  $95^\circ\text{C} \pm 5^\circ\text{C}$ . After digestion, each sample was diluted to 40 mL with Milli-Q water and then further diluted as necessary.

The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, and matrix matched reference materials, duplicates and sample matrix spikes, was carried through the same set of



procedures and analysed at the same time as the samples. A summary of the instrument conditions used and the ion/wavelength monitored for each analyte is given in Table 62.

Table 62 Instrumental Technique used for Acid Extractable Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	S1/2 Final Dilution Factor	S3 Final Dilution Factor	Ion (m/z)/ Wavelength (nm)
Ag	ICP-MS	Rh	ORS	He	800	NA	107 m/z
Al	ICP-MS	Rh	NA	NA	800	NA	27 m/z
As	ICP-MS	Rh	ORS	He	800	NA	75 m/z
B	ICP-MS	Rh	NA	NA	800	NA	11 m/z
Ba	ICP-MS	Rh	ORS	He	800	NA	137 m/z
Be	ICP-MS	Rh	NA	NA	800	NA	9 m/z
Ca	ICP-MS	Rh	ORS	He	NA	800	43 m/z
Cd	ICP-MS	Rh	NA	NA	800	NA	111 m/z
Co	ICP-MS	Rh	ORS	He	800	NA	59 m/z
Cr	ICP-MS	Rh	ORS	He	800	NA	52 m/z
Cu	ICP-MS	Rh	ORS	He	800	NA	65 m/z
Fe	ICP-MS	Rh	NA	NA	NA	800	56 m/z
Hg	ICP-MS	Rh	NA	NA	800	NA	201 m/z
K	ICP-MS	Rh	ORS	He	NA	800	39 m/z
La	ICP-MS	Rh	ORS	He	800	NA	139 m/z
Li	ICP-MS	Rh	ORS	He	800	NA	7 m/z
Mg	ICP-MS	Rh	ORS	He	NA	800	24 m/z
Mn	ICP-MS	Rh	ORS	He	800	NA	55 m/z
Mo	ICP-MS	Rh	ORS	He	800	NA	95 m/z
Na	ICP-MS	Rh	ORS	He	NA	800	23 m/z
Ni	ICP-MS	Rh	ORS	He	800	NA	60 m/z
P	ICP-MS	Rh	ORS	HEHe	NA	800	31 m/z
Rb	ICP-MS	Rh	ORS	He	800	NA	85 m/z
S	ICP-OES	Y	NA	NA	NA	800	181.972 nm
Sb	ICP-MS	Ir	ORS	He	800	NA	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	800	NA	78 m/z
Sn	ICP-MS	Rh	NA	NA	800	NA	118 m/z
Sr	ICP-MS	Rh	ORS	He	NA	800	88 m/z
Th	ICP-MS	Ir	ORS	He	800	NA	232 m/z
V	ICP-MS	Rh	ORS	He	800	NA	51 m/z
Zn	ICP-MS	Rh	ORS	He	800	NA	66 m/z

NA= Not applicable

### Sample Analysis for Water Soluble Anions

A test portion of 10 g was weighed into a 50 mL polypropylene container. The container was then filled with deionised water. The suspension was shaken, at room temperature for 1 h, centrifuged, and filtered through 0.45 µm filter. A summary of the measurement methods and instrumental techniques is presented in Table 63.

Table 63 Summary of the Measurement Methods and Instrumental Techniques used by NMI

Anion	Measurement Method	Instrument
Water Soluble Chloride	Ion Chromatographic Method	IC
Water Soluble Orthophosphate-P	Colorimetric, Ascorbic Acid Reduction	DA
Water Soluble Sulphate	Ion Chromatographic Method	IC

## APPENDIX 2 - 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 'ISO13528:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.<sup>6</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

$S_{rob\ av}$  robust average standard deviation

$p$  number of results

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

A worked example is set out below in Table 64.

Table 64 Uncertainty of Assigned Value for As in Sample S1

No. results (p)	22
Robust Average	56.8 mg/kg
$S_{rob\ av}$	4.45 mg/kg
$u_{rob\ av}$	1.19 mg/kg
$k$	2
$U_{rob\ av}$	2.4 mg/kg

The assigned value for As in Sample S1 is **56.8 ± 2.4 mg/kg**.

### 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 1 and Equation 2 respectively (see page 18). A worked example is set out below in Table 65.

Table 65 z-Score and E<sub>n</sub>-score for As Result Reported by Laboratory 17 in S1

As Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E <sub>n</sub> -Score
56 ± 8.5	56.8 ± 2.4	15% as CV or 0.15 x 56.8 = =8.52 mg/kg	$z = \frac{(56 - 56.8)}{8.52}$  $z = -0.09$	$E_n = \frac{(56 - 56.8)}{\sqrt{8.5^2 + 2.4^2}}$  $E_n = -0.09$

### APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.<sup>10</sup> An example is given. Between 2009 and 2022 NMI carried out 27 proficiency tests of metals in soil. These studies involved analyses of acid-extractable elements at low and high levels in dried soil, moist soil, biosoil, sediment, clay and sludge.

**Laboratory X** submitted results for As in all of these PTs. All reported results returned satisfactory z-scores. This data can usefully be separated into two ranges of results 0.5 to 10 mg/kg and 10 to 100 mg/kg (Tables 66 and 67). Taking the average of the robust CV over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 12% and 9.3% respectively. Using a coverage factor of two gives relative expanded uncertainties of 24% and 19% respectively, at a level of confidence of approximately 95%.

Table 66 Laboratory X Reported Results for As at 0.5 to 10 mg/kg Level.

Study No.	Sample	Laboratory result mg/kg	Assigned value mg/kg	Robust CV of all results (%)	Number of Results
AQA 09-13	S1 - Biosoil	4.091	3.64	16	11
	S2 - Soil	4.29	4.57	15	12
AQA 11-01	S1 - Biosoil	3.54	3.57	19.7	18
AQA 13-05	S1 - Soil	9.22	9.21	14	22
AQA 14-11	S1 - Sediment	7.91	7.37	11.8	21
AQA 15-02	S1 - Moist Sludge	8.29	7.02	13	22
	S2 - Moist Sludge	7.42	7.02	11.3	17
AQA 15-14	S1 - Sediment	10	9.95	6.7	17
	S2 - Soil	4.53	4.47	6.4	14
AQA 16-02	S2 - Clay	2.67	2.11	14	20
AQA 16-14	S1 - Soil	6.03	5.61	20	17
AQA 17-02	S2 - Soil	3.71	3.76	10	13
AQA 18-02	S1 - Compost	2.22	2.73	11	17
AQA 19-02	S1 - Soil	2.83	2.65	11	24
AQA 19-12	S1 - Soil	2.32	2.12	16	16
AQA 20-13	S1 - Biosoil	2.85	3.29	11	17
AQA 21-01	S1 – Sediment	7.02	6.26	6.9	18
AQA 21-01	S2 – Moist Sludge	3.99	3.58	12.6	13
AQA 22-02	S1 – Sediment	3.57	4.02	9.5	15
AQA 22-02	S2 – Moist Soil	3.57	3.56	6.2	13
AQA 22-15	S2 – Clay	4.29	3.63	17	19
Average				12*	

\* The mean value of robust CV was used.

Table 67 Laboratory X Reported Results for As at 10 to 100 mg/kg Level.

Study No.	Sample	Laboratory result mg/kg	Assigned value* mg/kg	Robust CV of all results (%)	Number of Results
AQA 10-12	S1 - Soil	16.6	14.4	8.5	19
AQA 11-12	S1 - Moist Sludge	25	21.6	15	13
AQA 12-01	S1 - Sediment	18.4	17.3	8.1	21
AQA 12-14	S2 - Soil	16.6	14.8	11	20
AQA 13-14	S1 - Sandy Soil	16.6	15.1	10.4	21
AQA 14-05	S1 - Soil	13.2	12.3	7.8	25
AQA 17-11	S1 - Sediment	18.1	17.4	11	22
AQA 18-12	S2 - Soil	10.4	9.6	8	20
AQA 19-12	S2 - Sediment	21	19.9	9	19
AQA 20-02	S1 - Soil	18.8	21.6	8.8	23
AQA 20-02	S2 - Moist Soil	16.5	17.8	6.7	24
AQA 21-14	S1 - Sediment	19.5	20.9	8.9	21
AQA 22-15	S1 -Sediment	58.6	56.8	7.8	22
Average				9.3**	

\*The mean value of robust CV was used.

Table 69 sets out the expanded uncertainty for results of the measurement of As in soil, biosoil, clay, sediment, sludge, sandy soil, moist soil, compost and agricultural soil over the ranges 0.5 to 10 mg/kg and 10 to 100 mg/kg.

Table 68 Uncertainty of As Results Estimated Using PT Data.

Results mg/kg	Uncertainty mg/kg
1.00	0.25
5.0	1.3
20.0	4.8
75	18
100	24

The estimates of 24% and 19% relative passes the test of being reasonable, and the analysis of the 34 different PT samples over fourteen years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrators etc.), and so complies with AS ISO/IEC 17025:2018.<sup>8</sup>

## APPENDIX 4 - INSTRUMENT DETAILS

Table 69 Instrument Conditions Ag

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Rh	ORS	He	800	NA	107
3	ICP-MS	In	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	328.289
5	ICP-MS			He		NA	
6	ICP-MS	<sup>72</sup> Ge/ <sup>103</sup> Rh/ <sup>201</sup> Hg	ORS	He	100	NA	107
7	ICP-MS	Rhodium	ORS	standard mode		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	328.069nm
12	ICP-OES-AV	Lu	NA	NA	50	50	328.289
14	ICP-MS	Rh	NA	NA	625	NA	109
17	ICP-MS	Rh	NA	standard mode	2000	NA	109
18	ICP-MS	In		He	1000	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	328.289
20	ICP-MS	Rh	ORS			NA	107
22	ICP-OES-AV	CsCl	NA	NA	50	50	328.068
23	ICP-OES-AV	Lu			83.3	NA	328.068
27	ICP-OES-RV					NA	328.068
28	ICP-OES-AV	Yb	NA		10	NA	338.289 nm

Table 70 Instrument Conditions A1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc-2 45	KED		1000	NA	27
2	ICP-OES-AV	Y	NA	NA	800	NA	396.152
3	ICP-MS	Sc	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	236.705
5	ICP-OES					NA	
6	ICP-OES-AV	Y371 / Te214			100	NA	308.215
7	ICP-MS	Scandium	ORS	standard mode		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	236.707, 308.215, 396.15nm
10	ICP-MS	Sc	CRI	He	500	NA	27
12	ICP-OES-AV	Lu	NA	NA	50	50	236.705
13	ICP-OES-AV	Eu	NA	NA	50	NA	237
14	ICP-MS	Sc	KED	He	625	NA	27
17	ICP-MS	Sc	NA	standard mode	2000	NA	27
19	ICP-OES-AV	Lu	NA	NA	50	50	236.705
20	ICP-OES-RV	Y377	NA			NA	396.152
21	ICP-MS	Sc	ORS	He	NA	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	236.705
23	ICP-OES-AV	Lu			333.2	NA	396.152
25	ICP-OES-AV	NA				NA	308.215
27	ICP-OES-RV	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA		10	NA	396.152 nm

Table 71 Instrument Conditions As

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge-1 72	KED		10	NA	75
2	ICP-MS	Rh	ORS	He	800	NA	75
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	188.98
5	ICP-MS			He		NA	
6	ICP-MS	<sup>72</sup> Ge/ <sup>103</sup> Rh/ <sup>201</sup> Hg	ORS	He	100	NA	75
7	ICP-MS	Telerium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	188.89nm
10	ICP-MS	Rh	CRI	He	500	NA	75
12	ICP-OES-AV	Lu	NA	NA	50	50	188.98
13	ICP-MS	Sc	ORS	He	50	NA	75
14	ICP-MS	Ge	KED	He	625	NA	75
17	ICP-MS	Rh	KED	He	1000	NA	75
18	ICP-MS	In		He	1000	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	188.98
20	ICP-MS	Rh	ORS			NA	75
21	ICP-MS	Rh	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	188.98
23	ICP-OES-AV	Lu			83.3	NA	188.98
25	ICP-OES-AV	NA				NA	188.982
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	188.98 nm

Table 72 Instrument Conditions B

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Y 89	KED		10	NA	11
3	ICP-MS	Sc	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	182.577
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	100	NA	11
8	ICP-OES	Eu & Cs	NA	NA	50	NA	249.773nm
10	ICP-MS	Sc	CRI	NA	500	NA	11
12	ICP-OES-AV	Lu	NA	NA	50	50	182.577
14	ICP-MS	Sc	NA	NA	625	NA	10
17	ICP-MS	Sc	KED	He	1000	NA	11
19	ICP-OES-AV	Lu	NA	NA	50	50	182.577
20	ICP-OES-RV	Te214	NA			NA	249.678
21	ICP-MS	Sc	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	249.772
23	ICP-OES-AV	Lu			83.3	NA	182.577
25	ICP-OES-AV	NA				NA	208.957
27	ICP-OES-RV					NA	249.772
28	ICP-OES-AV	Yb	NA			NA	249.772 nm



Table 73 Instrument Conditions Ba

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	In-1 115	KED		1	NA	138
2	ICP-MS	Rh	ORS	He	800	NA	134Mini
3	ICP-MS	Tb	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	230.424
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	5000	NA	137
7	ICP-MS	Rhodium	ORS	standard mode		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	585.369nm
10	ICP-MS	Rh	CRI	He	500	NA	135
12	ICP-OES-AV	Lu	NA	NA	50	50	230.424
14	ICP-MS	Rh	NA	NA	625	NA	138
17	ICP-MS	Tb	NA	standard mode	2000	NA	137
19	ICP-OES-AV	Lu	NA	NA	50	50	230.424
20	ICP-OES-RV	Y371	NA			NA	493.408
21	ICP-MS	Rh	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	585.367
23	ICP-OES-AV	Lu			83.3	NA	493.408
25	ICP-OES-AV	NA				NA	233.527
27	ICP-MS					NA	585.367
28	ICP-OES-AV	Yb	NA			NA	493.408 nm

Table 74 Instrument Conditions Be

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc-2 45	KED		10	NA	9
2	ICP-MS	Rh	NA	NA	800	NA	9
3	ICP-MS	Sc	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	313.107
6	ICP-MS	72Ge/10 3Rh/201I r	ORS	standard mode	100	NA	9
8	ICP-OES	Eu & Cs	NA	NA	50	NA	313.042nm
10	ICP-MS	Sc	CRI	NA	500	NA	9
12	ICP-OES-AV	Lu	NA	NA	50	50	313.107
14	ICP-MS	Sc	NA	NA	625	NA	9
17	ICP-MS	Sc	NA	standard mode	2000	NA	9
19	ICP-OES-AV	Lu	NA	NA	50	50	313.107
20	ICP-MS	Rh	NA			NA	9
21	ICP-MS	Sc	ORS	NoGas	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	313.042
23	ICP-OES-AV	Lu			83.3	NA	313.042
25	ICP-OES-AV	NA				NA	313.105
27	ICP-MS					NA	585.367
28	ICP-OES-AV	Yb	NA			NA	313.042 nm

Table 75 Instrument Conditions Ca

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-OES-AV	Y	NA	NA	NA	800	422.673
4	ICP-OES-AV	Lu	NA	NA	50	50	315.887
5	ICP-OES				NA		
6	ICP-OES-AV	Y371 / Te214			NA	200	315.887
8	ICP-OES	Eu & Cs	NA	NA	NA	50	315.887, 370.602nm
9					NA	15	422.7
11	ICP-OES-AV	Y 371.029			NA		430.253
12	ICP-OES-AV	Lu	NA	NA	50	50	315.887
13	ICP-MS	SC	ORS	He	NA	50	44
14	ICP-MS	Sc	KED	He	NA	625	44
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	315.887
20	ICP-OES-RV	Y377	NA		NA		317.933
22	ICP-OES-AV	CsCl	NA	NA	50	50	315.887
23	ICP-OES-AV	Lu			NA	83.3	317.933
24	ICP-OES-RV	Lu	NA	NA	NA	200	317.94 nm
25	ICP-OES-RV	NA			NA		317.933
27	ICP-OES-RV	NA	NA	NA	NA		NA

Table 76 Instrument Conditions Cd

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	In-1 115	KED		10	NA	111
2	ICP-MS	Rh	ORS	He	800	NA	111
3	ICP-MS	In	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	228.802
5	ICP-MS			He		NA	
6	ICP-MS	<sup>72</sup> Ge/ <sup>103</sup> Rh/ <sup>201</sup> Hg	ORS	He	100	NA	111
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	226.502nm
12	ICP-OES-AV	Lu	NA	NA	50	50	228.802
13	ICP-MS	Rh	ORS	He	50	NA	111
14	ICP-MS	Rh	NA	NA	625	NA	111
17	ICP-MS	Rh	KED	He	1000	NA	111
18	ICP-MS	In			1000	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	228.802
20	ICP-MS	Rh	ORS			NA	111
21	ICP-MS	Rh	ORS	NA	NA	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	226.502
23	ICP-OES-AV	Lu			83.3	NA	214.439
25	ICP-OES-AV	NA				NA	228.803
27	ICP-MS					NA	226.502
28	ICP-OES-AV	Yb	NA			NA	214.439 nm

Table 77 Instrument Conditions Co

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		10	NA	59
2	ICP-MS	Rh	ORS	He	800	NA	59
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	228.615
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	1000	NA	59
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	228.616nm
10	ICP-MS	Sc	CRI	He	500	NA	59
12	ICP-OES-AV	Lu	NA	NA	50	50	228.615
13	ICP-MS	Sc	ORS	He	50	NA	59
14	ICP-MS	Ge	KED	He	625	NA	59
17	ICP-MS	Ga	KED	He	2000	NA	59
19	ICP-OES-AV	Lu	NA	NA	50	50	228.615
20	ICP-OES-RV	Te214	NA			NA	228.615
21	ICP-MS	Sc	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	228.615
23	ICP-OES-AV	Lu			83.3	NA	230.786
25	ICP-OES-AV	NA				NA	228.616
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	228.615

Table 78 Instrument Conditions Cr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		10	NA	52
2	ICP-MS	Rh	ORS	He	800	NA	52
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	205.56
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	1000	NA	52
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	267.716nm
12	ICP-OES-AV	Lu	NA	NA	50	50	205.56
13	ICP-MS	Sc	ORS	He	50	NA	51
14	ICP-MS	Sc	KED	He	625	NA	52
17	ICP-MS	Sc	KED	He	1000	NA	52
18	ICP-OES-AV	Sc			100	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	205.56
20	ICP-OES-RV	Te214	NA			NA	267.716
22	ICP-OES-AV	CsCl	NA	NA	50	50	267.716
23	ICP-OES-AV	Lu			83.3	NA	267.716
25	ICP-OES-AV	NA				NA	267.709
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	267.716 nm

Table 79 Instrument Conditions Cu

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		10	NA	63
2	ICP-MS	Rh	ORS	He	800	NA	63Mini
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	324.754
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	1000	NA	63
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	327.395nm
12	ICP-OES-AV	Lu	NA	NA	50	50	324.754
13	ICP-MS	Sc	ORS	He	50	NA	63
14	ICP-MS	Ge	KED	He	625	NA	63
17	ICP-MS	Ga	KED	He	1000	NA	63
18	ICP-OES-AV	Sc			100	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	324.754
20	ICP-OES-RV	Y377	NA			NA	327.395
22	ICP-OES-AV	CsCl	NA	NA	50	50	327.395
23	ICP-OES-AV	Lu			83.3	NA	327.395
25	ICP-OES-AV	NA				NA	324.752
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	324.754

Table 80 Instrument Conditions Fe

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-OES-AV	Y	NA	NA	NA	800	238.204
4	ICP-OES-AV	Lu	NA	NA	50	50	261.382
5	ICP-OES				NA		
6	ICP-OES-AV	Y371 / Te214			NA	2000	240.489
8	ICP-OES	Eu & Cs	NA	NA	NA	50	238.204, 258.588, 259.940nm
9					NA	15	248.3
10	ICP-MS	Sc	CRI	He	NA	500	56
11	ICP-OES-AV	Y 371.029				NA	370.792
12	ICP-OES-AV	Lu	NA	NA	50	50	261.382
13	ICP-MS	Sc	ORS	He	NA	50	56
14	ICP-MS	Sc	KED	He	NA	625	56
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	261.382
20	ICP-OES-RV	Te214	NA		NA		259.94
21	ICP-MS	Sc	ORS	He	NA	500	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	258.588
23	ICP-OES-AV	Lu			NA	833.3	238.204
24	ICP-MS	Sc	DRC	He	NA	200	m/z 56
25	ICP-OES-AV	NA			NA		
27	ICP-OES-RV	NA	NA	NA	NA		NA



Table 81 Instrument Conditions Ga

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Rh	ORS	He	800	NA	71
3	NA		KED	He		NA	
4	ICP-MS	Ge	ORS	standard mode	50	50	69
8	ICP-MS	Ir, Rh & Sc	NA	NA	50	NA	71 m/z
12	ICP-MS	Ge	ORS	standard mode	50	50	69
17	KED	He	2000	NA	59		
19	ICP-MS	Ge	ORS	standard mode	50	50	69
22	ICP-MS	Sc, Rh, Ir	ORS	NA	50	50	71
27	ICP-MS	Rh, Sc, Ir	ORS	He	NA	NA	71
28	ICP-MS	Y	ORS	NA		NA	71 m/z

Table 82 Instrument Conditions Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir 193	KED		10	NA	202
2	ICP-MS	Ir	ORS	He	800	NA	202
4	CVAAS	NA	NA	NA	50	50	253.7
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	100	NA	202
7	ICP-MS	Iridium	ORS	standard mode		NA	
8	FIMS-AAS	NA	NA	NA	50	NA	253.7nm
12	CVAAS	NA	NA	NA	50	50	253.7
13	CVAAS	NA	NA	NA	50	NA	453
14	ICP-MS	Ir	NA	NA	625	NA	201
17	ICP-MS	Tb	KED	He	1000	NA	201
18	ICP-MS	In			1000	NA	
19	CVAAS	NA	NA	NA	50	50	253.7
20	ICP-MS	Ir	ORS			NA	202
22	CVAAS	NA	NA	NA	50	50	253.7
23	Cetac Hg Analyser	NA			83.3	NA	253.7
25	FIMS	NA				NA	253.7
27	CVAAS					NA	
28	CVAAS	SnCl2	NA			NA	

Table 83 Instrument Conditions K

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-OES-AV	Y	NA	NA	NA	800	766.491
4	ICP-OES-AV	Lu	NA	NA	50	50	766.491
5	ICP-OES				NA		
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	NA	200	766.491
8	ICP-OES	Eu & Cs	NA	NA	NA	50	404.721nm, 766.491nm
9					NA	15	766.5
11	ICP-OES-AV	Y 371.029				NA	769.897
12	ICP-OES-AV	Lu	NA	NA	50	50	766.491
13	ICP-MS	Sc	ORS	NA	NA	50	39
14	ICP-MS	Sc	KED	He	NA	625	39
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	766.491
20	ICP-OES-RV	Y377	NA		NA		766.491
22	ICP-OES-AV	CsCl	NA	NA	50	50	766.491
23	ICP-OES-AV	Lu			NA	83.3	769.897
24	ICP-OES-RV	Lu	NA	NA	NA	20	766.525 nm
25	ICP-OES-RV	NA			NA		766.49
27	ICP-OES-RV	NA	NA	NA	NA		NA

Table 84 Instrument Conditions La

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Rh	ORS	He	800	NA	139
3	ICP-MS	Tb	KED	He		NA	
4	ICP-MS	Lu	ORS	standard mode	50	50	139
8	ICP-MS	Ir, Rh & Sc	NA	NA	50	NA	139 m/z
12	ICP-MS	Lu	ORS	standard mode	50	50	139
14	ICP-MS	Rh	NA	NA	625	NA	139
17	ICP-MS	Tb	NA	standard mode	2000	NA	139
19	ICP-MS	Lu	ORS	standard mode	50	50	139
20	ICP-MS	Rh	ORS			NA	139
22	ICP-MS	Sc, Rh, Ir	ORS	NA	50	50	139
27	ICP-MS	Rh, Sc, Ir	ORS	He	NA	NA	139
28	ICP-MS	Ir	ORS	NA		NA	139 m/z

Table 85 Instrument Conditions Li

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	NA	NA	He	800	NA	7
3	ICP-MS	Sc	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	670.783
5	ICP-OES					NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	standard mode	100	NA	7
7	ICP-MS	Scandium	ORS	standard mode		NA	
8	ICP-MS	Ir, Rh & Sc	NA	NA	50	NA	7 m/z
10	ICP-MS	Sc	CRI	NA	500	NA	7
12	ICP-OES-AV	Lu	NA	NA	50	50	670.783
14	ICP-MS	Sc	NA	NA	625	NA	7
17	ICP-MS	Sc	NA	standard mode	2000	NA	7
19	ICP-OES-AV	Lu	NA	NA	50	50	670.783
20	ICP-MS	Rh	ORS			NA	7
21	ICP-MS	Sc	ORS	NoGas	500	NA	NA
22	ICP-MS	Sc, Rh, Ir	ORS	NA	50	50	7
27	ICP-MS	Rh, Sc, Ir	ORS	NA	NA	NA	7
28	ICP-OES-AV	Yb	NA			NA	670.783 nm

Table 86 Instrument Conditions Mg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-OES-RV	Y	NA	NA	NA	800	285.213
4	ICP-OES-AV	Lu	NA	NA	50	50	279.8
5	ICP-OES				NA		
6	ICP-OES-AV	Y371 / Te214			NA	2000	383.829
8	ICP-OES	Eu & Cs	NA	NA	NA	50	383.829nm
9	NA				NA	40	285.2
11	ICP-OES-AV	Y 371.029				NA	277.983
12	ICP-OES-AV	Lu	NA	NA	50	50	279.8
13	ICP-MS	Sc	ORS	He	NA	50	24
14	ICP-MS	Sc	KED	He	NA	625	25
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	279.8
20	ICP-OES-RV	Y377	NA		NA		280.27
21	NA	Sc	NA	NA	NA	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	383.829
23	ICP-OES-AV	Lu			NA	83.3	383.829
24	ICP-OES-RV	Lu	NA	NA	NA	200	279.08 nm
25	ICP-OES-AV	NA			NA		279.077
27	ICP-OES-RV	NA	NA	NA	NA		NA

Table 87 Instrument Conditions Mn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		100/10	NA	55
2	ICP-MS	Rh	ORS	He	800	NA	55
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	257.61
5	ICP-MS			He		NA	
6	ICP-OES-AV	Y371 / Te214			100	NA	293.931
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	261.021nm
10	ICP-MS	Sc	CRI	He	500	NA	NA
12	ICP-OES-AV	Lu	NA	NA	50	50	257.61
13	ICP-MS	Sc	ORS	He	50	NA	55
14	ICP-MS	Sc	KED	He	625	NA	55
17	ICP-MS	Sc	KED	He	2000	NA	55
18	ICP-OES-AV	Sc			100	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	257.61
20	ICP-OES-RV	Te214	NA			NA	191.446
21	ICP-MS	Sc	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	261.02
23	ICP-OES-AV	Lu			83.3	NA	260.568
25	ICP-OES-AV	NA				NA	257.61
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	257.61 nm

Table 88 Instrument Conditions Mo

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Y 89	KED		10	NA	98
2	ICP-MS	Rh	ORS	He	800	NA	95
3	ICP-MS	Rh	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	202.032
5	ICP-MS			He		NA	
6	ICP-MS	<sup>72</sup> Ge/ <sup>103</sup> Rh/ <sup>201</sup> Hg	ORS	He	100	NA	95
7	ICP-MS	Telurium	ORS	standard mode		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	202.032nm
12	ICP-OES-AV	Lu	NA	NA	50	50	202.032
13	ICP-MS	Rh	ORS	He	50	NA	95
14	ICP-MS	Rh	NA	NA	625	NA	95
17	ICP-MS	Rh	NA	standard mode	2000	NA	98
18	ICP-MS	In			1000	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	202.032
20	ICP-OES-RV	Te214	NA			NA	204.598
22	ICP-OES-AV	CsCl	NA	NA	50	50	202.032
23	ICP-OES-AV	Lu			83.3	NA	202.032
25	ICP-OES-AV	NA				NA	202.031
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	202.032 nm



Table 89 Instrument Conditions Na

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
4	ICP-OES-AV	Lu	NA	NA	50	50	588.995
5	ICP-OES				NA		
6	ICP-OES-AV	Y371 / Te214			NA	200	589.592
8	ICP-OES	Eu & Cs	NA	NA	50	50	330.237, 589.592nm
9					NA		589
11	ICP-OES-AV	Y 371.029				NA	588.995
12	ICP-OES-AV	Lu	NA	NA	50	50	588.995
13	ICP-MS	Sc	ORS	NA	NA	50	23
14	ICP-MS	Sc	KED	He	NA	625	23
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	588.995
20	ICP-OES-RV	Y377	NA		NA		589.592
22	ICP-OES-AV	CsCl	NA	NA	50	50	589.592
23	ICP-OES-AV	Lu			NA	83.3	330.237
24	ICP-OES-RV	Lu	NA	NA	NA	20	589.61 nm
25	ICP-OES-RV	NA			NA		589.592
27	ICP-OES-RV	NA	NA	NA	NA		NA

Table 90 Instrument Conditions Ni

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		10	NA	60
2	ICP-MS	Rh	ORS	He	800	NA	60
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	231.604
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	1000	NA	60
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	231.604nm
12	ICP-OES-AV	Lu	NA	NA	50	50	231.604
13	ICP-MS	Sc	ORS	He	50	NA	60
14	ICP-MS	Ge	KED	He	625	NA	60
17	ICP-MS	Ga	KED	He	1000	NA	60
18	ICP-OES-AV	Sc			100	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	231.604
20	ICP-OES-RV	Te214	NA			NA	216.555
21	NA	NA	ORS	NA	NA	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	231.604
23	ICP-OES-AV	Lu			83.3	NA	231.604
25	ICP-OES-AV	NA				NA	231.603
27	ICP-MS					NA	231.604
28	ICP-OES-AV	Yb	NA			NA	231.604 nm

Table 91 Instrument Conditions P

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Rh	ORS	HEHe	NA	800	31
4	ICP-OES-AV	Lu	NA	NA	50	50	182.143
5	ICP-OES				NA		
6	ICP-OES-AV	Y371 / Te214			NA	200	213.618
8	ICP-OES	Eu & Cs	NA	NA	NA	50	185.827nm
9	NA				NA	1	
11	ICP-OES-AV	Y 371.029				NA	213.618
12	ICP-OES-AV	Lu	NA	NA	50	50	182.143
13	ICP-OES-AV	Eu	NA	NA	NA	50	186
14	ICP-MS	Sc	KED	He	NA	625	31
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	182.143
20	ICP-OES-RV	Te214	NA		NA		177.434
21	ICP-MS	Sc	ORS	He	NA	500	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	185.827
23	ICP-OES-AV	Lu			NA	83.3	178.222
24	ICP-OES-AV	Lu	NA	NA	NA	20	178.226 nm
27	ICP-OES-RV	NA	NA	NA	NA		NA

Table 92 Instrument Conditions Pb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir 193	KED		10	NA	208
2	ICP-MS	Ir	ORS	He	800	NA	208
3	ICP-MS	Tb	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	220.353
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	1000	NA	208
7	ICP-MS	Iridium	ORS	standard mode		NA	
8	ICP-MS	Ir, Rh & Sc	NA	NA	50	NA	220.353nm
12	ICP-OES-AV	Lu	NA	NA	50	50	220.353
13	ICP-MS	Ir	ORS	He	50	NA	208
14	ICP-MS	Ir	NA	NA	625	NA	206+207+208
17	ICP-MS	Tb	KED	He	1000	NA	206+207+208
18	ICP-OES-AV	Sc			100	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	220.353
20	ICP-OES-RV	Te214	NA			NA	220.353
22	ICP-OES-AV	CsCl	NA	NA	50	50	220.353
23	ICP-OES-AV	Lu			83.3	NA	220.353
25	ICP-OES-AV	NA				NA	220.353
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	220.353 nm

Table 93 Instrument Conditions Rb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Rh	ORS	He	800	NA	85
4	ICP-MS	Ge	ORS	standard mode	50	50	85
8	ICP-MS	Ir, Rh & Sc	NA	NA	50	NA	85 m/z
12	ICP-MS	Ge	ORS	standard mode	50	50	85
17	ICP-MS	Rh	NA	standard mode	2000	NA	85
19	ICP-MS	Ge	ORS	standard mode	50	50	85
22	ICP-MS	Sc, Rh, Ir	ORS	He	50	50	85
27	ICP-MS					NA	
28	ICP-MS	In	ORS	NA		NA	85 m/z

Table 94 Instrument Conditions S

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-OES-RV	Y	NA	NA	NA	800	181.972
4	ICP-OES-AV	Lu	NA	NA	50	50	181.972
6	ICP-OES-AV	Y371 / Te214			NA	200	180.669
8	ICP-OES	Eu & Cs	NA	NA	NA	50	178.165,181.972nm
11	ICP-OES-AV	Y 371.029				NA	181.972
12	ICP-OES-AV	Lu	NA	NA	50	50	181.972
13	ICP-OES-AV	Eu	NA	NA	NA	50	207
14	ICP-OES-AV	Y	NA	NA	NA	62.5	181.975
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	181.972
20	ICP-OES-RV	Te214	NA		NA		180.669
22	ICP-OES-AV	CsCl	NA	NA	50	50	181.972
23	ICP-OES-AV	Lu			NA	83.3	181.972
24	ICP-OES-AV	Lu	NA	NA	NA	20	181.976 nm

27	ICP-OES-RV	NA	NA	NA	NA		NA
----	------------	----	----	----	----	--	----

Table 95 Instrument Conditions Sb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Rh	ORS	He	800	NA	121
3	ICP-MS	Tb	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	206.834
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	100	NA	121
7	ICP-MS	Telurium	ORS	standard mode		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	206.834nm
12	ICP-OES-AV	Lu	NA	NA	50	50	206.834
13	ICP-MS	Sc	ORS	He	50	NA	121
14	ICP-MS	Rh	NA	NA	625	NA	121
17	ICP-MS	Rh	NA	standard mode	2000	NA	121
18	ICP-MS	In			1000	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	206.834
22	ICP-OES-AV	CsCl	NA	NA	50	50	206.834
23	ICP-OES-AV	Lu			83.3	NA	206.834
25	ICP-OES-AV	NA				NA	206.836
27	ICP-MS					NA	206.834
28	ICP-OES-AV	Yb	NA			NA	206.834 nm

Table 96 Instrument Conditions Se

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge-1 72	KED		1	NA	82
2	ICP-MS	Rh	ORS	He	800	NA	78
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	196.026
5	ICP-MS			He		NA	
6	ICP-MS	72Ge/103Rh/201Ir	ORS	HEHe	100	NA	78
7	ICP-MS	Telerium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	196.026nm
12	ICP-OES-AV	Lu	NA	NA	50	50	196.026
13	ICP-MS	Sc	ORS	He	50	NA	78
14	ICP-MS	Rh	NA	NA	625	NA	82
17	ICP-MS	Te	NA	standard mode	2000	NA	82
18	ICP-MS	In			1000	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	196.026
20	ICP-MS	Rh	ORS			NA	78
22	ICP-OES-AV	CsCl	NA	NA	50	50	196.026
23	ICP-OES-AV	Lu			83.3	NA	196.026
25	ICP-OES-AV	NA				NA	196.029
27	ICP-MS					NA	196.026
28	ICP-OES-AV	Yb	NA			NA	196.026 nm

Table 97 Instrument Conditions Sn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	In-1 115	KED		1	NA	118
2	ICP-MS	Rh	ORS	He	800	NA	118
3	ICP-MS	Tb	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	189.925
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	100	NA	118
7	ICP-MS	Telurium	ORS	standard mode		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	189.926nm
10	ICP-MS	Rh	CRI	He	500	NA	118
12	ICP-OES-AV	Lu	NA	NA	50	50	189.925
14	ICP-MS	Rh	NA	NA	625	NA	118
17	ICP-MS	Rh	NA	standard mode	2000	NA	120
19	ICP-OES-AV	Lu	NA	NA	50	50	189.925
20	ICP-MS	Rh	ORS			NA	118
21	ICP-MS	Rh	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	189.925
23	ICP-OES-AV	Lu			83.3	NA	189.925
25	ICP-OES-AV	NA				NA	189.927
27	ICP-MS					NA	189.925
28	ICP-OES-AV	Yb	NA			NA	189.925 nm



Table 98 Instrument Conditions Sr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-OES-RV	Y	NA	NA	NA	800	421.552
4	ICP-OES-AV	Lu	NA	NA	50	50	421.552
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	NA	200	88
8	ICP-OES	Eu & Cs	NA	NA	NA	50	430.545nm
10	ICP-MS	Rh	CRI	He	NA	500	88
11	ICP-OES-AV	Y 371.029			NA		407.771
12	ICP-OES-AV	Lu	NA	NA	50	50	421.552
13	NA	NA	ORS	He	NA	50	88
14	ICP-MS	Rh	NA	NA	NA	625	88
18	ICP-OES-AV	Sc			NA	100	
19	ICP-OES-AV	Lu	NA	NA	50	50	421.552
20	ICP-OES-RV	Y371	NA		NA		407.771
21	ICP-MS	Rh	ORS	He	NA	500	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	430.544
23	ICP-OES-AV	Lu			NA	83.3	407.771
24	ICP-MS	Sc	DRC	He	NA	20	m/z 88
27	ICP-OES-RV	NA	NA	NA	NA		NA

Table 99 Instrument Conditions Th

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
2	ICP-MS	Ir	ORS	He	800	NA	232
3	ICP-MS	Tb	KED	He		NA	
4	ICP-MS	Lu	ORS	standard mode	50	50	232
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	100	NA	232
8	ICP-MS	Ir, Rh & Sc	NA	NA	50	NA	232 m/z
12	ICP-MS	Lu	ORS	standard mode	50	50	232
13	ICP-MS	Ir	ORS	He	50	NA	232
14	ICP-MS	Ir	NA	NA	625	NA	232
19	ICP-MS	Lu	ORS	standard mode	50	50	232
20	ICP-MS	Ir				NA	232
22	ICP-MS	Sc, Rh, Ir	ORS	He	50	50	232
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-MS	Ir	ORS	NA		NA	232 m/z

Table 100 Instrument Conditions V

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		10	NA	51
2	ICP-MS	Rh	ORS	He	800	NA	51
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	292.401
6	ICP-MS	72Ge/103Rh/201Ir	ORS	He	1000	NA	51
7	ICP-MS	Scandium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	311.837nm
10	ICP-MS	Sc	CRI	He	500	NA	51
12	ICP-OES-AV	Lu	NA	NA	50	50	292.401
13	ICP-MS	Sc	ORS	He	50	NA	51
14	ICP-MS	Sc	KED	He	625	NA	51
17	ICP-MS	Sc	KED	He	2000	NA	51
19	ICP-OES-AV	Lu	NA	NA	50	50	292.401
20	ICP-OES-RV	Y371				NA	310.229
21	ICP-MS	Sc	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	311.837
23	ICP-OES-AV	Lu			83.3	NA	292.401
25	ICP-OES-AV	NA				NA	292.399
27	ICP-MS	NA	NA	NA	NA	NA	NA
28	ICP-OES-AV	Yb	NA			NA	292.401 nm

Table 101 Instrument Conditions Zn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Sc 45	KED		10	NA	66
2	ICP-MS	Rh	ORS	He	800	NA	64Mini
3	ICP-MS	Y	KED	He		NA	
4	ICP-OES-AV	Lu	NA	NA	50	50	206.2
5	ICP-OES					NA	
6	ICP-OES-AV	Y371 / Te214			1000	NA	66
7	ICP-MS	Rhodium	ORS	He		NA	
8	ICP-OES	Eu & Cs	NA	NA	50	NA	206.2, 334.502nm
10	ICP-MS	Sc	CRI	He	500	NA	66
12	ICP-OES-AV	Lu	NA	NA	50	50	206.2
13	ICP-MS	Sc	ORS	He	50	NA	66
14	ICP-MS	Ge	KED	He	625	NA	66
17	ICP-MS	Ga	KED	He	1000	NA	66
18	ICP-OES-AV	Sc			100	NA	
19	ICP-OES-AV	Lu	NA	NA	50	50	206.2
20	ICP-OES-RV	Te214				NA	202.548
21	ICP-MS	Sc	ORS	He	500	NA	NA
22	ICP-OES-AV	CsCl	NA	NA	50	50	206.2
23	ICP-OES-AV	Lu			83.3	NA	213.857
25	ICP-OES-AV	NA				NA	213.857
27	ICP-MS					NA	206.2
28	ICP-OES-AV	Yb	NA			NA	213.857 nm

**END OF REPORT**