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National Measurement Institute

Proficiency Test Final Report AQA 23-16 Metals, Nutrients and Anions in Soil

December 2023

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Luminita Antin

Andrew Evans

Hamish Lenton

Mai Nielsen

Wei Huang

Jeffrey Merrick

Jessica Todorovski

Raluca Iavetz

Manager, Chemical Proficiency Testing

Phone: 61-2-9449 0111
proficiency@measurement.gov.au

Accredited for compliance with ISO/IEC 17043

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SUMMARY

This report presents the results of the proficiency test AQA 23-16 Metals, Nutrients and Anions in Soil. The study covers the measurement of acid extractable elements: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Th, Tl, V, U and Zn. Measurement of pH, electrical conductivity (EC), water soluble bromide (Br^-), chloride (Cl^-), fluoride (F^-), iodide (I^-), orthophosphate-P (PO_4^{3-}-P), and sulphate (SO_4^{2-}) and of total Kjeldahl nitrogen (TKN), 2M KCl extractable ammonium nitrogen (NH_4^+-N) and 2M KCl extractable nitrate nitrogen (NO_3^--N) were also included in the program.

The sample set consisted of two dried soil samples 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_n-scores.

Of 631 z-scores, 587 (93%) were satisfactory with $|z| \leq 2.0$.

Of 631 E_n-scores, 506 (80%) were satisfactory with $| E_n | \leq 1.0$.

Laboratories **10** and **23** returned the highest number of satisfactory z scores (46 out of 47 reported and 46 out of 46 reported, respectively).

Laboratory 23 also returned the highest number of satisfactory E_n-scores, 46.

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

Most participants analysed acid extractable elements by using a sample size of between 0.5 g to 1 g, an extraction temperature of between 95ºC to 120ºC, an extraction time of between 60 min to 120 min and a ratio of HNO_3 to HCl of 1:1. Low-level Sb, Sn and Th were the analytes which presented the most analytical difficulty to participating laboratories.

The level of chloride in study sample S3 was low and challenged participants' analytical techniques. Caution should be exercised when a colorimetric method is used to measure low-level chloride in soil. Spectrophotometry has low specificity and is liable to interference from coloured species. Alternatively, ICP-OES might not be the right instrumental technique for sulphate measurement in soil; false positive results can be produced using this technique as it measures total S and not just S from sulphate compounds.

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

Over the last 24 studies of inorganic analytes in soil, the average proportion of satisfactory scores was 90% for z-scores and 80% for E_n-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 659 numerical results, 599 (91%) were reported with an expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 0.1% to 333% 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."[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment and food safety. NMI offers studies in:

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

AQA 23-16 is the 33rd 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.[2] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[3] These documents have been prepared with reference to ISO Standard 17043[1] and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4]

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

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The 51 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)[5] 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:	15 August 2023
Samples dispatched:	4 September 2023
Results due:	6 October 2023
Interim report issued:	11 October 2023
Preliminary report issued:	17 October 2023

The due date for results was extended to 6 October 2023. This is a large and complex study and we received multiple requests for the results deadline to be extended.

2.3 Test Material Specification

Three samples were provided for analysis:

Sample S1 was 30 g of dried soil;

Sample S2 was 30 g of dried soil; 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 water soluble anions with the exception of water-soluble iodide 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 all acid extractable elements in S1 and S2.

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 4 September 2023.

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 (NO_3^--N) and (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 (NH_4^+-N) and 2M KCl extractable nitrate-N (NO_3^--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 µS/cm.

SAMPLE S1 Dried Soil		**SAMPLE S2 Dried Soil**		**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**
As	2-50	Ag	0.5-20	Ca (acid extractable)	250-10000
B	1-25	Al	1000-40000	Fe (acid extractable)	1000-40000
Cd	1-25	As	2-50	K (acid extractable)	250-10000
Cr	5-100	B	0.5-20	Mg (acid extractable)	250-10000
Cu	2-80	Ba	50-1000	Na (acid extractable)	50-2000
Hg	0.5-20	Be	0.5-20	P(acid extractable)	250-10000
Mn	50-1000	Bi	0.5-20	S (acid extractable)	NA
Mo	2-50	Co	0.5-20	Sr (acid extractable)	NA
Ni	2-50	Cu	2-50	Water Soluble Bromide (Br^-) - 1:5 soil/water extract	0.5-20
Pb	50-1000	Cs	0.5-20	Water Soluble Chloride (Cl^-) - 1:5 soil/water extract	2-80
Sb	2-50	La	2-80	Water Soluble Fluoride (F^-) - 1:5 soil/water extract	0.5-20
Se	2-50	Li	2-50	Water Soluble Iodide (I^-) - 1:5 soil/water extract	0.5-20
Tl	0.5-20	Rb	5-100	Water Soluble Sulphate (SO_4^{2-}) - 1:5 soil/water extract	5-100
V	5-100	Sn	0.5-20	Water Soluble Orthophosphate-P (PO_4^{3-}-P) - 1:5 soil/water extract	2-80
Zn	50-1000	Th	2-50	pH of 1:5 soil/water suspension	>2
		U	0.5-20	EC of 1:5 soil/water extract	50-1000
		Zn	50-1000	Kjeldahl nitrogen, total (TKN)	1000-40000
				2M KCl Extractable (Nitrate-N)	2-80
				2M KCl Extractable (Ammonium-N)	5-100

2.9 Interim and Preliminary Reports

An interim report was emailed participants on 11 October 2023. A preliminary report was issued on 17 October 2023. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants. There was a change in the uncertainty of the assigned values for As in S1 and S2, from 0.6 mg/kg to 0.7 mg/kg for both samples. There was no significant change in participants' E_n-scores.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summaries

Summaries of test methods are transcribed in Tables 1 to 10.

Table 1 Methodology for Acid Extractable Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO3 (mL)	Vol. HCl (mL)	Vol. HNO3 (1:1) (mL)	Vol. H2O2 (mL)	Other (mL)
2	US EPA 3050B	0.5	95	120	3	3			
3	Acid Digestion of sediment,sludges and soil-USEPA 3050	1	95	90	3	3			
4	USEPA 3050B	1	98	100		5.0	10.0		
5		1	95		7.5	2.5			
8	USEPA-6010C (Except Mercury by USEPA-7471B)	1	95		5	5		3	
9	Inhouse Method with Reference to USEPA 6010,6020	0.5	95	60	1	1.5		1	
10		1	100	120	3	3			
11	In House S6 referencing APHA 3125	0.4	120	60	2.5	7.5			
12	US-EPA Method 200.2	1	95	50	2	2			10
13	EPA (Environmental Protection Agency) 1994 Method 200.8	2	109	60	800	400			1200
14	USEPA Method 6010c, USEPA Methods 7471B, 7470A, 7471B	1	90-98	90	3	3			
15	In house Method	0.25	100-120-140	180	2.5			2.5	
16	EPA 200.2	0.5	95	60	1	1			
17	US EPA 3050B	0.5	95	120	7.5	5		1.5	
18	US EPA 200.7	1	95	45	2.5	2.5			45
19	EPA 3050B,3010A,245.7,7062	0.5	70-90	60	2.5	7.5			
20	in house	2	95	180	6	6		5	
21	AS 4479.2-1997, AS4479.4-1999	0.5	95	120	1	3			
23	USEPA Method 6010c, USEPA Methods 7471B, 7470A, 7471B	1	90 - 98	90	3	3			
24	Soil Chemmical Methods - Australasia (Rayment &Lyons) method 17B1	0.5014	95	120	3.75	1.25			
25	In House Method	1	112.5	240	2.5	7.5			
26	EPA200.2, (1:1 Nitric:Hydrochloric Acid)	0.5	96	30	1	1			
27	USEPA 3050	3	85	120	10	5	10	6	
28	200.2	0.5	98	90	3	3			

*Additional information in Table 10

Table 2 Methodology for Total Kjeldahl Nitrogen

Lab. Code	Method Reference	Digestion	Distillation	Measurement Method	Instrument
3	APHA 4500	Yes		Colorimetric - salicylate method	DA
5	QWI-EN-WK061E	Yes	Yes	Titrimetric method	Manual Analysis
10		Yes	Yes	Titrimetric method	foss
11				TKN = TN-NOx (Dumas)	LECO
14	APHA latest Edition. Analytical Methods for Waters and Wastewates 4500-Inorg-D	Yes	No	Colorimetric - salicylate method	DA
15	According to EN 13342 and DIN ISO 11261, modified by BUCHI (BUCHI 2013)	Yes	Yes	Titrimetric method	
23	APHA latest Edition. Analytical Methods for Waters and Wastewates 4500-Inorg-D	Yes	No	Colorimetric - salicylate method	DA
24	In-house method based on APHA 23rd edition 4500-Norg B	Yes	Yes	Colorimetric - salicylate method	DA

*Additional information in Table 10

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	
	NH4+-N	NO3--N				NH4+-N	NO3--N	NH4+-N	NO3--N
3	APHA	APHA	5	50	2	Colorimetric - Phenate method	Colorimetric - Vanadium III method	DA	DA
10			10	100	1 hour	SFA with Fluorescence Detector	Colorimetric-Sulfanilamide-NEDD Cd reduction	SFA	SFA
11	In House S37	In House S37	2	20	1	Colorimetric - Salicylate method	Colorimetric - Vanadium III method	FIA	FIA
14	APHA latest Edition. Analytical Methods for Waters and Wastewates 4500-Inorg-D	APHA latest Edition. Analytical Methods for Waters and Wastewates 4500-Inorg-D	5	25	1.5	Colorimetric - Phenate method	Colorimetric - Vanadium III method	DA	DA
15	HACH Method 10205 TNT Plus	HACH Method 8192	5	50	1	Colorimetric - Salicylate method	Other (please type)	Manual Analysis	Manual Analysis
22	7C2b	7C2b	10	100	1	Colorimetric - Salicylate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA

Lab. Code	Method Reference		Sample Mass (g)	Extraction Solution 2M KCl Volume (mL)	Shake time (hours)	Measurement Method		Measurement Instrument	
	NH4+-N	NO3--N				NH4+-N	NO3--N	NH4+-N	NO3--N
23	APHA latest Edition. Analytical Methods for Waters and Wastewates 4500-Inorg-D	APHA latest Edition. Analytical Methods for Waters and Wastewates 4500-NO2-B, 4500-NO3 E and 4500-N C	5.09	25	1.5	Colorimetric - Phenate method	Colorimetric - Vanadium III method	DA	DA
24	Soil Chemical Methods, Rayment & Lyons method 7C1 & 7C2	Soil Chemical Methods, Rayment & Lyons method 7C1 & 7C2	4.99	50	1	Colorimetric - Salicylate method	Colorimetric - Vanadium III method	DA	DA

*Additional information in Table 10

Table 4 Methodology for Water Soluble Bromide

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
3	APHA	5	25	2	Ion Chromatographic Method	IC
10		10	50	1 hour	Ion Chromatographic Method	IC
11		2	10	1		
14	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	20	100	1.5	Ion Chromatographic Method	IC
15	AN 133 71691	10	50	1	Ion Chromatographic Method	IC
17	NT	12	60	1		
23	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	9.98	50	1.5	Ion Chromatographic Method	IC
24	NA	39.95	200	1		
28	APHA 4110B and C	5	25	3	Ion Chromatographic Method	IC

Table 5 Methodology for Water Soluble Chloride

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
3	APHA	5	25	2	Ion Chromatographic Method	IC
5	QWI-EN-WD045G				Ferricyanide Colorimetric Method	DA
10		10	50	1 hour	Ion Chromatographic Method	IC

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
11		2	10	1	Mercuric Thiocyanate	Segmented Flow Analyser
14	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	20	100	1.5	Ion Chromatographic Method	IC
15	AN 133 71691	10	50	1	Ion Chromatographic Method	IC
17	APHA 4110 B	12	60	1	Ion Chromatographic Method	IC
23	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	9.98	50	1.5	Ion Chromatographic Method	IC
24	Soil Chemical Methods, Rayment & Lyons method 5A1	39.95	200	1	Potentiometric Method	Titration
28	APHA 4110B and C	5	25	3	Ion Chromatographic Method	IC

Table 6 Methodology for Water Soluble Fluoride

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
3	APHA	5	25	2	Ion Selective Electrode Method	Fluoride Selective Electrode
5	QWI-EN-WK040T				Ion Selective Electrode Method	Fluoride Selective Electrode
6	APHA 4500-F C				Ion Selective Electrode Method	Fluoride Selective Electrode
10		10	50	1 hour	Ion Selective Electrode Method	Omnis
11		2	10	1		
14	APHA	20	100	1.5	Ion Selective Electrode Method	Fluoride Selective Electrode
15	AN 133 71691	10	50	1	Ion Chromatographic Method	IC
17	NT	12	60	1		
23		9.98	50	1.5	Ion Selective Electrode Method	Fluoride Selective Electrode
24	Soil Chemical Methods, Rayment & Lyons	39.95	200	1	Ion Selective Electrode Method	Fluoride Selective Electrode
28	APHA 4110B and C	5	25	3	Ion Selective Electrode Method	IC

Table 7 Methodology for Water Soluble Iodide

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
3	APHA	5	25	2	Ion Chromatographic Method	IC
5	QWI-EN-.D010				Ion Selective Electrode Method	Iodide Selective Electrode
10		10	50	1 hour	Ion Chromatographic Method	IC
11		2	10	1		
14	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with UV-Vis detection	20	100	1.5	Ion Chromatographic Method	IC
15		10	50	1		
17	NT	12	60	1		
23	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	9.98	50	1.5	Ion Chromatographic Method	IC
24	NA	39.95	200	1		
28		5	25	3		

Table 8 Methodology for Water Soluble Orthophosphate-P

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
3	APHA	5	25	2	Ascorbic Acid Colorimetric Method	DA
5	QWI-EN-WK071SG				Ascorbic Acid Colorimetric Method	DA
10		10	50	1 hour	Ion Chromatographic Method	IC
11		2	10	1	Vanadomolybdophosphoric Colorimetric Method	FIA
14	APHA	20	100	1.5	Ascorbic Acid Colorimetric Method	DA
15	AN 133 71691	10	50	1	Ion Chromatographic Method	IC
17	NT	12	60	1		
23		9.98	50	1.5	Ascorbic Acid Colorimetric Method	DA
24	Soil Chemical Methods, Rayment & Lyons	39.95	200	1	Ascorbic Acid Colorimetric Method	DA
28	APHA 4110B and C	5	25	3	Ion Chromatographic Method	IC

Table 9 Methodology for Water Soluble SO_4^{2-}

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
3	APHA	5	25	2	Ion Chromatographic Method	IC
4	In-House Method NSW.AES.032				Turbidimetric Method	Turbidimeter
5	QWI-EN-WD041G				Turbidimetric Method	DA
10		10	50	1 hour	Ion Chromatographic Method	IC
11		2	10	1	ICP-Method	ICP-OES
14	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	20	100	1.5	Ion Chromatographic Method	IC
15	AN 133 71691	10	50	1	Ion Chromatographic Method	IC
17	APHA 4110 B	12	60	1	Ion Chromatographic Method	IC
23	APHA latest Edition. Analytical Methods for Waters and Wastewates, 4110b. Ion Cromatography with Chemical Suppression of Eluent Conductivity	9.98	50	1.5	Ion Chromatographic Method	IC
24	Soil Chemical Methods, Rayment & Lyons	39.95	200	1	Turbidimetric Method	Turbidimeter
28	APHA 4110B and C	5	25	3	Ion Chromatographic Method	IC

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 10.

Table 10 Additional information

Lab Code	Additional Information
11	Total Kjeldahl Nitrogen: TKN = TN by LECO and NOx by FIA
15	Total Kjeldahl Nitrogen: Analysed using automatic pH endpoint titration 2M KCl Extractable Nitrate-N: Cadmium Reduction Method 8192 (HACH). Instrument: DR 1900 HACH
19	Methodology: After digestion, make up to 50mL graduation with distilled water.
24	Methodology: Once digested the sample is made up to 25 mL with DI Water
28	Methodology: Acid ratio for ICP-MS extraction 2 mL HNO3 to 0.5 mL HCl
7	Sample S1: Method: EPA 7473, DMA80
16	Sample S1: Results reported on a single pass / Boron not reported due to low concs. Producing negative concs. Ie software does all calcs (approx x 1000 dilution factors applied to instrument levels)
19	Sample S1: Analyte concentration contributed by spike and an acceptable 70-130% recovery for all elements are determined.

3.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 11).

Table 11 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
2	SD of replicate analyses x 2 x 100/85 x 100/mean	Control Samples	CRM Instrument Calibration	
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	ISO/GUM
4	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS Standard Purity	Eurachem/CITAC Guide
5	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis Instrument Calibration	CRM Recoveries of SS	Eurachem/CITAC Guide
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM Recoveries of SS	NMI Uncertainty Course
7	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
8	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
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Variation in Sample Moisture Content Recoveries of SS	Nordtest Report TR537
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	Instrument Calibration Standard Purity	Nordtest Report TR537

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
12	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
13	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis	Recoveries of SS	
14	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS		Eurachem/CITAC Guide
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	other please type
16	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Instrument Calibration	CRM Instrument Calibration Recoveries of SS	ISO/GUM
17	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	Variation in Sample Moisture Content Recoveries of SS	
18	Professional judgment	Control Samples	Recoveries of SS	Eurachem/CITAC Guide
19	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	
20	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	CRM	
21	Calculated from Standard deviation and concentration of long-term in-house QC samples	Control Samples - RM Duplicate Analysis	CRM Instrument Calibration Laboratory Bias from PT Studies	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
22	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Nordtest Report TR537
23	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	NATA Technical Note 33
24	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis	Recoveries of SS	NATA General Accreditation Guidance,

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
				Estimating and Reporting MU
25	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
26	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis		
27	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Instrument Calibration	
28	No uncertainty values available	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	

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

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.

No feedback was provided for this study.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 12 to 61 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 51. An example chart with interpretation guide is shown in Figure 1.

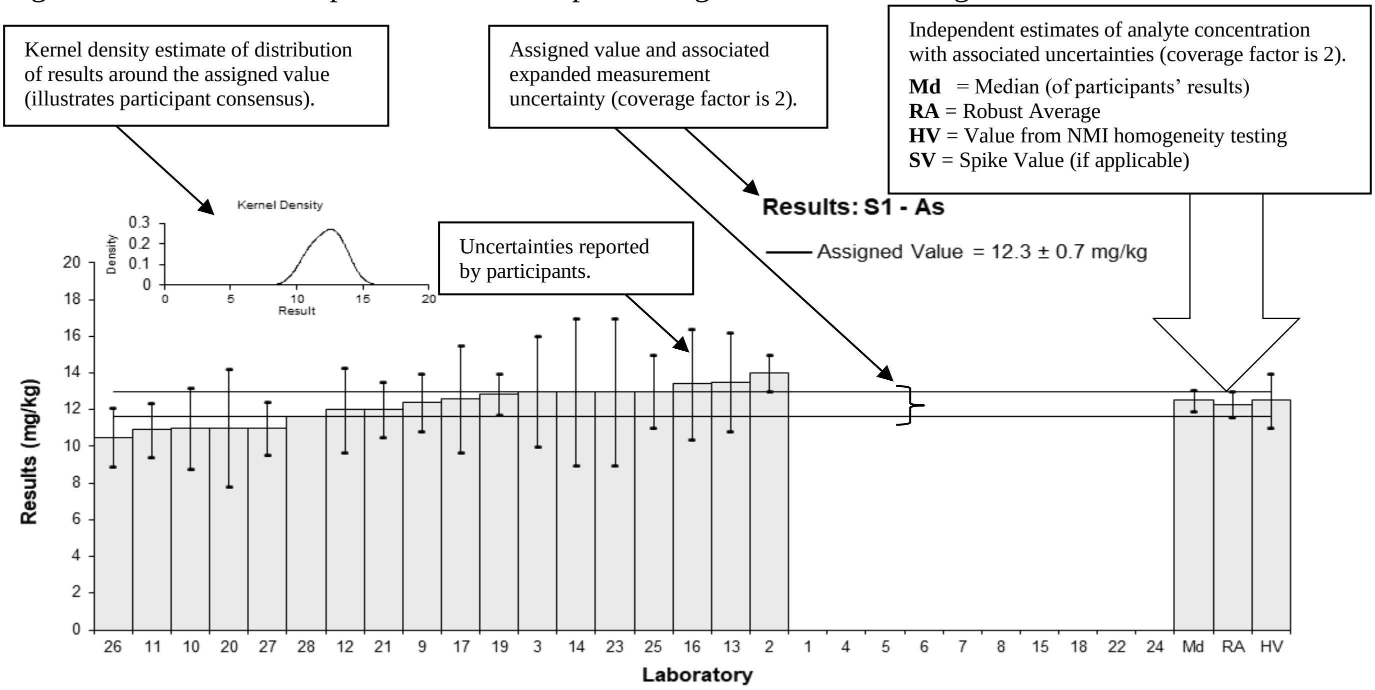


Figure 1 Guide to Presentation of Results

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.[3, 4, 6]

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.'[1] 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.[4, 6]

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.[6] The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528.[6]

4.5 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value (X) and the performance coefficient of variation (PCV). This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

$\sigma = X * PCV$ 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.[7]

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:

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

Where:

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

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

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

4.7 E_n-Score

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

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

where:

E_n is E_n-score;
χ is a participant's result;
X is the study assigned value;
U_χ is the expanded uncertainty of the participant's result;
U_X is the expanded uncertainty of the assigned value.

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

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

4.8 Traceability and Measurement Uncertainty

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

5 TABLES AND FIGURES

Table 12

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	As
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	14	1	1.38	1.39
3	13	3	0.57	0.23
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	12.4	1.6	0.08	0.06
10	11	2.2	-1.06	-0.56
11	10.9	1.5	-1.14	-0.85
12	12.0	2.3	-0.24	-0.12
13	13.5	2.7	0.98	0.43
14	13	4	0.57	0.17
15	NT	NT		
16	13.4	3.0	0.89	0.36
17	12.6	2.9	0.24	0.10
18	NT	NT		
19	12.825	1.118	0.43	0.40
20	11	3.2	-1.06	-0.40
21	12.0	1.5	-0.24	-0.18
22	NT	NT		
23	13	4	0.57	0.17
24	NT	NT		
25	13	2	0.57	0.33
26	10.5	1.6	-1.46	-1.03
27	11	1.463	-1.06	-0.80
28	11.6	NR	-0.57	-1.00

Statistics

Assigned Value	12.3	0.7
Spike Value	Not Spiked	
Homogeneity Value	12.5	1.5
Robust Average	12.3	0.7
Median	12.5	0.6
Mean	12.3	
N	18	
Max	14	
Min	10.5	
Robust SD	1.2	
Robust CV	9.7%	

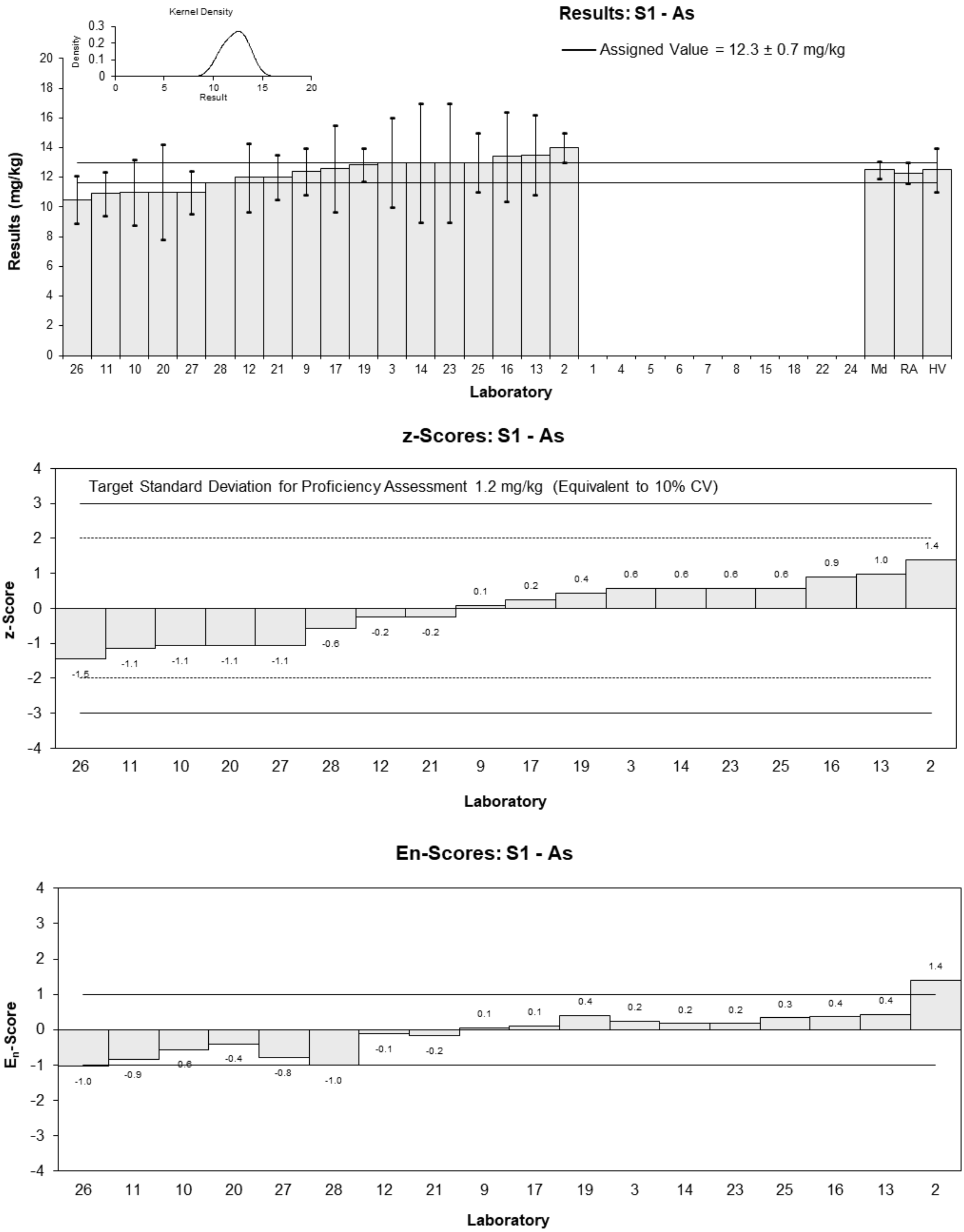

Results: S1 - As
Assigned Value = 12.3 ± 0.7 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S1 - As
Target Standard Deviation for Proficiency Assessment 1.2 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S1 - As
E_n-Score
Laboratory

Figure 2

Table 13

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	B
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	4.045	NR	0.28	0.25
2	NT	NT		
3	<10	10		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	NT	NT		
9*	6.23	0.90	4.04	2.09
10	4.3	0.86	0.72	0.39
11	3.46	0.5	-0.72	-0.50
12	<20	3.6		
13	3.9	0.8	0.03	0.02
14	<10	NR		
15	NT	NT		
16	NR	NR		
17	<10	NR		
18	NT	NT		
19**	59.361	2.580	95.33	20.81
20	NT	NT		
21	3.5	0.4	-0.65	-0.49
22	NT	NT		
23	4.1	4	0.38	0.05
24	NT	NT		
25	NT	NT		
26	2.73	0.74	-1.98	-1.15
27	5	1.07	1.92	0.89
28	NR	NR		

* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	3.88	0.67
Spike Value	Not Spiked	
Homogeneity Value	3.44	0.41
Robust Average	4.05	0.77
Median	4.05	0.67
Mean	4.14	
N	9	
Max	6.23	
Min	2.73	
Robust SD	0.92	
Robust CV	23%	

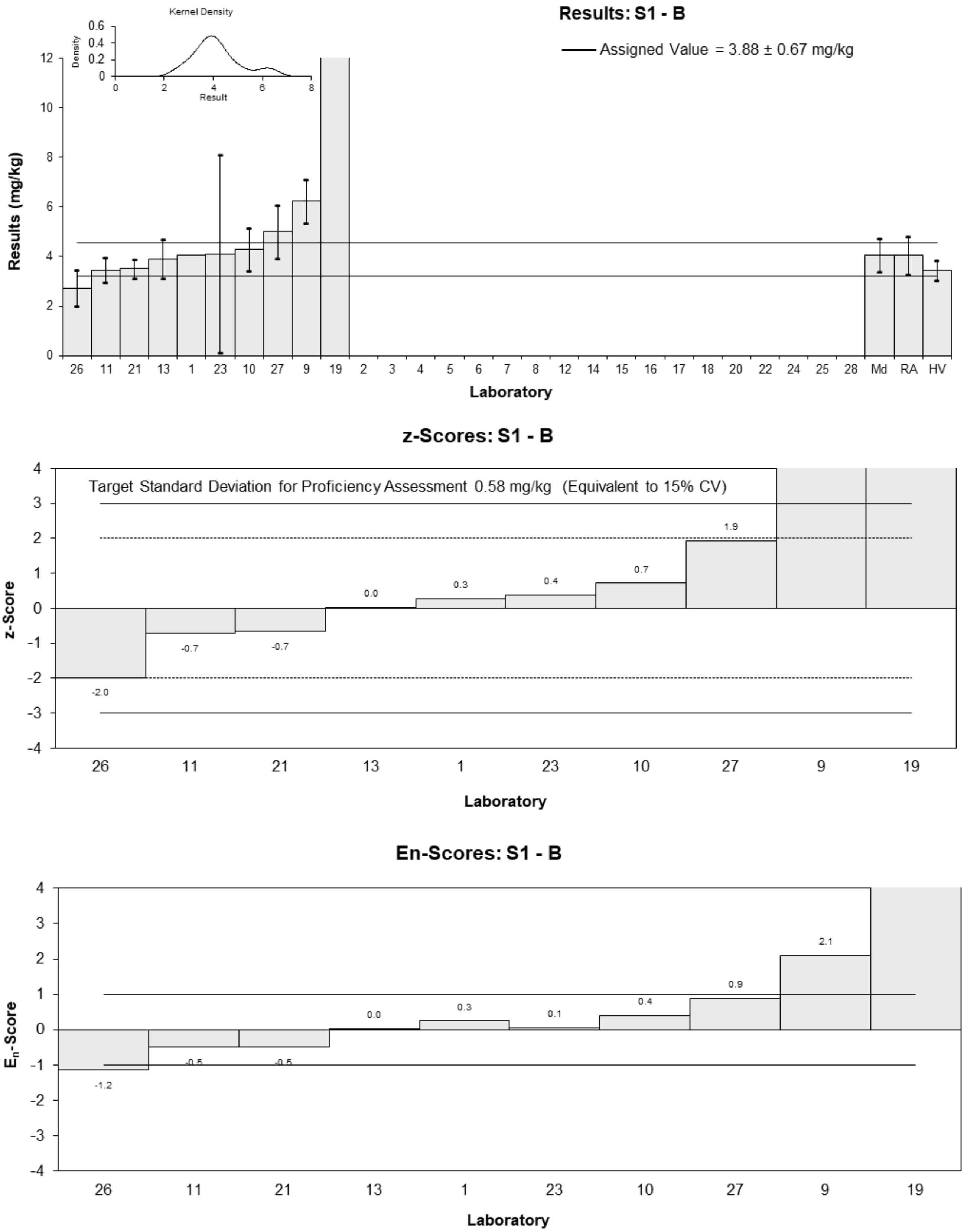

Results: S1 - B
Assigned Value = 3.88 ± 0.67 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 11 21 13 1 23 10 27 9 19 2 3 4 5 6 7 8 12 14 15 16 17 18 20 22 24 25 28 Md RA HV
z-Scores: S1 - B
Target Standard Deviation for Proficiency Assessment 0.58 mg/kg (Equivalent to 15% CV)
z-Score
-2.0 -0.7 -0.7 0.0 0.3 0.4 0.7 1.9
26 11 21 13 1 23 10 27 9 19
Laboratory
En-Scores: S1 - B
En-Score
-1.2 -0.5 -0.5 0.0 0.3 0.1 0.4 0.9 2.1
26 11 21 13 1 23 10 27 9 19
Laboratory

Figure 3

Table 14

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Cd
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.385	NR	0.83	2.68
2	3.0	0.2	-0.02	-0.04
3	3.1	0.6	0.20	0.15
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	2.6	0.1	-0.91	-2.38
9	3.04	0.90	0.07	0.03
10	2.8	0.56	-0.47	-0.36
11	3.11	0.4	0.22	0.24
12	2.88	0.41	-0.29	-0.30
13	3.06	0.61	0.11	0.08
14	3.3	0.6	0.64	0.47
15	NT	NT		
16	3.0	0.9	-0.02	-0.01
17	3.1	0.3	0.20	0.27
18	NT	NT		
19	3.379	0.173	0.82	1.66
20	2.8	0.86	-0.47	-0.24
21	2.9	0.3	-0.24	-0.33
22	NT	NT		
23	3.2	0.6	0.42	0.31
24	NT	NT		
25	3.0	1.0	-0.02	-0.01
26	2.73	0.55	-0.62	-0.49
27	2.6	0.3822	-0.91	-1.01
28	3.1	NR	0.20	0.64

Statistics

Assigned Value	3.01	0.14
Spike Value	Not Spiked	
Homogeneity Value	2.86	0.34
Robust Average	3.01	0.14
Median	3.02	0.11
Mean	3.00	
N	20	
Max	3.385	
Min	2.6	
Robust SD	0.25	
Robust CV	8.2%	

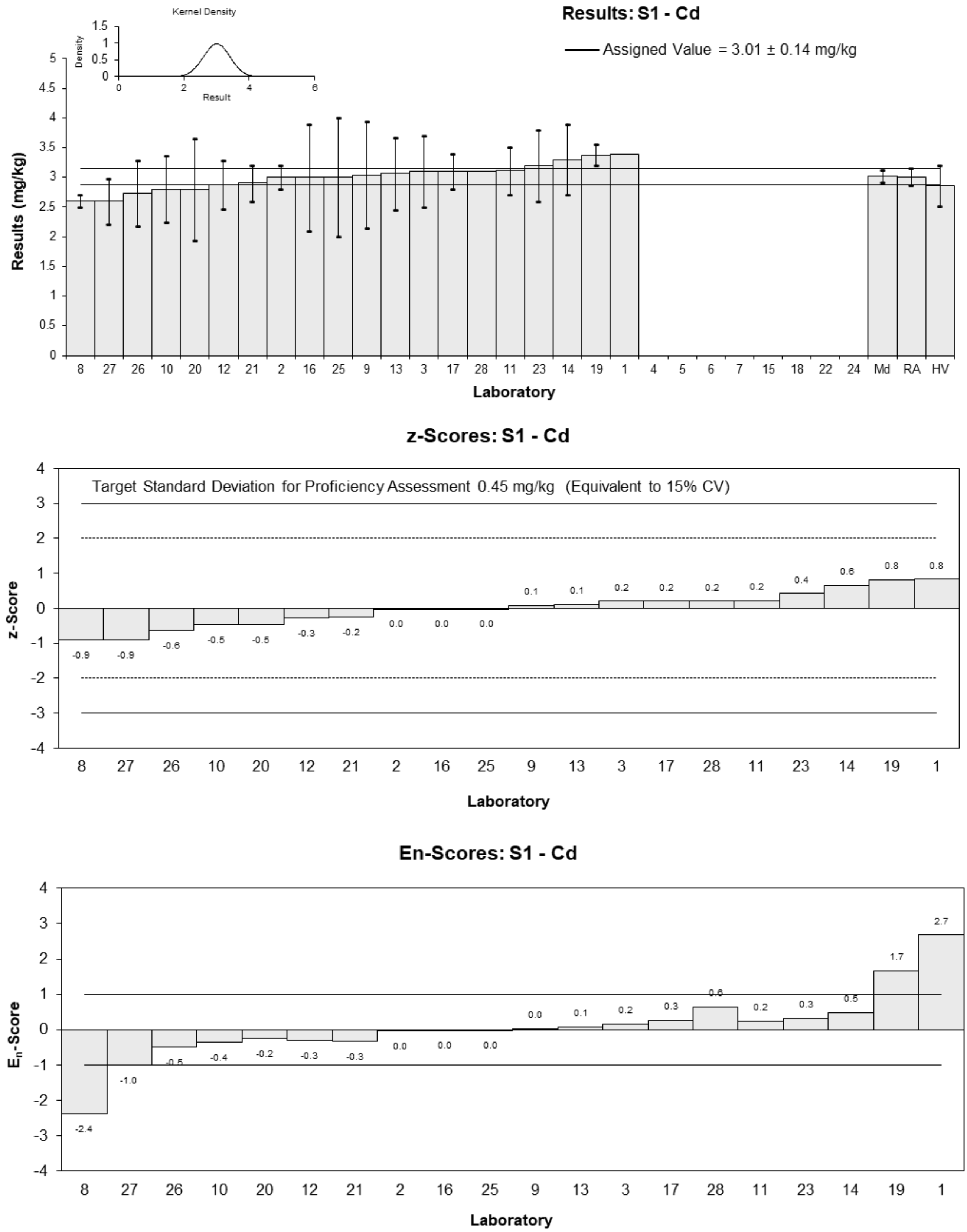

Results: S1 - Cd
Assigned Value = 3.01 ± 0.14 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S1 - Cd
Target Standard Deviation for Proficiency Assessment 0.45 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Cd
E_n-Score
Laboratory

Figure 4

Table 15

Sample Details

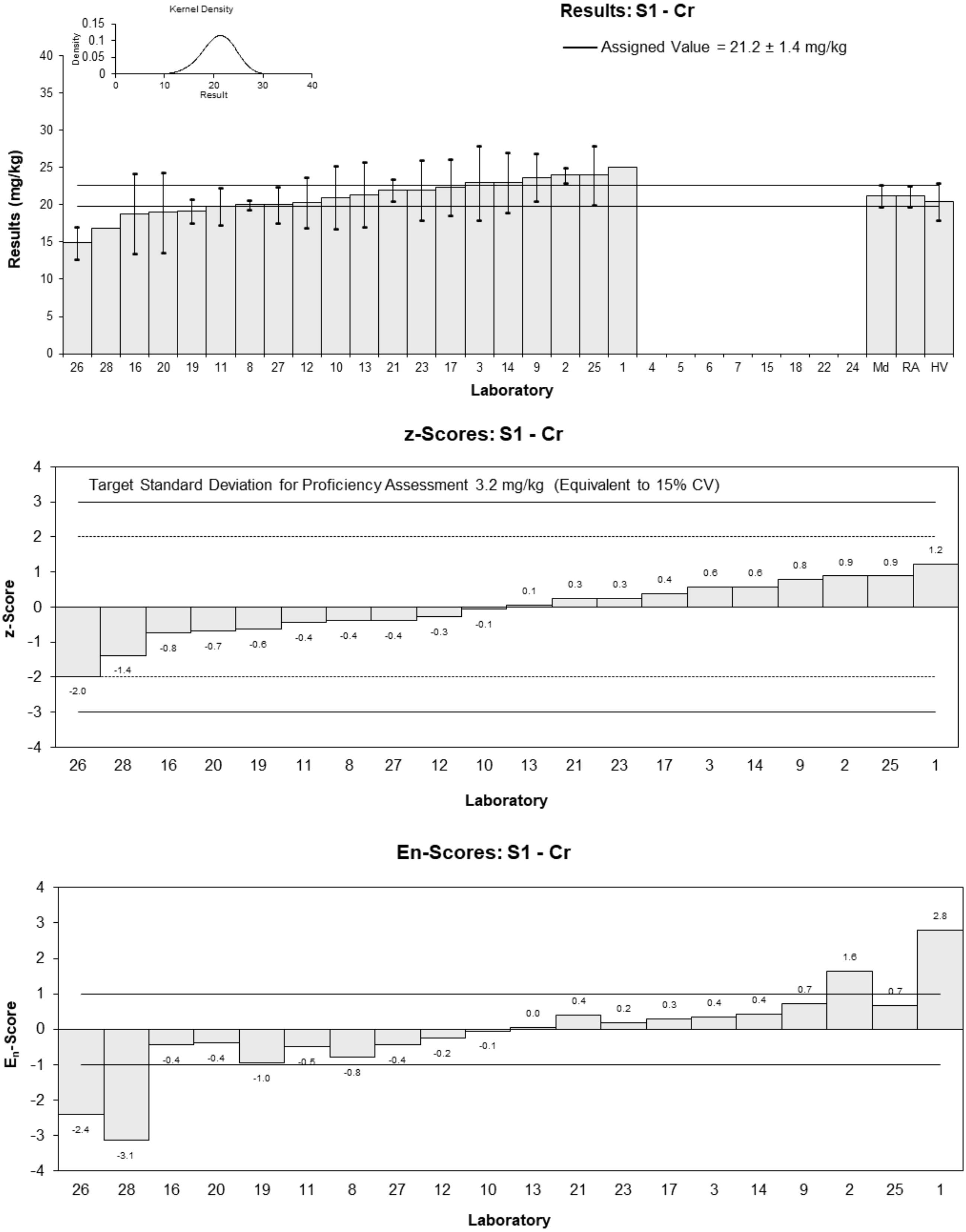
Sample No.	S1
Matrix	Soil
Analyte	Cr
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	25.1	NR	1.23	2.79
2	24	1	0.88	1.63
3	23	5	0.57	0.35
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	20	0.6	-0.38	-0.79
9	23.7	3.2	0.79	0.72
10	21	4.2	-0.06	-0.05
11	19.8	2.5	-0.44	-0.49
12	20.3	3.4	-0.28	-0.24
13	21.4	4.3	0.06	0.04
14	23	4	0.57	0.42
15	NT	NT		
16	18.8	5.4	-0.75	-0.43
17	22.4	3.8	0.38	0.30
18	NT	NT		
19	19.157	1.627	-0.64	-0.95
20	19	5.4	-0.69	-0.39
21	22.0	1.5	0.25	0.39
22	NT	NT		
23	22	4	0.25	0.19
24	NT	NT		
25	24	4	0.88	0.66
26	14.9	2.2	-1.98	-2.42
27	20	2.38	-0.38	-0.43
28	16.8	NR	-1.38	-3.14

Statistics

Assigned Value	21.2	1.4
Spike Value	Not Spiked	
Homogeneity Value	20.5	2.5
Robust Average	21.2	1.4
Median	21.2	1.5
Mean	21.0	
N	20	
Max	25.1	
Min	14.9	
Robust SD	2.5	
Robust CV	12%	



Results: S1 - Cr
Assigned Value = 21.2 ± 1.4 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 28 16 20 19 11 8 27 12 10 13 21 23 17 3 14 9 2 25 1 4 5 6 7 15 18 22 24 Md RA HV
z-Scores: S1 - Cr
Target Standard Deviation for Proficiency Assessment 3.2 mg/kg (Equivalent to 15% CV)
z-Score
-2.0 -1.4 -0.8 -0.7 -0.6 -0.4 -0.4 -0.4 -0.3 -0.1 0.1 0.3 0.3 0.4 0.6 0.6 0.8 0.9 0.9 1.2
Laboratory
26 28 16 20 19 11 8 27 12 10 13 21 23 17 3 14 9 2 25 1
En-Scores: S1 - Cr
En-Score
-2.4 -3.1 -0.4 -0.4 -1.0 -0.5 -0.8 -0.4 -0.2 -0.1 0.0 0.4 0.2 0.3 0.4 0.4 0.7 1.6 0.7 2.8
Laboratory
26 28 16 20 19 11 8 27 12 10 13 21 23 17 3 14 9 2 25 1

Figure 5

Table 16

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Cu
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	29.05	NR	2.47	4.79
2	25	1	0.73	1.09
3	24	5	0.30	0.14
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	25.2	2.6	0.82	0.66
10	24	4.8	0.30	0.14
11	22.7	2.5	-0.26	-0.22
12	22.0	3.3	-0.56	-0.37
13	25.0	5	0.73	0.33
14	24	5	0.30	0.14
15	NT	NT		
16	21.4	11.0	-0.82	-0.17
17	24	4	0.30	0.17
18	NT	NT		
19	19.423	1.314	-1.66	-2.18
20	23	5.6	-0.13	-0.05
21	23.0	1.0	-0.13	-0.19
22	NT	NT		
23	25	5	0.73	0.33
24	NT	NT		
25	25	4	0.73	0.41
26	18.3	2.7	-2.15	-1.69
27	23	2.875	-0.13	-0.10
28	18.1	NR	-2.23	-4.33

Statistics

Assigned Value	23.3	1.2
Spike Value	Not Spiked	
Homogeneity Value	23.8	2.9
Robust Average	23.3	1.2
Median	24.0	0.9
Mean	23.2	
N	19	
Max	29.05	
Min	18.1	
Robust SD	2.1	
Robust CV	9.1%	

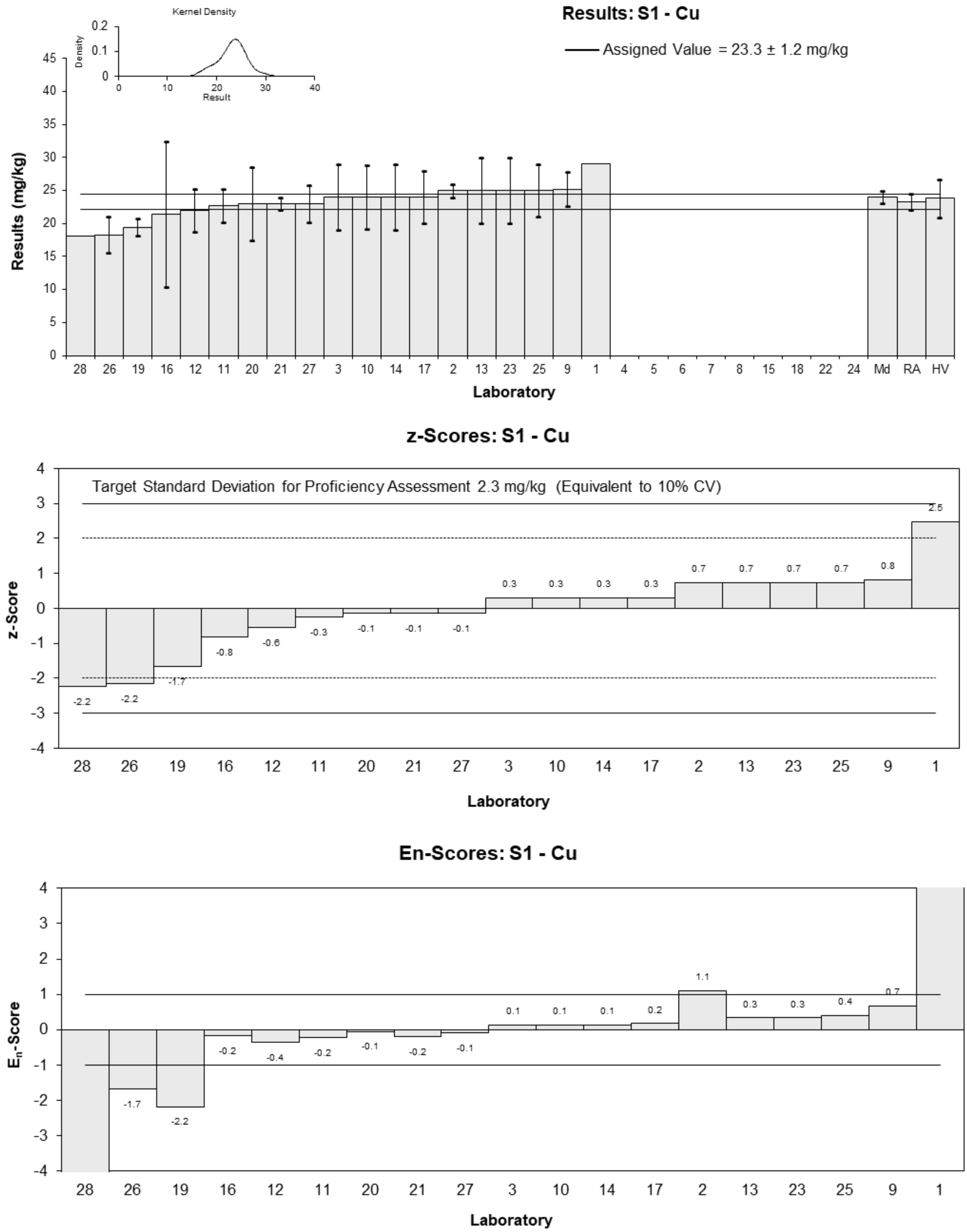

Results: S1 - Cu
Assigned Value = 23.3 ± 1.2 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
28 26 19 16 12 11 20 21 27 3 10 14 17 2 13 23 25 9 1 4 5 6 7 8 15 18 22 24 Md RA HV
z-Scores: S1 - Cu
Target Standard Deviation for Proficiency Assessment 2.3 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
28 26 19 16 12 11 20 21 27 3 10 14 17 2 13 23 25 9 1
-2.2 -2.2 -1.7 -0.8 -0.6 -0.3 -0.1 -0.1 -0.1 0.3 0.3 0.3 0.3 0.7 0.7 0.7 0.7 0.8 2.5
En-Scores: S1 - Cu
En-Score
Laboratory
28 26 19 16 12 11 20 21 27 3 10 14 17 2 13 23 25 9 1
-1.7 -2.2 -0.2 -0.4 -0.2 -0.1 -0.2 -0.1 0.1 0.1 0.1 0.2 1.1 0.3 0.3 0.4 0.7

Figure 6

Table 17

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Hg
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.0256	NR	0.19	0.62
2	1.9	0.2	-0.24	-0.32
3	2.2	0.4	0.78	0.56
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	1.79	0.06	-0.61	-1.66
8	2.1	0.3	0.44	0.42
9	2.05	0.58	0.27	0.14
10	1.8	0.36	-0.58	-0.46
11	2.07	0.25	0.34	0.38
12	1.96	0.32	-0.03	-0.03
13	2.07	0.4	0.34	0.24
14	2.2	0.6	0.78	0.38
15	NT	NT		
16	1.7	0.78	-0.91	-0.34
17	2.06	0.21	0.30	0.39
18	NT	NT		
19	1.816	0.077	-0.52	-1.30
20	1.9	0.69	-0.24	-0.10
21	1.9	0.2	-0.24	-0.32
22	NT	NT		
23	2	0.6	0.10	0.05
24	NT	NT		
25	1.98	0.6	0.03	0.02
26	1.72	0.29	-0.85	-0.82
27	2.3	0.3864	1.12	0.83
28	1.9	NR	-0.24	-0.78

Statistics

Assigned Value	1.97	0.09
Spike Value	2.01	0.10
Homogeneity Value	1.98	0.24
Robust Average	1.97	0.09
Median	1.98	0.07
Mean	1.97	
N	21	
Max	2.3	
Min	1.7	
Robust SD	0.17	
Robust CV	8.7%	

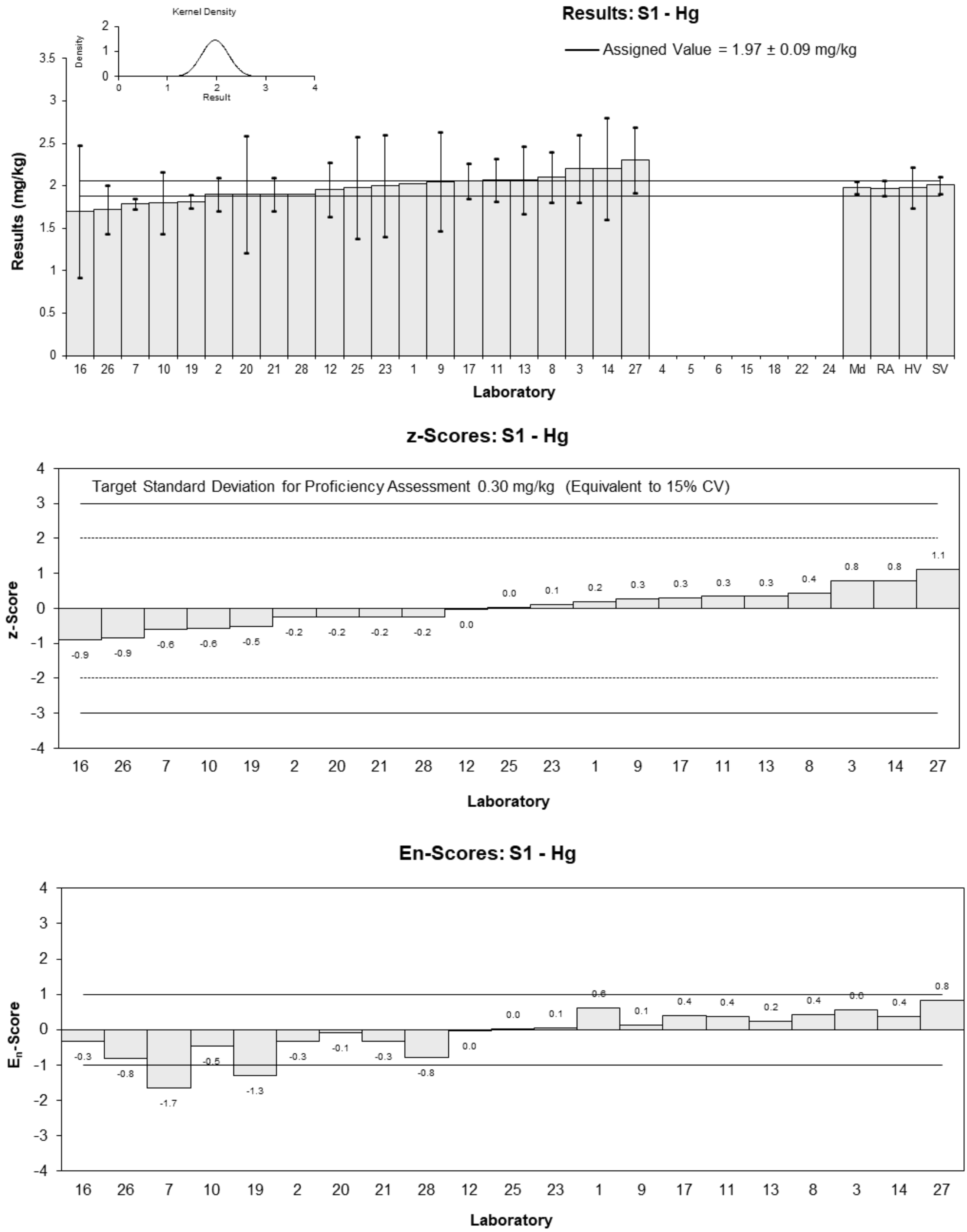

Kernel Density
Density
Result
Results: S1 - Hg
Assigned Value = 1.97 ± 0.09 mg/kg
Results (mg/kg)
16 26 7 10 19 2 20 21 28 12 25 23 1 9 17 11 13 8 3 14 27 4 5 6 15 18 22 24 Md RA HV SV
Laboratory
z-Scores: S1 - Hg
Target Standard Deviation for Proficiency Assessment 0.30 mg/kg (Equivalent to 15% CV)
z-Score
-0.9 -0.9 -0.6 -0.6 -0.5 -0.2 -0.2 -0.2 -0.2 0.0 0.0 0.1 0.2 0.3 0.3 0.3 0.3 0.4 0.8 0.8 1.1
16 26 7 10 19 2 20 21 28 12 25 23 1 9 17 11 13 8 3 14 27
Laboratory
En-Scores: S1 - Hg
En-Score
-0.3 -0.8 -1.7 -0.5 -1.3 -0.3 -0.1 -0.3 -0.8 0.0 0.0 0.1 0.6 0.1 0.4 0.4 0.2 0.4 0.6 0.4 0.8
16 26 7 10 19 2 20 21 28 12 25 23 1 9 17 11 13 8 3 14 27
Laboratory

Figure 7

Table 18

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Mn
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	613.55	NR	1.20	1.77
2	635	127	1.59	0.66
3	580	200	0.58	0.16
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	512	20	-0.66	-0.86
9	614	100	1.20	0.62
10	510	102	-0.69	-0.35
11	515	55	-0.60	-0.50
12	533	54	-0.27	-0.23
13	556	111	0.15	0.07
14	600	200	0.95	0.26
15	NT	NT		
16	507	34.8	-0.75	-0.81
17	554	35	0.11	0.12
18	NT	NT		
19	496.355	44.809	-0.94	-0.89
20	NT	NT		
21	558	10	0.18	0.26
22	NT	NT		
23	570	200	0.40	0.11
24	NT	NT		
25	802	200	4.64	1.25
26	404	89	-2.63	-1.49
27	500	56	-0.88	-0.72
28	454	NR	-1.72	-2.54

Statistics

Assigned Value	548	37
Spike Value	Not Spiked	
Homogeneity Value	555	67
Robust Average	548	37
Median	554	39
Mean	553	
N	19	
Max	802	
Min	404	
Robust SD	65	
Robust CV	12%	

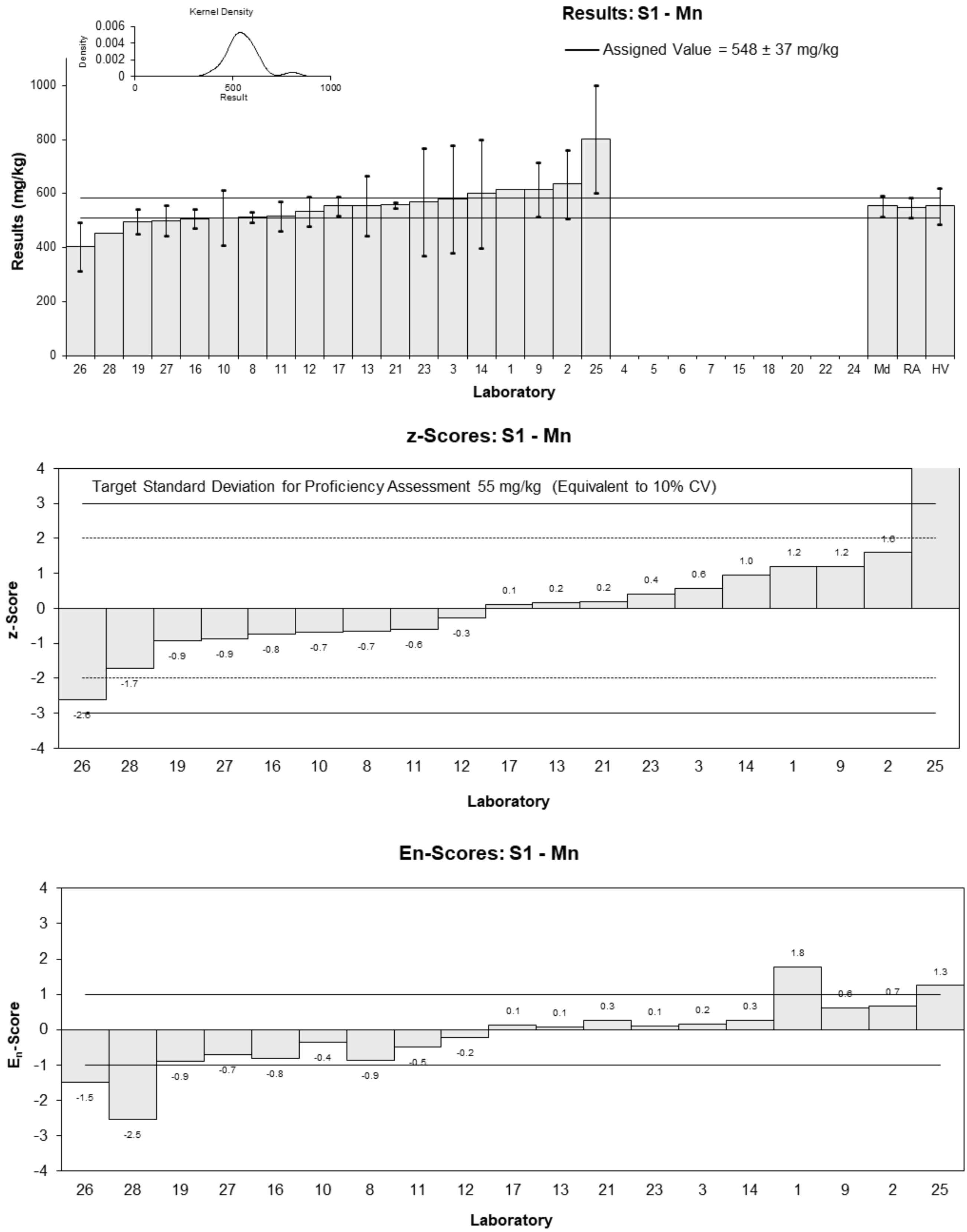

Results: S1 - Mn
Assigned Value = 548 ± 37 mg/kg
Kernel Density
Results (mg/kg)
Laboratory
z-Scores: S1 - Mn
Target Standard Deviation for Proficiency Assessment 55 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S1 - Mn
En-Score
Laboratory

Figure 8

Table 19

Sample Details

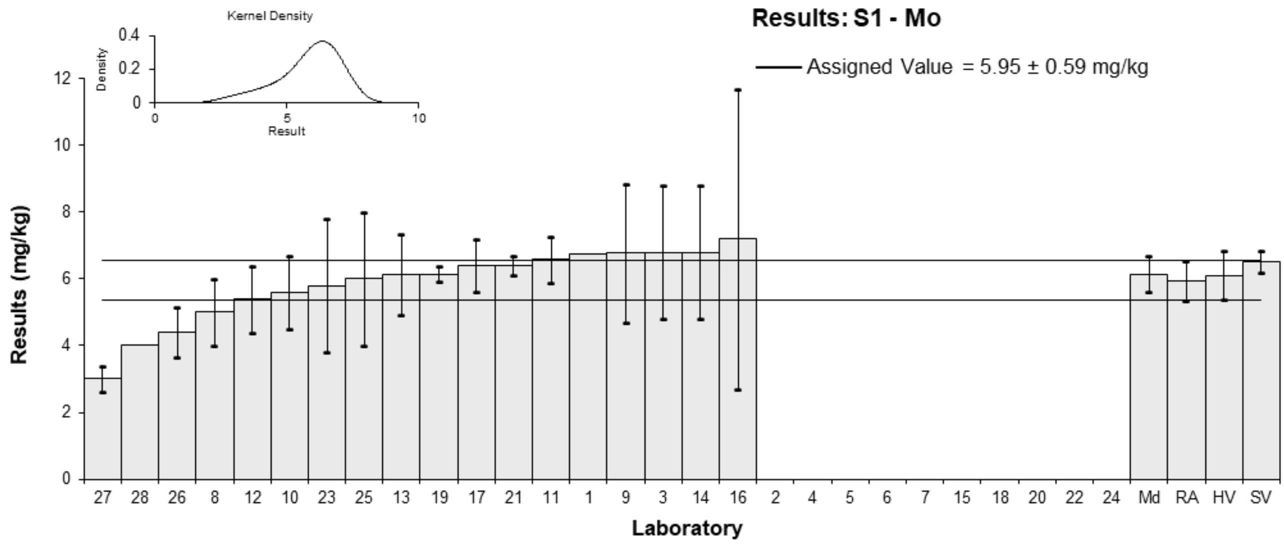
Sample No.	S1
Matrix	Soil
Analyte	Mo
Unit	mg/kg

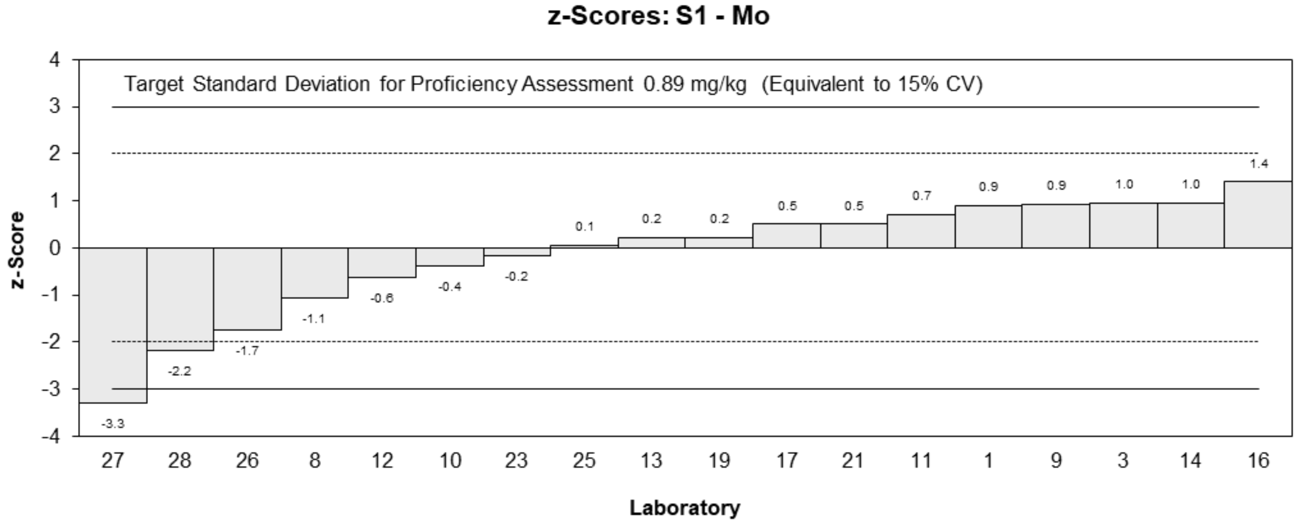
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	6.75	NR	0.90	1.36
2	NT	NT		
3	6.8	2	0.95	0.41
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	5	1	-1.06	-0.82
9	6.78	2.07	0.93	0.39
10	5.6	1.1	-0.39	-0.28
11	6.58	0.7	0.71	0.69
12	5.4	1.0	-0.62	-0.47
13	6.14	1.2	0.21	0.14
14	6.8	2	0.95	0.41
15	NT	NT		
16	7.2	4.5	1.40	0.28
17	6.4	0.8	0.50	0.45
18	NT	NT		
19	6.144	0.224	0.22	0.31
20	NT	NT		
21	6.4	0.3	0.50	0.68
22	NT	NT		
23	5.8	2	-0.17	-0.07
24	NT	NT		
25	6	2	0.06	0.02
26	4.4	0.75	-1.74	-1.62
27	3	0.387	-3.31	-4.18
28	4.0	NR	-2.18	-3.31

Statistics

Assigned Value	5.95	0.59
Spike Value	6.52	0.33
Homogeneity Value	6.10	0.73
Robust Average	5.95	0.59
Median	6.14	0.54
Mean	5.84	
N	18	
Max	7.2	
Min	3	
Robust SD	1.0	
Robust CV	17%	


Results: S1 - Mo
Assigned Value = 5.95 ± 0.59 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
27 28 26 8 12 10 23 25 13 19 17 21 11 1 9 3 14 16 2 4 5 6 7 15 18 20 22 24 Md RA HV SV


z-Scores: S1 - Mo
Target Standard Deviation for Proficiency Assessment 0.89 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-3.3 -2.2 -1.7 -1.1 -0.6 -0.4 -0.2 0.1 0.2 0.2 0.5 0.5 0.7 0.9 0.9 1.0 1.0 1.4
27 28 26 8 12 10 23 25 13 19 17 21 11 1 9 3 14 16

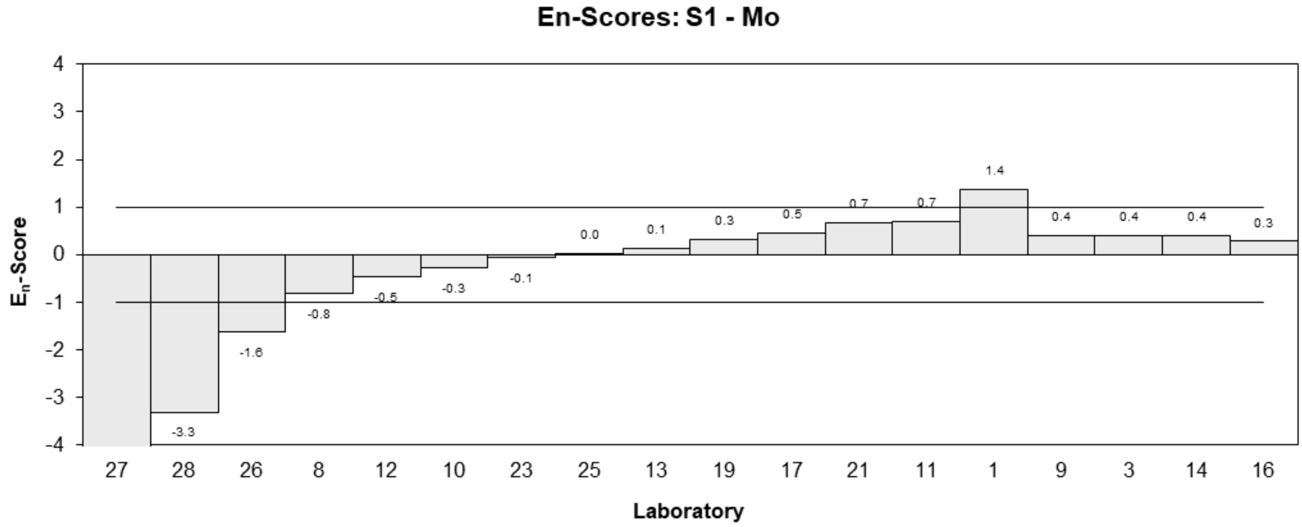

En-Scores: S1 - Mo
E_n-Score
Laboratory
-3.3 -1.6 -0.8 -0.5 -0.3 -0.1 0.0 0.1 0.3 0.5 0.7 0.7 1.4 0.4 0.4 0.4 0.3
27 28 26 8 12 10 23 25 13 19 17 21 11 1 9 3 14 16

Figure 9

Table 20

Sample Details

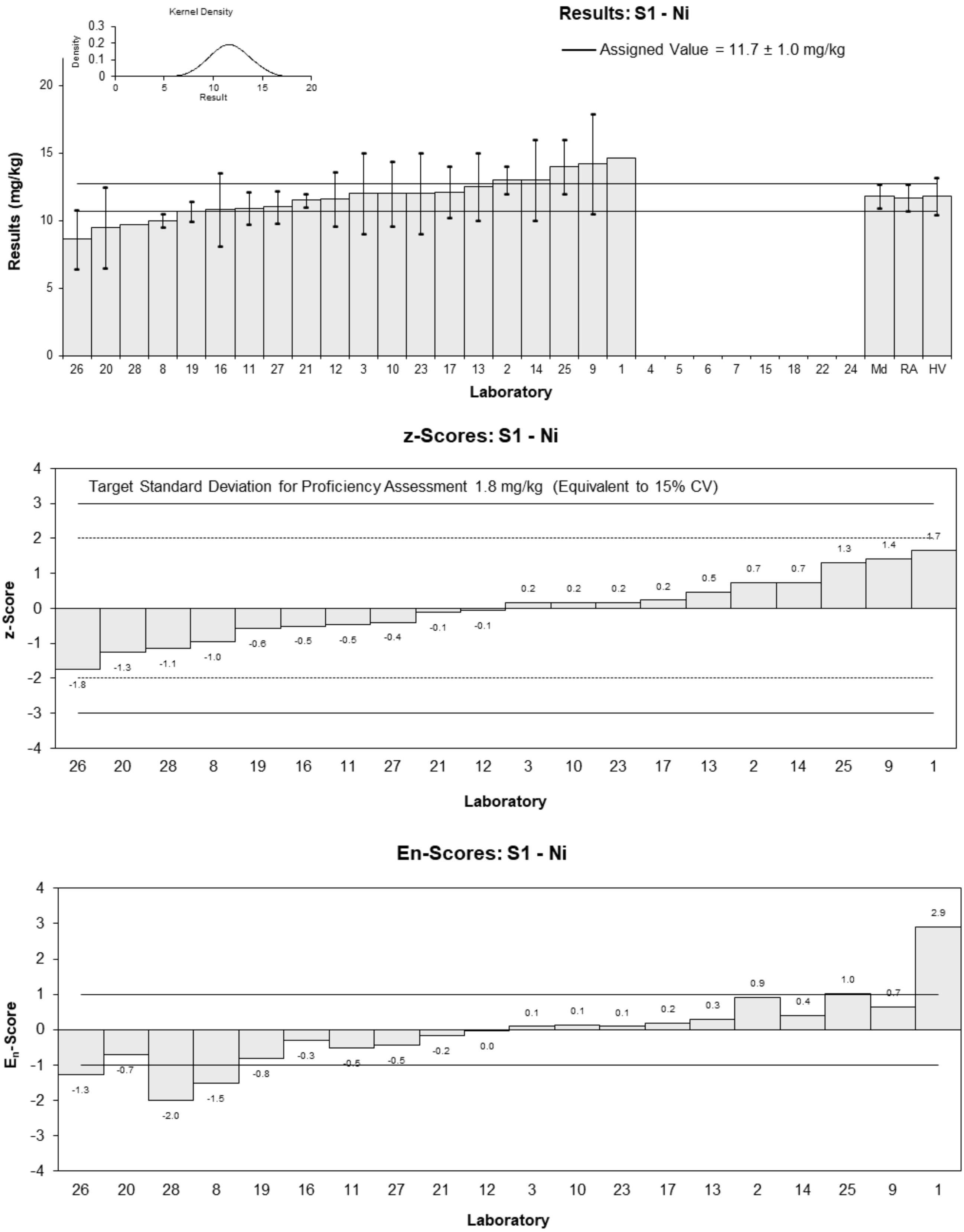
Sample No.	S1
Matrix	Soil
Analyte	Ni
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	14.6	NR	1.65	2.90
2	13	1	0.74	0.92
3	12	3	0.17	0.09
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	10	0.5	-0.97	-1.52
9	14.2	3.7	1.42	0.65
10	12	2.4	0.17	0.12
11	10.9	1.2	-0.46	-0.51
12	11.6	2.0	-0.06	-0.04
13	12.5	2.5	0.46	0.30
14	13	3	0.74	0.41
15	NT	NT		
16	10.8	2.7	-0.51	-0.31
17	12.1	1.9	0.23	0.19
18	NT	NT		
19	10.676	0.739	-0.58	-0.82
20	9.5	3.0	-1.25	-0.70
21	11.5	0.5	-0.11	-0.18
22	NT	NT		
23	12	3	0.17	0.09
24	NT	NT		
25	14	2	1.31	1.03
26	8.61	2.2	-1.76	-1.28
27	11	1.188	-0.40	-0.45
28	9.7	NR	-1.14	-2.00

Statistics

Assigned Value	11.7	1.0
Spike Value	Not Spiked	
Homogeneity Value	11.8	1.4
Robust Average	11.7	1.0
Median	11.8	0.9
Mean	11.7	
N	20	
Max	14.6	
Min	8.61	
Robust SD	1.7	
Robust CV	15%	



Kernel Density
Density
Result
Results: S1 - Ni
Assigned Value = 11.7 ± 1.0 mg/kg
Results (mg/kg)
Laboratory
z-Scores: S1 - Ni
Target Standard Deviation for Proficiency Assessment 1.8 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Ni
E_n-Score
Laboratory

Figure 10

Table 21

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Pb
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	591	NR	-0.13	-0.50
2	626	31	0.45	0.77
3	610	200	0.18	0.05
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	565	30	-0.57	-1.00
9	623	79	0.40	0.30
10	590	118	-0.15	-0.08
11	583	55	-0.27	-0.28
12	577	87	-0.37	-0.25
13	625	125	0.43	0.21
14	610	200	0.18	0.05
15	NT	NT		
16	648	19.1	0.82	1.97
17	592	44	-0.12	-0.15
18	NT	NT		
19	591.124	38.539	-0.13	-0.19
20	600	140	0.02	0.01
21	582	8.0	-0.28	-0.95
22	NT	NT		
23	620	200	0.35	0.10
24	NT	NT		
25	543	60	-0.93	-0.90
26	503	80	-1.60	-1.18
27	600	81.6	0.02	0.01
28	637	NR	0.63	2.38

Statistics

Assigned Value	599	16
Spike Value	Not Spiked	
Homogeneity Value	590	71
Robust Average	599	16
Median	596	14
Mean	596	
N	20	
Max	648	
Min	503	
Robust SD	29	
Robust CV	4.8%	

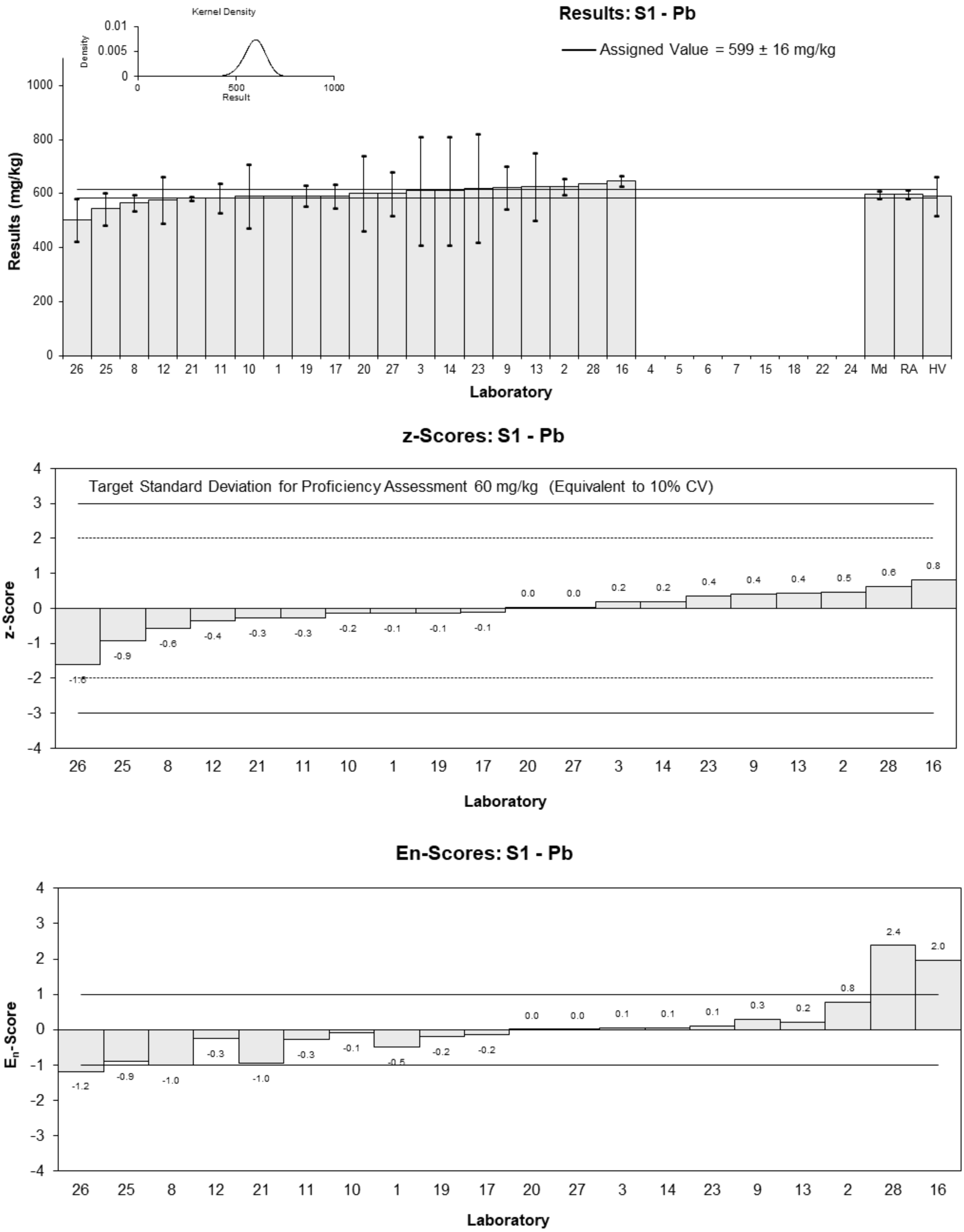

Kernel Density
Density
Result
Results: S1 - Pb
Assigned Value = 599 ± 16 mg/kg
Results (mg/kg)
Laboratory
z-Scores: S1 - Pb
Target Standard Deviation for Proficiency Assessment 60 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S1 - Pb
En-Score
Laboratory

Figure 11

Table 22

Sample Details

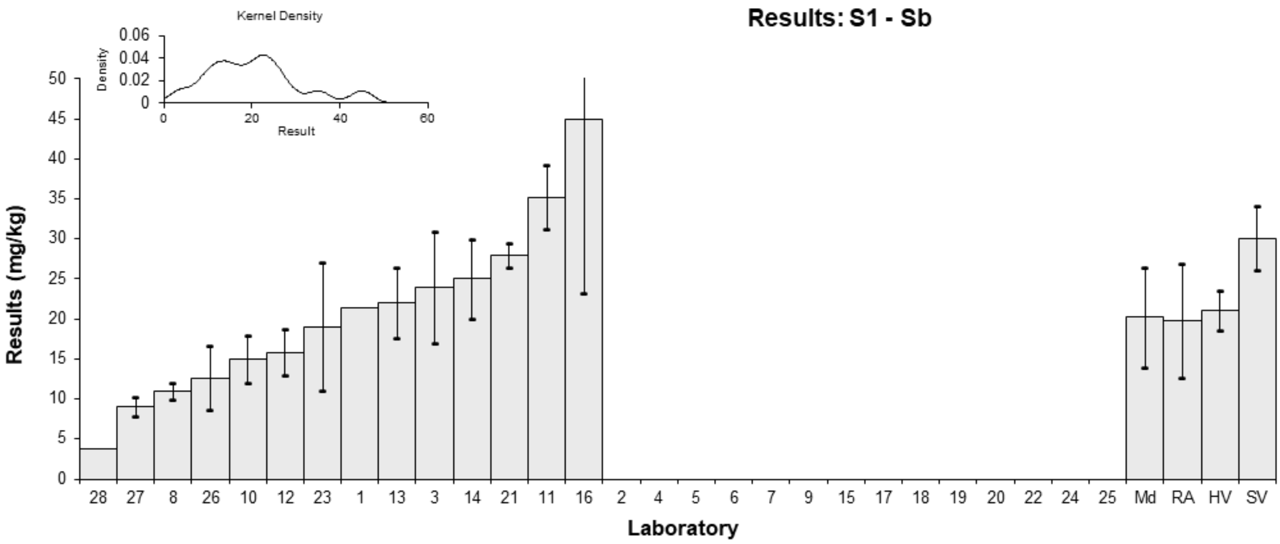
Sample No.	S1
Matrix	Soil
Analyte	Sb
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	21.4	NR
2	NT	NT
3	24	7
4	NT	NT
5	NT	NT
6	NT	NT
7	NR	NR
8	11	1
9	NT	NT
10	15	3
11	35.2	4.0
12	15.8	2.9
13	22.0	4.4
14	25	5
15	NT	NT
16	45.0	21.7
17	NT	NT
18	NT	NT
19	NT	NT
20	NT	NT
21	28	1.5
22	NT	NT
23	19	8
24	NT	NT
25	NT	NT
26	12.6	4.0
27	9	1.224
28	3.7	NR

Statistics

Assigned Value	Not Set	
Spike Value	30.1	4.0
Homogeneity Value	21.1	2.5
Robust Average	19.8	7.1
Median	20.2	6.3
Mean	20.5	
N	14	
Max	45	
Min	3.7	
Robust SD	11	
Robust CV	54%	



Kernel Density
Results: S1 - Sb
Density
Result
Results (mg/kg)
Laboratory
28
27
8
26
10
12
23
1
13
3
14
21
11
16
2
4
5
6
7
9
15
17
18
19
20
22
24
25
Md
RA
HV
SV

Figure 12

Table 23

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Se
Unit	mg/kg

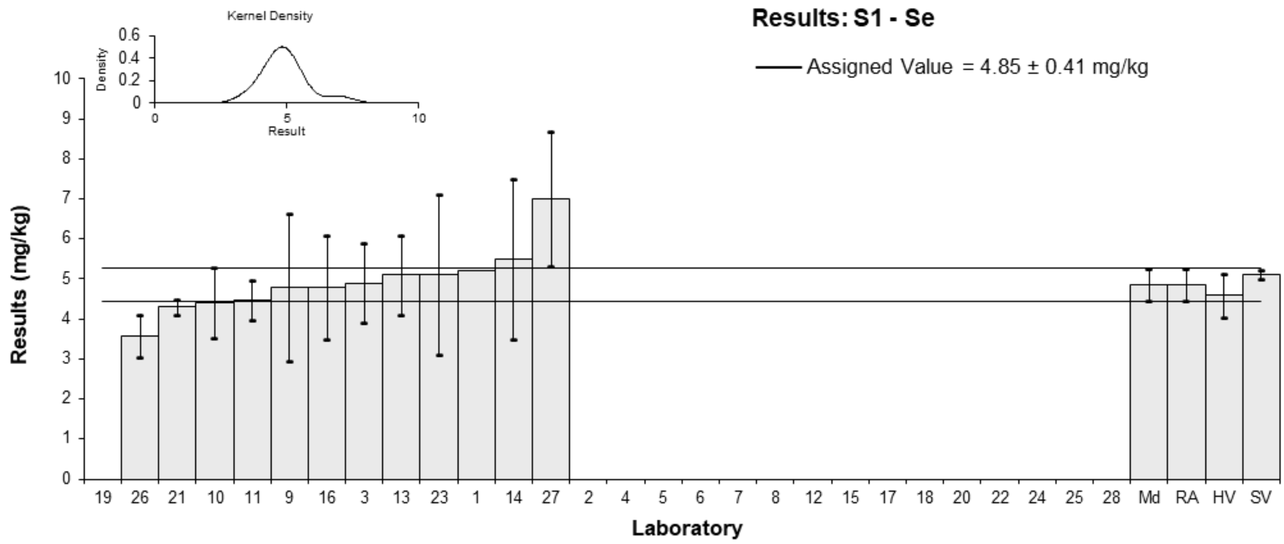
Participant Results

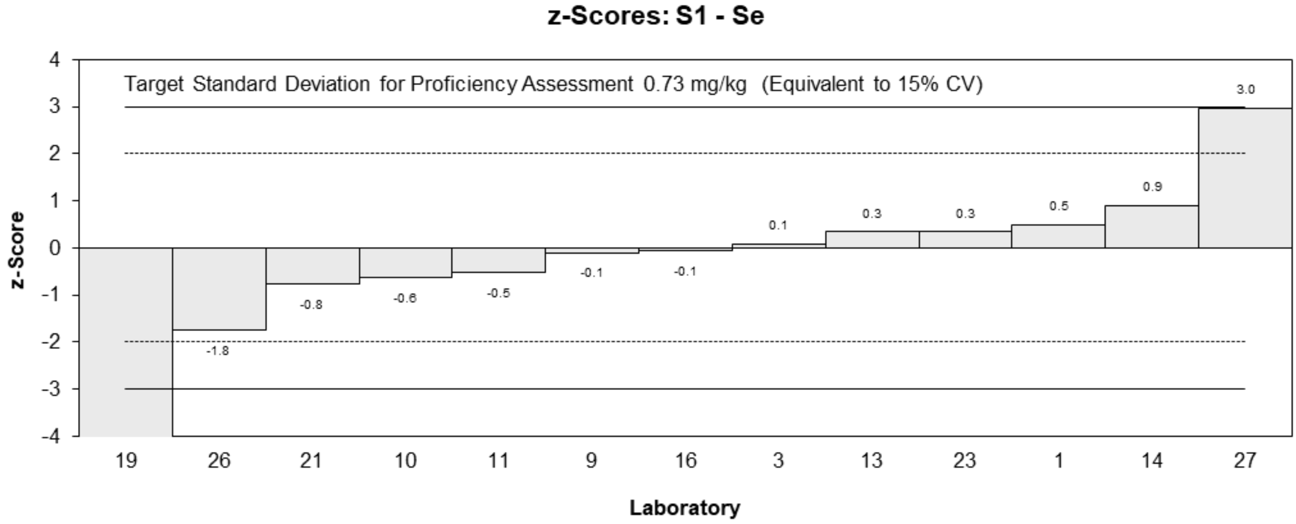
Lab. Code	Result	Uncertainty	z	E_n
1	5.2	NR	0.48	0.85
2	NT	NT		
3	4.9	1	0.07	0.05
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	4.78	1.84	-0.10	-0.04
10	4.4	0.88	-0.62	-0.46
11	4.47	0.5	-0.52	-0.59
12	<20	14		
13	5.1	1.0	0.34	0.23
14	5.5	2	0.89	0.32
15	NT	NT		
16	4.8	1.3	-0.07	-0.04
17	<10	NR		
18	NT	NT		
19**	-5.894	1.778	-14.77	-5.89
20	NT	NT		
21	4.3	0.2	-0.76	-1.21
22	NT	NT		
23	5.1	2	0.34	0.12
24	NT	NT		
25	<5	NR		
26	3.57	0.54	-1.76	-1.89
27	7	1.687	2.96	1.24
28	NR	NR		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	4.85	0.41
Spike Value	5.12	0.11
Homogeneity Value	4.59	0.55
Robust Average	4.85	0.41
Median	4.85	0.39
Mean	4.93	
N	12	
Max	7	
Min	3.57	
Robust SD	0.57	
Robust CV	12%	


Results: S1 - Se
Assigned Value = 4.85 ± 0.41 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
19 26 21 10 11 9 16 3 13 23 1 14 27 2 4 5 6 7 8 12 15 17 18 20 22 24 25 28 Md RA HV SV
Laboratory


z-Scores: S1 - Se
Target Standard Deviation for Proficiency Assessment 0.73 mg/kg (Equivalent to 15% CV)
z-Score
-1.8
-0.8
-0.6
-0.5
-0.1
-0.1
0.1
0.3
0.3
0.5
0.9
3.0
19 26 21 10 11 9 16 3 13 23 1 14 27
Laboratory

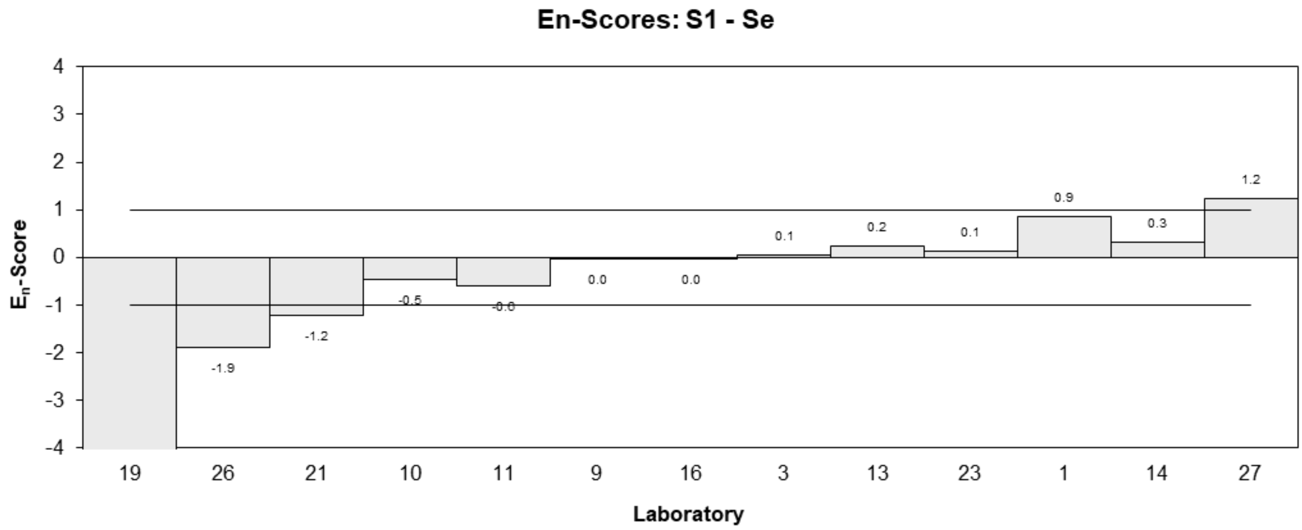

En-Scores: S1 - Se
E_n-Score
-1.9
-1.2
-0.5
-0.0
0.0
0.0
0.1
0.2
0.1
0.9
0.3
1.2
19 26 21 10 11 9 16 3 13 23 1 14 27
Laboratory

Figure 13

Table 24

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Tl
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.649	NR	-2.16	-2.39
2	NT	NT		
3	<2	2		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	NT	NT		
9	1.13	0.45	1.18	0.36
10	0.88	0.18	-0.56	-0.36
11	0.99	0.2	0.21	0.13
12	0.89	0.17	-0.49	-0.33
13	1.0	0.2	0.28	0.17
14	<2	NR		
15	NT	NT		
16	1.2	0.4	1.67	0.57
17	0.96	0.12	0.00	0.00
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	0.90	0.1	-0.42	-0.37
22	NT	NT		
23	<2	2		
24	NT	NT		
25	NT	NT		
26	<0.88	NR		
27**	480	79.68	3,326.67	6.01
28	NT	NT		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	0.96	0.13
Spike Value	0.999	0.041
Homogeneity Value	0.95	0.11
Robust Average	0.96	0.13
Median	0.960	0.087
Mean	0.96	
N	9	
Max	1.2	
Min	0.649	
Robust SD	0.16	
Robust CV	17%	

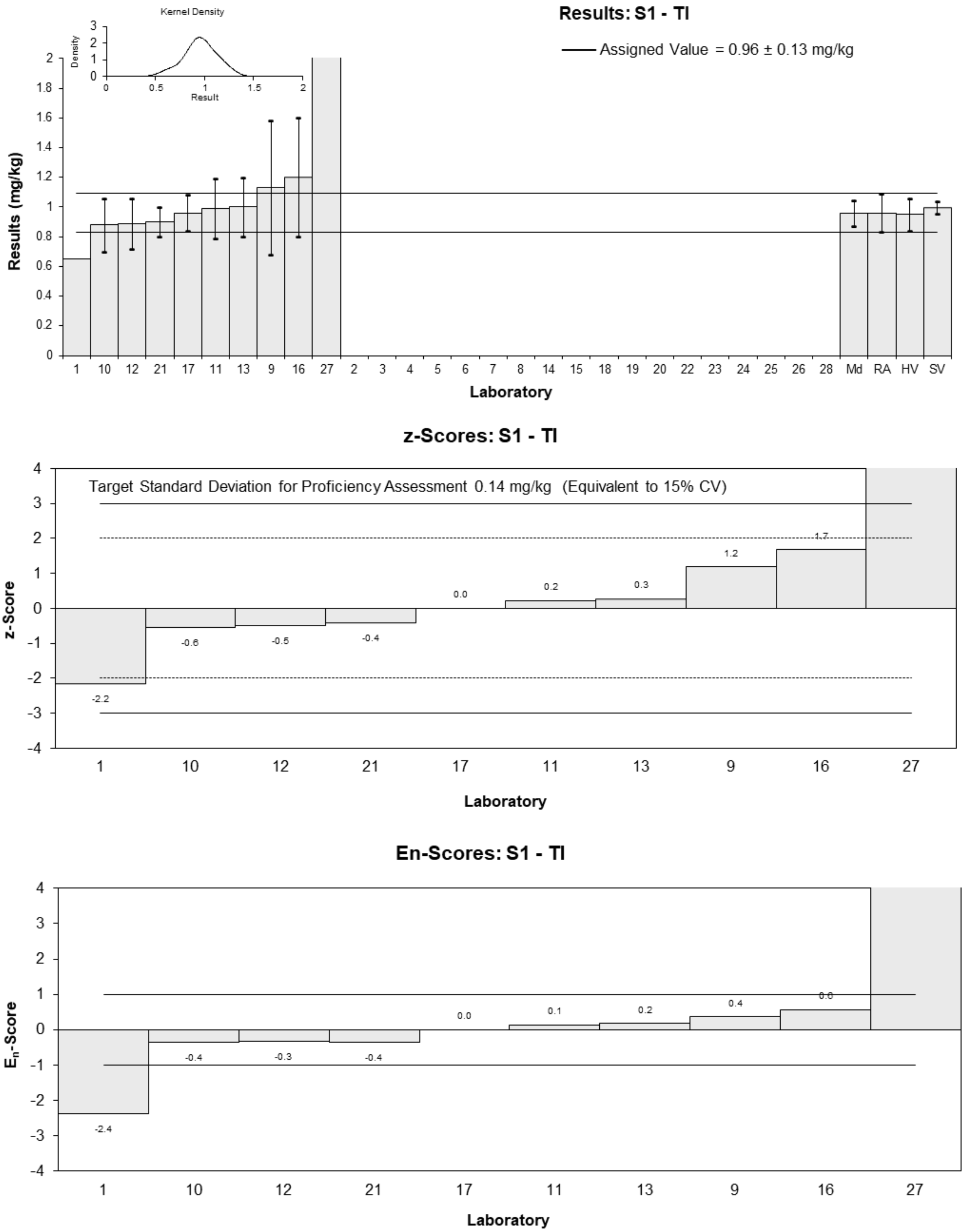

Results: S1 - Tl
Assigned Value = 0.96 ± 0.13 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S1 - Tl
Target Standard Deviation for Proficiency Assessment 0.14 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
En-Scores: S1 - Tl
E_n-Score
Laboratory

Figure 14

Table 25

Sample Details

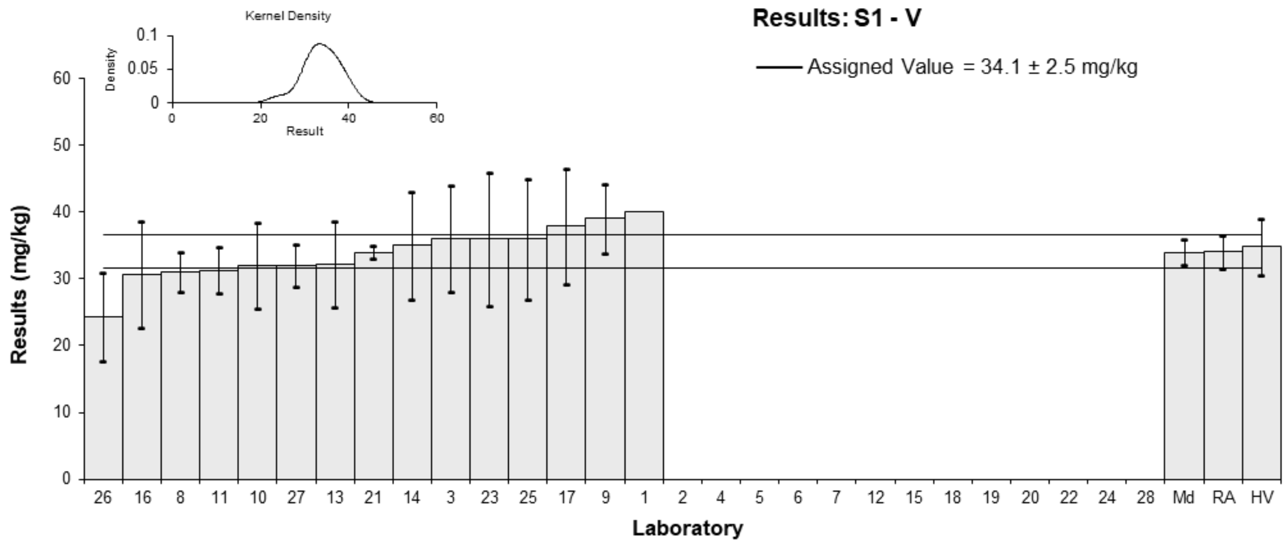
Sample No.	S1
Matrix	Soil
Analyte	V
Unit	mg/kg

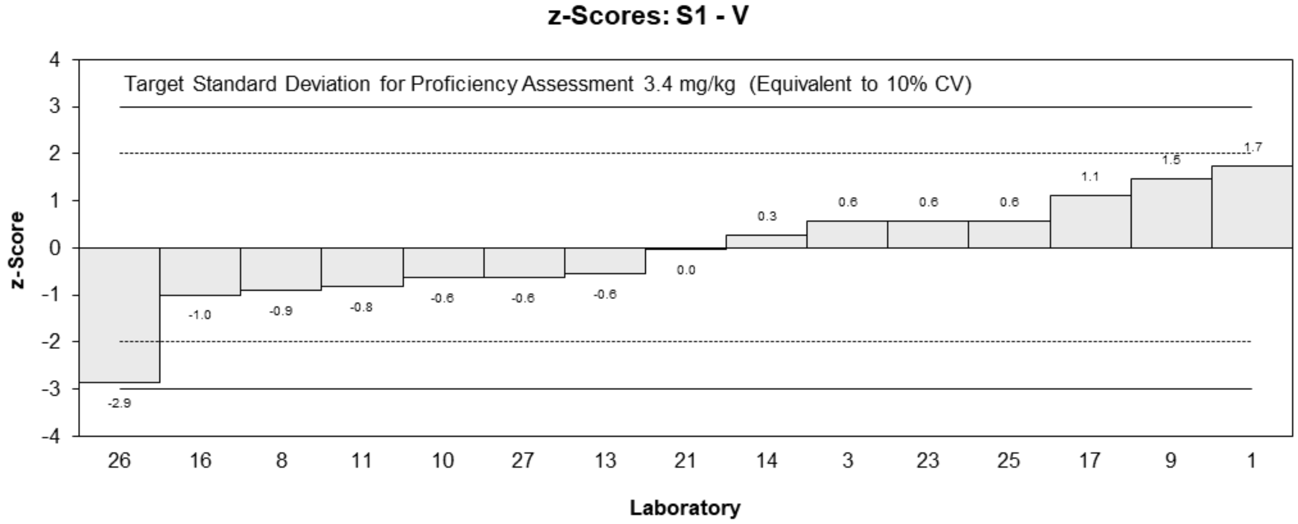
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	40	NR	1.73	2.36
2	NT	NT		
3	36	8	0.56	0.23
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	31	3	-0.91	-0.79
9	39.1	5.2	1.47	0.87
10	32	6.4	-0.62	-0.31
11	31.3	3.5	-0.82	-0.65
12	<100	67		
13	32.2	6.4	-0.56	-0.28
14	35	8	0.26	0.11
15	NT	NT		
16	30.7	8.0	-1.00	-0.41
17	37.9	8.7	1.11	0.42
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	34	1.0	-0.03	-0.04
22	NT	NT		
23	36	10	0.56	0.18
24	NT	NT		
25	36	9	0.56	0.20
26	24.3	6.6	-2.87	-1.39
27	32	3.2	-0.62	-0.52
28	NT	NT		

Statistics

Assigned Value	34.1	2.5
Spike Value	Not Spiked	
Homogeneity Value	34.8	4.2
Robust Average	34.1	2.5
Median	34.0	1.9
Mean	33.8	
N	15	
Max	40	
Min	24.3	
Robust SD	3.8	
Robust CV	11%	


Results: S1 - V
Assigned Value = 34.1 ± 2.5 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 16 8 11 10 27 13 21 14 3 23 25 17 9 1 2 4 5 6 7 12 15 18 19 20 22 24 28 Md RA HV


z-Scores: S1 - V
Target Standard Deviation for Proficiency Assessment 3.4 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
-2.9 -1.0 -0.9 -0.8 -0.6 -0.6 -0.6 0.0 0.3 0.6 0.6 0.6 1.1 1.5 1.7
26 16 8 11 10 27 13 21 14 3 23 25 17 9 1

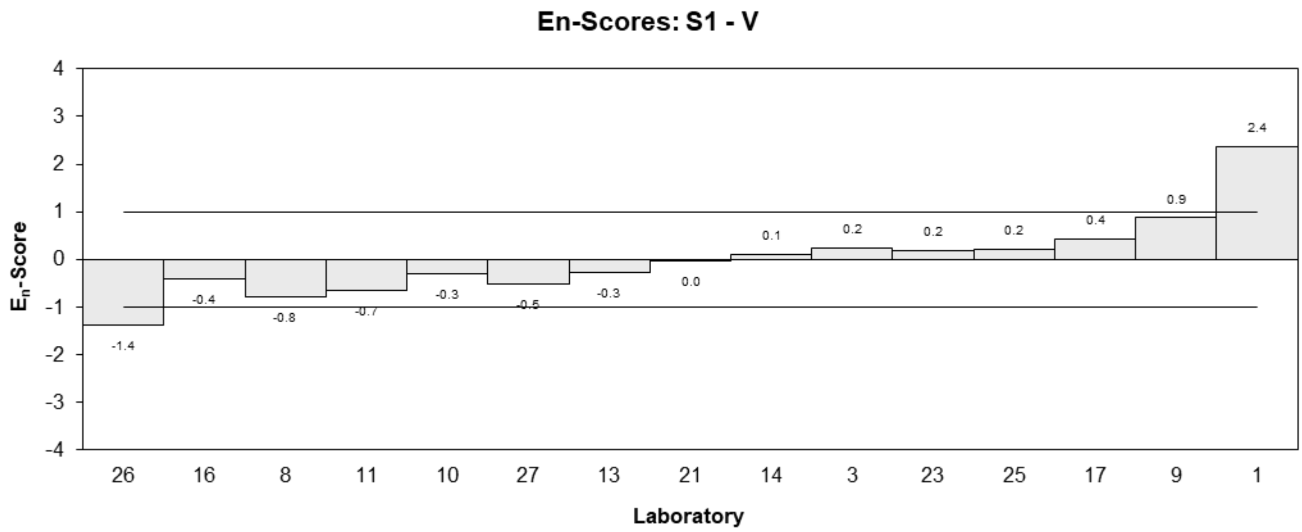

En-Scores: S1 - V
En-Score
Laboratory
-1.4 -0.4 -0.8 -0.7 -0.3 -0.5 -0.3 0.0 0.1 0.2 0.2 0.2 0.4 0.9 2.4
26 16 8 11 10 27 13 21 14 3 23 25 17 9 1

Figure 15

Table 26

Sample Details

Sample No.	S1
Matrix	Soil
Analyte	Zn
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	773.5	NR	-0.21	-0.75
2	850	43	0.76	1.24
3	820	200	0.38	0.15
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
8	712	21	-0.99	-2.56
9	802	95	0.15	0.12
10	760	152	-0.38	-0.20
11	768	75	-0.28	-0.28
12	791	56	0.01	0.02
13	814	163	0.30	0.15
14	790	200	0.00	0.00
15	NT	NT		
16	848	25.1	0.73	1.74
17	776	42	-0.18	-0.30
18	NT	NT		
19	806.413	47.437	0.21	0.31
20	770	140	-0.25	-0.14
21	765	10	-0.32	-1.03
22	NT	NT		
23	800	200	0.13	0.05
24	NT	NT		
25	769	110	-0.27	-0.19
26	732	190	-0.73	-0.30
27	780	140.4	-0.13	-0.07
28	919	NR	1.63	5.86

Statistics

Assigned Value	790	22
Spike Value	Not Spiked	
Homogeneity Value	776	93
Robust Average	790	22
Median	785	15
Mean	792	
N	20	
Max	919	
Min	712	
Robust SD	39	
Robust CV	4.9%	

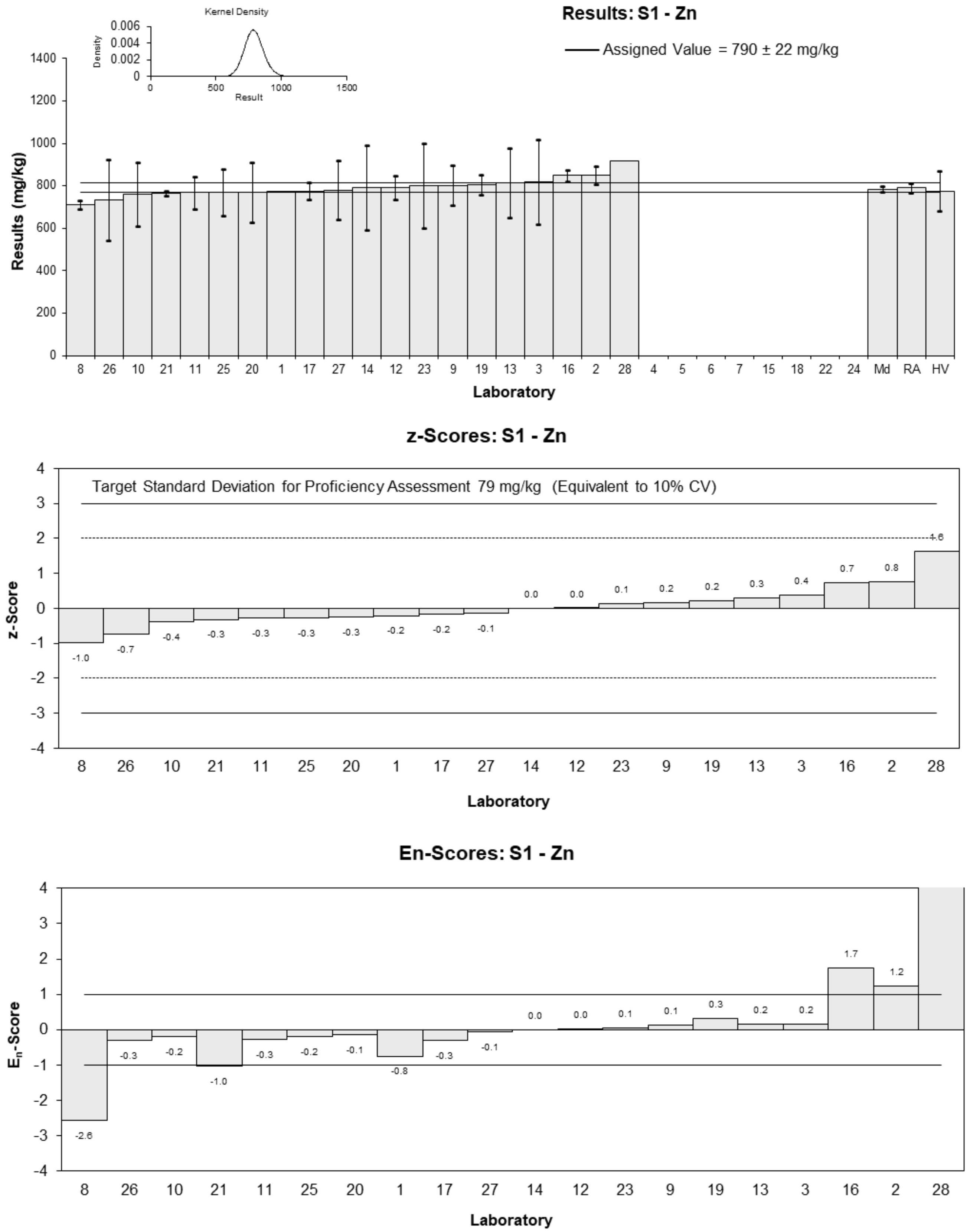

Results: S1 - Zn
Assigned Value = 790 ± 22 mg/kg
Kernel Density
Density
0.006
0.004
0.002
0
0
500
1000
1500
Result
Results (mg/kg)
1400
1200
1000
800
600
400
200
0
8 26 10 21 11 25 20 1 17 27 14 12 23 9 19 13 3 16 2 28 4 5 6 7 15 18 22 24 Md RA HV
Laboratory
z-Scores: S1 - Zn
Target Standard Deviation for Proficiency Assessment 79 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0 -0.7 -0.4 -0.3 -0.3 -0.3 -0.3 -0.2 -0.2 -0.1 0.0 0.0 0.1 0.2 0.2 0.3 0.4 0.7 0.8 1.6
8 26 10 21 11 25 20 1 17 27 14 12 23 9 19 13 3 16 2 28
Laboratory
En-Scores: S1 - Zn
En-Score
4
3
2
1
0
-1
-2
-3
-4
-2.6 -0.3 -0.2 -1.0 -0.3 -0.2 -0.1 -0.8 -0.3 -0.1 0.0 0.0 0.1 0.1 0.3 0.2 0.2 1.7 1.2
8 26 10 21 11 25 20 1 17 27 14 12 23 9 19 13 3 16 2 28
Laboratory

Figure 16

Table 27

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Ag
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.775	NR	-1.70	-3.31
2	NT	NT		
3	1.1	0.3	0.38	0.19
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	1.04	0.40	0.00	0.00
10	1.1	0.22	0.38	0.26
11	1.19	0.2	0.96	0.70
12	1.14	0.36	0.64	0.27
13**	15.6	3.1	93.33	4.70
14	1.2	0.4	1.03	0.39
15	NT	NT		
16	NT	NT		
17	0.90	0.09	-0.90	-1.16
18	0.93	0.2	-0.71	-0.51
19	NT	NT		
20	NT	NT		
21	1.0	0.1	-0.26	-0.31
22	NT	NT		
23	1	0.3	-0.26	-0.13
24	NT	NT		
25	NT	NT		
26	1.03	0.36	-0.06	-0.03
27	1	0.181	-0.26	-0.20
28	1.0	NR	-0.26	-0.50

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.04	0.08
Spike Value	Not Spiked	
Homogeneity Value	0.97	0.12
Robust Average	1.04	0.08
Median	1.02	0.08
Mean	1.03	
N	14	
Max	1.2	
Min	0.775	
Robust SD	0.12	
Robust CV	11%	

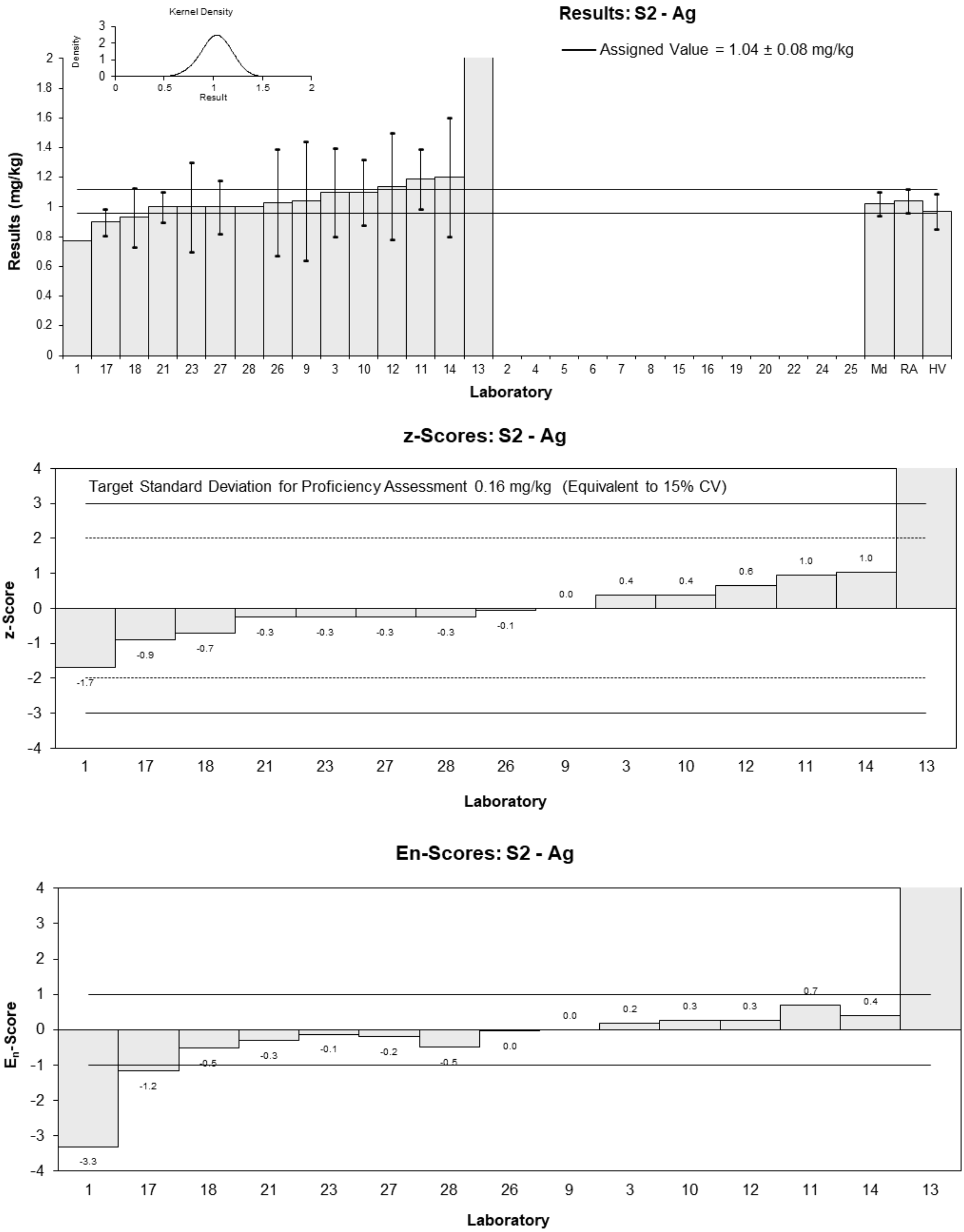

Results: S2 - Ag
Assigned Value = 1.04 ± 0.08 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
1 17 18 21 23 27 28 26 9 3 10 12 11 14 13 2 4 5 6 7 8 15 16 19 20 22 24 25 Md RA HV
z-Scores: S2 - Ag
Target Standard Deviation for Proficiency Assessment 0.16 mg/kg (Equivalent to 15% CV)
z-Score
-1.7 -0.9 -0.7 -0.3 -0.3 -0.3 -0.3 -0.1 0.0 0.4 0.4 0.6 1.0 1.0
1 17 18 21 23 27 28 26 9 3 10 12 11 14 13
Laboratory
En-Scores: S2 - Ag
En-Score
-3.3 -1.2 -0.5 -0.3 -0.1 -0.2 -0.5 0.0 0.0 0.2 0.3 0.3 0.7 0.4
1 17 18 21 23 27 28 26 9 3 10 12 11 14 13
Laboratory

Figure 17

Table 28

Sample Details

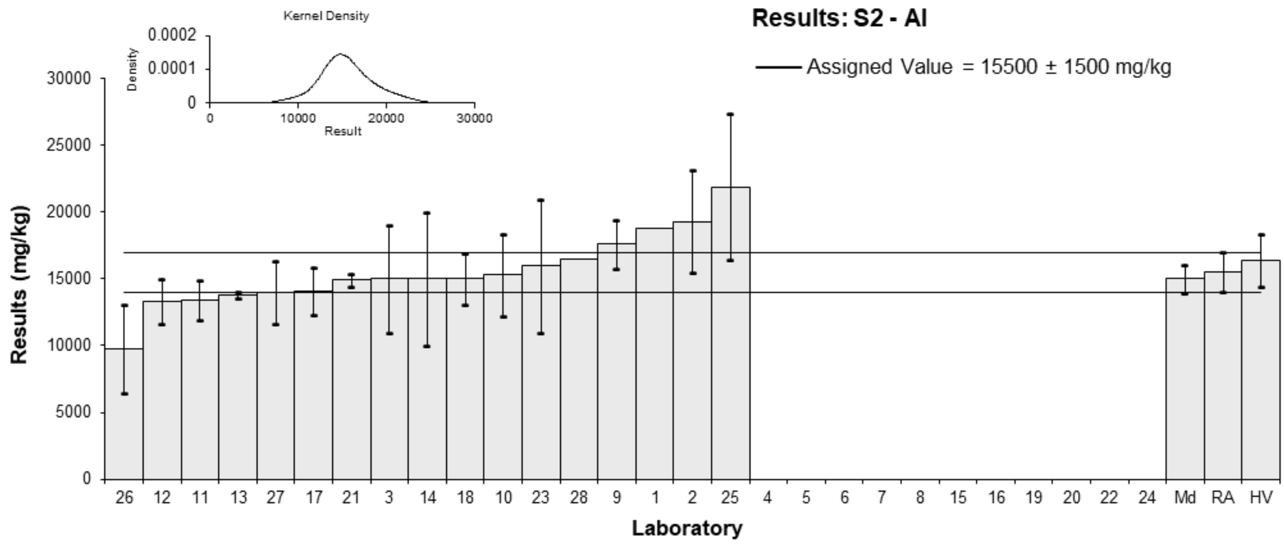
Sample No.	S2
Matrix	Soil
Analyte	Al
Unit	mg/kg

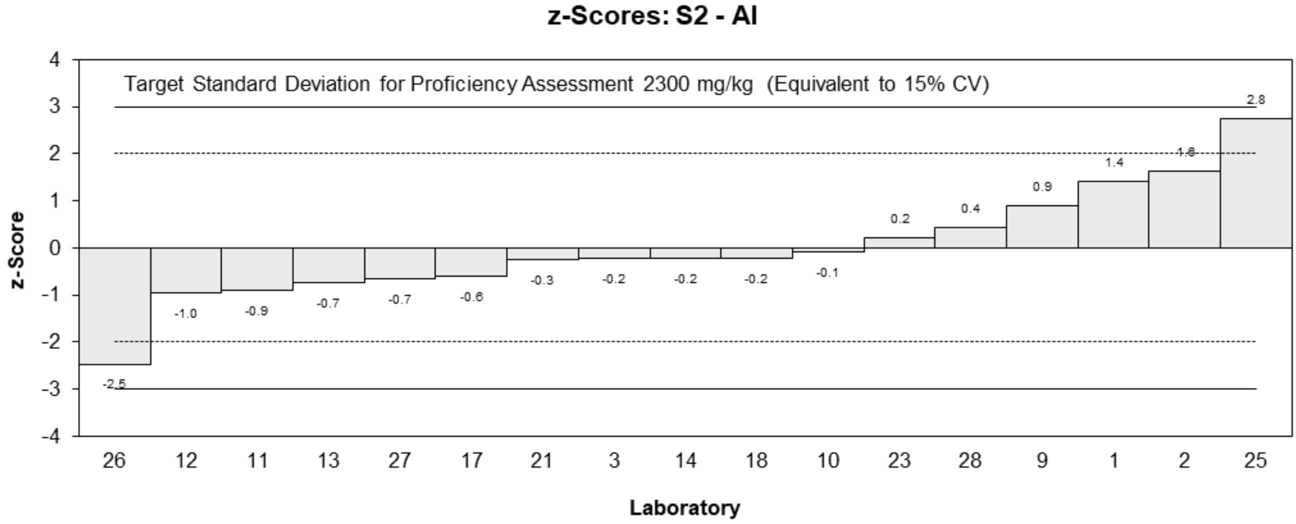
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	18800	NR	1.42	2.20
2	19300	3860	1.63	0.92
3	15000	4000	-0.22	-0.12
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	17600	1850	0.90	0.88
10	15300	3060	-0.09	-0.06
11	13384	1500	-0.91	-1.00
12	13300	1700	-0.95	-0.97
13	13800	275	-0.73	-1.11
14	15000	5000	-0.22	-0.10
15	NT	NT		
16	NT	NT		
17	14100	1800	-0.60	-0.60
18	15000	1900	-0.22	-0.21
19	NT	NT		
20	NT	NT		
21	14900	500	-0.26	-0.38
22	NT	NT		
23	16000	5000	0.22	0.10
24	NT	NT		
25	21900	5500	2.75	1.12
26	9750	3300	-2.47	-1.59
27	14000	2366	-0.65	-0.54
28	16530	NR	0.44	0.69

Statistics

Assigned Value	15500	1500
Spike Value	Not Spiked	
Homogeneity Value	16400	2000
Robust Average	15500	1500
Median	15000	1100
Mean	15500	
N	17	
Max	21900	
Min	9750	
Robust SD	2400	
Robust CV	16%	


Results: S2 - Al
Assigned Value = 15500 ± 1500 mg/kg
Kernel Density
Results (mg/kg)
Laboratory


z-Scores: S2 - Al
Target Standard Deviation for Proficiency Assessment 2300 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory

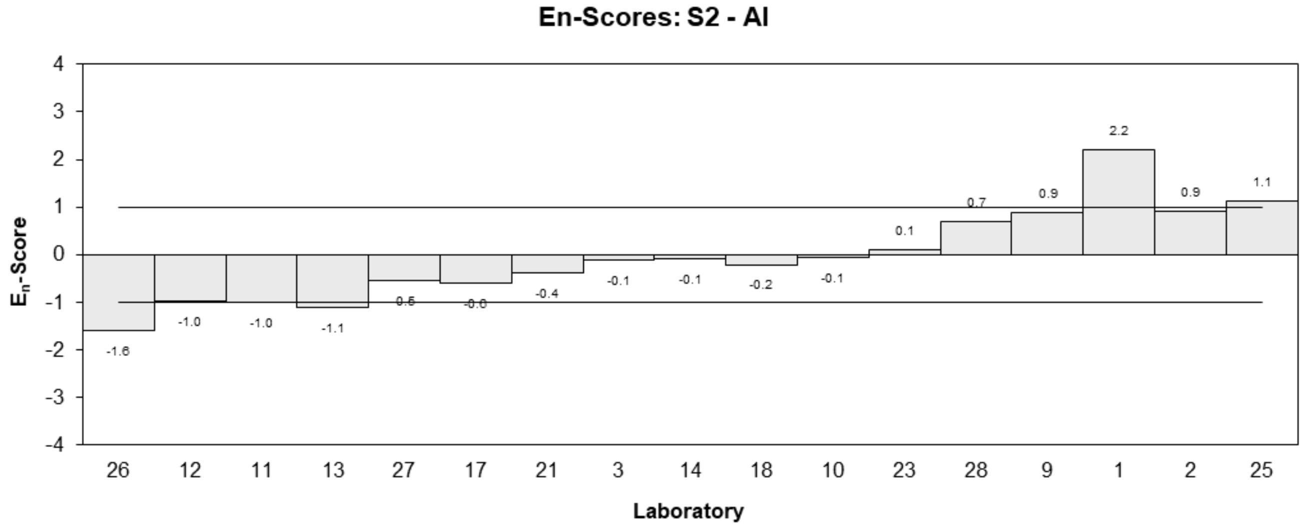

En-Scores: S2 - Al
En-Score
Laboratory

Figure 18

Table 29

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	As
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	12.0	NR	-0.24	-0.43
2	14	1	1.38	1.39
3	12	3	-0.24	-0.10
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	12.2	1.6	-0.08	-0.06
10	12	2.4	-0.24	-0.12
11	12.4	1.5	0.08	0.06
12	12.2	2.3	-0.08	-0.04
13	12.8	2.6	0.41	0.19
14	12	4	-0.24	-0.07
15	NT	NT		
16	NT	NT		
17	14.6	3.4	1.87	0.66
18	12	1.5	-0.24	-0.18
19	NT	NT		
20	NT	NT		
21	11.5	1.5	-0.65	-0.48
22	NT	NT		
23	13	4	0.57	0.17
24	NT	NT		
25	14	2	1.38	0.80
26	9.01	1.4	-2.67	-2.10
27	12	1.596	-0.24	-0.17
28	8.7	NR	-2.93	-5.14

Statistics

Assigned Value	12.3	0.7
Spike Value	Not Spiked	
Homogeneity Value	12.4	1.5
Robust Average	12.3	0.7
Median	12.0	0.4
Mean	12.1	
N	17	
Max	14.6	
Min	8.7	
Robust SD	1.2	
Robust CV	9.4%	

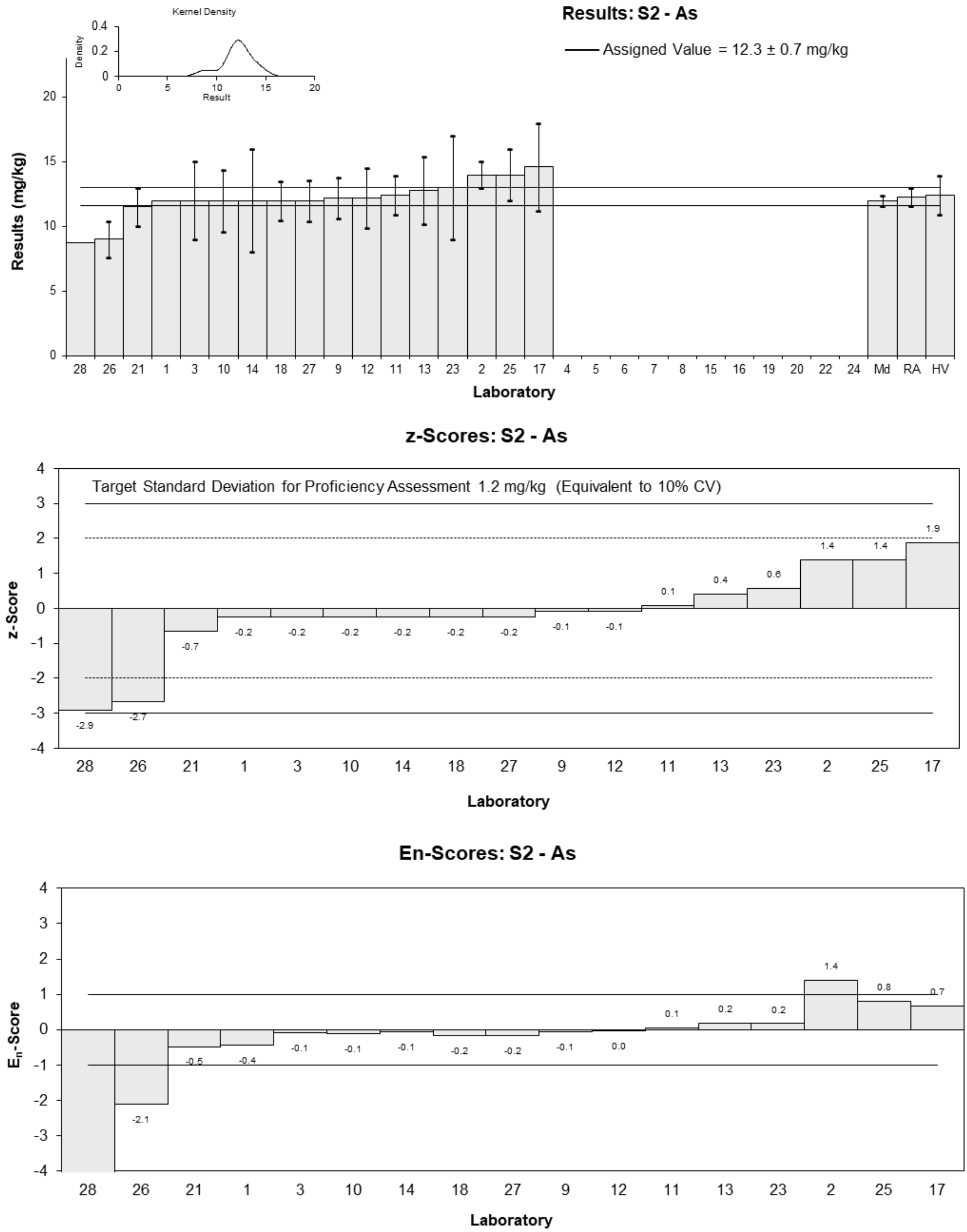

Kernel Density
Density
Result
Results: S2 - As
Assigned Value = 12.3 ± 0.7 mg/kg
Results (mg/kg)
28 26 21 1 3 10 14 18 27 9 12 11 13 23 2 25 17 4 5 6 7 8 15 16 19 20 22 24 Md RA HV
Laboratory
z-Scores: S2 - As
Target Standard Deviation for Proficiency Assessment 1.2 mg/kg (Equivalent to 10% CV)
z-Score
-2.9 -2.7 -0.7 -0.2 -0.2 -0.2 -0.2 -0.2 -0.2 -0.1 -0.1 0.1 0.4 0.6 1.4 1.4 1.9
28 26 21 1 3 10 14 18 27 9 12 11 13 23 2 25 17
Laboratory
En-Scores: S2 - As
En-Score
-2.1 -0.5 -0.4 -0.1 -0.1 -0.1 -0.2 -0.2 -0.1 0.0 0.1 0.2 0.2 1.4 0.8 0.7
28 26 21 1 3 10 14 18 27 9 12 11 13 23 2 25 17
Laboratory

Figure 19

Table 30

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	B
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.9704	NR	-0.32	-0.40
2	NT	NT		
3	<10	10		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	6.04	0.89	2.12	1.62
10	4.6	0.92	0.42	0.32
11	3.52	0.4	-0.85	-0.92
12	<20	3.6		
13	4.3	0.9	0.07	0.05
14	<10	NR		
15	NT	NT		
16	NT	NT		
17	<10	NR		
18	4.7	0.6	0.54	0.51
19	NT	NT		
20	NT	NT		
21	3.6	0.4	-0.75	-0.82
22	NT	NT		
23	4.2	4	-0.05	-0.01
24	NT	NT		
25	NT	NT		
26	3.03	0.82	-1.43	-1.14
27	5	5	0.90	0.15
28	NR	NR		

Statistics

Assigned Value	4.24	0.67
Spike Value	Not Spiked	
Homogeneity Value	4.30	0.52
Robust Average	4.24	0.67
Median	4.25	0.64
Mean	4.30	
N	10	
Max	6.04	
Min	3.03	
Robust SD	0.85	
Robust CV	20%	

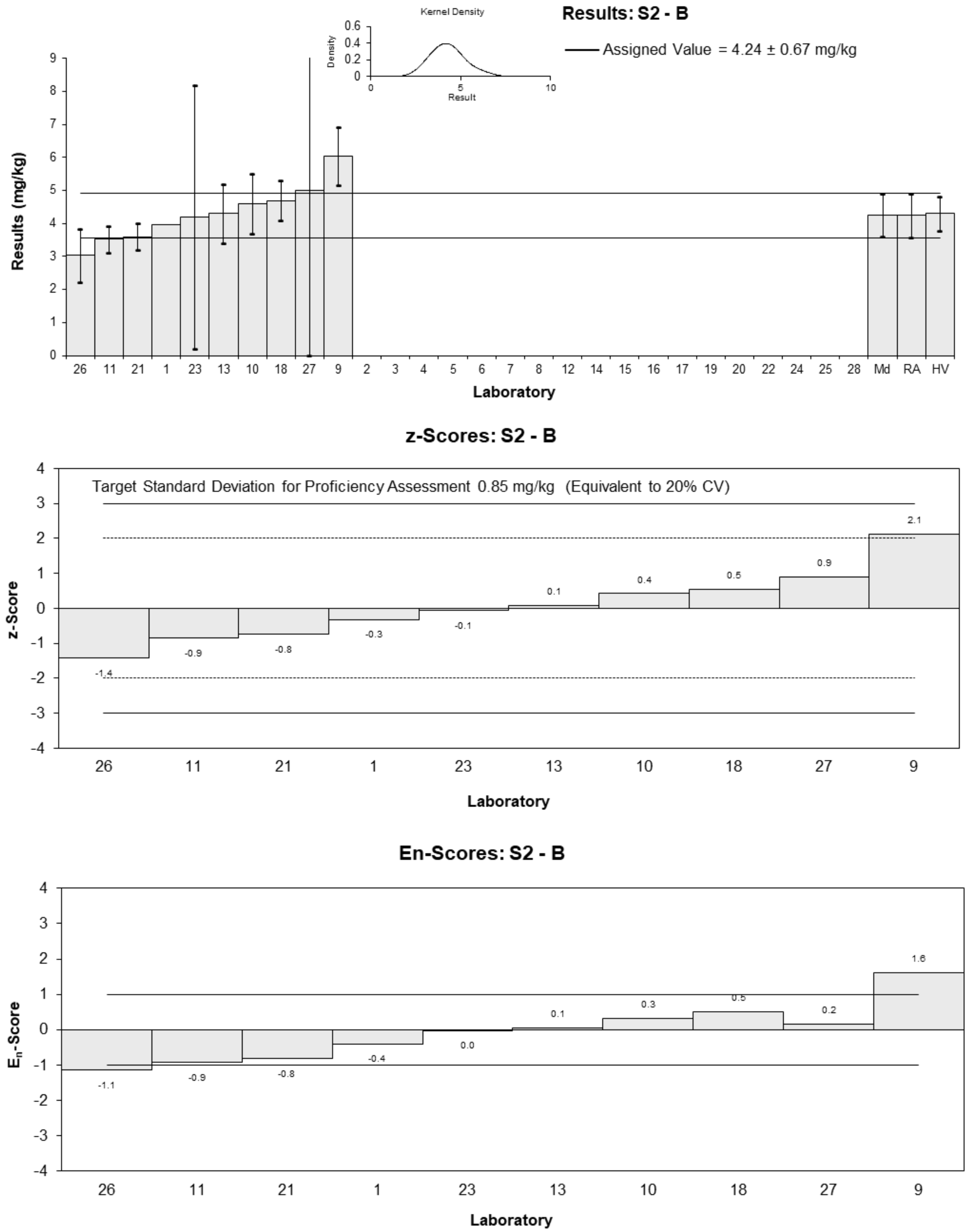

Results: S2 - B
Assigned Value = 4.24 ± 0.67 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 11 21 1 23 13 10 18 27 9 2 3 4 5 6 7 8 12 14 15 16 17 19 20 22 24 25 28 Md RA HV
z-Scores: S2 - B
Target Standard Deviation for Proficiency Assessment 0.85 mg/kg (Equivalent to 20% CV)
z-Score
-1.4 -0.9 -0.8 -0.3 -0.1 0.1 0.4 0.5 0.9 2.1
26 11 21 1 23 13 10 18 27 9
Laboratory
En-Scores: S2 - B
En-Score
-1.1 -0.9 -0.8 -0.4 0.0 0.1 0.3 0.5 0.2 1.6
26 11 21 1 23 13 10 18 27 9
Laboratory

Figure 20

Table 31

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Ba
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	116	NR	0.36	0.80
2	NT	NT		
3	110	20	-0.18	-0.10
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	120	13	0.71	0.57
10	110	22	-0.18	-0.09
11	109	12	-0.27	-0.23
12	101.3	6.1	-0.96	-1.36
13	107	22	-0.45	-0.22
14	110	20	-0.18	-0.10
15	NT	NT		
16	NT	NT		
17	114	9	0.18	0.19
18	110	10	-0.18	-0.18
19	NT	NT		
20	NT	NT		
21	105	5.0	-0.62	-0.99
22	NT	NT		
23	110	20	-0.18	-0.10
24	NT	NT		
25	119	30	0.62	0.23
26	95.7	23	-1.46	-0.69
27	120	14.76	0.71	0.51
28	126.3	NR	1.28	2.86

Statistics

Assigned Value	112	5
Spike Value	Not Spiked	
Homogeneity Value	118	14
Robust Average	112	5
Median	110	4
Mean	111	
N	16	
Max	126.3	
Min	95.7	
Robust SD	7.6	
Robust CV	6.8%	

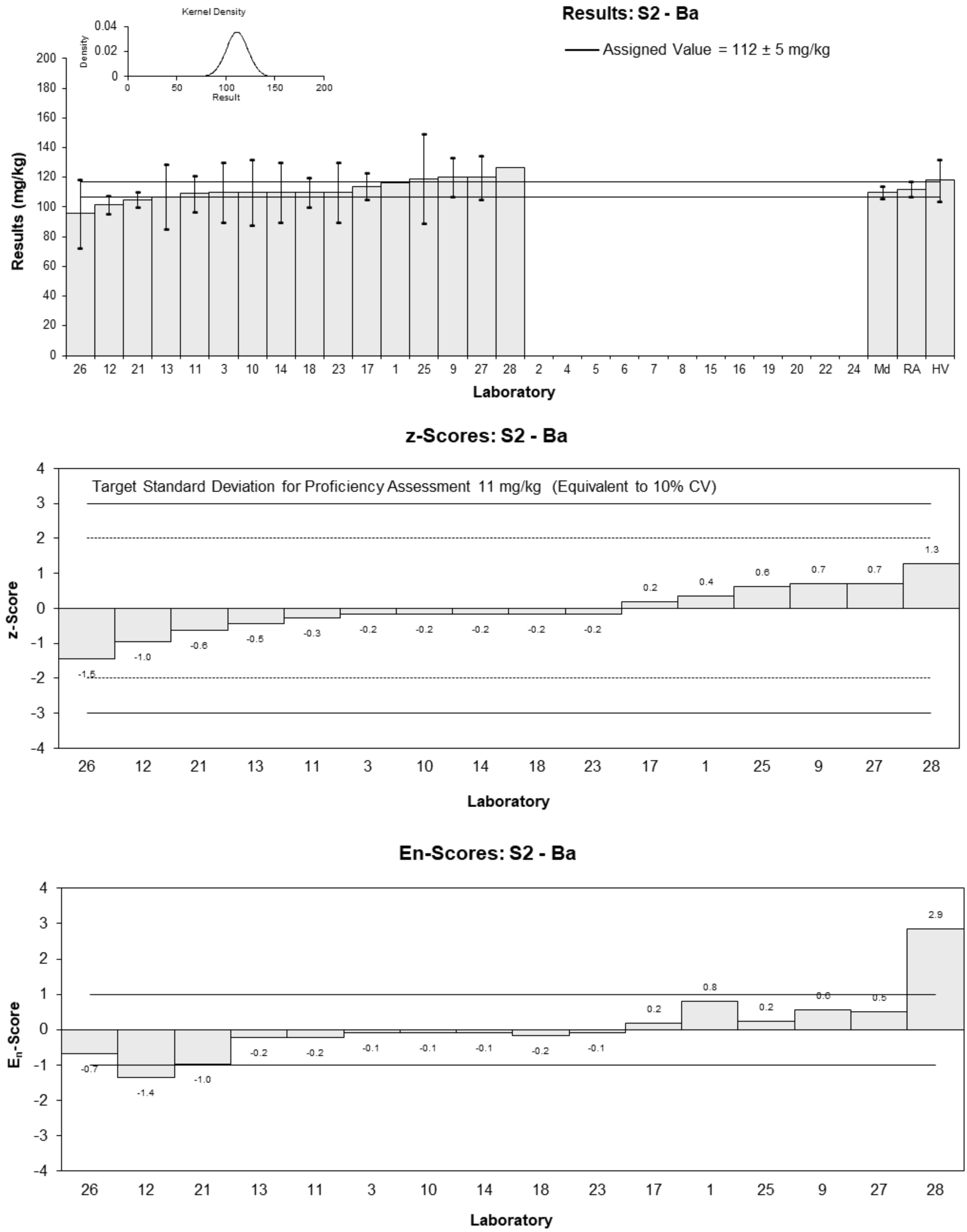

Results: S2 - Ba
Assigned Value = 112 ± 5 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 12 21 13 11 3 10 14 18 23 17 1 25 9 27 28 2 4 5 6 7 8 15 16 19 20 22 24 Md RA HV
z-Scores: S2 - Ba
Target Standard Deviation for Proficiency Assessment 11 mg/kg (Equivalent to 10% CV)
z-Score
-1.5 -1.0 -0.6 -0.5 -0.3 -0.2 -0.2 -0.2 -0.2 -0.2 0.2 0.4 0.6 0.7 0.7 1.3
26 12 21 13 11 3 10 14 18 23 17 1 25 9 27 28
Laboratory
En-Scores: S2 - Ba
E_n-Score
-0.7 -1.4 -1.0 -0.2 -0.2 -0.1 -0.1 -0.1 -0.2 -0.1 0.2 0.8 0.2 0.6 0.5 2.9
26 12 21 13 11 3 10 14 18 23 17 1 25 9 27 28
Laboratory

Figure 21

Table 32

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Be
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.685	NR	0.82	1.44
2	NT	NT		
3	<1	1		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	0.6	0.1	-0.52	-0.31
9	0.67	0.15	0.58	0.24
10	0.67	0.134	0.58	0.27
11	0.69	0.1	0.90	0.54
12	0.65	0.18	0.27	0.09
13	0.67	0.13	0.58	0.27
14	<1	NR		
15	NT	NT		
16	NT	NT		
17	0.66	0.07	0.43	0.34
18	0.59	0.2	-0.68	-0.21
19	NT	NT		
20	NT	NT		
21	0.60	0.05	-0.52	-0.54
22	NT	NT		
23	0.55	1	-1.31	-0.08
24	NT	NT		
25	<1	NR		
26	0.584	0.19	-0.77	-0.25
27	0.6	0.078	-0.52	-0.38
28	NT	NT		

Statistics

Assigned Value	0.633	0.036
Spike Value	Not Spiked	
Homogeneity Value	0.607	0.073
Robust Average	0.633	0.036
Median	0.650	0.041
Mean	0.632	
N	13	
Max	0.69	
Min	0.55	
Robust SD	0.051	
Robust CV	8.1%	

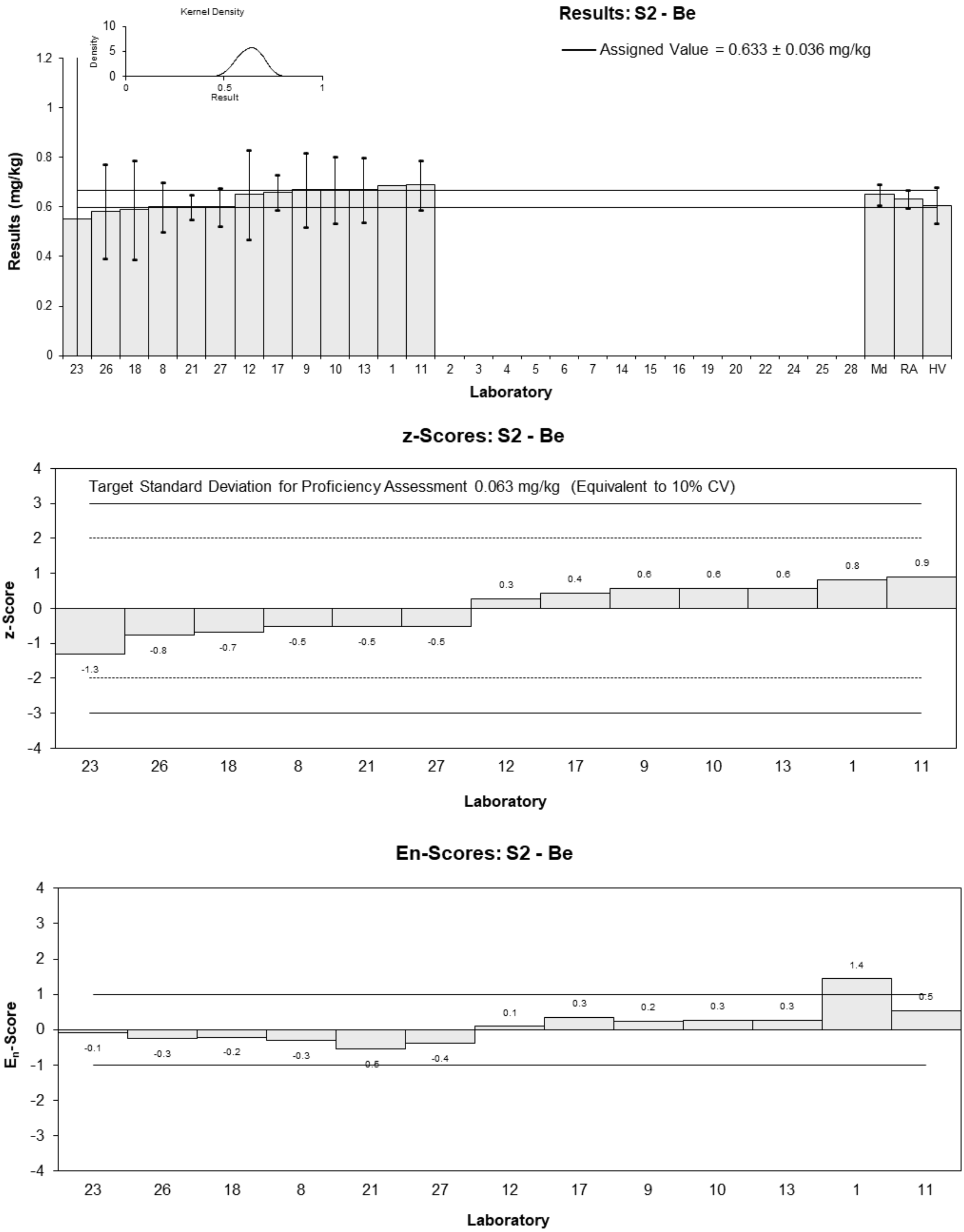

Results: S2 - Be
Assigned Value = 0.633 ± 0.036 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S2 - Be
Target Standard Deviation for Proficiency Assessment 0.063 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S2 - Be
E_n-Score
Laboratory

Figure 22

Table 33

Sample Details

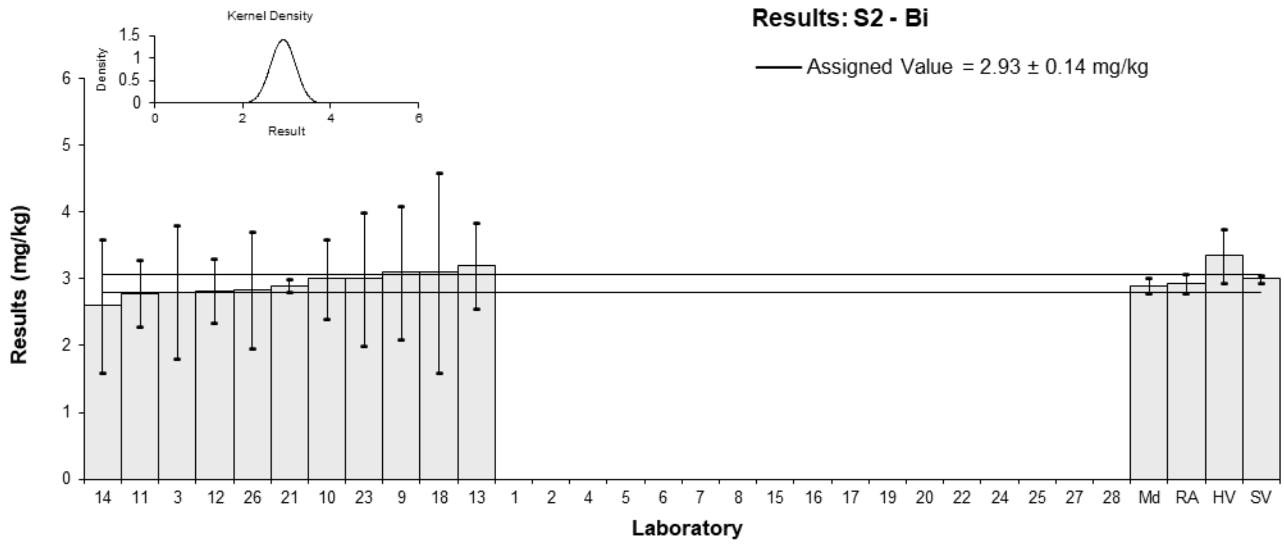
Sample No.	S2
Matrix	Soil
Analyte	Bi
Unit	mg/kg

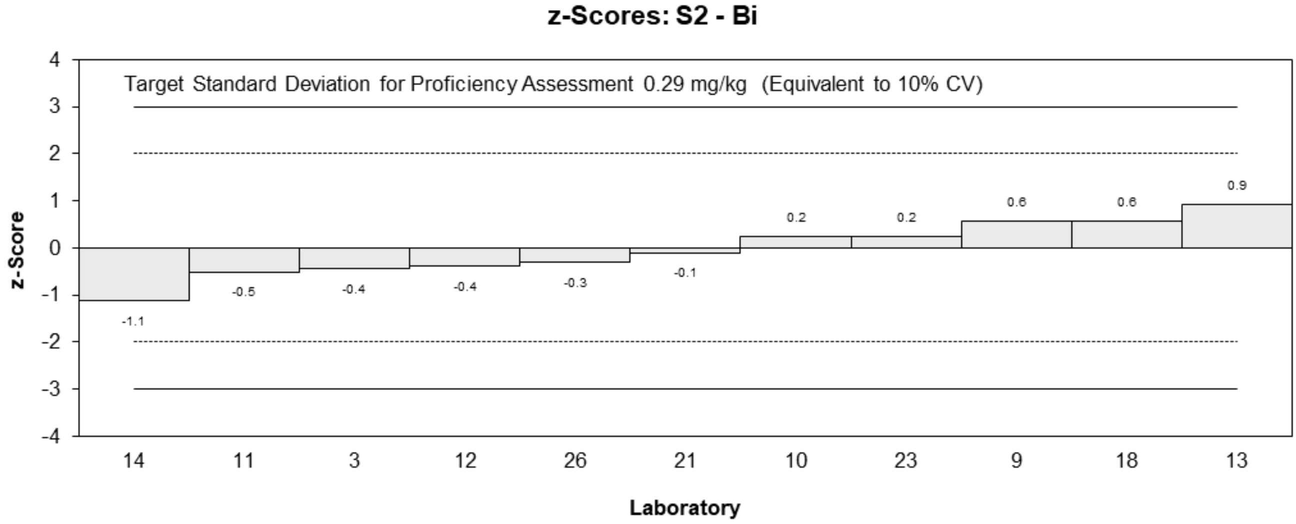
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	2.8	1	-0.44	-0.13
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	3.10	1.00	0.58	0.17
10	3.0	0.6	0.24	0.11
11	2.78	0.5	-0.51	-0.29
12	2.82	0.48	-0.38	-0.22
13	3.2	0.65	0.92	0.41
14	2.6	1	-1.13	-0.33
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	3.1	1.5	0.58	0.11
19	NT	NT		
20	NT	NT		
21	2.9	0.1	-0.10	-0.17
22	NT	NT		
23	3	1	0.24	0.07
24	NT	NT		
25	NT	NT		
26	2.84	0.88	-0.31	-0.10
27	NT	NT		
28	NT	NT		

Statistics

Assigned Value	2.93	0.14
Spike Value	3.00	0.06
Homogeneity Value	3.35	0.40
Robust Average	2.93	0.14
Median	2.90	0.11
Mean	2.92	
N	11	
Max	3.2	
Min	2.6	
Robust SD	0.19	
Robust CV	6.6%	


Results: S2 - Bi
Assigned Value = 2.93 ± 0.14 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 11 3 12 26 21 10 23 9 18 13 1 2 4 5 6 7 8 15 16 17 19 20 22 24 25 27 28 Md RA HV SV


z-Scores: S2 - Bi
Target Standard Deviation for Proficiency Assessment 0.29 mg/kg (Equivalent to 10% CV)
z-Score
-1.1
-0.5
-0.4
-0.4
-0.3
-0.1
0.2
0.2
0.6
0.6
0.9
14 11 3 12 26 21 10 23 9 18 13
Laboratory

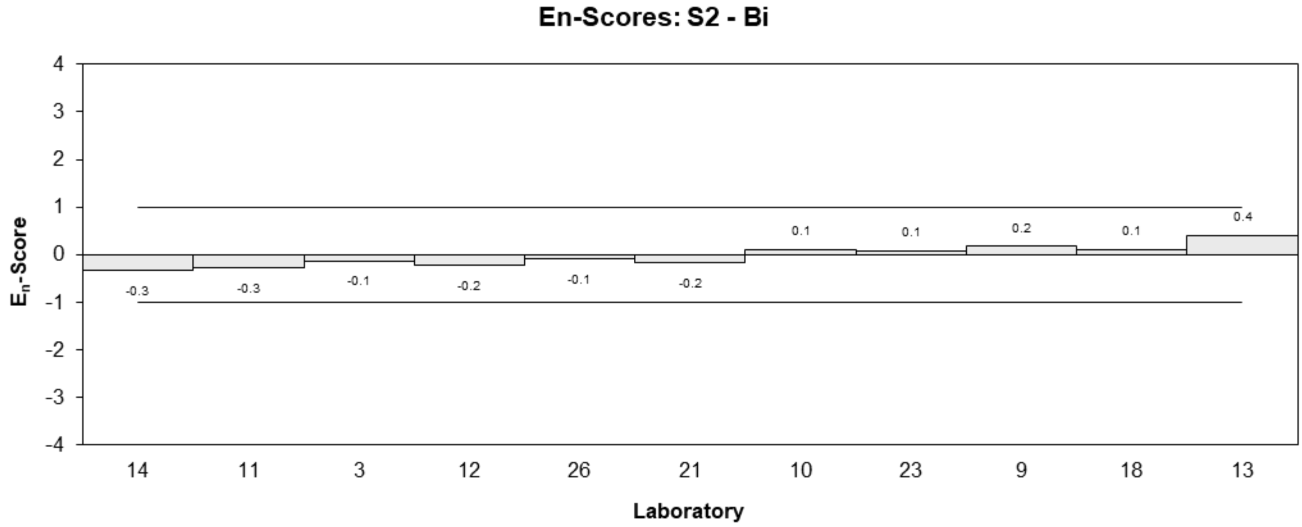

En-Scores: S2 - Bi
En-Score
-0.3
-0.3
-0.1
-0.2
-0.1
-0.2
0.1
0.1
0.2
0.1
0.4
14 11 3 12 26 21 10 23 9 18 13
Laboratory

Figure 23

Table 34

Sample Details

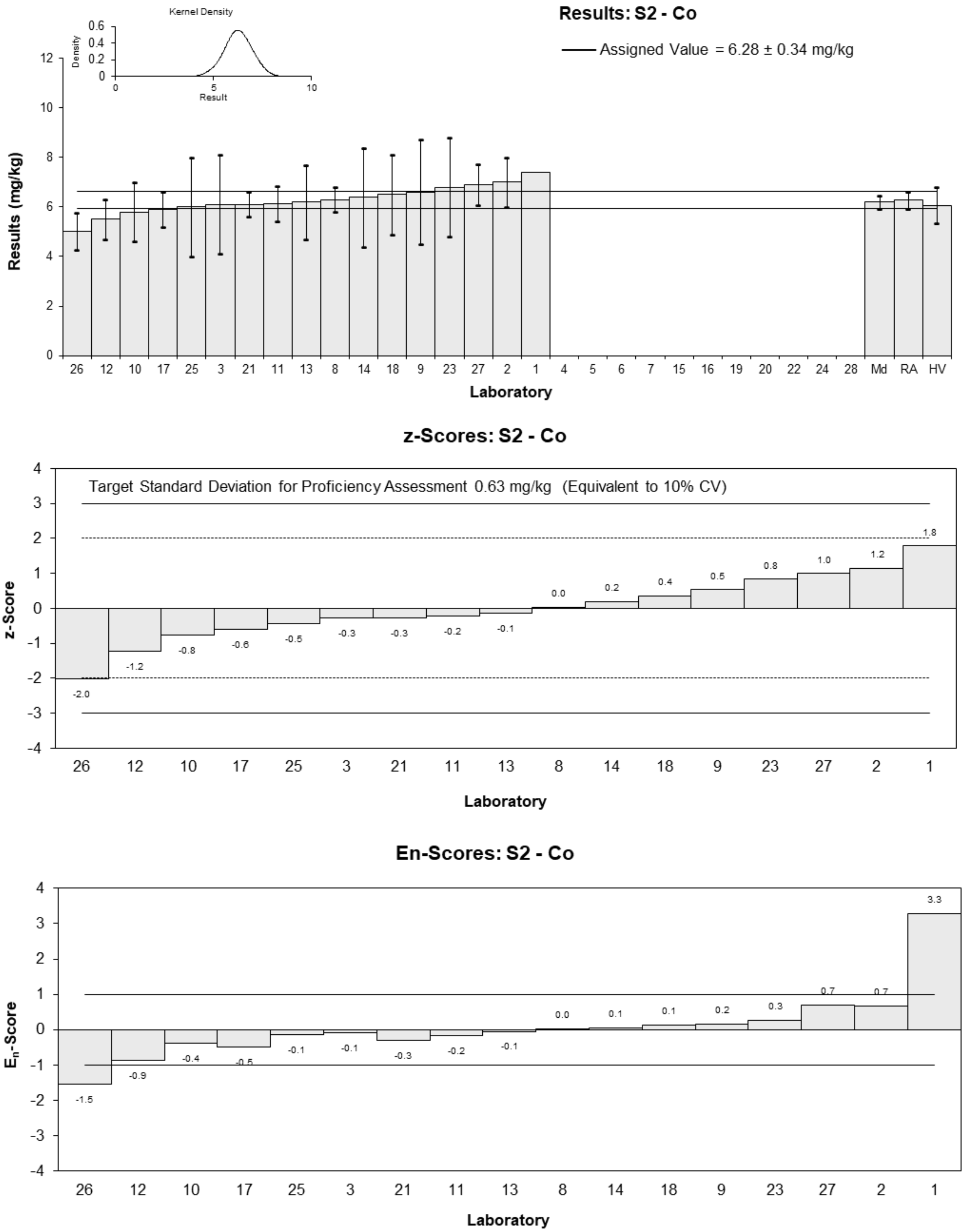
Sample No.	S2
Matrix	Soil
Analyte	Co
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	7.4	NR	1.78	3.29
2	7	1	1.15	0.68
3	6.1	2	-0.29	-0.09
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	6.3	0.5	0.03	0.03
9	6.61	2.10	0.53	0.16
10	5.8	1.2	-0.76	-0.38
11	6.14	0.7	-0.22	-0.18
12	5.50	0.82	-1.24	-0.88
13	6.2	1.5	-0.13	-0.05
14	6.4	2	0.19	0.06
15	NT	NT		
16	NT	NT		
17	5.9	0.7	-0.61	-0.49
18	6.5	1.6	0.35	0.13
19	NT	NT		
20	NT	NT		
21	6.1	0.5	-0.29	-0.30
22	NT	NT		
23	6.8	2	0.83	0.26
24	NT	NT		
25	6	2	-0.45	-0.14
26	5.01	0.75	-2.02	-1.54
27	6.9	0.8142	0.99	0.70
28	NT	NT		

Statistics

Assigned Value	6.28	0.34
Spike Value	Not Spiked	
Homogeneity Value	6.06	0.73
Robust Average	6.28	0.34
Median	6.20	0.27
Mean	6.27	
N	17	
Max	7.4	
Min	5.01	
Robust SD	0.56	
Robust CV	8.9%	



Results: S2 - Co
Assigned Value = 6.28 ± 0.34 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 12 10 17 25 3 21 11 13 8 14 18 9 23 27 2 1 4 5 6 7 15 16 19 20 22 24 28 Md RA HV
z-Scores: S2 - Co
Target Standard Deviation for Proficiency Assessment 0.63 mg/kg (Equivalent to 10% CV)
z-Score
-2.0 -1.2 -0.8 -0.6 -0.5 -0.3 -0.3 -0.2 -0.1 0.0 0.2 0.4 0.5 0.8 1.0 1.2 1.8
26 12 10 17 25 3 21 11 13 8 14 18 9 23 27 2 1
Laboratory
En-Scores: S2 - Co
En-Score
-1.5 -0.9 -0.4 -0.5 -0.1 -0.1 -0.3 -0.2 -0.1 0.0 0.1 0.1 0.2 0.3 0.7 0.7 3.3
26 12 10 17 25 3 21 11 13 8 14 18 9 23 27 2 1
Laboratory

Figure 24

Table 35

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Cs
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	1.3	1	-0.43	-0.09
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	1.5	0.3	0.53	0.31
11	NT	NT		
12	1.37	0.19	-0.10	-0.07
13	1.5	0.3	0.53	0.31
14	1.5	5	0.53	0.02
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	1.7	0.9	1.49	0.34
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NT	NT		
23	1.2	0.5	-0.91	-0.35
24	NT	NT		
25	NT	NT		
26	1.05	0.21	-1.63	-1.17
27	NT	NT		
28	NT	NT		

Statistics

Assigned Value	1.39	0.20
Spike Value	Not Spiked	
Homogeneity Value	1.59	0.19
Robust Average	1.39	0.20
Median	1.44	0.13
Mean	1.39	
N	8	
Max	1.7	
Min	1.05	
Robust SD	0.23	
Robust CV	17%	

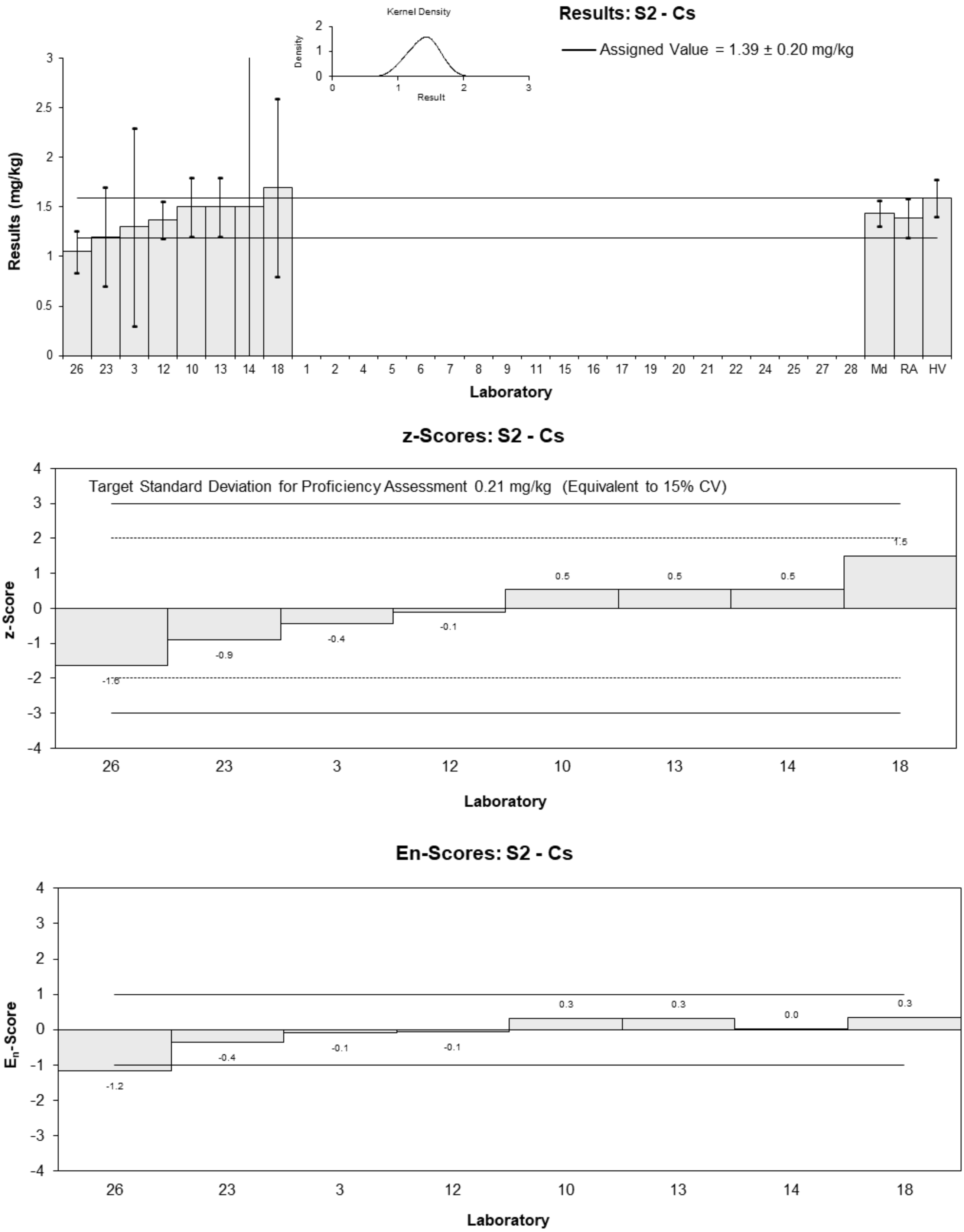

Kernel Density
Density
Result
Results: S2 - Cs
Assigned Value = 1.39 ± 0.20 mg/kg
Results (mg/kg)
Laboratory
26 23 3 12 10 13 14 18 1 2 4 5 6 7 8 9 11 15 16 17 19 20 21 22 24 25 27 28 Md RA HV
z-Scores: S2 - Cs
Target Standard Deviation for Proficiency Assessment 0.21 mg/kg (Equivalent to 15% CV)
z-Score
-1.6 -0.9 -0.4 -0.1 0.5 0.5 0.5 1.5
En-Scores: S2 - Cs
E_n-Score
-1.2 -0.4 -0.1 -0.1 0.3 0.3 0.0 0.3

Figure 25

Table 36

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Cu
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	25	NR	0.64	1.36
2	26	1	1.06	1.68
3	24	5	0.21	0.10
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	24.1	2.5	0.26	0.22
10	24	4.8	0.21	0.10
11	21.9	2.5	-0.68	-0.59
12	22.3	3.4	-0.51	-0.34
13	25	5	0.64	0.29
14	24	0.5	0.21	0.41
15	NT	NT		
16	NT	NT		
17	22.5	4.0	-0.43	-0.24
18	22	3	-0.64	-0.47
19	NT	NT		
20	NT	NT		
21	22.5	1.0	-0.43	-0.67
22	NT	NT		
23	25	5	0.64	0.29
24	NT	NT		
25	24	4	0.21	0.12
26	19.4	2.9	-1.74	-1.32
27	25	3.125	0.64	0.45
28	19.0	NR	-1.91	-4.09

Statistics

Assigned Value	23.5	1.1
Spike Value	Not Spiked	
Homogeneity Value	23.1	2.8
Robust Average	23.5	1.1
Median	24.0	0.9
Mean	23.3	
N	17	
Max	26	
Min	19	
Robust SD	1.8	
Robust CV	7.6%	

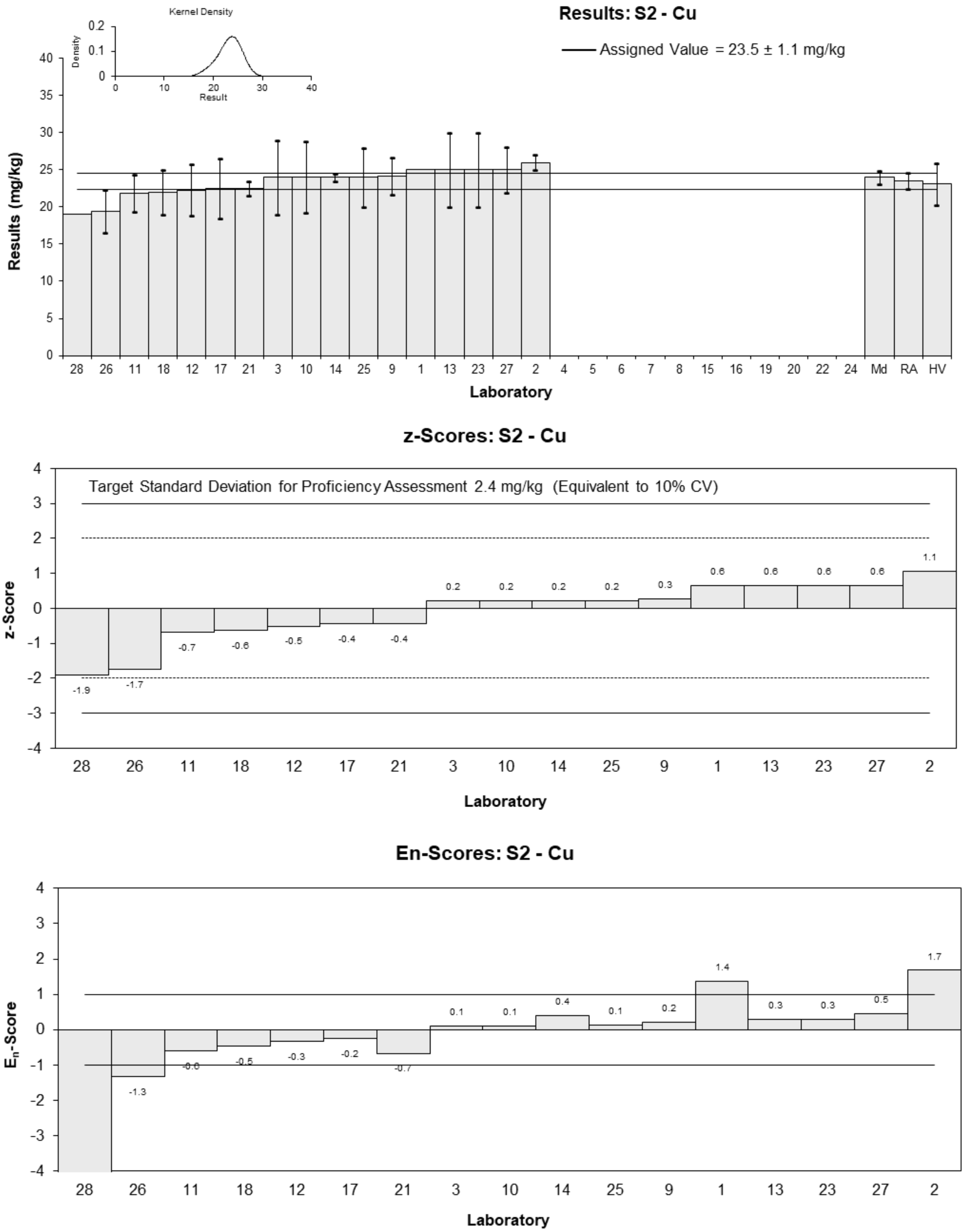

Results: S2 - Cu
Assigned Value = 23.5 ± 1.1 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
28 26 11 18 12 17 21 3 10 14 25 9 1 13 23 27 2 4 5 6 7 8 15 16 19 20 22 24 Md RA HV
z-Scores: S2 - Cu
Target Standard Deviation for Proficiency Assessment 2.4 mg/kg (Equivalent to 10% CV)
z-Score
-1.9 -1.7 -0.7 -0.6 -0.5 -0.4 -0.4 0.2 0.2 0.2 0.2 0.3 0.6 0.6 0.6 0.6 1.1
28 26 11 18 12 17 21 3 10 14 25 9 1 13 23 27 2
Laboratory
En-Scores: S2 - Cu
En-Score
-1.3 -0.6 -0.5 -0.3 -0.2 -0.7 0.1 0.1 0.4 0.1 0.2 1.4 0.3 0.3 0.5 1.7
28 26 11 18 12 17 21 3 10 14 25 9 1 13 23 27 2
Laboratory

Figure 26

Table 37

Sample Details

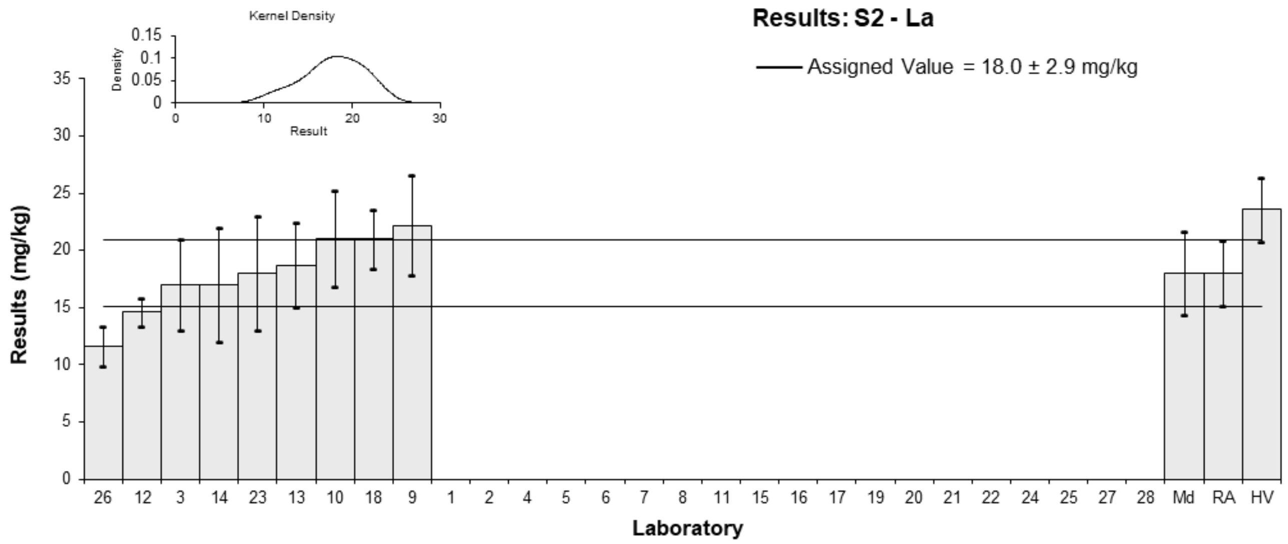
Sample No.	S2
Matrix	Soil
Analyte	La
Unit	mg/kg

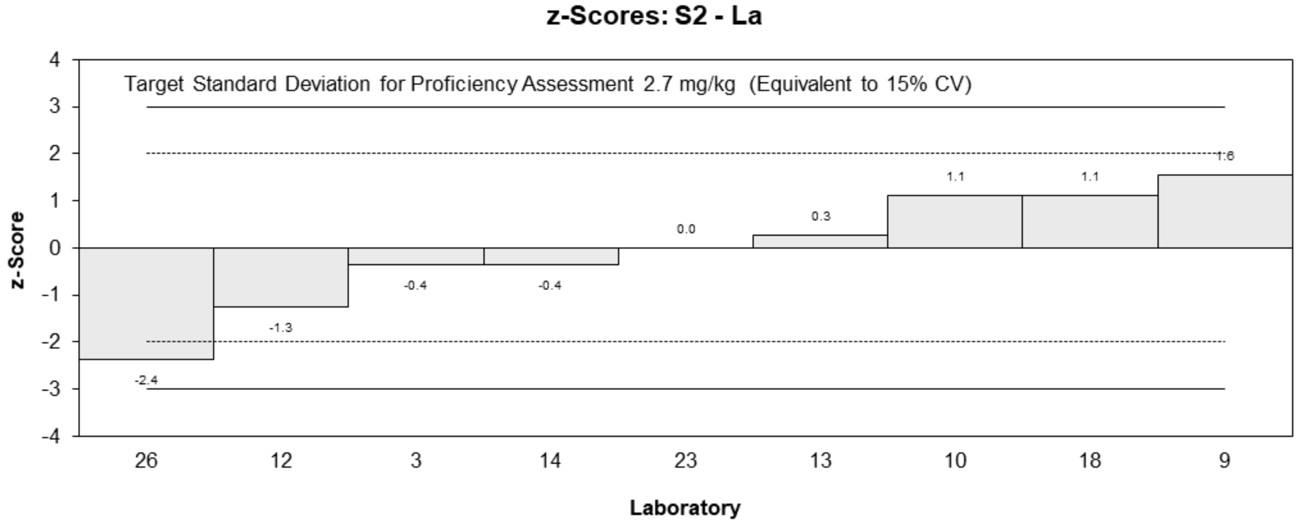
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	17	4	-0.37	-0.20
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	22.2	4.4	1.56	0.80
10	21	4.2	1.11	0.59
11	NT	NT		
12	14.6	1.2	-1.26	-1.08
13	18.7	3.7	0.26	0.15
14	17	5	-0.37	-0.17
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	21	2.6	1.11	0.77
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NT	NT		
23	18	5	0.00	0.00
24	NT	NT		
25	NT	NT		
26	11.6	1.7	-2.37	-1.90
27	NT	NT		
28	NT	NT		

Statistics

Assigned Value	18.0	2.9
Spike Value	Not Spiked	
Homogeneity Value	23.6	2.8
Robust Average	18.0	2.9
Median	18.0	3.7
Mean	17.9	
N	9	
Max	22.2	
Min	11.6	
Robust SD	3.5	
Robust CV	20%	


Results: S2 - La
Assigned Value = 18.0 ± 2.9 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory


z-Scores: S2 - La
Target Standard Deviation for Proficiency Assessment 2.7 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory

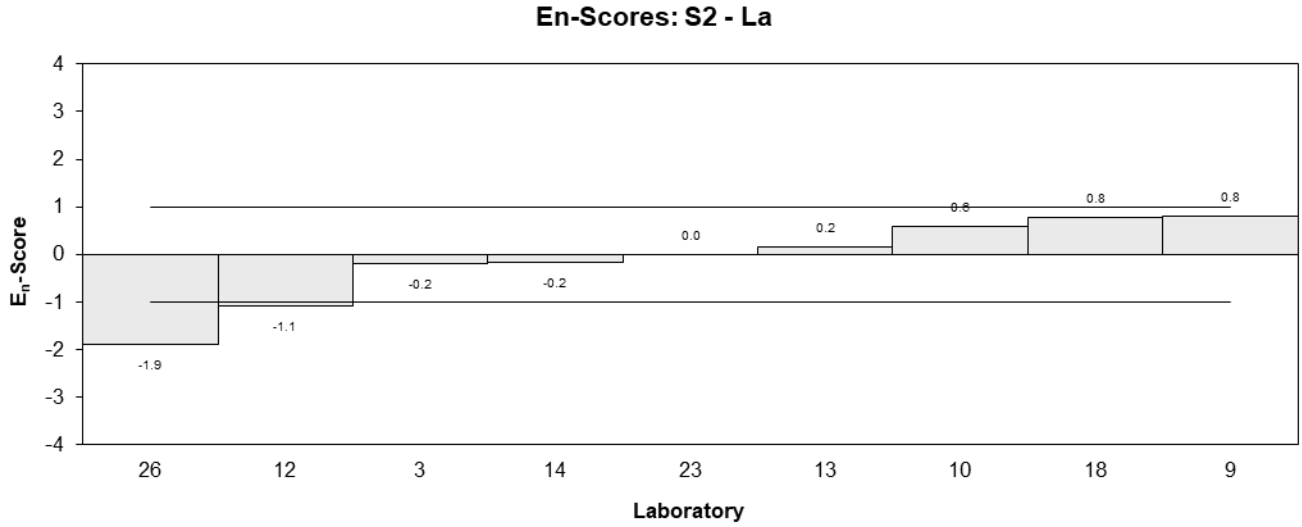

En-Scores: S2 - La
En-Score
Laboratory

Figure 27

Table 38

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Li
Unit	mg/kg

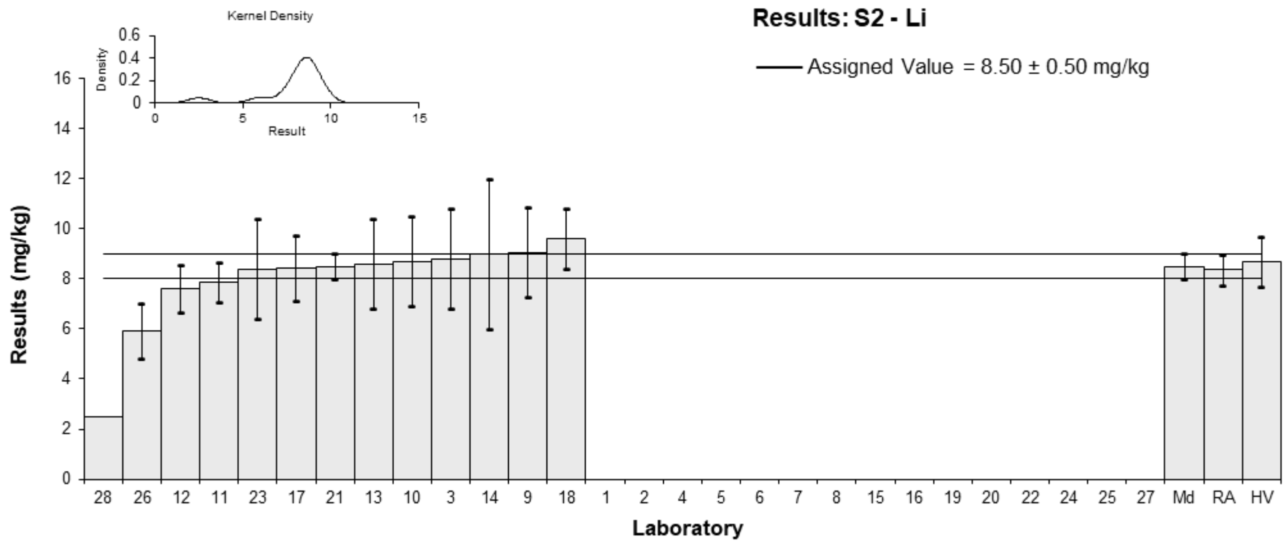
Participant Results

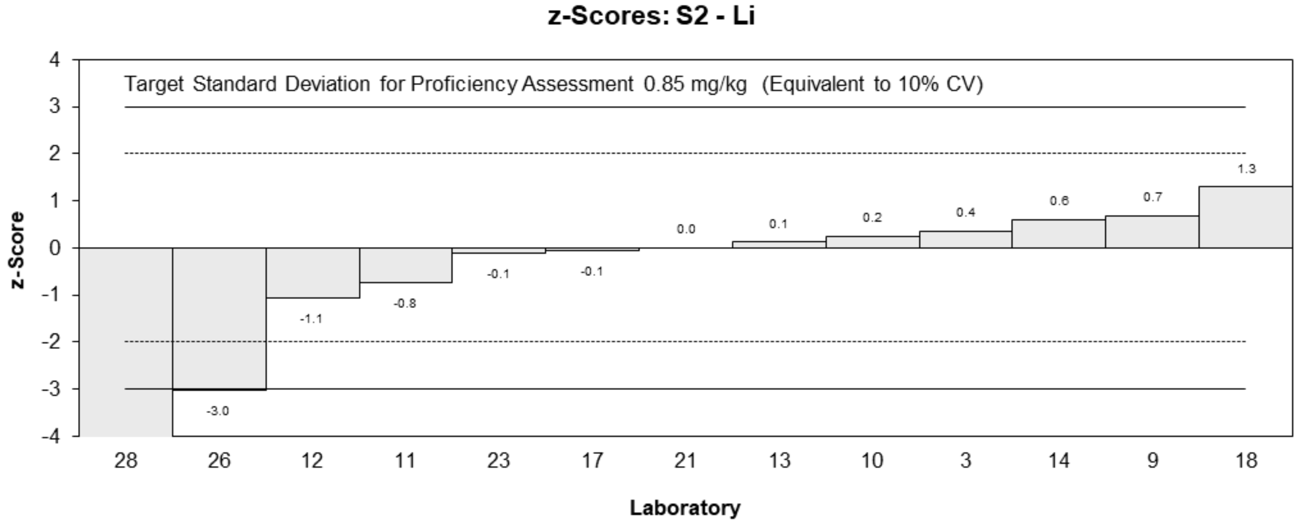
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	8.8	2	0.35	0.15
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	9.07	1.81	0.67	0.30
10	8.7	1.8	0.24	0.11
11	7.86	0.8	-0.75	-0.68
12	7.59	0.95	-1.07	-0.85
13	8.6	1.8	0.12	0.05
14	9	3	0.59	0.16
15	NT	NT		
16	NT	NT		
17	8.45	1.3	-0.06	-0.04
18	9.6	1.2	1.29	0.85
19	NT	NT		
20	NT	NT		
21	8.5	0.5	0.00	0.00
22	NT	NT		
23	8.4	2	-0.12	-0.05
24	NT	NT		
25	NT	NT		
26	5.93	1.1	-3.02	-2.13
27	NT	NT		
28*	2.5	NR	-7.06	-12.00

* Outlier, see Section 4.2

Statistics

Assigned Value	8.50	0.50
Spike Value	Not Spiked	
Homogeneity Value	8.7	1.0
Robust Average	8.36	0.61
Median	8.50	0.51
Mean	7.9	
N	13	
Max	9.6	
Min	2.5	
Robust SD	0.87	
Robust CV	10%	


Results: S2 - Li
Assigned Value = 8.50 ± 0.50 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
28 26 12 11 23 17 21 13 10 3 14 9 18 1 2 4 5 6 7 8 15 16 19 20 22 24 25 27 Md RA HV


z-Scores: S2 - Li
Target Standard Deviation for Proficiency Assessment 0.85 mg/kg (Equivalent to 10% CV)
z-Score
-3.0 -1.1 -0.8 -0.1 -0.1 0.0 0.1 0.2 0.4 0.6 0.7 1.3
Laboratory
28 26 12 11 23 17 21 13 10 3 14 9 18

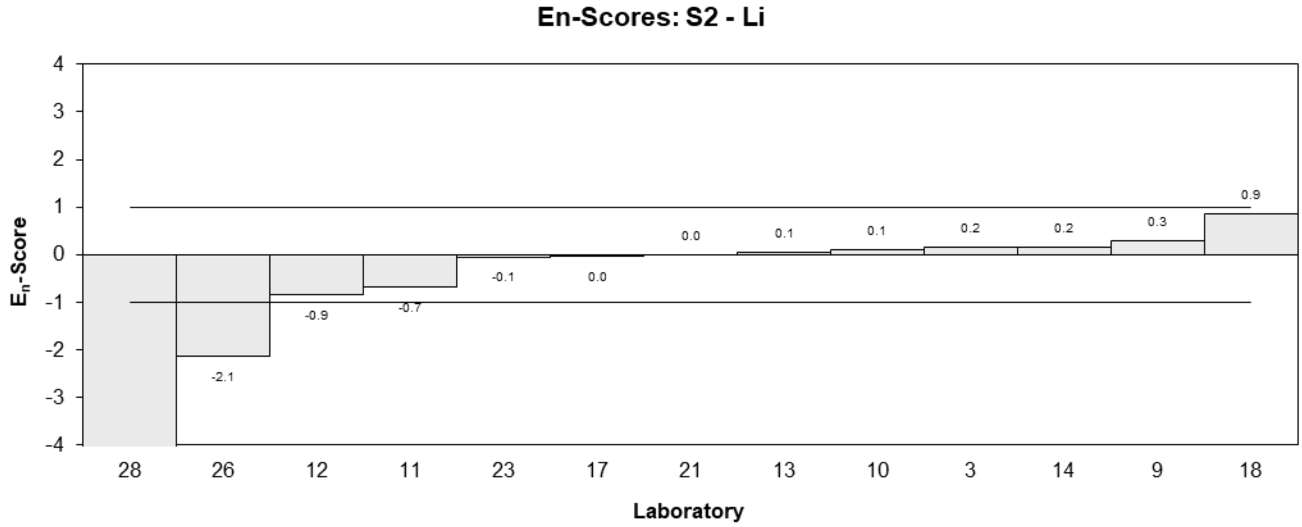

En-Scores: S2 - Li
En-Score
-2.1 -0.9 -0.7 -0.1 0.0 0.0 0.1 0.1 0.2 0.2 0.3 0.9
Laboratory
28 26 12 11 23 17 21 13 10 3 14 9 18

Figure 28

Table 39

Sample Details

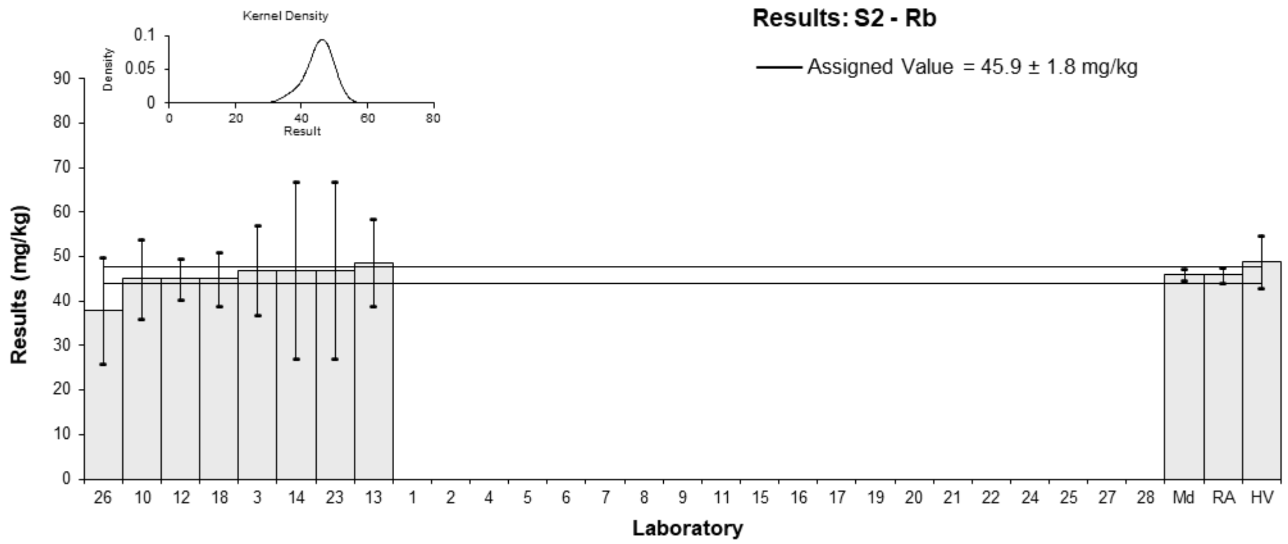
Sample No.	S2
Matrix	Soil
Analyte	Rb
Unit	mg/kg

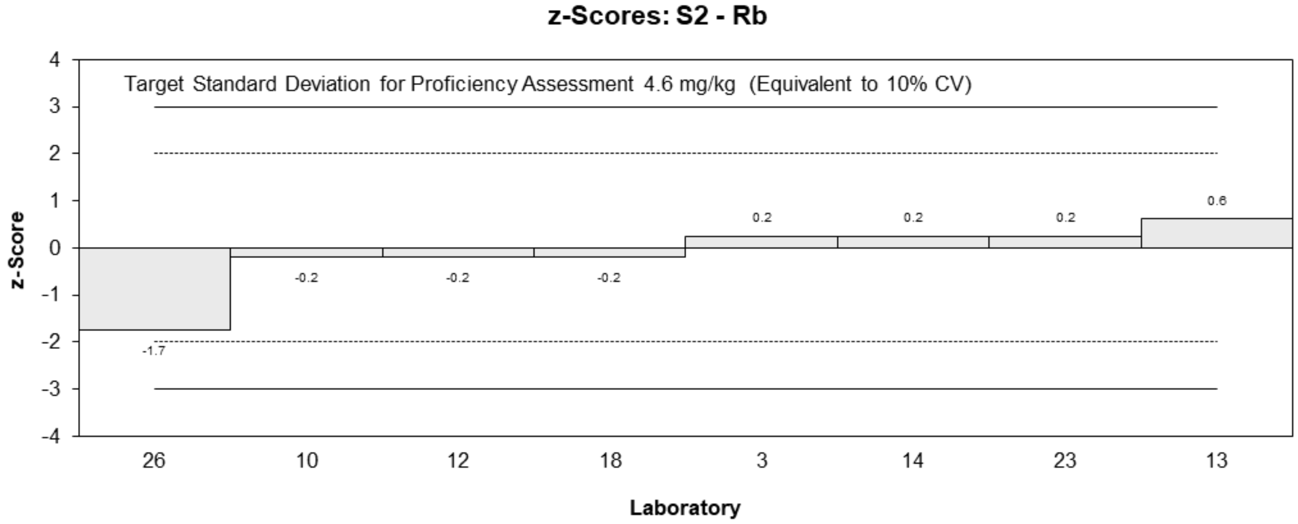
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	47	10	0.24	0.11
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	45	9	-0.20	-0.10
11	NT	NT		
12	45.0	4.6	-0.20	-0.18
13	48.7	9.7	0.61	0.28
14	47	20	0.24	0.05
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	45	6	-0.20	-0.14
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NT	NT		
23	47	20	0.24	0.05
24	NT	NT		
25	NT	NT		
26	37.9	12	-1.74	-0.66
27	NT	NT		
28	NT	NT		

Statistics

Assigned Value	45.9	1.8
Spike Value	Not Spiked	
Homogeneity Value	49.0	5.9
Robust Average	45.9	1.8
Median	46.0	1.3
Mean	45.3	
N	8	
Max	48.7	
Min	37.9	
Robust SD	2.1	
Robust CV	4.5%	


Results: S2 - Rb
Assigned Value = 45.9 ± 1.8 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
26 10 12 18 3 14 23 13 1 2 4 5 6 7 8 9 11 15 16 17 19 20 21 22 24 25 27 28 Md RA HV
Laboratory


z-Scores: S2 - Rb
Target Standard Deviation for Proficiency Assessment 4.6 mg/kg (Equivalent to 10% CV)
z-Score
-1.7
-0.2
-0.2
-0.2
0.2
0.2
0.2
0.6
26 10 12 18 3 14 23 13
Laboratory

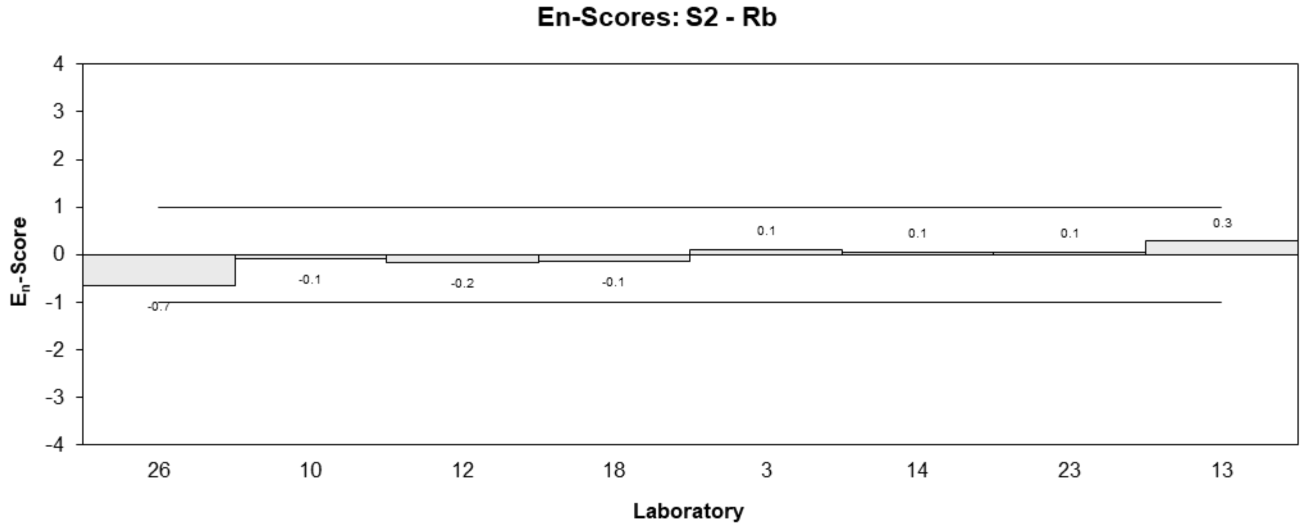

En-Scores: S2 - Rb
E_n-Score
-0.7
-0.1
-0.2
-0.1
0.1
0.1
0.1
0.3
26 10 12 18 3 14 23 13
Laboratory

Figure 29

Table 40

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Sn
Unit	mg/kg

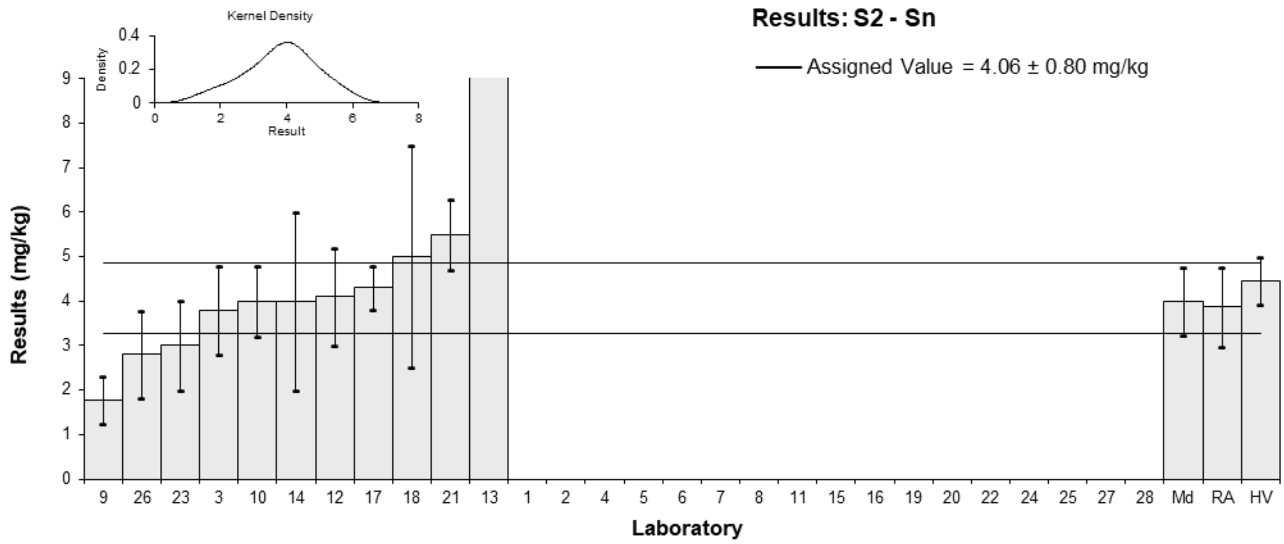
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	3.8	1	-0.32	-0.20
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9*	1.77	0.53	-2.82	-2.39
10	4.0	0.8	-0.07	-0.05
11	NT	NT		
12	4.1	1.1	0.05	0.03
13**	22.5	0.9	22.71	15.31
14	4	2	-0.07	-0.03
15	NT	NT		
16	NT	NT		
17	4.3	0.5	0.30	0.25
18	5	2.5	1.16	0.36
19	NT	NT		
20	NT	NT		
21	5.5	0.8	1.77	1.27
22	NT	NT		
23	3	1	-1.31	-0.83
24	NT	NT		
25	NT	NT		
26	2.81	0.98	-1.54	-0.99
27	NT	NT		
28	NT	NT		

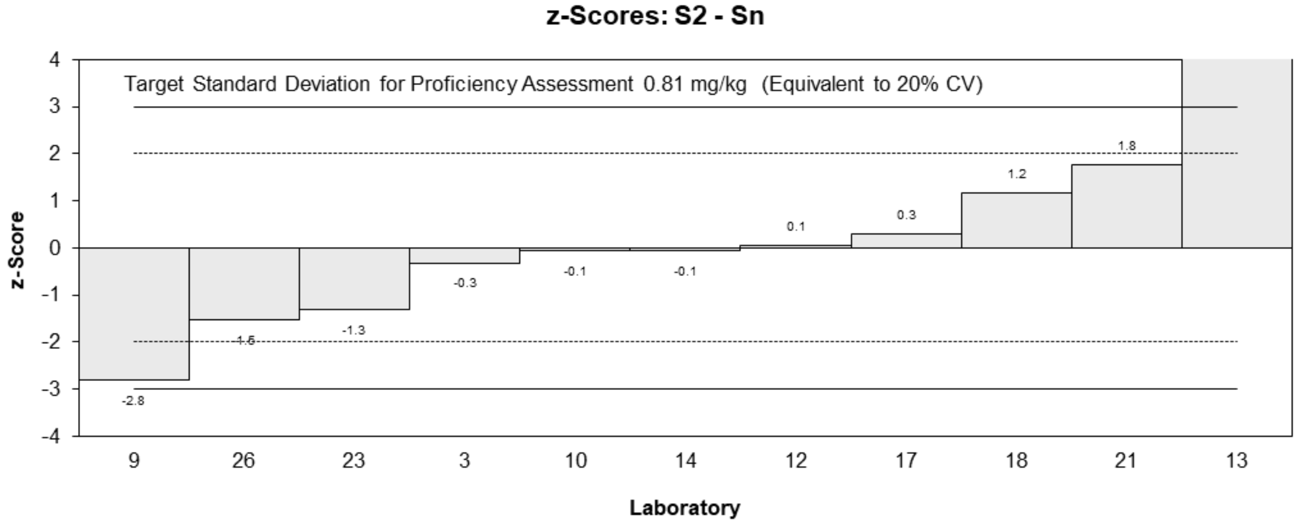
* Outlier, ** Extreme Outlier, see Section 4.2

Statistics

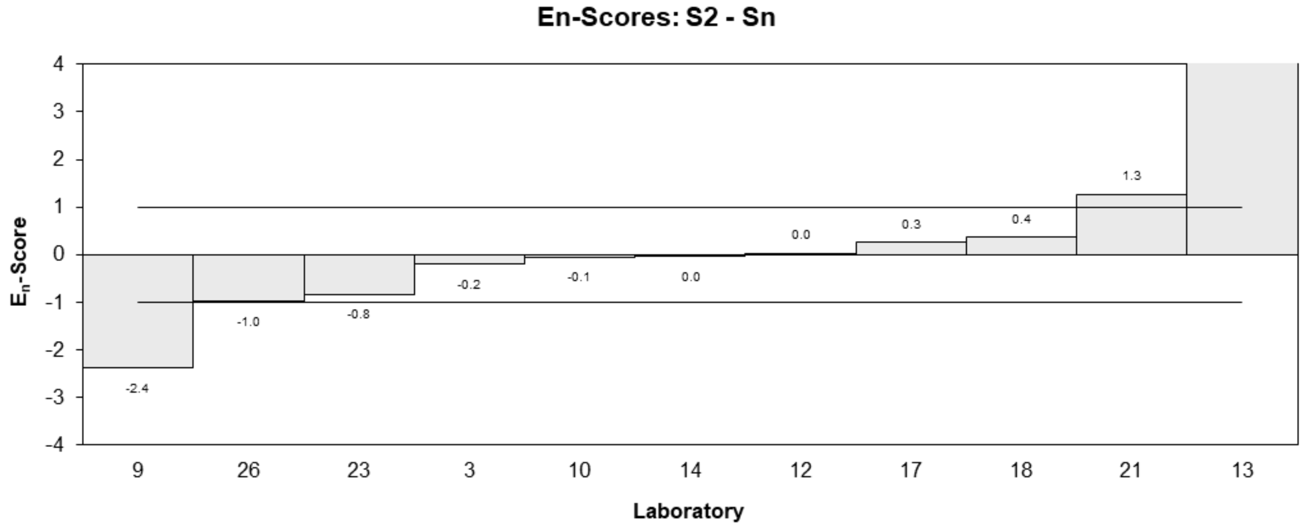
Assigned Value	4.06	0.80
Spike Value	Not Spiked	
Homogeneity Value	4.45	0.53
Robust Average	3.87	0.89
Median	4.00	0.76
Mean	3.83	
N	10	
Max	5.5	
Min	1.77	
Robust SD	1.1	
Robust CV	29%	



Results: S2 - Sn
Assigned Value = 4.06 ± 0.80 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
9 26 23 3 10 14 12 17 18 21 13 1 2 4 5 6 7 8 11 15 16 19 20 22 24 25 27 28 Md RA HV
Laboratory



z-Scores: S2 - Sn
Target Standard Deviation for Proficiency Assessment 0.81 mg/kg (Equivalent to 20% CV)
z-Score
-2.8 -1.5 -1.3 -0.3 -0.1 -0.1 0.1 0.3 1.2 1.8
9 26 23 3 10 14 12 17 18 21 13
Laboratory



En-Scores: S2 - Sn
En-Score
-2.4 -1.0 -0.8 -0.2 -0.1 0.0 0.0 0.3 0.4 1.3
9 26 23 3 10 14 12 17 18 21 13
Laboratory

Figure 30

Table 41

Sample Details

Sample No.	S2
Matrix	Soil
Analyte	Th
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	6.3	2	-0.50	-0.29
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	7.7	1.55	0.50	0.35
11*	12.1	3.0	3.64	1.56
12	NT	NT		
13	NT	NT		
14	6.2	3	-0.57	-0.24
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	6.0	1.5	-0.71	-0.50
19	NT	NT		
20	NT	NT		
21	9.2	0.8	1.57	1.44
22	NT	NT		
23	7	3	0.00	0.00
24	NT	NT		
25	NT	NT		
26	NR	NR		
27	NT	NT		
28	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	7.0	1.3
Spike Value	Not Spiked	
Homogeneity Value	8.4	1.1
Robust Average	7.5	1.8
Median	7.0	1.1
Mean	7.8	
N	7	
Max	12.1	
Min	6	
Robust SD	1.9	
Robust CV	25%	

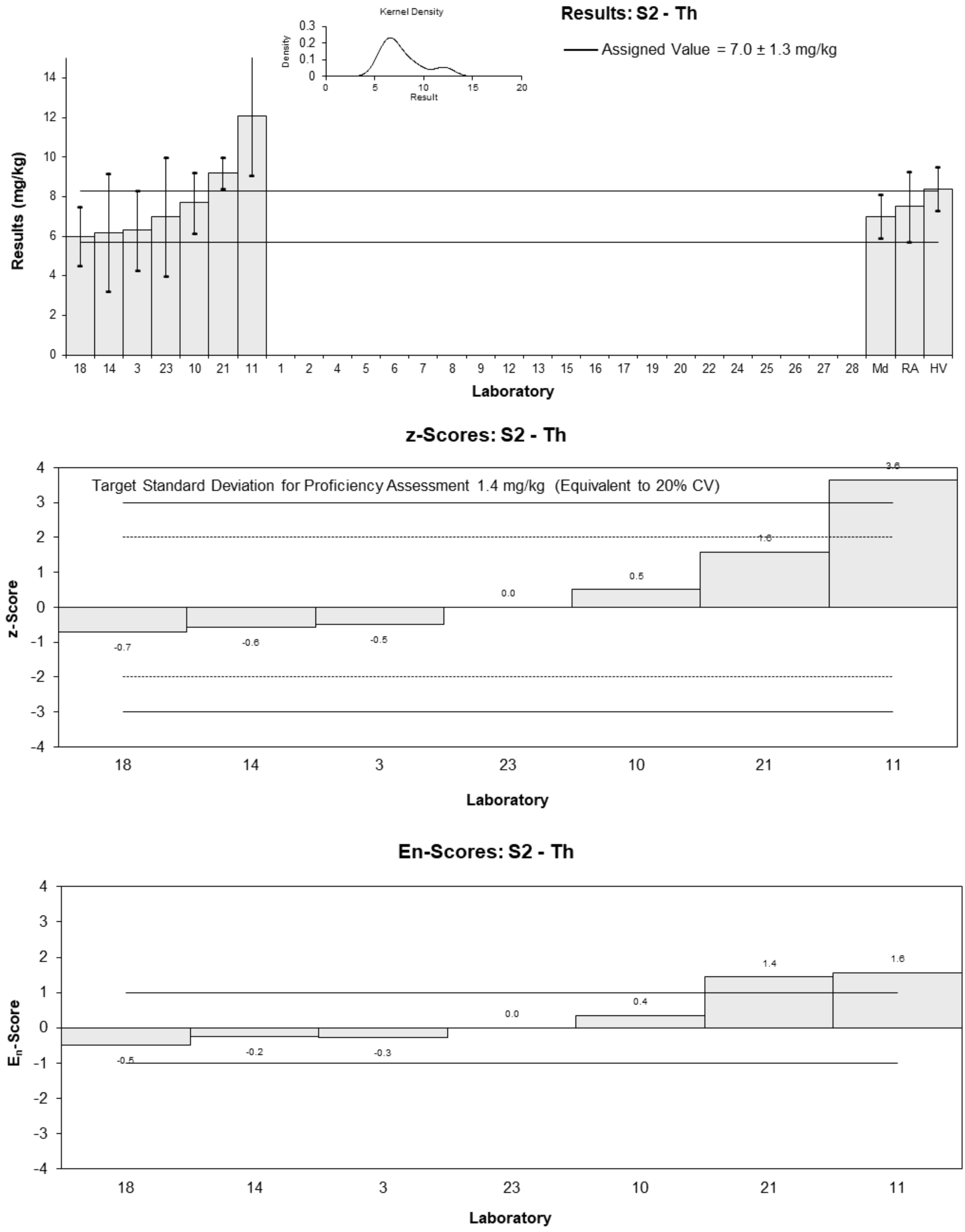

Results: S2 - Th
Assigned Value = 7.0 ± 1.3 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
18 14 3 23 10 21 11 1 2 4 5 6 7 8 9 12 13 15 16 17 19 20 22 24 25 26 27 28 Md RA HV
z-Scores: S2 - Th
Target Standard Deviation for Proficiency Assessment 1.4 mg/kg (Equivalent to 20% CV)
z-Score
-0.7 -0.6 -0.5 0.0 0.5 1.6 3.6
18 14 3 23 10 21 11
Laboratory
En-Scores: S2 - Th
En-Score
-0.5 -0.2 -0.3 0.0 0.4 1.4 1.6
18 14 3 23 10 21 11
Laboratory

Figure 31

Table 42

Sample Details

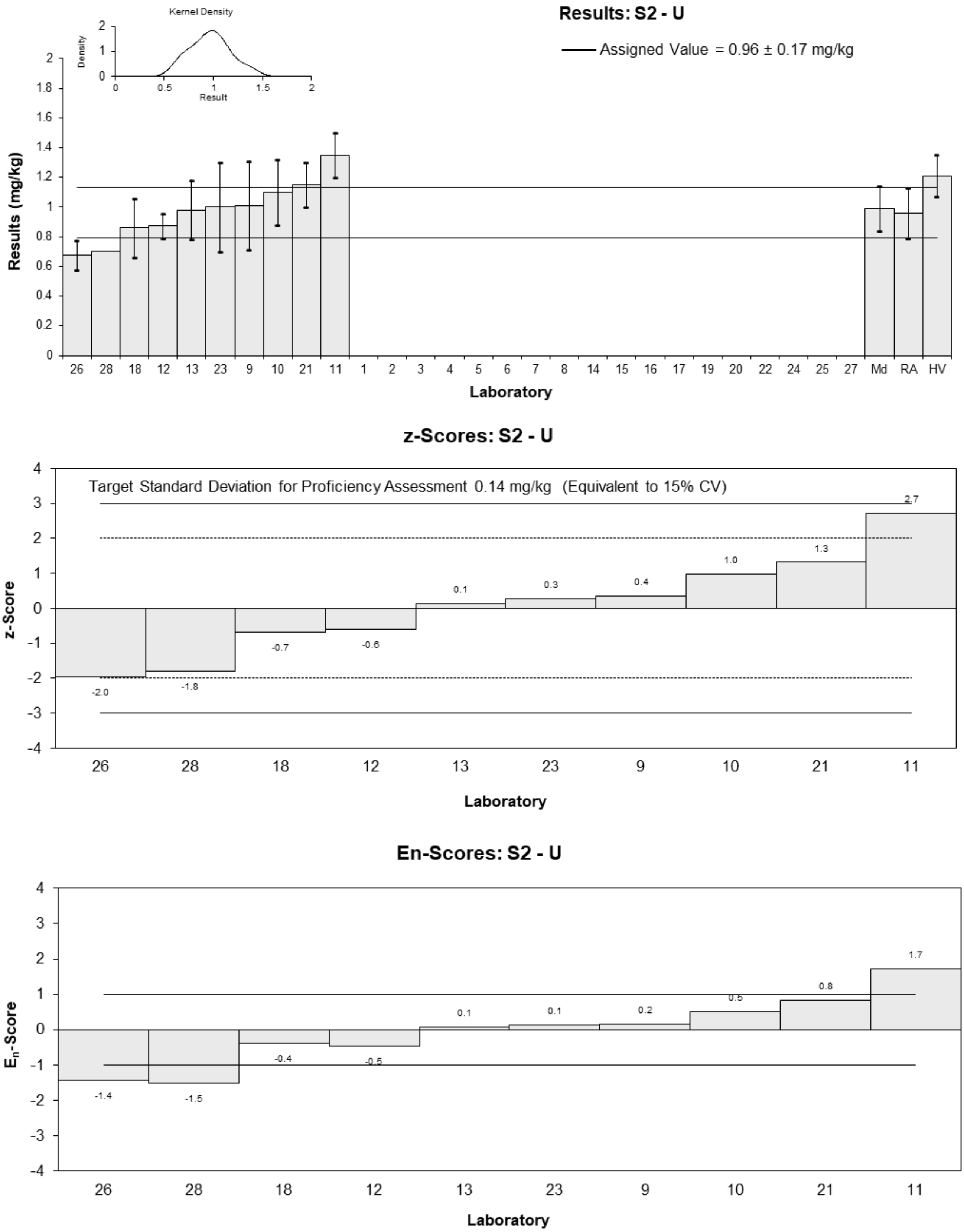
Sample No.	S2
Matrix	Soil
Analyte	U
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	<1	1		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	1.01	0.30	0.35	0.15
10	1.1	0.22	0.97	0.50
11	1.35	0.15	2.71	1.72
12	0.872	0.085	-0.61	-0.46
13	0.98	0.2	0.14	0.08
14	<1	NR		
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	0.86	0.2	-0.69	-0.38
19	NT	NT		
20	NT	NT		
21	1.15	0.15	1.32	0.84
22	NT	NT		
23	1	0.3	0.28	0.12
24	NT	NT		
25	NT	NT		
26	0.678	0.10	-1.96	-1.43
27	NT	NT		
28	0.7	NR	-1.81	-1.53

Statistics

Assigned Value	0.96	0.17
Spike Value	Not Spiked	
Homogeneity Value	1.21	0.14
Robust Average	0.96	0.17
Median	0.99	0.15
Mean	0.97	
N	10	
Max	1.35	
Min	0.678	
Robust SD	0.22	
Robust CV	23%	



Results: S2 - U
Assigned Value = 0.96 ± 0.17 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
26 28 18 12 13 23 9 10 21 11 1 2 3 4 5 6 7 8 14 15 16 17 19 20 22 24 25 27 Md RA HV
z-Scores: S2 - U
Target Standard Deviation for Proficiency Assessment 0.14 mg/kg (Equivalent to 15% CV)
z-Score
-2.0 -1.8 -0.7 -0.6 0.1 0.3 0.4 1.0 1.3 2.7
26 28 18 12 13 23 9 10 21 11
Laboratory
En-Scores: S2 - U
En-Score
-1.4 -1.5 -0.4 -0.5 0.1 0.1 0.2 0.5 0.8 1.7
26 28 18 12 13 23 9 10 21 11
Laboratory

Figure 32

Table 43

Sample Details

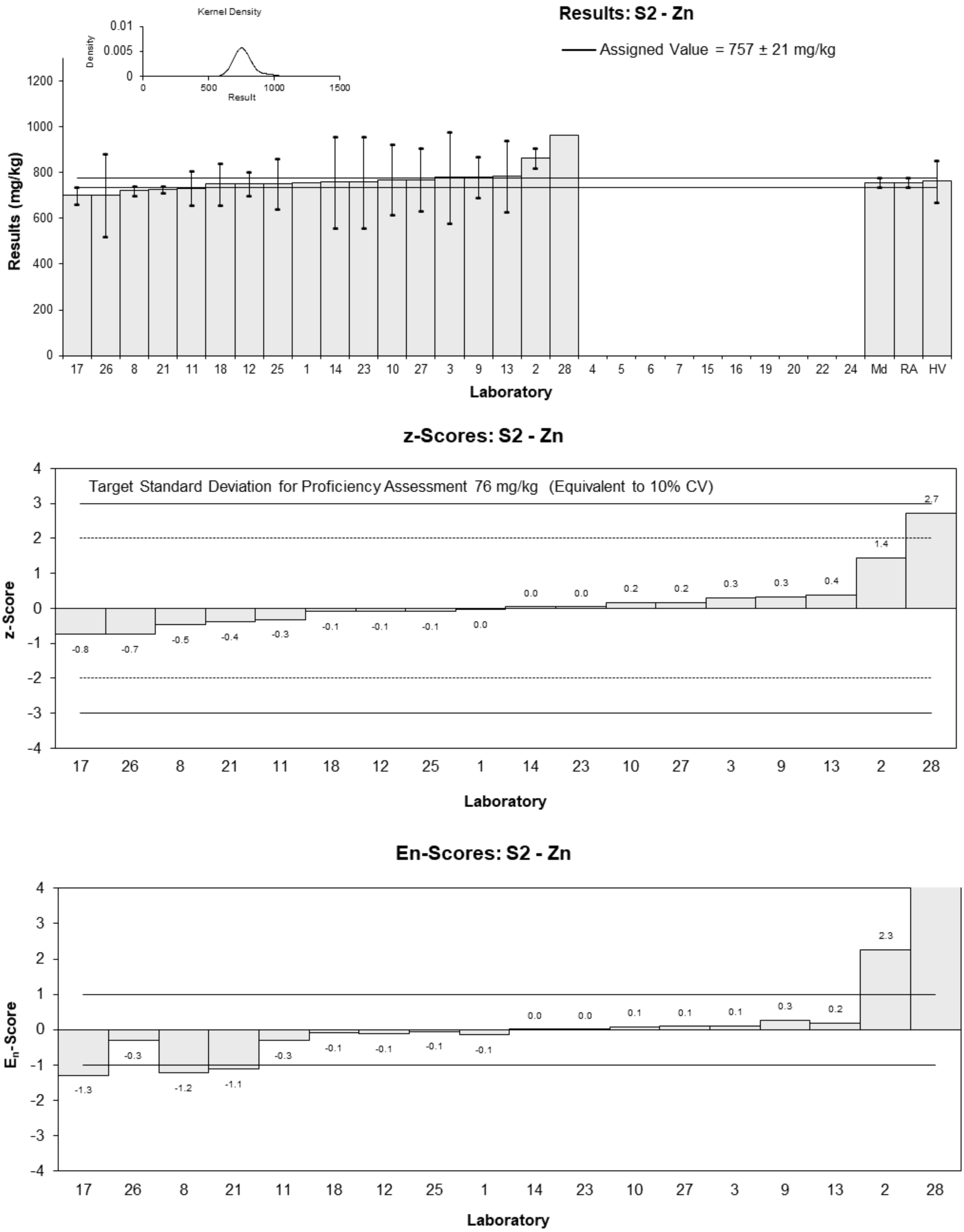
Sample No.	S2
Matrix	Soil
Analyte	Zn
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	754	NR	-0.04	-0.14
2	865	43	1.43	2.26
3	780	200	0.30	0.11
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	721	21	-0.48	-1.21
9	782	90	0.33	0.27
10	770	154	0.17	0.08
11	733	75	-0.32	-0.31
12	751	53	-0.08	-0.11
13	785	157	0.37	0.18
14	760	200	0.04	0.01
15	NT	NT		
16	NT	NT		
17	700	39	-0.75	-1.29
18	750	90	-0.09	-0.08
19	NT	NT		
20	NT	NT		
21	728	15	-0.38	-1.12
22	NT	NT		
23	760	200	0.04	0.01
24	NT	NT		
25	751	110	-0.08	-0.05
26	701	180	-0.74	-0.31
27	770	138.6	0.17	0.09
28	963	NR	2.72	9.81

Statistics

Assigned Value	757	21
Spike Value	Not Spiked	
Homogeneity Value	763	92
Robust Average	757	21
Median	757	21
Mean	768	
N	18	
Max	963	
Min	700	
Robust SD	35	
Robust CV	4.6%	



Results: S2 - Zn
Assigned Value = 757 ± 21 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
17 26 8 21 11 18 12 25 1 14 23 10 27 3 9 13 2 28 4 5 6 7 15 16 19 20 22 24 Md RA HV
z-Scores: S2 - Zn
Target Standard Deviation for Proficiency Assessment 76 mg/kg (Equivalent to 10% CV)
z-Score
-0.8 -0.7 -0.5 -0.4 -0.3 -0.1 -0.1 -0.1 0.0 0.0 0.0 0.2 0.2 0.3 0.3 0.4 1.4 2.7
17 26 8 21 11 18 12 25 1 14 23 10 27 3 9 13 2 28
Laboratory
En-Scores: S2 - Zn
E_n-Score
-1.3 -0.3 -1.2 -1.1 -0.3 -0.1 -0.1 -0.1 -0.1 0.0 0.0 0.1 0.1 0.1 0.3 0.2 2.3
17 26 8 21 11 18 12 25 1 14 23 10 27 3 9 13 2 28
Laboratory

Figure 33

Table 44

Sample Details

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

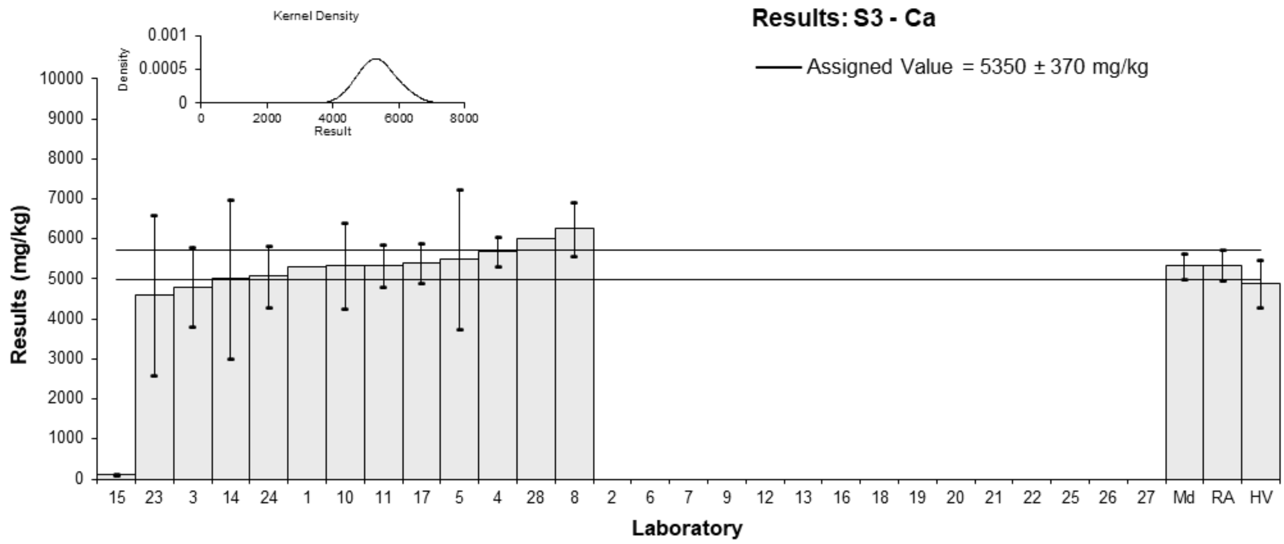
Participant Results

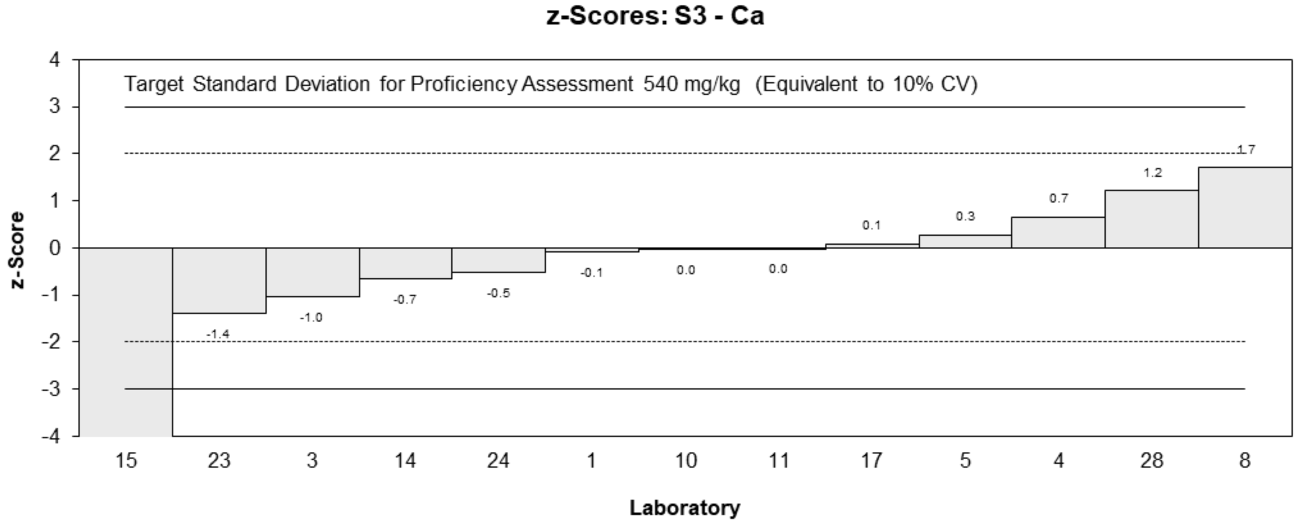
Lab. Code	Result	Uncertainty	z	E_n
1	5300	NR	-0.09	-0.14
2	NT	NT		
3	4800	1000	-1.03	-0.52
4	5700	365	0.65	0.67
5	5500	1738	0.28	0.08
6	NT	NT		
7	NT	NT		
8	6260	670	1.70	1.19
9	NT	NT		
10	5330	1066	-0.04	-0.02
11	5339	530	-0.02	-0.02
12	NT	NT		
13	NT	NT		
14	5000	2000	-0.65	-0.17
15**	110.98	4.68	-9.79	-14.16
16	NT	NT		
17	5400	500	0.09	0.08
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	4600	2000	-1.40	-0.37
24	5070	761	-0.52	-0.33
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	6000	NR	1.21	1.76

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	5350	370
Spike Value	Not Spiked	
Homogeneity Value	4890	590
Robust Average	5350	370
Median	5330	320
Mean	5360	
N	12	
Max	6260	
Min	4600	
Robust SD	510	
Robust CV	9.5%	


Results: S3 - Ca
Assigned Value = 5350 ± 370 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 23 3 14 24 1 10 11 17 5 4 28 8 2 6 7 9 12 13 16 18 19 20 21 22 25 26 27 Md RA HV


z-Scores: S3 - Ca
Target Standard Deviation for Proficiency Assessment 540 mg/kg (Equivalent to 10% CV)
z-Score
-1.4
-1.0
-0.7
-0.5
-0.1
0.0
0.0
0.1
0.3
0.7
1.2
1.7
15 23 3 14 24 1 10 11 17 5 4 28 8
Laboratory

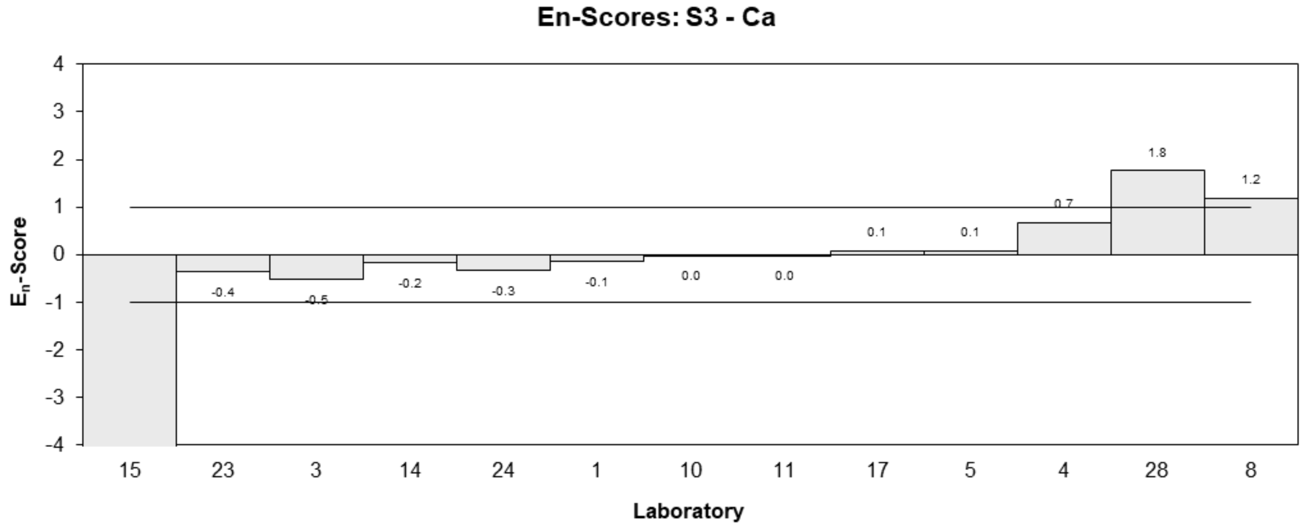

En-Scores: S3 - Ca
En-Score
-0.4
-0.5
-0.2
-0.3
-0.1
0.0
0.0
0.1
0.1
0.7
1.8
1.2
15 23 3 14 24 1 10 11 17 5 4 28 8
Laboratory

Figure 34

Table 45

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	24100	NR	0.76	1.00
2	24500	1225	0.94	1.00
3	22000	5000	-0.18	-0.08
4	23000	1640	0.27	0.25
5	17000	3315	-2.41	-1.45
6	NT	NT		
7	NT	NT		
8	25800	3900	1.52	0.80
9	NT	NT		
10	21000	4200	-0.62	-0.31
11	22882	2500	0.22	0.16
12	NT	NT		
13	NT	NT		
14	20500	6000	-0.85	-0.30
15	19512.49	23.56	-1.29	-1.70
16	NT	NT		
17	20700	1000	-0.76	-0.86
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	22000	6000	-0.18	-0.06
24	22400	3360	0.00	0.00
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	26800	NR	1.96	2.59

Statistics

Assigned Value	22400	1700
Spike Value	Not Spiked	
Homogeneity Value	21000	2500
Robust Average	22400	1700
Median	22200	1600
Mean	22300	
N	14	
Max	26800	
Min	17000	
Robust SD	2600	
Robust CV	11%	

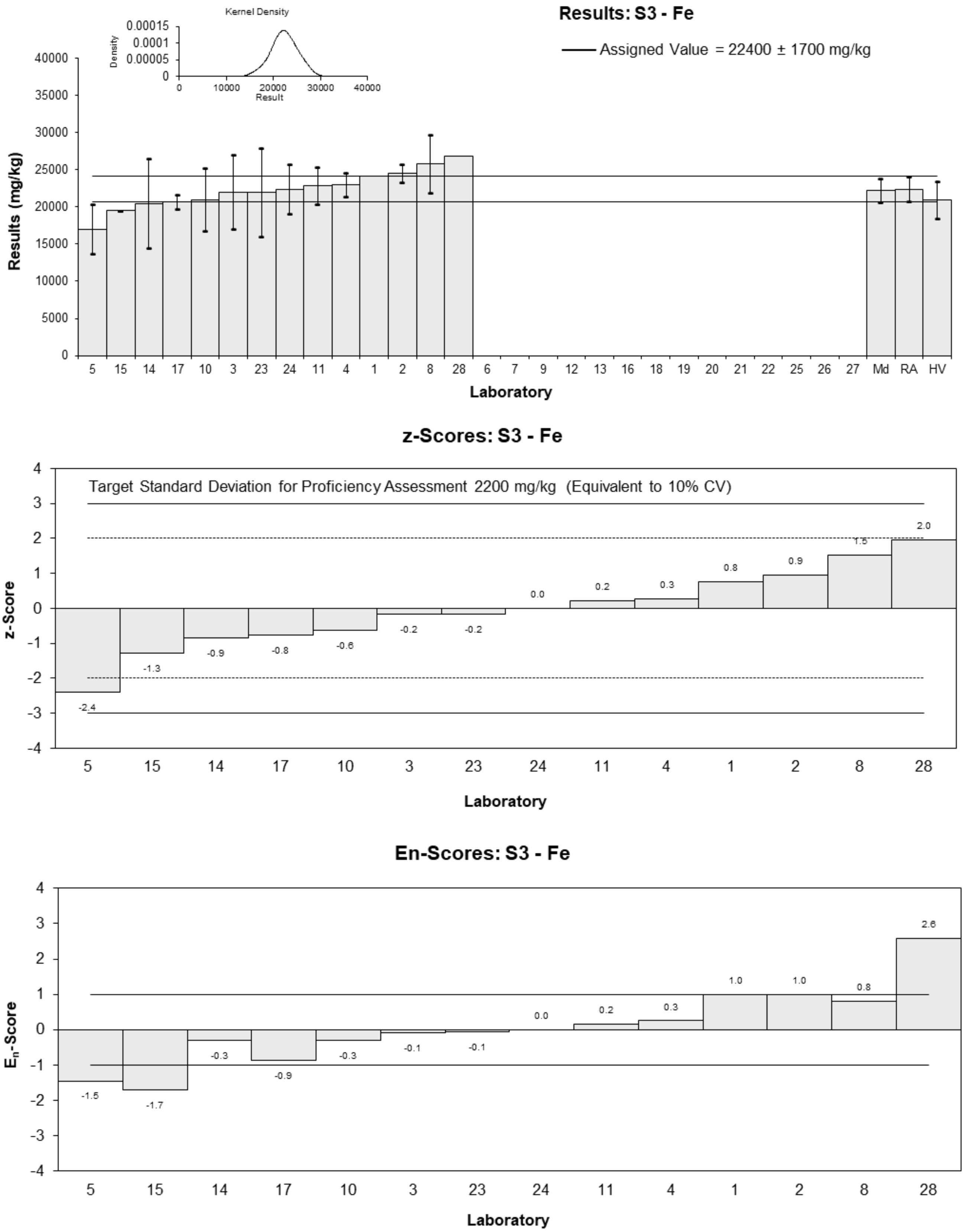

Results: S3 - Fe
Assigned Value = 22400 ± 1700 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S3 - Fe
Target Standard Deviation for Proficiency Assessment 2200 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - Fe
En-Score
Laboratory

Figure 35

Table 46

Sample Details

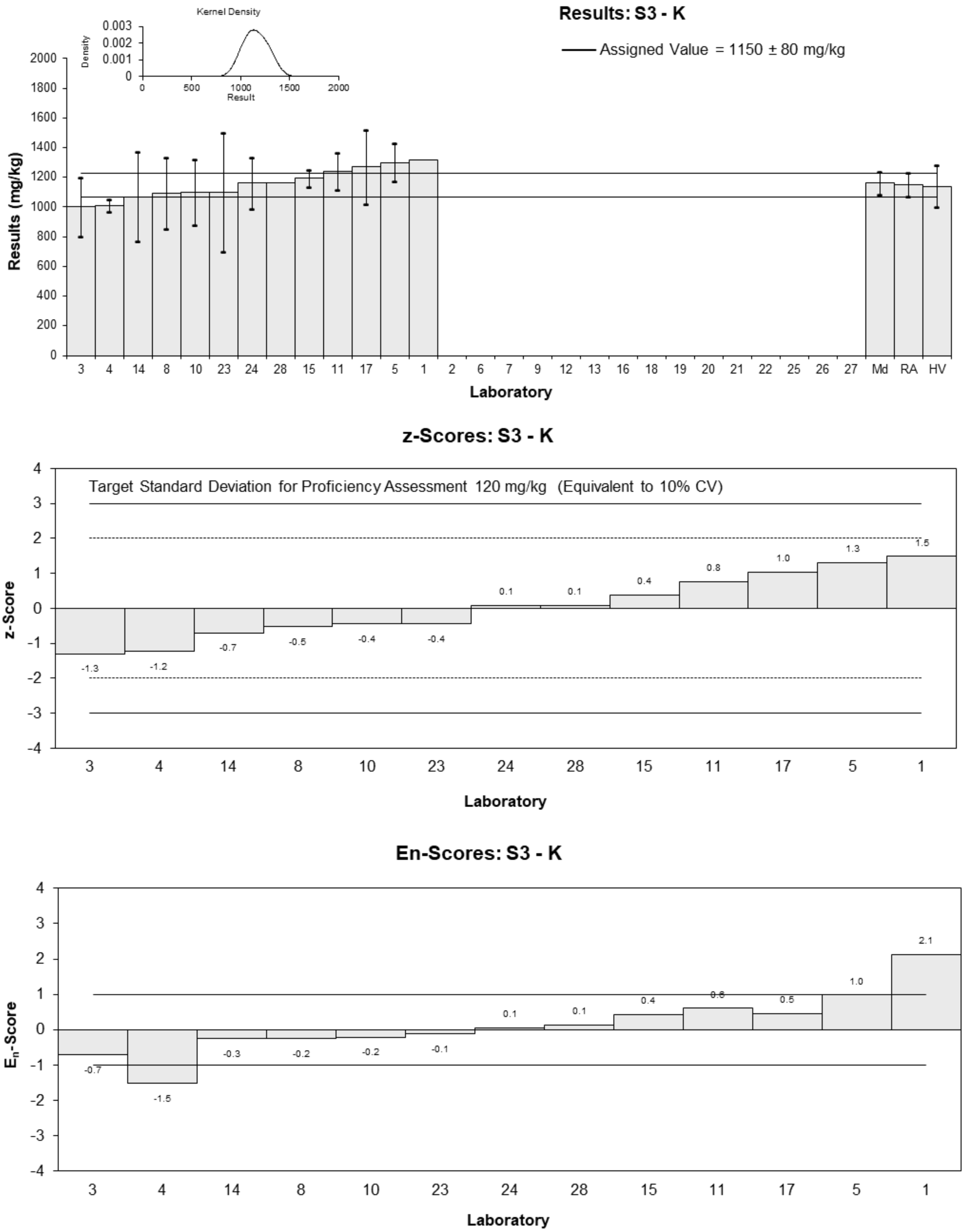
Sample No.	S3
Matrix	Soil
Analyte	K
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1320	NR	1.48	2.12
2	NT	NT		
3	1000	200	-1.30	-0.70
4	1010	44	-1.22	-1.53
5	1300	130	1.30	0.98
6	NT	NT		
7	NT	NT		
8	1090	240	-0.52	-0.24
9	NT	NT		
10	1100	220	-0.43	-0.21
11	1239	125	0.77	0.60
12	NT	NT		
13	NT	NT		
14	1070	300	-0.70	-0.26
15	1192.55	58.62	0.37	0.43
16	NT	NT		
17	1270	250	1.04	0.46
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	1100	400	-0.43	-0.12
24	1160	174	0.09	0.05
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	1160	NR	0.09	0.12

Statistics

Assigned Value	1150	80
Spike Value	Not Spiked	
Homogeneity Value	1140	140
Robust Average	1150	80
Median	1160	80
Mean	1150	
N	13	
Max	1320	
Min	1000	
Robust SD	120	
Robust CV	10%	



Results: S3 - K
Assigned Value = 1150 ± 80 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S3 - K
Target Standard Deviation for Proficiency Assessment 120 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - K
E_n-Score
Laboratory

Figure 36

Table 47

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1320	NR	1.58	2.00
2	NT	NT		
3	1000	200	-1.23	-0.64
4	1090	70	-0.44	-0.44
5	1300	408.2	1.40	0.38
6	NT	NT		
7	NT	NT		
8	1140	200	0.00	0.00
9	NT	NT		
10	1130	226	-0.09	-0.04
11	1167	115	0.24	0.18
12	NT	NT		
13	NT	NT		
14	1100	300	-0.35	-0.13
15	828.15	20.61	-2.74	-3.38
16	NT	NT		
17	1120	340	-0.18	-0.06
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	1100	400	-0.35	-0.10
24	1120	168	-0.18	-0.10
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	1340	NR	1.75	2.22

Statistics

Assigned Value	1140	90
Spike Value	Not Spiked	
Homogeneity Value	1150	140
Robust Average	1140	90
Median	1120	30
Mean	1140	
N	13	
Max	1340	
Min	828.15	
Robust SD	130	
Robust CV	12%	

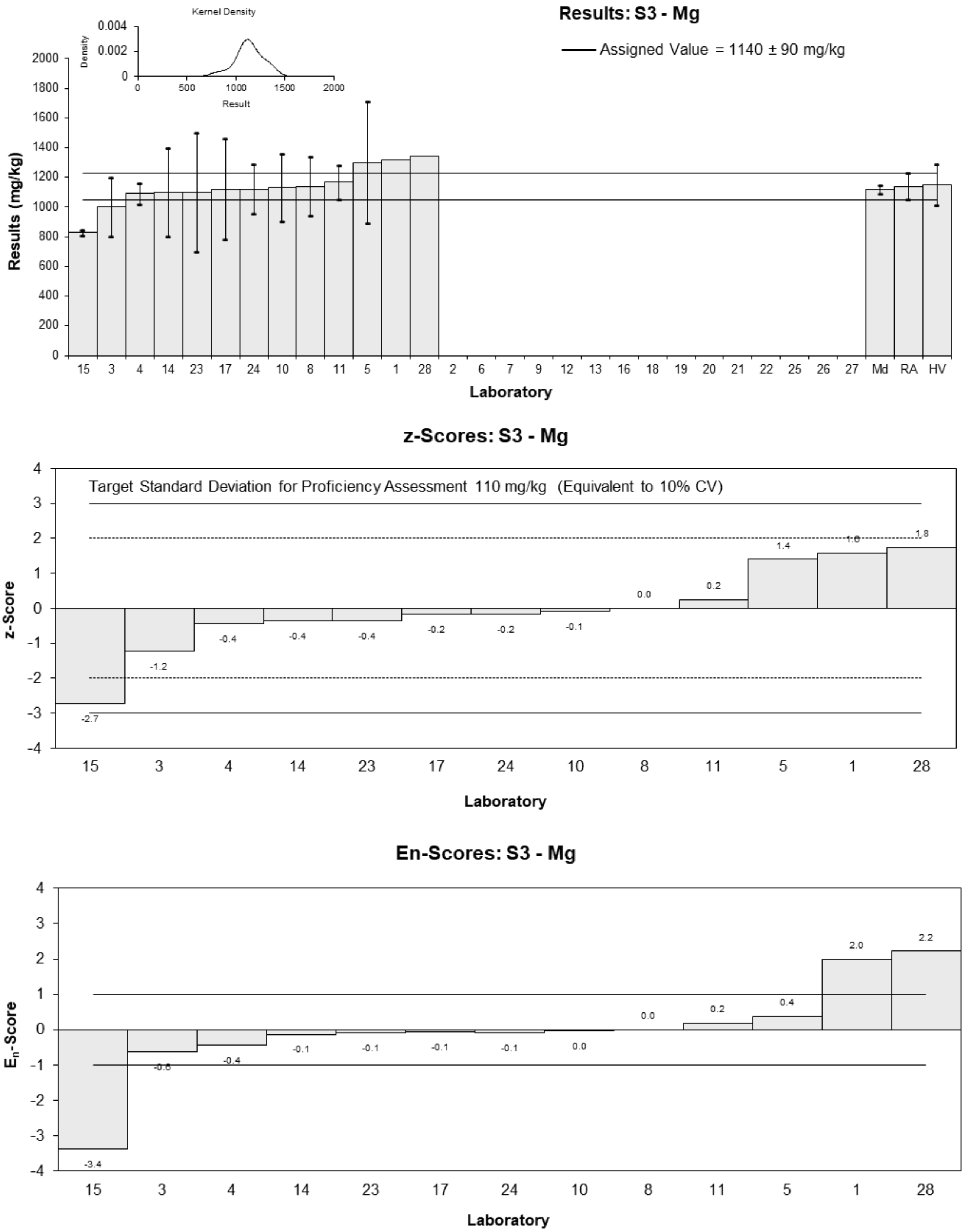

Results: S3 - Mg
Assigned Value = 1140 ± 90 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 3 4 14 23 17 24 10 8 11 5 1 28 2 6 7 9 12 13 16 18 19 20 21 22 25 26 27 Md RA HV
z-Scores: S3 - Mg
Target Standard Deviation for Proficiency Assessment 110 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
15 3 4 14 23 17 24 10 8 11 5 1 28
En-Scores: S3 - Mg
E_n-Score
Laboratory
15 3 4 14 23 17 24 10 8 11 5 1 28

Figure 37

Table 48

Sample Details

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

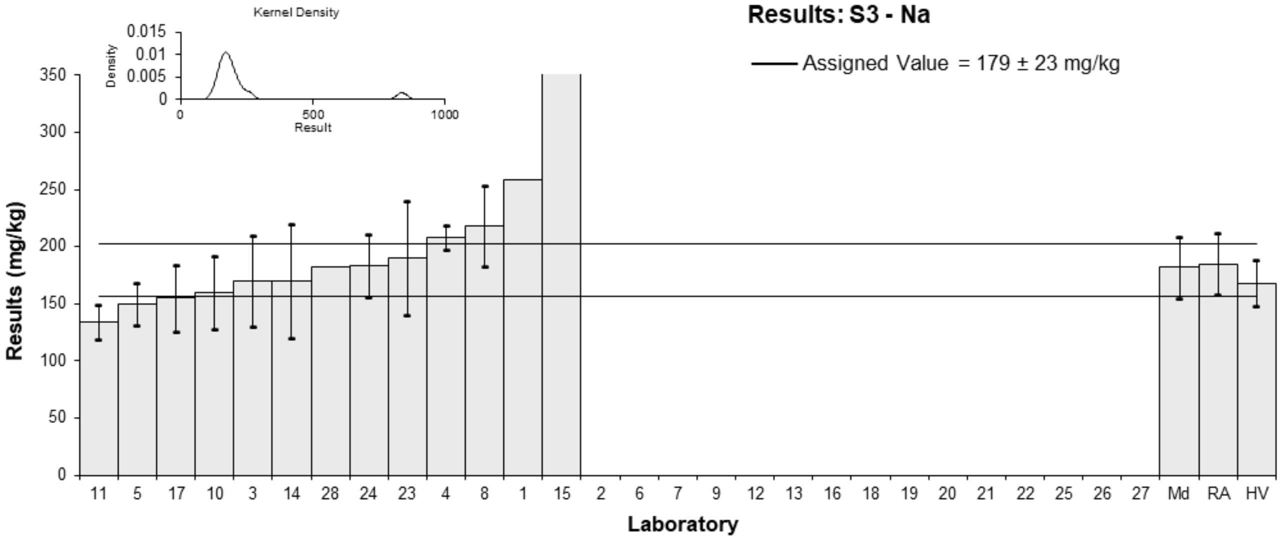
Participant Results

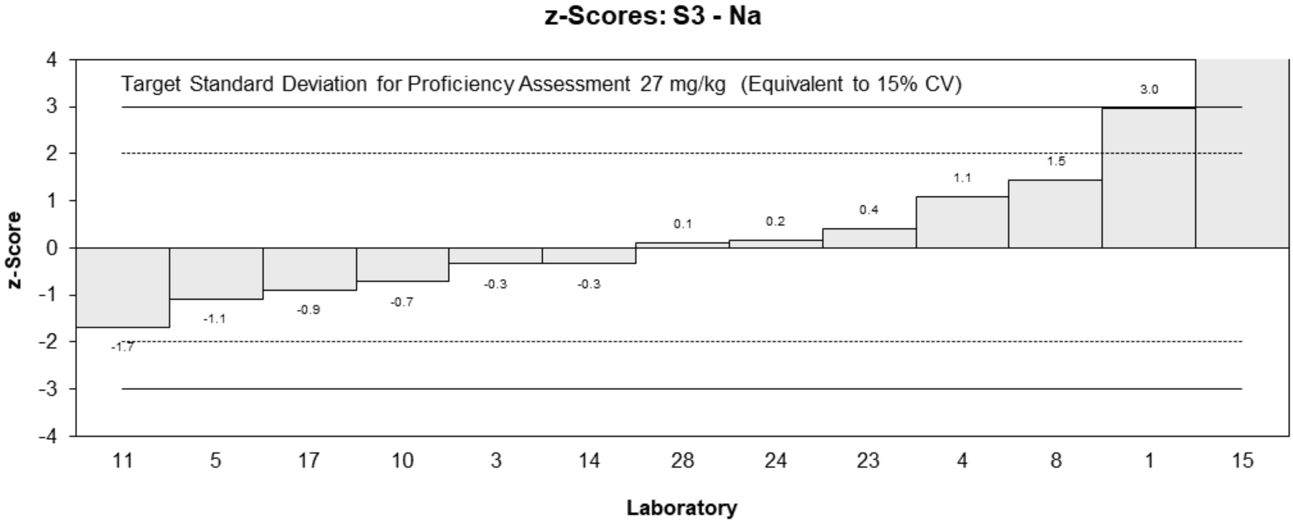
Lab. Code	Result	Uncertainty	z	E_n
1	258.5	NR	2.96	3.46
2	NT	NT		
3	170	40	-0.34	-0.20
4	208	11	1.08	1.14
5	150	18.3	-1.08	-0.99
6	NT	NT		
7	NT	NT		
8	218	35	1.45	0.93
9	NT	NT		
10	160	32	-0.71	-0.48
11	134	15	-1.68	-1.64
12	NT	NT		
13	NT	NT		
14	170	50	-0.34	-0.16
15*	838.81	94.21	24.57	6.80
16	NT	NT		
17	155	29	-0.89	-0.65
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	190	50	0.41	0.20
24	183	27.5	0.15	0.11
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	182	NR	0.11	0.13

* Outlier, see Section 4.2

Statistics

Assigned Value	179	23
Spike Value	Not Spiked	
Homogeneity Value	168	20
Robust Average	185	27
Median	182	27
Mean	230	
N	13	
Max	838.81	
Min	134	
Robust SD	39	
Robust CV	21%	


Results: S3 - Na
Assigned Value = 179 ± 23 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 5 17 10 3 14 28 24 23 4 8 1 15 2 6 7 9 12 13 16 18 19 20 21 22 25 26 27 Md RA HV


z-Scores: S3 - Na
Target Standard Deviation for Proficiency Assessment 27 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-1.7 -1.1 -0.9 -0.7 -0.3 -0.3 0.1 0.2 0.4 1.1 1.5 3.0
11 5 17 10 3 14 28 24 23 4 8 1 15

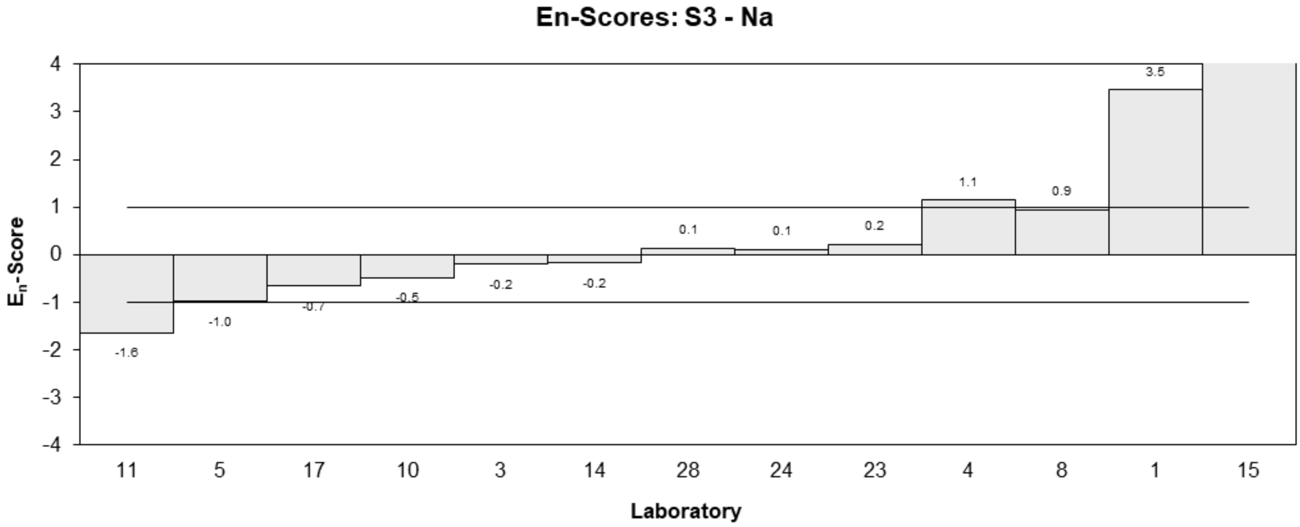

En-Scores: S3 - Na
E_n-Score
Laboratory
-1.6 -1.0 -0.7 -0.5 -0.2 -0.2 0.1 0.1 0.2 1.1 0.9 3.5
11 5 17 10 3 14 28 24 23 4 8 1 15

Figure 38

Table 49

Sample Details

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

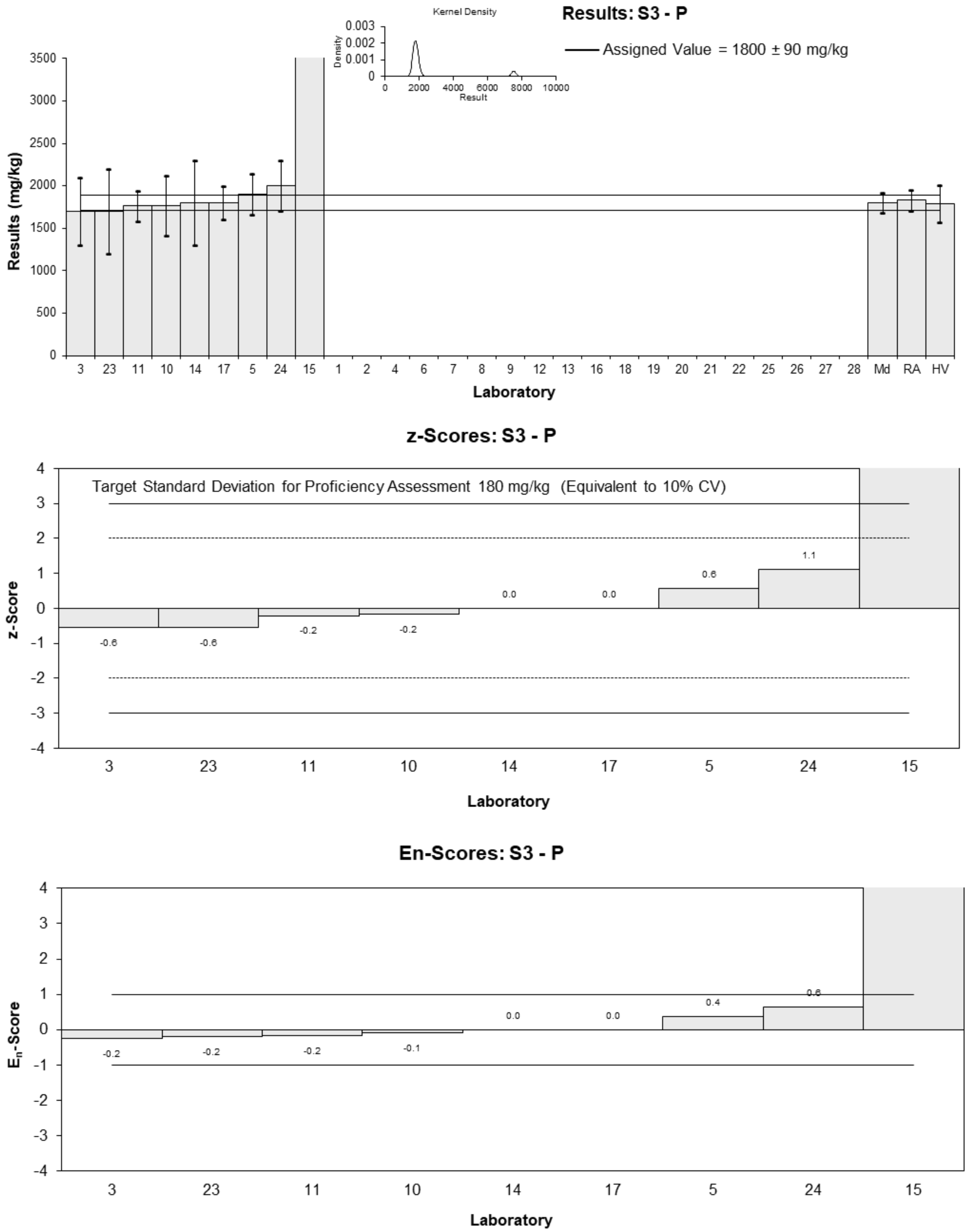
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	1700	400	-0.56	-0.24
4	NR	NR		
5	1900	245	0.56	0.38
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	1770	354	-0.17	-0.08
11	1763	180	-0.21	-0.18
12	NT	NT		
13	NT	NT		
14	1800	500	0.00	0.00
15*	7545.71	809.40	31.92	7.06
16	NT	NT		
17	1800	200	0.00	0.00
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	1700	500	-0.56	-0.20
24	2000	300	1.11	0.64
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	1800	90
Spike Value	Not Spiked	
Homogeneity Value	1790	220
Robust Average	1830	120
Median	1800	120
Mean	2400	
N	9	
Max	7545.71	
Min	1700	
Robust SD	140	
Robust CV	7.6%	



Results: S3 - P
Assigned Value = 1800 ± 90 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
z-Scores: S3 - P
Target Standard Deviation for Proficiency Assessment 180 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
En-Scores: S3 - P
E_n-Score
Laboratory

Figure 39

Table 50

Sample Details

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

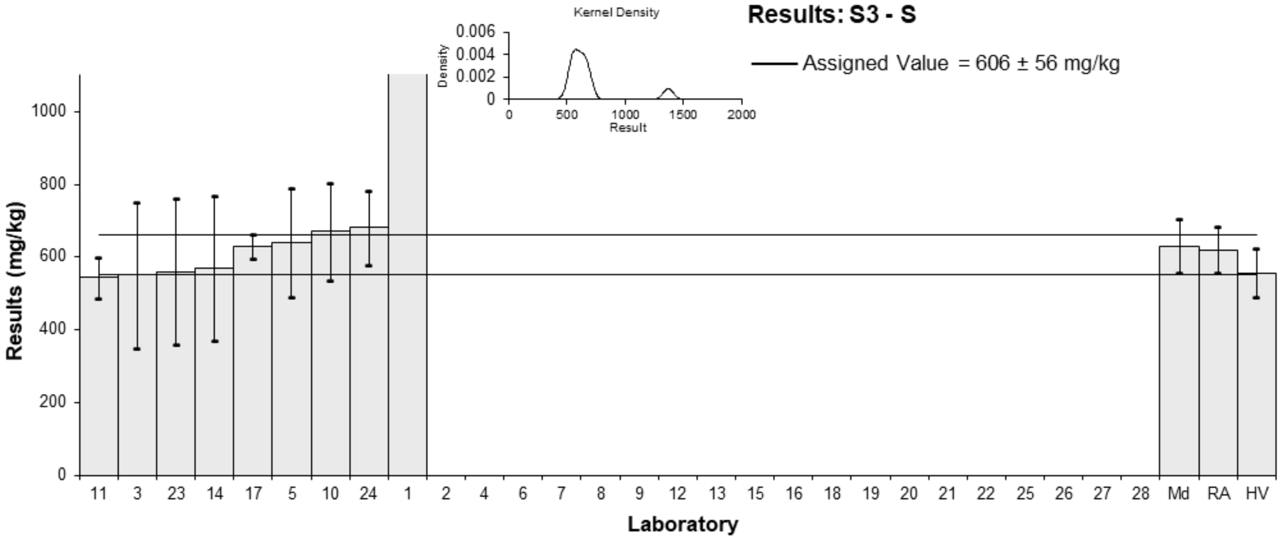
Participant Results

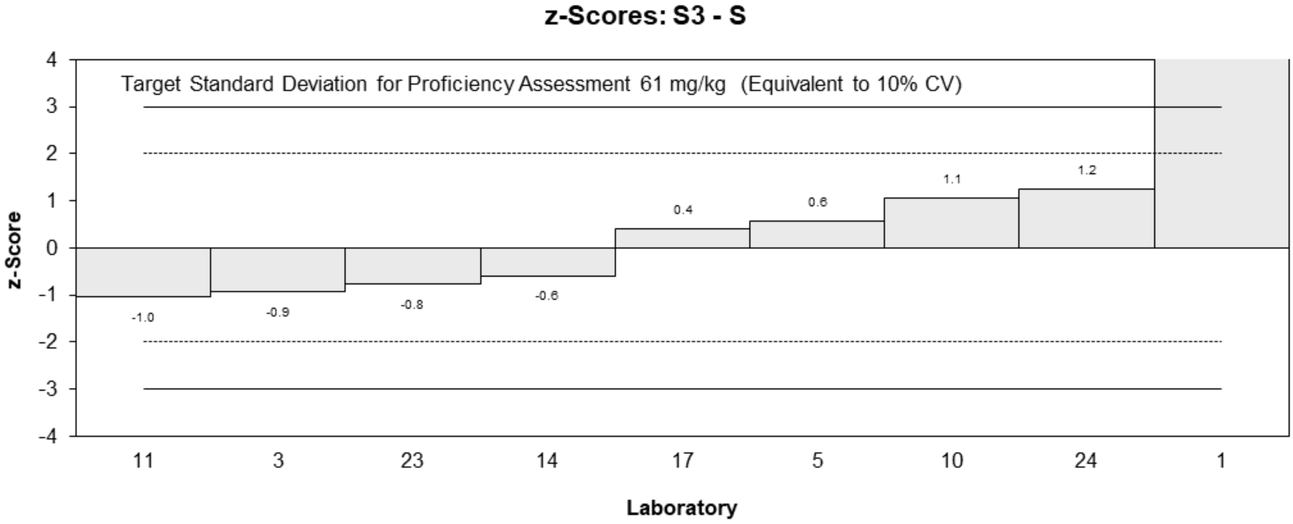
Lab. Code	Result	Uncertainty	z	E_n
1*	1370	NR	12.61	13.64
2	NT	NT		
3	550	200	-0.92	-0.27
4	NR	NR		
5	640	149.76	0.56	0.21
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	670	134	1.06	0.44
11	543	55	-1.04	-0.80
12	NT	NT		
13	NT	NT		
14	570	200	-0.59	-0.17
15	NT	NT		
16	NT	NT		
17	630	33	0.40	0.37
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	560	200	-0.76	-0.22
24	681	102	1.24	0.64
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	606	56
Spike Value	Not Spiked	
Homogeneity Value	556	67
Robust Average	620	64
Median	630	74
Mean	690	
N	9	
Max	1370	
Min	543	
Robust SD	77	
Robust CV	12%	


Kernel Density
Density
Result
Results: S3 - S
Assigned Value = 606 ± 56 mg/kg
Results (mg/kg)
Laboratory
11 3 23 14 17 5 10 24 1 2 4 6 7 8 9 12 13 15 16 18 19 20 21 22 25 26 27 28 Md RA HV


z-Scores: S3 - S
Target Standard Deviation for Proficiency Assessment 61 mg/kg (Equivalent to 10% CV)
z-Score
-1.0
-0.9
-0.8
-0.6
0.4
0.6
1.1
1.2
Laboratory
11 3 23 14 17 5 10 24 1

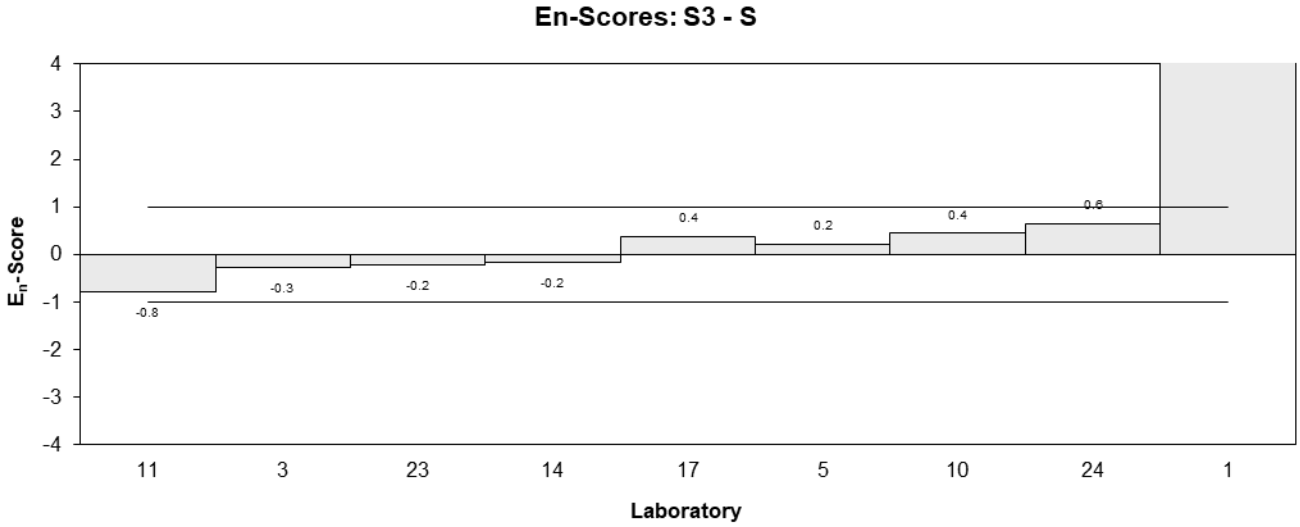

En-Scores: S3 - S
En-Score
-0.8
-0.3
-0.2
-0.2
0.4
0.2
0.4
0.6
Laboratory
11 3 23 14 17 5 10 24 1

Figure 40

Table 51

Sample Details

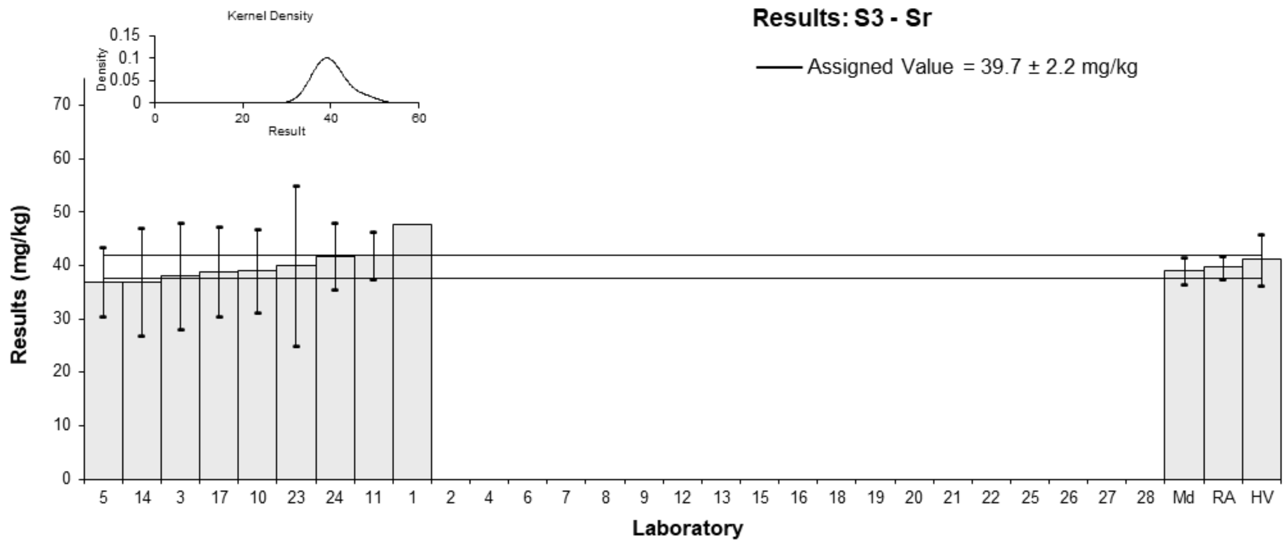
Sample No.	S3
Matrix	Soil
Analyte	Sr
Unit	mg/kg

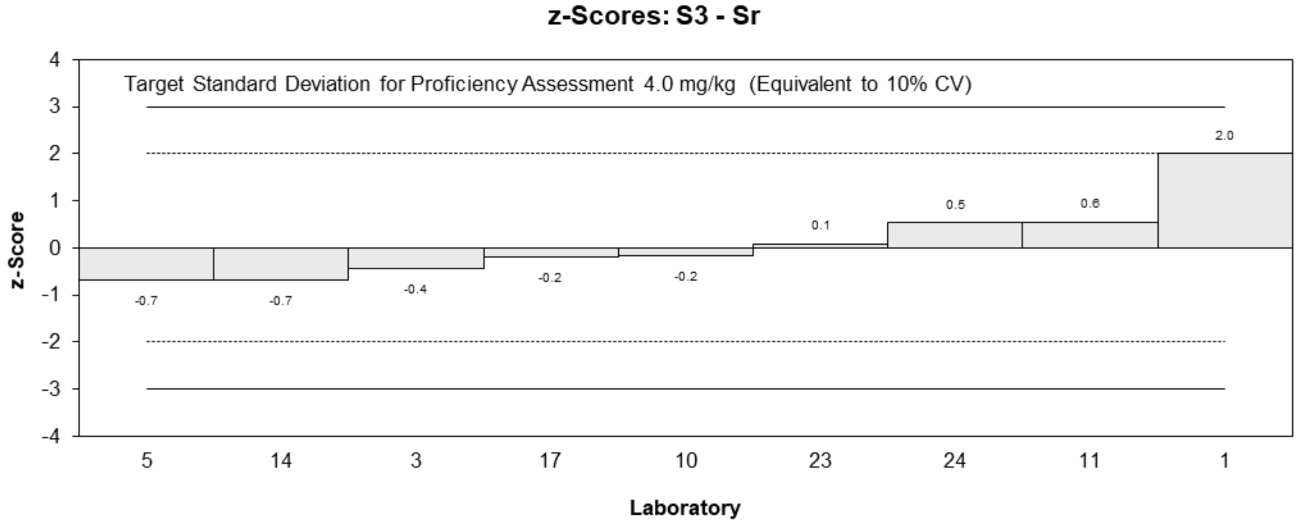
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	47.65	NR	2.00	3.61
2	NT	NT		
3	38	10	-0.43	-0.17
4	NR	NR		
5	37	6.401	-0.68	-0.40
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	39	7.8	-0.18	-0.09
11	41.9	4.5	0.55	0.44
12	NT	NT		
13	NT	NT		
14	37	10	-0.68	-0.26
15	NT	NT		
16	NT	NT		
17	38.9	8.4	-0.20	-0.09
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	40	15	0.08	0.02
24	41.8	6.27	0.53	0.32
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	NT	NT		

Statistics

Assigned Value	39.7	2.2
Spike Value	Not Spiked	
Homogeneity Value	41.1	4.9
Robust Average	39.7	2.2
Median	39.0	2.5
Mean	40.1	
N	9	
Max	47.65	
Min	37	
Robust SD	2.6	
Robust CV	6.7%	


Results: S3 - Sr
Assigned Value = 39.7 ± 2.2 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5 14 3 17 10 23 24 11 1 2 4 6 7 8 9 12 13 15 16 18 19 20 21 22 25 26 27 28 Md RA HV


z-Scores: S3 - Sr
Target Standard Deviation for Proficiency Assessment 4.0 mg/kg (Equivalent to 10% CV)
z-Score
-0.7 -0.7 -0.4 -0.2 -0.2 0.1 0.5 0.6 2.0
5 14 3 17 10 23 24 11 1
Laboratory

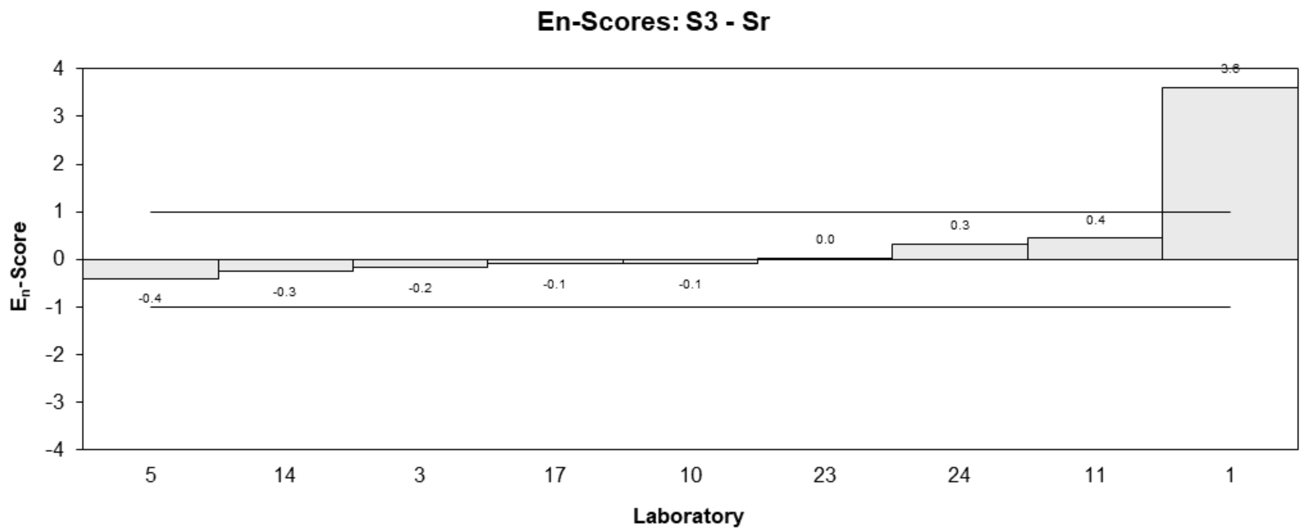

En-Scores: S3 - Sr
En-Score
-0.4 -0.3 -0.2 -0.1 -0.1 0.0 0.3 0.4 3.6
5 14 3 17 10 23 24 11 1
Laboratory

Figure 41

Table 52

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Bromide
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	NT	NT
2	NT	NT
3	1.5	0.5
4	NR	NR
5	NR	NR
6	NT	NT
7	NT	NT
8	NT	NT
9	NT	NT
10	1.2	0.24
11	NT	NT
12	NT	NT
13	NT	NT
14	1.1	1
15**	24.25	0.53
16	NT	NT
17	NT	NT
18	NT	NT
19	NT	NT
20	NT	NT
21	NT	NT
22	NR	NR
23	1.1	0.5
24	NT	NT
25	NT	NT
26	NT	NT
27	NT	NT
28	2.2	NR

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Homogeneity Value	1.10	0.22
Median	1.20	0.17
Mean	1.42	
N	5	
Max	2.2	
Min	1.1	

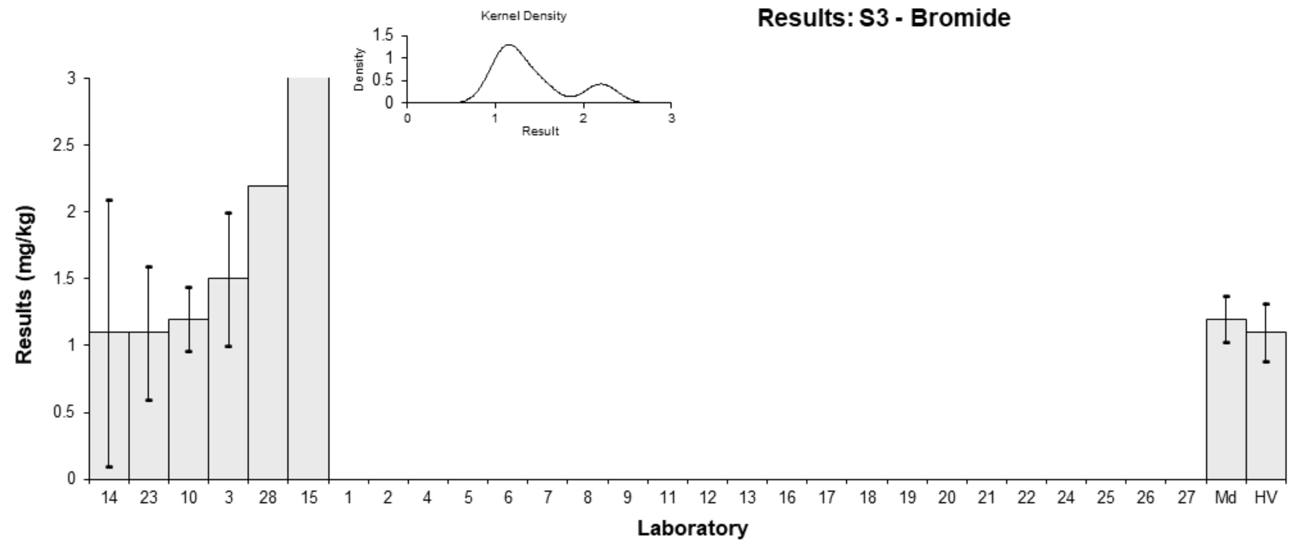

Results: S3 - Bromide
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 23 10 3 28 15 1 2 4 5 6 7 8 9 11 12 13 16 17 18 19 20 21 22 24 25 26 27 Md HV

Figure 42

Table 53

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	19	5	0.70	0.33
4	NR	NR		
5*	35	7	6.90	2.42
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	15	3	-0.85	-0.58
11	17	2.0	-0.08	-0.07
12	NT	NT		
13	NT	NT		
14	19	10	0.70	0.18
15	28.33	0.39	4.31	4.77
16	NT	NT		
17	14.3	1.4	-1.12	-1.08
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	16	6	-0.47	-0.19
24	<20	NR		
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	16	NR	-0.47	-0.52

* Outlier, see Section 4.2

Statistics

Assigned Value	17.2	2.3
Spike Value	Not Spiked	
Homogeneity Value	14.4	2.9
Robust Average	19.2	5.1
Median	17.0	2.5
Mean	20.0	
N	9	
Max	35	
Min	14.3	
Robust SD	6.2	
Robust CV	32%	

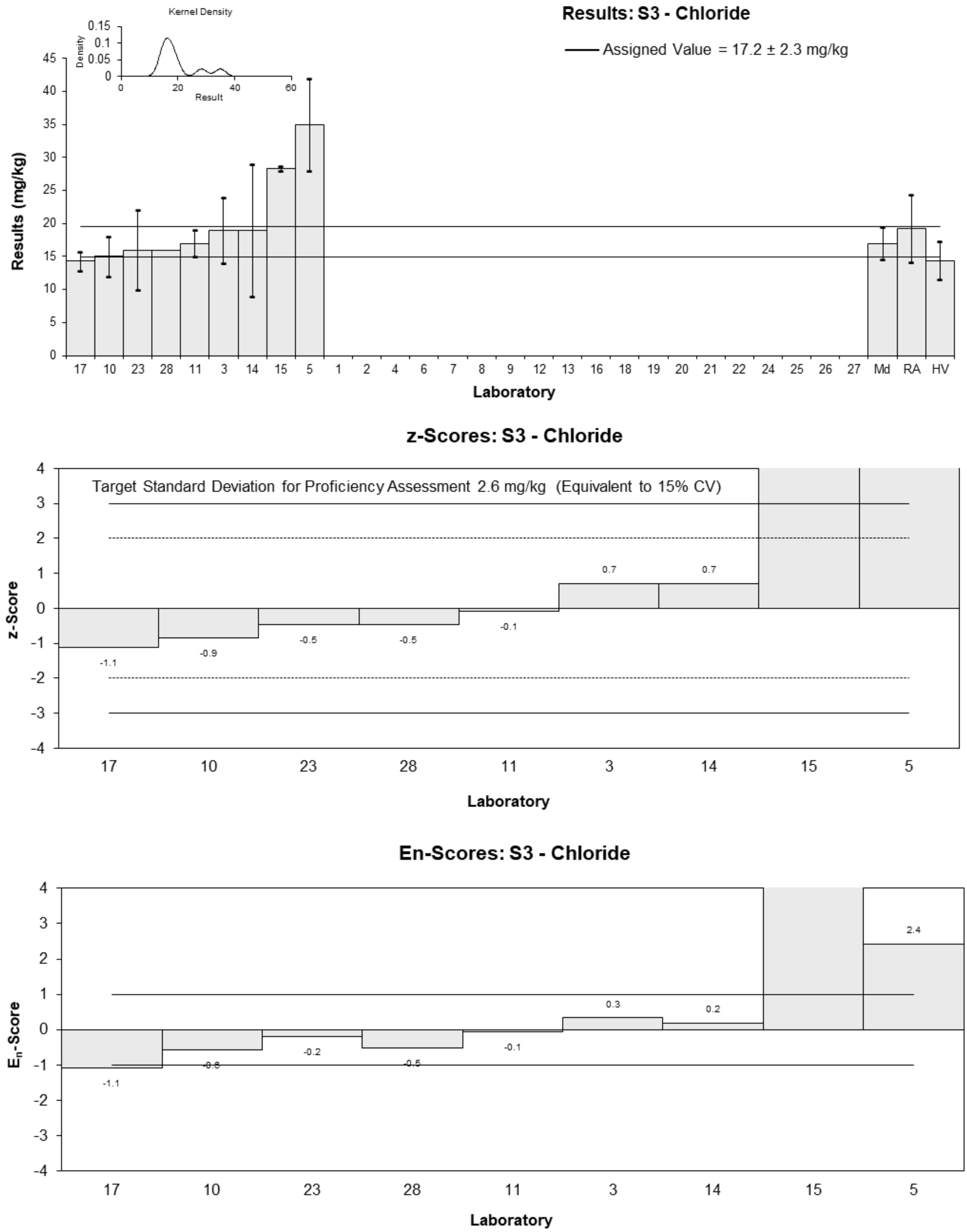

Results: S3 - Chloride
Assigned Value = 17.2 ± 2.3 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
17 10 23 28 11 3 14 15 5 1 2 4 6 7 8 9 12 13 16 18 19 20 21 22 24 25 26 27 Md RA HV
z-Scores: S3 - Chloride
Target Standard Deviation for Proficiency Assessment 2.6 mg/kg (Equivalent to 15% CV)
z-Score
-1.1
-0.9
-0.5
-0.5
-0.1
0.7
0.7
Laboratory
17 10 23 28 11 3 14 15 5
En-Scores: S3 - Chloride
E_n-Score
-1.1
-0.6
-0.2
-0.5
-0.1
0.3
0.2
2.4
Laboratory
17 10 23 28 11 3 14 15 5

Figure 43

Table 54

Sample Details

Sample No.	S3
Matrix	Soil
Analyte	Fluoride
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	NT	NT
2	NT	NT
3	1.0	0.5
4	NR	NR
5**	180	40.32
6	1.6	1
7	NT	NT
8	NT	NT
9	NT	NT
10	1.5	0.3
11	NT	NT
12	NT	NT
13	NT	NT
14	1.3	1
15	8.9	0.28
16	NT	NT
17	NT	NT
18	NT	NT
19	NT	NT
20	NT	NT
21	NT	NT
22	NR	NR
23	1.1	0.5
24	<1	NR
25	NT	NT
26	NT	NT
27	NT	NT
28	NR	NR

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Homogeneity Value	1.50	0.30
Robust Average	1.44	0.48
Median	1.40	0.38
Mean	2.6	
N	6	
Max	8.9	
Min	1	
Robust SD	0.47	
Robust CV	32%	

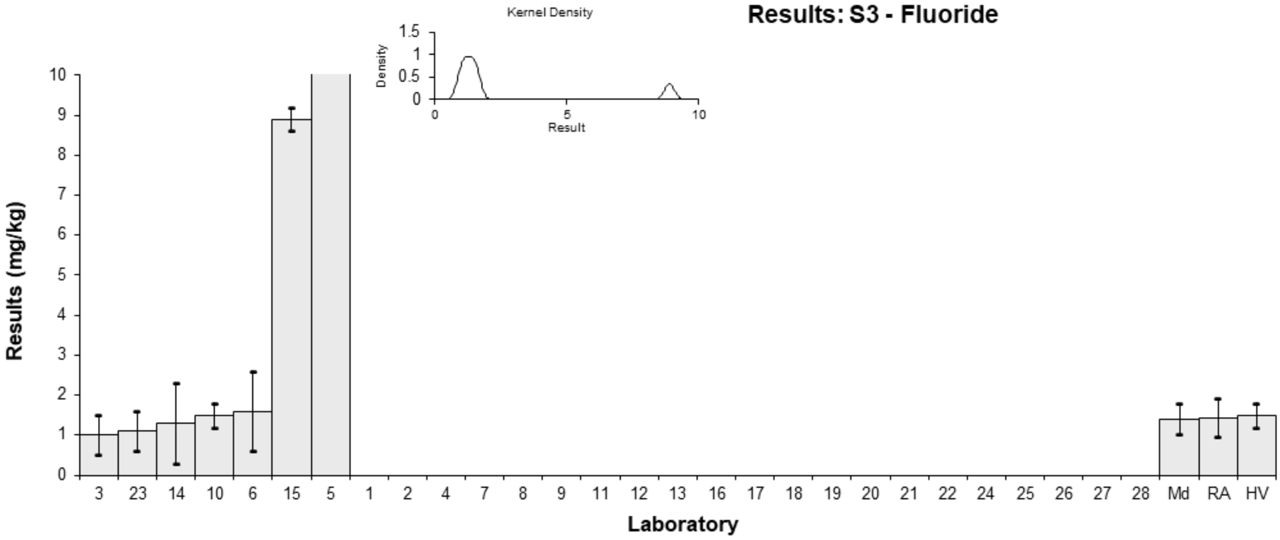

Results: S3 - Fluoride
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
3
23
14
10
6
15
5
1
2
4
7
8
9
11
12
13
16
17
18
19
20
21
22
24
25
26
27
28
Md
RA
HV

Figure 44

Table 55

Sample Details

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

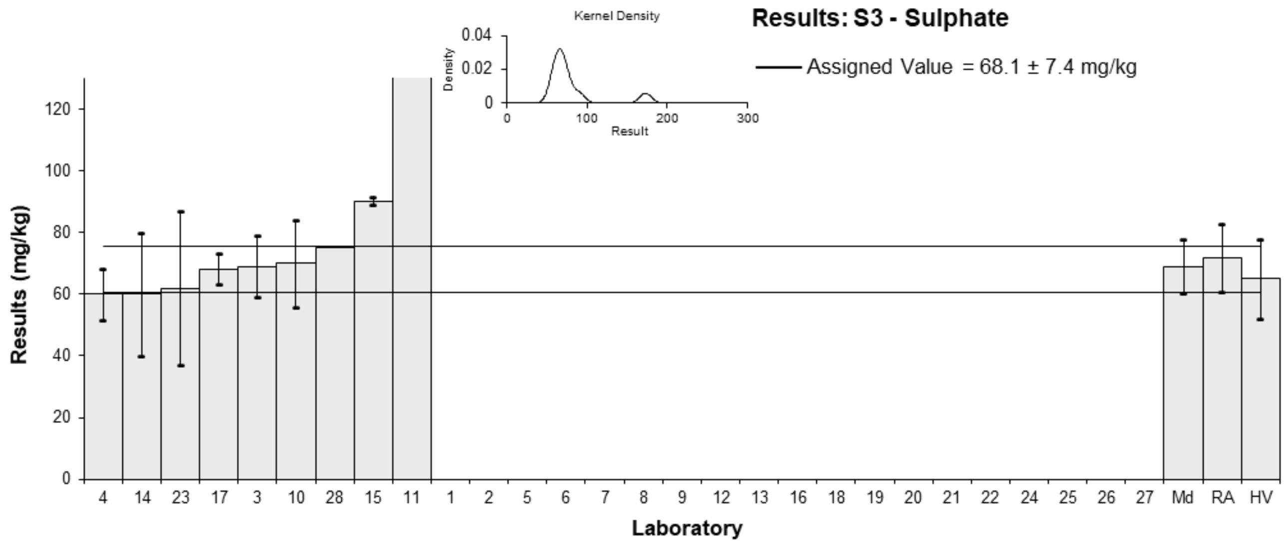
Participant Results

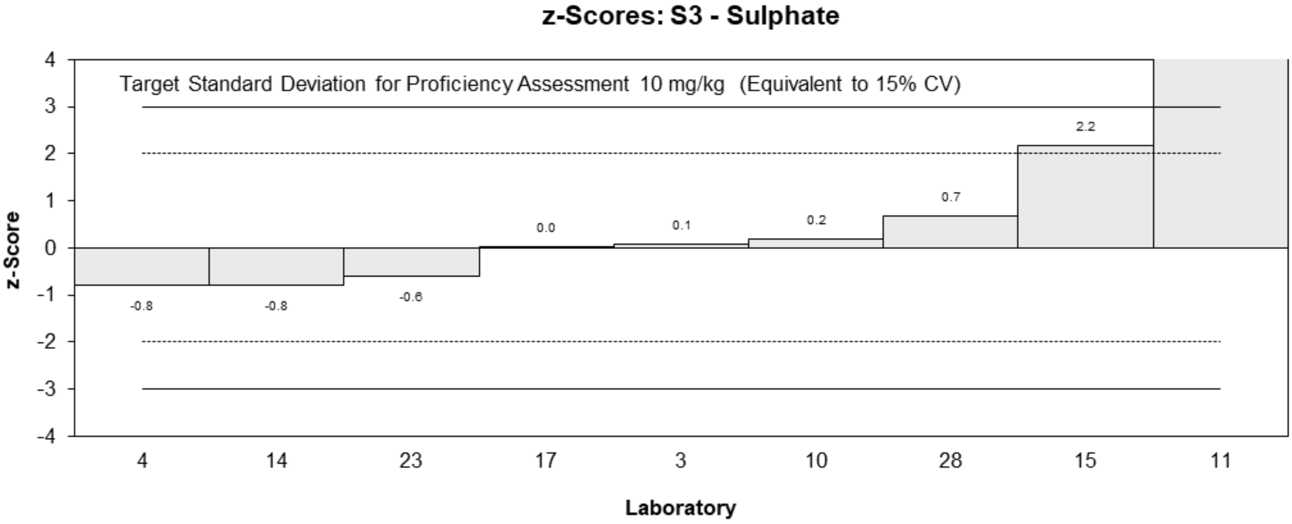
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	69	10	0.09	0.07
4	60	8.5	-0.79	-0.72
5	<100	NR		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	70	14	0.19	0.12
11*	173	20	10.27	4.92
12	NT	NT		
13	NT	NT		
14	60	20	-0.79	-0.38
15	90.35	1.30	2.18	2.96
16	NT	NT		
17	68.3	5.1	0.02	0.02
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	62	25	-0.60	-0.23
24	<20	NR		
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	75	NR	0.68	0.93

* Outlier, see Section 4.2

Statistics

Assigned Value	68.1	7.4
Spike Value	Not Spiked	
Homogeneity Value	65	13
Robust Average	72	11
Median	69.0	8.7
Mean	81	
N	9	
Max	173	
Min	60	
Robust SD	14	
Robust CV	19%	


Results: S3 - Sulphate
Assigned Value = 68.1 ± 7.4 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4 14 23 17 3 10 28 15 11 1 2 5 6 7 8 9 12 13 16 18 19 20 21 22 24 25 26 27 Md RA HV


z-Scores: S3 - Sulphate
Target Standard Deviation for Proficiency Assessment 10 mg/kg (Equivalent to 15% CV)
z-Score
-0.8
-0.8
-0.6
0.0
0.1
0.2
0.7
2.2
4 14 23 17 3 10 28 15 11
Laboratory

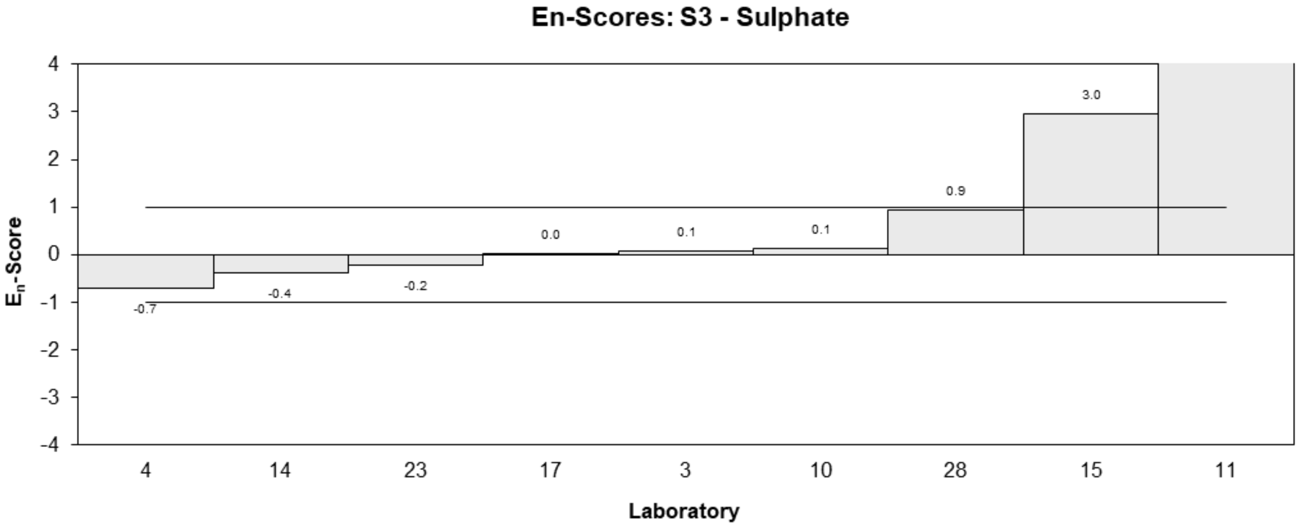

En-Scores: S3 - Sulphate
En-Score
-0.7
-0.4
-0.2
0.0
0.1
0.1
0.9
3.0
4 14 23 17 3 10 28 15 11
Laboratory

Figure 45

Table 56

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	10	2	0.00	0.00
4	NR	NR		
5	6.6	1.32	-2.27	-1.64
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	11	2.2	0.67	0.37
11	10.9	1.5	0.60	0.41
12	NT	NT		
13	NT	NT		
14	9.3	3	-0.47	-0.21
15	13.0	0.14	2.00	1.87
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	10	4	0.00	0.00
24	9.05	1.36	-0.63	-0.45
25	NT	NT		
26	NT	NT		
27	NT	NT		
28*	40	NR	20.00	18.75

* Outlier, see Section 4.2

Statistics

Assigned Value	10.0	1.6
Spike Value	Not Spiked	
Homogeneity Value	12.0	2.4
Robust Average	10.5	2.1
Median	10.0	1.2
Mean	13.3	
N	9	
Max	40	
Min	6.6	
Robust SD	2.5	
Robust CV	24%	

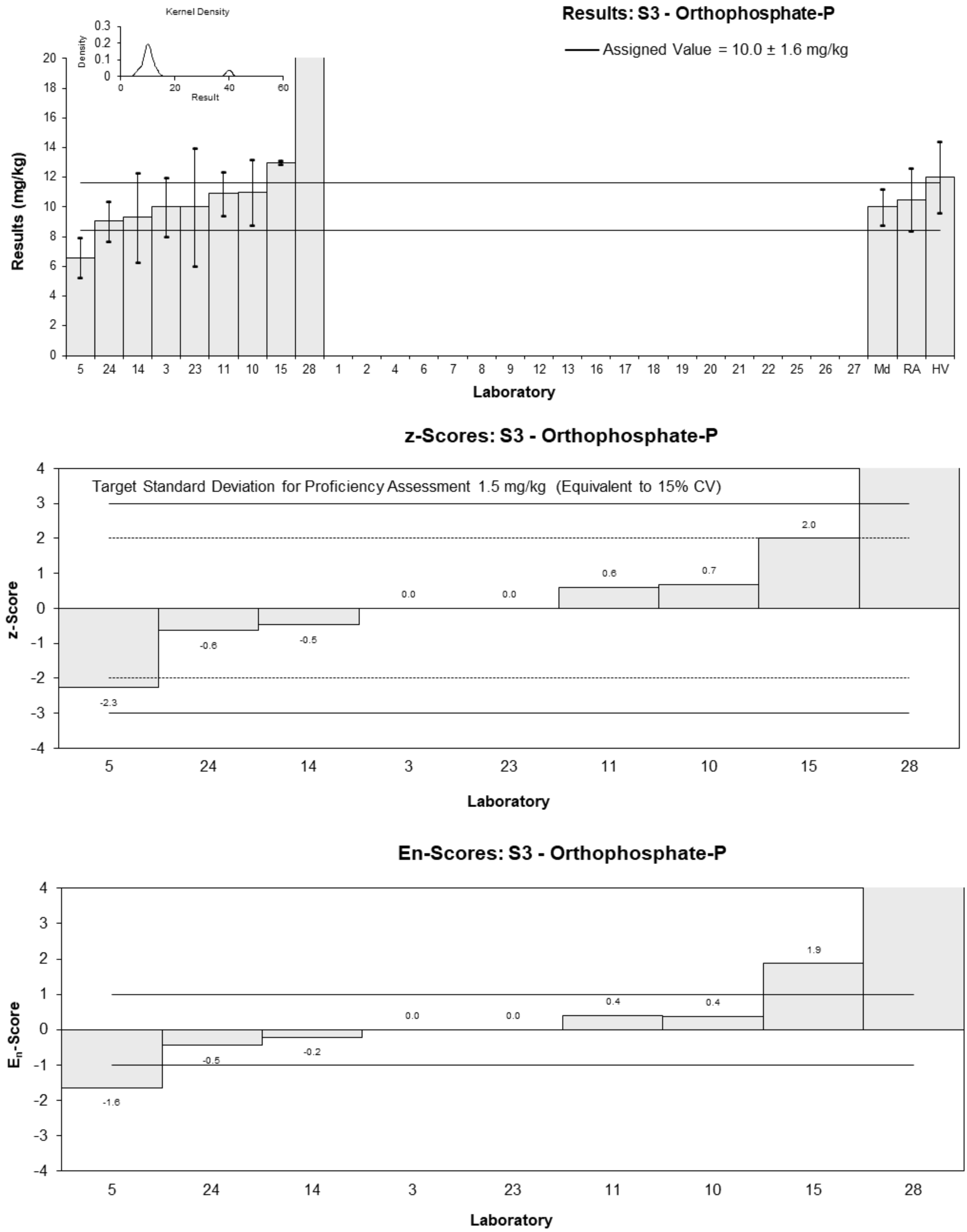

Results: S3 - Orthophosphate-P
Assigned Value = 10.0 ± 1.6 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5 24 14 3 23 11 10 15 28 1 2 4 6 7 8 9 12 13 16 17 18 19 20 21 22 25 26 27 Md RA HV
z-Scores: S3 - Orthophosphate-P
Target Standard Deviation for Proficiency Assessment 1.5 mg/kg (Equivalent to 15% CV)
z-Score
-2.3 -0.6 -0.5 0.0 0.0 0.6 0.7 2.0
5 24 14 3 23 11 10 15 28
Laboratory
En-Scores: S3 - Orthophosphate-P
E_n-Score
-1.6 -0.5 -0.2 0.0 0.0 0.4 0.4 1.9
5 24 14 3 23 11 10 15 28
Laboratory

Figure 46

Table 57

Sample Details

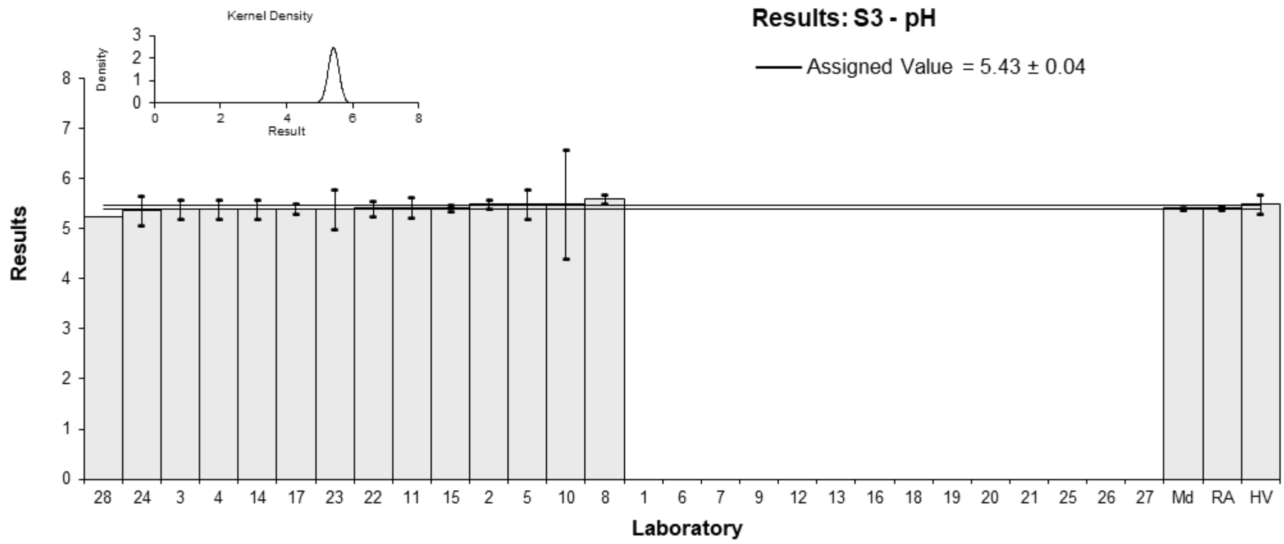
Sample No.	S3
Matrix	Soil
Analyte	pH

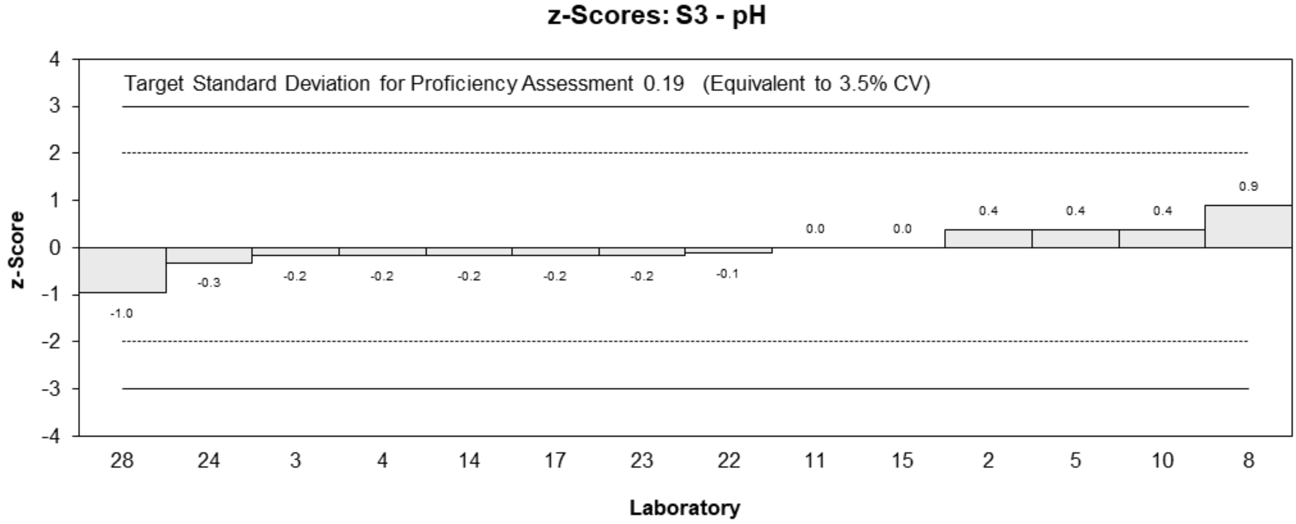
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	5.5	0.1	0.37	0.65
3	5.4	0.2	-0.16	-0.15
4	5.4	0.2	-0.16	-0.15
5	5.5	0.3	0.37	0.23
6	NT	NT		
7	NT	NT		
8	5.6	0.1	0.89	1.58
9	NT	NT		
10	5.5	1.1	0.37	0.06
11	5.43	0.2	0.00	0.00
12	NT	NT		
13	NT	NT		
14	5.4	0.2	-0.16	-0.15
15	5.43	0.06	0.00	0.00
16	NT	NT		
17	5.4	0.1	-0.16	-0.28
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	5.41	0.15	-0.11	-0.13
23	5.4	0.4	-0.16	-0.07
24	5.37	0.3	-0.32	-0.20
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	5.25	NR	-0.95	-4.50

Statistics

Assigned Value	5.43	0.04
Spike Value	Not Spiked	
Homogeneity Value	5.50	0.19
Robust Average	5.43	0.04
Median	5.41	0.02
Mean	5.43	
N	14	
Max	5.6	
Min	5.25	
Robust SD	0.064	
Robust CV	1.2%	


Results: S3 - pH
Assigned Value = 5.43 ± 0.04
Kernel Density
Density
Result
Results
Laboratory
28 24 3 4 14 17 23 22 11 15 2 5 10 8 1 6 7 9 12 13 16 18 19 20 21 25 26 27 Md RA HV


z-Scores: S3 - pH
Target Standard Deviation for Proficiency Assessment 0.19 (Equivalent to 3.5% CV)
z-Score
-1.0 -0.3 -0.2 -0.2 -0.2 -0.2 -0.2 -0.1 0.0 0.0 0.4 0.4 0.4 0.9
28 24 3 4 14 17 23 22 11 15 2 5 10 8
Laboratory

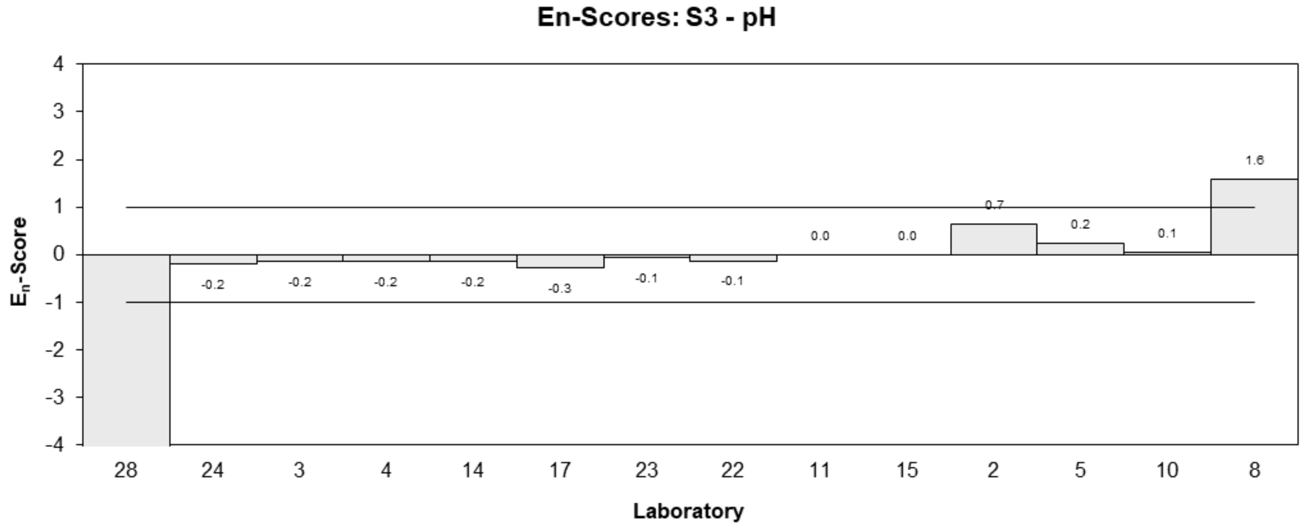

En-Scores: S3 - pH
En-Score
-0.2 -0.2 -0.2 -0.2 -0.3 -0.1 -0.1 0.0 0.0 0.7 0.2 0.1 1.6
28 24 3 4 14 17 23 22 11 15 2 5 10 8
Laboratory

Figure 47

Table 58

Sample Details

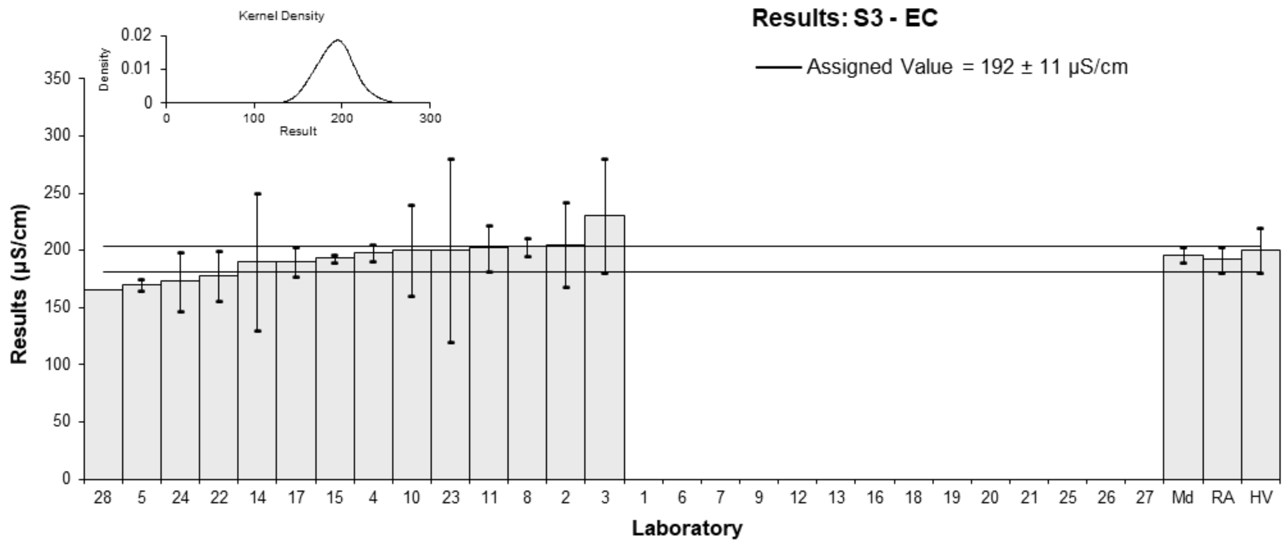
Sample No.	S3
Matrix	Soil
Analyte	EC
Unit	µS/cm

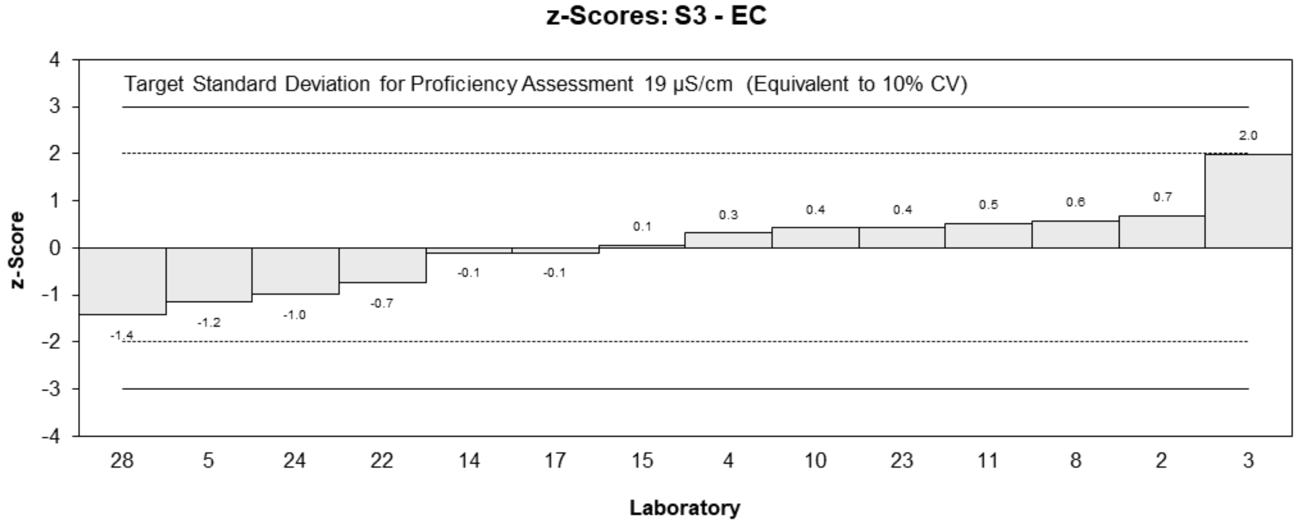
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	205.1	37	0.68	0.34
3	230	50	1.98	0.74
4	198	6.9	0.31	0.46
5	170	5	-1.15	-1.82
6	NT	NT		
7	NT	NT		
8	203	8	0.57	0.81
9	NT	NT		
10	200	40	0.42	0.19
11	202	20	0.52	0.44
12	NT	NT		
13	NT	NT		
14	190	60	-0.10	-0.03
15	193.2	3.4	0.06	0.10
16	NT	NT		
17	190	13	-0.10	-0.12
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	178	22	-0.73	-0.57
23	200	80	0.42	0.10
24	173	26	-0.99	-0.67
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	165	NR	-1.41	-2.45

Statistics

Assigned Value	192	11
Spike Value	Not Spiked	
Homogeneity Value	200	20
Robust Average	192	11
Median	196	7
Mean	193	
N	14	
Max	230	
Min	165	
Robust SD	17	
Robust CV	8.8%	


Results: S3 - EC
Assigned Value = 192 ± 11 µS/cm
Kernel Density
Density
Result
Results (µS/cm)
Laboratory
28 5 24 22 14 17 15 4 10 23 11 8 2 3 1 6 7 9 12 13 16 18 19 20 21 25 26 27 Md RA HV


z-Scores: S3 - EC
Target Standard Deviation for Proficiency Assessment 19 µS/cm (Equivalent to 10% CV)
z-Score
Laboratory
-1.4 -1.2 -1.0 -0.7 -0.1 -0.1 0.1 0.3 0.4 0.4 0.5 0.6 0.7 2.0
28 5 24 22 14 17 15 4 10 23 11 8 2 3

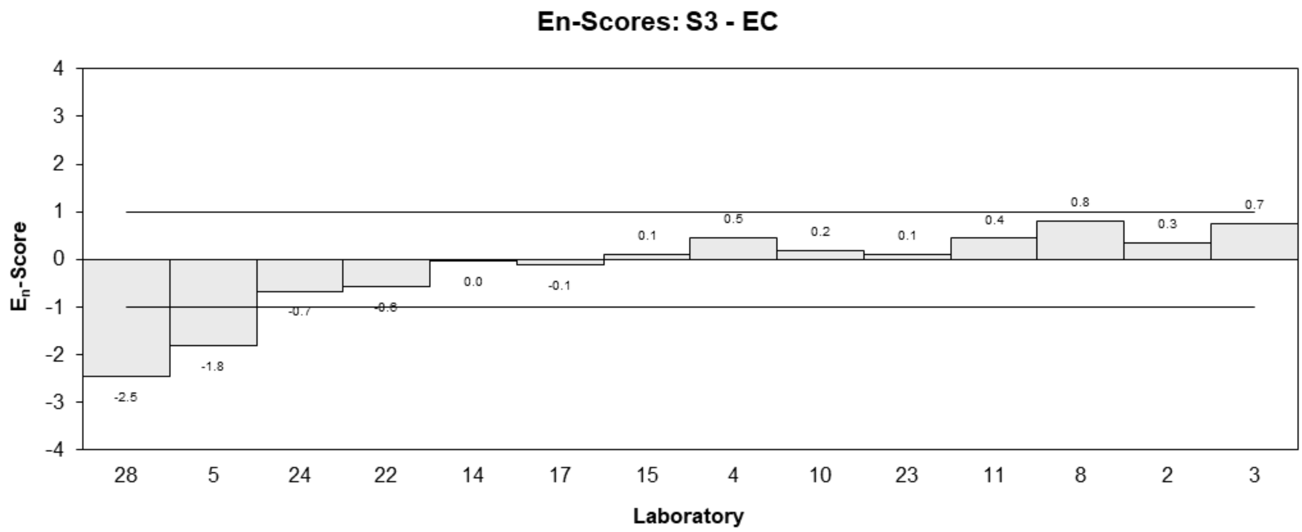

En-Scores: S3 - EC
En-Score
Laboratory
-2.5 -1.8 -0.7 -0.6 0.0 -0.1 0.1 0.5 0.2 0.1 0.4 0.8 0.3 0.7
28 5 24 22 14 17 15 4 10 23 11 8 2 3

Figure 48

Table 59

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	3300	700	-0.62	-0.41
4	NR	NR		
5	4700	921	1.23	0.72
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	4300	640	0.70	0.48
11	4899	490	1.50	1.09
12	NT	NT		
13	NT	NT		
14	2400	1000	-1.82	-1.01
15	4027.50	148.91	0.34	0.28
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	2700	1000	-1.42	-0.79
24	3800	874	0.04	0.02
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	NT	NT		

Statistics

Assigned Value	3770	910
Spike Value	Not Spiked	
Homogeneity Value	4800	960
Robust Average	3770	910
Median	3910	920
Mean	3770	
N	8	
Max	4899	
Min	2400	
Robust SD	1000	
Robust CV	27%	

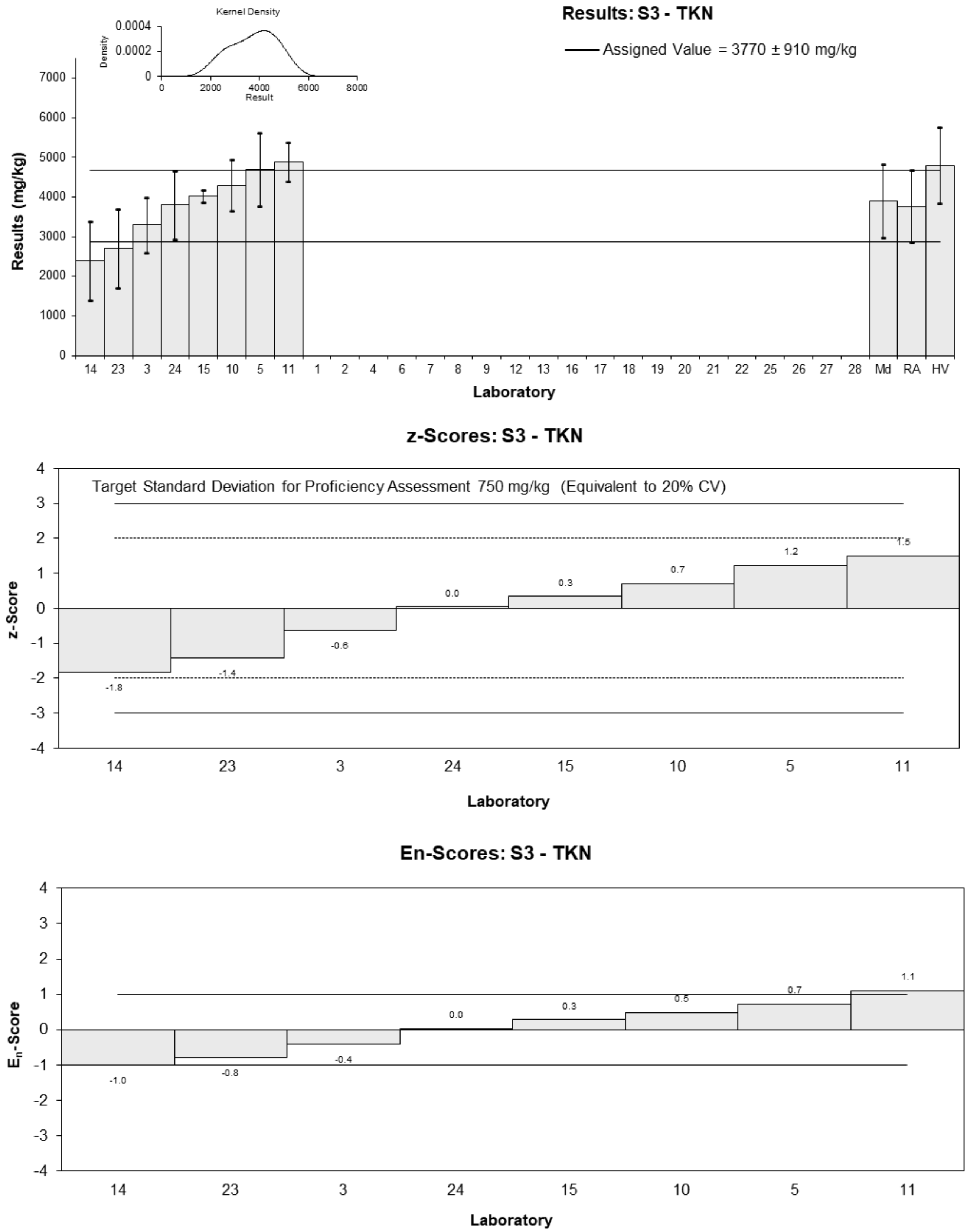

Results: S3 - TKN
Assigned Value = 3770 ± 910 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
14 23 3 24 15 10 5 11 1 2 4 6 7 8 9 12 13 16 17 18 19 20 21 22 25 26 27 28 Md RA HV
z-Scores: S3 - TKN
Target Standard Deviation for Proficiency Assessment 750 mg/kg (Equivalent to 20% CV)
z-Score
-1.8 -1.4 -0.6 0.0 0.3 0.7 1.2 1.5
14 23 3 24 15 10 5 11
Laboratory
En-Scores: S3 - TKN
En-Score
-1.0 -0.8 -0.4 0.0 0.3 0.5 0.7 1.1
14 23 3 24 15 10 5 11
Laboratory

Figure 49

Table 60

Sample Details

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

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	1.1	0.2	-0.74	-0.54
4	NR	NR		
5	NR	NR		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	1.9	0.38	1.63	0.97
11	0.9	0.1	-1.33	-1.04
12	NT	NT		
13	NT	NT		
14	1.4	0.5	0.15	0.08
15**	11.67	0.06	30.58	24.32
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	1.6	1.11	0.74	0.21
23	1.2	0.5	-0.44	-0.23
24	<1	NR		
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	NT	NT		

** Extreme Outlier, see Section 4.2

Statistics

Assigned Value	1.35	0.42
Spike Value	Not Spiked	
Robust Average	1.35	0.42
Median	1.30	0.38
Mean	1.35	
N	6	
Max	1.9	
Min	0.9	
Robust SD	0.41	
Robust CV	30%	

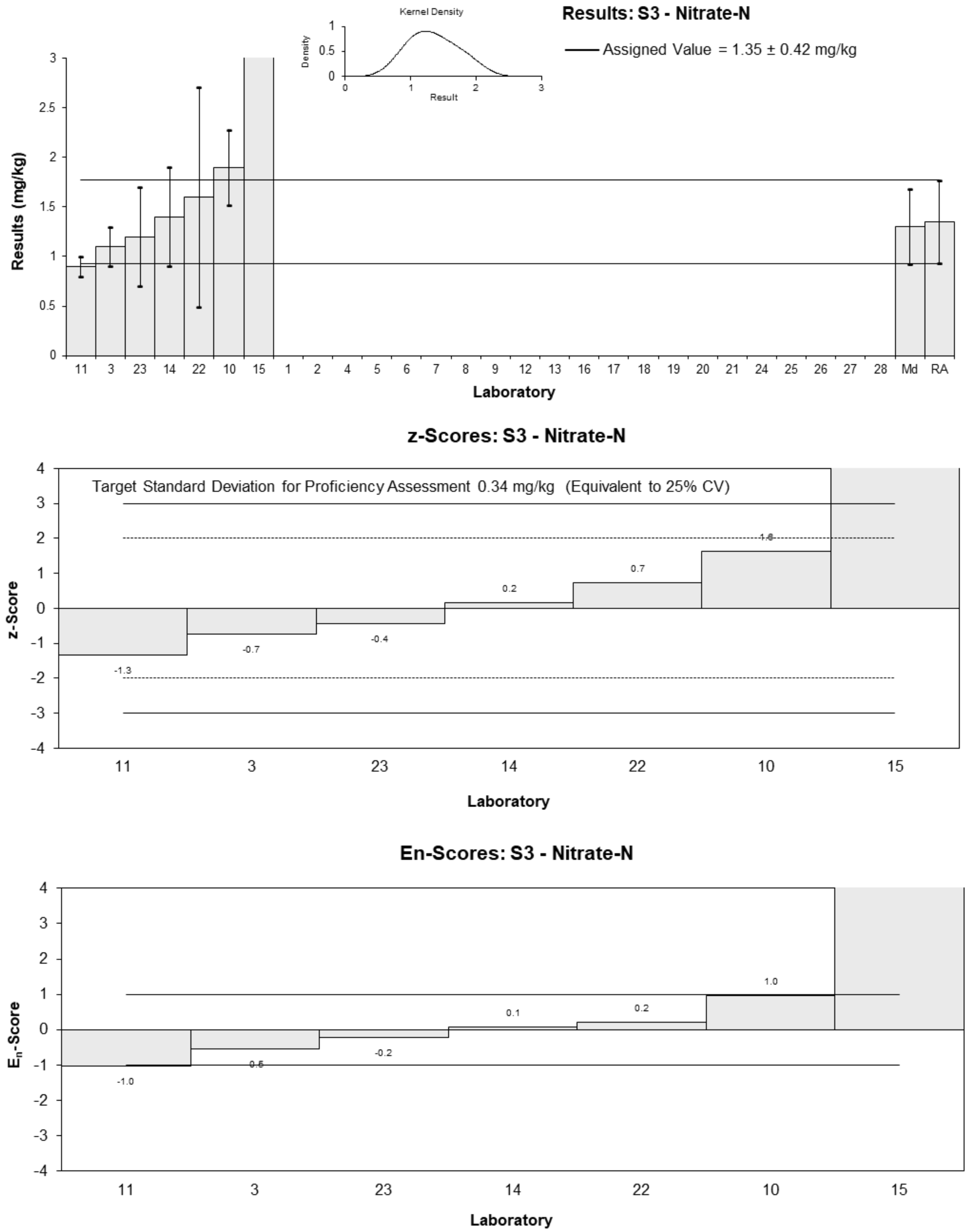

Results: S3 - Nitrate-N
Assigned Value = 1.35 ± 0.42 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
11 3 23 14 22 10 15 1 2 4 5 6 7 8 9 12 13 16 17 18 19 20 21 24 25 26 27 28 Md RA
z-Scores: S3 - Nitrate-N
Target Standard Deviation for Proficiency Assessment 0.34 mg/kg (Equivalent to 25% CV)
z-Score
-1.3 -0.7 -0.4 0.2 0.7 1.6
11 3 23 14 22 10 15
Laboratory
En-Scores: S3 - Nitrate-N
En-Score
-1.0 -0.5 -0.2 0.1 0.2 1.0
11 3 23 14 22 10 15
Laboratory

Figure 50

Table 61

Sample Details

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

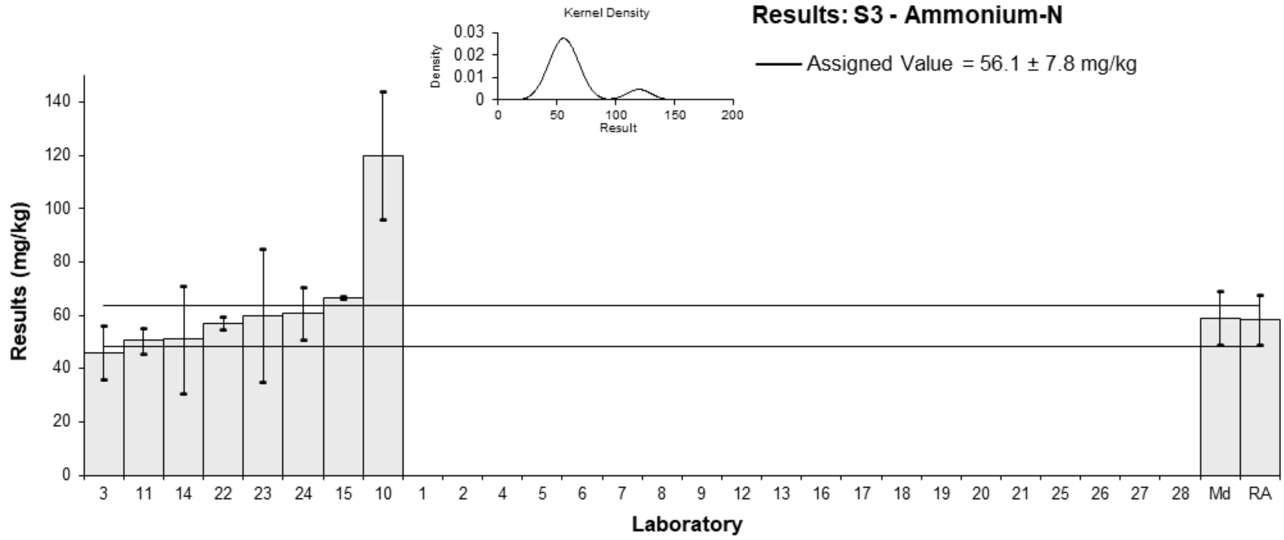
Participant Results

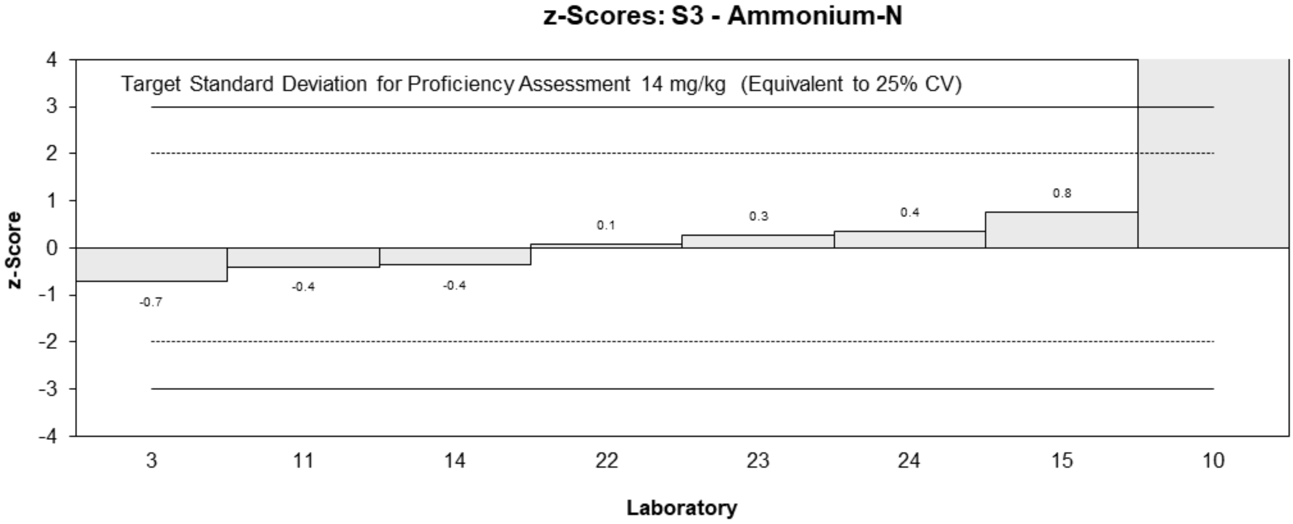
Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	46	10	-0.72	-0.80
4	NR	NR		
5	NR	NR		
6	NT	NT		
7	NT	NT		
8	NT	NT		
9	NT	NT		
10*	120	24	4.56	2.53
11	50.5	5.0	-0.40	-0.60
12	NT	NT		
13	NT	NT		
14	51	20	-0.36	-0.24
15	66.8	0.28	0.76	1.37
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	57.1	2.36	0.07	0.12
23	60	25	0.28	0.15
24	61.0	9.88	0.35	0.39
25	NT	NT		
26	NT	NT		
27	NT	NT		
28	NT	NT		

* Outlier, see Section 4.2

Statistics

Assigned Value	56.1	7.8
Spike Value	Not Spiked	
Robust Average	58.3	9.3
Median	59	10
Mean	64	
N	8	
Max	120	
Min	46	
Robust SD	11	
Robust CV	18%	


Results: S3 - Ammonium-N
Assigned Value = 56.1 ± 7.8 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
3 11 14 22 23 24 15 10 1 2 4 5 6 7 8 9 12 13 16 17 18 19 20 21 25 26 27 28 Md RA


z-Scores: S3 - Ammonium-N
Target Standard Deviation for Proficiency Assessment 14 mg/kg (Equivalent to 25% CV)
z-Score
-0.7
-0.4
-0.4
0.1
0.3
0.4
0.8
Laboratory
3 11 14 22 23 24 15 10

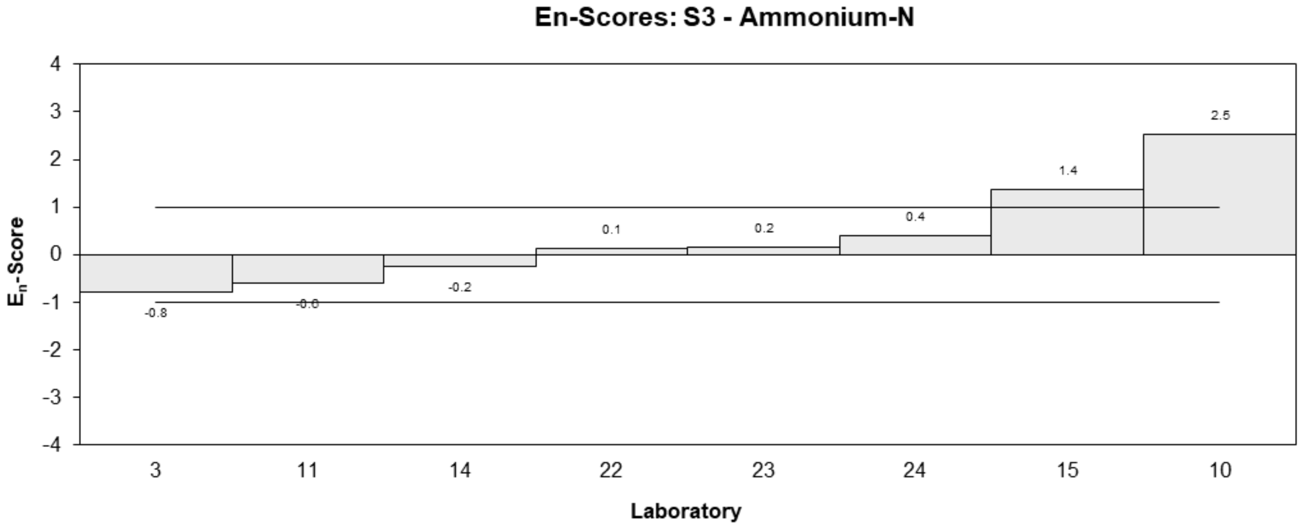

En-Scores: S3 - Ammonium-N
En-Score
-0.8
-0.6
-0.2
0.1
0.2
0.4
1.4
2.5
Laboratory
3 11 14 22 23 24 15 10

Figure 51

6 DISCUSSION OF RESULTS

6.1 Assigned Value and Traceability

Sample S1 was soil from a contaminated site fortified for 6 elements, ground and then sieved through a 0.350 µm sieve. **Sample S2** was prepared from the same soil material and sieved through a sieve size of 0.250 µm.

Sample S3 was unspiked agricultural soil.

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 '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.[6] 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 Sb in S1, and bromide, fluoride, and iodide in S3 because the reported results were either too few or too variable. Descriptive statistics for these elements are presented in Section 5. No descriptive statistics were presented for iodide in S3 due to only one result (0.06 mg/kg) being reported.

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 659 numerical results, 599 (91%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.1% to 333% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 11.

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

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 51). 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, 19 laboratories reported results for Mn in S1. The uncertainty of the assigned value estimated from the robust standard deviation of the 19 laboratories' results is 37 mg/kg (6.8% of the reported value). If Laboratory 8 result is coming from one measurement, then they might have under-estimated their expanded measurement uncertainties reported for Mn in S1 (20 mg/kg or 3.9% of the reported value) as an uncertainty estimated from one measurement cannot be smaller than the uncertainty estimated from 19 measurements. Alternatively, estimates of uncertainties for As in S2 larger than 3.8 mg/kg (the uncertainty of the assigned value, 0.70 mg/kg plus the allowable variation from the assigned value, the target standard deviation of 1.23 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 laboratories 14 and 23 for As in S2 (4 mg/kg) might have been over-estimated.

Laboratory 15 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 of these studies alone, can also be used to estimate the uncertainty of their measurement results. [10] An example of estimating measurement uncertainty using only proficiency testing is given in Appendix 3.

Laboratories 3 and 12 attached estimates of the expanded measurement uncertainty to results reported as a range ("less than"). An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[9]

Laboratories 14, 23 and 27 reported estimates of expanded uncertainty for some of their measurement results which were equal to larger than the results themselves.

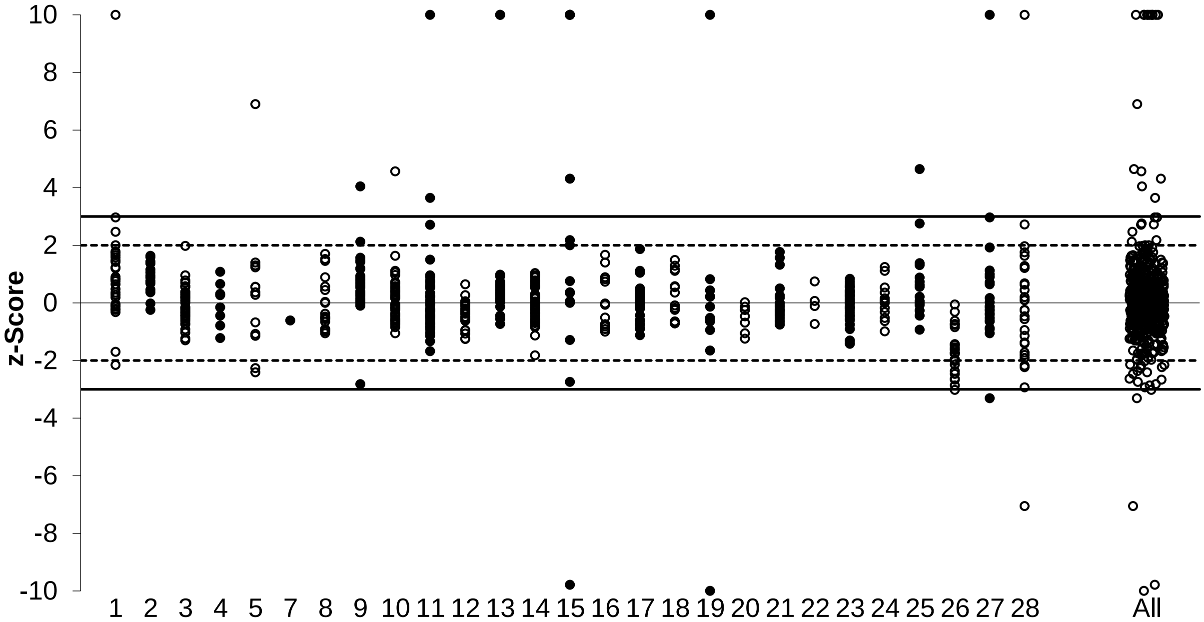
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 2495.52 ± 374.33 mg/kg,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

6.3 z-Score

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

The target standard deviation defines 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[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 62.



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

Figure 52 z-Score Dispersal by Laboratory

The dispersal of participants' z-scores is presented in Figure 52 (by laboratory code) and in Figure 54 (by test). Of 631 results for which z-scores were calculated, 587 (93%) returned satisfactory score of $|z| \leq 2.0$ and 23 (4%) 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.

Summary of participants' reported results and performance is presented in Figure 55.

Laboratories **10** and **23** returned the highest number of satisfactory z scores (46 out of 47 reported and 46 out of 46 reported, respectively).

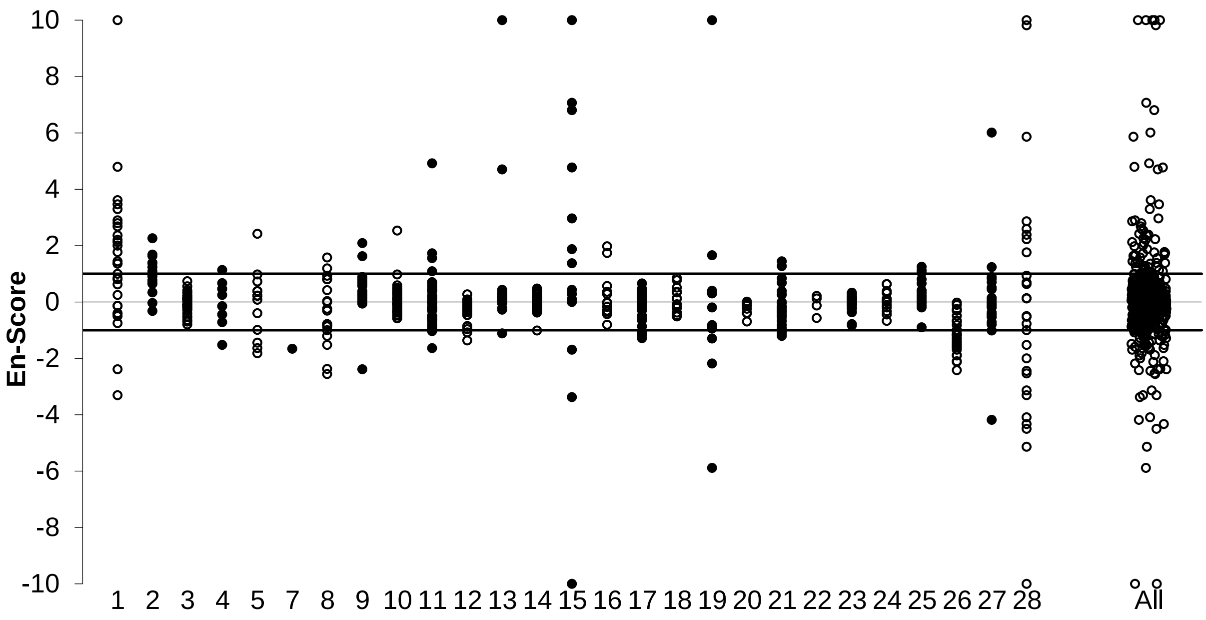
All results reported by L**aboratories 23** (46), **3, 14** (42), **17** (34), **21** (28), **12** (26), **8** (19), **2, 18** (17), **16, 24** (13) **4, 20** (8) and **22** (4) returned satisfactory z scores.

6.4 E_n-score

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

The dispersal of participants' E_n-scores is graphically presented in Figure 53. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 631 results for which E_n-scores were calculated, 507 (80%) 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 53 E_n-Score Dispersal by Laboratory

Laboratory 23 returned the highest number of satisfactory E_n-scores, 46.

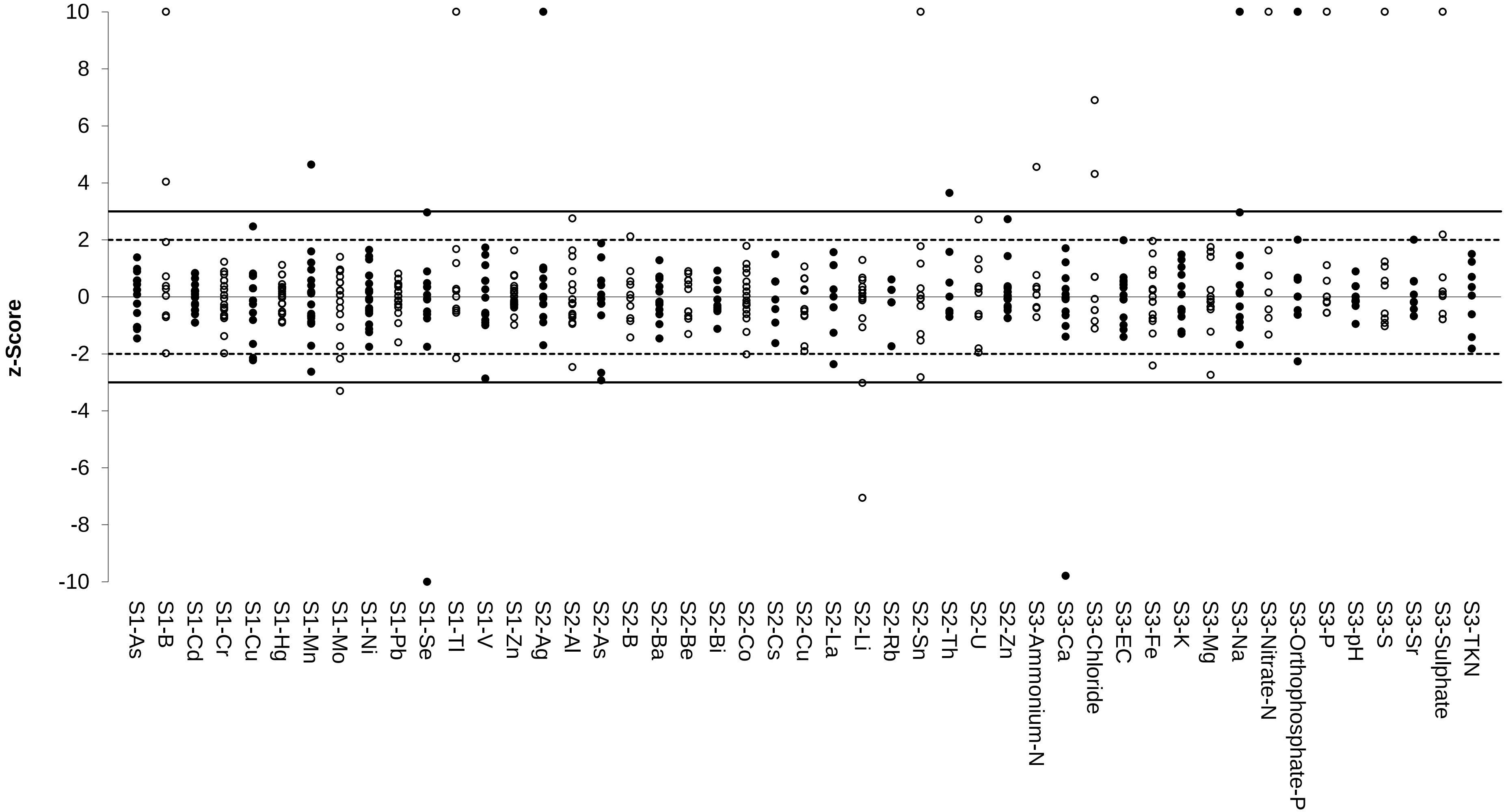
All results reported by **Laboratories 3** (42), **18** (17), 24 (13) **20** (8) and **22** (4) returned satisfactory E_n-scores.

Table 62 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	As	12.3	9.7%	11%	10%
S1	B	3.88	23%	13%	15%

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Cd	3.01	8.2%	14%	15%
S1	Cr	21.2	12%	10%	15%
S1	Cu	23.3	9.1%	10%	10%
S1	Hg	1.97	8.7%	14%	15%
S1	Mn	548	12%	6.2%	10%
S1	Mo	5.95	17%	12%	15%
S1	Ni	11.7	15%	11%	15%
S1	Pb	599	4.8%	6.1%	10%
S1	Sb	Not Set	54%	NA	Not Set
S1	Se	4.85	12%	13%	15%
S1	Tl	0.96	17%	16%	15%
S1	V	34.1	11%	9.4%	10%
S1	Zn	790	4.9%	5.9%	10%
S2	Ag	1.04	11%	16%	15%
S2	Al	15500	16%	3.7%	15%
S2	As	12.3	9.4%	11%	10%
S2	B	4.24	20%	13%	20%
S2	Ba	112	6.8%	7.9%	10%
S2	Be	0.633	8.1%	17.%	10%
S2	Bi	2.93	6.6%	14%	10%
S2	Co	6.28	8.9%	12%	10%
S2	Cs	1.39	17%	15%	15%
S2	Cu	23.5	7.6%	9.9%	10%
S2	La	18	20%	10%	15%
S2	Li	8.5	10%	12%	10%
S2	Rb	45.9	4.5%	9%	10%
S2	Sn	4.06	29%	13%	20%
S2	Th	7	25%	12%	20%
S2	U	0.96	23%	16.	15%
S2	Zn	757	4.6%	5.9%	10%
S3	Ammonium-N	56.1	18%	8.7%	25%
S3	Bromide	Not Set	37%	NA	Not Set
S3	Ca	5350	9.5%	4.4%	10%
S3	Chloride	17.2	32%	10%	15%
S3	EC	192	8.8%	7.3%	10%
S3	Fe	22400	11%	3.5%	10%
S3	Fluoride	Not Set	32%	NA	Not Set
S3	K	1150	10%	5.5%	10%
S3	Mg	1140	12%	5.5%	10%
S3	Na	179	21%	7.3%	15%
S3	Nitrate-N	1.35	30%	15%	25%
S3	Orthophosphate-P	10	24%	11%	15%
S3	P	1800	7.6%	5.2%	10%
S3	pH	5.43	1.2%	12%	3.5%
S3	S	606	12%	6.1%	10%
S3	Sr	39.7	6.7%	9.2%	10%
S3	Sulphate	68.1	19%	8.5%	15%
S3	TKN	3770	27%	4.6%	20%

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



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

Figure 54 z-Score Dispersal by Test

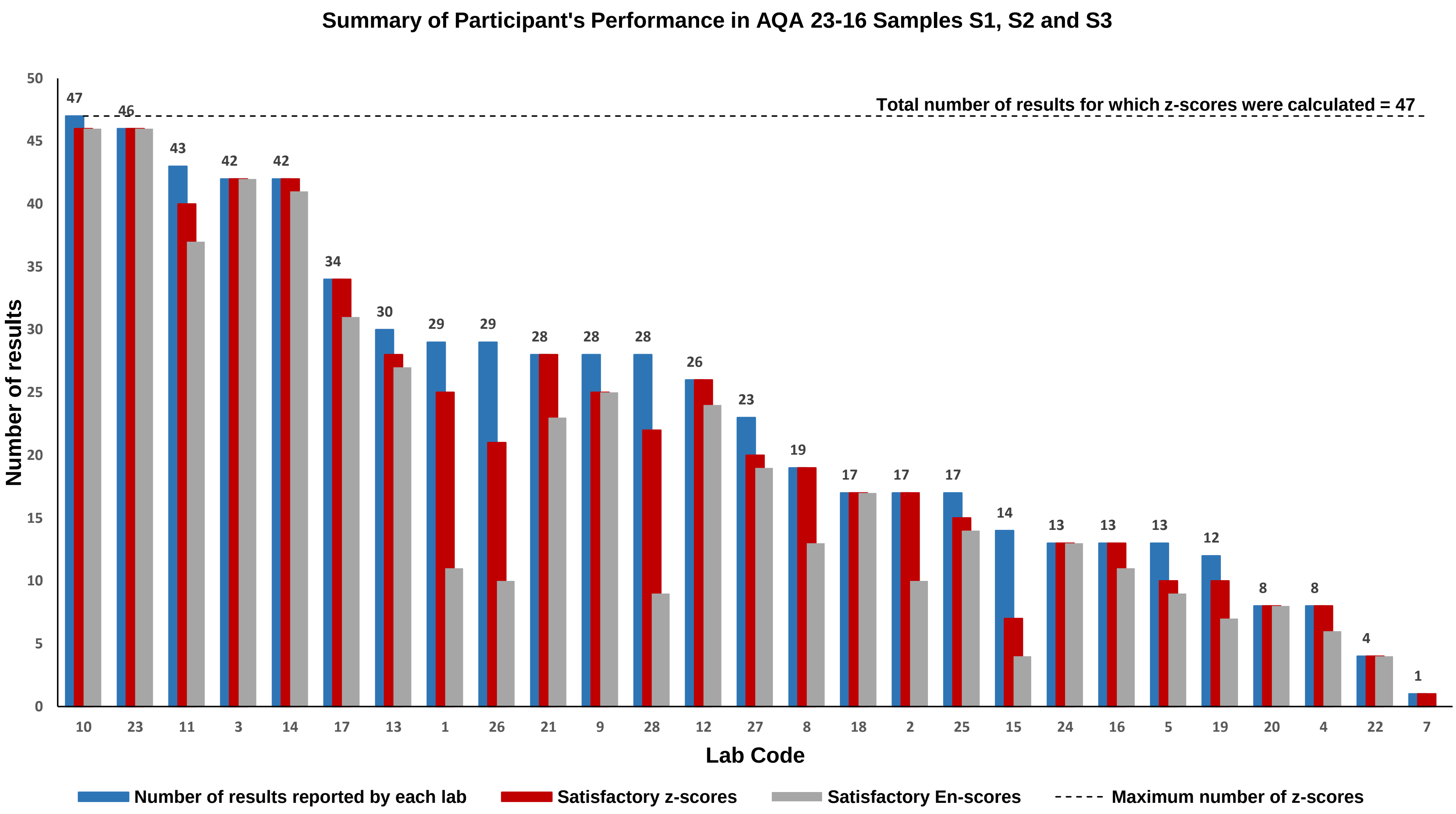


Figure 55 Summary of Participants' Performance

Table 63 Summary of Participants' Results and Performance in Sample S1

Lab Code	As (mg/kg)	B (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Se (mg/kg)	Tl (mg/kg)	V (mg/kg)	Zn (mg/kg)
A.V.	12.3	3.88	3.01	21.2	23.3	1.97	548	5.95	11.7	599	Not Set	4.85	0.96	34.1	790
H.V.	12.5	3.44	2.86	20.5	23.8	1.98	555	6.1	11.8	590	21.1	4.59	0.95	34.8	776
1	NT	4.045	3.385	25.1	29.05	2.0256	613.55	6.75	14.6	591	21.4	5.2	0.649	40	773.5
2	14	NT	3	24	25	1.9	635	NT	13	626	NT	NT	NT	NT	850
3	13	<10	3.1	23	24	2.2	580	6.8	12	610	24	4.9	<2	36	820
4	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NR	NR	NR	NR	NR	1.79	NR	NR	NR	NR	NR	NR	NR	NR	NR
8	NT	NT	2.6	20	NT	2.1	512	5	10	565	11	NT	NT	31	712
9	12.4	6.23	3.04	23.7	25.2	2.05	614	6.78	14.2	623	NT	4.78	1.13	39.1	802
10	11	4.3	2.8	21	24	1.8	510	5.6	12	590	15	4.4	0.88	32	760
11	10.9	3.46	3.11	19.8	22.7	2.07	515	6.58	10.9	583	35.2	4.47	0.99	31.3	768
12	12	<20	2.88	20.3	22	1.96	533	5.4	11.6	577	15.8	<20	0.89	<100	791
13	13.5	3.9	3.06	21.4	25	2.07	556	6.14	12.5	625	22	5.1	1	32.2	814
14	13	<10	3.3	23	24	2.2	600	6.8	13	610	25	5.5	<2	35	790
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	13.4	NR	3	18.8	21.4	1.7	507	7.2	10.8	648	45	4.8	1.2	30.7	848
17	12.6	<10	3.1	22.4	24	2.06	554	6.4	12.1	592	NT	<10	0.96	37.9	776
18	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
19	12.825	59.361	3.379	19.157	19.423	1.816	496.355	6.144	10.676	591.124	NT	-5.894	NT	NT	806.413
20	11	NT	2.8	19	23	1.9	NT	NT	9.5	600	NT	NT	NT	NT	770
21	12	3.5	2.9	22	23	1.9	558	6.4	11.5	582	28	4.3	0.9	34	765
22	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
23	13	4.1	3.2	22	25	2	570	5.8	12	620	19	5.1	<2	36	800
24	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
25	13	NT	3	24	25	1.98	802	6	14	543	NT	<5	NT	36	769
26	10.5	2.73	2.73	14.9	18.3	1.72	404	4.4	8.61	503	12.6	3.57	<0.88	24.3	732
27	11	5	2.6	20	23	2.3	500	3	11	600	9	7	480	32	780
28	11.6	NR	3.1	16.8	18.1	1.9	454	4	9.7	637	3.7	NR	NT	NT	919

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 64 Summary of Participants' Results and Performance in Sample S2

Lab Code	Ag (mg/kg)	Al (mg/kg)	As (mg/kg)	B (mg/kg)	Ba (mg/kg)	Be (mg/kg)	Bi (mg/kg)	Co (mg/kg)	Cs (mg/kg)	Cu (mg/kg)	La (mg/kg)	Li (mg/kg)	Rb (mg/kg)	Sn (mg/kg)	Th (mg/kg)	U (mg/kg)	Zn (mg/kg)
A.V.	1.04	15500	12.3	4.24	112	0.633	2.93	6.28	1.39	23.5	18	8.5	45.9	4.06	7	0.96	757
H.V.	0.97	16400	12.4	4.3	118	0.607	3.35	6.06	1.59	23.1	23.6	8.7	49	4.45	8.4	1.21	763
1	0.775	18800	12	3.9704	116	0.685	NT	7.4	NT	25	NT	NT	NT	NT	NT	NT	754
2	NT	19300	14	NT	NT	NT	NT	7	NT	26	NT	NT	NT	NT	NT	NT	865
3	1.1	15000	12	<10	110	<1	2.8	6.1	1.3	24	17	8.8	47	3.8	6.3	<1	780
4	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	NT	NT	NT	NT	NT	0.6	NT	6.3	NT	NT	NT	NT	NT	NT	NT	NT	721
9	1.04	17600	12.2	6.04	120	0.67	3.1	6.61	NT	24.1	22.2	9.07	NT	1.77	NT	1.01	782
10	1.1	15300	12	4.6	110	0.67	3	5.8	1.5	24	21	8.7	45	4	7.7	1.1	770
11	1.19	13384	12.4	3.52	109	0.69	2.78	6.14	NT	21.9	NT	7.86	NT	NT	12.1	1.35	733
12	1.14	13300	12.2	<20	101.3	0.65	2.82	5.5	1.37	22.3	14.6	7.59	45	4.1	NT	0.872	751
13	15.6	13800	12.8	4.3	107	0.67	3.2	6.2	1.5	25	18.7	8.6	48.7	22.5	NT	0.98	785
14	1.2	15000	12	<10	110	<1	2.6	6.4	1.5	24	17	9	47	4	6.2	<1	760
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	0.9	14100	14.6	<10	114	0.66	NT	5.9	NT	22.5	NT	8.45	NT	4.3	NT	NT	700
18	0.93	15000	12	4.7	110	0.59	3.1	6.5	1.7	22	21	9.6	45	5	6	0.86	750
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
21	1	14900	11.5	3.6	105	0.6	2.9	6.1	NT	22.5	NT	8.5	NT	5.5	9.2	1.15	728
22	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
23	1	16000	13	4.2	110	0.55	3	6.8	1.2	25	18	8.4	47	3	7	1	760
24	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
25	NT	21900	14	NT	119	<1	NT	6	NT	24	NT	NT	NT	NT	NT	NT	751
26	1.03	9750	9.01	3.03	95.7	0.584	2.84	5.01	1.05	19.4	11.6	5.93	37.9	2.81	NR	0.678	701
27	1	14000	12	5	120	0.6	NT	6.9	NT	25	NT	NT	NT	NT	NT	NT	770
28	1	16530	8.7	NR	126.3	NT	NT	NT	NT	19	NT	2.5	NT	NT	NT	0.7	963

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

Table 65 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.	5350	22400	1150	1140	179	1800	606	39.7
H.V.	4890	21000	1140	1150	168	1790	556	41.1
1	5300	24100	1320	1320	258.5	NT	1370	47.65
2	NT	24500	NT	NT	NT	NT	NT	NT
3	4800	22000	1000	1000	170	1700	550	38
4	5700	23000	1010	1090	208	NR	NR	NR
5	5500	17000	1300	1300	150	1900	640	37
6	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	NT	NT	NT	NT	NT
8	6260	25800	1090	1140	218	NT	NT	NT
9	NT	NT	NT	NT	NT	NT	NT	NT
10	5330	21000	1100	1130	160	1770	670	39
11	5339	22882	1239	1167	134	1763	543	41.9
12	NT	NT	NT	NT	NT	NT	NT	NT
13	NT	NT	NT	NT	NT	NT	NT	NT
14	5000	20500	1070	1100	170	1800	570	37
15	110.98	19512.49	1192.55	828.15	838.81	7545.71	NT	NT
16	NT	NT	NT	NT	NT	NT	NT	NT
17	5400	20700	1270	1120	155	1800	630	38.9
18	NT	NT	NT	NT	NT	NT	NT	NT
19	NT	NT	NT	NT	NT	NT	NT	NT
20	NT	NT	NT	NT	NT	NT	NT	NT
21	NT	NT	NT	NT	NT	NT	NT	NT
22	NR	NR	NR	NR	NR	NR	NR	NR
23	4600	22000	1100	1100	190	1700	560	40
24	5070	22400	1160	1120	183	2000	681	41.8
25	NT	NT	NT	NT	NT	NT	NT	NT
26	NT	NT	NT	NT	NT	NT	NT	NT
27	NT	NT	NT	NT	NT	NT	NT	NT
28	6000	26800	1160	1340	182	NT	NT	NT

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

Table 65 Summary of Participants' Results and Performance for Sample S3 (continued)

Lab Code	Bromide (mg/kg)	Chloride (mg/kg)	Fluoride (mg/kg)	Iodide (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	17.2	Not Set	Not Set	68.1	10	5.43	192	3770	1.35	56.1
H.V.	1.1	14.4	1.5	NA	65	12	5.5	200	4800	NA	NA
1	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
2	NT	NT	NT	NT	NT	NT	5.5	205.1	NT	NT	NT
3	1.5	19	1	<1	69	10	5.4	230	3300	1.1	46
4	NR	NR	NR	NR	60	NR	5.4	198	NR	NR	NR
5	NR	35	180	0.06	<100	6.6	5.5	170	4700	NR	NR
6	NT	NT	1.6	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
8	NT	NT	NT	NT	NT	NT	5.6	203	NT	NT	NT
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	1.2	15	1.5	<1	70	11	5.5	200	4300	1.9	120
11	NT	17	NT	NT	173	10.9	5.43	202	4899	0.9	50.5
12	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	1.1	19	1.3	<1	60	9.3	5.4	190	2400	1.4	51
15	24.25	28.33	8.9	NT	90.35	13	5.43	193.2	4027.5	11.67	66.8
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	14.3	NT	NT	68.3	NT	5.4	190	NT	NT	NT
18	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
21	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
22	NR	NR	NR	NR	NR	NR	5.41	178	NR	1.6	57.1
23	1.1	16	1.1	<1	62	10	5.4	200	2700	1.2	60
24	NT	<20	<1	NT	<20	9.05	5.37	173	3800	<1	61
25	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
26	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
27	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
28	2.2	16	NR	NT	75	40	5.25	165	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 63 to 65 and in Figures 52 to 55.

Low level Sb, Sn and Th were the analytes which presented the most analytical difficulty to participating laboratories.

Lead, Rb and Zn were the tests which presented the least analytical difficulty to participating laboratories, with a between-laboratory CV of 4.5 to 4.8 %.

All unsatisfactory results reported by Laboratory 26 for acid extractable elements were lower than the assigned value by the same factor of approximately 0.65. This laboratory should check their dilution and/or standard preparation procedure. The unsatisfactory 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.

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.[5, 15-18] 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_3, HCl, in combination or alone and most of these methods produce comparable results.[19-21]

In the present study most participants used a sample size of between 0.5 g to 1 g, an extraction temperature between of 95ºC to 120ºC, an extraction time between 60 min to 120 min and a ratio HNO_3 to HCl of 1:1.

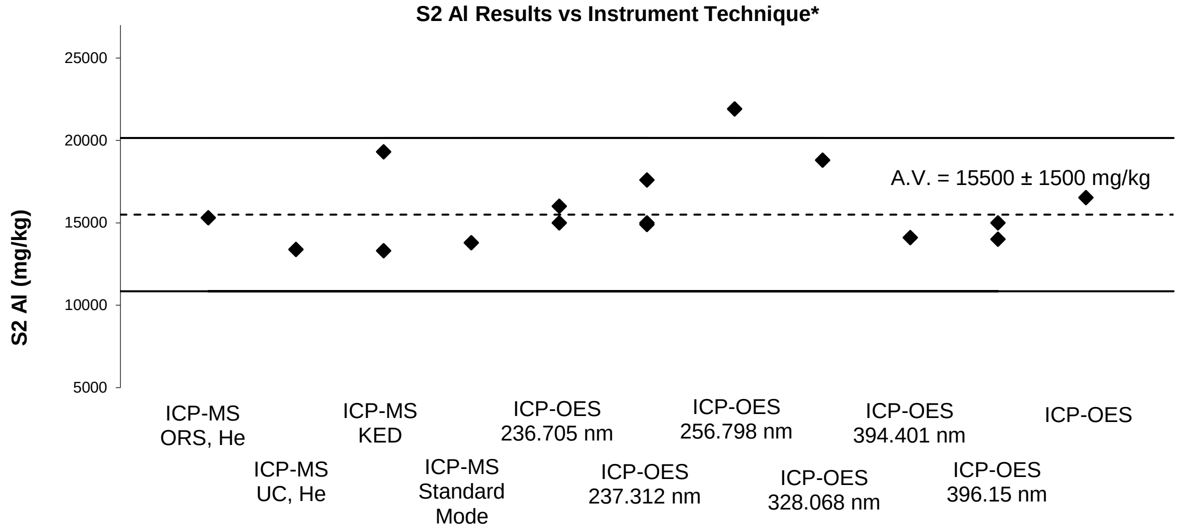
Laboratory 19 extracted their sample at a temperature of between 70ºC to 90ºC for 60 min.

Laboratory 15 used a staggered digestion regime, extracted their sample at 100ºC, 120ºC and 140ºC temperatures for 180 min and used a sample size of only 0.25 g. They also reported using only HNO_3 as extraction agent. Caution should be exercised when such a small sample size is taken for analysis as this might not be representative of the whole sample. Some acid extractable elements can be partially recovered from the soil when only HNO_3 is used for extraction.

Individual Element Commentary

Aluminium is an element strongly dependent on digestion regime. The between-laboratory coefficient of variation for Al in Sample S2 was higher (16%) than that predicted by Thomson and Horwitz (3.7%).[7] A more aggressive digestion regime that involved a longer extraction time (240 min) may explain the high results reported by Laboratory 25.

Plots of Al results versus instrumental techniques used are presented in Figure 56.



*The result reported by Laboratory 26 was excluded. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 56 S2-Al z-Results vs. Instrumental Technique

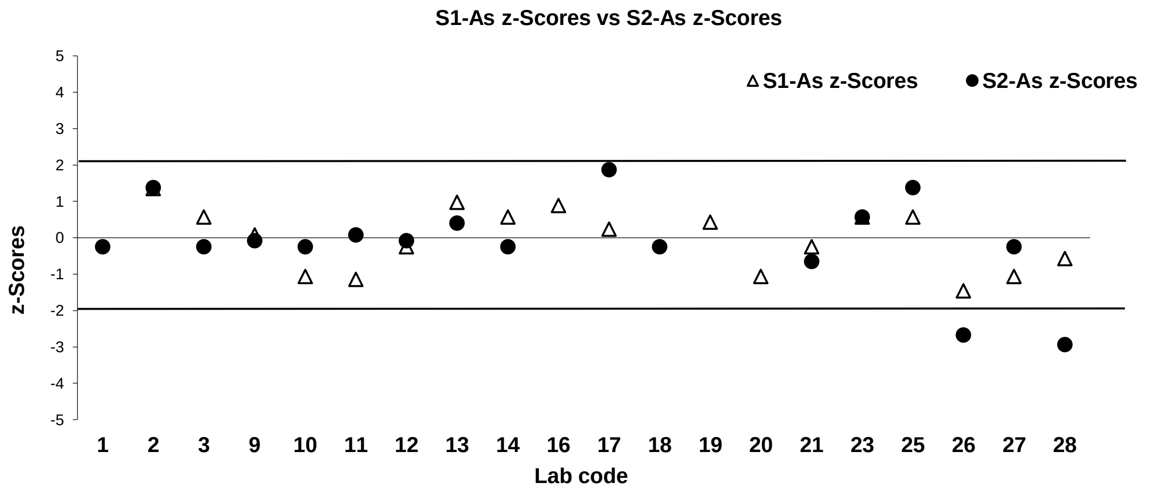
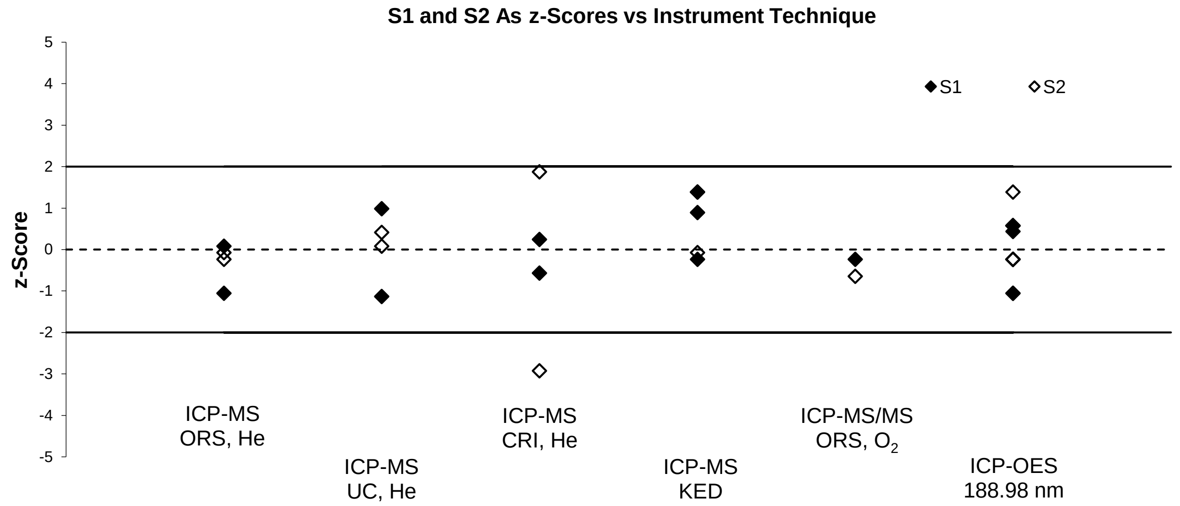


Figure 57 S1 and S2 As z-Scores vs. Laboratory Code



*The results reported by Laboratory 26 were excluded.

Figure 58 S1and S2 As z-Scores vs. Instrumental Technique

Arsenic level in S1 and in S2 was similar at 12.3 mg/kg. Laboratories 26 and 28 should review their procedure for measuring As in soil as the results they have reported returned a satisfactory z-score in S1 and unsatisfactory z-score in S2 (Figure 57).

Plots of participants' performance versus instrumental techniques used for As measurements in S1 and S2 are presented in Figure 58. Most participants used ICP-MS in collision mode.

Antimony results in S1 were variable with a large between-laboratory CV of 54%. No assigned value was set for this test. Antimony is an element whose recovery strongly depends on the acids employed for digestion. It is known that when only nitric acid is used, Sb is transformed into 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 an aqueous solution, sufficient hydrogen ion concentration must be maintained in order to prevent $SbCl_6^-$ hydrolysis.[22-24] Laboratories should consider using matrix matched control samples to assess their digestion regime and increase their estimates of uncertainty for Sb measurements in soil.

Most participants reported using ICP-MS for Sb measurement. ICP-OES with a wavelength of 206.834 nm may not be the right instrumental technique for low-level Sb measurement in soil (Figure59). Large variation was noticed between the result produced by ICP-MS in standard mode.

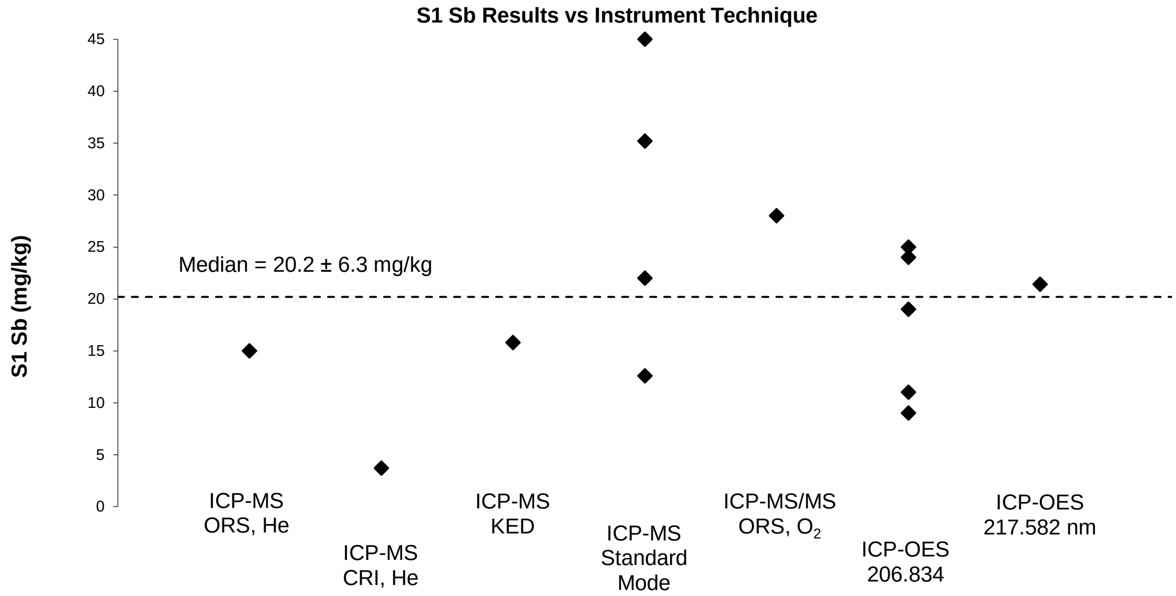


Figure 59 Sb Results vs. Instrumental Technique

Boron The between-laboratory coefficient of variation for S1 and S2 was 23% and 20% respectively, while the between -laboratory coefficient of variation predicted by Thompson and Horwitz was 13%. 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 the 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 60. Laboratory 9 should review their procedure for B measurement in soil as both of their results reported for this test in S1 and S2 returned high unsatisfactory z-scores. (Figure 61).

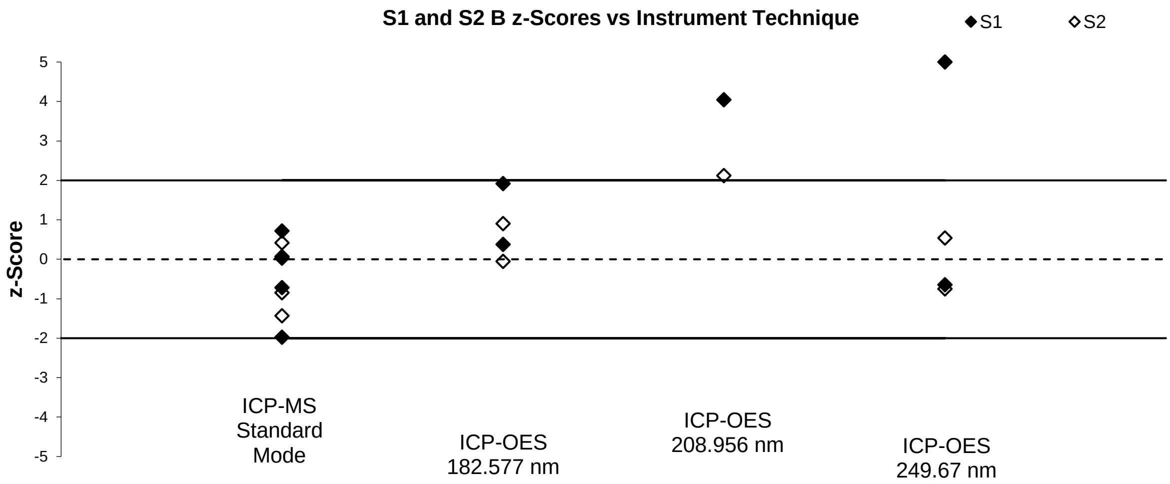


Figure 60 S1and S2 B z-Scores vs. Instrumental Technique

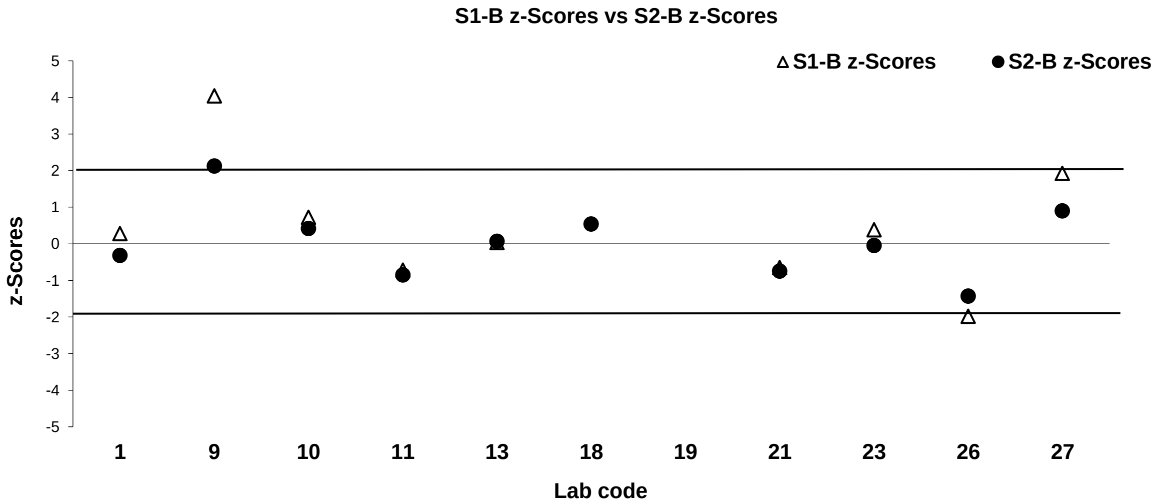


Figure 61 S1and S2 B z-Scores vs. Instrumental Technique

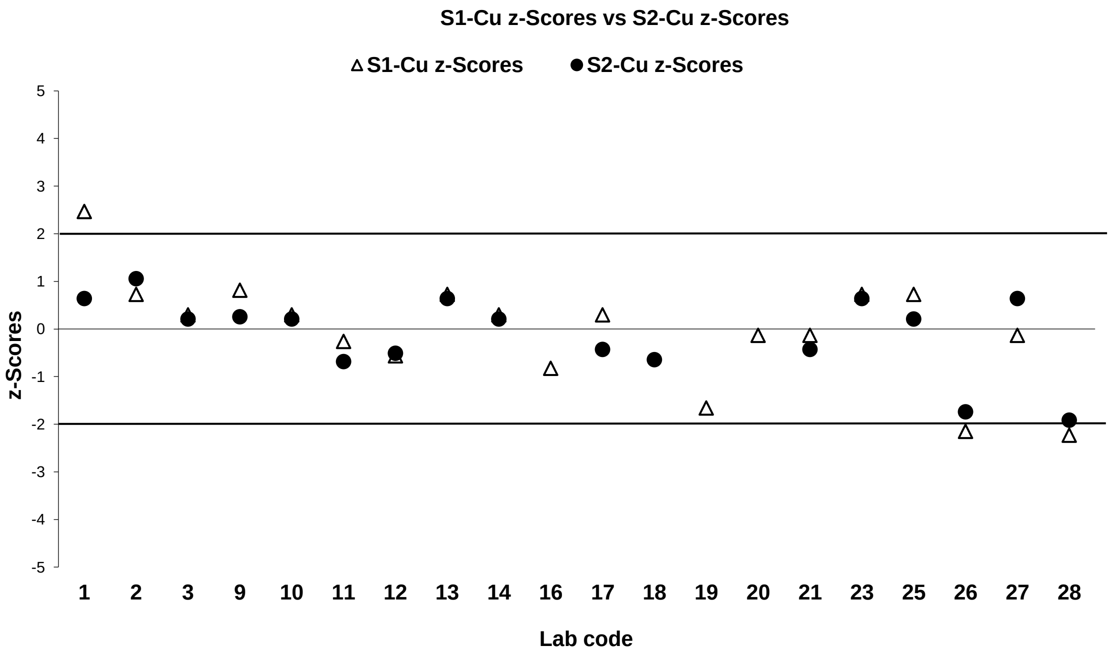
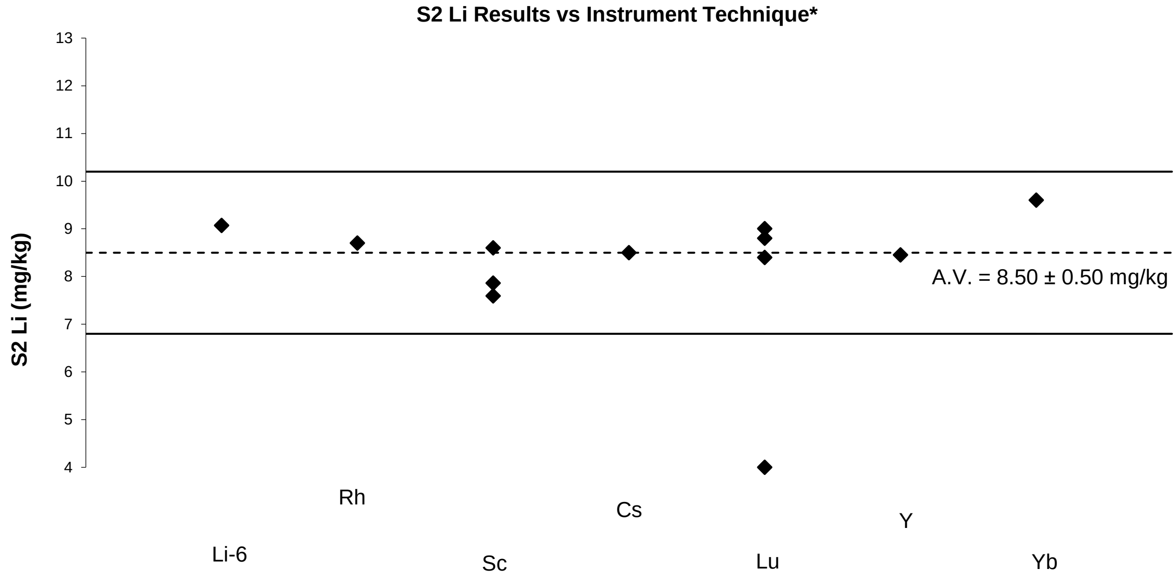


Figure 62 S1 and S2 Cu z-Scores vs. Laboratory Code

Copper The results reported by Laboratories 26 and 28, returned low z-scores in both study samples, an indication of method or laboratory bias (Figure 62). These laboratories should check their procedure for Cu measurements in soil.

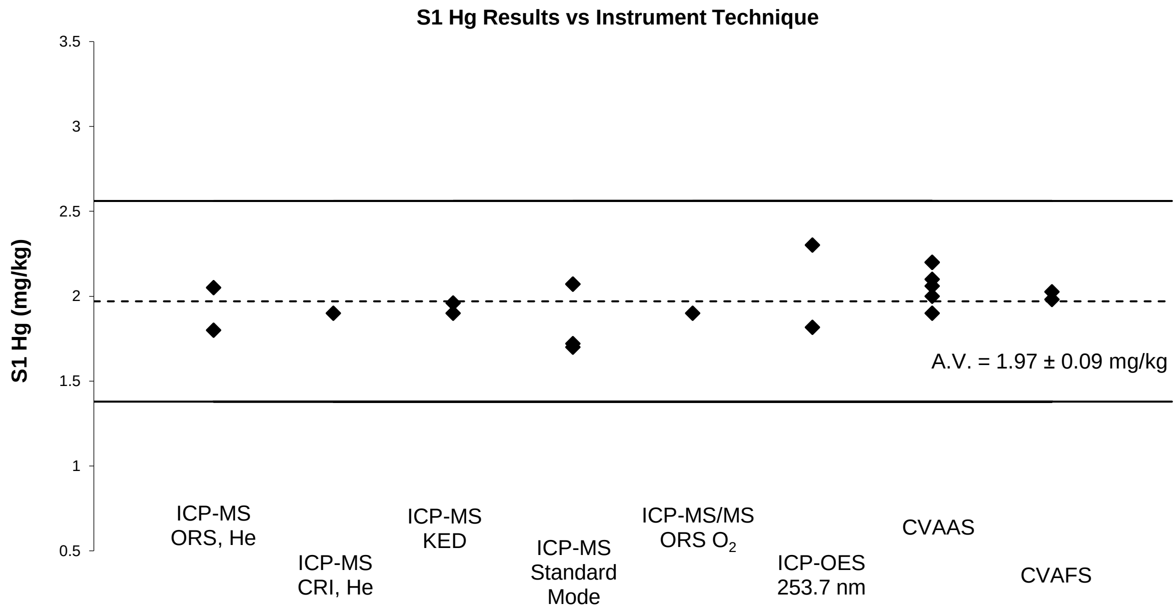
Lithium ICP-MS has low sensitivity for light elements like Li due to space-charge effects. An internal standard with similar behaviour may overcome this problem. Figure 63 presents plots of participants' results versus the internal standard used for Li measurements.



*The results reported by Laboratory 26 were excluded. Laboratory 28 result of 2.5 mg/Kg has been plotted as 4 mg/Kg. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 63 S2 Li Results vs. Internal Standard

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 64).

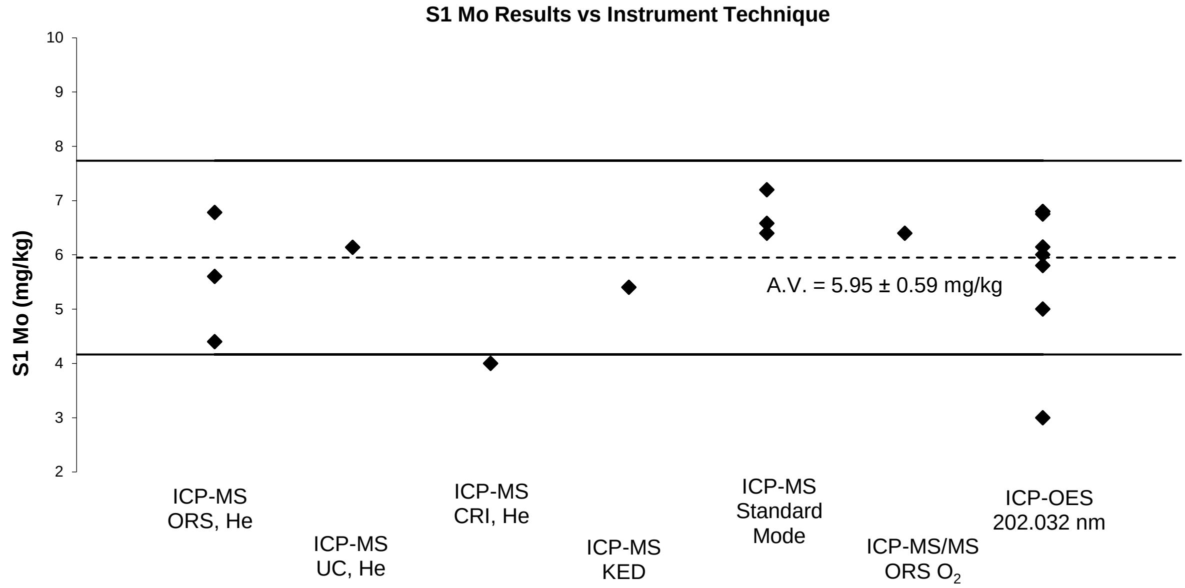


Horizontal lines on charts are the results corresponding to z-scores of 2 and -2

Figure 64 S1 Hg Results vs. Instrumental Technique

Molybdenum level in S1 was 5.95 mg/kg. Nine participants reported results using ICP-MS measurements and eight using ICP-OES measurements. All but two reported results returned satisfactory z-scores.

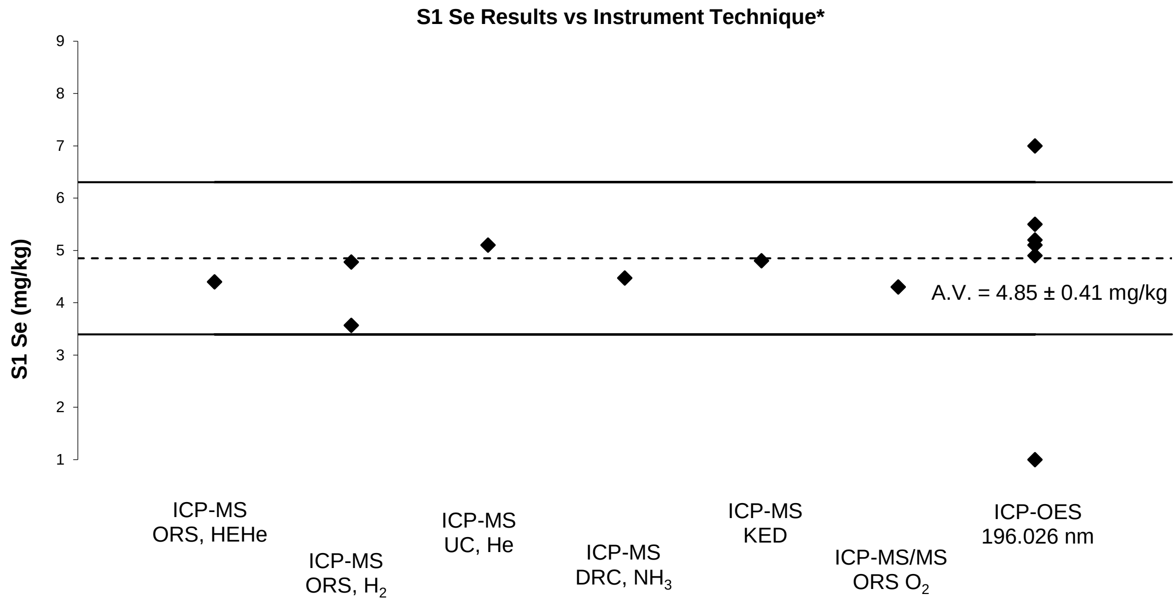
All results from ICP-MS measurements in standard mode were higher than the assigned value (Figure 65).



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

Figure 65 S1 Mo Results vs. Instrumental Technique

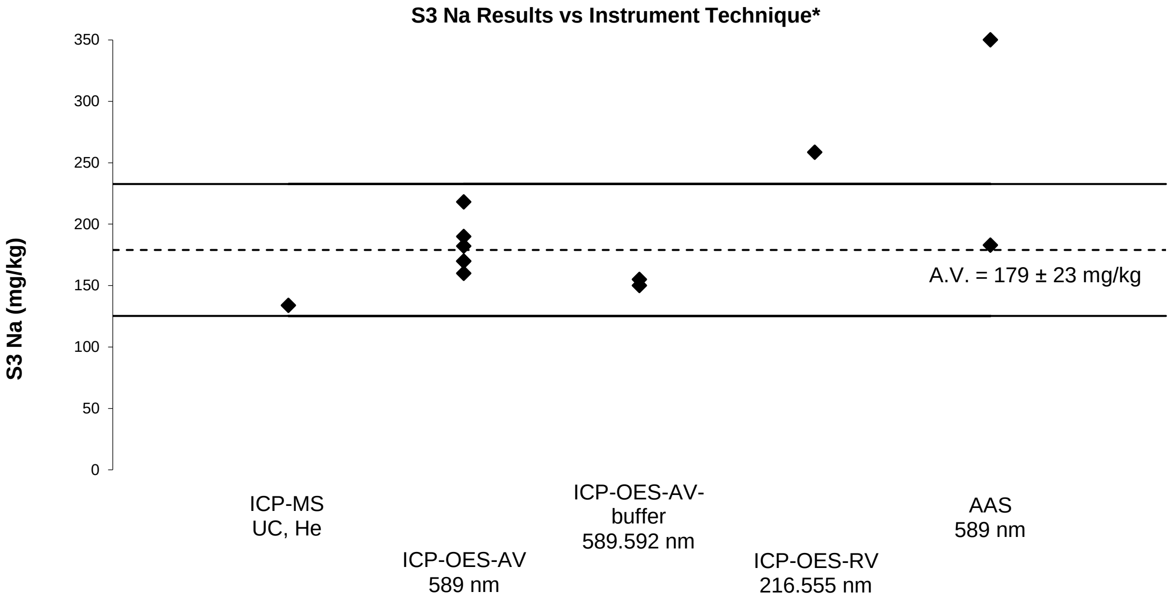
Selenium Participants' results versus the instrumental techniques used for Se measurement in S1 are presented in Figure 66. Six laboratories used ICP-OES and all used a wavelength of 196.026 nm.



*Laboratory 19 result of -5.894 mg/Kg has been plotted as 1 mg/Kg. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 66 S1 Se Results vs. Instrumental Technique

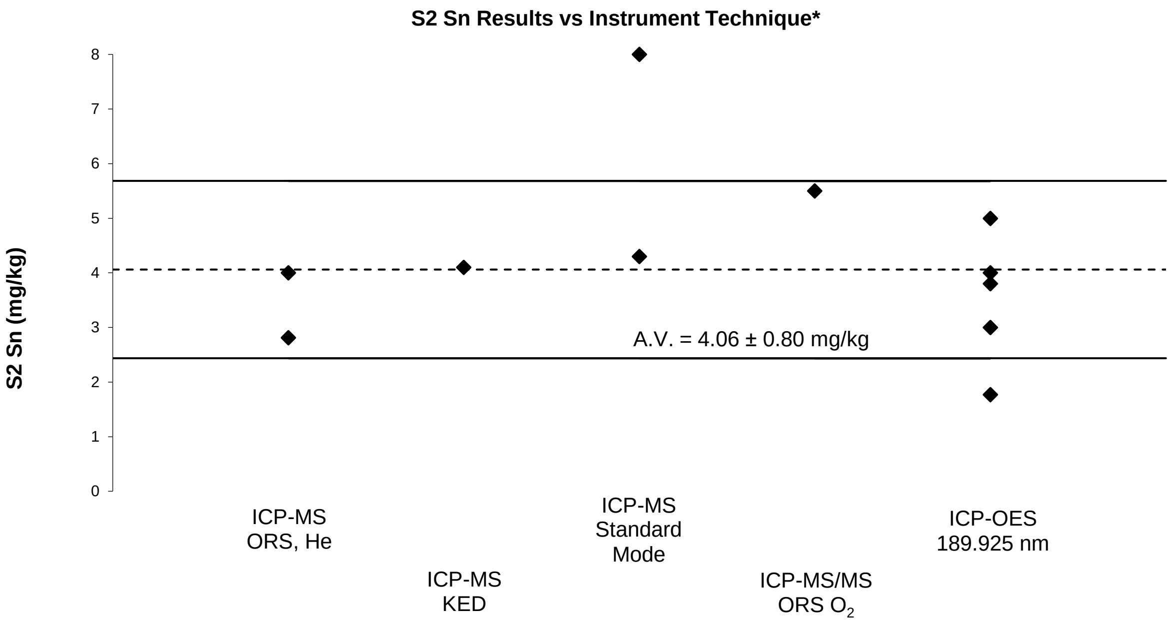
Sodium Participants' results versus the instrumental techniques used for Na measurement in S3 are presented in Figure 67. ICP-OES was the preferred measurement technique.



*Laboratory 15 result of 838.8 mg/kg has been plotted as 350 mg/kg. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 67 S3 Na Results vs. Instrumental Technique

Tin Figure 68 presents Sn results versus instrumental techniques used. ICP-OES with wavelength 189.925 nm was the preferred instrumental technique.



*Laboratory 13 result of 22.5 mg/kg has been plotted as 8 mg/kg. Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 68 S3 Sn Results vs. Instrumental Technique

Zinc z-scores versus laboratory code are presented in Figure 69. Laboratories whose Zn results are consistently lower or higher than the assigned value should check for method or laboratory bias.

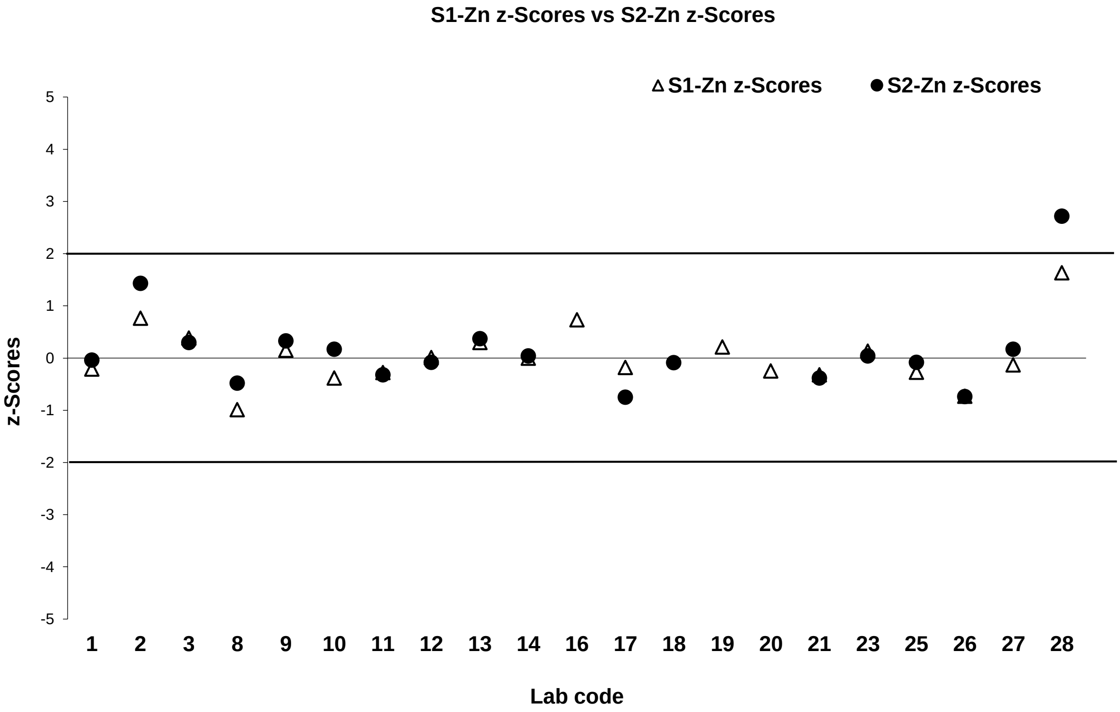


Figure 69 S1 and S2 Zn z-Scores vs Laboratory Code

6.6 Participants' Within – Laboratory Repeatability

Sample S2 was the same soil material used for Sample S1 preparation, sieved through a 250 µm sieve. Laboratories were asked to report results for As, B, Cu and Zn in both soil samples. The concentration of these analytes in the two study samples was expected to be similar.

Results reported for As, B, Cu and Zn and the expanded MU in both study samples are presented in the bar charts in Figures 70 to 73. In some cases, the results reported for these tests in the two study samples were significantly different. The results reported by Laboratories 26 and 28 for As returned satisfactory z-scores in S1 but not in S2 while the results reported by Laboratories 1, 26 and 28 for Cu returned satisfactory z-scores in S2 but not in S1. Laboratory 28 reported a satisfactory result for Zn in S1 and an unsatisfactory result is S2. The estimated uncertainties reported by Laboratory 14 for Cu in S1 and S2 were also significantly different.

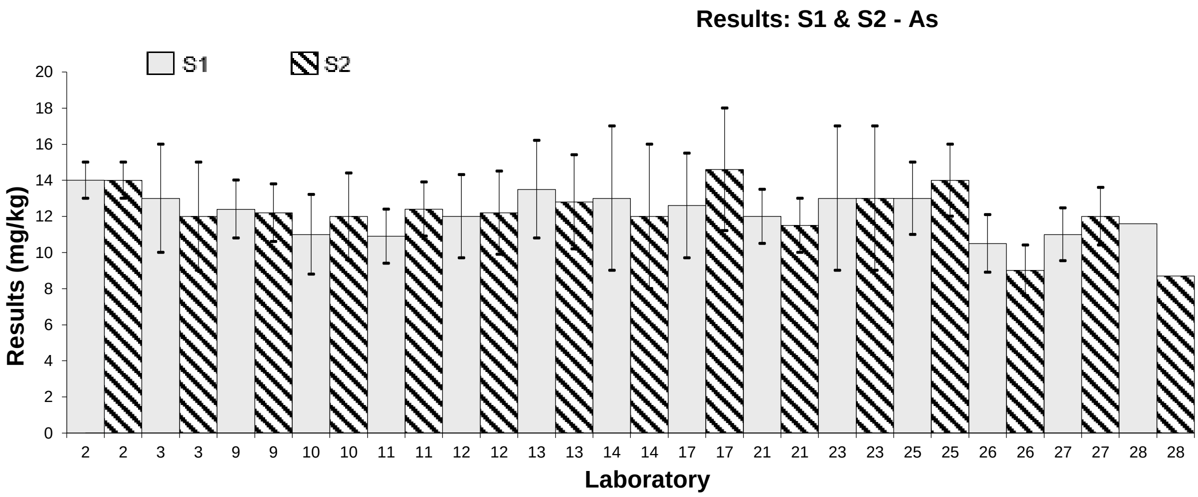


Figure 70 Bar Charts of Results for S1 and S2 – As

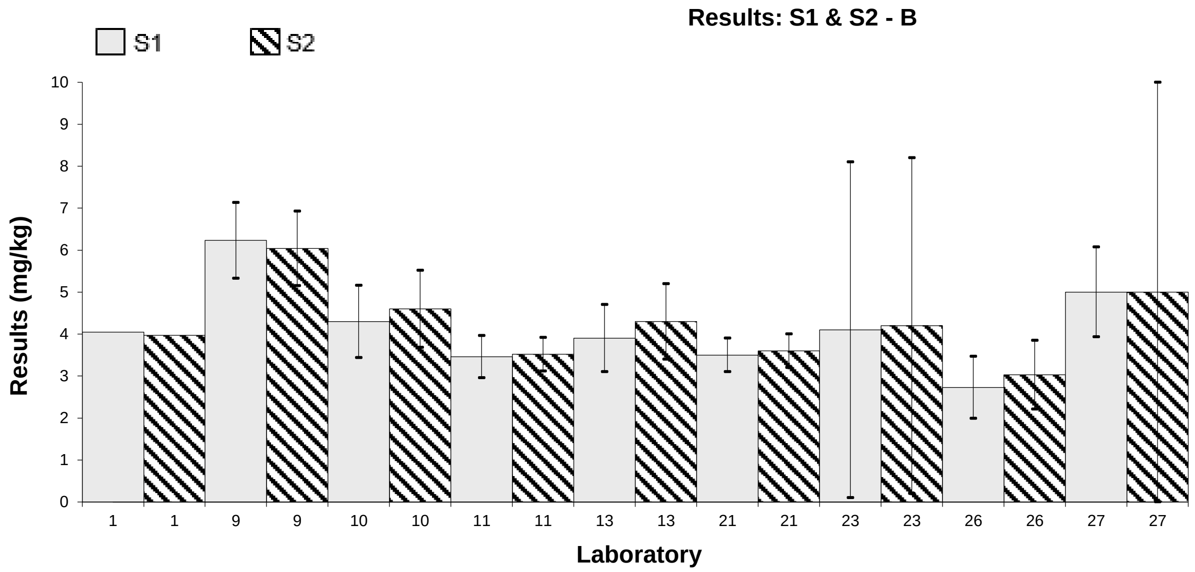


Figure 71 Bar Charts of Results for S1 and S2 – B

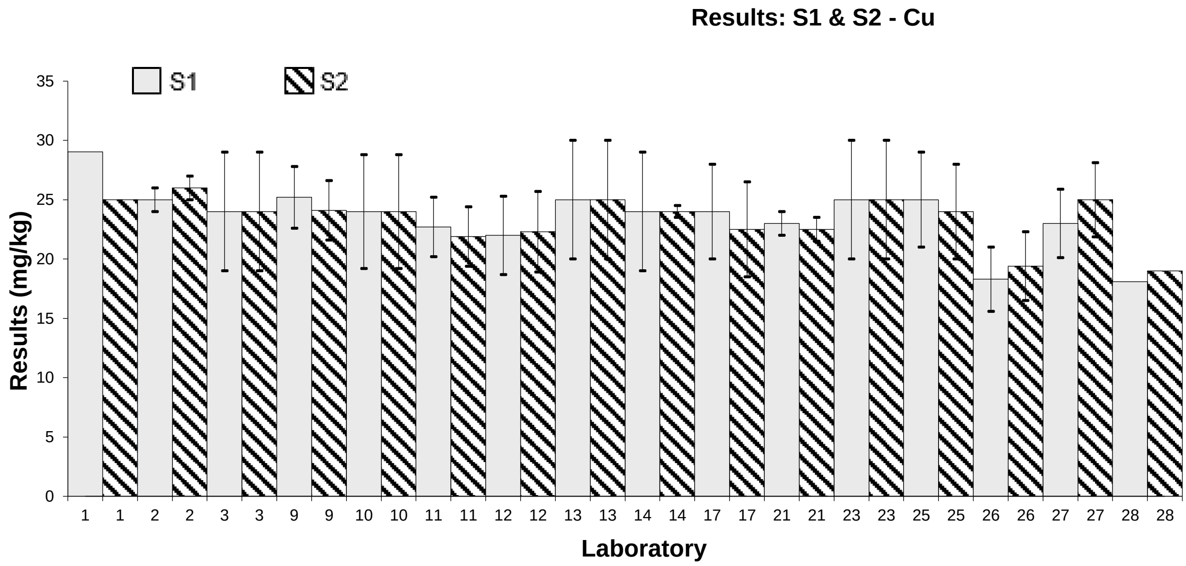


Figure 72 Bar Charts of Results for S1 and S2 –Cu

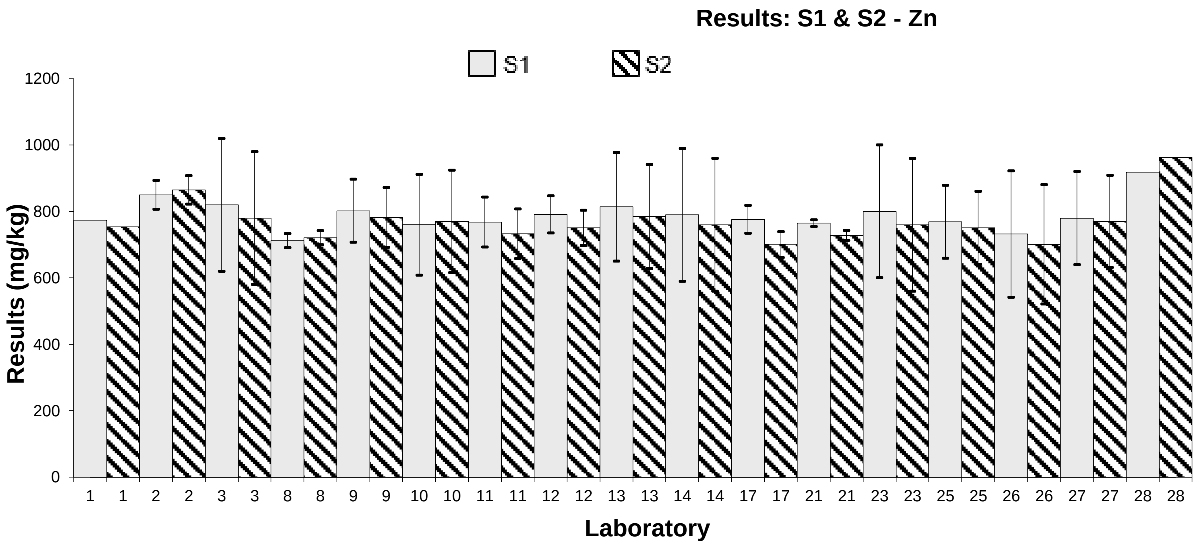


Figure 73 Bar Charts of Results for S1 and S2 –Zn

Scatter plots of z-scores in Samples S1 and S2 for As, B, Cu and Zn are presented in Figure 74 to 77. Points close to the diagonal axis represent excellent repeatability, and points close to zero represent excellent repeatability and accuracy.

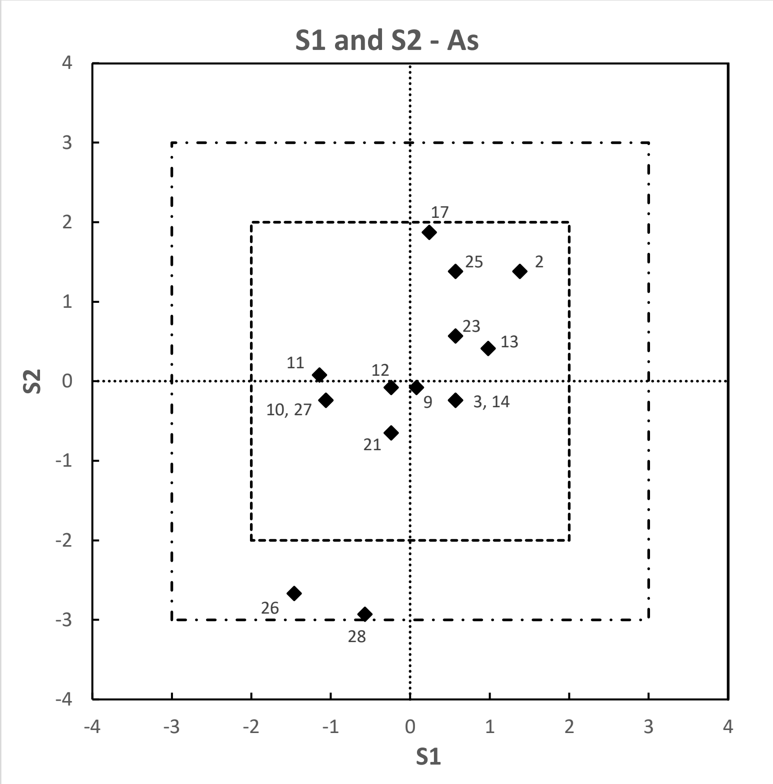


Figure 74 Scatter Plots of z-Scores for As in S1 and S2

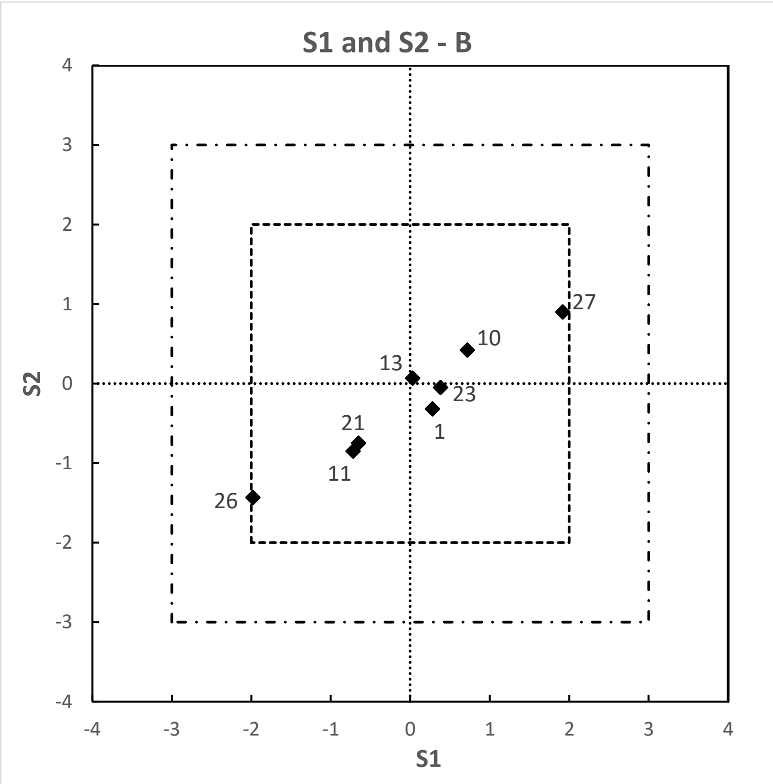


Figure 75 Scatter Plots of z-Scores for B in S1 and S2

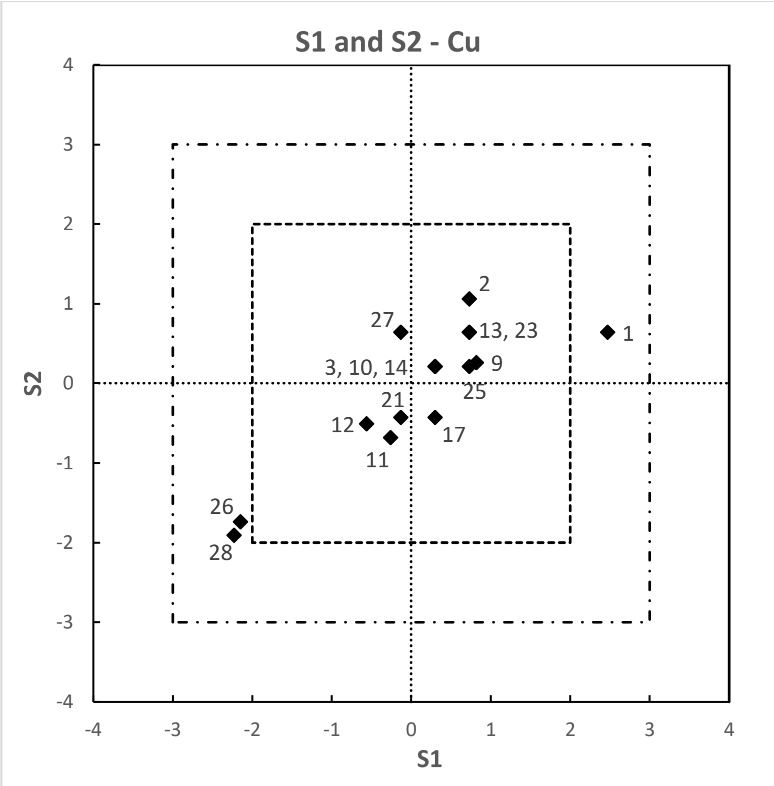


Figure 76 Scatter Plots of z-Scores for Cu in S1 and S2

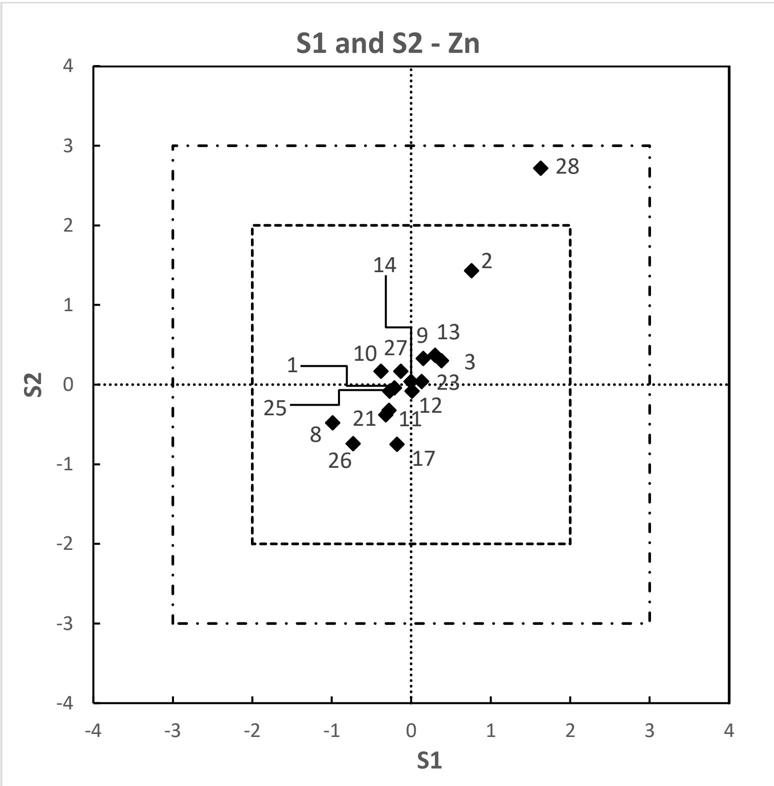


Figure 77 Scatter Plots of z-Scores for Zn in S1 and S2

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

Mineral nitrogen components, ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-), are of particular interest when soil fertility is assessed. While water can extract NO_3^--N and NO_2^- -N from a majority of soils, NH_4^+-N has to be displaced by another cation when the surface soil colloids are negatively charged.[25]

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 2 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 78.

Problems with sample preparation/dilution procedure may explain laboratory 10 result of 120 mg/kg.

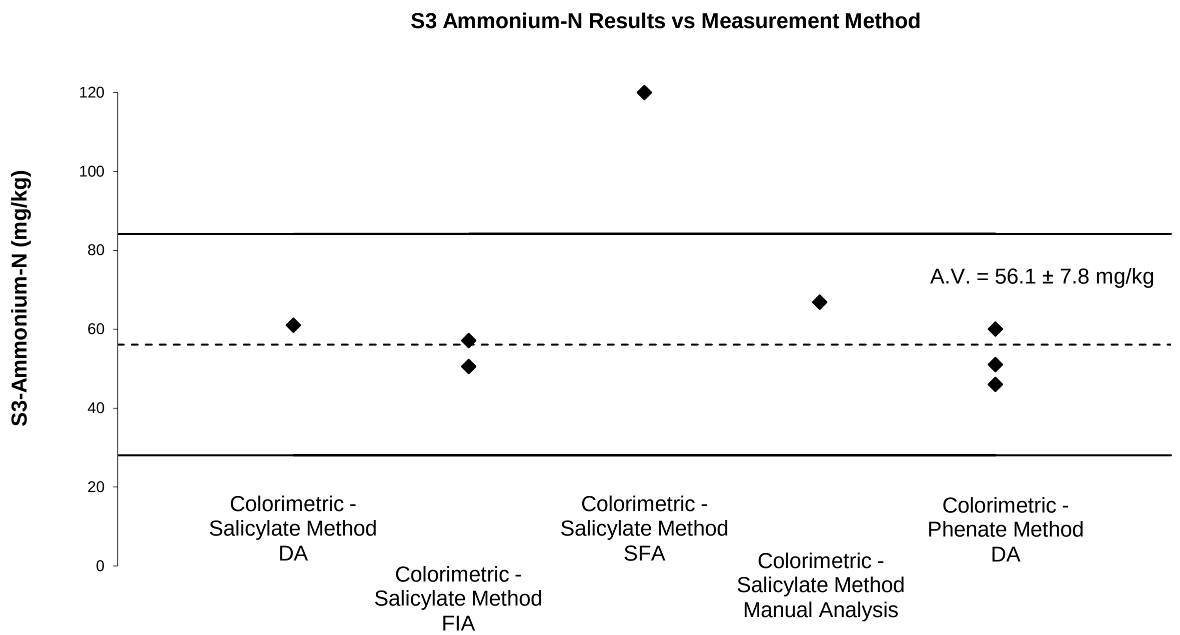
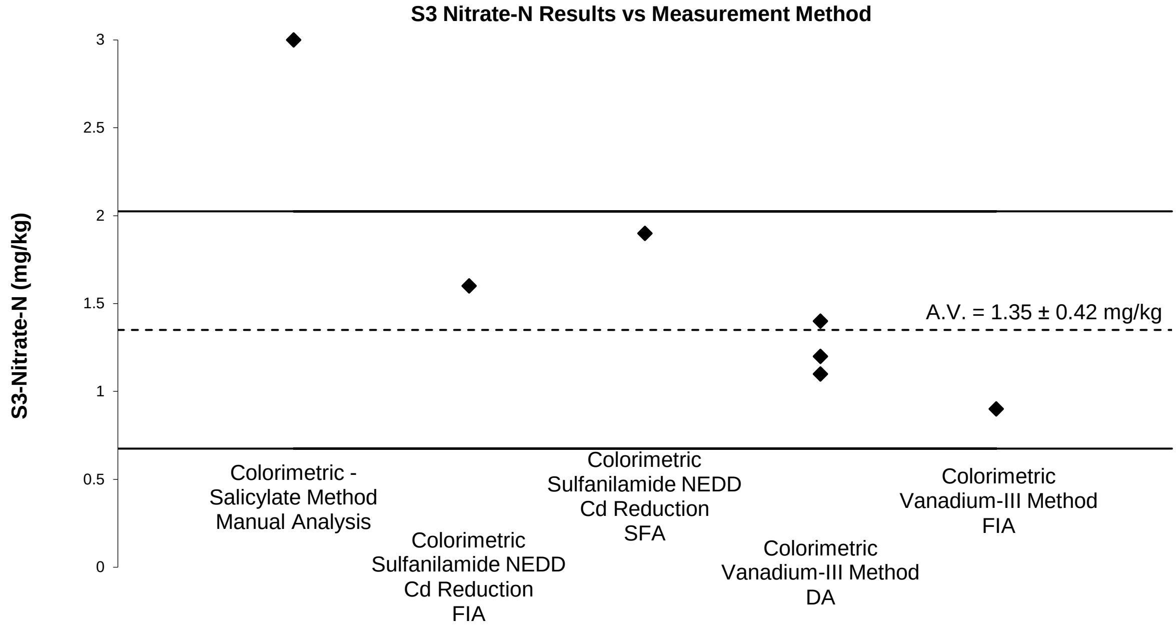


Figure 78 S3-NH_4^+-N Results vs. Analytical Method and Measurement Technique

2M KCl Extractable Nitrate-Nitrogen The measurement method used by most laboratories involved NO_3^--N reduction to NO_2^--N by passage of the clarified soil extract through a Cd-Cu reduction column followed by NO_x (the reduced NO_2^--N plus original NO_2^--N) measurements. NO_x was determined colorimetrically based on Griess-Ilosvay reaction and NO_3^--N calculated by subtracting NO_2^--N value (obtained by analysis without passing the sample through the Cd-Cu reduction column), from the NO_x value.

Three laboratories used trivalent V for NO_3^--N reduction to NO_2^--N (Figure 79).



*Laboratory 3 result of 11.67 has been plotted as 3 mg/kg.

Figure 79: S3-NO_3^--N Results vs. Measurement Technique

6.8 Participants' Results and Analytical Methods for Total Kjeldahl Nitrogen

TKN assigned value was 3770 mg/kg. All results reported for TKN in S3, returned satisfactory z-score. Plots of participants' results versus analytical method and measurement technique used are presented in Figure 80.

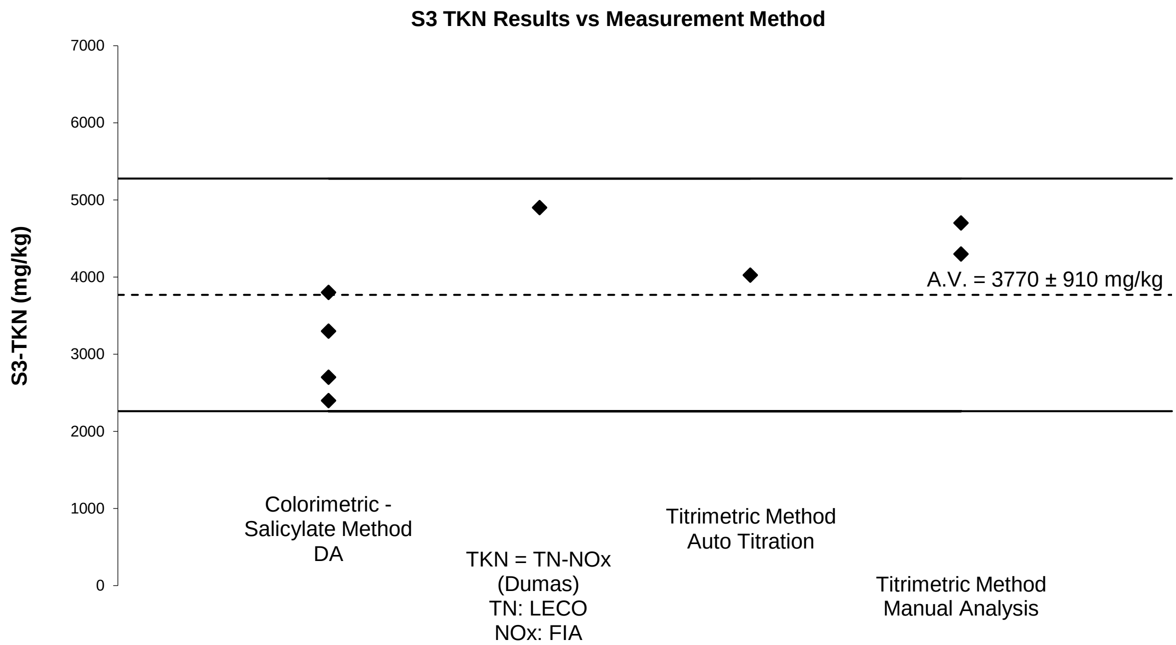


Figure 80 S3-TKN Results vs. Measurement Technique

6.9 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.[24, 25] 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 a 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

Bromide Only 6 laboratories reported results for bromide in S3. The results reported by Laboratories 3, 10, 14 and 23 were in good agreement with each other and with the homogeneity value of 1.1 mg/kg. All laboratories used the Ion chromatographic Method.

Chloride level in S3 was low, close to the reporting level of many participants, which may have challenged their analytical techniques (Figure 81).

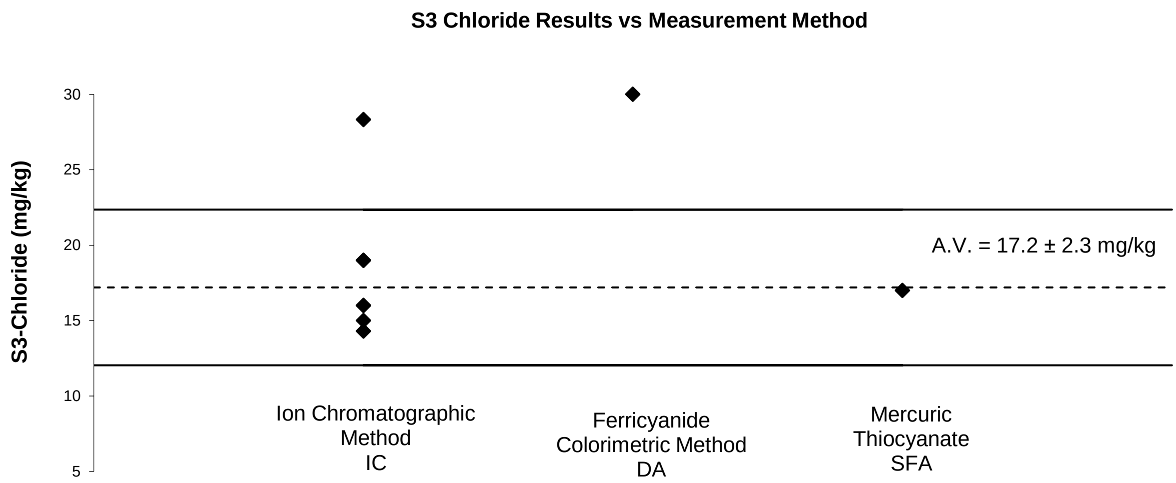


Figure 81 S3-Chloride Results vs. Measurement Technique

Caution should be exercised when a colorimetric method is used for the measurements of low-level chloride in soil samples. Spectrophotometry has low specificity and is liable to interference from coloured species.

Table 66 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 66 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.

Sulphate A distribution of participants' results with the analytical method used is presented in Figure 82.

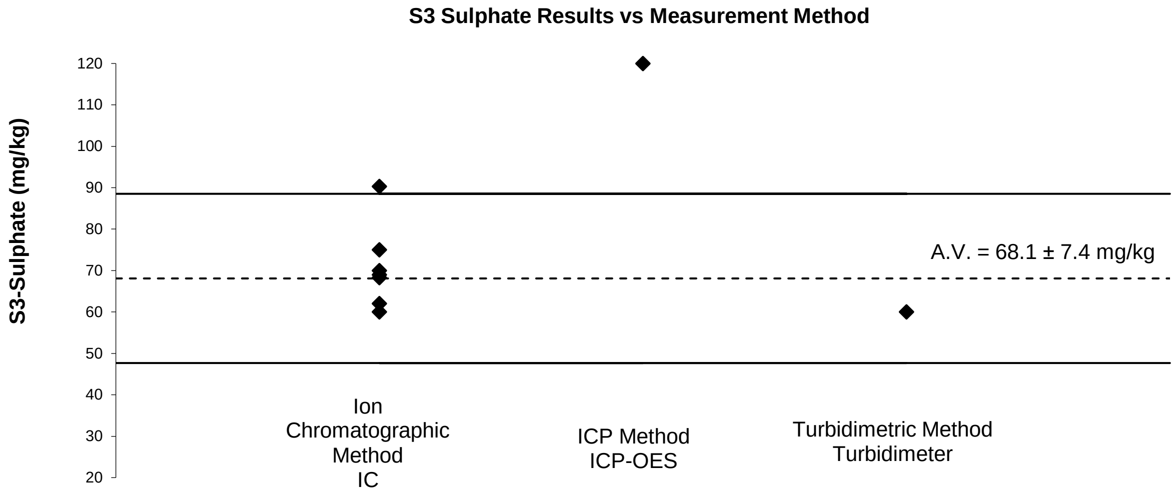


Figure 82 S3-Sulphate Results vs. Measurement Technique

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.

Orthophosphate-P level in S3 was low, which may explain the variability in participants' results with a the between-laboratory CV of 24%. Ascorbic acid colorimetric method was the most popular method used by participants for the measurement of orthophosphate-P (Figure 83).

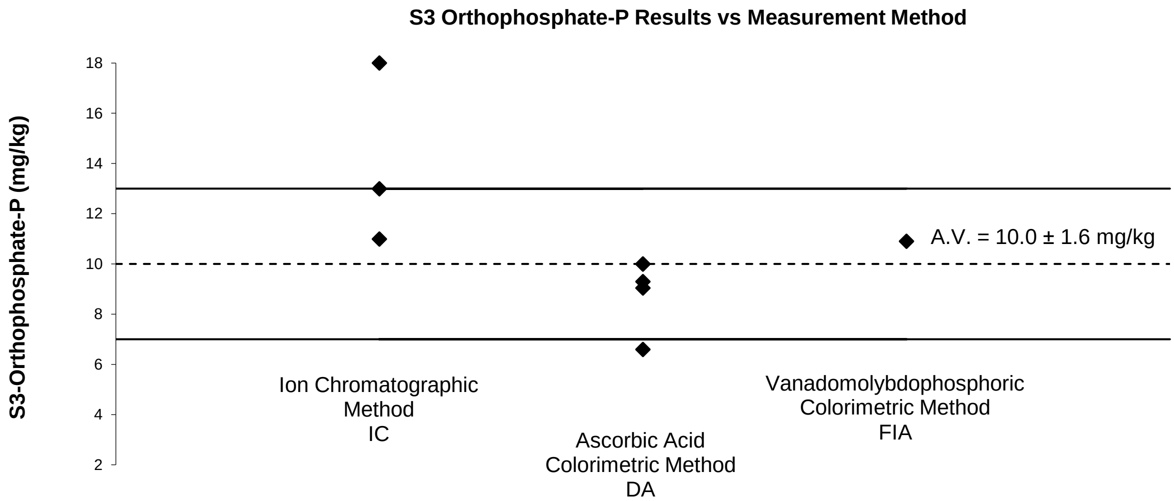


Figure 83 S3-Orthophosphate-P Results vs. Method

6.10 Comparison with Previous NMI Proficiency Tests Studies of Metals in Soil

AQA 23-16 is the 33rd NMI proficiency study of inorganic analytes in soil. A summary of participants' performance over the last 24 studies (2012 to 2023) is presented in Figure 84.

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.

6.11 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 67).

Table 67 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1, 4, 6, 7	CRM
2	Trace Metals - Sandy Loam 10. Lot # LRAB2288
8	AGAL-10, AGAL-12
10	Agal 10 & Agal 12
11	AGAL 12 (metals) In house AG reference
12	Agal-12 Biosoil
14	SS
15	Clean Sandy Loam
16	AGAL 10 / AGAL 12
17	CRM036
18	AGAL-12
20	RM
21	AQA 19-02 S2, AQA 20-13 S1,S2 and In house QC soil samples
22	ASPAC 7098-C1
24	SS
25	RM

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'*[26]

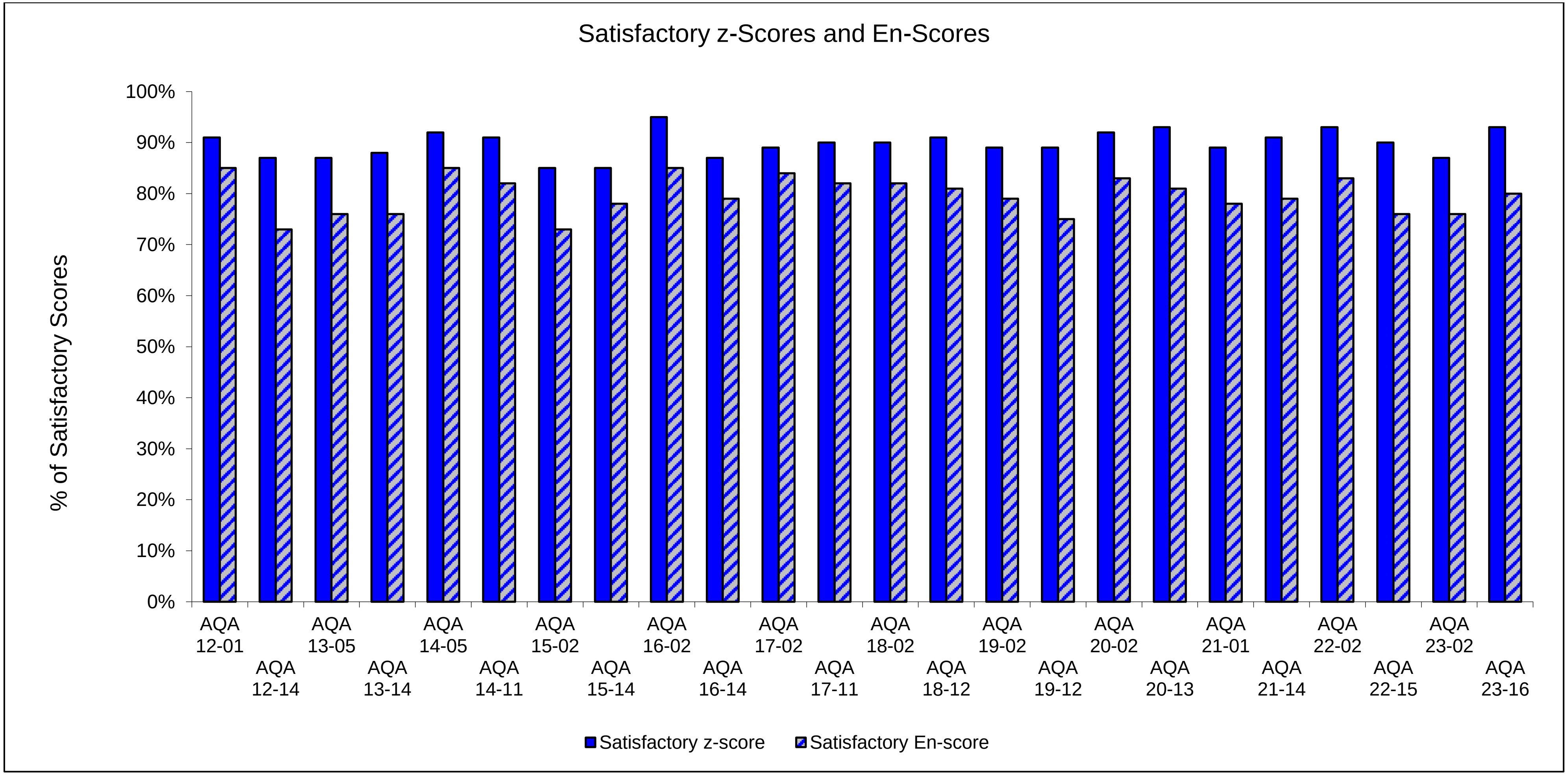


Figure 84 Participants' Performance over Time

7 REFERENCES

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

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Samples S1 and S2 were prepared as part of a preparation trial run for the reference material for acid extractable elements in soil MX 022. Sample S1 was soil from a contaminated site fortified for 6 elements, ground and then sieved through a 0.350 µm sieve. Sample S2 was prepared from the same soil material and sieved through a sieve size of 0.250 µm.

Sample S3 was an agricultural soil material grind, sieved, 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 water-soluble anions sample S3 with the exception of exception of iodide 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 all acid extractable elements in S1 and S2. Homogeneity testing was based on that described in the International Harmonised Protocol from Proficiency Testing.[4] Minimum 6 bottles from S1 and S2 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 68 sets out an example for the testing of the homogeneity of chloride in Sample S3.

Table 68 Homogeneity Testing of chloride in Sample S3

BOTTLE	A Cd (mg/kg)	B Cd (mg/kg)
1	2.80	2.90
17	2.60	2.90
27	2.90	2.90
38	2.70	2.80
43	3.10	2.80
54	2.71	2.90
69	2.80	2.90

	Value	Critical	Result
Cochran	0.27	0.60	**Pass**
S_{an}/σ	0.45	0.5	**Pass**
s^2_{sam}	0.001	0.03	**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°C ± 5°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 69.

Table 69 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
Bi	ICP-MS	Ir	ORS	He	800	NA	209 m/z
Ca	ICP-OES	Y	NA	NA	NA	800	422.673 nm
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
Cs	ICP-MS	Rh	ORS	He	800	NA	133 m/z
Cu	ICP-MS	Rh	ORS	He	800	NA	65 m/z
Fe	ICP-OES	Y	NA	NA	NA	800	238.204 nm
Hg	ICP-MS	Rh	NA	NA	800	NA	201 m/z
K	ICP-OES	Y	NA	NA	NA	800	766.491 nm
La	ICP-MS	Rh	ORS	He	800	NA	139 m/z
Li	ICP-MS	Rh	ORS	He	800	NA	7 m/z
Mg	ICP-OES	Y	NA	NA	NA	800	279.078 nm
Mn	ICP-MS	Rh	ORS	He	800	NA	55 m/z
Mo	ICP-MS	Rh	ORS	He	800	NA	95 m/z
Na	ICP-OES	Y	NA	NA	NA	800	588.995 nm
Ni	ICP-MS	Rh	ORS	He	800	NA	60 m/z
P	ICP-OES	Y	NA	NA	NA	800	177.434 nm
Pb	ICP-MS	Ir	ORS	He	800	NA	Average of 206, 207, 208 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-OES	Y	NA	NA	NA	800	430.544 nm
Th	ICP-MS	Ir	ORS	He	800	NA	232 m/z
Tl	ICP-MS	Rh	ORS	He	800	NA	205 m/z
U	ICP-MS	Ir	ORS	He	800	NA	238 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

Analyses for all the tests other than acid extractable elements were conducted by NMI Inorganics section.

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 70.

Table 70 Summary of the Measurement Methods and Instrumental Techniques used by NMI

Anion	Measurement Method	Instrument
Total Kjeldahl Nitrogen	Titrimetric Method	Manual Analysis
Water Soluble Bromide	Ion Chromatographic Method	IC
Water Soluble Chloride	Ion Chromatographic Method	IC
Water Soluble Fluoride	Ion Selective Electrode 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_N 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'.[6] The uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 71.

Table 71 Uncertainty of Assigned Value for As in Sample S1

No. results (p)	18
Robust Average	12.3 mg/kg
$S_{rob\ av}$	1.19 mg/kg
$u_{rob\ av}$	0.35 mg/kg
k	2
$U_{rob\ av}$	0.7 mg/kg

The assigned value for **As** in Sample S1 is **12.3 ± 0.7 mg/kg**.

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 1 and Equation 2 respectively (see page 18). A worked example is set out below in Table 72.

Table 72 z-Score and E_n-score for As Result Reported by Laboratory 2 in S1

As Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E_n-Score
14 ± 1	12.3 ± 0.7	10% as CV or 0.10 x 12.3= =1.23 mg/kg	$z = \frac{(14 - 12.3)}{1.23}$ z = 1.38	$En = \frac{(14 - 12.3)}{\sqrt{1^2 + 0.7^2}}$ E_n=1.39

APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10] An example is given. Between 2009 and 2023 NMI carried out 29 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 73 and 74).

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 73 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
AQA 23-02	S1 – Soil	4.41	4.12	5.9	16
AQA 23-02	S2 - Sludge	4.41	4.8	24	8
Average				12*	

* The mean value of robust CV was used. ** The mean value of Robust CV was used.

Table 74 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. ** The mean value of Robust CV was used.

Table 75 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 75 Uncertainty of As Results Estimated Using PT Data.

Results mg/kg	Uncertainty mg/kg
1.00	0.24
5.0	1.2
20.0	3.8
75	14
100	19

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.[8]

APPENDIX 4 - INSTRUMENT DETAILS

Table 76 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)
3	ICP-OES-AV	Lutetium	NA	NA	NA	50-1000	328.068nm
9	ICP-MS	Rh	ORS	He	0.1	NA	107
10	ICP-MS	Rh	ORS	He	800	NA	107
11	ICP-MS	Rh	NA	NA	625	NA	109
12	ICP-MS	Rh	KED	He	2000	NA	109
13	ICP-MS	Rh	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	328.068
17	ICP-MS	In	NA	standard mode	10	NA	107
18	ICP-MS	Y	CRI	O2	50	NA	107
21	ICP-MS/MS	Rh103	ORS	O2	1600	NA	Ag 107/107(m/z)
23	ICP-OES-AV	Lu	NA	NA	NA	25	328.289
26	ICP-MS	103	ORS	He	1000	NA	107
27	ICP-OES-AV	Lu			83	NA	328.068
28	ICP-MS		CRI			NA	

Table 77 Instrument Conditions Al

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		He	1000	NA	26.982
3	ICP-OES-AV	Lutetium	NA	NA	NA	50	236.705nm
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	237.312
10	ICP-MS	Rh	ORS	He	800	NA	27
11	ICP-MS	Sc	UC	He	625	NA	27
12	ICP-MS	Sc	KED	He	2000	NA	27
13	ICP-MS	Sc	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	237.312
17	ICP-OES-AV-buffer	Y				NA	394.401
18	ICP-OES-AV	Yb			50	NA	396.15
21	ICP-OES-AV	In 303.936	NA	NA	80	NA	Al 237.312
23	ICP-OES-AV	Lu	NA	NA	NA	2500	236.705
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	256.798 (nm)
26	ICP-MS	72	ORS	standard mode	1000	NA	27
27	ICP-OES-AV	Lu			83	NA	396.152
28	ICP-OES-AV					NA	

Table 78 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)
2	ICP-MS	Rh		He	1000	NA	74.922
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	188.98nm
8	ICP-OES-AV	NA				NA	188.982
9	ICP-MS	Ge	ORS	He	0.1	NA	75
10	ICP-MS	Rh	ORS	He	800	NA	75
11	ICP-MS	Ge	UC	He	625	NA	75
12	ICP-MS	Rh	KED	He	1000	NA	75
13	ICP-MS	Rh	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	188.98
17	ICP-MS	Ge	CRI	He	10	NA	75
18	ICP-OES-AV	Yb			50	NA	188.98
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	188.979
20	ICP-OES-AV	nil	NA		20	NA	
21	ICP-MS/MS	Rh103	ORS	O2	1600	NA	As 75/91(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	25	188.98
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	188.98 (nm)
26	ICP-MS	72	ORS	He	1000	NA	75
27	ICP-OES-AV	Lu			83	NA	188.98
28	ICP-MS		CRI			NA	

Table 79 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	208.956nm
8	ICP-OES-AV	NA				NA	208.957
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	208.956
10	ICP-MS	NA	NA	NA	800	NA	11
11	ICP-MS	Sc	NA	NA	625	NA	10
12	ICP-MS	Sc	KED	He	1000	NA	11
13	ICP-MS	Sc	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	208.956
17	ICP-OES-AV	Y				NA	208.957
18	ICP-OES-AV	Yb			50	NA	249.67
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	249.677
21	ICP-OES-AV	In 303.936	NA	NA	80	NA	B 249.678
23	ICP-OES-AV	Lu	NA	NA	20	NA	182.577
26	ICP-MS	89	ORS	standard mode	500	NA	11
27	ICP-OES-AV	Lu			83	NA	182.577
28	ICP-MS		CRI			NA	

Table 80 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)
3	ICP-OES-AV	Lutetium	NA	NA	NA	50-1000	230.424nm
8	ICP-OES-AV	NA				NA	233.527
9	ICP-OES-RV	Lu	NA	NA	0.1	NA	455.403
10	ICP-MS	Rh	ORS	He	800	NA	134Mini
11	ICP-MS	Rh	NA	NA	625	NA	138
12	ICP-MS	Tb	KED	He	2000	NA	137
13	ICP-MS	In	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	455.403
17	ICP-OES-AV-buffer	Y				NA	233.527
18	ICP-OES-AV	Yb			50	NA	493.4
21	ICP-OES-AV	Eu 390.711	NA	NA	80	NA	Ba 455.403
23	ICP-OES-AV	Lu	NA	NA	NA	25	230.424
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	585.367 (nm)
26	ICP-MS	159	ORS	He	1000	NA	137
27	ICP-OES-AV	Lu			83	NA	493.408
28	ICP-MS		CRI			NA	

Table 81 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	313.042nm
8	ICP-OES-AV	NA				NA	313.107
9	ICP-MS	Li6	ORS	He	0.1	NA	9
10	ICP-MS	NA	NA	NA	800	NA	9
11	ICP-MS	Sc	NA	NA	625	NA	9
12	ICP-MS	Sc	KED	He	2000	NA	9
13	ICP-MS	Sc	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	234.861
17	ICP-MS	Sc	NA	standard mode	10	NA	9
18	ICP-OES-AV	Yb			50	NA	313.04
21	ICP-MS/MS	Sc 45/61	ORS	No Gas	1600	NA	Be 9/9(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	NA	313.107
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	234.861 (nm)
26	ICP-MS	72	ORS	standard mode	1000	NA	9
27	ICP-OES-AV	Lu			83	NA	313.042

Table 82 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)
3	ICP-OES-AV	Lutetium	NA	NA	50	NA	315.887nm
5	ICP-OES	Cs, Y	NA	NA	NA	500	315.887 nm
8	ICP-OES-RV	NA			NA		317.933
10	ICP-MS	Rh	ORS	He	NA	800	43Mini
11	ICP-MS	Sc	UC	He	NA	625	44
14	ICP-OES-RV	Lu	NA	NA	50	50	315.887
15	Other				NA		422.7
17	ICP-OES-AV-buffer	Y			NA		315.887
23	ICP-OES-AV	Lu	NA	NA	400	NA	315.887
24	AAS	NA	NA	NA	NA	20	422.7
28	ICP-OES-AV				NA		

Table 83 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)
2	ICP-MS	Rh		He	1000	NA	110.904
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	214.439nm
8	ICP-OES-AV	NA				NA	228.802
9	ICP-MS	In	ORS	He	0.1	NA	111
10	ICP-MS	Rh	ORS	He	800	NA	111
11	ICP-MS	Rh	NA	NA	625	NA	111
12	ICP-MS	Rh	KED	He	1000	NA	111
13	ICP-MS	Rh	NA		250	NA	
14	ICP-OES-AV-equation	Lu	NA	NA	50	50	214.439
17	ICP-MS	In	UC	standard mode	10	NA	111
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	288.802
20	ICP-OES-AV	nil			20	NA	
21	ICP-OES-AV	Lu219.55 6	NA	NA	80	NA	Cd 226.502
23	ICP-OES-AV	Lu	NA	NA	20	25	228.802
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	228.802 (nm)
26	ICP-MS	103	ORS	He	1000	NA	111
27	ICP-OES-AV	Lu			83	NA	214.439
28	ICP-MS		CRI			NA	

Table 84 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)
2	ICP-MS	Rh		He	1000	NA	58.933
3	ICP-OES-AV	Lutetium	NA	NA	NA	50-1000	231.160nm
8	ICP-OES-AV	NA				NA	228.616
9	ICP-MS	Ge	ORS	He	0.1	NA	59
10	ICP-MS	Rh	ORS	He	800	NA	59
11	ICP-MS	Ge	UC	He	625	NA	59
12	ICP-MS	Ga	KED	He	2000	NA	59
13	ICP-MS	Rh	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	230.786
17	ICP-MS	Ga	CRI	He	10	NA	59
18	ICP-OES-AV	Yb			50	NA	228.8
21	ICP-OES-AV	Lu219.55 6	NA	NA	80	NA	Co 228.615
23	ICP-OES-AV	Lu	NA	NA	NA	25	228.615
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	230.786 (nm)
26	ICP-MS	103	ORS	He	1000	NA	59
27	ICP-OES-AV	Lu			83	NA	230.786

Table 85 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)
2	ICP-MS	Rh		He	1000	NA	51.941
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	205.560nm
8	ICP-OES-AV	NA				NA	267.716
9	ICP-MS	Ge	ORS	He	0.1	NA	52
10	ICP-MS	Rh	ORS	He	800	NA	52
11	ICP-MS	Sc	UC	He	625	NA	52
12	ICP-MS	Sc	KED	He	1000	NA	52
13	ICP-MS	Sc	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	267.716
17	ICP-OES-AV-buffer	Y				NA	205.56
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	267.716
20	ICP-OES-AV	nil			20	NA	
21	ICP-MS/MS	Sc 45	ORS	O2	1600	NA	Cr 52/52(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	NA	205.56
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	267.716 (nm)
26	ICP-MS	72	ORS	He	1000	NA	52
27	ICP-OES-AV	Lu			83	NA	267.716
28	ICP-MS		CRI			NA	

Table 86 Instrument Conditions Cs

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)
3	ICP-MS		ORS	No Gas	NA	1000	133m/z
10	ICP-MS	Rh	ORS	He	800	NA	133
12	ICP-MS	Tb	KED	He	2000	NA	133
13	ICP-MS	Rh	NA	He	250	NA	
14	ICP-MS	Lu	ORS	standard mode	1000	1000	133
18	ICP-OES-AV	Tb			50	NA	133
23	ICP-MS	Ge	NA	NA	20	NA	107.846
26	ICP-MS	159	ORS	He	1000	NA	133
27	ICP-OES-AV	Lu			NT	NA	NT

Table 87 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)
2	ICP-MS	Rh		He	1000	NA	62.93
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	324.754nm
8	ICP-OES-AV	NA				NA	324.752
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	324.754
10	ICP-MS	Rh	ORS	He	800	NA	63Mini
11	ICP-MS	Ge	UC	He	625	NA	63
12	ICP-MS	Ga	KED	He	1000	NA	63
13	ICP-MS	Ga	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	324.754
17	ICP-OES-AV-buffer	Y				NA	324.752
18	ICP-OES-AV	Yb			50	NA	324.75
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	327.393
20	ICP-OES-AV	nil			20	NA	
21	ICP-OES-AV	In 303.936	NA	NA	80	NA	Cu 327.395
23	ICP-OES-AV	Lu	NA	NA	20	25	324.754
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	327.395 (nm)
26	ICP-MS	103	ORS	He	1000	NA	63
27	ICP-OES-AV	Lu			83	NA	327.395
28	ICP-MS		CRI			NA	

Table 88 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-MS	Rh		He	NA	1000	55.935
3	ICP-OES-AV	Lutetium	NA	NA	50	NA	234.350nm
5	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	NA	500	57 m/z
8	ICP-OES-RV	NA			NA		238.204
10	ICP-MS	Rh	ORS	He	NA	800	56Mini
11	ICP-MS	Sc	UC	He	NA	625	56
14	ICP-OES-RV	Lu	NA	NA	50	50	261.187
15	Other				NA		248.3
17	ICP-OES-AV-buffer	Y			NA		273.955
23	ICP-OES-AV	Lu	NA	NA	2000	NA	261.382
24	ICP-OES-AV	NA	NA	NA	NA	500	238.204
28	ICP-OES-AV				NA		

Table 89 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)
2	ICP-MS	Ir		He	1000	NA	201.971
3	CVAAS	NA	NA	NA	500	500	253.7nm
8	FIMS	NA				NA	253.7
9	ICP-MS	Ir	ORS	He	0.1	NA	202
10	ICP-MS	Ir	ORS	He	800	NA	202
11	ICP-MS	Ir	NA	NA	625	NA	201
12	ICP-MS	Tb	KED	He	1000	NA	201
13	ICP-MS	Ir	NA		250	NA	
14	CVAAS	NA	NA	NA	500	500	
17	CVAAS					NA	253.7nm
19	ICP-OES-AV	NA	NA	NA	0.1	NA	253.652
20	CVAAS	nil			100	NA	
21	ICP-MS/MS	Ir 193	ORS	O2	1600	NA	Hg 202/202(m/z)
23	CVAAS	NA	NA	NA	200	250	253.7
25	CVAFS	NA	NA	NA	500	NA	254 (nm)
26	ICP-MS	193	ORS	standard mode	1000	NA	202
27	ICP-OES-AV	Lu			83	NA	253.7
28	ICP-MS		CRI			NA	

Table 90 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)
3	ICP-OES-AV	Caesium	NA	NA	50	NA	766.491nm
5	ICP-OES	Cs, Y	NA	NA	NA	500	766.491 nm
8	ICP-OES-RV	NA			NA		766.49
10	ICP-MS	Rh	ORS	He	NA	800	39
11	ICP-MS	Sc	UC	He	NA	625	39
14	ICP-OES-RV	Lu	NA	NA	50	50	766.491
15	Other				NA		766.5
17	ICP-OES-AV-buffer	Y			NA		766.49
23	ICP-OES-AV	Lu	NA	NA	20	NA	766.491
24	AAS	NA	NA	NA	NA	10	766.5
28	ICP-OES-AV				NA		

Table 91 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)
3	ICP-MS	Lutetium	ORS	No Gas	NA	1000	139m/z
9	ICP-MS	Ir	ORS	He	0.1	NA	139
10	ICP-MS	Rh	ORS	He	800	NA	139
12	ICP-MS	Tb	KED	He	2000	NA	139
13	ICP-MS	In	NA		250	NA	
14	ICP-MS	Lu	ORS	standard mode	1000	1000	139
18	ICP-MS	Tb	CRI		50	NA	139
23	ICP-MS	Lu	NA	NA	21	NA	139
26	ICP-MS	159	ORS	He	1000	NA	139
27	ICP-OES-AV	Lu			NT	NA	NT

Table 92 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	670.783nm
9	ICP-MS	Li6	ORS	He	0.1	NA	7
10	ICP-MS	NA	NA	NA	800	NA	7
11	ICP-MS	Sc	NA	NA	625	NA	7
12	ICP-MS	Sc	KED	He	2000	NA	7
13	ICP-MS	Sc	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	670.783
17	ICP-OES-AV-buffer	Y				NA	670.784
18	ICP-OES-AV	Yb			50	NA	670.78
21	ICP-OES-AV	Cs672.328	NA	NA	80	NA	Li 670.783(nm)
23	ICP-OES-AV	Lu	NA	NA	NA	25	670.783
26	ICP-MS	72	ORS	H2	1000	NA	7
27	ICP-OES-AV	Lu			NT	NA	NT
28	ICP-OES-AV					NA	

Table 93 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)
3	ICP-OES-AV	Lutetium	NA	NA	50	NA	279.800nm
5	ICP-OES	Cs, Y	NA	NA	NA	500	383.829 nm
8	ICP-OES-RV	NA			NA		279.077
10	ICP-MS	Rh	ORS	He	NA	800	24
11	ICP-MS	Sc	UC	He	NA	625	25
14	ICP-OES-AV	Lu	NA	NA	50	50	285.213
15	Other				NA		285.2
17	ICP-OES-AV-buffer	Y			NA		285.213
23	ICP-OES-AV	Lu	NA	NA	20	NA	279.8
24	AAS	NA	NA	NA	NA	10	285.2
28	ICP-OES-AV				NA		

Table 94 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)
2	ICP-MS	Rh		He	1000	NA	54.938
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	257.610nm
8	ICP-OES-AV	NA				NA	257.61
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	257.61
10	ICP-MS	Rh	ORS	He	800	NA	55
11	ICP-MS	Sc	UC	He	625	NA	55
12	ICP-MS	Sc	KED	He	2000	NA	55
13	ICP-MS	Rh	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	257.61
17	ICP-OES-AV-buffer	Y				NA	257.61
19	ICP-OES-RV	Lu 20mglKg	NA	NA	100	NA	257.61
21	ICP-OES-AV	Eu 271.700	NA	NA	80	NA	Mn 257.610
23	ICP-OES-AV	Lu	NA	NA	20	25	257.61
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	293.931 (nm)
26	ICP-MS	72	ORS	standard mode	1000	NA	55
27	ICP-OES-AV	Lu			83	NA	260.568
28	ICP-MS		CRI			NA	

Table 95 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	202.032nm
8	ICP-OES-AV	NA				NA	202.031
9	ICP-MS	Rh	ORS	He	0.1	NA	95
10	ICP-MS	Rh	ORS	He	800	NA	95
11	ICP-MS	Rh	NA	NA	625	NA	95
12	ICP-MS	Rh	KED	He	2000	NA	98
13	ICP-MS	Rh	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	202.032
17	ICP-MS	In	NA	standard mode	10	NA	95
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	202.031
21	ICP-MS/MS	Rh103	ORS	O2	1600	NA	Mo 95/95(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	NA	202.032
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	202.032 (nm)
26	ICP-MS	89	ORS	He	1000	NA	95
27	ICP-OES-AV	Lu			83	NA	202.032
28	ICP-MS		CRI			NA	

Table 96 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)
3	ICP-OES-AV	Lutetium	NA	NA	50	NA	588.995nm
5	ICP-OES	Cs, Y	NA	NA	NA	500	589.592 nm
8	ICP-OES-AV	NA			NA		589.592
10	ICP-OES-AV	Y	NA	NA	NA	800	588.995
11	ICP-MS	Sc	UC	He	NA	625	23
14	ICP-OES-AV	Lu	NA	NA	50	50	589.592
15	Other				NA		589
17	ICP-OES-AV-buffer	Y			NA		589.592
23	ICP-OES-AV	Lu	NA	NA	400	NA	588.995
24	AAS	NA	NA	NA	NA	neat	589
28	ICP-OES-AV				NA		

Table 97 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)
2	ICP-MS	Rh		He	1000	NA	59.933
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	231.604nm
8	ICP-OES-AV	NA				NA	231.604
9	ICP-MS	Ge	ORS	He	0.1	NA	60
10	ICP-MS	Rh	ORS	He	800	NA	60
11	ICP-MS	Ge	UC	He	625	NA	60
12	ICP-MS	Ga	KED	He	1000	NA	60
13	ICP-MS	Rh	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	231.604
17	ICP-MS	Ga	CRI	He	10	NA	60
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	231.604
20	ICP-OES-AV	nil			20	NA	
21	ICP-OES-AV	Lu219.55 6	NA	NA	80	NA	Ni 231.604
23	ICP-OES-AV	Lu	NA	NA	20	25	231.604
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	231.604 (nm)
26	ICP-MS	103	ORS	He	1000	NA	60
27	ICP-OES-AV				83	NA	231.604
28	ICP-MS		CRI			NA	

Table 98 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)
3	ICP-OES-AV	Lutetium	NA	NA	50	NA	213.618nm
5	ICP-OES	Cs, Y	NA	NA	NA	500	185.827 nm
8	ICP-OES-AV	NA			NA		
10	ICP-MS	Rh	ORS	HEHe	NA	800	31
11	ICP-MS	Sc	UC	He	NA	625	31
14	ICP-OES-AV	Lu	NA	NA	50	50	213.618
15	Other			NA	NA		
17	ICP-OES-AV-buffer	Y			NA		214.914
23	ICP-OES-AV	Lu	NA	NA	2000	NA	182.143
24	ICP-OES-AV	NA	NA	NA	NA	10	213.618

Table 99 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)
2	ICP-MS	Ir		He	1000	NA	207.977
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	220.353nm
8	ICP-OES-AV	NA				NA	220.353
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	220.353
10	ICP-MS	Ir	ORS	He	800	NA	208
11	ICP-MS	Ir	NA	NA	625	NA	206+207+208
12	ICP-MS	Tb	KED	He	1000	NA	206+207+208
13	ICP-MS	Ir	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	220.353
17	ICP-OES-AV-buffer	Y				NA	220.353
19	ICP-OES-AV	Lu 20 mg/Kg	NA	NA	100	NA	220.353
20	ICP-OES-AV	nil			20	NA	
21	ICP-OES-AV	Eu271.70	NA	NA	80	NA	Pb 220.353
23	ICP-OES-AV	Lu	NA	NA	20	NA	220.353
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	220.353 (nm)
26	ICP-MS	159	ORS	standard mode	1000	NA	208
27	ICP-OES-AV	Lu			83	NA	220.353
28	ICP-MS		CRI			NA	

Table 100 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)
3	ICP-MS	Germaniu m	ORS	He	1000	NA	85m/z
10	ICP-MS	Rh	ORS	He	800	NA	85
12	ICP-MS	Rh	KED	He	2000	NA	85
13	ICP-MS	Rh	NA		250	NA	
14	ICP-MS	Ge	ORS	He	1000	1000	85
18	ICP-MS	Y	CRI	O2	50	NA	87
23	ICP-MS	Ge	ORS	standard mode	200	NA	85
26	ICP-MS	89	ORS	He	1000	NA	85
27	ICP-OES-AV	Lu			NT	NA	NT

Table 101 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)
3	ICP-OES-AV	Lutetium	NA	NA	50	NA	181.972nm
5	ICP-OES	Cs, Y	NA	NA	NA	500	181.972 nm
10	ICP-OES-AV	Y	NA	NA	NA	800	181.972
11	ICP-OES-AV	Y	NA	NA	NA	62.5	181.975
14	ICP-OES-AV	Lu	NA	NA	50	50	181.972
17	ICP-OES-AV-buffer	Y			NA		181.975
23	ICP-OES-AV	Lu	NA	NA	20	NA	181.972
24	ICP-OES-AV	NA	NA	NA	NA	10	181.972

Table 102 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	206.834nm
8	ICP-OES-AV	NA				NA	206.836
10	ICP-MS	Rh	ORS	He	800	NA	121
11	ICP-MS	Rh	NA	NA	625	NA	121
12	ICP-MS	Rh	KED	He	2000	NA	121
13	ICP-MS	Rh	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	206.834
21	ICP-MS/MS	Rh103	ORS	O2	1600	NA	Sb 121/121(m/z)
23	ICP-OES-AV	Lu	NA	NA	NA	25	206.834
26	ICP-MS	193	ORS	standard mode	1000	NA	121
27	ICP-OES-AV	Lu			83	NA	206.834
28	ICP-MS		CRI			NA	

Table 103 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	196.026nm
8	ICP-OES-AV	NA				NA	196.026
9	ICP-MS	Ge	ORS	H2	0.1	NA	78
10	ICP-MS	Rh	ORS	HEHe	800	NA	78
11	ICP-MS	Rh	DRC	NH3	625	NA	82
12	ICP-MS	Te	KED	He	2000	NA	82
13	ICP-MS	Rh	UC	He	250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	196.026
17	ICP-MS	Ga	DRC	NH3	10	NA	82
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	196.026
21	ICP-MS/MS	Rh103	ORS	O2	1600	NA	Se 78/94(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	25	196.026
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	196.026 (nm)
26	ICP-MS	72	ORS	H2	1000	NA	78
27	ICP-OES-AV	Lu			83	NA	196.026
28	ICP-MS		CRI			NA	

Table 104 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	189.925nm
8	ICP-OES-AV	NA				NA	189.927
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	189.925
10	ICP-MS	Rh	ORS	He	800	NA	118
12	ICP-MS	Rh	KED	He	2000	NA	120
13	ICP-MS	Rh	NA		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	189.925
17	ICP-MS	In	NA	standard mode	10	NA	118
18	ICP-OES-AV	Yb			50	NA	189.92
21	ICP-MS/MS	Rh103	ORS	O2	1600	NA	Sn 118/134(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	NA	189.925
26	ICP-MS	103	ORS	He	1000	NA	120
27	ICP-OES-AV	Lu			83	NA	189.925

Table 105 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)
3	ICP-OES-AV	Lutetium	NA	NA	NA	50-1000	407.771nm
5	ICP-MS	Sc, Ga, Ge, Y, Rh, Ce, Ho, Ir	NA	He	NA	500	88 m/z
10	ICP-MS	Rh	ORS	He	NA	800	88
11	ICP-MS	Rh	NA	NA	NA	625	88
14	ICP-OES-AV	Lu	NA	NA	50	50	407.771
17	ICP-OES-AV-buffer	Y			NA		421.552
23	ICP-OES-AV	Lu	NA	NA	NA	25	421.552
24	ICP-OES-AV	NA	NA	NA	NA	10	407.771

Table 106 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)
3	ICP-MS	Lutetium	ORS	No Gas	NA	1000	232m/z
10	ICP-MS	Ir	ORS	He	800	NA	232
11	ICP-MS	Ir	NA	NA	625	NA	232
13	ICP-MS	NA	NA	NA	250	NA	NA
14	ICP-MS	Lu	ORS	standard mode	1000	1000	232
18	ICP-MS	Ir	CRI		50	NA	232
21	ICP-MS/MS	Ir 193	ORS	He	1600	NA	Th 232/232(m/z)
23	ICP-MS	Lu	ORS	standard mode	200	NA	232
27	ICP-OES-AV	Lu			NT	NA	NT

Table 107 Instrument Conditions Tl

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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	190.764nm
9	ICP-MS	Ir	ORS	He	0.1	NA	205
10	ICP-MS	Ir	ORS	He	800	NA	205
11	ICP-MS	Ir	NA	NA	625	NA	205
12	ICP-MS	Tb	KED	He	2000	NA	205
13	ICP-MS	Ir	NA		250	NA	
14	ICP-MS	Lu	ORS	standard mode	1000	1000	205
17	ICP-MS	Ir	NA	standard mode	10	NA	203
21	ICP-MS/MS	Ir 193	ORS	O2	1600	NA	Tl 205/205(m/z)
23	ICP-OES-AV	Lu	NA	NA	NA	25	190.794
26	ICP-MS	159	ORS	standard mode	500	NA	205
27	ICP-OES-AV	Lu			83	NA	336.122

Table 108 Instrument Conditions U

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)
3	ICP-MS	Lutetium	ORS	No Gas	NA	1000	238m/z
9	ICP-MS	Ir	ORS	He	0.1	NA	238
10	ICP-MS	Ir	ORS	He	800	NA	238
11	ICP-MS	Ir	NA	NA	625	NA	238
12	ICP-MS	Tb	KED	He	2000	NA	238
13	ICP-MS	Ir	NA		250	NA	
14	ICP-MS	Lu	ORS	standard mode	1000	1000	238
18	ICP-MS	Ir	CRI		50	NA	238
21	ICP-MS/MS	Ir 193	ORS	He	1600	NA	U 238/238(m/z)
23	ICP-MS	Lu	ORS	standard mode	NA	250	238
26	ICP-MS	159	ORS	standard mode	1000	NA	238
27	ICP-OES-AV	Lu			NT	NA	NT
28	ICP-MS		CRI			NA	

Table 109 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)
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	NA	292.401nm
8	ICP-OES-AV	NA				NA	292.402
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	292.401
10	ICP-MS	Rh	ORS	He	800	NA	51
11	ICP-MS	Sc	UC	He	625	NA	51
12	ICP-MS	Sc	KED	He	2000	NA	51
13	ICP-MS	Sc	UC		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	292.401
17	ICP-OES-AV-buffer	Y				NA	292.402
21	ICP-MS/MS	Sc 45	ORS	O2	1600	NA	V 51/67(m/z)
23	ICP-OES-AV	Lu	NA	NA	20	NA	292.401
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	311.837 (nm)
26	ICP-MS	72	ORS	He	1000	NA	51
27	ICP-OES-AV	Lu			83	NA	292.401

Table 110 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)
2	ICP-MS	Rh		He	1000	NA	65.926
3	ICP-OES-AV	Lutetium	NA	NA	50-1000	50-1000	206.200nm
8	ICP-OES-AV	NA				NA	213.857
9	ICP-OES-AV	Lu	NA	NA	0.1	NA	206.2
10	ICP-MS	Rh	ORS	He	800	NA	64Mini
11	ICP-MS	Ge	UC	He	625	NA	66
12	ICP-MS	Ga	KED	He	1000	NA	66
13	ICP-MS	Rh	UC		250	NA	
14	ICP-OES-AV	Lu	NA	NA	50	50	206.2
17	ICP-OES-AV-buffer	Y				NA	213.857
18	ICP-OES-AV	Yb			50	NA	213.85
19	ICP-OES-AV	Lu 20mglKg	NA	NA	100	NA	206.2
20	ICP-OES-AV	nil			20	NA	
21	ICP-OES-AV	Lu219.55 6	NA	NA	80	NA	Zn 206.200
23	ICP-OES-AV	Lu	NA	NA	20	25	206.2
25	ICP-OES-AV	Y 371.029	NA	NA	50	NA	334.557 (nm)
26	ICP-MS	72	ORS	He	1000	NA	66
27	ICP-OES-AV	Lu			83	NA	213.857
28	ICP-OES-AV					NA	

END OF REPORT