



Australian Government
Department of Industry,
Innovation and Science

**National
Measurement
Institute**

Proficiency Test Report AQA 18-12 Metals, Anions and Nutrients in Soil

December 2018

ACKNOWLEDGMENTS

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

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

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

Luminita Antin

Jeffrey Merrick

Ian White

Andrew Evans

Michael Wu

Alexander Sadler

Paul Armishaw

Manager, Chemical Proficiency Testing

Phone: 61-2-9449 0149

proficiency@measurement.gov.au



Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

1	SUMMARY	5
2	INTRODUCTION	6
2.1	NMI Proficiency Testing Program	6
2.2	Study Aims	6
2.3	Study Conduct	6
3	STUDY INFORMATION	6
3.1	Selection of Matrices and Inorganic Analytes	6
3.2	Participation	6
3.3	Test Material Specification	7
3.4	Laboratory Code	7
3.5	Sample Preparation, Analysis and Homogeneity Testing	7
3.6	Stability of Analytes	7
3.7	Sample Storage, Dispatch and Receipt	7
3.8	Instructions to Participants	7
3.9	Interim Report	8
4	PARTICIPANT LABORATORY INFORMATION	9
4.1	Test Method Summaries	9
4.2	Instruments Used for Measurements	14
4.3	Additional Information	14
4.4	Basis of Participants' Measurement Uncertainty Estimates	15
4.5	Participant Comments on this PT Study or Suggestions for Future Studies	16
5	PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS	18
5.1	Results Summary	18
6	TABLES AND FIGURES	20
7	DISCUSSION OF RESULTS	134
7.1	Assigned Value	134
7.2	Measurement Uncertainty Reported by Participants	134
7.3	E_n -score	135
7.4	z-Score	135
7.1	Participants' Results and Analytical Methods for Acid Extractable Elements	139
7.2	Participants' Results and Analytical Methods for 2M KCl Extractable Ammonium-N and Nitrate-N	153
7.4	Participants' Results and Analytical Methods for Water Soluble Anions	154
7.5	Comparison with Previous NMI Proficiency Tests Studies of Metals in Soil	157
7.6	Reference Materials and Certified Reference Materials	157
8	REFERENCES	159
APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING		161
APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND E_n SCORE CALCULATION		163
APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION		164
APPENDIX 4 - INSTRUMENT DETAILS		166

1 SUMMARY

This report presents the results of the proficiency test AQA 18-12 Metals, Anions and Nutrients in Soil. The study focused on the measurement of acid extractable elements: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, Th, U, V and Zn. Measurement of pH, electrical conductivity (EC), water soluble bromide (Br^-), chloride (Cl^-), fluoride (F^-), iodide (I^-), sulfate (SO_4^{2-}), orthophosphate-P ($\text{PO}_4^{3-}\text{-P}$) and total Kjeldahl nitrogen and 2M KCl extractable ammonium nitrogen ($\text{NH}_4^+\text{-N}$) and 2M KCl extractable nitrate nitrogen ($\text{NO}_3^-\text{-N}$) were also included in the program.

The sample set consisted of three dried soil samples.

Twenty six 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 821 results, 751 (91%) returned a satisfactory score of $|z| \leq 2$.

Of 821 E_n -scores, 671 (82%) were satisfactory with $|E_n| \leq 1$.

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

Unsolved interference problems were the main cause of variability in the results reported for Ag, As, Hg and Se in the highly contaminated soil sample S1.

When measuring low level As in soil by ICP-MS in collision mode, laboratories should consider screening for lanthanides in the sample and adjusting the instrument conditions to minimise the doubly charged atomic ions formation. Interferences from tungsten (WO^+ and WHO^+) on Hg are poorly removed when the conventional He collision gas is used. Zr and Nb concentrations in the soil sample S1 were elevated; oxide based interferences from these elements on Ag cannot be effectively removed by ICP-MS in collision mode. The good level of agreement between Cu and Zn results indicates that overall participants overcame the interferences caused by the presence of significant quantities of TiO^+ in the sample. ICP-MS with collision/reaction cell and He as collision gas cannot remove interferences from the doubly charged atomic ions on Se. Improved recoveries of ^{78}Se in the presence of lanthanide can be obtained if ICP-MS is used in reaction mode with H_2 at a high flow rate, 8.1 mL/min. When measuring elements in soil, participants should also consider including lanthanides, Zr, Nb and W to the method set up for their instruments. When these elements are present in the sample at an elevated level then laboratories should consider using an alternative technique/instrumental conditions or increasing their level of reporting for the elements affected by interference from these analytes.

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

On average participants' performance remained fairly consistent.

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

Of 887 numerical results, 852 (96%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 3.

2 INTRODUCTION

2.1 NMI Proficiency Testing Program

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

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

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

AQA 18-12 is the 23rd NMI proficiency study of inorganic analytes in soil.

2.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories' methods used in determination of inorganic analytes in soil;
- compare the performance of participant laboratories with their past performance;
- evaluate within-laboratory reproducibility; and
- develop the practical application of traceability and measurement uncertainty.

2.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.² The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.³ These documents have been prepared with reference to ISO Standard 17043¹ and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.⁴

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

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

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The 58 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.

3.2 Participation

Twenty-six laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued: 06 August 2018
Samples dispatched: 27 August 2018
Results due: 21 September 2018
Interim report issued: 25 September 2018

3.3 Test Material Specification

Three samples were provided for analysis:

- Sample S1 was 25 g of dried highly contaminated soil;
- Sample S2 was 25 g of dried soil, previously distributed as Sample S1 of AQA 16-02;⁶
- Sample S3 was 50 g of dried agricultural soil, previously distributed as Sample S3 of proficiency testing study AQA 16-02.⁶

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

A partial homogeneity testing was conducted for Sample S1 in this study. The same validated sample preparation procedure was followed as in previous studies where the test samples were demonstrated to be sufficiently homogeneous for evaluation of participants' performance.^{6, 7}

Samples S2 and S3 were previously distributed as Samples S1 and S3 respectively of PT study AQA 16-02. These samples were formerly tested for homogeneity by NMI except for 2M KCl extractable ammonium nitrogen ($\text{NH}_4^+ \text{-N}$), 2M KCl extractable nitrate nitrogen ($\text{NO}_3^- \text{-N}$), pH, EC and total Kjeldahl nitrogen.

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

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

No stability study was carried out 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.^{6, 7}

3.7 Sample Storage, Dispatch and Receipt

The samples were dispatched by courier on 27 August 2018.

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.

3.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- For S3 determination of the 2M KCl extractable ammonium nitrogen ($\text{NH}_4^+ \text{-N}$) and nitrate nitrogen ($\text{NO}_3^- \text{-N}$), participants are asked to follow the 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 to 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 results for all the other tests in S1, S2 and S3 on a as received basis in units of mg/kg.

SAMPLE S1 (soil)		SAMPLE S2 (soil)		SAMPLE S3 (soil)	
Test Acid Extractable	Approximate Conc. Range mg/kg	Test Acid Extractable	Approximate Conc. Range mg/kg	Test	Approximate Conc. Range mg/kg
Ag	20-400	As	1-20	Ca (acid extractable)	2500-50000
Al	2500-50000	B	5-100	Fe (acid extractable)	5000-100000
As	2-40	Cd	0.5-10	K (acid extractable)	500-10000
Ba	50-1000	Cr	10-200	Mg (acid extractable)	50-1000
Be	0.5-10	Co	1-20	Na (acid extractable)	50-1000
Bi	0.25-5	Cu	1-20	P (acid extractable)	50-1000
Ca	2500-50000	Hg	<1	S (acid extractable)	50-1000
Cr	500-10000	Mn	20-400	Water Soluble Bromide (Br ⁻)-1:5 soil/water extract	0.5-10
Cu	10-200	Ni	5-100	Water Soluble Chloride (Cl ⁻)-1:5 soil/water extract	10-200
Fe	5000-100000	Pb	10-200	Water Soluble Fluoride (F ⁻)-1:5 soil/water extract	0.5-10
Ga	5-100	Sb	5-100	Water Soluble Iodide (I ⁻)-1:5 soil/water extract	0.5-10
Hg	0.1-2	Se	1-20	Water Soluble Sulphate (SO ₄ ²⁻)-1:5 soil/water extract	25-300
K	2500-50000	Sr	25-1000	Water Soluble Orthophosphate-P (PO ₄ ³⁻ -P)-1:5 soil/water extract	0.5-10
Mn	2500-50000	V	5-100	pH of 1:5 soil/water suspension	>3
Mo	20-400	Zn	5-100	EC of 1:5 soil/water extract (µS/cm)	>250
Ni	20-400			2M KCl Extractable (Nitrate-N)	NA
Pb	10-200			2M KCl Extractable (Ammonium-N)	NA
S	2500-50000			Kjeldahl nitrogen, total (TKN)	NA
Se	0.5-10				
Sn	50-1000				
Sr	50-1000				
Th	50-1000				
U	20-400				
V	2500-50000				
Zn	50-1000				

NA=not available

- Report results as you would report to a client.
- For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (eg 5.21 ± 0.51 mg/kg). Report the basis of your uncertainty estimates (i.e. control charts, proficiency testing).
- Please send us all the requested details regarding the test method.
- Return the completed results sheet by 21 September 2018.

3.9 Interim Report

An interim report was emailed to participants on 25 September 2018.

4 PARTICIPANT LABORATORY INFORMATION

4.1 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)	Digestion Temp. (°C)	Digestion Time (min)	Vol. HNO ₃ (mL)	Vol. HNO ₃ (1:1) (mL)	Vol. HCl (mL)	Vol. HCl (1:1) (mL)	Vol. H ₂ O ₂ (mL)	Other (mL)
1	USEPA 3050	1	95	60	10				6	
2	Reference to USEPA 3050B	1	95	120	2		3		2	
3 ^a	US EPA 3050, 6010B	2.5	90	120	2		6			
4	USEPA 3051A (Modification)	1	170	15		8		2		
6	APHA 3215 (modified)	0.5	95	30	1		1			
7	In-House	1	98	60	3		3			
8	In house reverse aqua regia	0.25	110	60	3.5		1.5			
9		1.2	95-100	120	3		3			
11	USEPA 200.7	1	95	0.5	2.5		2.5			
12		1	112.5	120	7.5		2.5			
14	EPA (Environmental Protection Agency) 1994 Method 200.8	2	109	60	800		400			1200
15	In House S6 - referencing APHA 3125	0.4	120	60	2.5		7.5			
16	200.7, 3051, 6010C and 7471B	2	100	60	4		12			24 (H ₂ O)
17	USEPA 3050B	0.5	95	120	3		3			1 (H ₂ O)
18 ^a	EPA3050B, 6020B	2	90-95	60	4		12			
19		2	95	120	2		6			
20	US EPA 200.2	1-1.1	95	50	2		2			10
21	EPA Method 3050B Acid Digestion of Sediments, Sludges and Soils	0.5	85	240	5		5			
22 ^a	US EPA 3050B	0.5	95	120	7.5		5		1.5	
23	USEPA method 200.2 Revision 2.8	1	95	60		2		10	2	
24 ^a	In-house referenced to US EPA 200.8 In-house referenced to APHA 3120B	0.2	105	120	3		9			
25	US EPA 200.2 adaptation for Hot Block	~0.5000	95 / 85	30 / 30	3		3		2	
26	In-house Method	0.1	140	180	5				5	

^aAdditional information in Table 10

Table 2 Methodology for Total Kjeldahl Nitrogen

Lab. Code	Method Reference	Digestion	Distillation	Measurement Method	Instrument
1	APHA 4500B	Yes	Yes	Titrimetric method	Manual Analysis
2	APHA 4500-Norg D	Yes		Block Digestion & FIA	FIA
4	APHA Method 4500-N Org B and Method 4500-NH3 F	Yes	Yes	Colorimetric - phenate method	DA
6	APHA (online edition) 4500-N org	Yes		Colorimetric - salicylate method	DA
9		Yes	Yes	Titrimetric method	Manual Analysis
12	NA	Yes		Colorimetric - salicylate method	DA
13	APHA 4500 Norg B	Yes	Yes		
15					LECO
17		Yes	No	Colorimetric - phenate method	FIA
21	A.P.H.A 21st Edition 2005, method 4500-Norg B	Yes	Yes	Titrimetric method	Auto Kjeldahl
23	APHA 4500 -NOrg. A & D,	Yes	No	colourmetric method	DA
24	In-house referenced to APHA-N org A	Yes	No	Colorimetric - salicylate method	SFA
26	AOAC 955.04-D (Method normally used for fertilizer N Analysis) but in our context this method has been adopted to soil and has been use since. It will be good to see its efficacy through this PT.	Yes	Yes	Titrimetric method	Methrom Automated titration system (Titrino Plus 877)

^aAdditional 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	
	NH ₄ ⁺ -N	NO ₃ ⁻ -N				NH ₄ ⁺ -N	NO ₃ ⁻ -N	NH ₄ ⁺ -N	NO ₃ ⁻ -N
1	APHA 4500G	APHA 4500F	10	100	1	Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA
2	APHA 4500-NH3 H	APHA 4500-NO ₃ I	3	30	1	Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA
4	7C2a	7B1a	3	30	1	Colorimetric - Salicylate method	Colorimetric-Sulfanilamide-NEDD hydrazine reduction	SFA	SFA

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

Lab. Code	Method Reference		Sample Mass (g)	Extraction Solution 2M KCl Volume (mL)	Shake time (hours)	Measurement Method		Measurement Instrument	
	NH ₄ ⁺ -N	NO ₃ ⁻ -N				NH ₄ ⁺ -N	NO ₃ ⁻ -N	NH ₄ ⁺ -N	NO ₃ ⁻ -N
9			4	40	1	Segmented Flow Analyzer	Colorimetric-Sulfanilamide-NEDD Cd reduction	Segmented Flow Analyzer	FIA
12	NA	NA	3	30	1	Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	DA
13	APHA 4500 NH3 B/C	APHA 4500 NH3 B/C	25.001	250	1				
15	In House S37	In House S37	2	20	1	Colorimetric - Salicylate method	Colorimetric - vanadium III method	FIA	FIA
18	APHA 4500-NH3 F		3	30	1	Colorimetric - Phenate method		DA	
19			10	100	1				
24	In-house referenced to APHA-4500 NH3 G	In-house referenced to APHA-4500-NO ₃ I	5	50	1	Colorimetric - Phenate method	Colorimetric-Sulfanilamide-NEDD Cd reduction	DA	SFA

Table 4 Methodology for Water Soluble Br⁻

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
5	APHA 4110 B	5	25	1	Ion Chromatographic Method	IC
7	In-House	5	25	3	Ion Chromatographic Method	IC
9	APHA	8	40	1	Ion Chromatographic Method	IC
18	USEPA 9056A	4	20	1	Ion Chromatographic Method	IC
21	APHA 4110	10	50	1	Ion Chromatographic Method	IC
22	APHA 4110B	12	60	1	Ion Chromatographic Method	IC
24	In-house referenced to US EPA 300.1	20	100	1	Ion Chromatographic Method	IC

Table 5 Methodology for Water Soluble I⁻

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
5	APHA 4110 B	5	25	1	Ion Chromatographic Method	IC
9	APHA	8	40	1	Ion Chromatographic Method	IC
18	USEPA 9056A	4	20	1	Ion Chromatographic Method	IC
24	In-house from US EPA 300.1	20	100	1	Ion Chromatographic Method	IC

Table 6 Methodology for Water Soluble Cl⁻

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
1	APHA 4110B	10	50	1	Ion Chromatographic Method	IC
5	APHA 4110 B	5	25	1	Ion Chromatographic Method	IC
6	APHA (online edition) 4110 B (modified)	50	250	1	Ion Chromatographic Method	IC
7	In-House	5	25	3	Ion Chromatographic Method	IC
9	APHA	8	40	1	Ion Chromatographic Method	IC
13	NSW.AES.030	15.0003	75.0	1		
15		2	10	1	Ion Chromatographic Method	
18	USEPA 9056A	4	20	1	Ion Chromatographic Method	IC
19		10	100	1		
21	APHA 4110	10	50	1	Ion Chromatographic Method	IC
22	APHA 4110B	12	60	1	Ion Chromatographic Method	IC
23	APHA 4500-Cl	10	50	1	Ferricyanide Colorimetric Method	DA
24	In-house from APHA-4500-Cl E	20	100	1	Ferricyanide Colorimetric Method	DA
26	USEPA Method 9253	5	25	1	Silver nitrate titration method	titration apparatus

Table 7 Methodology for Water Soluble F⁻

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
1	APHA 4500C	10	50	1	Ion Selective Electrode Method	Fluoride Selective Electrode
5	APHA 4110 B	5	25	1	Ion Chromatographic Method	IC
7	In-House	5	25	3	Ion Chromatographic Method	IC
9	APHA	8	40	1	Ion Chromatographic Method	IC
15		2	10	1	Ion Chromatographic Method	IC
23	APHA 4500-F	10	50	1		Fluoride Selective Electrode
24	In-house from-4500-F C	20	100	1	Ion Selective Electrode Method	Fluoride Selective Electrode

Table 8 Methodology for Water Soluble SO₄²⁻

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
1	APHA 4110B	10	50	1	Ion Chromatographic Method	IC
5	APHA 4110 B	5	25	1	Ion Chromatographic Method	IC
7	In-House	5	25	3	Ion Chromatographic Method	IC
9	APHA	8	40	1	Ion Chromatographic Method	IC
13	APHA 4500 SO42-E	15.0003	75.0	1		
15		2	10	1	ICP-Method	ICP-OES
18	USEPA 9056A	4	20	1	Ion Chromatographic Method	IC
19		10	100	1		
21	APHA 4110	10	50	1	Ion Chromatographic Method	IC
22	APHA 4110B	12	60	1	Ion Chromatographic Method	IC
23	USEPA 200.2	10	50	1	ICP-Method	ICP-OES
24	In-house referenced to APHA 3120B	20	100	1	ICP-Method	ICP-OES

Table 9 Methodology for Water Soluble Orthophosphate-P

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
1	APHA 4500F	10	50	1	Ascorbic Acid Colorimetric Method	FIA
5	APHA 4110 B	5	25	1	Ion Chromatographic Method	IC
7	In-House	5	25	3	Ion Chromatographic Method	IC
9	APHA	8	40	1	Ascorbic Acid Colorimetric Method	FIA
12	NA	8	40	1	Ascorbic Acid Colorimetric Method	DA
15		2	10	1	Vanadomolybdophosphoric Colorimetric Method	FIA
18	APHA 4500-P E	4	20	1	Ascorbic Acid Colorimetric Method	DA
19		10	100	1		
21	APHA 4110	10	50	1	Ion Chromatographic Method	IC
22	APHA 4110B	12	60	1	Ion Chromatographic Method	IC
23	APHA 4500-P	10	50	1	Ascorbic Acid Colorimetric Method	DA
24	In-house US EPA	20	100	1	Ascorbic Acid Colorimetric Method	SFA
26	USEPA Method 365.3	5	25	1	Ascorbic Acid Colorimetric Method	Analytik Jena Specord 50 UV/Vis Spectrophotometer

4.2 Instruments Used for Measurements

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

4.3 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
2	S3: Sample preparation method reference - Soil Chemical Methods Australia, G. E. Rayment & David J Lyons
3	S1: There are possible spectral interferences in Ag, Pb and Th
4	S3: Insufficient sample for water soluble anions.
5	S3: Bigger amount of sample is needed
6	S1: Sulphur is not accredited. This is an experimental method
18	S1: Be in No Gas mode
22	S1: The sample matrix made Hg analysis by CVAAS not possible. Sample, as described, was highly contaminated and contained interferences which made reporting some elements (Ag, Be and Se) not possible using this laboratories standard method so have not been reported.
23	S1: The laboratory was unable to report Bismuth as the sample had contained interferences which impeded on the recovery of the internal standard for ICPMS. The extract was diluted however the limit of reporting was raised. A "NT" was entered instead of a raised limit of reporting.
24	S1: Dilution Factor is dilution of digested sample ICP-MS used for sample 2 copper, Mass 65, Gas He, IS Germanium. ICP-MS used for sample 2 manganese, Mass 55, Gas He, IS Scandium. ICP-OES-AV used for sample 2 Nickel, line 231.604, IS Scandium. ICP-MS used for sample 2, Mass 66, Gas He, IS Terbium
26	S1: This is a method adopted by our Lab for the soil type found in our country. The soil has very low nutrient status and low CEC and the use of are more aggressive method might cause overestimation of the extractable cation. S3: We had some challenges with the analysis of calcium so we therefore drop it. For the majority of the anion we are not yet equipment to run the test we hope to participate fully in the next PT.

4.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Tables 11 and 12).

Table 11 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision ^a	Method Bias ^a	
1*	Top Down Approach	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS Instrument Calibration Variation in sample moisture content	Eurochem Guide 2007
2	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS Instrument Calibration	Eurachem/CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis Instrument Calibration	CRM Laboratory bias from PT studies Recoveries of SS Instrument Calibration	NATA Technical Note 33
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM	NMI Uncertainty Course
5	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate Analysis	CRM	Eurachem/CITAC Guide
6	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – RM Duplicate Analysis	Instrument Calibration	IANZ technical guide
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Laboratory bias from PT studies Recoveries of SS	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	Recoveries of SS Instrument Calibration	Nordtest Report TR537
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis	Recoveries of SS	ISO/GUM
11	NATA Technical Note 33	Control Samples Duplicate Analysis	CRM Standard Purity Instrument Calibration	NATA Technical Note 33
12	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – RM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS Instrument Calibration	NATA Technical Note 33
13		Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Standard Purity Instrument Calibration	
14	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – RM Duplicate Analysis	Recoveries of SS	
15	Top Down - precision and estimates of the method and laboratory bias	Control Samples – RM Duplicate Analysis	Instrument Calibration	Nordtest Report TR537
16*		Control Samples – CRM	CRM Laboratory bias from PT studies	

			Recoveries of SS Instrument Calibration	
17	Standard deviation from PT studies	Control Samples Duplicate Analysis		
18*		Control Samples Duplicate Analysis Instrument Calibration	CRM	
19	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control Samples – CRM Duplicate Analysis Instrument Calibration		ISO/GUM
20	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	CRM Laboratory bias from PT studies	Eurachem/CITAC Guide
21	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis	Laboratory bias from PT studies	NATA Technical Note 33
22	Top Down - precision and estimates of the method and laboratory bias	Control Samples – CRM Duplicate Analysis	CRM Recoveries of SS Instrument Calibration	NATA Technical Note 33
23	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS Duplicate Analysis	CRM Instrument Calibration	Eurachem/CITAC Guide
24	Top Down - precision and estimates of the method and laboratory bias	Control Samples – SS	CRM Recoveries of SS	NATA Technical Note 33
25	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – CRM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS Instrument Calibration	NATA Technical Note 33
26	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples – SS Duplicate Analysis Instrument Calibration	Recoveries of SS Instrument Calibration	

*RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples; * Additional Information

Table 12 Additional Information for Basis of Uncertainty Estimate

Lab. Code	Additional Information
1	The standard deviations from this study may prove pretty helpful with MU in the future.
7	Uncertainty not reported for this PT study. To include it in future PT studies.
16	Estimation of MU from within-laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques
18	Estimation of MU from within-laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

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

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

Participants' comments are reproduced in Table 13.

Table 13 Participants' Comments

Lab Code	Participants' Comments	Study Co-ordinator's Response
5	The time for measurement should be longer	Your feedback is important to us. We attempt to accommodate most of our participants' requests including when extra time for samples' analyses is needed. The reporting date for this study was extended for one week. In the present study participants were asked to report results 3 weeks after the dispatch date.
26	Our Lab at this stage is not fully equipped for Anion analysis. We are in the process of procuring our first Ion chromatograph, which will allow us to participate fully in the next PT study. This being our First PT participation it is somewhat a challenge but we hope to produce our best work. I have to say that the coordination and assistance from Institute has been very good.	Your feedback is greatly appreciated.

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 14 to 70 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 58.

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

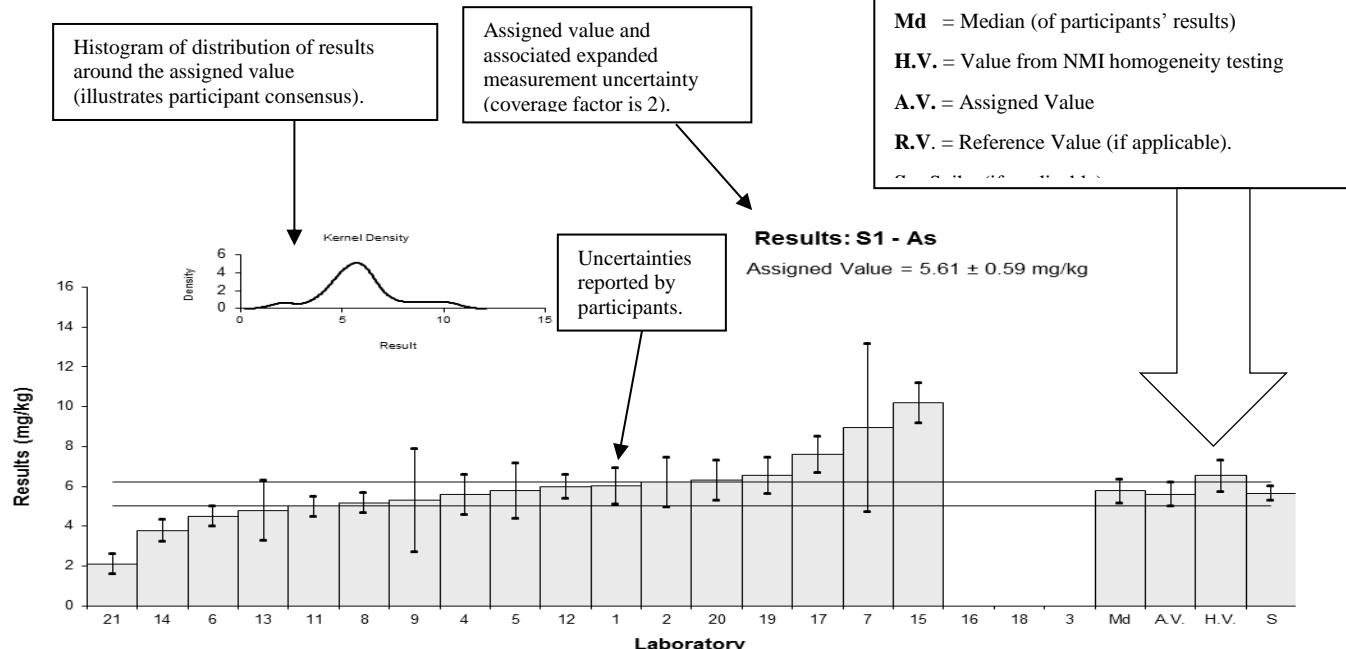


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

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

5.3 Robust Average

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

5.4 Robust Between-Laboratory Coefficient of Variation

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

5.5 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the performance coefficient of variation (PCV) as presented in Equation 1. This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

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

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.⁹ By setting a fixed and realistic value for the PCV, the participants' performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 2.

For each participant's result a z-score is calculated according to Equation 2 below:

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

where:

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

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

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

5.7 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:

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

where:

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

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

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

5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017¹⁰ 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.¹¹

6 TABLES AND FIGURES

Table 14

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Ag
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	0.30	0.07
3	3.74	0.56
4	0.50	0.04
5	NT	NT
6	<2.3	NR
7	NR	NR
8	1.86	0.19
9	0.14	0.03
10	<0.2	0.02
11	<1	1
12	NT	NT
13	NT	NT
14	NT	NT
15	1.05	0.2
16	< 5	< 1
17	NT	NT
18	<5	0.5
19	NT	NT
20	1.09	0.35
21	0.50	0.07
22	NR	NR
23	2	0.28
24	0.5	0.145
25	NT	NT
26	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	<0.3	
Robust Average	1.03	0.71
Median	0.78	0.42
Mean	1.17	
N	10	
Max.	3.74	
Min.	0.14	
Robust SD	0.032	
Robust CV	87%	

Results: S1 - Ag

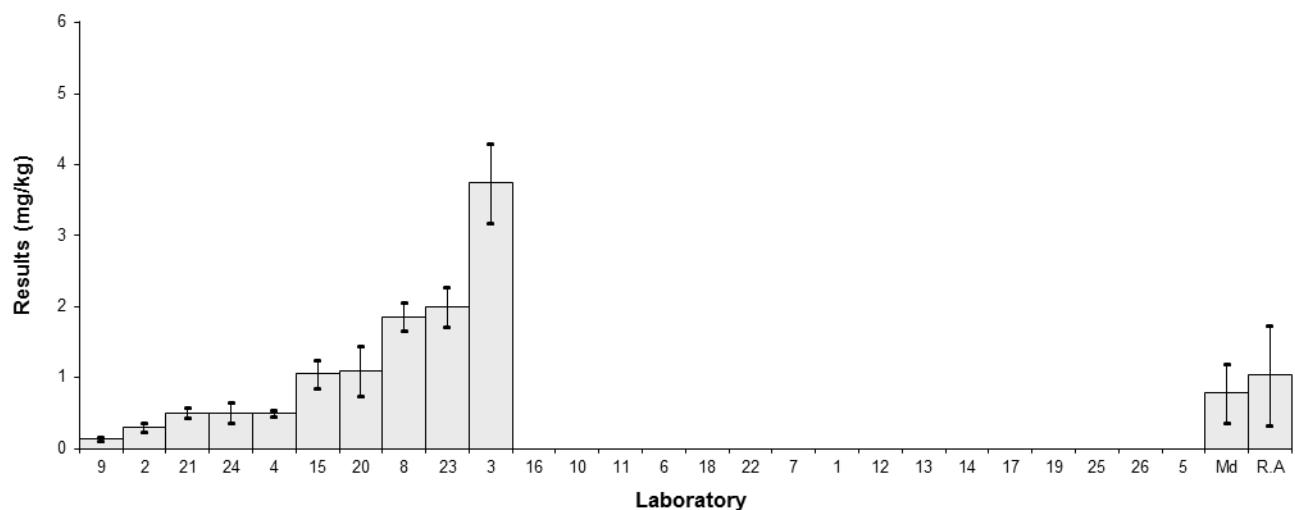


Figure 2

Table 15

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Al
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	11540	1210	1.10	1.16
3	9910	1486.50	0.01	0.01
4	NR	NR		
5	NT	NT		
6	8510	2900	-0.94	-0.46
7	9117	NR	-0.53	-1.07
8	9160	920	-0.50	-0.63
9	10800	2240	0.61	0.38
10	8200	820	-1.14	-1.55
11	9347	500	-0.37	-0.62
12	12700	1900	1.89	1.38
13	NT	NT		
14	10960	1100	0.71	0.80
15	11400	1500	1.01	0.90
16	10100	2000	0.13	0.09
17	NT	NT		
18	10129	1501	0.15	0.14
19	9100	1820	-0.54	-0.41
20	9200	1100	-0.47	-0.53
21	9677	1452	-0.15	-0.14
22	1300	160	-5.79	-11.51
23	9480	1186	-0.28	-0.30
24	26100	5742	10.91	2.80
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	9900	730
Spike	Not Spiked	
Homogeneity Value	11200	1300
Robust Average	9920	820
Median	9680	410
Mean	10350	
N	19	
Max.	26100	
Min.	1300	
Robust SD	1200	
Robust CV	12%	

*Robust Average excluding Laboratories 22 and 24.

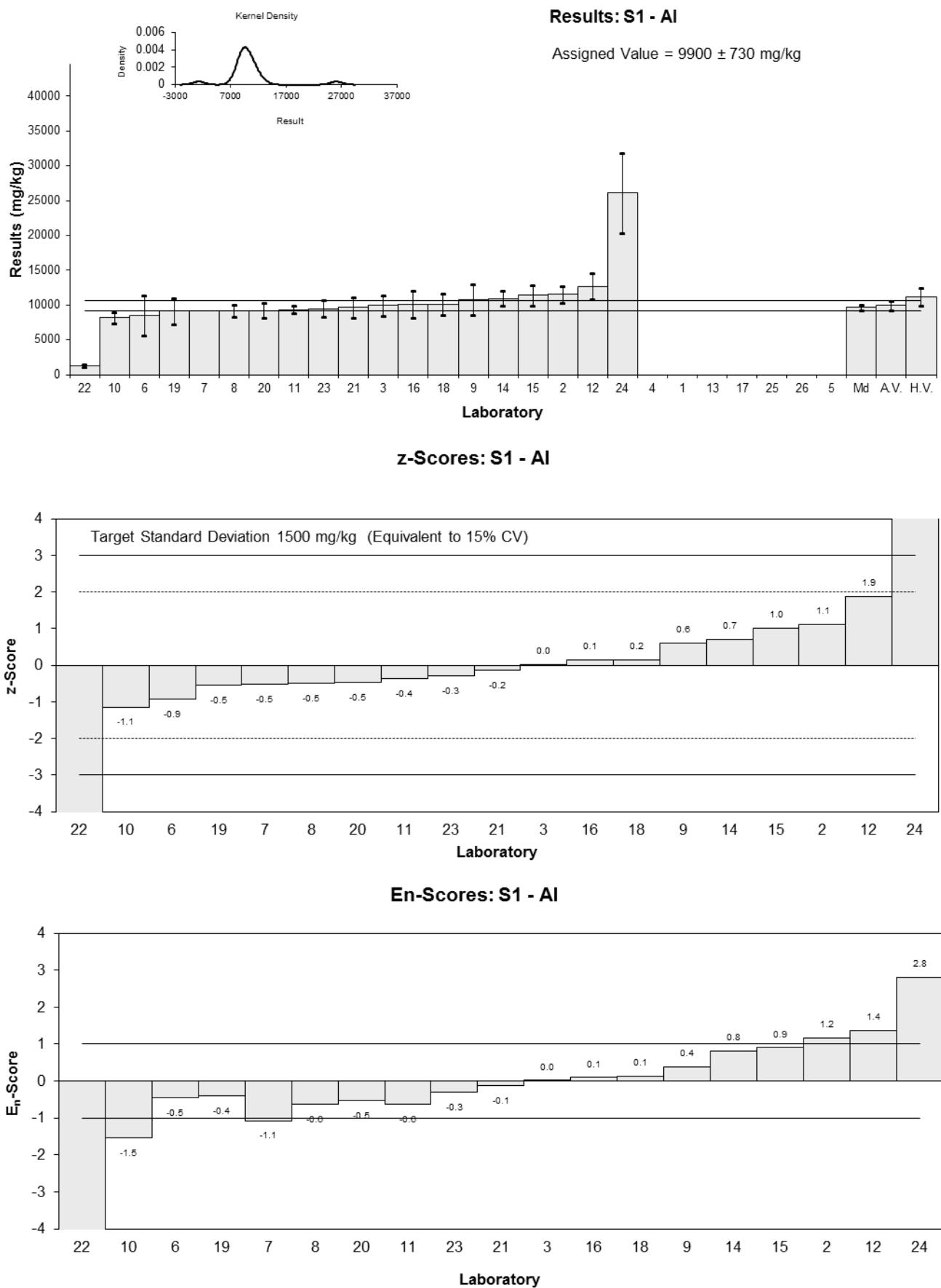


Figure 3

Table 16

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	8.65	1.69
3	5.44	0.81
4	8.2	0.4
5	NT	NT
6	5.91	0.890
7	NR	NR
8	7.65	0.77
9	3.5	0.51
10	9.4	1.41
11	<1	5
12	<5	NR
13	NT	NT
14	5.12	0.51
15	6.89	1.0
16	8.99	1.44
17	NT	NT
18	8.3	1.7
19	19.4	3.88
20	6.3	1.7
21	5.08	0.76
22	10	2
23	<5	NR
24	11.8	1.18
25	NT	NT
26	NT	NT

Statistics

Assigned Value	Not set	
Spike	Not Spiked	
Homogeneity Value	5.6	1.4
Robust Average	7.7	1.7
Median	7.9	1.4
Mean	8.2	
N	16	
Max.	19.4	
Min.	3.5	
Robust SD	1.9	
Robust CV	35%	

*Robust Average excluding Laboratories 9, 19 and 24.

Results: S1 - As

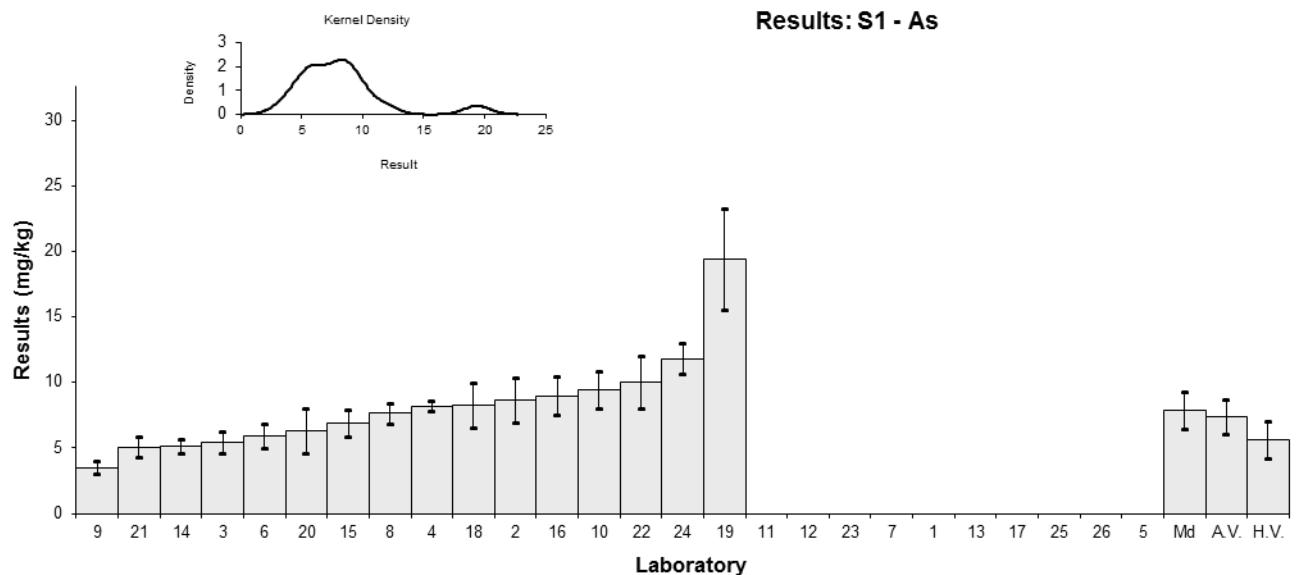


Figure 4

Table 17

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Ba
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	112	12	0.77	0.60
3	93.0	13.95	-1.06	-0.72
4	104	7	0.00	0.00
5	NT	NT		
6	93.6	22	-1.00	-0.46
7	159	NR	5.29	9.17
8	93.6	9.4	-1.00	-0.93
9	110	17	0.58	0.33
10	110	11	0.58	0.48
11	93	5	-1.06	-1.41
12	111	17	0.67	0.39
13	NT	NT		
14	116	11.6	1.15	0.92
15	112	15	0.77	0.50
16	100	16	-0.38	-0.23
17	NT	NT		
18	110	22	0.58	0.26
19	64.3	12.86	-3.82	-2.80
20	101.7	6.2	-0.22	-0.27
21	106	15.90	0.19	0.12
22	110	9	0.58	0.55
23	100	10.2	-0.38	-0.34
24	125	16	2.02	1.23
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	104	6
Spike	Not Spiked	
Homogeneity Value	101	12
Robust Average	105	6
Median	108	5
Mean	106	
N	20	
Max.	159	
Min.	64.3	
Robust SD	10	
Robust CV	9.5%	

*Robust Average excluding Laboratory 7.

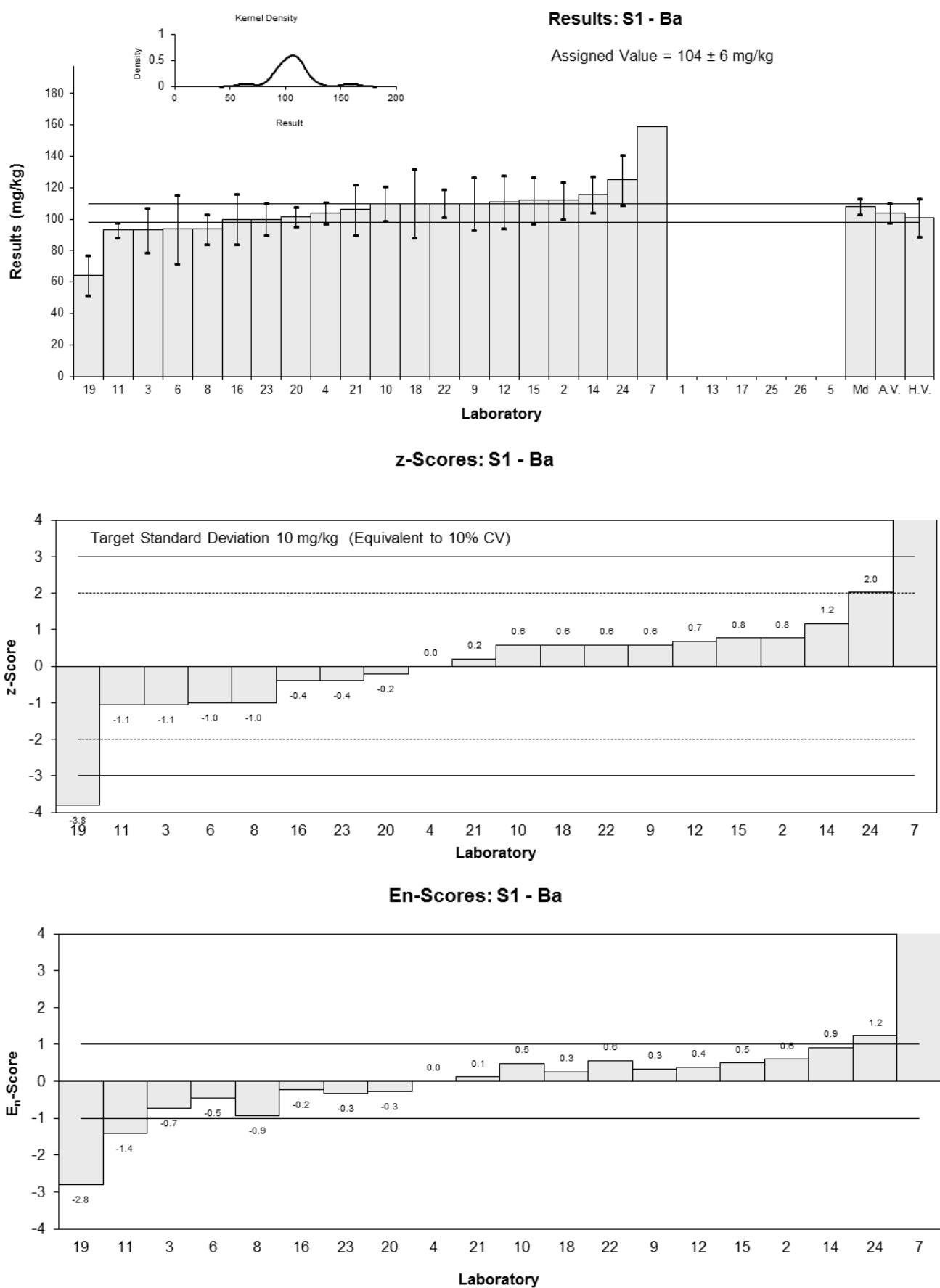


Figure 5

Table 18

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Be
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	1.47	0.44	0.59	0.25
3	1.66	0.24	1.53	1.05
4	1.3	0.5	-0.25	-0.09
5	NT	NT		
6	1.28	0.420	-0.35	-0.15
7	NT	NT		
8	1.49	0.15	0.69	0.62
9	1.6	0.31	1.23	0.71
10	<5	0.5		
11	1.2	2	-0.74	-0.07
12	<5	NR		
13	NT	NT		
14	1.48	0.15	0.64	0.57
15	1.49	0.3	0.69	0.41
16	< 2	< 0.4		
17	NT	NT		
18	<2	0.2		
19	15.3	3.06	68.89	4.55
20	1.46	0.30	0.54	0.32
21	1.18	0.18	-0.84	-0.69
22	NR	NR		
23	1	0.14	-1.73	-1.59
24	0.99	11	-1.78	-0.03
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	1.35	0.17
Spike	Not Spiked	
Homogeneity Value	1.24	0.15
Robust Average	1.38	0.18
Median	1.47	0.15
Mean	2.35	
N	14	
Max.	15.3	
Min.	0.99	
Robust SD	0.24	
Robust CV	17%	

*Robust Average excluding Laboratory 19.

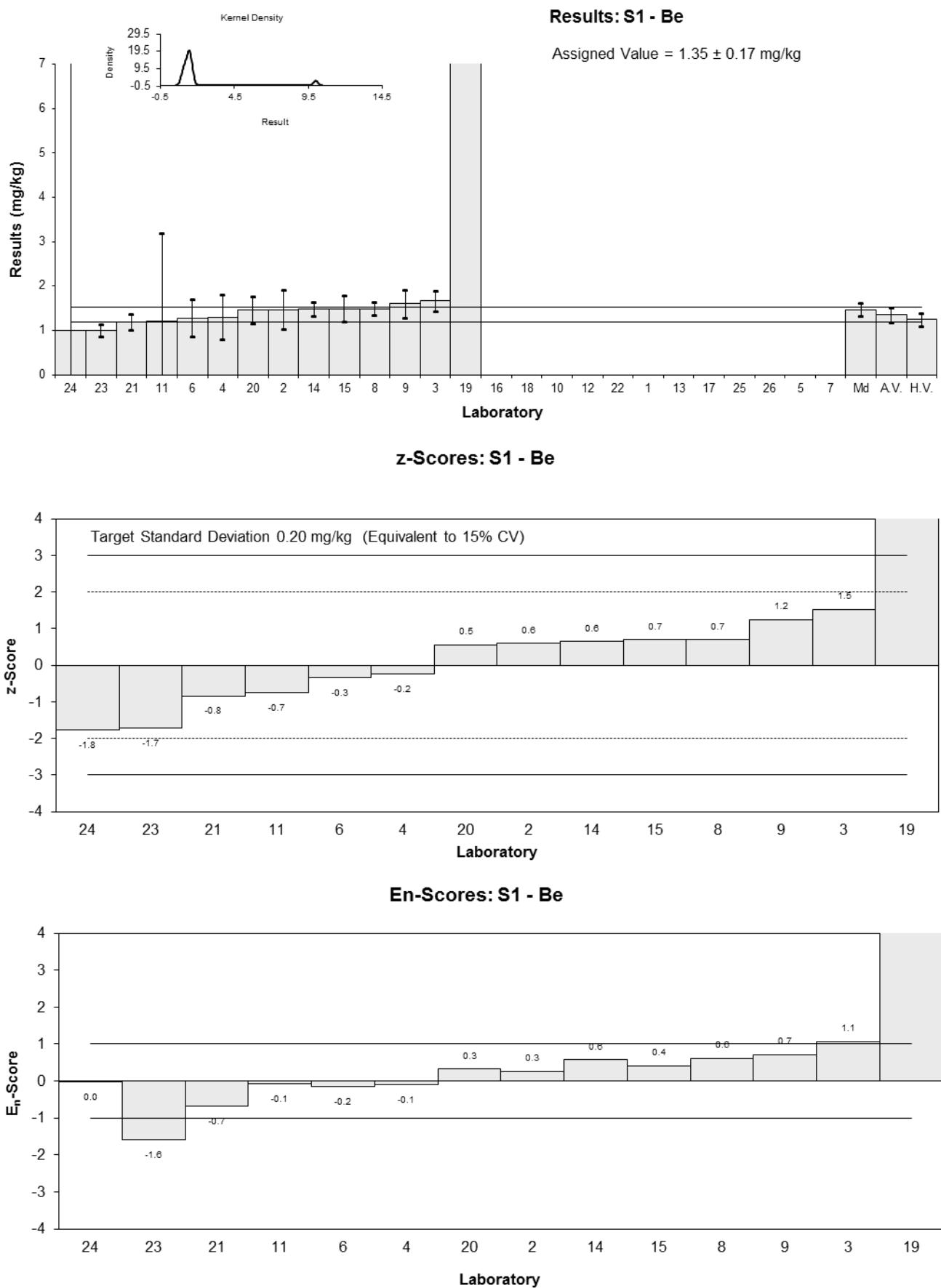


Figure 6

Table 19

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Bi
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	0.33	0.08	0.84	0.40
3	<1.0	0.15		
4	0.3	0.06	0.16	0.09
5	NT	NT		
6	<0.46	NR		
7	NT	NT		
8	0.258	0.03	-0.80	-0.63
9	0.31	0.08	0.39	0.18
10	<5	0.5		
11	<1	2		
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	0.33	0.06	0.84	0.49
16	< 10	< 2		
17	NT	NT		
18	<10	1		
19	NT	NT		
20	<0.4	0.27		
21	0.23	0.03	-1.43	-1.13
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	0.293	0.047
Spike	Not Spiked	
Homogeneity Value	0.355	0.043
Robust Average	0.293	0.047
Median	0.305	0.039
Mean	0.293	
N	6	
Max.	0.33	
Min.	0.23	
Robust SD	0.046	
Robust CV	16%	

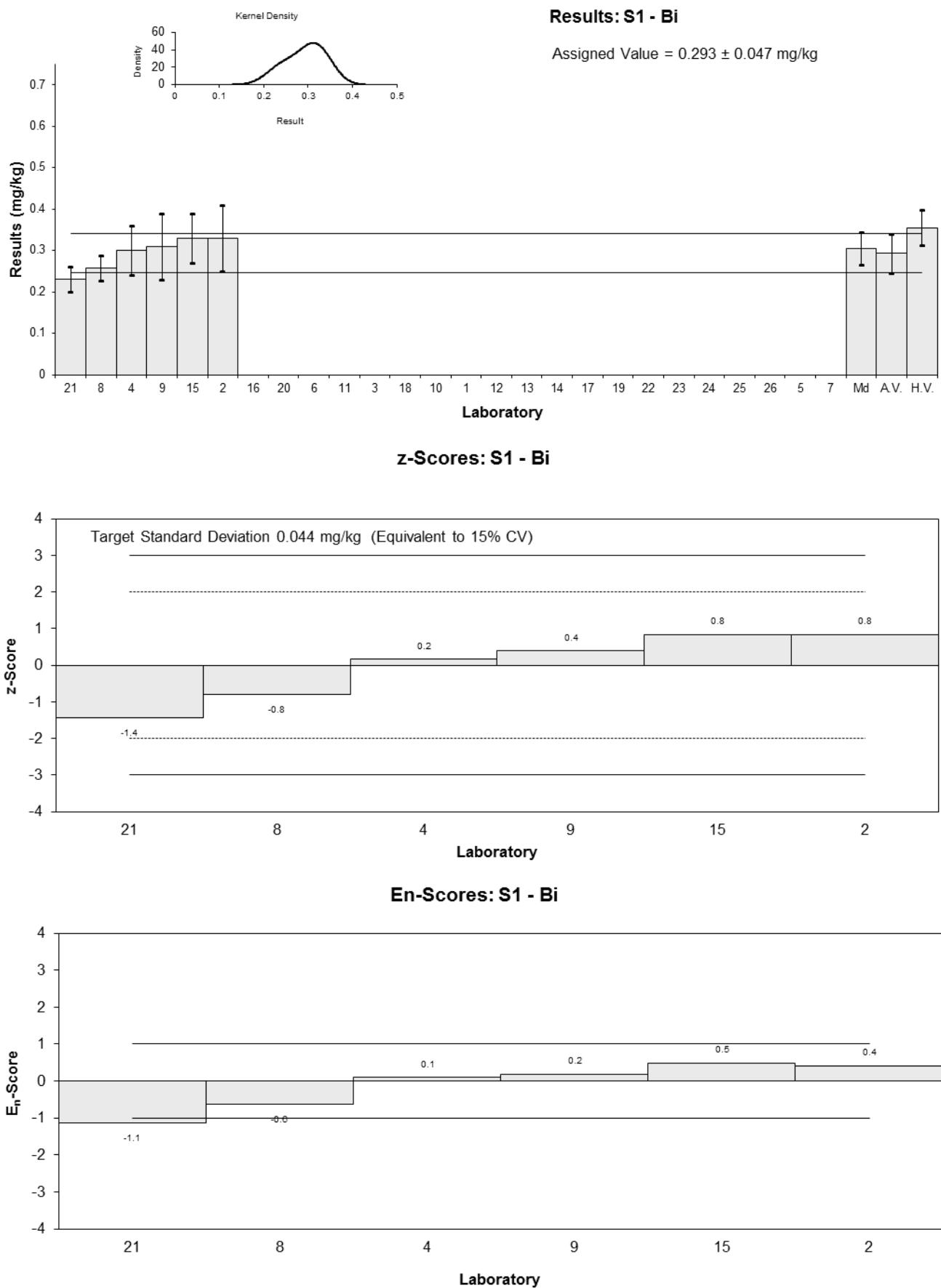


Figure 7

Table 20

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Ca
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	30500	3320	0.82	0.64
3	28809.1	4321.36	0.22	0.13
4	23300	1400	-1.74	-2.47
5	NT	NT		
6	26300	5800	-0.67	-0.32
7	31540	NR	1.18	2.39
8	29700	3000	0.53	0.45
9	27800	4900	-0.14	-0.08
10	NT	NT		
11	27070	1000	-0.40	-0.66
12	28600	4300	0.14	0.09
13	NT	NT		
14	26280	2630	-0.68	-0.64
15	28000	3000	-0.07	-0.06
16	30800	6200	0.92	0.41
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	28200	4000	0.00	0.00
21	27900	4185	-0.11	-0.07
22	26000	1700	-0.78	-1.00
23	25900	7224	-0.82	-0.31
24	30900	3708	0.96	0.68
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	28200	1400
Spike	Not Spiked	
Homogeneity Value	30200	3600
Robust Average	28200	1400
Median	28000	1300
Mean	28100	
N	17	
Max.	31540	
Min.	23300	
Robust SD	2300	
Robust CV	8.2%	

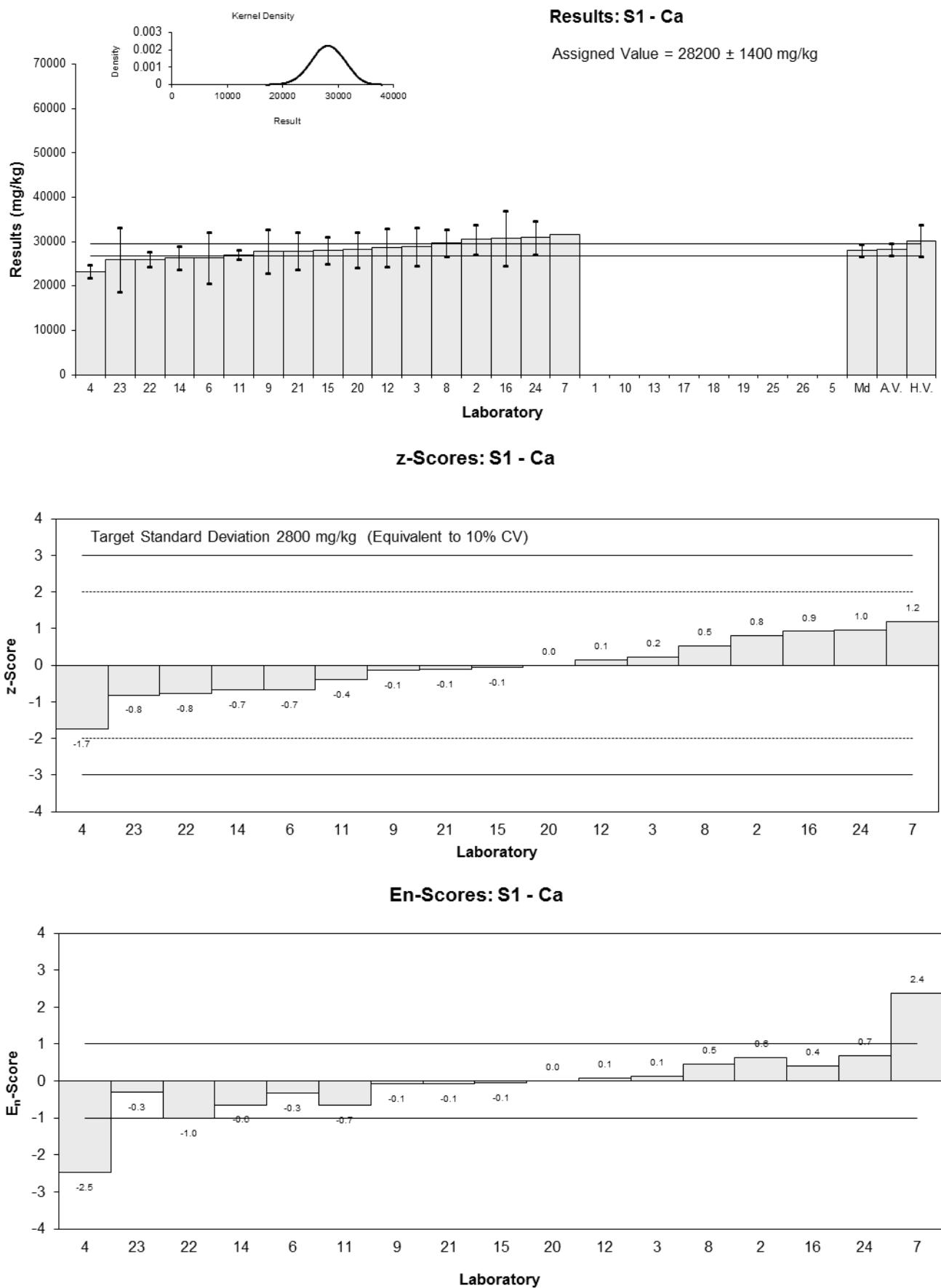


Figure 8

Table 21

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	977	220	0.87	0.35
3	1000	150	1.12	0.64
4	913	71	0.16	0.16
5	NT	NT		
6	782	120	-1.30	-0.90
7	1035	NR	1.51	2.67
8	936	94	0.41	0.35
9	920	147	0.23	0.13
10	810	121.5	-0.99	-0.68
11	830	2	-0.77	-1.35
12	871	131	-0.31	-0.20
13	NT	NT		
14	862	86.2	-0.41	-0.37
15	910	90	0.12	0.11
16	1030	170	1.46	0.74
17	NT	NT		
18	792	107	-1.19	-0.90
19	553	110.6	-3.85	-2.84
20	960	150	0.68	0.39
21	870	131	-0.32	-0.21
22	940	35	0.46	0.66
23	856	98.9	-0.48	-0.39
24	923	111	0.27	0.20
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	899	51
Spike	Not Spiked	
Homogeneity Value	945	100
Robust Average	899	51
Median	912	36
Mean	889	
N	20	
Max.	1035	
Min.	553	
Robust SD	91	
Robust CV	10%	

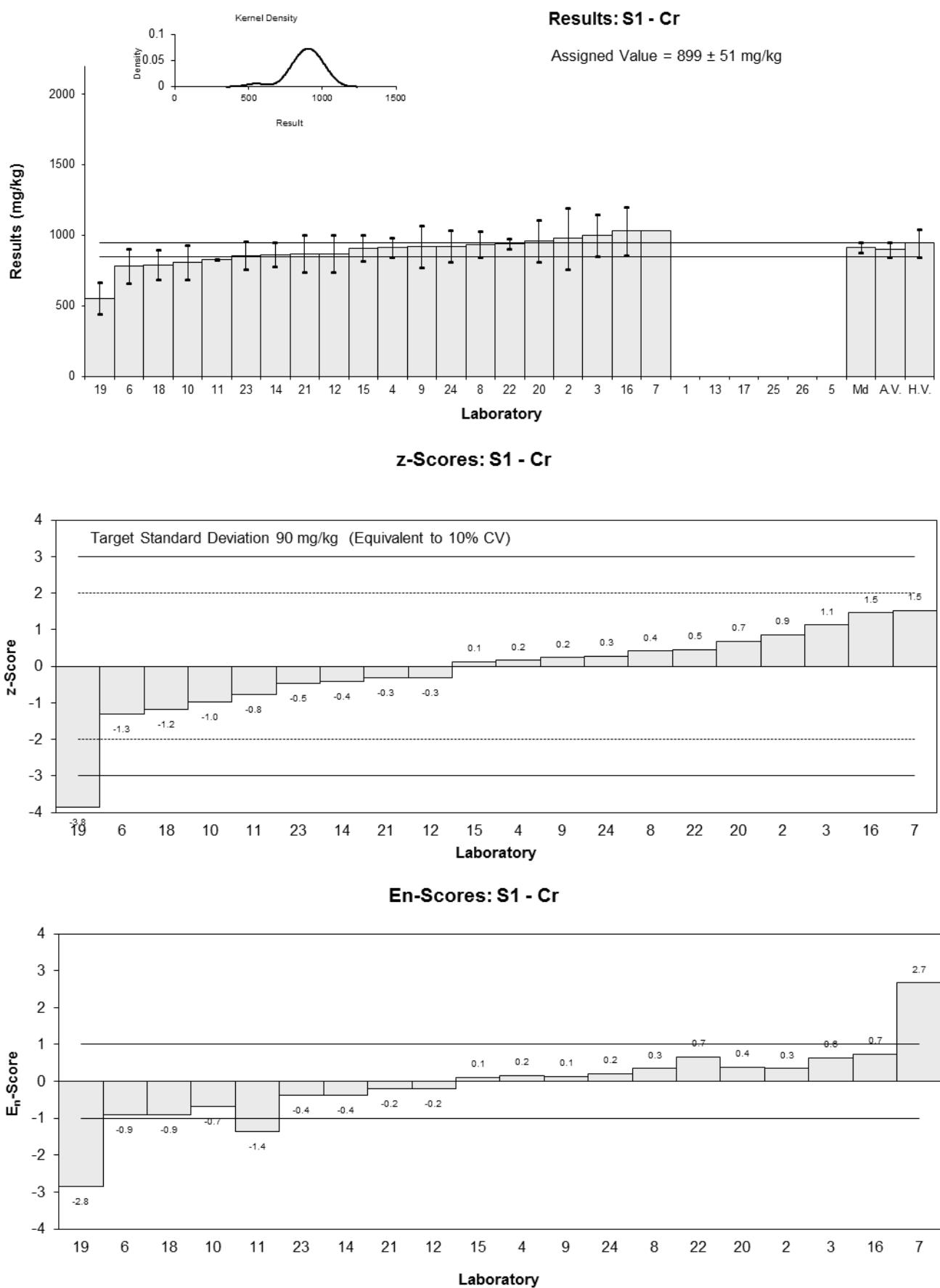


Figure 9

Table 22

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	14.2	2.7	0.35	0.24
3	15.3	2.29	0.89	0.70
4	12.8	0.7	-0.35	-0.50
5	NT	NT		
6	11.4	1.70	-1.04	-1.01
7	NR	NR		
8	13.4	1.3	-0.05	-0.06
9	13	2.1	-0.25	-0.21
10	11	1.65	-1.23	-1.23
11	11.6	2	-0.94	-0.81
12	14	2	0.25	0.21
13	NT	NT		
14	14.7	1.47	0.59	0.63
15	14.8	2.0	0.64	0.56
16	13.3	2.4	-0.10	-0.07
17	NT	NT		
18	12.1	1.64	-0.69	-0.69
19	15.7	3.14	1.09	0.65
20	14.0	2.4	0.25	0.19
21	11.2	1.68	-1.14	-1.11
22	18	4	2.22	1.08
23	11	1.35	-1.23	-1.38
24	16.6	3.7	1.53	0.80
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	13.5	1.2
Spike	Not Spiked	
Homogeneity Value	13.2	1.6
Robust Average	13.5	1.2
Median	13.4	1.0
Mean	13.6	
N	19	
Max.	18	
Min.	11	
Robust SD	2.1	
Robust CV	16%	

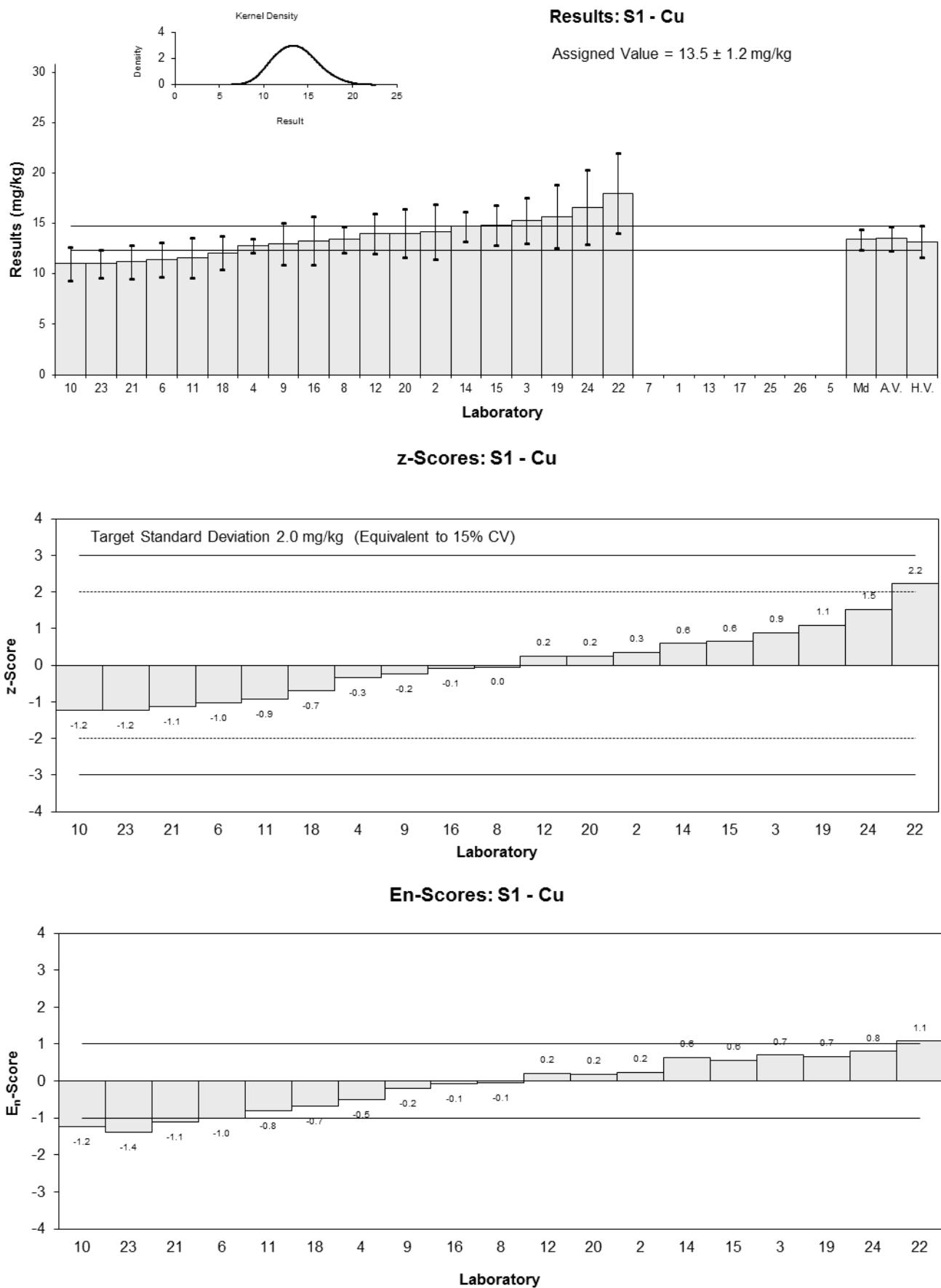


Figure 10

Table 23

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Fe
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	42186	5610	0.52	0.35
3	43700	6555	0.90	0.52
4	NR	NR		
5	NT	NT		
6	35100	7700	-1.25	-0.63
7	43101	NR	0.75	1.43
8	42800	4300	0.67	0.56
9	40900	9650	0.20	0.08
10	35000	3500	-1.27	-1.25
11	36850	1000	-0.81	-1.40
12	40400	7700	0.07	0.04
13	NT	NT		
14	39220	3922	-0.22	-0.20
15	42500	4500	0.60	0.48
16	39300	7900	-0.20	-0.10
17	NT	NT		
18	35603	4066	-1.12	-0.98
19	NT	NT		
20	37200	3800	-0.72	-0.67
21	38276	5741	-0.45	-0.30
22	43000	2000	0.72	1.00
23	41400	4413	0.32	0.27
24	50800	9652	2.67	1.08
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	40100	2100
Spike	Not Spiked	
Homogeneity Value	43200	5200
Robust Average	40100	2100
Median	40700	1700
Mean	40400	
N	18	
Max.	50800	
Min.	35000	
Robust SD	3600	
Robust CV	9%	

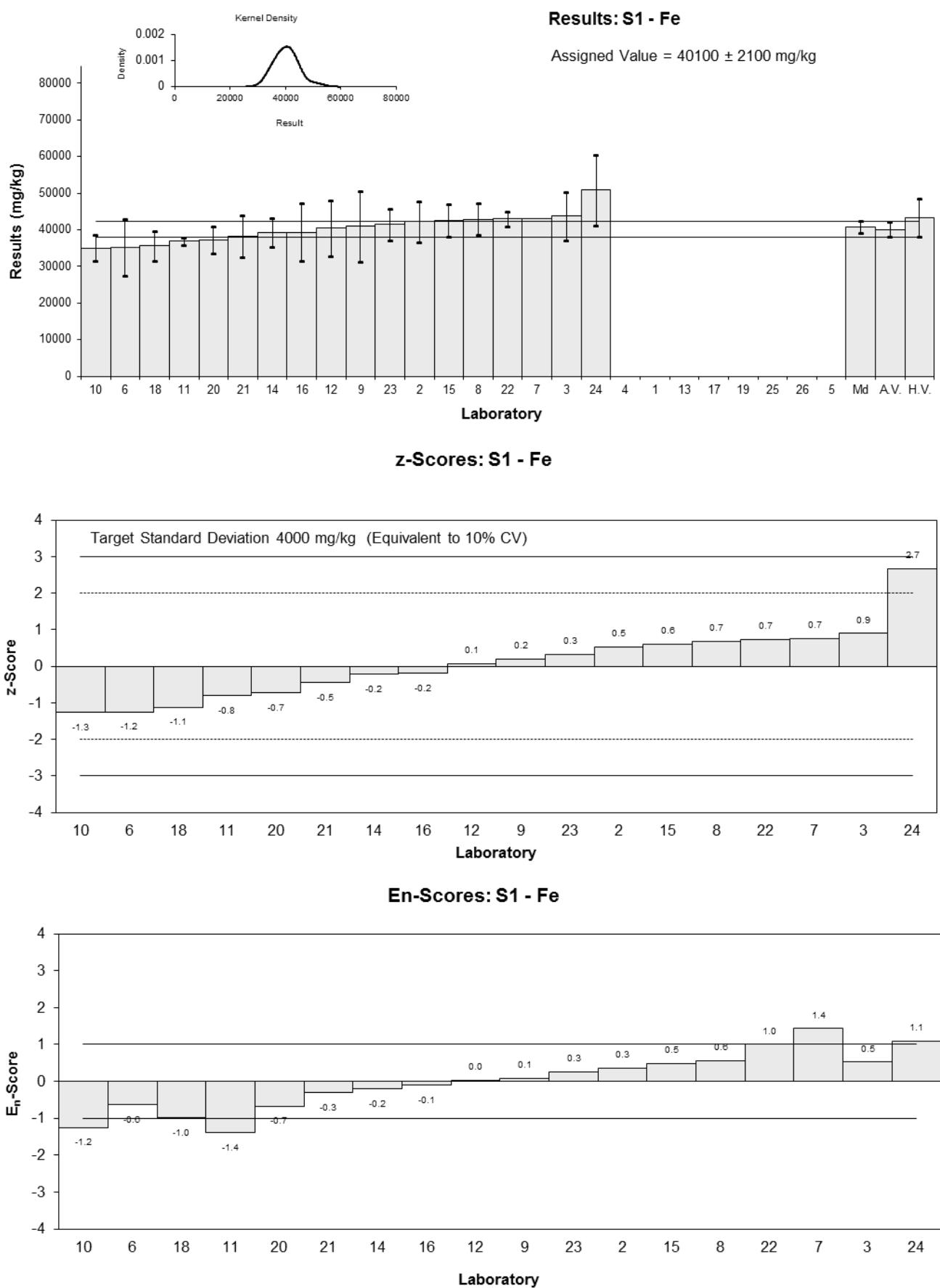


Figure 11

Table 24

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Ga
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	NT	NT		
3	17.34	2.60	1.47	0.79
4	14	2.8	-0.09	-0.05
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NR	NR		
9	10	2.4	-1.97	-1.09
10	NT	NT		
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	14.2	2.84	0.00	0.00
19	NT	NT		
20	NT	NT		
21	16.5	2.47	1.08	0.59
22	NT	NT		
23	12.9	1.94	-0.61	-0.36
24	NT	NT		
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	14.2	3.0
Spike	Not Spiked	
Homogeneity Value	12.0	1.4
Robust Average	14.2	3.0
Median	14.1	2.8
Mean	14.2	
N	6	
Max.	17.34	
Min.	10	
Robust SD	3	
Robust CV	21%	

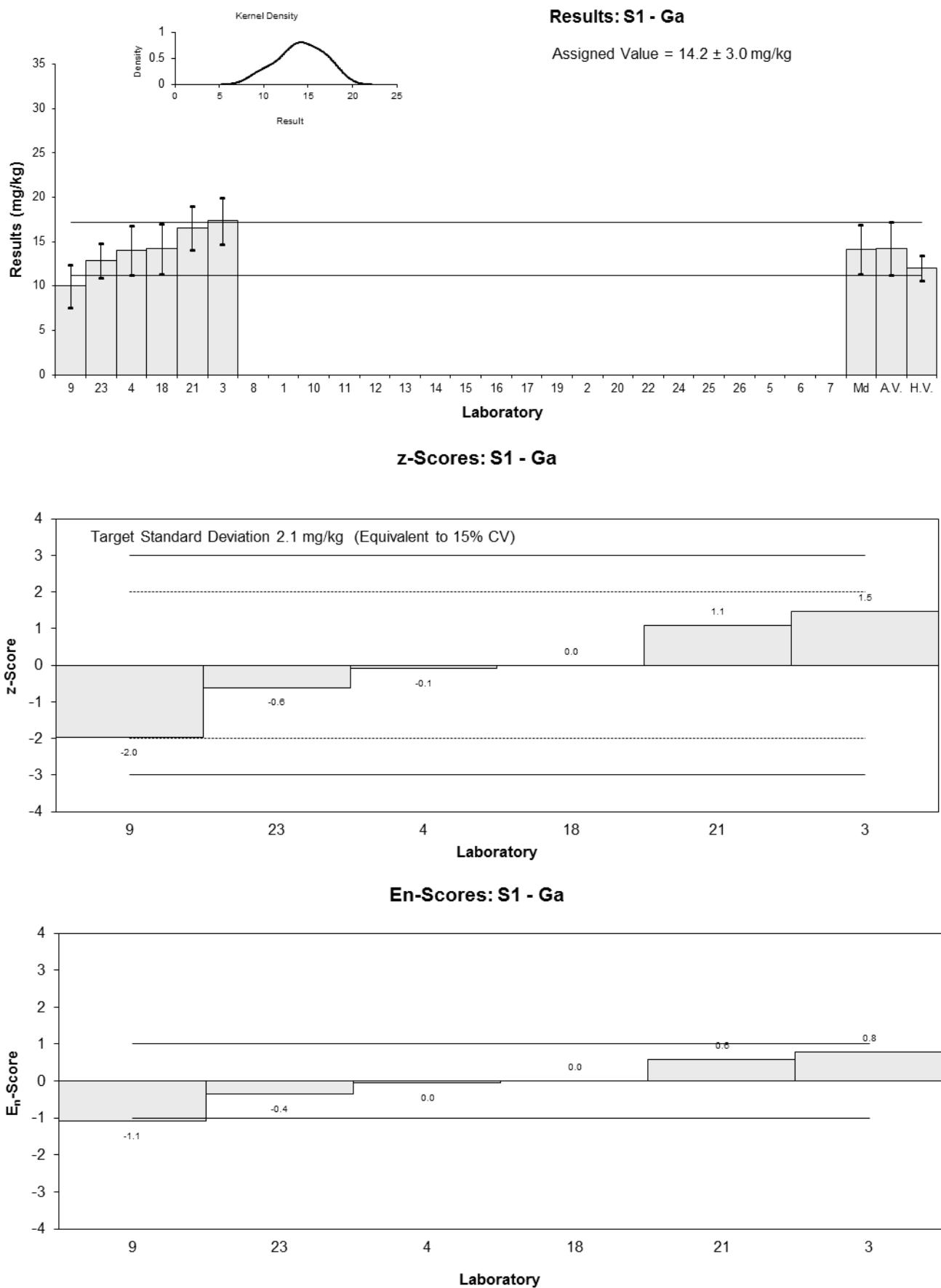


Figure 12

Table 25

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	0.054	0.005
3	0.040	0.006
4	0.05	0.005
5	NT	NT
6	<0.23	NR
7	NR	NR
8	0.058	0.02
9	0.05	0.01
10	0.2	0.03
11	NT	NT
12	0.04	0.01
13	NT	NT
14	0.18	0.018
15	0.07	0.03
16	< 0.1	< 0.02
17	NT	NT
18	0.22	0.04
19	NT	NT
20	<0.10	0.067
21	0.28	0.04
22	NR	NR
23	<0.1	NR
24	0.32	0.07
25	NT	NT
26	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	<0.001	
Robust Average	0.128	0.082
Median	0.064	0.023
Mean	0.130	
N	12	
Max.	0.32	
Min.	0.04	
Robust SD	0.088	
Robust CV	69%	

Results: S1 - Hg

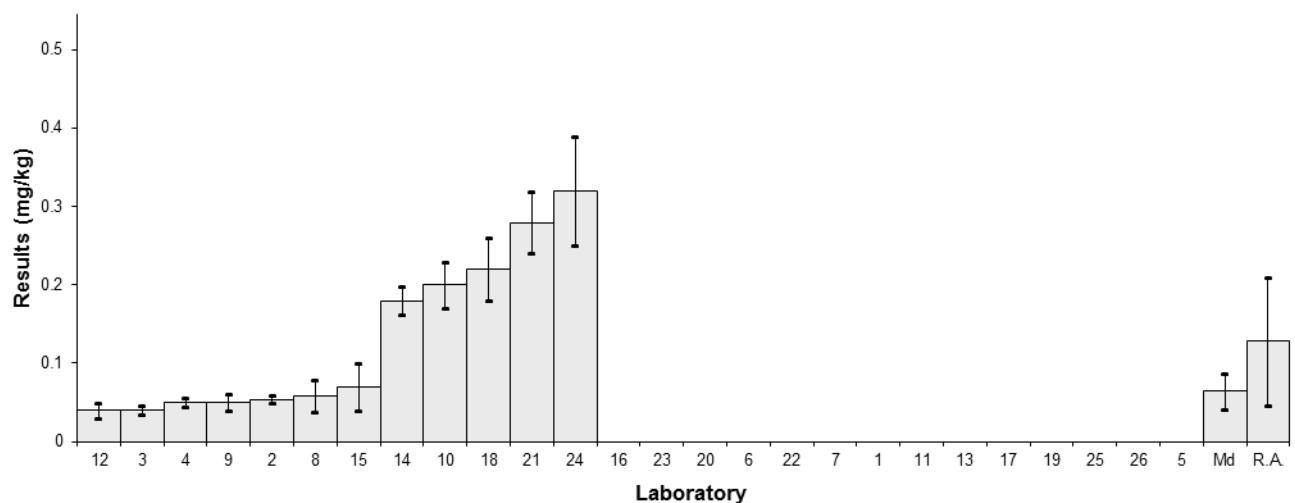


Figure 13

Table 26

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	K
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	2394	800	1.85	0.46
3	2094.08	314.11	0.37	0.21
4	NR	NR		
5	NT	NT		
6	1610	240	-2.03	-1.39
7	2176	NR	0.77	0.92
8	2160	220	0.69	0.50
9	1850	352	-0.84	-0.43
10	NT	NT		
11	1980	200	-0.20	-0.15
12	2310	350	1.44	0.75
13	NT	NT		
14	1838	184	-0.90	-0.73
15	1950	200	-0.35	-0.27
16	2050	410	0.15	0.07
17	NT	NT		
18	NT	NT		
19	1660	332	-1.78	-0.97
20	1960	290	-0.30	-0.18
21	1997	300	-0.11	-0.07
22	2500	360	2.38	1.21
23	1850	490	-0.84	-0.33
24	3420	410	6.93	3.15
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	2020	170
Spike	Not Spiked	
Homogeneity Value	2120	260
Robust Average	2050	180
Median	2000	120
Mean	2100	
N	17	
Max.	3420	
Min.	1610	
Robust SD	270	
Robust CV	13%	

*Robust Average excluding Laboratory 24.

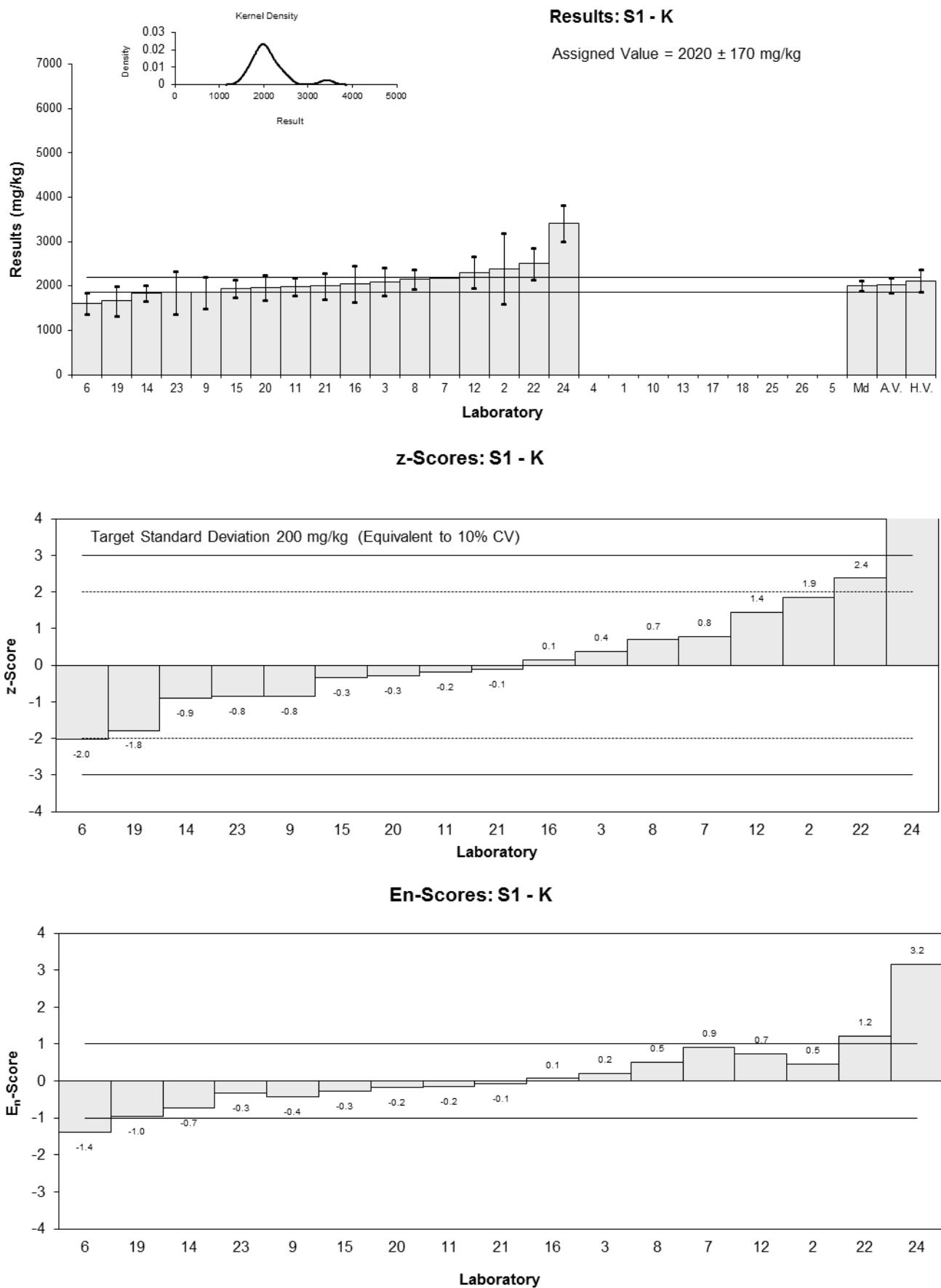


Figure 14

Table 27

Sample Details

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

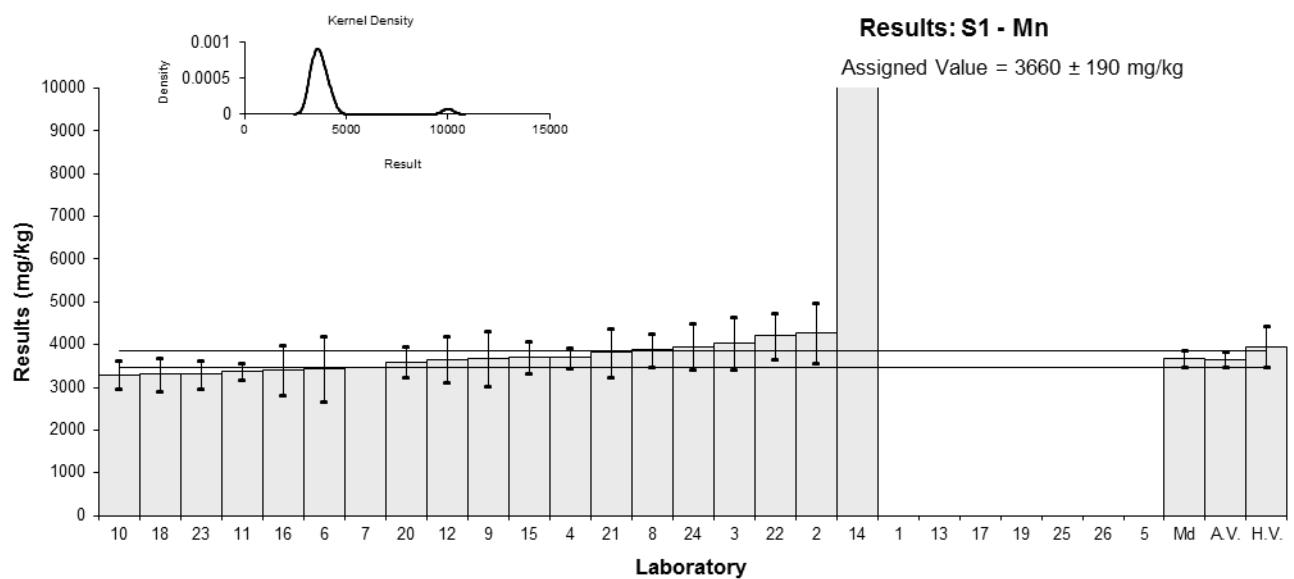
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	4269	696	1.66	0.84
3	4040.0	606	1.04	0.60
4	3700	240	0.11	0.13
5	NT	NT		
6	3440	760	-0.60	-0.28
7	3473	NR	-0.51	-0.98
8	3880	390	0.60	0.51
9	3670	640	0.03	0.01
10	3300	330	-0.98	-0.95
11	3375	200	-0.78	-1.03
12	3660	550	0.00	0.00
13	NT	NT		
14	35890	3589	88.06	8.97
15	3700	370	0.11	0.10
16	3410	580	-0.68	-0.41
17	NT	NT		
18	3306	384	-0.97	-0.83
19	NT	NT		
20	3590	360	-0.19	-0.17
21	3811	572	0.41	0.25
22	4200	530	1.48	0.96
23	3310	327	-0.96	-0.93
24	3960	554	0.82	0.51
25	NT	NT		
26	NT	NT		

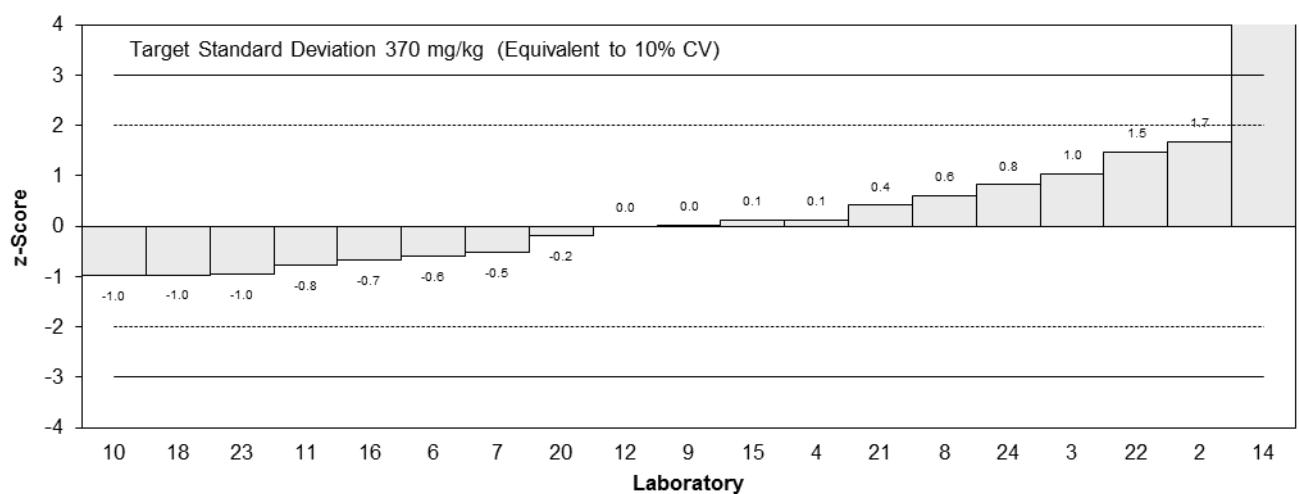
Statistics

Assigned Value*	3660	190
Spike	Not Spiked	
Homogeneity Value	3960	480
Robust Average	3700	210
Median	3670	190
Mean	5370	
N	19	
Max.	35890	
Min.	3300	
Robust SD	330	
Robust CV	8.9%	

*Robust Average excluding Laboratory 14.



z-Scores: S1 - Mn



En-Scores: S1 - Mn

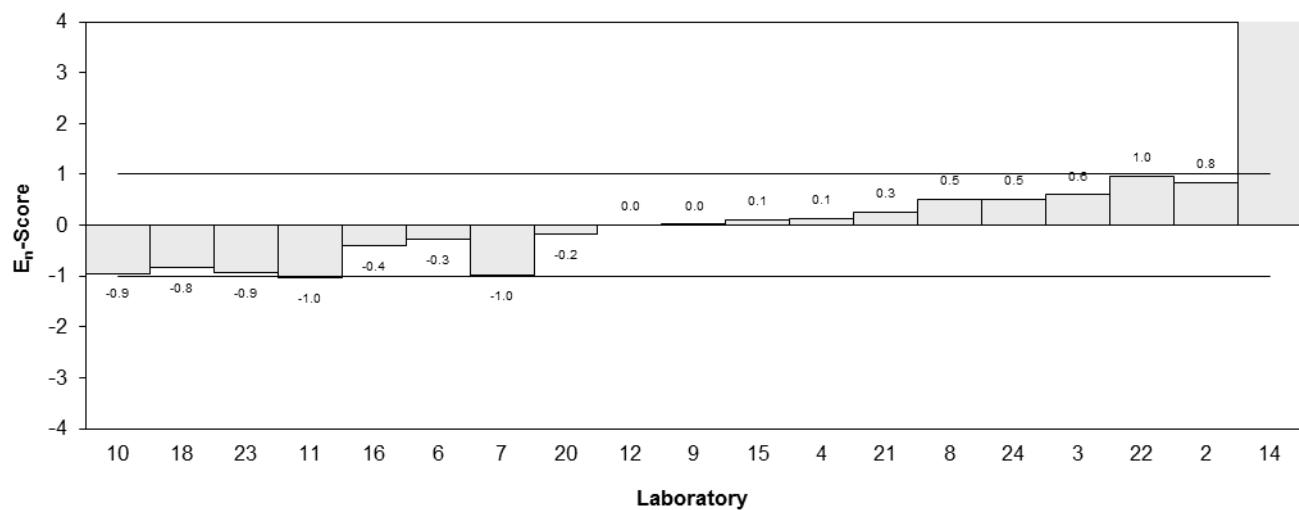


Figure 15

Table 28

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	14.3	3.5	-1.46	-0.99
3	14.9	2.23	-1.24	-1.14
4	17	1.7	-0.47	-0.50
5	NT	NT		
6	14.8	2.5	-1.28	-1.09
7	NR	NR		
8	21.3	2.1	1.09	1.03
9	17	2.6	-0.47	-0.40
10	25	3.75	2.44	1.58
11	15.1	2	-1.17	-1.13
12	17	2	-0.47	-0.46
13	NT	NT		
14	20.9	2.09	0.95	0.90
15	21.1	2.2	1.02	0.94
16	21.5	3.6	1.17	0.78
17	NT	NT		
18	22.1	3.76	1.38	0.89
19	NT	NT		
20	18.4	3.4	0.04	0.03
21	17.4	2.61	-0.33	-0.27
22	18	3	-0.11	-0.08
23	14	2.24	-1.57	-1.43
24	21.2	2.3	1.06	0.95
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	18.3	2.0
Spike	Not Spiked	
Homogeneity Value	18.1	2.2
Robust Average	18.3	2.0
Median	17.7	2.2
Mean	18.4	
N	18	
Max.	25	
Min.	14	
Robust SD	3.5	
Robust CV	19%	

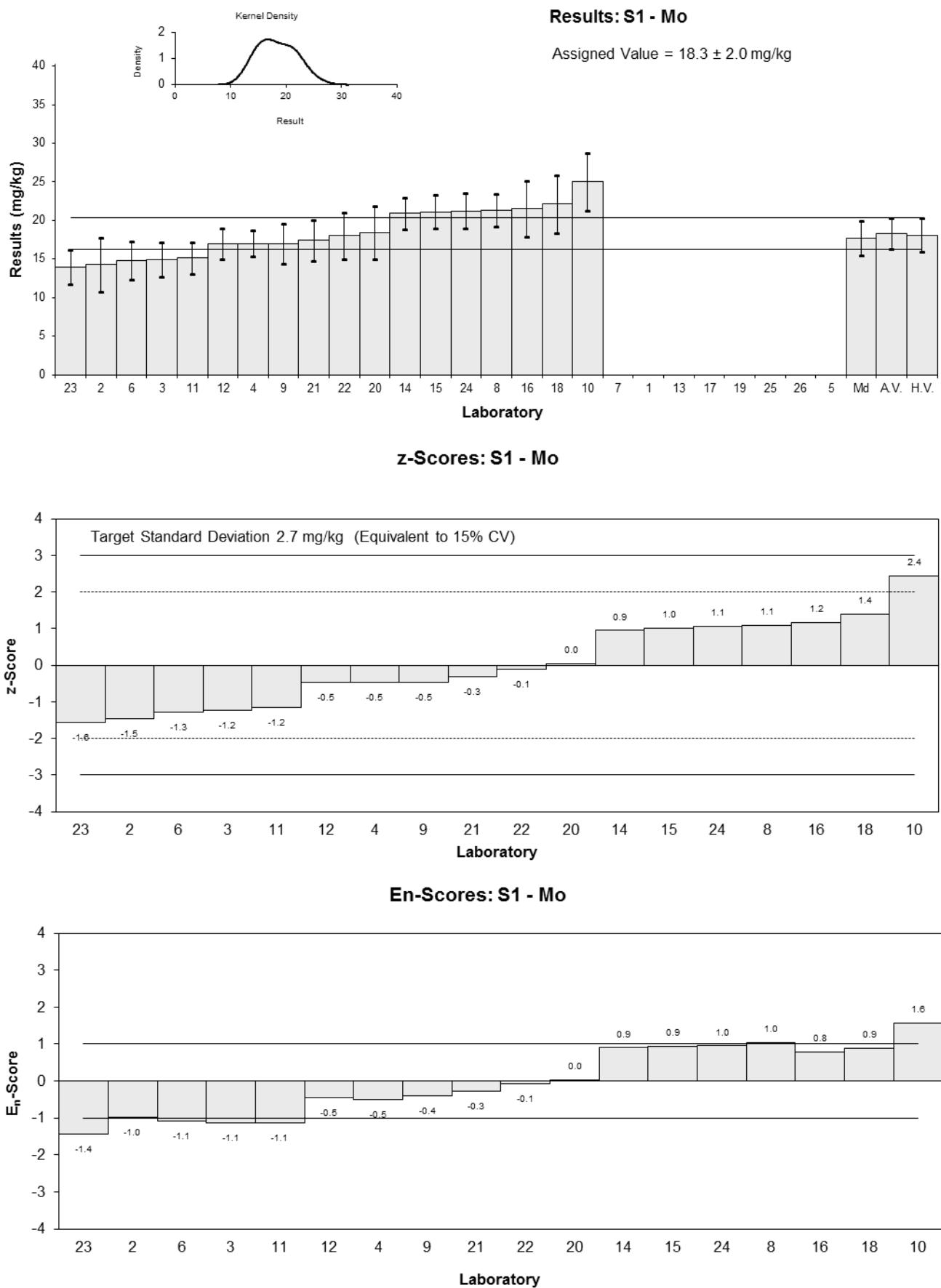


Figure 16

Table 29

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	101	18	0.24	0.12
3	89.2	13.38	-0.95	-0.61
4	92	9.9	-0.67	-0.53
5	NT	NT		
6	95.5	25	-0.31	-0.12
7	NR	NR		
8	105	10.5	0.65	0.49
9	110	19	1.16	0.56
10	88	13.2	-1.08	-0.69
11	87	10	-1.18	-0.92
12	102	12	0.34	0.24
13	NT	NT		
14	112	11.2	1.36	0.99
15	121	15	2.27	1.33
16	98.8	16.6	0.02	0.01
17	NT	NT		
18	90.6	11.5	-0.81	-0.58
19	57	11.4	-4.22	-3.02
20	113	15	1.46	0.85
21	82	12.26	-1.68	-1.15
22	100	9	0.14	0.12
23	92	9.09	-0.67	-0.55
24	118	12	1.97	1.36
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	98.6	7.7
Spike	Not Spiked	
Homogeneity Value	113	14
Robust Average	98.6	7.7
Median	98.8	6.9
Mean	97.6	
N	19	
Max.	121	
Min.	57	
Robust SD	13	
Robust CV	13%	

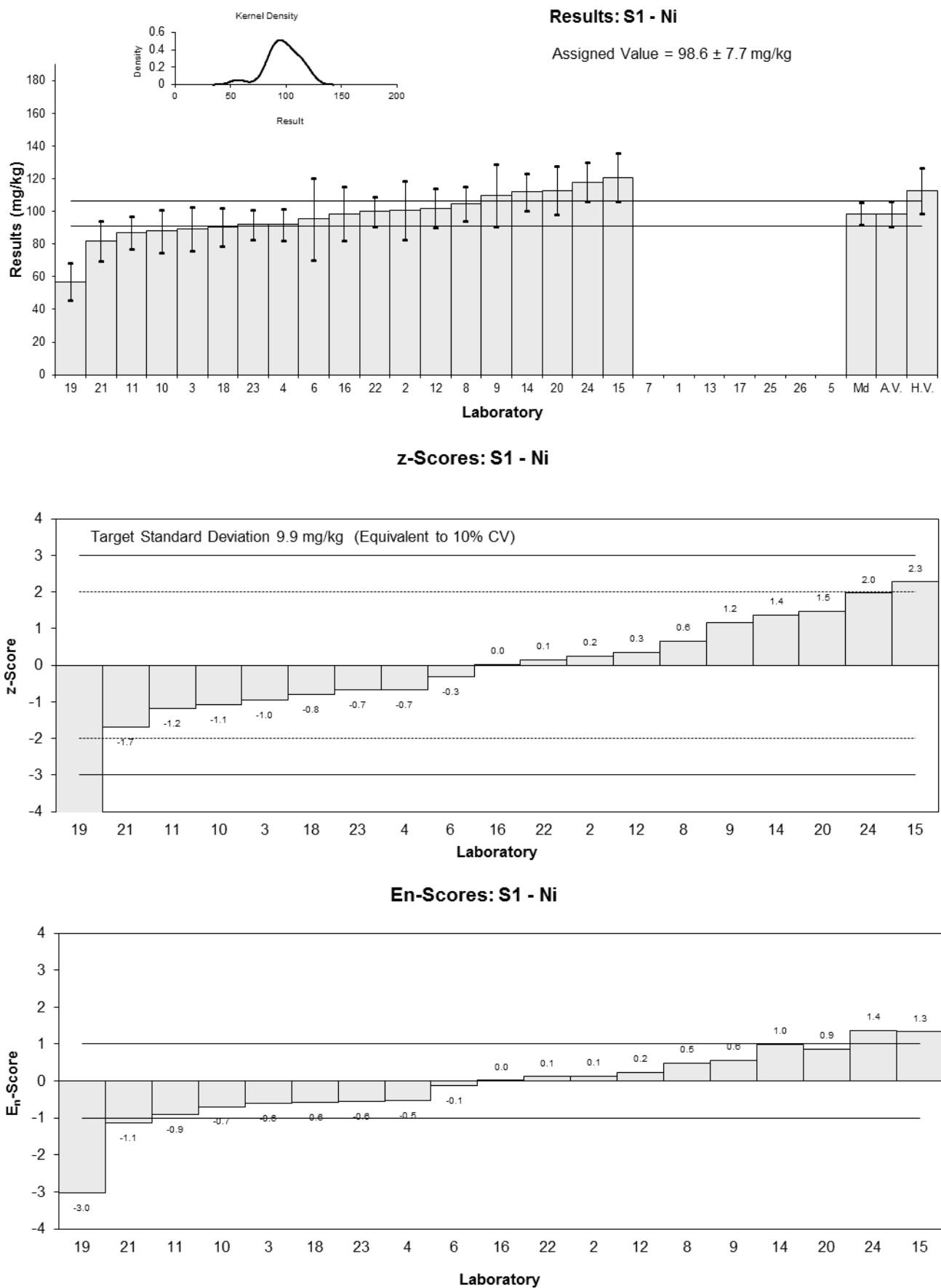


Figure 17

Table 30

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	21.6	5.3	-0.05	-0.02
3	20.4	3.06	-0.60	-0.40
4	21	2	-0.32	-0.31
5	NT	NT		
6	19.2	3.1	-1.15	-0.76
7	36.0	NR	6.59	13.00
8	21.6	2.2	-0.05	-0.04
9	21	2.8	-0.32	-0.23
10	23	3.45	0.60	0.36
11	20	2	-0.78	-0.74
12	22	2	0.14	0.13
13	NT	NT		
14	24.0	2.40	1.06	0.87
15	28.8	3.0	3.27	2.22
16	20.6	3.4	-0.51	-0.31
17	NT	NT		
18	23.4	2.92	0.78	0.54
19	19.7	3.94	-0.92	-0.49
20	23.0	3.5	0.60	0.35
21	21.5	3.22	-0.09	-0.06
22	23	4	0.60	0.31
23	19	2.25	-1.24	-1.08
24	23.3	4.2	0.74	0.37
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	21.7	1.1
Spike	Not Spiked	
Homogeneity Value	22.2	2.7
Robust Average	21.9	1.1
Median	21.6	1.0
Mean	22.6	
N	20	
Max.	36	
Min.	19	
Robust SD	1.8	
Robust CV	8.2%	

*Robust Average excluding Laboratory 7.

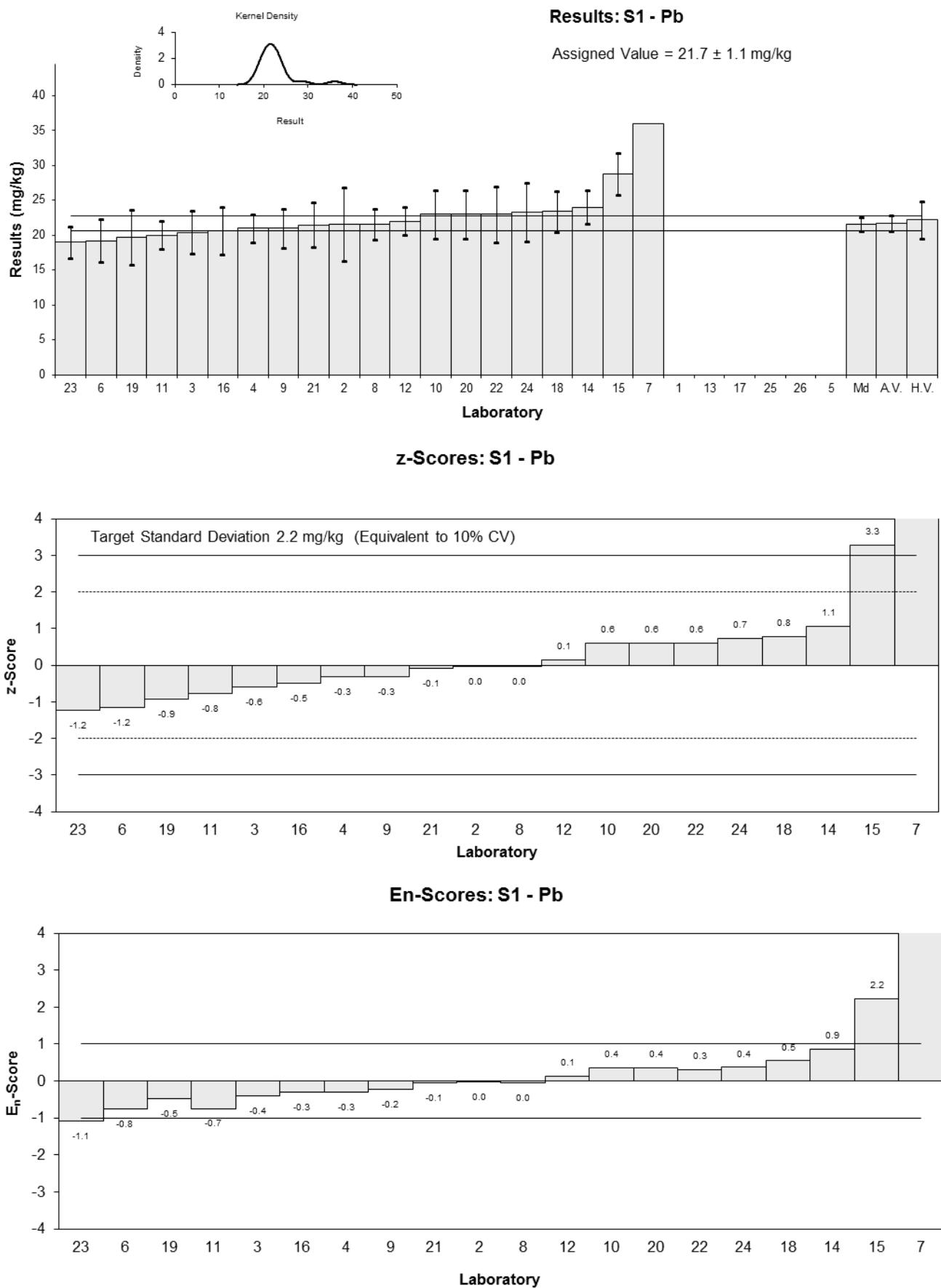


Figure 18

Table 31

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	S
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	3400	680	0.15	0.07
3	3337.64	500.64	-0.04	-0.02
4	2700	270	-1.94	-1.64
5	NT	NT		
6	3890	778	1.61	0.65
7	NT	NT		
8	3440	344	0.27	0.20
9	3060	730	-0.87	-0.37
10	NT	NT		
11	3160	300	-0.57	-0.46
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	3200	300	-0.45	-0.36
16	3830	770	1.43	0.58
17	NT	NT		
18	NT	NT		
19	NT	NT		
20	<2000	NR		
21	3416	512	0.20	0.11
22	3100	160	-0.75	-0.75
23	3000	270	-1.04	-0.88
24	4270	1110	2.75	0.80
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	3350	290
Spike	Not Spiked	
Homogeneity Value	2790	330
Robust Average	3350	290
Median	3340	210
Mean	3370	
N	13	
Max.	4270	
Min.	2700	
Robust SD	420	
Robust CV	13%	

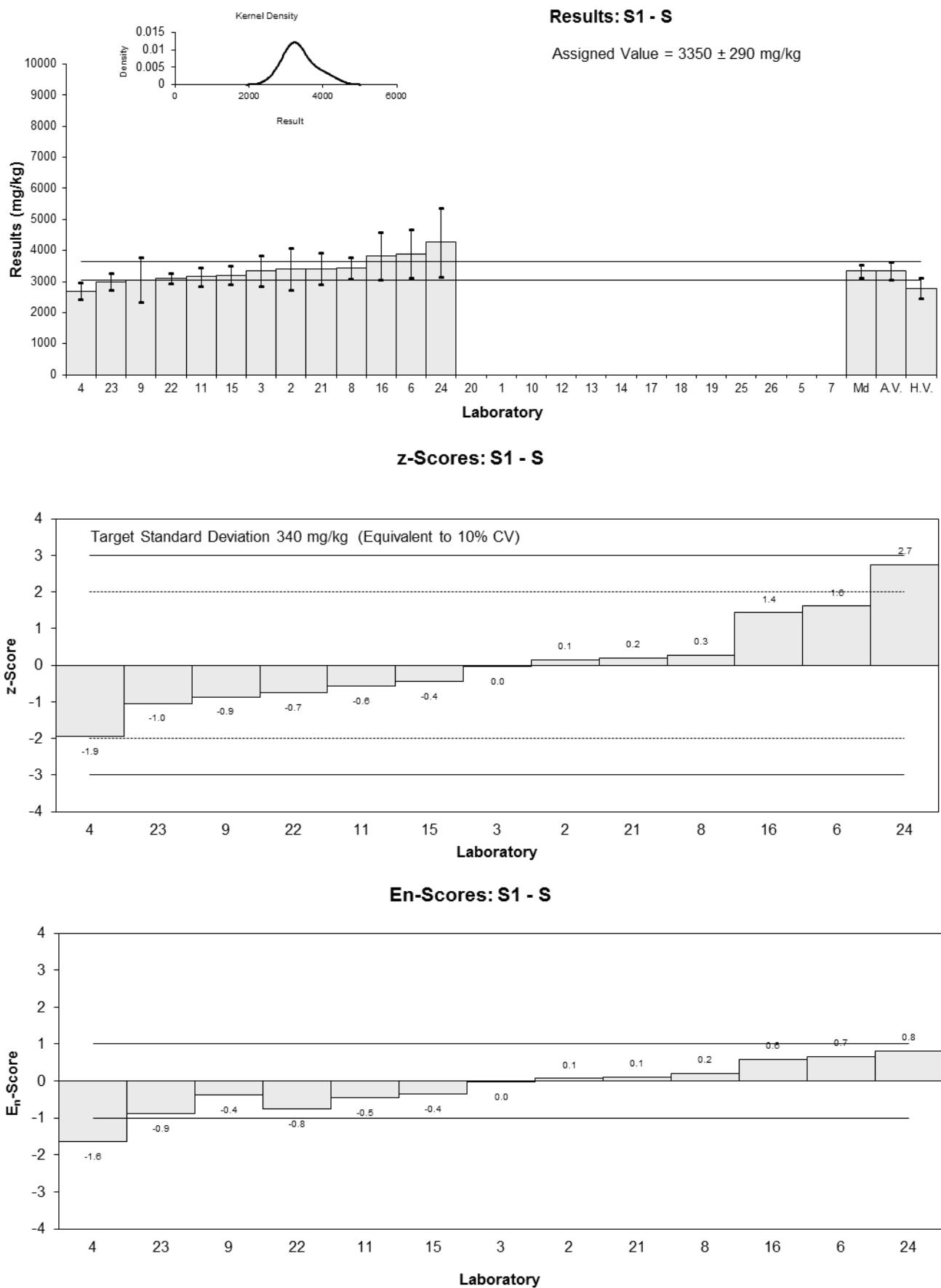


Figure 19

Table 32

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	0.27	0.06
3	<1.0	0.15
4	0.2	0.02
5	NT	NT
6	<0.92	NR
7	NR	NR
8	3.32	0.33
9	0.43	0.08
10	<2	0.2
11	13	1
12	<25	NR
13	NT	NT
14	1.25	0.13
15	1.11	0.2
16	< 2	< 0.4
17	NT	NT
18	<2	0.2
19	NT	NT
20	<2	1.4
21	1.32	0.20
22	NR	NR
23	<5	NR
24	2.1	0.5
25	NT	NT
26	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.081	0.037
Robust Average	1.5	1.2
Median	1.25	0.97
Mean	2.56	
N	9	
Max.	13	
Min.	0.2	
Robust SD	0.5	
Robust CV	33%	

Results: S1 - Se

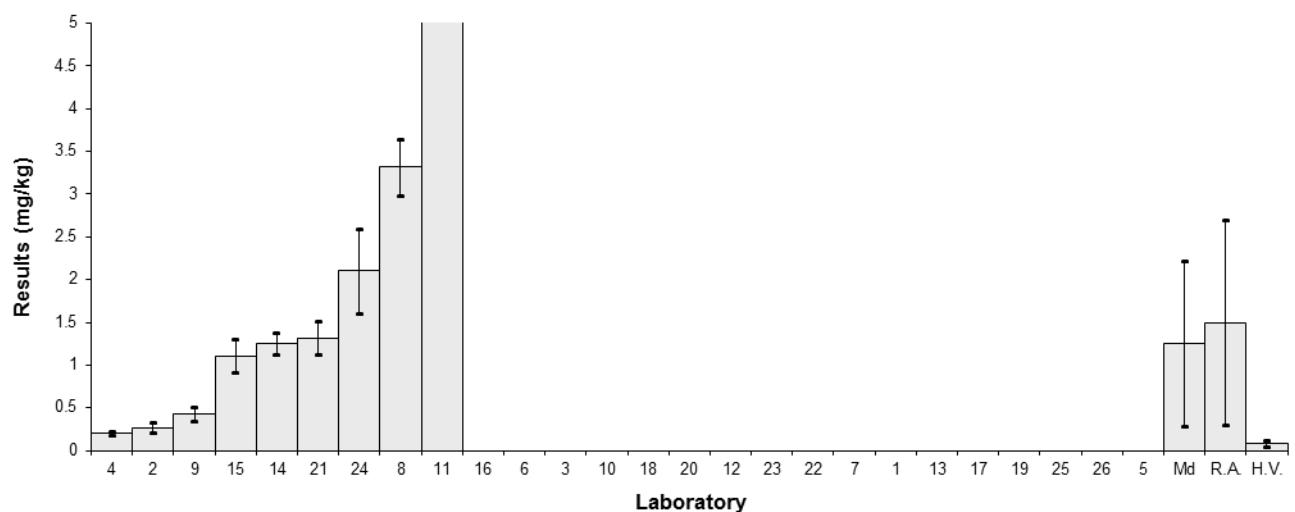


Figure 20

Table 33

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Sn
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	94.2	28.5	-1.16	-0.66
3	105.573	15.83	-0.49	-0.45
4	110	20	-0.23	-0.18
5	NT	NT		
6	97.3	28	-0.98	-0.56
7	NT	NT		
8	118	11.8	0.23	0.26
9	100	21	-0.82	-0.60
10	140	14	1.52	1.51
11	108	10	-0.35	-0.42
12	NT	NT		
13	NT	NT		
14	126	12.6	0.70	0.75
15	137	15	1.35	1.28
16	114	19	0.00	0.00
17	NT	NT		
18	128	14	0.82	0.81
19	75	15	-2.28	-2.16
20	124	25	0.58	0.37
21	110	16.5	-0.23	-0.21
22	120	8	0.35	0.47
23	102	15.2	-0.70	-0.66
24	128	24	0.82	0.54
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	114	10
Spike	Not Spiked	
Homogeneity Value	120	14
Robust Average	114	10
Median	112	9
Mean	113	
N	18	
Max.	140	
Min.	75	
Robust SD	20	
Robust CV	18%	

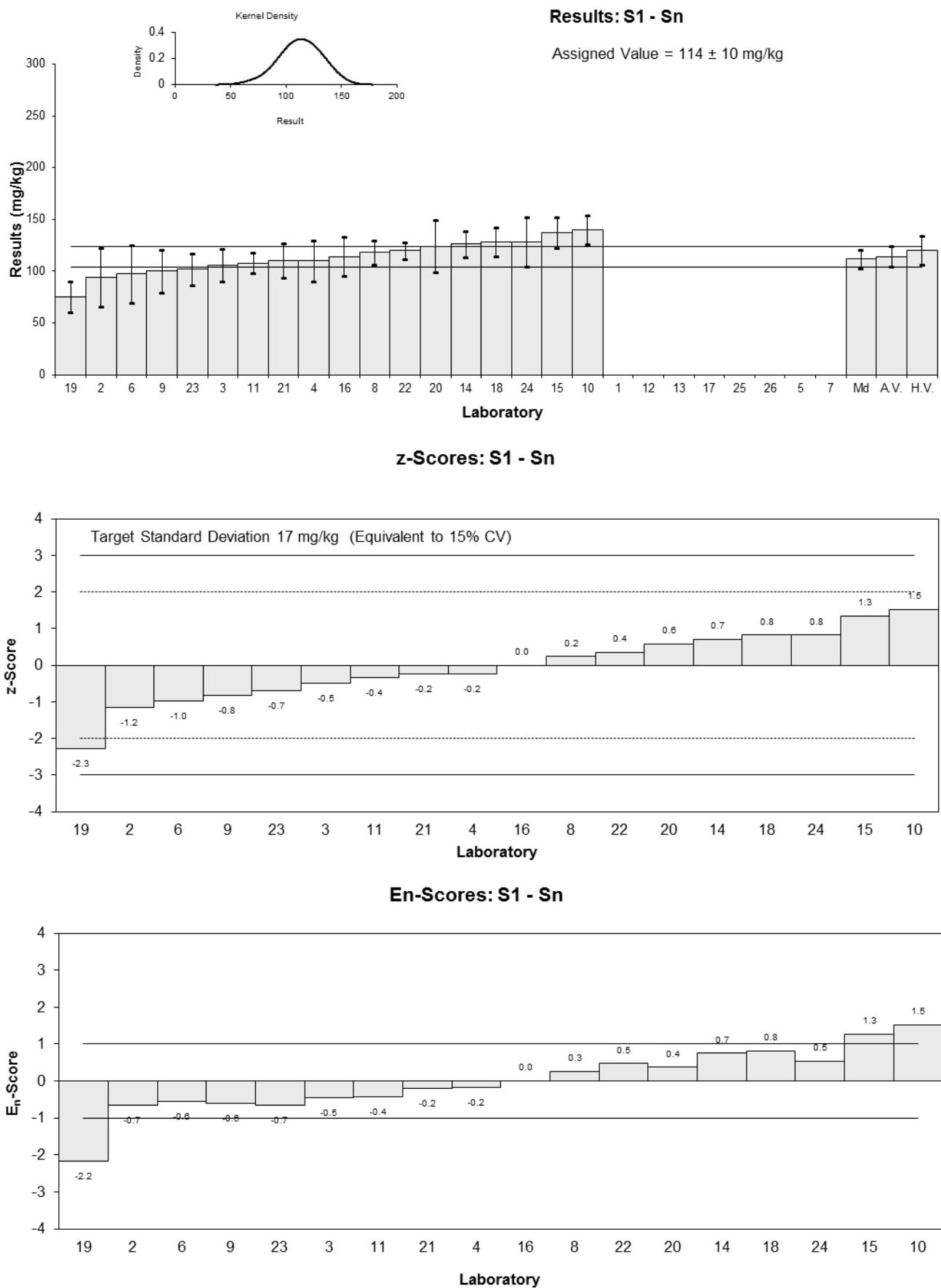


Figure 21

Table 34

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Sr
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	242	65	0.17	0.06
3	236.368	35.45	-0.07	-0.04
4	190	13	-2.02	-2.61
5	NT	NT		
6	196	35	-1.76	-1.12
7	250	NR	0.50	0.92
8	262	26	1.01	0.83
9	260	49	0.92	0.43
10	260	39	0.92	0.54
11	244	20	0.25	0.25
12	NT	NT		
13	NT	NT		
14	262	26.2	1.01	0.82
15	251	30	0.55	0.40
16	221	44	-0.71	-0.37
17	NT	NT		
18	244	20	0.25	0.25
19	NT	NT		
20	241	25	0.13	0.11
21	235	35.3	-0.13	-0.08
22	220	28	-0.76	-0.58
23	208	17.2	-1.26	-1.39
24	235	33	-0.13	-0.08
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	238	13
Spike	Not Spiked	
Homogeneity Value	251	30
Robust Average	238	13
Median	242	10
Mean	237	
N	18	
Max.	262	
Min.	190	
Robust SD	22	
Robust CV	9.2%	

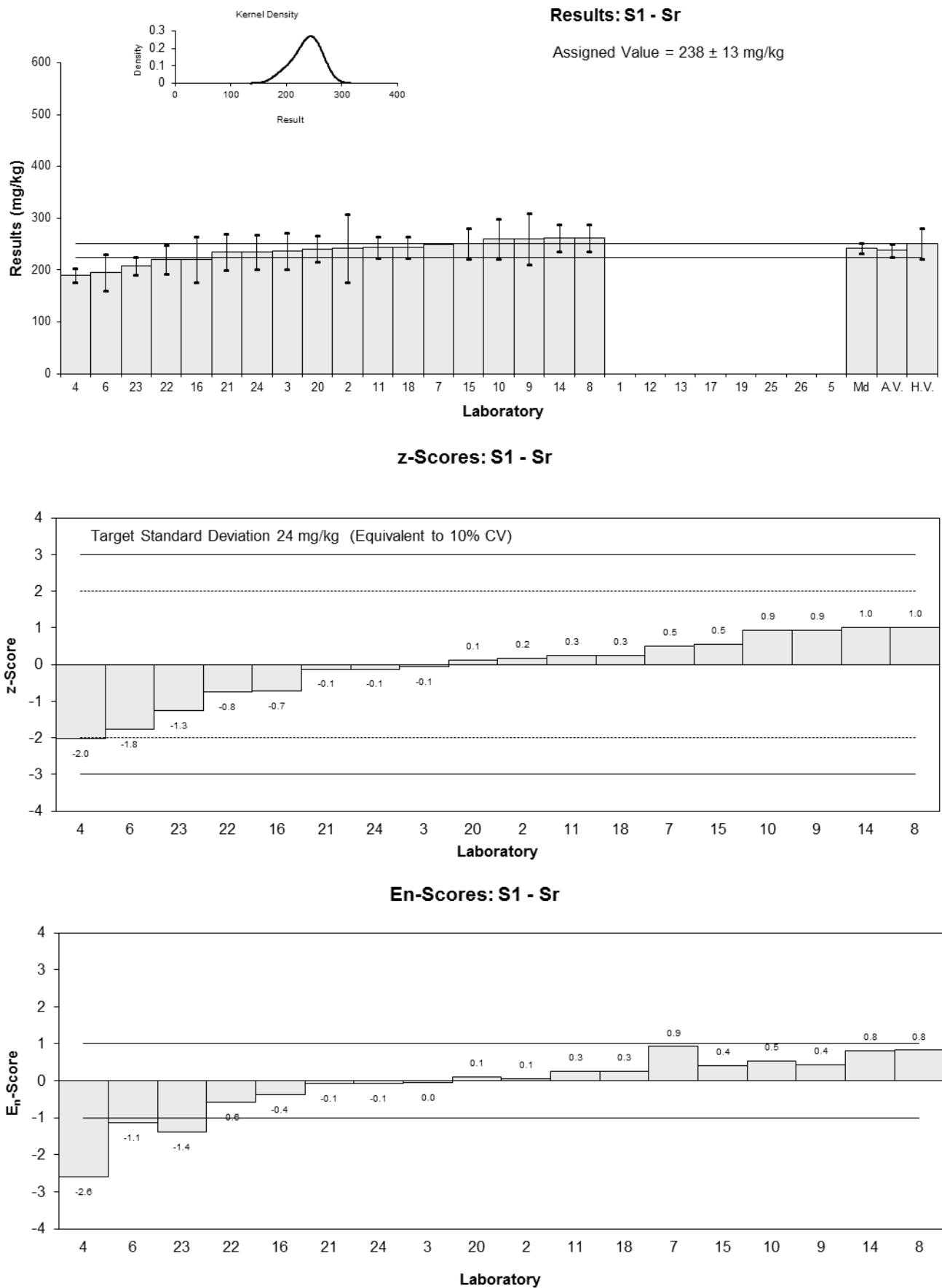


Figure 22

Table 35

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Th
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	NT	NT		
3	76.79	11.51	2.53	1.16
4	40	6	-1.08	-0.55
5	NT	NT		
6	NT	NT		
7	NT	NT		
8	NR	NR		
9	43	10	-0.78	-0.37
10	NT	NT		
11	NR	NR		
12	NT	NT		
13	NT	NT		
14	NT	NT		
15	37.8	8.0	-1.29	-0.64
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	67.5	13.5	1.62	0.71
20	NT	NT		
21	92.0	13.80	4.02	1.75
22	NT	NT		
23	45.4	4.1	-0.55	-0.29
24	NT	NT		
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	51	19
Spike	Not Spiked	
Homogeneity Value	42.7	5.1
Robust Average	57	23
Median	45	10
Mean	57.5	
N	7	
Max.	92	
Min.	37.8	
Robust SD	18	
Robust CV	32%	

*Robust Average excluding Laboratory 21.

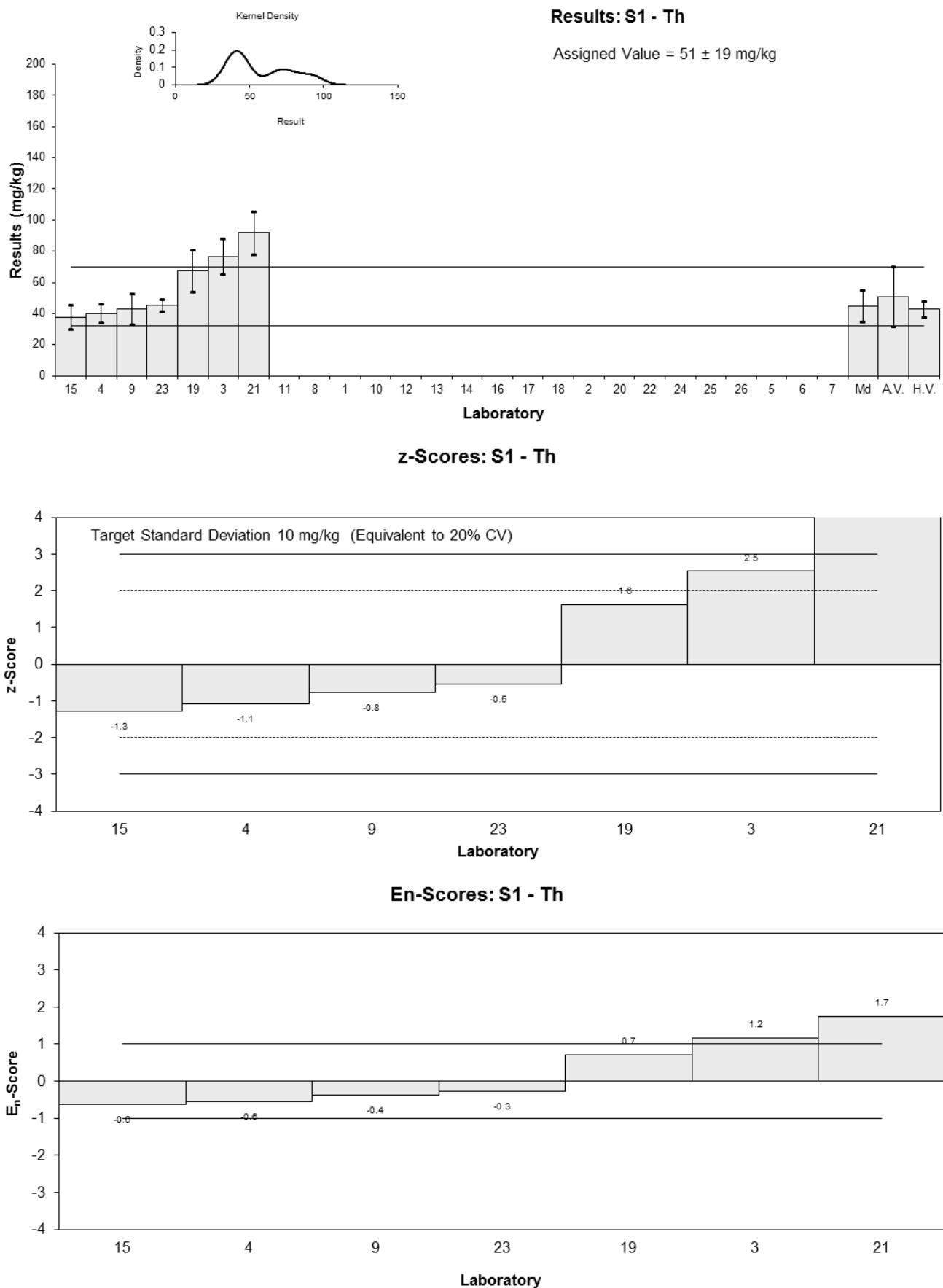


Figure 23

Table 36

Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	U
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	31.4	7.9	0.16	0.06
3	NT	NT		
4	28	1.2	-0.94	-1.16
5	NT	NT		
6	27.5	4.9	-1.10	-0.63
7	50.0	NR	6.18	8.68
8	26.3	2.6	-1.49	-1.35
9	31	7.4	0.03	0.01
10	31	4.65	0.03	0.02
11	NR	NR		
12	NT	NT		
13	NT	NT		
14	34.8	3.48	1.26	0.95
15	27.6	3.0	-1.07	-0.89
16	27.8	5.6	-1.00	-0.52
17	NT	NT		
18	33.4	6.01	0.81	0.39
19	31.3	6.26	0.13	0.06
20	30.4	1.9	-0.16	-0.17
21	31.6	4.74	0.23	0.13
22	NT	NT		
23	36.8	10.3	1.91	0.56
24	34.8	6.6	1.26	0.56
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	30.9	2.2
Spike	Not Spiked	
Homogeneity Value	31.8	3.8
Robust Average	31.3	2.4
Median	31.2	2.6
Mean	32.1	
N	16	
Max.	50	
Min.	26.3	
Robust SD	3.4	
Robust CV	11%	

*Robust Average excluding Laboratory 7.

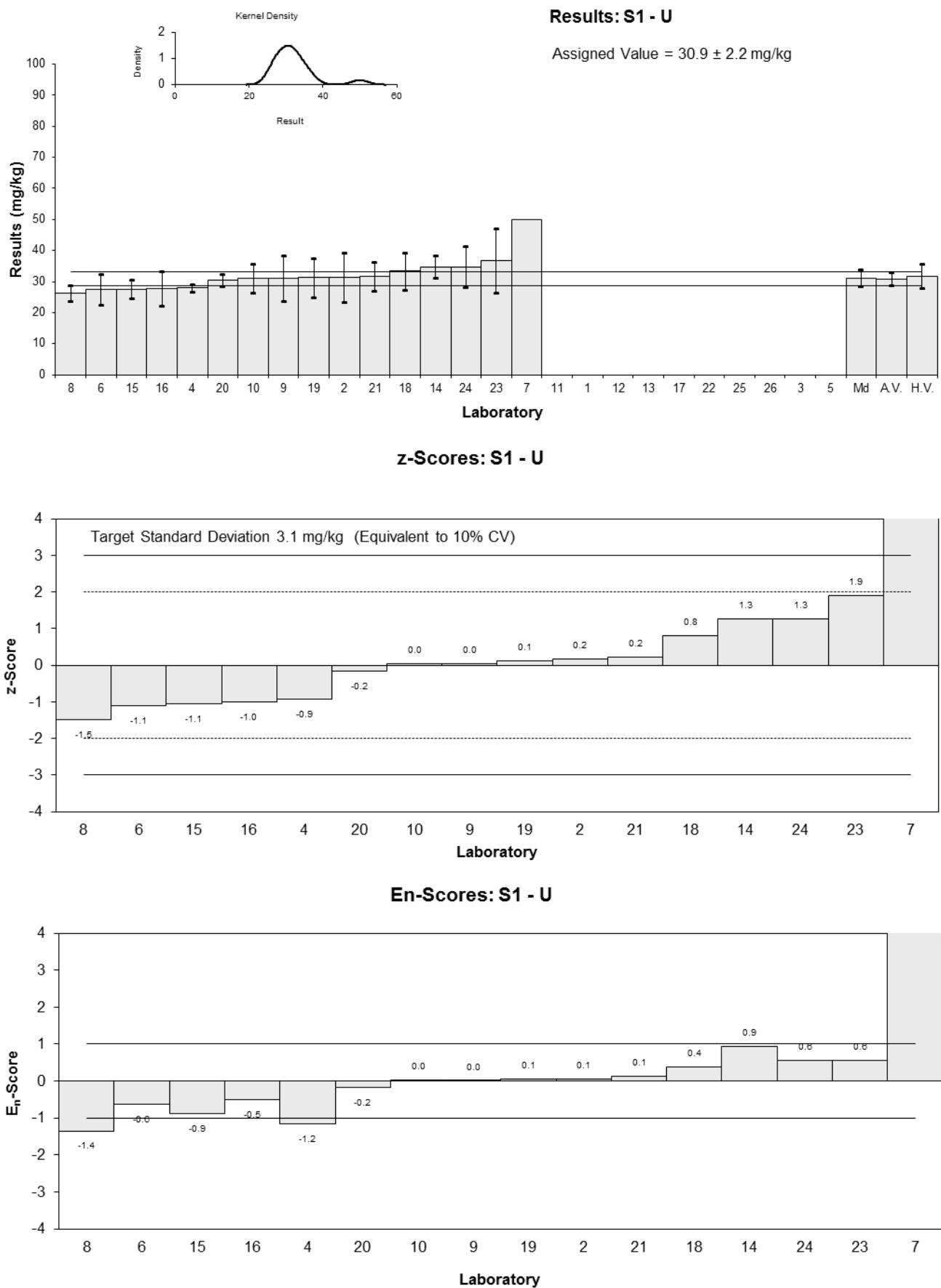


Figure 24

Table 37

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	2833	630	0.53	0.22
3	3040	456	1.30	0.72
4	2600	190	-0.33	-0.36
5	NT	NT		
6	2360	610	-1.23	-0.52
7	NT	NT		
8	2670	270	-0.07	-0.06
9	2710	580	0.07	0.03
10	2400	240	-1.08	-1.01
11	NR	NR		
12	2650	400	-0.15	-0.09
13	NT	NT		
14	2540	254	-0.56	-0.50
15	2900	290	0.78	0.63
16	3020	520	1.23	0.61
17	NT	NT		
18	2411	278	-1.04	-0.87
19	NT	NT		
20	2550	220	-0.52	-0.51
21	2828	424	0.51	0.30
22	3000	410	1.15	0.70
23	2350	227	-1.26	-1.22
24	2900	290	0.78	0.63
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	2690	160
Spike	Not Spiked	
Homogeneity Value	2720	330
Robust Average	2690	160
Median	2670	180
Mean	2690	
N	17	
Max.	3040	
Min.	2350	
Robust SD	270	
Robust CV	10%	

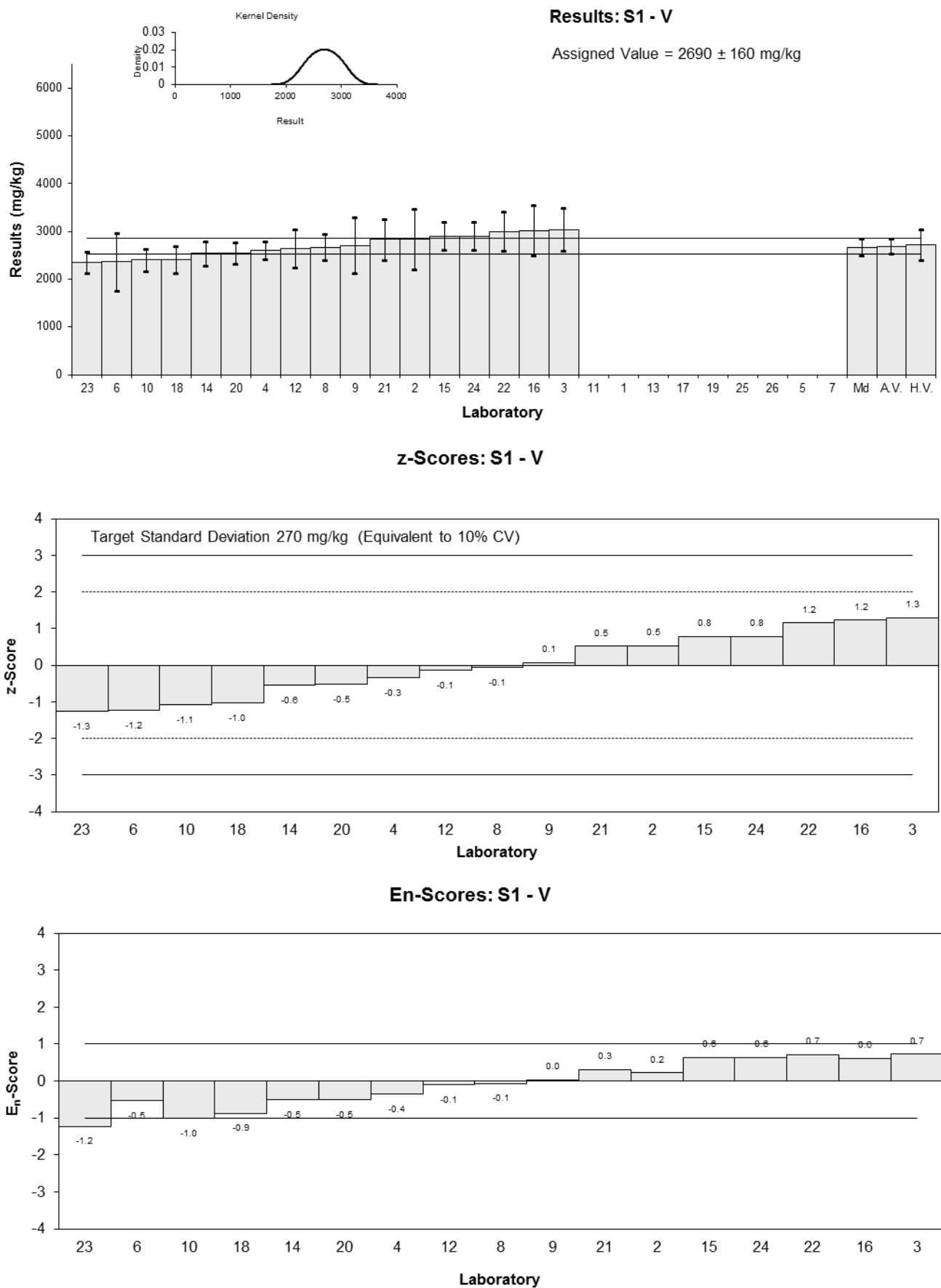


Figure 25

Table 38

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	35.8	6.3	-0.06	-0.04
3	28.5	4.27	-1.40	-1.14
4	40	3	0.72	0.66
5	NT	NT		
6	<34	NR		
7	44.6	NR	1.57	1.67
8	44.5	4.5	1.55	1.24
9	41	5.7	0.90	0.64
10	27	4.05	-1.68	-1.40
11	20.5	2	-2.88	-2.85
12	43	6	1.27	0.88
13	NT	NT		
14	39.0	3.90	0.54	0.45
15	39.0	4.0	0.54	0.45
16	33.8	5.6	-0.42	-0.30
17	NT	NT		
18	31.6	3.87	-0.83	-0.70
19	NT	NT		
20	37.6	3.8	0.28	0.24
21	25.3	3.80	-1.99	-1.70
22	42	6	1.09	0.75
23	26	3.18	-1.87	-1.68
24	47.9	11	2.18	0.97
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	36.1	5.1
Spike	Not Spiked	
Homogeneity Value	39.0	4.7
Robust Average	36.1	5.1
Median	38.3	4.0
Mean	36.0	
N	18	
Max.	47.9	
Min.	20.5	
Robust SD	8.6	
Robust CV	24%	

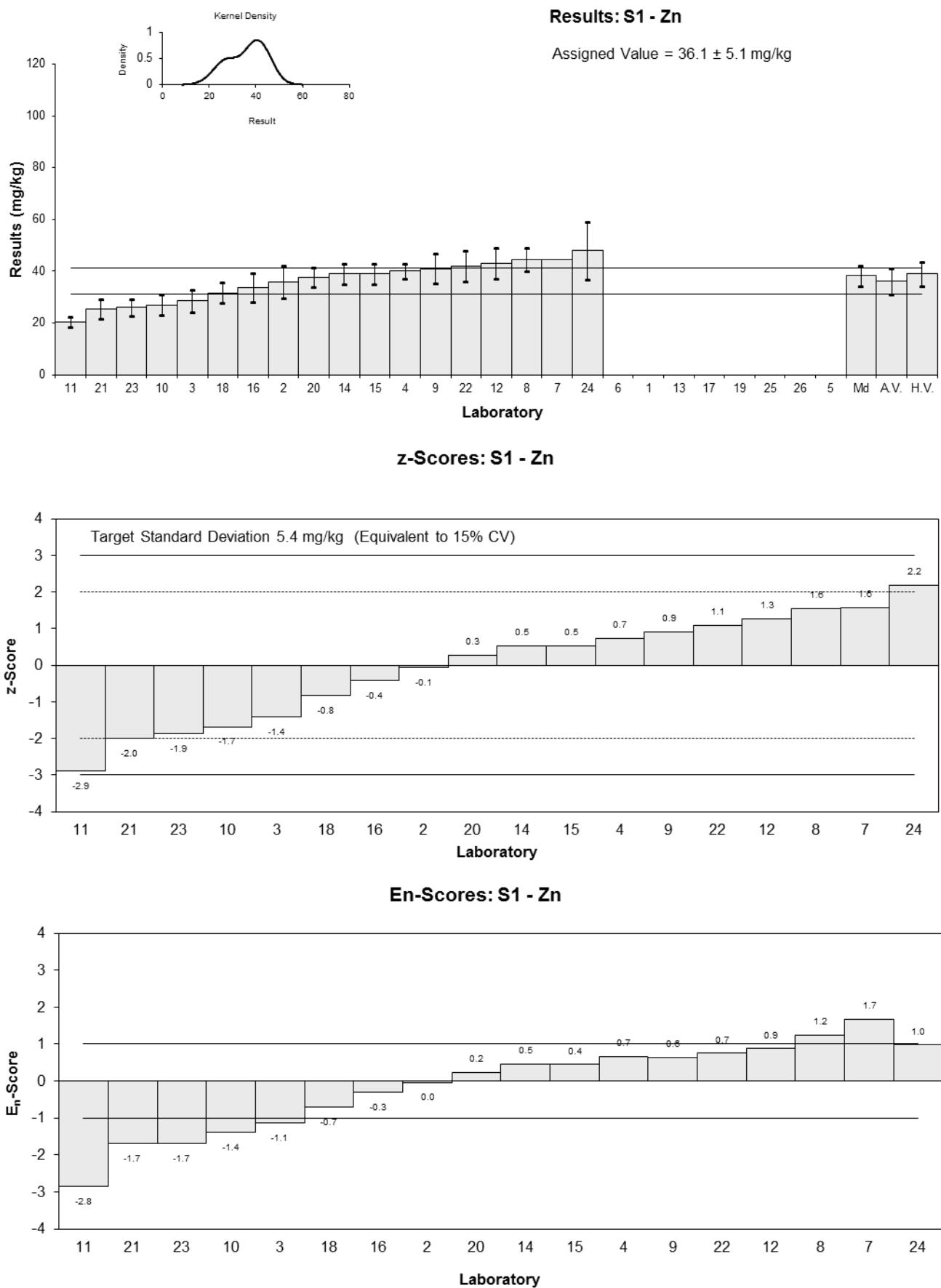


Figure 26

Table 39

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	9.0	2.8	-0.62	-0.21
2	9.34	1.80	-0.27	-0.14
3	9.84	1.47	0.25	0.15
4	8.0	0.4	-1.67	-2.30
5	NT	NT		
6	11.5	1.75	1.98	1.03
7	NR	NR		
8	9.48	0.95	-0.12	-0.11
9	8.4	2.0	-1.25	-0.58
10	11	1.65	1.46	0.80
11	NT	NT		
12	9	2	-0.62	-0.29
13	NT	NT		
14	9.49	0.95	-0.11	-0.10
15	10.4	1.5	0.83	0.50
16	10.1	1.6	0.52	0.29
17	9.57	1.91	-0.03	-0.02
18	9.97	1.4	0.39	0.24
19	NT	NT		
20	11.0	2.1	1.46	0.64
21	9.08	1.36	-0.54	-0.35
22	9	2	-0.62	-0.29
23	8	1.65	-1.67	-0.92
24	9.8	1	0.21	0.17
25	10.2	4.2	0.62	0.14
26	NT	NT		

Statistics

Assigned Value	9.60	0.57
Spike	Not Spiked	
Homogeneity Value	8.6	1.0
Robust Average	9.60	0.57
Median	9.53	0.37
Mean	9.61	
N	20	
Max.	11.5	
Min.	8	
Robust SD	1	
Robust CV	10%	

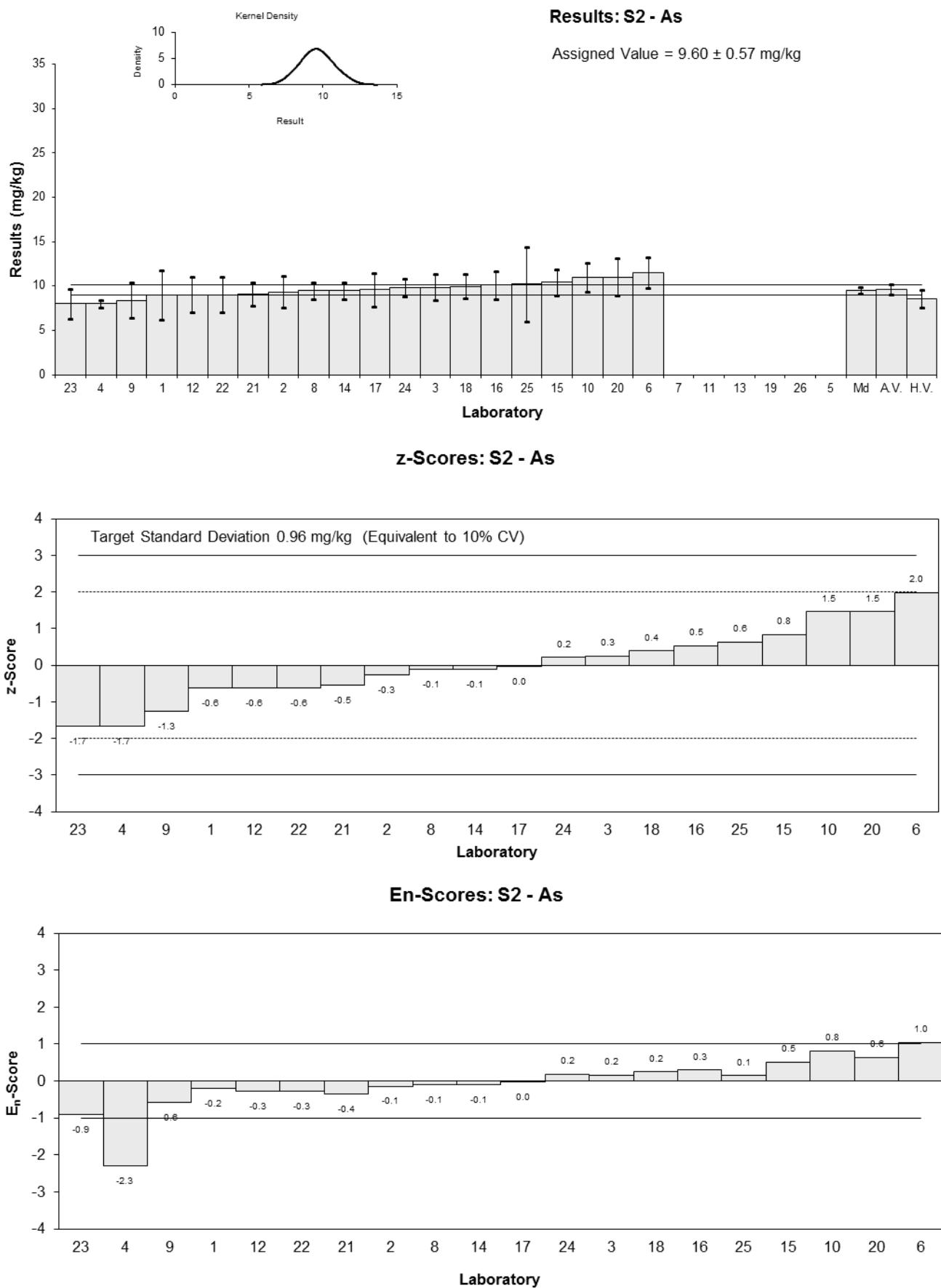


Figure 27

Table 40

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	19	4.4	1.64	1.04
2	15.1	3.8	0.28	0.20
3	13.3	1.99	-0.35	-0.45
4	17	3	0.94	0.85
5	NT	NT		
6	<22	NR		
7	NR	NR		
8	13.2	1.3	-0.38	-0.67
9	14	2.8	-0.10	-0.10
10	12	2.4	-0.80	-0.88
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	15.0	1.50	0.24	0.39
15	14.4	2.0	0.03	0.04
16	15.0	2.8	0.24	0.24
17	12.7	3.2	-0.56	-0.48
18	14.9	2.2	0.21	0.25
19	NT	NT		
20	<20	3.6		
21	13.2	1.98	-0.38	-0.50
22	14	3	-0.10	-0.09
23	<50	NR		
24	24	6	3.39	1.59
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	14.3	1.0
Spike	Not Spiked	
Homogeneity Value	16.5	2.0
Robust Average	14.6	1.2
Median	14.4	0.9
Mean	15.1	
N	15	
Max.	24	
Min.	12	
Robust SD	1.5	
Robust CV	10%	

*Robust Average excluding Laboratory 24.

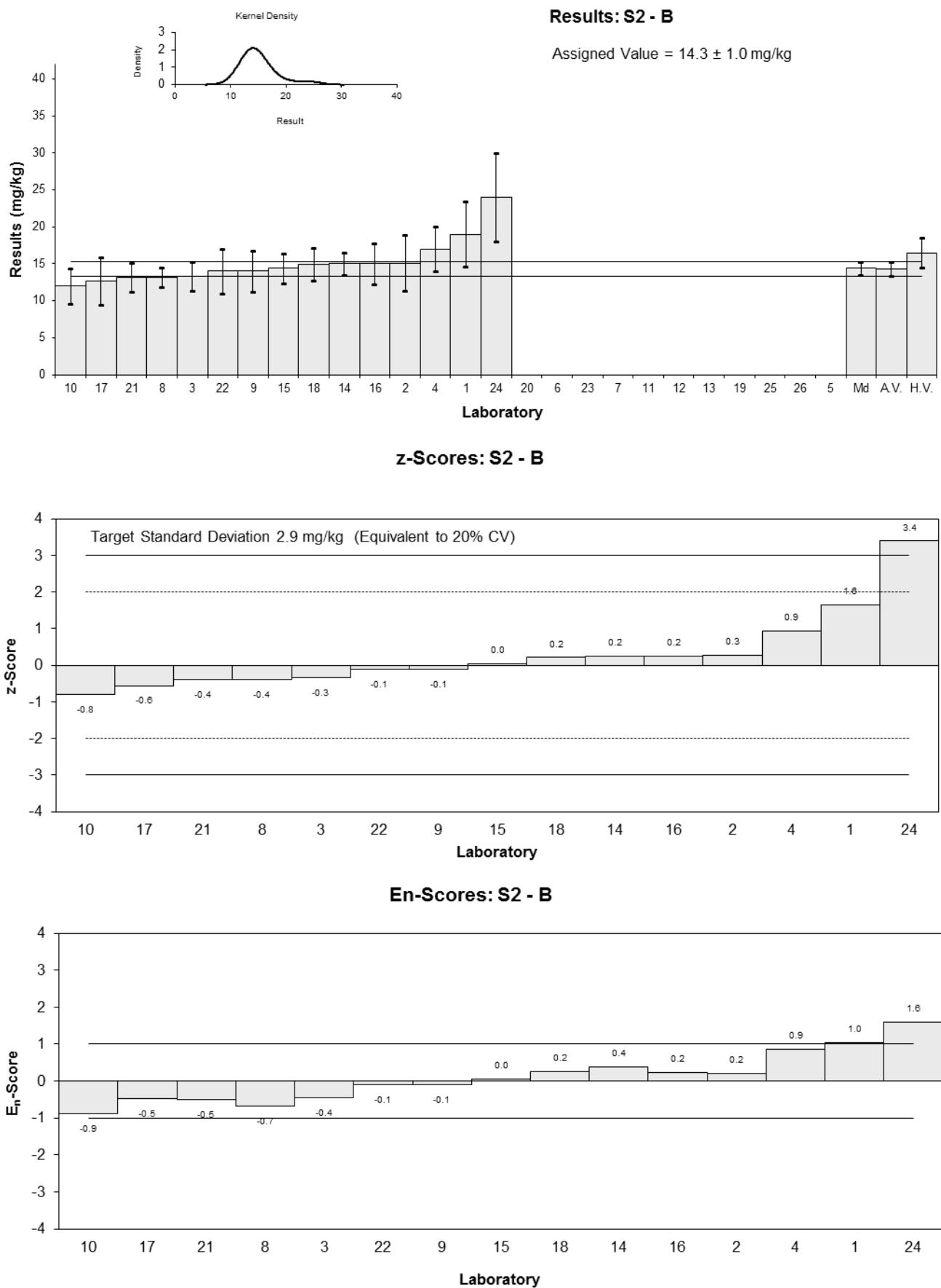


Figure 28

Table 41

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Cd
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	2.0	0.34	-0.05	-0.03
2	1.96	0.39	-0.25	-0.12
3	2.10	0.31	0.45	0.28
4	1.6	0.2	-2.04	-1.87
5	NT	NT		
6	1.80	0.34	-1.04	-0.60
7	NR	NR		
8	1.98	0.20	-0.15	-0.14
9	1.8	0.3	-1.04	-0.67
10	2.1	0.315	0.45	0.27
11	NT	NT		
12	2	1	-0.05	-0.01
13	NT	NT		
14	2.04	0.20	0.15	0.14
15	2.09	0.2	0.40	0.36
16	1.85	0.29	-0.80	-0.53
17	1.95	0.41	-0.30	-0.14
18	2.02	0.28	0.05	0.03
19	NT	NT		
20	2.23	0.32	1.09	0.66
21	2.03	0.30	0.10	0.06
22	2	1.5	-0.05	-0.01
23	2	0.19	-0.05	-0.05
24	2.6	0.4	2.94	1.44
25	2.25	0.5	1.19	0.47
26	NT	NT		

Statistics

Assigned Value	2.01	0.09
Spike	Not Spiked	
Homogeneity Value	1.93	0.23
Robust Average	2.01	0.09
Median	2.00	0.05
Mean	2.02	
N	20	
Max.	2.6	
Min.	1.6	
Robust SD	0.20	
Robust CV	10%	

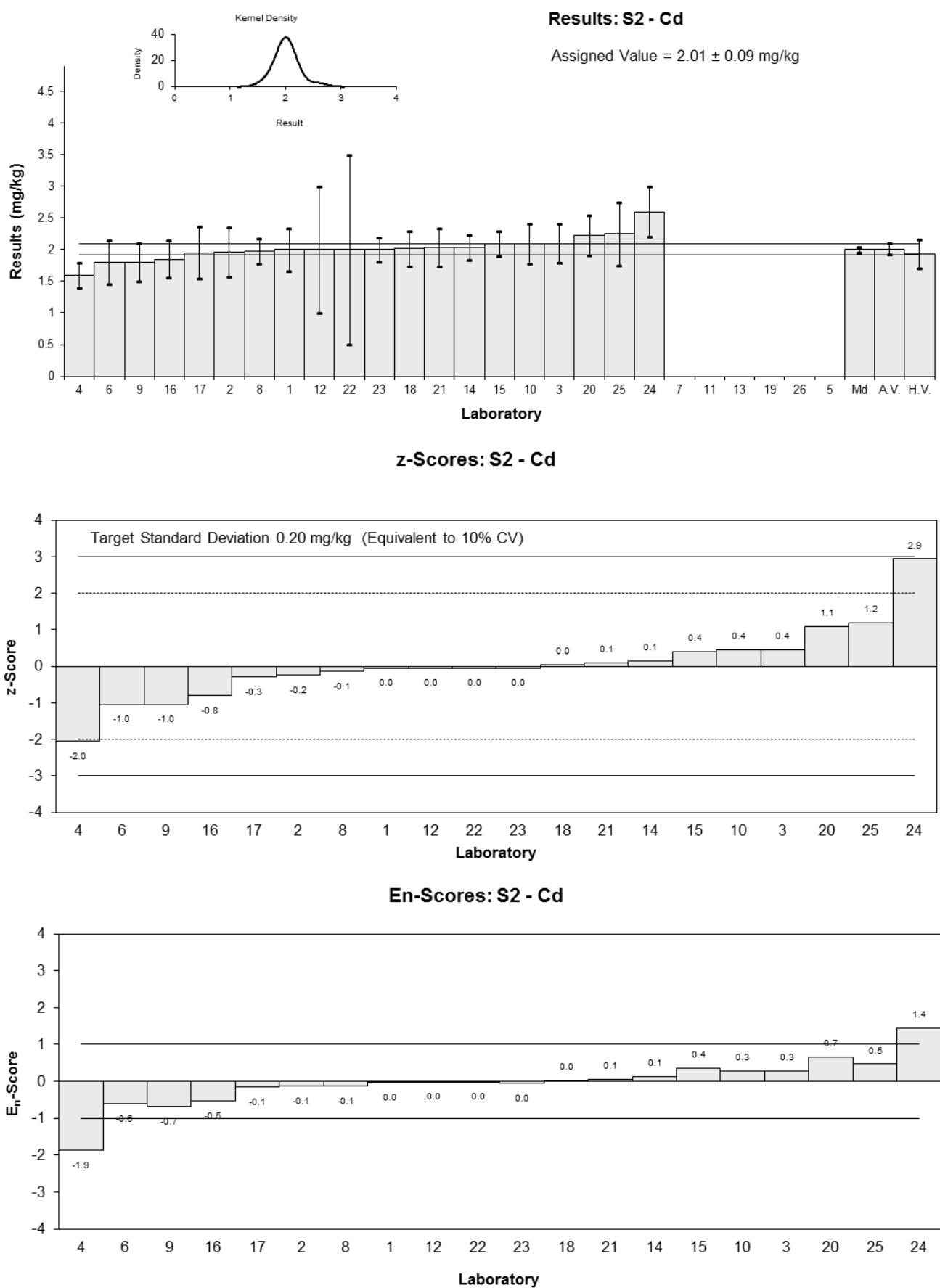


Figure 29

Table 42

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	2.5	0.54	0.68	0.28
2	2.33	0.43	-0.04	-0.02
3	2.18	0.32	-0.68	-0.43
4	2.9	0.2	2.39	2.03
5	NT	NT		
6	2.13	0.32	-0.90	-0.56
7	NR	NR		
8	2.11	0.21	-0.98	-0.81
9	2.3	0.4	-0.17	-0.09
10	<5	0.5		
11	NT	NT		
12	2	1	-1.45	-0.33
13	NT	NT		
14	2.62	0.26	1.20	0.87
15	2.62	0.3	1.20	0.79
16	< 5	< 1		
17	2.37	0.48	0.13	0.06
18	<5	0.5		
19	NT	NT		
20	2.50	0.44	0.68	0.33
21	2.03	0.30	-1.32	-0.87
22	3	2	2.82	0.33
23	2	0.28	-1.45	-1.00
24	2.2	0.2	-0.60	-0.51
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	2.34	0.19
Spike	Not Spiked	
Homogeneity Value	2.93	0.35
Robust Average	2.34	0.19
Median	2.32	0.15
Mean	2.36	
N	16	
Max.	3	
Min.	2	
Robust SD	0.31	
Robust CV	13%	

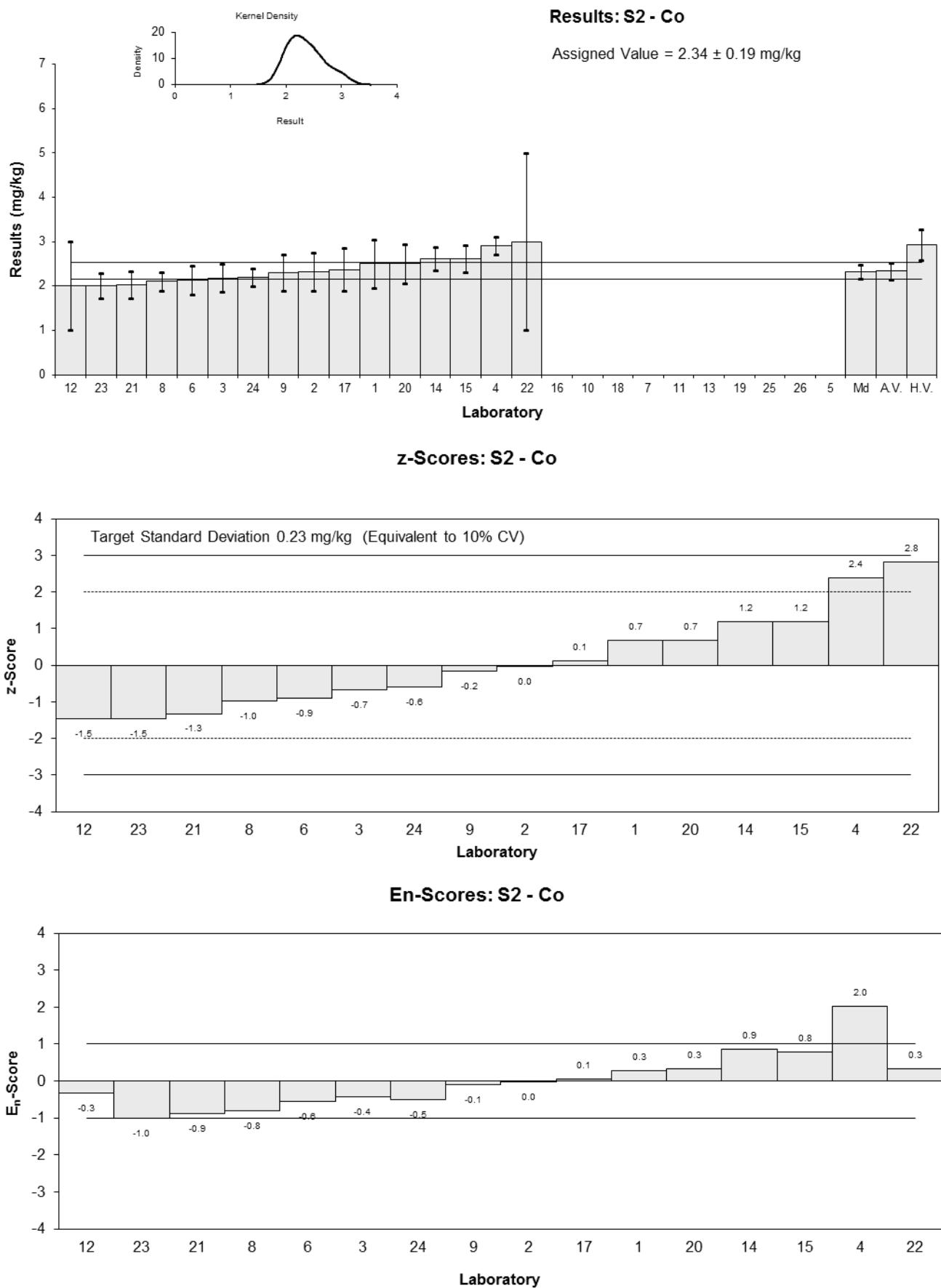


Figure 30

Table 43

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Cr
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	37	8.2	0.25	0.11
2	31.4	7.2	-1.30	-0.63
3	36.0	5.40	-0.03	-0.02
4	38	3	0.53	0.53
5	NT	NT		
6	28.5	4.15	-2.11	-1.65
7	45.8	NR	2.69	4.85
8	35.1	3.5	-0.28	-0.25
9	33	5.3	-0.86	-0.55
10	37	5.55	0.25	0.15
11	NT	NT		
12	36	5	-0.03	-0.02
13	NT	NT		
14	38.2	3.82	0.58	0.49
15	39.1	4.0	0.83	0.67
16	40.4	6.7	1.19	0.61
17	36.0	7.2	-0.03	-0.01
18	37.3	5.01	0.33	0.22
19	NT	NT		
20	35.6	5.7	-0.14	-0.08
21	33.9	5.08	-0.61	-0.40
22	41	5	1.36	0.91
23	32	3.71	-1.14	-0.97
24	31.2	3.1	-1.36	-1.33
25	36.94	0.6	0.23	0.40
26	NT	NT		

Statistics

Assigned Value	36.1	2.0
Spike	Not Spiked	
Homogeneity Value	38.5	4.6
Robust Average	36.1	2.0
Median	36.0	1.4
Mean	36.2	
N	21	
Max.	45.8	
Min.	28.5	
Robust SD	3.6	
Robust CV	10%	

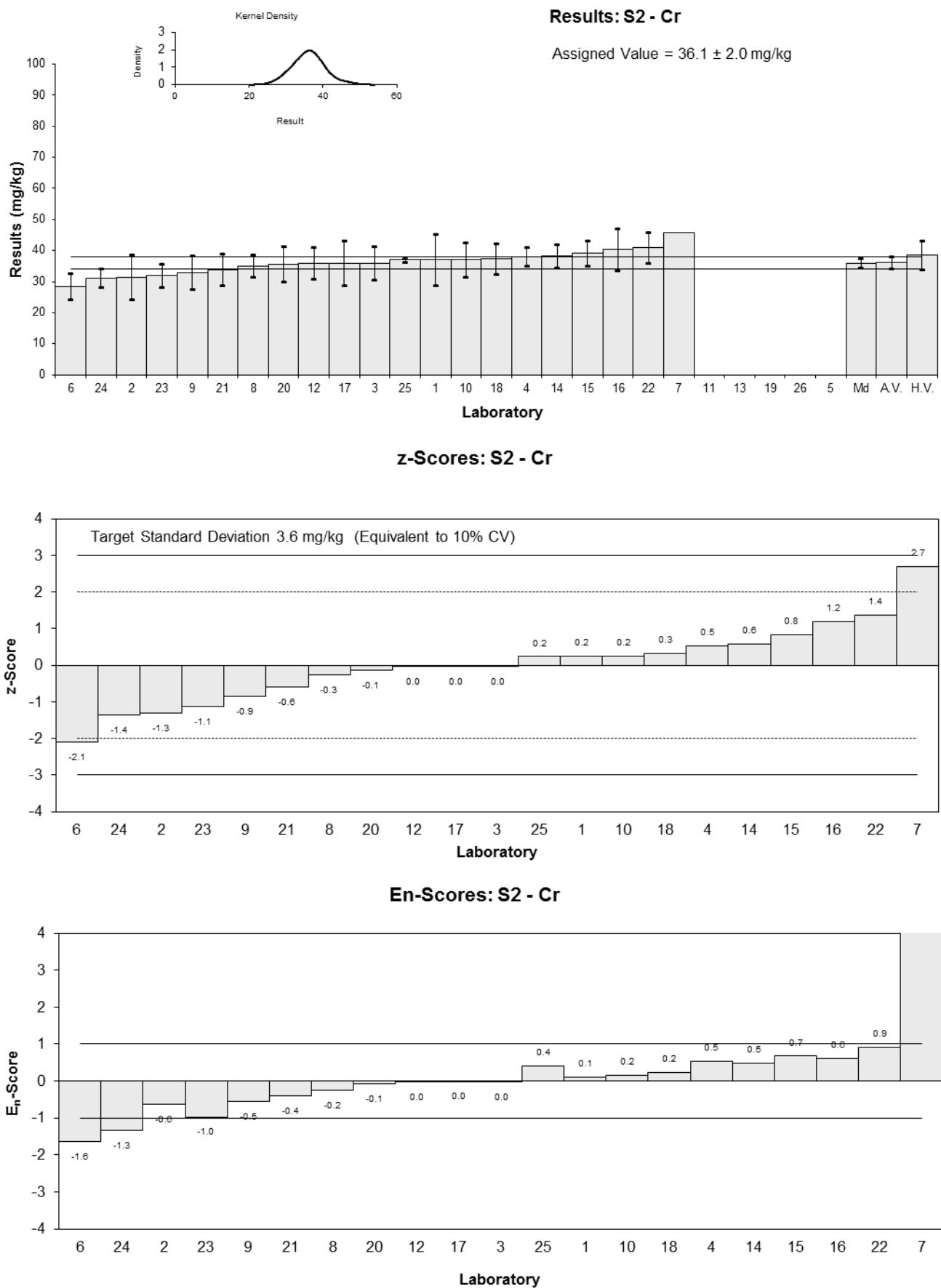


Figure 31

Table 44

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	50	9.2	-0.84	-0.49
2	58.5	11.0	0.71	0.35
3	54.3	8.14	-0.05	-0.04
4	47	3	-1.39	-2.04
5	NT	NT		
6	49.9	7.45	-0.86	-0.61
7	76.6	NR	4.03	10.00
8	53.3	5.3	-0.24	-0.23
9	51	8.2	-0.66	-0.42
10	55	8.25	0.07	0.05
11	NT	NT		
12	53	8	-0.29	-0.19
13	NT	NT		
14	56.3	5.63	0.31	0.28
15	58.6	6.0	0.73	0.63
16	58.3	10.3	0.68	0.35
17	54.3	11.4	-0.05	-0.03
18	58.2	8.2	0.66	0.42
19	NT	NT		
20	58.3	8.1	0.68	0.44
21	53.0	7.95	-0.29	-0.19
22	56	7	0.26	0.19
23	49	5.88	-1.03	-0.89
24	52.7	5.3	-0.35	-0.33
25	57.98	0.5	0.62	1.50
26	NT	NT		

Statistics

Assigned Value	54.6	2.2
Spike	Not Spiked	
Homogeneity Value	55.8	6.7
Robust Average	54.6	2.2
Median	54.3	2.5
Mean	55.3	
N	21	
Max.	76.6	
Min.	47	
Robust SD	4.1	
Robust CV	7.5%	

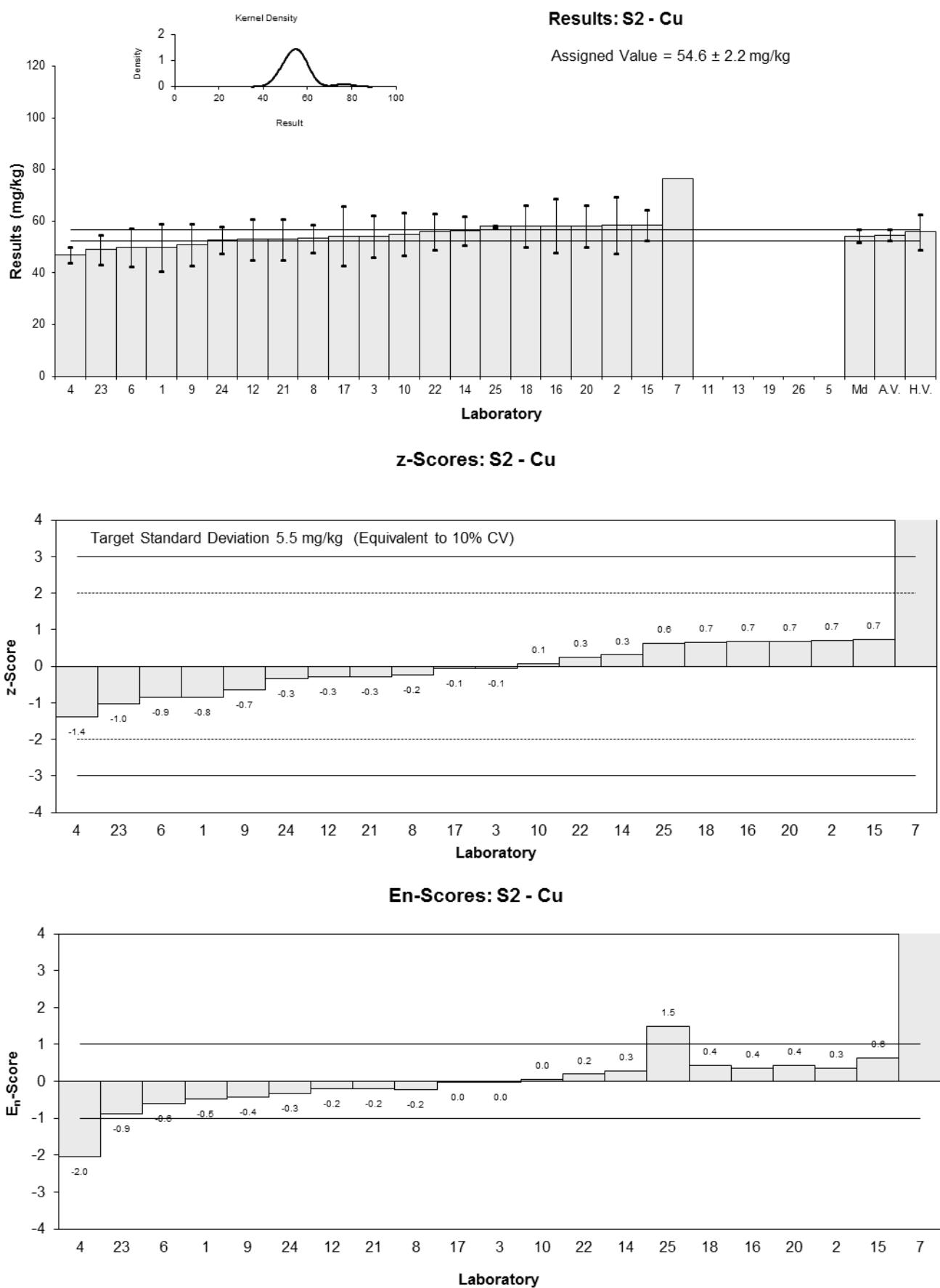


Figure 32

Table 45

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Hg
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.025	0.005	1.16	0.77
2	0.023	0.002	0.67	0.67
3	0.015	0.002	-1.31	-1.31
4	0.02	0.002	-0.07	-0.07
5	NT	NT		
6	<0.22	NR		
7	NR	NR		
8	0.021	0.01	0.17	0.07
9	<0.1	NR		
10	<0.1	0.015		
11	NT	NT		
12	<0.02	NR		
13	NT	NT		
14	0.023	0.002	0.67	0.67
15	<0.05	NR		
16	<0.1	<0.02		
17	0.019	0.009	-0.32	-0.13
18	<0.1	0.01		
19	NT	NT		
20	<0.10	0.067		
21	0.09	0.01	17.17	6.58
22	0.016	0.016	-1.06	-0.26
23	<0.1	NR		
24	<0.03	0.01		
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	0.0203*	0.0035
Spike	Not Spiked	
Homogeneity Value	0.0205	0.0031
Robust Average	0.0212	0.0040
Median	0.0210	0.0023
Mean	0.0280	
N	9	
Max.	0.09	
Min.	0.015	
Robust SD	0.004	
Robust CV	19%	

*Robust Average excluding Laboratory 21.

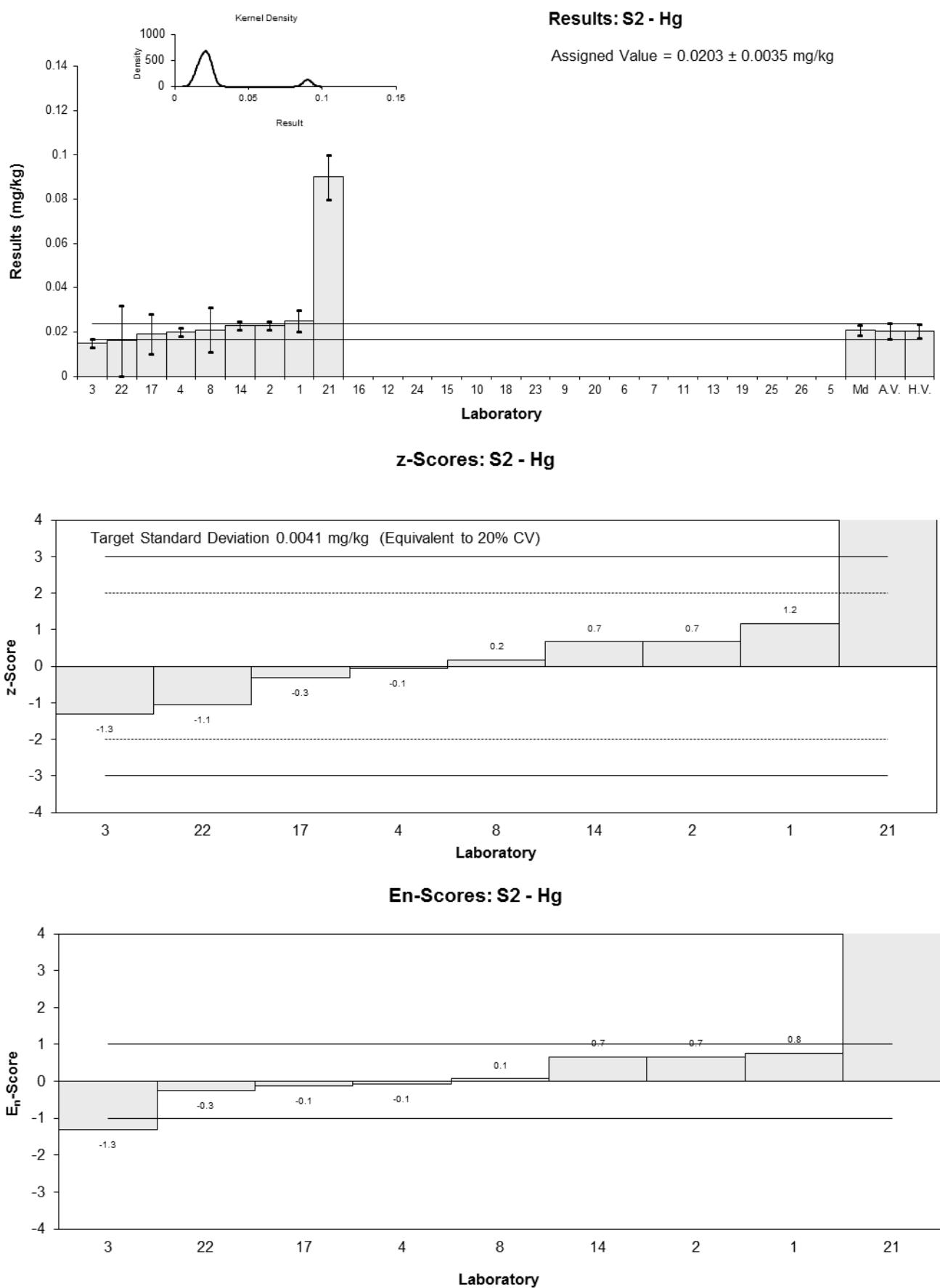


Figure 33

Table 46

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Mn
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	150	28	-0.07	-0.04
2	149	24	-0.13	-0.08
3	154	23.10	0.20	0.13
4	140	9	-0.73	-1.07
5	NT	NT		
6	153	34	0.13	0.06
7	149	NR	-0.13	-0.40
8	149	15	-0.13	-0.13
9	140	24	-0.73	-0.45
10	160	16	0.60	0.54
11	NT	NT		
12	139	21	-0.79	-0.56
13	NT	NT		
14	159	15.9	0.53	0.48
15	150	15	-0.07	-0.06
16	161	27	0.66	0.36
17	150	30	-0.07	-0.03
18	161	18.7	0.66	0.52
19	NT	NT		
20	160	17	0.60	0.51
21	147	22.0	-0.26	-0.18
22	160	13	0.60	0.65
23	147	14.6	-0.26	-0.26
24	147	14.7	-0.26	-0.26
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	151	5
Spike	Not Spiked	
Homogeneity Value	150	18
Robust Average	151	5
Median	150	2
Mean	151	
N	20	
Max.	161	
Min.	139	
Robust SD	8	
Robust CV	5.3%	

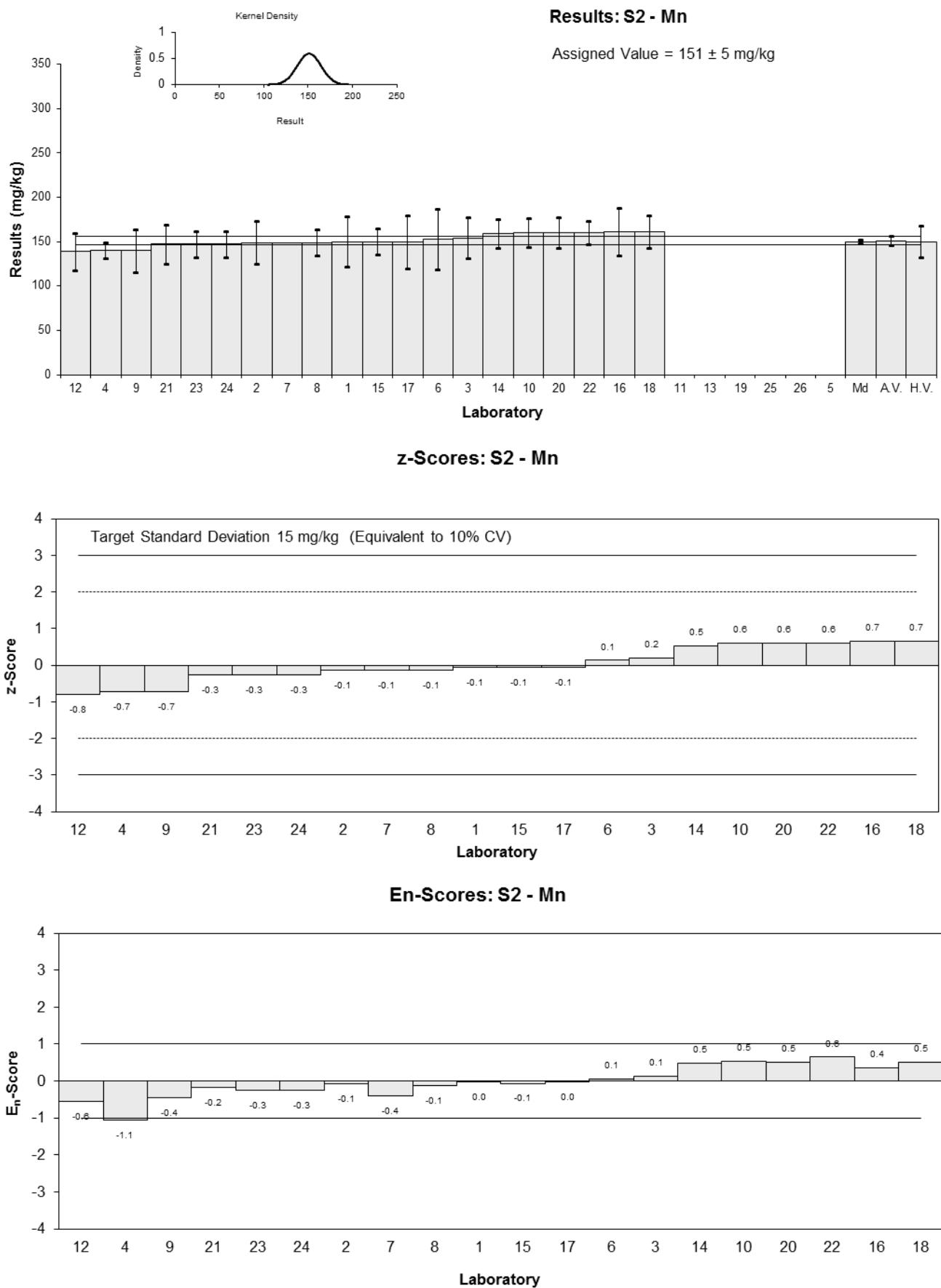


Figure 34

Table 47

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Ni
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	19	3.9	0.05	0.03
2	18.8	3.9	-0.05	-0.03
3	18.4	2.76	-0.26	-0.17
4	17	2	-1.01	-0.88
5	NT	NT		
6	16.3	3.9	-1.38	-0.65
7	20.9	NR	1.06	2.50
8	18.1	1.8	-0.42	-0.41
9	18	3.2	-0.48	-0.27
10	20	3	0.58	0.35
11	NT	NT		
12	17	3	-1.01	-0.61
13	NT	NT		
14	19.2	1.92	0.16	0.14
15	21.8	2.5	1.53	1.10
16	20.3	3.4	0.74	0.40
17	19.1	4.0	0.11	0.05
18	20.3	2.57	0.74	0.52
19	NT	NT		
20	19.4	2.8	0.26	0.17
21	17.6	2.64	-0.69	-0.47
22	20	4	0.58	0.27
23	18	1.80	-0.48	-0.46
24	19	2	0.05	0.05
25	18.70	2.8	-0.11	-0.07
26	NT	NT		

Statistics

Assigned Value	18.9	0.8
Spike	Not Spiked	
Homogeneity Value	19.5	2.3
Robust Average	18.9	0.8
Median	19.0	0.7
Mean	18.9	
N	21	
Max.	21.8	
Min.	16.3	
Robust SD	1.0	
Robust CV	5.3%	

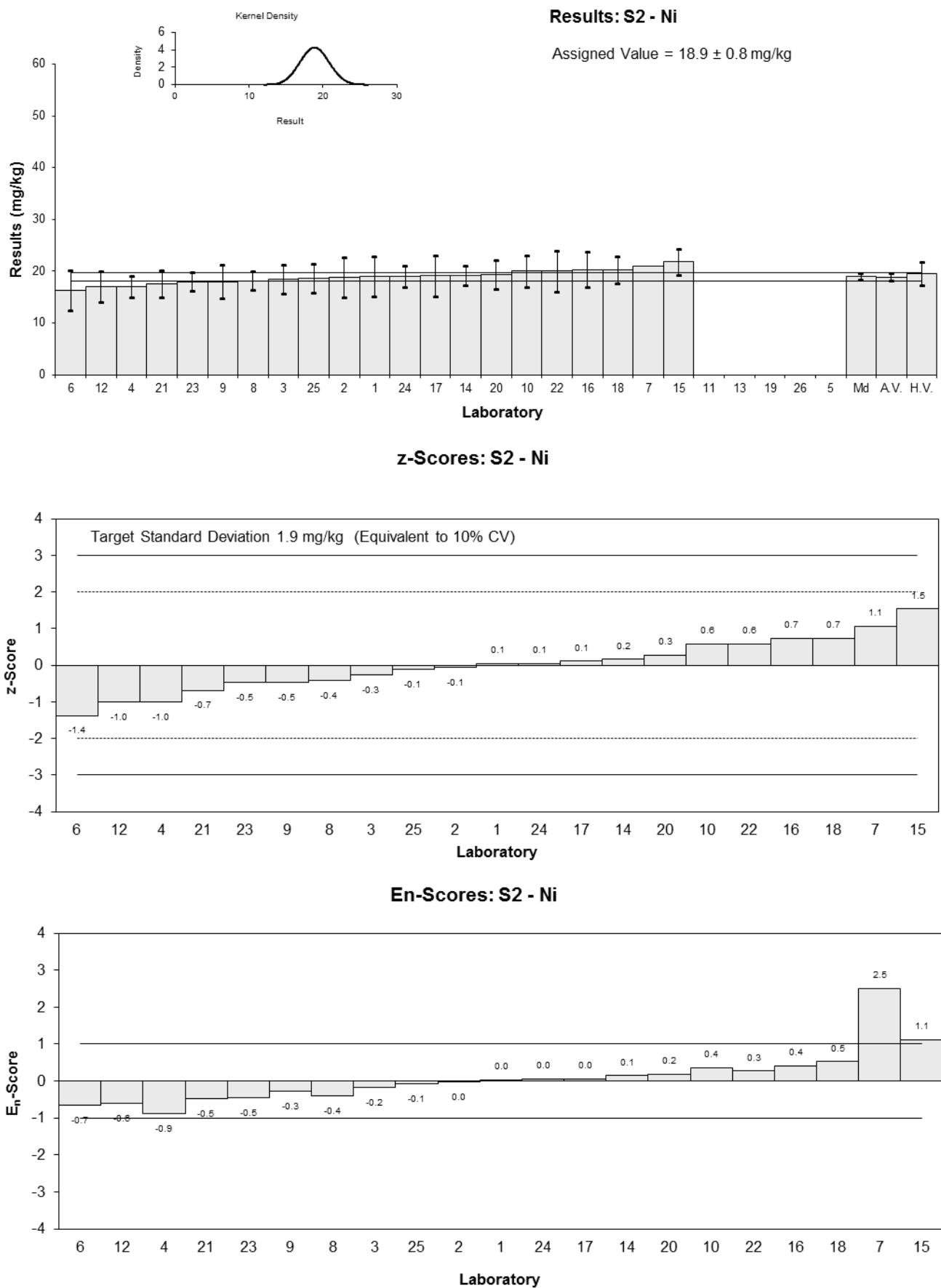


Figure 35

Table 48

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Pb
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	75	17	-0.31	-0.14
2	73.8	15.5	-0.47	-0.23
3	76.1	11.41	-0.17	-0.11
4	70	4	-0.96	-1.48
5	NT	NT		
6	73.3	11.5	-0.53	-0.34
7	99.0	NR	2.79	7.20
8	74.1	7.4	-0.43	-0.41
9	72	9.6	-0.70	-0.54
10	78	11.7	0.08	0.05
11	NT	NT		
12	72	11	-0.70	-0.47
13	NT	NT		
14	83.1	8.31	0.74	0.65
15	78.8	8.0	0.18	0.16
16	81.5	13.5	0.53	0.30
17	78.3	15.7	0.12	0.06
18	80.9	10.1	0.45	0.33
19	NT	NT		
20	86	13	1.11	0.64
21	84.1	12.6	0.87	0.52
22	77	8	-0.05	-0.05
23	77	8.26	-0.05	-0.05
24	62.8	11.3	-1.89	-1.25
25	79.06	3.3	0.21	0.37
26	NT	NT		

Statistics

Assigned Value	77.4	3.0
Spike	Not Spiked	
Homogeneity Value	78.5	9.4
Robust Average	77.4	3.0
Median	77.0	2.5
Mean	77.7	
N	21	
Max.	99	
Min.	62.8	
Robust SD	5.6	
Robust CV	7.2%	

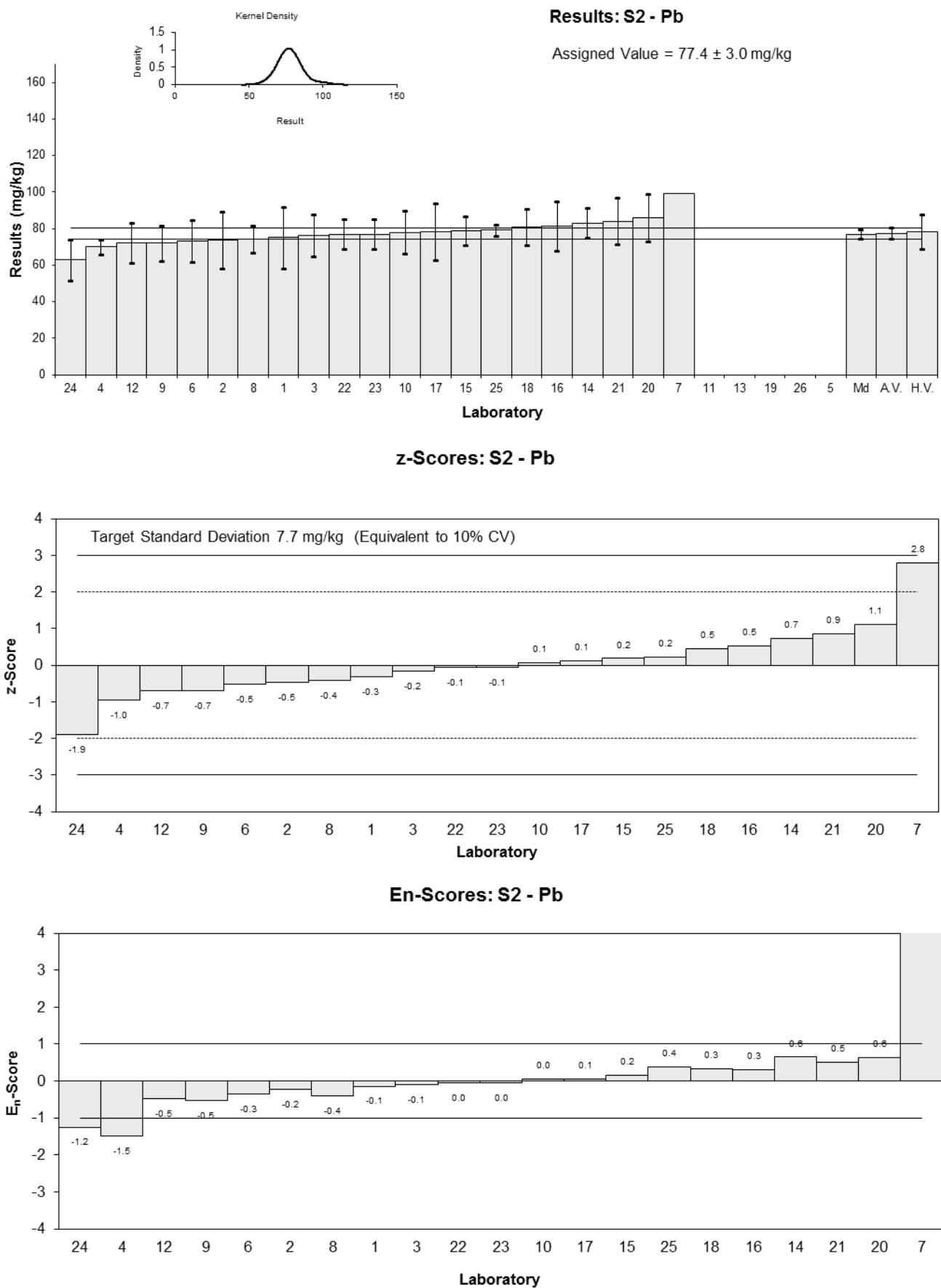


Figure 36

Table 49

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Sb
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	16	4.7	-0.09	-0.06
2	5.64	1.40	-3.27	-4.67
3	12.9	1.93	-1.04	-1.29
4	16	2	-0.09	-0.11
5	NT	NT		
6	13.1	4.5	-0.98	-0.66
7	NR	NR		
8	17.5	1.8	0.37	0.47
9	7.4	1.3	-2.73	-4.01
10	19	2.85	0.83	0.80
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	17.0	1.70	0.21	0.28
15	19.6	3.0	1.01	0.94
16	19.3	3.2	0.92	0.82
17	17.8	7.3	0.46	0.20
18	17	3.4	0.21	0.18
19	NT	NT		
20	13.4	2.5	-0.89	-0.94
21	17.9	2.69	0.49	0.49
22	5	3	-3.47	-3.23
23	12	5.21	-1.32	-0.78
24	15.8	3.8	-0.15	-0.12
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	16.3	1.8
Spike	Not Spiked	
Homogeneity Value	12.9	1.6
Robust Average	15.1	2.4
Median	16.0	2.0
Mean	14.6	
N	18	
Max.	19.6	
Min.	5	
Robust SD	2.7	
Robust CV	18%	

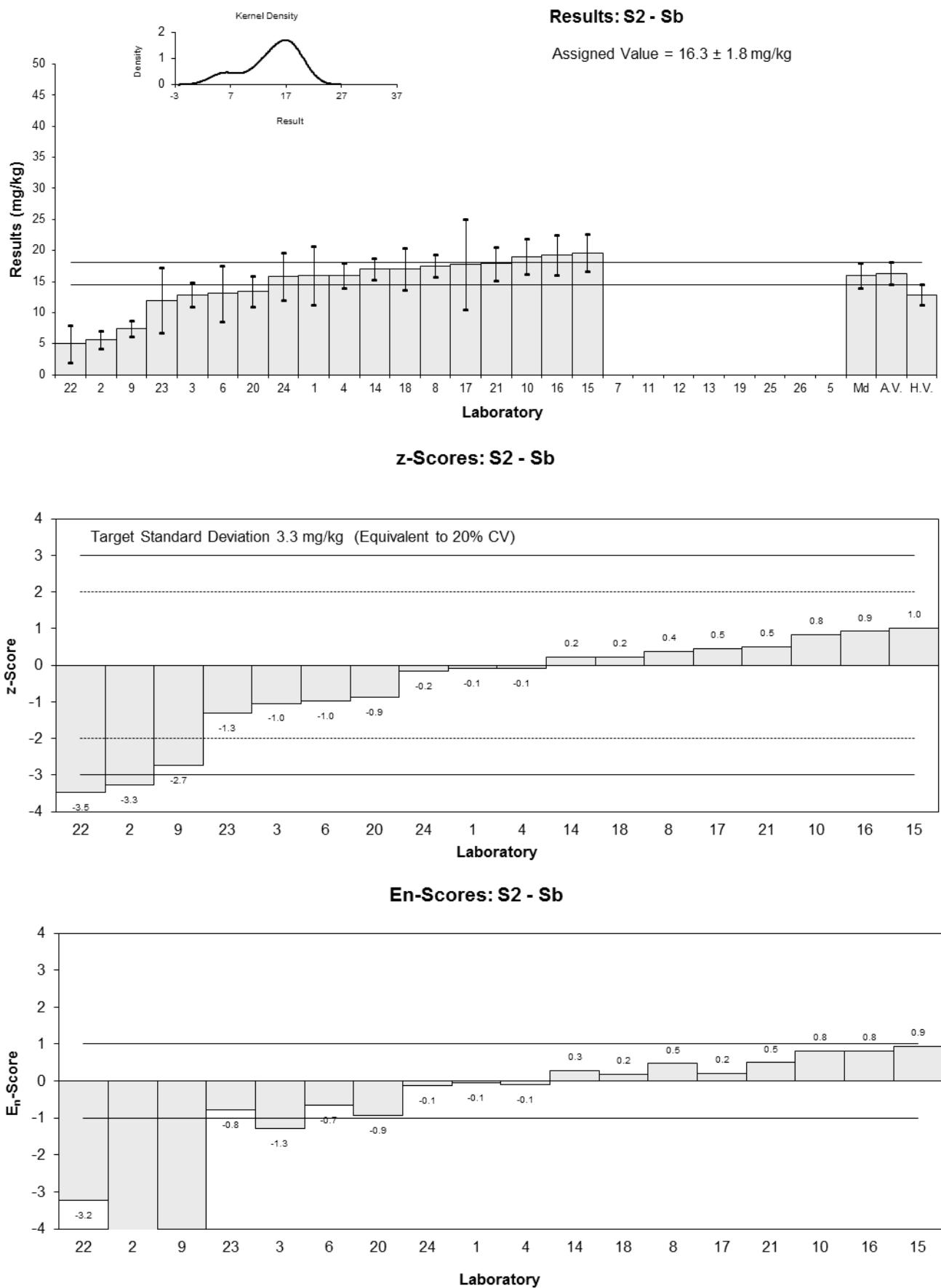


Figure 37

Table 50

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Se
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	5.0	1.6	-1.25	-0.69
2	7.36	1.74	1.31	0.67
3	5.05	0.75	-1.19	-1.26
4	5.8	0.5	-0.38	-0.52
5	NT	NT		
6	6.71	1.2	0.61	0.44
7	NR	NR		
8	6.49	0.65	0.37	0.43
9	6.0	1.2	-0.16	-0.12
10	6.4	0.64	0.27	0.32
11	NT	NT		
12	<5	NR		
13	NT	NT		
14	6.39	0.64	0.26	0.31
15	6.56	0.8	0.44	0.45
16	6.65	0.97	0.54	0.47
17	5.98	1.85	-0.18	-0.09
18	6.38	0.77	0.25	0.26
19	NT	NT		
20	6.9	1.8	0.81	0.40
21	6.61	0.99	0.50	0.42
22	4	3	-2.33	-0.71
23	6	1.71	-0.16	-0.08
24	5.4	1.2	-0.81	-0.59
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	6.15	0.45
Spike	Not Spiked	
Homogeneity Value	6.18	0.74
Robust Average	6.15	0.45
Median	6.39	0.28
Mean	6.09	
N	18	
Max.	7.36	
Min.	4	
Robust SD	0.76	
Robust CV	12%	

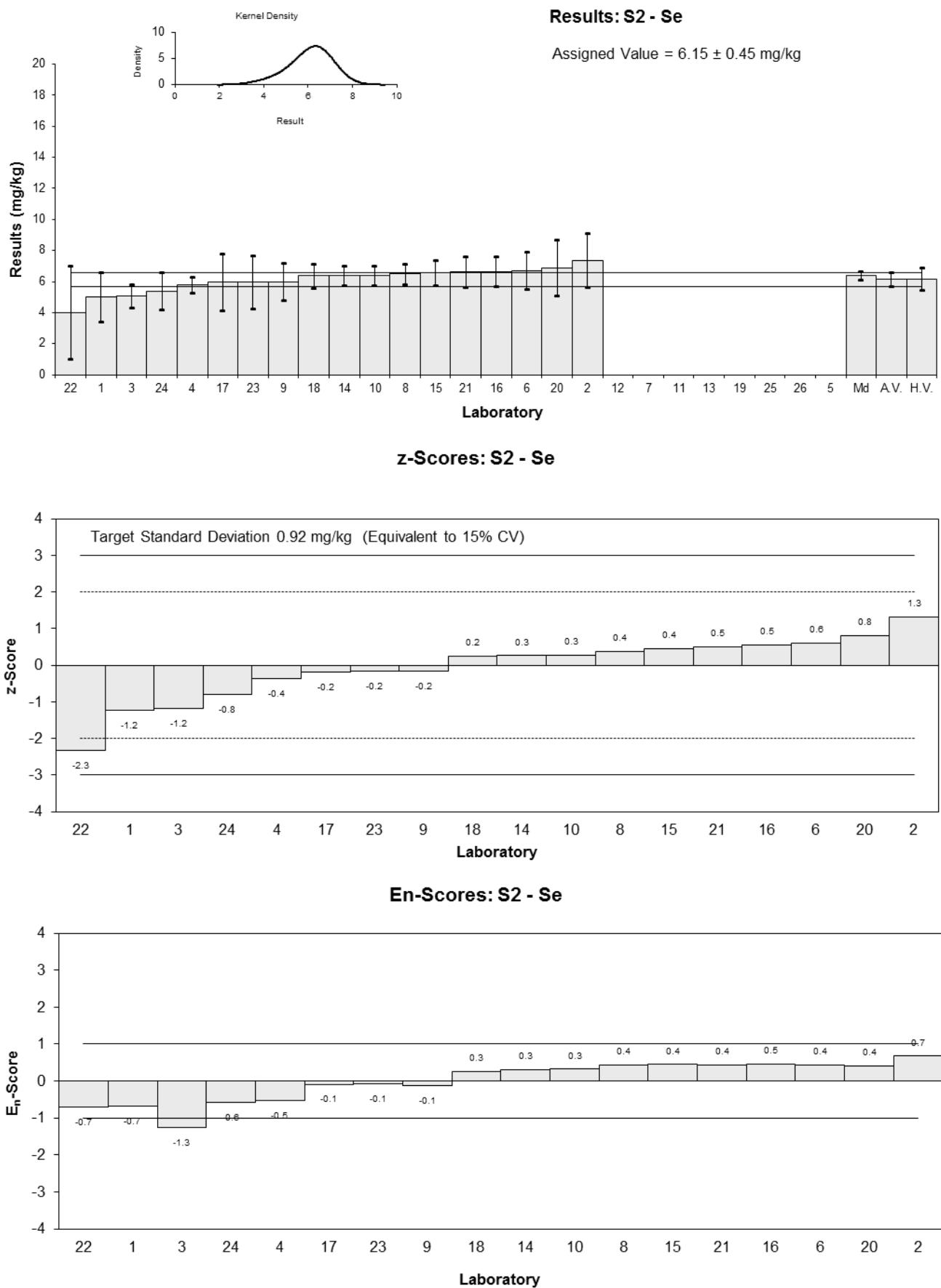


Figure 38

Table 51

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	Sr
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	17	3.8	0.49	0.21
2	15.4	3.9	-0.49	-0.20
3	15.57	2.33	-0.39	-0.26
4	16	1.1	-0.12	-0.16
5	NT	NT		
6	14.0	2.5	-1.36	-0.86
7	17.2	NR	0.62	1.67
8	16.0	1.6	-0.12	-0.12
9	16	3	-0.12	-0.07
10	16	2.4	-0.12	-0.08
11	NT	NT		
12	NT	NT		
13	NT	NT		
14	17.0	1.70	0.49	0.44
15	16.4	2.0	0.12	0.10
16	17.8	3.6	0.99	0.44
17	15.8	2.4	-0.25	-0.16
18	16.8	1.37	0.37	0.40
19	NT	NT		
20	17.0	1.9	0.49	0.40
21	15.0	2.25	-0.74	-0.52
22	17	6	0.49	0.13
23	16	1.33	-0.12	-0.14
24	9.9	1.4	-3.89	-4.14
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	16.2	0.6
Spike	Not Spiked	
Homogeneity Value	16.8	2.0
Robust Average	16.2	0.6
Median	16.0	0.6
Mean	15.9	
N	19	
Max.	17.8	
Min.	9.9	
Robust SD	1.0	
Robust CV	6.2%	

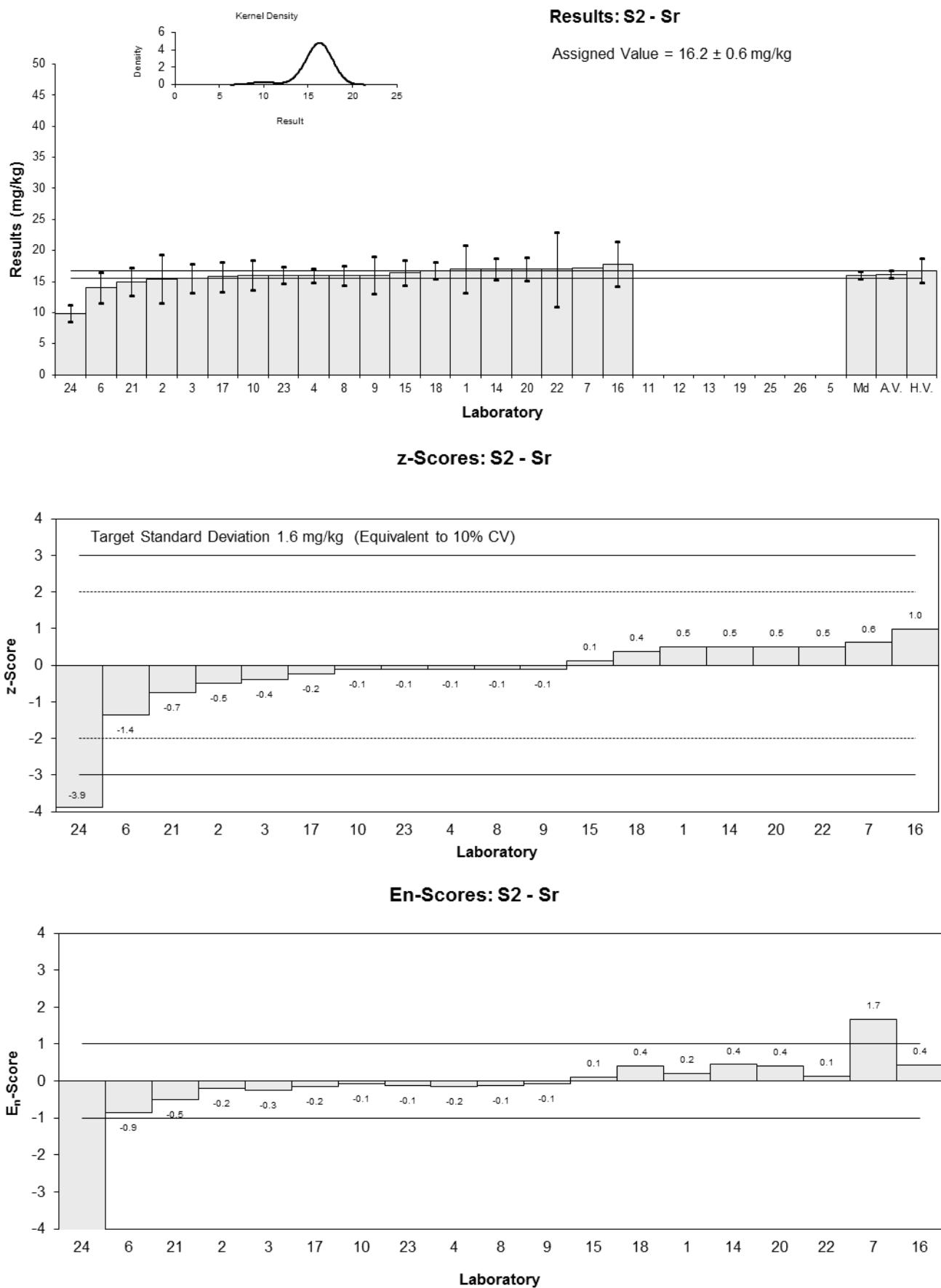


Figure 39

Table 52

Sample Details

Sample No.	S2
Matrix.	Soil
Analyte.	V
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	38	9.6	-0.21	-0.08
2	34.4	8.6	-1.13	-0.50
3	40.3	6.04	0.39	0.24
4	40	2.9	0.31	0.35
5	NT	NT		
6	34.5	9.3	-1.11	-0.45
7	NT	NT		
8	35.6	3.6	-0.82	-0.80
9	35	7.5	-0.98	-0.49
10	41	4.1	0.57	0.49
11	NT	NT		
12	36	5	-0.72	-0.53
13	NT	NT		
14	42.6	4.26	0.98	0.82
15	41.2	8.0	0.62	0.29
16	43.3	7.5	1.16	0.58
17	39.4	7.9	0.15	0.07
18	41.2	4.75	0.62	0.47
19	NT	NT		
20	40.5	9.8	0.44	0.17
21	36.9	5.54	-0.49	-0.33
22	41	9	0.57	0.24
23	39	3.79	0.05	0.05
24	36.4	3.6	-0.62	-0.60
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	38.8	1.8
Spike	Not Spiked	
Homogeneity Value	41.3	5.0
Robust Average	38.8	1.8
Median	39.4	1.3
Mean	38.8	
N	19	
Max.	43.3	
Min.	34.4	
Robust SD	3.2	
Robust CV	8.2%	

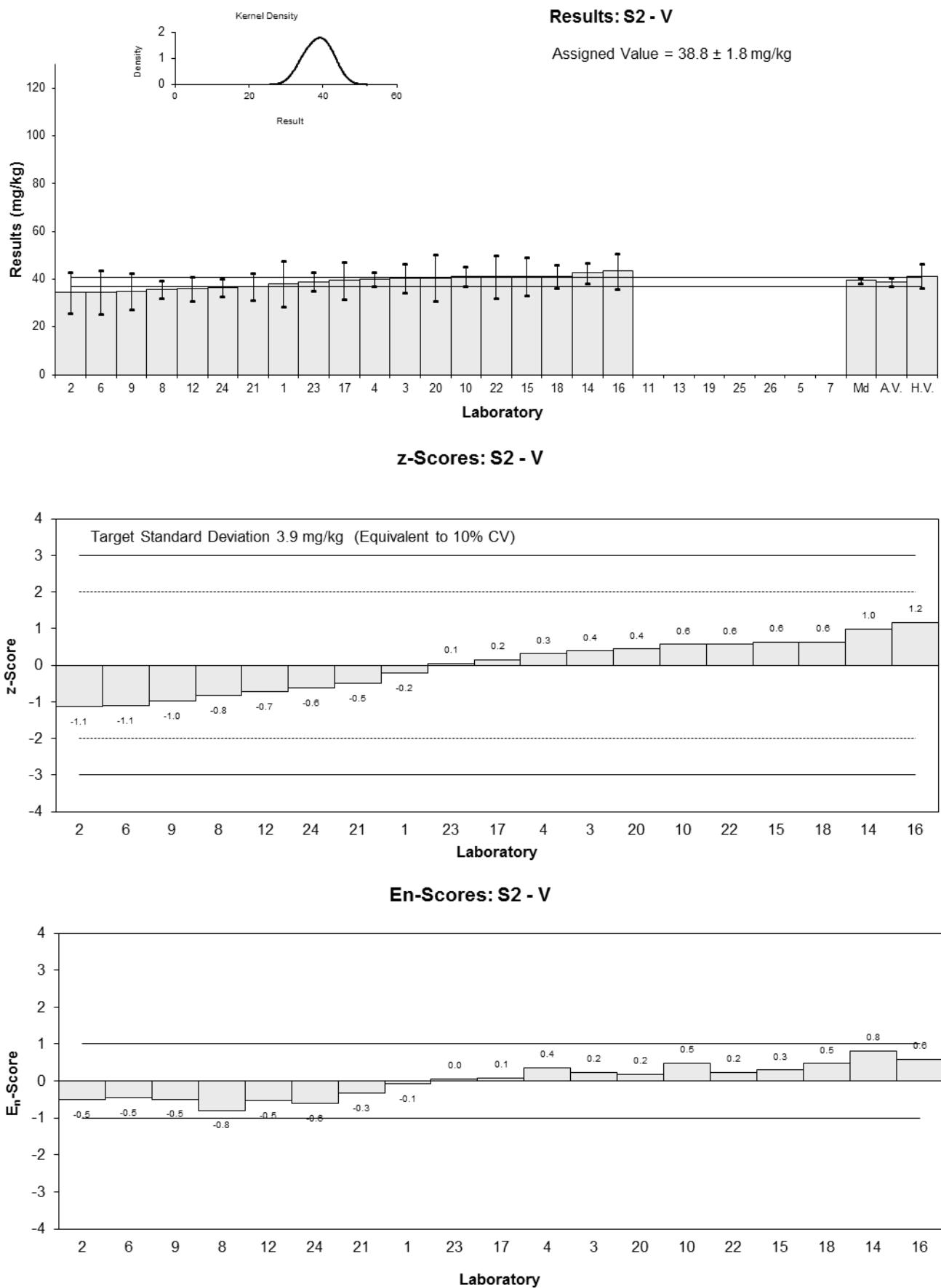


Figure 40

Table 53

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	70	12	-0.01	-0.01
2	73.4	13.0	0.47	0.25
3	70.7	10.60	0.09	0.05
4	63	4.6	-1.01	-1.28
5	NT	NT		
6	38.0	10	-4.58	-3.07
7	75.1	NR	0.71	1.61
8	61.8	6.2	-1.18	-1.20
9	68	9.4	-0.30	-0.21
10	73	10.95	0.41	0.25
11	NT	NT		
12	67	10	-0.44	-0.30
13	NT	NT		
14	72.5	7.25	0.34	0.30
15	78.2	8.0	1.16	0.94
16	72.9	12.0	0.40	0.23
17	69.1	14.5	-0.14	-0.07
18	73.1	8.73	0.43	0.32
19	NT	NT		
20	77.8	6.1	1.10	1.13
21	73.3	11.0	0.46	0.28
22	68	8	-0.30	-0.24
23	74	7.77	0.56	0.47
24	58.7	12.3	-1.63	-0.90
25	67.42	0.7	-0.38	-0.84
26	NT	NT		

Statistics

Assigned Value	70.1	3.1
Spike	Not Spiked	
Homogeneity Value	72.2	8.7
Robust Average	70.1	3.1
Median	70.7	1.8
Mean	68.8	
N	21	
Max.	78.2	
Min.	38	
Robust SD	5.7	
Robust CV	8.1%	

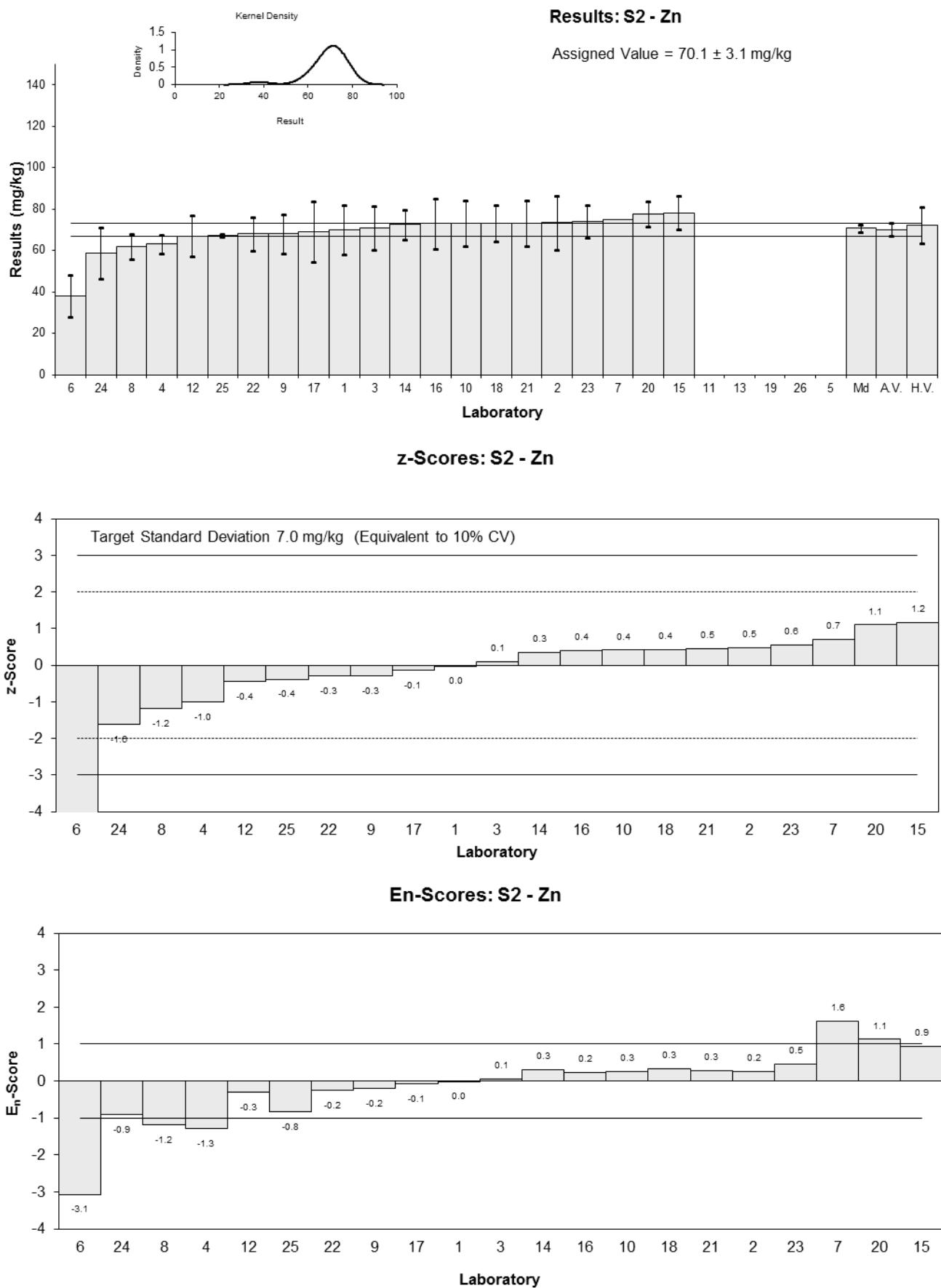


Figure 41

Table 54

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	NT	NT
2	NR	NR
3	NR	NR
4	NR	NR
5	1.34	1.25
6	NT	NT
7	<0.5	NR
8	NR	NR
9	<1	0.2
10	NR	NR
11	NT	NT
12	NR	NR
13	NT	NT
14	NT	NT
15	NT	NT
16	NT	NT
17	NR	NR
18	< 5	0.5
19	NT	NT
20	NT	NT
21	0.58	0.087
22	<2.5	NR
23	NT	NT
24	0.53	0.1
25	NT	NT
26	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.70	0.14
Robust Average	0.82	0.74
Median	0.58	0.18
Mean	0.82	
N	3	
Max.	1.34	
Min.	0.53	
Robust SD	0.040	
Robust CV	4.9%	

Results: S3 - Bromide

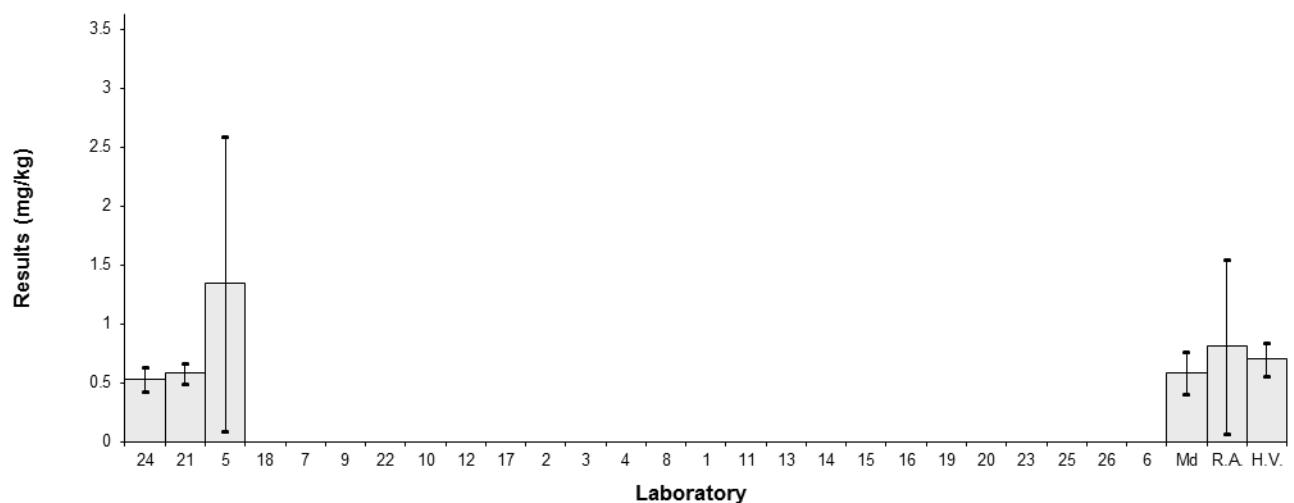


Figure 42

Table 55

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	3100	870	-0.22	-0.08
2	3229	350	0.19	0.15
3	3116.84	467.52	-0.17	-0.11
4	2670	160	-1.58	-2.08
5	NT	NT		
6	3160	695	-0.03	-0.01
7	3901	NR	2.31	4.06
8	NR	NR		
9	3030	730	-0.44	-0.19
10	NR	NR		
11	NT	NT		
12	3530	530	1.14	0.64
13	NT	NT		
14	NT	NT		
15	3200	320	0.09	0.08
16	3050	610	-0.38	-0.19
17	3150	470	-0.06	-0.04
18	NT	NT		
19	NT	NT		
20	3330	480	0.50	0.31
21	NT	NT		
22	2900	290	-0.85	-0.79
23	3530	986	1.14	0.36
24	2910	873	-0.82	-0.29
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	3170	180
Spike	Not Spiked	
Homogeneity Value	3000	360
Robust Average	3170	180
Median	3150	100
Mean	3190	
N	15	
Max.	3901	
Min.	2670	
Robust SD	270	
Robust CV	8.5%	

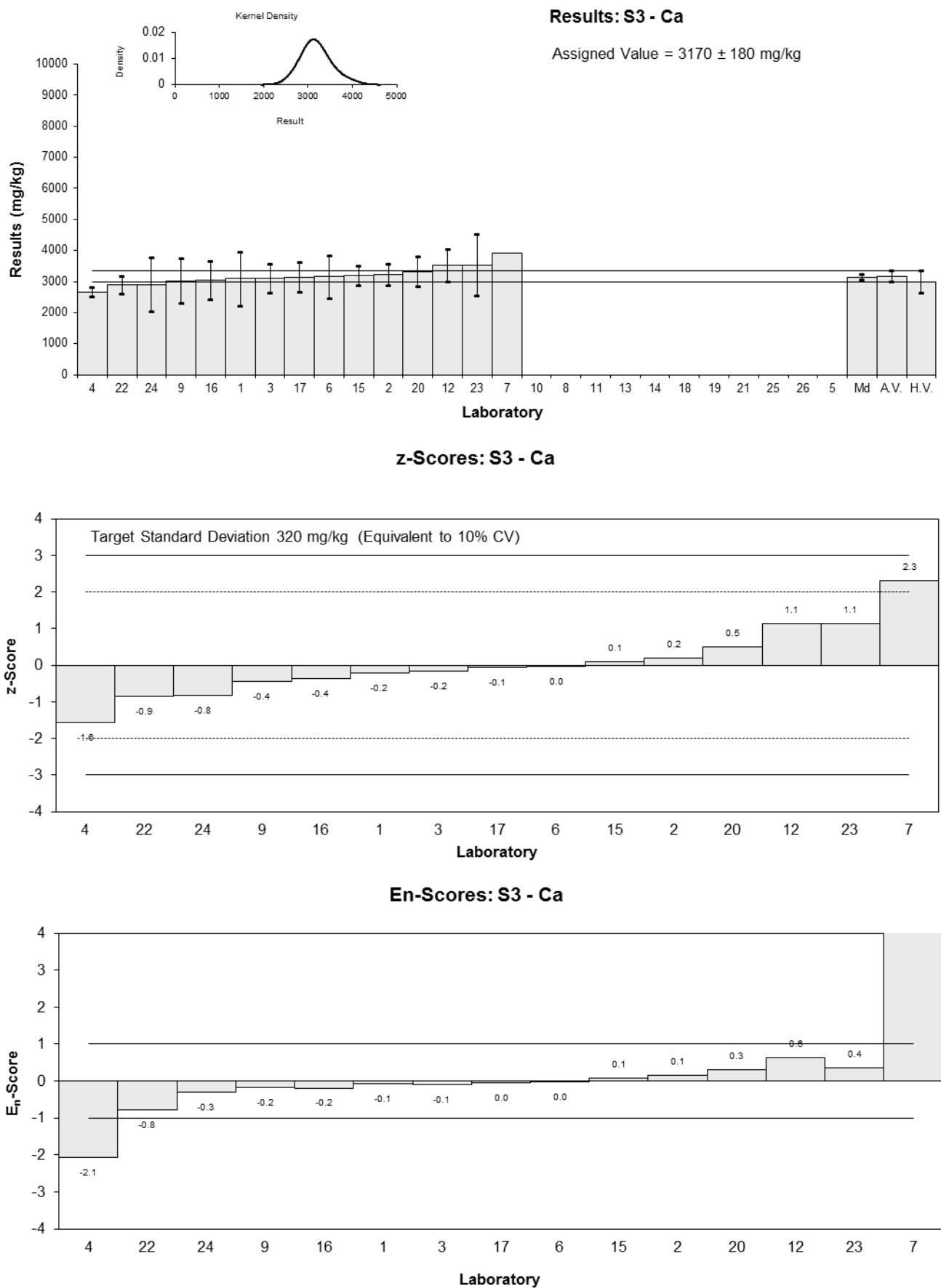


Figure 43

Table 56

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	89	18	-0.73	-0.37
2	NR	NR		
3	NR	NR		
4	NR	NR		
5	100.11	30.81	0.43	0.13
6	360	NR	27.50	47.14
7	17.6	NR	-8.17	-14.00
8	NR	NR		
9	85	13	-1.15	-0.78
10	NR	NR		
11	NT	NT		
12	NR	NR		
13	104	15	0.83	0.50
14	NT	NT		
15	97	10	0.10	0.09
16	89.4	14.2	-0.69	-0.43
17	NR	NR		
18	88.4	10.9	-0.79	-0.62
19	101	20.1	0.52	0.24
20	NT	NT		
21	94.8	23.7	-0.13	-0.05
22	90	10	-0.62	-0.52
23	100	17.3	0.42	0.22
24	101	15	0.52	0.31
25	NT	NT		
26	123.2	5.3	2.83	3.53

Statistics

Assigned Value*	96.0	5.6
Spike	Not Spiked	
Homogeneity Value	98	15
Robust Average	96.3	6.8
Median	97.0	5.7
Mean	109	
N	15	
Max.	360	
Min.	17.6	
Robust SD	8.0	
Robust CV	8.3%	

*Robust Average excluding Laboratories 6 and 7.

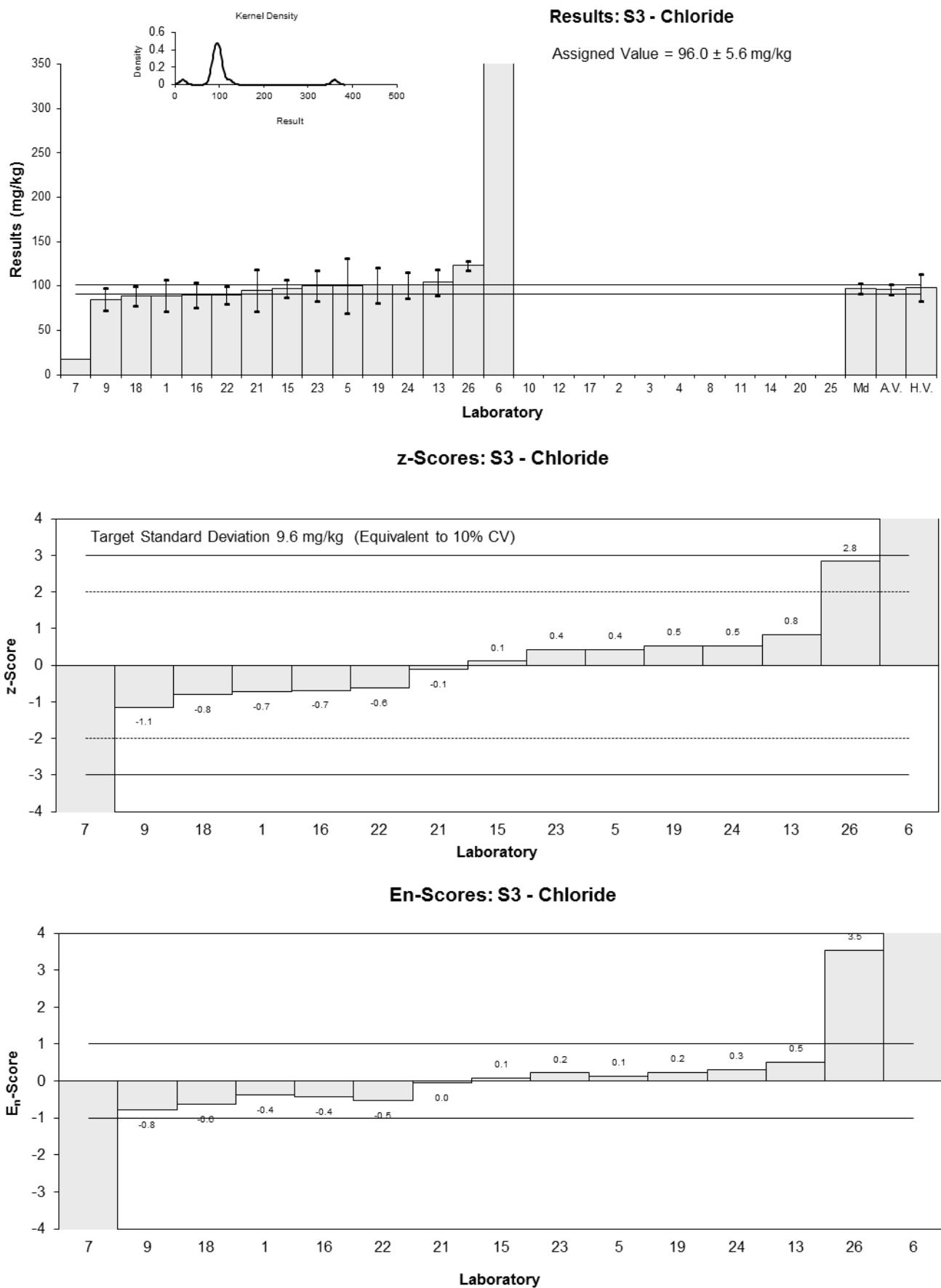


Figure 44

Table 57

Sample Details

Sample No.	S3
Matrix.	Soil
Analyte.	EC
Units	uS/cm

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	295	55	-4.99	-4.90
2	572	57.2	-0.29	-0.27
3	NR	NR		
4	NR	NR		
5	NT	NT		
6	NT	NT		
7	601	NR	0.20	0.50
8	NR	NR		
9	580	58	-0.15	-0.14
10	NR	NR		
11	NT	NT		
12	555	NR	-0.58	-1.42
13	603	21	0.24	0.44
14	NT	NT		
15	553	55	-0.61	-0.60
16	660	123	1.21	0.57
17	NR	NR		
18	630	31.2	0.70	1.04
19	657	131.4	1.15	0.51
20	NT	NT		
21	608	30	0.32	0.49
22	570	52	-0.32	-0.33
23	589	23.8	0.00	0.00
24	580	64	-0.15	-0.13
25	NT	NT		
26	573	3	-0.27	-0.66

Statistics

Assigned Value	589	24
Spike	Not Spiked	
Robust Average	589	24
Median	580	19
Mean	575	
N	15	
Max.	660	
Min.	295	
Robust SD	38	
Robust CV	6.5%	

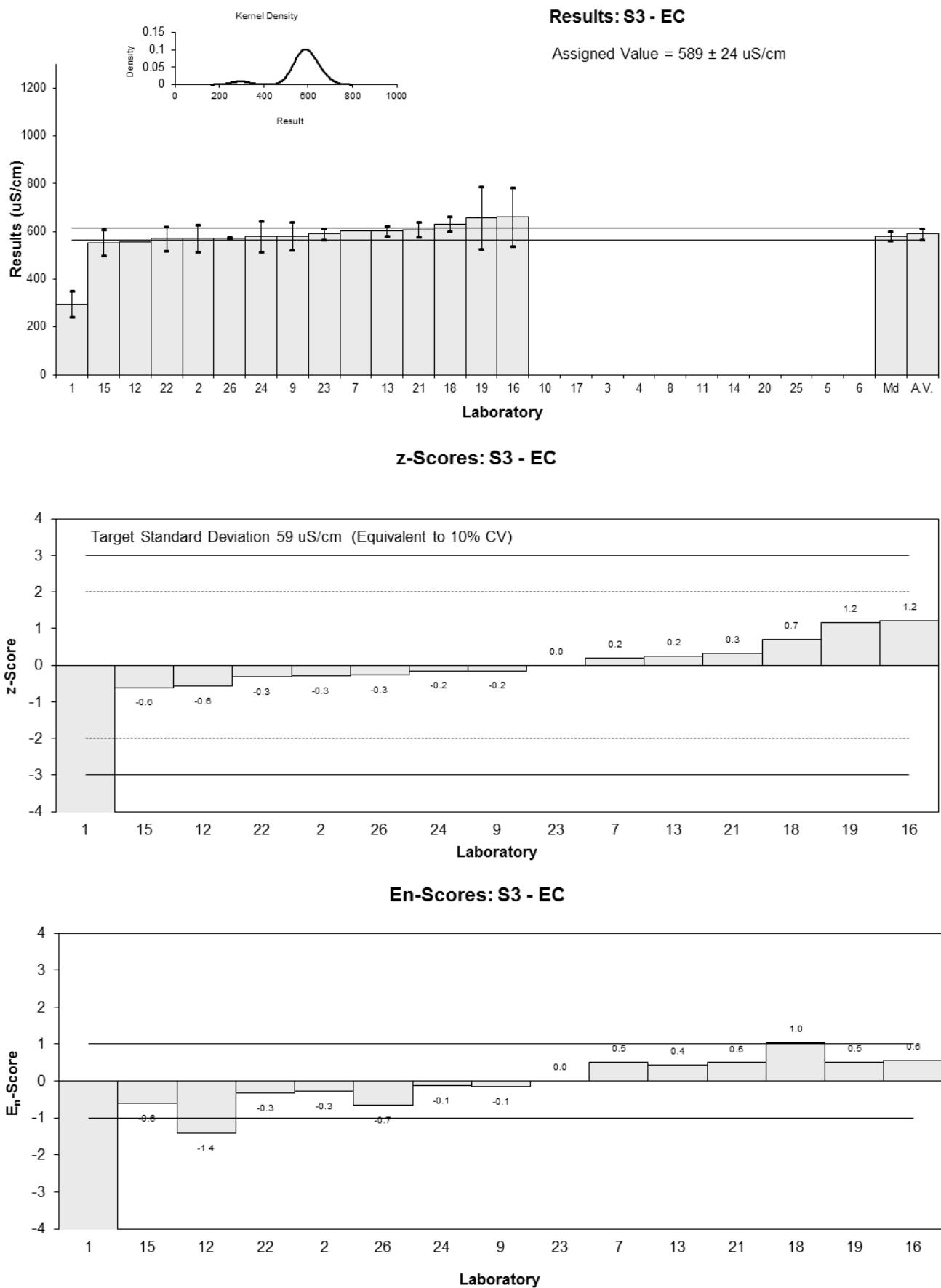


Figure 45

Table 58

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	19800	3200	-0.15	-0.09
2	19196	2550	-0.45	-0.33
3	20600	3090	0.25	0.15
4	NR	NR		
5	NT	NT		
6	18300	4000	-0.90	-0.44
7	22308	NR	1.10	2.21
8	NR	NR		
9	18600	4390	-0.75	-0.33
10	NR	NR		
11	NT	NT		
12	19200	3600	-0.45	-0.24
13	NT	NT		
14	NT	NT		
15	20200	2000	0.05	0.04
16	21200	4200	0.55	0.25
17	20300	3100	0.10	0.06
18	20153	2302	0.03	0.02
19	NT	NT		
20	19700	2000	-0.20	-0.18
21	NT	NT		
22	20000	950	-0.05	-0.07
23	24200	2579	2.04	1.48
24	22100	4199	1.00	0.46
25	NT	NT		
26	12030.4	363.5	-4.01	-7.58

Statistics

Assigned Value	20100	1000
Spike	Not Spiked	
Homogeneity Value	20500	2500
Robust Average	20100	1000
Median	20100	700
Mean	19900	
N	16	
Max.	24200	
Min.	12030.4	
Robust SD	2000	
Robust CV	10%	

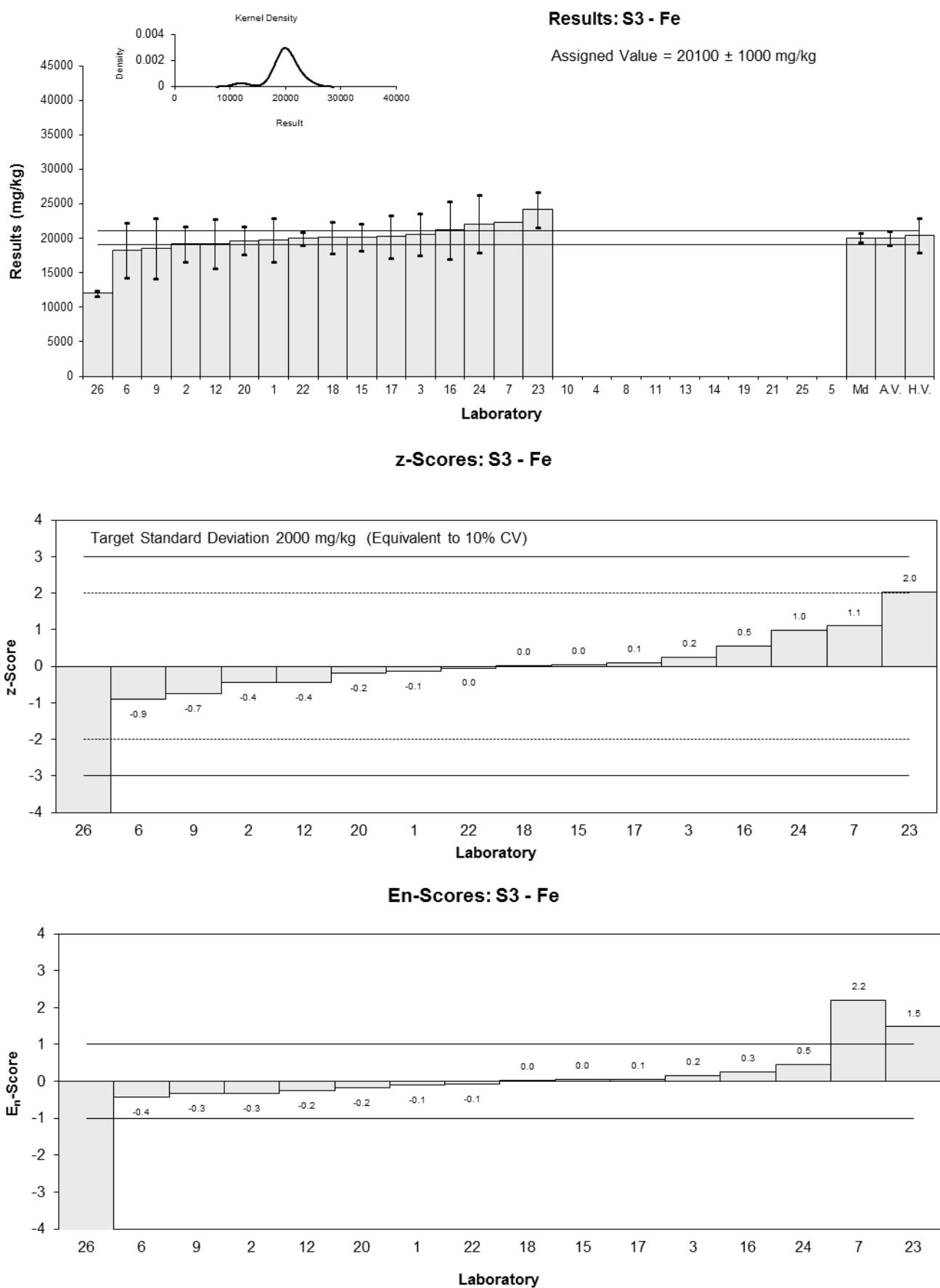


Figure 46

Table 59

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	1.3	0.4
2	NR	NR
3	NR	NR
4	NR	NR
5	3.09	0.41
6	NT	NT
7	<0.5	NR
8	NR	NR
9	2.4	0.36
10	NR	NR
11	NT	NT
12	NR	NR
13	NT	NT
14	NT	NT
15	<0.25	NR
16	<20	4
17	NR	NR
18	NT	NT
19	NT	NT
20	NT	NT
21	NT	NT
22	NT	NT
23	3	0.52
24	2.4	0.3
25	NT	NT
26	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	1.70	0.34
Robust Average	2.44	0.91
Median	2.4	1.1
Mean	2.44	
N	5	
Max.	3.09	
Min.	1.3	
Robust SD	0.81	
Robust CV	33%	

Results: S3 - Fluoride

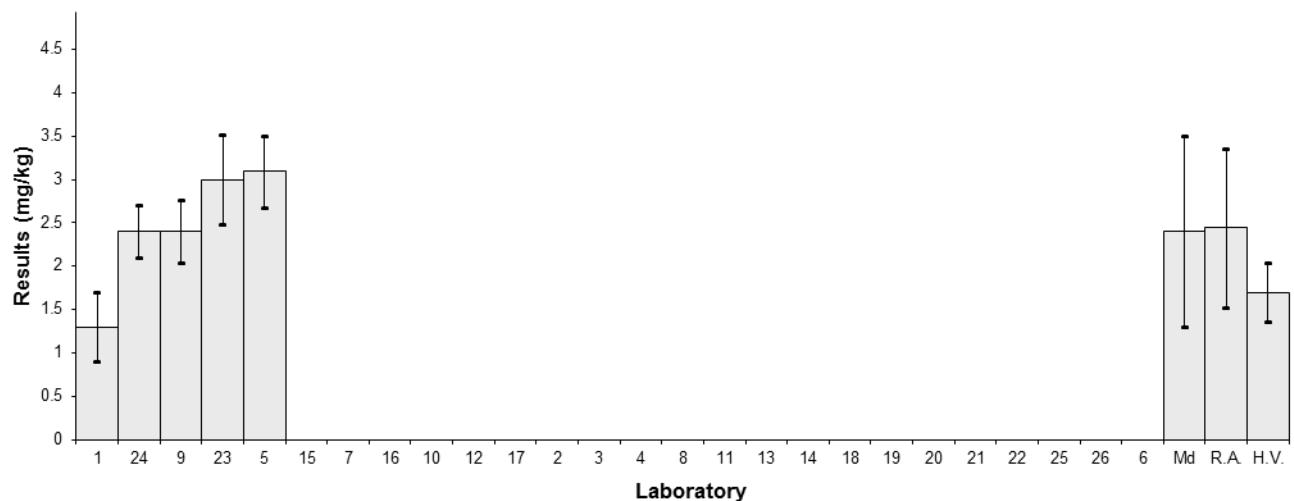


Figure 47

Table 60

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	1540	390	1.00	0.35
2	1472	370	0.51	0.19
3	1290.37	193.55	-0.78	-0.51
4	NR	NR		
5	NT	NT		
6	1280	183	-0.86	-0.59
7	1485	NR	0.61	0.94
8	NR	NR		
9	1270	240	-0.93	-0.51
10	NR	NR		
11	NT	NT		
12	2380	360	7.00	2.64
13	NT	NT		
14	NT	NT		
15	1400	140	0.00	0.00
16	1420	280	0.14	0.07
17	1470	370	0.50	0.18
18	NT	NT		
19	1260	252	-1.00	-0.52
20	1500	220	0.71	0.42
21	NT	NT		
22	1700	290	2.14	0.99
23	1450	385	0.36	0.13
24	3610	433	15.79	5.00
25	NT	NT		
26	870.6	20.4	-3.78	-5.74

Statistics

Assigned Value*	1400	90
Spike	Not Spiked	
Homogeneity Value	1660	200
Robust Average	1450	130
Median	1460	100
Mean	1590	
N	16	
Max.	3610	
Min.	870	
Robust SD	140	
Robust CV	9.7%	

*Robust Average excluding Laboratories 12 and 24.

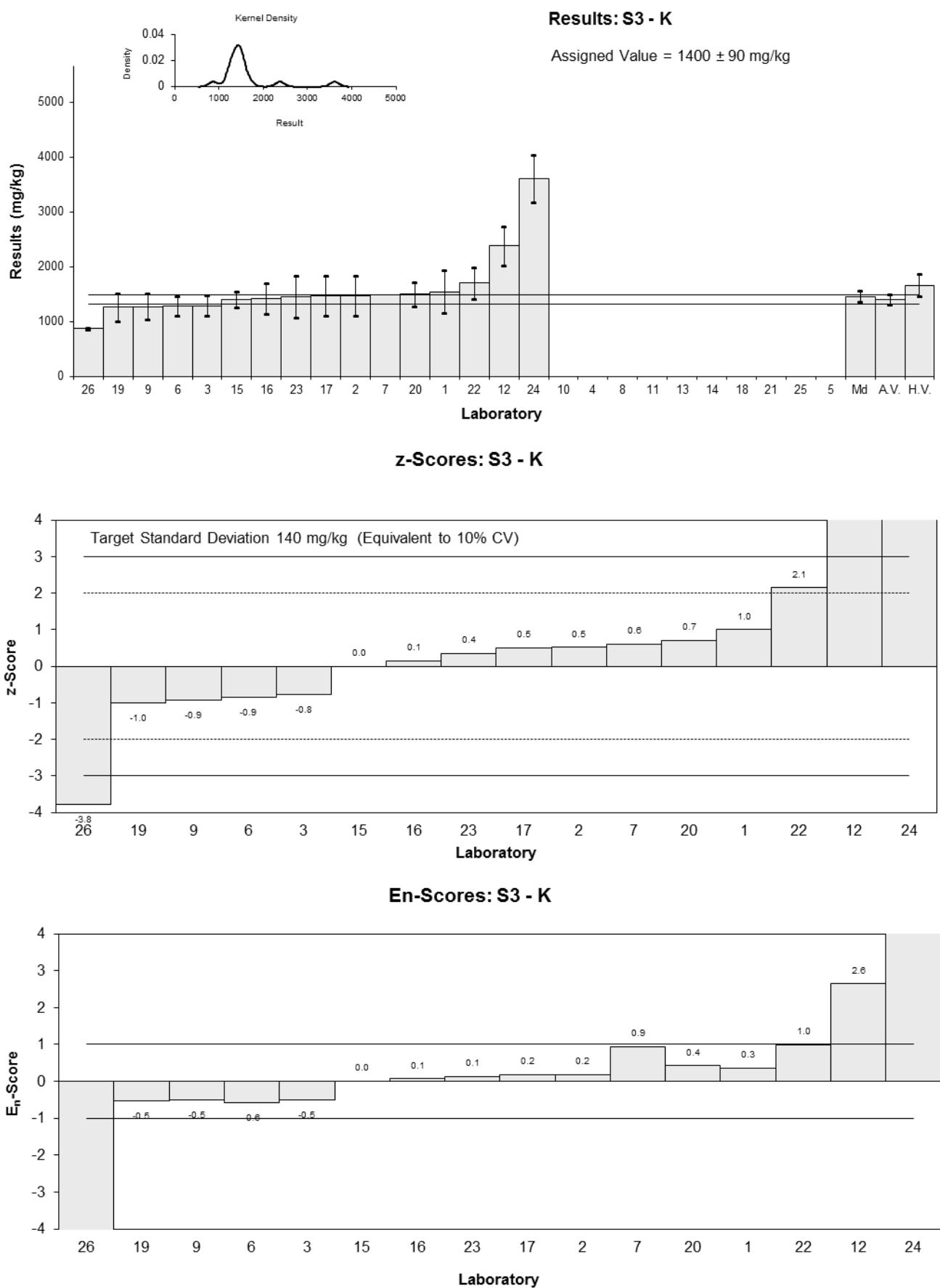


Figure 48

Table 61

Sample Details

Sample No.	S3
Matrix.	Soil
Analyte.	KCl Ext Ammonium-N
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	22	3.8	0.39	0.28
2	22.0	4.4	0.39	0.26
3	NR	NR		
4	18.4	1.9	-0.49	-0.42
5	NT	NT		
6	14.1	NR	-1.54	-1.43
7	NT	NT		
8	NR	NR		
9	<30	6		
10	NR	NR		
11	NT	NT		
12	13	2	-1.81	-1.53
13	26.7	4.0	1.54	1.06
14	NT	NT		
15	2.0	0.2	-4.51	-4.18
16	25.2	2.52	1.18	0.95
17	NR	NR		
18	19.0	2.93	-0.34	-0.26
19	66.0	13.2	11.18	3.28
20	NT	NT		
21	NT	NT		
22	NT	NT		
23	NT	NT		
24	23	6	0.64	0.35
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	20.4	4.4
Spike	Not Spiked	
Robust Average	20.4	5.5
Median	22.0	3.6
Mean	22.9	
N	11	
Max.	66	
Min.	2	
Robust SD	5.3	
Robust CV	26%	

*Robust Average excluding Laboratories 15 and 19.

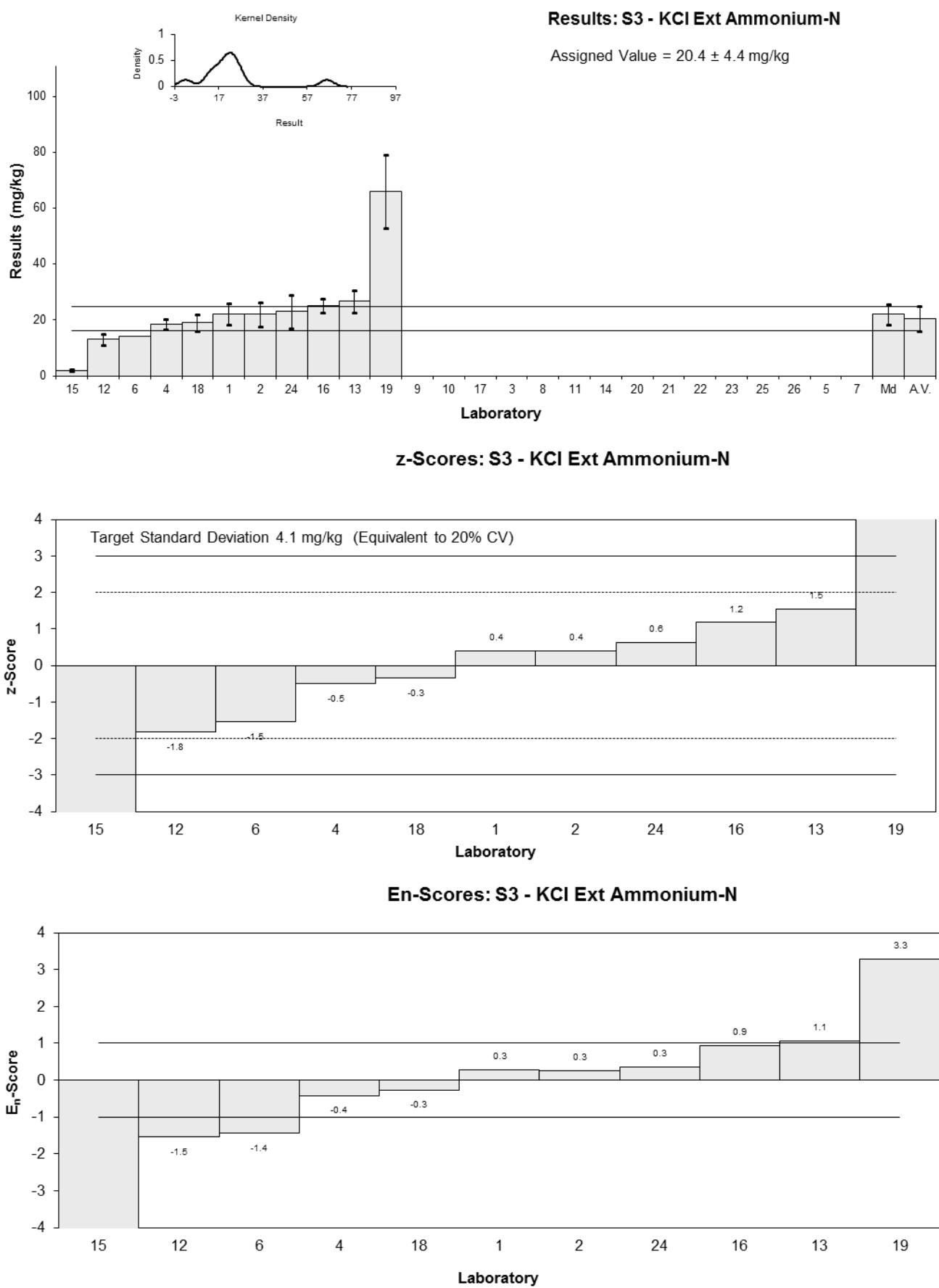


Figure 49

Table 62

Sample Details

Sample No.	S3
Matrix.	Soil
Analyte.	KCl Ext Nitrate-N
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	150	31	-0.62	-0.31
2	168.8	25.3	0.55	0.32
3	NR	NR		
4	195	15	2.19	1.94
5	NT	NT		
6	144	NR	-1.00	-1.60
7	NT	NT		
8	NR	NR		
9	160	32	0.00	0.00
10	NR	NR		
11	NT	NT		
12	150	20	-0.62	-0.45
13	154	18	-0.38	-0.29
14	NT	NT		
15	19.1	2.0	-8.81	-13.82
16	170	17	0.62	0.51
17	NR	NR		
18	NT	NT		
19	158	61.6	-0.12	-0.03
20	NT	NT		
21	NT	NT		
22	NT	NT		
23	NT	NT		
24	165	25	0.31	0.19
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	160	10
Spike	Not Spiked	
Robust Average	158	11
Median	158	8
Mean	149	
N	11	
Max.	195	
Min.	19.1	
Robust SD	12	
Robust CV	7.6%	

*Robust Average excluding Laboratory 15.

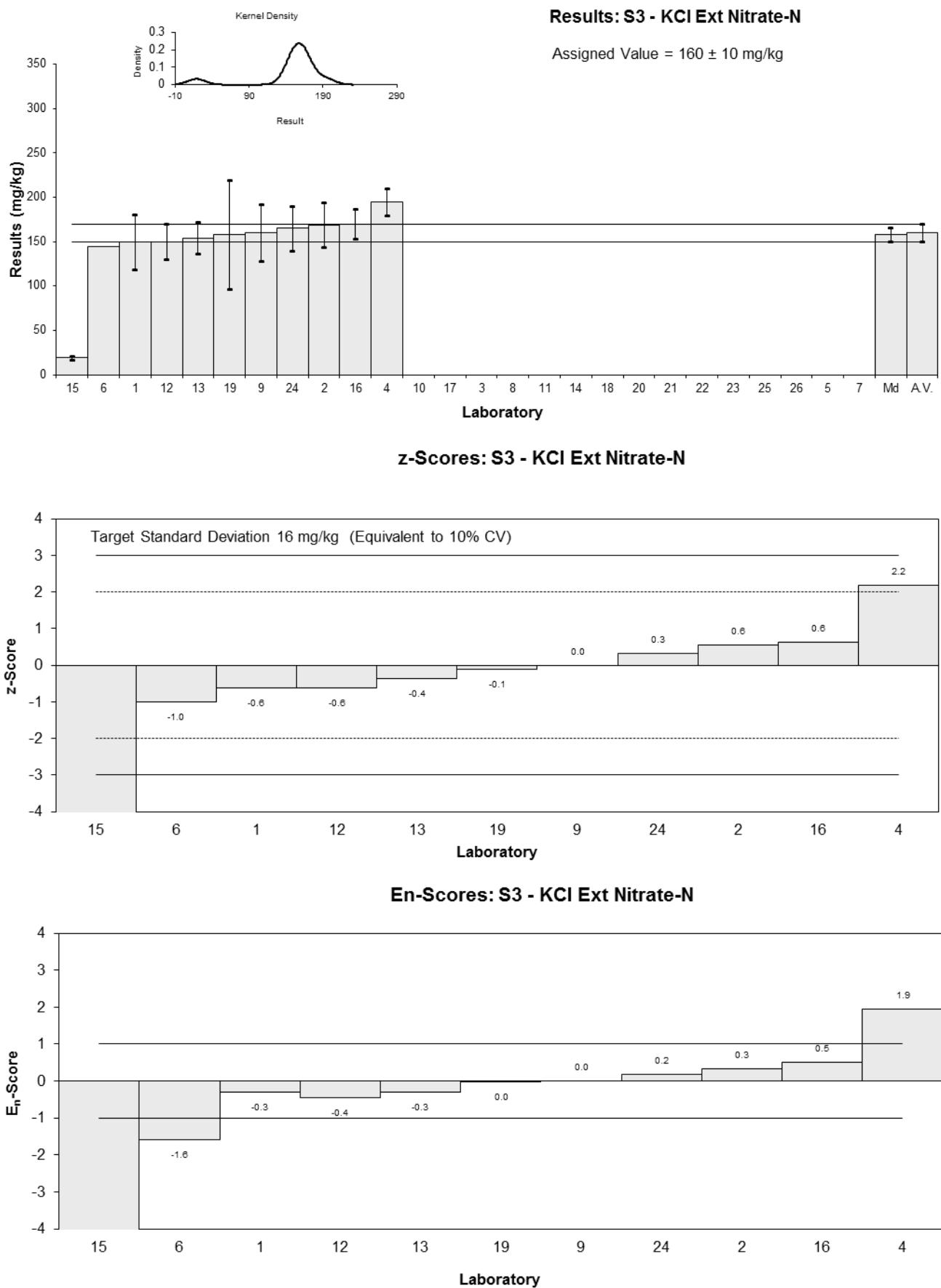


Figure 50

Table 63

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	700	195	-1.07	-0.40
2	714	75	-0.89	-0.63
3	678.46	101.76	-1.35	-0.80
4	NR	NR		
5	NT	NT		
6	606	170	-2.27	-0.94
7	818	NR	0.43	0.41
8	NR	NR		
9	800	140	0.20	0.10
10	NR	NR		
11	NT	NT		
12	1020	150	3.01	1.38
13	NT	NT		
14	NT	NT		
15	720	70	-0.82	-0.59
16	712	142	-0.92	-0.44
17	755	106	-0.37	-0.22
18	NT	NT		
19	1090	218	3.90	1.31
20	812	86	0.36	0.23
21	NT	NT		
22	740	230	-0.56	-0.18
23	770	257	-0.18	-0.05
24	1110	333	4.16	0.95
25	NT	NT		
26	341.8	13.4	-5.64	-5.26

Statistics

Assigned Value*	784	83
Spike	Not Spiked	
Homogeneity Value	850	100
Robust Average	772	91
Median	748	46
Mean	774	
N	16	
Max.	1110	
Min.	341.8	
Robust SD	130	
Robust CV	17%	

*Robust Average excluding Laboratory 26.

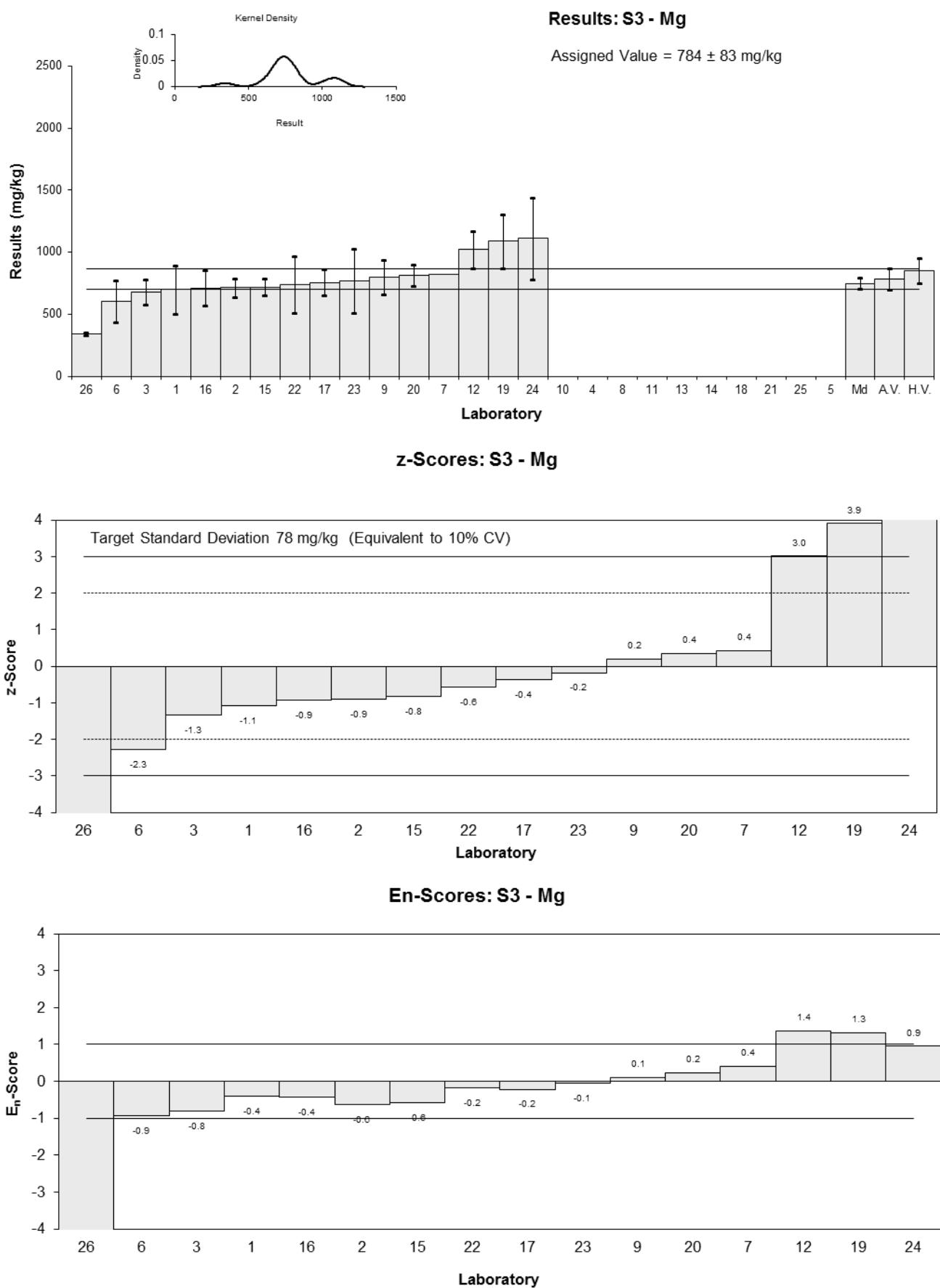


Figure 51

Table 64

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	145	42	-0.46	-0.16
2	210	22	3.82	2.40
3	151.739	22.76	-0.02	-0.01
4	150	15	-0.13	-0.11
5	NT	NT		
6	<900	NR		
7	165	NR	0.86	1.30
8	NR	NR		
9	150	32	-0.13	-0.06
10	NR	NR		
11	NT	NT		
12	171	NR	1.25	1.90
13	NT	NT		
14	NT	NT		
15	130	15	-1.45	-1.22
16	136	27	-1.05	-0.56
17	146	31	-0.39	-0.18
18	NT	NT		
19	NT	NT		
20	147	35	-0.33	-0.14
21	NT	NT		
22	760	120	40.00	5.05
23	150	60.1	-0.13	-0.03
24	609	183	30.07	2.49
25	NT	NT		
26	165.5	11.0	0.89	0.91

Statistics

Assigned Value*	152	10
Spike	Not Spiked	
Homogeneity Value	173	21
Robust Average	160	16
Median	150	11
Mean	226	
N	15	
Max.	760	
Min.	130	
Robust SD	15	
Robust CV	9.4%	

*Robust Average excluding Laboratories 22 and 24.

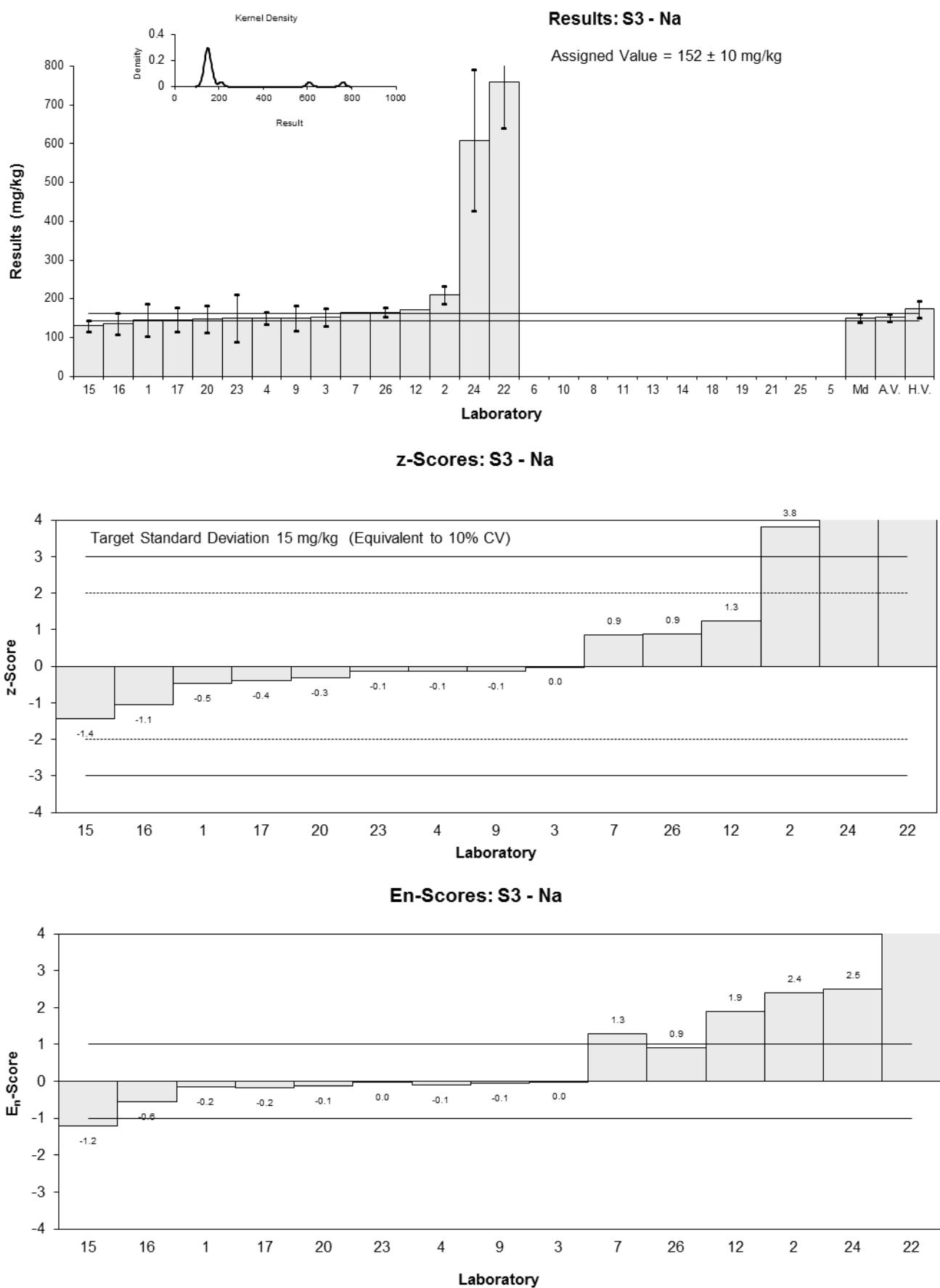


Figure 52

Table 65

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty
1	1.0	0.5
2	NR	NR
3	NR	NR
4	NR	NR
5	3.66	0.72
6	NT	NT
7	NT	NT
8	NR	NR
9	1.0	0.2
10	NR	NR
11	NT	NT
12	<1	NR
13	NT	NT
14	NT	NT
15	1.4	0.3
16	<10	2
17	NR	NR
18	0.84	0.09
19	1.59	.318
20	NT	NT
21	0.59	0.17
22	<1.0	NR
23	0.5	0.04
24	0.75	0.12
25	NT	NT
26	6.3	1.3

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.70	0.11
Robust Average	1.28	0.67
Median	1.00	0.43
Mean	1.76	
N	10	
Max.	6.3	
Min.	0.5	
Robust SD	0.37	
Robust CV	45%	

Results: S3 - Orthophosphate-P

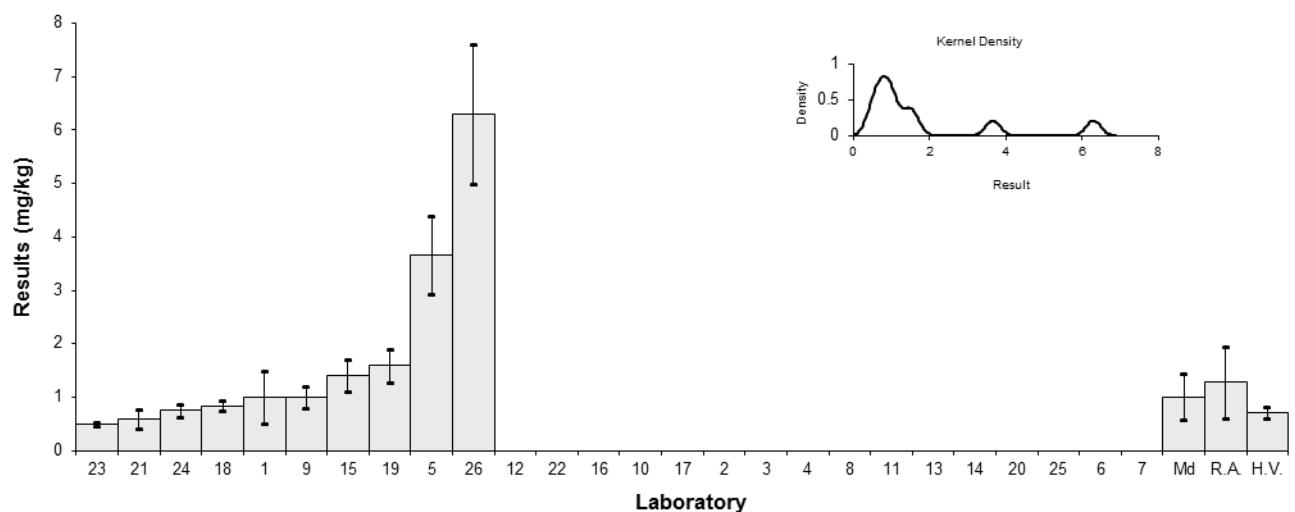


Figure 53

Table 66

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	550	93	-0.50	-0.29
2	569	60	-0.17	-0.14
3	611	91.65	0.55	0.32
4	495	15	-1.45	-1.92
5	NT	NT		
6	516	77	-1.09	-0.72
7	595	NR	0.28	0.39
8	NR	NR		
9	530	69	-0.85	-0.61
10	NR	NR		
11	NT	NT		
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	550	50	-0.50	-0.45
16	514	103	-1.12	-0.59
17	627	94	0.83	0.47
18	638	128	1.02	0.44
19	529	105.8	-0.86	-0.44
20	657	71	1.35	0.95
21	NT	NT		
22	550	70	-0.50	-0.36
23	680	61.1	1.74	1.37
24	555	150	-0.41	-0.15
25	NT	NT		
26	779.28	14.1	3.46	4.62

Statistics

Assigned Value	579	41
Spike	Not Spiked	
Homogeneity Value	591	71
Robust Average	579	41
Median	555	30
Mean	585	
N	17	
Max.	779	
Min.	495	
Robust SD	68	
Robust CV	12%	

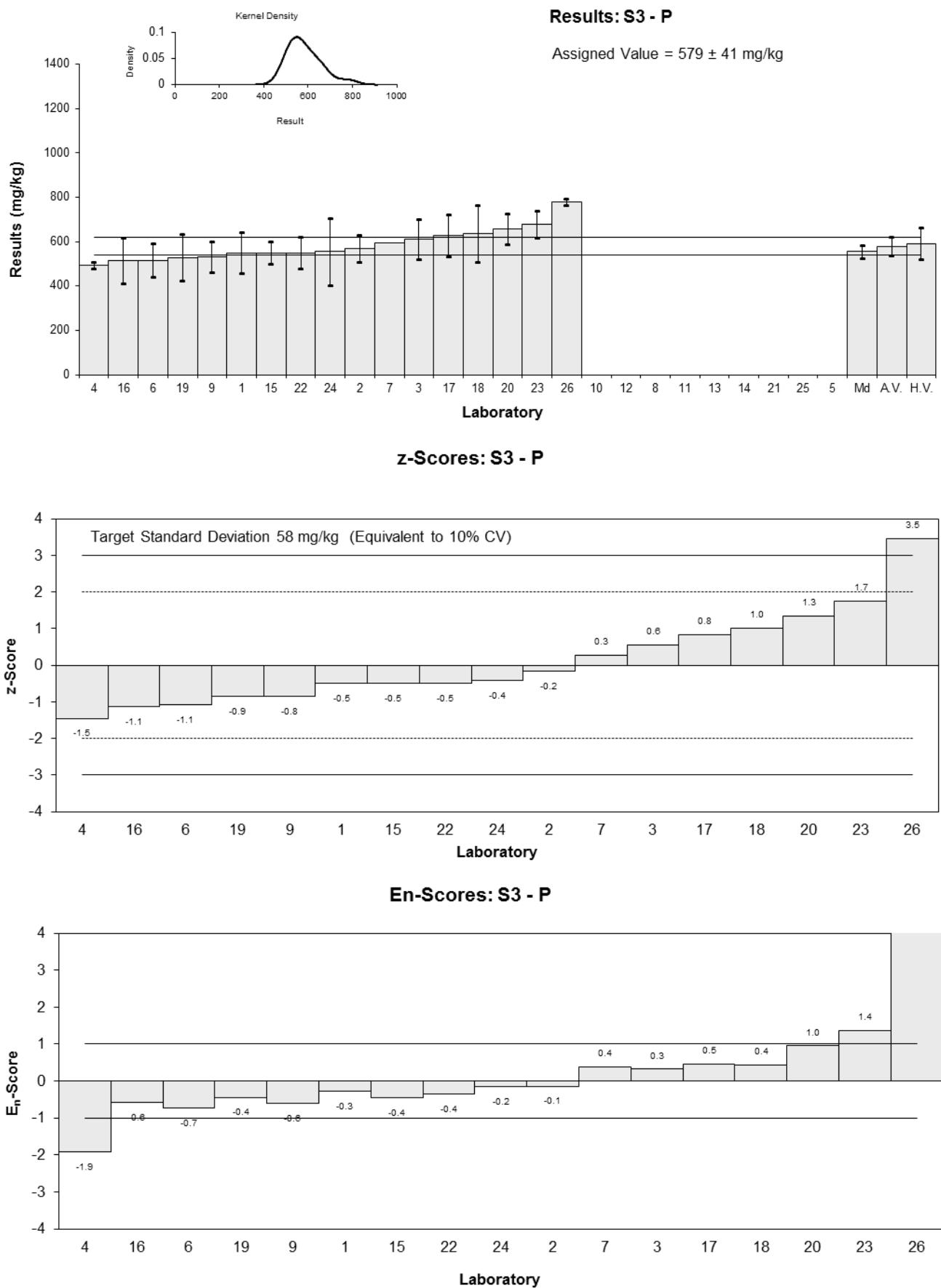


Figure 54

Table 67

Sample Details

Sample No.	S3
Matrix.	Soil
Analyte.	pH

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	7.3	0.2	-0.08	-0.28
2	7.40	0.06	0.05	0.43
3	NR	NR		
4	NR	NR		
5	NT	NT		
6	7.2	NR	-0.22	-2.29
7	7.25	NR	-0.15	-1.57
8	NR	NR		
9	7.3	0.2	-0.08	-0.28
10	NR	NR		
11	NT	NT		
12	7.5	NR	0.19	2.00
13	7.4	0.1	0.05	0.33
14	NT	NT		
15	7.43	0.4	0.10	0.17
16	7.34	0.2	-0.03	-0.09
17	NR	NR		
18	7.15	0.178	-0.29	-1.10
19	7.33	0.2	-0.04	-0.14
20	NT	NT		
21	7.38	0.36	0.03	0.05
22	7.4	0.1	0.05	0.33
23	7.5	0.16	0.19	0.80
24	7.3	0.2	-0.08	-0.28
25	NT	NT		
26	7.65	0.15	0.39	1.75

Statistics

Assigned Value	7.36	0.07
Spike	Not Spiked	
Robust Average	7.36	0.07
Median	7.36	0.05
Mean	7.36	
N	16	
Max.	7.65	
Min.	7.15	
Robust SD	0.10	
Robust CV	1.4%	

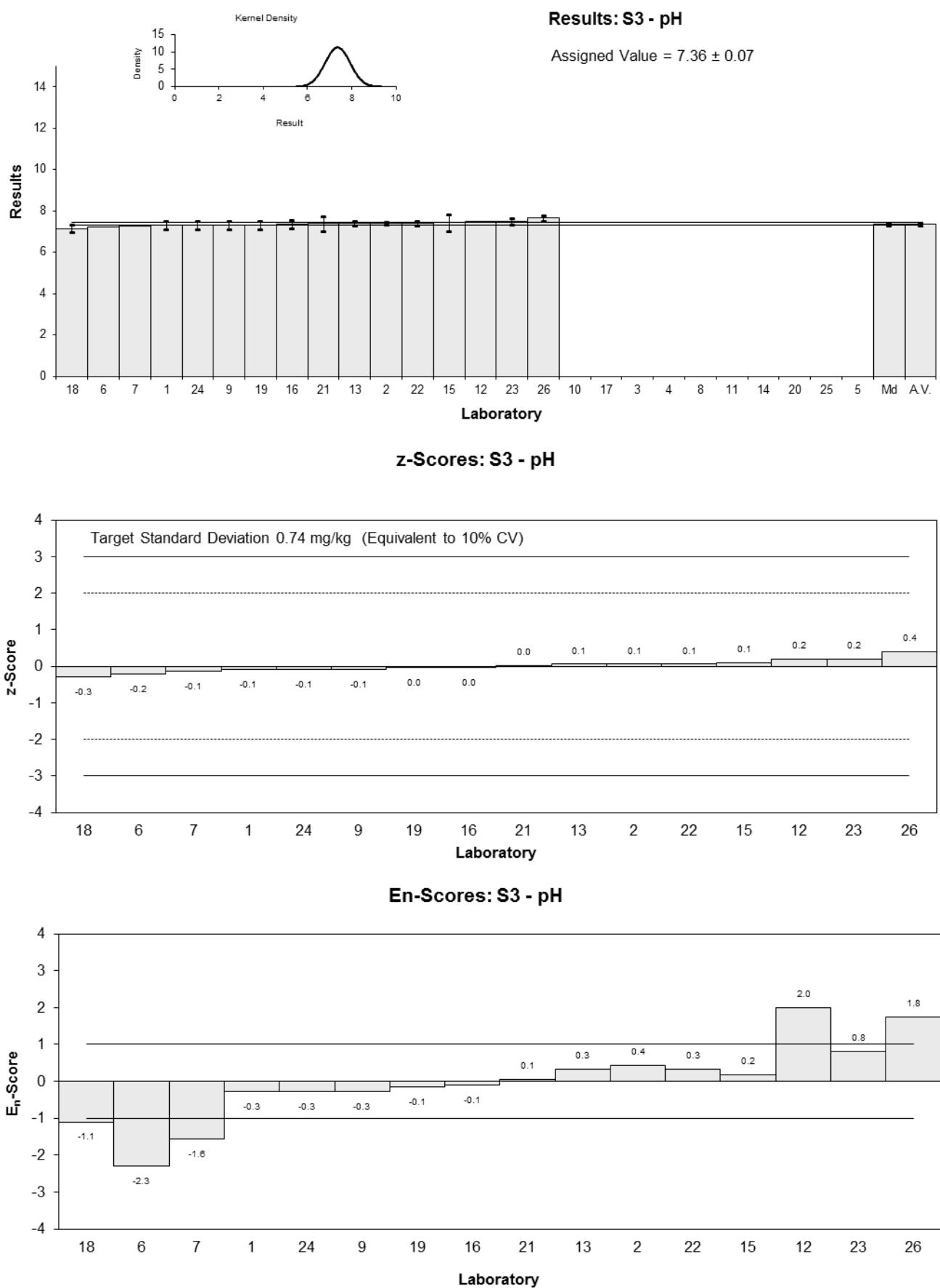


Figure 55

Table 68

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	270	58	-0.36	-0.17
2	265	28	-0.54	-0.49
3	271.780	40.76	-0.29	-0.19
4	250	25	-1.07	-1.06
5	NT	NT		
6	291	99	0.39	0.11
7	NT	NT		
8	NR	NR		
9	280	67	0.00	0.00
10	NR	NR		
11	NT	NT		
12	NR	NR		
13	NT	NT		
14	NT	NT		
15	275	30	-0.18	-0.15
16	302	60	0.79	0.36
17	291	59	0.39	0.18
18	NT	NT		
19	270	54	-0.36	-0.18
20	<2000	NR		
21	NT	NT		
22	350	20	2.50	2.93
23	280	83.5	0.00	0.00
24	880	229	21.43	2.62
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value*	280	13
Spike	Not Spiked	
Homogeneity Value	277	33
Robust Average	283	16
Median	280	10
Mean	329	
N	13	
Max.	880	
Min.	250	
Robust SD	17	
Robust CV	6%	

*Robust Average excluding Laboratory 24.

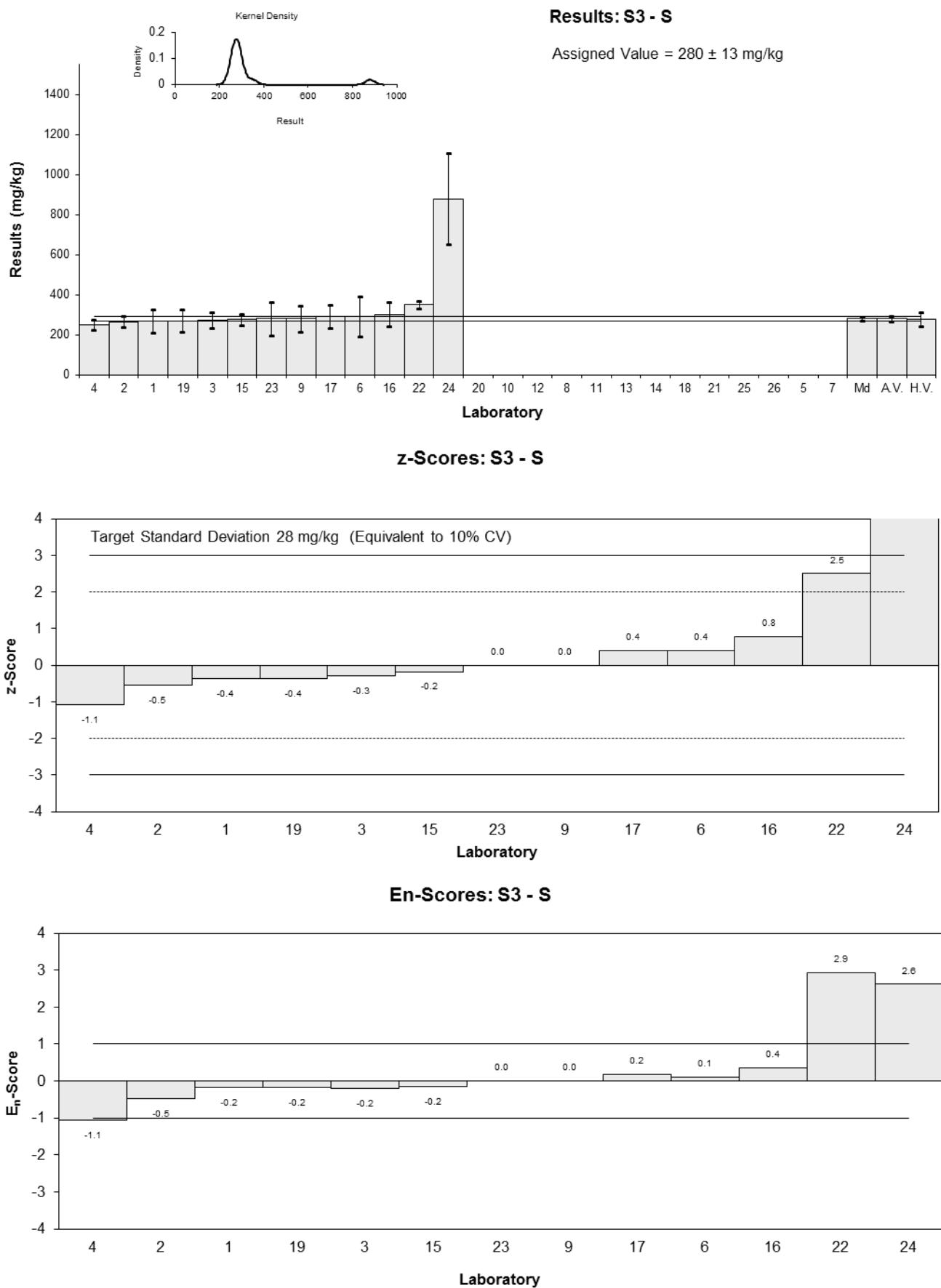


Figure 56

Table 69

Sample Details

Sample No.	S3
Matrix.	Soil
Analyte.	Sulfate
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	120	25	-0.24	-0.19
2	NR	NR		
3	NR	NR		
4	NR	NR		
5	125.14	51.09	-0.03	-0.02
6	NT	NT		
7	<25	NR		
8	NR	NR		
9	110	22	-0.63	-0.55
10	NR	NR		
11	NT	NT		
12	NR	NR		
13	84.0	12.0	-1.67	-1.87
14	NT	NT		
15	99	10	-1.07	-1.26
16	129	26	0.12	0.09
17	NR	NR		
18	160	20.4	1.35	1.22
19	106	21.2	-0.79	-0.70
20	NT	NT		
21	143.4	35.7	0.69	0.43
22	130	9	0.16	0.19
23	160	10.7	1.35	1.56
24	143	37	0.67	0.41
25	NT	NT		
26	NT	NT		

Statistics

Assigned Value	126	19
Spike	Not Spiked	
Homogeneity Value	160	24
Robust Average	126	19
Median	127	16
Mean	126	
N	12	
Max.	160	
Min.	84	
Robust SD	26	
Robust CV	21%	

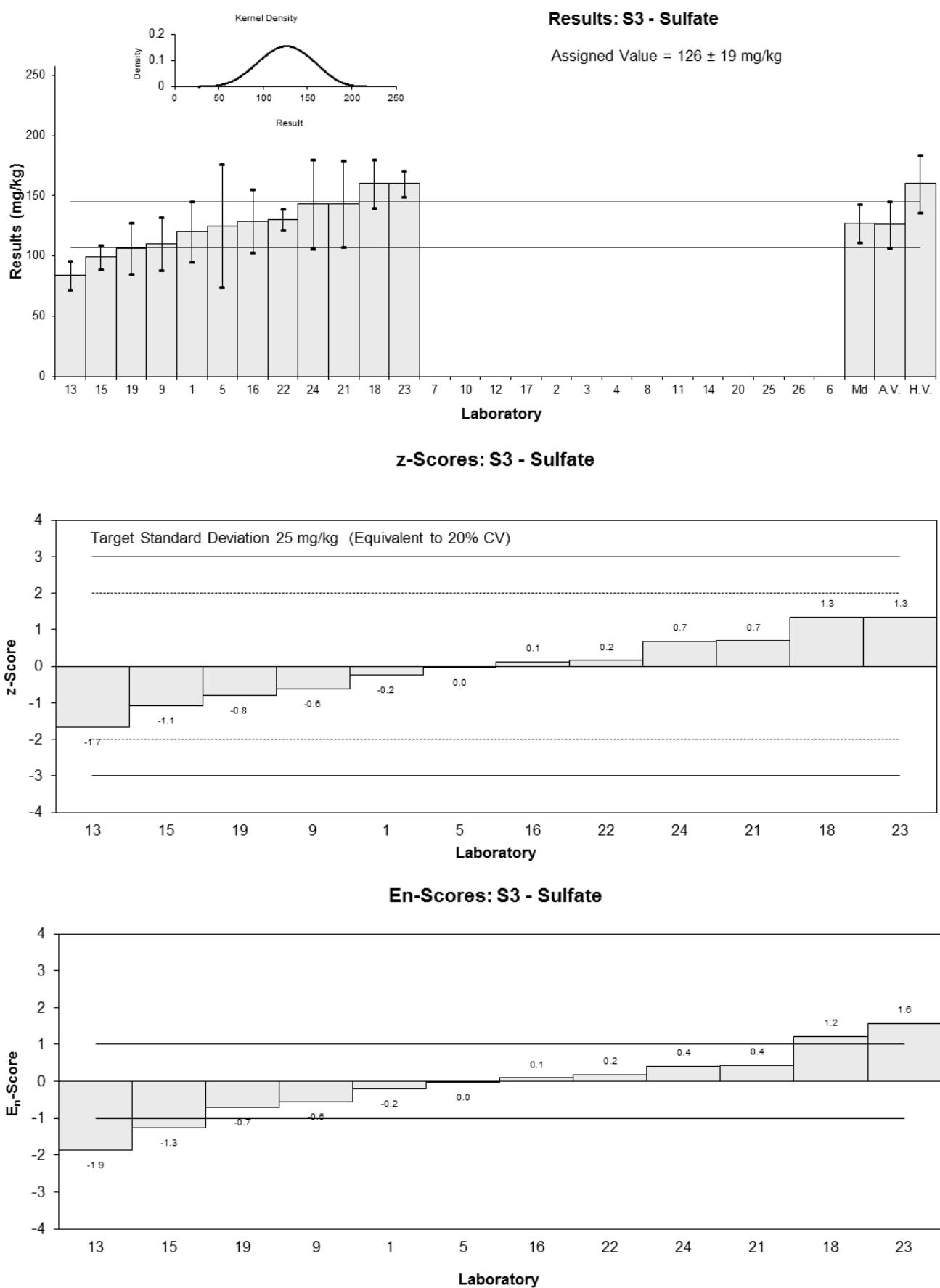


Figure 57

Table 70

Sample Details

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

Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	1880	340	-0.11	-0.06
2	2053	218	0.81	0.67
3	NR	NR		
4	1800	490	-0.53	-0.20
5	NT	NT		
6	1950	NR	0.26	0.71
7	NT	NT		
8	NR	NR		
9	1800	270	-0.53	-0.36
10	NR	NR		
11	NT	NT		
12	1900	300	0.00	0.00
13	1812	181	-0.46	-0.45
14	NT	NT		
15	1800	180	-0.53	-0.52
16	640	115	-6.63	-9.36
17	1920	530	0.11	0.04
18	NT	NT		
19	1980	396	0.42	0.20
20	NT	NT		
21	1863	186	-0.19	-0.19
22	NT	NT		
23	1900	172	0.00	0.00
24	2030	284	0.68	0.44
25	NT	NT		
26	917.4	40.9	-5.17	-12.12

Statistics

Assigned Value*	1900	70
Spike	Not Spiked	
Robust Average	1870	80
Median	1880	70
Mean	1750	
N	15	
Max.	2053	
Min.	640	
Robust SD	100	
Robust CV	5.3%	

*Robust Average excluding Laboratories 16 and 26.

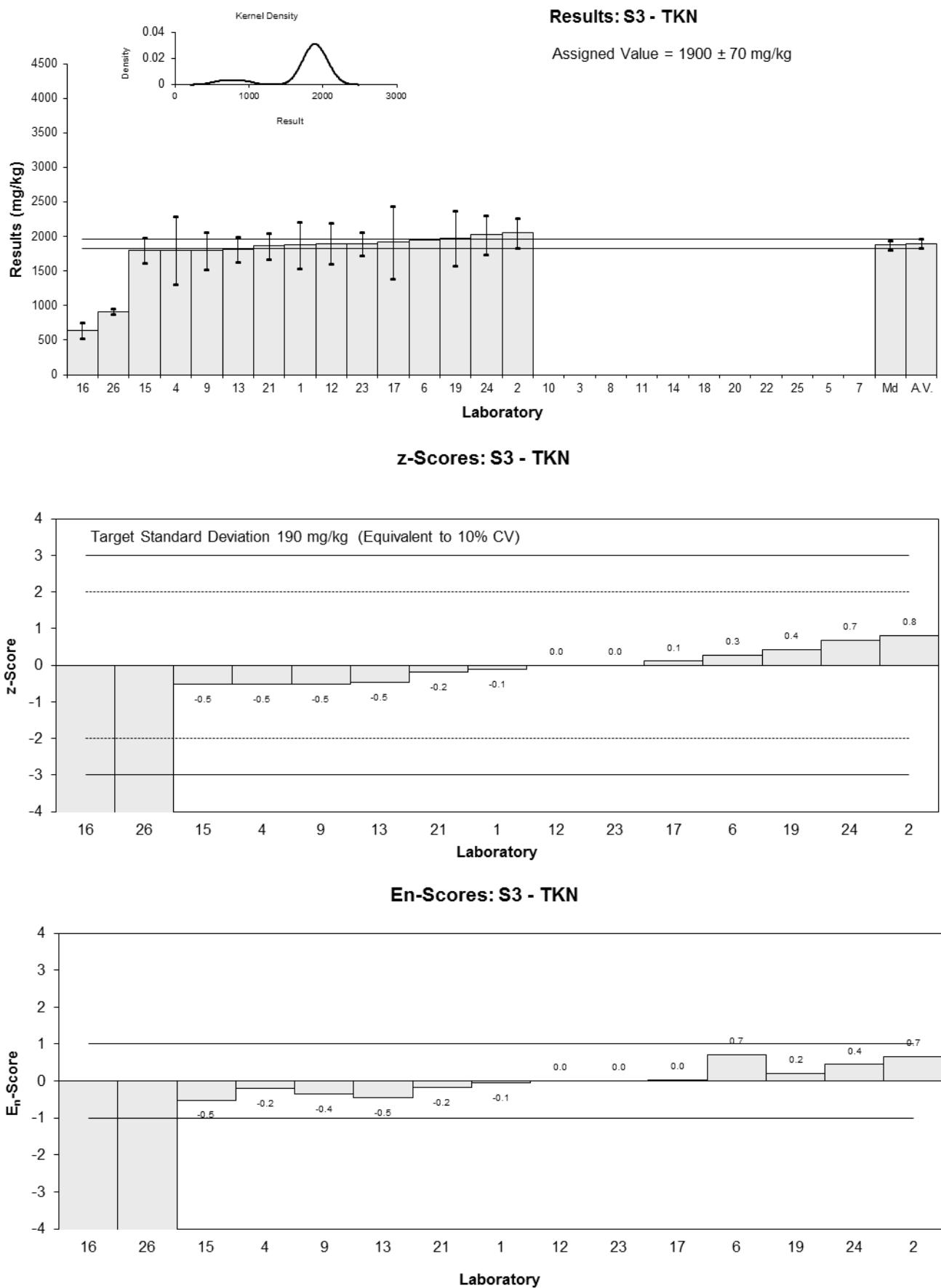


Figure 58

7 DISCUSSION OF RESULTS

7.1 Assigned Value

Samples S1 was highly contaminated dried soil.

Sample S2 and S3 were dried soil samples previously distributed as Sample S1 and S3 respectively of PT study AQA 16-02.

Assigned Values of the inorganic analytes in the study samples S1, S2 and S3 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 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'. Results less than 50% and more than 150% of the robust average were investigated and then removed before calculation of the assigned value.⁸ Appendix 2 sets out the calculation for the robust average of As in Sample S2 and its associated uncertainty.

No assigned value was set for Ag, As, Hg or Se in S1 because the reported results for these elements were too variable. No assigned value was also set for bromide or fluoride in S3 because too few results were 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.

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 887 numerical results, 852 (96%) were reported with an expanded measurement uncertainty, indicating that most laboratories have addressed this requirement of ISO 17025.¹⁰ The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Tables 11 and 12.

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

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 58). In this study, the reported expanded measurement uncertainty has been over-estimated in some cases (e.g. Lab 12 and 22 for Cd in S2, Lab 23 for Ca in S1, Lab 2 for K in S1) or under-estimated (e.g. Lab 11 for Cr, Fe, Zn in S1, Lab 22 for Al, S in S1). As a simple rule of thumb, when the uncertainty estimate is smaller than the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be reviewed as suspect.

Overestimation of the precision and/or laboratory or method bias is the most common error seen in the laboratories' estimated uncertainty budgets. According to NATA Technical Note 33¹⁴ and to NORDTEST TR 537,¹² the most common sources used to estimate the precision component are from:

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

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

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

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies alone, can also be used to estimate the uncertainty of their measurement results.^{12, 14}

Laboratories 3, 10, 11, 18 and 20 attached estimates of the expanded measurement uncertainty to results reported as less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.¹¹

Laboratories 11 and 24 reported an estimate of expanded uncertainty for their Be measurement result larger than the result itself.

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 64.3 ± 12.86 mg/kg, it is better to report 64 ± 13 mg/kg or instead of 9910 ± 1486.50 mg/kg, it is better to report 9910 ± 1500 mg/kg.¹¹

7.3 E_n-score

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

The dispersal of participants' E_n-scores is graphically presented in Figure 59. 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 821 results for which E_n-scores were calculated, 671 (82%) returned a satisfactory score of $|E_n| \leq 1$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

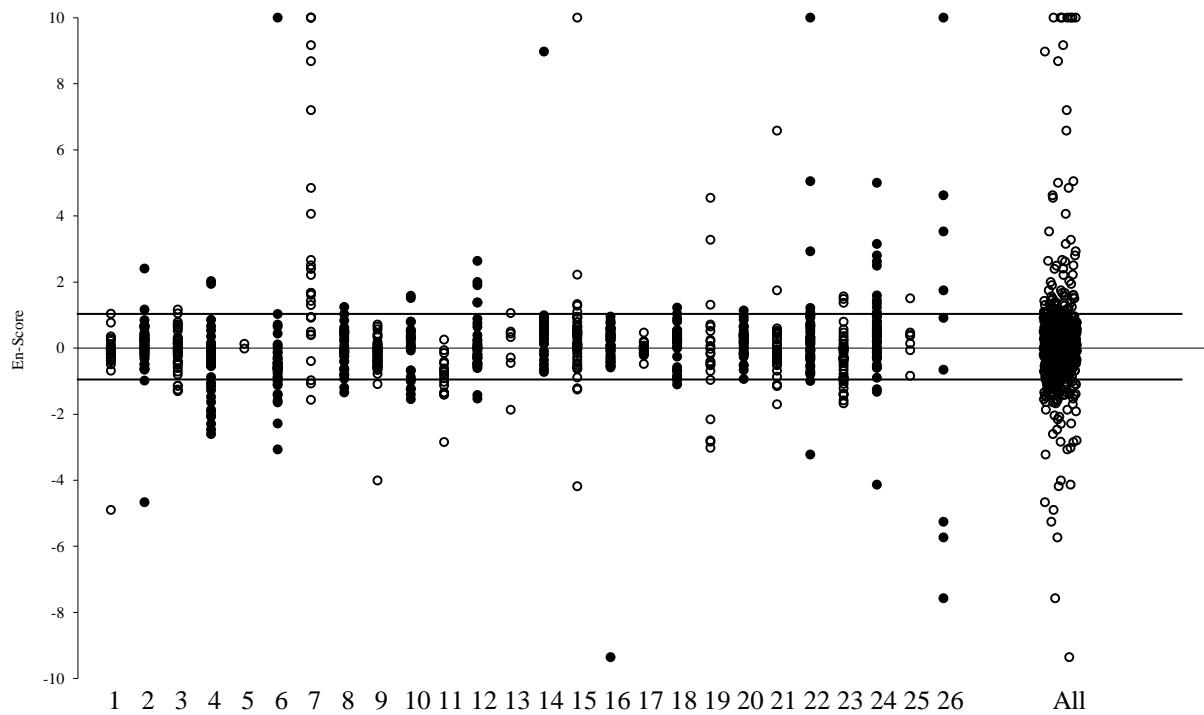
7.4 z-Score

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

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

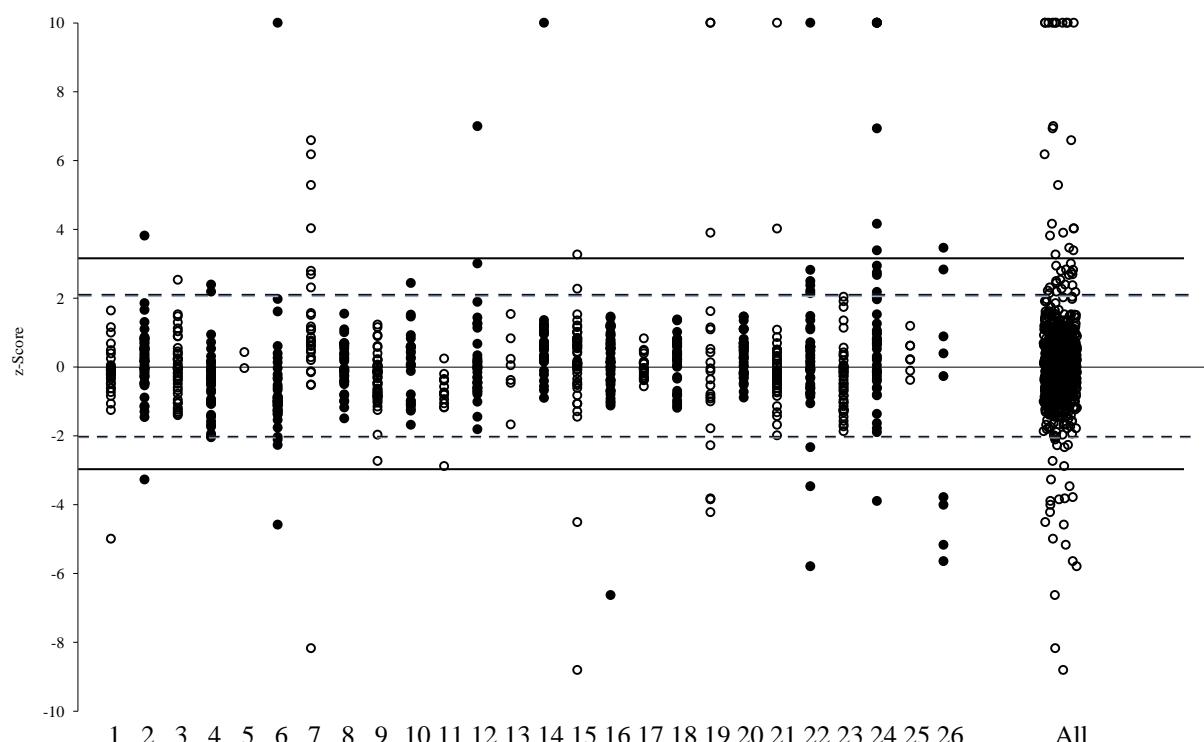
The between laboratory coefficient of variation predicted by the Thompson equation⁸ and the participants' coefficient of variation resulted in this study are presented for comparison in Table 71.

The dispersal of participants' z-scores is presented in Figure 60 (by laboratory code) and in Figure 61 (by test). Of 821 results for which z-scores were calculated, 751 (91%) returned a satisfactory score of $|z| \leq 2$ and 31 (4%) were questionable of $2 < |z| \leq 3$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.



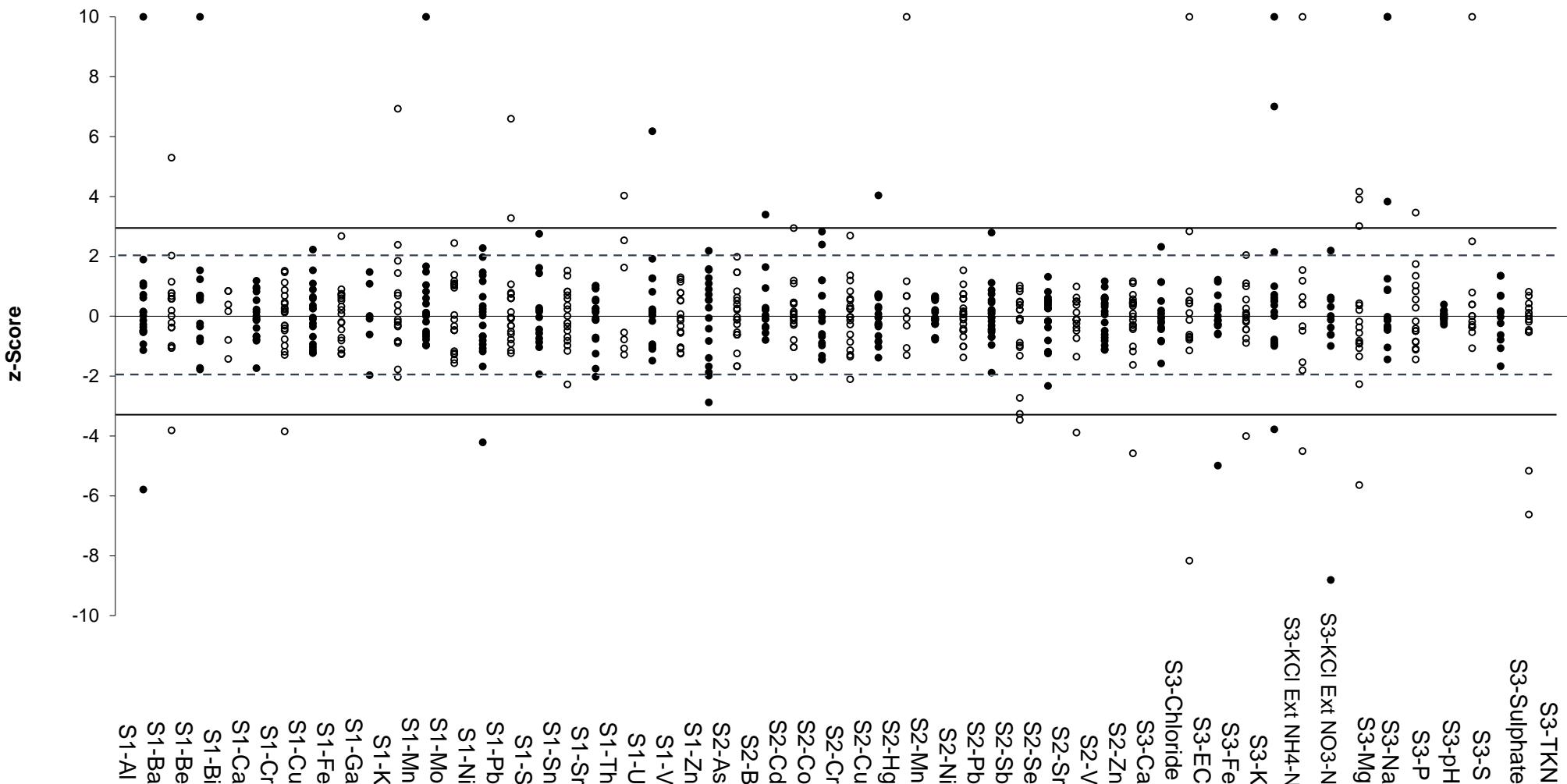
Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 59 E_n -Score Dispersal by Laboratory



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

Figure 60 z-Score Dispersal by Laboratory



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

Figure 61 z-Score Dispersal by Test

Table 71 Between Laboratory CV of this Study, Thompson CV and Set Target SD

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Ag	Not Set	87%	NA	Not Set
S1	Al	9900	12%	4%	20%
S1	As	Not Set	35%	NA	Not Set
S1	Ba	104	9.5%	8%	15%
S1	Be	1.35	17%	15%	15%
S1	Bi	0.293	16%	19%	10%
S1	Ca	28200	8.2%	3.4%	10%
S1	Cr	899	10%	5.7%	15%
S1	Cu	13.5	16%	11%	10%
S1	Fe	40100	9%	3.2%	15%
S1	Ga	14.2	21%	11%	20%
S1	Hg	Not Set	88%	NA	Not Set
S1	K	2020	13%	5.1%	10%
S1	Mn	3660	8.9%	4.7%	15%
S1	Mo	18.3	19%	10%	10%
S1	Ni	98.6	13%	8%	10%
S1	Pb	21.7	8.2%	10%	10%
S1	S	3350	13%	4.7%	20%
S1	Se	Not Set	33%	NA	Not Set
S1	Sn	114	18%	7.8%	10%
S1	Sr	238	9.2%	7.0%	20%
S1	Th	51	32%	8.9%	10%
S1	U	30.9	11%	9.5%	10%
S1	V	2690	10%	4.9%	15%
S1	Zn	36.1	24%	9.3%	15%
S2	As	9.6	10%	11%	10%
S2	B	14.3	10%	11%	20%
S2	Cd	2.01	10%	14%	10%
S2	Co	2.34	13%	14%	10%
S2	Cr	36.1	10%	9%	10%
S2	Cu	54.6	7.5%	9%	10%
S2	Hg	0.0203	19%	29%	20%
S2	Mn	151	5.3%	8%	10%
S2	Ni	18.9	5.3%	10%	10%
S2	Pb	77.4	7.2%	8%	10%
S2	Sb	16.3	18%	11%	20%
S2	Se	6.15	12%	12%	15%
S2	Sr	16.2	6.2%	11%	10%
S2	V	38.8	8.2%	9%	10%
S2	Zn	70.1	8.1%	8%	10%
S3	Bromide	Not Set	4.9%	NA	Not Set
S3	Ca	3170	8.5%	5%	10%
S3	Chloride	96	8.3%	8%	10%
S3	EC	589*	6.5%	6%	10%
S3	Fe	20100	10%	4%	10%

* μ S/cm

Table 71 Between Laboratory CV of this study, Thompson CV and Set Target SD (continued)

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as CV)
S3	Fluoride	Not Set	33%	NA	Not Set
S3	K	1400	9.7%	5%	10%
S3	KCl Ext Ammonium-N	20.4	26%	10%	20%
S3	KCl Ext Nitrate-N	160	7.6%	7%	10%
S3	Mg	784	17%	6%	10%
S3	Na	152	9.4%	8%	10%
S3	Orthophosphate-P	Not Set	45%	NA	Not Set
S3	P	579	12%	6%	10%
S3	pH	7.36	1.4%	12%	10%
S3	S	280	6%	7%	10%
S3	Sulfate	126	21%	8%	20%
S3	TKN	1900	5.3%	5%	10%

NA = Not Available, * μ S/cm

7.5 Participants' Results and Analytical Methods for Acid Extractable Elements

A summary of participants' results and performance is presented in Tables 72 and 73 and in Figures 59 to 61.

Unsolved interference problems were the main cause of variability in the results reported by participants in this study. Sample S1 was a highly contaminated soil sample and presented analytical difficulty to participating laboratories. Elements including Nb, Ti, Zr and W and some of the lanthanides (Sm, Nd, Gd, Dy, Eu, Er, Ho) were present in high levels in this sample and challenged participants' analytical techniques. No agreement could be found between the results reported by participants for Ag, As, Hg and Se in S1.

All the unsatisfactory results reported by Laboratories 7 and 24 were greater than the assigned value. This is an indication of method or laboratory bias.

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 can lead to misleading conclusions – since metals can be extracted from the fraction naturally present in the soil matrix.^{5, 18-21} 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 HNO₃, HCl, in combination or alone and most of these methods produce comparable results.²²⁻²⁴

The method descriptions provided by participants are presented in Tables 1 and 10 while the instrumental conditions are presented in Appendix 4.

Table 72 Summary of Participants' Results and Performance for Acid Extractable Elements in Samples S1

Lab Code	S1-Ag mg/kg	S1-Al mg/kg	S1-As mg/kg	S1-Ba mg/kg	S1-Be mg/kg	S1-Bi mg/kg	S1-Ca mg/kg	S1-Cr mg/kg	S1-Cu mg/kg	S1-Fe mg/kg	S1-Ga mg/kg	S1-Hg mg/kg
H.V.	<0.3	11200	5.6	101	1.24	0.355	30200	945	13.2	43200	12	<0.001
A.V	Not Set	9900	Not Set	104	1.35	0.293	28200	899	13.5	40100	14.2	Not Set
1	NT											
2	0.3	11540	8.65	112	1.47	0.33	30500	977	14.2	42186	NT	0.054
3	3.74	9910	5.44	93	1.66	<1.0	28809.1	1000	15.3	43700	17.34	0.04
4	0.5	NR	8.2	104	1.3	0.3	23300	960	12.8	NR	14	0.05
5	NT											
6	<2.3	8510	5.91	93.6	1.28	<0.46	26300	782	11.4	35100	NT	<0.23
7	NR	9117	NR	159	NT	NT	31540	1035	NR	43101	NT	NR
8	1.86	9160	7.65	93.6	1.49	0.258	29700	936	13.4	42800	NR	0.058
9	0.14	10800	3.5	110	1.6	0.31	27800	920	13	40900	10	0.05
10	<0.2	8200	9.4	110	<5	<5	NT	810	11	35000	NT	0.2
11	<1	9347	<1	93	1.2	<1	27070	830	11.6	36850	NR	NR
12	NT	12700	<5	111	<5	NT	28600	871	14	40400	NT	0.04
13	NT											
14	NT	10960	5.12	116	1.48	NT	26280	862	14.7	39220	NT	0.18
15	1.05	11400	6.89	112	1.49	0.33	28000	910	14.8	42500	NT	0.07
16	< 5	10100	8.99	100	< 2	< 10	30800	1030	13.3	39300	NT	< 0.1
17	NT											
18	<5	10129	8.3	110	<2	<10	NT	792	12.1	35603	14.2	0.22
19	NT	9100	19.4	64.3	15.3	NT	NT	553	15.7	NT	NT	NT
20	1.09	9200	6.3	101.7	1.46	<0.4	28200	960	14	37200	NT	<0.10
21	0.5	9677	5.08	106	1.18	0.23	27900	870	11.2	38276	16.5	0.28
22	NR	1300	10	110	NR	NT	26000	940	18	43000	NT	NR
23	2	9480	<5	100	1	NT	25900	856	11	41400	12.9	<0.1
24	0.5	26100	11.8	125	0.99	NT	30900	923	16.6	50800	NT	0.32
25	NT											
26	NT											

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

Table 72 Summary of Participants' Results and Performance for Acid Extractable Elements in Sample S1 (continued)

Lab Code	S1-K mg/kg	S1-Mn mg/kg	S1-Mo mg/kg	S1-Ni mg/kg	S1-Pb mg/kg	S1-S mg/kg	S1-Se mg/kg	S1-Sn mg/kg	S1-Sr mg/kg	S1-Th mg/kg	S1-U mg/kg	S1-V mg/kg	S1-Zn mg/kg
H.V.	2120	3960	18.1	113	22.2	2790	0.081	120	251	42.7	31.8	2720	39
A.V.	2020	3660	18.3	98.6	21.7	3350	Not Set	114	238	51	30.9	2690	36.1
1	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
2	2394	4269	14.3	101	21.6	3400	0.27	94.2	242	NT	31.4	2833	35.8
3	2094.08	4040	14.9	89.2	20.4	3337.64	<1.0	105.573	236.368	76.79	NT	3040	28.5
4	NR	3700	17	92	21	2700	0.2	110	190	40	28	2600	40
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	1610	3440	14.8	95.5	19.2	3890	<0.92	97.3	196	NT	27.5	2360	<34
7	2176	3473	NR	NR	36	NT	NR	NT	250	NT	50	NT	44.6
8	2160	3880	21.3	105	21.6	3440	3.32	118	262	NR	26.3	2670	44.5
9	1850	3670	17	110	21	3060	0.43	100	260	43	31	2710	41
10	NT	3300	25	88	23	NT	<2	140	260	NT	31	2400	27
11	1980	3375	15.1	87	20	3160	13	108	244	NT	NT	NT	20.5
12	2310	3660	17	102	22	NT	<25	NT	NT	NT	NT	2650	43
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	1838	35890	20.9	112	24.0	NT	1.25	126	262	NT	34.8	2540	39.0
15	1950	3700	21.1	121	28.8	3200	1.11	137	251	37.8	27.6	2900	39
16	2050	3410	21.5	98.8	20.6	3830	<2	114	221	NT	27.8	3020	33.8
17	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
18	NT	3306	22.1	90.6	23.4	NT	<2	128	244	NT	33.4	2411	31.6
19	1660	NT	NT	57	19.7	NT	NT	75	NT	67.5	31.3	NT	NT
20	1960	3590	18.4	113	23	<2000	<2	124	241	NT	30.4	2550	37.6
21	1997	3811	17.4	82	21.5	3416	1.32	110	235	92	31.6	2828	25.3
22	2500	4200	18	100	23	3100	NR	120	220	NT	NT	3000	42
23	1850	3310	14	92	19	3000	<5	102	208	45.4	36.8	2350	26
24	3420	3960	21.2	118	23.3	4270	2.1	128	235	NT	34.8	2900	47.9
25	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
26	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

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

Table 73 Summary of Participants' Results and Performance for Acid Extractable Elements in Samples S2 and S3

Lab Code	S2-As mg/kg	S2-B mg/kg	S2-Cd mg/kg	S2-Cr mg/kg	S2-Co mg/kg	S2-Cu mg/kg	S2-Hg mg/kg	S2-Mn mg/kg	S2-Ni mg/kg	S2-Pb mg/kg	S2-Sb mg/kg
H.V.	8.6	16.5	1.93	38.5	2.93	55.8	0.0205	150	19.5	78.5	12.9
A.V	9.6	14.3	2.01	36.1	2.34	54.6	0.0203	151	18.9	77.4	16.3
1	9	19	2	37	2.5	50	0.025	150	19	75	16
2	9.34	15.1	1.96	31.4	2.33	58.5	0.023	149	18.8	73.8	5.64
3	9.84	13.3	2.1	36	2.18	54.3	0.015	154	18.4	76.1	12.9
4	8	17	1.6	38	2.9	47	0.02	140	17	70	16
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	11.5	<22	1.8	28.5	2.13	49.9	<0.22	153	16.3	73.3	13.1
7	NR	NR	NR	45.8	NR	76.6	NR	149	20.9	99	NR
8	9.48	13.2	1.98	35.1	2.11	53.3	0.021	149	18.1	74.1	17.5
9	8.4	14	1.8	33	2.3	51	<0.1	140	18	72	7.4
10	11	12	2.1	37	<5	55	<0.1	160	20	78	19
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	9	NT	2	36	2	53	<0.02	139	17	72	NT
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	9.49	15.0	2.04	28.2	2.62	56.3	0.023	159	19.2	83.1	17.0
15	10.4	14.4	2.09	39.1	2.62	58.6	<0.05	150	21.8	78.8	19.6
16	10.1	15	1.85	40.4	< 5	58.3	< 0.1	161	20.3	81.5	19.3
17	9.57	12.7	1.95	36	2.37	54.3	0.019	150	19.1	78.3	17.8
18	9.97	14.9	2.02	37.3	<5	58.2	<0.1	161	20.3	80.9	17
19	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
20	11	<20	2.23	35.6	2.5	58.3	<0.10	160	19.4	86	13.4
21	9.08	13.2	2.03	33.9	2.03	53	0.09	147	17.6	84.1	17.9
22	9	14	2	41	3	56	0.016	160	20	77	5
23	8	<50	2	32	2	49	<0.1	147	18	77	12
24	9.8	24	2.6	31.2	2.2	52.7	<0.03	147	19	62.8	15.8
25	10.2	NT	2.25	36.94	NT	57.98	NT	NT	18.7	79.06	NT
26	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
29	8.6	16.5	1.93	38.5	2.93	55.8	0.0205	150	19.5	78.5	12.9

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

Table 73 Summary of Participants' Results and Performance for Acid Extractable Elements in Samples S2 and S3 (continued)

Lab Code	S2-Se mg/kg	S2-Sr mg/kg	S2-V mg/kg	S2-Zn mg/kg	S3-Ca mg/kg	S3-Fe mg/kg	S3-K mg/kg	S3-Mg mg/kg	S3-Na mg/kg	S3-P mg/kg	S3-S mg/kg
H.V.	6.18	16.8	41.3	72.2	3000	20500	1660	850	173	591	277
A.V.	6.15	16.2	38.8	70.1	3170	20100	1400	784	152	579	280
1	5	17	38	70	3100	19800	1540	700	145	550	270
2	7.36	15.4	34.4	73.4	3229	19196	1472	714	210	569	265
3	5.05	15.57	40.3	70.7	3116.84	20600	1290.37	678.46	151.739	611	271.78
4	5.8	16	40	63	2670	NR	NR	NR	150	495	250
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	6.71	14	34.5	38	3160	18300	1280	606	<900	516	291
7	NR	17.2	NT	75.1	3901	22308	1485	818	165	595	NT
8	6.49	16	35.6	61.8	NA	NA	NA	NA	NA	NA	NA
9	6	16	35	68	3030	18600	1270	800	150	530	280
10	6.4	16	41	73	NA	NA	NA	NA	NA	NA	NA
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	<5	NT	36	67	3530	19200	2380	1020	171	NA	NA
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	6.39	17.0	42.6	72.5	NT	NT	NT	NT	NT	NT	NT
15	6.56	16.4	41.2	78.2	3200	20200	1400	720	130	550	275
16	6.65	17.8	43.3	72.9	3050	21200	1420	712	136	514	302
17	5.98	15.8	39.4	69.1	3150	20300	1470	755	146	627	291
18	6.38	16.8	41.2	73.1	NT	20153	NT	NT	NT	638	NT
19	NT	NT	NT	NT	NT	NT	1260	1090	NT	529	270
20	6.9	17	40.5	77.8	3330	19700	1500	812	147	657	<2000
21	6.61	15	36.9	73.3	NT	NT	NT	NT	NT	NT	NT
22	4	17	41	68	2900	20000	1700	740	760	550	350
23	6	16	39	74	3530	24200	1450	770	150	680	280
24	5.4	9.9	36.4	58.7	2910	22100	3610	1110	609	555	880
25	NT	NT	NT	67.42	NT	NT	NT	NT	NT	NT	NT
26	NT	NT	NT	NT	NT	12030.4	870.6	341.8	165.5	779.28	NT

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

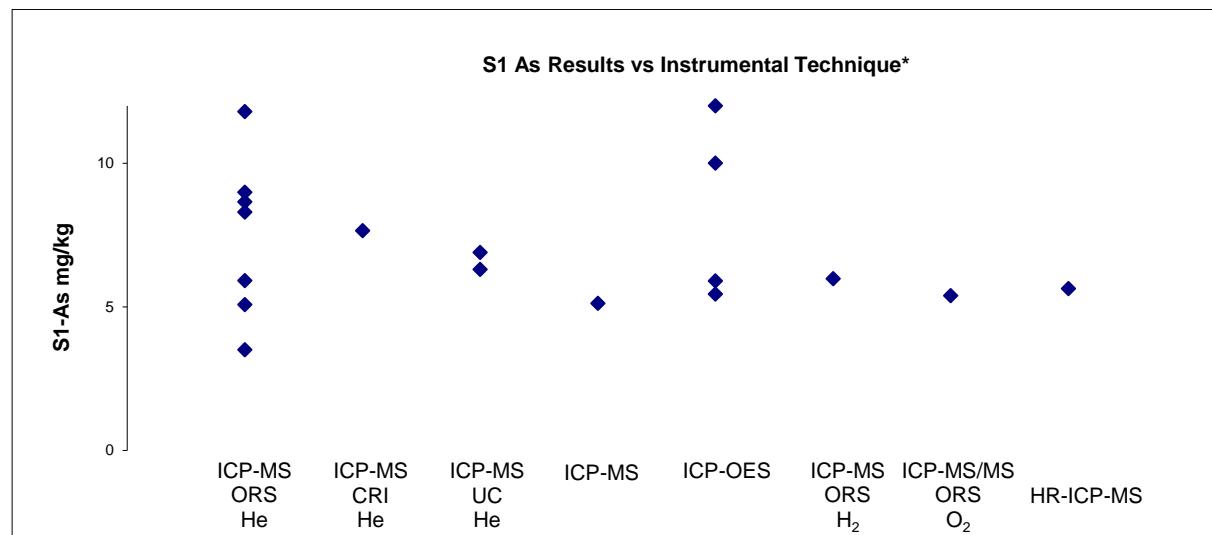
Table 74 Summary of Participants' Results and Performance for Sample S3

Lab Code	S3-Br mg/kg	S3-Cl ⁻ mg/kg	S3-F ⁻ mg/kg	S3-I ⁻ mg/kg	S3-PO ₄ ³⁻ -P mg/kg	S3-SO ₄ ²⁻ mg/kg	S3-pH	S3-EC µS/cm	S3-TKN mg/kg	S3-KCl Ext NH ₄ ⁺ -N mg/kg	S3-KCl Ext NO ₃ ⁻ -N mg/kg
H.V.	0.7	98	1.7	<1	0.7	160	NA	NA	NA	NA	NA
A.V.	Not Set	96	Not Set	Not Set	Not Set	126	7.36	589	1900	20.4	160
1	NT	89	1.3	NT	1	120	7.3	295	1880	22	150
2	NR	NR	NR	NR	NR	NR	7.4	572	2053	22	168.8
3	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
4	NR	NR	NR	NR	NR	NR	NR	NR	1800	18.4	195
5	1.34	100.11	3.09	NR	3.66	125.14	NT	NT	NT	NT	NT
6	NT	360	NT	NT	NT	NT	7.2	NT	1950	14.1	144
7	<0.5	17.6	<0.5	NT	NT	<25	7.25	601	NT	NT	NT
8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9	<1	85	2.4	<1	1	110	7.3	580	1800	<30	160
10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	NA	NA	NA	NA	<1	NA	7.5	555	1900	13	150
13	NT	104	NT	NT	NT	84	7.4	603	1812	26.7	154
14	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
15	NT	97	<0.25	NT	1.4	99	7.43	553	1800	2	19.1
16	NT	89.4	<20	NT	<10	129	7.34	660	640	25.2	170
17	NR	NR	NR	NR	NR	NR	NR	NR	1920	NR	NR
18	< 5	88.4	NT	< 5	0.84	160	7.15	630	NT	19	NT
19	NT	101	NT	NT	1.59	106	7.33	657	1980	66	158
20	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
21	0.58	94.8	NT	NT	0.59	143.4	7.38	608	1863	NT	NT
22	<2.5	90	NT	NT	<1.0	130	7.4	570	NT	NT	NT
23	NT	100	3	NT	0.5	160	7.5	589	1900	NT	NT
24	0.53	101	2.4	1.4	0.75	143	7.3	580	2030	23	165
25	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
26	NT	123.2	NT	NT	6.3	NT	7.65	573	917.4	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

Individual Element Commentary

Arsenic With the latest developments of instrumental techniques (collision/reaction cells for ICP-MSs), Arsenic typically no longer presents analytical difficulties to participating laboratories. However, while all reported results for As in S2 returned satisfactory z-scores, no assigned value could be set for this element in the highly contaminated soil sample S1, because the reported results were too variable (between 3.5 mg/kg and 19.4 mg/kg). Most participants used ICP-MS for As measurements with various collision/reaction cells and He as collision gas (Figure 62). No relationship was noticed between the participants' results and the instrumental technique used.



*NMI study results included; Result larger than 12 mg/kg has been plotted as 12 mg/kg.

Figure 62 S1-As Results vs. Instrumental Technique

An investigation study was conducted by NMI using the same extraction procedure (see Appendix 1) but various instrumental techniques and conditions. The results are presented in Table 75.

Table 75 NMI As Results vs. Instrumental Technique

Instrumental technique used	ICP-MS-ORS He*	ICP-MS-ORS H ₂ (7.8 mL/min)	ICP-MS/MS-ORS O ₂ (25%)	HR-ICP-MS** HR mode	ICP-OES (188.98 nm)
Result (mg/kg)	7.80	6.0	5.4	5.6	5.9

*The high As result is an indication of unsolved interferences. **Homogeneity Value.

The result from ICP-MS-ORS He measurements was significantly different from results produced by other instrumental techniques. In many matrices encountered in routine testing of As, the largest and most common interference to overcome in analysis by ICP-MS is $^{40}\text{Ar}^{35}\text{Cl}^+$. ICP-MS with collision/reaction cells and He as collision gas is the most popular instrumental technique used to solve this interference. While He is generally an effective interference removal strategy for polyatomic interferences, the fact that the primary mechanism of interference removal is based on atomic size means it will struggle to remove interferences from doubly charged atomic ions.^{25, 26} This situation is observed in the S1 soil sample where significant amounts of a number of lanthanides were present (Table 76).

Table 76 NMI Lanthanides Measurements in S1

Element	Result* (mg/kg)
Sm	9.6
Eu	1.7
Nd	49
Gd	8.3
Dy	8.6
Ho	1.8
Er	5.6

* From standard addition analyses by HR-ICP-MS.

Doubly charged lanthanides (Sm^{++} , Nd^{++} , Eu^{++}) appearing at half of their true mass (nominal m/z of 74.5 and 75.5) can produce spectral overlap at nominal m/z 75.^{27,28} The typical quadrupole mass spectrometers have a resolution between 0.7 and 1.0 amu and may not completely solve these interferences (Figures 63 and 64). Figure 63 from HR spectra approximately represents the window measured in a standard quadrupole mass spectrometer (this solution has a composition similar to the soil digest but contains negligible Cl^- to better visualise the interfering peaks). The spectrum in Figure 64 is essentially the centre peak from Figure 63 with the different species resolved out in HR mode in HR-ICP-MS (this solution is the actual digest of S1).

Hydrogen as reaction gas has been proven to reduce Ar-based interferences and with increased higher flows was also found to effectively remove the doubly charged lanthanides.²⁶ However, the increase in the H_2 flow rate can be detrimental to the As signal. The mass shifting of $^{75}\text{As}^+$ to m/z 91 as $^{75}\text{AsO}^{16+}$, by O_2 is considered an effective solution for overcoming As interferences as long as Zr background in the sample is negligible.²⁹

ICP-MS technique operated in collision mode has gained popularity, as it is a simple and effective way to remove most of the common interferences encountered in routine testing. However, because the interferences are removed based upon differences in atomic size, collision mode is not so effective in removing doubly charged ions' interferences. When measuring low level As in soil, laboratories should consider screening for lanthanides in the sample and adjusting the instrument condition to minimise the doubly charged atomic ions formation.

The results from ICP-MS in collision mode reported by **Laboratories 6, 8, 9, 14, 5, 20, 21**, were in good agreement with the homogeneity value of 5.63 mg/kg when a PCV of 20% is considered.

Beryllium and Bismuth Some laboratories reported problems overcoming interferences encountered for Be and Bi in S1. No spectral interferences on nominal mass 9 m/z and on nominal mass 209 m/z were seen in the HR-ICP-MS for Be and Bi respectively in S1 (Figures 65).

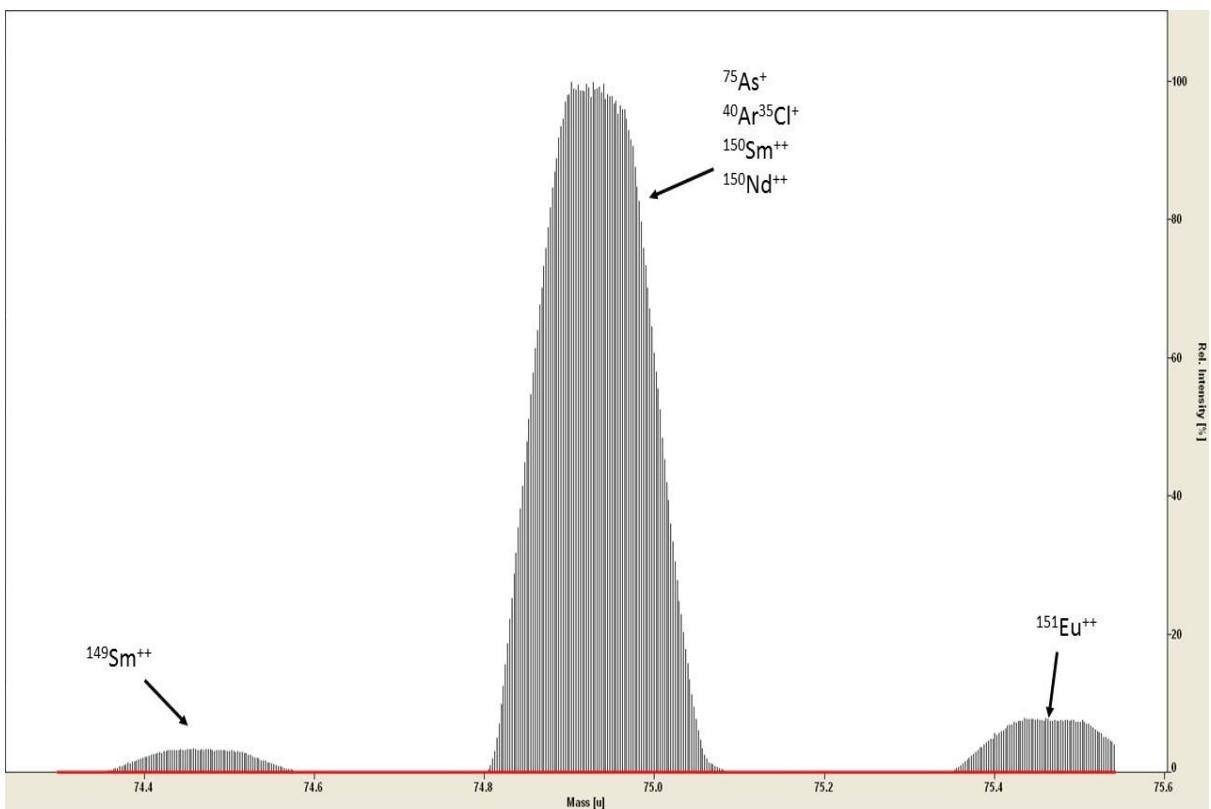


Figure 63 HR-ICP-MS Low Resolution Mode Wide Scan of m/z 75
(nominally m/z 74.5-75.5)

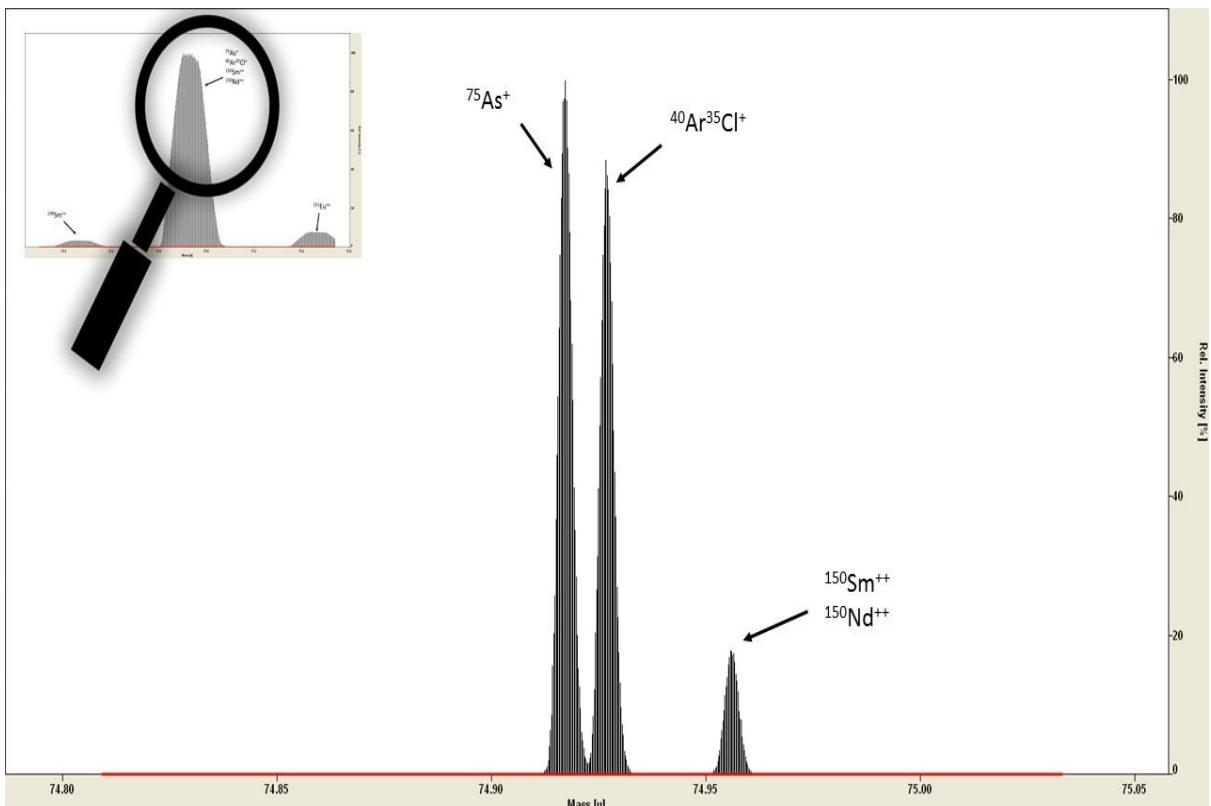


Figure 64 HR-ICP-MS High Resolution Mode Wide Scan of m/z 75
(nominally m/z 74.5-75.05)

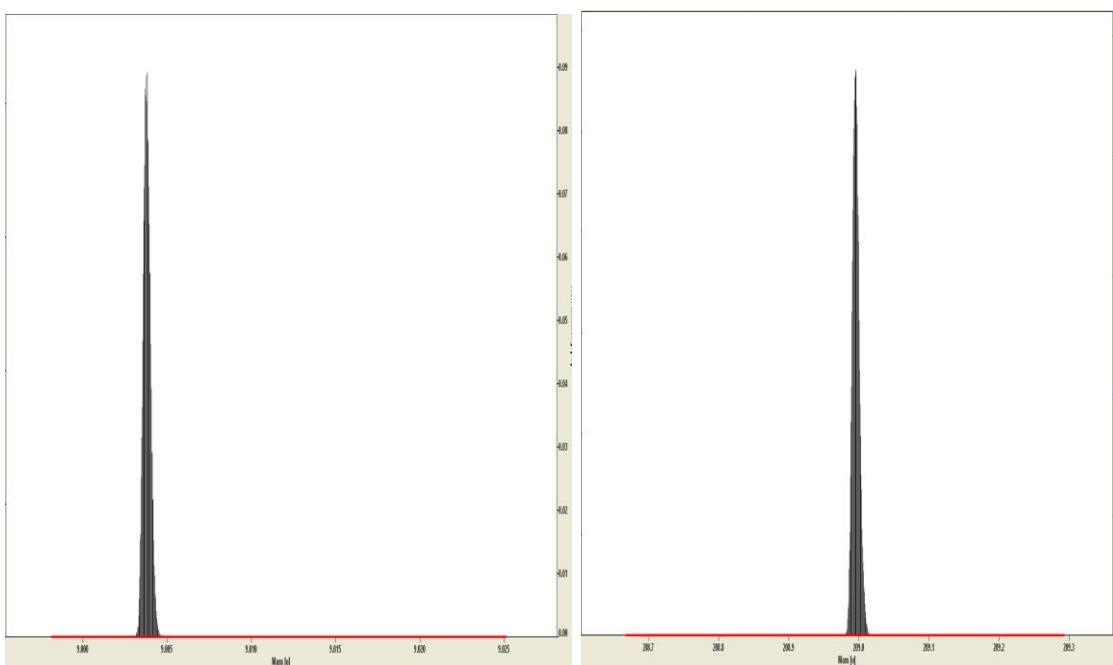


Figure 65 HR-ICP-MS High Resolution Mode Wide Scans of m/z 9 and m/z 209

Mercury The robust average of the reported results for Hg in S1 was 0.128 mg/kg and the robust coefficient of between laboratories variation was high (88%). No assigned value was set for this analyte in S1. Plots of participants' results versus the instrumental technique used are presented in Figure 66.

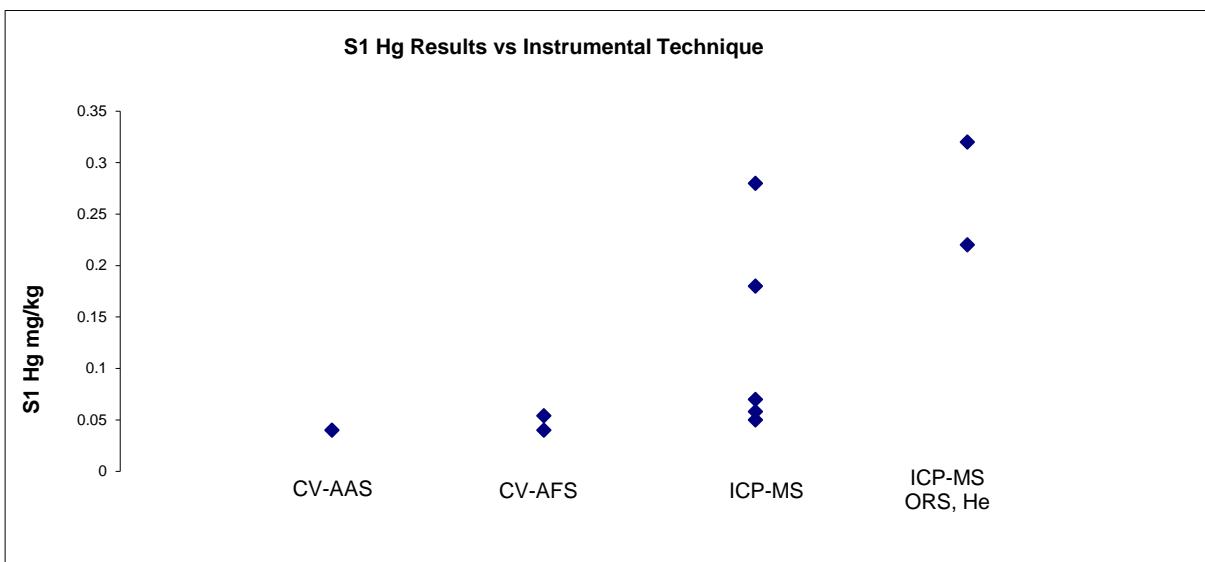


Figure 66 S1-Hg Results vs. Instrumental Technique

Tungsten concentration in the study sample was high, 10.6 mg/kg and Hg measurements in samples with high W content can be challenging due to polyatomic interferences from WO^+ and WHO^+ formed in plasma. These interferences are poorly removed when conventional He collision gas is used; much higher than the true value or false positives are frequently obtained for Hg when measured by ICP-MS in collision mode.³⁰

Table 77 presents the results of Hg from measurements conducted by NMI using various instrumental techniques and conditions.

Table 77 NMI Hg results vs. Instrumental Technique

Instrumental technique used	ICP-MS-ORS He*	CV-AFS**	ICP-MS/MS-ORS O ₂ (25%)
Result (mg/kg)	0.078	<0.001	<0.001

*The higher Hg result is an indication of unsolved interferences. **Homogeneity Value.

Vapour generator techniques are known to be effective in solving the polyatomic interference from W; it removes Hg from the matrix and then measures it in the vapour state.

Except for one, all results reported for Hg in S2 were satisfactory.

Potassium Plots of participants' results versus the instrumental technique used are presented in Figure 67.

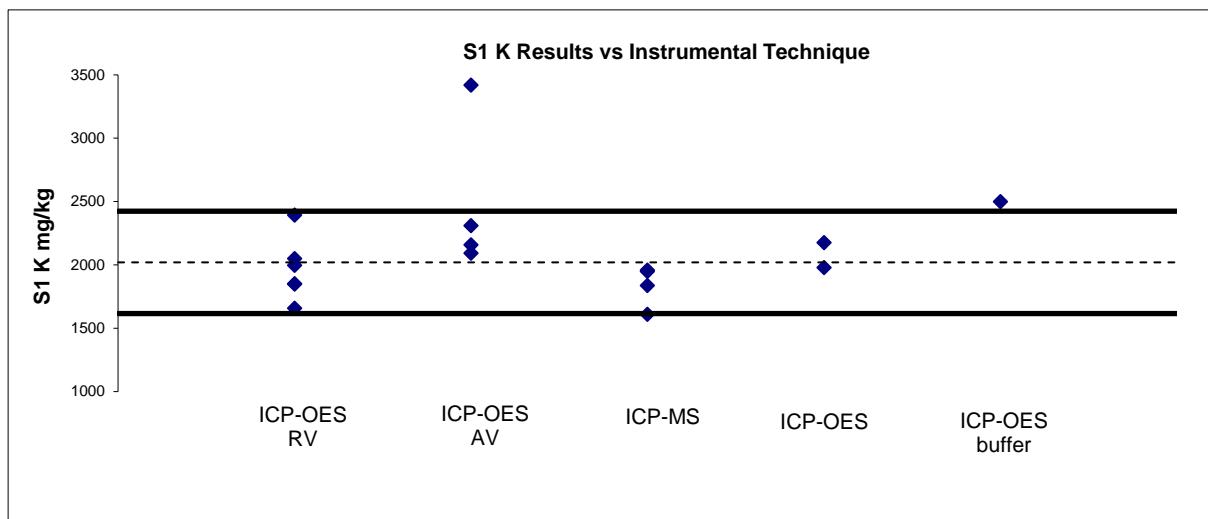


Figure 67 S1-K Results vs. Instrumental Technique

Unsolved ionization interferences might explain the high unsatisfactory results reported for K.

Thorium All high Th results were from ICP-OES measurements (Figure 68)

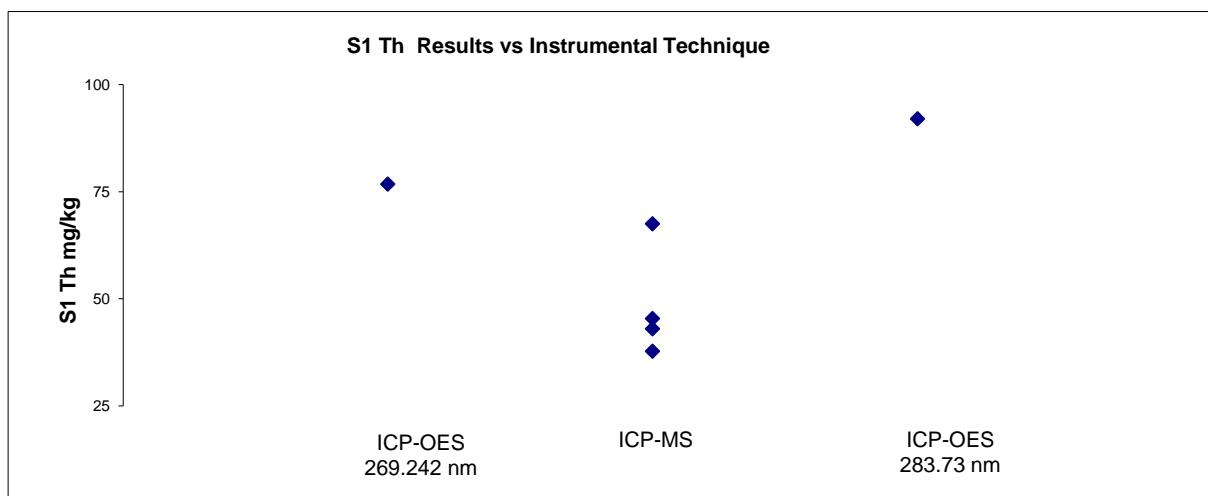


Figure 68 S1-Th Results vs. Instrumental Technique

Silver Plots of participants' results for Ag in S1 versus instrumental technique used are presented in Figure 69.

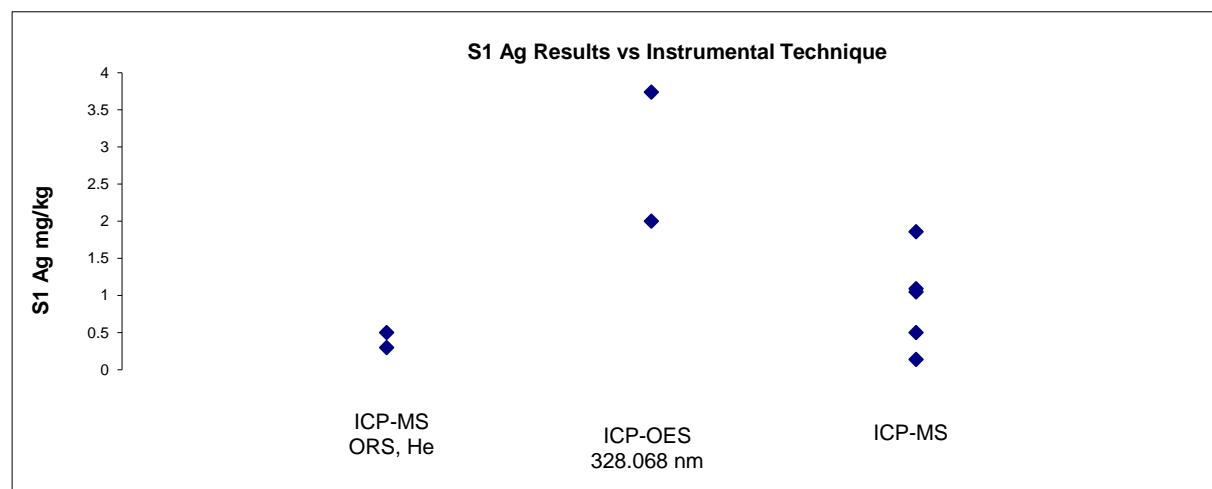
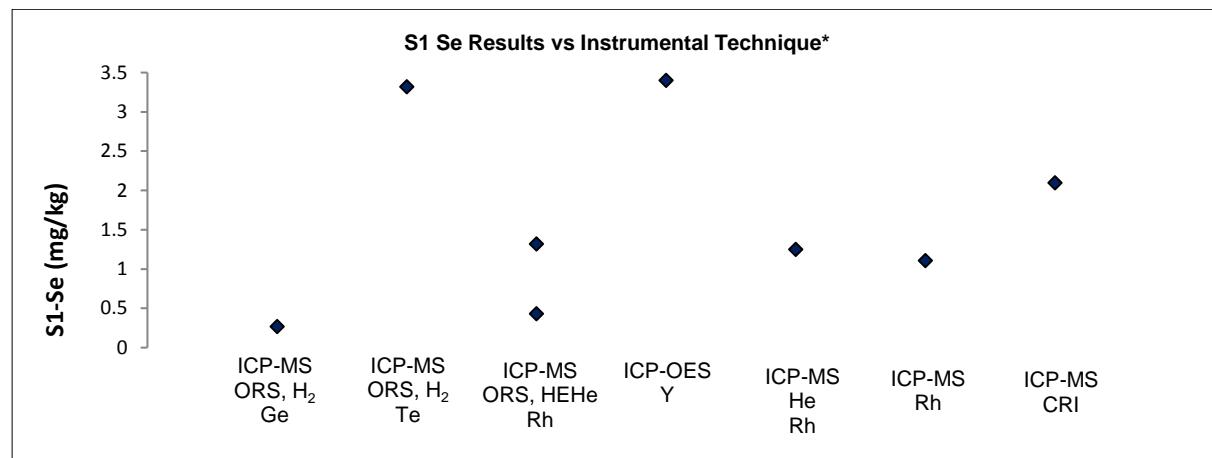


Figure 69 S1-Ag Results vs. Instrumental Technique

Ag suffers from significant oxide-based interferences, especially when measured in matrices with high Zr and/or Nb content.³¹ Zr and Nb concentration in the soil sample S1 were elevated 1780 mg/kg and 13.7 mg/kg respectively, which might explain the large between-laboratory coefficients of variation of reported results for Ag (87%).

ICP-MS with He as collision gas is not too effective in removing oxide-based interferences from Zr and Nb on Ag. ICP-MS with O₂ or NH₃ as reaction gases might be a better option.

Selenium Similar to As, Ag and Hg results, Se results in S1 were variable (between 0.2 mg/kg and 13 mg/kg) and no assigned value could be set.



*Result >3.5 has been plotted as 3.5 mg/kg.

Figure 70 S1-Se Results vs. Instrumental Technique

Most participants reported using ICP-MS with various collision cells and He or high energy He as collision gas and some reported using ICP-MS in reaction mode with H₂. Plots of participants' results versus instrumental technique and internal standard used are presented in Figure 70. Tellurium is often present in soil samples and might not be suitable to use it as internal standard.

Se results in S1 from measurements conducted by NMI using the same extraction procedure (see Appendix 1) but various instrumental techniques and conditions are presented in

Table 78. The ^{78}Se result from ICP-MS-ORS with H_2 as reaction gas is in relatively good agreement with the Se result from HR-ICP-MS measurements.

Table 78 NMI Se results vs. Instrumental Technique

Instrumental technique used	ICP-MS-ORS He*	ICP-MS/MS ORS H_2 (8.1 mL/min) ^{78}Se	HR-ICP-MS HR mode**
Result (mg/kg)	0.49	0.10	0.08

*The high Se result is an indication of unsolved interferences. **Homogeneity Value.

Se analysis is known to suffer from a very significant ArAr^+ dimer interference and as in the case of As, the focus on such a high profile interference can result in overlooking other interferences. Doubly charged lanthanides (Gd^{++} , Dy^{++} , Ho^{++} and Er^{++}) can also produce spectral overlap on ^{78}Se and ^{82}Se (Figures 71 and 72).^{25, 26} High concentrations of Gd, Dy, Ho and Er were measured in S1 and this might explain the variability in Se results (Table 76). Furthermore, measurement of ^{82}Se can also lead to higher than expected results due to $^{81}\text{Br}^{\text{H}}\text{H}^+$ formation and due to ^{82}Kr presence in Ar when proper background correction is not applied.

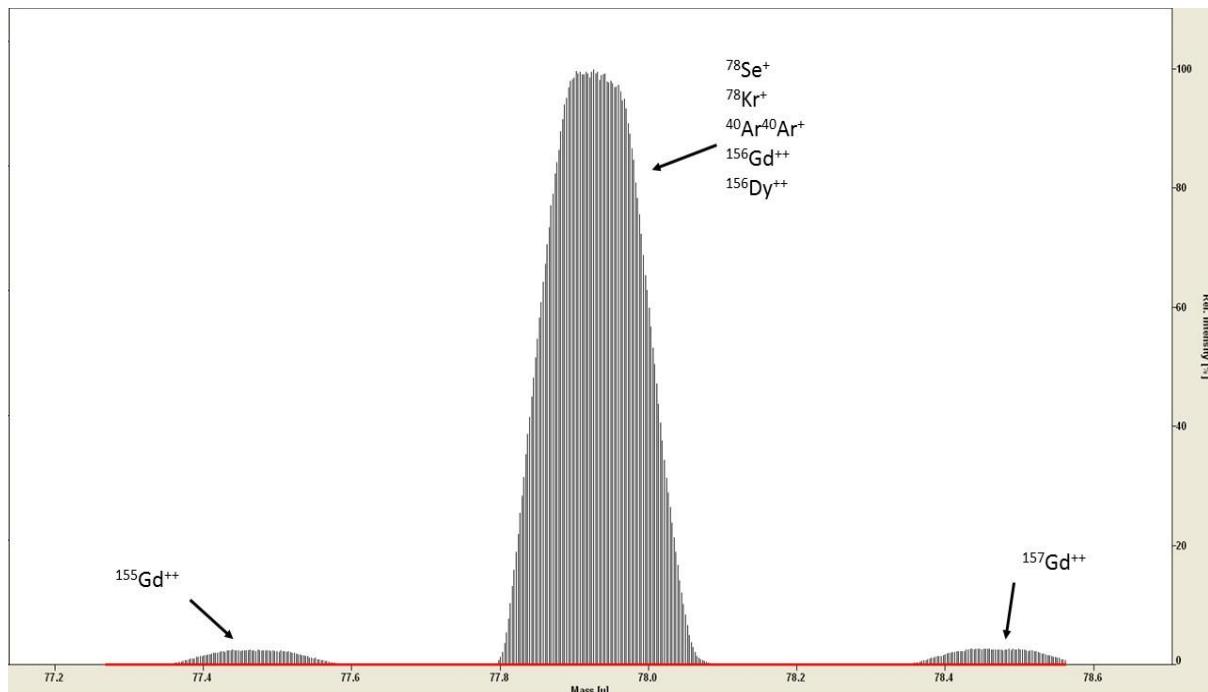


Figure 71 HR-ICP-MS Low Resolution Mode Wide Scan of m/z 78 (nominally m/z 77.5-78.5).

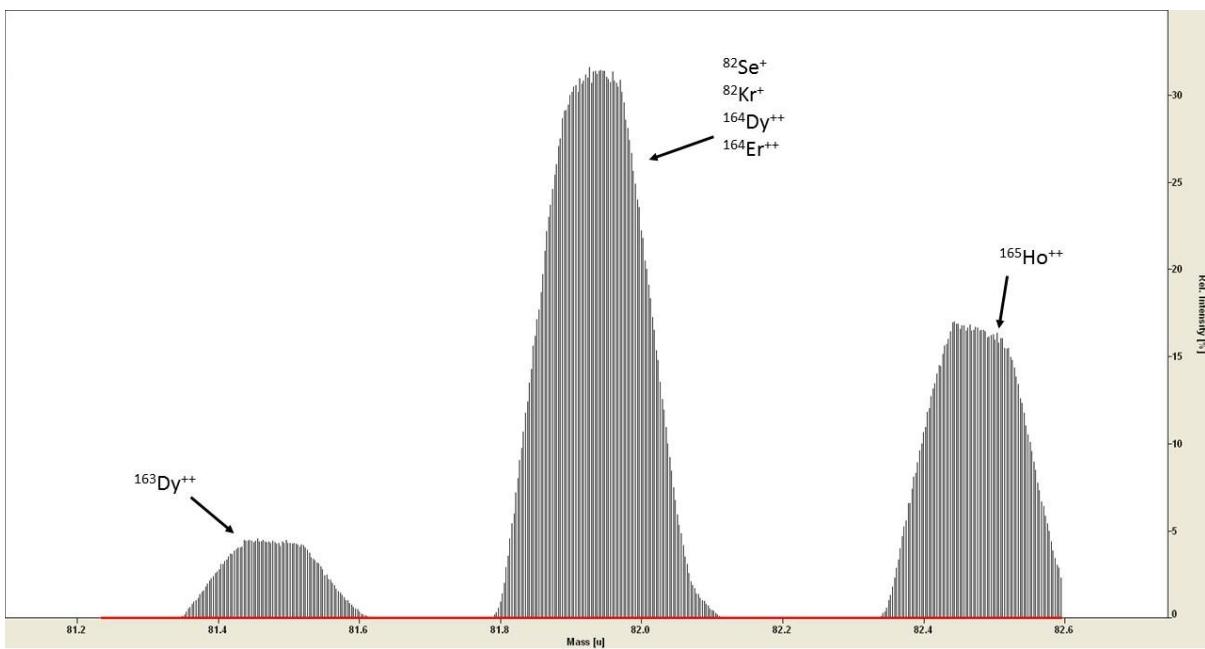


Figure 72 HR-ICP-MS Low Resolution Mode Wide Scan of m/z 82 (nominally m/z 81.5-82.5).

ICP-MS with collision/reaction cell and He as collision gas is relatively effective in removing ArAr^+ dimer interference on Se, but cannot remove interferences from the doubly charged atomic ions.^{25, 26} Improved recoveries of ^{78}Se in the presence of lanthanide can be obtained if ICP-MS is used in collision mode with H_2 at a high flow rate, 8.1 mL/min.²⁶

None of the reported results for Se were in agreement with the Se result from the HR-ICP-MS measurement (0.081 ± 0.037 mg/kg).

Copper and Zinc Titanium concentration in S1 was high at 4560 mg/kg. In samples containing high amounts of Ti, analysis of Zn and Cu can be complicated by the presence of significant quantities of TiO^+ when measured by ICP-MS. The good agreement between Cu and Zn results indicates that overall participants overcame this problem.

All high Zn results were from ICP-OES measurements with wavelength 213.857 nm (Figure 73). Zn 213.857 nm can have significant interferences from Cr 213.844 nm ; Zn 206.2 nm is a better option when it is measured by ICP-OES in matrices with high Cr content. Cr level in Sample S1 was 899 mg/kg which might explain the high Zn results.

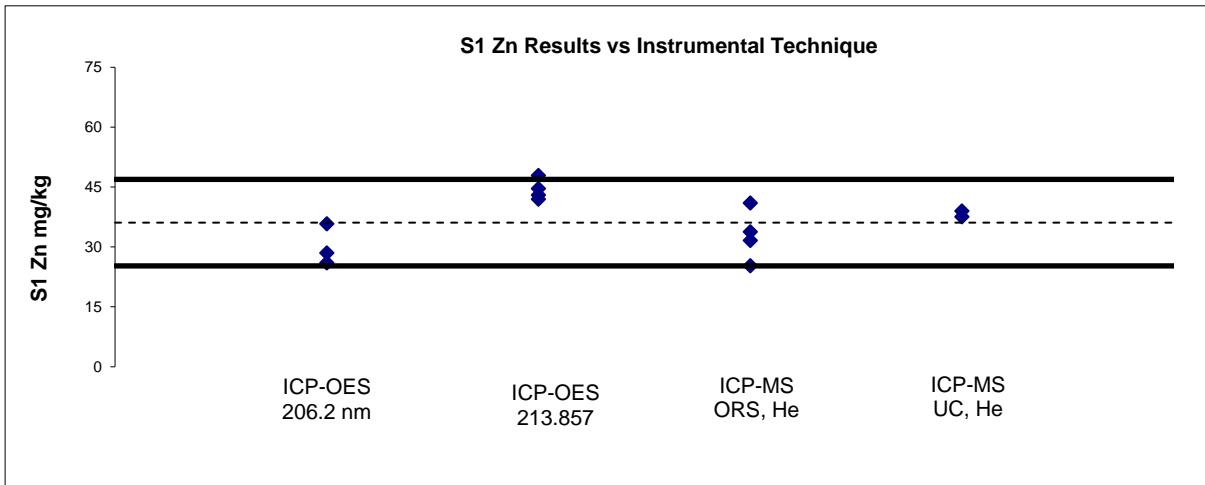


Figure 73 S1-Zn Results vs. Instrumental Technique

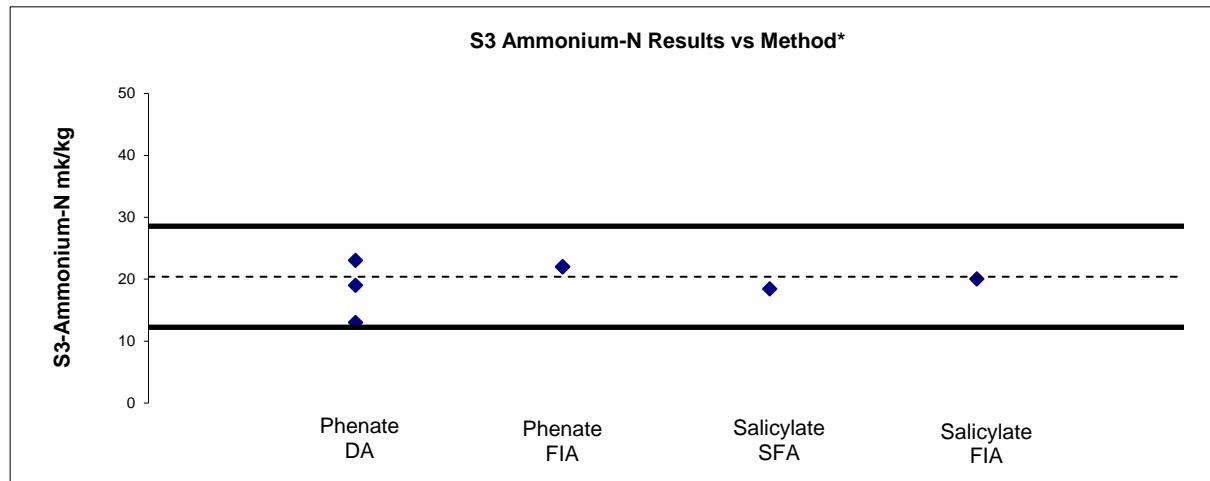
7.6 Participants' Results and Analytical Methods for 2M KCl Extractable Ammonium-N and Nitrate-N

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.³² 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 participants used a soil/2M KCl ratio of 1:10.

The results reported by Laboratory 15 for 2M KCl extractable ammonium-N and nitrate-N in S3 were 10 times lower than the assigned values. They might have correctly measured these tests in S3 but forgot to include the dilution factor in the calculation of the final results.

2M KCl Extractable Ammonium-Nitrogen Plots of participants' results versus the analytical methods and instrumental technique used are presented in Figure 74. Although participants used various analytical methods and measurement technique most produced comparable results.

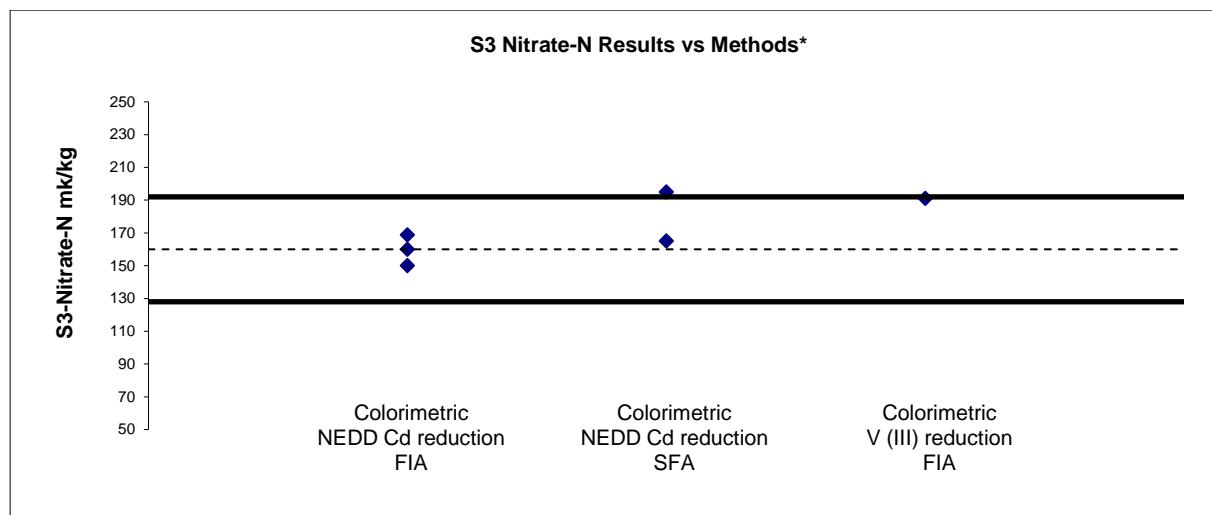


*Results of 2 mg/kg has been plotted as 20 mg/kg.

Figure 74 S3- NH_4^+ -N Results vs. Analytical Method and Measurement Technique

2M KCl Extractable Nitrate-Nitrogen Except for two, all participants performed satisfactorily for NO_3^- -N measurements. 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.

One laboratory used trivalent V for NO_3^- -N reduction to NO_2^- -N (Figure 75).



*Results of 19.1 mg/kg has been plotted as 191 mg/kg.

Figure 75: S3- NO_3^- -N Results vs. Measurement Technique

7.7 Participants' Results and Analytical Methods for Total Kjeldahl Nitrogen

TKN assigned value was 1900 mg/kg. Fifteen participants reported results for TKN and thirteen performed satisfactorily. Seven participants used a colorimetric method, four a titrimetric method and one reported using LECO. Plots of participants' results versus analytical method and measurement technique are presented in Figure 76.

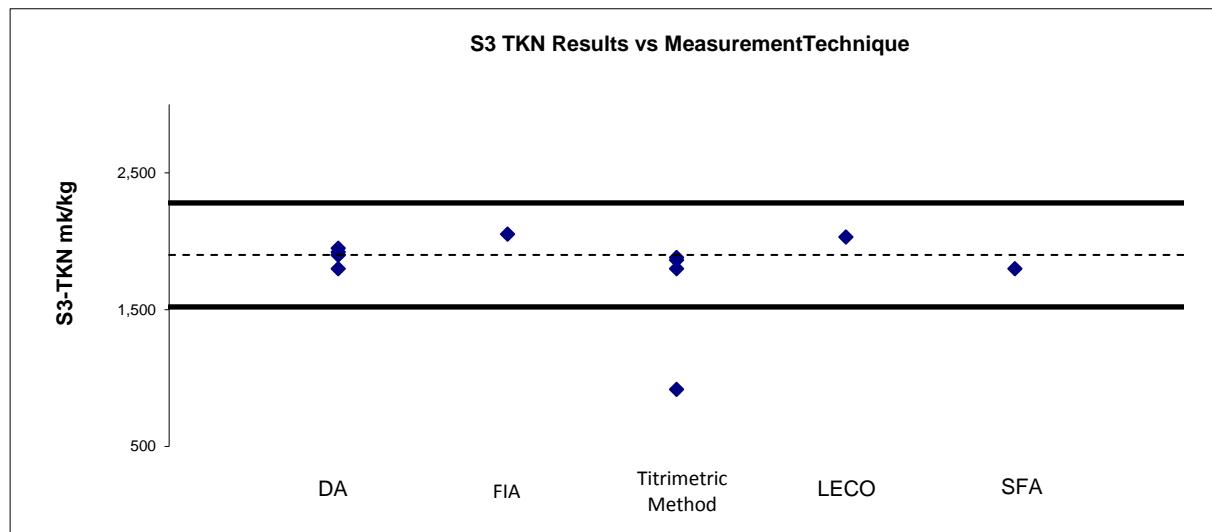


Figure 76 S3-TKN Results vs. Measurement Technique

7.8 Participants' Results and Analytical Methods for Water Soluble Anions

Measurement of water soluble anions in soil is an empirical measurement – where the method of extraction defines the measurand.^{32, 33} With testing laboratories using different methods, each could be considered to be measuring a different measurand that is their version of 'water soluble anions in soil'. This lack of uniformity in the procedures can make the comparison of participants' results difficult.

In the previous study of metals and anions in soil AQA 11-12, NMI conducted a study on water soluble anions content in soil using the same instrumental technique but 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 sulfate results were found to change in direct proportion with the amount of water used in the extraction procedure.⁷

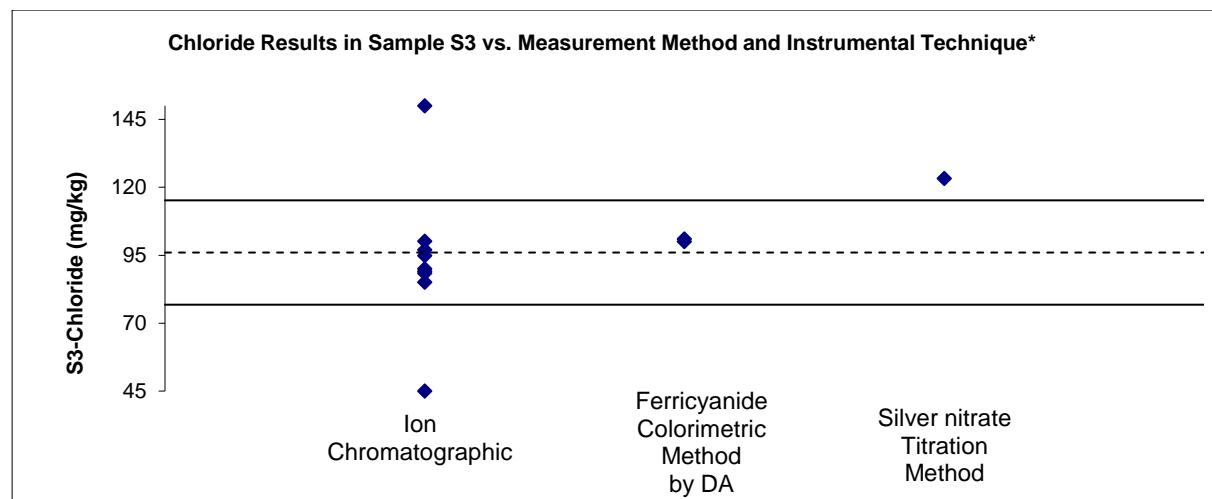
In the present study participating laboratories were asked to analyse the sample using their normal measurement technique but to follow the same preparation procedure for the soil extract which involved: a soil/water ratio of 1:5 and a mixing time of one hour.

The method descriptions and instrumental techniques provided by participants are presented in Tables 4 to 10. Except for one all participants used a soil/water ratio of 1 to 5; one participant used a soil/water ratio of 1 to 10

Individual Water Soluble Anion Commentary

Bromide Three participants reported results for water soluble bromide. All used IC.

Chloride Thirteen participants reported results for chloride and 10 performed satisfactorily. Figure 77 presents a plot of participants' results versus measurement method and instrumental technique used for chloride analysis in S3.



*Results >150 mg/kg and <45 mg/kg have been plotted as 150 mg/kg and 45 mg/kg.

Figure 77 S3-Chloride Results vs. Measurement Method

Fluoride level in S3 was low and this might have challenged participants' analytical techniques. 5 results were reported for this test and 4 were in good agreement with each other, centred on 2.44 mg/kg value. Participants' results versus measurement method are presented in Figure 78.

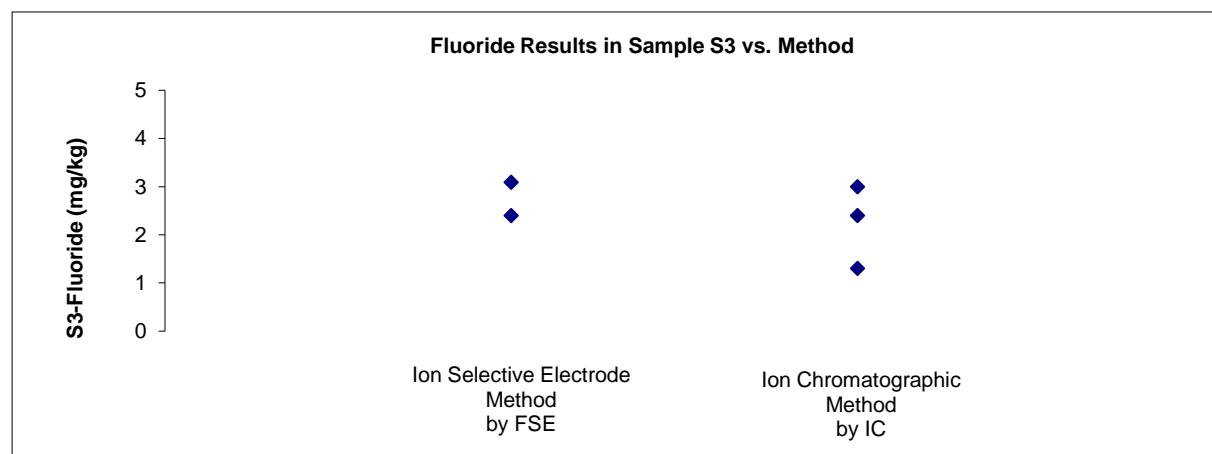
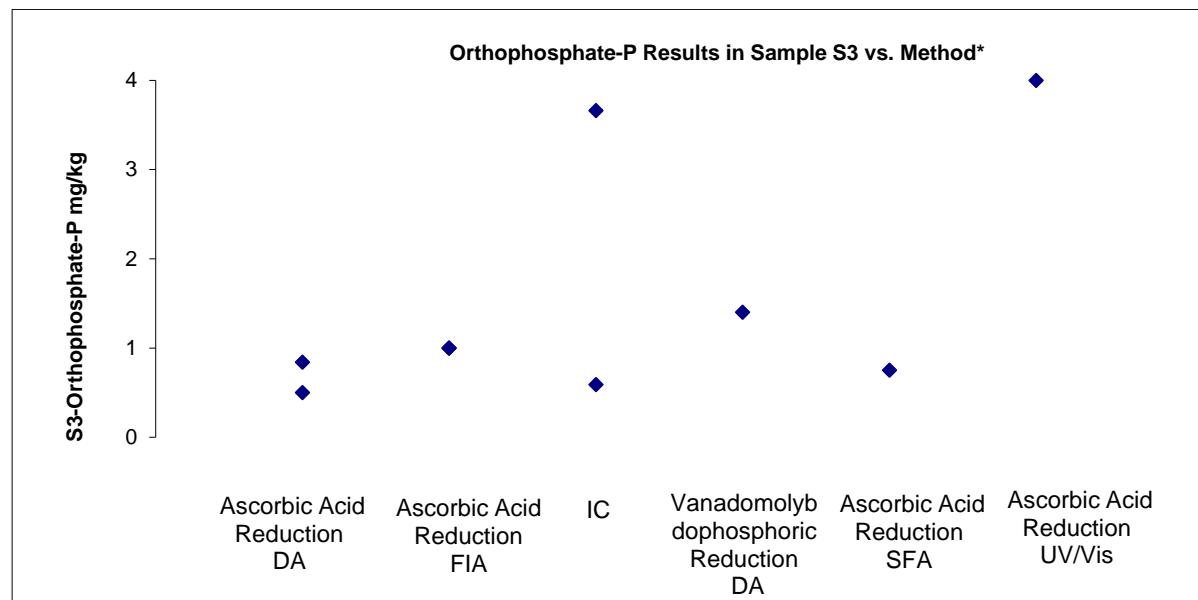


Figure 78 S3-Fluoride Results vs. Measurement Method

Iodide level in S3 was below level of detection of most instrumental techniques used by participants. The result reported by Laboratory 24 was a false positive.

Orthophosphate-P No assigned value could be set for orthophosphate-P in S3 because the reported results were too variable between 0.5 mg/kg and 6.3 mg/kg. Participants used a wide variety of measurement methods and instrumental techniques (Figure 79). Some laboratories might have reported phosphate and not orthophosphate-P.



*Result >4 mg/kg has been plotted as 4 mg/kg.

Figure 79 S3-Orthophosphate-P Results vs. Method

Sulfate Plots of participants' results with the instrumental technique used are presented in Figure 80. Although most of the S in soil samples is from sulfate compounds, false positive results can be produced when this is measured by ICP-OES: this technique measures total S and not only S from sulfate compounds.

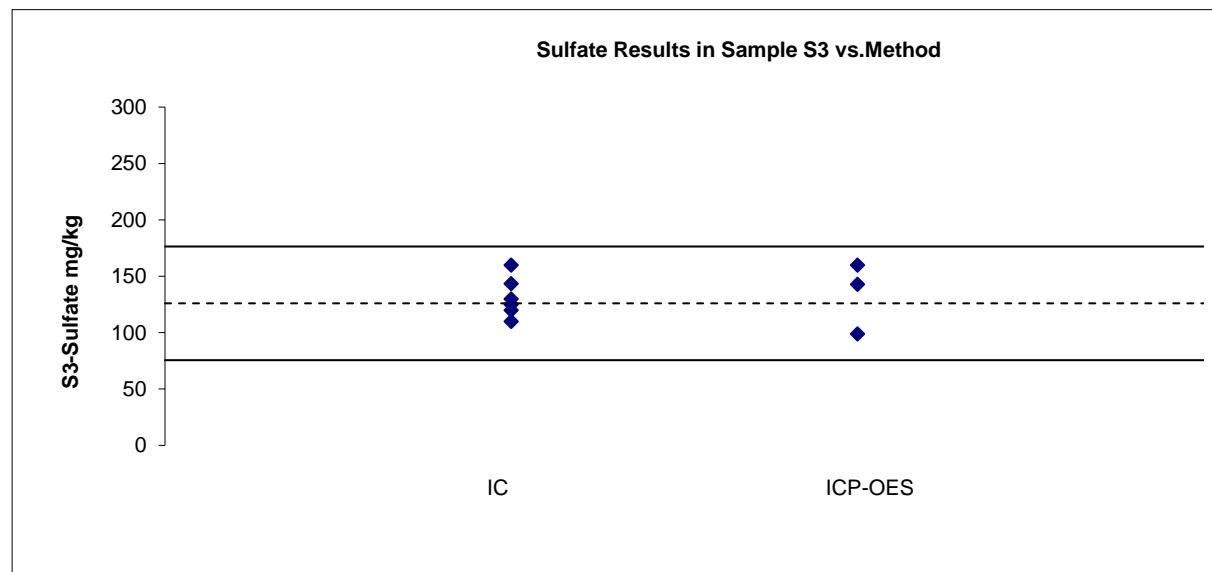


Figure 80 S3-Sulfate Results vs. Measurement Method and Instrumental Technique

pH measurements in soil did not present a difficulty to the participating laboratories. All the reported results were in agreement with the assigned value except for one.

EC Of 15 reported results for EC in S3, 14 returned satisfactory z-scores.

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

AQA 18-12 is the twenty-third NMI proficiency test of metals in soil. For most of the analytes the same fixed target standard deviation was used in the present study as in the previous studies of metals in soil. This allowed a comparison of participants' performance (z-score) over time and provided a benchmark for progressive improvement.

Participants' performance in measurement of metals in soil over time is presented in Figure 81. On average participants' performance remained fairly consistent.

Over time laboratories should expect at least 95% of its scores to lay with the range $|z| \leq 2$. Scores in the range $2 < |z| \leq 3$ 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.

7.10 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 79).

Table 79 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	AGAL-10/In-house SRMs
2	Novachem CRM029
3	Agal - 10
4	PACS2 Marine Sediment and NIST SRM 2704 Buffalo River Sediment
5	Sigma Aldrich (anion standard solution)
8	NIST SRM 2711a (Montana Soil)
9	Previous PT samples
11	AQA-17-11
13	SQC014: Nutrients in Soil for TKN and Ammonia as N
15	AGAL 12
16	AGAL-10
18	AGAL 10 & AGAL 12
20	AGAL-10 Hawkesbury River Sediment
22	CRM 036
23	CRM
24	AGAL-10, AGAL-12, ERA Metals in Soil, ERA Metals in Sludge

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'³⁴

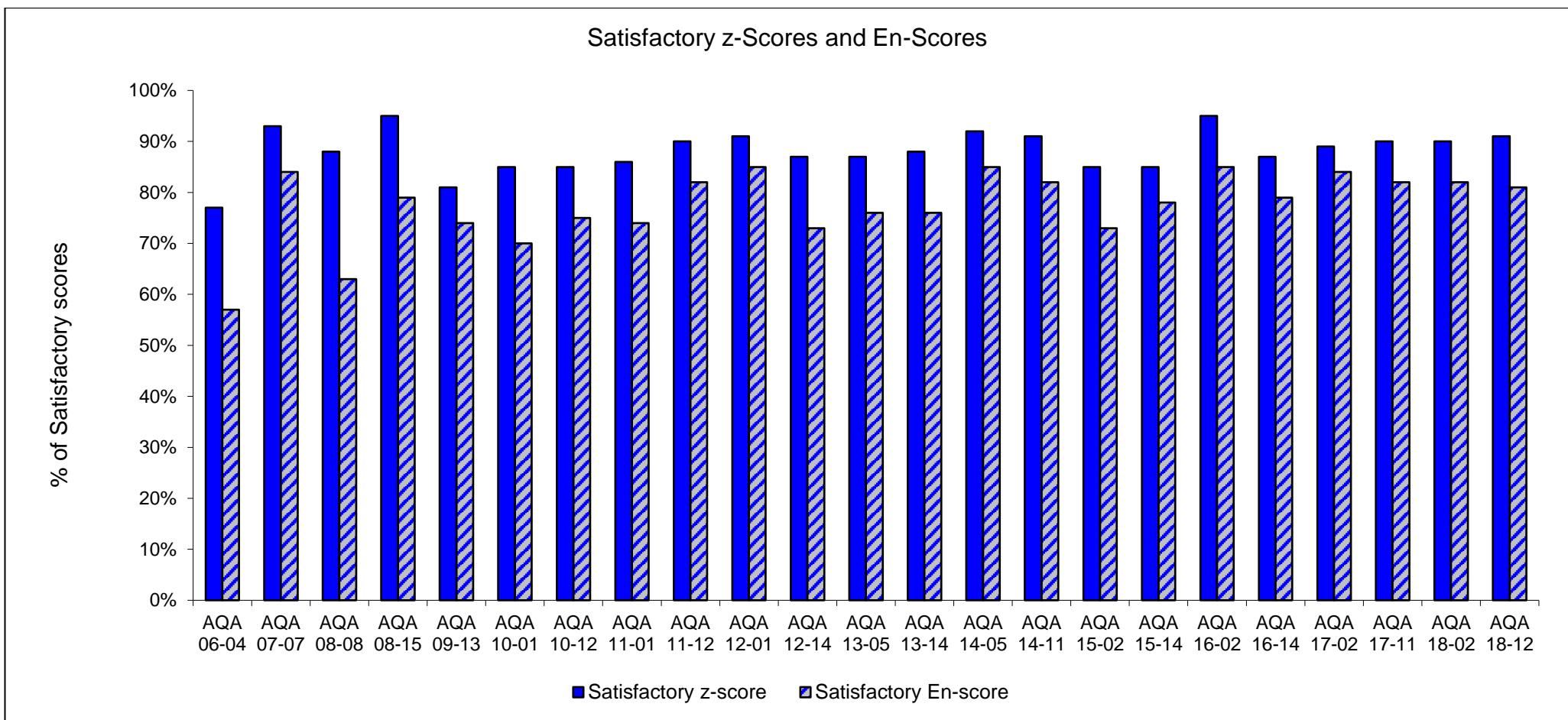


Figure 81 Participants' Performance over Time

8 REFERENCES

- [1] ISO17043:2010, Conformity assessment – *General requirements for proficiency testing*.
- [2] NMI 2016, *NMI Chemical Proficiency Testing Study Protocol*, viewed 7 November 2018, <<http://www.measurement.gov.au>>.
- [3] NMI 2016, *NMI Chemical Proficiency Testing Statistical Manual*, viewed 7 November 2018, <<http://www.measurement.gov.au>>.
- [4] Thompson, M, Ellison, S & Wood, R 2006, ‘The international harmonized protocol for proficiency testing of (chemical) analytical laboratories’, *Pure Appl. Chem*, vol 78, pp 145-196.
- [5] National Environmental Protection Council, Schedule B(1) – *Guidelines on the Investigation Levels for Soil and Groundwater*, viewed November 2017, <<http://www.ephc.gov.au/nepms>>.
- [6] NMI, (2012), *AQA 16-02 Metals in Soil*, <<http://www.measurement.gov.au>>.
- [7] NMI (2014), *AQA 12-14 Metals in Soil*, <<http://www.measurement.gov.au>>.
- [8] ISO13528:2015(E), *Statistical methods for use in proficiency testing by interlaboratory comparisons*.
- [9] Thompson, M 2000, Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing, *Analyst*, vol 125, pp 385-386.
- [10] ISO/IEC 17025:2015, *General requirements for the competence of testing and calibration laboratories*
- [11] Eurachem 2012, *Quantifying uncertainty in Analytical Measurement*, 3rd edition, viewed 10 May 2017, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.
- [12] Betil, M, Naykki, T, Hovind, H & Krysell, M 2004, *Nordtest Report Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories*, Nordest Tekniikantie, Finland, Esopo.
- [13] Hibbert, B 2007, *Quality Assurance for the Analytical Chemistry Laboratory*, Oxford University Press.
- [14] NATA 2009, *Technical Note 33*.
- [15] ISO (2008), *Guide to the Expression of Uncertainty in Measurement (GUM)*, Geneva, Switzerland.
- [16] Eurolab 2002, Technical Report No 1/2002 - *Measurement Uncertainty in Testing*.
- [17] NMI, *Estimating Measurement Uncertainty for Chemists* – viewed March 2017, <www.measurement.gov.au>.
- [18] Australian and New Zealand Environment and Conservation Council, and National Health and Medical Research Council -ANZECC/NMHRC 1992, *Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites*.
- [19] Australian Health Commission 1995, *Contaminated Sites Monograph No4: Trace Element Concentrations in Soils from Rural and Urban Areas of Australia*

- [20] European Commission, DG Research, Brussels Belgium 2002, *Methodologies for Soil and Sediment Fraction Studies*.
- [21] Gaudino, S, Galas, C 2007, ‘The role of different soil sample digestion methods on trace element analysis: a comparison of ICP-MS and INAA measurement results’, *Accred Qual Assur* vol 12, pp 84-93.
- [22] Chen, M, Ma, L 2001, ‘Comparison of Three Aqua Regia Digestion Methods for Twenty Florida Soil’, *Soil Sci. Soc. Am J*, vol 65, pp 491-499.
- [23] Charun, Y 2006, ‘A comparative study of acid-extractable and total digestion methods for the determination of inorganic elements in peat material by inductively coupled plasma-optical emission spectrometry’, *Analytica Chimica Acta*, vol 557, pp 296-303.
- [24] Roje, V 2010, ‘Multi-elemental analysis of marine sediment reference material MESS-3: one-step microwave digestion and determination by high resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS)’, *Chemical papers* vol 64 (4), pp.409-414.
- [25] Spectroscopy, *Reducing the Effects of Interferences in Quadrupole ICP-MS* – viewed November 2018, <<http://www.spectroscopyonline.com/reducing-effects-interferences-quadrupole-icp-ms?id=&sk=&date=&pageID=3>>
- [26] Jackson, B & Liba, A 2015, ‘Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods’ *J. Anal. At. Spectrometry*, vol. 30, pp1179-1183.
- [27] Crustal Geophysics and Geochemistry Centre, *High Resolution ICP-MS Laboratory* – viewed November 2018, <https://crustal.usgs.gov/laboratories/icpms/high_resolution.html>
- [28] Spectroscopy, *A Beginner’s Guide to ICP-MS* – viewed November 2018, <http://matematicas.udea.edu.co/~carlopez/beginer_guide_icpms.pdf>
- [29] Manecki, M., Lofthouse, S., Boening, P & Ducos, S., McS., ‘Accurate Determination of Arsenic and Selenium in Environmental Samples Using the Thermo Scientific iCAP TQ’ ICP-MS – *Thermoscientific Application Note 43285*.
- [30] Wei, G & Hu S 2011, ‘Application of ion molecule reaction to eliminate WO interference on mercury determination in soil and sediment samples by ICP-MS’ *J. Anal. At. Spectrometry*, vol. 26, pp1198-1203.
- [31] Chang, CC, Jiang & SJ 2013, ‘Bandpass reaction cell inductively coupled plasma mass spectrometry for the determination of silver and cadmium in samples in the presence of excess Zr, Nb and Mo’ *Analytica Chimica Acta*, vol. 493, pp213-218.
- [32] Rayment, G. E. & Lyons, D. J 2011 *Soil Chemical Methods – Australasia*, CSIRO Publishing, Collingwood VIC Australia
- [33] Afzal M., Yasin M, (2002), *Effect of soil to water ratios on chemical properties of saline-sodic and normal soil* Pakistan J. agric. Res. 17, 379-386.
- [34] JCGM 200:2008, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition.

APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Samples S1 was a highly contaminated soil, it was a composite of soil samples submitted to NMI for chemical analyses. The material was mixed, dried, ground, sieved and further mixed and divided in portions of approximately 30 g each.

Sample S2 and S3 were dried soil samples previously distributed as Sample S1 and S3 respectively of PT study AQA 16-02. The procedures for preparation and analysis of these samples were provided in the report of AQA 16-02.⁵

Sample Analysis and Homogeneity Testing

The same procedure was followed for Sample S1 preparation as in the previous NMI PT studies.^{5,6} Partial homogeneity testing was conducted for the elements of interest. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value. Measurements were made under repeatability conditions in random order.

Samples S2 and S3 were previously distributed as Samples S1 and S3 respectively of PT study AQA 16-02. These samples were previously tested for homogeneity by NMI except for 2M KCl extractable ammonium nitrogen ($\text{NH}_4^+ \text{-N}$), 2M KCl extractable nitrate nitrogen ($\text{NO}_3^- \text{-N}$), pH, EC and total Kjeldahl nitrogen.

Sample Analysis for Acid Extractable Elements

Measurements for acid extractable elements were made using NMI method: NT2.49.³¹ NMI holds third party (NATA) accreditation for this method. Testing using NMI Method NT2.49 involve solubilisation of metals and metal complexes using a mixture of nitric acid and hydrochloric acid. Metals were then measured using ICP-MS, ICP-OES, ICP-MS/MS and HR-ICP-MS.

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

The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, and matrix matched reference materials, duplicates and sample matrix spikes, was carried through the same set of procedures and analysed at the same time as the samples. A summary of the instrument conditions used and the ion/wavelength monitored for each analyte is given in Table 80.

Table 80 Instrumental Technique used for Acid Extractable Elements in S1

Analyte	Instrument	Internal Standard	Reaction/Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1Final Dilution Factor	Ion (m/z)/Wavelength (nm)
Ag	ICP-MS/MS	Co, Y	ORS	O ₂	40	109 m/z
Ag*	ICP-MS/MS	Co, Y	ORS	NH ₃	40	107 m/z
Al	ICP-MS	Rh	NA	NA	800	27 m/z
As	HR-ICP-MS	Co, Y	NA	NA	100	75 m/z
Ba	ICP-OES	Y	NA	NA	800	445.403 nm
Be	ICP-OES	Y	NA	NA	800	313.107 nm
Bi	ICP-MS	Ir	NA	NA	800	209 m/z
Ca	ICP-OES	Y	NA	NA	800	43 m/z
Cr	ICP-MS	Rh	ORS	He	800	52 m/z

Table 80 Instrumental Technique used for Acid Extractable Elements in S1 (continued)

Analyte	Instrument	Internal Standard	Reaction/Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1Final Dilution Factor	Ion (m/z)/Wavelength (nm)
Cu	ICP-MS	Rh	ORS	He	800	65 m/z
Fe	ICP-MS	Rh	ORS	He	800	56 m/z
Ga	ICP-MS	Rh	ORS	He	800	71 m/z
Hg	CV-AFS	NA	NA	NA	800	253.7 nm
Hg*	ICP-MS/MS	Co, Y	ORS	O ₂	40	202 m/z
K	ICP-MS	Rh	ORS	He	800	39 m/z
Mn	ICP-MS	Rh	ORS	He	800	55 m/z
Mo	ICP-MS	Rh	ORS	He	800	95 m/z
Ni	ICP-MS	Rh	ORS	He	800	60 m/z
Pb	ICP-MS	Ir	NA	NA	800	Average of 206, 207, 208 m/z
S	ICP-OES	Y	NA	NA	800	180.669 nm
Se	HR-ICP-MS	Co, Y	NA	NA	100	78 m/z
Sn	ICP-MS	Rh	NA	NA	800	118 m/z
Sr	ICP-MS	Rh	ORS	He	800	88 m/z
Th	ICP-MS	Ir	ORS	He	800	232 m/z
U	ICP-MS	Ir	ORS	He	800	238 m/z
V	ICP-MS	Rh	ORS	He	800	51 m/z
Zn	ICP-MS	Rh	ORS	He	800	66 m/z

*Confirmation technique

APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND E_N SCORE CALCULATION

The assigned value was calculated as the robust average using the procedure described in ‘ISO13258:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons – Annex C’⁸ the uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 81.

Table 81 Uncertainty of Assigned Value for As in Sample S2

No. results (p)	20
Robust Average	9.60 mg/kg
$S_{rob\ av}$	1.01 mg/kg
$u_{rob\ av}$	0.29 mg/kg
k	2
$U_{rob\ av}$	0.57 mg/kg

The assigned value for As in Sample S1 is **9.60 ± 0.57 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 19).

A worked example is set out below in Table 82.

Table 82 z-Score and E_n-score for As Result Reported by Laboratory 1 in S2

As Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E _n -Score
9.0 ± 2.8	9.60 ± 0.57	10% as CV or 0.10x9.60 = =0.96 mg/kg	$z = \frac{(9.00 - 9.60)}{0.96}$ $z = -0.63$	$E_n = \frac{(9.00 - 9.60)}{\sqrt{2.8^2 + 0.57^2}}$ $E_n = -0.21$

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.^{12, 14} An example is given.

Between 2009 and 2017 NMI carried out fifteen 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 and sludge. Laboratory X submitted results for As in fourteen 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.

Table 83 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	Biosoil	4.091 ± 0.41	3.64 ± 0.43	16	11
	Soil	4.29 ± 0.43	4.57 ± 0.50	15	12
AQA 11-01	Biosoil	3.54 ± 0.35	3.57 ± 0.26	20	18
AQA 13-05	Soil	9.22 ± 1.4	9.21 ± 0.68	14	22
AQA 14-11	Sediment	7.91 ± 1.2	7.37 ± 0.32	12	21
AQA 15-02	Sludge	8.29 ± 1.2	7.02 ± 0.29	13	22
	Sludge	7.42 ± 1.1	7.02 ± 0.29	11	17
AQA 15-14	Sediment	10 ± 1.5	9.95 ± 0.40	6.7	17
	Soil	4.53 ± 0.9	4.47 ± 0.19	6.4	14
AQA 16-02	Agricultural Soil	2.67 ± 0.4	2.11 ± 0.17	14	20
AQA 16-14	Soil	6.03 ± 0.9	5.61 ± 0.59	15	17
Average				13**	

* Expanded uncertainty at approximately 95% confidence.

** The mean value of Robust CV was used. The pooled standard deviation could also be used. In this case the pooled standard deviation is 13%. Using a coverage factor of 2 gives an estimate of 26%.

Table 84 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	Soil	16.6 ± 1.66	14.4 ± 0.7	8.5	19
AQA 11-12	Moist Soil	25 ± 3.6	21.6 ± 2.2	15	13
AQA 12-01	Sediment	18.4 ± 2.7	17.3 ± 0.8	8.1	21
AQA 12-14	Soil	16.6 ± 2.4	14.8 ± 0.9	11	20
AQA 13-14	Sandy Soil	16.6 ± 2.4	15.1 ± 0.9	10	21
AQA 14-05	Soil	13.2 ± 1.9	12.3 ± 0.5	7.8	25
Average				10**	

* Expanded uncertainty at approximately 95% confidence.

** The mean value of Robust CV was used. The pooled standard deviation could also be used. In this case the pooled standard deviation is 10%. Using a coverage factor of 2 gives an estimate of 20%.

Taking the average of the robust CV over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 13% and 10% respectively. Using a coverage factor of two gives relative expanded uncertainties of 26% and 20% respectively, at a level of confidence of approximately 95%. Table 83 and Table 84 sets out the expanded uncertainty for results of the measurement of As in soil, biosoil, sediment, sludge, sandy soil, moist soil and agricultural soil over the ranges 0.5 to 10 mg/kg and 10 to 30 mg/kg.

Table 85 Uncertainty of As Results Estimated Using PT Data.

Results mg/kg	Uncertainty mg/kg
1.00	0.26
5.0	1.3
20	4
75	15

The estimates of 26% and 20% relative passes the test of being reasonable, and the analysis of the 16 different PT samples over seven years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrators etc.), and so complies with ISO 17025:2015.¹⁰

APPENDIX 4 - INSTRUMENT DETAILS

Table 86 Instrument Conditions Ag

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-MS	In	ORS	He	0.09	NA	107
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	328.068
4						NA	
5					NA	NA	
6	ICP-MS	Rh	ORS	He	5000	NA	107
7	ICP-MS	Ir193			400	NA	
8	ICP-MS	Rh	CRI			NA	
9	ICP-MS	Rh				NA	107
10						NA	
11	ICPAES	Y			50	NA	
12						NA	
13					NA	NA	
14						NA	
15	ICP-MS	Rh	NA	NA	625	NA	109
16	ICP-MS	Rh	ORS	He	20	NA	107
17					NA	NA	
18	ICP-MS	Rh	ORS	He	500	NA	107
19						NA	
20	ICP-MS	Rh			2000	NA	109
21	ICP-MS	Ge 72	ORS			NA	107 m/z
22	ICP-OES-AV-buffer	Y			100	NA	328.068
23	ICP-OES-RV					NA	328.068
24	ICP-MS	Indium	ORS	He	10	NA	107
25					NA	NA	
26					NA	NA	

Table 87 Instrument Conditions Al

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-OES-SVDV	Lu			1.9	NA	308.215
3	ICP-OES-AV	Lu 261.541	NA	NA	2000	NA	396.152
4						NA	
5					NA	NA	
6	ICP-MS	Sc	ORS	NA	5000	NA	27
7	ICP-AES	Lu			40	NA	396.153
8	ICP-MS	Sc	CRI		1600	NA	
9	ICP-MS	Rh				NA	27
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	256.798
13					NA	NA	
14	ICP-MS	Sc	NA	NA	250	NA	
15	ICP-MS	Sc	UC	He	625	NA	27
16	ICP-MS	Sc	ORS	He	200	NA	27
17					NA	NA	
18	ICP-MS	Sc	ORS	He	500	NA	27
19	ICP-OES-RV					NA	
20	ICP-MS	Sc			2000	NA	27
21	ICP-OES-RV	Y377	NA			NA	308.215 nm
22	ICP-OES-AV-buffer	Y			100	NA	308.215
23	ICP-OES-RV					NA	308.215
24	ICP-OES-AV	Scandium			10	NA	167.019
25					NA	NA	
26					NA	NA	

Table 88 Instrument Conditions As

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	193.7
2	ICP-MS	Ge	ORS	He	0.09	0.09	75
3	ICP-OES-AV	Lu 261.541	NA	NA	20	20	188.98
5					NA	NA	
6	ICP-MS	Ge	ORS	He	5000	5000	75
7	ICP-MS	Y89			80000	400	
8	ICP-MS	Rh	CRI		160	160	
9	ICP-MS	Rh	ORS	He			75
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		188.98
13					NA	NA	
14	ICP-MS	Rh	NA	He	250	250	
15	ICP-MS	Ge	UC	He	625	625	75
16	ICP-MS	Ge	ORS	He	20	20	75
17	ICP-MS	72	ORS	He	NA	100	75
18	ICP-MS	Rh	ORS	He	500	500	75
19	ICP-OES-RV					NA	
20	ICP-MS	Rh	UC	He	1000	1000	75
21	ICP-MS	Ge 72	ORS				75m/z
22	ICP-OES-AV-buffer				100	100	189.042
23	ICP-OES-RV						188.98
24	ICP-MS	Germanium	ORS	He	10	10	75
25	ICP-OES-AV-buffer				NA		188.979
26					NA	NA	

Table 89 Instrument Conditions B

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-OES-AV	Lu			NA	20	249.772
2	ICP-MS	Ge	ORS	He	NA	0.09	10
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	249.678
4					NA		
5					NA	NA	
6	ICP-MS	Y	ORS	NA	NA	5000	11
7	ICP-MS	Y89			NA	400	
8	ICP-MS	Rh	CRI		NA	160	
9	ICP-MS	Rh			NA		11
10					NA		
11					NA	NA	
12					NA		
13					NA	NA	
14	ICP-MS	Sc	NA	NA	NA	250	
15	ICP-MS	Sc	NA	NA	NA	625	10
16	ICP-MS	Sc	ORS	NA	NA	20	11
17	ICP-OES-AV-buffer	Lu			NA	100	249.678
18	ICP-MS	Sc	ORS	He	NA	500	11
19					NA	NA	
20	ICP-MS	Sc	UC	He	NA	1000	11
21	ICP-OES-RV	Te214	NA		NA		249.678
22	ICP-OES-AV-buffer	Y			NA	100	208.959
23	ICP-OES-RV				NA		249.772
24	ICP-MS	Scandium	ORS	H2	NA	10	11
25					NA		
26					NA	NA	

Table 90 Instrument Conditions Ba

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-OES-SVDV	Lu			0.09	NA	455.403
3	ICP-OES	Lu 261.541	NA	NA	20	NA	233.527
4						NA	
5					NA	NA	
6	ICP-MS	Tb	ORS	He	5000	NA	137
7	ICP-MS	In115			400	NA	
8	ICP-MS	Rh	CRI		160	NA	
9	ICP-MS	Rh				NA	134
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	585.367
13					NA	NA	
14	ICP-MS	In	NA	NA	250	NA	
15	ICP-MS	Rh	NA	NA	625	NA	138
16	ICP-MS	Rh	ORS	He	20	NA	137
17					NA	NA	
18	ICP-MS	Lu	ORS	He	500	NA	135
19	ICP-OES-RV					NA	
20	ICP-MS	Lu			2000	NA	137
21	ICP-MS	Ge 72	ORS			NA	137m/z
22	ICP-OES-AV-buffer	Y			100	NA	233.527
23	ICP-OES-RV					NA	585.367
24	ICP-MS	Indium	ORS	He	10	NA	137
25					NA	NA	
26					NA	NA	

Table 91 Instrument Conditions Be

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-MS	Ge			0.09	NA	9
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	313.107
4						NA	
5					NA	NA	
6	ICP-MS	Ge	ORS	NA	5000	NA	9
7	NT					NA	
8	ICP-MS	Sc	CRI		160	NA	
9	ICP-MS	Rh				Na	9
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	313.107
13					NA	NA	
14	ICP-MS	Sc	NA	NA	250	NA	
15	ICP-MS	Sc	NA	NA	625	NA	9
16	ICP-MS	Sc	ORS	NA	20	NA	9
17					NA	NA	
18	ICP-MS	Sc	ORS	other	500	NA	9
19	ICP-MS					NA	
20	ICP-MS	Sc			2000	NA	9
21	ICP-MS	Ge 72	ORS			NA	9m/z
22	ICP-OES-AV-buffer	Y			100	NA	313.042
23	ICP-OES-RV					NA	585.367
24	ICP-MS	Sc	ORS	H2	10	NA	9
25					NA	NA	
26					NA	NA	

Table 92 Instrument Conditions Bi

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorban ce(nm)
1					NA	NA	NA
2	ICP-MS	Ir	ORS	He	0.09	NA	209
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	223.061
4						NA	
5					NA	NA	
6	ICP-MS	Tb	ORS	NA	5000	NA	209
7	NT					NA	
8	ICP-MS	Rh	CRI		160	NA	
9	ICP-MS	Rh				NA	209
10						NA	
11	ICPAES	Y			50	NA	
12						NA	
13					NA	NA	
14						NA	
15	ICP-MS	Ir	NA	NA	625	NA	209
16	ICP-MS	Lu	ORS	He	20	NA	209
17					NA	NA	
18	ICP-MS	Lu	ORS	He	500	NA	209
19						NA	
20	ICP-MS	Lu			2000	NA	209
21	ICP-MS	Rh 103	ORS			NA	209m/z
22						NA	
23	ICP-MS	Rh, Sc, In	ORS			NA	209
24						NA	
25					NA	NA	
26					NA	NA	

Table 93 Instrument Conditions Ca

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-OES-RV	Lu			NA	40	317.933
2	ICP-OES-SVDV	Lu			1.9	1.9	315.887
3	ICP-OES-AV	Lu 261.541	NA	NA	2000	200	315.887
4							
5					NA		
6	ICP-MS	Sc	ORS	H2	5000	5000	40
7	ICP-AES	Lu			40	40	317.933
8	ICP-OES-AV	Cs			1600	NA	
9	ICP-OES-RV	Y					315.887
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	210.324
13					NA		
14	ICP-MS	Sc	NA	He	250	NA	
15	ICP-MS	Sc	UC	He	625	625	44
16	ICP-OES-RV	Y	NA	NA	200	20	317.933
17	ICP-OES-AV-buffer	Lu			Na	100	430.253
18							
19							
20	ICP-MS	Sc			2000	2000	43
21	ICP-OES-RV	Y377	NA				317.933 nm
22	ICP-OES-AV-buffer	y			100	100	317.933
23	ICP-OES-RV						315.887
24	ICP-OES-AV	Scandium			10	10	
25					NA	NA	
26					NA	NT	

Table 94 Instrument Conditions Cd

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	228.8
2	ICP-MS	Ir	ORS	He	NA		111
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	228.802
4					NA		
5					NA	NA	
6	ICP-MS	Rh	ORS	NA	NA	5000	111
7	ICP-MS	In115			NA	400	
8	ICP-MS	Rh	CRI		NA	160	
9	ICP-MS	Rh	ORS	He	NA		111
10					NA		
11					NA	NA	
12					NA		
13					NA	NA	
14	ICP-MS	Rh	NA	NA	NA	250	
15	ICP-MS	Rh	NA	NA	NA	625	111
16	ICP-MS	Rh	ORS	He	NA	20	111
17	ICP-MS	103	ORS	He	NA	100	114
18	ICP-MS	Rh	ORS	He	NA	500	111
19					NA	NA	
20	ICP-MS	Rh	UC	He	NA	1000	111
21	ICP-MS	Rh 103	ORS		NA		111m/z
22	ICP-OES-AV-buffer	Y			NA	100	228.802
23	ICP-OES-RV				NA		226.502
24	ICP-MS	Gold	ORS	He	NA	10	111
25	ICP-OES-AV-buffer				NA		228.802
26					NA	NA	

Table 95 Instrument Conditions Co

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	240.7
2	ICP-MS	Ge	ORS	He	NA		59
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	231.16
4					NA		
5					NA	NA	
6	ICP-MS	Rh	ORS	He	NA	5000	59
7	ICP-AES	Lu			NA	40	228.616
8	ICP-MS	Rh	CRI		NA	160	
9	ICP-MS	Rh	ORS	He	NA		59
10					NA		
11					NA	NA	
12					NA		
13					NA	NA	
14	ICP-MS	Rh	NA	He	NA	250	
15	ICP-MS	Ge	UC	He	NA	625	59
16	ICP-MS	Ge	ORS	He	NA	20	59
17	ICP-MS	103	ORS	He	NA	100	59
18	ICP-MS	Sc	ORS	He	NA	500	59
19					NA	NA	
20	ICP-MS	Ga	UC		NA	2000	59
21	ICP-MS	Ge 72	ORS		NA		59m/z
22	ICP-OES-AV-buffer	Y			NA	100	230.786
23	ICP-OES-RV				NA		228.615
24	ICP-MS	Germanium	ORS	He	NA	10	65
25					NA		
26					NA	NA	

Table 96 Instrument Conditions Cr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	357.9
2	ICP-OES-SVDV	Lu			1.9	0.09	205.56
3	ICP-OES-AV	Lu 261.541	NA	NA	200	20	267.716
4							
5					NA	NA	
6	ICP-MS	Ge	ORS	He	5000	5000	52
7	ICP-MS	Y89			80000	400	
8	ICP-MS	Rh	CRI		160	160	
9	ICP-MS	Rh	ORS	He			52
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		267.716
13					NA	NA	
14	ICP-MS	Sc	Na	He	250	250	
15	ICP-MS	Sc	UC	He	625	625	52
16	ICP-MS	Sc	ORS	He	200	20	52
17	ICP-MS	103	ORS	He	NA	100	52
18	ICP-MS	Sc	ORS	He	500	500	52
19	ICP-OES-RV					NA	
20	ICP-MS	Sc	UC	He	1000	1000	52
21	ICP-MS	Ge 72	ORS				52m/z
22	ICP-OES-AV-buffer	Y			100	100	205.618
23	ICP-OES-RV						267.716
24	ICP-MS	Germanium	ORS	He	10	10	52
25	ICP-OES-AV-buffer				NA		267.716
26					NA	NA	

Table 97 Instrument Conditions Cu

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	324.7
2	ICP-OES-SVDV	Lu			0.09	0.09	324.754
3	ICP-OES-AV	Lu 261.541	NA	NA	20	20	327.395
4							
5					NA	NA	
6	ICP-MS	Rh	ORS	He	5000	5000	63
7	ICP-AES	Lu			40	40	327.393
8	ICP-MS	Rh	CRI		160	160	
9	ICP-MS	Rh	ORS	He			65
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		327.395
13					NA	NA	
14	ICP-MS	Rh	NA	He	250	250	
15	ICP-MS	Ge	UC	He	625	625	63
16	ICP-MS	Sc	ORS	He	20	20	63
17	ICP-MS	103	ORS	He	NA	100	65
18	ICP-MS	Sc	ORS	He	500	500	63
19	ICP-MS					NA	
20	ICP-MS	Ga	UC	He	1000	1000	63
21	ICP-MS	Ge 72	ORS				63m/z
22	ICP-OES-AV-buffer	Y			100	100	324.754
23	ICP-OES-RV						327.395
24	ICP-OES-AV	Scandium			10	10	327.395
25	ICP-OES-AV-buffer				NA		327.393
26					NA	NA	

Table 98 Instrument Conditions Fe

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	40	248.3
2	ICP-OES-SVDV	Lu			1.9	1.9	259.94
3	ICP-OES-AV	Lu 261.541	NA	NA	2000	2000	238.204
4							
5					NA		
6	ICP-MS	Rh	ORS	H2	5000	5000	56
7	ICP-AES	Lu			40	40	238.204
8	ICP-OES-AV	Cs	CRI		1600	NA	
9	ICP-MS	Rh					56
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	370.792
13					NA		
14	ICP-MS	Sc	NA	He	250	NA	
15	ICP-MS	Sc	UC	He	625	625	56
16	ICP-MS	Sc	ORS	He	200	200	56
17	ICP-OES-AV-buffer				NA	500	239.563
18	ICP-MS	Sc	ORS	He	500	500	
19							
20	ICP-MS	Sc					
21	ICP-OES-AV	Te214	NA				238.204nm
22	ICP-OES-AV-buffer	Y			100	100	259.941
23	ICP-OES-RV						258.588
24	ICP-OES-AV	Scandium			10	10	238.204
25					NA	NA	
26	AAS	Spiked sample			NA	1250	248.3

Table 99 Instrument Conditions Ga

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2						NA	
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	294.363
4						NA	
5					NA	NA	
6							
7	NT					NA	
8						NA	
9	ICP-MS	Rh				NA	71
10						NA	
11						NA	
12						NA	
13					NA	NA	
14						NA	
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS	Rh	ORS	He	500	NA	71
19						NA	
20	ICP-MS				NT	NA	NA
21	ICP-MS	Rh 103	ORS			NA	69m/z
22						NA	
23	ICP-MS	Rh, Sc, Ir	ORS	He		NA	71
24						NA	
25					NA	NA	
26					NA	NA	

Table 100 Instrument Conditions Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorban ce(nm)
1	AAS	None			NA	25	253.6
2	AFS				1.9	1.9	253.7
3	AAS		NA	NA	100	100	
4							
5					NA	NA	
6	ICP-MS	Ir	ORS	NA	5000	5000	202
7	ICP-MS	Ir193			400	400	
8	ICP-MS	Rh	CRI		160	160	
9	ICP-MS	Rh					201
10							
11						NA	
12	CVAFS	NA			500		254
13					NA	NA	
14	ICP-MS	Ir	NA	NA	250	250	
15	ICP-MS	Ir	NA	NA	625	625	201
16	ICP-MS	Lu	ORS	He	20	20	201
17	VGA-ICP-OES				NA	100	194.164
18	ICP-MS	Lu	ORS	He	500	500	202
19						NA	
20	ICP-MS	Lu	UC	He	1000	1000	201
21	ICP-MS	Ir 193	ORS				202m/z
22	AAS					100	254.7
23	AAS						253.7
24	ICP-MS	Gold	ORS	He	10	10	202
25					NA		
26					NA	NA	

Table 101 Instrument Conditions K

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-OES-RV	Lu			NA	40	766.490
2	ICP-OES-RV	Y			1.9	1.9	766.491
3	ICP-OES-AV	Lu 261.541	NA	NA	200	200	766.491
4							
5					NA		
6	ICP-MS	Sc	ORS	He	5000	5000	39
7	ICP-AES	Lu			40	40	766.49
8	ICP-OES-AV	Cs			160	NA	
9	ICP-OES-RV	Y					766.491
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	769.897
13					NA		
14	ICP-MS	Sc	NA	NA	250	NA	
15	ICP-MS	Sc	UC	He	625	625	39
16	ICP-OES-RV	Y	NA	NA	20	20	766.485
17	ICP-OES-AV-buffer	Lu	ORS	He	NA	100	766.491
18							
19	ICP-OES-RV						
20	ICP-MS	Sc	UC	He	2000	2000	39
21	ICP-OES-RV	Y377	NA				766.491nm
22	ICP-OES-AV-buffer	Y			100	100	769.896
23	ICP-OES-RV						766.491
24	ICP-OES-AV	Scandium			10	10	766.491
25					NA	NA	
26	AAS (Emission)	spiked sample			NA	500	766.5

Table 102 Instrument Conditions Mg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorban ce(nm)
1	ICP-OES-RV	Lu			NA	40	279.077
2	ICP-OES-SVDV	Lu			NA	0.09	285.213
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	279.078
4					NA		
5					NA		
6	ICP-MS	Y	ORS	He	NA	5000	24
7	ICP-AES	Lu			NA	40	285.213
8					NA	NA	
9	ICP-OES-RV	Y			NA		279.8
10					NA	NA	
11					NA	NA	
12	ICP-OES-AV	Y 371.029			NA	NA	277.983
13					NA		
14					NA	NA	
15	ICP-MS	Sc	UC	He	NA	625	25
16	ICP-OES-RV	Y	NA	NA	NA	20	285.211
17	ICP-OES-AV-buffer	Lu	ORS	He	NA	100	279.078
18					NA		
19	ICP-OES-RV				NA		
20	ICP-MS	Sc			NA	2000	25
21	-				NA		
22	ICP-OES-AV-buffer	Y			NA	100	285.213
23	ICP-OES-RV				NA		383.829
24	ICP-OES-AV	Scandium			NA	10	279.8
25					NA	NA	
26	AAS	spiked sample			NA	500	285.2

Table 103 Instrument Conditions Mn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	279.5
2	ICP-OES-SVDV	Lu			1.9	1.9	257.61
3	ICP-OES-AV	Lu 261.541	NA	NA	200	20	257.61
4							
5					NA	NA	
6	ICP-MS	Ge	ORS	NA	5000	5000	55
7	ICP-MS	Y89			80000	400	
8	ICP-MS	Rh	CRI		1600	160	
9	ICP-MS	Rh	ORS	He			55
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		293.931
13					NA	NA	
14	ICP-MS	Rh	NA	He	250	250	
15	ICP-MS	Sc	UC	He	625	625	55
16	ICP-MS	Sc	ORS	He	200	20	55
17	ICP-MS	103			NA	100	55
18	ICP-MS	Sc	ORS	He	500	500	55
19						NA	
20	ICP-MS	Sc			2000	2000	55
21	ICP-OES-AV	Te214	NA				259.372nm
22	ICP-OES-AV-buffer	Y			100	100	257.611
23	ICP-OES-RV						261.02
24	ICP-OES-AV	Scandium			10	10	257.61
25					NA		
26					NA	NA	

Table 104 Instrument Conditions Mo

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-MS	In	ORS	He	0.09	NA	95
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	202.032
4						NA	
5					NA	NA	
6	ICP-MS	Y	ORS	He	5000	NA	95
7	ICP-MS	Y89			80000	NA	
8	ICP-MS	Rh	CRI		160	NA	
9	ICP-MS	Rh	ORS	He		NA	95
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	202.032
13					NA	NA	
14	ICP-MS	Rh	NA	NA	250	NA	
15	ICP-MS	Rh	NA	NA	625	NA	95
16	ICP-MS	Ge	ORS	He	20	NA	95
17					NA	NA	
18	ICP-MS	Rh	ORS	He	500	NA	95
19						NA	
20	ICP-MS	Rh			2000	NA	98
21	ICP-MS	Ge 72	ORS			NA	95m/z
22	ICP-OES-AV-buffer	Y			100	NA	202.095
23	ICP-OES-RV					NA	202.032
24	ICP-MS	Indium	ORS	He	10	NA	98
25					NA	NA	
26					NA	NA	

Table 105 Instrument Conditions Na

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorban ce(nm)
1	ICP-OES-RV	Lu			NA	20	589.592
2	ICP-OES-RV	Lu			NA	0.09	589.592
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	589.592
4					NA		
5					NA		
6	ICP-MS	Sc	ORS	H2	NA	5000	23
7	ICP-AES	Lu			NA	40	589.592
8					NA	NA	
9	ICP-OES-RV	Y			NA		588.995
10					NA	NA	
11					NA	NA	
12	ICP-OES-AV	Y 371.029			NA	NA	588.995
13					NA		
14					NA	NA	
15	ICP-MS	Sc	UC	He	NA	625	23
16	ICP-OES-RV	Y	NA	NA	NA	20	589.611
17	ICP-OES-AV-equation	Lu			NA	100	589.592
18					NA		
19					NA		
20	ICP-MS	Sc	UC	He	NA	2000	23
21	-				NA		
22	ICP-OES-AV-buffer	Y			NA	100	589.592
23	ICP-OES-RV				NA		589.592
24	ICP-OES-AV	Scandium			NA	10	588.995
25					NA	NA	
26	AAS (Emission)	spiked sample			NA	250	589

Table 106 Instrument Conditions Ni

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	232
2	ICP-MS	Ge	ORS	He	0.09	0.09	231.604
3	ICP-OES-AV	Lu 261.541	NA	NA	20	20	231.604
4							
5					NA	NA	
6	ICP-MS	Ge	ORS	He	5000	5000	60
7	ICP-MS	Y89			80000	400	
8	ICP-MS	Rh	CRI		160	160	
9	ICP-MS	Rh					60
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		231.604
13					NA	NA	
14	ICP-MS	Rh	NA	He	250	250	
15	ICP-MS	Ge	UC	He	625	625	60
16	ICP-MS	Ge	ORS	He	20	20	60
17	ICP-MS	103	ORS	He	NA	100	60
18	ICP-MS	Sc	ORS	He	500	500	60
19	ICP-OES-RV					NA	
20	ICP-MS	Ga	UC	He	1000	1000	60
21	ICP-MS	Ge 72	ORS				60m/z
22	ICP-OES-AV-buffer	Y			100	100	231.604
23	ICP-OES-RV						231.604
24	ICP-MS	Germanium	ORS	He	10	10	60
25	ICP-OES-AV-buffer				NA		231.604
26					NA	NA	

Table 107 Instrument Conditions P

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-OES-AV	Lu			NA	40	214.914
2	ICP-OES-SVDV	Lu			NA	0.09	177.434
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	213.618
4					NA		
5					NA		
6	ICP-MS	Ge	ORS	He	NA	5000	31
7	ICP-AES	Lu			NA	40	213.617
8					NA	NA	
9	ICP-MS	Rh			NA		31
10					NA	NA	
11					NA	NA	
12					NA	NA	
13					NA		
14					NA	NA	
15	ICP-MS	Sc	UC	He	NA	625	31
16	ICP-OES-RV	Y	NA	NA	NA	20	178.219
17	ICP-OES-AV-equation	Lu			NA	100	213.618
18	ICP-MS	Sc	ORS	He	NA	500	31
19	ICP-OES-RV				NA		
20	ICP-MS	Sc			NA	2000	31
21	-				NA		
22	ICP-OES-AV-buffer	Y			NA	100	177.495
23	ICP-OES-RV				NA		185.827
24	ICP-MS	Germanium	ORS	He	NA	10	31
25					NA	NA	
26	UV/VIS spectrophotometer	spiked sample			NA		880

Table 108 Instrument Conditions Pb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	283.3
2	ICP-MS	Ir	ORS	He	0.09	0.09	208
3	ICP-OES-AV	Lu 261.541	NA	NA	20	20	220.353
4							
5					NA	NA	
6	ICP-MS	Tb	ORS	NA	5000	5000	206+207+208
7	ICP-MS	Ir193			400	400	
8	ICP-MS	Tb	CRI		160	160	
9	ICP-MS	Ir	ORS	He			207
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		220.353
13					NA	NA	
14	ICP-MS	Ir	NA	NA	250	250	
15	ICP-MS	Ir	NA	NA	625	625	206+207+208
16	ICP-MS	Lu	ORS	He	20	20	208
17	ICP-MS	103	ORS	He	NA	100	208
18	ICP-MS	Lu	ORS	He	500	500	208
19	ICP-OES-RV					NA	
20	ICP-MS	Lu	UC	He	1000	1000	206+207+208
21	ICP-MS	Ir 193	ORS				208m/z
22	ICP-OES-AV-buffer	Y			100	100	220.353
23	ICP-OES-RV						220.353
24	ICP-MS	Gold	ORS	He	10	10	208
25	ICP-OES-AV-buffer				NA		220.355
26					NA	NA	

Table 109 Instrument Conditions S

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-OES-AV	Lu			NA	20	181.975
2	ICP-OES-SVDV	Lu			1.9	1.9	181.972
3	ICP-OES-AV	Lu 261.541	NA	NA	200	20	181.972
4							
5					NA		
6	ICP-MS/MS	Y	ORS	O2	5000	5000	32/48
7	NT						
8	ICP-OES-AV	Cs			1600	NA	
9	ICP-OES-RV	Y					181.972
10						NA	
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250	NA	181.972
13					NA		
14						NA	
15	ICP-OES-AV	Y	NA	NA	62.5	5.5	181.975
16	ICP-OES-RV	Y	NA	NA	20	20	180.668
17	ICP-OES-AV-equation	Lu			NA	100	181.972
18							
19							
20	ICP-MS	Sc			2000	2000	34
21	ICP-OES-AV	Te214	NA				181.972nm
22	ICP-OES-AV-buffer	Y			100	100	180.731
23	ICP-OES-RV						178.165
24	ICP-OES-AV	Scandium			10	10	181.972
25					NA	NA	
26					NA	NT	

Table 110 Instrument Conditions Sb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	217.6
2	ICP-MS	In	ORS	He	NA	0.09	121
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	20	217.852
4					NA		
5					NA	NA	
6	ICP-MS	Ir	ORS	NA	NA	5000	121
7	ICP-MS	In115			NA	400	
8	ICP-MS	Rh	CRI		NA	160	
9	ICP-MS	Rh			NA		121
10					NA		
11					NA	NA	
12					NA		
13					NA	NA	
14	ICP-MS	Rh	NA	NA	NA	250	
15	ICP-MS	Rh	NA	NA	NA	625	121
16	ICP-MS	Rh	ORS	He	NA	20	121
17	ICP-MS	103	ORS	He	NA	100	121
18	ICP-MS	Rh	ORS	He	NA	500	123
19					NA	NA	
20	ICP-MS	Rh			NA	2000	121
21	ICP-MS	Rh 103	ORS		NA		121m/z
22	ICP-OES-AV-buffer	Y			NA	100	217.581
23	ICP-OES-RV				NA		206.834
24	ICP-MS	Indium	ORS	He	NA	10	121
25					NA		
26					NA	NA	

Table 111 Instrument Conditions Se

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	196
2	ICP-MS	Ge	ORS	H2	0.09	0.09	78
3	ICP-OES-AV	Lu 261.541	NA	NA	20	20	196.026
4							
5					NA	NA	
6	ICP-MS	Ge	ORS	H2	5000	5000	78
7	ICP-MS	Y89			80000	400	
8	ICP-MS	Rh	CRI		1600	1600	
9	ICP-MS	Rh	ORS	He			78
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		196.026
13					NA	NA	
14	ICP-MS	Rh	NA	He	250	250	
15	ICP-MS	Rh	NA	NA	625	625	82
16	ICP-MS	Ge	ORS	HEHe	20	20	78
17	ICP-MS	72	ORS	He	NA	100	78
18	ICP-MS	Rh	ORS	H2	500	500	78
19	ICP-MS					NA	
20	ICP-MS	Te			2000	2000	82
21	ICP-MS	Rh 103	ORS	HEHe			78m/z
22	ICP-OES-AV-buffer	Y			100	100	196.09
23	ICP-OES-RV						196.026
24	ICP-MS	Tellurium	ORS	H2	10	10	78
25					NA		
26					NA	NA	

Table 112 Instrument Conditions Sn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-OES-SVDV	Lu			0.09	NA	189.925
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	189.927
4						NA	
5					NA	NA	
6	ICP-MS	Rh	ORS	He	5000	NA	118
7	NT					NA	
8	ICP-MS	Rh	CRI		1600	NA	
9	ICP-MS	Rh				NA	118
10						NA	
11	ICPAES	Y			50	NA	
12						NA	
13					NA	NA	
14	ICP-MS	Rh	NA	NA	250	NA	
15	ICP-MS	Ge	NA	NA	625	NA	118
16	ICP-MS	Rh	ORS	He	20	NA	118
17					NA	NA	
18	ICP-MS	Rh	ORS	He	500	NA	118
19	ICP-OES-RV					NA	
20	ICP-MS	Rh			2000	NA	120
21	ICP-MS	Rh 103	ORS			NA	118m/z
22	ICP-OES-AV-buffer	Y			100	NA	189.991
23	ICP-OES-RV					NA	189.925
24	ICP-MS	Indium	ORS	He	10	NA	118
25					NA	NA	
26					NA	NA	

Table 113 Instrument Conditions Sr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	460.7
2	ICP-OES-SVDV	Lu			0.09		421.552
3	ICP-OES-AV	Lu 261.541	NA	NA	200	20	407.771
4							
5					NA	NA	
6	ICP-MS	Y	ORS	He	5000	5000	88
7	ICP-AES	Lu			40	40	407.771
8	ICP-MS	Rh	CRI		1600	160	
9	ICP-MS	Rh					88
10							
11	ICPAES	Y			50	NA	
12							
13					NA	NA	
14	ICP-MS	Rh	NA	NA	250	250	
15	ICP-MS	Rh	NA	NA	625	625	88
16	ICP-MS	Ge	ORS	He	20	20	88
17	ICP-OES-AV-equation	Lu			NA	100	407.771
18	ICP-MS	Rh	ORS	He	500	500	88
19						NA	
20	ICP-MS	Rh			2000	2000	88
21	ICP-MS	Ge 72	ORS				88m/z
22	ICP-OES-AV-buffer	Y			100	100	407.771
23	ICP-OES-RV						430.544
24	ICP-MS	Indium	ORS	He	10	10	88
25					NA		
26					NA	NA	

Table 114 Instrument Conditions Th

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2							
3	ICP-OES-AV	Lu 261.541	NA	NA	20	NA	269.242
4						NA	
5					NA	NA	
6							
7	NT					NA	
8						NA	
9	ICP-MS	Rh				NA	232
10						NA	
11	ICPAES	Y			50	NA	
12						NA	
13					NA	NA	
14						NA	
15	ICP-MS	Ir	NA	NA	625	NA	232
16						NA	
17					NA	NA	
18						NA	
19	ICP-MS					NA	
20	ICP-MS				NT	NA	NA
21	ICP-OES-RV	Y377	NA			NA	283.730nm
22						NA	
23	ICP-MS	Rh, Sc, Ir	ORS			NA	232
24						NA	
25					NA	NA	
26					NA	NA	

Table 115 Instrument Conditions U

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1					NA	NA	NA
2	ICP-MS	Ir	ORS	He	0.09	NA	238
3	ICP-OES-AV	Lu 261.541	NA	NA	NA	NA	385.957
4						NA	
5					NA	NA	
6	ICP-MS	Tb	ORS	NA	5000	NA	238
7	ICP-MS	Ir193			400	NA	
8	ICP-MS	Rh	CRI		160	NA	
9	ICP-MS	Rh				NA	238
10						NA	
11						NA	
12						NA	
13					NA	NA	
14	ICP-MS	Ir	NA	NA	250	NA	
15	ICP-MS	Ir	NA	NA	625	NA	238
16	ICP-MS	Lu	ORS	He	20	NA	238
17					NA	NA	
18	ICP-MS	Lu	ORS	He	500	NA	238
19	ICP-MS					NA	
20	ICP-MS	Lu			2000	NA	238
21	ICP-MS	Ir 193	ORS			NA	238m/z
22						NA	
23	ICP-MS	Rh, Sc, Ir	ORS	He		NA	238
24	ICP-MS	Terbium	ORS	He	10	NA	238
25					NA	NA	
26					NA	NA	

Table 116 Instrument Conditions V

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	318.4
2	ICP-OES-SVDV	Lu			1.9	1.9	292.401
3	ICP-OES-AV	Lu 261.541	NA	NA	200	20	290.881
4							
5					NA	NA	
6	ICP-MS	Ge	ORS	He	5000	5000	51
7	NT						
8	ICP-MS	Rh	CRI		1600	160	
9	ICP-MS	Rh					51
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		311.837
13					NA	NA	
14	ICP-MS	Sc	NA	He	250	250	
15	ICP-MS	Sc	UC	He	625	625	51
16	ICP-MS	Sc	ORS	He	200	20	51
17	ICP-MS	103	ORS	He	NA	100	51
18	ICP-MS	Sc	ORS	He	500	500	51
19						NA	
20	ICP-MS	Sc			2000	NA	51
21	ICP-OES-RV	Y377	NA				292.401 nm
22	ICP-OES-AV-buffer	Y			100	100	292.402
23	ICP-OES-RV			He			311.837
24	ICP-OES-AV	Scandium			10	10	292.401
25					NA		
26					NA	NA	

Table 117 Instrument Conditions Zn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2/S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	AAS	None			NA	20	213.9
2	ICP-OES-SVDV	Lu			0.09	0.09	206.2
3	ICP-OES-AV	Lu 261.541	NA	NA	20	20	206.2
4							
5					NA	NA	
6	ICP-MS	Ge	ORS	He	5000	5000	66
7	ICP-AES	Lu			40	40	213.857
8	ICP-MS	Rh	CRI		160	160	
9	ICP-MS	Rh	ORS	He			66
10							
11	ICPAES	Y			50	NA	
12	ICP-OES-AV	Y 371.029			250		213.857
13					NA	NA	
14	ICP-MS	Rh	NA	He	250	250	
15	ICP-MS	Ge	UC	He	625	625	66
16	ICP-MS	Ge	ORS	He	20	20	66
17	ICP-MS	103	ORS	He	NA	100	66
18	ICP-MS	Sc	ORS	He	500	500	66
19						NA	
20	ICP-MS	Ga	UC	He	1000	1000	66
21	ICP-MS	Ge 72	ORS				66m/z
22	ICP-OES-AV-buffer	Y			100	100	213.856
23	ICP-OES-RV			He			206.2
24	ICP-OES-AV	Scandium			10	10	213.857
25	ICP-OES-AV-buffer				NA		206.2
26					NA	NA	

END OF REPORT