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# Proficiency Test Final Report AQA 20-13 Metals, Nutrients and Anions in Soil

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## 1 SUMMARY

This report presents the results of the proficiency test AQA 20-13 Metals, Nutrients and Anions in Soil. The study focused on the measurement of acid extractable elements: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Th, Tl, U, V and Zn. Measurement of pH, electrical conductivity (EC), water soluble bromide ( $\text{Br}^-$ ), chloride ( $\text{Cl}^-$ ), orthophosphate-P ( $\text{PO}_4^{3-}\text{-P}$ ), sulphate ( $\text{SO}_4^{2-}$ ) 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 two dried biosoil samples and one agricultural soil sample.

Twenty five laboratories registered to participate and twenty four 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 559 z-scores, 519 (93%) were satisfactory with  $|z| \leq 2.0$ .

Of 559  $E_n$ -scores, 453 (81%) were satisfactory with  $|E_n| \leq 1.0$ .

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

In previous studies conducted by NMI for trace elements in garden soil, compost, sediment or clay, relationships were found between the results reported for Al, Cr, Ni, V and extraction regime employed. In the present study, the samples were dried biosoil. Participants used various sample sizes, digestion temperatures and digestion times, there was no relationship evident between the extraction method employed and the results reported for targeted analytes.

Measurement of low level Na in soil presented analytical difficulty to participating laboratories.

- iii. *evaluate within laboratory reproducibility;*

Sample S3 of the present study was distributed as Sample S3 of AQA 20-02. Although the assigned values set for the two samples were not significantly different, in some cases, the reported results varied greatly.

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

On average participants' performance remained fairly consistent.

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

Of 586 numerical results, 538 (92%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 3.

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

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

## **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 inter-laboratory comparison."<sup>1</sup> NMI PT studies target chemical testing in areas of high public significance such as trade, environment and food safety. NMI offers studies in:

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

AQA 20-13 is the 27<sup>th</sup> 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;
- evaluate within-laboratory reproducibility;
- compare the performance of participant laboratories with their past performance; 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.<sup>2</sup> The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.<sup>3</sup> These documents have been prepared with reference to ISO Standard 17043<sup>1</sup> and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.<sup>4</sup>

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

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

## **3 STUDY INFORMATION**

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

The 47 tests were selected from those for which an investigation level is published in the Guideline on the Investigation Levels for Soil and Groundwater, promulgated by the National Environmental Protection Council (NEPC)<sup>5</sup> and from analytes commonly measured in soil.

### **3.2 Participation**

Twenty-five laboratories participated and twenty-four submitted results.

The timetable of the study was:

Invitation issued: 03 August 2020  
Samples dispatched: 31 August 2020  
Results due: 29 September 2020  
Interim report issued: 30 September 2020

### **3.3 Test Material Specification**

Three samples were provided for analysis:

- Sample S1 was 20 g of dried biosoil;
- Sample S2 was 20 g of dried biosoil; and
- Sample S3 was 75 g of dried agricultural soil, previously distributed as Sample S3 of proficiency testing study AQA 20-02.

### **3.4 Laboratory Code**

All participant laboratories were assigned a confidential code number.

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

Test samples from previous studies have been demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. Therefore, only a partial homogeneity test was conducted for all elements in S1, S2 and S3 with the exception of Th in S1, Tl in S2 and 2M KCl extractable ammonium nitrogen ( $\text{NH}_4^+ \text{-N}$ ) and 2M KCl extractable nitrate nitrogen ( $\text{NO}_3^- \text{-N}$ ), EC, pH, Na and S in S3. The results from the partial homogeneity test for these samples are reported in the present study as the homogeneity value.

The preparation, analysis and homogeneity testing of the study samples 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.

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

The samples were dispatched by courier on 31 August 2020.

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 Sample S3 for 2M KCl Extractable ( $\text{NO}_3^- \text{-N}$ ) and ( $\text{NH}_4^+ \text{-N}$ ), participants are asked to follow the extraction procedure described below:

"Prepare a 1:10 w/v soil/2M KCl extracting solution. For example, weigh 5 g of soil into a suitable bottle or jar and add 50 mL of 2M KCl extracting solution. Mechanically shake (end-over-end preferred), at room temperature for 1 h. Allow around 20-30 min for soil to settle and clarify and then take a known aliquot for the measurement technique employed. Further dilution of the aliquot may be required."

Measure the analytes using a colorimetric method; and 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 ( $\text{NH}_4^+$ -N) and 2M KCl extractable nitrate-N ( $\text{NO}_3^-$ -N).

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

SAMPLE S1 (biosoil)		SAMPLE S2 (biosoil)		SAMPLE S3 (agricultural soil)	
Test Acid Extractable	Approximate Conc. Range mg/kg	Test Acid Extractable	Approximate Conc. Range mg/kg	Test	Approximate Conc. Range mg/kg
As	0.5-20	Al	250-10000	Ca (acid extractable)	400-3000
Bi	0.5-20	Ag	0.5-20	Fe (acid extractable)	3000-12000
Cd	0.5-20	B	10-400	K (acid extractable)	200-500
Cr	10-400	Ba	10-400	Mg (acid extractable)	100-1000
Cs	0.05-2	Be	0.05-2	Na (acid extractable)	20-200
Cu	25-1000	Co	0.5-20	P (acid extractable)	100-1000
Hg	0.5-20	Ga	0.5-20	S (acid extractable)	NA
La	0.5-20	Li	0.5-20	Sr (acid extractable)	0.5-20
Mn	25-1000	Mo	0.5-20	Water Soluble Bromide ( $\text{B}^-$ )- 1:5 soil/water extract	0.5-20
Ni	10-400	Sb	0.5-20	Water Soluble Chloride ( $\text{Cl}^-$ )- 1:5 soil/water extract	20-200
Pb	10-400	Sn	10-400	Water Soluble Orthophosphate-P ( $\text{PO}_4^{3-}$ -P) - 1:5 soil/water extract	0.5-20
Rb	0.5-20	Sr	10-400	Water Soluble Sulphate ( $\text{SO}_4^{2-}$ ) - 1:5 soil/water extract	20-200
Se	0.5-20	Tl	0.05-2	pH of 1:5 soil/water suspension	NA
Th	0.05-2	U	0.05-2	EC of 1:5 soil/water extract ( $\mu\text{S}/\text{cm}$ )	>500 $\mu\text{S}/\text{cm}$
Zn	50-2000	V	0.5-20	2M KCl Extractable (Nitrate-N)	NA
				2M KCl Extractable (Ammonium-N)	NA
				Total Kjeldahl nitrogen (TKN)	400-3000

NA = Not Available

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

### 3.9 Interim Report

An interim report was emailed to participants on 30 September 2020.

## 4 PARTICIPANT LABORATORY INFORMATION

### 4.1 Test Method Summaries

Summaries of test methods are transcribed in Tables 1 to 8.

Table 1 Methodology for Acid Extractable Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO <sub>3</sub> (mL)	Vol. HCl (mL)	Vol. HNO <sub>3</sub> (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H <sub>2</sub> O <sub>2</sub> (mL)	Other (mL)
1	USEPA 3050B	0.5	95	120	3	3				1 (H <sub>2</sub> O)
2		2	95	180	2	6				
3	USEPA method 200.2 Revision 2.8	1	95	60			2		2	10 (HCl (1:4))
4	AS 4479.2-1997, AS4479.4-1999	0.5	95	120	1.25	3.75				
5	USEPA Method 3050	2.5	90	120	2	6				
6	200.2 Revision 2.8	1	95 ± 5	60	2	10			2	
7	USEPA-6010C (Except Mercury by USEPA-7471B)	ICP=1g, FIMS=0.5g	95		5	5		3		
9	USEPA Method 200.2	1	95	60			2	10	2	
10	EPA (Environmental Protection Agency) 1994 Method 200.8		109	60	800	400				1200 (H <sub>2</sub> O)
11	ICPOES/ICPMS/AFS In-house methods referenced to USEPA 6010,6020 and 7474	1	95	90	2	3			2	
12	In house referencing APHA 3125	0.4	120	60	2.5	7.5				
13	USEPA 3051A (Modification)	1	170	15			8	2		
14	EPA Method 3050B Acid Digestion of Sediments, Sludges and Soils	0.5	85	240	5	5				
15	US EPA 200.2 adaption for Hot Block	~0.5000gm	95/85	30/30	3	3			2	
16	USEPA3050	1	95	60	10				6	
17		1	112.5	120	2.5	7.5				
18*	In-house	1	98	90	3	3				
19*		1	95 - 100	120	3	3				
20*	In-house based on US EPA 3051 acid ratio but using similar temperature to US EPA 200.2		80	60	6	2				
21	US-EPA Method 200.2	1	95	50	2	2				10 (H <sub>2</sub> O)
23	In-house	2.16	95	90	5	5			5	
24	USEPA Method 200.2	1	95	60			2	10	2	
25*	USEPA 200.7	1	95	30	2	2				

\*Additional information in Table 8

Table 2 Methodology for Total Kjeldahl Nitrogen

Lab. Code	Method Reference	Digestion	Distillation	Measurement Method	Instrument
1	Inhouse	Yes	No	Colorimetric – Phenate Method	FIA
2		Yes		Colorimetric – Phenate Method	DA
3	APHA 4500	Yes		Colorimetric – Phenate Method	DA
6	APHA 22 <sup>nd</sup> edition 4500 Norg A & D with Jirka Modification- Jirka et al. (1976) and the appropriate Discrete Analyser method.	Yes	No	Colorimetric – Phenate Method	DA
9	APHA 4500 Norg, A & D	Yes	No	Colorimetric – Salicylate Method	DA
12	In House	No	No	TKN = TN-NOx (Dumas Combustion)	LECO
13	APHA Method 4500-N Org B and Method 4500-NH3 F	Yes	Yes	Colorimetric – Phenate Method	DA
14	European Standard – Determination of Kjeldahl Nitrogen in soil, biowaste and sewage sludge 2005-08	Yes	Yes	Titrimetric Method	Buchi
16	APHA4500B	Yes	Yes	Titrimetric Method	Manual Analysis
17	Soil Chem Methods Australasia (Rayment and Lyons) and EPA Methods 351.2 and 365.3	Yes		Colorimetric – Salicylate Method	DA
19	APHA 4500-N B, C	Yes	Yes	Titrimetric Method	Foss Auto Distillation and Titration
24	APHA 4500 –Norg. A & D	Yes	No	Colorimetric – Salicylate Method	DA

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

Lab. Code	Method Reference		Sample Mass (g)	Extraction Solution 2M KCl Volume (mL)	Shake time (hours)	Measurement Method		Measurement Instrument
	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N				NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	
2			10	100	20	Colorimetric – Phenate Method	Colorimetric – Vanadium III Method	DA DA
12	In House	In House	2	20	1	Colorimetric – Salicylate Method	Colorimetric – Vanadium III Method	FIA FIA
13	7C2a	7B1a	3	30	1	Colorimetric – Salicylate Method	Colorimetric-Sulphanilamide-NEDD Hydrazine Reduction	SFA SFA
14			10	50	1	Colorimetric – Phenate Method	Colorimetric – Phenate Method	FIA FIA
16	APHA4500G	APHA4500F	10	100	1	Colorimetric – Phenate Method	Colorimetric-Sulphanilamide-NEDD Cd Reduction	FIA FIA

Lab. Code	Method Reference		Sample Mass (g)	Extraction Solution 2M KCl Volume (mL)	Shake time (hours)	Measurement Method		Measurement Instrument	
	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N				NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N
17	Australian Soil and Land Survey Handbook: Australian Laboratory Handbook of Soil and Water Chemical Methods, method 7C2. G. E. Rayment and F. R. Higginson. 1992	Australian Soil and Land Survey Handbook: Australian Laboratory Handbook of Soil and Water Chemical Methods, method 7C2. G. E. Rayment and F. R. Higginson. 1992	3	30	1	Colorimetric – Phenate Method	Colorimetric-Sulphanilamide-NEDD Cd Reduction	DA	DA
19	Seal	Seal	5	50	1	Ammonia reacts with o-phthalaldehyde at 75°C in the presence of borate buffer and sodium sulphite to form a fluorescent species. The fluorescence is measured at 460 nm following excitation at 370 nm	Colorimetric-Sulphanilamide-NEDD Cd Reduction	SFA	SFA
22	7C2b	7C2b	10	100	1	Colorimetric – Salicylate Method	Colorimetric-Sulphanilamide-NEDD Cd Reduction	FIA	FIA

Table 4 Methodology for Water Soluble Br<sup>-</sup>

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2		10	100	1	ICP-Method	ICP-MS
3	APHA 4110	10	50	1	Ion Chromatographic Method	IC
6	APHA 4110	10	50	1	Ion Chromatographic Method	IC
13	APHA 4110B	10	50	1	Ion Chromatographic Method	IC
14		10	50	1	Ion Chromatographic Method	IC
17		5	25	1	Ion Chromatographic Method	IC
18	In-house	5	25	3	Ion Chromatographic Method	IC
19		4	20	1	Ion Chromatographic Method	IC

**Table 5 Methodology for Water Soluble Cl<sup>-</sup>**

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2		10	100	1	Ferricyanide Colorimetric Method	DA
3	APHA 4110	10	50	1	Ion Chromatographic Method	FIA
6	APHA 4500 - Cl	10	50	1	Ferricyanide Colorimetric Method	DA
9	APHA 4500-Cl <sup>-</sup> E and others	10	50	1	Mercuric Thiocyanate	DA
12		2	10	1	Mercuric Thiocyanate	Plate Reader
13	APHA 4110B	10	50	1	Ion Chromatographic Method	IC
14		10	50	1	Mercuric Thiocyanate	DA
16	APHA4110B	10	50	1	Ion Chromatography	IC
17		5	25	1	Ion Chromatographic Method	IC
18	In-house	5	25	3	Ion Chromatographic Method	IC
19		4	20	1	Ion Chromatographic Method	IC
22	5A2b	8	40	1	Ferricyanide Colorimetric Method	FIA
24	APHA 4500	10	50	1	Mercuric Thiocyanate	DA

**Table 6 Methodology for Water Soluble Orthophosphate-P**

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2		10	100	1	Ascorbic Acid Colorimetric Method	DA
3	APHA 4110	10	50	1	Ion Chromatographic Method	FIA
6	APHA 4500 - P	10	50	1	Ascorbic Acid Colorimetric Method	DA
9	APHA -P A, B & F	10	50	1	Ascorbic Acid Colorimetric Method	DA
12		2	10	1	Vanadomolybdophosphoric Colorimetric Method	FIA
13	APHA 4500-P G	10	50	1	Ascorbic Acid Colorimetric Method	FIA
14		10	50	1	Ion Chromatographic Method	IC
16	APHA4500F	10	50	1	Ascorbic Acid Colorimetric Method	FIA
19		4	20	1	Ascorbic Acid Colorimetric Method	DA
24	APHA 4500	10	50	1	Ascorbic Acid Colorimetric Method	DA

**Table 7 Methodology for Water Soluble SO<sub>4</sub><sup>2-</sup>**

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
2		10	100	1	Turbidimetric Method	DA
3	APHA 4110	10	50	1	Ion Chromatographic Method	IC
6	USEPA 200.2	10	50	1	ICP-Method	ICP-OES
9	APHA 4500-SO <sub>4</sub> <sup>2-</sup> E and others	10	50	1	Turbidimetric Method	DA
12		2	10	1	ICP-Method	ICP-OES

Lab. Code	Method Reference	Sample Mass (g)	Water Volume (mL)	Shake Time (hours)	Measurement Method	Measurement Instrument
13	APHA 4110B	10	50	1	Ion Chromatographic Method	IC
16	APHA4110B	10	50	1	Ion Chromatography	IC
17		5	25	1	Ion Chromatographic Method	IC
18	In-house	5	25	3	Ion Chromatographic Method	IC
19		4	20	1	Ion Chromatographic Method	IC
24	In House	10	50	1	ICP-Method	ICP-OES

## 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 8.

Table 8 Additional information

Lab Code	Additional Information
18	Methodology for Acid Extractable Elements: Made up to final volume 40 mL with Milli-Q Water.
19	Methodology for Acid Extractable Elements: 10 mL H <sub>2</sub> O added after 1 hour digestion.
20	Sample S1: We also performed a US EPA 200.2 Digestion on Sample S1, which gave lower results for Cr 21.6 mg/kg & Thorium 0.13 mg/kg, than our in-house block digestion method. All other elements were similar. US EPA 200.2 uses 2 mL of (1+1) nitric acid and 5 mL of (1+4) hydrochloric acid so less acid is used in the digest. Sample S2: We also performed a US EPA 200.2 digestion on Sample 2 which gave lower results for Sn with 29.4 mg/kg and U 0.69 mg/kg, as compared to our in-house method but interestingly higher results for Li 1.03 mg/kg. Methodology for Acid Extractable Elements: Same acid ratio as US EPA 3051, however, samples heated in block digestor unit.
25	Methodology for Acid Extractable Elements: Samples diluted to 50 mL following digestion.

#### 4.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Tables 9 and 10).

Table 9 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation <sup>a</sup>		Guide Document for Estimating MU
		Precision	Method Bias	
1	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis		
2	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control Samples - CRM	CRM	Eurachem/CITAC Guide
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis		Eurachem/CITAC Guide
4	Calculated from Standard deviation and concentration of long term in house QC samples	Control Samples - RM Duplicate Analysis	Instrument Calibration Laboratory Bias from PT Studies	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
5	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Variation in Sample Moisture Content Laboratory Bias from PT Studies Recoveries of SS Standard Purity	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	Eurachem/CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Recoveries of SS	NMI Uncertainty Course
9	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	Eurachem/CITAC Guide
10	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM	Recoveries of SS	
11	Bottom Up (ISO/GUM, fish bone/cause and effect diagram)	Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	Instrument Calibration	Nordtest Report TR537
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	NMI Uncertainty Course
14	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	Laboratory Bias from PT Studies	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
15	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance,

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation <sup>a</sup>		Guide Document for Estimating MU
		Precision	Method Bias	
				Estimating and Reporting MU (Replace TN 33)
16	Top Down Approach	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Variation in Sample Moisture Content Recoveries of SS	Eurochem Guide 2007
17	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
19	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	Instrument Calibration Variation in Sample Moisture Content Recoveries of SS	Nordtest Report TR537
20	Top Down - reproducibility (standard deviation) from PT studies used directly	Duplicate Analysis		Nordtest Report TR537
21	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration Laboratory Bias from PT Studies	Eurachem/CITAC Guide
22	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples - CRM Duplicate Analysis Instrument Calibration	Laboratory Bias from PT Studies	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
23	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM	CRM	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
24	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS	CRM	Eurachem/CITAC Guide
25	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)

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

Table 10 Additional Information for Basis of Uncertainty Estimate

Lab Code	Additional Information
18	Measurement Uncertainty not provided in this round. To be provided in future PT Studies.

#### **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 11.

Table 11 Participants' Comments

Lab Code	Participants' Comments	Study Co-ordinator's Response
16	<p>Service was great and the study is reasonably priced. Just enough time was provided to complete the testing given our current workloads, although the reporting phase does take quite a while to complete, mainly because of the uncertainty calculations involved.</p> <p>This study will be used in future to aid in calculation of MU in the laboratory.</p>	<p>Thank you!</p> <p>One of the aims of the proficiency testing studies is to support laboratories to develop their procedure for estimating uncertainty of their measurement results and to provide participants with information that will be useful in assessing how realistic their uncertainty estimates are.</p>
25	<p>We use these samples for our CRM's. A larger mass of supplied sample would be good.</p>	<p>One of the aims of the proficiency testing studies is to produce materials that can be used in method validation and as control samples.</p> <p>The test samples of this study were checked for homogeneity and are well characterised, both by in-house testing and from the results of the proficiency round and qualifies as reference materials. Surplus of these test samples are available for purchase from NMI.</p>

## 5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 5.1 Results Summary

Participant results are listed in Tables 12 to 58 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 48. An example chart with interpretation guide is shown in Figure 1.

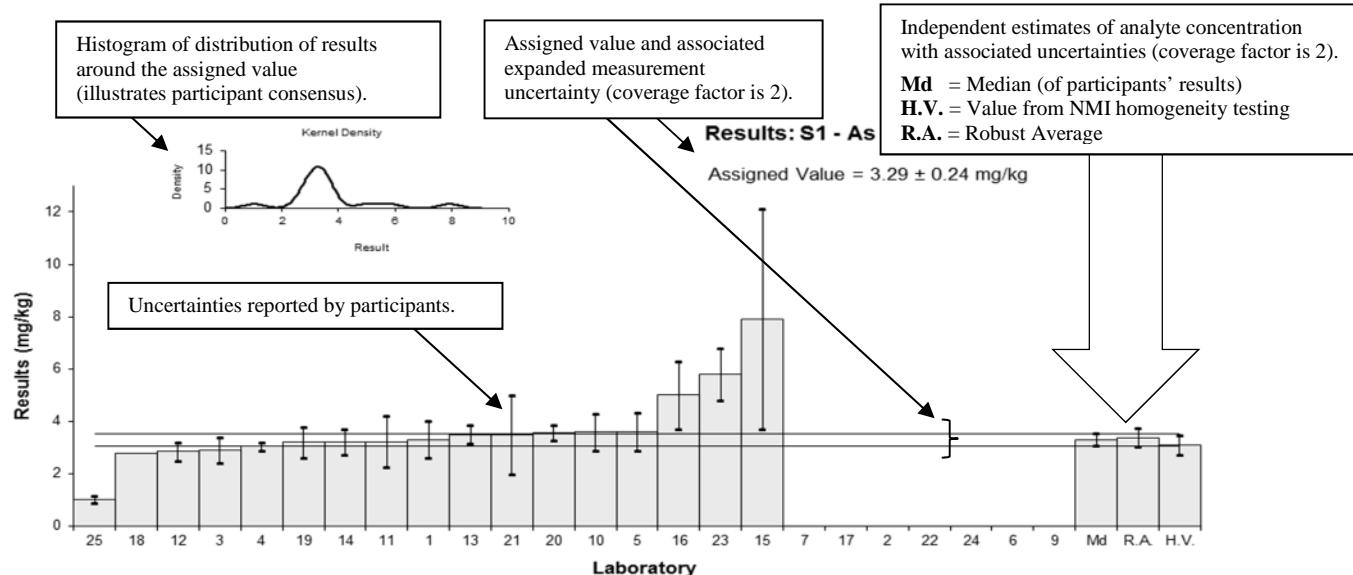


Figure 1 Guide to Presentation of Results

### 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.'<sup>1</sup> 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 inter-laboratory comparisons, ISO13528:2015(E)'.<sup>6</sup>

### 5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2015(E).<sup>6</sup>

### 5.5 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratory variation that in the judgement of the study coordinator would be expected from participants. It is important to note that is not the coefficient of variation of participant results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation.<sup>7</sup> By setting a fixed and realistic value for the PCV, the participant's performance does not depend

on other participants' performance and can be compared from study to study and against achievable performance.

### 5.6 Target Standard Deviation

The target standard deviation ( $\sigma$ ) is the product of the assigned value ( $X$ ) and the performance coefficient of variation (PCV) as presented in Equation 1

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

### 5.7 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
- $\chi$  is participants' result
- $X$  is the study assigned value
- $\sigma$  is the target standard deviation

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

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

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

An example of E<sub>n</sub>-score calculation using data from the present study is given in Appendix 2.

The E<sub>n</sub>-score is complementary to the z-score in assessment of laboratory performance.

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

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

where:

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

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

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

### 5.9 Traceability and Measurement Uncertainty

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

## 6 TABLES AND FIGURES

Table 12

### Sample Details

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	As
<b>Units</b>	mg/kg

### Participant Results

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.3	0.7	0.02	0.01
2	NT	NT		
3	2.9	0.476	-0.79	-0.73
4	3.05	0.16	-0.49	-0.83
5	3.60	0.72	0.63	0.41
6	NT	NT		
7	<3	NR		
9	NT	NT		
10	3.6	0.7	0.63	0.42
11	3.22	0.98	-0.14	-0.07
12	2.85	0.35	-0.89	-1.04
13	3.5	0.35	0.43	0.49
14	3.21	0.5	-0.16	-0.14
15	7.917	4.2	9.38	1.10
16	5.0	1.3	3.47	1.29
17	NT	NT		
18	2.78	NR	-1.03	-2.13
19	3.2	0.6	-0.18	-0.14
20	3.57	0.28	0.57	0.76
21	3.5	1.5	0.43	0.14
22	NT	NT		
23	5.8	1.0	5.09	2.44
24	NT	NT		
25	1.02	0.15	-4.60	-8.02

### Statistics

<b>Assigned Value*</b>	3.29	0.24
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	3.08	0.37
<b>Robust Average</b>	3.39	0.37
<b>Median</b>	3.30	0.23
<b>Mean</b>	3.65	
<b>N</b>	17	
<b>Max.</b>	7.917	
<b>Min.</b>	1.02	
<b>Robust SD</b>	0.61	
<b>Robust CV</b>	18%	

\*Robust Average excluding Laboratories 15, 23 and 25.

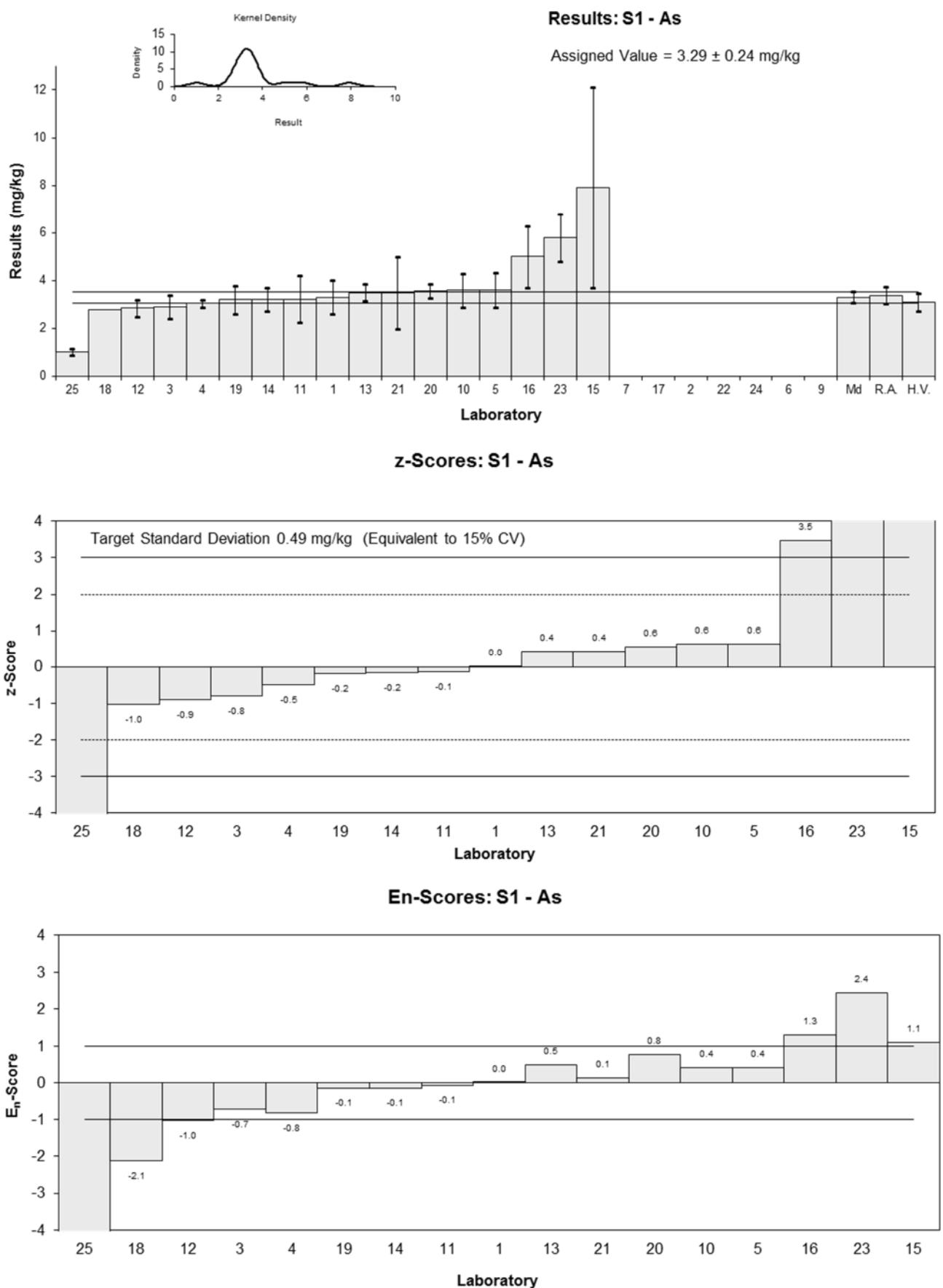


Figure 2

Table 13

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Bi
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.4	0.8	0.24	0.13
2	NT	NT		
3	2.6	NR	-1.38	-1.55
4	3.31	0.33	0.06	0.05
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	3.4	0.7	0.24	0.15
11	3.91	0.78	1.28	0.70
12	2.90	0.40	-0.77	-0.64
13	2.7	0.3	-1.18	-1.09
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	2.9	0.6	-0.77	-0.51
20	3.62	0.03	0.69	0.77
21	4.02	0.63	1.50	0.96
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	3.28	0.44
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	3.50	0.42
<b>Robust Average</b>	3.28	0.44
<b>Median</b>	3.36	0.48
<b>Mean</b>	3.28	
<b>N</b>	10	
<b>Max.</b>	4.02	
<b>Min.</b>	2.6	
<b>Robust SD</b>	0.56	
<b>Robust CV</b>	17%	

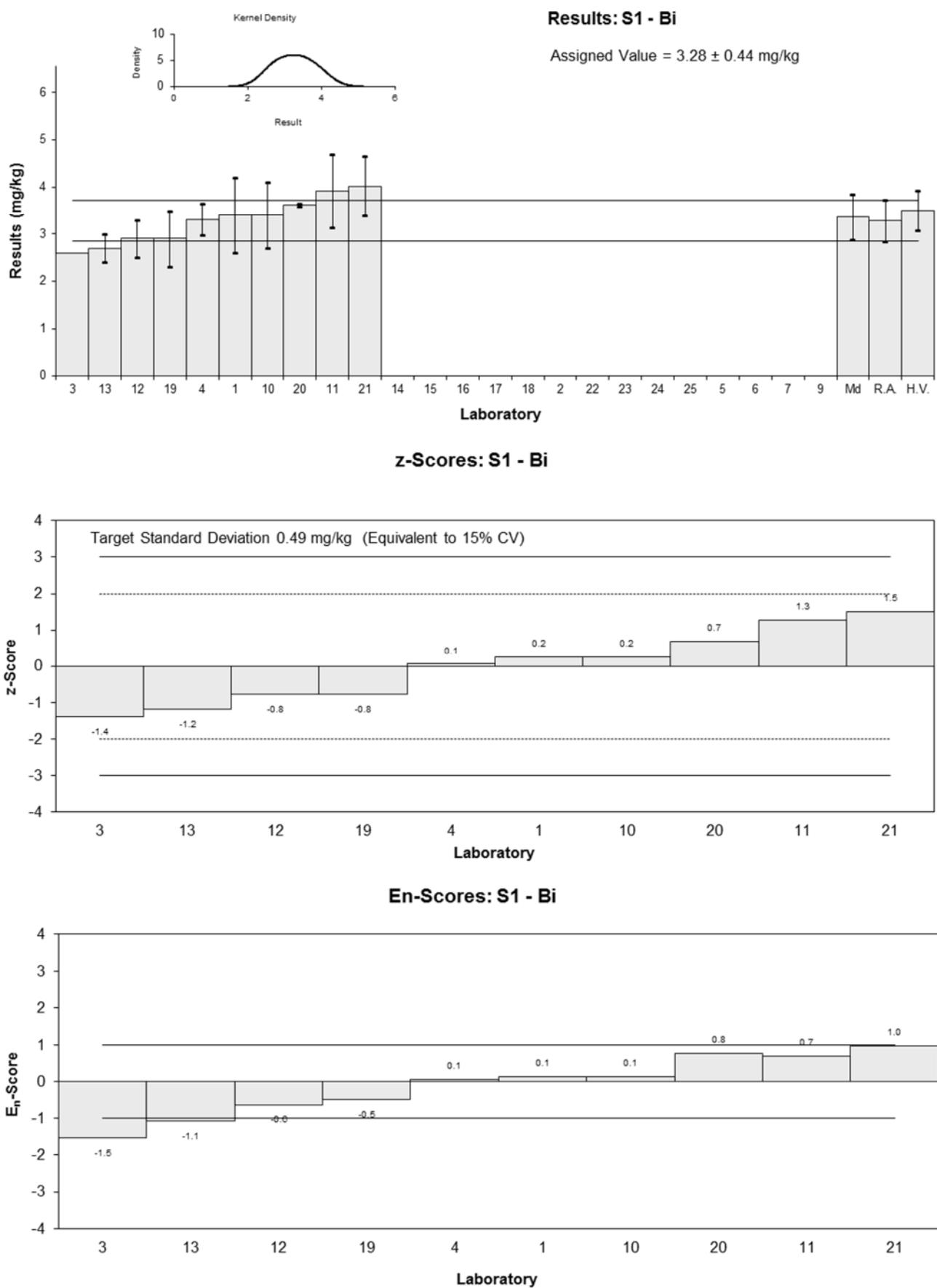


Figure 3

Table 14

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Cd
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.71	0.16	-1.03	-0.76
2	NT	NT		
3	0.7	0.1	-1.11	-1.20
4	0.836	0.13	-0.03	-0.03
5	0.88	0.18	0.32	0.21
6	NT	NT		
7	1.0	0.2	1.27	0.77
9	NT	NT		
10	0.91	0.2	0.56	0.33
11	0.85	0.26	0.08	0.04
12	0.78	0.2	-0.48	-0.29
13	0.78	0.1	-0.48	-0.51
14	0.88	0.1	0.32	0.34
15	0.994	0.5	1.22	0.31
16	0.75	0.15	-0.71	-0.56
17	NT	NT		
18	0.66	NR	-1.43	-2.95
19	0.83	0.17	-0.08	-0.06
20	0.88	0.07	0.32	0.43
21	0.85	0.14	0.08	0.07
22	NT	NT		
23	0.9	0.2	0.48	0.29
24	NT	NT		
25	0.91	0.09	0.56	0.64

**Statistics**

<b>Assigned Value</b>	0.840	0.061
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.803	0.096
<b>Robust Average</b>	0.840	0.061
<b>Median</b>	0.850	0.044
<b>Mean</b>	0.839	
<b>N</b>	18	
<b>Max.</b>	1	
<b>Min.</b>	0.66	
<b>Robust SD</b>	0.10	
<b>Robust CV</b>	12%	

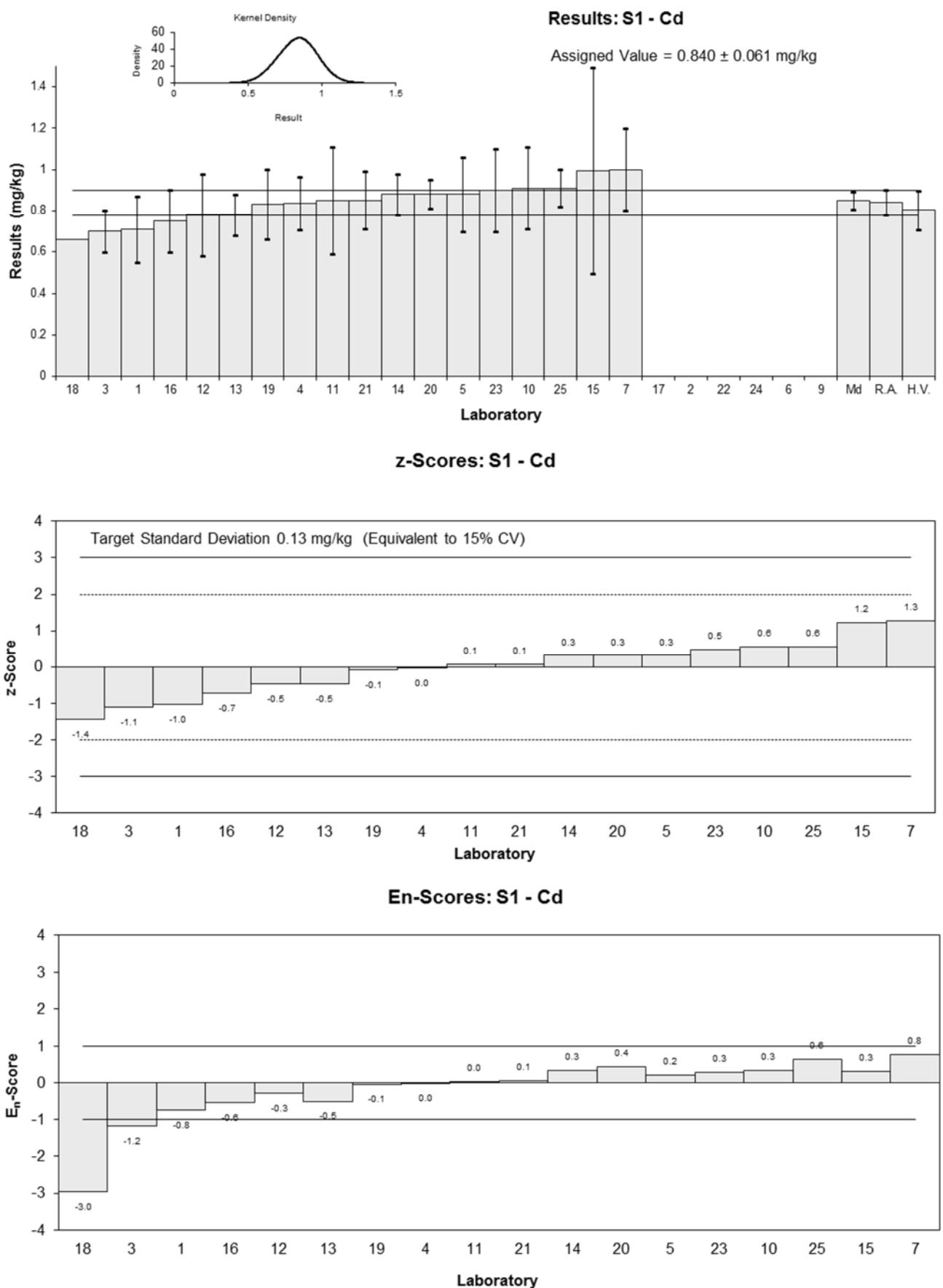


Figure 4

Table 15

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Cr
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	27	6	0.63	0.26
2	NT	NT		
3	20.7	5.79	-1.85	-0.78
4	26.6	2.7	0.47	0.38
5	28.52	5.70	1.23	0.53
6	NT	NT		
7	25	3.7	-0.16	-0.10
9	NT	NT		
10	23.2	4.6	-0.87	-0.45
11	20.6	5.5	-1.89	-0.84
12	26.1	3.5	0.28	0.18
13	22.23	1.7	-1.25	-1.36
14	26.9	4.0	0.59	0.35
15	NT	NT		
16	26	5.7	0.24	0.10
17	NT	NT		
18	25.4	NR	0.00	0.00
19	26	5	0.24	0.11
20	28.7	0.3	1.30	2.03
21	26.7	4.4	0.51	0.28
22	NT	NT		
23	28	8.0	1.02	0.32
24	NT	NT		
25	23	2	-0.94	-0.94

**Statistics**

<b>Assigned Value</b>	25.4	1.6
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	25.5	3.1
<b>Robust Average</b>	25.4	1.6
<b>Median</b>	26.0	0.8
<b>Mean</b>	25.3	
<b>N</b>	17	
<b>Max.</b>	28.7	
<b>Min.</b>	20.6	
<b>Robust SD</b>	2.7	
<b>Robust CV</b>	11%	

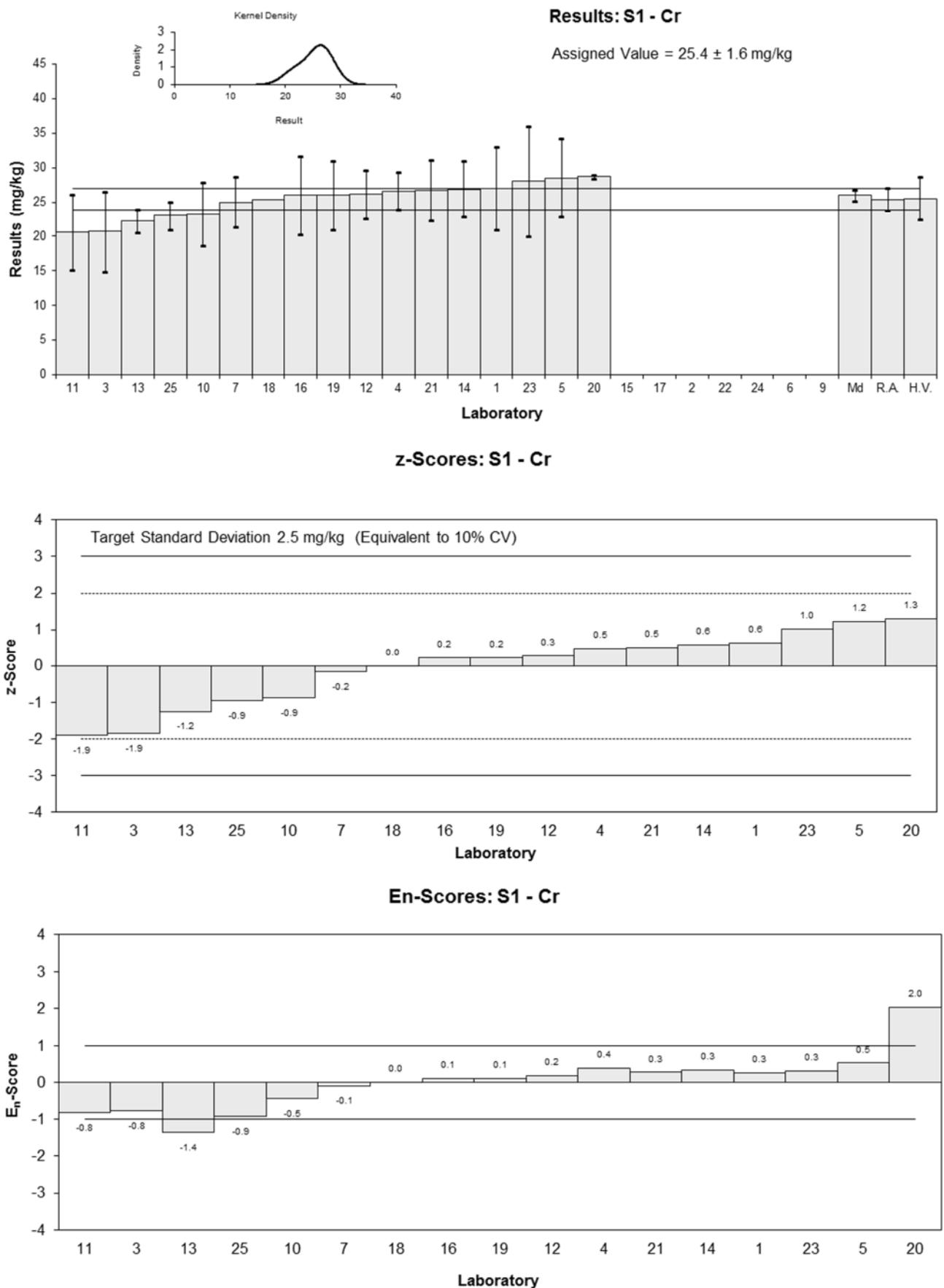


Figure 5

Table 16

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Cs
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NR	NR
2	NT	NT
3	<0.1	NR
4	NT	NT
5	NT	NT
6	NT	NT
7	NT	NT
9	NT	NT
10	0.15	0.03
11	NR	NR
12	NT	NT
13	0.15	0.02
14	NT	NT
15	NT	NT
16	NT	NT
17	NT	NT
18	NT	NT
19	<0.5	NR
20	0.127	0.008
21	<0.2	0.14
22	NT	NT
23	NT	NT
24	NT	NT
25	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.14	0.02
<b>Median</b>	0.15	0.001
<b>Mean</b>	0.14	
<b>N</b>	3	
<b>Max.</b>	0.15	
<b>Min.</b>	0.127	

\*Insufficient data to calculate statistics.

**Results: S1 - Cs**

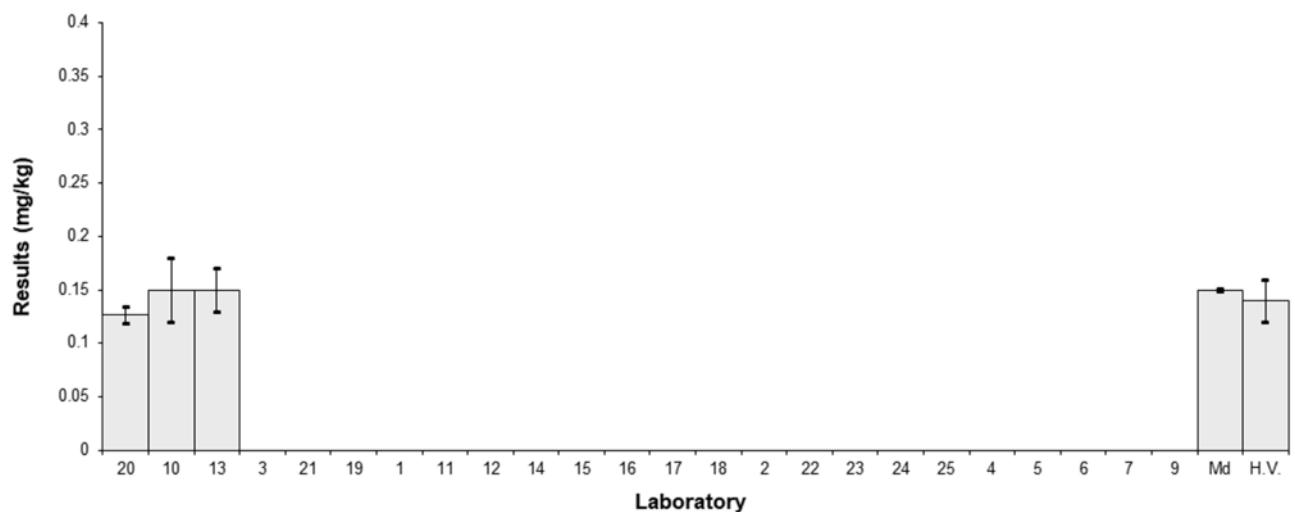


Figure 6

Table 17

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Cu
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	590	120	-0.58	-0.29
2	NT	NT		
3	537	90.4	-1.42	-0.93
4	622	35	-0.06	-0.09
5	582.43	116.49	-0.70	-0.36
6	NT	NT		
7	679.7	85.2	0.86	0.59
9	NT	NT		
10	662.9	132.6	0.59	0.27
11	668	69	0.67	0.56
12	573	60	-0.85	-0.78
13	613	33	-0.21	-0.29
14	615	92.3	-0.18	-0.11
15	701.3	0.5	1.20	2.43
16	590	90	-0.58	-0.38
17	NT	NT		
18	580	NR	-0.73	-1.48
19	600	120	-0.42	-0.21
20	644	5	0.29	0.57
21	629	86	0.05	0.03
22	NT	NT		
23	670	98	0.70	0.43
24	NT	NT		
25	825	50	3.18	3.38

**Statistics**

<b>Assigned Value</b>	626	31
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	610	73
<b>Robust Average</b>	626	31
<b>Median</b>	619	27
<b>Mean</b>	632	
<b>N</b>	18	
<b>Max.</b>	825	
<b>Min.</b>	537	
<b>Robust SD</b>	53	
<b>Robust CV</b>	8.5%	

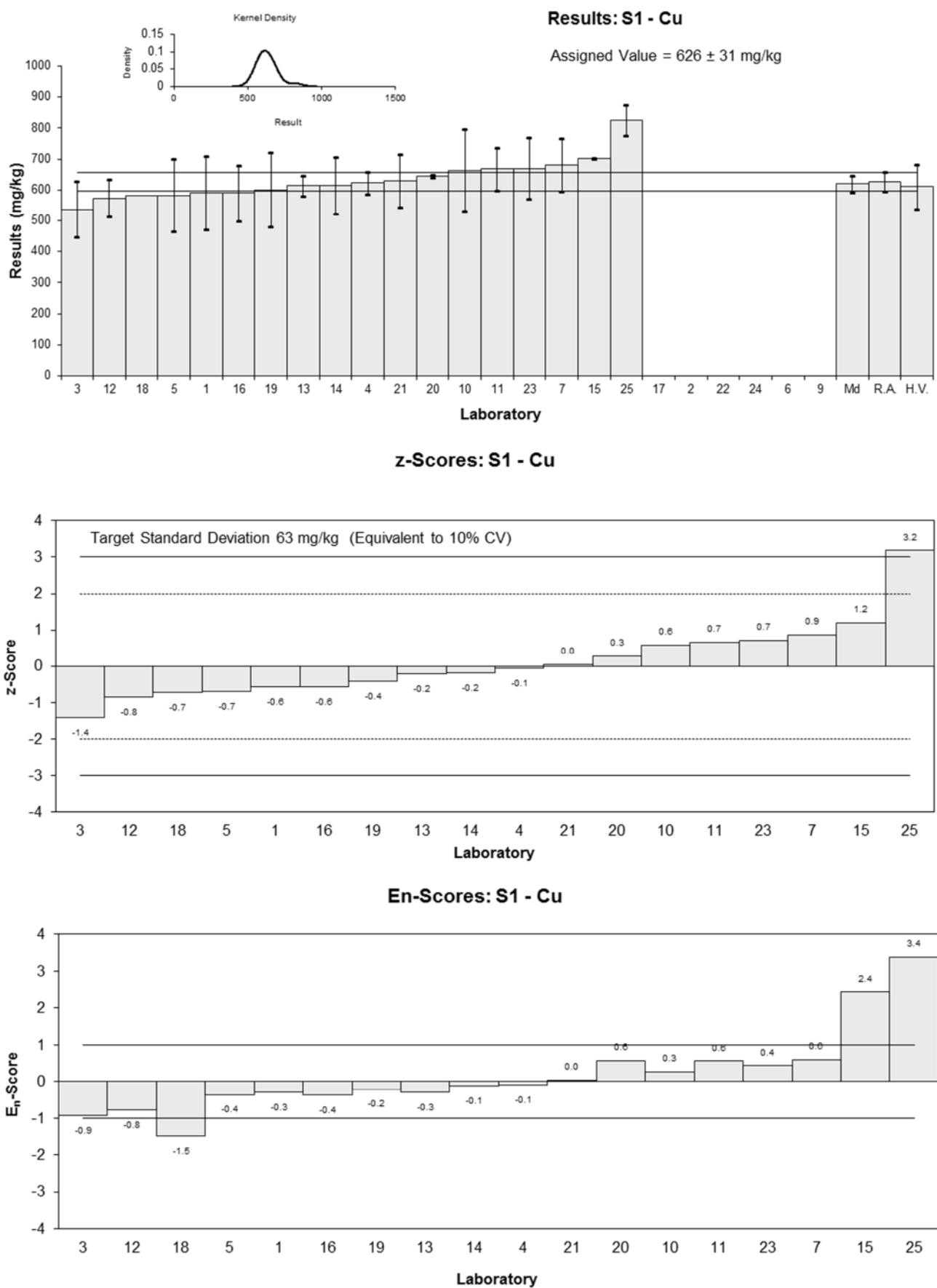


Figure 7

Table 18

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Hg
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.58	0.08	-2.84	-3.16
2	NT	NT		
3	1.0	0.13	-0.07	-0.06
4	1.02	0.1	0.07	0.07
5	0.88	0.18	-0.86	-0.62
6	NT	NT		
7	0.8	0.4	-1.39	-0.51
9	NT	NT		
10	1.1	0.2	0.59	0.39
11	1.02	0.06	0.07	0.08
12	1.42	0.40	2.71	0.99
13	1.01	0.15	0.00	0.00
14	1.10	0.2	0.59	0.39
15	NT	NT		
16	0.55	0.11	-3.04	-2.96
17	NT	NT		
18	1.26	NR	1.65	2.27
19	1.1	0.2	0.59	0.39
20	1.09	0.22	0.53	0.33
21	1.04	0.18	0.20	0.14
22	NT	NT		
23	1.0	0.33	-0.07	-0.03
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	1.01	0.11
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1.00	0.12
<b>Robust Average</b>	1.01	0.11
<b>Median</b>	1.02	0.06
<b>Mean</b>	1.00	
<b>N</b>	16	
<b>Max.</b>	1.42	
<b>Min.</b>	0.55	
<b>Robust SD</b>	0.18	
<b>Robust CV</b>	18%	

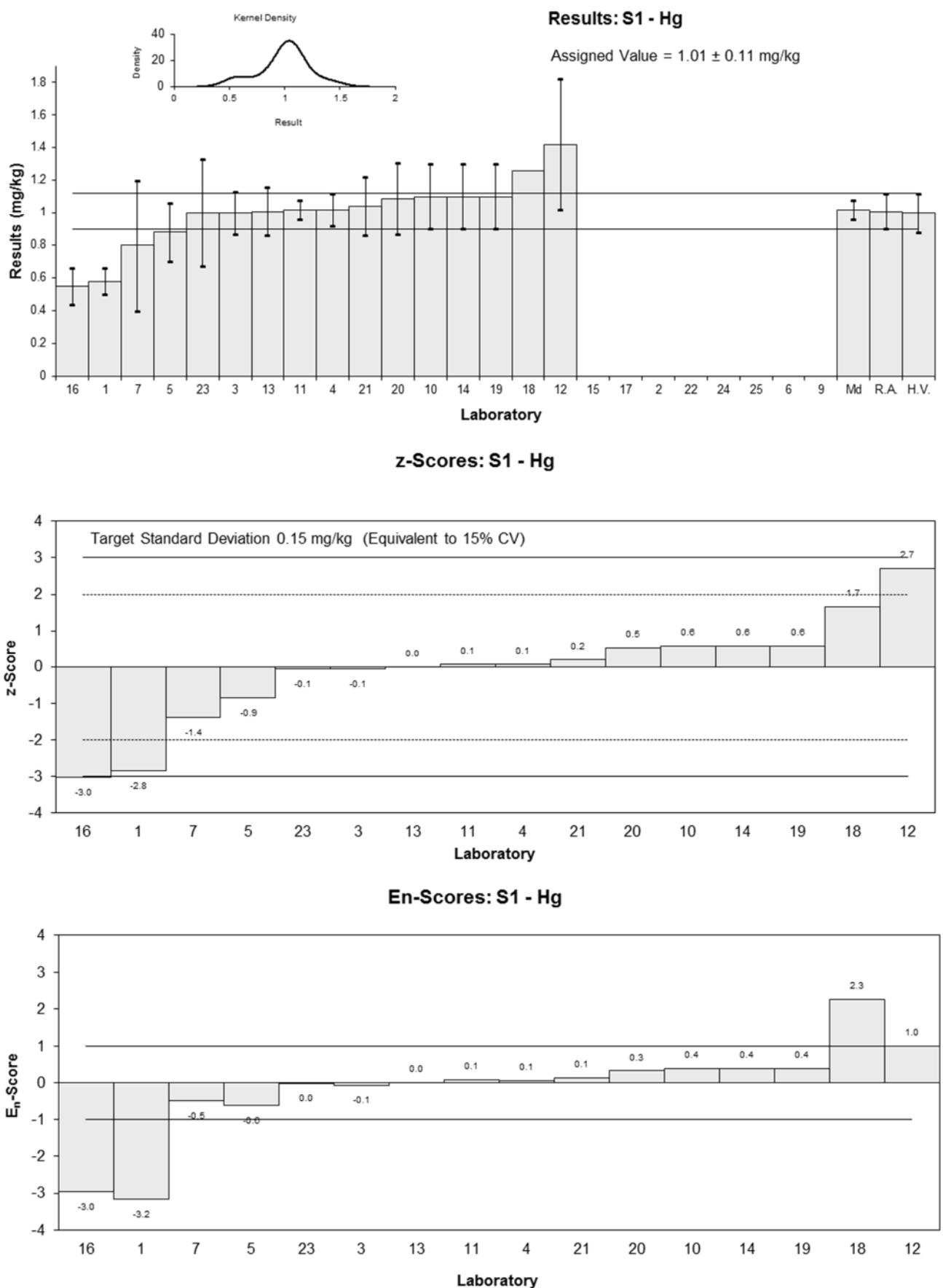


Figure 8

Table 19

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	La
<b>Units</b>	mg/kg

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NR	NR		
2	NT	NT		
3	8.0	NR	-1.08	-1.14
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	9.9	2	1.04	0.43
11	9.07	3.12	0.11	0.03
12	NT	NT		
13	NR	NR		
14	9.04	1.4	0.08	0.04
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	8.9	1.8	-0.08	-0.04
20	9.95	0.06	1.09	1.15
21	9.40	0.77	0.48	0.37
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	7.5	1	-1.64	-1.12

**Statistics**

<b>Assigned Value</b>	8.97	0.85
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	9.3	1.1
<b>Robust Average</b>	8.97	0.85
<b>Median</b>	9.06	0.74
<b>Mean</b>	8.97	
<b>N</b>	8	
<b>Max.</b>	9.95	
<b>Min.</b>	7.5	
<b>Robust SD</b>	0.96	
<b>Robust CV</b>	11%	

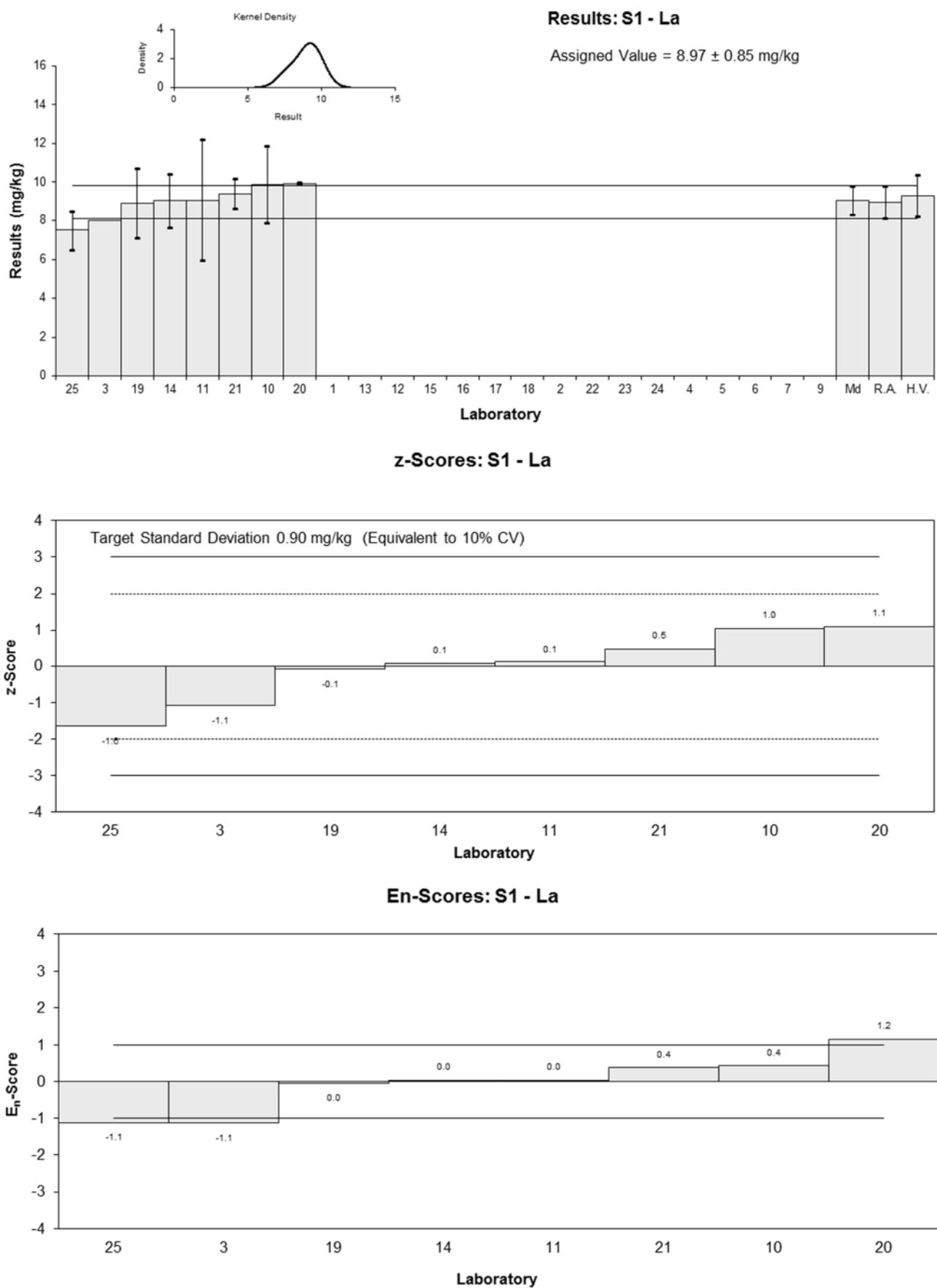


Figure 9

Table 20

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Mn
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	440	90	0.00	0.00
2	NT	NT		
3	408	68.7	-0.73	-0.46
4	455	23	0.34	0.56
5	426.39	85.28	-0.31	-0.16
6	NT	NT		
7	468	68.6	0.64	0.40
9	NT	NT		
10	449.1	89.8	0.21	0.10
11	490	80	1.14	0.62
12	426	50	-0.32	-0.27
13	432	29	-0.18	-0.25
14	440	66.0	0.00	0.00
15	NT	NT		
16	430	81	-0.23	-0.12
17	NT	NT		
18	433	NR	-0.16	-0.50
19	420	80	-0.45	-0.25
20	442	4	0.05	0.14
21	488	49	1.09	0.94
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	418	20	-0.50	-0.90

**Statistics**

<b>Assigned Value</b>	440	14
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	477	57
<b>Robust Average</b>	440	14
<b>Median</b>	437	9
<b>Mean</b>	442	
<b>N</b>	16	
<b>Max.</b>	490	
<b>Min.</b>	408	
<b>Robust SD</b>	22	
<b>Robust CV</b>	5%	

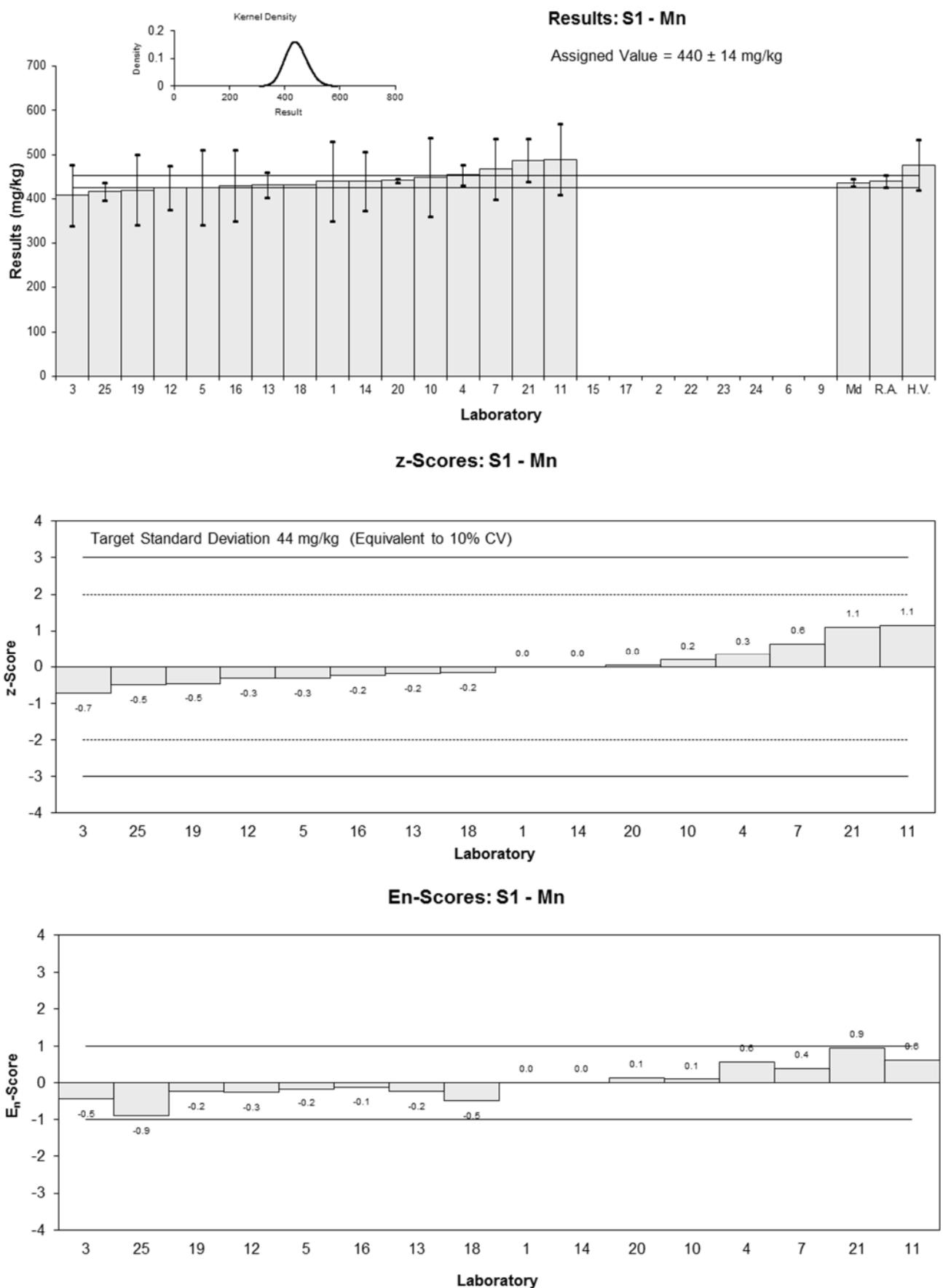


Figure 10

Table 21

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Ni
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	27	6	0.04	0.02
2	NT	NT		
3	22.3	4.3	-1.71	-1.05
4	27.9	2.8	0.37	0.34
5	26.77	5.35	-0.05	-0.02
6	NT	NT		
7	27.9	6.5	0.37	0.15
9	NT	NT		
10	27.7	5.5	0.30	0.14
11	25.3	6.5	-0.59	-0.24
12	26.5	3.5	-0.15	-0.11
13	25.6	2.8	-0.48	-0.44
14	28.1	4.2	0.45	0.28
15	NT	NT		
16	26	5.3	-0.33	-0.17
17	NT	NT		
18	26.8	NR	-0.04	-0.11
19	28	6	0.41	0.18
20	28.8	0.3	0.71	2.00
21	29.0	4.0	0.78	0.51
22	NT	NT		
23	27	9.9	0.04	0.01
24	NT	NT		
25	23	2	-1.45	-1.78

**Statistics**

<b>Assigned Value</b>	26.9	0.9
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	26.8	3.2
<b>Robust Average</b>	26.9	0.9
<b>Median</b>	27.0	0.8
<b>Mean</b>	26.7	
<b>N</b>	17	
<b>Max.</b>	29	
<b>Min.</b>	22.3	
<b>Robust SD</b>	1.5	
<b>Robust CV</b>	5.6%	

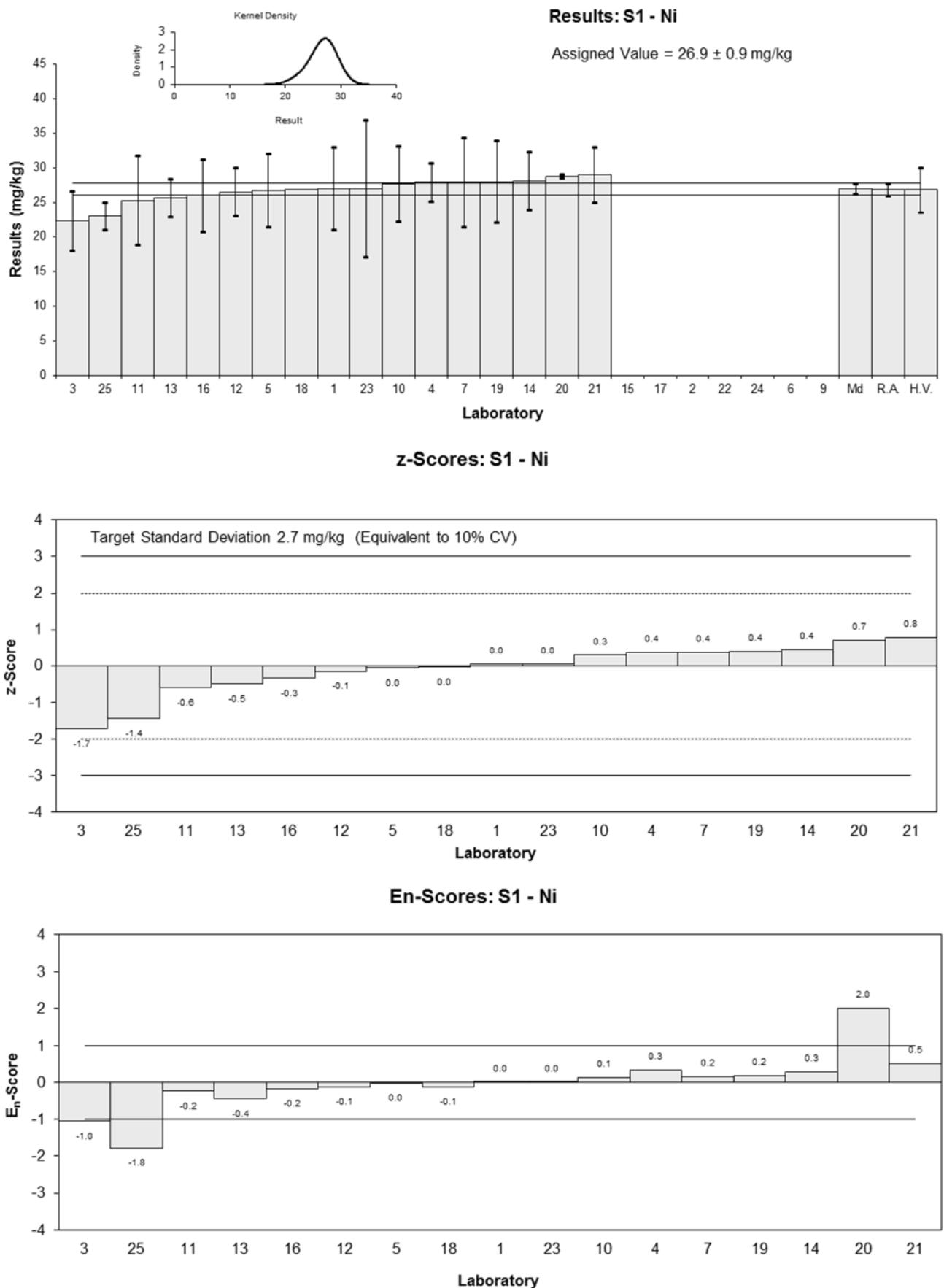


Figure 11

Table 22

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Pb
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	23	5	0.18	0.08
2	NT	NT		
3	19.9	3.31	-1.19	-0.76
4	22.15	2.3	-0.20	-0.17
5	21.53	4.31	-0.47	-0.24
6	NT	NT		
7	26.3	4.1	1.64	0.86
9	NT	NT		
10	24.5	4.9	0.84	0.37
11	23.0	6.3	0.18	0.06
12	20.0	2.5	-1.15	-0.92
13	23	1.3	0.18	0.22
14	23.4	3.5	0.35	0.21
15	24.10	3.3	0.66	0.42
16	23	4.8	0.18	0.08
17	NT	NT		
18	21.5	NR	-0.49	-0.85
19	23	5	0.18	0.08
20	25.6	0.7	1.33	2.03
21	24.7	3.8	0.93	0.52
22	NT	NT		
23	20	4.7	-1.15	-0.53
24	NT	NT		
25	19	2	-1.59	-1.51

**Statistics**

<b>Assigned Value</b>	22.6	1.3
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	22.5	2.7
<b>Robust Average</b>	22.6	1.3
<b>Median</b>	23.0	1.1
<b>Mean</b>	22.6	
<b>N</b>	18	
<b>Max.</b>	26.3	
<b>Min.</b>	19	
<b>Robust SD</b>	2.2	
<b>Robust CV</b>	9.7%	

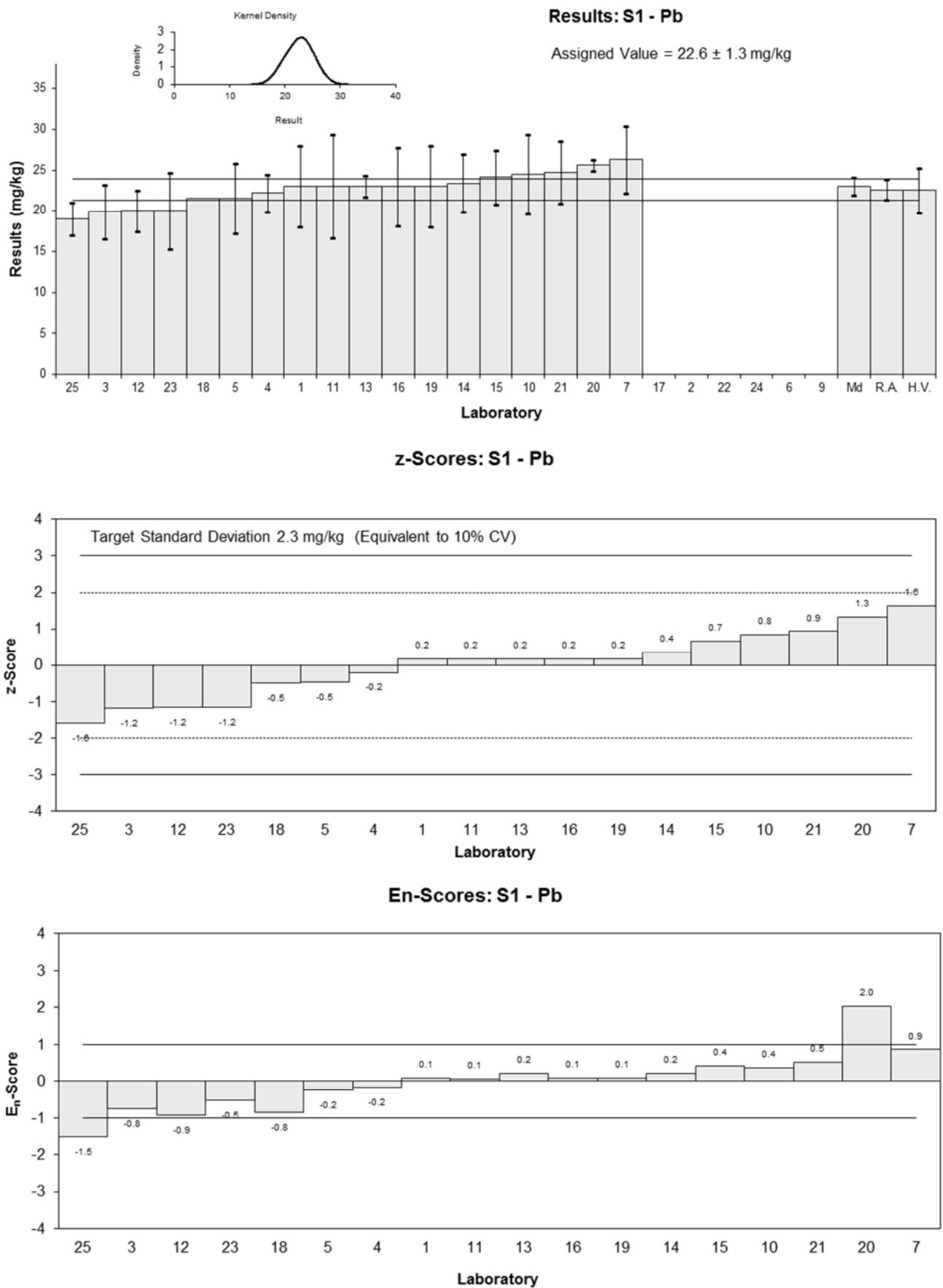


Figure 12

Table 23

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Rb
<b>Units</b>	mg/kg

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NR	NR		
2	NT	NT		
3	8.7	NR	-1.71	-1.38
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	11.4	2.3	0.86	0.34
11	NR	NR		
12	NT	NT		
13	10.3	1	-0.19	-0.12
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	10	2	-0.48	-0.21
20	11.0	0.1	0.48	0.38
21	11.8	1.3	1.24	0.71
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	23	2	11.90	5.24

**Statistics**

<b>Assigned Value*</b>	10.5	1.3
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	11.7	1.4
<b>Robust Average</b>	11.0	1.6
<b>Median</b>	11.0	1.1
<b>Mean</b>	12.3	
<b>N</b>	7	
<b>Max.</b>	23	
<b>Min.</b>	8.7	
<b>Robust SD</b>	1.7	
<b>Robust CV</b>	15%	

\*Robust Average excluding Laboratory 25.

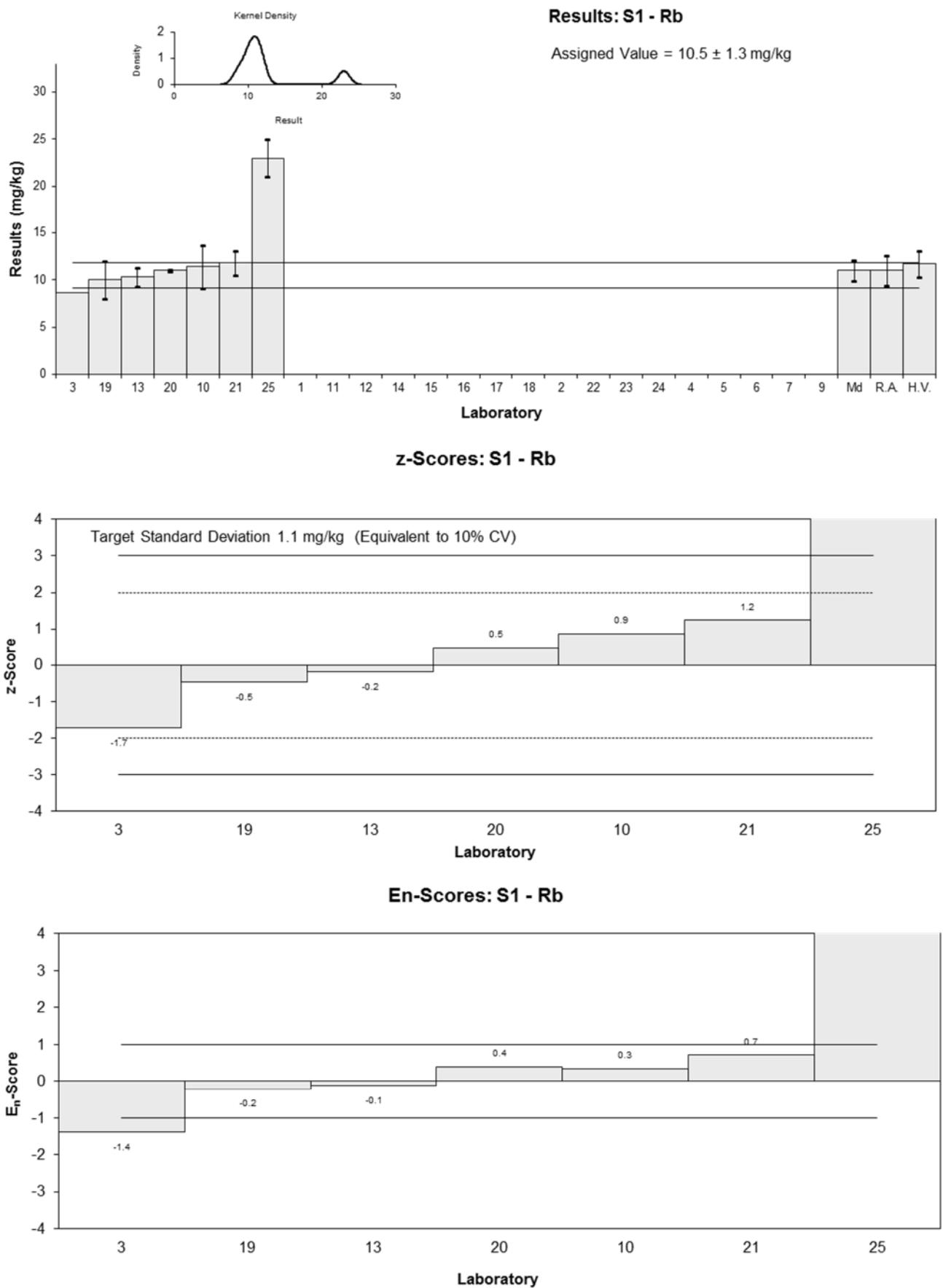


Figure 13

Table 24

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Se
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.8	1.2	0.09	0.04
2	NT	NT		
3	2	0.5	-3.11	-3.11
4	3.24	0.17	-0.91	-1.64
5	4.62	0.92	1.55	0.91
6	NT	NT		
7	8.9	2.5	9.16	2.05
9	NT	NT		
10	3.8	0.8	0.09	0.06
11	3.43	1.32	-0.57	-0.24
12	3.75	0.50	0.00	0.00
13	3.8	0.3	0.09	0.13
14	4.05	0.6	0.53	0.46
15	NT	NT		
16	6.2	1.5	4.36	1.61
17	NT	NT		
18	4.03	NR	0.50	1.08
19	3.6	0.6	-0.27	-0.23
20	3.94	0.14	0.34	0.64
21	3.3	1.5	-0.80	-0.30
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	8.8	1	8.98	4.89

**Statistics**

<b>Assigned Value*</b>	3.75	0.26
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	3.28	0.39
<b>Robust Average</b>	4.00	0.56
<b>Median</b>	3.80	0.24
<b>Mean</b>	4.45	
<b>N</b>	16	
<b>Max.</b>	8.9	
<b>Min.</b>	2	
<b>Robust SD</b>	0.90	
<b>Robust CV</b>	23%	

\*Robust Average excluding Laboratories 3, 7, 16 and 25.

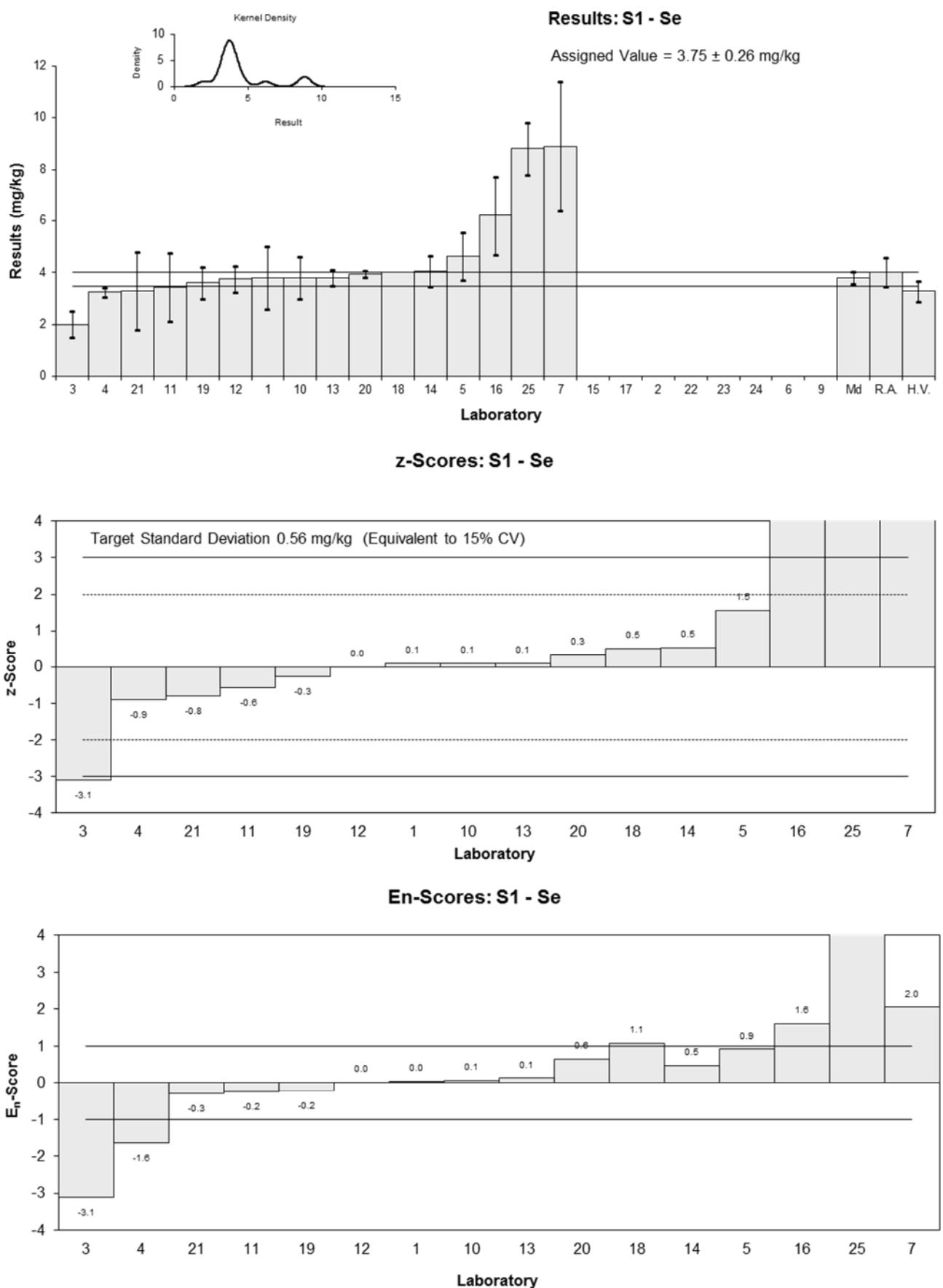


Figure 14

Table 25

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Th
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NR	NR
2	NT	NT
3	0.1	NR
4	0.183	0.028
5	NT	NT
6	NT	NT
7	NT	NT
9	NT	NT
10	NT	NT
11	NR	NR
12	NT	NT
13	<0.5	0.5
14	NT	NT
15	NT	NT
16	NT	NT
17	NT	NT
18	NT	NT
19	<0.5	NR
20	0.31	0.08
21	NT	NT
22	NT	NT
23	NT	NT
24	NT	NT
25	2.3	.5

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Median</b>	0.25	0.25
<b>Mean</b>	0.723	
<b>N</b>	4	
<b>Max.</b>	2.3	
<b>Min.</b>	0.1	

\*Insufficient data to calculate statistics.

**Results: S1 - Th**

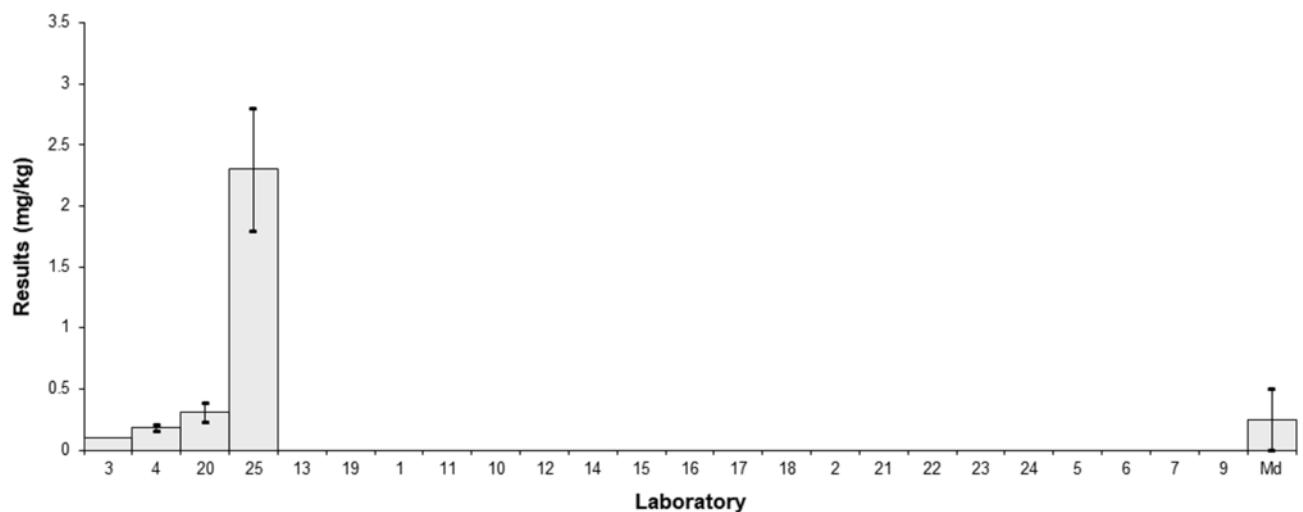


Figure 15

Table 26

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Zn
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	570	120	-0.70	-0.35
2	NT	NT		
3	516	80	-1.58	-1.14
4	589	59	-0.39	-0.37
5	658.50	131.70	0.74	0.34
6	NT	NT		
7	626	114.4	0.21	0.11
9	NT	NT		
10	651.2	130.2	0.62	0.29
11	653	77	0.65	0.49
12	588	60	-0.41	-0.38
13	612	45	-0.02	-0.02
14	647	97.1	0.55	0.34
15	637.0	0.7	0.39	0.86
16	540	88	-1.19	-0.79
17	NT	NT		
18	697	NR	1.37	3.00
19	640	130	0.44	0.20
20	606	4	-0.11	-0.25
21	637	45	0.39	0.45
22	NT	NT		
23	560	170	-0.86	-0.31
24	NT	NT		
25	594	50	-0.31	-0.33

**Statistics**

<b>Assigned Value</b>	613	28
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	506	61
<b>Robust Average</b>	613	28
<b>Median</b>	619	22
<b>Mean</b>	612	
<b>N</b>	18	
<b>Max.</b>	697	
<b>Min.</b>	516	
<b>Robust SD</b>	47	
<b>Robust CV</b>	7.7%	

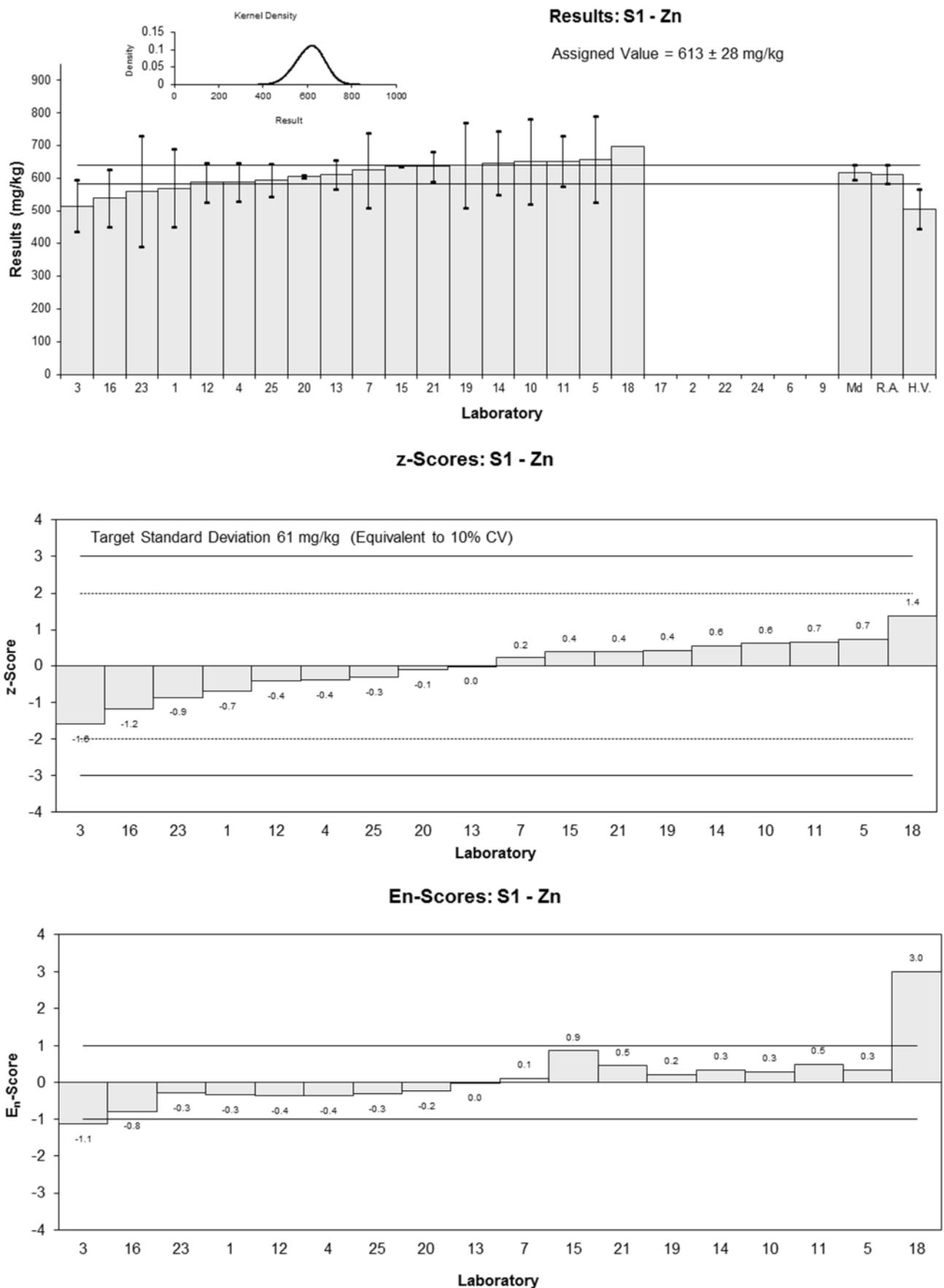


Figure 16

Table 27

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Ag
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2.7	0.8	-0.14	-0.07
2	NT	NT		
3	3.0	0.68	0.58	0.34
4	2.655	0.399	-0.25	-0.24
5	3.39	0.68	1.52	0.89
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	2.88	0.29	0.29	0.34
11	2.25	0.71	-1.23	-0.69
12	2.76	0.35	0.00	0.00
13	NT	NT		
14	2.90	0.4	0.34	0.31
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	2.43	NR	-0.80	-1.65
19	2.6	0.5	-0.39	-0.30
20	2.99	0.10	0.56	1.03
21	3.00	0.71	0.58	0.33
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	2.5	.2	-0.63	-0.92

**Statistics**

<b>Assigned Value</b>	2.76	0.20
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2.85	0.34
<b>Robust Average</b>	2.76	0.20
<b>Median</b>	2.76	0.21
<b>Mean</b>	2.77	
<b>N</b>	13	
<b>Max.</b>	3.39	
<b>Min.</b>	2.25	
<b>Robust SD</b>	0.29	
<b>Robust CV</b>	11%	

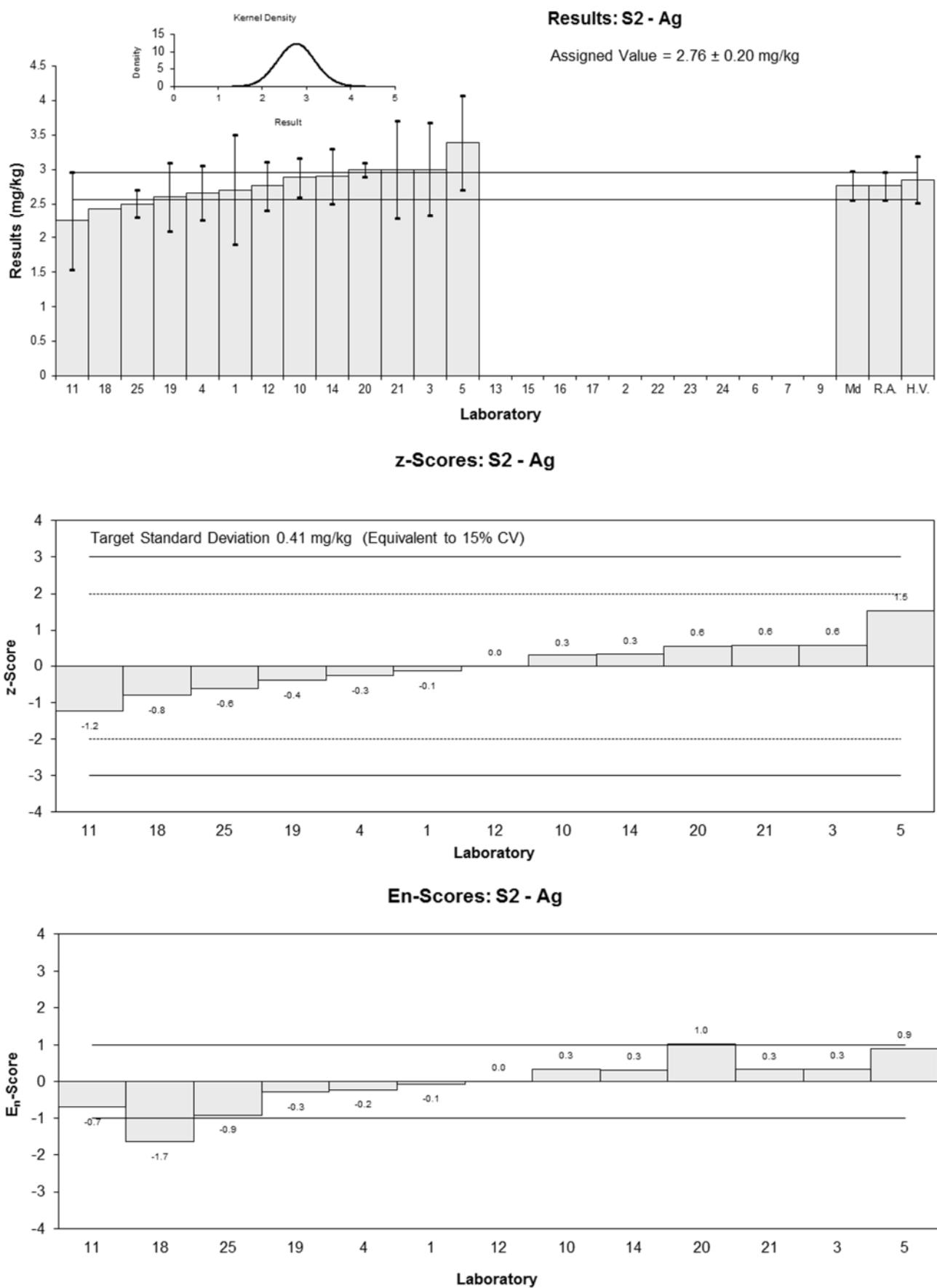


Figure 17

Table 28

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Al
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3700	800	-0.61	-0.29
2	NT	NT		
3	4060	801	0.30	0.14
4	4172	418	0.59	0.48
5	3990.18	798.04	0.13	0.06
6	NT	NT		
7	3689	193.2	-0.64	-0.81
9	NT	NT		
10	4500	900	1.42	0.60
11	4460	470	1.32	0.99
12	4180	450	0.61	0.47
13	NT	NT		
14	3478	522	-1.17	-0.80
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	3893	NR	-0.12	-0.20
19	3940	790	0.00	0.00
20	3661	216	-0.71	-0.86
21	3970	480	0.08	0.06
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	3520	350	-1.07	-0.99

**Statistics**

<b>Assigned Value</b>	3940	240
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	4400	530
<b>Robust Average</b>	3940	240
<b>Median</b>	3960	210
<b>Mean</b>	3944	
<b>N</b>	14	
<b>Max.</b>	4500	
<b>Min.</b>	3478	
<b>Robust SD</b>	360	
<b>Robust CV</b>	9.1%	

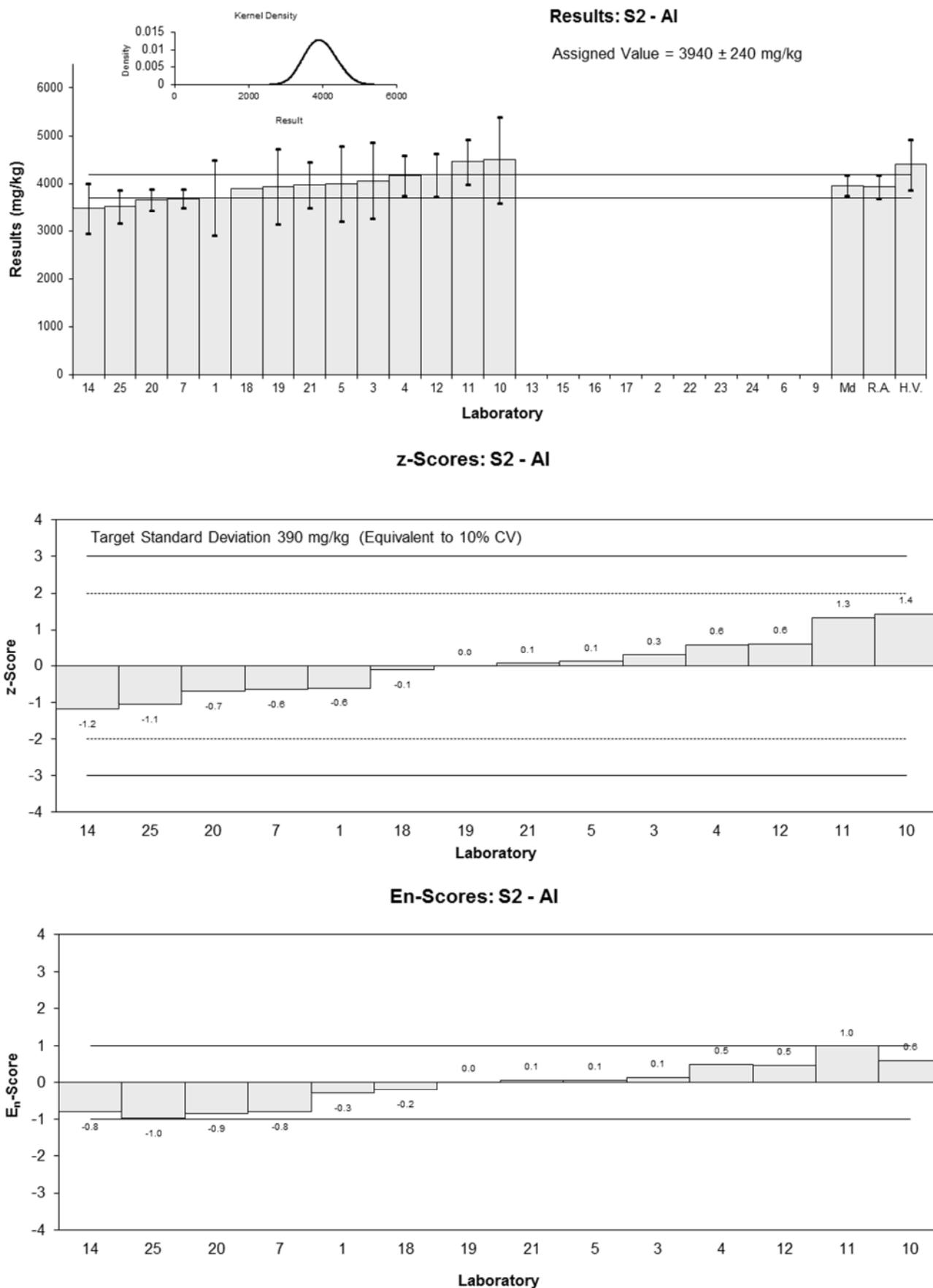


Figure 18

Table 29

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	B
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	86	18	-0.93	-0.47
2	NT	NT		
3	83	NR	-1.24	-2.36
4	98	9.8	0.34	0.29
5	120.77	24.16	2.74	1.05
6	NT	NT		
7	92.6	37.5	-0.23	-0.06
9	NT	NT		
10	95.5	19	0.07	0.04
11	87.3	28	-0.79	-0.26
12	95.4	10	0.06	0.05
13	NT	NT		
14	98.6	15	0.40	0.24
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	97.8	NR	0.32	0.60
19	88	18	-0.72	-0.36
20	98.2	6	0.36	0.44
21	104	18	0.97	0.49
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	96	10	0.13	0.11

**Statistics**

<b>Assigned Value</b>	94.8	5.0
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	79.0	9.4
<b>Robust Average</b>	94.8	5.0
<b>Median</b>	95.8	2.6
<b>Mean</b>	95.8	
<b>N</b>	14	
<b>Max.</b>	120.77	
<b>Min.</b>	83	
<b>Robust SD</b>	7.5	
<b>Robust CV</b>	7.9%	

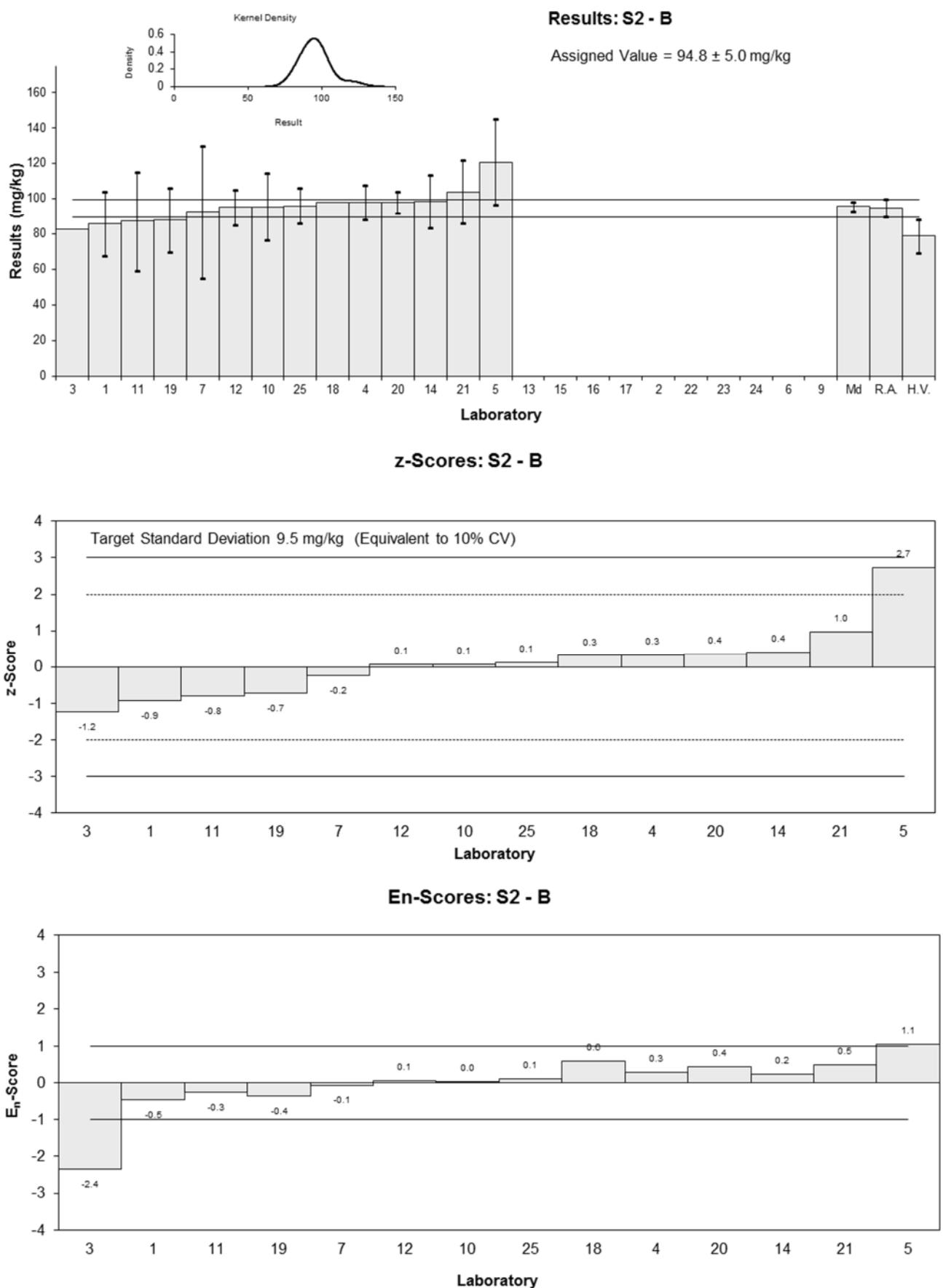


Figure 19

Table 30

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Ba
<b>Units</b>	mg/kg

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NR	NR		
2	NT	NT		
3	140	24.7	0.07	0.04
4	116	6.0	-1.65	-1.61
5	85.78	17.16	-3.83	-2.47
6	NT	NT		
7	133	71.5	-0.43	-0.08
9	NT	NT		
10	163	33	1.73	0.68
11	155	16	1.15	0.78
12	116	15	-1.65	-1.16
13	NT	NT		
14	134	20	-0.36	-0.21
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	149	NR	0.72	0.77
19	140	30	0.07	0.03
20	155	8	1.15	1.05
21	150.9	9.1	0.86	0.75
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	144	10	0.36	0.30

**Statistics**

<b>Assigned Value</b>	139	13
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	147	18
<b>Robust Average</b>	139	13
<b>Median</b>	140	10
<b>Mean</b>	137	
<b>N</b>	13	
<b>Max.</b>	163	
<b>Min.</b>	85.78	
<b>Robust SD</b>	19	
<b>Robust CV</b>	14%	

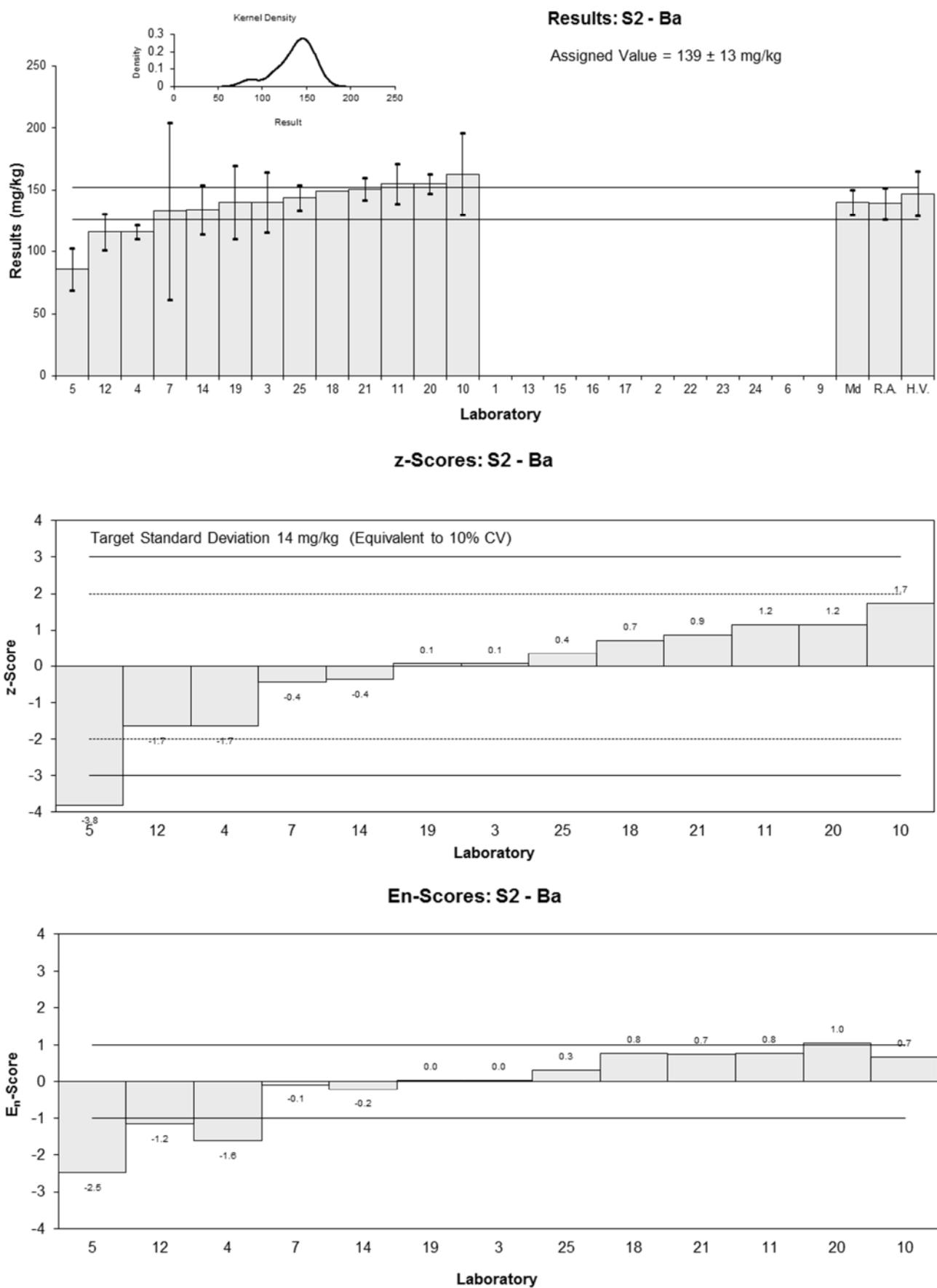


Figure 20

Table 31

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Be
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.10	0.03	-0.71	-0.37
2	NT	NT		
3	<0.1	NR		
4	0.104	0.01	-0.48	-0.51
5	0.12	0.02	0.48	0.34
6	NT	NT		
7	<1	NR		
9	NT	NT		
10	0.12	0.02	0.48	0.34
11	0.11	0.03	-0.12	-0.06
12	0.10	0.02	-0.71	-0.51
13	NT	NT		
14	<0.1	NR		
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	<0.5	NR		
20	0.130	0.002	1.07	1.48
21	<0.2	0.14		
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.112	0.012
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.106	0.013
<b>Robust Average</b>	0.112	0.012
<b>Median</b>	0.110	0.014
<b>Mean</b>	0.112	
<b>N</b>	7	
<b>Max.</b>	0.13	
<b>Min.</b>	0.1	
<b>Robust SD</b>	0.013	
<b>Robust CV</b>	12%	

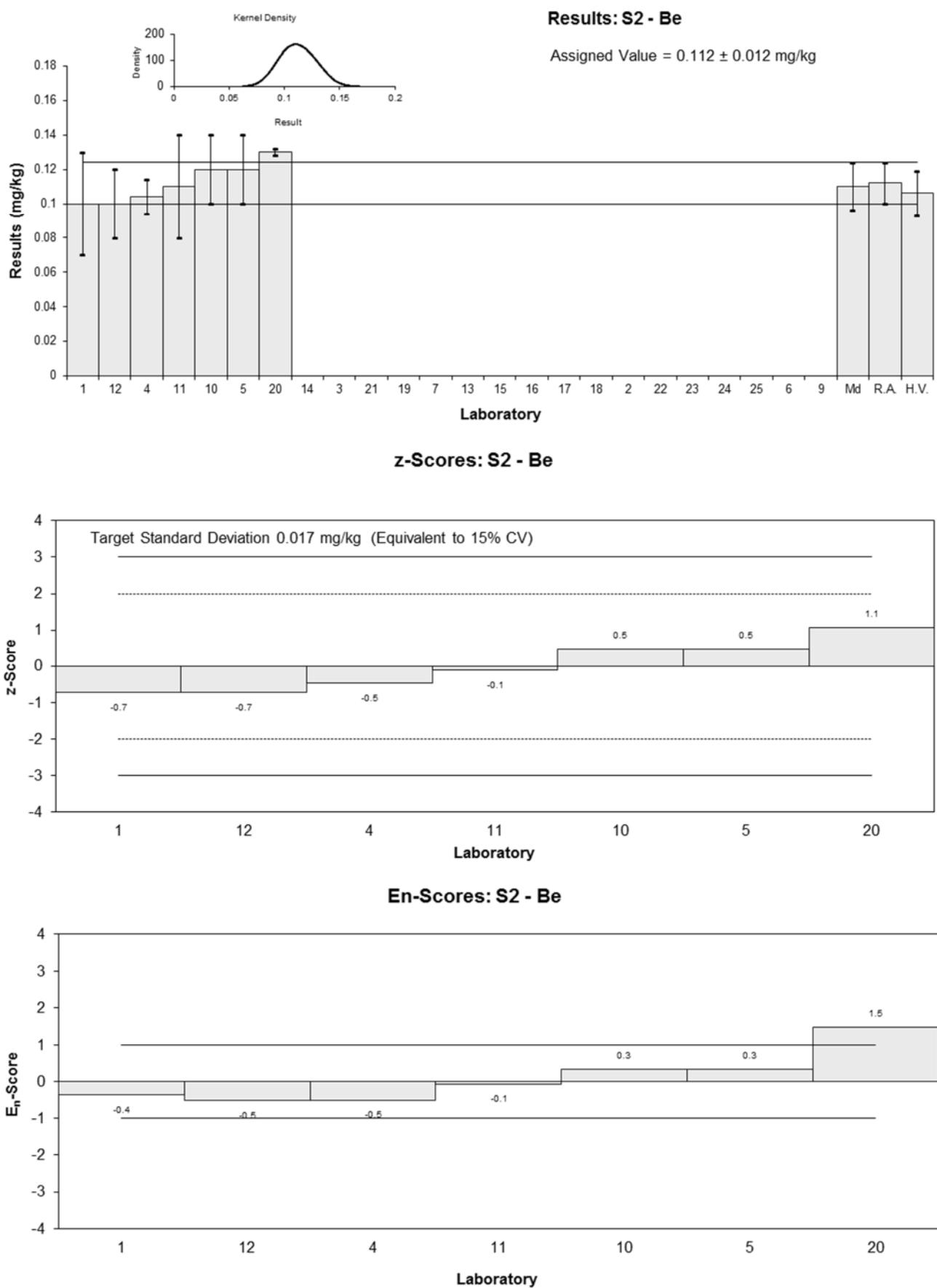


Figure 21

Table 32

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Co
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	4.4	0.9	-0.18	-0.09
2	NT	NT		
3	3.8	0.60	-1.52	-1.06
4	4.41	0.44	-0.16	-0.14
5	4.17	0.83	-0.69	-0.36
6	NT	NT		
7	5.0	0.8	1.16	0.62
9	NT	NT		
10	4.8	1	0.71	0.31
11	4.39	1.42	-0.20	-0.06
12	4.44	0.7	-0.09	-0.05
13	NT	NT		
14	4.25	0.6	-0.51	-0.36
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	4.64	NR	0.36	0.70
19	4.5	0.9	0.04	0.02
20	5.12	0.11	1.43	2.51
21	4.59	0.70	0.25	0.15
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	4.2	.5	-0.63	-0.51

**Statistics**

<b>Assigned Value</b>	4.48	0.23
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	4.25	0.51
<b>Robust Average</b>	4.48	0.23
<b>Median</b>	4.43	0.17
<b>Mean</b>	4.48	
<b>N</b>	14	
<b>Max.</b>	5.12	
<b>Min.</b>	3.8	
<b>Robust SD</b>	0.34	
<b>Robust CV</b>	7.6%	

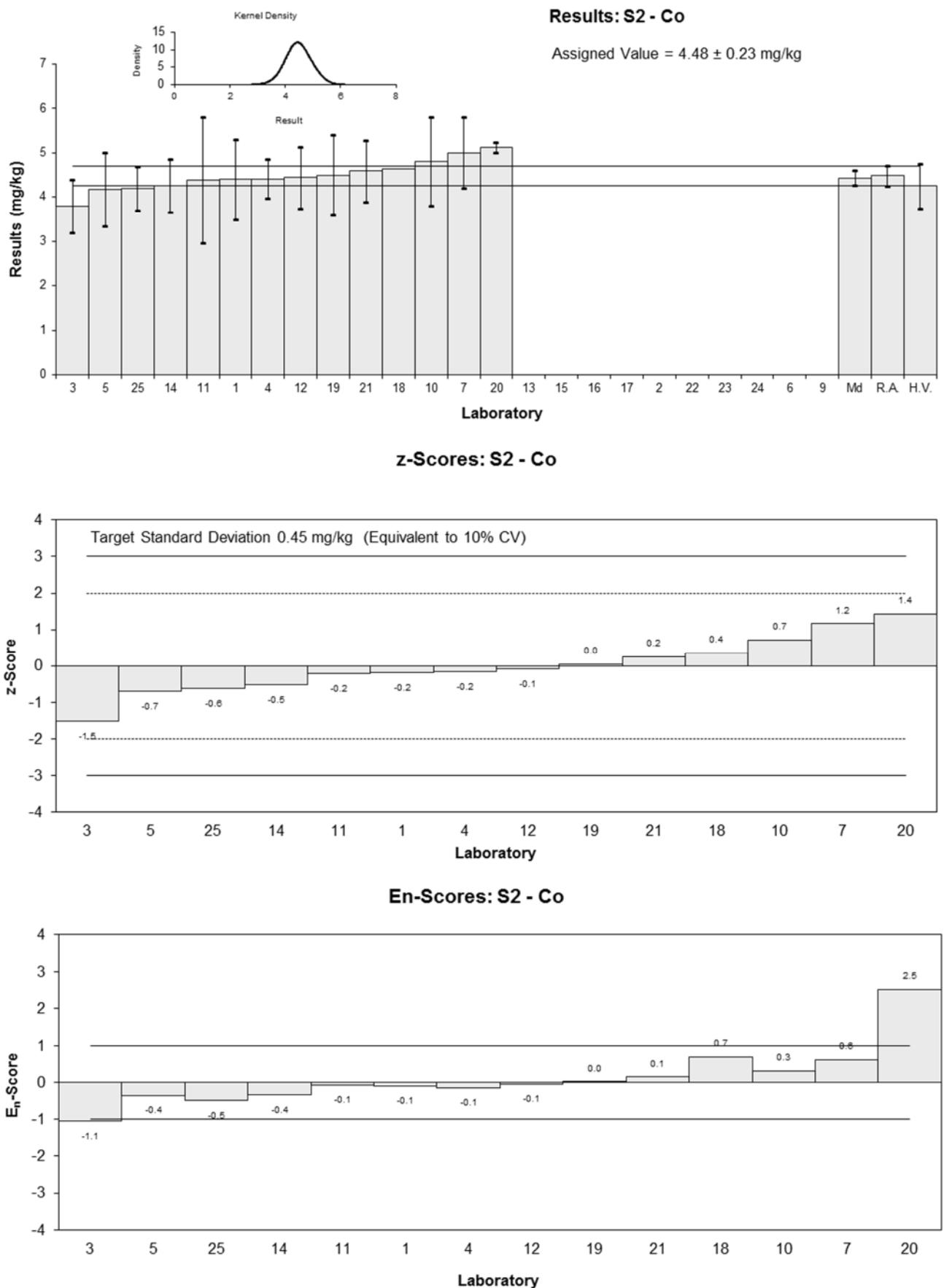


Figure 22

Table 33

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Ga
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NR	NR
2	NT	NT
3	0.9	NR
4	NT	NT
5	NT	NT
6	NT	NT
7	NT	NT
9	NT	NT
10	NT	NT
11	NR	NR
12	NT	NT
13	NT	NT
14	NT	NT
15	NT	NT
16	NT	NT
17	NT	NT
18	NT	NT
19	1.1	0.2
20	0.97	0.05
21	NT	NT
22	NT	NT
23	NT	NT
24	NT	NT
25	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1.13	0.14
<b>Median</b>	0.97	0.26
<b>Mean</b>	0.99	
<b>N</b>	3	
<b>Max.</b>	1.1	
<b>Min.</b>	0.9	

\*Insufficient data to calculate statistics.

**Results: S2 - Ga**

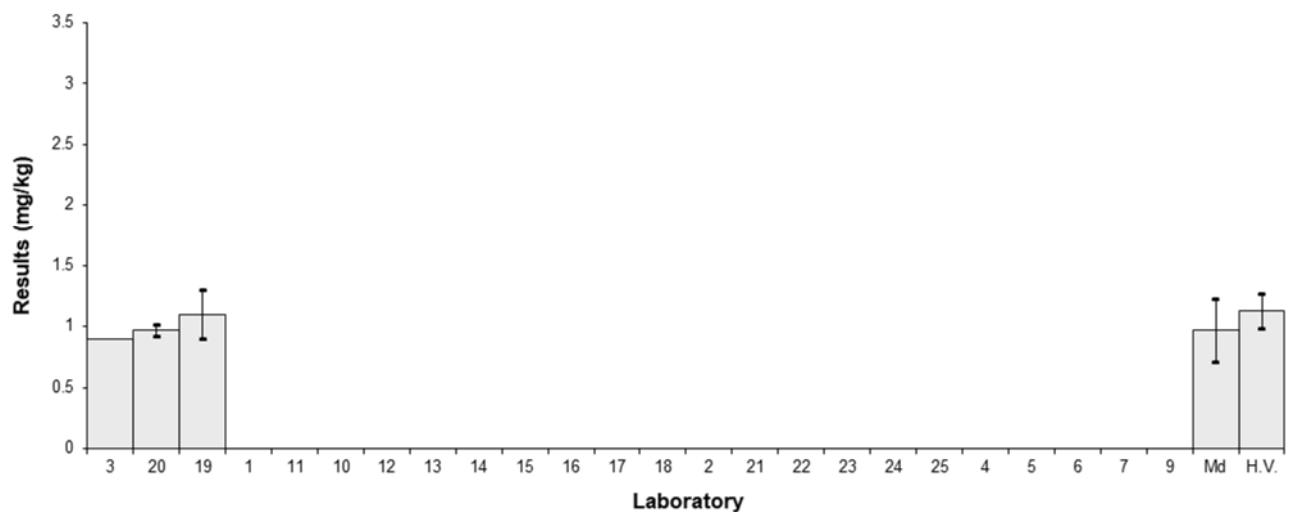


Figure 23

Table 34

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Li
<b>Units</b>	mg/kg

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NR	NR		
2	NT	NT		
3	0.5	NR	-2.45	-2.67
4	1.037	0.052	0.29	0.30
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	1.13	0.23	0.77	0.51
11	1.20	0.24	1.12	0.73
12	0.86	0.1	-0.61	-0.58
13	NT	NT		
14	0.614	0.1	-1.87	-1.78
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	1.91	NR	4.74	5.17
19	0.99	0.20	0.05	0.04
20	0.77	0.04	-1.07	-1.14
21	1.10	0.30	0.61	0.34
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	2.1	.2	5.71	4.16

**Statistics**

<b>Assigned Value*</b>	0.98	0.18
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.99	0.12
<b>Robust Average</b>	1.06	0.34
<b>Median</b>	1.04	0.18
<b>Mean</b>	1.11	
<b>N</b>	11	
<b>Max.</b>	2.1	
<b>Min.</b>	0.5	
<b>Robust SD</b>	0.45	
<b>Robust CV</b>	42%	

\*Robust Average excluding Laboratories 3, 18 and 25.

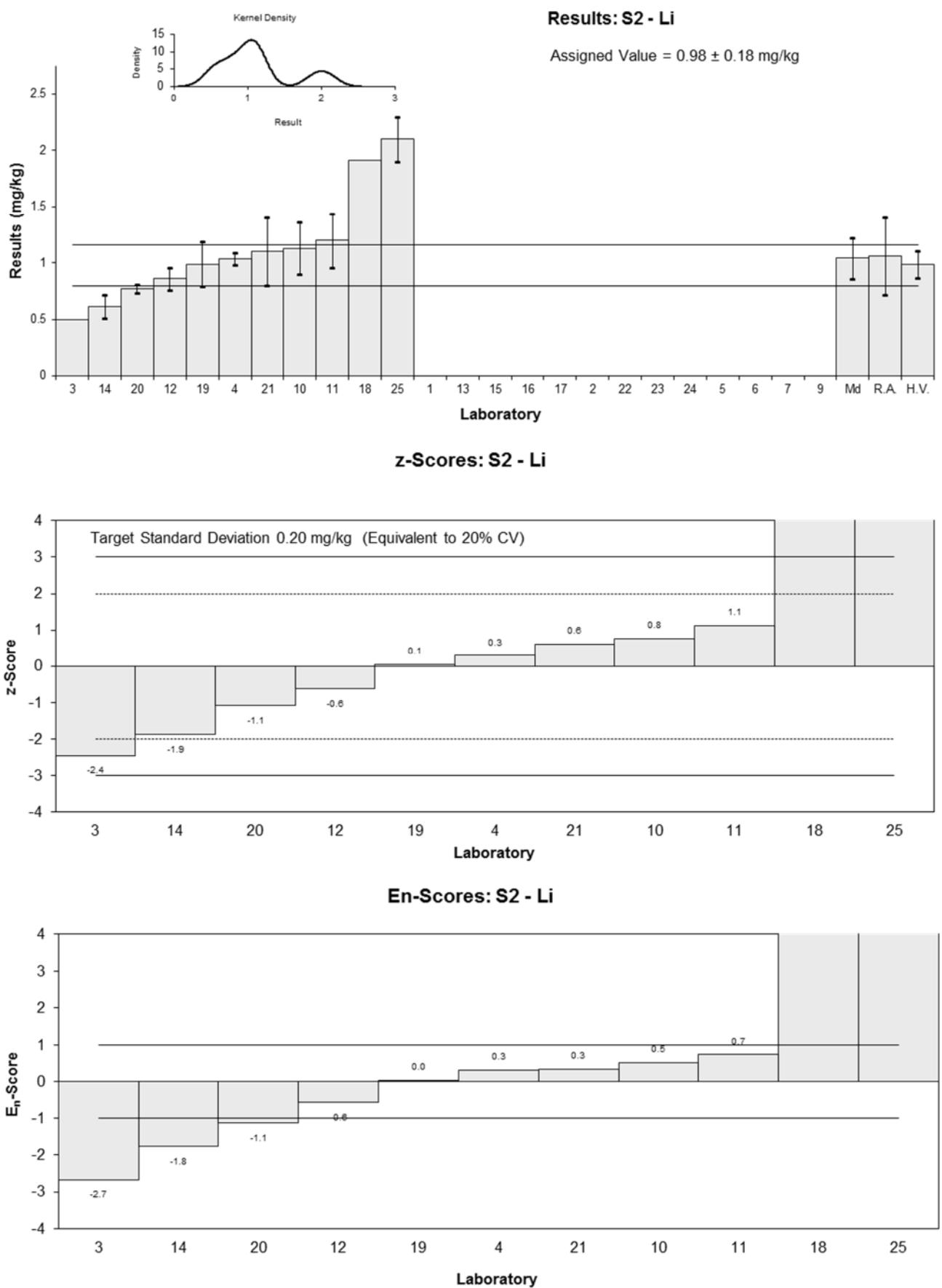


Figure 24

Table 35

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Mo
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	5.1	1.2	-0.34	-0.21
2	NT	NT		
3	4.2	0.90	-1.45	-1.15
4	5.156	0.26	-0.27	-0.40
5	5.02	1.00	-0.43	-0.32
6	NT	NT		
7	5.6	1.6	0.29	0.14
9	NT	NT		
10	6.1	1.2	0.91	0.57
11	4.83	0.83	-0.67	-0.57
12	5.34	0.8	-0.04	-0.03
13	NT	NT		
14	5.91	0.9	0.67	0.53
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	5.14	NR	-0.29	-0.49
19	5.4	1.1	0.04	0.03
20	6.95	0.23	1.96	3.02
21	6.2	1.2	1.03	0.64
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	4.6	.5	-0.96	-1.12

**Statistics**

<b>Assigned Value</b>	5.37	0.47
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	5.20	0.62
<b>Robust Average</b>	5.37	0.47
<b>Median</b>	5.25	0.33
<b>Mean</b>	5.40	
<b>N</b>	14	
<b>Max.</b>	6.95	
<b>Min.</b>	4.2	
<b>Robust SD</b>	0.70	
<b>Robust CV</b>	13%	

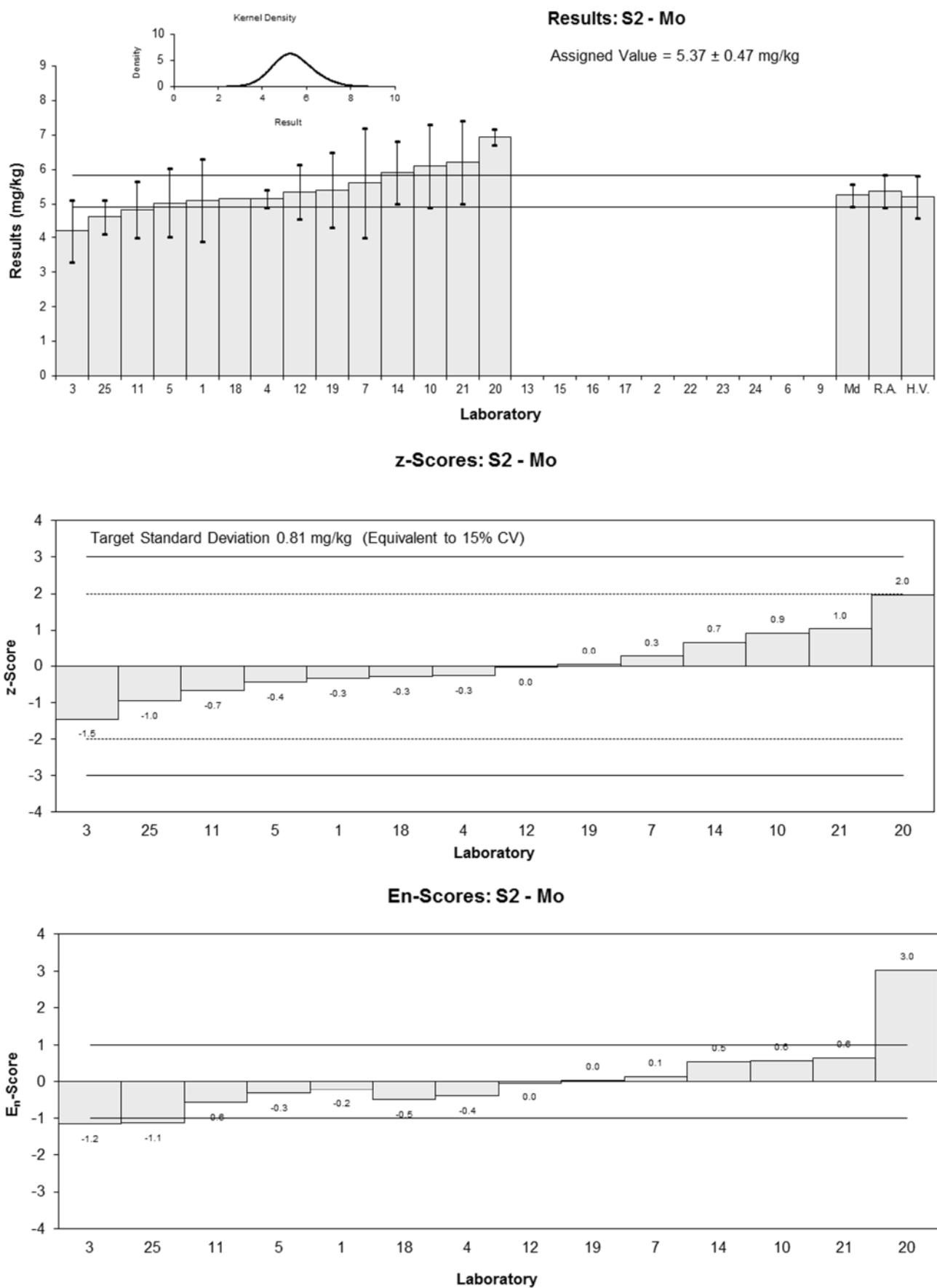


Figure 25

Table 36

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Sb
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1.1	0.5	0.19	0.08
2	NT	NT		
3	0.8	0.2	-1.23	-1.09
4	0.873	0.088	-0.88	-1.19
5	1.11	0.22	0.24	0.20
6	NT	NT		
7	1.0	0.9	-0.28	-0.07
9	NT	NT		
10	1.2	0.2	0.66	0.59
11	1.10	0.38	0.19	0.10
12	0.62	0.1	-2.08	-2.68
13	NT	NT		
14	1.12	0.2	0.28	0.25
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	1.38	NR	1.51	2.46
19	1.0	0.2	-0.28	-0.25
20	1.26	0.04	0.94	1.47
21	1.21	0.34	0.71	0.41
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	0.95	0.1	-0.52	-0.67

**Statistics**

<b>Assigned Value</b>	1.06	0.13
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.95	0.11
<b>Robust Average</b>	1.06	0.13
<b>Median</b>	1.10	0.09
<b>Mean</b>	1.05	
<b>N</b>	14	
<b>Max.</b>	1.38	
<b>Min.</b>	0.62	
<b>Robust SD</b>	0.19	
<b>Robust CV</b>	18%	

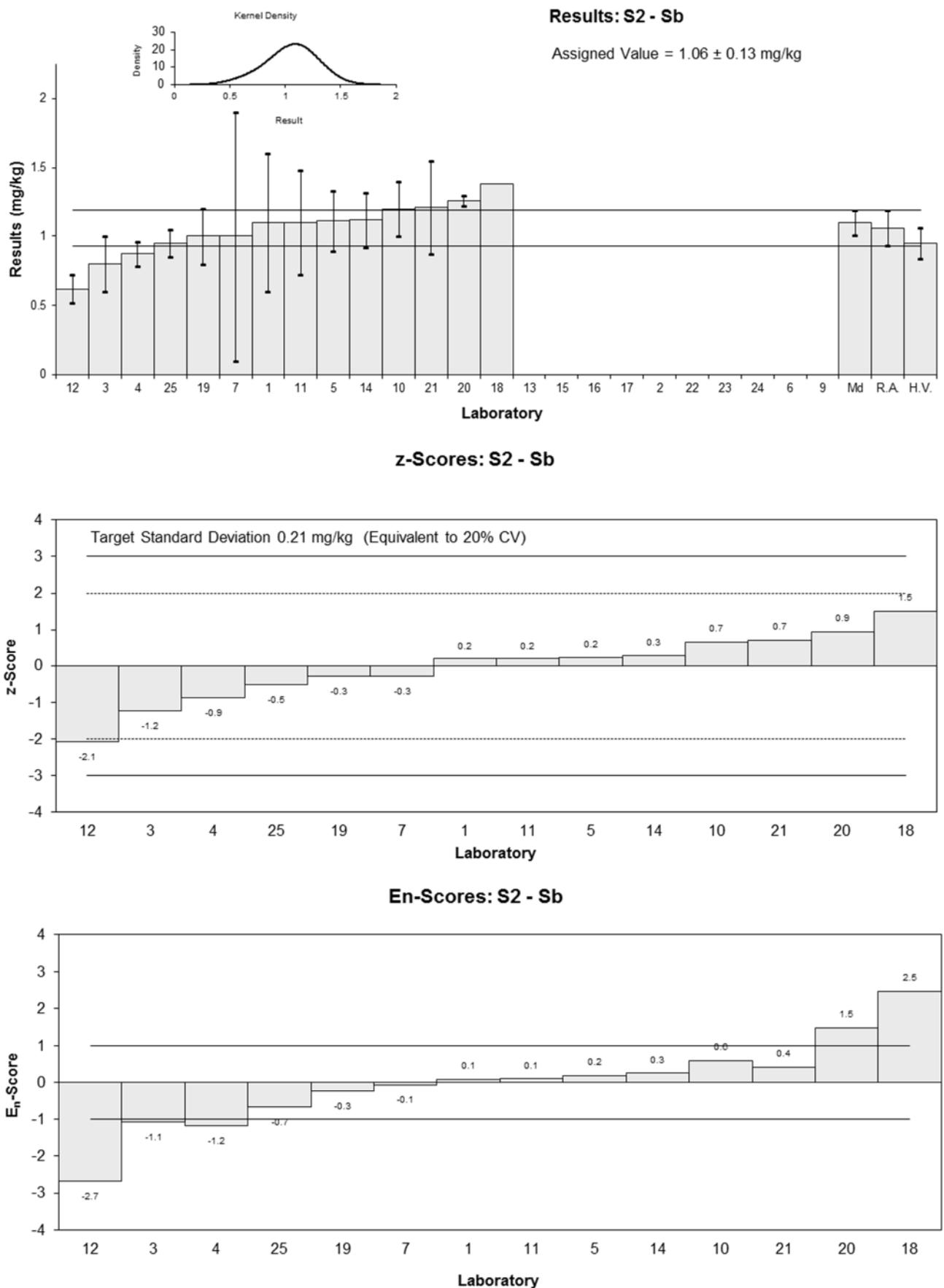


Figure 26

Table 37

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Sn
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	30	7	-0.42	-0.25
2	NT	NT		
3	27.7	4.4	-0.90	-0.75
4	30.79	4.62	-0.25	-0.20
5	NT	NT		
6	NT	NT		
7	36.9	14.7	1.02	0.32
9	NT	NT		
10	33.5	6.7	0.31	0.20
11	25.3	5.8	-1.40	-0.97
12	35.8	5.0	0.79	0.61
13	NT	NT		
14	28.0	4.2	-0.83	-0.71
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	30	6	-0.42	-0.28
20	37.8	1.6	1.21	1.44
21	39.3	7.9	1.52	0.84
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	29	.3	-0.62	-0.81

**Statistics**

<b>Assigned Value</b>	32.0	3.7
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	22.5	2.7
<b>Robust Average</b>	32.0	3.7
<b>Median</b>	30.4	2.7
<b>Mean</b>	32.0	
<b>N</b>	12	
<b>Max.</b>	39.3	
<b>Min.</b>	25.3	
<b>Robust SD</b>	5.1	
<b>Robust CV</b>	16%	

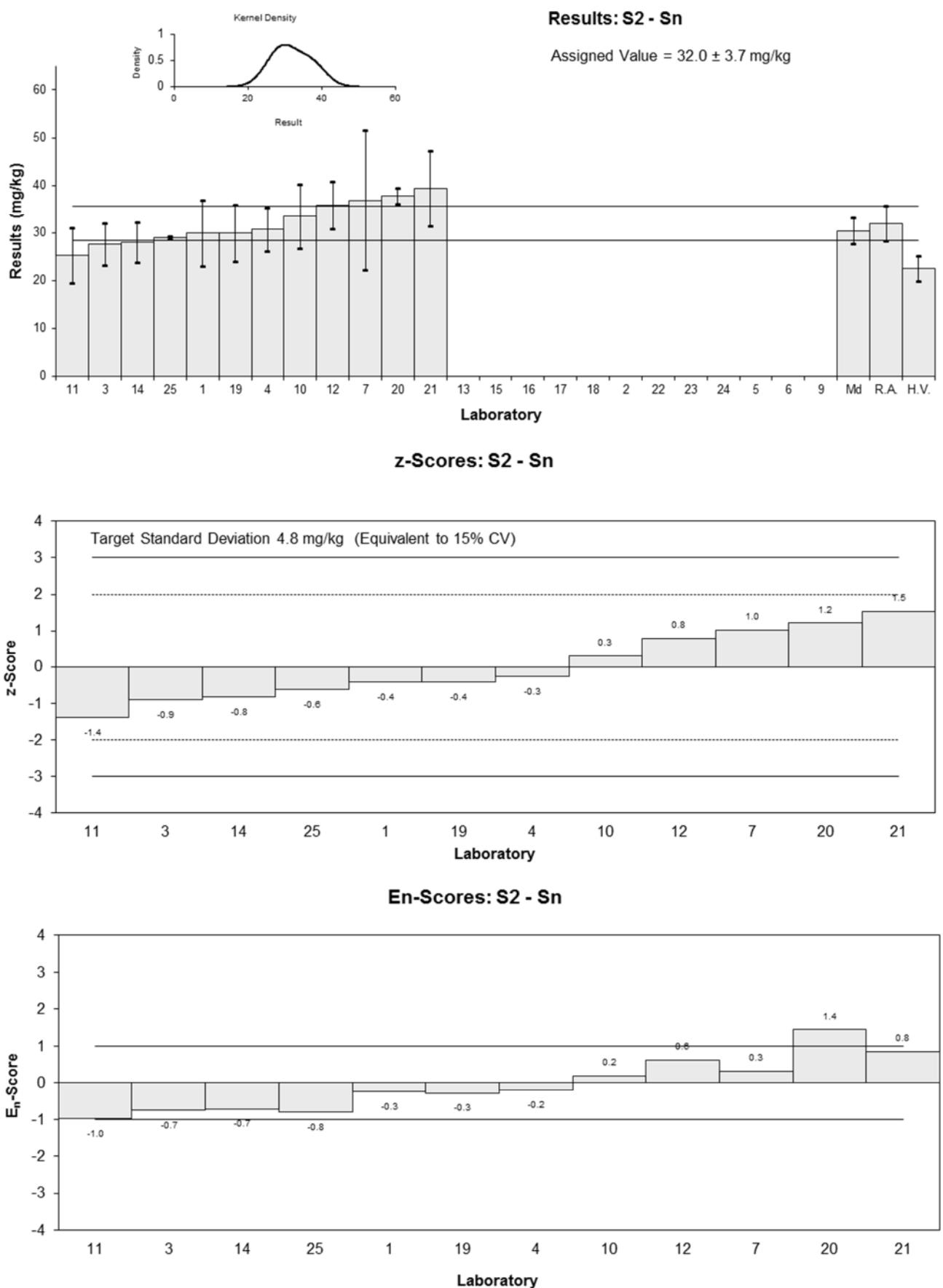


Figure 27

Table 38

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Sr
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	86	13	-1.37	-0.87
2	NT	NT		
3	76.9	14.2	-2.28	-1.37
4	96.4	4.82	-0.32	-0.32
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	109	22	0.94	0.40
11	108	18	0.84	0.42
12	88.9	10	-1.07	-0.81
13	NT	NT		
14	104	16	0.44	0.24
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	96.8	NR	-0.28	-0.33
19	110	200	1.04	0.05
20	115	4	1.55	1.62
21	105	11	0.54	0.39
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	94	10	-0.56	-0.42

**Statistics**

<b>Assigned Value</b>	99.6	8.6
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	96	12
<b>Robust Average</b>	99.6	8.6
<b>Median</b>	100	8
<b>Mean</b>	99.2	
<b>N</b>	12	
<b>Max.</b>	115	
<b>Min.</b>	76.9	
<b>Robust SD</b>	12	
<b>Robust CV</b>	12%	

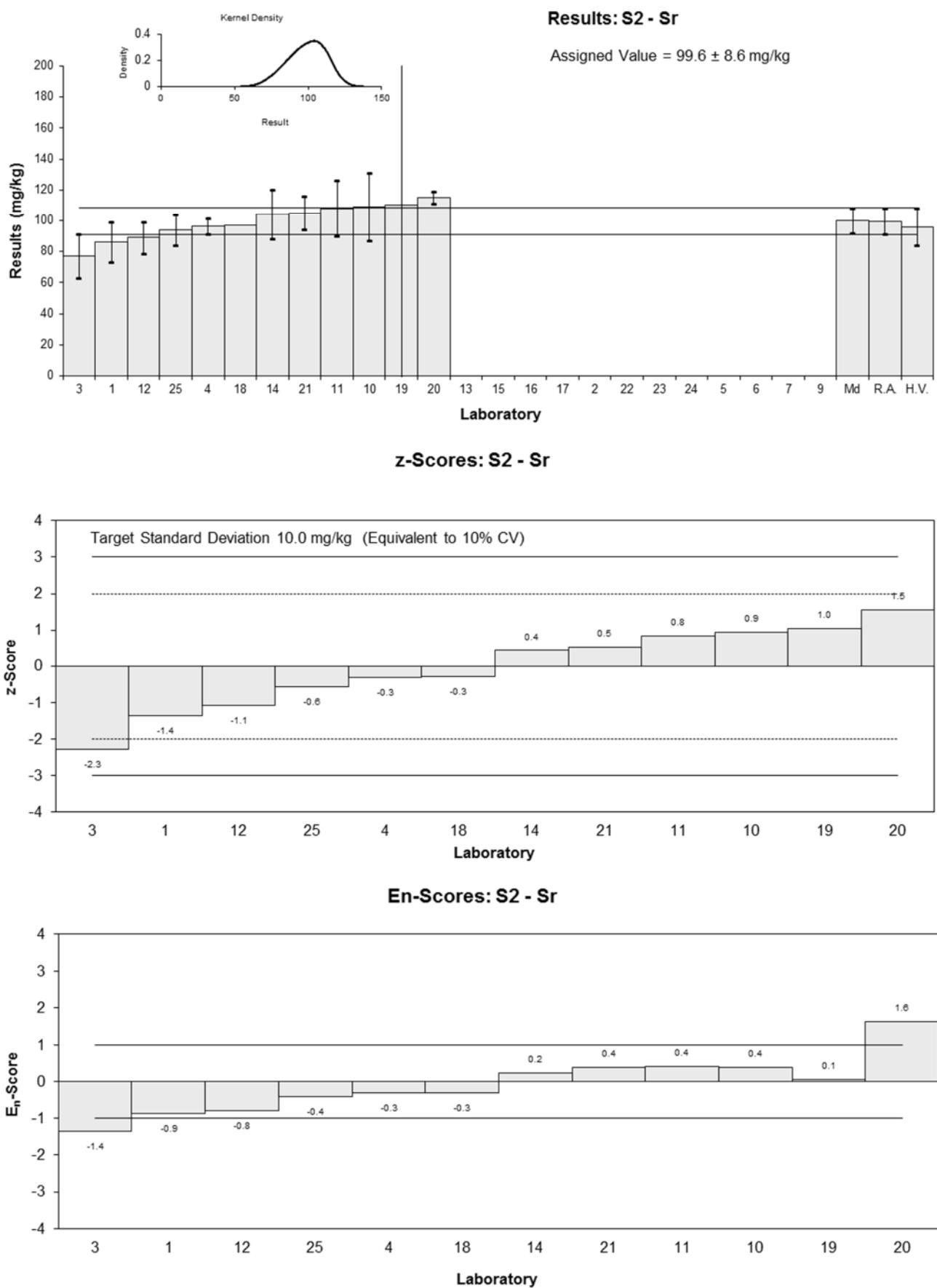


Figure 28

Table 39

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	Tl
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.09	0.04	0.19	0.09
2	NT	NT		
3	<0.1	NR		
4	0.077	0.008	-0.42	-0.38
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	0.094	0.019	0.37	0.28
11	0.11	0.04	1.12	0.53
12	0.05	0.02	-1.67	-1.21
13	NT	NT		
14	NT	NT		
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	<0.5	NR		
20	0.090	0.003	0.19	0.18
21	<0.2	0.14		
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.086	0.022
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	0.086	0.022
<b>Median</b>	0.090	0.013
<b>Mean</b>	0.085	
<b>N</b>	6	
<b>Max.</b>	0.11	
<b>Min.</b>	0.05	
<b>Robust SD</b>	0.022	
<b>Robust CV</b>	26%	

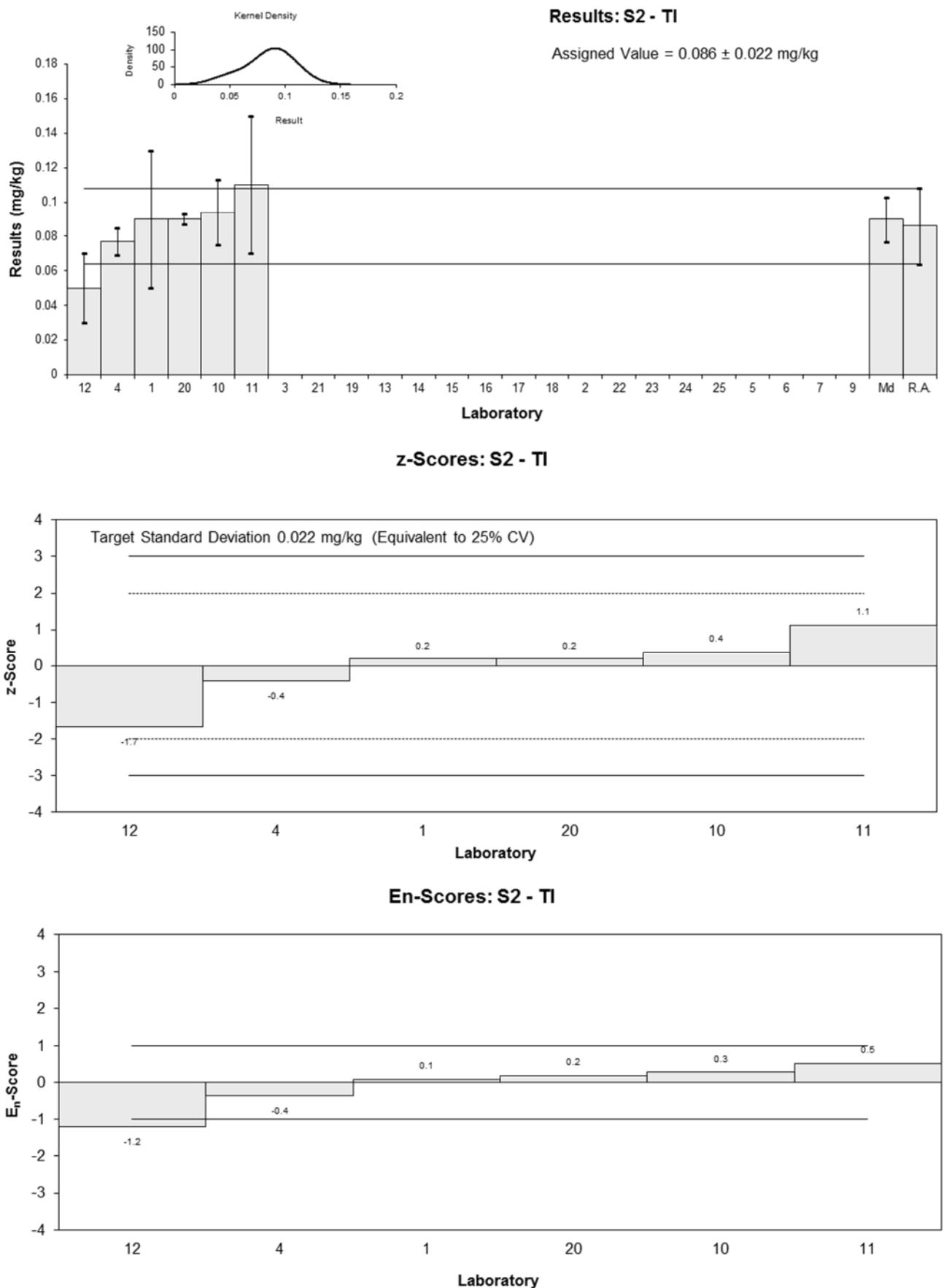


Figure 29

Table 40

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	U
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.6	0.2	-0.62	-0.28
2	NT	NT		
3	0.5	NR	-1.63	-1.88
4	0.632	0.032	-0.30	-0.33
5	NT	NT		
6	NT	NT		
7	NT	NT		
9	NT	NT		
10	0.67	0.13	0.08	0.05
11	0.65	0.23	-0.12	-0.05
12	0.58	0.1	-0.83	-0.62
13	NT	NT		
14	0.664	0.1	0.02	0.02
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	0.84	NR	1.79	2.07
19	0.59	0.12	-0.73	-0.49
20	0.81	0.03	1.49	1.62
21	0.750	0.081	0.89	0.74
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.662	0.086
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.627	0.075
<b>Robust Average</b>	0.662	0.086
<b>Median</b>	0.650	0.060
<b>Mean</b>	0.662	
<b>N</b>	11	
<b>Max.</b>	0.84	
<b>Min.</b>	0.5	
<b>Robust SD</b>	0.11	
<b>Robust CV</b>	17%	

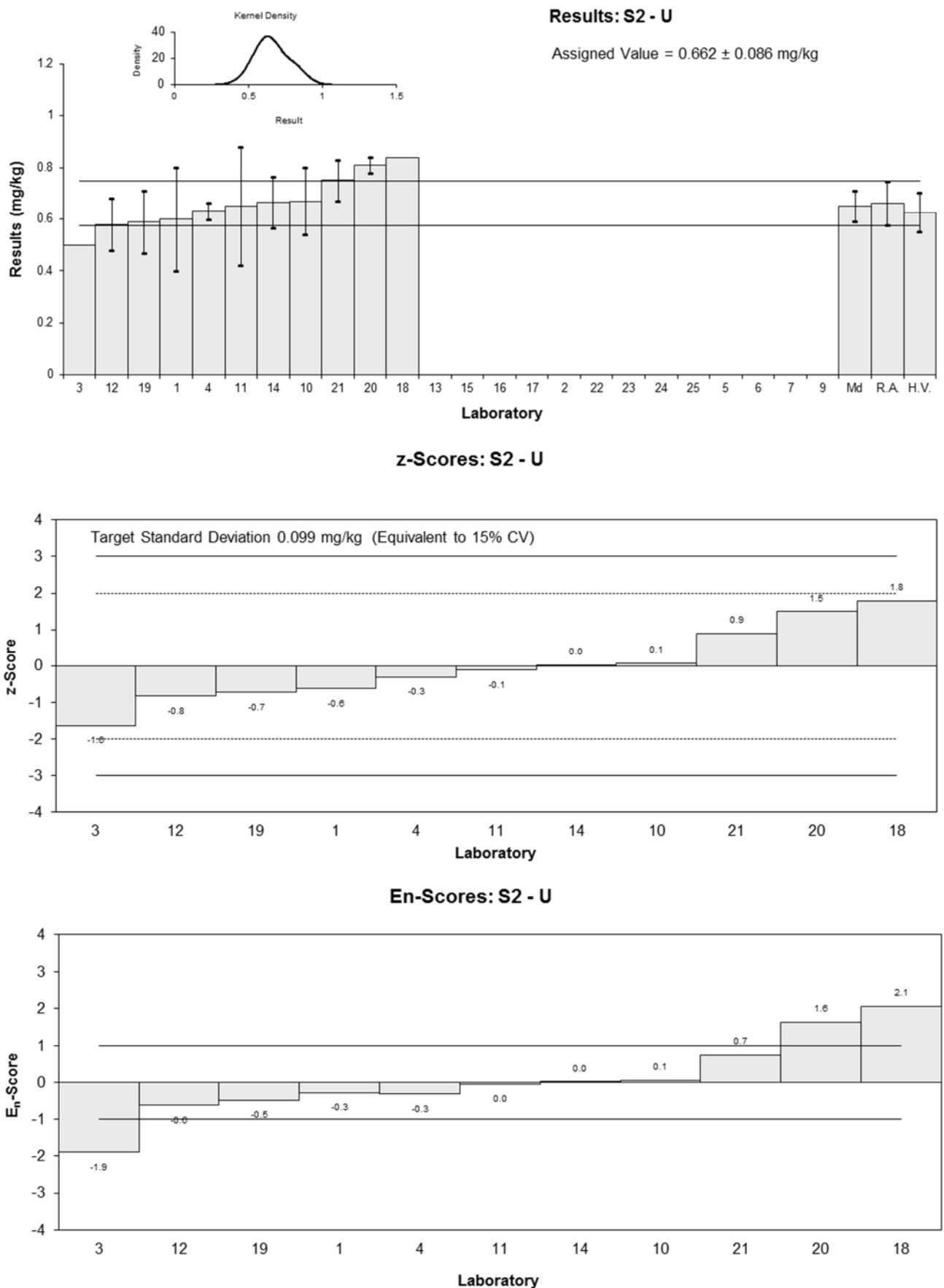


Figure 30

Table 41

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biosoil
<b>Analyte.</b>	V
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	11	3	-0.76	-0.29
2	NT	NT		
3	11	2.0	-0.76	-0.42
4	11.07	0.56	-0.70	-0.93
5	12.64	2.53	0.62	0.28
6	NT	NT		
7	13	2.3	0.92	0.46
9	NT	NT		
10	12.2	2.4	0.25	0.12
11	13.1	2.9	1.01	0.40
12	12.0	2.0	0.08	0.05
13	NT	NT		
14	11.1	1.7	-0.67	-0.44
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	NT	NT		
19	11	2	-0.76	-0.42
20	13.1	0.9	1.01	1.05
21	12.1	6.8	0.17	0.03
22	NT	NT		
23	NT	NT		
24	NT	NT		
25	11.2	2	-0.59	-0.33

**Statistics**

<b>Assigned Value</b>	11.9	0.7
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	11.0	1.3
<b>Robust Average</b>	11.9	0.7
<b>Median</b>	12.0	0.8
<b>Mean</b>	11.9	
<b>N</b>	13	
<b>Max.</b>	13.1	
<b>Min.</b>	11	
<b>Robust SD</b>	0.98	
<b>Robust CV</b>	8.2%	

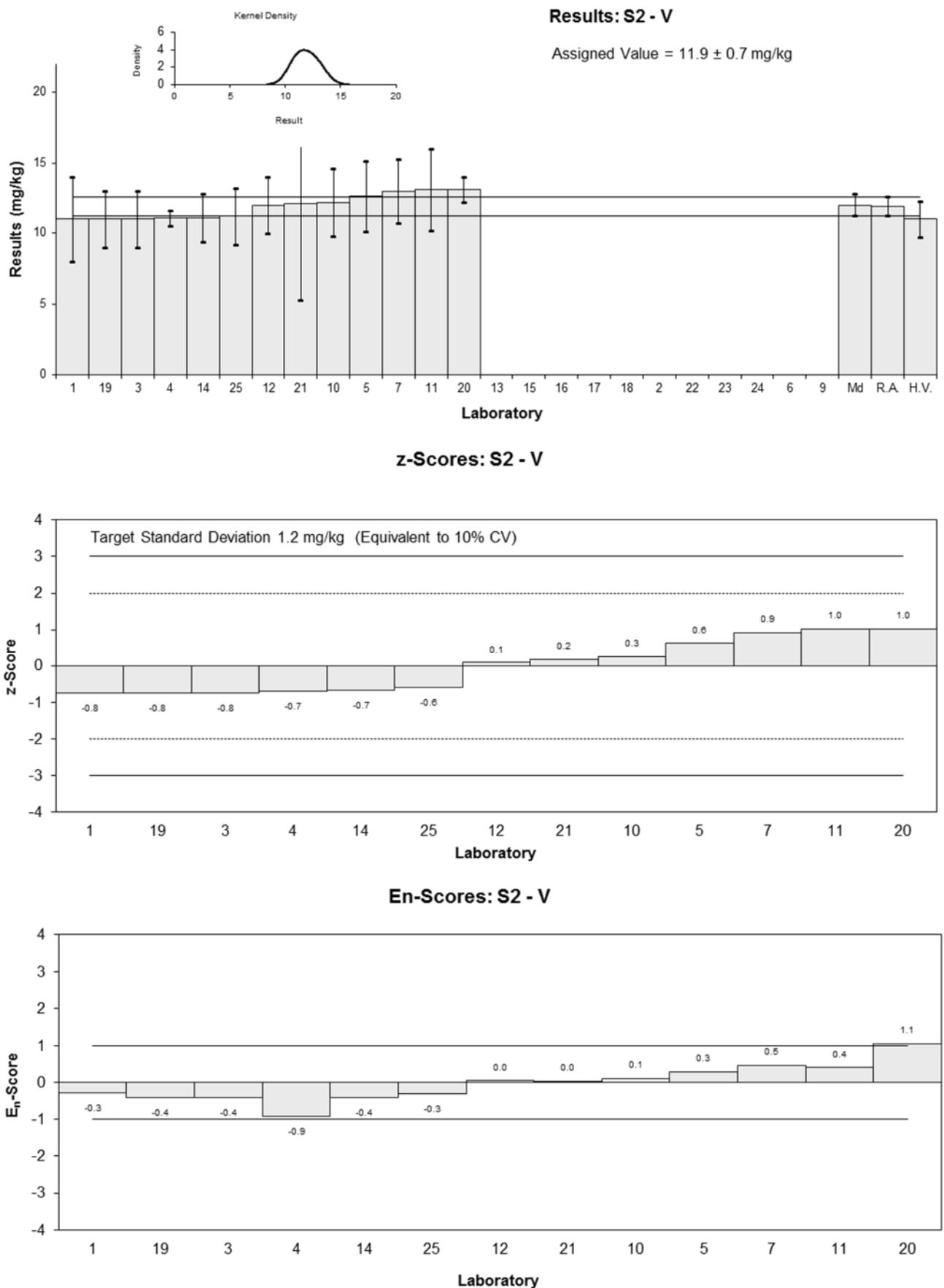


Figure 31

Table 42

**Sample Details**

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

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NR	NR		
2	33	6	0.57	0.38
3	NT	NT		
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
9	NT	NT		
10	NT	NT		
11	NR	NR		
12	29	3.0	-0.10	-0.08
13	15	2.4	-2.47	-2.08
14	39.3	5.9	1.64	1.10
15	NT	NT		
16	33	5.6	0.57	0.39
17	22	2.2	-1.28	-1.09
18	NT	NT		
19	31	5	0.24	0.17
20	NT	NT		
21	NT	NT		
22	31.3	NR	0.29	0.26
23	NT	NT		
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	29.6	6.6
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	29.6	6.6
<b>Median</b>	31.2	2.5
<b>Mean</b>	29.2	
<b>N</b>	8	
<b>Max.</b>	39.3	
<b>Min.</b>	15	
<b>Robust SD</b>	7.5	
<b>Robust CV</b>	25%	

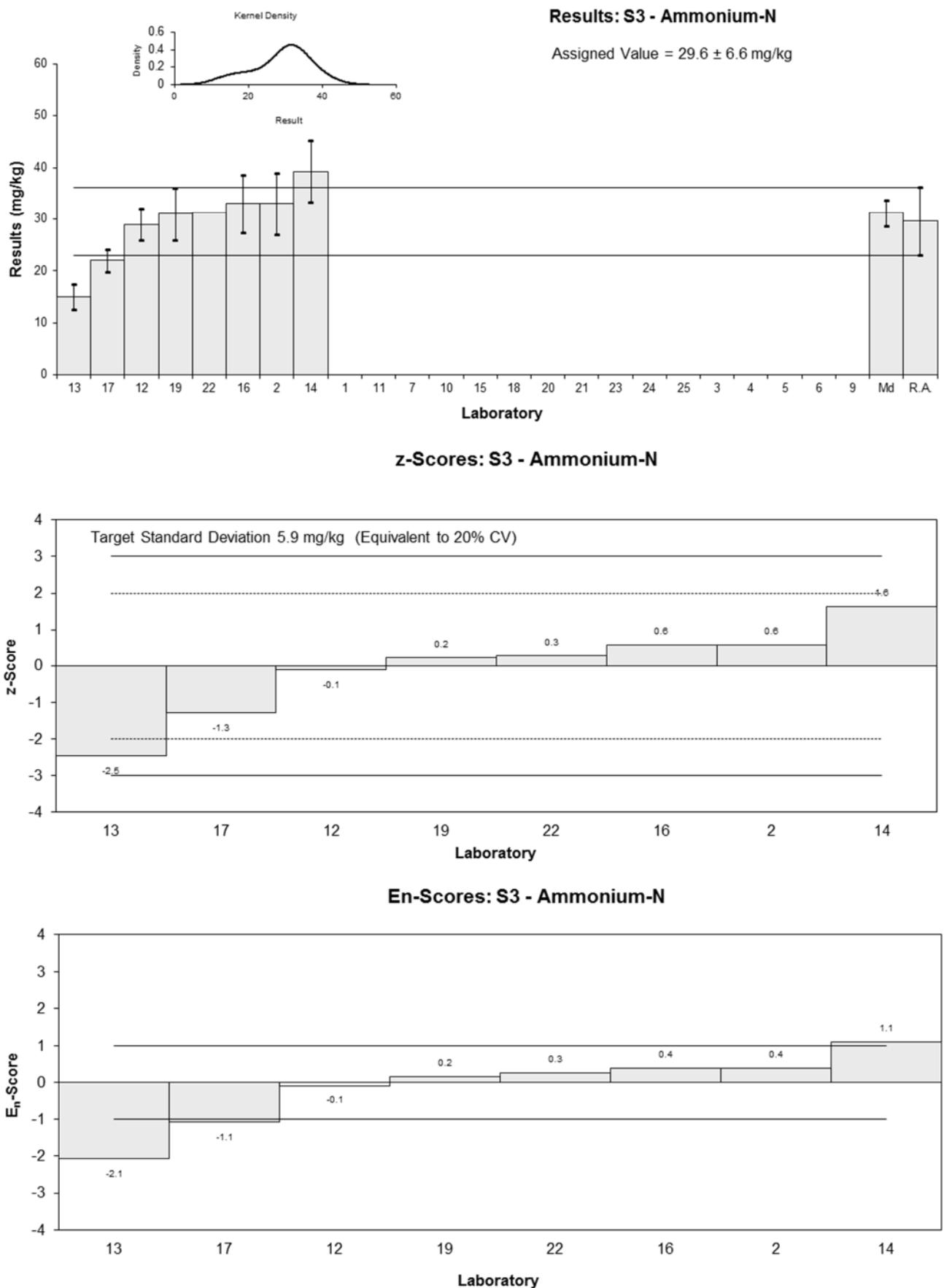


Figure 32

Table 43

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NR	NR
2	1.5	0.6
3	0.9	0.08
4	NT	NT
5	NT	NT
6	0.85	0.07
7	NR	NR
9	NT	NT
10	NT	NT
11	NR	NR
12	NT	NT
13	35	3.5
14	1.02	0.2
15	NT	NT
16	NT	NT
17	<2	NR
18	1.75	NR
19	1.1	0.2
20	NT	NT
21	NT	NT
22	NR	NR
23	NT	NT
24	NT	NT
25	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2.40	0.29
<b>Robust Average</b>	1.33	0.53
<b>Median</b>	1.10	0.34
<b>Mean</b>	6.02	
<b>N</b>	7	
<b>Max.</b>	35	
<b>Min.</b>	0.85	
<b>Robust SD</b>	0.56	
<b>Robust CV</b>	42%	

### Results: S3 - Bromide

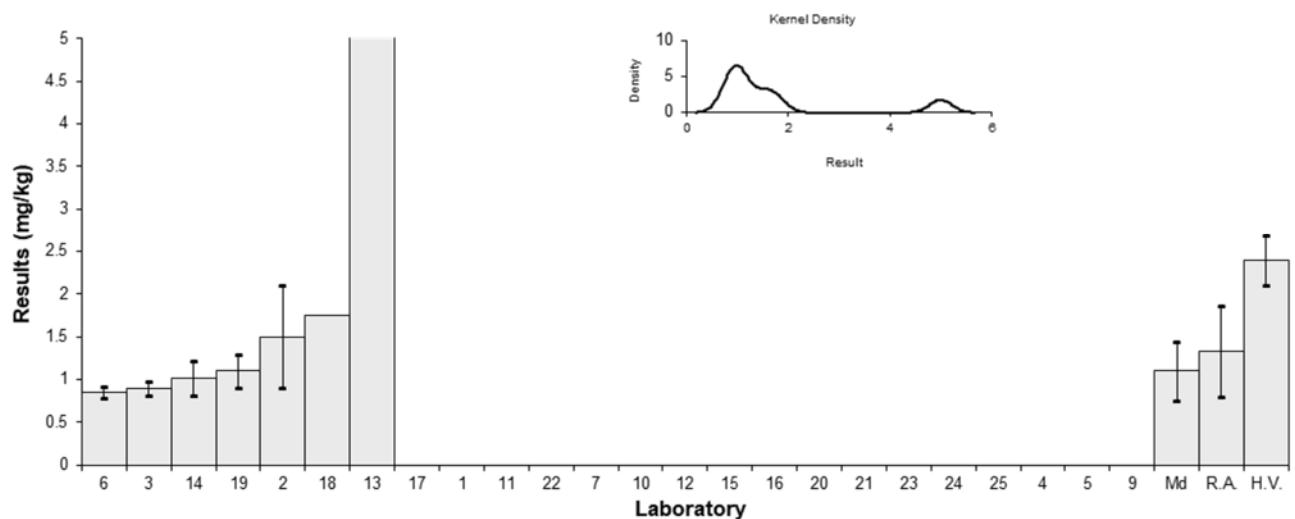


Figure 33

Table 44

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1020	130	-0.29	-0.22
2	1186	220	1.30	0.61
3	1070	204	0.19	0.10
4	NT	NT		
5	NT	NT		
6	1020	139	-0.29	-0.21
7	1061	229.3	0.10	0.05
9	1040	292	-0.10	-0.03
10	NT	NT		
11	1100	120	0.48	0.40
12	1030	120	-0.19	-0.16
13	791	50	-2.47	-4.44
14	1010	152	-0.38	-0.26
15	NT	NT		
16	1050	240	0.00	0.00
17	973	180	-0.73	-0.42
18	1087	NR	0.35	1.23
19	1070	210	0.19	0.09
20	1064	41	0.13	0.28
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	1110	130	0.57	0.45
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	1050	30
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1000	100
<b>Robust Average</b>	1050	30
<b>Median</b>	1060	30
<b>Mean</b>	1043	
<b>N</b>	16	
<b>Max.</b>	1186	
<b>Min.</b>	791	
<b>Robust SD</b>	50	
<b>Robust CV</b>	4.8%	

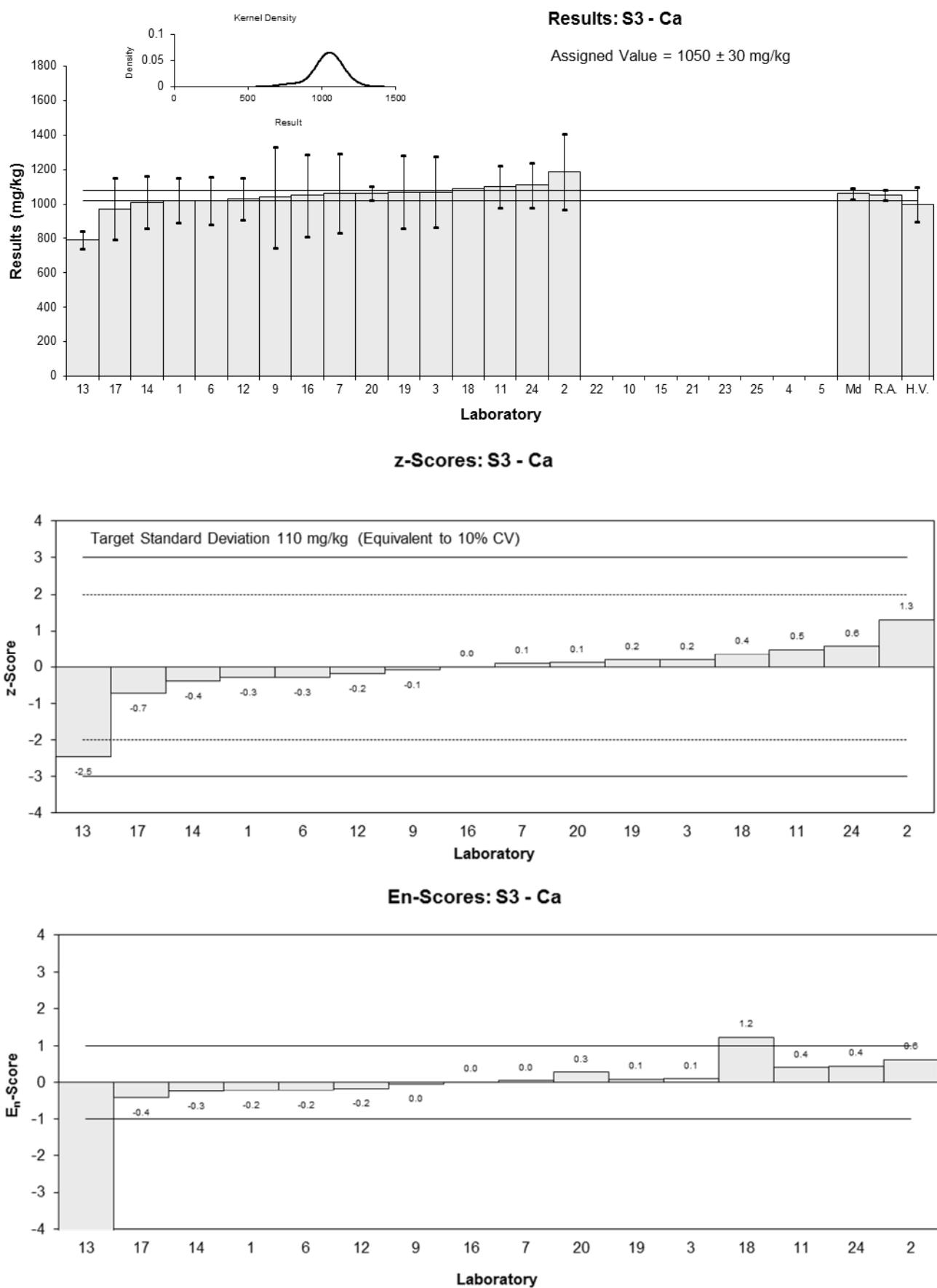


Figure 34

Table 45

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NR	NR		
2	47.5	13	0.61	0.36
3	44.1	5.18	0.21	0.23
4	NT	NT		
5	NT	NT		
6	45.8	4.4	0.41	0.48
7	NR	NR		
9	50	7.3	0.91	0.82
10	NT	NT		
11	NR	NR		
12	52	10	1.15	0.84
13	<5	5		
14	38.3	5.7	-0.47	-0.49
15	NT	NT		
16	32	7.9	-1.22	-1.04
17	35	7	-0.86	-0.80
18	44.3	NR	0.24	0.34
19	34	5	-0.98	-1.07
20	NT	NT		
21	NT	NT		
22	34.14	7.8	-0.96	-0.83
23	NT	NT		
24	50	3.5	0.91	1.12
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	42.3	5.9
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	43.0	5.2
<b>Robust Average</b>	42.3	5.9
<b>Median</b>	44.2	5.5
<b>Mean</b>	42.3	
<b>N</b>	12	
<b>Max.</b>	52	
<b>Min.</b>	32	
<b>Robust SD</b>	8.2	
<b>Robust CV</b>	19%	

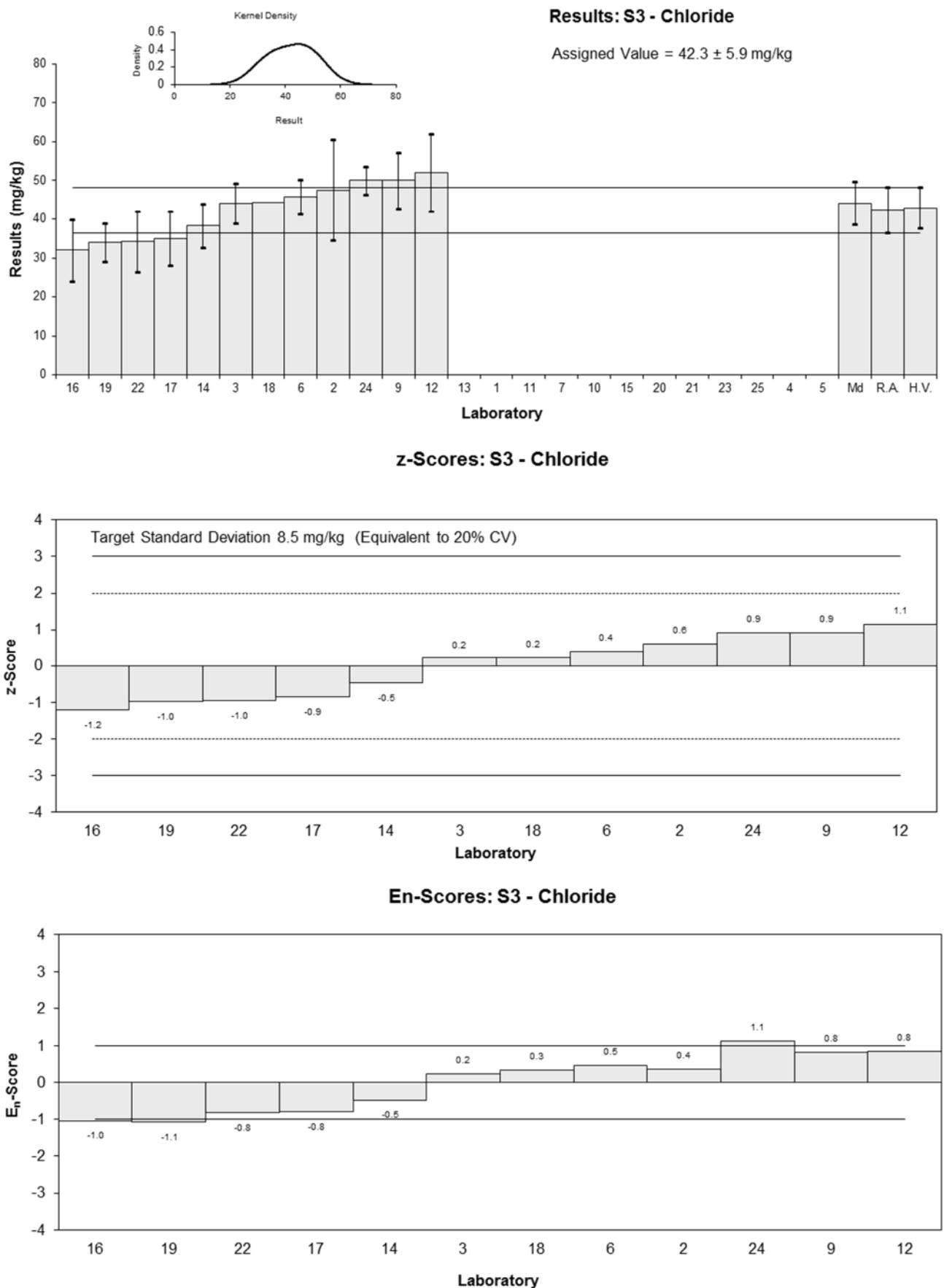


Figure 35

Table 46

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NR	NR		
2	NT	NT		
3	196	18.2	-0.58	-0.58
4	NT	NT		
5	NT	NT		
6	203	5	-0.24	-0.45
7	NR	NR		
9	214	15.2	0.29	0.33
10	NT	NT		
11	NR	NR		
12	196	20	-0.58	-0.54
13	233	23	1.20	1.00
14	217	33	0.43	0.26
15	NT	NT		
16	195	36	-0.62	-0.35
17	197	10	-0.53	-0.78
18	212	NR	0.19	0.40
19	200	20	-0.38	-0.36
20	NT	NT		
21	NT	NT		
22	205	6	-0.14	-0.26
23	NT	NT		
24	234	9.97	1.25	1.84
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	208	10
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	208	10
<b>Median</b>	204	8
<b>Mean</b>	209	
<b>N</b>	12	
<b>Max.</b>	234	
<b>Min.</b>	195	
<b>Robust SD</b>	14	
<b>Robust CV</b>	6.7%	

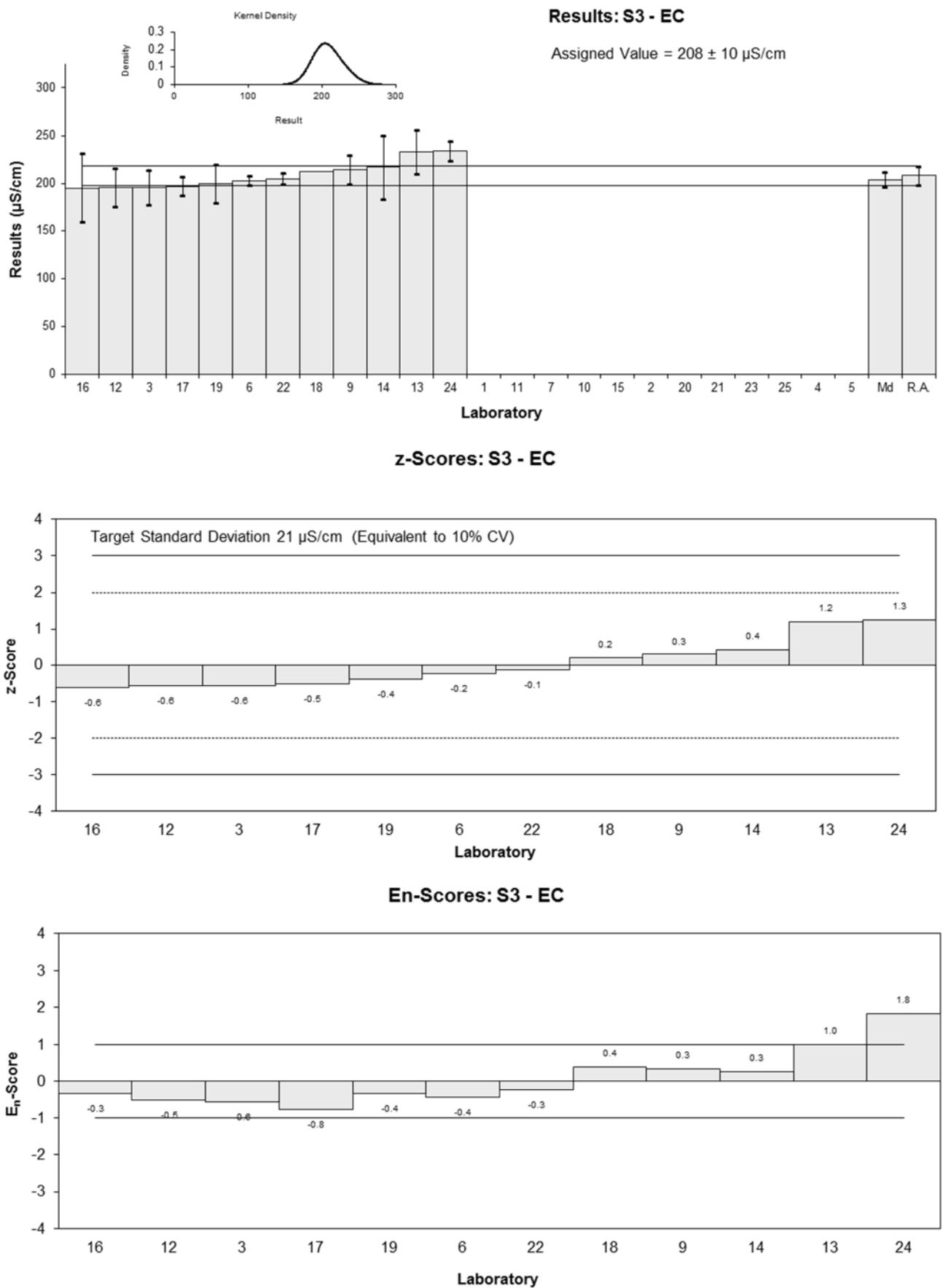


Figure 36

Table 47

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	5590	840	0.71	0.41
2	4767	530	-0.87	-0.74
3	4670	1625	-1.05	-0.33
4	NT	NT		
5	NT	NT		
6	4210	483	-1.93	-1.76
7	5366	821.6	0.28	0.17
9	5240	794	0.04	0.02
10	NT	NT		
11	6270	830	2.01	1.19
12	5260	500	0.08	0.07
13	NR	NR		
14	5122	768	-0.19	-0.12
15	NT	NT		
16	4850	780	-0.71	-0.44
17	5840	1110	1.19	0.54
18	5536	NR	0.61	1.02
19	5160	1030	-0.11	-0.06
20	4945	127	-0.53	-0.82
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	5510	587	0.56	0.44
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	5220	310
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	5000	600
<b>Robust Average</b>	5220	310
<b>Median</b>	5240	240
<b>Mean</b>	5222	
<b>N</b>	15	
<b>Max.</b>	6270	
<b>Min.</b>	4210	
<b>Robust SD</b>	480	
<b>Robust CV</b>	9.2%	

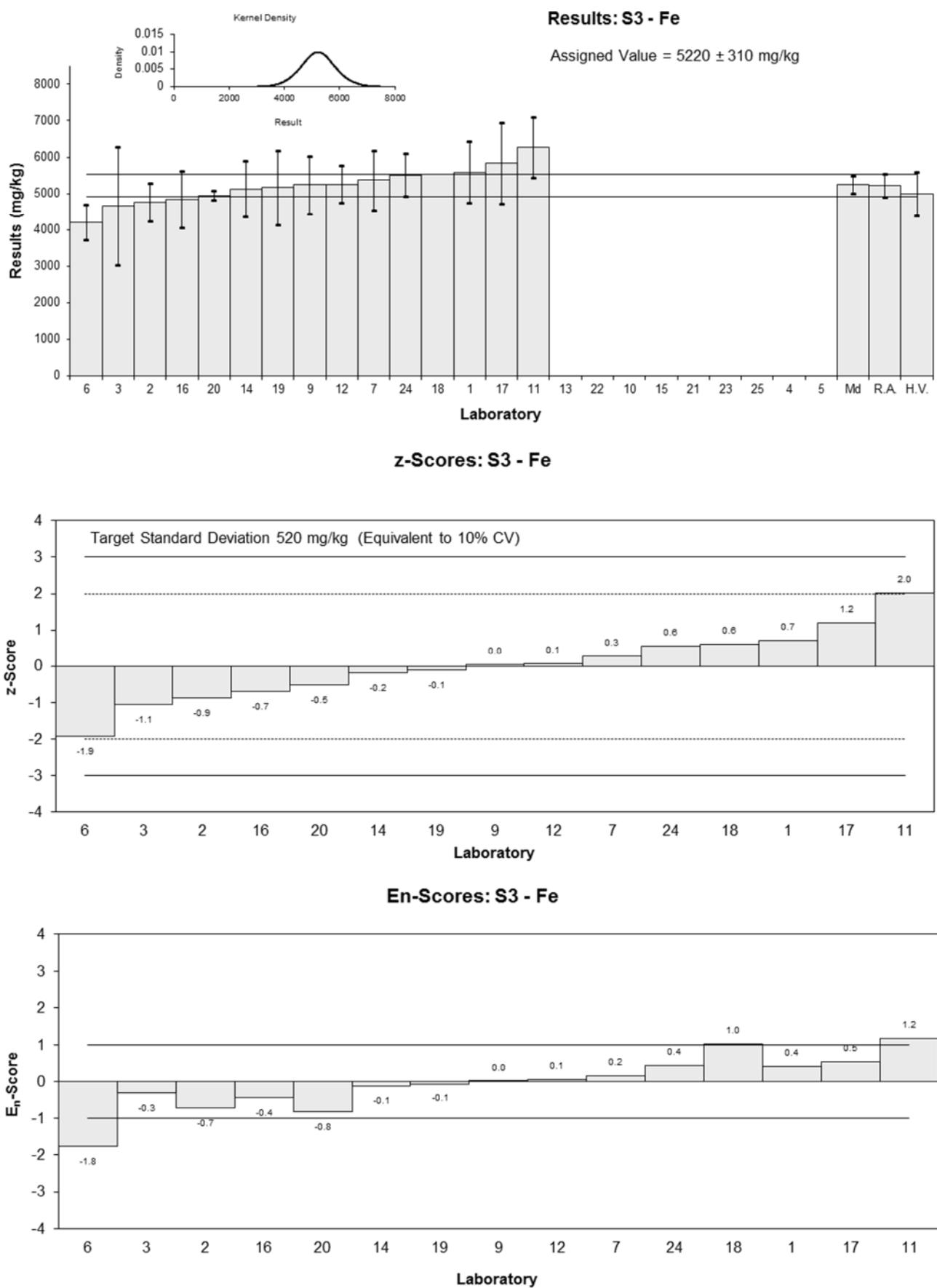


Figure 37

Table 48

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	267	67	0.15	0.06
2	258	48	-0.19	-0.09
3	260	42.5	-0.11	-0.06
4	NT	NT		
5	NT	NT		
6	231	19	-1.22	-1.05
7	219	48.2	-1.67	-0.82
9	250	76	-0.49	-0.16
10	NT	NT		
11	319	107	2.13	0.51
12	280	30	0.65	0.44
13	NR	NR		
14	279	42	0.61	0.33
15	NT	NT		
16	240	52	-0.87	-0.40
17	375	70	4.26	1.51
18	266	NR	0.11	0.12
19	250	50	-0.49	-0.23
20	198	51	-2.47	-1.15
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	300	36.4	1.41	0.85
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	263	24
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	270	32
<b>Robust Average</b>	263	24
<b>Median</b>	260	16
<b>Mean</b>	266	
<b>N</b>	15	
<b>Max.</b>	375	
<b>Min.</b>	198	
<b>Robust SD</b>	37	
<b>Robust CV</b>	14%	

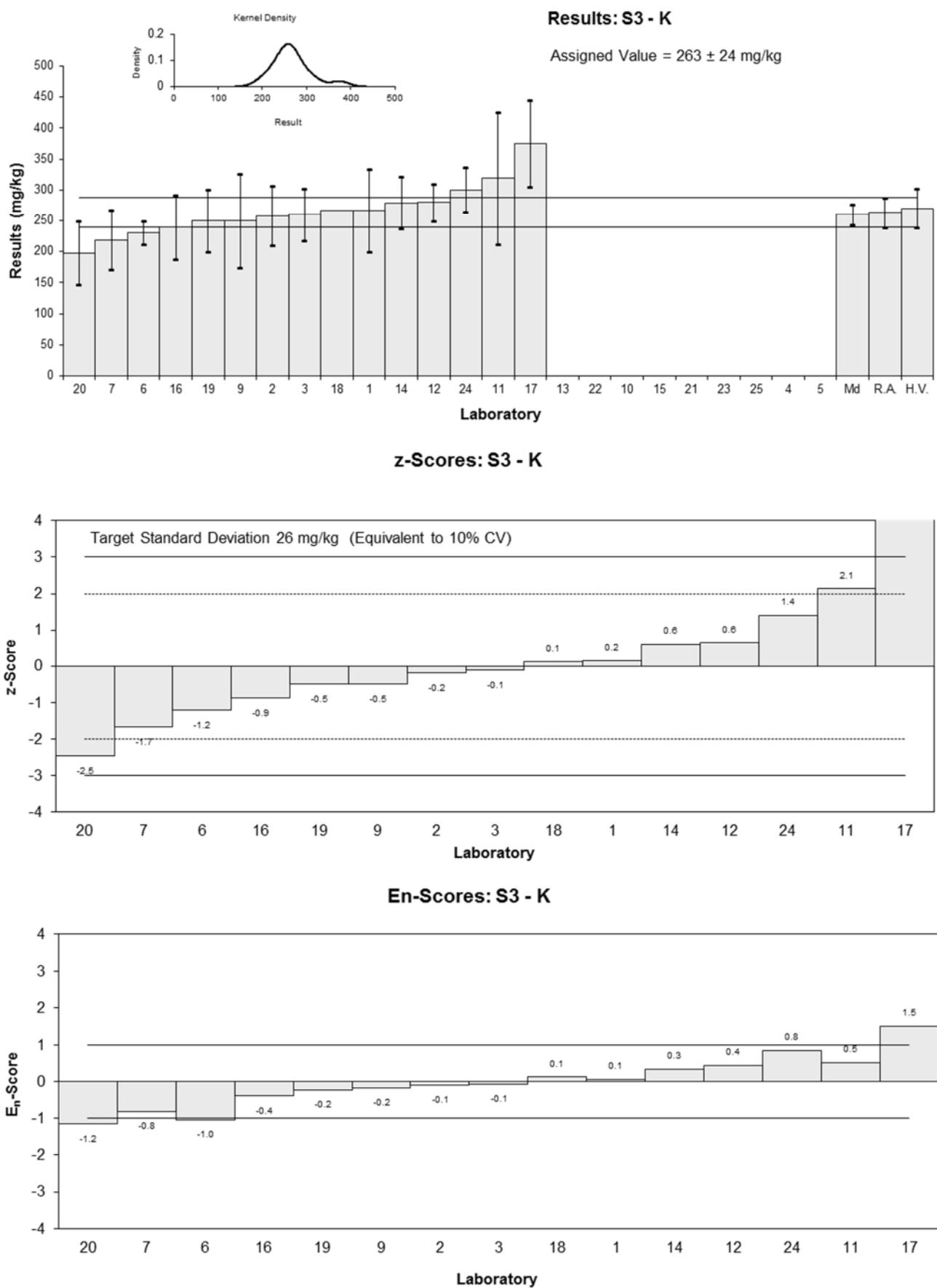


Figure 38

Table 49

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	408	41	0.15	0.12
2	436	65	0.85	0.49
3	400	73.4	-0.05	-0.03
4	NT	NT		
5	NT	NT		
6	305	25	-2.41	-2.74
7	375	62.2	-0.67	-0.40
9	360	121	-1.04	-0.34
10	NT	NT		
11	474	105	1.79	0.67
12	410	45	0.20	0.16
13	415	29	0.32	0.34
14	14950	2243	361.89	6.49
15	NT	NT		
16	400	81	-0.05	-0.02
17	543	100	3.51	1.37
18	419	NR	0.42	0.68
19	380	80	-0.55	-0.26
20	360	4	-1.04	-1.66
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	400	42.1	-0.05	-0.04
25	NT	NT		

**Statistics**

<b>Assigned Value*</b>	402	25
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	400	40
<b>Robust Average</b>	409	31
<b>Median</b>	404	21
<b>Mean</b>	1315	
<b>N</b>	16	
<b>Max.</b>	14950	
<b>Min.</b>	305	
<b>Robust SD</b>	49	
<b>Robust CV</b>	12%	

\*Robust Average excluding Laboratory 14

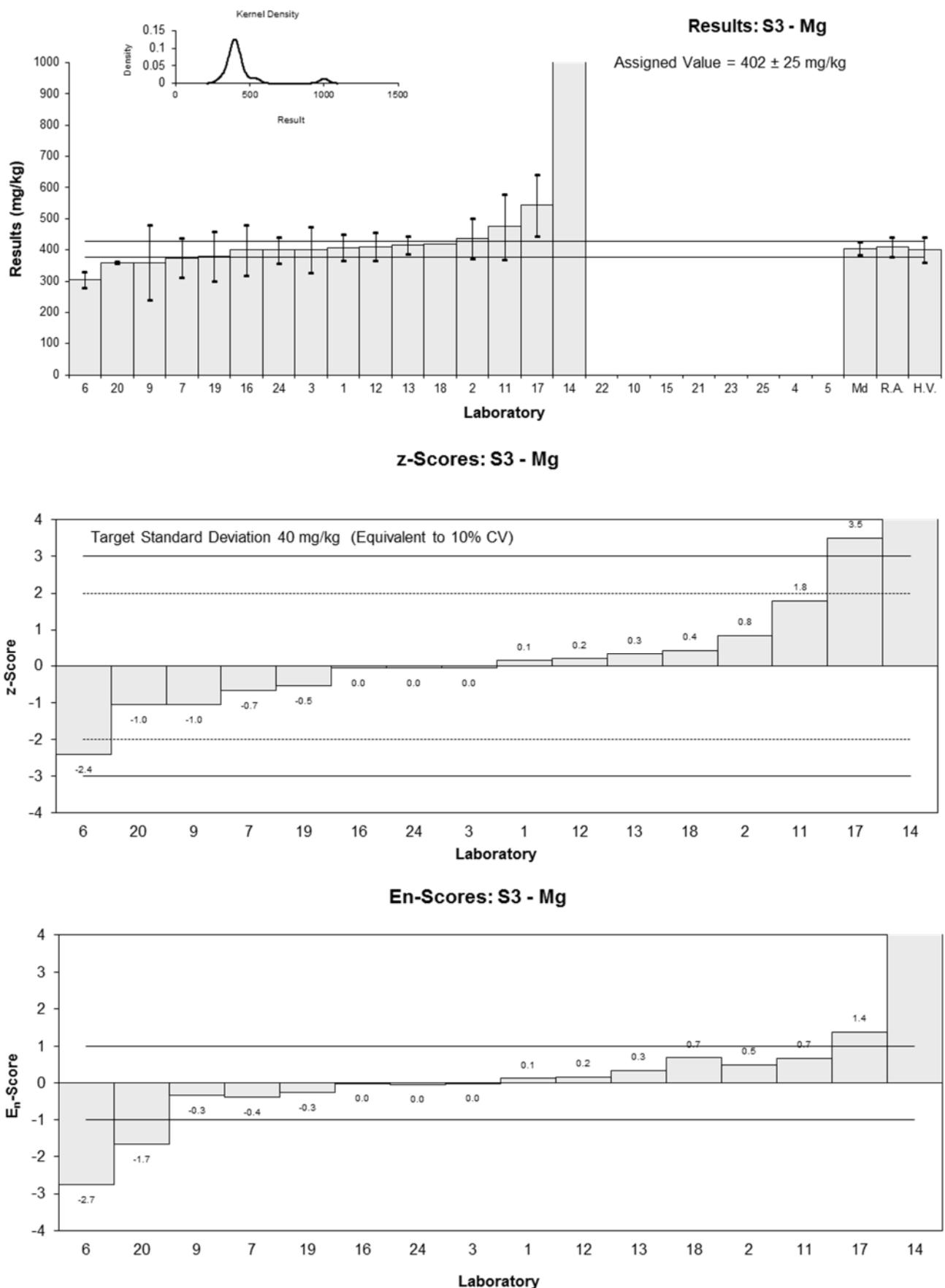


Figure 39

Table 50

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	106	23	1.82	0.66
2	68	22	-2.42	-0.91
3	90	13.5	0.03	0.02
4	NT	NT		
5	NT	NT		
6	91.8	6.9	0.23	0.18
7	174	27.5	9.40	2.90
9	70	46	-2.20	-0.42
10	NT	NT		
11	131	29	4.60	1.35
12	86	10	-0.41	-0.27
13	90	15	0.03	0.02
14	106	16	1.82	0.88
15	NT	NT		
16	92	28	0.26	0.08
17	93	18	0.37	0.16
18	83.0	NR	-0.75	-0.71
19	78	16	-1.30	-0.63
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	90	9	0.03	0.02
25	NT	NT		

**Statistics**

<b>Assigned Value*</b>	89.7	9.5
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	92	11
<b>Median</b>	90.0	5.7
<b>Mean</b>	96.6	
<b>N</b>	15	
<b>Max.</b>	174	
<b>Min.</b>	68	
<b>Robust SD</b>	17	
<b>Robust CV</b>	18%	

\*Robust Average excluding Laboratory 7.

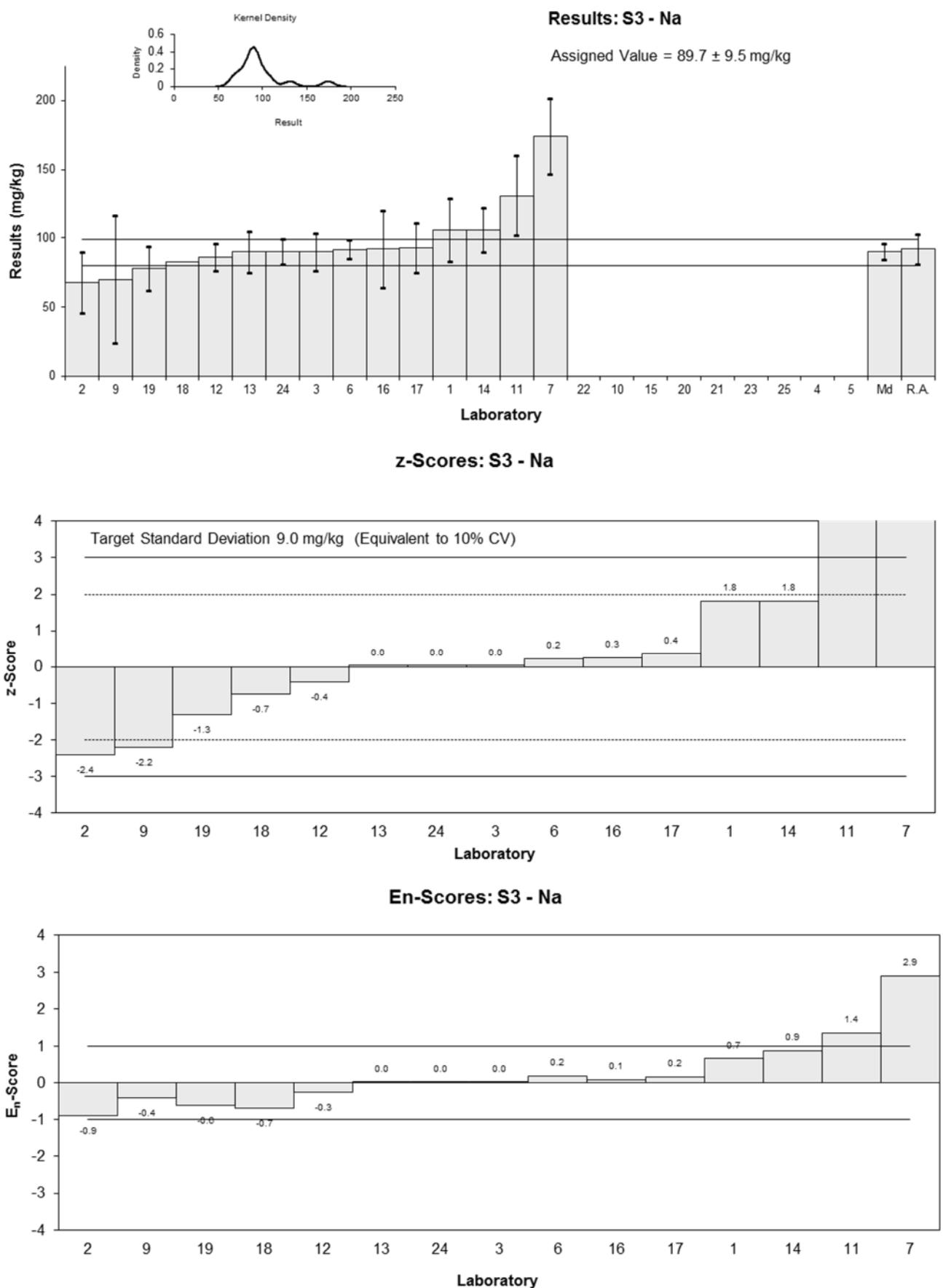


Figure 40

Table 51

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NR	NR		
2	1.4	0.4	-9.23	-16.96
3	17.7	NR	-0.22	-0.44
4	NT	NT		
5	NT	NT		
6	NT	NT		
7	NR	NR		
9	NT	NT		
10	NT	NT		
11	NR	NR		
12	17	2.0	-0.61	-0.50
13	18	1.8	-0.06	-0.05
14	18.2	2.7	0.06	0.04
15	NT	NT		
16	19	3.9	0.50	0.22
17	17	2.6	-0.61	-0.40
18	NT	NT		
19	20	3	1.05	0.61
20	NT	NT		
21	NT	NT		
22	18.2	NR	0.06	0.11
23	NT	NT		
24	NT	NT		
25	NT	NT		

**Statistics**

<b>Assigned Value*</b>	18.1	0.9
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	17.9	1.1
<b>Median</b>	18.0	1.1
<b>Mean</b>	16.3	
<b>N</b>	9	
<b>Max.</b>	20	
<b>Min.</b>	1.4	
<b>Robust SD</b>	1.3	
<b>Robust CV</b>	7.3%	

\*Robust Average excluding Laboratory 2.

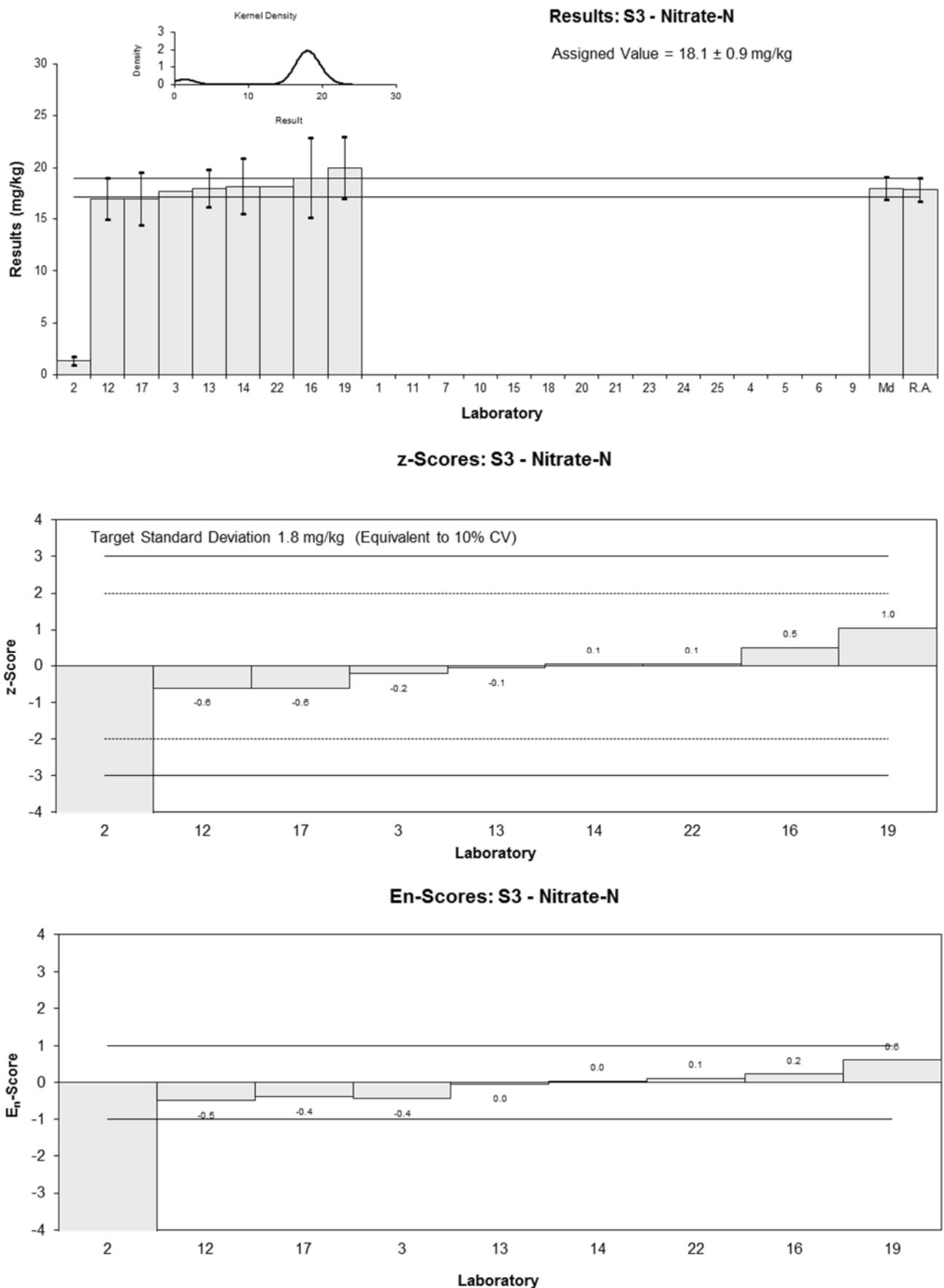


Figure 41

Table 52

**Sample Details**

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

**Participant Results**

Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	NR	NR		
2	3.2	0.7	5.32	1.91
3	1.9	0.18	0.45	0.39
4	NT	NT		
5	NT	NT		
6	1.48	0.14	-1.12	-1.05
7	NR	NR		
9	1.5	0.189	-1.05	-0.89
10	NT	NT		
11	NR	NR		
12	2.1	0.4	1.20	0.68
13	1.67	0.14	-0.41	-0.38
14	2.06	0.3	1.05	0.72
15	NT	NT		
16	<0.5	NR		
17	NT	NT		
18	NR	NR		
19	1.6	0.2	-0.67	-0.56
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	1.9	0.2	0.45	0.37
25	NT	NT		

**Statistics**

<b>Assigned Value*</b>	1.78	0.25
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1.10	0.13
<b>Robust Average</b>	1.84	0.28
<b>Median</b>	1.90	0.26
<b>Mean</b>	1.93	
<b>N</b>	9	
<b>Max.</b>	3.2	
<b>Min.</b>	1.48	
<b>Robust SD</b>	0.34	
<b>Robust CV</b>	18%	

\*Robust Average excluding Laboratory 2.

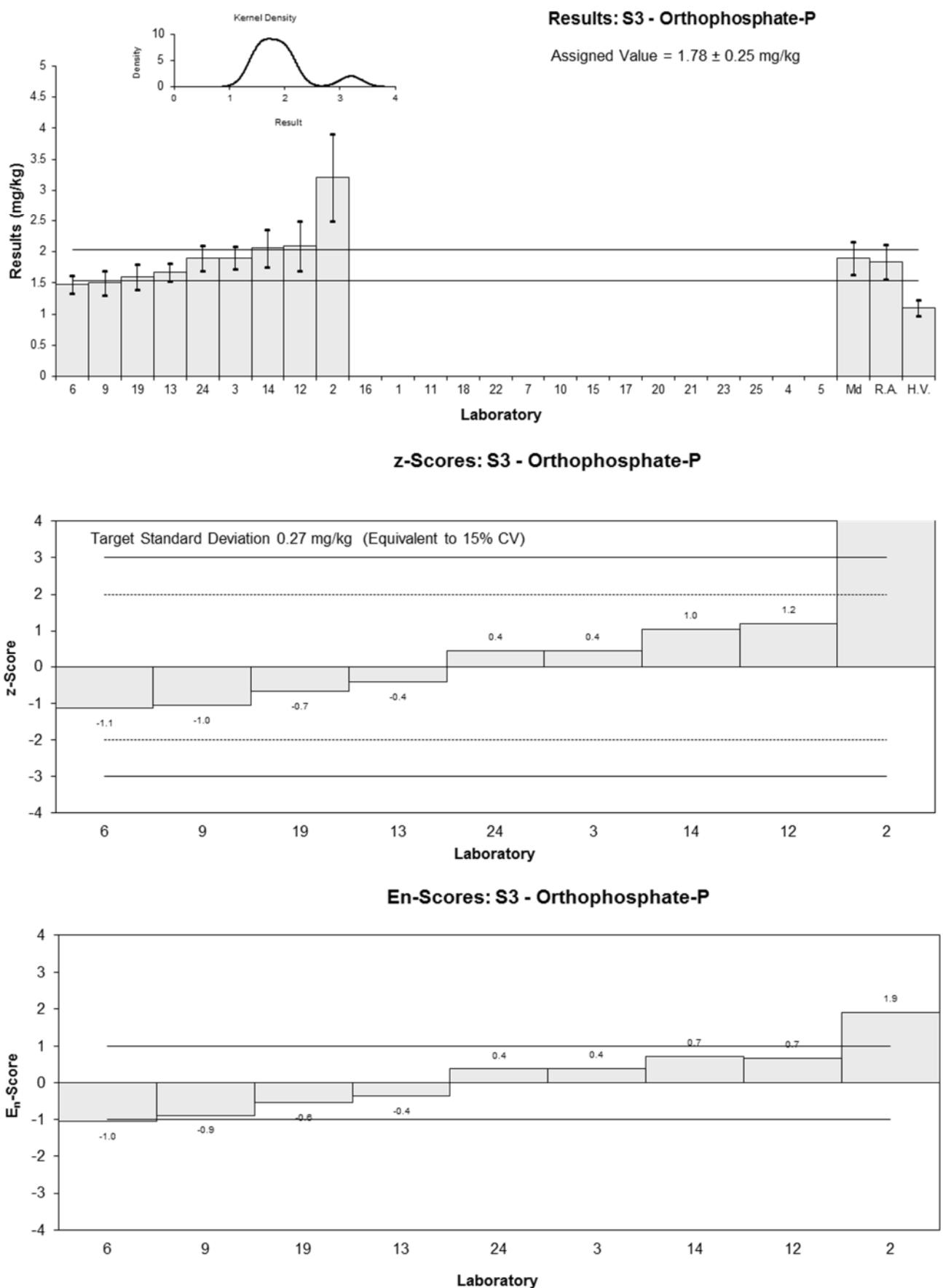


Figure 42

Table 53

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	282	43	-0.07	-0.04
2	333	56	1.73	0.83
3	260	NR	-0.85	-1.26
4	NT	NT		
5	NT	NT		
6	232	57	-1.83	-0.87
7	NR	NR		
9	300	11.2	0.56	0.73
10	NT	NT		
11	279	71	-0.18	-0.07
12	340	40	1.97	1.26
13	219	29	-2.29	-1.87
14	289	43	0.18	0.11
15	NT	NT		
16	290	49	0.21	0.11
17	282	54	-0.07	-0.03
18	306	NR	0.77	1.16
19	270	50	-0.49	-0.26
20	278	8	-0.21	-0.29
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	290	NR	0.21	0.32
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	284	19
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	255	31
<b>Robust Average</b>	284	19
<b>Median</b>	282	10
<b>Mean</b>	283	
<b>N</b>	15	
<b>Max.</b>	340	
<b>Min.</b>	219	
<b>Robust SD</b>	30	
<b>Robust CV</b>	11%	

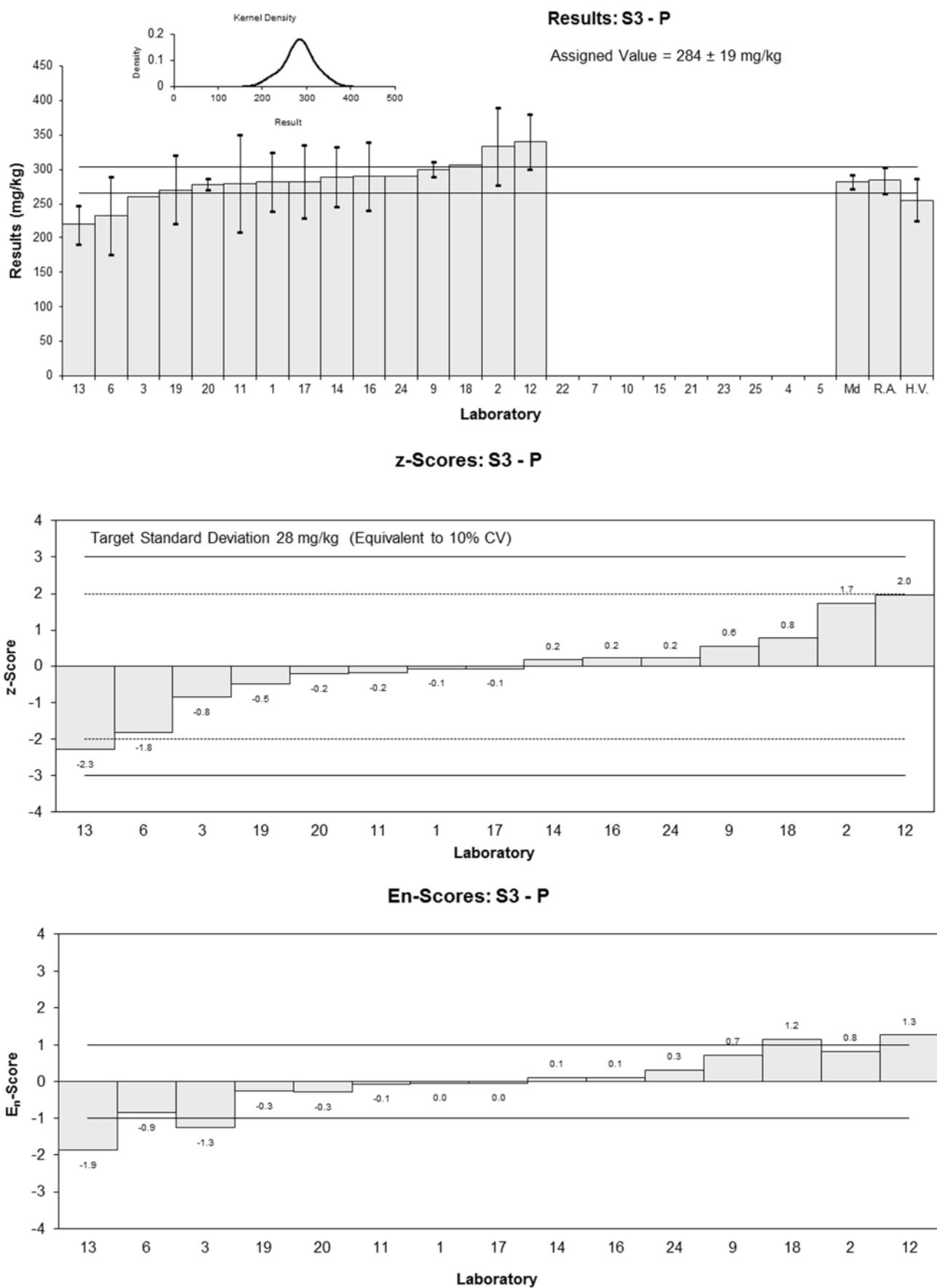


Figure 43

Table 54

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	NR	NR		
2	4.75	0.2	-1.48	-1.19
3	5.0	NR	-0.06	-0.11
4	NT	NT		
5	NT	NT		
6	4.77	0.04	-1.37	-2.44
7	5.4	0.1	2.22	2.90
9	5	0.087	-0.06	-0.08
10	NT	NT		
11	NR	NR		
12	5.0	0.2	-0.06	-0.05
13	4.9	0.5	-0.63	-0.22
14	5.07	0.1	0.34	0.45
15	NT	NT		
16	5.2	0.2	1.08	0.87
17	5	0.12	-0.06	-0.07
18	5.00	NR	-0.06	-0.11
19	5.1	0.2	0.51	0.41
20	NT	NT		
21	NT	NT		
22	5.0	0.1	-0.06	-0.07
23	NT	NT		
24	5.1	0.11	0.51	0.63
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	5.01	0.09
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	5.01	0.09
<b>Median</b>	5.00	0.07
<b>Mean</b>	5.02	
<b>N</b>	14	
<b>Max.</b>	5.4	
<b>Min.</b>	4.75	
<b>Robust SD</b>	0.14	
<b>Robust CV</b>	2.8%	

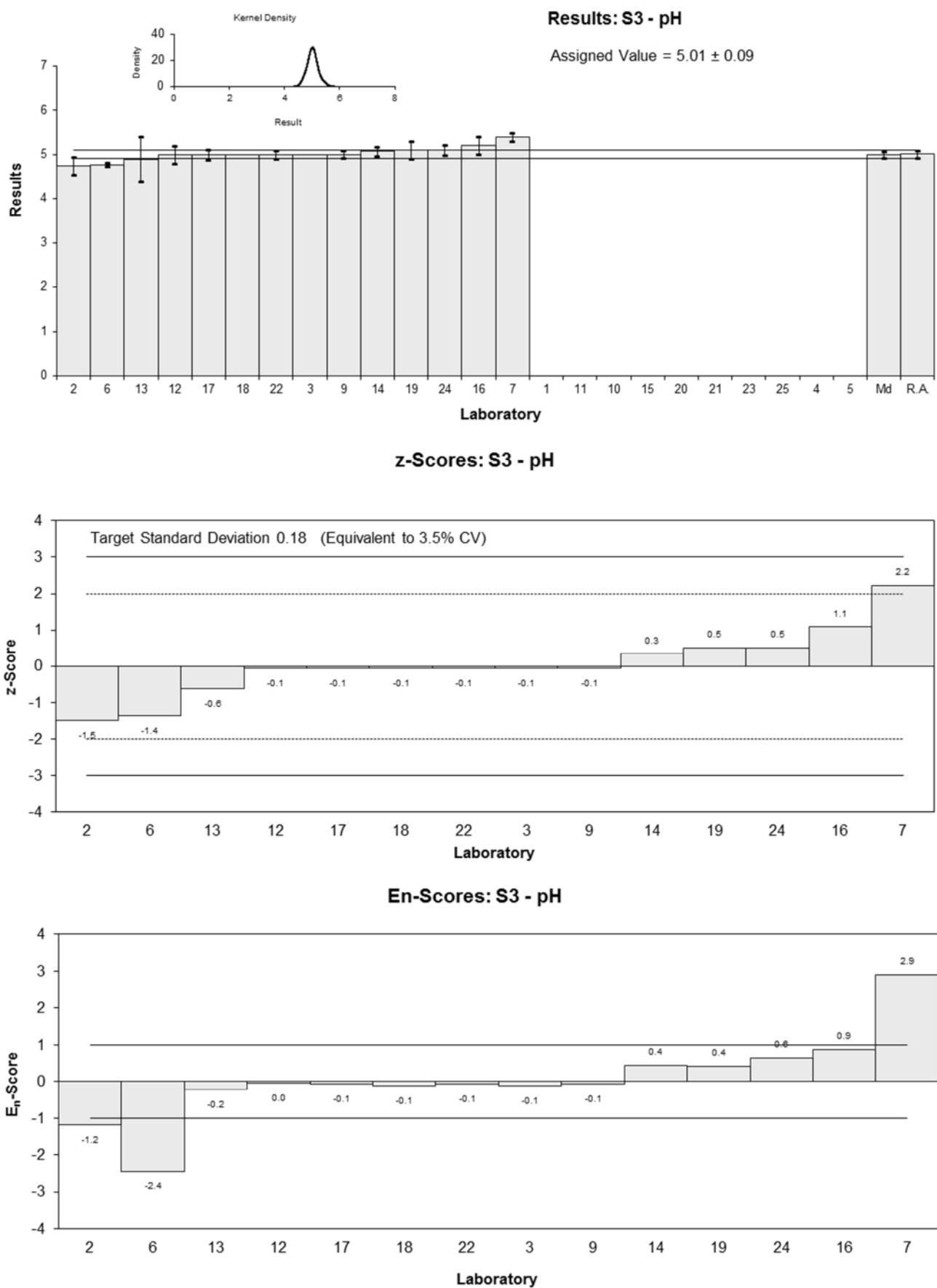


Figure 44

Table 55

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	312	47	0.26	0.16
2	270	42	-1.12	-0.72
3	280	NR	-0.79	-1.14
4	NT	NT		
5	NT	NT		
6	270	86	-1.12	-0.38
7	NR	NR		
9	320	10.87	0.53	0.68
10	NT	NT		
11	325	65	0.69	0.31
12	340	40	1.18	0.80
13	261	26	-1.41	-1.29
14	337	51	1.09	0.60
15	NT	NT		
16	300	64	-0.13	-0.06
17	NT	NT		
18	NT	NT		
19	320	60	0.53	0.25
20	311	6	0.23	0.32
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	310	24.7	0.20	0.19
25	NT	NT		

**Statistics**

<b>Assigned Value</b>	304	21
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	304	21
<b>Median</b>	311	13
<b>Mean</b>	304	
<b>N</b>	13	
<b>Max.</b>	340	
<b>Min.</b>	261	
<b>Robust SD</b>	30	
<b>Robust CV</b>	9.9%	

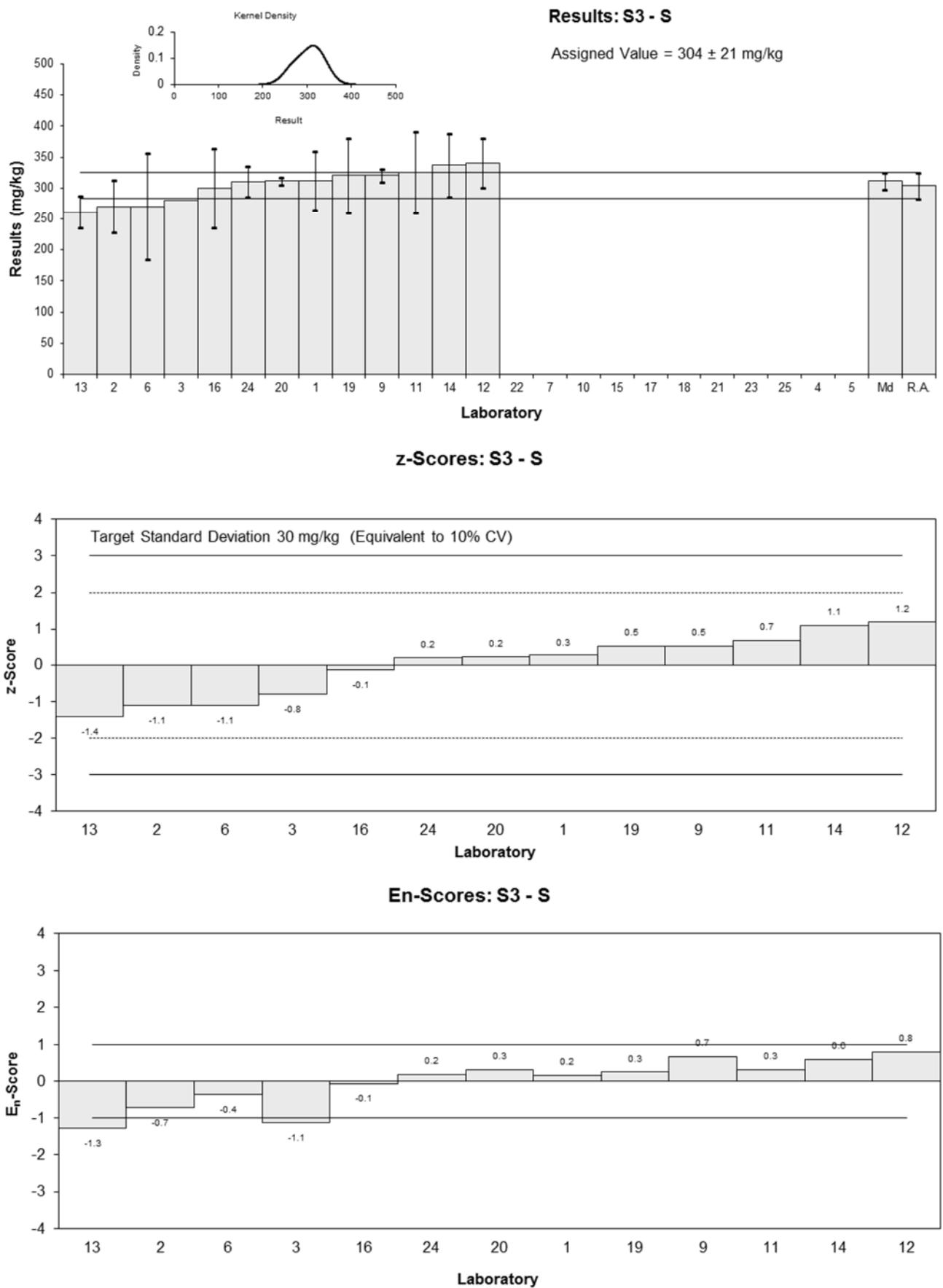


Figure 45

Table 56

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	10.7	1.3	-0.45	-0.29
2	3.7	0.8	-6.70	-5.51
3	9.0	1.6	-1.96	-1.13
4	NT	NT		
5	NT	NT		
6	9.34	1.27	-1.66	-1.11
7	NR	NR		
9	13	1.56	1.61	0.94
10	NT	NT		
11	13.1	2.2	1.70	0.77
12	10.2	1.5	-0.89	-0.54
13	10.8	0.7	-0.36	-0.31
14	NT	NT		
15	NT	NT		
16	10.9	3.5	-0.27	-0.08
17	13	2	1.61	0.79
18	11.0	NR	-0.18	-0.18
19	12	2	0.71	0.35
20	10.7	0.4	-0.45	-0.43
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	12	1	0.71	0.54
25	NT	NT		

**Statistics**

<b>Assigned Value*</b>	11.2	1.1
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	12.0	1.4
<b>Robust Average</b>	11.0	1.1
<b>Median</b>	10.9	1.0
<b>Mean</b>	10.7	
<b>N</b>	14	
<b>Max.</b>	13.1	
<b>Min.</b>	3.7	
<b>Robust SD</b>	1.7	
<b>Robust CV</b>	15%	

\*Robust Average excluding Laboratory 2.

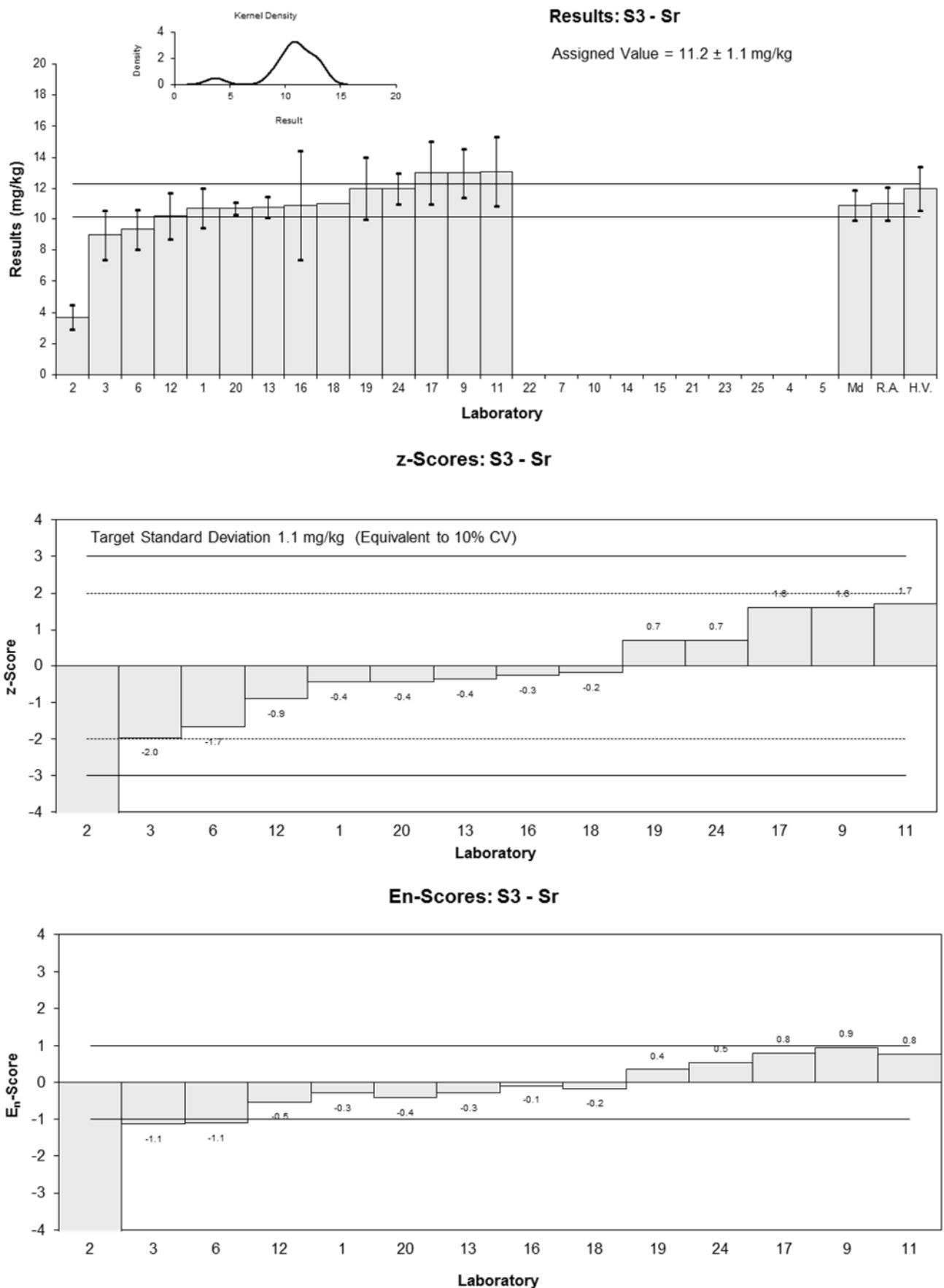


Figure 46

Table 57

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	NR	NR
2	NT	NT
3	110	19.5
4	NT	NT
5	NT	NT
6	107	7
7	NR	NR
9	130	8.75
10	NT	NT
11	NR	NR
12	37	8.0
13	59	5.9
14	NT	NT
15	NT	NT
16	60	12
17	61	12
18	83.3	NR
19	63	10
20	NT	NT
21	NT	NT
22	NR	NR
23	NT	NT
24	120	9.6
25	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	80	9
<b>Robust Average</b>	83	28
<b>Median</b>	73	25
<b>Mean</b>	83	
<b>N</b>	10	
<b>Max.</b>	130	
<b>Min.</b>	37	
<b>Robust SD</b>	36	
<b>Robust CV</b>	43%	

### Results: S3 - Sulphate

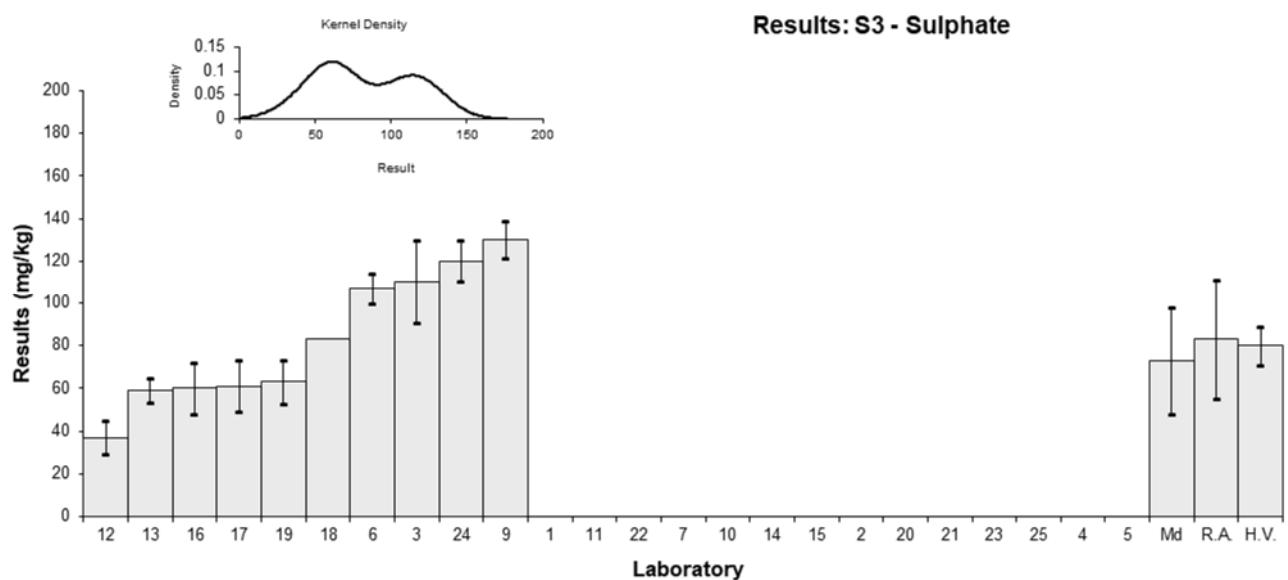


Figure 47

Table 58

**Sample Details**

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

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2510	480	0.87	0.39
2	3600	800	5.58	1.57
3	1980	NR	-1.43	-1.83
4	NT	NT		
5	NT	NT		
6	2320	411	0.04	0.02
7	NR	NR		
9	2370	760	0.26	0.08
10	NT	NT		
11	NR	NR		
12	2183	220	-0.55	-0.45
13	2125	574	-0.80	-0.31
14	2190	329	-0.52	-0.32
15	NT	NT		
16	2180	250	-0.56	-0.42
17	2300	350	-0.04	-0.03
18	NT	NT		
19	2600	390	1.26	0.68
20	NT	NT		
21	NT	NT		
22	NR	NR		
23	NT	NT		
24	3060	761	3.25	0.96
25	NT	NT		

**Statistics**

<b>Assigned Value*</b>	2310	180
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2200	260
<b>Robust Average</b>	2370	220
<b>Median</b>	2310	150
<b>Mean</b>	2452	
<b>N</b>	12	
<b>Max.</b>	3600	
<b>Min.</b>	1980	
<b>Robust SD</b>	310	
<b>Robust CV</b>	13%	

\*Robust Average excluding Laboratory 2.

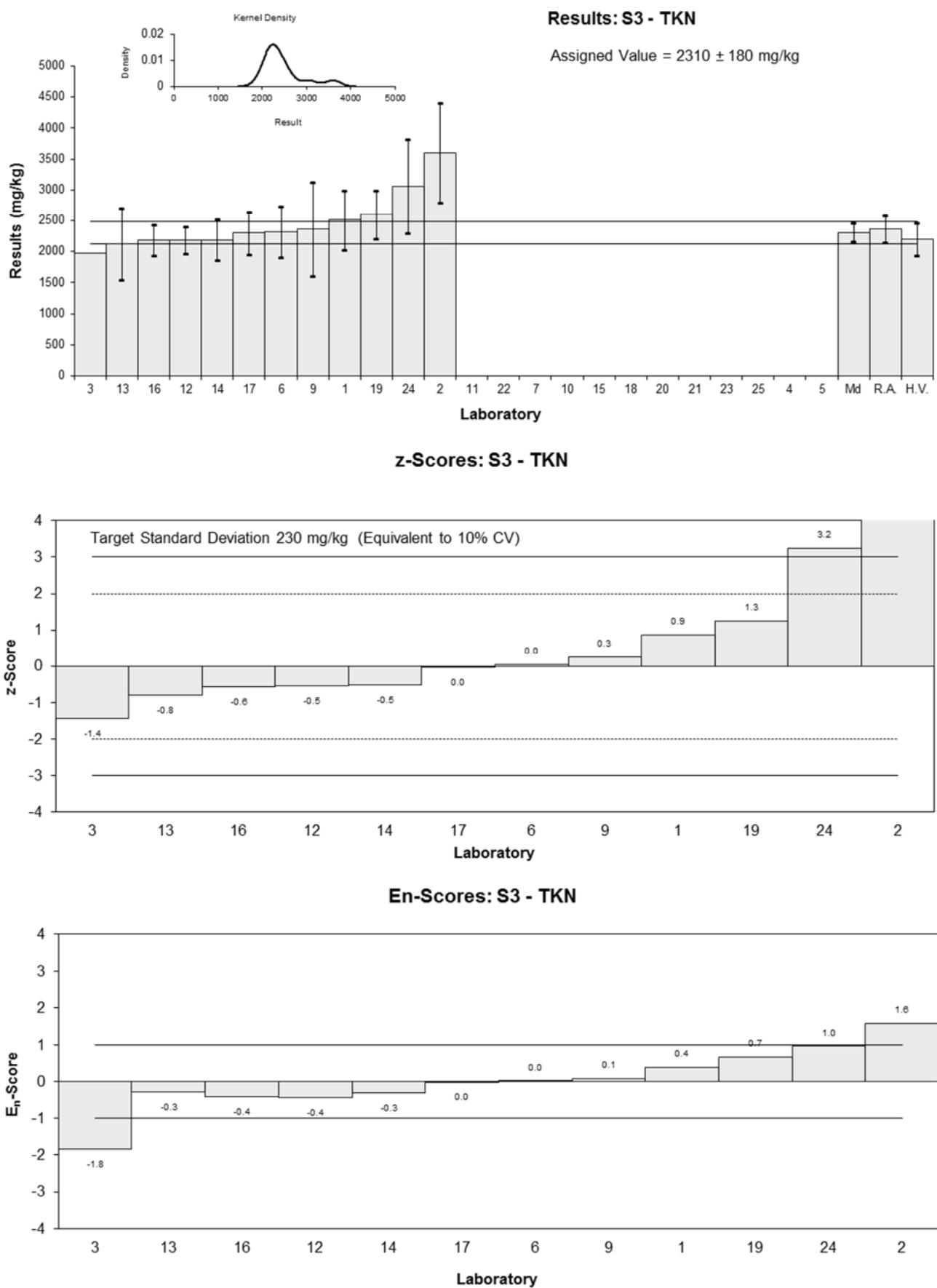


Figure 48

## 7 DISCUSSION OF RESULTS

### 7.1 Assigned Value and Traceability

**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.<sup>6</sup> Appendix 2 sets out the calculation of the robust average of Bi in Sample S1 and its associated uncertainty.

No assigned value was set for Cs, Th, in S1 and Ga in S2 because too few results were reported for these elements; no assigned value was set for bromide and sulphate in S3 either because the reported results were not compatible.

**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 586 numerical results, 538 (92%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 0.071% to 182% of the reported value. Participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Tables 9 and 10.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias and top down approach using only the reproducibility from inter-laboratory comparisons studies.<sup>9–15</sup>

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 48). In this study, the reported expanded measurement uncertainty has been under-estimated in some cases (e.g. Lab 20 for Bi, Cr, Cu in S1 or Lab 15 for Cu in S1) or over-estimated (e.g. Lab 7 for Sb in S2). As a simple rule of thumb, when the uncertainty estimate is either 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 According to General Accreditation Guidance, Estimating and reporting measurement uncertainty of chemical test results<sup>12</sup> and to NORDTEST TR 537,<sup>10</sup> 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.<sup>10, 12</sup>

Laboratories 13 and 21 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.<sup>9</sup>

Laboratory 19 reported an estimate of expanded uncertainty for their Sr in S2 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  $64.3 \pm 12.86$  mg/kg, it is better to report  $64 \pm 13$  mg/kg or instead of  $9910 \pm 1486.50$  mg/kg, it is better to report  $9910 \pm 1500$  mg/kg.<sup>9</sup>

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

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

The dispersal of participants' E<sub>n</sub>-scores is graphically presented in Figure 49. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E<sub>n</sub>-score.

Of 559 results for which E<sub>n</sub>-scores were calculated, 453 (81%) returned a satisfactory score of  $|E_n| \leq 1.0$  indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

### 7.4 z-Score

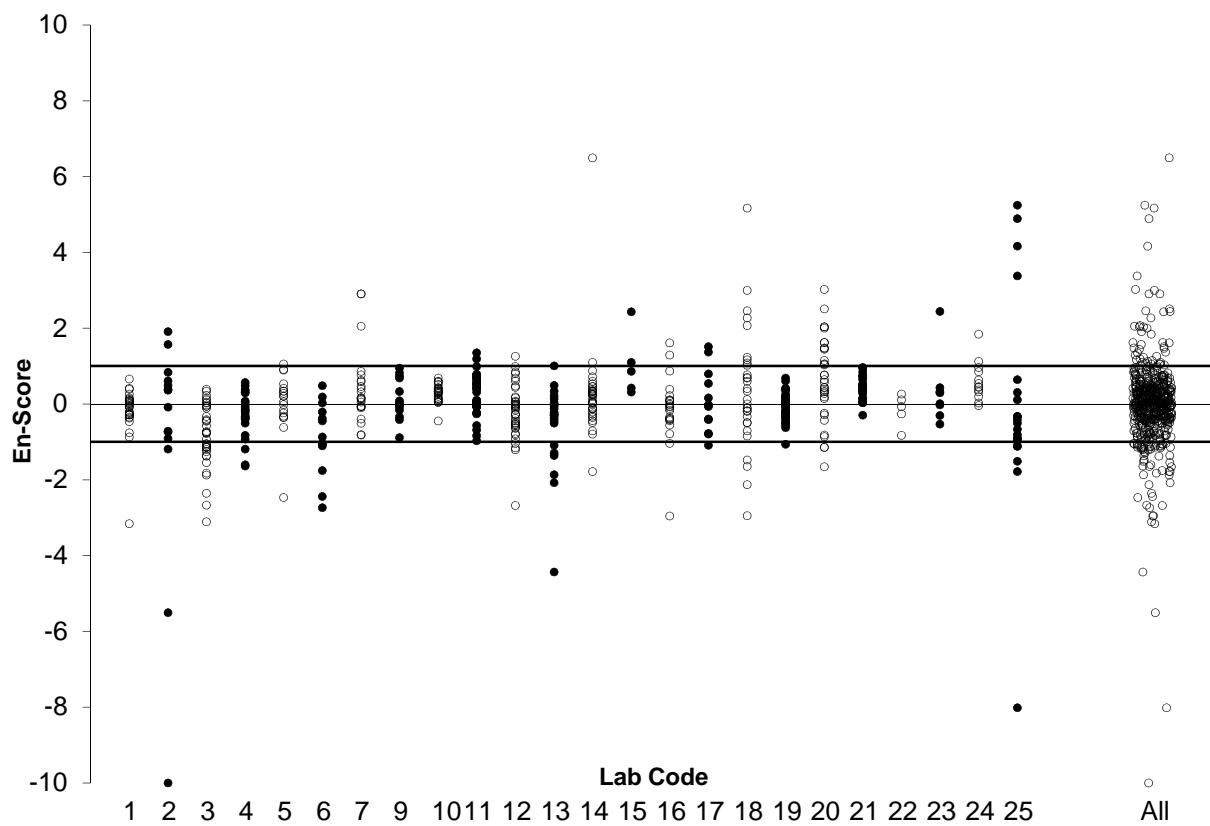
The z-score compares the participant's deviation from the assigned value with the target standard deviation set for proficiency assessment.

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 3.5% to 25% PCV were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation as a realistic, set value enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson equation<sup>7</sup> and the participants' coefficient of variation resulted in this study are presented for comparison in Table 59.

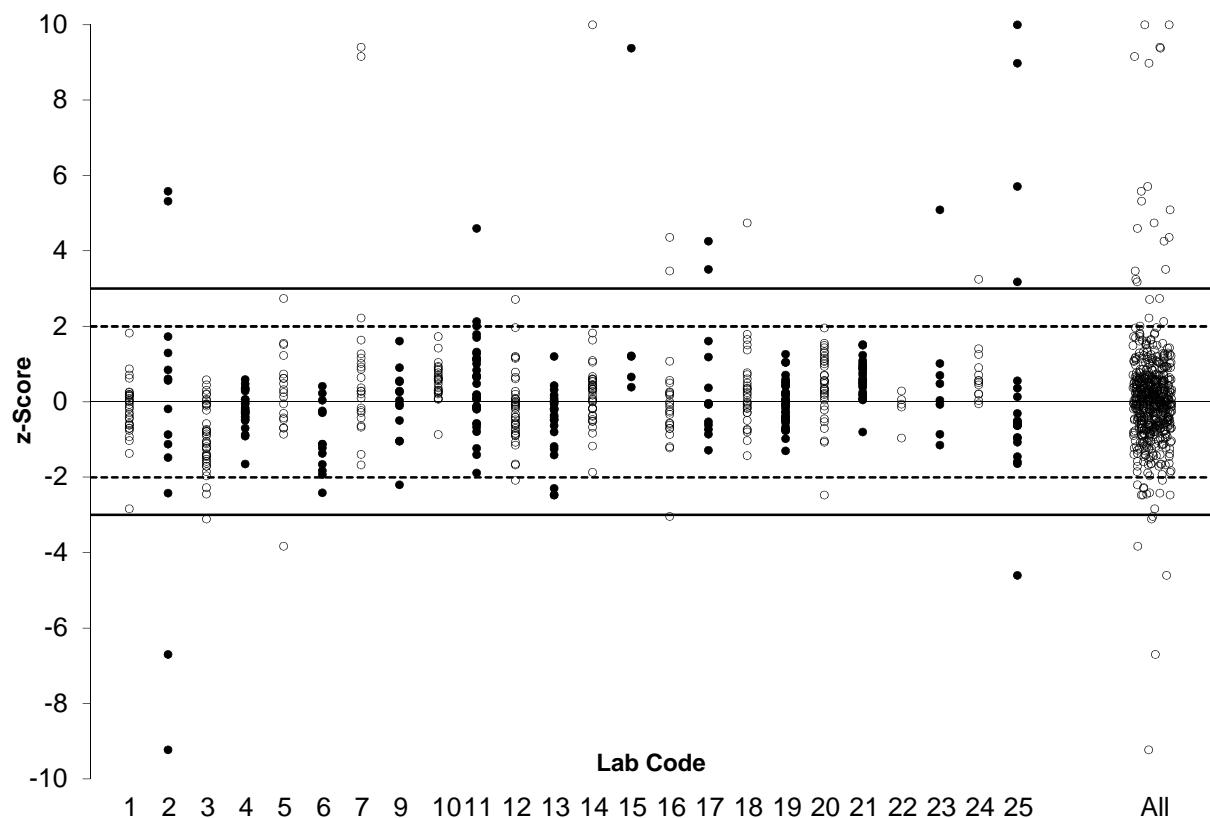
The dispersal of participants' z-scores is presented in Figure 50 (by laboratory code) and in Figure 51 (by test). Of 559 results for which z-scores were calculated, 519 (93%) returned

satisfactory score of  $|z| \leq 2.0$  and 16 (3%) were questionable of  $2.0 < |z| < 3.0$ . Participants with multiple z-scores larger than 2.0 or smaller than -2.0 should check for laboratory bias.



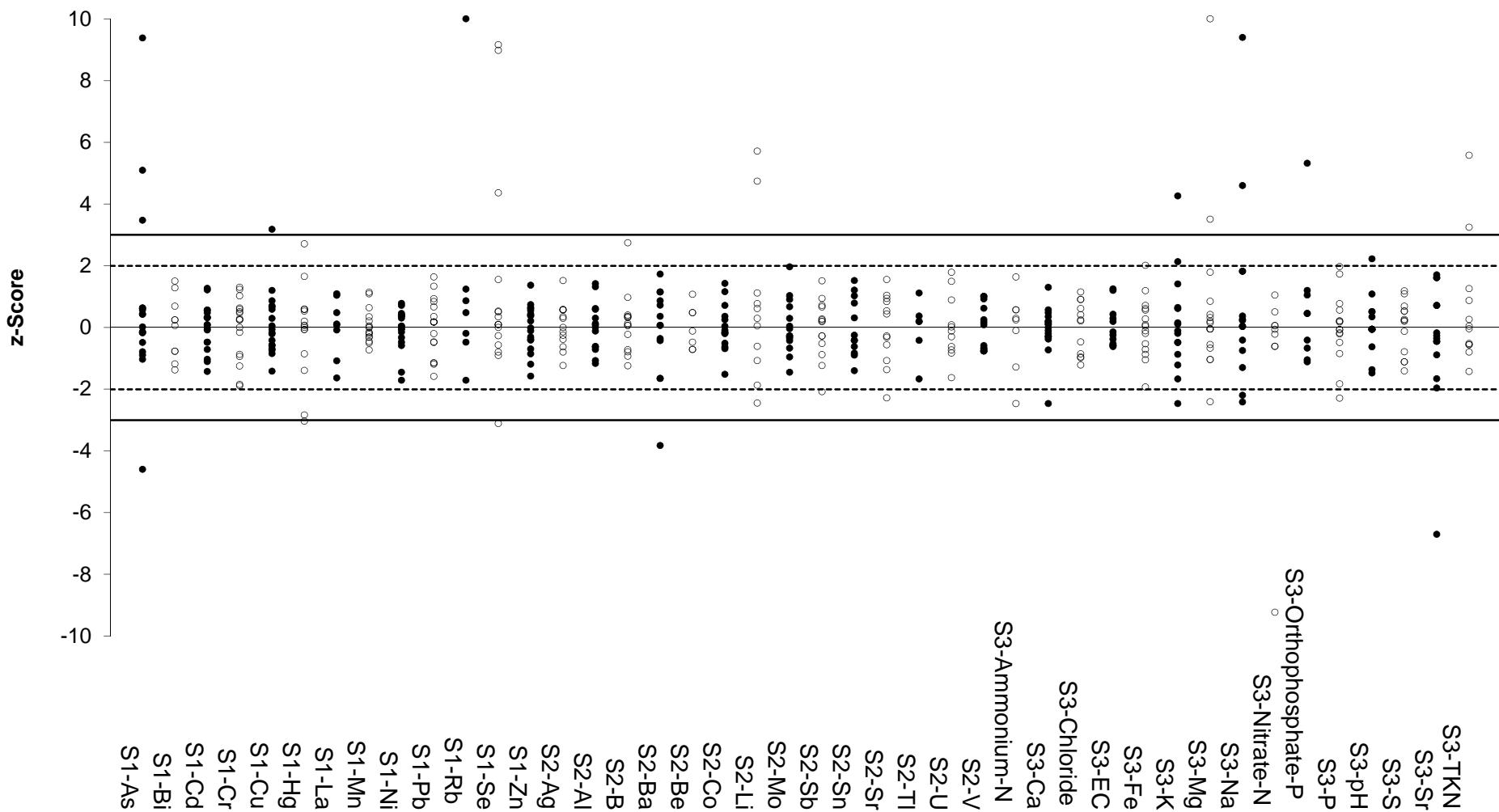
Scores of  $>10$  or  $<-10$  have been plotted as 10 or -10.

Figure 49 E<sub>n</sub>-Score Dispersal by Laboratory



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

Figure 50 z-Score Dispersal by Laboratory



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

Figure 51 z-Score Dispersal by Test

Table 59 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 CV)
S1	As	3.29	11%	13%	15%
S1	Bi	3.28	17%	13%	15%
S1	Cd	0.840	12%	16%	15%
S1	Cr	25.4	11%	9.8%	10%
S1	Cs	Not Set	NA	NA	NA
S1	Cu	626	8.5%	6.1%	10%
S1	Hg	1.01	18%	16%	15%
S1	La	8.97	11%	12%	10%
S1	Mn	440	5%	6.4%	10%
S1	Ni	26.9	5.6%	9.8%	10%
S1	Pb	22.6	9.7%	10%	10%
S1	Rb	10.5	12%	11%	10%
S1	Se	3.75	9.5%	13%	15%
S1	Th	Not Set	NA	NA	NA
S1	Zn	613	7.7%	6.1%	10%
S2	Ag	2.76	11%	14%	15%
S2	Al	3940	9.1%	4.6%	10%
S2	B	94.8	7.9%	8.1%	10%
S2	Ba	139	14%	7.6%	10%
S2	Be	0.112	12%	22%	15%
S2	Co	4.48	7.6%	13%	10%
S2	Ga	Not Set	NA	NA	NA
S2	Li	0.98	21%	16%	20%
S2	Mo	5.37	13%	12%	15%
S2	Sb	1.06	18%	16%	20%
S2	Sn	32.0	16%	9.5%	15%
S2	Sr	99.6	12%	8%	10%
S2	Tl	0.086	26%	22%	25%
S2	U	0.662	17%	17%	15%
S2	V	11.9	8.2%	11%	10%
S3	Ca	1050	4.8%	5.6%	10%
S3	Fe	5220	9.2%	4.4%	10%
S3	K	263	14%	6.9%	10%
S3	Mg	402	9.8%	6.5%	10%
S3	Na	89.7	16%	8.1%	10%
S3	P	284	11%	6.8%	10%
S3	S	304	9.9%	6.8%	10%
S3	Sr	11.2	14%	11%	10%
S3	Bromide	Not Set	42%	NA	NA
S3	Chloride	42.3	19%	9.1%	20%
S3	Orthophosphate-P	1.78	16%	15%	15%
S3	Sulphate	Not Set	43%	NA	NA
S3	pH	5.01	2.8%	13%	3.5%
S3	EC	208 µS/cm	6.7%	7.2%	10%
S3	TKN	2310	10%	5%	10%
S3	Ammonium-N	29.6	25%	9.6%	20%
S3	Nitrate-N	18.1	5.7%	10%	10%

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

Table 60 Summary of Participants' Results and Performance in Sample S1

Lab Code	As (mg/kg)	Bi (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cs (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	La (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Rb (mg/kg)	Se (mg/kg)	Th (mg/kg)	Zn (mg/kg)
A.V.	3.29	3.28	0.840	25.4	Not Set	626	1.01	8.97	440	26.9	22.6	10.5	3.75	Not Set	613
H.V.	3.08	3.50	0.803	25.5	0.14	610	1.00	9.3	477	26.8	22.5	11.7	3.28	NA	506
1	3.3	3.4	0.71	27	NR	590	0.58	NR	440	27	23	NR	3.8	NR	570
2	NT														
3	2.9	2.6	0.7	20.7	<0.1	537	1.0	8.0	408	22.3	19.9	8.7	2	0.1	516
4	3.05	3.31	0.836	26.6	NT	622	1.02	NT	455	27.9	22.15	NT	3.24	0.183	589
5	3.60	NT	0.88	28.52	NT	582.43	0.88	NT	426.39	26.77	21.53	NT	4.62	NT	658.50
6	NT														
7	<3	NT	1.0	25	NT	679.7	0.8	NT	468	27.9	26.3	NT	8.9	NT	626
9	NT														
10	3.6	3.4	0.91	23.2	0.15	662.9	1.1	9.9	449.1	27.7	24.5	11.4	3.8	NT	651.2
11	3.22	3.91	0.85	20.6	NR	668	1.02	9.07	490	25.3	23.0	NR	3.43	NR	653
12	2.85	2.90	0.78	26.1	NT	573	1.42	NT	426	26.5	20.0	NT	3.75	NT	588
13	3.5	2.7	0.78	22.23	0.15	613	1.01	NR	432	25.6	23	10.3	3.8	<0.5	612
14	3.21	NT	0.88	26.9	NT	615	1.10	9.04	440	28.1	23.4	NT	4.05	NT	647
15	7.917	NT	0.994	NT	NT	701.3	NT	NT	NT	NT	24.10	NT	NT	NT	637.0
16	5.0	NT	0.75	26	NT	590	0.55	NT	430	26	23	NT	6.2	NT	540
17	NT														
18	2.78	NT	0.66	25.4	NT	580	1.26	NT	433	26.8	21.5	NT	4.03	NT	697
19	3.2	2.9	0.83	26	<0.5	600	1.1	8.9	420	28	23	10	3.6	<0.5	640
20	3.57	3.62	0.88	28.7	0.127	644	1.09	9.95	442	28.8	25.6	11.0	3.94	0.31	606
21	3.5	4.02	0.85	26.7	<0.2	629	1.04	9.40	488	29.0	24.7	11.8	3.3	NT	637
22	NT														
23	5.8	NT	0.9	28	NT	670	1.0	NT	NT	27	20	NT	NT	NT	560
24	NT														
25	1.02	NT	0.91	23	NT	825	NT	7.5	418	23	19	23	8.8	2.3	594

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

Table 61 Summary of Participants' Results and Performance in Sample S2

Lab Code	Ag (mg/kg)	Al (mg/kg)	B (mg/kg)	Ba (mg/kg)	Be (mg/kg)	Co (mg/kg)	Ga (mg/kg)	Li (mg/kg)	Mo (mg/kg)	Sb (mg/kg)	Sn (mg/kg)	Sr (mg/kg)	Tl (mg/kg)	U (mg/kg)	V (mg/kg)
A.V.	2.76	3940	94.8	139	0.112	4.48	Not Set	0.98	5.37	1.06	32.0	99.6	0.086	0.662	11.9
H.V.	2.85	4400	79.0	147	0.106	4.25	1.13	0.99	5.20	0.95	22.5	96	NA	0.627	11.0
1	2.7	3700	86	NR	0.10	4.4	NR	NR	5.1	1.1	30	86	0.09	0.6	11
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	3.0	4060	83	140	<0.1	3.8	0.9	0.5	4.2	0.8	27.7	76.9	<0.1	0.5	11
4	2.655	4172	98	116	0.104	4.41	NT	1.037	5.156	0.873	30.79	96.4	0.077	0.632	11.07
5	3.39	3990.18	120.77	85.78	0.12	4.17	NT	NT	5.02	1.11	NT	NT	NT	NT	12.64
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	NT	3689	92.6	133	<1	5.0	NT	NT	5.6	1.0	36.9	NT	NT	NT	13
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	2.88	4500	95.5	163	0.12	4.8	NT	1.13	6.1	1.2	33.5	109	0.094	0.67	12.2
11	2.25	4460	87.3	155	0.11	4.39	NR	1.20	4.83	1.10	25.3	108	0.11	0.65	13.1
12	2.76	4180	95.4	116	0.10	4.44	NT	0.86	5.34	0.62	35.8	88.9	0.05	0.58	12.0
13	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
14	2.90	3478	98.6	134	<0.1	4.25	NT	0.614	5.91	1.12	28.0	104	NT	0.664	11.1
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
18	2.43	3893	97.8	149	NT	4.64	NT	1.91	5.14	1.38	NT	96.8	NT	0.84	NT
19	2.6	3940	88	140	<0.5	4.5	1.1	0.99	5.4	1.0	30	110	<0.5	0.59	11
20	2.99	3661	98.2	155	0.130	5.12	0.97	0.77	6.95	1.26	37.8	115	0.090	0.81	13.1
21	3.00	3970	104	150.9	<0.2	4.59	NT	1.10	6.2	1.21	39.3	105	<0.2	0.750	12.1
22	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
23	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
24	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
25	2.5	3520	96	144	NT	4.2	NT	2.1	4.6	0.95	29	94	NT	NT	11.2

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

Table 62 Summary of Participants' Results and Performance for Sample S3

Lab Code	Ca (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)	P (mg/kg)	S (mg/kg)	Sr (mg/kg)	Bromide (mg/kg)	Chloride (mg/kg)	Orthophosphate-P (mg/kg)	Sulphate (mg/kg)	pH	EC (µS/cm)	TKN (mg/kg)	Ammonium-N (mg/kg)	Nitrate-N (mg/kg)
A.V.	1050	5220	263	402	89.7	284	304	11.2	Not Set	42.3	1.78	Not Set	5.01	208	2310	29.6	18.1
H.V.	1000	5000	270	400	NA	255	NA	12.0	2.40	43.0	1.10	80	NA	NA	2200	NA	NA
1	1020	5590	267	408	106	282	312	10.7	NR	NR	NR	NR	NR	NR	2510	NR	NR
2	1186	4767	258	436	68	333	270	3.7	1.5	47.5	3.2	NT	4.75	NT	3600	33	1.4
3	1070	4670	260	400	90	260	280	9.0	0.9	44.1	1.9	110	5.0	196	1980	NT	17.7
4	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
5	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
6	1020	4210	231	305	91.8	232	270	9.34	0.85	45.8	1.48	107	4.77	203	2320	NT	NT
7	1061	5366	219	375	174	NR	NR	NR	NR	NR	NR	NR	5.4	NR	NR	NR	NR
9	1040	5240	250	360	70	300	320	13	NT	50	1.5	130	5	214	2370	NT	NT
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	1100	6270	319	474	131	279	325	13.1	NR	NR	NR	NR	NR	NR	NR	NR	NR
12	1030	5260	280	410	86	340	340	10.2	NT	52	2.1	37	5.0	196	2183	29	17
13	791	NR	NR	415	90	219	261	10.8	35	<5	1.67	59	4.9	233	2125	15	18
14	1010	5122	279	14950	106	289	337	NT	1.02	38.3	2.06	NT	5.07	217	2190	39.3	18.2
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	1050	4850	240	400	92	290	300	10.9	NT	32	<0.5	60	5.2	195	2180	33	19
17	973	5840	375	543	93	282	NT	13	<2	35	NT	61	5	197	2300	22	17
18	1087	5536	266	419	83.0	306	NT	11.0	1.75	44.3	NR	83.3	5.00	212	NT	NT	NT
19	1070	5160	250	380	78	270	320	12	1.1	34	1.6	63	5.1	200	2600	31	20
20	1064	4945	198	360	NT	278	311	10.7	NT	NT	NT	NT	NT	NT	NT	NT	NT
21	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
22	NR	NR	NR	NR	NR	NR	NR	NR	NR	34.14	NR	NR	5.0	205	NR	31.3	18.2
23	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
24	1110	5510	300	400	90	290	310	12	NT	50	1.9	120	5.1	234	3060	NT	NT
25	NT	NT	NT	NT	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.

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

A summary of participants' results and performance is presented in Tables 60 to 63 and in Figures 50 and 51.

Measurement of Na in S3 presented the most analytical difficulty.

### 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.<sup>5, 16-19</sup> While an aggressive digestion regime can produce high, misleading results, weak digestion regimes (low digestion temperature, reduced digestion time, diluted acids and/or a low ratio of acid to sample size) may extract just a fraction of the contaminants from the soil. There is no standardisation of methods for acid extractable elements. In general methods are conventionally defined by procedures involving extractions: with aqua regia or with various amounts of HNO<sub>3</sub>, HCl, in combination or alone and most of these methods produce comparable results.<sup>20-22</sup>

In previous studies conducted by NMI for trace elements in garden soil, compost, sediment or clay, relationships were found to exist between the results reported for Al, Cr, Ni, V and extraction regime employed.

In the present study, the samples were dried biosoil. Although participants used various sample sizes (from 0.5 g to 2.16 g), digestion temperatures (from 80°C to 170°C) and digestion times (from 30 min to 240 min) no relationship was evident between extraction method employed and the results reported for targeted analytes including for the method dependent ones.

The method descriptions provided by participants are presented in Tables 1 and 8 while the instrumental conditions are presented in Appendix 4.

Laboratory 20 reported for Sample S1: "We also performed a US EPA 200.2 Digestion on Sample S1, which gave lower results for Cr 21.6 mg/kg & Thorium 0.13 mg/kg, than our in-house block digestion method. All other elements were similar. US EPA 200.2 uses 2 mL of (1+1) nitric acid and 5 mL of (1+4) hydrochloric acid so less acid is used in the digest." For Sample S2, Laboratory 20 also reported: "We also performed a US EPA 200.2 digestion on Sample 2 which gave lower results for Sn with 29.4 mg/kg and U 0.69 mg/kg, as compared to our in-house method but interestingly higher results for Li 1.03 mg/kg."

### Individual Element Commentary

**Aluminium** is an element which is strongly dependent on digestion regime. The between-laboratory coefficient of variation for Al in Sample S2 (9.1%) was in good agreement with that predicted by Thomson (10%).<sup>7</sup>

Plots of Al participants' performance versus instrumental technique used are presented in Figure 52

**Arsenic** measurements at a level of 3.29 mg/kg in soil Sample S1 presented difficulties to some participating laboratories. Of 17 reported results, 4 returned unsatisfactory z-scores.

Arsenic level in S1 is likely to be too low for accurate determination by ICP-OES and GF-AAS. (Figure 53).

### S2 Al z-Scores vs Instrumental Technique

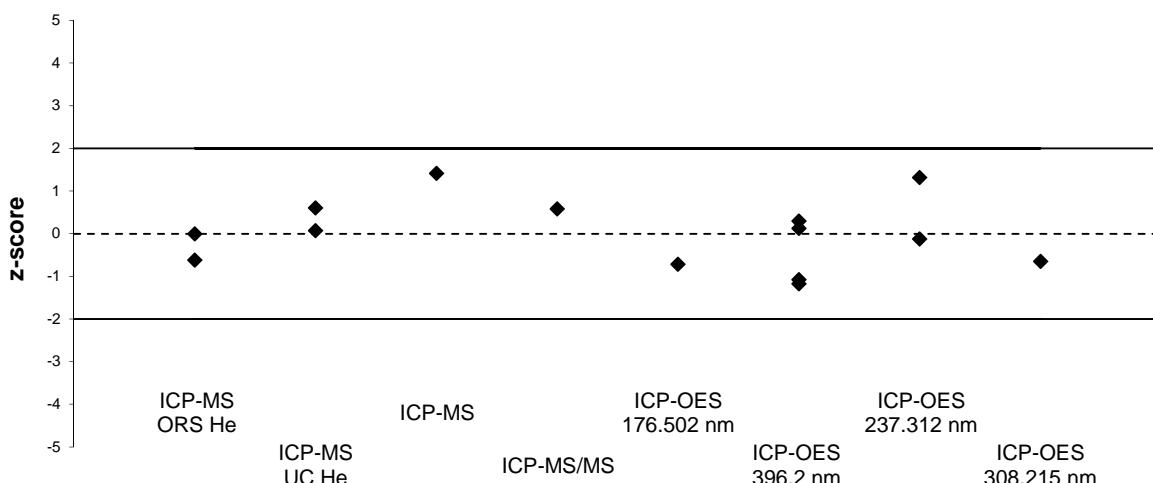
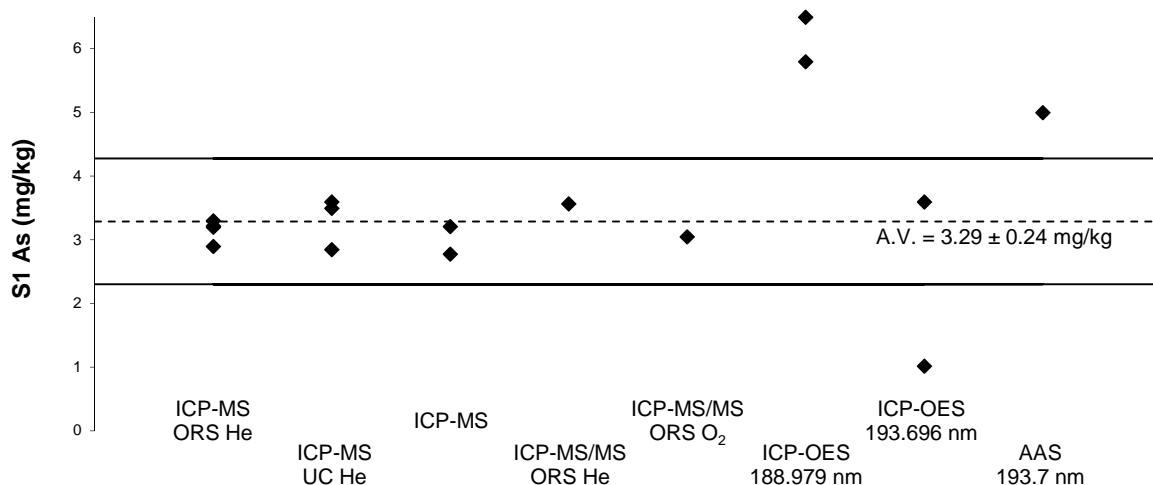


Figure 52 S2-Al z-Scores vs. Instrumental Technique

### S1 As Results vs Instrumental Technique



\*Result > 6.5 mg/kg has been plotted as 6.5 mg/kg.

Figure 53 S1-As Results vs. Instrumental Technique

**Boron.** Caution should be exercised when ICP-OES with wavelength 249.7 nm is used for B measurement. Iron line 249.771 has direct overlap interference on B line 249.7. Plots of participants' results versus instrumental technique are presented in Figure 54.

**Mercury** The unsatisfactory Hg results reported in S1 were approximately 0.5 or 2 times higher than the assigned value; this indicates problems with the laboratory's dilution, standard preparation and/or calculation procedure.

Plots of participants' results versus instrumental technique used are presented in Figure 55.

### S2 B Results vs Instrumental Technique

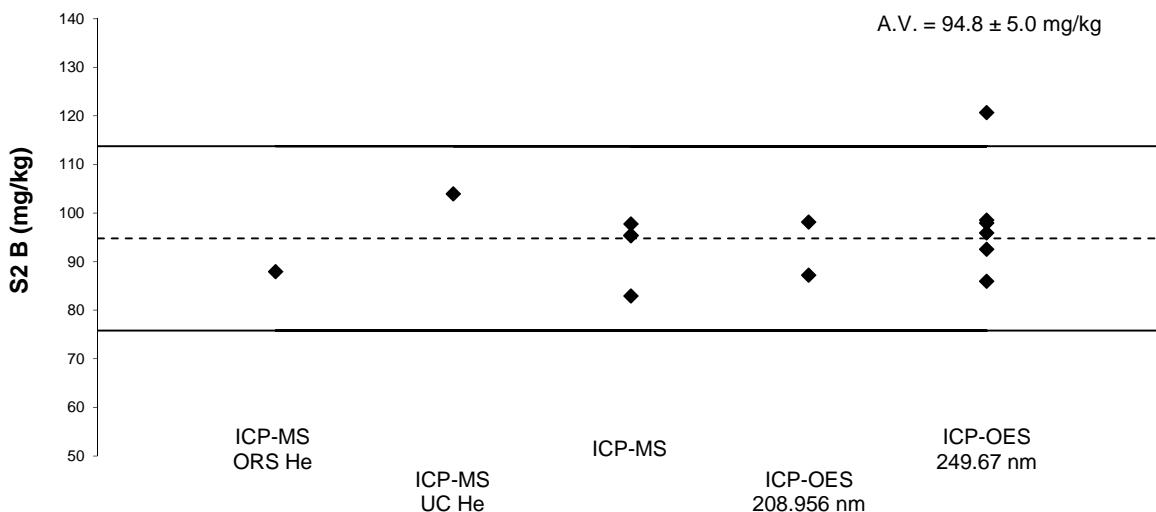


Figure 54 B z-Scores vs. Instrumental Technique

### S1 Hg Results vs Instrumental Technique

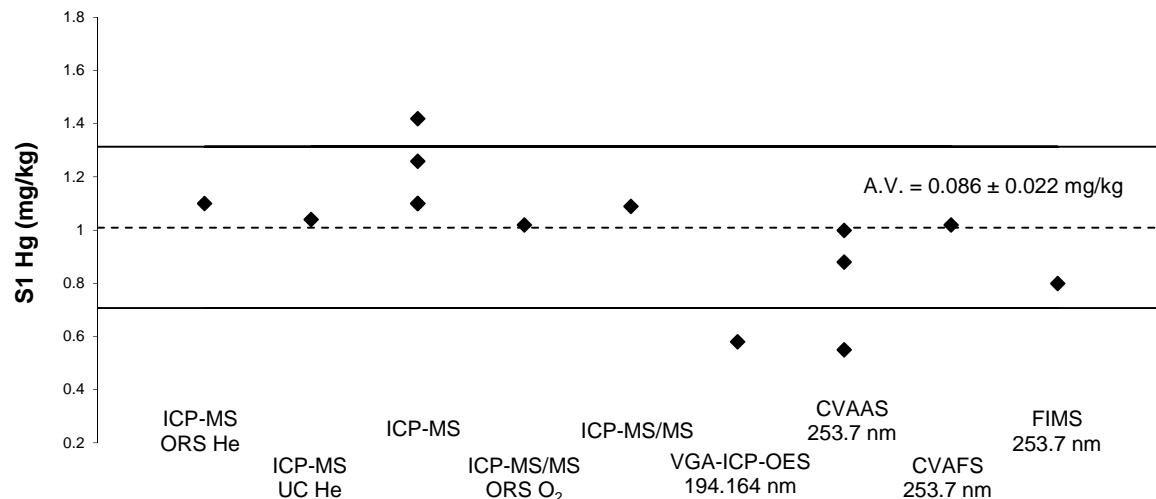


Figure 55 S2 Hg Results vs. Instrumental Technique

### S3 Na Results vs Instrumental Technique

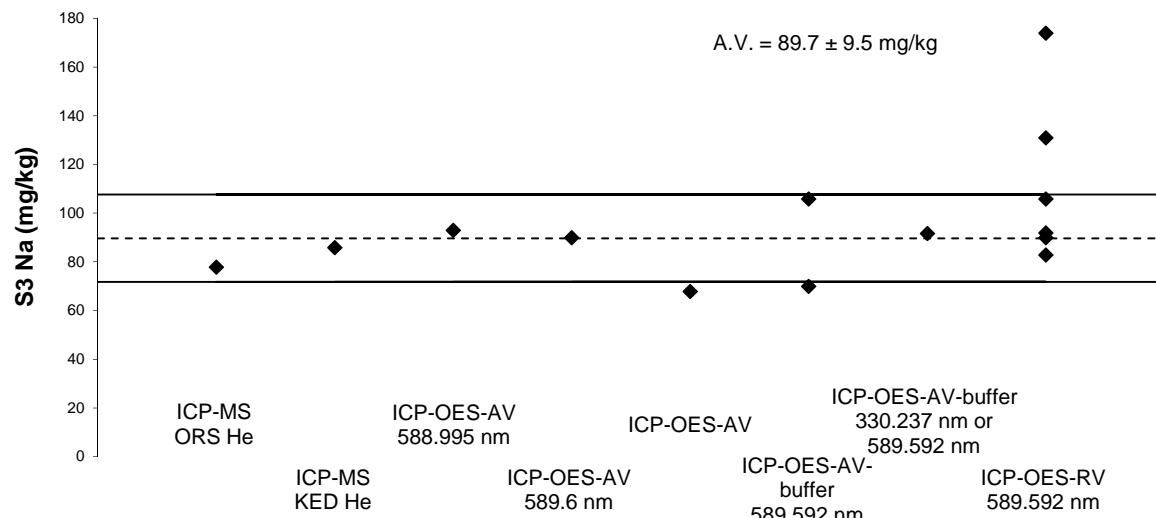


Figure 56 S3 Na Results vs. Instrumental Technique

**Sodium, Magnesium and Potassium** challenged participants' analytical techniques. Four results returned unsatisfactory z-scores for Na and 3 for Mg and K.

Sodium level in S3 was low (89.7 mg/kg) and challenged participants in the present study. The between laboratory coefficient (16%) was double that predicted by Thomson of 8.1%. With one exception all unsatisfactory results were from ICP-OES with wavelength 589.612. Caution should be exercised when low level Na is measured by ICP-OES-RV with wavelength 589.592 nm because this wavelength has interferences from Ba 589.612 nm.

Caution should be also exercised when the level of K in solution is below 1 ppm and it is measured by ICP-OES-RV with wavelength 766.491 nm because this line has low intensity (Figure 57).

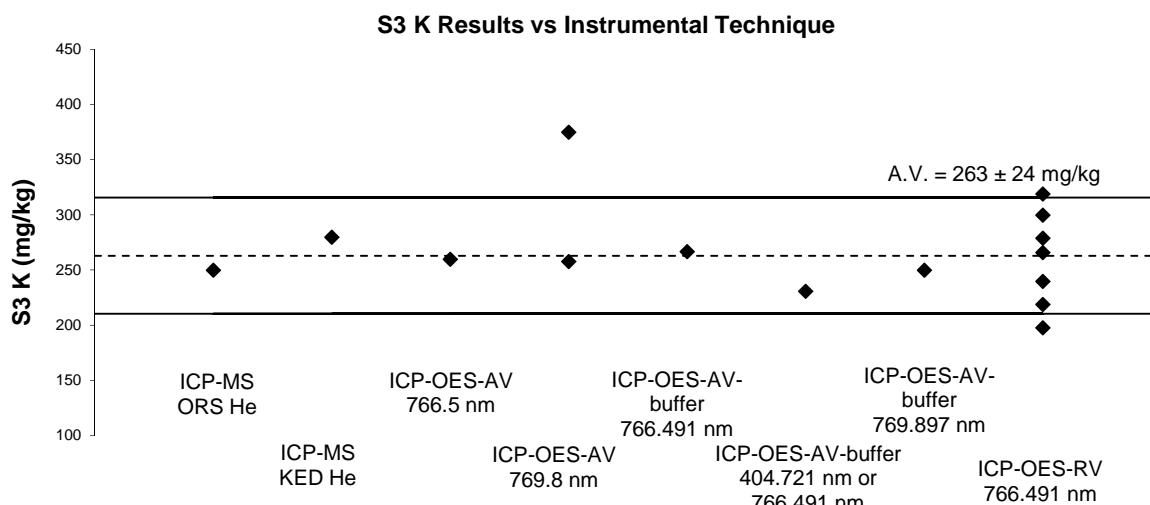
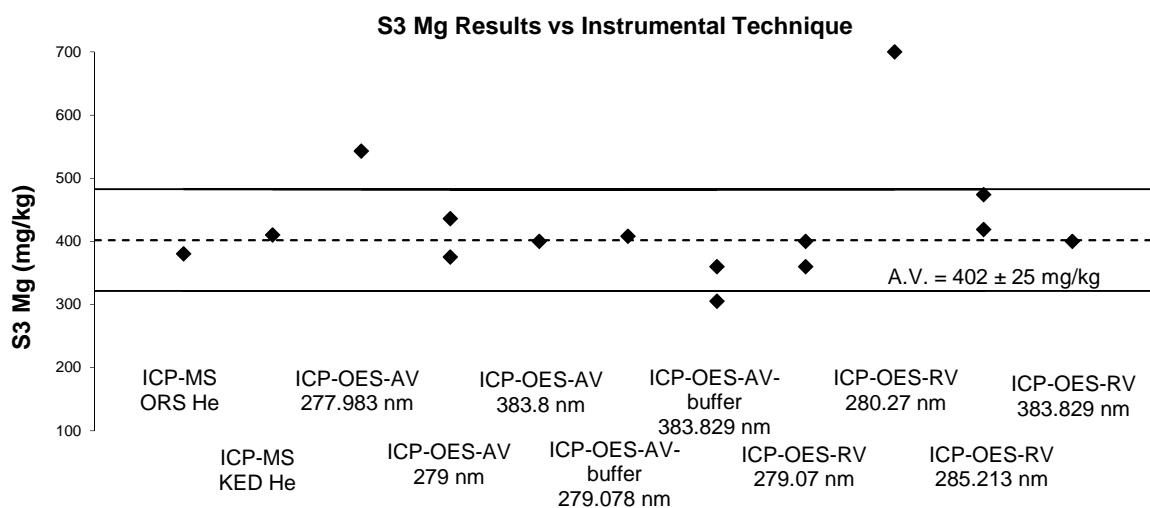


Figure 57 S3 K Results vs. Instrumental Technique

Plots of participants' results versus instruments used for Mg measurements in S3 are presented in Figure 58. Unsatisfactory Mg results may be explained by high dilution factors which produced solution concentration outside the instrument's calibration range.



\*Result >700 mg/kg has been plotted as 700 mg/kg.

Figure 58 S3 Mg Results vs. Instrumental Technique

**Lithium** measurements at a level of 0.98 mg/kg in soil sample S2 presented difficulties to some participating laboratories. Of 11 results reported for lithium in S2, 3 returned unsatisfactory results. Figure 59 presents plots of participants results versus instrumental technique used.

### S2 Li Results vs Instrumental Technique

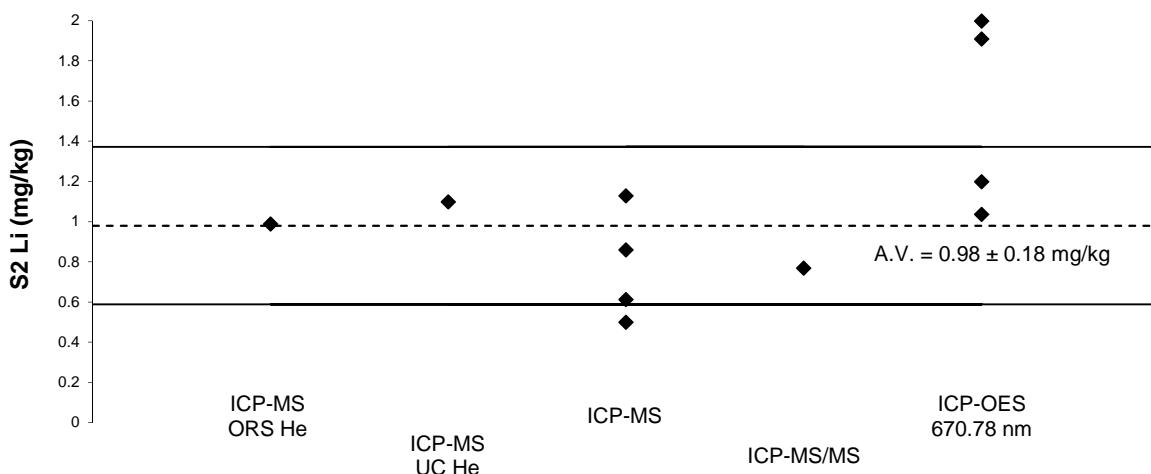


Figure 59 S3 Li Results vs. Instrumental Technique

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

### S1 Se Results vs Instrumental Technique

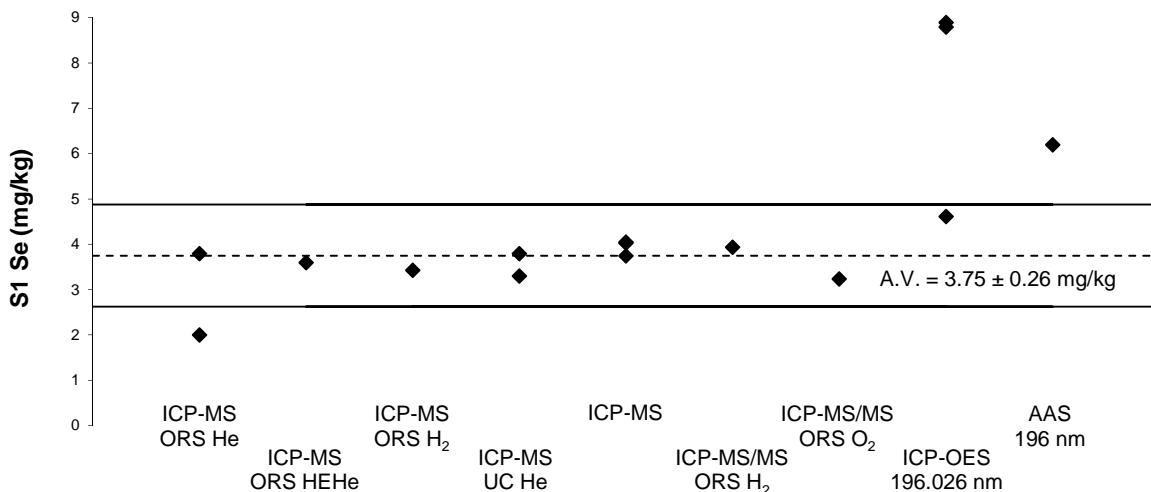


Figure 60 S3 Li Results vs. Instrumental Technique

Selenium level in soil may be too low for ICP-OES and GF-AAS measurements (Figure 60).

## 7.6 Participants' Within-Laboratory Reproducibility

Sample S3 was a soil sample previously distributed as S3 of AQA 20-02. The same target standard deviation was used to calculate z-scores for analytes in both samples. This allowed evaluation of the within laboratory reproducibility of participants.

Of 16 laboratories who reported results in the present study in S3, 9 reported results in AQA 20-02 (Laboratories 2, 3, 6, 12, 13, 14, 19, 20 and 24).

Bar charts of laboratories results in the two studies are presented in Figure 61. In some cases the participants' results reported in the two studies are significantly different.

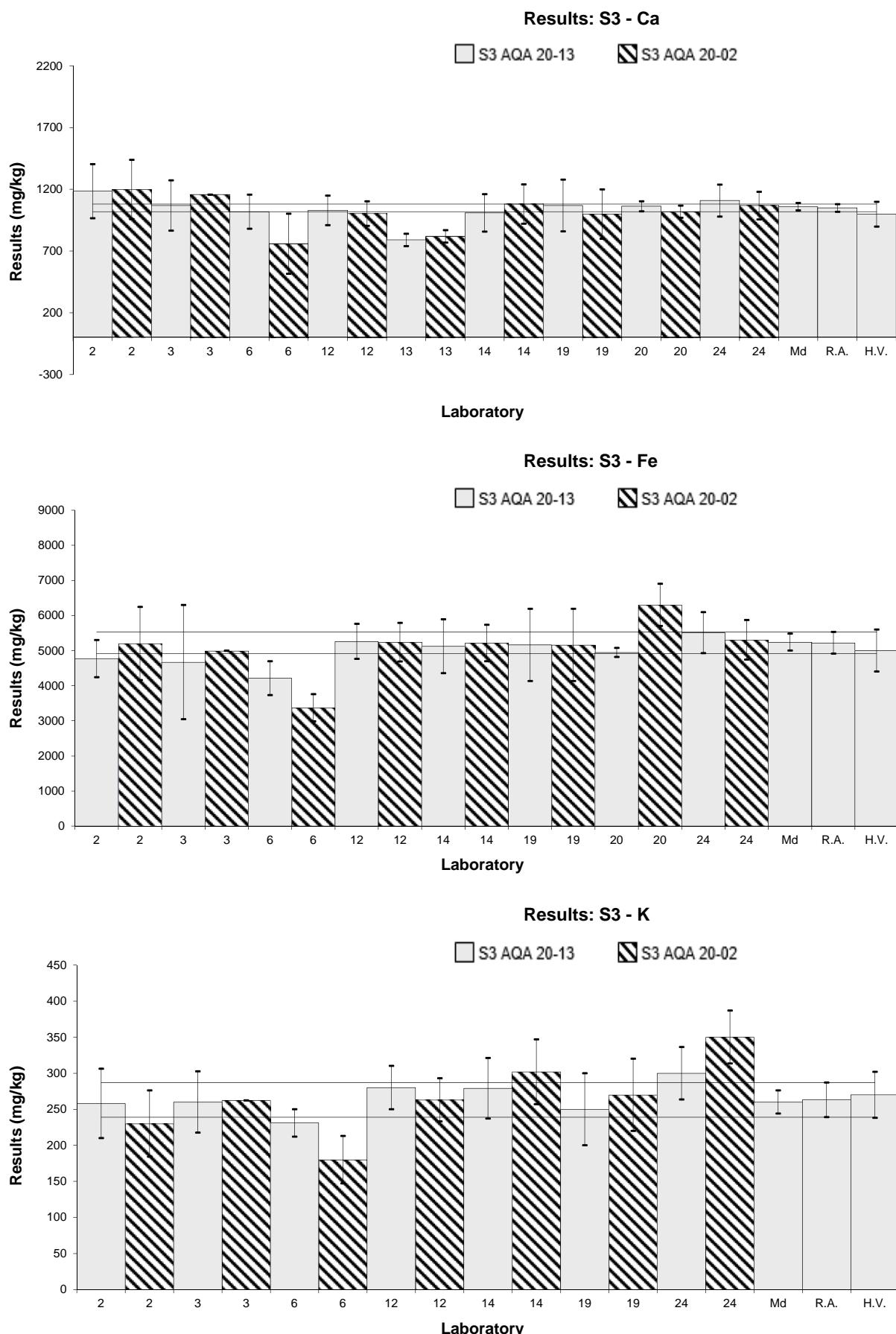


Figure 61 Bar charts of Results in S3 of AQA 20-13 and S3 of AQA 20-02

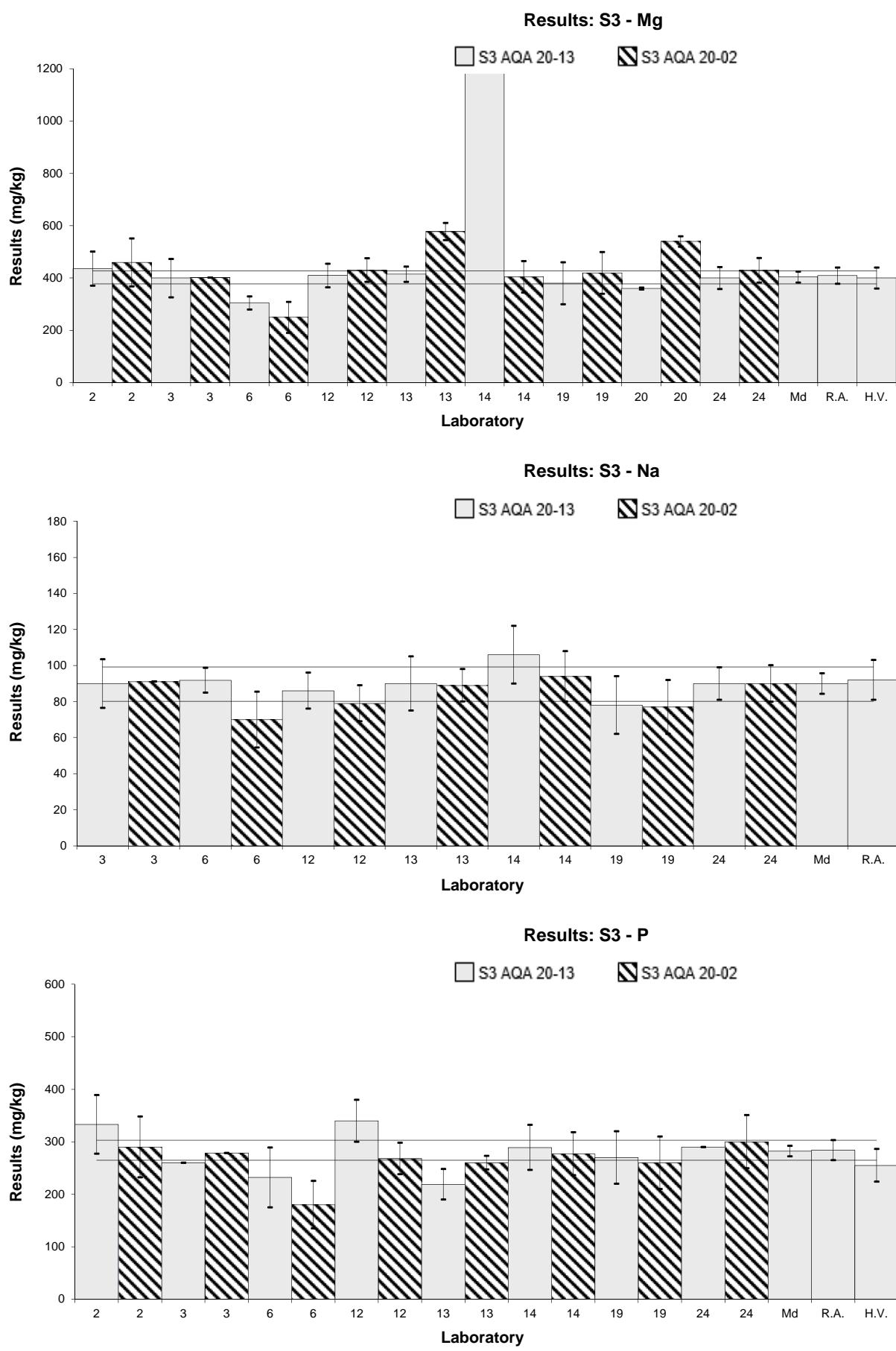


Figure 61 Bar charts of Results in S3 of AQA 20-13 and S3 of AQA 20-02 (continued)

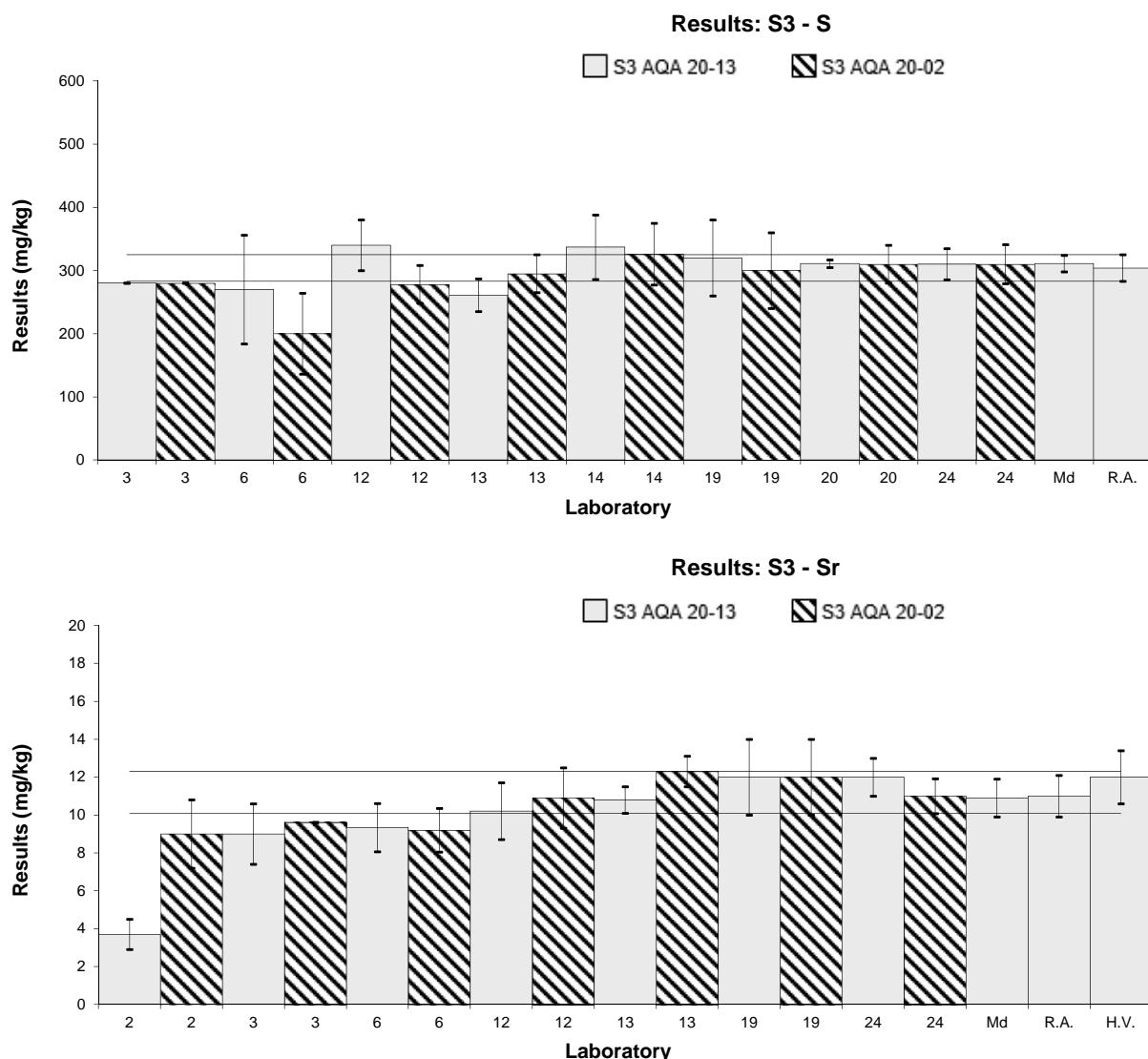


Figure 61 Bar Charts of Results in S3 of AQA 20-13 and S3 of AQA 20-02 (continued)

Figure 62 presents scatter plots of z-scores in Sample S3 of AQA 20-13 and S3 of AQA 20-02. Points close to the diagonal axis represent excellent reproducibility and points close to zero represent excellent reproducibility and accuracy.

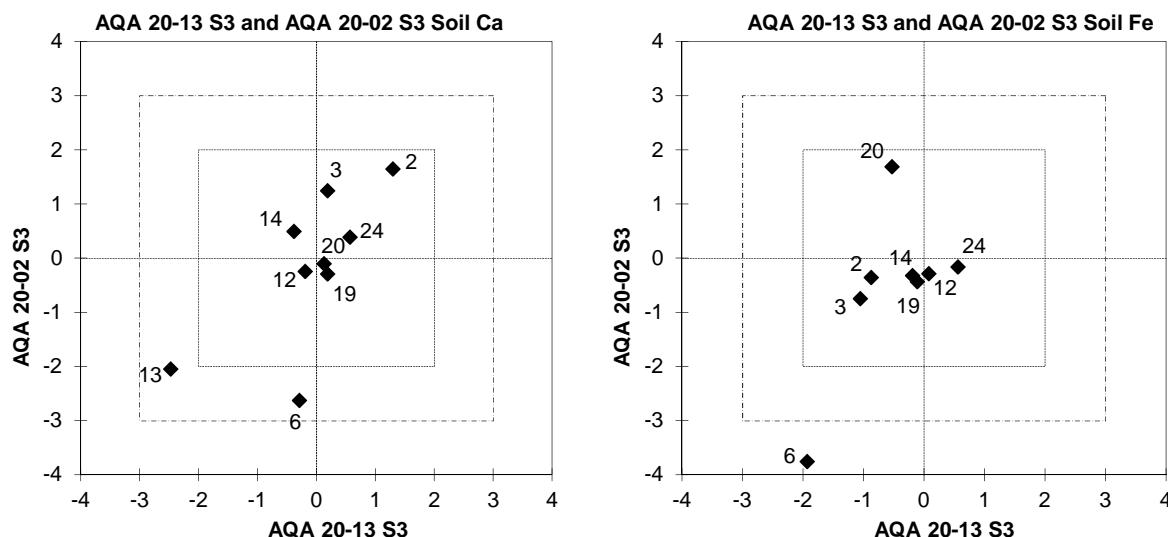


Figure 62 Scatter Plots of: z-Score in S3 of AQA 20-13 and S3 of AQA 20-02

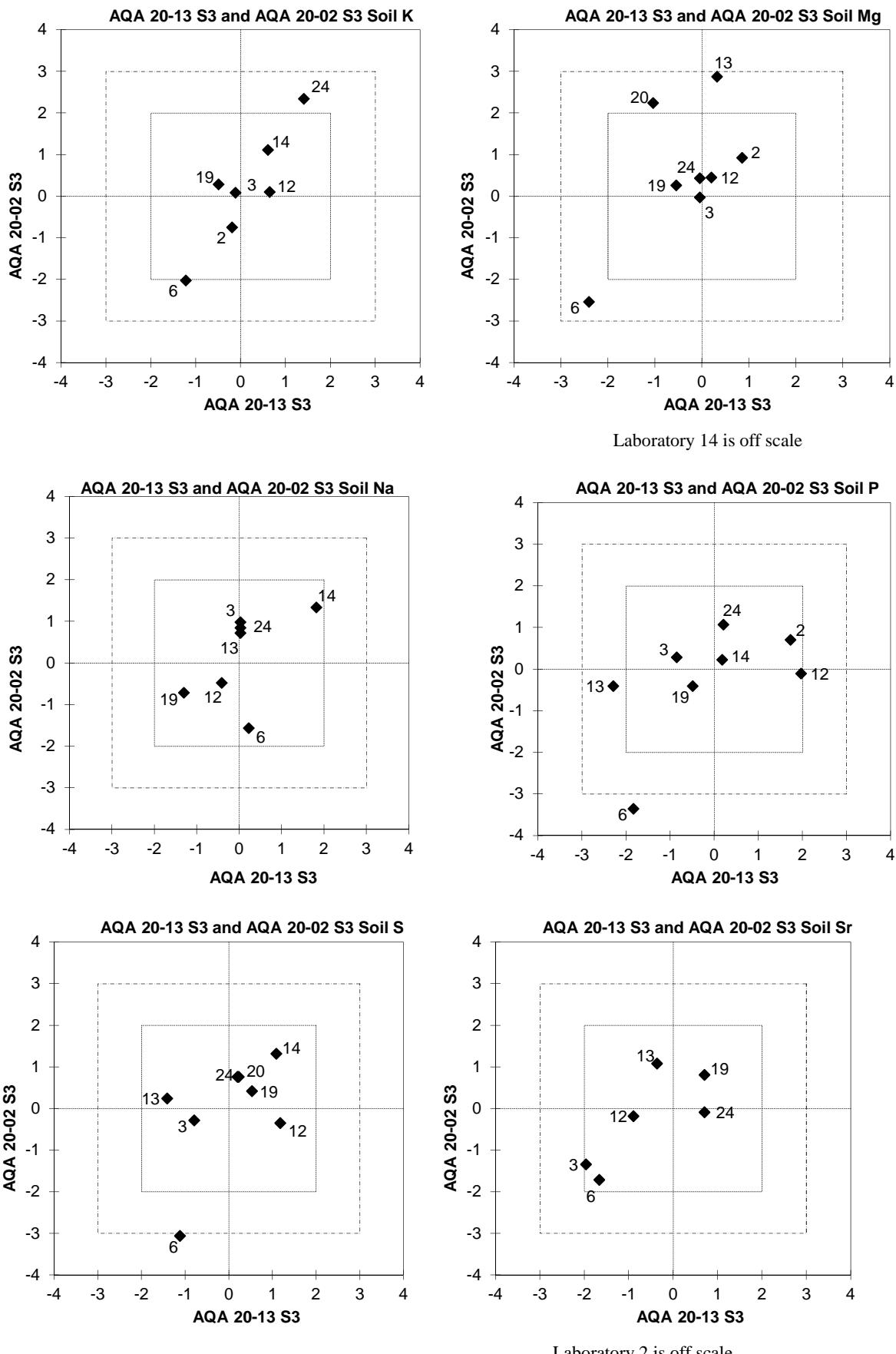


Figure 62 Scatter Plots of: z-Score in S3 of AQA 20-13 and S3 of AQA 20-02 (continued)

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

Mineral nitrogen components, ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ), are of particular interest when soil fertility is assessed. While water can extract  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N from a majority of soils,  $\text{NH}_4^+$ -N has to be displaced by another cation when the surface soil colloids are negatively charged.<sup>23</sup> The participating laboratories were asked to analyse the sample using their normal measurement technique but to follow the preparation procedure for the soil extract which involved: a soil/2M KCl ratio of 1:10 and a mixing time of one hour.

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

**2M KCl Extractable Ammonium-Nitrogen** Plots of participants' results versus the analytical methods and instrumental technique used are presented in Figure 63. Although participants used various analytical methods and measurement technique all produced comparable results with the exception of one.

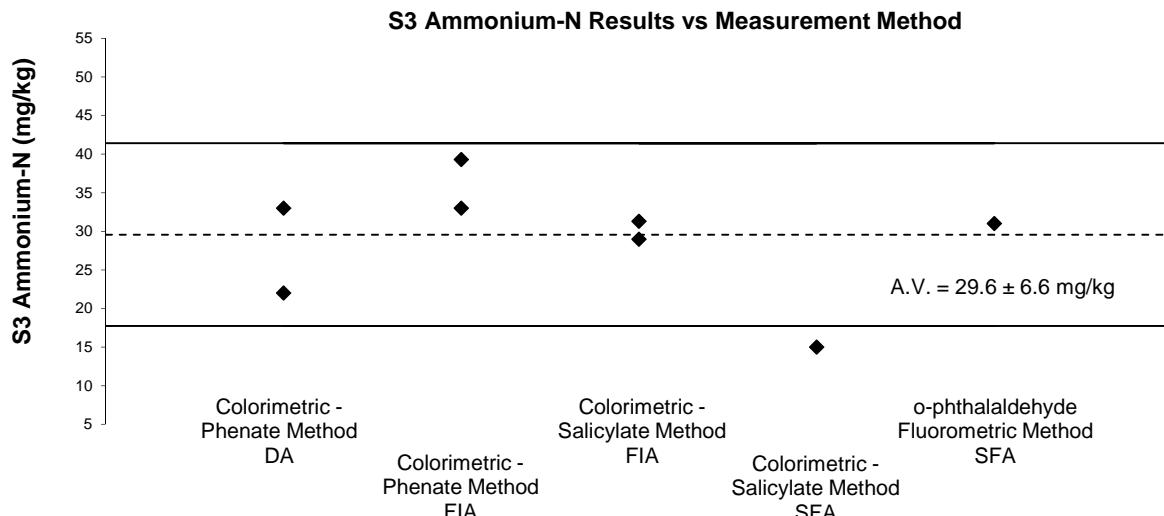
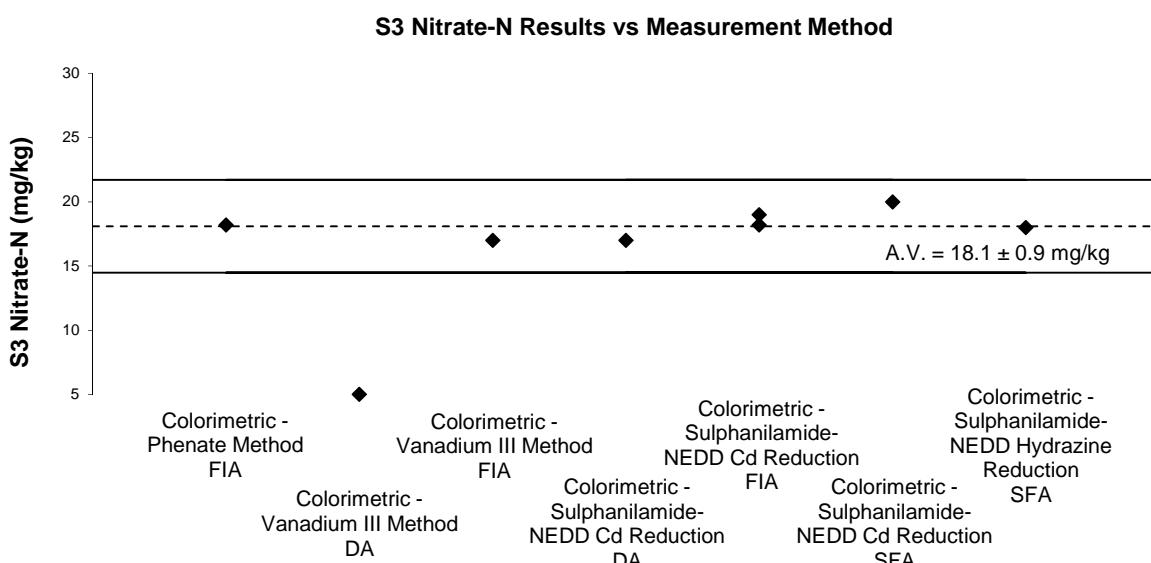


Figure 63 S3- $\text{NH}_4^+$ -N Results vs. Analytical Method and Measurement Technique



\*Result <5 mg/kg has been plotted as 5 mg/kg.

Figure 64: S3- $\text{NO}_3^-$ -N Results vs. Measurement Technique

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

Two laboratories used trivalent V for  $\text{NO}_3^-$ -N reduction to  $\text{NO}_2^-$ -N (Figure 64).

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

TKN assigned value was 2310 mg/kg. Two results both returned unsatisfactory results, both from DA measurements. Plots of participants' results versus analytical method and measurement technique are presented in Figure 71.

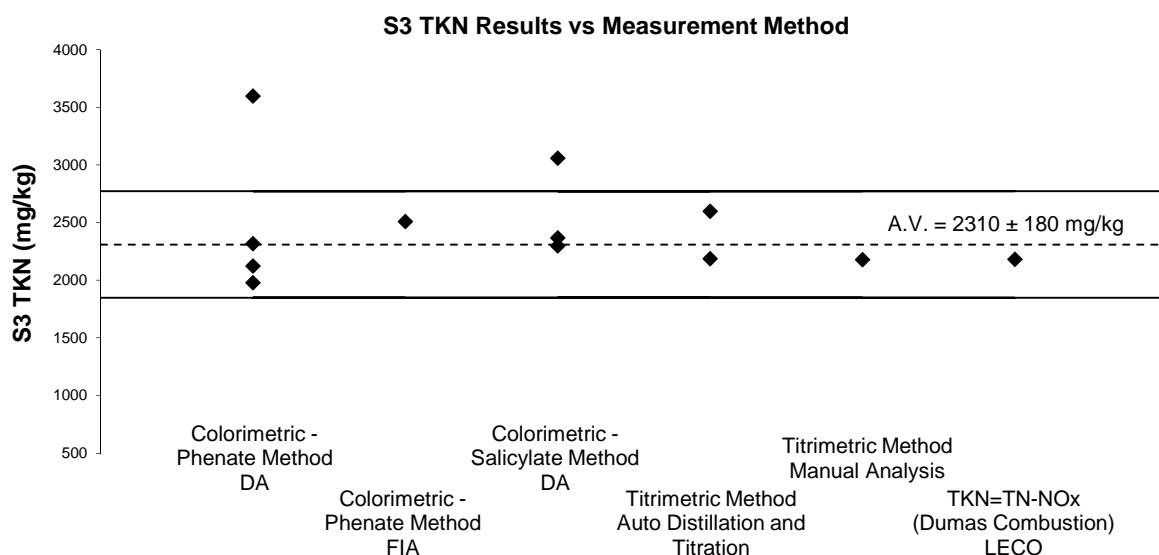


Figure 65 S3-TKN Results vs. Measurement Technique

Interferences from the coloured species in the extract might be the cause of the high, unsatisfactory TKN z-scores.

### 7.9 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.<sup>23, 24</sup> With testing laboratories using different methods, each could be considered to be measuring a different measurand that is their version of ‘water soluble anions in soil’. This lack of uniformity in the procedures can make the comparison of participants’ results difficult.

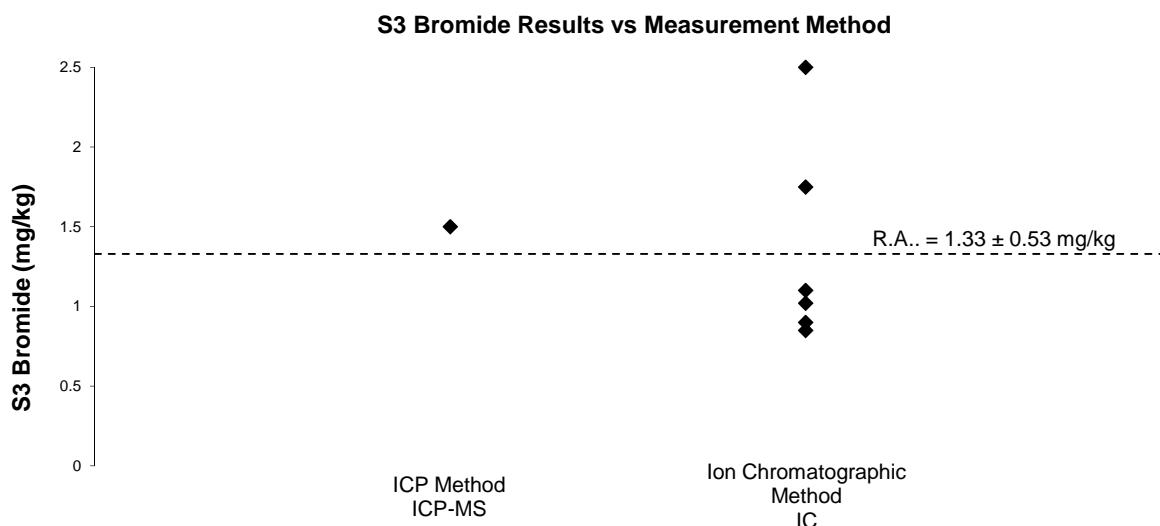
In the previous study of metals and anions in soil AQA 11-12, NMI conducted a study on water soluble anions content in soil using the same instrumental technique but two extraction procedures: one involved a soil/water ratio of 1: 5 and the other a soil/water ratio of 1:10. The **fluoride, orthophosphate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

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

The method descriptions and instrumental techniques provided by participants are presented in Tables 4 to 7. All laboratories used a soil/water ratio of 1:5 with the exception of one.

## Individual Water Soluble Anion Commentary

**Bromide.** No assigned value could be set for this test because the reported results were too variable, the between laboratory CV was 34%. Figure 66 presents a plot of participants' results versus measurement method and instrumental technique used for bromide analysis in S3.



\*Results >2.5 mg/kg has been plotted as 2.5 mg/kg.

Figure 66 S3-Bromide Results vs. Measurement Method

**Chloride** For water soluble chloride measurements in soil, participants used the ion colorimetric method or various colorimetric methods. All produced comparable results (Figure 73).

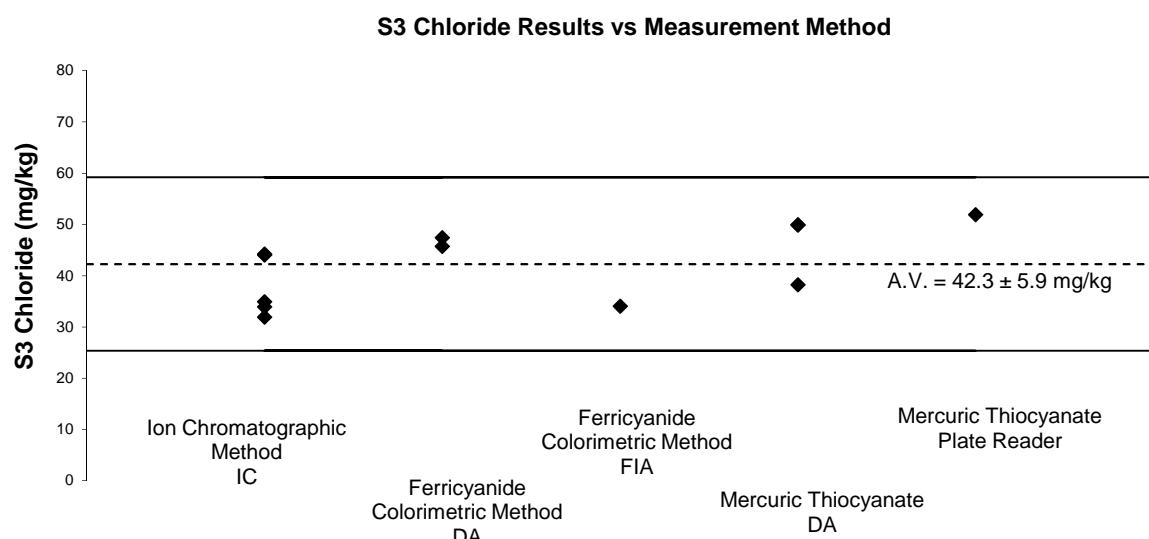


Figure 67 S3-Chloride Results vs. Measurement Method

**Orthophosphate-P** Participants used a wide variety of measurement methods and instrumental techniques (Figure 68). Most participants used for orthophosphate-P measurements ascorbic acids colorimetric method.

Laboratory 2 used a ratio of soil to water of 1 to 10 and this may explain the high result (3.2 mg/kg) reported by them for this test, double of the assigned value.

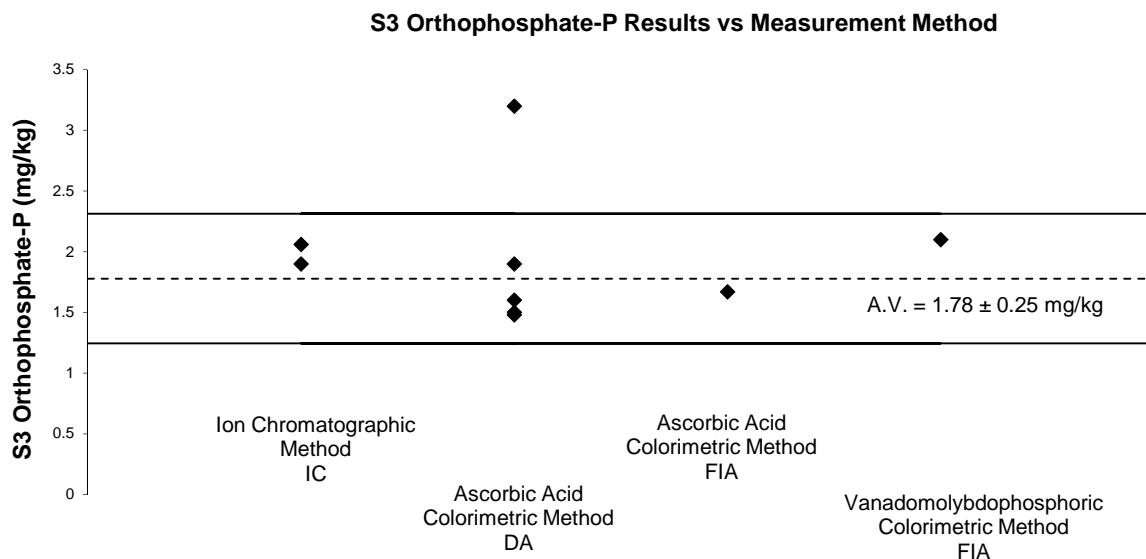


Figure 68 S3-Orthophosphate-P Results vs. Method

**Sulphate** No assigned value was set for this test because the results were too variable. Plots of participants' results with the instrumental technique used are presented in Figure 69. Although most of the S in soil samples is from sulphate compounds, false positive results can be produced when this is measured by ICP-OES: this technique measures total S and not only S from sulphate compounds.

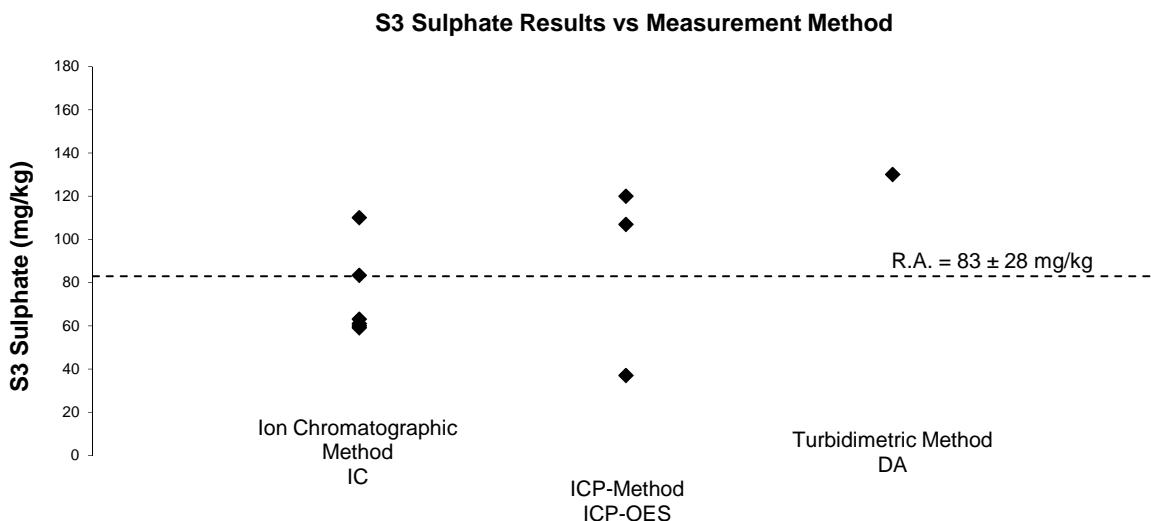


Figure 69 S3-Sulphate Results vs. Measurement Method and Instrumental Technique

**pH and EC** measurements in soil did not present a difficulty to the participating laboratories. All the reported results were in agreement with the assigned value with the exception of one.

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

AQA 20-13 is the twenty-seventh 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 70. On average participants' performance remained fairly consistent.

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

## 7.11 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 63).

Table 63 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	AQA, Inhouse
2	CRM - ERA
4	RM - AQA 19-02 S2 – AQA 19-12 S1,S2 – In house QC soil samples
5	CRM
6	CRM – Choice Analytical CRMs
7	CRM – AGAL 10
9	CRM - Various
10	RM
11	Novachem SQC001S
12	RM – AGAL 12
13	CRM – PACS2 Marine Sediment and NIST SRM 2704 Buffalo River Sediment
15	CRM
16	CRM – AGAL-10/In-house SRMs
17	CRM
19	RM – agal10, agal12
21	CRM – Agal-10 Hawkesbury River Sediment
22	CRM – ASPAC 6052 and AQA 19-12 and ASAPAC ASS 7098
23	RM – Previous AQA PT scheme samples
24	SS – CRM
25	NMI Proficiency samples

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

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

*'a reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'<sup>25</sup>*

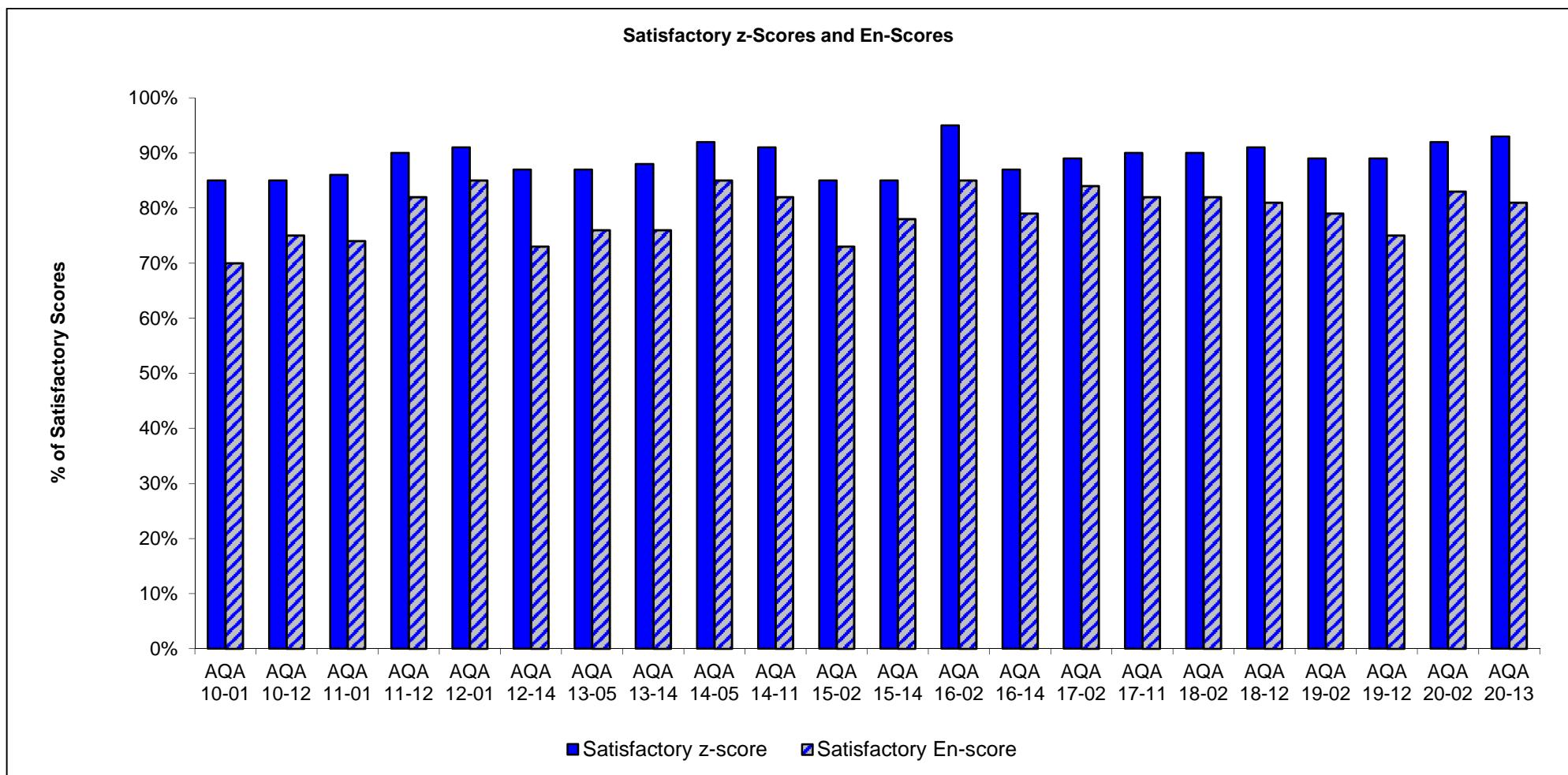


Figure 70 Participants' Performance over Time

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

### Sample Preparation

**Samples S1** and **S2** were a composite of biosoil samples submitted to NMI for chemical analysis. The material was mixed, dried at 105°C, ground, sieved and divided into portions of 20 g each.

**Sample S3** was an agricultural soil material. This sample was previously distributed as sample S3 for AQA 20-02. The preparation procedure of this sample is provided in the report for AQA 20-02.<sup>26</sup>

### Sample Analysis and Homogeneity Testing

The same preparation procedure was followed for Samples S1, S2 and S3 as in previous NMI PT studies. Partial homogeneity testing was conducted for the elements of interest with the exception of Th in S1, Tl in S2 and 2M KCl extractable ammonium nitrogen ( $\text{NH}_4^+ \text{-N}$ ) and 2M KCl extractable nitrate nitrogen ( $\text{NO}_3^- \text{-N}$ ), EC, pH, Na and S in S3. Three bottles were analysed in duplicate and the average of these results was reported as the homogeneity value. Measurements were made under repeatability conditions in random order.

### Sample Analysis for Acid Extractable Elements

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

The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, and matrix matched reference materials, duplicates and sample matrix spikes, was carried through the same set of procedures and analysed at the same time as the samples. A summary of the instrument conditions used and the ion/wavelength monitored for each analyte is given in Table 65.

Table 64 Instrumental Technique used for Acid Extractable Elements

Analyte	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	S1/2 Final Dilution Factor	S3 Final Dilution Factor	Ion (m/z)/Wavelength (nm)
Ag	ICP-MS	Rh	ORS	He	800	NA	107 m/z
Al	ICP-MS	Rh	NA	NA	800	NA	27 m/z
As	ICP-MS	Rh	ORS	He	800	NA	75 m/z
B	ICP-MS	Rh	NA	NA	800	NA	11 m/z
Ba	ICP-OES	Y	NA	NA	800	NA	445.403 nm
Be	ICP-MS	Rh	NA	NA	800	NA	9 m/z
Bi	ICP-MS	Ir	NA	He	800	NA	209 m/z
Ca	ICP-OES	Y	NA	NA	NA	800	422.673 nm
Cd	ICP-MS	Rh	NA	NA	800	NA	111 m/z
Co	ICP-MS	Rh	ORS	He	800	NA	59 m/z
Cr	ICP-MS	Rh	ORS	He	800	NA	52 m/z
Cs	ICP-MS	Rh	ORS	He	800	NA	113 m/z
Cu	ICP-MS	Rh	ORS	He	800	NA	65 m/z
Fe	ICP-MS	Rh	NA	NA	NA	800	56 m/z
Ga	ICP-MS	Rh	ORS	He	800	NA	71 m/z
Hg	ICP-MS	Rh	NA	NA	800	NA	201 m/z
K	ICP-MS	Rh	ORS	He	NA	800	39 m/z
La	ICP-MS	Rh	ORS	He	800	NA	139 m/z
Li	ICP-MS	Rh	ORS	He	800	NA	7 m/z

Analyte	Instrument	Internal Standard	Reaction/Collision Cell	Cell Mode/Gas	S1/2 Final Dilution Factor	S3 Final Dilution Factor	Ion (m/z)/Wavelength (nm)
Mg	ICP-OES	Y	NA	NA	NA	800	280.270 nm
Mn	ICP-MS	Rh	ORS	He	800	NA	55 m/z
Mo	ICP-MS	Rh	ORS	He	800	NA	95 m/z
Ni	ICP-MS	Rh	ORS	He	800	NA	60
P	ICP-OES	Rh	NA	NA	NA	800	213.618
Pb	ICP-MS	Ir	NA	NA	800	NA	Average of 206, 207, 208 m/z
Rb	ICP-MS	Rh	ORS	He	800	NA	85 m/z
Sb	ICP-MS	Rh	ORS	He	800	NA	212 m/z
Se	ICP-MS	Rh	ORS	HEHe	800	NA	78 m/z
Sn	ICP-MS	Rh	NA	NA	800	NA	118 m/z
Sr	ICP-MS	Rh	ORS	He	800	800	88 m/z
U	ICP-MS	Ir	NA	NA	800	NA	238 m/z
V	ICP-MS	Rh	ORS	He	800	NA	51 m/z
Zn	ICP-MS	Rh	ORS	He	800	NA	66 m/z

### Sample Analysis for Water Soluble Anions

A test portion of 10 g was weighed into a 50 mL polypropylene container. The container was then filled with deionised water. The suspension was shaken, at room temperature for 1 h, centrifuged, and filtered through 0.45 µm filter. A summary of the measurement methods and instrumental techniques is presented in Table 66.

Table 65 Summary of the Measurement Methods and Instrumental Techniques used by NMI

Anion	Measurement Method	Instrument
Water Soluble Bromide	Ion Chromatographic Method	IC
Water Soluble Chloride	Ion Chromatographic Method	IC
Water Soluble Nitrate-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Water Soluble Orthophosphate-P	Colorimetric, Ascorbic Acid Reduction	DA
Water Soluble Sulphate	Ion Chromatographic Method	IC

## APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND E<sub>n</sub> SCORE CALCULATION

The assigned value was calculated as the robust average using the procedure described in ‘ISO13258:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C’.<sup>6</sup> The uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 66.

Table 66 Uncertainty of Assigned Value for Bi in Sample S1

No. results (p)	10
Robust Average	3.28 mg/kg
$S_{rob\ av}$	0.56 mg/kg
$u_{rob\ av}$	0.22 mg/kg
$k$	2
$U_{rob\ av}$	0.44 mg/kg

The assigned value for Bi in Sample S1 is **3.28 ± 0.44 mg/kg**

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

For each participant’s result a z-score and E<sub>n</sub>-score are calculated according to Equation 1 and Equation 2 respectively (see page 14).

A worked example is set out below in Table 67.

Table 67 z-Score and E<sub>n</sub>-score for Bi Result Reported by Laboratory 1 in S1

Bi Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E <sub>n</sub> -Score
3.4 ± 0.8	3.28 ± 0.44	15% as CV or 0.15x3.28 = =0.49 mg/kg	$z = \frac{(3.4 - 3.28)}{0.49}$  $z = 0.24$	$E_n = \frac{(3.4 - 3.28)}{\sqrt{0.8^2 + 0.44^2}}$  $E_n = 0.13$

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.<sup>10, 12</sup> An example is given. Between 2009 and 2020 NMI carried out 22 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 all of these PTs. All reported results returned satisfactory z-scores. This data can usefully be separated into two ranges of results 0.5 to 10 mg/kg and 10 to 100 mg/kg.

Table 68 Laboratory X Reported Results for As at 0.5 to 10 mg/kg Level.

Study No.	Sample	Laboratory result mg/kg	Assigned value* mg/kg	Robust CV of all results (%)	Number of Results
AQA 09-13	S1 - Biosoil	4.091	3.64	16	11
	S2 - Soil	4.29	4.57	15	12
AQA 11-01	S1 - Biosoil	3.54	3.57	19.7	18
AQA 13-05	S1 - Soil	9.22	9.21	14	22
AQA 14-11	S1 - Sediment	7.91	7.37	11.8	21
AQA 15-02	S1 - Moist Sludge	8.29	7.02	13	22
	S2 - Moist Sludge	7.42	7.02	11.3	17
AQA 15-14	S1 - Sediment	10	9.95	6.7	17
	S2 - Soil	4.53	4.47	6.4	14
AQA 16-02	S2 - Clay	2.67	2.11	14	20
AQA 16-14	S1 - Soil	6.03	5.61	20	17
AQA 17-02	S2 - Soil	3.71	3.76	10	13
AQA 18-02	S1 - Compost	2.22	2.73	11	17
AQA 19-02	S1 - Soil	2.83	2.65	11	24
AQA 19-12	S1 - Soil	2.32	2.12	16	16
AQA 20-13	S1 - Biosoil	2.85	3.29	11	17
Average				12.4**	

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

Table 69 Laboratory X Reported Results for As at 10 to 100 mg/kg Level.

Study No.	Sample	Laboratory result mg/kg	Assigned value* mg/kg	Robust CV of all results (%)	Number of Results
AQA 10-12	S1 - Soil	16.6	14.4	8.5	19
AQA 11-12	S1 - Moist Sludge	25	21.6	15	13
AQA 12-01	S1 - Sediment	18.4	17.3	8.1	21
AQA 12-14	S2 - Soil	16.6	14.8	11	20
AQA 13-14	S1 - Sandy Soil	16.6	15.1	10.4	21
AQA 14-05	S1 - Soil	13.2	12.3	7.8	25
AQA 17-11	S1 - Sediment	18.1	17.4	11	22
AQA 18-12	S2 - Soil	10.4	9.6	8	20
AQA 19-12	S2 - Sediment	21	19.9	9	19
AQA 20-02	S1 - Soil	18.8	21.6	8.8	23
AQA 20-02	S2 - Moist Soil	16.5	17.8	6.7	24
Average				9.5**	

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

Taking the average of the robust CV over these PT samples for each concentration range gives estimates of the relative standard uncertainty of 12% and 10% respectively. Using a coverage factor of two gives relative expanded uncertainties of 25% and 20% respectively, at a level of confidence of approximately 95%. Table 70 sets out the expanded uncertainty for results of the measurement of As in soil, biosoil, clay, sediment, sludge, sandy soil, moist soil, compost and agricultural soil over the ranges 0.5 to 10 mg/kg and 10 to 100 mg/kg.

Table 70 Uncertainty of As Results Estimated Using PT Data.

Results mg/kg	Uncertainty mg/kg
1.00	0.24
5.0	1.2
20	4
75	15

The estimates of 25% and 20% relative passes the test of being reasonable, and the analysis of the 25 different PT samples over ten years can be assumed to include all the relevant uncertainty components (different matrices, operators, reagents, calibrators etc.), and so complies with ISO 17025:2018.<sup>8</sup>

## APPENDIX 4 - INSTRUMENT DETAILS

Table 71 Instrument Conditions Ag

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	107
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-OES-AV	Eu			50	NA	328.1
4	ICP-MS/MS	Rh103	ORS	O2	4000	NA	Ag 107/107(m/z)
5	ICP-OES-AV	Lu 261.541				NA	328.068
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	NA		N/A	250	
11	ICP-MS	In	ORS	He	0.1	NA	107
12	ICP-MS	Rh	NA	standard mode	625	NA	109
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS	Ge 72	ORS		N/A		107 m/z
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Ir193			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	107
20	ICP-MS/MS		ORS		1000	NA	107
21	ICP-MS	Rh	UC	He	2000	NA	109
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	328.068

**Table 72 Instrument Conditions Al**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	45	ORS	He	100	NA	27
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-OES-AV	Eu			50	NA	396.2
4	ICP-MS/MS	Sc 45	ORS	NA	80000	NA	Al 27/27(m/z)
5	ICP-OES-AV	Lu 261.541				NA	396.152
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	308.215
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Sc	NA		N/A	250	
11	ICP-OES-AV	Lu			0.1	NA	237.312
12	ICP-MS	Sc	UC	He	625	NA	27
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV	Y377	NA		N/A		396.152 nm
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-OES-AV	Lu			400	NA	237.313
19	ICP-MS	Sc	ORS	He	800	NA	27
20	ICP-OES-AV				1000	NA	176.502
21	ICP-MS	Sc	UC	He	2000	NA	27
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	396.153

**Table 73 Instrument Conditions As**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	72	ORS	He	100	NA	75
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	75
4	ICP-MS/MS	Rh103	ORS	O2	4000	NA	As 75/91(m/z)
5	ICP-OES-AV	Lu 261.541				NA	193.696
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	188.979
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	250	250	
11	ICP-MS	Ge	ORS	He	0.1	NA	75
12	ICP-MS	Ge	UC	He	625	NA	75
13						NA	
14	ICP-MS	Ge 72	ORS				75m/z
15	ICP-OES-AV				50	NA	188.979
16	AAS	None			20	NA	193.7
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			400	NA	
19	ICP-MS	Rh	ORS	He	800	NA	75
20	ICP-MS/MS		ORS	He	1000	NA	75
21	ICP-MS	Rh	UC	He	1000	NA	75
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-AV	Y	NA	NA	18.5	NA	188.979
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	193.696

**Table 74 Instrument Conditions B**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			100	NA	249.678
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc			50	NA	11
4	ICP-OES-AV	Lu261.541	NA	NA	80	NA	B 249.678
5	ICP-OES-AV	Lu 261.541				NA	249.678
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	249.678
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Sc	NA		250	N/A	
11	ICP-OES-AV	Lu			0.1	NA	208.956
12	ICP-MS	Sc	NA	standard mode	625	NA	10
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV	Te214	NA			N/A	249.678nm
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Sc	ORS	He	800	NA	11
20	ICP-OES-AV				1000	NA	208.956
21	ICP-MS	Sc	UC	He	1000	NA	11
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	249.677

**Table 75 Instrument Conditions Ba**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	138
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	137
4	ICP-OES-AV	Eu 390.711	NA	NA	80	NA	Ba 455.403
5	ICP-OES-AV	Lu 261.541				NA	233.527
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	233.527
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	In	NA		N/A	250	
11	ICP-OES-RV	Lu			0.1	NA	455.403
12	ICP-MS	Rh	NA	standard mode	625	NA	138
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV	Y371	NA		N/A		493.408 nm
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	In115			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	134
20	ICP-OES-AV				1000	NA	455.403
21	ICP-MS	Tb	UC	He	2000	NA	137
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	232.572

**Table 76 Instrument Conditions Be**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			100	NA	313.107
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc			50	NA	8
4	ICP-OES-AV	Lu307.760	NA	NA	80	NA	Be 313.107(nm)
5	ICP-OES-AV	Lu 261.541				NA	313.042
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	313.107
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Sc	NA		250	N/A	
11	ICP-MS	Ge			0.1	NA	9
12	ICP-MS	Sc	NA	standard mode	625	NA	9
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS	Ge 72	ORS			N/A	9m/z
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Sc	ORS	He	800	NA	9
20	ICP-MS/MS		ORS	He	1000	NA	9
21	ICP-MS	Sc	UC	He	2000	NA	9
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 77 Instrument Conditions Bi**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	193	ORS	He	100	NA	209
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	209
4	ICP-MS/MS	Ir 193	ORS	O <sub>2</sub>	4000	NA	Bi 209/209(m/z)
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir	NA		N/A	250	
11	ICP-MS	Ir	ORS	He	0.1	NA	209
12	ICP-MS	Ir	NA	standard mode	625	NA	209
13						NA	
14	NA					NA	
15	NT				NT	NA	NT
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Ir	ORS	He	800	NA	209
20	ICP-MS/MS		ORS		1000	NA	209
21	ICP-MS	Tb	UC	He	2000	NA	209
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 78 Instrument Conditions Ca**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	100	430.253
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	370.6
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	315.887, 370.602nm
7	ICP-OES-RV	NA			NA		317.933
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-RV	Lu			NA	0.1	422.673
12	ICP-MS	Sc	KED	He	NA	625	44
13					NA		
14	ICP-OES-RV	Y377	NA			N/A	317.933 nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-RV	Lu			NA	50	317.933
17	ICP-OES-AV	Y 371.029			NA	1	430.253
18	ICP-OES-RV	Lu			NA	40	315.887
19	ICP-MS	Rh	ORS	He	NA	800	43
20	ICP-OES-RV				NA	1000	315.887
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		315.887
25	NA	NA	NA	NA	NA	NA	NA

**Table 79 Instrument Conditions Cd**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	114
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	111
4	ICP-OES-AV	Lu291.139	NA	NA	80	NA	Cd 226.502(nm)
5	ICP-OES-AV	Lu 261.541				NA	228.802
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	228.802
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	NA		250	250	
11	ICP-MS	Ir	ORS	He	0.1	NA	111
12	ICP-MS	Rh	NA	standard mode	625	NA	111
13						NA	
14	ICP-MS	Rh 103	ORS				111m/z
15	ICP-OES-AV				50	NA	228.802
16	AAS	None			20	NA	228.8
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	In115			400	NA	
19	ICP-MS	Rh	ORS	He	800	NA	111
20	ICP-MS/MS		ORS	He	1000	NA	111
21	ICP-MS	Rh	UC	He	1000	NA	111
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-AV	Y	NA	NA	18.5	NA	228.802
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	228.802

**Table 80 Instrument Conditions Co**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	59
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	59
4	ICP-OES-AV	Lu219.556	NA	NA	80	NA	Co 228.615(nm)
5	ICP-OES-AV	Lu 261.541				NA	231.16
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	228.616
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	N/A	250	
11	ICP-MS	Ge	ORS	He	0.1	NA	59
12	ICP-MS	Ge	KED	He	625	NA	59
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-OES-AV	Te214	NA		N/A		228.615 nm
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	59
20	ICP-MS/MS		ORS	He	1000	NA	59
21	ICP-MS	Ga	UC	He	2000	NA	59
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	225.616

**Table 81 Instrument Conditions Cr**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	52
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	52
4	ICP-MS/MS	Sc 45/61	ORS	O2	1600	NA	Cr 52/52(m/z)
5	ICP-OES-AV	Lu 261.541				NA	267.716
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	267.716
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Sc	UC	He	250	250	
11	ICP-MS	Ge	ORS	He	0.1	NA	52
12	ICP-MS	Sc	KED	He	625	NA	52
13						NA	
14	ICP-OES-AV	Te214	NA				267.716 nm
15	NT				NT	NA	NT
16	AAS	None			20	NA	357.9
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	52
20	ICP-MS/MS		ORS	He	1000	NA	52
21	ICP-MS	Sc	UC	He	1000	NA	52
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-RV	Y	NA	NA	185	NA	267.716
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	267.716

**Table 82 Instrument Conditions Cs**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						NA	
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Rh	ORS	He	50	NA	133
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	250	250	
11						NA	
12						NA	
13						NA	
14	NA					NA	
15	NT				NT	NA	NT
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Rh	ORS	He	800	NA	133
20	ICP-MS/MS		ORS		1000	NA	133
21	ICP-MS	Tb	UC	He	2000	NA	133
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 83 Instrument Conditions Cu**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	65
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	93
4	ICP-OES-AV	Lu 307.760	NA	NA	80	NA	Cu 327.395
5	ICP-OES-AV	Lu 261.541				NA	327.395
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	324.752
9	NA	NA	NA	NA	NA	NA	NA
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-AV	Lu			0.1	NA	324.754
12	ICP-MS	Ge	KED	He	625	NA	63
13						NA	
14	ICP-OES-RV	Y377	NA				327.395 nm
15	ICP-OES-AV				50	NA	327.393
16	AAS	None			20	NA	324.7
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	63
20	ICP-OES-AV				1000	NA	315
21	ICP-MS	Ga	UC	He	1000	NA	63
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-RV	Y	NA	NA	185	NA	324.752
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	327.393

**Table 84 Instrument Conditions Fe**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	500	239.563
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	258.6
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	238.204, 258.588, 259.940nm
7	ICP-OES-AV	NA			NA		259.94
9					NA		
10	NA	NA	NA	NA	NA	NA	NA
11	ICP-OES-AV	Lu			NA	0.1	259.94
12	ICP-MS	Sc	KED	He	NA	625	56
13					NA		
14	ICP-OES-AV	Te214	NA			N/A	259.940nm
15	NA	NA	NA	NA	NA	NA	NA
16	AAS	None			NA	50	248.3
17	ICP-OES-AV	Y 371.029			NA	1	370.792
18	ICP-OES-AV	Lu			NA	800	238.204
19	ICP-MS	Rh	ORS	He	NA	800	56
20	ICP-OES-AV				NA	1000	238.204
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		258.588
25	NA	NA	NA	NA	NA	NA	NA

**Table 85 Instrument Conditions Ga**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						NA	
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	71
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	NA	NA	NA	NA	NA	NA	NA
11						NA	
12						NA	
13	NA	NA	NA	NA	NA	NA	NA
14	NA					NA	
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Rh	ORS	He	800	NA	71
20	ICP-MS/MS		ORS	H2	1000	NA	71
21	UC	He	2000	NA	59		
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 86 Instrument Conditions Hg**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	VGA-ICP-OES				100	NA	194.164
2	NA	NA	NA	NA	NA	NA	NA
3	CVAAS				50	NA	253.7
4	ICP-MS/MS	Ir 193	ORS	O2	4000	NA	Hg 202/202(m/z)
5	CVAAS					NA	253.7
6	NA	NA	NA	NA	NA	NA	NA
7	FIMS	NA				NA	253.7
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir	NA		250	250	
11	CVAFS				0.1	NA	253.7
12	ICP-MS	Ir	NA	standard mode	625	NA	201
13						NA	
14	ICP-MS	Ir 193	ORS				202m/z
15	NT				NT	NA	NT
16	AAS	None			25	NA	253.6
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Bi209			4000	NA	
19	ICP-MS	Ir	ORS	He	800	NA	202
20	ICP-MS/MS		ORS		1000	NA	202
21	ICP-MS	Tb	UC	He	1000	NA	201
22	NA	NA	NA	NA	NA	NA	NA
23	Hydride	NA	NA	NA	111	NA	253.7
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 87 Instrument Conditions K**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer				NA	100	766.491
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	766.5
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	404.721nm, 766.491nm
7	ICP-OES-RV	NA			NA		766.49
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-RV	Lu			NA	0.1	766.491
12	ICP-MS	Sc	KED	He	NA	625	39
13					NA		
14	ICP-OES-RV	Y377	NA			N/A	766.491nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-RV	Lu			NA	20	766.49
17	ICP-OES-AV	Y 371.029			NA	1	769.897
18	ICP-OES-RV	Lu			NA	40	766.49
19	ICP-MS	Rh	ORS	He	NA	800	39
20	ICP-OES-RV				NA	1000	766.491
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		766.491
25	NA	NA	NA	NA	NA	NA	NA

**Table 88 Instrument Conditions La**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						NA	
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	139
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	In	N/A		250	250	
11	ICP-MS	In	ORS	He	0.1	NA	139
12						NA	
13						NA	
14	NA					NA	
15	NT				NT	NA	NT
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Rh	ORS	He	800	NA	139
20	ICP-MS/MS		ORS		1000	NA	139
21	ICP-MS	Tb	UC	He	2000	NA	139
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	398.832

**Table 89 Instrument Conditions Li**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						NA	
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc			50	NA	7
4	ICP-OES-AV	Cs697.327	NA	NA	80	NA	Li 670.783(nm)
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Sc	NA		N/A	250	
11	ICP-OES-RV	Lu			0.1	NA	670.783
12	ICP-MS	Sc	NA	standard mode	625	NA	7
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS	Ge 72	ORS		N/A		7 m/z
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-OES-RV	Lu			40	NA	670.784
19	ICP-MS	Sc	ORS	He	800	NA	7
20	ICP-MS/MS		ORS		1000	NA	7
21	ICP-MS	Sc	UC	He	2000	NA	7
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	670.784

Table 90 Instrument Conditions Mg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	100	279.078
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	383.8
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	383.829nm
7	ICP-OES-AV	NA			NA		279.077
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-RV	Lu			NA	0.1	285.213
12	ICP-MS	Sc	KED	He	NA	625	25
13					NA		
14	ICP-OES-RV	Y377	NA			N/A	280.27 nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-RV	Lu			NA	50	279.077
17	ICP-OES-AV	Y 371.029			NA	1	277.983
18	ICP-OES-RV	Lu			NA	40	285.213
19	ICP-MS	Rh	ORS	He	NA	800	24
20	ICP-OES-RV				NA	1000	279.078
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		383.829
25	NA	NA	NA	NA	NA	NA	NA

**Table 91 Instrument Conditions Mn**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	55
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	55
4	ICP-OES-AV	Eu 271.700	NA	NA	80	NA	Mn 257.610
5	ICP-OES-AV	Lu 261.541				NA	257.61
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	257.61
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	250	N/A	
11	ICP-OES-AV	Lu			0.1	NA	257.61
12	ICP-MS	Sc	KED	He	625	NA	55
13						NA	
14	ICP-OES-AV	Te214	NA			N/A	191.446 nm
15	NT				NT	NA	NT
16	AAS	None			20	NA	279.5
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	55
20	ICP-OES-AV				1000	NA	257.61
21	ICP-MS	Sc	UC	He	2000	NA	55
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	253.61

**Table 92 Instrument Conditions Mo**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	98
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Rh	ORS	He	50	NA	95
4	ICP-MS/MS	Rh103	ORS	O2	4000	NA	Mo 95/95(m/z)
5	ICP-OES-AV	Lu 261.541				NA	202.032
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	202.031
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	NA		250	N/A	
11	ICP-OES-AV	Lu			0.1	NA	202.032
12	ICP-MS	Rh	NA	standard mode	625	NA	95
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-OES-AV	Te214	NA			N/A	204.598 nm
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	95
20	ICP-MS/MS		ORS		1000	NA	98
21	ICP-MS	Rh	UC	He	2000	NA	98
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	203.031

**Table 93 Instrument Conditions Na**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	100	589.592
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	589.6
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	330.237, 589.592nm
7	ICP-OES-RV	NA			NA		589.592
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-RV	Lu			NA	0.1	589.592
12	ICP-MS	Sc	KED	He	NA	625	23
13					NA		
14	ICP-OES-RV	Y377	NA			N/A	589.592 nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-RV	Lu			NA	20	589.592
17	ICP-OES-AV	Y 371.029			NA	1	588.995
18	ICP-OES-RV	Lu			NA	40	589.592
19	ICP-MS	Rh	ORS	He	NA	800	23
20	ICP-OES-RV				NA	1000	588.995
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		589.592
25	NA	NA	NA	NA	NA	NA	NA

**Table 94 Instrument Conditions Ni**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	60
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	60
4	ICP-OES-AV	Lu219.556	NA	NA	80	NA	Ni 231.604(nm)
5	ICP-OES-AV	Lu 261.541				NA	231.604
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	231.604
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	250	250	
11	ICP-MS	Ge	ORS	He	0.1	NA	60
12	ICP-MS	Ge	KED	He	625	NA	60
13						NA	
14	ICP-OES-AV	Te214	NA				216.555 nm
15	NT				NT	NA	NT
16	AAS	None			20	NA	232
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			4000	NA	
19	ICP-MS	Rh	ORS	He	800	NA	60
20	ICP-MS/MS		ORS	He	1000	NA	60
21	ICP-MS	Ga	UC	He	1000	NA	60
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-RV	Y	NA	NA	18.5	NA	231.604
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	231.604

**Table 95 Instrument Conditions P**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	100	213.618
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	185.8
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	185.827nm
7	NA	NA			NA		
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-AV	Lu			NA	0.1	177.434
12	ICP-MS	Sc	KED	He	NA	625	31
13					NA		
14	ICP-OES-AV	Te214	NA			N/A	177.434 nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-AV	Lu			NA	50	214.914
17	ICP-OES-AV	Y 371.029			NA	1	213.618
18	ICP-OES-AV	Lu			NA	40	178.221
19	ICP-MS	Rh	ORS	HEHe	NA	800	31
20					NA	1000	
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		185.827
25	NA	NA	NA	NA	NA	NA	NA

**Table 96 Instrument Conditions Pb**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	208
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	208
4	ICP-OES-AV	Eu271.70	NA	NA	80	NA	Pb 20.353(nm)
5	ICP-OES-AV	Lu 261.541				NA	220.353
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	220.353
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir	NA		250	250	
11	ICP-MS	Ir	ORS	He	0.1	NA	208
12	ICP-MS	Ir	NA	standard mode	625	NA	206+207+208
13						NA	
14	ICP-OES-AV	Te214	NA				220.353 nm
15	ICP-OES-AV				50	NA	220.353
16	AAS	None			20	NA	283.3
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Bi209			4000	NA	
19	ICP-MS	Ir	ORS	He	800	NA	208
20	ICP-MS/MS		ORS		1000	NA	208
21	ICP-MS	Tb	UC	He	1000	NA	206+207+208
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-AV	Y	NA	NA	18.5	NA	220.353
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	220.353

**Table 97 Instrument Conditions Rb**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						NA	
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Rh	ORS	He	50	NA	85
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	NA		250	N/A	
11						NA	
12						NA	
13						NA	
14	NA					NA	
15	NT				NT	NA	NT
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Rh	ORS	He	800	NA	85
20	ICP-MS/MS		ORS	He	1000	NA	85
21	ICP-MS	Rh	UC	He	2000	NA	85
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	

**Table 98 Instrument Conditions S**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	100	181.972
2	ICP-OES-AV				NA		
3	ICP-OES-AV	Eu			NA	50	178.2
4	NA	NA	NA	NA	NA	NA	NA
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	178.165,181.972nm
7	NA	NA			NA		
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-AV	Lu			NA	0.1	181.972
12	ICP-OES-AV	Y	NA	NA	NA	62.5	181.975
13					NA		
14	ICP-OES-AV	Te214	NA			N/A	180.669 nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-AV	Lu			NA	50	181.975
17					NA		
18					NA		
19	ICP-OES-AV	Y			NA	800	181.792
20	ICP-OES-AV				NA	1000	181.972
21	NA	NA	NA	NA	NA	NA	NA
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		178.165
25	NA	NA	NA	NA	NA	NA	NA

**Table 99 Instrument Conditions Sb**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	121
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Rh	ORS	He	50	NA	121
4	ICP-MS/MS	Rh103	ORS	O2	4000	NA	Sb 121/121(m/z)
5	ICP-OES-AV	Lu 261.541				NA	206.834
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	206.836
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	NA		250	N/A	
11	ICP-MS	In	ORS	He	0.1	NA	121
12	ICP-MS	Rh	NA	standard mode	625	NA	121
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS	Rh 103	ORS			N/A	122m/z
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	In115			400	NA	
19	ICP-MS	Rh	ORS	He	800	NA	121
20	ICP-MS/MS		ORS	He	1000	NA	121
21	ICP-MS	Rh	UC	He	2000	NA	121
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	206.836

Table 100 Instrument Conditions Se

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	72	ORS	He	100	NA	78
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	78
4	ICP-MS/MS	Rh103	ORS	O2	4000	NA	Se 78/94(m/z)
5	ICP-OES-AV	Lu 261.541				NA	196.026
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	196.026
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	250	250	
11	ICP-MS	Ge	ORS	H2	0.1	NA	78
12	ICP-MS	Rh	NA	standard mode	625	NA	82
13						NA	
14	ICP-MS	Rh 103	ORS				78m/z
15	NT				NT	NA	NT
16	AAS	None			20	NA	196
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Y89			400	NA	
19	ICP-MS	Rh	ORS	HEHe	800	NA	78
20	ICP-MS/MS		ORS	H2	1000	NA	78
21	ICP-MS	Te	UC	He	200	NA	82
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	196.026

Table 101 Instrument Conditions Sn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	118
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Rh	ORS	He	50	NA	118
4	ICP-OES-AV	Lu219.556	NA	NA	80	NA	Sn 189.927(nm)
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	189.927
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	NA		250	N/A	
11	ICP-MS	In	ORS	He	0.1	NA	118
12	ICP-MS	Rh	NA	standard mode	625	NA	118
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS	Rh 103	ORS			N/A	118m/z
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Rh	ORS	He	800	NA	118
20	ICP-MS/MS		ORS	He	1000	NA	118
21	ICP-MS	Rh	UC	He	2000	NA	120
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	189.927

**Table 102 Instrument Conditions Sr**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV-buffer	Lu			NA	100	407.771
2	ICP-OES-AV				NA		
3	ICP-MS	Sc	ORS	He	50	50	88
4	ICP-OES-AV	Lu219.556	NA	NA	80	NA	Sr 218.596(nm)
5	NA	NA	NA	NA	NA	NA	NA
6	ICP-OES-AV-buffer	Eu & Cs	NA	NA	NA	50	430.545nm
7	NA	NA					
9					NA		
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11	ICP-OES-AV	Lu			0.1	0.1	88
12	ICP-MS	Rh	NA	standard mode	625	625	88
13					NA		
14	ICP-OES-RV	Y371	NA			N/A	407.771 nm
15	NA	NA	NA	NA	NA	NA	NA
16	ICP-OES-AV	Lu			NA	20	407.771
17	ICP-OES-AV	Y 371.029			NA	1	407.771
18	ICP-OES-RV	Lu			40	40	421.552
19	ICP-MS	Rh	ORS	He	800	800	88
20	ICP-MS/MS		ORS		1000	1000	88
21	ICP-MS	Rh	UC	He	2000	NA	88
22					NA		
23	NA	NA	NA	NA	NA	NA	NA
24	ICP-OES-RV				NA		430.544
25	ICP-OES-AV	Yttrium			50	NA	407.271

Table 103 Instrument Conditions Th

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						NA	
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	232
4	ICP-MS/MS	Ir 193	ORS	He	1600	NA	Th 232/232(m/z)
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	N/A	N/A	N/A	N/A	N/A	N/A	N/A
11						NA	
12						NA	
13						NA	
14	NA					NA	
15	NT				NT	NA	NT
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Ir	ORS	He	800	NA	232
20	ICP-MS/MS		ORS		1000	NA	232
21	NA	NA	NA	NA	NA	NA	NA
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	283.73

**Table 104 Instrument Conditions Tl**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	205
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	205
4	ICP-MS/MS	Ir 193	ORS	O2	1600	NA	Tl 205/205(m/z)
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir	NA		N/A	250	
11	ICP-MS	Ir	ORS	He	0.1	NA	205
12	ICP-MS	Ir	NA	standard mode	625	NA	205
13	NA	NA	NA	NA	NA	NA	NA
14	NA					NA	
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Ir	ORS	He	800	NA	205
20	ICP-MS/MS		ORS		1000	NA	203
21	ICP-MS	Tb	UC	He	2000	NA	205
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 105 Instrument Conditions U**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	238
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Lu	ORS	He	50	NA	232
4	ICP-MS/MS	Ir 193	ORS	He	4000	NA	U 238/238(m/z)
5	NA	NA	NA	NA	NA	NA	NA
6	NA	NA	NA	NA	NA	NA	NA
7	NA	NA				NA	
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Ir	NA		N/A	250	
11	ICP-MS	Ir	ORS	He	0.1	NA	238
12	ICP-MS	Ir	NA	standard mode	625	NA	238
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-MS	Ir 193	ORS		N/A		238m/z
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-MS	Bi209			4000	NA	
19	ICP-MS	Ir	ORS	He	800	NA	238
20	ICP-MS/MS		ORS		1000	NA	238
21	ICP-MS	Tb	UC	He	2000	NA	238
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25						NA	

**Table 106 Instrument Conditions V**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	51
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	51
4	ICP-MS/MS	Sc 45/61	ORS	O2	4000	NA	V 51/67(m/z)
5	ICP-OES-AV	Lu 261.541				NA	298.881
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	292.402
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Sc	UC	He	250	250	
11	ICP-OES-AV	Lu			0.1	NA	292.401
12	ICP-MS	Sc	KED	He	625	NA	51
13	NA	NA	NA	NA	NA	NA	NA
14	ICP-OES-RV	Y371	NA				310.229 nm
15	NA	NA	NA	NA	NA	NA	NA
16	NA	NA	NA	NA	NA	NA	NA
17	NA	NA	NA	NA	NA	NA	NA
18						NA	
19	ICP-MS	Rh	ORS	He	800	NA	51
20	ICP-MS/MS		ORS	He	1000	NA	51
21	ICP-MS	Sc	UC	He	200	NA	51
22	NA	NA	NA	NA	NA	NA	NA
23	NA	NA	NA	NA	NA	NA	NA
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	292.464

**Table 107 Instrument Conditions Zn**

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1/S2 Final Dilution Factor	S3 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	103	ORS	He	100	NA	66
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS	Sc	ORS	He	50	NA	66
4	ICP-OES-AV	Lu219.556	NA	NA	80	NA	Zn 206.200(nm)
5	ICP-OES-AV	Lu 261.541				NA	206.2
6	NA	NA	NA	NA	NA	NA	NA
7	ICP-OES-AV	NA				NA	213.857
9	NA	NA	NA	NA	NA	NA	NA
10	ICP-MS	Rh	UC	He	250	250	
11	ICP-OES-AV	Lu			0.1	NA	206.2
12	ICP-MS	Ge	KED	He	625	NA	66
13						NA	
14	ICP-OES-AV	Te214	NA				202.548 nm
15	ICP-OES-AV				50	NA	213.86
16	AAS	None			20	NA	213.9
17	NA	NA	NA	NA	NA	NA	NA
18	ICP-OES-AV	Lu			4000	NA	213.857
19	ICP-MS	Rh	ORS	He	800	NA	64
20	ICP-MS/MS		ORS		1000	NA	213
21	ICP-MS	Ga	UC	He	1000	NA	66
22	NA	NA	NA	NA	NA	NA	NA
23	ICP-OES-RV	Y	NA	NA	185	NA	213.857
24	NA	NA	NA	NA	NA	NA	NA
25	ICP-OES-AV	Yttrium			50	NA	206.2

**END OF REPORT**