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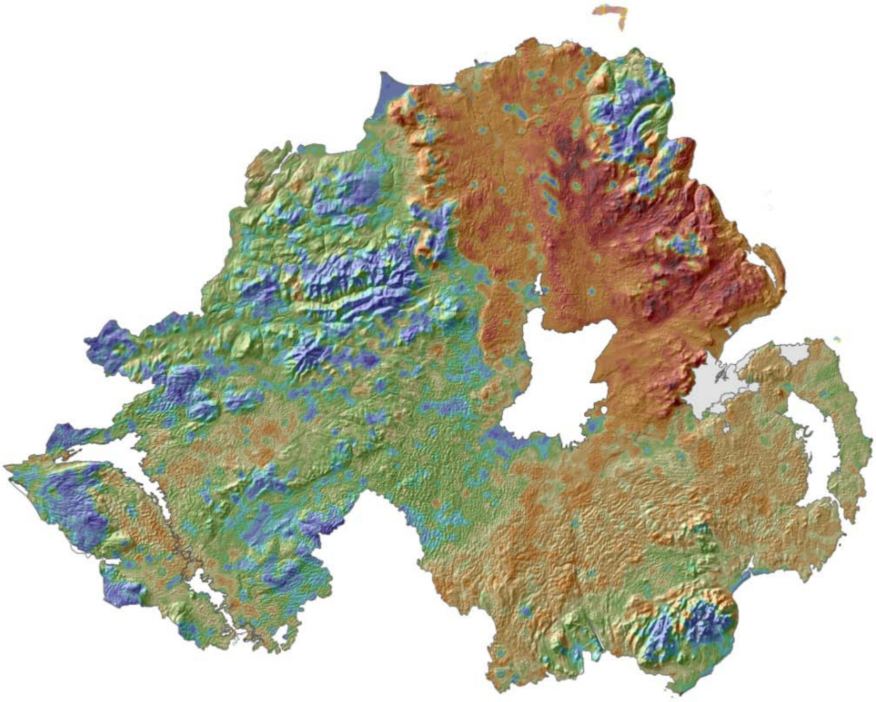
Tellus Soil Geochemistry - Quality Assessment and Map Production of ICP data

Tellus Geochemistry Programme

Internal Report IR/11/01



Tellus 'S' soil Aluminium data for Northern Ireland analysed using aqua regia digest and ICP-AES

BRITISH GEOLOGICAL SURVEY

TELLUS GEOCHEMISTRY PROGRAMME

INTERNAL REPORT IR/11/01

Tellus Soil Geochemistry - Quality Assessment and Map Production of ICP data

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Irish Grid Reference

SW corner 190000,310000
Centre point 280000,382500
NE corner 370000,455000

Map
Sheet: Northern Ireland, 1:250 000 scale, Geological Map of Northern Ireland

Front cover
Tellus S soils for Aluminium for Northern Ireland analysed using aqua regia digest and ICP-AES.

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Foreword

The following report presents the methodology employed for the chemical analysis and quality assurance of samples of surface and deep soils collected by urban and rural sampling in Northern Ireland and analysed by ICP. These samples were collected and analysed under the Tellus project by the Geological Survey of Northern Ireland (GSNI) and British Geological Survey (BGS). Maps of selected elemental concentrations are presented and compared with previously published XRFS maps. The Tellus geochemical project was implemented to provide a regional scale, geochemical baseline for Northern Ireland.

Acknowledgements

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Summary

Soil samples (surface'A' and deep 'S') were collected across Northern Ireland during the Tellus Project, 2004-7 according to the G-BASE protocol. The results of analyses 'A' samples analysed by XRFS were previously published in 2007. Both 'A' and 'S' samples were also analysed by ICP, using *aqua regia* digests and the 'S' samples by multi-acid ('near-total') digest. The quality assurance process applied to these analyses and the results are presented here. Almost all the ICP data fell within acceptable experimental errors in the context of controls provided by Certified Reference Materials and replicate samples. Minor discrepancies are noted.

A summary of correction factors which have been approved and applied to the data for the purpose of data preparation and map production is given opposite.

Correction Factors which have been applied in data preparation:

Aqua regia digest ICP analysis of Tellus 'A' soil
Cs [Cs] (measured from July 2006) x 1.238
Aqua regia digest ICP analysis of Tellus 'S' soil
Cs [Cs] (analysed after 09/06) x 1.296
Mixed acid 'near total' digest ICP analysis for Tellus 'S' soil
Al ([Al] x 1.1235) – 0.4732
Ca ([Ca] x 1.0527) – 0.0041
Co ([Co] x 1.0867) – 0.1952
Cr ([Cr] x 1.5095) – 10.73
Cu ([Cu] x 0.9653) + 1.5439
Fe ([Fe] x 1.0484) – 0.0389
Mg ([Mg] x 1.0418) + 0.0084
Sr ([Sr] x 1.0168) – 6.5825

Small scale maps of selected elements analysed by ICP are presented and compared with the earlier XRFS maps.

1 Introduction

The Tellus project comprised regional scale geochemical sampling and airborne geophysical surveys of Northern Ireland. The objective of the geochemical surveys was to generate baseline data for environmental management and to promote mineral exploration. Soil samples were analysed by XRFS and by ICP. The results of the XRFS analyses were published as digital datasets and maps in 2007 but the processing of the ICP analyses was deferred. This report now describes the analytical methodology, assessment of data quality, and map production of ICP data. Samples were analysed by ICP using both *aqua regia* and mixed acid digests. Soil sulphate was analysed by a hydrochloric acid digest.

Details of the field sampling programmes are described by Knights (2007 a, b, c). The methodology of sampling and analysis are described by Smyth (2007). The results of the inorganic geochemical surveys of the Belfast Metropolitan Area are described by Nice (2010).

Regional soil sampling of Northern Ireland was conducted between 2004 and 2006. Rural samples were collected at a density of 1 per 2 km^2 on the Irish OS grid. The urban areas of Belfast and Londonderry were excluded from the regional survey. Two separate urban surveys were made of the Belfast Metropolitan Area (Belfast, Bangor, Carrickfergus, Carryduff, Castlereagh, Greenisland, Holywood, Lisburn and Newtownabbey) and the urban area of Londonderry. The sampling density of the urban surveys was 4 sites per km^2.

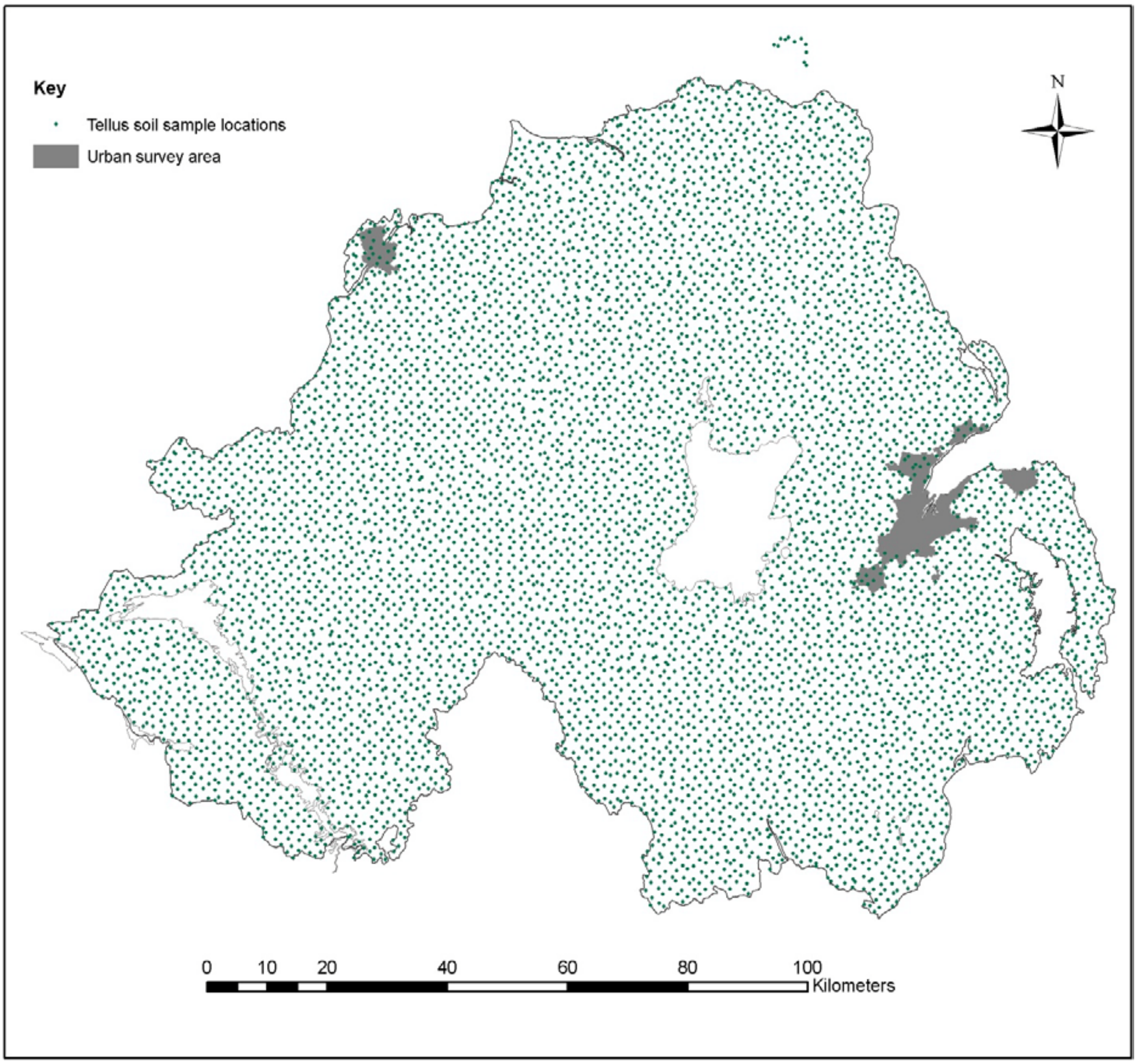


Figure 1 Location of Tellus regional survey soil sample points with urban survey areas highlighted in grey.

6940 regional sample localities and 1172 urban sample localities were visited with two discrete soil samples collected at each. Surface ‘A’ soil samples were collected from a depth of 5 – 20cm. Deep ‘S’ Soil samples were collected from a depth of 35 – 50cm from the same auger holes as the ‘A’ sample. Each sample comprised a composite of five auger flights collected at the corner points and centre of a 20 x 20m square. Following collection the samples were transported in batches of 100 to the GSNI core-store at Carrickfergus where they were air-dried in advance of dispatch to analytical laboratories.

2 Analytical methodology

A range of analytical techniques were employed to determine major and trace element concentrations in the Tellus soil samples. In addition pH and LOI were determined for the surface soil. These analyses are summarised below (Table 1) with analytical methods discussed within the content of this report denoted in bold.

Table 1 Summary of analytical techniques employed to determine major and trace element concentrations in Tellus soil samples.

Analytical method	Tellus 'S' soil		Tellus 'A' soil	
	Regional	Urban	Regional	Urban
Aqua regia partial digest ICP analysis	**X**		**X***	**X**
Mixed acid '*near-total*' digest ICP analysis	**X***	**X**		
Fire assay for Pt, Pd, Au	X			
HCl acid digest for SO_4	**X**			
XRFS analysis, pH and LOI			X	X

** denotes additional sample set comprising of a resample survey conducted during the equivalent urban survey*

This report deals specifically with the methodology, results and quality assessment of data derived by analytical procedures detailed in Table 2, all of which were conducted at SGS Laboratories, Toronto.

Table 2 Summary of analytical methods employed by SGS laboratories and discussed in this report.

SGS Method	Details
ICM12B: Multi-Element Determination using a Mixture of Hydrochloric and Nitric Acids	*Aqua regia* partial digest of Tellus 'S' soil for regional survey and Tellus 'A' soil for regional and urban survey – trace element analysis by ICP-AES and ICP-MS following *aqua regia* digest of a 1 g sub-sample
ICM40B: Multi-Element Determination using a Mixture of Hydrochloric, Nitric, Perchloric and Hydrofluoric acids	Mixed acid "Near-total" digest of Tellus 'S' soil for regional and urban survey – Multi acid (HF-$HCLO_4$-HCL-HNO_3) digest followed by trace element analysis by ICP-AES and ICP-MS.
CHAY50: Determination of Sulphate	Sulphate by dilute hydrochloric acid leach of Tellus 'S' soil for regional survey – Analysis of a 1 g sub-sample by ICP-AES following hydrochloric acid digest.

A summary of determinands, and the relevant detection limits, units and determination methods are reported in Table 3. Some additional elements were analysed by these methods, (for example Au, Pt and Pd) but better data sets were derived by previous fire assay/ICP-MS analysis.

Table 3 Summary of determinants, analytical method, detection limit and units.

Element	Units	Detection Limit		Method	Element	Units	Detection Limit		Method
		Aqua regia	*Near-total*				*Aqua regia*	*Near-total*	
Ag	mg kg^{-1}	0.01	0.02	ICP-MS	Mo	mg kg^{-1}	0.05	0.05	ICP-MS
Al	%	0.01	0.01	ICP-AES	Na	%	0.01	0.01	ICP-AES
As	mg kg^{-1}	0.1	1	ICP-MS	Nb	mg kg^{-1}	0.05	0.05	ICP-MS
B	mg kg^{-1}	10	n/a	ICP-AES	Ni	mg kg^{-1}	0.5	0.5	ICP-MS ICP-AES
Ba	mg kg^{-1}	5	5	ICP-AES					
Be	mg kg^{-1}	0.1	0.1	ICP-MS	P	mg kg^{-1}	50	50	ICP-AES
Bi	mg kg^{-1}	0.02	0.04	ICP-MS	Pb	mg kg^{-1}	0.2	0.5	ICP-MS
Ca	%	0.01	0.01	ICP-AES	Rb	mg kg^{-1}	0.2	0.2	ICP-MS
Cd	mg kg^{-1}	0.01	0.02	ICP-MS	S	%	0.01	0.01	ICP-AES
Ce	mg kg^{-1}	0.05	0.05	ICP-MS	Sb	mg kg^{-1}	0.05	0.05	ICP-MS
Co	mg kg^{-1}	0.1	0.1	ICP-MS	Sc	mg kg^{-1}	0.1	0.1	ICP-MS
Cr	mg kg^{-1}	1	1	ICP-AES	Se	mg kg^{-1}	1	2	ICP-MS
Cs	mg kg^{-1}	0.05	5	ICP-MS	Sn	mg kg^{-1}	0.3	0.3	ICP-MS
Cu	mg kg^{-1}	0.5	0.5	ICP-AES	Sr	mg kg^{-1}	0.5	0.5	ICP-AES
Fe	%	0.01	0.01	ICP-AES	Ta	mg kg^{-1}	0.05	0.05	ICP-MS
Ga	mg kg^{-1}	0.1	0.1	ICP-MS	Tb	mg kg^{-1}	0.02	0.02	ICP-MS
Ge	mg kg^{-1}	0.1	0.1	ICP-MS	Te	mg kg^{-1}	0.05	0.05	ICP-MS
Hf	mg kg^{-1}	0.05	0.02	ICP-MS	Th	mg kg^{-1}	0.1	0.2	ICP-MS
Hg	mg kg^{-1}	0.01		ICP-MS	Tl	mg kg^{-1}	0.02	0.02	ICP-MS
In	mg kg^{-1}	0.02	0.02	ICP-MS	U	mg kg^{-1}	0.05	0.1	ICP-MS
K	%	0.01	0.01	ICP-AES	V	mg kg^{-1}	1	1	ICP-AES
La	mg kg^{-1}	0.1	0.1	ICP-MS	W	mg kg^{-1}	0.1	0.1	ICP-MS
Li	mg kg^{-1}	1	1	ICP-AES	Y	mg kg^{-1}	0.05	0.05	ICP-MS
Lu	mg kg^{-1}	0.01	0.01	ICP-MS	Yb	mg kg^{-1}	0.1	0.1	ICP-MS
Mg	%	0.01	0.01	ICP-AES	Zn	mg kg^{-1}	1	1	ICP-AES
Mn	mg kg^{-1}	5	5	ICP-AES	Zr	mg kg^{-1}	0.5	0.5	ICP-AES

Determinant	Units	Detection limit	Method
SO_4	%	0.01	ICP analysis following dilute HCL digest

2.1 *AQUA REGIA* PARTIAL DIGEST

The required samples were prepared for and subjected to *aqua regia* partial digest using the in-house method ICM12B of SGS Laboratories. A 1g aliquot of sample was weighed and added to a 50ml centrifuge tube with 8ml of concentrated nitric acid. The tube was heated in a water bath at 80 – 90°C for 30 minutes and then cooled before adding 4ml of hydrochloric acid. Following the addition of hydrochloric acid, the tube was then heated in the water bath with mixing every half hour for two hours. The solution was then allowed to cool to room temperature before being diluted to 50ml with deionised water and shaken. Analysis was then conducted using either ICP-MS or ICP-AES.

2.2 MIXED ACID ‘*NEAR-TOTAL*’ DIGEST

The required samples were subjected to mixed acid dissolution using the in-house method ICM40B at SGS Laboratories. A 0.20 ± 0.001g aliquot of sample was weighed into a 50 ml P.T.F.E. dish where 2ml of nitric, hydrochloric and hydrofluoric acids, plus 1ml of perchloric acid were added. The inner wall of the dish was rinsed with deionised water and then heated at 200 – 250°C until dry. After allowing the dish to cool, a further 1ml of perchloric acid was added and the dish was re-heated to dryness at the same temperature. After cooling, 2ml of hydrochloric acid and 1ml of nitric acid were then added. The dish was left to stand for a few minutes before adding 10ml of deionised water; the solution was heated to dissolve the salts, and then transferred to a graduated tube and diluted to 12ml. Analysis was then conducted using ICP-AES or ICP-MS.

2.3 DILUTE HYDROCHLORIC ACID LEACH

Hydrochloric acid digest (in-house method CHAY50) was used to prepare the Tellus 'S' soil samples for ICP analysis of sulphate (SO_4). A 0.1g sample was weighed into a test tube where 2ml of distilled water was added. The sample was agitated and then heated to boiling point for a few minutes. Following this 1ml of concentrated hydrochloric acid was added and the solution heated to boiling point where its temperature was sustained for 15 to 20 minutes. The solution was cooled and diluted to 20 ml using distilled water. Samples were then analysed using ICP-AES. Following analysis sulphate was calculated from the sulphur value.

2.4 ICP ANALYSIS

Following partial or *near-total* digest by one of the above techniques, samples were subjected to analysis by either ICP-AES or ICP-MS.

- ICP-AES

At the beginning of each run, consisting of approximately 300 samples, the instrument was calibrated. Calibration solutions comprised of a blank and either a 50ppm standard for major elements (Al, Ca, Fe, Mg, Na, P, S and Ti) or a 5ppm standard for trace elements. A calibration check standard was included after every 24 samples to ensure drift was no greater than 10%. Lutetium at 5ppm was used as an internal standard to compensate for variations in the plasma caused by different sample types. Results for major elements were reported as % element, results for trace elements were reported in mg kg^{-1}.

- ICP-MS

The samples for ICP-MS were diluted using 1% nitric acid containing rhodium and rhenium as internal standards. The instrument was calibrated at the beginning of every run; typically a run included 200 – 300 samples. The calibration was based on four points: 0, 10, 25 and 50 µg L^{-1} (0, 1, 2.5 and 5 µg L^{-1} for Ag and Hg), and a check was performed at 10 µg L^{-1} after every 48 analyses to ensure there was no drift. All results were reported in mg kg^{-1}.

3 Quality control methodology

Analytical data must be assessed in terms of quality and integrity to ascertain they are suitable for the intended end use. The accuracy and precision of data are typically tested by a series of plots and statistical tests. (Johnson *et al*. 2005). For each analytical dataset lab reported data were sent in a series of individual spreadsheets containing the results for an individual analytical run. Spreadsheets were sorted into run order and compiled in a 'master' spreadsheet with detection limits and additional duplicate and replicate sample data. By sorting the analytical data into run order any step changes or drift could be identified and their impact on data quality assessed. Throughout the entire analytical period, analytical instruments were routinely calibrated and control samples such as certified reference materials and replicate samples were analysed routinely alongside the Tellus soil samples. A detailed study of control samples allows for the identification of errors introduced at either the extraction or the analysis stage and corrections to be made where appropriate.

3.1 REFERENCE MATERIALS

A range of reference materials was used, as summarised in Table 4. Reference values for both the certified and the secondary reference materials are based on XRFS data which represent true total elemental analysis. The reference materials were included for analysis alongside the Tellus soil samples, extracted and analysed in the same way as the samples. Therefore they can be used to identify and potentially adjust for any errors introduced at the extraction or analysis stage.

Table 4 Reference materials summary

Certified reference materials	**Secondary reference materials**
TILL-1*	ANTBAS (Antrim basalt)
TILL-2	CURR (Peaty soil)
TILL-3*	DAL (Dalradian metasediment)
TILL-4	DERMOT S4
SGS in-house standard	LWRPAL (Lower Palaeozoic)
XRAL01A	[1]S13B (Carboniferous limestone)

** sample represents combined "B" and "C" horizons.*

[1] British Geological Survey G-BASE internal SRM, <150μm bulk stream sediment from an area of mineralised Carboniferous limestone, grid reference in British National Grid.

3.2 CONTROL CHARTS

Control charts (Shewhart charts) are time sequenced and are used to assess the presence of step changes or evidence of analytical drift over time (Miller and Miller, 2005). Shewhart charts were plotted for each element for a range of certified reference materials and secondary reference materials to give good coverage of concentration ranges (Figure 2). The red line depicts the analysed values in chronological order; the blue lines indicate the mean and the mean ± twice the standard deviation. Quantitative acceptance criteria are applied to the graphs to identify any problems with the data.

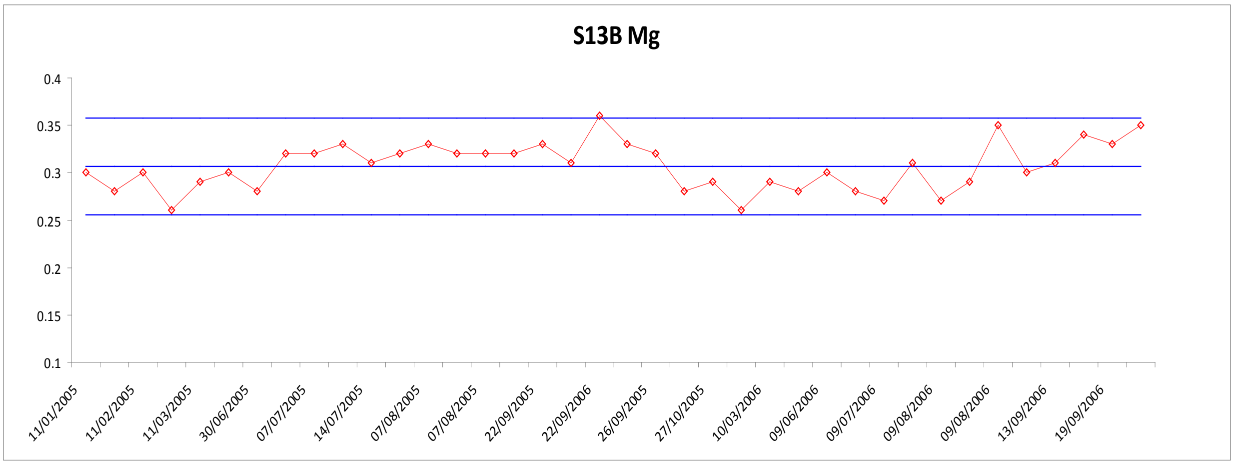


Figure 2 Example Shewhart chart.

The acceptance criteria were as follows:

- Points falling between the mean ± 2sd lines were accepted.
- If one point fell outside the mean ± 2sd line, but not outside the mean ± 3sd then the data were accepted.
- Where points consistently fell outside the mean ±2sd line then data for all the reference materials were reviewed for that element and a decision made on the validity of the data.
- Individual points falling outside the mean ±3sd were also reviewed by comparing with other available data to determine if the problem was systematic.

3.3 CORRECTION FACTORS

Where certified values are available, data can be corrected for errors which occurred either during dissolution and/or analysis by determining and applying a correction factor. The correction factor is obtained by plotting the measured value for an element against the certified values for a range of Certified Reference Materials (CRM). The equation of the line on the regression graph gives a formula to correct the results for the samples (Figure 3). For this to be a useful exercise data need to be available for reference materials and the range must be sufficient to give a reliable regression. The equation was tested by applying to the raw data for the other reference materials to determine if the entire data set would be noticeably improved. The correction factor was only applied where it is clear that in doing so, data quality will improve.

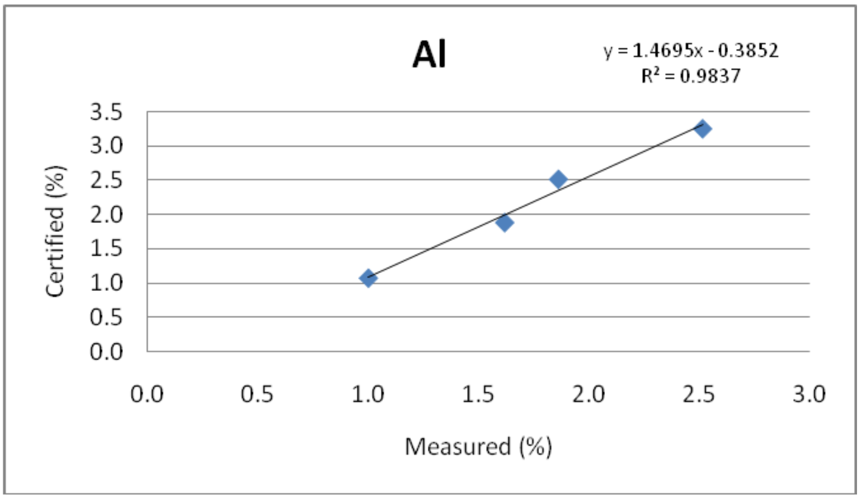


Figure 3 An example regression plot for measured values against certified values for Till-1, 2, 3 and 4.

Where Certified Reference Material data for the Till materials are not available, histograms were produced using secondary reference materials (Figure 4). Histogram analysis gives a clear view of both the accuracy of the results and their distribution compared to a normal curve, however no correction factor can be derived.

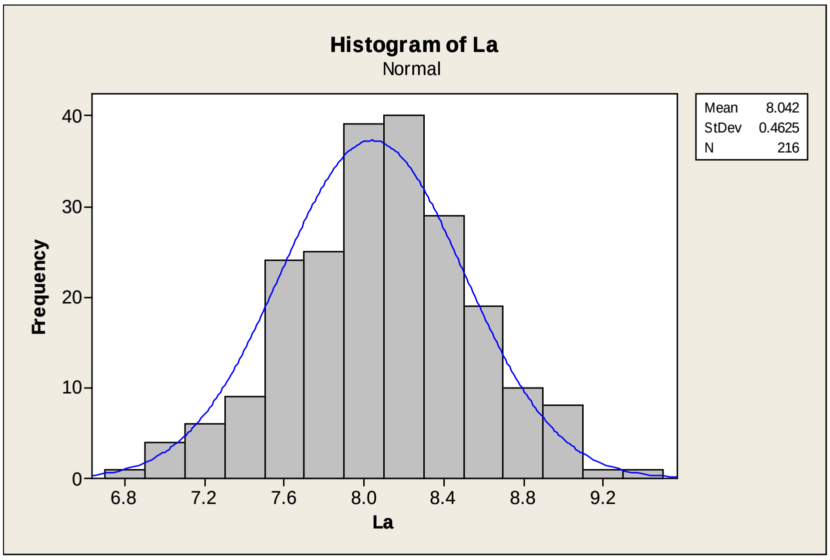


Figure 4 Example histogram showing measured lanthanum data in XRAL01A against the expected value. Values are in mg kg^{-1}. A normal distribution is observed with no bias.

4 Quality assessment of Tellus ICP data

A detailed quality assessment was undertaken for the data derived for each analytical element. For full details of the quality assessments of each, refer to the Appendices. For each analytical procedure it is important to note that error can be introduced at both the extraction stage (partial or *near-total* acid digest) and the analytical stage (ICP analysis).

4.1 TELLUS 'A' SOIL – *AQUA REGIA* PARTIAL DIGEST

4.1.1 **Quality control**

Reference materials routinely extracted and analysed in the same way as the samples for this method included the certified reference materials; Till-1, Till-2, Till-3 and Till-4, along with the six secondary reference materials. Finally SGS ran their own in-house standard, XRAL01A, for which there are reported expected values. These reference materials were used in the data quality assessment.

Where Certified Reference Material data are not available to plot regression graphs, a histogram has been produced for the data for XRAL01A. These are shown in Appendix 1, giving a clear view of both the accuracy of the results and their distribution compared to a normal curve for individual elements. Histograms have been included as well as regression graphs where they are helpful. XRAL01A was selected as it was the only material other than the Certified Reference Materials for which expected *aqua regia* extraction data were available; the XRFS data for total element content quoted for the other materials would not give a useful comparison. Also, there were far more results available for this than any other reference material.

Shewhart charts were plotted for all elements for the certified reference materials, ANTBAS, S13B and XRAL01A and, where necessary, for the other secondary reference materials to give good coverage of concentration ranges. These charts give a clear indication of any step changes or analytical drift. An example of a Shewhart Chart for the 'A' soil *aqua regia* data is given in Figure 5.

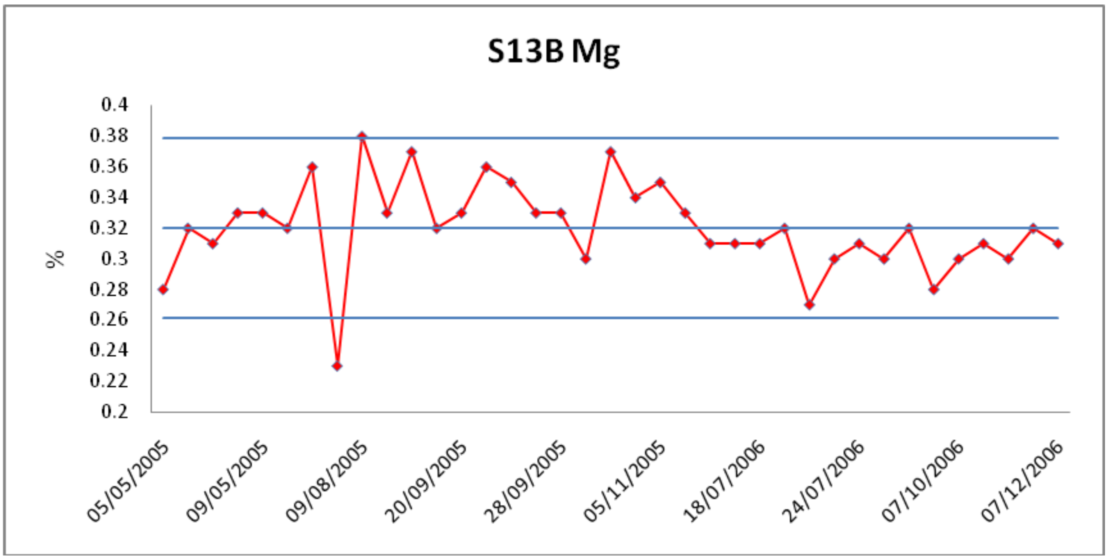


Figure 5 Shewhart chart for Mg concentration in S13B.

On 9/5/2005 S13B gave a noticeably low result for several elements, including magnesium as shown above but this is not seen for other materials analysed on the same day. Also in September 2005, S13B showed an increase in measured values, sometimes accompanied by XRAL01A and DAL, but not by Antbas or LWRPALA. The magnitude of this increase varied between materials; therefore no correction factor can be applied. Although in some cases poor precision was observed, this problem was not systematic.

Shewhart charts reveal a step change in caesium and zirconium reflective of the fact that sample analysis was conducted over two periods May-Sept 2005 and July-Feb 2006-2007. This break was indiscernible for all other elements. Ideally this should be corrected for.

Caesium data are also observed to display evidence of under recovery however this may be explained by the caesium being contained in a silica matrix and therefore not being fully extracted by the *aqua regia* digest.

Shewhart charts for phosphorus concentration in primary and most secondary reference materials indicate that results were more widely scattered than usual with varying precision. No cause has been identified and this is not possible to correct for.

An unusually high molybdenum result was recorded in each of the reference materials during July 2006, this may represent a dissolution batch that was contaminated. Insufficient data were available to assess the situation fully but unusually high results should be treated with caution.

Poor precision was observed across the antimony data.

For a detailed discussion of data quality on an element by element basis using a combination of Shewhart plots, regression graphs with correction factors and histograms where appropriate, refer to Appendix 1.

4.1.2 **Corrections based on certified reference materials**

Where data are available and the range is sufficient to give a reliable regression correction factors have been derived using the Certified Reference Materials Till-1, Till-2, Till-3 and Till-4. On the whole the correction factors produced in this manner are small and insufficient corroborative evidence is available from other reference materials to indicate whether applying a correction factor really gives an improvement. They have, therefore, not been applied to the sample data. Where regression graphs have been plotted the correlation factors are close to 1 showing that the data are consistent across the concentration range covered.

4.1.3 **Recommendations**

Following a detailed study of the quality control data, obtained from certified and secondary reference materials, data have been shown to be fit for purpose. Where sufficient certified reference material data are available, correction factors have been generated from linear regressions based on the mean of the measured results plotted against certified values. These correction factors however have not been applied to the data set as there were no certified reference materials with *aqua regia* data available included with the samples, other than those used to generate the correction factors. Therefore, it is not possible to ascertain whether applying the factor gives an overall improvement in the results; it is possible that applying a factor, without sufficient evidence of improvement, could have an adverse effect on data quality. This does not preclude the application of these factors at a later date if further evidence suggests they would give an improvement.

There is, however, one exception; the reference material data for caesium clearly shows a step change between the analysis conducted during 2005 and the subsequent analysis from 2006. Applying a correction factor of 1.238 to all caesium data for samples analysed from 2006 onwards corrects for this step and improves the data quality.

Table 5 Correction factors for analytical data for Tellus A soil following *aqua regia* partial digest and ICP analysis.

Element	**Correction Factor**
Ag	([Ag] × 1.3959) – 0.1186
As	([As] × 1.0803) – 0.595
Ba	([Ba] × 1.0116) + 5.3883
Co	([Co] × 1.0668) + 0.1162
Cr	([Cr] × 1.2444) – 2.3288
Cs	[Cs] (measured from July 2006) × 1.238
Cu	([Cu] × 1.0642) + 1.4204
Fe	([Fe] × 0.9129) + 0.2893
K	([K] × 1.1983) + 0.049
Mg	([Mg] × 1.071) + 0.0435
Mn	([Mn] × 0.8071) + 47.433
Ni	([Ni] × 1.0081) + 0.6422
Pb	([Pb] × 0.9554) – 0.9875
V	([V] × 0.7692) + 8.6253

4.2 TELLUS ‘S’ SOIL – *AQUA REGIA* PARTIAL DIGEST

4.2.1 Quality control

Certified reference materials; Till-1, Till-2, Till-3, and Till-4, and six secondary reference materials were included routinely with the samples and extracted and analysed by the same method. In addition the SGS in-house standard XRAL01A was included. These reference materials were then used in the quality control process to identify and correct for error where possible. Regression graphs were plotted using data for the certified reference materials. Histograms were plotted for this reference material to assess data quality where there was insufficient data for certified reference materials.

Shewhart charts were plotted individually for each element for; each of the certified reference materials, ANTBAS, S13B and XRAL01A and, where necessary, for the other secondary reference materials to give good coverage of concentration ranges and assess data quality over time (Figure 6).

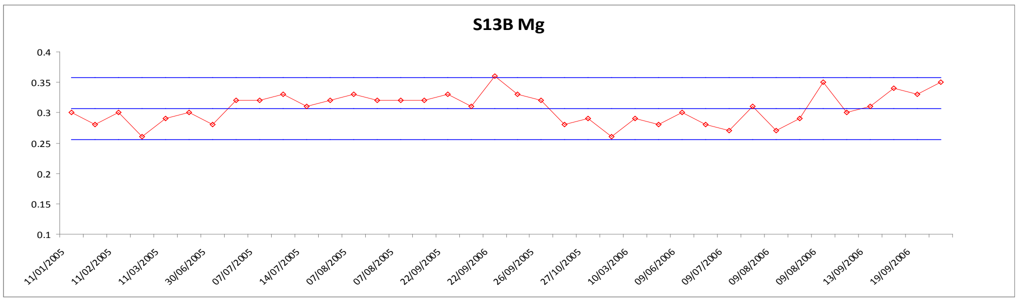


Figure 6 Example Shewhart plot for Mg concentration in S13B. Values in % Mg

For several elements some Shewhart plots, particularly those for XRAL01A, appeared to show a step change from 19/09/06 onwards. During this period few of the other reference materials were analysed more than once or twice which makes it difficult to judge if the issue is material or extraction based or a result of analytical error. Some possible explanations include the opening of a new pot of reference material, a change of acid or low water bath temperature. Insufficient information to accurately assess the cause or magnitude of this step means it cannot be corrected for.

Phosphorous data reported below the detection limit should be treated with caution. In the reference materials several points are reported as being below detection limit despite the usual value being well above it. This cannot be corrected for as it is not a systematic issue.

For a detailed discussion of data quality on an element by element basis using a combination of Shewhart plots, regression graphs with correction factors and histograms where appropriate refer to Appendix 2.

4.2.2 Corrections based on certified reference materials

Where certified values are available, data can be corrected for errors which may have occurred during dissolution and analysis. Certified Reference Materials Till-1, Till-2, Till-3 and Till-4 were used where data were sufficient to give a reliable regression. Where Certified Reference Material data were not available a histogram was produced for the data using the in-house standard XRAL01A. XRAL01A was selected as it was the only material, other than the Certified Reference Materials, for which expected *aqua regia* extraction data were available; the XRFS data for total element content quoted for the other materials would not give a useful comparison. Also, there were far more results available for this than any other reference material.

Table 6 Correction factors for *aqua regia* analytical data

Element	Correction Factor
Ag	([Ag] × 1.1548) - 0.0507
As	([As] × 1.1397) - 1.611
Ba	([Ba] × 0.9503) + 7.8456
Bi	([Bi] × 1.0499) - 1.3196
Co	([Co] × 1.0811) + 0.2179
Cr	([Cr] × 1.2614) - 4.1432
Cu	([Cu] × 1.055) + 0.5091
Cs	[Cs] (analysed after 09/06) × 1.296
Fe	([Fe] × 0.8368) + 0.4527
Mn	([Mn] × 0.8125) + 45.138
Ni	([Ni] × 0.9781) + 0.589
Pb	([Pb] × 0.9832) - 2.0578
V	([V] × 0.7769) + 8.5222
Zn	([Zn] × 0.9868) + 8.2446

4.2.3 Recommendations

A detailed study of quality control data obtained from certified and secondary reference materials included with the samples submitted from the regional soil sampling of Northern Ireland has shown the data to be fit for purpose. Where sufficient certified reference material data are available, correction factors have been generated from linear regressions based on the mean of the measured results plotted against certificate values. These correction factors have not been applied to the data set as there were no certified reference materials with *aqua regia* data available included with the samples, other than those used to generate the correction factors. Therefore, it is not possible to ascertain whether applying the factor gives an overall improvement in the results; it is possible that applying a factor, without sufficient evidence of improvement, could have an adverse effect on data quality. This does not preclude the application of these factors at a later date if further evidence suggests they would give an improvement.

One exception is the correction factor used to correct for the step change noted in the caesium data. This correction can be applied to all data analysed from September to remove the effects of step change and improve the data quality.

4.3 TELLUS 'S' SOIL – MIXED ACID '*NEAR-TOTAL*' DIGEST

It is worth noting that while the mixed acid dissolution can be described as "near-total", for most elements, there will be some minerals that cannot be dissolved by the given method and so under-recoveries should be expected for those elements. Volatile elements may be partially lost during the dissolution process, also leading to under recoveries.

4.3.1 Quality control

Shewhart charts were plotted for all elements for the certified reference materials, ANTBAS, Dal and S13B and, where necessary, for the other secondary reference materials to give good coverage of concentration ranges. These charts give a clear indication of step changes or drift.

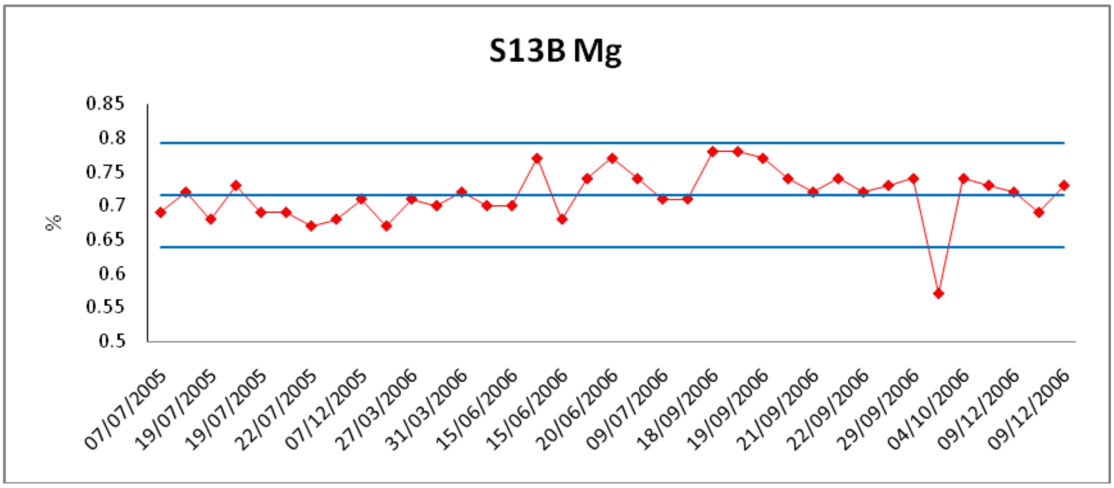


Figure 7 Shewhart plot for Mg concentration in S13B.

Some reference materials were mis-labelled; in some of these cases the correct label could be assigned as the concentrations closely matched those measured in other materials, but others appeared to be unknowns. These were removed from the calculations, but some concern remains regarding the accuracy in naming the unknown samples. Results falling outside the expected concentration range should be treated with caution.

The data for the reference material S13B analysed by ICP-AES on 4th April 2006 and by ICP-MS on 10th April 2006 were anomalous for several elements; they were frequently high, but occasionally low. These data have been removed from the calculations. The data for a separate dissolution of S13B analysed in the same runs gave results within the expected range. Till-2 was also analysed twice in these runs and gave results within the expected range.

For almost every element, even after these erroneous data have been removed, there are fliers in the Shewhart plots. There is no identifiable pattern between elements, samples, or analytical batches for example. Therefore the data have been retained for the calculations as there is no valid reason to remove them. However, if the same is happening for the unknown samples there could be spurious results in the data set. Results that stand out as unusually high or low must be treated with caution. For example the arsenic data include several results which fall outside the acceptable range but no systematic error is identified and so these results are included.

Several elements show low or under recovery but often these observations can be explained. Yttrium and zirconium data show a generally low and often erratic recovery. However, this is expected as these elements are often bound up in resistate minerals such as zircon and will remain unaffected by the mixed acid dissolution method. Low recoveries in antimony can be accounted for by the loss of antimony pentafluoride by aggressive heating during the dissolution process. Under-recovery and poor precision in silver data is likely to reflect the precipitation of silver chloride during dissolution. Lastly cobalt demonstrated poor recovery, this is however, typical when subjected to mixed acid dissolution.

It was noted that nickel was initially determined by ICP-MS but later by ICP-AES however no discernable step change was identified and therefore no data conditioning is required.

During the analytical period the detection limit for caesium was initially quoted as 0.05 mg kg^{-1} however it changed to 5 mg kg^{-1}. The precision of the data at the initial lower detection limit was good but during subsequent analysis with the higher detection limit many results were lost below this limit.

4.3.2 Corrections based on certified reference materials

During mixed acid ‘*near-total*’ digest, errors can occur during both the dissolution and analysis stages. Regression plots based on Certified Reference Materials Till-1, Till-2, Till-3 and Till-4 were used where data range was sufficient to obtain a reliable result. The equation obtained from this plot was applied to the raw data for the other reference materials to determine if the data set would be improved by applying the equation to the entire data set. Several of the correction factors derived from the regression plots were ascertained to improve data quality and therefore have been applied to the data. These are summarised in Table 7.

Table 7 Summary of recommended correction factors for ‘*near-total*’ 'S' soil data

Element	Correction Factors
Al	([Al] × 1.1235) – 0.4732
Ca	([Ca] × 1.0527) – 0.0041
Co	([Co] × 1.0867) – 0.1952
Cr	([Cr] × 1.5095) – 10.73
Cu	([Cu] × 0.9653) + 1.5439
Fe	([Fe] × 1.0484) – 0.0389
Mg	([Mg] × 1.0418) + 0.0084
Sr	([Sr] × 1.0168) – 6.5825

Where Certified Reference Material data for the Till materials were not available, a histogram was produced for the data using S13B which, although does not give a correction factor, can be used to asses the accuracy of the results. S13B was selected as it had been included frequently with the samples; also total data from XRFS analysis were readily available.

A more detailed discussion on data quality on an element by element basis can be found in Appendix 3.

4.3.3 Recommendations

A detailed study of the quality control data obtained from certified and secondary reference materials has shown the data to be fit for purpose. Where sufficient data are available for the Till certified reference materials, correction factors have been generated from linear regressions based on the mean of the measured results plotted against certified values. These correction factors were evaluated by applying them to the mean raw results for the other reference materials. Table 7 shows the recommended correction factors; these are based on the graphs in Appendix 3. The correction should be applied to Al, Ca, Co, Cr, Cu, Fe, Mg and Sr as this gives an improvement across the concentration range for which data are available. The caesium data should be used with caution as the detection limit was changed during the analytical period.

4.4 DILUTE HCl DIGEST – TELLUS ‘S’ SOILS - SULPHATE

4.4.1 Quality control

There is a lack of available Certified Reference Material data for this particular analytical method so it is not possible to comment on accuracy. The CCRMP reference material PD-1 was included with the samples but this is not certified for sulphate. However the given value in the approximate chemical composition of 4.27% sulphate sulphur agrees well with the average measured value of 4.12% sulphate sulphur. This is well above the concentration seen in the samples. Shewhart plots were created using secondary reference materials to assess precision of the data (Figure 8).

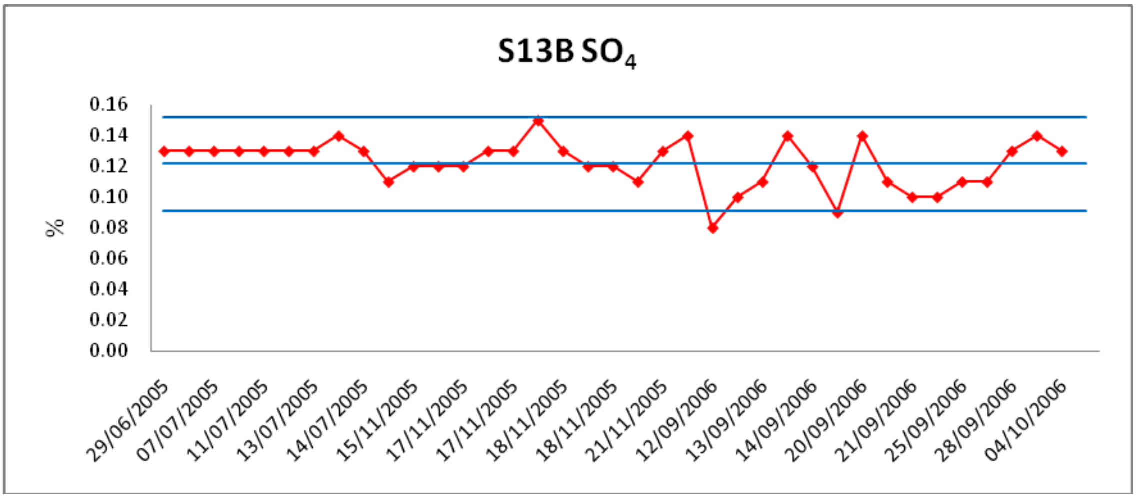


Figure 8 Shewhart plot showing measured acid soluble sulphate data in S13B.

The data indicates that precision remains good throughout the analytical time period however it is clear that the precision became more variable during the 2006 analytical period. For a short period in November 2005 the detection limit was raised by from 0.01 to 0.05%. This higher value is the one normally quoted by the analytical laboratory, although several of the reference materials show good precision down to at least 0.02%.

4.4.2 Recommendations

Without values for Certified Reference Materials it has not been possible to assess the accuracy of the analytical data. However, the Shewhart charts indicate that the data quality is consistent and should therefore be useful.

5 Map production

The regional scale data sets cover all of Northern Ireland aside from the major urban areas of Belfast Metropolitan Area and Bangor. Data sets are provided separately for urban areas which were sampled at a greater density: Belfast, Bangor, Carrickfergus, Carryduff, Castlereagh, Greenisland, Holywood, Lisburn, Newtonabbey and Londonderry. These are shown in Figure 9. The quality assessments described above apply to both regional and urban data.

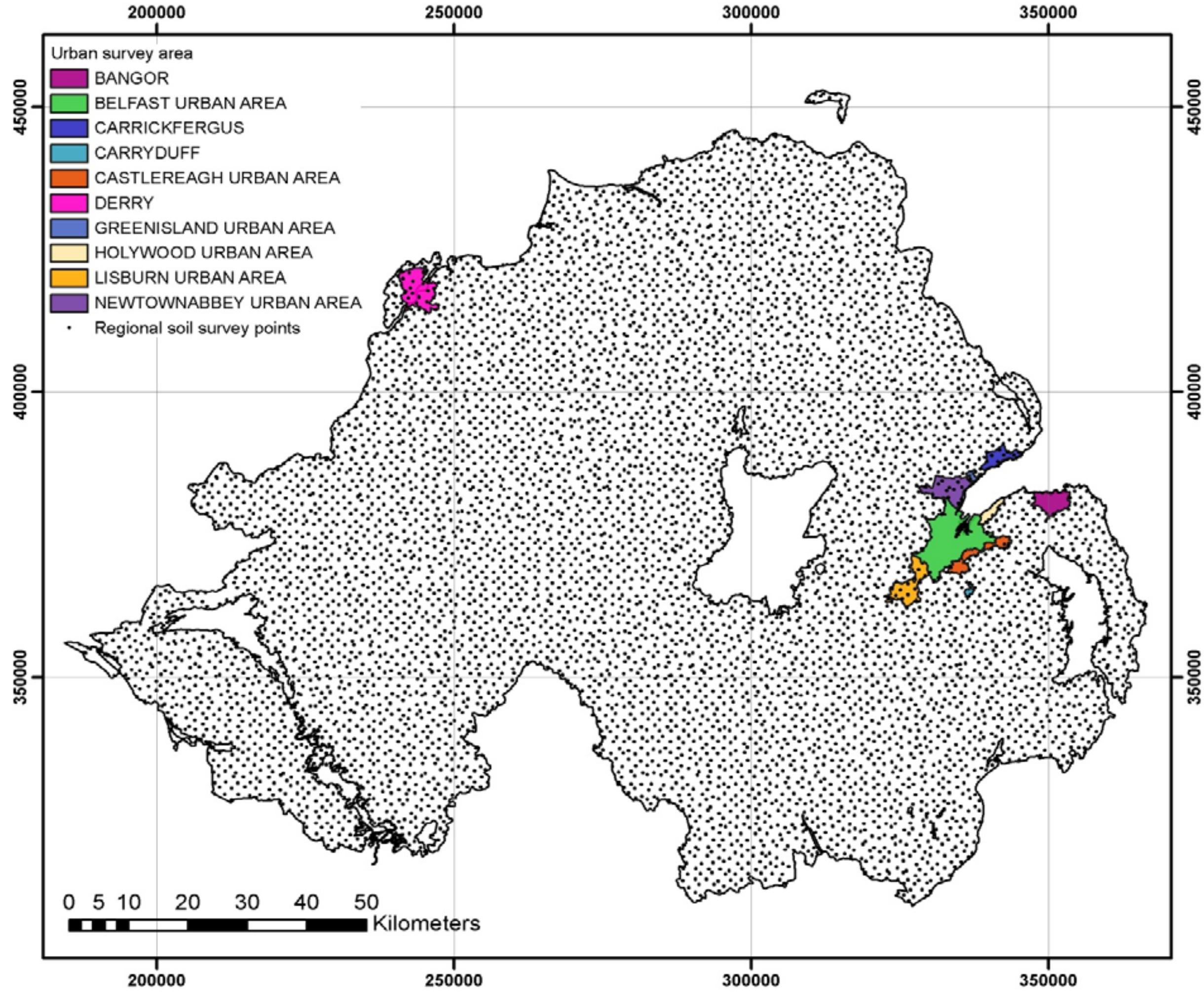


Figure 9 Distribution of Tellus regional survey sample points and the location of urban survey areas

5.1 DATA PREPARATION

Prior to map production correction factors were applied to the data, where appropriate, and all values below detection limit were given a quantitative value of half detection limit for the purpose of statistical investigation and gridding. This method is based on the knowledge that any value below detection limit will lie between zero and detection limit, this is consistent with the traditional method used in older soil and stream sediment data (Johnson et al. 2005). It is important to note however that discernable trends can sometimes be seen in data reported below detection limit and in some cases it may be of interest to refer back to the original lab reported values. The use of data below the detection limited is discussed by AMC (2001) A summary of correction factors can be observed in Table 8.

Table 8 Correction factors applied to data for data preparation and map production

Aqua regia digest ICP analysis of Tellus 'A' soil	
Cs	[Cs] (Analysed after June 2006) × 1.238
Aqua regia digest ICP analysis of Tellus 'S' soil	
Cs	[Cs] (analysed after September 2006) × 1.296
Mixed acid 'near total' digest ICP analysis for Tellus 'S' soil	
Al	([Al] × 1.1235) – 0.4732
Ca	([Ca] × 1.0527) – 0.0041
Co	([Co] × 1.0867) – 0.1952
Cr	([Cr] × 1.5095) – 10.73
Cu	([Cu] × 0.9653) + 1.5439
Fe	([Fe] × 1.0484) – 0.0389
Mg	([Mg] × 1.0418) + 0.0084
Sr	([Sr] × 1.0168) – 6.5825

5.2 IMAGE PRODUCTION AND PRESENTATION

5.2.1 Regional geochemical maps

Regional scale geochemical maps were produced using ArcGIS™ v.9.3 developed by Environmental Systems Research Institute, Inc. (ESRI). Grids were produced using Spatial Analyst using the same methods as those employed by the G-BASE program. Data were interpolated using Inverse Distance Weighting (IDW) with power 2, a grid cell size of 250m and a fixed search radius of 1500m. A standard G-BASE colour scheme was used to plot the percentiles.

Data were imported into ArcGIS™ v9.3 and a geochemical database created using the Geosoft module 'Geochemistry for ArcGIS v1.0'. This allowed the generation of percentiles calculated individually for each element. A standard percentile suite was used for regional data including; 1st, 2nd, 5th, 10th, 15th, 20th, 25th, 40th, 50th, 60th, 75th, 85th, 90th, 95th, 98th, 99th and 100th percentiles. This classification was based on the G-BASE scheme however additional percentiles were used in keeping with the previous Tellus geochemistry data preparation process. The G-Base classification includes 5th, 10th, 15th, 25th, 50th, 75th, 90th, 95th, 99th, 100th percentiles. The use of additional percentiles allows for a more detailed presentation of concentration distribution. On occasion the spread of data was not sufficient to generate 17 percentile classes or lower percentile classes fell below detection limit. Adjustments were made accordingly to best represent the data and no percentile classes containing data below detection limit are displayed.

The regional scale data sets provide coverage for the entire of Northern Ireland aside from the major urban areas of Belfast and Bangor which are greyed out.

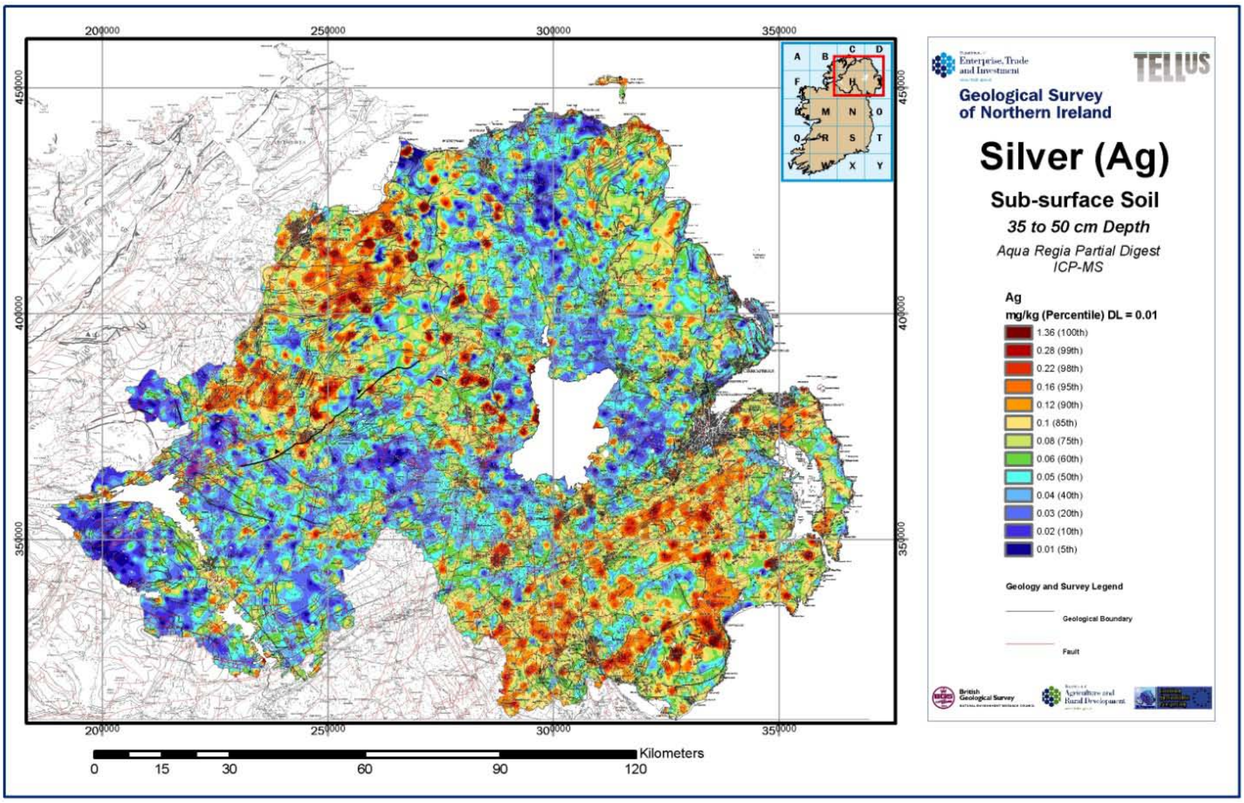


Figure 10 Example regional scale map of silver content in sub surface soil

Interpolated maps allow for identification of regional scale geochemical trends. Several additional features were added to the display including fault boundaries, geological boundaries, lakes, urban areas and 1:250K OSNI topographical information. Such information allows for initial identification of possible anthropogenic, structural or geological controls on the soil geochemistry of the Northern Ireland region.

5.2.2 **Urban geochemical maps**

Urban soils often display localised variations in geochemical composition as a result of anthropogenic activity. Of most importance is the identification of enhanced levels of potentially harmful elements in areas with residential or allotment land uses. It is important however to take into consideration the background level concentration of these elements as certain geological formations can be naturally elevated in lead or arsenic for example. One method of addressing this issue could be the classification of the urban soil samples in terms of underlying geology and the subsequent normalisation of the urban geochemical values based on the average value observed in the surrounding rural area. Additionally the urban data sets can be presented in terms of acceptable thresholds provided by the Environment Agency to highlight hot spots of serious environmental concern. A detailed overview of the urban geochemical baseline is essential for many activities, such as land use planning, as certain elements are toxic at high levels to plants and animals. Additional variables such as pH and salinity should also be taken into account as these control bioavailability. These urban data can be used for site specific investigation such as a contaminated land assessment of a residential development site. Interpolation of data therefore is not a suitable technique for map presentation as extrapolation between sample points could give misleading information. The extent of an elevated arsenic anomaly may be exaggerated for example.

Proportional symbols are used to display data for each individual data point. This allows for visual representation of actual soil geochemistry at each sample location. Maps were produced using ArcGIS v.9.3. For the urban maps the standard G-Base classification including 5th, 10th, 15th, 25th, 50th, 75th, 90th, 95th, 99th, 100th percentiles appears more appropriate in best displaying the data at this local scale, Figure 11. Alternatively data can be displayed in terms of Soil

Guideline Values to provide a useful visual context essential in the study of contaminated land and potentially harmful elements. An example for the Belfast Metropolitan Area is shown in **Figure 12**. The urban sampling survey and results are described by Nice (2010).

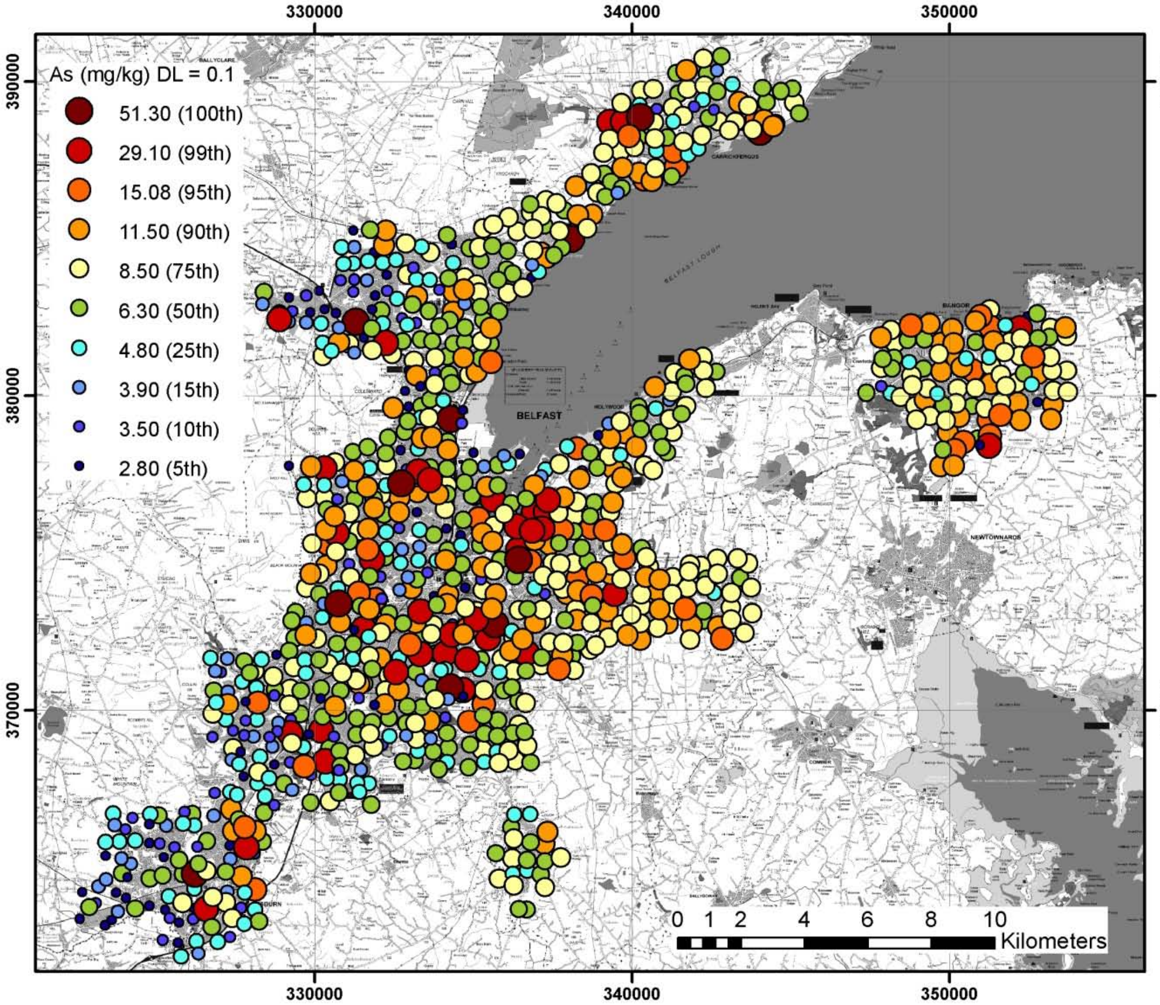


Figure 11 Urban soils map for arsenic levels in Tellus 'A' soil for the Belfast Metropolitan Area displayed using proportional symbols.

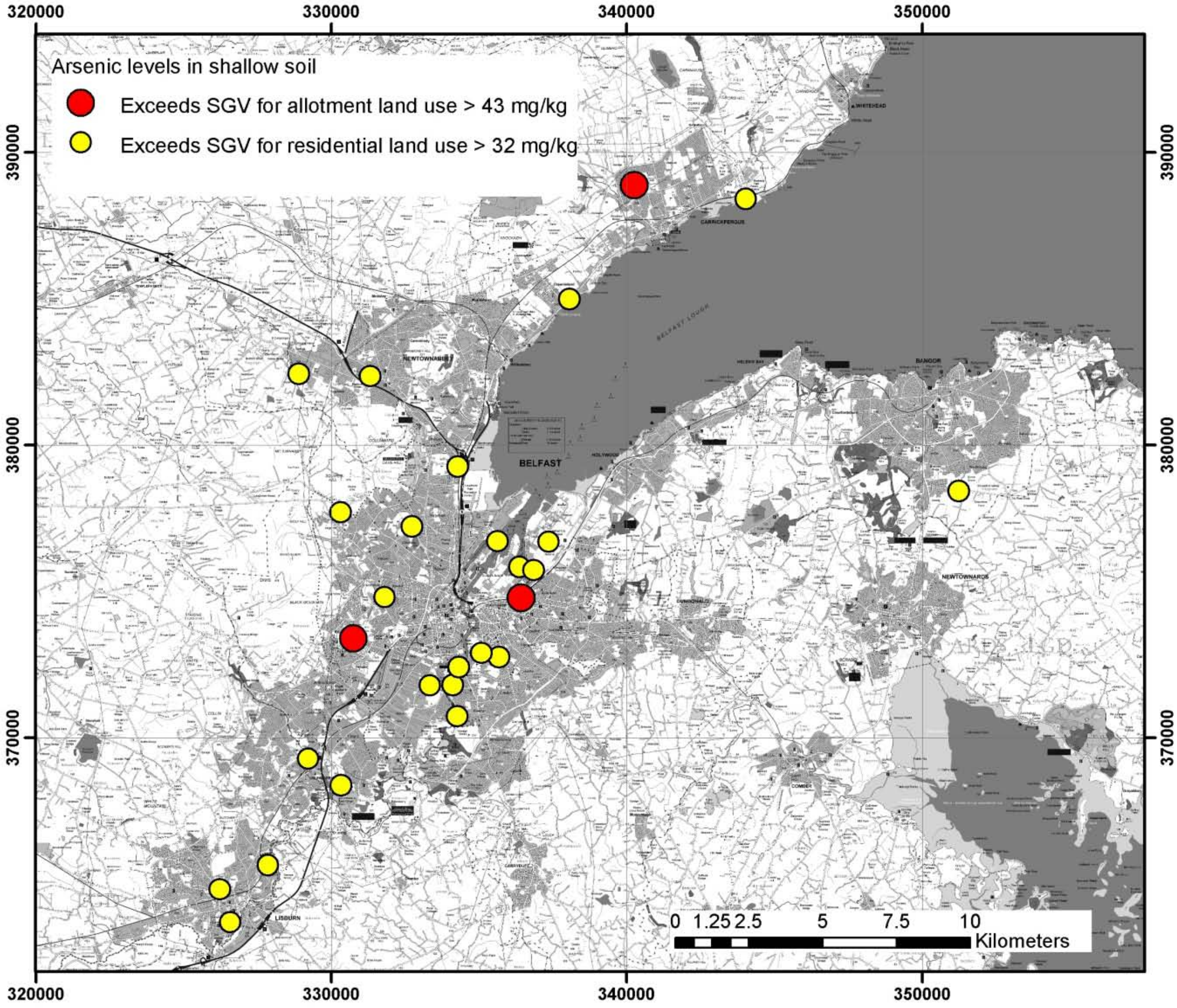


Figure 12 Urban soil map for the Belfast Metropolitan Area depicting sample points where arsenic concentration exceeds guideline values for either residential or allotment land use as specified by the Environment Agency 2009.

6 Comparisons between regional datasets

The following section compares the various analytical data sets for selected elements of the Tellus regional soil survey.

Data sets include:

- *Aqua regia* partial digest ICP-MS/ICP-AES analysis of Tellus ‘S’ soil
- Mixed acid “*Near-total*” digest ICP-MS/ICP-AES analysis of Tellus ‘S’ soil
- XRFS analysis of Tellus ‘A’ soil
- *Aqua regia* partial digest ICP-AES/ICP-MS data of Tellus ‘A’ soil.

Comparisons between the surface and deep soils can be beneficial for many reasons including the vertical extent of anthropogenic shallow soil anomalies, or perhaps subsurface anomalies which are not expressed in the shallow soil. Interpretations can then be made based on geological, structural, geogenic, and anthropogenic factors.

The detection limits for each element by each technique are given at the top of the legend for each map. It is important to note that for some elements there is a significant difference between the detection limits for XRFS and ICP-AES/MS. As the maps are based on percentiles, these differences have an impact on the appearance of the maps for some elements.

6.1 ARSENIC

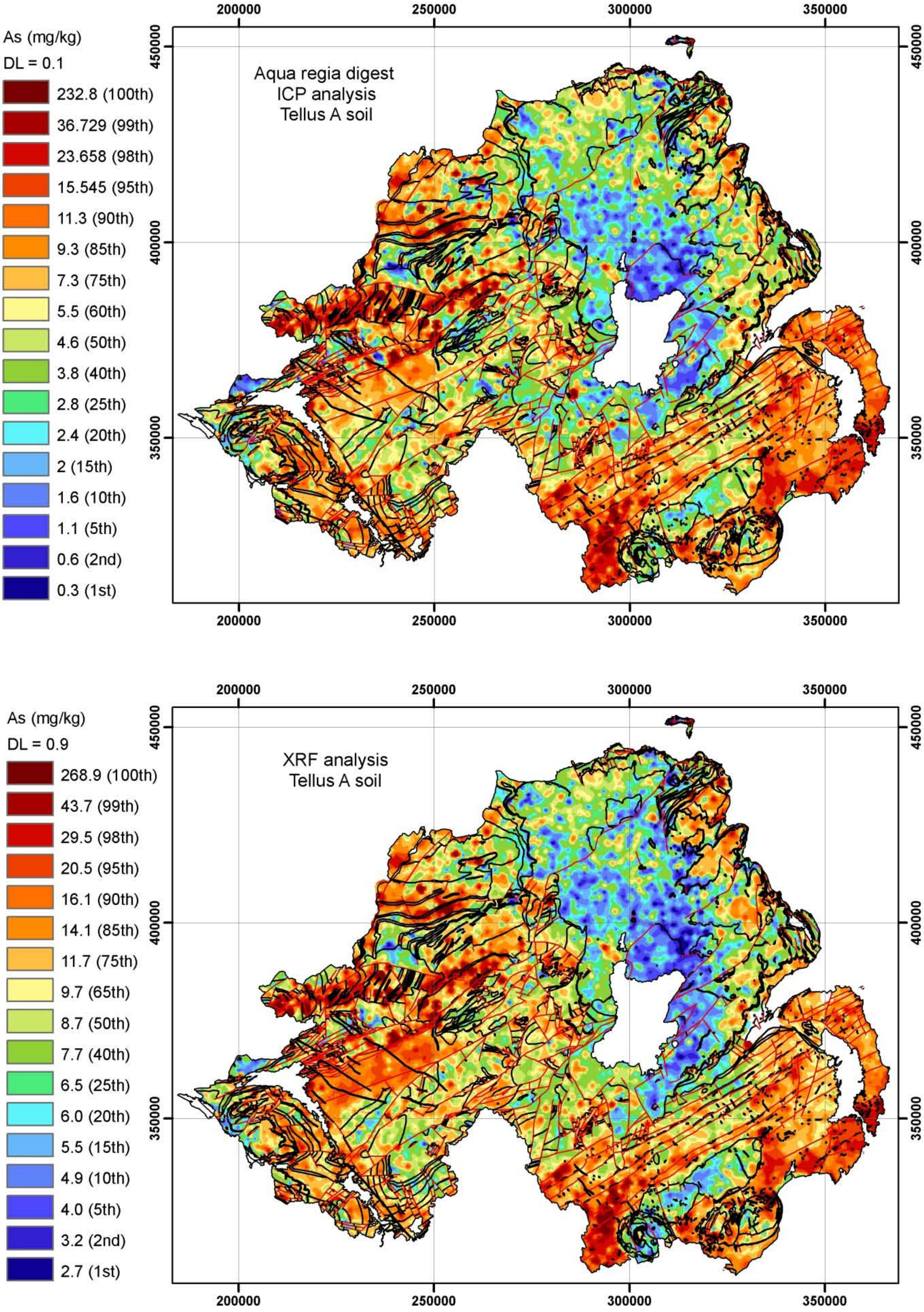


Figure 13 Comparison of Tellus 'A' soil regional data for As

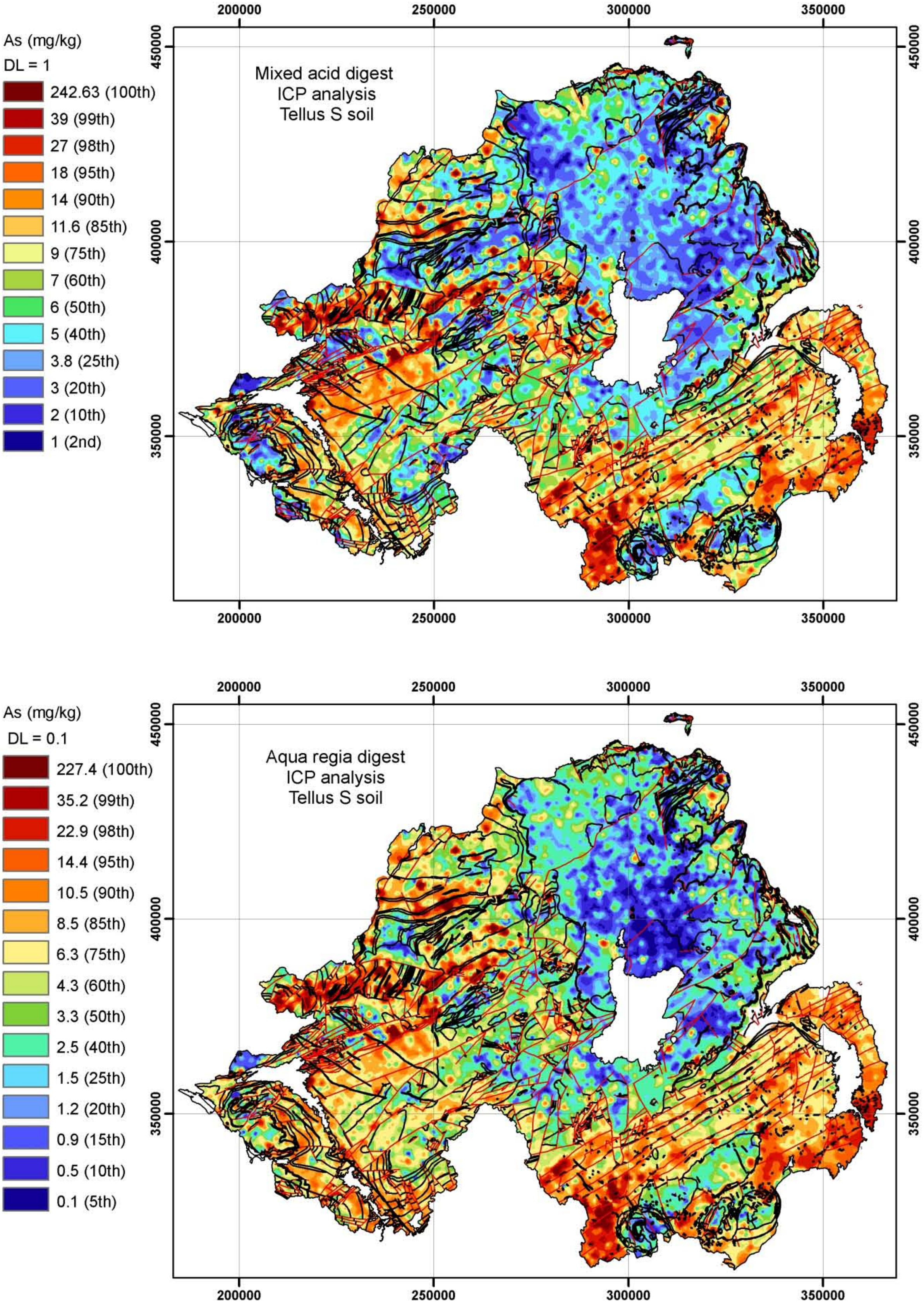


Figure 14 Comparison of Tellus ‘S’ soil regional data for As

6.2 CADMIUM

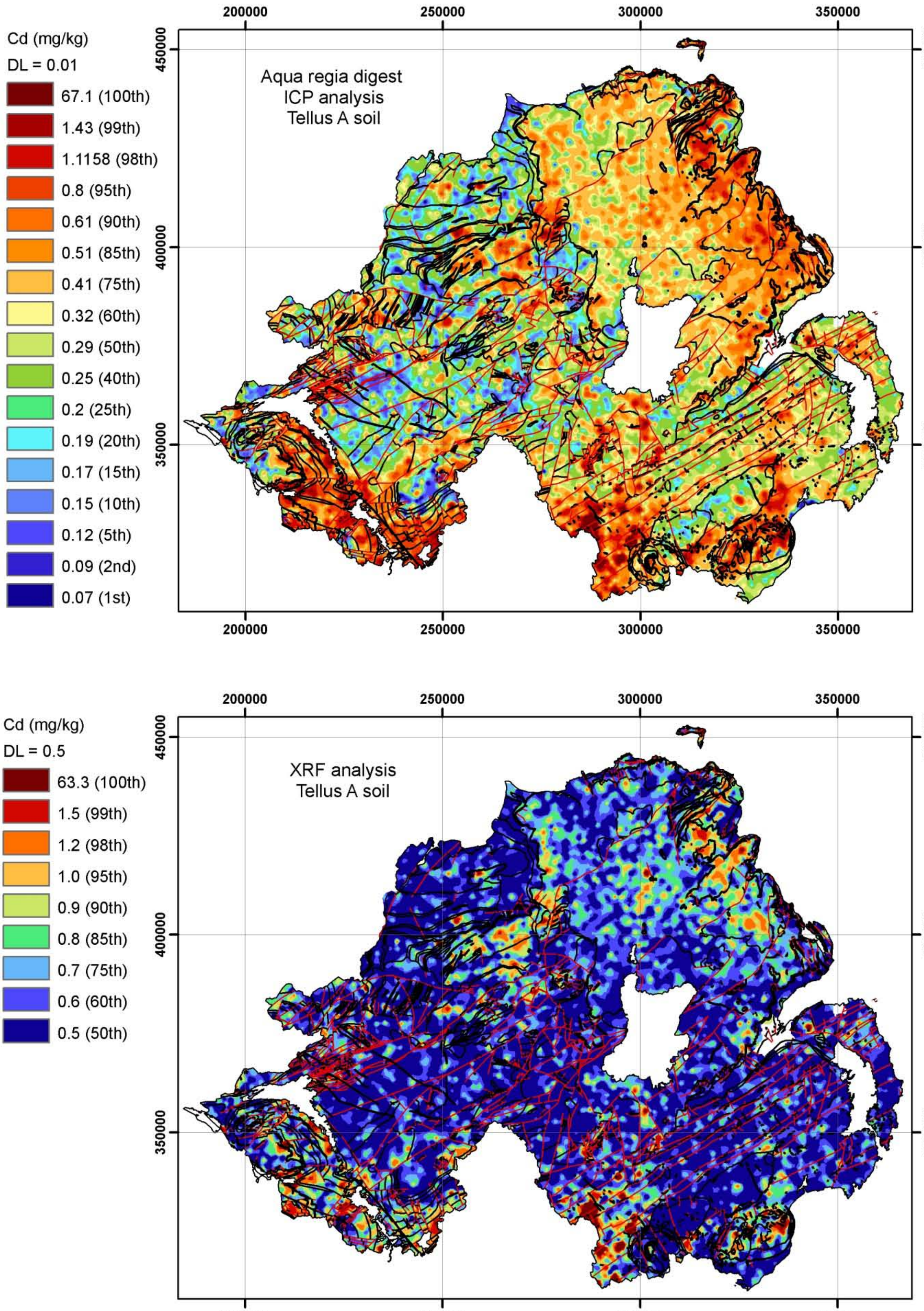


Figure 15 Comparison of Tellus 'A' soil regional data for Cd

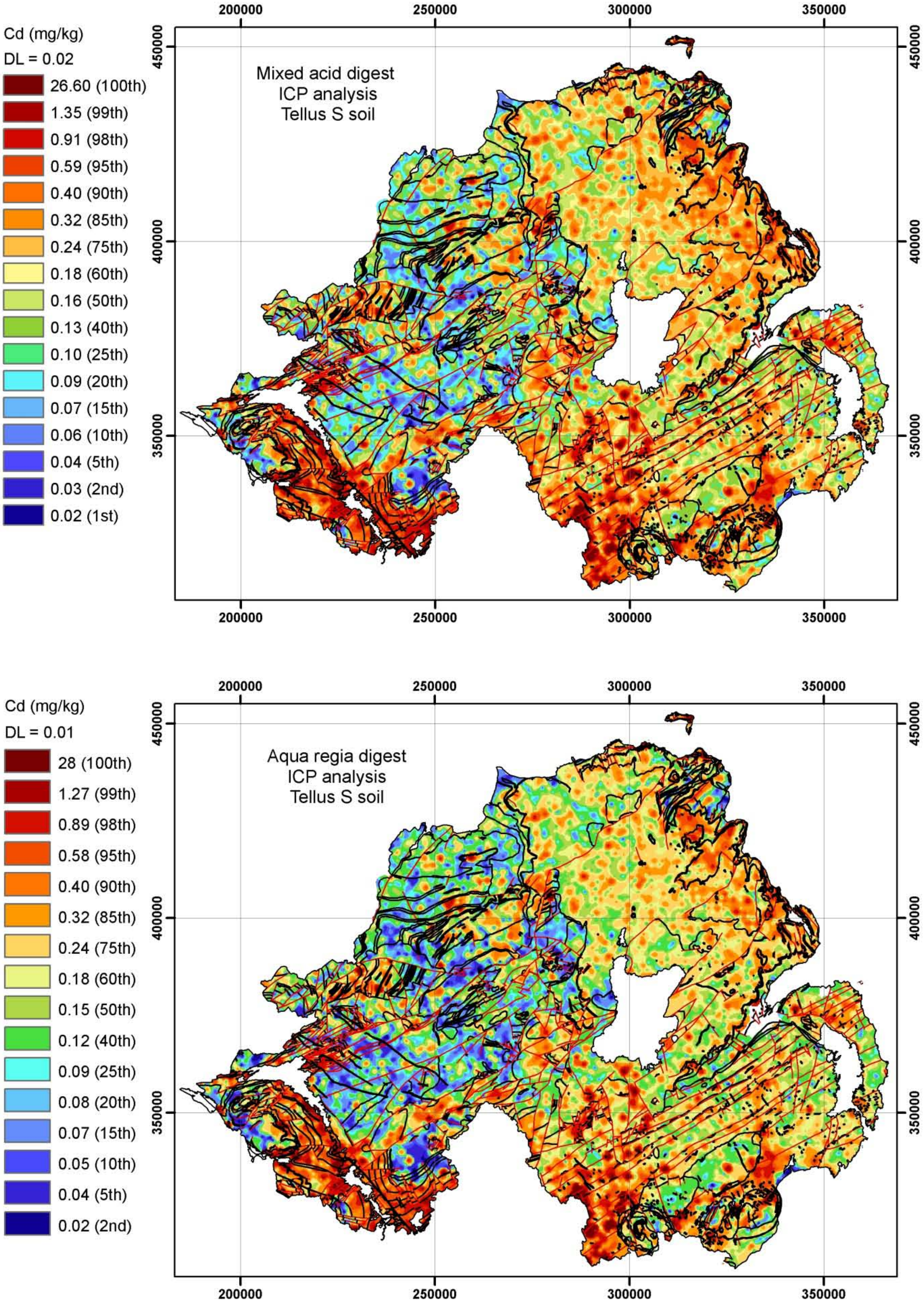


Figure 16 Comparison of Tellus 'S' soil regional data for Cd

6.3 CHROMIUM

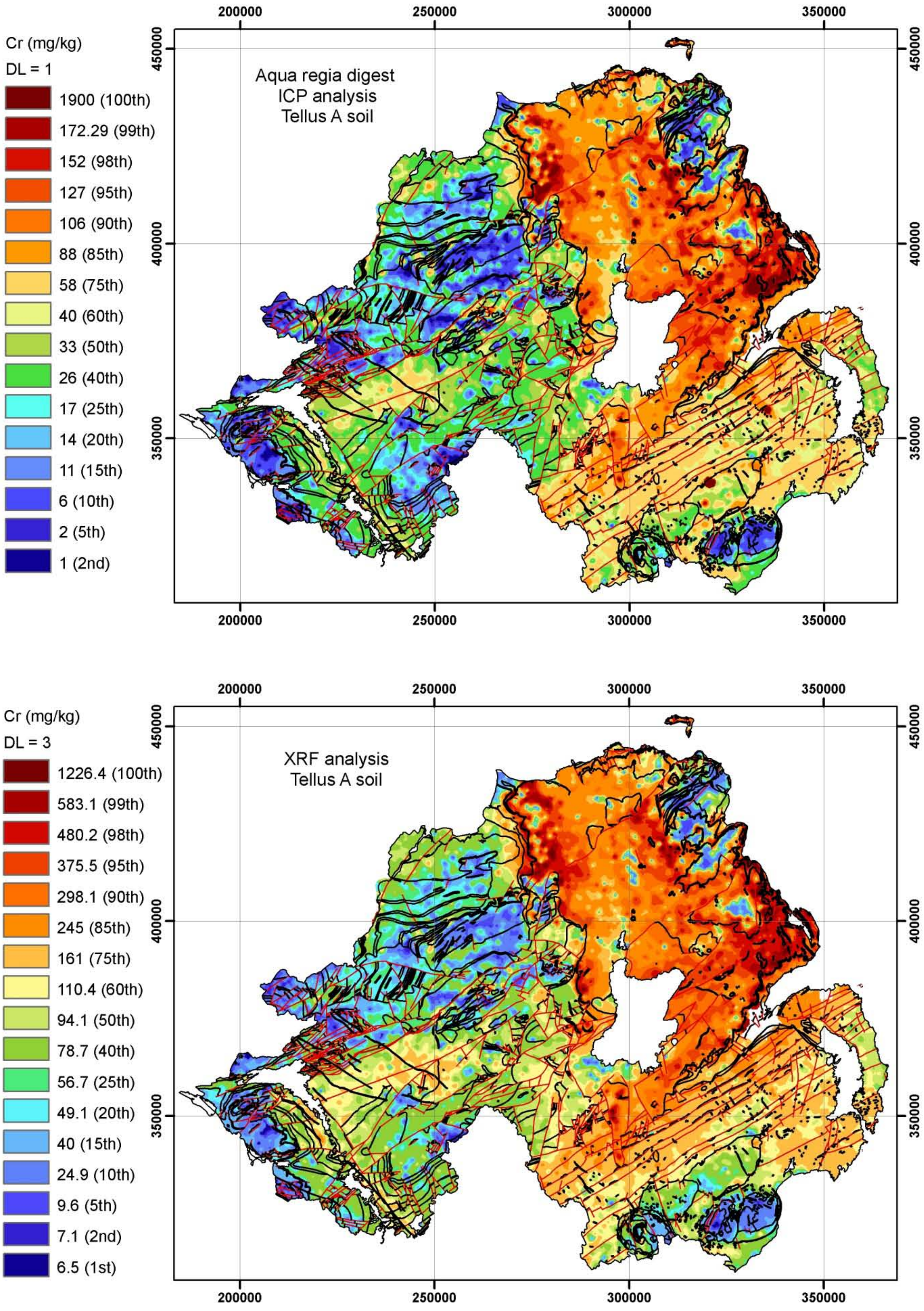
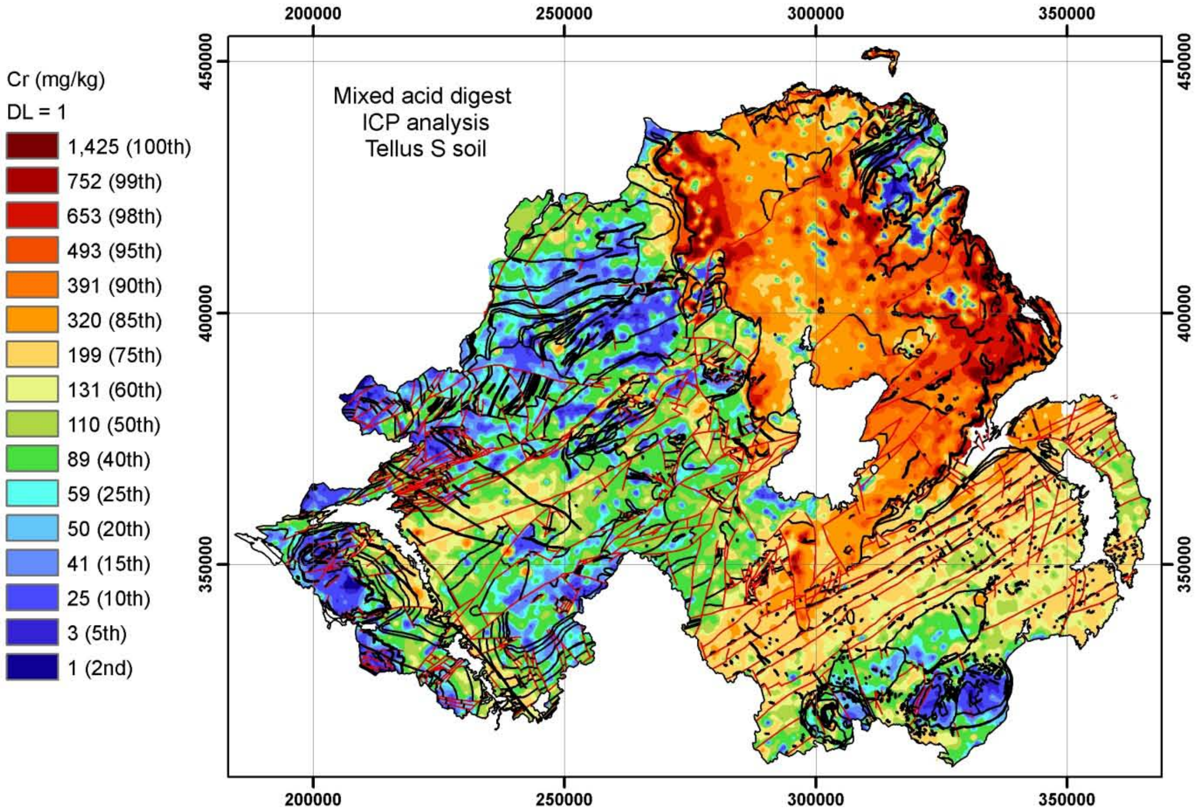
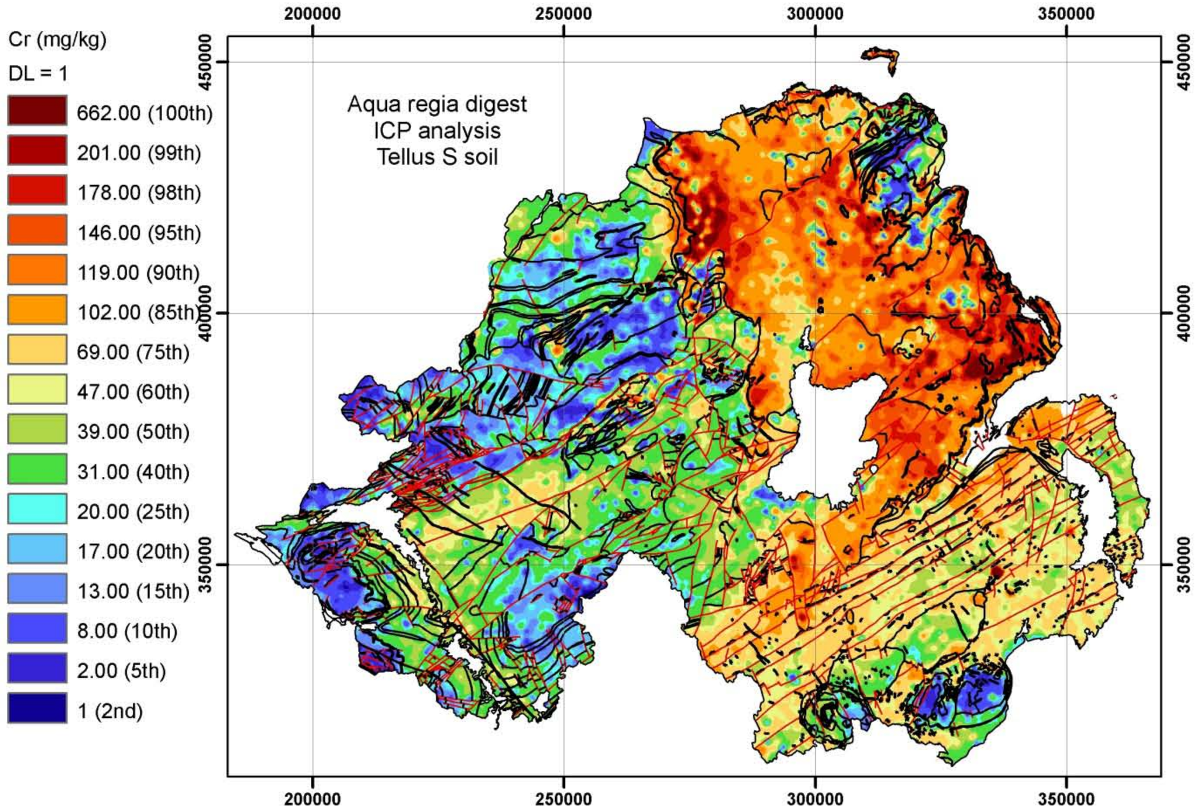


Figure 17 Comparison of Tellus 'A' soil regional data for Cr


Cr (mg/kg)
DL = 1
1,425 (100th)
752 (99th)
653 (98th)
493 (95th)
391 (90th)
320 (85th)
199 (75th)
131 (60th)
110 (50th)
89 (40th)
59 (25th)
50 (20th)
41 (15th)
25 (10th)
3 (5th)
1 (2nd)
Mixed acid digest
ICP analysis
Tellus S soil
200000
250000
300000
350000
450000
400000
350000


Cr (mg/kg)
DL = 1
662.00 (100th)
201.00 (99th)
178.00 (98th)
146.00 (95th)
119.00 (90th)
102.00 (85th)
69.00 (75th)
47.00 (60th)
39.00 (50th)
31.00 (40th)
20.00 (25th)
17.00 (20th)
13.00 (15th)
8.00 (10th)
2.00 (5th)
1 (2nd)
Aqua regia digest
ICP analysis
Tellus S soil
200000
250000
300000
350000
450000
400000
350000

6.4 COPPER

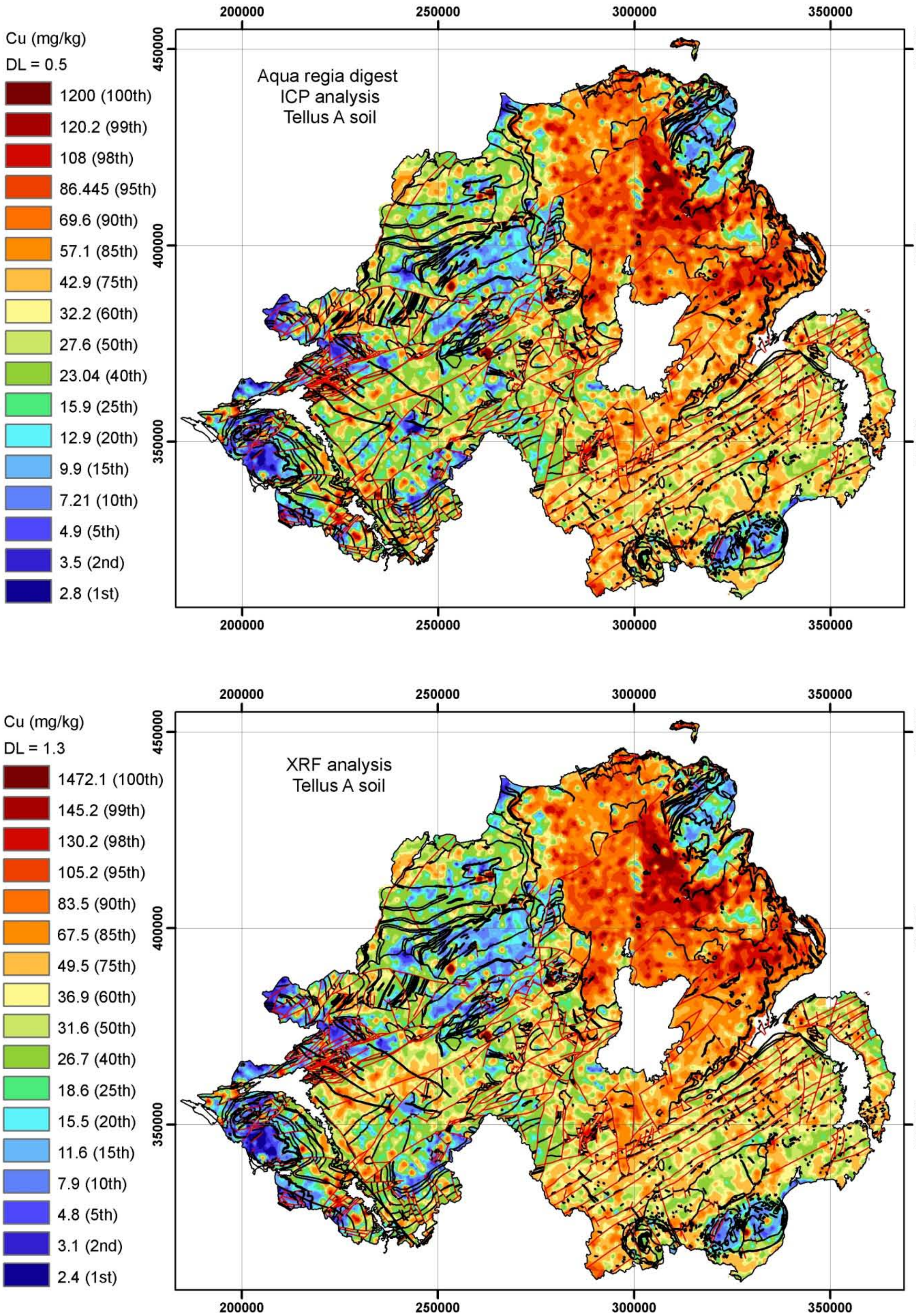


Figure 18 Comparison of Tellus 'A' soil regional data for Cu

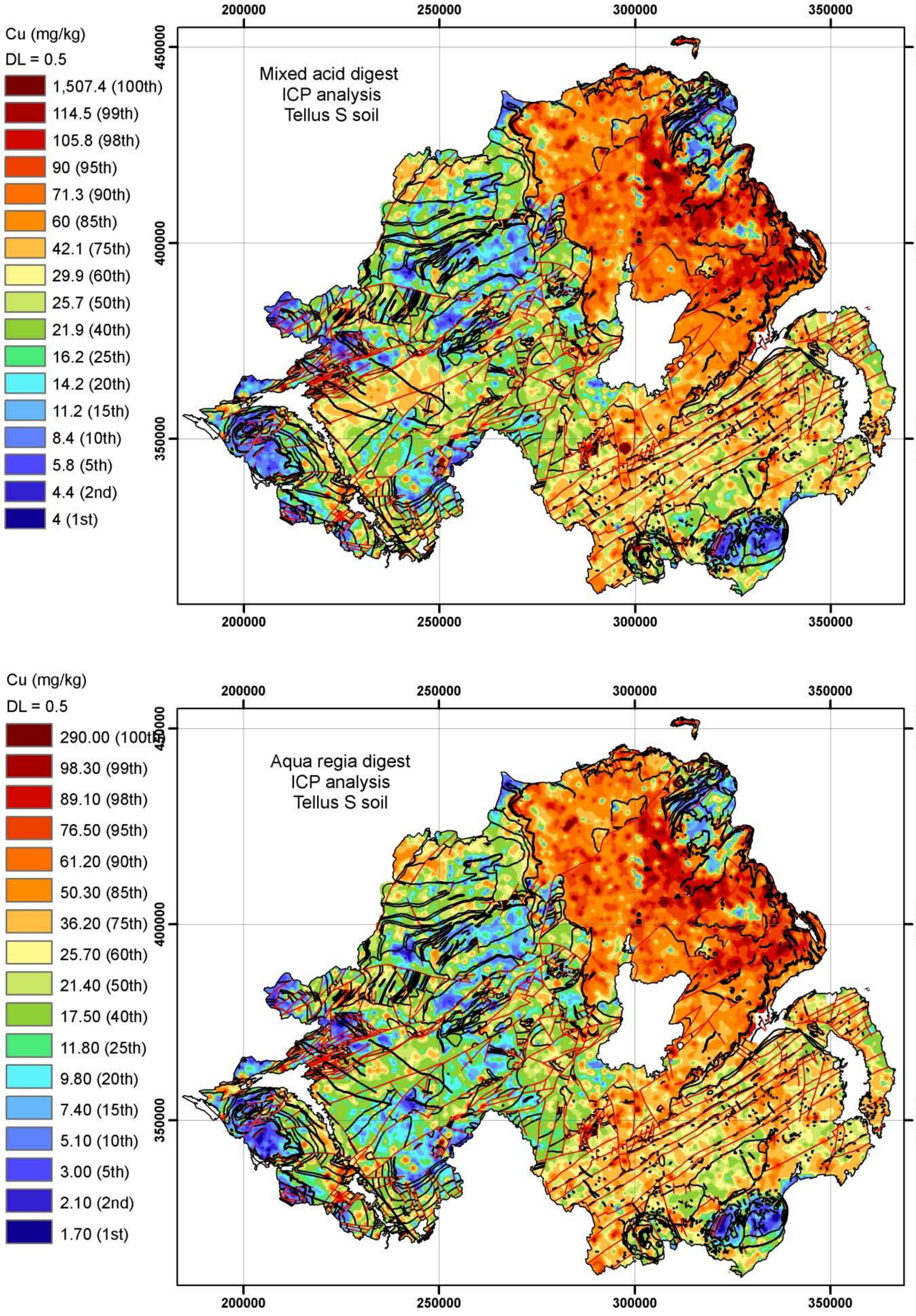


Figure 19 Comparison of Tellus 'S' soil regional data for Cu

6.5 MOLYBDENIUM

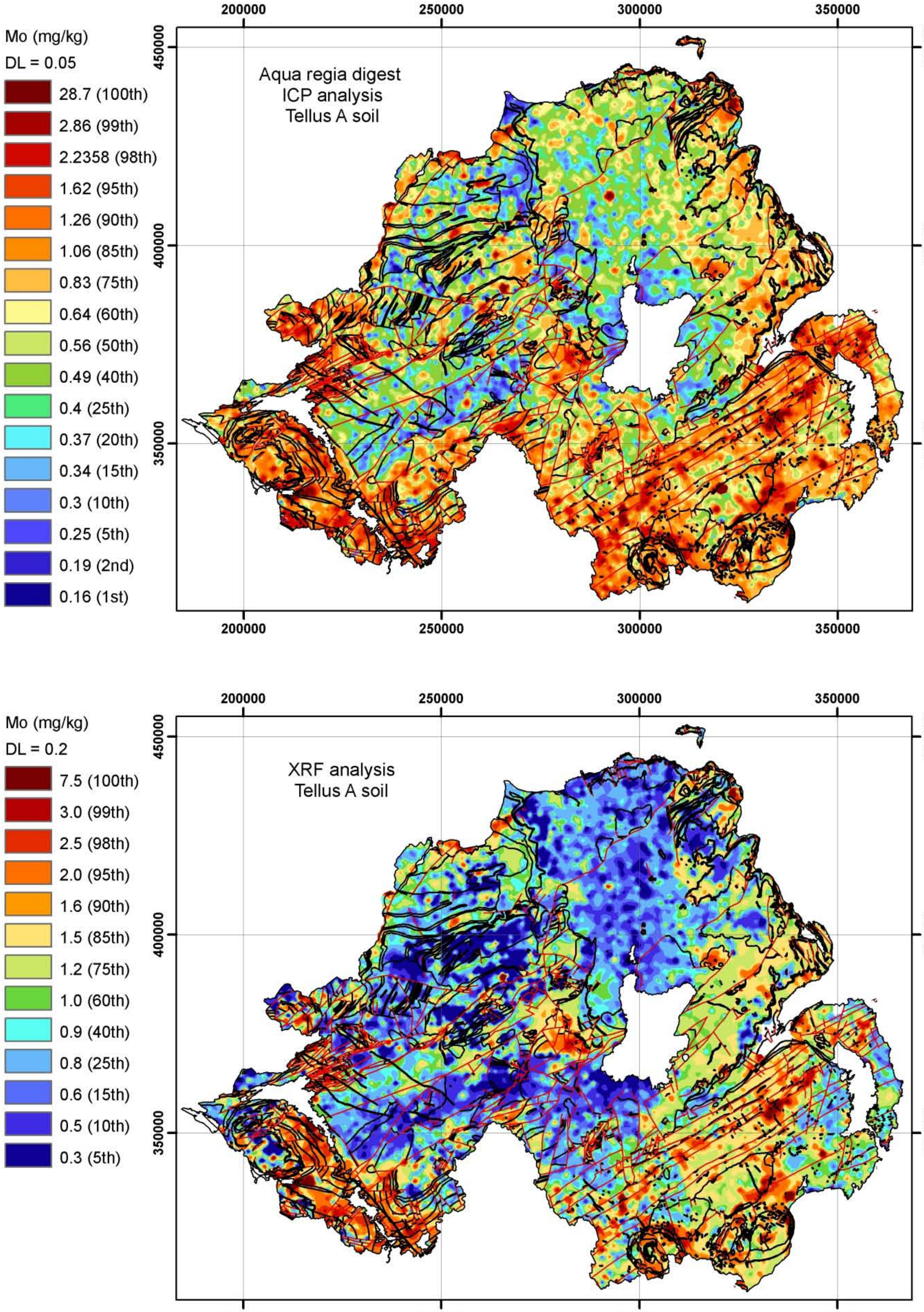
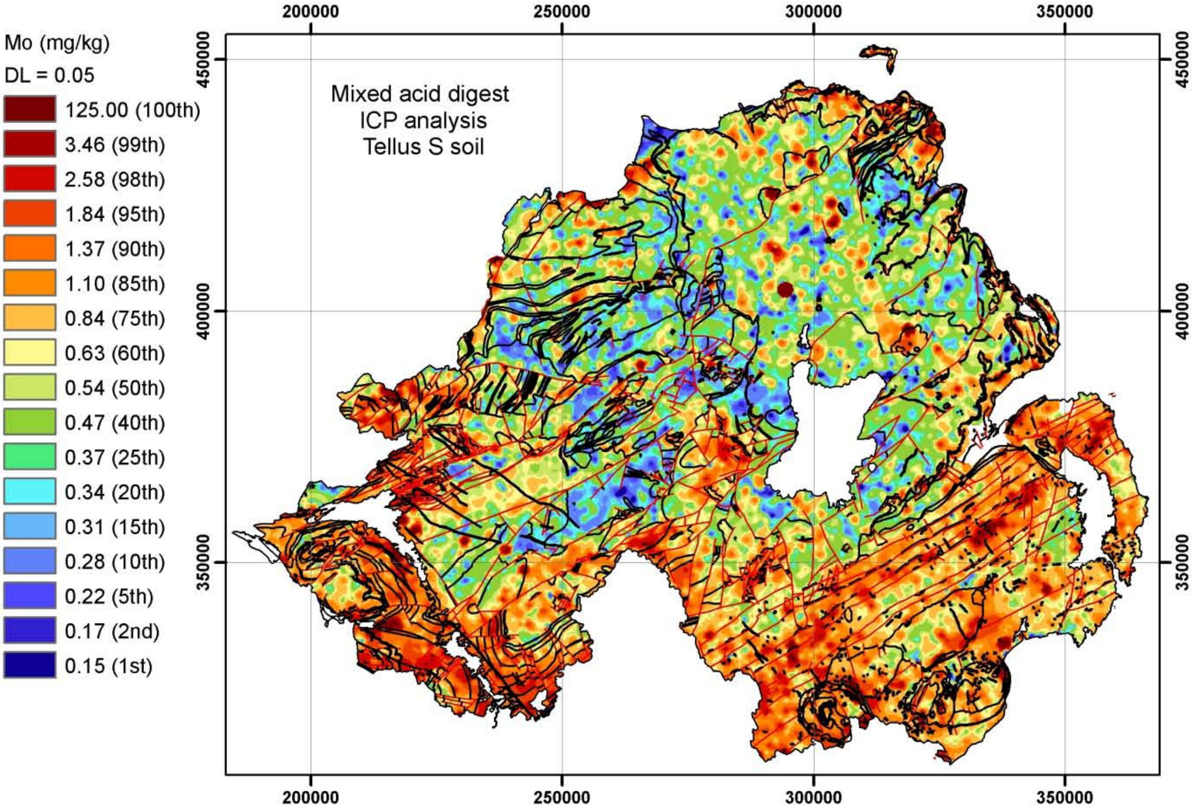


Figure 20 Comparison of Tellus ‘A’ soil regional data for Mo



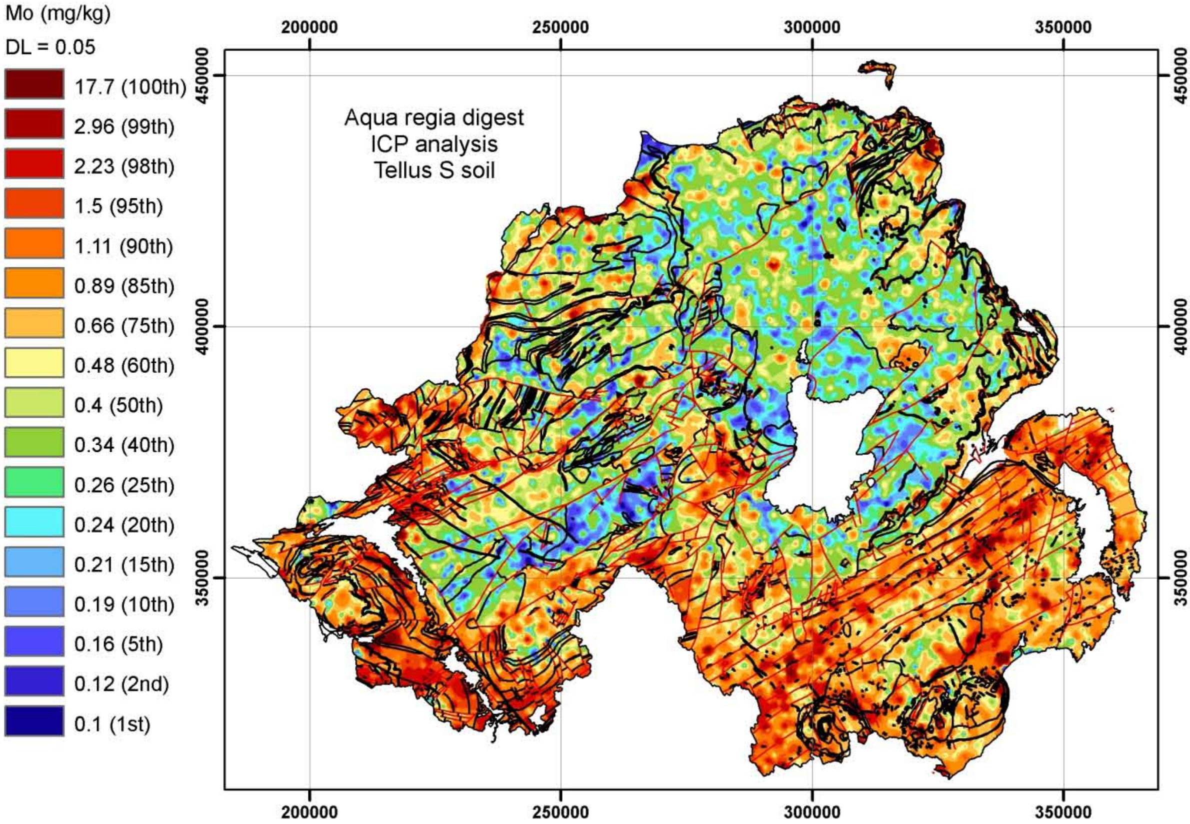


Figure 21 Comparison of Tellus 'S' soil regional data for Mo

6.6 NICKEL

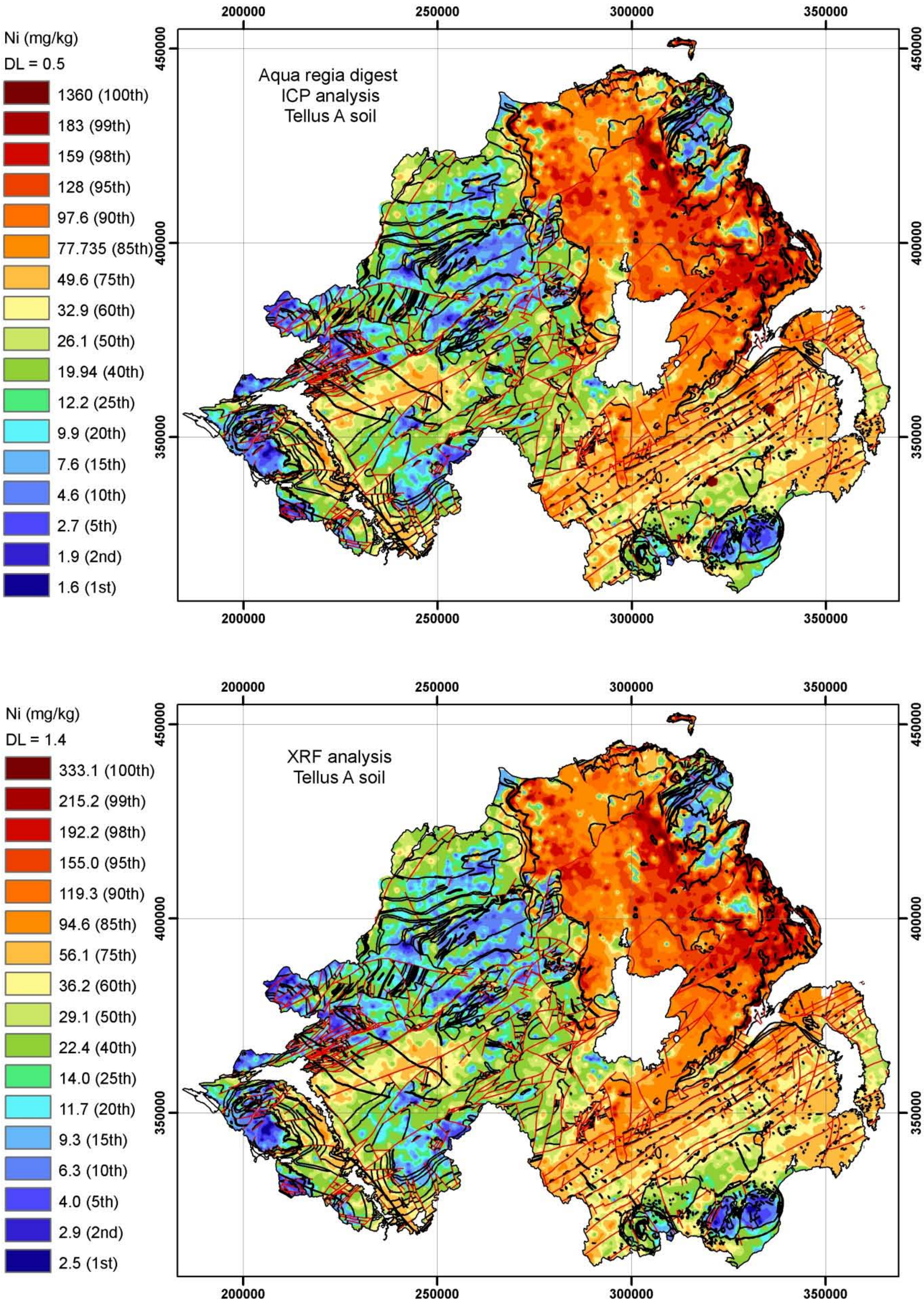


Figure 22 Comparison of Tellus 'A' soil regional data for Ni

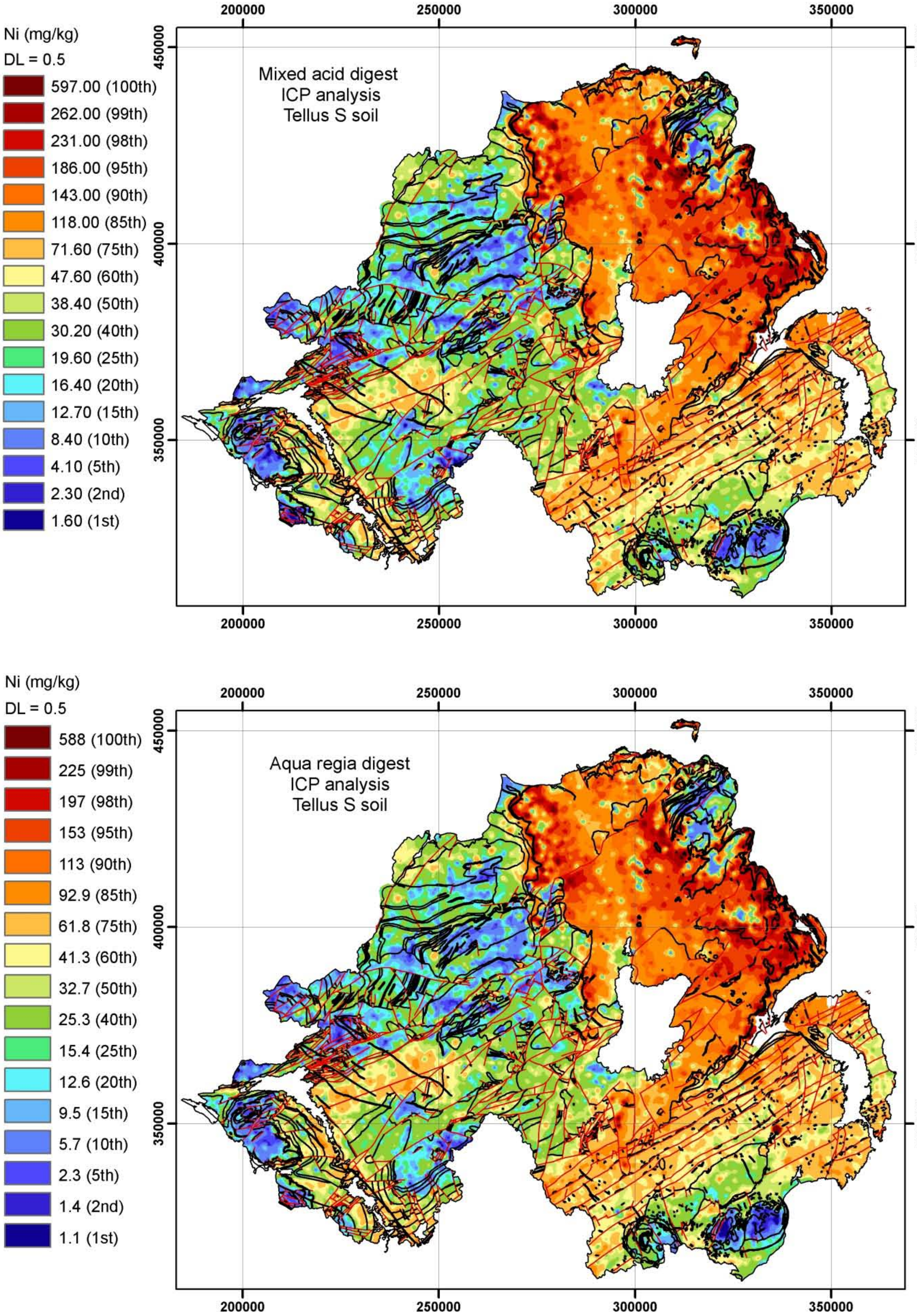


Figure 23 Comparison of Tellus 'S' soil regional data for Ni

6.7 LEAD

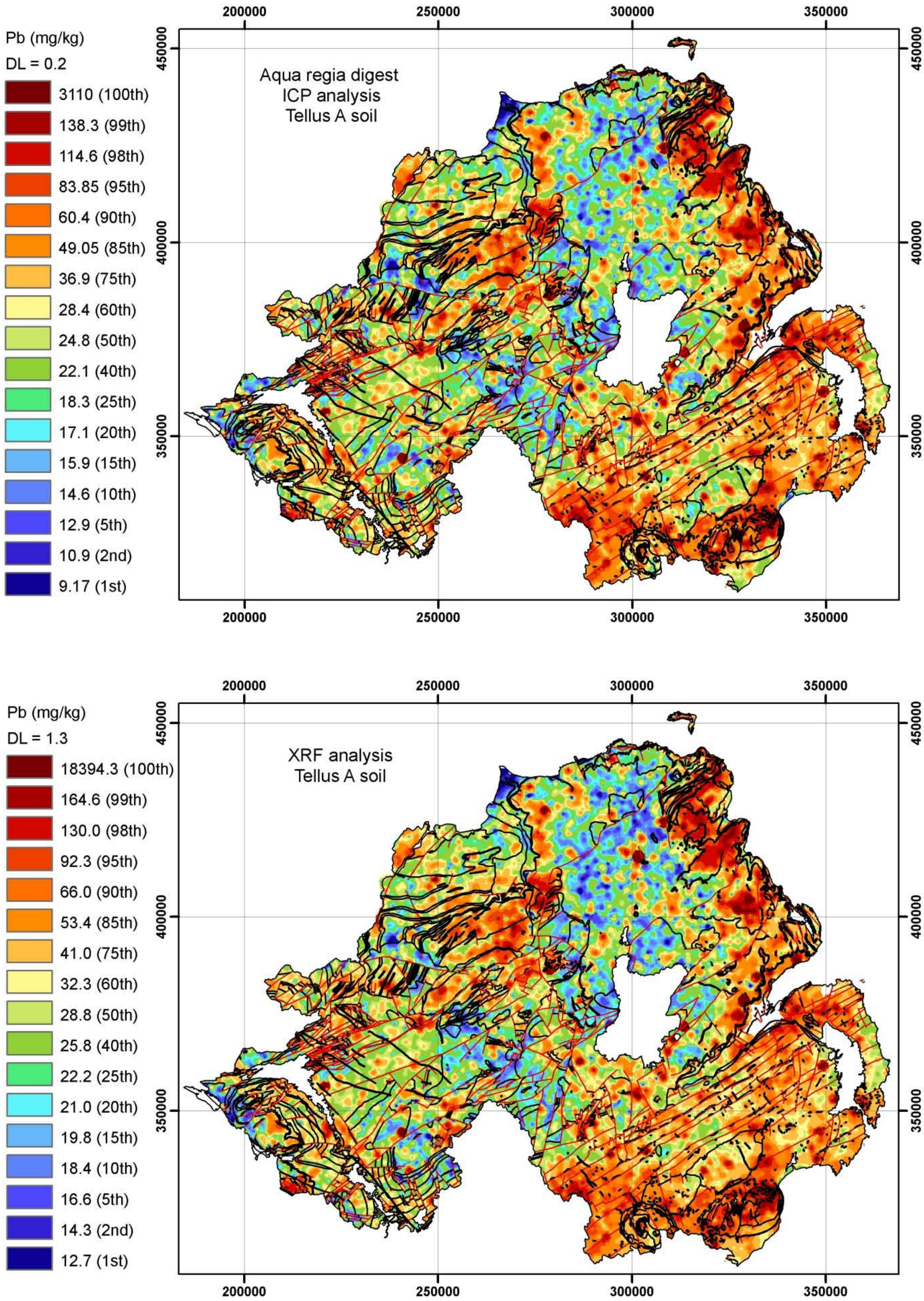


Figure 24 Comparison of Tellus 'A' soil regional data for Pb

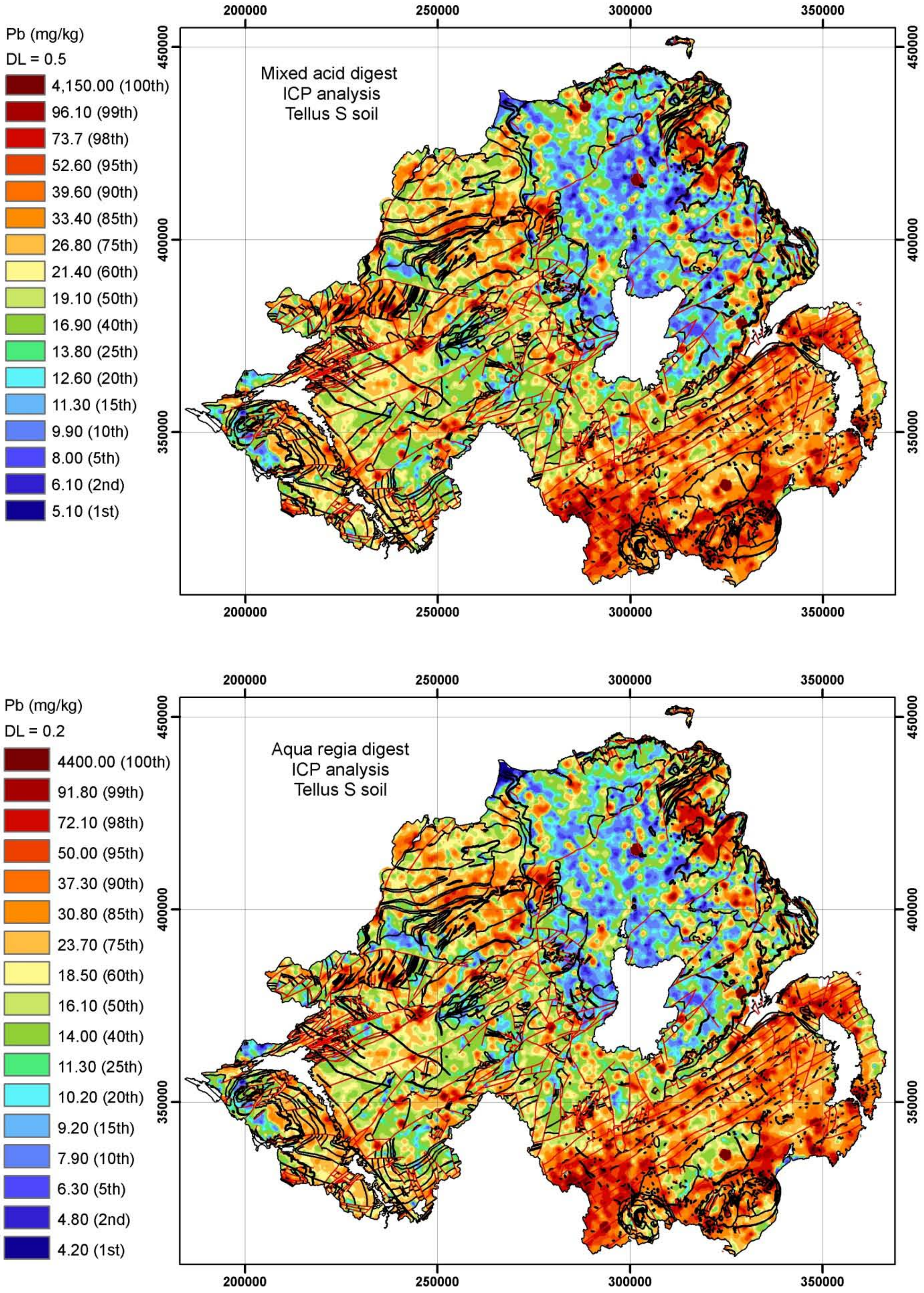


Figure 25 Comparison of Tellus 'S' soil regional data for Pb

6.8 ANTIMONY

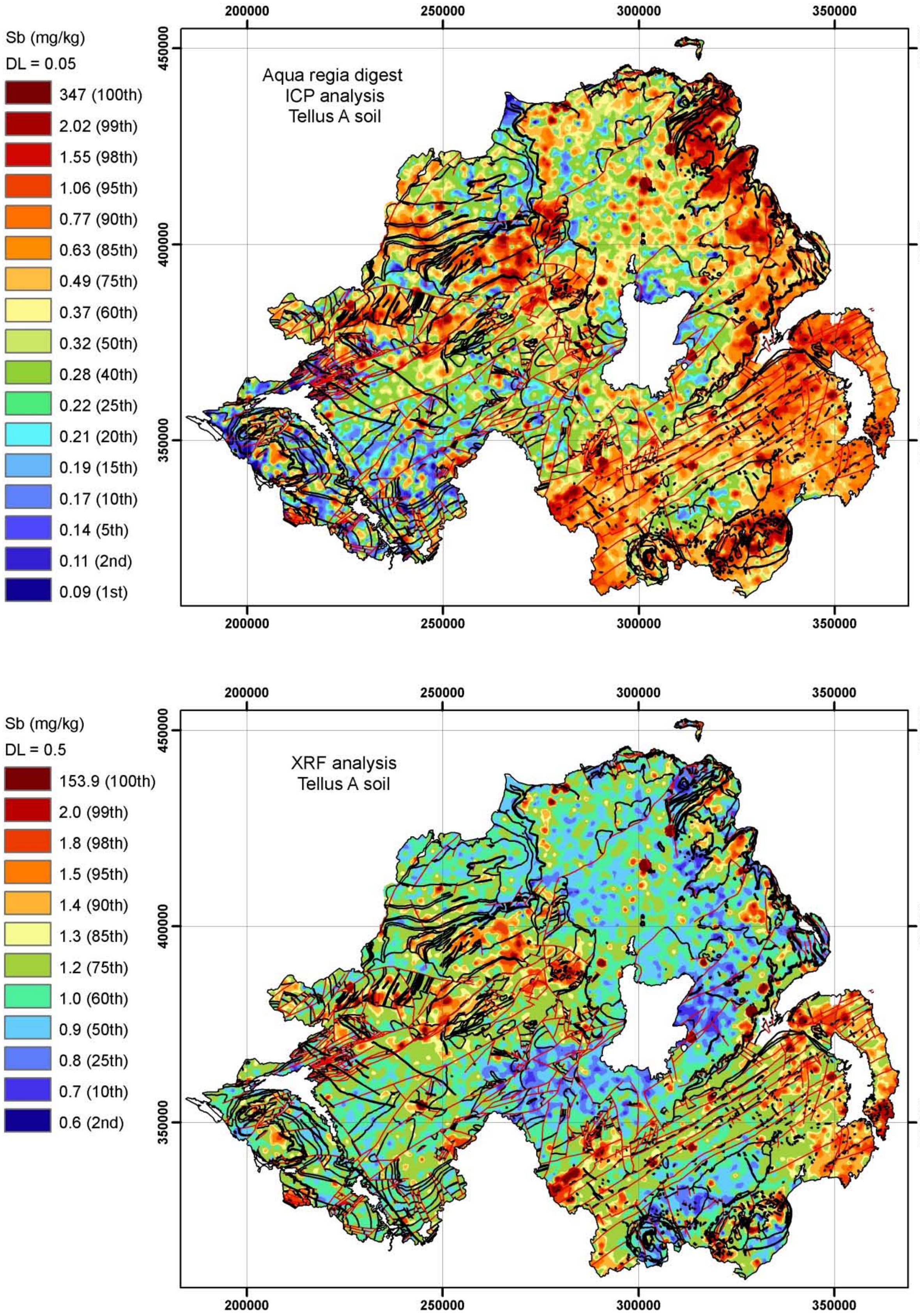


Figure 26 Comparison of Tellus ‘A’ soil regional data for Sb

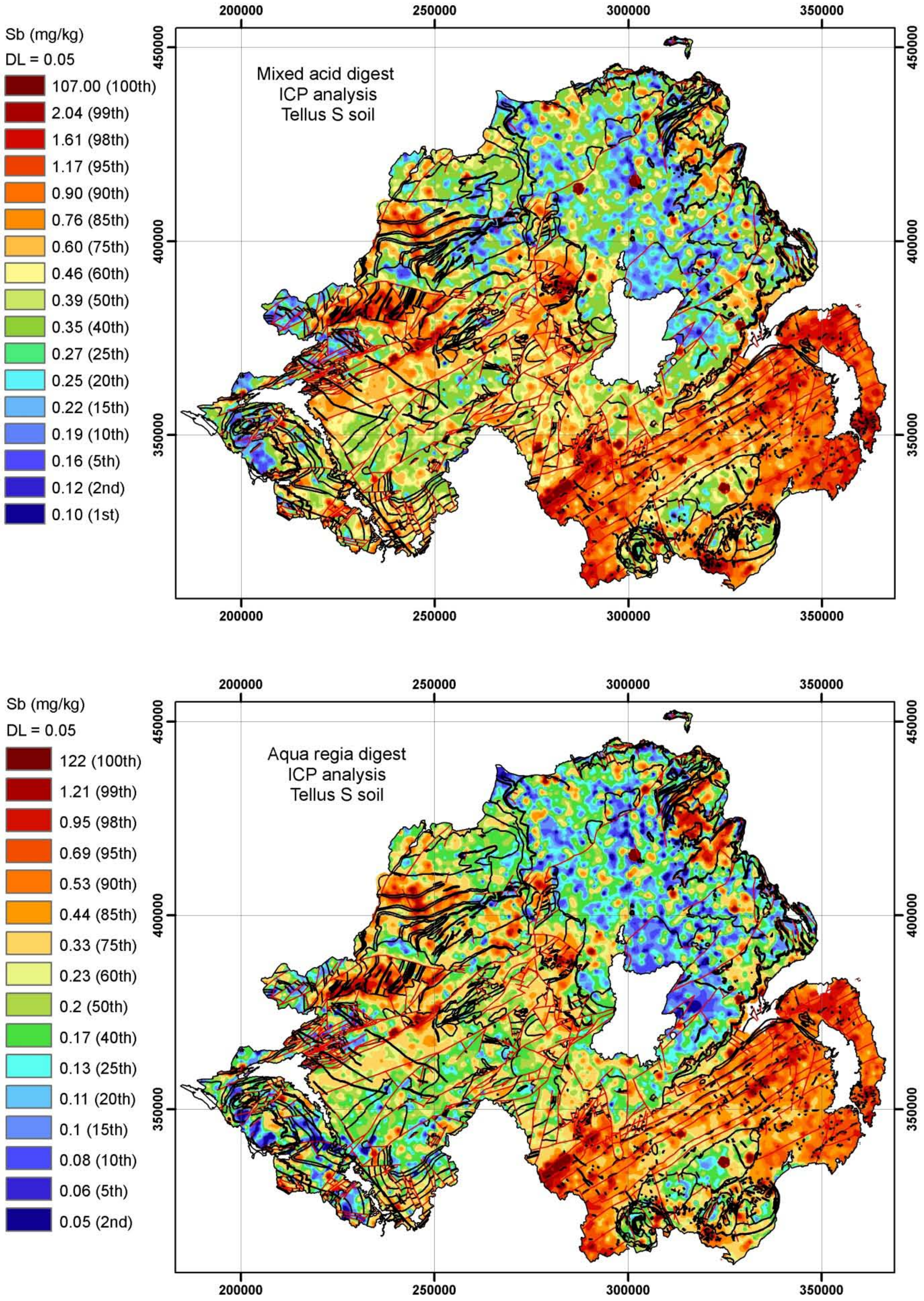


Figure 27 Comparison of Tellus 'S' soil regional data for Sb

6.9 SELENIUM

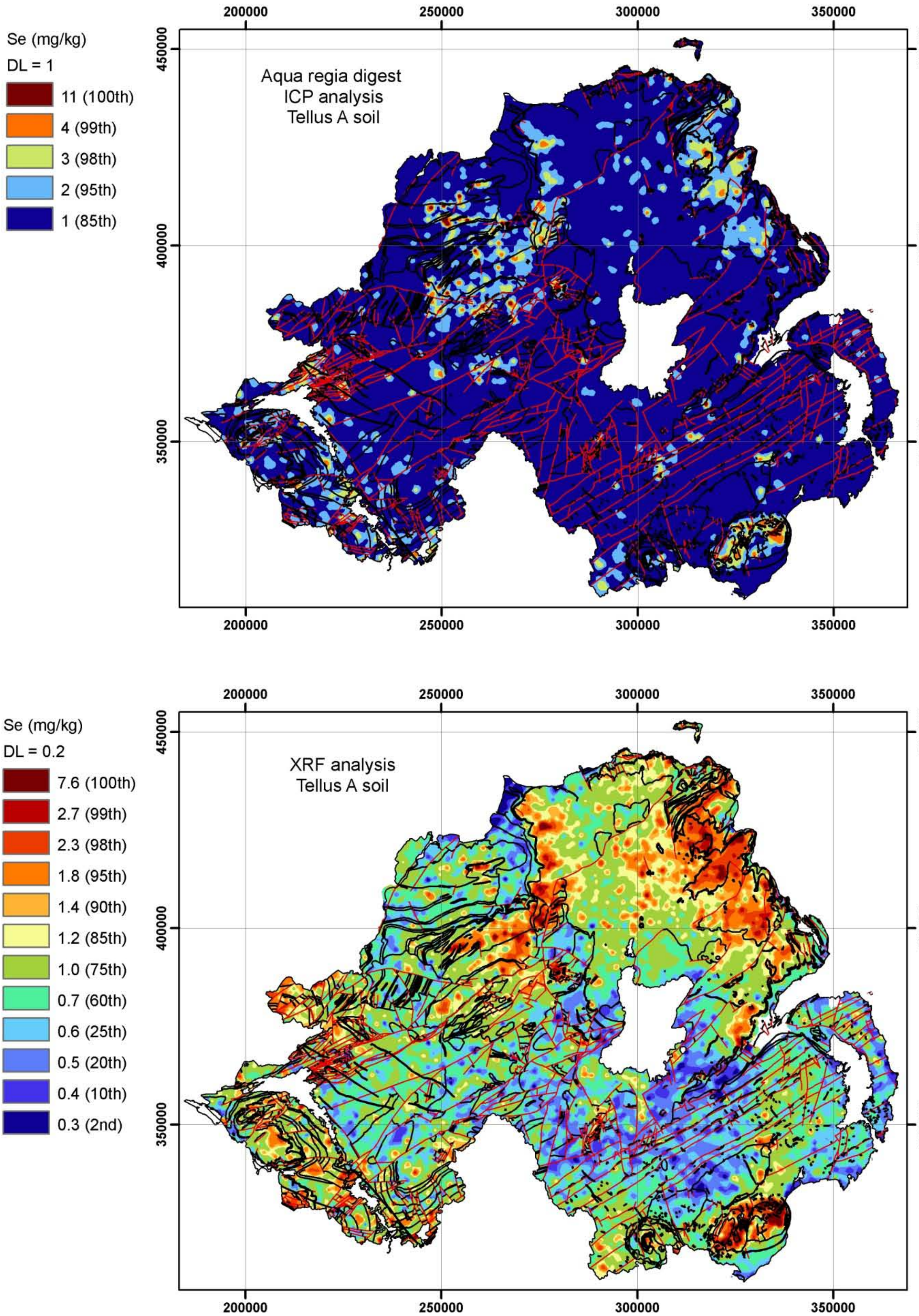


Figure 28 Comparison of Tellus 'A' soil regional data for Se

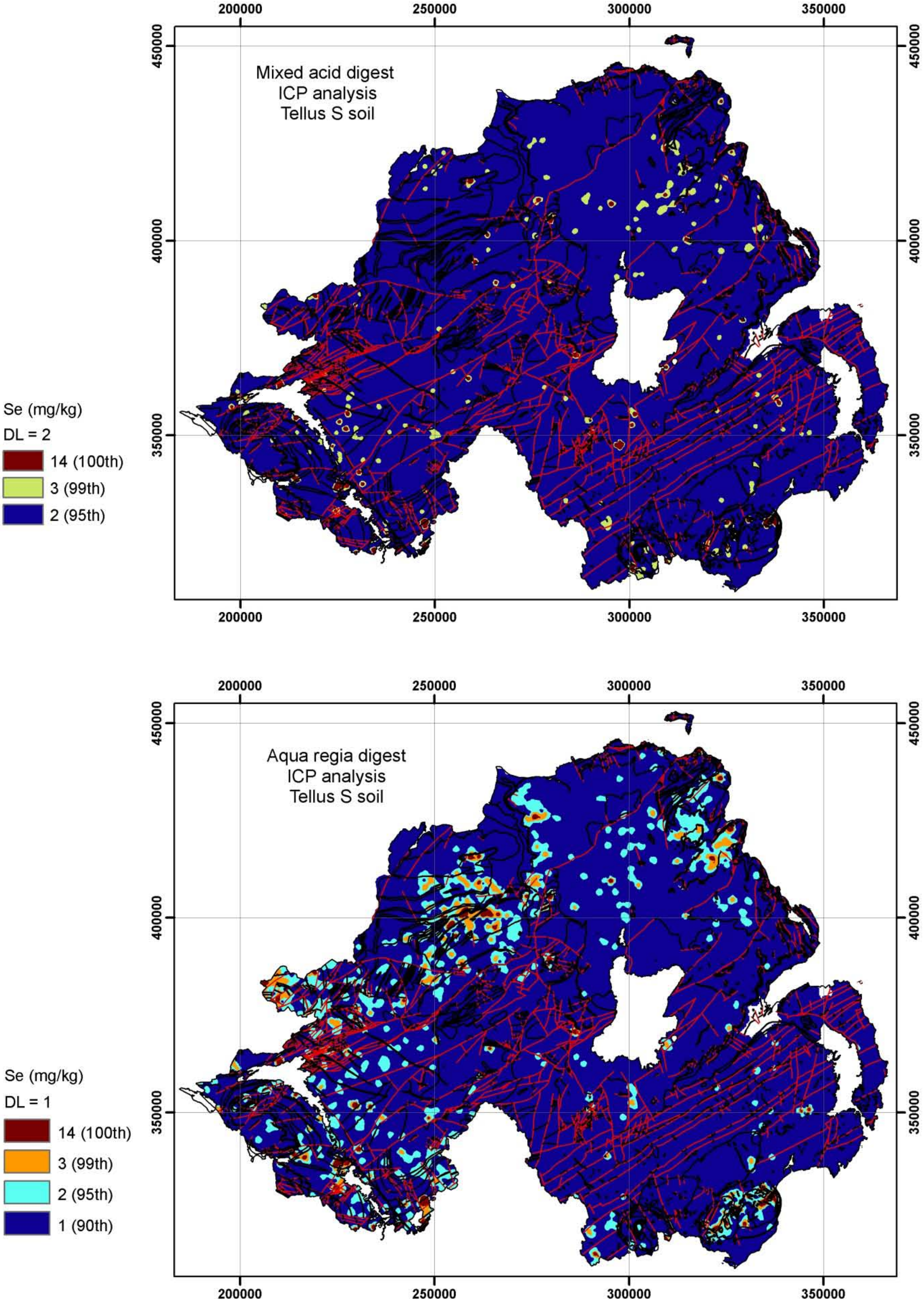


Figure 29 **Comparison of Tellus 'S' soil regional data for Se**

6.10 TIN

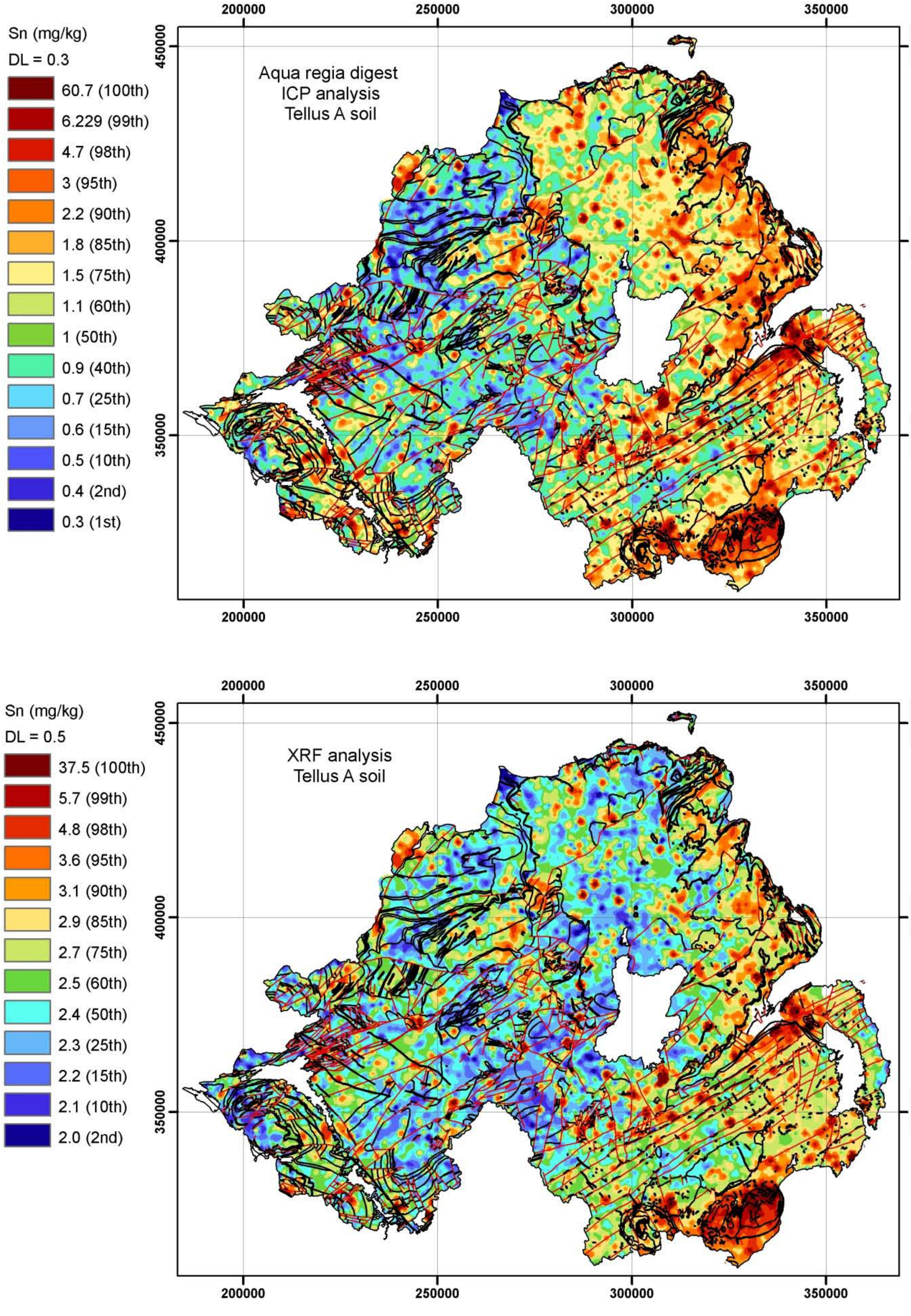


Figure 30 Comparison of Tellus ‘A’ soil regional data for Sn

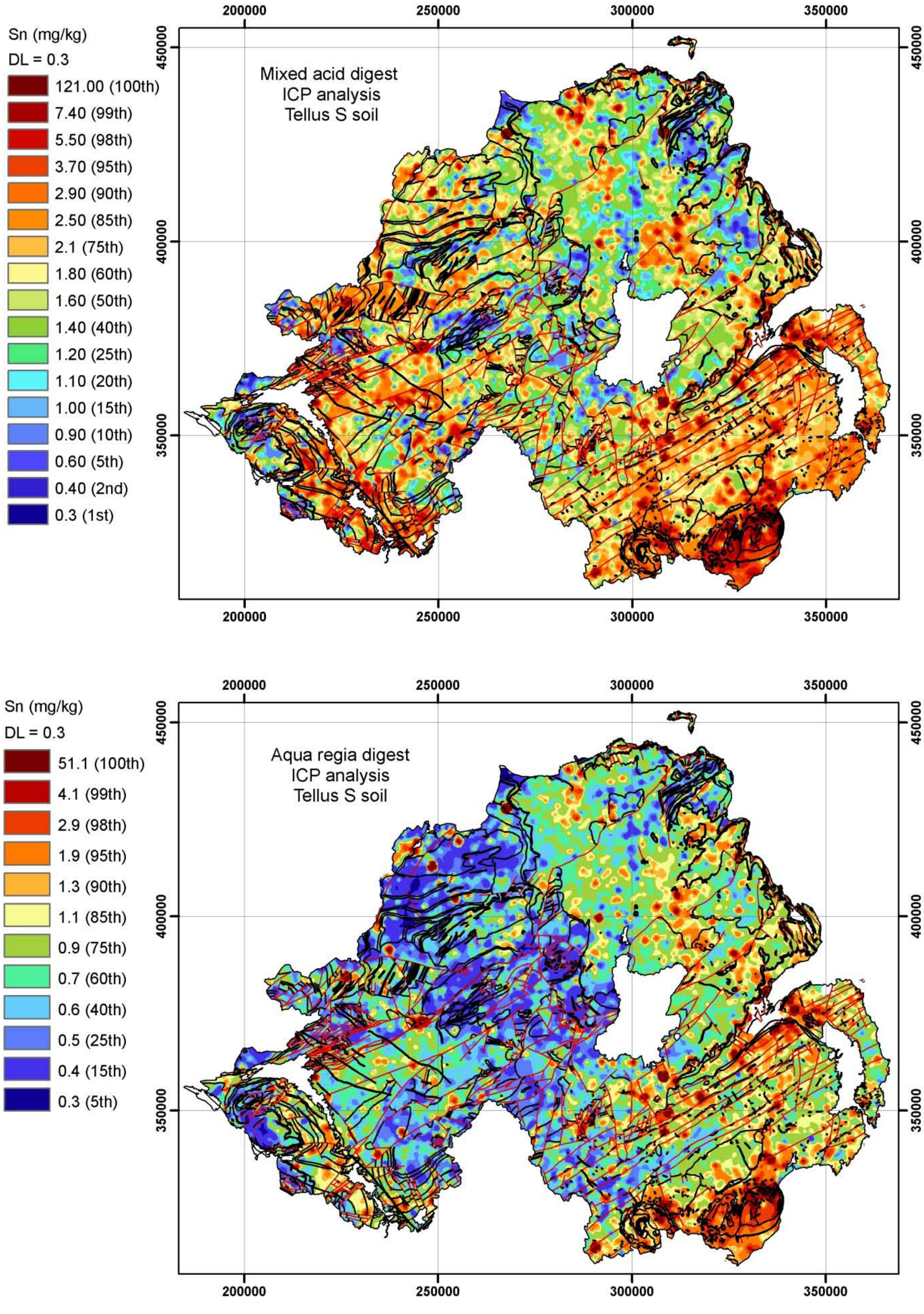


Figure 31 Comparison of Tellus 'S' soil regional data for Sn

6.11 URANIUM

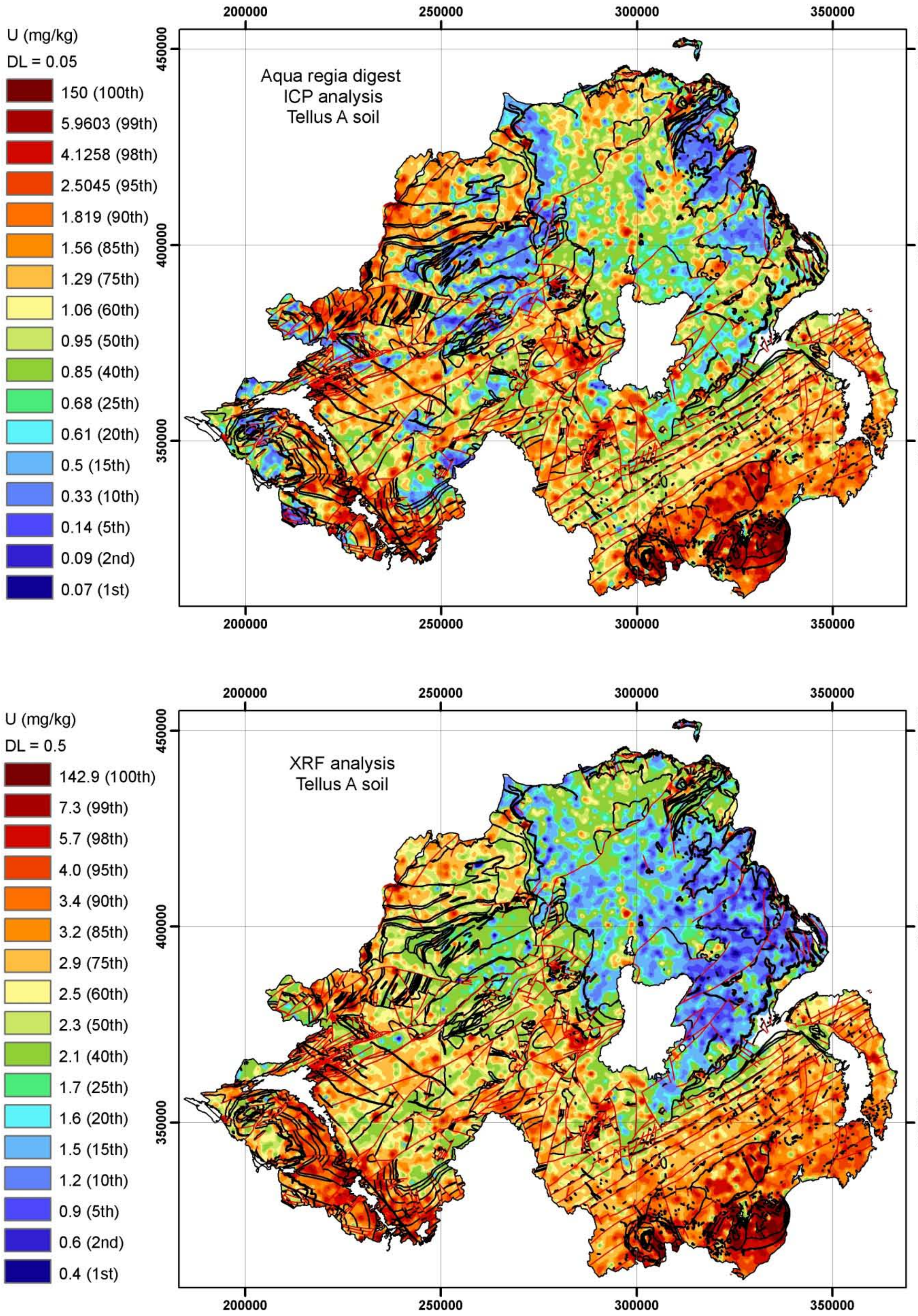


Figure 32 Comparison of Tellus ‘A’ soil regional data for U

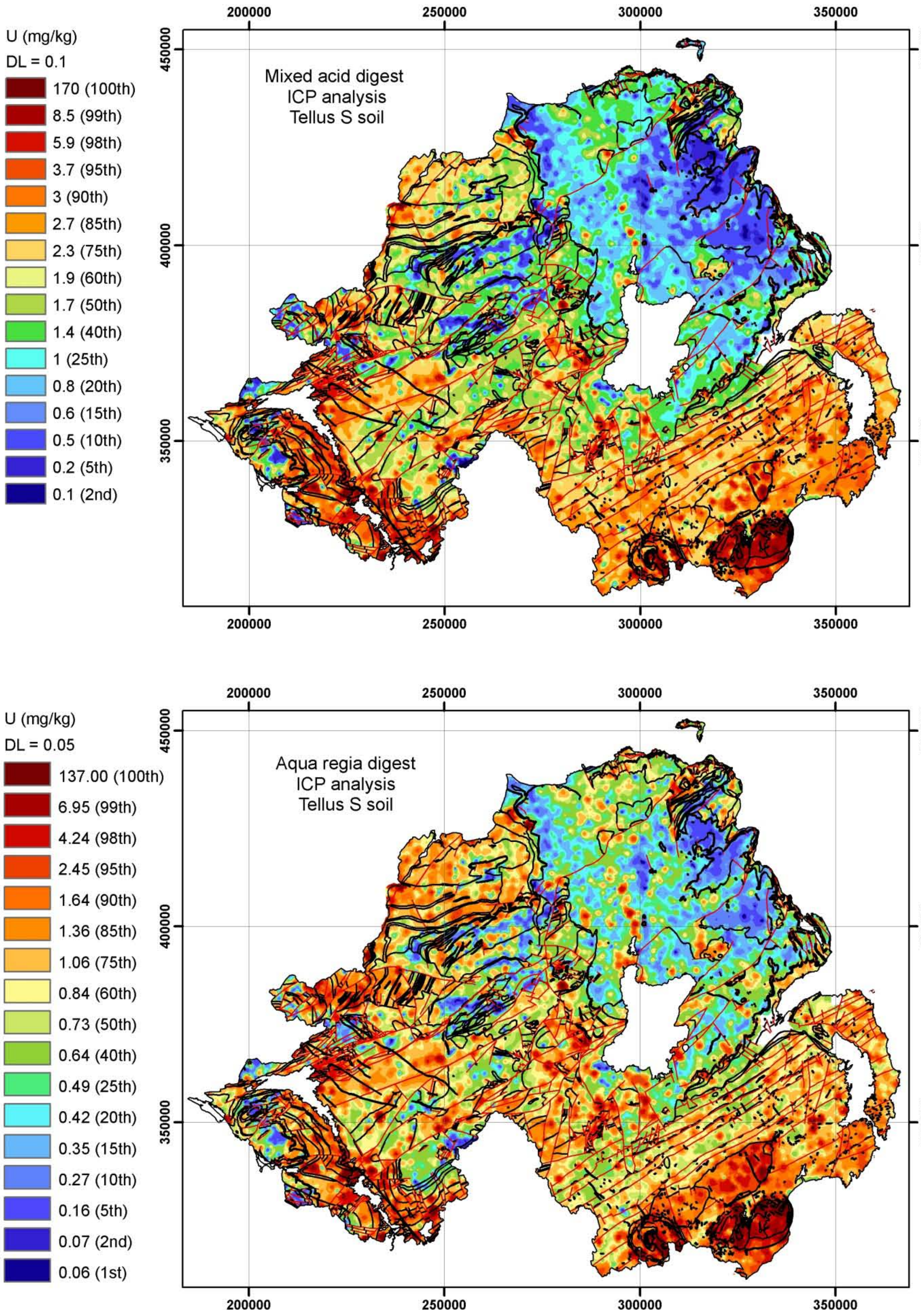


Figure 33 Comparison of Tellus 'S' soil regional data for U

6.12 ZINC

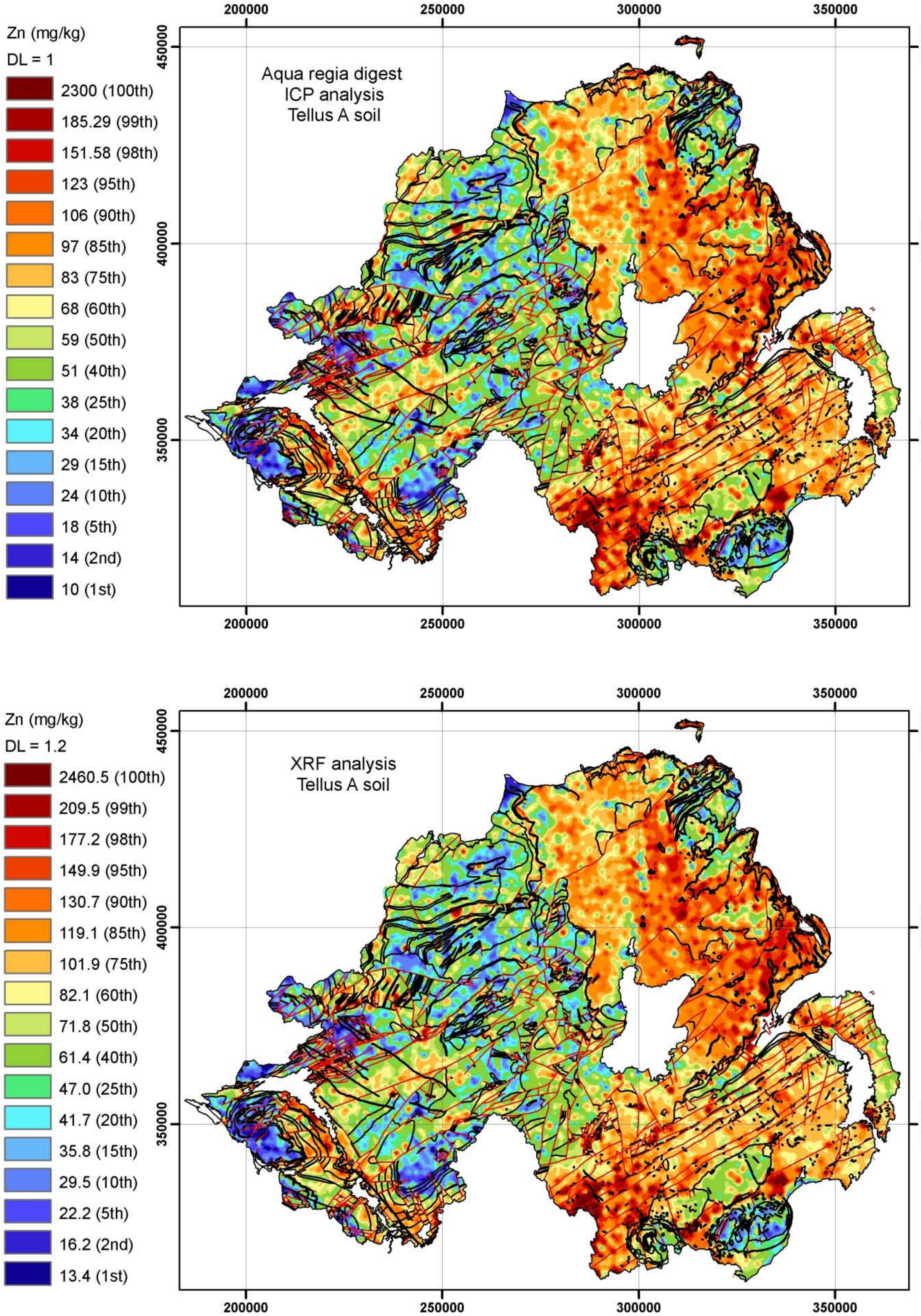


Figure 34 Comparison of Tellus ‘A’ soil regional data for Zn

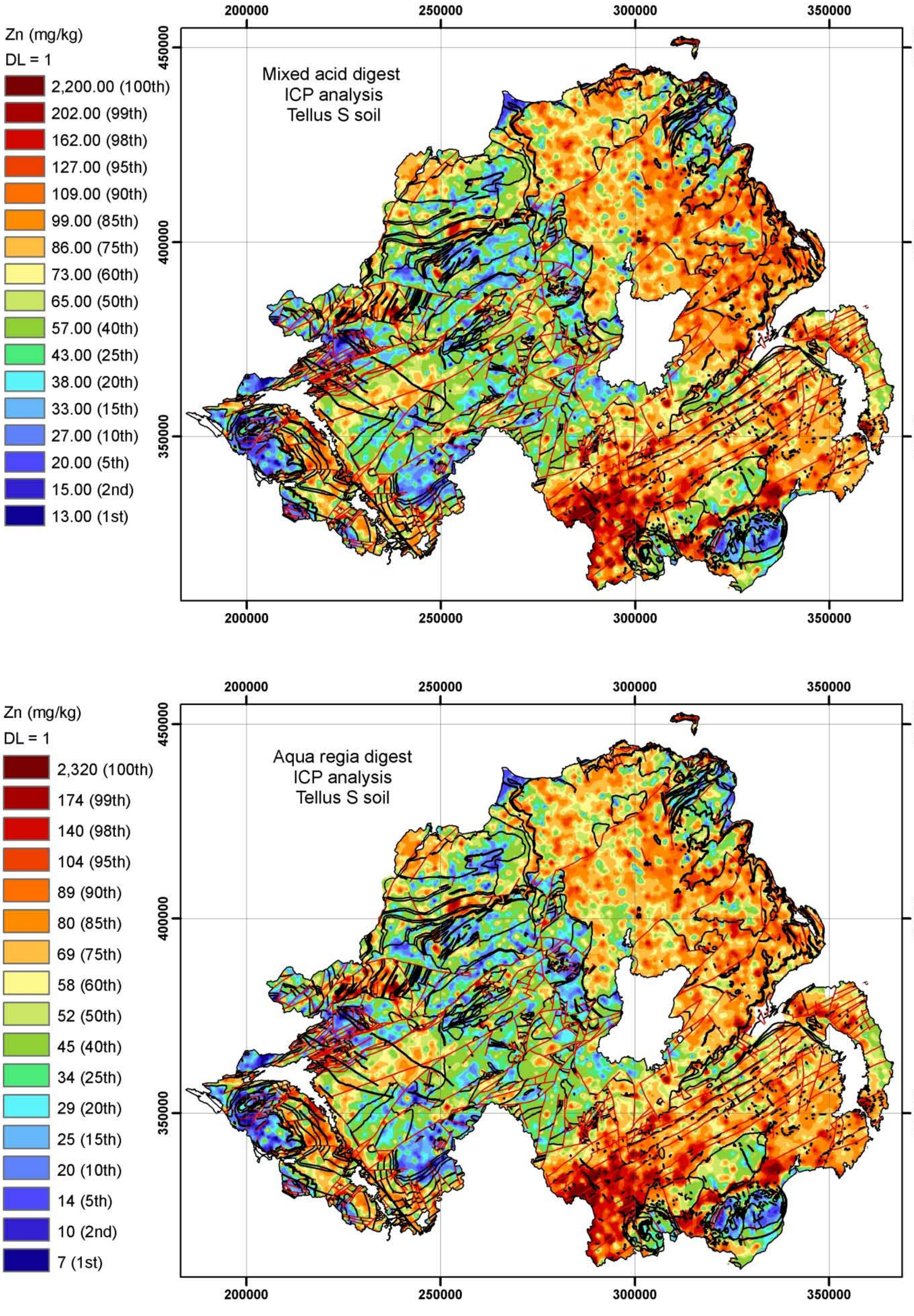


Figure 35 Comparison of Tellus 'S' soil regional data for Zn

7 Conclusions

Analysis of Tellus soil geochemistry data provides a regional scale multi-element resource detailing the spatial distribution of principal chemical elements and compounds. Geochemical mapping can be applied to a wide range of disciplines, namely mineral exploration and environmental geochemistry. A regional scale baseline allows for the evaluation of regional trends and the assessment of geological or anthropogenic influences. The geochemical composition of soil reflects the soil forming environment and the processes which have shaped it over time. In addition, a more detailed urban survey provides valuable data for the assessment of anthropogenic influence against the natural background values.

These new ICP data sets are complementary to the XRFS data sets previously published. It is important to take into consideration which data set is the most appropriate for each specific element. By nature the acid digest process can lead to under recovery or volatilisation depending on the severity of the digest. As a result certain analytical techniques will produce data which have varying degrees of accuracy.

Aqua regia digest is considered a 'partial' digest; it is suitable for the analysis of sulphide minerals and iron oxides however it will not digest the silicate minerals or resistate minerals such as zircon. Therefore the leach should be considered partial for elements commonly bound in silicate or resistate minerals. It is also worth noting that *aqua regia* digest can break down gold and while the detection limit may hamper the spread of data it is still useful.

Mixed acid digest is typically referred to as "*Near-total*" due to the ability to break down silicate minerals with the specific combination of acids (perchloric, hydrochloric, hydrofluoric and nitric acid). Although a very effective dissolution process for a wide range of mineral species it is worth noting that for some, volatile loss can lead to under recovery, (e.g. As and Sb). Under-recovery may also be observed in Al, Ba, Be, Cr, Hf, In, Mn, Sn, and Te depending on the matrix in which these elements are bound.

The maps for cadmium, molybdenum, antimony and selenium show apparent anomalies between the data obtained from XRFS and those from ICP-MS. These differences are caused by the contrast in detection limits between the methods combined with low concentrations in the samples. For example, for cadmium 50% of the XRFS results fall below the detection limit, while the maps produced from the ICP methods give detail down to the 1st percentile. For selenium the situation is reversed with the ICP methods losing all detail below the 85th percentile while XRFS provides results down to the 2nd percentile. Antimony and molybdenum are also both affected to a lesser extent.

Appendix 1: Detailed quality assessment for *aqua regia* partial digest ICP analysis of Tellus 'A' soils

This appendix contains detailed information on the quality assessment of the *aqua regia* partial digest ICP analytical data for Tellus 'S' soils on an element by element basis. While correction factors are discussed they should only be applied where it is certain they will improve data quality. Recommendations and approved correction factors are discussed in Chapter 4.1.3.

SILVER Ag

Shewhart plots of primary and secondary reference material data revealed some data points which lie either well above or well below the normal spread of data. The dates of these analyses were compared between materials and with other elements for the materials but the problems were found to be non-systematic. The Shewhart chart for XRAL01A showed a step change of approximately 15% starting on 15/2/07. Unfortunately none of the other reference materials were analysed beyond this point so it is not possible to determine whether this step occurred just for this material or for all samples.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data:

Correction factor = ([Ag] x 1.3959) – 0.1186

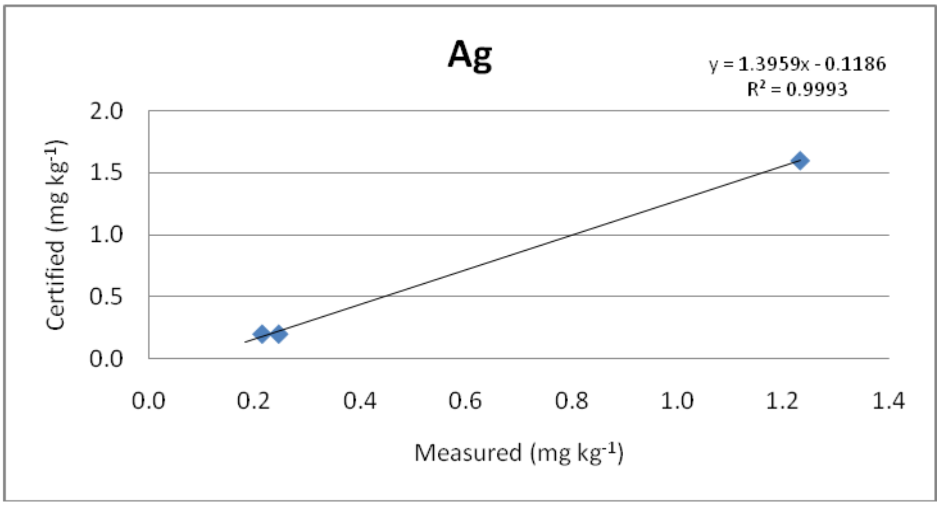


Figure 36 Regression plot for measured values against certified values for silver in Till-1, 2, 3 and 4.

However the regression is based on just three points, two of which are very close together, and there are no reference data to confirm that applying the factor will improve the sample data

The histogram for data from the analysis of XRAL01A shows a broad spread of data peaking below the expected value of 2.18mg kg^{-1}.

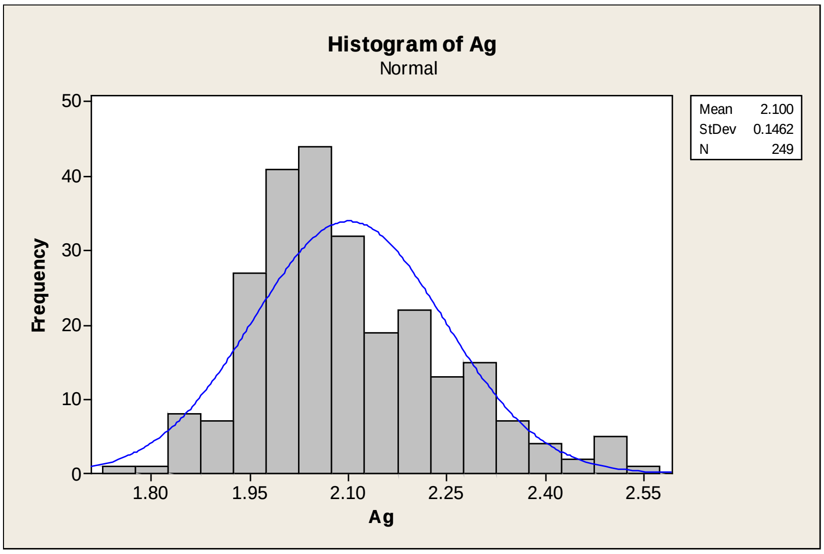


Figure 37 Histogram showing measured silver data in XRAL01A. Values are in mg kg^{-1}.

ALUMINIUM Al

Shewhart plots of primary and secondary reference material data indicated that for most materials there were no issues with the precision of data as reported direct from the laboratory. The Shewhart plots for the reference material S13B showed a period of poor precision between 9/8/2005 and 28/9/2005, this is repeated for several elements for this material, but does not occur for the other materials that were analysed during this period.

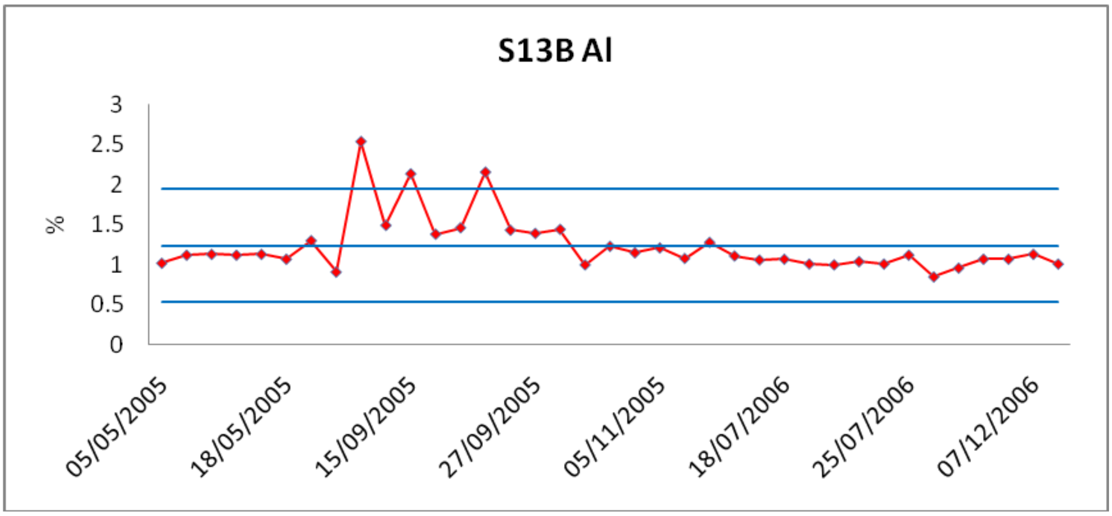


Figure 38 Shewhart chart for aluminium in S13B.

The regression line for the four Till materials suggests some bias, but the histogram for XRAL01A gives a peak coincident with the expected value of 0.53% Al.

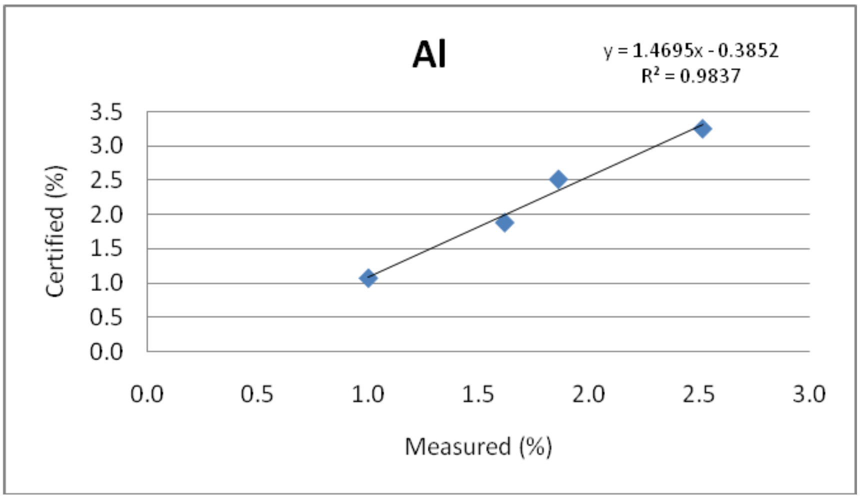


Figure 39 Regression plot for measured values against certified values for aluminium in Till-1, 2, 3 and 4.

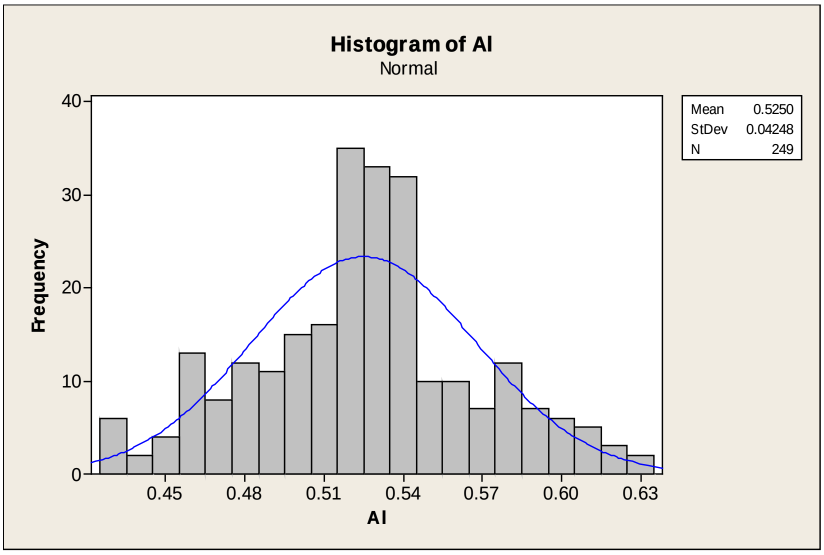


Figure 40 Histogram showing measured aluminium data in XRAL01A. Values are % Al.

ARSENIC As

Shewhart plots of the Till materials and S13B indicated that there were no issues with the precision of data as reported directly from the laboratory. The secondary reference materials Antbas and Dal contained little arsenic, but the variable data, between below the quoted detection limit and twenty times the quoted detection limit, suggests that the detection limit quoted is over optimistic and data less than 2mg kg^{-1} should be treated with caution. At the other end of the scale, the data for XRAL01A also gave poor precision and under recovery, but, with an expected value of 1081mg kg^{-1} this is much higher than the concentration range seen in the samples. The reference materials containing intermediate levels of arsenic did not exhibit these problems; most of the sample data fell within this range.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data:

$$\text{Correction factor} = ([\text{As}] \times 1.0803) - 0.595$$

However the correction is small and the concentrations, even in the lowest Till material, are above those in the samples. Therefore with no certified reference material to validate applying the correction, it should not be applied.

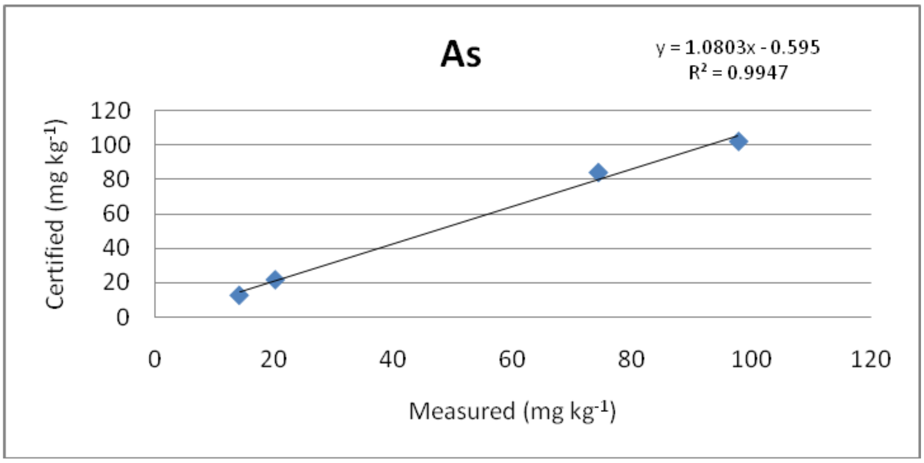


Figure 41 Regression plot for measured values against certified values for arsenic in Till-1, 2, 3 and 4.

BARIUM Ba

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory for most of the materials. However, as for some other elements, S13B exhibited values higher than usual between 9/8/2005 and 28/9/2005. Also XRAL01A gave a broad spread of data mostly falling below the expected value. This could be due to the unusually high concentration in this material, which falls well above the calibration range.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Ba] x 1.0116) + 5.3883

Without evidence from an independent Certified Reference Material it is not possible to assess whether applying this factor to the data gives any improvement.

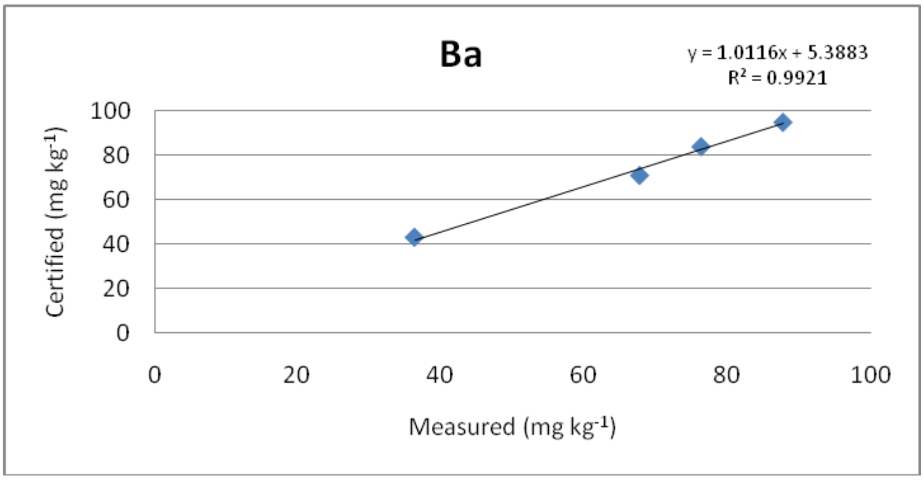


Figure 42 Regression plot for measured values against certified values for barium in Till-1, 2, 3 and 4.

BISMUTH Bi

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. As has been seen for other elements, XRAL01A gave a period of high results in September 2005. There were insufficient data available to plot a regression.

The histogram of data from the analysis of XRAL01A shows most data to fall below the expected value of 11.71mg kg^{-1}, but with a small peak at 11.9mg kg^{-1} relating to the unusually high results from September 2005.

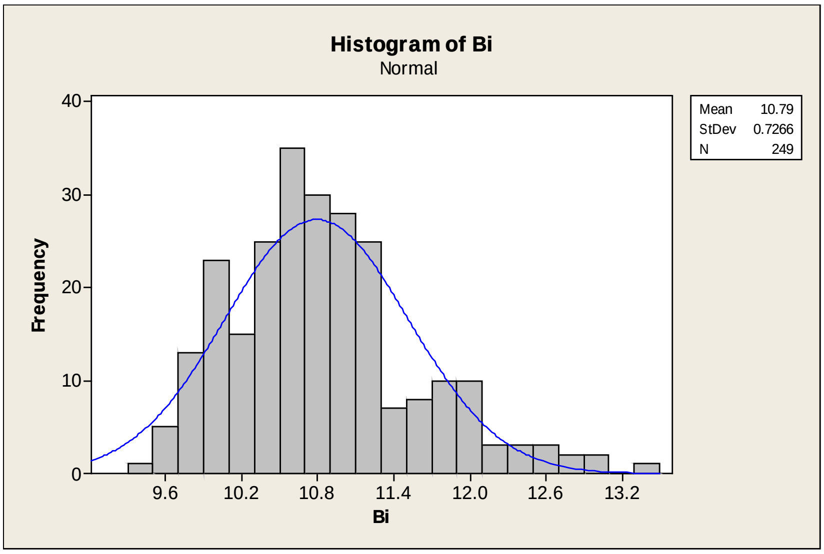


Figure 43 Histogram showing measured bismuth data in XRAL01A. Values are in mg kg^{-1}.

CALCIUM Ca

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported directly from the laboratory. The regression plot for calcium shows a flier for the material Till-1 (reference value 0.145%, mean measured value 0.276%). There are no indications in the data to suggest why this discrepancy occurred.

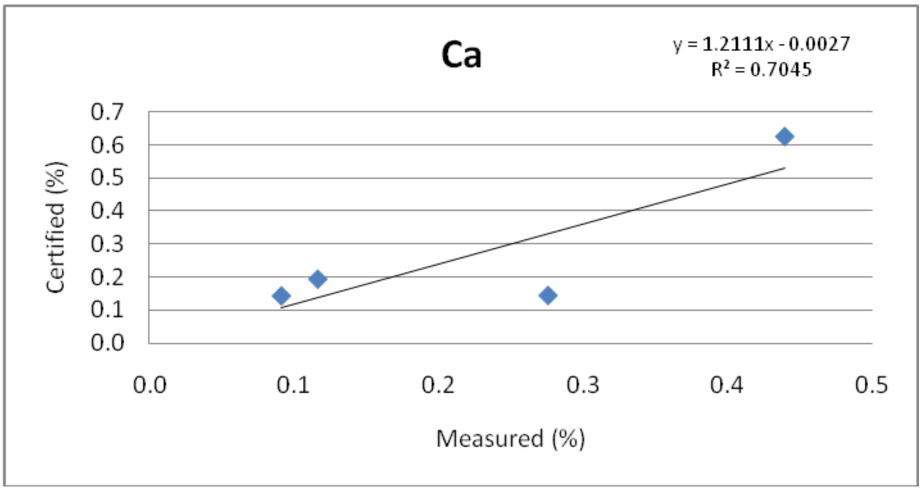


Figure 44 Regression plot for measured values against certified values for calcium in Till-1, 2, 3 and 4.

The histogram for the reference material XRAL01A shows the data to be centred just below the expected value of 1.91%.

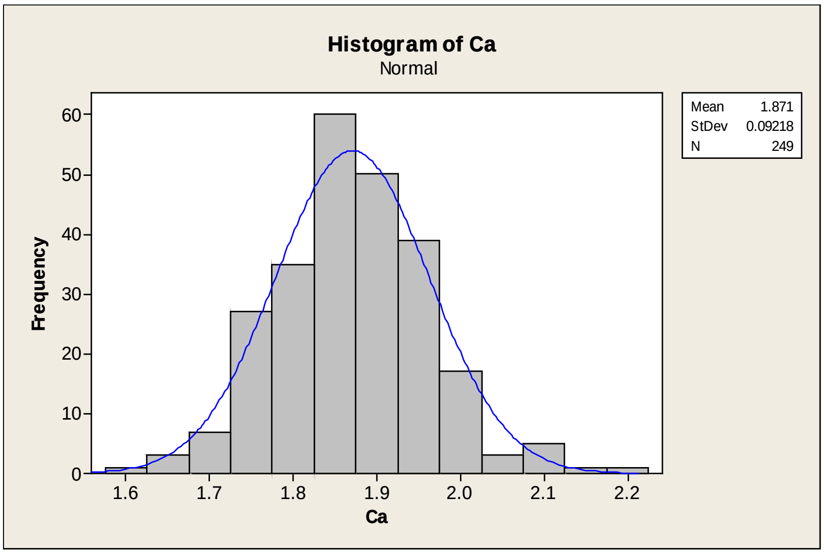


Figure 45 Histogram showing measured calcium data in XRAL01A. Values are % Ca.

CADMIUM Cd

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

There were insufficient values for the reference materials to plot a regression. The histogram for XRAL01A shows the data to be distributed approximately 0.3mg kg^{-1} above the expected value of 2.82mg kg^{-1}.

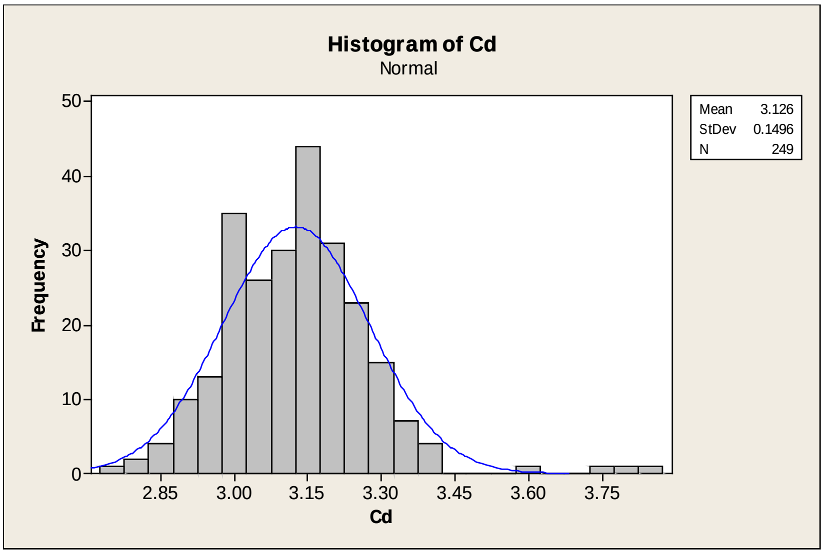


Figure 46 Histogram showing measured cadmium data in XRAL01A. Values are in mg kg^{-1}.

CERIUM Ce

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. This is confirmed by the histogram for XRAL01A which shows the majority of the data to lie close to the expected value of 14.64mg kg-1.

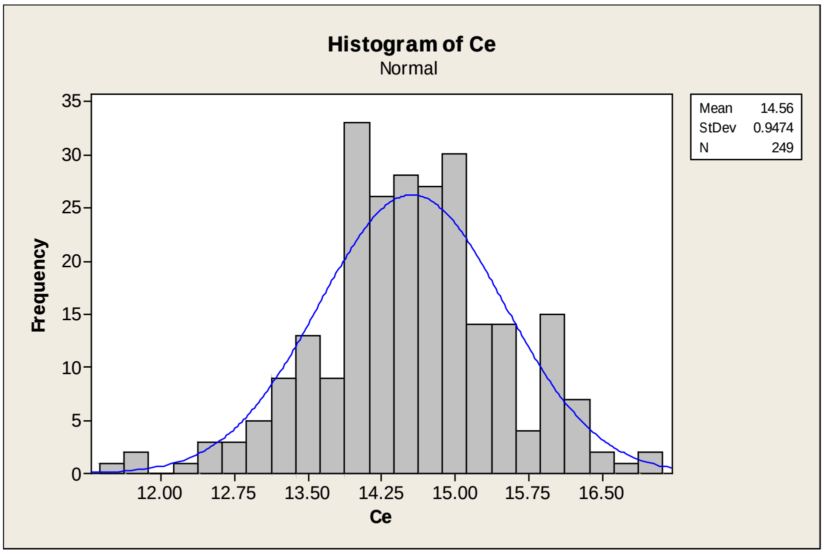


Figure 47 Histogram showing measured cerium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

COBALT Co

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Co] x 1.0668) + 0.1162

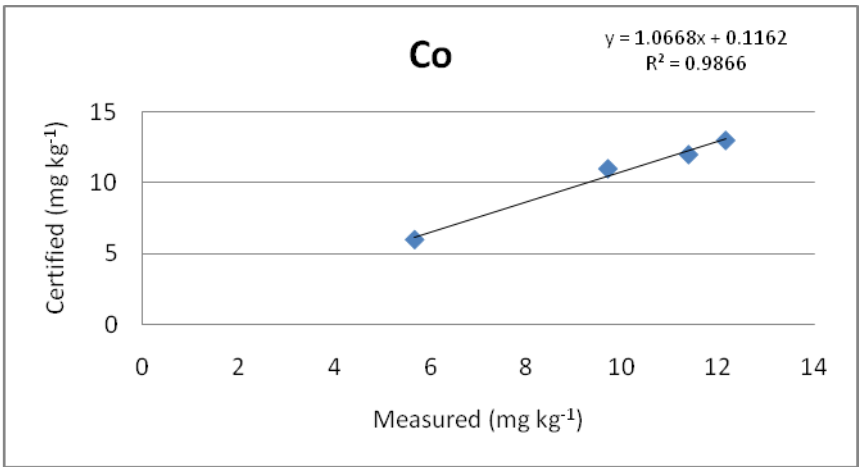


Figure 48 Regression plot for measured values against certified values for cobalt in Till-1, 2, 3 and 4.

The histogram for XRAL01A shows the data to be close to the expected value of 6.48mg kg^{-1}.

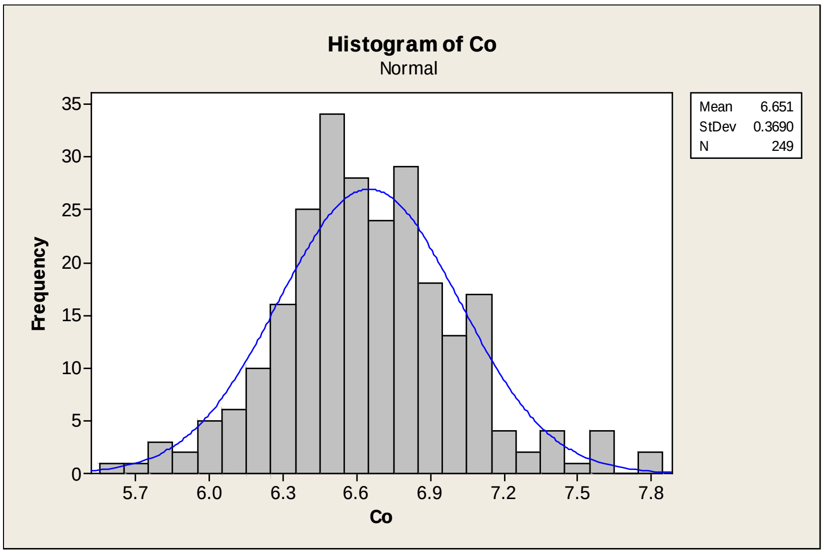


Figure 49 Histogram showing measured cobalt data in XRAL01A. Values are in mg kg^{-1}.

CHROMIUM Cr

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. However, the results for XRAL01A included one point that fell abnormally below the mean; this was not seen for other elements or other materials. Also, the data between 9/8/2005 and 20/9/2005 for S13B showed the same poor precision seen for other elements in this standard during this period.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Cr] x 1.2444) – 2.3288

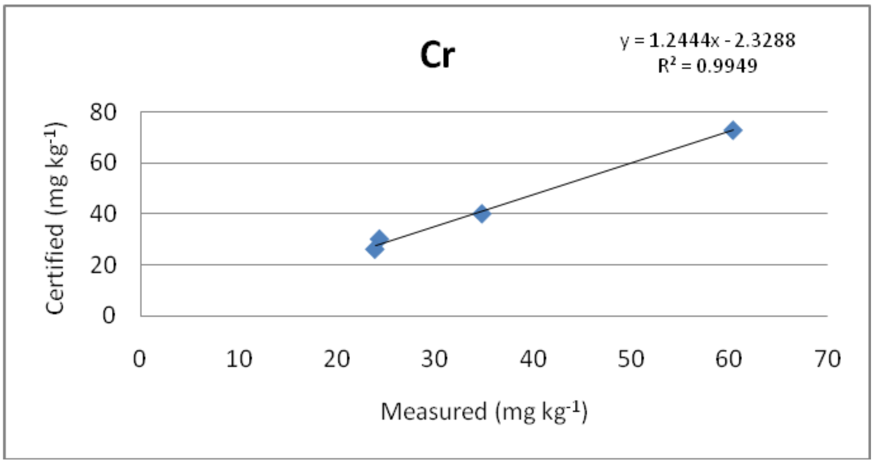


Figure 50 Regression plot for measured values against certified values for chromium in Till-1, 2, 3 and 4.

CAESIUM Cs

The analysis of the samples took place over two periods, May to September 2005 and July 2006 to February 2007. For all other elements, except perhaps zirconium, this break was indiscernible. However, for caesium there is a clear step change of approximately 20% seen in all reference materials analysed during both periods. For XRAL01A, for which there are most results available, the change is 23.8%. In addition to this the mean for caesium, even during the early period was just 1.4 mg kg^{-1} compared to an expected value of 1.84 mg kg^{-1}, this could be due to dissolution problems as caesium occurs in the silica matrix and may not be extracted fully by *aqua regia*. The step change should be accounted for by multiplying all caesium results measured from July 2006 onwards by a factor of 1.238. However, this still leaves the overall mean for caesium measured in XRAL01A as 1.4. Without corroborating data from other materials it is not possible to say whether applying a further factor to the entire data set would improve the sample results.

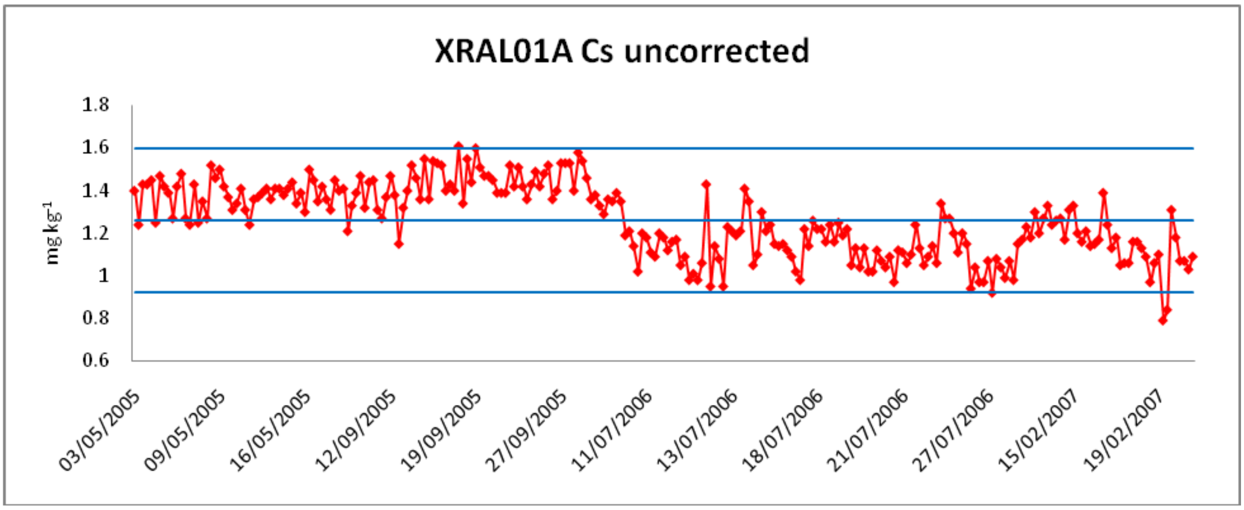


Figure 51 Shewhart chart for caesium in XRAL01A without correction.

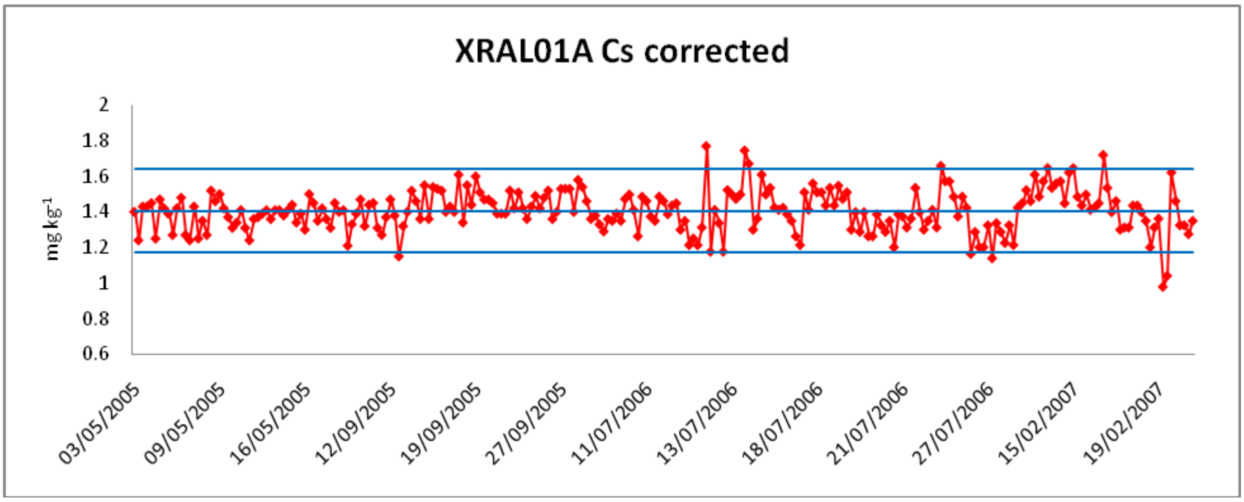


Figure 52 Shewhart chart for caesium in XRAL01A with correction.

COPPER Cu

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Cu] x 1.0642) + 1.4204

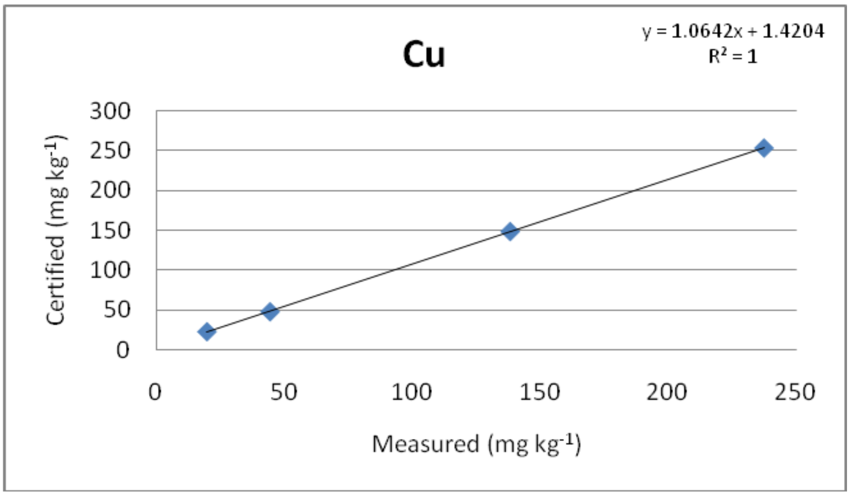


Figure 53 Regression plot for measured values against certified values for copper in Till-1, 2, 3 and 4

The histogram for copper measured in XRAL1A shows an even distribution centred on the expected value of 105mg kg^{-1}.

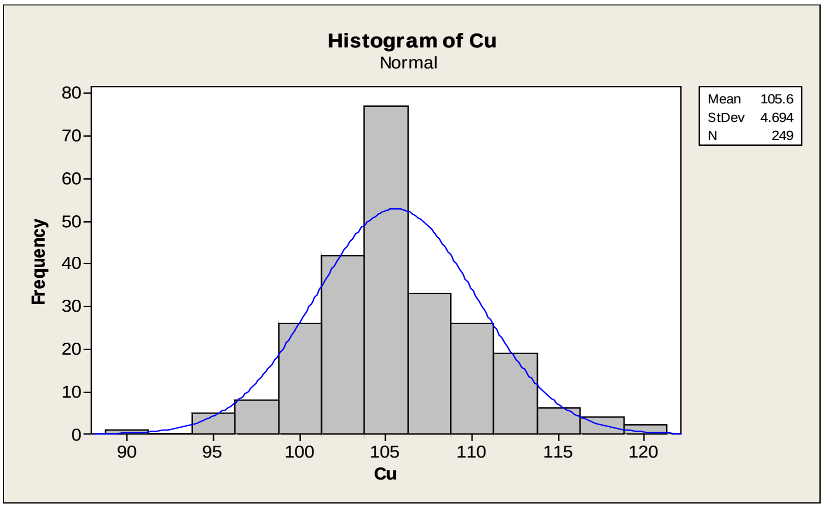


Figure 54 Histogram showing measured copper data in XRAL01A. Values are in mg kg^{-1}.

IRON Fe

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Fe] x 0.9129) + 0.2893

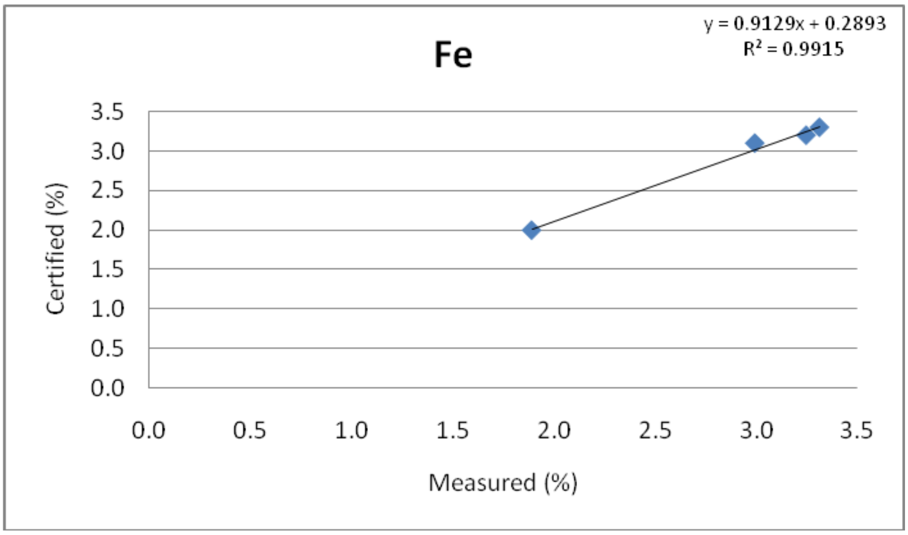


Figure 55 Regression plot for measured values against certified values for iron in Till-1, 2, 3 and 4.

The histogram for iron in XRAL01A shows a broad peak, close to the expected value of 1.91% iron.

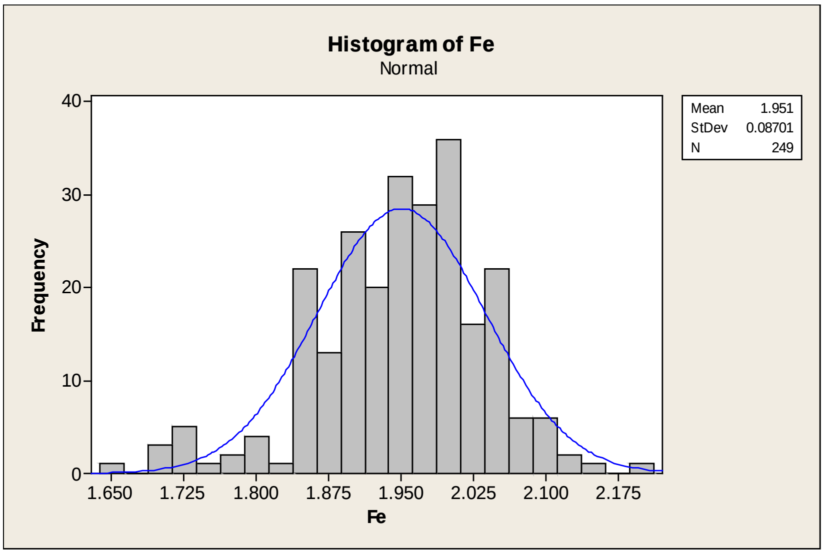


Figure 56 Histogram showing measured iron data in XRAL01A. Values are % iron.

GALLIUM Ga

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory, although, as for some other elements, S13B showed poor precision in September 2005. The histogram of gallium data for XRAL01A shows a distribution of data close to the expected value of 1.68mg kg^{-1}.

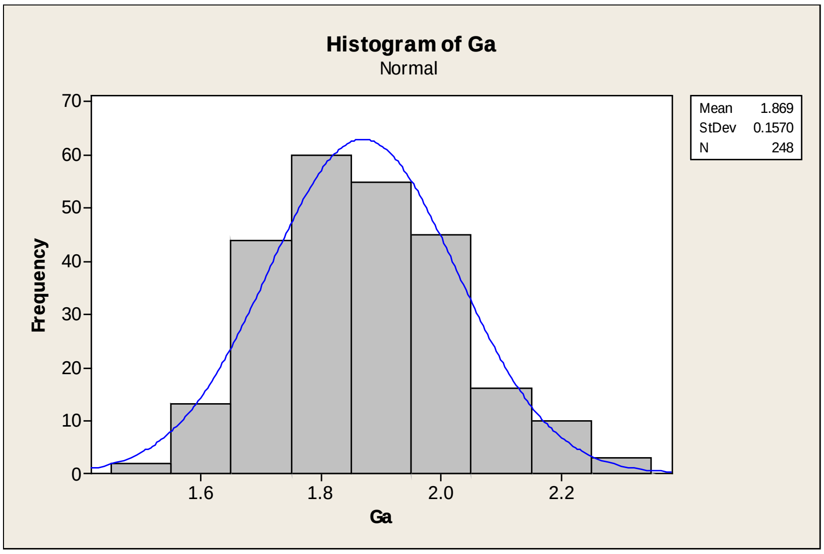


Figure 57 Histogram showing measured gallium data in XRAL01A. Values are in mg kg^{-1}.

POTASSIUM K

As for several other elements, the Shewhart plot for potassium data for reference material S13B showed poor precision during the period between 9/8/2005 and 20/9/2005. Otherwise the Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([K] x 1.1983) + 0.049

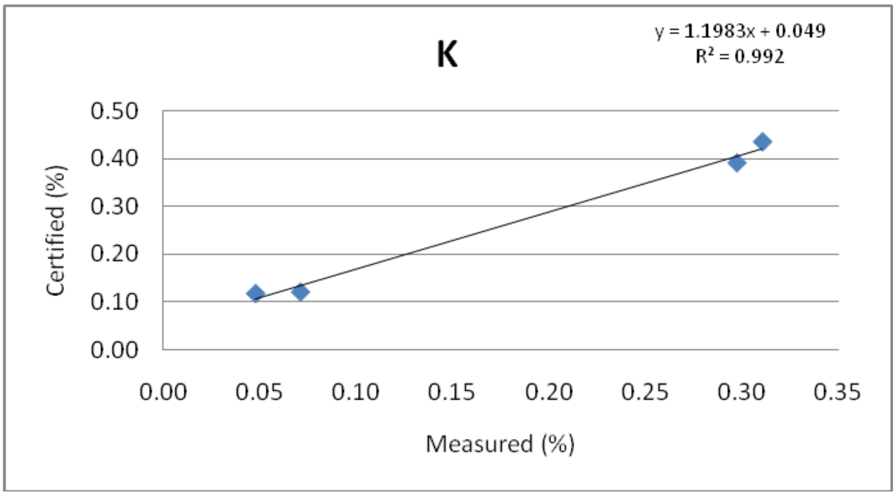


Figure 58 Regression plot for measured values against certified values for potassium in Till-1, 2, 3 and 4.

The histogram for potassium data for XRAL01A shows a distribution centred on the expected value of 1.6% K.

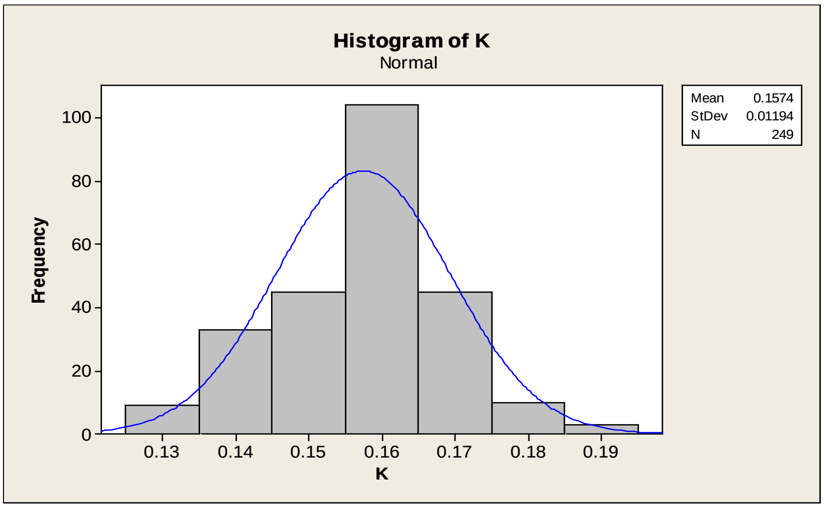


Figure 59 Histogram showing measured potassium data in XRAL01A. Values are % K.

LANTHANUM La

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. There is no significant bias shown on the histogram for XRAL01A with the peak coincident with the expected value of 8 mg kg^{-1}.

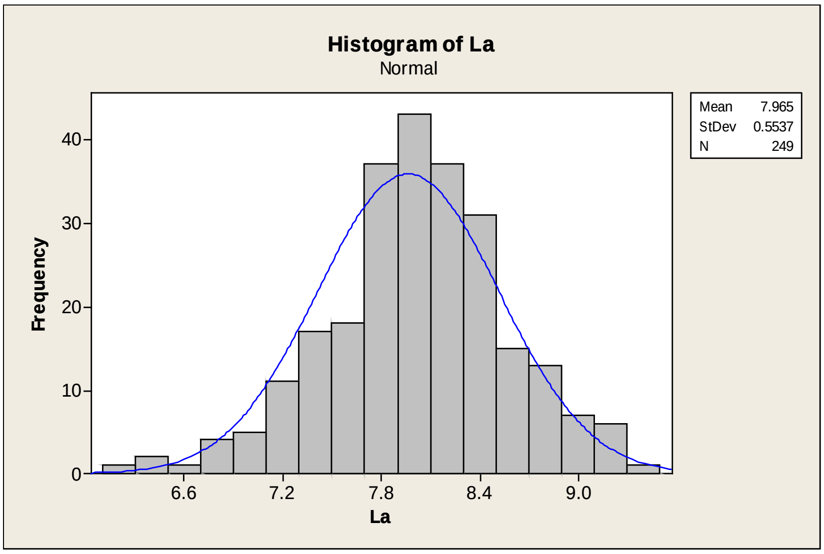


Figure 60 Histogram showing measured lanthanum data in XRAL01A. Values are in mg kg^{-1}.

LITHIUM Li

Other than the aforementioned issues with precision for S13B between 9/8/2005 and 28/9/2005, Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. Unfortunately, XRAL01A was the only reference material used for which an expected value for lithium was quoted and that was just 3.5 times the limit of detection. However, the histogram shows the data to be remarkably accurate at this level when compared to the expected value of 3.5mg kg $^{-1}$.

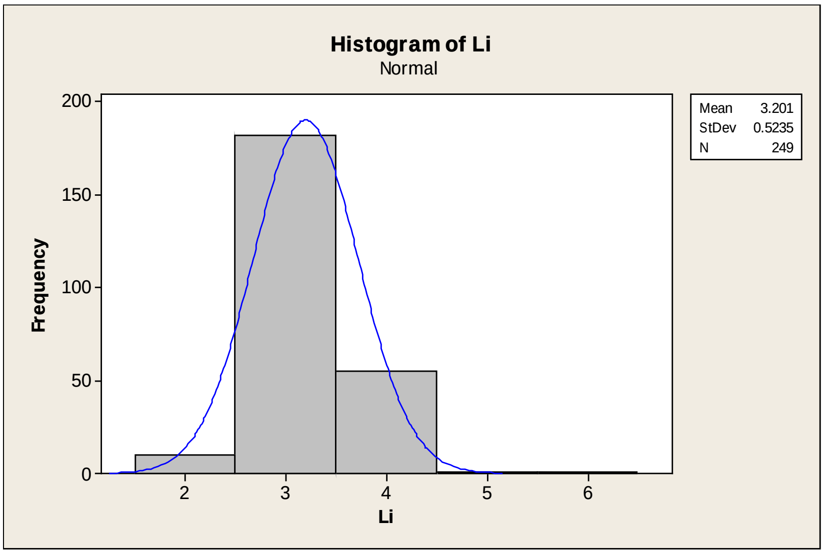


Figure 61 Histogram showing measured lithium data in XRAL01A. Values are in mg kg^{-1}.

MAGNESIUM Mg

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. As for several other elements, a single unusually low result occurred on 9/07/05 for S13B. A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data, however the till materials all contain similar amounts of magnesium and so are not fully representative of the samples.

Correction factor = ([Mg] x 1.071) + 0.0435

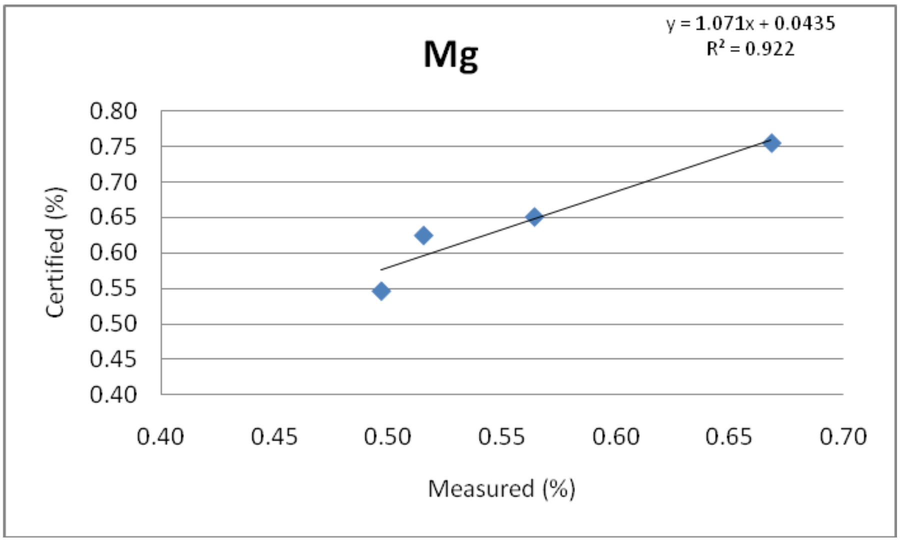


Figure 62 Regression plot for measured values against certified values for magnesium in Till-1, 2, 3 and 4.

The histogram for XRAL01A shows that the data are distributed close to, but just above the expected value of 0.27% Mg.

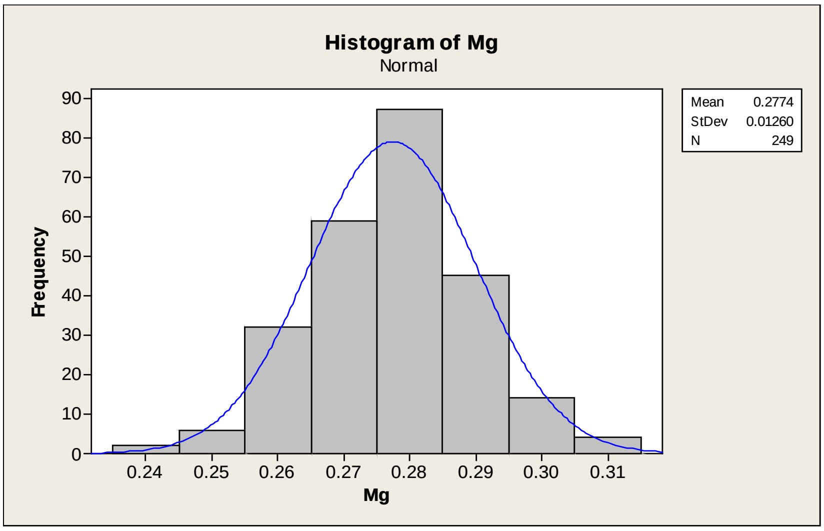


Figure 63 Histogram showing measured magnesium data in XRAL01. Values are % Mg.

MANGANESE Mn

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Mn] x 0.8071) + 47.433

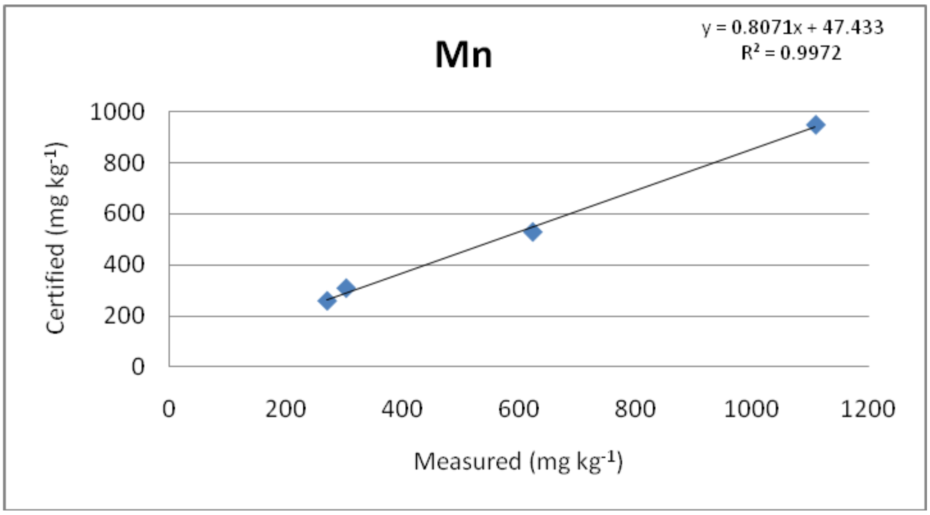


Figure 64 Regression plot for measured values against certified values for manganese in Till-1, 2, 3 and 4.

The histogram showing the distribution of manganese results determined in the reference material XRAL01A shows a broad spread of data around the expected value of 304.7mg kg^{-1} with a slight negative bias.

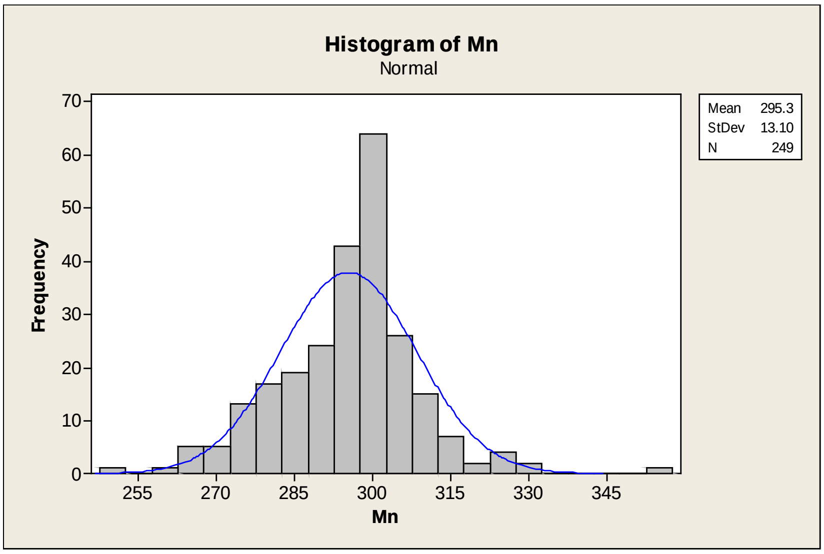


Figure 65 Histogram showing measured manganese data in XRAL01A. Values are in mg kg^{-1}.

MOLYBDENUM Mo

Generally, Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. However, each of the reference materials, Till-1, Till-2, Antbas and XRAL01A gave a result well above the normal range during July 2006. These were not all analysed on the same day, but may represent a dissolution batch that was contaminated. Without further evidence it is not possible to judge whether any samples will have been affected during this period, but unusually high results should be treated with caution. Insufficient data were available to carry out a regression. The histogram shows the data to be tightly grouped around the expected value of 9.79mg kg^{-1}, and highlights the unusually high result at 19.579mg kg^{-1}.

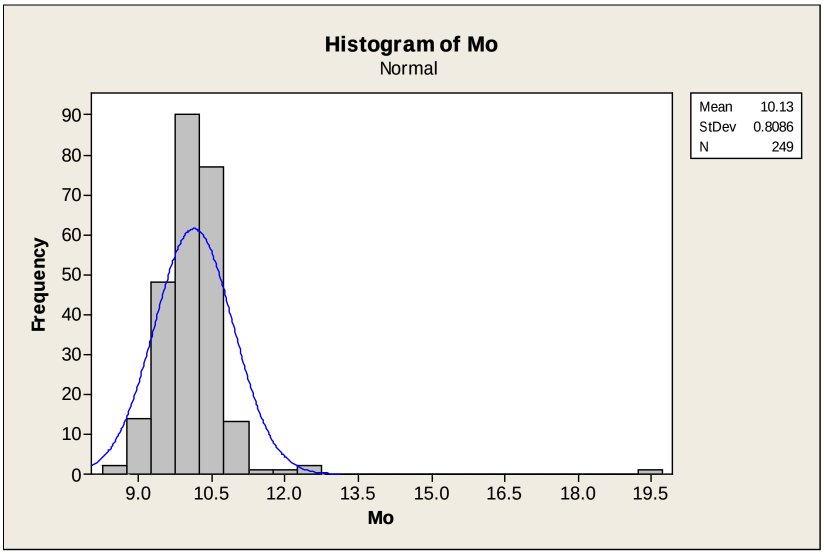


Figure 66 Histogram showing measured molybdenum data in XRAL01A. Values are in mg kg^{-1}

NICKEL Ni

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A single low point on 9/7/05 for S13B was identified as for several other elements in that standard, but did not occur for other standards analysed that day.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Ni] x 1.0081) + 0.6422

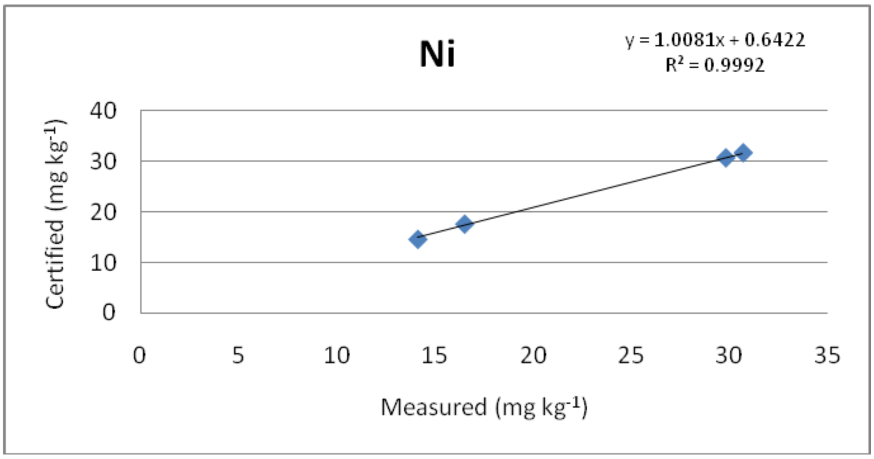


Figure 67 Regression plot for measured values against certified values for nickel in Till-1, 2, 3 and 4.

The histogram of data for XRAL01A shows the mean to sit close to the expected value of 41.52mg kg^{-1}.

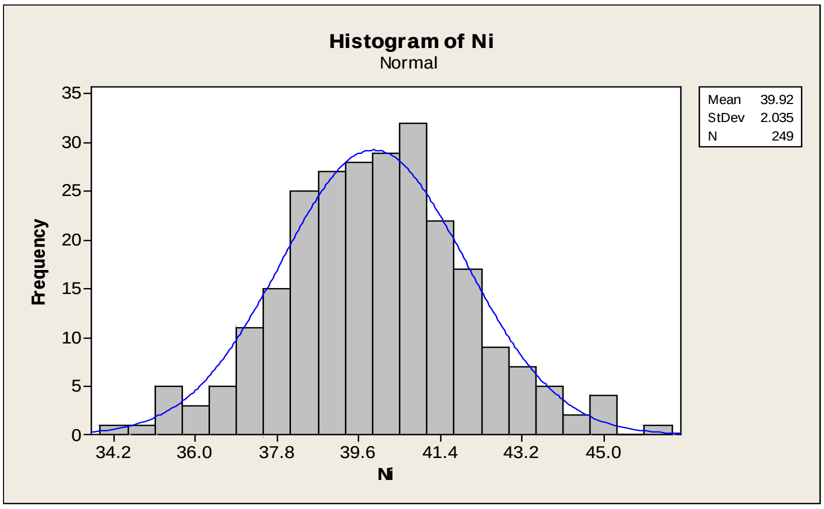


Figure 68 Histogram showing measured nickel data in XRAL01A. Values are in mg kg^{-1}.

PHOSPHORUS P

Shewhart plots of primary and most secondary reference material data showed results that were more widely scattered than usual. The plots for materials that were analysed a lot included periods that were more precise and, being below the long term mean, were nearer to the expected value. This shows clearly on the histogram for XRAL01A where the expected value is 700mg kg^{-1}. It is difficult to identify a cause for the high data, and, as it covers a wide concentration range, it is not possible to make an appropriate correction.

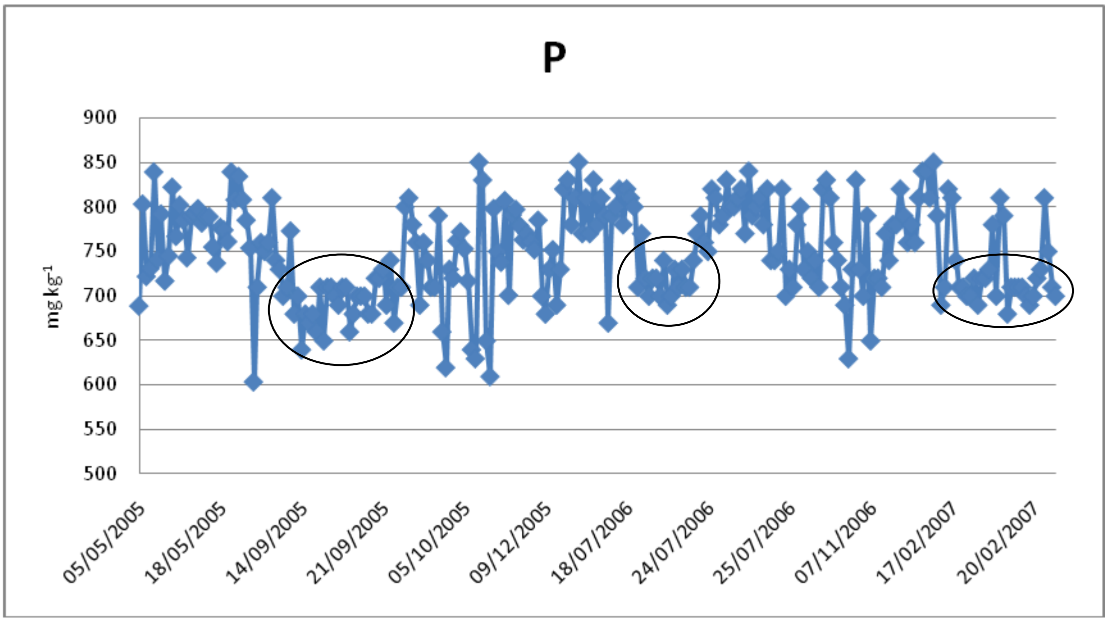


Figure 69 Shewhart chart for phosphorus in XRAL01A.

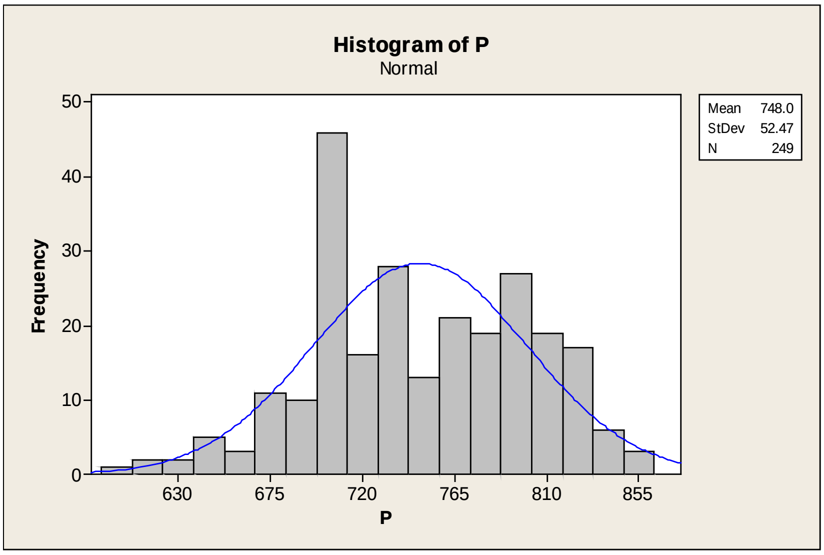


Figure 70 Histogram showing measured phosphorus data in XRAL01A.Values are in mg kg^{-1}.

LEAD Pb

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Pb] x 0.9554) – 0.9875

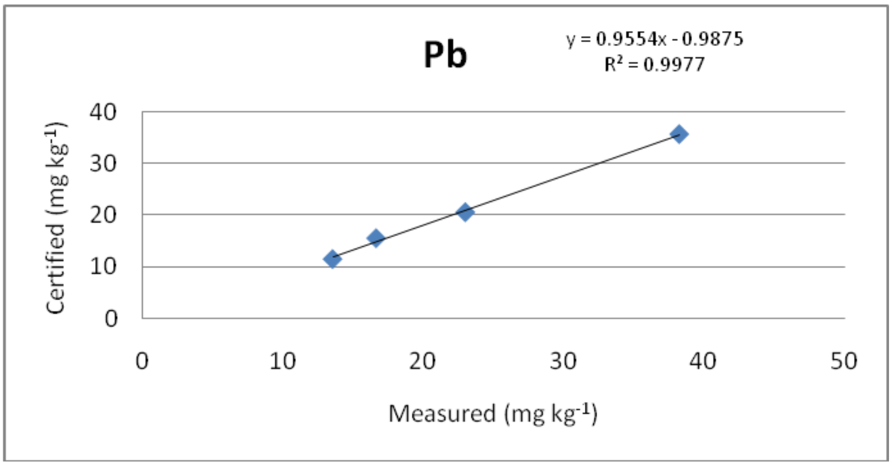


Figure 71 Regression plot for measured values against certified values for lead in Till-1, 2, 3 and 4.

The histogram shows a broad spread of data centred just below the expected value of 72.43mg kg^{-1}.

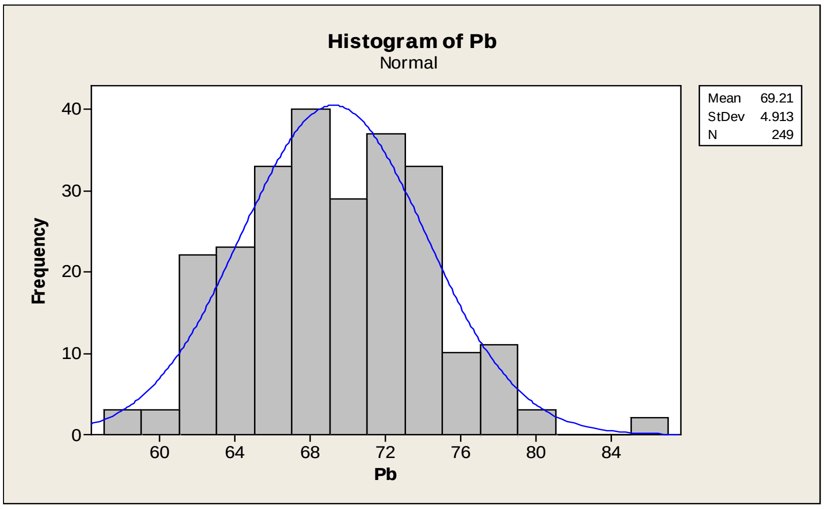


Figure 72 Histogram showing measured lead data in XRAL01A. Values are in mg kg^{-1}.

RUBIDIUM Rb

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. As for several other elements, the Shewhart plot for rubidium data for reference material S13B showed poor precision during September 2005. The histogram for XRAL01A shows a distribution of concentrations centred above the expected value of 7.23mg kg^{-1}.

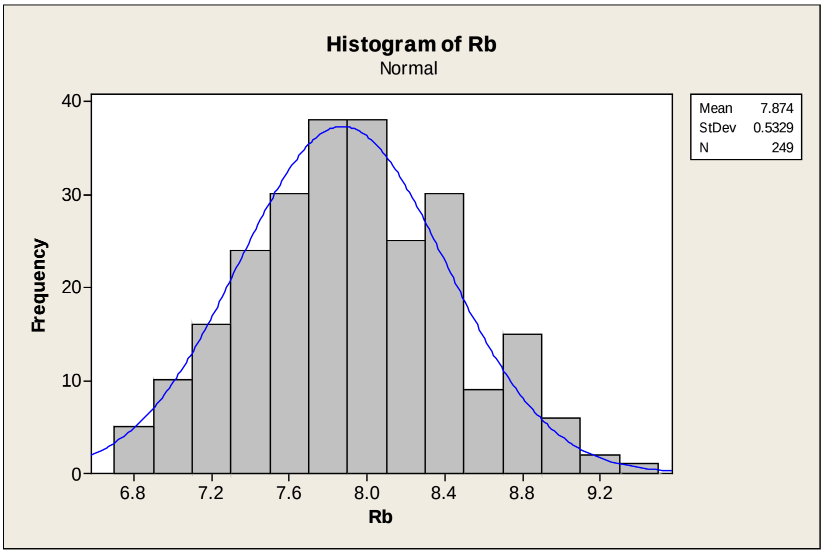


Figure 73 Histogram showing measured rubidium data in XRAL01A. Values are in mg kg^{-1}.

SULPHUR S

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. The results obtained from the analysis of the reference material Antbas were erratic during September 2005, but settled down for the rest of the analytical period. The histogram of measured concentrations for XRAL01A shows a slight negative bias compared to the expected value of 0.18%.

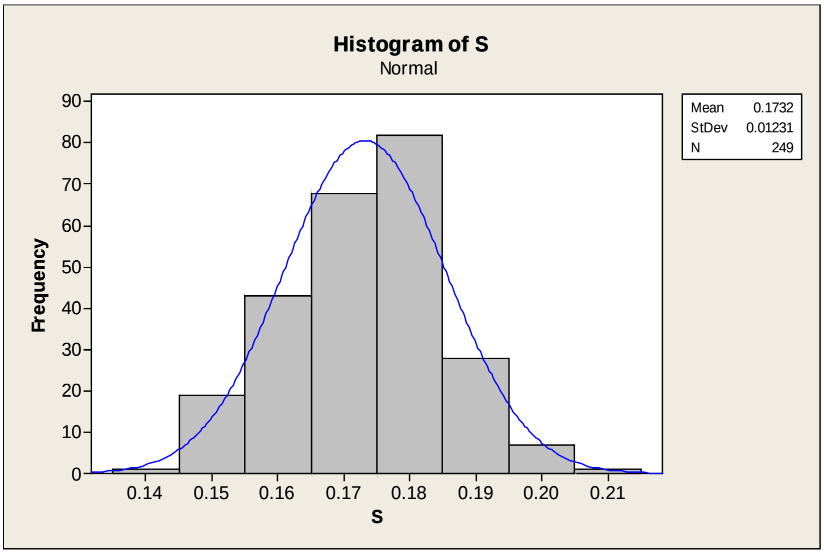


Figure 74 Histogram showing measured sulphur data in XRAL01A. Values are % S.

ANTIMONY Sb

The Shewhart plots for antimony showed poor precision across the range. Most reference materials contained levels close to the detection limit, XRAL01A contained levels that exceeded forty times the calibration range, but Till-1 and LWRPALA were just above the calibration range and within the range respectively and still demonstrated poor precision.

SELENIUM Se

Due to low concentrations present in most of the reference materials only the Shewhart chart for XRAL01A could be plotted. This was pixellated since the data were only quoted to one significant figure but, as the histogram shows, there were no issues with the accuracy or the precision of data as reported direct from the laboratory. The expected value for Selenium in this material is 4.05mg kg^{-1}.

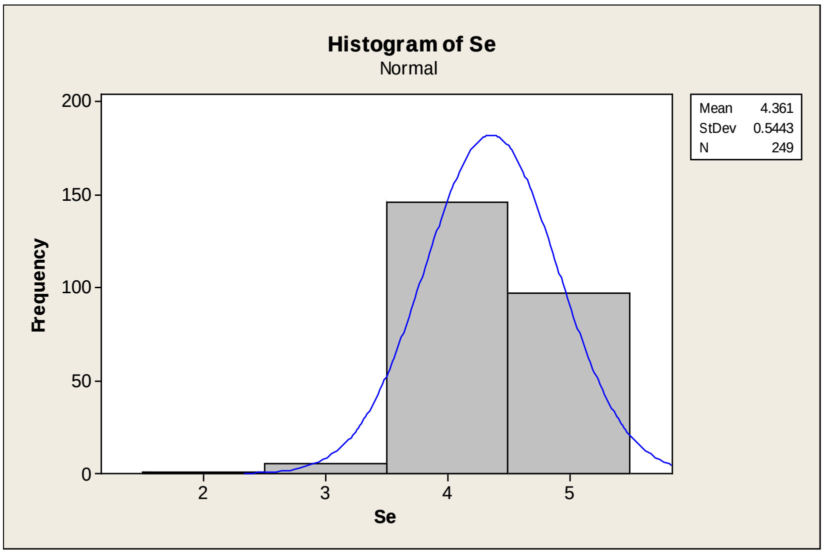


Figure 75 Histogram showing measured selenium data in XRAL01A. Values are in mg kg^{-1}.

TIN Sn

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory, although, as has been the case with some previous elements, reference material S13B gave high recoveries in September 2005. The histogram for data obtained from reference material XRAL01A shows a clear peak above the expected value of 2.39mg kg^{-1}.

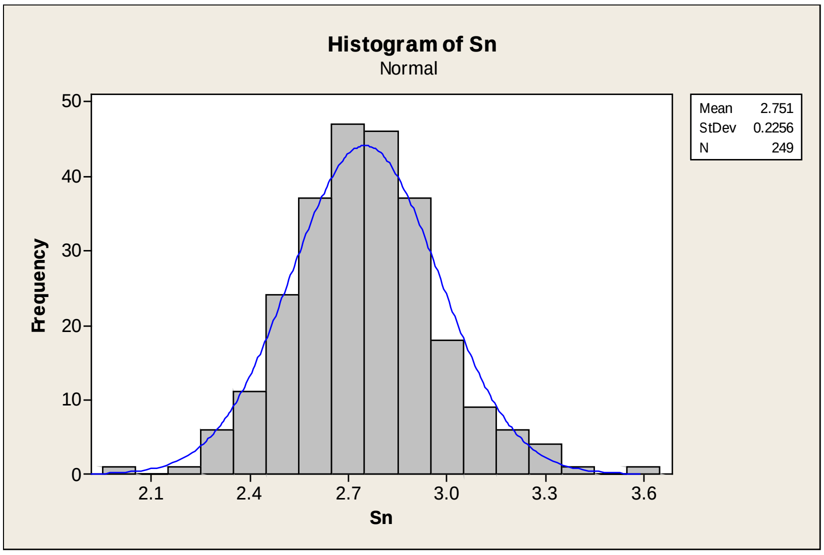


Figure 76 Histogram showing measured tin data in XRAL01A. Values are in mg kg^{-1}.

STRONTIUM Sr

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. As for some other elements, the reference material S13B gave one low result on 9/7/05, this is not seen for the other materials used. Although the Shewhart plot for XRAL01A looks evenly spread, the histogram reveals a bimodal distribution with a peak at the expected value of 62.39mg kg^{-1} and a second broad peak around 56mg kg^{-1}.

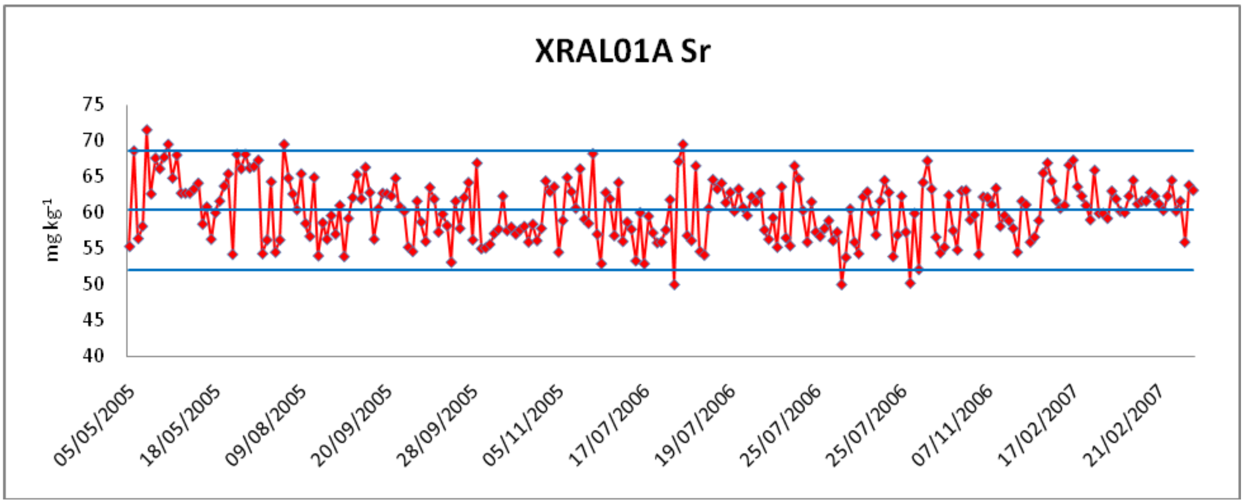


Figure 77 Shewhart chart for strontium in XRAL01A.

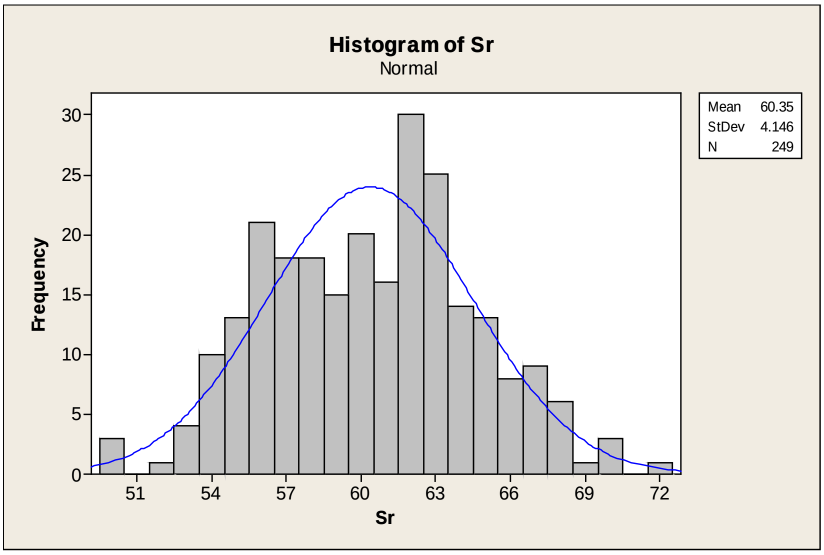


Figure 78 Histogram showing measured strontium data in XRAL01A. Values are in mg kg^{-1}.

THORIUM Th

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. There is a small positive bias compared to the expected value of 2.73mg kg^{-1} shown on the histogram for XRAL01A.

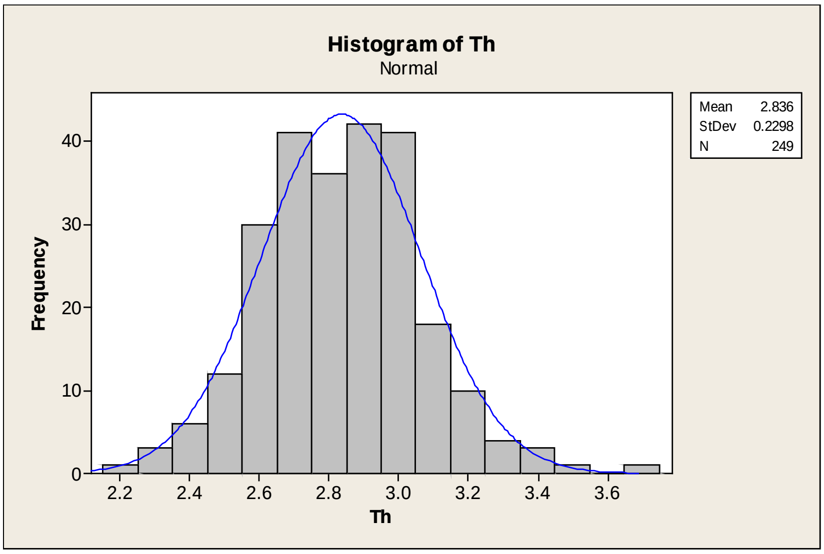


Figure 79 Histogram showing measured thorium data in XRAL01A. Values are in mg kg^{-1}.

URANIUM U

Shewhart plots of primary and secondary reference material data indicated that for most of the analytical period there were no systematic issues with the precision of data as reported direct from the laboratory. However, the plots for the secondary reference materials XRAL01A, S13B and DAL show an overall increase in reported concentration between 9/9/05 and 20/9/05, the changes are approximately 4%, 18% and 18% respectively. This is not seen for LWRPALA and Curr, the other materials included for analysis during this period. The histogram of data for XRAL01A shows that, although the data are centred on the expected concentration 3.57mg kg^{-1}, they are spread across a significant concentration range.

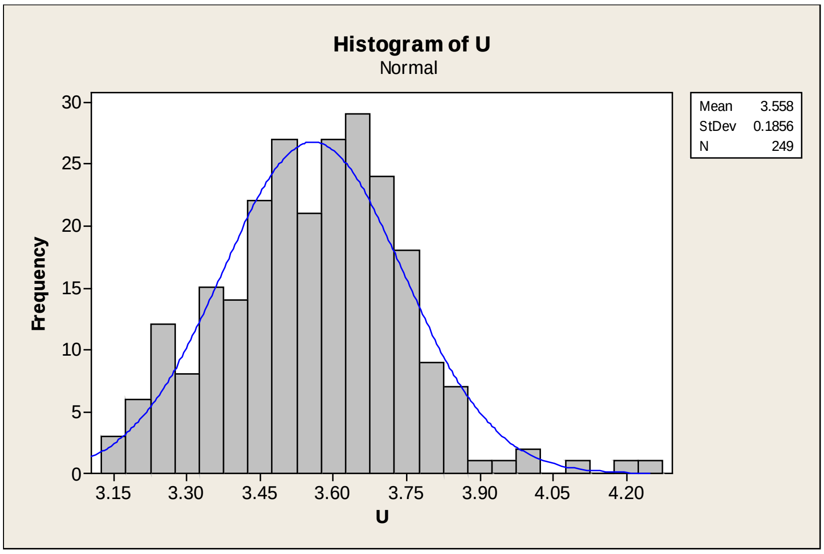


Figure 80 Histogram showing measured uranium data in XRAL01A. Values are in mg kg^{-1}.

VANADIUM V

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory, although, as has been the case with some previous elements, reference material S13B gave high recoveries in September 2005. A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

$$\text{Correction factor} = ([V] \times 0.7692) + 8.6253$$

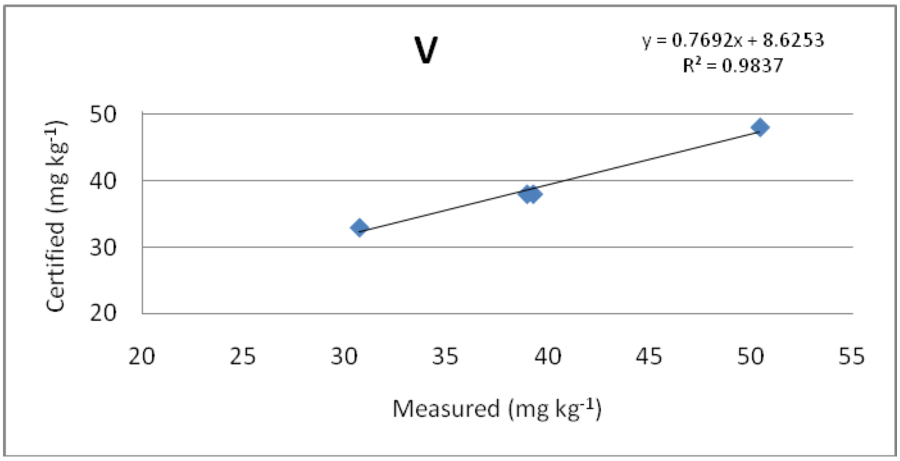


Figure 81 Regression plot for measured values against certified values for vanadium in Till-1, 2, 3 and 4.

The histogram of measured values for XRAL01A shows the data to be evenly distributed and centred on a mean close to the expected value of 225.5mg kg^{-1}.

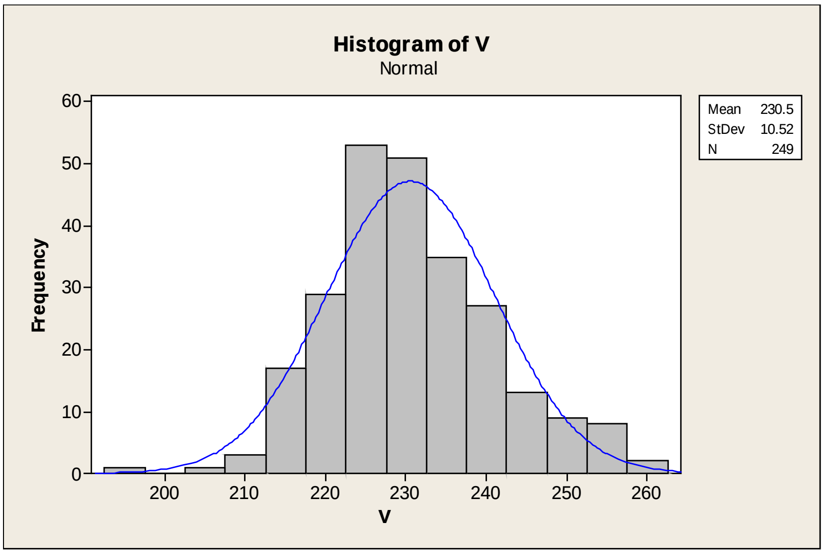


Figure 82 Histogram showing measured vanadium data in XRAL01A. Values are in mg kg^{-1}.

YTTRIUM Y

As for uranium, the Shewhart charts for the materials S13B, XRAL01A and Dal show above average values during September 2005. This pattern is not seen for the other reference materials. The histogram of measured data from XRAL01A shows a broad spread of data above the expected vale of 9.38mg kg^{-1}.

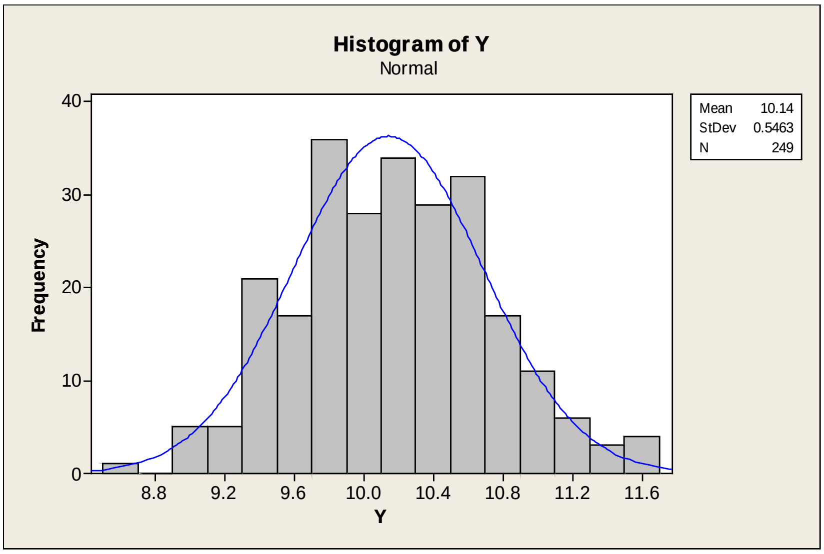


Figure 83 Histogram showing measured yttrium data in XRAL01A. Values are in mg kg^{-1}.

ZINC Zn

Shewhart plots of primary and secondary reference material data indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. As for some other elements, the reference material S13B gave one low result on 9/7/05, this is not seen for the other materials used.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Zn] x 1.0547) + 2.3118

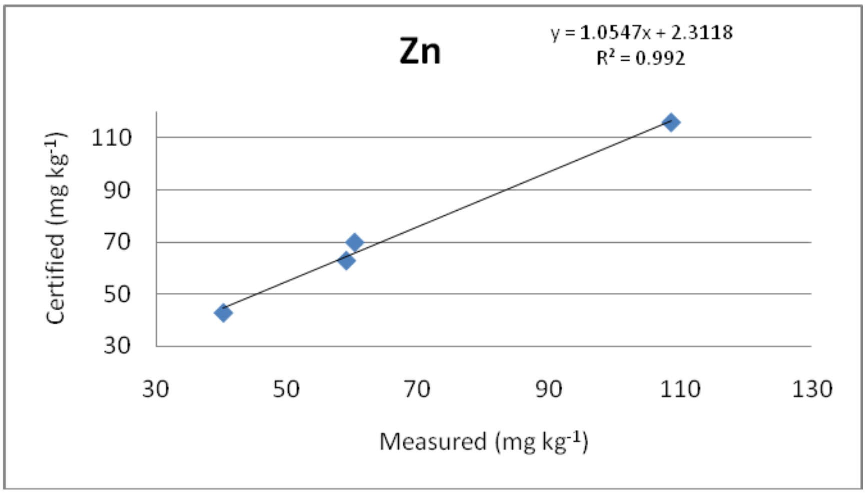


Figure 84 Regression plot for measured values against certified values for zinc in Till-1, 2, 3 and 4.

The histogram shows the data to cover a broad spread, but with a clear peak close to the expected value of 179.2mg kg^{-1}.

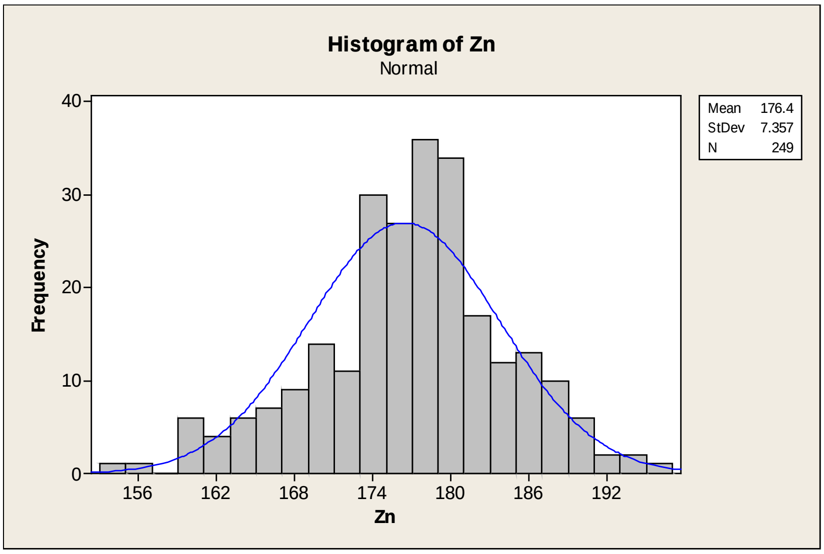


Figure 85 Histogram showing measured zinc data in XRAL01A. Values are in mg kg^{-1}

ZIRCONIUM Zr

As for caesium, the Shewhart charts for XRAL01A and DAL show a step change between the samples that were analysed during 2005 and those that were analysed later. However, the step is not in the same direction for the two materials and so it is not possible to determine a factor to correct between the two analytical periods. The other reference materials did not show any change between the sets of data.

The histogram shows a fairly broad spread of data centred close to the expected value of 6.5mg kg^{-1}.

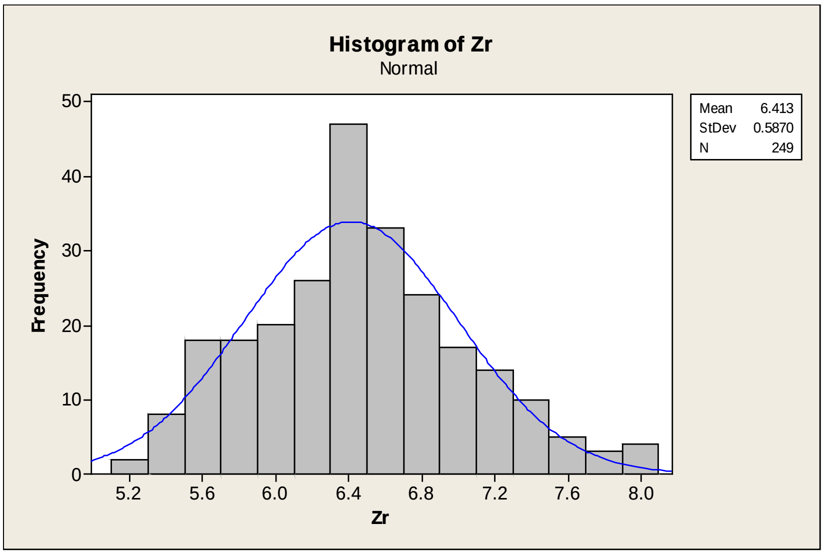


Figure 86 Histogram showing measured zirconium data in XRAL01A. Values are in mg kg^{-1}.

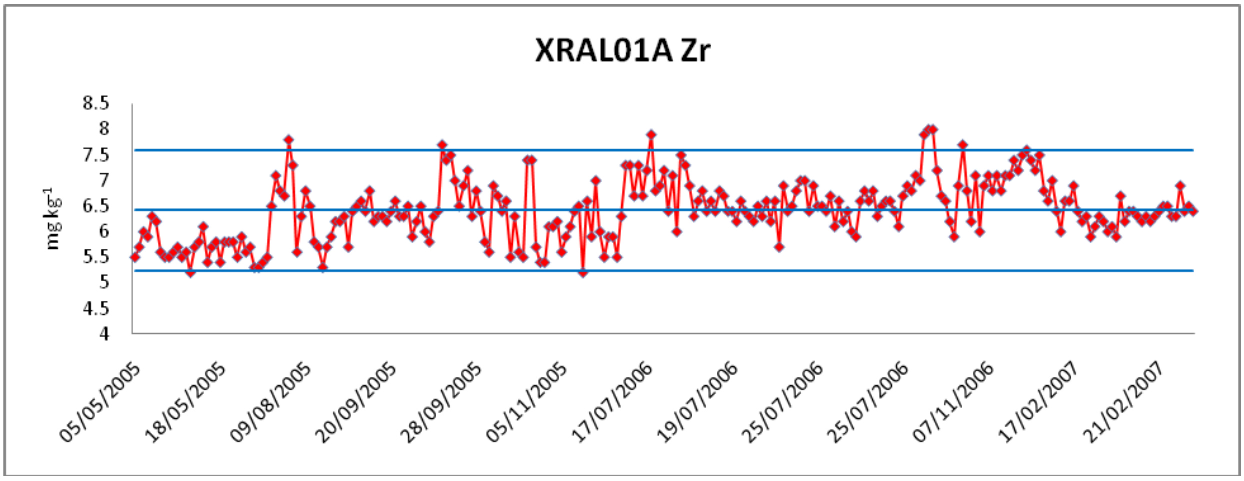


Figure 87 Shewhart plot for zirconium in XRAL01A.

Appendix 2: Detailed quality assessment for *aqua regia* partial digest ICP analysis of Tellus 'S' soils

The following section includes a discussion of data quality on an element by element basis. Correction factors are supplied where appropriate however they should not be applied unless recommended based on the certainty data quality will improve. Recommended correction factors are discussed in **Chapter 4.2.3**

SILVER Ag

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Ag] x 1.1548) – 0.0507

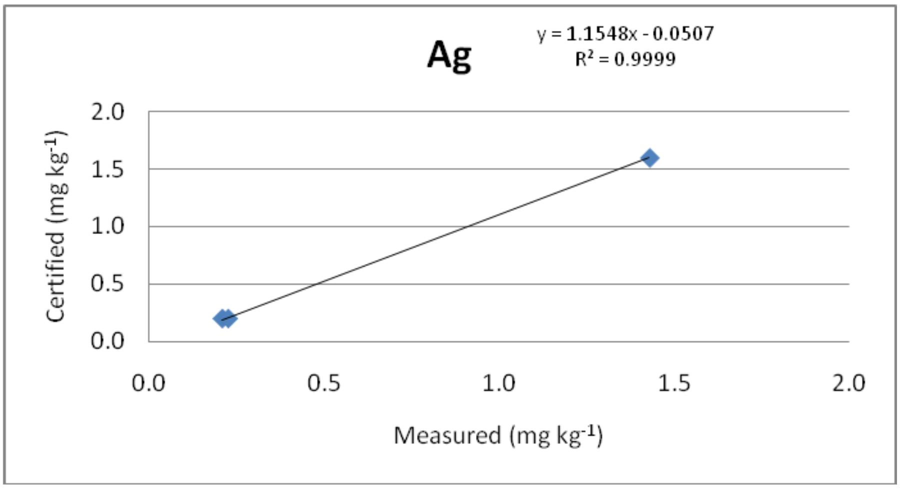


Figure 88 Regression plot for measured values against certified values for silver in Till-1, 2, 3 and 4.

ALUMINIUM Al

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram for measured concentrations from XRAL01A shows a peak near the expected value but with a second peak approximately 10% lower. The Shewhart charts do not indicate a particular period of low concentration data; therefore no correction can be made for this.

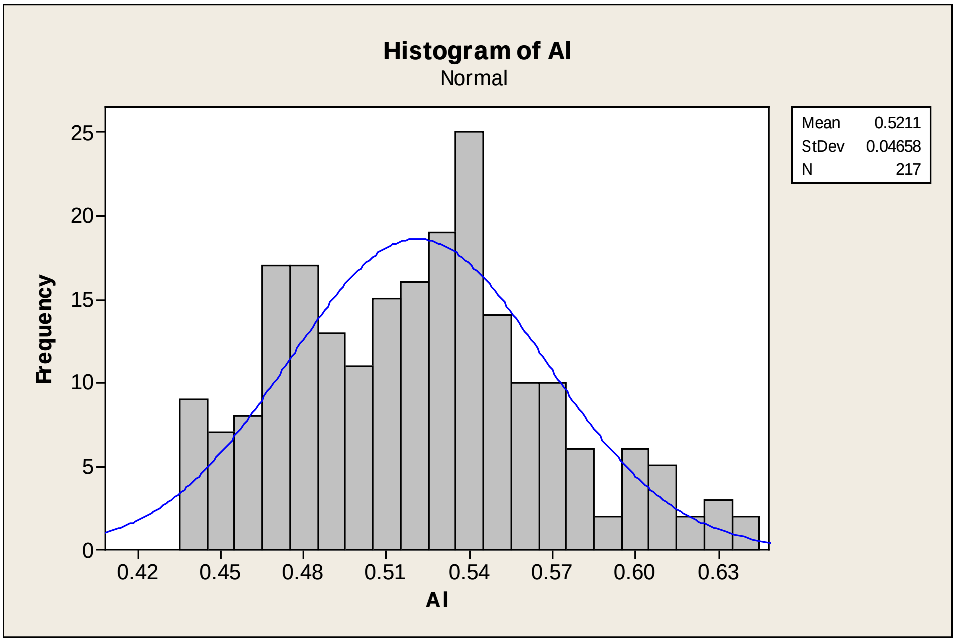


Figure 89 Histogram showing measured aluminium data in XRAL01A against the expected value. Values are % Al.

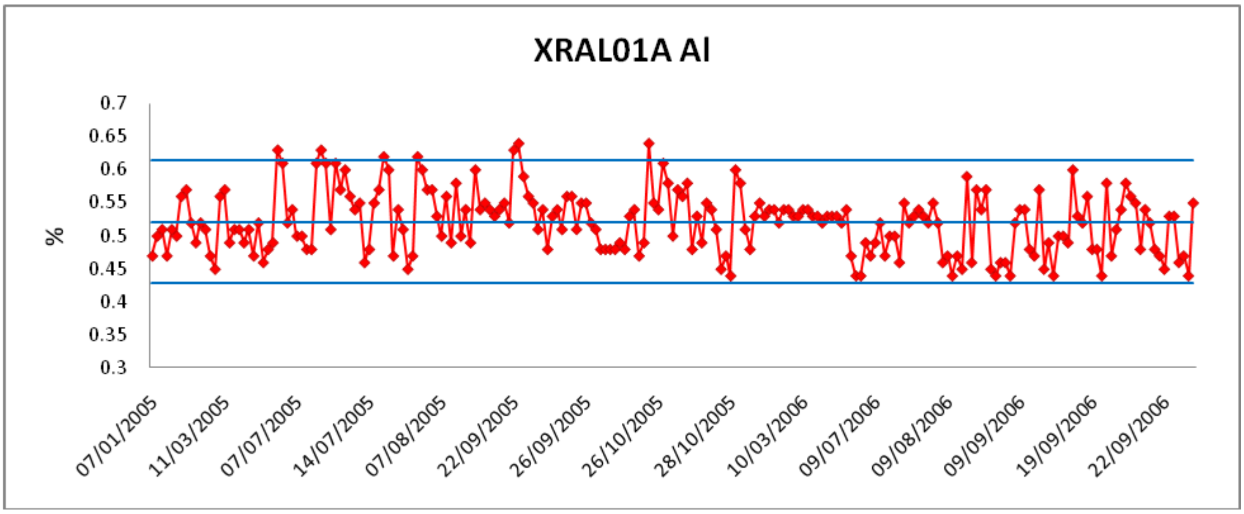


Figure 90 Shewhart chart for aluminium in XRAL01A.

ARSENIC As

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([As] x 1.1397) – 1.611

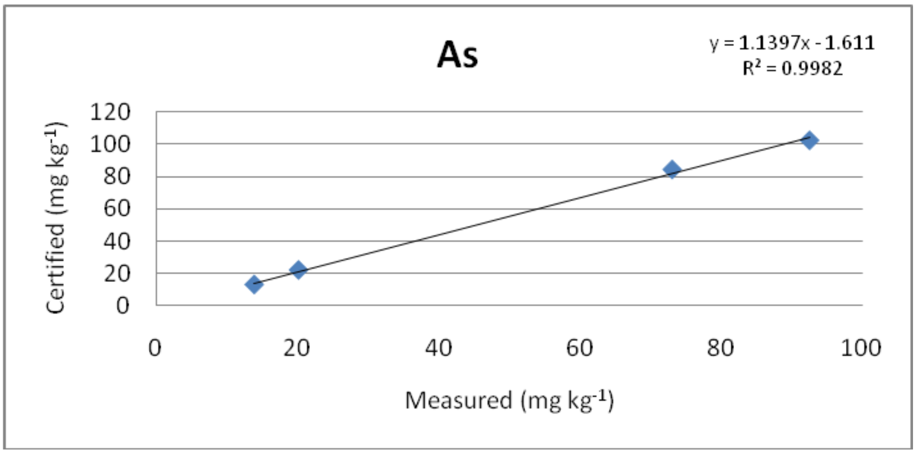


Figure 91 Regression plot for measured values against certified values for arsenic in Till-1, 2, 3 and 4.

BARIUM Ba

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory for most of the materials. However, there is an apparent step change that occurs on 19/09/2006 for the reference material XRAL01A. This step represents a concentration change of approximately 10% at this level. Only one primary reference material, Till-2, was analysed beyond this period, this also exhibits a step change. It should also be noted that the mean for the barium concentration in XRAL01A was 2747mg kg^{-1}, well below the expected value of 3540 mg kg^{-1}, even if the correction factor is applied to it. This could be due to the unusually high concentration in this sample, which falls well above the calibration range. The wide spread of results at this level is clear from the histogram for XRAL01A.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Ba] x 0.9503) + 7.8456

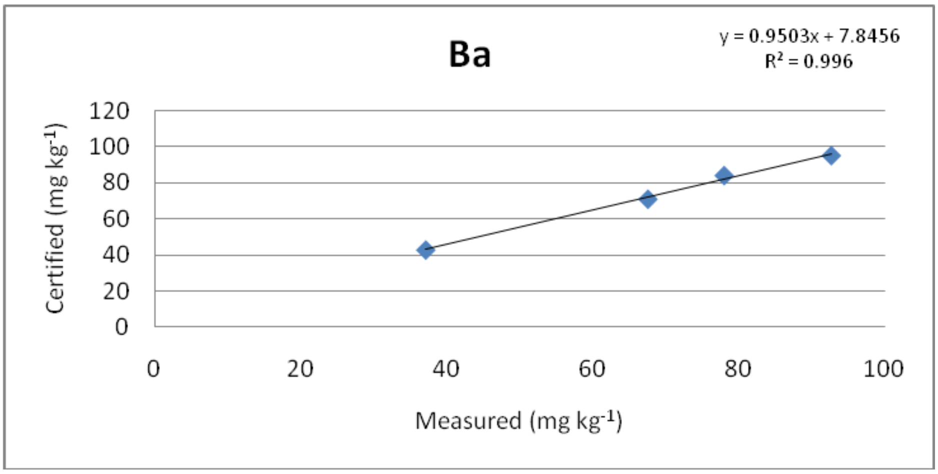


Figure 92 Regression plot for measured values against certified values for barium in Till-1, 2, 3 and 4.

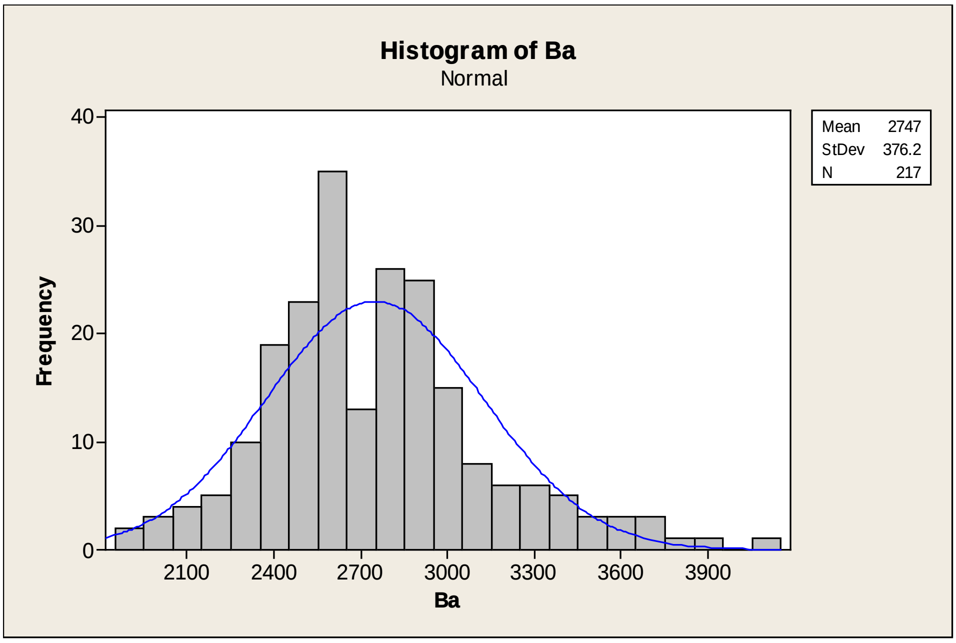


Figure 93 Histogram showing measured barium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

BISMUTH Bi

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Bi] x 1.0499) – 1.3196

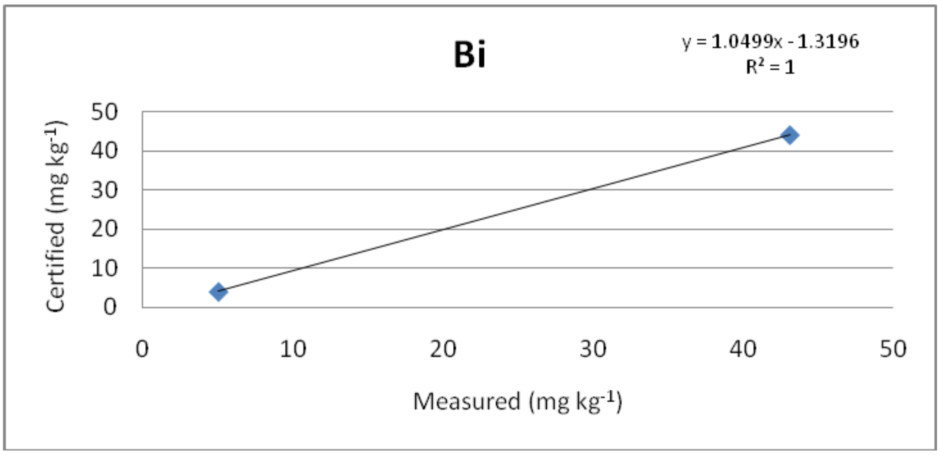


Figure 94 Regression plot for measured values against certified values for bismuth in Till-2 and 4.

CALCIUM Ca

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

The histogram for the reference material XRAL01A shows a wide distribution of data centred just below the expected value.

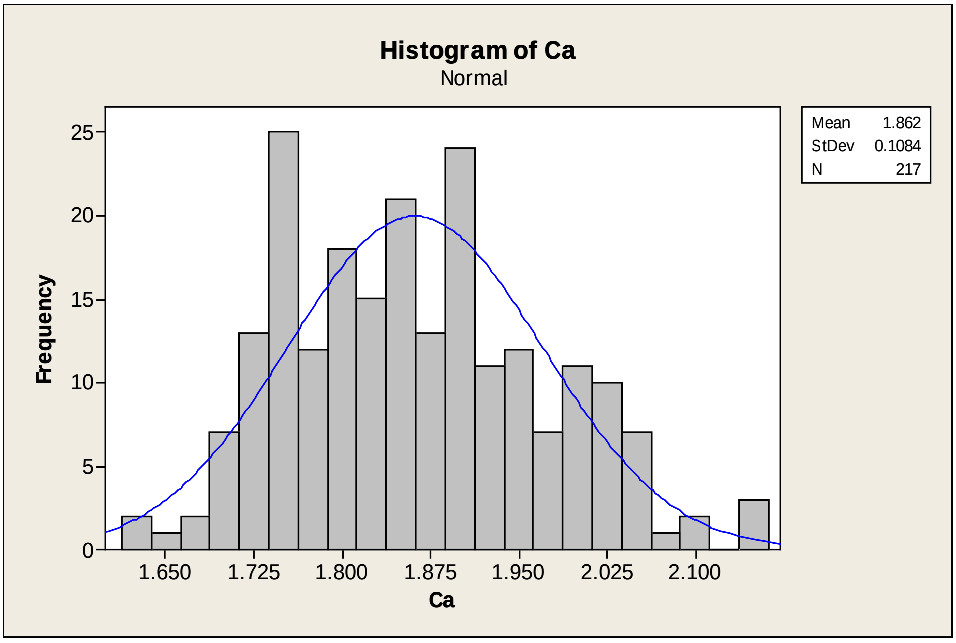


Figure 95 Histogram showing measured calcium data in XRAL01A against the expected value. Values are % Ca.

CADMIUM Cd

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

There were insufficient values for the reference materials to plot a regression. The histogram for XRAL01A shows the data to be distributed approximately 0.2mg kg^{-1} above the expected value.

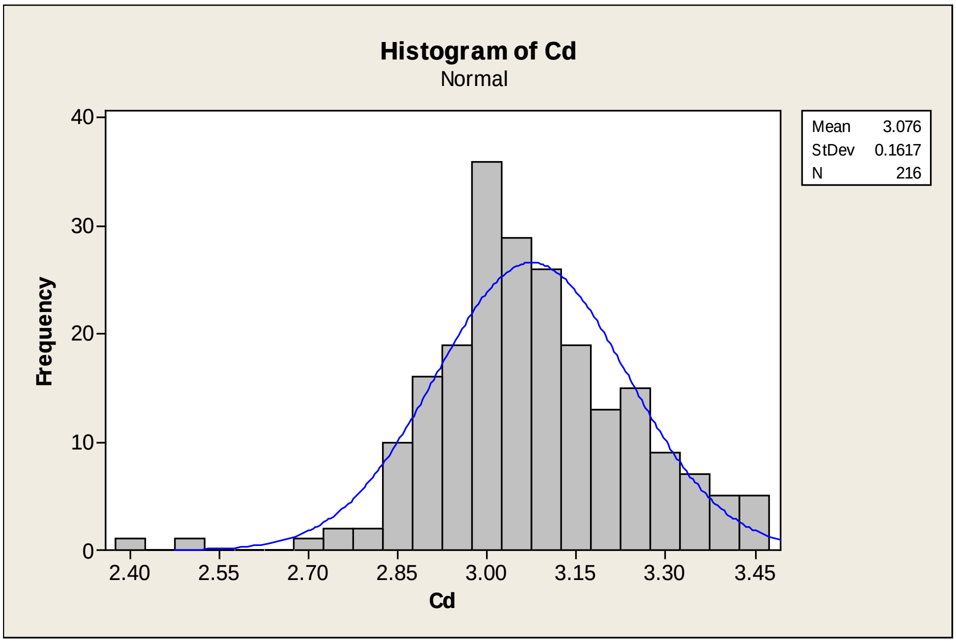


Figure 96 Histogram showing measured cadmium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

CERIUM Ce

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. This is confirmed by the histogram for XRAL01A.

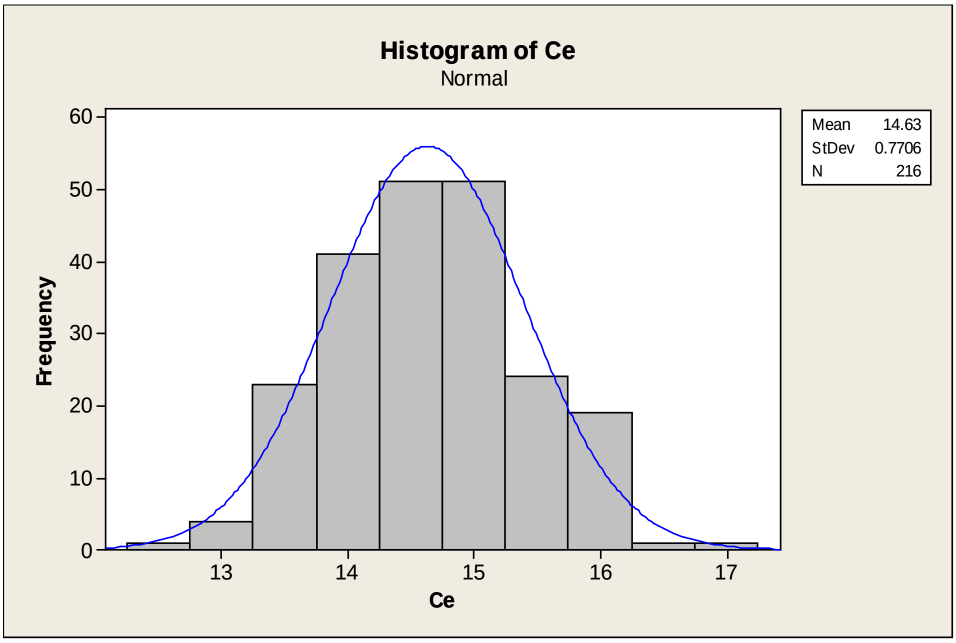


Figure 97 Histogram showing measured cerium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

COBALT Co

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Co] x 1.0811) + 0.2179

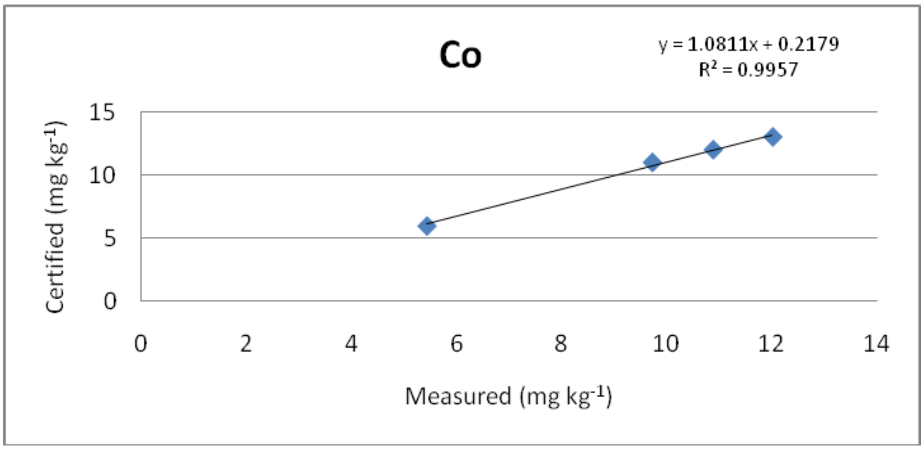


Figure 98 Regression plot for measured values against certified values for cobalt in Till-1, 2, 3 and 4.

CHROMIUM Cr

Shewhart plots of primary and secondary reference material data indicated no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Cr] x 1.2614) – 4.1432

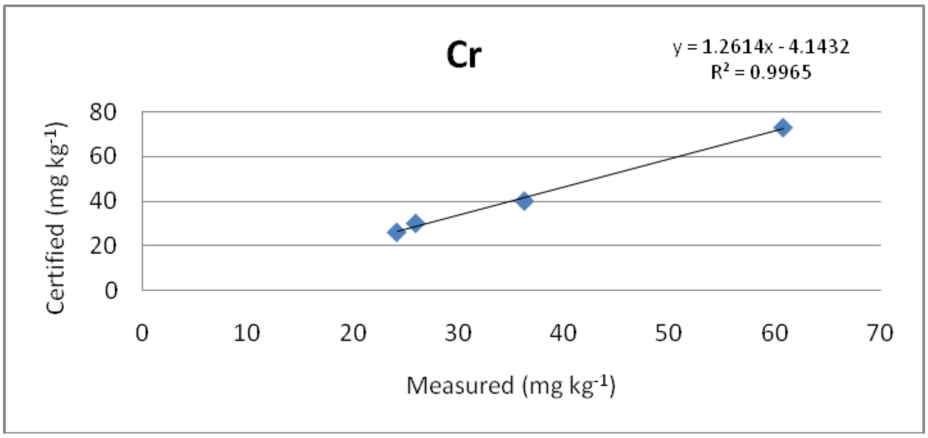


Figure 99 Regression plot for measured values against certified values for chromium in Till-1, 2, 3 and 4.

CAESIUM Cs

The histogram for XRAL01A shows a bimodal distribution and all values falling well below the expected concentration of 1.84mg kg^{-1}. The lower peak is probably due to measurements made in late September and October 2006, a period characterised by a step change in the Shewhart charts for several elements, particularly in this standard. Ideally the data should have factors applied to them to correct for this error and the low data throughout the measurement period, but there is insufficient data to reliably gauge the magnitude of the correction.

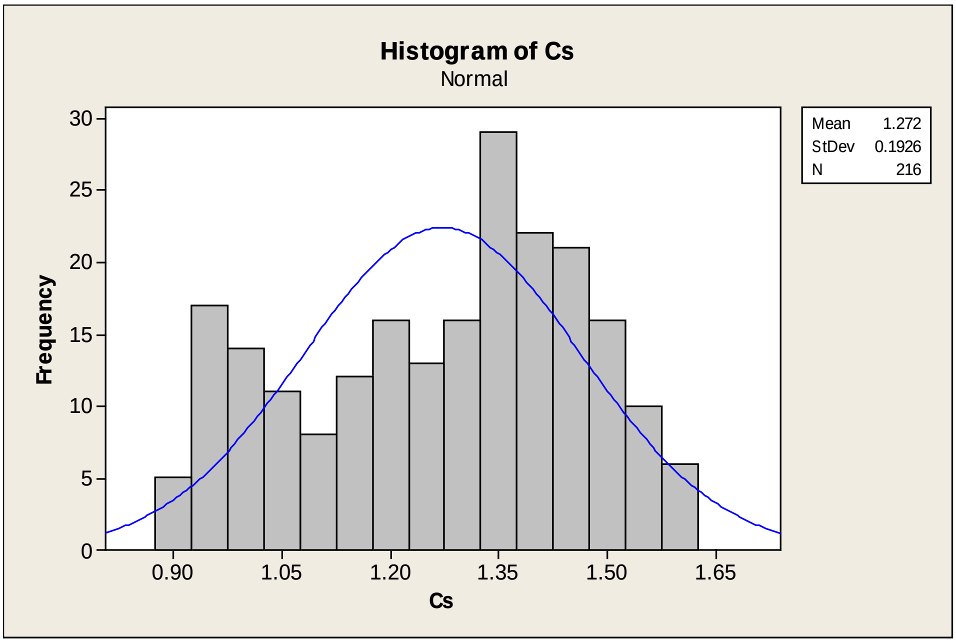


Figure 100 Histogram showing measured caesium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

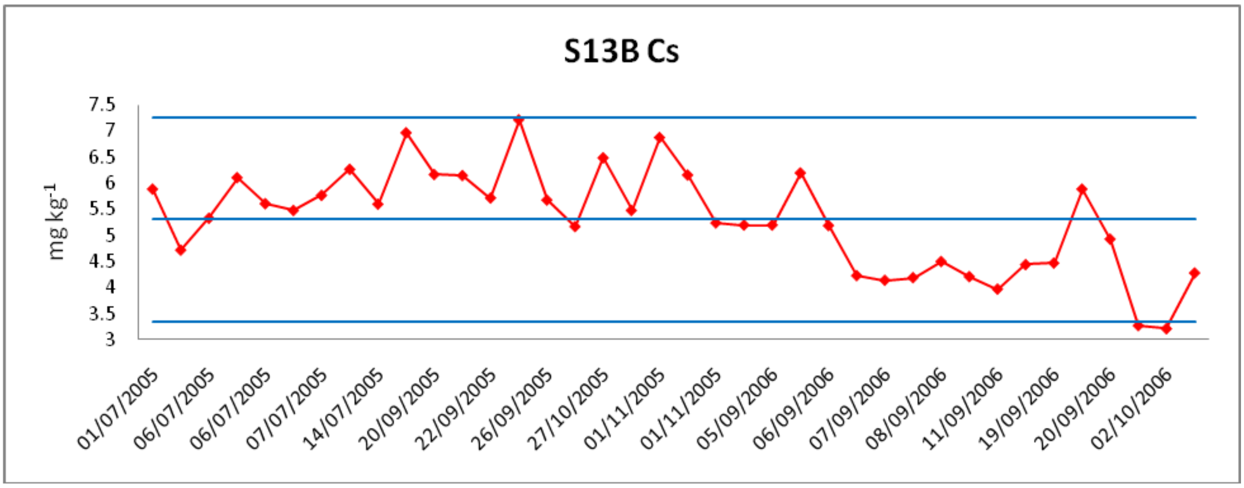


Figure 101 **Shewhart chart for caesium in S13B.**

COPPER CU

Some Shewhart charts showed brief periods where the measured values fell outside the accepted range. However, these were not consistent between materials and so have not been corrected for. A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Cu] x 1.055) + 0.5091

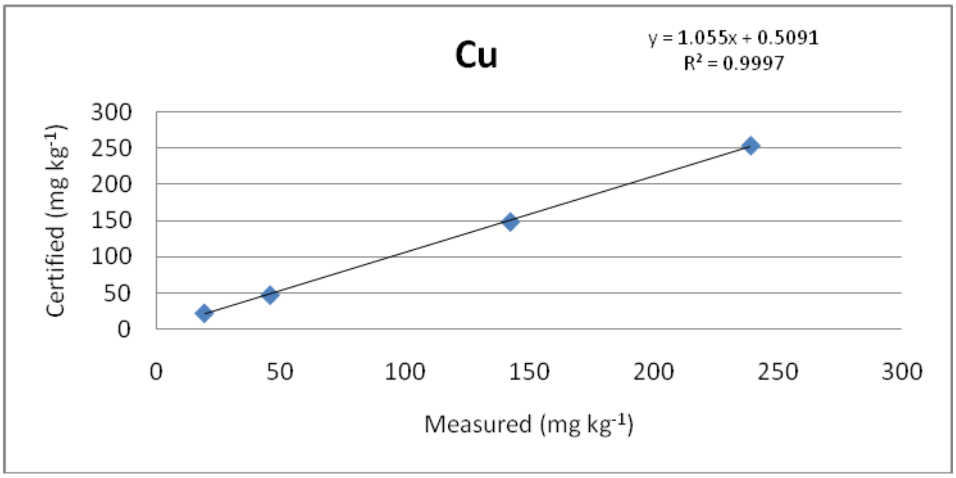


Figure 102 Regression plot for measured values against certified values for copper in Till-1, 2, 3 and 4.

IRON Fe

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Fe] x 0.8368) + 0.4527

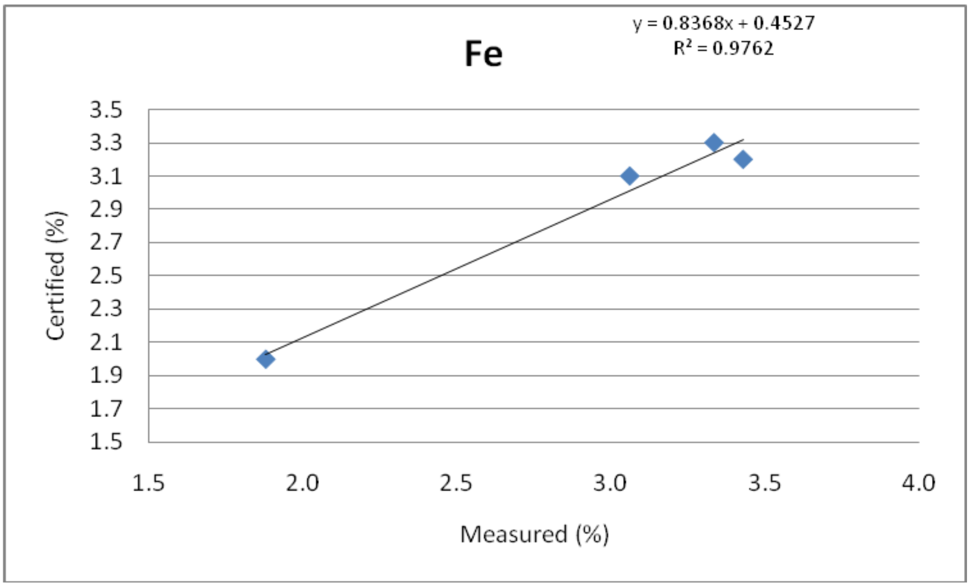


Figure 103 Regression plot for measured values against certified values for iron in Till-1, 2, 3 and 4.

GALLIUM Ga

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram indicates a positive bias in the data for XRAL01A, with most concentrations lying above the expected concentration.

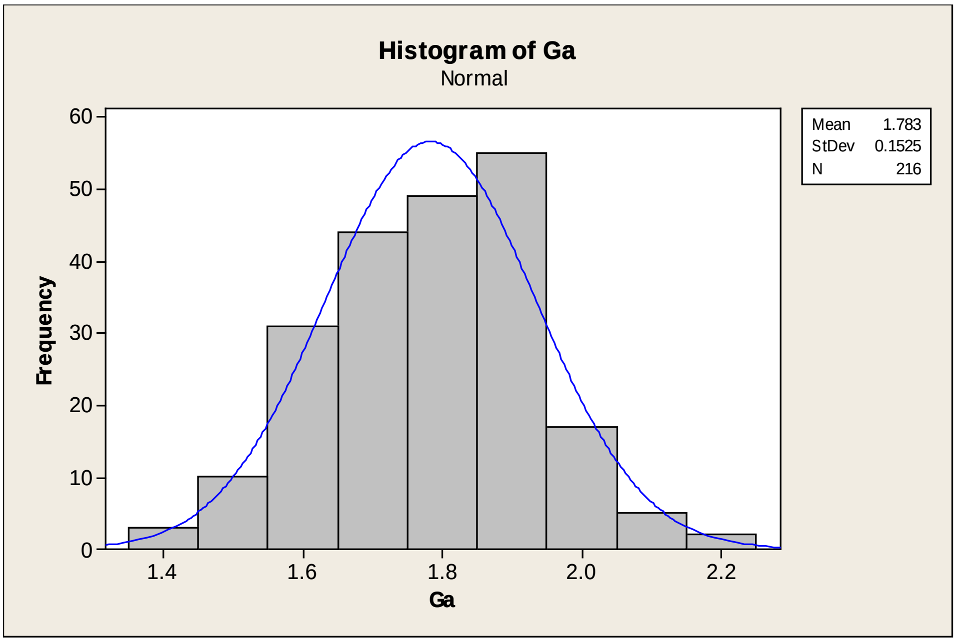


Figure 104 Histogram showing measured gallium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

POTASSIUM K

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

The histogram for XRAL01A is slightly skewed to the left, but with the majority of the data within 0.01% of the expected value.

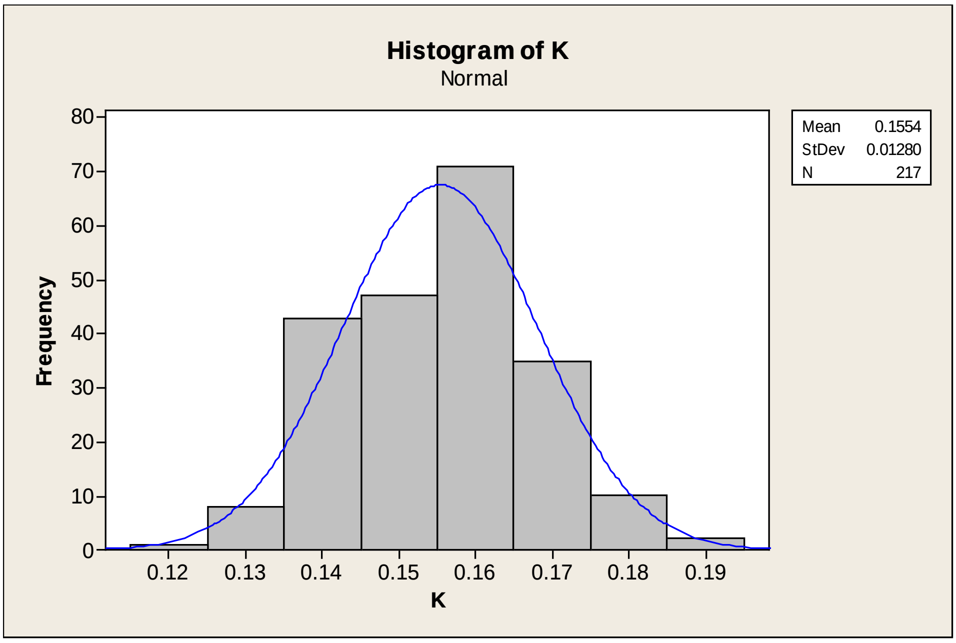


Figure 105 Histogram showing measured potassium data in XRAL01A against the expected value. Values are % K.

LANTHANUM La

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. There is no significant bias shown on the histogram for XRAL01A.

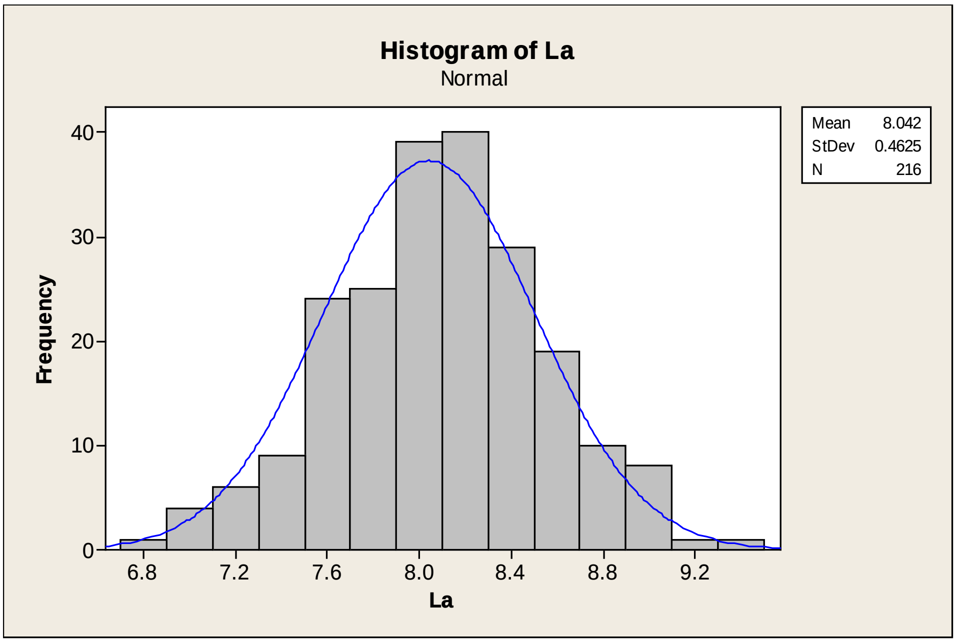


Figure 106 Histogram showing measured lanthanum data in XRAL01A against the expected value. Values are in mg kg^{-1}.

LITHIUM Li

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. Unfortunately XRAL01A was the only reference material for which an expected value for lithium was quoted and that was just 3.5 times the limit of detection. However, the histogram shows the data to be remarkably accurate at this level.

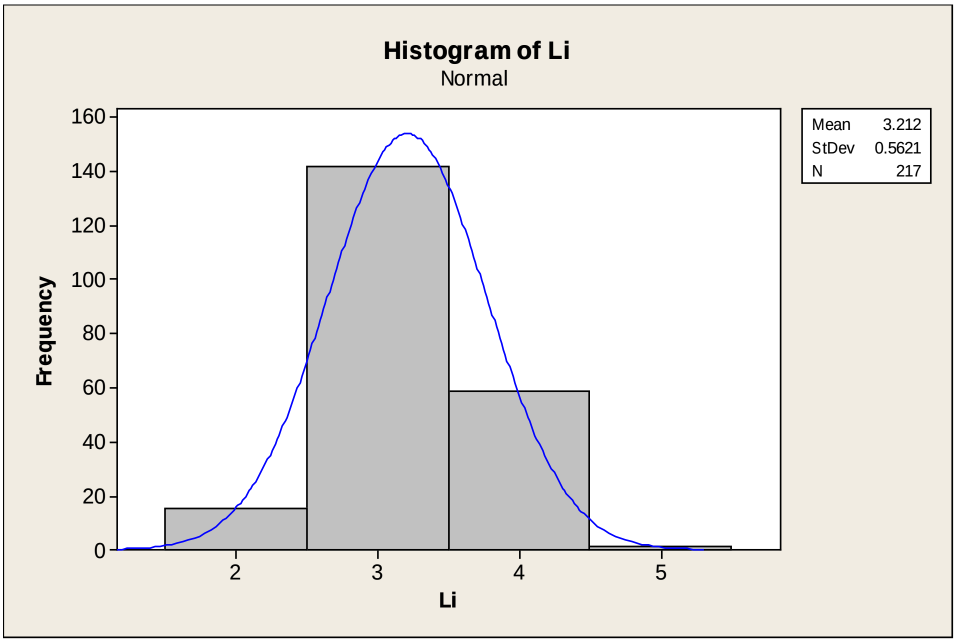


Figure 107 Histogram showing measured lithium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

MAGNESIUM Mg

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

The histogram for XRAL01A shows that the data are skewed slightly to the right of the expected value, but with the majority of the data within 0.01% of the expected value.

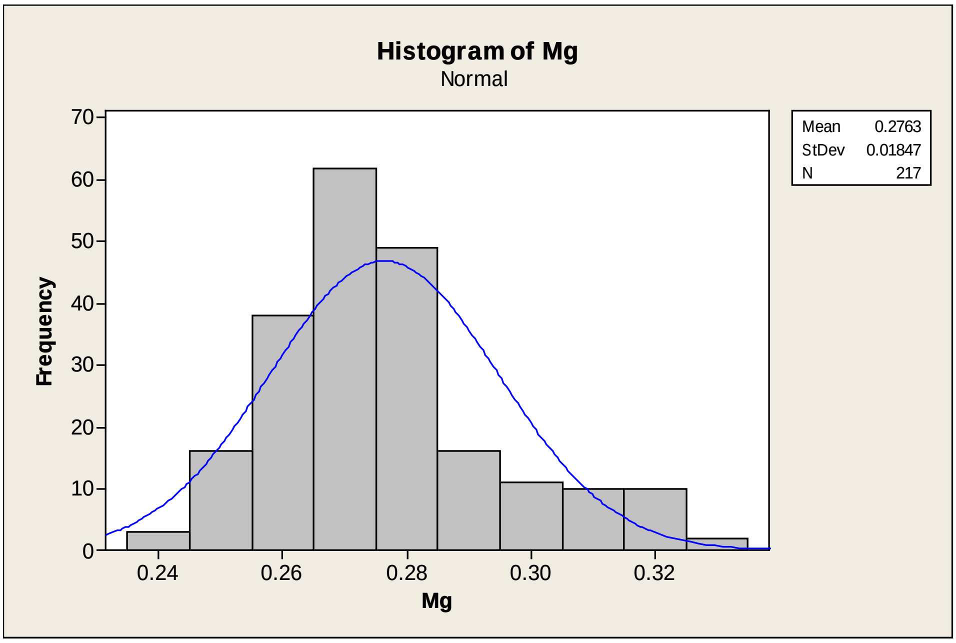


Figure 108 Histogram showing measured magnesium data in XRAL01A against the expected value. Values are % Mg.

MANGANESE Mn

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory for most of the materials. However, there is an apparent step change that occurs on 19/09/2006 for the reference material XRAL01A and less obviously for S13B. This step represents a concentration change of approximately 10% at this level. Only one primary reference material, Till-2, was analysed beyond this period, this also exhibits a step change. The effect of the step change is clear on the histogram for XRAL01A with a cluster of data points occurring separate from the main group. Insufficient data are available to make a valid correction to the sample data during this period.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Mn] x 0.8125) + 45.138

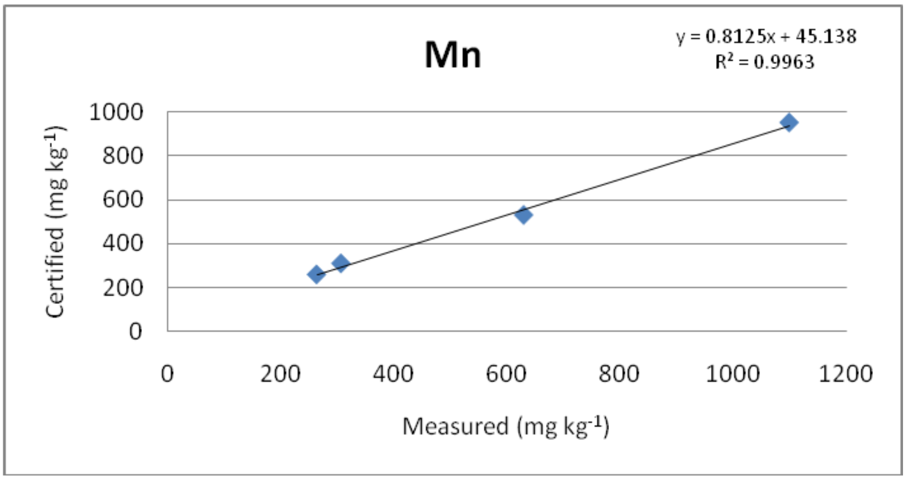


Figure 109 Regression plot for measured values against certified values for manganese in Till-1, 2, 3 and 4.

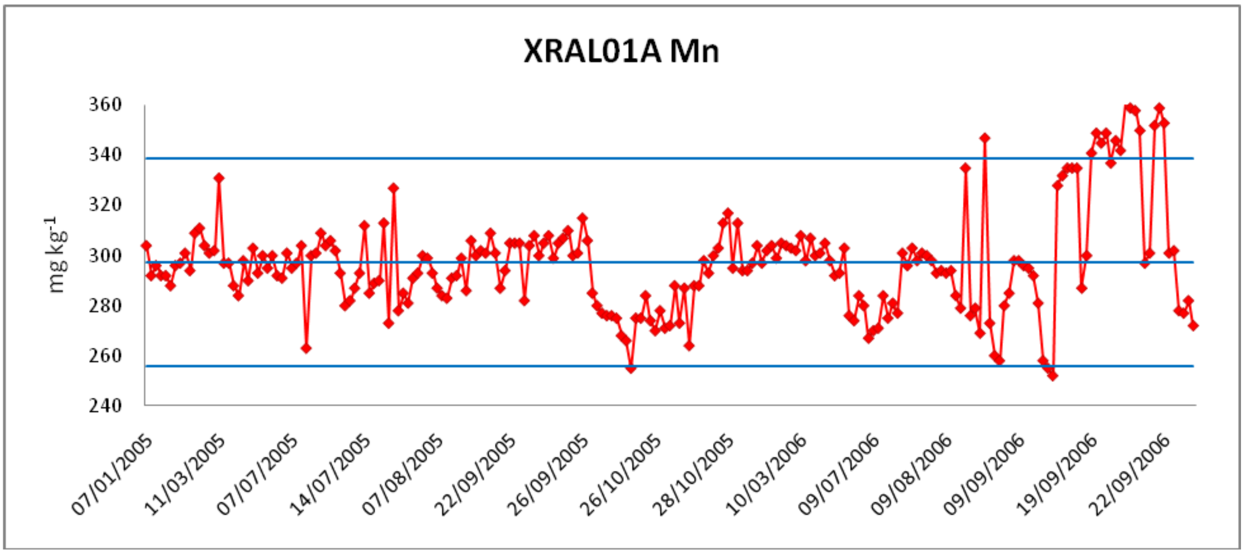


Figure 110 Shewhart chart for manganese in XRAL01A.

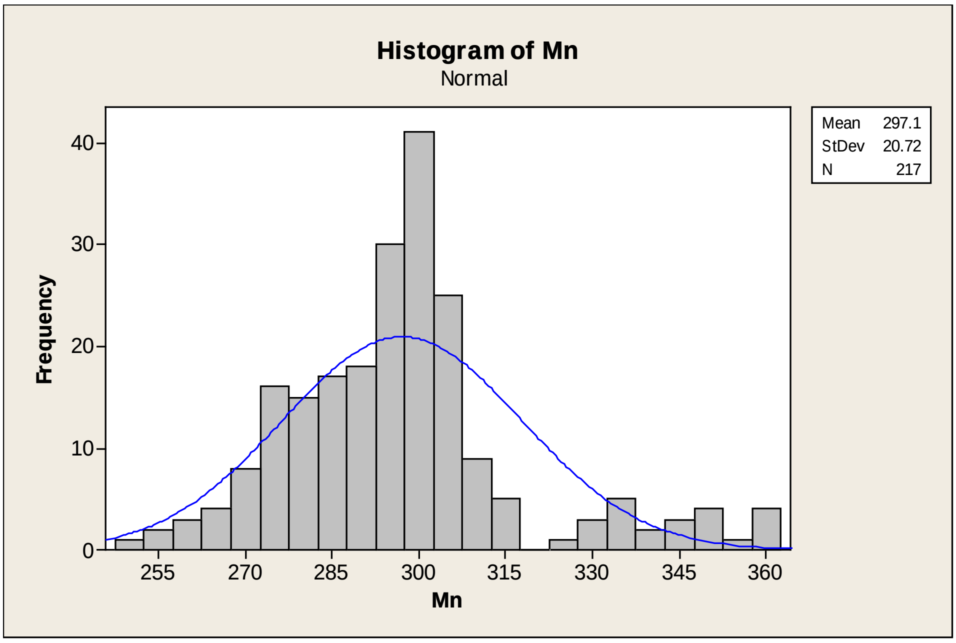


Figure 111 Histogram showing measured manganese data in XRAL01A against the expected value. Values are in mg kg^{-1}.

MOLYBDENUM Mo

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out, but only two relatively similar data points were available. The histogram for the data obtained for XRAL01A, shows a broad spread of results either side of the expected value showing the poor precision for molybdenum analysis at this level. No correction factor was applied to the sample data.

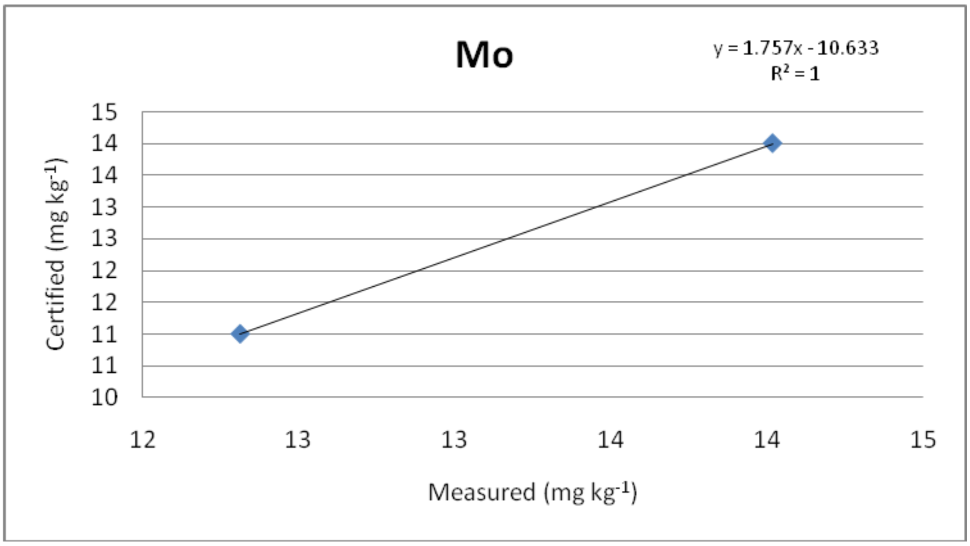


Figure 112 Regression plot for measured values against certified values for molybdenum in Till-2 and 4.

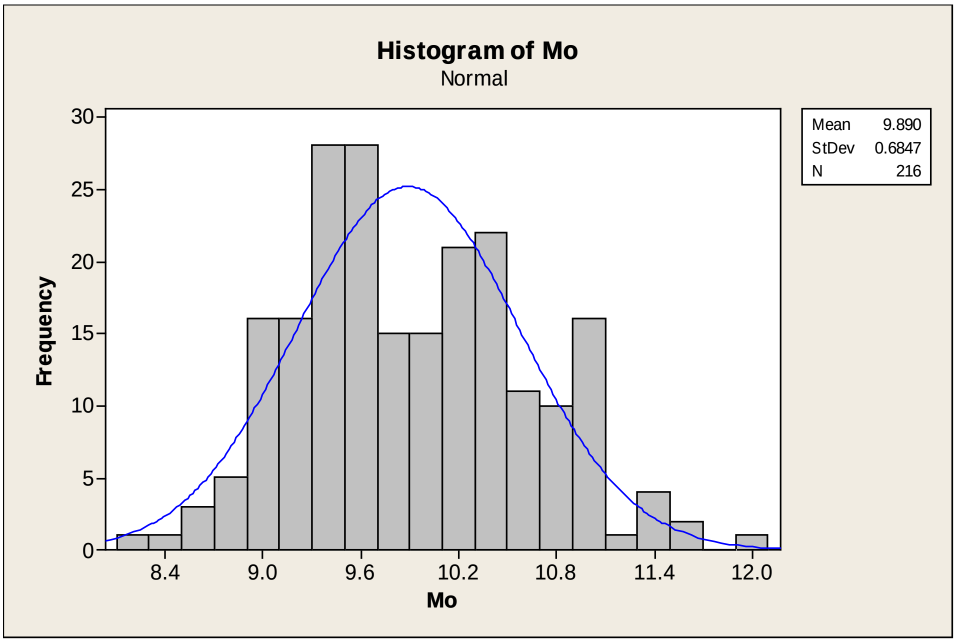


Figure 113 Histogram showing measured molybdenum data in XRAL01A against the expected value. Values are in mg kg^{-1}.

NICKEL NI

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Ni] x 0.9781) + 0.589

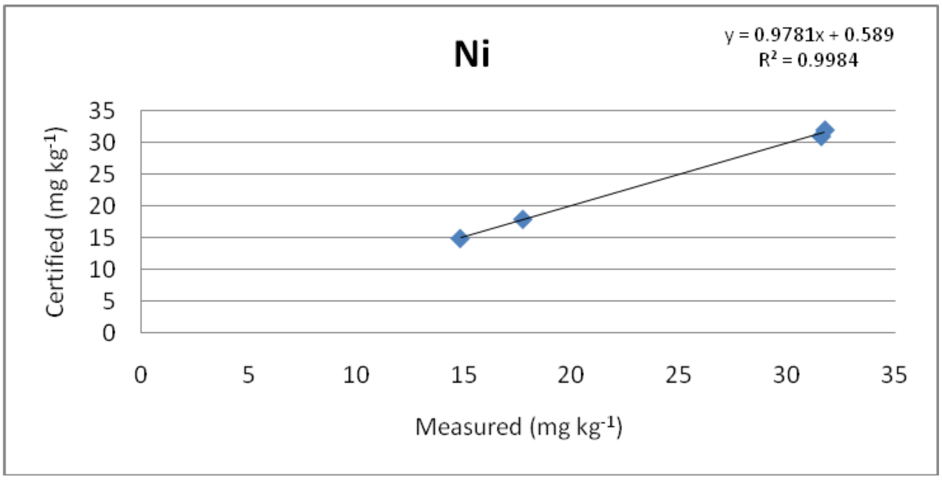


Figure 114 Regression plot for measured values against certified values for nickel in Till-1, 2, 3 and 4.

PHOSPHORUS P

There are several places in the reference materials where the phosphorus concentration is reported as below the detection limit, despite the usual value being well above it. These occur on 13/9/06 and 09/12/06, although there are other data points on these days that are good. It is not possible to correct for this in any way, but any phosphorus data reported as below the detection limit should be treated with caution. There are times during the measurement period that the reference material XRAL01A consistently measured up to 14% above the mean value. This is reflected in the shape of the histogram, but this pattern did not occur for the other reference materials.

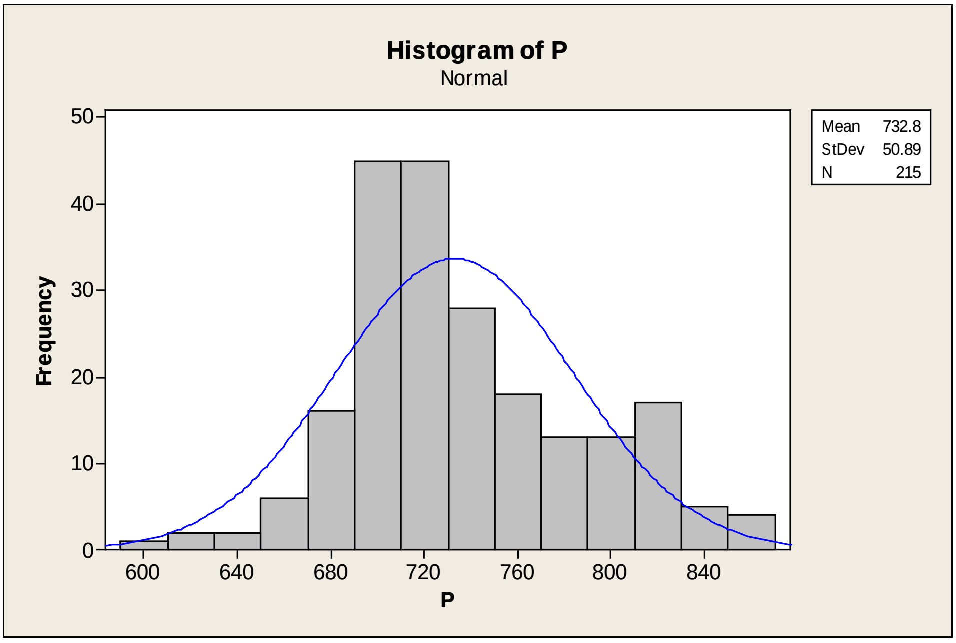


Figure 115 Histogram showing measured phosphorus data in XRAL01A against the expected value. Values are in mg kg^{-1}.

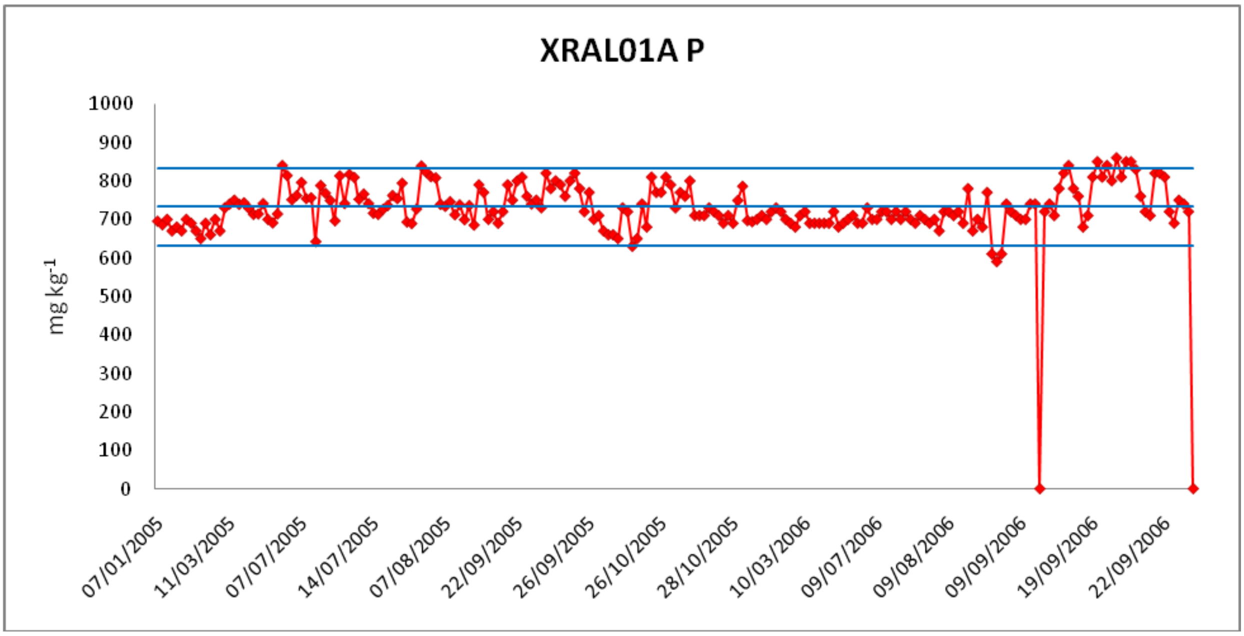


Figure 116 Shewhart chart for phosphorus in XRAL01A.

LEAD Pb

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values was carried out and gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Pb] x 0.9832) – 2.0578

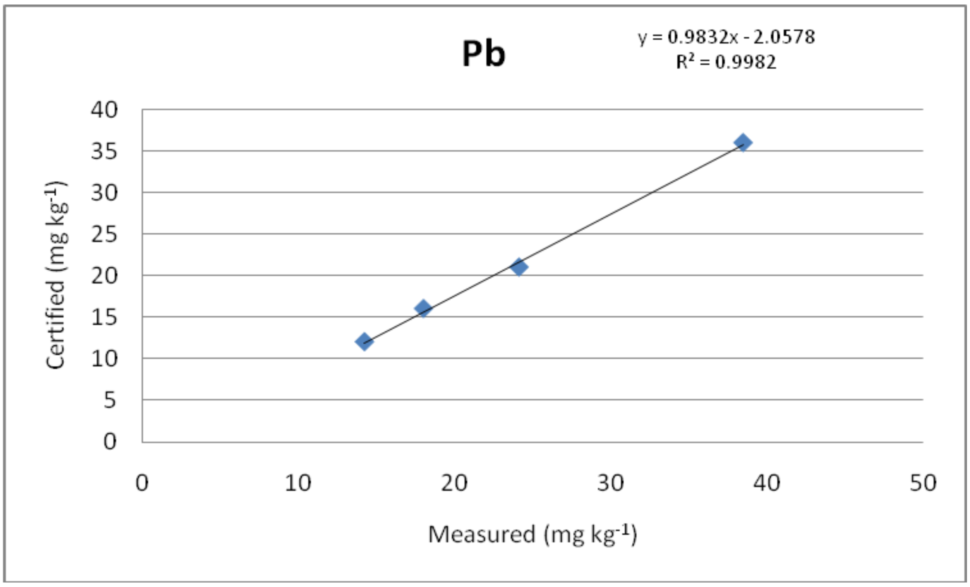


Figure 117 Regression plot for measured values against certified values for lead in Till-1, 2, 3 and 4.

RUBIDIUM Rb

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram for XRAL01A shows a bimodal distribution of concentrations, but with the mean coincident with the expected concentration.

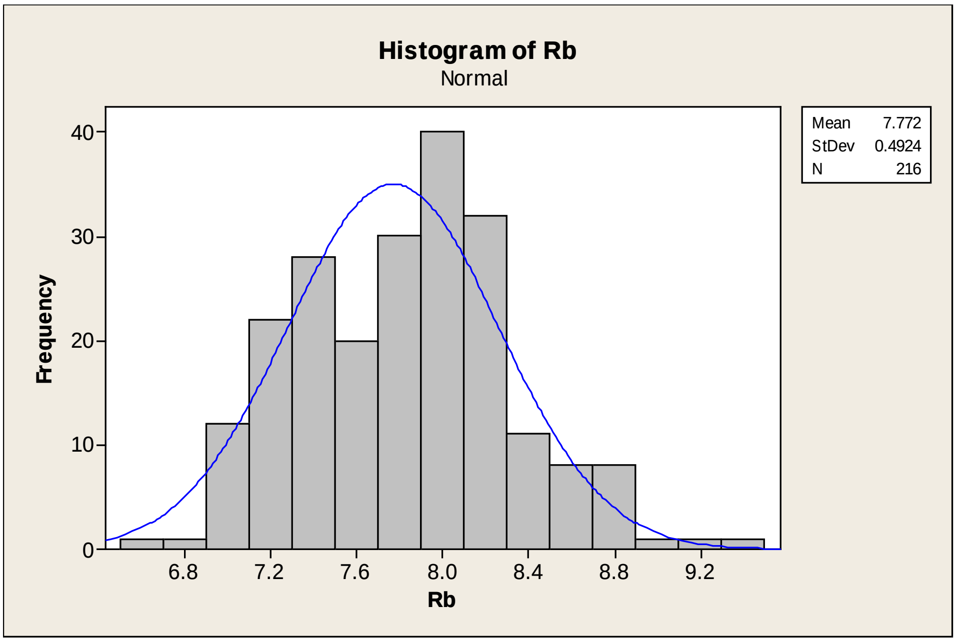


Figure 118 Histogram showing measured rubidium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

SULPHUR S

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram of measured concentrations for XRAL01A shows a slight negative bias.

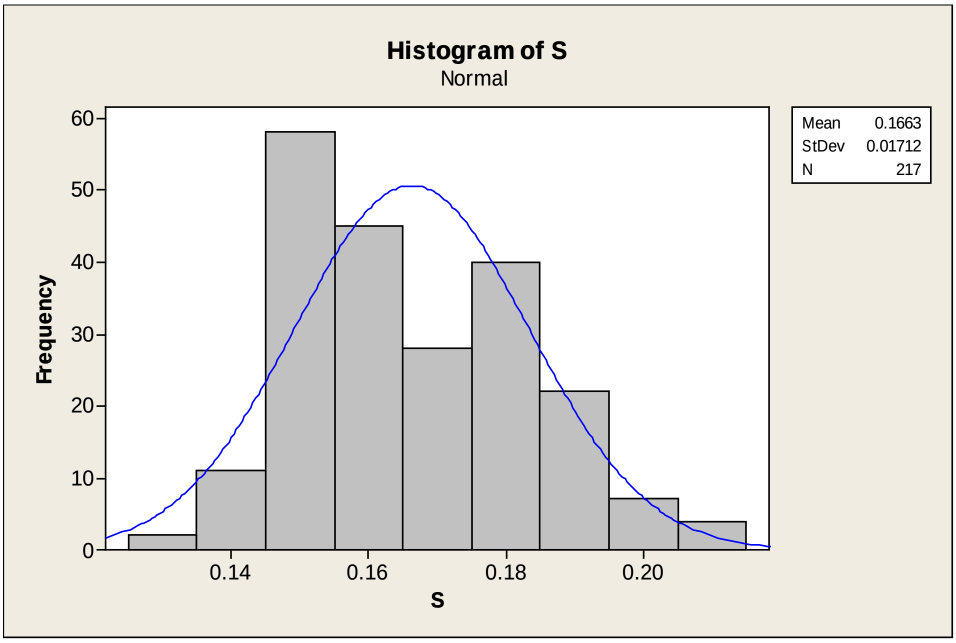


Figure 119 Histogram showing measured sulphur data in XRAL01A against the expected value. Values are % S.

ANTIMONY Sb

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram for XRAL01A indicates a slight negative bias, with the majority of results falling below the expected concentration.

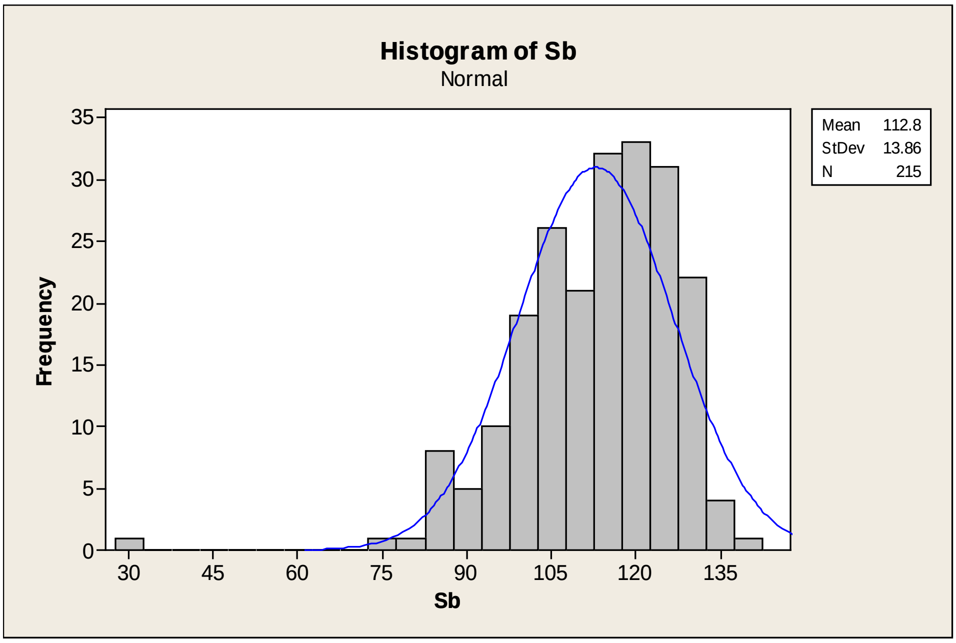


Figure 120 Histogram showing measured antimony data in XRAL01A against the expected value. Values are in mg kg^{-1}.

SELENIUM Se

Due to low concentrations present in most of the reference materials only the Shewhart chart for XRAL01A could be plotted. This was pixellated since the data were only quoted to one significant figure but, as the histogram shows, there were no issues with the accuracy or the precision of data as reported direct from the laboratory.

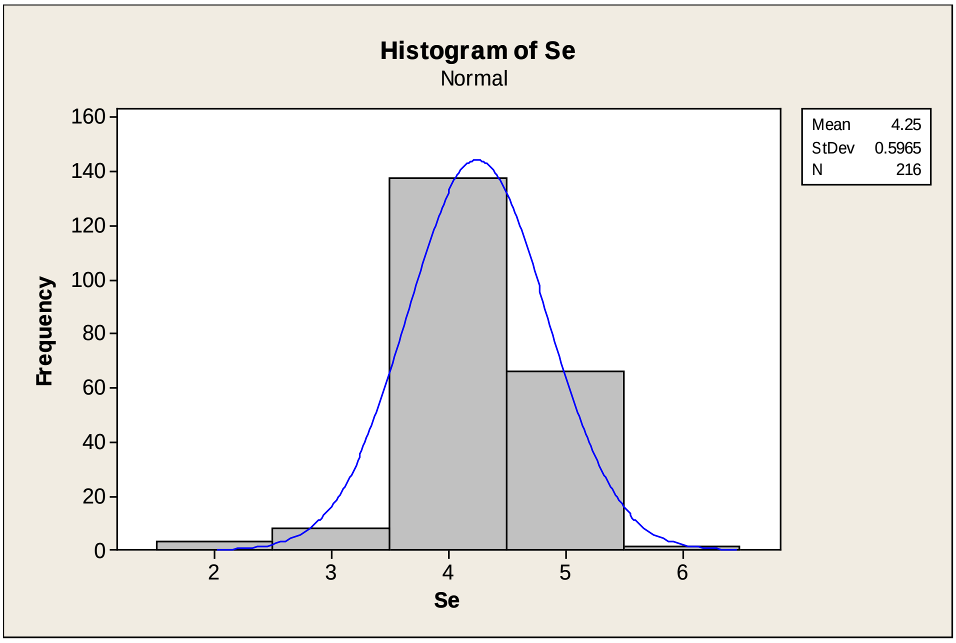


Figure 121 Histogram showing measured selenium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

TIN Sn

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram for XRAL01A indicates a positive bias in the data, with most results lying above the expected concentration.

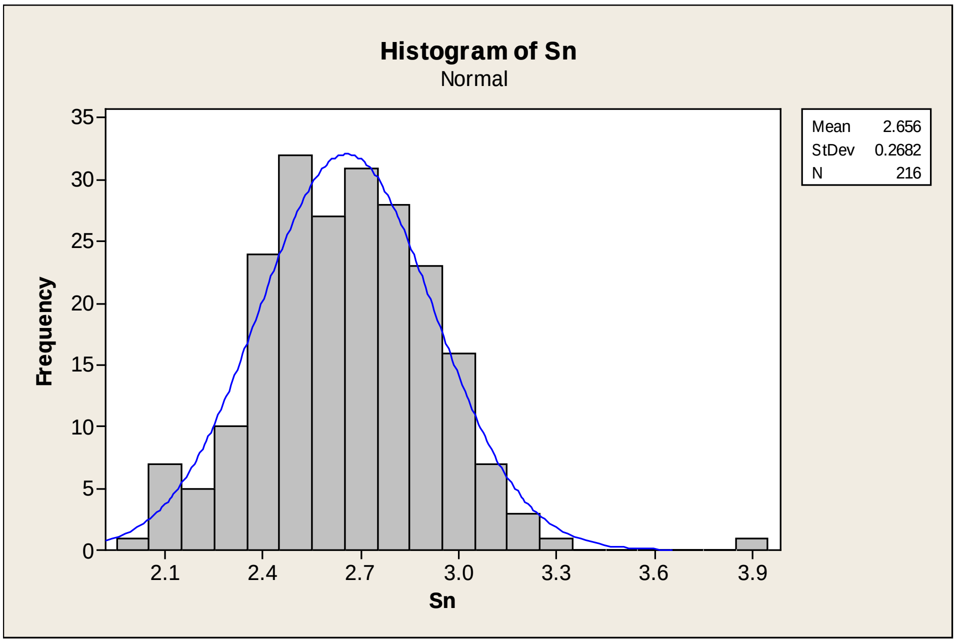


Figure 122 Histogram showing measured tin data in XRAL01A against the expected value. Values are in mg kg^{-1}.

STRONTIUM Sr

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram for XRAL01A results indicates a slight negative bias, with the majority of results falling below the expected concentration.

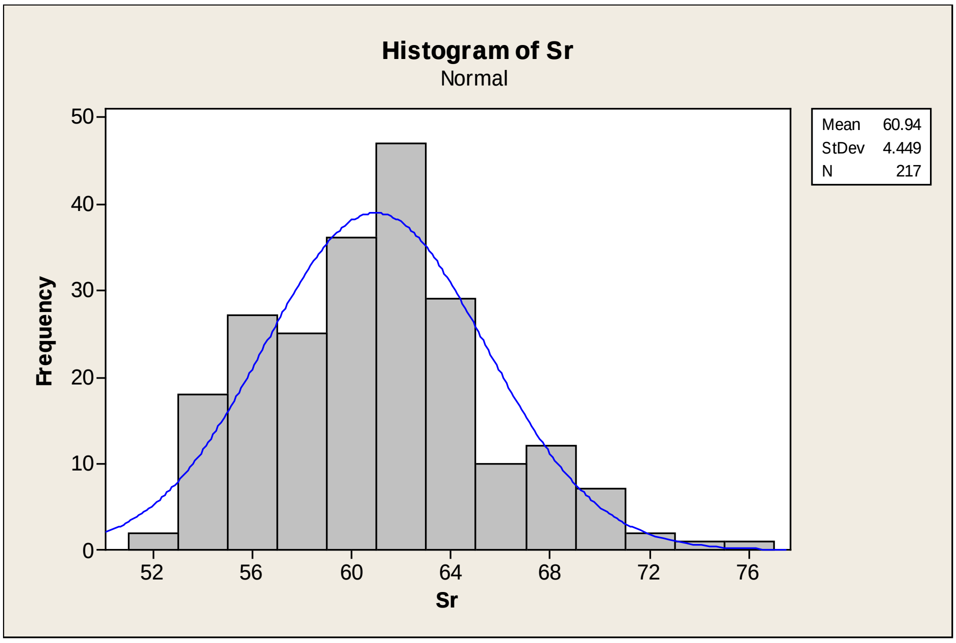


Figure 123 Histogram showing measured strontium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

THORIUM Th

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. There is a small positive bias shown on the histogram for XRAL01A.

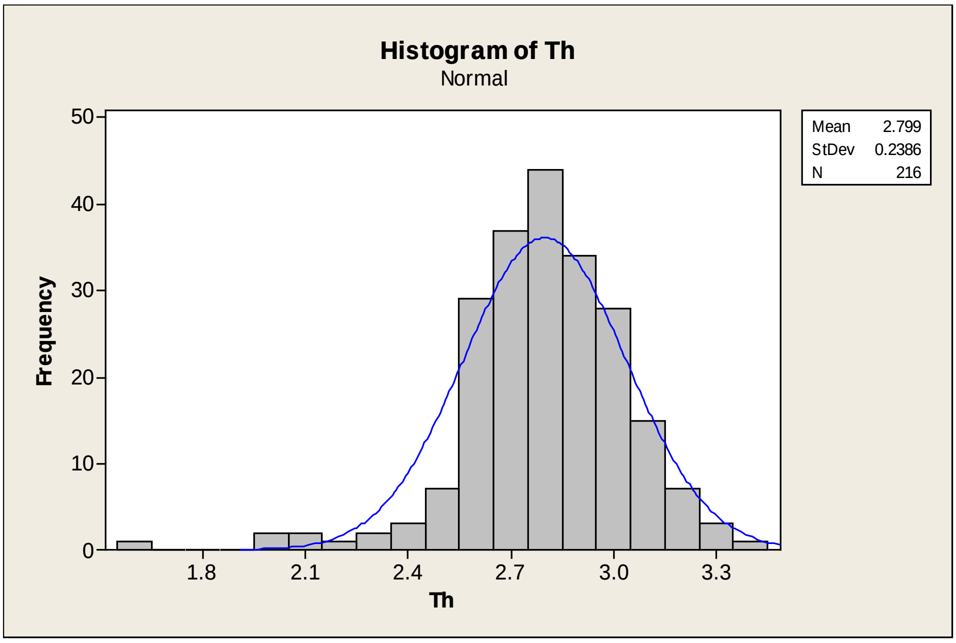


Figure 124 Histogram showing measured thorium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

URANIUM U

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. However, the histogram of data for XRAL01A shows that, although the data are centred on the expected concentration, they are spread across a significant concentration range.

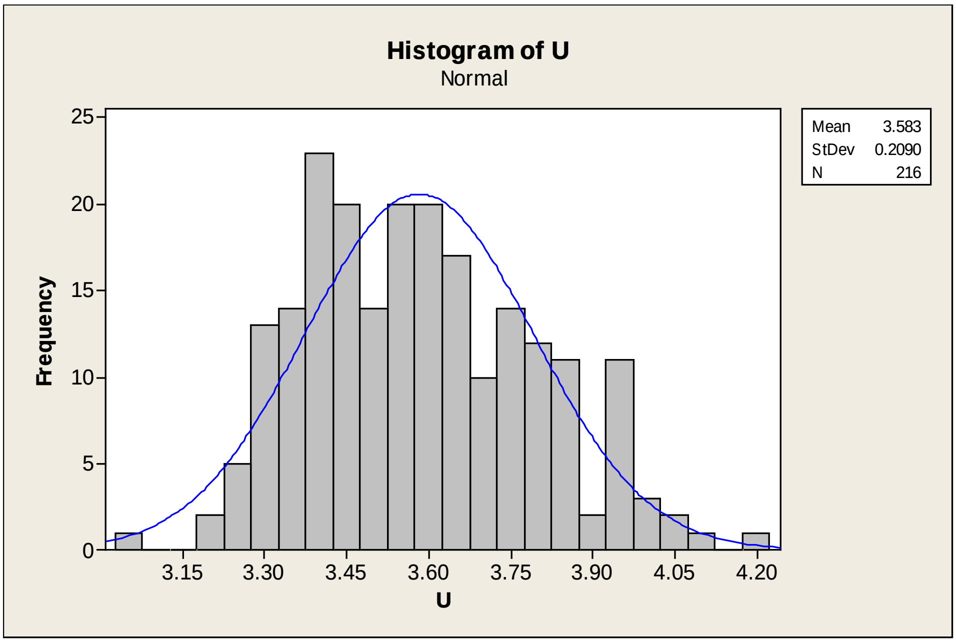


Figure 125 Histogram showing measured uranium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

VANADIUM V

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([V] x 0.7769) + 8.5222

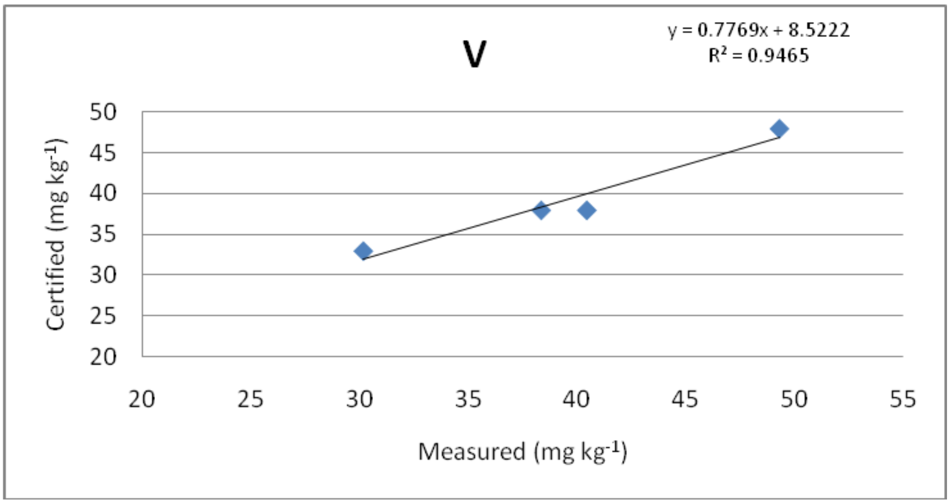


Figure 126 Regression plot for measured values against certified values for vanadium in Till-1, 2, 3 and 4.

YTTRIUM Y

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

The histogram indicates a positive bias in the data for XRAL01A, with most results lying above the expected concentration.

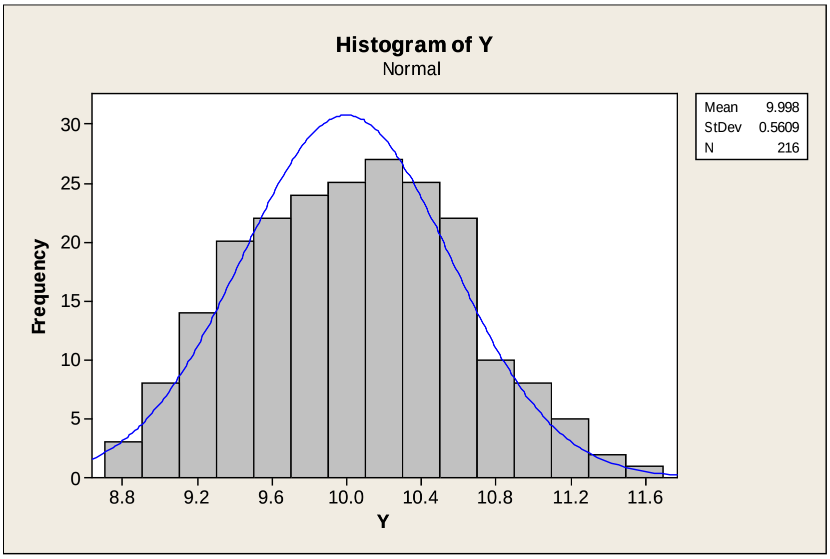


Figure 127 Histogram showing measured yttrium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

ZINC Zn

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory.

A regression of reported CRM values against certified values gave the following factor which could be applied as a correction to the measured data.

Correction factor = ([Zn] x 0.9868) + 8.2446

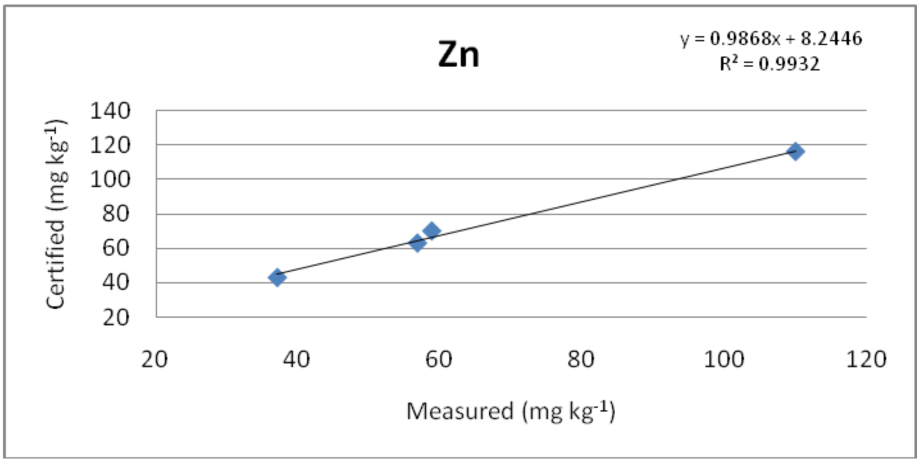


Figure 128 Regression plot for measured values against certified values for zinc in Till-1, 2, 3 and 4.

ZIRCONIUM Zr

Shewhart plots of primary and secondary reference material data indicated that there were no issues with the precision of data as reported direct from the laboratory. There is a small rise in the RM data from 19/9/2006 onwards for XRAL01A, this is not reproduced in the other RMs and is not large enough to correct for.

The histogram indicates a positive bias in the data for XRAL01A, with most results lying above the expected concentration; this is probably due to the increased values already mentioned.

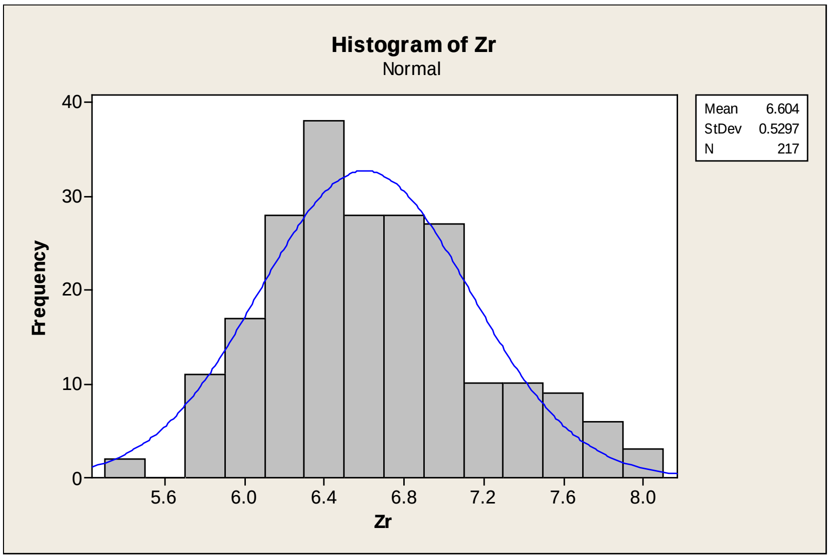


Figure 129 Histogram showing measured zirconium data in XRAL01A against the expected value. Values are in mg kg^{-1}.

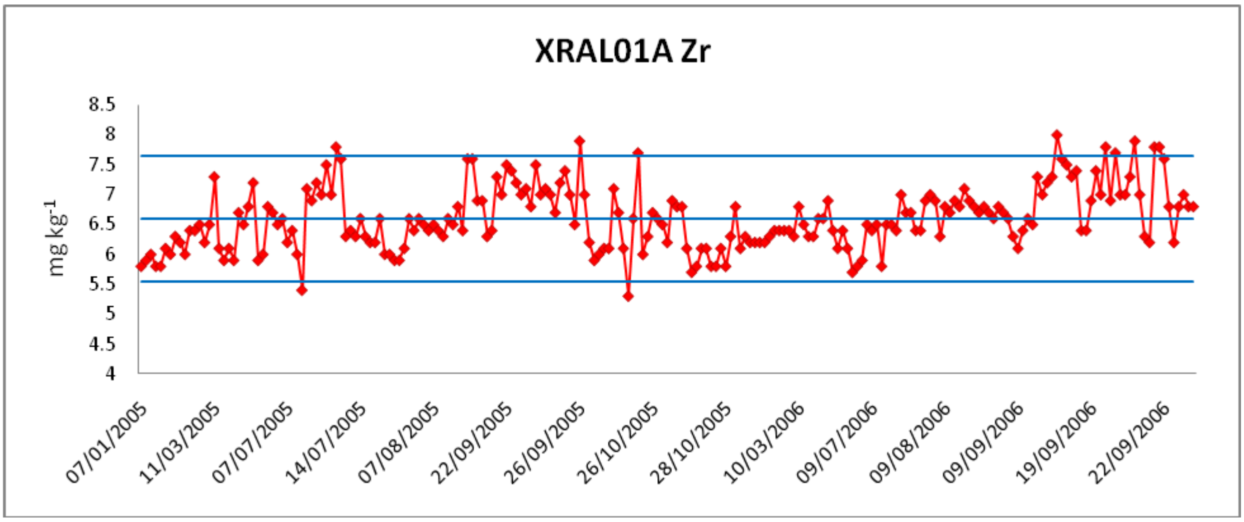


Figure 130 Histogram showing measured zirconium data in XRAL01A against the expected value.

Appendix 3: Detailed quality assessment for mixed acid ‘*near-total*’ digest ICP analysis of Tellus ‘S’ soils

The following section includes an element by element discussion for mixed acid ‘*near-total*’ digest ICP analyses. Correction factors are included but should not be applied unless it has been shown a significant improvement will be made to the data. Recommendations are given in Chapter 4.3.3.

SILVER Ag

The Shewhart charts for silver for several materials showed results that fell outside the acceptable range. However the failures occurred at different times for different materials and do not indicate a systematic error. The histogram of data for S13B shows the majority of the data sitting well below the expected value of 0.9 mg kg^{-1}. This and the poor precision showed by the Shewhart charts, is probably due to precipitation of silver chloride during the dissolution and could occur for all samples. There are no reference values for silver in the Till certified reference materials.

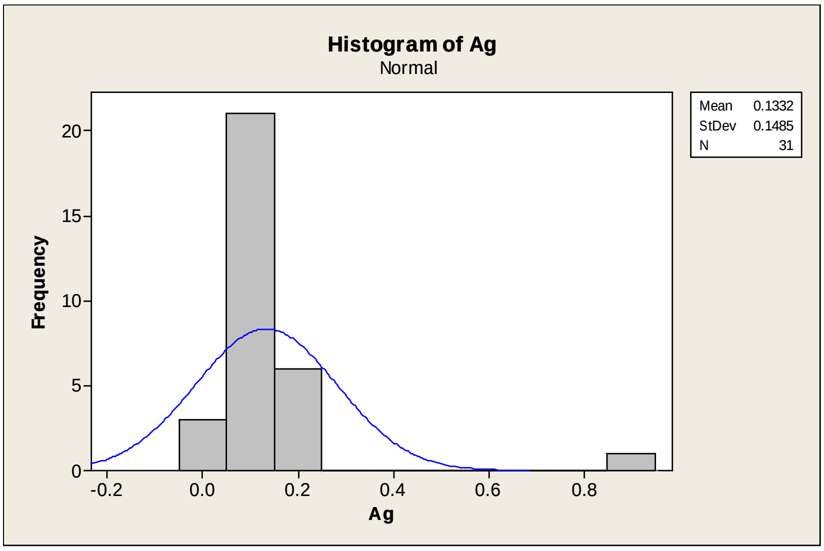


Figure 131 Histogram showing measured silver data in S13B. Values are in mg kg^{-1}.

ALUMINIUM Al

Shewhart plots of primary and secondary reference material data indicate that there were no systematic issues with the precision of data as reported by the laboratory. The results for the Till certified reference materials plotted against reference values fall on a straight line, although the concentration range is small. Applying the equation of the line to the certified reference materials gives a slight overall improvement in data quality. The histogram showing data obtained for the reference material S13B during this period shows a reasonably even distribution but with all data falling below the expected value of 10.96%. The correction factor should be applied to the raw data.

Correction factor = ([Al] x 1.1235) – 0.4732

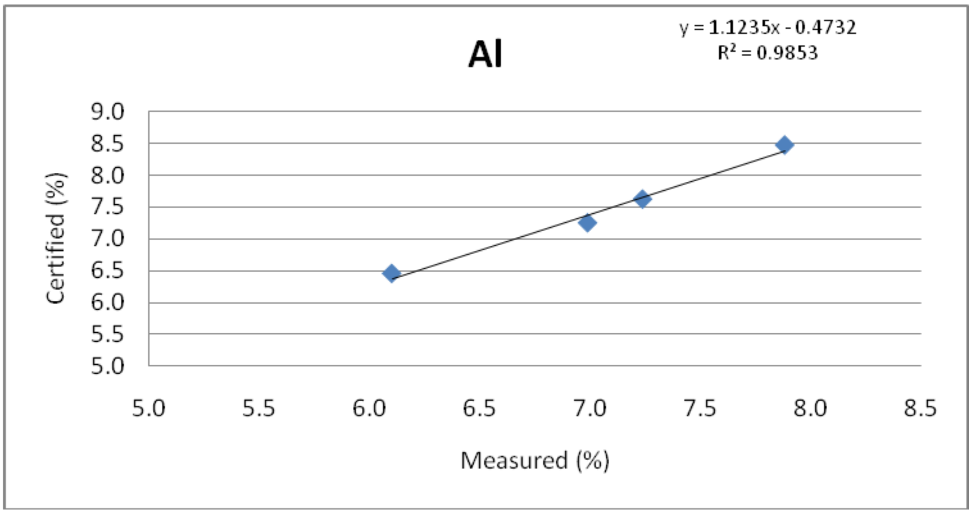


Figure 132 Regression plot for measured values against certified values for aluminium in Till-1, 2, 3 and 4.

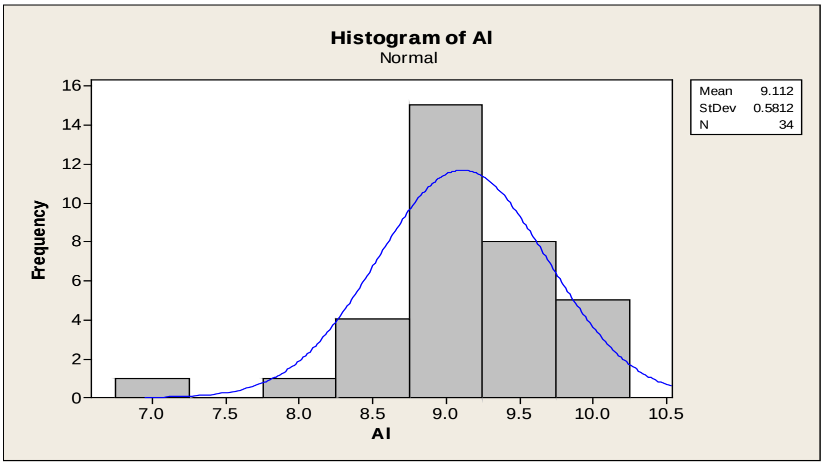


Figure 133 Histogram showing measured aluminium data in S13B. Values are % Al.

ARSENIC As

The Shewhart charts for arsenic for several materials showed results that fell outside the acceptable range. However the failures occurred at different times for different materials and do not indicate a systematic error. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the correction factor to the results for the other reference materials does not improve data quality. The histogram of data for S13B shows that the great majority of results are close to the expected value of 14 mg kg^{-1}.

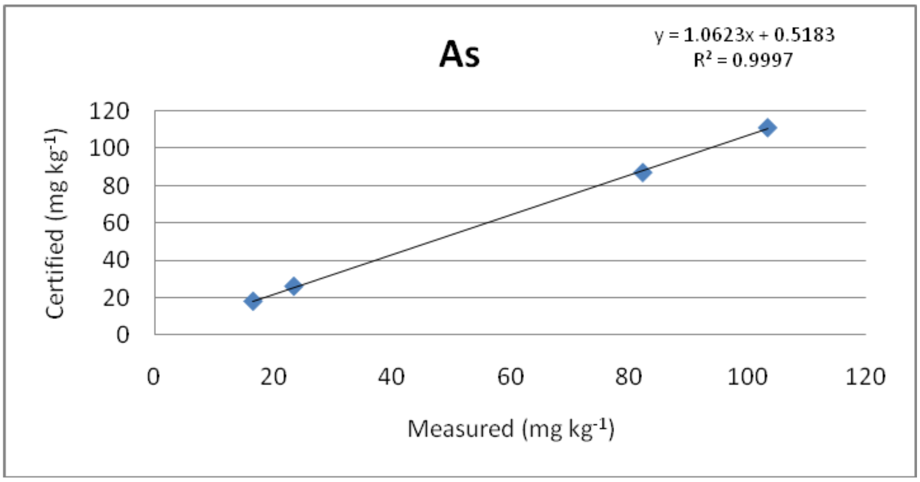


Figure 134 Regression plot for measured values against certified values for arsenic in Till-1, 2, 3 and 4.

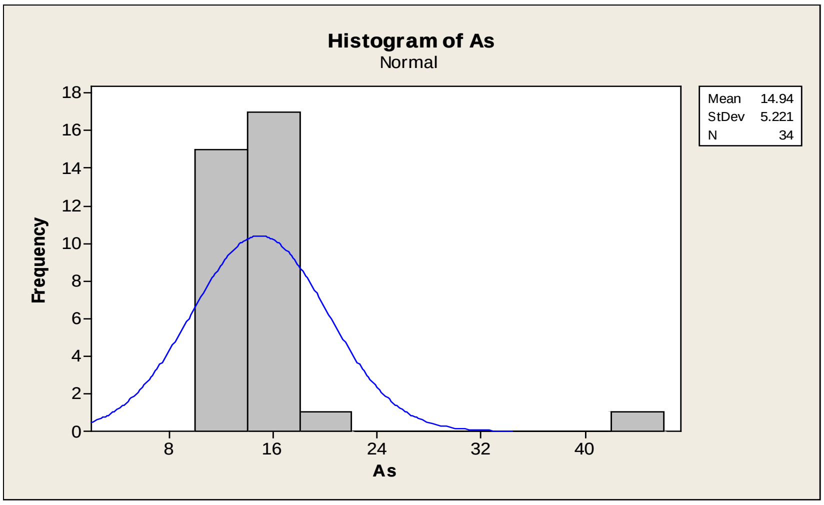


Figure 135 Histogram showing measured arsenic data in S13B. Values are in mg kg^{-1}.

BARIUM Ba

Shewhart plots of primary and secondary reference material data indicate that there were no systematic issues with the precision of data as reported by the laboratory. The regression of reported Till CRM values against certified/provisional values gave a straight line but applying the equation of the graph to the other reference materials available did not give an overall improvement in the data quality. The histogram shows that the majority of the data for S13B fall well above the expected value of 744mg kg^{-1}.

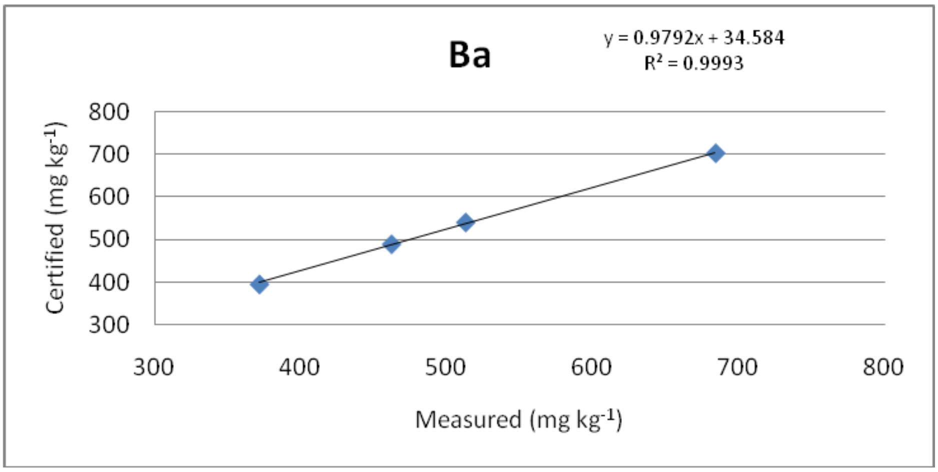


Figure 136 Regression plot for measured values against certified values for barium in Till-1, 2, 3 and 4.

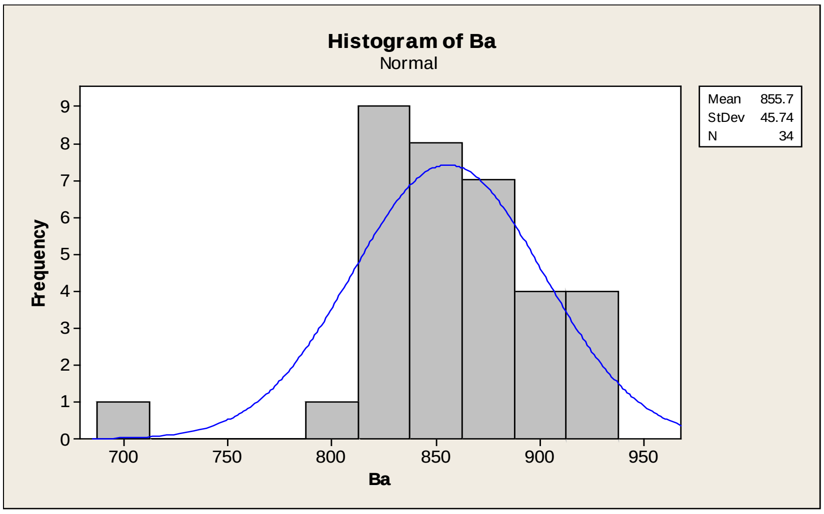


Figure 137 Histogram showing measured barium data in S13B. Values are in mg kg^{-1}.

BERYLLIUM Be

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values gave a correlation coefficient close to one suggesting that the equation of the line could be applied to the raw data. However there are no data available from the other reference materials to validate this.

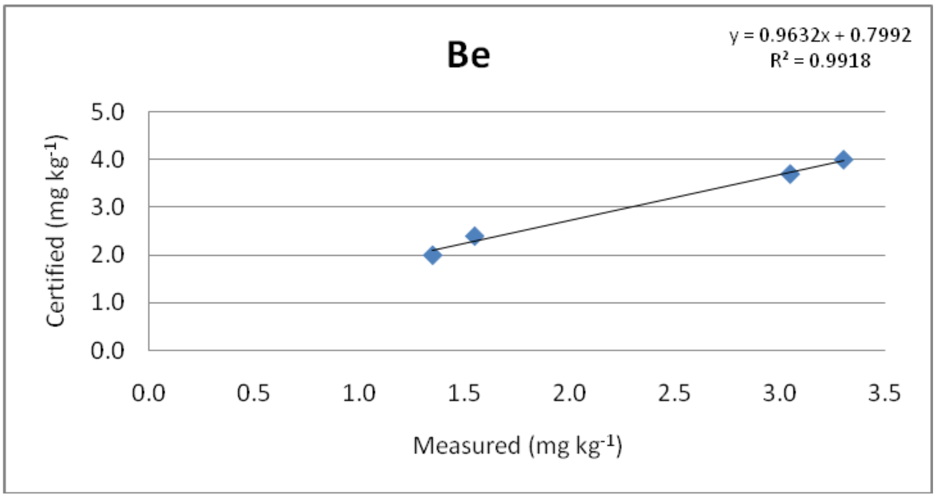


Figure 138 Regression plot for measured values against certified values for beryllium in Till-1, 2, 3 and 4.

BISMUTH Bi

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. There were one or two results that fell outside the accepted range but these were not repeated in other materials and did not indicate a systematic error. There was insufficient bismuth in three of the Till materials to produce a regression. All the data for the reference material S13B fell below the expected value of 0.5 mg kg^{-1}.

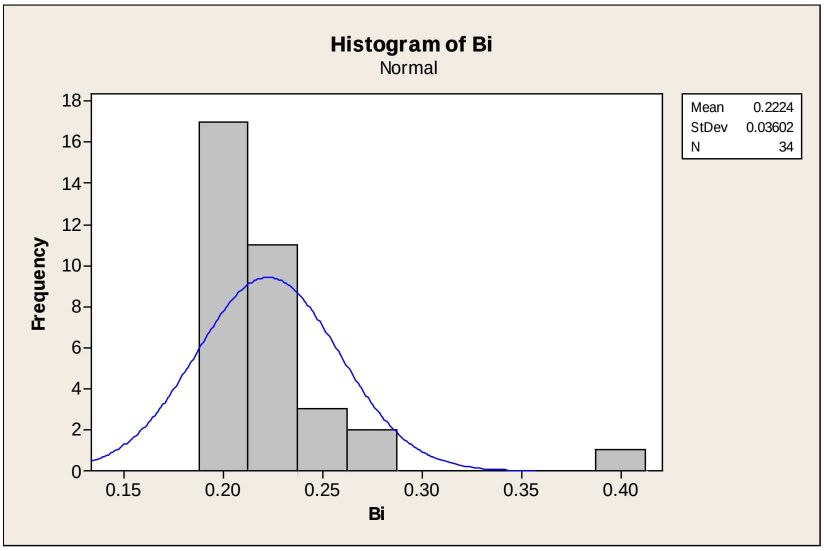


Figure 139 Histogram showing measured bismuth data in S13B. Values are in mg kg^{-1}.

CALCIUM Ca

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out and applying the resulting factor to the reported data for the other reference materials gave an improvement in the data quality. The factor should therefore be applied to all the data as reported by the laboratory.

Correction factor = ([Ca] x 1.0527) – 0.0041

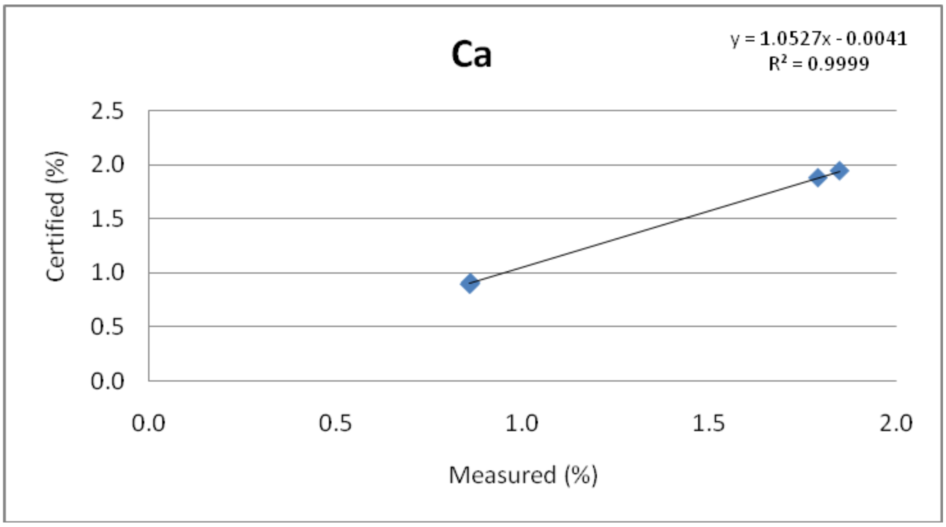


Figure 140 Regression plot for measured values against certified values for calcium in Till-1, 2, 3 and 4.

CADMIUM Cd

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. Data were not available for a regression to be plotted. The histogram shows the majority of the data to fall below the expected value of 0.5mg kg^{-1}.

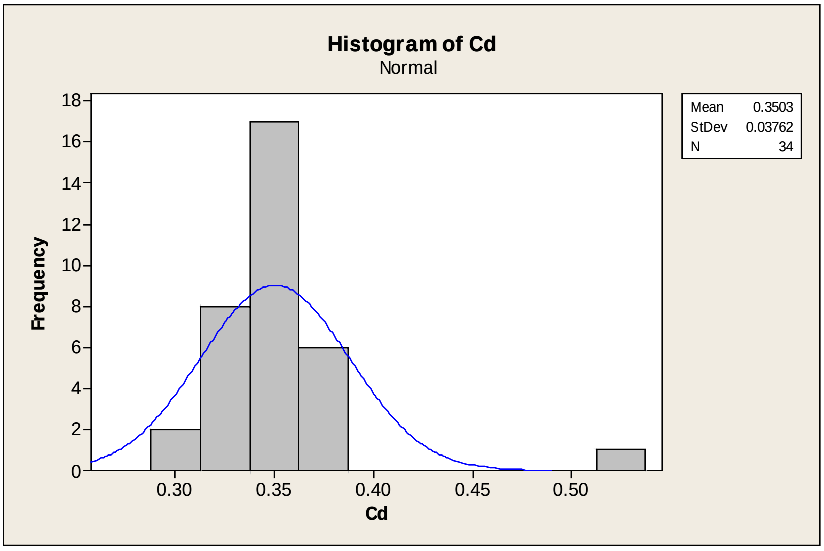


Figure 141 Histogram showing measured cadmium data in S13B. Values are in mg kg^{-1}.

CERIUM Ce

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. The histogram of results obtained by the analysis of S13B shows most data to lie just below the expected value of 100mg kg^{-1}.

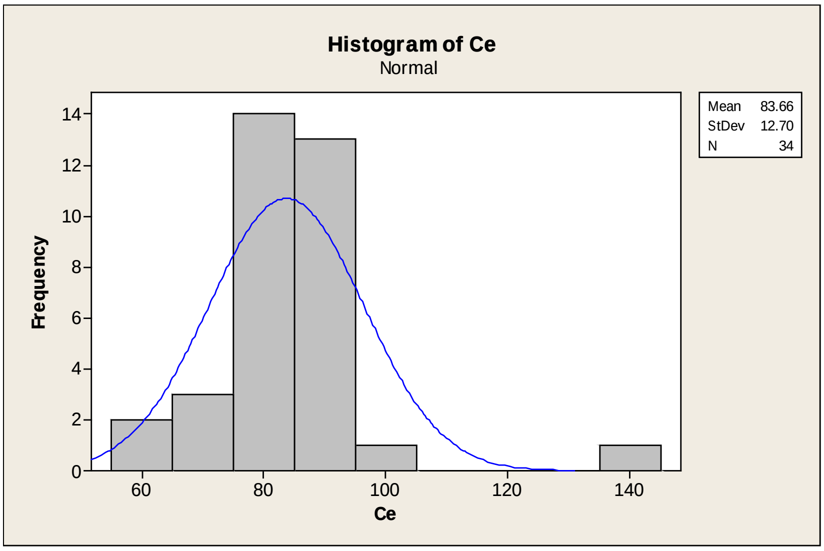


Figure 142 Histogram showing measured cerium data in S13B. Values are in mg kg^{-1}.

COBALT Co

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. The resulting factor was tested against the measured value for the other reference materials and gave a small improvement in the overall data quality. This factor should, therefore be applied to all the raw data. The poor recovery, typical for cobalt using this type of dissolution, is indicated by comparing the values for S13B on the histogram with the target value of 24.6 mg kg^{-1}.

Correction factor = ([Co] x 1.0867) – 0.1952

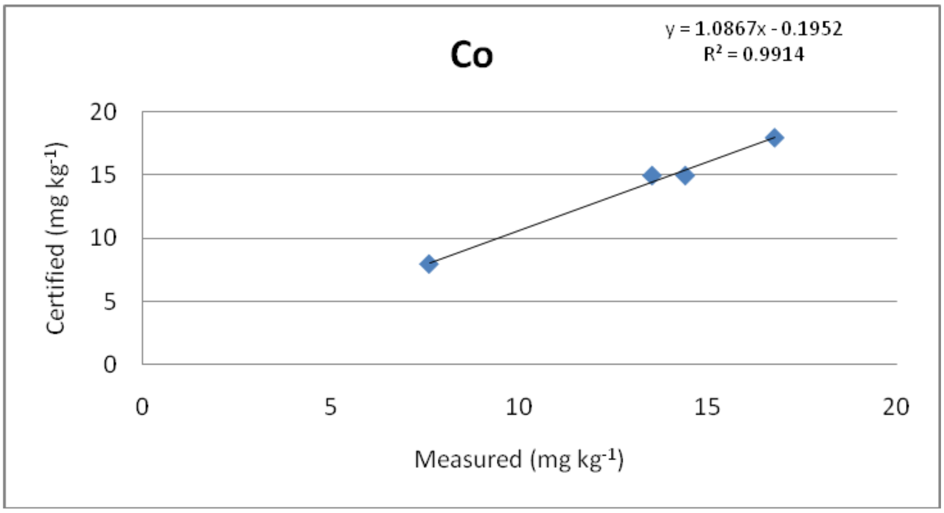


Figure 143 Regression plot for measured values against certified values for cobalt in Till-1, 2, 3 and 4.

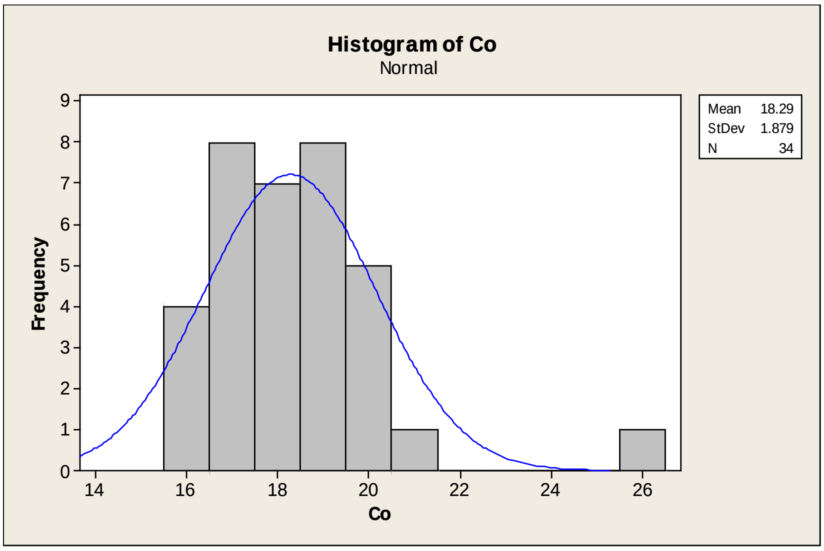


Figure 144 Histogram showing measured cobalt data in S13B. Values are in mg kg^{-1}.

CHROMIUM Cr

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory, except for SO-3 which exhibits an unusually wide spread of data. This is not repeated for any of the other reference materials and appears to be random, despite being well above the detection limit. A regression of reported Till CRM values against certified/provisional values was carried out. The resulting factor was tested against the measured values for the other reference materials and improved the results noticeably. The histogram of raw data for S13B shows the majority of the data to lie below the expected value of 100mg kg^{-1}; this is typical for chromium for this type of dissolution.

Correction factor = ([Cr] x 1.5095) – 10.73

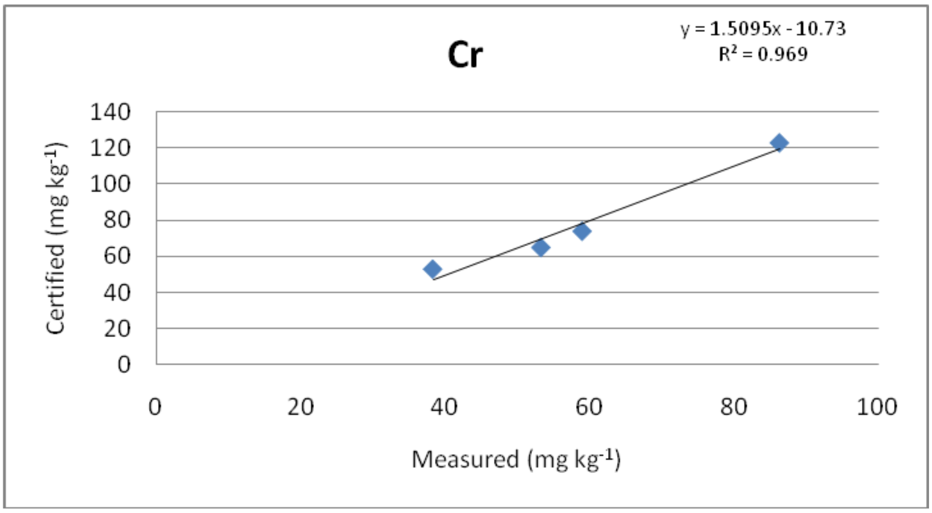


Figure 145 Regression plot for measured values against certified values for chromium in Till-1, 2, 3 and 4.

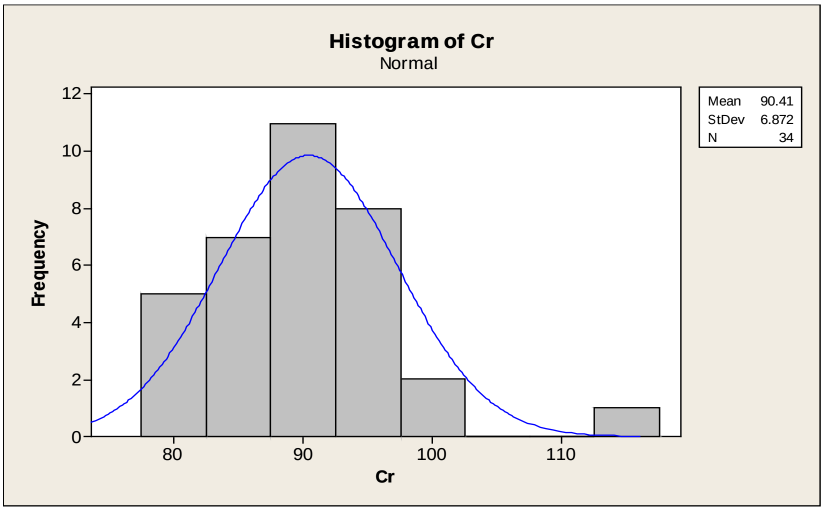


Figure 146 Histogram showing measured chromium data in S13B. Values are in mg kg^{-1}.

CAESIUM Cs

Shewhart plots of primary and secondary reference materials where data were available indicated that there were no issues with the precision of data as reported direct from the laboratory. However, during the analysis period the quoted detection limit changed from 0.05 to 5mg kg^{-1}, meaning that all the data in the reference materials with less than 5 mg kg^{-1} have been lost. This is unfortunate as the plots indicate no problems with the results at lower levels. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the equation from this to the other reference materials did not improve the data quality. The histogram shows that all results were above the expected value of 4mg kg^{-1}.

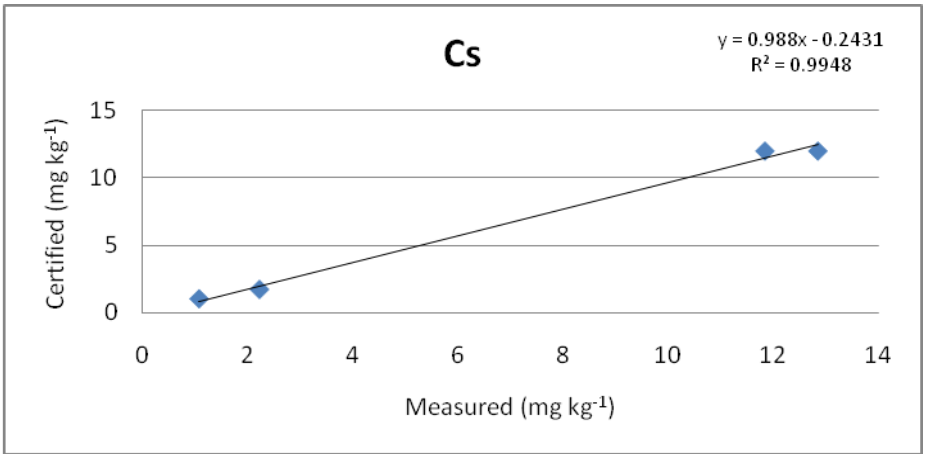


Figure 147 Regression plot for measured values against certified values for caesium in Till-1, 2, 3 and 4.

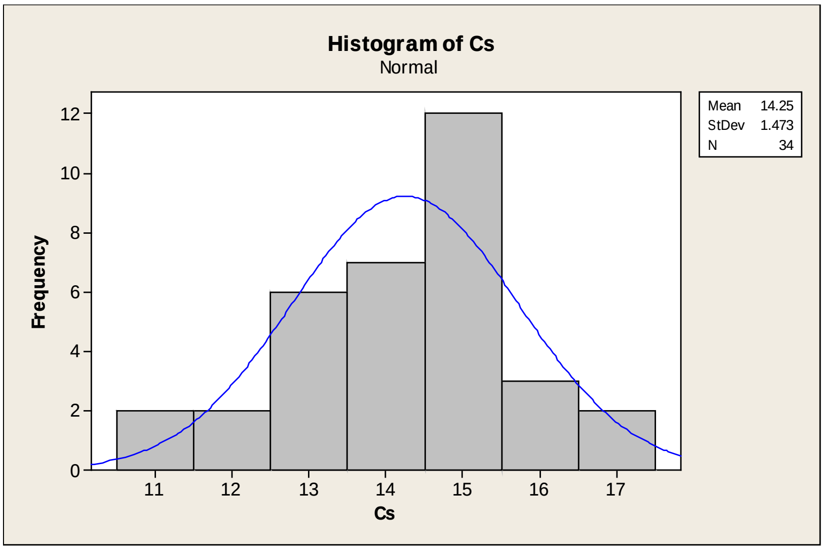


Figure 148 Histogram showing measured caesium data in S13B. Values are in mg kg^{-1}.

COPPER Cu

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. However, it is noticeable that there were several data points that fell wide of the accepted range, these points occurred on different dates for different materials. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the equation to the raw data for the other reference materials gave a small improvement in data quality. The histogram of the results for S13B shows the majority of the results to be close to the target value of 17.1mg kg^{-1}.

Correction factor = ([Cu] x 0.9653) + 1.5439

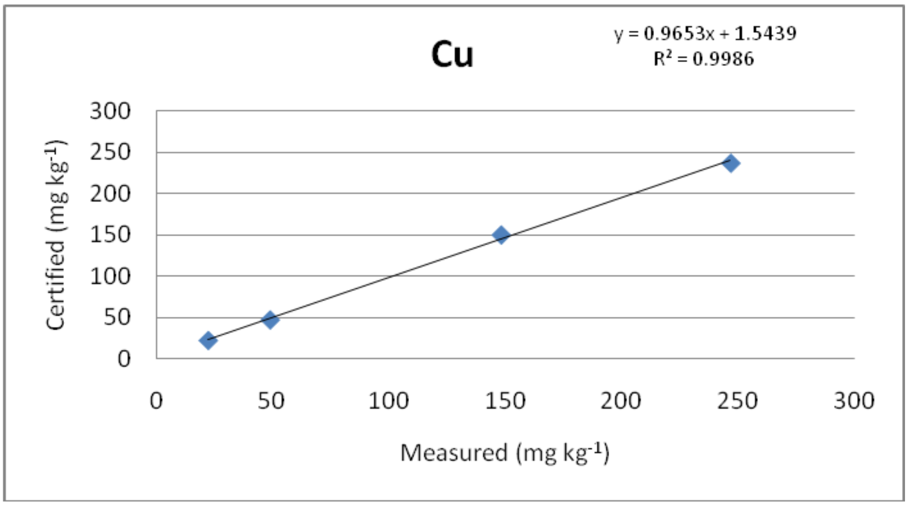


Figure 149 Regression plot for measured values against certified values for copper in Till-1, 2, 3 and 4.

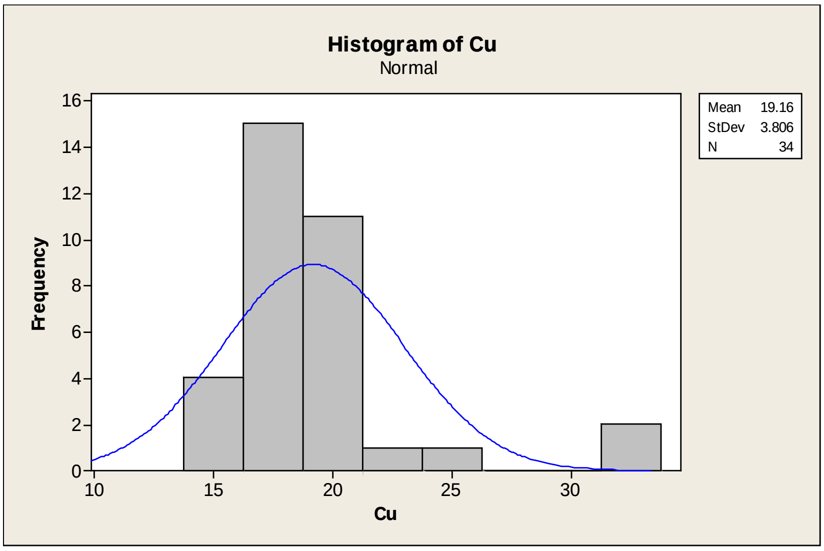


Figure 150 Histogram showing measured copper data in S13B. Values are in mg kg^{-1}.

IRON Fe

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. However, once again there were data points that fell wide of the accepted range. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results gave improvements for most reference materials and so this should be applied to all data. The histogram of results for S13B shows a general under-recovery compared with the target value of 5.22% which is still the case even after the regression factor has been applied.

Correction factor = ([Fe] x 1.0484) – 0.0389

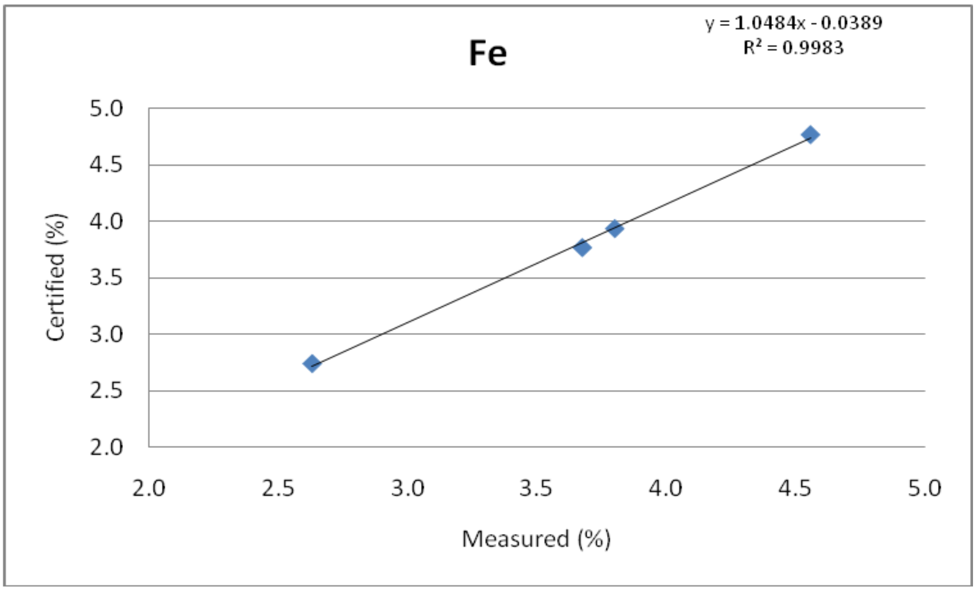


Figure 151 Regression plot for measured values against certified values for iron in Till-1, 2, 3 and 4.

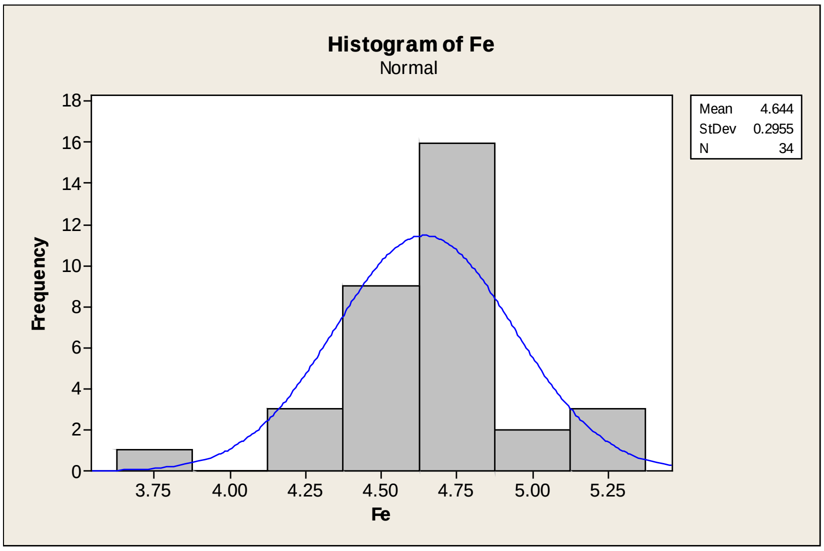


Figure 152 Histogram showing measured iron data in S13B. Values are % Fe.

GALLIUM Ga

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. The histogram for results for reference material S13B shows the majority of results to lie close to the expected value of 21.9mg kg^{-1}.

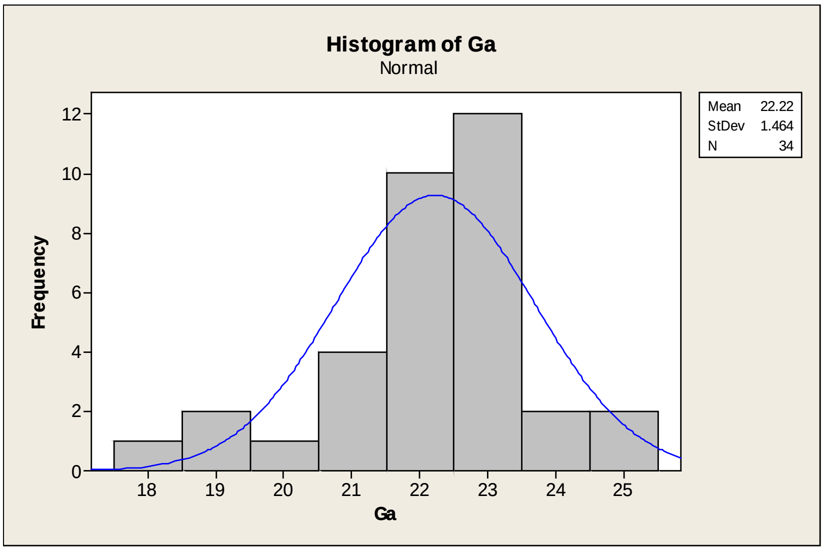


Figure 153 Histogram showing measured gallium data in S13B. Values are in mg kg^{-1}.

POTASSIUM K

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the majority of results to lie close to the expected value of 1.90%.

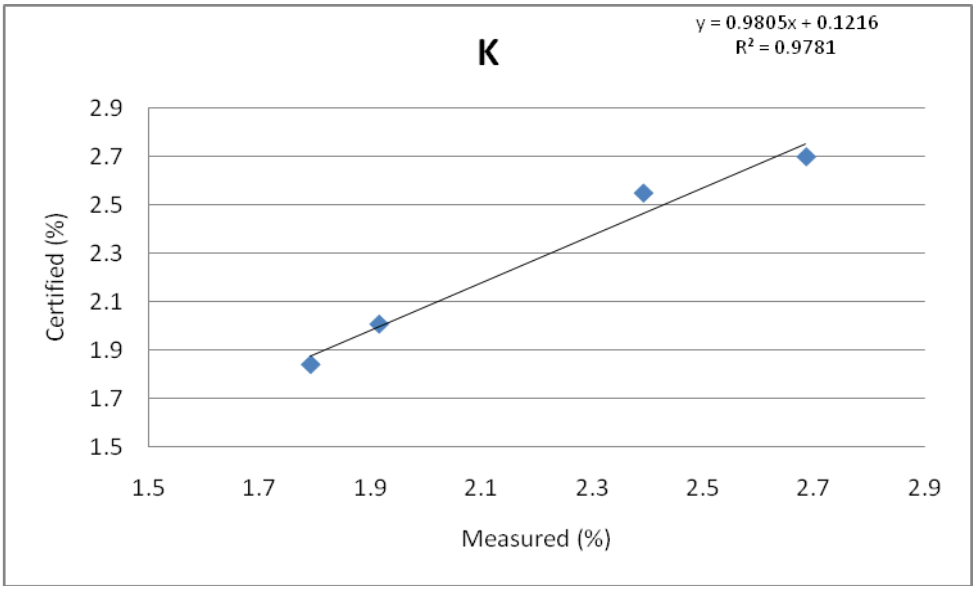


Figure 154 Regression plot for measured values against certified values for potassium in Till-1, 2, 3 and 4.

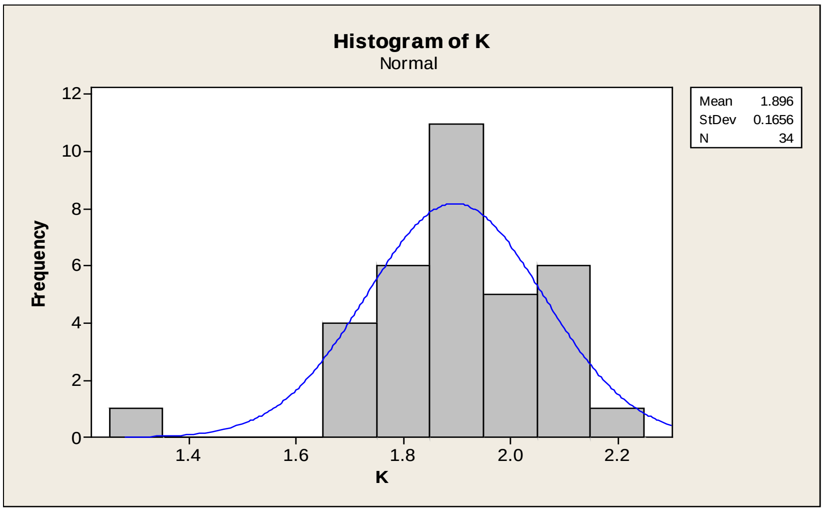


Figure 155 Histogram showing measured potassium data in S13B. Values are % K.

LANTHANUM La

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured result for the other reference materials gave no improvement in accuracy compared to the expected values. The histogram for S13B results shows the majority of data lying below the expected value of 48mg kg^{-1}.

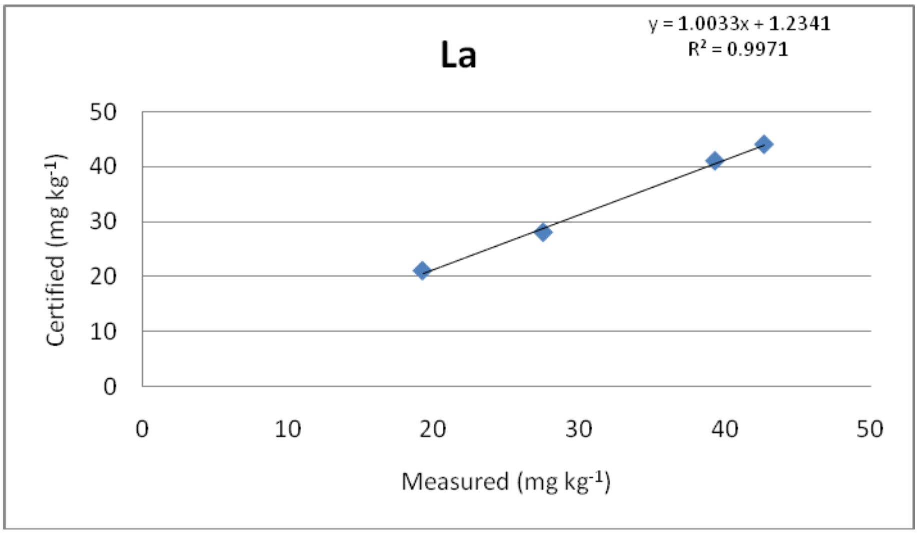


Figure 156 Regression plot for measured values against certified values for lanthanum in Till-1, 2, 3 and 4.

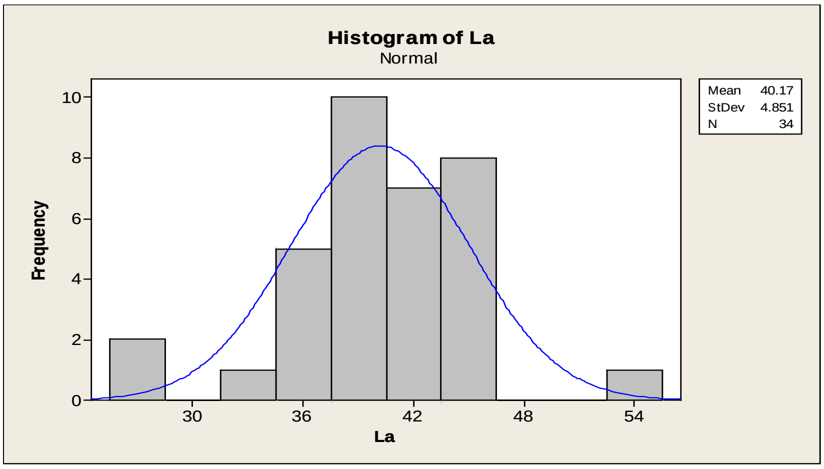


Figure 157 Histogram showing measured lanthanum data in S13B. Values are in mg kg^{-1}.

LITHIUM Li

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. The histogram for S13B shows a reasonably normal distribution of data. A regression of reported Till CRM values against certified/provisional values was carried out. Unfortunately no expected values are available for lithium in the other reference materials so it is difficult to assess the validity of applying the correction factor given by the regression plot to the data for the samples.

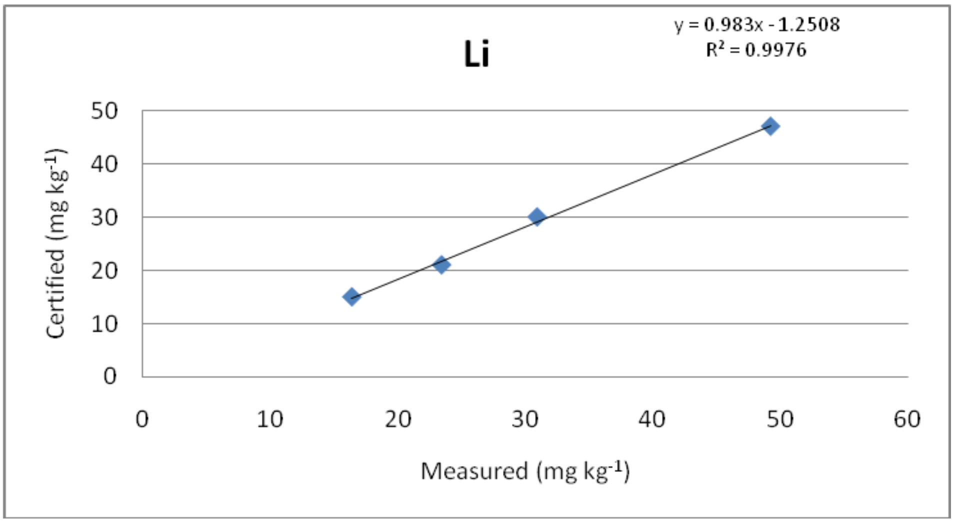


Figure 158 Regression plot for measured values against certified values for lithium in Till-1, 2, 3 and 4.

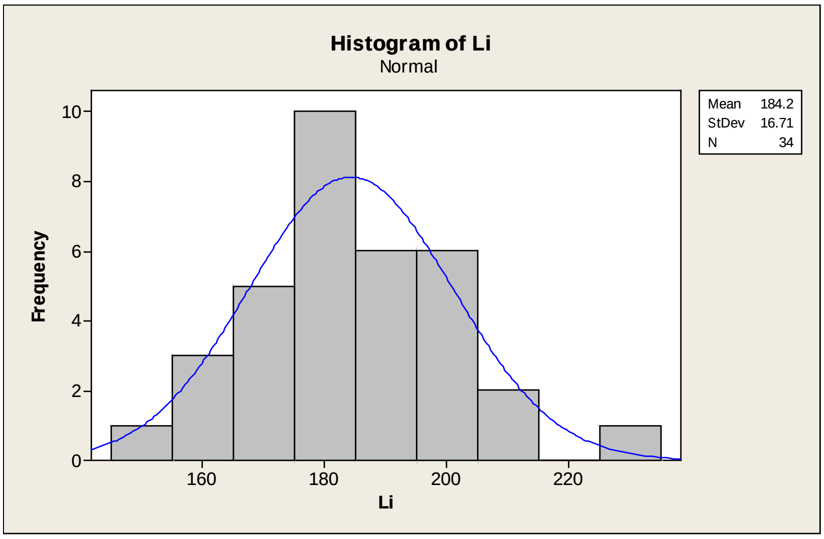


Figure 159 Histogram showing measured lithium data in S13B. Values are in mg kg^{-1}.

MAGNESIUM Mg

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results gave improvements for the other reference materials and so this should be applied to all data. The histogram of results for S13B shows a general under-recovery compared with the expected value of 0.784% which is still the case, though to a lesser extent, after the regression factor has been applied.

Correction factor = ([Mg] x 1.0418) + 0.0084

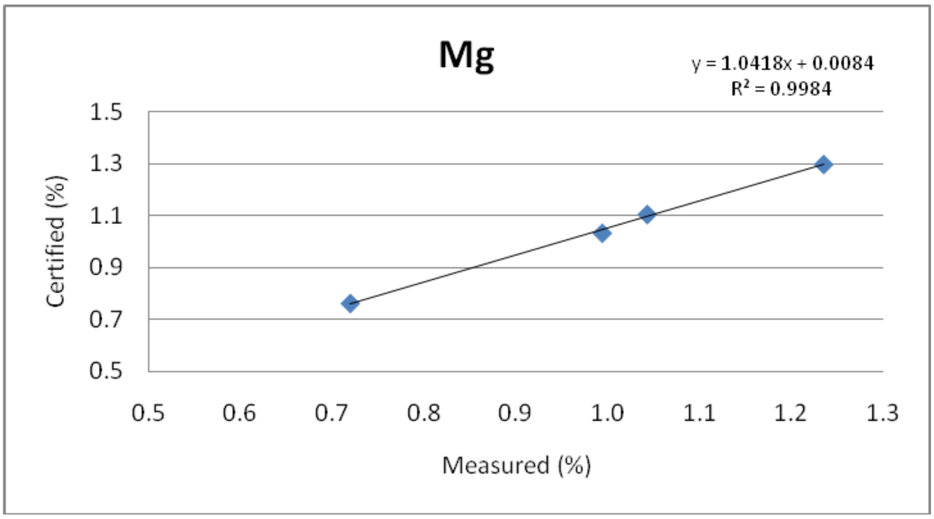


Figure 160 Regression plot for measured values against certified values for magnesium in Till-1, 2, 3 and 4.

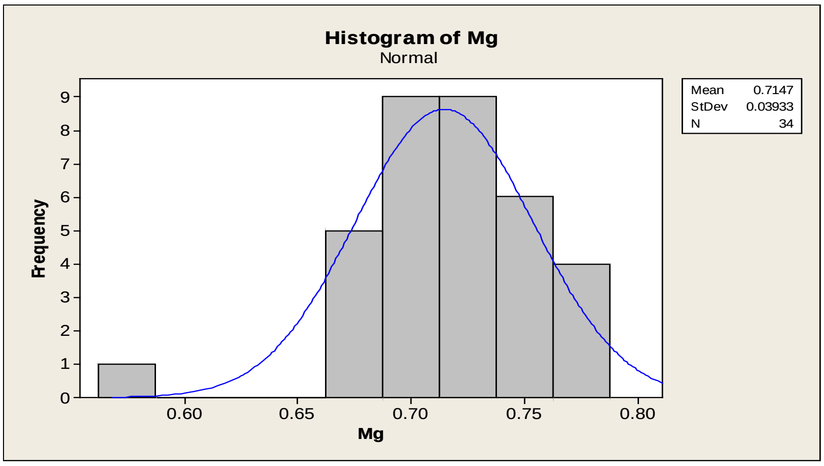


Figure 161 Histogram showing measured magnesium data in S13B. Values are % Mg.

MANGANESE Mn

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the majority of results to lie below the expected value of 836mg kg^{-1}.

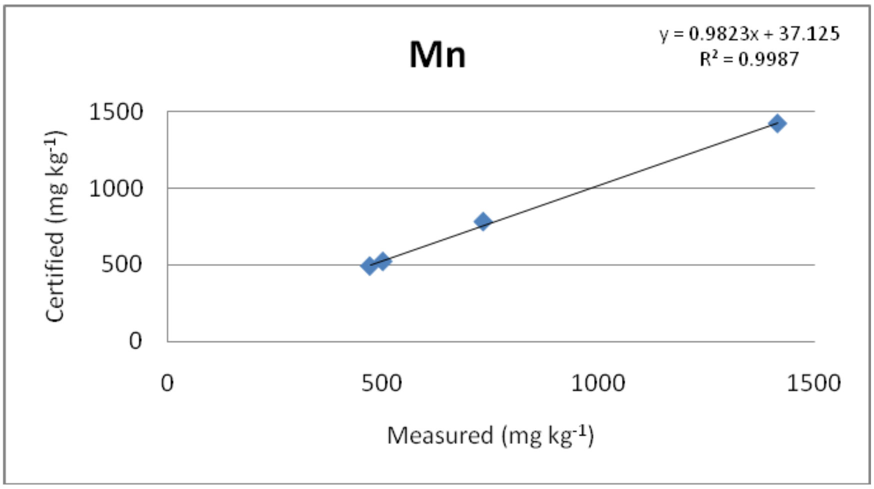


Figure 162 Regression plot for measured values against certified values for manganese in Till-1, 2, 3 and 4.

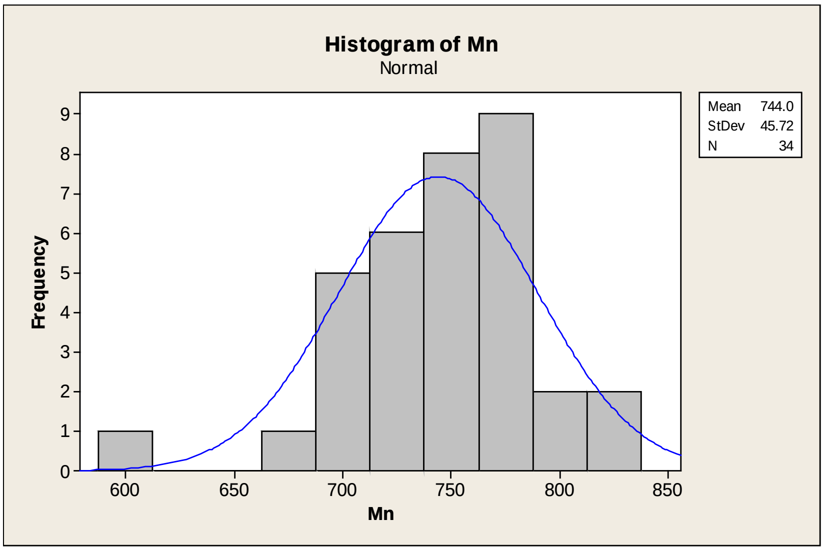


Figure 163 Histogram showing measured manganese data in S13B. Values are in mg kg^{-1}.

MOLYBDENIUM Mo

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured result for the other reference materials did not improve their accuracy compared to the expected value. The histogram of results for S13B shows the results follow a normal distribution, but are well below the expected value of 1.5mg kg^{-1}.

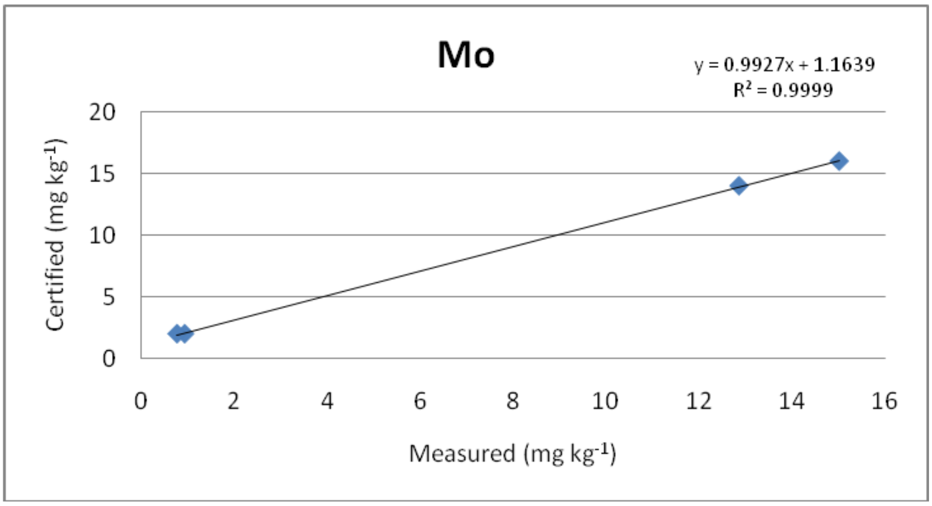


Figure 164 Regression plot for measured values against certified values for molybdenum in Till-1, 2, 3 and 4.

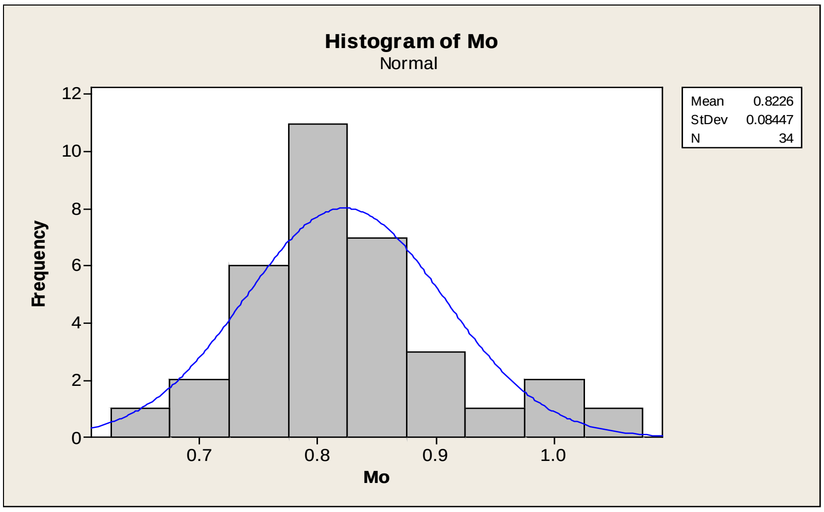


Figure 165 Histogram showing measured molybdenum data in S13B. Values are in mg kg^{-1}.

SODIUM Na

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory.

A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the results follow a normal distribution, close to the expected value of 0.223%.

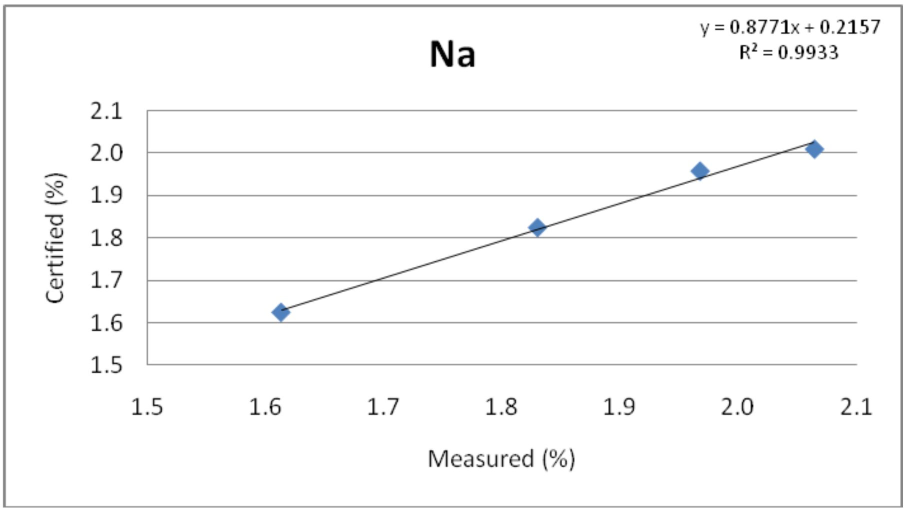


Figure 166 Regression plot for measured values against certified values for sodium in Till-1, 2, 3 and 4.

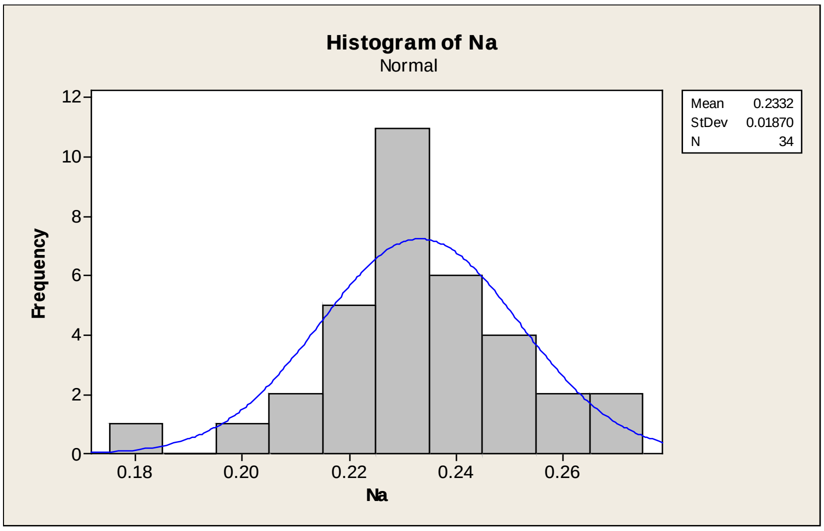


Figure 167 Histogram showing measured sodium data in S13B. Values are % Na.

NICKEL Ni

Early nickel results were determined by ICP-MS, later ones by ICP-AES. There was no discernable step change between the two sets of data and so no data conditioning is required. Shewhart plots of primary and secondary reference materials indicated that there were generally no systematic issues with the precision of data as reported direct from the laboratory. However, some reference materials gave unusually high results during the second week in September 2006. Unfortunately, as the date the problem occurred varies between reference materials, the problem cannot be assigned to a specific batch. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the results shows values clustered around and just above the expected value of 45.7mg kg^{-1}.

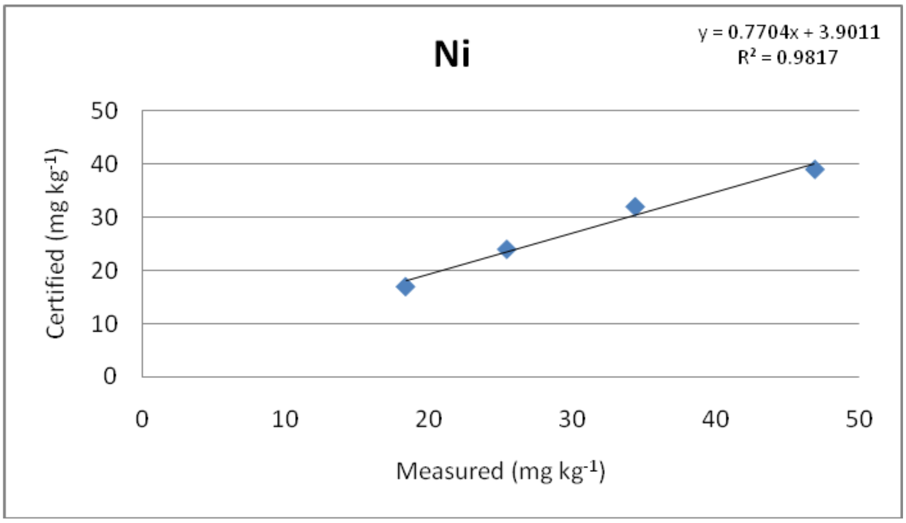


Figure 168 Regression plot for measured values against certified values for nickel in Till-1, 2, 3 and 4.

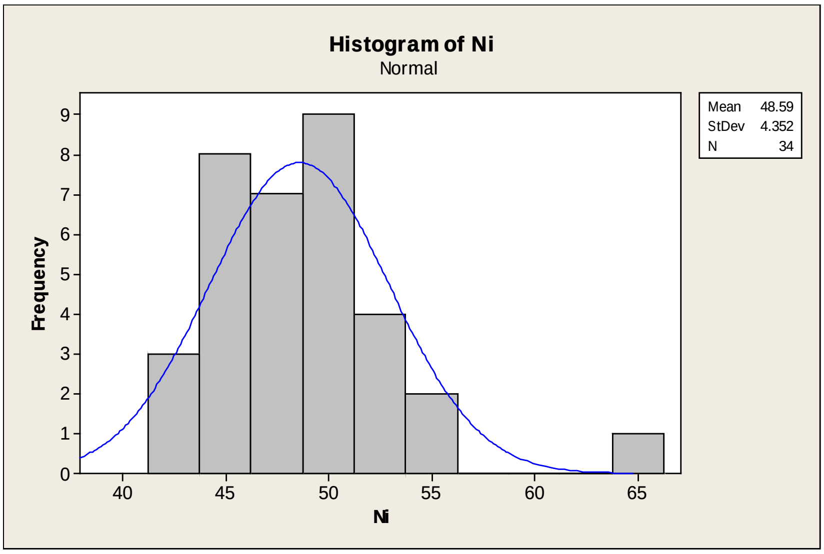


Figure 169 Histogram showing measured nickel data in S13B. Values are in mg kg^{-1}.

PHOSPHOROUS P

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the results follow a normal distribution, but the target value from XRFS analysis only shows the correct value to fall between 437 and 656mg kg^{-1}. Most of the data fall within this range.

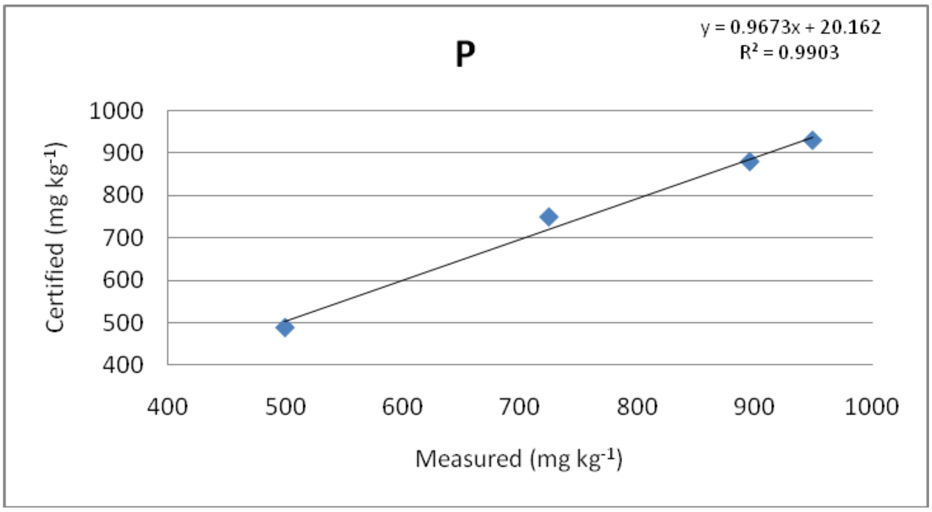


Figure 170 Regression plot for measured values against certified values for phosphorus in Till-1, 2, 3 and 4.

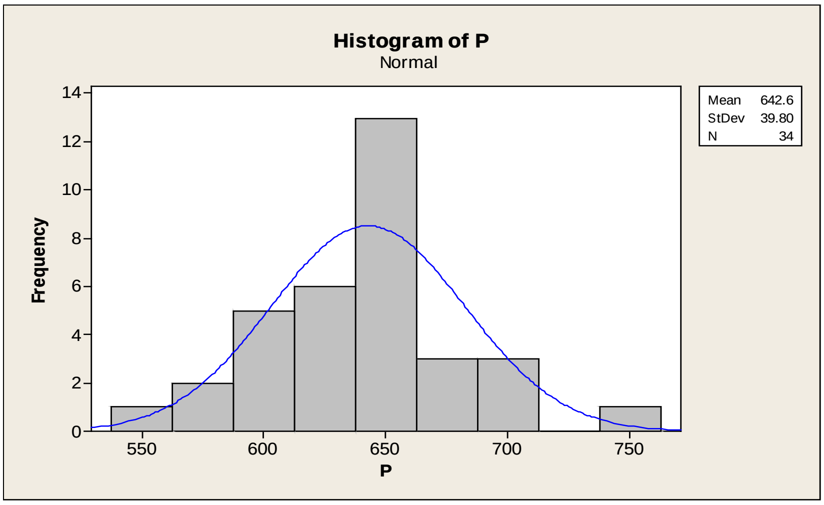


Figure 171 Histogram showing measured phosphorus data in S13B. Values are in mg kg^{-1}.

LEAD Pb

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the results are broadly distributed but centred on the expected value of 62.9mg kg^{-1}.

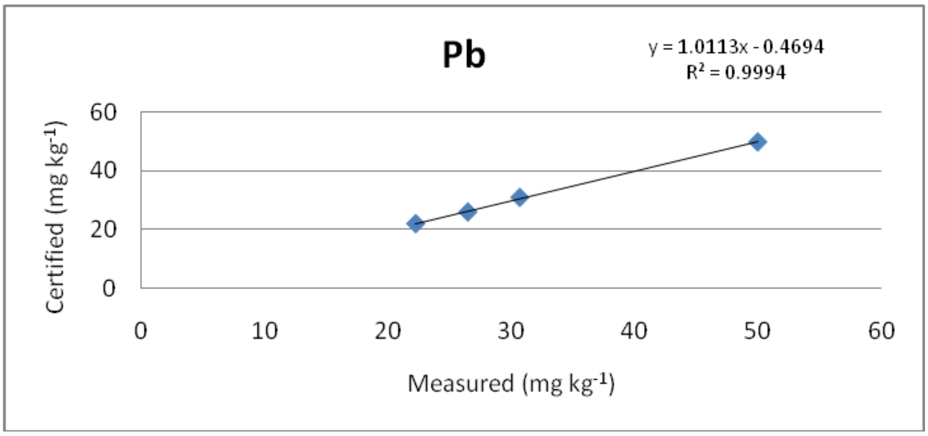


Figure 172 Regression plot for measured values against certified values for lead in Till-1, 2, 3 and 4.

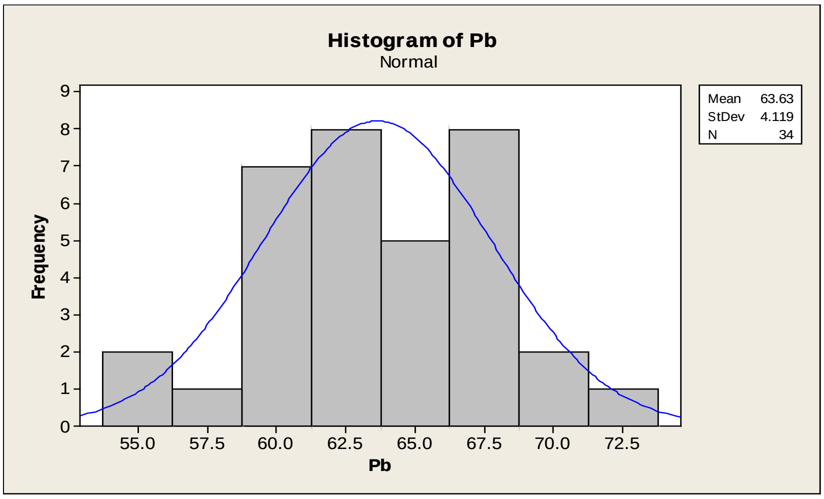


Figure 173 Histogram showing measured lead data in S13B. Values are in mg kg^{-1}.

RUBIDIUM Rb

Shewhart plots of primary and secondary reference materials indicated that there were generally no issues with the precision of data as reported direct from the laboratory for most materials. However, the results for the reference material antbas showed a considerable reduction in precision for the later part of the analytical period. This change was not seen for any other material. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results did not improve their accuracy compared to the expected values. The histogram of results for S13B shows the majority of fall close to or just above the expected value of 111.4 mg kg^{-1}.

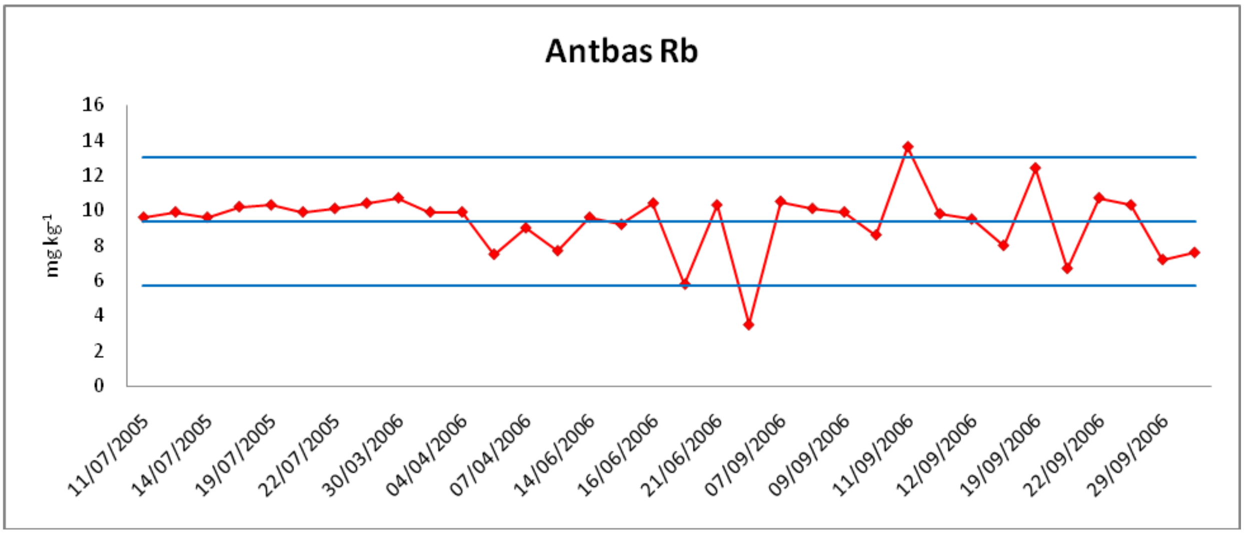


Figure 174 Shewhart Chart for Rubidium in Antbas.

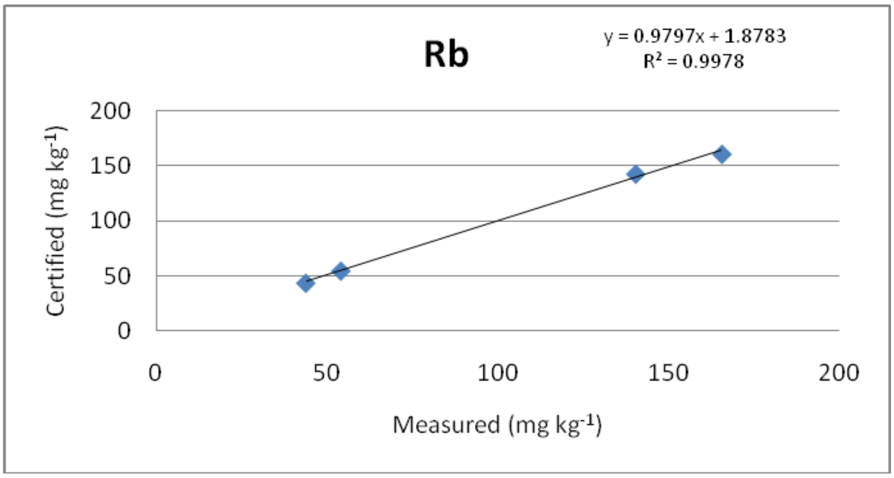


Figure 175 Regression plot for measured values against certified values for rubidium in Till-1, 2, 3 and 4.

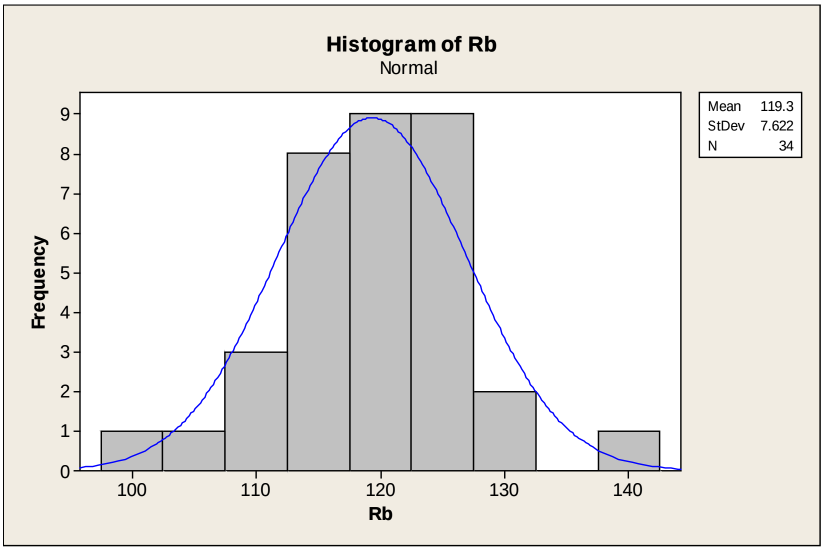


Figure 176 Histogram showing measured rubidium data in S13B. Values are in mg kg^{-1}.

SULPHUR S

Shewhart plots of primary and secondary reference materials indicated that there were generally no issues with the precision of data as reported direct from the laboratory. There were insufficient data available to plot a regression of reported Till CRM values against certified/provisional values; therefore no correction can be attempted. The histogram of results for S13B shows a clearly defined peak, with just two outlying low values. There are no data available to compare these values to.

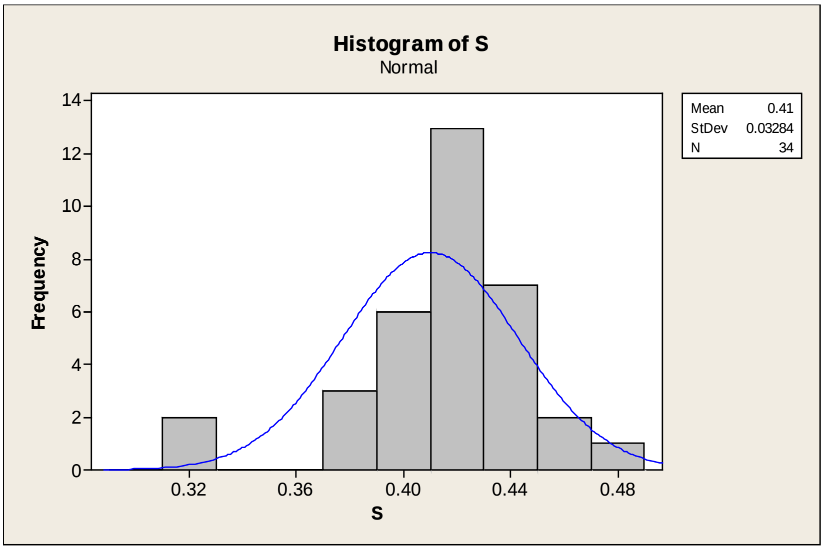


Figure 177 Histogram showing measured sulphur data in S13B. Values are % S.

ANTIMONY Sb

Shewhart plots of primary and secondary reference materials indicated no systematic issues with the precision of data as reported direct from the laboratory. The plot for SO-3 showed four unusually high points, all with approximately the same concentration; this was not seen for any of the other reference materials. A regression of reported Till CRM values against certified/provisional values was carried out, although the results for three of the materials used were similar. Applying the obtained factor did not improve the data for the other reference materials. The histogram of the results for S13B shows a normal distribution centred tightly on 0.5mg kg^{-1}. The results for the materials for which target values were available show the data to be approximately 30% low. This is probably due to antimony being lost as antimony pentafluoride (boiling point 149.5°C) during the aggressive heating in the dissolution process.

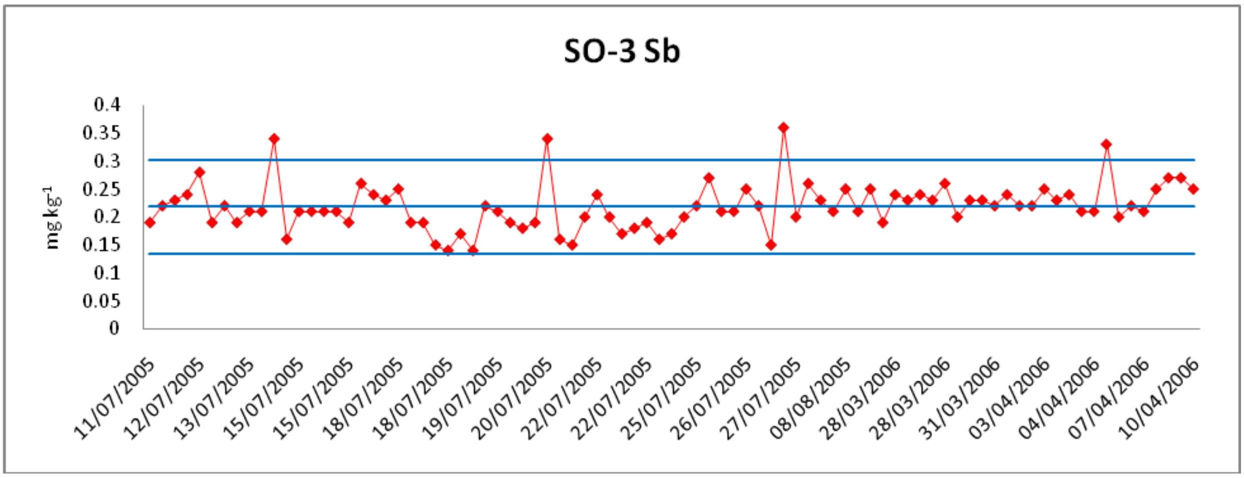


Figure 178 Shewhart Chart for antimony in SO-3.

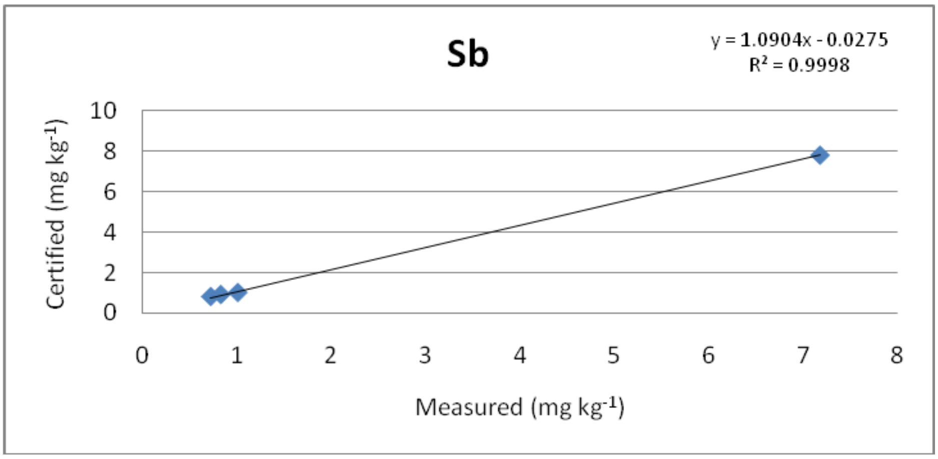


Figure 179 Regression plot for measured values against certified values for antimony in Till-1, 2, 3 and 4.

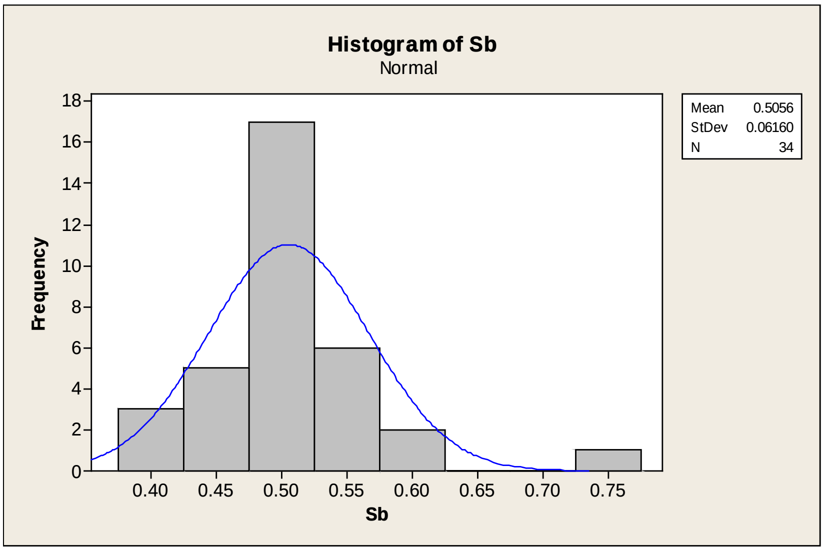


Figure 180 Histogram showing measured antimony data in S13B. Values are in mg kg^{-1}.

SELENIUM Se

All the results for selenium in the reference materials and most of the samples fell below the detection limit.

TIN Sn

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory, although for some materials, occasional results fell well above the expected values. This is seen on the histogram of the results for S13B, where the majority of the results fall just below the expected value of 2.9mg kg^{-1} but there are outliers at around 4 and 6mg kg $^{-1}$. Data were not available for a regression to be plotted.

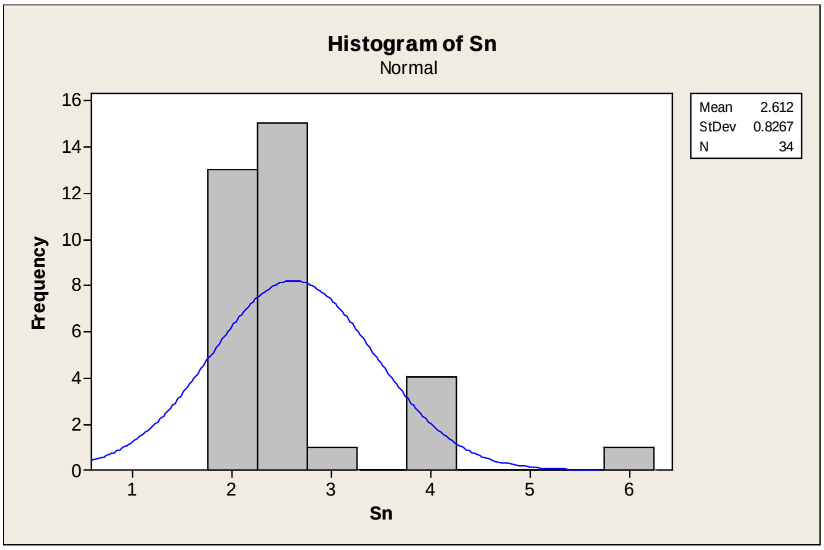


Figure 181 Histogram showing measured tin data in S13B. Values are in mg kg^{-1}.

STRONTIUM Sr

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory, although two materials had results that fell well away from the mean which is notable in an element with an otherwise high level of precision. A regression of reported Till CRM values against certified/provisional values was carried out. The factor, when applied to the mean laboratory data for the other reference materials slightly improved the results compared to the expected values. The histogram of results for S13B shows the distribution to be skewed above the expected value of 122mg kg^{-1}.

Correction factor = ([Sr] x 1.0168) – 6.5825

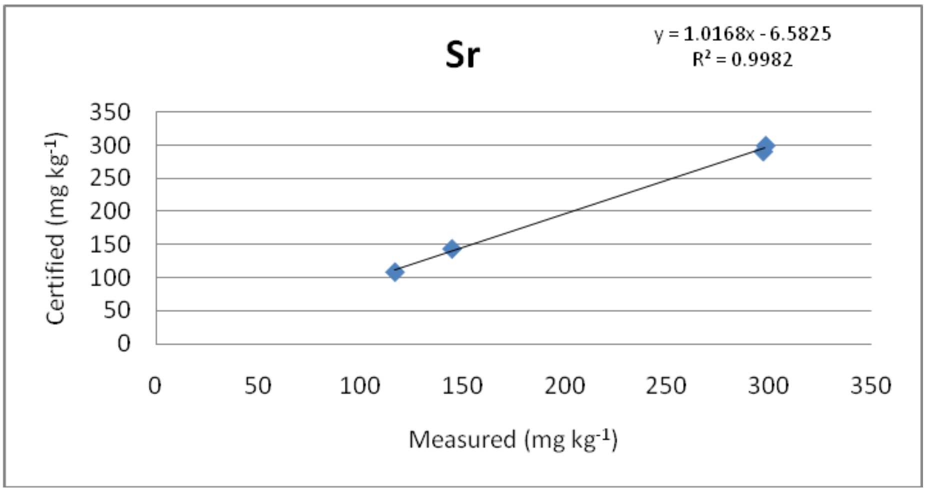


Figure 182 Regression plot for measured values against certified values for strontium in Till-1, 2, 3 and 4.

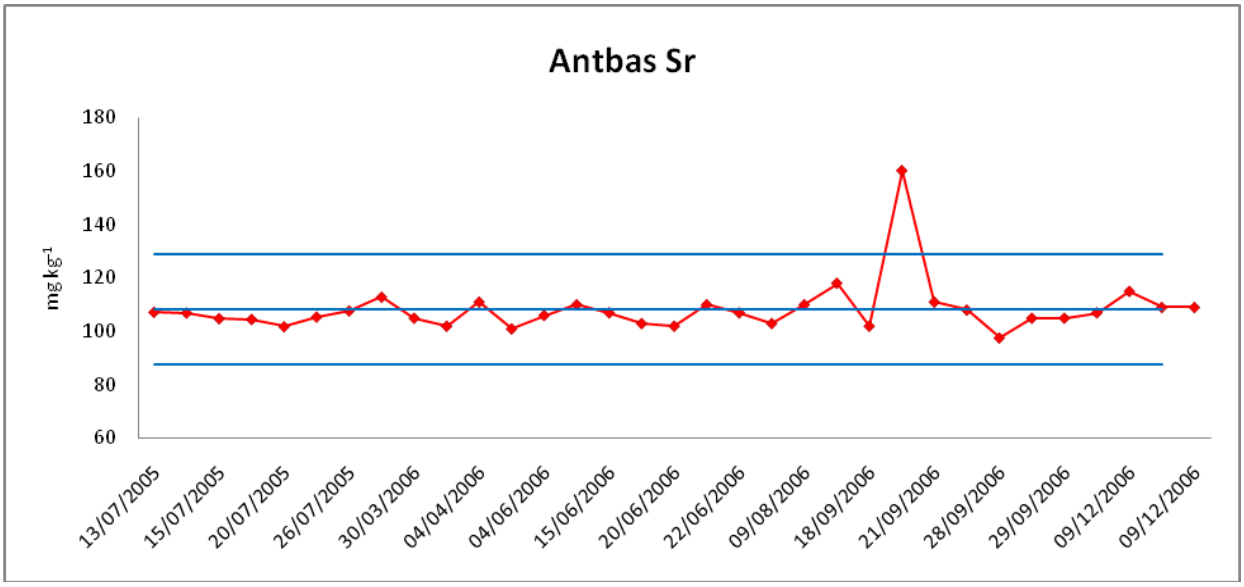


Figure 183 Shewhart Chart for strontium in antbas.

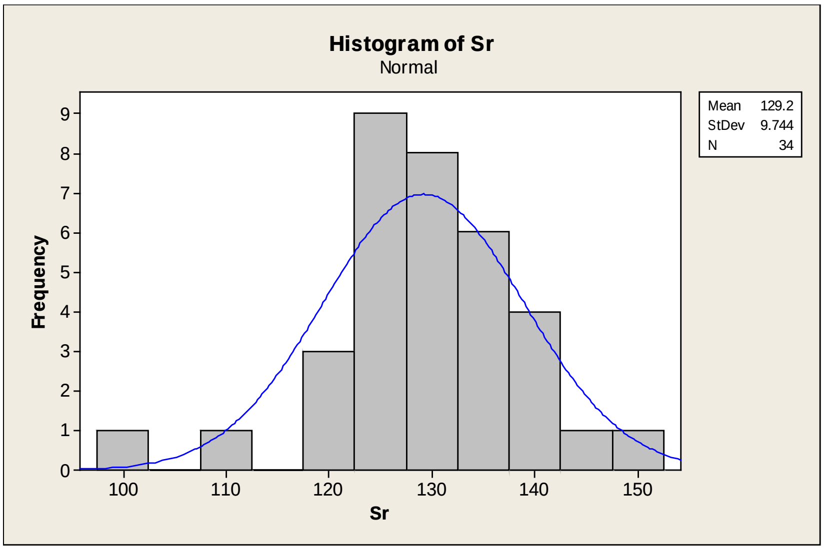


Figure 184 Histogram showing measured strontium data in S13B. Values are in mg kg^{-1}.

THORIUM Th

Shewhart plots of primary and secondary reference materials indicated that there were no systematic issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials gave some improvement towards the expected values for those with higher levels of thorium, but made the results much worse for those with lower levels. The histogram for the measured results for S13B gave a normal distribution which sits above the expected value of 10.6mg kg^{-1}.

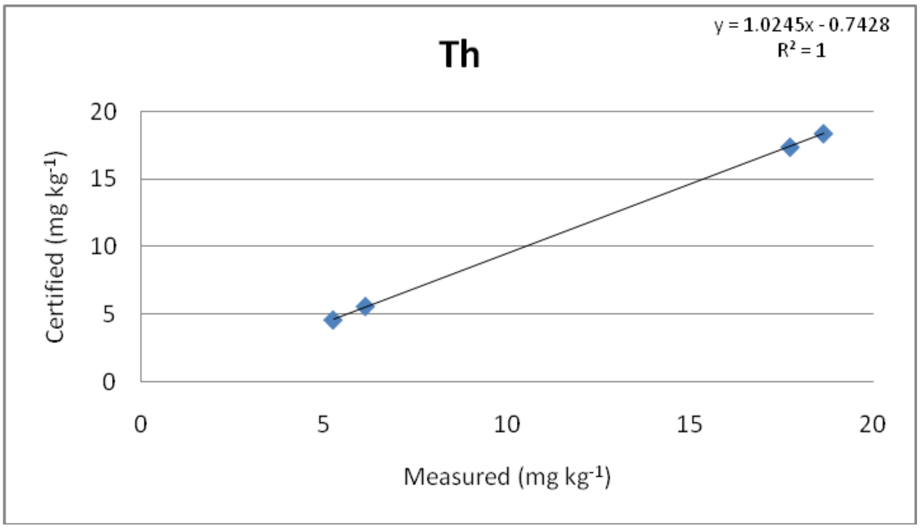


Figure 185 Regression plot for measured values against certified values for thorium in Till-1, 2, 3 and 4.

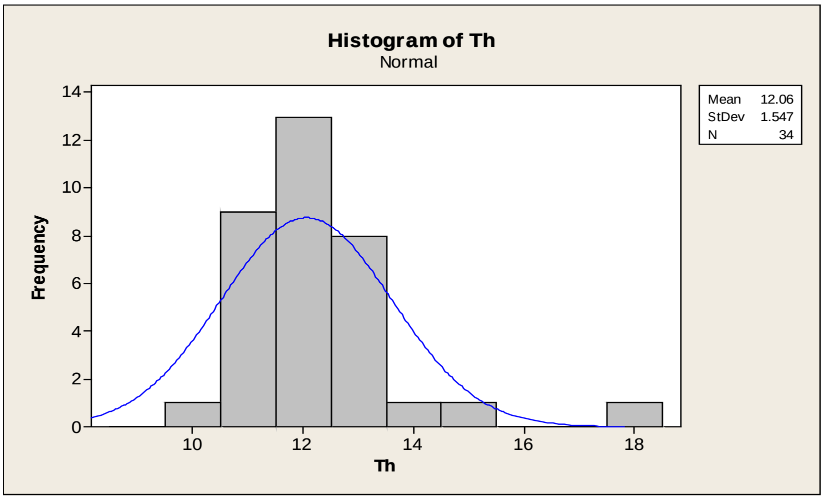


Figure 186 Histogram showing measured thorium data in S13B. Values are in mg kg^{-1}.

URANIUM U

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram for results for S13B shows most values to lie above the expected value of 2.8mg kg^{-1}.

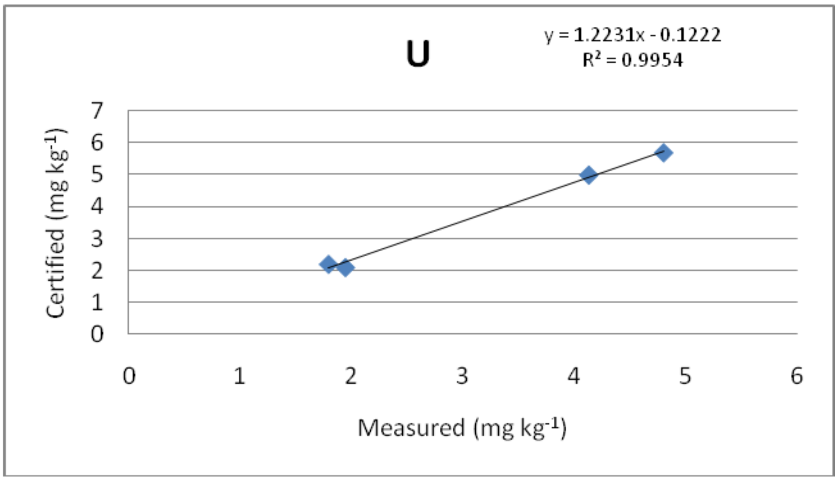


Figure 187 Regression plot for measured values against certified values for uranium in Till-1, 2, 3 and 4.

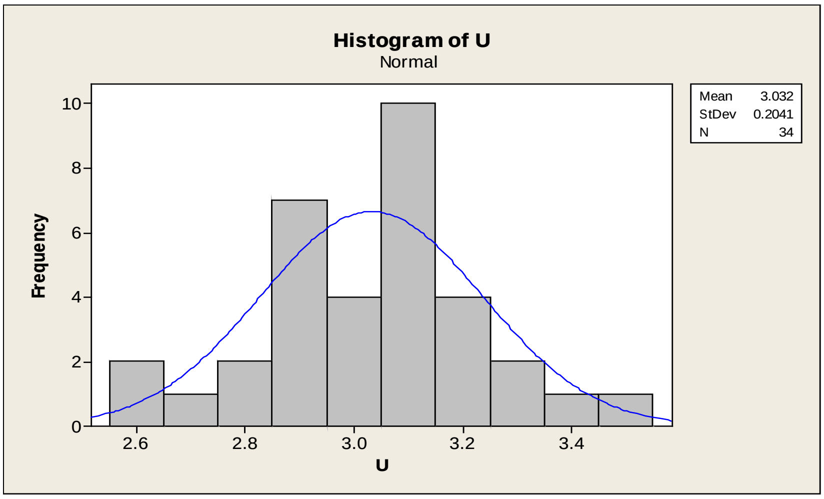


Figure 188 Histogram showing measured uranium data in S13B. Values are in mg kg^{-1}.

VANADIUM V

Shewhart plots of primary and secondary reference materials indicated that there were generally no systematic issues with the precision of data as reported direct from the laboratory. However it is noticeable that on the 19 and 20 September 2006 some of the reference materials produced unusually high results, this was not the case for all the materials. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of measured results for S13B shows a broad spread of data, mostly below the expected value of 99mg kg^{-1}.

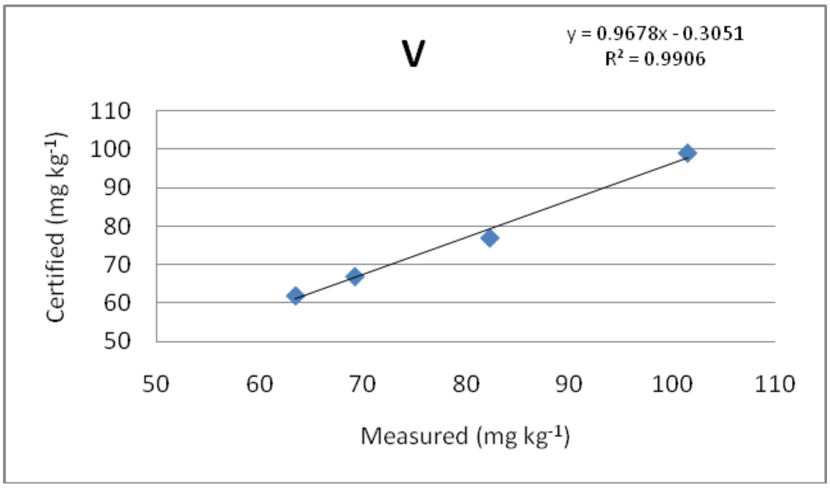


Figure 189 Regression plot for measured values against certified values for vanadium in Till-1, 2, 3 and 4.

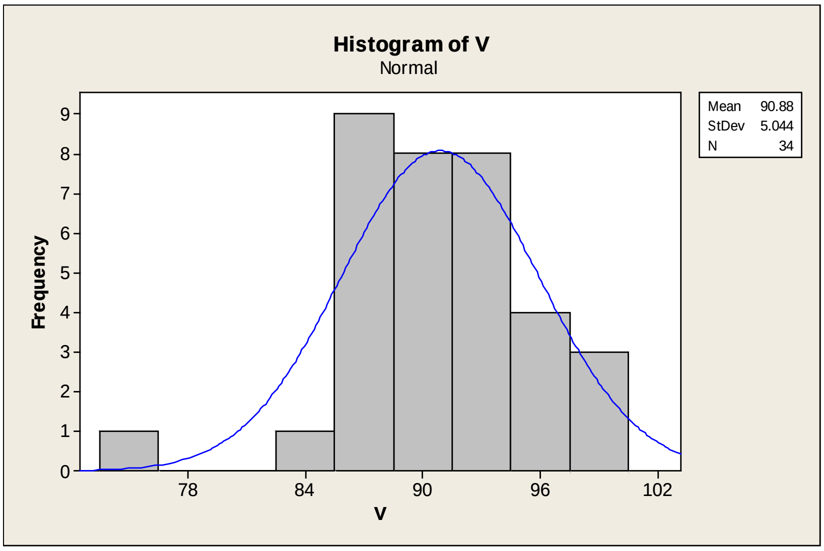


Figure 190 Histogram showing measured vanadium data in S13B. Values are in mg kg^{-1}.

YTTRIUM Y

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out and, although the data were well above the detection limit, the correlation coefficient was too low to allow the factor to be applied. The histogram of results for S13B shows a normal distribution, but is below the expected value of 22.6mg kg^{-1}. The low and erratic recoveries seen for this element are probably due to yttrium being bound up in the resistate minerals.

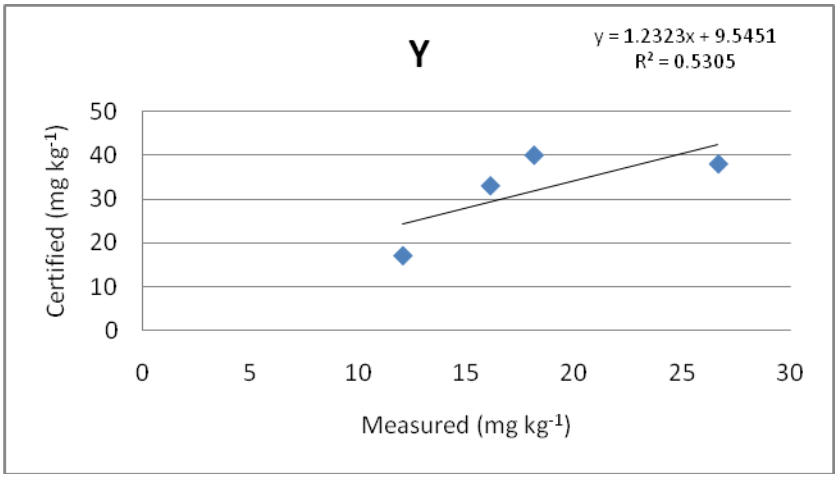


Figure 191 Regression plot for measured values against certified values for yttrium in Till-1, 2, 3 and 4.

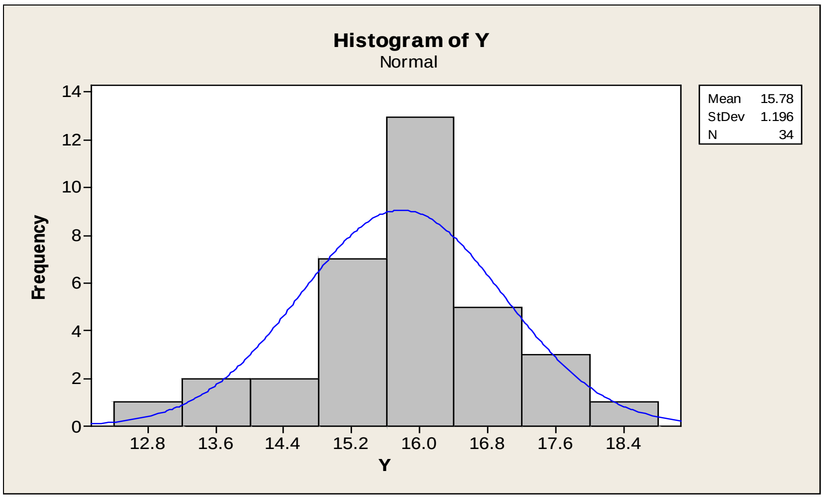


Figure 192 Histogram showing measured yttrium data in S13B. Values are in mg kg^{-1}.

ZINC Zn

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. Applying the factor to the measured results for the other reference materials did not improve their accuracy compared to the expected values. The histogram of measured results for S13B shows a broad spread of data, above the expected value of 99.7mg kg^{-1}, although it should be noted that at 115% recovery this was the worst of the reference materials, the average recovery being 102.9%.

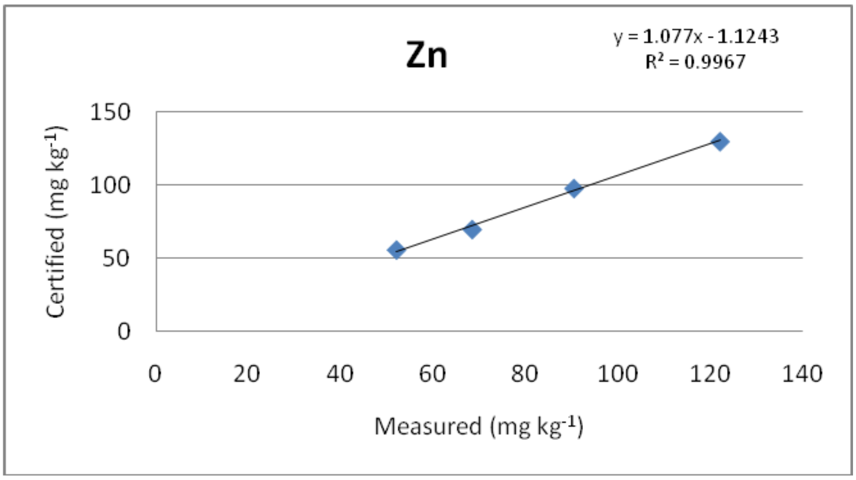


Figure 193 Regression plot for measured values against certified values for zinc in Till-1, 2, 3 and 4.

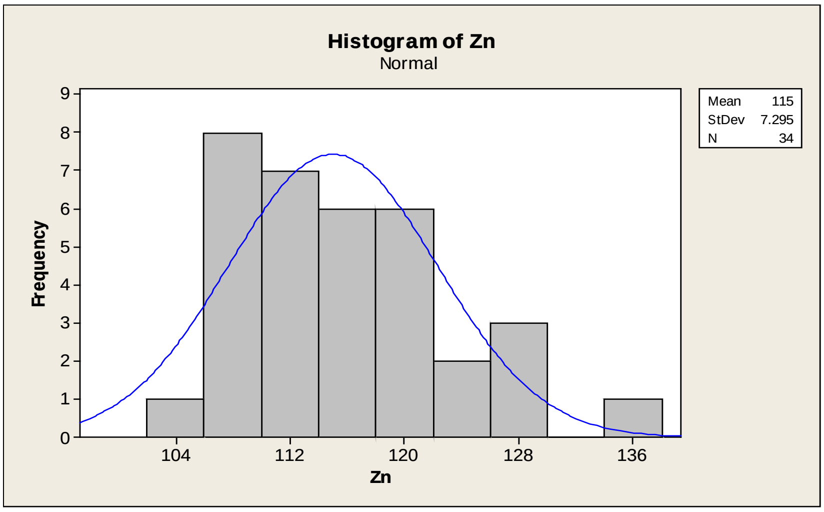


Figure 194 Histogram showing measured zinc data in S13B. Values are in mg kg^{-1}.

ZIRCONIUM Zr

Shewhart plots of primary and secondary reference materials indicated that there were no issues with the precision of data as reported direct from the laboratory. A regression of reported Till CRM values against certified/provisional values was carried out. This gave an unusually large correction factor which does not improve the results for the other reference materials when applied to the raw data. It is not unusual for zirconium values to be low for '*near-total*' dissolutions, as resistate materials such as zircons will be unaffected by the mixed acid dissolution method. The histogram reflects this problem, giving a normal distribution, but below the expected value of 159.6mg kg^{-1}.

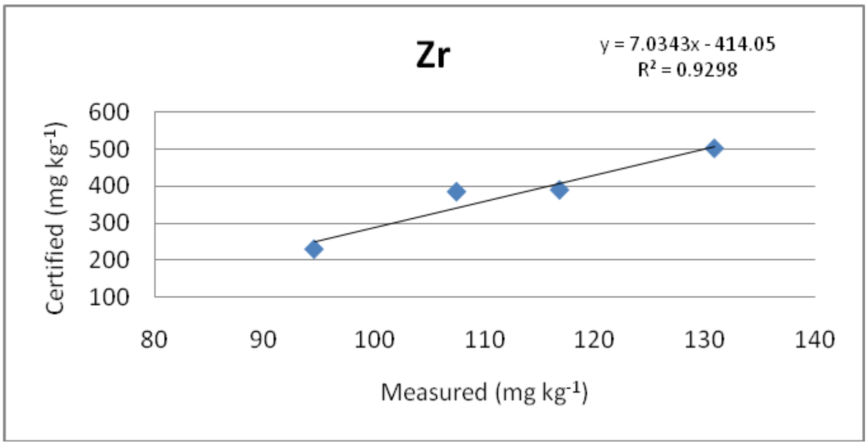


Figure 195 Regression plot for measured values against certified values for zirconium in Till-1, 2, 3 and 4.

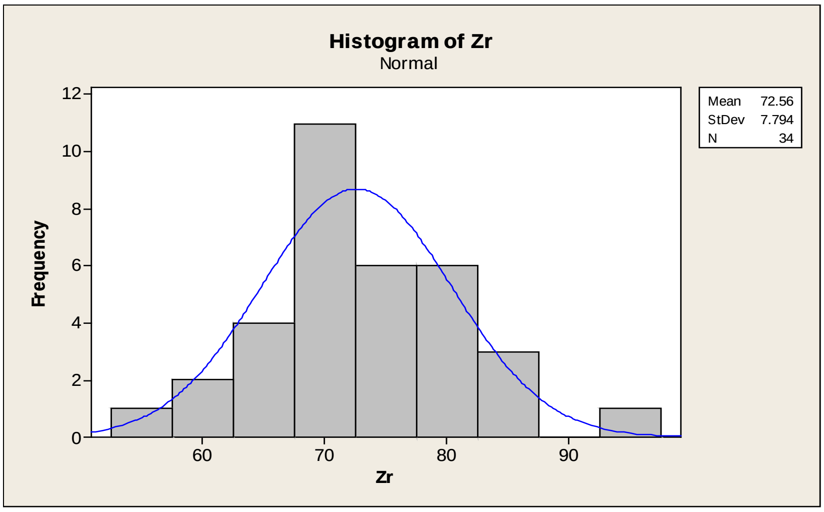


Figure 196 Histogram showing measured zirconium data in S13B. Values are in mg kg^{-1}.

Appendix 4: Detailed quality assessment of acid extracted sulphate analysis by ICP-OES of Tellus ‘S’ soils

Shewhart plots of secondary reference material data indicated that there were no significant issues with the precision of the data as reported direct from the laboratory, although it is noticeable that the precision for several reference materials was better earlier in the analytical period than later. This is clearly shown by the Shewhart plot for reference material S13B shown below.

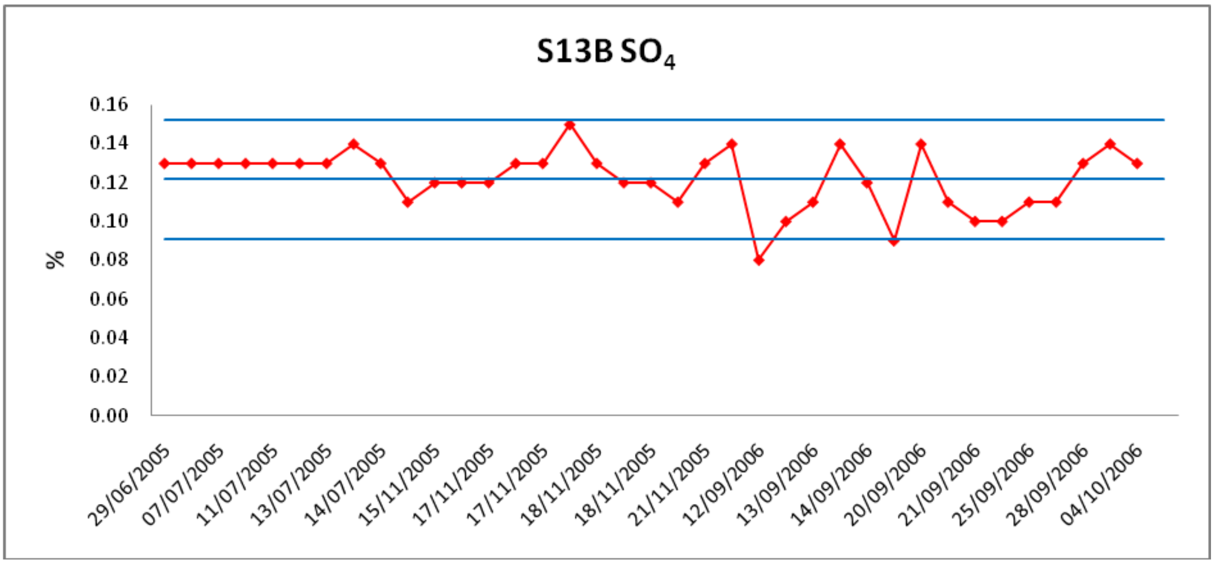


Figure 197. Shewhart chart for sulphate in S13B

There were insufficient values for the certified reference materials to plot a regression. For a short period in November 2005 the detection limit was raised from 0.01 to 0.05%. This higher value is the one normally quoted by the analytical laboratory, although several of the reference materials show good precision down to at least 0.02%.

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