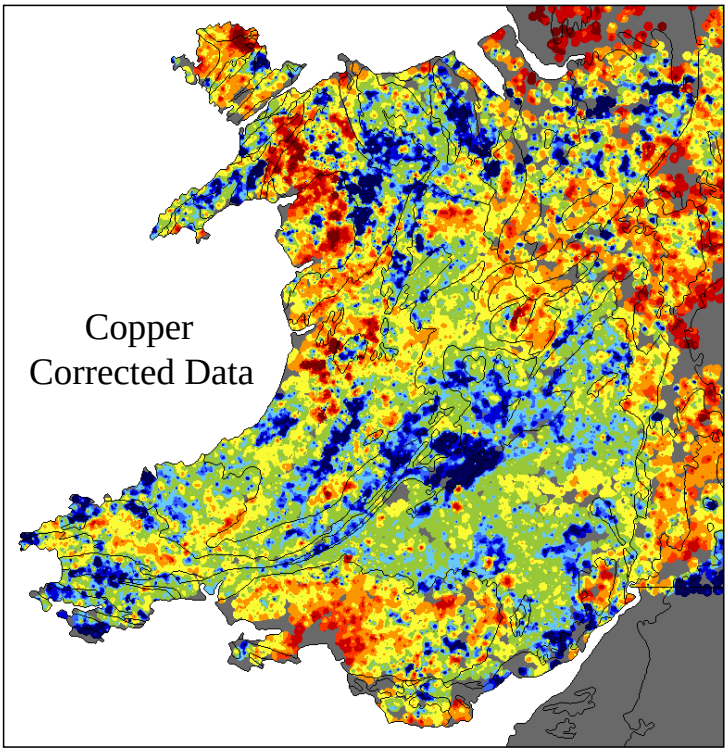
British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Quality Control of G-BASE Data

Procedures Followed for XRF Data From Wales and Welsh Borders Area Stream Sediment Samples

G-BASE

Internal Report IR/02/105



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/105

Quality Control of G-BASE Data

Procedures Followed for XRF Data From Wales and Welsh Borders Area Stream Sediment Samples

T R Lister

Key words

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Front cover

Colour enhanced digital image of corrected copper data.

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Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

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1 Introduction

Analysis of all G-BASE solid (stream sediment, soil, rock) samples is carried out in laboratories at BGS, Keyworth. The analytical method routinely used is Wavelength Dispersive X-Ray Fluorescence (WD-XRF) (Ingham & Vrebos 1994).

To accommodate the full range of elemental data requested by G-BASE, it has been necessary for the laboratory to develop three separate analytical programmes for particular suites of elements. The result is the generation of three discrete data files, each containing analytical data for the elemental suite analysed within each particular programme.

Each batch of samples is identified by a unique laboratory number which is assigned by laboratory staff on receipt of an analytical request. When data is reported by the laboratory, three data files corresponding to each laboratory number are sent digitally to the G-BASE data manager who will then begin the overall task of data quality control.

This document outlines the procedures applied to all G-BASE solid sample data once reported by the laboratory to the G-BASE data manager. The correction factors applied to the raw data prior to loading to the BGS Geochemistry Database are listed in this report.

2 Transfer of Data

Three data files for each laboratory number are generated by the analytical instruments, and are differentiated by an alpha-numerical code combined with the laboratory number.

The data files contain information on date and time of analysis, as well as the analytical determinations for each element. Files are transferred digitally, generally as e-mail attachments, in a space-delimited text format containing rows and columns of data.

In this format, the data can be accessed directly by Excel or used as the input file for an Access data table.

3 Creating the Database

Access relational database software enables the text-format data files to be used to create data tables for each laboratory number. Three individual data-table template files are generated, into which data from each of the three different analytical programmes may be appended.

As a relational database, links can be created to join data fields between the analytical data tables and the G-BASE field observations data table (created at the time of sample collection) containing sample type code data, locational data and a wide range of sample site observations.

4 Linking Tables

The only prerequisite for linking data tables is that the field by which the tables are to be related must have the same identity in all linked tables. In the case of G-BASE data, the linked field is the sample identification number. This field is given the identity SAMPLE_NO in all tables to be linked. SAMPLE_NO is a unique number assigned to the sample at time of collection, and includes a two-digit project code followed by a four-digit sample code.

Once a relation has been set up between tables, data fields can be copied between the related tables. In this way, the sample type code field from the field data table is appended to the analytical data tables.

5 Creating Control Tables

From the analytical tables with appended sample type code fields, new tables are created containing only G-BASE control sample data. Control samples are labelled ‘STD’ (Internal Standard), and can be copied to new tables by using simple queries from within Access. The end products of these functions are three control data-tables, which contain data only for the G-BASE internal control standards analysed as part of the laboratory number under scrutiny.

Two control samples are present in each batch of 100 samples submitted to the laboratory. Control samples consist of material of known elemental concentrations. There are approximately 8 different control material types used routinely within G-BASE. For any particular atlas area generally four different control standards are used for data quality control procedures.

6 Generating Control Graphs

Control graphs for all elements are created by plotting element concentration against time of analysis. This produces a ‘time-series’ plot for each element for each control standard. Access control tables may be opened as Excel spreadsheets, within which the functionality exists to construct time-series plots, an example of which is shown below. This example is a simple time-series plot for copper concentration in control standard S15. Further information such as trend lines and error bars may be added to the graphs.

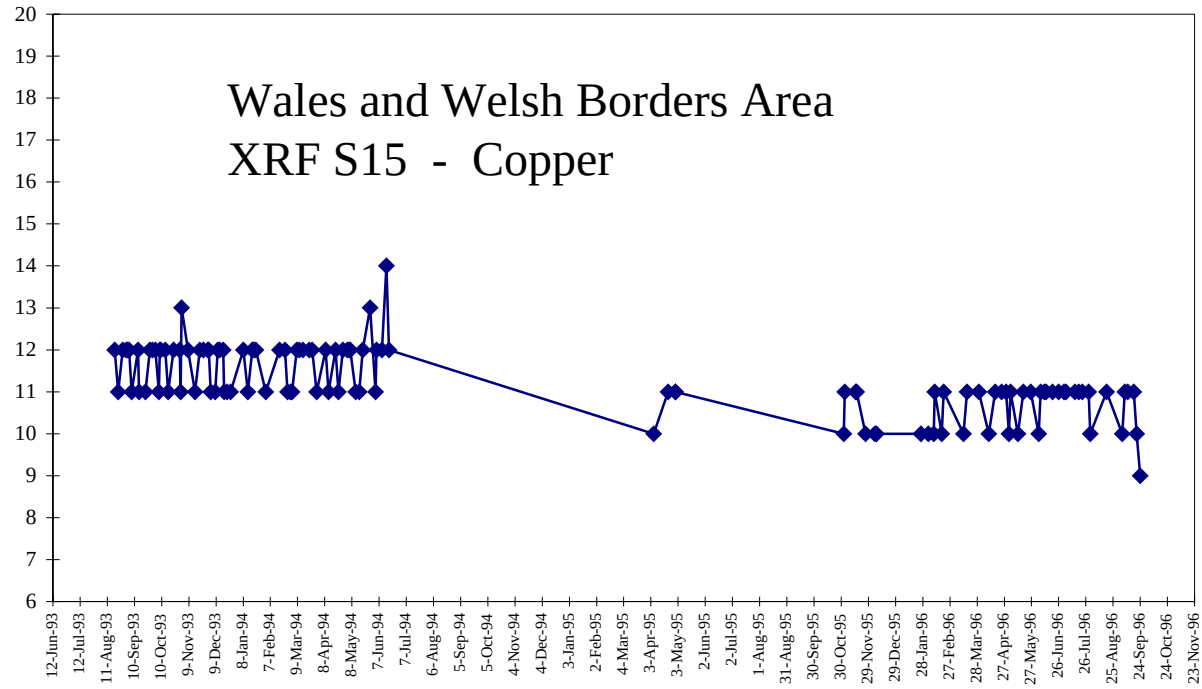


Fig. 1. Excel generated time-series control plot for Wales and Welsh Borders area XRF data. S15 - Copper

Theoretically, if the analytical instruments are performing to the optimum level and have been calibrated/recalibrated correctly, the control graphs should display little variation in element concentration throughout the period of analysis.

In reality however, the control graphs often show clearly identifiable shifts in the data. Most often this is coincident with a recalibration event which has been necessary due to instrument breakdown or after instrument service/overhaul. In the case of Wales and Welsh Borders area samples, several recalibrations of the analytical instruments were carried out during the entire

period of analysis of approximately 21,500 samples. A total of 49 individual laboratory numbers constitute the total number of samples analysed for this particular project over a 3-year period.

7 Generating Colour Enhanced Digital Images

Colour enhanced images of the geographical distribution of each element, when examined together with the respective time-series graphs, can give an immediate visual impact as to the nature of underlying analytical problems, and a possible indication of the corrective steps required to amend the data. When creating images, it is essential that factors such as analytical detection limits and reported units be considered before classifying data.

The public-domain software package NIH-Image, with added routines, has been utilised for the purpose of image generation. (Herd 1997)

Examples of colour enhanced images and associated time-series graphs are shown in appendix 1.

8 Normalising Data

In conjunction with data from analysis of International Reference Material, definitive concentrations of each element, for all G-BASE control standards may be attained. It is with respect to these definitive concentrations that any subsequent normalisation of data will be made.

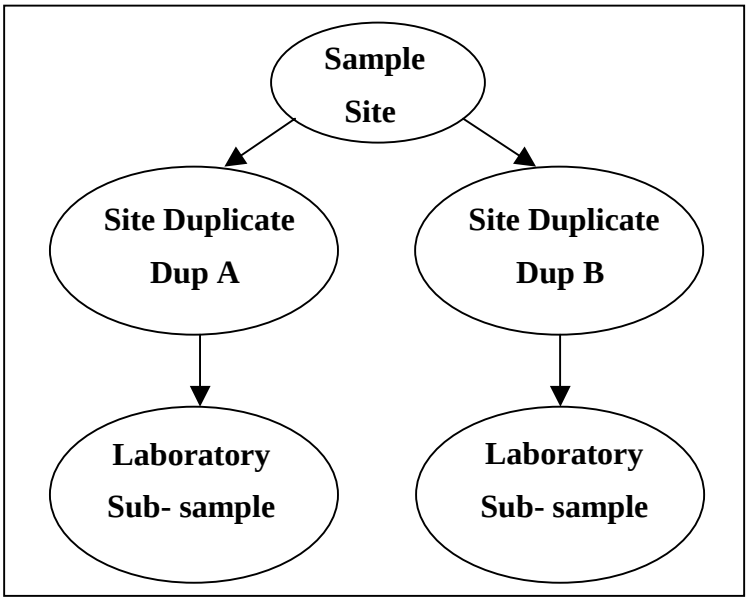
Several stages of normalisation may be necessary before data for a particular element satisfy quality control checks. Firstly, shifts in concentration within the period of analysis must be eliminated. This may involve breaking the time-series plots into a series of segments, within which the concentrations are fairly constant over time. Calculation of the mean concentrations within each segment will provide adequate information to enable ‘within analysis’ correction factors to be applied. An example of this procedure is shown in appendix 2.

Normalisation of data was undertaken for all elements displaying discontinuous time-series control graphs, with evident ‘shifts’ in concentration. The normalisation factors for all elements are presented as appendix 3.

9 Analysis of Variance (ANOVA)

At one sample site in each discrete batch of 100 samples, a site sample duplicate was collected. Each of the duplicate pair was subsequently sub-sampled at the sample preparation laboratory to produce a replicate set of four samples for each duplicate site. (Figure 2.)

Figure 2. Sample replicate methodology



In order to quantify sampling and analytical precision, analysis of variance (ANOVA) was carried out on the replicate data. For stream sediments, a total of 186 replicate sets, collected at random throughout the area of sampling, were used in the ANOVA calculations.

A random nested model of ANOVA was selected, since all the analyses form part of a single randomised dataset (Snedecor & Cochran, 1989). The NESTED procedure from the MINITAB™ statistical software package was used to perform the ANOVA.

Within-sample variance (represented by multiple components including inhomogeneities introduced during sample handling and preparation, and analytical errors), between-sample variance (representing within-site variation and any variation incorporated during collection of the sample) and between-site variance (the natural distribution of elements in stream sediments) were calculated.

Because the frequency distribution of most elements is multi-modal and none fit the Gaussian model perfectly, there is an unquantifiable overstatement of the between-site variance - a problem that is inherent in using ANOVA on geochemical data.

Statistical F-tests have not been quoted because the data do not satisfy this and other assumptions required for formal analysis of variance.

Table 1. Percentage of variance in stream sediment samples attributable to between-site, between-sample and within-sample variance.

Element	Between Site (%)	Between Sample (%)	Within Sample (%)
MgO	98.01	1.11	0.88
P_2O_5	86.77	9.32	3.91
K_2O	95.41	3.21	1.37
CaO	93.39	6.12	0.49
TiO_2	97.44	1.54	1.02
MnO	93.62	6.07	0.31
Fe_2O_3	95.52	3.94	0.55
V	96.11	2.47	1.42
Cr	95.74	2.61	1.65
Co	95.69	3.99	0.32
Ba	88.31	10.41	1.29
Ni	92.95	5.73	1.32
Cu	93.37	5.25	1.37
Zn	95.32	4.37	0.31
Ga	94.60	2.19	3.21
As	92.73	6.85	0.42
Se	72.79	12.86	14.35
Rb	93.64	3.75	2.62
Sr	91.38	7.71	0.91
Y	91.20	2.52	6.28
Zr	87.68	4.87	7.44
Nb	82.67	3.59	13.75
Mo	79.27	1.88	18.85
Pb	98.41	1.44	0.15
Bi			
Th	81.88	4.62	13.51
U	69.34	7.64	23.02
Ag			
Cd	84.70	2.44	12.86
Sn	77.01	11.80	11.20
Sb			
Cs			
La	84.82	6.00	9.17
Ce	82.98	10.06	6.96

Due to the large amount of data reported below the lower limit of detection, ANOVA calculation was not performed on Bi, Ag, Sb and Cs.

Complete ANOVA calculations are presented as appendix 4.

10 Transfer of Data to Geochemistry Database

On completion of all the quality control procedures described in this report, data is accepted by the G-BASE data manager as being fit for transfer to the BGS corporate Geochemistry Database.

The normalised data is passed on to the Geochemistry Database manager for loading to the Oracle data tables. This report represents a record of the correction factors applied to the raw analytical data generated from stream sediment samples, prior to incorporation into the corporate Geochemistry Database.

Appendix 1

Comparison of raw data and corrected data colour enhanced digital images for Cu in stream sediments over the Wales and Welsh Borders area.

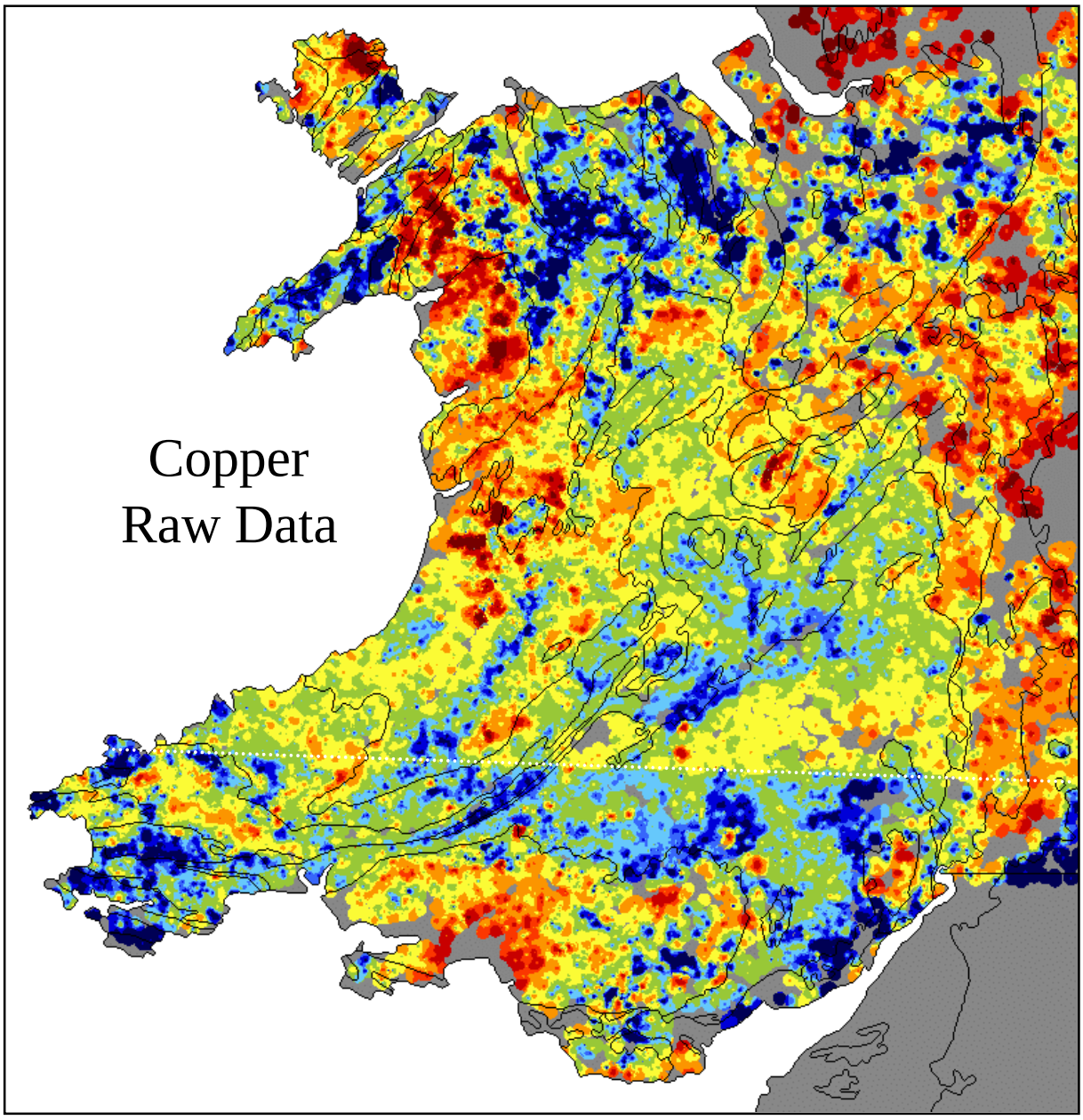


Fig. 3. Colour enhanced digital image displaying raw data distribution of Cu in stream sediments over the Wales and Welsh Borders area. A linear feature related to changes in instrument calibration is clearly evident (highlighted as white dashed line) when compared to the image generated using corrected data. The image has been classified using standard G-BASE percentile ranges (5,10,15,25,50,75,90,95,99%), with dark blue representing the lowest class, through to deep red indicating the highest levels. Areas where no samples have been collected are coloured grey.

Time-series control graphs for G-BASE control standards: Wales and Welsh Borders area.

Data trend lines are represented by dashed green lines, and it can be seen that a general decrease in the measured concentration of Cu in S13, S15, and S3B control standards occurs over the period of analysis. In the case of S26, variation at considerably higher Cu concentrations is less noticeable.

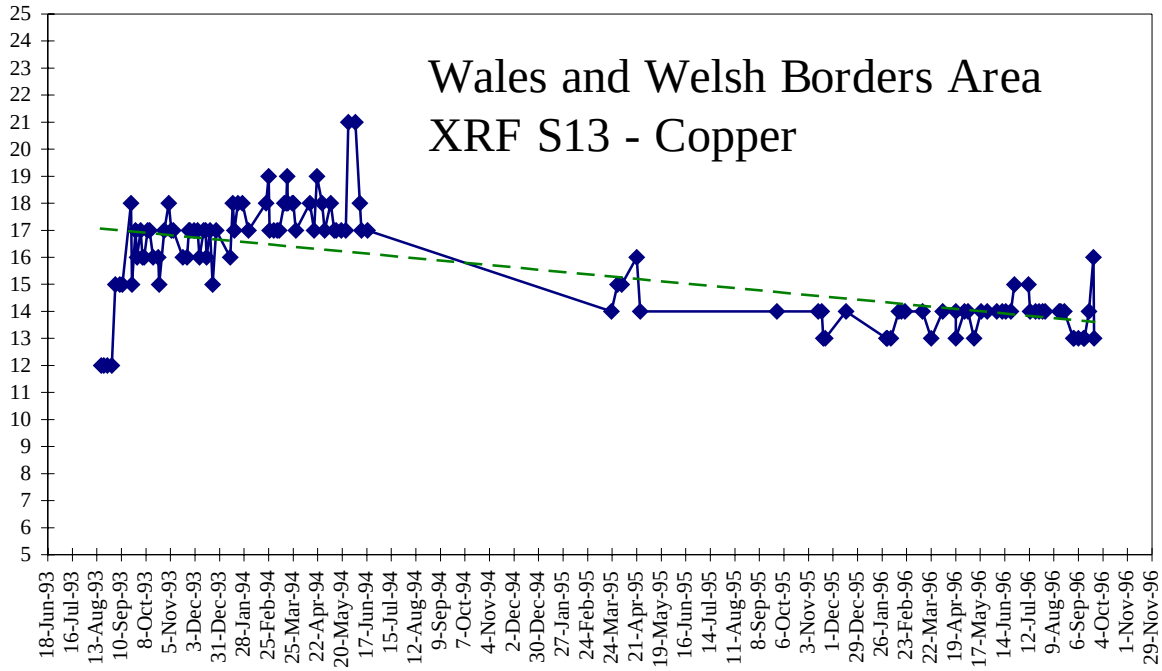


Fig. 4. Time-series control graph for Cu in control standard S13 from Wales and Welsh Borders area samples.

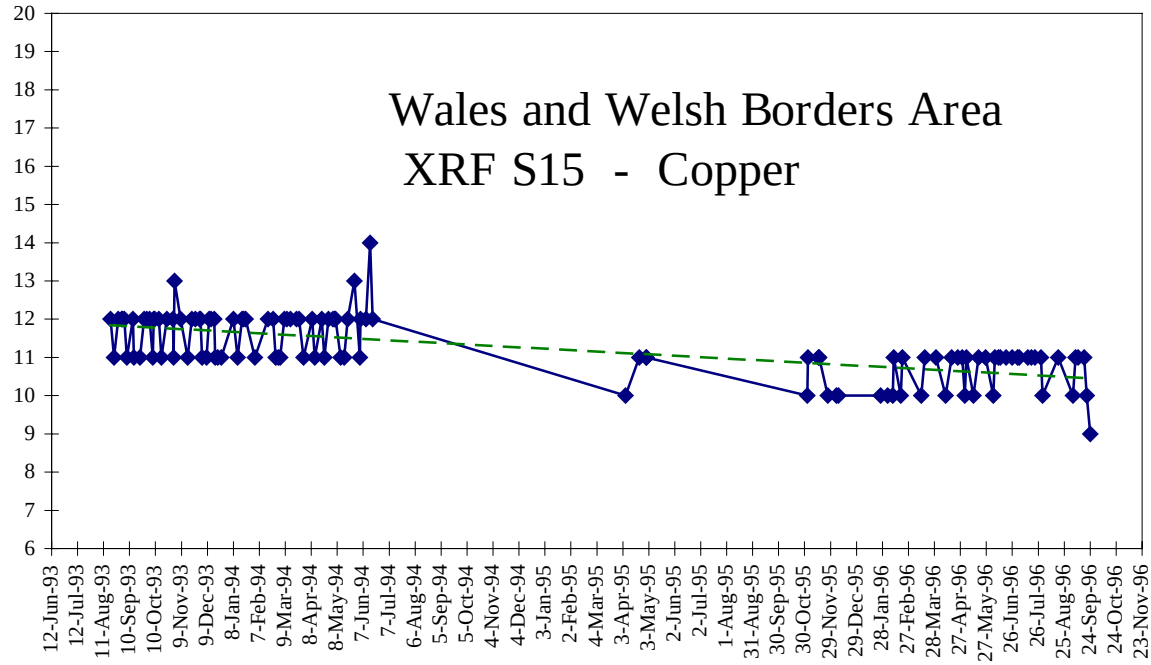


Fig. 5. Time-series control graph for Cu in control standard S15 from Wales and Welsh Borders area samples.

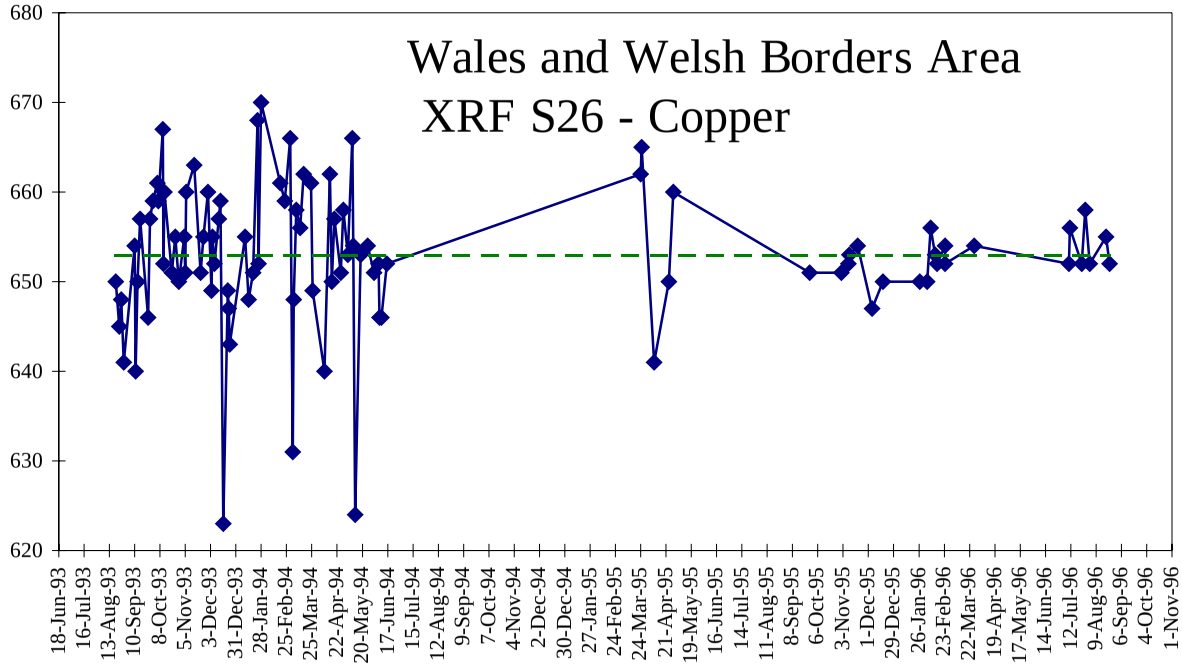


Fig 6. Time-series control graph for Cu in control standard S26 from Wales and Welsh Borders area samples

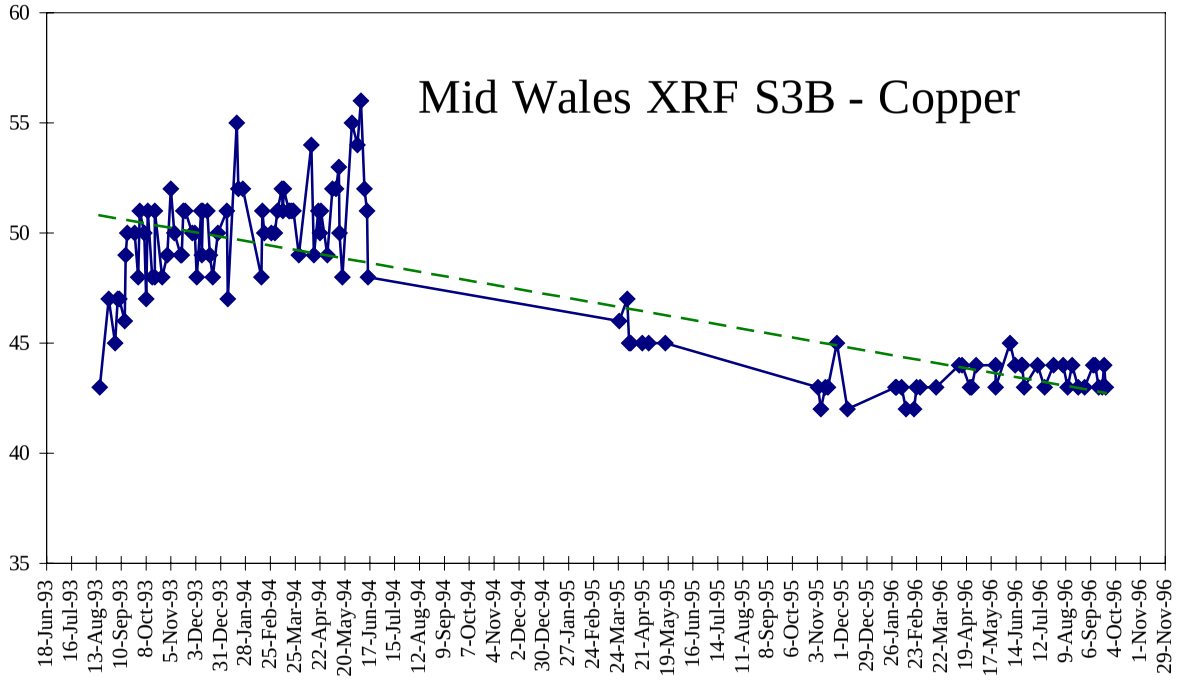


Fig. 7. Time-series control graph for Cu in control standard S3B from Wales and Welsh Borders area samples

Data from G-BASE control standards S13, S15, S2 and S3b were normalised as described in appendix 2. The appropriate correction factors were applied to the raw copper data to generate the image displayed in figure 8.

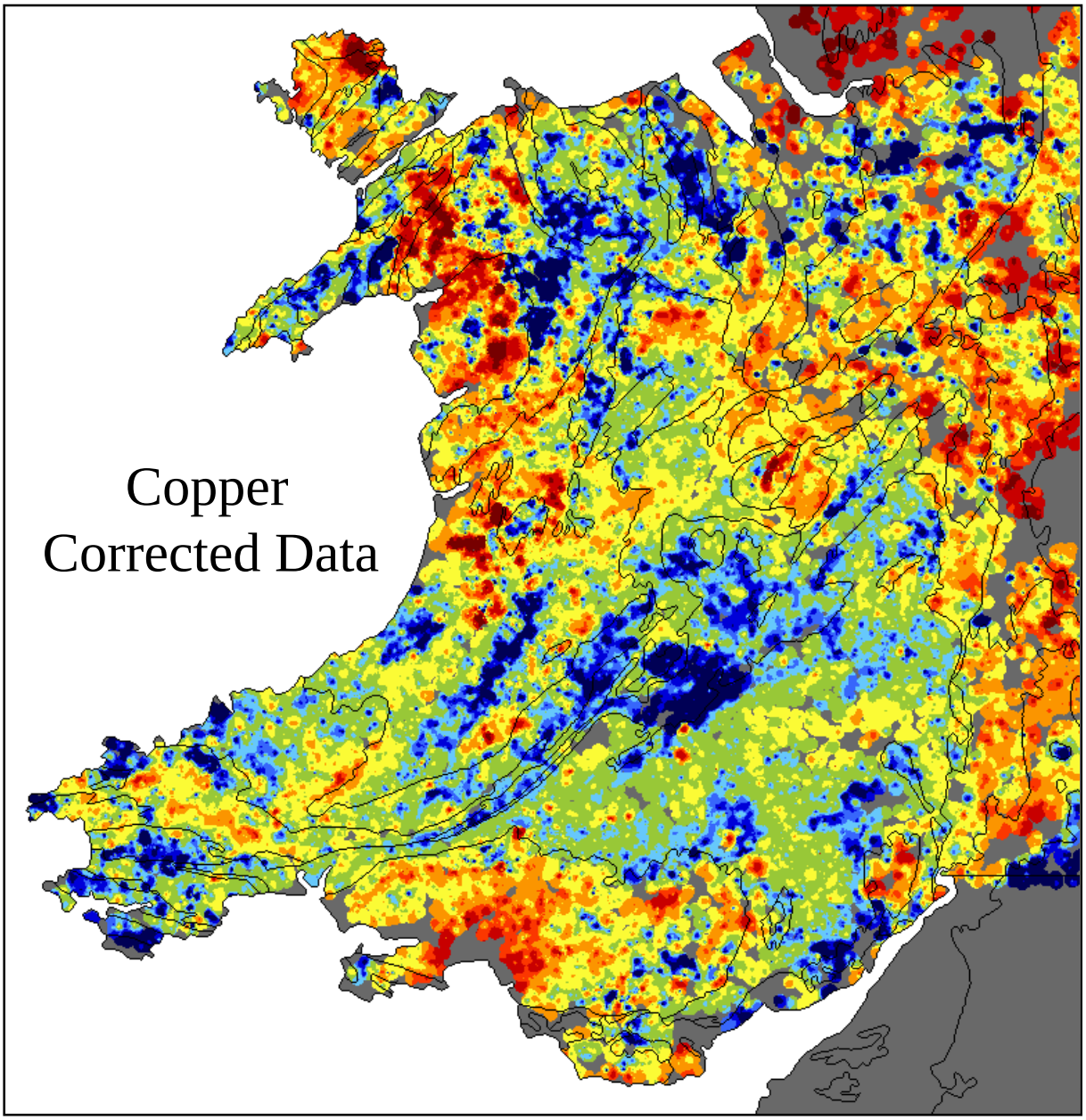


Fig. 8. Colour enhanced digital image displaying corrected data distribution of Cu in stream sediments over the Wales and Welsh Borders area. Linear features related to changes in instrument calibration evident in the raw data image are now invisible. The image has been classified using standard G-BASE percentile ranges (5,10,15,25,50,75,90,95,99%), with dark blue representing the lowest class, through to deep red indicating the highest levels. Areas where no samples have been collected are coloured grey.

Appendix 2

An example of the method by which time-series charts may be split into segments is illustrated below. Charts for G-BASE controls S13, S15, S26 and S3B, for the element Cobalt, are shown. Figures 9 – 12 show the concentration of Co throughout the entire period of analysis. From these charts, it is evident that there are three discrete populations of Co concentration, namely August 1993 – November 1993, November 1993 – November 1994, and November 1994 - August 1996.

New time-series plots were generated for each of the three identified periods of analysis, and mean values of element concentration calculated. A factor was then calculated to normalise each segment of the period of analysis to the accepted concentration. Figures 13 – 24 show plots for each segment for G-BASE controls S13, S15, S26 and S3B.

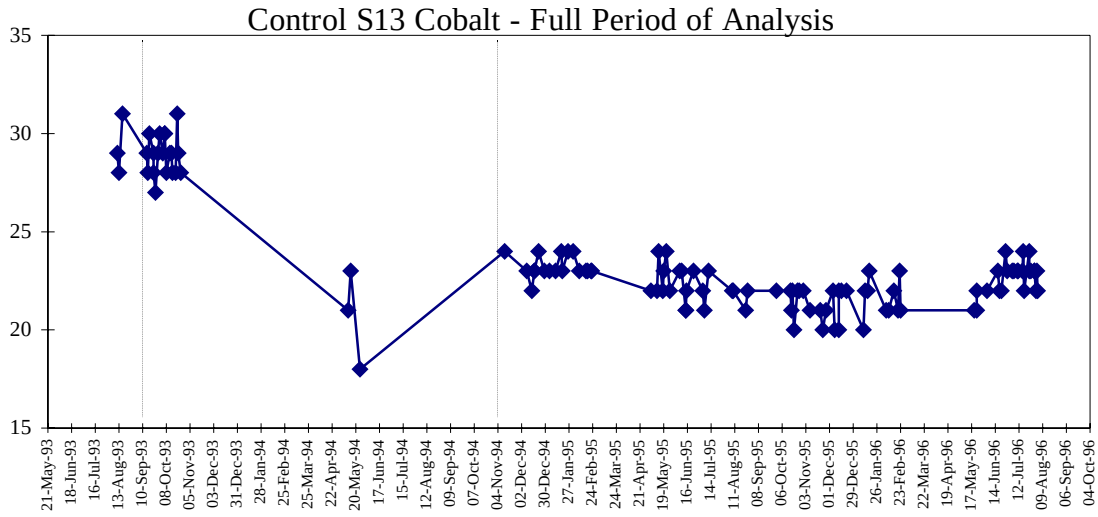


Fig. 9. Control S13 for Co in Wales and Welsh Borders area samples.

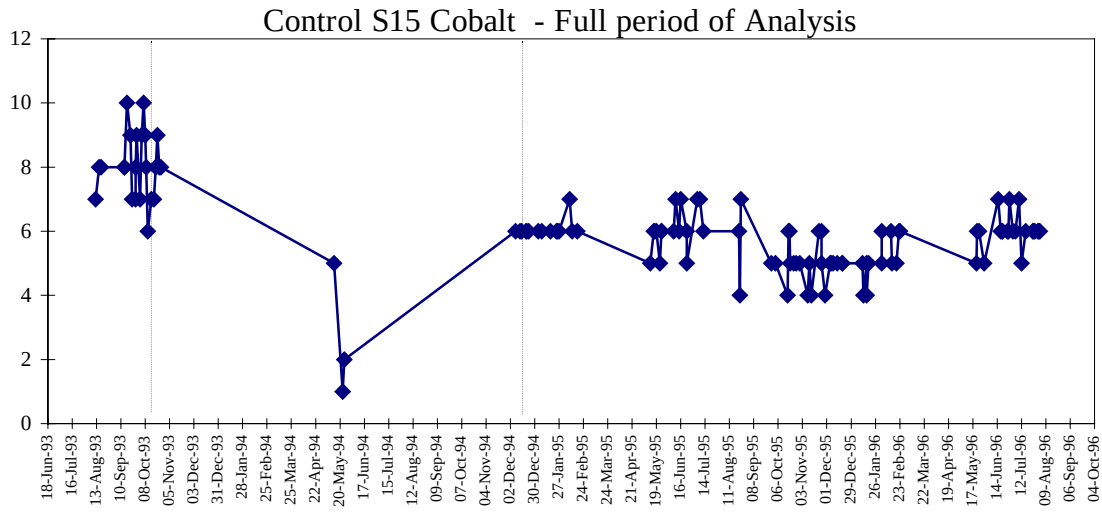


Fig. 10. Control S15 for Co in Wales and Welsh Borders area samples.

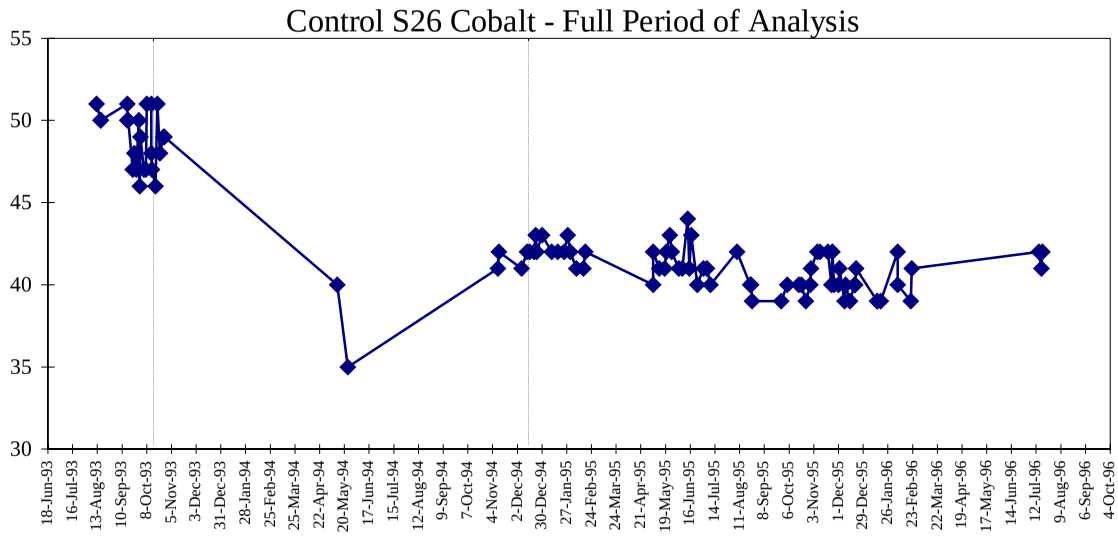


Fig. 11. Control S26 for Co in Wales and Welsh Borders area samples.

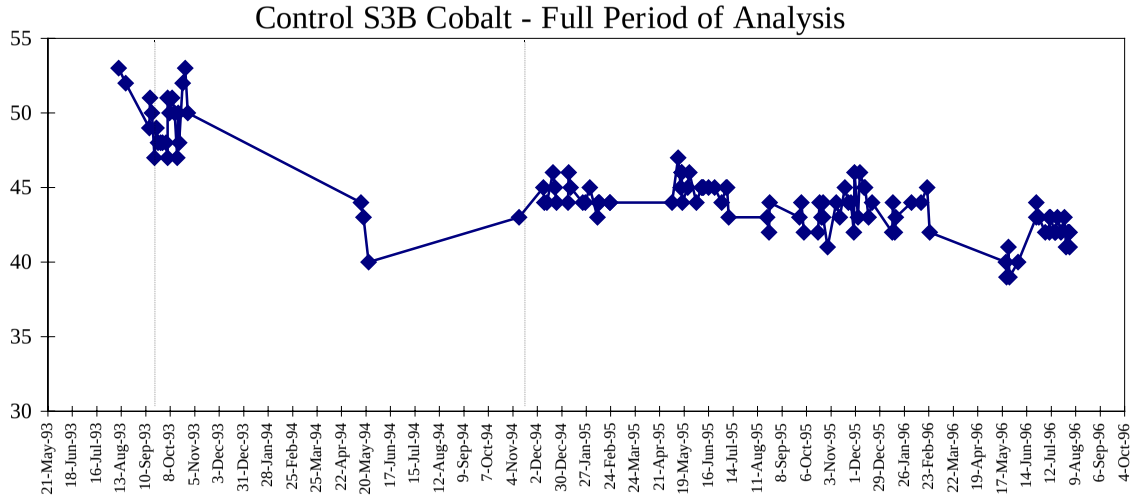


Fig. 12. Control S3B for Co in Wales and Welsh Borders area samples.

Control Standard S13 Segments

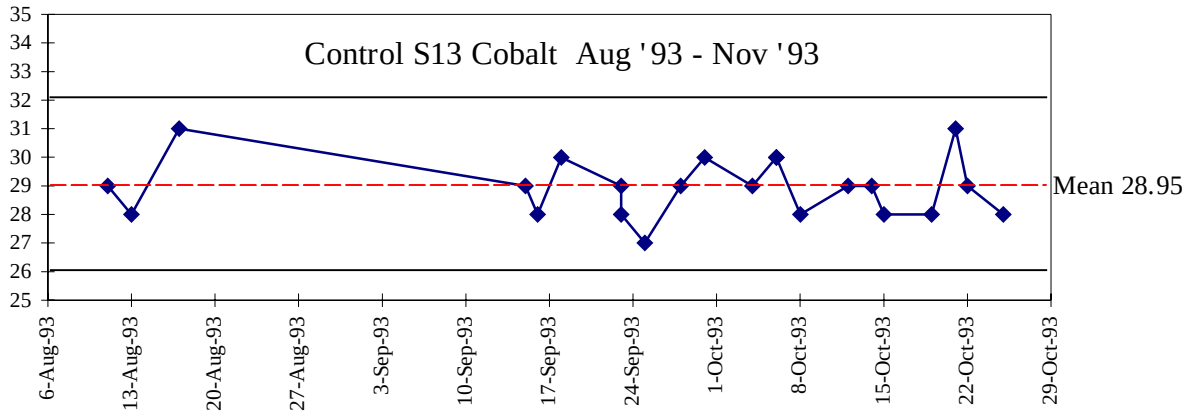


Fig. 13. Cobalt concentration in control S13, Aug ’93 – Nov ‘93

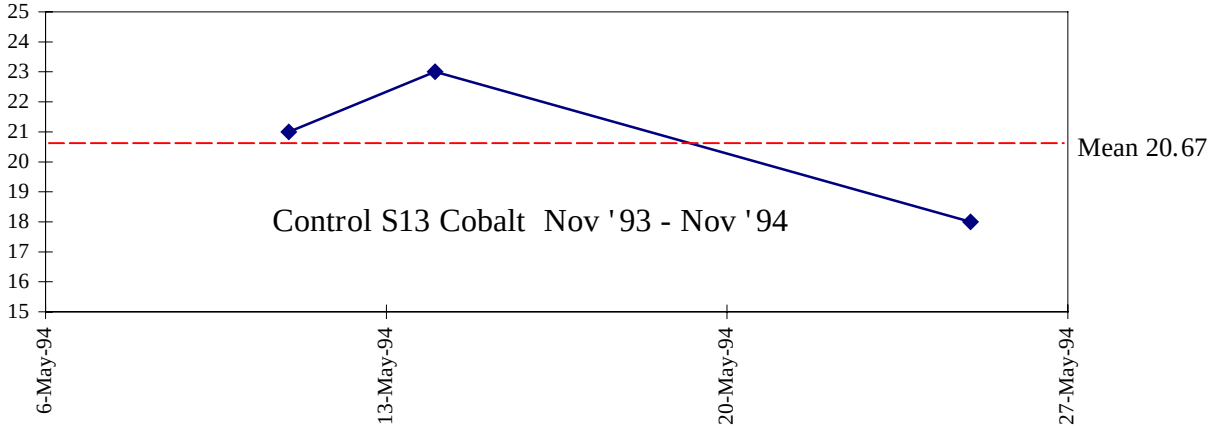


Fig. 14. Cobalt concentration in control S13, Nov ’93 – Nov ‘94

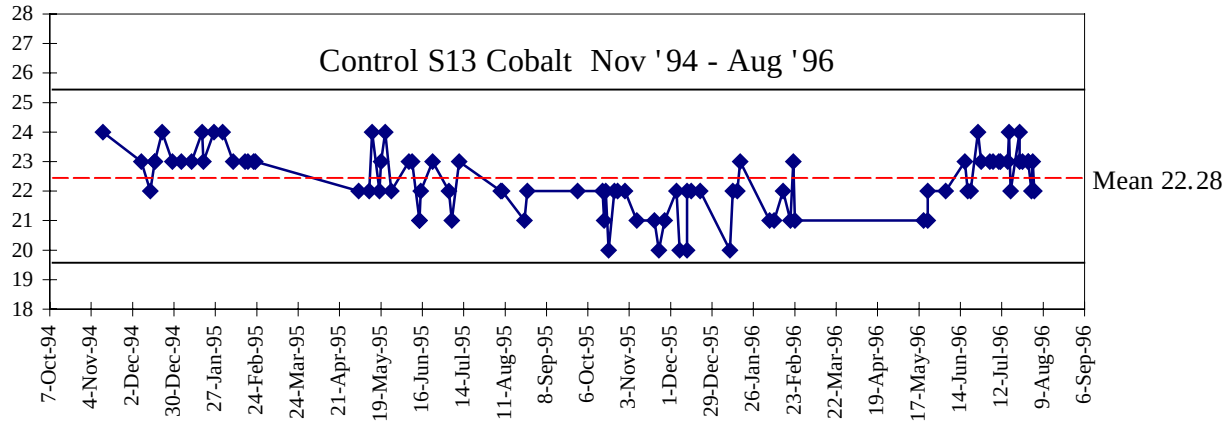


Fig. 15. Cobalt concentration in control S13, Nov ’94 – Aug ‘96

Control Standard S15 Segments

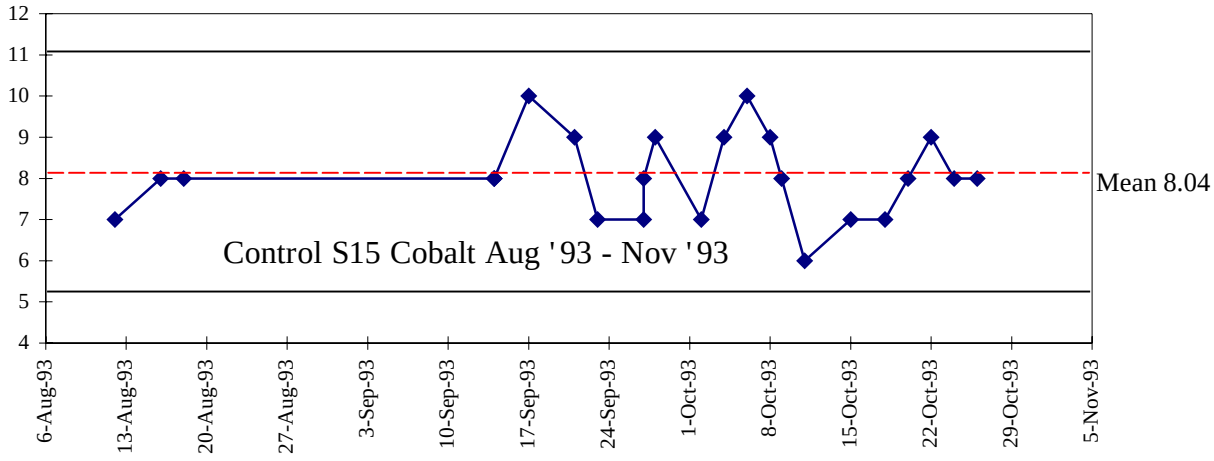


Fig. 16. Cobalt concentration in control S15, Aug ’93 – Nov ’93

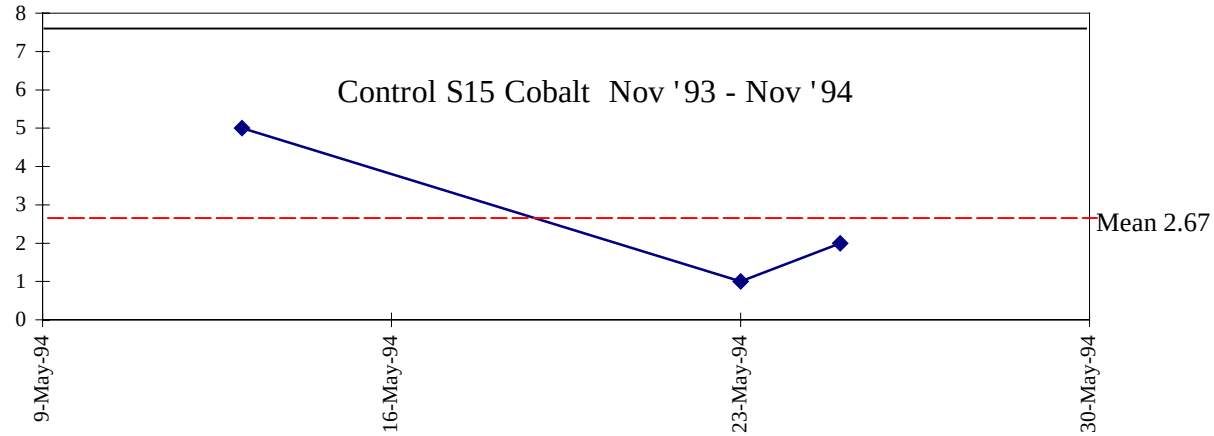


Fig. 17. Cobalt concentration in control S15, Nov ’93 – Nov ‘94

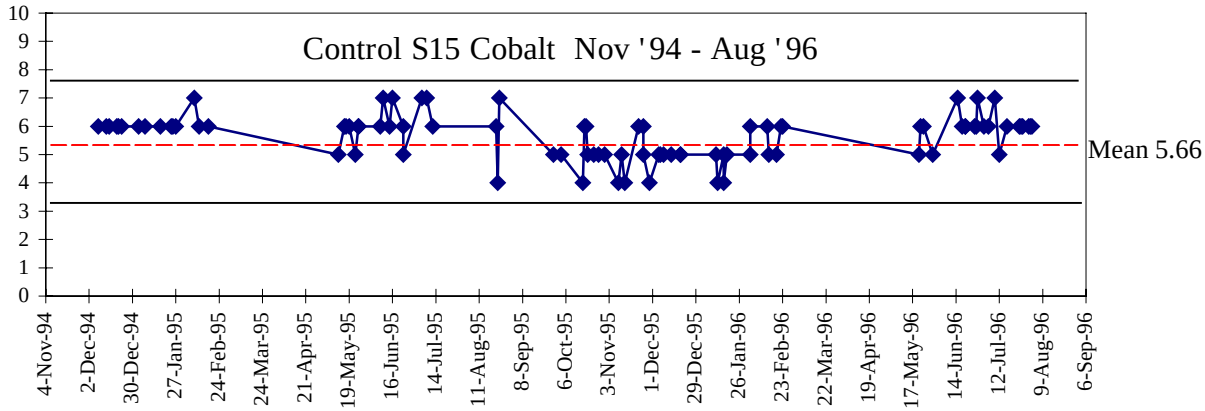


Fig. 18. Cobalt concentration in control S15, Nov ’94 – Aug ‘96

Control Standard S26 Segments

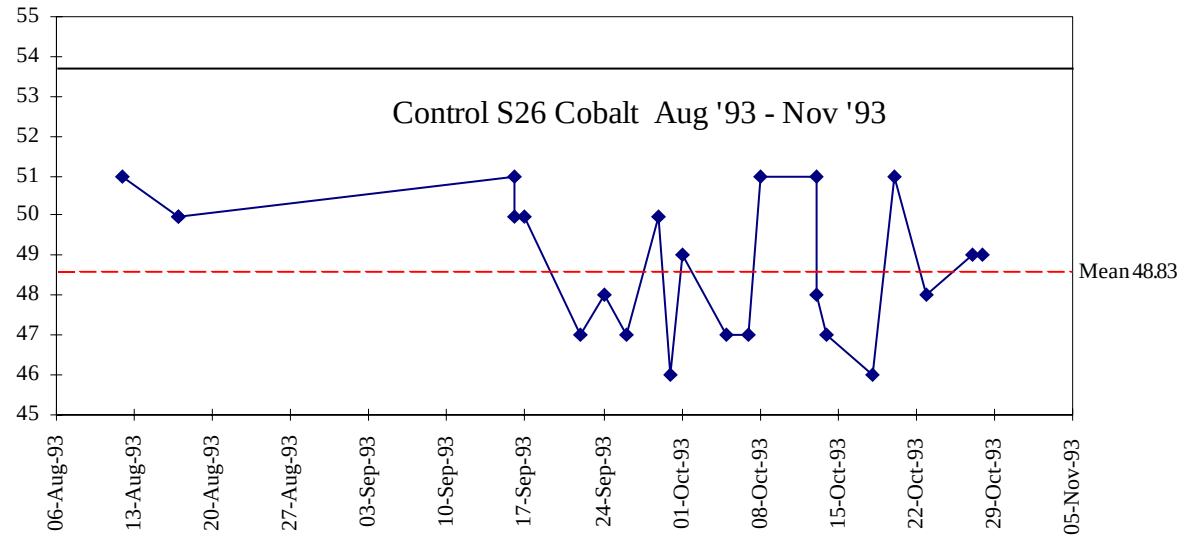


Fig. 19. Cobalt concentration in control S26, Aug ’93 – Nov ’93

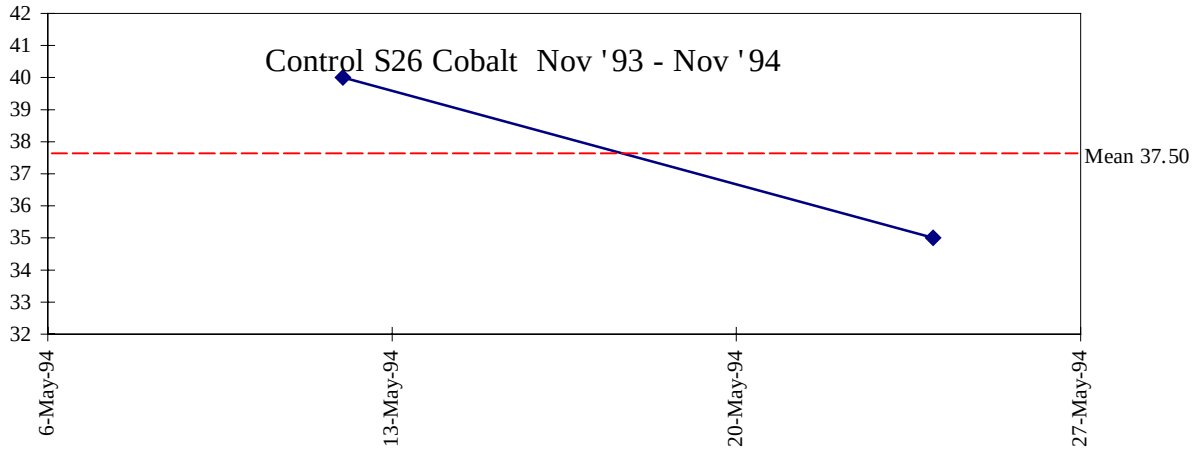


Fig. 20. Cobalt concentration in control S26, Nov ’93 – Nov ’94

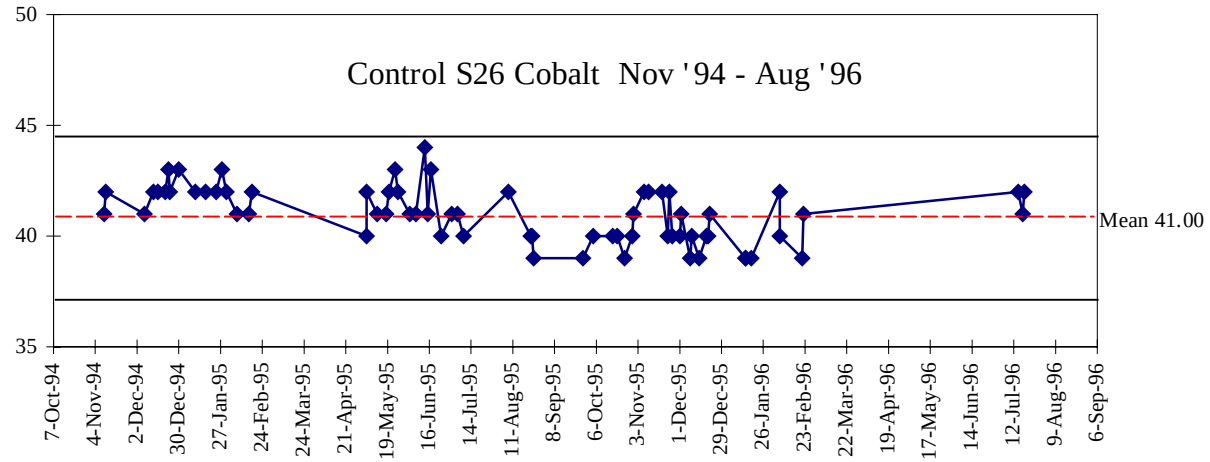


Fig. 21. Cobalt concentration in control S26, Nov ’94 – Aug ’96

Control Standard S3B Segments

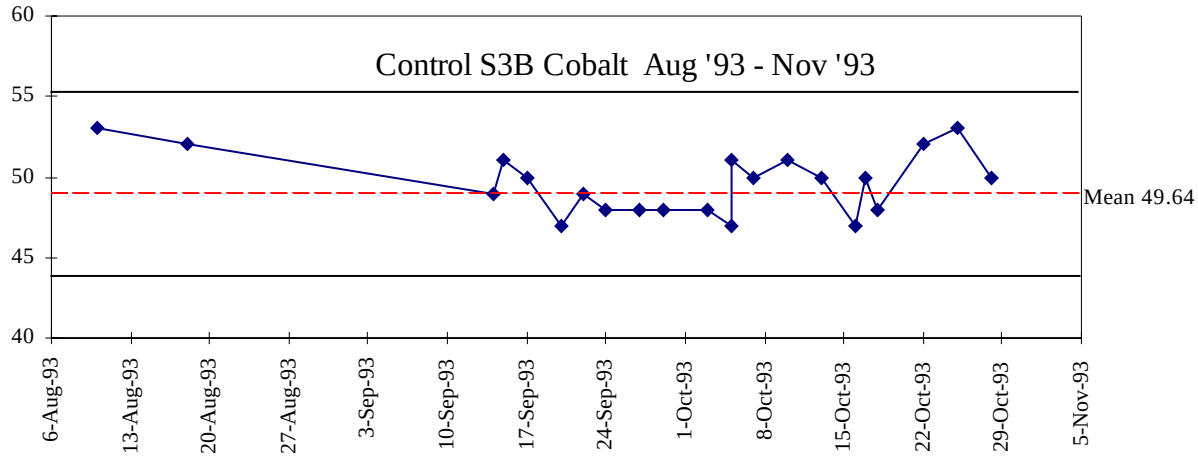


Fig. 22. Cobalt concentration in control S3b, Aug ’93 – Nov ’93

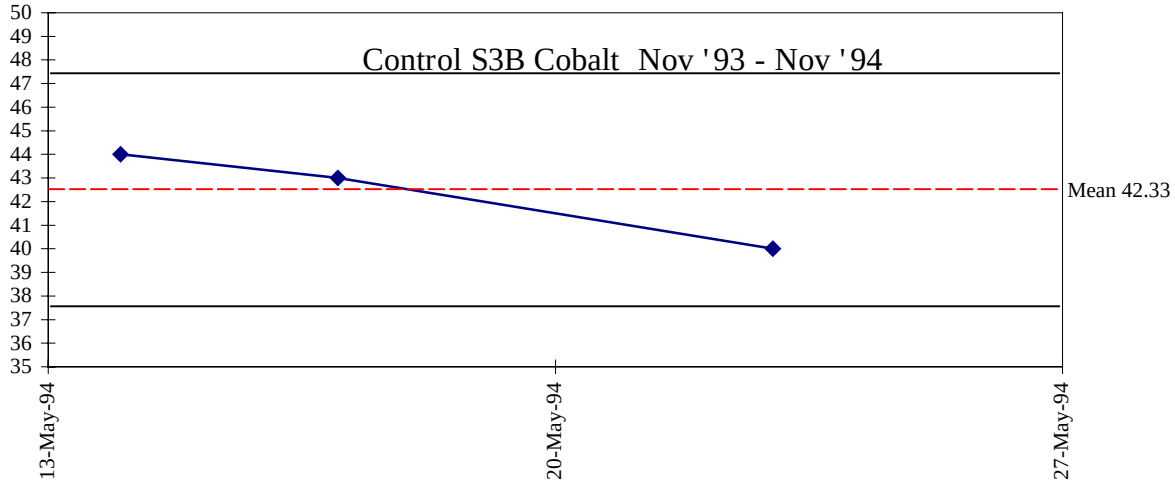


Fig. 23. Cobalt concentration in control S3B, Nov ’93 – Nov ’94

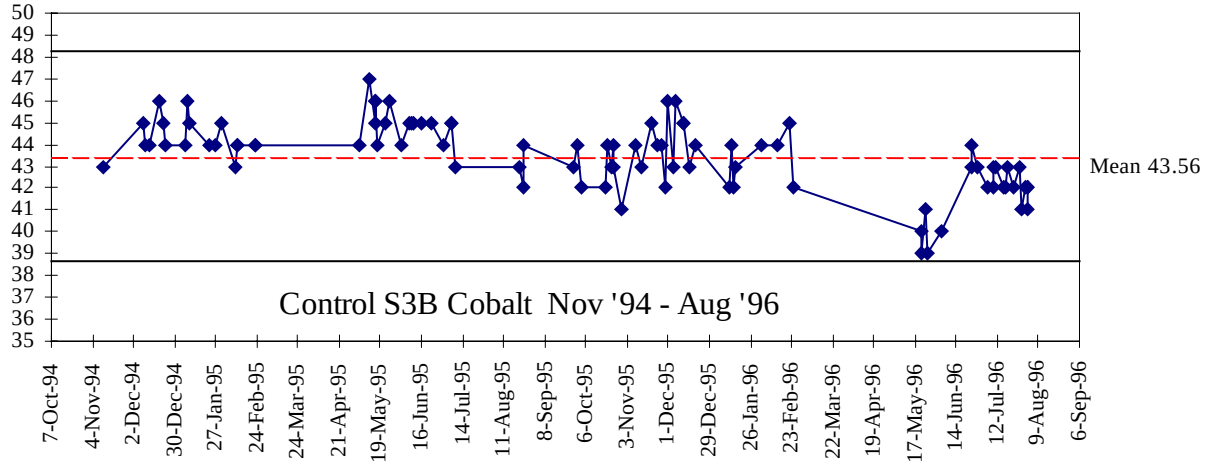


Fig. 24. Cobalt concentration in control S3B, Nov ’94 – Aug ’96

Mid Wales XRF Cobalt Segment Calibration Means			
Control ID	Segment 1 (Aug '93 – Nov '93)	Segment 2 (Nov '93 – Nov '94)	Segment 3 (Nov '94 – Aug '96)
S13	28.95	20.67	22.28
S15	8.04	2.67	5.66
S26	48.83	37.50	41.00
S3B	49.64	42.33	43.56

Table 2. Segment mean values for control standards.

Using data from table 2, regression plots were generated to normalise data within the time periods of segments 2 and 3 to that of segment 1, the initial calibration of the XRF instruments at the commencement of analysis of samples from the Wales and Welsh Borders area. As can be seen from table 2, Co concentrations in S26 and S3B are very similar. Following consultation with the analysts, data for S3B were omitted from the regression calculations. (The dense nature of the sample matrix of control S3B causes interference between some elements at high concentrations).

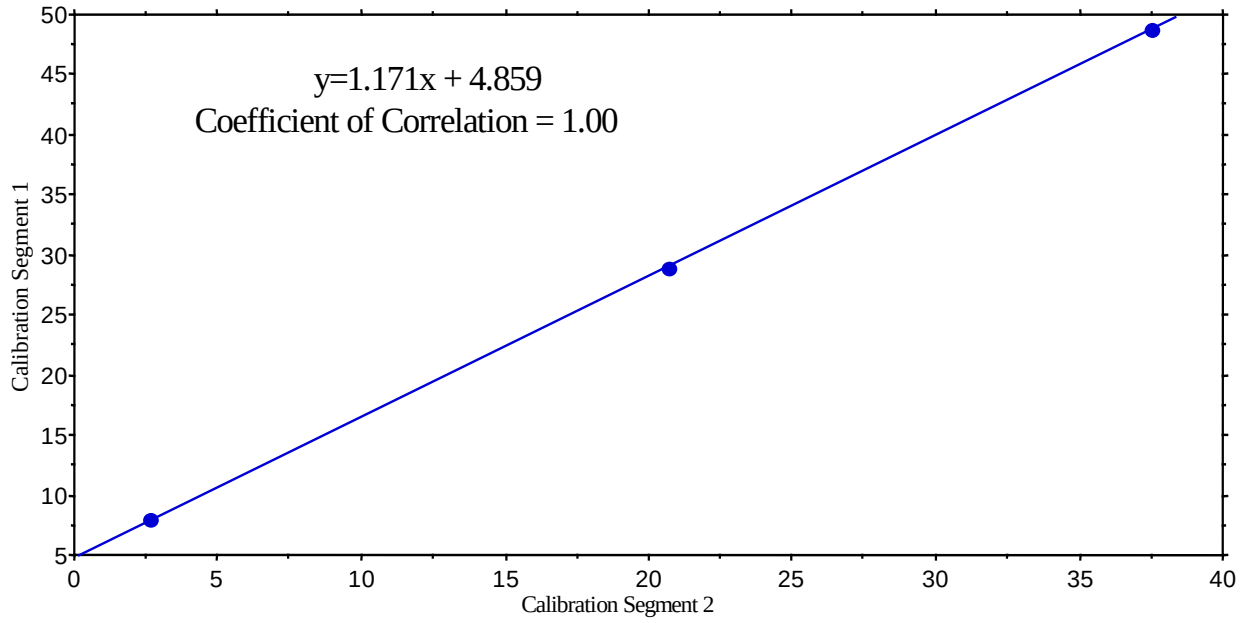


Fig 25.Linear regression for correction of segment 2 data.

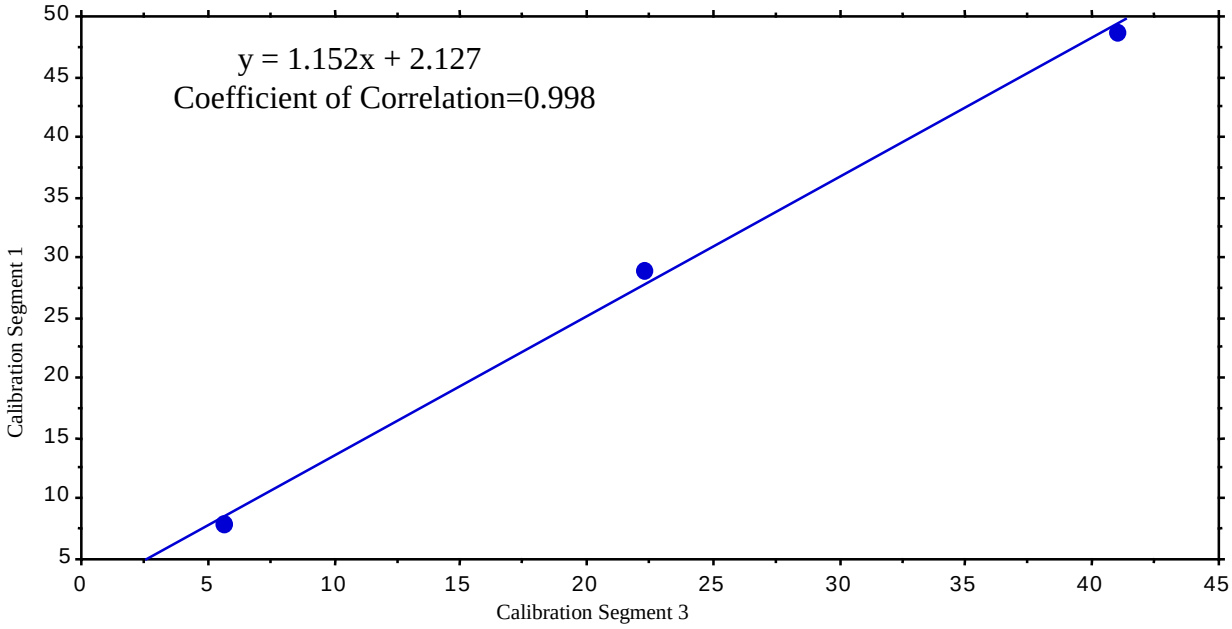


Fig 26. Linear regression for correction of segment 3 data

The correction factors calculated by regression (shown graphically in figures 25 & 26) were applied to the data within time segments 2 and 3. Figures 27 – 30 show the resulting normalised data time-series plots for G-BASE control standards S13, S15, S26 and S3B. (Although data for control S3B were omitted from the regression calculations, for consistency, the correction factors were applied to S3B data in order to validate the accuracy of the normalisation).

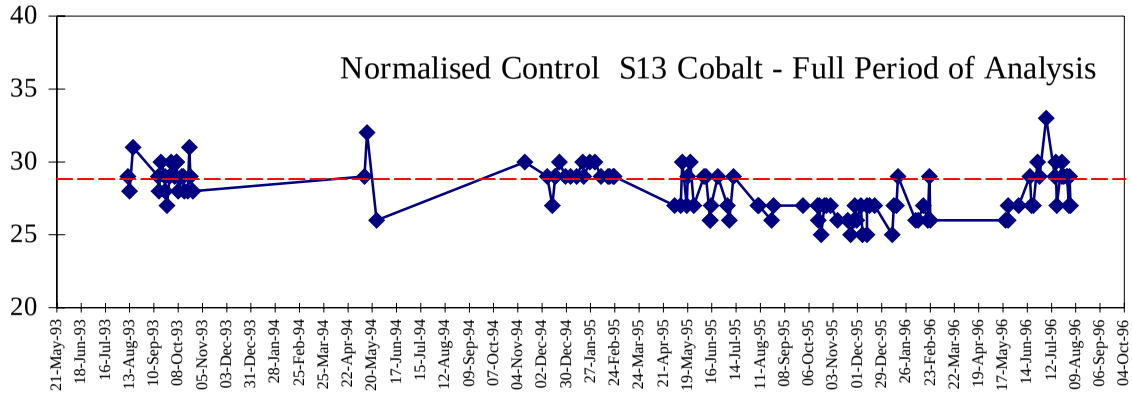


Fig 27. Recalculated S13 control chart using normalised data

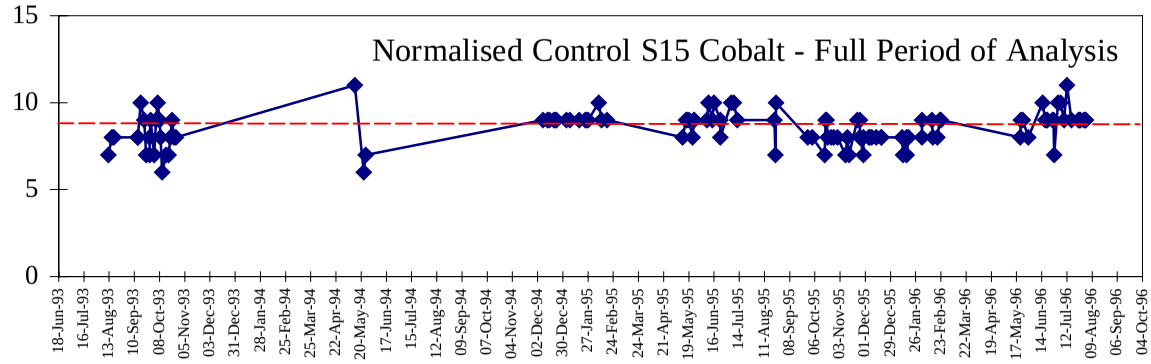


Fig 28. Recalculated S15 control chart using normalised data

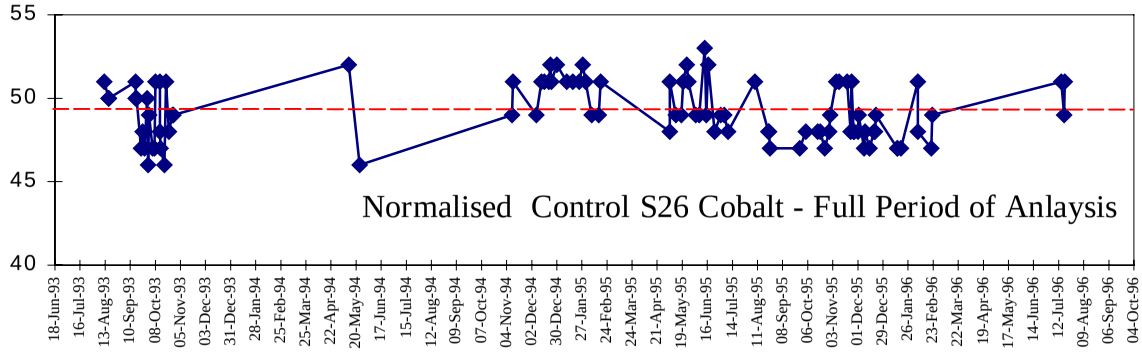


Fig 29. Recalculated S26 control chart using normalised data

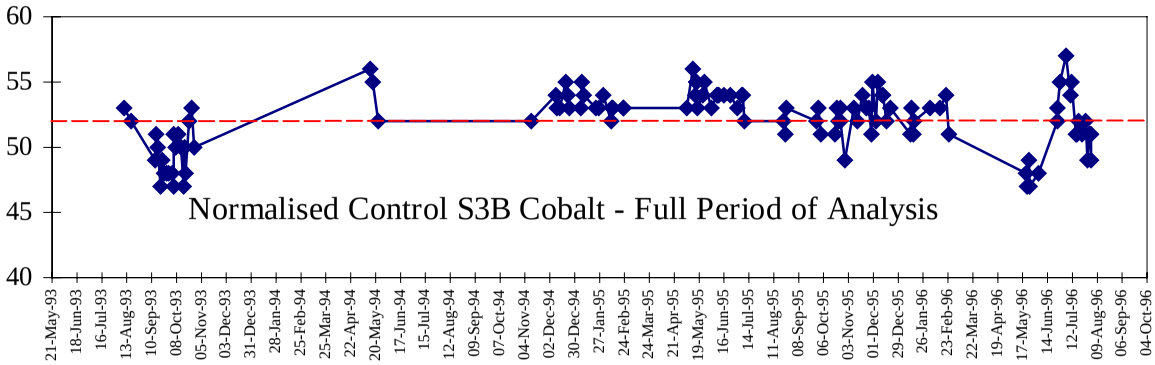


Fig 30. Recalculated S3B control chart using normalised data

Appendix 3

Correction factors for all affected elements -Wales and Welsh Borders area stream sediment data.

Correction to Th

Samples analysed between 29-Aug-93 and 19-Jun-94 **No change**.

Samples analysed between 14-Dec-94 and 17-May-95 **(Th*0.5623)+1.9809**

All samples analysed from 26-Sep-95 to end of analysis. The following correction based on line overlap information from analysts.

(Th*1.082)+(Pb*0.00916)+(Bi*0.1131)

Correction to Sn

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632 **No Change**.

Lab numbers 3633, 3668, 3669, 3670, 3671, 3672, 3673, 3674, 3675, 3716 **Sn + 1.00**

Lab numbers 3717, 3718, 3719, 3720, 3721, 3770 **No Change.**

Lab numbers 3771, 3772, 3773, 3774, 3803 **Sn + 1.00.**

Lab numbers 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913 **Sn + 2.00.**

Lab numbers 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **Sn + 1.00.**

Correction to Sb

Pilot Liverpool Bay Samples: **Sb + 1.00**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632 **No Change**.

Lab numbers 3633, 3668, 3669, 3670 ,3671, 3672, 3673, 3674, 3675, 3716 **Sb + 1.00**

Lab numbers 3717, 3718, 3719, 3720, 3721, 3770 **Sb + 3.00**

Lab numbers 3771, 3772, 3773, 3774, 3803, 3804, 3805, 3806, 3807, 3808,
3911, 3912, 3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **Sb + 4.00**

A further correction to the following lab numbers has been applied after more detailed examination of the sediment and soil images.

Lab number 3628 **Sb – 2.00**

Lab numbers 3631, 3675 **Sb + 2.00**

Correction to Ni

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670, 3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771 **No Change**.

Lab number 3772 - samples 373915 - 374017 **No Change**.

Lab number 3772 - samples 374018 - 374460 **Ni + 2.00**

Lab numbers 3773, 3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **Ni + 2.00**

Correction to Cu

Pilot Liverpool Bay Samples:		**Cu + 3.00**
Lab numbers 3624, 3625		**Cu + 4.00**
Lab numbers 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670		**No Change**
Lab numbers 3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771		**Cu - 2.00**
Lab number 3772	Samples 373915 -> 374017	**Cu - 2.00**
	Samples 374018 -> 374460	**Cu + 3.00**
Lab number 3773	Samples 374461 -> 374639	**Cu + 1.00**
	Samples 374640 -> 374670	**Cu + 3.00**
	Sample 374671	**Cu + 1.00**
	Samples 374672 -> 374673	**Cu + 3.00**
	Samples 374674 -> 374723	**Cu + 1.00**
	Samples 374724 -> 374818	**Cu + 3.00**
	Samples 374819 -> 375024	**Cu + 1.00**
Lab numbers 3774, 3803		**Cu + 1.00**
Lab numbers 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023		**Cu + 3.00**

Appendix C

Correction to Cd

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670, 3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3773, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913 **No Change**

Lab numbers 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **Cd - 2.00**

Correction to Fe_2O_3

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668 **No Change**

Lab numbers, 3670, 3671, 3672, 3673, 3674, 3675, 3716 **(Fe2O3 * 1.104) - 0.057**

Lab numbers 3625, 3626, 3669, 3717, 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3773,3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3913 **No Change**

Lab numbers 3912, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **(Fe2O3 * 0.990) - 0.109**

Correction to Bi

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670, 3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771 **No Change**

Lab number	3772	373915 - 374017	**No Change**
	3772	374018 - 374460	**(Bi * 0.79194) + 0.4152**
Lab number	3773	374461 - 374639	**(Bi * 0.80119) + 0.70698**
	3773	374640 – 374670	**(Bi * 0.79194) + 0.4152**
	3773	374671	**(Bi * 0.80119) + 0.70698**
	3773	374672 - 374673	**(Bi * 0.79194) + 0.4152**
	3773	374674 - 374723	**(Bi * 0.80119) + 0.70698**
	3773	374724 - 374818	**(Bi * 0.79194) + 0.4152**
	3773	374819 - 375024	**(Bi * 0.80119) + 0.70698**
Lab numbers	3774, 3803		**(Bi * 0.80119) + 0.70698**

Lab numbers 3804, 3805, 3806, 3807, 3808, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 3911, 3913, 3912, 4021, 4022, 4023 **(Bi * 0.79194) + 0.4152**

Correction to TiO_2

Pilot Liverpool Bay Samples:	**No Change**
Lab numbers 3624,3627, 3628, 3629, 3630, 3631, 3632, 3633	**No Change**
Lab number 3668	**(0.9584*TiO2)-0.0042897**
Lab numbers, 3670, 3671, 3672, 3673, 3674, 3675, 3716	**(TiO2*1.0036) - 0.0072214**
Lab numbers 3717,3773, 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3625,3626,3669,3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911,3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132,3912, 4021, 4022, 4023	**(TiO2*0.92562) + 0.00035623**

Correction to Co

Pilot Liverpool Bay Samples: **(1.0146*Co)+1.3845**

Lab numbers 3624,3627, 3628, 3629, 3630, 3631, 3632, 3633 **No Change**

Lab number 3668 **(1.171*Co) + 4.8586**

Lab numbers 3670, 3671, 3672, 3673, 3674, 3675, 3716, 3717,3773, 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3625, 3626, 3669, 3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132,3912, 4021, 4022, 4023 **(1.1523*Co) + 2.1272**

Correction to Y

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670 ,3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771 **No Change**.

Lab number 3772 - samples 373915 - 374017 - **No Change**.

Lab number 3772 - samples 374018 - 374460 **(Y*1.0625) + 2.2642**

Lab numbers 3773, 3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023. **(Y*1.0625) + 2.2642**

Correction to V

Pilot Liverpool Bay Samples:	**No Change**
Lab numbers 3624, 3627, 3628, 3629, 3630, 3631, 3632, 3633	**No Change**
Lab numbers, 3668, 3670, 3671, 3672, 3673, 3674, 3675, 3716,	**(1.029*V) + 3.9986**
Lab numbers 3717, 3773, 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3625, 3626, 3669, 3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3913	**(1.0101*V) + 4.1144**
Lab numbers 3934, 3938	**(1.0352*V) + 6.5693**
Lab numbers 3939, 3940, 4130, 4131, 4132, 3912, 4021, 4022, 4023	**(1.1102*V) - 2.5689**

Correction to Ag

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670, 3671, 3672, 3673, 3674, 3675, 3716 **No Change**

Lab numbers 3717, 3718, 3719, 3720, 3721, 3770 **Ag + 2.00**

Lab numbers 3771, 3772, 3773, 3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913 **Ag + 1.00**

Lab numbers 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **No Change**.

Correction to K_2O

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670 ,3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3773, 3774, 3803, 3804, 3805, 3806, 3807, 3808, 3911, 3913 **No Change**.

Lab numbers 3934, 3938, 3939 up to 353427 **K2O+0.14**.

Lab numbers 3939 (>=353427), 3940, 4130, 4131, 4132,3912, 4021, 4022, 4023 **No Change**.

Correction to U

Pilot Liverpool Bay Samples: **No Change**

Lab numbers 3624, 3625, 3626, 3627, 3628, 3629, 3630, 3631, 3632, 3633, 3668, 3669, 3670 **No Change**

Lab numbers 3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719, 3720, 3721, 3770, 3771 **(U*0.98154)+0.60741**

Lab number 3772

Samples 373915 -> 374017 **(U*0.98154)+0.60741**

Samples 374018 -> 374460 **(U*1.0395)-0.18888**

Lab number 3773

Samples 374461 -> 374639 **(U*1.1566)-1.0024**

Samples 374640 -> 374670 **(U*1.0395)-0.18888**

Sample 374671 **(U*1.1566)-1.0024**

Samples 374672 -> 374673 **(U*1.0395)-0.18888**

Samples 374674 -> 374723 **(U*1.1566)-1.0024**

Samples 374724 -> 374818 **(U*1.0395)-0.18888**

Samples 374819 -> 375024 **(U*1.1566)-1.0024**

Lab numbers 3774, 3803 **(U*1.1566)-1.0024**

Lab numbers 3804, 3805, 3806, 3807, 3808, 3911, 3912, 3913, 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023 **(U*1.1566)-1.0024**

Correction to La

Pilot Liverpool Bay Samples:	**No Change**
Lab numbers 3624, 3625, 3626, 3627	**No Change**
Lab numbers 3628, 3629, 3630	**(0.93161*La)-0.039064**
Lab numbers 3631	**(0.81214*La)+0.25951**
Lab numbers 3632, 3633, 3668, 3669, 3670, 3671, 3672	**(0.93161*La)-0.039064**
Lab numbers 3673	**(1.0646*La)+2.6332**
Lab numbers 3718, 3719, 3720, 3721, 3770, 3771, 3772, 3773, 3774, 3803, 3674, 3675, 3716, 3717, 3804, 3805(<=381114)	**(0.99378*La)+0.58258**
Lab numbers 3805(>381114), 3806, 3807, 3808, 3912, 3911, 3913	**(0.91315*La)-1.0171**
Lab numbers 3934, 3938, 3939, 3940, 4130, 4131, 4132, 4021, 4022, 4023	**(1.0095*La)+0.49178**

Correction to Mo

Stage I

Pilot Liverpool Bay Samples:		**Mo + 0.6**
Labno 3624		**Mo - 0.95**
Labnos 3625, 3626, 3627, 3628, 3629, 3630		**No Change**
Labno 3631		**Mo - 0.3**
Labno 3632		**No Change**
Labnos 3633, 3668, 3669, 3670		**Mo - 0.7**
Labnos 3671, 3672, 3673, 3674, 3675, 3716, 3717, 3718, 3719 (excl 371500, 371619-371624), 3720		**Mo - 0.5**
Labno 3719 (371500, 371619-371624)		**No Change**
Labno 3721		**Mo - 1.0**
Labnos 3770, 3771		**Mo - 0.2**
Labno 3772		**No Change**
Labno 3773	Samples 374461 - 374639	**Mo + 2.0**
	Sample 374671	**Mo + 2.0**
	Samples 374674 - 374723	**Mo + 2.0**
	Samples 374819 - 375024	**Mo + 2.0**
	Samples 374640 - 374670	**No Change**
	Samples 374672 - 364673	**No Change**
	Samples 374724 - 374818	**No Change**

Correction to Mo

Stage I

Labnos 3774, 3803	**Mo + 2.0**
Labnos 3804, 3805	**No Change**
Labno 3806	**Mo - 0.6**
Labnos 3807, 3808, 3911, 3912, 3913, 3934	**Mo - 0.8**
Labno 3938	**No Change**
Labnos 3939, 3940	**Mo - 0.8**
Labnos 4021, 4022, 4023	**Mo - 1.2**
Labnos 4130 ,4131	**Mo - 0.8**

Correction to Mo

Stage II

All Stage I corrected data	**Mo - 1.0**

Appendix 4

MINITAB™ ANOVA calculations

Nested ANOVA: MGO

Analysis of Variance for MGO

Source	DF	SS	MS
Sample	172	1817.2026	10.5651
Site	172	14.2775	0.0830
Error	344	8.0850	0.0235
Total	688	1839.5651	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	2.632	98.01	1.622
Site	0.030	1.11	0.173
Error	0.024	0.88	0.153
Total	2.685		1.639

Nested ANOVA: P2O5

Analysis of Variance for P2O5

Source	DF	SS	MS
Sample	172	7.9075	0.0460
Site	172	0.4838	0.0028
Error	344	0.1679	0.0005
Total	688	8.5592	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.011	86.77	0.104
Site	0.001	9.32	0.034
Error	0.000	3.91	0.022
Total	0.012		0.112

Nested ANOVA: K2O

Analysis of Variance for K2O

Source	DF	SS	MS
Sample	172	230.3791	1.3394
Site	172	4.6285	0.0269
Error	344	1.6322	0.0047
Total	688	236.6398	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.330	95.41	0.574
Site	0.011	3.21	0.105
Error	0.005	1.37	0.069
Total	0.345		0.588

Nested ANOVA: CAO

Analysis of Variance for CAO

Source	DF	SS	MS
Sample	172	2169.6598	12.6143
Site	172	71.6859	0.4168
Error	344	5.4924	0.0160
Total	688	2246.8381	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	3.063	93.39	1.750
Site	0.201	6.12	0.448
Error	0.016	0.49	0.126
Total	3.279		1.811

Nested ANOVA: TIO2

Analysis of Variance for TIO2

Source	DF	SS	MS
Sample	172	15.9708	0.0929
Site	172	0.1666	0.0010
Error	344	0.0830	0.0002
Total	688	16.2204	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.023	97.44	0.152
Site	0.000	1.54	0.019
Error	0.000	1.02	0.016
Total	0.024		0.154

Nested ANOVA: MNO

Analysis of Variance for MNO

Source	DF	SS	MS
Sample	172	50.3548	0.2928
Site	172	1.6234	0.0094
Error	344	0.0800	0.0002
Total	688	52.0582	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.071	93.62	0.267
Site	0.005	6.07	0.068
Error	0.000	0.31	0.015
Total	0.076		0.276

Nested ANOVA: FE2O3

Analysis of Variance for FE2O3

Source	DF	SS	MS
Sample	172	3081.2996	17.9145
Site	172	66.5893	0.3871
Error	344	8.6781	0.0252
Total	688	3156.5670	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	4.401	95.52	2.098
Site	0.181	3.94	0.426
Error	0.025	0.55	0.159
Total	4.607		2.146

Nested ANOVA: V

Analysis of Variance for V

Source	DF	SS	MS
Sample	172	584090.8177	3395.8768
Site	172	9522.9167	55.3658
Error	344	4269.0000	12.4099
Total	688	597882.7344	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	838.762	96.11	28.961
Site	21.520	2.47	4.639
Error	12.410	1.42	3.523
Total	872.692		29.541

Nested ANOVA: CR

Analysis of Variance for CR

Source	DF	SS	MS
Sample	172	638603.6080	3712.8117
Site	172	11291.9167	65.6507
Error	344	5415.5000	15.7427
Total	688	655311.0247	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	915.758	95.74	30.261
Site	25.002	2.61	5.000
Error	15.743	1.65	3.968
Total	956.503		30.927

Nested ANOVA: CO

Analysis of Variance for CO

Source	DF	SS	MS
Sample	172	319658.4832	1858.4796
Site	172	6797.9167	39.5228
Error	344	526.5000	1.5305
Total	688	326982.8999	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	456.715	95.69	21.371
Site	19.033	3.99	4.363
Error	1.531	0.32	1.237
Total	477.278		21.847

Nested ANOVA: BA

Analysis of Variance for BA

Source	DF	SS	MS
Sample	172	13307303.8272	77368.0455
Site	172	785375.9167	4566.1391
Error	344	91630.5000	266.3677
Total	688	14184310.2438	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	18278.863	88.31	135.199
Site	2154.060	10.41	46.412
Error	266.368	1.29	16.321
Total	20699.291		143.872

Nested ANOVA: NI

Analysis of Variance for NI

Source	DF	SS	MS
Sample	172	137406.2716	798.8737
Site	172	4576.1667	26.6056
Error	344	950.0000	2.7616
Total	688	142932.4383	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	193.904	92.95	13.925
Site	11.945	5.73	3.456
Error	2.762	1.32	1.662
Total	208.611		14.443

Nested ANOVA: CU

Analysis of Variance for CU

Source	DF	SS	MS
Sample	172	70459.3211	409.6472
Site	172	2177.7500	12.6613
Error	344	504.0000	1.4651
Total	688	73141.0711	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	99.677	93.37	9.984
Site	5.609	5.25	2.368
Error	1.465	1.37	1.210
Total	106.751		10.332

Nested ANOVA: ZN

Analysis of Variance for ZN

Source	DF	SS	MS
Sample	172	7151822.2206	41580.3617
Site	172	166309.0000	966.9128
Error	344	11283.0000	32.7994
Total	688	7329414.2206	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	10197.450	95.32	100.982
Site	467.964	4.37	21.632
Error	32.799	0.31	5.727
Total	10698.213		103.432

Nested ANOVA: GA

Analysis of Variance for GA

Source	DF	SS	MS
Sample	172	14313.8087	83.2198
Site	172	282.1667	1.6405
Error	344	239.0000	0.6948
Total	688	14834.9753	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	20.484	94.60	4.526
Site	0.474	2.19	0.688
Error	0.695	3.21	0.834
Total	21.652		4.653

Nested ANOVA: AS

Analysis of Variance for AS

Source	DF	SS	MS
Sample	172	441892.4523	2569.1422
Site	172	16246.1667	94.4545
Error	344	973.5000	2.8299
Total	688	459112.1190	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	621.350	92.73	24.927
Site	45.901	6.85	6.775
Error	2.830	0.42	1.682
Total	670.081		25.886

Nested ANOVA: SE

Analysis of Variance for SE

Source	DF	SS	MS
Sample	172	176.3714	1.0254
Site	172	21.3950	0.1244
Error	344	15.3450	0.0446
Total	688	213.1114	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.226	72.79	0.476
Site	0.040	12.86	0.200
Error	0.045	14.35	0.211
Total	0.311		0.557

Nested ANOVA: RB

Analysis of Variance for RB

Source	DF	SS	MS
Sample	172	394440.5004	2293.2587
Site	172	10398.7500	60.4578
Error	344	5390.5000	15.6701
Total	688	410229.7504	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	560.626	93.64	23.678
Site	22.437	3.75	4.737
Error	15.670	2.62	3.959
Total	598.733		24.469

Nested ANOVA: SR

Analysis of Variance for SR

Source	DF	SS	MS
Sample	172	767665.3124	4463.1704
Site	172	32899.2500	191.2747
Error	344	3660.5000	10.6410
Total	688	804225.0624	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	1072.591	91.38	32.750
Site	90.492	7.71	9.513
Error	10.641	0.91	3.262
Total	1173.724		34.260

Nested ANOVA: Y

Analysis of Variance for Y

Source	DF	SS	MS
Sample	172	18893.9702	109.8487
Site	172	570.5000	3.3169
Error	344	634.0000	1.8430
Total	688	20098.4702	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	26.749	91.20	5.172
Site	0.738	2.52	0.859
Error	1.843	6.28	1.358
Total	29.330		5.416

Nested ANOVA: ZR

Analysis of Variance for ZR

Source	DF	SS	MS
Sample	172	57692214.0610	335419.8492
Site	172	2703478.0000	15717.8953
Error	344	2344460.0000	6815.2907
Total	688	62740152.0610	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	80272.157	87.68	283.323
Site	4459.946	4.87	66.783
Error	6815.291	7.44	82.555
Total	91547.393		302.568

Nested ANOVA: NB

Analysis of Variance for NB

Source	DF	SS	MS
Sample	172	3430.8102	19.9466
Site	172	204.8567	1.1910
Error	344	269.4250	0.7832
Total	688	3905.0919	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	4.709	82.67	2.170
Site	0.204	3.59	0.452
Error	0.783	13.75	0.885
Total	5.697		2.387

Nested ANOVA: MO

Analysis of Variance for MO

Source	DF	SS	MS
Sample	172	1555.4281	9.0432
Site	172	103.9517	0.6044
Error	344	173.3750	0.5040
Total	688	1832.7547	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	2.119	79.27	1.456
Site	0.050	1.88	0.224
Error	0.504	18.85	0.710
Total	2.673		1.635

Nested ANOVA: PB

Analysis of Variance for PB

Source	DF	SS	MS
Sample	172	2706589.1084	15735.9832
Site	172	20744.1667	120.6056
Error	344	2091.5000	6.0799
Total	688	2729424.7750	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	3920.855	98.41	62.617
Site	57.374	1.44	7.575
Error	6.080	0.15	2.466
Total	3984.309		63.121

Nested ANOVA: TH

Analysis of Variance for TH

Source	DF	SS	MS
Sample	172	1823.0165	10.5989
Site	172	118.7442	0.6904
Error	344	141.1900	0.4104
Total	688	2082.9507	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	2.488	81.88	1.577
Site	0.140	4.62	0.374
Error	0.410	13.51	0.641
Total	3.039		1.743

Nested ANOVA: U

Analysis of Variance for U

Source	DF	SS	MS
Sample	172	421.5080	2.4506
Site	172	51.3125	0.2983
Error	344	61.7150	0.1794
Total	688	534.5355	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.540	69.34	0.735
Site	0.060	7.64	0.244
Error	0.179	23.02	0.424
Total	0.779		0.883

Nested ANOVA: CD

Analysis of Variance for CD

Source	DF	SS	MS
Sample	172	638.2560	3.7108
Site	172	31.8750	0.1853
Error	344	46.2500	0.1344
Total	688	716.3810	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	0.885	84.70	0.941
Site	0.025	2.44	0.160
Error	0.134	12.86	0.367
Total	1.045		1.022

Nested ANOVA: SN

Analysis of Variance for SN

Source	DF	SS	MS
Sample	172	4114.6356	23.9223
Site	172	418.6875	2.4342
Error	344	269.8750	0.7845
Total	688	4803.1981	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	5.395	77.01	2.323
Site	0.826	11.80	0.909
Error	0.785	11.20	0.886
Total	7.006		2.647

Nested ANOVA: LA

Analysis of Variance for LA

Source	DF	SS	MS
Sample	172	47727.2507	277.4840
Site	172	2812.4792	16.3516
Error	344	2439.1250	7.0905
Total	688	52978.8549	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	65.566	84.82	8.097
Site	4.640	6.00	2.154
Error	7.090	9.17	2.663
Total	77.296		8.792

Nested ANOVA: CE

Analysis of Variance for CE

Source	DF	SS	MS
Sample	172	187576.4875	1090.5610
Site	172	14187.4167	82.4850
Error	344	7298.0000	21.2151
Total	688	209061.9042	

Variance Components

Source	Var Comp.	% of Total	StDev
Sample	253.104	82.98	15.909
Site	30.694	10.06	5.540
Error	21.215	6.96	4.606
Total	305.014		17.465

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