Normal background concentrations of contaminants in the soils of England. Results of the data exploration for Cd, Cu, Hg and Ni

Science Facilities Directorate

Commissioned Report CR/12/041N

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Foreword

This report is part of the outputs from the Defra-funded Science and Research project SP1008 to establish normal background contaminant concentrations in the soils of England, carried out between October 2011 and March 2012 and consisting of four work packages. Work package 1 (WP1) was concerned with a review of available contaminant data for the soils of England and Work package 2 (WP2) explored the principal available data sets, using the examples of arsenic, lead, benzo[*a*]pyrene and asbestos. A robust statistical methodology for defining normal background concentrations of contaminants in soil was established as part of Work package 3 (WP3). The final deliverable has been a series of technical guidance sheets (TGSs) describing the determined normal background concentrations (NBCs) for a selected number of contaminants (WP4) and a project final report.

This report documents the data sources, exploratory data analysis and application of the statistical methodology for Cd, Cu, Hg and Ni. These additional contaminants were studied during WP 4, and thus the data exploration for these contaminants has not been reported in the initial data exploration/methodology project reports covering As, BaP, Pb and asbestos.

Acknowledgements

In addition to the authors named on this report, a number of other Natural Environment Research Council (NERC) staff have contributed to parts of this project, namely, Don Appleton, Murray Lark, Barry Rawlins, Chris Vane (all British Geological Survey) and Stephen Lofts (Centre for Ecology and Hydrology (CEH)). We are also grateful to the insight and comments from Paul Nathanial of Land Quality Management, Nottingham regarding how the determinations of normal background concentrations for contaminants fits within the revised Part 2A contaminated land Statutory Guidance. The Project also acknowledges the contribution of the Project "Steering Group" who have provided us with valuable feedback on our work to determine NBCs. Finally, we thank the Defra Soils Policy Team who have directed the Project to a successful conclusion.

We acknowledge the great efforts of those who have contributed to producing the soil data sets described in our metadata database (summarised in Appendix 2 of our WP1&2 report). We realise some information in this will need correcting and updating and we would appreciate any contributions that help us to improve this metadata.

The following licences have been issued with respect to some of the data sets investigated:

- Environmental Change Network (ECN): CEH – ECN:CJ10/11 – issued 6th December 2011 for one year
- Countryside Survey 10 km grid references for CS plot: CEH – issued 1st December 2011 for one year
- NSI Topsoil data – Datalease Code: L0212/00657 issued 12th December 2011 for one year (Cranfield ref: WU13058V)
- For the mineralisation and mining data layer based on the Department of Environment Ove Arup "Mining Instability in Britain" contract, copyright ownership of the "derived product" - the ArcView mining instability data set - is vested in NERC/BGS (BGS IPR reference IPR35-10)

The Generalised Land Use Database Statistics (file 154329.xlsx) was used under the Open Government licence.The topsoil Hg data that was reported in summarised fashion in Tipping et al. 2011, was supplied by Professor Edward Tipping (CEH, Lancaster) to whom we are grateful for his assistance.

Contents

FIGURES

TABLES

Summary

The British Geological Survey (BGS) has been commissioned by the Department for Environment, Food and Rural Affairs (Defra) to give guidance on what are normal levels of contaminants in English soils in support of the Part 2A Contaminated Land Statutory Guidance. This has initially been done by studying the distribution of four contaminants – arsenic (As), lead (Pb), benzo[*a*]pyrene (BaP) and asbestos – in topsoils from England. The work was extended further to include cadmium (Cd), copper (Cu), nickel (Ni) and mercury (Hg) enabling methodologies developed by the project to be tested on a larger range of contaminants.

This report serves to record the information collected on the additional four contaminants (Cd, Cu, Ni and Hg) that was undertaken in order to define their Normal Background Concentrations (NBCs). Other earlier Project reports should be consulted for the full background to methods used to analyse these data, in particular Work package 1&2, and Work package 3 reports. The Technical Guidance Sheets, and Technical Guidance Sheet Supplementary Information for each of these additional contaminants provide the final synthesis of this exploratory data analysis, and should be considered as the definitive resource for the Normal Background Concentrations.

1 Introduction

In April 2012 revised Part 2A Contaminated Land Statutory Guidance (SG) was issued by the Secretary of State for Environment, Food and Rural Affairs (Defra, 2012). This Guidance explains how the contaminated land regime should be implemented in England. Within the SG references are made to the "normal" presence and levels of contaminants in soils and the British Geological Survey (BGS) has been commissioned by Defra to give guidance on what are "normal" levels of contaminants in English soils. Eight contaminants were selected for study, namely, arsenic (As), asbestos, benzo[*a*]pyrene (BaP), cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni) and lead (Pb). The work is summarised in Johnson *et al*. (2012).

This report is a record of the outputs from the activities essential to data gathering, exploratory data analysis and statistical analysis of data on four of those contaminants: Cd, Cu, Hg and Ni. This work was part of Work package 4 and directly analogous to that undertaken on As, BaP and Pb in Work packages 1 – 3 of the first phase of the Project during methodology development, as reported in Ander *et al*. (2011) and Cave *et al.* (2012). This report should be read in conjunction with those reports.

2 Cadmium (Cd)

2.1 EXPLORATORY DATA ANALYSIS

Cadmium data from the G-BASE and NSI(XRFS) projects have greatly varying detection limits, with the lowest (0.25 mg/kg) being from the NSI(XRFS) project. This was an intentional result of applying a longer data acquisition time for Cd during the XRFS analytical phase of that work.

Some of the G-BASE data has a high (1 mg/kg) maximum detection limit in relation to the natural abundance of Cd in English soils – and it is this highest detection limit that restricts the use of the entire data set (Table 1a), unlike for most other inorganic elements (*e.g.* Cu and Ni). It is also the case that data just above the detection limit was reported to only one significant figure – leading to multiple identical concentrations being reported from these surveys.

Table 1 shows the summary data for the various subsets of the G-BASE data, and for a combined data set. Where data are greater than the detection limit, but numerically identical for multiple quartiles this is as a result of reporting to one significant figure those lower measurable concentrations. The impact of multiple detection limits (high relative to the overall data set) and truncation of the reporting values is also shown for G-BASE urban topsoil Cd concentration data in Figure 1.

In light of these complexities a decision was made to use the NSI(XRFS) as the main data set to determine domains, along with the most recent urban G-BASE data (since the NSI sampling strategy excluded urban areas). The data which were selected for use are shown in bold in Table 1. The G-BASE data used have a detection limit of 0.5 mg/kg, whilst the NSI(XRFS) is 0.25 mg/kg.

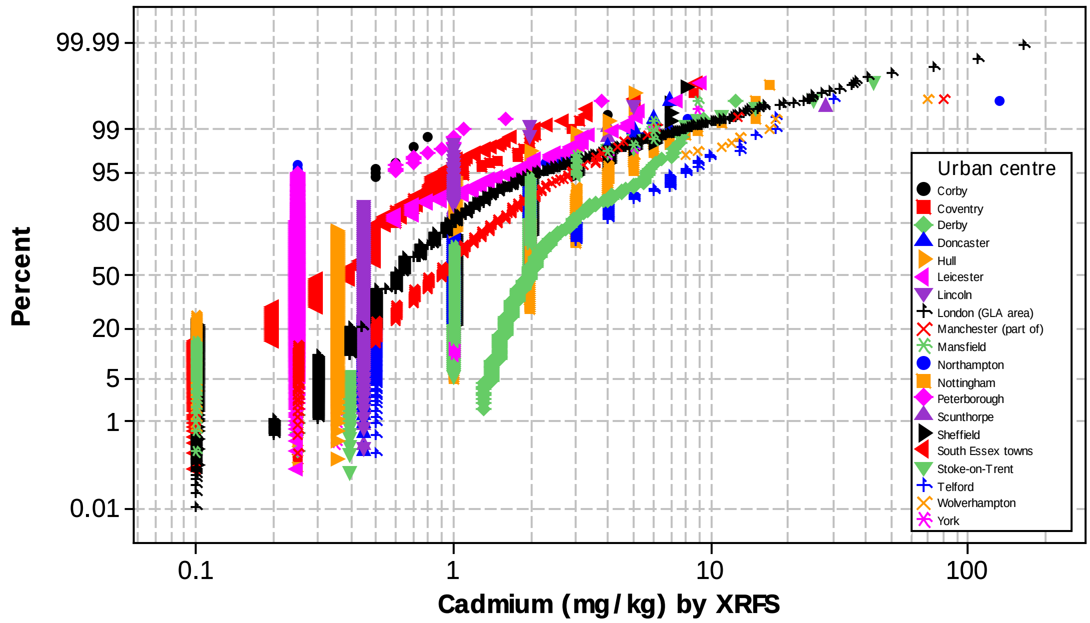

Figure 1: Probability plot of Cd concentrations in urban centres sampled by G-BASE. Vertical lines indicate detection limits, 0.5 × detection limit and truncated reporting to one significant figure.

(a) All Data	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
All data	42151	<1	<1	<1	<1	<1	170	42
(b) Data set	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
LOW DENSITY NATIONAL (NSI XRFS)	**4864**	**0.51**	**<0.25**	**0.25**	**0.33**	**0.49**	**48**	**25**
Regional (G-BASE rural)	23686	<0.7	<0.7	<0.7	<0.7	0.7	140	55
Urban (G-BASE)	13601	1.1	<1	<1	<1	1	170	31
(c) Urban area	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
CORBY	**133**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**4**	**10**
COVENTRY	**395**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**8.6**	**8**
Derby	276	2.4	<0.9	1.6	2	2.6	12	3
Doncaster	279	1.1	<0.9	1	1	1	7	4
Hull	408	<0.7	<0.7	<0.7	<0.7	<0.7	5	4
LEICESTER	**656**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**9.3**	**6**
Lincoln	215	<0.9	<0.9	<0.9	<0.9	<0.9	5	8
LONDON (GLA AREA)	**6494**	**1**	**<0.5**	**0.5**	**0.6**	**0.84**	**170**	**31**
MANCHESTER (PART)	**300**	**1.4**	**<0.5**	**0.6**	**0.9**	**1.3**	**80**	**16**
Mansfield	257	1.3	<1	1	1	2	9	3
NORTHAMPTON	**275**	**0.87**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**130**	**16**
Nottingham	636	2.2	<0.5	1	2	3	17	4
PETERBOROUGH	**275**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**3.8**	**11**
Scunthorpe	196	1.2	<0.9	<0.9	1	1	28	12
Sheffield	575	1.2	<1	1	1	2	8	3
SOUTH ESSEX TOWNS	**715**	**<0.5**	**<0.5**	**<0.5**	**<0.5**	**0.5**	**8.9**	**9**
Stoke-on-Trent	746	1.7	<1	1	2	2	43	14
Telford	294	2.4	<1	1	1	3	30	4
Wolverhampton	285	1.9	<1	<1	1	2	70	12
York	191	1.3	<1	1	1	2	9	4

Data in bold is that which was used in the calculation of NBCs.

Table 1: Statistical summary of topsoil Cd in the main data sets. (a) All data; (b) G-BASE and NSI XRFS; and (c) by urban centres sampled by G-BASE (Cd concentrations in mg/kg).

The distribution of concentrations is shown in Figure 2 and the k-means cluster output in Figure 3. The latter guided the definition of domains associated with background concentrations higher than the Principal Domain in English soils.

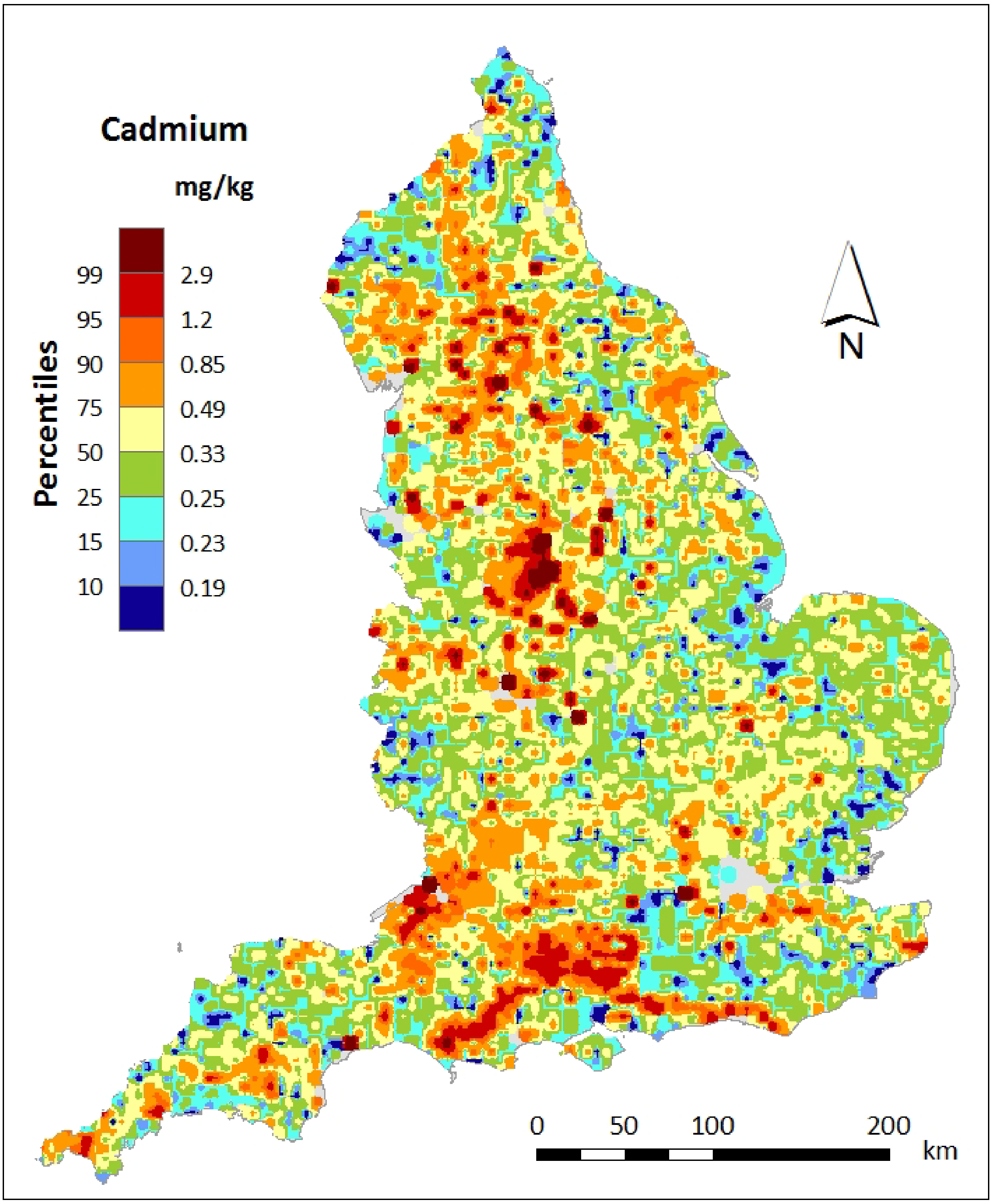

Figure 2: Interpolated map of topsoil Cd, using only NSI(XRFS) data. Colour thresholds are designed for highly skewed data.

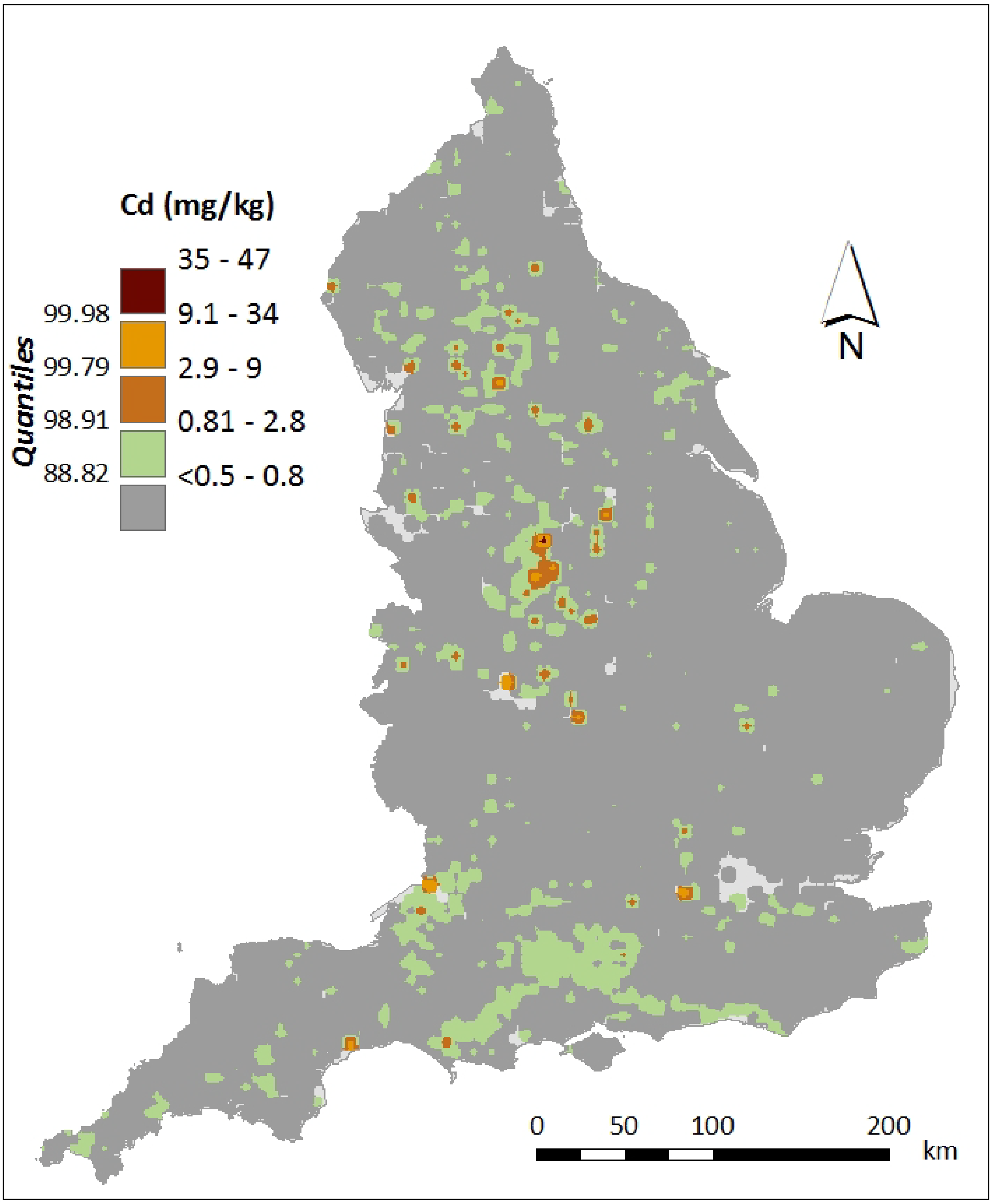

Figure 3: Interpolated map of topsoil NSI(XRFS) Cd data only. Thresholds determined by using k-means cluster analysis.

2.2 DOMAIN SELECTION

The following information was used to compile the evidence for domains:

- non-ferrous metalliferous mineralisation and mining;
- higher topsoil Cd concentrations in soils over the Cretaceous Chalk of southern England than the rest of the Chalk outcrop (spatial extent); and
- urban areas.

2.2.1 Non-ferrous metalliferous mineralisation and mining

Results of analysis show that Peak District soil are much higher in Cd than the other areas (Figure 4 and Figure 5), although some other regions also have higher concentrations than the non-mineralised data, and in relation to k-means – confirming observations from Figure 3. However, low sample numbers associated with the Peak District samples (Table 2) mean that for classification of this as one mineralised domain, as suggested by Figure 4 and Figure 5, it is desirable to use some G-BASE data to have sufficient sample numbers for NBC quantification.

The North Pennines and Mendips, on the basis of these data, appear to have a higher topsoil Cd concentration than is typical in English soils, whilst being somewhat lower than those for the Peak District. They have therefore been combined into a second mineralisation domain ("Min Gp2"), with the Peak District forming "Min Gp1". That these areas have higher than typical background concentrations is entirely consistent with the metalliferous mineralisation that occurs in these orefields and previous stream sediment geochemical surveys. Neither Mendips nor the North Pennines areas have G-BASE soil samples, so the sample numbers for these cannot be augmented as for the Peak District.

The Peak District data are shown in Table 3 and it can be seen that the two surveys' data have a similar distribution, allowing for the higher detection limit (0.7 mg/kg) and lower sensitivity (reported to one significant figure at concentrations up to 10 mg/kg) of G-BASE results, which is confirmed by Figure 6.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
1 SW England	79	0.6	<0.25	0.27	0.46	0.73	2.54	2
2 North Devon	4	0.3	0.3	0.26	0.29	0.33	0.34	1
3 Mendips	8	1.2	<0.25	0.32	0.90	1.19	4.85	2
4 Shelve	3	0.6	0.5	0.51	0.58	0.68	0.68	1
5 Peak District	21	5.4	0.7	1.23	3.12	4.65	47.5	4
6 Lake District	26	0.6	<0.25	0.32	0.47	0.75	3.90	4
7 North Pennines	87	0.9	<0.25	0.31	0.50	0.87	12.5	6
Non-mineralised	4636	0.5	<0.25	<0.25	0.32	0.48	20.2	15

Table 2: Summary statistics of topsoil Cd concentrations (in mg/kg) using NSI(XRFS) data for metalliferous mineralisation and mining areas.

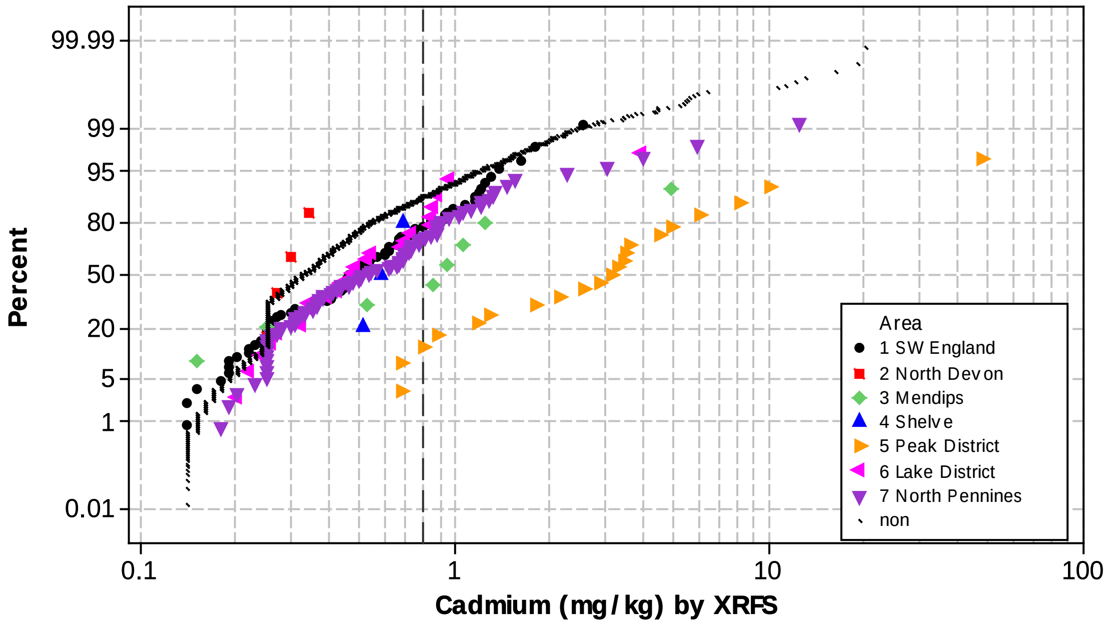

Figure 4: Probability plot of topsoil Cd concentrations in the mineralisation domains (using NSI(XRFS) data). k-means threshold of 0.8 mg/kg shown as dashed line.

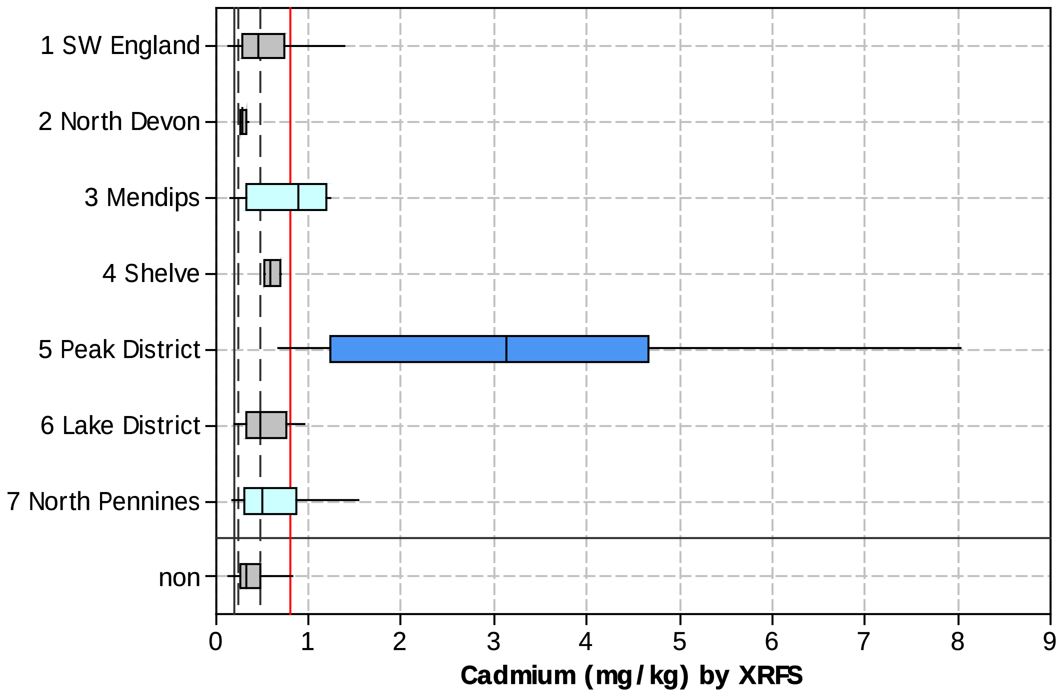

Figure 5: Boxplot of topsoil Cd concentrations in the mineralisation domains (using NSI(XRFS) data). k-means threshold of 0.8 mg/kg shown as red line. Interquartile range of "non" samples (not within a mineralisation area) projected vertically as black dashed lines.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Peak District – NSI(XRFS)	21	5.4	0.7	1.23	3.12	4.65	47.5	4
Peak District – G-BASE (regional)	203	4.394	<0.7	2.0	3.0	5.0	35	3

Table 3: Summary statistics of topsoil Cd concentrations (in mg/kg) in the Peak District metalliferous mineralisation and mining from NSI(XRFS) and G-BASE (regional).

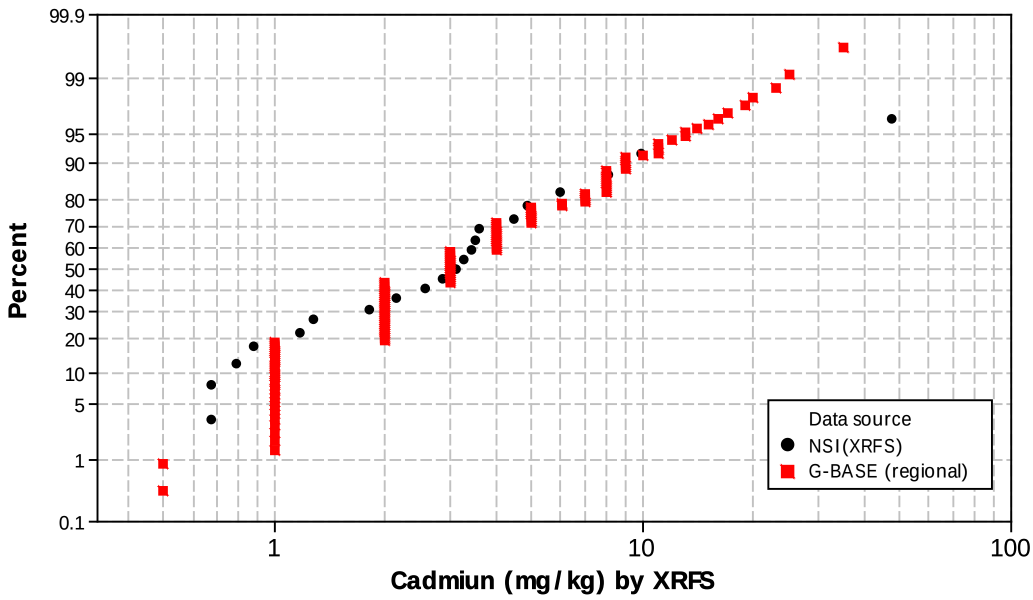

Figure 6: Probability plot of topsoil Cd concentrations in the Peak District mineralisation domains, by data source.

2.2.2 Southern extent of Cretaceous Chalk

This can be seen to have a typically elevated background Cd concentration in Figure 3. The extent of the Chalk is shown in Figure 7, and by comparison with Figure 3 it can be seen that the southernmost extent of the Chalk in that which is associated with systematically elevated Cd concentrations. Although the available data for this area is largely that derived from the NSI(XRFS) information, this geological control has been noted in the G-BASE London data[1], where the Chalk outcrop extends north into the south of London, and is seen to give higher topsoil Cd concentrations. The NSI(XRFS) data provide sufficient samples to quantify a NBC, and have a high median concentration (Table 4) in relation to that of the overall NSI(XRFS) data set (0.33 mg/kg).

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Chalk South – NSI(XRFS)	265	0.97	<0.25	0.48	0.86	1.35	5.58	2

Table 4: Summary statistics of topsoil Cd concentrations (in mg/kg) over the southern Chalk extent.

[1] http://www.bgs.ac.uk/gbase/londonearth.html

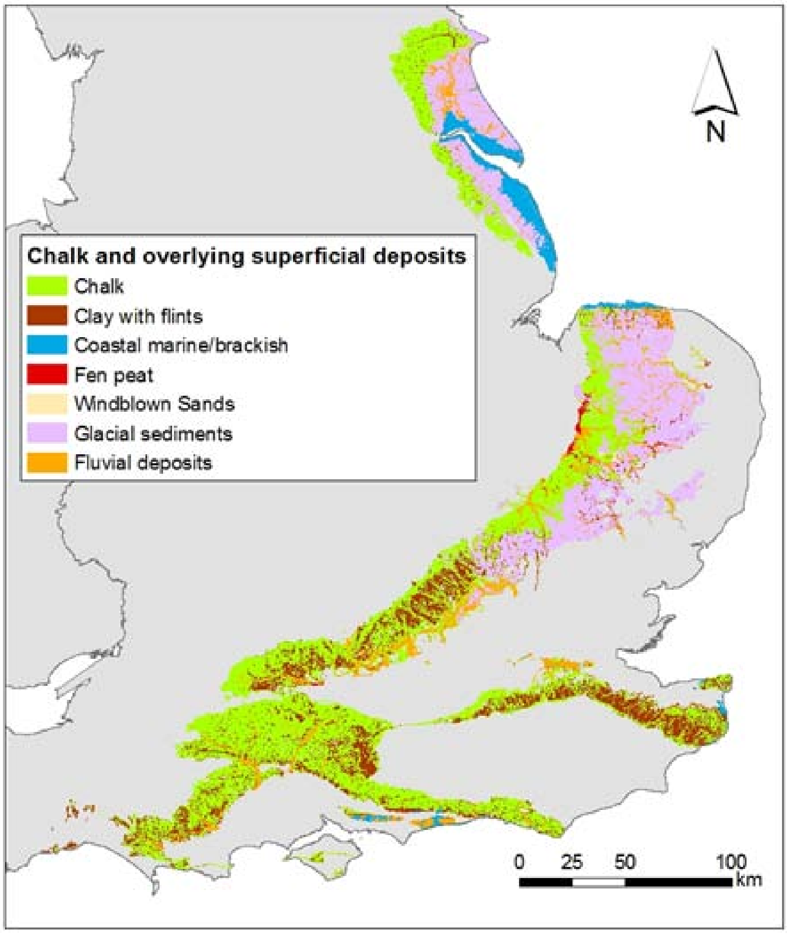

Figure 7: The extent of the Cretaceous Chalk and overlying superficial deposits in England.

2.2.3 Urban areas

The NSI sampling did not include urban areas – thus the few samples to fall within this category have been augmented with the more recent G-BASE urban data sets, which benefit from having a lower detection limit than earlier data (Table 1).

It can be seen that there appear to be trends within these data, with Manchester and London (GLA area) data having the systematically highest concentrations (Figure 8). Summary statistics are provided in Section 2.3.

Note that the London urban area and the southern Chalk areas intersect. As the Chalk South Domain is associated with typically higher concentrations of Cd, the area of intersection is assigned to the Chalk South Domain rather than the Urban Domain.

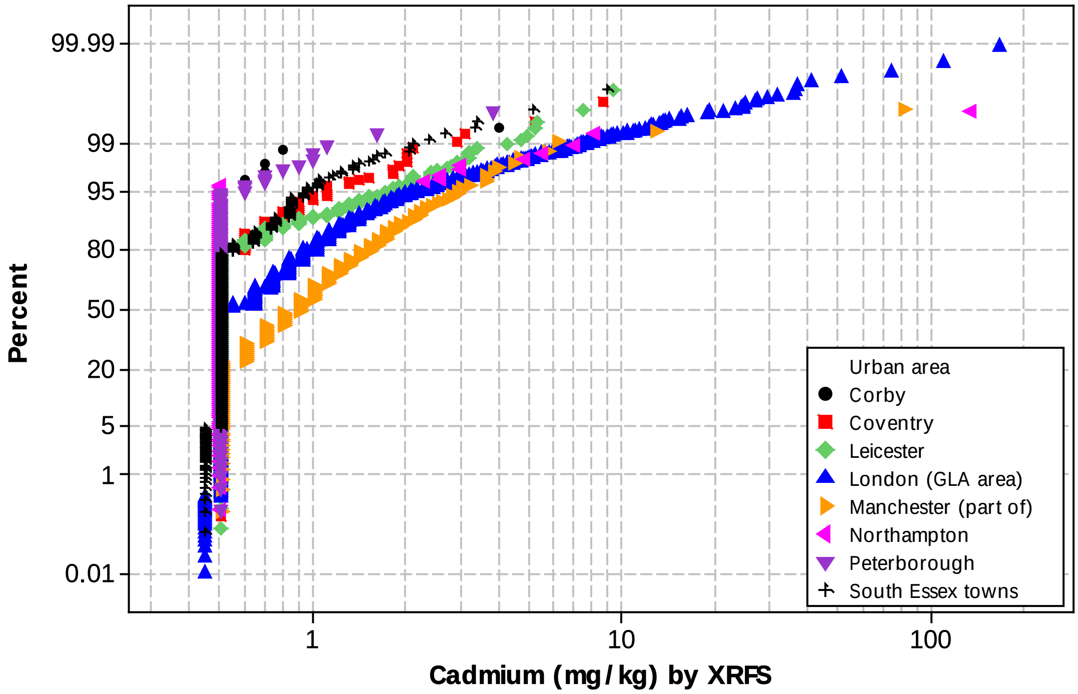

Figure 8: Probability plot of topsoil Cd concentrations in the G-BASE urban data with sampling area shown.

2.3 DOMAIN DATA SUMMARY

The data summarised into the domains described above are presented in Table 5 and Figure 9, and have the extent shown in Figure 10.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Chalk South	265	1.0	0.3	0.5	0.9	1.4	5.6	2
Min_Gp1	224	4.5	<0.5	2.0	3.0	5.0	48	4
Min_Gp2	95	0.9	0.3	0.3	0.5	0.9	13	6
Urban	9308	0.9	<0.5	<0.5	<0.5	0.8	165	33
Principal	4418	0.5	0.3	0.3	0.3	0.5	20	17

Table 5: Summary statistics of topsoil Cd concentrations (in mg/kg) in the domains.

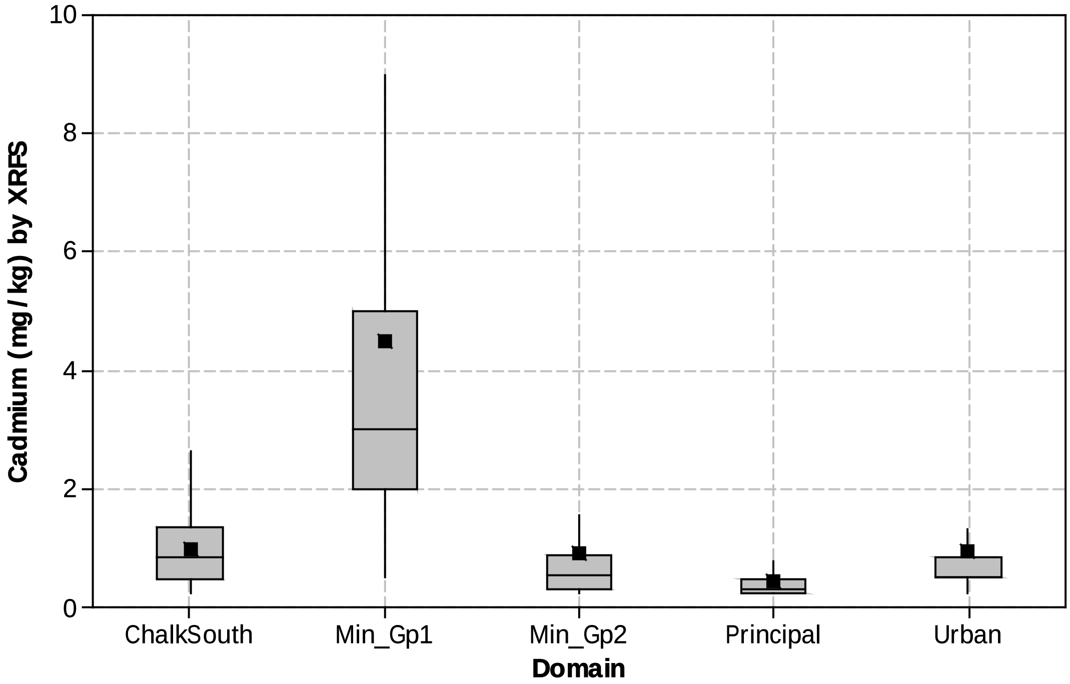

Figure 9: Boxplot of topsoil Cd concentrations by domain.

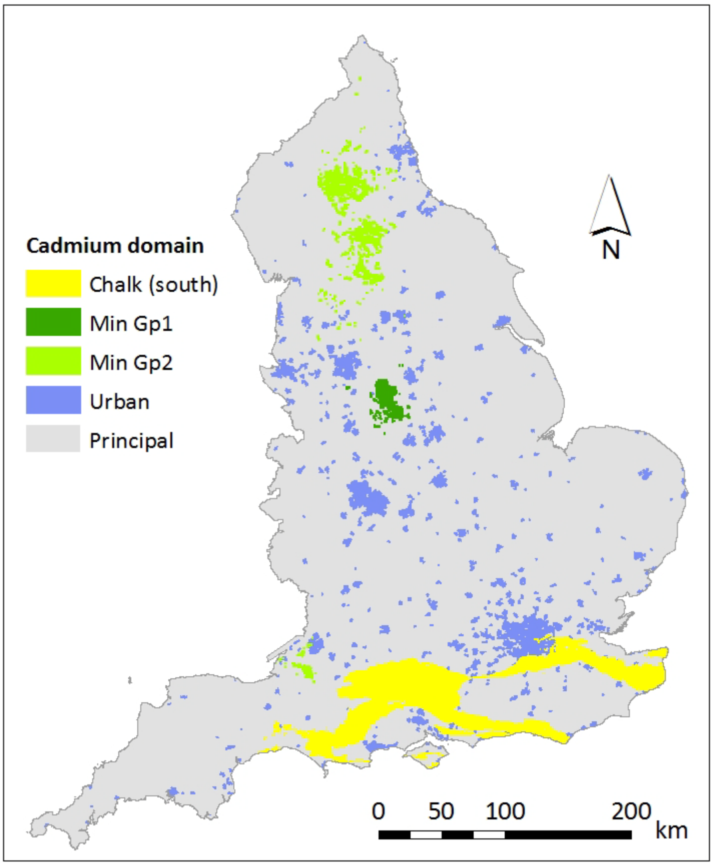

Figure 10: Map of Cd domains in England.

2.4 CADMIUM NBC CALCULATION

2.4.1 Principal domain

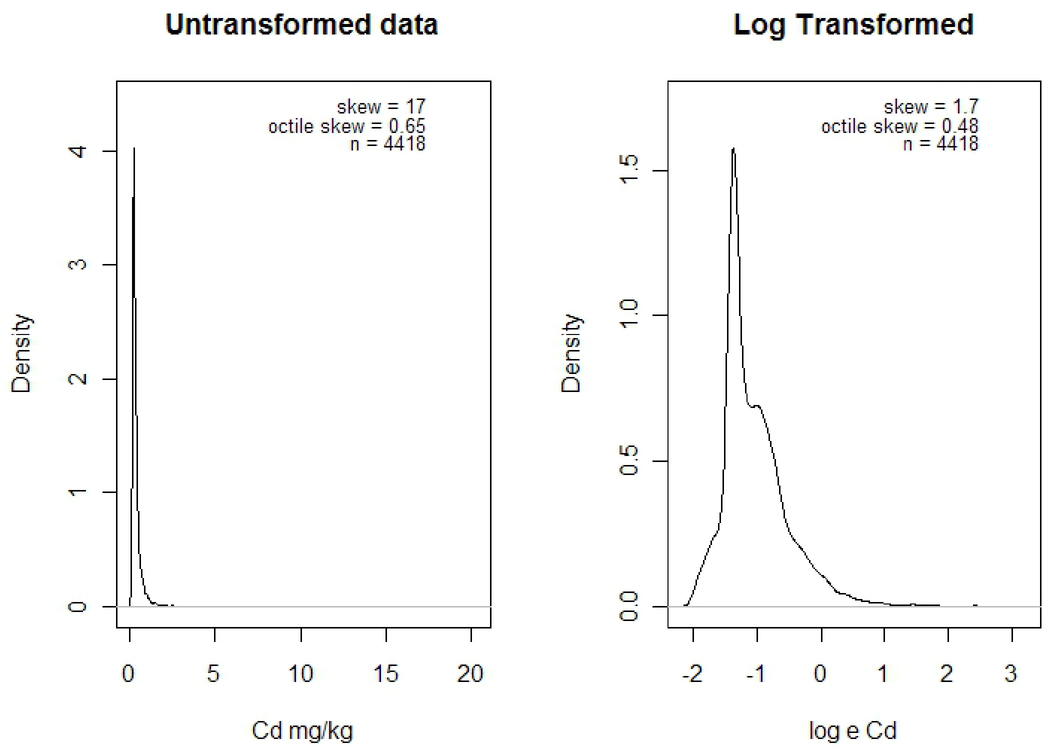

Figure 11: Density distributions for the raw data and the $\log_e$ transformed data for Cd in the Principal Domain (n = number of samples).

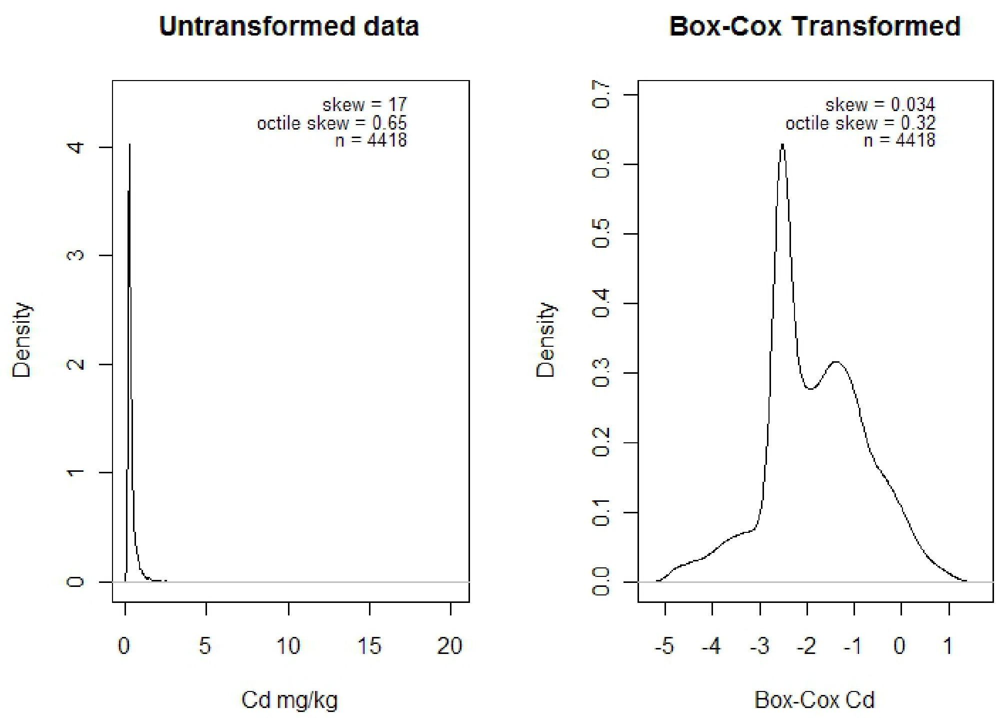

Figure 12: Density distributions for the raw data and the Box-Cox transformed data for Cd in the Principal Domain (n = number of samples).

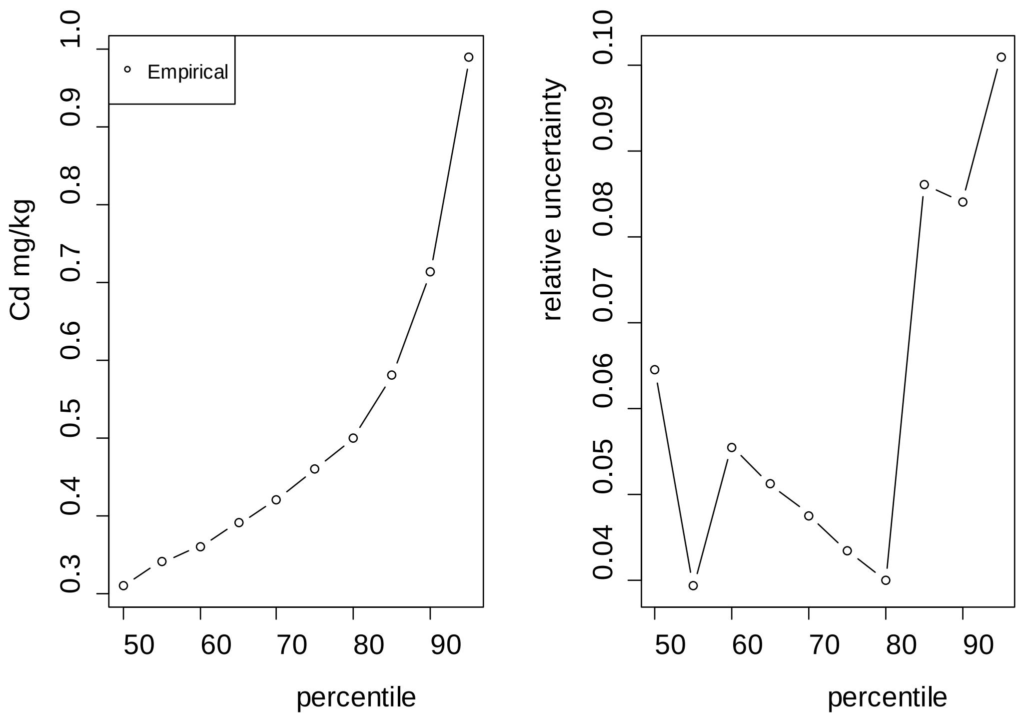

Figure 13: Empirical percentiles and relative uncertainty for Cd in the Principal Domain.

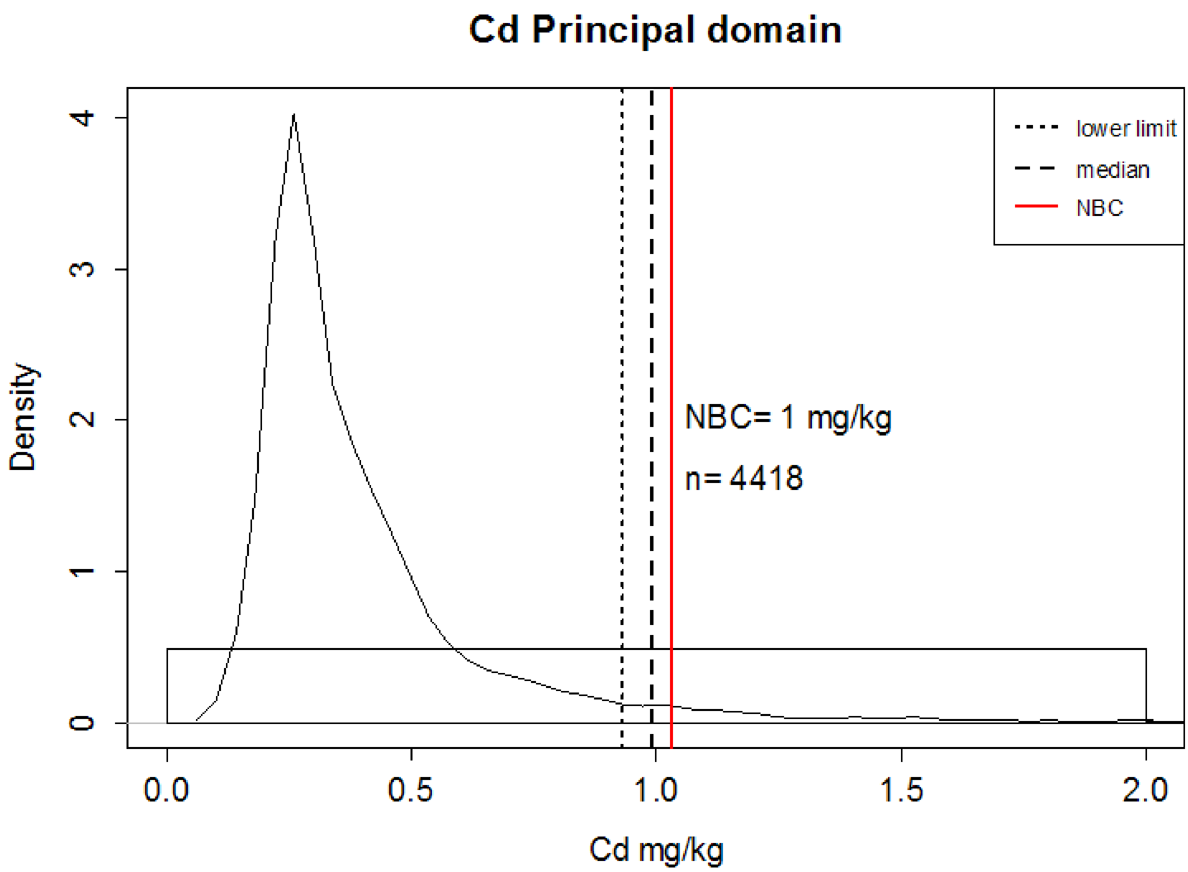

Figure 14: Summary density plot and histogram of the distribution for Cd in the Principal Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H
50	0.3	0.3	0.3
55	0.3	0.3	0.3
60	0.4	0.4	0.4
65	0.4	0.4	0.4
70	0.4	0.4	0.4
75	0.5	0.5	0.5
80	0.5	0.5	0.5
85	0.6	0.6	0.6
90	0.7	0.7	0.7
95	0.9	1.0	1.0

Low (L) and High (H) values represent confidence intervals around the median.

Table 6: Empirical (Emp) percentile values for Cd in the Principal Domain (concentrations in mg/kg).

2.4.2 Chalk South domain

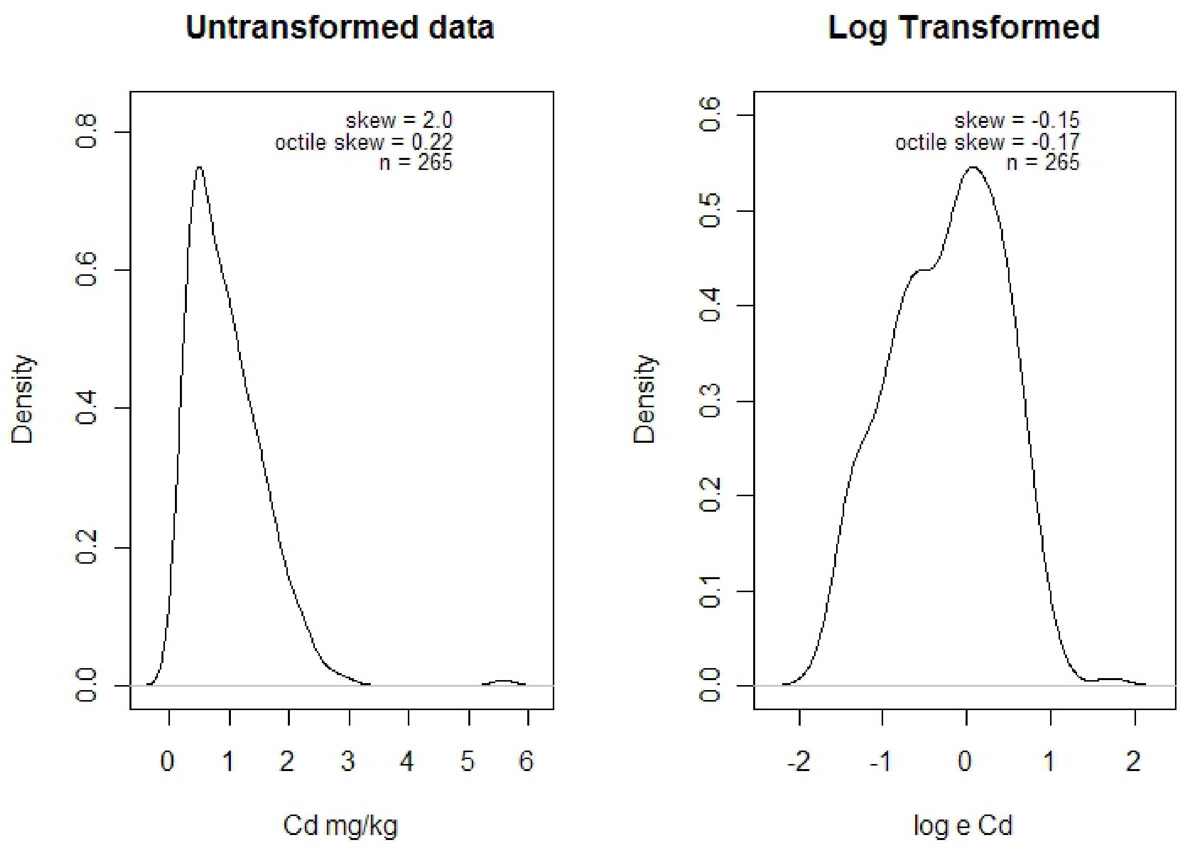

Figure 15: Density distributions for the raw data and the $\log_e$ transformed data for Cd in the Chalk South Domain (n = number of samples).

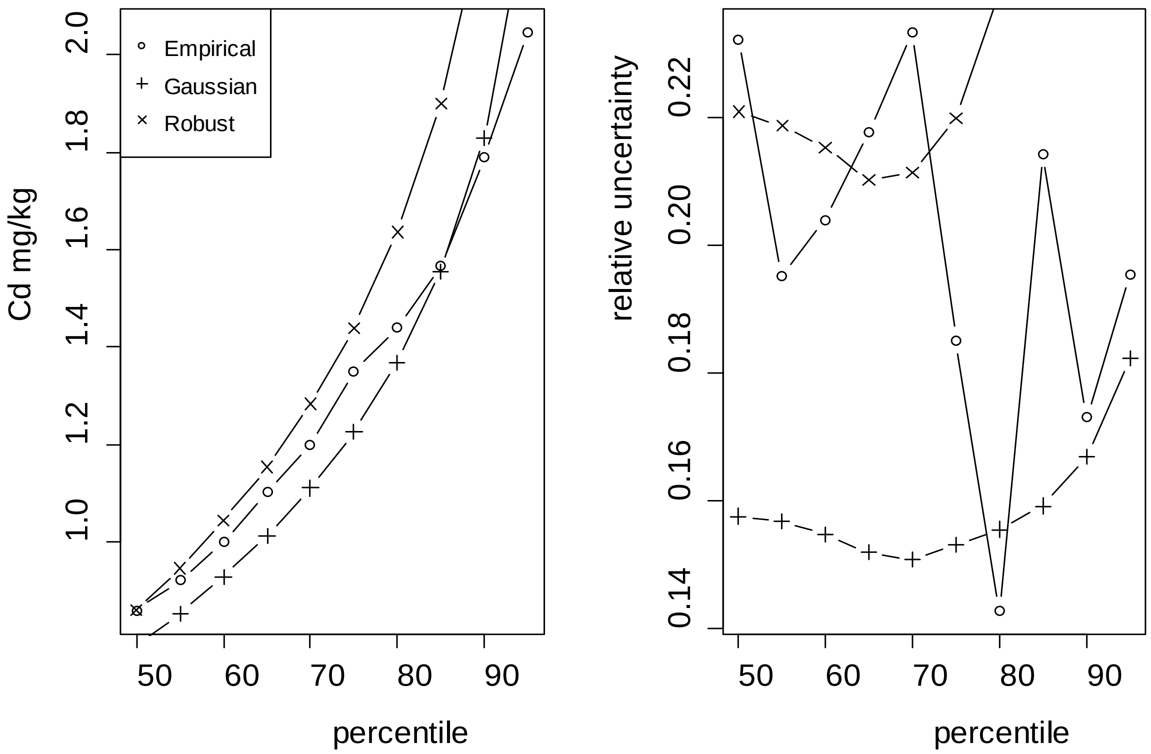

Figure 16: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Cd in the Chalk South Domain.

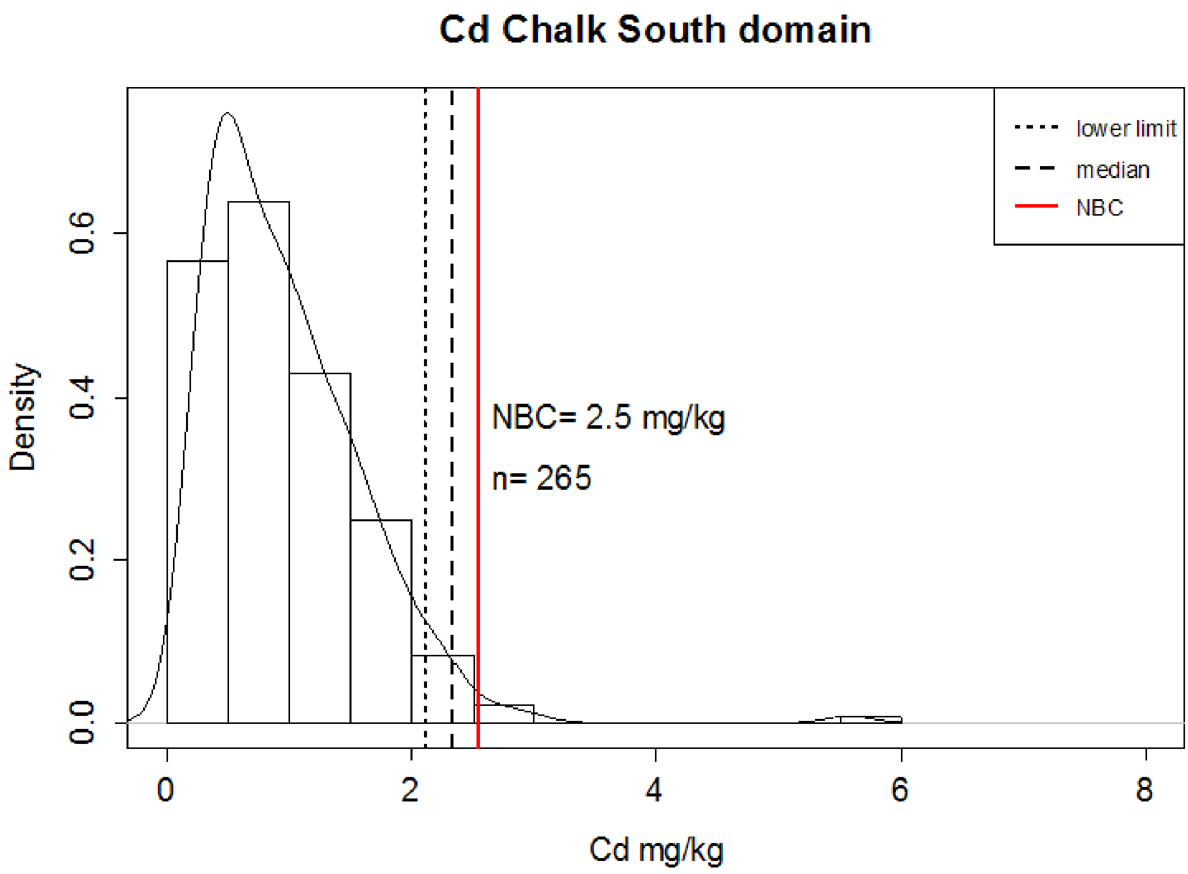

Figure 17: Summary density plot and histogram of the distribution for Cd in the Chalk South Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	0.75	0.86	0.95	**0.73**	**0.79**	**0.85**	0.75	0.86	0.94
55	0.85	0.92	1.03	**0.79**	**0.85**	**0.92**	0.82	0.95	1.02
60	0.91	1.00	1.11	**0.86**	**0.93**	**1.00**	0.90	1.04	1.12
65	0.97	1.10	1.21	**0.94**	**1.01**	**1.09**	0.99	1.15	1.23
70	1.07	1.20	1.35	**1.03**	**1.11**	**1.20**	1.10	1.28	1.37
75	1.20	1.35	1.45	**1.13**	**1.23**	**1.32**	1.22	1.44	1.53
80	1.33	1.44	1.54	**1.26**	**1.37**	**1.47**	1.36	1.64	1.75
85	1.44	1.57	1.78	**1.43**	**1.56**	**1.68**	1.58	1.90	2.06
90	1.62	1.79	1.93	**1.68**	**1.83**	**1.98**	1.88	2.29	2.52
95	1.83	2.05	2.23	**2.11**	**2.32**	**2.54**	2.42	3.02	3.39

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 7: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Cd in the Chalk South Domain (concentrations in mg/kg).

2.4.3 Mineralisation Group 1 (Min Gp1) Domain

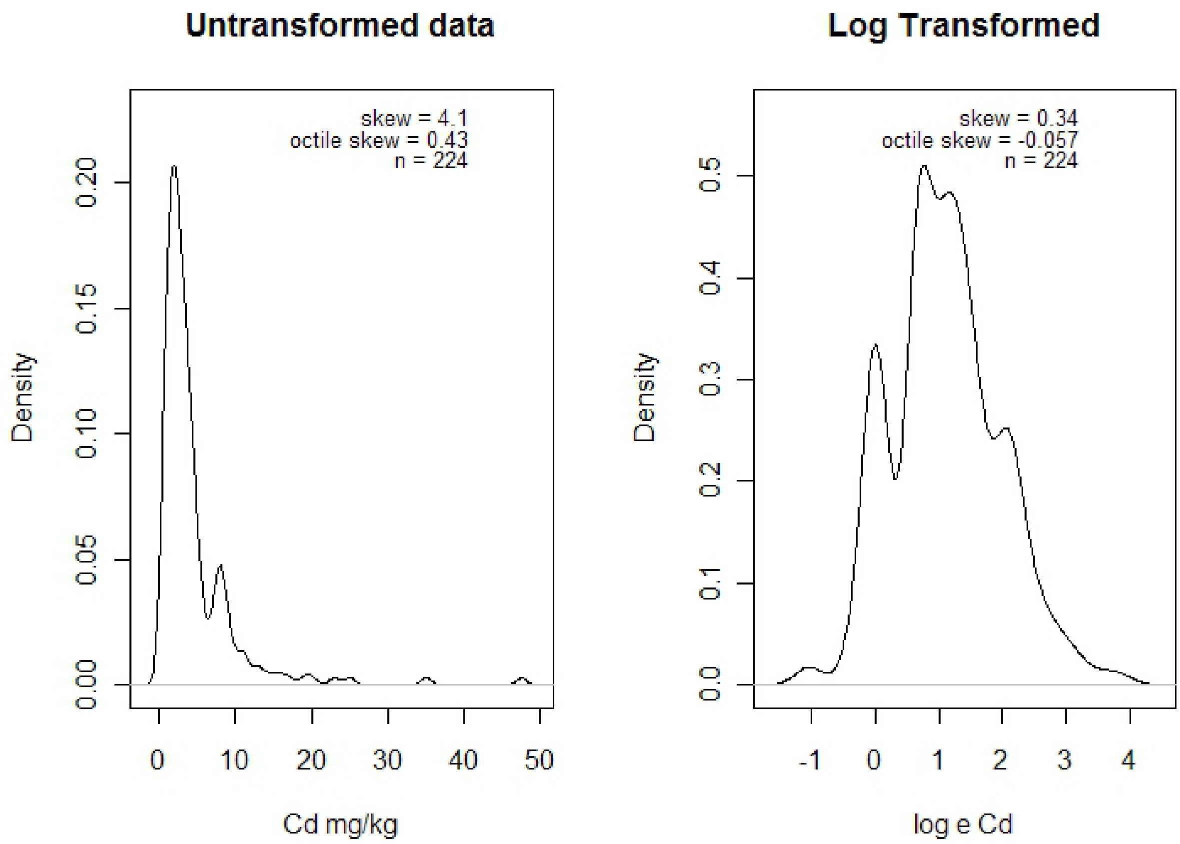

Figure 18: Density distributions for the raw data and the $\log_e$ transformed data for Cd in the Mineralisation Group 1 Domain (n = number of samples).

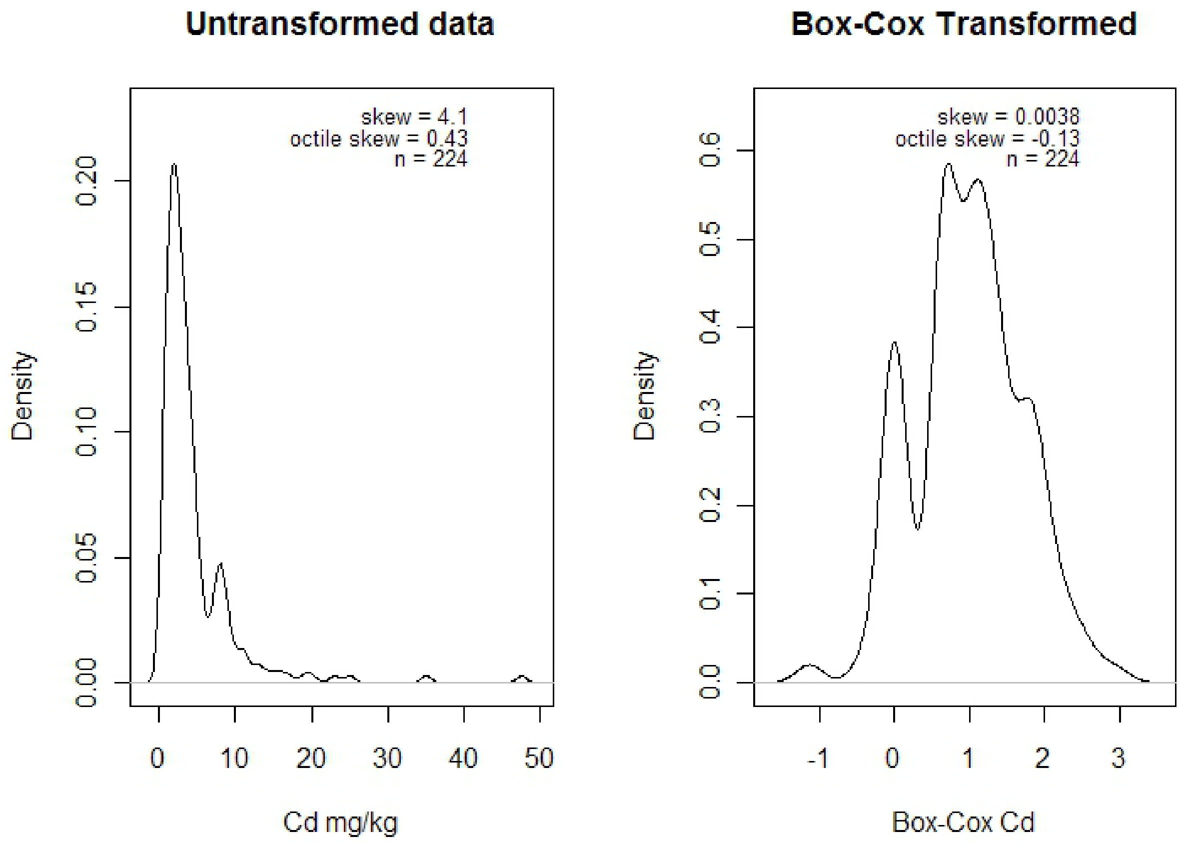

Figure 19: Density distributions for the raw data and the Box-Cox transformed data for Cd in the Mineralisation Group 1 Domain (n = number of samples).

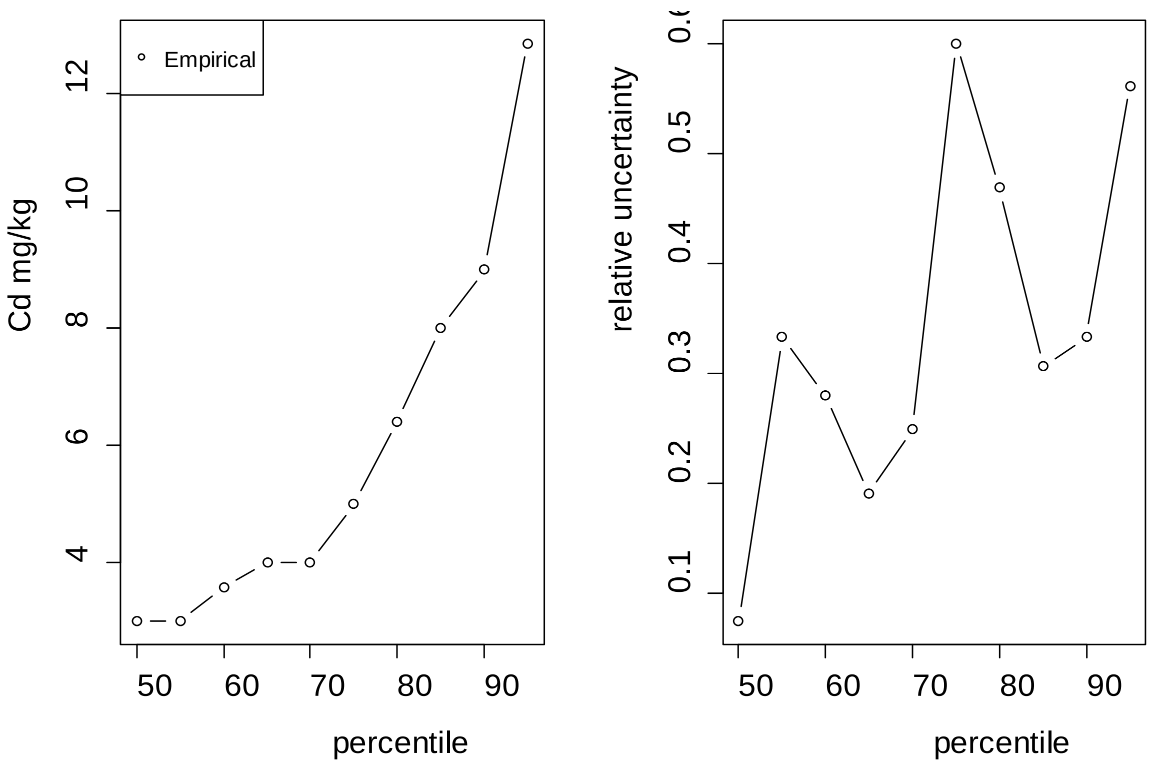

Figure 20: Empirical percentiles and relative uncertainty for Cd in the Mineralisation Group 1 Domain.

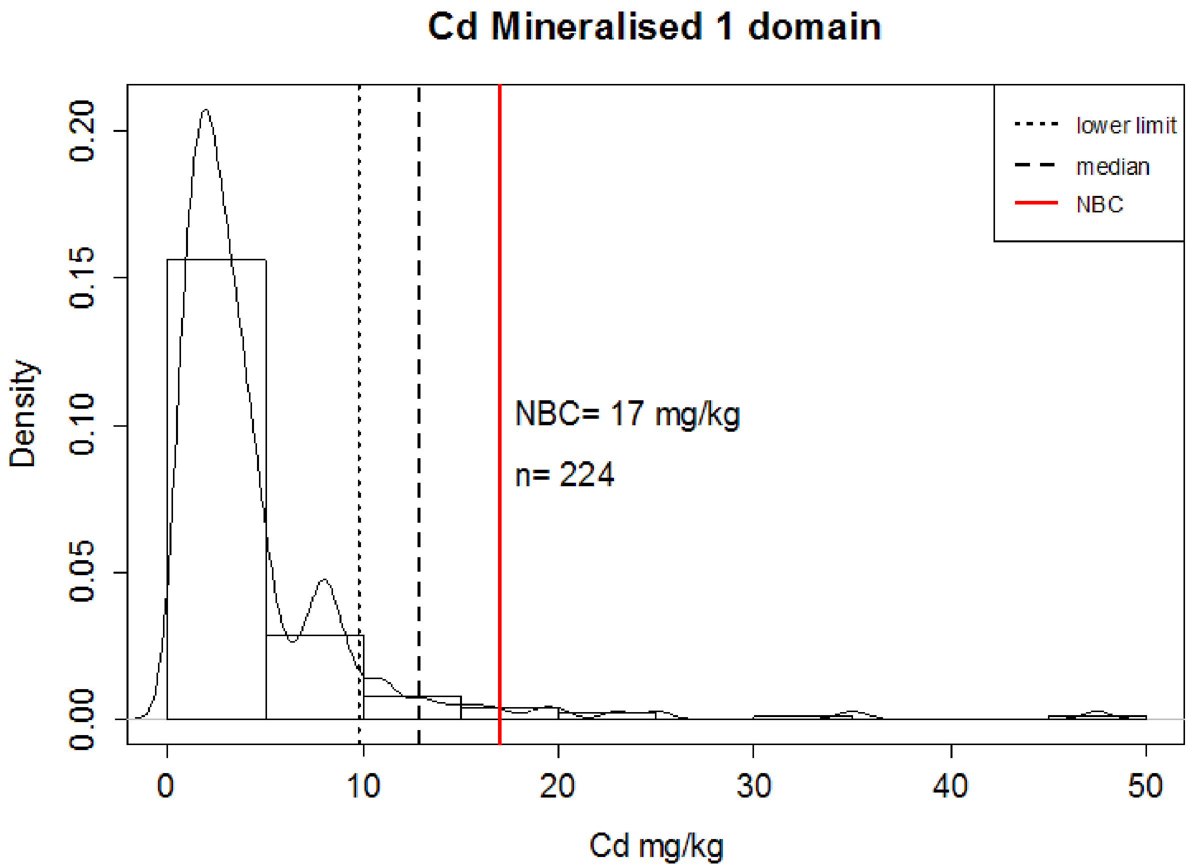

Figure 21: Summary density plot and histogram of the distribution for Cd in the Mineralisation Group 1 Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H
50	3	3	3
55	3	3	4
60	3	4	4
65	3	4	4
70	4	4	5
75	4	5	7
80	5	6	8
85	7	8	9
90	8	9	11
95	10	13	17

Low (L) and High (H) values represent confidence intervals around the median.

Table 8: Empirical (Emp) percentile values for Cd in the Mineralisation Group 1 Domain (concentrations in mg/kg).

2.4.4 Mineralisation Group 2 (Min Gp2) Domain

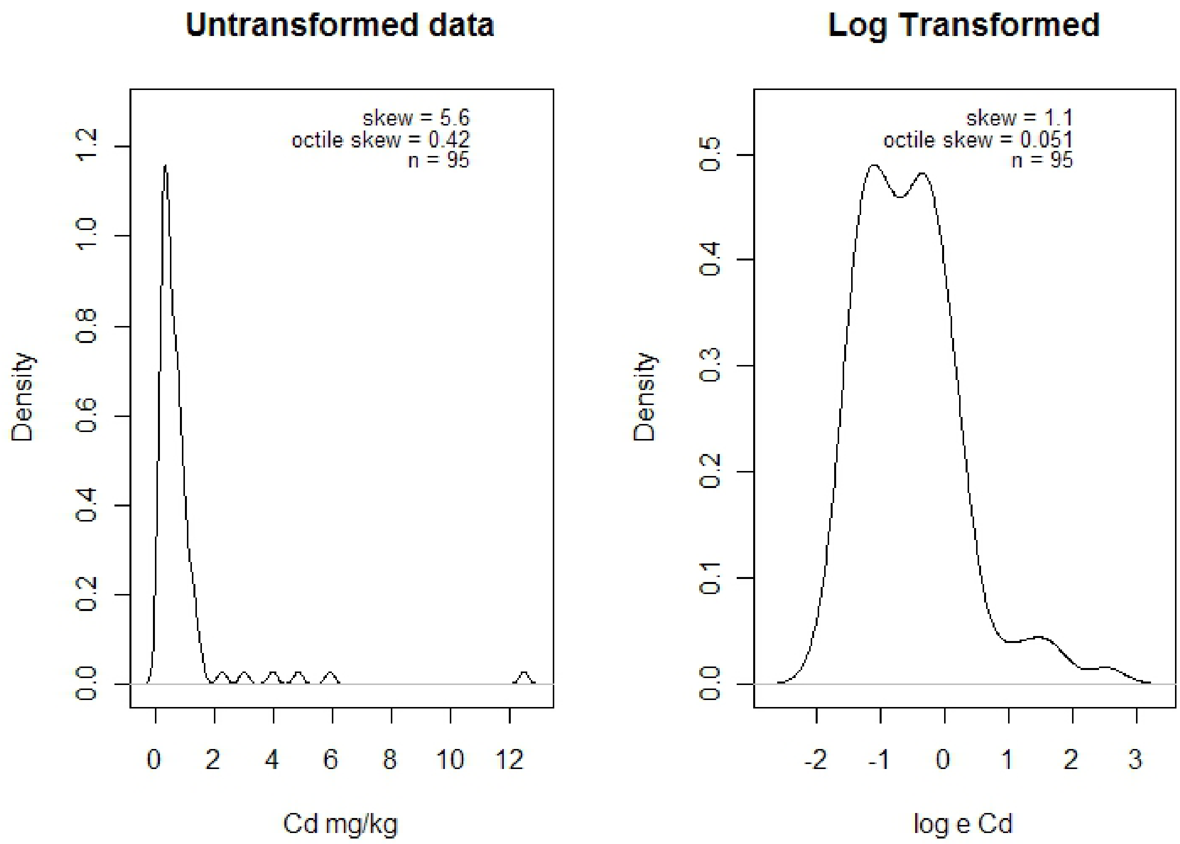

Figure 22: Density distributions for the raw data and the $\log_e$ transformed data for Cd in the Mineralisation Group 2 Domain (n = number of samples).

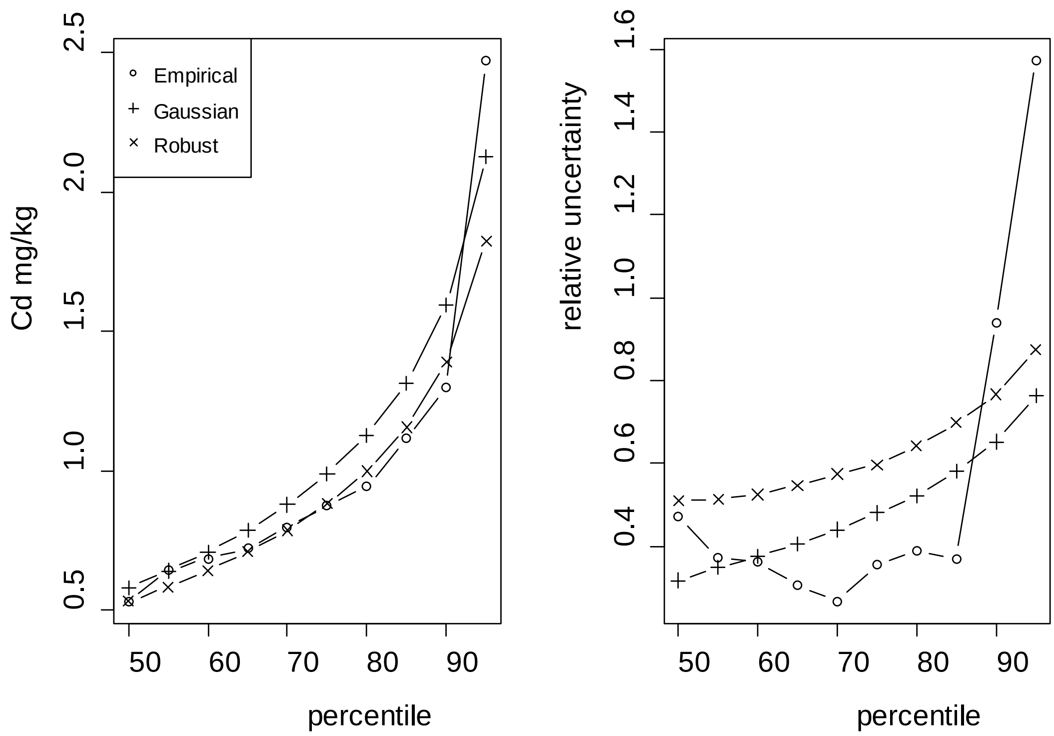

Figure 23: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Cd in the Mineralisation Group 2 Domain.

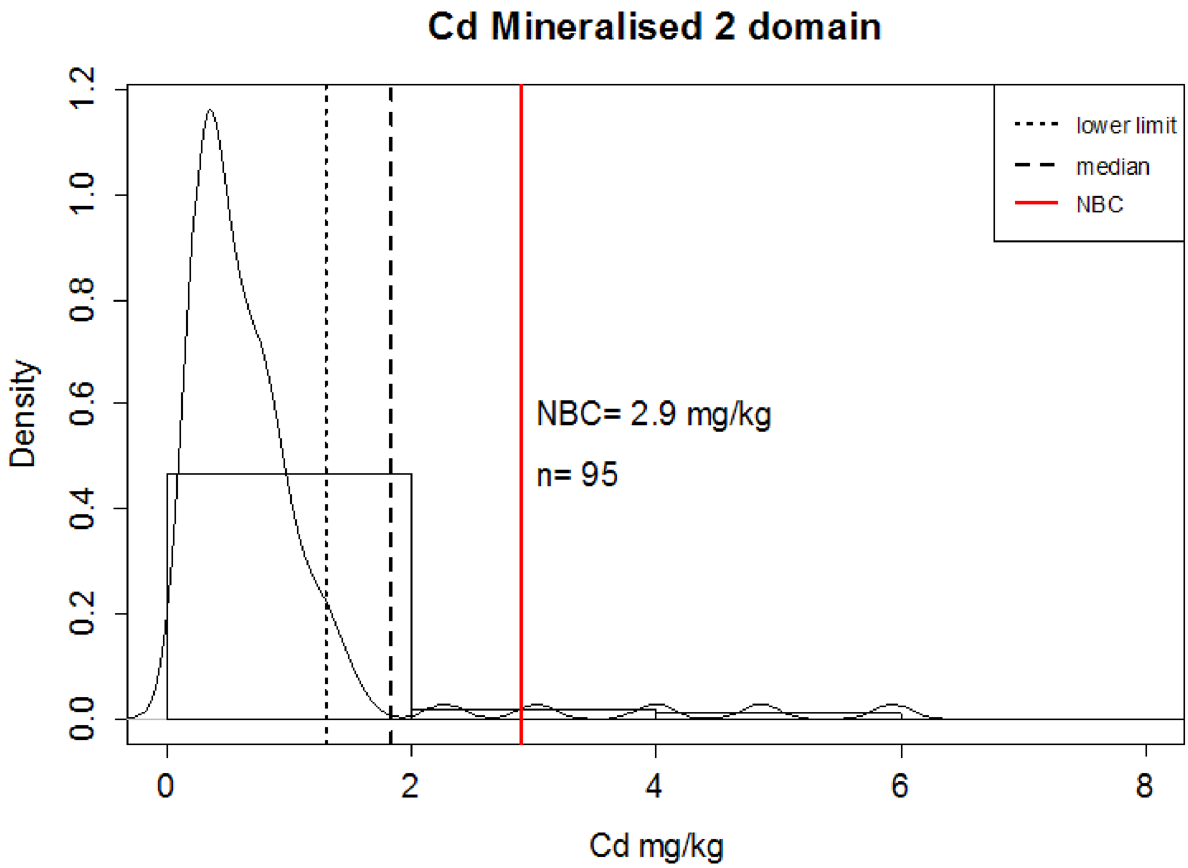

Figure 24: Summary density plot and histogram of the distribution for Cd in the Mineralisation Group 2 Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	0.4	0.5	0.7	0.5	0.6	0.7	**0.4**	**0.5**	**0.7**
55	0.5	0.6	0.7	0.5	0.6	0.8	**0.5**	**0.6**	**0.8**
60	0.5	0.7	0.8	0.6	0.7	0.9	**0.5**	**0.6**	**0.9**
65	0.7	0.7	0.9	0.6	0.8	1.0	**0.6**	**0.7**	**1.0**
70	0.7	0.8	0.9	0.7	0.9	1.1	**0.6**	**0.8**	**1.1**
75	0.7	0.9	1.1	0.8	1.0	1.2	**0.7**	**0.9**	**1.2**
80	0.8	0.9	1.2	0.9	1.1	1.5	**0.8**	**1.0**	**1.4**
85	0.9	1.1	1.3	1.0	1.3	1.7	**0.9**	**1.2**	**1.7**
90	1.1	1.3	2.3	1.1	1.6	2.2	**1.0**	**1.4**	**2.1**
95	1.3	2.5	5.2	1.4	2.1	3.1	**1.3**	**1.8**	**2.9**

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 9: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Cd in the Mineralisation Group 2 Domain (concentrations in mg/kg).

2.4.5 Urban Domain

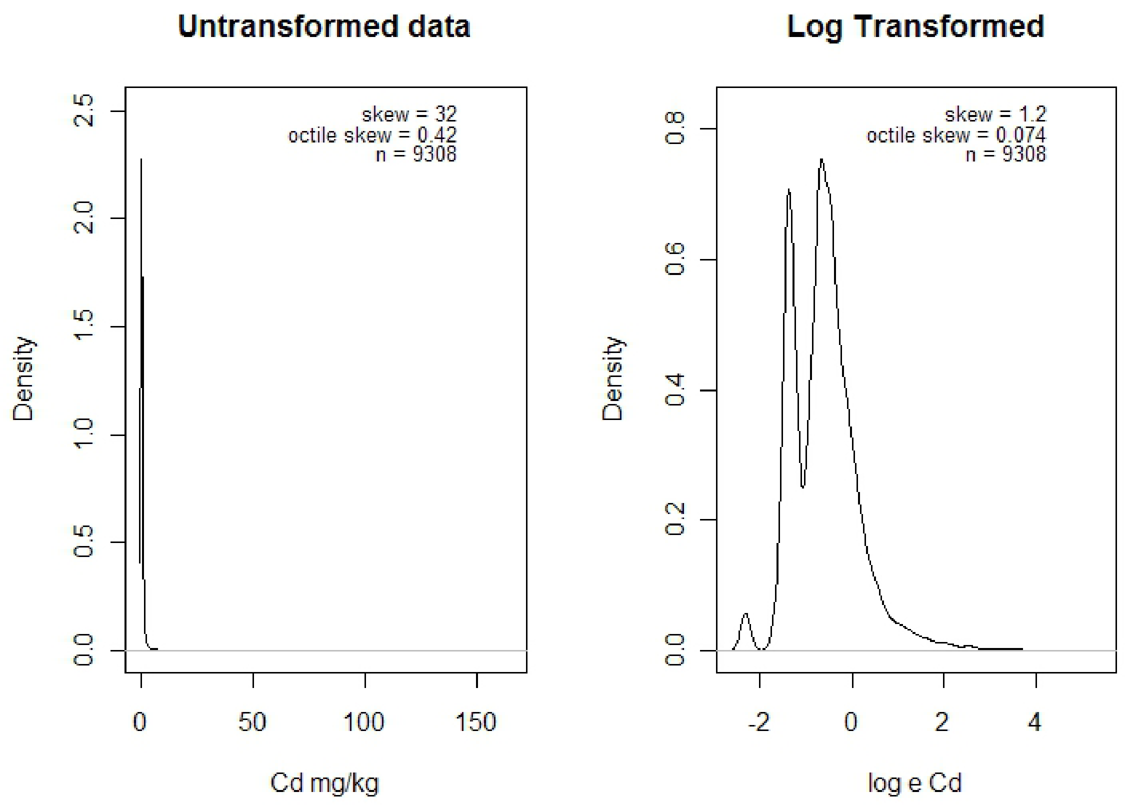

Figure 25: Density distributions for the raw data and the $\log_e$ transformed data for Cd in the Urban Domain (n = number of samples).

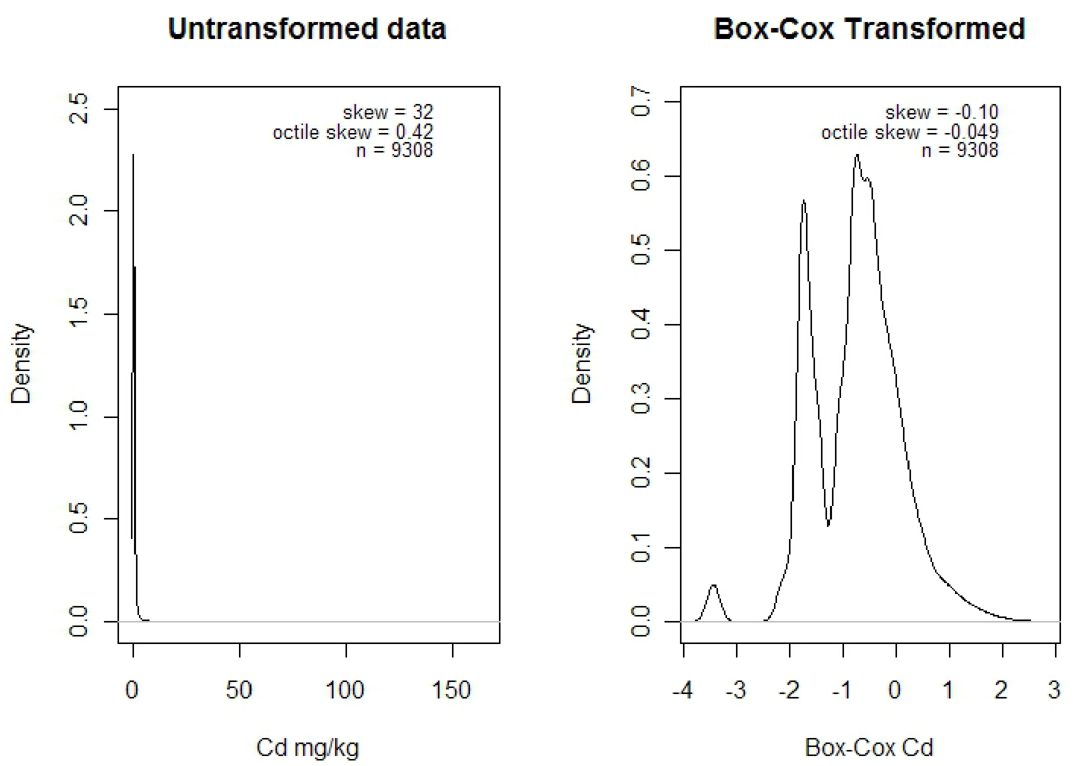

Figure 26: Density distributions for the raw data and the Box-Cox transformed data for Cd in the Urban Domain (n = number of samples).

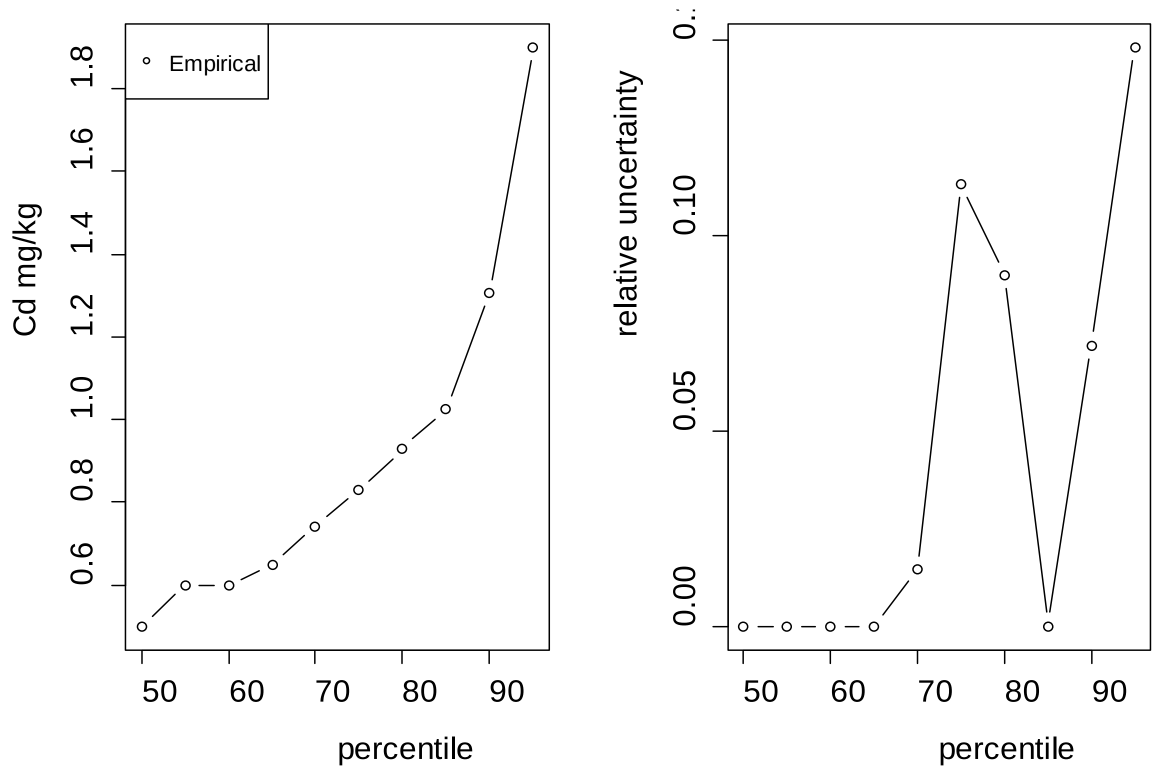

Figure 27: Empirical percentiles and relative uncertainty for Cd in the Urban Domain.

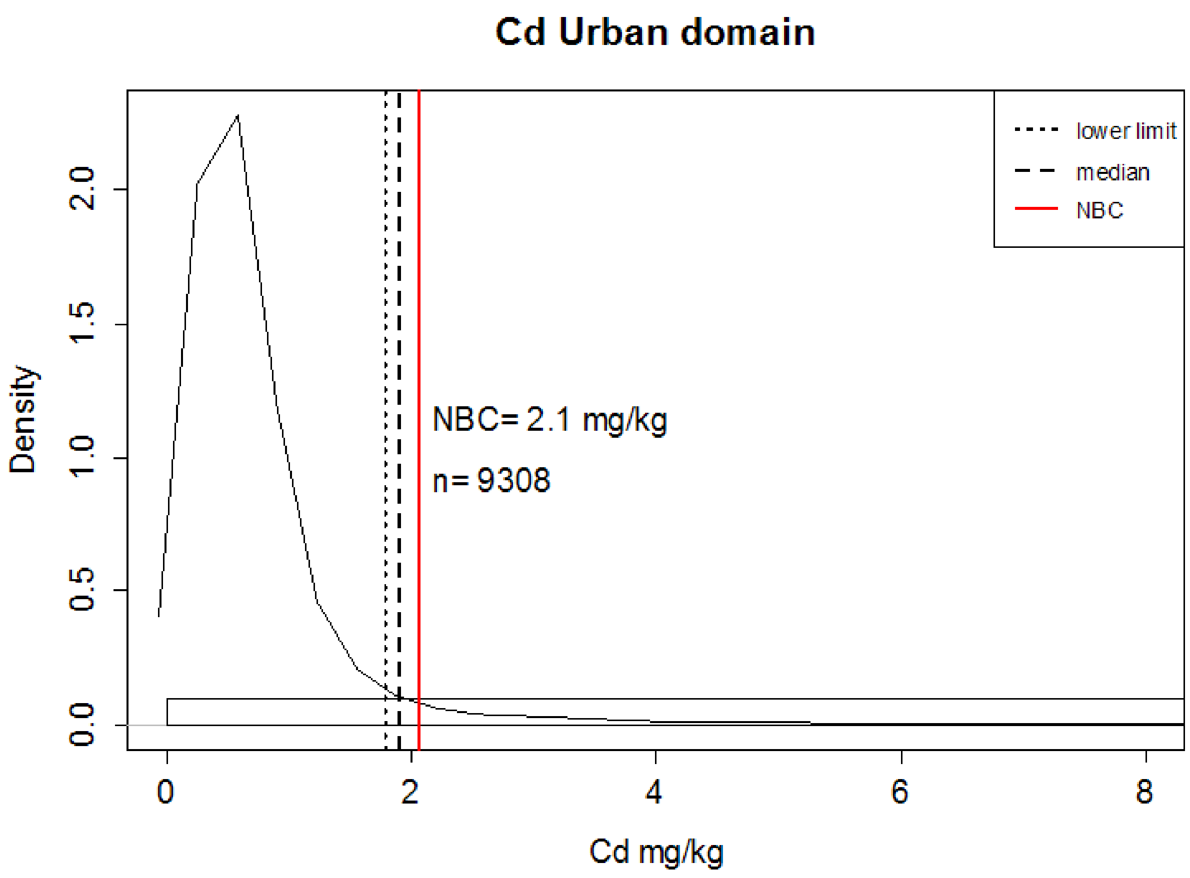

Figure 28:Summary density plot and histogram of the distribution for Cd in the Urban Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H
50	0.5	0.5	0.5
55	0.6	0.6	0.6
60	0.6	0.6	0.6
65	0.7	0.7	0.7
70	0.7	0.7	0.7
75	0.7	0.8	0.8
80	0.9	0.9	0.9
85	1.0	1.0	1.0
90	1.2	1.3	1.3
95	1.8	1.9	2.1

Low (L) and High (H) values represent confidence intervals around the median.

Table 10: Empirical (Emp) percentile values for Cd in the Urban Domain (concentrations in mg/kg).

3 Copper (Cu)

3.1 EXPLORATORY DATA ANALYSIS

Copper data from G-BASE and NSI(XRFS) were used to determine domains. These show typically higher concentrations in the urban areas relative to the data from rural areas provided by G-BASE (regional) and NSI(XRFS) (Figure 29, Figure 30 and Table 11).

The data are mapped in Figure 31, and show strong spatial controls on concentration variations. When k-means cluster analysis is used to identify data populations higher in concentration than those which are typical across England, this has the result of highlighting some metalliferous mineralisation and mining areas, as well as urbanisation controls, as shown in Figure 32.

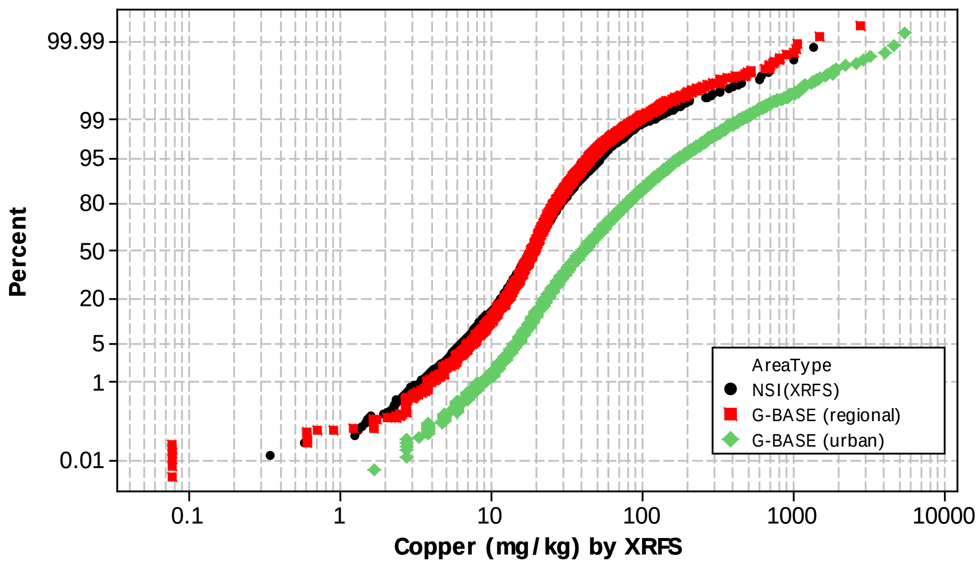

Figure 29: Probability plot of topsoil Cu concentrations for different data sets.

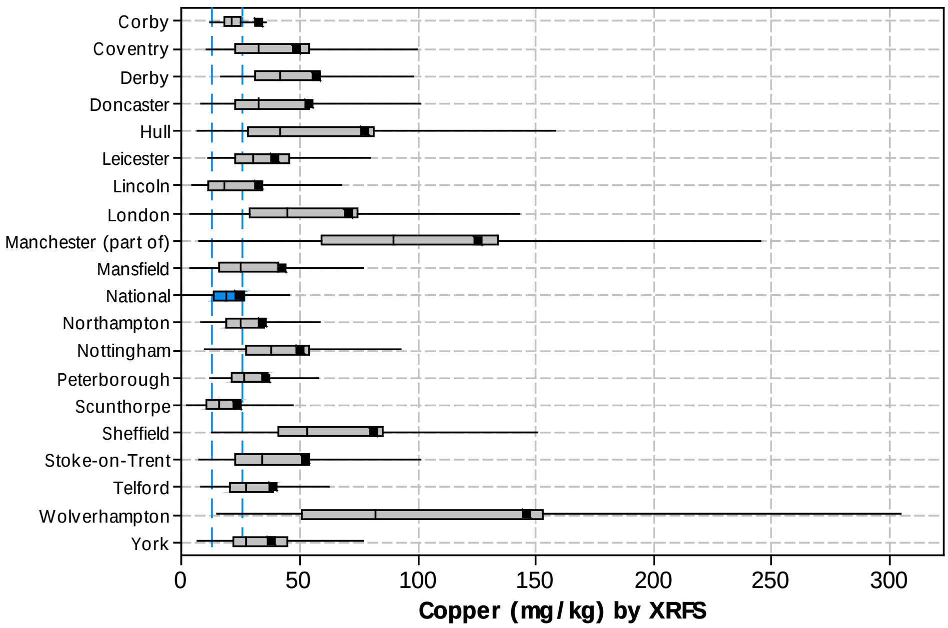

Figure 30: Boxplot of urban topsoil Cu data collected by the G-BASE project. Dashed blue lines extend the interquartile range of the national NSI(XRFS) data.

(a) All data	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
All data	41848	35.3	<1	15.3	21.5	34.8	5330	27
(b) Data set	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
NSI(XRFS)	4864	23.9	<1	12.9	18.6	25.9	1380	19
Regional	23685	22.4	<1	13.7	18.5	24.4	2770	36
Urban	13299	62.5	1.64	24.7	39.1	66.1	5330	19
(c) Urban area	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
Corby	133	32.0	11.4	17.8	20.8	24.7	908	10
Coventry	390	48.0	9.98	22.5	31.9	53.7	464	4
Derby	275	56.2	16.1	30.4	41.3	57.7	659	6
Doncaster	279	53.5	7.89	22.5	31.9	53.7	1280	10
Hull	407	76.9	5.81	27.7	41.2	80.8	1170	5
Leicester	652	38.9	10.7	22.4	29.6	45.1	508	6
Lincoln	215	32.4	3.72	11.0	17.3	33.9	362	4
London (GLA area)	6494	72.6	3.24	29.1	46.2	76.6	5330	19
Manchester (part)	300	125	7.06	59.0	89.1	134	2160	8
Mansfield	257	41.8	2.68	15.2	24.6	40.7	1800	13
Northampton	275	33.9	7.47	18.3	24.7	34.7	1070	14
Nottingham	636	49.6	8.93	26.7	37.1	53.7	1010	9
Peterborough	272	34.9	11.5	20.4	26.1	35.6	270	4
Scunthorpe	196	22.9	1.64	10.0	15.2	24.6	451	9
Sheffield	575	81.0	12.1	40.2	52.7	85.0	1640	8
South Essex towns	715	50.1	4.71	21.8	30.9	49.2	2590	16
Stoke-on-Trent	745	52.1	6.85	22.5	33.9	53.7	1800	12
Telford	292	38.3	7.89	19.6	26.7	38.1	434	5
Wolverhampton	284	146	14.1	50.6	81.9	153	3180	8
York	191	37.7	5.81	21.4	26.7	44.4	236	3

Table 11: Statistical summary of topsoil Cu in the main data sets: (a) all data (b) data set (c) urban areas sampled by G-BASE (Cu concentrations in mg/kg).

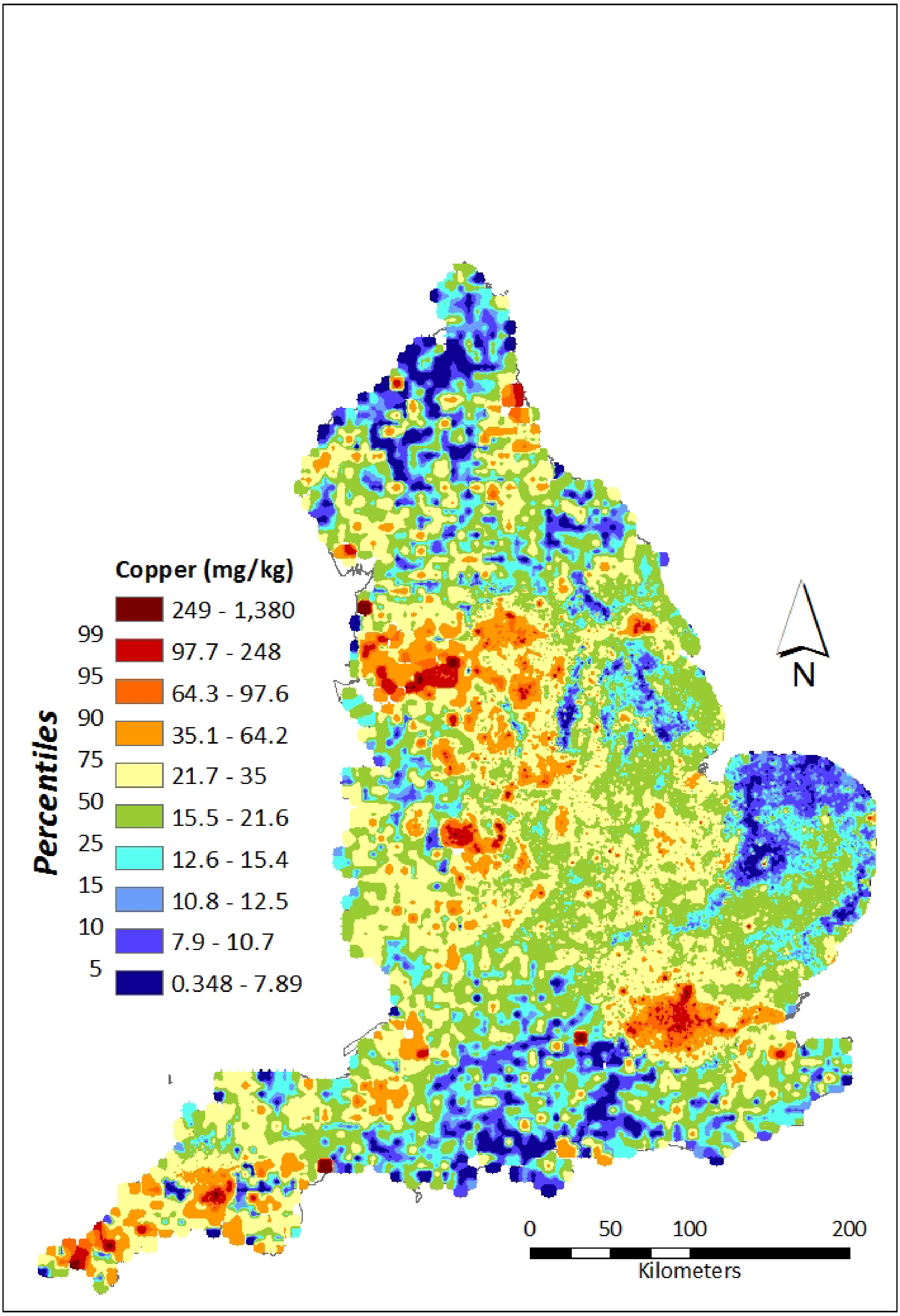

Figure 31: Interpolated map of topsoil Cu data. Colour thresholds are designed for highly skewed data.

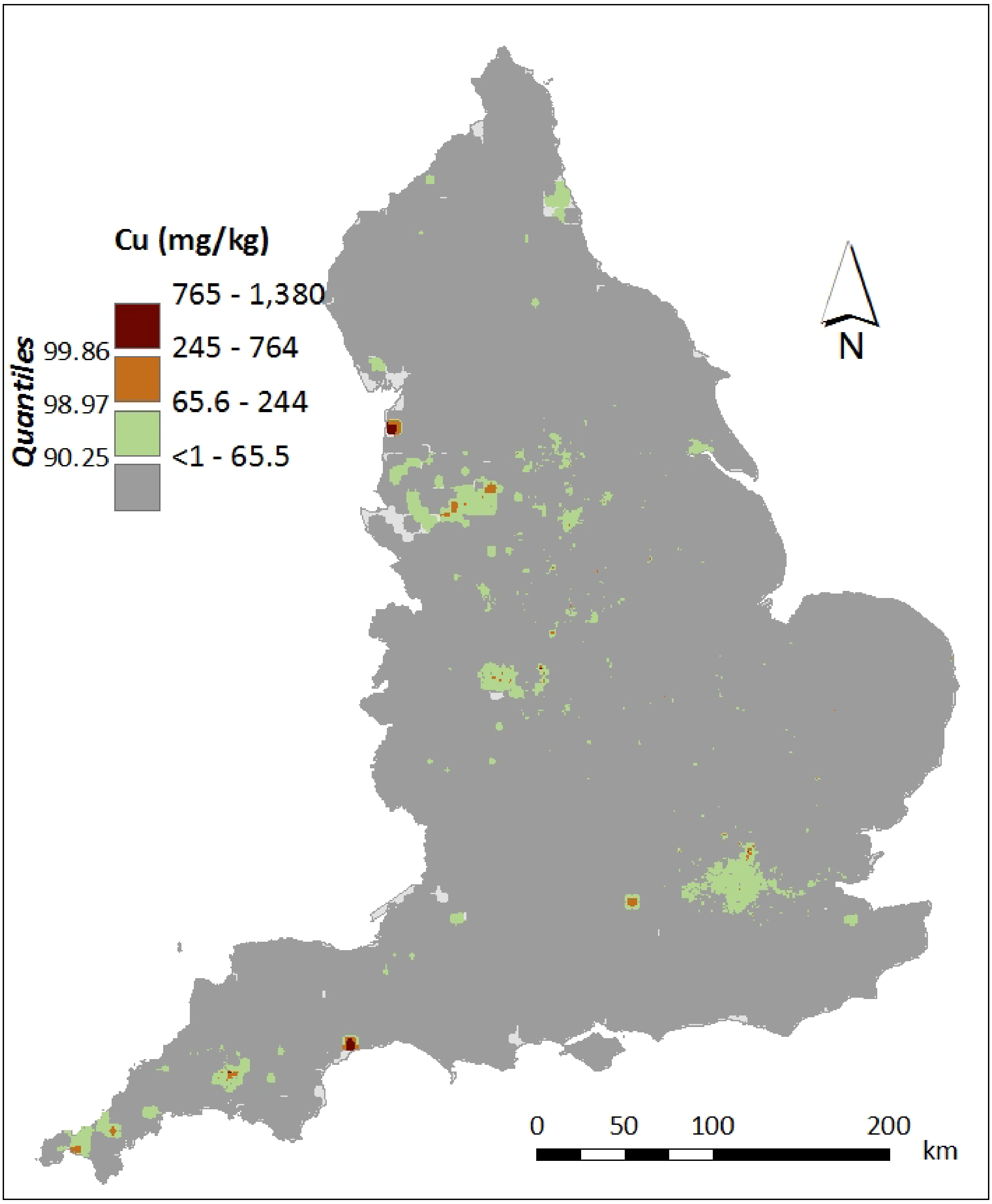

Figure 32: Interpolated map of topsoil Cu concentrations. Thresholds determined by using k-means cluster analysis.

3.2 DOMAIN SELECTION

The information shown below was used to compile the data for domains, with higher topsoil Cu concentrations than typical, in:

- non-ferrous metalliferous mineralisation and mining
- urban areas.

3.2.1 Non-ferrous metalliferous mineralisation and mining

It can be seen that southwest England is the area that has higher than typical topsoil Cu concentration (Figure 33 and Table 12), with a median concentration (47 mg/kg) that is greater than the 75th percentile of the remainder of the data. This is consistent with what is known about mineralisation in the south-west England orefield.

More surprisingly are orefield associated with Cu mineralisation/working which do not show up as having higher topsoil concentrations than nationally typical (Figure 33), such as the Lake District. This is presumed to result from the relatively low-density sampling (1 per 25 km^2) available for these areas, and it should be considered likely that ‘mineralisation’ domains may be identified by more localised sampling in these areas.

Coniston Cu mine, Lake District, was once the world’s largest Cu mine (British Geological Survey, 1992) and higher environmental Cu has previously been observed associated with the Shelve mineralisation district (British Geological Survey, 2000). Copper mineralisation has also been recorded in the North Pennines by other surveys, and high concentrations found in the G-BASE stream sediment survey (British Geological Survey, 1996). Areas like Alderley Edge, Cheshire, are associated with Cu mineralisation and historically worked, but too small to feature on this mapping – nor widely observed in deeper soil samples (British Geological Survey, 2000). Copper is not expected to be excessively high over the Mendips orefield, with a previous local survey median topsoil Cu concentration of 12 mg/kg (Davies and Ballinger, 1990).

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
1 SW England	153	91.6	3.0	30.4	47.4	77.6	2770	10
2 North Devon	4	22.0	14.1	15.4	19.9	30.5	33.9	1
3 Mendips	8	22.2	9.1	11.5	24.9	30.2	35.6	0
4 Shelve	3	22.9	17.5	17.5	24.3	26.8	26.8	-1
5 Peak District	224	36.8	3.7	20.0	29.8	43.1	272	4
6 Lake District	26	22.3	7.7	15.3	20.1	29.0	48.6	1
7 North Pennines	89	19.7	1.5	10.4	16.2	23.8	96.8	2
non	41625	35.9	<1	15.3	21.5	35.0	5330	26

Table 12: Summary statistics of topsoil Cu concentrations for metalliferous mineralisation and mining areas (concentrations in mg/kg).

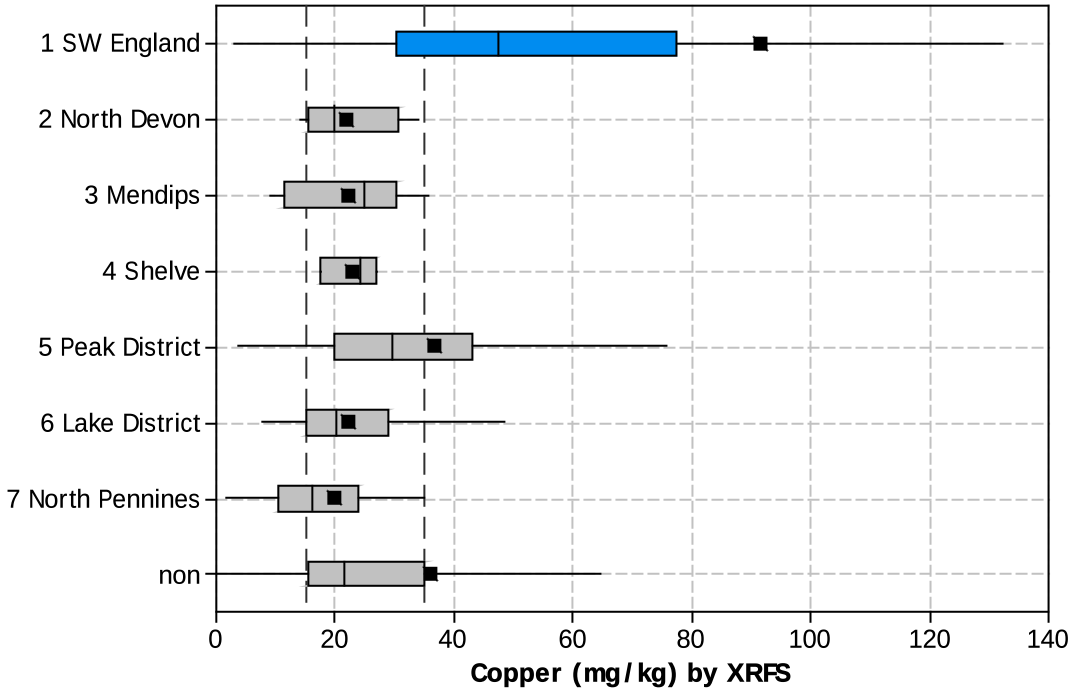

Figure 33: Boxplot of topsoil Cu concentrations in the mineralisation domains (Interquartile range of "non" samples not within a mineralisation area projected vertically as dashed lines).

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3.2.2 Urban areas

Urban areas can be seen to have higher concentration of Cu in Table 11, and these are summarised by spatial attribution to urban areas, or not, in Table 13 and Figure 34. These show a much higher concentration in the urban data set compared to all the other data.

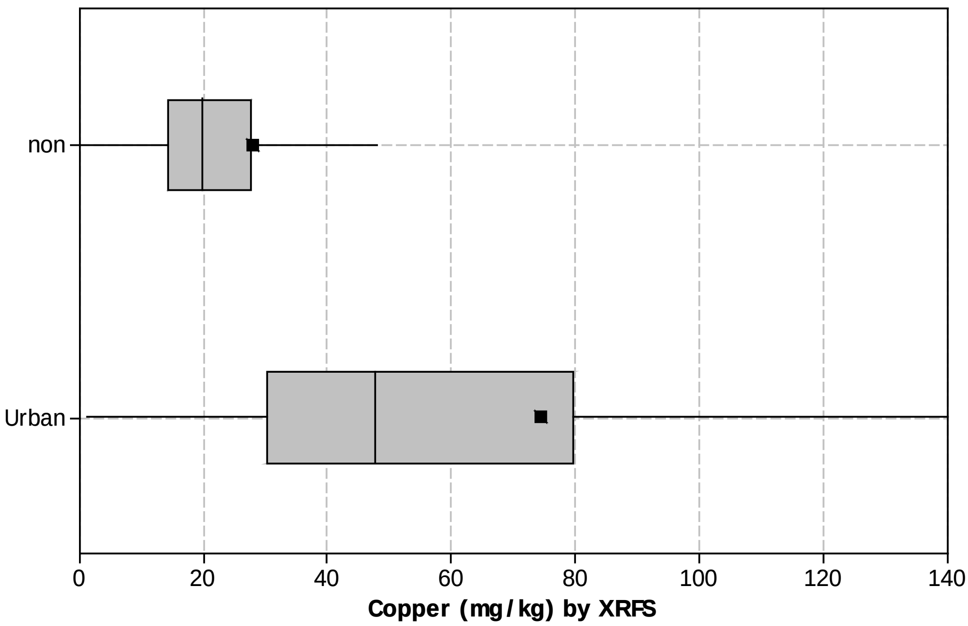

Figure 34: Boxplot of topsoil Cu concentrations over urban and non-urban areas.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Urban	7475	74.4	1.22	30.3	47.5	79.7	4580	14
Non-urban	34657	27.8	<1	14.3	19.8	27.7	5330	39

Table 13: Summary statistics for topsoil Cu concentrations (in mg/kg) over urban and non-urban areas.

3.3 DOMAIN DATA SUMMARY

It can be seen that the Mineralisation and Urban domains are higher in typical concentration than the residual sample data (Table 14, Figure 35), which form the Principal domain data set. Whilst the Mineralisation and Urban data sets have a very similar distribution (Figure 36) they have not been combined, as they are caused by different processes. The location of these domains is shown in Figure 37.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Mineralisation	153	92	3.0	30.4	47.4	77.6	2766	10
Urban	7475	74	1.2	30.3	47.5	79.7	4577	14
Principal	34504	27	<1	14.3	19.8	27.7	5326	41

Table 14: Summary statistics of topsoil Cu concentrations (in mg/kg) in the domains.

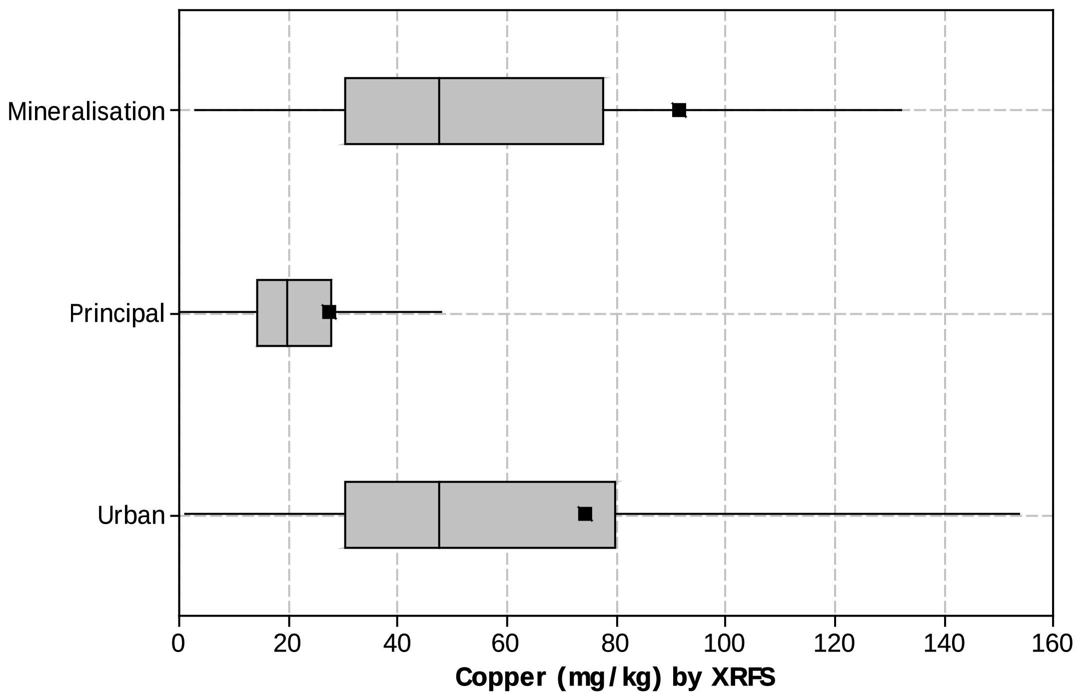

Figure 35: Boxplot of Cu data classified by domains

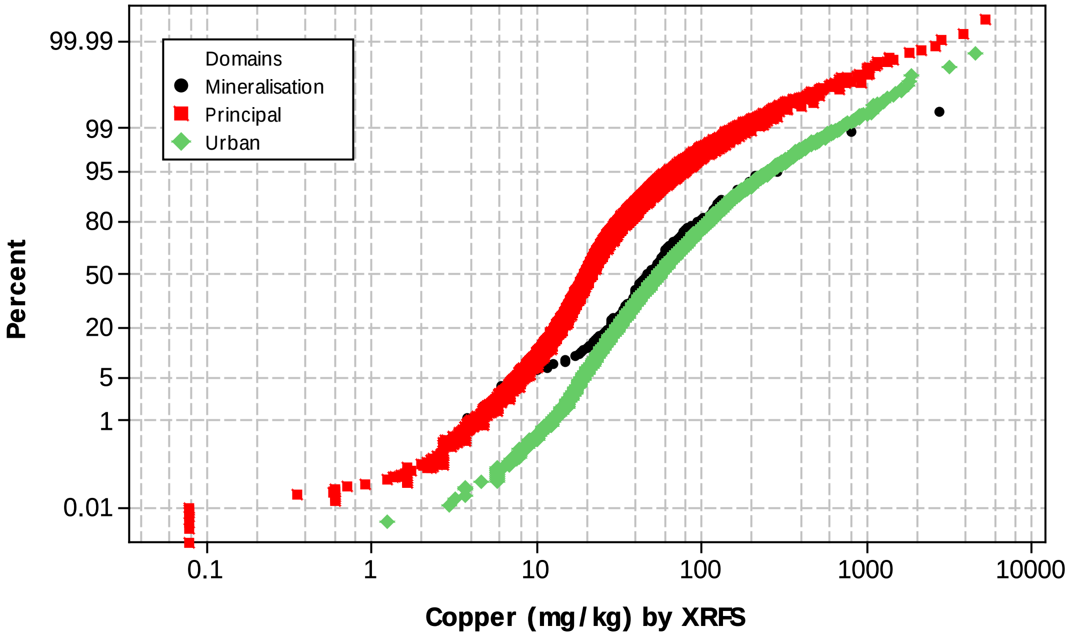

Figure 36: Probability plot of Cu topsoil data classified by domains

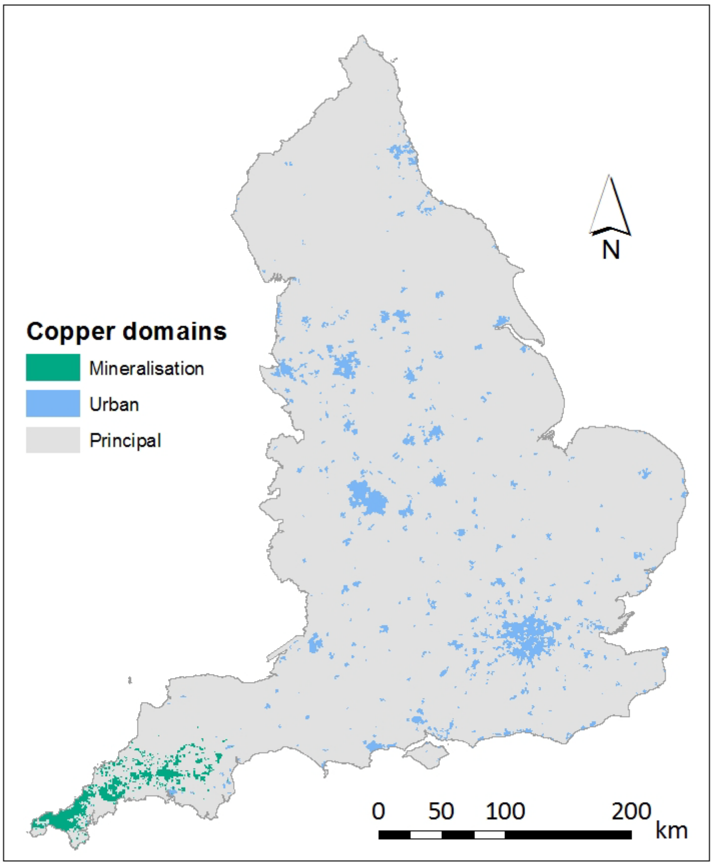

Figure 37: Map of Cu domains

3.4 COPPER NBC CALCULATION

3.4.1 Principal domain

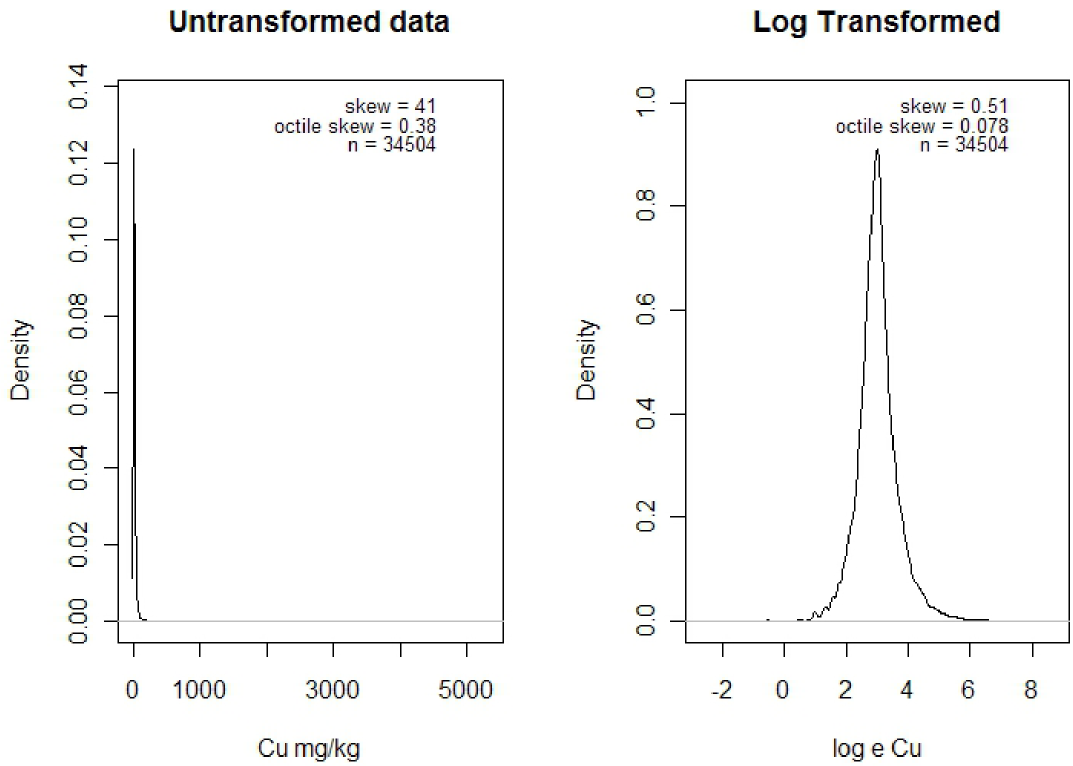

Figure 38: Density distributions for the raw data and the $\log_e$ transformed data for Cu in the Principal Domain (n = number of samples).

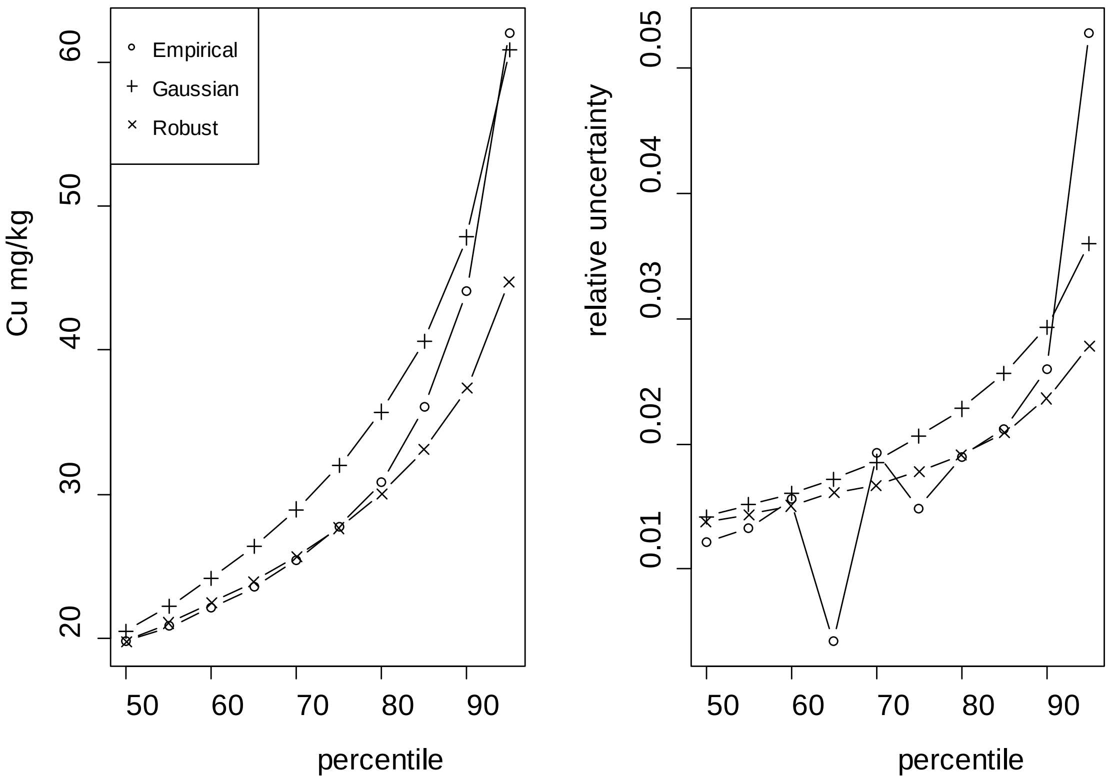

Figure 39: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Cu in the Principal Domain

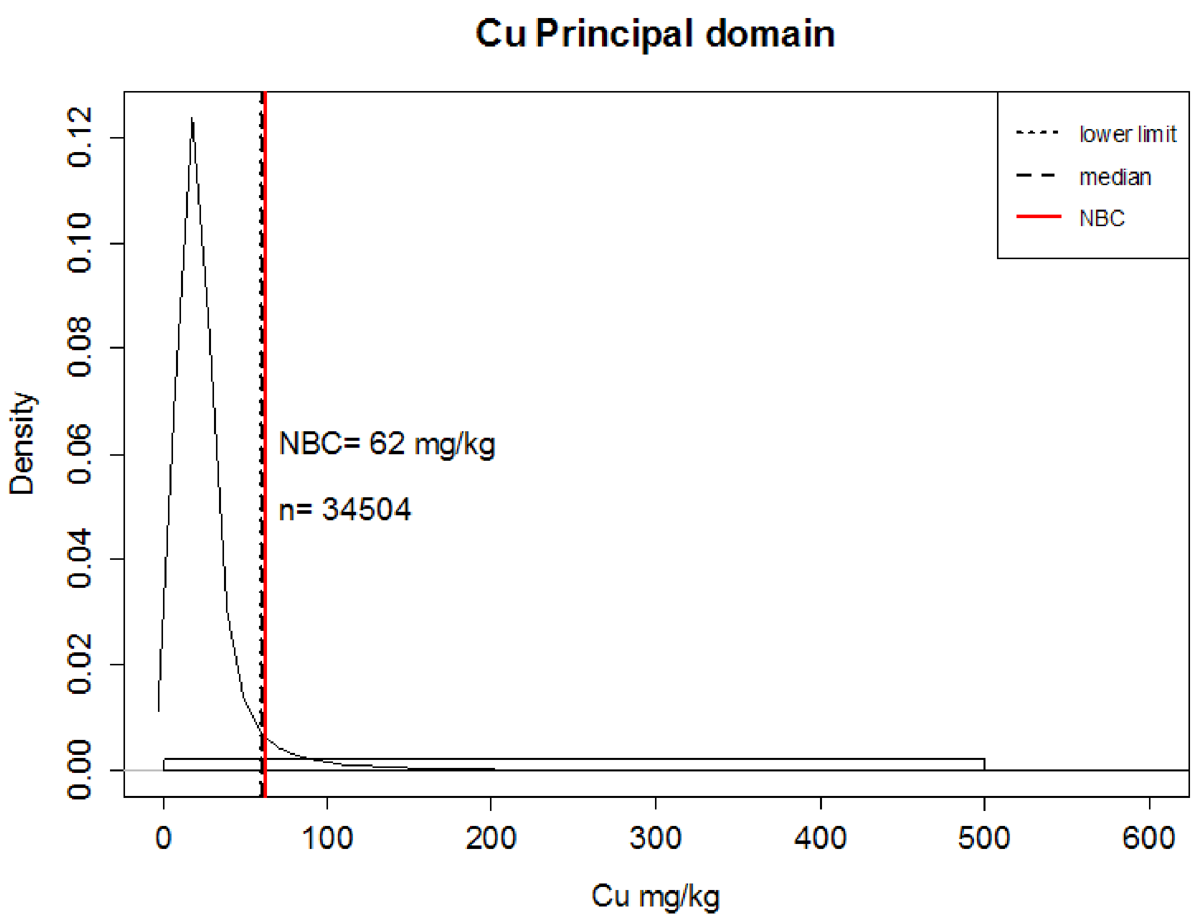

Figure 40: Summary density plot and histogram of the distribution for Cu in the Principal Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	19.6	19.8	19.9	20.3	20.4	20.6	19.6	19.8	19.9
55	20.7	20.8	21	22	22.2	22.4	20.9	21	21.2
60	21.9	22.1	22.3	24	24.2	24.4	22.2	22.4	22.5
65	23.5	23.5	23.6	26.2	26.4	26.6	23.7	23.9	24.1
70	25.1	25.4	25.6	28.7	28.9	29.2	25.3	25.7	25.7
75	27.5	27.7	27.9	31.7	32	32.3	27.2	27.6	27.7
80	30.7	30.8	31.3	35.3	35.7	36.2	29.5	30	30.1
85	35.4	36	36.2	40.2	40.7	41.2	32.5	33.1	33.2
90	43.3	44.2	44.5	47.2	47.8	48.6	36.6	37.4	37.4
95	60.7	62.1	64	59.9	60.9	62.1	43.6	44.7	44.9

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 15: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Cu in the Principal Domain (concentrations in mg/kg).

3.4.2 Urban domain

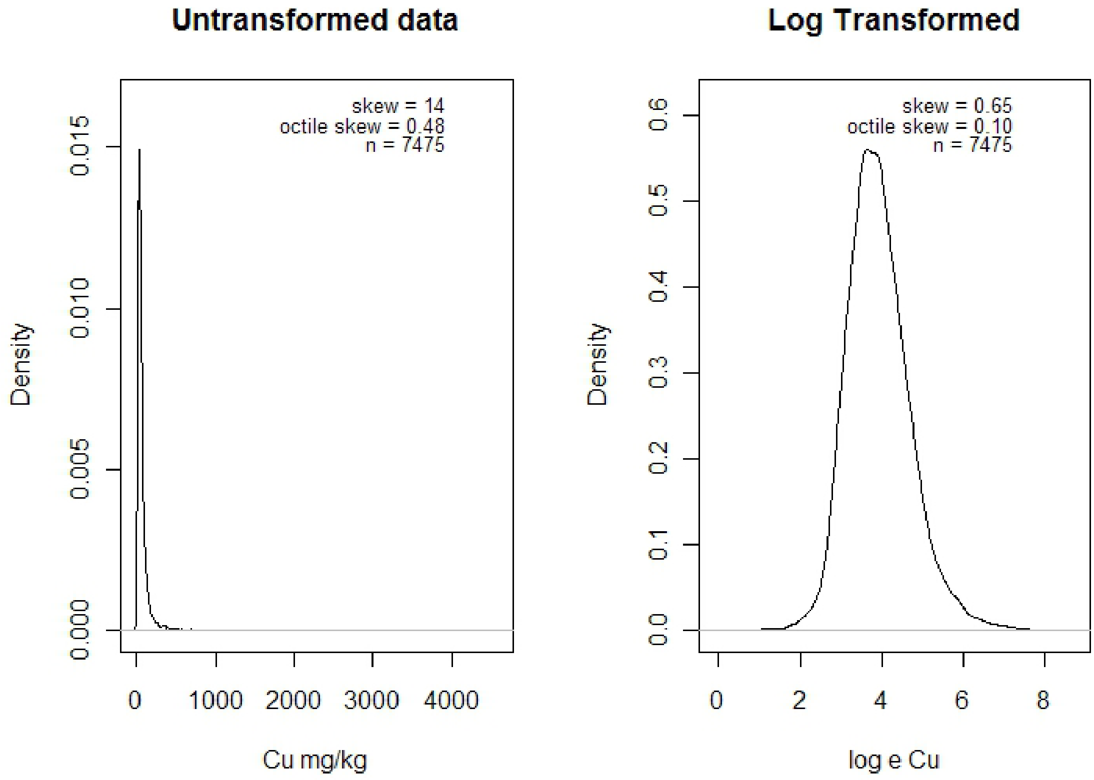

Figure 41: Summary density plot and histogram of the distribution for Cu in the Urban Domain showing an example NBC (n = number of samples).

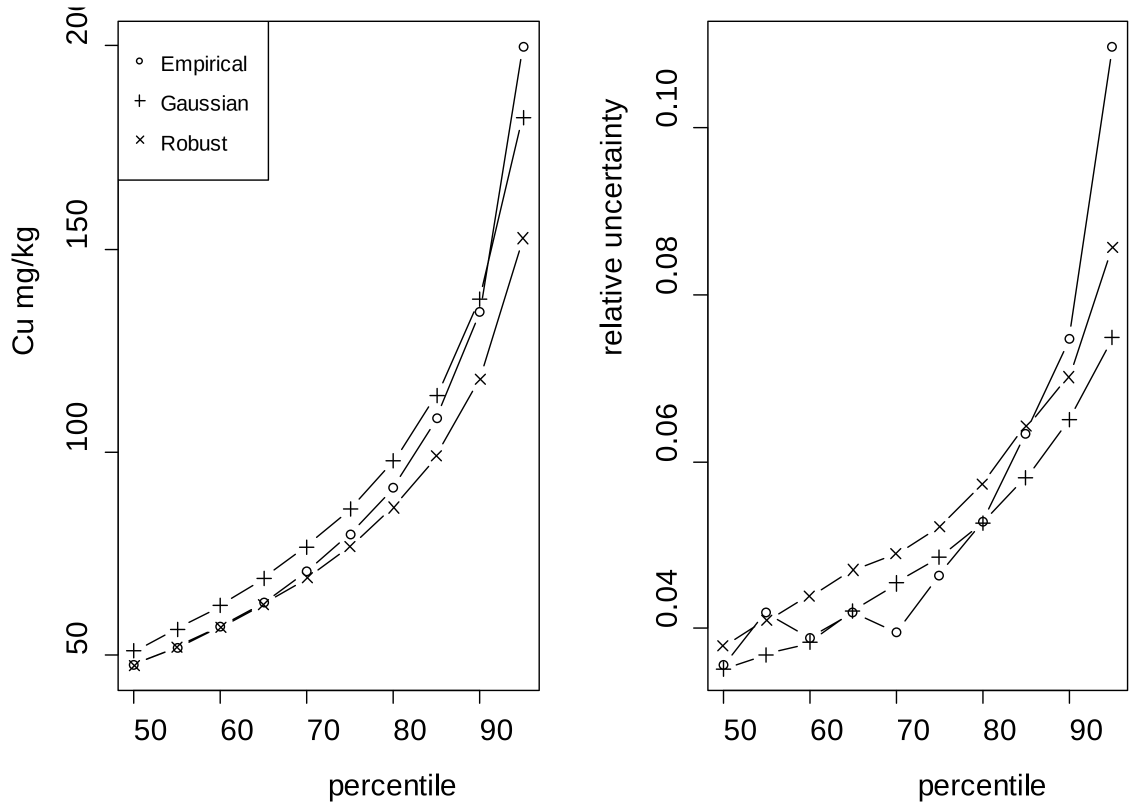

Figure 42: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Cu in the Urban Domain.

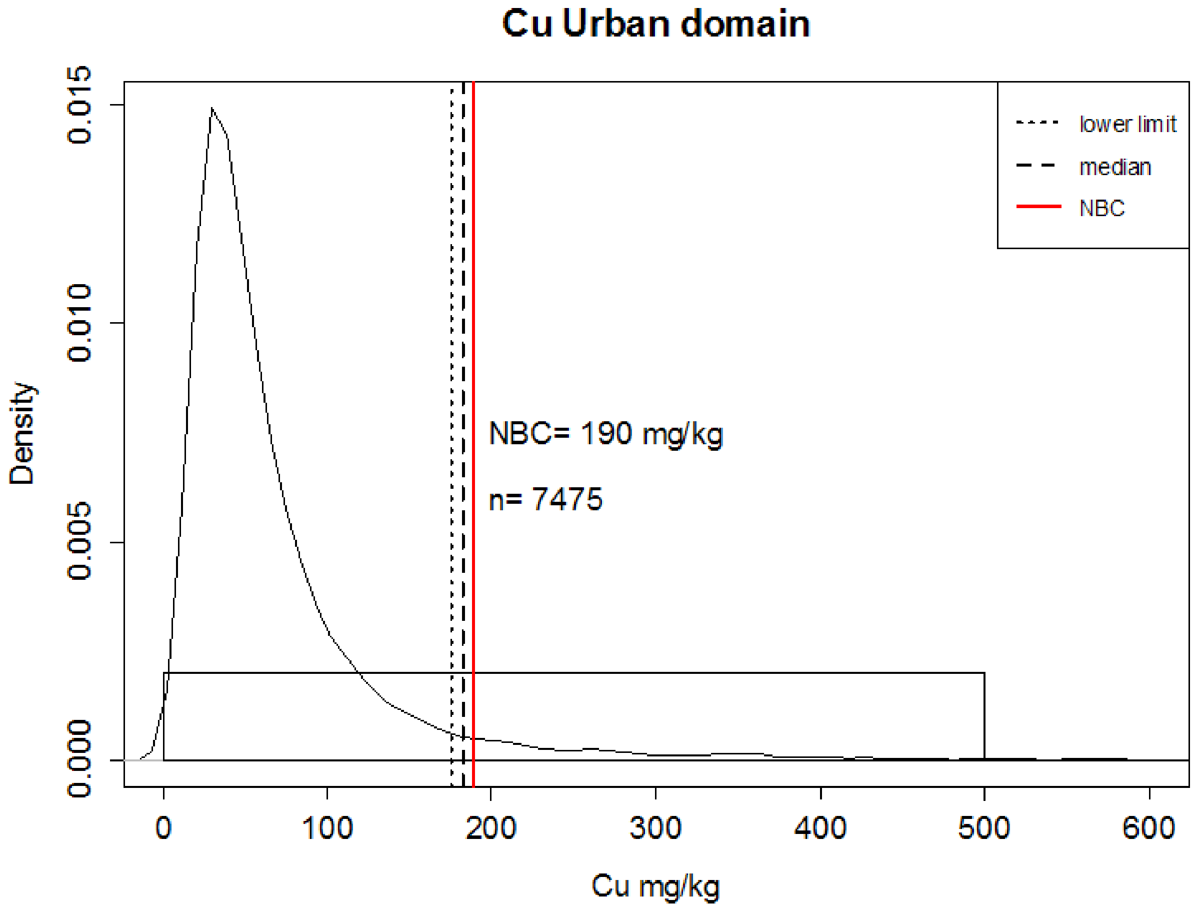

Figure 43: Summary density plot and histogram of the distribution for Cu in the Urban Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	46.8	47.5	48.5	**50.2**	**51**	**51.9**	46.7	47.5	48.5
55	50.8	51.8	52.9	**55.2**	**56.3**	**57.3**	51	51.9	53.2
60	56	57	58.2	**60.9**	**62.1**	**63.3**	55.8	56.8	58.3
65	61.5	62.7	64.2	**67.3**	**68.8**	**70.2**	61.2	62.4	64.1
70	69.1	70.4	71.9	**74.8**	**76.6**	**78.3**	67.5	68.9	70.9
75	77.7	79.7	81.4	**83.9**	**86.1**	**88.1**	75.1	76.7	79.1
80	88.9	91.1	93.7	**95.3**	**97.9**	**100**	84.3	86.3	89.2
85	105	108	112	**111**	**114**	**117**	96	99	103
90	131	135	141	**133**	**138**	**142**	115	118	123
95	189	200	211	**176**	**182**	**189**	147	153	160

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 16: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Cu in the Urban Domain (concentrations in mg/kg).

3.4.3 Mineralisation domain

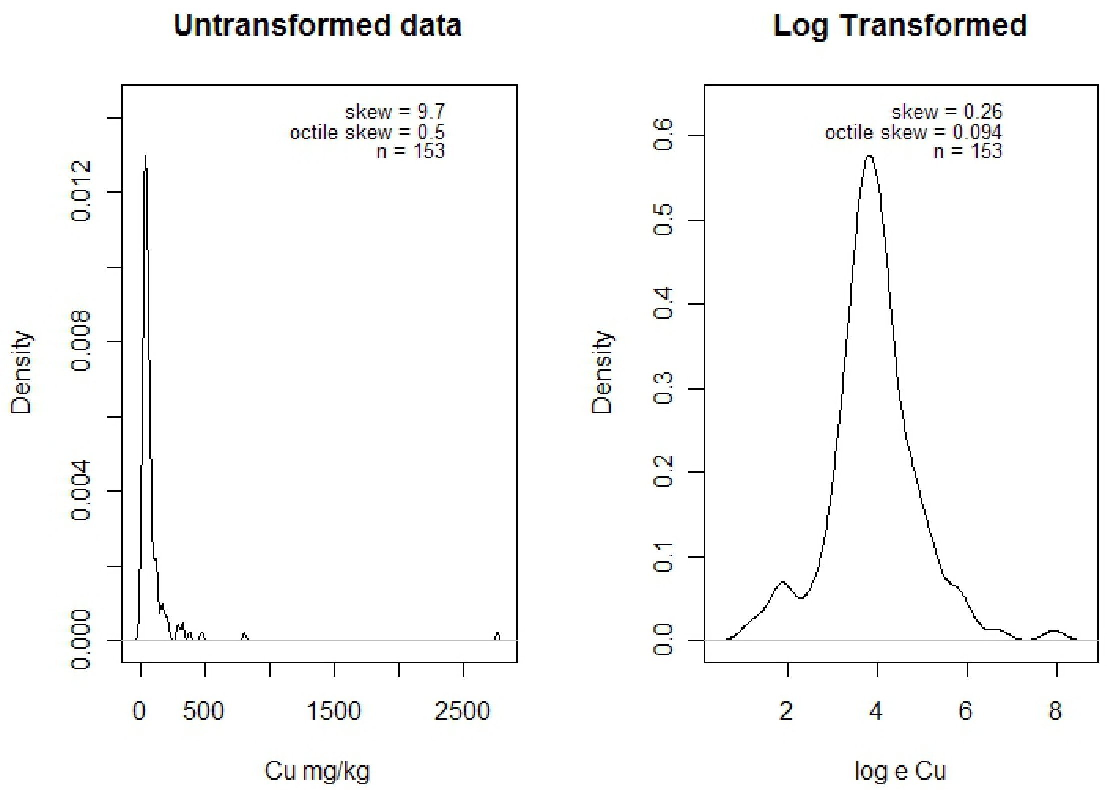

Figure 44: Density distributions for the raw data and the $\log_e$ transformed data for Cu in the Mineralisation Domain (n = number of samples).

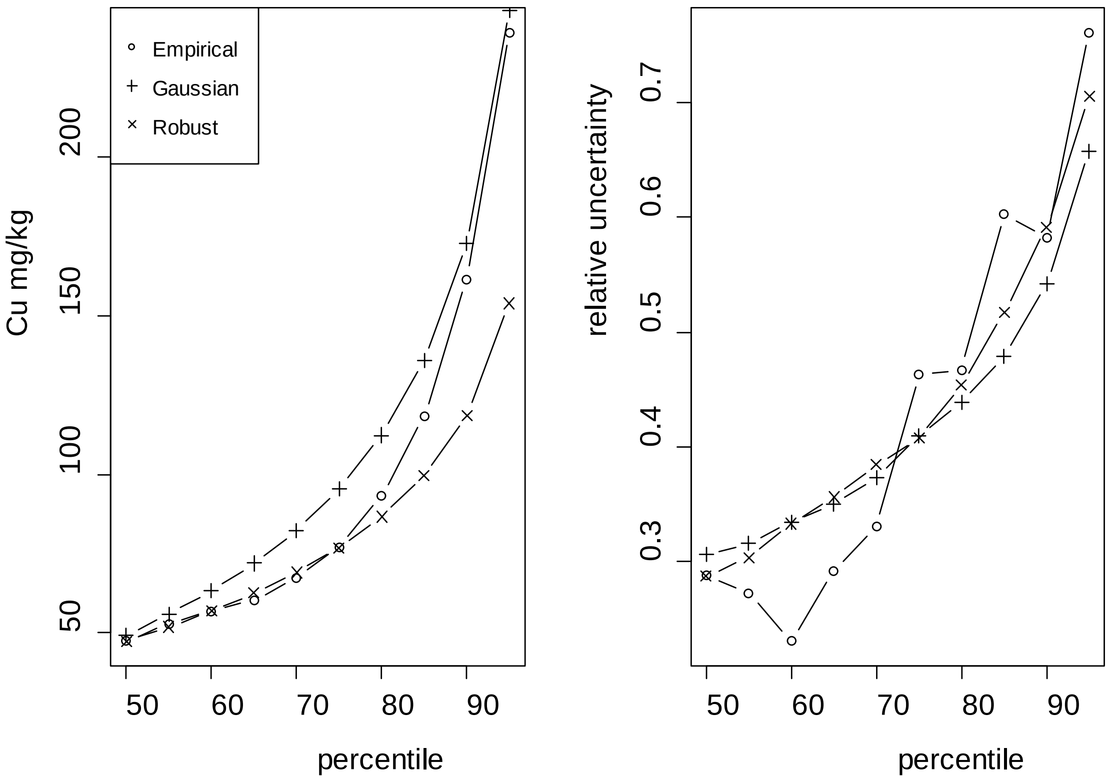

Figure 45: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Cu in the Mineralisation Domain.

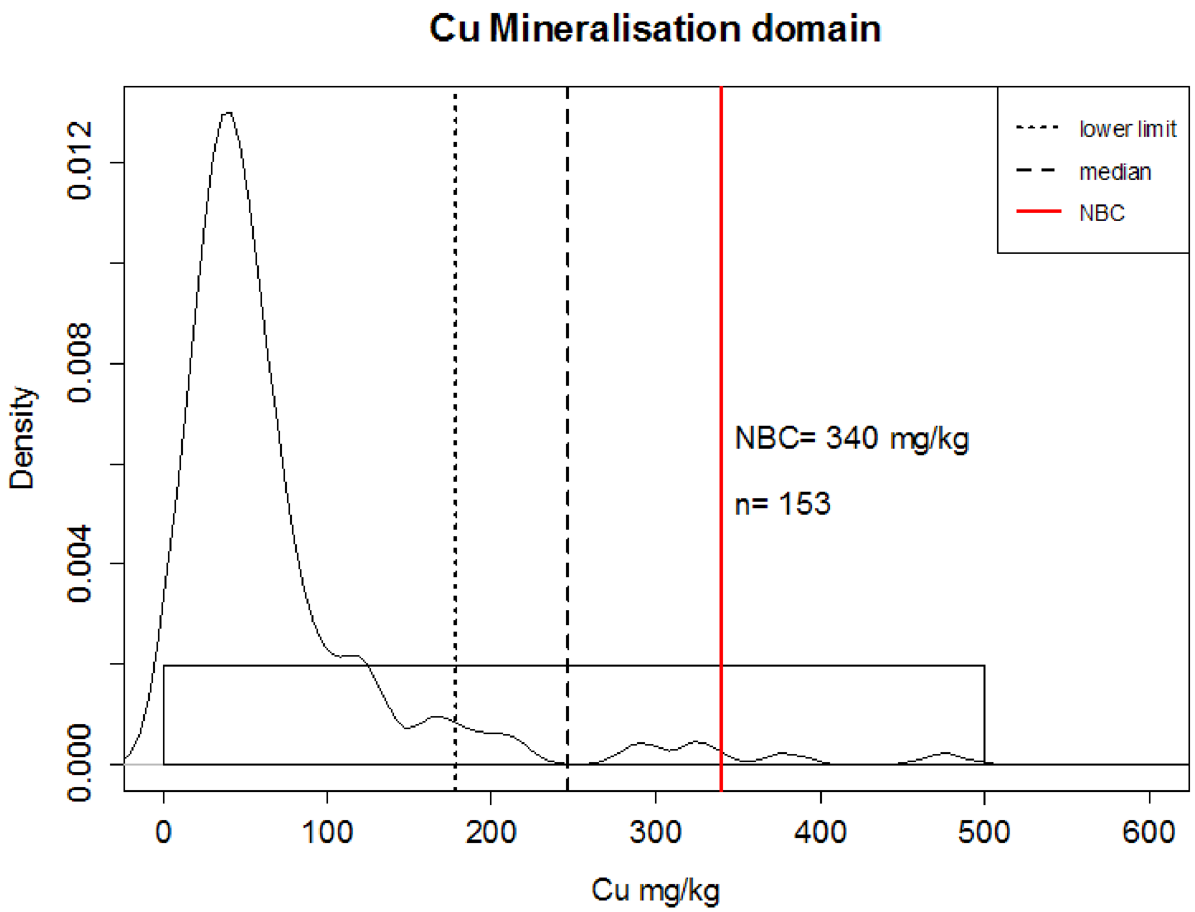

Figure 46: Summary density plot and histogram of the distribution for Cu in the Mineralisation Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	41.3	47.4	55	**42.3**	**49.4**	**57.4**	41.3	47.4	55
55	44.9	52.8	59.3	**47.6**	**55.8**	**65.2**	44.8	51.9	60.5
60	49.7	56.8	62.8	**53.6**	**63.2**	**74.7**	48.3	56.8	67.2
65	54.9	60.2	72.5	**60.3**	**71.9**	**85.5**	52.2	62.5	74.4
70	58.9	67.3	81.1	**68.3**	**82.4**	**99.1**	56.7	69	83.3
75	63.3	77.1	99.1	**77.8**	**95.4**	**117**	61.9	76.9	93.2
80	75.5	93.2	119	**90.5**	**112**	**140**	68.2	86.6	108
85	93	118	164	**107**	**136**	**172**	76	100	128
90	115	161	209	**131**	**173**	**225**	88	119	158
95	164	239	347	**178**	**246**	**340**	108	154	217

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 17: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Cu in the Mineralisation Domain (concentrations in mg/kg).

4 Mercury (Hg)

4.1 EXPLORATORY DATA ANALYSIS

The G-BASE project has soil Hg results for only two urban areas (Stoke and London) and so data has been gathered from a variety of sources. These are summarised in Table 18 - Project data sources are reviewed in more detail in Ander *et al.* (2011) and sample locations are shown in Figure 47. It can be seen that detection limits vary by over ten times (Table 18), and that the different data sources have different statistical properties, with considerable variation in reported central tendency and range values (Table 19).

There is an inherent problem in that, other than the Soil Herbage Survey (SHS) rural data, these sites have targeted specific geographical areas and/or land uses. It is therefore very difficult to establish the extent to which systematic bias arising from sample collection, preparation, digestion and analytical methods contribute to the apparent difference between these data sources.

Although Hg was determined on both phases of NSI original samples, the method had a relatively high detection limit (0.1 mg/kg), with over 50% of the data falling below that detection limit, and the remainder of the data being reported to only one significant figure; these data were thus not used.

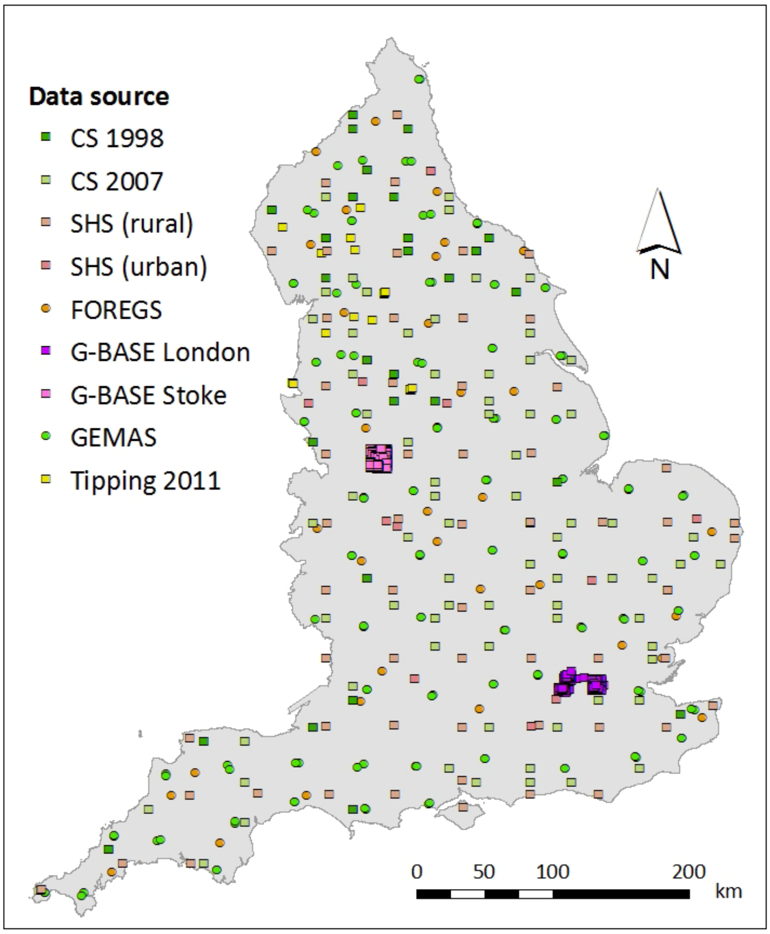

Figure 47: Location of samples, classified by originating project, used to establish Hg normal background concentrations.

Data source	Depth, support & prep	Digestion step	Instrument & Laboratory	Detection limit (mg/kg)
CS 1998	15 cm deep (× 8 cm diameter) core. Single core. Drying temperature/ sieving not recorded.	not specified.	not specified.	not specified.
CS 2007	15 cm deep. 15 cm deep (× 8 cm diameter) core. Single core. Air dried. Sieving not recorded.	*Aqua-regia* microwave digestion.	ICP-MS. Laboratory not reported.	0.067
SHS	5 cm deep. 3 cores per sample, support not specified but 3 samples collected within a 20×20 m square. Stored 4°C. Not specified whether sieved/dried.	*Aqua-regia*.	Cold-vapour atomic absorption spectrometry (CV-AAS). EA laboratory.	0.07
FOREGS	0-25 cm. 3-5 sample composite. Dried at 40°C, sieved <2 mm.	n/a. Heated to 850°C to drive off Hg.	Hg analyser. Hungarian Geological Survey laboratory.	0.0001
G-BASE London	15 cm deep. 5 augers in 20×20 m area. 30°C dried. <2 mm sieved and ground in agate.	n/a. Heated to 850°C to drive off Hg.	Hg analyser. Hungarian Geological Survey laboratory.	0.0001
G-BASE Stoke	15cm deep. 9 composite on 2×2m grid. Air-dried. <2 mm sieved and ground in agate.	*Aqua-regia*.	CV-AAS. Bondar Clegg laboratory, Canada.	0.01
GEMAS	0-20 cm on arable; 0-10 cm permanent pasture. Five spade-dug pits in 10 × 10 m, ~3.5kg sample collected. Air-dried & <2 mm sieved.	n/a. Heated to 850°C to drive off Hg.	Hg analyser. Hungarian Geological Survey laboratory.	0.0001
Tipping 2011	Generally 10 cm; range 9-19 cm. Single pit dug and sampled. Air-dry. <2 mm sieved.	*Aqua-regia*, microwave digestion.	ICP-MS.	0.07

Table 18: Summary of data used to establish normal background concentration exploratory data analysis.

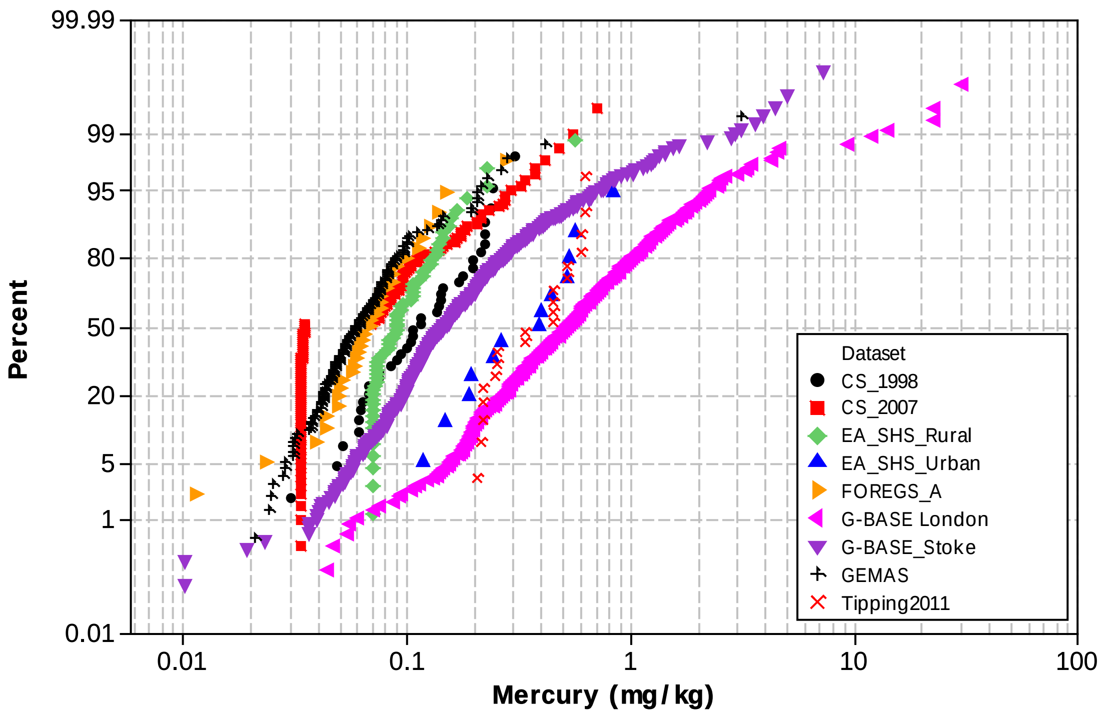

Figure 48: Probability plot of Hg data by source data set.

Data source	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
CS 1998	36	0.13	0.03	0.07	0.11	0.19	0.30	1
CS 2007	175	0.09	<0.07	<0.07	<0.07	0.10	0.70	3
SHS (rural)	61	0.11	0.07	0.07	0.09	0.12	0.56	5
SHS (urban)	13	0.37	0.12	0.19	0.39	0.52	0.84	1
FOREGS	33	0.077	0.011	0.050	0.067	0.087	0.274	3
G-BASE London	440	0.959	0.045	0.290	0.522	0.900	30.8	9
G-BASE Stoke	737	0.25	0.01	0.10	0.14	0.23	7.22	8
GEMAS	131	0.098	0.021	0.044	0.059	0.081	3.12	11
Tipping 2011	20	0.39	0.21	0.23	0.39	0.52	0.63	0

Summary statistics are presented with significant figures proportional to the detection limit sensitivity (Table 18).

Table 19: Summary statistics of Hg results by source data set (in mg/kg)

4.2 DOMAIN SELECTION

The data shown above suggests urbanisation as an important likely domain for Hg, whilst knowledge of orefield mineralisation and pre-existing studies have suggested that these may have a higher concentrations of Hg.

Coal-burning is considered major atmospheric source of Hg in the EU, and other industrial/domestic sources exist (Rodrigues *et al.*, 2006). These authors show high short-distance variation in concentrations (greater than ten times within 50 m) and also that concentrations that vary greatly between two parks in Glasgow. This is significant in the context of the other urban area parks in Europe which were sampled.

4.2.1 Urbanisation

Results of analysis show that topsoil Hg concentrations have a positive relationship with the extent of urbanisation (Figure 49 and Figure 50).

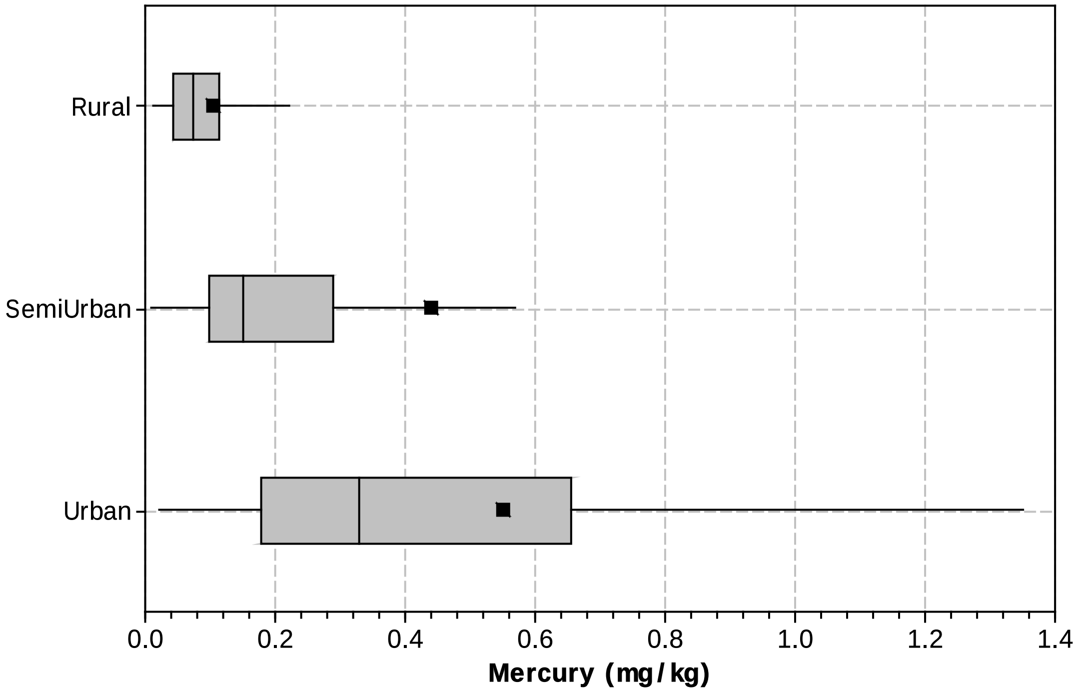

Figure 49: Boxplot of topsoil Hg data characterised by extent of urbanisation (GLUD data)

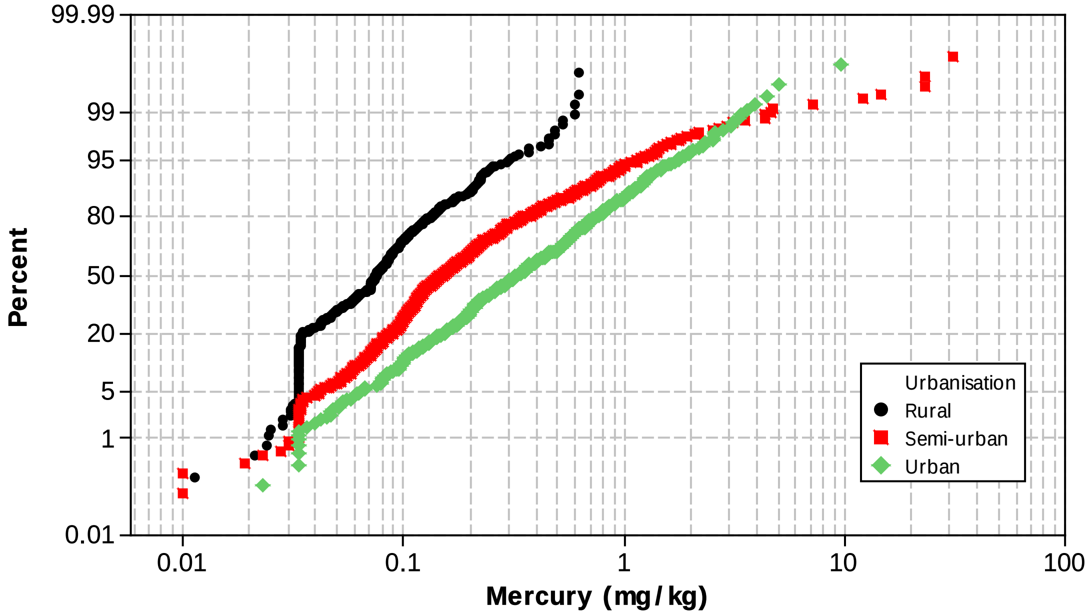

Figure 50: Probability plot of topsoil Hg categorised by extent of urbanisation

4.2.2 Non-ferrous metalliferous mineralisation and mining

A positive relationship between topsoil Hg concentrations and metalliferous mineralisation may be expected from an understanding of orefield mineral chemistry and from previous work (Davies, 1976; Thornton, 1991), although Davies does note that the relative increase of Hg concentration he observed (maximum of nineteen times the background) is low in relation the relative increase seen in ore-forming elements (*e.g.* Pb, As, Cu) or major accessory elements (*e.g.* Cd). It is suggested that a combination of very few analyses available for Hg over the mapped mineralisation areas, combined with this likely relatively low increase gives rise to the lack of discrimination seen in the data assembled for this Project (Table 20, Figure 51).

Therefore, there is no evidence within our data that mining areas form a separate domain. This, however, may be due to the lack of data, and further domains may be defined with more comprehensive coverage of sampling sites.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
1 SW England	13	0.08	<0.07	<0.07	0.07	0.1	0.24	2
2 North Devon	0							
3 Mendips	0							
4 Shelve	2	<0.07	<0.07	*	<0.07	*	<0.07	*
5 Peak District	0							
6 Lake District	1	0.21	<0.07	*	0.21	*	0.21	*
7 North Pennines	12	0.18	<0.07	0.08	0.14	0.2	0.45	1
non	1619	0.41	<0.07	0.09	0.16	0.4	30.8	15

Table 20: Summary statistics of topsoil Hg concentrations (in mg/kg) classified by metalliferous mineralisation/mining areas

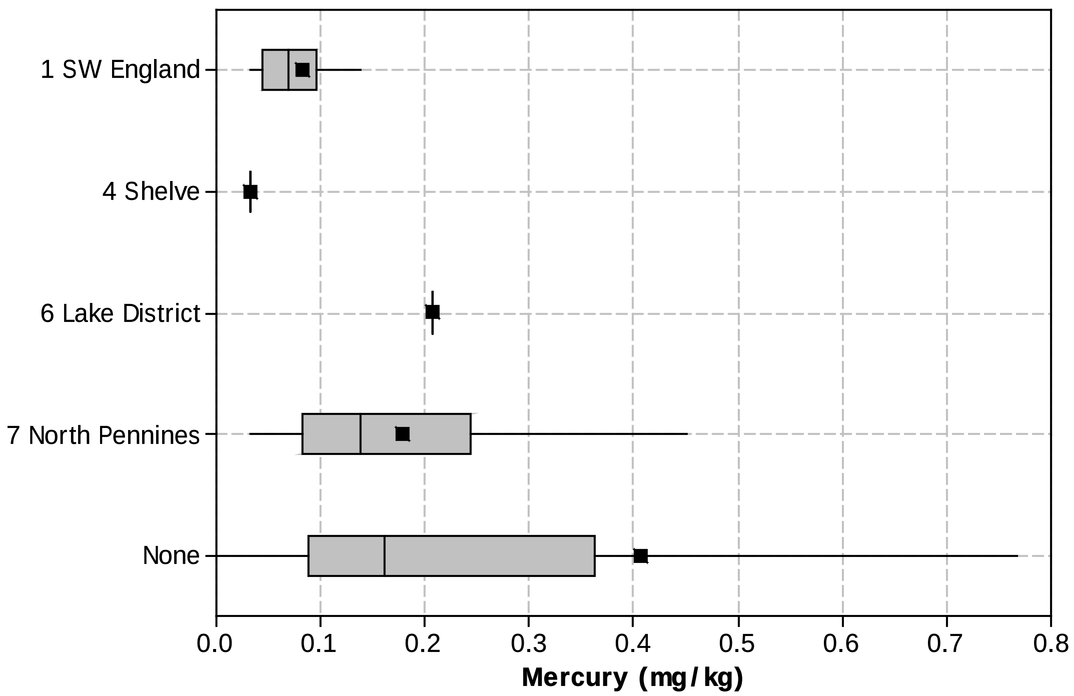

Figure 51: Boxplot of topsoil Hg data categorised by metalliferous mineralisation/mining areas

4.3 DOMAIN DATA SUMMARY

It can be seen that the Urban Domain has a higher typical concentration than the residual sample data (Figure 52, Figure 53 and Table 21), which form the Principal Domain data set. The location of these domains is shown in Figure 54.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Urban	512	0.55	<0.07	0.18	0.33	0.65	9.6	5
Principal	1134	0.34	<0.07	0.07	0.12	0.23	31	15

Table 21: Summary statistics of topsoil Hg concentrations (in mg/kg) in the domains.

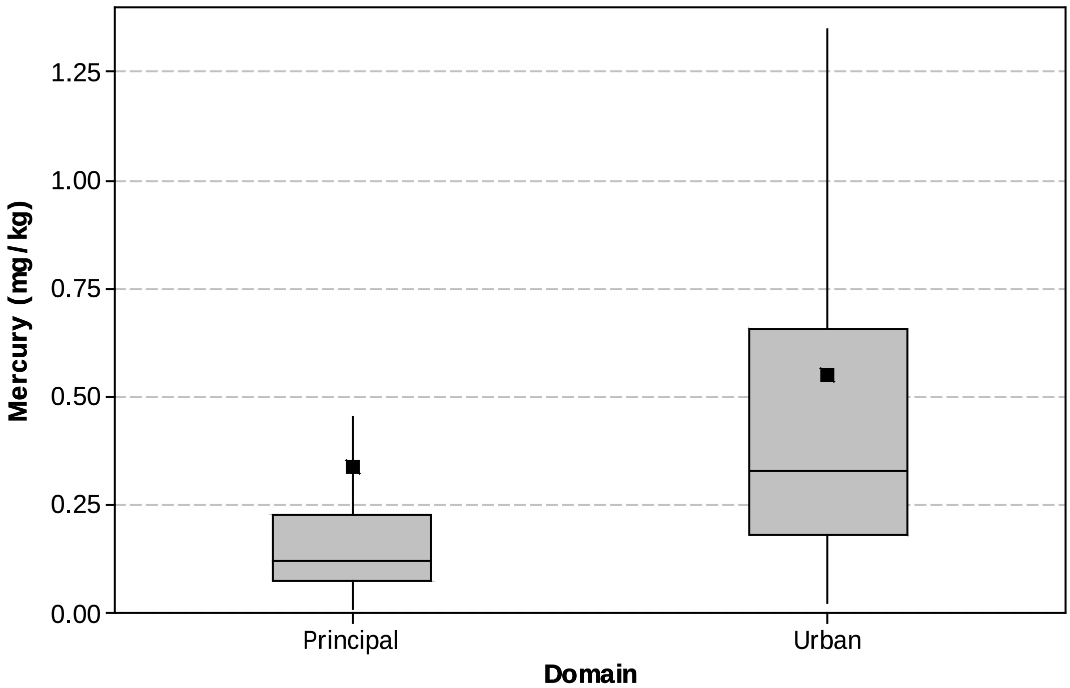

Figure 52: Boxplot of Hg topsoil data classified by domains.

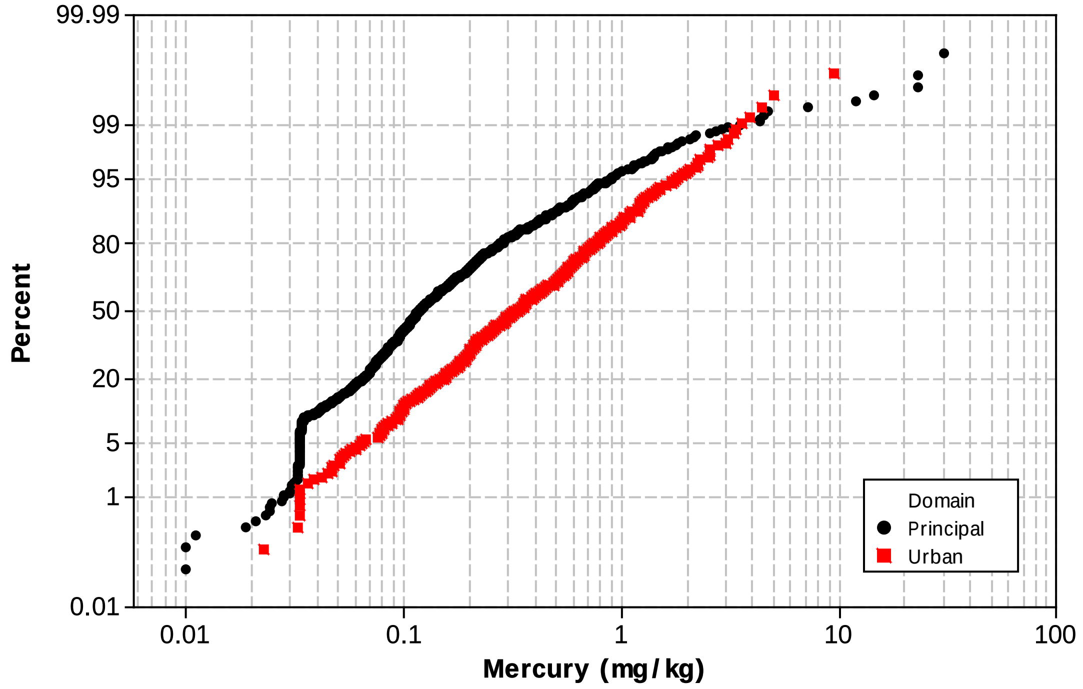

Figure 53: Probability plot of Hg topsoil data classified by domains.

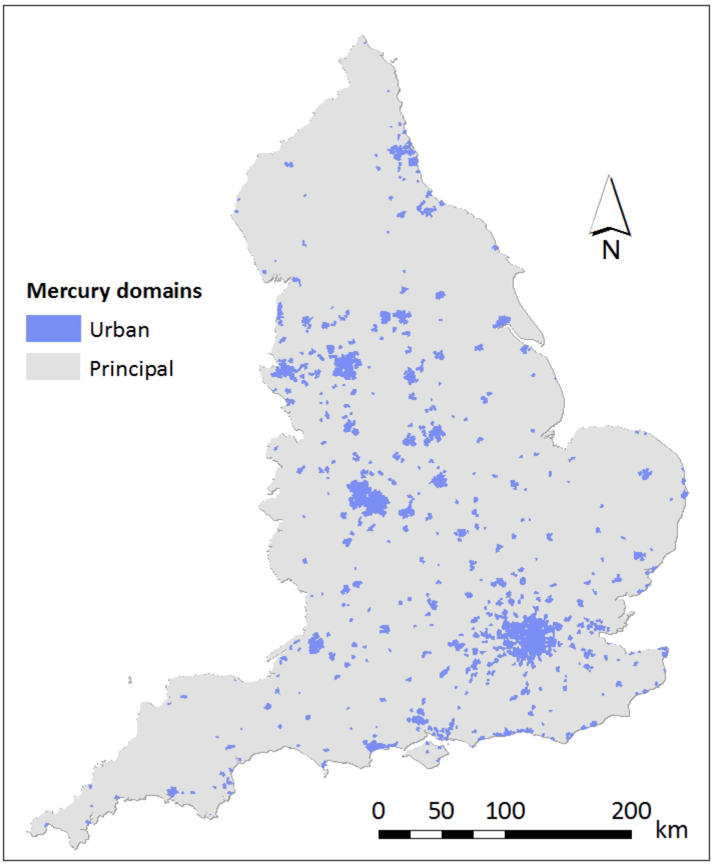

Figure 54: Map of Hg domains.

4.4 MERCURY NBC CALCULATION

4.4.1 Principal domain

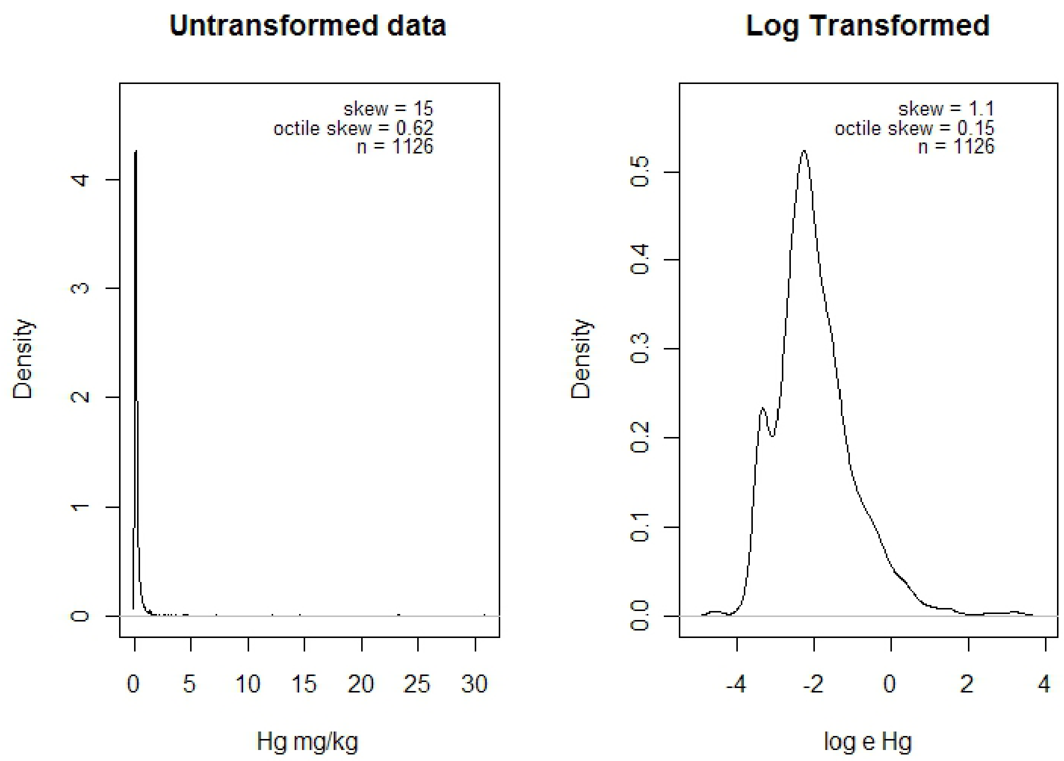

Figure 55: Density distributions for the raw data and the log$_e$ transformed data for Hg in the Principal Domain (n = number of samples).

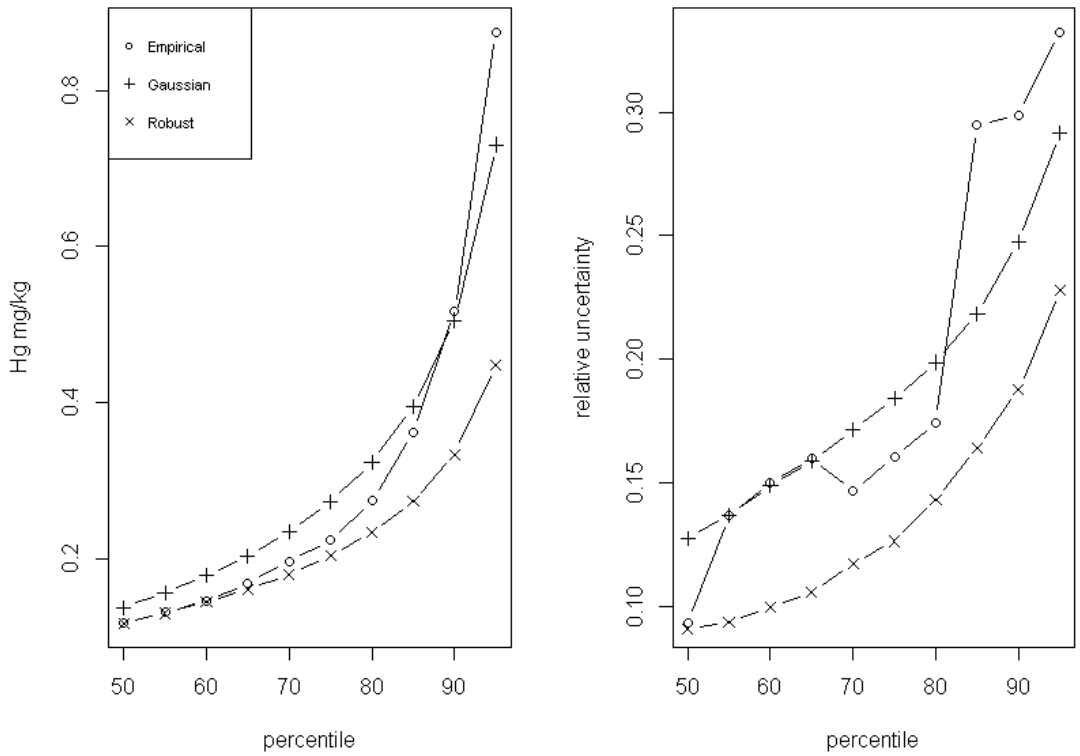

Figure 56: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Hg in the Principal Domain.

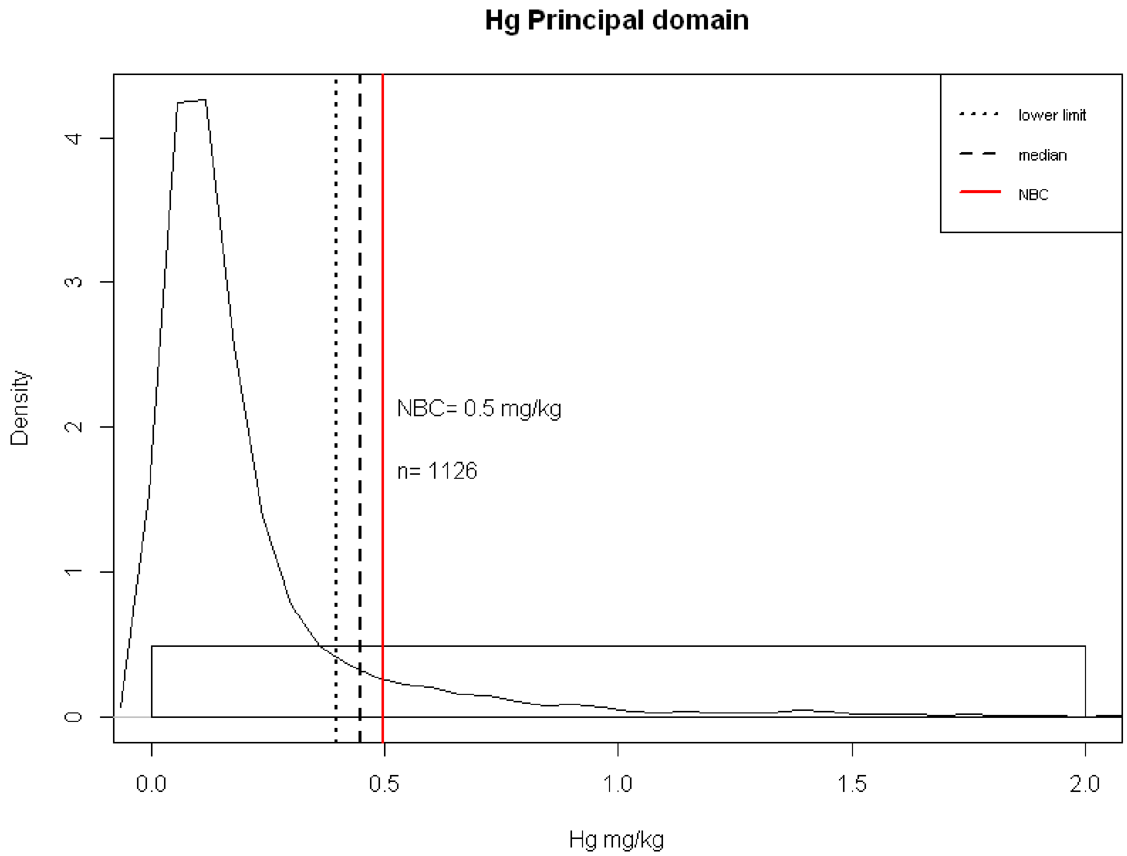

Figure 57: Summary density plot and histogram of the distribution for Hg in the Principal Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	0.11	0.12	0.12	0.13	0.14	0.15	**0.11**	**0.12**	**0.12**
55	0.12	0.13	0.14	0.15	0.16	0.17	**0.12**	**0.13**	**0.14**
60	0.14	0.15	0.16	0.16	0.18	0.19	**0.14**	**0.14**	**0.15**
65	0.16	0.17	0.18	0.19	0.20	0.22	**0.15**	**0.16**	**0.17**
70	0.18	0.20	0.21	0.21	0.23	0.25	**0.17**	**0.18**	**0.19**
75	0.21	0.22	0.25	0.25	0.27	0.30	**0.19**	**0.20**	**0.22**
80	0.25	0.28	0.30	0.29	0.32	0.36	**0.22**	**0.23**	**0.25**
85	0.31	0.36	0.41	0.35	0.39	0.44	**0.25**	**0.27**	**0.29**
90	0.45	0.52	0.60	0.44	0.51	0.57	**0.30**	**0.33**	**0.36**
95	0.72	0.87	1.01	0.63	0.73	0.84	**0.40**	**0.45**	**0.50**

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 22: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Hg in the Principal Domain (concentrations in mg/kg).

4.4.2 Urban domain

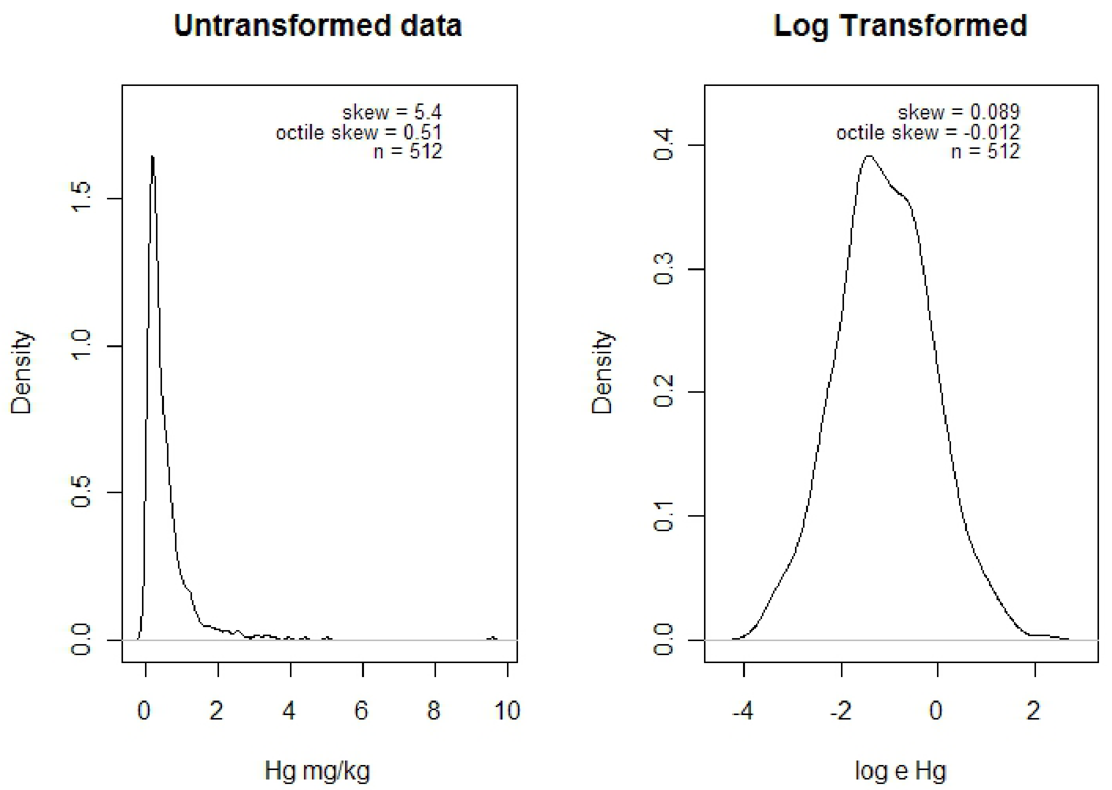

Figure 58: Density distributions for the raw data and the $\log_e$ transformed data for Hg in the Urban Domain (n = number of samples).

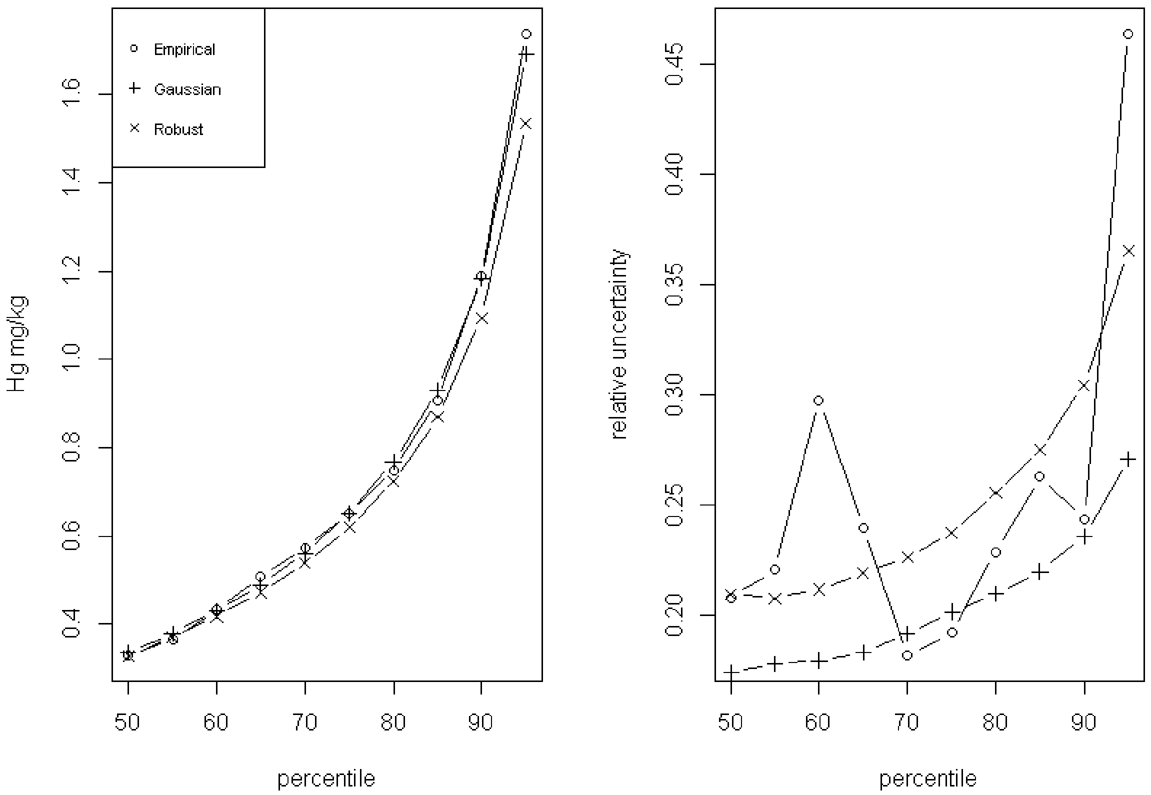

Figure 59: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Hg in the Urban Domain.

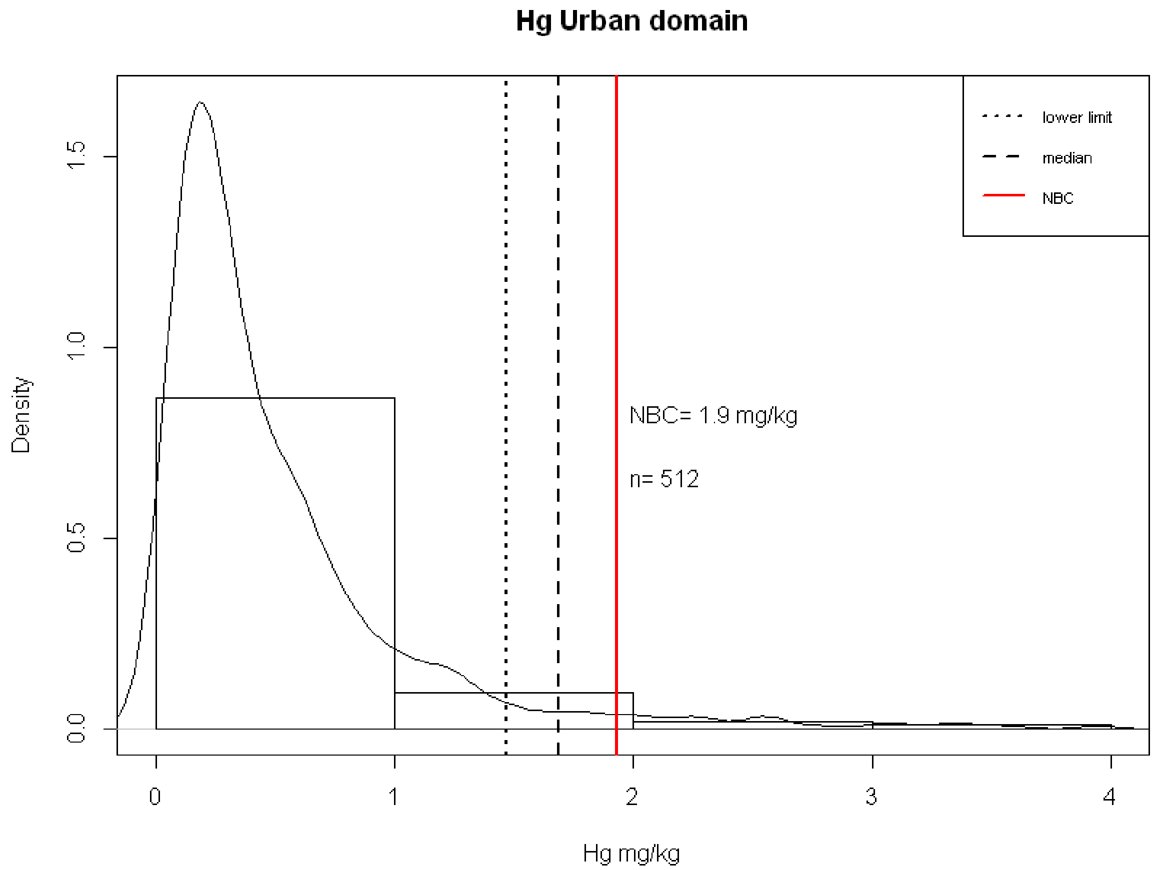

Figure 60: Summary density plot and histogram of the distribution for Hg in the Urban Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	0.29	0.33	0.36	**0.31**	**0.34**	**0.37**	0.29	0.33	0.36
55	0.33	0.37	0.41	**0.35**	**0.38**	**0.41**	0.33	0.37	0.41
60	0.37	0.43	0.49	**0.39**	**0.43**	**0.47**	0.37	0.42	0.46
65	0.44	0.51	0.56	**0.45**	**0.49**	**0.54**	0.42	0.47	0.53
70	0.51	0.57	0.62	**0.51**	**0.56**	**0.62**	0.48	0.54	0.60
75	0.58	0.65	0.70	**0.59**	**0.65**	**0.72**	0.56	0.62	0.70
80	0.67	0.75	0.84	**0.69**	**0.77**	**0.85**	0.65	0.72	0.84
85	0.79	0.91	1.0	**0.83**	**0.93**	**1.0**	0.78	0.87	1.0
90	1.0	1.2	1.3	**1.1**	**1.2**	**1.3**	0.98	1.1	1.3
95	1.3	1.7	2.2	**1.5**	**1.7**	**1.9**	1.3	1.5	1.9

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 23: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Hg in the Urban Domain (concentrations in mg/kg).

5 Nickel (Ni)

5.1 EXPLORATORY DATA ANALYSIS

Nickel data from the G-BASE and NSI(XRFS) were used to determine domains. These show no significant systematic differences between rural and urban data (Figure 61, Figure 62 and Table 24). It is noticeable that Ni has a relatively restricted absolute range (less then three orders of magnitude) and very few high concentration outliers. The data are mapped in Figure 63, and show strong spatial controls on concentration variations, which are largely explained by underlying geology. When k-means cluster analysis is applied to these data, the breaks are identified at more evenly distributed concentrations than observed for the other contaminants worked on in this project, and therefore encapsulate much of England (Figure 64). Since the objective is to identify those much higher concentrations which require separating into different domains, in this instance only the upper clusters have been used – as shown in Figure 65.

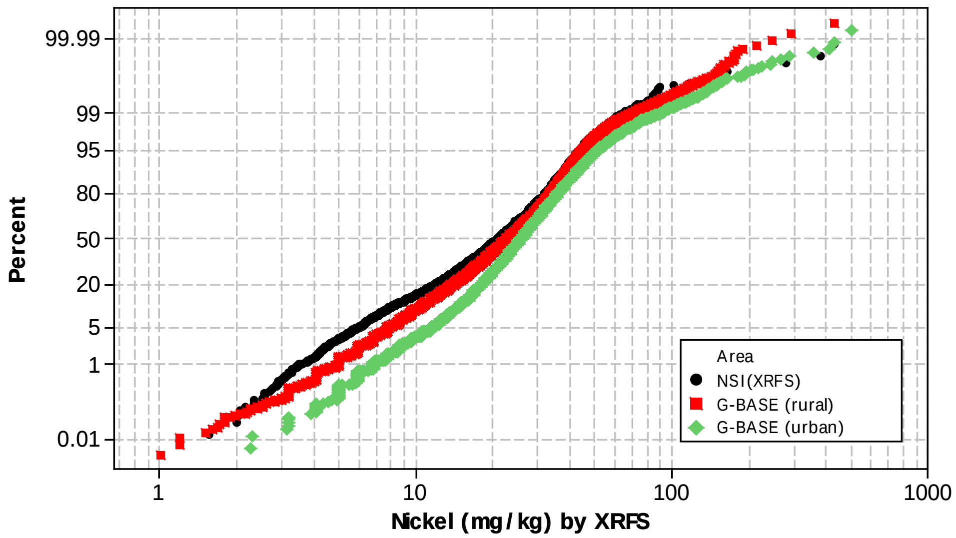

Figure 61: Probability plot of topsoil Ni concentrations by data density.

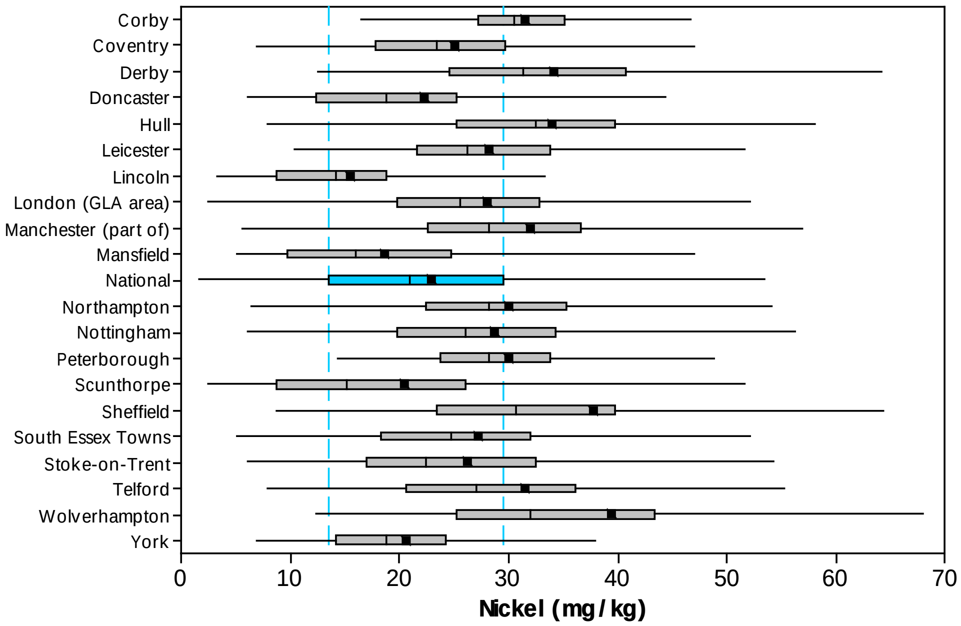

Figure 62: Boxplot of urban topsoil Ni data collected by the G-BASE project. Dashed lines extend the interquartile range of the national NSI(XRFS) data.

(a) All data	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
All data	42133	25.6	1.00	16.7	23.5	31.9	506	6
(b) Data set	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
NSI(XRFS)	4864	22.8	1.56	13.5	20.8	29.5	430	8
G-BASE (regional)	23686	24.6	1.00	15.6	22.6	31.5	431	4
G-BASE (urban)	13583	28.3	2.24	19.5	25.6	33.3	506	7
(c) Urban area	**Number**	**Mean**	**Minimum**	**25th percentile**	**Median**	**75th percentile**	**Maximum**	**Skewness**
Corby	133	31.5	16.4	27.1	30.5	35.2	63.5	1
Coventry	390	24.9	6.81	17.8	23.3	29.7	157	5
Derby	275	34.1	12.5	24.6	31.3	40.6	180	4
Doncaster	279	22.1	5.90	12.3	18.7	25.1	150	4
Hull	407	34.0	7.73	25.1	32.4	39.7	130	2
Leicester	652	28.2	10.2	21.5	26.2	33.7	87.3	1
Lincoln	215	15.4	3.15	8.6	14.1	18.7	93.7	3
London (GLA area)	6494	28.0	2.28	19.7	25.5	32.7	506	8
Manchester (part)	300	32.0	5.44	22.4	28.2	36.6	137	3
Mansfield	257	18.5	4.98	9.6	16.0	24.6	94.6	2
Northampton	275	29.9	6.26	22.4	28.1	35.2	76.7	1
Nottingham	636	28.6	5.90	19.6	26.0	34.2	146	3
Peterborough	272	29.9	14.3	23.6	28.2	33.8	64.5	1
Scunthorpe	196	20.4	2.24	8.6	15.0	26.0	186	4
Sheffield	575	37.7	8.64	23.3	30.6	39.7	434	6
South Essex towns	715	27.1	5.01	18.1	24.7	31.9	210	5
Stoke-on-Trent	745	26.1	5.90	16.9	22.4	32.4	115	2
Telford	292	31.4	7.73	20.5	26.9	36.1	141	3
Wolverhampton	284	39.3	12.3	25.1	32.0	43.4	243	4
York	191	20.5	6.81	14.1	18.7	24.2	78.1	3

Table 24: Statistical summary of topsoil Ni in the main data sets: (a) All data; (b) Data sets; and (c) urban areas sampled by G-BASE (Ni concentrations in mg/kg).

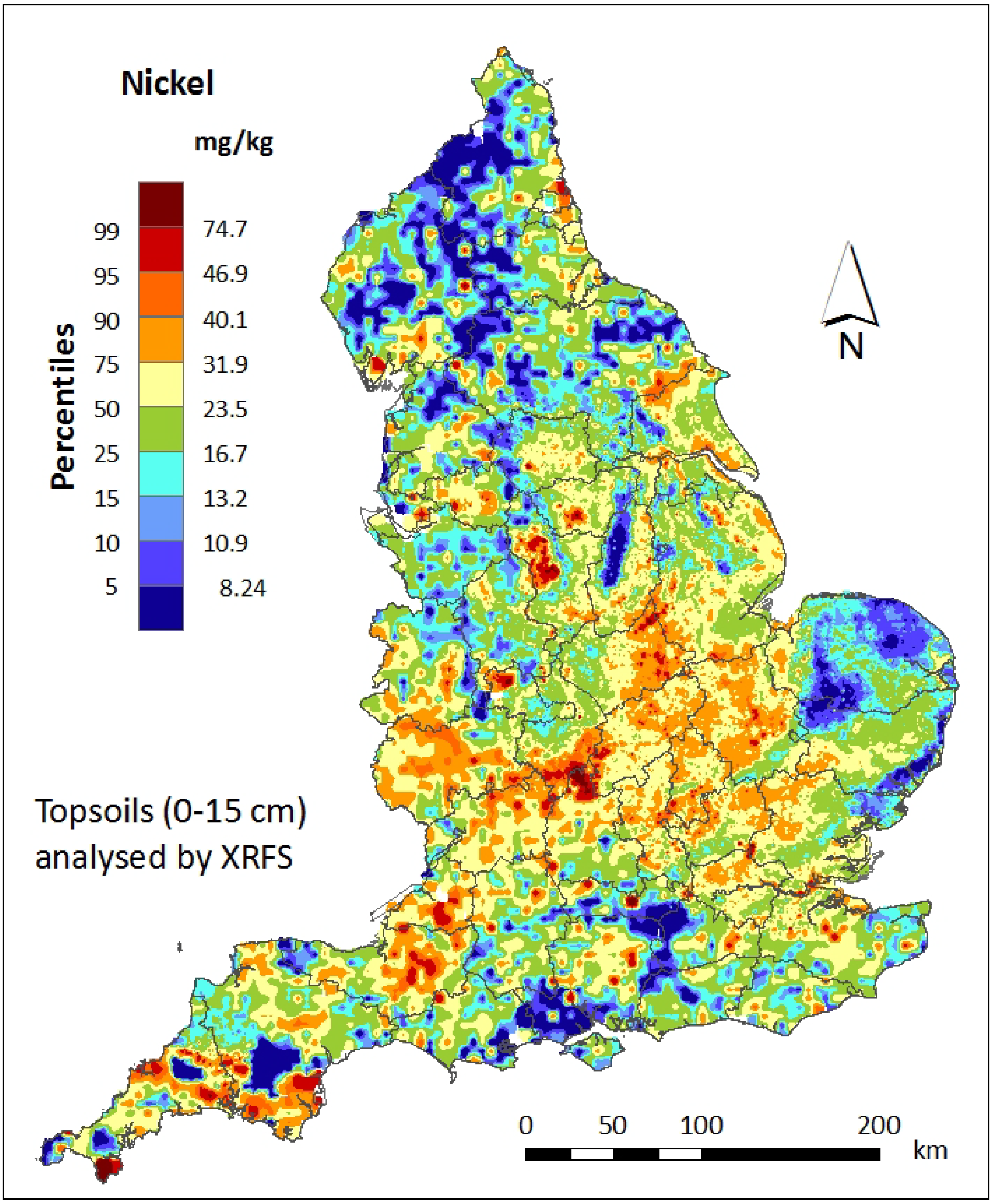

Figure 63: Interpolated map of topsoil Ni data. Colour thresholds are designed for highly skewed data.

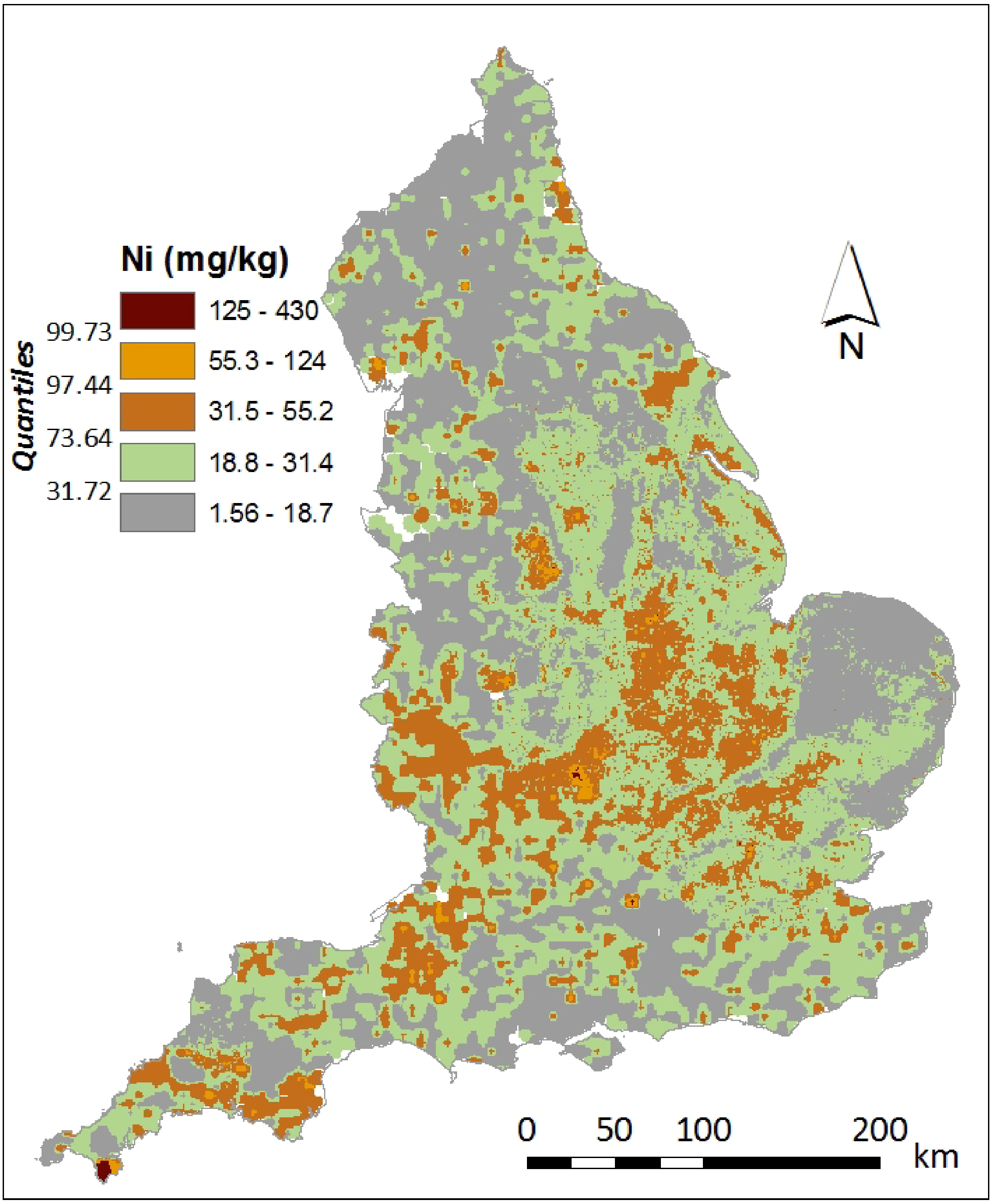

Figure 64: Interpolated map of topsoil Ni concentrations. Thresholds determined by using k-means cluster analysis.

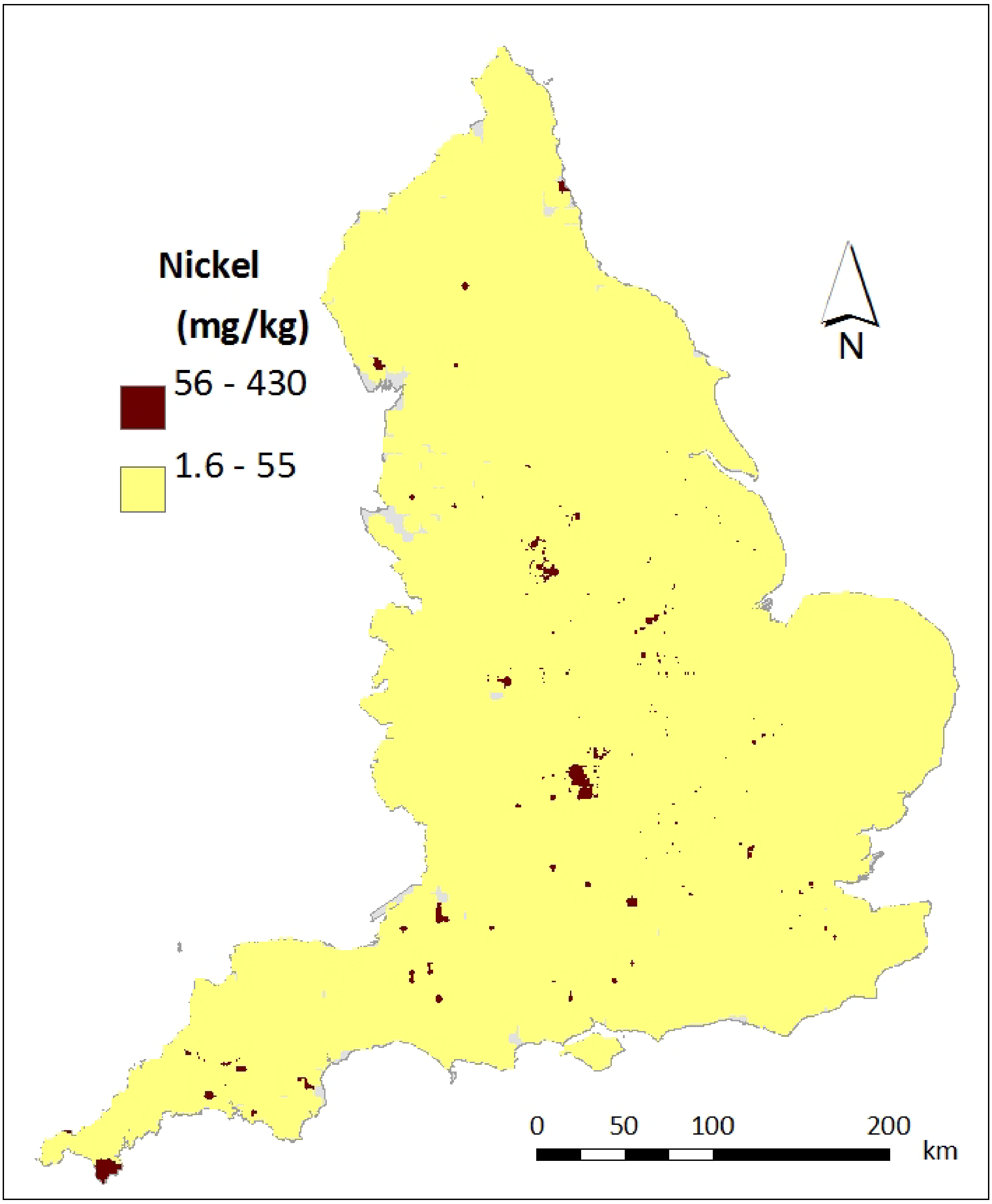

Figure 65: Interpolated map of topsoil Ni concentrations. Threshold determined by using k-means cluster analysis 97th percentile (cf. Figure 64).

5.2 DOMAIN SELECTION

The information shown below was used to compile the data for domains, with higher topsoil Ni concentrations than typical, in:

- basic rocks
- ultrabasic rocks
- ironstones
- Peak District (non-ferrous metalliferous mineralisation and mining area).

5.2.1 Basic and ultrabasic rocks

Basic rocks have Ni-bearing minerals within their matrix – the proportion of this is further increased in ultrabasic rocks. Elevated concentrations are seen in other areas/studies of soils and sediments (*e.g.* Northern Ireland). It can be seen that, although there are very few data, the median of 63 mg/kg is elevated in comparison with the main data set. However, when these data are further subdivided into 'basic' and 'ultrabasic' these have very different data distributions, as shown in Table 25 and Figure 66. They have therefore been identified as separate domains.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
All	*27*	*83.5*	*20.5*	*33.4*	*63.2*	*87.0*	*430*	*3*
Basic	23	60.9	20.5	33.4	62.5	80.9	107	0.1
Ultrabasic	4	213	25.4	48.2	199	393	430	0.3

'All' data subdivided into 'Basic' and 'Ultrabasic'.

Table 25: Summary statistics of topsoil Ni concentrations (in mg/kg) over basic/ultrabasic rocks

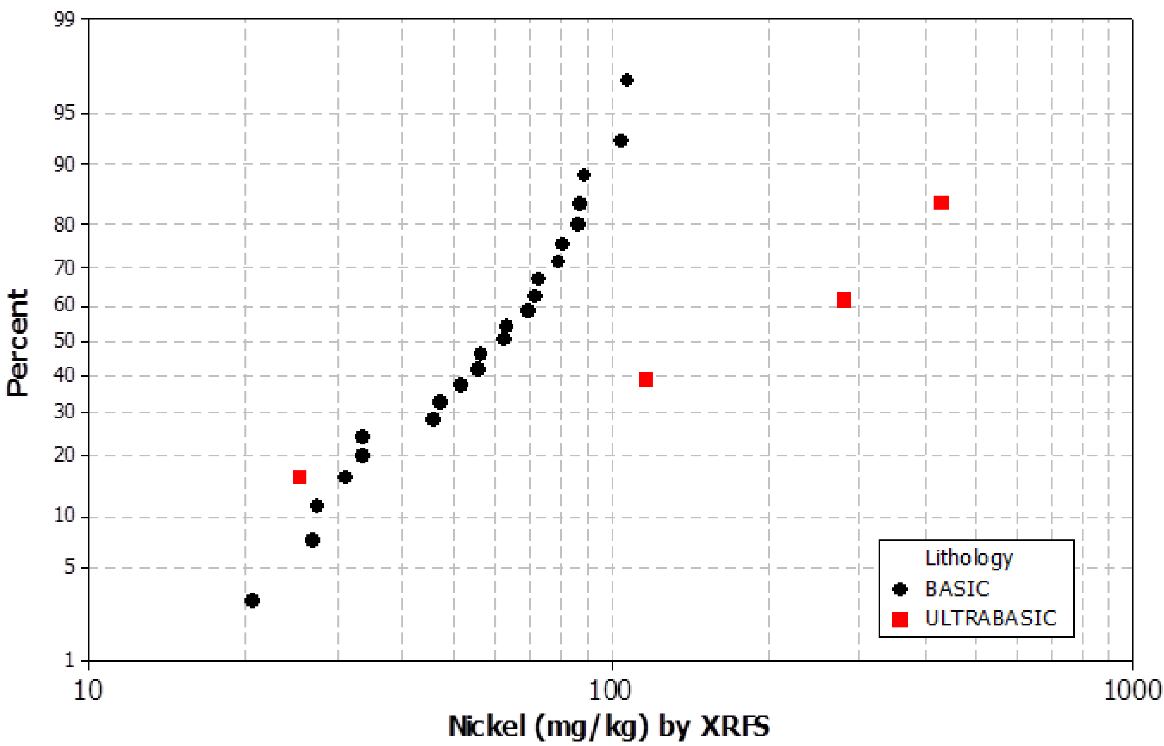

Figure 66: Probability plot of topsoil Ni concentrations over basic and ultrabasic rocks in England.

In order to try to overcome difficulties in quanitifying the NBC for these domains due to the low sample numbers, the BGS Mineral Recconnaissance Programme (MRP) soil data (see Ander *et al.*, 2011) from the Lizard complex (both basic and ultrabasic rocks) has been explored. The sample locations with Ni data are shown in Figure 67, and it should be noted that they are targeted at areas considered 'prospective' for metalliferous mineral deposits and so located primarily along transects considered most likely to identify higher soil metal concentrations for the target metals. Also, although sample depth and sieving fraction is not recorded in the BGS

Geochemistry Database, there are two publications which use some/all of these data to aid geological mapping of the geological complex lithologies of this area (Smith and Leake, 1984; Shepherd *et al*., 1987). It appears that the soil samples reflect material from up to 1 m depth – so quite different to those of the main data sets. Additionally, a finer seiving mesh size has been used for some of the samples; this will often have the benefit of increasing the geochemical contrast in the data, which is helpful to the main purpose of the samples collected, but does not reflect a 0 - 15 cm soil sieved to <2 mm. It is therefore very difficult to establish whether the systematically elevated concentrations over both basic and ultrabasic rocks shown in Figure 68 and Table 26 reflect a methodological bias or are more representative of the range of Ni concentrations that could be expected over these rock types.

Comparisons are available from elsewhere in the UK – the topsoil samples over basalt (basic domain analogy) in Northern Ireland have an interquartile range of 65 – 140 mg/kg and median of 102 mg/kg. A review of soil chemistry from Scotland (Berrow and Ure, 1985) had an arithmetic mean of 1540 mg/kg Ni over ultrabasic rocks, with basic rock parent materials with an arithmetic mean of 51-57 mg/kg.

The literature and MRP data therefore support the definition of basic and ultrabasic domains, but the inability to ascertain the source of bias between the main data sets used in this work from the concentrations in the Ni data mean that they have not been used to contribute to the NBC calculation.

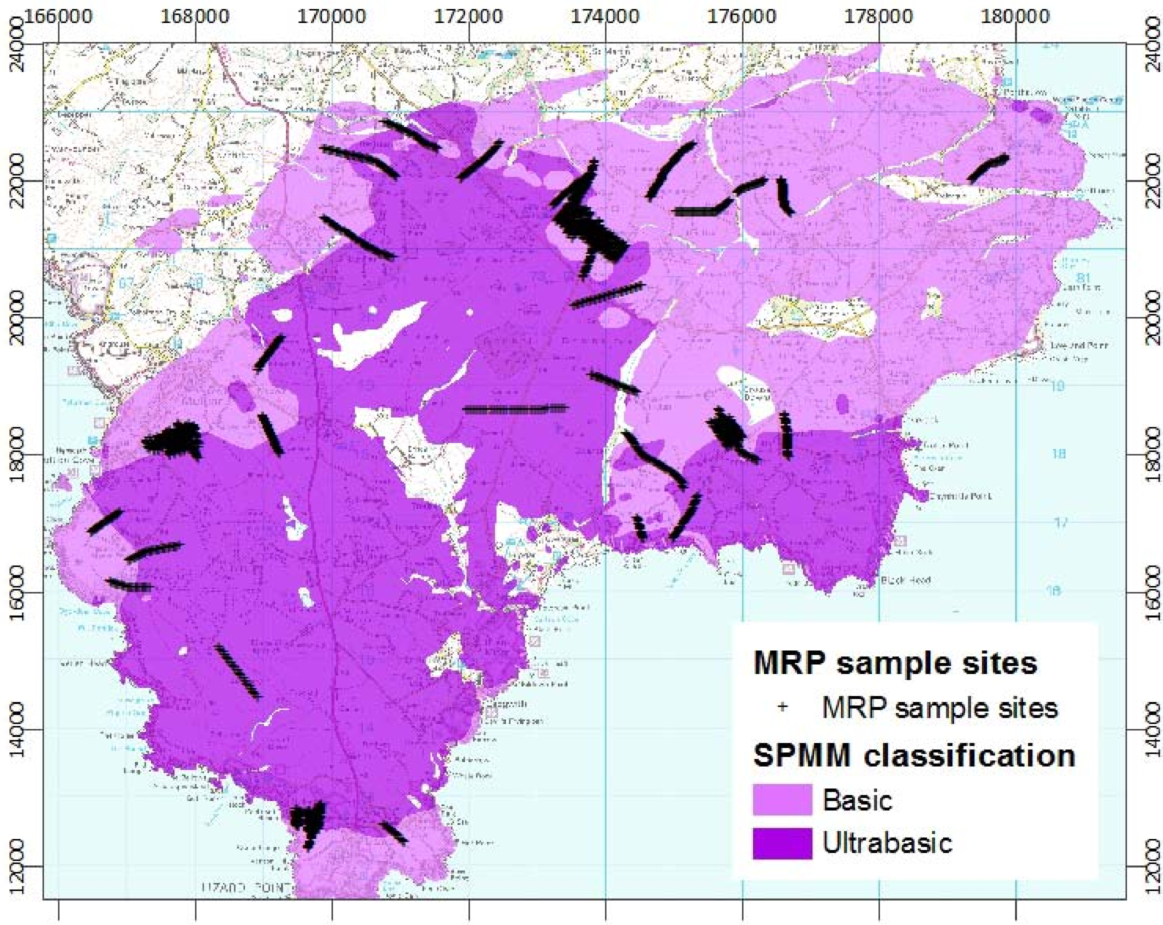

Figure 67: MRP sampling sites in the Lizard area.

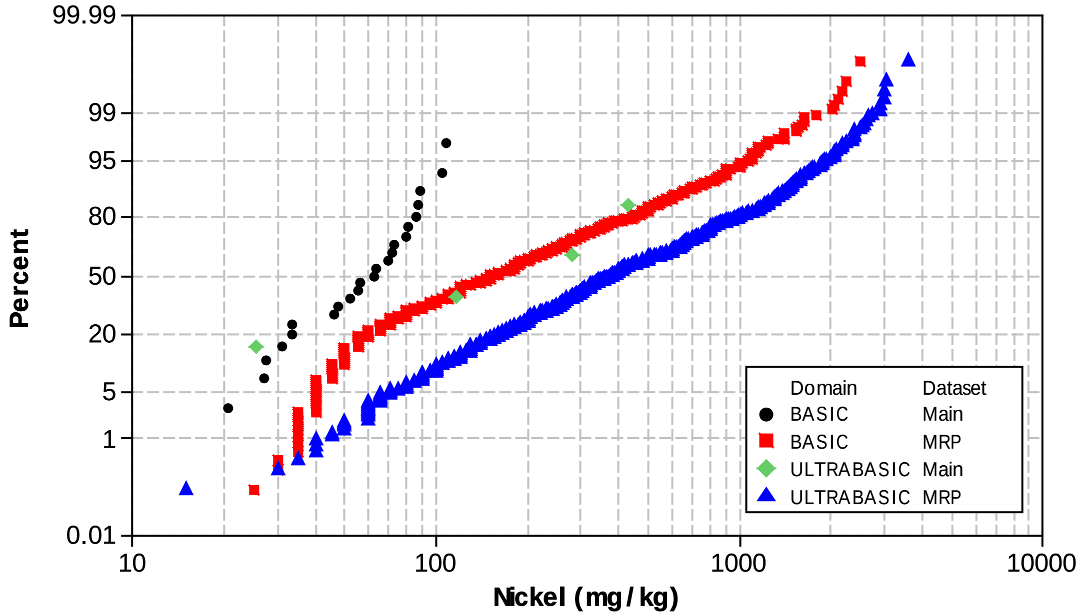

Figure 68: Probability plot of the main data set and MRP soil Ni concentration data over basic and ultrabasic rocks.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Basic (main)	23	60.9	20.5	33.4	62.5	80.9	107	0
Basic (MRP)	637	290	25.0	70.0	150	350	2500	3
Ultrabasic (main)	4	213	25.4	48.2	199	393	430	0
Ultrabasic (MRP)	632	619	15.0	195	380	800	3600	2

Table 26: Summary statistics of MRP soil Ni concentrations (in mg/kg) over basic/ultrabasic rocks compared to the main data set Ni concentrations.

5.2.2 Ironstones

Whilst higher concentrations are observed over ironstones, they do not appear to be ubiquitously elevated in comparison to typical concentrations, in contrast to As. Hence, these data have been examined in more detail and show that soils over formations which are recorded as having both the major and minor mineral cement of iron oxide are typically elevated in concentration in comparison to those which are not (Figure 69: “MNR_MNRL” = ‘f’) – which are in themselves not elevated in comparison to the main data set (Figure 70).

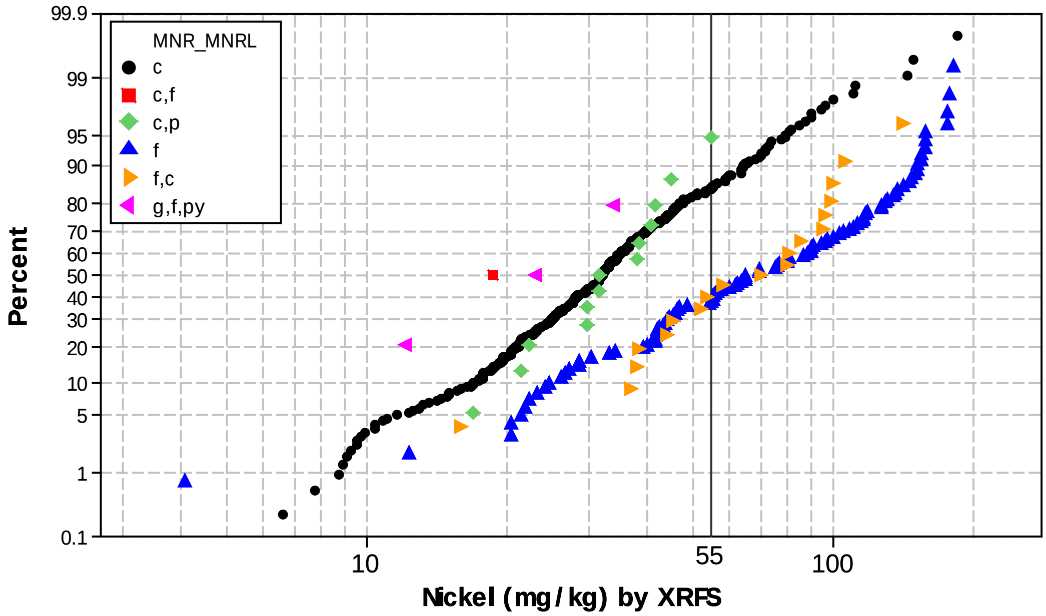

Figure 69: Probability plot of topsoil Ni concentrations, categorised by ironstone minor mineralogy (k-cluster mean threshold shown as a vertical line). Cement codes: c = calcite; f = ferroan; p = phosphatic; g = gypsiferous; and py = pyrite.

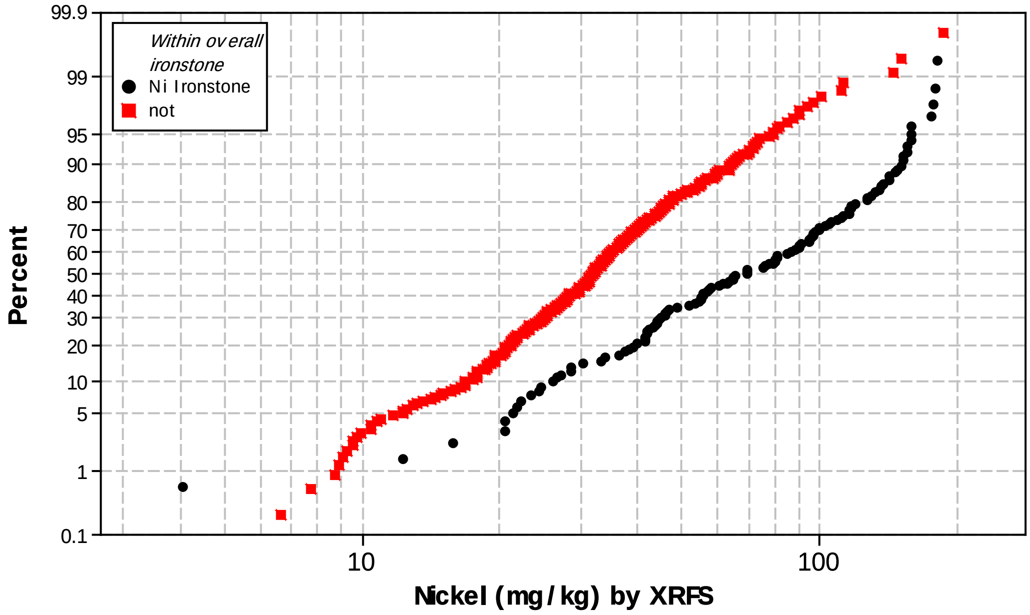

Figure 70: Probability plot of all ironstone area topsoil Ni concentrations, categorised by whether the major and minor mineralogy is iron-cement, or not.

5.2.3 Peak District

The area of the Peak District can be seen as distinct region of elevated Ni soil concentrations. When combined with the Peak District metalliferous mineralisation and mining data set, as well as the simplified solid geology (Figure 71) it can be seen that it is difficult to distinguish the underlying process controlling elevated topsoil Ni concentrations. It is evident that occurrence of either extrusive or intrusive basic igneous rocks is not uniquely associated with the higher concentrations – although there may be occurrences of these more Ni-rich rocks which are too localised to be identified and/or mapped at 1:50,000 (the Soil Parent Material Model (SPPM) scale). Alternatively, there may be relatively minor Ni associated with mineralisation in this area – or a secondary enrichment through sorption to manganese or iron oxides. Finally, the possibility of an intrinsic occurrence within the limestone/dolomitic carbonate minerals has also been suggested (Edmunds, 1971). Preliminary analysis of stream sediment data from this area (BGS, unpublished) could not unequivocally attribute the Ni source(s).

Therefore, the mineralisation and mining spatial data has been used to define a domain called 'Peak District' – although it should be recognised that those areas of the Carboniferous Limestone which lie outwith the area of the mineralisation may also have Ni natural background concentrations which are more applicable to this domain. Summary statistics are given in Section 5.3.

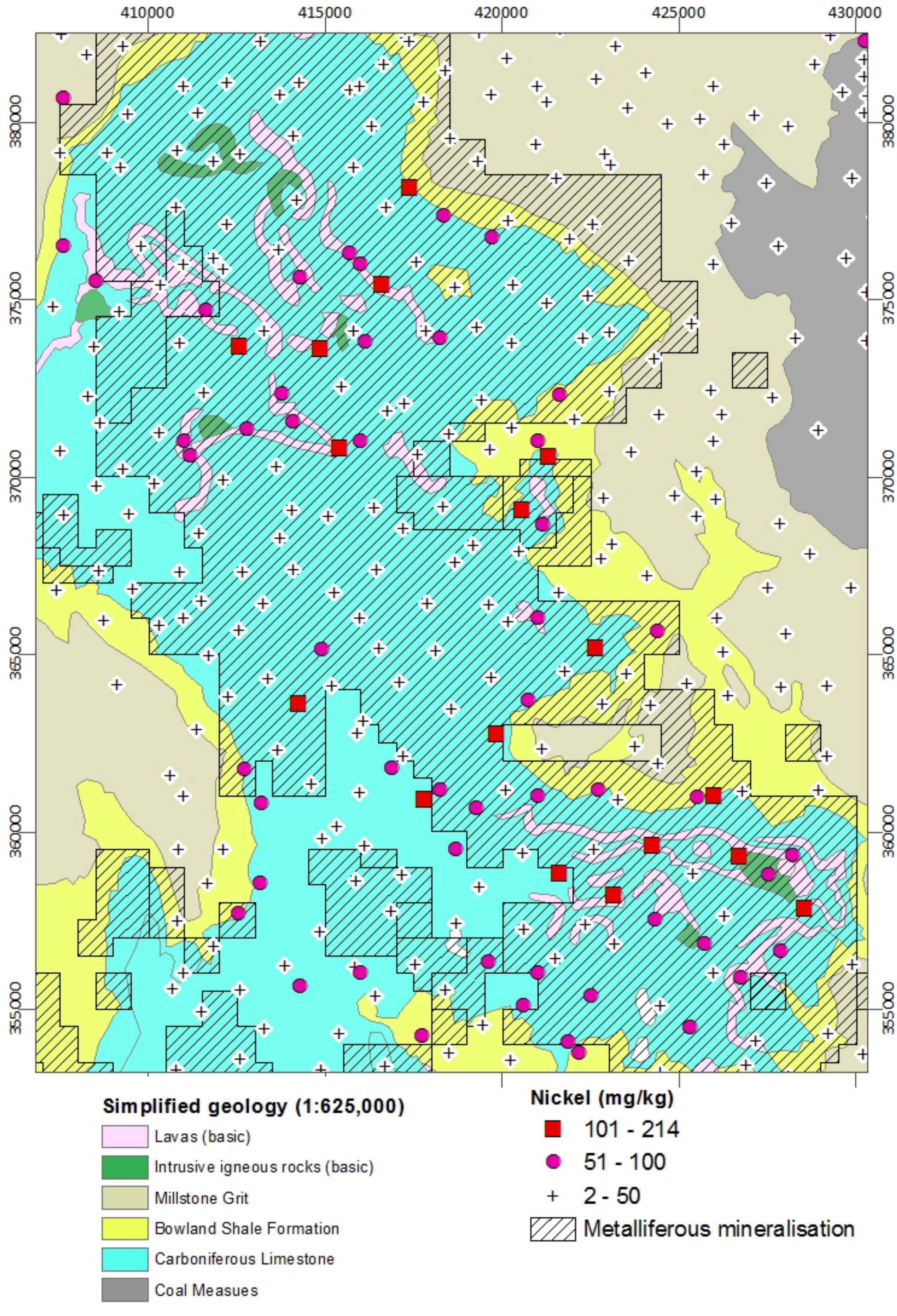

Figure 71: Map of topsoil Ni concentrations in the Peak District area, with simplified geology and extent of metalliferous mineralisation and mining.

5.3 DOMAIN DATA SUMMARY

The summary statistics for the domains are shown in Table 27, and it should be noted that there are <30 samples for the basic and ultrabasic domains disqualifying a satisfactory NBC calculation (see Cave *et al.*, 2012). The ironstone domain is listed as 'Ironstone(Ni)' since it occupies a smaller areas than the full ironstone outcrop area which is characteristic of higher arsenic concentrations (see Ander *et al.*, 2011).

These domains appear (notwithstanding some low sample numbers) to have characteristic concentration distributions, as shown in Figure 72 and Figure 73.

The spatial occurrence of the domains is shown in Figure 74.

Area name	Number	Mean	Minimum	25th percentile	Median	75th percentile	Maximum	Skewness
Basic	23	60.9	20.5	33.4	62.5	80.9	107	0
Ultrabasic	4	213	25.4	48.2	199	393	430	0
Ironstone (Ni)	117	78.9	4.1	42.3	69.4	112	182	1
Peak District	221	44.5	5.9	22.4	34.2	51.2	384	4
Principal	41768	25.3	1.0	16.6	23.4	31.7	506	5

Table 27: Summary statistics of topsoil Ni concentrations (in mg/kg) in the domains.

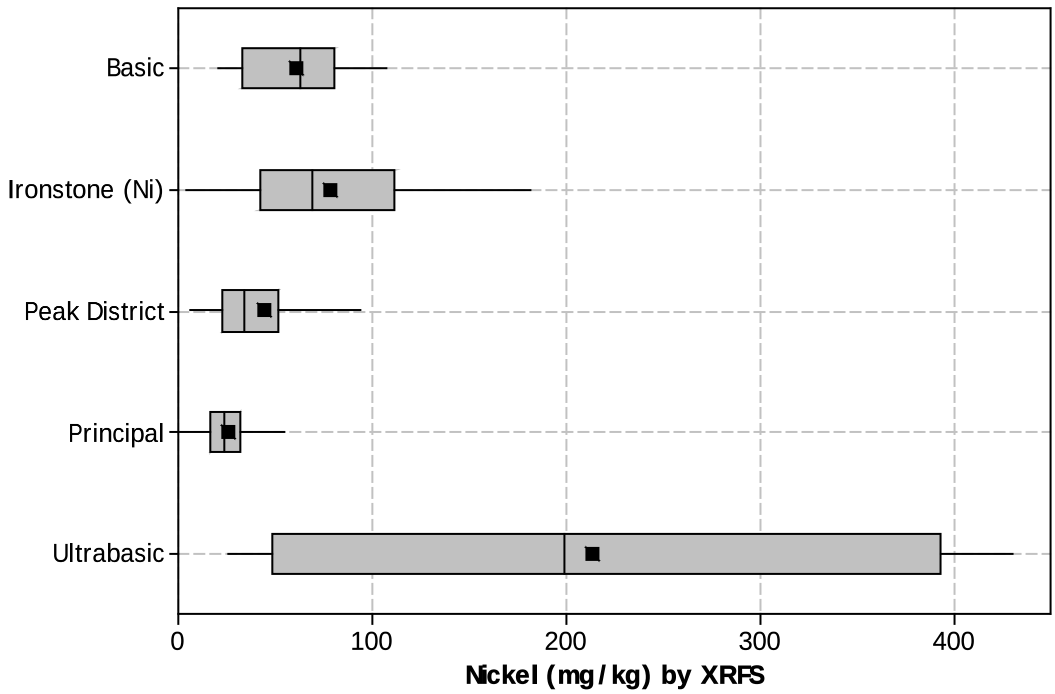

Figure 72: Boxplot of topsoil Ni data classified by domains.

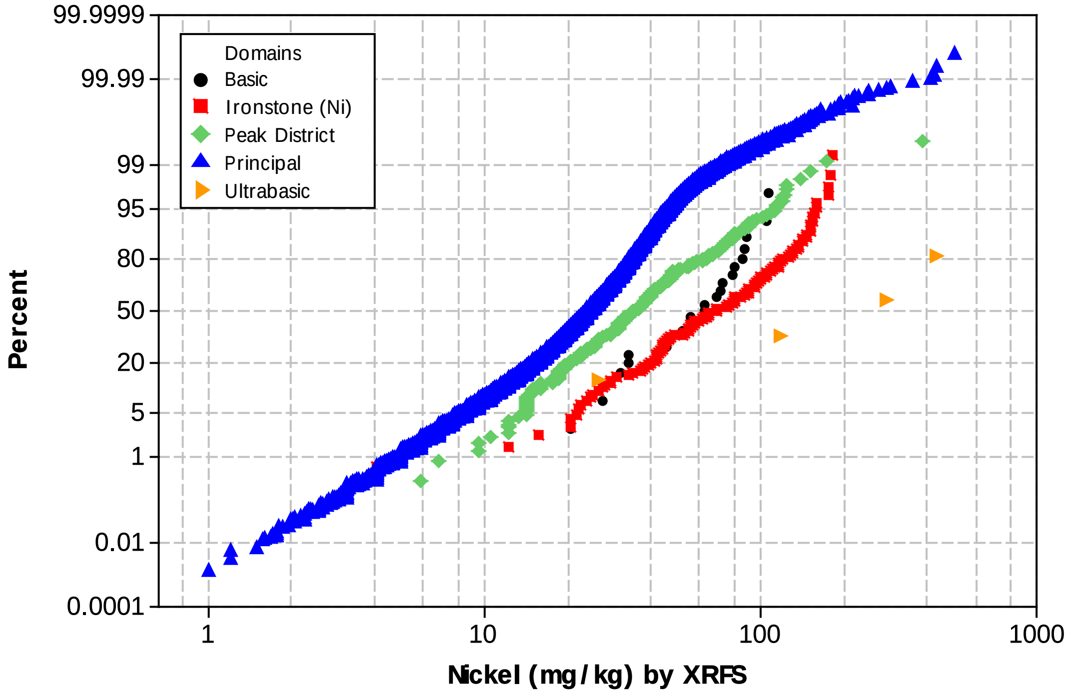

Figure 73: Probability plot of Ni topsoil data classified by domains.

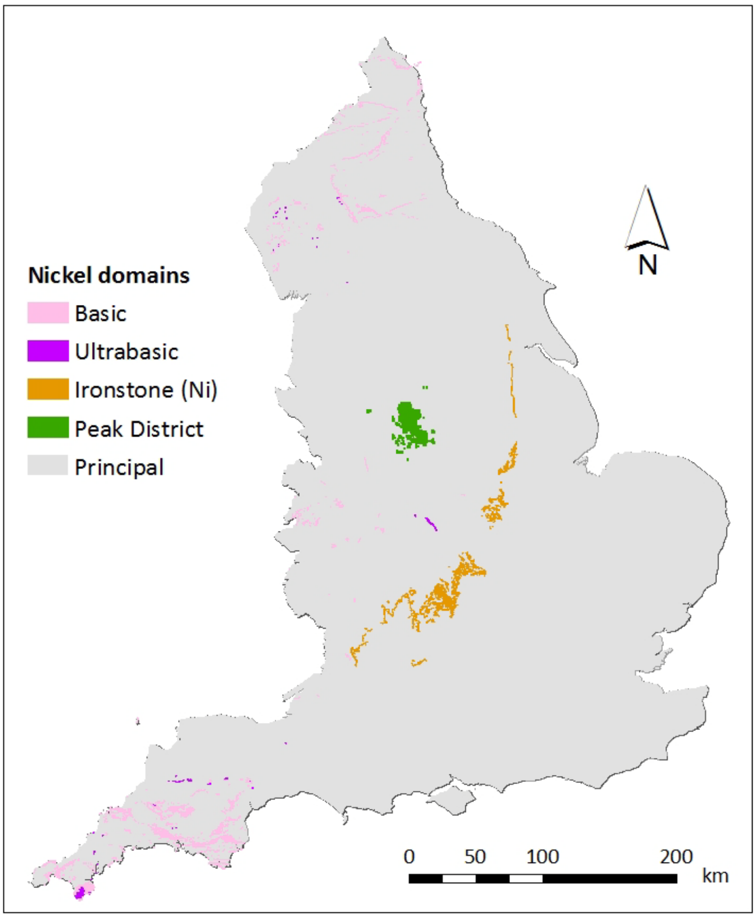

Figure 74: Map of Ni domains.

5.4 Nickel NBC CALCULATION

5.4.1 Principal Domain

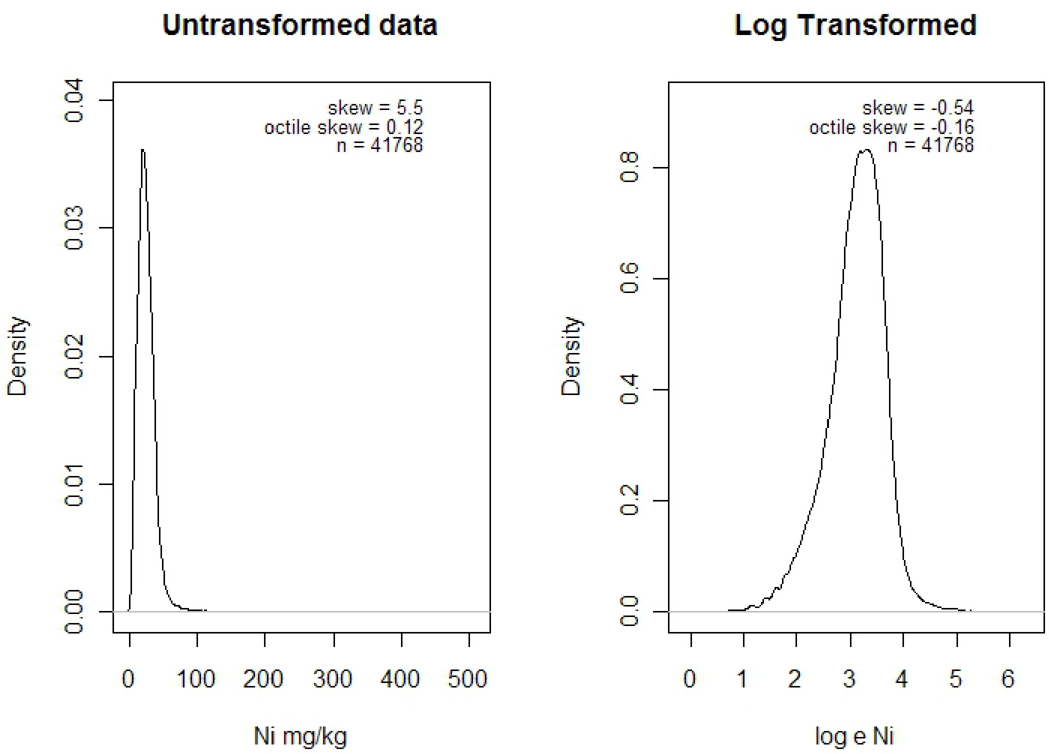

Figure 75: Density distributions for the raw data and the $\log_e$ transformed data for Ni in the Principal Domain (n = number of samples).

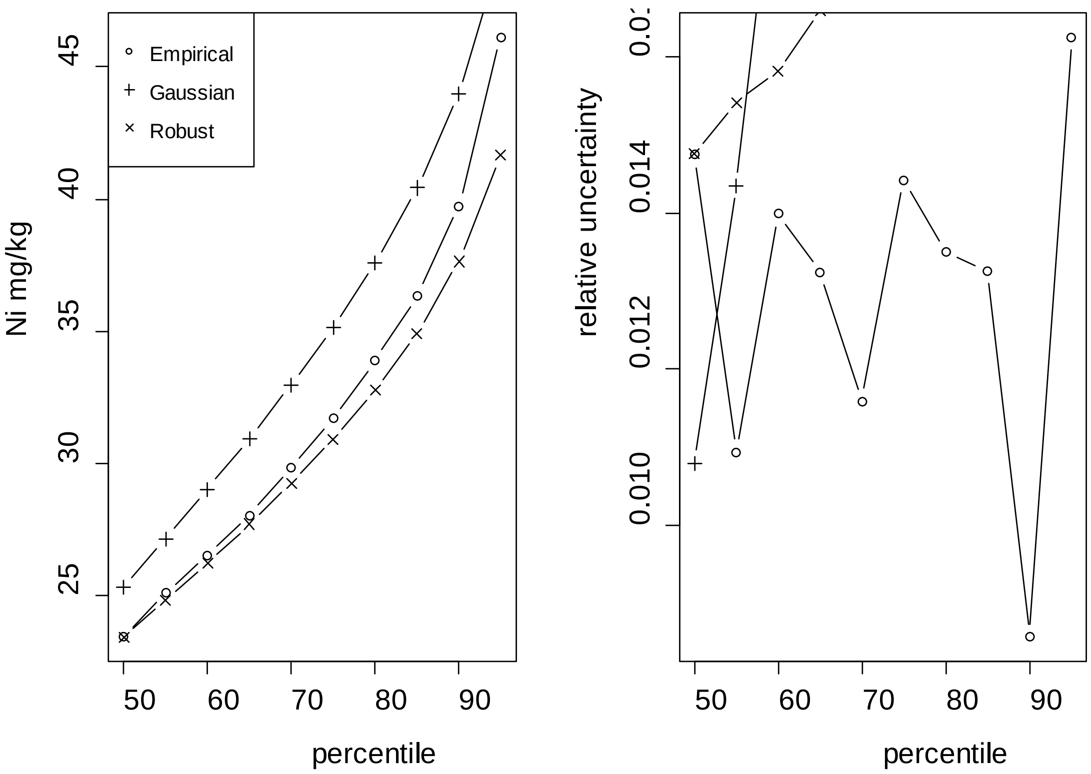

Figure 76: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Ni in the Principal Domain.

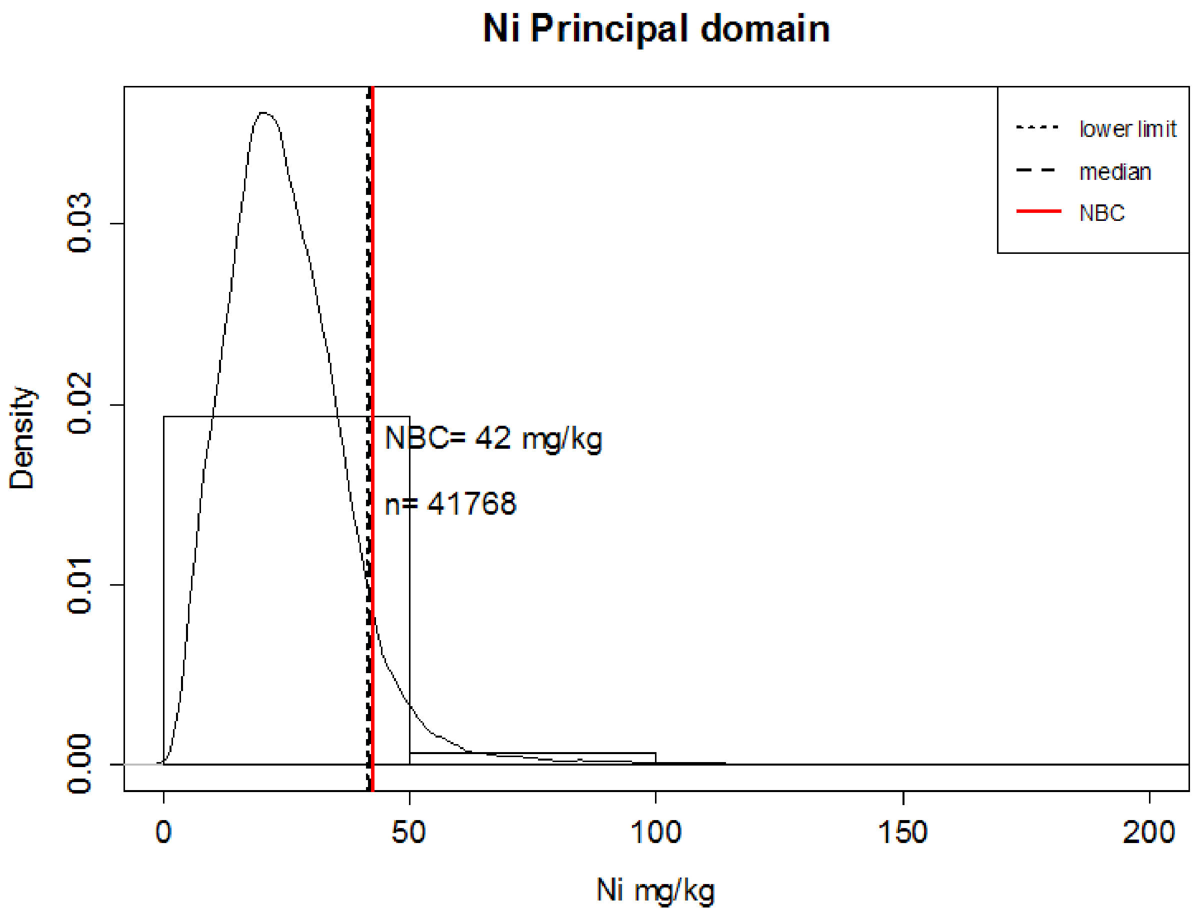

Figure 77: Summary density plot and histogram of the distribution for Ni in the Principal Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	23.3	23.4	23.6	25.2	25.3	25.4	**23.3**	**23.4**	**23.6**
55	24.8	25.1	25.1	27.0	27.1	27.3	**24.6**	**24.8**	**25.0**
60	26.3	26.5	26.7	28.8	29.0	29.3	**26.0**	**26.2**	**26.5**
65	27.9	28.0	28.3	30.6	30.9	31.3	**27.5**	**27.7**	**28.0**
70	29.7	29.8	30.0	32.5	33.0	33.5	**29.0**	**29.2**	**29.5**
75	31.5	31.7	32.0	34.6	35.1	35.7	**30.6**	**30.9**	**31.2**
80	33.7	33.9	34.2	37.0	37.6	38.3	**32.5**	**32.8**	**33.1**
85	36.1	36.3	36.6	39.7	40.4	41.3	**34.6**	**34.9**	**35.3**
90	39.7	39.7	40.0	43.1	44.0	45.0	**37.3**	**37.6**	**38.1**
95	45.7	46.1	46.5	48.1	49.3	50.6	**41.3**	**41.7**	**42.1**

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 28: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Ni in the Principal Domain (concentrations in mg/kg).

5.4.2 Basic Domain

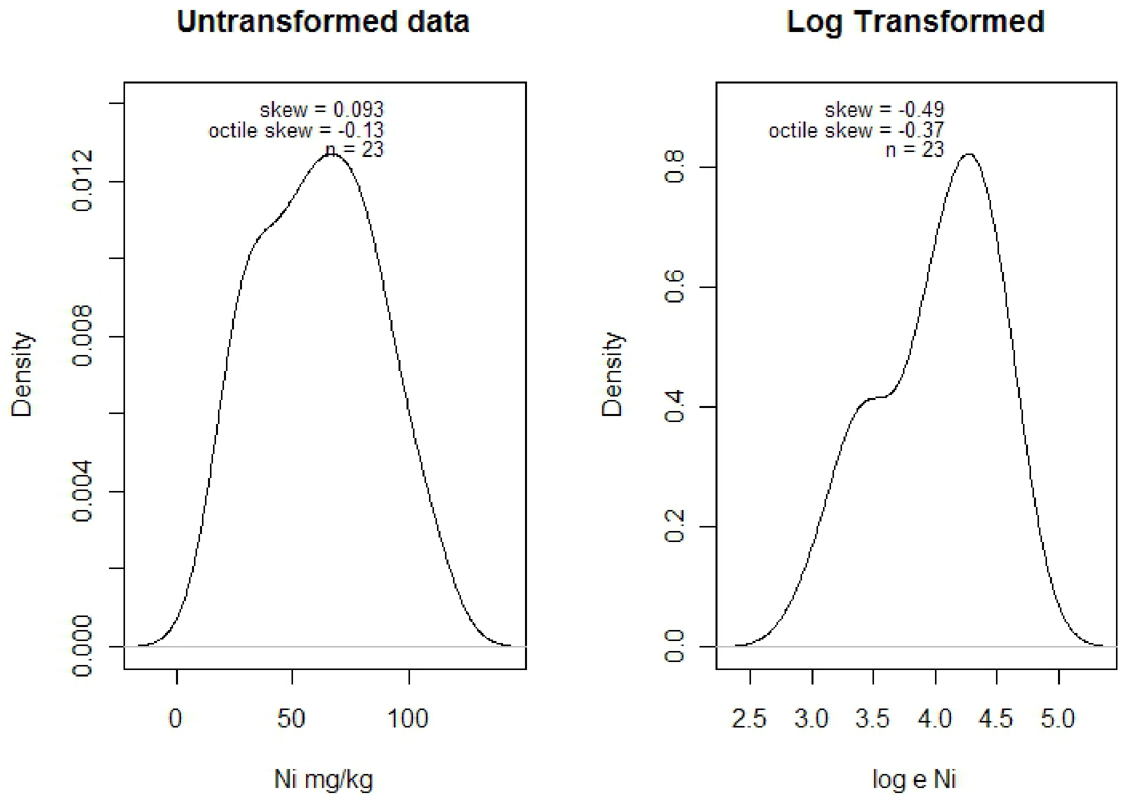

Figure 78: Density distributions for the raw data and the $\log_e$ transformed data for Ni in the Basic Domain (n = number of samples).

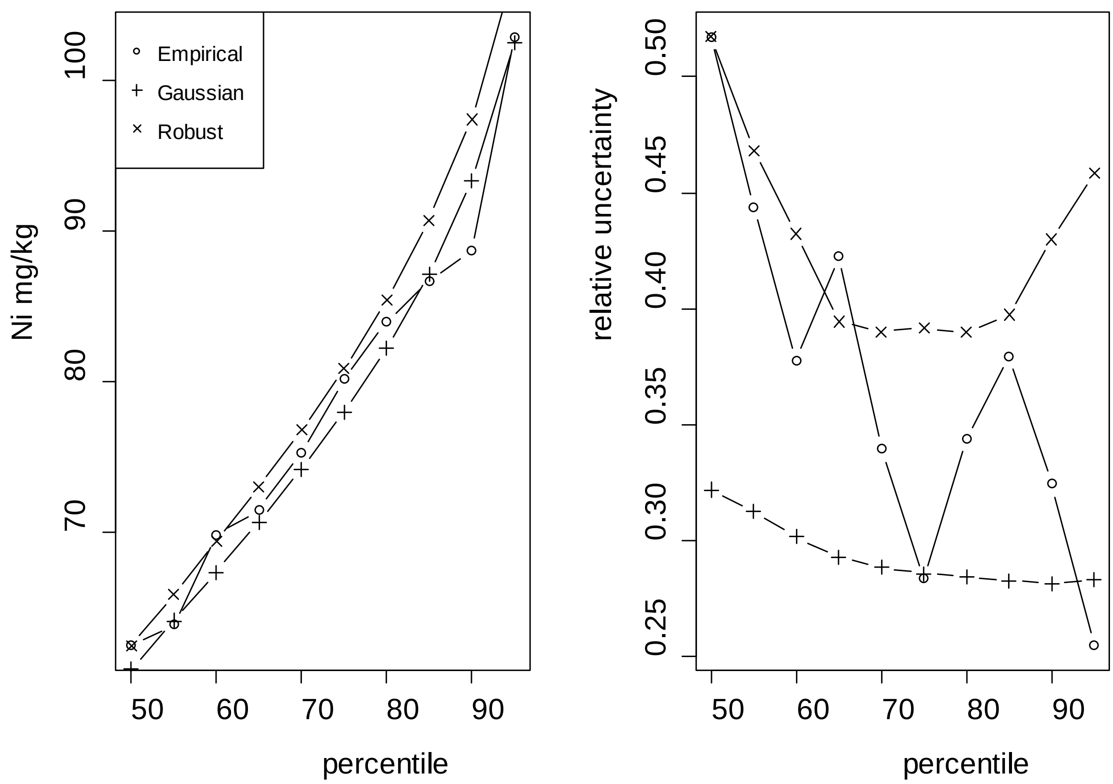

Figure 79: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Ni in the Basic Domain.

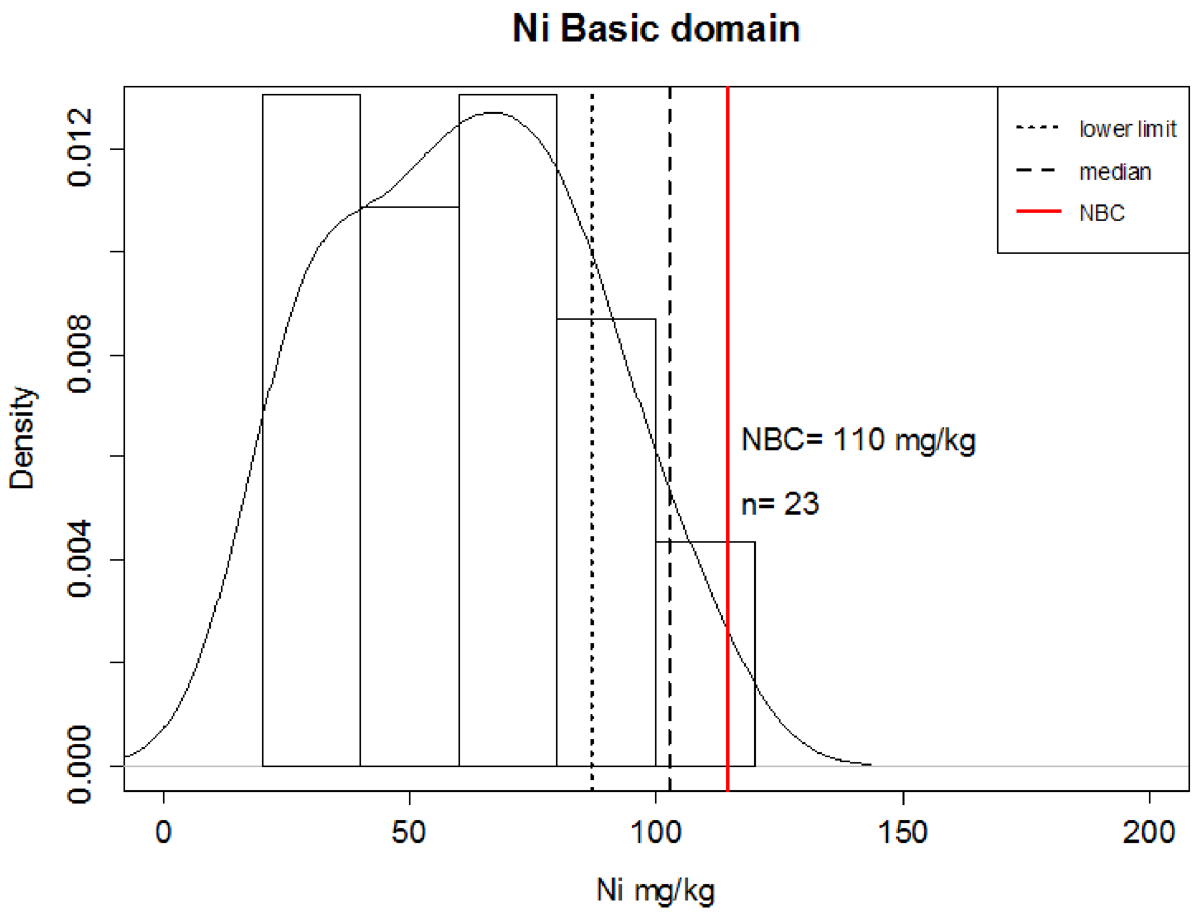

Figure 80: Summary density plot and histogram of the distribution for Ni in the Basic Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	45.7	62.5	72.4	**50.4**	**60.9**	**71.3**	45.7	62.5	79.5
55	47.6	63.9	79.6	**53.5**	**64.1**	**74.3**	49.2	65.9	81.3
60	54.0	69.8	81.9	**56.6**	**67.4**	**77.3**	52.6	69.4	83.2
65	56.1	71.5	86.3	**59.7**	**70.7**	**80.5**	56.2	73.0	87.7
70	58.7	75.3	87.0	**62.8**	**74.2**	**84.2**	59.7	76.8	92.1
75	62.9	80.2	89.1	**66.1**	**78.0**	**88.1**	63.2	80.9	96.5
80	68.5	84.0	98.3	**69.9**	**82.2**	**92.0**	67.2	85.4	103
85	71.1	86.7	104	**74.2**	**87.2**	**97.4**	70.7	90.7	110
90	78.1	88.7	107	**79.6**	**93.4**	**104**	74.2	97.4	120
95	80.9	103	107	**86.9**	**103**	**114**	81.4	107	134

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 29: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Ni in the Basic Domain (concentrations in mg/kg).

5.4.3 Ironstone(Ni) domain

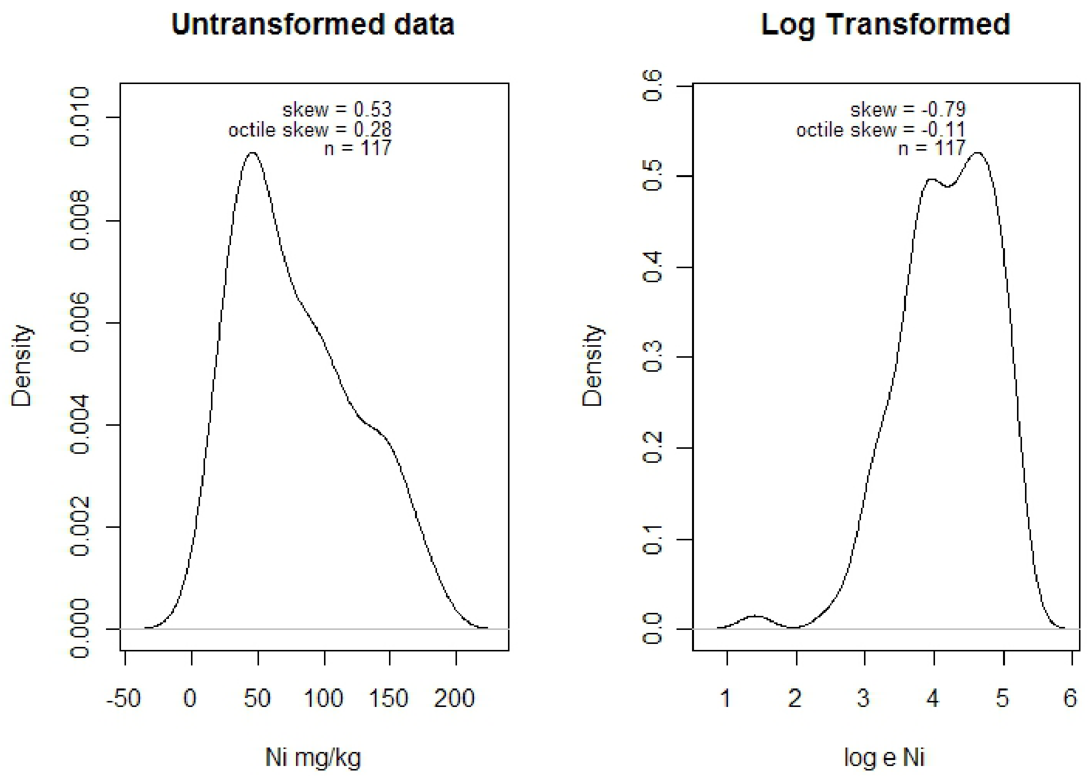

Figure 81: Density distributions for the raw data and the $\log_e$ transformed data for Ni in the Ironstone(Ni) Domain (n = number of samples).

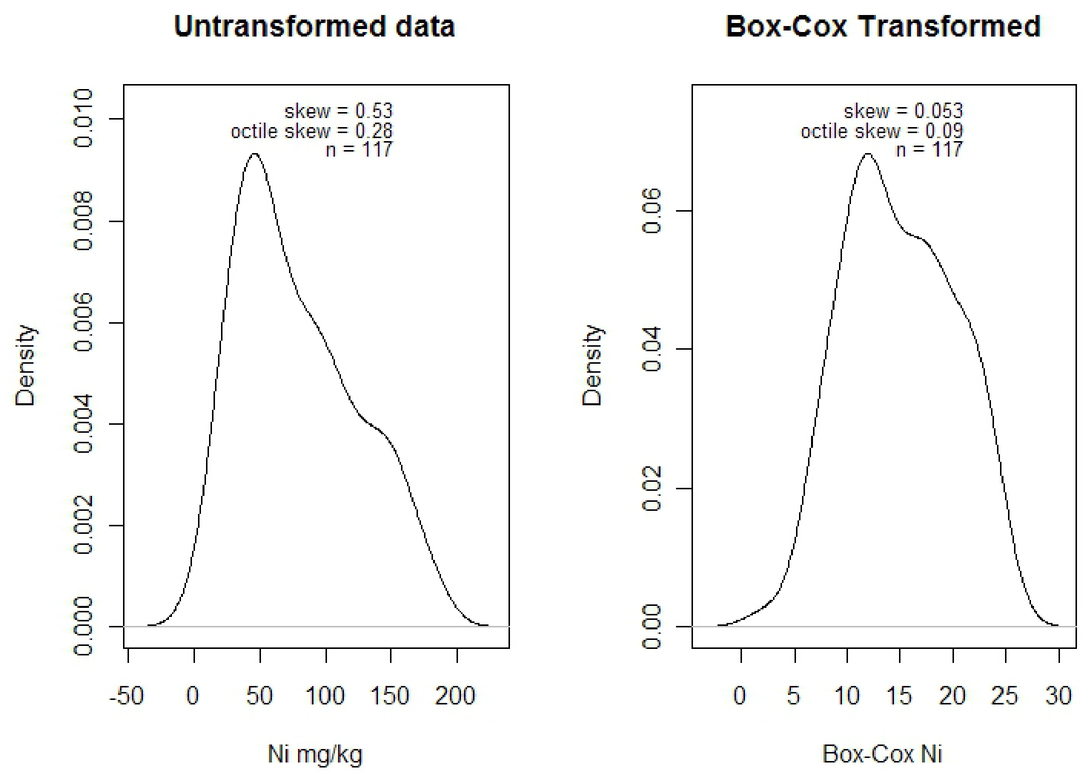

Figure 82: Density distributions for the raw data and the Box-Cox transformed data for Ni in the Ironstone(Ni) Domain (n = number of samples).

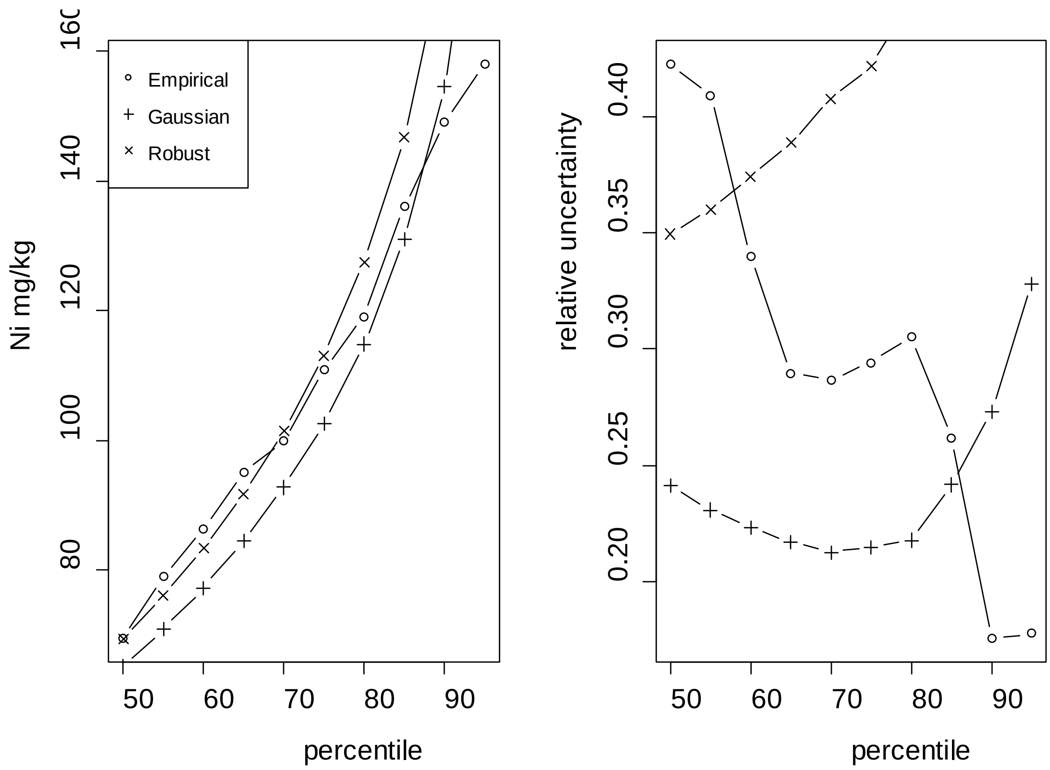

Figure 83: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Ni in the Ironstone(Ni) Domain.

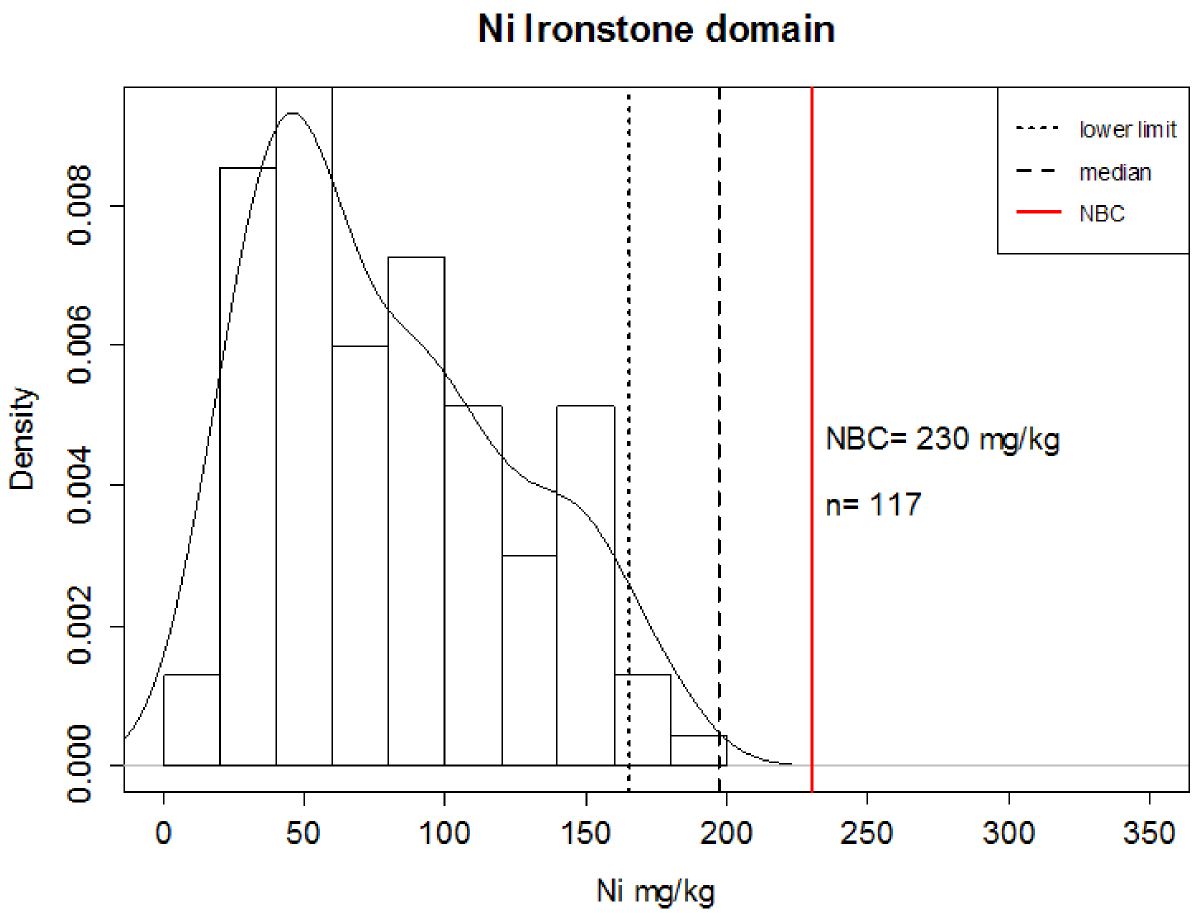

Figure 84: Summary density plot and histogram of the distribution for Ni in the Ironstone(Ni) Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	**P L**	**Parametric**	**P H**	R L	Robust	R H
50	55.8	69.4	85.2	**57.4**	**65.1**	**73.1**	56.8	69.4	81.1
55	61.7	78.9	93.9	**62.7**	**70.8**	**79.1**	62.0	76.0	89.3
60	69.4	86.3	98.8	**68.6**	**77.2**	**85.8**	67.9	83.4	99.1
65	80.1	94.9	108	**75.1**	**84.4**	**93.4**	74.2	91.7	110
70	88.6	100	117	**82.5**	**92.7**	**102**	81.4	101	123
75	97.2	111	130	**91**	**103**	**113**	89.9	113	138
80	105	119	141	**102**	**115**	**127**	100	127	157
85	116	136	152	**114**	**131**	**146**	112	147	184
90	132	149	158	**133**	**154**	**175**	131	175	224
95	148	158	176	**165**	**197**	**230**	166	228	301

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 30: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Ni in the Ironstone(Ni) Domain (concentrations in mg/kg).

5.4.4 Peak District Domain

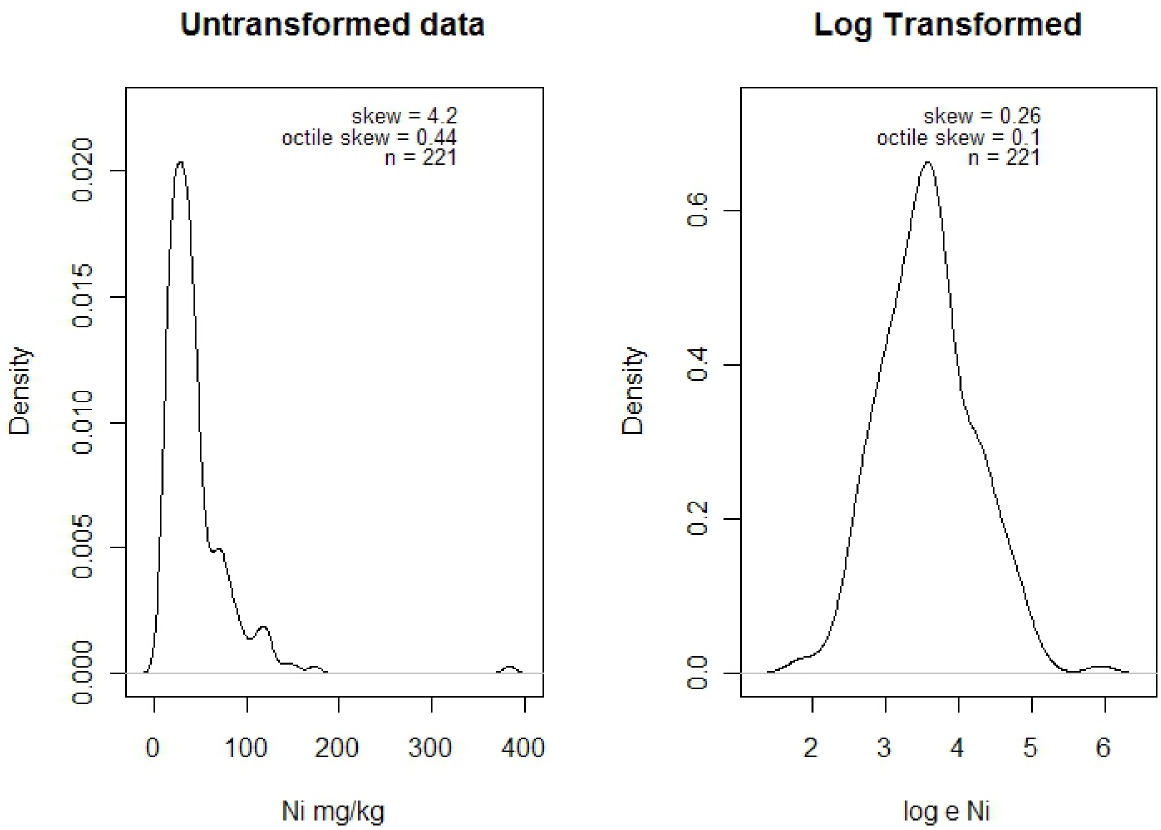

Figure 85: Density distributions for the raw data and the $\log_e$ transformed data for Ni in the Peak District Domain (n = number of samples).

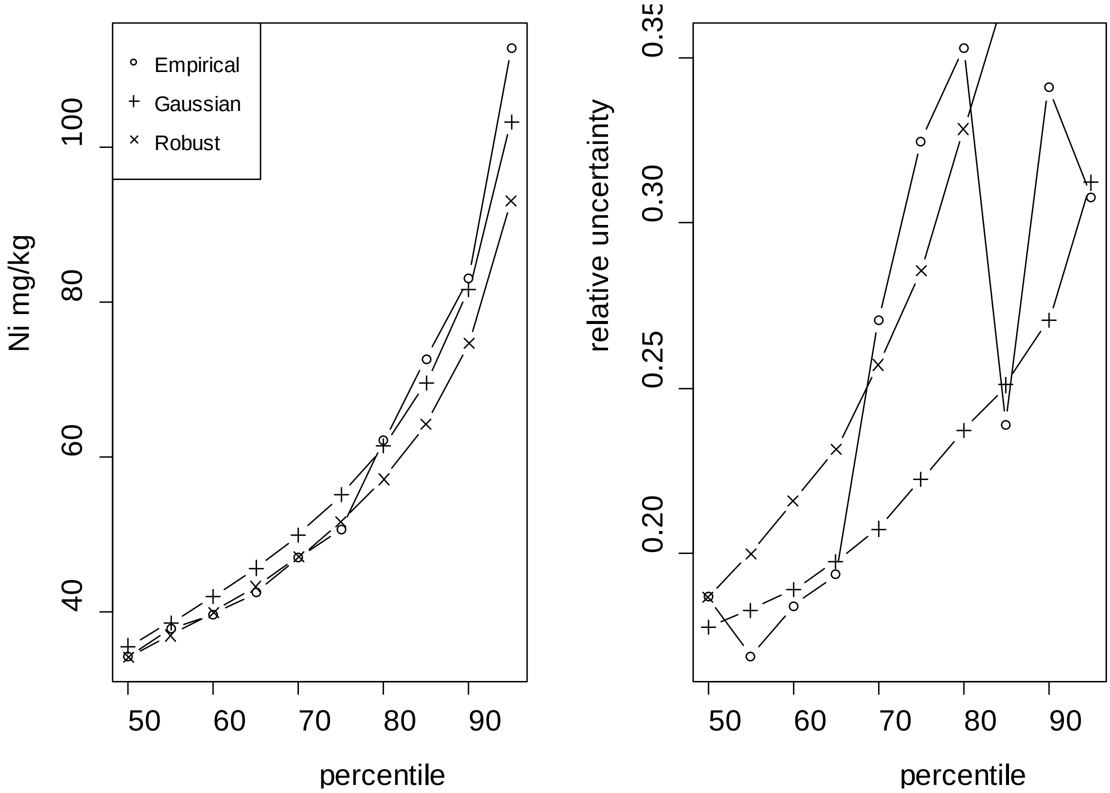

Figure 86: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Ni in the Peak District Domain.

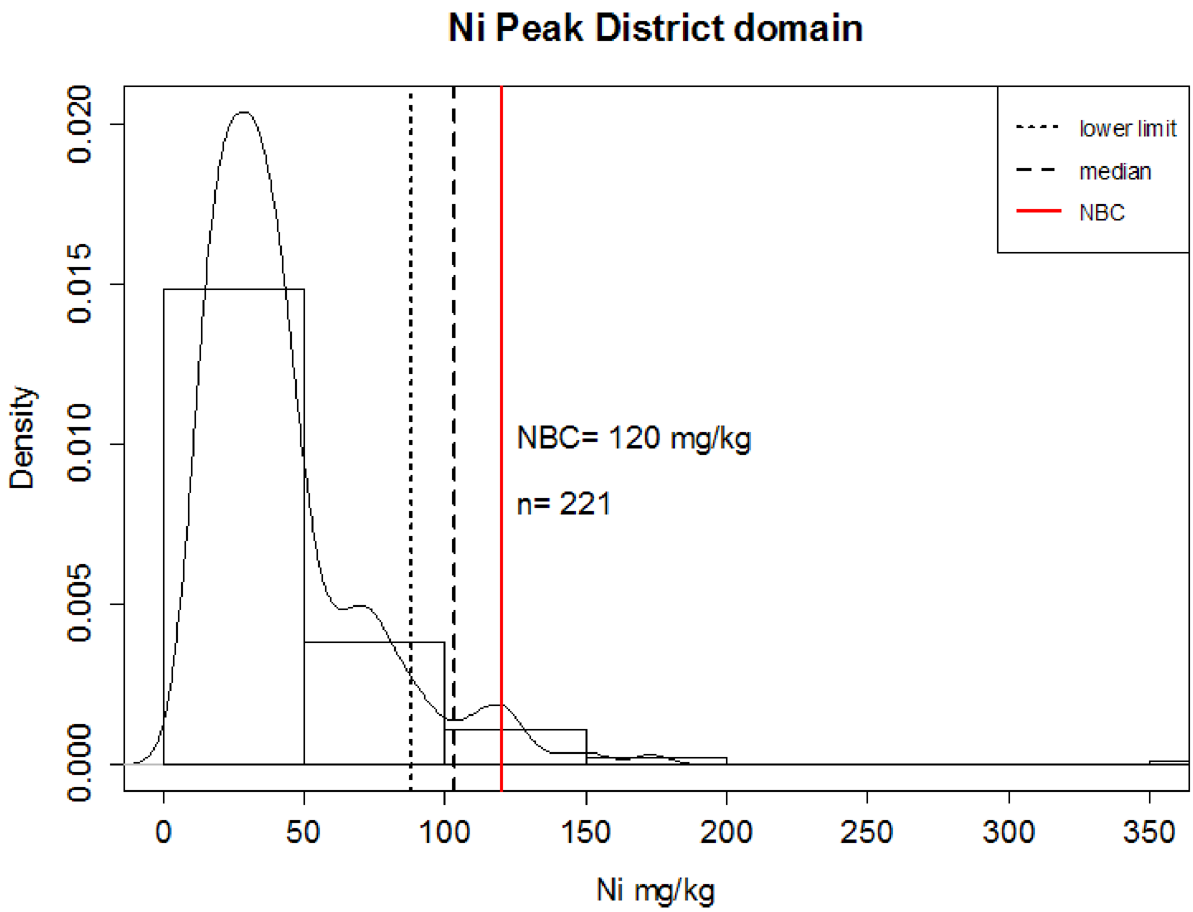

Figure 87: Summary density plot and histogram of the distribution for Ni in the Peak District Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	31.5	34.2	37.9	**32.5**	**35.6**	**38.8**	31.5	34.2	37.9
55	34.2	37.9	40.6	**35.2**	**38.6**	**42.2**	34.1	37.0	41.5
60	37.0	39.7	44.3	**38.1**	**42.0**	**46.0**	36.9	39.9	45.5
65	38.8	42.5	47.0	**41.2**	**45.7**	**50.3**	40.1	43.3	50.1
70	41.6	47.0	54.3	**45.0**	**50.0**	**55.3**	43.3	47.1	55.4
75	47.0	50.7	63.5	**49.1**	**55.1**	**61.4**	47.0	51.6	61.7
80	50.7	62.2	72.6	**54.3**	**61.4**	**68.9**	50.9	57.1	69.7
85	63.5	72.6	80.9	**61.2**	**69.6**	**78.7**	56.4	64.3	80.2
90	73.6	83.1	101.9	**70.9**	**81.6**	**93.0**	63.4	74.7	96.3
95	90.0	113	125	**87.9**	**103**	**120**	75.0	93.2	126

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 31: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Ni in the Peak District Domain (concentrations in mg/kg).

5.4.5 Ultrabasic domain

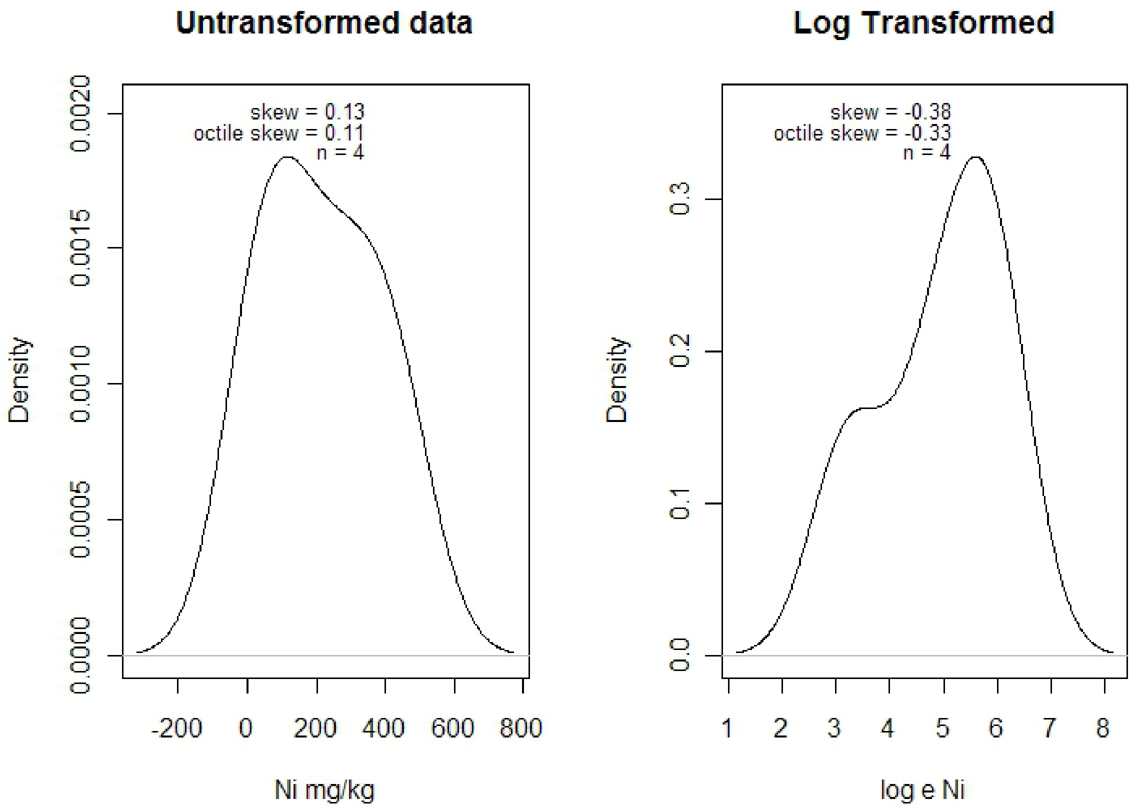

Figure 88: Density distributions for the raw data and the $\log_e$ transformed data for Ni in the Ultrabasic Domain (n = number of samples).

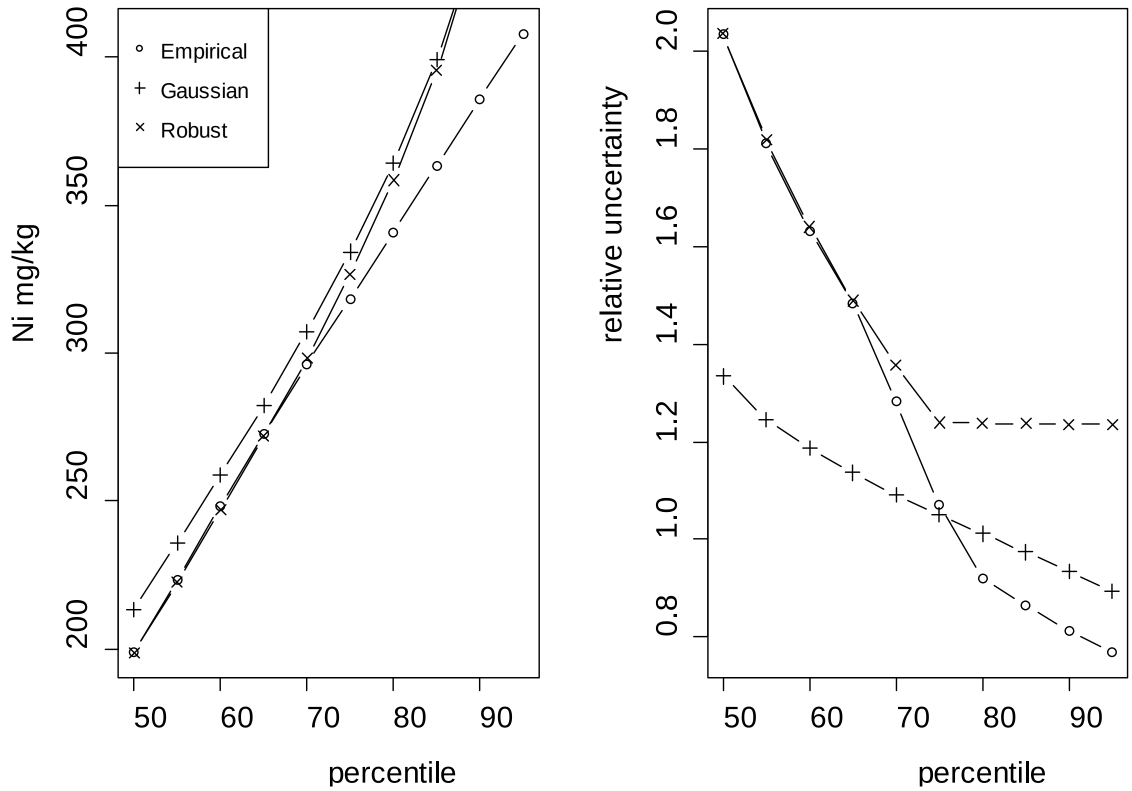

Figure 89: Comparison of empirical, Gaussian and Robust percentiles and relative uncertainty for Ni in the Ultrabasic Domain.

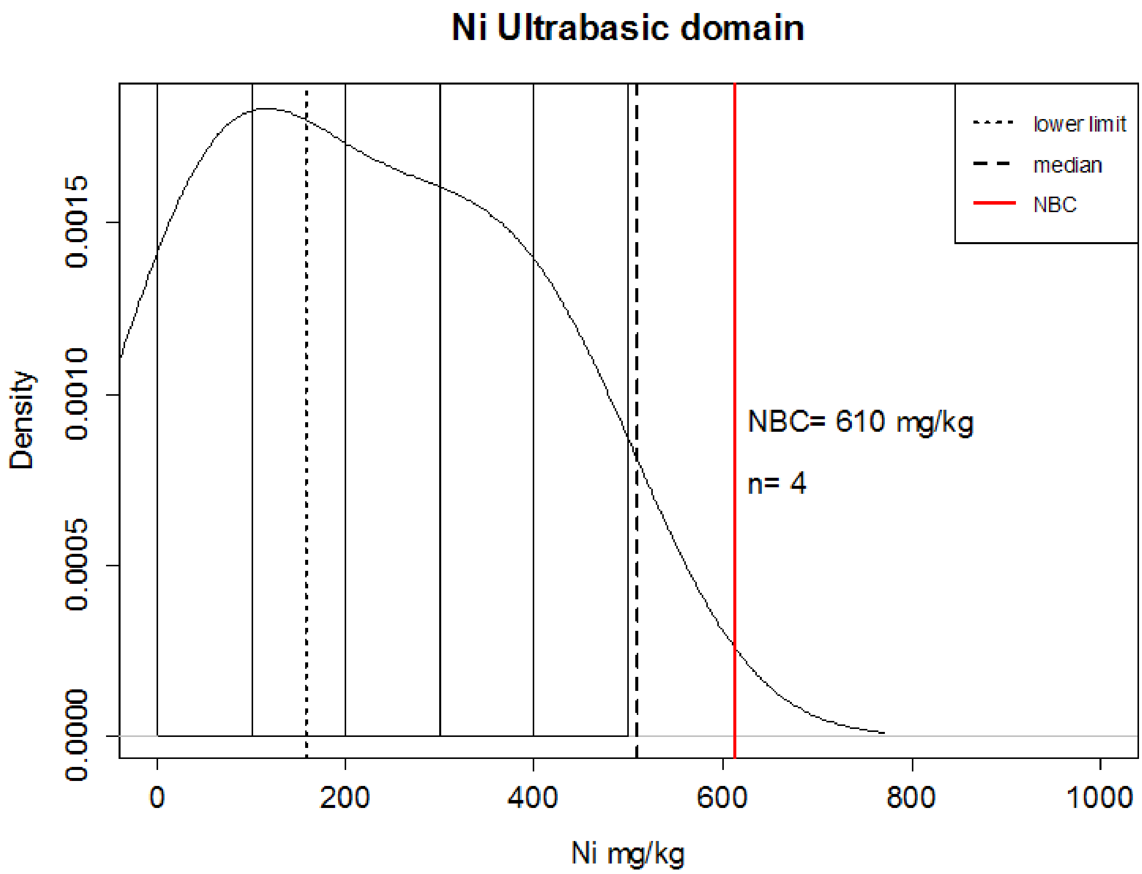

Figure 90: Summary density plot and histogram of the distribution for Ni in the Ultrabasic Domain showing an example NBC (n = number of samples).

Percentile	Emp L	Empirical	Emp H	P L	Parametric	P H	R L	Robust	R H
50	25.4	199	430	**71.1**	**213**	**356**	25.4	199	430
55	25.4	224	430	**77.7**	**236**	**372**	25.4	223	430
60	25.4	248	430	**84.5**	**259**	**392**	25.4	247	430
65	25.4	273	430	**91.4**	**282**	**412**	25.4	272	430
70	50.9	296	430	**98.8**	**307**	**434**	25.4	298	430
75	89.3	318	430	**107**	**334**	**458**	25.4	327	430
80	117	341	430	**116**	**364**	**484**	25.4	358	469
85	117	363	430	**126**	**399**	**514**	25.4	395	514
90	117	386	430	**139**	**443**	**553**	25.4	442	571
95	117	408	430	**158**	**508**	**612**	25.4	511	656

Low (L) and High (H) values represent confidence intervals around the median. Shaded/bold values indicate data used to calculate NBC.

Table 32: Empirical (Emp), parametric Gaussian (P) and Robust Gaussian (R) percentile values for Ni in the Ultrabasic Domain (concentrations in mg/kg).

6 Summary

Exploratory data analysis of the whole data sets and domains, followed by summary statistics of the domains and NBC calculation are presented in this report for Cd, Cu, Hg and Ni. The relevant Technical Guidance Sheets (and Supplementary Information sheets) should be seen as the definitive NBC resource for these elements. The information in this report is provided only for completeness of record, and as an analogous summary to some of the content on As, Pb and BaP found in Ander *et al*. (2011) and Cave *et al.* (2012), there is therefore limited commentary provided on the information within this output.

Cd	**DOMAIN**				
	Principal	**Min. Grp. 1**	**Min. Grp. 2**	**Urban**	**Chalk South**
NBC	**1.0**	**17**	**2.9**	**2.1**	**2.5**
N	*4,418*	*224*	*95*	*9,308*	*265*
Cu	**DOMAIN**				
	Principal	**Mineralisation**	**Urban**		
NBC	**62**	**340**	**190**		
N	*34,504*	*153*	*7,475*		
Hg	**DOMAIN**				
	Principal	**Urban**			
NBC	**0.5**	**1.9**			
N	*1,126*	*512*			
Ni	**DOMAIN**				
	Principal	**Ironstone (Ni)**	**Peak District**	**Basic**	**Ultrabasic**
NBC	**42**	**230**	**120**	*	*
N	*41,768*	*117*	*221*	*23*	*4*

Table 33: Summary Normal Background Concentrations (NBCs) determined for Cd, Cu, Hg and Ni (concentrations in mg/kg). NBCs have been determined for the Ni Basic and Ultrabasic Domains but are not presented here has insufficient (<30) data were available for each domain (N=number of samples).

References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.

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