



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL

The advanced soil geochemical atlas of England and Wales

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Bibliographic reference: RAWLINS, B G, McGRATH, S P, SCHEIB, A J, BREWARD, N, CAVE, M, LISTER, T R, INGHAM, M, GOWING, C and CARTER, S. 2012. The advanced soil geochemical atlas of England and Wales. British Geological Survey, Keyworth.
www.bgs.ac.uk/gbase/advsoilatlasEW.html

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ISBN 978 0 85272 709 6

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BRITISH GEOLOGICAL SURVEY

The advanced soil geochemical atlas of England and Wales

The advanced soil geochemical atlas of England and Wales

PERIOD	GROUP									
1	1									
1	1									
	H HYDROGEN									
2	3	4								
	Li LITHIUM	Be BERYLLIUM								
3	11	12								
	Na SODIUM	Mg MAGNESIUM								
4	19	20	21	22	23	24	25	26	27	
	K POTASSIUM	Ca CALCIUM	Sc SCANDIUM	Ti TITANIUM	V VANADIUM	Cr CHROMIUM	Mn MANGANESE	Fe IRON	Co COBALT	
5	37	38	39	40	41	42	43	44	45	
	Rb RUBIDIUM	Sr STRONTIUM	Y YTTRIUM	Zr ZIRCONIUM	Nb NIOBIUM	Mo MOLYBDENUM	Tc TECHNETIUM	Ru RUTHENIUM	Rh RHODIUM	
6	55	56	57-71	72	73	74	75	76	77	
	Cs CAESIUM	Ba BARIUM	La-Lu LANTHANIDE	Hf HAFNIUM	Ta TANTALUM	W TUNGSTEN	Re RHENIUM	Os OSMIUM	Ir IRIDIUM	
7	87	88	89-103	104	105	106	107	108	109	
	Fr FRANCIUM	Ra RADIUM	Ac-Lr ACTINIDE	Rf RUTHERFORDIUM	Db DUBIUM	Sg SEABORGIUM	Bh BOHRIUM	Hs HASSIUM	Mt MEITNERIUM	

Elements in the original and advanced atlas

Elements only in the advanced atlas

Not determined

LANTHANIDE

6	57	58	59	60	61	62
	La LANTHANUM	Ce CERIUM	Pr PRASEODYMIUM	Nd NEODYMIUM	Pm PROMETHIUM	Sm SAMARIUM

7	89	90	91	92	93	94
	Ac ACTINIUM	Th THORIUM	Pa PROTACTINIUM	U URANIUM	Np NEPTUNIUM	Pu PLUTONIUM

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Analysis

Data conditioning

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Creating the geochemical maps

Reference maps

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									2 He HELIUM
			13	14	15	16	17		
			5 B BORON	6 C CARBON	7 N NITROGEN	8 O OXYGEN	9 F FLUORINE	10 Ne NEON	
			13 Al ALUMINIUM	14 Si SILICON	15 P PHOSPHORUS	16 S SULPHUR	17 Cl CHLORINE	18 Ar ARGON	
28 Ni NICKEL	29 Cu COPPER	30 Zn ZINC	31 Ga GALLIUM	32 Ge GERMANIUM	33 As ARSENIC	34 Se SELENIUM	35 Br BROMINE	36 Kr KRYPTON	
46 Pd PALLADIUM	47 Ag SILVER	48 Cd CADMIUM	49 In INDIUM	50 Sn TIN	51 Sb ANTIMONY	52 Te TELLURIUM	53 I IODINE	54 Xe XENON	
78 Pt PLATINUM	79 Au GOLD	80 Hg MERCURY	81 Tl THALLIUM	82 Pb LEAD	83 Bi BISMUTH	84 Po POLONIUM	85 At ASTATINE	86 Rn RADON	
110 Uun UNUNNIUM	111 Uuu UNUNUNIUM	112 Uub UNUNBIUM		114 Uuq UNUNQUADIUM					
63 Eu EUROPIUM	64 Gd GADOLINIUM	65 Tb TERBIUM	66 Dy DYSPROSIUM	67 Ho HOLMIUM	68 Er ERBIUM	69 Tm THULIUM	70 Yb YTTERBIUM	71 Lu LUTETIUM	
95 Am AMERICIUM	96 Cm CURIUM	97 Bk BERKELIUM	98 Cf CALIFORNIUM	99 Es EINSTEINIUM	100 Fm FERMIUM	101 Md MENDELEVIUM	102 No NOBELIUM	103 Lr LAWRENCIUM	

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Foreword

This publication is the outcome of collaborative research between the British Geological Survey (BGS) and Rothamsted Research. BGS is a research institute partly funded by the Natural Environment Research Council (NERC). Rothamsted Research receives strategic funding from the Biotechnology and Biological Sciences Research Council (BBSRC). The analyses presented in this atlas were funded from the NERC core grant provided to the British Geological Survey. Details of the availability of the geochemical data are available from the website:

www.bgs.ac.uk/gbase/advsoilatlasEW

Introduction

The total concentration of different elements in the soil – its geochemistry – has implications for both human and animal health. For example, soil geochemistry influences the availability of a range of essential and potentially toxic elements which has implications for their uptake by grazing animals and crops. Understanding the natural or geogenic concentrations of elements in the soil can help to determine whether, and the extent to which, soil may have been contaminated by anthropogenic activities. Much of the variation in the concentration of major and trace elements in the soil is accounted for by the parent material from which the soil formed (Rawlins et al., 2003).

The analyses presented in this – the advanced atlas are for those soil samples collected for the National Soil Inventory (NSI) by the Soil Survey of England and Wales (now the National Soil Resources Institute, Cranfield University, UK) as described in McGrath and Loveland (1992) in the *Soil Geochemical Atlas of England and Wales*. The geochemical analyses presented in the original atlas were for a series of 17 elements. The advanced atlas presents analyses for a total of 53 elements which includes the original 17 elements. A periodic table shows those elements for which analyses are available. The geochemical maps, descriptions of the spatial distribution of each element and summary statistics can be accessed through clicking the symbol for each element.

Sampling and sample preparation

Soil sampling took place between 1978 and 1982 and was restricted to the uppermost 15 cm of *mineral* soil (or less if rock intervened), or of peat, as appropriate, i.e. litter layers were not sampled, as they were regarded as ephemeral. The actual sampling depth was recorded. Twenty-five cores of soil were taken at the nodes of a 4 m grid within a 20 m x 20 m square centred on each OS 5-km grid point across England and Wales. A total of 5691 samples were collected; large urban areas were avoided. The cores were taken with a screw-type, mild-steel auger, to avoid contamination from traces of elements such as chromium and manganese present in stainless, plated or similar special steels. The cores of soil were bulked and mixed well in the field, double-bagged in food-grade polythene bags, and a waterproof and rot-proof label ('Synteape') placed between the bags. The target sample mass was 450 g of air-dried soil. In organic or other loosely packed layers, it was often necessary to take many more than 25 auger cores. In such cases, the interval of the subsampling grid decreased in 1 m steps (e.g. 3 m x 3 m) and the whole grid resampled. This procedure was repeated until sufficient soil was judged to have been taken.

Field-moist samples of soil were refrigerated (to 4°C) on the day of sampling, and transported to the Soil Survey laboratory within the following two weeks. On receipt, each sample was allocated a unique sample number, cross-referenced to the National Grid reference of the site. Samples were spread out on sheets of 'Kraft' paper to air-dry, after which each was split into two equal portions. One of these was kept as a reference sample, without further treatment, in case of contamination or loss during subsequent analysis. The other sample was milled in a mild-steel roller-mill to pass a 2-mm aperture sieve. Preliminary work had shown that no detectable contamination of the samples arose from this procedure. A further 25 g subsample was taken from the <2 mm air-dry sample by coning and quartering, and ground to <150 micrometres in an all-agate planetary ball mill. These samples were transferred to the BGS laboratories for determination of total element concentrations by X-Ray Fluorescence Spectrometry (XRFS). At the sample preparation facility, BGS, Keyworth, a 10 g subsample of milled material was mixed thoroughly with 3 g of binder for three minutes in an agate planetary ball mill. This mixture was then pressed into a 32 mm diameter pellet at 250 kN using a Herzog (HTP-40) semi-automatic press. The binder consists of nine parts EMU120FD styrene co-polymer (BASF plc) and one part Ceridust 3620, a micronised polyethylene wax (Hoechst), after van Zyl (1982).

Around thirty years have passed since the samples were taken, and in that time they were stored air dry. It is unlikely that any changes took place in the total concentrations of the elements that were determined in this advanced analysis. In that time it is unlikely also that the concentrations of most of the elements have changed markedly at the field sites. Possible exceptions are the plant nutrients Ca, K, Mg, P and S which are often added in fertilisers or liming materials, and in the

case of S, any sulphates added to soil rapidly wash out under most conditions. Examples of those elements that do not change rapidly are Co, Ni and V where soil samples were retaken some 15 years later in the Humber–Trent region. The mean and median concentrations measured varied little between the two dates, often within the limit of expected analytical variation (Lark et al, 2006). This reanalysis therefore provides a good benchmark for the concentrations of most of the elements determined in the soils of England and Wales that is unlikely to have been altered by such processes as natural or industrially derived deposition from the atmosphere or the deposition of waste materials, which tends to be localised.

Analysis

Major, minor and trace-element determinations for the NSI samples were carried out by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRFS) and energy-dispersive (polarised) X-ray fluorescence spectrometry (ED-P-XRFS) (Ingham and Vrebos, 1994). A Philips *MagiX PRO* and a PANalytical *Axios Advanced* sequential wavelength-dispersive x-ray fluorescence spectrometer both fitted with rhodium-anode X-ray tubes (4 kW 60 kV) were used for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Nd, Sm, Yb, Hf, Ta, W, Tl, Pb, Bi, Th and U. The spectrometers were controlled using PANalytical *SuperQ* application software package, version 4.00, running under MicroSoft™ WindowsXP Pro operating system. A PANalytical *Epsilon5* energy-dispersive, polarised, x-ray fluorescence spectrometer fitted with a gadolinium-anode X-ray tube (600 W 100 kV) was used for Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, and Ce. The PANalytical *Epsilon5* was controlled using *Epsilon5* application software package, version 2.0A, running under MicroSoft™ WindowsXP Pro operating system.

Reported values of the lower limit of detection (LLD) for each element are listed in Table 1. To achieve improved LLDs for Se and Tl, the channel analysis times were increased significantly. This yielded an improvement in LLDs of 0.1 and 0.15 mg/kg respectively. The ED-XRFS analytes were also adjusted, improving the LLDs for example for Cd from 0.5 to 0.25 mg/kg. Conversely, channel counting times were decreased for As, Nd and Hf with a reduction of LLDs of 1.5, 1.4 and 1 mg/kg respectively. Remaining LLDs for major elements reflect the standard values routinely reported for soil and sediment samples analysed for the Geochemical Baseline Survey of the Environment (G-BASE) project.

Table 1 Values of lower limit of detection (LLD) for all elements (mg/kg, or where stated %).

Element	LLD	**Method	Element	LLD	**Method
Ag	0.25	ED-XRFS	*Ni	1.3	WD-XRFS
*Al (%)	0.05	WD-XRFS	*P (%)	0.0087	WD-XRFS
*As	2.4	WD-XRFS	*Pb	1.2	WD-XRFS
Ba	0.5	ED-XRFS	Pd	0.25	ED-XRFS
Bi	0.3	WD-XRFS	Rb	0.7	WD-XRFS
Br	0.7	WD-XRFS	S	801	WD-XRFS
*Ca (%)	0.025	WD-XRFS	Sb	0.25	ED-XRFS
*Cd	0.25	ED-XRFS	*Sc	2.4	WD-XRFS
*Ce	0.6	ED-XRFS	Se	0.1	WD-XRFS
*Co	1.5	WD-XRFS	Si (%)	0.023	WD-XRFS
*Cr	2.8	WD-XRFS	Sm	3.0	WD-XRFS
*Cs	0.5	ED-XRFS	*Sn	0.25	ED-XRFS
*Cu	1.2	WD-XRFS	Sr	0.8	WD-XRFS
*Fe (%)	0.0049	WD-XRFS	*Ta	1.1	WD-XRFS
Ga	1.0	WD-XRFS	Te	0.35	ED-XRFS
Ge	0.5	WD-XRFS	Th	0.7	WD-XRFS
Hf	2.0	WD-XRFS	*Th	0.7	WD-XRFS
I	0.35	ED-XRFS	Ti (%)	0.0036	WD-XRFS
In	0.25	ED-XRFS	Tl	0.35	WD-XRFS
*K (%)	0.0066	WD-XRFS	*U	0.7	WD-XRFS
La	0.6	ED-XRFS	*V	2.7	WD-XRFS
*Mg(%)	0.109	WD-XRFS	*W	0.6	WD-XRFS
*Mn (%)	0.0054	WD-XRFS	Y	0.8	WD-XRFS
*Mo	0.2	WD-XRFS	Yb	1.3	WD-XRFS
*Na (%)	0.2	WD-XRFS	*Zn	1.1	WD-XRFS
Nb	0.7	WD-XRFS	*Zr	0.8	WD-XRFS
*Nd	5.0	WD-XRFS			

* denotes those elements for which a correction factor was applied to ensure the reported analyses were consistent with previous analyses of internal reference materials.

** WD- and ED-XRFS refer to wavelength and energy dispersive X-ray fluorescence spectrometry respectively.

Data conditioning

Once the data had been checked, verified and accepted from the laboratory analyses, further checks and conditioning of the data was carried out. Data from the reanalysis of NSI samples

underwent two processes. First, comparison with the contemporaneous measurements of both primary and secondary reference materials to quantify analytical accuracy and precision. Second, normalisation and levelling of the data to previous XRF geochemical analyses of geochemical samples from across England and Wales as part of the G-BASE survey (Johnson et al., 2005) which ensures that direct comparisons can be made between the data.

Reference materials (RMs) are samples that have been collected, prepared and analysed according to documented procedures, and analysed repeatedly, to give what become accepted values (Johnson, 2011). Table 2 lists reference materials used during the analysis. Primary reference materials (PRMs) were four international certified standards with recognised and accepted elemental concentrations. Each of these was analysed twice by XRF after each batch of 500 samples. The four secondary reference materials (SRM), also listed in Table 2, were BGS in-house reference samples developed for internal use by the Geochemical Baselines Survey of the Environment (G-BASE) project. These are bulk stream sediments and soil standards collected at various places in the UK. The SRMs were inserted into the NSI samples at a frequency of two standards per 100 samples and importantly, were 'blind' to the laboratory analysts.

Table 2 Summary information for the reference materials (RMs) included in the XRF analysis.

Primary RMs		Secondary RMs	
ID	Description	ID	Description
GSS-1 (GBW07401)	Soil reference material. National Research Centre for CRMs, Office for China	S15B	Stream sediment reference material. Penrith sandstone, UK
GSS-4 (GBW07404)	Lake sediment reference material from CCRMP*. Composite of two lake sediments from Ontario, Canada.	S57A	Surface soil reference material, UK
LKSD-1	Lake sediment reference material from CCRMP*. Composite of two lake sediments from Ontario, Canada.	S57A	Surface soil reference material, UK
LKSD-4	Lake sediment reference material CCRMP*. Composite of two lake sediments from Ontario and Saskatchewan, Canada.	S58A	Profile soil reference material, UK

* Canadian Certified Reference Material Project; Natural Resources Canada.

The results of the analysis of the SRMs are crucial for the process of assessing the accuracy of the data and normalisation and levelling of the latter to existing national geochemical datasets. To assess the accuracy, SRM results are checked against accepted values for each element (values

listed in Lister and Johnson, 2005) graphically, using Shewhart control plots. These plots also help to identify any bias in the data, where laboratory batches may need to be levelled using a linear transformation. Levelling is generally required following major changes in analytical procedures and to level new datasets relative to regional-scale geochemical data held by BGS. In such cases, the normalisation of SRM results gives levelling factors that are applied to the data (Lister and Johnson, 2005). Those samples for which the reported values were below the detection limit for each analysis were set to half the detection limit (see Table 1) for creating the maps and calculating summary statistics.

Table 3 Coefficient of variation (%) for each of the 53 elements from repeated analyses (n=25) of the four certified reference materials (Table 2).

Element	Reference material			
	GSS-1	GSS-6	LKSD-1	LKSD-4
Ag	39	NA	16	49
Al	2.7	2.3	3.4	3.9
As	3.9	2	5	5
Ba	1.2	0.79	1.1	1.3
Bi	20	1.7	41	85
Br	20	5.6	6.7	1.5
Ca	1.2	2.9	1.5	1.2
Cd	2.5	NA	8.9	5.5
Ce	1.3	1.2	2.6	1.9
Cl	25	44	4.2	13
Co	5.9	12	4.9	8.3
Cr	4	2.9	3.5	4.8
Cs	2.4	2.4	18	12
Cu	3.6	1.9	2	3
Fe	0.92	1.5	1.2	1.7
Ga	2.3	3.3	5	5.2
Ge	39	12	75	33
Hf	20	13	32	29
I	6.6	1.6	7.8	2.2
In	29	35	40	33
K	2.9	3.5	3	3.4
La	1.3	1.6	2.5	1.5
Mg	3.5	NA	5.1	4
Mn	2.1	2	2.7	3.3

Element	Reference material			
	GSS-1	GSS-6	LKSD-1	LKSD-4
Mo	6.9	1.2	1.7	8.6
Na	6.2	NA	6.2	NA
Nb	2.2	1.5	7.4	5.4
Nd	7.3	12	13	6.3
Ni	3.6	2.2	3.6	2.8
P	2.8	7.8	4.3	3.3
Pb	1.3	0.64	1.5	1.4
Pd	NA	NA	NA	NA
Rb	0.63	0.8	1.8	1.8
S	9.8	11	NA	0.7
Sb	8	0.85	13	8.6
Sc	7.6	6.1	24	12
Se	67	5.9	6.1	2
Si	2.5	2.3	3.2	3.3
Sm	39	47	44	19
Sn	2.7	0.92	4.4	2.9
Sr	0.64	1.3	1.4	1.5
Ta	30	15	63	99
Te	16	37	NA	NA
Th	3.2	2.3	22	7
Ti	2.9	3.1	3.1	3.7
Tl	26	14	46	15
U	7.8	6.1	2	1.7
V	1.8	1.8	2.2	1.5
W	6.9	2	15	15
Y	2	3.2	2.6	1.9
Yb	29	22	31	18
Zn	2.3	3.7	3.8	4.1
Zr	0.79	0.47	3.2	2

NA not analysed

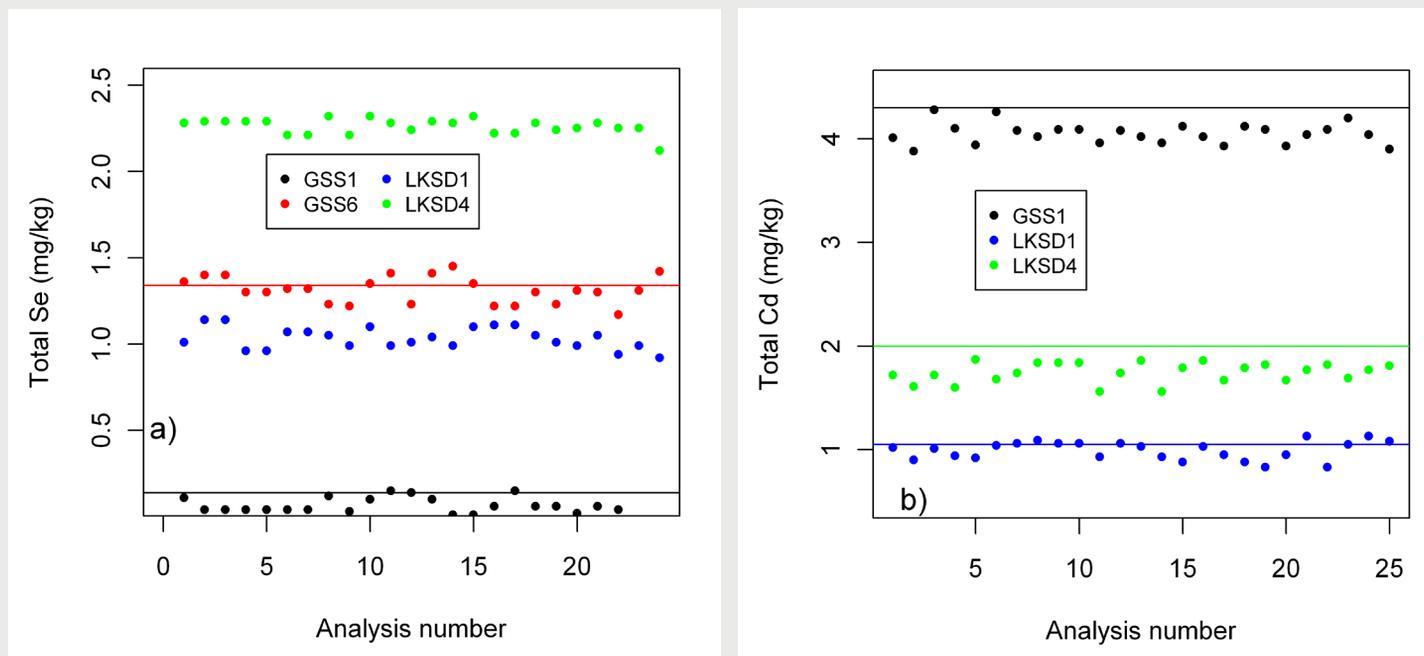


Figure 1 XRFS repeat analyses of the certified reference materials (Table 1) at intervals spanning the period of analysis of the NSI samples for a) Se, and b) Cd. The coloured lines denote the certified values of each of the reference materials; lines are only displayed for those elements for which certified values are available.

To provide a quantitative estimate of analytical precision for the XRFS analyses for each element, we calculated the coefficient of variation (CV- %) based on repeated analyses of the four reference materials which were undertaken at regular intervals throughout analyses of all the NSI samples. The CV values are presented in Table 3; in general they indicate that the analytical precision is very good (CV <5%). Larger (>10%) values show that the precision is somewhat poorer and suggests care should be taken in placing too much interpretation on small differences in the reported values for those elements.

To assess analytical precision we can compare the reported values from repeated analyses of reference materials with their certified values. Examples of this are shown in Figure 1 above for Se and Cd. In both cases, the repeated analyses are close to or slightly below the certified values suggesting that the reported values are generally accurate.

Summary statistics and plots for each element

Summary statistics and plots were created using the R environment (R core team, 2010) and bespoke scripts which include functions from the fBasics and Hmisc packages. Three plots, including a histogram with boxplot, a normal Q-Q plot and cumulative frequency plot as well as a list of descriptive statistics were calculated in R for each element. These are all aligned and displayed on one page for each element.

Creating the geochemical maps

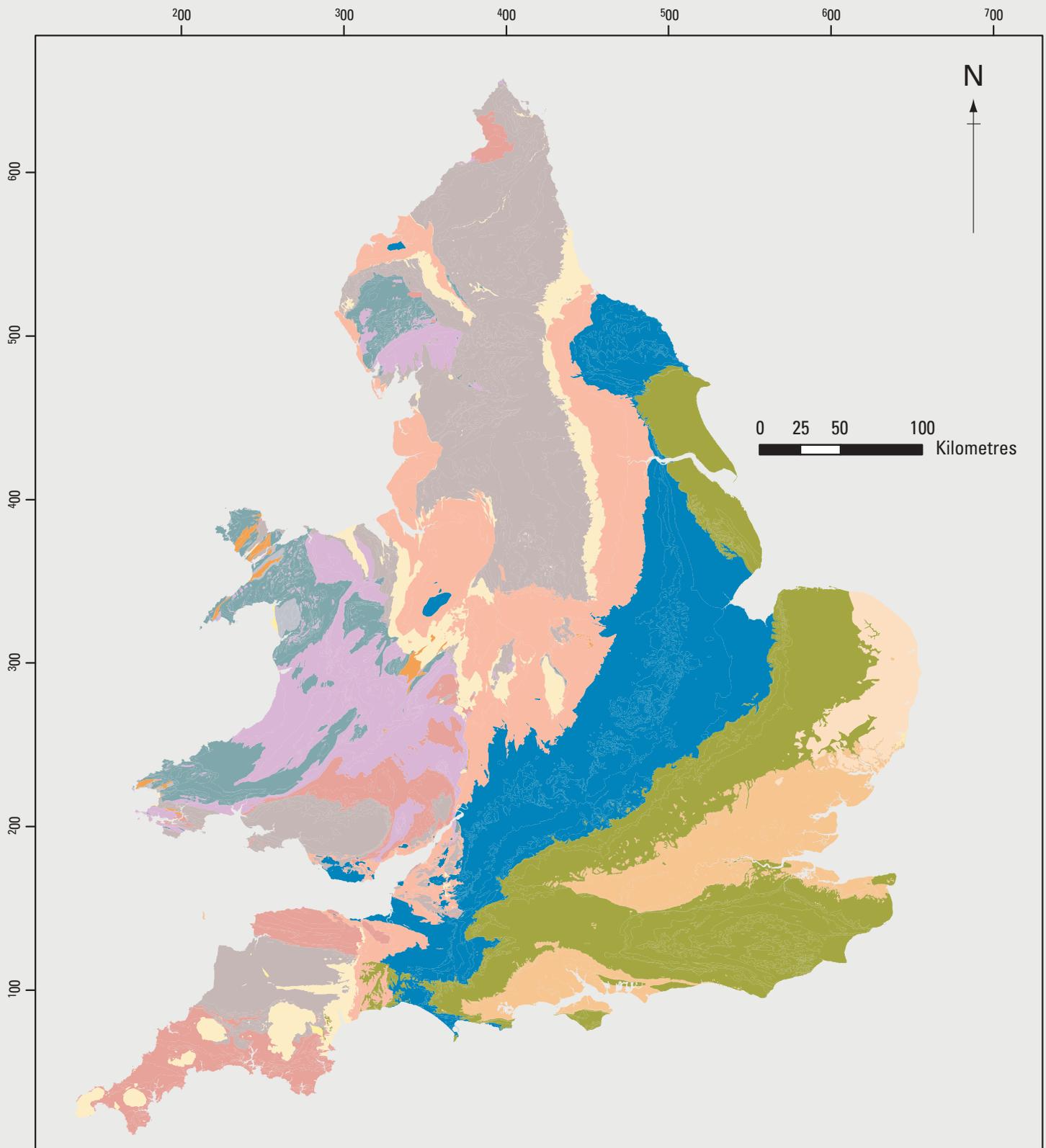
The geochemical maps were created using the R environment (R core team, 2010) and bespoke scripts which include functions under the 'sp' (Pebesma and Bivand, 2005) and 'gstat' (Pebesma, 2004) packages. For each element, the skewness of its frequency distribution was calculated and if this was greater than 1 the values were log transformed. Distributions for which the skewness was less than 1 were not transformed. Predictions were made on a 2.5 km by 2.5 km grid using the data and by applying inverse distance weighted (IDW) interpolation. A search radius of 30 km was used with a minimum of eight and a maximum of 24 sampling points within this. For those elements which were log transformed, the estimates were back transformed by applying the exponential function (e^x).

For each element two maps were plotted. The first uses an arithmetic scale for the colour scheme which separates the distribution into ten arithmetic intervals – this is particularly effective if the data are not strongly skewed as each interval is represented on the map and the each interval is the same. The second map has a percentile scale – in this case the intervals are calculated as the deciles (10th percentile, 20th percentile ... 90th percentile) of the cumulative frequency distribution. This approach is useful if the data are strongly skewed because the colours account for the non-linear variation; the viewer must always remember that the *concentration* intervals are not equal. The advantage of presenting maps in both these forms can be appreciated when considering the maps of cadmium (Cd). The arithmetic map indicates that the largest number of high values occur in Derbyshire (central England), but the subtle variations are obscured when compared to the percentile scale map which highlights other features of the spatial distribution.

The concentrations of the most abundant elements are expressed as percentages in soil (%) whilst the concentrations of those elements of lower abundance are expressed in milligrams per kilogram of soil (mg/kg).

Reference maps

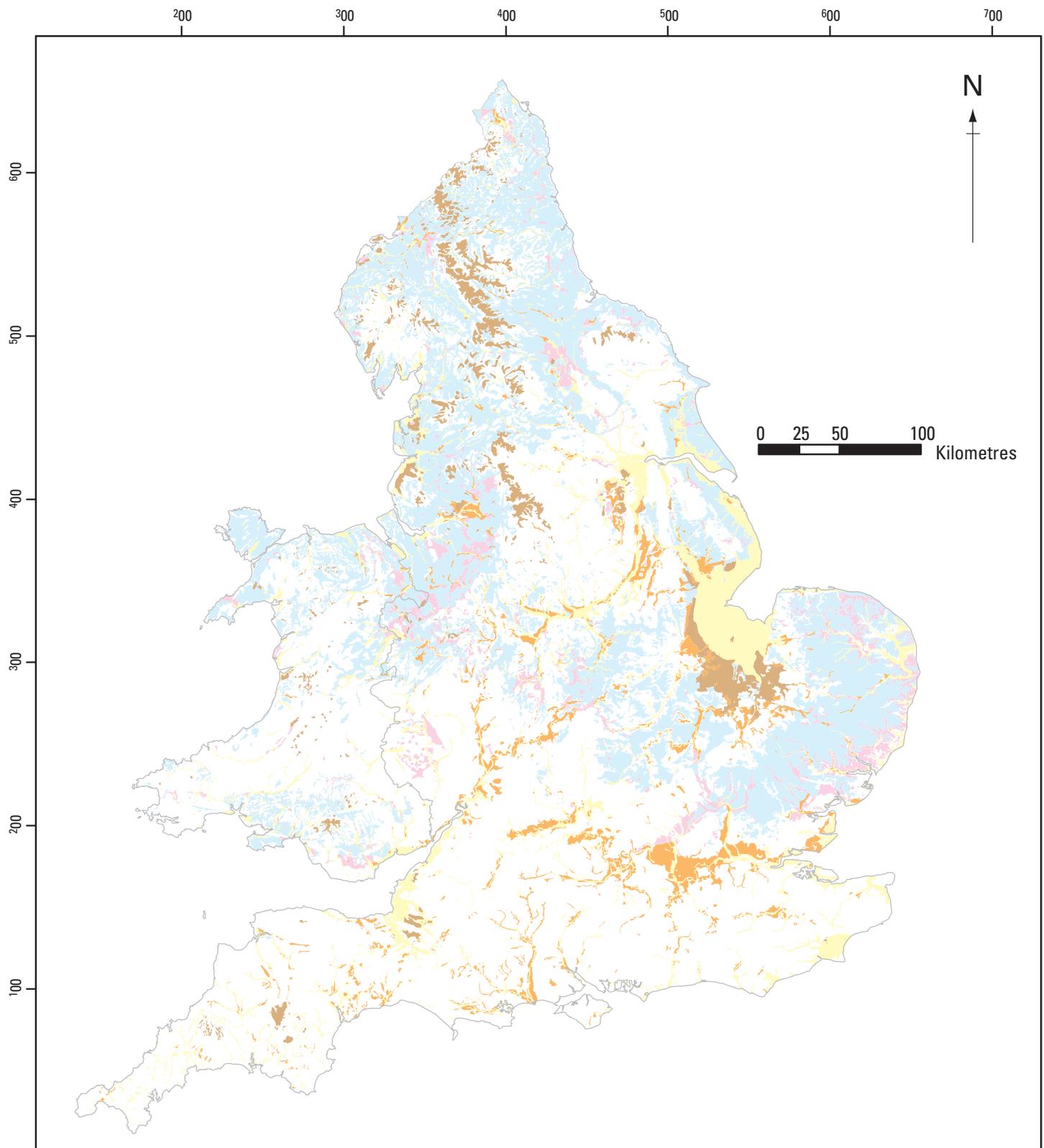
To aid the descriptions of the spatial distributions of each element, a series of three reference maps covering England and Wales are referred to in the text. Two of these maps show the distribution of the major types of bedrock geology and superficial deposits across England and Wales. The third map shows the topography, major rivers and roads, and the large urban areas and their names. These can be accessed through the map icons on the periodic table of elements.



Bedrock geology map for England and Wales

Key

 Quaternary	 Carboniferous
 Neogene	 Devonian
 Palaeogene	 Silurian
 Cretaceous	 Ordovician
 Jurassic	 Cambrian
 Triassic	 Lewisian Complex
 Permian	



Superficial geology map for England and Wales

Key

- Glacial sand and gravel
- Alluvium
- Peat
- River terrace deposits (undifferentiated)
- Till



Topographic map for England and Wales

Key

- Urban area
- Topographic features
- Main road
- River
- Metres above sea level
- 0-75
- 75-150
- 150-300
- 300-450
- 450-600
- Over 600

Aluminium (Al)

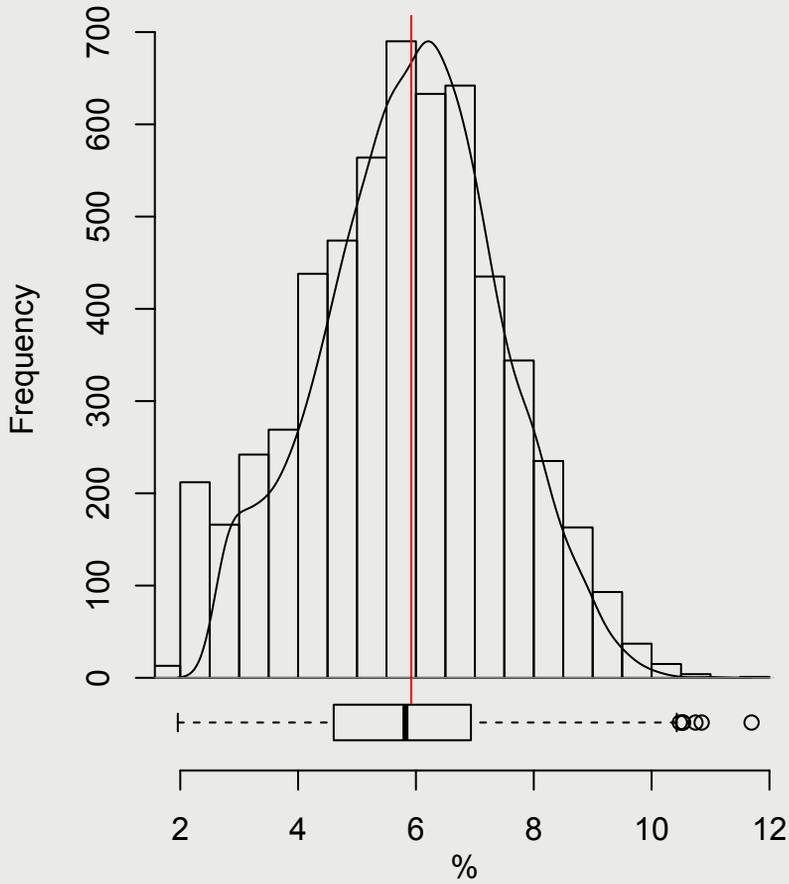
Aluminium is a major element, typically present at about 8% by weight in the Earth's upper continental crust and at similar levels in most rock types, though lower in sandstones and limestones. Aluminium is also abundant in soils, being present in the matrix of clays and other silicate minerals and consequently most of this is not biologically available. Total aluminium in soil reflects the type of soil and the underlying geology.

Soils formed over the mainly argillaceous rocks of Devonian and Carboniferous age in the South West peninsula, Ordovician sediments in the Lake District, the Silurian rocks of western and central Wales, the Yorkshire–Nottinghamshire coalfield and the Jurassic outcrop of the Midlands show generally high Al concentrations.

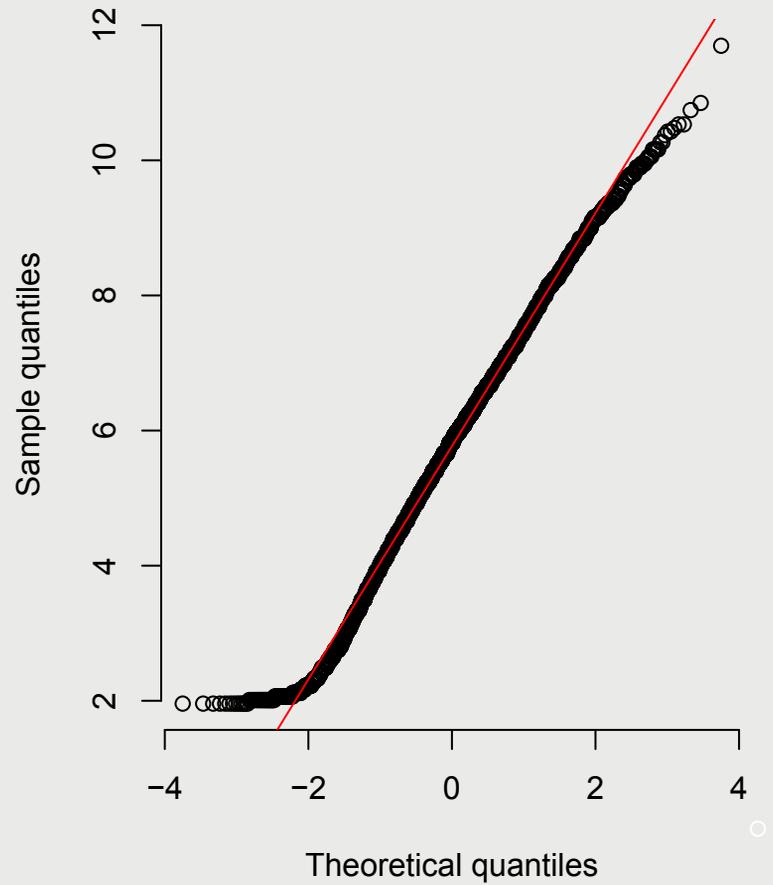
At the opposite extreme, low Al is a marker of organic-rich soils, which contain a smaller proportion of aluminosilicate minerals (McGrath and Loveland, 1992). Clear examples of these are the upland peats in the Pennines and over the major granite intrusions of Dartmoor and Bodmin Moor in Devon and Cornwall, the lowland peats in the Fens and Brecklands of East Anglia and the heath lands to the south-west of London near Bracknell and Guildford. The Chalk outcrop in southern and eastern England also shows low Al concentrations.

Aluminium is not completely extracted from the soil matrix during aqua regia digestion (McGrath and Loveland, 1992), so the values reported here (using the XRF-S method) are higher than those reported in McGrath and Loveland (1992). The differences are large (median concentrations of 2.9 and 5.8% respectively).

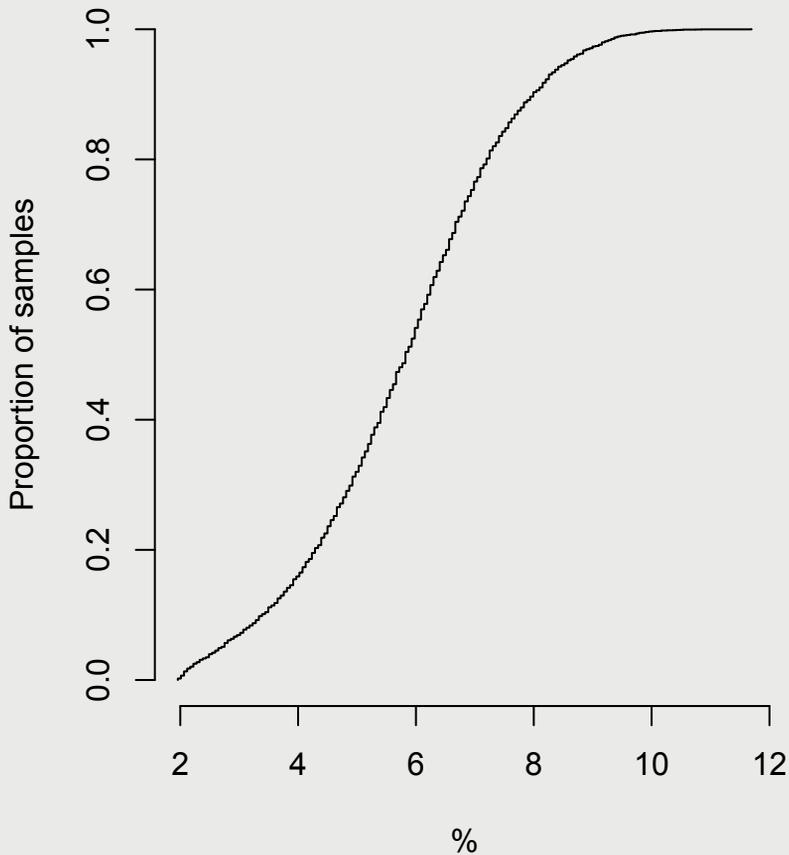
Histogram and boxplot



Normal Q-Q plot



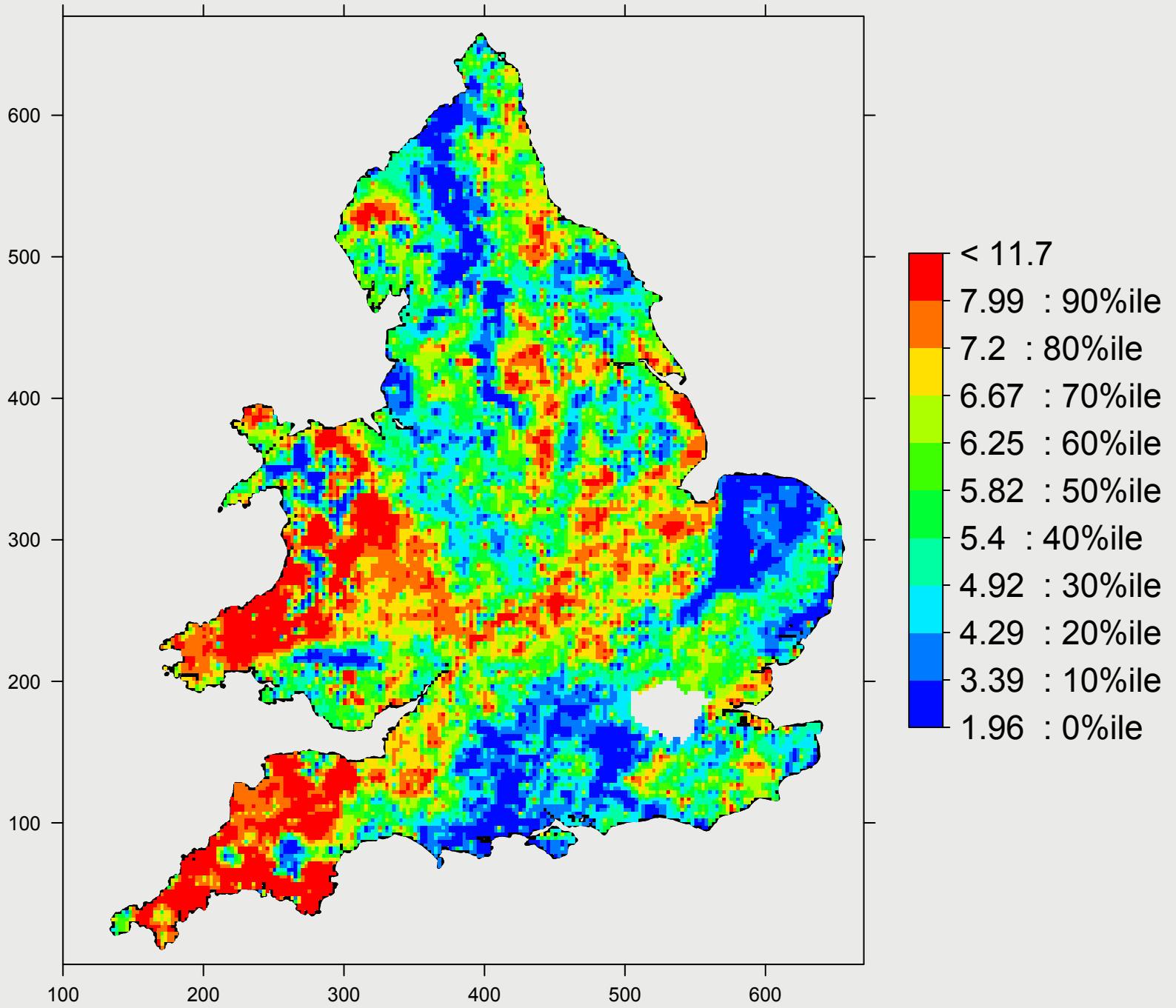
Cumulative frequency



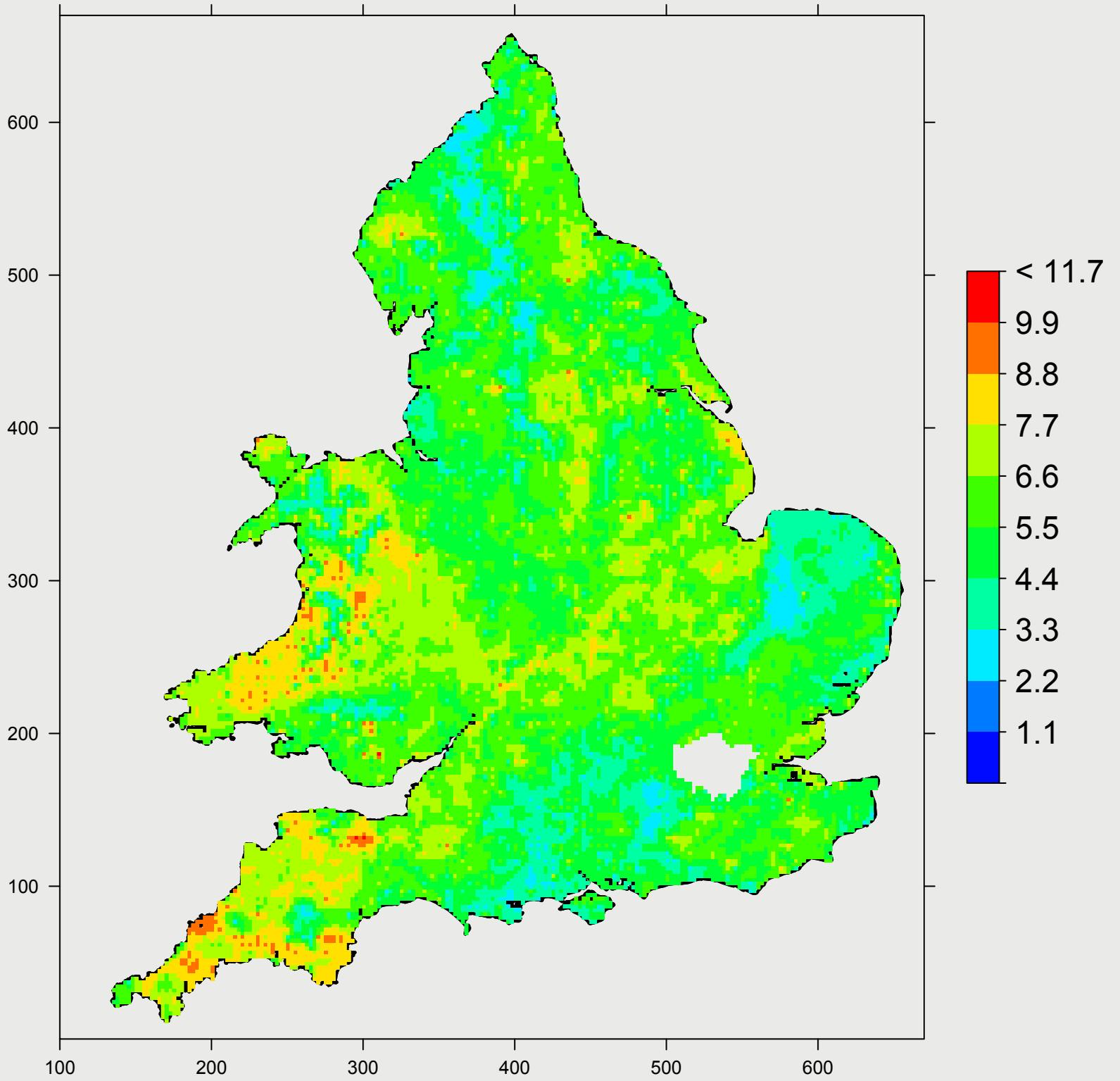
Al - Aluminium %

- mean= 5.8
- median= 5.8
- 10th percentile= 3.4
- 25th percentile= 4.6
- 75th percentile= 6.9
- 90th percentile= 8
- min= 2
- max= 12
- skewness= -0.061
- n= 5670

Topsoil aluminium (% ; percentile scale)



Topsoil aluminium (% ; arithmetic scale)



Antimony (Sb)

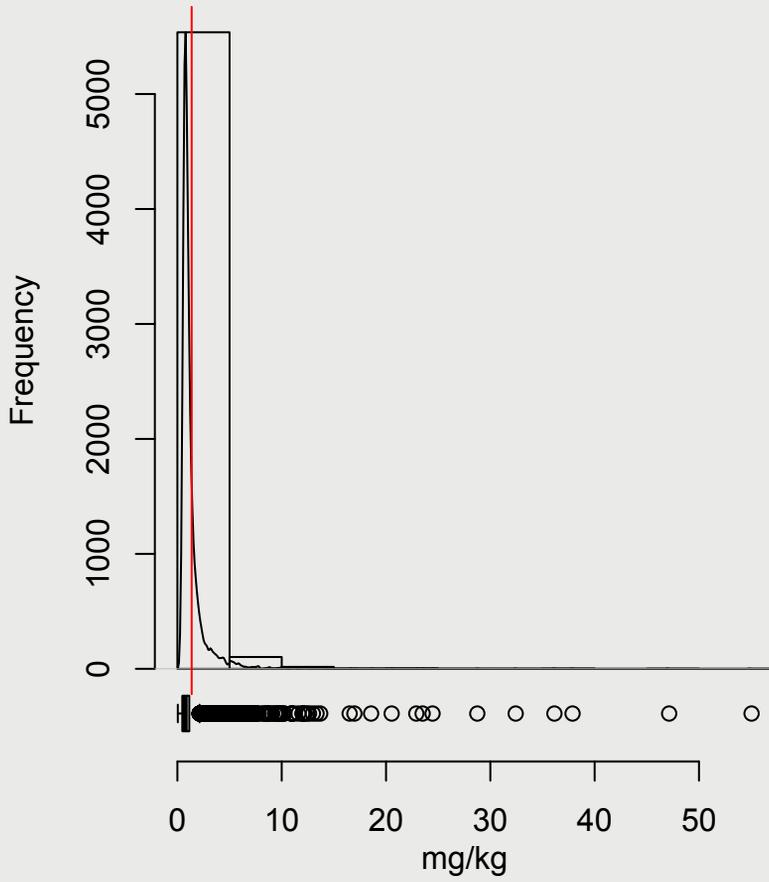
Antimony (Sb) is a rather rare nonmetallic element, geochemically closely associated with arsenic and sulphur. It is toxic and some of its compounds are known to be carcinogenic. It is used in alloys and batteries, semiconductors and pharmaceuticals. The estimated upper continental crust concentrations of Sb are typically between 0.2 and 0.3 mg/kg. Its concentration in the soils of England and Wales ranges from <0.1 mg/kg to 55 mg/kg.

The highest natural concentrations in soil (>2 mg/kg) occur in parts of north-west England (the Lake District, the Northern Pennines and the Peak District), and smaller areas in Wales, Shropshire and the Mendips, where the high Sb levels are associated with metal-sulphide mineralisation and former mining for lead, zinc and copper. High natural levels also occur in the mineralised regions of Devon and Cornwall, which also have a long history of metal mining. Other naturally high Sb concentrations are associated with black shale lithologies, for example in south Derbyshire.

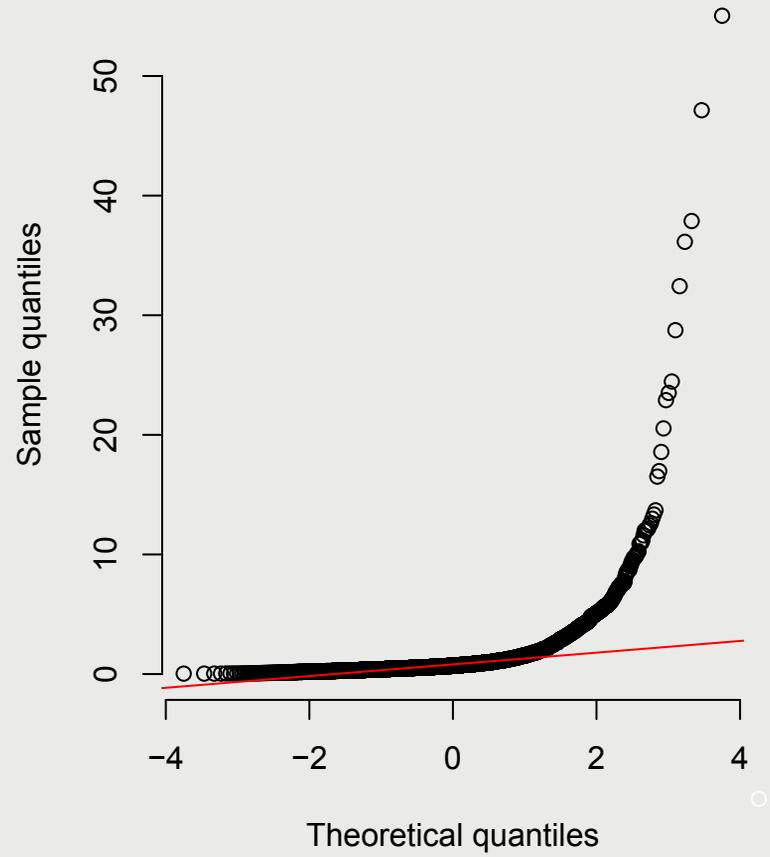
Other areas of high Sb concentrations extend over the major industrial centres around Greater Manchester and Liverpool, the north-east around Newcastle and Sunderland, the Yorkshire coalfield and Birmingham. High concentrations also occur in soils over the south Wales coalfield. The location of these high Sb values, cutting across the bedrock and superficial geology, strongly suggests that these are mainly industrial signatures derived mainly from coal-burning, metal-working and smelting operations.

The lowest Sb concentrations (<0.5 mg/kg) generally occur in central, eastern and southern England where the soils have developed from a range of sedimentary and glacial parent material types. Most notable of these are the Chalk outcrops and younger Tertiary and Quaternary deposits.

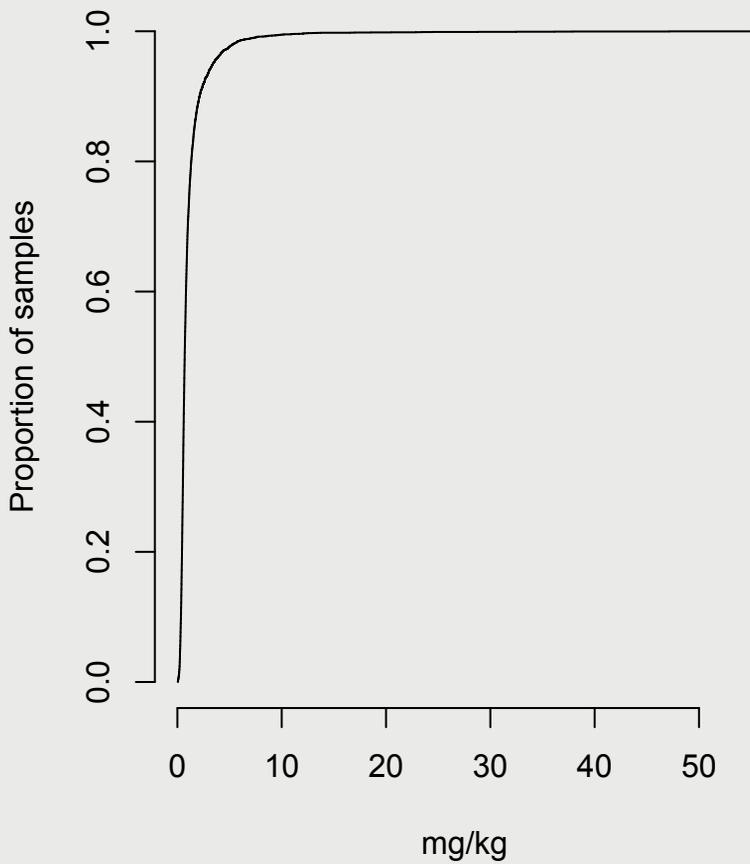
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Sb - Antimony mg/kg

mean= 1.1

median= 0.7

10th percentile= 0.34

25th percentile= 0.48

75th percentile= 1.1

90th percentile= 2.1

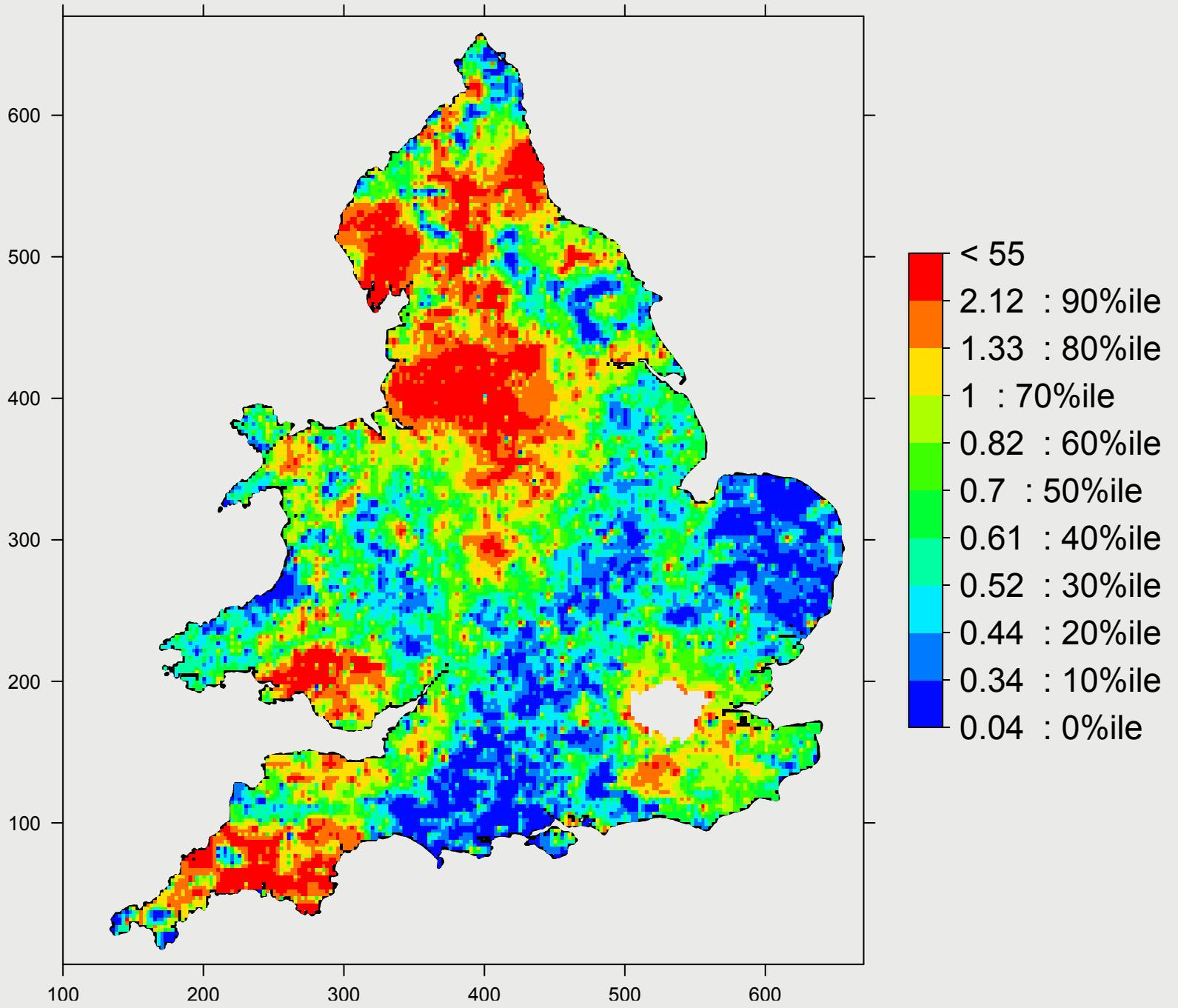
min= 0.04

max= 55

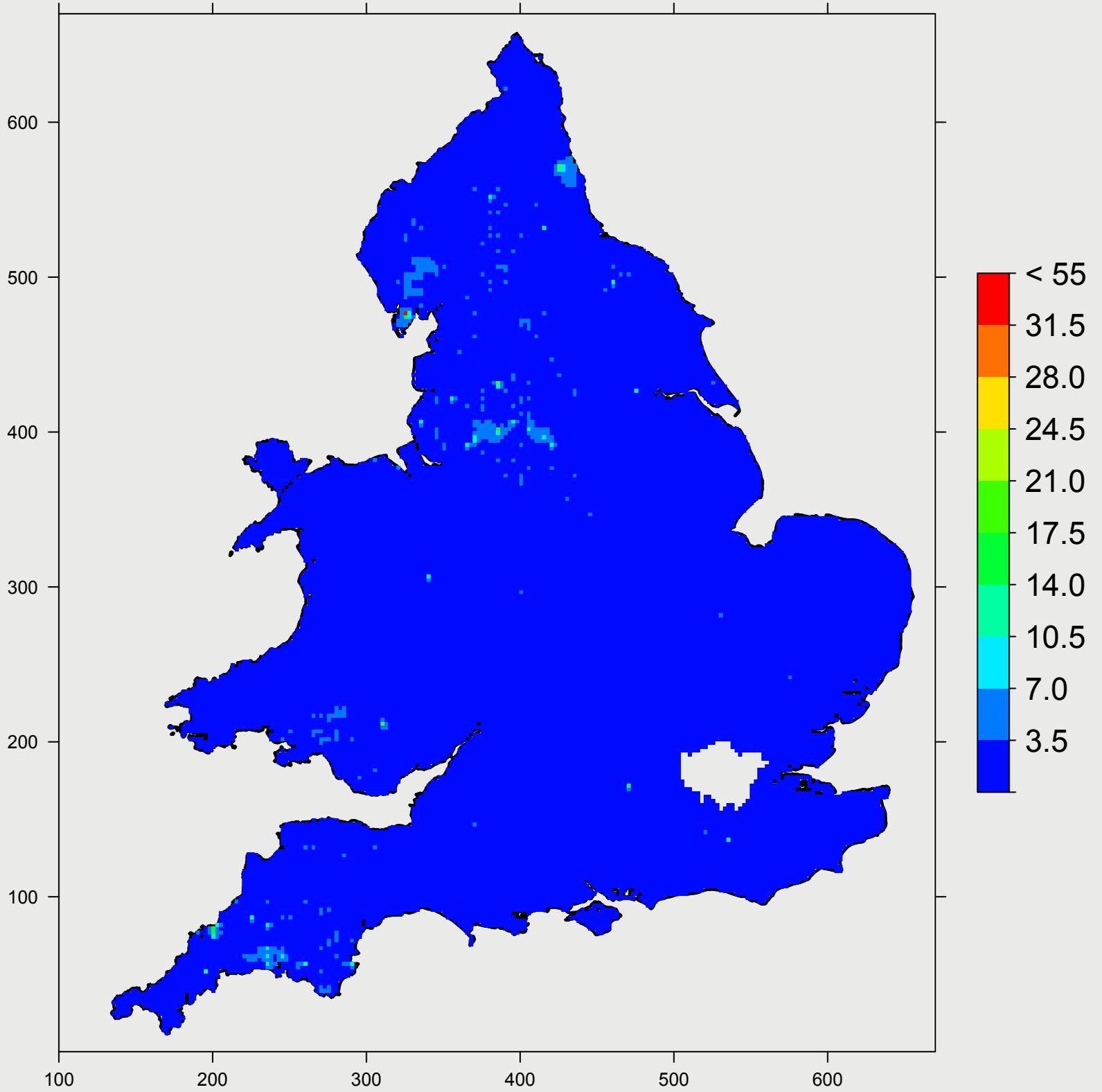
skewness= 12

n= 5670

Topsoil antimony (mg/kg ; percentile scale)



Topsoil antimony (mg/kg ; arithmetic scale)



Arsenic (As)

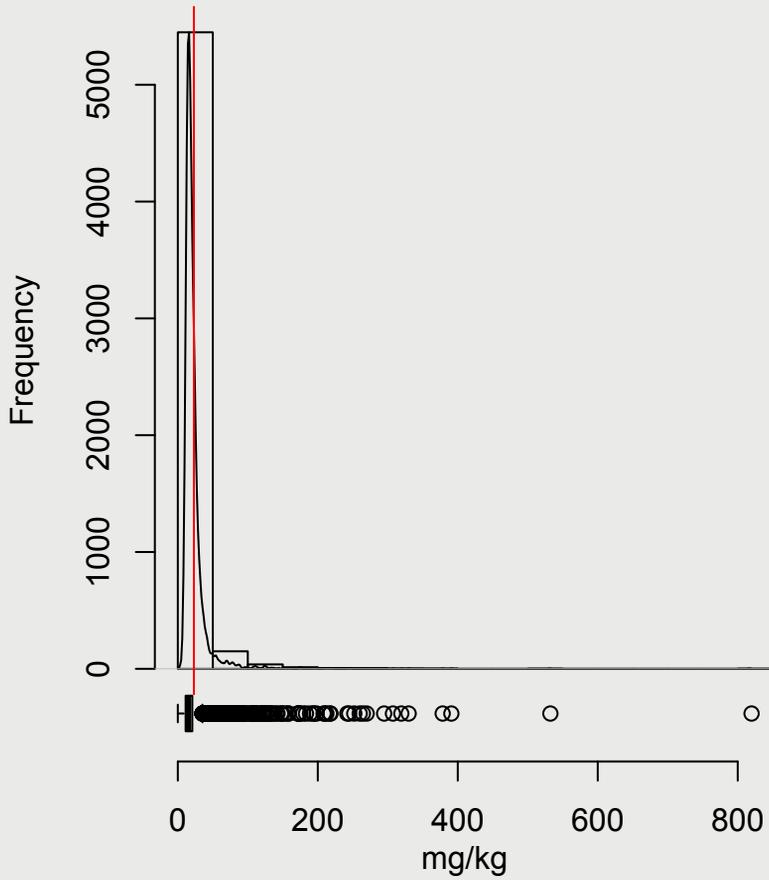
Arsenic is a nonmetallic element, strongly associated with sulphide minerals, which occurs at an estimated upper continental crustal concentration of about 2 mg/kg, but is more abundant in shale and coal (10–13 mg/kg). Its toxic character is well known. Topsoil covering half of England and Wales contains less than 15 mg/kg As dry weight. Soils which contain much higher concentrations occur in parts of Cornwall, Devon and in south Wales, parts of central and north Wales, and the Lake District, due to mineralisation, mining and smelting of minerals. Some areas in Cornwall and south Devon produced large amounts of As, particularly in the 19th century, and much of this was exported by sea. The Swansea Valley area in south Wales was very active in smelting and processing metals such as copper, and the high As levels in soils in this area are certainly related to this industrial history.

The region of higher concentrations which runs in a broad band over the Lower Jurassic outcrop from the Bristol area to the east of Nottingham to Scunthorpe is linked to the presence of underlying ironstones that are known to contain elevated As concentrations, compared to other rock types. Similar rocks of Early Cretaceous age in the Lincoln Wolds also show high soil As concentrations. Other areas with slight enrichment are most easily seen on the percentile map; these include parts of the industrial belt of Lancashire and Yorkshire, and the Fens east of Peterborough. Fortunately, much of the As in soil is not bioavailable, except under reducing conditions (Zhao et al., 2010).

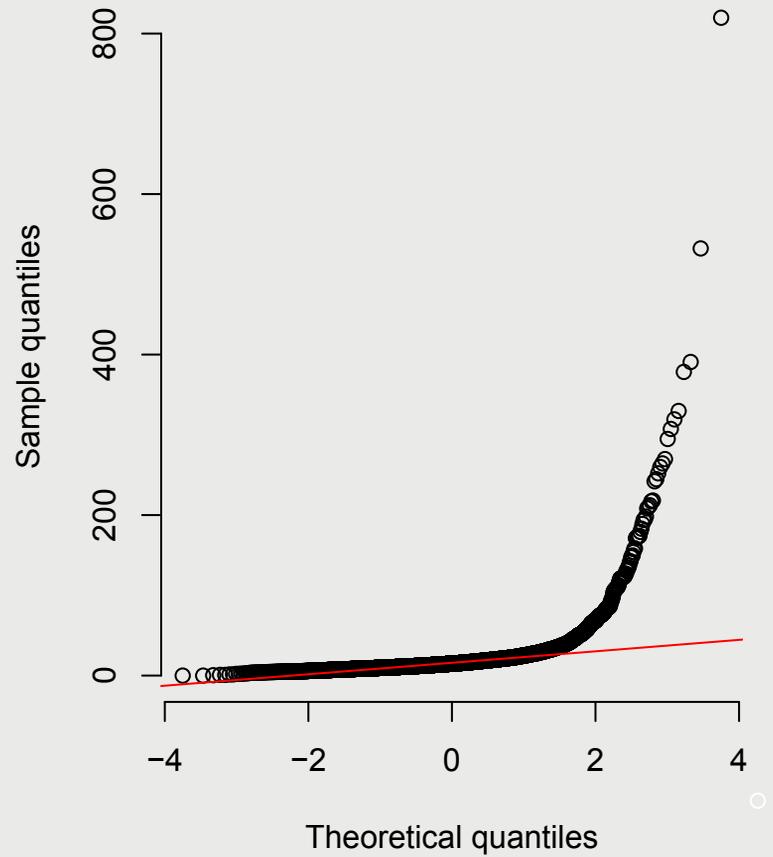
Low As concentrations in soils are associated with sedimentary rocks of the lower Carboniferous, the Permo-Triassic, Chalk and younger sediments of the Hampshire Basin and East Anglia.



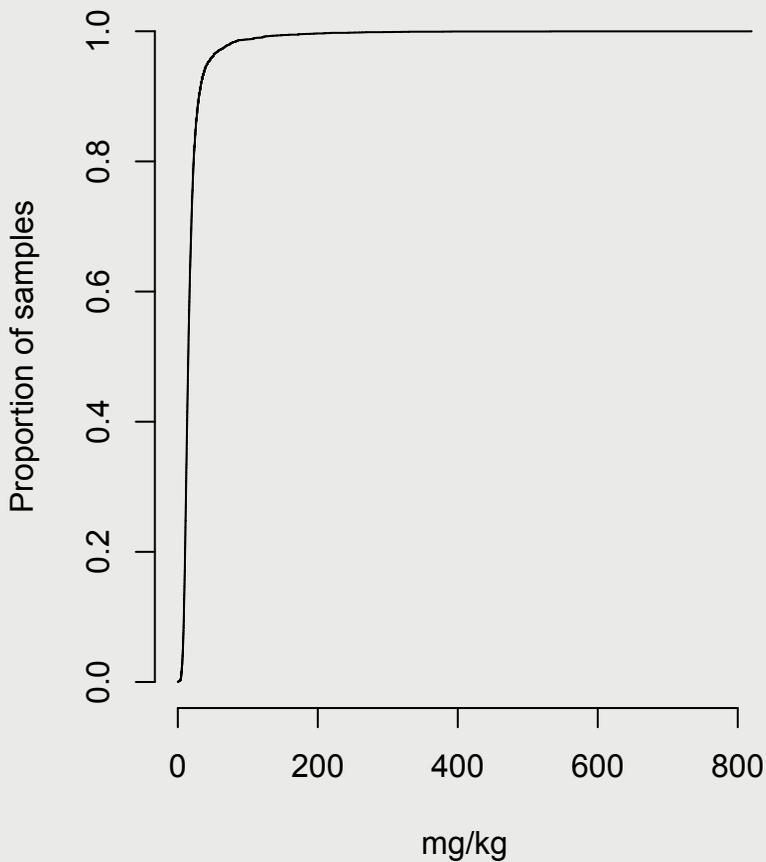
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



As - Arsenic mg/kg

mean= 20

median= 15

10th percentile= 8.6

25th percentile= 11

75th percentile= 21

90th percentile= 30

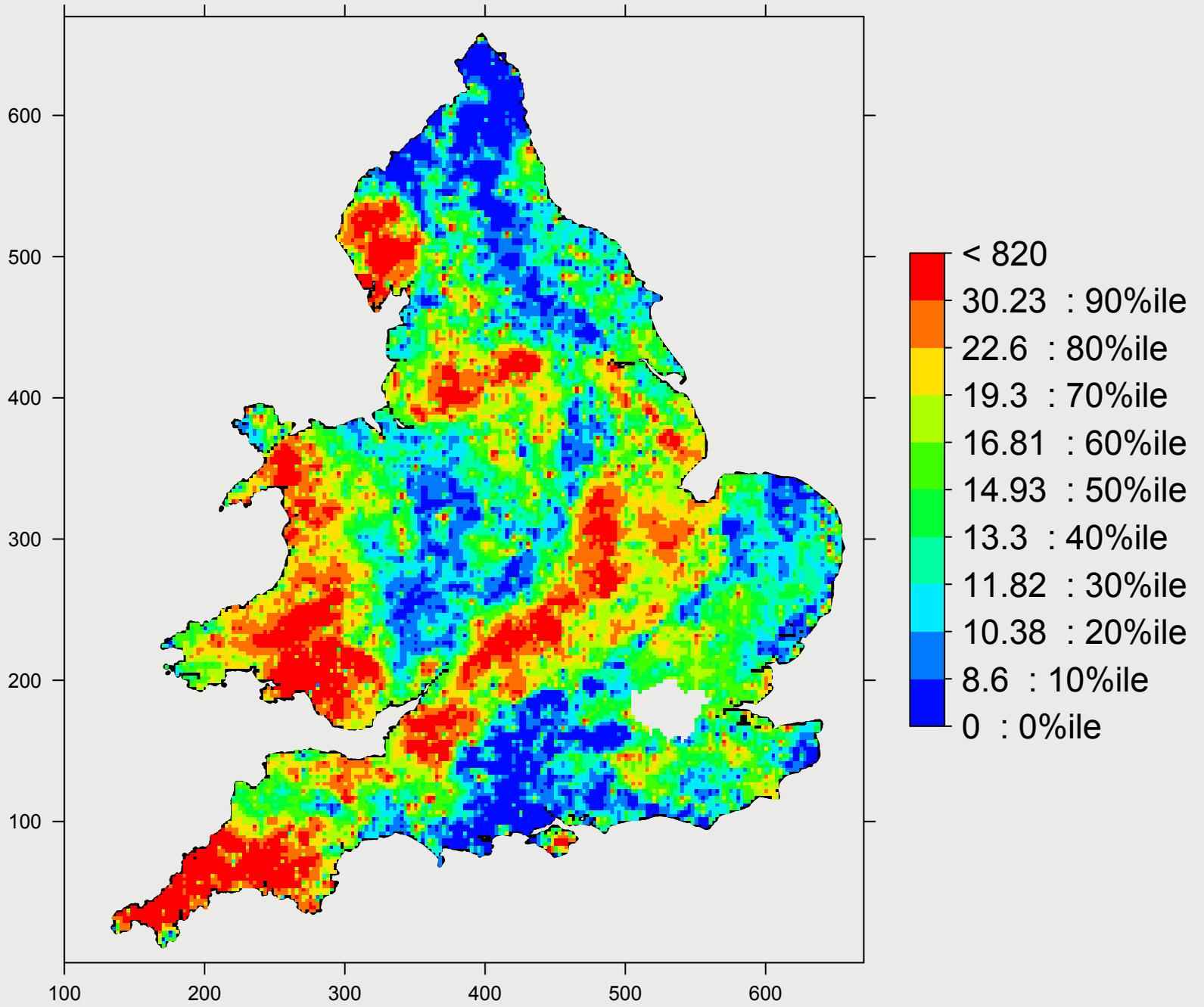
min= 0

max= 820

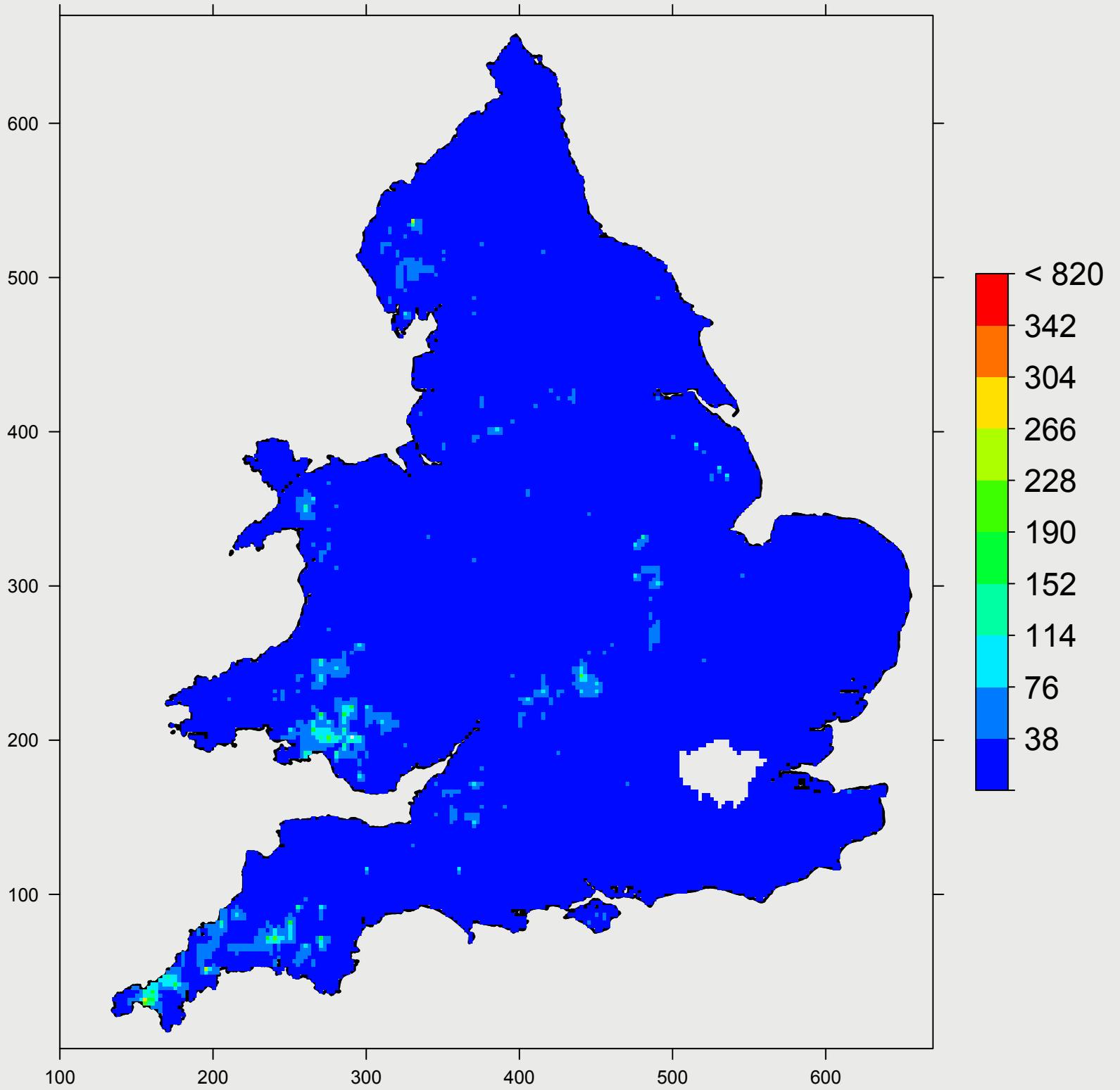
skewness= 12

n= 5670

Topsoil arsenic (mg/kg ; percentile scale)



Topsoil arsenic (mg/kg ; arithmetic scale)



Barium (Ba)

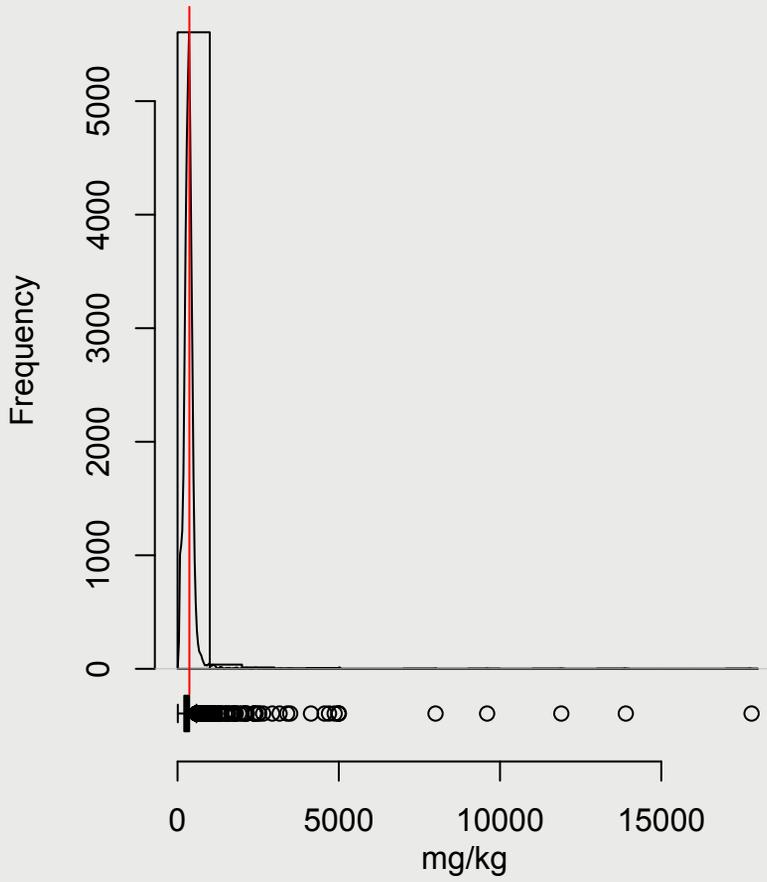
Barium is a metallic element, present at an estimated concentration of about 600 mg/kg in upper continental crust. Its geochemistry is dominated by low-solubility sulphate (barytes) and carbonate (witherite) minerals, though it is also present in K-feldspars and micas and is more abundant in granites (600 mg/kg) than in basic igneous rocks (330 mg/kg). It may be essential for some organisms at trace levels, but soluble Ba compounds are toxic. Barium is widely used in industry, notably in impure form in drilling mud, and in glass, ceramics, paint, paper and electronics (Reimann and De Caritat, 1998).

Elevated levels of Ba occur in the south-west England, the Mendips, parts of Wales, the Peak District, over the Permo-Triassic outcrop between Nottingham and Derbyshire extending to the Humber, and near York. The origin of some of these may be natural deposits of barytes, perhaps associated with mineralisation, or with black shale lithologies, but others could reflect industrial uses (Ba compounds are commonly used in paints and other industrial processes). Relatively high concentrations are found in lowland areas having recent marine alluvium as a parent material, e.g. in the Somerset Levels and around The Wash and Lincolnshire coastal marshes.

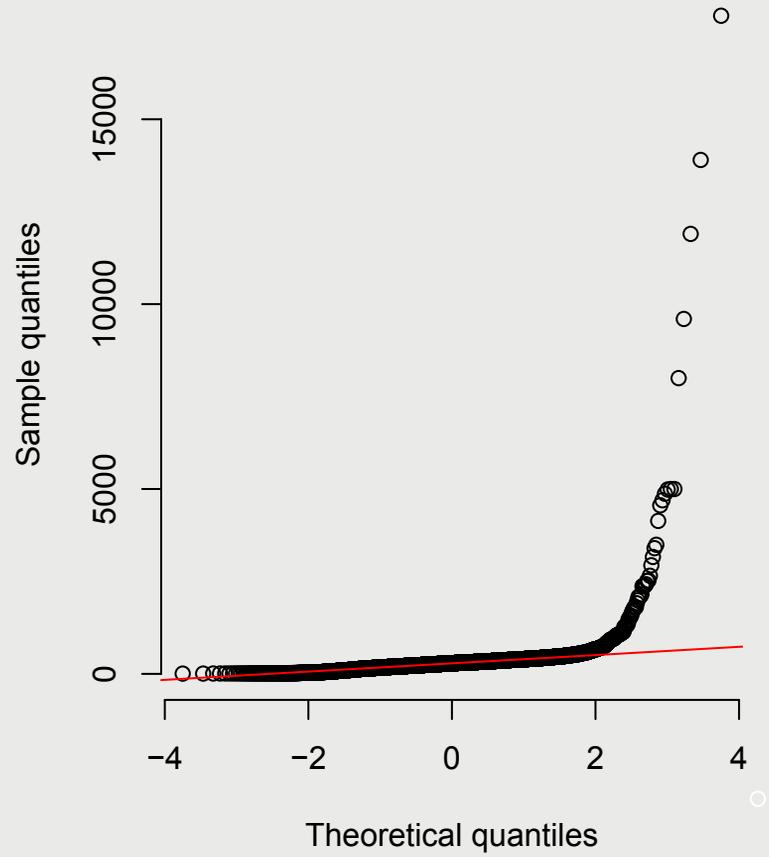
Barium occurs at low concentrations in upland peat soils, for example over the Pennines, North York Moors, parts of Wales and the granite Moors in south-west England, but not in lowland peat (e.g. the Fens), though the latter may also contain some marine alluvium. Elsewhere, soils on Chalk bedrock show notably low Ba concentrations, as do some of the sandy soils of East Anglia.

It appears that Ba is inefficiently extracted from the soil matrix during aqua regia digestion, and the values reported here (using the XRF-S method) are higher than in McGrath and Loveland (1992). For example, the median concentrations in soil analysed by these methods are 288 and 121 mg/kg respectively).

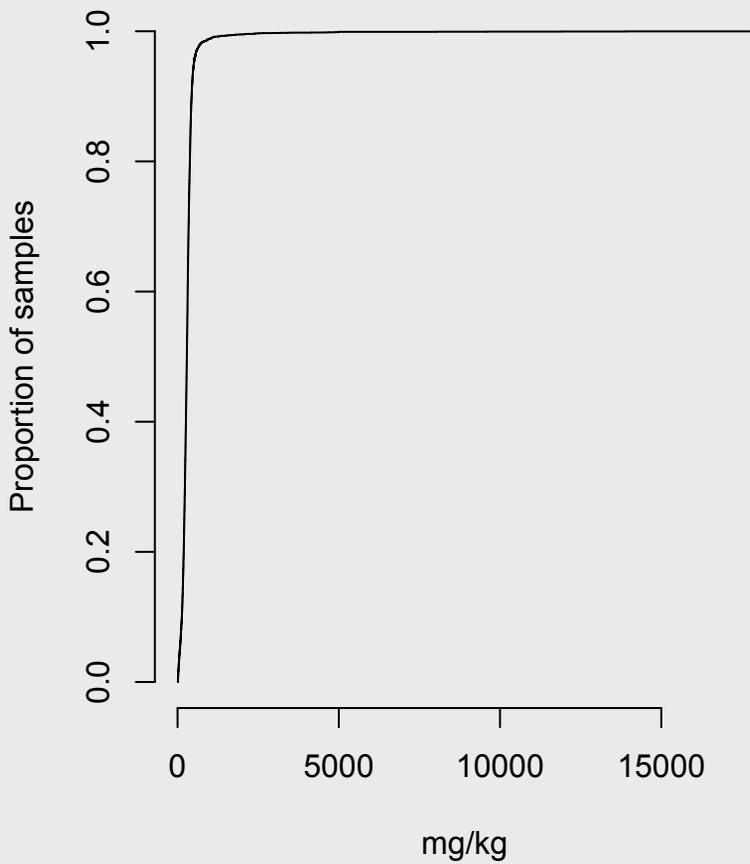
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ba - Barium mg/kg

mean= 316

median= 288

10th percentile= 133

25th percentile= 210

75th percentile= 360

90th percentile= 435

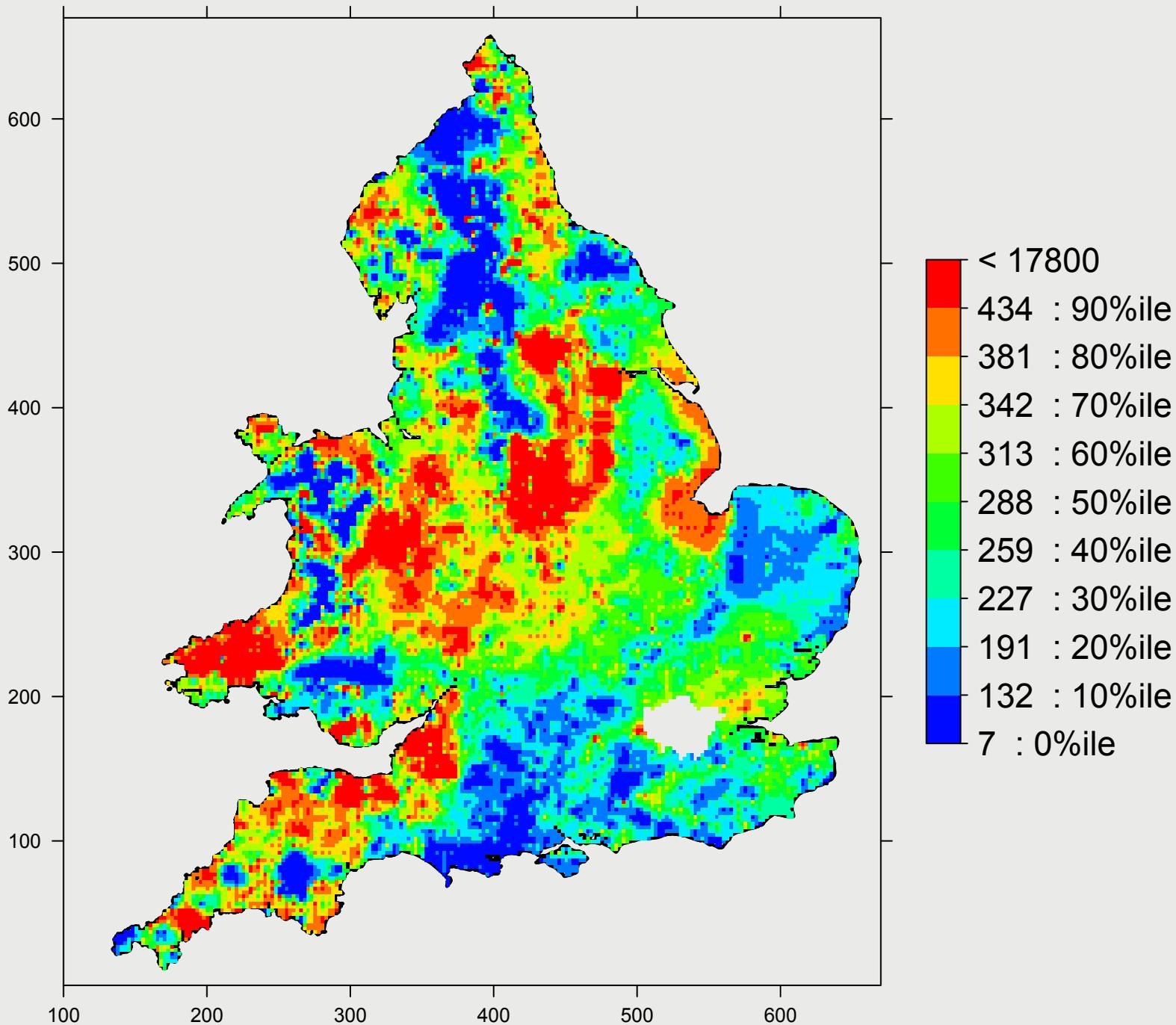
min= 7.9

max= 17800

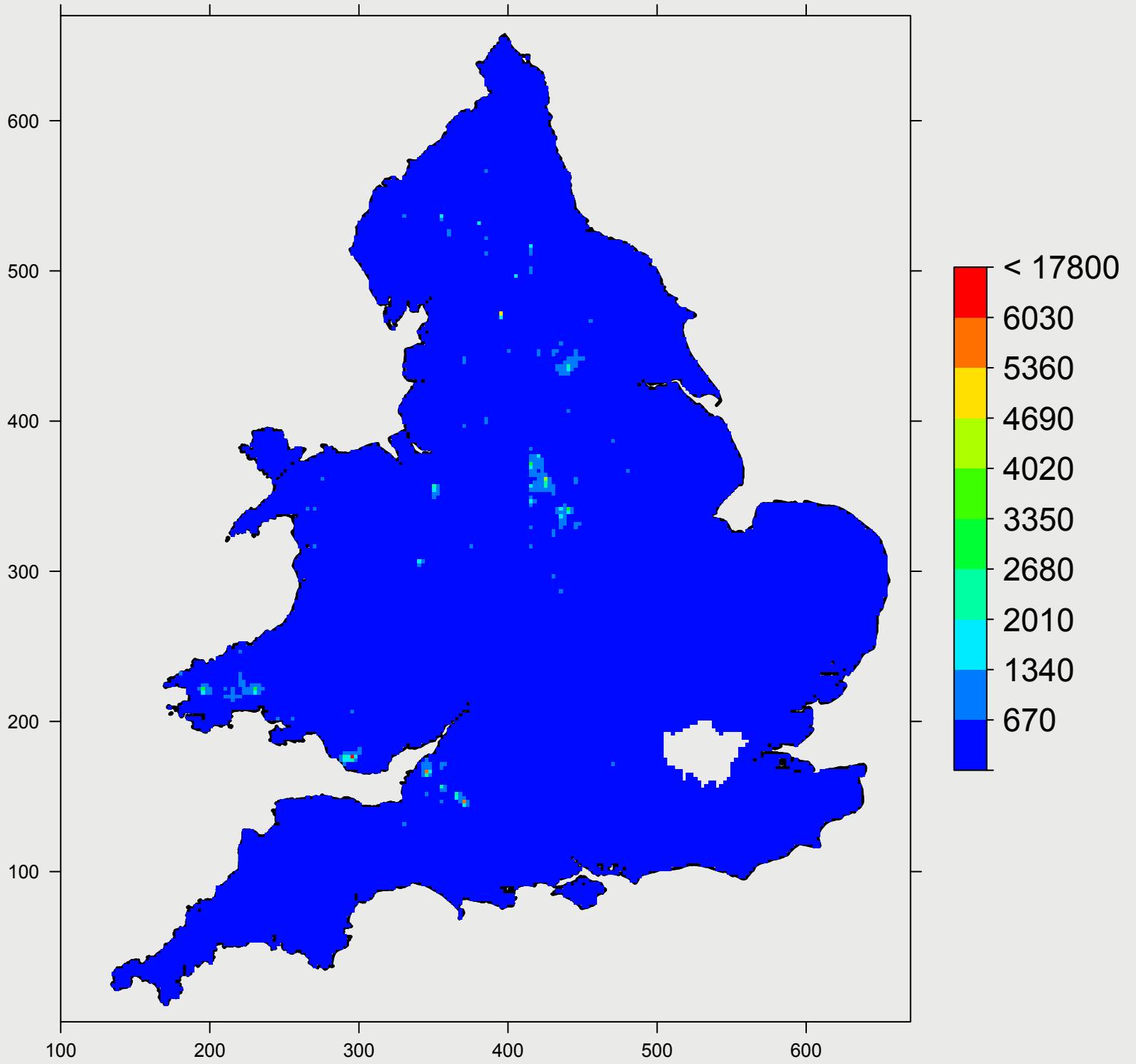
skewness= 23

n= 5670

Topsoil barium (mg/kg ; percentile scale)



Topsoil barium (mg/kg ; arithmetic scale)



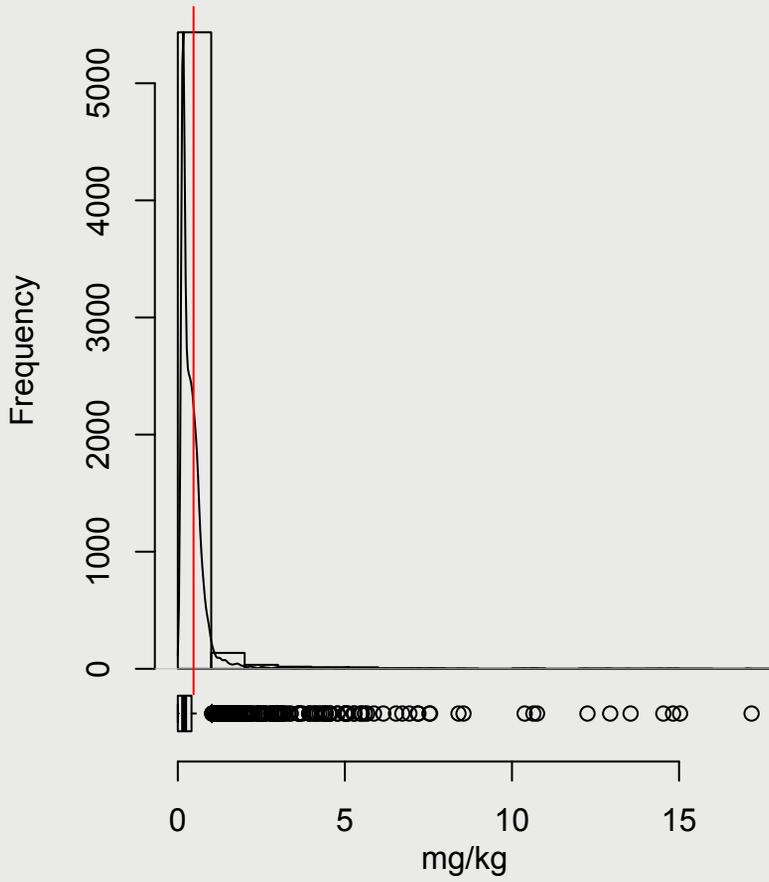
Bismuth (Bi)

Bismuth is a rather rare metallic element with an estimated crustal abundance of only 0.125 mg/kg, though concentrations are somewhat higher in shales (0.25 mg/kg; Reimann and De Caritat, 1998) and it is most often associated with lead, arsenic and sulphides. The XRF-S instrument used for the analyses reported a lower limit of detection (LLD) for Bi of 0.3 mg/kg. Exploratory statistical analysis showed that over half of the samples had concentrations below the LLD, so consequently the precision of values below this level is poorer and this is reflected in the 'noise' levels in the map.

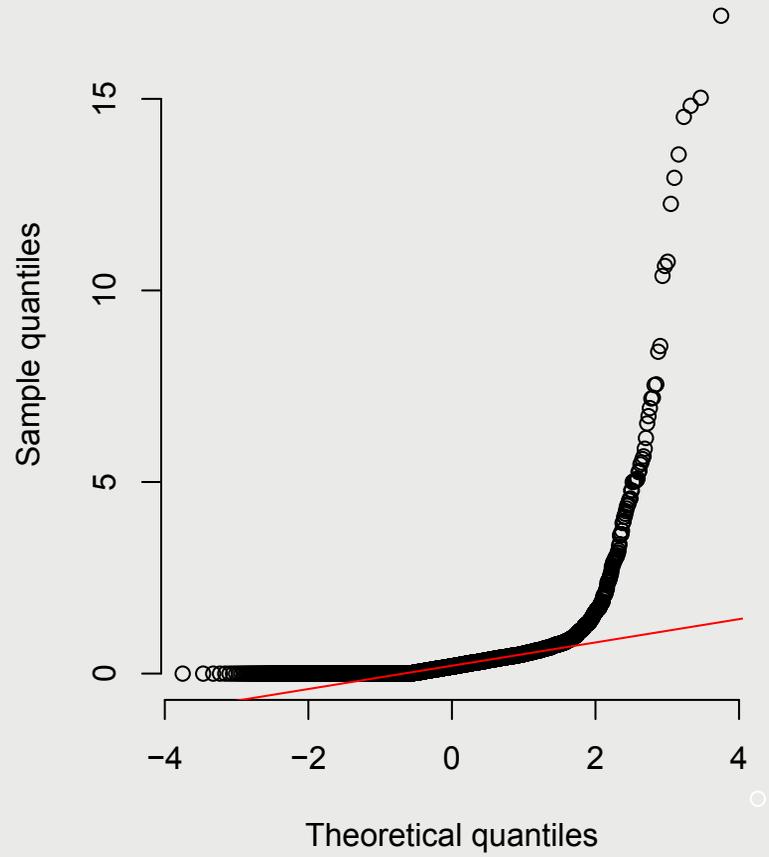
The major areas where Bi concentrations in soils are elevated (above 0.65 mg/kg – the 95th percentile) relate to samples from the granite outcrops and the mineralised area of south-west England, south Wales, the Bristol area, the Lake District, Peak District and the industrial areas of Lancashire and Yorkshire. Smelting may be largely responsible for the high values around Bristol and the Swansea area.

Low Bi values are mainly associated with soils in East Anglia and eastern England generally, but the distribution patterns are unreliable at these low values.

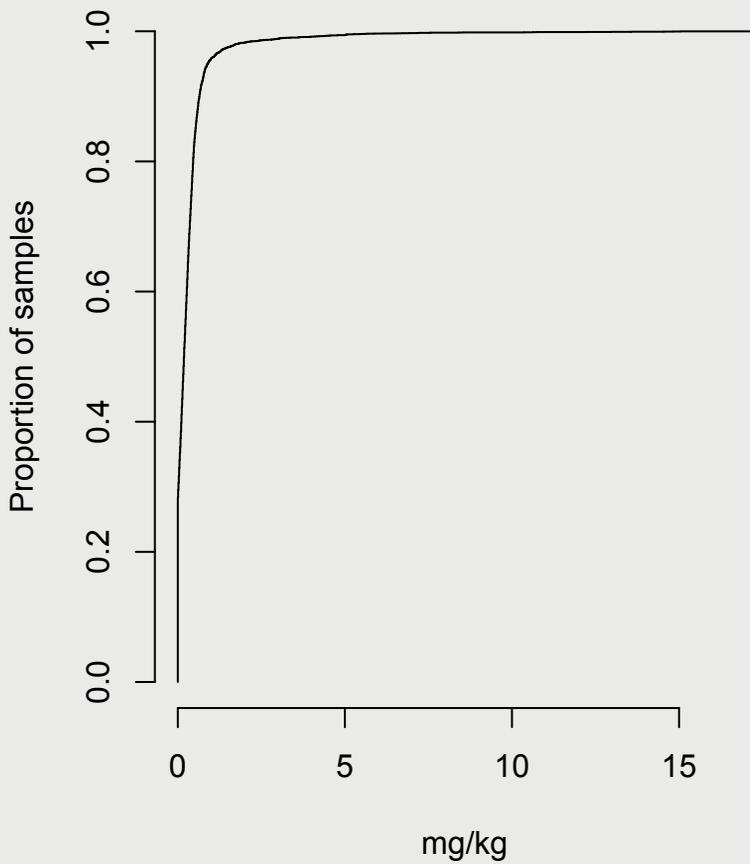
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Bi - Bismuth mg/kg

mean= 0.33

median= 0.19

10th percentile= 0

25th percentile= 0

75th percentile= 0.41

90th percentile= 0.65

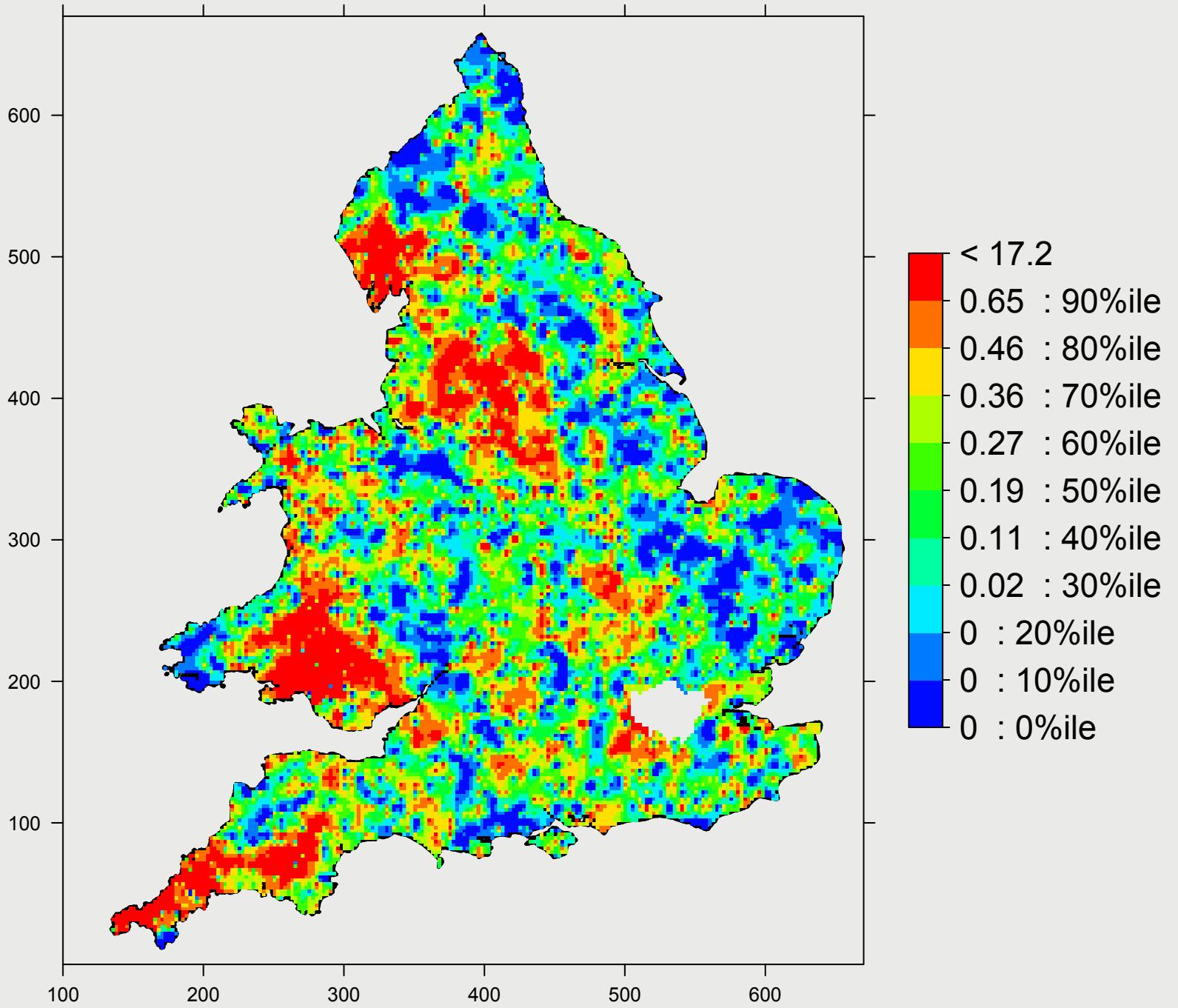
min= 0

max= 17

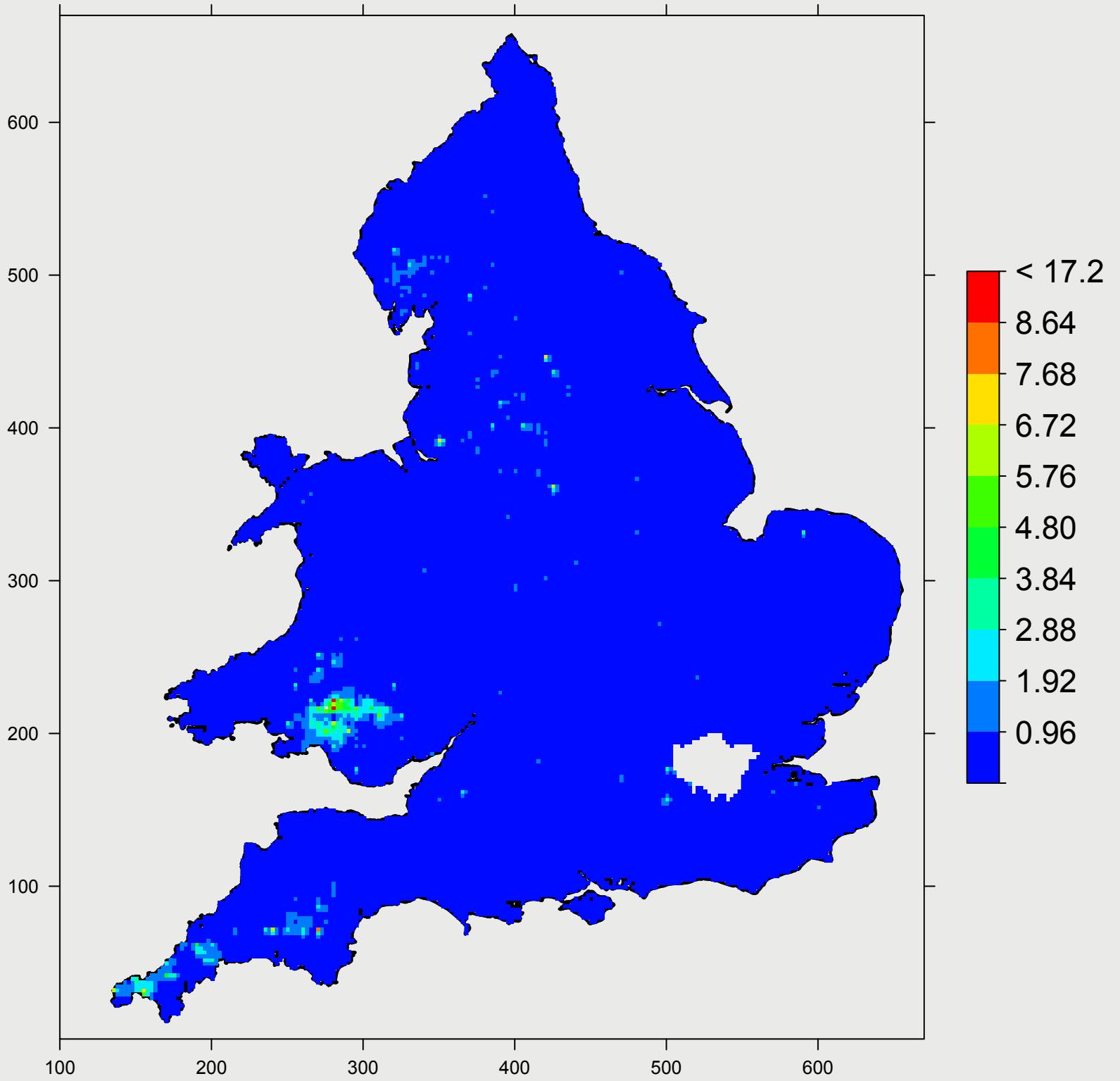
skewness= 11

n= 5670

Topsoil bismuth (mg/kg ; percentile scale)



Topsoil bismuth (mg/kg ; arithmetic scale)



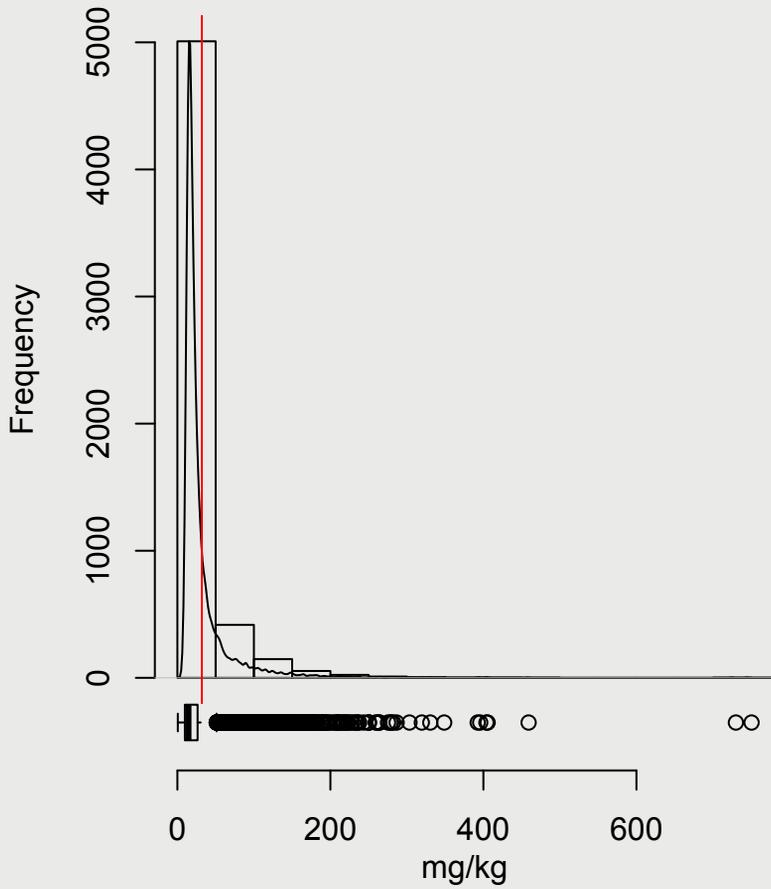
Bromine (Br)

Bromine is a nonmetallic halogen element and occurs naturally in many inorganic substances. In crustal rocks Br occurs as bromide salts, at an estimated upper continental crustal abundance of about 1.6–2 mg/kg, but higher in shale and limestone (6 mg/kg), and especially coals (20 mg/kg; Reimann and De Caritat, 1998). For soils across England and Wales the total Br concentration ranges from 0.6 to 750 mg/kg with a median and mean of 15 and 27 mg/kg, respectively.

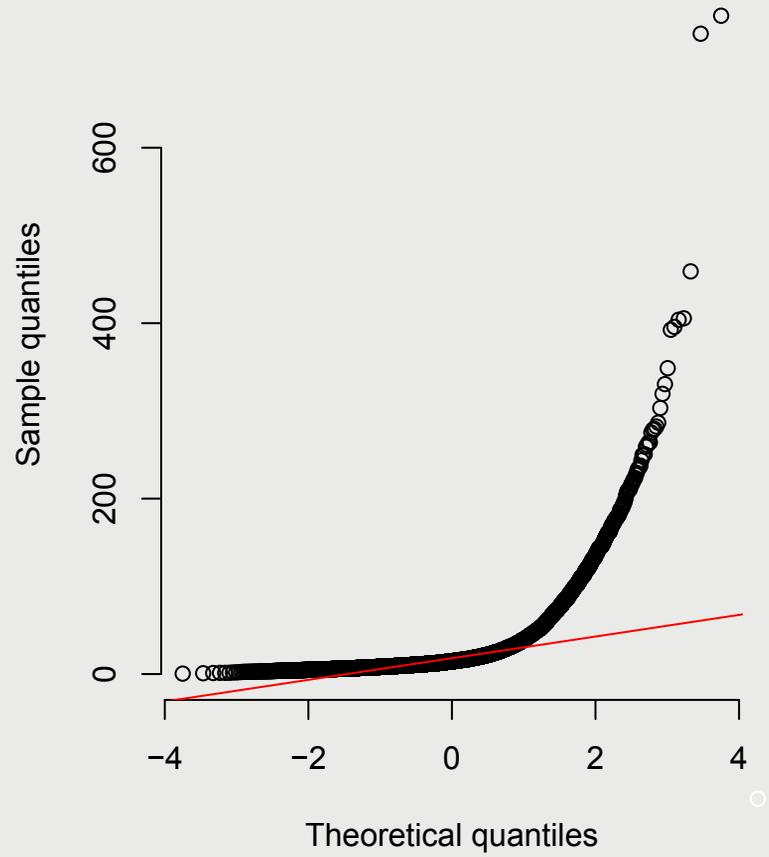
The percentile map of Br shows elevated levels of Br in soils over the igneous intrusions and the Devonian sedimentary rocks of south-west England, the Ordovician and Silurian strata of western Wales, the Carboniferous rocks of the Pennines and Ordovician and Silurian volcanic rocks of the Lake District. Elevated levels across the Fen Basin and Norfolk Broads, as well as many coastal regions in the south-east, relate to the influence of marine alluvium or recent ingression of Br-enriched salt water. By comparison, the arithmetic map of Br shows that highest concentrations (> 200 mg/kg) were reported for soils collected across the granite intrusions of Cornwall (Dartmoor, Bodmin Moor, Land's End), Snowdonia and the Ordovician mafic volcanic rocks of the Lake District.

Low Br concentrations are notable over the Permo-Triassic of the Midlands and eastern England, and the post-Cretaceous deposits of East Anglia.

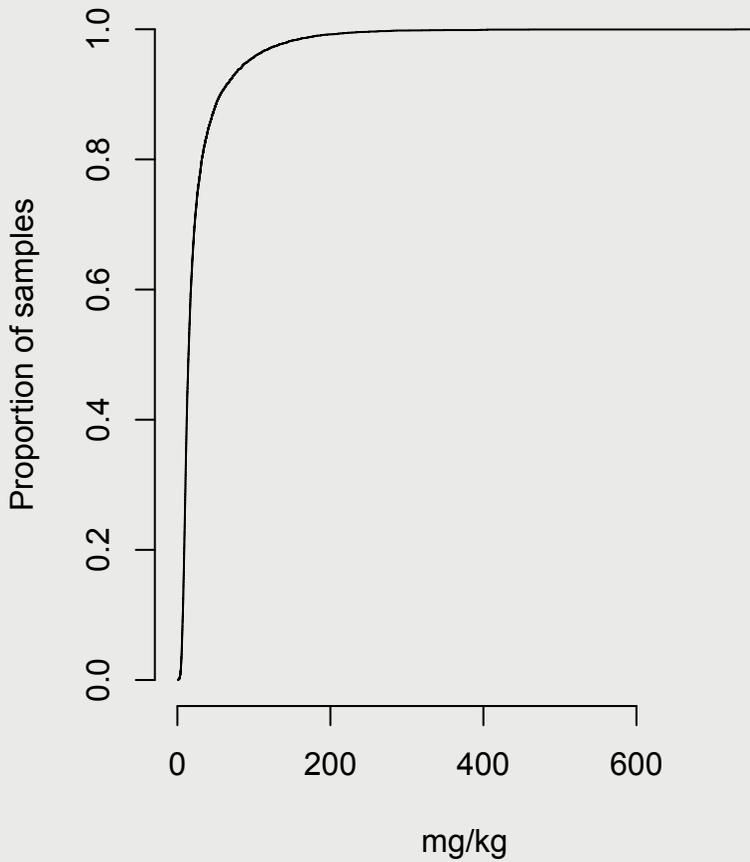
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Br - Bromine mg/kg

mean= 27

median= 15

10th percentile= 7.1

25th percentile= 9.8

75th percentile= 26

90th percentile= 56

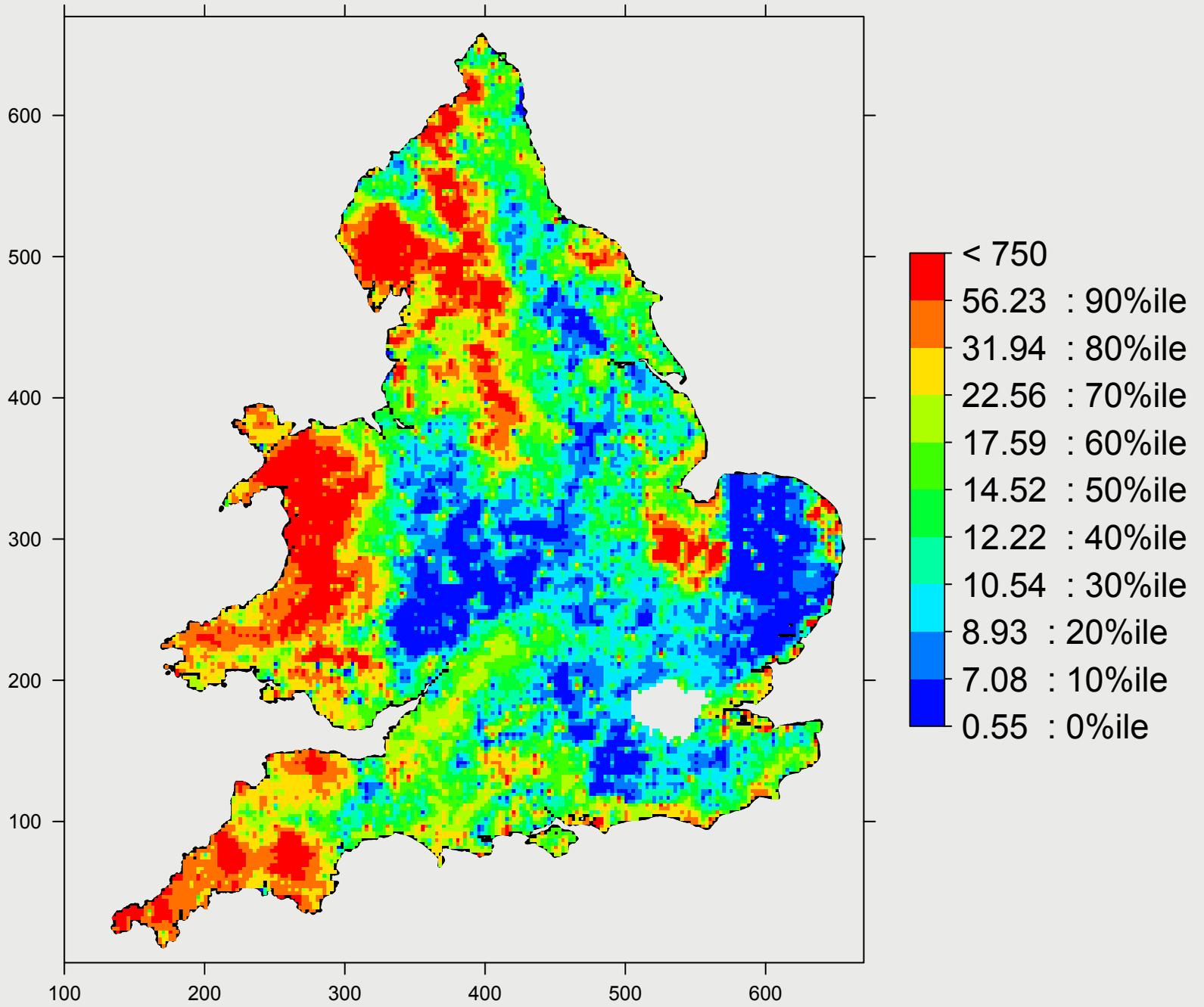
min= 0.55

max= 750

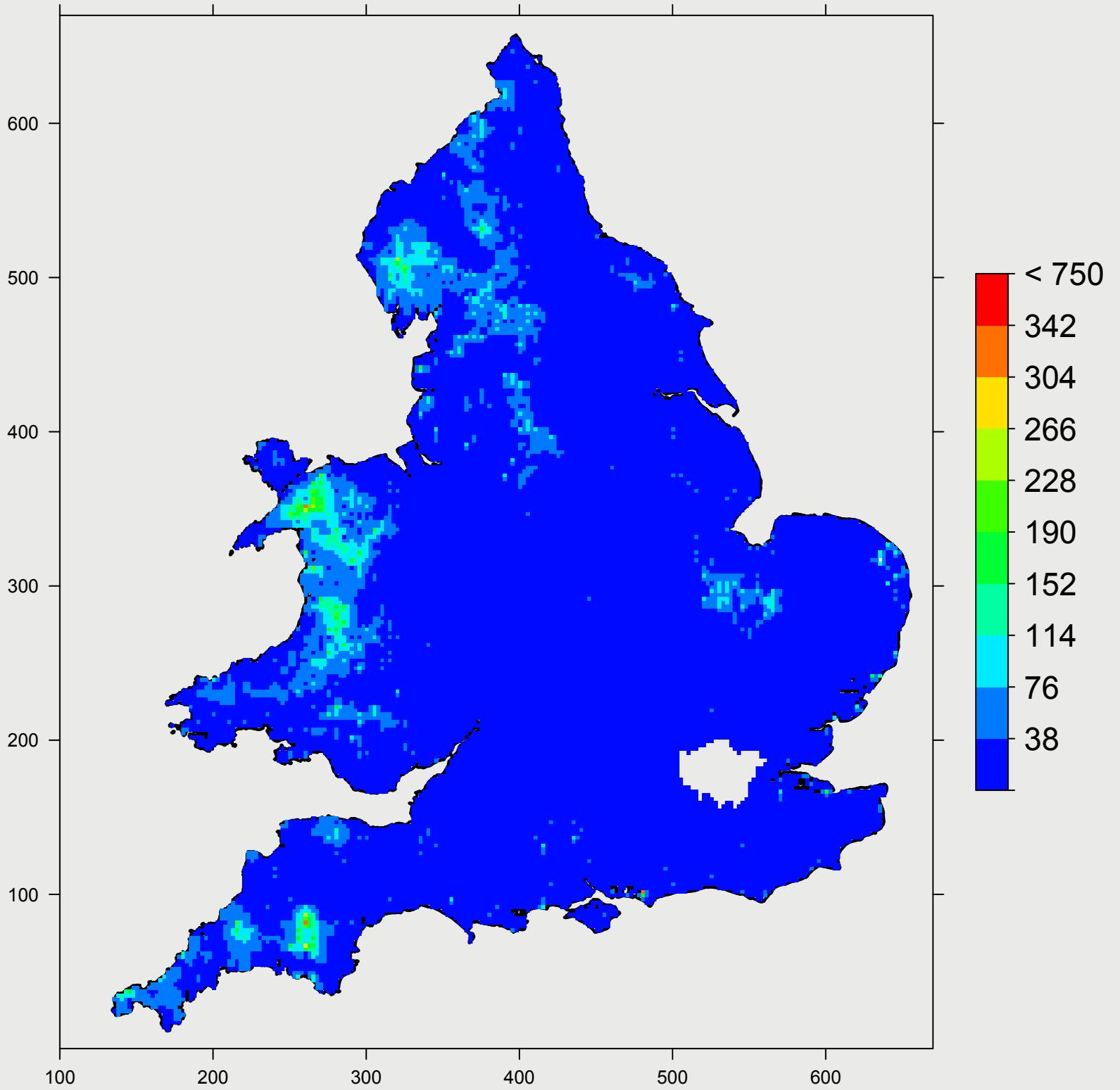
skewness= 5.9

n= 5670

Topsoil bromine (mg/kg ; percentile scale)



Topsoil bromine (mg/kg ; arithmetic scale)



Cadmium (Cd)

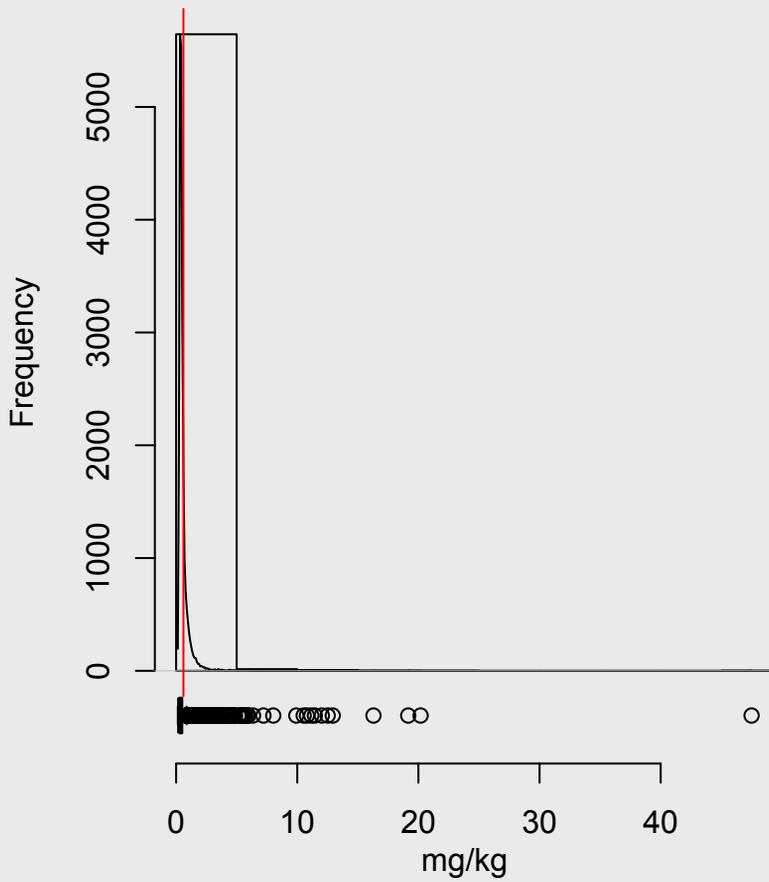
Cadmium is a rather rare metallic element, most closely associated with zinc and other metal sulphide minerals, present in the Earth's upper continental crustal rocks at around 0.1 mg/kg. It is biologically non-essential and toxic, and high concentrations in food are of concern due to its potential impacts on human health (EFSA, 2009). For example, the Statutory Instrument (SI 1263, 1989) gives a maximum Cd concentration for agricultural soils receiving sewage sludge of 3 mg/kg dry weight. A total concentration of 10 mg/kg (for sandy loam soil) was adopted as the Soil Guideline Value for residential soils (Environment Agency, 2009), and is well above the concentration found in most soils.

The main areas in which soils appear to be above this value are those with high, naturally occurring (geogenic) Cd concentrations in the underlying rocks, and other areas where metals were processed, but not necessarily mined. The most extensive locations of mining and smelting of (mainly) zinc and lead in the past include the Derbyshire Peak District region in central/northern England, the Mendips, the Halkyn Mountain region and Snowdonia in north Wales, the mining districts of central Wales and Shropshire, the Lake District and parts of the northern Pennines.

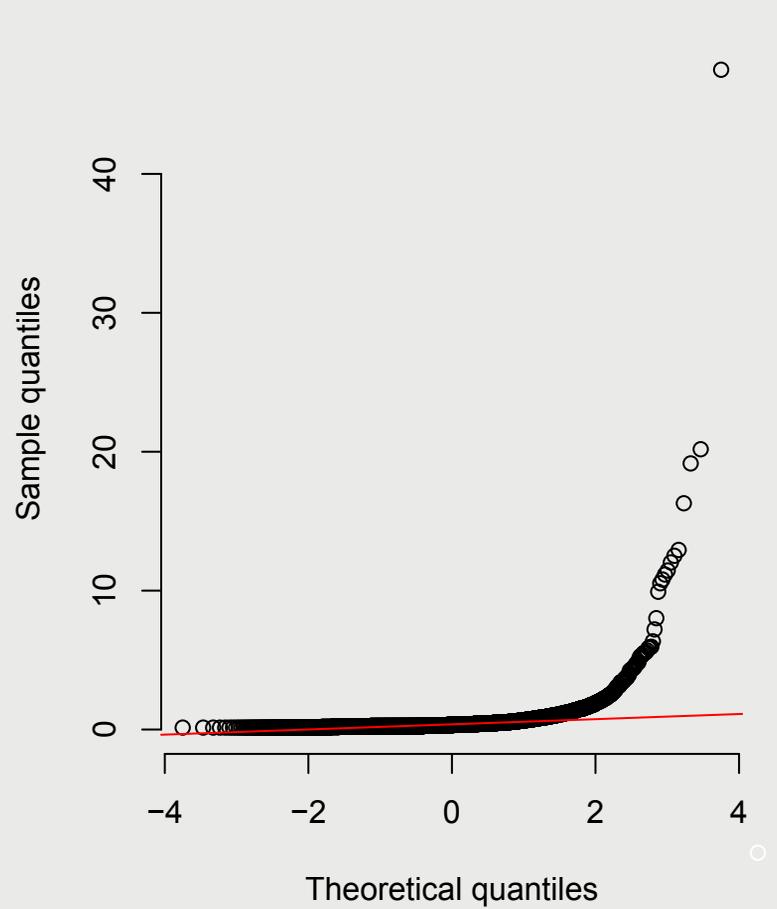
Other non-mining industrially affected regions that are apparent include an area centred on Avonmouth near Bristol, where lead and zinc smelting was carried out for a large part of the 20th century, and areas of south Wales (notably the Swansea Valley and the Vale of Glamorgan, where many smelting and metal working industries were formerly active). In all of these mining and smelting operations, the dust and wastes generated contained cadmium as a contaminant. Industrial cities such as Birmingham, Wolverhampton, Coventry, Manchester and Sheffield also show slightly elevated soil Cd concentrations due to its use in plating and metal-working.

Another region of slight geogenic enrichment in soils follows the outcrop of the Cretaceous Chalk of southern England and the Yorkshire and Lincolnshire Wolds, where shallow soils have a Cd concentration of up to 2 mg/kg. Many other areas that are slightly enriched (1-2 mg/kg), are readily apparent on the percentile map, such as the major granites of Cornwall and Devon. The concentrations reported here are lower than those published in the original *Soil geochemical atlas*. Although the same soil samples were analysed, the technique used originally for Cd determination was flame atomic absorption spectroscopy (McGrath and Loveland, 1992). The mean and median concentrations by XRF-S are 0.52 and 0.33 mg/kg respectively, compared to 0.8 and 0.7 mg/kg reported in the original *Soil geochemical atlas*.

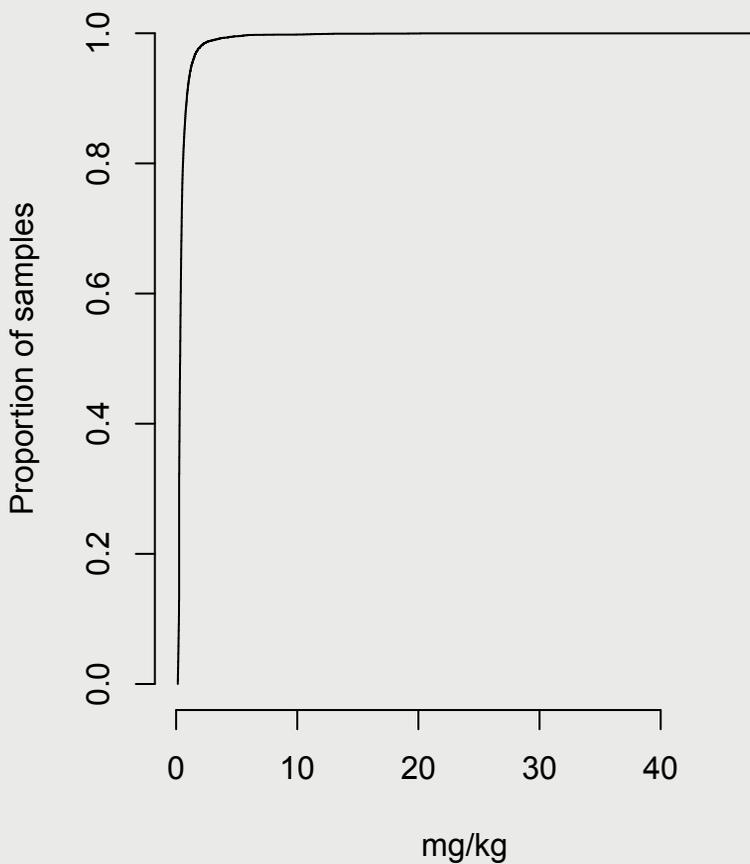
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Cd - Cadmium mg/kg

mean= 0.52

median= 0.33

10th percentile= 0.23

25th percentile= 0.25

75th percentile= 0.5

90th percentile= 0.88

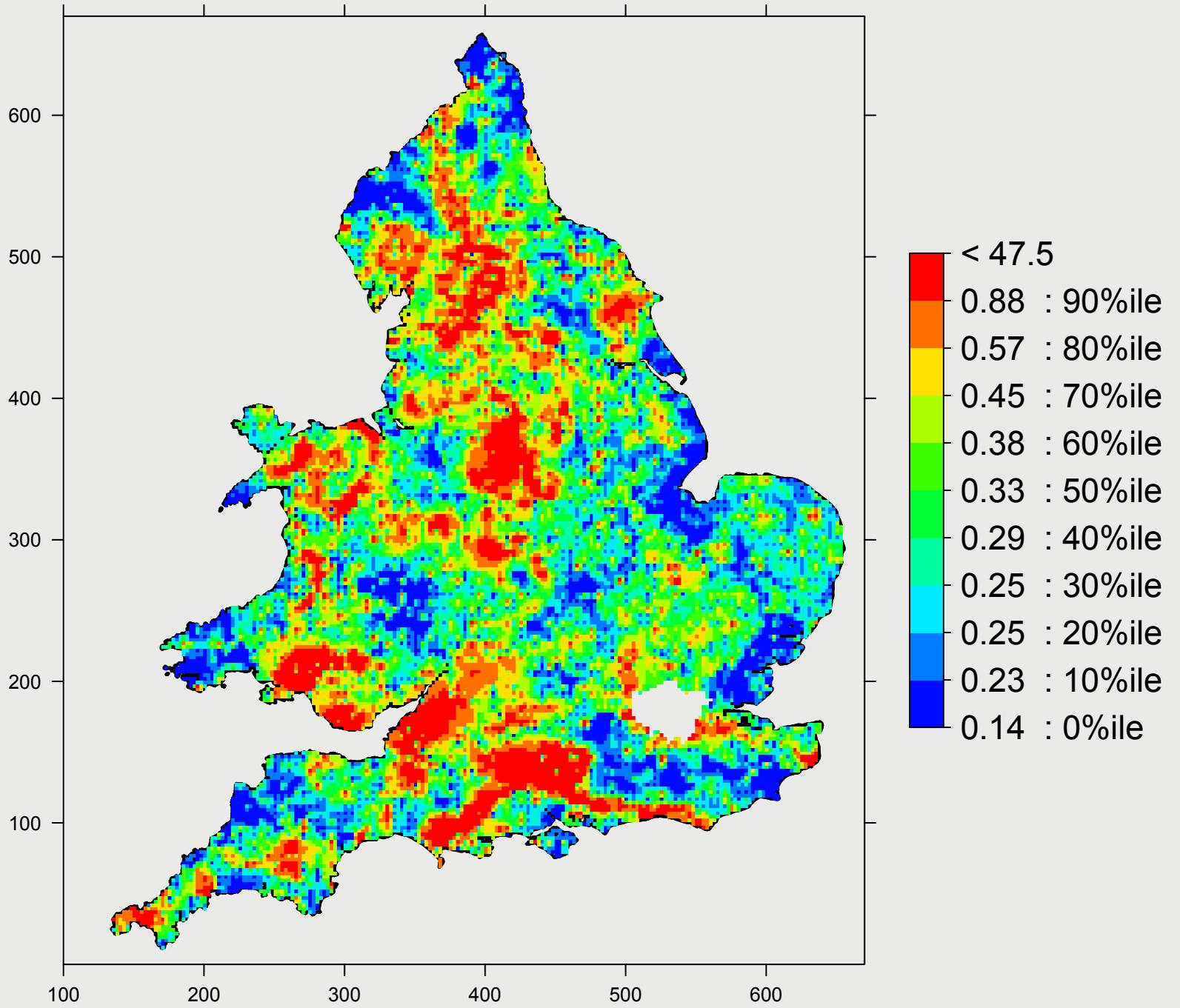
min= 0.14

max= 48

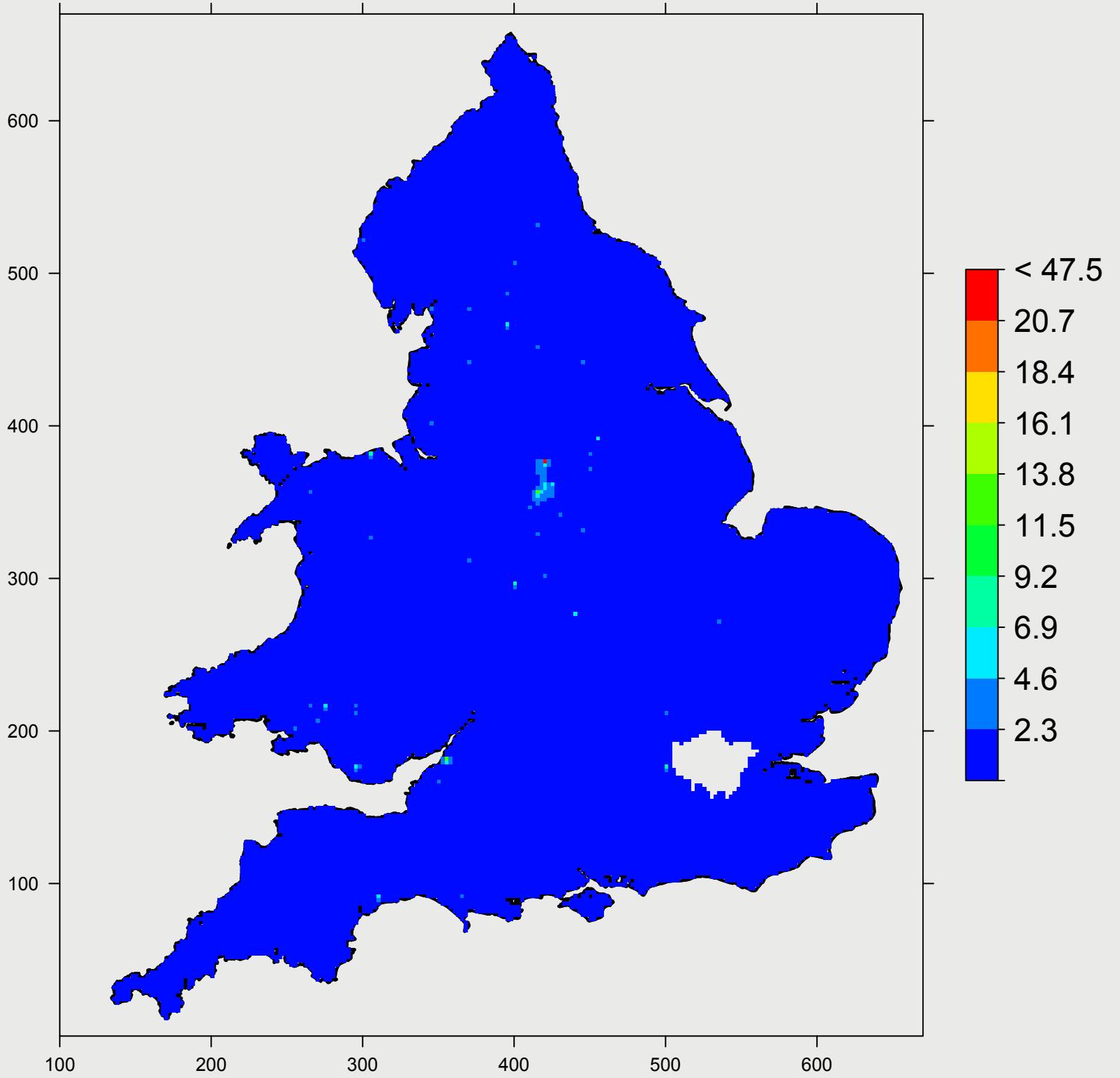
skewness= 24

n= 5670

Topsoil cadmium (mg/kg ; percentile scale)



Topsoil cadmium (mg/kg ; arithmetic scale)



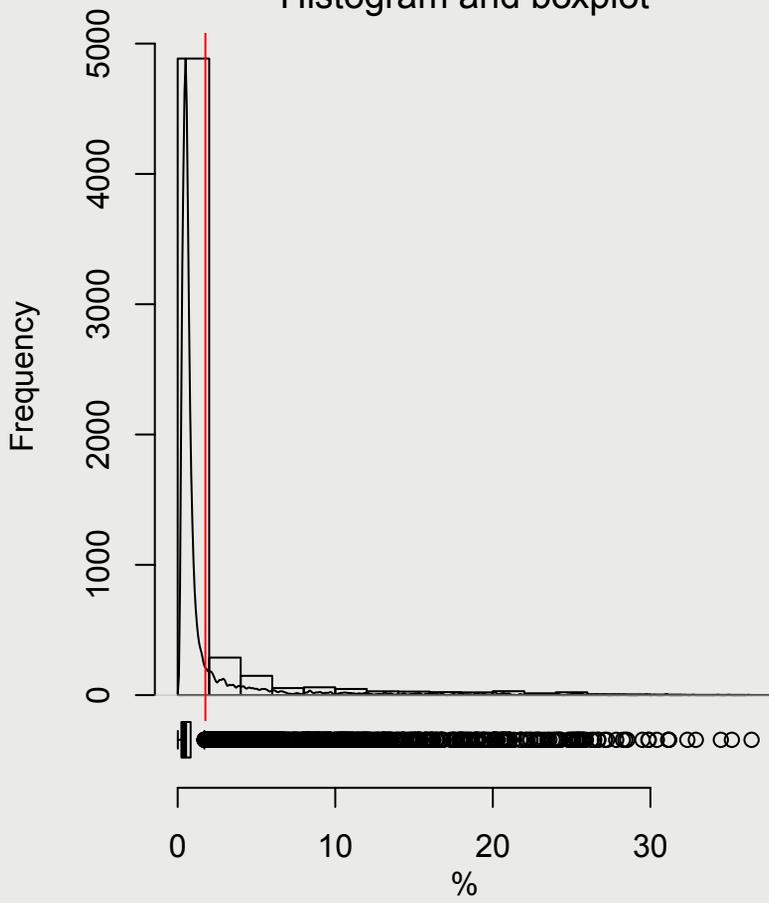
Calcium (Ca)

Calcium is a major, abundant metallic element, present at about 3.0% by weight in the Earth's upper continental crust and widespread in many minerals especially as carbonates in limestones, and in feldspars, amphiboles and pyroxenes. Calcium compounds are widely used for example in agricultural lime, fertilisers, cements, concrete, plaster and desulphurisation plants for power stations. It is essential for all living organisms.

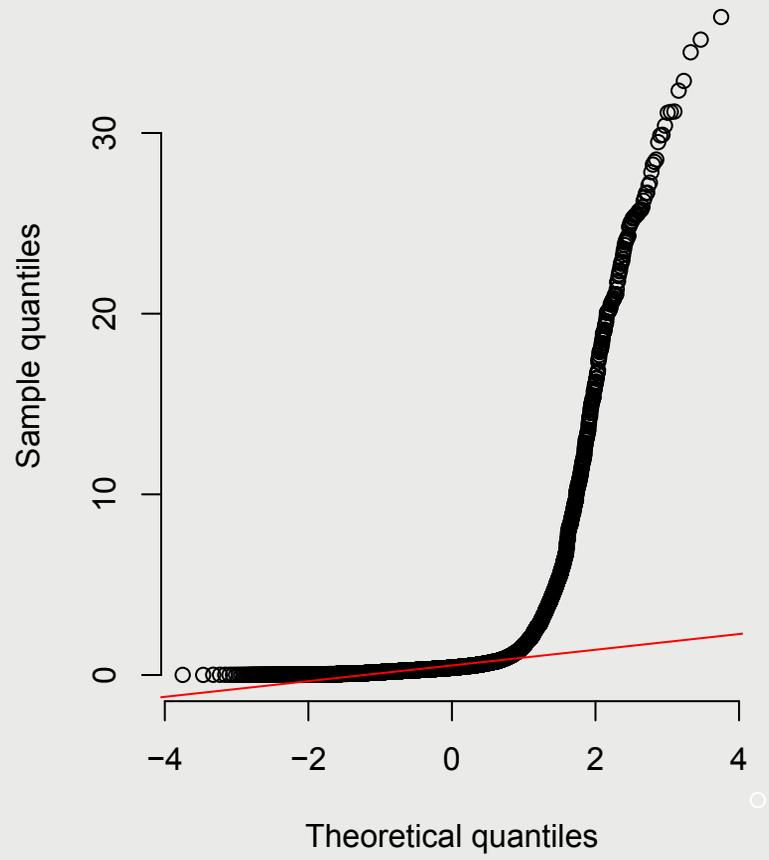
Although Ca has been applied to soils through the addition of lime for many years, the map for calcium largely reflects high levels in areas of underlying Permian, Jurassic and Cretaceous limestone and chalk bedrock, and where they are not covered deeply with drift and till. These occur mainly in the south and east of England, and the soils in these areas tend to have naturally high pH values. The arithmetic map highlights areas with very high concentrations of Ca that denote soils that are thin and chalky, and in which the bioavailability of cationic trace elements will be decreased. The percentile map is slightly different because it shows most of the soils underlain by limestone or chalk that have slightly lower concentrations of Ca.

Very low Ca concentrations are present over large areas of Wales, the Pennines, Cumbria, the North York Moors, Devon and Cornwall, the Hampshire Basin and the Weald of Kent and Sussex. These represent geogenic control, for example from Ca-poor Palaeozoic greywackes, and sandstones of Devonian, Carboniferous, Jurassic, Early Cretaceous and Tertiary ages.

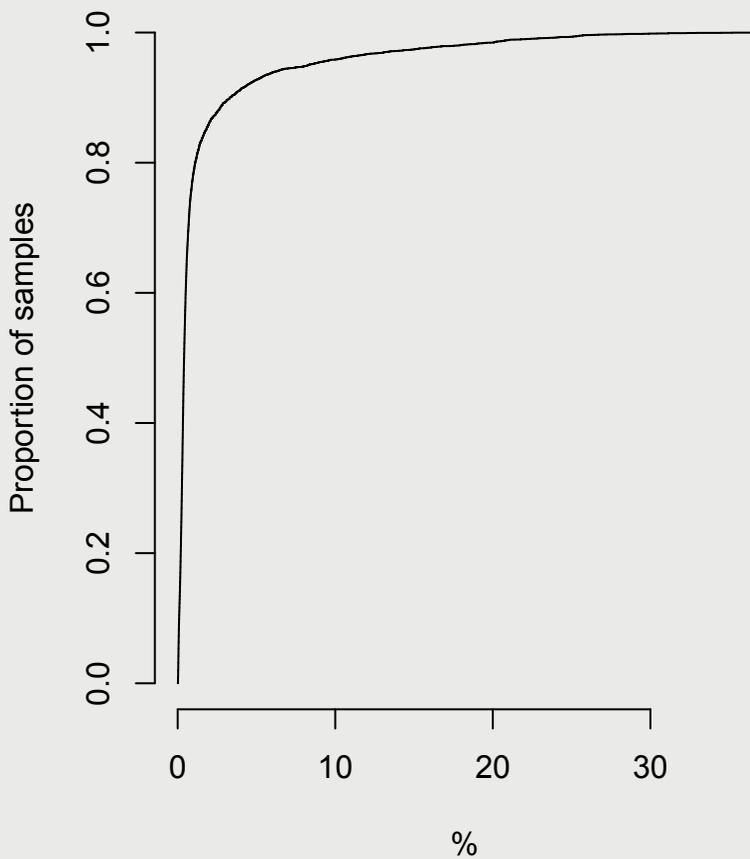
Histogram and boxplot



Normal Q-Q plot



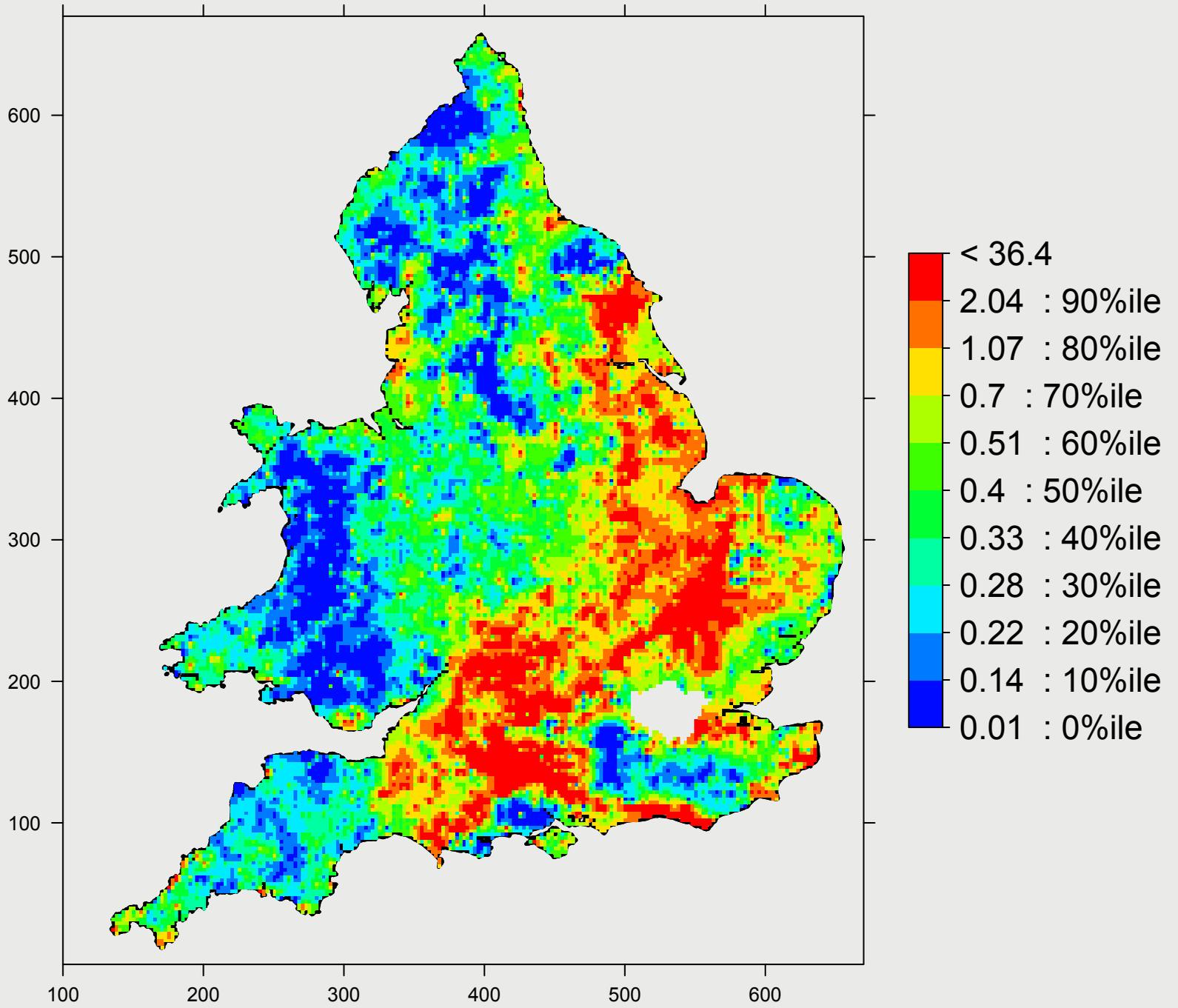
Cumulative frequency



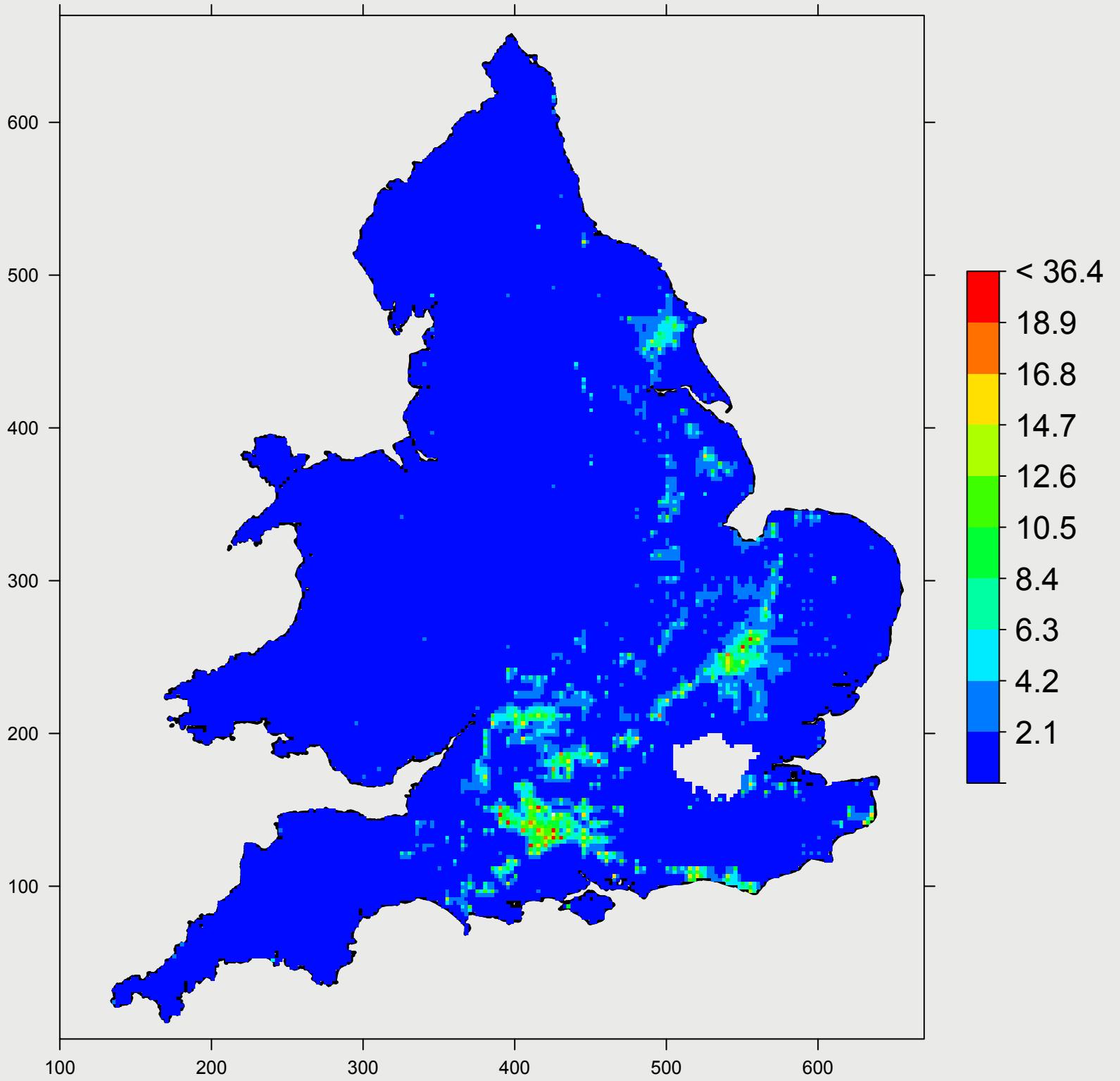
Ca - Calcium %

- mean= 1.6
- median= 0.41
- 10th percentile= 0.093
- 25th percentile= 0.24
- 75th percentile= 0.82
- 90th percentile= 3.3
- min= 0.0071
- max= 36
- skewness= 4.6
- n= 5670

Topsoil calcium (% ; percentile scale)



Topsoil calcium (% ; arithmetic scale)



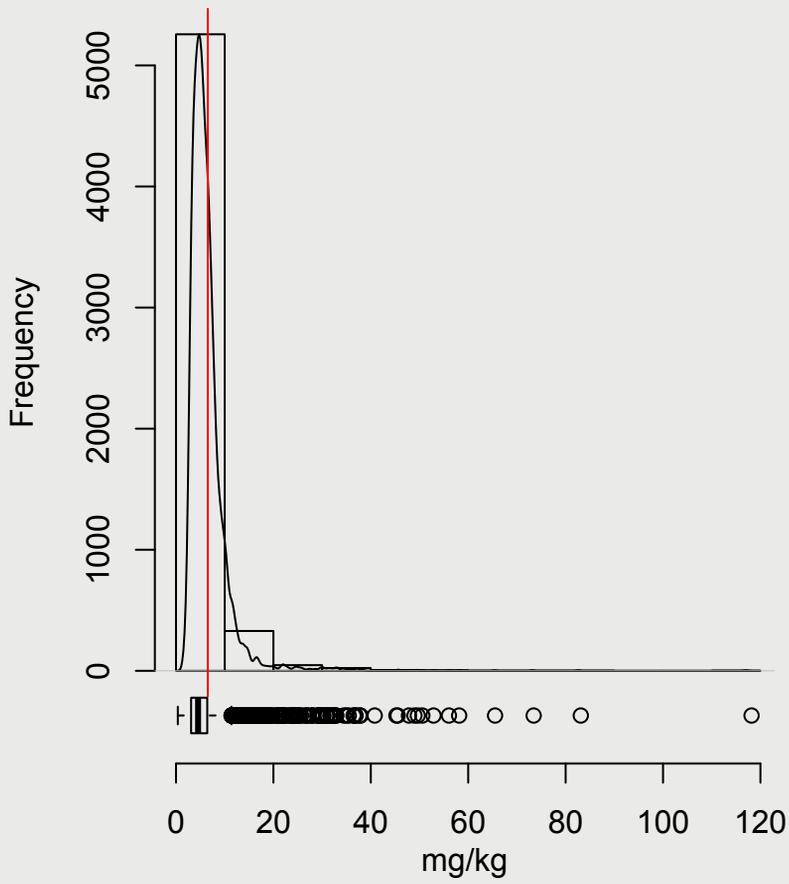
Caesium (Cs)

Natural Caesium (mainly the stable isotope ^{133}Cs) is an alkali metal and due to its physical and chemical properties behaves in a geochemically similar way to Rb and K, but its concentrations are generally lower. Reimann and de Caritat (1998) suggest an upper continental crustal abundance of between 3.7 and 5.8 mg/kg.

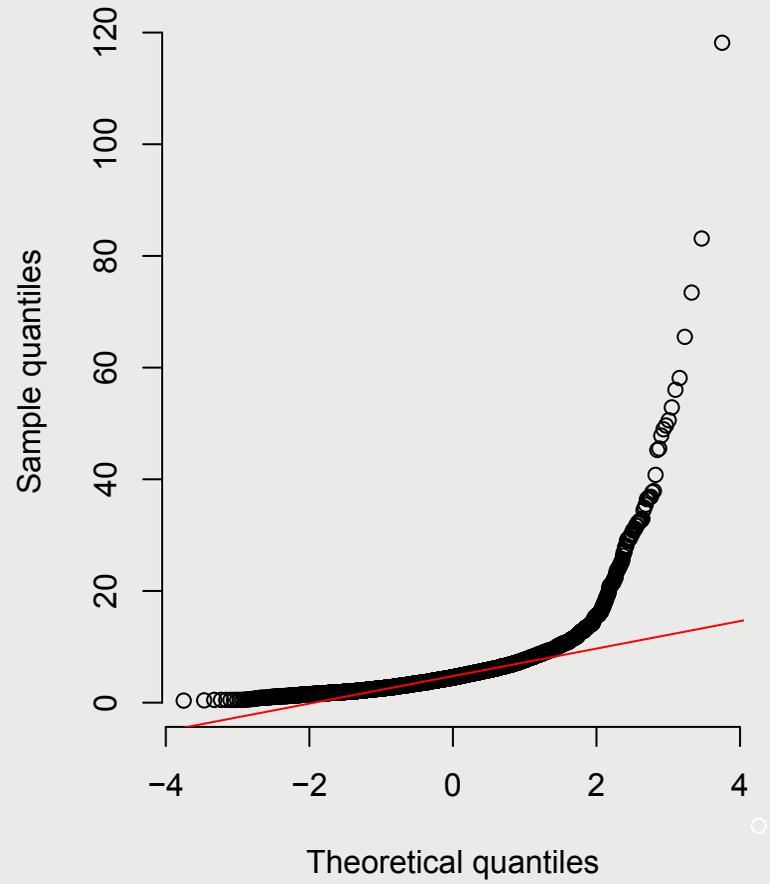
More than 20% of concentrations measured in the NSI soils exceed 6 mg/kg and most of these samples were collected from south-west England and south-east England (the Wealden district), western Wales, parts of central England and the Lake District. However, concentrations greater than 18.6 mg/kg (see arithmetic scale map) only occur across Devon and Cornwall and are associated with the major granite intrusions. The highest concentrations were measured in soils collected in the Torbay area to the south-east of the large granite intrusion of Dartmoor. This pattern is therefore close to those shown by potassium and rubidium. High Cs levels over the Somerset Levels (also associated with high Rb and K) and north-west Somerset are more problematical. The high Cs concentrations over soils in the Wealden district reflect the mineralogy of the Early Cretaceous nonmarine lacustrine and deltaic sandstones and clays. These contain material derived by river erosion from both the south-west peninsular and the area of Jurassic outcrop north of London, where Cs-rich rocks are now present at outcrop as they were in Early Cretaceous times (Brenchley and Rowson, 2006).

Very low Cs values are present over the Chalk, the Namurian sandstones, and those parts of East Anglia where the soils are derived from chalky or sandy Quaternary deposits.

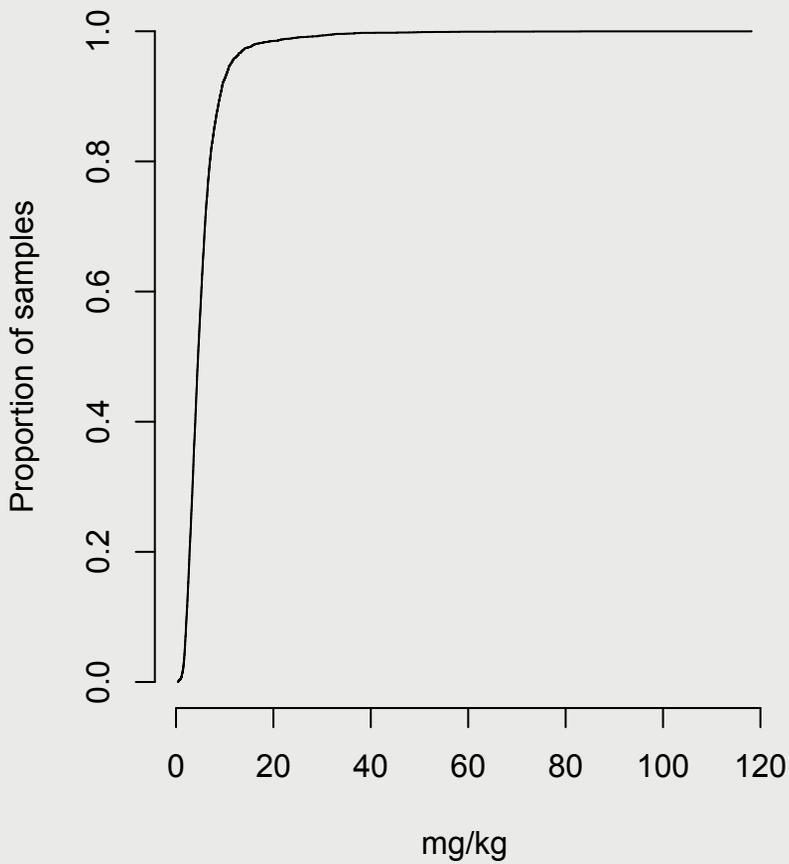
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Cs - Caesium mg/kg

mean= 5.5

median= 4.5

10th percentile= 2.2

25th percentile= 3.1

75th percentile= 6.4

90th percentile= 9

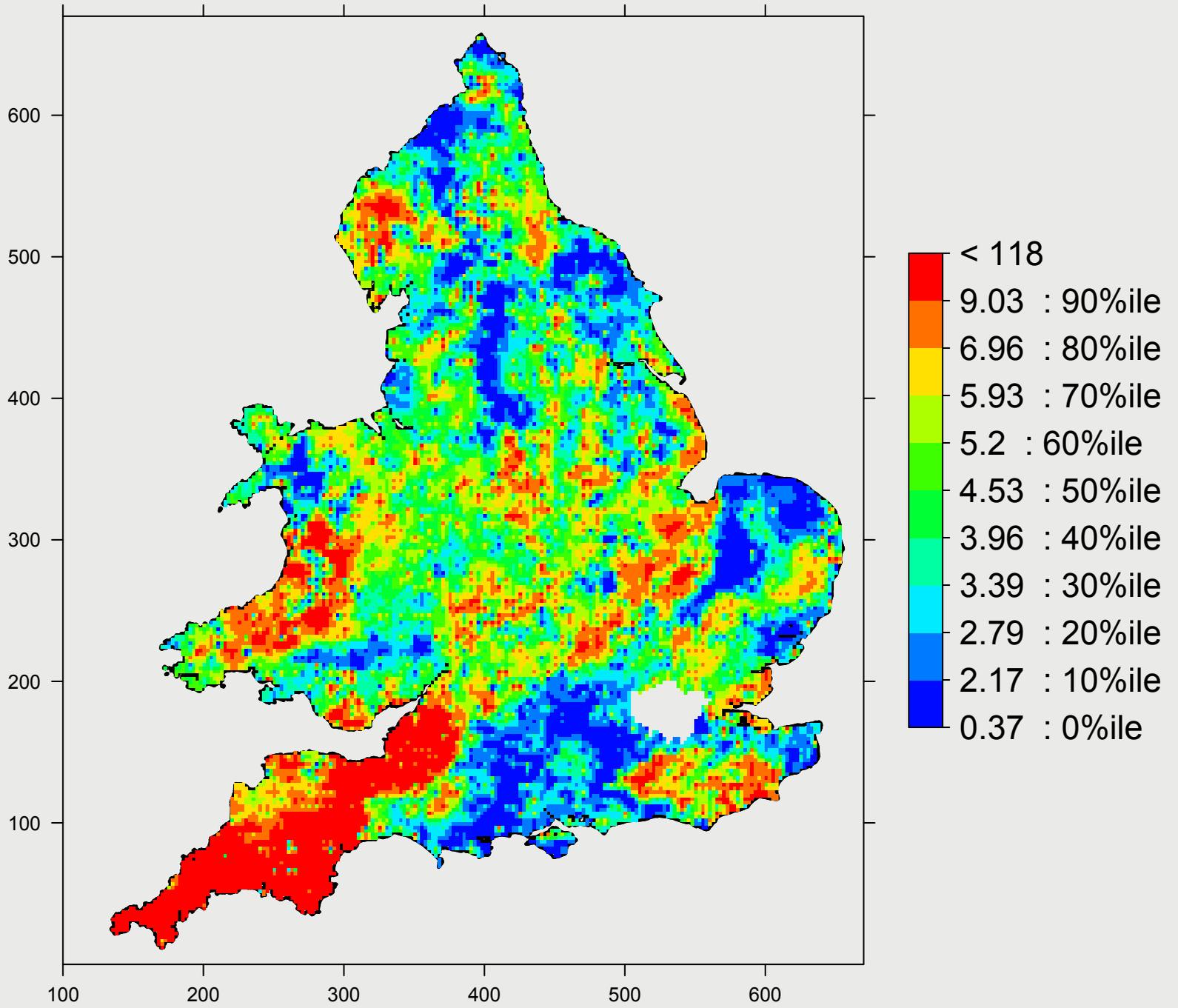
min= 0.37

max= 118

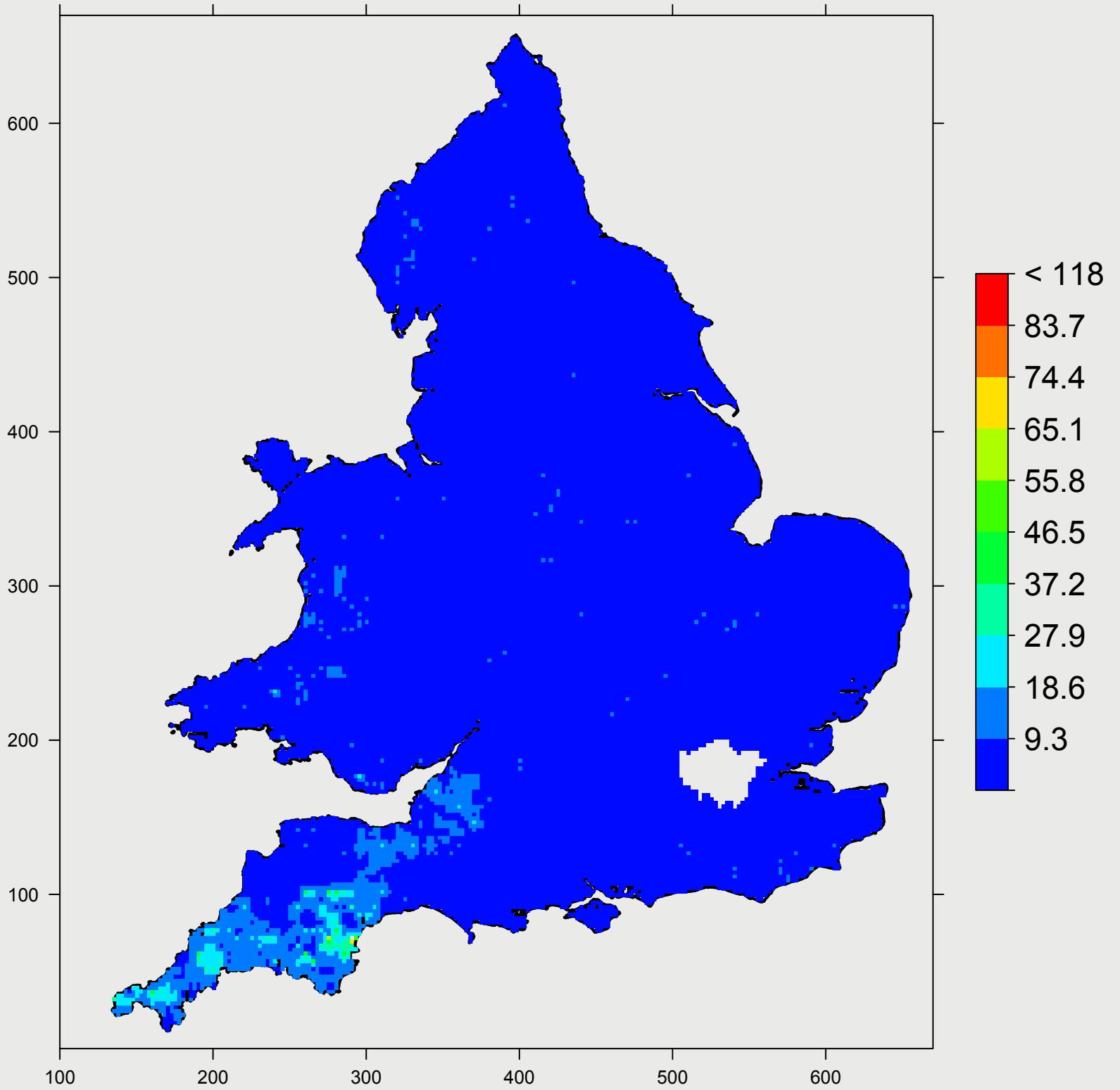
skewness= 7.2

n= 5670

Topsoil caesium (mg/kg ; percentile scale)



Topsoil caesium (mg/kg ; arithmetic scale)



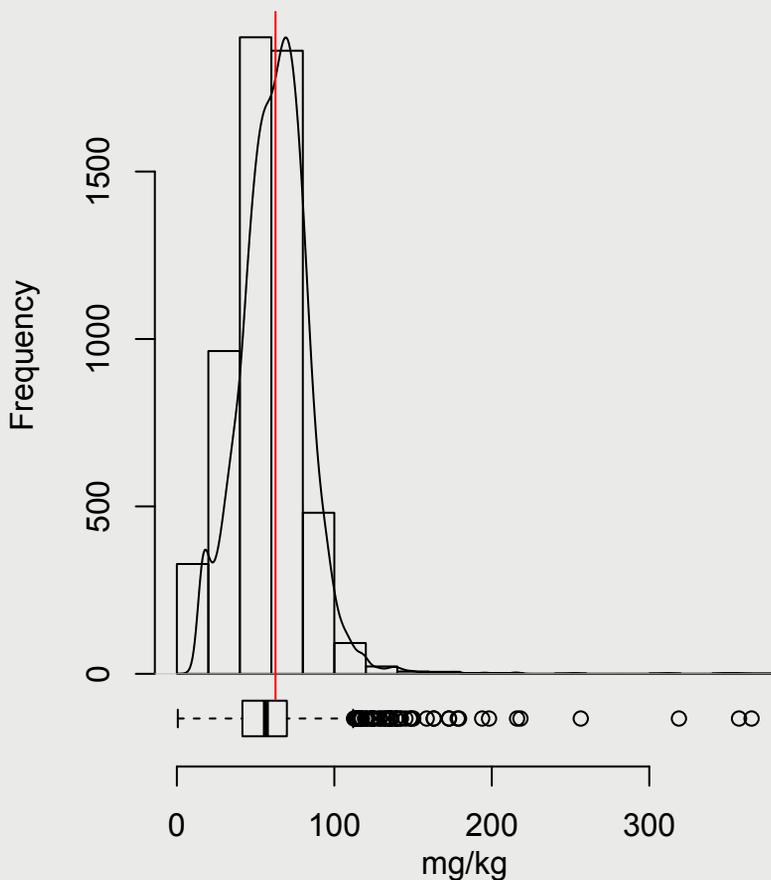
Cerium (Ce)

Cerium is the most abundant of the rare earth elements with an average crustal abundance of 65 mg/kg (Reimann and De Caritat, 1998). It is found in a number of minerals including monazite, xenotime, feldspars, apatite, sphene and zircon. Whilst it has no known biological role, it can accumulate in soils and the environment from its various uses in domestic electrical appliances and petrol producing industries. Concentrations measured in the NSI samples range from only 0.6 to 365 mg/kg with a mean and median of 56 and 57 mg/kg respectively, showing a near 'normal' concentration distribution.

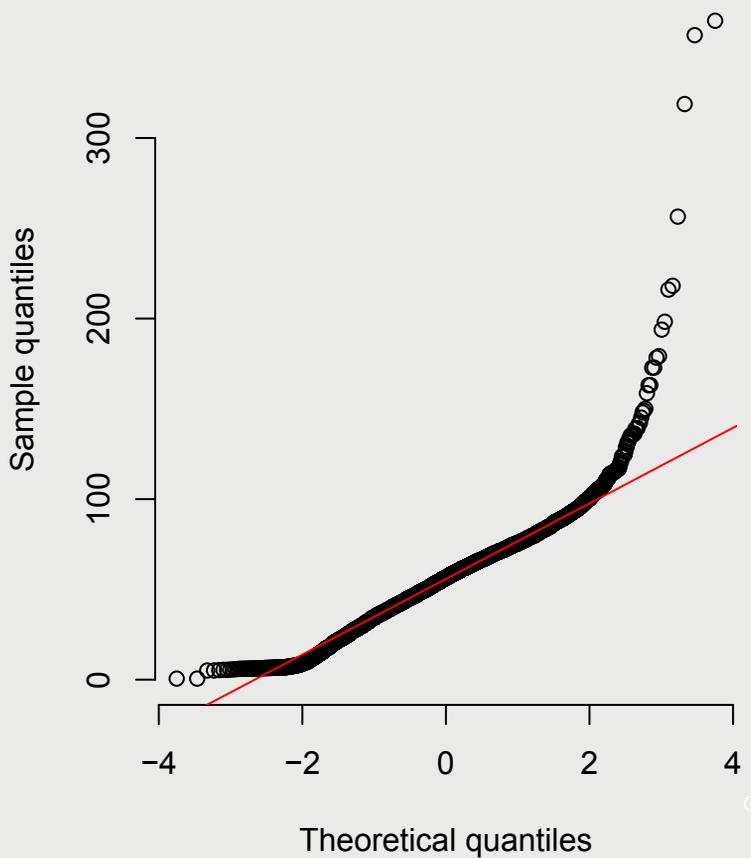
The highest Ce concentrations (>80 mg/kg) are in soils overlaying Lower Cretaceous strata in the Wealden district in south-east England, the Lias and Middle Jurassic oolites and ironstones of central England, Upper Ordovician and Silurian strata of western Wales and the Devonian slates and sandstone across Devon and Cornwall.

In contrast, very low Ce concentrations are present in soils over Snowdonia, parts of central Wales and the Brecon Beacons, much of the Pennines and the Permo-Triassic sandstone and mudstone outcrop, East Anglia, the Hampshire Basin and the granites of south-west England.

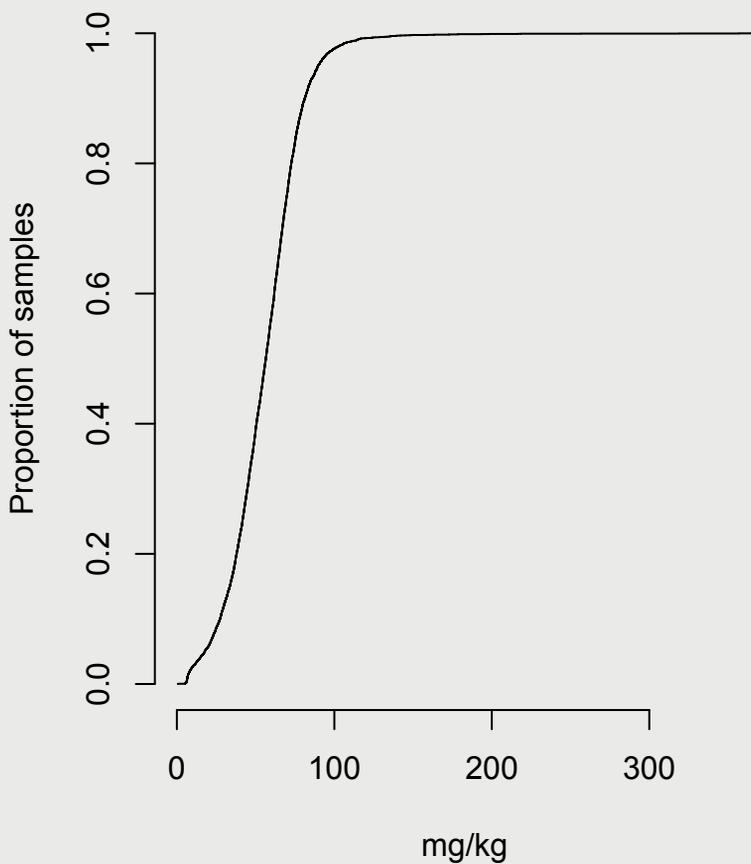
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ce - Cerium mg/kg

mean= 56

median= 57

10th percentile= 27

25th percentile= 42

75th percentile= 70

90th percentile= 81

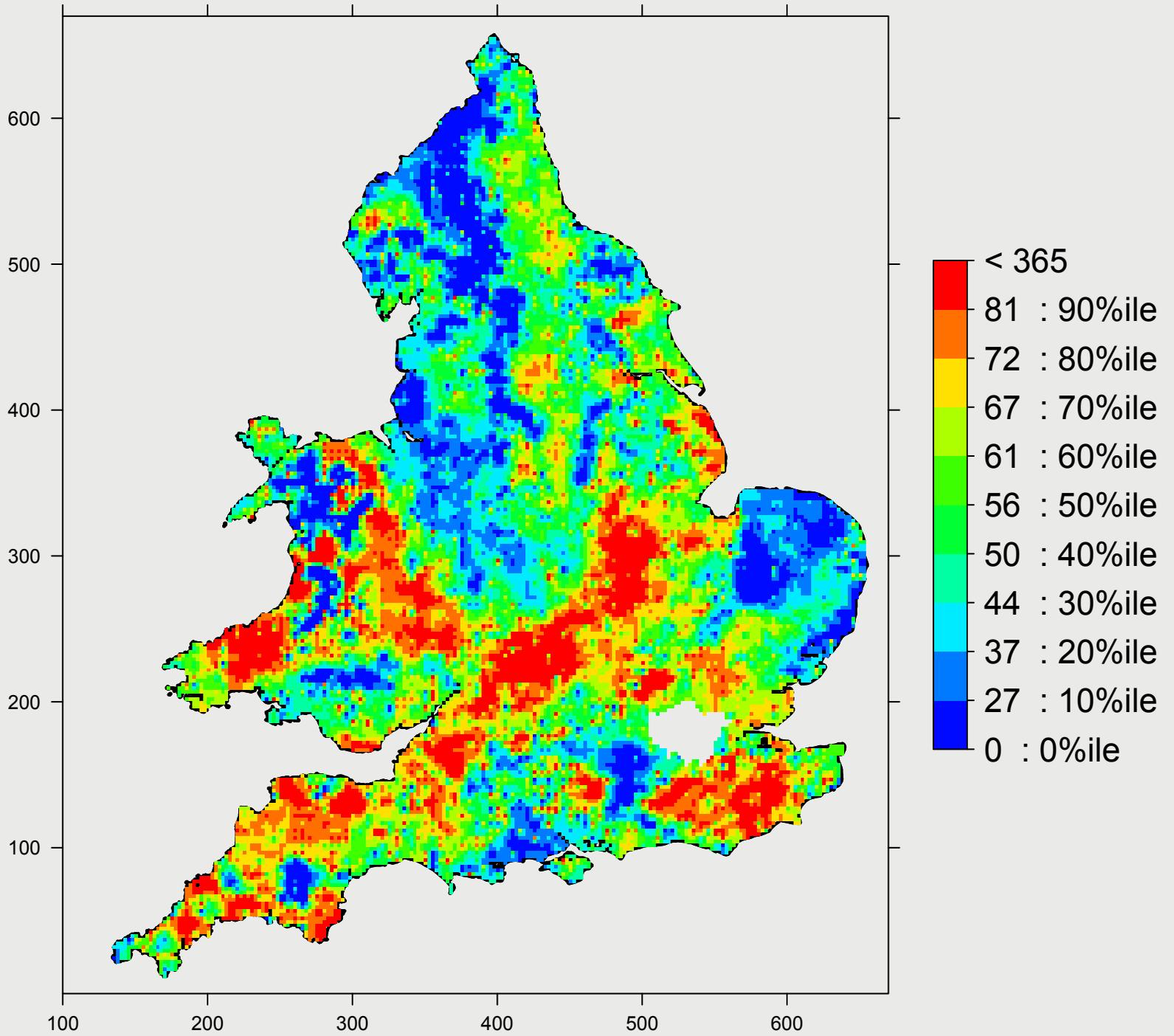
min= 0.6

max= 365

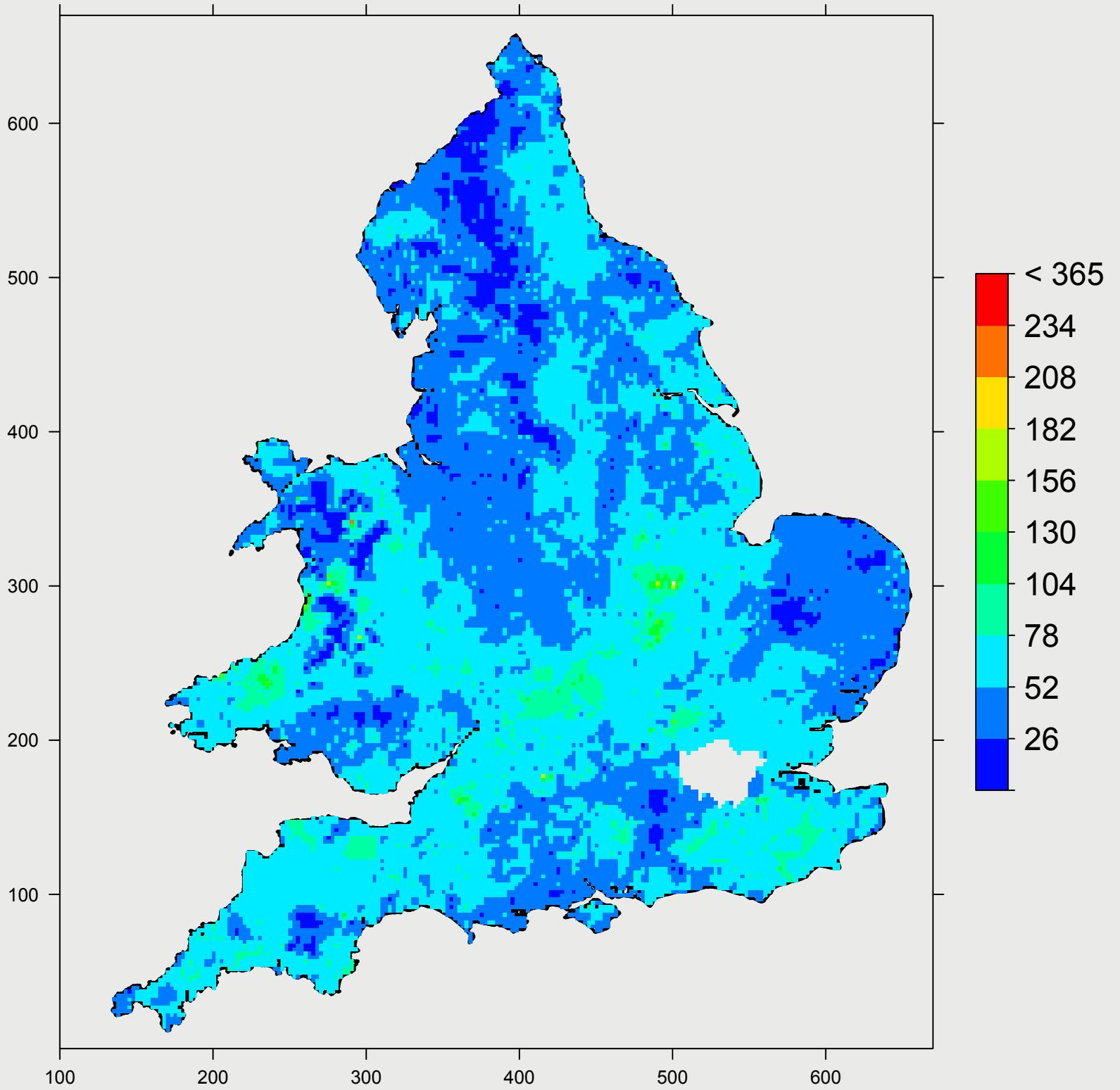
skewness= 1.5

n= 5670

Topsoil cerium (mg/kg ; percentile scale)



Topsoil cerium (mg/kg ; arithmetic scale)



Chlorine (Cl)

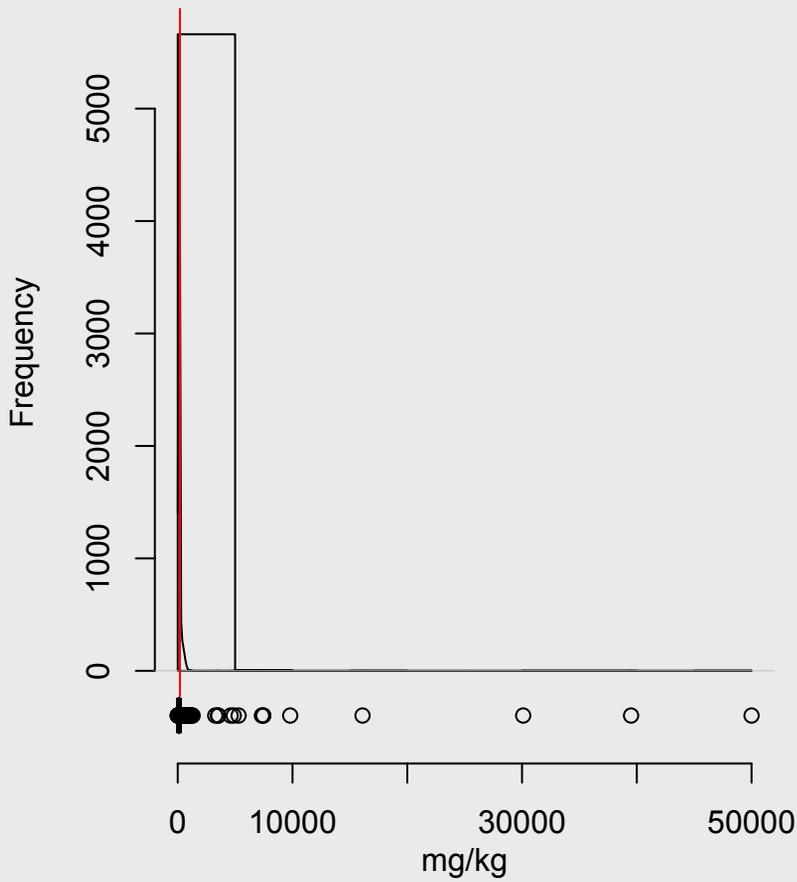
Chlorine is a nonmetallic, gaseous element forming a wide range of ionic compounds – chlorides, for example – and is an essential element in the biosphere. Typical upper continental crustal concentrations of Cl range from 140 to 640 mg/kg. In the geosphere, sandstones tend to be low in Cl (10 mg/kg) and granites, shales (150-200 mg/kg) and especially coals (1000 mg/kg) considerably richer (Reimann and De Caritat, 1998).

The dominant factors which are likely to control the spatial distribution of total Cl concentrations across England and Wales are inputs from marine aerosols in areas close to the coast with large annual average rainfall, and Cl derived from geological deposits of marine origin or recent marine incursions. The highest Cl concentrations (>200 mg/kg) occur in upland areas of northern England (Pennines, Lake District) and Wales, Devon and Cornwall. High concentrations also occur inland of The Wash where the superficial deposits are of recent marine origin, and marine alluvial soils also show high Cl levels on the coasts of Hampshire, Essex and north Kent. Inland, soils over the granite outcrops of Devon and Cornwall all show high Cl concentrations, but whether this is due to Cl-enriched rocks, or the topography giving increased marine mist input is not clear.

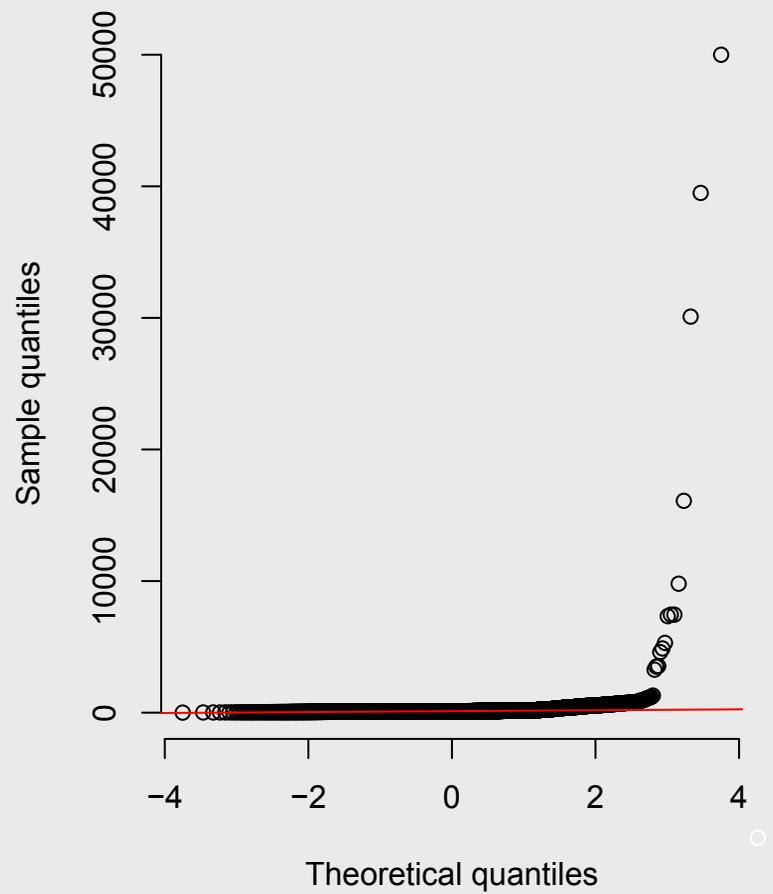
Low soil Cl concentrations are most closely associated with the Old Red Sandstone in SE Wales and the Welsh Borders, and SE Devon; and over the Weald, the Chalk and Quaternary deposits in southern and eastern England.

There appears to be considerable short-scale variation in Cl concentrations in parts of southern England; the causes of this variation may be due to local geological sources but further investigation would be required to confirm this. It is noteworthy that there is relatively small, three-fold variation in Cl concentrations between the 10th and 90th percentiles of its cumulative frequency distribution.

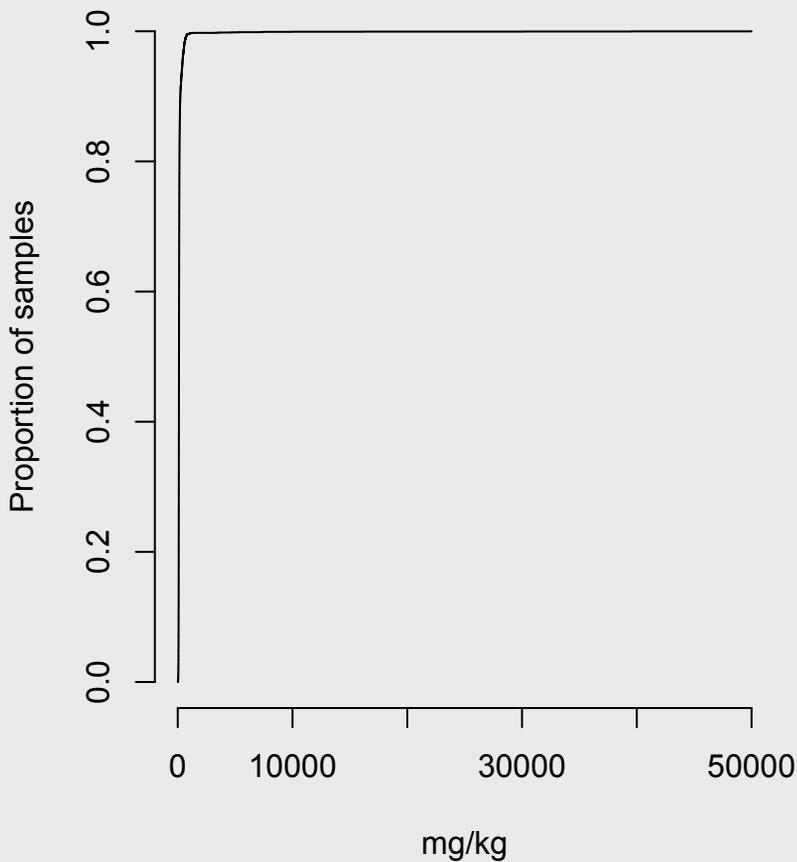
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Cl - Chlorine mg/kg

mean= 174

median= 108

10th percentile= 74

25th percentile= 90

75th percentile= 136

90th percentile= 225

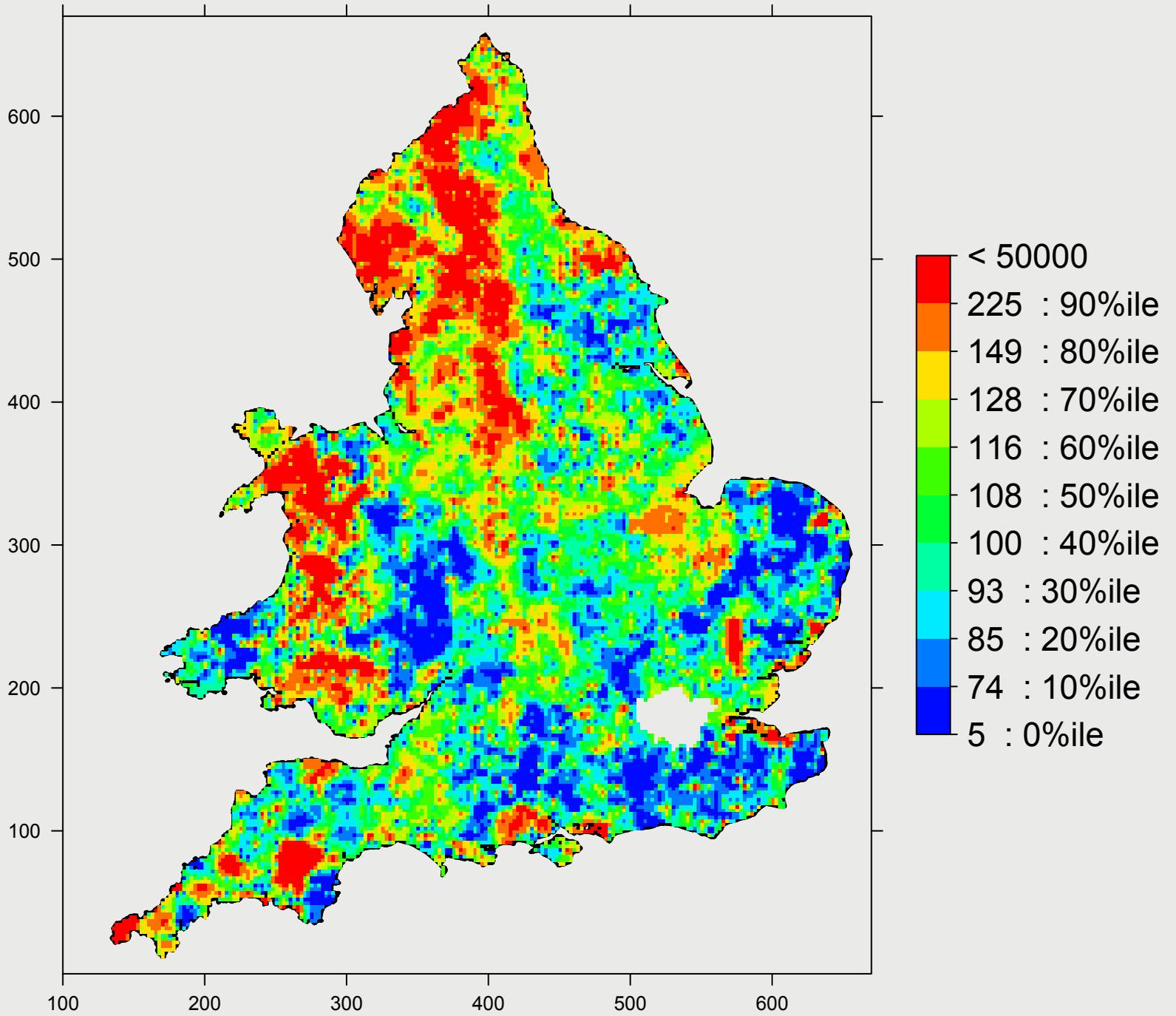
min= 5.4

max= 50000

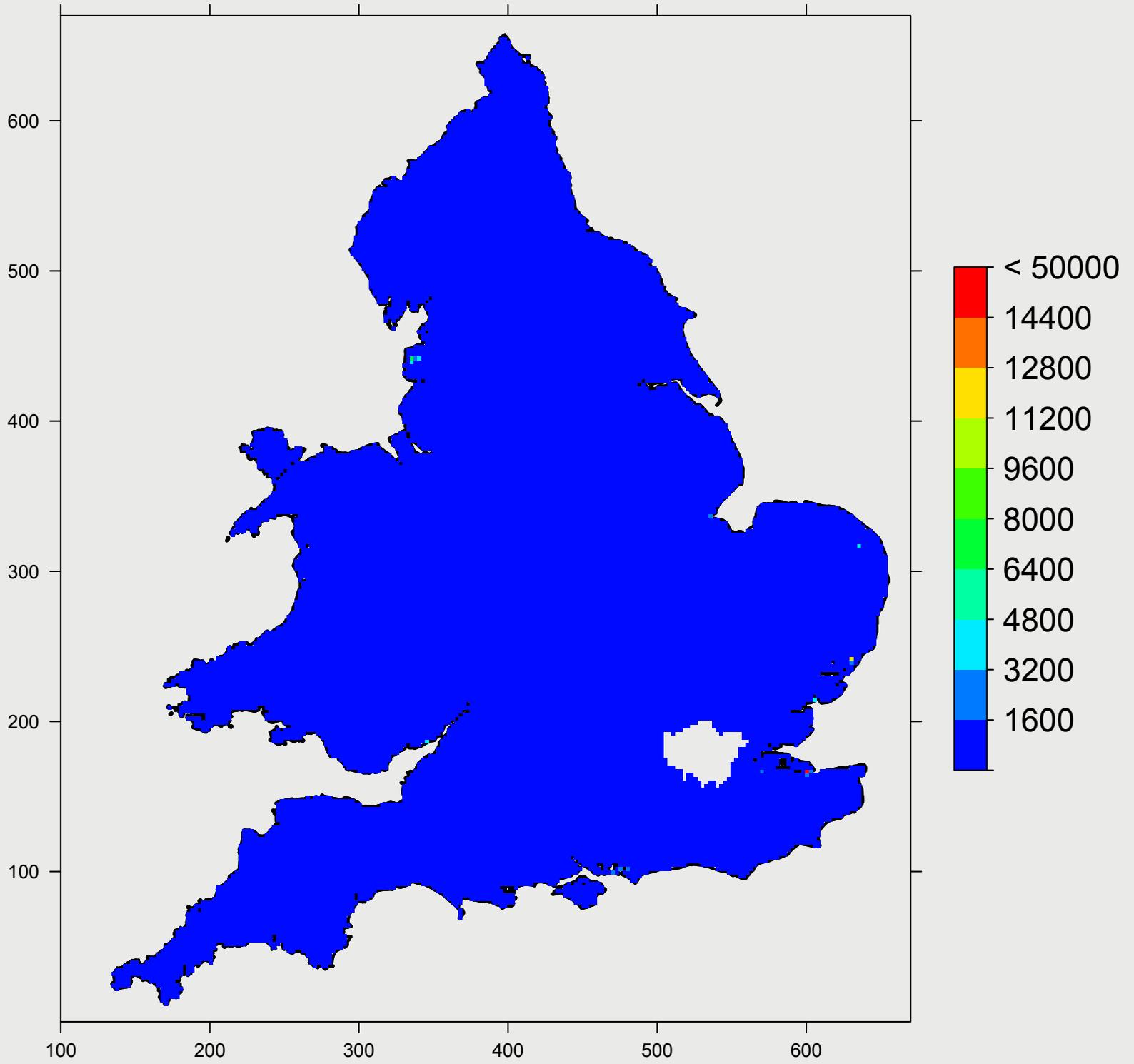
skewness= 39

n= 5670

Topsoil chlorine (mg/kg ; percentile scale)



Topsoil chlorine (mg/kg ; arithmetic scale)



Chromium (Cr)

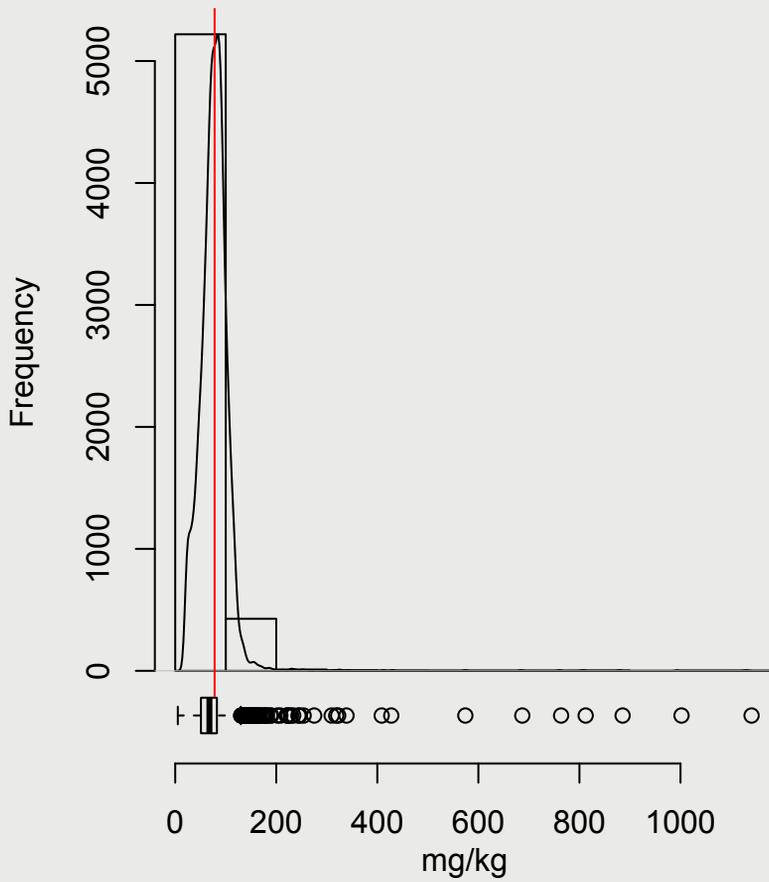
Chromium is a metallic element, present at about 35 mg/kg in the upper continental crust, but is more abundant in basic (250–300 mg/kg) and ultrabasic (2300 mg/kg) igneous rocks and shales (100 mg/kg) than in granites and sandstones (10–35 mg/kg) (Reimann and De Caritat, 1998). It is an essential element for animals at trace levels, but its bioavailability from the soil is generally low because it exists mainly in insoluble reduced forms (Cr III) in soil.

The Cr concentrations in topsoils appear to mirror the clay content (Oliver et al., 2002) and are low in sandy, thin chalky and upland soils. Small areas with high Cr concentrations occur in soil over the Lizard peninsula in the south-west due to serpentine parent materials, and a few small areas across central England, all of these are related to high P and Fe in soils and some are also linked with high Co, Ni and As. The latter group infers that a geochemical linkage is responsible, and all of these zones of high concentration are located on the belt of clay across England that includes ironstones. The percentile map shows additional features in that the alluvium in the Thames estuary and coast of Lincolnshire have relatively large Cr concentrations, possibly also associated with fine clay minerals. Further examples are the areas underlain by Devonian rocks in Devon and Cornwall and the area of mudstone, siltstone and sandstones stretching from Bridgnorth to Brecon and Newport in the Welsh Borders region. There are also areas of high Cr which are most likely anthropogenic, for example in Sheffield.

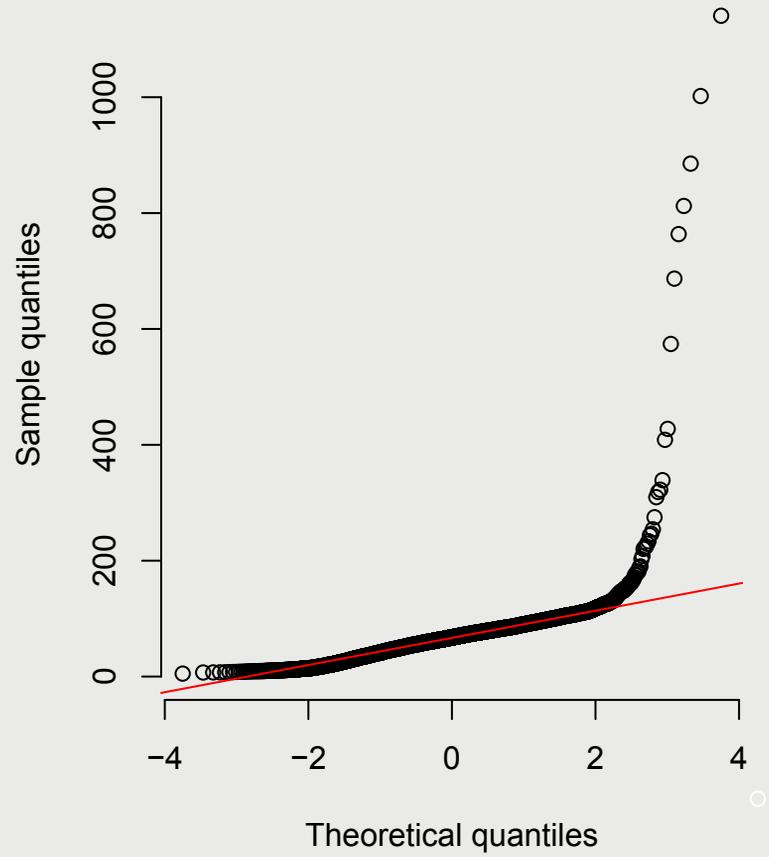
Low Cr concentrations in soils are associated with the granites of south-west England, much of north and central Wales, the Pennines, the Permo-Triassic outcrop and much of East Anglia.

The data suggest that Cr is not completely extracted from the soil matrix during aqua regia digestion; the values reported here using the XRF-S method are higher than those reported in McGrath and Loveland(1992) for which analysis was undertaken after aqua regia extraction. For example the median concentrations are 68 and 39 mg/kg respectively.

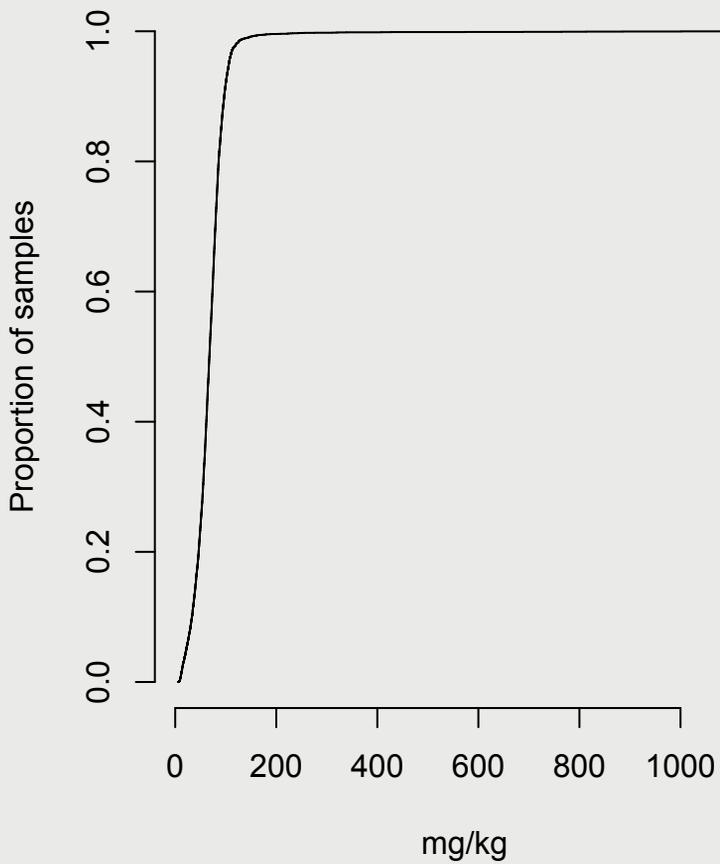
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Cr- Chromium mg/kg

mean= 68

median= 68

10th percentile= 33

25th percentile= 51

75th percentile= 83

90th percentile= 97

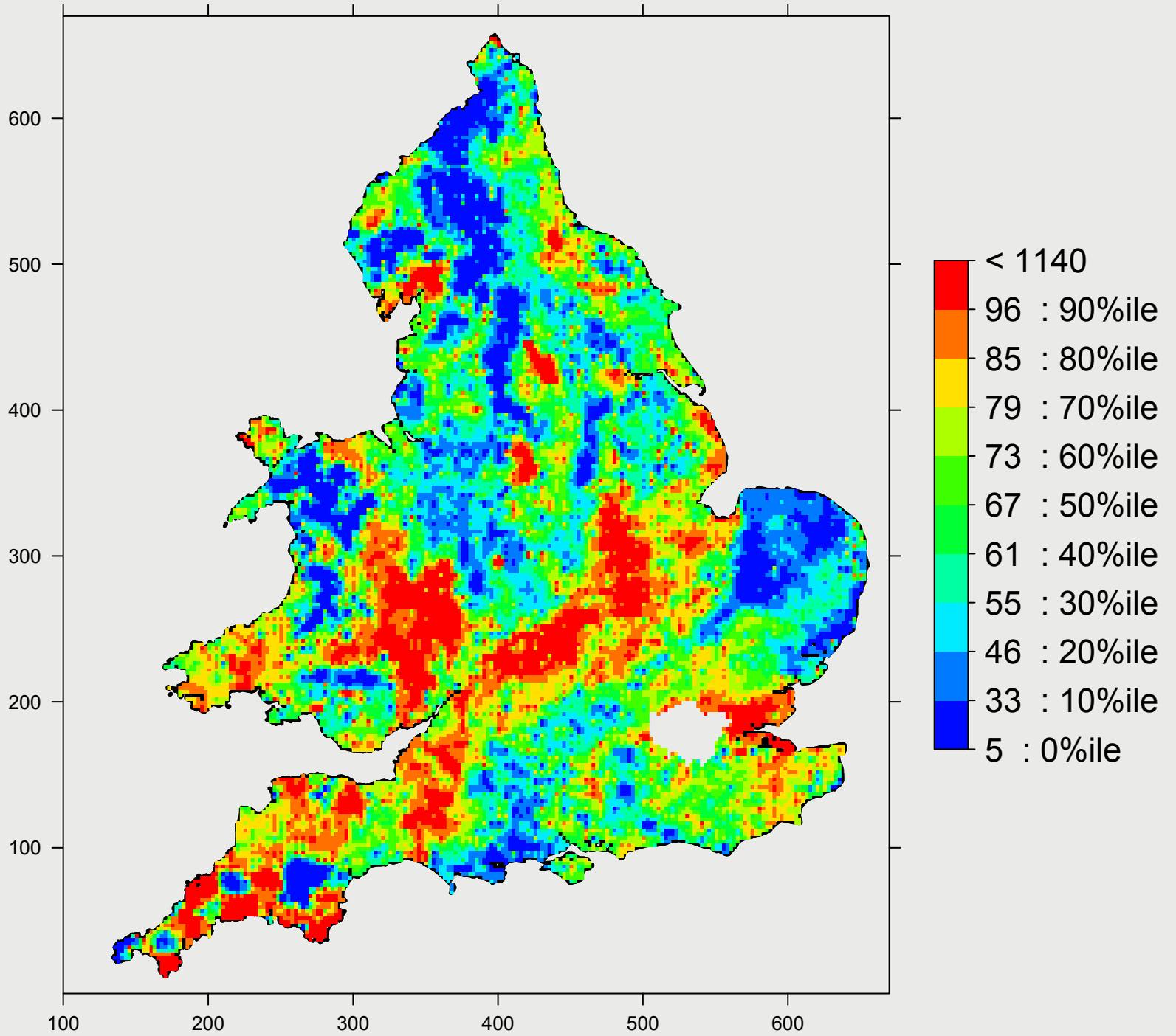
min= 5.1

max= 1141

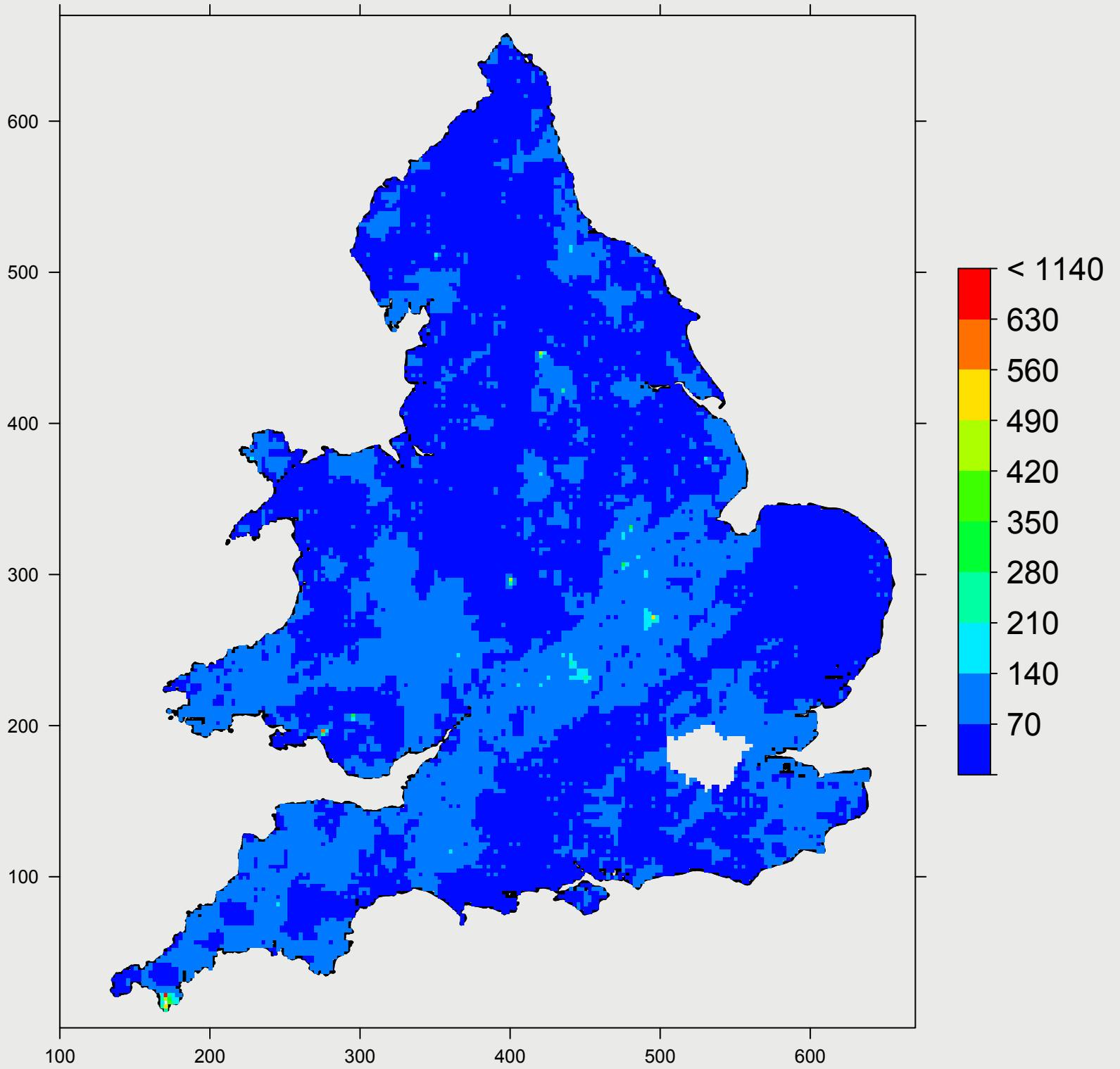
skewness= 11

n= 5670

Topsoil chromium (mg/kg ; percentile scale)



Topsoil chromium (mg/kg ; arithmetic scale)



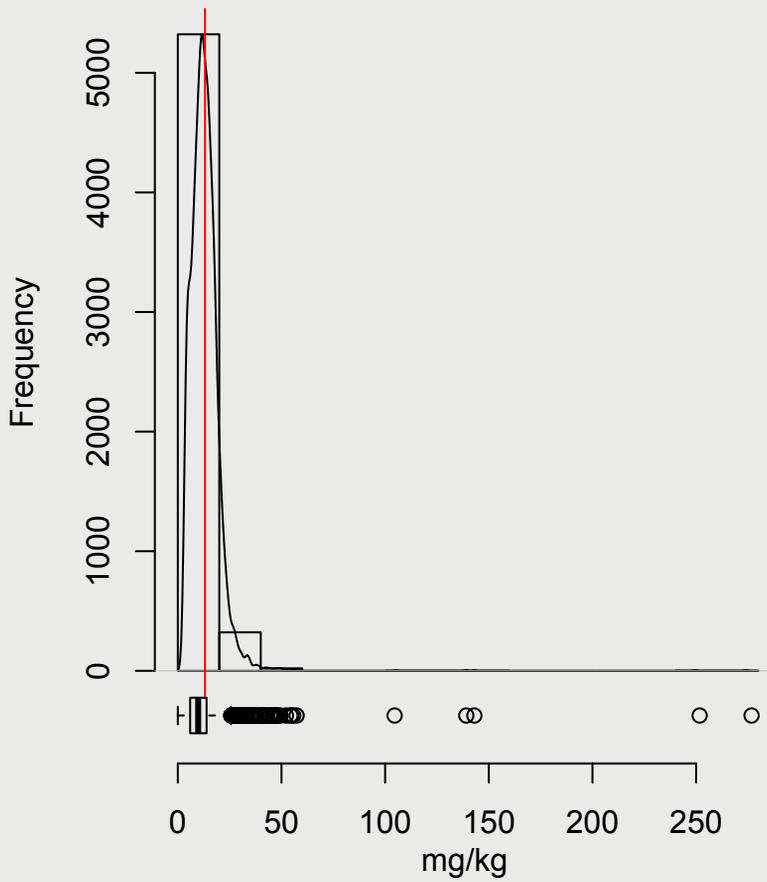
Cobalt (Co)

Cobalt is a metallic element with an estimated upper continental crustal abundance of about 11 mg/kg, though it is more abundant in basic and ultrabasic igneous rocks and less abundant in granites, sandstones and limestones (Reimann and De Caritat, 1998). Cobalt is an essential micronutrient, and Co deficiencies can be a major agricultural problem with some grazing animals, especially sheep, being particularly vulnerable.

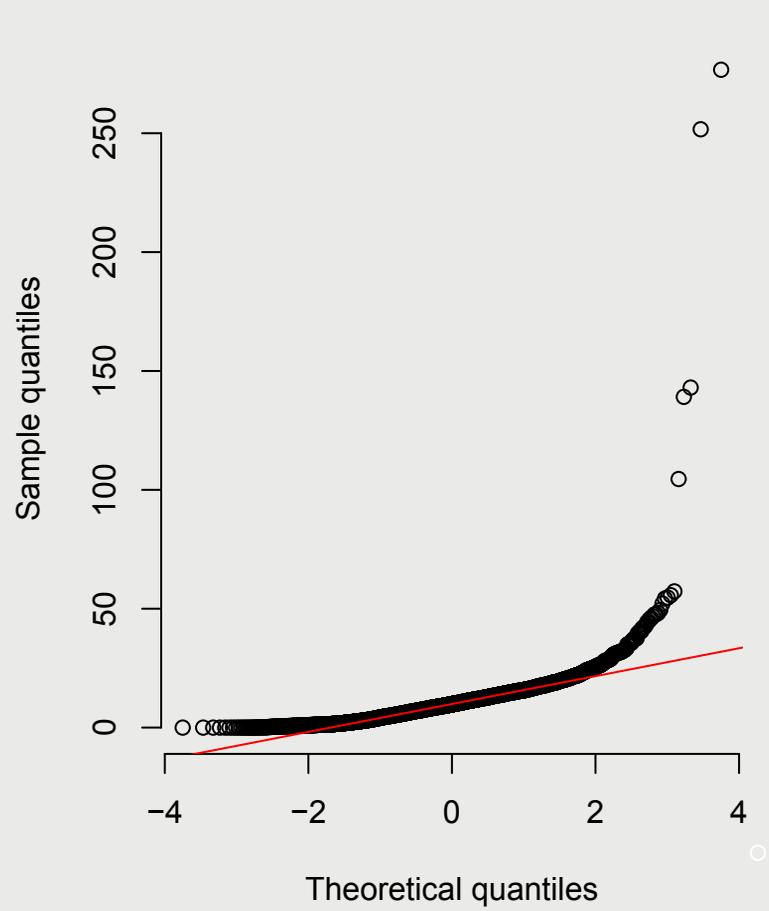
The concentrations of Co are generally low across much of England and Wales, with a few areas of higher concentrations (>13 mg/kg); for example near Banbury in Oxfordshire where there is an association with high Fe and Ni concentrations in soil linked with the occurrence and mining of Lower Jurassic ironstone. The percentile map shows that many of the clay-rich soils have reasonably high Co concentrations. This enrichment extends over much of the Jurassic outcrop between Bath in the south-west and Grantham (Lincolnshire). An area of high Co values near Hemel Hempstead in Hertfordshire is more problematical. The Peak District (basalt lavas within the mainly limestone sequence) and the Yorkshire–Derbyshire–Nottinghamshire coalfield show elevated Co levels. High Co concentrations are also present over the Serpentine soils of the Lizard in Cornwall, and in a few areas in south and central Devon. Cobalt shows broad similarity in its spatial distribution to that of As, Fe and Ni.

Low Co concentrations occur in many of the upland areas of the north of England, Wales and the south-west (especially the granite outcrops), which may be of importance for animal nutrition in these regions of pastoral agriculture. Lowland areas with low concentrations (<6 mg/kg) include the sandy soils in the New Forest, the heaths between Reading and Woking and the Quaternary sands and tills of East Anglia.

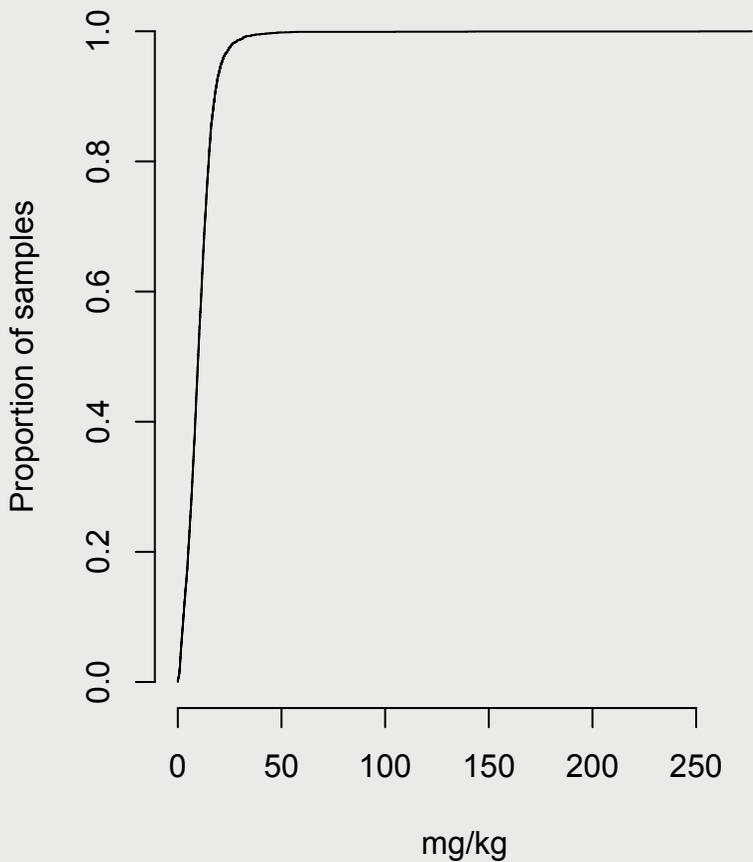
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Co - Cobalt mg/kg

mean= 11

median= 9.8

10th percentile= 2.7

25th percentile= 6

75th percentile= 14

90th percentile= 18

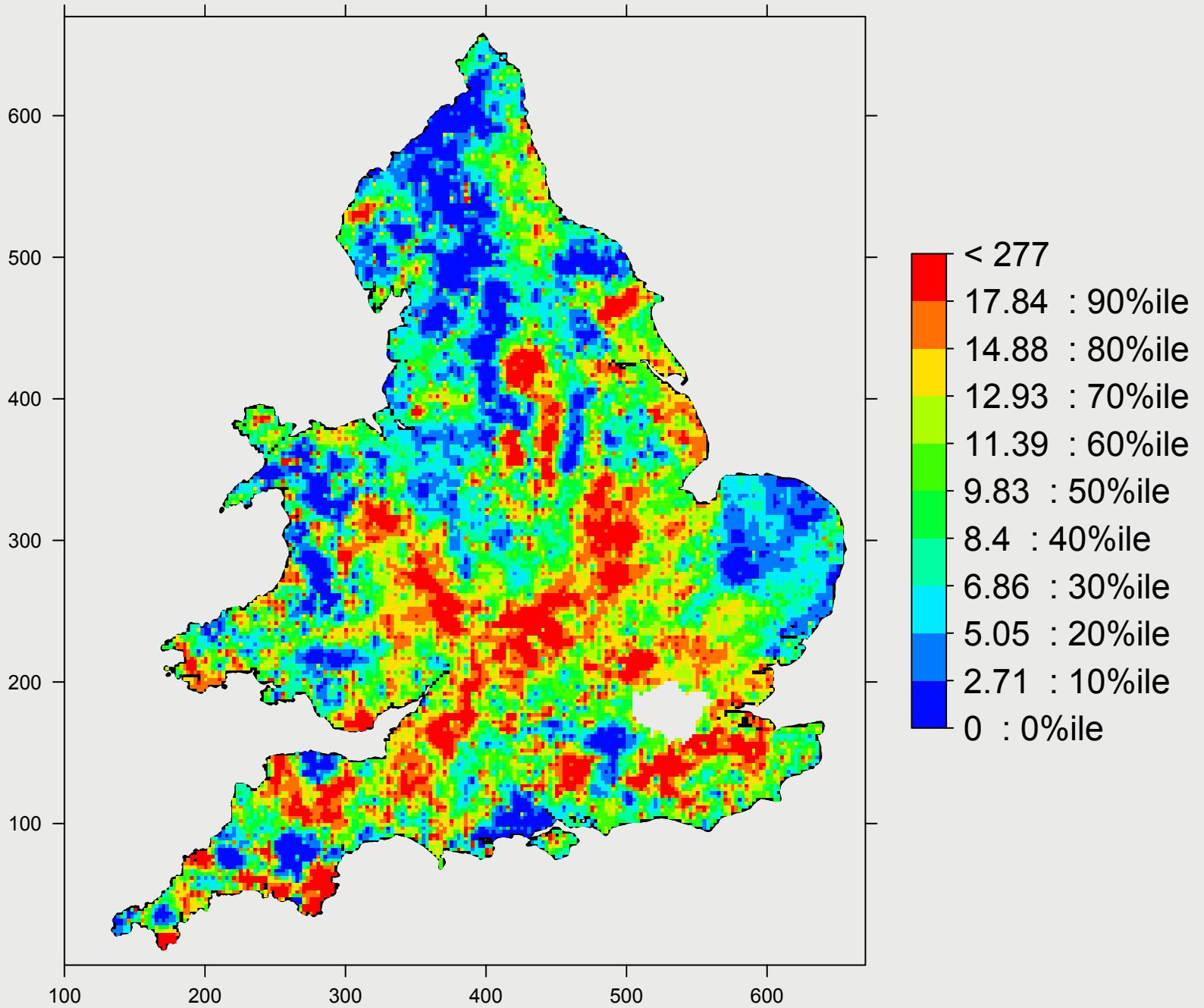
min= 0

max= 277

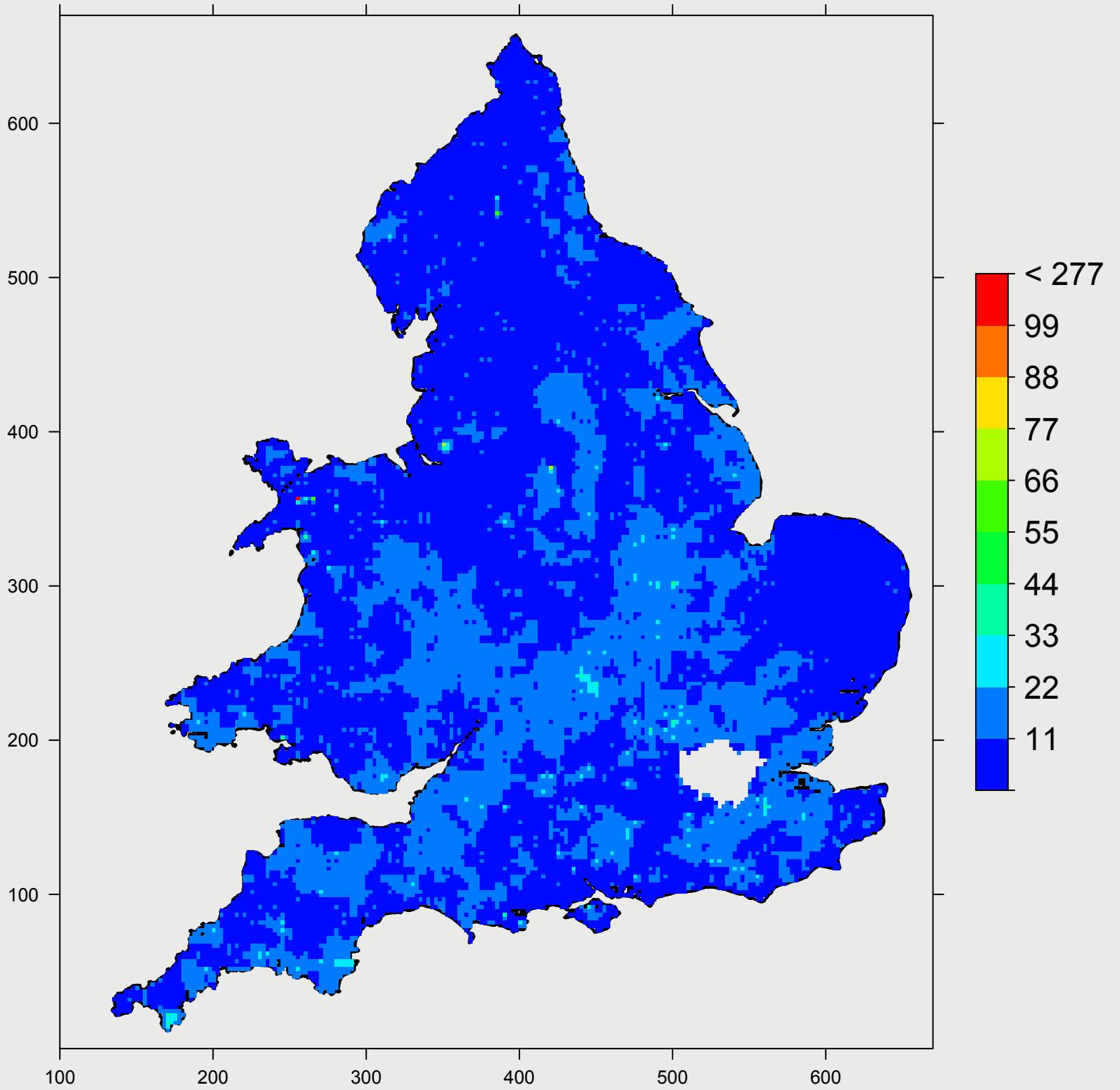
skewness= 12

n= 5670

Topsoil cobalt (mg/kg ; percentile scale)



Topsoil cobalt (mg/kg ; arithmetic scale)



Copper (Cu)

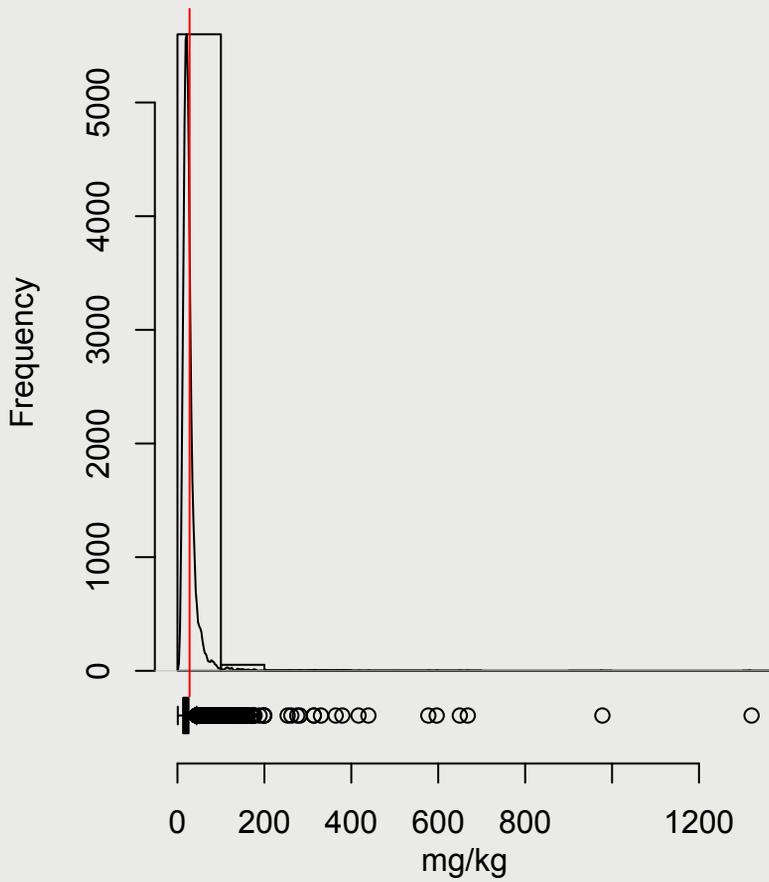
Copper is a biologically essential metallic micronutrient element with an estimated upper continental crustal abundance of about 15 mg/kg, though it is much more abundant in basalts (90 mg/kg) and shales (45 mg/kg) relative to other rock types (Reimann and De Caritat, 1998). Copper also has strong affinities with sulphur in mineralisation centres and with humified organic matter in some lowland peats.

Most of the areas of very high soil Cu concentrations are those where mining, smelting or the industrial uses of Cu have been practiced for long periods, including south Cornwall, the Tamar Valley, Anglesey and Snowdonia, south Wales (particularly the Swansea valley), Bristol, Birmingham, around northern industrial towns in a wide zone from Liverpool through Manchester to Leeds, and a smaller area of the north-east coalfield around Newcastle and Sunderland.

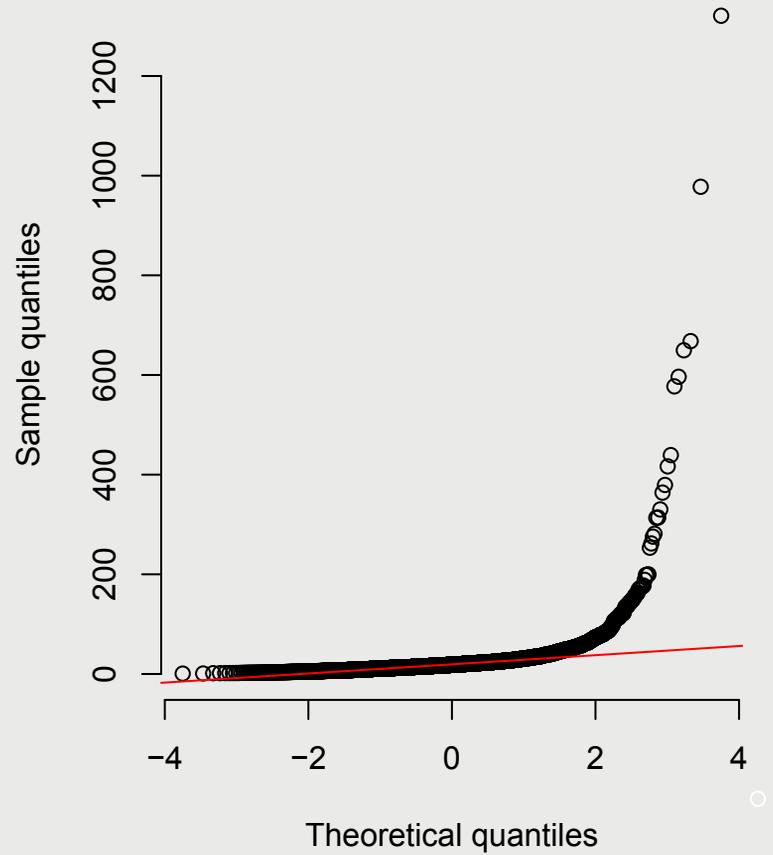
There are upper limit values for soil Cu concentrations and Statutory Instrument (SI 1263, 1989) gives a maximum Cu concentration for agricultural soils receiving sewage sludge of 135 mg/kg dry weight, as excess Cu intake can induce other trace-element deficiencies (e.g. Mo) in livestock. Most soils away from the mining areas are well below this value, almost 90% being less than 30 mg/kg. Soils with relatively high Cu are exaggerated somewhat on the percentile map, and it is interesting that the organic soils in the Fens and the Somerset Levels also appear to contain ~30 mg/kg Cu over most of the area, suggesting that the fen peats may have accumulated Cu through sorption of Cu from groundwater, or from the agricultural application of Cu-containing fertilisers during the twentieth century.

Soils with low copper concentrations occur mainly on high moorlands with organic soils (the Pennines, Wales, North Yorkshire, the south-west (Bodmin Moor, Dartmoor)) or in lowland areas that have sandy or thin chalk soils (East Anglia, Hampshire, New Forest, west Surrey and Sussex).

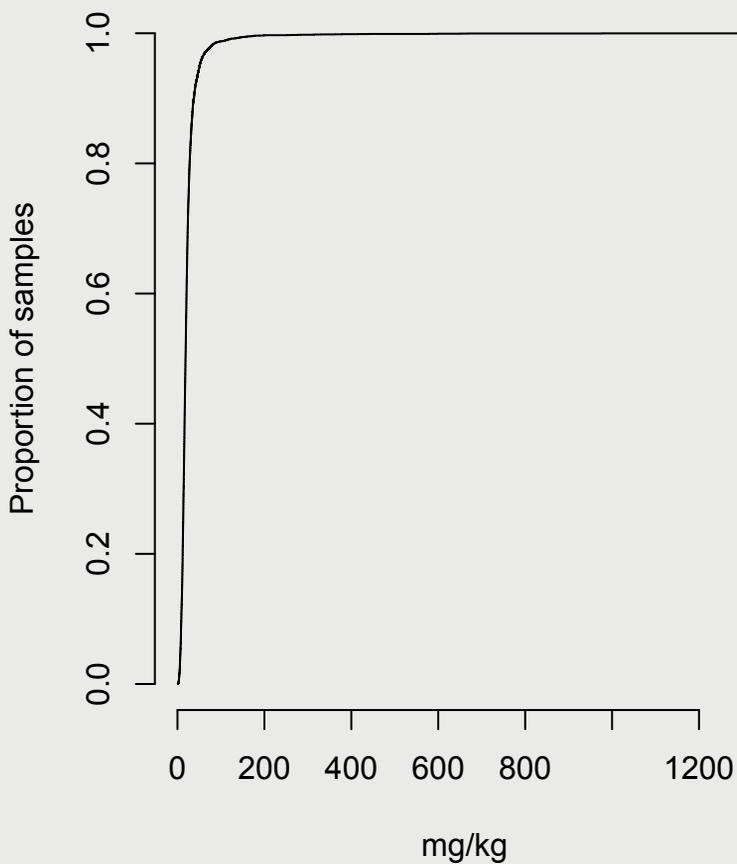
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Cu - Copper mg/kg

mean= 24

median= 19

10th percentile= 8.8

25th percentile= 13

75th percentile= 26

90th percentile= 38

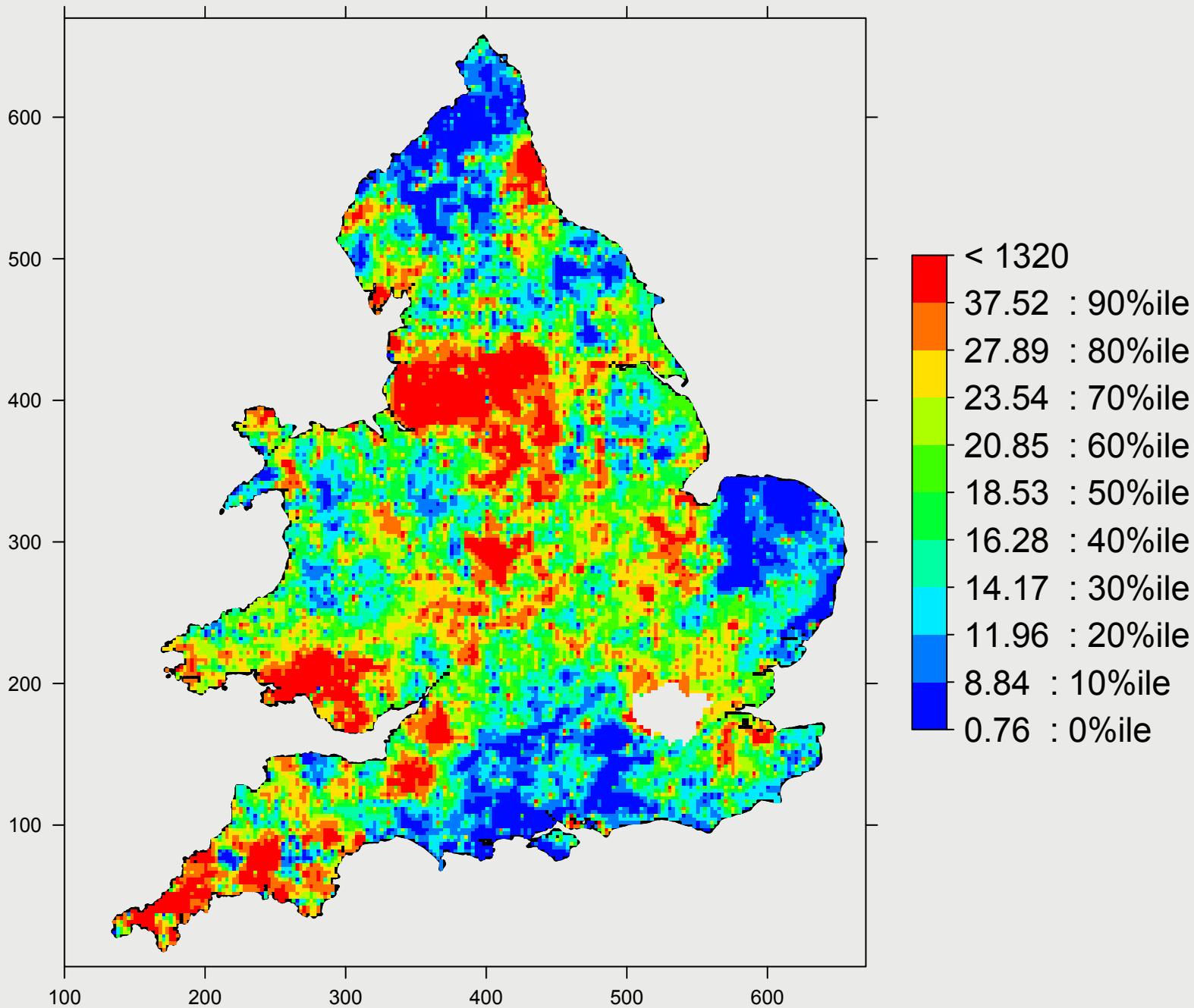
min= 0.76

max= 1321

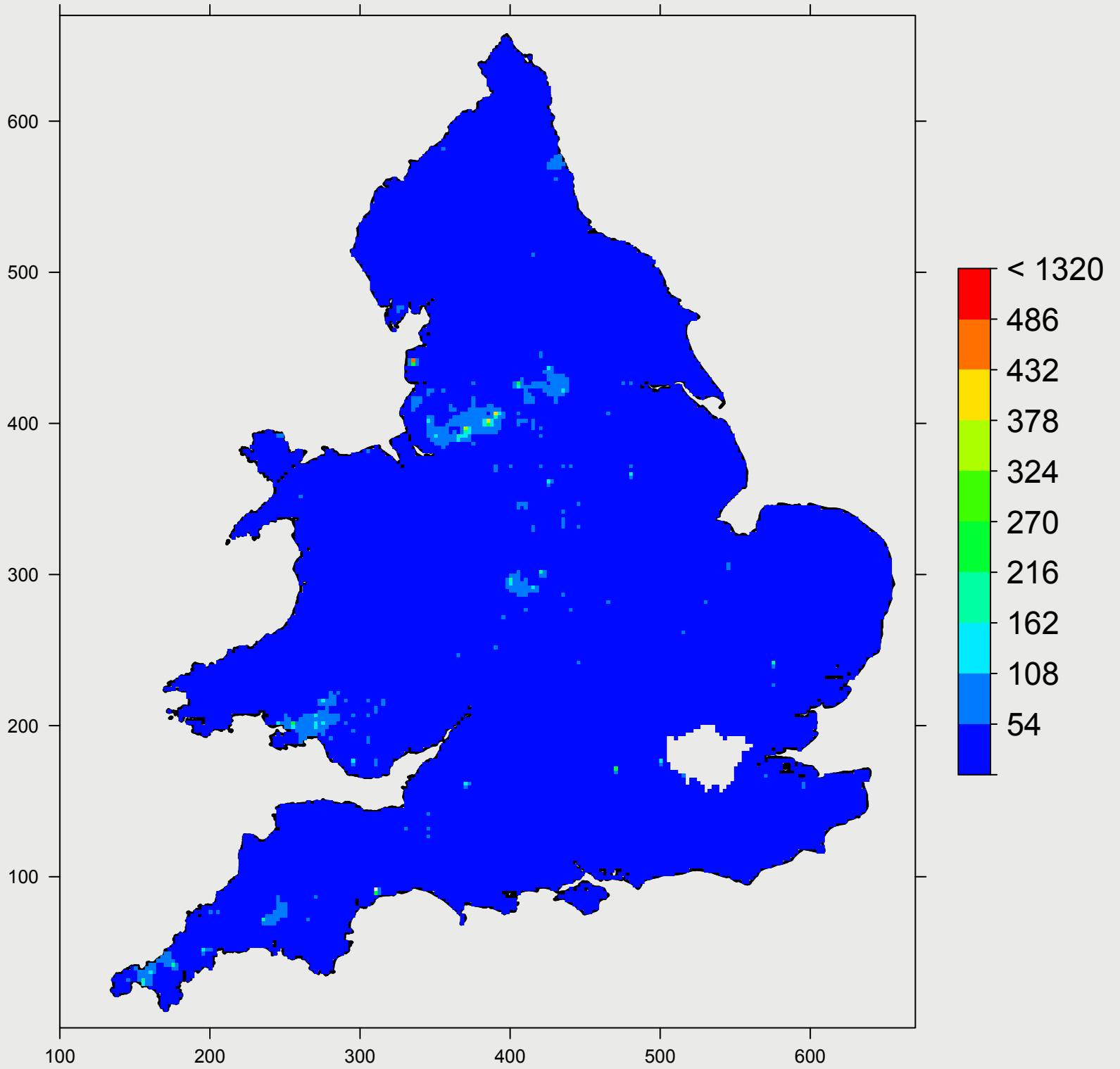
skewness= 19

n= 5670

Topsoil copper (mg/kg ; percentile scale)



Topsoil copper (mg/kg ; arithmetic scale)



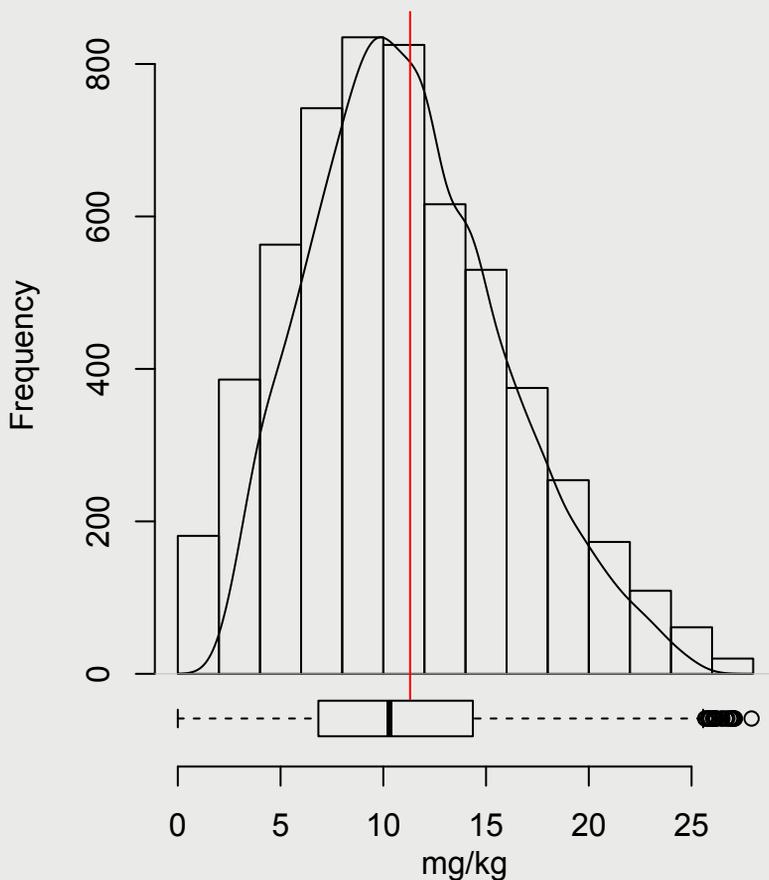
Gallium (Ga)

Gallium is a non-toxic, non-essential metallic element with an average upper continental crustal abundance of between 14 and 17 mg/kg (Reimann and De Caritat, 1998). The primary source of Ga is its occurrence as a trace component in bauxite (aluminium ore minerals) and to a smaller extent in sphalerite (a Zn sulphide mineral). Hence, the spatial distribution of elevated concentrations of Ga in soils corresponds well to those shown for Al and to a lesser extent to areas of Zn mineralisation. There is very little published information on its occurrence in soils and its environmental effects.

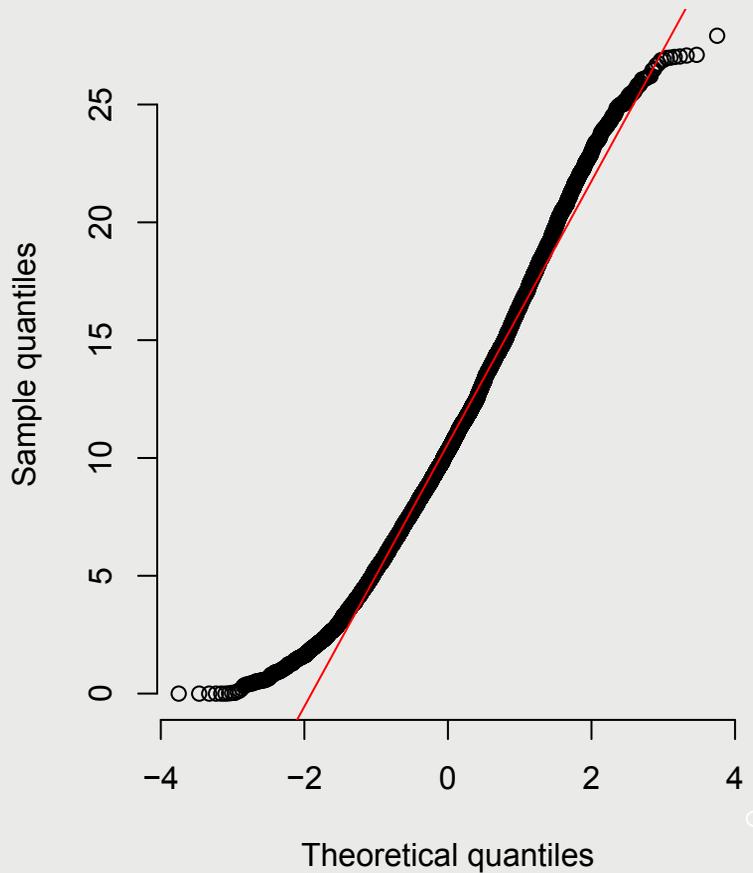
Median concentrations measured in the NSI soils are 10 mg/kg. The data is only slightly skewed and so has a nearly normal distribution. Elevated concentrations (>18 mg/kg) occur mainly in relation to soils developed over Devonian mudstone and sandstone in the south-west of England, and Lower Palaeozoic mudstone and greywacke of western Wales and the Lake District, where there may also be a local sphalerite-related overprint due to mineralisation. Lesser patterns of enrichment can be seen over the coalfields of Lancashire, Yorkshire, the north-east and parts of south Wales; and over the Jurassic mudstones of the Midlands.

The lowest concentrations were measured in soils from East Anglia and southern England as well as from the Pennines in the north of England, which are underlain by chalky and sandy Quaternary deposits, Cretaceous Chalk and Carboniferous (Namurian sandstone) strata, respectively.

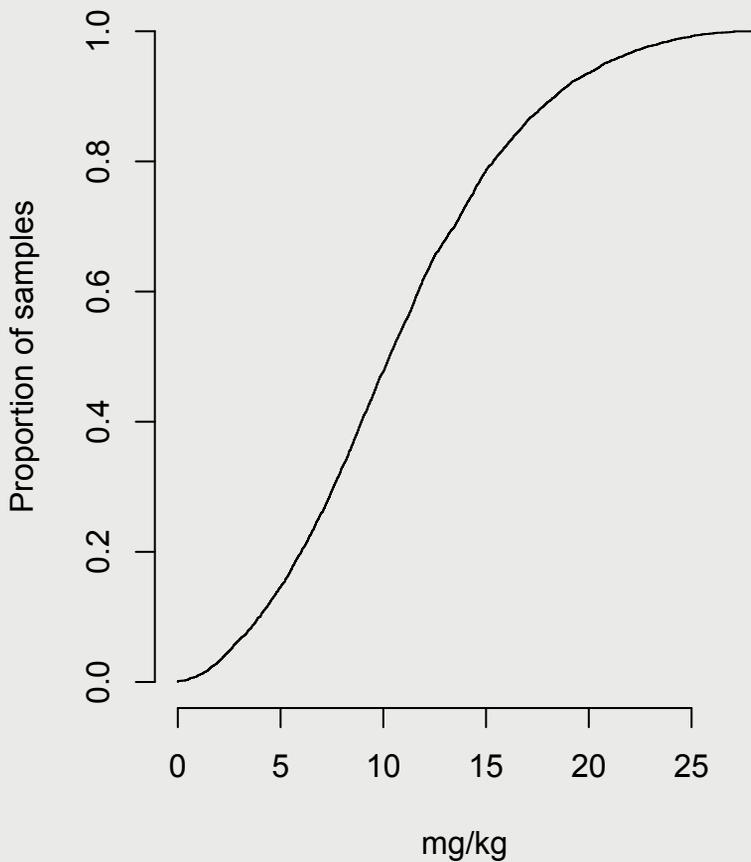
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ga - Gallium mg/kg

mean= 11

median= 10

10th percentile= 4

25th percentile= 6.8

75th percentile= 14

90th percentile= 18

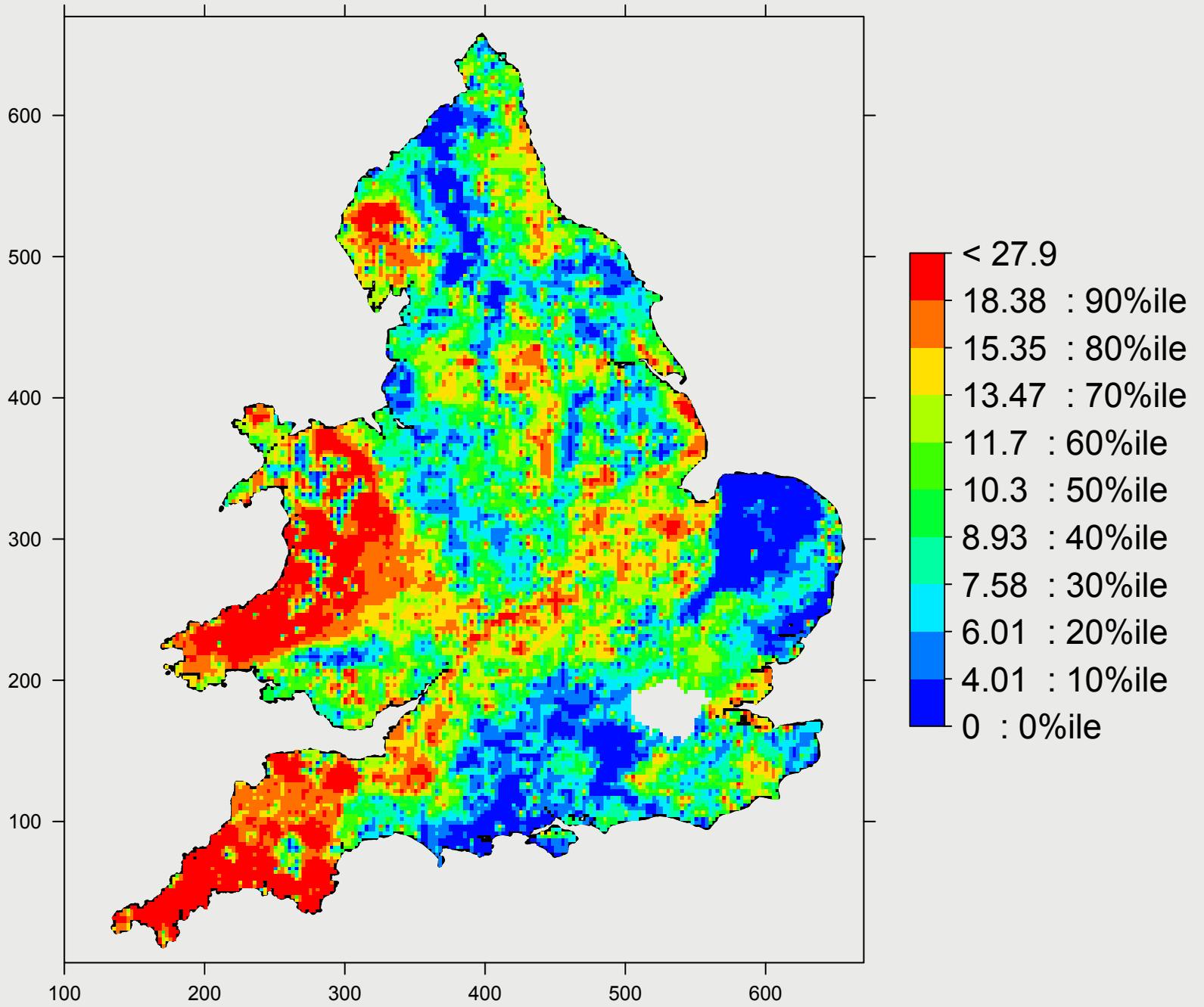
min= 0

max= 28

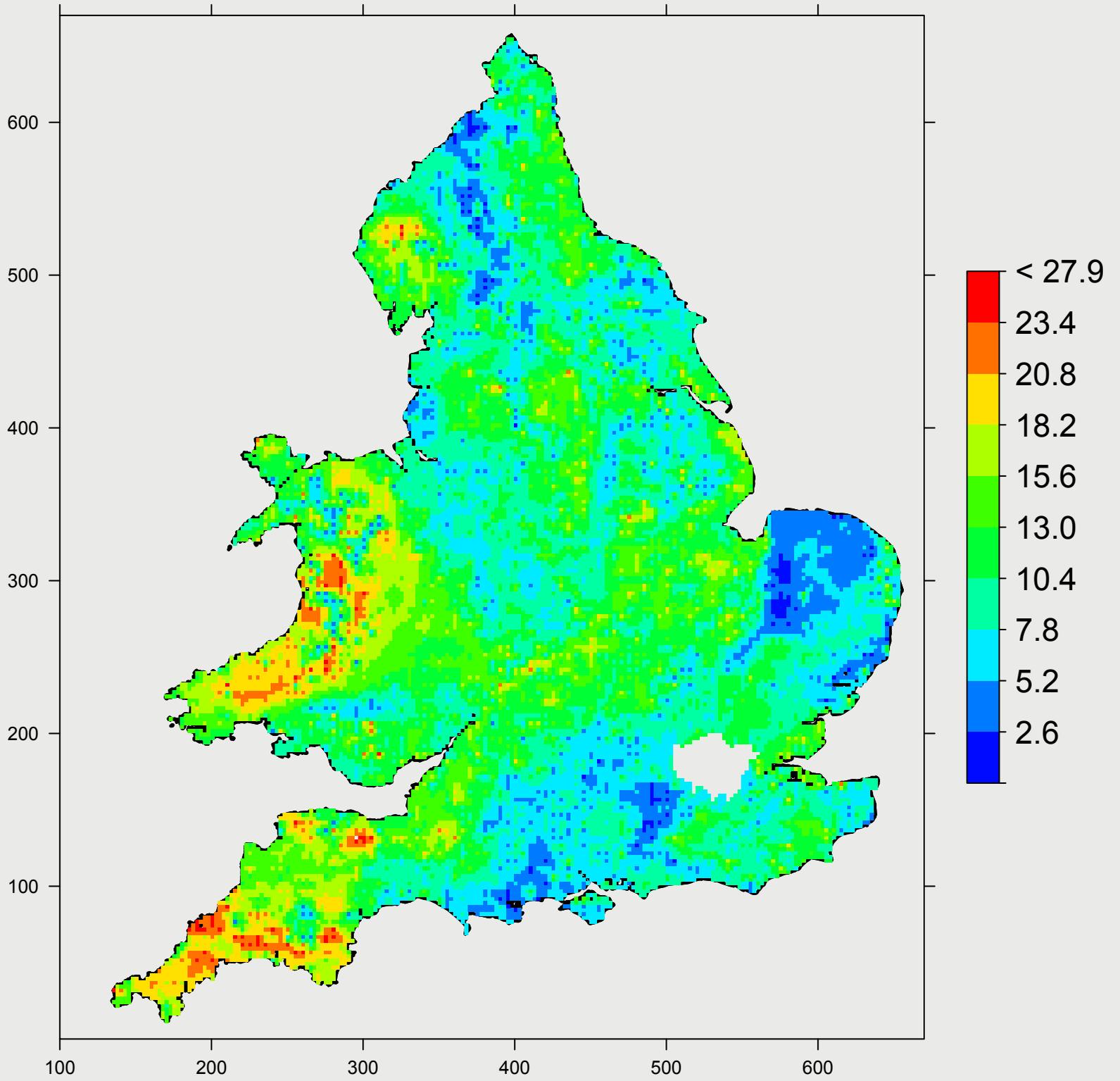
skewness= 0.43

n= 5670

Topsoil gallium (mg/kg ; percentile scale)



Topsoil gallium (mg/kg ; arithmetic scale)



Germanium (Ge)

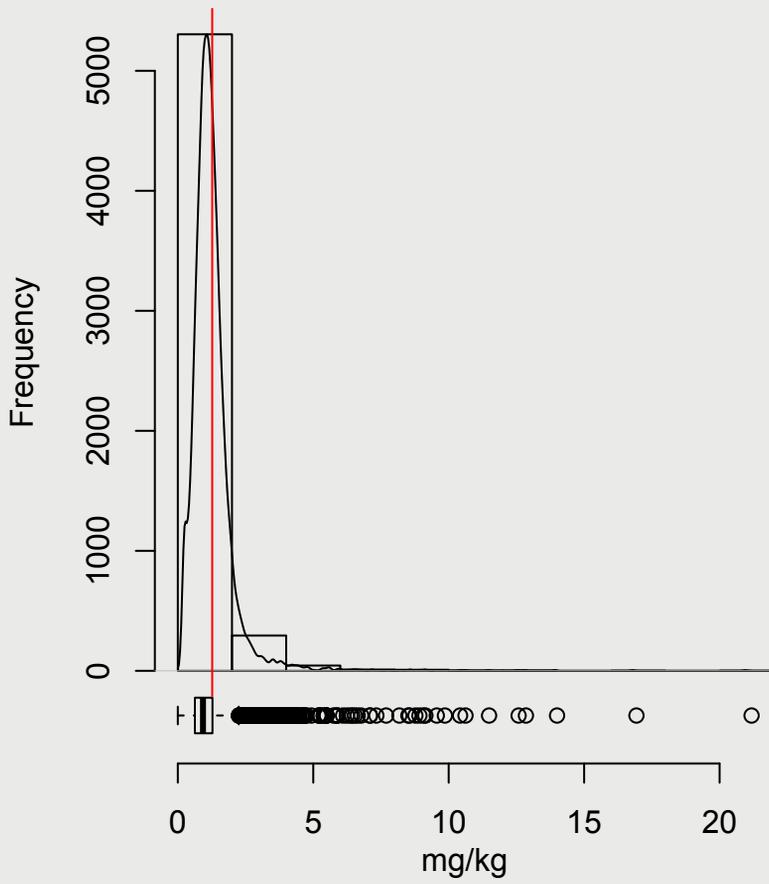
Germanium is a low-abundance semimetallic element which is not considered an essential trace element for animal health. The average upper continental crustal abundance is 1.4–1.6 mg/kg, and shows little differentiation between rock types (Reimann and De Caritat, 1998). There is little published material regarding its geochemical behaviour in soils but although it has affinities with silicon it also (unlike Si) forms sulphides. It is obtained mainly as a by-product of the mining of sphalerite ((Zn,Fe)S), and is also recovered from silver, lead and copper ores. Occupational health studies suggest that inorganic Ge is a cumulative toxin causing serious, and potentially fatal, adverse effects on the kidney, the muscle and the nervous system in both animals and man. Naturally occurring Ge present at normal levels in food does not appear to be associated with any adverse effects, but there are insufficient data to define a safe upper level for any amount of Ge (EVM, 2003).

Mean and median concentrations in NSI soils are 1.1 and 0.93 mg/kg respectively. Maps showing the spatial distribution of Ge highlight a few sites with elevated concentrations (>2.4 mg/kg) including the heavily industrialised area between Liverpool, Manchester, Derby, Nottingham and Leeds, and also between Durham and Newcastle in northern England. These are likely to be related to geogenic sources in the bedrock (Carboniferous Coal Measures) with an additional industrial component. There is also a natural geogenic enrichment in the Lake District, The Pennines, mid Wales and the south-west, associated with sulphide mineralisation.

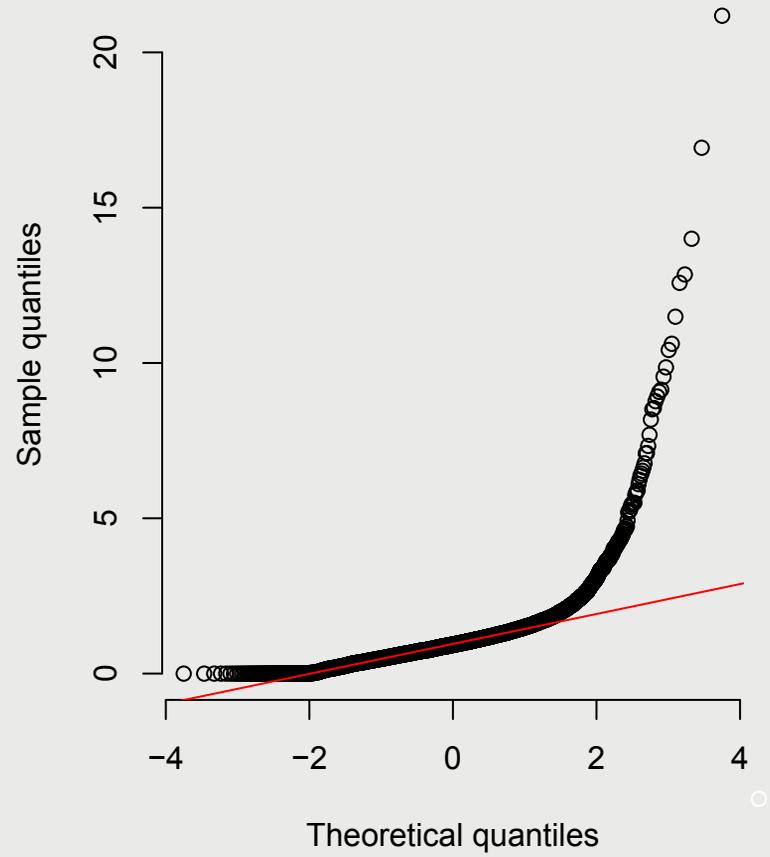
Areas of low Ge concentrations are much less well defined but include much of southern England and East Anglia.



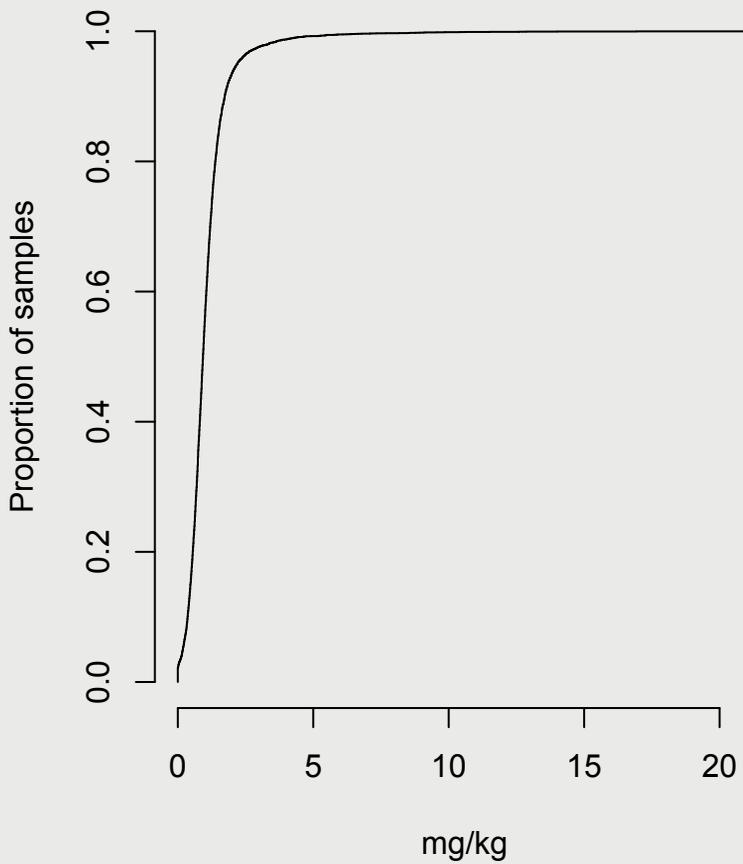
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ge - Germanium mg/kg

mean= 1.1

median= 0.93

10th percentile= 0.36

25th percentile= 0.63

75th percentile= 1.3

90th percentile= 1.7

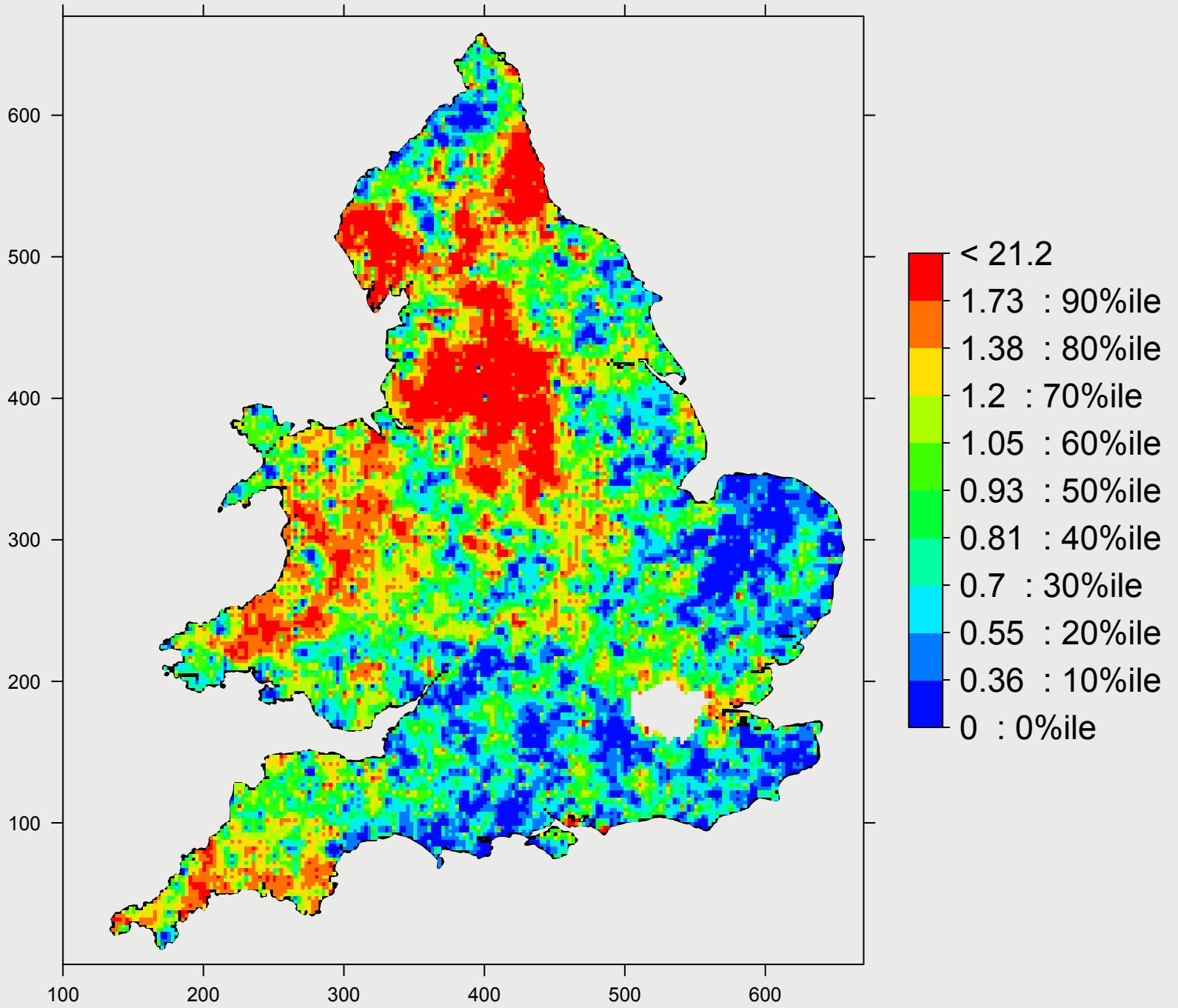
min= 0

max= 21

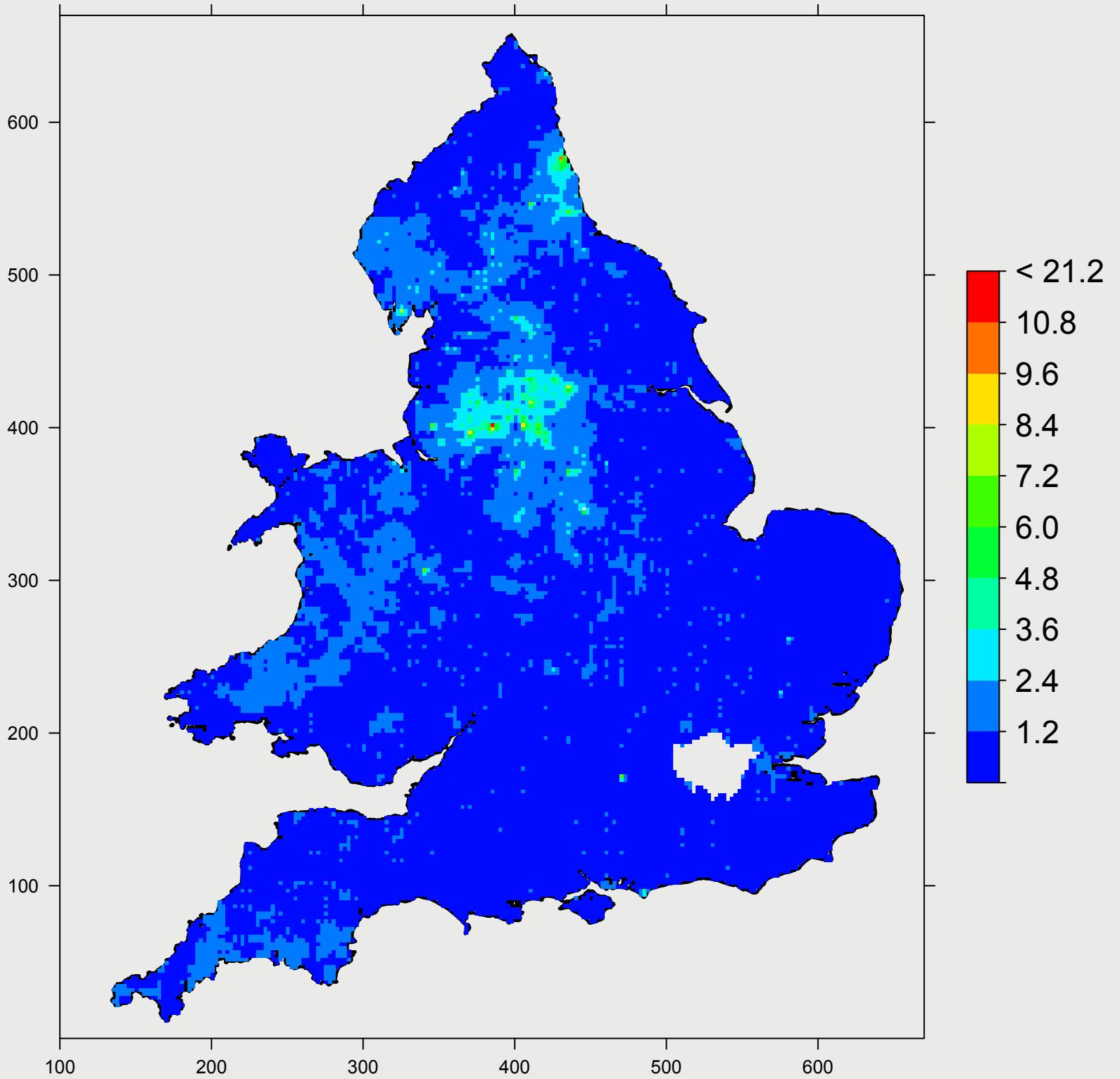
skewness= 6.8

n= 5670

Topsoil germanium (mg/kg ; percentile scale)



Topsoil germanium (mg/kg ; arithmetic scale)



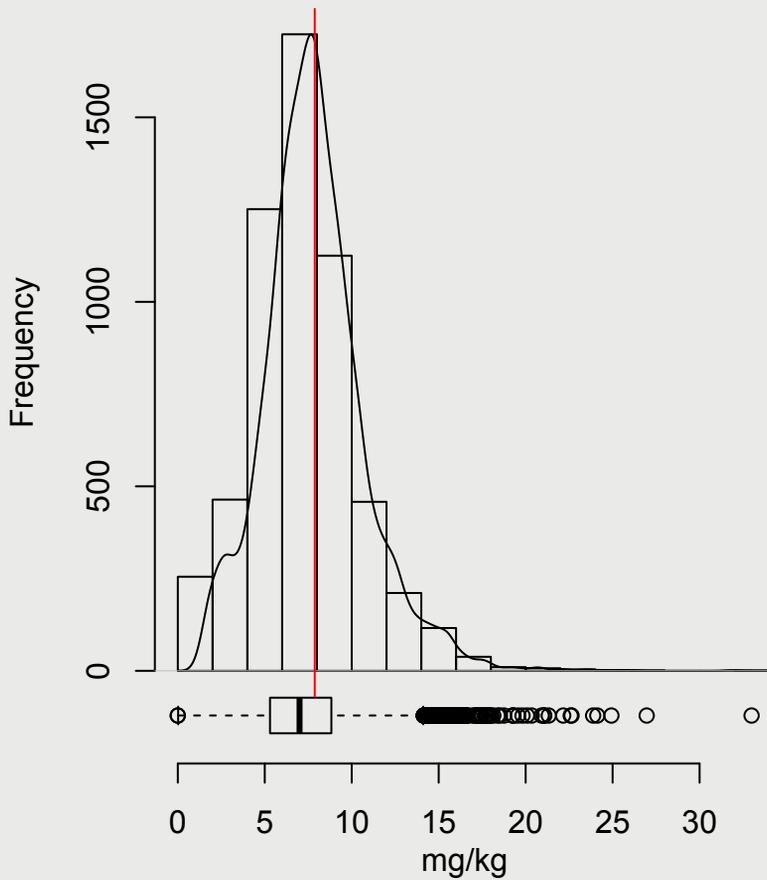
Hafnium (Hf)

Hafnium is a fairly low-abundance lithophile metal, present at a concentration of about 5.8 mg/kg in the upper continental crust (Reimann and De Caritat, 1998) and is the third-row group equivalent of Zr in the Periodic Table. Since it possesses similar properties of ionic radius and oxidation state to that of Zr, its behaviour is almost identical, although it has lower natural abundance. Consequently Hf occurs mainly in resistant, detrital heavy minerals such as zircon and sphene. In eastern England, Scheib and Lee (2010) showed that elevated Hf concentrations relate to wind-blown (aeolian) deposits, such as loess and cover-sand, and indicate soils of predominantly silt to fine-sand grain size fractions.

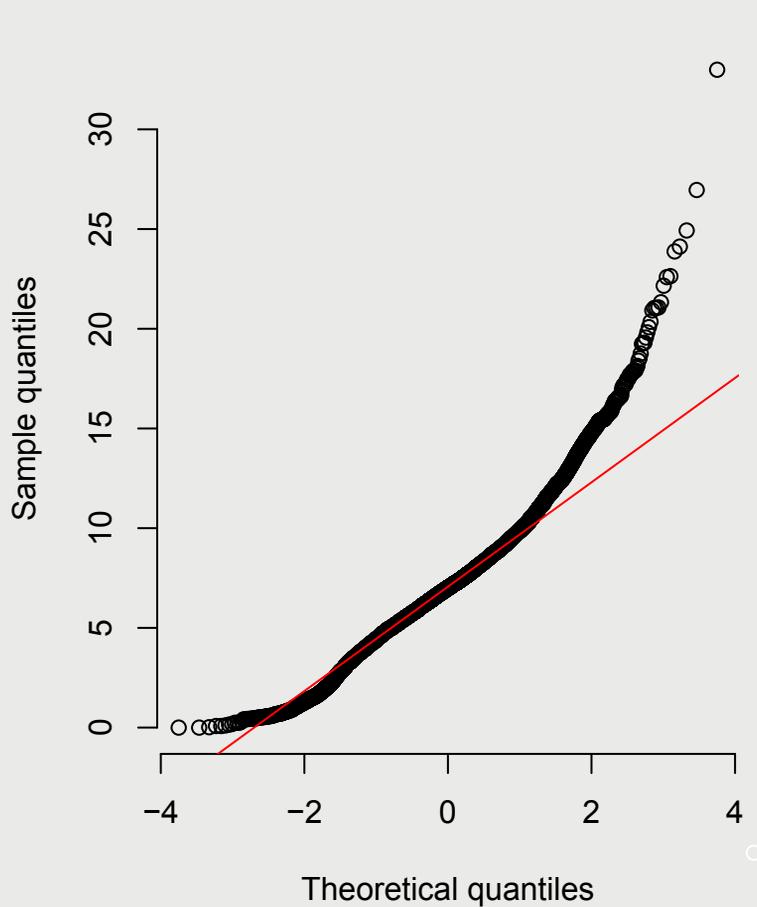
Geochemical maps of Hf show elevated concentrations (>10 mg/kg) were measured in soils across a) most of southern England, especially in the Wealden district of Sussex and Kent b) north-eastern England between Hull (loess or residual soils over the chalk outcrop) and the North Yorks Moors (the deltaic series of the Jurassic) c) Breckland (north-east of Cambridge) – cover sands, d) the southern Peak District (Loess over the limestone bedrock) as well as around e) Hereford in western England (Old Red Sandstone). In the Weald, the highest Hf levels appear to be associated with the Lower Greensand outcrop though similar rocks to the north of London do not show such Hf enrichments.

Very low soil Hf concentrations are associated with the Lower Palaeozoic greywackes of Wales, the Namurian gritstones of the Pennines, lowland Cheshire and Lancashire, Dartmoor, and parts of East Anglia.

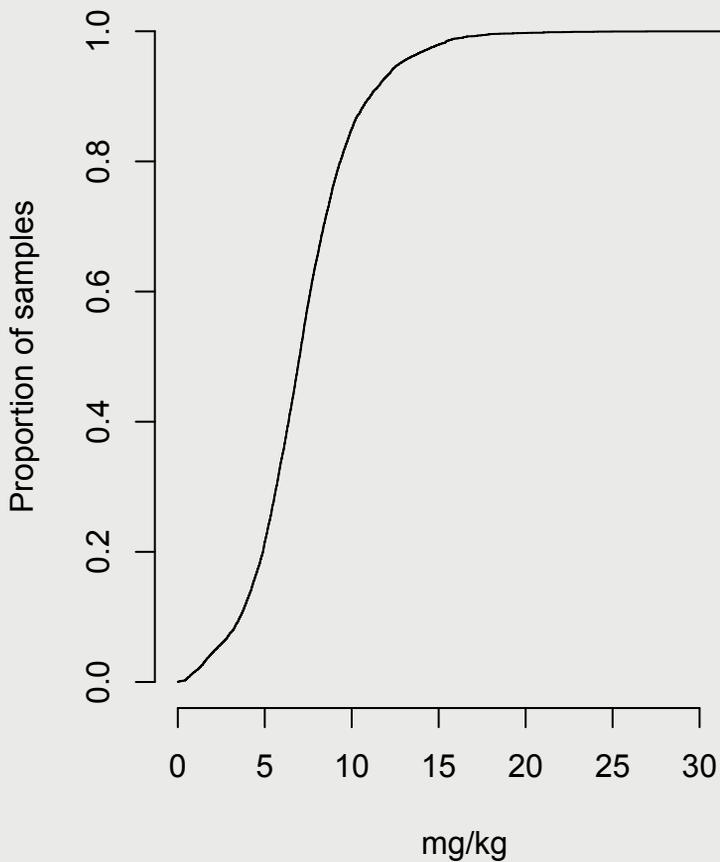
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Hf - Hafnium mg/kg

mean= 7.2

median= 7

10th percentile= 3.6

25th percentile= 5.3

75th percentile= 8.8

90th percentile= 11

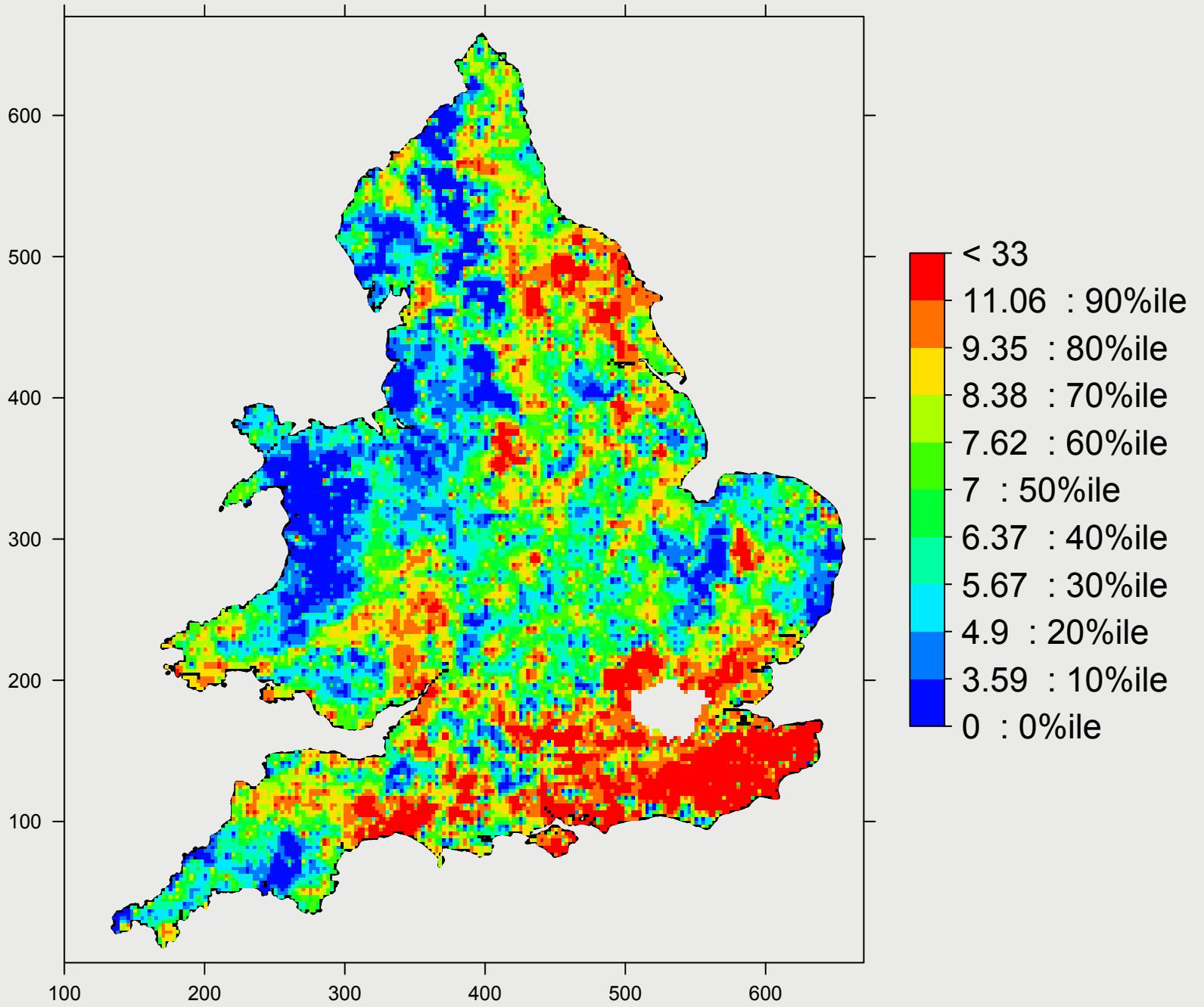
min= 0

max= 33

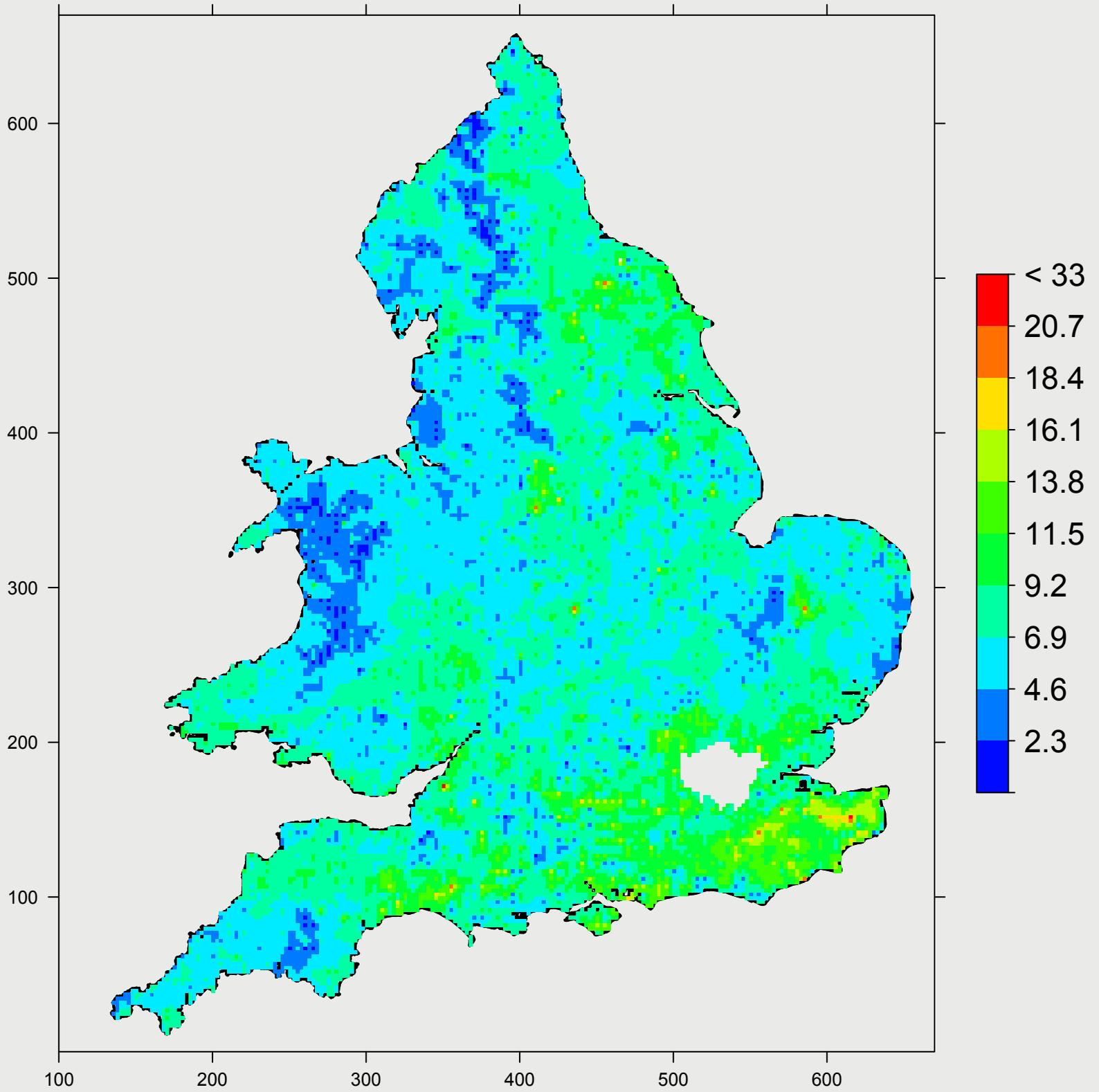
skewness= 0.81

n= 5668

Topsoil hafnium (mg/kg ; percentile scale)



Topsoil hafnium (mg/kg ; arithmetic scale)

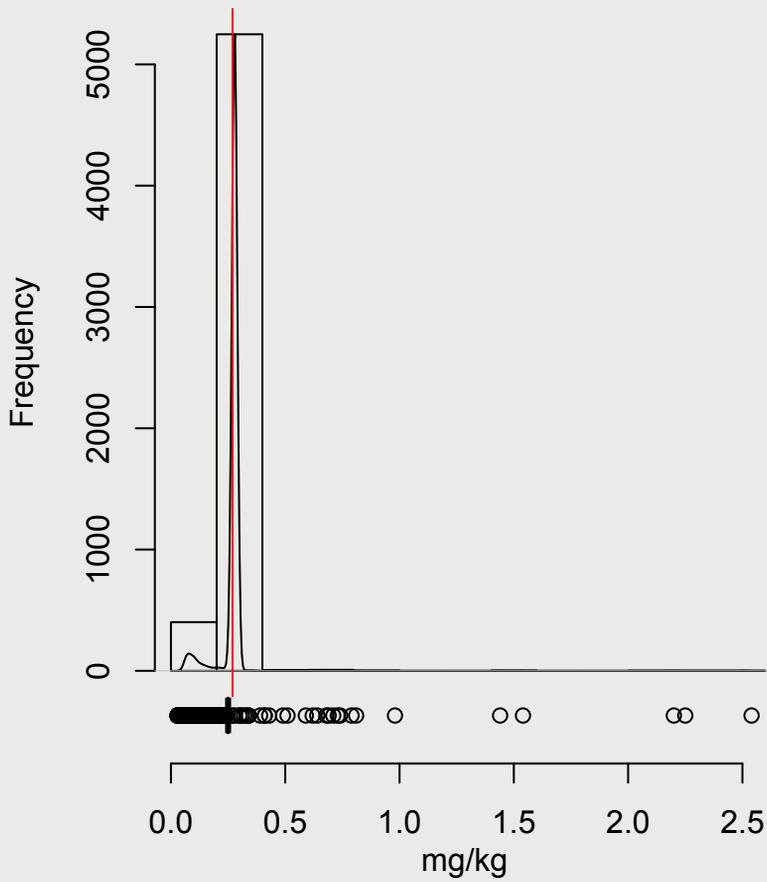


Indium (In)

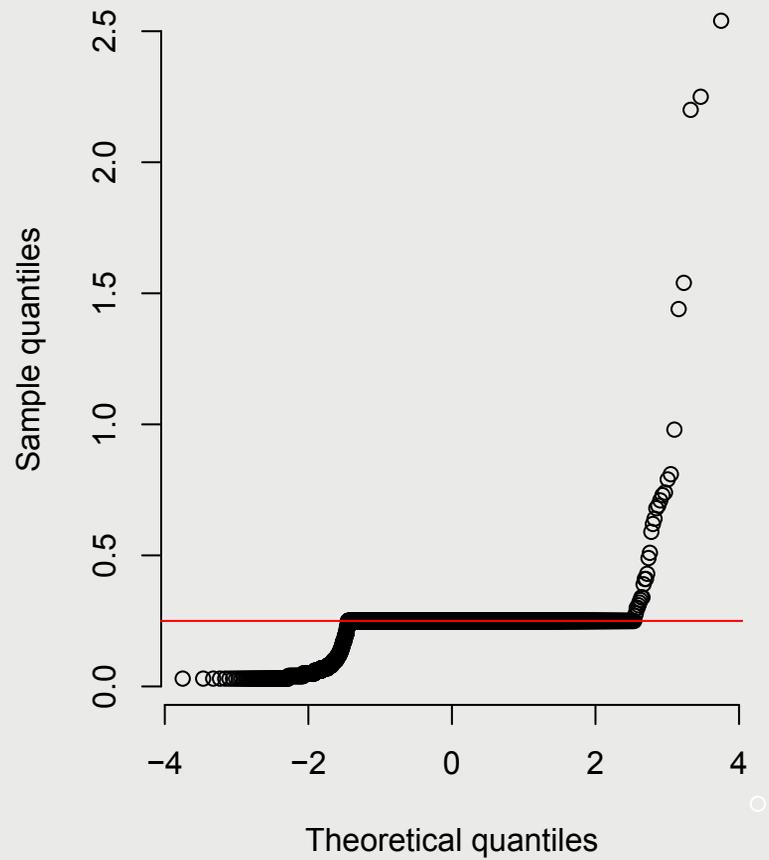
Indium is a rare metallic element, with an estimated average upper continental crustal abundance of between 0.5 and 0.6 mg/kg (Reimann and De Caritat, 1998). It is predominantly found in Zn ores and is recovered as by-product in the smelting process. It is considered biologically non-essential; though few research studies have been undertaken to assess its environmental effects.

Indium concentrations in NSI soils are so low that the vast majority of samples were below the detection limit for the XRF-S analysis. For this reason, the percentile map is not presented. The arithmetic geochemical map displays a few sites that have concentrations above the lower limit of detection (0.25 mg/kg). Some 20 soil samples had concentrations of greater than 0.5 mg/kg, with a maximum of 2.5 mg/kg. These occur in two areas; one over the Carboniferous Coal Measures of south Wales but which may be associated with atmospheric 'fallout' from the former intensive smelting industries of the Swansea valley, and the other is likely to be related to Zn mineralisation and smelting in the vicinity of granite intrusions across the west of Cornwall (Hayle, St Austell–Redruth).

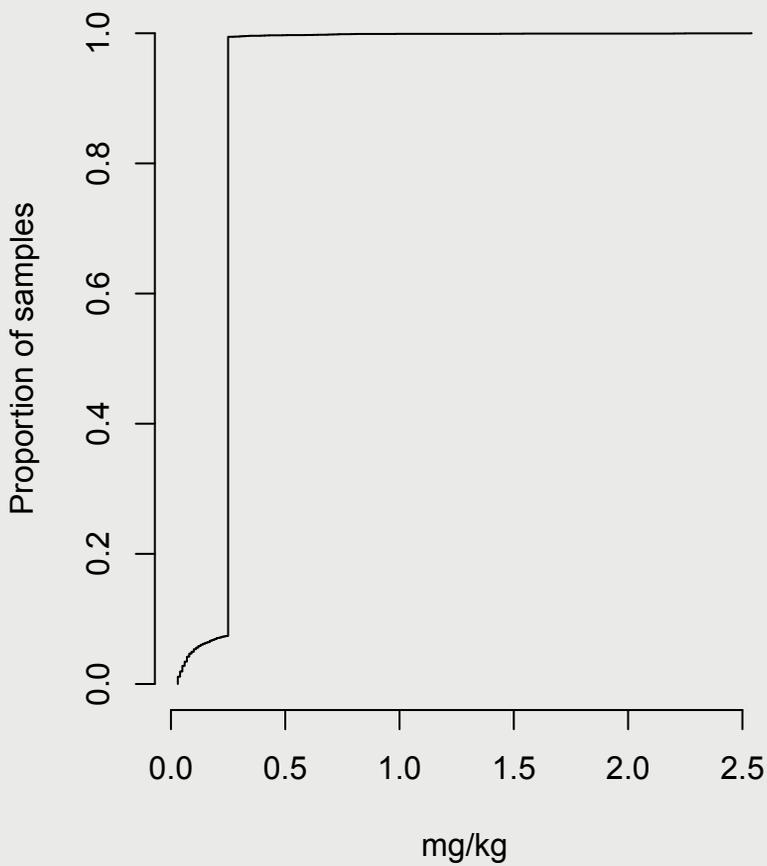
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



In - Indium mg/kg

mean= 0.24

median= 0.25

10th percentile= 0.25

25th percentile= 0.25

75th percentile= 0.25

90th percentile= 0.25

min= 0.03

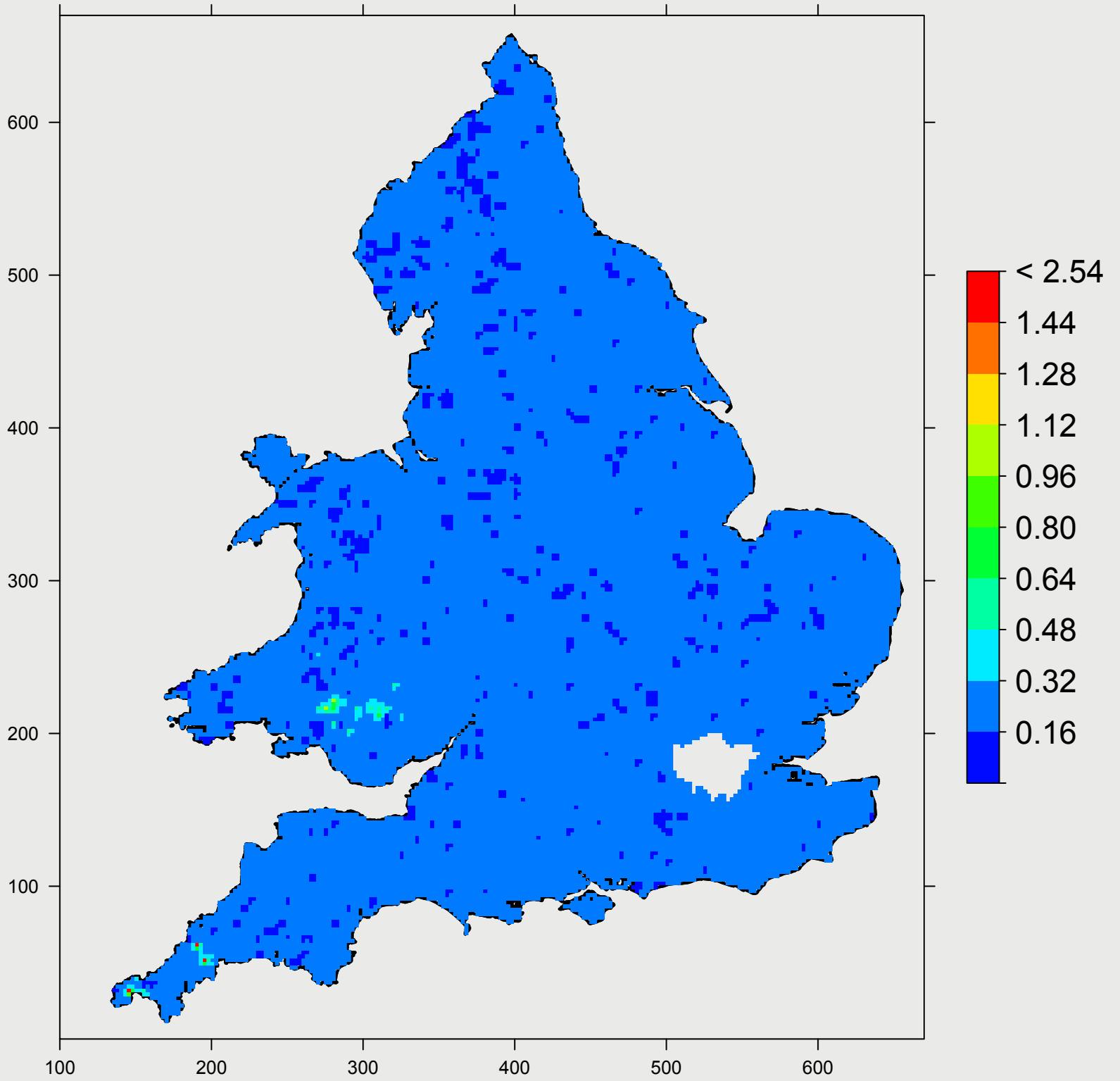
max= 2.5

skewness= 14

n= 5670

A map of soil indium concentrations on a percentile scale is not shown because the vast majority of the values were below the limit of detection. Presentation of such a map could lead to erroneous interpretations.

Topsoil indium (mg/kg ; arithmetic scale)



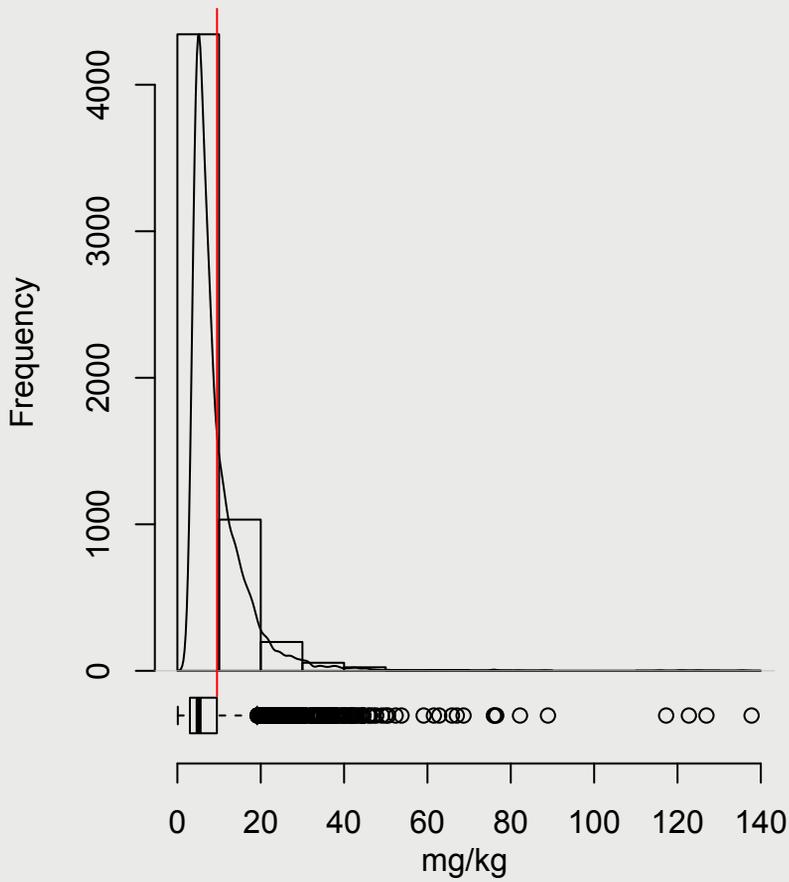
Iodine (I)

Iodine is a rare, nonmetallic halogen element and is biologically essential for many organisms. The average crustal abundance is very low, between 0.15 and 1.4 mg/kg (Reimann and De Caritat, 1998). For livestock and humans, only a trace of I is required, however a lack of I intake can cause a series of medical conditions such as goitre, generally grouped into iodine deficiency disorders (Johnson, 2003). Its main industrial application is as catalyst and stabilising agent as well as a nutritional supplement.

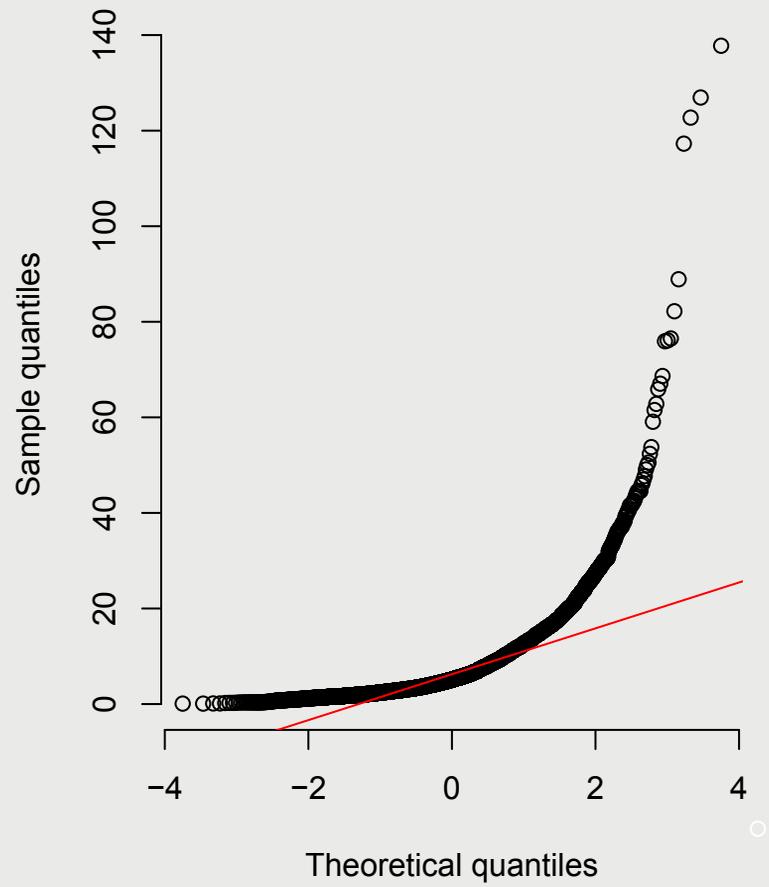
The mean and median concentrations measured in NSI soils are 7.5 and 5.1 mg/kg respectively. The upper 10% of the data range from 16 to 138 mg/kg. The spatial distribution of these elevated concentrations is very distinct and corresponds with various geological settings. The percentile map shows these in the Lake District, the Peak District, the Cotswolds, the Salisbury and Basingstoke area (Chalk outcrop) and all of south-west England other than central Devon. The largest concentrations (arithmetic map) relate to soils collected over Ordovician tuffs that crop out in Snowdonia and the Lake District but in these areas the topography may be a factor allowing marine aerosols to increase the soil I concentration. In Cornwall, marine-derived aerosols may also have an influence on the I content in soils as the high concentrations are not only confined to soils overlying the granitic intrusions. In the case of the Fen Basin, the Norfolk Broads, the wider Thames estuary and Romney Marsh south of Folkestone, elevated concentrations correspond to recent marine sediments, as well as the possible influence from marine inundation, and possibly sorption of I by organic material. A large number of the highest concentrations (> 62.1 mg/kg) are indeed measured in soils collected near the coast.

Low concentrations of I (<3 mg/kg) in soils correspond well with the extent of the Triassic outcrop across west and central England, the sandy heaths of southern England and the chalky and sandy Quaternary deposits of East Anglia.

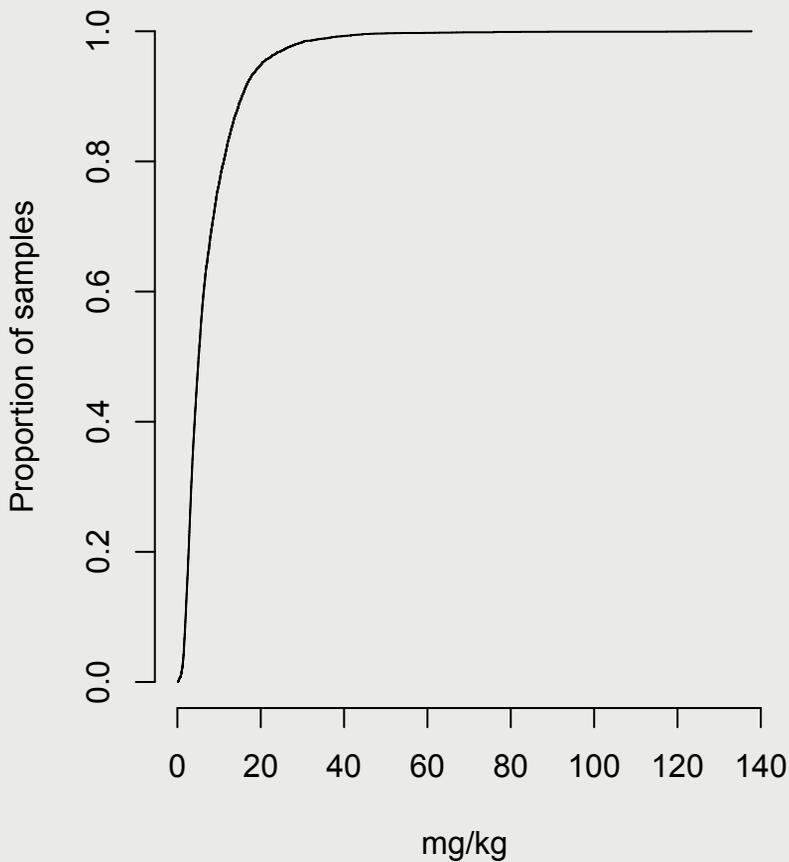
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



I - Iodine mg/kg

mean= 7.5

median= 5.1

10th percentile= 2

25th percentile= 3

75th percentile= 9.5

90th percentile= 16

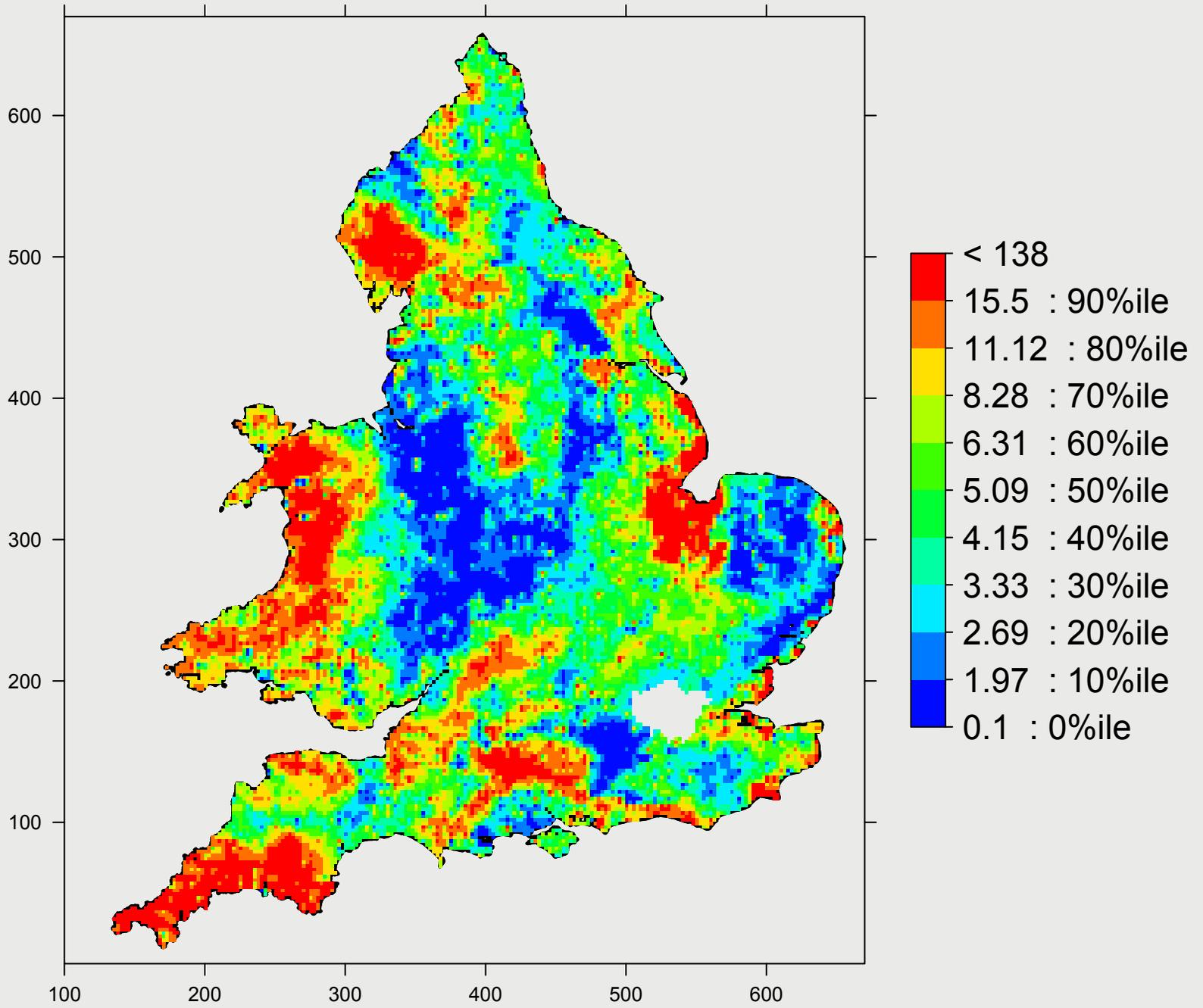
min= 0.1

max= 138

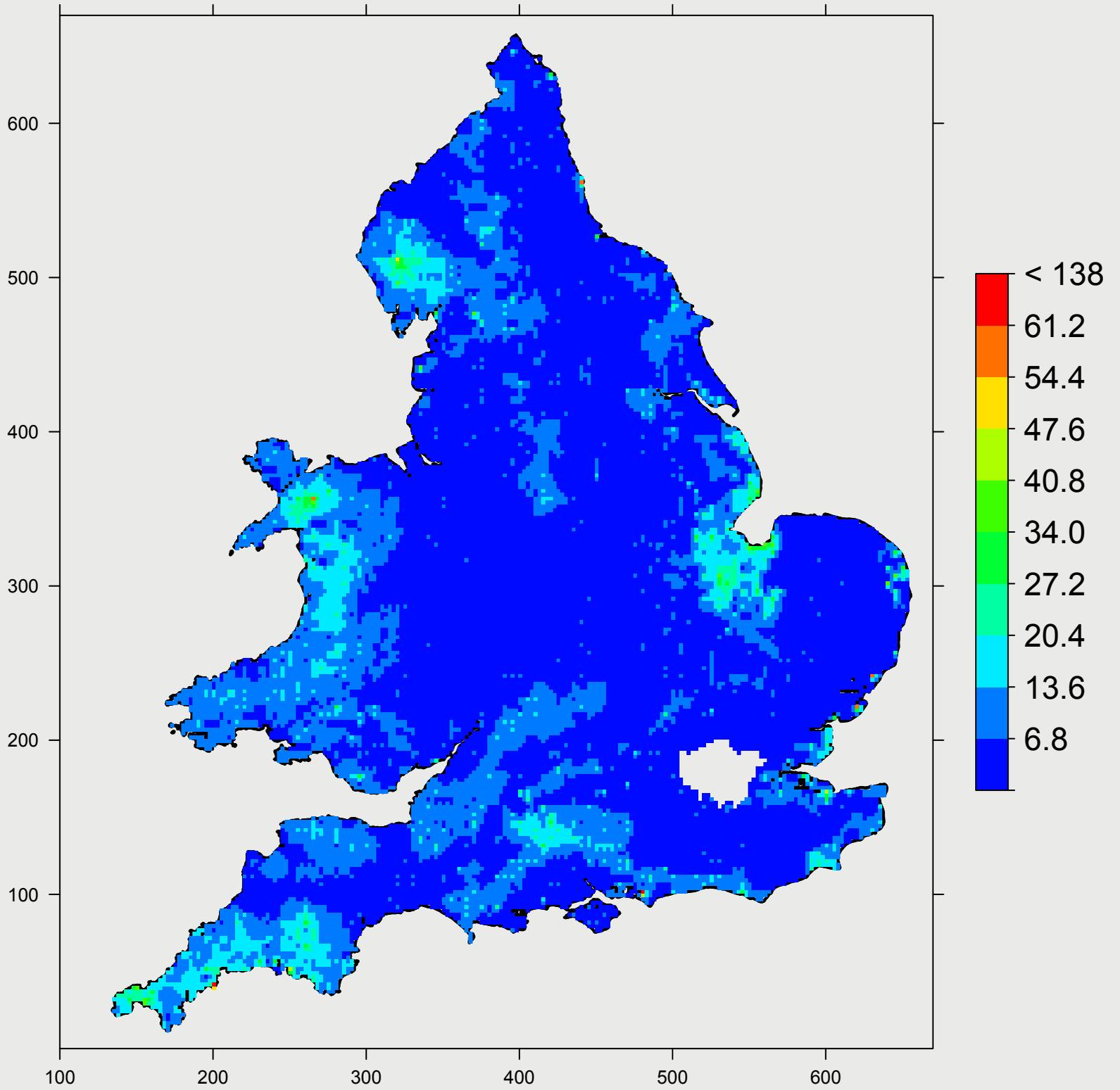
skewness= 5

n= 5670

Topsoil iodine (mg/kg ; percentile scale)



Topsoil iodine (mg/kg ; arithmetic scale)



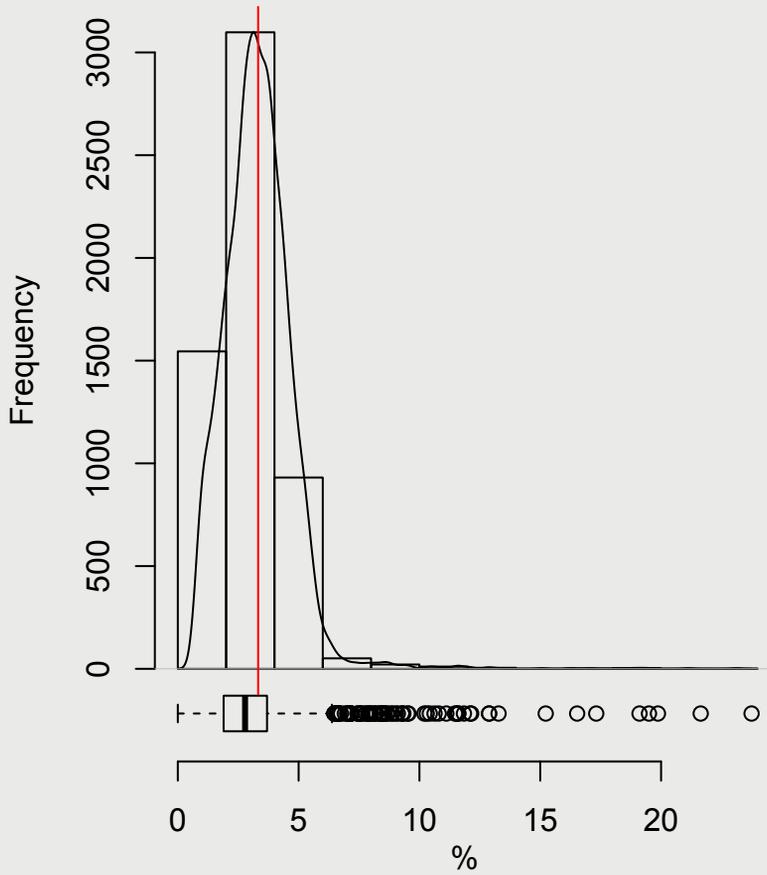
Iron (Fe)

Iron is a major element, present at about 3.5% Fe by weight in the Earth's upper continental crust, but is more abundant in basic igneous rocks (7–9%) than in granites (2%), and more abundant in shales and greywackes (~5%) than in sandstones (1%) or limestones (0.5%) (Reimann and De Caritat, 1998). Although soils generally contain large concentrations of Fe, only a small proportion of it is bioavailable. Iron shows broad similarity in its spatial distribution to that of As, Co and Ni.

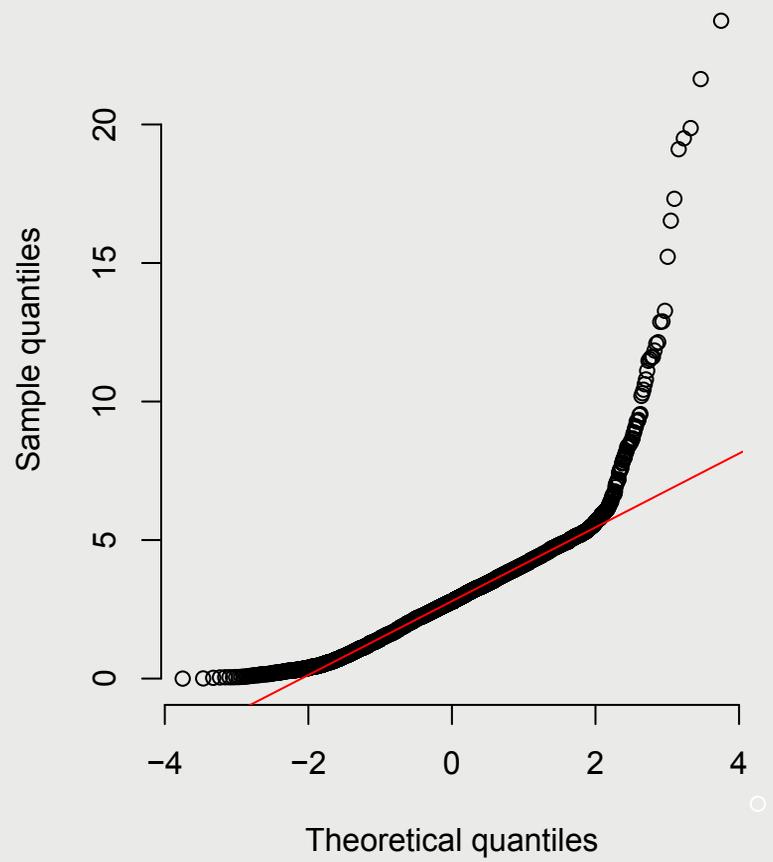
Relatively high concentrations (>3.5%) occur in a prominent broad band over most of the Jurassic sedimentary outcrop running from Somerset in the south-west to Lincolnshire. The highest concentrations within this band may be associated with the occurrence of ironstones and iron-rich clays, limestones and sandstones, for example those near Banbury, in Northamptonshire and at Scunthorpe. High concentrations of soil Fe are also present in parts of the south-west, mid and west Wales, west of Sheffield and Cumbria. The local bedrock geology is influential in most of these areas, but there may also be a contribution from industrial activity such as coalfield iron ore mining, steelmaking and engineering (Sheffield) and secondary iron oxide precipitation in localised areas across central England and Wales, such as the coastal marshes of Lincolnshire, Essex and north Kent.

Low Fe concentrations (<1%) occur in many of the upland areas of the north of England, Wales and the south-west peninsular (notably over the granite outcrops), which may be related to the leaching of Fe from topsoil or due to the presence of organic matter-dominated soil such as peats. Areas with low topsoil Fe concentration also include the sandy soils in the New Forest (Hampshire), the heaths between Reading and Woking and the sandy soils and tills of East Anglia.

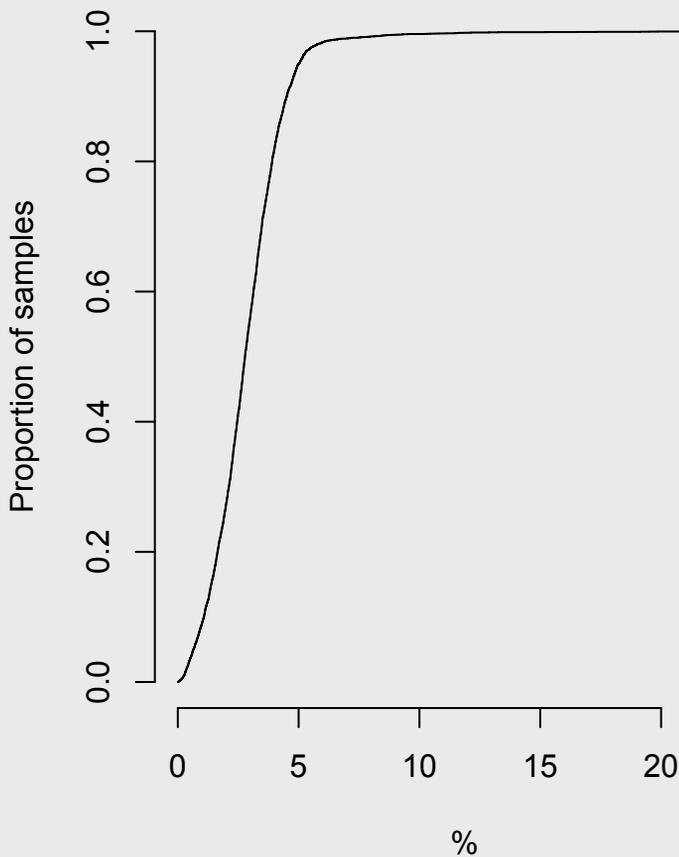
Histogram and boxplot



Normal Q-Q plot



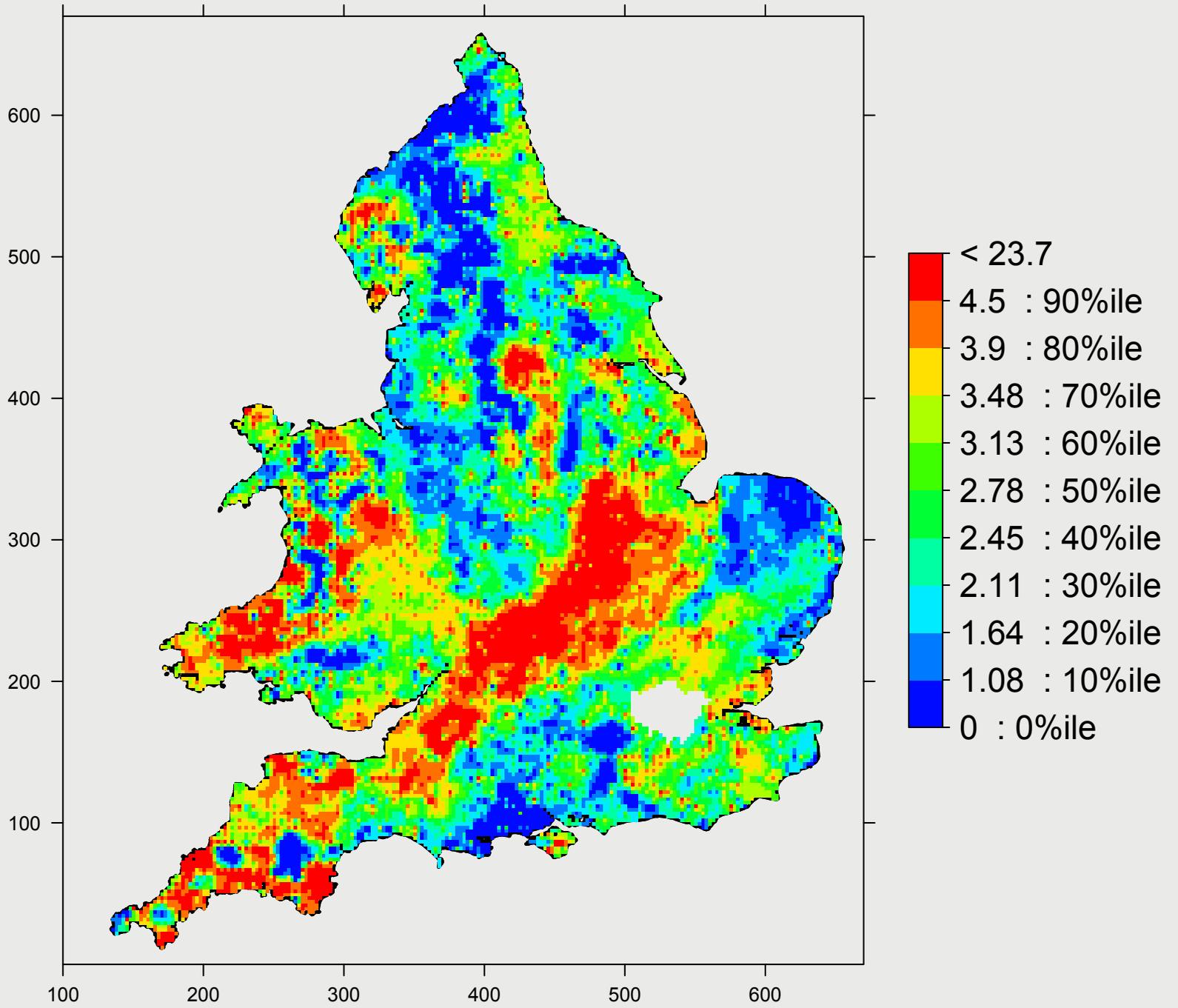
Cumulative frequency



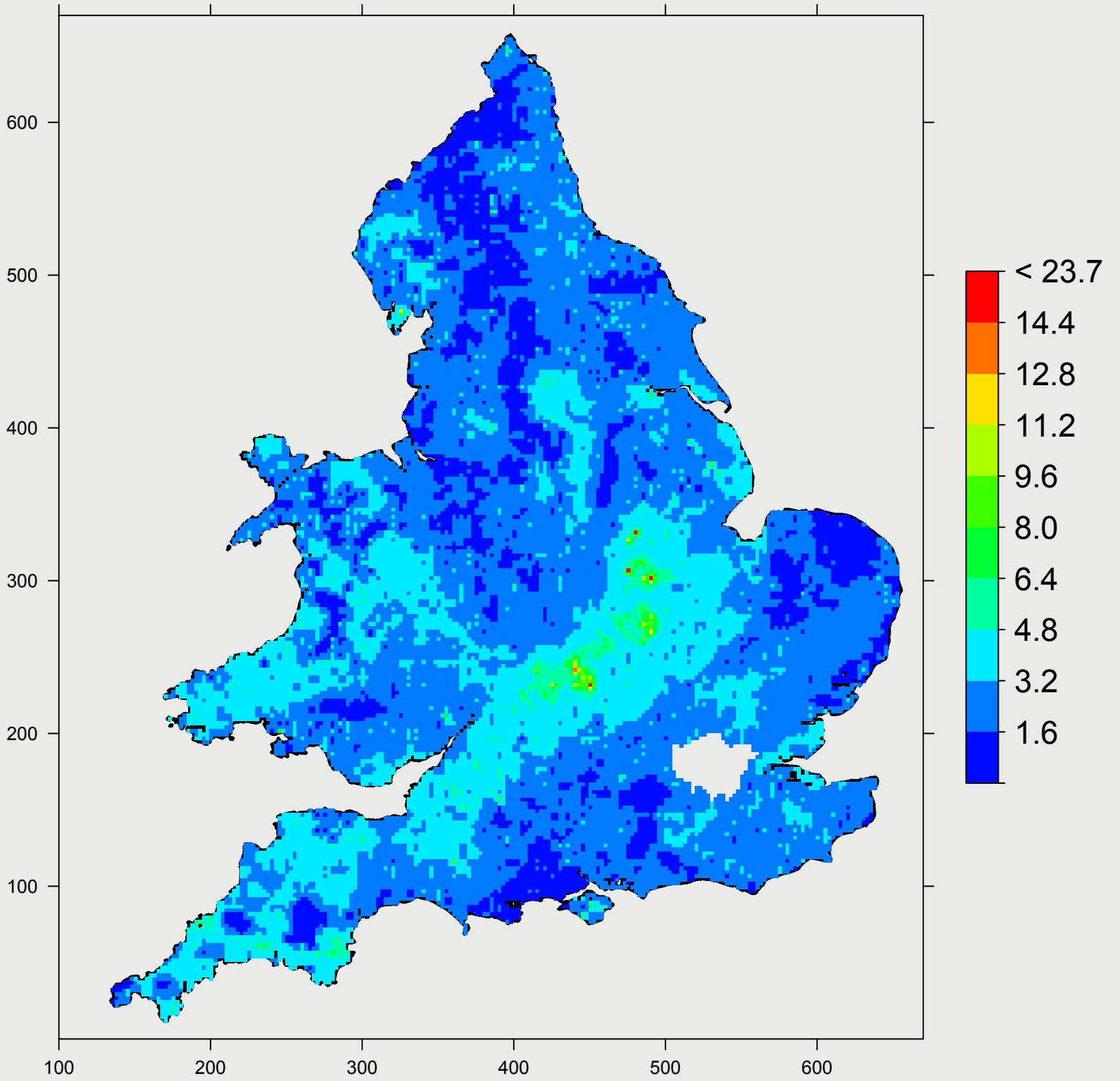
Fe - Iron %

mean= 2.9
median= 2.8
10th percentile= 1.1
25th percentile= 1.9
75th percentile= 3.7
90th percentile= 4.5
min= 0
max= 24
skewness= 2.5
n= 5670

Topsoil iron (% ; percentile scale)



Topsoil iron (% ; arithmetic scale)



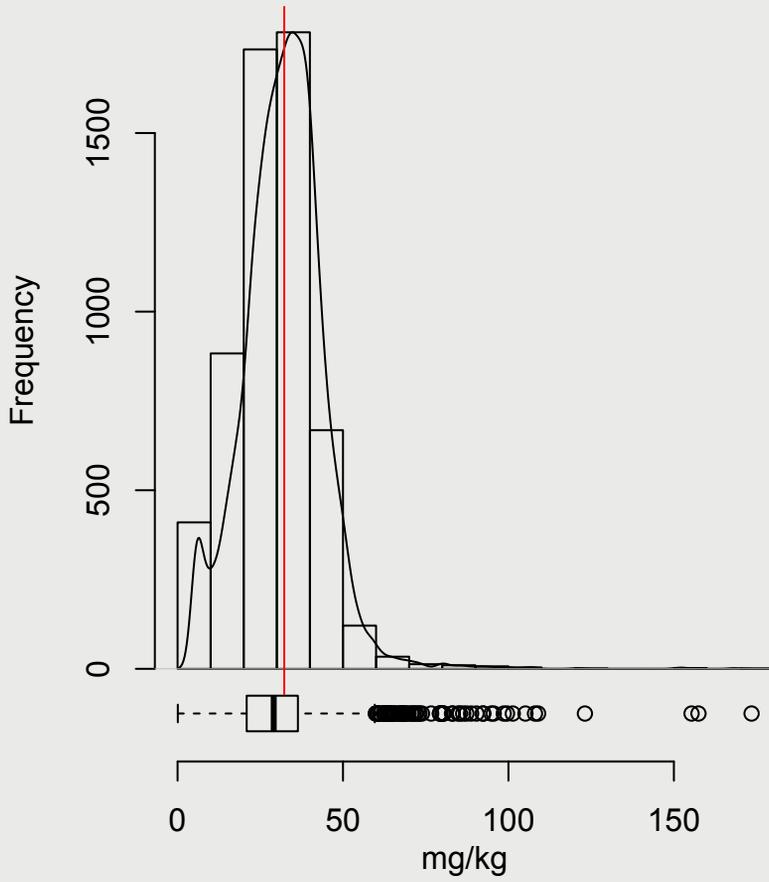
Lanthanum (La)

Lanthanum is one of the more common rare earth elements for which there are many industrial applications and uses, for example as conductors, catalysts and batteries. It is considered non-essential with generally low toxicity. It is mainly found in the resistate minerals monazite and bastnäesite and has an average crustal abundance of around 30 mg/kg (Reimann and De Caritat, 1998). This is very similar to the median and mean concentrations of 29 mg/kg measured in the NSI soils.

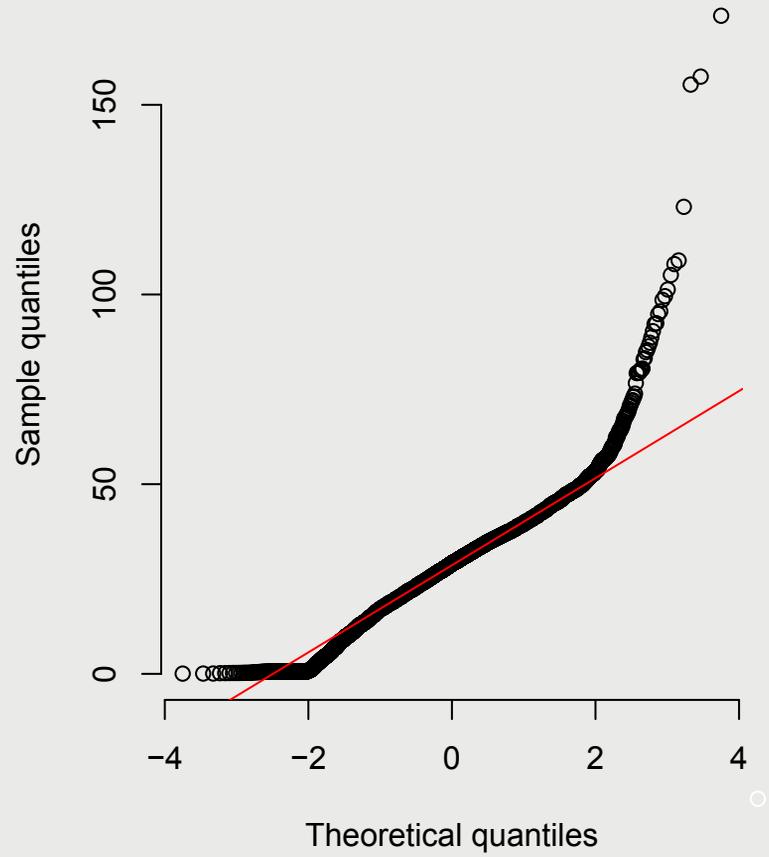
Total La concentrations in the NSI soils range from <1 to 173 mg/kg with levels > 43 mg/kg (90th percentile) occurring mainly in areas of sedimentary rocks across the southern half of England and central and south-west Wales. In central England a prominent belt of elevated concentrations correspond to the outcrop of Jurassic sedimentary strata. In south-east England, elevated concentrations (>35 mg/kg) relate to soils collected over a) the Lower Cretaceous nonmarine sandstones and clays of the Wealden District, b) the Chalk between Winchester and Salisbury and c) the Chalk and Palaeogene clays to the north of London, though whether this is due to Quaternary deposits is not clear. The Chalk outcrop of the Yorkshire and Lincolnshire Wolds is also marked by high La concentrations, probably indicating a residual soil rich in resistate minerals. In the south-west, high concentrations relate to soils collected from Devonian and Carboniferous sedimentary strata, with low concentrations over the granitic intrusions. In Wales, high concentrations correspond to Ordovician and Silurian mudstones that crop out in the south-west, and along the Welsh–English border. High soil La levels are also present over parts of the Old Red Sandstone outcrop of the Welsh Borders.

The lowest concentrations (<15 mg/kg) were reported in soils across most of East Anglia, the Welsh uplands (e.g. Snowdonia), the Pennines and North York Moors, the Permo-Triassic outcrop of the Midlands, the granites of Devon and Cornwall, and the Paleocene outcrops of the Surrey heaths and the Hampshire Basin.

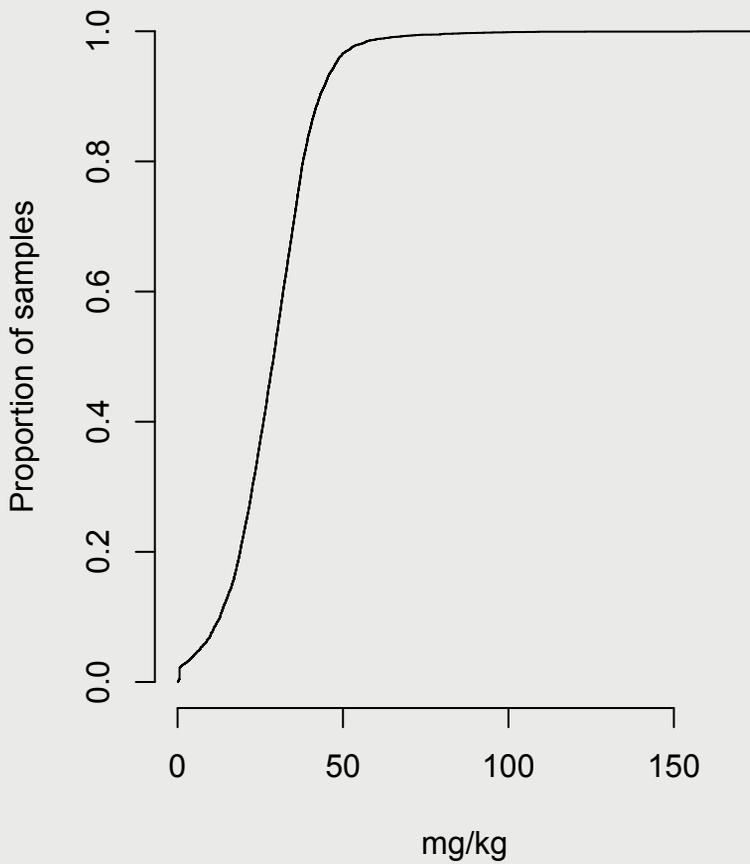
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



La- Lanthanum mg/kg

mean= 29

median= 29

10th percentile= 13

25th percentile= 21

75th percentile= 36

90th percentile= 43

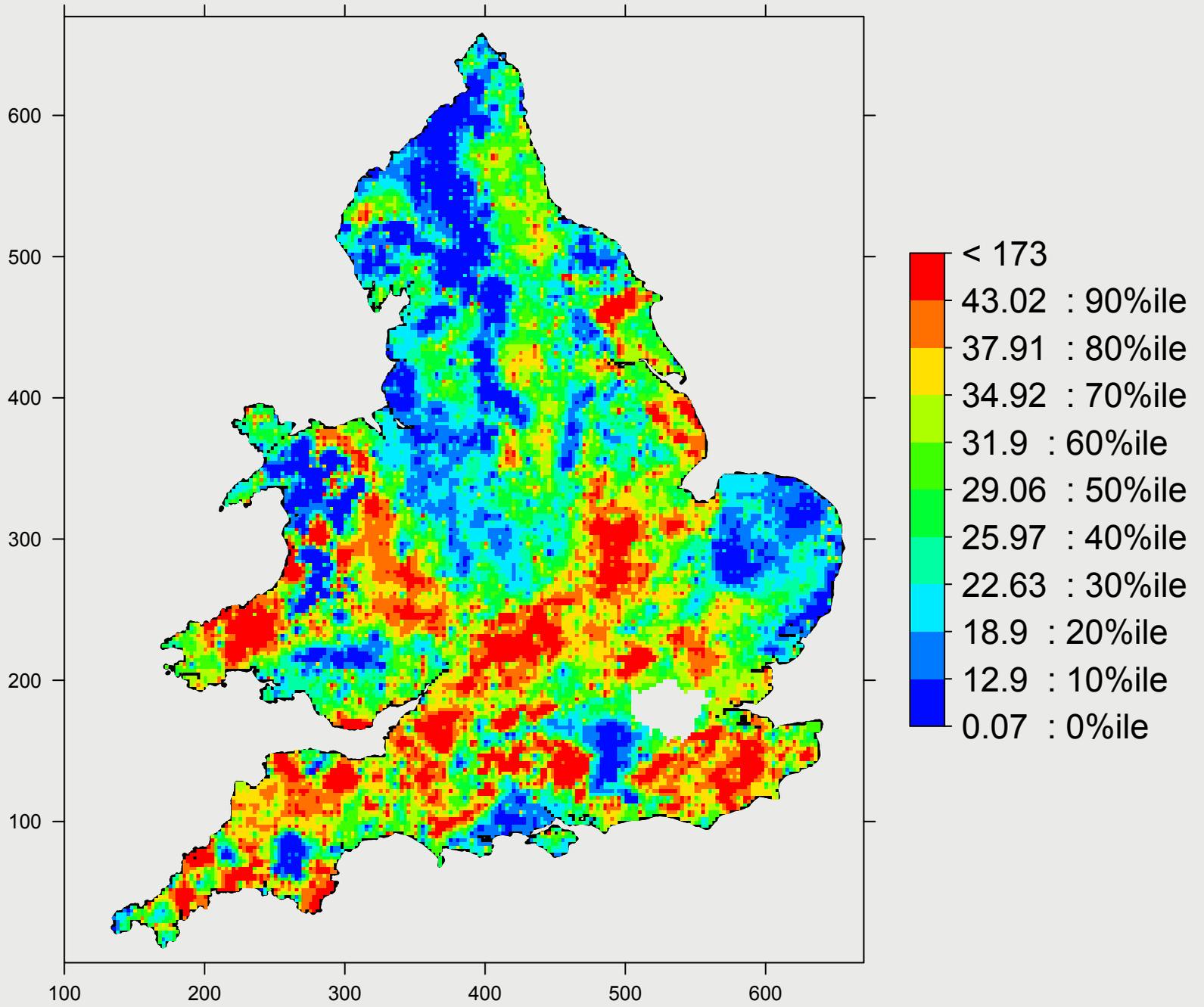
min= 0.07

max= 173

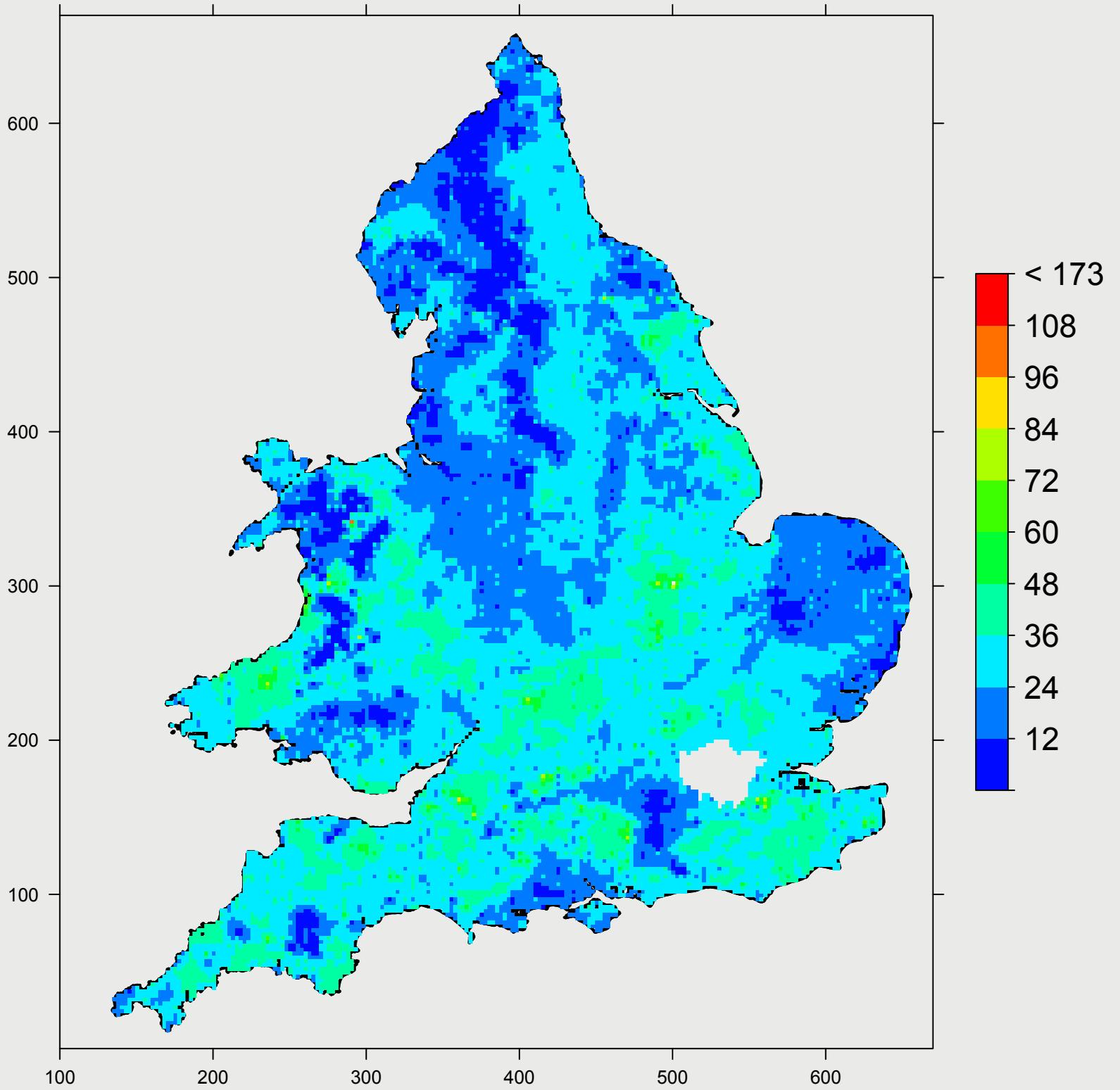
skewness= 1

n= 5670

Topsoil lanthanum (mg/kg ; percentile scale)



Topsoil lanthanum (mg/kg ; arithmetic scale)



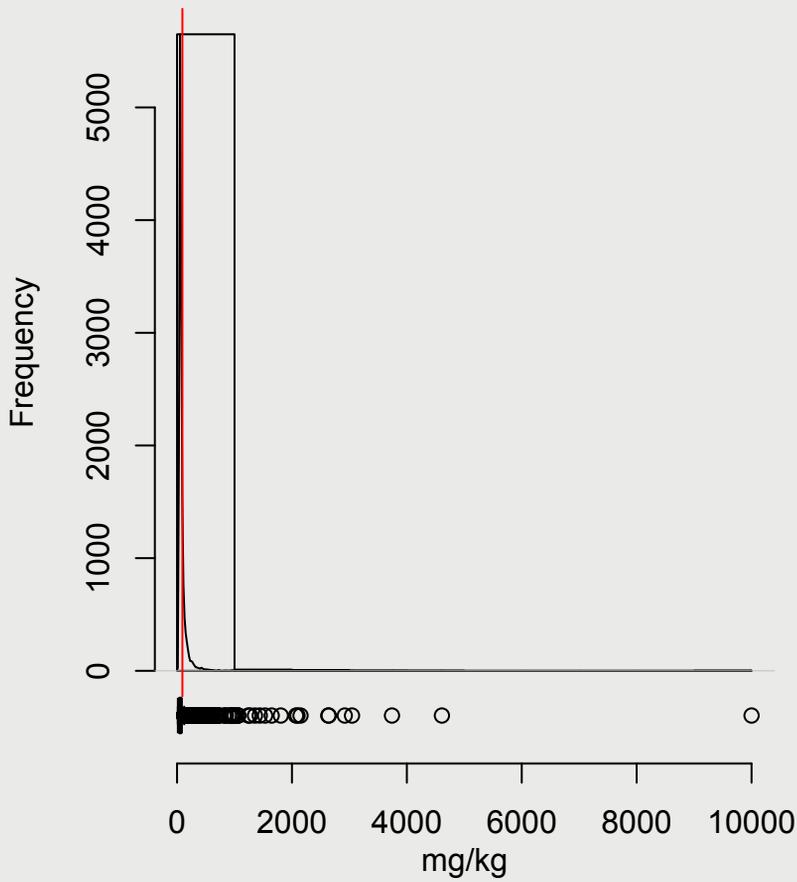
Lead (Pb)

Lead is a heavy metallic element, having an estimated upper continental crustal abundance of about 15 mg/kg, though it is less abundant in basic igneous rocks (1–4 mg/kg) than in granites (20 mg/kg), and shales (22 mg/kg). It is biologically non-essential and toxic (Reimann and De Caritat, 1998).

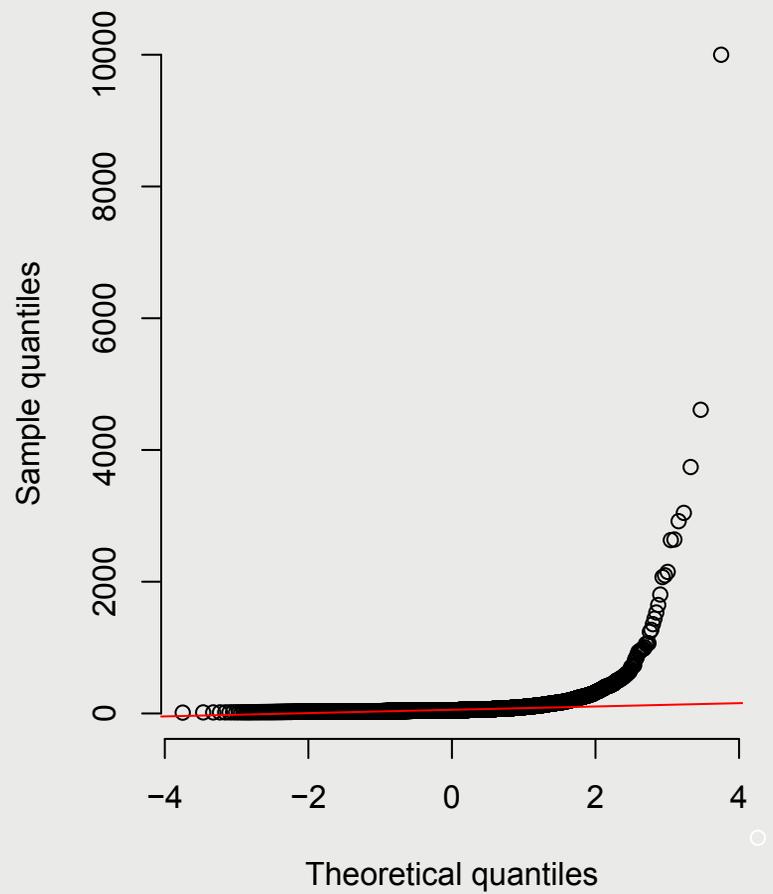
In England and Wales, soils with the highest lead concentrations are all close to historical areas of mining and smelting such as Avonmouth near Bristol, south Wales, Derbyshire (southern Peak District), the northern Pennines and in Snowdonia and the Halkyn Mountain district of north Wales. Other areas such as the Lake District, Shropshire, mid Wales, the Mendip Hills and Cornwall, which were also subject to Pb mining and smelting are also shown clearly by high Pb concentrations on the percentile map (>40 mg/kg). Organic-rich soils on high land in Wales, Cumbria and the Pennines also have some high Pb concentrations away from mining centres, where Pb may have been dispersed locally (from smelting) and long-range from tetraethyl Pb which was added to petrol and accumulated in the surface layers of peat (McGrath and Loveland, 1992). Relatively high Pb concentrations in soils are also associated with densely populated industrial conurbations, e.g. Birmingham, London, Newcastle, and wider areas around Liverpool, Manchester and Swansea. This 'anthropogenic signature' for Pb in urban areas is ubiquitous and is related to coal burning, old paint, piping, solders, fuel lead and more general use of this important metal.

Low Pb concentrations (<20 mg/kg) occur in sandy soils and over chalk soils, particularly in the south and east, as shown in the percentile map.

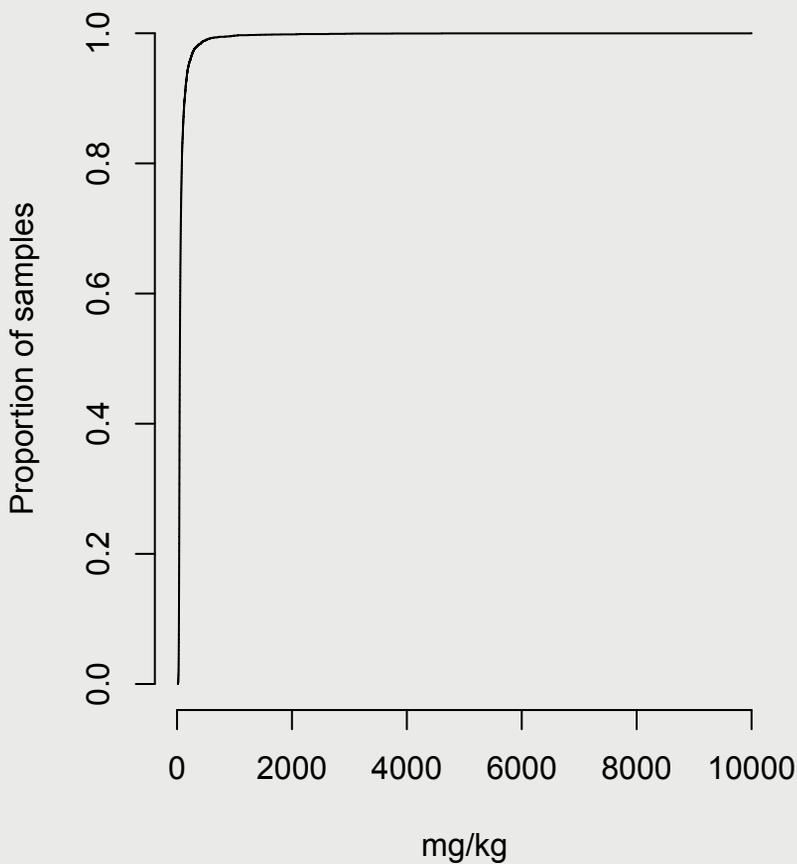
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Pb - Lead mg/kg

mean= 81

median= 49

10th percentile= 33

25th percentile= 39

75th percentile= 73

90th percentile= 134

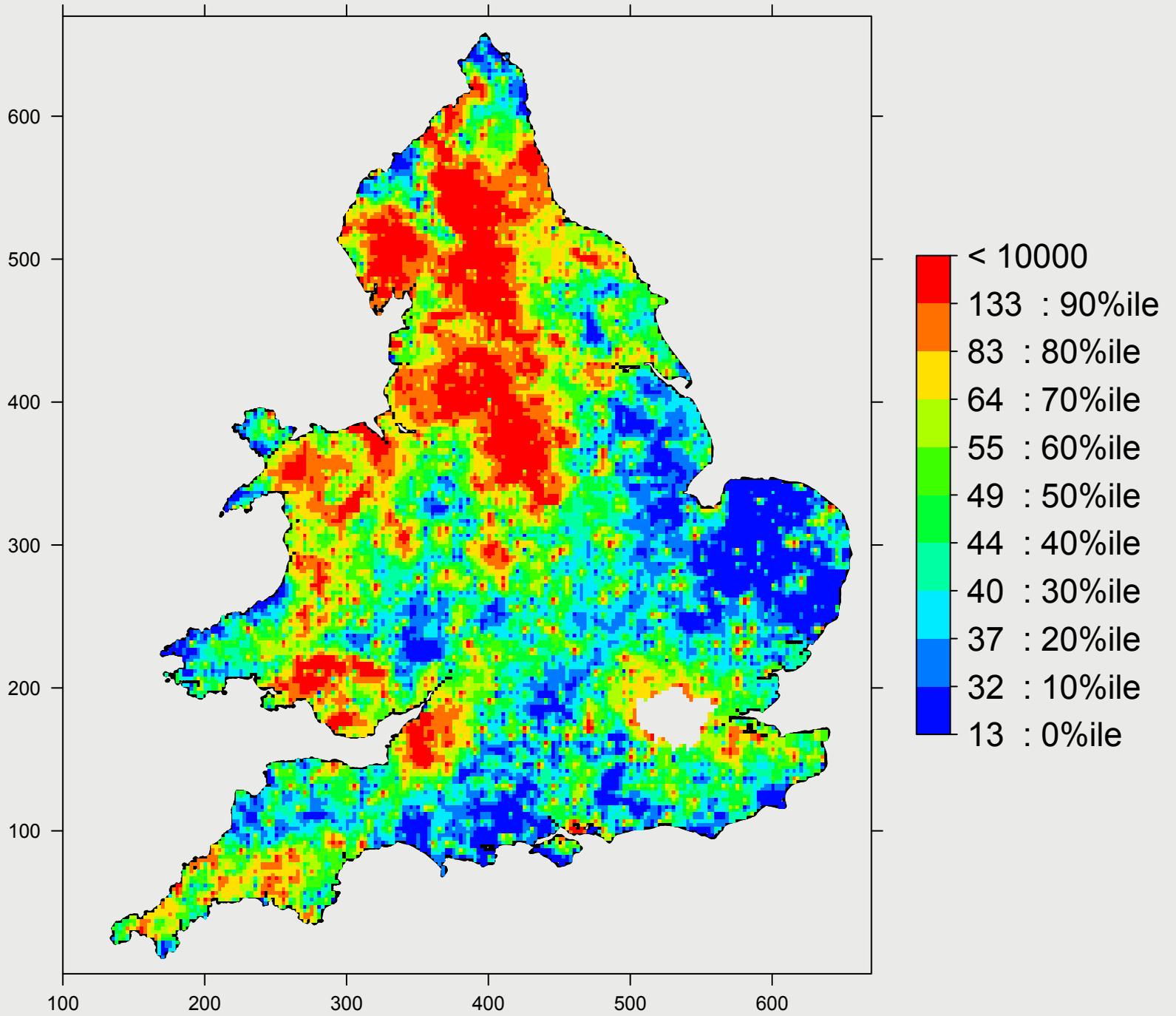
min= 13

max= 10000

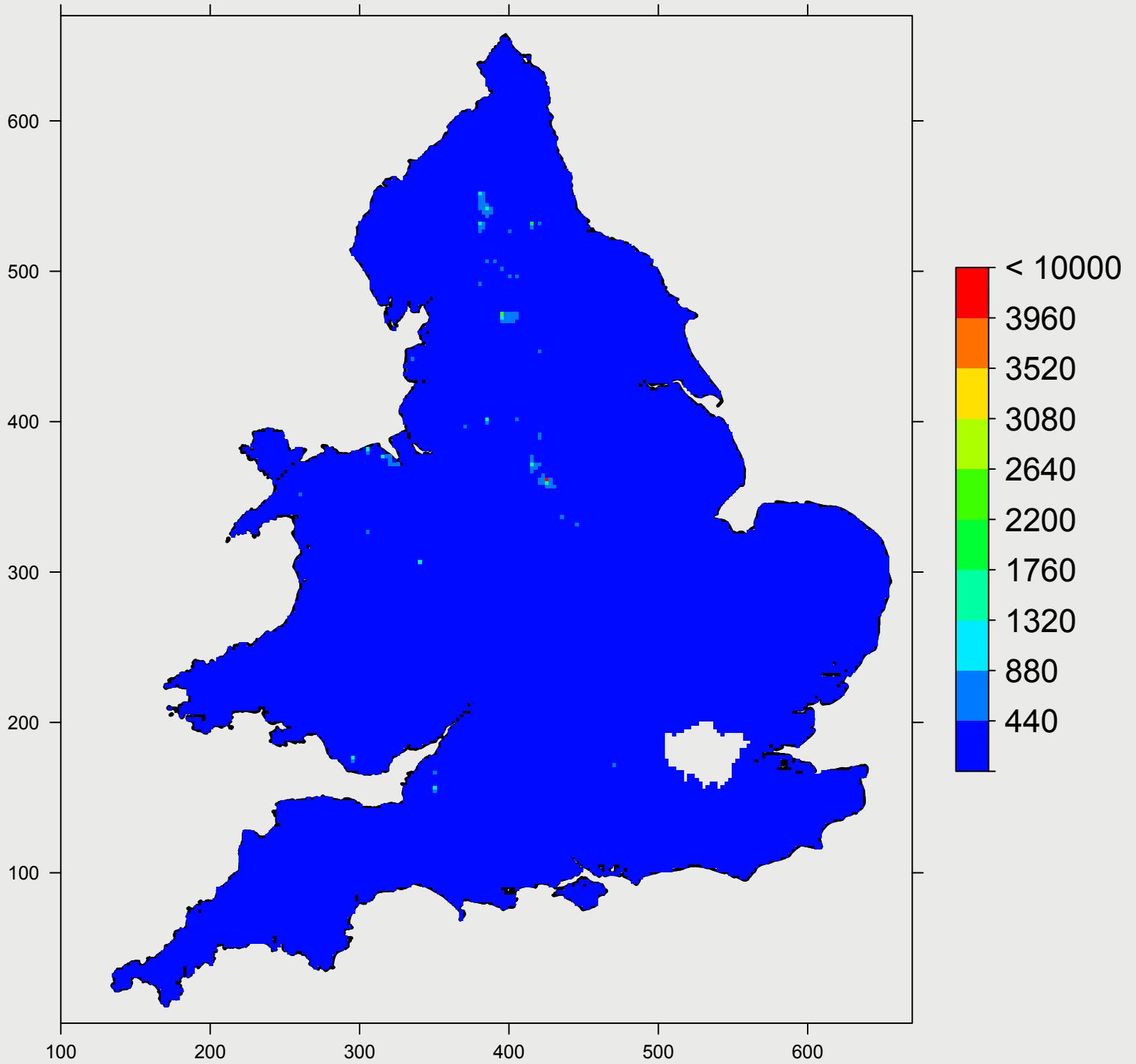
skewness= 28

n= 5670

Topsoil lead (mg/kg ; percentile scale)



Topsoil lead (mg/kg ; arithmetic scale)



Magnesium (Mg)

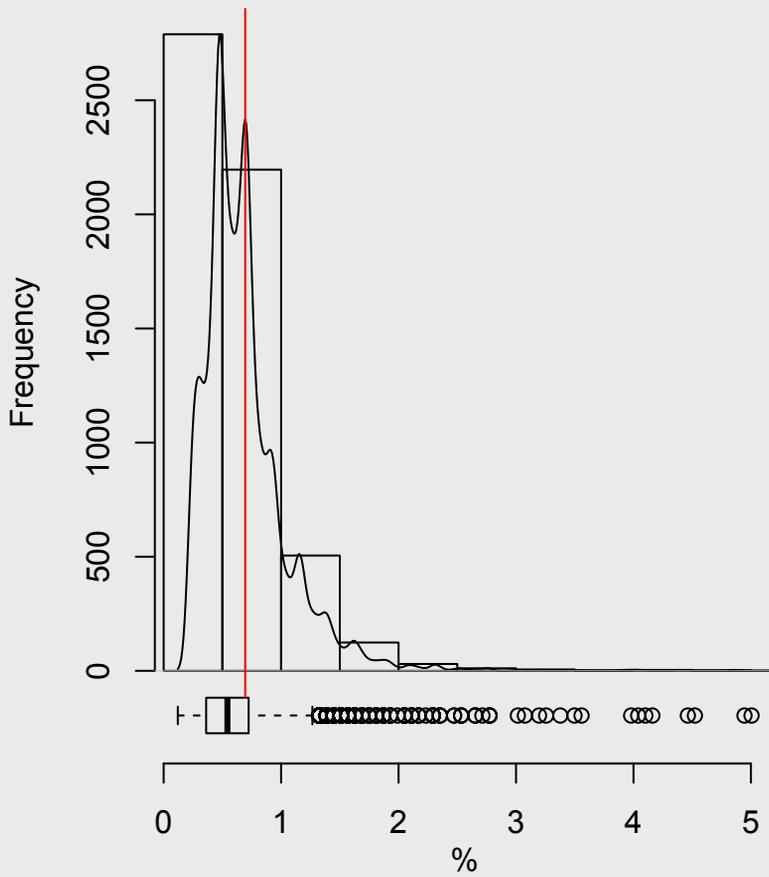
Magnesium is a major metallic element, present at about 1.3% by weight in the upper continental crust, but much more abundant in basic igneous rocks (4.6%) than in granites (0.5%) and sandstones (0.7%), and more common in shales (1.6%) than in pure limestones (0.4%) and coals (Reimann and De Caritat, 1998). However, dolomitic limestones, which contain magnesium carbonate, are naturally rich in Mg (up to 10% Mg). Magnesium is biologically essential to both plants and animals, and as a highly mobile element, deficiencies (perhaps due to soil leaching) may be a common problem.

A band of high soil Mg occurs along the Permian Magnesian Limestone (dolomite) outcrop in a narrow band extending from the north of Nottingham to Wetherby, then after a gap due to narrowing of the outcrop and poor exposure, continuing to the north-east coast at Sunderland. Other areas of high Mg concentrations include Permo-Triassic Mercia Mudstone Group (mudstone and siltstone) in an area of the Midlands and the Avon–Somerset area, and the Old Red Sandstone of the Welsh Borders centred on Hereford. Some of the Mg enrichment in soils of the Somerset Levels may be related to Quaternary marine inundation and this is also an important controlling factor in the Thames estuary (Essex and north Kent marshes), the Lincolnshire coastal marshes and the Fens, where marine alluvium is particularly high in Mg.

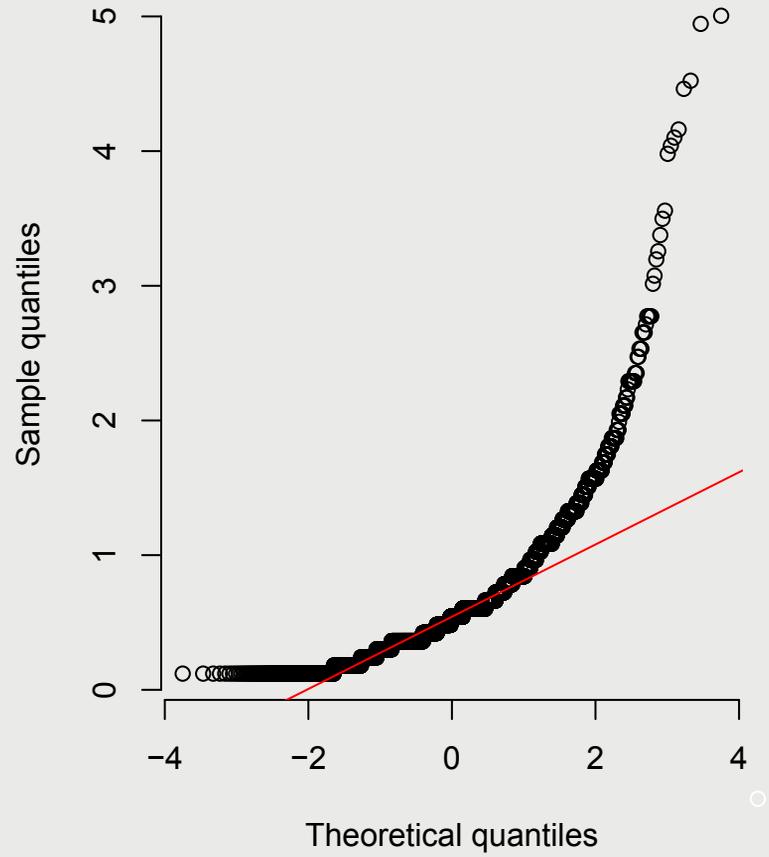
Very low Mg concentrations mark the outcrop of the Namurian grits of the Pennines, the deltaic Jurassic sediments of the North York Moors, the Lower Palaeozoic greywackes of north and central Wales, the south Wales coalfield, the Wealden Series (nonmarine Lower Cretaceous sands and clays) the Paleocene sands of the Surrey heaths and the Hampshire Basin, and much of the Quaternary deposits of East Anglia.

However, the total Mg concentration in soil is not a good guide of the likelihood of a response in crops to added Mg in fertilisers. A system of “index values” based on the concentrations of Mg extracted by ammonium nitrate solution is used in agriculture to determine when Mg should be applied, and this information is supplied in McGrath and Loveland (1992). It appears that Mg is inefficiently extracted from the soil matrix during aqua regia digestion, because the median values reported here based on XRF-S analysis (0.54%) are significantly higher than those reported (0.3%) in McGrath and Loveland (1992).

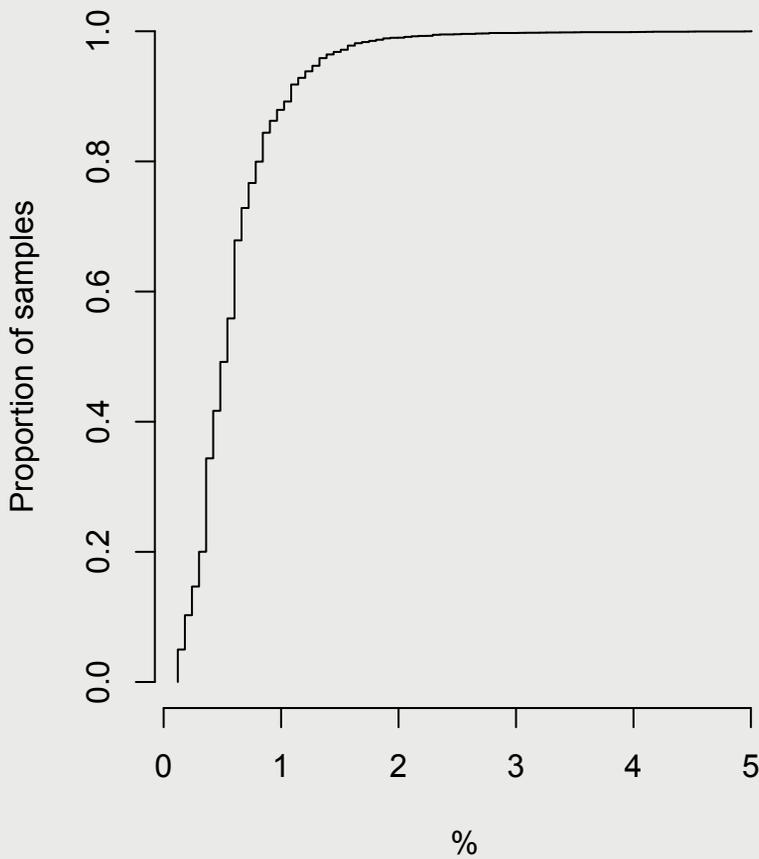
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Mg- Magnesium %

mean= 0.6

median= 0.54

10th percentile= 0.18

25th percentile= 0.36

75th percentile= 0.72

90th percentile= 1.1

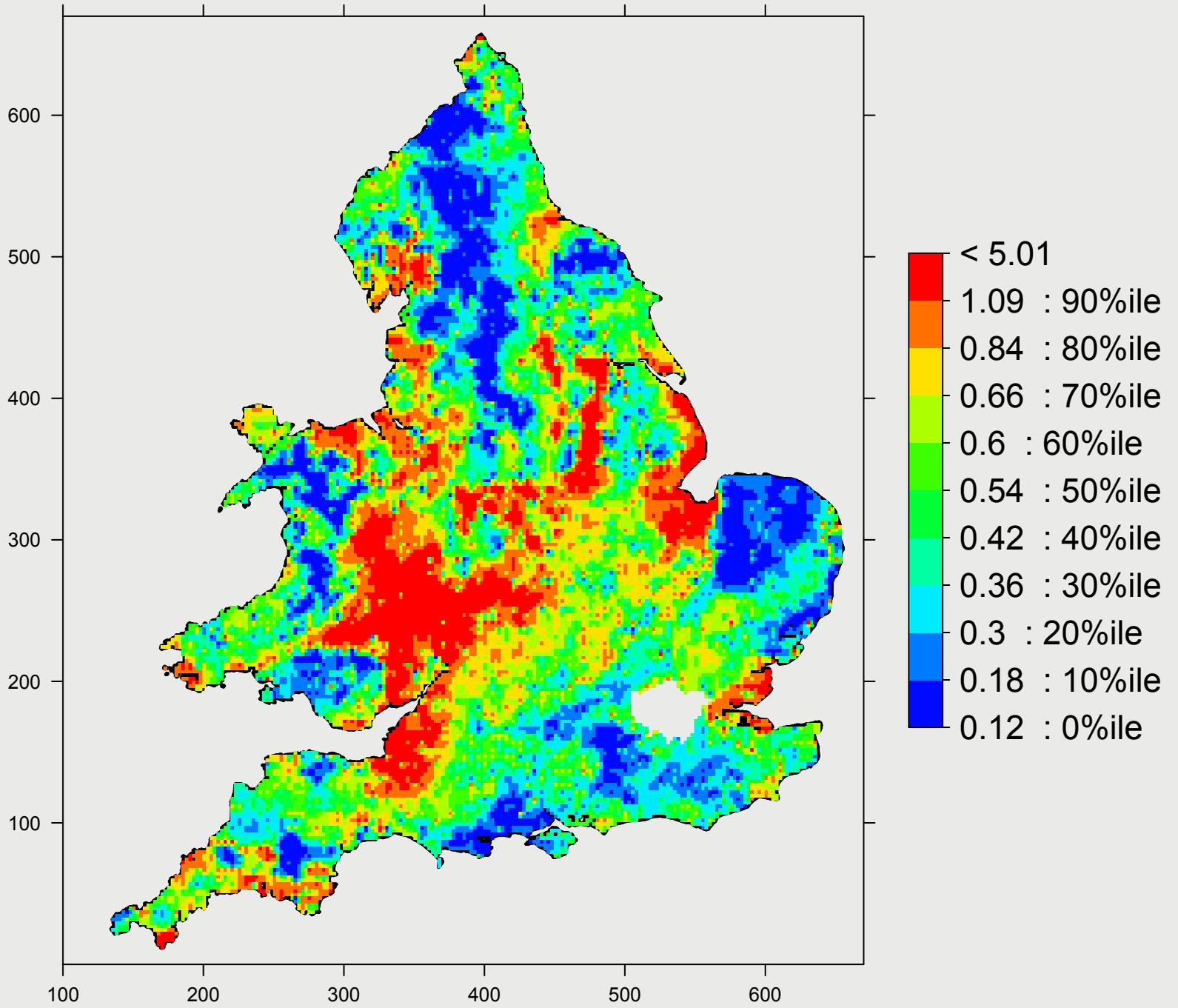
min= 0.12

max= 5

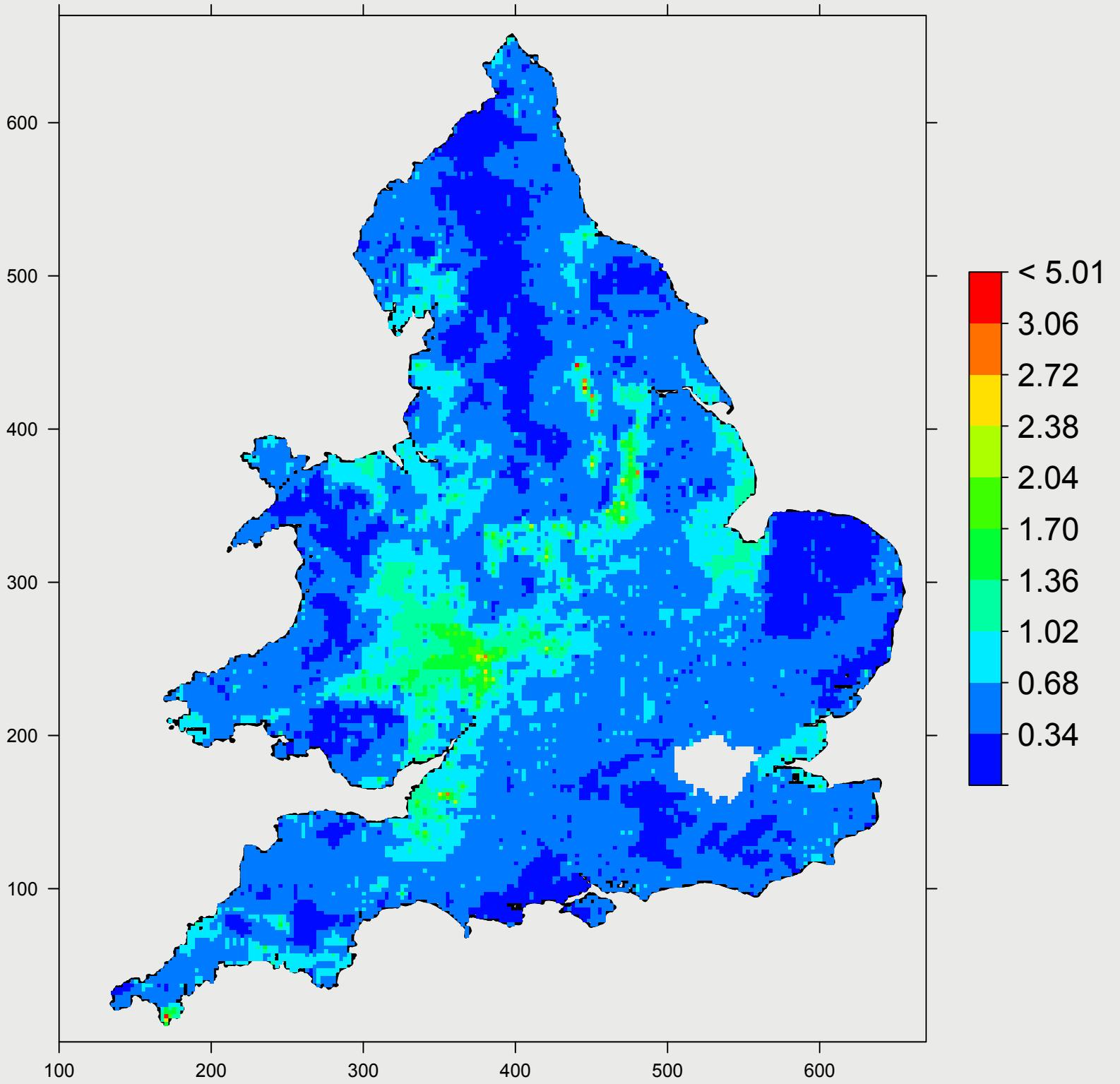
skewness= 2.8

n= 5670

Topsoil magnesium (% ; percentile scale)



Topsoil magnesium (% ; arithmetic scale)



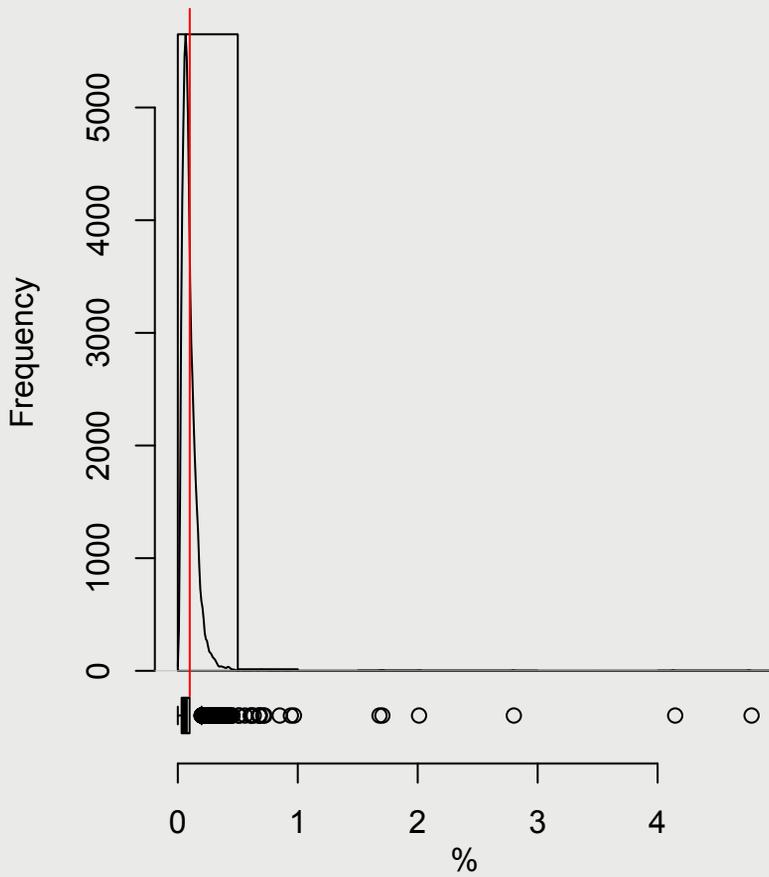
Manganese (Mn)

Manganese is a common metallic element, present at about 550–600 mg/kg in the upper continental crust, with higher levels in basic igneous rocks (1500 mg/kg) than in granites (400 mg/kg) and low levels in sandstones (100 mg/kg). Concentrations in greywacke, shale and limestone are generally in the 700–850 mg/kg range (Reimann and De Caritat, 1998). Manganese is a biologically important element and is essential for all organisms, with deficiency problems far more likely than toxic effects.

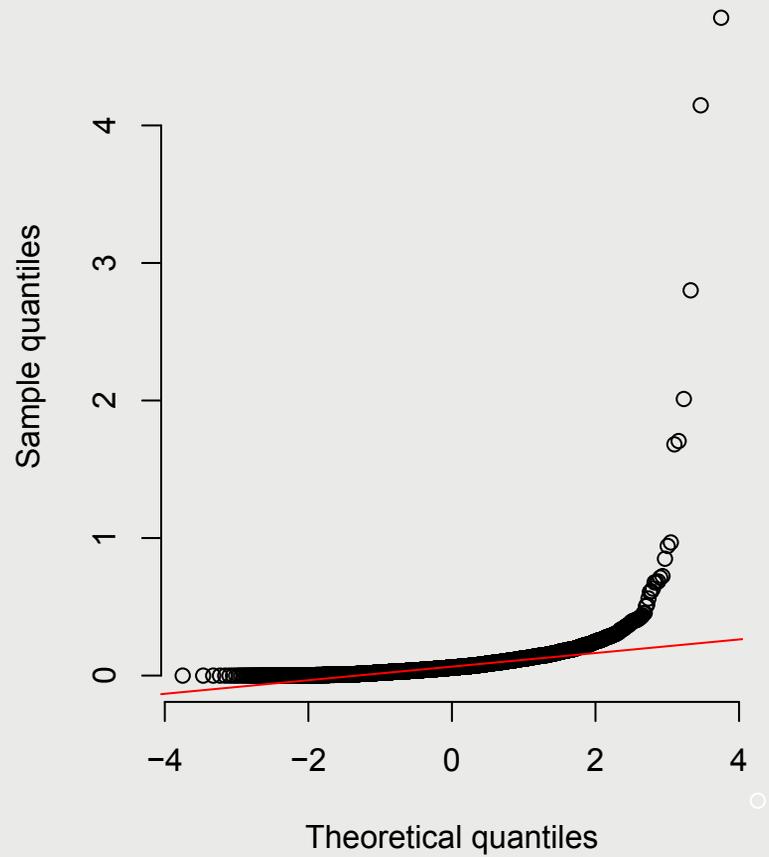
Soils with the highest Mn concentrations (>0.11%) are not spatially extensive and are likely to be related to historical mineral extraction and processing. Manganese ore was worked near Dolgellau in west Wales and appears to be associated with the valleys near Barmouth and Aberdovey, perhaps having been redeposited in sediments. Manganese was also mined in the 18 and 19th century, mainly associated with lead mines, west of Matlock in Derbyshire (Ford, 2001). More generally, elevated soil Mn concentrations are associated with the Carboniferous Limestone outcrop in Cumbria and Derbyshire, the Devonian limestones of south-east Devon, the Permian Magnesian Limestone in Yorkshire, and part of the Coal Measures outcrop in the Yorkshire–Nottinghamshire Coalfield with Jurassic limestones in the Bath and Cotswolds area, and with the Chalk outcrop in Lincolnshire and southern England. Other areas of high Mn levels include an area of Carboniferous shales in central Devon and parts of the Old Red Sandstone outcrop of the Welsh Borders.

Areas with low Mn concentrations include most of the high moorlands (mainly on granites or sandstones) and lowland heaths in England and Wales (mainly sandy substrates), and the sandy soils with low clay contents in East Anglia. Low manganese availability in soil can be a problem in crop production, but total soil concentrations is not necessarily a good indicator of the likelihood of crop deficiency for this element.

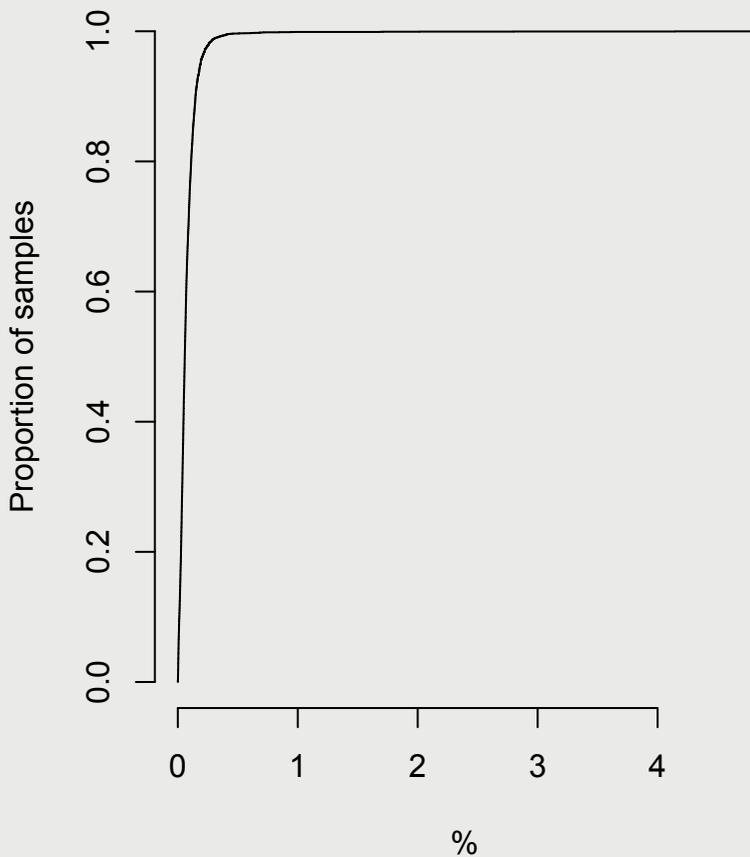
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Mn- Manganese %

mean= 0.077

median= 0.058

10th percentile= 0.012

25th percentile= 0.032

75th percentile= 0.098

90th percentile= 0.15

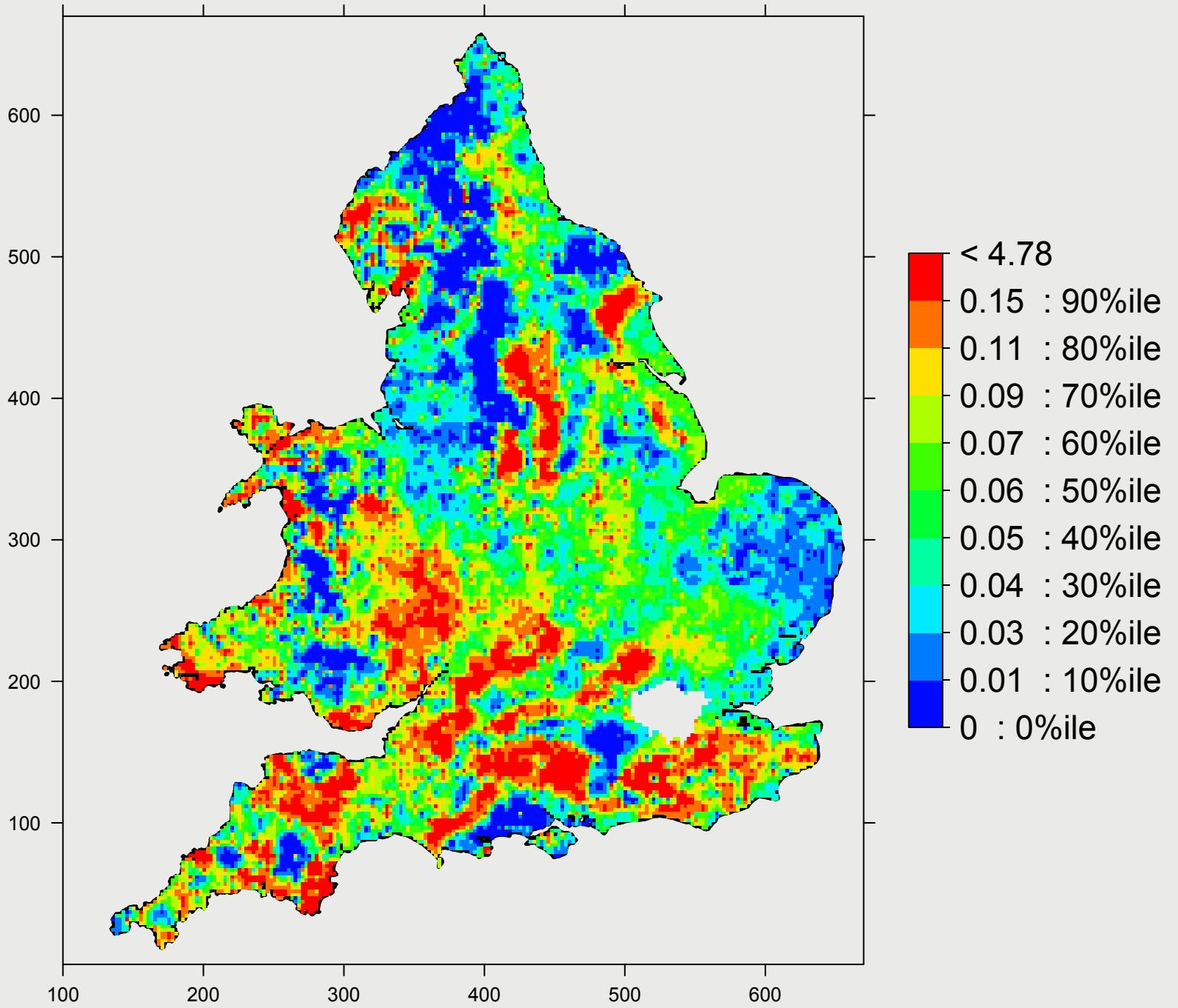
min= 0

max= 4.8

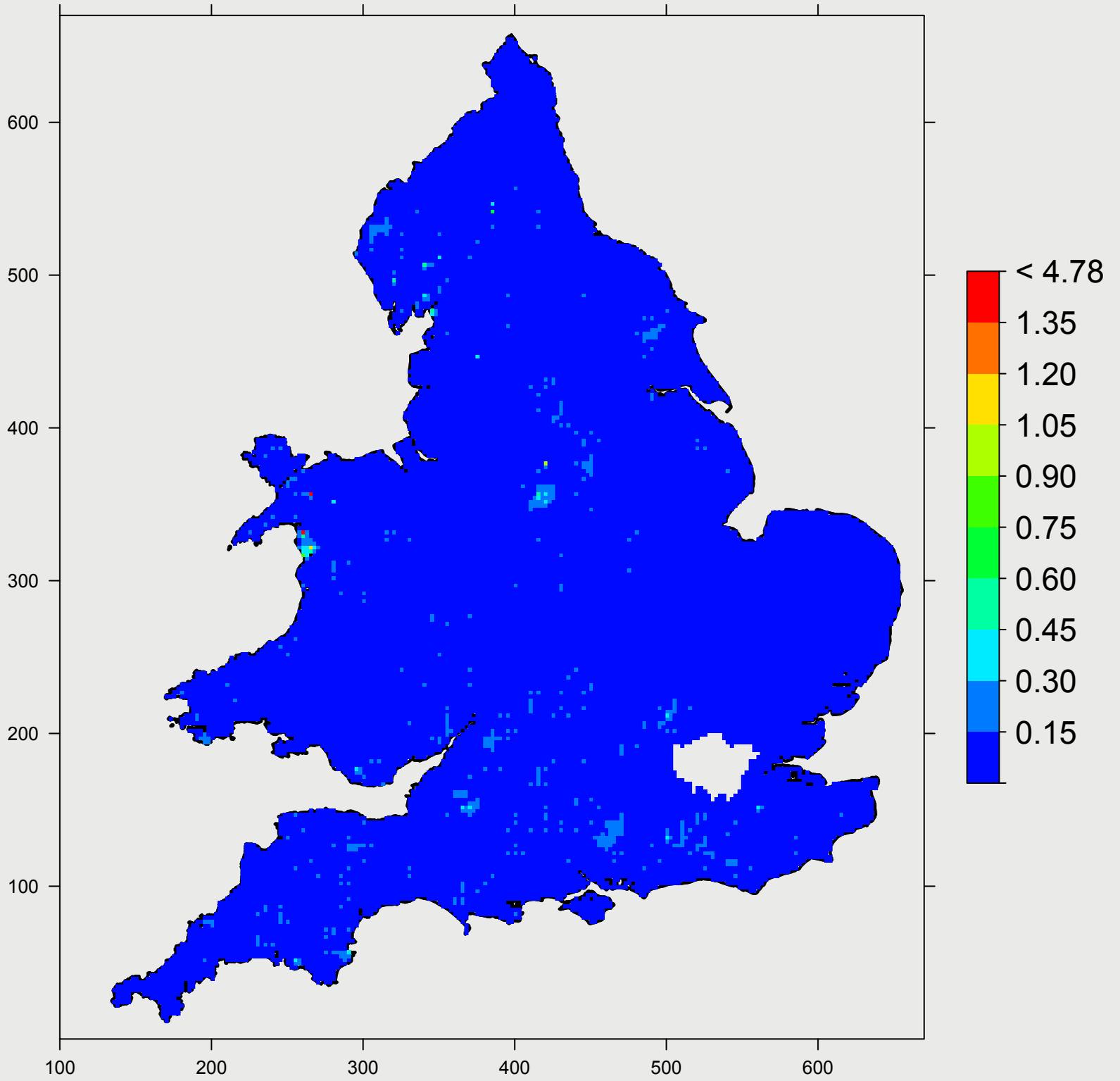
skewness= 22

n= 5670

Topsoil manganese (% ; percentile scale)



Topsoil manganese (% ; arithmetic scale)



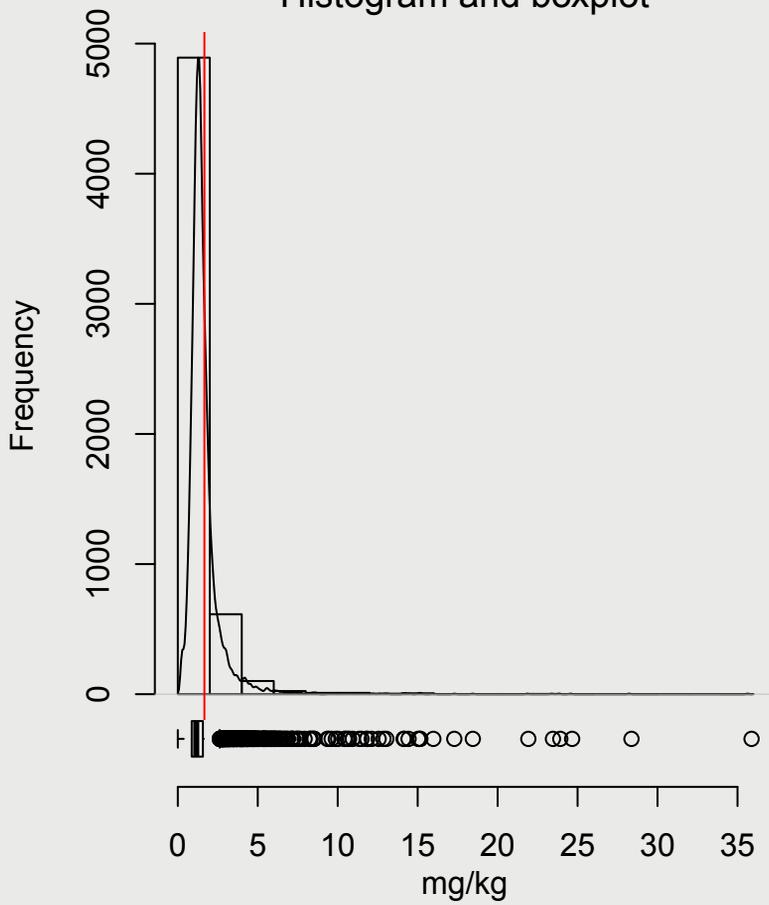
Molybdenum (Mo)

Molybdenum is a relatively rare metallic element, present at about 1.5 mg/kg in the Earth's upper continental crust, and at similar concentrations in most rock types, though it has a strong affinity with sulphur and organic matter, and consequently is enriched in black shales and coals (>3 mg/kg) (Reimann and De Caritat, 1998). Molybdenum is a biologically important trace element, essential for almost all organisms, and both deficiency and toxicity problems are common and well documented.

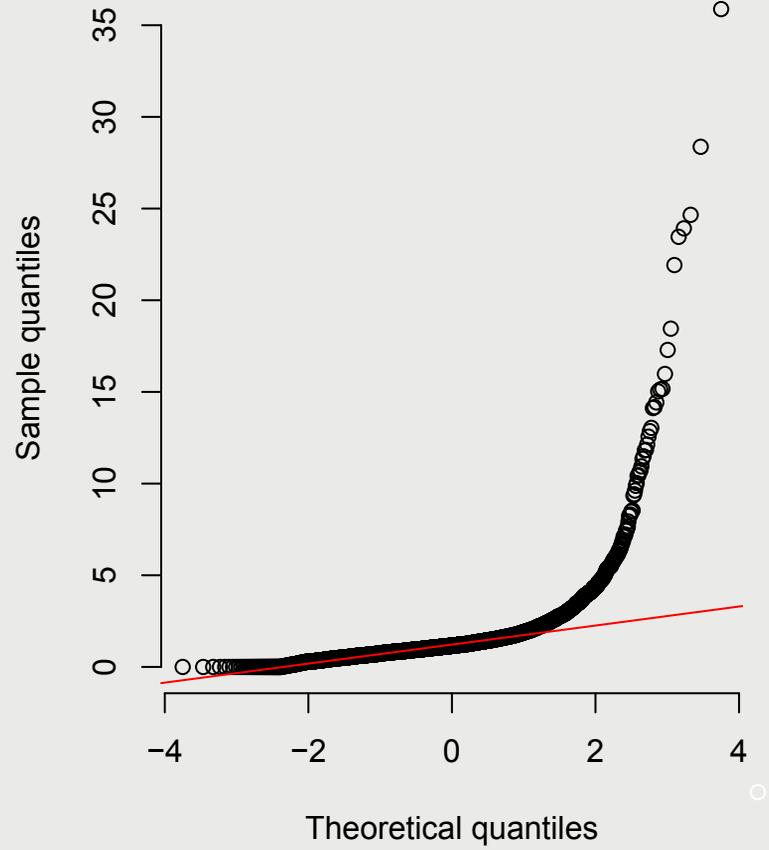
Areas which have high Mo concentrations in soils include the well-known area of Somerset with so-called "teart" pastures, where naturally high Mo in soil can induce Cu deficiency in ruminants grazing there. Sulphur and selenium concentrations in soils are also relatively elevated in the most affected area. The soil Mo concentrations reach up to 37.5 mg/kg in this area which is underlain by black shales of the Lower Lias (the most likely Mo source) and Mercia Mudstone Group (Triassic) mudstones, but additional sorption and concentration by the peaty soils may be responsible for the very high levels. Black shales of Carboniferous age also occur in south Derbyshire and the Craven Basin in Lancashire, again with soil Mo concentrations up to 16.5 mg/kg, while Lower Palaeozoic black shales also show high Mo levels in south-west Wales. Elevated Mo concentrations (>2 mg/kg) also occur in soils in the region of northern industrial cities stretching from Manchester to Sheffield and Leeds (seen on the percentile map), which is mainly anthropogenic and related to coal-burning and industrial use of this element. Similar anthropogenic enrichment can be seen in Birmingham and the Sunderland–Newcastle area. Clay-rich soils across central England extending from Gloucester in a broad band to Lincolnshire follow the outcrop of Lower Jurassic mudstones (with subsidiary black shales) and also have slightly elevated Mo concentrations (>1.5 mg/kg), with similar distribution to As in this region (Oliver et al., 2002). High levels in the Peterborough to Cambridge areas are more closely associated with the peat soils of the Fens, where Mo has been concentrated by sorption from groundwater.

Soils with low Mo concentrations are associated with two situations: 1) soils in the high Pennines with high organic matter contents, underlain by grits and sandstones and 2) those that are sandy in texture and low in organic matter (Oliver et al., 2002). The latter include parts of the Permo-Triassic outcrop in the Midlands, the Brecklands and sandy soils of East Anglia, the sandy heathland soils in the south of England, and the Old Red Sandstone outcrop of the Welsh borders.

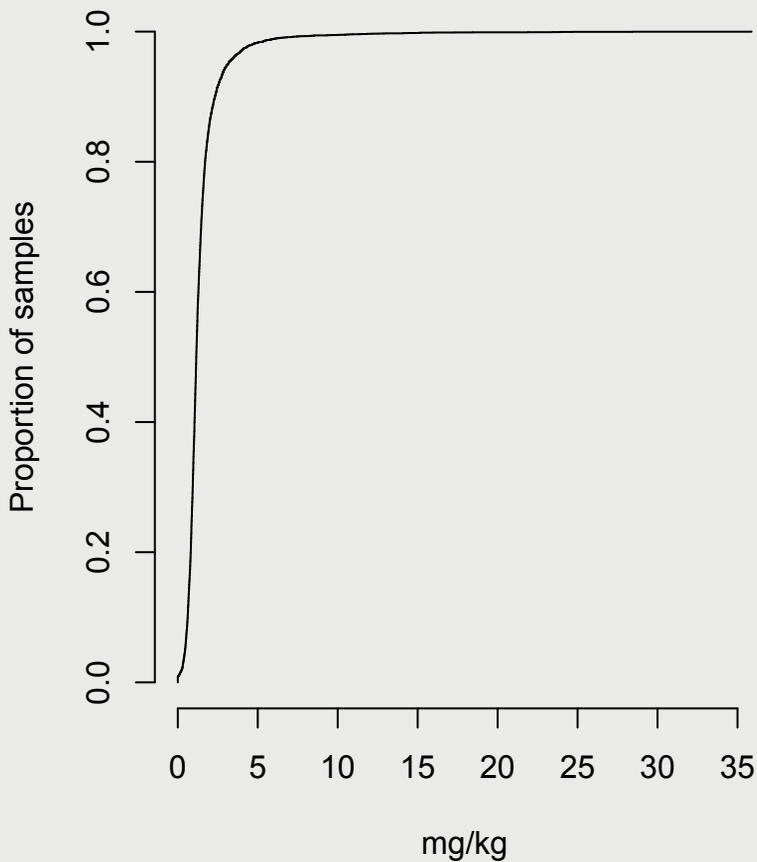
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Mo- Molybdenum mg/kg

mean= 1.4

median= 1.2

10th percentile= 0.62

25th percentile= 0.87

75th percentile= 1.6

90th percentile= 2.3

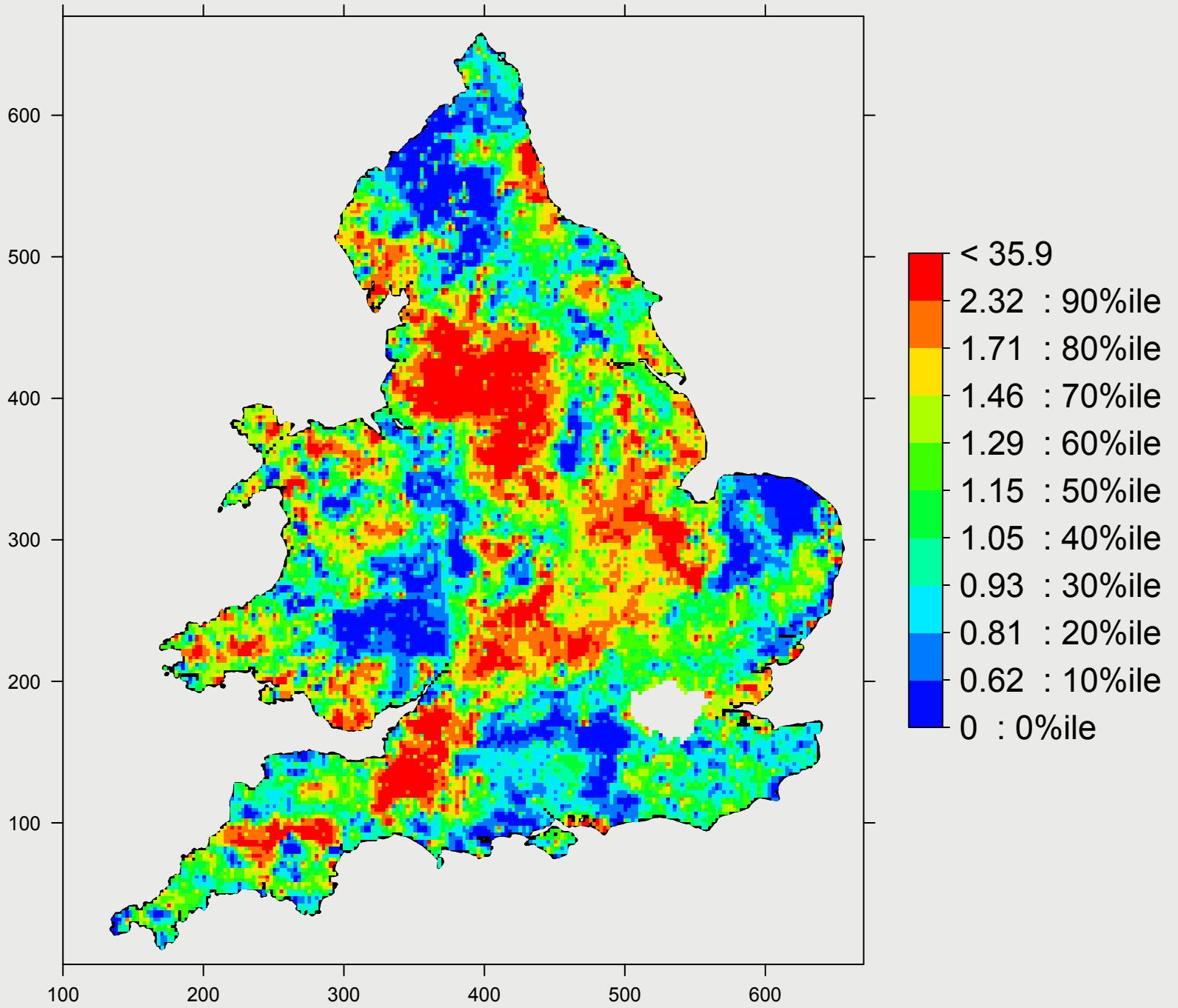
min= 0

max= 36

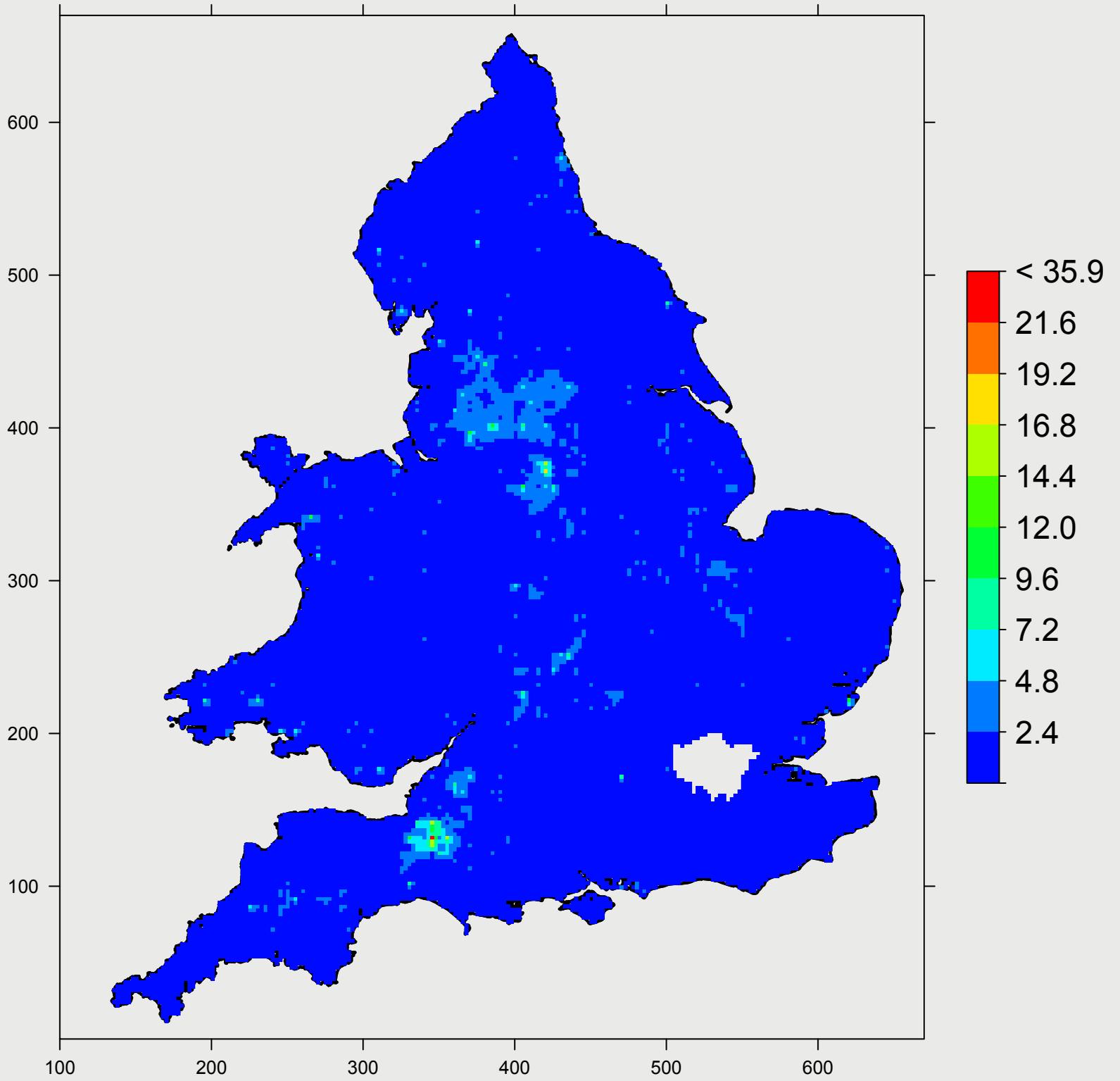
skewness= 9

n= 5670

Topsoil molybdenum (mg/kg ; percentile scale)



Topsoil molybdenum (mg/kg ; arithmetic scale)



Neodymium (Nd)

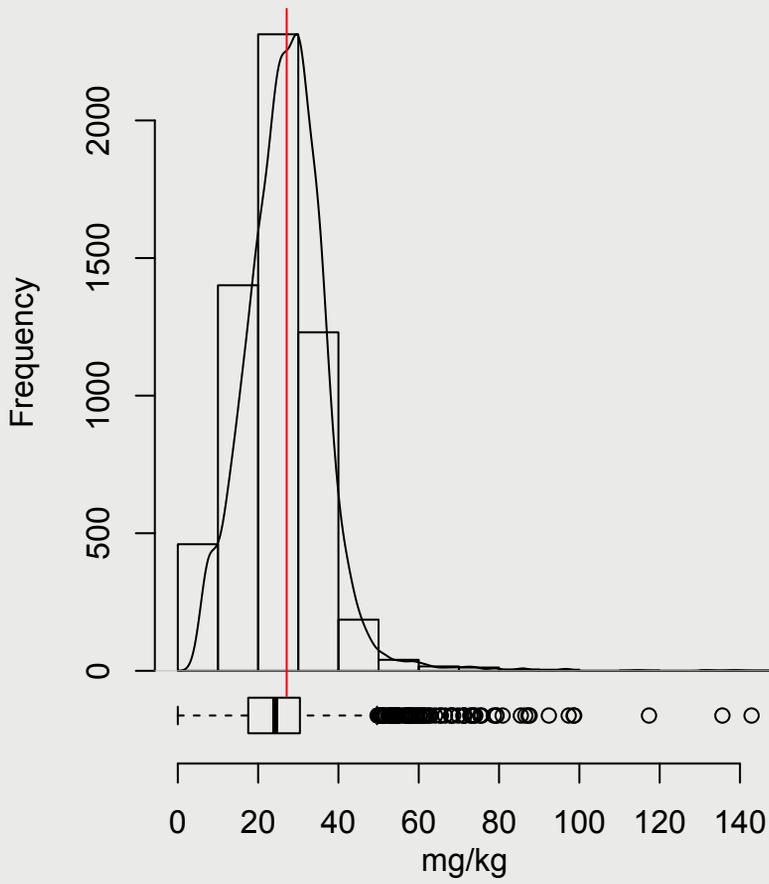
Neodymium is a rare earth element (REE) that occurs in the Earth's upper continental crust at about 26 mg/kg. It is considered non-essential, with only scarce data on its potential toxicity. Like La and Sm, it is generally found in the resistate minerals monazite and bastnäesite. Its main industrial application is in magnets and lasers (Reimann and De Caritat, 1998). The mean and median concentration measured in NSI soils is 24 and 23 mg/kg respectively, implying a near-normal concentration distribution.

The most prominent area of high soil Nd concentration follows the line of the Jurassic outcrop from Somerset to Lincolnshire, with high values also present over the Chalk outcrop in the Yorkshire and Lincolnshire Wolds and in southern England, the southern Peak District (Carboniferous Limestone), south-west Wales, parts of Devon and Cornwall, Bedfordshire, and the nonmarine Lower Cretaceous sandstones and clays of the Wealden District of Sussex and Kent.

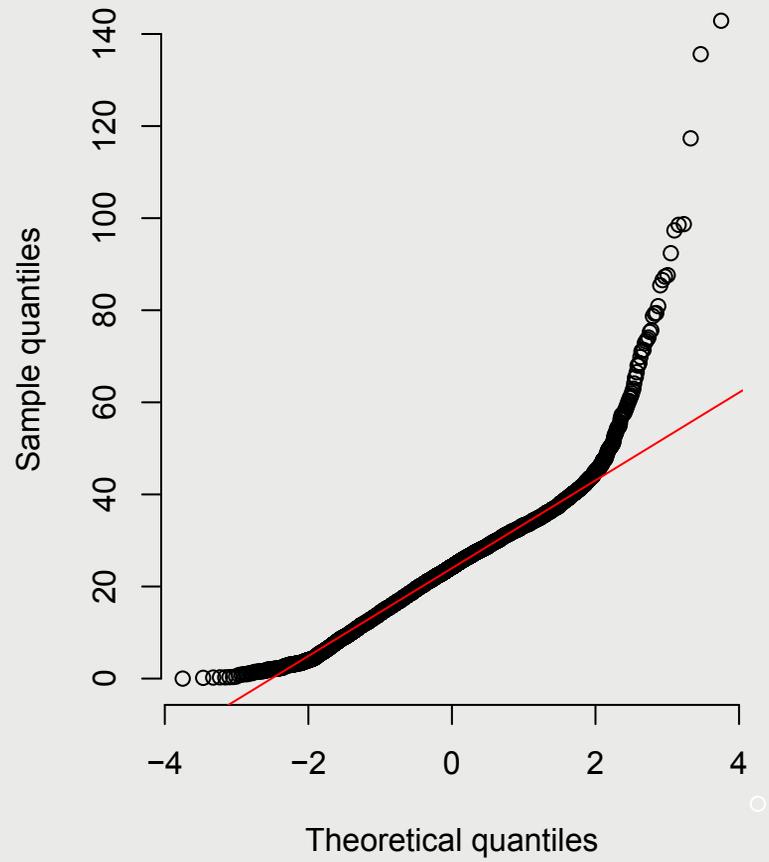
Low Nd values follow the gritstone uplands of the Pennines, the Permo-Triassic outcrop of the Midlands, the granites of south-west England, and the sandy soils of the Hampshire Basin, the Surrey heaths and large areas of East Anglia. The overall pattern is very similar to that shown by other resistate-mineral hosted elements such as Ce and Nb.



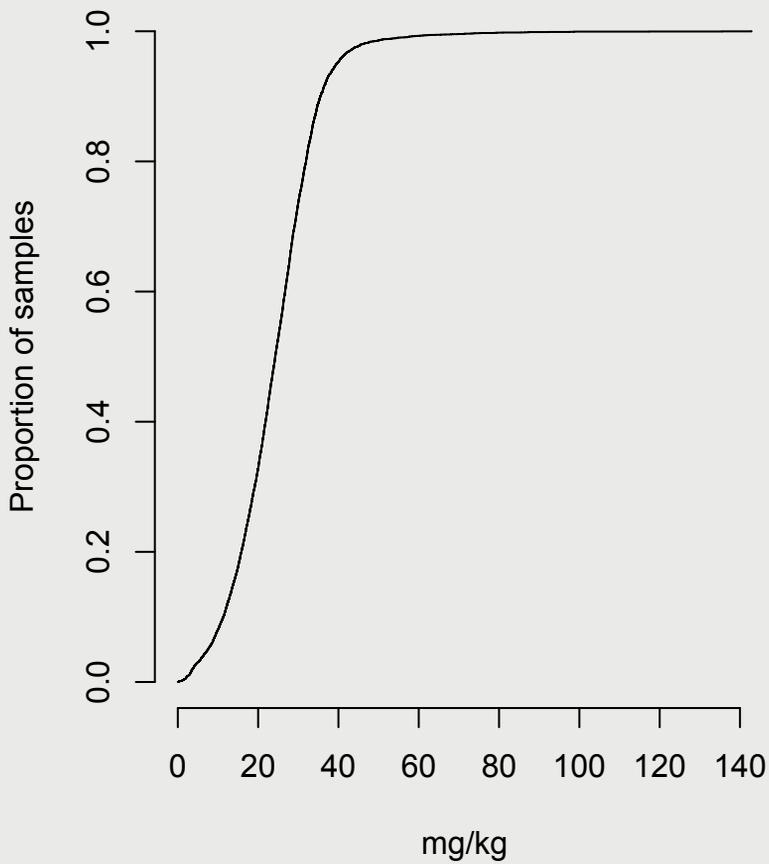
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Nd - Neodymium mg/kg

mean= 24

median= 24

10th percentile= 11

25th percentile= 18

75th percentile= 30

90th percentile= 35

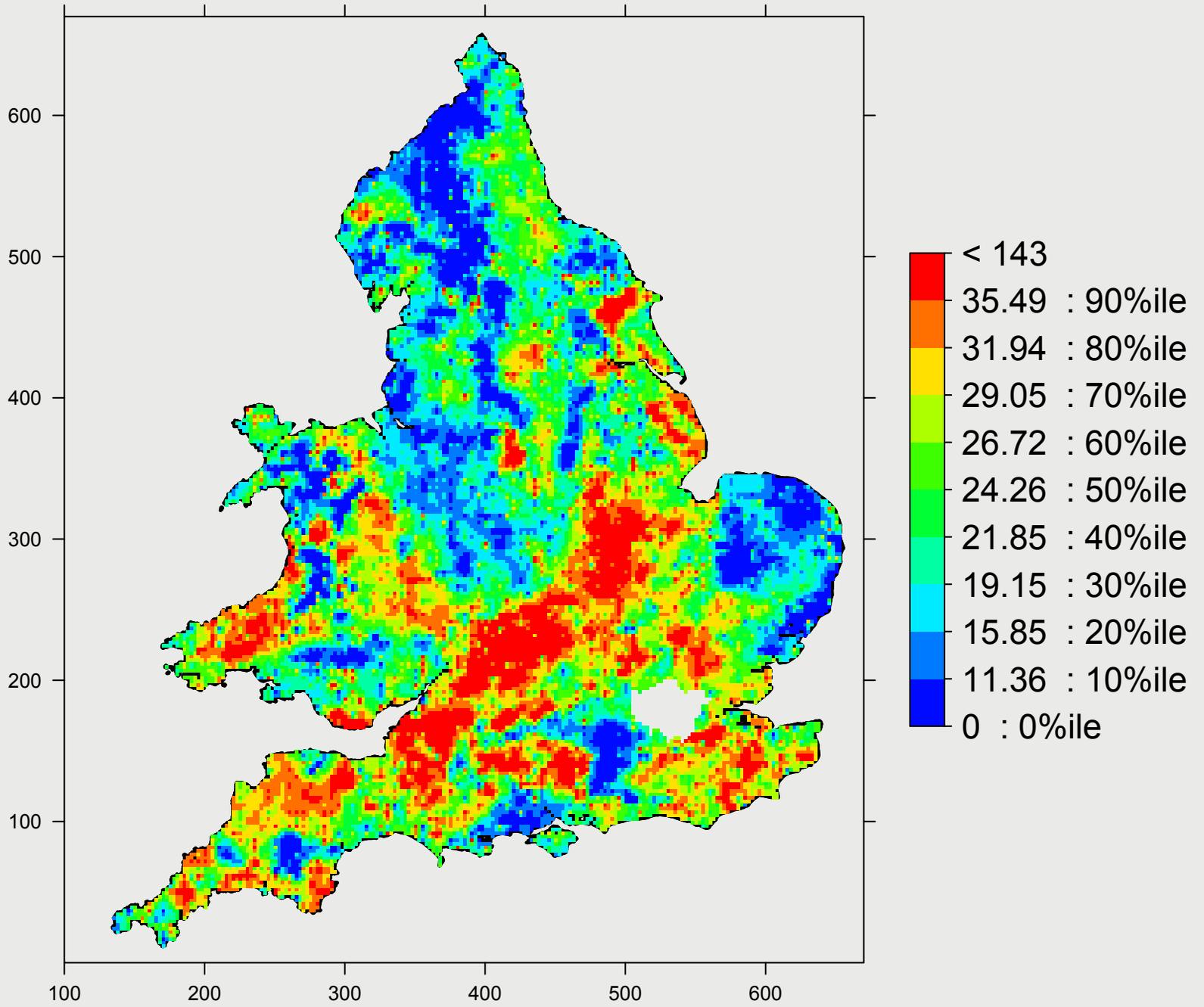
min= 0

max= 143

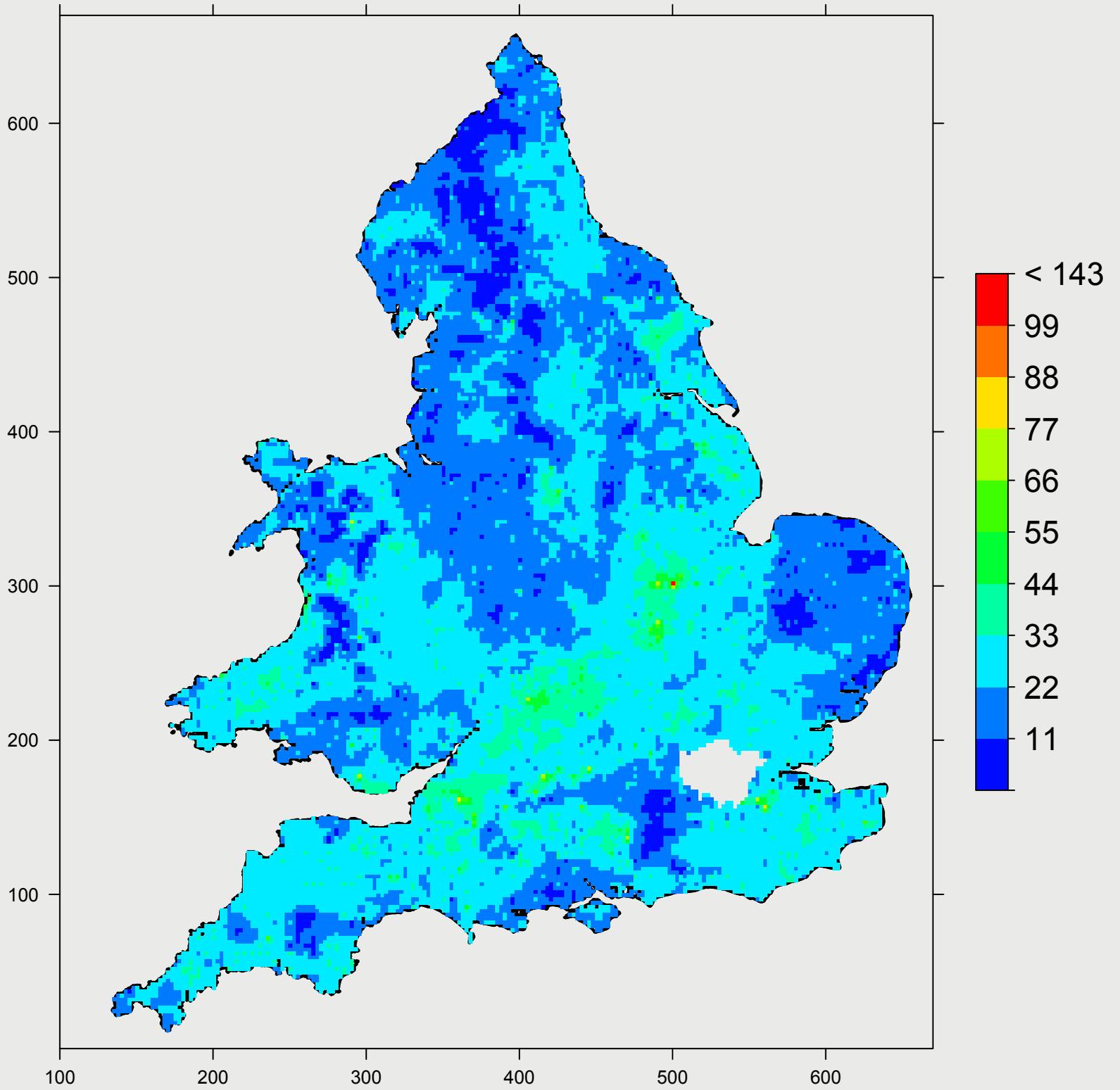
skewness= 1.3

n= 5670

Topsoil neodymium (mg/kg ; percentile scale)



Topsoil neodymium (mg/kg ; arithmetic scale)



Nickel (Ni)

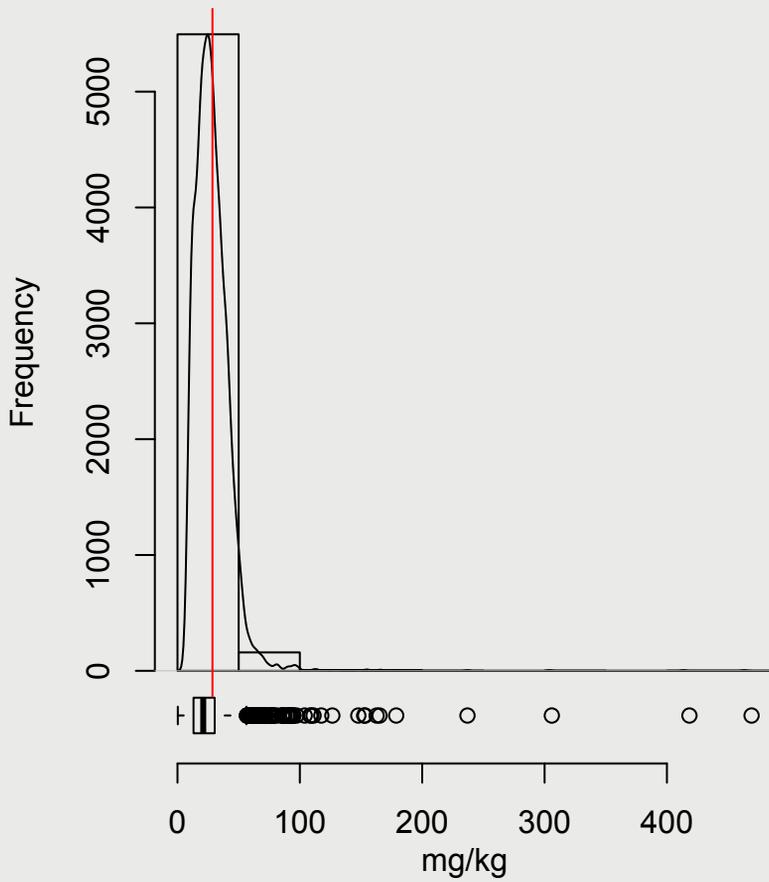
Nickel is a metallic element, closely related to iron, present at about 20 mg/kg in the Earth's upper continental crust. It is very strongly enriched in ultrabasic rocks (2000 mg/kg in dunite and serpentine), less so in basic rocks (130–140 mg/kg), rare in granites, sandstones and limestone (2–5 mg/kg) and generally around 50–70 mg/kg in shales (Reimann and De Caritat, 1998). It is an essential trace element for some organisms. It is widely used in metallurgy as an alloying metal and in plating, in batteries and pigments, and as a catalyst. The median value in the NSI soils is near the crustal average of 20 mg/kg.

High concentrations of soil Ni (maximum 510 mg/kg) occur in the Lizard peninsula, related to the serpentine bedrock there, and in south Wales near Swansea (max 179 mg/kg), where Ni smelting took place for many decades. Two other examples are near Banbury in Oxfordshire (associated with Jurassic ironstone of the Marlstone Rock Formation) and in north Derbyshire, where one site has >400 mg/kg associated with very high Pb and Zn values close to a former mine and quarry.

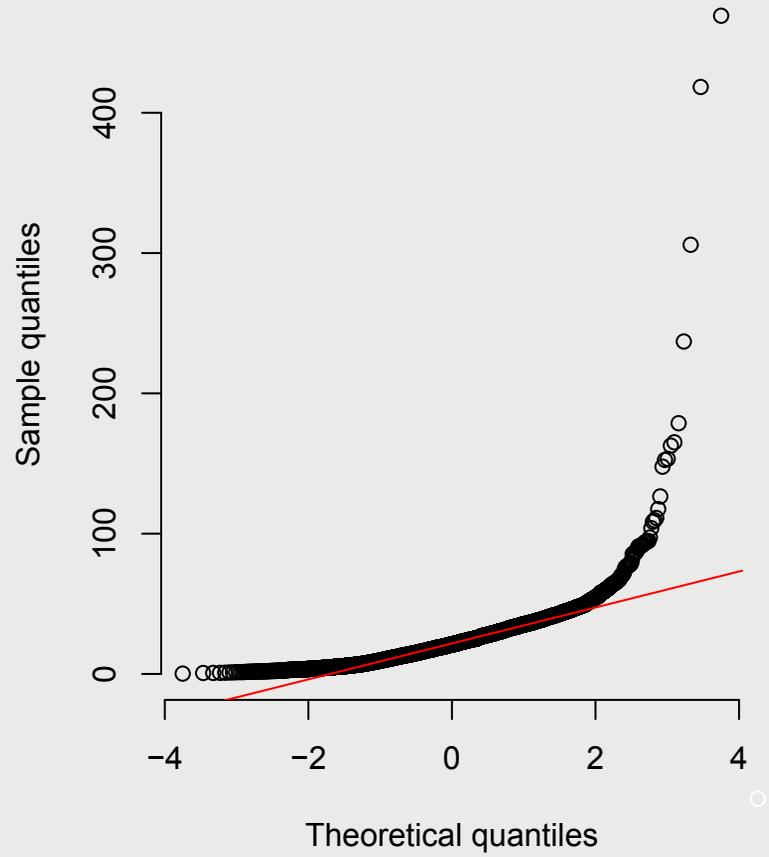
The clay-rich soils over the Jurassic outcrop in central England have reasonably high Ni concentrations (>30 mg/kg) especially in areas of ironstone outcrop, and other areas of high natural Ni levels include the Old Red Sandstone outcrop of the Welsh Borders (see also Cr), parts of south Devon and Cornwall, the southern Peak District, the Chalk Wolds of Lincolnshire and Yorkshire (but not the Chalk outcrop of southern England) and parts of Bedfordshire and Cambridgeshire (for reasons not yet clear). Curiously, the marine alluvium of the Lincolnshire coast also shows relatively high soil Ni values. Other areas of high Ni values include the industrial centres of Manchester, Birmingham, Derby, Nottingham and Tyneside where the elevated Ni values are likely to be of industrial origin.

Relatively low Ni concentrations occur in many of the upland areas of the north of England, Wales and south-west England (notably the major granite units). Other areas of low Ni concentrations are the sandy soils in the New Forest, the heaths between Reading and Woking, and the sandy soils and tills of East Anglia. Nickel in soil has a similar spatial distribution to the elements As, Co, and Fe.

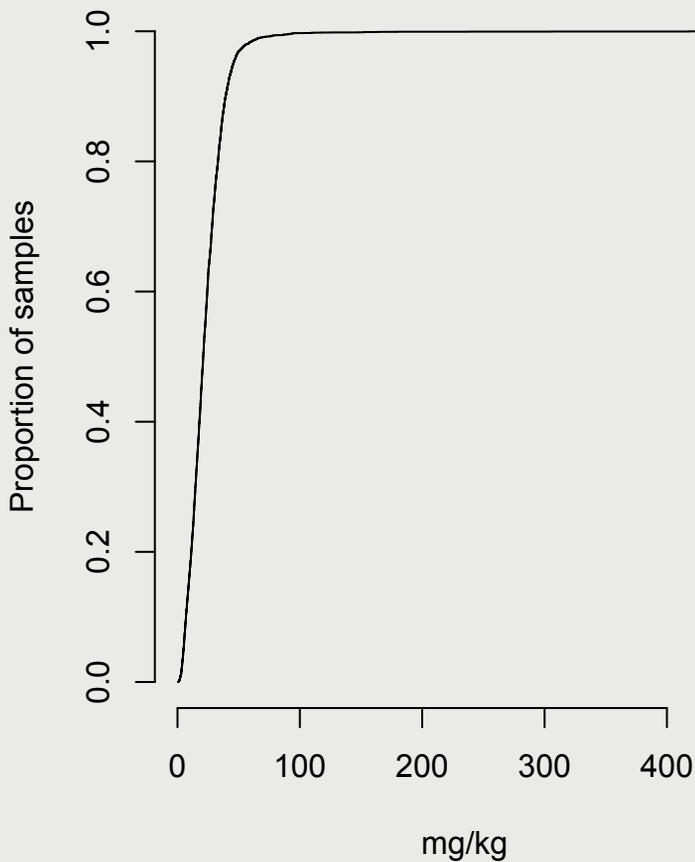
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ni - Nickel mg/kg

mean= 23

median= 21

10th percentile= 6.9

25th percentile= 13

75th percentile= 30

90th percentile= 39

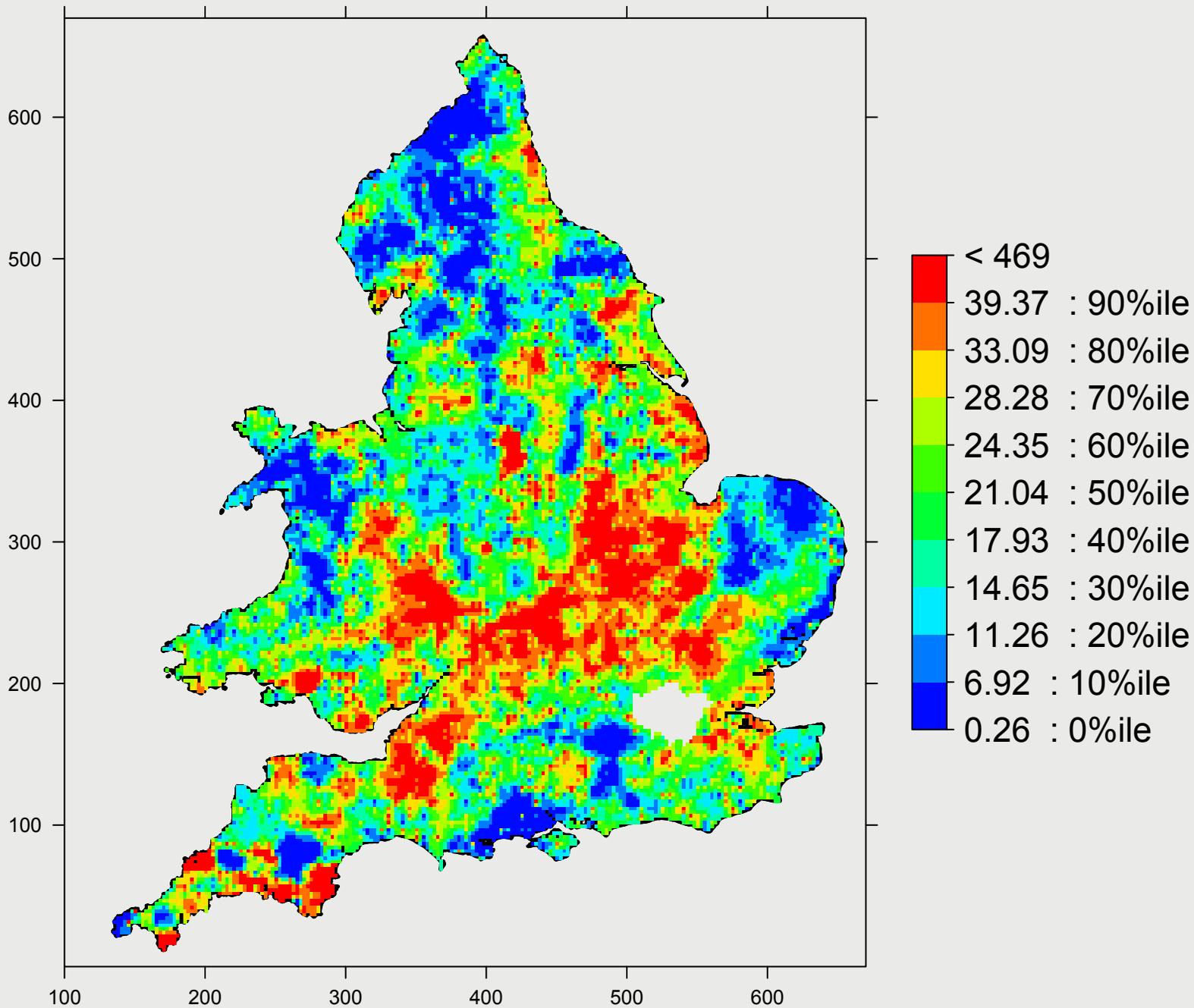
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max= 469

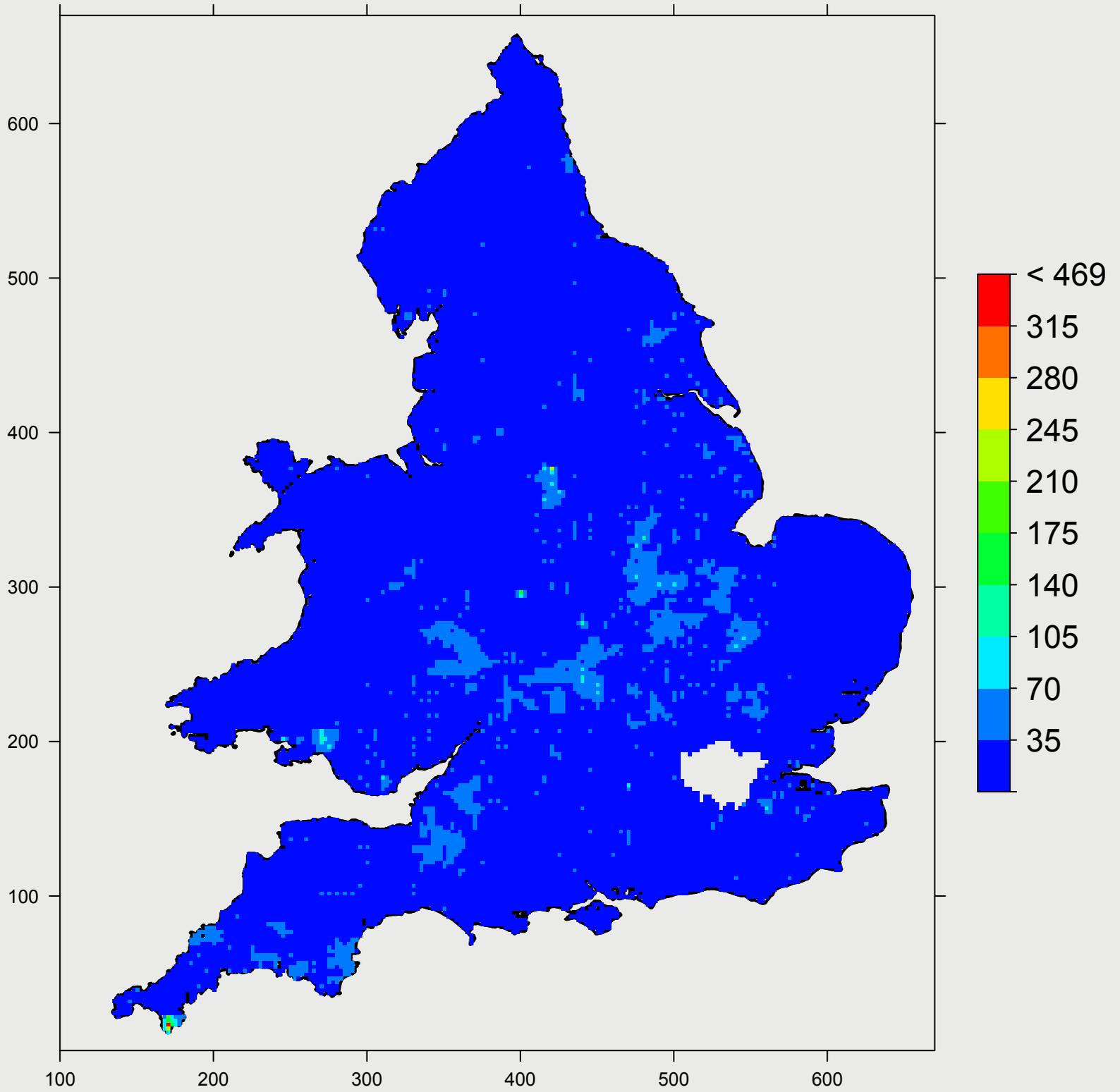
skewness= 7.9

n= 5670

Topsoil nickel (mg/kg ; percentile scale)



Topsoil nickel (mg/kg ; arithmetic scale)



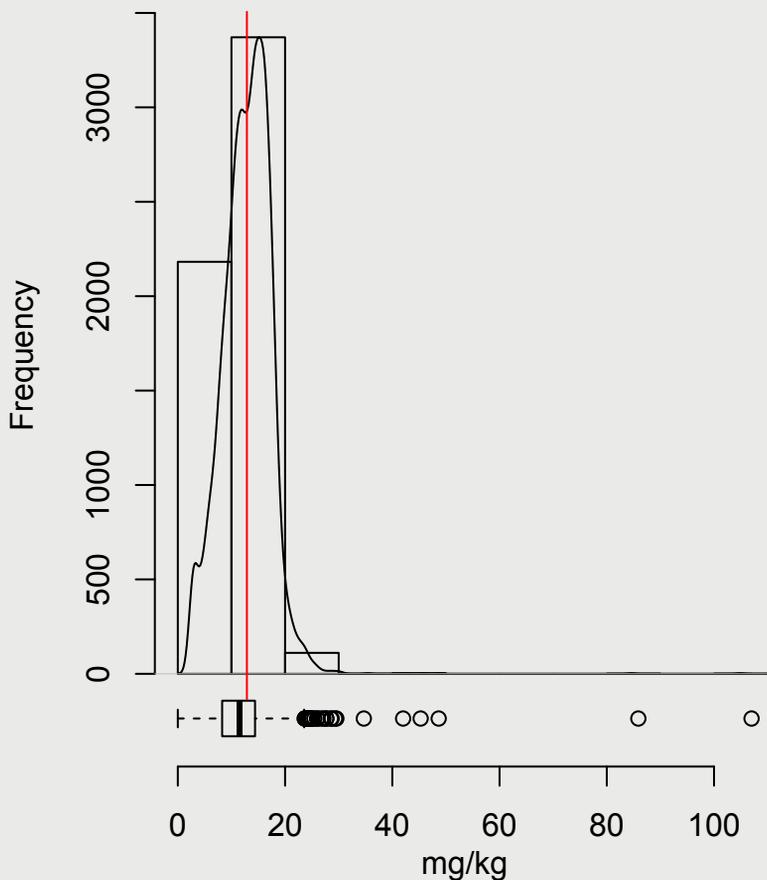
Niobium (Nb)

Niobium is a transition metal with no known biological role. It forms the rare minerals columbite and pyrochlore, and occurs in association with the more common minerals zircon and apatite. Its estimated concentration in the Earth's upper continental crust is 20 mg/kg (Emsley, 2001), and it is more abundant in granitic rocks (18 mg/kg) and shales (17 mg/kg) than in basalts (4–10 mg/kg) and very low in limestones (0.1 mg/kg) (Reimann and De Caritat, 1998). Estimated mean concentrations in soils vary from 24 mg/kg (Emsley, 2001) to 12 mg/kg stated by Reimann and De Caritat (1998). The dominant industrial use of niobium is as an alloy in high-grade structural steel and in smaller amounts in electronic components. Mean and median concentrations measured in NSI soils for England and Wales are 11 and 12 mg/kg respectively with a maximum of 107 mg/kg, suggesting a near-normal concentration distribution.

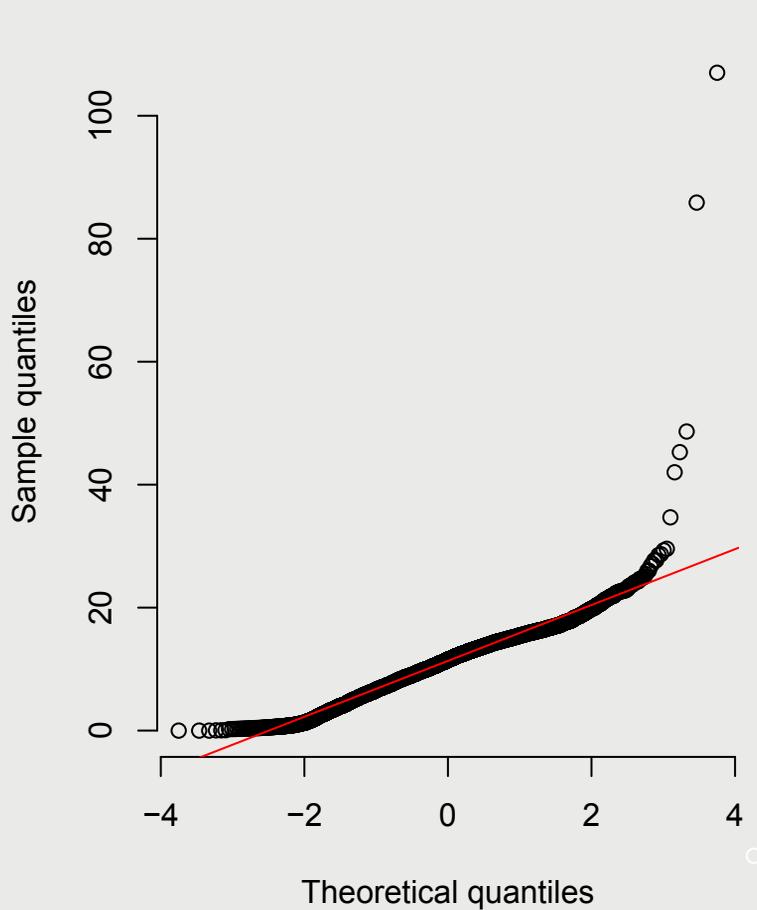
The highest soil Nb concentrations predominantly occur in four main areas. In Wales, high Nb concentrations occur in Dyfed and Powys, north of a very sharp geochemical gradient initially following the Devonian–Carboniferous boundary east from Pembroke, but then running north of east through the Old Red Sandstone outcrop to Hereford. The reason for this line is not yet clear. High Nb concentrations are present over the Devonian and Carboniferous sedimentary terrane of Devon and Cornwall, with much lower values over the major granites. In the Wealden District of Sussex and Kent, nonmarine Lower Cretaceous sands and clays clearly host an abundant suite of resistate minerals (see also Ce, Hf, La, Ti, Th, Ta, W) believed to be derived from a south-west provenance (Brenchley and Rowson, 2006). The other notable enrichment is a broad trend following the Jurassic outcrop from Somerset to Lincolnshire, possibly related to a resistate mineral component in the clays and ironstones. Less obvious high Nb values are present over the coastal marshes of Lincolnshire, part of the Fens, and in Essex.

Very low Nb values follow the gritstone uplands of the Pennines and the Permo-Triassic outcrop of the Midlands, parts of upland Wales, and large areas of East Anglia.

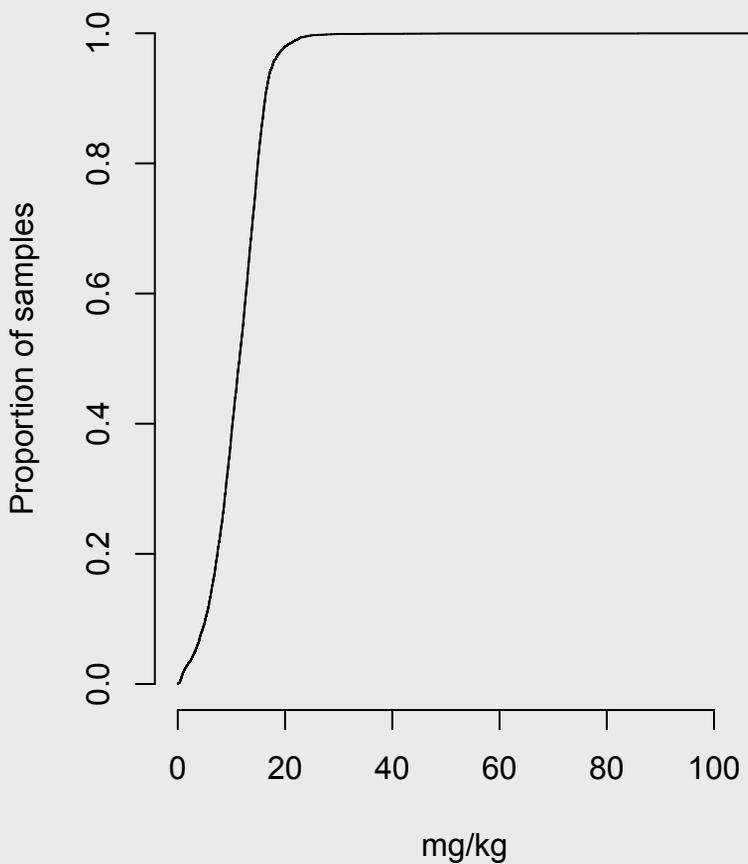
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Nb - Niobium mg/kg

mean= 11

median= 12

10th percentile= 5.2

25th percentile= 8.3

75th percentile= 14

90th percentile= 16

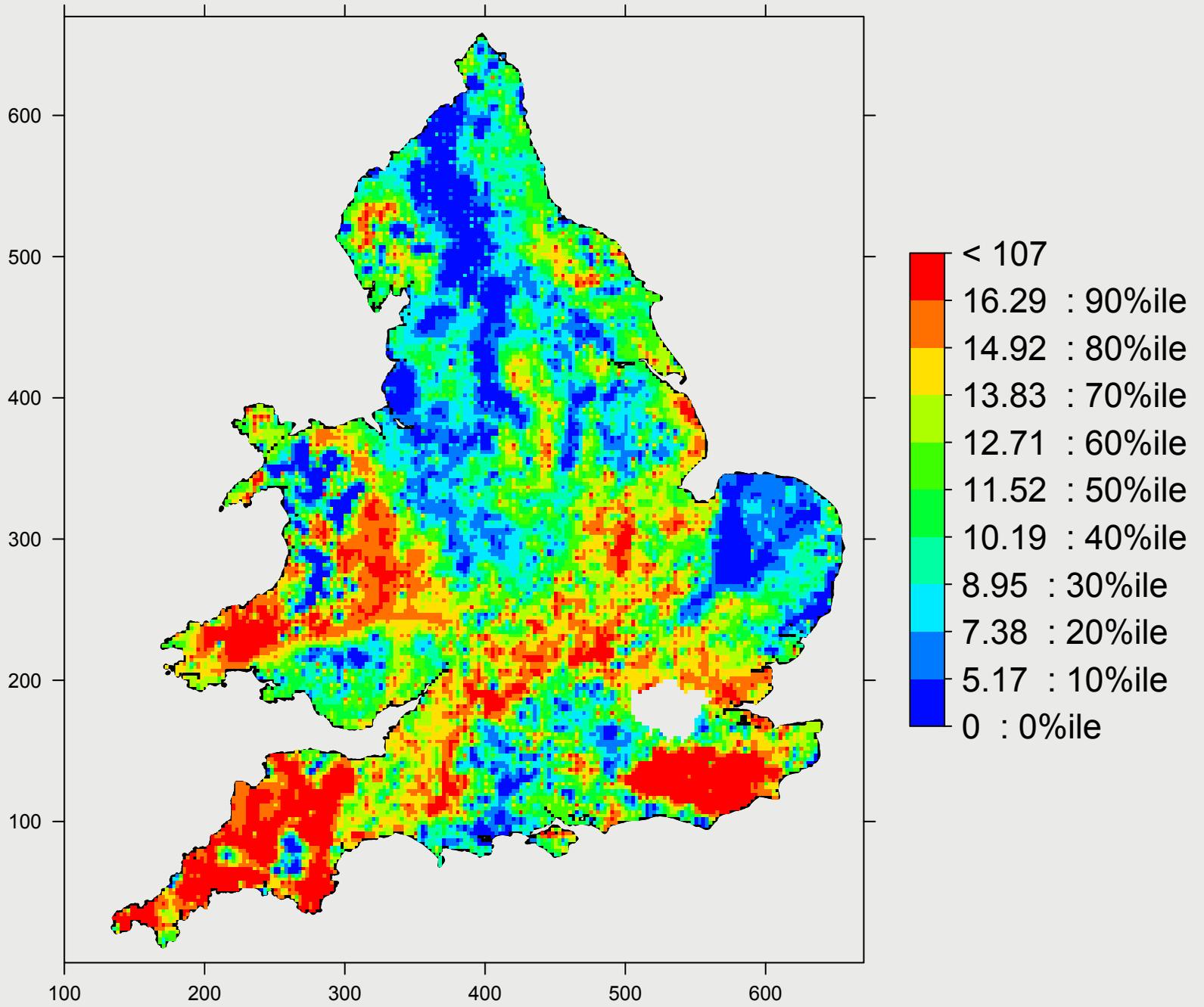
min= 0

max= 107

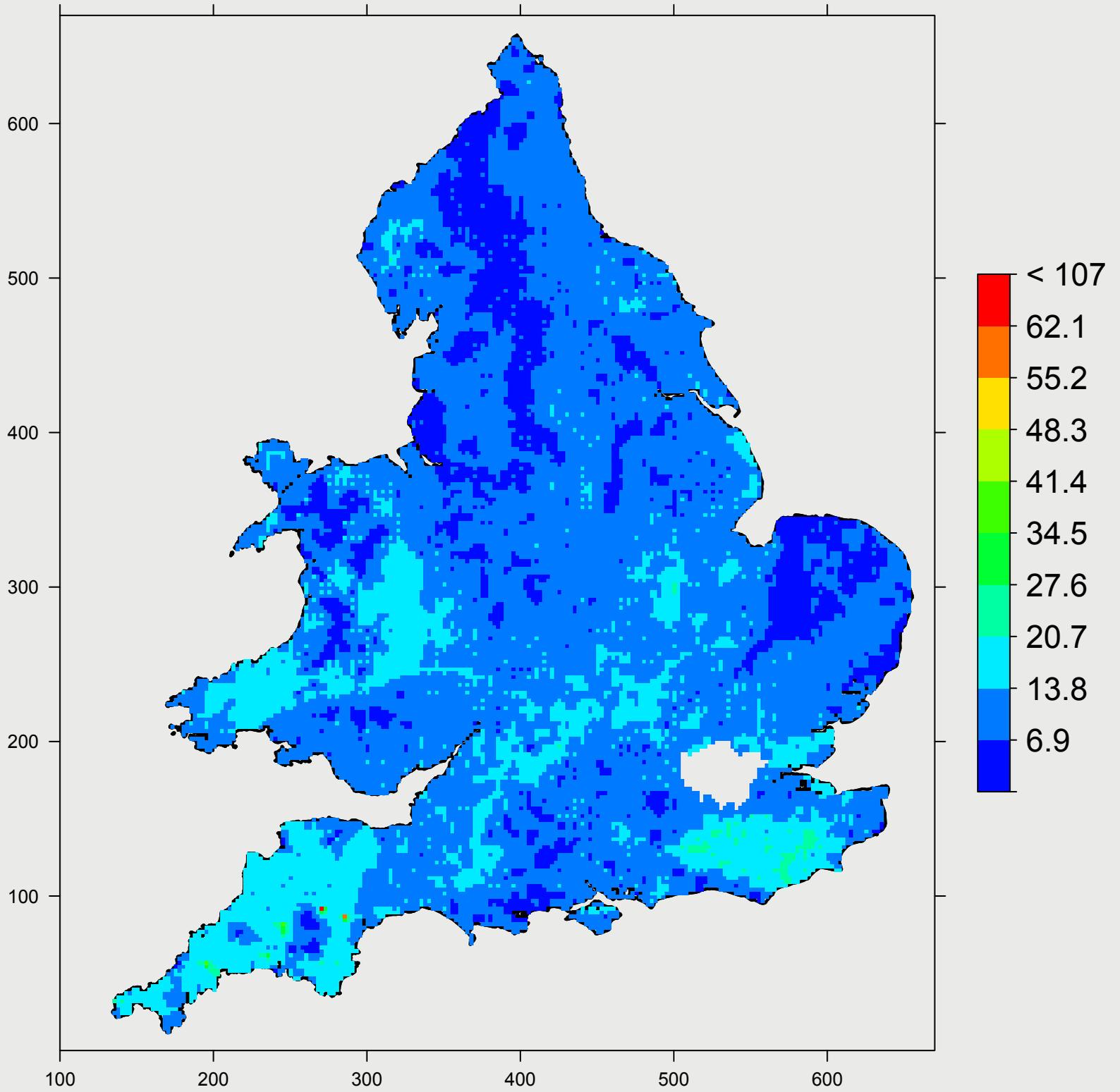
skewness= 2.1

n= 5670

Topsoil niobium (mg/kg ; percentile scale)



Topsoil niobium (mg/kg ; arithmetic scale)

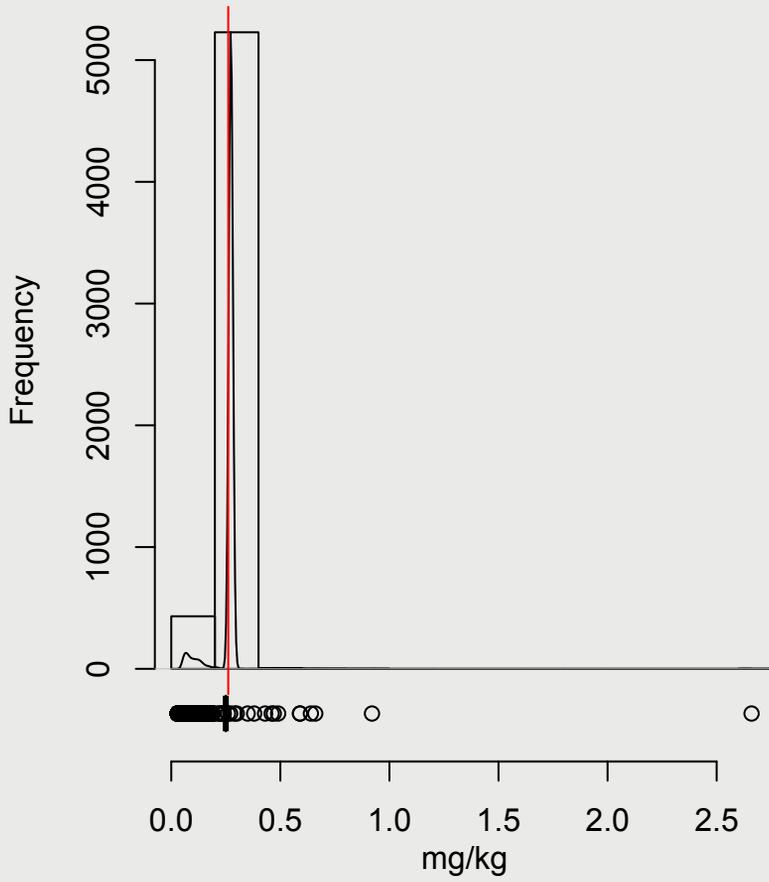


Palladium (Pd)

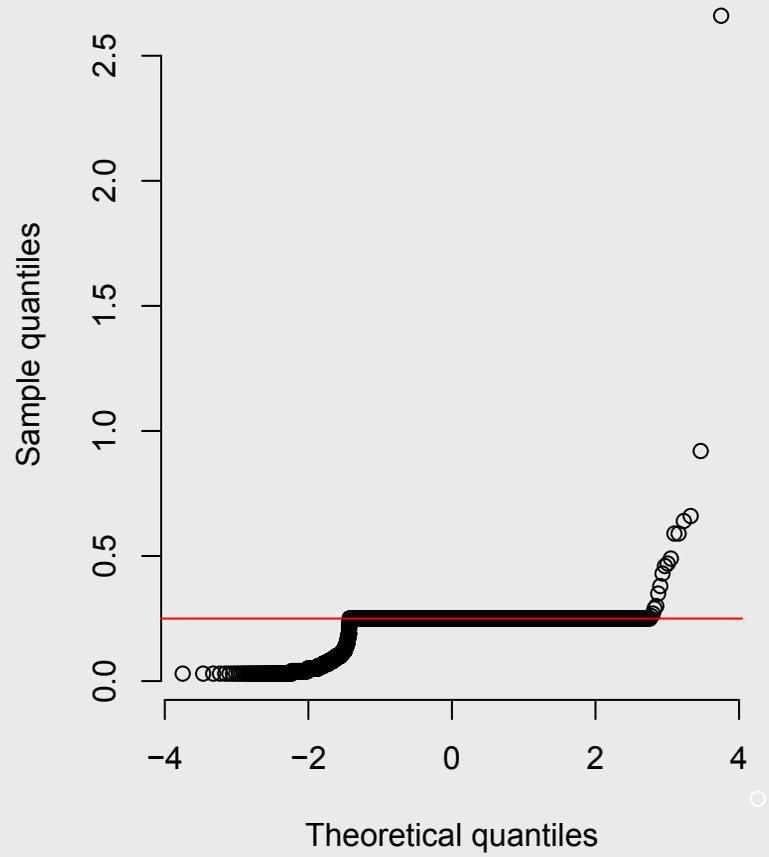
Palladium is one of the 'platinum group' of very rare metals which include Pt, Pd, Os, Ir, Rh and Ru. The average upper continental crustal abundance of Pd is less than 0.001 mg/kg (Reimann and De Caritat, 1998), although there is relative enrichment to about 0.002 mg/kg in ultrabasic rocks (dunite, serpentine) and it can also be enriched in Ni ore minerals such as braggite (Pt,Pd,Ni)S. A more recent environmental source of Pd is anthropogenic — it is used widely as a catalyst, most notably along with platinum in vehicle exhaust converters.

Around 90% of the reported values for total Pd were below the 0.25 mg/kg limit of detection for XRF analysis. For this reason, the percentile map is not presented. The arithmetic map highlights a number of areas where Pd concentrations are believed to be reliably greater than 0.25 mg/kg. The most significant of these are in south Wales, where historic nickel smelting took place. The largest concentration (2.66 mg/kg) occurs in Somerset, at the eastern end of the Mendip Hills, in an area of limestone quarrying. This is associated with high concentrations of Ag, As and Sb; and moderately high Pb and Zn concentrations, suggesting that both mineralisation and possibly anthropogenic inputs are responsible. Other rather isolated anomalies in south Devon, Shropshire, Derbyshire and the Pennines are also associated with high concentrations of Ag, Pb, Sb and Zn at mining and quarry sites, but others — near Leeds, for example — are not. There is no evidence of significant Pd enrichment in west Cornwall, associated with the serpentine bedrock of The Lizard peninsular.

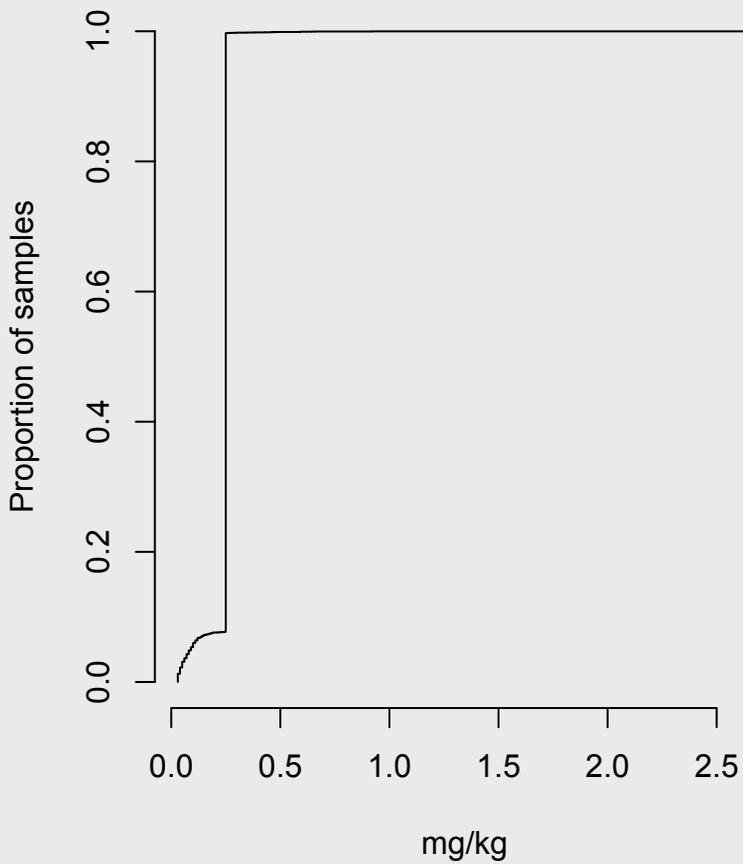
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Pd - Palladium mg/kg

mean= 0.24

median= 0.25

10th percentile= 0.25

25th percentile= 0.25

75th percentile= 0.25

90th percentile= 0.25

min= 0.03

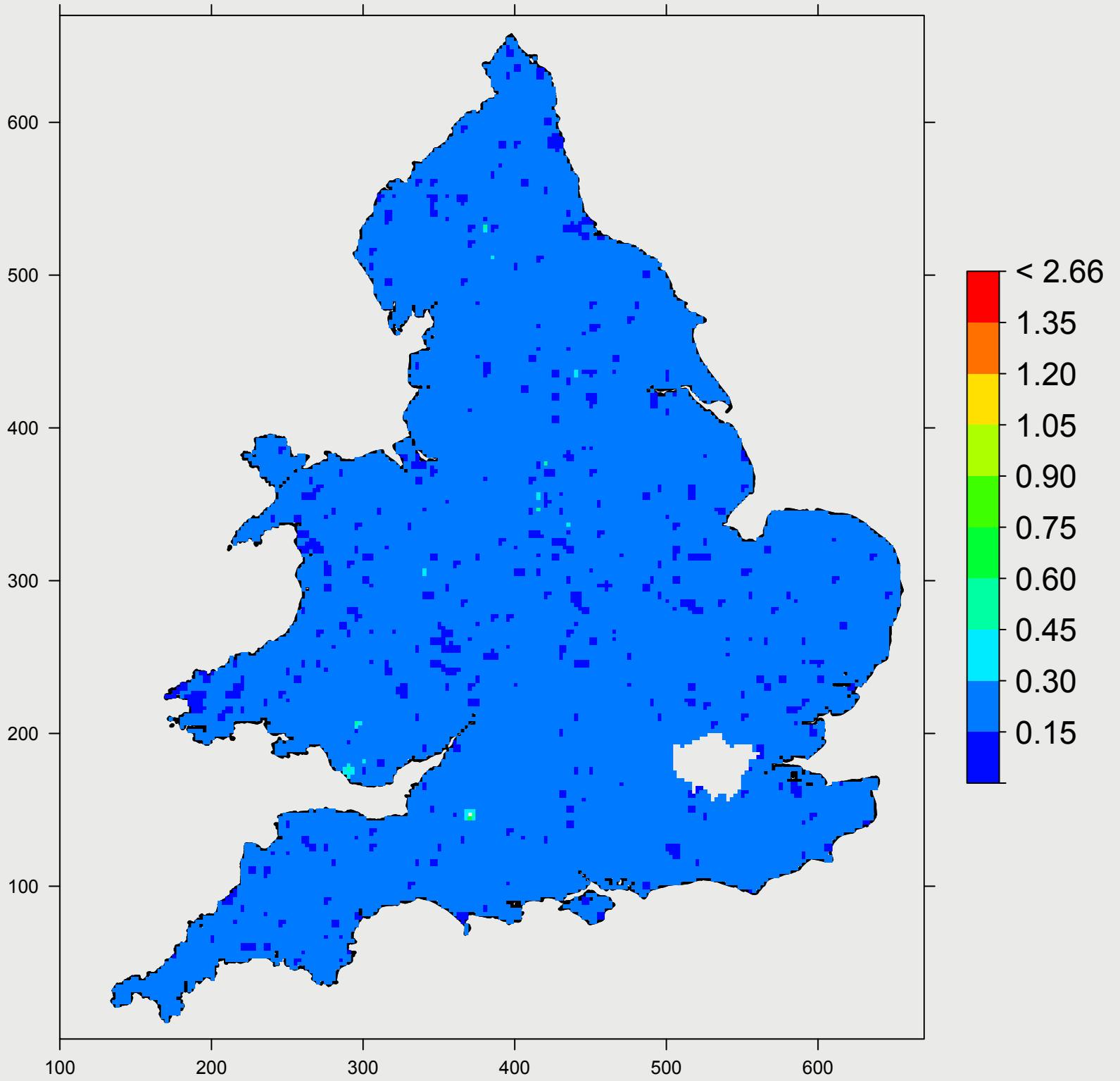
max= 2.7

skewness= 11

n= 5669

A map of soil palladium concentrations on a percentile scale is not shown because the vast majority of the values were below the limit of detection. Presentation of such a map could lead to erroneous interpretations.

Topsoil palladium (mg/kg ; arithmetic scale)



Phosphorus (P)

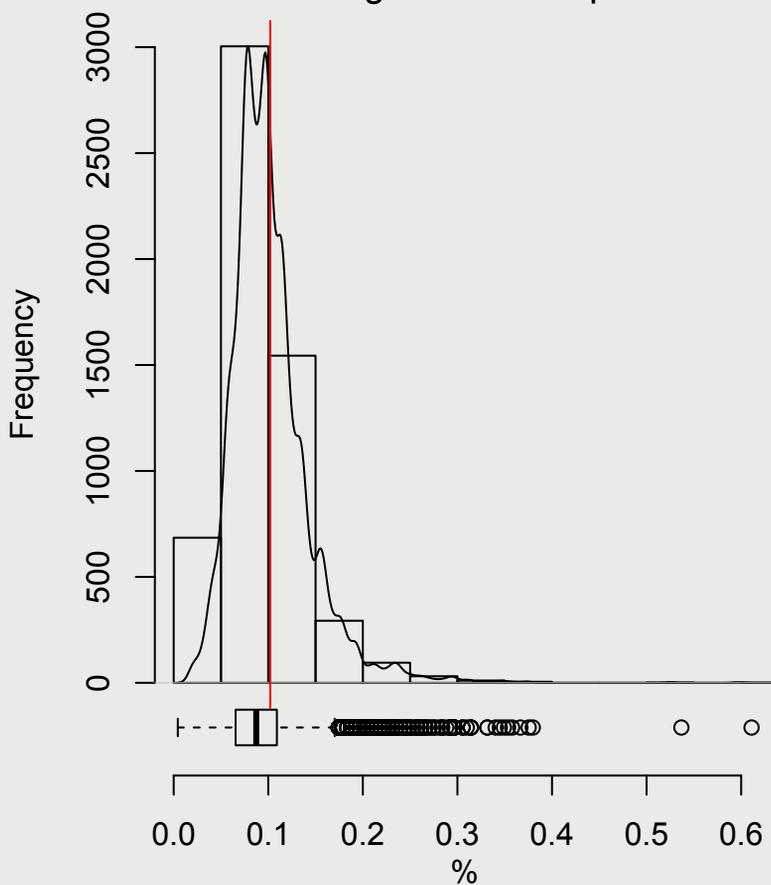
Phosphorus is a major non-metal, essential to all living organisms, though it is toxic in elemental form and in some compounds. It is present at about 700 mg/kg in the Earth's upper continental crust, rather higher in basic igneous rocks (1200 mg/kg) than in granites (750 mg/kg) and much lower in sandstones (30 mg/kg) than in shales (800 mg/kg; Reimann and De Caritat, 1998). It is widely used in industry, especially in detergents and fertilisers.

Total P concentration in topsoil has a similar spatial distribution to total Fe in soils, but most of the lowland and upland agricultural areas of England and Wales will have been subject to addition of P-bearing fertilisers, modifying the natural distribution of P. There is clearly an association of P with Fe in areas of high Fe concentrations over the Jurassic outcrop in central England, especially with the ironstones, e.g. near Banbury in Oxfordshire and in Northamptonshire. Elsewhere the distribution pattern is poorly defined, though the Chalk outcrop is shown by rather discontinuous elevated P concentrations and high levels are also present over the Lancashire coastal lowlands. Low levels mark the Pennines, the Old Red Sandstone of the Welsh Borders, and the sandy heathland soils of Surrey, the Hampshire Basin, the Wealden district of Sussex and Kent, and parts of East Anglia.

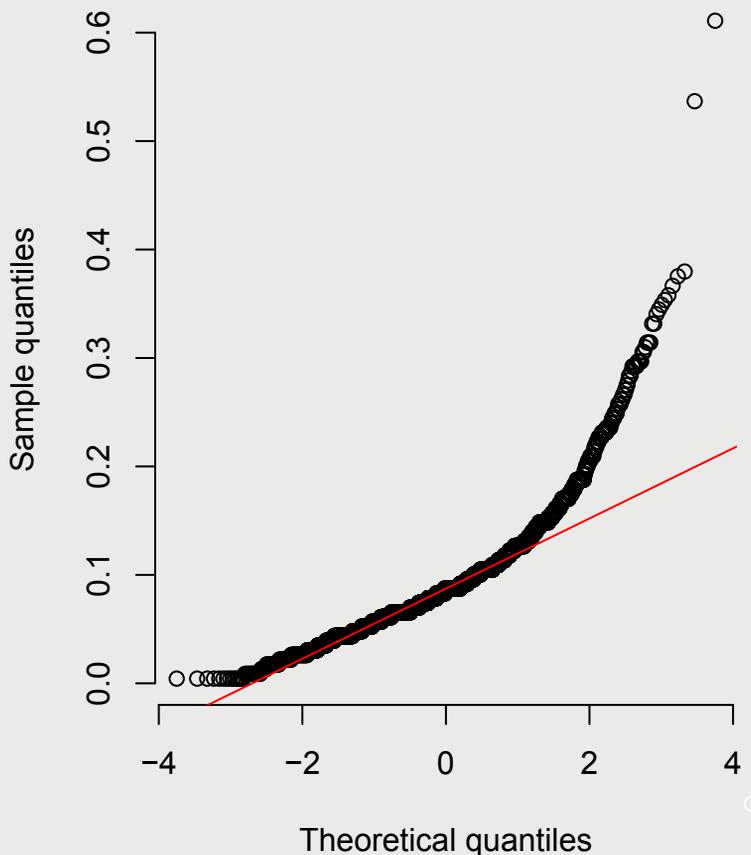
However, the total P concentration in soil is not a good guide of the likelihood of a response in crops to added P in fertilisers. A system of 'index values' based on the concentrations of 'available' P extracted by sodium bicarbonate solution is used agriculturally to determine where P should be applied; this information is presented in McGrath and Loveland (1992). Comparing the results obtained by XRF-S analysis with those of aqua regia digestion followed by ICP-AES analysis (McGrath and Loveland, 1992) shows that the former had a slightly larger median value than the latter (medians 0.08 and 0.07% respectively).



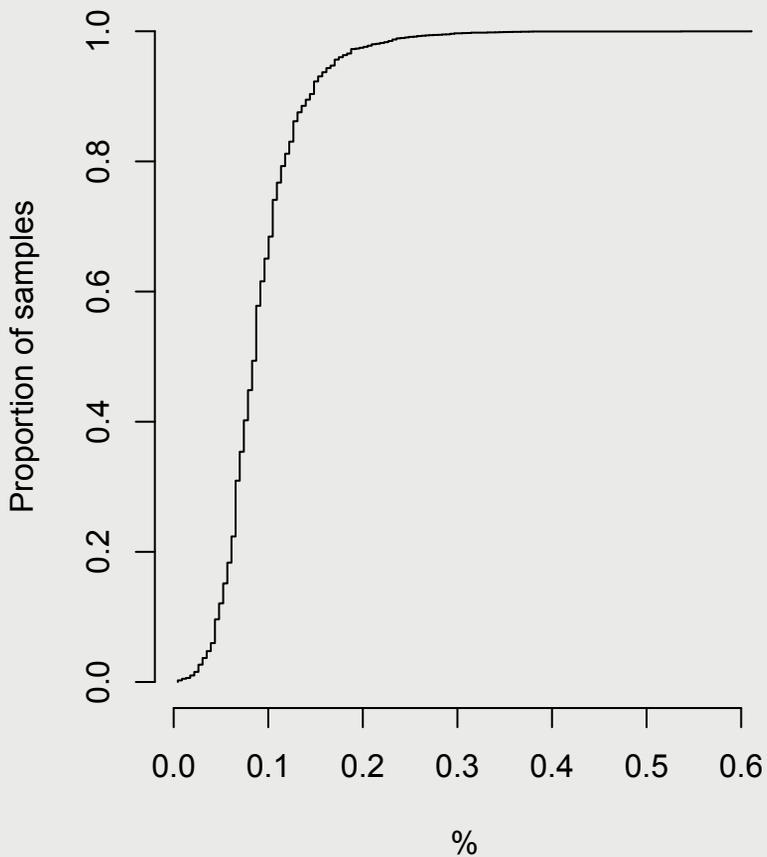
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



P- Phosphorus %

mean= 0.091

median= 0.087

10th percentile= 0.048

25th percentile= 0.065

75th percentile= 0.11

90th percentile= 0.14

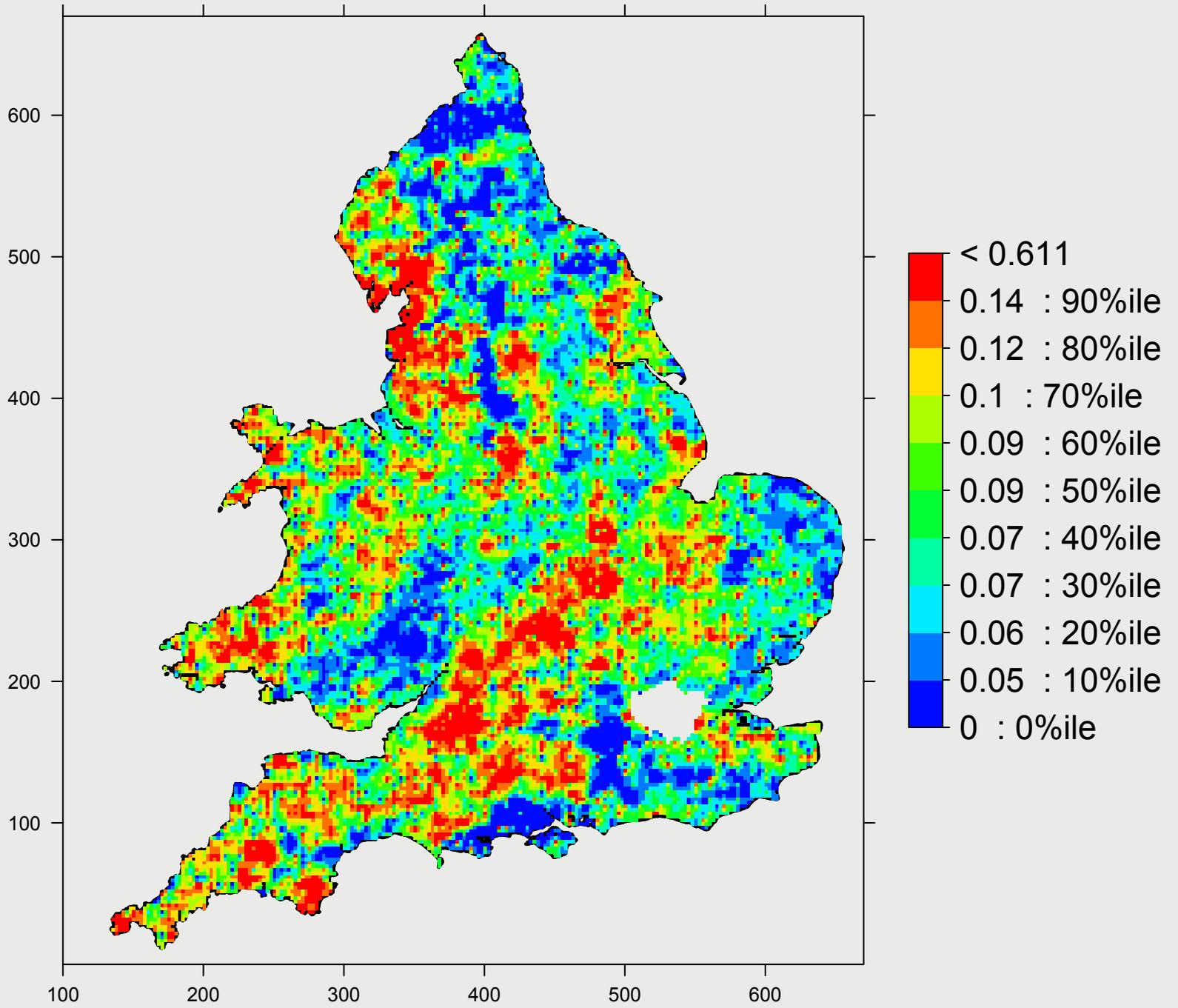
min= 0.0044

max= 0.61

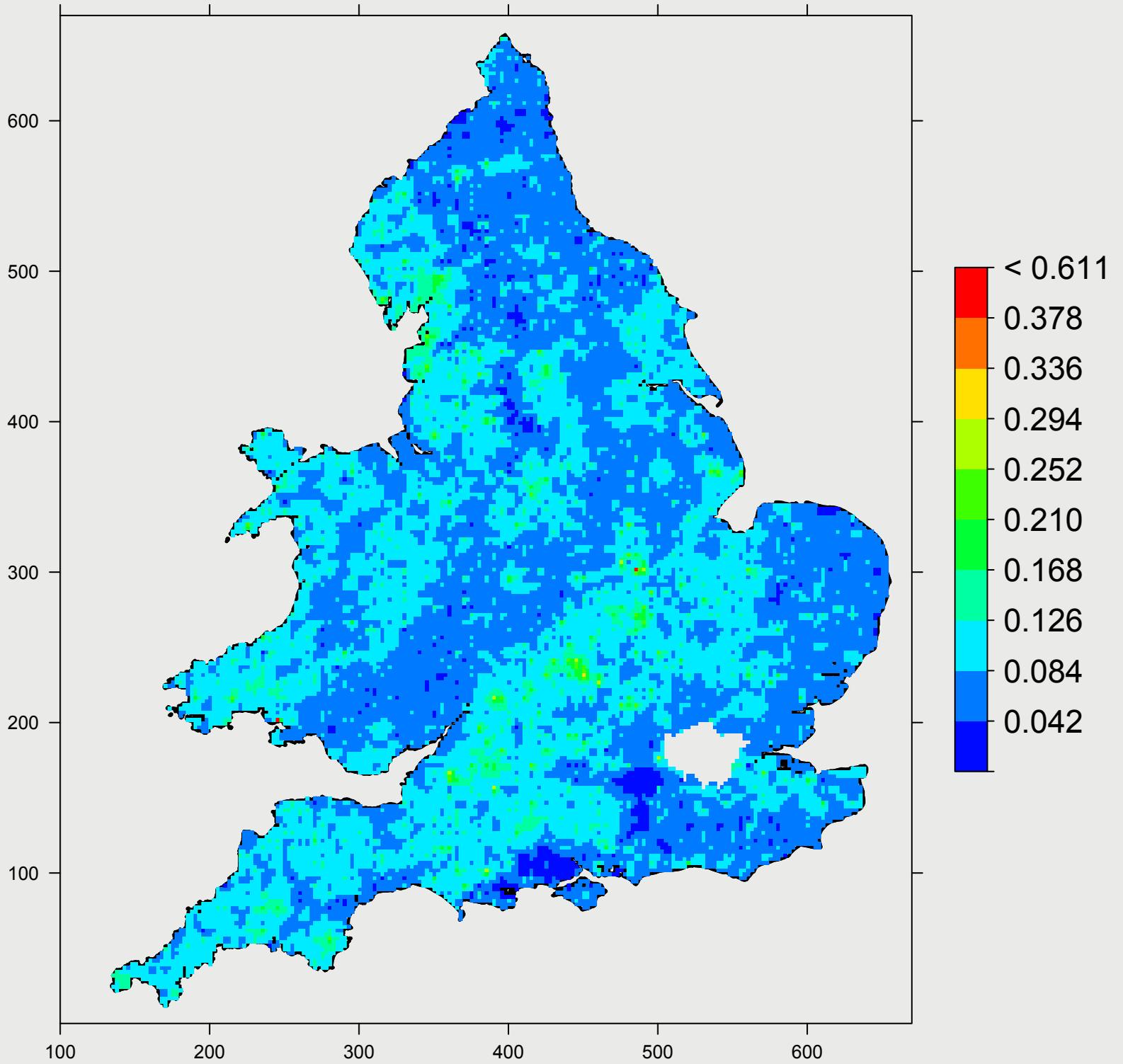
skewness= 2

n= 5670

Topsoil phosphorus (% ; percentile scale)



Topsoil phosphorus (% ; arithmetic scale)



Potassium (K)

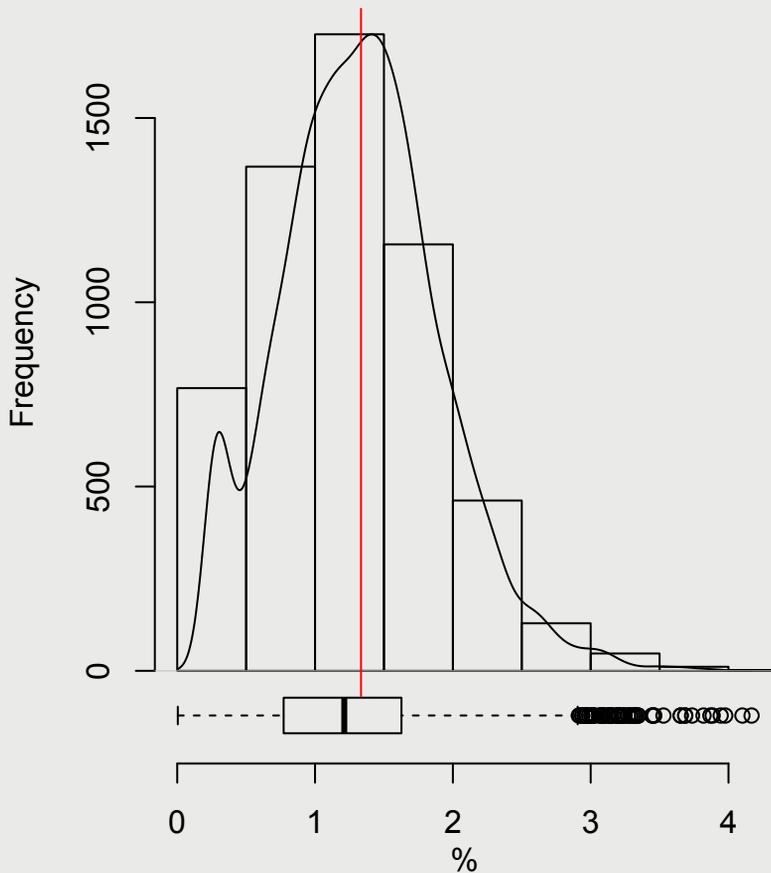
Potassium is a major metallic element, essential for all organisms, and is present at about 2.8% in the Earth's upper continental crust, being more abundant in granites (3.3%) than in basic igneous rocks (0.8%: Reimann and De Caritat, 1998), as it is present in the abundant rock-forming mineral orthoclase feldspar (KAlSi_3O_8) and in micas. The measurement of K by XRF that was used here gives higher concentrations (median=1.2%) than those reported for aqua regia extraction (median=0.46%) used in McGrath and Loveland (1992).

The areas with high concentrations (>1.6%) are mainly associated with soils formed on underlying rocks consisting of undifferentiated mudstone, siltstone and sandstone, the largest areas of which include the south-west in the form of Devonian strata, and rocks of Triassic age (Mercia Mudstone Group) extending from Avon and Somerset, and intermittently in the Midlands to north Nottinghamshire. Similar mudstone, siltstone and sandstone lithologies of Lower Palaeozoic age with high K concentrations occur in mid Wales and rocks of Carboniferous age in the Northumberland trough south of Berwick-upon-Tweed. Other soils formed throughout the country on areas with coastal marine alluvium show high K values, notably in Lincolnshire and the Fens, and in Essex.

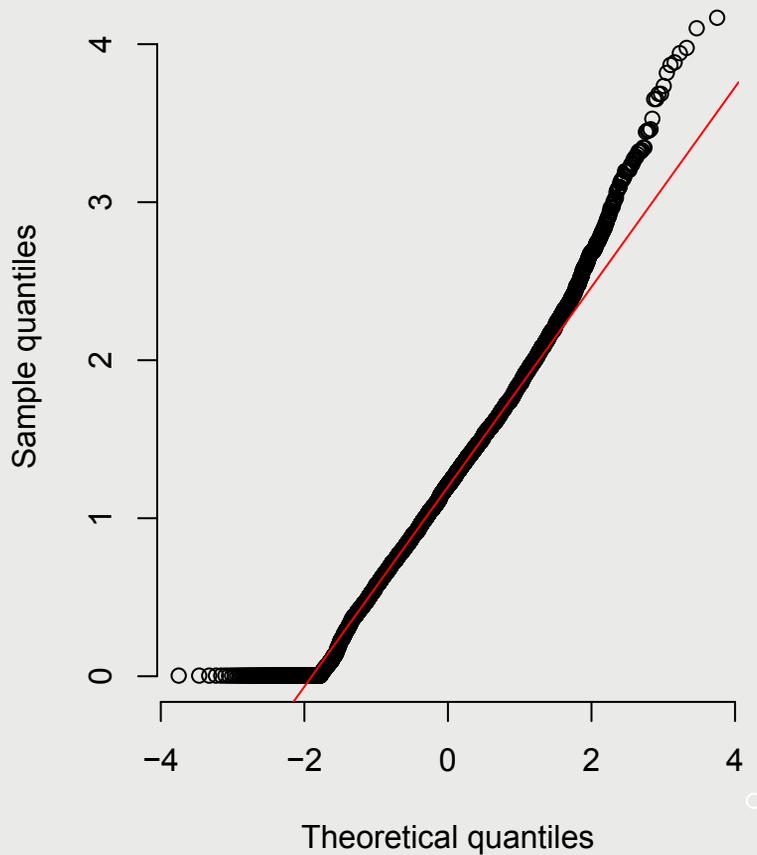
Regions with low K concentrations in soil include those soils with a low proportion of clay minerals (Oliver et al., 2002) that occur south and west of London, parts of East Anglia and many of the mountains and moors in Wales and northern England.

However, the total K concentration in soil is not an effective measure of its availability to crops. A system of 'index values' based on the concentrations of 'available' K extracted by ammonium nitrate solution is used agriculturally to determine when K should be applied, and this information is supplied in McGrath and Loveland (1992), who noted that the areas in East Anglia with low concentrations of total K appear to have slightly higher extractable K, presumably because of the use of fertilisers.

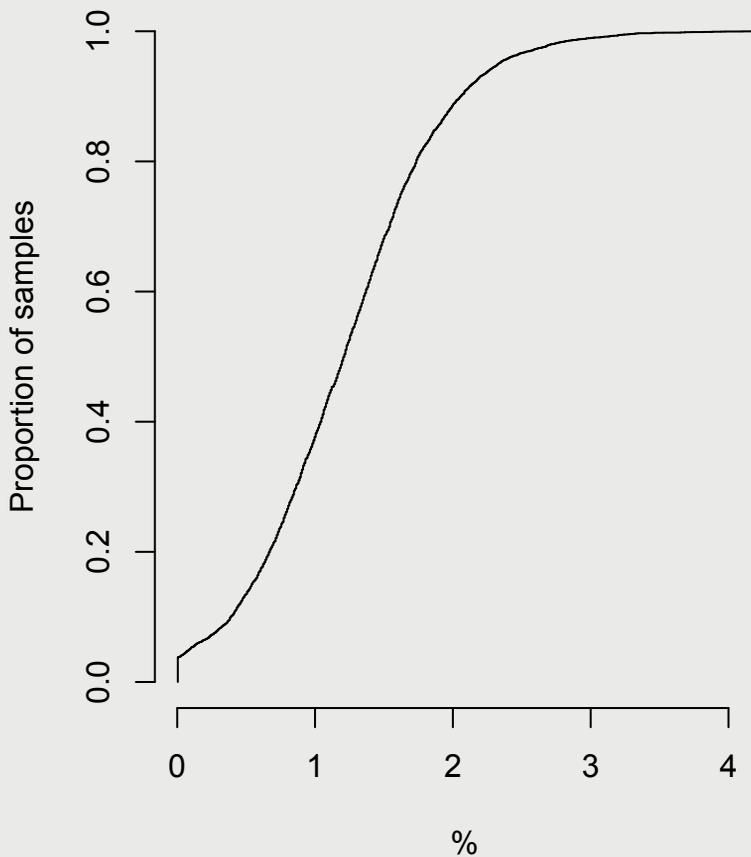
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



K - Potassium %

mean= 1.2

median= 1.2

10th percentile= 0.39

25th percentile= 0.77

75th percentile= 1.6

90th percentile= 2.1

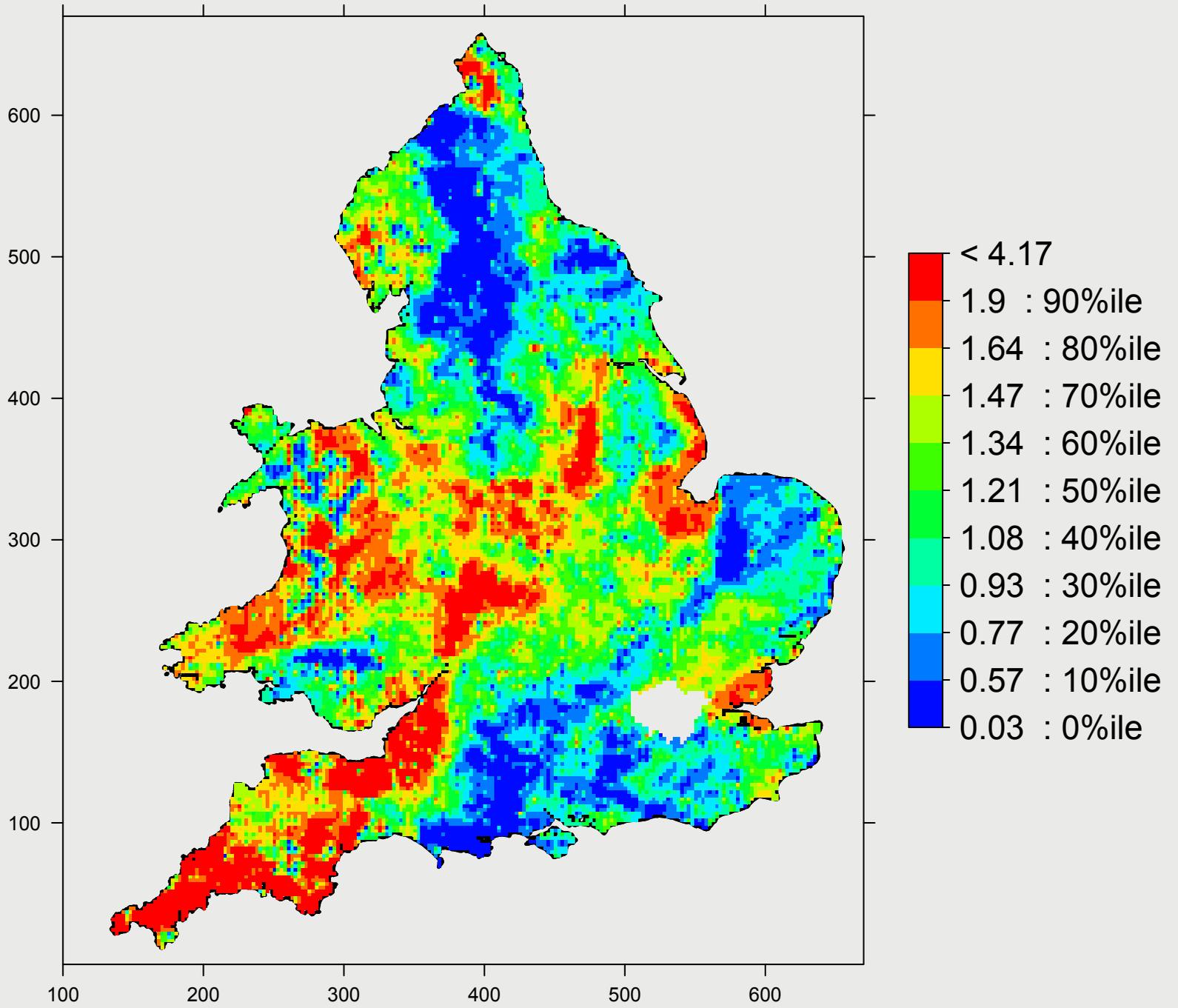
min= 0.0042

max= 4.2

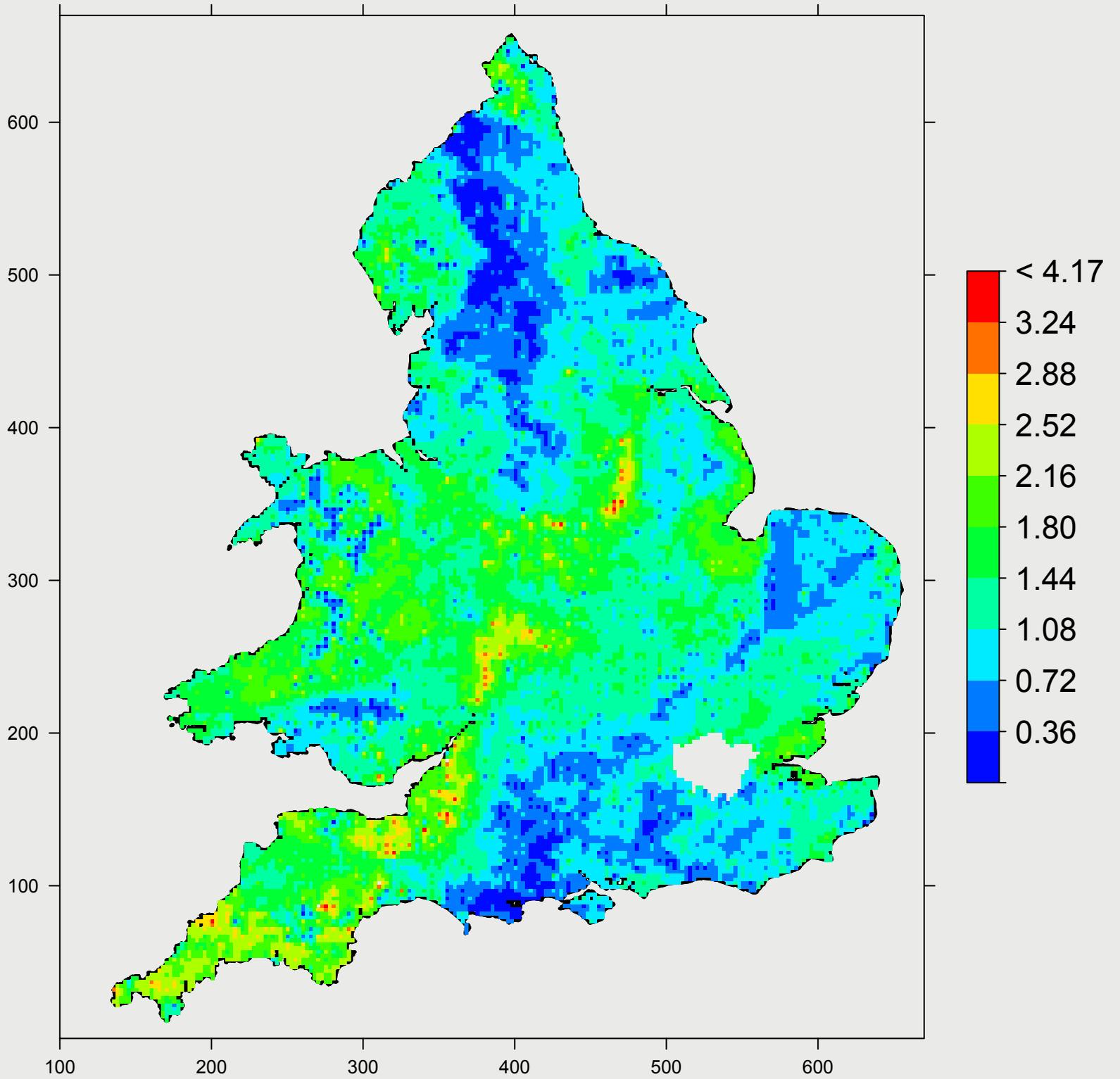
skewness= 0.4

n= 5670

Topsoil potassium (% ; percentile scale)



Topsoil potassium (% ; arithmetic scale)



Rubidium (Rb)

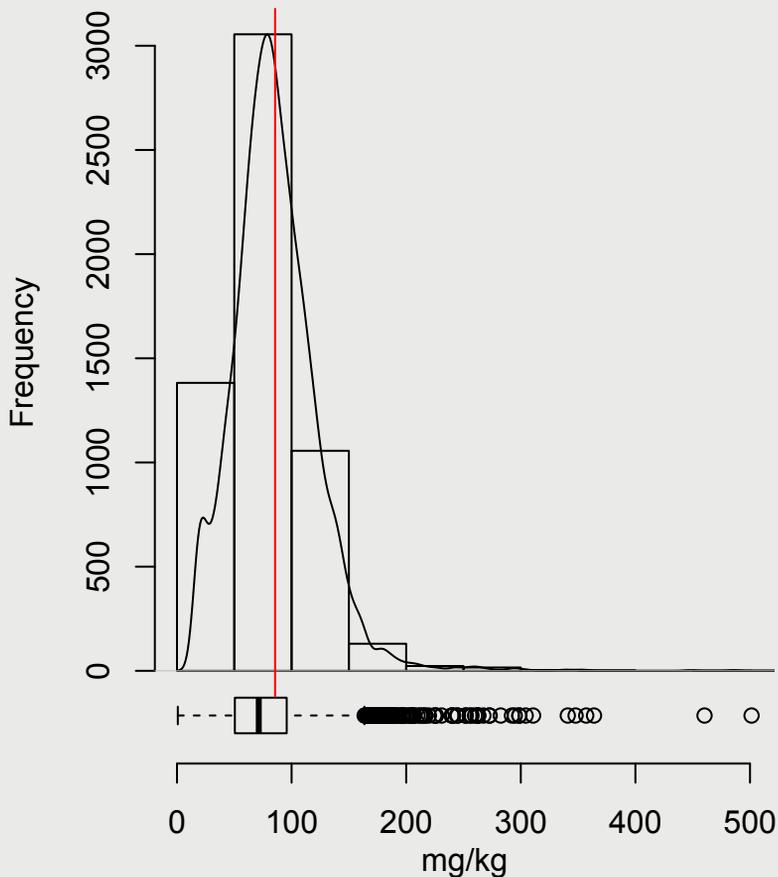
Rubidium is a metallic element, present at about 110 mg/kg in the Earth's upper continental crust. It is much more abundant in granite (120 mg/kg) than in basic igneous rocks (30 mg/kg), and more in shales (140 mg/kg) than in sandstones (40 mg/kg; Reimann and De Caritat, 1998), and is considered non-essential and non-toxic. It is chemically very similar to potassium, which it tends to substitute for in rock-forming K-silicate minerals (K-feldspar, muscovite, biotite etc.). Due to this fact, the spatial distribution of soil Rb across England and Wales is similar to that of K. Median and mean concentrations reported for XRF-S analysis of the NSI soils are 71 and 75 mg/kg, respectively, with the upper 10% of soils having concentrations >121 mg/kg.

The maps show that these highest levels are predominantly associated with Devonian and Carboniferous sedimentary strata of south-west England, Ordovician and Silurian mudstones of mid and south-west Wales as well as the Ordovician Silurian mudstone of the Lake District.

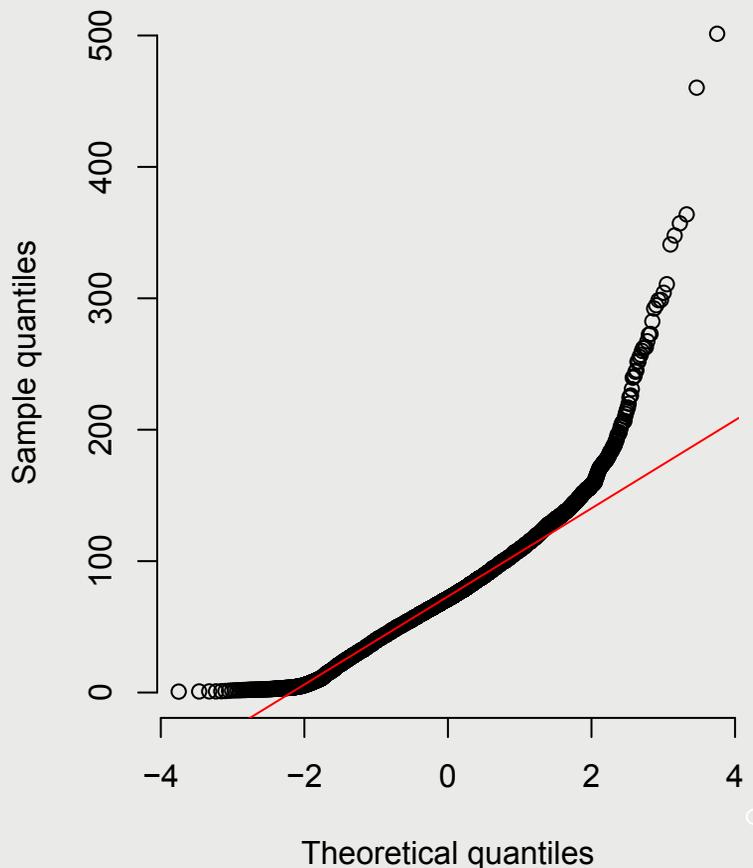
The lowest concentrations (<50 mg/kg) were reported in soils across the areas of Cretaceous bedrock in north-east, central and southern England, the Carboniferous of the Pennines, the Coal Measures of south Wales and Snowdonia.

Reimann and De Caritat (1998) state a K/Rb ratio for most common continental rocks between 160 and 300. The K/Rb ratio for NSI data is 84, which is likely to be the result of weathering.

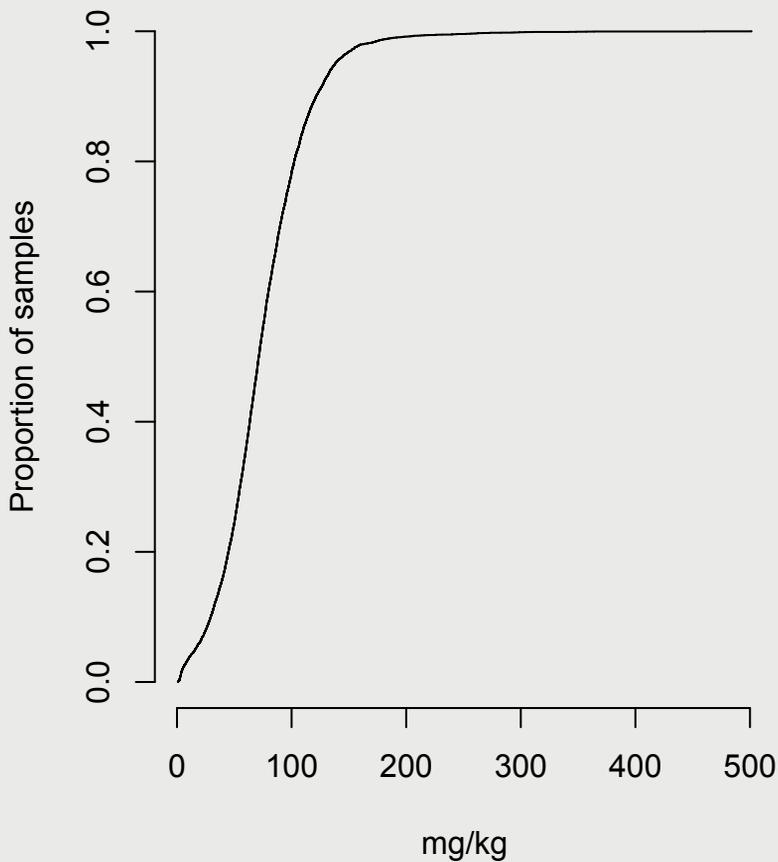
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Rb - Rubidium mg/kg

mean= 75

median= 71

10th percentile= 29

25th percentile= 51

75th percentile= 96

90th percentile= 121

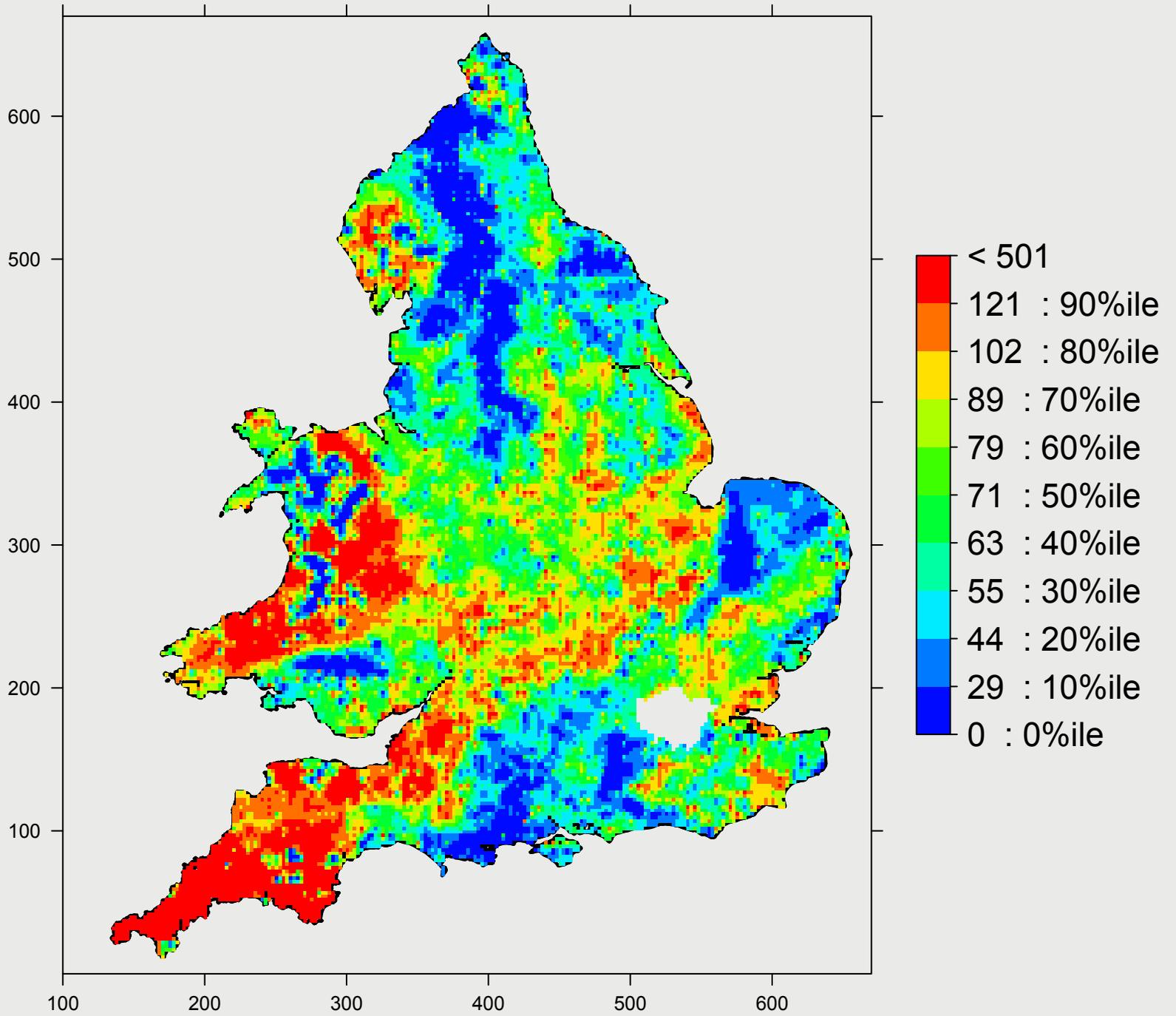
min= 0.72

max= 501

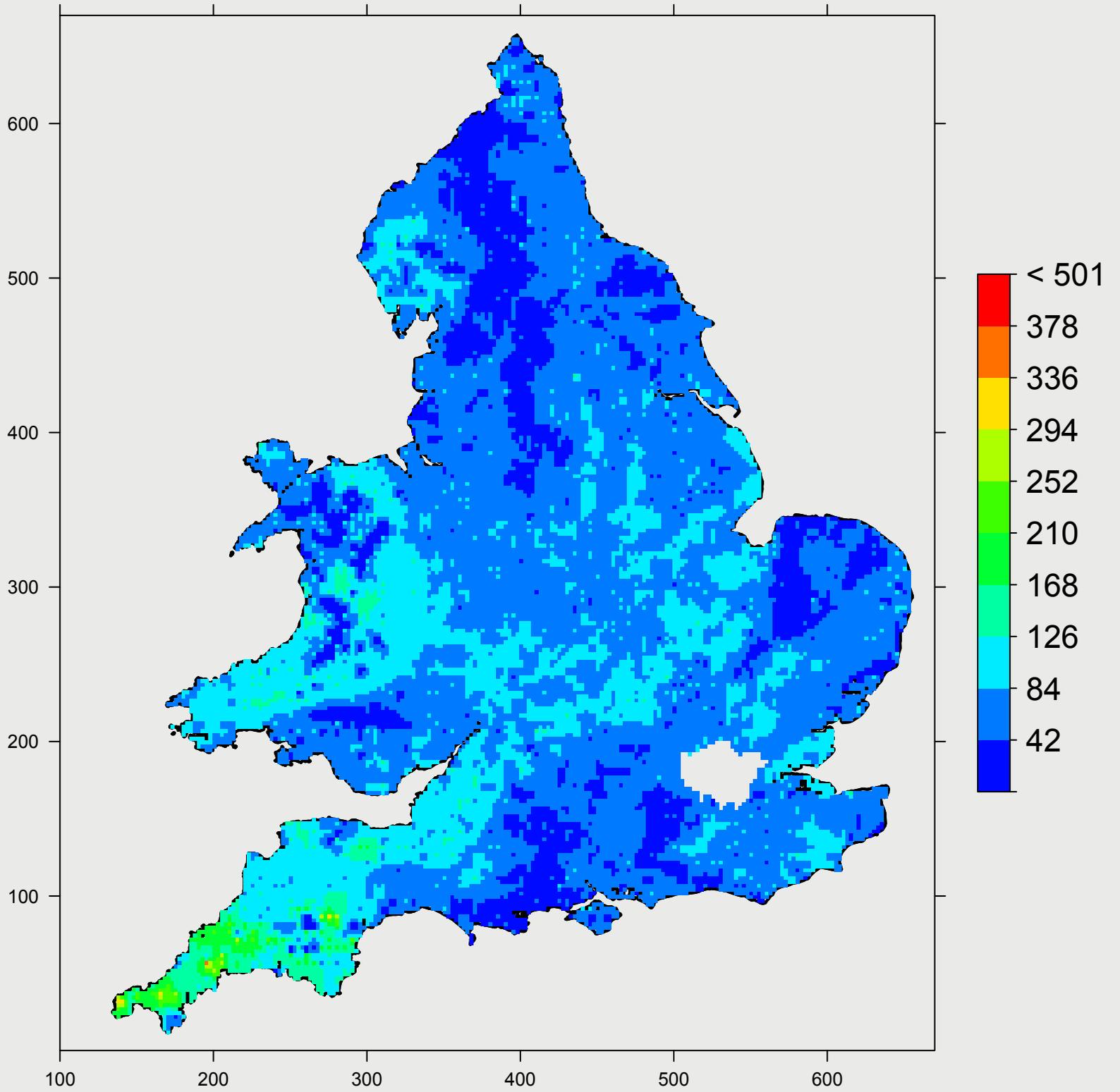
skewness= 1.4

n= 5670

Topsoil rubidium (mg/kg ; percentile scale)



Topsoil rubidium (mg/kg ; arithmetic scale)



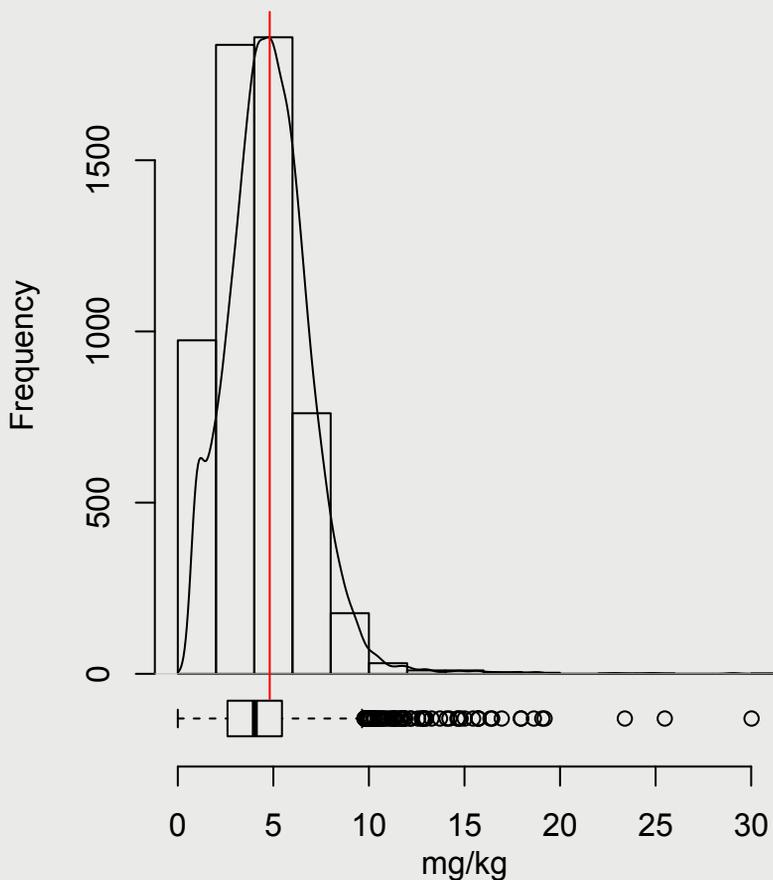
Samarium (Sm)

Samarium is a rare earth element (REE), and like the other REEs (La and Ce), it is mainly found in the minerals monazite and bastnäesite. However it has a lower average crustal abundance of around 4.6 mg/kg (Reimann and De Caritat, 1998) with higher concentrations in granites (8 mg/kg) than in basic igneous rocks (3.5 mg/kg). It is considered non-essential with generally low toxicity, and has industrial applications in magnets, condensers and nuclear reactor control rods. In NSI soils, measured mean and median concentrations of Sm were 4.1 and 4.0 mg/kg, respectively and the upper 10 % of the data range from 6.4 to a maximum of 30 mg/kg.

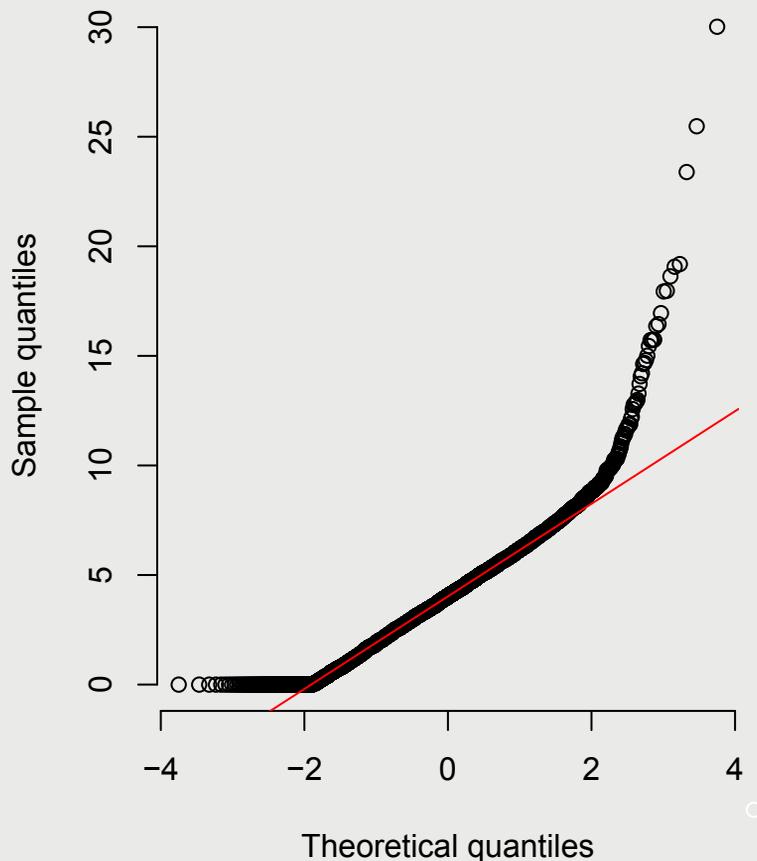
The maps show three main areas of elevated soil concentrations of Sm (>5 mg/kg) in a) south-east England, in the Wealden District of Sussex and Kent which is underlain by nonmarine Lower Cretaceous sediments, b) an area stretching across central England from Peterborough to the Bristol Channel, underlain predominantly by Jurassic limestone, clays and sandstone and c) north-east England, where high values are shown across the Lincolnshire coast and the over the Wolds as far north as the River Derwent. Whilst the latter area is underlain by mainly Cretaceous Chalk, it is more likely that residual or aeolian deposits are responsible for these distribution patterns.

Low Sm concentrations follow the gritstone uplands of the Pennines, much of the Permo-Triassic outcrop of the Midlands, and the sandy soils of the Surrey heaths and much of East Anglia.

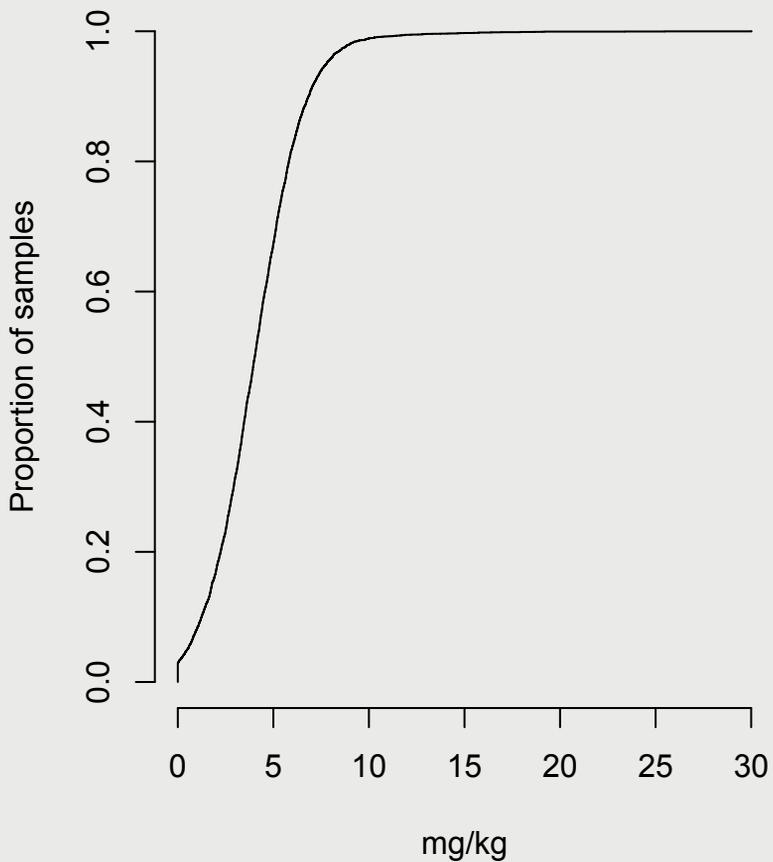
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Sm - Samarium mg/kg

mean= 4.1

median= 4

10th percentile= 1.2

25th percentile= 2.6

75th percentile= 5.4

90th percentile= 6.8

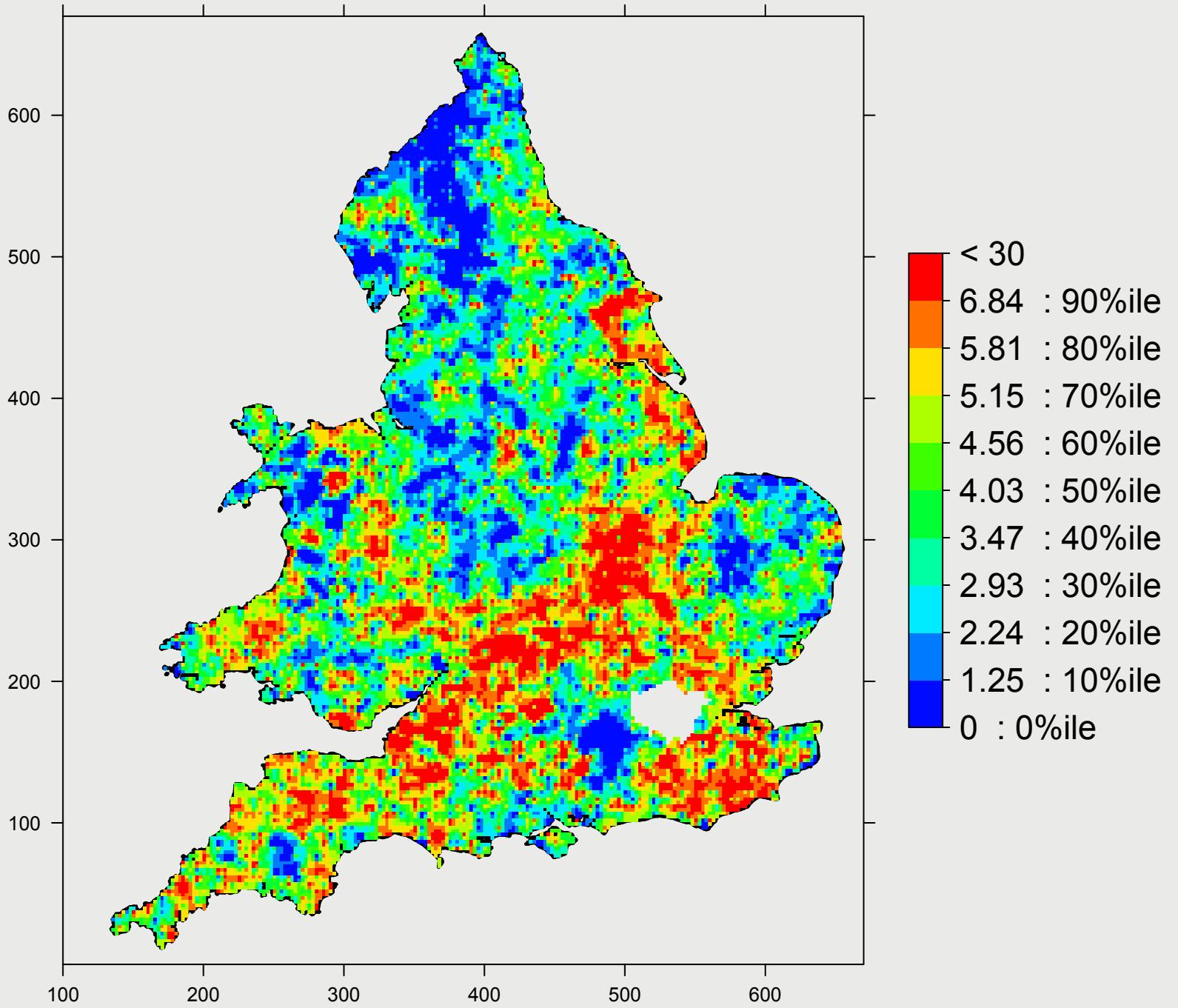
min= 0

max= 30

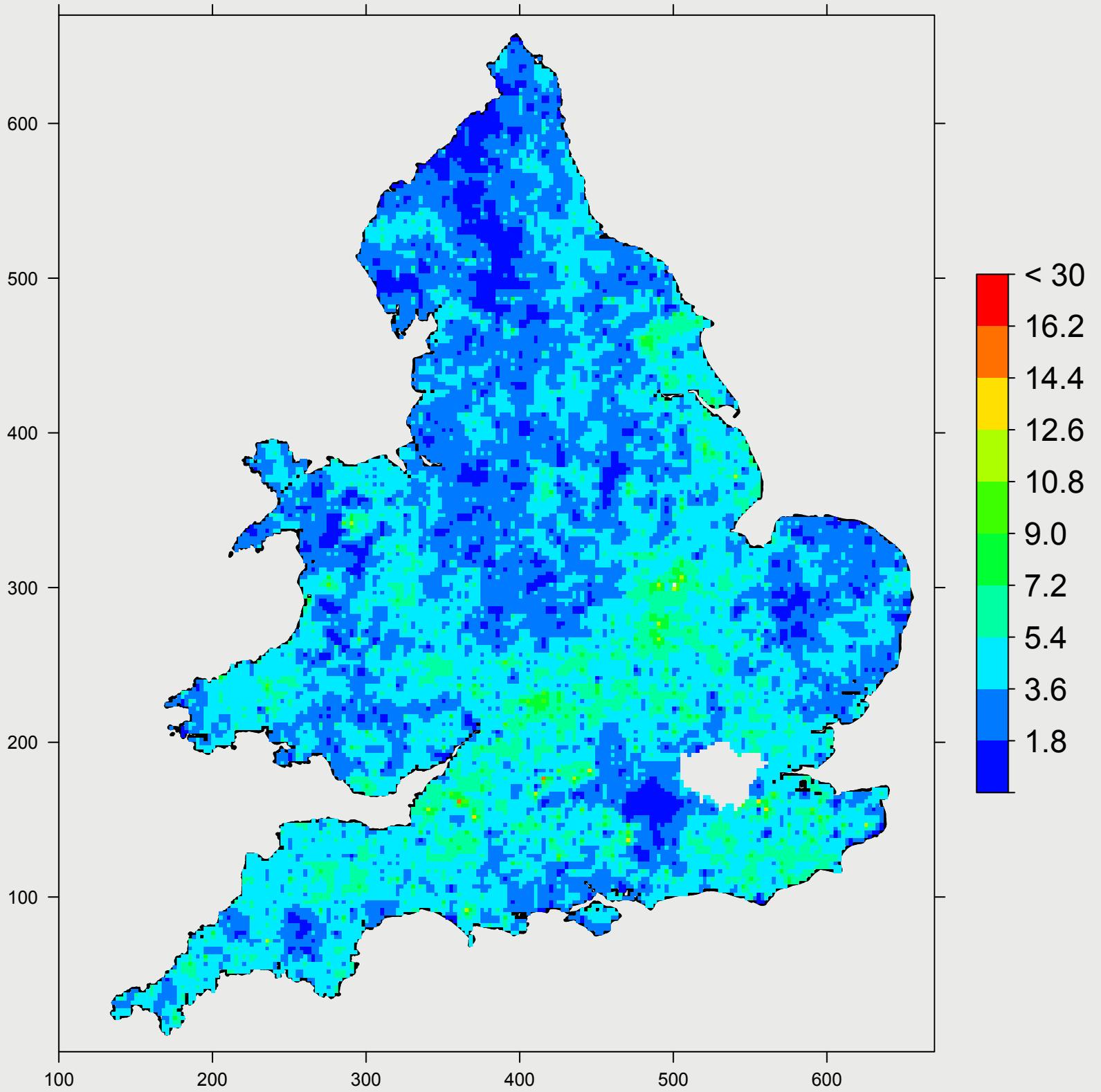
skewness= 1.2

n= 5670

Topsoil samarium (mg/kg ; percentile scale)



Topsoil samarium (mg/kg ; arithmetic scale)



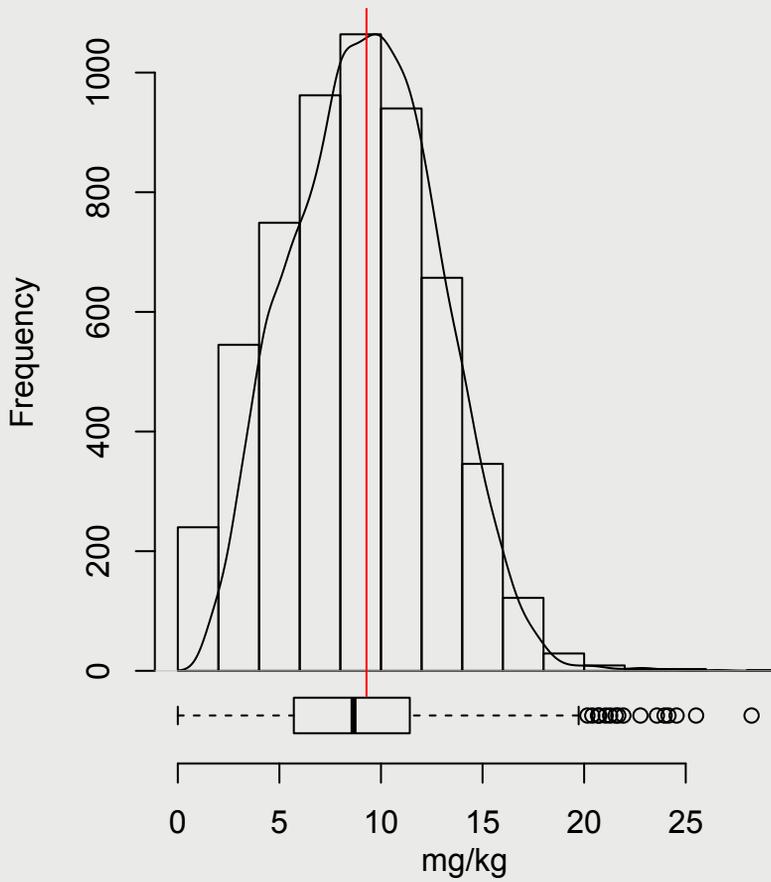
Scandium (Sc)

Scandium is a transition metal and is considered non-essential, although little is known of its potential toxicity and importance in the environment. The estimated average upper continental crustal abundance is between 7 and 11 mg/kg. Thorveitite (a silicate of Sc) is the main Sc mineral, but this is very rare and Sc is usually hosted by common rock-forming minerals such as pyroxenes, amphiboles, biotite garnet, zircon and monazite (Reimann and De Caritat, 1998). It is more abundant in basic igneous rocks (35 mg/kg) than in granites (5 mg/kg) or sandstones (3 mg/kg), and at intermediate levels in shales (15 mg/kg).

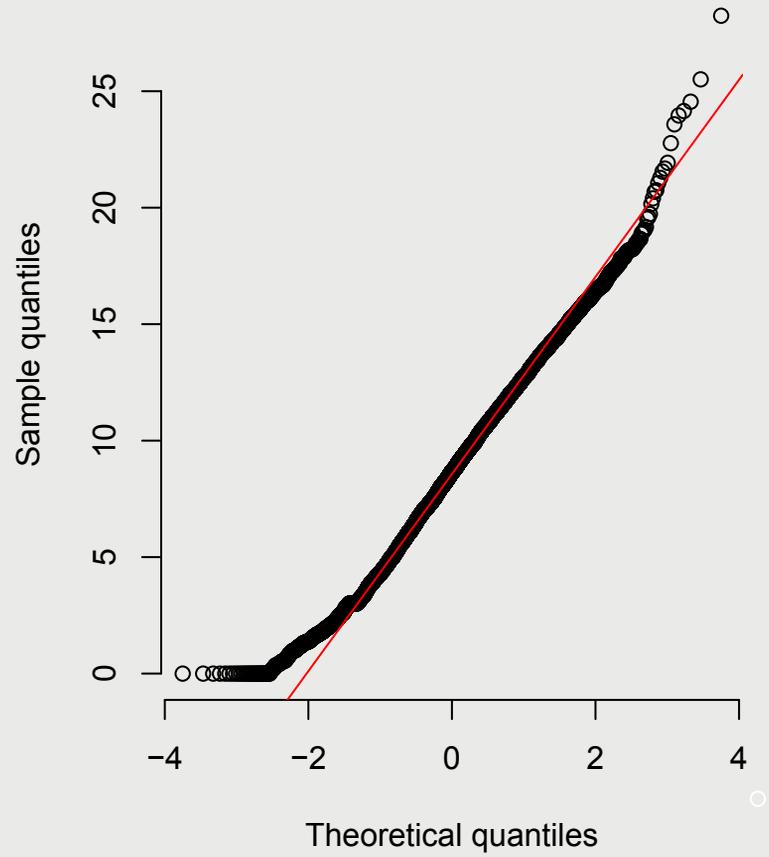
Scandium measured in NSI soils is near-normally distributed with both mean and median concentrations of 8.6 mg/kg. The upper 10% of the data range from 14 to 28 mg/kg. The percentile map shows that elevated concentrations (>14 mg/kg) occur in soils collected from Jurassic strata spanning most of central England, Devonian sediments of the south-west, Ordovician and Silurian mudstones of Wales and the Lake District, more recent clay-rich sediments of the Thames estuary as well as along the Lincolnshire coast between Grimsby and Skegness.

Most of the low concentrations (<5 mg/kg) correspond to soils collected from areas underlain by Carboniferous and Permo-Triassic strata of northern England. In the south and east of England, low concentrations also relate to the outcrop of Cretaceous Chalk. Further to the south-west, the granite intrusions also give rise to low values in soils.

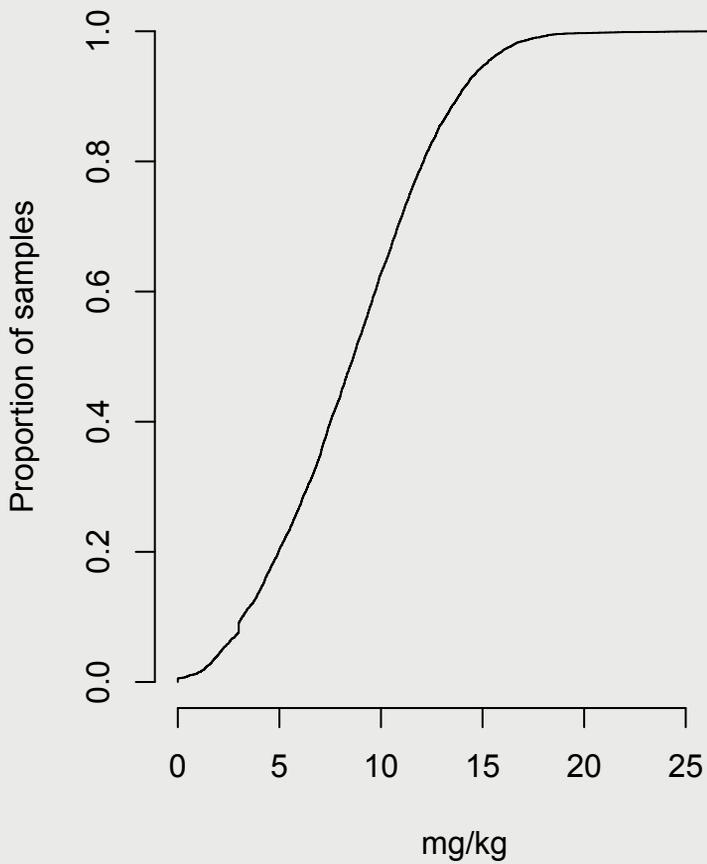
Histogram and boxplot



Normal Q-Q plot



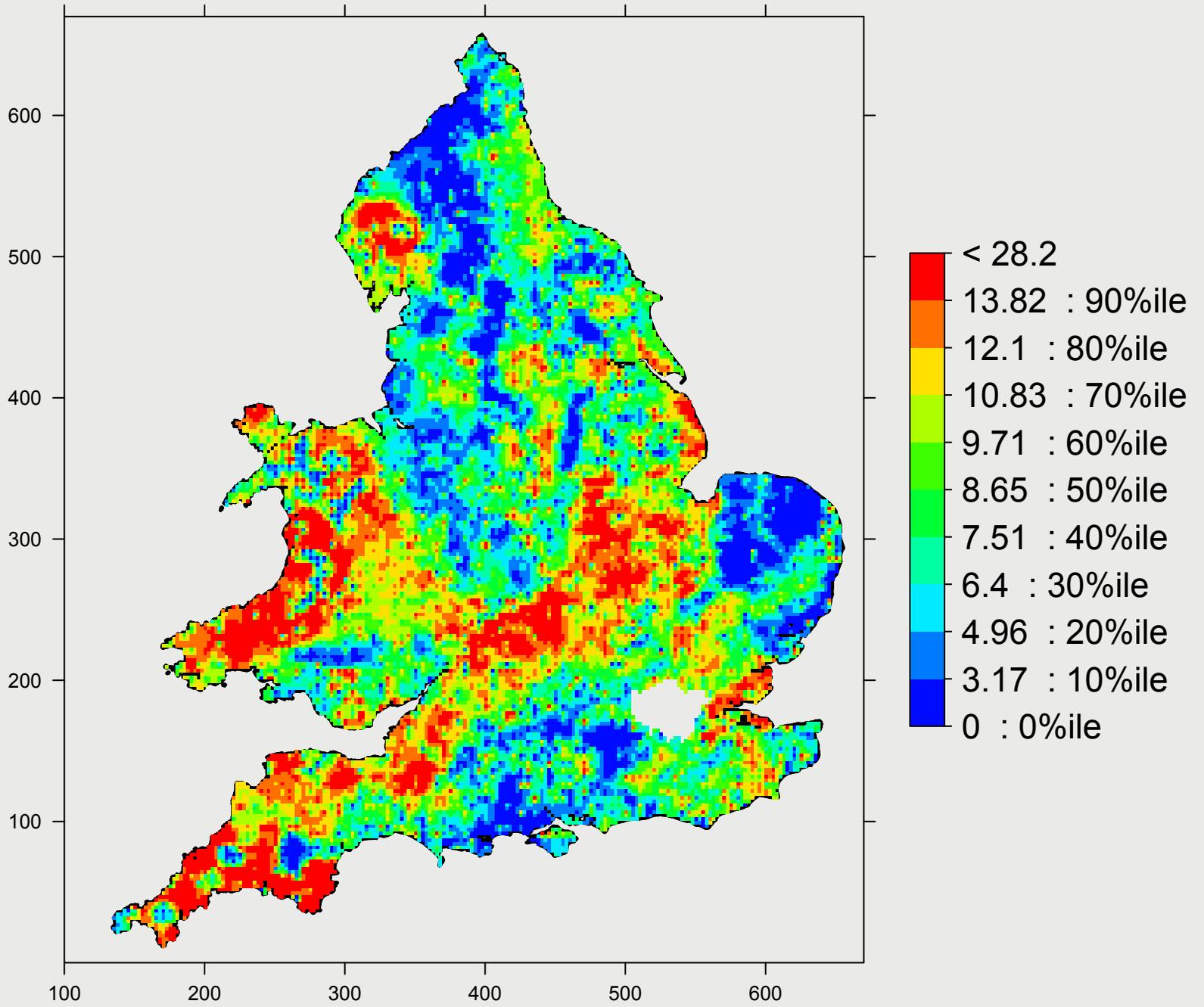
Cumulative frequency



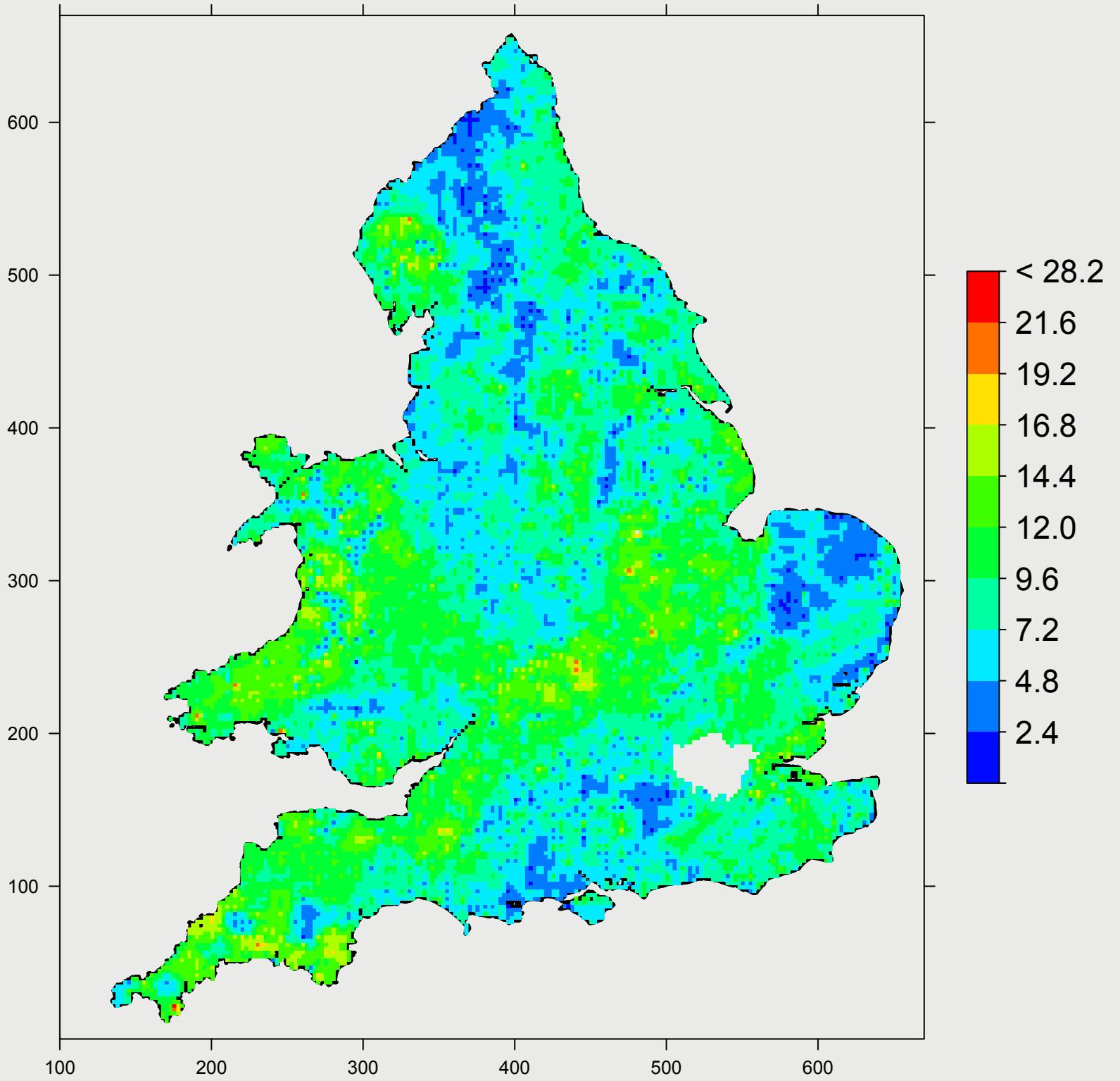
Sc - Scandium mg/kg

- mean= 8.6
- median= 8.6
- 10th percentile= 3.2
- 25th percentile= 5.7
- 75th percentile= 11
- 90th percentile= 14
- min= 0
- max= 28
- skewness= 0.16
- n= 5670

Topsoil scandium (mg/kg ; percentile scale)



Topsoil scandium (mg/kg ; arithmetic scale)



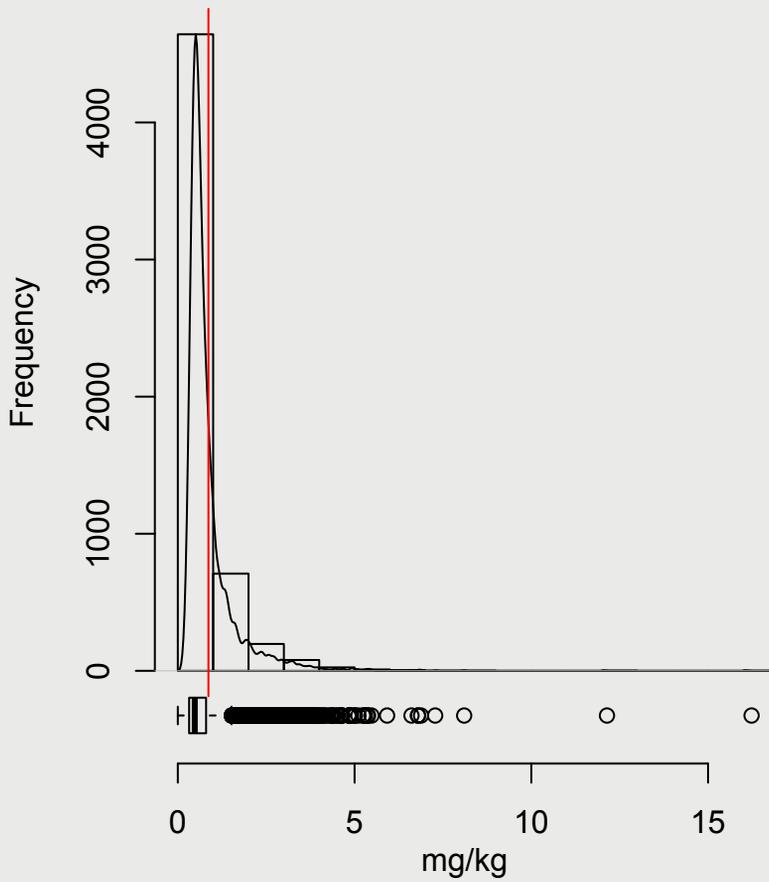
Selenium (Se)

Selenium is a rather low-abundance nonmetallic element, present at only 0.1 mg/kg in the Earth's upper continental crust. It is strongly associated with sulphur and has an affinity with organic matter, so it is relatively enriched in shales (0.3 mg/kg) and especially coals (3 mg/kg). It is an essential micronutrient for many organisms, but it has a narrow optimum intake range and both deficiency and excess toxicity problems are well documented.

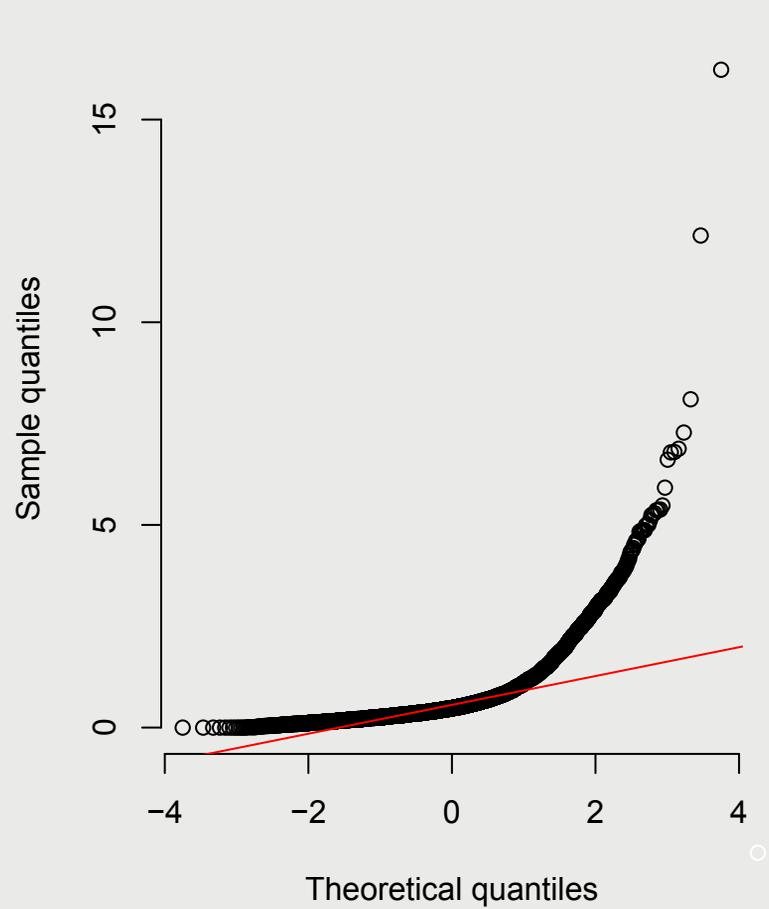
The highest Se concentrations in soils of England and Wales are strongly spatially correlated with sulphur. They occur over much of the higher altitude land in the south-west, Wales, Cumbria and the Pennines, and may therefore also have an atmosphere deposition component (RoTAP, 2011). In addition to this pattern, relatively large Se concentrations occur in the Fens, the Norfolk Broads, and Teesside, associated with organic matter. Molybdenum and sulphur concentrations in soils, along with Se, are also relatively elevated in the area in Somerset most affected by 'teart' in ruminants (see Molybdenum). The origin of high Mo, S and Se concentrations in this area may be the underlying black shales of the Lower Liassic (Jurassic).

Most soils in the lowland agricultural areas are low in Se, especially over sandy soils derived from the Old Red Sandstone and Permo-Triassic and Quaternary deposits. It is known that this results in low concentrations in staple crops such as wheat that can lead to element deficiencies in animals and humans (Adams et al., 2002). In addition, it can be seen that the majority of soils in these lowland areas have concentrations below 0.6 mg Se/kg which has been suggested can lead to dietary deficiencies (Lyons et al., 2003).

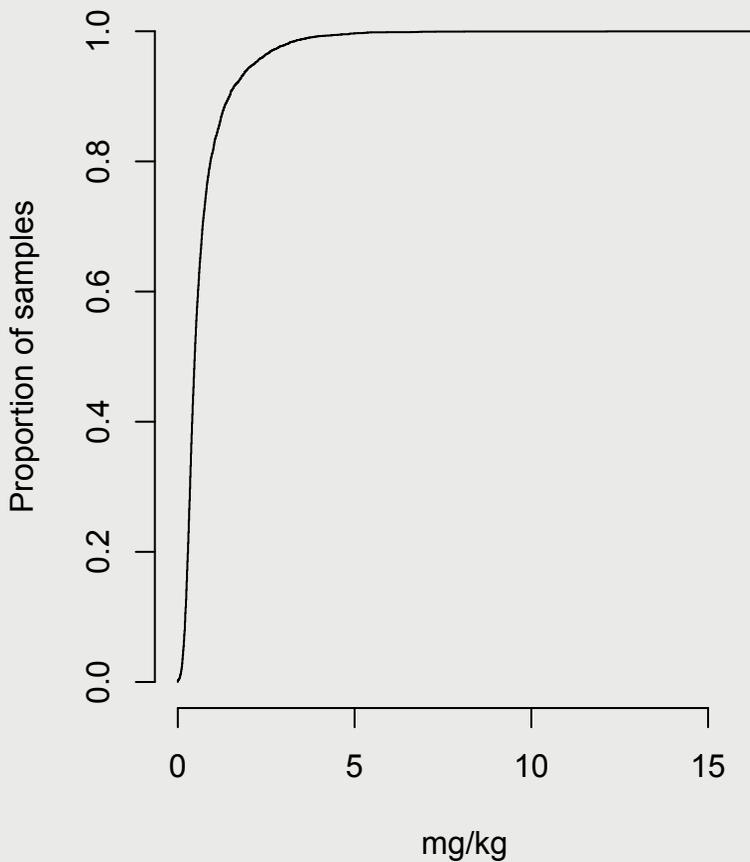
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Se - Selenium mg/kg

mean= 0.71

median= 0.48

10th percentile= 0.21

25th percentile= 0.32

75th percentile= 0.8

90th percentile= 1.5

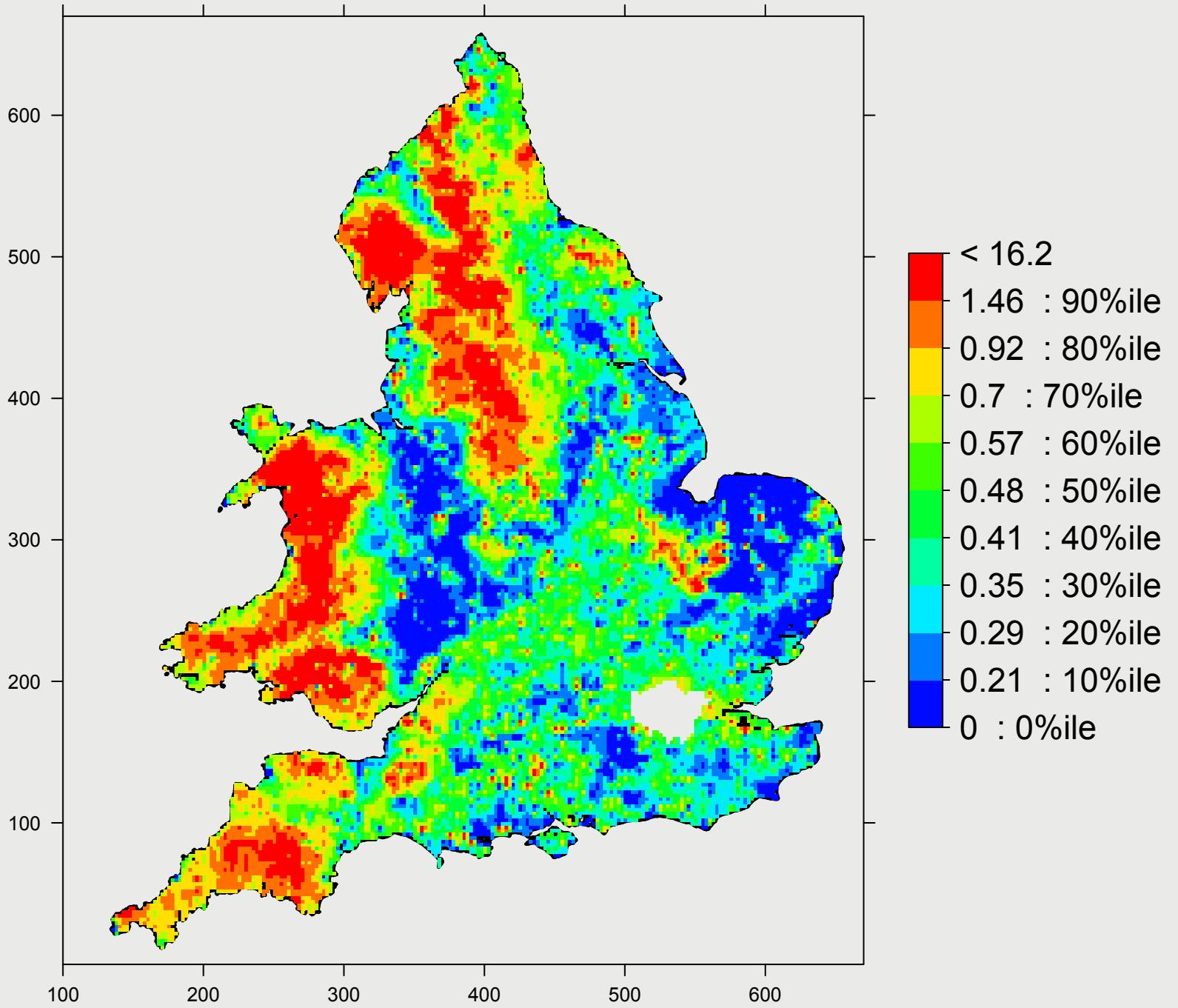
min= 0

max= 16

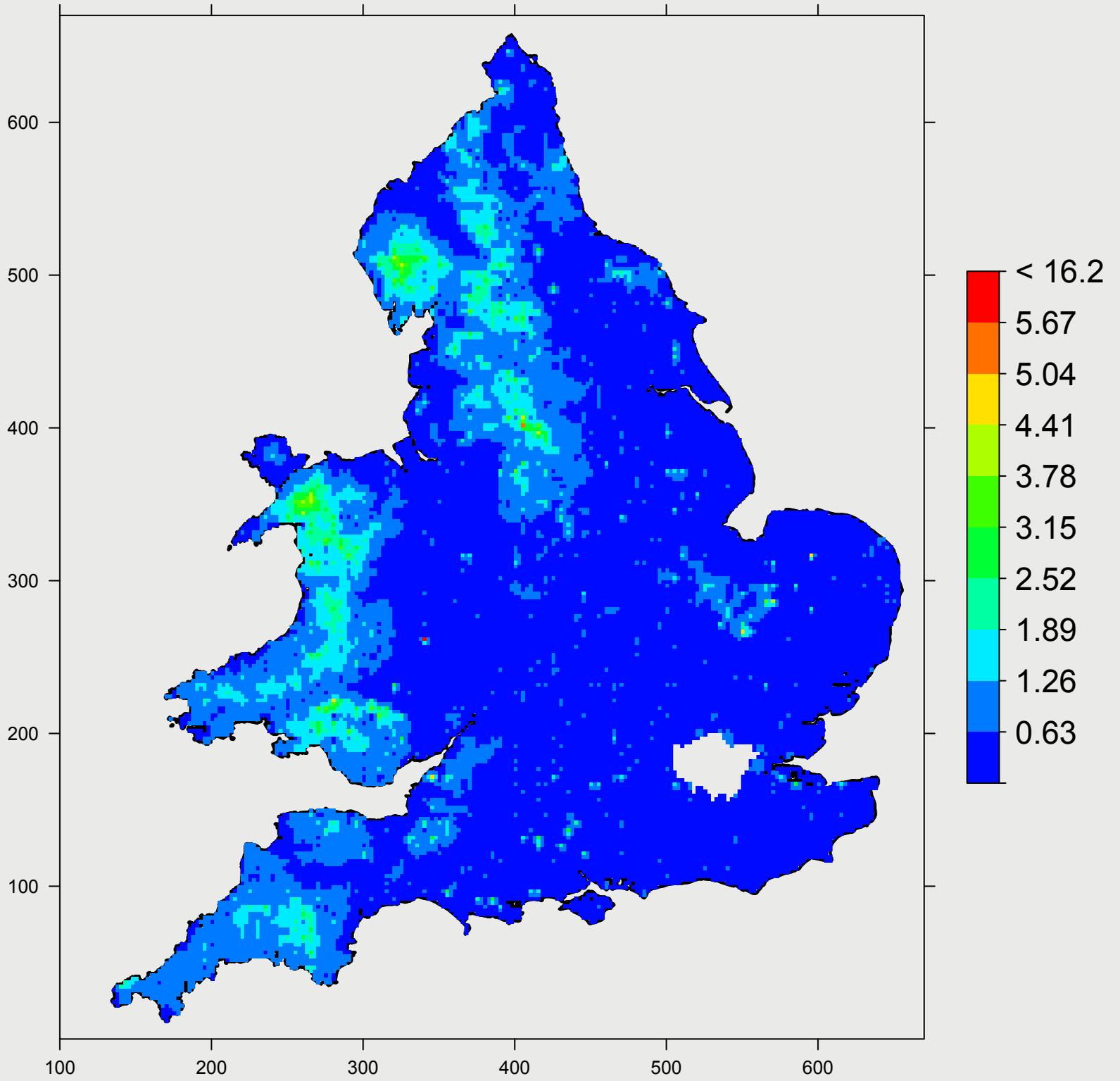
skewness= 4.8

n= 5670

Topsoil selenium (mg/kg ; percentile scale)



Topsoil selenium (mg/kg ; arithmetic scale)



Silicon (Si)

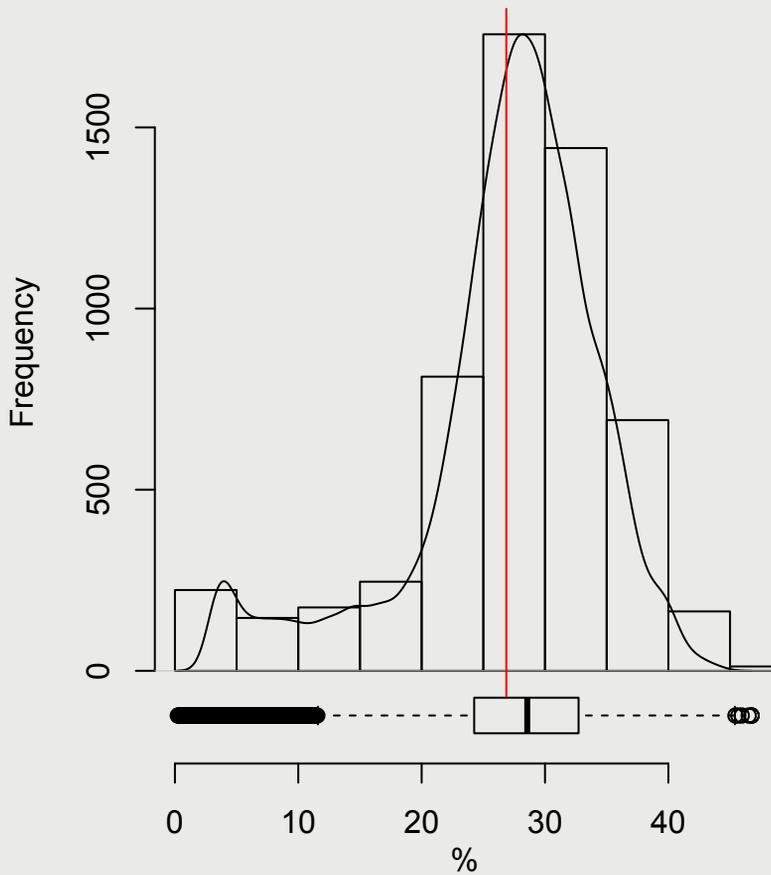
Silicon is the most common metalloid (semi-metal) in the Earth's crust, having an estimated average crustal abundance of around 30% (300 000 mg/kg). and predominantly occurs as oxides (silicates) in most rock-forming minerals such as quartz, feldspar, olivine, muscovite, orthoclase (and many more). It is a beneficial element for some organisms and essential for some, such as diatoms.

The mean and median concentrations of Si in NSI soils are 27 and 29% respectively, with a maximum of 47%. High Si concentrations indicate a greater abundance of sand grains (mainly quartz) in the soil, which is shown by the arithmetic map, where the highest Si concentrations (>36%) correlate particularly well with the sandstone outcrops. Its spatial distribution outlines a) the Permo-Triassic sandstone cropping out in Cumbria and then from Liverpool around the Peak District and north towards Sunderland, b) the Old Red Sandstone of the Welsh Borders, c) the Lower Cretaceous nonmarine sandstones in the Wealden District of Sussex and Kent and d) the Palaeogene sandstone of the Hampshire Basin and the Slough and Reading areas. The largest area of elevated Si concentrations however covers almost the entire eastern half of East Anglia with the exception of the Norfolk Broads. These either relate to Quaternary marine sands or gravels or, certainly in the Breckland, Cromer and Ipswich areas, to known wind-blown loess and cover-sand deposits (Scheib and Lee, 2010).

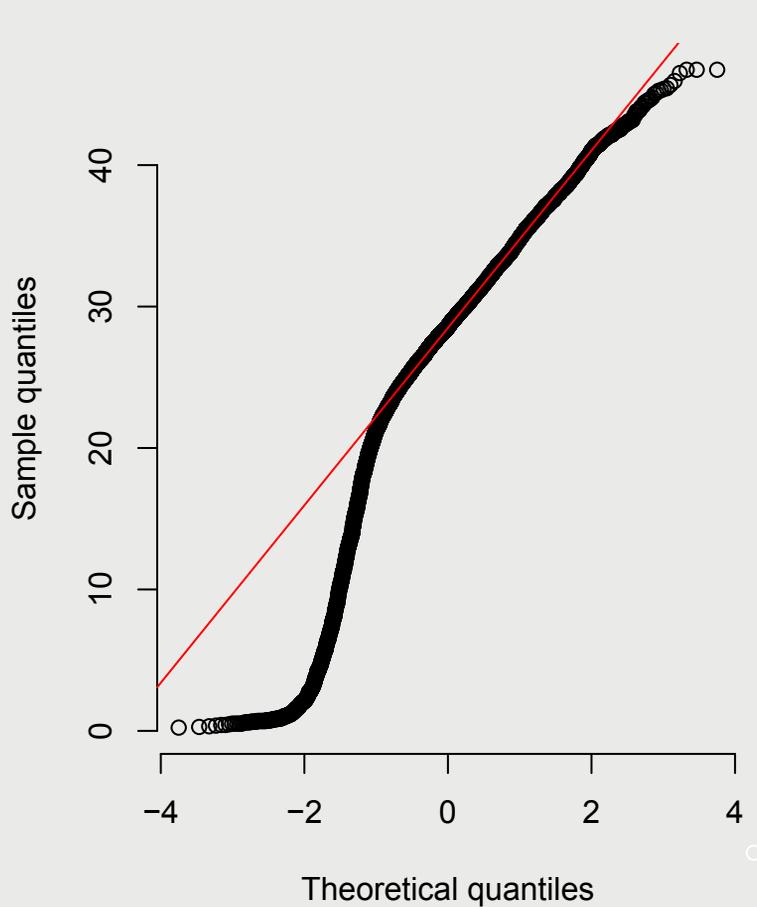
Low-Si soils include those over much of upland Wales, the Lake District and the Pennines, plus the limestones and clays of the Jurassic, and the Chalk. Peaty soils may be largely responsible for this in the uplands, which are often underlain by Si-rich sandstones and granites.



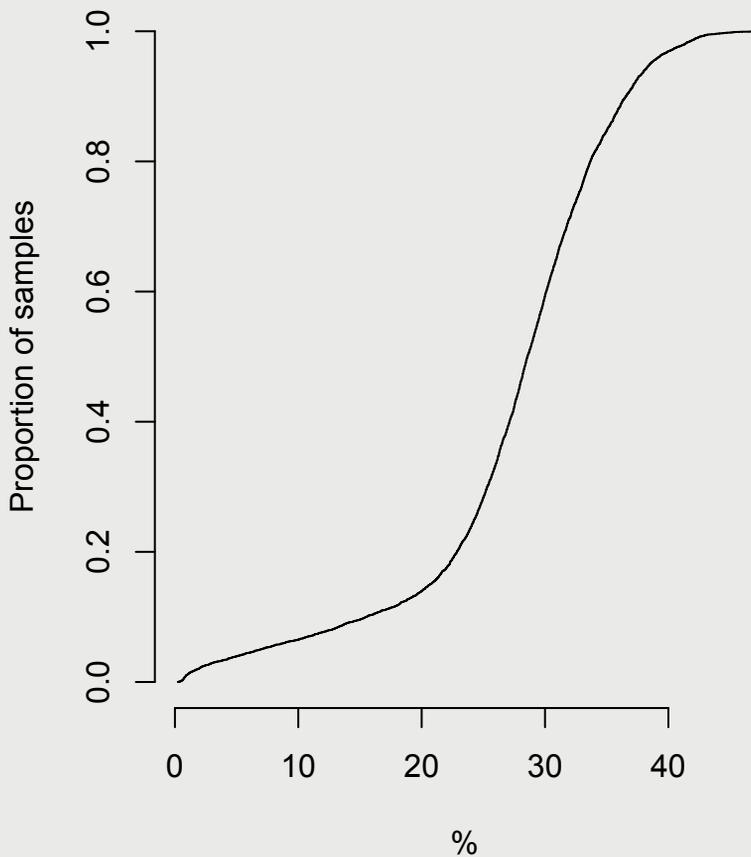
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Si - Silicon %

mean= 27

median= 29

10th percentile= 16

25th percentile= 24

75th percentile= 33

90th percentile= 37

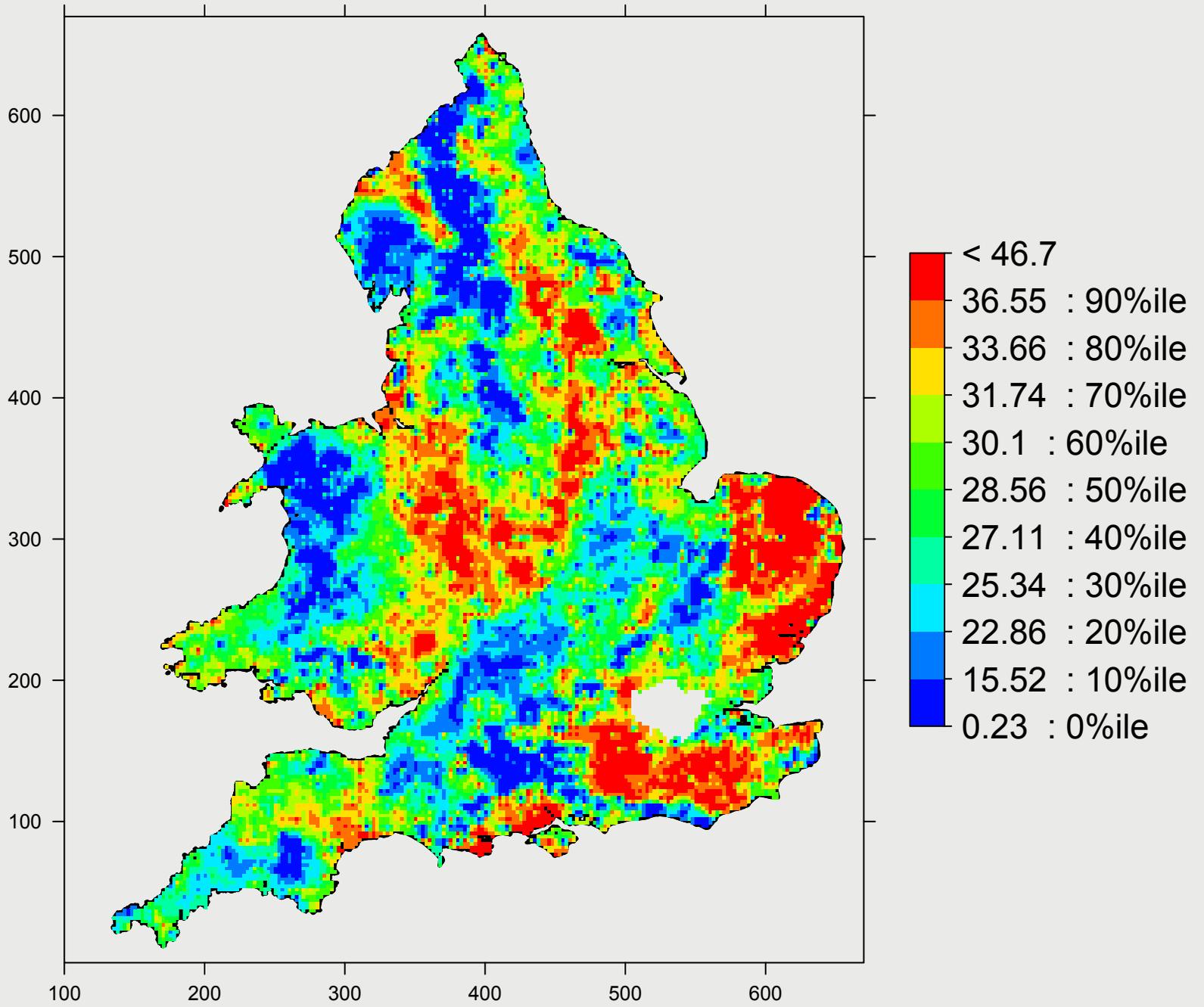
min= 0.23

max= 47

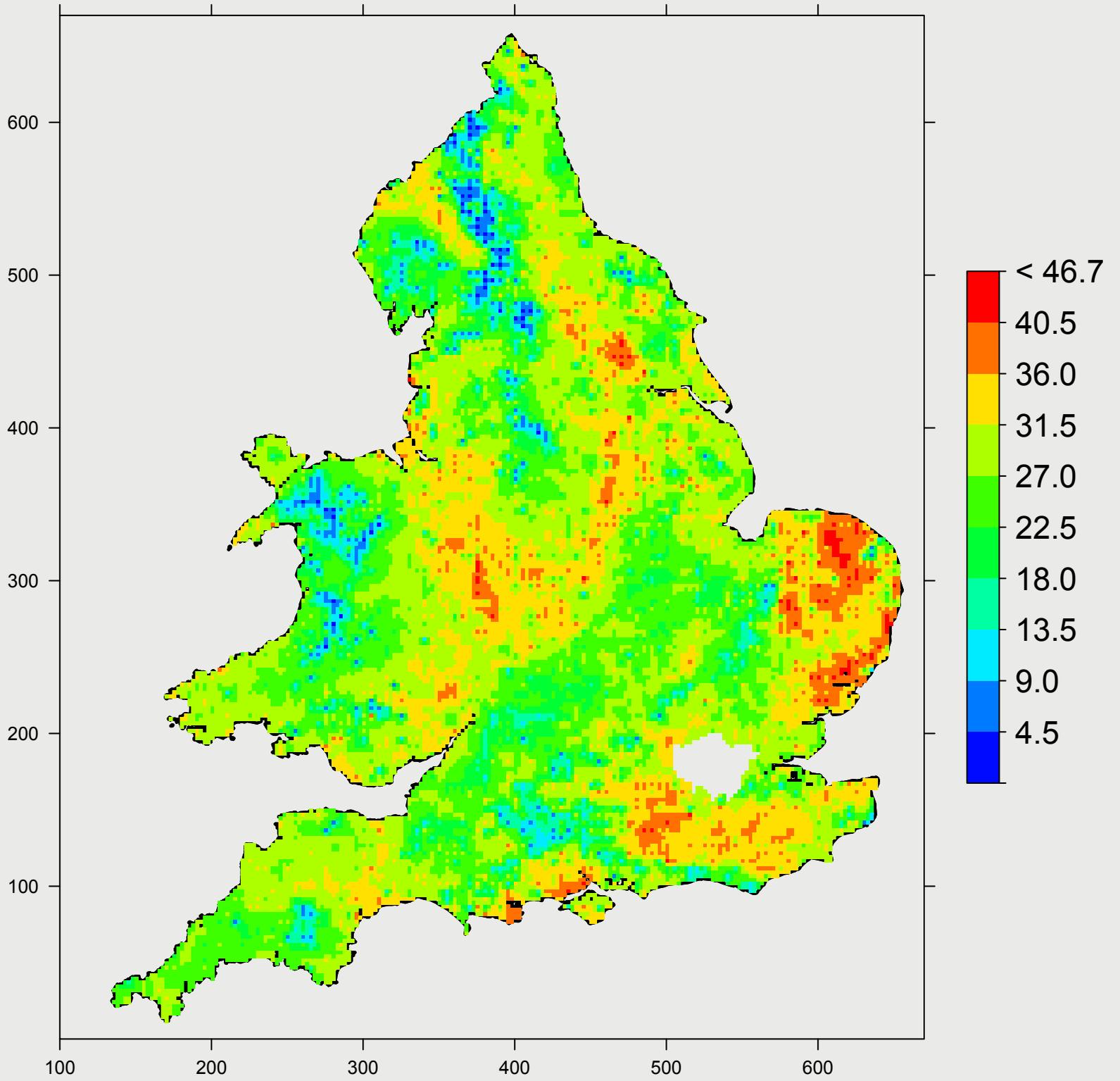
skewness= -1.1

n= 5670

Topsoil silicon (% ; percentile scale)



Topsoil silicon (% ; arithmetic scale)

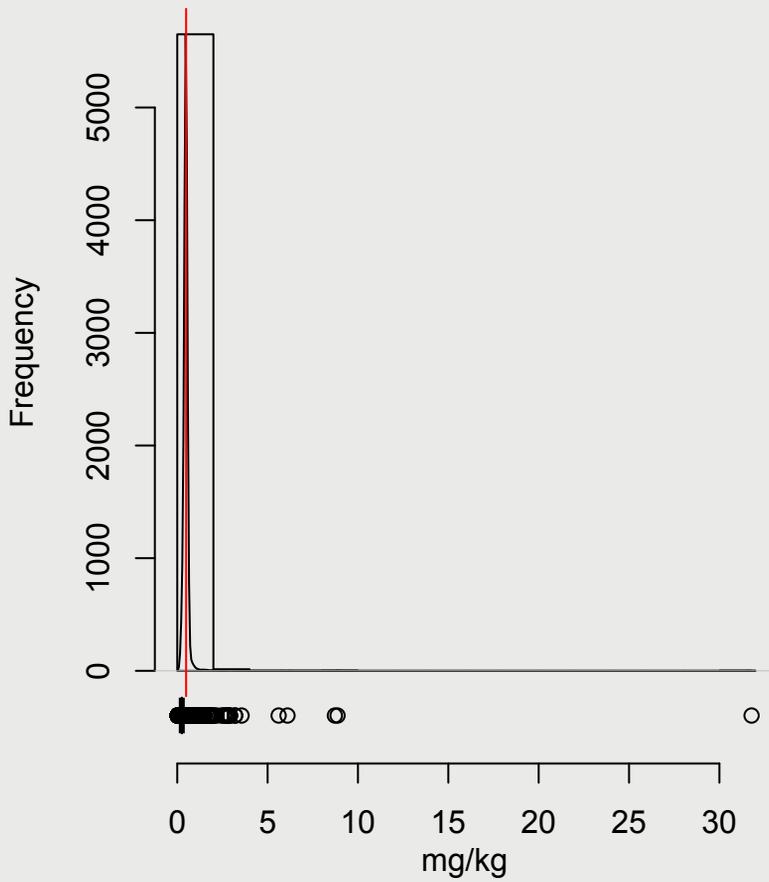


Silver (Ag)

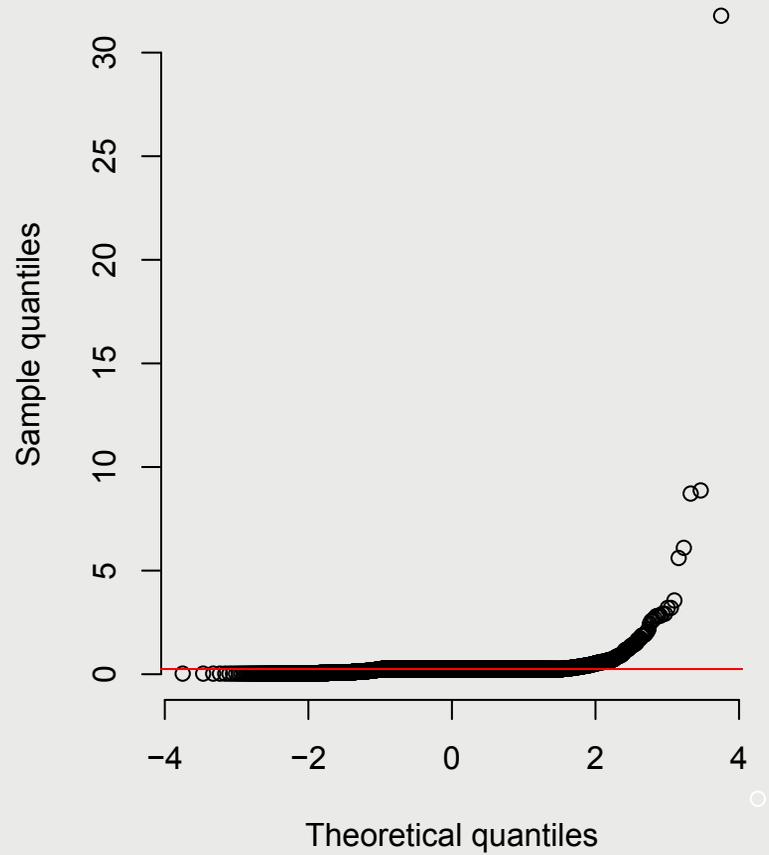
Silver is a rare metallic element with an estimated average upper continental crustal abundance of 0.05 mg/kg (Reimann and De Caritat, 1998). It is biologically non-essential and is toxic to many micro-organisms. Silver has a strong affinity for sulphur, and is often associated with lead and zinc sulphide minerals such as galena and sphalerite. Around 90% of the reported values for total Ag were below the limit of detection for XRFS analysis. Any interpretation of the spatial distribution of Ag concentrations should be extremely cautious because the patterns displayed are likely to include artefacts due to the large uncertainties associated with the analyses.

The areas with the highest Ag concentrations (>0.25 mg/kg) occur predominantly in parts of central and northern England and areas of south Wales and the south-west peninsula where they are most closely associated with lead–zinc mining, but there is also a notable moderate urban-industrial signature in Birmingham and several very high values on the periphery of London, including one site to the west with 31.8 mg/kg Ag (and 15 mg/kg Cd, 44 mg/kg Sn) near Wraysbury.

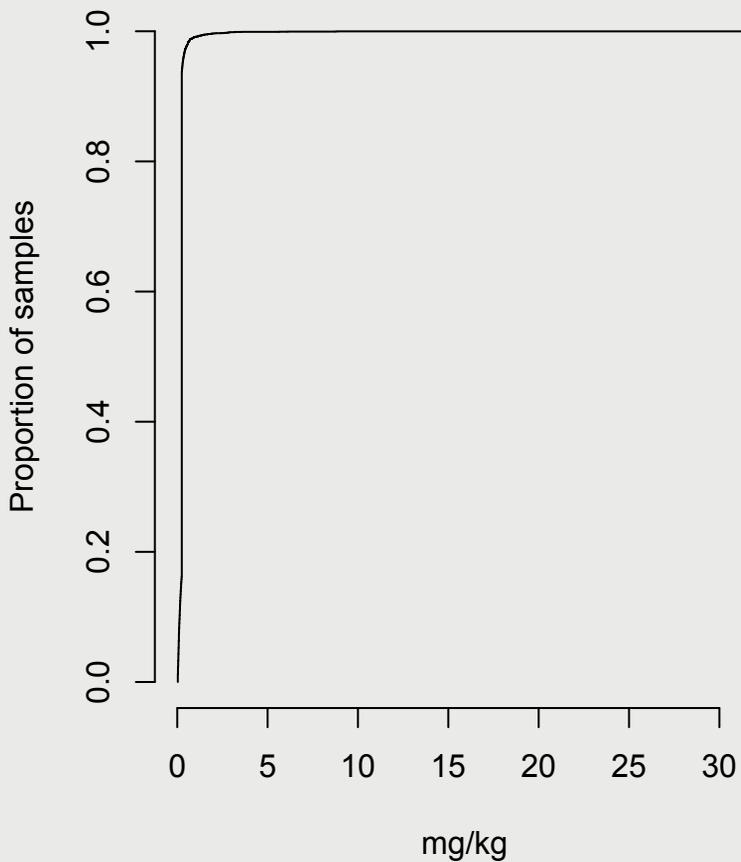
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ag - Silver mg/kg

mean= 0.26

median= 0.25

10th percentile= 0.13

25th percentile= 0.25

75th percentile= 0.25

90th percentile= 0.25

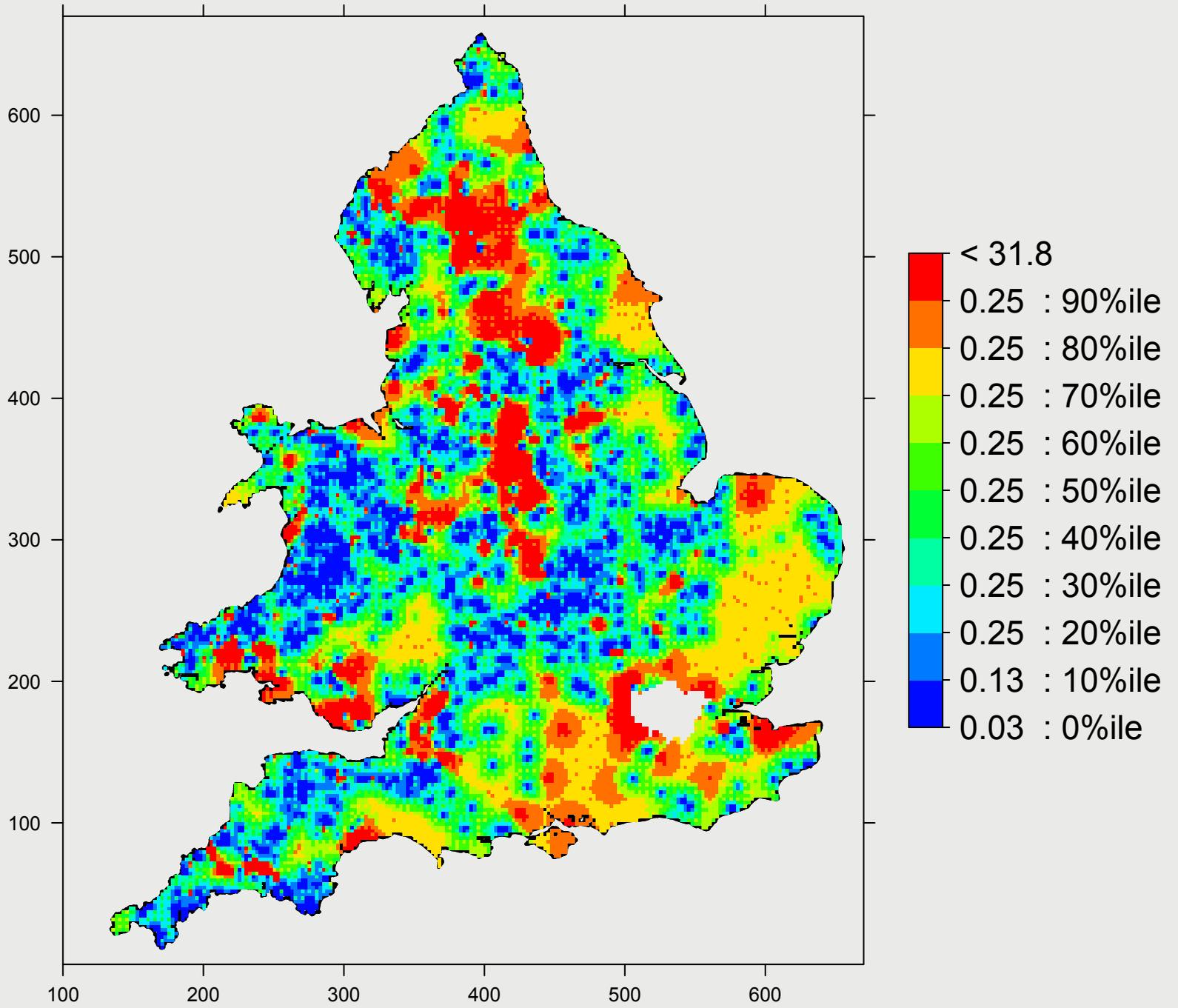
min= 0.03

max= 32

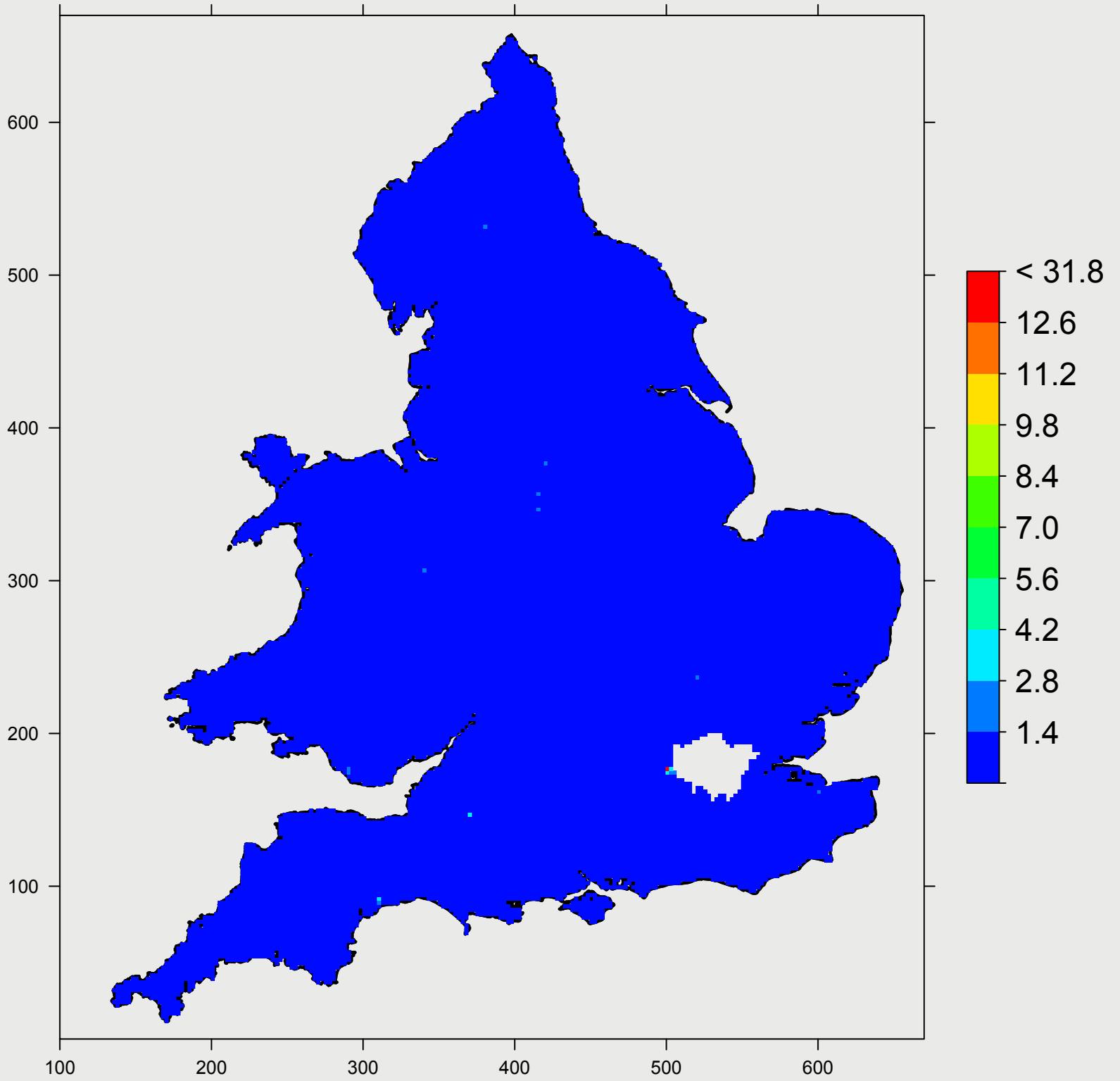
skewness= 49

n= 5669

Topsoil silver (mg/kg ; percentile scale)



Topsoil silver (mg/kg ; arithmetic scale)



Sodium (Na)

Sodium is a major metallic element, present at about 2.6–2.9% by weight in the Earth's upper continental crust, and present in many rock-forming minerals, especially feldspars. It is essential for many organisms, but toxic to plants and animals at high concentrations.

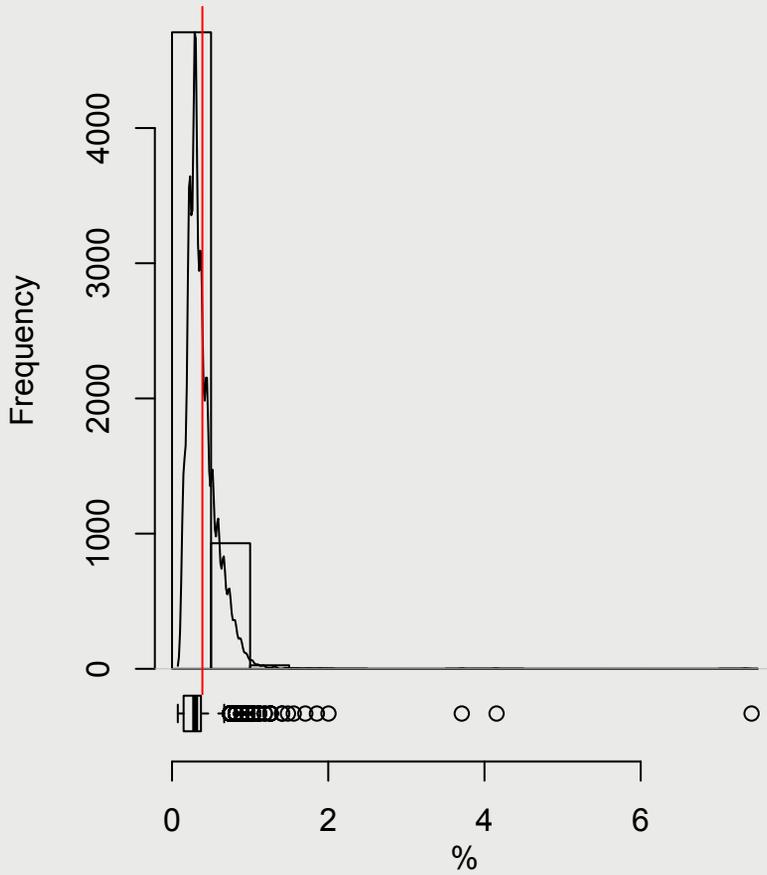
The highest concentrations of Na in soils occur in small areas of marine alluvium in salt marshes around the Thames estuary, the north-east Norfolk and Suffolk coasts, and the Fens. Large parts of south-west England, Wales and Welsh Borders, Cumbria and the Cheviot hills also appear to have relatively high Na concentrations (>0.5%), but these may not be in soluble forms, occurring in minerals of igneous origin, though atmospheric deposition may be significant in some areas.

Areas with low Na concentrations appear to be linked to Cretaceous Chalk and sandy drift deposits in East Anglia, central-southern England and the Weald.

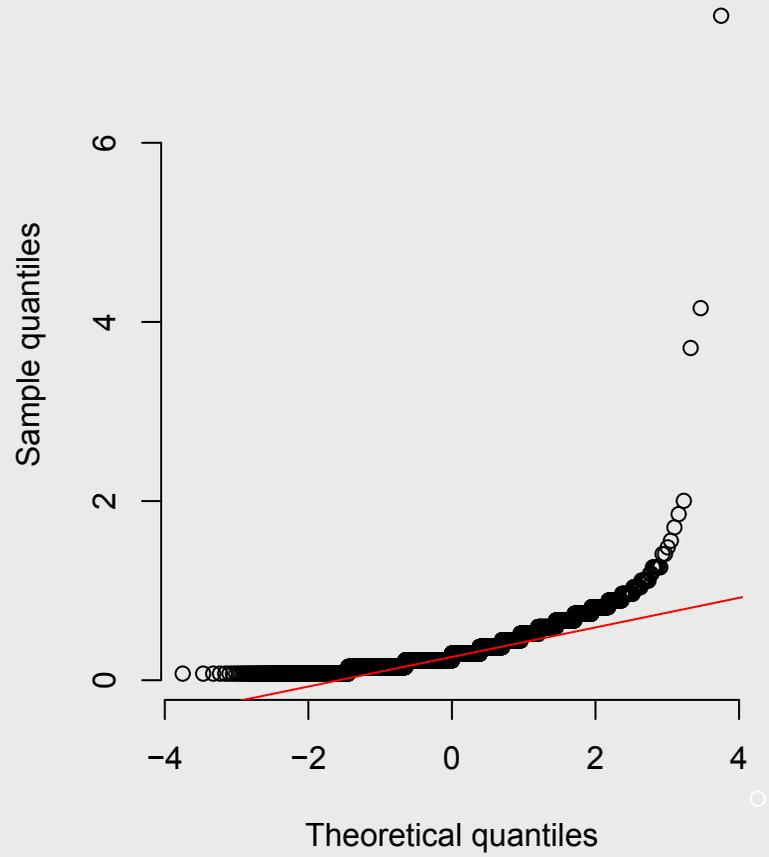
Sodium is inefficiently extracted from the soil matrix during aqua regia digestion (McGrath and Loveland, 1992), and the values reported here (using the XRF-S method) are higher than those reported using aqua regia. For example, the median concentrations in soil are 0.3 and 0.02%, respectively.



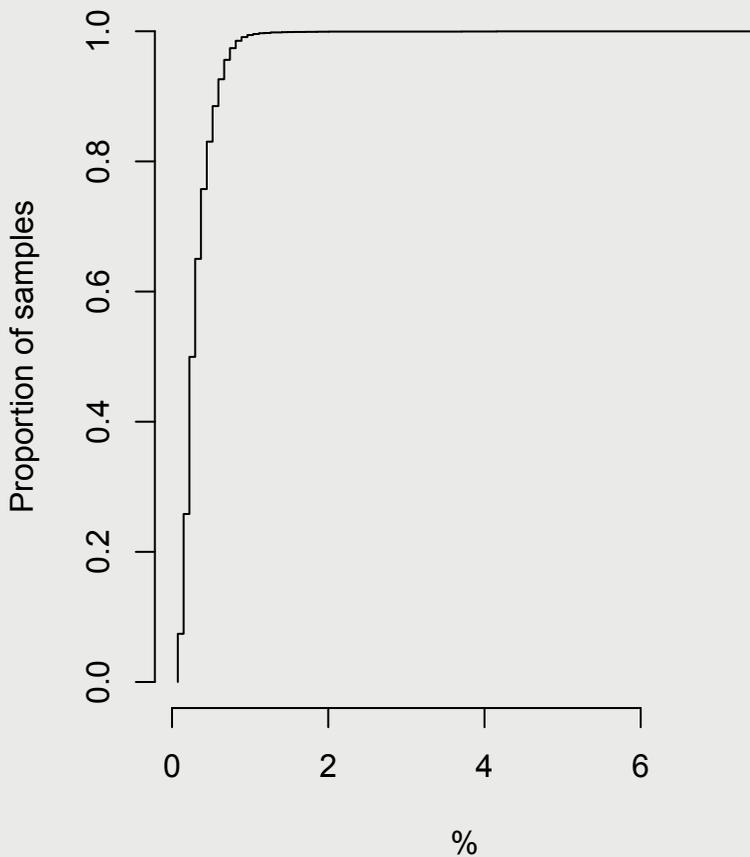
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Na - Sodium %

mean= 0.32

median= 0.3

10th percentile= 0.15

25th percentile= 0.15

75th percentile= 0.37

90th percentile= 0.59

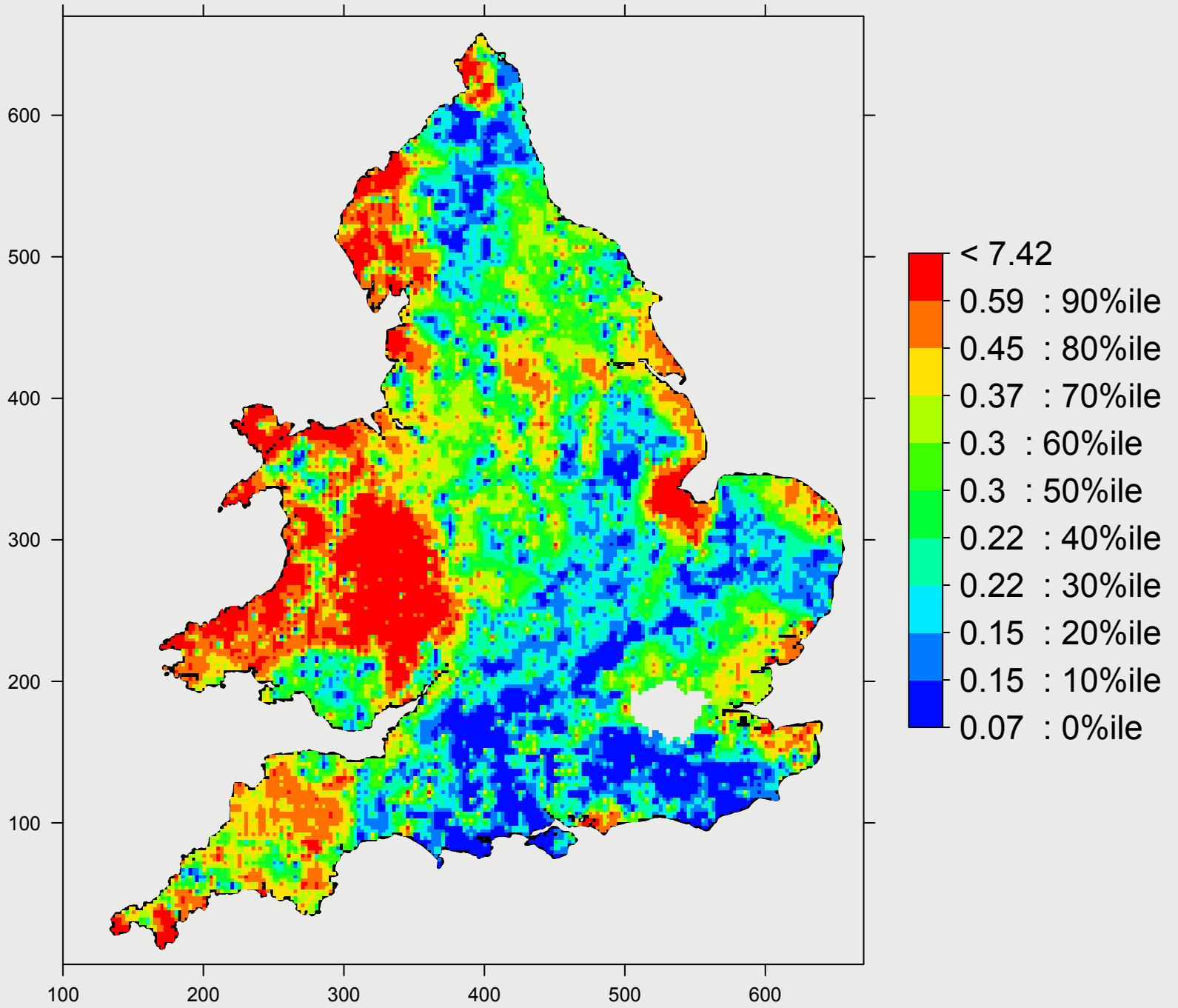
min= 0.074

max= 7.4

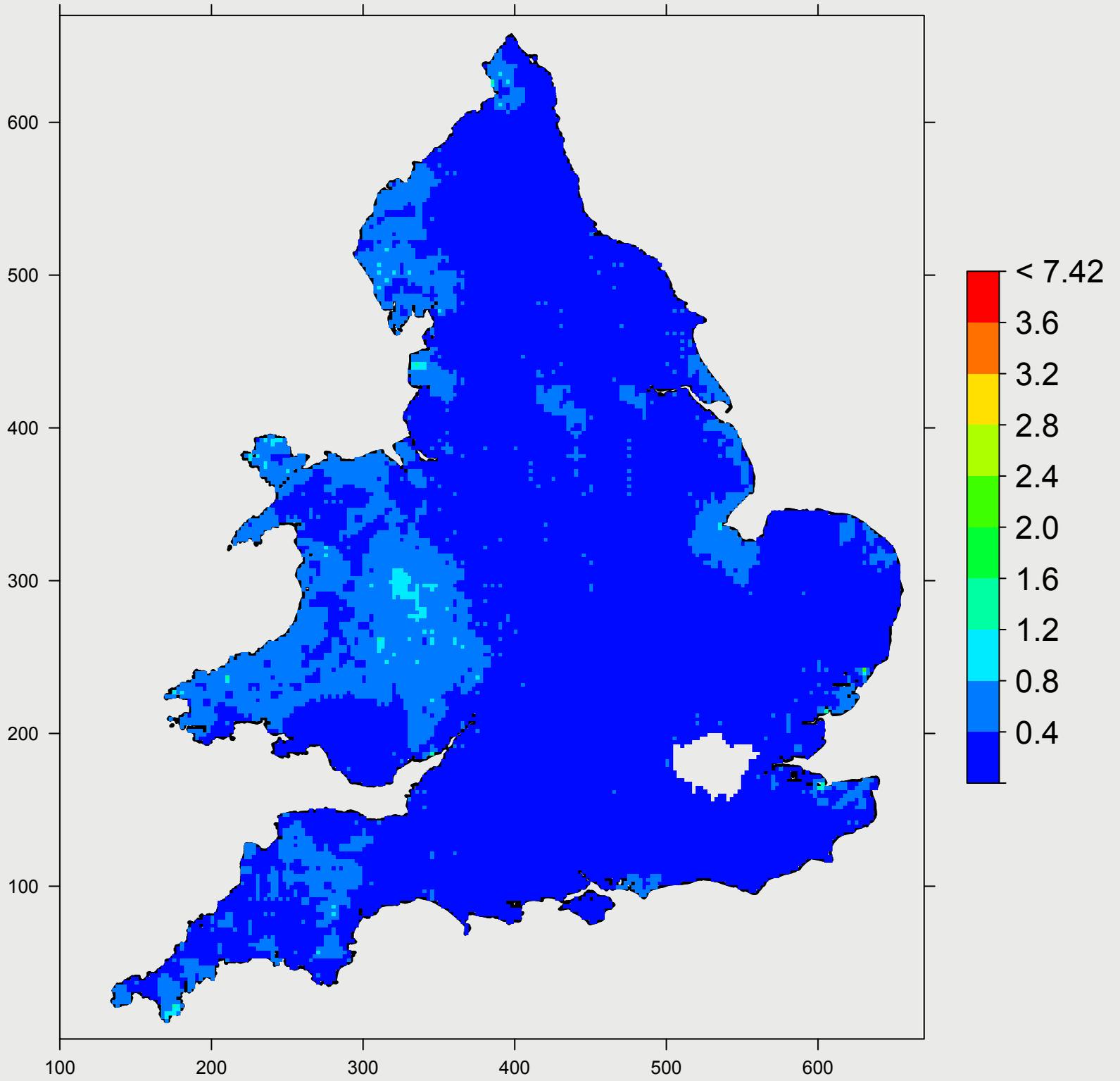
skewness= 8.1

n= 5670

Topsoil sodium (% ; percentile scale)



Topsoil sodium (% ; arithmetic scale)



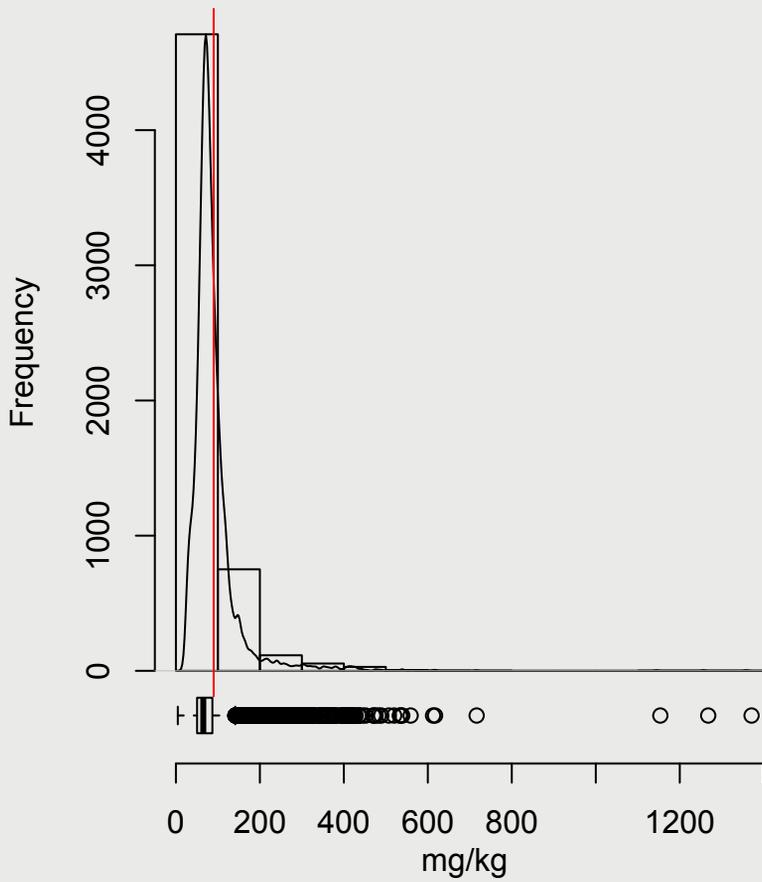
Strontium (Sr)

Strontium is a metallic element, present at about 330–350 mg/kg in the upper continental crust (Reimann and De Caritat, 1998). Strontium is geochemically similar to calcium and substitutes for Ca in many Ca-bearing minerals, including sulphates (gypsum), carbonates and feldspars. It also has some affinity with barium (Ba), and also occurs with this element in barytes (BaSO_4) deposits. It is biologically non-essential for most organisms.

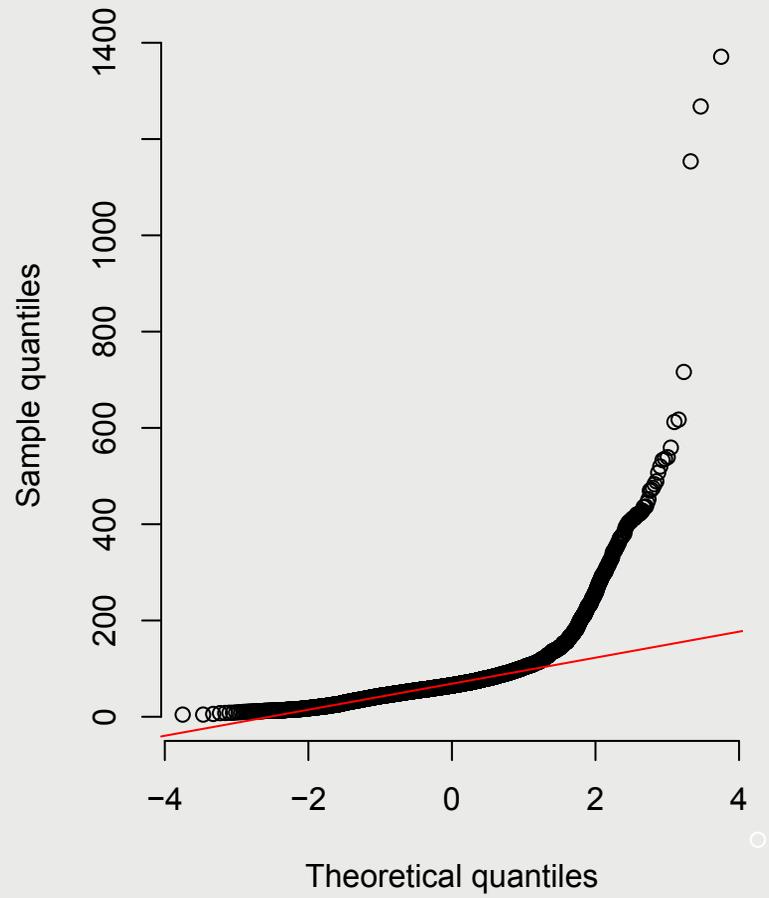
The strontium maps are essentially similar to those for Ca, because it has similar geological and pedological associations as Ca. The exceptions occur where Sr concentrations are elevated relative to the concentrations of Ca occur in the Cheviot Hills in Northumberland (Devonian age igneous rocks) and the areas underlain by Devonian rocks in Devon and Cornwall. The enrichment with Sr may have been associated with the processes associated with the igneous rocks in these areas. Soils with higher Sr are mainly concentrated to the south and east of the Jurassic boundary that runs from the Bristol Channel roughly to Scarborough on the Yorkshire coast. Other enrichments are present in the Peak District and Yorkshire where they are associated with high Ba levels due to barytes mineralisation.

Low Sr concentrations are mostly associated with the Ca-poor sandstones of the Pennines and North York Moors, the Lower Palaeozoic uplands of Wales and Cumbria, the Old Red Sandstone and Permo-Triassic outcrop of the Midlands, the major granites of the south-west, especially Dartmoor, and the sandy heathland soils of southern England, the Weald and East Anglia.

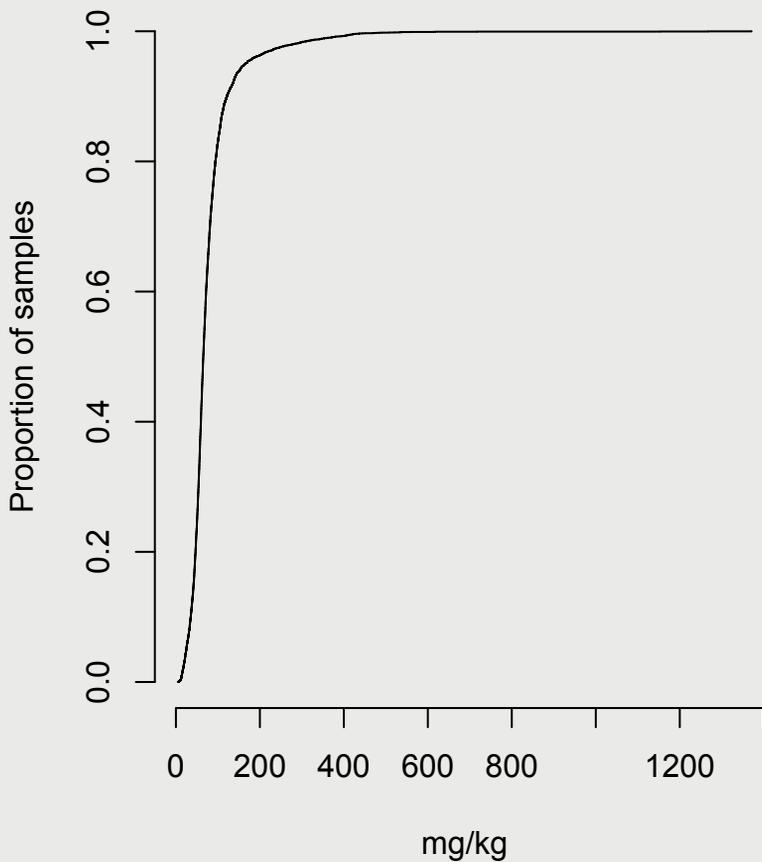
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Sr - Strontium mg/kg

mean= 79

median= 65

10th percentile= 35

25th percentile= 50

75th percentile= 87

90th percentile= 122

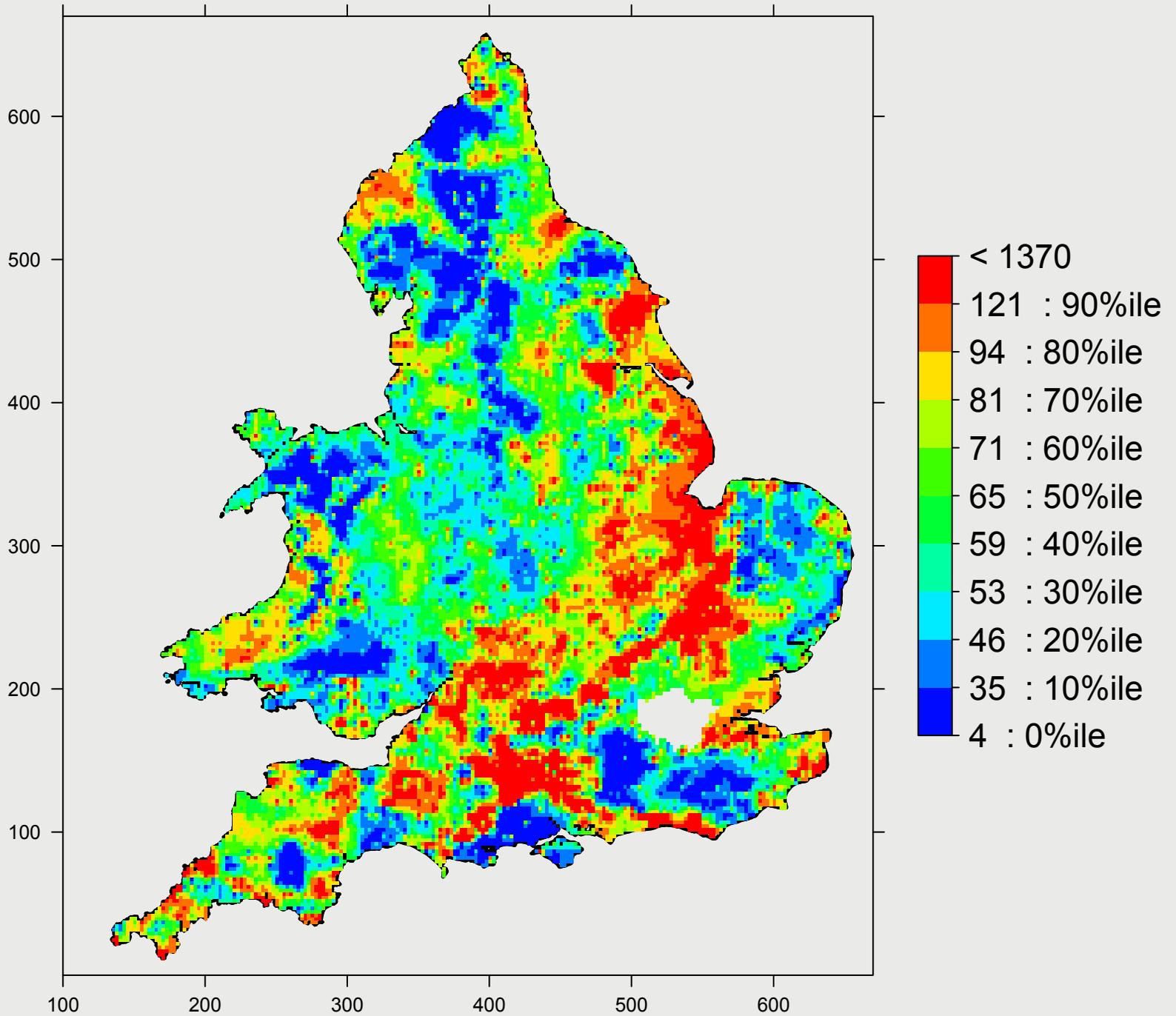
min= 4.5

max= 1371

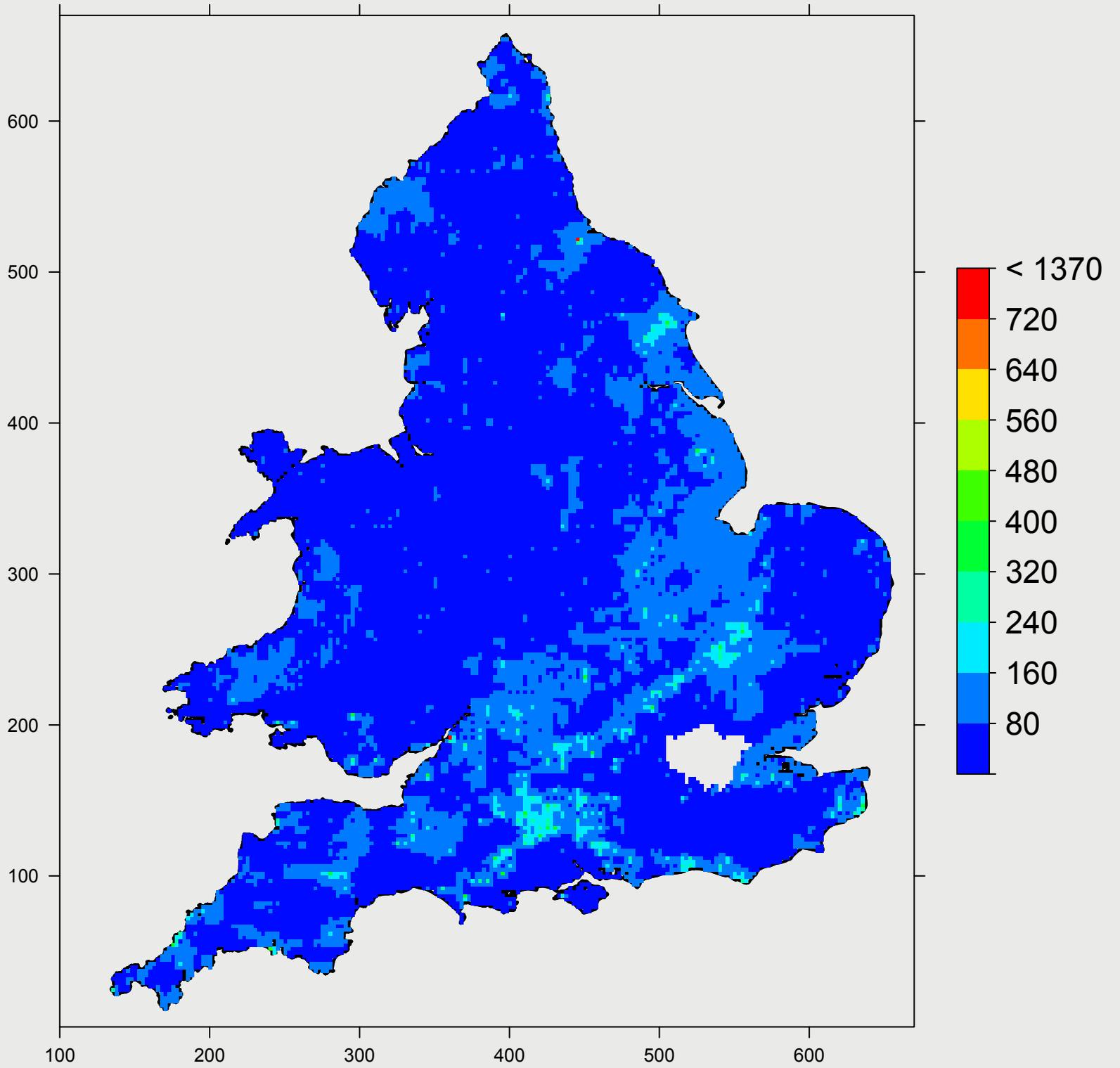
skewness= 6.3

n= 5670

Topsoil strontium (mg/kg ; percentile scale)



Topsoil strontium (mg/kg ; arithmetic scale)



Sulphur (S)

Sulphur is a major nonmetallic element, present at about 900 mg/kg in the upper crust. It is enriched in basic igneous rocks (900 mg/kg) relative to granites (100 mg/kg), but is much more abundant in shales (1100 mg/kg) and especially coals (20 000 mg/kg: Reimann and De Caritat, 1998). It forms many important sulphide ore minerals such as galena, sphalerite and pyrite, and sulphates such as gypsum and anhydrite. It is also a constituent of organic matter, and is an essential element for all organisms.

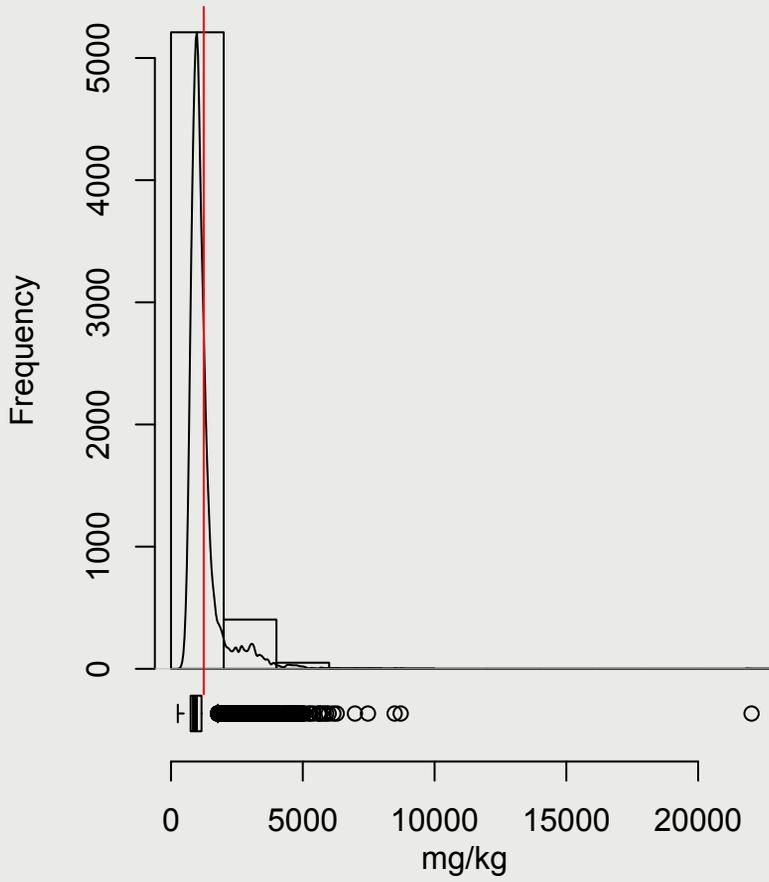
The concentrations reported for S analyses by XRFs should be treated with some caution as their intrinsic variability and uncertainty is higher than for many other elements. No correction is applied for the sample matrix, and consequently the reported S values will be influenced to varying extents by the types of S-bearing minerals (e.g. pyrite and gypsum) present in the soil samples. Furthermore, the binder used to prepare the samples for XRFs analysis also contains variable traces of sulphur, which is likely to have resulted in increased concentrations of sulphur being reported in the samples. However, the broad trends in the data are sufficiently reliable for general interpretation.

Soils containing high concentrations of S are present in the peaty areas of the Fens south of The Wash, rather scattered areas in the 'Fens' or 'Mosses' of the Lancashire plain and also the peaty soils of the Pennines and upland Wales and the granite moors of the south-west, related to binding of S by the organic matter. More locally, high sulphur concentrations mark the presence of Pb and Zn sulphide minerals in the mining districts of Wales, the Peak District, northern Pennines and Shropshire. There may also be some atmospheric deposition of S, related to rainfall, which is higher in the north and west than in the south and east of England and Wales (RoTAP, 2011).

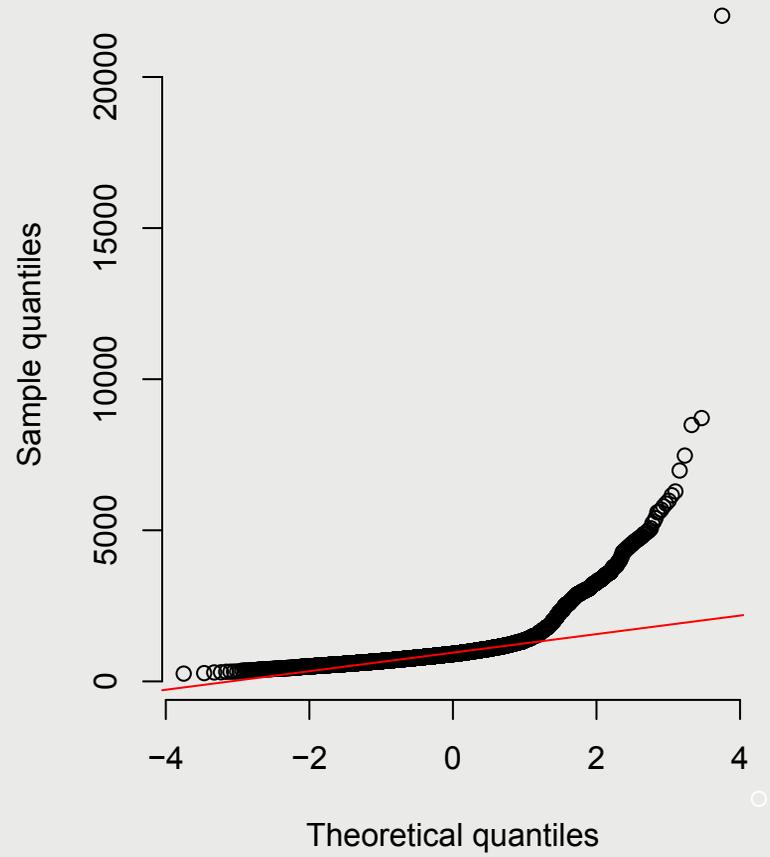
Organic-rich black shales and coals may contain high S concentrations, This may also be the case in the area of Somerset most affected by 'teart' in ruminants (see Mo) where high S, Mo, and Se may be derived from the underlying black shales of the Lower Lias (Jurassic).

Low S concentrations in soil occur throughout East Anglia, parts of the Old Red Sandstone of the Welsh Borders, the Midlands and Devon; and also in the Weald of Sussex and Kent; and in Surrey. It is known that crops respond to S fertiliser applications (McGrath and Zhao, 1995) so agricultural S deficiency may be a significant problem in these areas.

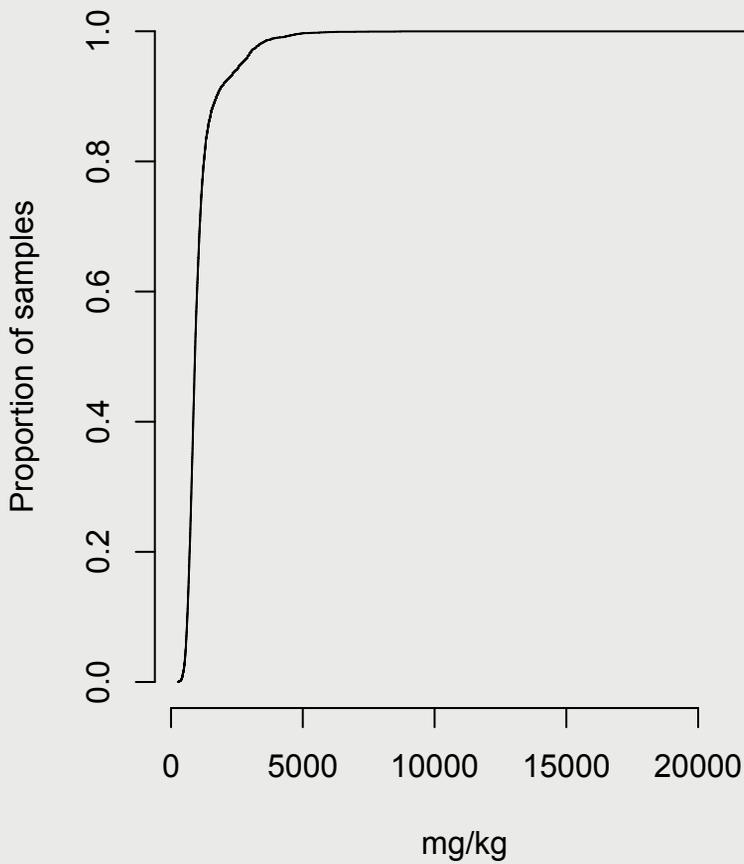
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



S - Sulphur mg/kg

mean= 1107

median= 909

10th percentile= 619

25th percentile= 744

75th percentile= 1158

90th percentile= 1731

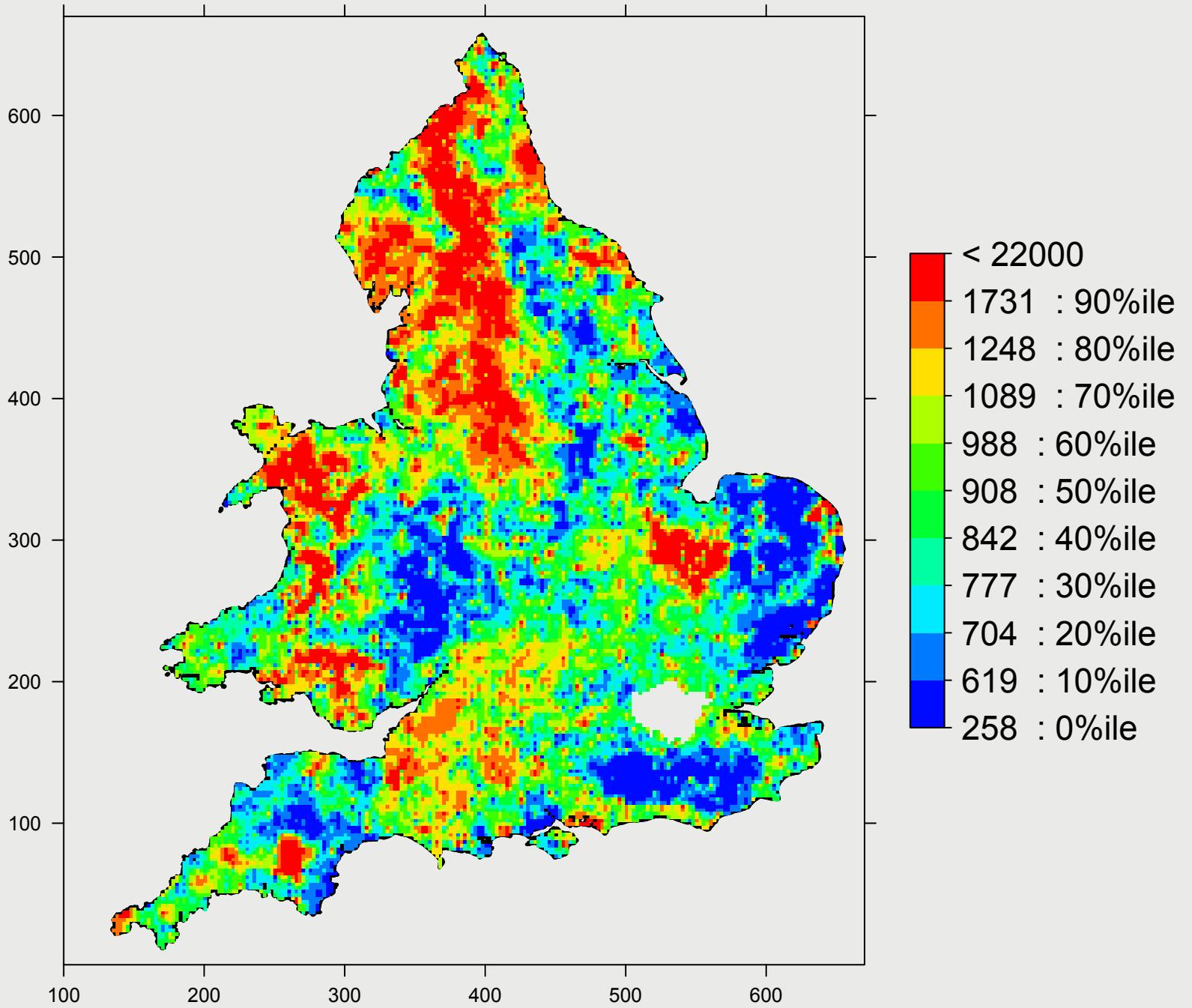
min= 258

max= 22027

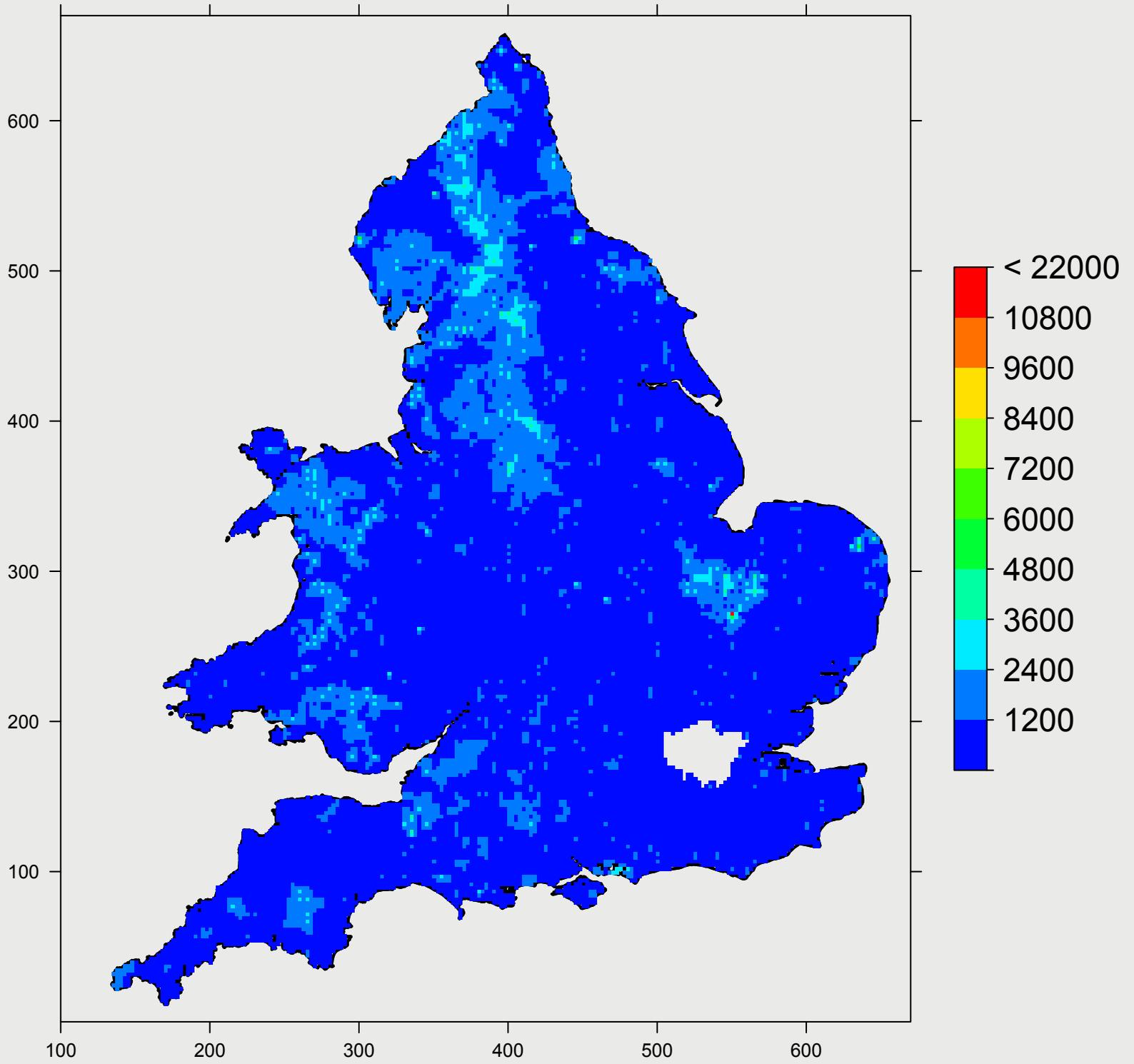
skewness= 6.5

n= 5670

Topsoil sulphur (mg/kg ; percentile scale)



Topsoil sulphur (mg/kg ; arithmetic scale)



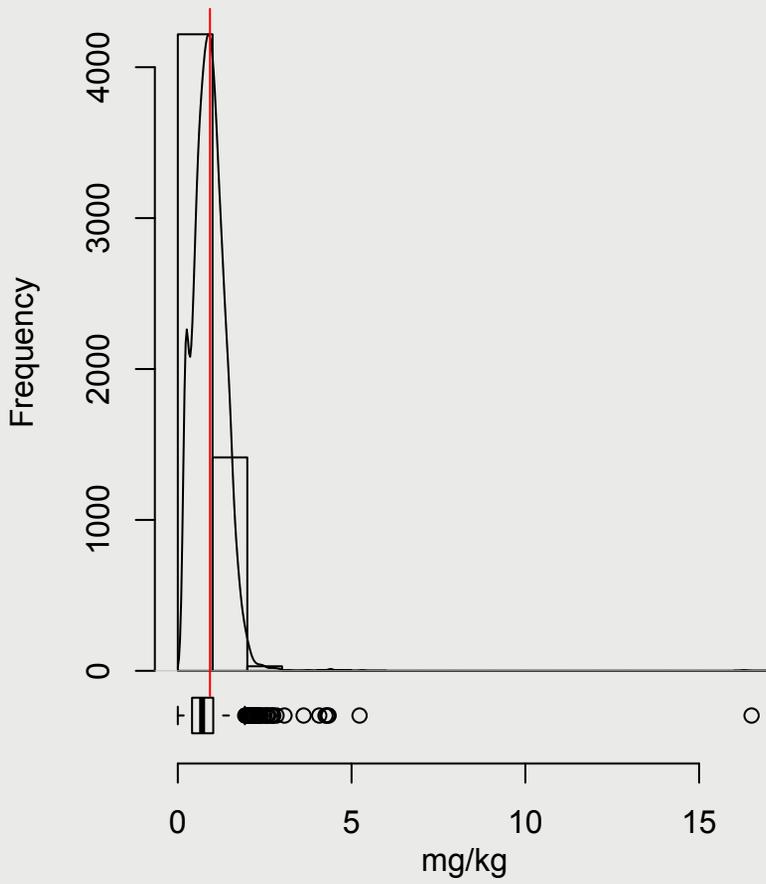
Tantalum (Ta)

Tantalum is a rare transition metal with an estimated average upper continental crustal abundance of 1.5–2.2 mg/kg. It is a highly refractory element and, due to almost identical geochemical properties, always occurs together with Nb in nature and is likewise considered non-essential with no known biological function and low toxicity. Tantalum is mainly found in the rare columbite-tantalite minerals, but is also present at trace levels in biotite and resistate minerals such as zircon, rutile, ilmenite and sphene. It is of growing interest because of its application and use in electronic components and in the production of superalloys, e.g. for the aviation industry.

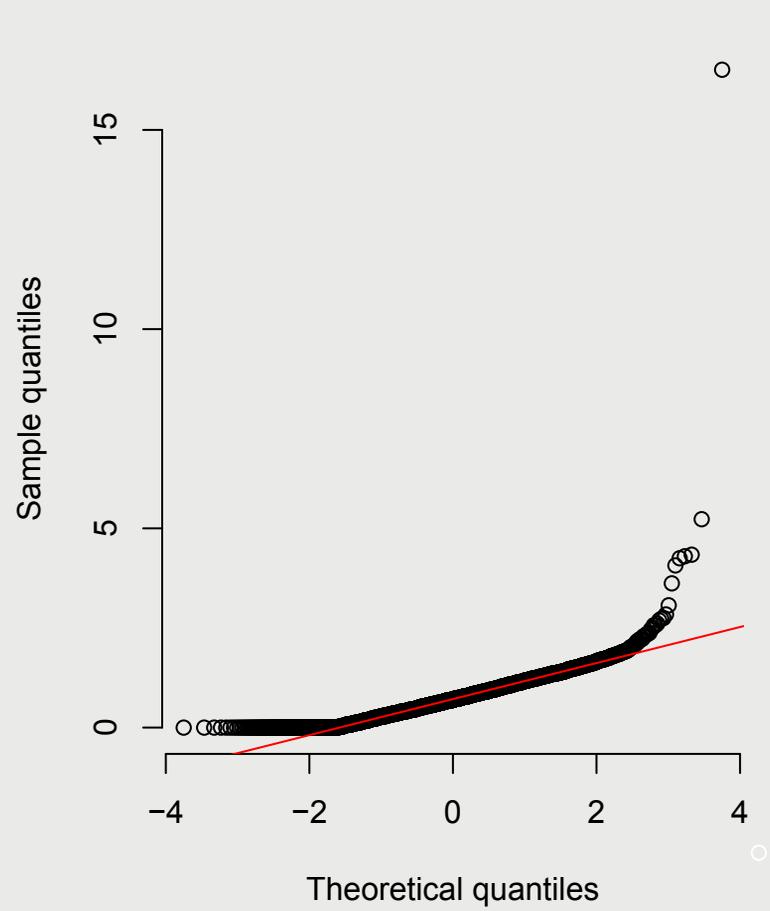
The mean and median concentrations of Ta in NSI soils are 0.73 and 0.7 mg/kg (about half the crustal abundance), implying a near-normal concentration distribution. Only few areas across England and Wales have soil concentrations above its typical crustal abundance. In comparison with geochemical maps of Nb, Ta concentrations seem to be more dispersed and less geologically defined. However, similarly to Nb, the highest concentrations (>1 mg/kg) relate to the Devonian terrane of the south-west (where the highest value, 16.5 mg/kg, occurs over the St Austel granite), the nonmarine Lower Cretaceous sandstones and clays of the Weald in the south-east, and Ordovician and Silurian strata of south-west and mid Wales. Elevated concentrations are also visible over marine alluvium along the Lincolnshire and Essex coasts.

Areas with low soil Ta values are poorly defined, being mostly below the practical analytical detection limit, but appear to be most prominent over the Pennines and East Anglia.

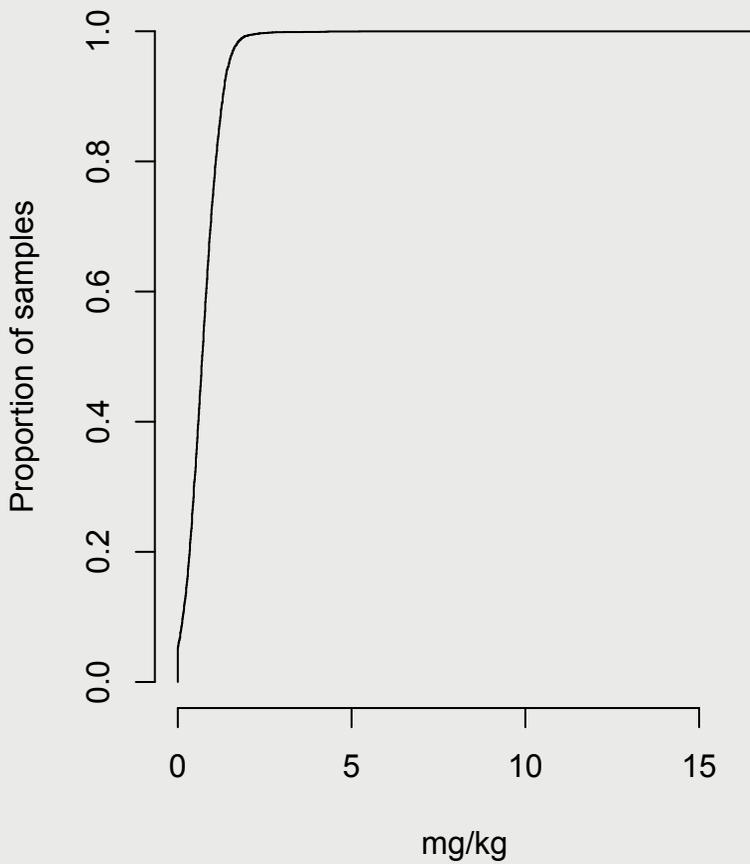
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Ta - Tantalum mg/kg

mean= 0.73

median= 0.7

10th percentile= 0.14

25th percentile= 0.41

75th percentile= 1

90th percentile= 1.3

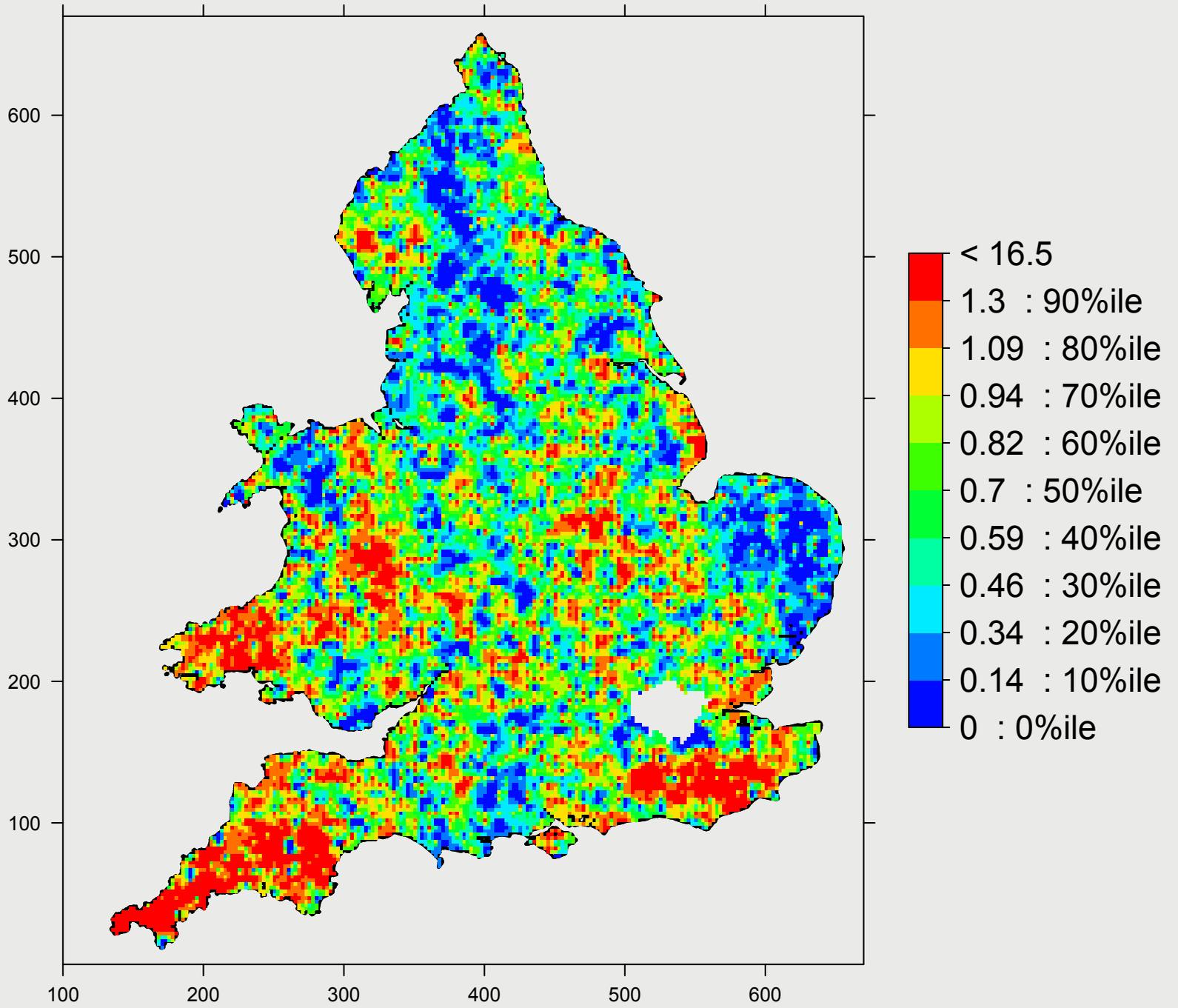
min= 0

max= 17

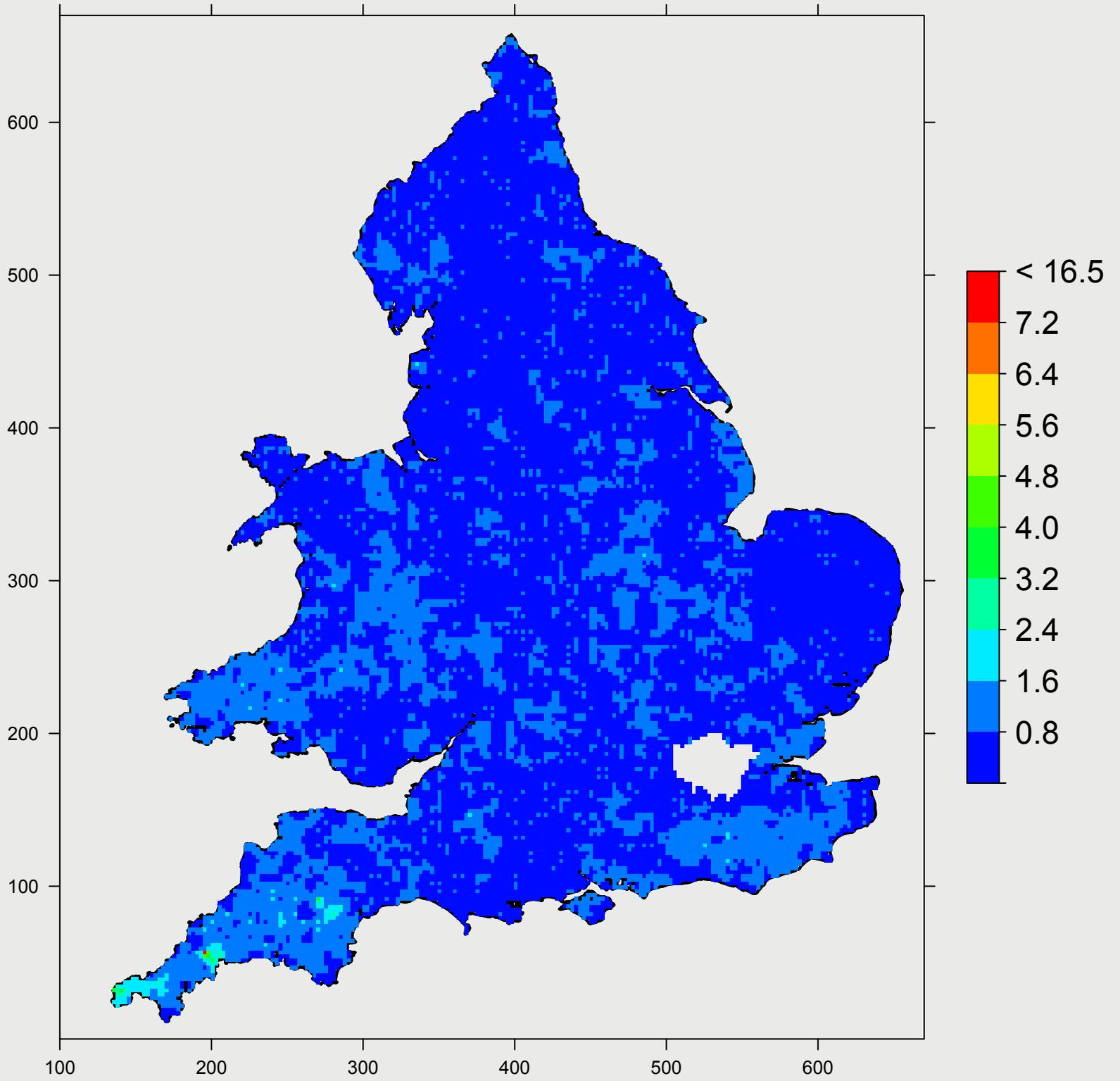
skewness= 6.3

n= 5670

Topsoil tantalum (mg/kg ; percentile scale)



Topsoil tantalum (mg/kg ; arithmetic scale)



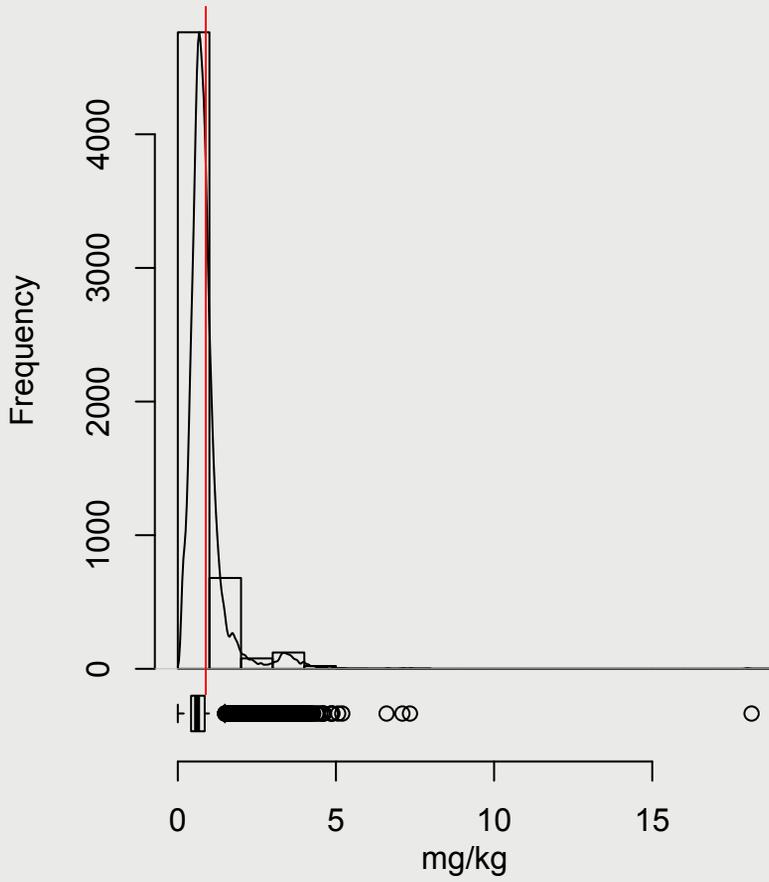
Thallium (Tl)

Thallium is a rare, very soft heavy metal with an estimated average upper continental crust content of about 0.75 mg/kg Tl. It is considered non-essential but highly toxic. Thallium forms rare minerals such as crookesite and iorandite; and also occurs in many sulphide ores (lead and zinc) as well as in common rock-forming minerals such as K-feldspar and micas. It is more abundant in granites (1.1 mg/kg) and shales (1 mg/kg) than in basic igneous rocks (0.18 mg/kg) but, as it has strong affinities for sulphur and organic matter and is enriched in coals (3 mg/kg: Reimann and De Caritat, 1998). It is used in industry in alloys, electronics, glass and pharmaceuticals. Mean and median concentrations in NSI topsoil are similar, being 0.75 and 0.61 mg/kg respectively.

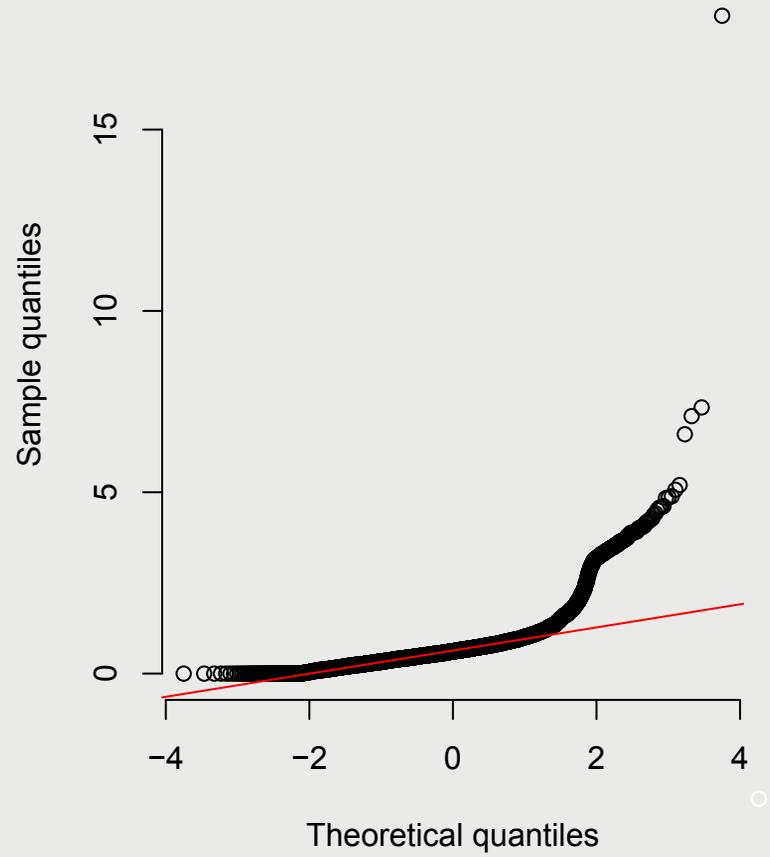
Elevated concentrations can be found in topsoils from a) the north-west covering most of the Lake District and the Pennines and Peak District, b) northern and mid Wales (Snowdonia), c) the Bristol area and the eastern Mendip Hills, and south-west England (Devon and Cornwall). In most cases these are associated with Pb-Zn mining and smelting, and other industrial activity. In Somerset and elsewhere there may also be an association with Lower Jurassic black shales. Across most of central and eastern England, elevated concentrations are more dispersed but seem to correlate with low-lying areas with organic-rich soils, such as the Fen Basin and Norfolk Broads.

Low-Tl areas are more poorly defined, but certainly include the Chalk outcrop and sandy soils in southern England.

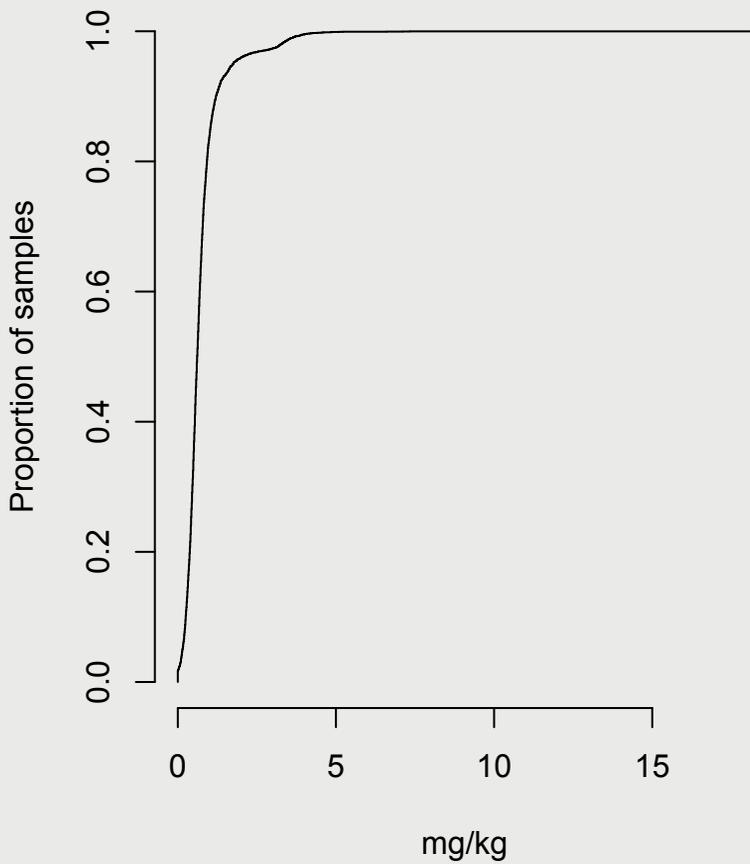
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Tl - Thallium mg/kg

mean= 0.75

median= 0.61

10th percentile= 0.25

25th percentile= 0.42

75th percentile= 0.85

90th percentile= 1.2

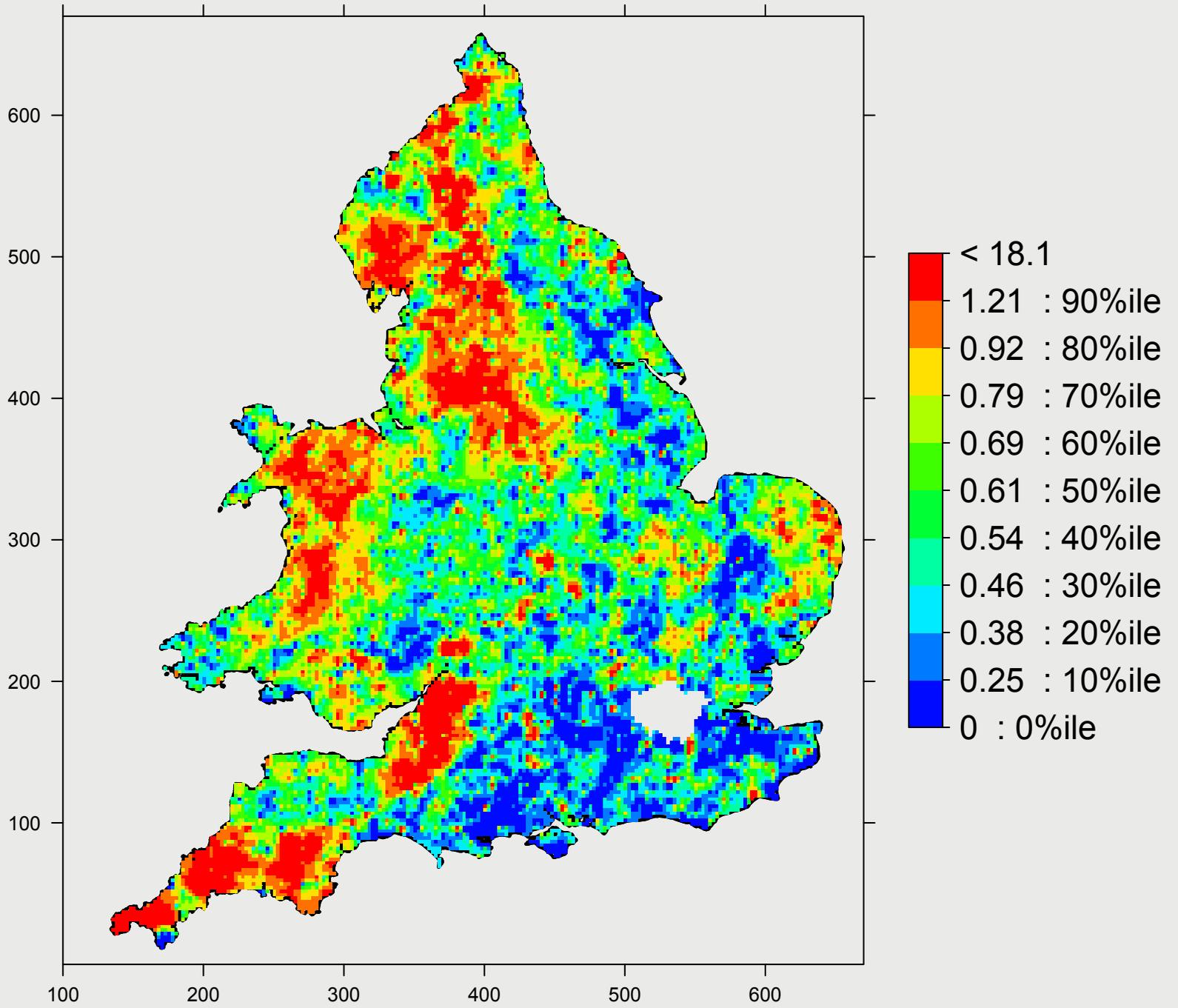
min= 0

max= 18

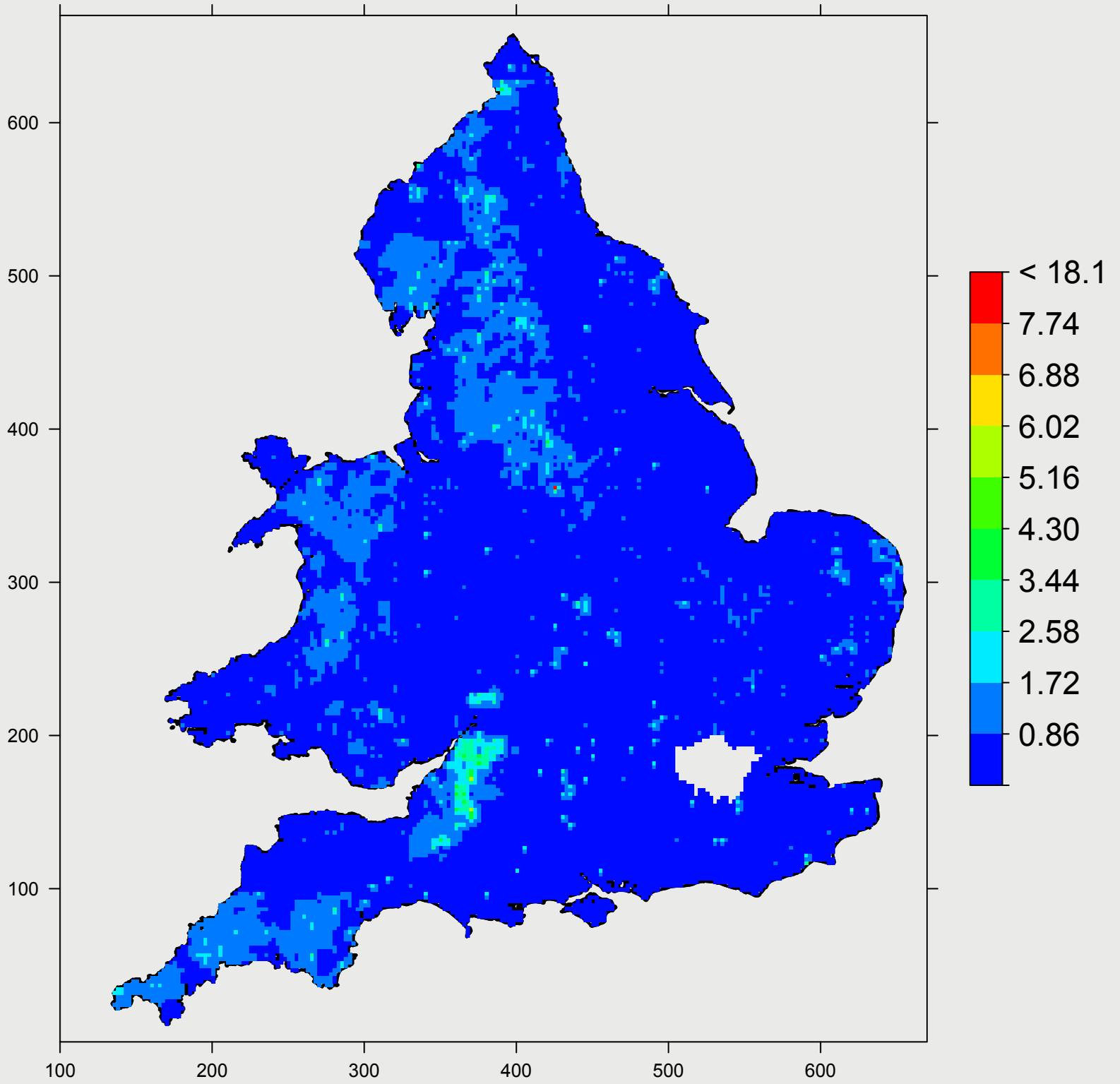
skewness= 5.8

n= 5670

Topsoil thallium (mg/kg ; percentile scale)



Topsoil thallium (mg/kg ; arithmetic scale)



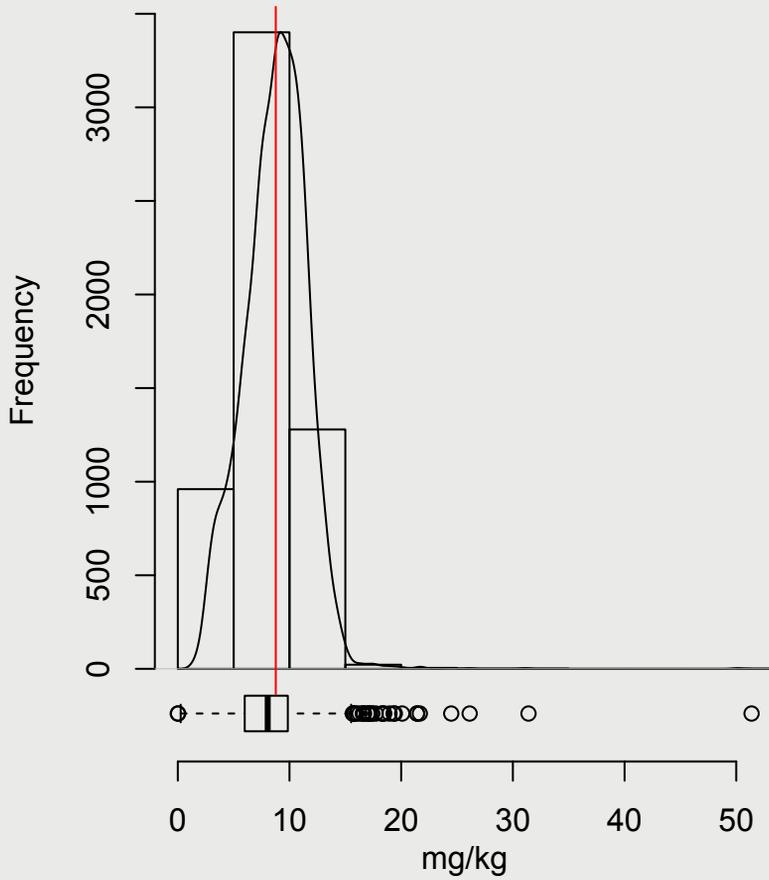
Thorium (Th)

Thorium is a radioactive heavy metallic element of the actinide group that is considered non-essential, but radiotoxic and carcinogenic, due to its slow decay and emission of alpha radiation, the most stable isotope being ^{232}Th . It has an average crustal abundance of around 10 mg/kg and is naturally associated with K, U and the rare earth elements, especially Ce. It occurs principally in silicate minerals such as thorite and monazite, but is also often present in zircon, sphene and epidote; and can be present in P fertilisers and as by-product of U mining and processing. Thorium is predominantly used in the nuclear industry and in special metallurgical alloys and coatings (Reimann and De Caritat, 1998). NSI soils contain mean and median concentrations of around 8 mg/kg with the upper 10th percentile concentrations ranging from 11 to a maximum of 51 mg/kg.

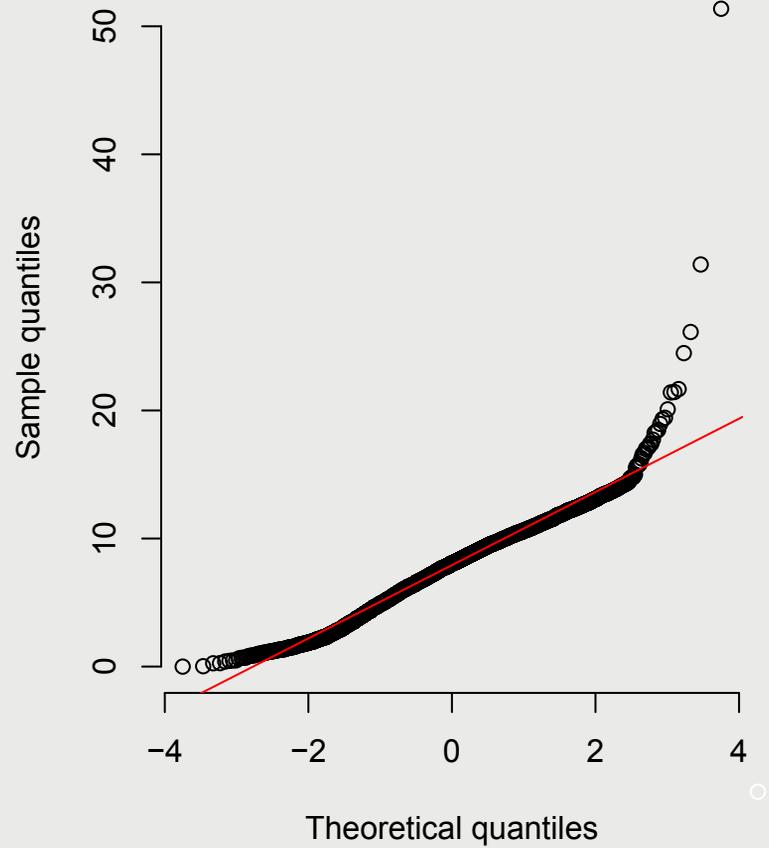
These higher concentrations relate to several principal areas: a) the Silurian of mid and south-west Wales and the Old Red Sandstone of the Welsh Borders b) the Devonian-Carboniferous sedimentary terrane in the south-west, excluding the major granitic intrusions c) the Jurassic outcrop of central England extending from Somerset to Lincolnshire, especially the ironstones and ferruginous sandstones and d) the nonmarine Lower Cretaceous sedimentary strata of the Wealden district of south-east England.

The lowest concentrations (<6 mg/kg) were measured in soils overlying the Cretaceous Chalk of southern England and East Anglia (including the post-Cretaceous cover) as well as the Triassic mudstones of the Midlands and the Carboniferous of the Pennines.

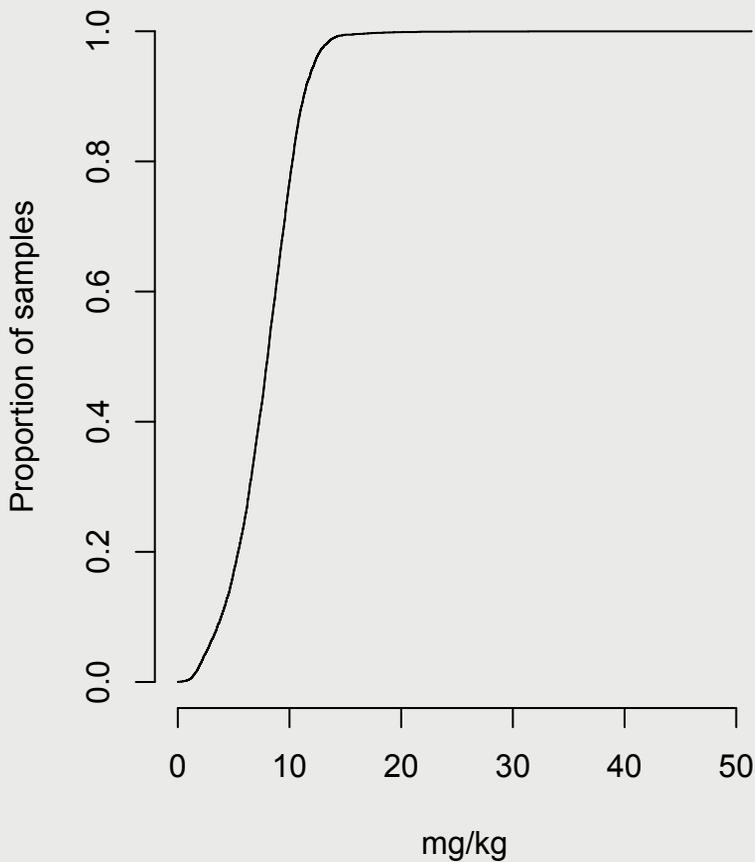
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Th - Thorium mg/kg

mean= 7.9

median= 8.1

10th percentile= 3.9

25th percentile= 6

75th percentile= 9.8

90th percentile= 11

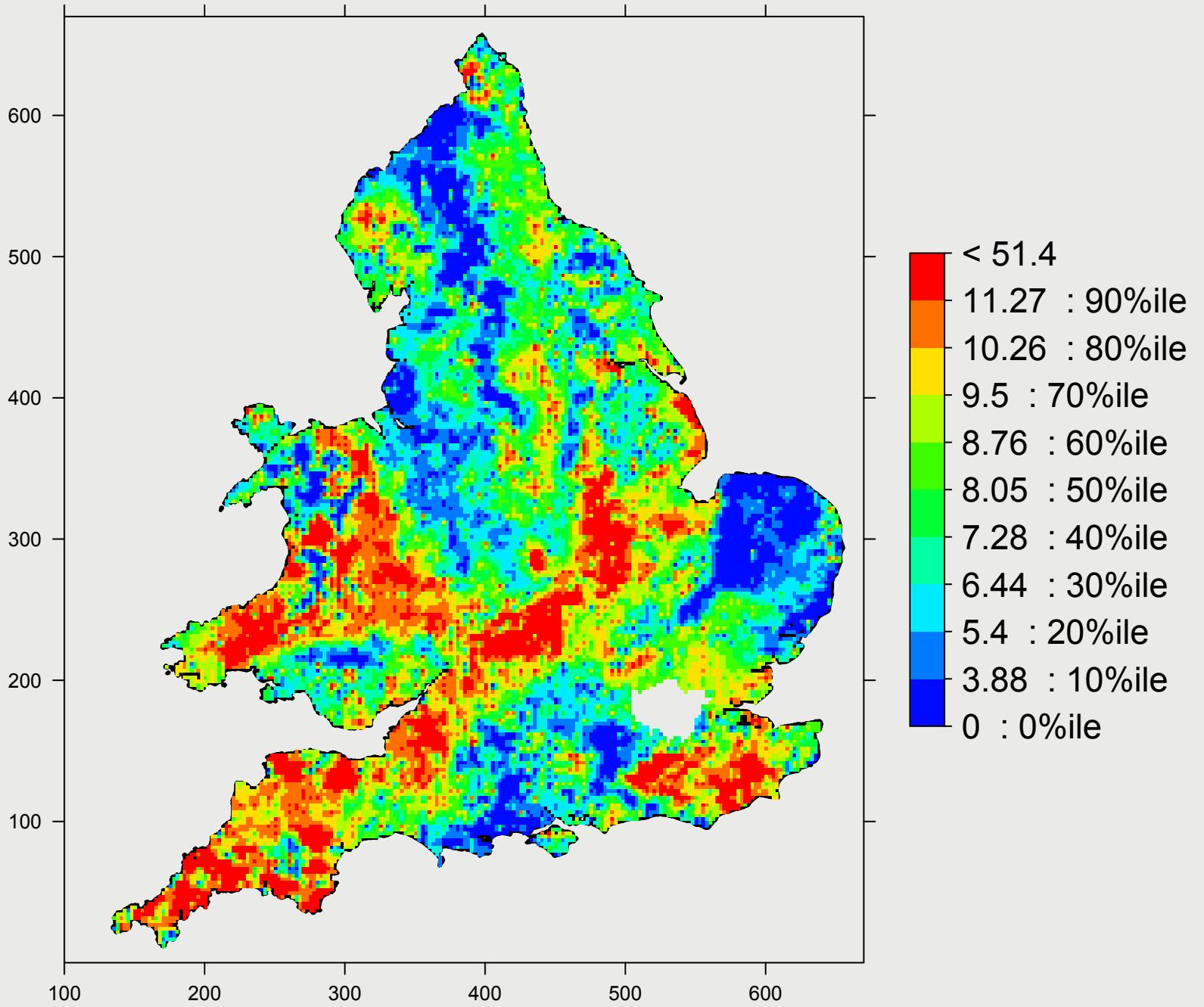
min= 0

max= 51

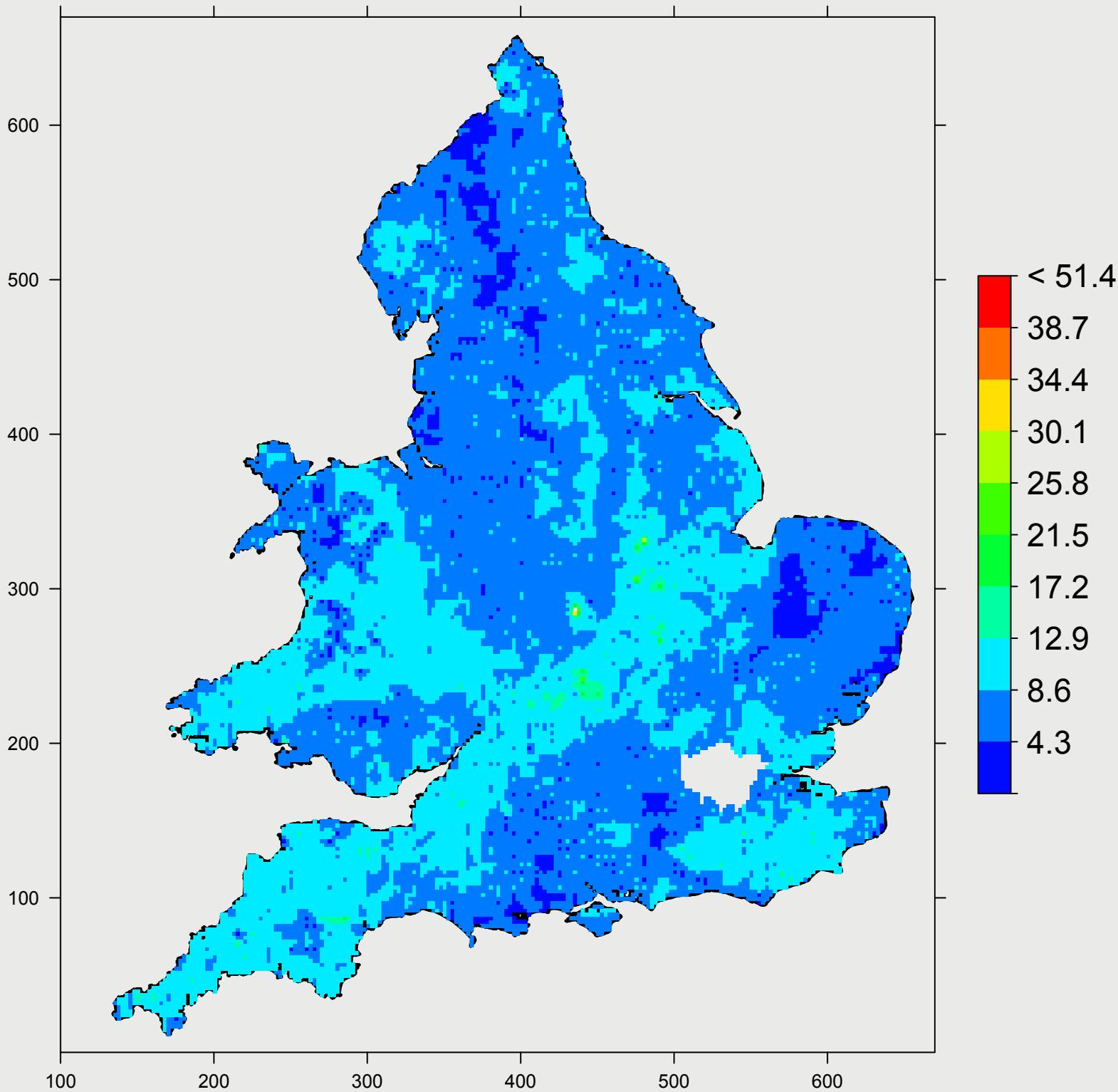
skewness= 0.63

n= 5670

Topsoil thorium (mg/kg ; percentile scale)



Topsoil thorium (mg/kg ; arithmetic scale)



Tin (Sn)

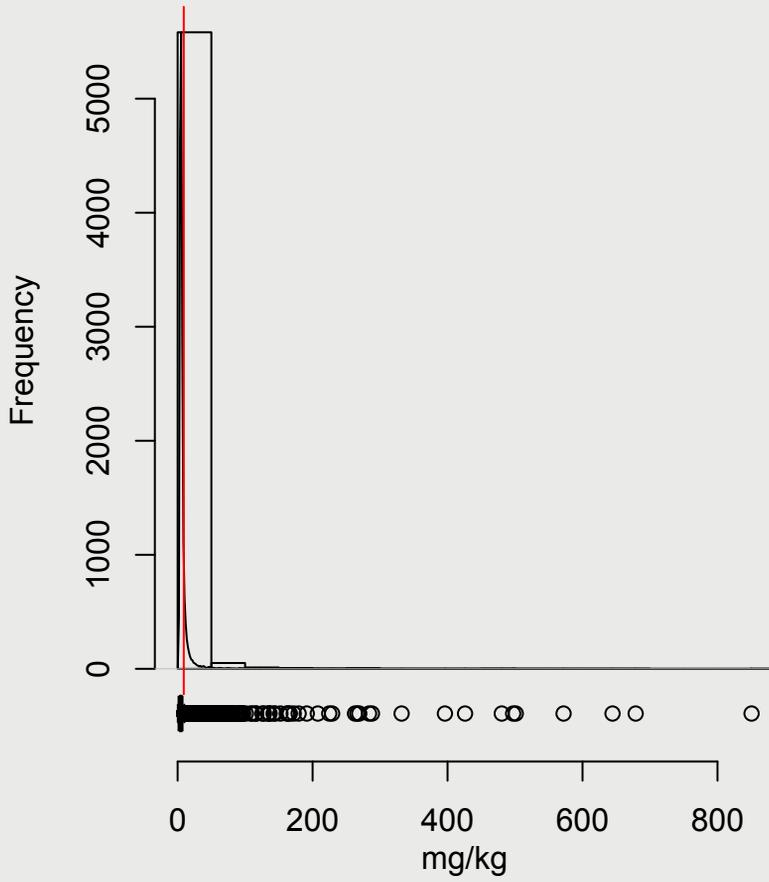
Tin is a metallic element with an estimated average upper continental crustal abundance of 2.5–5.5 mg/kg, and is more common in granites (3.6 mg/kg) than in basic igneous rocks (0.9 mg/kg). The principal Sn ore mineral is cassiterite (SnO_2) but it can also be present in more common rock-forming minerals such as micas, amphiboles, rutile and magnetite. Tin is possibly essential for some organisms, including humans, but is also toxic for 'lower' organisms (Reimann and De Caritat, 1998). Inorganic Sn compounds are thought to be mainly non-toxic, but organo-tins, used for industrial and agricultural purposes, are significantly more toxic (Cooney and Wuertz, 1989). Their use in antifouling marine paints had led to serious problems with accumulation in marine organisms, notably shellfish. Inorganic Sn is used in the production of steel, coatings and alloys (notably solders) as well as paints.

Mean and median concentrations for soils across England and Wales are 8.2 and 4.3 mg/kg respectively, indicating a large number of outliers, which are also reflected by a skewness coefficient of 17. The upper 10% of the data range almost over two magnitudes from 11 to 850 mg/kg. Whilst some of the elevated concentrations clearly correlate to bedrock geology in the Lake District, Snowdonia, the Cambrian Mountains of central Wales, and especially in south-west England where Sn mineralisation is present and was formerly extensively mined, others outline densely populated conurbations, which include all major cities, e.g. Bristol, Birmingham, London, Hull, Newcastle, and wider areas around Liverpool, Manchester and Swansea (a former centre of Sn smelting). This implies anthropogenic processes, such as smelting, engineering and coal burning as a source of Sn in these areas. The highest soil Sn concentrations (>120 mg/kg) however are best observed in the arithmetic map, which indicates that these are strongly associated with mining and smelting processes in Cornwall, south-west England.

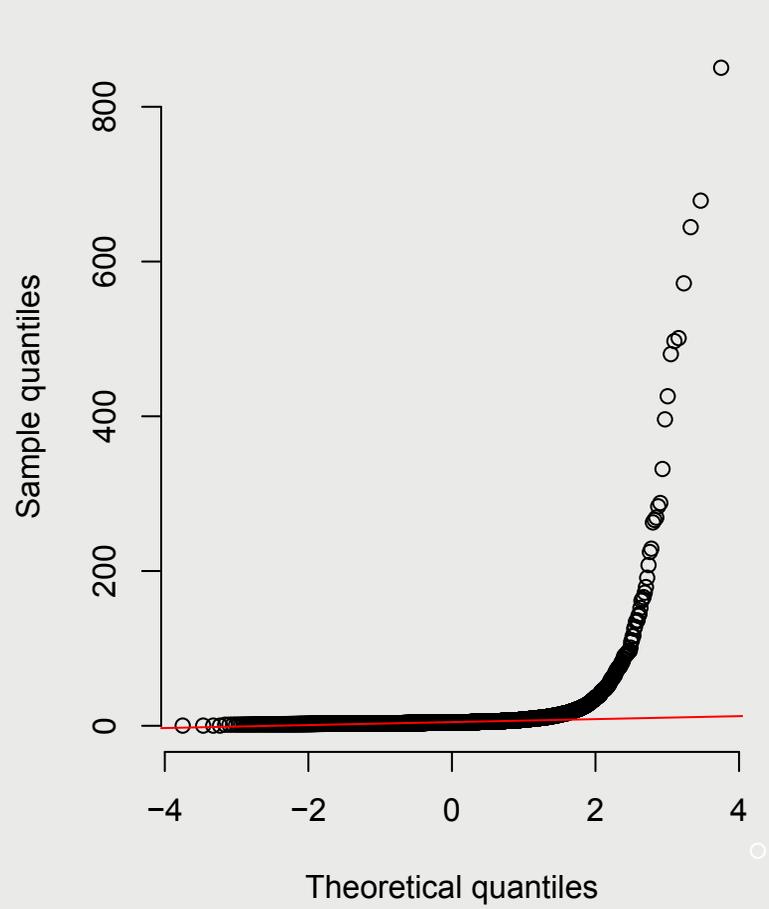
Very low Sn concentrations are present over large parts of eastern and southern England, especially in East Anglia.



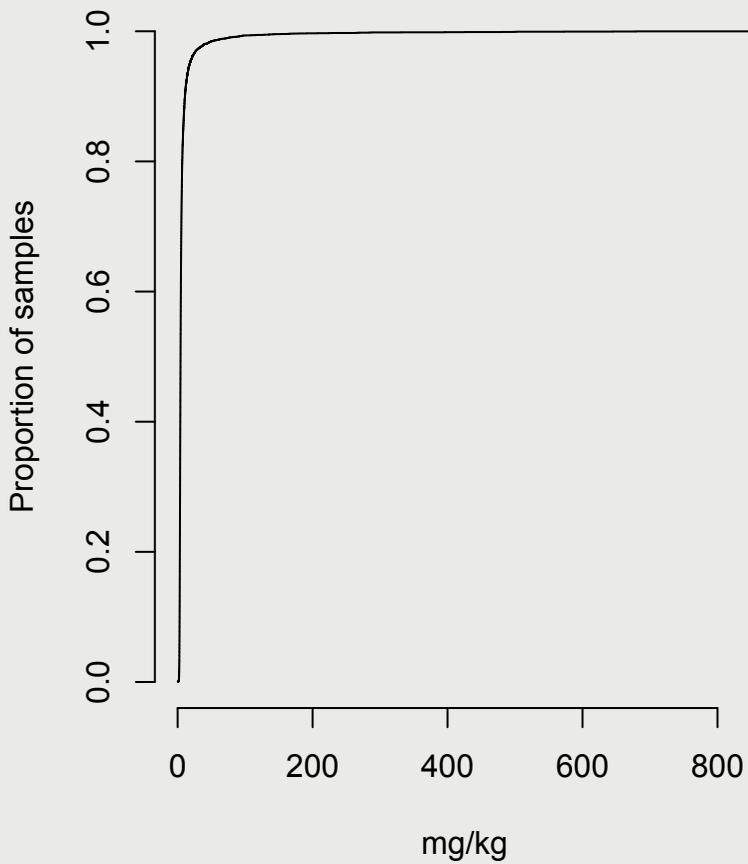
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Sn - Tin mg/kg

mean= 8.2

median= 4.3

10th percentile= 2.9

25th percentile= 3.5

75th percentile= 6

90th percentile= 11

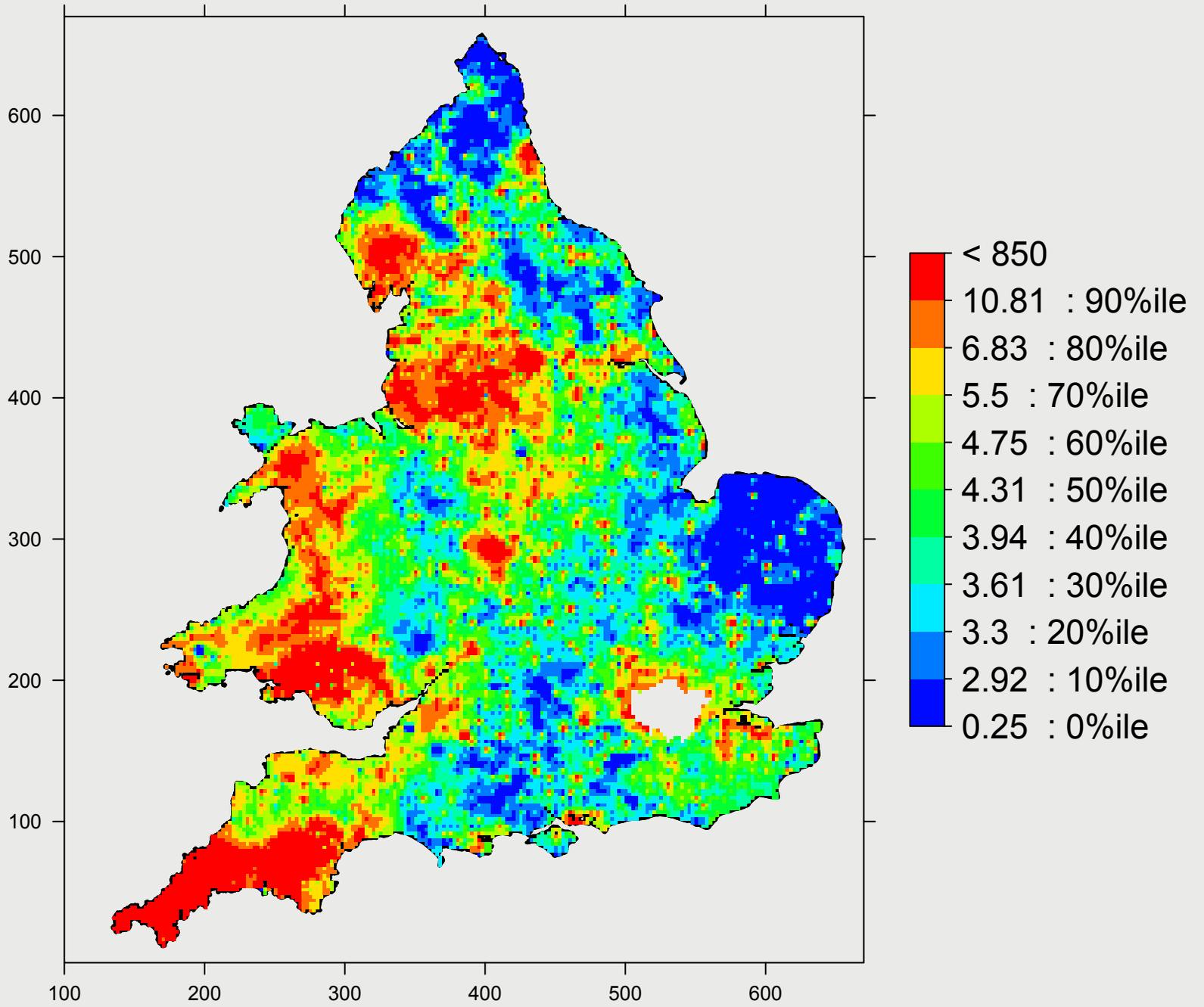
min= 0.25

max= 850

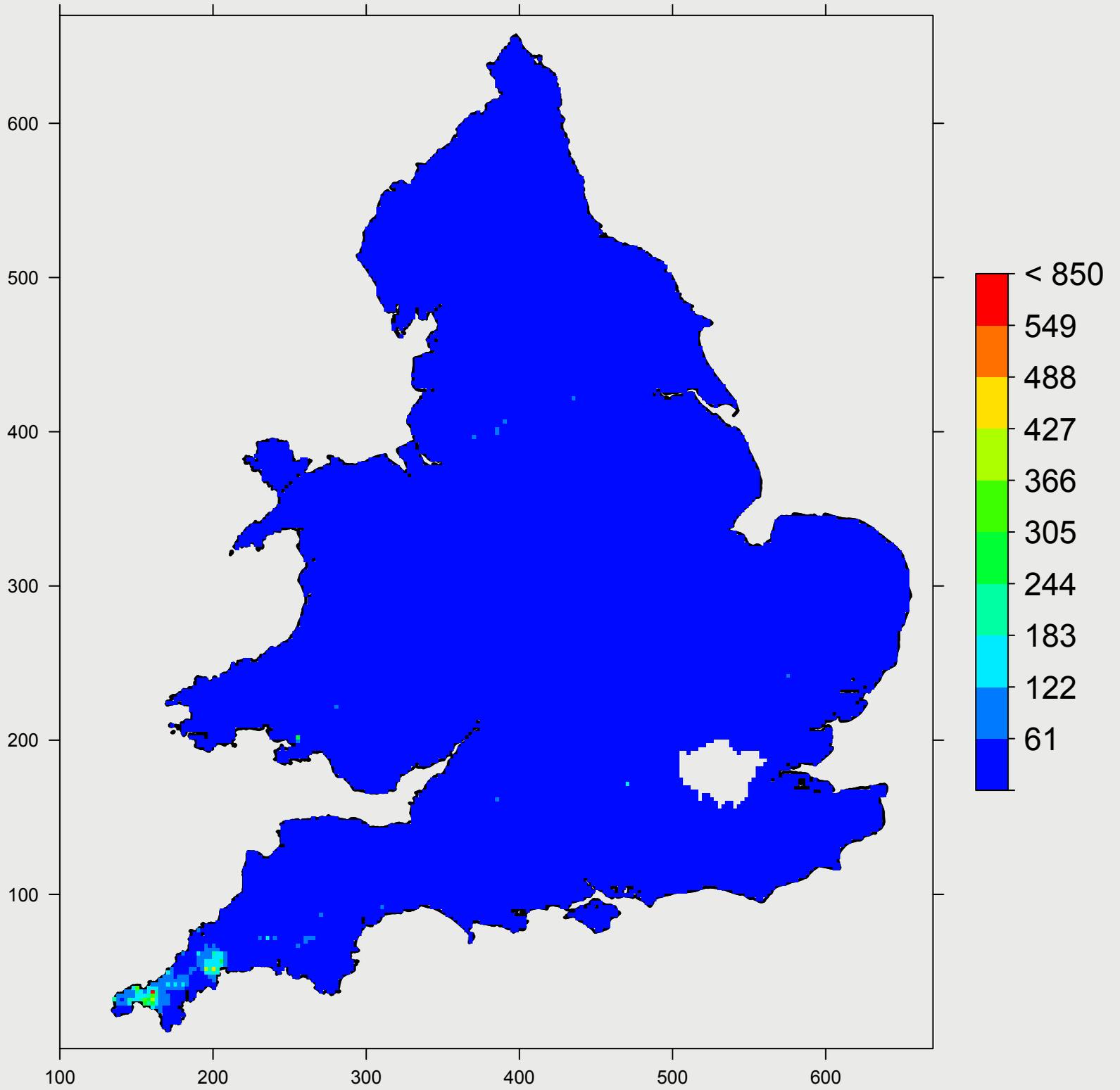
skewness= 17

n= 5670

Topsoil tin (mg/kg ; percentile scale)



Topsoil tin (mg/kg ; arithmetic scale)



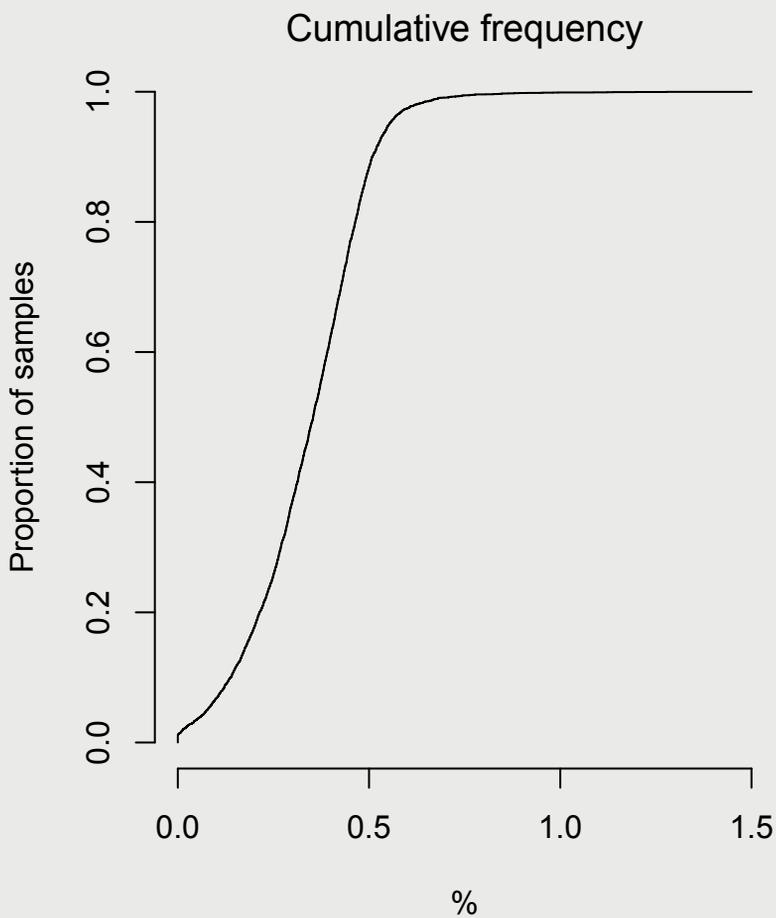
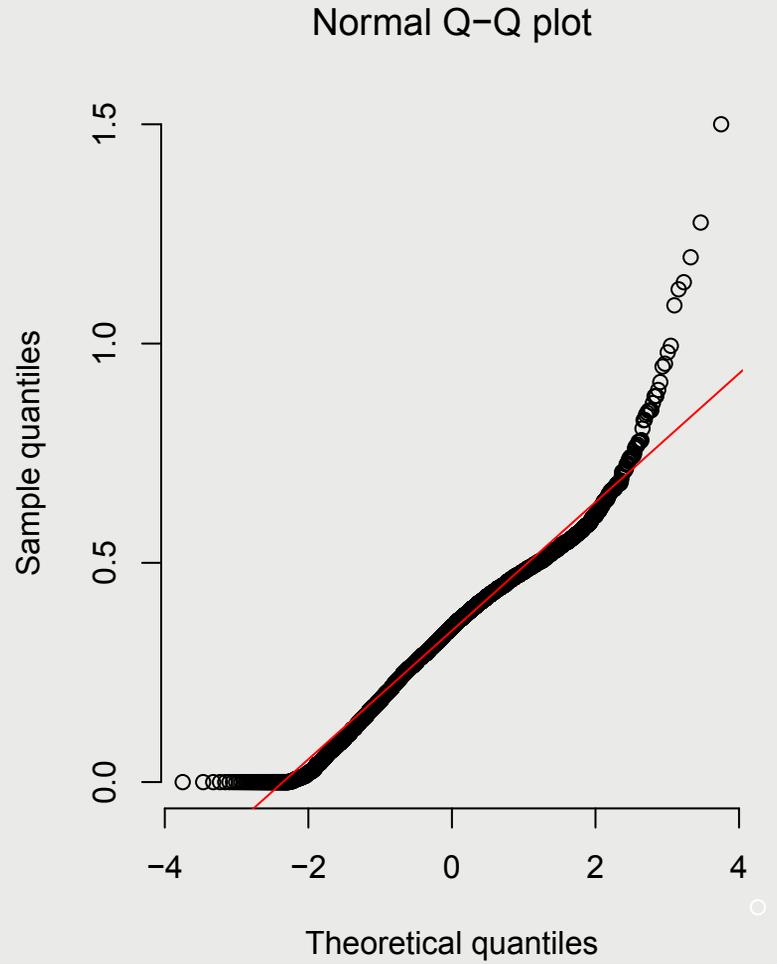
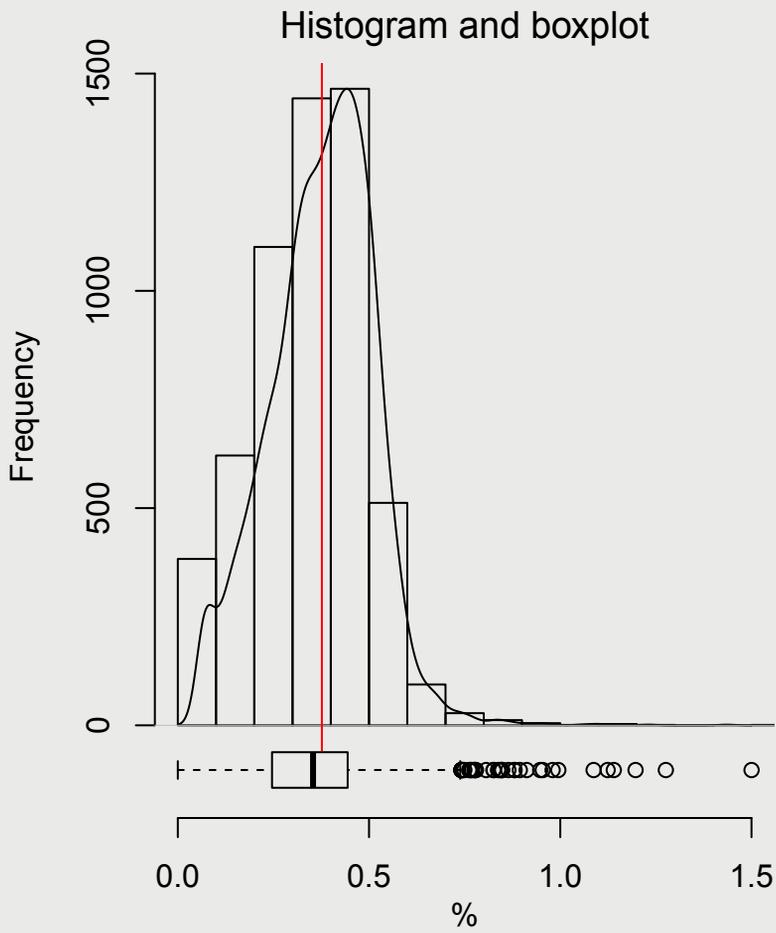
Titanium (Ti)

Titanium is one of the major metallic elements and is present at an estimated average concentration in the upper continental crust of between 0.3 and 0.31% by weight (Reimann and De Caritat, 1998), being more abundant in basic igneous rocks (1%) than in granites (0.3%). It is mainly found in the rather resistate minerals ilmenite, sphene and rutile. It is considered non-essential and non-toxic. In NSI topsoils, Ti concentrations are similar with mean and median concentrations of 0.34 and 0.35% respectively.

Overall the data are fairly normally distributed with elevated topsoil concentrations mainly related to Lower Cretaceous nonmarine sandstone and clays of the Wealden District of Sussex and Kent in south-east England, the Devonian and Carboniferous sedimentary terrane of south-west England and pre-Carboniferous sedimentary strata of mid and western Wales and the Welsh Borders. The pattern in Wales shows a very sharp gradient north of the south Wales coalfield which is shown by several other elements with 'resistate' mineral hosts. Other higher concentrations were reported in marine alluvium-based soils from the Lincolnshire coast, the Thames estuary, the Lower Palaeozoic sedimentary rocks of the Lake District, the Peak District and in parts of the Lower Jurassic of central England.

The lowest concentrations (<0.25%) relate to the northern part of East Anglia, the soils over the Cretaceous outcrops of southern England and the Triassic and Carboniferous strata of the northern half of England.





Ti - Titanium %

mean= 0.34

median= 0.35

10th percentile= 0.14

25th percentile= 0.25

75th percentile= 0.44

90th percentile= 0.51

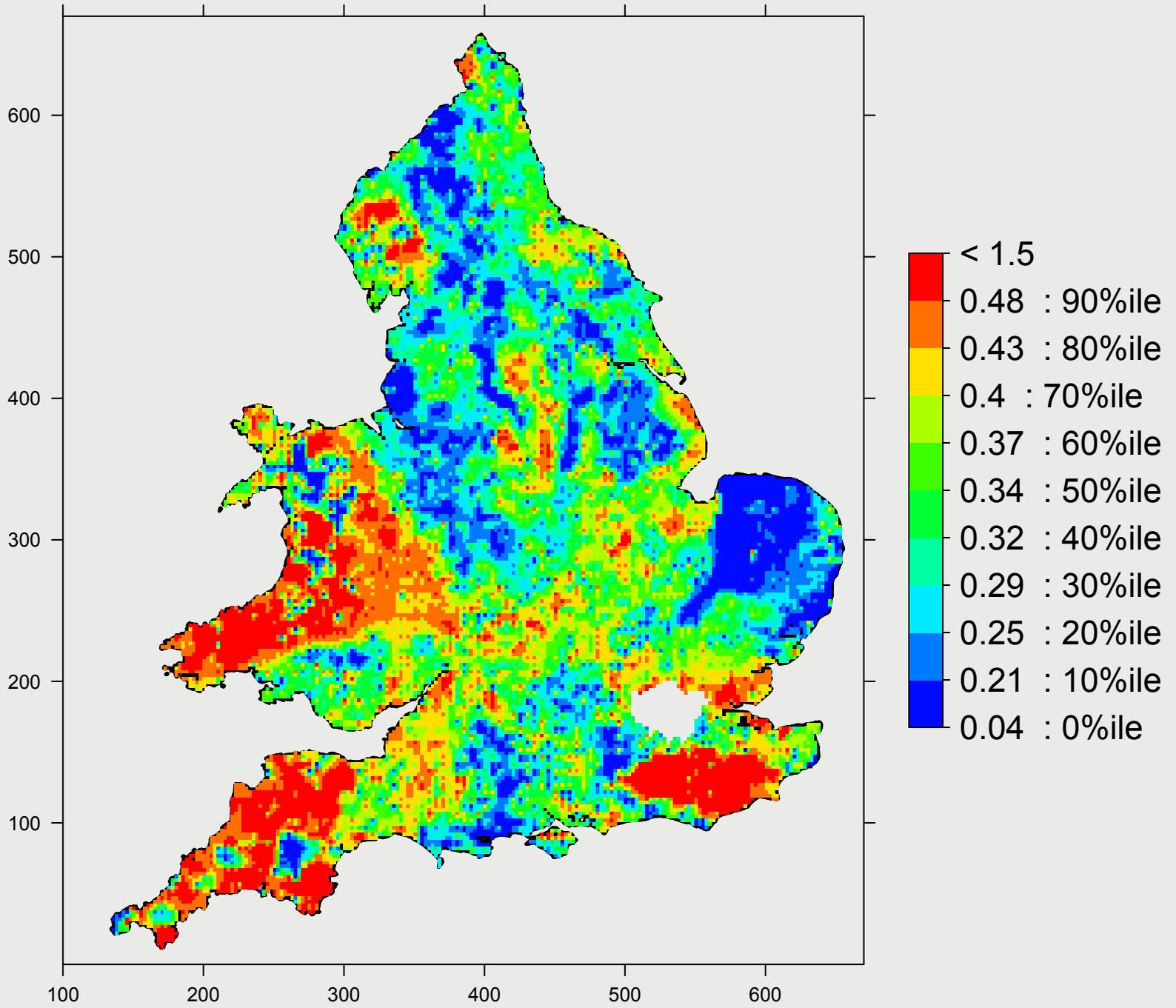
min= 0

max= 1.5

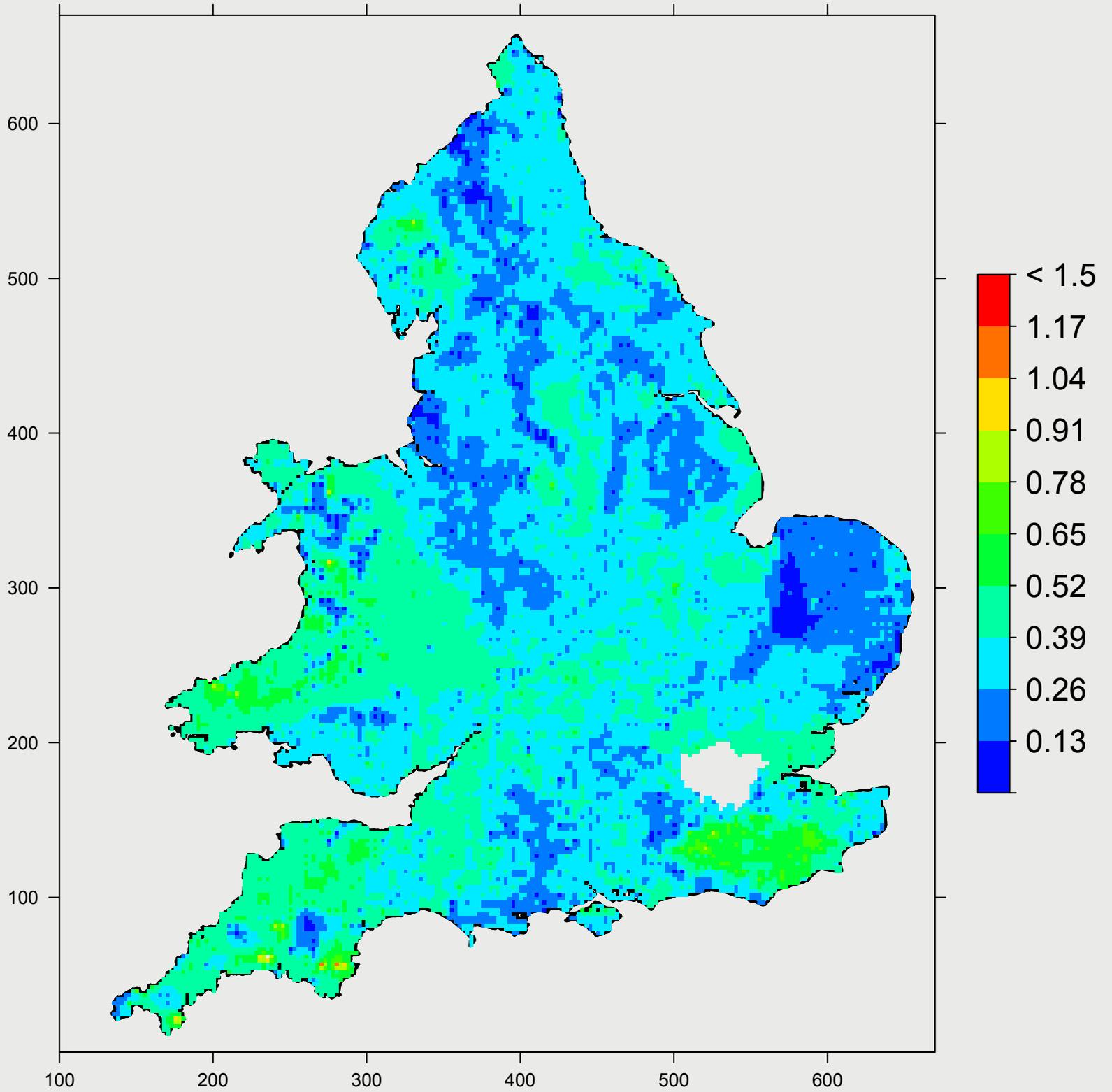
skewness= 0.11

n= 5670

Topsoil titanium (% ; percentile scale)



Topsoil titanium (% ; arithmetic scale)



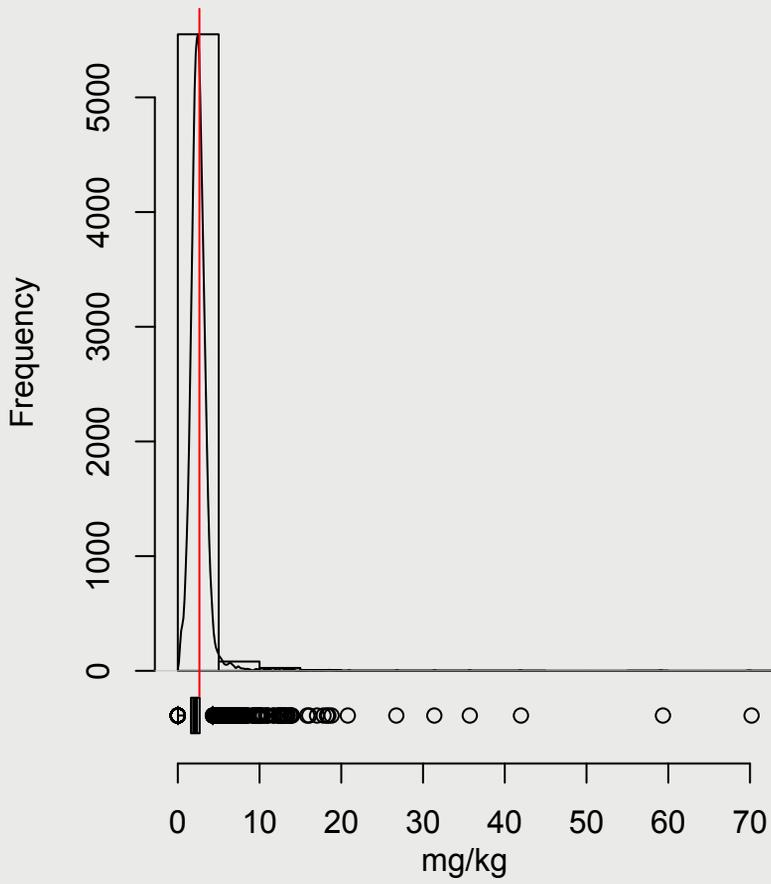
Tungsten (W)

Tungsten is a rather rare, hard and high melting-point heavy metallic element with an estimated upper continental crustal abundance of about 1.4–2.0 mg/kg. Its principal minerals are the tungstates scheelite (CaWO_4) and wolframite ($(\text{Fe},\text{Mn})\text{WO}_4$), but it is also present in micas, powellite (CaMoO_4), Mn-oxide minerals and possibly others. There are some geochemical similarities between W and Mo, but also major differences, notably W having a lower affinity for sulphur. There is some evidence that W is biologically active and may be an important trace element for some plants. The special properties of W metal give rise to many industrial applications, notably in tool steels, abrasives, light bulbs, X-ray tubes and catalysts.

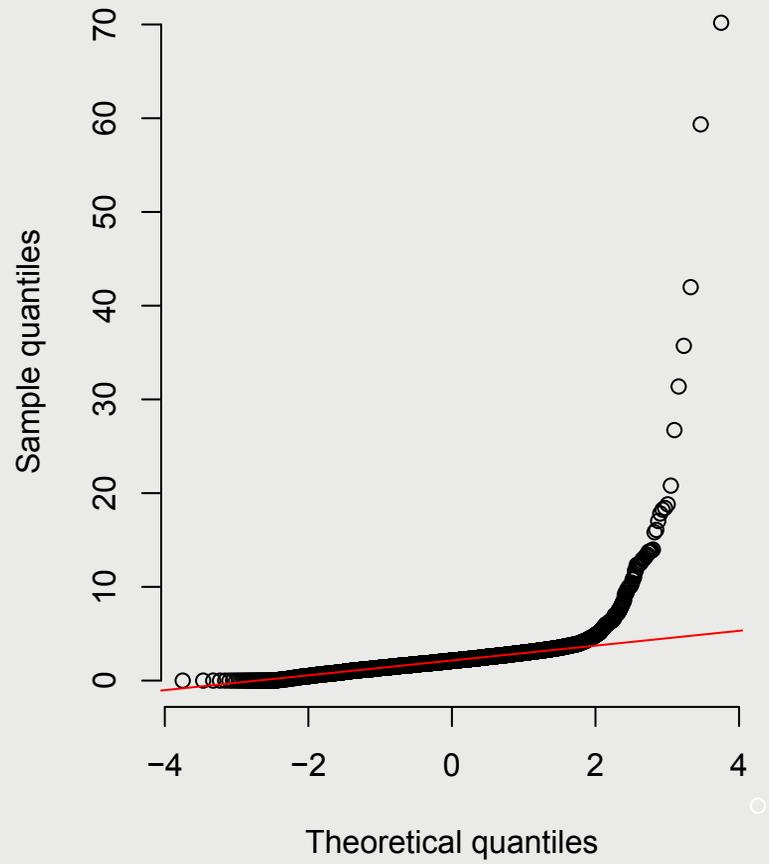
Despite the similarities of Mo and W, their spatial distribution is not similar in the NSI soils, except perhaps for part of Devon. In south Devon and Cornwall, W concentrations in soils are high and are associated with mining and extraction processes especially on and around the granite intrusions of Dartmoor, Bodmin Moor and St Austell (and in the lower Tamar Valley where a maximum value of 74 mg/kg W is present) and this correlates closely with Sn. Mineral veins related to the intrusions contain minerals such as cassiterite and wolframite (ores of Sn and W respectively) which have been mined extensively over time. The only other centre of W mineralisation in the UK is at Carrock Fell in the northern Lake District, and this is shown by the percentile map, although a higher value is present at nearby Shap Fell. Elsewhere there are elevated soil W levels in the Bristol area possibly related to smelting, and the Lower Cretaceous nonmarine sands and clays in the Weald also contain relatively high concentrations of W, suggesting (along with other elements) a significant resistate mineral suite in these sediments. Some isolated W anomalies are almost certainly anthropogenic.

Areas with very low W values are less well defined, but include much of eastern and central-southern England.

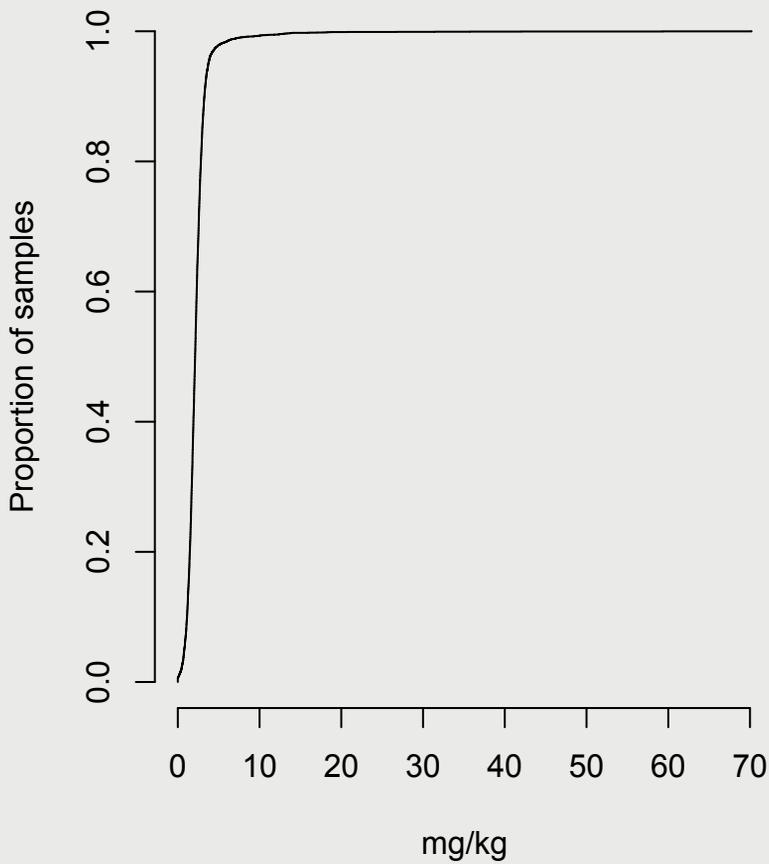
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



W - Tungsten mg/kg

mean= 2.3

median= 2.1

10th percentile= 1.1

25th percentile= 1.6

75th percentile= 2.7

90th percentile= 3.3

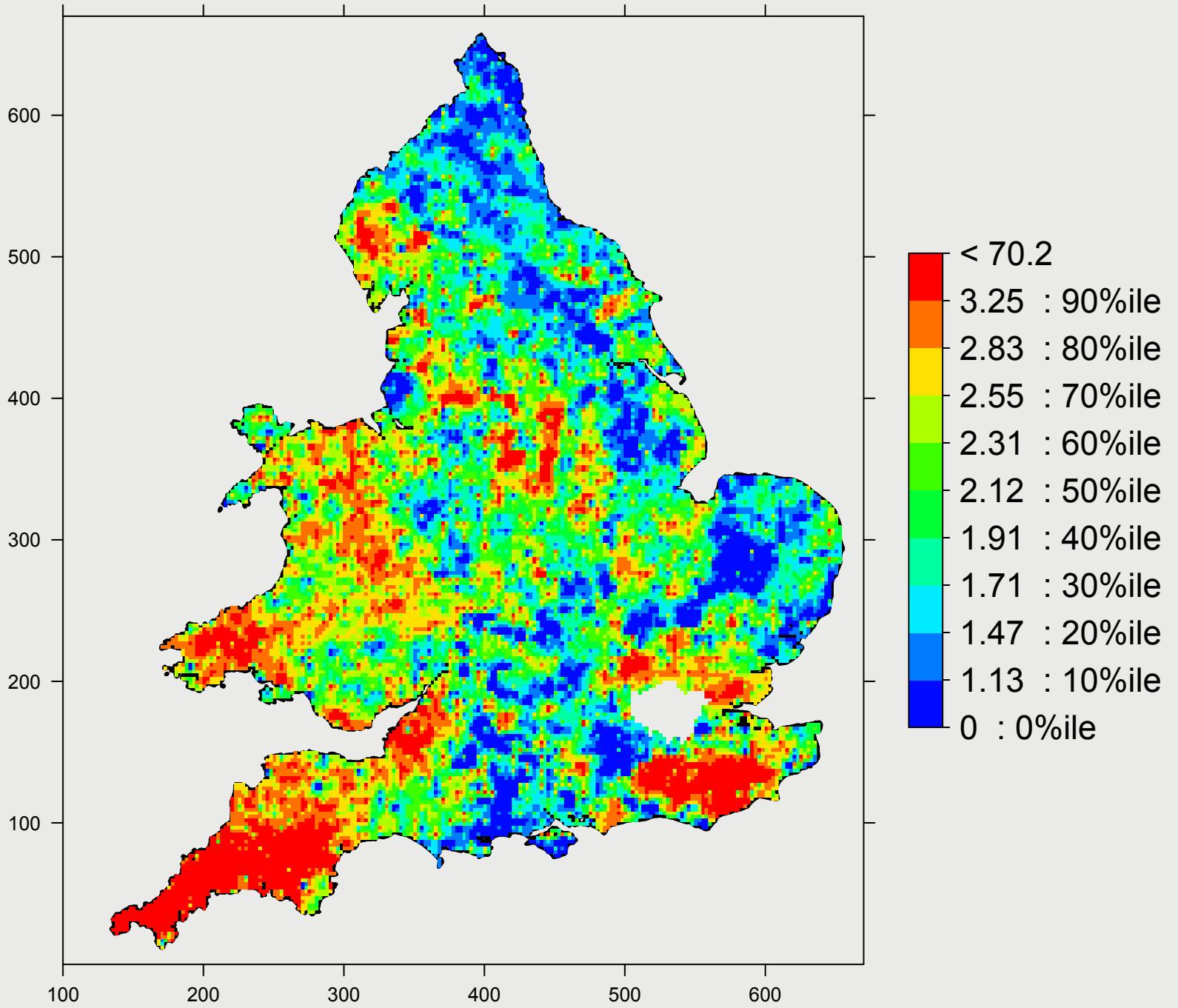
min= 0

max= 70

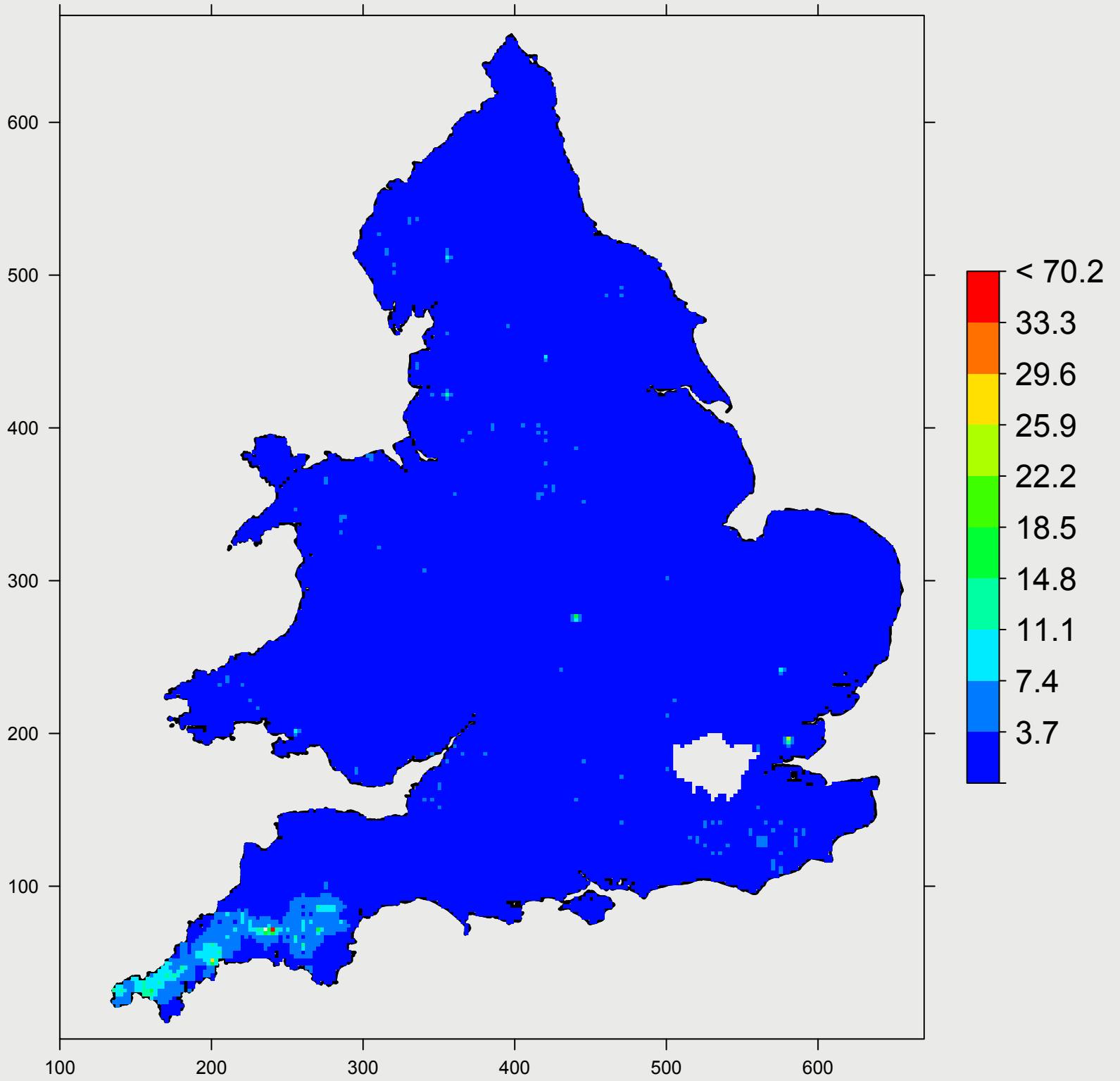
skewness= 16

n= 5670

Topsoil tungsten (mg/kg ; percentile scale)



Topsoil tungsten (mg/kg ; arithmetic scale)



Uranium (U)

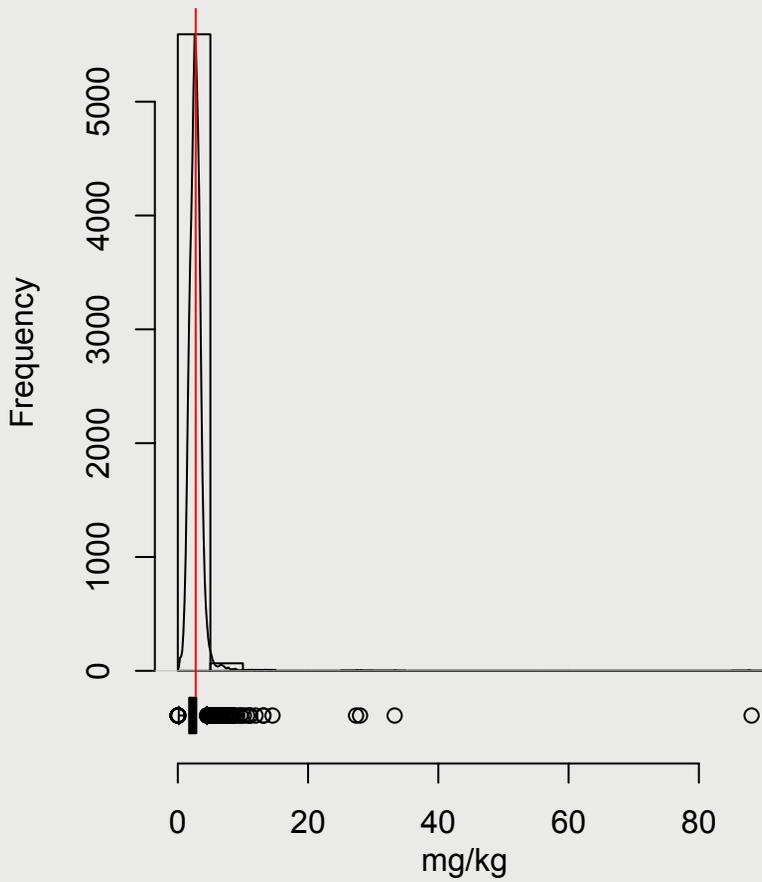
Uranium is a heavy, radioactive, metallic element of the actinide group with an estimated average upper continental crustal abundance between 2.5 and 2.8 mg/kg (Reimann and De Caritat, 1998). The most common isotope is ^{238}U , with a half life of 4.46 billion years. The primary uranium ore mineral is pitchblende (UO_2) and it is also present at trace levels in more common minerals such as zircon, apatite and monazite. It is considered non-essential, and chemo-/radiotoxic and carcinogenic. Uranium is one of the three naturally occurring radioactive elements (along with Th and K) contributing to natural terrestrial radioactivity.

Owing to its radioactive properties, U is mined for use in the nuclear industry as well as in aviation and military technologies. Mining of phosphate rock for fertilisers is an additional pathway into the environment. The mean and median values for the NSI soils are 2.4 and 2.3 mg/kg respectively, implying a near-normal concentration distribution. Over 90% of the data are below 3.3 mg/kg and only four samples above 20 mg/kg.

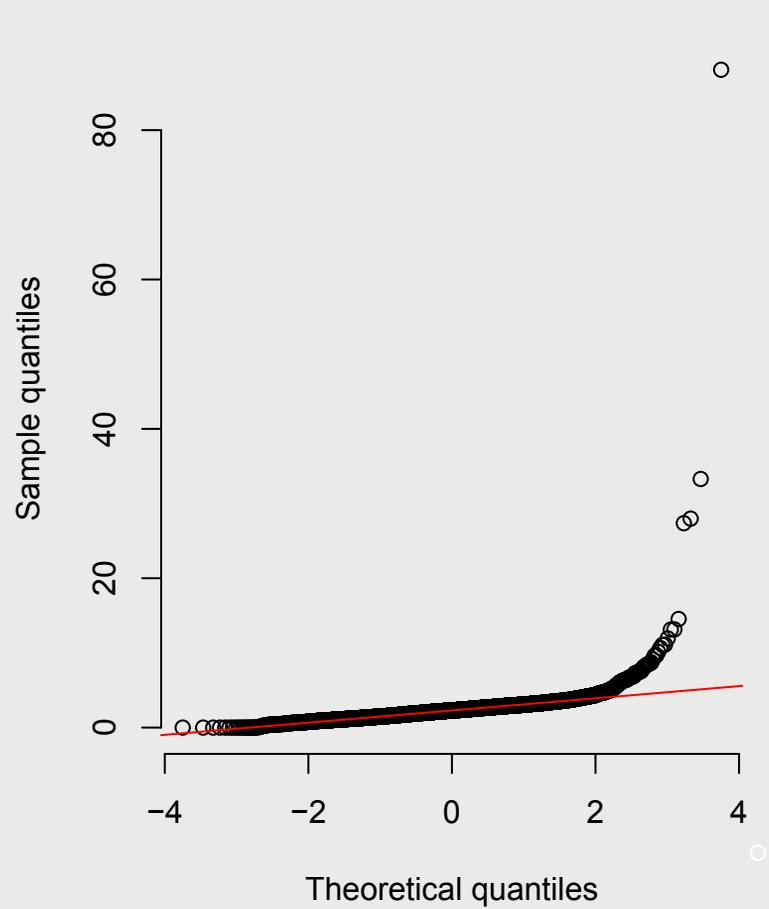
Elevated concentrations above 3.3 mg/kg mainly relate to a) Lower Cretaceous nonmarine sandstones and clays of the Wealden District in south-east England, b) the Devonian and Carboniferous terrane of Cornwall, including the granites c) Holocene peats of the Fen Basin, d) marine alluvium of the Lincolnshire coast, e) primarily Carboniferous and Permian limestone outcrops extending from the Peak district to Newcastle in the north and f) Silurian and Devonian strata between Welshpool and Hereford. The latter area also includes the highest concentration of 88 mg/kg U measured in a sample collected west of Leominster, associated with high Se and S values but with no obvious cause.

The lowest concentrations of U relate to soils from East Anglia, southern England, despite the potential input of U from phosphate fertilisers, and the high ground of the Pennines.

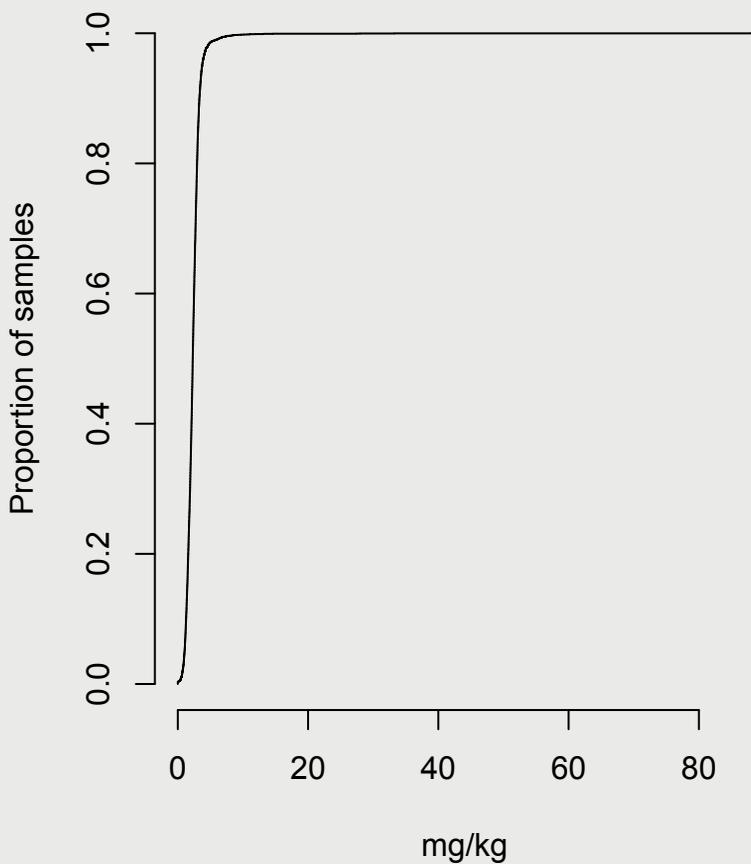
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



U - Uranium mg/kg

mean= 2.4

median= 2.3

10th percentile= 1.3

25th percentile= 1.7

75th percentile= 2.8

90th percentile= 3.3

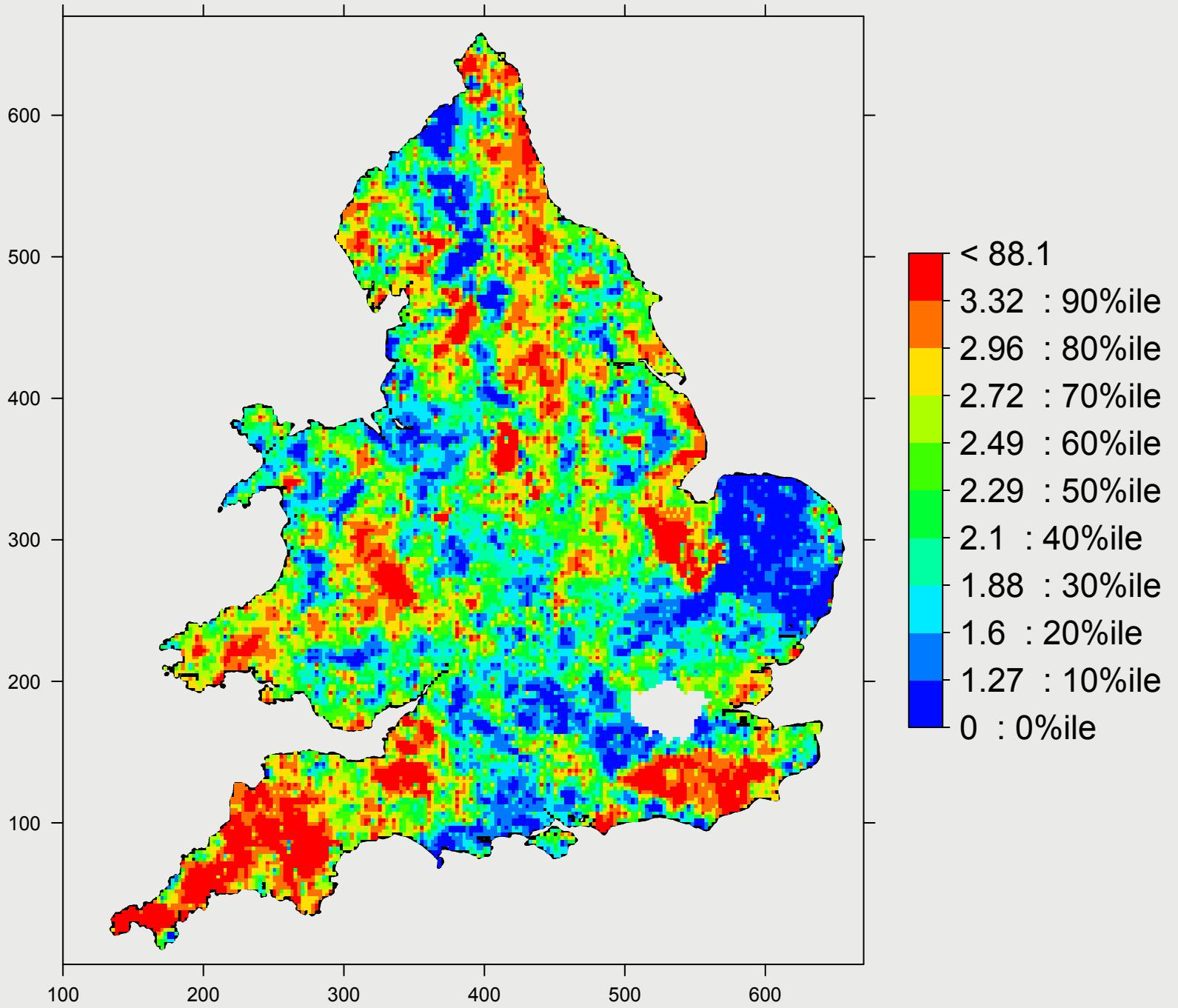
min= 0

max= 88

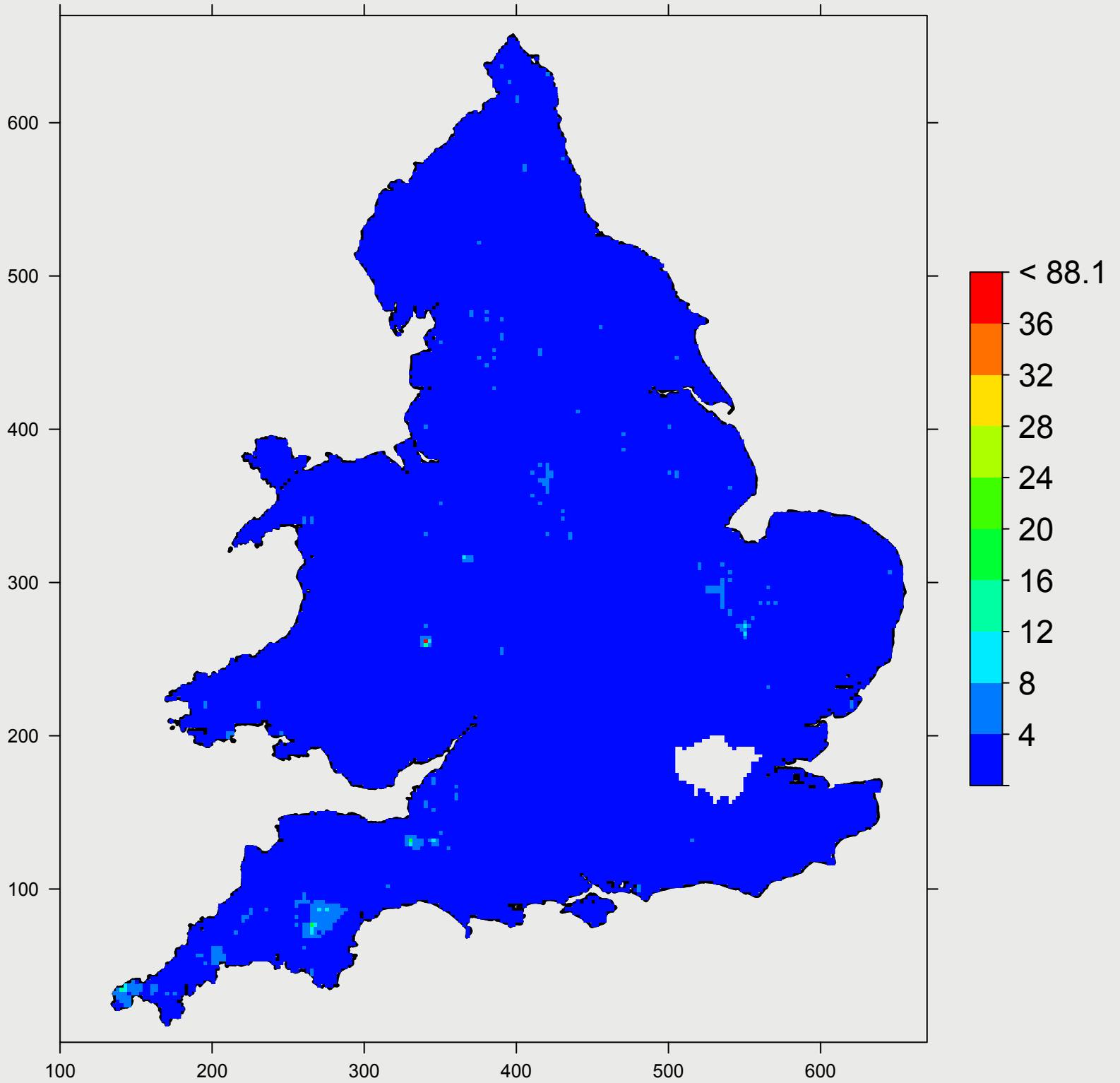
skewness= 28

n= 5670

Topsoil uranium (mg/kg ; percentile scale)



Topsoil uranium (mg/kg ; arithmetic scale)



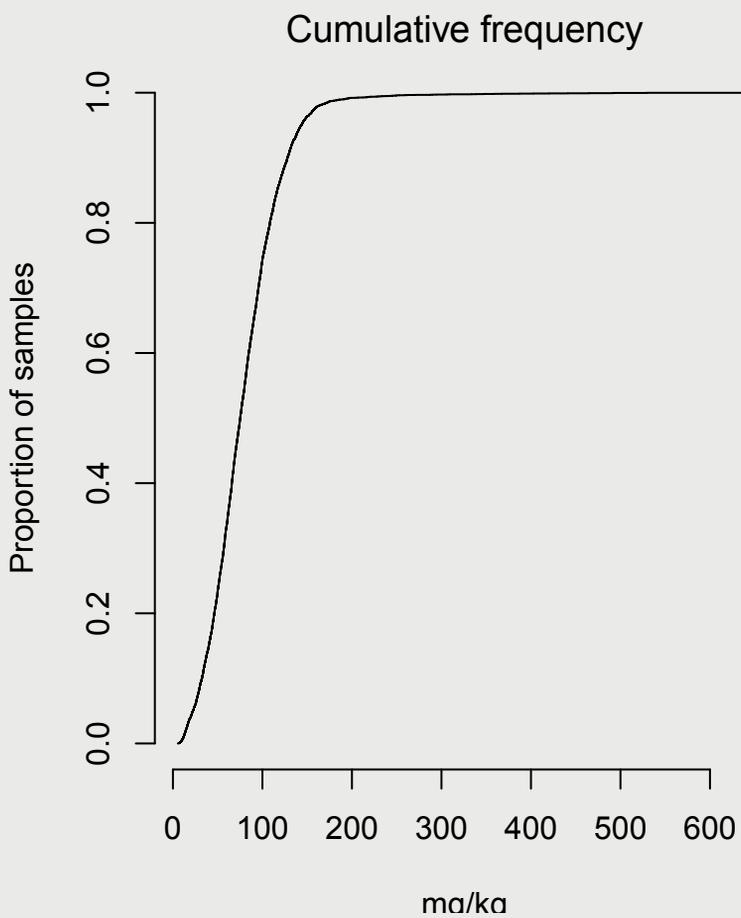
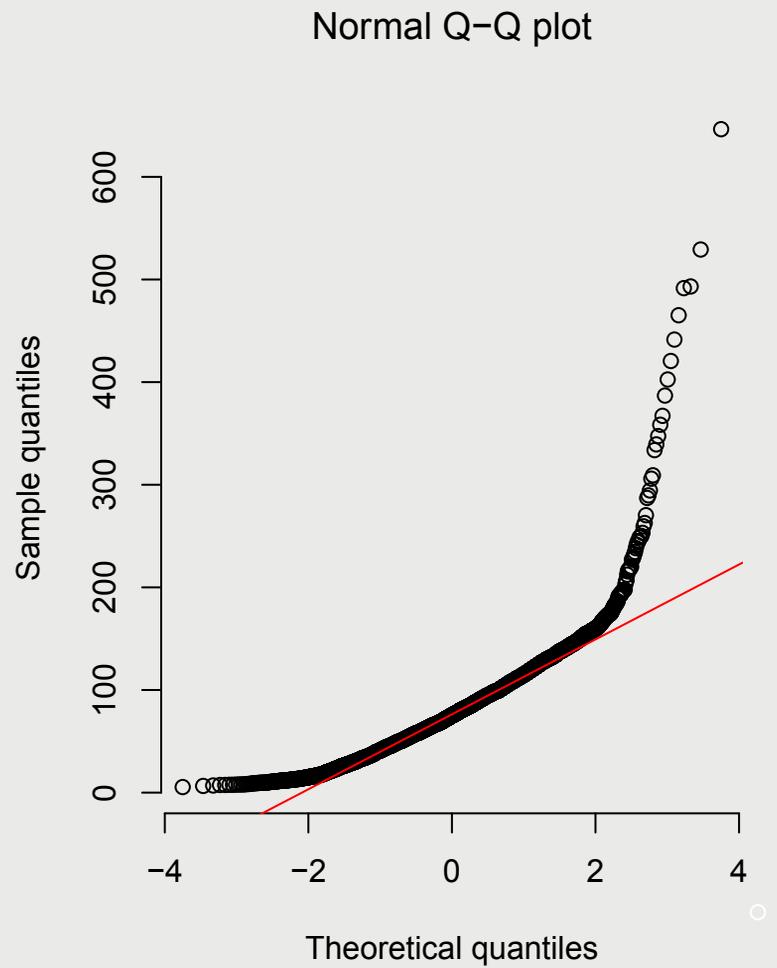
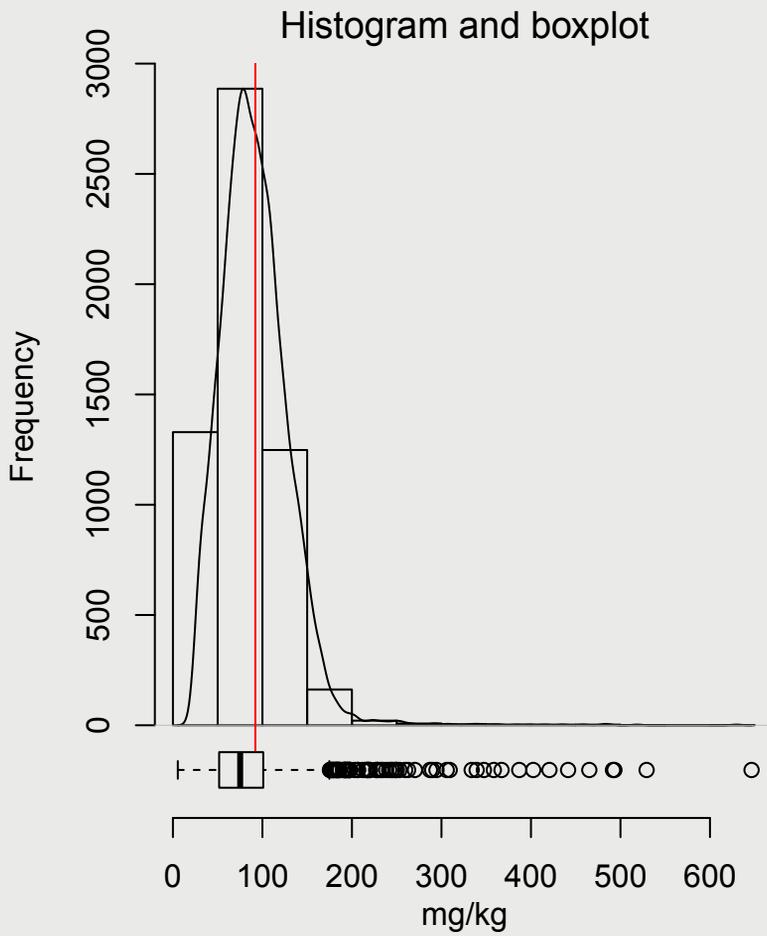
Vanadium (V)

Vanadium is a fairly abundant transition metal with an estimated average upper continental crustal abundance of 53 to 60 mg/kg, being much more abundant in basic igneous rocks (260 mg/kg) than in granites (70 mg/kg) and lower still in sandstones and limestones (20 and 15 mg/kg respectively), but usually around 130 mg/kg in shales (Reimann and De Caritat, 1998). It is found in many minerals, such as carnotite, vanadinite and magnetite; and rock-forming minerals such as pyroxenes and amphiboles, but is also associated with organic matter in black shales, coal and oil. It is an essential nutrient for some organisms; however, it is also considered toxic, which greatly depends on its speciation and oxidation state. Vanadium is mainly used in steel production and alloys as well as catalysts.

Mean and median concentration in NSI soils are higher than the nominal crustal abundance, measuring 79 and 75 mg/kg respectively. This is higher than most medians for agricultural and forest soils listed by Reimann and De Caritat (1998), which range from 26.1 mg/kg (Finland) to 94 mg/kg (Canada). In England and Wales, elevated concentrations (>128 mg/mg) occur mainly over the Jurassic strata especially between Banbury and Melton Mowbray (spatially associated with the ironstones: see also Breward, 2007), the Ordovician and Silurian strata of mid and south-west Wales, the Thames estuary and Devonian-Carboniferous sedimentary terrane of south-west England.

The lowest concentrations of V (<40 mg/kg) occur in soils over the Cretaceous strata of East Anglia and southern England, the igneous intrusions of Cornwall, the Triassic to Carboniferous strata of central and northern England, in particular the Pennines. There are close similarities in the distribution of V and Cr in soils.





V - Vanadium mg/kg

mean= 79

median= 75

10th percentile= 32

25th percentile= 52

75th percentile= 101

90th percentile= 128

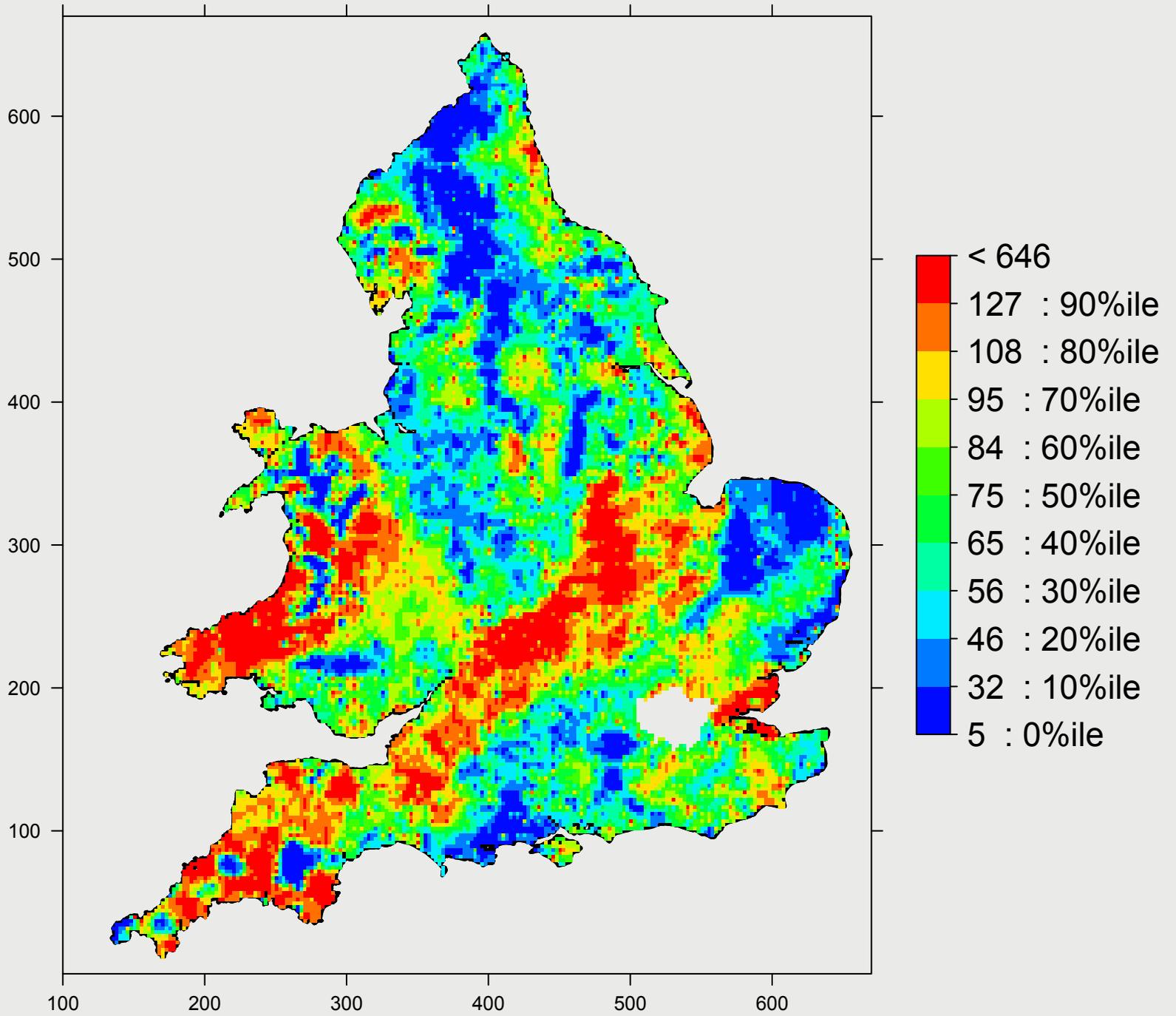
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max= 646

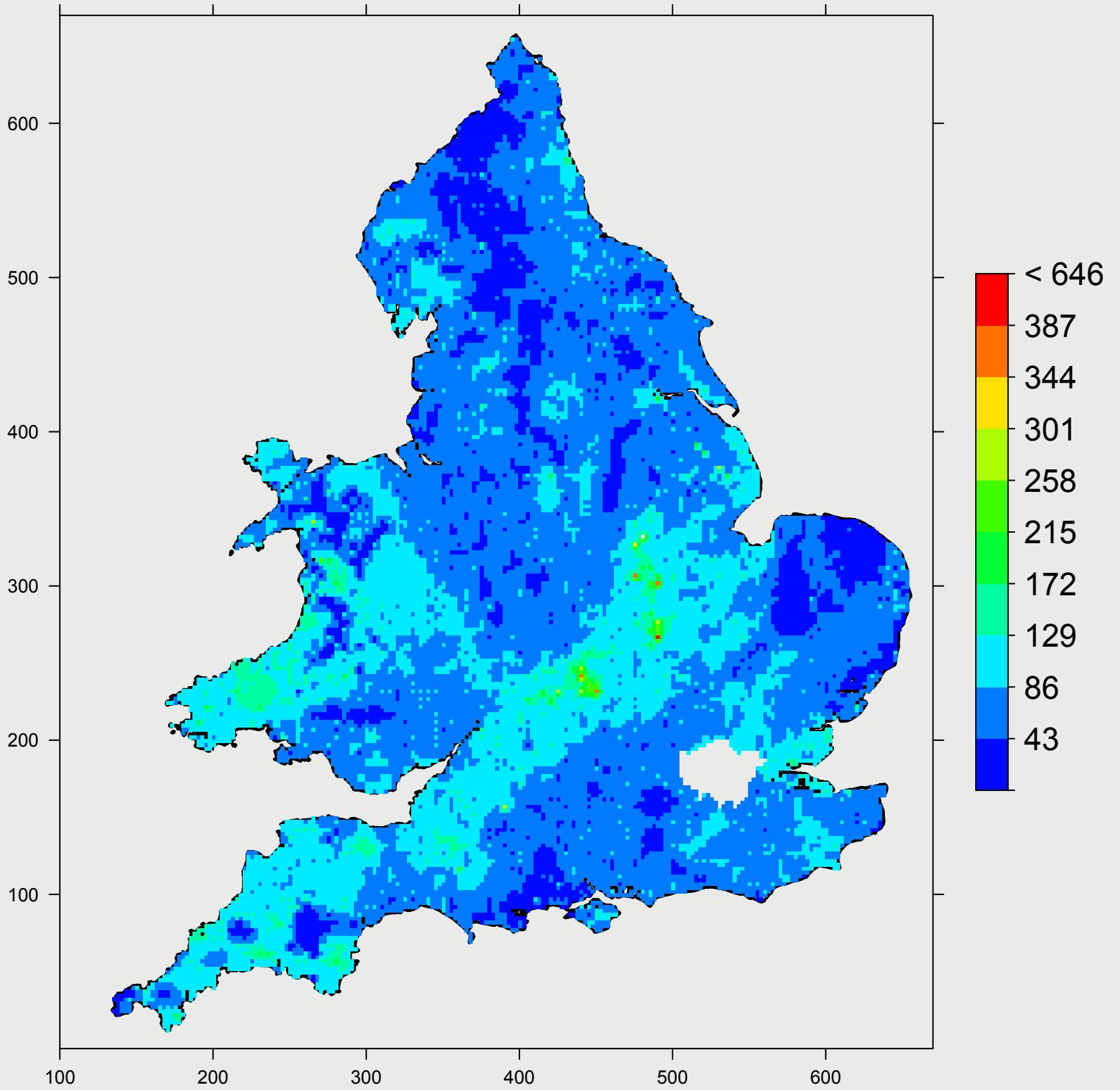
skewness= 2.3

n= 5670

Topsoil vanadium (mg/kg ; percentile scale)



Topsoil vanadium (mg/kg ; arithmetic scale)



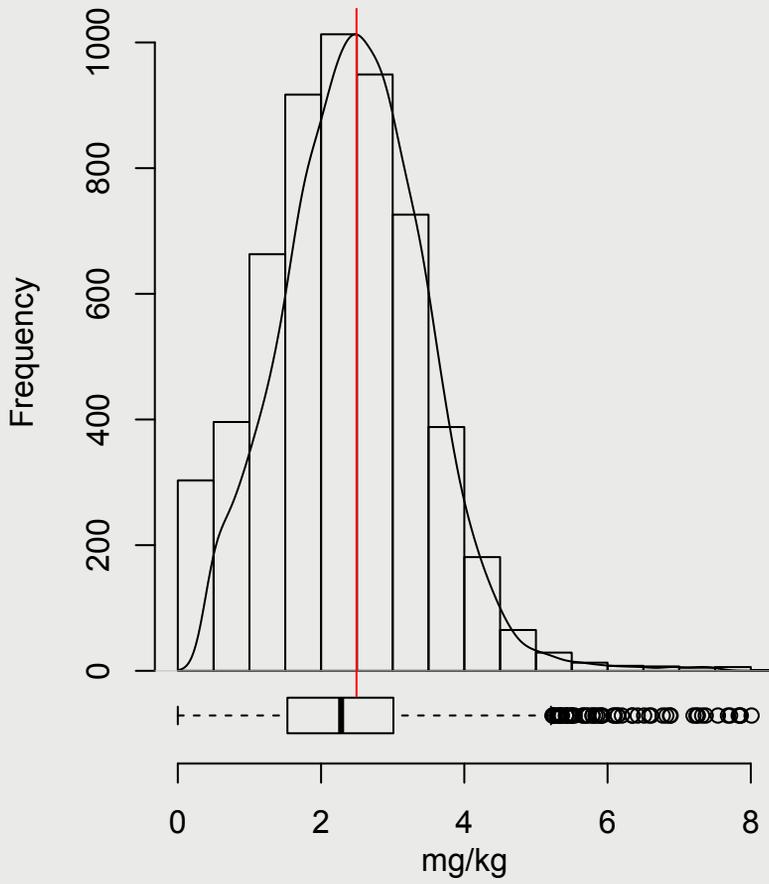
Ytterbium (Yb)

Ytterbium is one of the 15 rare earth elements (REEs) and has an estimated average crustal abundance of between 1.5 and 2.2 mg/kg (Reimann and De Caritat, 1998). Similar to other REEs such as La, Sm, Nd and Ce, Yb is primarily found in monazite and bastnäesite but is also present in more common minerals such as biotite, pyroxenes, feldspars and zircon. Like the other REEs, it is considered non-essential with a generally low toxicity. In industry it is used as a doping agent for stainless steel and in condensers. The mean and median concentrations in NSI soil are each 2.3 mg/kg, similar to the crustal abundance.

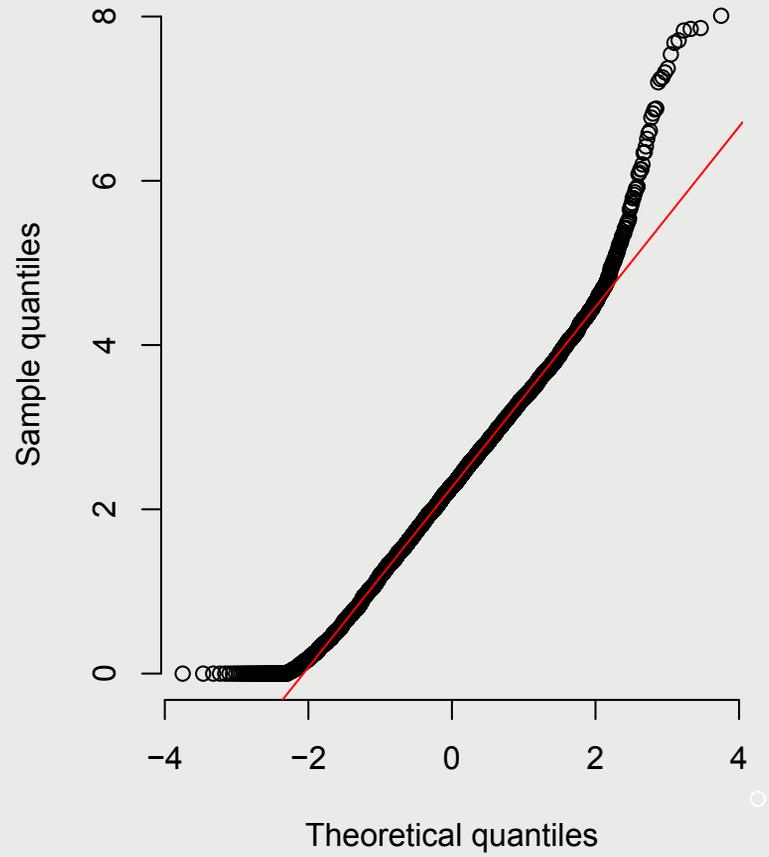
The spatial distribution of Yb is similar to the other REEs, in particular Sm. Elevated concentrations (>3.6 mg/kg) occur mainly in soils over Jurassic strata of central England, the Weald in south-east England, the Peak District, the Lincolnshire Wolds as well as the south-west of Wales and England.

Lowest concentrations (<2 mg/kg) occur in soils from East Anglia and the Triassic and Carboniferous of west and north England.

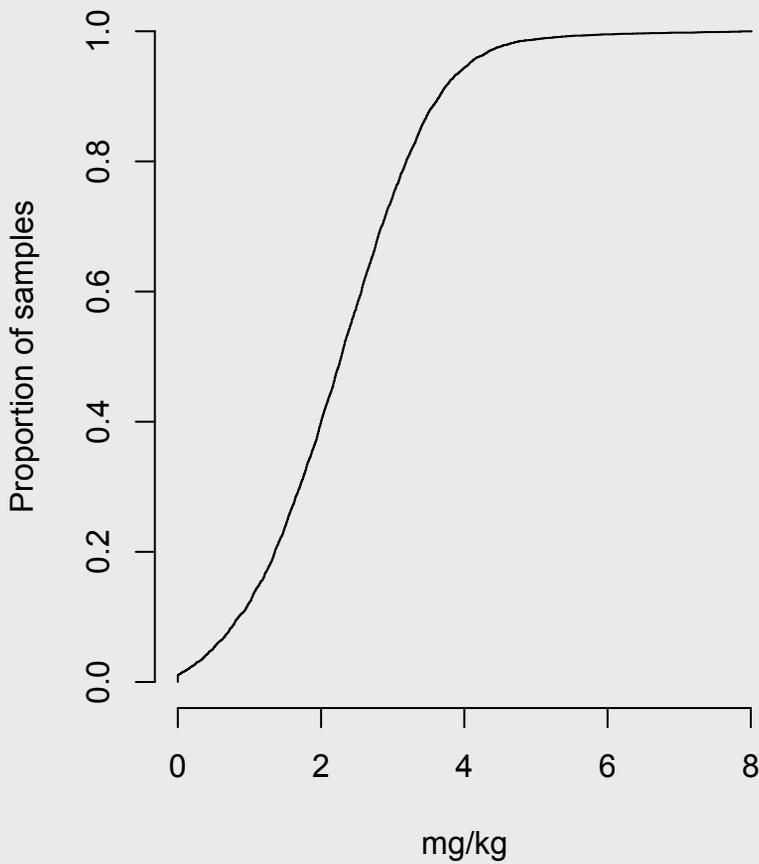
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Yb - Ytterbium mg/kg

mean= 2.3

median= 2.3

10th percentile= 0.85

25th percentile= 1.5

75th percentile= 3

90th percentile= 3.6

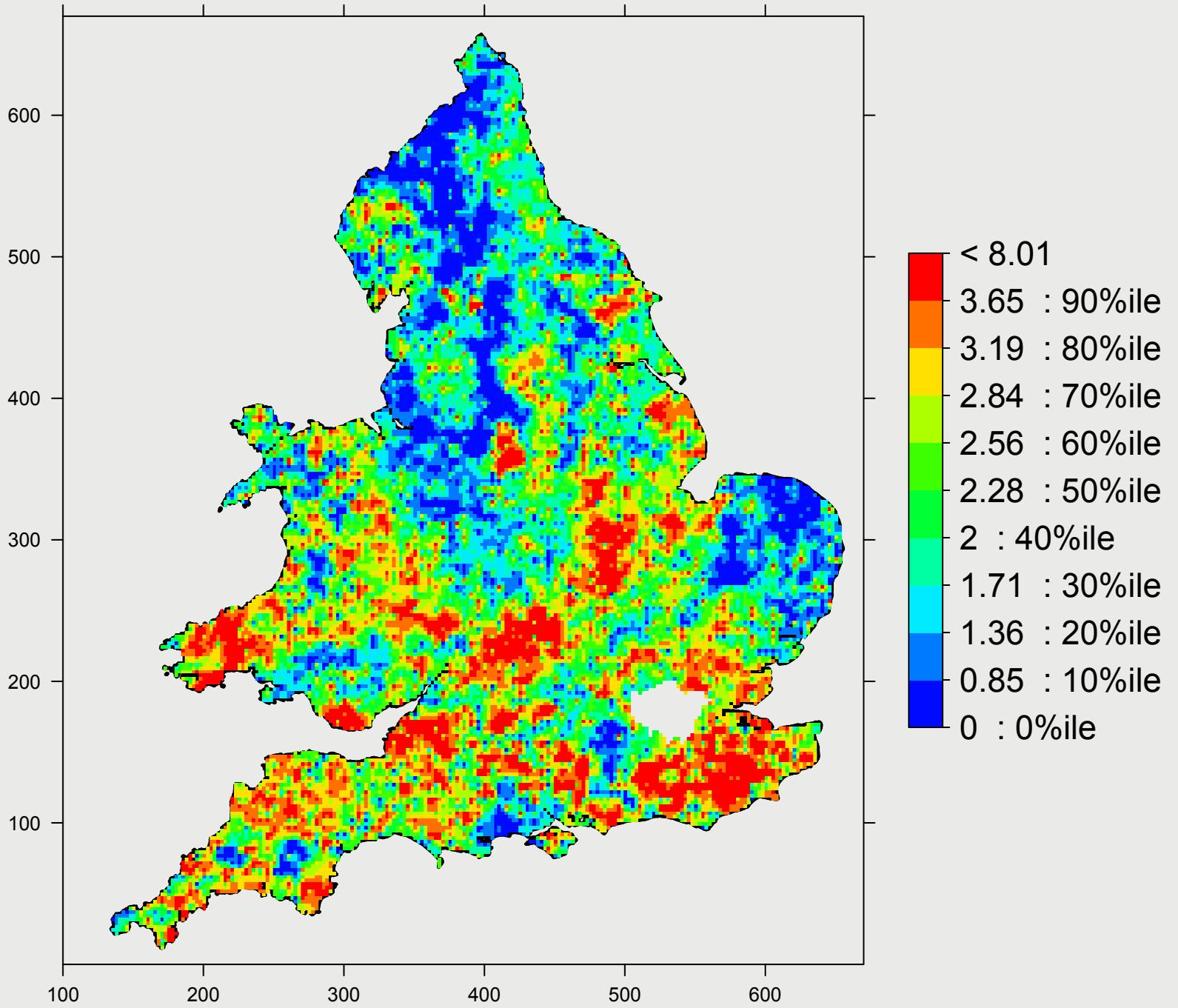
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max= 8

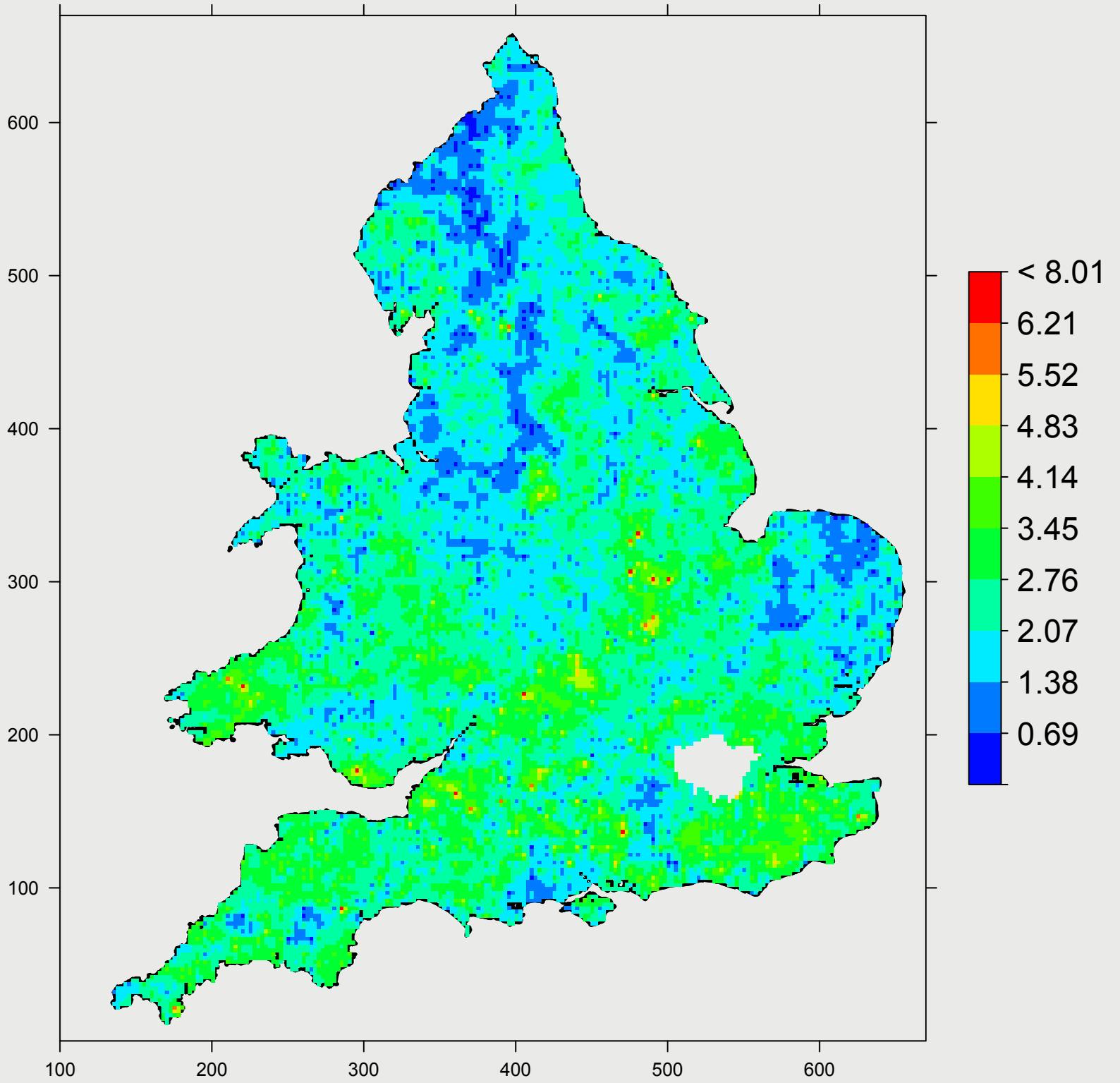
skewness= 0.42

n= 5670

Topsoil ytterbium (mg/kg ; percentile scale)



Topsoil ytterbium (mg/kg ; arithmetic scale)



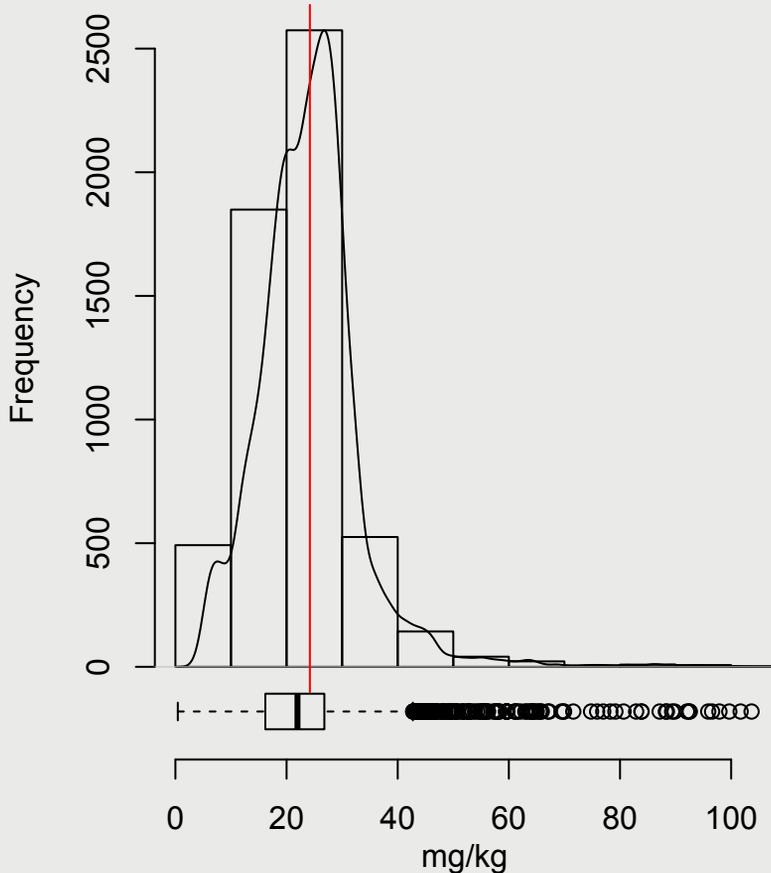
Yttrium (Y)

Yttrium is a metal, often classified as one of the rare earth elements, though it is not strictly within the lanthanide series, and has an average crustal abundance of 21 mg/kg (Reimann and De Caritat, 1998) with relatively little differentiation between granites and basic igneous rocks, and shales, although both limestones and coals (4 and 3 mg/kg respectively) are very low in Y. It is found primarily in a number of minerals including monazite, xenotime and garnet, and also in more common minerals such as biotite, feldspars, pyroxenes and apatite. It is widely used in the ceramic, metallurgical and electronic industries, and as a catalyst in plastics manufacturing. The concentrations reported in the NSI soils range from 0.43 to 104 mg/kg with mean and median concentrations of 22 mg/kg.

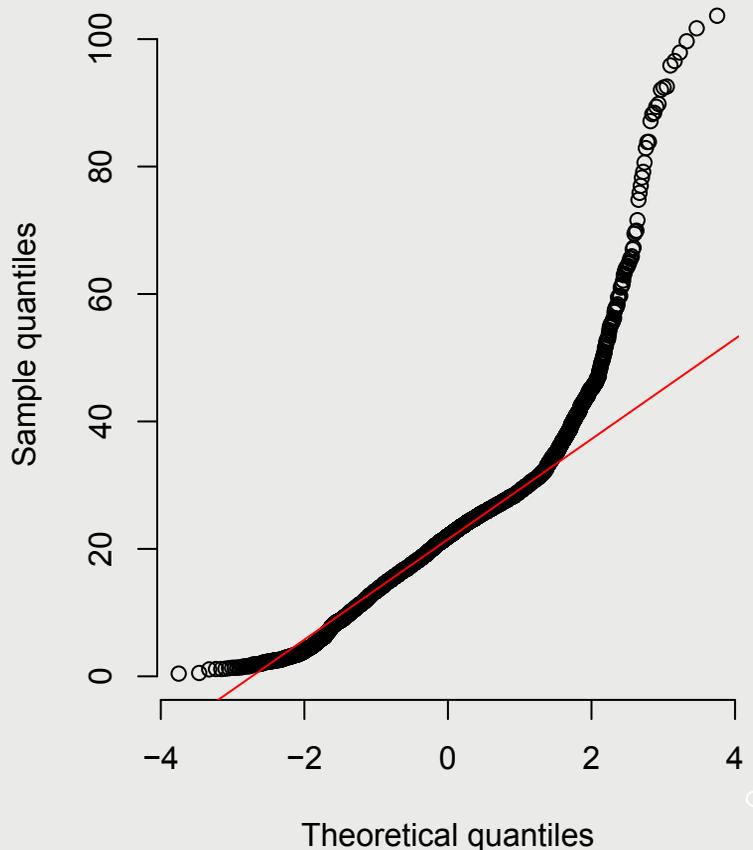
The highest Y concentrations (>25 mg/kg) occur in soils overlying a wide range of lithologies in central and southern England, including the nonmarine Lower Cretaceous rocks of the Wealden district (south-east England), the Lias and Middle Jurassic sediments, parts of the Cretaceous Chalk and the Carboniferous Limestone outcrop of the Peak District. As limestones are generally deficient in Y, this pattern suggests a residual or loess-type sandy soil development in these areas.

The lowest concentrations (<15 mg/kg) occur over the Pennines, the granites of south-west England (probably due to the peaty soils of the moors rather than the bedrock), the Triassic outcrop of the Midlands and Merseyside, much of East Anglia and the sandy soils of the Surrey heaths and the Hampshire Basin.

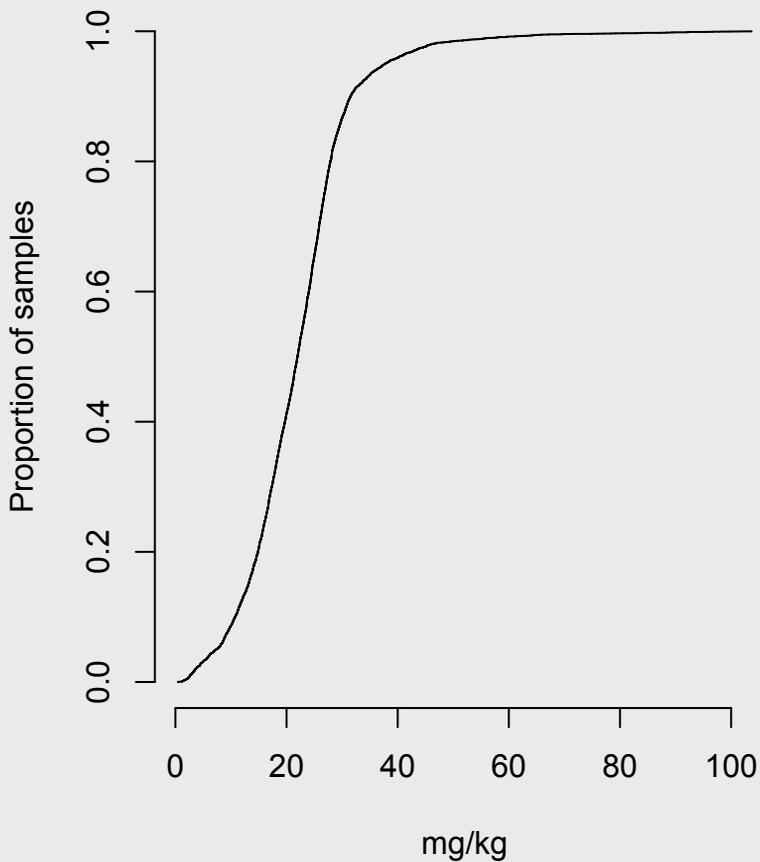
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Y - Yttrium mg/kg

mean= 22

median= 22

10th percentile= 11

25th percentile= 16

75th percentile= 27

90th percentile= 31

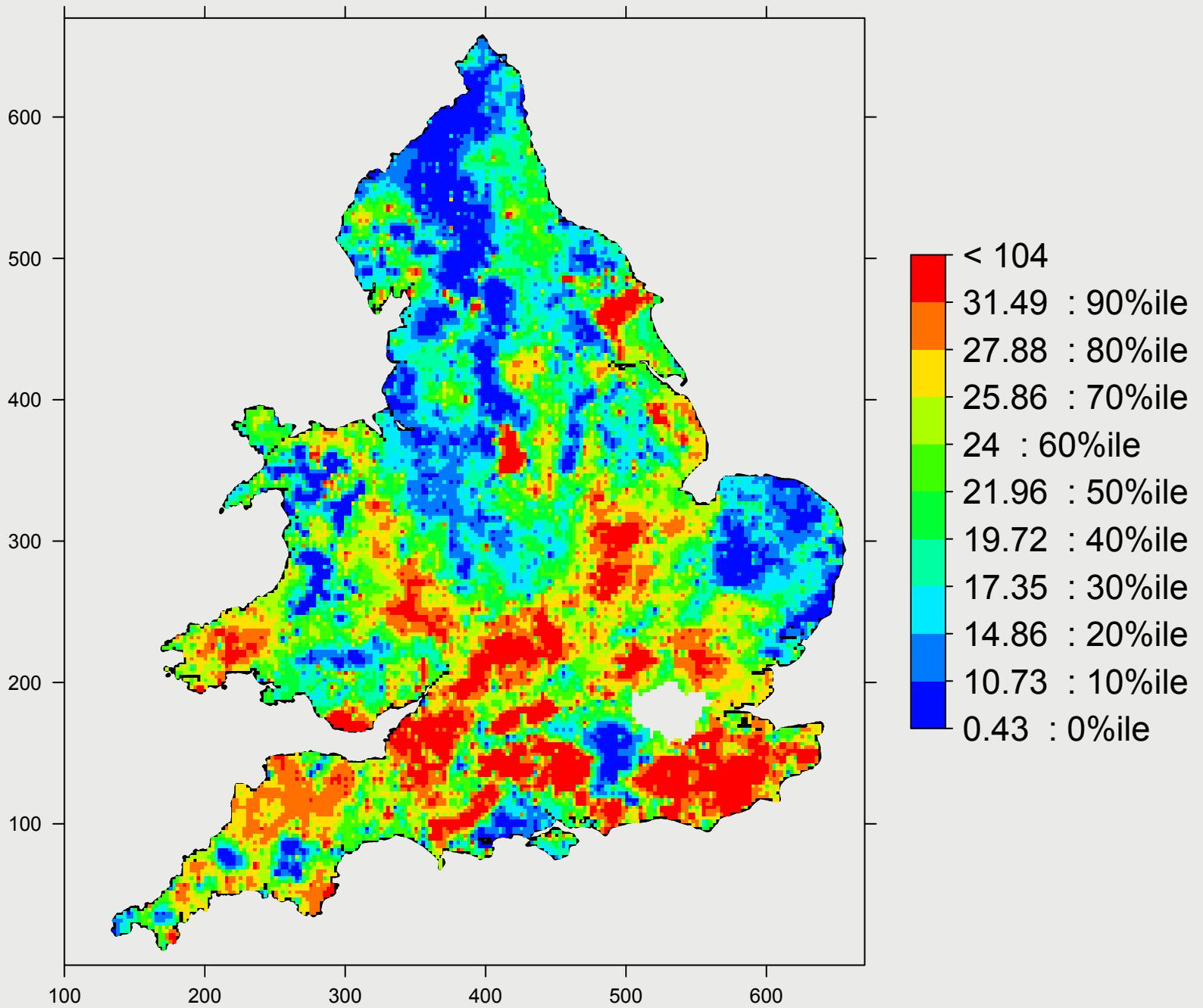
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max= 104

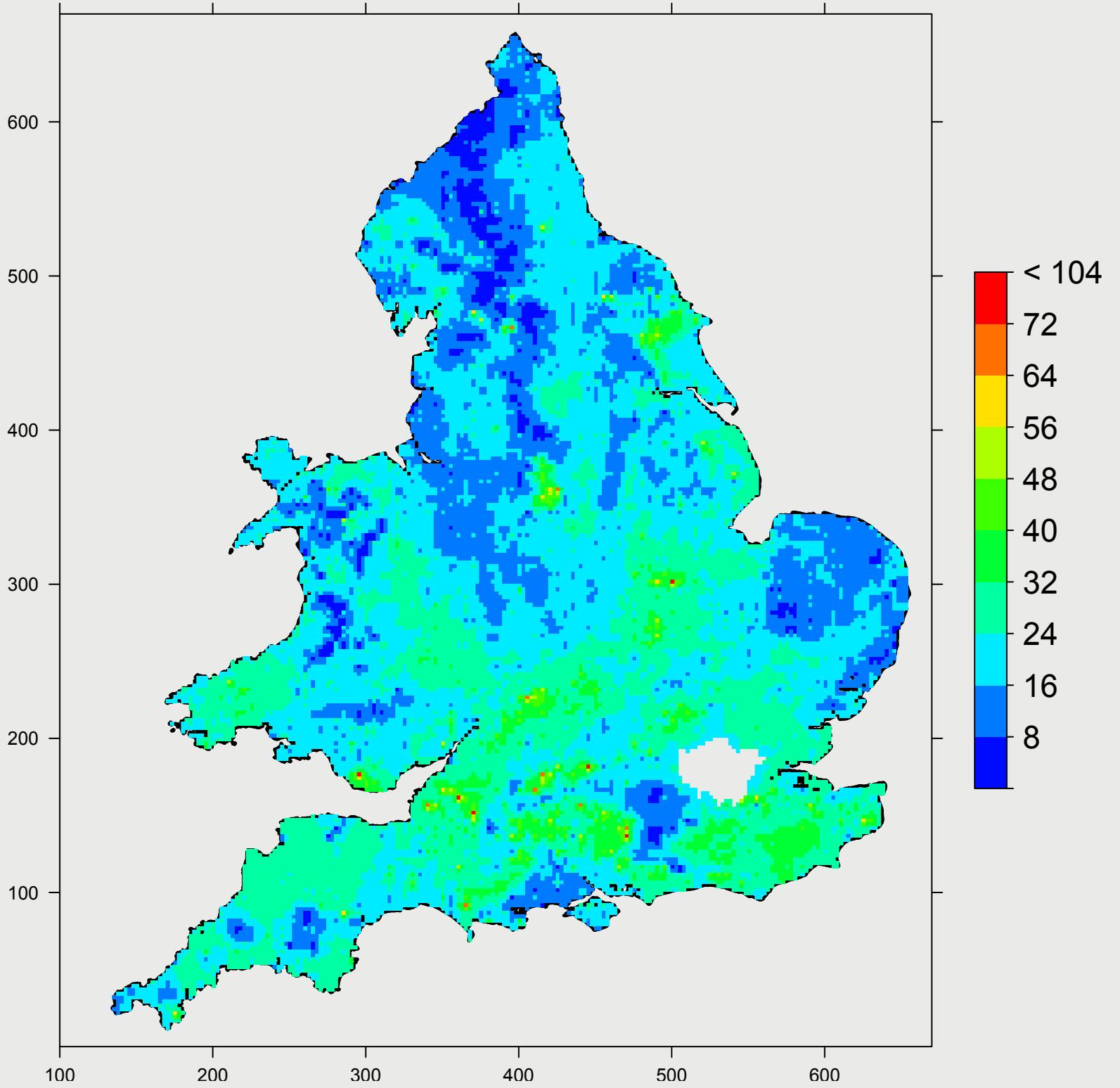
skewness= 1.7

n= 5670

Topsoil yttrium (mg/kg ; percentile scale)



Topsoil yttrium (mg/kg ; arithmetic scale)



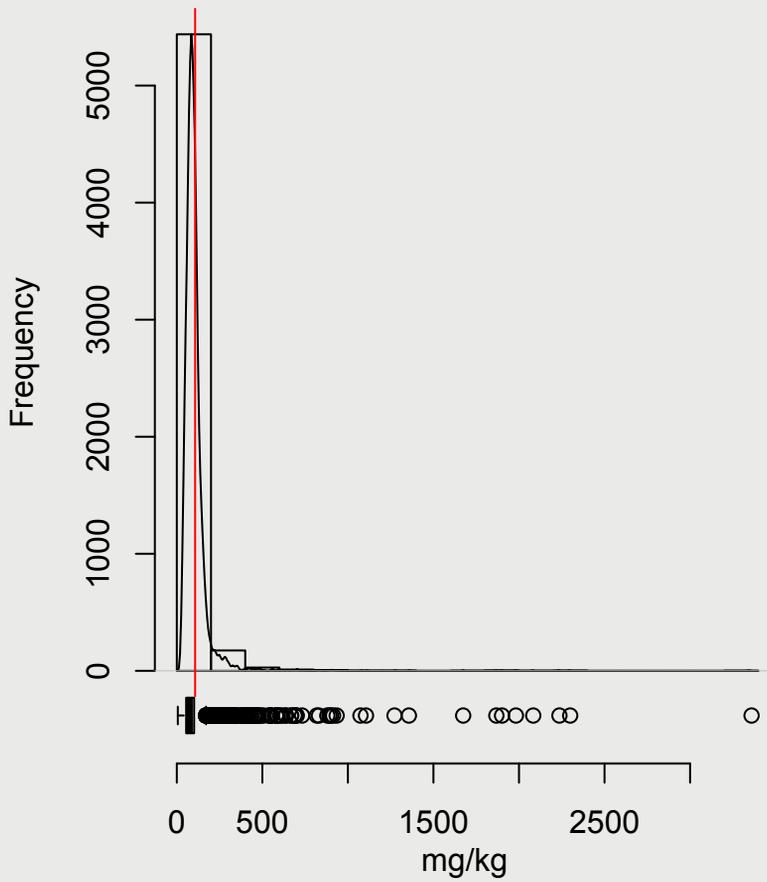
Zinc (Zn)

Zinc is a common metallic element, with an estimated abundance of 50–70 mg/kg in the Earth's upper continental crust, and rather more common in basic igneous rocks (100 mg/kg) and shales (100 mg/kg) than in granites (50 mg/kg) or sandstones (20 mg/kg). Zinc most commonly occurs in its sulphide ore mineral sphalerite (ZnS) but is also present in pyroxenes, amphiboles, micas, garnet and magnetite. It is essential for all organisms and has a low toxicity, deficiencies being more important than excess (Reimann and De Caritat, 1998). Zinc has many industrial uses, such as in galvanised (zinc-coated) iron, alloys, pigments and paint, batteries, glass and plastics. As such it is a ubiquitous contaminant in urban soils.

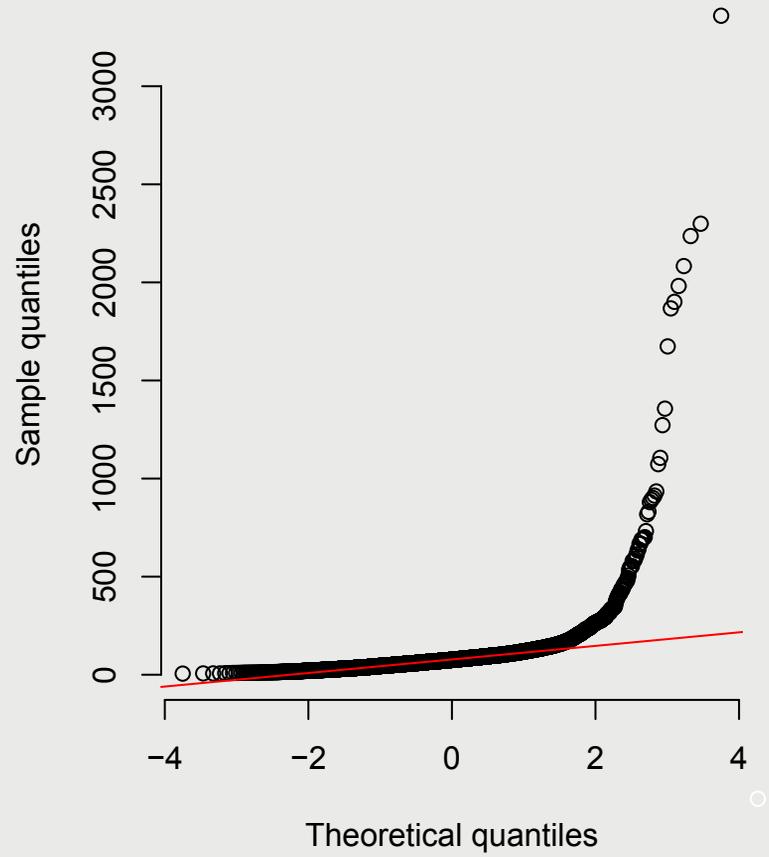
Soils with high Zn concentrations occur mainly where there has been a history of lead and zinc mining. The most obvious of these are the former mining fields of the Pennines, Peak District, Wales, Shropshire, the Mendips and south-west England. High levels are also present around major smelting sites, such as Swansea and Avonmouth (Bristol area). There is also a clear urban-industrial signature around major cities such as Manchester, Birmingham, Sheffield, Leeds, Sunderland and Newcastle. Many of the soils in a broad band following the Jurassic outcrop from the Bristol area to the Lincoln and Cambridge areas also have slightly elevated Zn concentrations, most likely associated with soils rich in clay (Oliver et al, 2002). Statutory Instrument (SI 1263, 1989) gives a maximum Zn concentration for agricultural soils receiving sewage sludge of 300 mg/kg dry weight. Most soils away from mining areas are below this value, many being less than 100 mg/kg.

Low Zn in soil occurs mainly in heathlands in the New Forest, south west of London, the Brecklands and north Norfolk, and the mountains in Wales and northern England. In these upland areas, low Zn concentrations appear to be related to high soil organic matter contents (McGrath and Loveland, 1992).

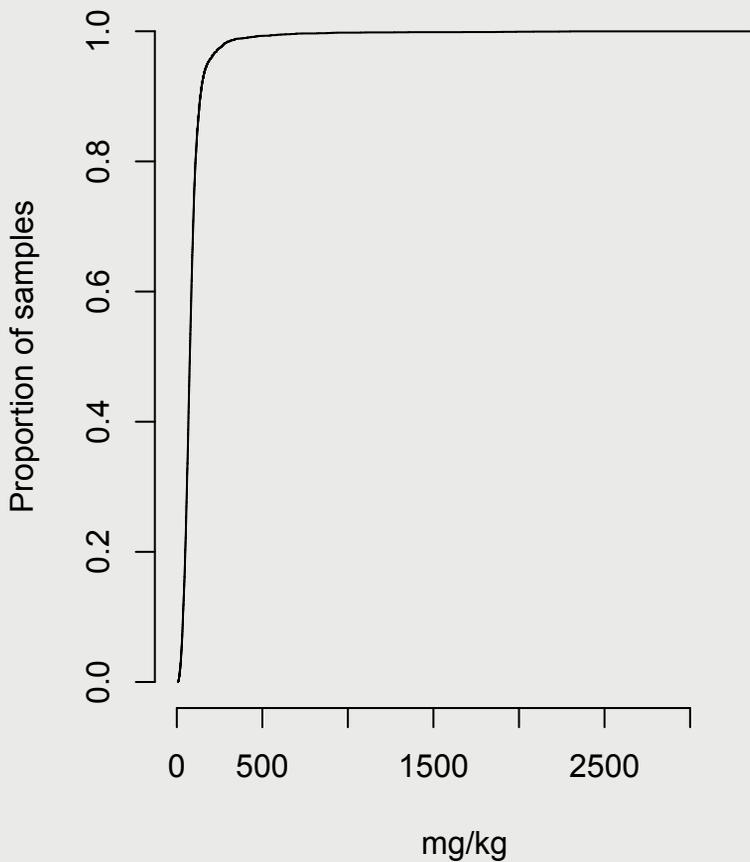
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Zn - Zinc mg/kg

mean= 91

median= 76

10th percentile= 36

25th percentile= 55

75th percentile= 101

90th percentile= 138

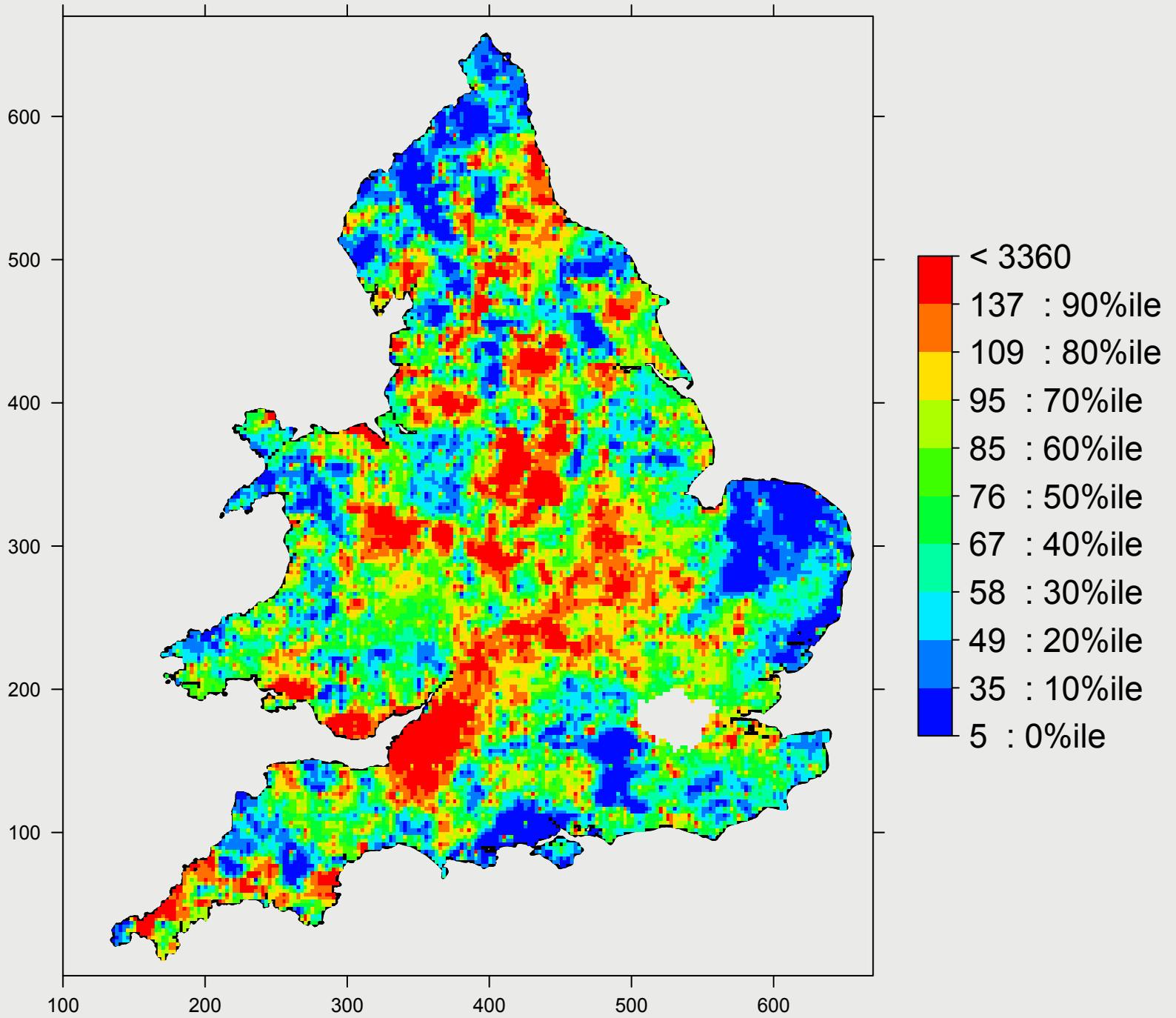
min= 5.8

max= 3359

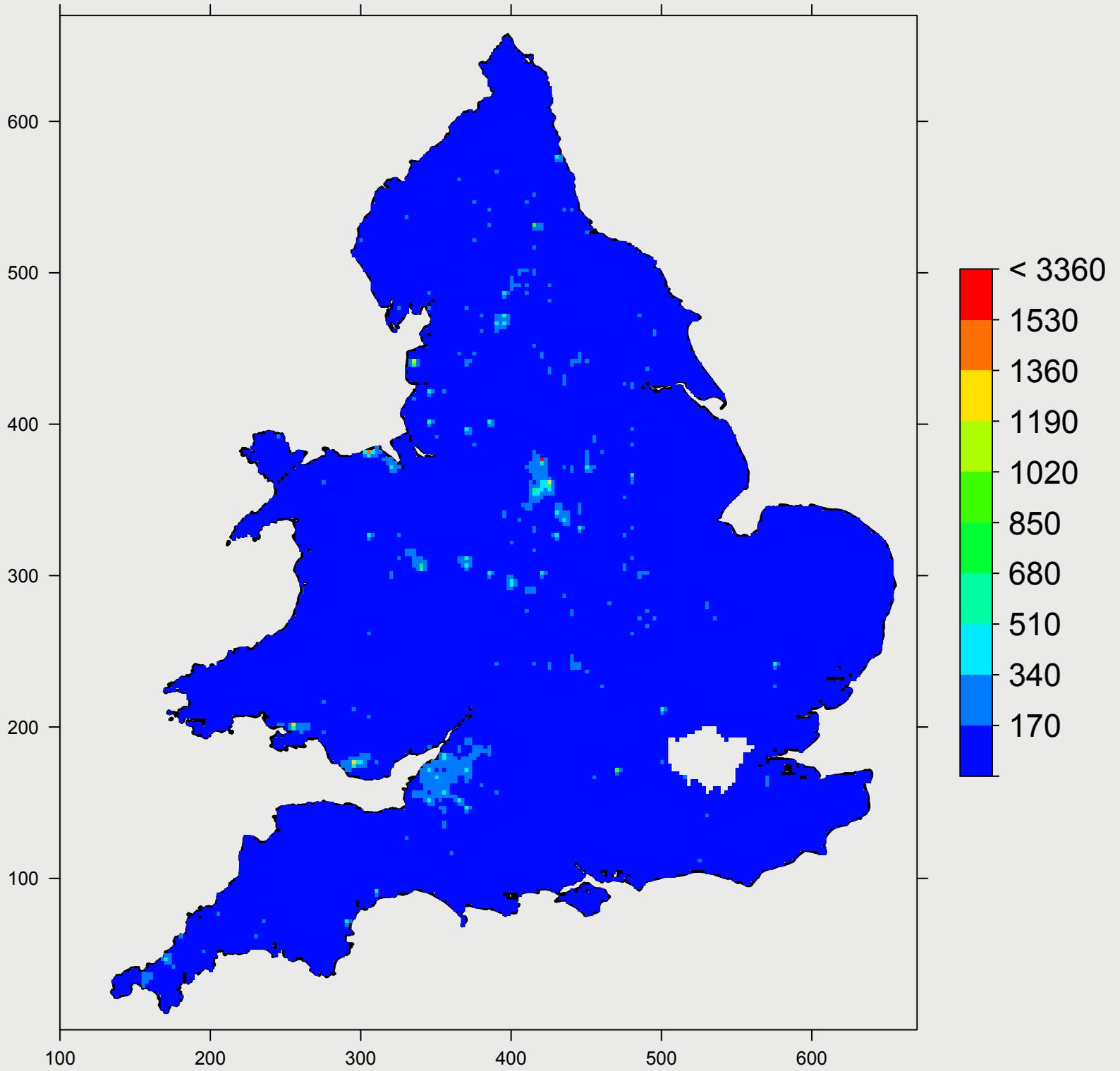
skewness= 14

n= 5670

Topsoil zinc (mg/kg ; percentile scale)



Topsoil zinc (mg/kg ; arithmetic scale)



Zirconium (Zr)

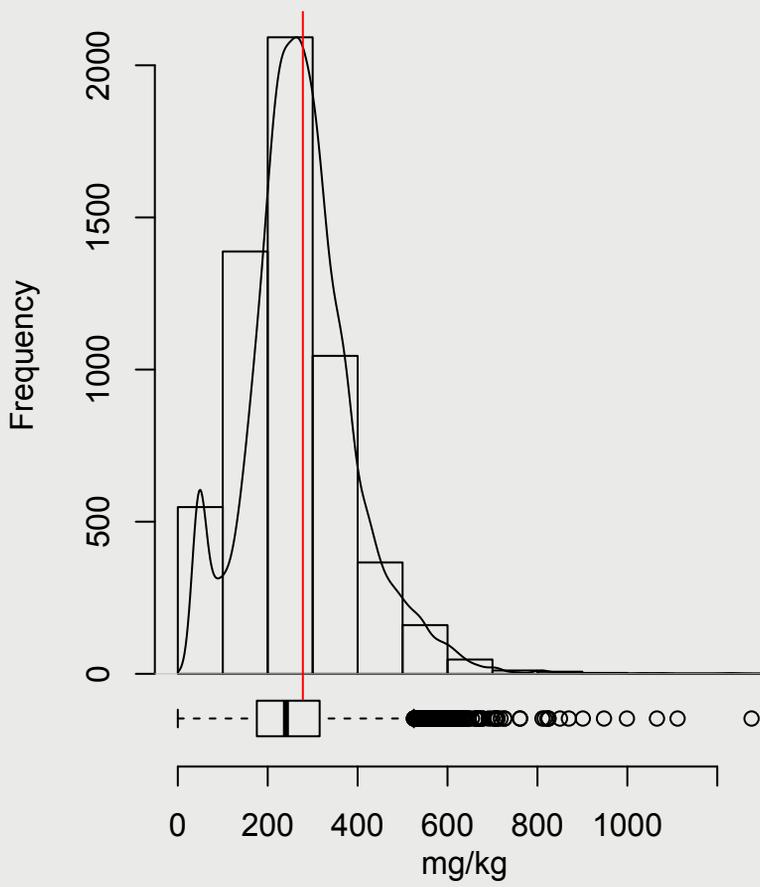
Zirconium is a relatively abundant, lithophile element with an estimated value of about 200 mg/kg in the upper continental crust which forms several typical minerals including the common resistate minerals zircon (ZrSiO_4) and rarer baddeleyite (ZrO_2). The Zr^{4+} ion is incompatible with most common rock-forming silicate mineral lattices, and it is therefore strongly partitioned into zircon and other accessory minerals such as sphene. It is more abundant in granites (200 mg/kg) than in basic igneous rocks (100 mg/kg) but is more concentrated in sandstones and greywackes (250–300 mg/kg) and depleted in limestones and coals (20 mg/kg: Reimann and De Caritat, 1998). In eastern England, Scheib and Lee (2010) showed that elevated Zr concentrations are a good indicator for wind-blown (aeolian) deposits, such as loess and cover-sand, that form soils of predominantly silt to fine sand-sized fractions. It is non-essential and is believed to have low toxicity, though such data are scarce. Zirconium is widely used in industries such as glass and ceramics, in abrasives, special alloys and in the nuclear industry.

Due to their almost identical geochemical properties, the maps of Zr show a very similar distribution to the ones for Hf. Elevated concentrations (>300 mg/kg) were measured in soils across a) most of southern England, especially in Dorset, the Wealden district in Sussex and Kent, west and north-west of London and in Essex b) north-eastern England between Hull and the North Yorkshire Moors and along the eastern margins of the Pennines, including the Chalk outcrop of the Yorkshire and Lincolnshire Wolds c) the Chalk outcrop, Breckland and the Norfolk Broads of East Anglia, d) the southern Peak District (Carboniferous Limestone outcrop) and e) the Old Red Sandstone outcrop around Hereford in western England.

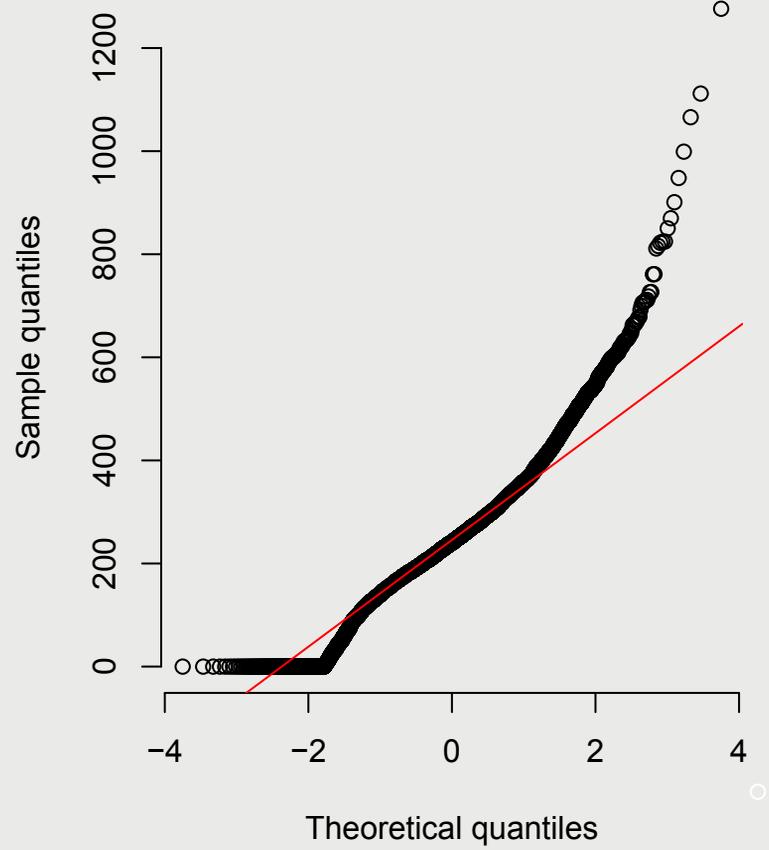
For the chalk and limestone areas, high levels may appear incongruous as Zr levels in carbonates are very low, but there are publications that describe the occurrence of aeolian deposits such as loess and cover-sand in which zircons are abundant. The highly resistate nature of zircon characterises the Zr distribution in soils and sediments.

Very low concentrations of Zr in soils follow much of the Lower Palaeozoic outcrop in Wales and Cumbria, both the sedimentary and granitic rocks of south-west England, and many clay-based soils, for example over the Triassic and Jurassic where these, rather than superficial deposits, are the parent materials, or peaty soils in both the upland moors and lowland fens.

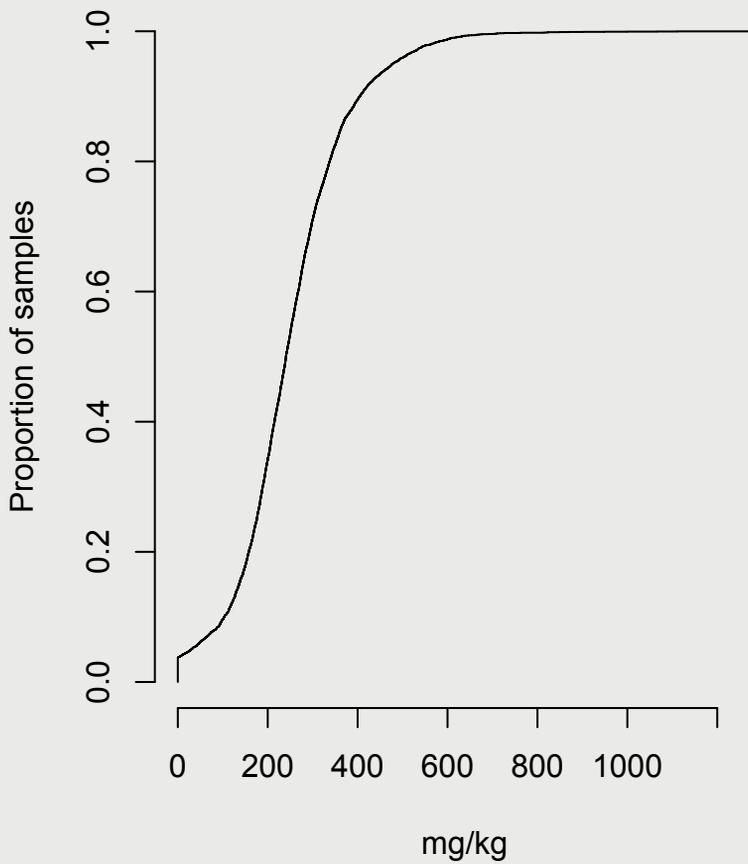
Histogram and boxplot



Normal Q-Q plot



Cumulative frequency



Zr - Zirconium mg/kg

mean= 250

median= 241

10th percentile= 104

25th percentile= 176

75th percentile= 316

90th percentile= 405

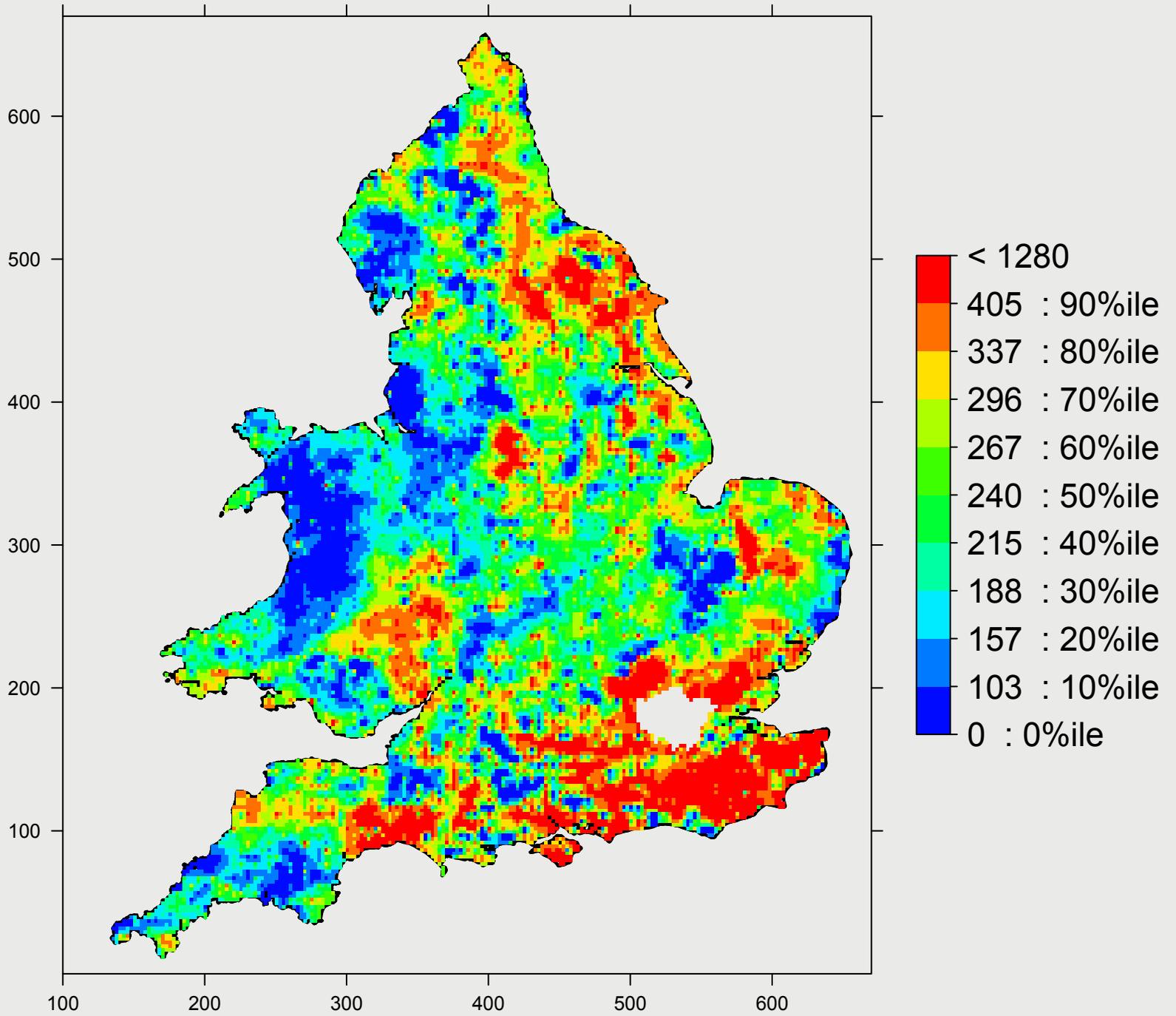
min= 0

max= 1276

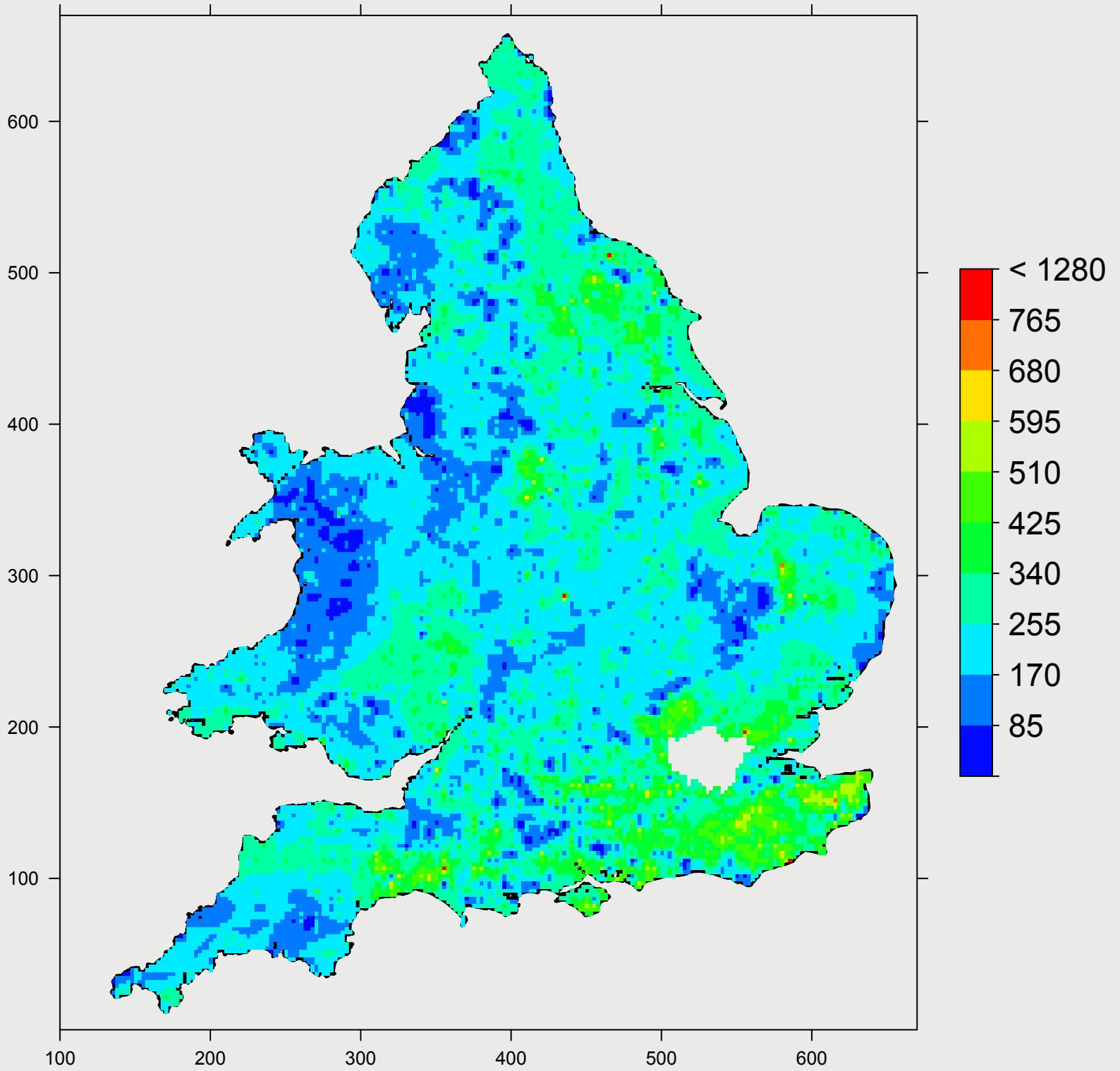
skewness= 0.78

n= 5670

Topsoil zirconium (mg/kg ; percentile scale)



Topsoil zirconium (mg/kg ; arithmetic scale)



References

- ADAMS, M L, LOMBI, E, ZHAO F-J, and McGRATH, S P. 2002. Evidence of low selenium concentrations in UK bread-making wheat grain. *Journal of the Science of Food and Agriculture*, Vol. 82, 1160–1165.
- BRENCHLEY, P J and ROWSON, P F (editors) 2006. *The Geology of England and Wales*. (London: The Geological Society.)
- BREWARD, N. 2007. Arsenic and presumed resistate trace element geochemistry of the Lincolnshire (UK) sedimentary ironstones, revealed by a regional geochemical survey using soil, water and stream sediment sampling. *Applied Geochemistry*, Vol. 22, 1970–1993.
- COONEY, J J, and WUERTZ, S. 1989. Toxic effects of tin compounds on microorganisms. *Journal of industrial microbiology and biotechnology*, Vol. 4(5), 375–402.
- EMSLEY, J. 2001. Niobium: Nature's Building Blocks: An A–Z Guide to the Elements
- ENVIRONMENT AGENCY. 2009. Updated technical background to the CLEA model. Science Report SC050021/SR3. Bristol: Environment Agency.
- ESFA (European Food Safety Authority). 2009. Scientific opinion on cadmium in food. *EFSA Journal* Vol. 980, 1–39.
- EVM (Expert Group on Vitamins and Minerals). 2003. Risk Assessment: Germanium. Food Standards Agency. http://www.food.gov.uk/multimedia/pdfs/evm_germanium.pdf
- FORD, T D. 2001 Derbyshire Wad and UMBER. *Bulletin of the Peak District Mines Historical Society*, Vol. 14, 39–45.
- INGHAM, M N, and VREBOS, B A R. 1994. High Productivity Geochemical XRF Analysis. *Advances in X-ray Analysis*, Vol. 37, 717–724.
- JOHNSON, C C. 2003. The geochemistry of iodine and its application to environmental strategies for reducing the risks from iodine deficiency disorders (IDD). *British Geological Survey Commissioned Report*, CR/03/057N.
- JOHNSON, C C. 2011. Understanding the quality of chemical data from the urban environment—Part 1: Quality control procedures. 61–76 In: *Mapping the urban chemical environment*. JOHNSON et al. (editors) (London: Wiley.)
- JOHNSON, C C, BREWARD, N, ANDER, E L and AULT, L. 2005. G-BASE: Baseline geochemical mapping of Great Britain and Northern Ireland. *Geochemistry: Exploration Environment, Analysis. Special Volume on Geochemical Mapping*. Vol. 5 Part 4 pp. 347–358.
- LARK, R M, BELLAMY, P H, and RAWLINS, B G. 2006. Spatio-temporal variability of some metal concentrations in the soil of eastern England, and implications for soil monitoring. *Geoderma*, Vol. 133, 363–379.

- LISTER, T R, and JOHNSON, C C. 2005. G-BASE data conditioning procedures for stream sediment and soil chemical analyses. *British Geological Survey Internal Report*, IR/05/150.
- LYONS, G, STANGOULIS, J, and GRAHAM, R. 2003. High-selenium wheat: biofortification for better health. *Nutrition Research Reviews*, Vol. 16, 45–60.
- MCGRATH, S P, and LOVELAND, P J. 1992. *The Soil Geochemical Atlas of England and Wales*. (Glasgow: Blackie.)
- MCGRATH, S P, and ZHAO, F J. 1995. A risk assessment of sulphur deficiency in cereals using soil and atmospheric deposition data. *Soil Use and Management*, Vol. 11, 110–114.
- OLIVER, M A, LOVELAND, P J, FROGBROOK, Z L, WEBSTER, R, and MCGRATH, S P. 2002. Statistical and geostatistical analysis of the National Soil Inventory of England and Wales. Final Report to Department of Environment, Food and Rural Affairs- DEFRA, available from the National Soil Resources Institute, Cranfield University.
- PEBESMA, E J. 2004. Multivariable geostatistics in S: the gstat package. *Computers & Geosciences*, Vol. 30, 683–691.
- PEBESMA, E J, and BIVAND, R S. 2005. Classes and methods for spatial data in R. *R News* 5 (2), <http://cran.r-project.org/doc/Rnews/>.
- R DEVELOPMENT CORE TEAM. 2006. *R: A language and environment for statistical computing*. (Vienna: R Foundation for Statistical Computing.)
- RAWLINS, B G, WEBSTER, R, and LISTER, T R. 2003. The influence of parent material on top soil geochemistry in eastern England. *Earth Surface Processes and Landforms*, Vol. 28, 1389–1409.
- REIMANN, C, and DE CARITAT, P. 1998. *Chemical elements in the environment*. (Berlin: Springer Verlag.)
- RoTAP. 2011. Review of Transboundary Air Pollution (RoTAP), A review of Acidification, Eutrophication, Heavy Metals and Ground-Level Ozone in the UK. <http://www.rotap.ceh.ac.uk/about>
- SCHEIB, A J, and LEE, J R. 2010. The application of regional-scale geochemical data in defining the extent of aeolian sediments: the Late Pleistocene loess and coversand deposits of East Anglia, UK. *Quaternary newsletter*, Vol. 120, 5–14.
- STATUTORY INSTRUMENTS. 1989. The Sludge (Use in Agriculture) Regulations. *Public Health, England and Wales*. (Scotland: Public Health.)
- VAN ZYL .1982. Rapid preparation of robust pressed powder briquettes containing a styrene and wax mixture as binder. *X-ray Spectrometry*, Vol. 11 (1).
- ZHAO, F J, MCGRATH, S P and MEHARG, A A. 2010. Arsenic as a food chain contaminant: Mechanisms of plant uptake and metabolism and mitigation strategies. *Annual Review of Plant Biology*, Vol. 61, 535–59.

