Geochemical Atlas
for Scottish Topsoils

Edward Paterson
Macaulay Land Use Research Institute
Craigiebuckler, Aberdeen AB15 8QH

Edited and updated by:
Colin Campbell
Malcolm Coull
Charles Shand

THE MACAULAY LAND USE
RESEARCH INSTITUTE

Contents

Introduction

Soils

The soils of Scotland have been extensively mapped at a range of scales. From a commission in 1978, national coverage was achieved in 1984 with the publication of the 1:250,000 series of maps (Macaulay Institute for Soil Research, 1984). Alongside the sampling and survey activities associated with the soil mapping, the National Soils Inventory of Scotland project was undertaken. The inventory consisted of examination and description of the soil profiles on a 5-km grid across the whole of Scotland and sampling and analysis of alternate profiles on this grid to give a 10-km grid of sampled sites.

Soil samples were taken from the principal genetic horizons of the soil profiles and were taken back to the Institute for processing, analysis and storage. Details of the sampling procedures and profile descriptions are available elsewhere (Lilly et al., 2010).

On receipt at the Institute, the soil samples were air-dried at a temperature around 30°C, rolled, sieved through a 2-mm aperture sieve and stored for analysis. The first-phase analysis consisted of measurements of particle size distribution, soil pH, exchangeable sodium, potassium, magnesium and calcium and the concentration of carbon and nitrogen. The remaining soil samples were archived for future work and it is this sample set that has been used for the geochemical dataset described here.

Aqua-regia extraction of soils

The methods used for sample preparation and analysis are very similar to those described by McGrath and Loveland (1992) in their geochemical atlas for the topsoils of England and Wales. Representative 5 g sub samples were taken from the archived soils using a spinning riffler and ground to <150 μm in an agate ball mill. Two-gram aliquots of these ground samples were then ignited at 400°C overnight to remove organic matter before transfer to Pyrex tubes for aqua regia extraction using the procedure described by McGrath and Cunliffe (1985). The residues after extraction were taken up in 2.4M HCl, diluted to 0.6M HCl and analysed using an inductively coupled plasma (ICP) optical emission spectrometer. Two sets of analytical quality control procedures were used – the first was that used for the calibration and monitoring of ICP performance using traceable standards, whilst the second used the procedure described by McGrath (1987). In the latter case a batch procedure was used where standard soils were incorporated in each batch along with repeat digests and repeat solutions in order to test various stages of the overall process. The concentration values for the elements in the Scottish topsoils presented here refer to the air-dried soil.

Limits of detection

In the preparation of these maps and data summaries the limits of detection for the element in the soils have been derived from the limits in analytical phase. This does not define the lower working limits as set out by McGrath and Loveland (1992). In the worst cases these lower working limits fall within the lower quartile.

Data handling and statistical analysis

Preliminary data analysis was carried out using Microsoft Excel before transfer to an ORACLE relational database management system for data storage. The data were then reclassified and displayed in ARC GIS 9.3 for mapping. Frequency analysis and calculation of mean and median values for individual elements were also carried out using Microsoft Excel.

Comparison with other datasets

There are important differences related to the soil sampling methods employed in Scotland compared with those in the survey of England and Wales. In Scotland, the National Soil Inventory archive contains single samples taken from the centre of the genetic soil horizons. In England and Wales, composite auger samples were taken from the top 15-cm of soil thus incorporating surface soil where anthropogenic inputs might be expected to be greatest. In Scotland, with its much higher proportions of semi-natural soils this procedure would have resulted in 'bulking' of, in some cases, two or three distinctly different horizons and the decision was taken to sample on a genetic horizon basis. It is important that this difference is borne in mind when attempting to compare the datasets. From an analytical point of view the dataset is directly comparable with that published for England and Wales.

1.1 Soil Mapping in Scotland

A number of different mapping units have been used through the various phases of soil survey in Scotland (Gauld and Paterson, 1996). However, one unit which has remained a keystone of the system throughout is the soil association, which groups together soils which have developed within a particular landform on the same or similar parent materials (Glentworth, 1962). This grouping conveys a mineralogical and/or geochemical signature, which has been extensively used in wide-area modelling of acid deposition on soils (Langan and Wilson, 1994). Although over 140 soil associations have been described for Scotland, many of these are relatively small or are subtle variations of one another and it is possible to simplify radically the overall picture by considering only those associations which cover >1% of the total land area. When this is done then over 70% of the land area is covered by 14 soil associations.

Geological Group	Association	Parent Material
Drifts derived from metamorphic rocks	Arkaig	Drifts derived from schists, gneisses, granulites and quartzites principally of the Moine Series
	Foudland	Drifts derived from slates, phyllites and other weakly metamorphosed argillaceous rocks
	Lochinver	Drifts derived from Lewisian gneisses
	Strichen	Drifts derived from arenaceous schists and strongly metamorphosed argillaceous schists of the Dalradian Series
Drifts derived from sedimentary materials	Balrownie	Drifts derived mainly from sandstones of Lower Old Red Sandstone age, often water-modified
	Ettrick	Drifts derived from Lower Paleozoic greywackes and shales
	Rowanhill	Drifts derived from Carboniferous sandstones, shales and limestones
	Torridon	Drifts derived from Torridonian sandstones and grits
Drifts derived from igneous rocks	Countesswells	Drifts derived from granites and granitic rocks
	Darleith	Drifts derived from basaltic rocks
	Sourhope	Drifts derived from Old Red Sandstone intermediate lavas
Other geological materials	Corby	Fluvioglacial and raised beach sands and gravels derived from acid rocks
	Tarves	Drifts derived from intermediate rocks or mixed acid and basic rocks, both metamorphic and igneous
	Peats	Plant Material

The accompanying maps, particularly those for the metamorphic and sedimentary parent materials, show clearly the strong NE - SW structure of the underlying geology of Scotland and this is echoed in the spatial distributions of individual elements within the geochemical datasets. However, it must be borne in mind that the data pertain to the surface horizons, where the influence of parent material may be affected by anthropogenic and pedogenic activities. Thus, without further evidence it would be difficult to provide explanations for all the factors that may have contributed to a single isolated value or observation.

Some of the other soil classification units that can be mapped, e.g. major soil sub groups (Langan et al., 1996), may show much greater differentiation for some elements, e.g. manganese is particularly susceptible to pedogenic processes, such as reduction/oxidation cycles due to waterlogging, and shows significant differences between major soils sub groups.

To aid interpretation a combined map of the 14 major soil associations along with a map of the soil types are given. Within the boundaries of Scotland, there are 793 possible sampling locations where the 10-km National Grid lines intersect. The map shown on page 11 gives the sampling positions of relevance to the data presented in this atlas: there is no data for Orkney and some of the possible sampling locations are bare rock, built on or under water (shown as blanks on the map). For all of the "major" and "trace" elements, data is given for all but two of the locations, comprising 291 mineral soils and 414 organic soils. For carbon, a few additional samples of organic soils from blank positions shown on the map are included in the analysis. The numbers of soil types in each of the categories are as follows:

Cultivated soils (Ap and variations)	176
Leached mineral soils (E and variations)	9
Litter soils (L, F and variations)	28
Mineral soils (A and variations)*	116
Organic soils, aerobic (FH, H and HO)	54
Peats and peaty soils, anaerobic (O and variations)	324
Total	707

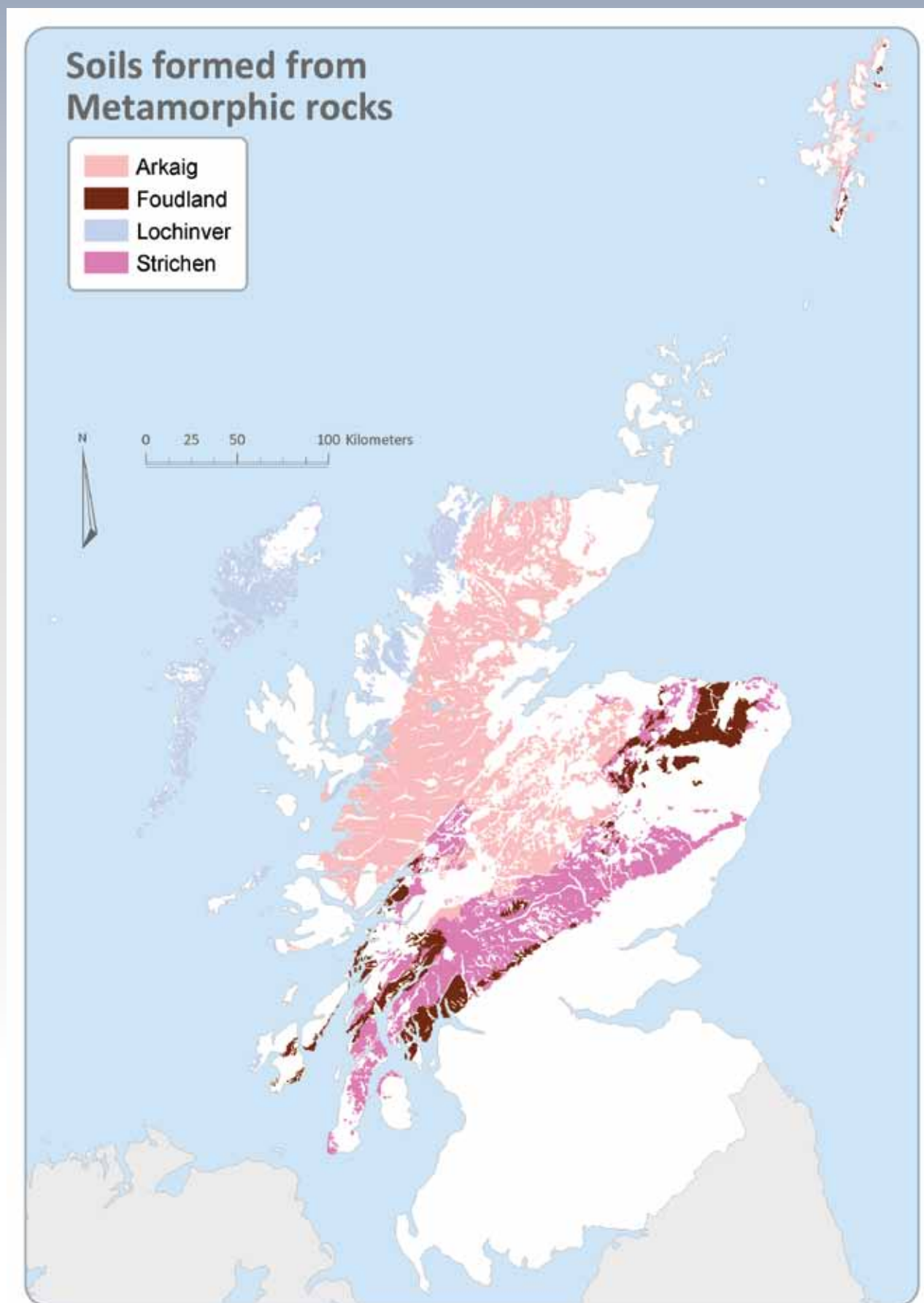*For an explanation of the horizon symbols see Macaulay Institute for Soil Research (1984).*

* Includes 2 samples of exposed subsoil.

In comparing soil survey maps with the geochemical data shown here it is important to recognise that:

1. Soil maps indicate the probability of occurrence of a particular soil type in an area rather than a certainty it will be found there;

2. The point data presented here should not be used for extrapolation or interpolation without a robust statistical basis;

3. Correlation between these two types of datasets must be carried out with care.
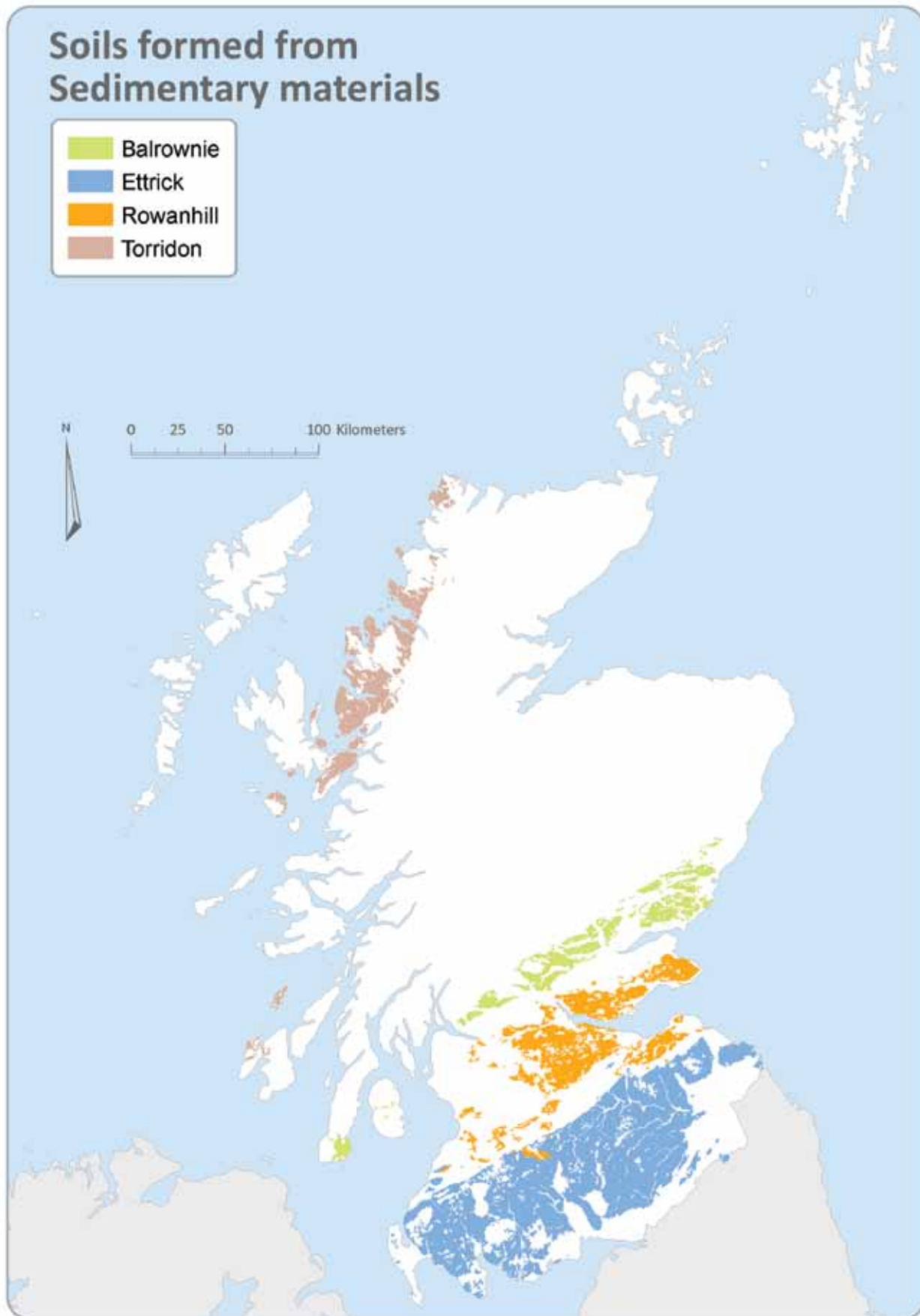
Soils formed from Metamorphic rocks

- Arkaig
- Foudland
- Lochinver
- Strichen

N

0   25   50   100 Kilometers

Geochemical Atlas for Scottish Topsoils

Soils formed from Sedimentary materials

- Balrownie
- Ettrick
- Rowanhill
- Torridon

N

0   25   50   100 Kilometers

Parent Materials of the Major Soil Associations

Soils formed from Igneous rocks

- Countesswells (green)
- Darleith (blue)
- Sourhope (red)

N

0 25 50 100 Kilometers
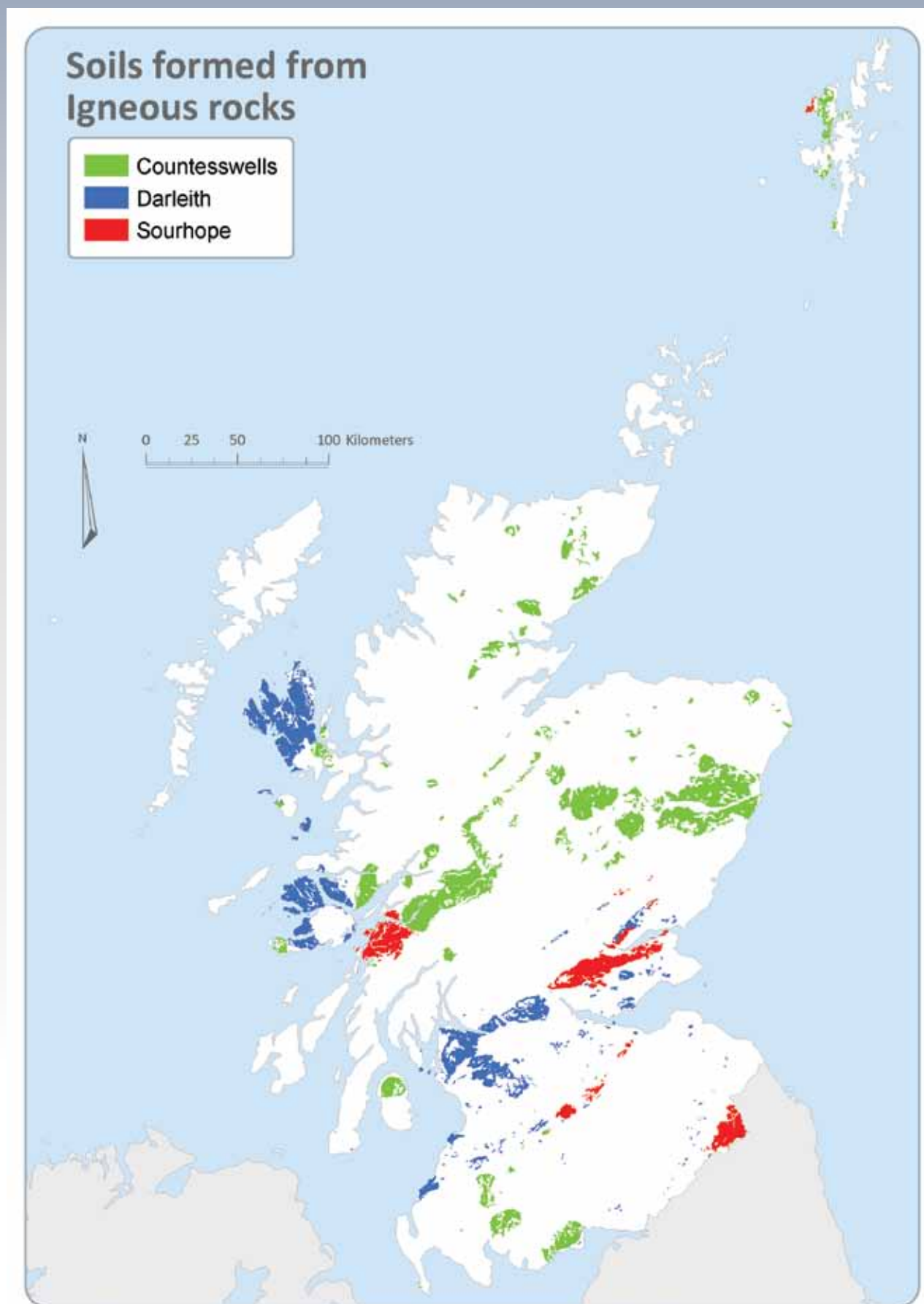
Soils formed from other materials

Corby
Tarves

N

0   25   50   100 Kilometers
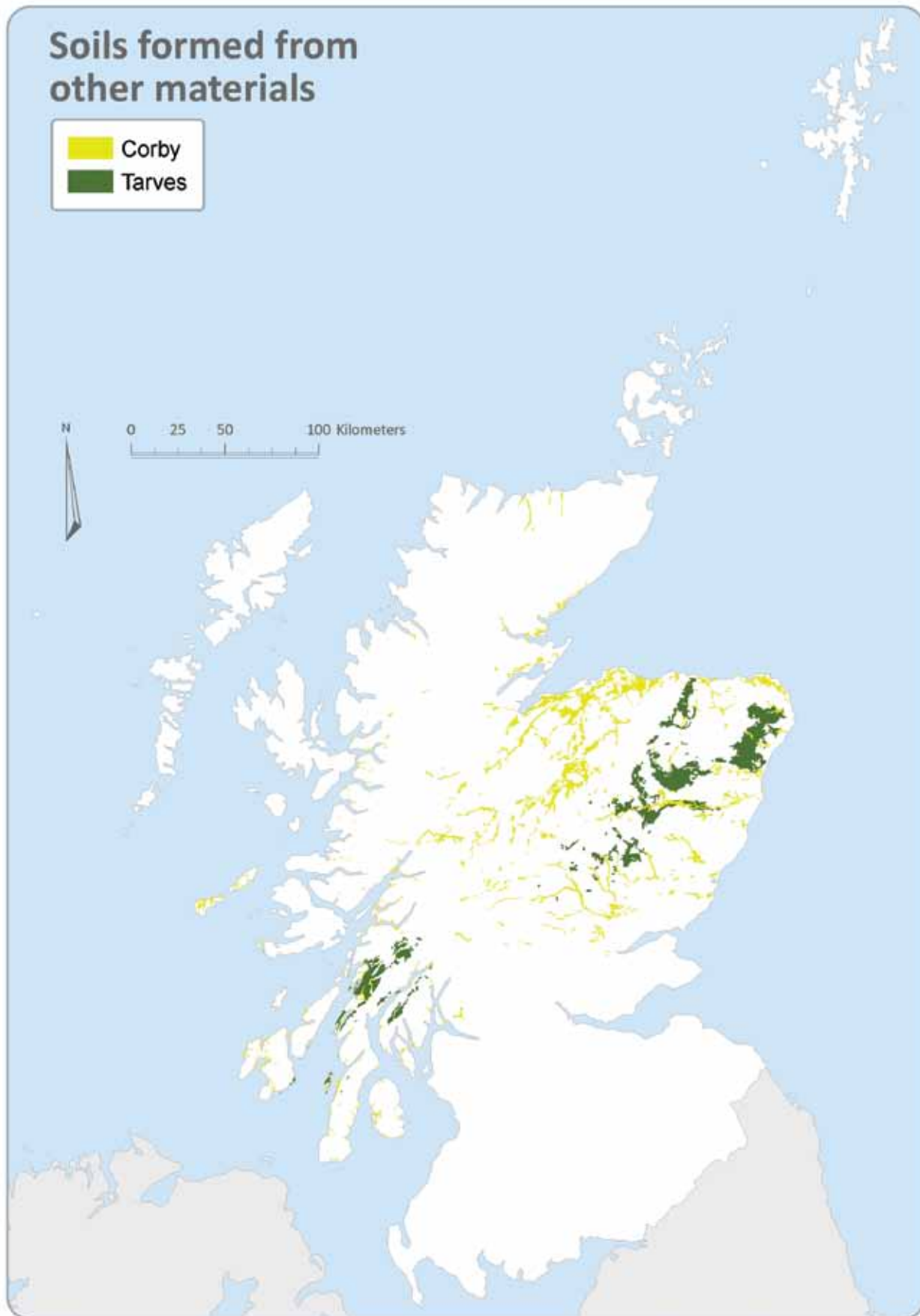
Major Soil Associations in Scotland

Legend:
- Arkaig
- Balrownie
- Corby
- Countesswells
- Darleith
- Ettrick
- Foudland
- Lochinver
- Rowanhill
- Sourhope
- Strichen
- Tarves
- Torridon

N

0   25   50   100 Kilometers

Geochemical Atlas for Scottish Topsoils
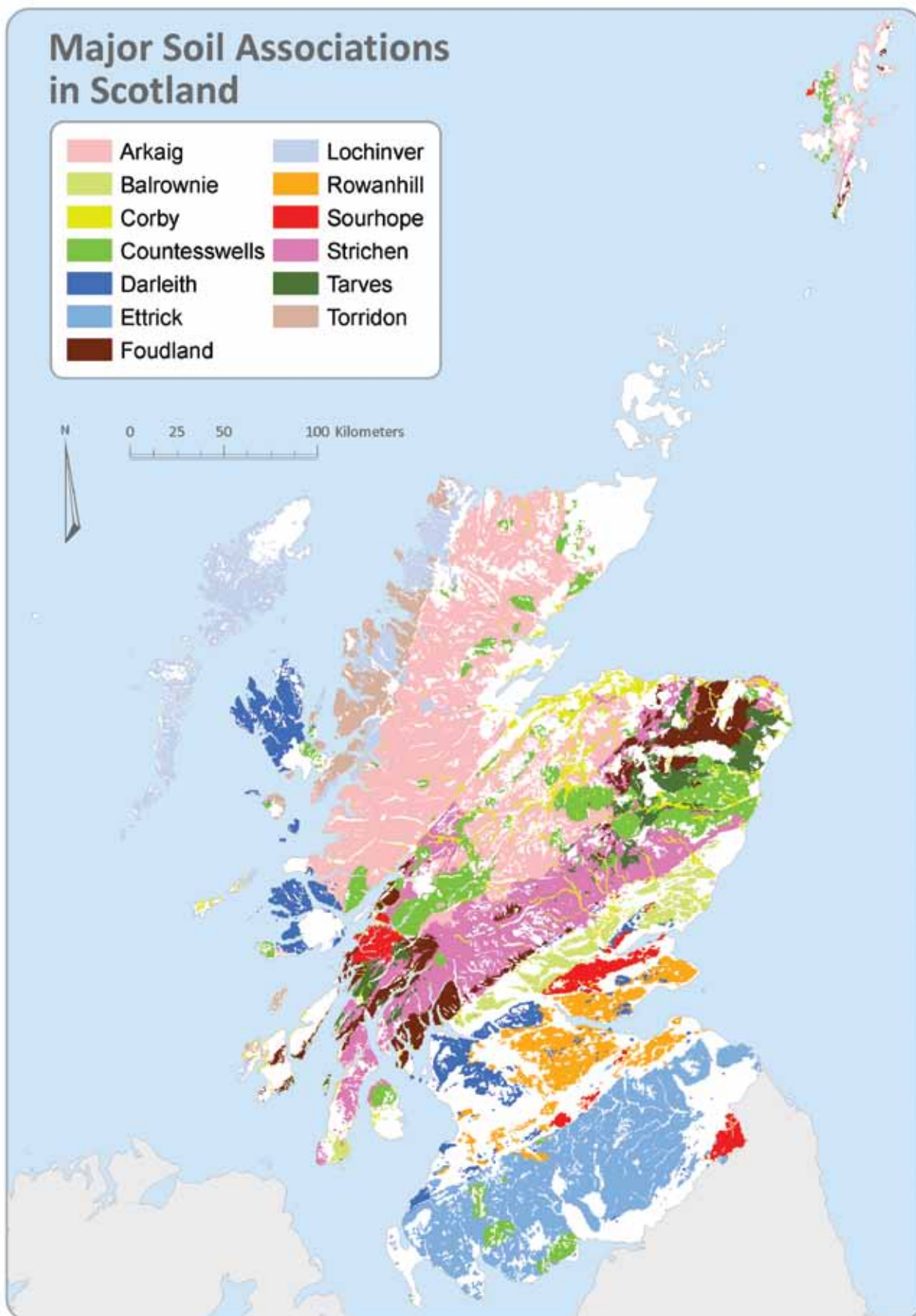
1.2 Sampling Locations and Soil Types

NSIS1
Soil types

- Cultivated soils
- Leached mineral soils
- Litter soils
- Mineral soils
- Organic soils (aerobic)
- Peats and peaty soils (anaerobic)

0 25 50 100 Kilometers

1.3 Carbon

Carbon (%)
in Scottish Topsoils

Carbon (%)
- Above 55.30 (> 95 percentile)
- 51.41 - 55.30 (75 - 95 percentile)
- 26.25 - 51.41 (50 - 75 percentile)
- 5.60 - 26.25 (25 - 50 percentile)
- 2.44 - 5.60 (5 - 25 percentile)
- Below 2.44 (< 5 percentile)
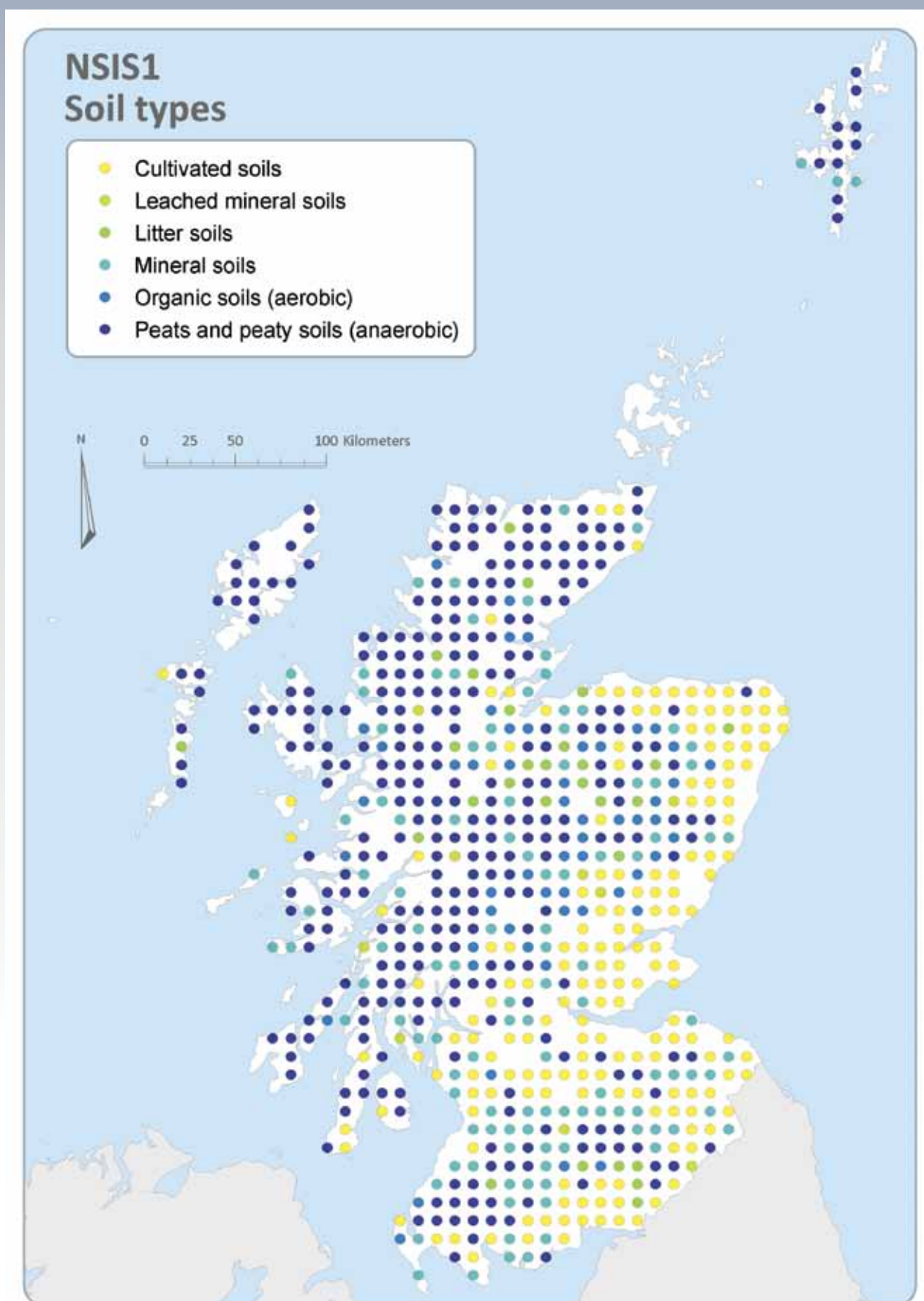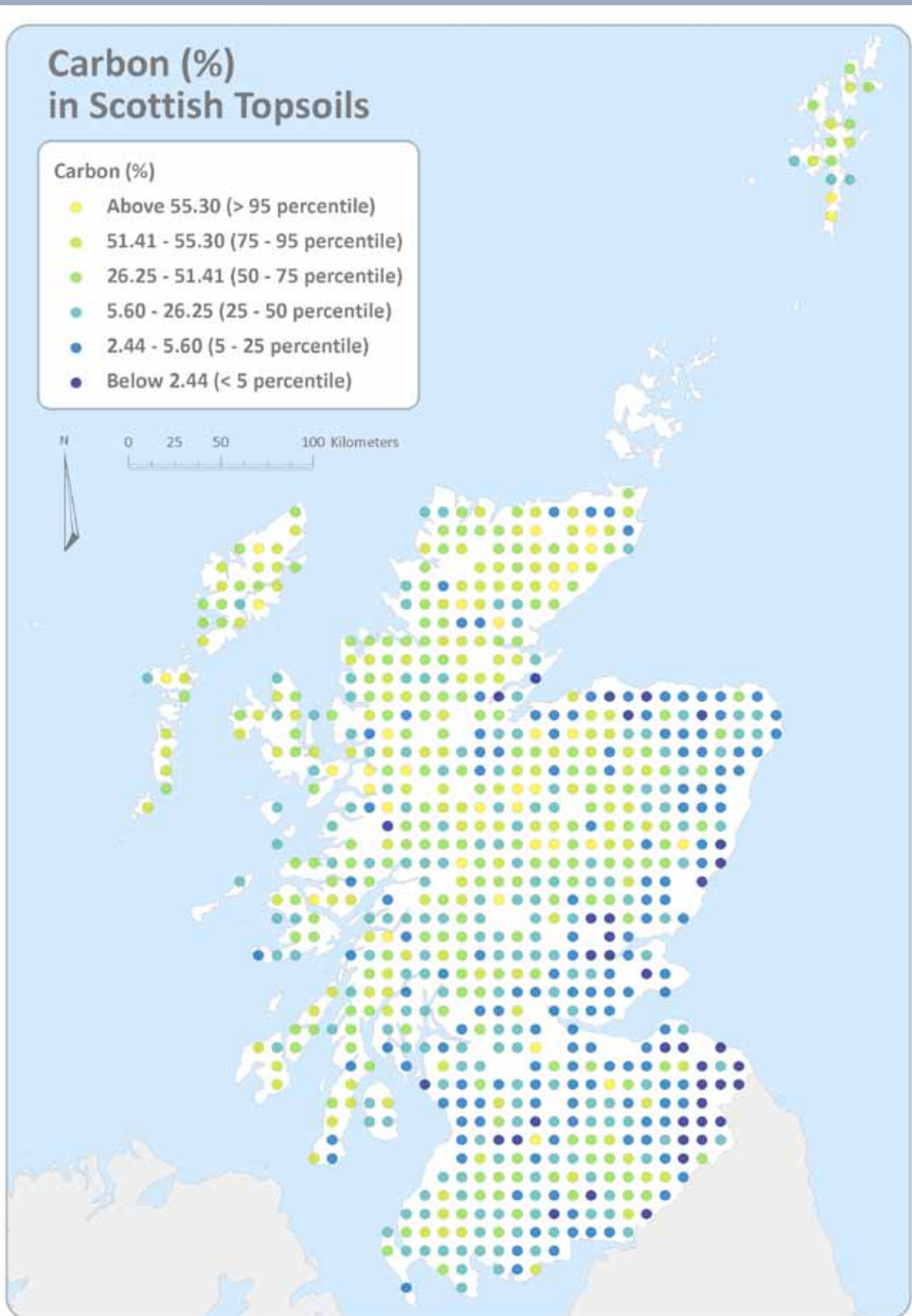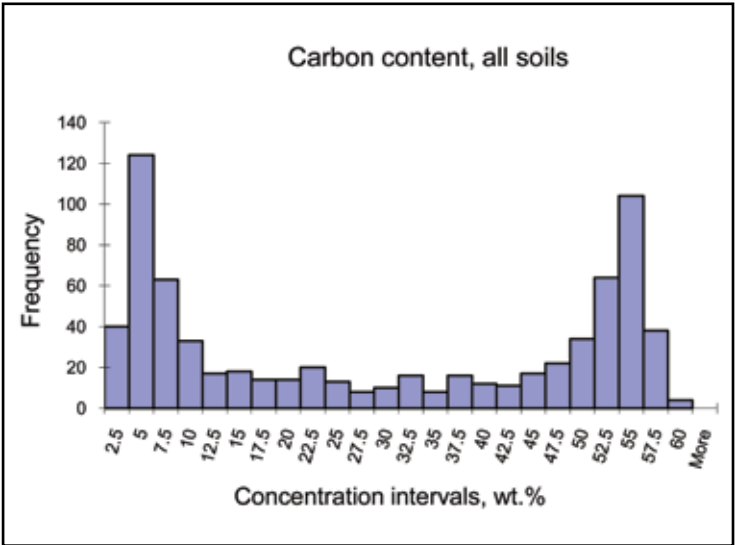
1.3 Carbon

Although most of the carbon in topsoils is not of geochemical origin, the presence and spatial distribution of carbon provides evidence for one of the key soil forming processes that occurs in Scottish soils viz. the accumulation of organic matter. Howard et al. (1995) have estimated that 87% of the total carbon in soils of Great Britain is found in Scotland and that 75% is in Scottish peatlands. Using data for the depth of peat, area of peat, dry peat bulk density and carbon concentration of peat, Chapman et al. (2009) have improved on previous estimates of the carbon content of peatland in Scotland and derived a value of 1620 Mt of carbon, representing 56% of the total carbon stock in Scottish soils estimated by Bradley et al. (2005). The data for the carbon content of topsoils reported here for the Scottish Atlas were obtained by combustion using a Hewlett Packard CHN analyser.

The spatial distribution of carbon concentrations, shows values in excess of the 50 percentile value in the upland soils in the north and west of the country. The concentration of carbon for the lowland soils in the eastern side of the country and across the Central Valley generally fall below the 50 percentile. This fact reflects the occurrence in the uplands of organic surface horizons, either in the form of peat, or as part of organo-mineral soils, such as humus-iron or peaty podzols and peaty gleys. In the lowlands, mineral soils predominate and lower carbon concentration values are observed. Most of the mineral soils have carbon concentrations less than the 25 percentile value of 5.6%, although there is some tendency for increased values at the interface between the lowlands and the uplands. Sporadic occurrences of values less than the 5 percentile value of 2.44%, can be seen on the Moray Firth coast near Inverness and Elgin and on the east coast near Arbroath. These low concentration values are probably associated with coarse textured sandy soils. Low carbon concentration values are also found in the Tay valley and in an area to the east of a line from North Berwick to Jedburgh, near the border with England.


C (wt.%)	mineral	organic
Mean	5.51	43.62
Median	4.65	49.60
Count	291	429

Summary of statistics

The histogram of the carbon contents for the whole dataset shows clearly a bimodal distribution. In these circumstances, summary statistics for the whole sample set would be misleading but it is interesting to compare the median value of 26% for the whole dataset with the value of 3.6% for the soils of England and Wales (McGrath and Loveland, 1992). However, the dataset has been subdivided into two groups - mineral soils with an organic matter content of <25% (<14.5% C) and organic soils. For the mineral soils, the mean carbon content is 5.5% while that for the organic soils is 43.6%.

pH
in Scottish Topsoils

pH
- Below 4
- 4 - 5
- 5 - 6
- 6 - 7
- Above 7
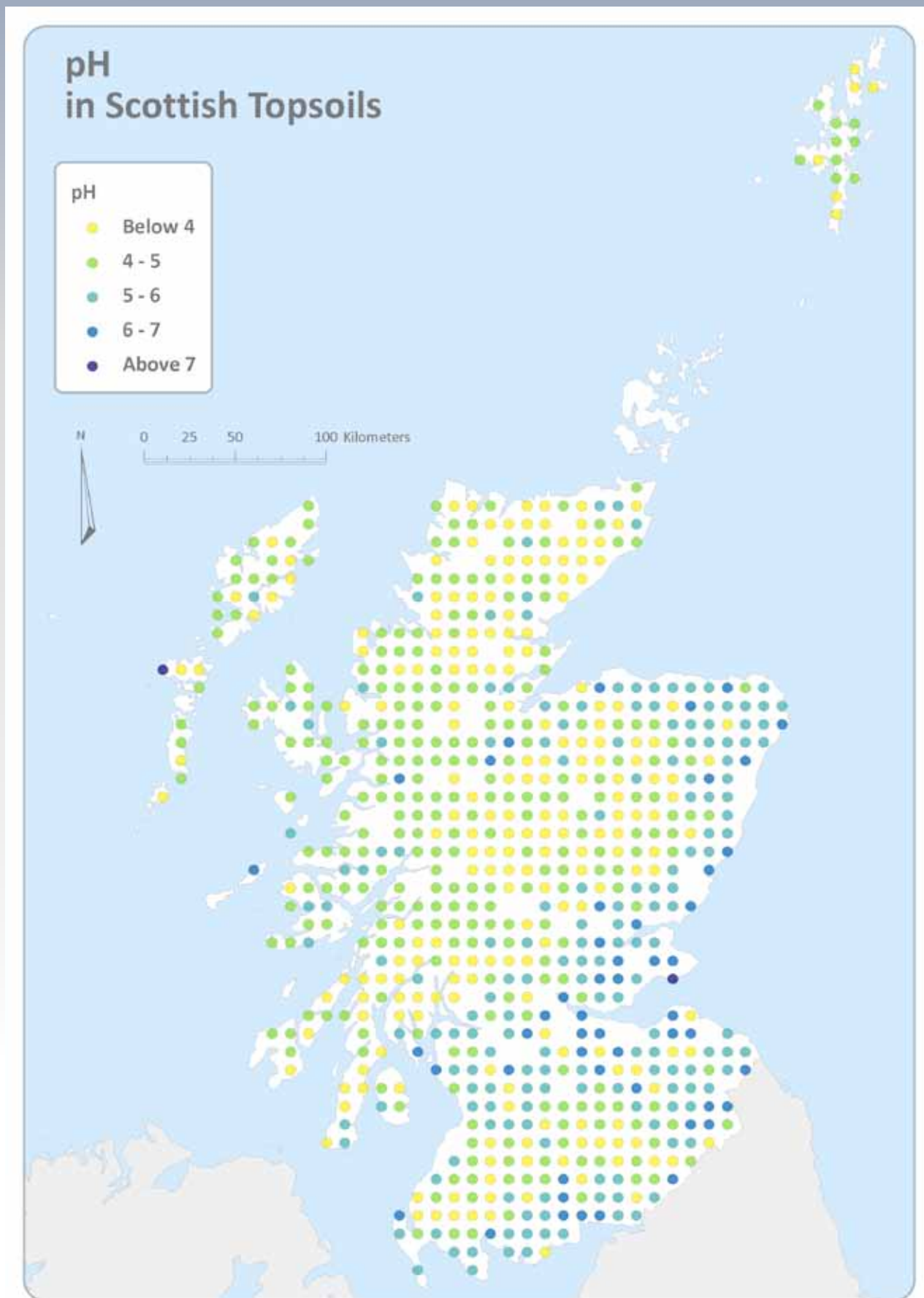
1.4 Soil pH

Soil pH is a key soil property which influences many important processes that occur in soils. These include soil development processes, such as mineral weathering, ion-exchange and specific adsorption as well as carbon turnover and biological processes, all of which significantly affect soil development, growth of crops in agricultural systems and habitat development in semi-natural systems.

The measured pH values found across Scotland show a broad correlation with the carbon contents and clearly delineate the highly organic soils of the Highlands and the Southern Uplands from the mineral soils of the lowland areas. Very few soils in Scotland are alkaline with only two sites where the pH >7; these sites are located on the coast, in Fife and North Uist and probably arise from calcareous sea shells in soils derived from coastal sands. In the cultivated soils of the Moray Firth, Buchan Platform, Fife, Lothians and across the Central Valley, soil pH values lie in the range 5-7 with the majority between 5 and 6. In the organic soils of the north and west the values of pH are almost all below 5 with many falling below 4. Comparison of soil pH values with their susceptibility to acidification as calculated during the Critical Loads for Acid Deposition programme (Langan and Wilson, 1994) shows that many of the vulnerable areas have already undergone considerable acidification. This change is particularly well-illustrated in the soils of the Southern Uplands, developed on greywackes and shales.
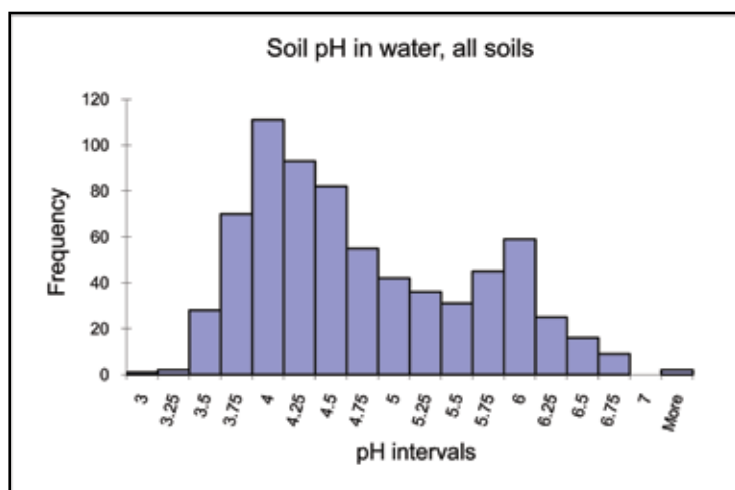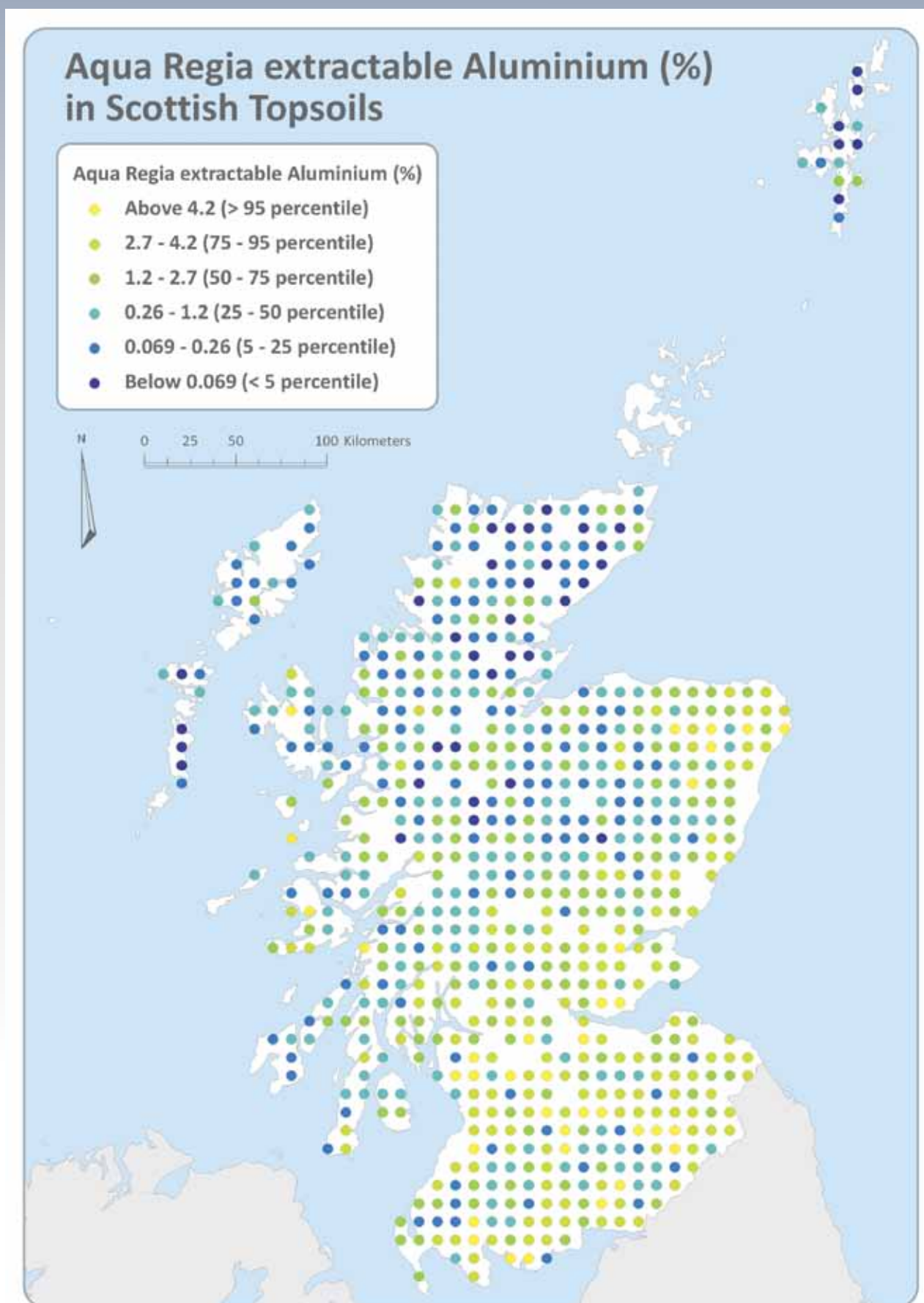

pH (water)	mineral	organic
Mean	5.38	3.45
Median	4.80	2.67
Count	291	416

Summary of statistics

The value of soil pH (measured in water) displays a bimodal distribution peaking at 4.0 and 6.0, respectively. This distribution points to the existence of two distinct populations, which correspond to the largely extensively managed organic soils resource and the more intensively managed mineral soils. In the latter case soil pH is frequently maintained by the addition of lime.

Aqua Regia extractable Aluminium (%) in Scottish Topsoils

Aqua Regia extractable Aluminium (%)
- Above 4.2 (> 95 percentile)
- 2.7 - 4.2 (75 - 95 percentile)
- 1.2 - 2.7 (50 - 75 percentile)
- 0.26 - 1.2 (25 - 50 percentile)
- 0.069 - 0.26 (5 - 25 percentile)
- Below 0.069 (< 5 percentile)

2.1 Aluminium

Aluminium is one of the most common elements in the lithosphere. In soils of the temperate zone, aluminium normally occurs in close association with silicon either in primary minerals, such as feldspars, phyllosilicates and clay minerals. Relatively small proportions of aluminium are found in active forms, although these can be of considerable importance in soil forming processes or in determining the impact of acidification on soils.

The aqua regia extraction method used in this study does not give quantitative recovery of total soil aluminium nor indeed can it be readily related to any of the conventional operationally defined fractions such as that extracted by acid ammonium oxalate (Paterson et al., 1993). Nevertheless, it is arguable (McGrath and Loveland, 1992) that the fraction may be ultimately equated to that which may be released during extreme weathering such as that in highly acidified soils.
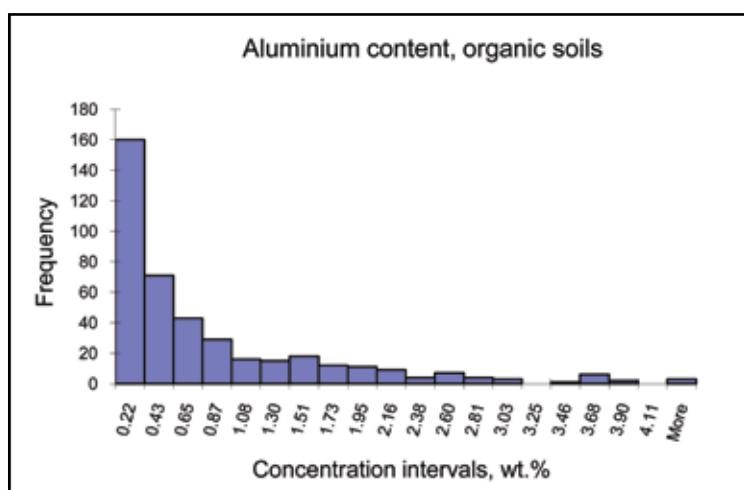
Examination of the inventory data shows the very marked differentiation between the organic soils of upland areas and the mineral surface horizons of the lowlands. The <5 percentile values are entirely associated with the organic soils of the Western Isles and the North West Highlands whereas, the >95 percentile values occur more widely across the Southern Uplands, the Buchan Platform in NE Scotland and the Inner Hebrides.
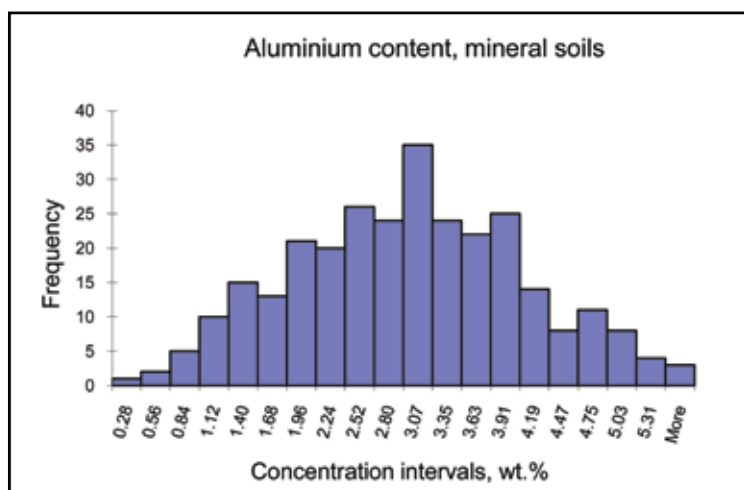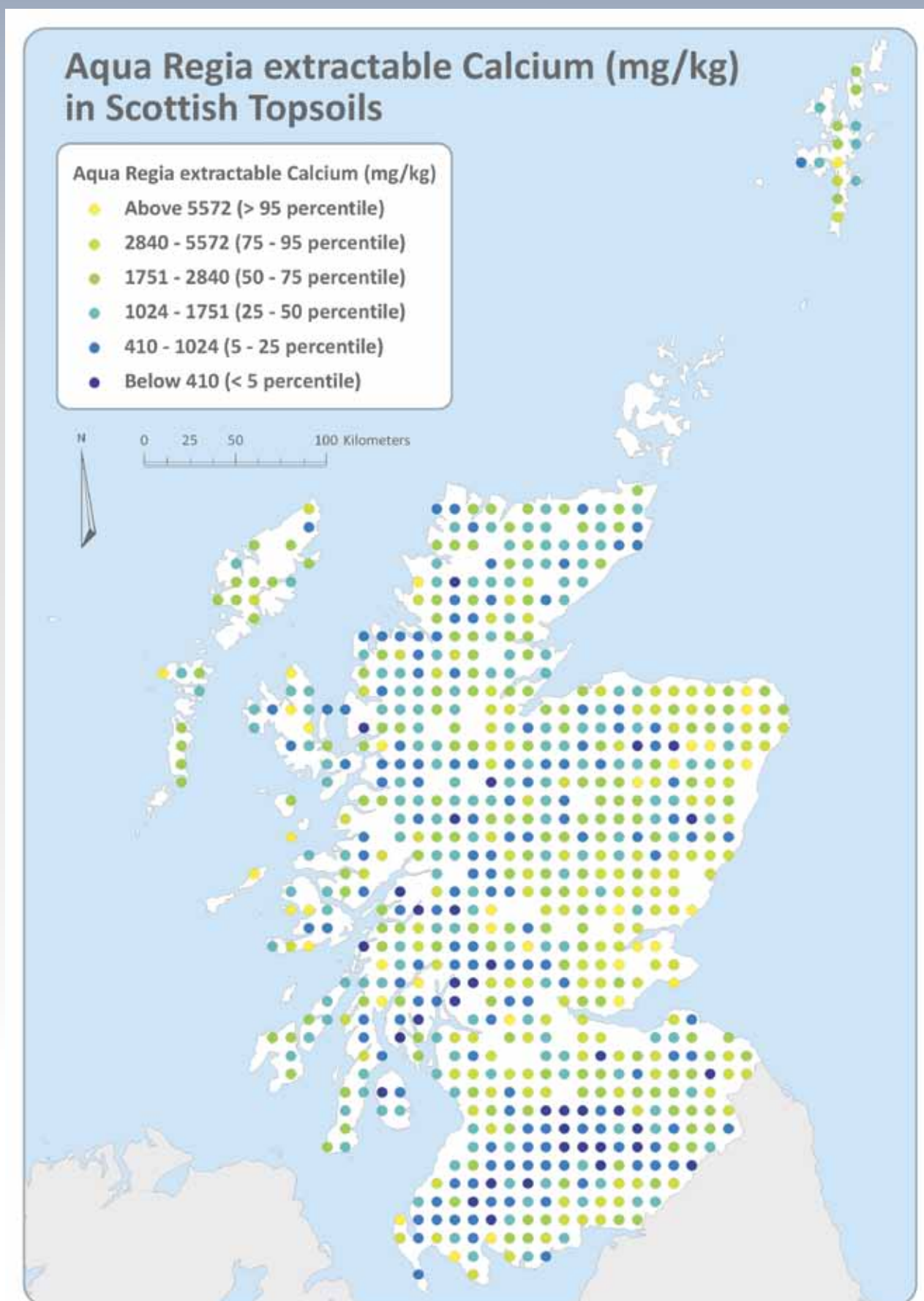

Al (wt.%)	mineral	organic
Mean	2.84	0.71
Median	2.90	0.35
Count	291	414

Summary statistics

The histogram and summary statistics for the mineral soils show an almost normal distribution of aluminium concentration with a mean value of 2.84% and a median value of 2.90%. On the other hand, in the organic soils of the Highlands and uplands a very strongly skewed distribution is obtained. The mean concentration is very much lower at 0.71% and the median even lower at 0.35%.

Aqua Regia extractable Calcium (mg/kg) in Scottish Topsoils

Aqua Regia extractable Calcium (mg/kg)

- Above 5572 (> 95 percentile)
- 2840 - 5572 (75 - 95 percentile)
- 1751 - 2840 (50 - 75 percentile)
- 1024 - 1751 (25 - 50 percentile)
- 410 - 1024 (5 - 25 percentile)
- Below 410 (< 5 percentile)

2.2 Calcium

Calcium is the fifth most abundant element in the Earth's crust and is an important constituent of many rock-forming minerals. Relatively few Scottish soils are developed on calcareous parent materials and only two examples are seen (in Fife and South Uist) where the combination of a high pH value (>7) and high Ca content (> 95 percentile) suggests a calcareous parent material. The most widespread mineral source of calcium in Scottish soils is plagioclase feldspar.
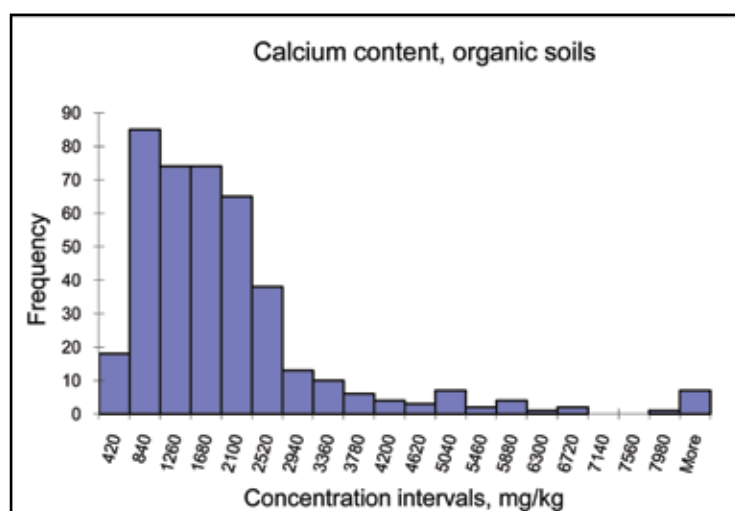
In many soils, calcium is the dominant cation in the exchange complex and its depletion due to acidification results in a strongly developed inverse relationship with soil pH. This relationship is particularly well illustrated across the Southern Uplands and in the Argyll peninsula where low calcium concentration (< 5 percentile) are associated with soil pH values of < 4. The relatively high values of calcium (> 75 percentile) observed in the soils of the north east and east of the country reflect the influence of farming where the addition of lime is a prerequisite for the growth of many arable crops, such as barley.
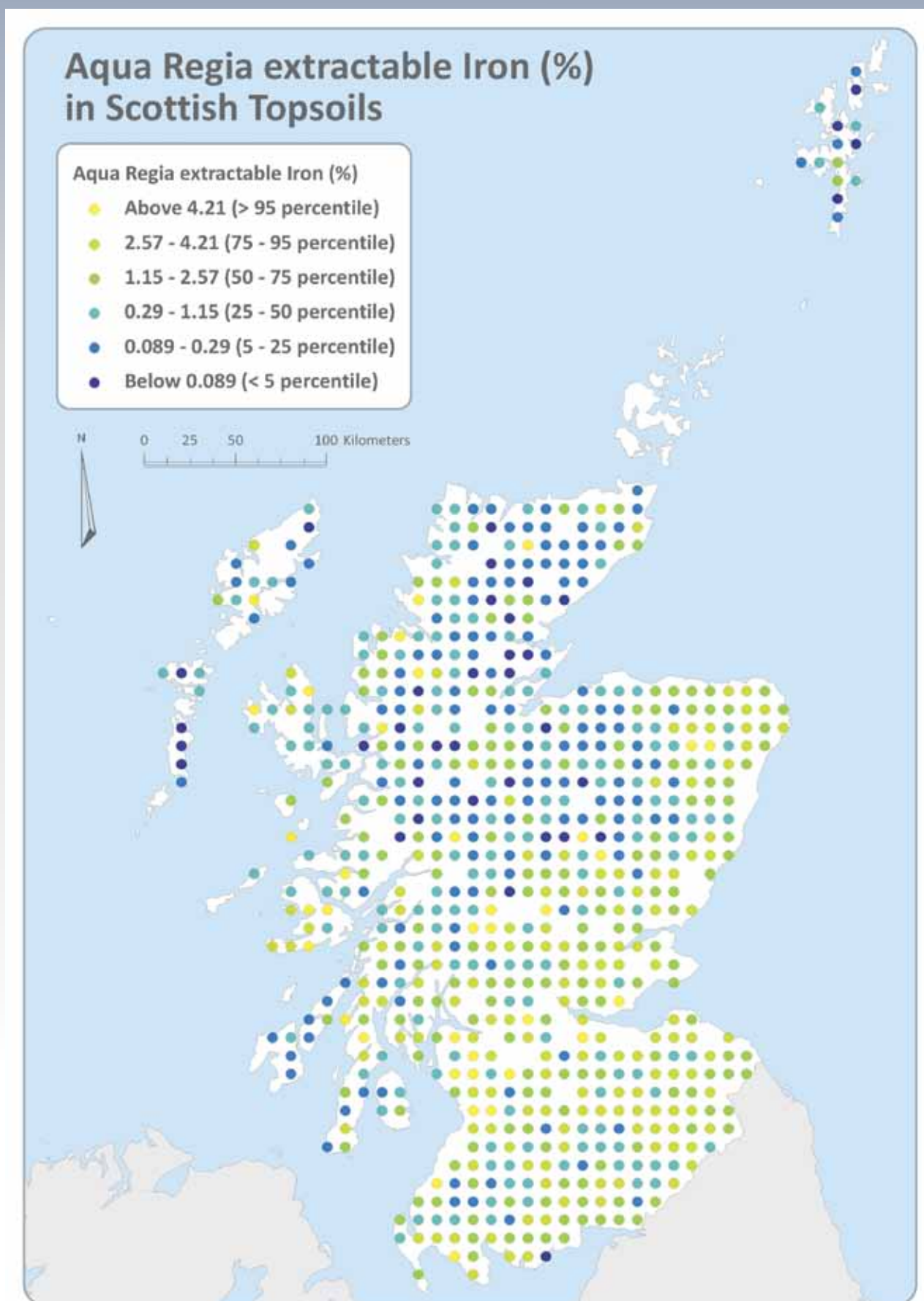

Calcium content, mineral soils
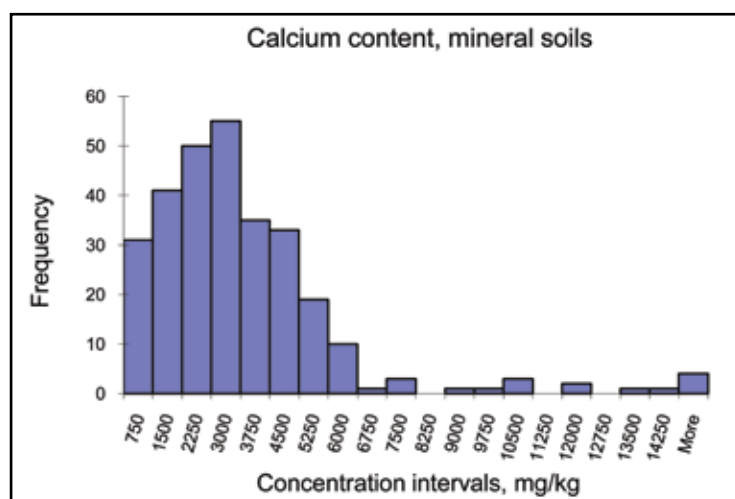
Ca (mg/kg)	mineral	organic
Mean	4439	1791
Median	2618	1433
Count	291	414

Summary statistics

The histogram and summary statistics for the mineral soils show a very narrow distribution of calcium concentration with mean and median values of 4439 mg/kg and 2618 mg/kg, respectively only two soils have a calcium concentration in excess of 100,000 mg/kg with almost all having values <10,000 mg/kg. In the organic soils the content of calcium is around half that observed for the mineral samples with mean and median values of 1791 mg/kg and 1433 mg/kg, respectively.


Calcium content, organic soils

Aqua Regia extractable Iron (%) in Scottish Topsoils

Aqua Regia extractable Iron (%)

- Above 4.21 (> 95 percentile)
- 2.57 - 4.21 (75 - 95 percentile)
- 1.15 - 2.57 (50 - 75 percentile)
- 0.29 - 1.15 (25 - 50 percentile)
- 0.089 - 0.29 (5 - 25 percentile)
- Below 0.089 (< 5 percentile)

N

0   25   50   100 Kilometers

2.3 Iron

Iron is the fourth most abundant element in the Earth's crust and occurs in a range of mineral types. It can occur in both divalent and trivalent forms and its geochemical and pedogenic behaviour is strongly influenced by its valency. The lower valency is normally associated with substitution in silicate structures, such as olivines and micas, while the trivalent form occurs extensively as oxide species. Iron plays an important role in the pedogenesis of soils where its mobilisation and reprecipitation within the soil profile is used as an important diagnostic criterion in soil classification. Many of the mineral species in which it occurs are acid labile and it is likely that high recoveries of iron are obtained using aqua regia.

The most notable feature in the geochemical dataset is again the differentiation between organic and mineral soils although there are a number of instances where very high values (> 95 percentile) are obtained in areas of predominantly organic soils. Many of these situations may arise because of the admixture of 'iron pan' subsoils with the organic surface horizons, which are sometimes very shallow. However, there are also a series of high iron concentration values associated with the basaltic lava-derived soils of the Inner Hebrides as well as the soils in North Ayrshire. It is noteworthy that many of these sites also show elevated concentration values for other elements, such as calcium. The higher iron concentration values found In the soils of the north-east of Scotland probably reflects the fact that many of these mineral soils are, in fact, cultivated podzols where admixture of iron-rich subsoils has resulted in elevated topsoil concentrations.
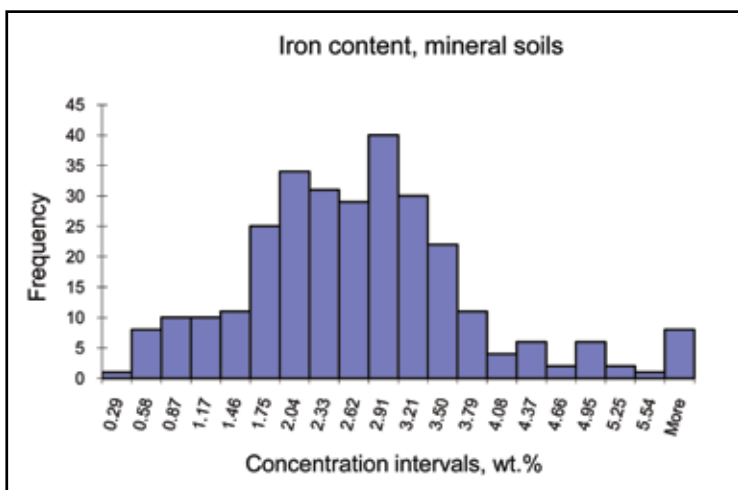
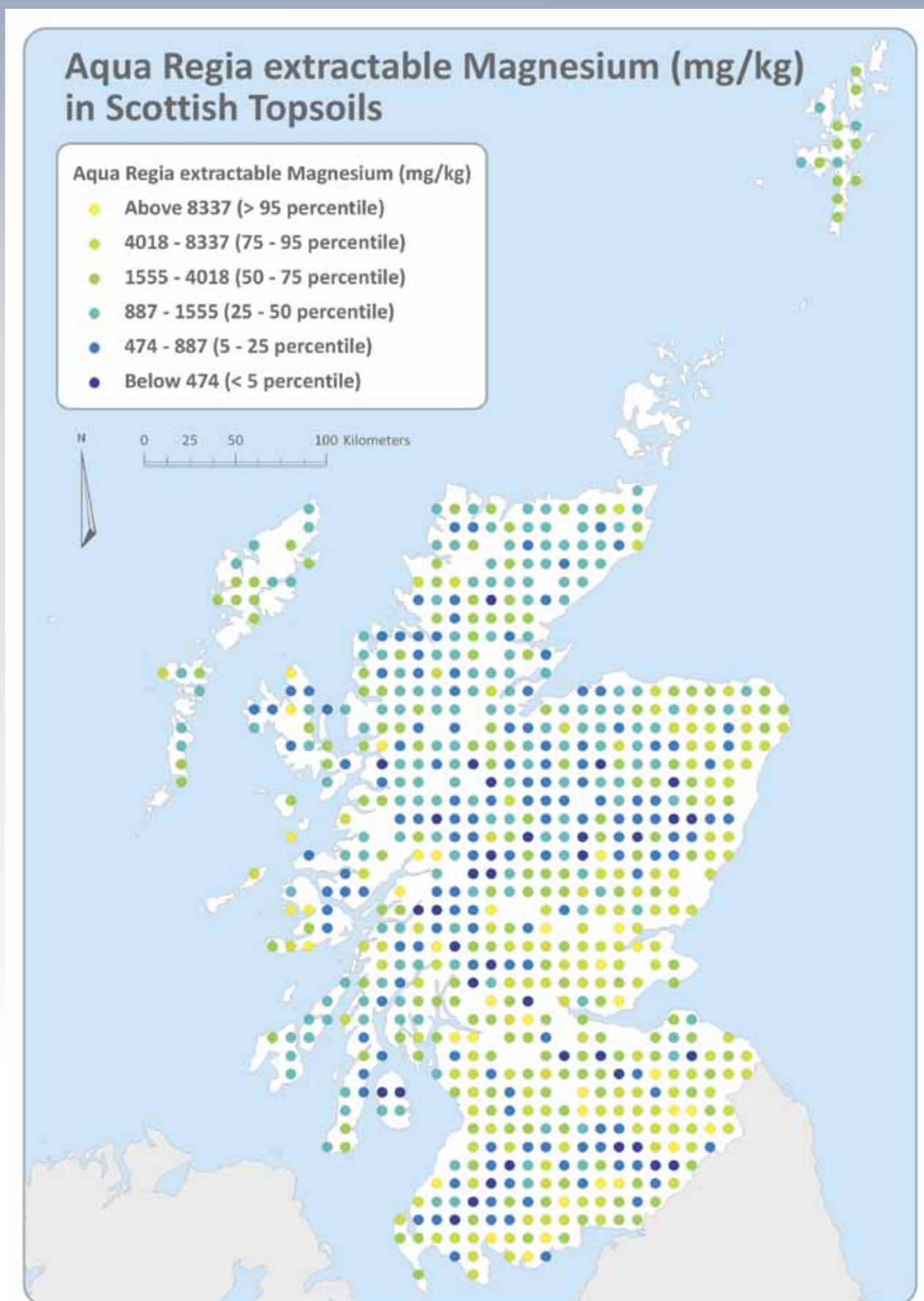| Fe (wt.%)	mineral	organic
Mean	2.55	0.972
Median	2.47	0.376
Count	291	414

Summary statistics

The summary statistics and the histogram for the mineral soils show an approximately log normal distribution with mean and median values near 2.5% with most soils having values lower than around 4%.
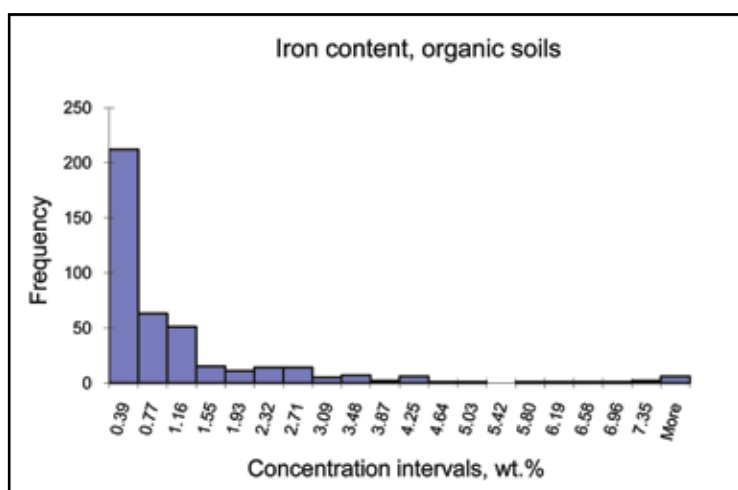
For the organic soils the mean is greater at 0.97% than the median at 0.38% and the histogram shows a very skewed distribution with most values less than 1%.

Aqua Regia extractable Magnesium (mg/kg) in Scottish Topsoils

Aqua Regia extractable Magnesium (mg/kg)

- Above 8337 (> 95 percentile)
- 4018 - 8337 (75 - 95 percentile)
- 1555 - 4018 (50 - 75 percentile)
- 887 - 1555 (25 - 50 percentile)
- 474 - 887 (5 - 25 percentile)
- Below 474 (< 5 percentile)

N   0   25   50   100 Kilometers

2.4 Magnesium

Magnesium occurs in a wide range of silicate minerals, where it frequently substitutes for Fe (II), and also in phyllosilicate minerals, such as biotite and chlorite. Its occurrence in acid labile mineral species should ensure reasonable recovery using aqua regia. Magnesium is an essential element for both plant and animal health; in the former, it is the central metallic constituent of the porphyrin complex, chlorophyll, and, in the latter, it plays a key role in enzymatic reactions.
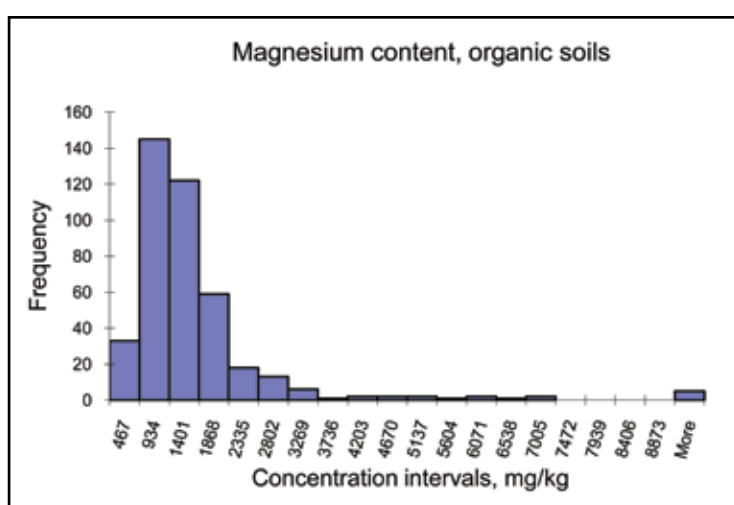
The upper quartile values for the magnesium concentrations are almost all located on the mineral soils of Scotland. On the other hand the lower quartile and the very low values (< 5 percentile) are associated with organic upland soils in both the Highland and Southern Uplands. However, it is noteworthy that on the periphery of the Southern Uplands very high magnesium concentration values are observed which are associated with the soils of the Ettrick association. High magnesium concentration values (> 95 percentile) are also observed in the Inner Hebrides, probably associated with basaltic rocks.
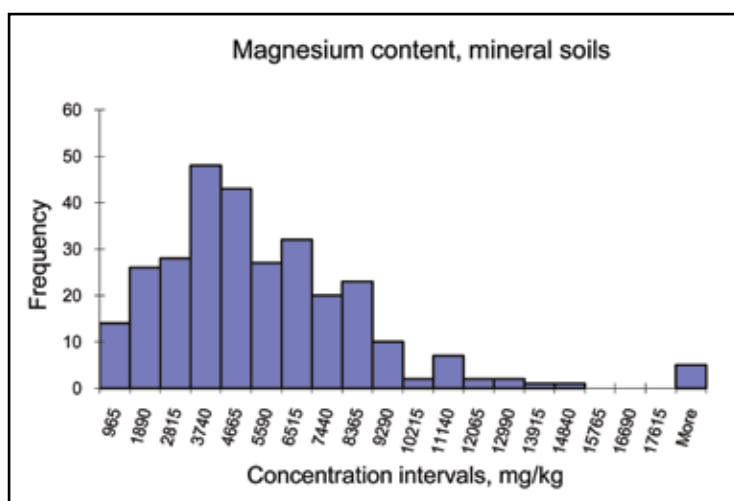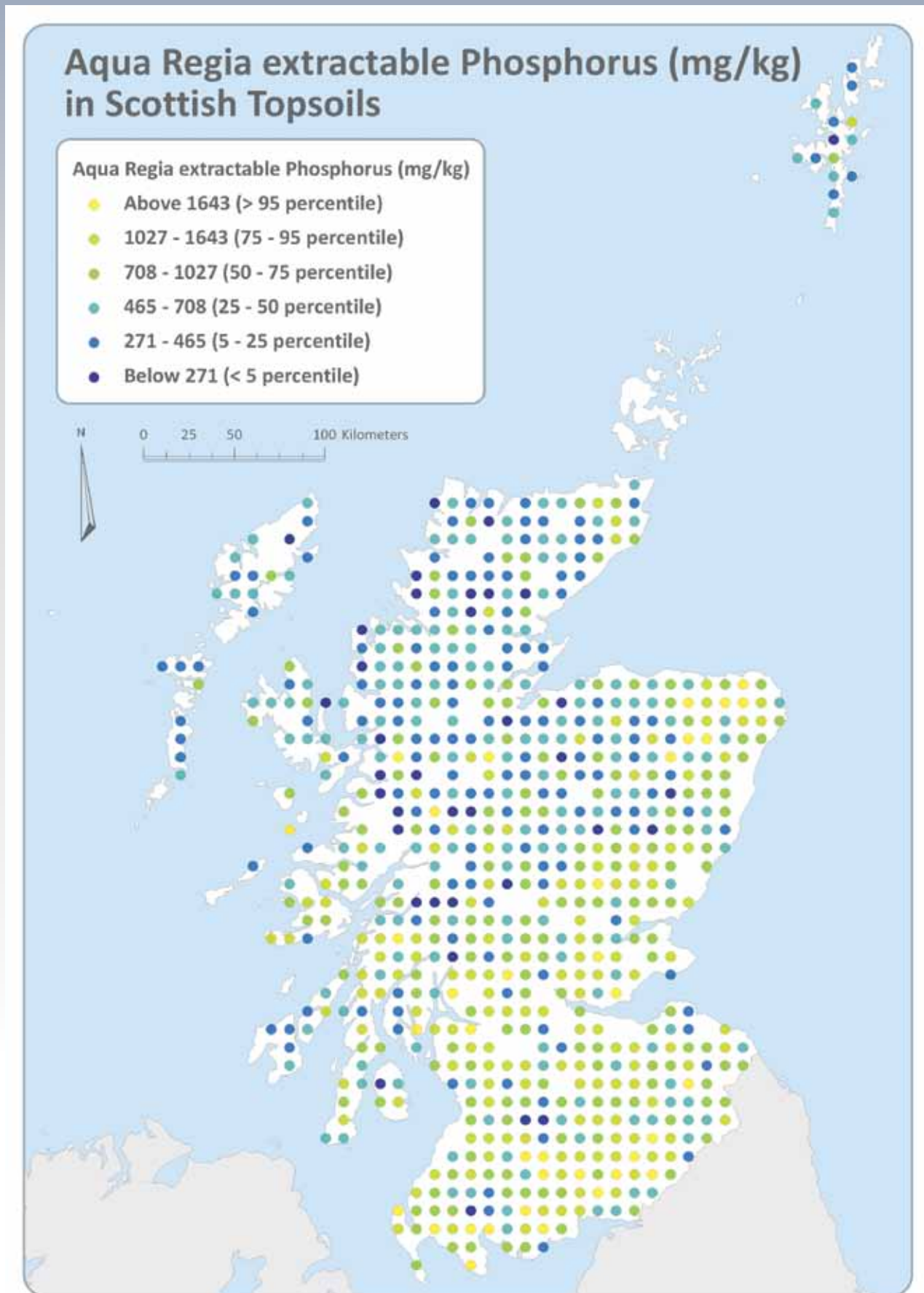

Mg (mg/kg)	mineral	organic
Mean	5127	1410
Median	4232	1009
Count	291	414

Summary statistics

The summary statistics and the histograms for the mineral soils show that the magnesium concentration is approximately normal with a mean value of 5127 mg/kg and a median of 4232 mg/kg. The upper limit for most of the concentrations is 15,000 mg/kg. However, in the organic soils much lower values of magnesium concentration are obtained with a mean of 1410 mg/kg and a median of 1009 mg/kg. Virtually all of the concentrations are less than 3300 mg/kg.

Aqua Regia extractable Phosphorus (mg/kg) in Scottish Topsoils

Aqua Regia extractable Phosphorus (mg/kg)

- Above 1643 (> 95 percentile)
- 1027 - 1643 (75 - 95 percentile)
- 708 - 1027 (50 - 75 percentile)
- 465 - 708 (25 - 50 percentile)
- 271 - 465 (5 - 25 percentile)
- Below 271 (< 5 percentile)

0   25   50   100 Kilometers

2.5 Phosphorus

The average crustal abundance of phosphorus is 1050 mg/kg and the only phosphorus compounds known to occur in natural systems involve the oxyanion, phosphate. Thus, minerals such as apatite form a major source of phosphorus. The role of phosphorus as a major nutrient in both plants and animals is well known and most arable and mixed agricultural systems in Scotland include substantial additions of phosphate fertilisers.
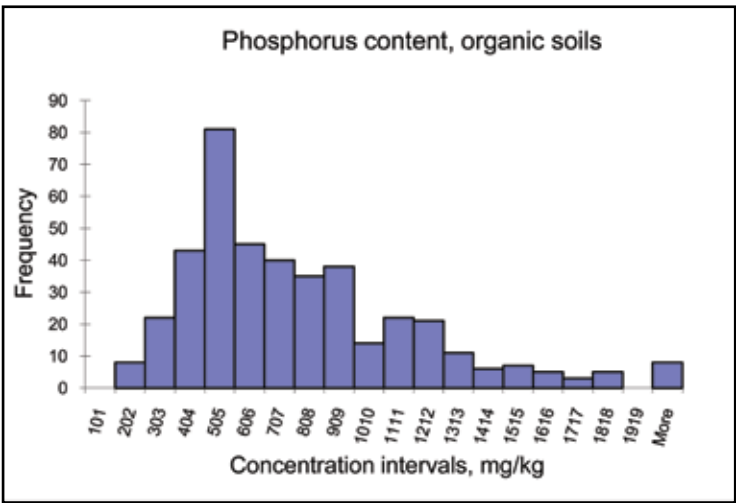
The lowest values of phosphorus concentration (< 5 percentile) are associated with highly organic upland soils in the north-west and central highlands. Much of the remaining organic soils north of the Highland Boundary Fault fall below the median value for Scotland. Upper quartile and very high values (> 95 per-centile values) are found in the Buchan and Upper Buchan Platforms in north-east Scotland which have probably arisen from agricultural activity over many years. The other areas of enrichment include parts of Fife and the southern part of the Southern Uplands.
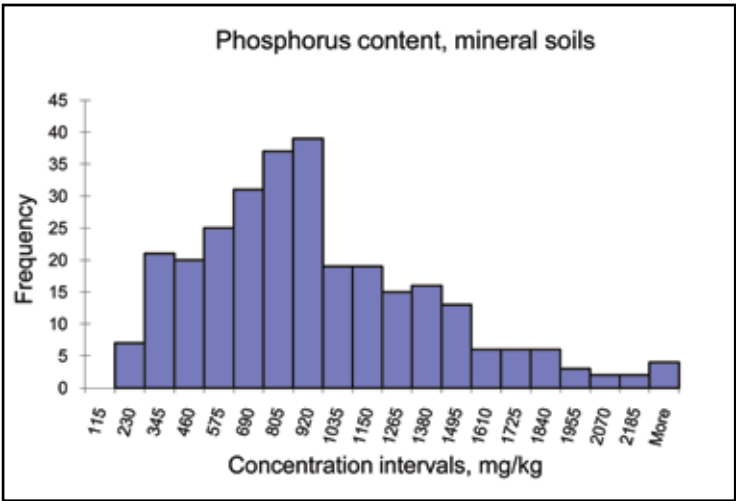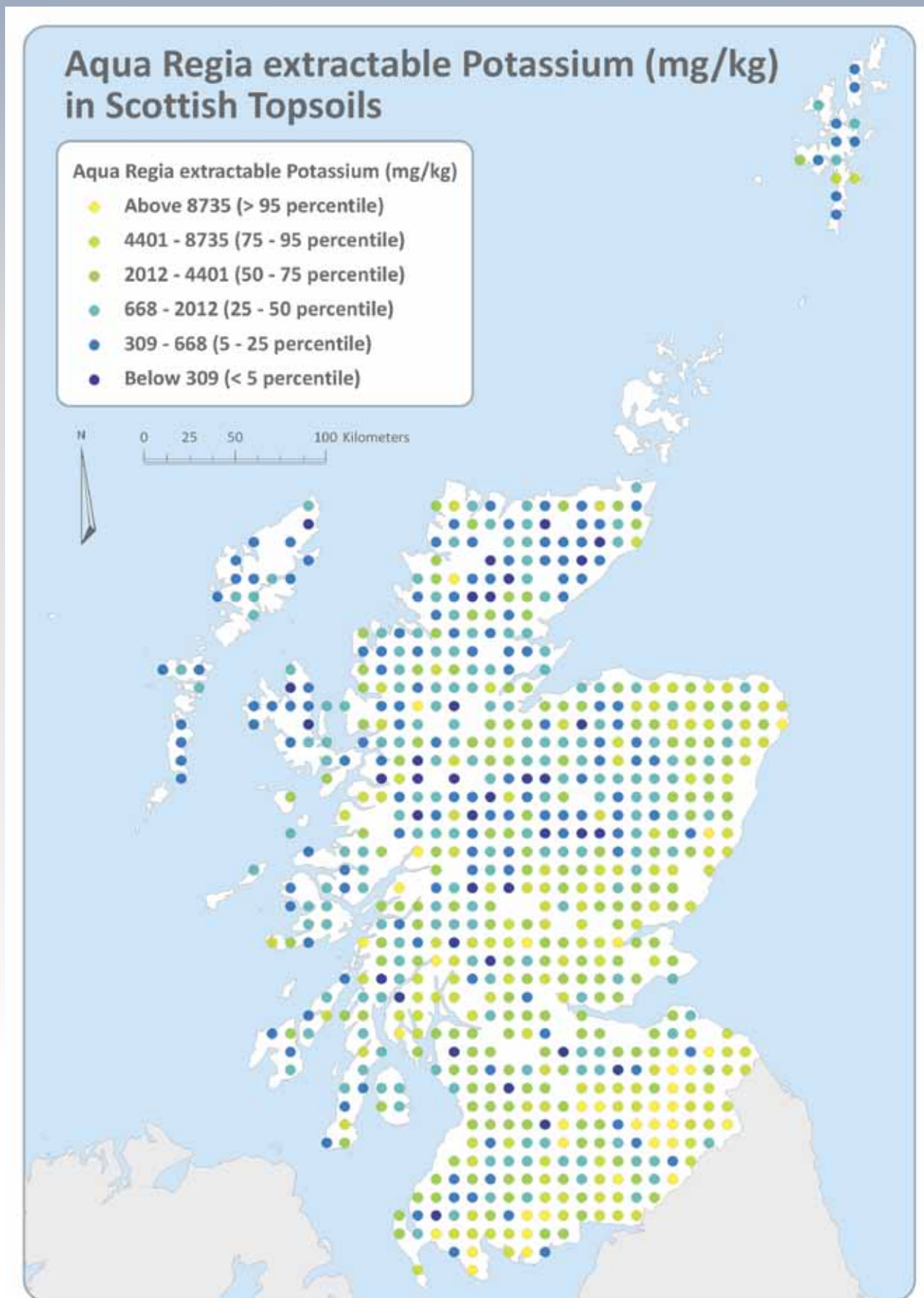

P (mg/kg)	mineral	organic
Mean	896	729
Median	813	630
Count	291	414

Summary statistics

It is clear from the summary statistics and the histograms that there is a slight enrich-ment of phosphorus in mineral soils com-pared to the concentration in organic soils. For the mineral soils the mean and median values are similar at 896 mg/kg and 813 mg/kg, respectively. In the organic soils there is a similar discrepancy with values of 729 mg/kg and 630 mg/kg, respec-tively. The distribution for the mineral soils tends to be flatter with a wide range of val-ues whereas for the organic soils a peak is observed at lower values.

Aqua Regia extractable Potassium (mg/kg) in Scottish Topsoils

Aqua Regia extractable Potassium (mg/kg)

- Above 8735 (> 95 percentile)
- 4401 - 8735 (75 - 95 percentile)
- 2012 - 4401 (50 - 75 percentile)
- 668 - 2012 (25 - 50 percentile)
- 309 - 668 (5 - 25 percentile)
- Below 309 (< 5 percentile)

N

0   25   50   100 Kilometers

2.6 Potassium

Potassium occurs in soils at concentrations that are only slightly lower than those of magnesium and sodium. It occurs almost entirely within the structure of silicates, such as alkali feldspars, and aluminosilicate minerals, e.g. mica, and is held in an exchangeable form on cation exchange sites. Potassium is an essential element for both plant growth and animal health. Potassium deficiency in plants results in a chlorosis of the older leaves whilst in animals, potassium (as K^+) is one of the principal extracellular salt components and is thought to offer some protection against sodium-induced hypertension. A detailed assessment of the potassium reserves in Scottish grassland soils, based on aqua regia extraction and mineralogical analysis of the soils by X-ray powder diffraction, has been published by Andrist-Rangel et al. (2010).

The lowest concentration values of potassium are associated with the organic soils of the north-west and central Highlands, where most of the soils have values in the lower quartiles and the < 5 percentile ranges. It is noteworthy that the organic soils of the Southern Uplands do not display similarly low concentration values. Particularly high concentration values are clustered at the eastern and southern edges of the Southern Uplands and at the edges of the Highland Boundary fault line running from Stonehaven in NE Scotland to Loch Lomond in the west. The upper quartile values found in the northern part of the Buchan Platform from Aberdeen to Banff may be associated with the proportion of acid igneous rocks found in the mixed till of the Tarves Association or may reflect fertiliser inputs.
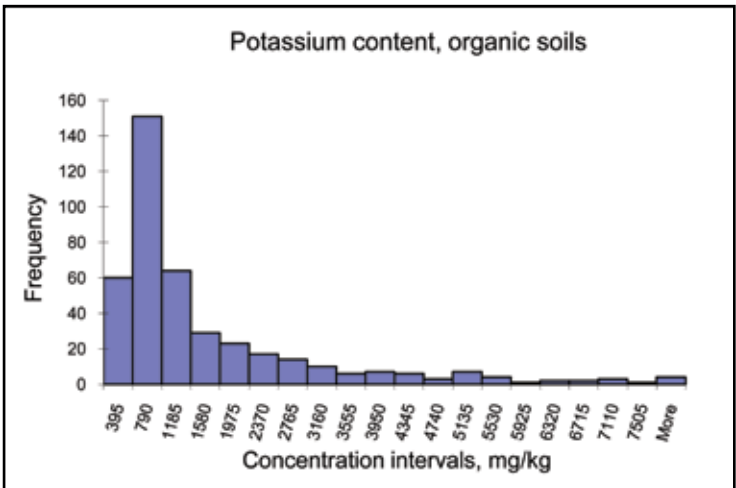

Potassium content, mineral soils

Potassium content, organic soils
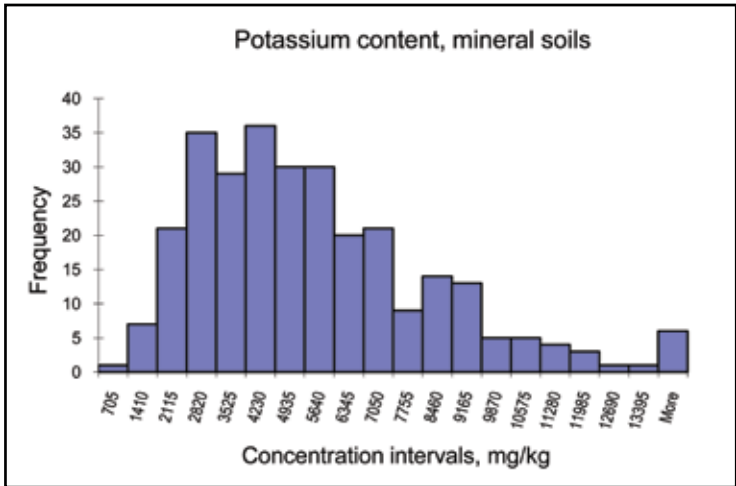
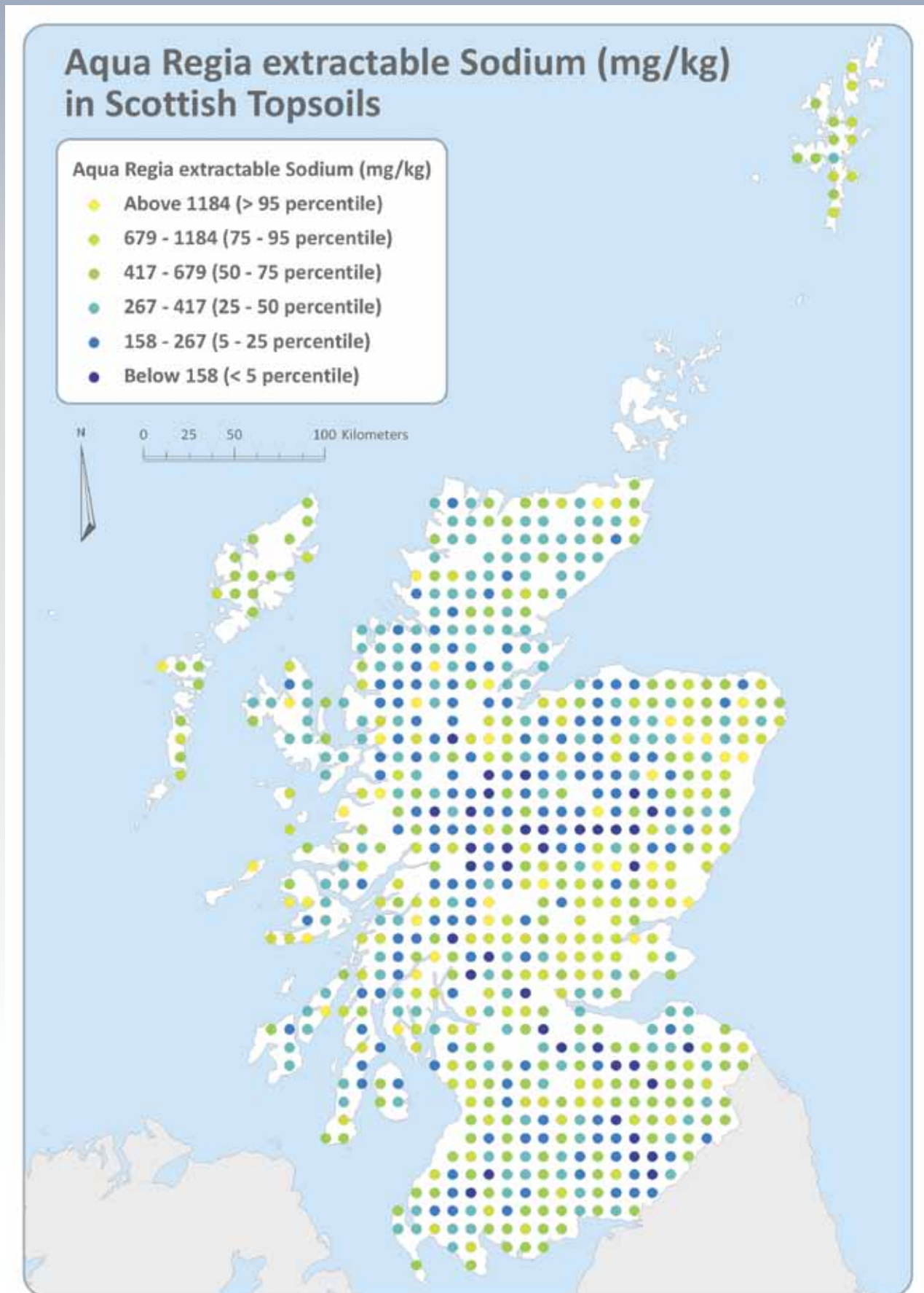| K (mg/kg)	mineral	organic
Mean	5150	1407
Median	4452	775
Count	291	414

Summary statistics

From both the summary statistics and the histograms it is clear that considerable differences are observed in the potassium content of mineral and organic soils.

The distribution of concentrations is relatively wide for mineral soils with some skewing towards lower values. The mean and median values are similar at 5150 mg/kg and 4452 mg/kg, respectively. For the organic soils, however, most values are <2000 mg/kg and are strongly skewed towards the lower values with a mean content of 1407 mg/kg and a median of 775 mg/kg.

Aqua Regia extractable Sodium (mg/kg) in Scottish Topsoils

Aqua Regia extractable Sodium (mg/kg)
- Above 1184 (> 95 percentile)
- 679 - 1184 (75 - 95 percentile)
- 417 - 679 (50 - 75 percentile)
- 267 - 417 (25 - 50 percentile)
- 158 - 267 (5 - 25 percentile)
- Below 158 (< 5 percentile)

2.7 Sodium

Sodium has an average crustal abundance of 2.3%, (23,000 mg/kg). In parent rocks most of the sodium is found in feldspars although it can also be found in amphibole and pyroxene. Sodium is also one of the four major cations found associated with cation exchange sites in soils. The recovery of sodium from soils using aqua regia extraction has been noted by McGrath and Loveland (1992) as very poor. Most of the sodium is likely in sodium feldspar, which is insoluble in aqua regia.

The highest concentrations of sodium (< 75 percentile) are associated with two groups of soils. The first of these is the coastal areas on the west, north and east of the country, where it is likely that marine inputs make a major contribution. The second is associated with the mineral soils located between the Forth-Clyde valley and the Highland Boundary fault and in the Buchan Platform in north-east Scotland. In the organic soils of the central Highlands particularly low values are found (< 5 percentile).
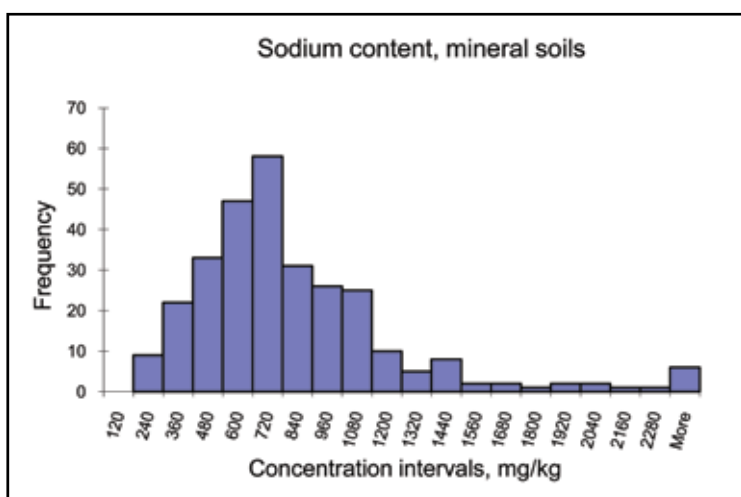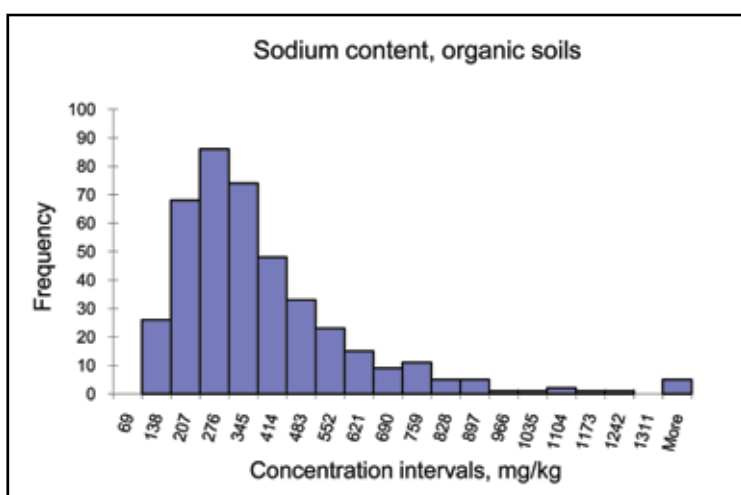

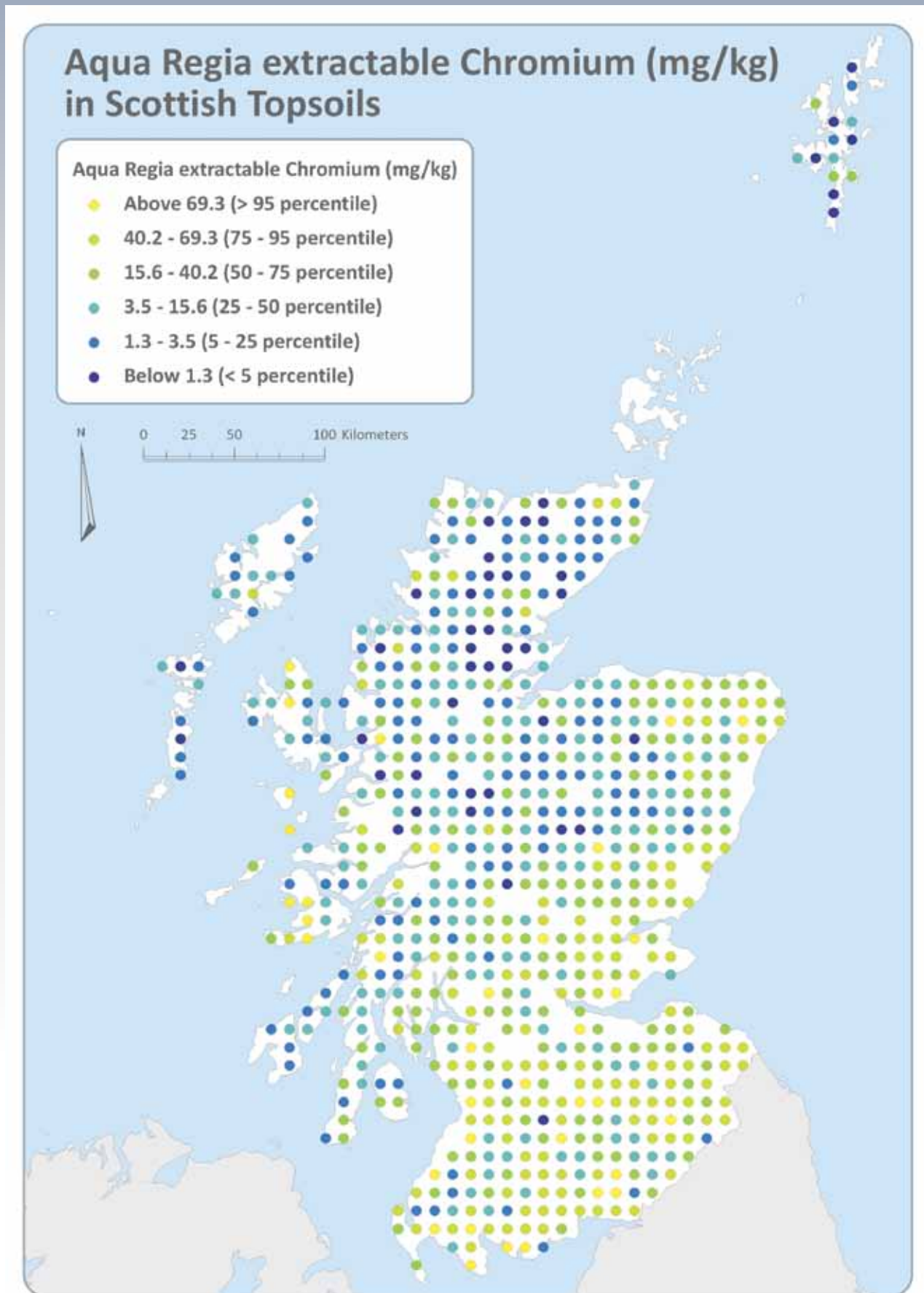| Na (mg/kg)	mineral	organic
Mean	776	364
Median	677	299
Count	291	414

Summary statistics

The difference between the mineral and organic soils is less marked for sodium than it is for many of the other elements in this dataset with only a twofold difference.

The histogram for the mineral soils shows an almost normal distribution with a mean vale of 776 mg/kg and a median value of 677 mg/kg. For the organic soils, the distribution is more skewed towards lower concentrations with a mean value of 364 mg/kg and a the median value of 299 mg/kg – approximately half that observed for mineral soils.

Aqua Regia extractable Chromium (mg/kg) in Scottish Topsoils

Aqua Regia extractable Chromium (mg/kg)
- ◆ Above 69.3 (> 95 percentile)
- ● 40.2 - 69.3 (75 - 95 percentile)
- ● 15.6 - 40.2 (50 - 75 percentile)
- ● 3.5 - 15.6 (25 - 50 percentile)
- ● 1.3 - 3.5 (5 - 25 percentile)
- ● Below 1.3 (< 5 percentile)

3.1 Chromium

Of the conventionally defined 'trace metals' chromium occurs with an average crustal abundance of 100 mg/kg but the concentration displays a wide variation with rock type. Chromium is found in two valency states in nature – with a valency of 3+ as the chromic cation, Cr^{3+}, and a valency of 6+ in the chromate oxyanion, CrO_4^{2-}. Although environmental standards for chromium contents of soils are set in terms of total contents, it is the hexavalent chromium which presents the greatest hazard to health both in terms of its mobility in the soil environment and its toxicity to organisms. Previous studies on the chromium content of Scottish soils (Berrow and Reaves, 1986) have utilised direct-current arc spectrometry and have concentrated on subsoils.
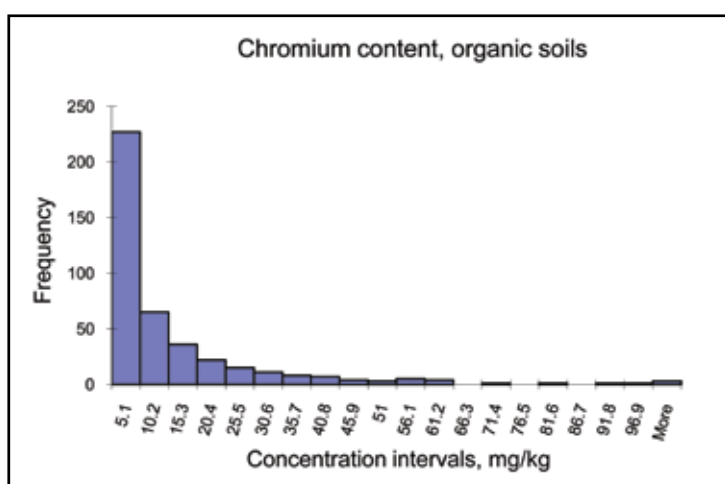
In common with many of the other elements reported here, chromium concentrations reflect the marked division between the organic soils of the upland areas and the mineral soils of the lowlands. Virtually all of the lowest concentration class (< 5 percentile) is found north of the Highland Boundary Fault. On the other hand the upper quartile values are grouped in areas on the east coast which are largely associated with more basic parent materials and across the Southern Uplands. This latter area is associated with the soils developed on the greywackes, shales and slates of the Ettrick association. These rocks tend to be rich in chlorite, which often contains substituted chromium.
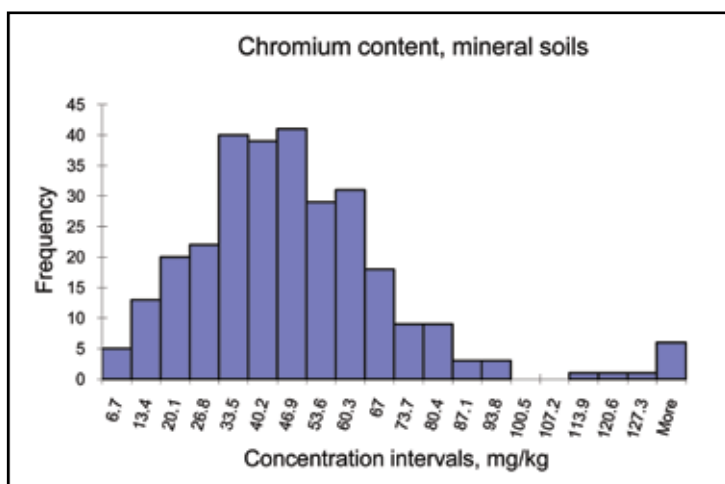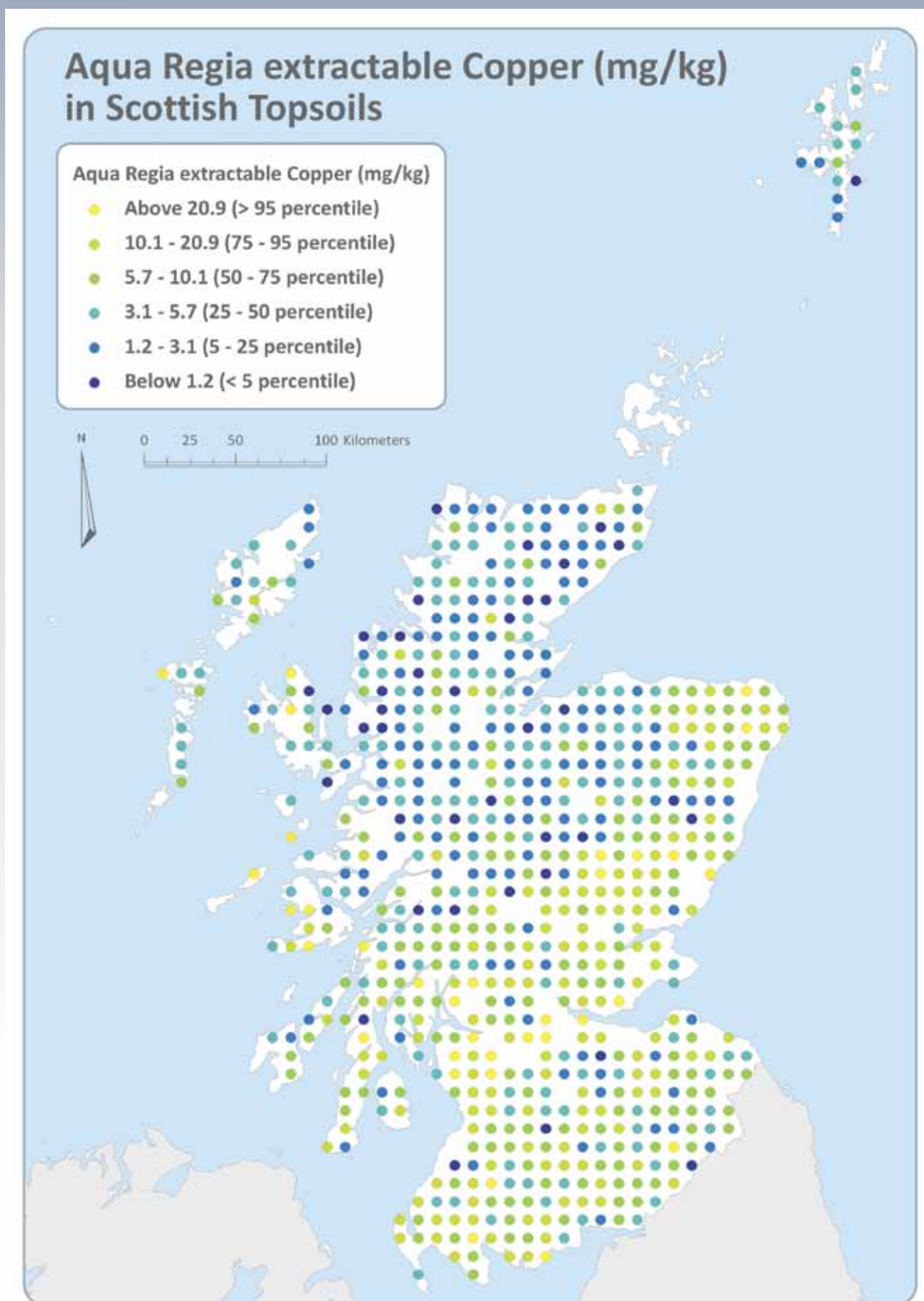

Cr (mg/kg)	mineral	organic
Mean	44.7	11.5
Median	41.2	4.3
Count	291	414

Summary statistics

From the summary statistics and the histograms it is clear that chromium shows a particularly clear differentiation between organic and mineral soils. In the mineral soil set, the distribution is approximately normal with mean and median values of 44.7 mg/kg and 41.2 mg/kg, respectively. In the organic soils, however, the distribution is extremely skewed to low concentrations with a wide discrepancy between the mean and median values. The median value for the chromium concentration of organic soils is an order of magnitude lower than that for mineral soils.

Aqua Regia extractable Copper (mg/kg) in Scottish Topsoils

Aqua Regia extractable Copper (mg/kg)

- Above 20.9 (> 95 percentile)
- 10.1 - 20.9 (75 - 95 percentile)
- 5.7 - 10.1 (50 - 75 percentile)
- 3.1 - 5.7 (25 - 50 percentile)
- 1.2 - 3.1 (5 - 25 percentile)
- Below 1.2 (< 5 percentile)

N   0   25   50   100 Kilometers

3.2 Copper

The average crustal abundance of copper is around 60 mg/kg but values encountered in soils are generally much lower. In an extensive survey of Scottish soils Reaves and Berrow (1984a) have given values for the geometric mean ranging from 5 to 12 mg/kg using a DC arc spectrographic method. Copper is an essential element for the healthy growth of plants and animals and deficiency symptoms have been observed in soils and plants in Scotland and elsewhere.

Copper concentrations show a similar pattern to that observed for many of the other elements in this study with effectively two groups of soils, one associated with the highly organic soils of the Highlands and the other with the mineral soils of the Lowlands. The < 5 percentile samples are almost all associated with organic soils whereas the upper quartile and the > 95 percentile samples are found more widely distributed across the mineral soils of the Central Valley, the Howe of the Mearns and in the extreme north east of Scotland. Although Reaves and Berrow (1984a) established a good relationship between parent material and copper content this was largely based on subsoil contents where the added complications of anthropogenic activity and dilution with organic matter are not felt.

Copper content, mineral soils

Copper content, organic soils
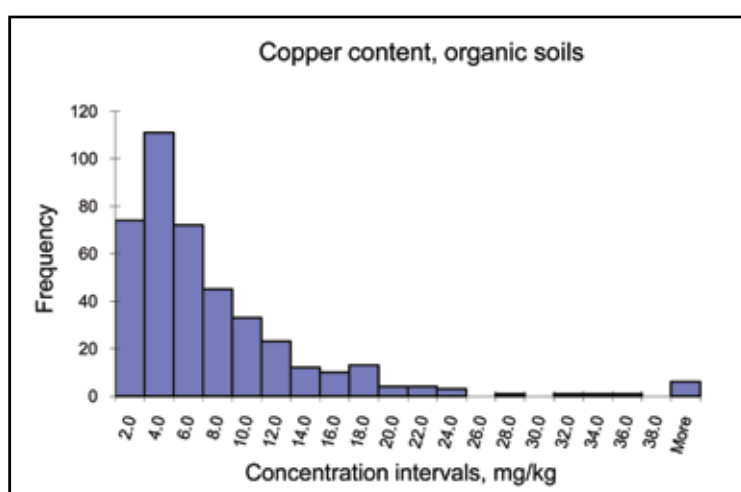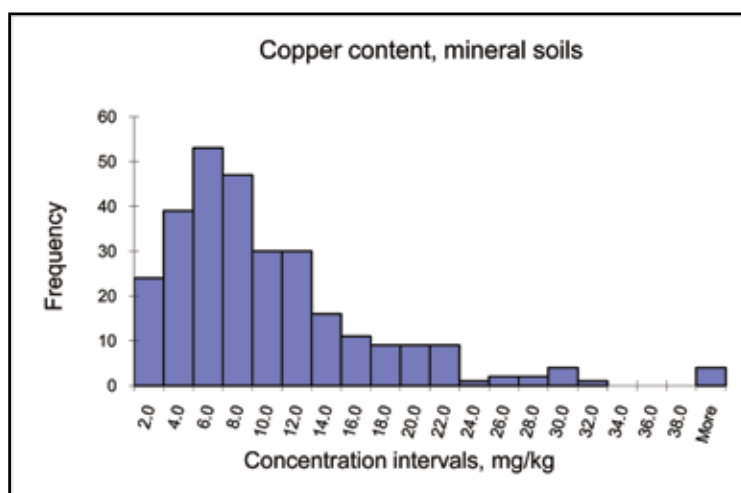
Cu (mg/kg)	mineral	organic
Mean	9.4	6.9
Median	7.5	4.5
Count	291	414

Summary statistics

From the summary statistics and the histograms it is clear that the difference between mineral and organic soils is not nearly so well developed for copper as it is for chromium - a result which is in accord with that of Reaves and Berrow (1984a) and reflects the ability of organic soils to retain copper very strongly due to the impact of complexation by organic matter. The mean and median concentrations in mineral soils are 9.4 and 7.5 mg/kg, respectively whereas in organic soils the values are slightly lower at 6.9 and 4.5 mg/kg with a wider divergence of the mean and median.
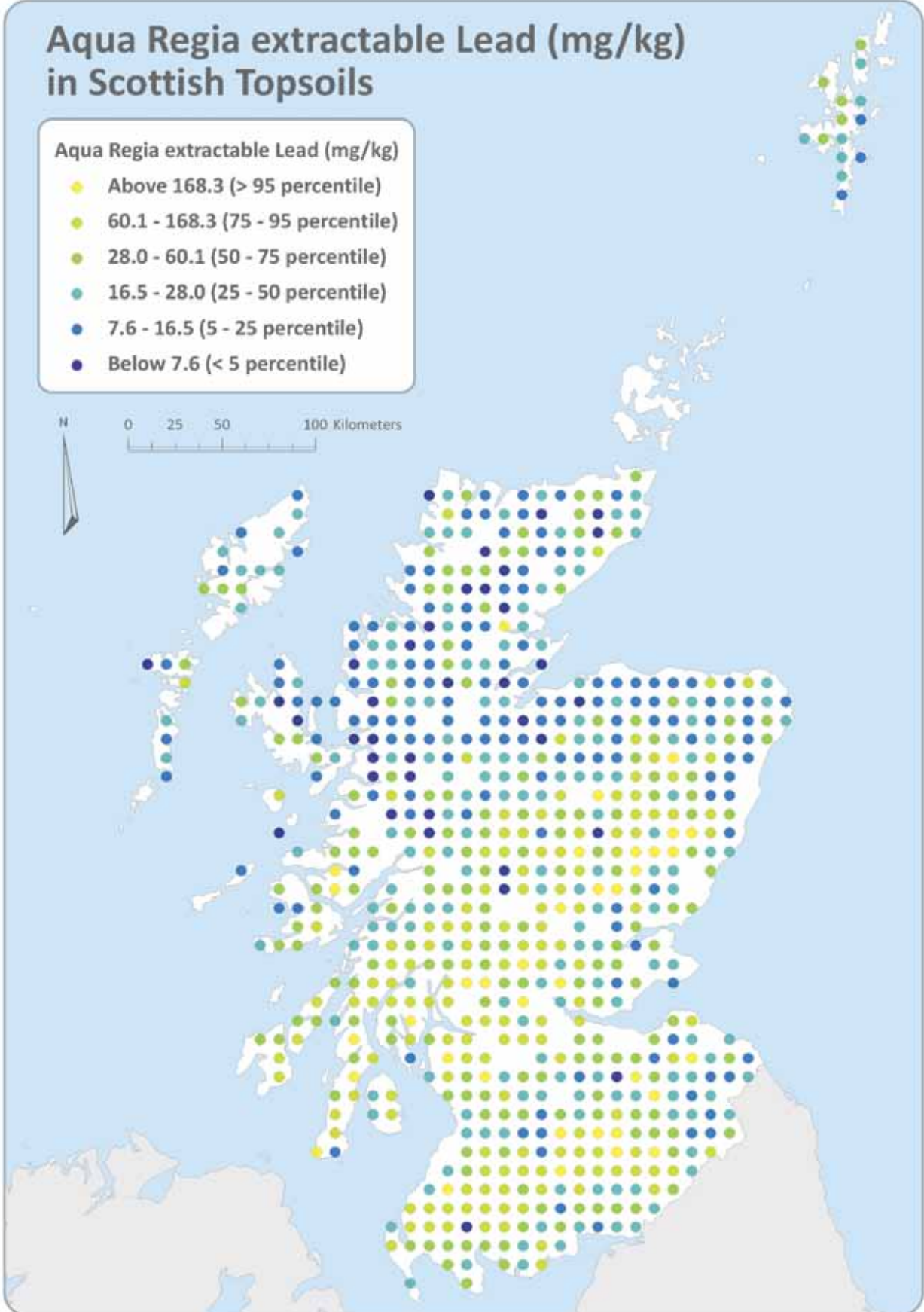
Aqua Regia extractable Lead (mg/kg) in Scottish Topsoils

Aqua Regia extractable Lead (mg/kg)

- ◆ Above 168.3 (> 95 percentile)
- ● 60.1 - 168.3 (75 - 95 percentile)
- ● 28.0 - 60.1 (50 - 75 percentile)
- ● 16.5 - 28.0 (25 - 50 percentile)
- ● 7.6 - 16.5 (5 - 25 percentile)
- ● Below 7.6 (< 5 percentile)

N

0   25   50   100 Kilometers

3.3 Lead

Although lead has a relatively low crustal abundance of around 13 mg/kg its distribution in surface soils throughout the world has prompted the suggestion by Davies (1995) that it is difficult to obtain any soil that may be deemed uncontaminated. Reaves and Berrow (1984b) have published data for Scottish soils based on a DC arc spectrographic method, where the range for Scottish soils is given as 2.5 - 85 mg/kg - a result in accord with the present results despite the difference in analytical procedures. The adverse impacts of lead on human development have been well documented (Royal Commission on Environmental Pollution, 1983) and have prompted many studies throughout the world.

The spatial distribution of topsoil lead concentration is difficult to reconcile with the underlying geology of Scotland as reflected in the soil association concept except in the Southern Uplands where lead minerali-sation is known to occur and where lead mining and smelting have been carried out for centuries. Another notable band of enrichment lies in the organic soils in the Central Highlands to the north of the Highland Boundary fault. Similarly, around Glasgow, values in the upper quartile are found. For organic soils in more remote areas in the north west Highlands the lead contents lie in the lower quartile and indeed the < 5 per-centile class. Whether these observations are consistent with Davies' hypothesis cannot be determined on these data alone.
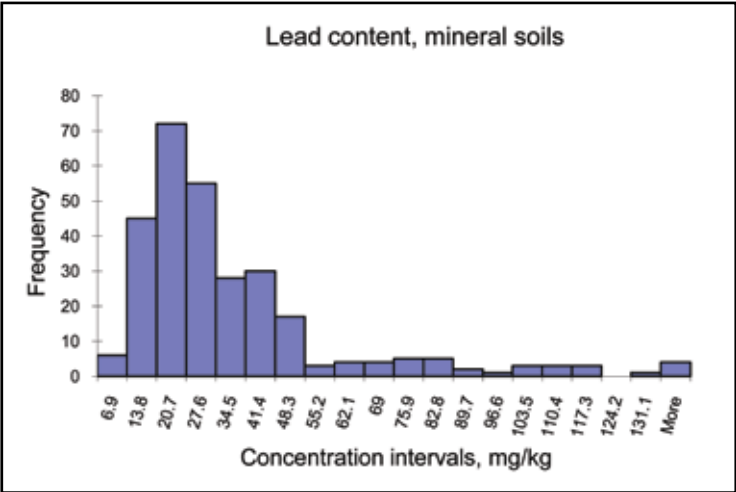
Pb (mg/kg)	mineral	organic
Mean	31.8	65.1
Median	23.0	34.7
Count	291	414

Summary statistics

From the summary statistics given above and the histograms given opposite there is clear differentiation between mineral and organic soils but, in contrast to the behaviour of other elements, it is some of the organic soils which are enriched in lead. The mean and median concentrations in mineral soils are 31.8 and 23.0 mg/kg, respectively whereas in organic soils values of 65.1 and 34.7 mg/kg were found. A similar observation has also been made by Reaves and Berrow (1984b) in their study and by McGrath and Loveland (1992) for the England and Wales dataset. The distribution of lead concentrations in the mineral soils is less skewed than that for the organic soils.
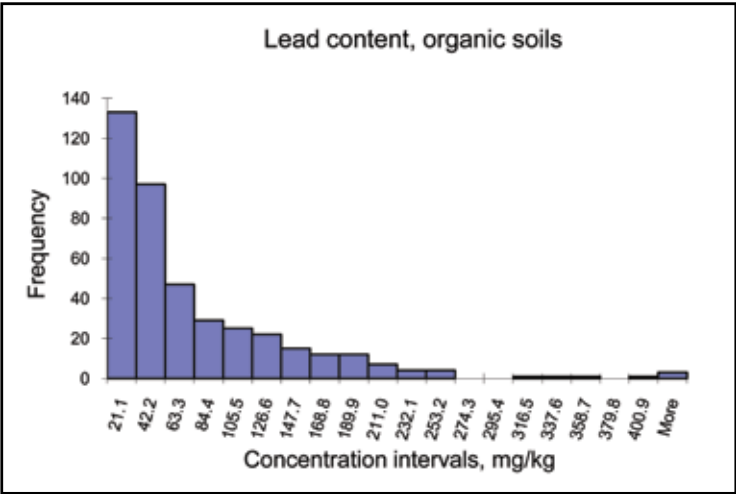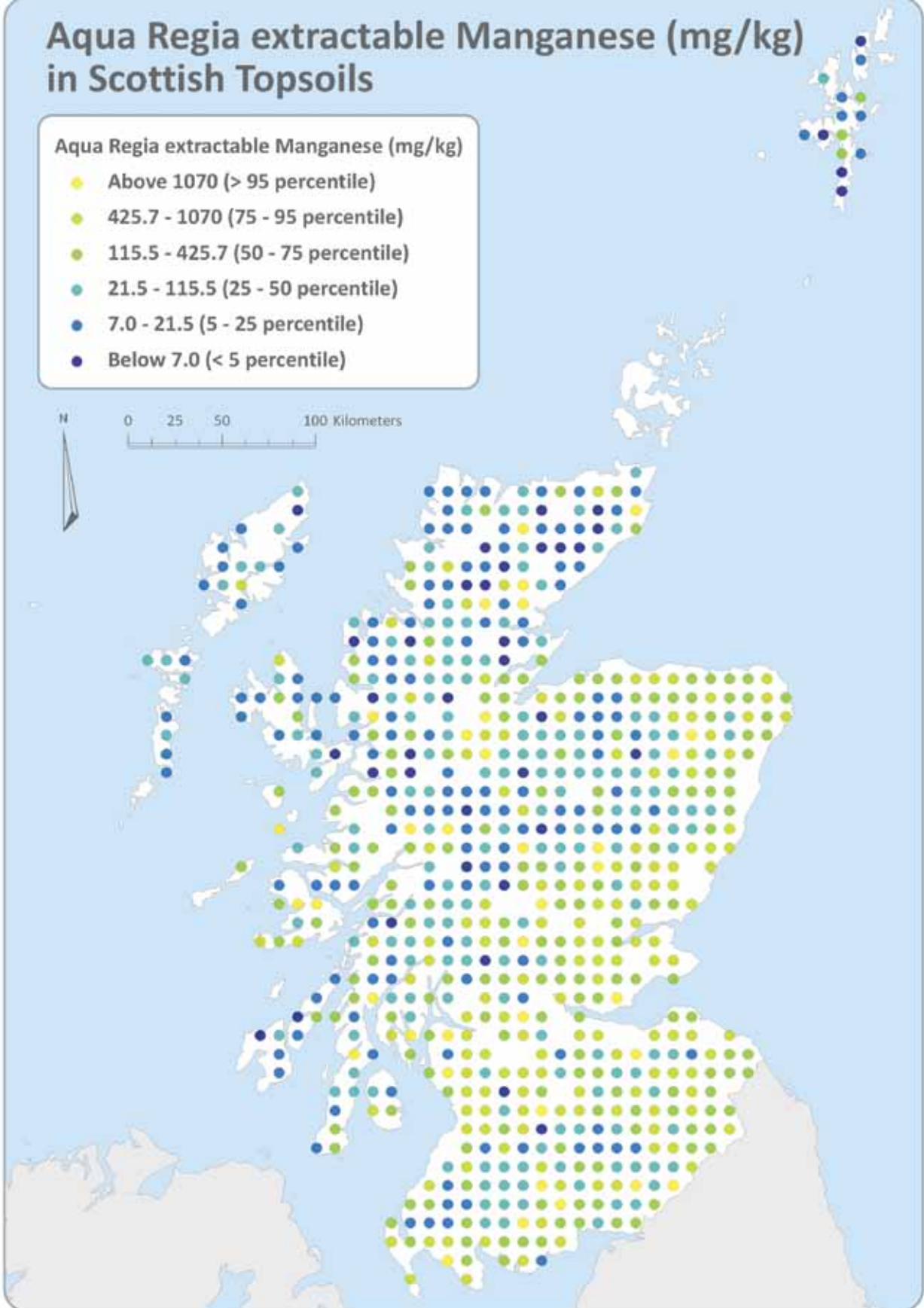
Aqua Regia extractable Manganese (mg/kg) in Scottish Topsoils

Aqua Regia extractable Manganese (mg/kg)
- Above 1070 (> 95 percentile)
- 425.7 - 1070 (75 - 95 percentile)
- 115.5 - 425.7 (50 - 75 percentile)
- 21.5 - 115.5 (25 - 50 percentile)
- 7.0 - 21.5 (5 - 25 percentile)
- Below 7.0 (< 5 percentile)

3.4 Manganese

Manganese is one of the most abundant trace metals with an average crustal abundance of around 1000 mg/kg. Its behaviour in soils is dominated by its variable valency and its subsequent susceptibility to redox alteration. In that sense its behaviour is similar to that of iron although it is more readily reduced to the mobile Mn^{2+} cation. In sedimentary and metamorphic rocks manganese is generally found as oxide inclusions whereas, in igneous rocks, it is a found as a structural component of other minerals. It is an essential element for both plants and animals and is involved in enzyme activities.
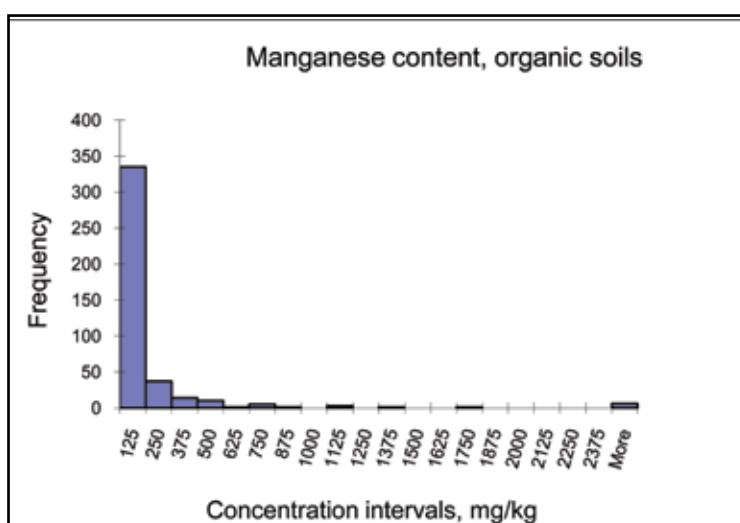
Although the majority of the > 95 percentile values for manganese are associated with soils in the uplands this is not reflected in the overall distribution of the upper quartile where significant concentrations can be seen in the soils of the Howe of the Mearns (Balrownie association) and in north east Scotland (Foudland association). Relatively low values are observed in the organic soils of the Highlands and the Southern Uplands. Again, in the coastal fringe of the soils of the Ettrick association higher values are found. The enrichment found in the Inner Hebrides and around Glasgow is consistent with the distribution of the basaltic igneous rocks of the Darleith association.
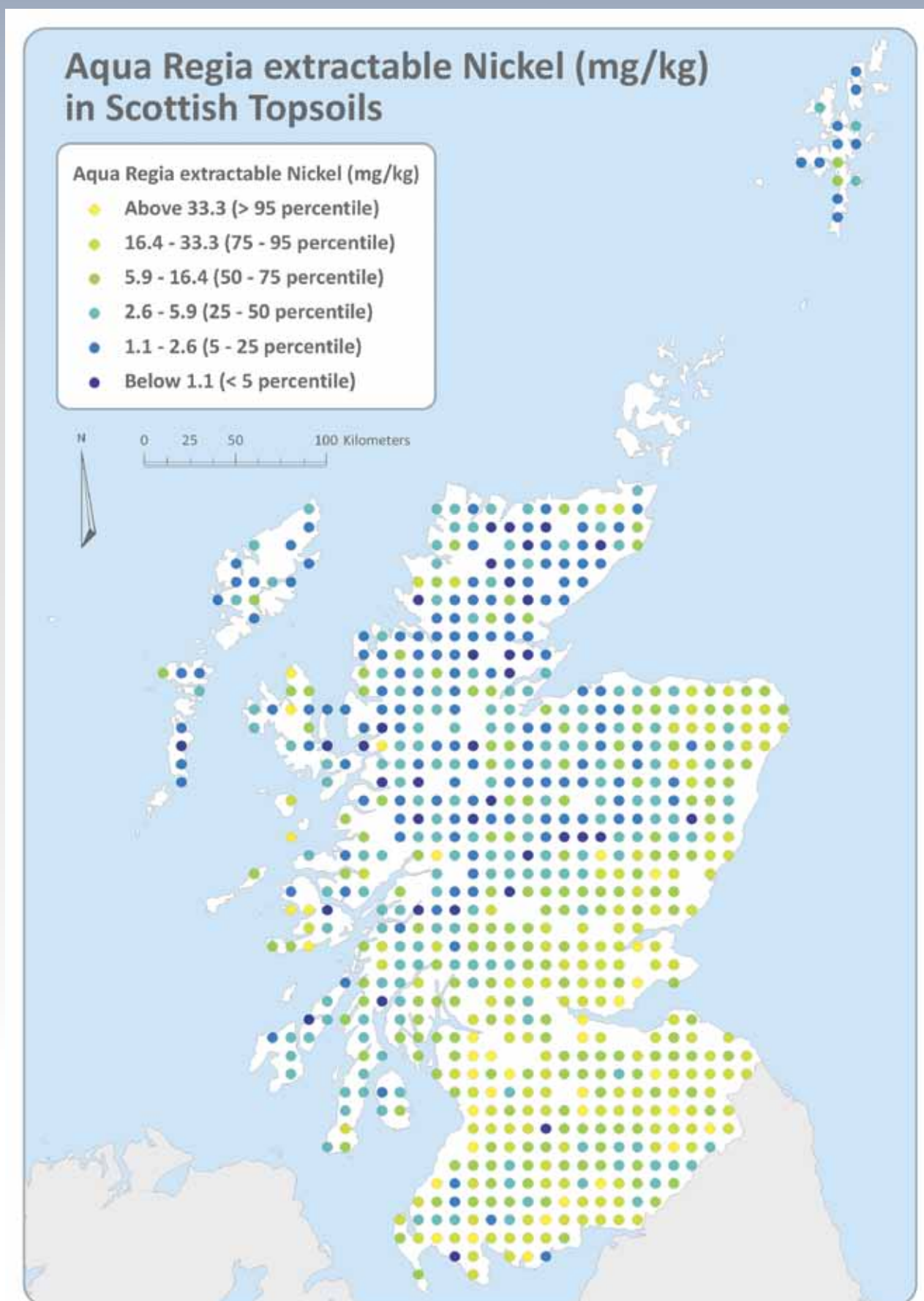

Manganese content, mineral soils

Manganese content, organic soils
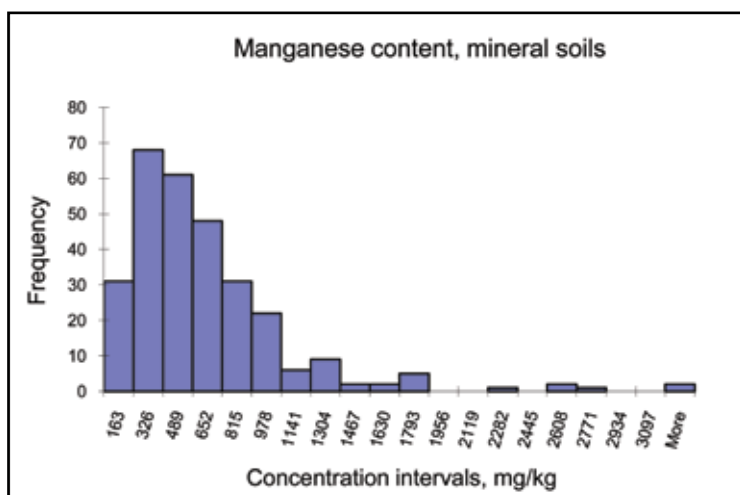
Mn (mg/kg)	mineral	organic
Mean	574	165
Median	450	31
Count	291	414

Summary statistics

From the summary statistics it is clear that there is a significant difference between the manganese contents of mineral and the organic soils with a four-fold change in the mean values at 574 and 165 mg/kg, respectively and a fifteen-fold change in the median values from 450 to 31 mg/kg, respectively. The histogram for the mineral soils shows a skewed distribution with a maximum of about 2000 mg/kg (excluding very high values). For the organic soils the skew towards low values is very much more pronounced with more than 70% of the contents < 200 mg/kg.

Aqua Regia extractable Nickel (mg/kg) in Scottish Topsoils

Aqua Regia extractable Nickel (mg/kg)
- Above 33.3 (> 95 percentile)
- 16.4 - 33.3 (75 - 95 percentile)
- 5.9 - 16.4 (50 - 75 percentile)
- 2.6 - 5.9 (25 - 50 percentile)
- 1.1 - 2.6 (5 - 25 percentile)
- Below 1.1 (< 5 percentile)

3.5 Nickel

Nickel has an average crustal abundance of around 90 mg/kg but is known to show a wide variation according to rock type with basic and ultrabasic rocks showing high to very high values. Indeed, in some areas of Scotland, toxic levels of nickel may be encountered in soils developed from serpentinite minerals (Wilson and Berrow, 1978). It is a siderophilic element and tends to associate with sulphidic phases. In sedimentary rocks it is frequently found associated with organic-rich deposits.

Previous work by Berrow and Reaves (1986) has used a DC-arc spectrographic method to study the nickel content of subsoils in Scotland. The nickel contents found in this study display a similar spatial pattern to those observed for other elements in that the lower quartiles of the distribution are almost all observed in the organic soils of the Highlands while the mineral soils of the lowlands show higher concentrations of nickel. However, these higher concentrations are observed in particular areas with upper quartile values in northern Buchan, probably associated with more basic parent materials as are the values observed in the Hebrides. The upper quartile values clustered in Fife and the Southern Uplands may be associated with sedimentary parent materials although the values around Glasgow may be anthropogenically enhanced.
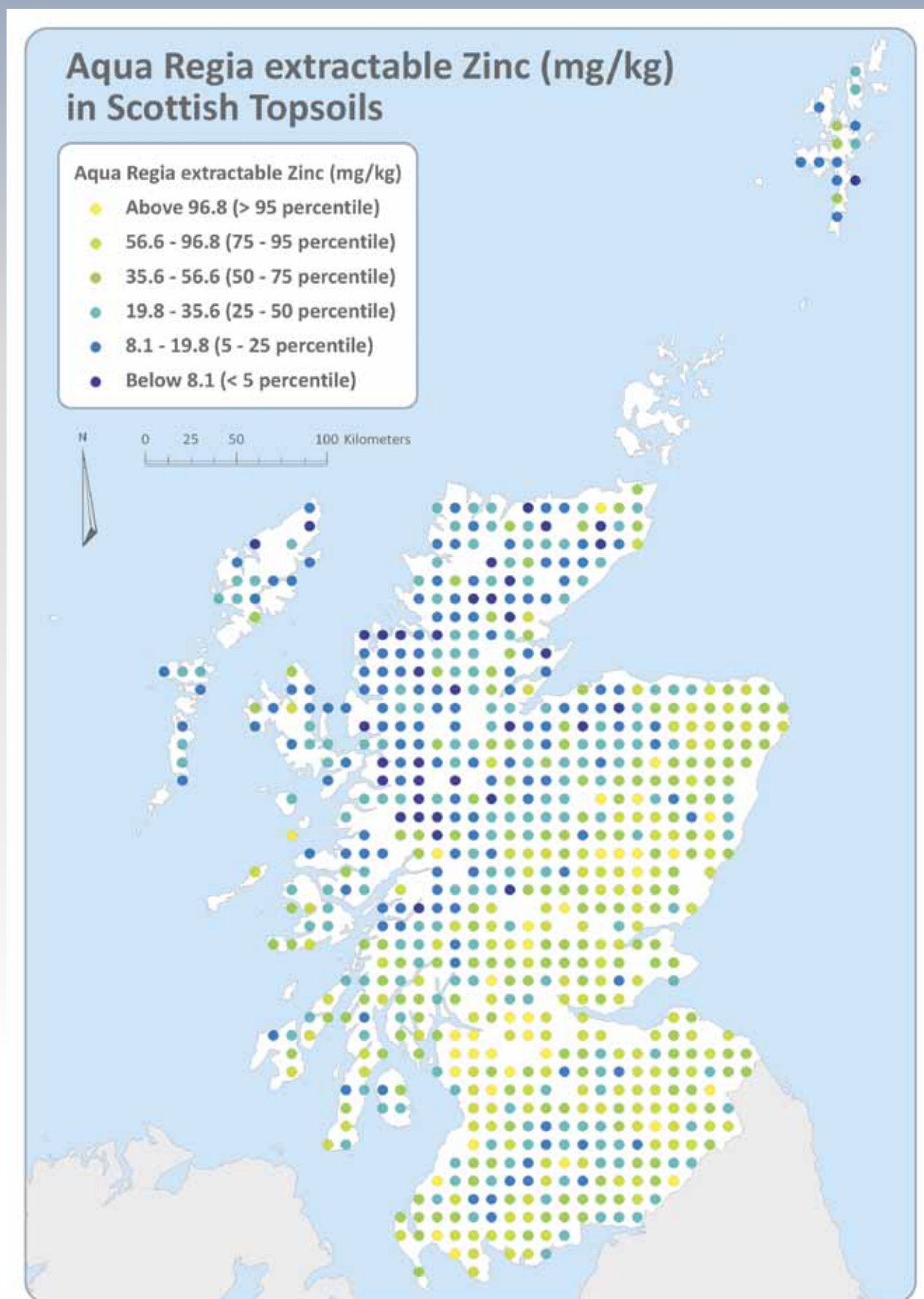

Nickel content, mineral soils
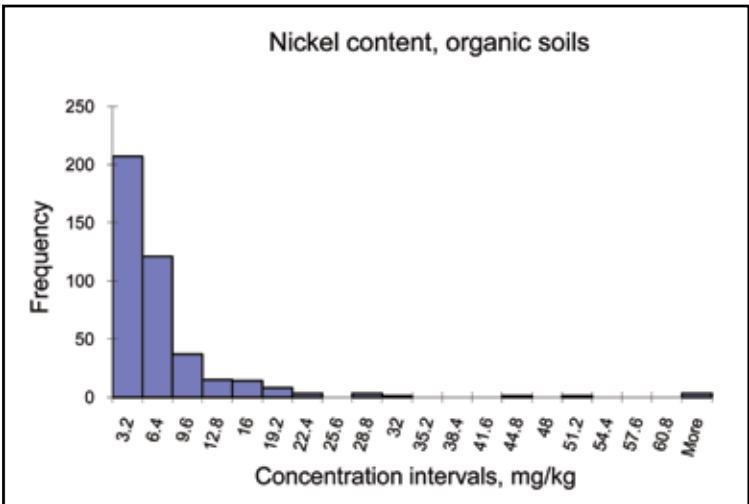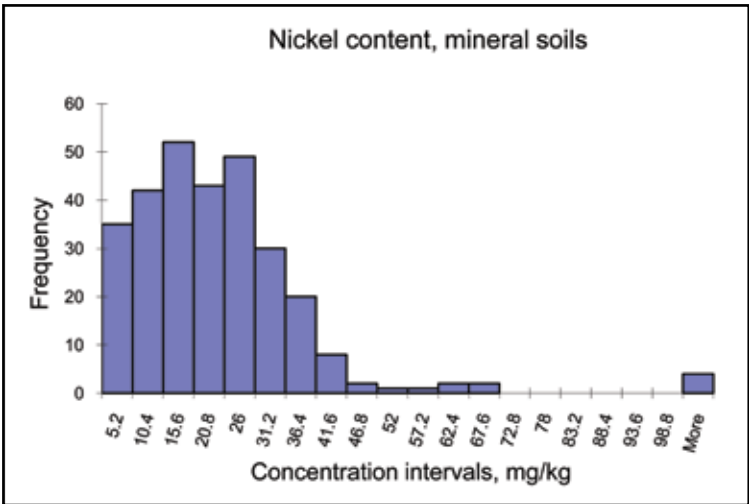
Ni (mg/kg)	mineral	organic
Mean	20.5	5.8
Median	17.4	3.3
Count	291	414

Summary statistics

From the summary statistics it is clear that nickel shows the marked distinction between mineral and organic soils that has been seen for a number of other elements. For the mineral soils almost all the values lie below 50 mg/kg and the distribution can be seen to be skewed towards lower concentrations with a mean of 20.5 and median of 17.4 mg/kg, respectively. However, for the organic soils with a mean of 5.8 and median of 3.3 mg/kg, the distribution can be seen to be strongly skewed towards low concentrations. In these soils few values exceed 20 mg/kg.

Nickel content, organic soils

Aqua Regia extractable Zinc (mg/kg) in Scottish Topsoils

Aqua Regia extractable Zinc (mg/kg)

- Above 96.8 (> 95 percentile)
- 56.6 - 96.8 (75 - 95 percentile)
- 35.6 - 56.6 (50 - 75 percentile)
- 19.8 - 35.6 (25 - 50 percentile)
- 8.1 - 19.8 (5 - 25 percentile)
- Below 8.1 (< 5 percentile)

N

0   25   50   100 Kilometers

3.6 Zinc

Zinc has an average crustal abundance of 70 mg/kg. Gabbros and basalts have zinc concentrations in the range 80 - 120 mg/kg, whereas, in granites the levels are slightly lower at 30 - 70 mg/kg. Zinc is found exclusively in the divalent state in nature and tends to substitute for iron and magnesium in silicates and oxides.

In common with many of the other elements reported here, the zinc concentrations in the organic soils of the upland areas are lower than those of the mineral soils of the lowlands. Virtually all of the lowest concentration classes are found in the Highlands. On the other hand, the highest concentrations are found around the Highland Boundary Fault and in areas across the Southern Uplands. There are notably high concentrations around Glasgow although whether these are lithogenic or anthropogenic cannot be determined from concentration alone.

Zinc content, mineral soils
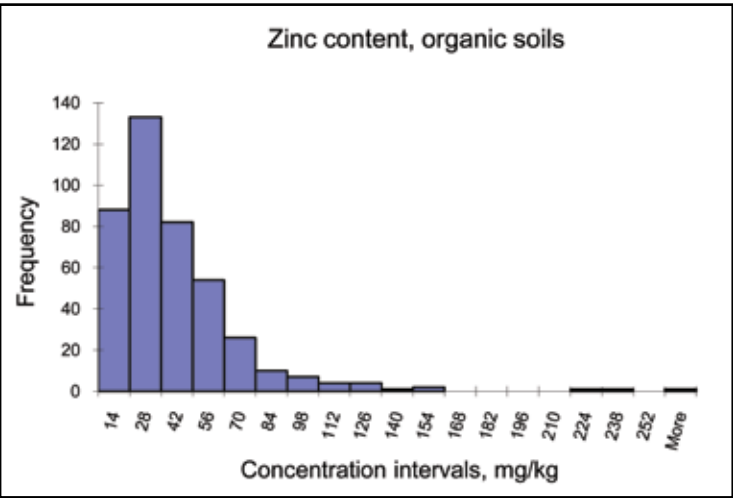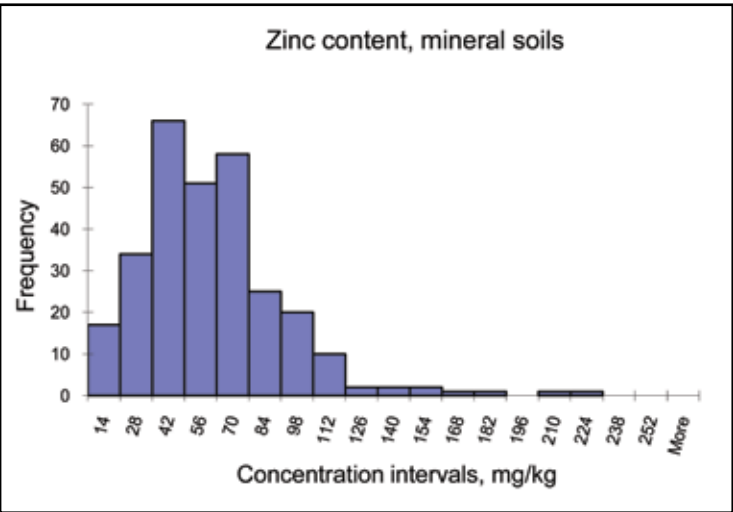
Zn (mg/kg)	mineral	organic
Mean	53.8	34.5
Median	48.0	26.7
Count	291	414

Summary statistics

From the summary statistics and the histograms it is clear that zinc does not show such clear differentiation between organic and mineral soils as that seen for some other metals. In mineral soils the distribution is approximately normal with mean and median values of 53.8 and 48.0 mg/kg, respectively. In organic soils, however, the distribution is more skewed to low concentrations. The mean and median values for the zinc content of organic soils, 34.5 and 26.7 mg/kg, respectively, are lower than those for mineral soils.

Zinc content, organic soils

4. Concluding Remarks

The results show that Scottish topsoils display a wide variation in their elemental composition as measured by aqua regia extraction and inductively coupled plasma optical emission spectometry. A number of factors contribute to the observed differences in composition including organic matter concentration, soil parent material and, possibly, anthropogenic inputs.

The main factor related to differences is the organic matter concentration of the soils. Although previous authors have referred to the 'dilution effect' of organic matter implying that the organic component does not contribute to the measured composition this is not always the case. For some elements, such as lead and copper, there is clear evidence that the organic soils have similar or even greater concentrations than the mineral ones. This observation probably reflects two processes. In the case of copper, copper/organic matter interactions are strong and copper is therefore accumulating in organic horizons whereas in the case of lead it may reflect the fact that much of lead in surface horizons is derived from atmospheric deposition and that, on a weight basis, this leads to higher concentrations in the less dense organic horizons.

The effect of organic matter accumulation obscures the effects of parent material, fully justifying the decision by Berrow and Reaves (1986) to focus their attention on subsoils in the search for links to parent material. However, for some elements where the element concentration in organic horizons is not greatly different from that in mineral horizons, a relationship between element concentration and parent material can be observed.

Although the question of anthropogenic enhancement cannot be directly addressed from concentration alone there is some circumstantial evidence in that high concentrations of many elements are observed around major centres of population such as Glasgow and to a lesser extent Edinburgh.

The data presented and discussed here form an extension to the data already held on Scottish soils as part of the National Soils Inventory of Scotland. The state of Scotland's soil resource has been reviewed (Towers et al., 2006). The report by Towers et al. (2006) includes comprehensive description of the quality-of-soil information held by the Macaulay Land Use Research Institute and other organisations including the Scottish Environment Protection Agency, the British Geological Survey, Scottish Natural Heritage and the Scottish Agricultural College.

It should be remembered that the aqua regia extraction method does not recover the total amounts of the elements in soils (Berrow and Stein, 1983), although for some elements recovery can be high. The data presented here represent a combination of concentration of the elements in soils with extractability, which will vary depending on mineralogy, and anthropogenic inputs where they exist.

5. References

Andrist-Rangel, Y., Hillier, S., Öborn, I., Lilly, A., Towers, W., Edwards, A.C. and Paterson, E. (2010) Assessing potassium reserves in northern temperate grassland soils: A perspective based on quantitative mineralogical analysis and aqua-regia extractable potassium. Geoderma, 158, 303–314.

Berrow, M.L. and Reaves, G.A. (1986) Total chromium and nickel contents of Scottish soils. Geoderma, 37, 15-27.

Berrow, M.L. and Stein, W.M. (1983) Extraction of metals from soils and sewage sludges by refluxing with aqua regia. Analyst 108, 277-285.

Bradley, R.I., Milne, R., Bell, J., Lilly, A., Jordan, C. and Higgins, A. (2005) A soil carbon and land use database for the United Kingdom. Soil Use and Management, 21, 363-369.

Chapman, S.J., Bell, J., Donnelly, D. and Lilly, A. (2009) Carbon stocks in Scottish peatlands. Soil Use and Management, 25, 105-112.

Davies, B.E. (1995) Lead. In: Heavy Metals in Soils, Second Edition, Ed. B.J. Alloway. Blackie, London, pp 206-223.

Gauld, J.H. and Paterson, E. (1996) The information base for Scottish soils. In: Soil Databases to Support Sustainable Development, (Eds C.Le Bas and M.Jamagne) European Commission Joint Research Centre & INRA, pp 93-97.

Glentworth, R. (1962) The principal genetic soil groups of Scotland. In: Proceedings International Soil Science Conference, Transactions Commissions IV and V. New Zealand, pp 2-9.

Howard, P.J.A., Loveland, P.J., Bradley, R.I., Dry, F.T., Howard, D.M. and Howard, D.C. (1995) The carbon content of soil and its geographical distribution in Great Britain. Soil Use and Management, 11, 9-15.

Langan, S.J. and Wilson, M.J. (1994) Critical loads of acid deposition on Scottish soils. Water, Air and Soil Pollution, 75, 177-191.

Langan, S.J., Paterson, E. and Taylor, A.G. (1996) The Scottish soil resource: current status and future priorities for its management. In: Soils, Sustainability and the Natural Heritage, Eds A.G. Taylor, J.E. Gordon and M.B. Usher, Edinburgh, HMSO, pp 69-91.

Lilly, A., Bell, J.S., Hudson, G., Nolan, A.J. and Towers, W. [Compilers]. (2010) National Soil Inventory of Scotland 1 (NSIS_1): site location, sampling and profile description protocols. (1978-1988). Technical Bulletin, Macaulay Institute. Available online (January 2011) at http://www.macaulay.ac.uk/issues/NSIS1_protocols.pdf.

Macaulay Institute for Soil Research (1984) Organization and Methods of the 1:250,000 Soil Survey of Scotland. Craigiebuckler, Aberdeen, 81pp.

McGrath, S.P. (1987) Computerized quality control, statistics and regional mapping of the concentrations of trace and major elements in the soil of England and Wales. Soil Use and Management, 3, 31-38.

McGrath, S.P. and Cunliffe, C.H. (1985) A simplified method for the extraction of the metals, Fe, Zn, Cu, Ni, Cd, Pb, Cr, Co and Mn from soils and sewage sludges. Journal of the Science of Food and Agriculture, 36, 794-798.

McGrath, S.P. and Loveland, P.J. (1992) The Soil Geochemical Atlas of England and Wales. Blackie, London, pp 101.

Paterson, E., Clark, L. and Birnie, A.C. (1993) Sequential selective dissolution of iron, aluminium and silicon from soils. Communications in Soil Science and Plant Analysis, 24, 2015-2023.

Reaves, G.A. and Berrow, M.L. (1984a) Total copper contents of Scottish soils. Journal of Soil Science, 35, 583 592.

Reaves, G.A. and Berrow, M.L. (1984b) Total lead concentrations in Scottish soils. Geoderma, 32, 1-8.

Royal Commission on Environmental Pollution (1983) Ninth Report: Lead in the Environment. HMSO, London, pp 185.

Towers, W., Grieve, I.C., Hudson, G., Campbell, C.D., Lilly, A., Davidson, D.A., Bacon, J.R., Langan, S.J. and Hopkins, D.W. (2006) Scotland's soil resource - current state and threats. Macaulay Institute and University of Stirling. Environmental Research Report 2006/01. Scottish Government, Edinburgh. http://www.scotland.gov.uk/Resource/Doc/149337/0039742.pdf.

Wilson, M.J. and Berrow, M.L. (1978) The mineralogy and heavy metal content of some serpentinite soils in North-East Scotland. Chemie der Erde, 37, 181 205.

Appendix

Other geochemical atlases

Fay, D., Kramers, G., Zhang, C., McGrath, D. and Greenan E. (2007) Soil Geochemical Atlas of Ireland. Ed G. Kramers. Teagasc and the Environmental Protection Agency, Wexford, pp 120.

McGrath, S.P. and Loveland, P.J. (1992) The Soil Geochemical Atlas of England and Wales, Blackie, London, pp 101.

Salminen, R. (chief editor) (2005) Forum of European Geological Survey Geochemical Atlas of Europe http://www.gtk.fi/pub/foregsatlas/ (at September 2010).

Design by:
Lauren Farr-Miller
Ian Williamson