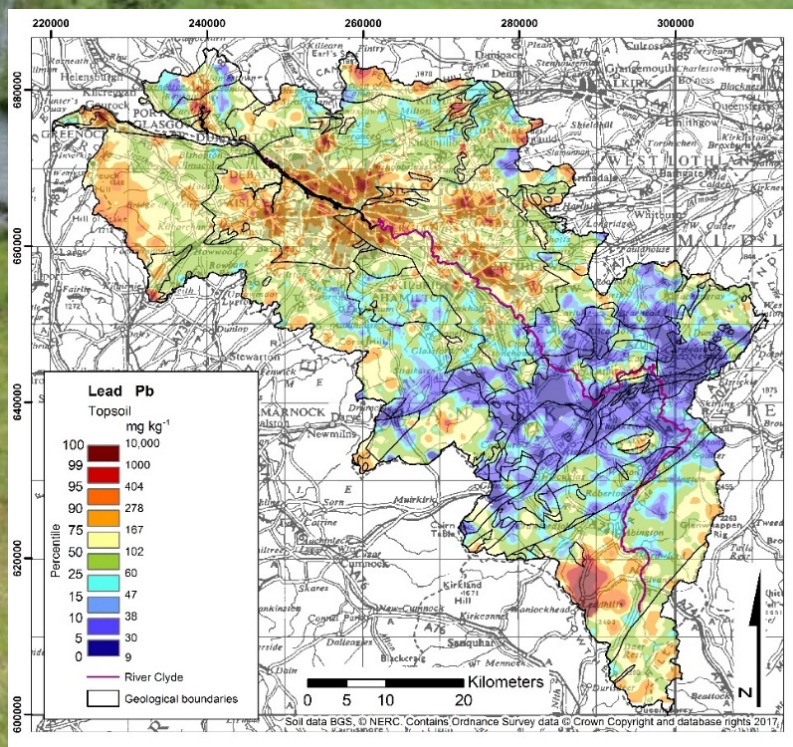




Soil geochemical atlas of the Clyde Basin



BRITISH GEOLOGICAL SURVEY

GEOANALYTICS AND MODELLING PROGRAMME

OPEN REPORT OR/14/032

Soil geochemical atlas of the Clyde Basin

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concentrations in topsoil of
the Clyde Basin

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Foreword

Soil quality is of interest because soil forms the foundation for building and infrastructure in both rural and urban environments, it is a fundamental resource for agriculture, energy production and climate change mitigation. Soil supports key ecosystems and biodiversity and mediates the flow and pollution of water resources. This volume presents an assessment of the chemical quality of soil across the River Clyde Basin in the West of Scotland, including Scotland's main conurbation of Glasgow.

Glasgow was a major powerhouse of the Industrial Revolution during the 18 – 20th centuries, where heavy industries such as shipbuilding and locomotive engineering were fed by local supplies of coal and iron ore. The Clyde Basin contains also the former mining area of Leadhills, where lead, silver and zinc ores were extracted until the 1950s. The twentieth century saw a decline in these heavy industries, and a realisation that whilst they brought prosperity to the area, they have left a substantially modified local environment.

The work presented here is the result of a project carried out in two phases over 10 years to determine the geochemistry of soil across the region. It was undertaken as part of the Clyde and Glasgow Urban Super Project (CUSP); a multi-disciplinary collaborative programme between the British Geological Survey (BGS) and Local Authorities to characterise the geo-environment of the Clyde Basin.

Soil is a weathering product of the underlying rocks. Therefore, the rocks, along with superficial materials deposited by rivers or glaciers over long periods of time, largely determine the chemical composition of soil. In addition to this natural control on soil chemistry, in city environments, urban pollution, transport and industry can have an impact on soil quality. Similarly, in rural areas, agricultural inputs and industries such as mining and mineral extraction can alter the concentrations of certain chemicals in soil. However, in rural areas not affected by industrialisation, we can establish a near-natural geochemical background. By comparing this to the geochemical composition of soil in mining and built-up urban areas, an assessment of the manmade (anthropogenic) modification can be made.

This volume compares the concentrations of chemical elements found in soil from the urban area of Glasgow with those from its rural hinterland. This enables an assessment of the anthropogenic pollution imprint on the environment. It also provides information on the essential nutrients in soil necessary for agricultural production. This fundamental background information is vital to aid land and resource management, and satisfy the legislatively driven demands for an improved and sustainable environment, where people can live and work with a better quality of life.

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1 Introduction

Information on the chemical quality of the environment is important because the 92 naturally occurring elements on Earth that form the various rocks, soil, waters and gases that are the building blocks of the planet are not distributed evenly across the globe. Concentrations in soil at any location are controlled by factors including geology, vegetation, soil forming processes and climate. Of these, the soil parent material (geology) plays a dominant role in determining soil geochemistry (Rawlins et al., 2003). In addition to natural sources of the elements, environmental concentrations can be enhanced by anthropogenic (human) activities such as mining, industrialisation, urbanisation and waste disposal.

The distribution of the elements is important because many are essential to life, and at least 41 of the naturally occurring elements are potentially harmful to plants, animals or humans in high doses (Table 1). Thus, on the one hand, soil geochemistry is important for agriculture, to provide the essential nutrients for healthy crop and animal growth for human food supply. On the other hand, soil pollution can be of concern in terms of environmental protection and sustainable resource management.

This volume describes the geochemistry of soil in the River Clyde Basin in the west of Scotland (Figure 1), forming an integral part of the British Geological Survey's (BGS) Geochemical Baseline Survey of the Environment (G-BASE) programme. The aim of the study was to provide an overview of soil quality in both the rural and urban environments of the Clyde Basin as an aid to planning and catchment management. It was carried out as part of the wider BGS Clyde and Glasgow Urban Super Project (CUSP). The CUSP is a multidisciplinary catchment-based project being undertaken by the BGS in collaboration with Glasgow City Council (GCC) and other Local Authorities in the region to characterise the geoenvironment of the Clyde Basin and deliver geoscience products to aid sustainable planning and development in Scotland's major conurbation (Campbell et al., 2010).

The soil survey was carried out in two phases. Samples were collected from the urban area of Glasgow and surrounding peri-urban rural environment during 2001 – 2002. The survey was subsequently extended to include the rest of the Clyde Basin rural and urban areas in 2010 – 2011. The soil samples were analysed to determine the concentration of approximately 50 chemical parameters. The results are presented here as a series of interpolated geochemical maps, statistical summaries and overview descriptions of the parameter distributions in soil across the Clyde Basin¹.

1. Note the results of the initial 2001 – 2002 Glasgow soil study have been reported in detail elsewhere (Fordyce et al., 2012).

Table 1. Selected essential and potentially harmful elements for plant, animal or human health.

Chemical symbol	Element name	Chemical symbol	Element name
Ag	Silver	Na	Sodium
Al	Aluminium	Nb	Niobium
As	Arsenic	Nd	Neodymium
B	Boron	Ni	Nickel
Ba	Barium	P	Phosphorus
Bi	Bismuth	Pb	Lead
Br	Bromine	Rb	Rubidium
Ca	Calcium	S	Sulphur
Cd	Cadmium	Sb	Antimony
Ce	Cerium	Sc	Scandium
Cl	Chlorine	Se	Selenium
Co	Cobalt	Sm	Samarium
Cr	Chromium	Si	Silicon
Cs	Caesium	Sn	Tin
Cu	Copper	Sr	Strontium
F	Fluorine	Ta	Tantalum
Fe	Iron	Ti	Titanium
Ga	Gallium	Te	Tellurium
Ge	Germanium	Th	Thorium
Hg	Mercury	Tl	Thallium
Hf	Hafnium	U	Uranium
I	Iodine	V	Vanadium
K	Potassium	W	Tungsten
La	Lanthanum	Y	Yttrium
Mg	Magnesium	Yb	Ytterbium
Mn	Manganese	Zn	Zinc
Mo	Molybdenum	Zr	Zirconium

The majority of elements are essential to health in small doses; those that can also be potentially harmful in high doses are shown in black text. Elements listed in purple are non-essential, but low toxicity. Elements listed in blue have no/limited biological function and are generally toxic to most organisms (Modified from Appleton, 1995)

1.1 CLYDE BASIN STUDY AREA

The CUSP study area encompasses the entire catchment of the River Clyde from the upper reaches in the Lowther Hills in the Southern Uplands of the Scottish Borders to the mouth of the estuary at Gourrock (see Figures 1, 2 and 3 and Tables 2 and 3 for locations). The 3130 km² area includes the settlements of Abington, Leadhills, Lanark, Carluke, Strathaven, Kilmacollm, Bridge-of-Weir, Kilsyth, Kirkintilloch and the new-towns of East Kilbride and Cumbernauld as well as the main Glasgow conurbation. The urban and built-up areas are concentrated in the north of the Basin around the lower reaches of the River Clyde, whereas the south of the area is predominately rural. The topography of the area ranges from the valley floor of the River Clyde to the upland volcanic-rock plateaux of the Campsie–Kilpatrick Hills to the north of Glasgow, and the Renfrewshire Hills to the southwest of Glasgow (Figure 2). The south of the area is dominated by the rolling hill-country of the Southern Uplands. These upland areas comprise rough grazing and open moorland, whereas agricultural pasture, and to a lesser extent, arable land and forestry dominate the centre of the Basin (Figure 4). In recent times, the upland area of Eaglesham Moor to the south of East Kilbride and Strathaven has become home to the United Kingdom (UK)'s largest windfarm covering 53 km² (Location 34, Figure 3).

The settlement of Glasgow has existed since the Bronze Age, it developed on high ground close to the most reliable seaward ford of the River Clyde. The City and Burgh were decreed by Royal Charter during the 12th century, but up until the establishment of the university in 1451, the city was essentially a small ecclesiastical centre (population 4500) based around the cathedral. By the end of the 16th century, coal was being exported in flat-bottomed barges, but development of the River Clyde was necessary to allow safe passage for larger vessels. Hence, in the west of the area, the City Fathers of Glasgow purchased land to build a port at Port Glasgow in 1667, as this marked the highest accessible point on the River Clyde for ocean-going ships. By 1775 Port Glasgow was the site of the principle Custom's House on the River Clyde. It became a centre for import/export and shipbuilding (Bowie, 1975). It was not until the 19th century that a dredged channel was cut to allow ocean-going ships access to Glasgow city centre. Similarly, Greenock was a small fishing village to the west of Glasgow until a pier and breakwater were built on the River Clyde during the 1600s and the town became heavily involved in shipbuilding. The small harbour was converted into a major port in early 1700s and Greenock flourished as a trading centre (Scotland Channel, 2014). By contrast, the neighbouring town of Gourock was not as industrialised as Greenock or Port Glasgow, but remained a centre of the fishing industry, with some shipbuilding as well as stone quarrying (Milne, 1958). Glasgow became the third most important port in the UK after London and Liverpool during the 18th and 19th centuries, with imports of tobacco, cotton, coffee, rum and sugar (Glasgow City Council, 2014).

The development of the Glasgow conurbation was based largely on the combination of transport via the River Clyde, and mineral extraction related to the local geology. The numerous and easily accessible coal and ironstone seams of the Scottish Coal Measures provided the fuel and raw materials to support a thriving industrial centre. From 1732 onwards, the establishment of ironworks and forges increased the local demand for coal and ironstone at the expense of the export trade, and by 1800, the population of Glasgow had grown to 84000, reflecting the gathering momentum of the industrial revolution (Browne et al., 1986; Glasgow City Council, 2014).

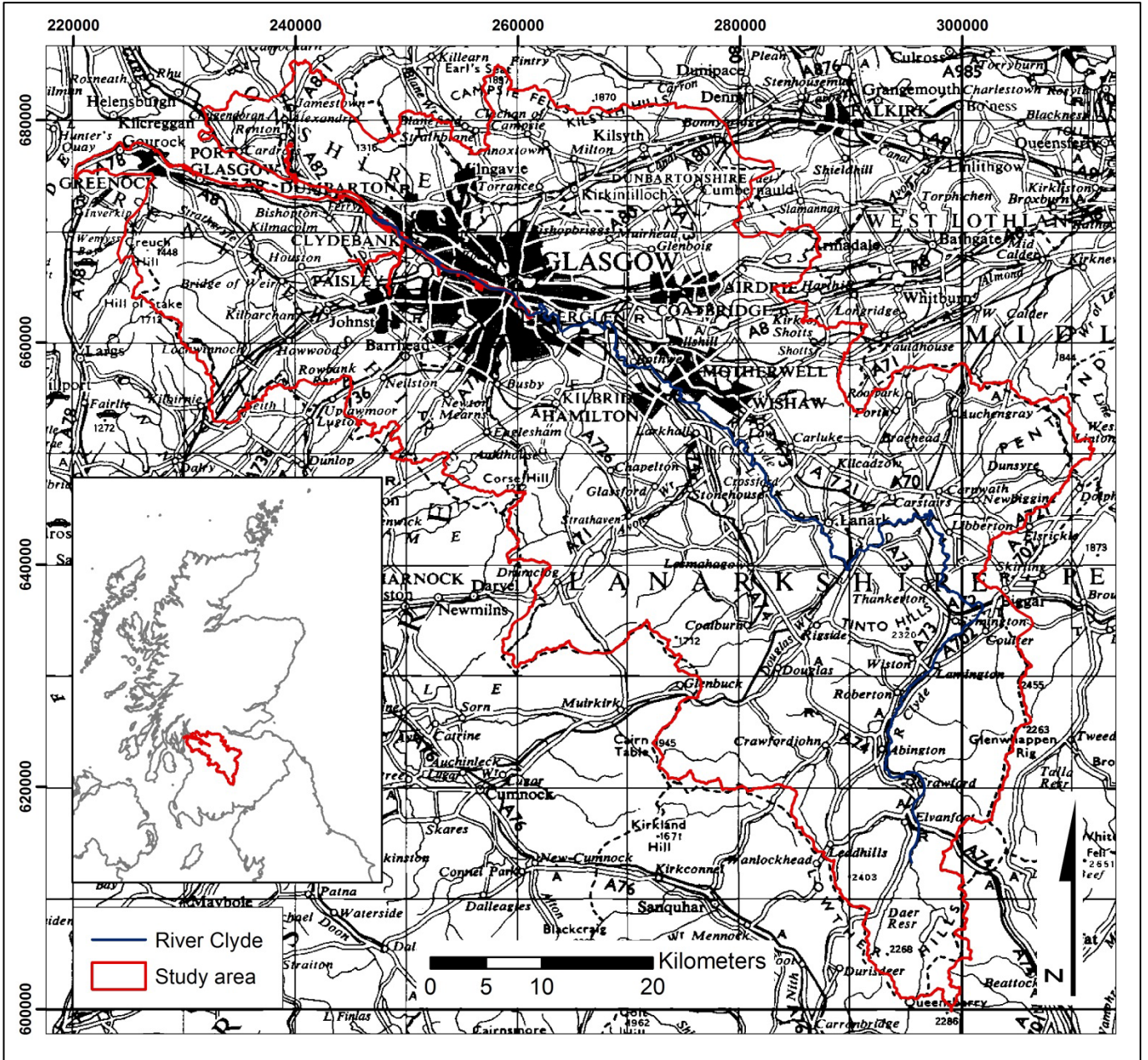
Similarly, in the east of the area, the Lanarkshire section of the Glasgow conurbation comprised small towns and hamlets until the start of the 1800s. In the case of Hamilton, this centred on the castle and estate of the powerful Dukes of Hamilton who expanded the town and established a college in 1451. However, the town grew rapidly in the mid-1800s with the arrival of the railways and coal mining and iron smelting industries. Motherwell remained a small hamlet to the southeast of Glasgow at the site of an ancient religious well, until the railways arrived in the 1830s. Motherwell became a junction station with a direct link to Glasgow, and these excellent transport routes led to the development of a number of major iron and steel works in the town. A wide range of other heavy engineering companies were established in the same area, building everything from munitions, to bridge components, and trams. To the east of Glasgow, Airdrie grew up as a farming settlement on the main Glasgow – Edinburgh road that was originally built by monks in the 12th century. It developed into a small market town during the 1600s, but by the middle of the 18th century it was a well-established weaving centre with flax grown on many local farms. At the same time, the expansion of the coal and iron industries led to a demand for machinery and tools, and Airdrie became important for engineering works. To the east of Glasgow also, Coatbridge emerged as a settlement following the construction of the Monklands Canal in 1788 to transport coal from the North Lanarkshire coalfield to Glasgow. Ironstone was discovered in the Coatbridge area, and by 1869, the Gartsherrie Ironworks had become the largest in Scotland at that time, employing 3200 people. Similarly, Wishaw was established in 1825 with the development of a distillery, but grew dramatically following the arrival of the railways, which opened up collieries in the 1830s (Lanarkshire Communities, 2014). To the northeast of Glasgow, Kirkintilloch began as a fort on the Antonine Wall built by the Romans, and became a small burgh market town in the 12th century situated on the main Glasgow – Edinburgh route. However, the arrival of the Forth and Clyde canal in 1788, and then the railways in the 1820s transformed the town into a centre of cotton weaving, iron working and boat building (East Dunbartonshire Council, 2014). Similarly, the neighbouring town of Kilsyth was a small hamlet until the advent of the Forth and Clyde canal, when it became a centre for weaving and coal mining (Lanarkshire Communities, 2014).

Across the whole Glasgow conurbation, the trend of increasing population and commercial success continued through the 19th century with the advent of steam trains and iron ships, which made further demands on the coal and iron resources. The mining of ironstone peaked around 1880, but declined rapidly as the ore proved unsuitable for steel production, and it finally ended after the First World War (1914-1918). By contrast, the subsurface mining of coal was at its height in the early 20th century and continued until 1983. Mining waste was used as stowing in the workings. Domestic coal ash was discarded and used as a soil conditioner in gardens/allotments and industrial coal ash was used as a fill material across the city. Several other materials were extracted in the area including limestone, seat-clay, sandstone, sand and gravel, and dolerite. Several of the quarries have been infilled and used for waste disposal, such as Greengairs near Airdrie (Location 22, Figure 3), which is the largest landfill site in Scotland (Browne et al., 1986; Philpott et al., 1992).

In the late 18th and early 19th centuries, Glasgow became the centre of a cotton spinning region; the number of cottonmills within a radius of twenty-five miles of the city rose from 19 to 134 between 1787 and 1834. The flourishing cotton industry stimulated the development of related industries such as bleaching, dyeing and fabric printing. Cotton spinning, weaving, calico printing and bleaching were based in the city centre in 1779, and moved to Renfrewshire (west of Glasgow), as business expanded. Paisley and the Vale of Leven (Alexandria and Dumbarton) to the west of Glasgow, attracted textile printworks partly because of the suitability of the water (Glasgow City Council, 2014).

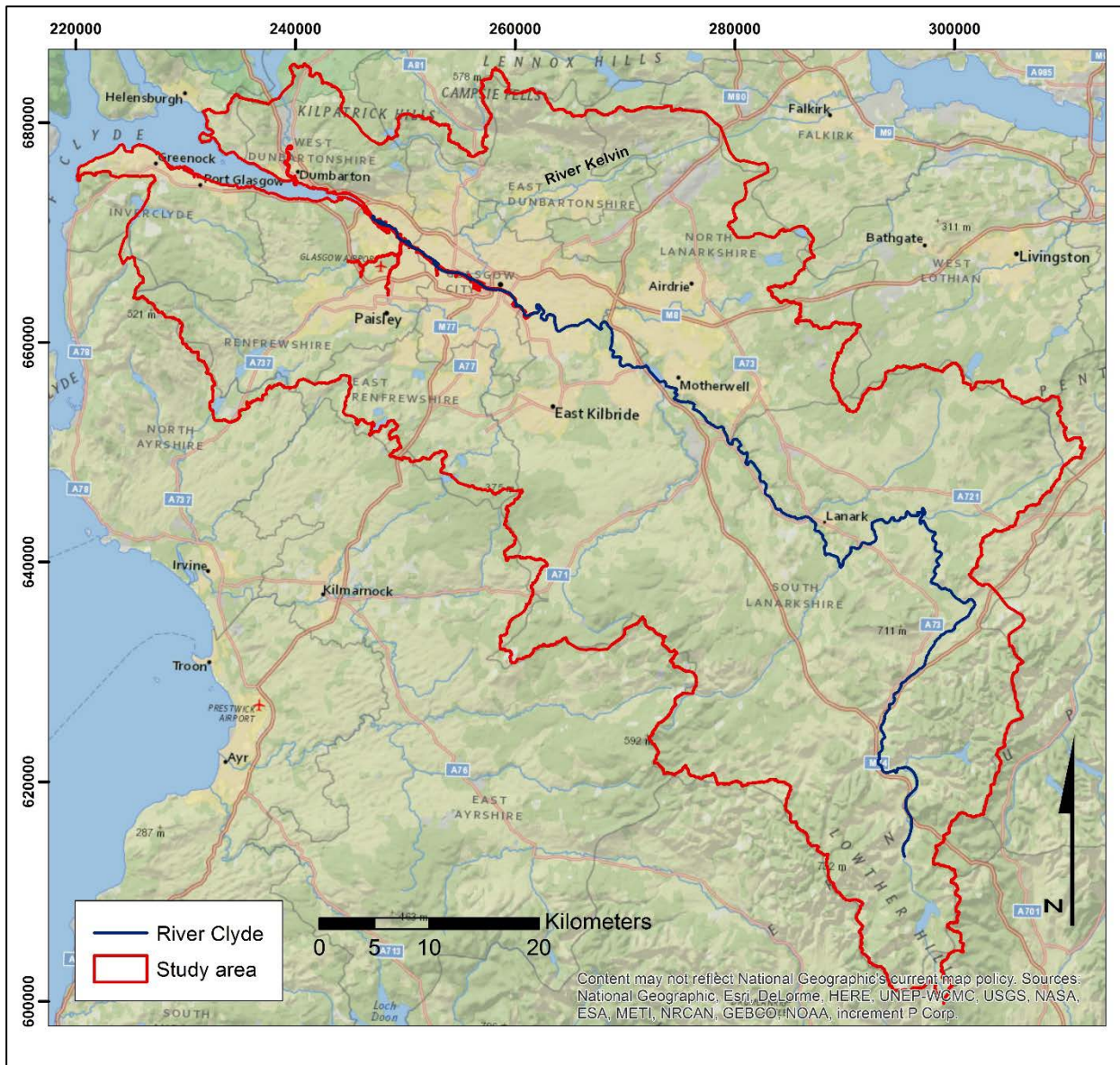
Heavy industry, particularly shipbuilding developed along the River Clyde during the 19th and first half of the 20th centuries and was focussed at Clydebank. Glasgow was renowned also for iron and steel manufacture including the Clydebridge, Westburn, Camlachie, Parkhead and Cathcart Holm works in the East End of the city. Parkhead Forge was the largest steelworks in Scotland employing over 20 000 people at its peak before it closed in 1975 (Glasgow City Archives, 2013). Iron and steel centres also developed to the east of Glasgow in Coatbridge (Gartcosh) and Ravenscraig in Motherwell (Location 26, Figure 3). Both mills were operated by Colville Steel, but were subsumed into British Steel in 1967 until their closure in 1986 and 1992, respectively. At the time of closure, Ravenscraig was the largest hot strip steel mill in Western Europe (Monklands Memories, 2014; Steelworks History, 2014). Heavy engineering developed at complexes such as the Shieldhall works at Renfrew (west of Glasgow), in the south of Glasgow city centre (Pollockshields works) and the St Rollox Royston–Cowlairs railway yards, north of Glasgow city centre, as well as works in the East End of the city. Glasgow was also a focus of mineral processing, the company of JJ Whites in Rutherglen (southeast Glasgow), was the world's largest chrome producer, during the 19th century and operated until 1968. Chromite-ore processing residues were extensively used as landfill material around southeast Glasgow and between 1880 and 1968 it is estimated that 2, 500 000 tonnes (dry weight) of chromite waste were dumped (Farmer et al., 1999).

The conurbation, and in particular Clydebank, sustained heavy bombing during the Second World War (1939 – 1945) and large tracts of the 19th century tenement housing were cleared between the 1950s and 1970s as part of the city's post-war regeneration programme. Much of the inner city population moved out to satellite new-town developments such as East Kilbride (to the south of Glasgow) and Cumbernauld (to the northeast of Glasgow) at this time. This, coupled with a decline in heavy industry over the same period, left the conurbation with a legacy of derelict land, which has been the target of regeneration schemes that continue to the present day. Areas, such as the former steel works in Coatbridge and Motherwell, to the east of Glasgow, are being redeveloped for light industry and housing. The metal processing heartland of the East End of Glasgow is the subject of major regeneration, centring on the site of the 2014 Commonwealth Games. The Glasgow conurbation today is a thriving business, retail, cultural and tourism centre with a modern mixed economy including biosciences, optoelectronics, contact centre management, software development, creative industries, construction and communication technologies (Glasgow City Council, 2014).



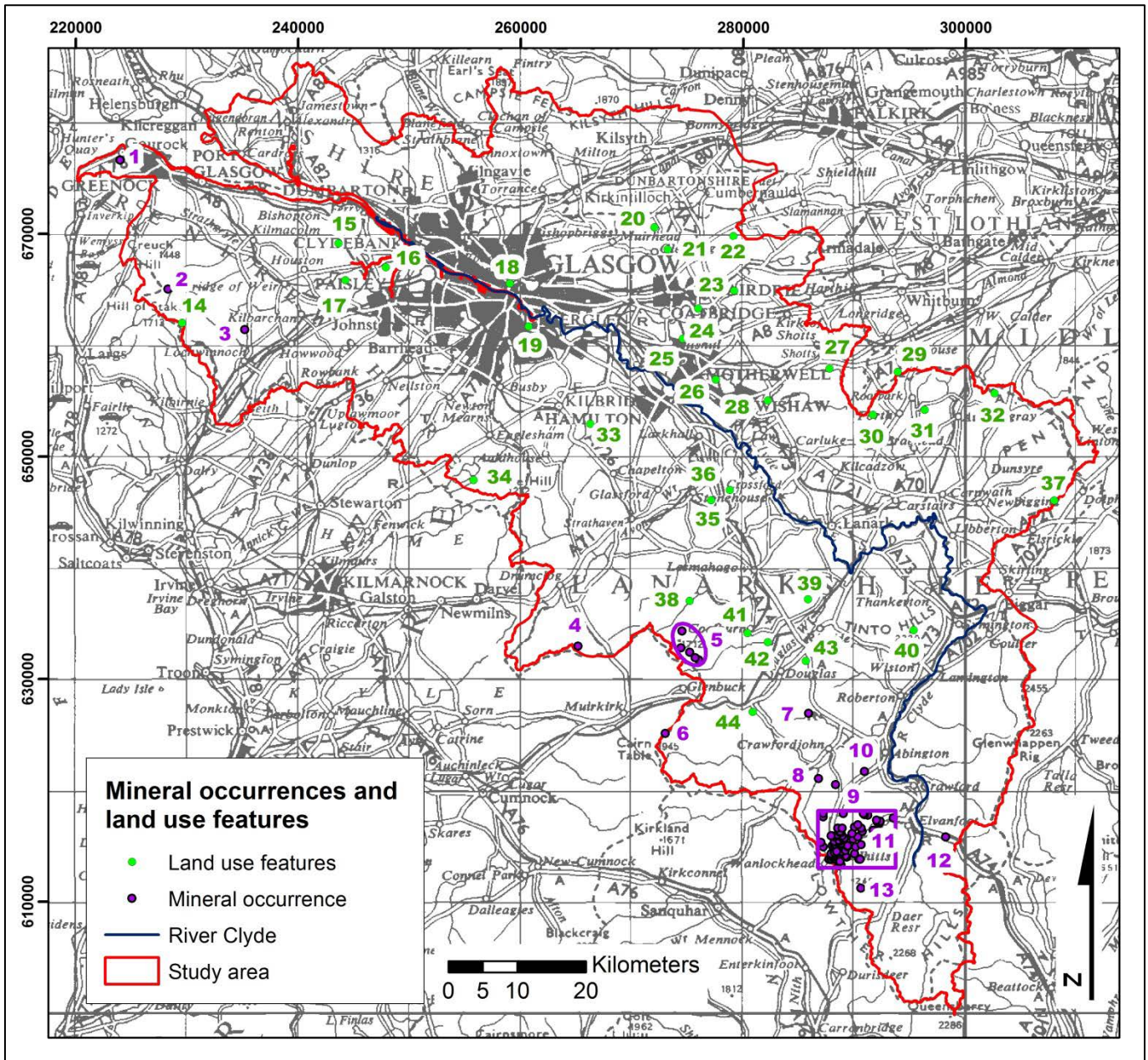
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Figure 1. Location map of the Clyde Basin study area.



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Figure 2. Topographic map of the Clyde Basin study area.



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See Tables 2 and 3 for locations

Figure 3. Selected mineral occurrences and land use features in the Clyde Basin study area.

Table 2. Main metalliferous mineral occurrences in the Clyde Basin study area

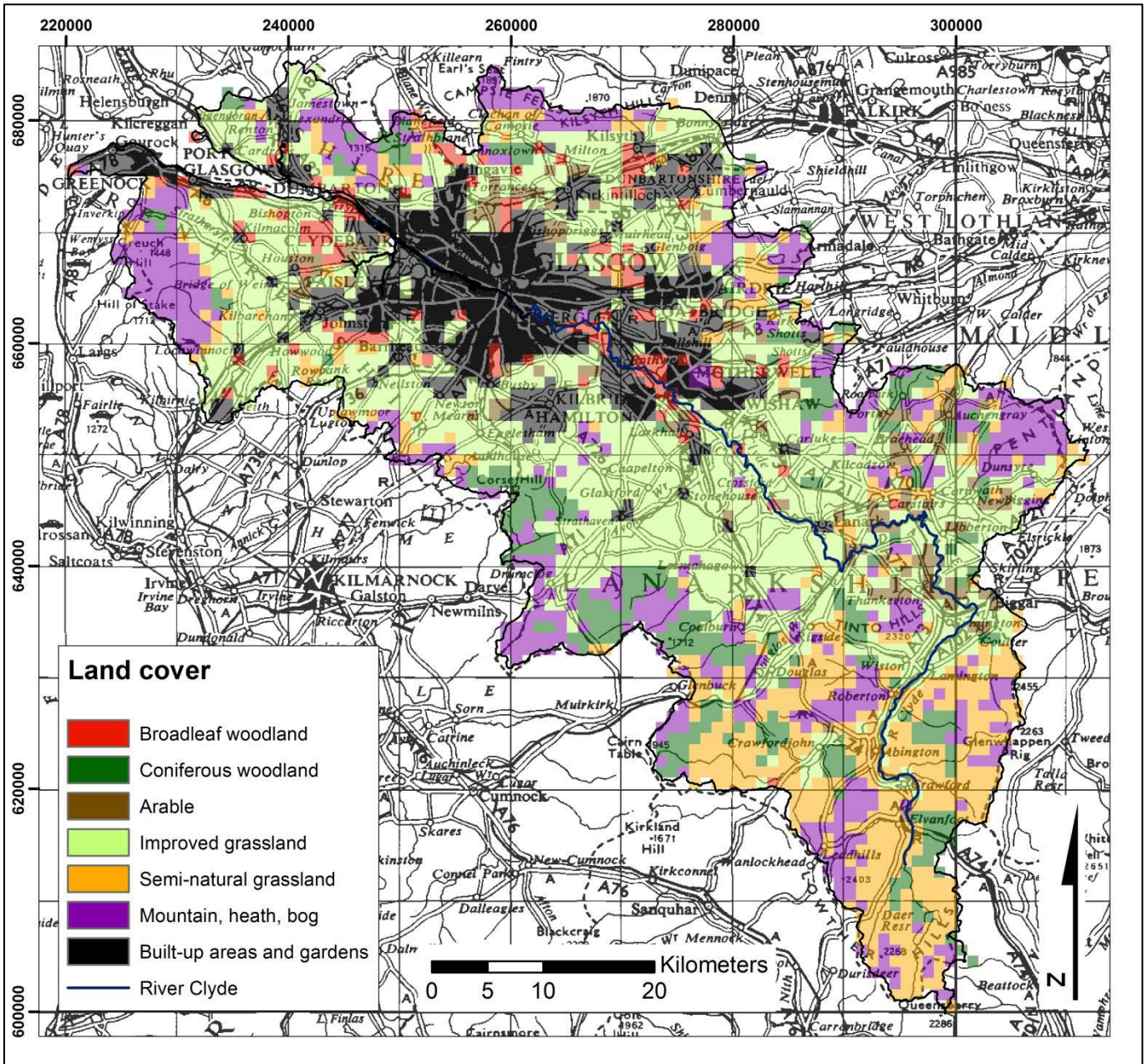
Number	Occurrence name	Mineralisation
1	Drumshantie, Gourrock	Cu
2	Muirshiel	Ba
3	Kaim	Ba, Cu
4	Spoutloch Burn	Ba, Pb
5	Nutberry Hill, River Nethan, Cumberhead, Meilke Auchentilloch, Coal Burn	Ba, Fe, Pb
6	Crossflat Burn	Ba
7	Paige Hill, Auchensaugh Hill	Ba veins
8	Snar Water	Au
9	Glendowran Mine	Pb
10	Drakeslaw Lead Mine	Pb
11	Leadhills–Wanlockhead	Pb, Zn, Cu, Au
12	Crawford Vein	Pb
13	Lang Cleugh	Pb, Au

From BGS (1993) and the BGS Mineral Occurrences Database
 For number locations, see Figure 3

Table 3. Selected land use features in the Clyde Basin Study area

Number	Name	Type
14	Misty Law	Upland
15	Bishopton	Former Royal Ordnance works
16	Glasgow Airport, Renfrew	Current industry
17	Linwood Moss	Capped landfill , restored 2009
18	Glasgow City Centre	Urban
19	Rutherglen	Former heavy industry, chromite works, mining
20	Bedlay Colliery	Former deep-shaft coal mining, tips
21	Glenboig	Former fireclay and silica-sand pit, now landfilled
22	Greengairs	Former opencast coal mine now landfill
23	Moffat Mills, Airdrie	Former paper mills, current distillery
24	Calderbank, Airdrie	Former ironstone and brick pit
25	Mossend, Motherwell	Former clay and brick pit
26	Ravenscraig, Motherwell	Former steel works
27	Dykehead	Opencast coal mine
28	Newmains Moss, Wishaw	Former opencast fireclay and coal mines and collieries
29	Levenseat	Former quarry, now landfill
30	Forth	Former opencast coal mine
31	Wilsontown	Opencast coal mine
32	Tarbrax	Former oil shale/coal workings
33	Blantyre Muir	Opencast coal mine
34	Whitelee	Windfarm, Eaglesham Moor
35	Overwood	Landfill, former sandstone quarry
36	Canderigg	Former opencast coal mines and collieries
37	Black Mount	Upland
38	Logan Water	River valley
39	Brokencrossmuir	Opencast coal mine
40	Tinto Hill	Upland
41	Coalburn	Opencast coal mine
42	Longhill Burn	Former lime works
43	Mainshill Wood	Opencast coal mine
44	Glespin	Opencast coal mine

For number locations, see Figure 3



Land cover data and classification based upon LCM2007 © NERC (CEH) 2011, all rights reserved. © Crown Copyright and/or database right 2011. Licence number 100,427 © third party licensors (Morton et al., 2011).

Figure 4. Land cover map of the Clyde Basin study area.

1.2 BEDROCK GEOLOGY OF THE CLYDE BASIN

For the purposes of this volume, the bedrock geology of the Clyde Basin study area has been simplified into major units based on the 1: 625 000 BGS DigMap® dataset (Table 4). The Clyde Basin study area includes part of the Lower Palaeozoic belt of the Southern Uplands, and to the north of this, the Upper Palaeozoic sequences of the Midland Valley of Scotland (mostly Carboniferous, along with Devonian and less commonly, Permian strata). The Lower Palaeozoic rocks (Ordovician and Silurian) are largely separated from the Upper Palaeozoic rocks by the Southern Upland and related major faults which trend northeastwards from southwest of Ballantrae to the coast east of Dunbar (Floyd, 1994). These faults also separate the higher ground of the Southern Uplands from the lowlands of the Midland Valley of Scotland (Figure 5).

The rocks of the Southern Uplands formed as an accretionary thrust complex at the Laurentian continental margin during Lower Palaeozoic subduction of the Iapetus Ocean, whereas the rocks of the Midland Valley largely formed during a period of extension in the Carboniferous, leading to the deposition of large volumes of sedimentary and volcanic rocks. The main geological components of the Clyde Basin are described in the following sections, in stratigraphic order from oldest to youngest. A brief summary of the Quaternary Geology of the region is contained in Section 1.3 of this atlas.

1.2.1 Sedimentary rocks

Ordovician – Silurian

Rocks of the Ordovician–Silurian Leadhills Supergroup crop out in the southeast of the Clyde Basin area, within the Southern Uplands massif. The distribution of the Leadhills Supergroup is controlled by the Southern Upland Fault and the Carcow, Leadhills, Fardingmullach and Orlock Bridge tract-bounding faults. For the purposes of this publication, the Leadhills Supergroup includes the Crawford Group and Moffat Shale Group, which underlie the Leadhills Supergroup.

Crawford and Moffat Shale Groups (Ordovician – Silurian)

The Crawford Group is of Arenig to Caradoc age and composed dominantly of volcanic rocks. These include hyaloclastites and basaltic pillow lavas with sheet-like dolerite intrusions or lava flows. Present also are blue-grey radiolarian cherts, red and grey cherts, red and green siliceous mudstones with chert nodules, and fossiliferous brown mudstones containing graptolites and conodonts (Floyd, 1995; Stone et al., 2012).

The Moffat Shale Group is of Caradoc to Llandovery age and is dominantly a black pelagic mudstone, with subordinate cherts, mudstones and siltstones, and within the Ettrickbridge Formation, a 55 m thick sandstone turbidite unit (Floyd, 1995). Individual formations within the Moffat Shale Group also contain abundant graptolite fauna, and thin layers of volcanic ash (metabentonite) are also found interbedded in the mudstones (Stone et al., 2012).

The Crawford Group represents the vestiges of the uppermost oceanic crust, and the Moffat Shale Group comprises its pelagic sedimentary cover. Both were formed in a deep oceanic plate environment (Stone et al., 2012).

Leadhills Supergroup (Ordovician)

The formations and groups comprising the Leadhills Supergroup in the Clyde Basin are, from older to younger, the Tappins Group (Marchburn Formation), Barrhill Group (Kirkcolm and Galdenoch Formations) and the Scaur Group (Portpatrick, Shinnel and Glenlee Formations). The strata of the Leadhills Supergroup strike parallel to the trace of the Southern Upland Fault, with the older Tappins Group adjacent to the Southern Upland Fault, and the younger Shinnel Formation adjacent to the Silurian Gala Group. The lithologies of the Leadhills Supergroup are dominated by greywacke sandstones, siltstones, cherts and mudstones with conglomerates. The lithostratigraphical characterisation of the rocks of the Leadhills Supergroup is based upon the variation of sedimentary provenance within the turbiditic sandstones, i.e. some formations are rich in quartzofeldspathic material whereas others contain abundant volcanic detritus. From north to south across the Leadhills Supergroup, the Marchburn Formation is composed of dark green, quartz-poor sandstone turbidites with clasts of chert and lava, as well as micro-conglomerates containing clasts of mudstones, chert and dacitic and basaltic lava. The Kirkcolm Formation is composed of well-bedded quartzose greywacke sandstone, whilst the Galdenoch Formation is characterised by a significant component of andesitic detritus, occasionally exceeding 25%. The Portpatrick Formation is dominantly volcanoclastic sandstone, exposed as a dark blue-grey sandstone turbidite deposit with detrital mafic

lithoclasts (typically 20%) and quartzofeldspathic lithoclasts (typically 80%). The Shinnel Formation is dominated by quartz-rich turbiditic sandstone and thick sequences of grey laminated siltstone, whilst the Glenlee Formation is rich in pyroxene, hornblende and quartzofeldspathic lithoclasts (Stone et al., 2012).

The Leadhills Supergroup was deposited as a series of huge submarine fans adjacent to the Laurentian continental margin, with turbidity currents as the principal depositional agents (Floyd, 1995, Stone et al., 2012).

Silurian

The Silurian rocks within the Clyde Basin catchment crop out in the central to south eastern region of the area, and are termed the Gala Group and the Midland Valley Silurian Inliers. The Gala Group is exposed to the south of the Southern Upland Fault (at the far south west limit of the Clyde Basin area), with the Midland Valley Silurian Inliers cropping out within the Midland Valley itself to the north of the Southern Upland Fault.

Gala Group (Silurian)

The Gala Group is of Llandovery age and occurs to the southeast of the Orlock Bridge Fault in the south of the catchment. From north to south the Gala Group comprises the Mindork Formation (Gala Unit 2) and the Queensberry Formation (Gala Units 4 and 6). The rocks are predominantly medium to thick-bedded, locally pebbly, quartzose greywacke sandstones and massive to laminated mudstones.

The rocks of the Gala Group were largely deposited as turbidites in inner-mid-fan sheets, lobes and slumps, with interlobe and channel deposits.

Midland Valley Silurian Inliers

Within the Clyde Basin, there are four Silurian Inliers of mostly Wenlock age: Lesmahagow, Hagshaw Hills, Carmichael and Eastfield. Both the Lesmahagow and Hagshaw Hills outliers have been folded into broad anticlinal structures. The inliers are typically composed of greywacke sandstones, conglomerates, sandstones, siltstones, mudstones and fish-bearing shale beds. Conglomerates within the Lesmahagow, Hagshaw Hills and Eastfield inliers contain pebbles of igneous origin (e.g. acid igneous rock, porphyrite, granite) as well as quartz and jasper clasts (Stone et al., 2012).

These sediments were laid down in a marine environment, with periods of deposition in shallow marine, deltaic and lagoonal environments.

Devonian

The Old Red Sandstone (ORS) Supergroup, comprising rocks of Lower Devonian and Upper Devonian age, is present to the north of the Southern Upland Fault and in the most northerly area of the Clyde Basin catchment (north of the Firth of Clyde).

ORS Supergroup

Rocks of the Lower Devonian Arbuthnott–Garvock and Strathmore Groups and the Upper Devonian Stratheden Group are present in the area around Alexandria to the north of Glasgow. The Lower Devonian Lanark Group rocks are located mainly around Lanarkshire to the mid-south of the Clyde Basin.

The Arbuthnott–Garvock, Strathmore and Lanark Groups rocks are composed of red-brown conglomerates, breccias, sandstones and mudstones with minor amounts of tuff and cornstone (BGS, 1993). The sandstones are lithic to sublithic, with clasts in the conglomerates composed of lava, sandstones, quartzite and vein quartz.

The Stratheden Group rocks north of the Firth of Clyde are formed of mudstones, cross-bedded sandstones and conglomerates containing clasts of Dalradian rock-types, vein quartz, quartzite, red sandstones and volcanic arenites (BGS, 1993). Proximal to the Southern Uplands, the Upper Devonian rocks are composed of conglomerates with greywacke clasts overlain by sandstones, pebbly sandstones, siltstones, mudstones and thin conglomerates (containing clasts of quartz, quartzite and chert).

The ORS rocks were formed in arid climates. On high ground, they were deposited in scree and piedmont fans; on lower ground, they were deposited as fluvial and lacustrine sediments via braided rivers on floodplains.

Carboniferous

Rocks of Carboniferous age underlie the major part of the Clyde Basin area, comprising the Inverclyde Group, Strathclyde Group, Clackmannan Group and Scottish Coal Measures Group. The rocks crop out in a broad syncline, which was forming during deposition of the Carboniferous strata.

Inverclyde Group

The Inverclyde Group comprises, in ascending order, the Kinnesswood, Ballagan, and Clyde Sandstone Formations. The Kinnesswood Formation is characterised by red, purple-red, yellow-brown and white commonly cross-bedded sandstones, along with siltstones with locally developed conglomerate, thin beds of palaeosol and characteristic pedogenic carbonate nodules and horizons. The Ballagan Formation is comprised mostly of grey silty mudstone with thin interbeds of argillaceous dolostone and sandstone, along with sparse lenticular bodies of cross-bedded channel fill sandstone. The Clyde Sandstone is composed of white sandstone with pebbles and beds of red-grey mudstone and nodules/beds of pedogenic limestone (Stone et al., 2012).

The Inverclyde Group was formed in a mix of alluvial, fluvial and fluviodeltaic environments, coupled with lacustrine, coastal plain and marine (peritidal) deposits. The clastic rocks were deposited by streams draining the Southern Upland landmass under semi-arid and seasonally wet weathering conditions.

Strathclyde and Clackmannan Groups

The Strathclyde Group is composed of both volcanic and sedimentary rocks. The volcanic rocks belong to the Clyde Plateau Volcanic Formation, and are described separately. The sedimentary rocks belong to the Kirkwood and Lawmuir Formations and are dominated by sandstones, siltstones and mudstones with a few coals, oil shales and seat rocks, as well as bioclastic limestones (Stone et al., 2012).

The rocks were deposited in a fluviodeltaic and marine transgressive environment (including freshwater lagoons where the oil shales were deposited).

The Clackmannan Group is composed of the Lower Limestone Formation, Limestone Coal Formation, Upper Limestone Formation and the Passage Formation. The Clackmannan Group comprises a variable succession of marine limestones, coals, mudstone, siltstone and sandstone (Browne et al., 1999).

The depositional environment is related to the advance and retreat of fluvio-deltaic systems in a varying salinity environment.

Scottish Coal Measures Group

Rocks of the Scottish Coal Measures Group crop out in the central region of the area and comprise repeated cycles of sandstone-mudstone-seatearth-coal cyclothems (Browne et al., 1999). The coals of these sequences have been historically worked throughout the central belt of Scotland.

The environment of deposition was that of a wetland forest, flood plain, river and delta, prograding deltas and shallow lakes.

Permian

Permian strata belonging to the Stewartry Group crop out in one small area in the southeast of the Clyde Basin (known as the 'Snar Valley outlier'), near Crawfordjohn within the Southern Uplands massif.

Stewartry Group

Regionally, the Stewartry Group consists of mostly red sandstones and breccio-conglomerates, formed in desert environments. The distribution of the Stewartry Group is confined to a series of fault-bounded, northwest or north-trending basins that cut across the Southern Uplands massif. These basin boundary faults followed reactivated Caledonian trends in response to broadly east-west extension, resulting in the formation of mainly half-graben structures. Locally, the Snar Valley outlier is composed of moderately well-

sorted breccio-conglomerate containing sub-angular clasts of wacke-type sandstone, mudstone and chert (Stone et al., 2012).

The Snar Valley outlier strata occupy a palaeotopographical depression above the underlying Ordovician turbidite sequence, and are believed to have originated as debris-flow and sheet-flood deposits.

1.2.2 Igneous rocks

Silurian to Devonian

The intrusive and extrusive igneous rocks formed in Silurian to Devonian times crop out immediately north of the Southern Upland Fault. The extrusive rocks form part of the Lanark Group, with the intrusives classified under the Midland Valley Siluro–Devonian Felsic Intrusion Suite and the South of Scotland Granitic Suite. For the most part, the extrusive volcanic rocks crop out between the Carmichael Fault and the Southern Upland Fault, and the intrusive volcanic rocks crop out near Lanark and westward toward Mauchline.

Silurian to Devonian Intrusive and Extrusive Igneous Rocks

The extrusive volcanic rocks consist of a suite of calc-alkaline, basaltic to andesitic lavas (commonly amygdaloidal), including olivine basalts, pyroxene andesites, trachytes and rhyolites, feldsparphyric lavas with subordinate volcanic breccias, tuffs, and minor intercalations of sandstone and conglomerate (Smith 1999; Smith and Monaghan, 2013). Local haematisation of the lavas is a common occurrence, and suggests a subaerial environment during deposition. The intrusive volcanic rocks consist of felsite, feldsparphyry, andesitic and microdioritic rocks.

These Silurian to Devonian volcanic rocks are interpreted as forming during the Late Caledonian calc-alkaline magmatic event, during partial melting of a subduction-contaminated source in a volcanic island-arc setting.

Carboniferous

The Clyde Plateau Volcanic Formation (CPV) crops out throughout most of the northern part of the Clyde Basin, extending from just north of the Southern Upland Fault near Strathaven to the Firth of Clyde, where it forms the bedrock of the Renfrew, Kilpatrick and Campsie Hills.

Clyde Plateau Volcanic Formation

The Clyde Plateau Volcanic Formation is composed of thick plateaux of alkali olivine-basalt lava flows, tuffs, felsic lava and felsic tuff, and volcanoclastic sedimentary rocks (Cameron and Stephenson, 1985). Tropical weathering between eruptions produced reddened flow tops, or persistent red-brown lateritic boles.

The CPV was erupted during Late Devonian to early Carboniferous magmatism, caused by north–south lithospheric extension, which led to continental rifting. This period of active magmatism resulted in the eruption and emplacement of extrusive rocks from a series of fissure eruptions and central volcanoes, which are preserved as vents and plugs throughout the Clyde Basin, typically following a basement Caledonian northeast to southwest trend.

Carboniferous – Permian

The Clyde Volcanics: igneous intrusions are distributed throughout the northern sector of the Clyde Basin, but are absent south of the Southern Upland Fault, and immediately north of it.

Clyde Volcanics: Igneous Intrusions

The Clyde Volcanics are composed of dolerite and tholeiitic basalt, felsic rock, mafic igneous rock, and pyroclastic rock. Most of the early Carboniferous minor intrusions (such as vents, plugs, dykes and sills), are compositionally alkali basalts, which cooled relatively slowly and are, therefore, texturally doleritic (Stephenson et al., 2003). These intrusions are also accompanied by more evolved trachytic intrusions, formed by phonolites or rhyolitic microgranitic rocks.

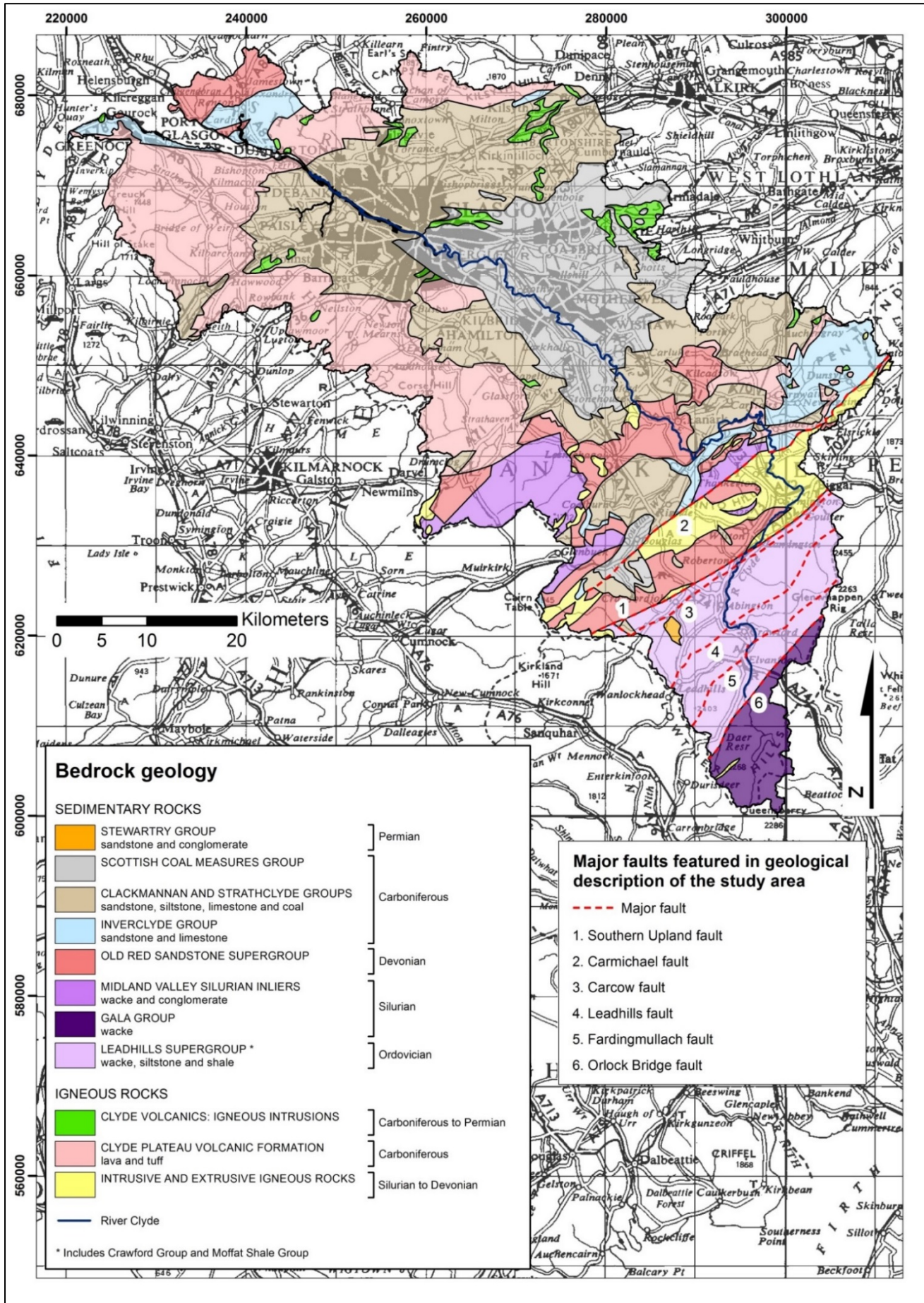
These intrusions arose due to a Late Devonian to early Carboniferous magmatism in an extensional tectonic setting, and ultimately led to the eruption of the Clyde Plateau Volcanic Formation.

Table 4. Simplified bedrock geology scheme for the Clyde Basin study area.

SEDIMENTARY ROCKS			
	Simplified Geological Unit	Description	Geological Grouping into Simplified Units
PERMIAN	STEWARTRY GROUP	Sandstone and conglomerate	STEWARTRY GROUP
	CARBONIFEROUS	SCOTTISH COAL MEASURES GROUP	SCOTTISH COAL MEASURES GROUP
DEVONIAN	CLACKMANNAN AND STRATHCLYDE GROUPS	Sandstone, siltstone, limestone and coal	CLACKMANNAN GROUP STRATHCLYDE GROUP
	INVERCLYDE GROUP	Sandstone and limestone	INVERCLYDE GROUP
	OLD RED SANDSTONE SUPERGROUP		STRATHEDEN GROUP STRATHMORE GROUP LANARK GROUP ARBUTHNOTT-GARVOCK GROUP
SILURIAN	MIDLAND VALLEY SILURIAN INLIERS	Greywacke and conglomerate	SILURIAN ROCKS (UNDIFFERENTIATED)
ORDOVICIAN	GALA GROUP	Greywacke	GALA GROUP
	LEADHILLS SUPERGROUP *	Greywacke, siltstone and shale	SCAUR GROUP BARRHILL GROUP TAPPINS GROUP CRAWFORD GROUP AND MOFFAT SHALE GROUP
	IGNEOUS ROCKS		
	CARBONIFEROUS TO PERMIAN	CLYDE VOLCANICS: IGNEOUS INTRUSIONS	
UNNAMED IGNEOUS INTRUSION, CARBONIFEROUS TO PERMIAN - FELSIC-ROCK			
UNNAMED IGNEOUS INTRUSION, CARBONIFEROUS TO PERMIAN - MAFIC IGNEOUS-ROCK			
UNNAMED IGNEOUS INTRUSION, CARBONIFEROUS TO PERMIAN - PYROCLASTIC ROCK			
CARBONIFEROUS	CLYDE PLATEAU VOLCANIC FORMATION	Lava and tuff	UNNAMED EXTRUSIVE ROCKS, DINANTIAN - FELSIC LAVA AND FELSIC TUFF
			UNNAMED EXTRUSIVE ROCKS, DINANTIAN - MAFIC LAVA AND MAFIC TUFF
SILURIAN TO DEVONIAN	INTRUSIVE AND EXTRUSIVE IGNEOUS ROCKS		UNNAMED EXTRUSIVE ROCKS, SILURIAN TO DEVONIAN - FELSIC LAVA AND FELSIC TUFF
			UNNAMED EXTRUSIVE ROCKS, SILURIAN TO DEVONIAN - MAFIC LAVA AND MAFIC TUFF
			UNNAMED IGNEOUS INTRUSION, LATE SILURIAN TO EARLY DEVONIAN

* For the purposes of this publication, the Leadhills Supergroup is classified to contain the Crawford Group and Moffat Shale Group, which underlie the Leadhills Supergroup.

The descriptions identify the dominant lithologies in each unit where the group name does not suggest a dominant lithology.



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Figure 5. Simplified bedrock geology map of the Clyde Basin study area.

1.3 QUATERNARY GEOLOGY OF THE CLYDE BASIN

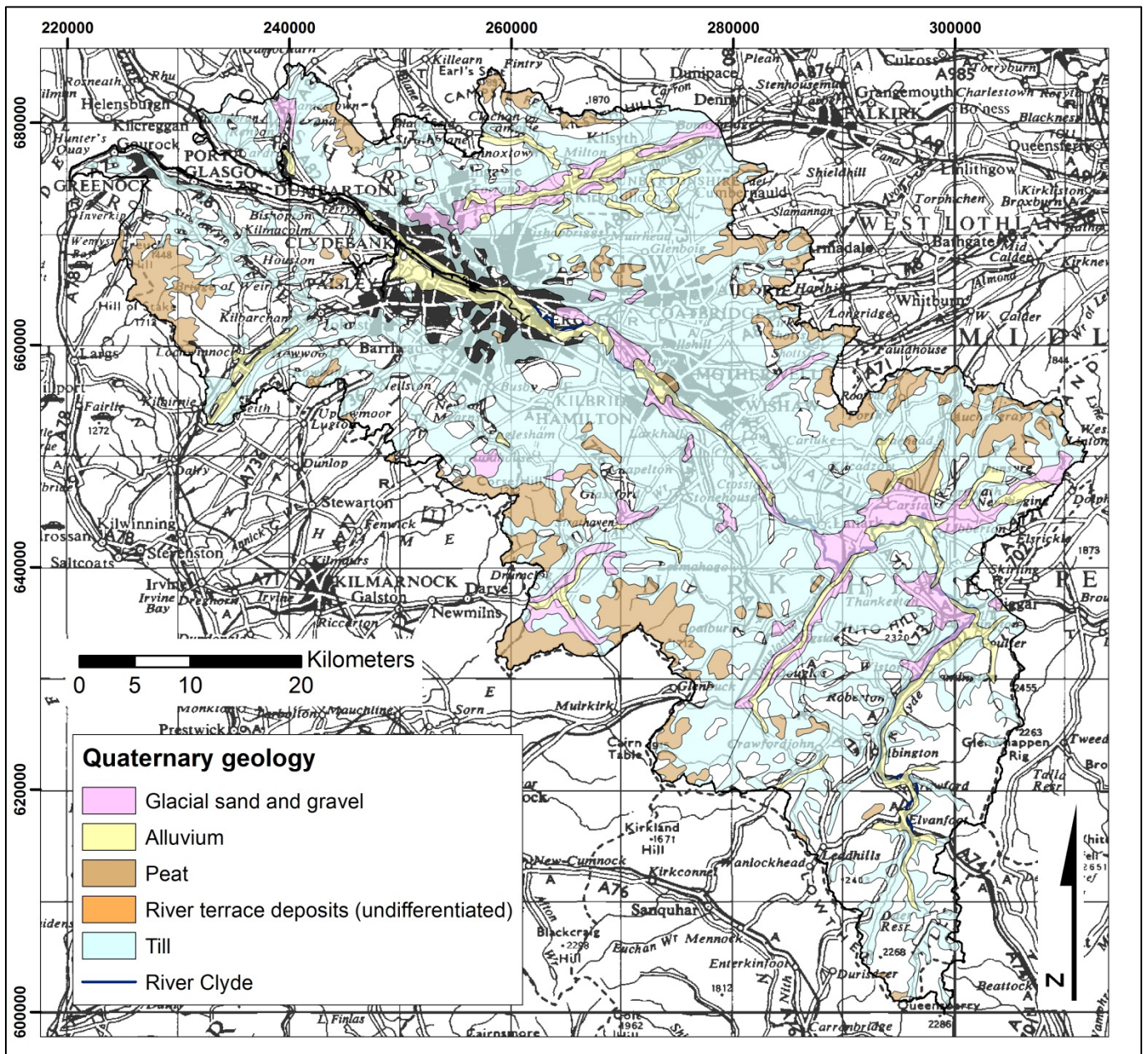
Quaternary (superficial) deposits occur throughout the Clyde Basin, comprising material deposited via glacial, fluvial and marine processes. The Quaternary deposits in the area predominately comprise glacial till and morainic material (typically deposited directly on bedrock), and cover much of the central portion of the Clyde Basin. In places, the till deposits have been moulded by sub-glacial action into typical glacial landforms such as drumlins, and elsewhere form gently undulating topography (Figure 6).

Shelly tills cover much of the low ground in the Glasgow area, from where ice flows picked up marine organisms from the sea, before spreading to Glasgow and Ayrshire and depositing them with the till (Cameron and Stephenson, 1985). Glaciofluvial sand and gravels overlie the tills throughout the area, particularly along present day valleys.

Peat is typically found over the high ground and moorland areas, such as the Clyde Muirshiel Regional Park (Location 2, Figure 3), as well as occurring in low-lying areas in hollows. Recent alluvium deposits (thin terraced deposits of silt and sand with lenses of gravel along river banks) occupy the present day river courses throughout the region, and in particular, the River Clyde valley in the centre of Glasgow (Cameron and Stephenson, 1985).

1.4 MINERAL OCCURRENCES AND MINING

As outlined in Section 1.1 of this volume, much of northeast of the Clyde Basin is underlain by the Scottish Coal Measures, which were extensively mined both in opencast and underground pits from the 17th – 20th centuries. Although much of the coal mining in the Clyde Basin area was in decline by the 1980s, several opencast pits are still in operation today, particularly to the south of Glasgow (Figure 3). In addition to the coal resources, oil was extracted from shale in the remote area of Tarbrax (Location 32, Figure 3) in the east of the Clyde Basin between 1864 and 1925 (Museum of the Scottish Shale Oil Industry, 2014). Several metalliferous mineral occurrences are also present in the area (Figure 3). A full description of these is given in BGS (1993) and summarised here. The most notable deposit is the Leadhills–Wanlockhead field (Location 11, Figure 3) in the south of the area comprising lead-zinc veins held in Ordovician-age greywacke rocks. Between 1700 and 1958 0.4 million tonnes of metallic lead; 10 000 tonnes of zinc and 25 tonnes of cupellated silver were produced from the Leadhills–Wanlockhead area (Mackay, 1959). Lead was also mined on a smaller scale from the Drakeslaw and Glendowran areas (Locations 9 and 10, Figure 3) during the 18th and early 19th century. Approximately 0.3 million tonnes of high-grade barite was mined from the Muirshiel deposit in the west of the area (Location 2, Figure 3) until 1969 and veins at the Nutberry Hill–Cumberhead deposit (Location 5, Figure 3) were exploited on a small scale during the 1980s for barite and lead. Similarly, copper was mined on a small scale from disseminated malachite in Carboniferous age sandstones at the Drumshantie deposit near Gourock in the northwest of the area (Location 1, Figure 3) and from veins associated with a Carboniferous age quartz-dolerite dyke intruding the Clyde Plateau lavas at Kaim on the Misty Law massif in the west of the area (Location 3, Figure 3). Minor occurrences of barite, lead and gold have also been noted at Spoutloch Burn, Crossflat Burn, Paige Hill, Snar Water and Lang Cleugh in the south of the area (Locations 4, 6, 7, 8 and 13, Figure 3).

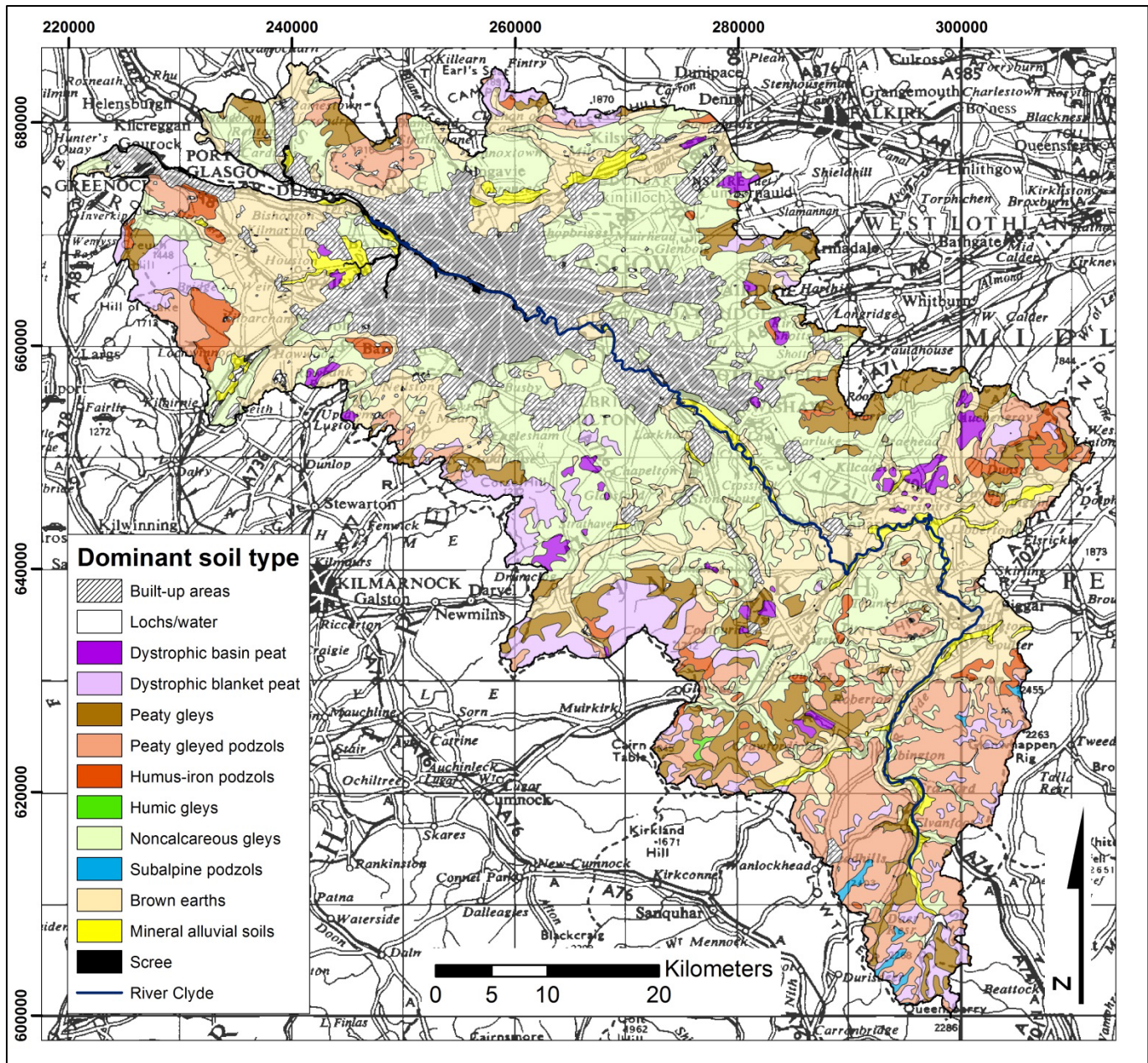


Based on BGS DiGMap 1: 625 000 data © NERC (Jackson and Green, 2003). Contains Ordnance Survey data © Crown Copyright and database rights 2017

Figure 6. Quaternary geology map of the Clyde Basin study area.

1.5 SOIL TYPES IN THE CLYDE BASIN

Soil types in the Clyde Basin are predominately controlled by variations in soil parent material (bedrock and superficial geology) as well as in climate and topography (Bown et al., 1982). Non-calcareous gleys are the dominant soil type in the area (Figure 7). This soil type is characterised by poor natural drainage and is developed over the extensive till deposits (Figure 6) overlying the Carboniferous strata (Figure 5) that occupy much of centre of the study area. Low permeability brown-earth soil is developed on these rock types also, but is particularly associated with red-brown sandy-clay-loam till over the Devonian Old Red Sandstone strata (Figure 5). The moderate leaching and acidity of this soil and mild climatic conditions, coupled with manmade drainage interventions, mean this soil type is well suited to agriculture over much of the region. Peaty gleyed podzol forms on the more freely draining steeper slopes of the Campsie–Kilpatrick and Renfrewshire Hills in the north of the area, except in rockier areas where humus iron podzol is associated with thin stony-sandy-loamy till deposits. Peaty gley is developed on poorly draining clayey till on moors and uplands in the area, which are also characterised by blanket peat bogs as a result of higher rainfall, cooler temperatures and greater soil wetness. Peaty gleyed podzol is the dominant soil type over the greywackes of the Southern Uplands in the south of the area, where the naturally undulating topography allows rapid water run-off and free soil drainage. However, high rainfall results in strong leaching of mineral elements from this soil type. Alluvial mineral soil is restricted to the valleys of the rivers and streams in the area. Its texture is highly variable, but loam and sandy loam predominate. Much of this soil is free draining in the upper layers, but can be waterlogged on low-lying land due to high river levels (Bown et al., 1982).



Soil type classification and polygon data from *Soil Survey of Scotland: 1:250,000 Soil Map*. Copyright James Hutton Institute 2013. Used with the permission of the James Hutton Institute. All rights reserved. Based on survey data from Soil Survey of Scotland Staff (1981).

Figure 7. Main soil types in the Clyde Basin study area.

2 Methods

2.1 CLYDE BASIN SOIL SURVEYS

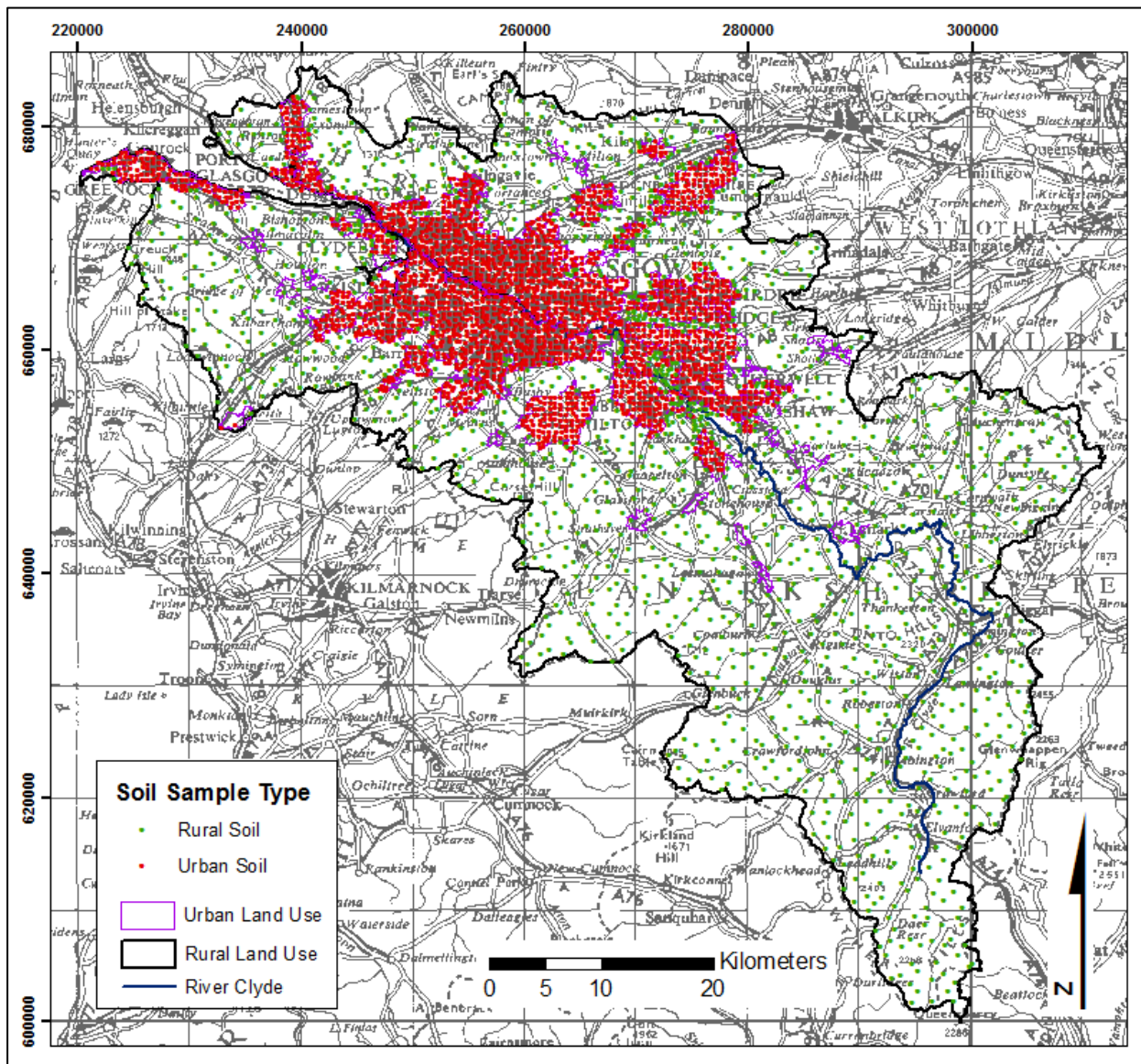
The BGS Clyde Basin soil geochemistry dataset is compiled from two separate field survey campaigns carried out under the CUSP programme. The first of these was a G-BASE survey of 1622 soil samples in the urban and immediate rural environment of Glasgow carried out in the summers of 2001 and 2002. This included the urban areas of Dumbarton, Glasgow, Paisley–Renfrew, Johnson and East Kilbride. The results of this survey have been reported in detail by Fordyce et al. (2012). In the summers of 2010 and 2011, the G-BASE project extended these surveys to include 2241 soil samples from rural areas across the Clyde Basin and urban soil from the towns of Hamilton, Airdrie, Motherwell, Coatbridge, Wishaw, Cumbernauld, Kirkintilloch, Kilsyth, Alexandria, Greenock, Gourock, Bishopton–Erskine and Port Glasgow (Bearcock et al., 2011; Bearcock et al., 2012). In addition, in 2011, 80 urban soil samples were collected from specific land use types within the GCC area for a separate project to examine organic pollutants in urban soil (OPUS). Samples were collected for both inorganic and persistent organic pollutant (POPs) analyses (Bearcock et al., 2012). The results of the inorganic element analysis are included in this atlas. A summary of the surveys that comprise the Clyde Basin soil dataset is given in Table 5 and soil sample locations are shown in Figure 8.

Table 5. Summary of surveys that comprise the G-BASE Clyde Basin soil dataset.

Survey name	Survey description	Date	Number
Glasgow Soil Survey	Sample density of 4 per km ² across the urban/peri-urban area and 1 per 2 km ² in the rural environment	2001–2002	1622
Clyde Soil Survey	Sample density of 4 per km ² across the urban/peri-urban area and 1 per 2 km ² in the rural environment	2010–2011	2241
OPUS Soil Survey	Eight samples collected from 10 different land uses in the GCC area	2011	80
Clyde Basin Soil			3943
Categorised as:			
Clyde Urban Soil			1611
Clyde Rural Soil			2332

Rural–urban sample categories based on the Scottish Government Urban Rural Land Use Classification (Scottish Government, 2015)

Whilst the data combined in this atlas are from two distinct time periods, great care has been taken to standardise sampling procedures for both quality assurance and direct comparison between surveys. The G-BASE field procedures manual clearly defines all protocols (Johnson, 2005), and was used to provide the basis for each survey. The procedures for collecting soil samples are outlined in the following section, and any deviations from standard protocol are identified.



Rural–urban sample categories based on the Scottish Government Urban Rural Land Use Classification (Scottish Government, 2015) Land Use© Scottish Government. Contains Ordnance Survey data © Crown Copyright and database rights 2016.

Figure 8. Map showing the location of soil samples collected for the Clyde Basin survey.

2.2 SAMPLE COLLECTION

According to standard G-BASE procedures (Johnson, 2005), sampling was carried out by a team of 8 – 10 university student voluntary workers (VWs) led by BGS staff. Samplers worked in pairs that were interchanged daily to reduce the possibility of sampling bias introduced by the use of individual procedures. All jewellery was removed prior to sampling to avoid possible metal contamination.

In the urban environment, soil samples were collected at a density of 4 per km² whereby, each 1 kilometre national grid-square on 1: 25 000 scale Ordnance Survey (OS) maps was subdivided into four sub-squares with 500 m x 500 m dimensions. A soil sample was collected as close as possible to the centre point of each 500 m square accepting access and ground characteristic limitations. Common sites for collection included gardens, parks, road verges, open spaces, school yards, sports fields and waste ground. For the OPUS soil survey, eight samples were collected from 10 different land use types across the GCC area (agriculture, parks, allotments, gardens, schools, roads, railways, heavy industry, gas works and petrol stations).

Rural soil sampling was carried out at a sample density of 1 per 2 km², whereby a soil sample was collected from every second 1 km grid square as marked on 1: 50 000 scale OS maps. Samples were collected at least 100 m away from obvious sources of contamination, such as habitation, industrial activity and roads/tracks.

At each site, two separate soil samples, a top and a deeper sample each of approximately 250 g of unsieved material, were collected into a Kraft® paper bag using a handheld Dutch auger. Each sample was a composite of five sub-samples collected from the corners and centre of a 20 x 20 m square. The top few centimetres of surface vegetation was discarded and sub-samples from standard depths of 5 – 20 cm for topsoil and 35 – 50 cm for deeper soil collected. The sub-samples were homogenised to form one top sample and one deeper sample from each site. The top samples were coded 'A' and the deeper samples coded 'S' upon collection. Observations of soil colour, depth and clast lithology and abundance were also recorded at site, and the samples were classified into seven qualitative textural groups (gravel, sand, sandy-silt, silt, silty-clay, sandy-clay and clay) (Johnson, 2005).

At each sample site, information on the location, geology, contamination, land use and other features required for data interpretation was entered on a computer-compatible field data card in standard G-BASE format. Locations were determined using a Garmin® global positioning system unit (GPS) and were plotted on master copies of the 1: 25 000 and 1: 50 000 OS maps at the end of sampling (Johnson, 2005). The field cards were pre-numbered according to a random number system and each site was assigned a 4-digit randomised number in sample batches of 100 (see Section 2.4 of this volume).

For quality assurance purposes, two sets of field duplicates per batch of 100 samples were collected in the same way as the original samples a few meters away from the original sites, following standard G-BASE procedures (Johnson, 2005).

During the Clyde Basin rural and urban surveys carried out in 2010–2011, measurements were made of the depth of the organic-rich layer (DOL) in the soil. This was to aid studies into the amount of carbon stored in soil. At each site, the depth of the dark-brown or black organic-rich layer was determined using the soil auger and a tape measure. The average depth of the five sub-samples was recorded on the field card. Where the bottom of the organic-rich layer could not be reached with an auger, a depth of >1.2 m was recorded. If no organic-rich layer was present, the DOL was recorded as 0 cm.

2.3 SAMPLE ANALYSIS

The Clyde Basin topsoil underwent analysis to determine soil pH and the total concentrations of approximately 50 major and trace elements. Loss on ignition (LOI) was measured also, as an indicator of organic matter content in the soil.

The G-BASE project does not routinely analyse the deeper soil samples, these are collected and stored in the BGS National Geoscience Data Centre (NGDC) sample archive. However, the deeper soil samples from the Glasgow soil survey in 2001–2002 underwent analysis for a full suite of approximately 50 inorganic chemical elements. Since information for deeper soil is not available across the whole of the Clyde Basin, these results are not included in this atlas. However, the deeper soil results from the Glasgow survey have been reported in full by Fordyce et al. (2012). Data for pH and LOI in deeper soil are included in this volume, as these parameters were determined in both the Glasgow survey of 2001–2002 and the Clyde Basin rural soil collected in 2010–2011.

2.3.1 Sample preparation

Following collection, the soil was air and oven-dried at <30 °C to prevent the volatilisation of selenium (Se). Samples were dry-sieved through nylon mesh to a <2 mm size fraction. The samples were then homogenised, coned and quartered and sub-samples taken for analyses. A 10 g split was taken for pH analysis and a further 2 g split for LOI. A 30 g sub-sample was ground in an agate planetary ball mill until 95% was <53 µm. This pulverised material was further sub-sampled to obtain a 12 g split for element analysis by X-ray Fluorescence Spectrometry (XRFS).

XRFS pellets were prepared by grinding the 12 g aliquot of milled material with 3 g of binder for 3 minutes in an agate planetary ball mill. This mixture was then pressed into a 40 mm diameter pellet at 250 kN using a Herzog (HTP-40) semi-automatic press. The binder consists of 9 parts EMU120FD styrene co-polymer (BASF plc) and 1 part Ceridust 3620, a micronised polyethylene wax (Hoechst, after Van Zyl (1982).

2.3.2 X-ray fluorescence spectrometry (XRFS) analysis

Major, minor and trace element determinations were carried out by Wavelength-Dispersive X-ray Fluorescence Spectrometry (WD-XRFS) (Ingham and Vrebos, 1994; Ingham et al., 2007a; Ingham et al., 2007b) for Na, Mg, Al, Si and P as one suite and K, Ca, Ti, Mn, Fe, S, Cl, 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 as another. Silver, Cd, In, Sn, Sb, Te, I, Cs, Ba, La and Ce were analysed by Energy-Dispersive X-ray Fluorescence Spectrometry (ED-XRFS). Concentrations of the major elements are expressed as oxide weight percent and for all other elements as mg kg⁻¹ (Table 6).

Given analytical capabilities at the time, the elements Cl, In, Nd, S, Sm and Yb were not determined in the Glasgow urban/peri-urban dataset in 2001–2002 (Table 6).

For both WD-XRFS and ED-XRFS, mineralogical and particle-size effects contribute to the overall analytical error. The calibrations were validated by analysis of reference materials and regularly corrected for instrumental drift.

The lower limits of detection (LLD) for the Glasgow soil survey analysis carried out in 2002 and the Clyde Basin soil survey determinations completed in 2012 are shown in Table 6. The LLDs are theoretical values for the concentration equivalent to three standard deviations above the background count rate for the analyte in a silica matrix. High instrumental stability results in practical values for these materials approaching the theoretical detection limit.

2.3.3 Soil pH

Soil pH was determined by adding 10 g of <2 mm sample to 25 ml of 0.01M CaCl₂.2H₂O (calcium chloride) (Taylor et al., 2005). The mixture was shaken to form a slurry prior to analysis by pH electrode. This method of pH determination generally gives lower results (0.5 pH units) than water-based methods (Rowell, 1994).

2.3.4 Soil loss on ignition (LOI)

LOI was determined on 2 g of <2 mm material heated in a furnace and kept at 450 °C for a minimum of 4 hours. The LOI is percentage difference in weight before and after heating.

Table 6. Clyde Basin soil analytes and limits of detection.

Analyte	Name	Method	Units	LLD 2002	LLD 2012
Al	Aluminium	WD-XRFS	wt % oxide	0.1	0.2
Ca	Calcium	WD-XRFS	wt % oxide	0.1	0.05
Fe	Iron	WD-XRFS	wt % oxide	0.01	0.01
K	Potassium	WD-XRFS	wt % oxide	0.05	0.01
Mg	Magnesium	WD-XRFS	wt % oxide	0.1	0.3
Mn	Manganese	WD-XRFS	wt % oxide	0.01	0.005
Na	Sodium	WD-XRFS	wt % oxide	0.1	0.3
P	Phosphorus	WD-XRFS	wt % oxide	0.05	0.05
Si	Silicon	WD-XRFS	wt % oxide	0.1	0.1
Ti	Titanium	WD-XRFS	wt % oxide	0.02	0.01
Ag	Silver	ED-XRFS	mg kg ⁻¹	0.5	0.5
As	Arsenic	WD-XRFS	mg kg ⁻¹	0.9	0.9
Ba	Barium	ED-XRFS	mg kg ⁻¹	5.1	1
Bi	Bismuth	WD-XRFS	mg kg ⁻¹	0.5	0.3
Br	Bromine	WD-XRFS	mg kg ⁻¹	0.5	0.8
Cd	Cadmium	ED-XRFS	mg kg ⁻¹	0.5	0.5
Ce	Cerium	ED-XRFS	mg kg ⁻¹	3.8	1
Cl	Chlorine	WD-XRFS	mg kg ⁻¹	nd	200
Co	Cobalt	WD-XRFS	mg kg ⁻¹	1.2	1.5
Cr	Chromium	WD-XRFS	mg kg ⁻¹	1.3	3
Cs	Caesium	ED-XRFS	mg kg ⁻¹	2	1
Cu	Copper	WD-XRFS	mg kg ⁻¹	0.8	1.3
Ga	Gallium	WD-XRFS	mg kg ⁻¹	0.7	1
Ge	Germanium	WD-XRFS	mg kg ⁻¹	0.6	0.5
Hf	Hafnium	WD-XRFS	mg kg ⁻¹	0.7	1
I	Iodine	ED-XRFS	mg kg ⁻¹	2	0.5
In	Indium	ED-XRFS	mg kg ⁻¹	nd	0.5
La	Lanthanum	ED-XRFS	mg kg ⁻¹	3.5	1
Mo	Molybdenum	WD-XRFS	mg kg ⁻¹	0.8	0.2
Nb	Niobium	WD-XRFS	mg kg ⁻¹	0.6	1
Nd	Neodymium	WD-XRFS	mg kg ⁻¹	nd	4
Ni	Nickel	WD-XRFS	mg kg ⁻¹	0.6	1.3
Pb	Lead	WD-XRFS	mg kg ⁻¹	0.5	1.3
Rb	Rubidium	WD-XRFS	mg kg ⁻¹	0.5	1
S	Sulphur	WD-XRFS	mg kg ⁻¹	nd	1000
Sb	Antimony	ED-XRFS	mg kg ⁻¹	1	0.5
Sc	Scandium	WD-XRFS	mg kg ⁻¹	1.3	3
Se	Selenium	WD-XRFS	mg kg ⁻¹	0.2	0.2
Sm	Samarium	WD-XRFS	mg kg ⁻¹	nd	3
Sn	Tin	ED-XRFS	mg kg ⁻¹	0.8	0.5
Sr	Strontium	WD-XRFS	mg kg ⁻¹	0.6	1
Ta	Tantalum	WD-XRFS	mg kg ⁻¹	1.2	1
Te	Tellurium	ED-XRFS	mg kg ⁻¹	1	0.5
Th	Thorium	WD-XRFS	mg kg ⁻¹	0.6	0.7
Tl	Thallium	WD-XRFS	mg kg ⁻¹	0.5	0.5
U	Uranium	WD-XRFS	mg kg ⁻¹	0.6	0.5
V	Vanadium	WD-XRFS	mg kg ⁻¹	1.3	3
W	Tungsten	WD-XRFS	mg kg ⁻¹	0.7	0.6
Y	Yttrium	WD-XRFS	mg kg ⁻¹	0.8	1
Yb	Ytterbium	WD-XRFS	mg kg ⁻¹	nd	1.5
Zn	Zinc	WD-XRFS	mg kg ⁻¹	0.5	1.3
Zr	Zirconium	WD-XRFS	mg kg ⁻¹	0.8	1
pH	pH	Slurry	pH	-	-
LOI	Loss on Ignition	Furnace	wt %	-	-

LLD = Lower limit of detection nd = not determined

2.4 ERROR CONTROL AND DATA QUALITY

2.4.1 Field and laboratory

Rigorous field-based control procedures at each stage of the sampling process are designed to minimise error (Johnson, 2005). Systematic error in analysis was monitored using a method based on randomised sample site numbers (Plant, 1973). Samples were collected in random number order but analysed in sequential order so that any within-batch analytical instrument drift can be distinguished from genuine geographic variances. No within-batch analytical drift problems were evident in the samples.

Long-term analytical drift between batches of samples was monitored using a series of standards representing a range of concentration for each element. The standards included several bulk soil samples collected over representative rock types, three of which were analysed in every batch of 100 samples. Time versus concentration plots for each of these reference samples were prepared. Tolerance limits arbitrarily set at the mean $\pm 2\sigma$ were used to assess data quality. Simple arithmetic correlations were applied to normalise the data to the rest of the UK geochemistry database for systematic drift (Lister and Johnson, 2005). Those applied to the Clyde topsoil datasets are outlined in Table 7.

Table 7. Normalisation factors applied to the Clyde topsoil datasets

Element	Topsoil normalisation factors	
	Glasgow Urban	Clyde Rural and Urban
Al	(Al x 0.9441) + 2.004	
Ba		(Ba x 0.8819) + 54.816
Bi	Bi + 0.4	
Ce	(Ce x 1.1724) + 7.898	(Ce x 1.2221) – 5.4103
Co	(Co x 1.4019) + 1.5711	(Co x 1.1354) + 3.8732
Cr	(Cr x 0.7111) + 18.192	(Cr x 0.8982) + 14.245
Fe	(Fe x 0.7363) + 2.2501	(Fe x 1.1) + 0.0257
Hf		(Hf x 0.8611) + 0.4138
K	(K x 0.9102) + 0.2398	
La	(La x 1.1506) + 1.8029	(La x 1.1144) – 1.9707
Mo	Mo + 1	
Sb	Sb – 0.5	
Se	Se + 0.3	
Si	(Si x 0.4829) + 26.695	
Sn	(Sn x 1.0381) + 0.7902	(Sn x 1.2453) – 0.1468
Sr		(Sr x 0.8603) + 3.2589
Tl	Tl + 0.5	
U*	U – 1	U - (-0.0004) x Pb
V		(V x 0.8949) + 18.586
Zn	(Zn x 0.8887) + 2.4903	(Zn x 0.8789) + 6.3742
Zr	(Zr x 1.0068) – 11.129	(Zr x 1.0746) – 29.272

* Includes XRF analytical correction factor for Pb interference

Certified reference materials (CRM) GSD-7, GSS-1, LKSD-1 and LKSD-4 were included in the XRF analytical runs and the results are in good agreement with the certified values (Table 8). However, In, Nb, Ta and Te show poorer accuracy due to the very low abundance of these elements in the standards, close to or below the limits of detection. Chlorine and S also show poorer accuracy due to the relatively high LLD by XRF for these elements. Consequently, the results for these elements should be treated with caution.

Individual results are not reliable below the quoted lower limits, but reliable estimates of average or typical values over an area may be obtained at lower levels of concentration; meaningful patterns may thus be recognised for some elements at levels lower than the LLD. Therefore, for data presentation/analysis purposes, concentrations below the LLD were set to half the least conservative of either the 2002 or 2012 LLD. Results for In and Te were all below the LLD and are not presented in this atlas.

Table 8. Results for certified reference materials included in the Clyde Basin soil XRFs analyses.

CRM		GSD-7		GSS-1		LKSD-1		LKSD-4	
Element	Units	Clyde measured	Certified value	Clyde measured	Certified value	Clyde measured	Certified value	Clyde measured	Certified value
Al	wt %	14.7 ± 0.08	13.4	13.7 ± 0.09	14.2	5.4 ± 0.10	7.8	5.0 ± 0.11	5.9
Ca	W t %	1.64 ± 0.01	1.67	1.74 ± 0.01	1.72	11.99 ± 0.10	10.80	1.85 ± 0.03	1.80
Fe	wt %	6.41 ± 0.02	6.51	5.05 ± 0.03	5.19	3.98 ± 0.03	4.10	4.21 ± 0.04	4.10
K	wt %	3.73 ± 0.05	3.54	2.55 ± 0.04	2.59	1.07 ± 0.02	1.10	0.79 ± 0.02	0.80
Mg	wt %	4.4 ± 0.04	3.1	2.1 ± 0	1.8	1.8 ± 0.04	1.7	1.0 ± 0.05	0.9
Mn	wt %	0.093 ± 0	0.089	0.237 ± 0	0.227	0.093 ± 0	0.100	0.070 ± 0	0.100
Na	wt %	1.2 ± 0.05	1.2	1.4 ± 0.05	1.7	1.5 ± 0.05	2.0	0.5 ± 0	0.7
P	wt %	0.21 ± 0	0.19	0.17 ± 0	0.17	0.15 ± 0	0.20	0.35 ± 0.01	0.30
Si	wt %	67.2 ± 0.22	64.7	55.3 ± 0.29	62.6	30.5 ± 0.52	40.1	44.1 ± 0.88	41.6
Ti	wt %	0.704 ± 0.01	0.747	0.757 ± 0.01	0.805	0.446 ± 0.01	0.500	0.301 ± 0	0.400
Ag	mg kg ⁻¹	1.3 ± 0.40	1.1	0.4 ± 0.21	0.4	0.5 ± 0.08	0.6	0.2 ± 0.11	0.2
As	mg kg ⁻¹	81.7 ± 0.72	84.0	34.7 ± 0.34	33.5	34.3 ± 0.59	40.0	16.9 ± 0.53	16.0
Ba	mg kg ⁻¹	697 ± 2.57	720	550 ± 3.85	590	381 ± 3.17	430	257 ± 2.16	330
Bi	mg kg ⁻¹	0.9 ± 0.28	0.7	1.2 ± 0.26	1.2	1.1 ± 0.21	no data	0.4 ± 0.15	no data
Br	mg kg ⁻¹	0.5 ± 0.42	no data	2.1 ± 0.28	2.9	10.0 ± 0.26	11.0	50.8 ± 0.68	49.0
Cd	mg kg ⁻¹	0.9 ± 0.11	1.1	4.0 ± 0.17	4.3	1.1 ± 0.13	1.2	1.9 ± 0.15	1.9
Ce	mg kg ⁻¹	76 ± 0.62	78	63 ± 0.63	70	24 ± 0.47	27	37 ± 0.86	48
Cl	mg kg ⁻¹	116 ± 9.51	no data	160 ± 16.13	78	459 ± 9.05	no data	238 ± 8.80	no data
Co	mg kg ⁻¹	20.4 ± 1.09	21.0	13.7 ± 0.79	14.2	11.6 ± 0.81	11.0	11.7 ± 0.71	11.0
Cr	mg kg ⁻¹	118.5 ± 1.46	122.0	57.2 ± 0.92	62.0	26.0 ± 0.81	31.0	30.6 ± 0.81	33.0
Cs	mg kg ⁻¹	5 ± 0.51	6	8 ± 0.36	9	ND	2	2 ± 0.51	2
Cu	mg kg ⁻¹	35.7 ± 0.48	38.0	19.4 ± 0.33	21.0	40.5 ± 0.57	44.0	30.3 ± 0.54	31.0
Ga	mg kg ⁻¹	16.8 ± 0.60	17.7	16.7 ± 0.46	19.3	8.7 ± 0.51	no data	7.7 ± 0.30	no data
Ge	mg kg ⁻¹	1.2 ± 0.43	1.4	0.7 ± 0.37	1.3	0.2 ± 0.41	no data	0.7 ± 0.35	no data
Hf	mg kg ⁻¹	4.2 ± 0.74	4.9	6.9 ± 0.68	6.8	3.7 ± 0.70	3.6	3.0 ± 0.50	2.8
I	mg kg ⁻¹	0.9 ± 0.17	no data	1.8 ± 0.24	1.9	2.0 ± 0.28	no data	9.6 ± 0.34	no data
In	mg kg ⁻¹	ND	no data	ND	no data	0.5 ± 0.22	no data	ND	no data
La	mg kg ⁻¹	42 ± 0.53	45	31 ± 0.83	34	14 ± 0.63	16	21 ± 0.50	26
Mo	mg kg ⁻¹	1.4 ± 0.17	1.4	1.4 ± 0.17	1.4	9.5 ± 0.14	10.0	1.6 ± 0.15	<5
Nb	mg kg ⁻¹	14.9 ± 0.27	17.0	14.3 ± 0.26	16.6	4.0 ± 0.23	7.0	4.4 ± 0.25	9.0
Nd	mg kg ⁻¹	33.5 ± 1.80	37.0	26.7 ± 1.31	28.0	21.3 ± 2.19	16.0	28.7 ± 1.81	25.0
Ni	mg kg ⁻¹	54.1 ± 0.75	53.0	19.4 ± 0.73	20.4	14.9 ± 0.40	16.0	33.2 ± 0.41	31.0
Pb	mg kg ⁻¹	351.8 ± 2.03	350.0	94.1 ± 0.72	98.0	80.3 ± 0.92	82.0	97.0 ± 1.19	91.0
Rb	mg kg ⁻¹	143.2 ± 0.93	147.0	134.2 ± 0.91	140.0	22.4 ± 0.32	24.0	25.0 ± 0.35	28.0
S	mg kg ⁻¹	491 ± 58.15	190	812 ± 57.75	310	9642 ±	1570	6127 ±	999
Sb	mg kg ⁻¹	2.7 ± 0.26	2.6	1.0 ± 0.20	0.9	1.1 ± 0.25	1.2	1.2 ± 0.22	1.7
Sc	mg kg ⁻¹	13.1 ± 1.44	14.6	10.4 ± 1.32	11.2	7.5 ± 1.30	9.0	6.9 ± 0.57	7.0
Se	mg kg ⁻¹	0.2 ± 0.06	0.3	0.1 ± 0.10	0.1	1.0 ± 0.10	no data	2.2 ± 0.12	no data
Sm	mg kg ⁻¹	4.4 ± 1.23	6.1	3.4 ± 1.33	5.2	2.7 ± 1.40	4.0	4.4 ± 1.02	5.0
Sn	mg kg ⁻¹	4.6 ± 0.21	5.4	5.8 ± 0.17	6.1	14.2 ± 0.19	16.0	4.5 ± 0.19	5.0
Sr	mg kg ⁻¹	217.8 ± 0.59	220.0	152.7 ± 0.82	155.0	255.9 ± 1.13	250.0	121.2 ± 1.09	110.0
Ta	mg kg ⁻¹	1.1 ± 0.48	1.4	0.8 ± 0.53	1.4	0.0 ± 0.45	0.3	0.0 ± 0.33	0.4
Te	mg kg ⁻¹	ND	no data	ND	no data	ND	no data	ND	no data
Th	mg kg ⁻¹	12.3 ± 0.33	12.6	10.5 ± 0.38	11.6	1.6 ± 0.41	2.2	4.9 ± 0.23	5.1
Tl	mg kg ⁻¹	0.9 ± 0.40	0.9	0.9 ± 0.28	1.0	0.4 ± 0.24	no data	1.0 ± 0.28	no data
U	mg kg ⁻¹	3.5 ± 0.33	3.5	3.5 ± 0.34	3.3	9.7 ± 0.27	9.7	31.5 ± 0.26	31
V	mg kg ⁻¹	91.9 ± 1.72	96.0	78.8 ± 2.62	86.0	47.4 ± 1.33	50.0	45.5 ± 1.35	49.0
W	mg kg ⁻¹	6.3 ± 0.41	5.5	4.2 ± 0.31	3.1	1.4 ± 0.16	<4	1.5 ± 0.26	<4
Y	mg kg ⁻¹	24.3 ± 0.41	24.0	25.0 ± 0.60	25.0	20.7 ± 0.32	19.0	22.3 ± 0.29	23.0
Yb	mg kg ⁻¹	2.5 ± 0.90	2.6	2.2 ± 0.66	2.7	1.9 ± 0.81	2.0	2.3 ± 0.49	2.0
Zn	mg kg ⁻¹	241.1 ± 1.19	238.0	650.7 ± 2.36	680.0	320.4 ± 2.28	331.0	193.3 ± 1.70	194.0
Zr	mg kg ⁻¹	154.9 ± 0.70	162.0	242.4 ± 1.20	245.0	130.2 ± 0.99	134.0	98.0 ± 0.92	105.0

Clyde Measured = mean ± standard deviation of 14 analyses ND = not detected

CRM = certified reference materials

GSD-7 = sediment, Institute of Geophysical and Geochemical Prospecting, China

GSS-1 = soil, National Research Centre for CRMs, China

LKSD-1 and LKSD-4 = lake sediment, Canadian Certified Reference Material Project, Natural Resources Canada

2.4.2 Analysis of variance

Variability in the sampling and analytical methods was monitored by means of field and analytical duplicate samples and analytical standards and reference materials. All field duplicate sample results were removed from the dataset prior to statistical treatment according to standard G-BASE procedures (Lister and Johnson, 2005).

Sampling and analytical precision were calculated using a procedure based on analysis of variance (ANOVA). Field duplicate soil samples were collected at approximately one site in 50; the sites were chosen using random number lists. Each field duplicate sample was dried and split into two portions, producing a total of four analytical replicates from each site. As a check against mis-labelling or other errors, the analyses of the replicates were plotted against each other, for selected elements of differing chemical properties, to assess whether any sample pairs were consistently out-lying. The results for the replicate pairs of samples were averaged, and the field duplicate sample pairs were examined in a similar manner. No labelling errors were found.

Plots of cumulative frequency versus concentration for each element in the soil were examined to assess the degree to which the distribution of the element conformed to a Gaussian distribution; as a result, the concentrations of all trace and major elements were log-transformed before undergoing ANOVA, to improve their conformity to the model distribution (Plant et al., 1975).

A random nested model of ANOVA was selected because all the analyses were part of a single randomised dataset (Snedecor and Cochran, 1989). The NESTED procedure from the SASTM statistical software package was used to perform the ANOVA (SAS Institute Inc., 1989). Residual variance (representing inter-alia inhomogeneities introduced in sample preparation and sub-sampling, and errors in chemical analysis), between-sample variance (representing within-site variability as well as any variability introduced by the process of sample collection) and between-site variance (representing the natural geochemical distribution of the elements in the soil) were calculated.

Since the frequency distribution of most elements is multi-modal and none fit the Gaussian model perfectly, there is an unquantifiable overstatement of the between-site variance, a problem that is inherent in using ANOVA on geochemical data. Statistical F-tests have not been quoted because the data do not satisfy this and other assumptions required for formal analysis of variance.

The percentages of variance attributable to geochemical (between-site), sampling (between-sample) and analytical (residual) variance are given in Table 9, and provide a general indication of the reliability of the geochemical data. There were insufficient replicate pairs to calculate ANOVA for Ag, In and Te. For data above the detection limit, it is expected that geographical geochemical differences between-site should account for $\geq 80\%$ of the variance, as opposed to $< 20\%$ sampling and analytical variance (Ramsay, 1998). For the Clyde Basin, in most cases over 80% of the variability can be attributed to between-site variance, demonstrating the robustness of the field sampling method. The between-site variance is $< 80\%$ for Bi, Cd, Cs, Hf, Sb, Sm, Ta, Tl, U, W and Yb and analytical variability is higher ($> 3\%$) for these elements, and for I, Mo, S, than the other parameters. This reflects the fact that concentrations of these elements in soil are close to the limit of detection. Therefore, results should be treated with more caution than for other analytes in the dataset.

Table 9. Percentage of variance in Clyde Basin topsoil samples attributable to between-site, between-sample and residual variance.

Element	N	Between Site %	Between Sample %	Residual %	Total %
Al	69	98.9	1.0	0.1	100
As	69	80.0	17.4	2.6	100
Ba	69	98.4	1.3	0.4	100
Bi	43	23.4	1.6	75.0	100
Br	69	94.6	4.6	0.9	100
Ca	69	92.2	7.6	0.2	100
Cd	25	59.5	2.1	38.4	100
Ce	69	98.2	1.0	0.9	100
Cl	35	95.0	1.8	3.2	100
Co	69	93.1	3.5	3.3	100
Cr	69	94.0	5.5	0.5	100
Cs	52	70.4	14.3	15.3	100
Cu	69	85.8	13.8	0.4	100
Fe	69	97.4	2.4	0.1	100
Ga	69	97.8	1.5	0.7	100
Ge	68	92.5	1.6	6.0	100
Hf	57	72.0	6.6	21.4	100
I	63	85.4	10.1	4.5	100
K	69	98.6	1.3	0.1	100
La	56	92.1	5.3	2.6	100
Mg	69	96.4	3.0	0.6	100
Mn	69	96.2	3.4	0.5	100
Mo	64	88.4	4.8	6.8	100
Na	58	94.4	4.4	1.2	100
Nb	69	99.4	0.4	0.2	100
Nd	35	96.9	1.3	1.7	100
Ni	69	92.8	6.7	0.5	100
P	69	90.1	8.7	1.2	100
Pb	69	92.5	4.6	2.9	100
Rb	69	98.3	1.6	0.1	100
S	35	85.3	11.1	3.6	100
Sb	67	77.3	10.9	11.9	100
Sc	69	92.0	1.5	6.4	100
Se	69	85.0	6.4	8.6	100
Si	69	99.6	0.1	0.3	100
Sm	32	45.4	-3.3	57.9	100
Sn	69	84.2	9.0	6.8	100
Sr	69	95.1	4.6	0.3	100
Ta	40	26.1	8.1	65.8	100
Th	69	96.8	1.3	1.9	100
Ti	69	99.3	0.6	0.1	100
Tl	50	35.1	11.2	53.7	100
U	69	76.7	-0.9	24.2	100
V	69	98.1	1.7	0.2	100
W	61	52.8	11.9	35.4	100
Y	69	98.0	1.6	0.5	100
Yb	33	54.1	8.1	37.8	100
Zn	69	84.6	14.3	1.1	100
Zr	69	99.5	0.3	0.2	100

N = number of replicate pairs. All data log-transformed.

2.5 DATA PRESENTATION

Once full error control and data quality procedures were completed, the Clyde soil geochemical results were formally loaded into the BGS Corporate Oracle® Geochemistry Database (Harris and Coats, 1992), where they may be retrieved by means of a database front-end.

To present the data spatially, interpolated surface geochemical maps showing the concentrations of the elements in soil across the Clyde Basin were created using the ArcGIS10.1 (ESRI®) geographic information system (GIS) software package. These convert the sample point data into a continuous surface across the area. The interpolation was carried out using inverse distance weighting (IDW) analysis. In this method, the map was split into a series of grid cells, whereby in this case, the cell size represented 250 x 250 m on the ground. Each grid cell (pixel) was then assigned a value, which was calculated from all the data within 1500 m of the cell. These data were weighted according to the distance of the sample site from the cell (r), the weighting was proportional to r^2 . Colour-classified maps were then produced, based on boundaries set at the 5, 10, 15, 25, 50, 75, 90, 95, and 99 percentiles of the data distribution for most elements, according to standard G-BASE procedures (Johnson et al., 2005). In addition, geological line-work, based on the simplified geological map (Figure 5), was overlain on each geochemical map. To present the differences between urban and rural soil chemistry, the Clyde Basin dataset was categorised into rural and urban samples based on land use domain polygons in GIS. The urban domain was determined using the Scottish Government Urban Rural Land Use Classification. This two-fold classification is based upon the National Records of Scotland settlement dataset, and defines areas of contiguous high-population density postcodes (> 3000 people) as urban and areas < 3000 people as rural (Scottish Government, 2015). The urban dataset for the present study comprises 2333 soil samples collected from within this urban domain. The peri-urban and rural samples collected in the non-built environment are referred to collectively as the rural soil dataset, which comprises 1611 samples (Table 5; Figure 8). The data were classified also according to the underlying bedrock geology to assess variation in soil chemistry over different parent material lithologies. Geological and rural–urban comparisons in soil chemistry are presented as a series of box plots. The boxes show the 25th, 50th and 75th percentiles, and the whiskers the lower ($Q1 - 1.5 \times IQR$) and upper limits ($Q3 + 1.5 \times IQR$) of the data distribution, where IQR is the inter-quartile range. The box plots and histograms showing the data distribution for each soil parameter were generated using the Minitab® software package.

This atlas has been published as an 'interactive pdf document', which allows the reader to access and display additional information in digital format. This comprises a clickable button on each element information page, which toggles to a new view of a location map showing the place names mentioned in the element description text.

3 Soil geochemistry

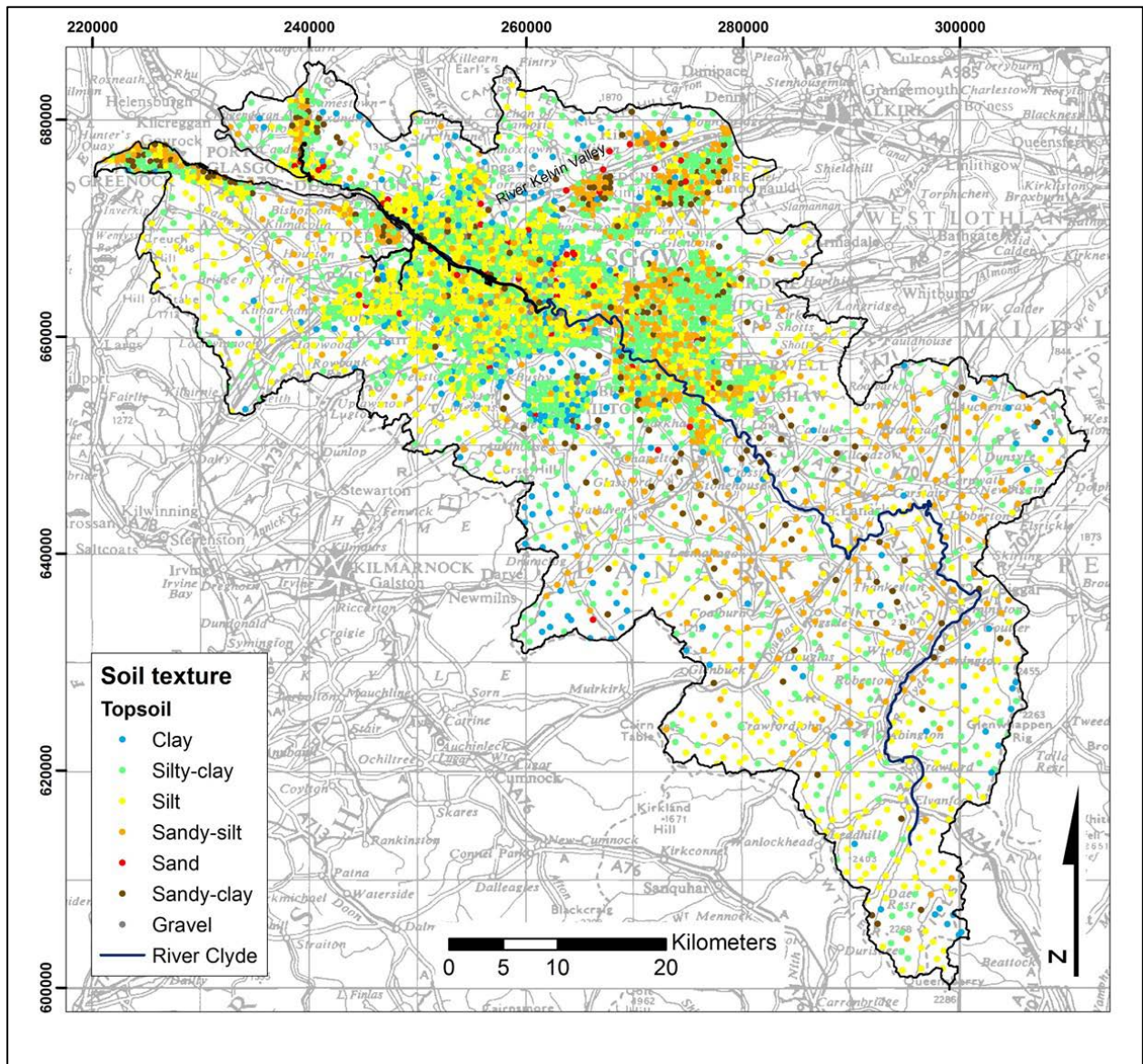
The results of the Clyde Basin geochemical survey are presented in this section of the atlas. Information on key soil parameters such as texture, pH and LOI is presented at the start of the section. For each chemical parameter measured in topsoil, a map showing the spatial distribution is accompanied by statistical tables and plots summarising the data and a description of the main controls on the parameter distributions. Reference to world soil median concentrations are taken from Reimann and Caritat (1998). Locations mentioned in the text are shown in Figures 1 – 3. Information is presented for a selection of 24 chemical elements showing the most interesting distributions in topsoil, including those that are important for agriculture/land quality assessments. Information is arranged in alphabetical order according to element name. Maps and statistical summaries of a further 26 topsoil-element concentrations, with similar spatial distributions to those discussed in the main body of the atlas, are included in Appendix 1. A guide to the information included in this section and in Appendix 1 is shown in Table 10. Results for major elements are reported in weight percent and for minor/trace elements in mg kg⁻¹.

Table 10. Guide to soil parameter information in this section and in Appendix 1

Parameter in this section	Parameters with similar spatial distributions in Appendix 1
Topsoil texture	
Depth of organic-rich layer	
Topsoil pH	
Deeper soil pH	
Topsoil LOI	
Deeper soil LOI	
Aluminium	Gallium, Scandium
Antimony	
Arsenic	
Barium	
Cadmium	Silver
Caesium	
Calcium	
Chromium	Nickel
Cobalt	Vanadium
Copper	Germanium, Zinc
Iodine	Bromine, Chlorine, Sulphur
Iron	
Lanthanum	Bismuth, Cerium, Neodymium, Samarium, Thorium, Yttrium, Ytterbium
Lead	
Manganese	
Molybdenum	
Phosphorus	Magnesium, Sodium, Strontium
Potassium	Rubidium
Selenium	Thallium
Silicon	Hafnium, Zirconium
Tin	
Titanium	Niobium, Tantalum
Tungsten	
Uranium	

Soil texture

Topsoil texture recorded at each sample site shows that sandy-silt, silt and silty-clay textures predominate in urban soil. Silt-grade soil is associated with upland areas on the edge of the Basin whereas sandy-silt textures dominate brown-earth soil developed over the Old Red Sandstone, Inverclyde and Clackmannan Group sedimentary rocks, that underlie the centre of the Basin, and the area southwest of Glasgow. Clay-textured soil is reported in the River Kelvin valley to the north of Glasgow.

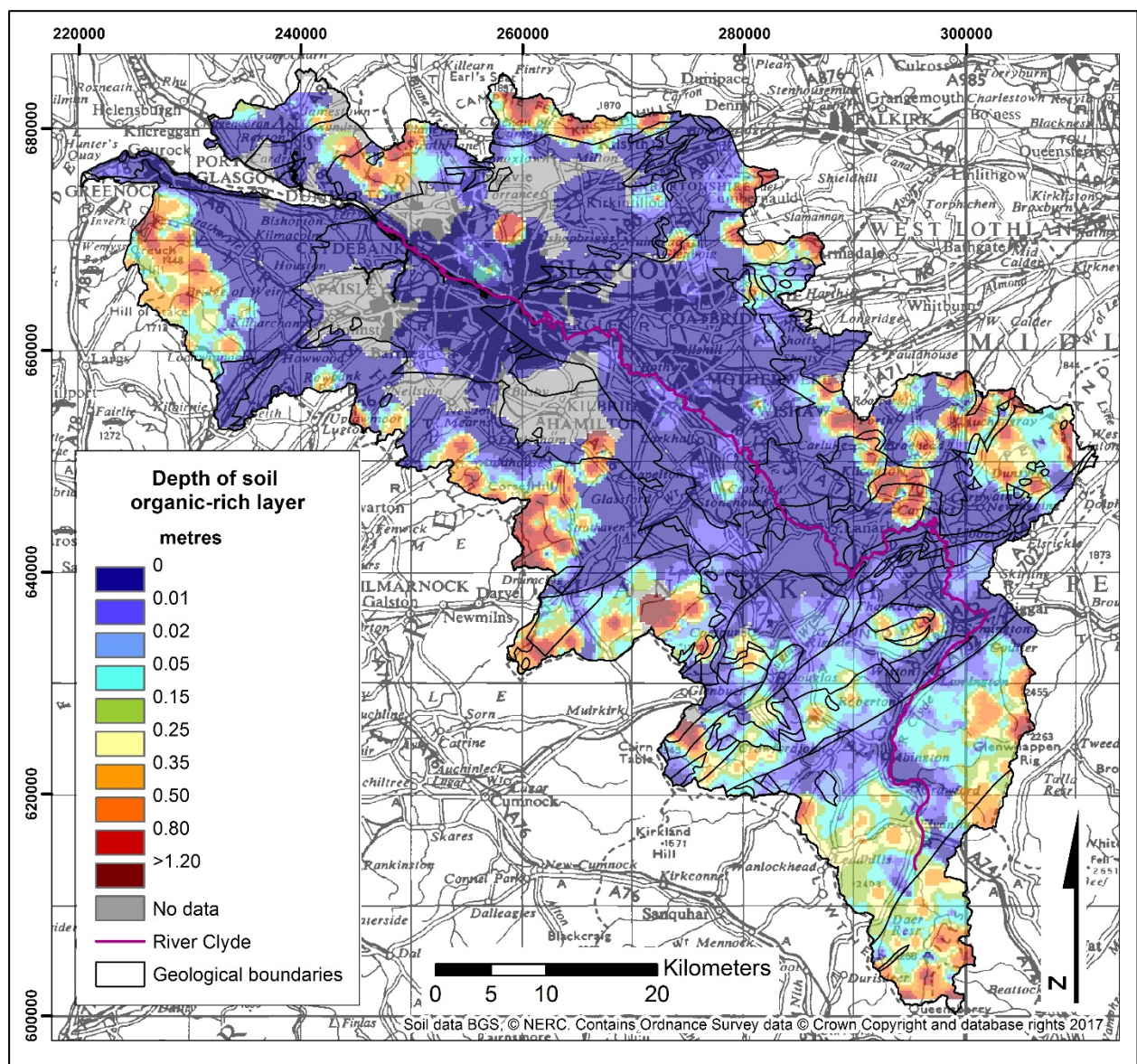


Depth of soil organic-rich layer

The DOL measurement was made at 2240 sampling locations forming part of the Clyde Basin soil survey. As the DOL methodology was not implemented until 2010, data are not available for the areas visited in the earlier Glasgow soil survey carried out in 2001–2002.

At 1776 locations, a well-defined dark-brown/black organic-rich layer was not present and the DOL measurement was recorded as zero. At 55 of the sampling sites the DOL was reported to be greater than 1.2 m, the maximum depth measureable using a 1.2 m soil auger.

The DOL data were used to produce an interpolated map to show the spatial variability of the depth of organic-rich soil across the Basin. Greatest depths are generally observed on the upland peripheries of the Basin and corresponded to areas of peat (Figure 7). Greater depths in the north of the Glasgow urban area are associated with low-lying lochs, where again peat accumulates. The DOL measurement shows a strong spatial coincidence with soil LOI as expected, as LOI can be used as an indicator of soil organic matter content. Interestingly, outside the areas of peat/upland soil, a noticeable organic-rich layer was absent in most soil types across the Basin.

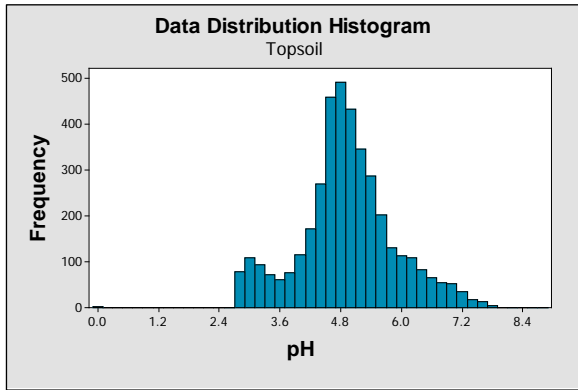
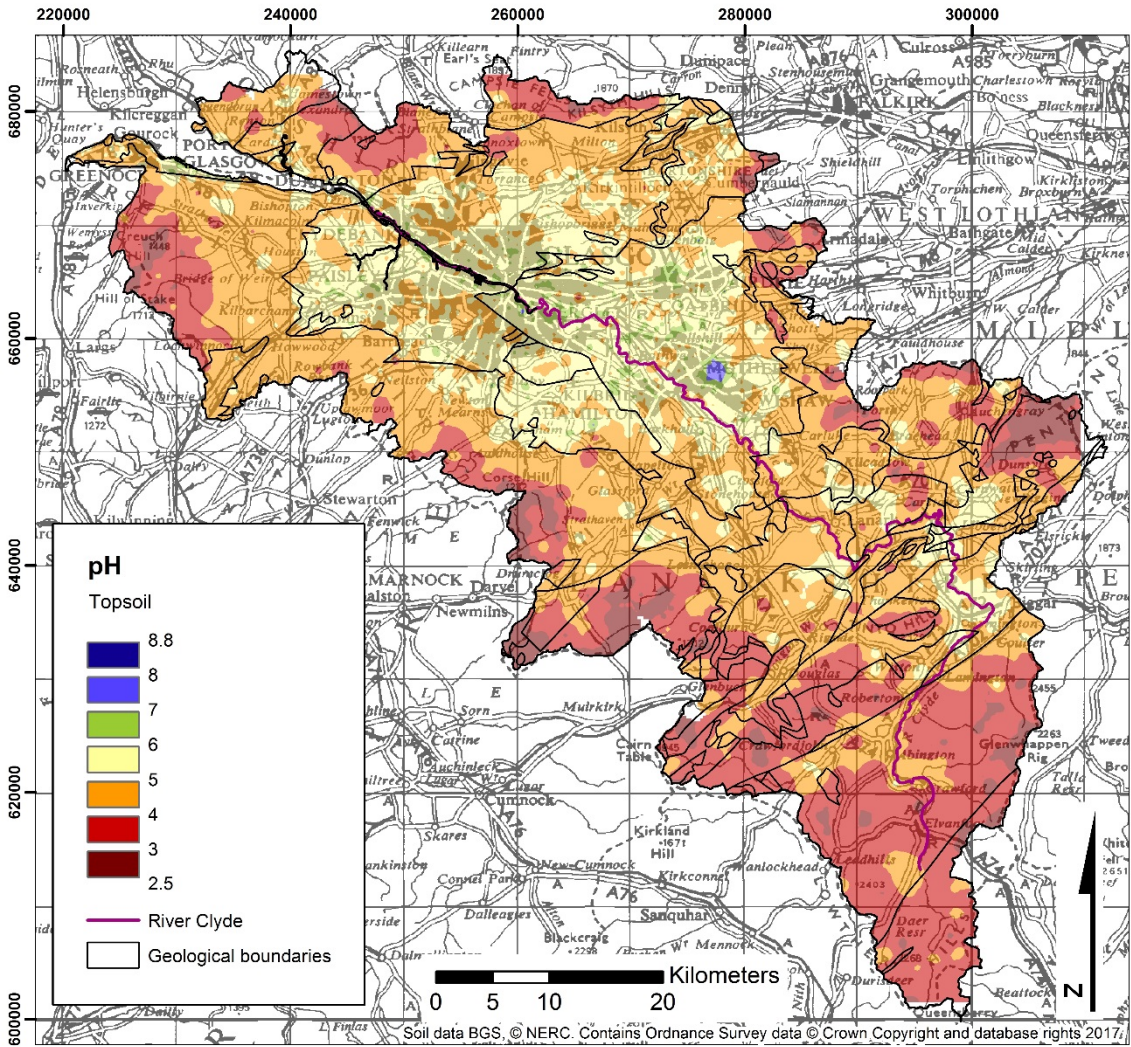


Soil pH

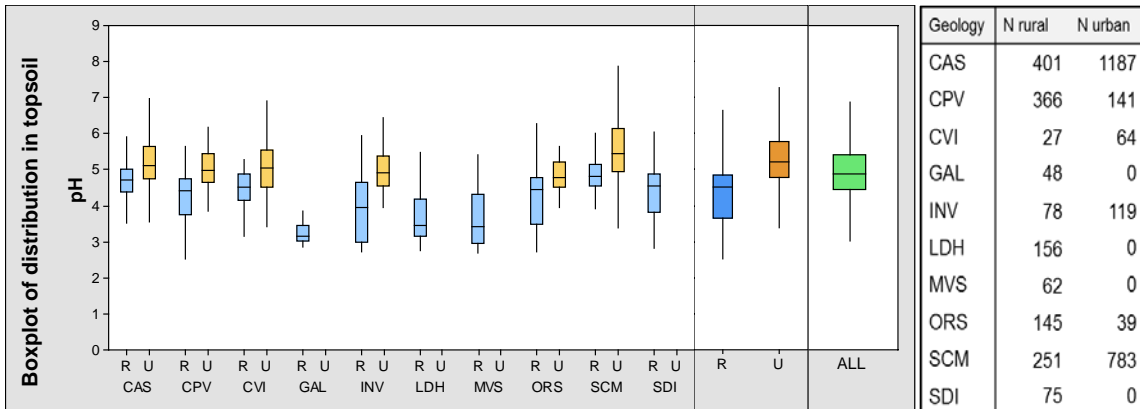
Topsoil (5 – 20 cm) and deeper soil (35 – 50 cm) pH values show similar ranges in the Clyde Basin of 2.53 – 8.79 and 2.67 – 8.88 respectively.

In both topsoil and deeper soil, pH values are generally acid (< pH 7) and lowest pH values (< pH 4) are controlled by the distribution of organic-rich/peaty soil in the upland areas on the periphery of the Basin. These are typical values for peat soil types due to the increased presence of humic acids (McBride, 1994) and are similar to results reported for Scottish topsoil (Paterson, 2011). Topsoil and deeper soil developed over the Clackmannan, Strathclyde and Scottish Coal Measure Group strata in the north of the area have marginally higher pH values (5 – 6), which may reflect the influence of calcareous sandstone and limestone parent materials.

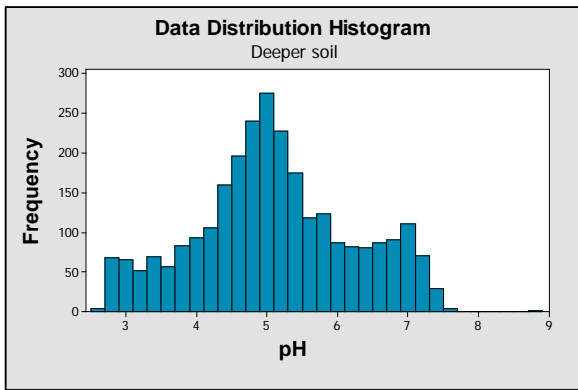
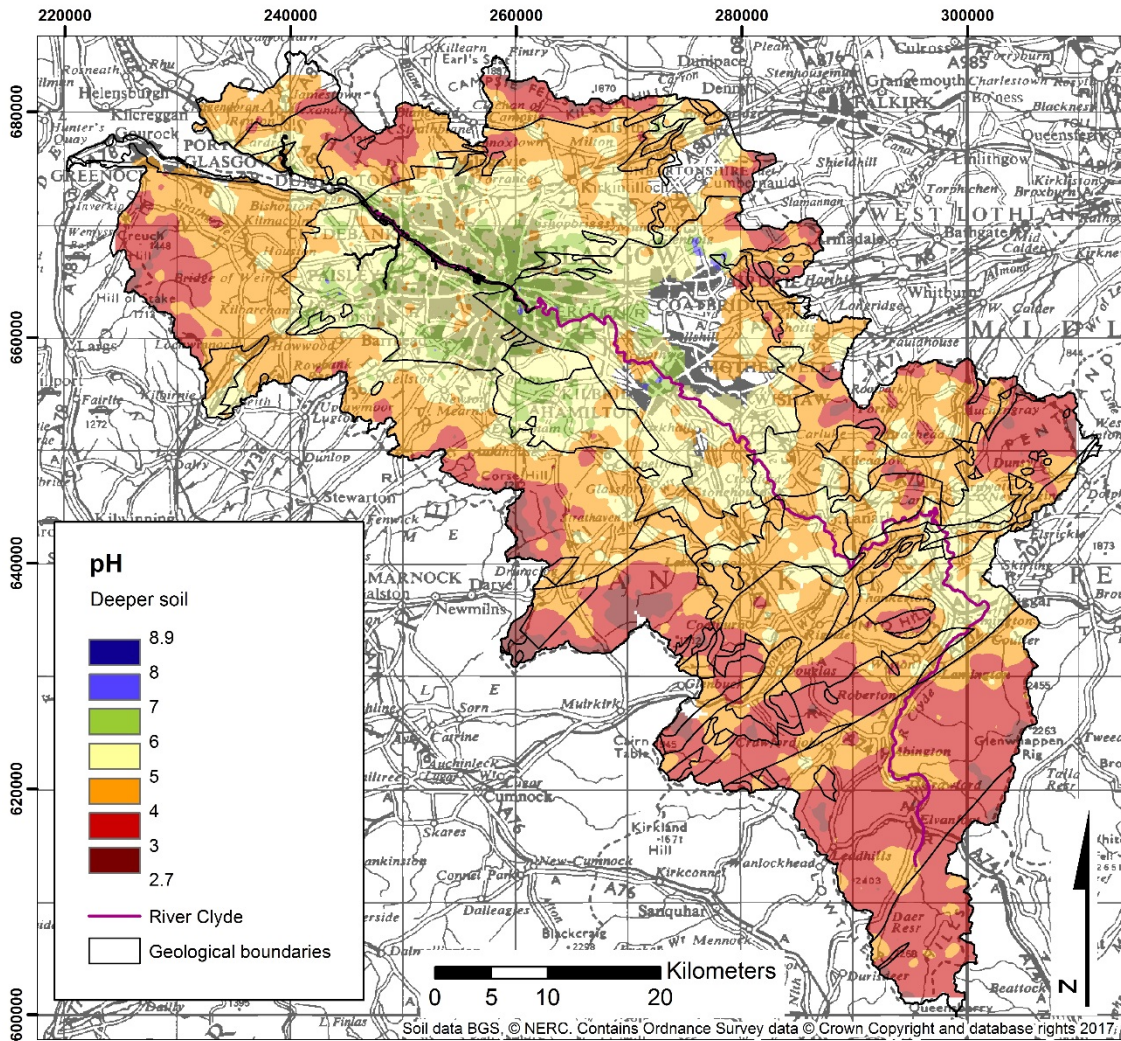
Topsoil and deeper soil pH values in the urban areas are generally between 5 and 7 and are typically higher than in rural soil. The former Ravenscraig Steelworks in Motherwell (Location 26, Figure 3) in the east of the area is characterised by topsoil pH values > 7. In addition to the presence of building rubble at this cleared site, these values almost certainly reflect the use of lime in the steel making process resulting in calcareous furnace slag noted in soil samples at this location, which was the largest steel mill in Western Europe until it closed in 1992. Higher soil pH in urban areas relative to rural soil is indicative of the presence of building rubble, slag and artificial ground materials in city soil, which are generally calcareous in nature. Similar relationships have been noted previously in Glasgow and other cities and is a typical characteristic of many urban environments (Fordyce et al., 2005, 2012; Birke et al., 2011).



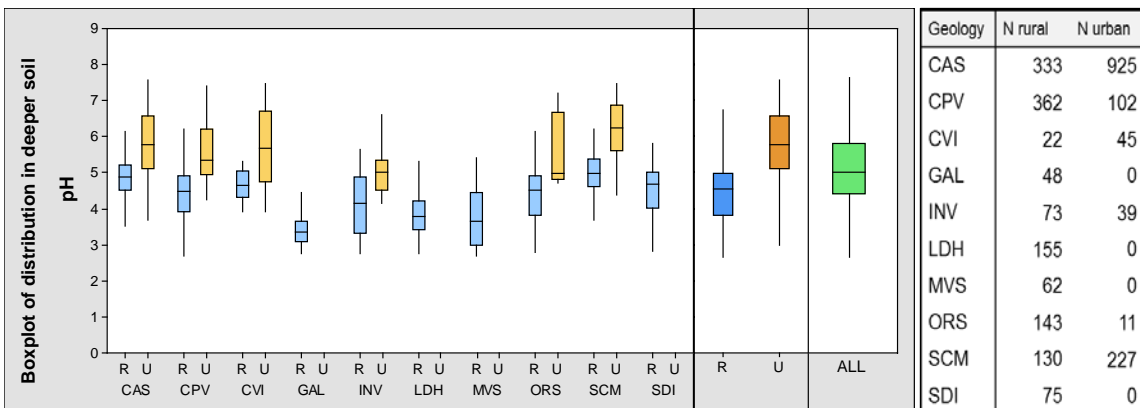
Statistics	pH: (topsoil)		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	3.39	2.53	2.53
Maximum	8.79	7.47	8.79
Standard Deviation	0.79	0.83	0.95
Mean	5.33	4.32	4.92
Median	5.20	4.51	4.88
World soil median			6.3



R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks



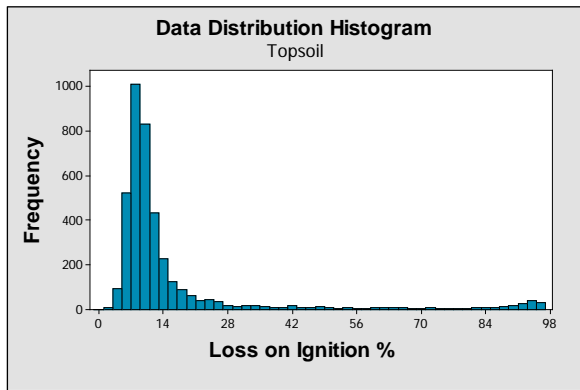
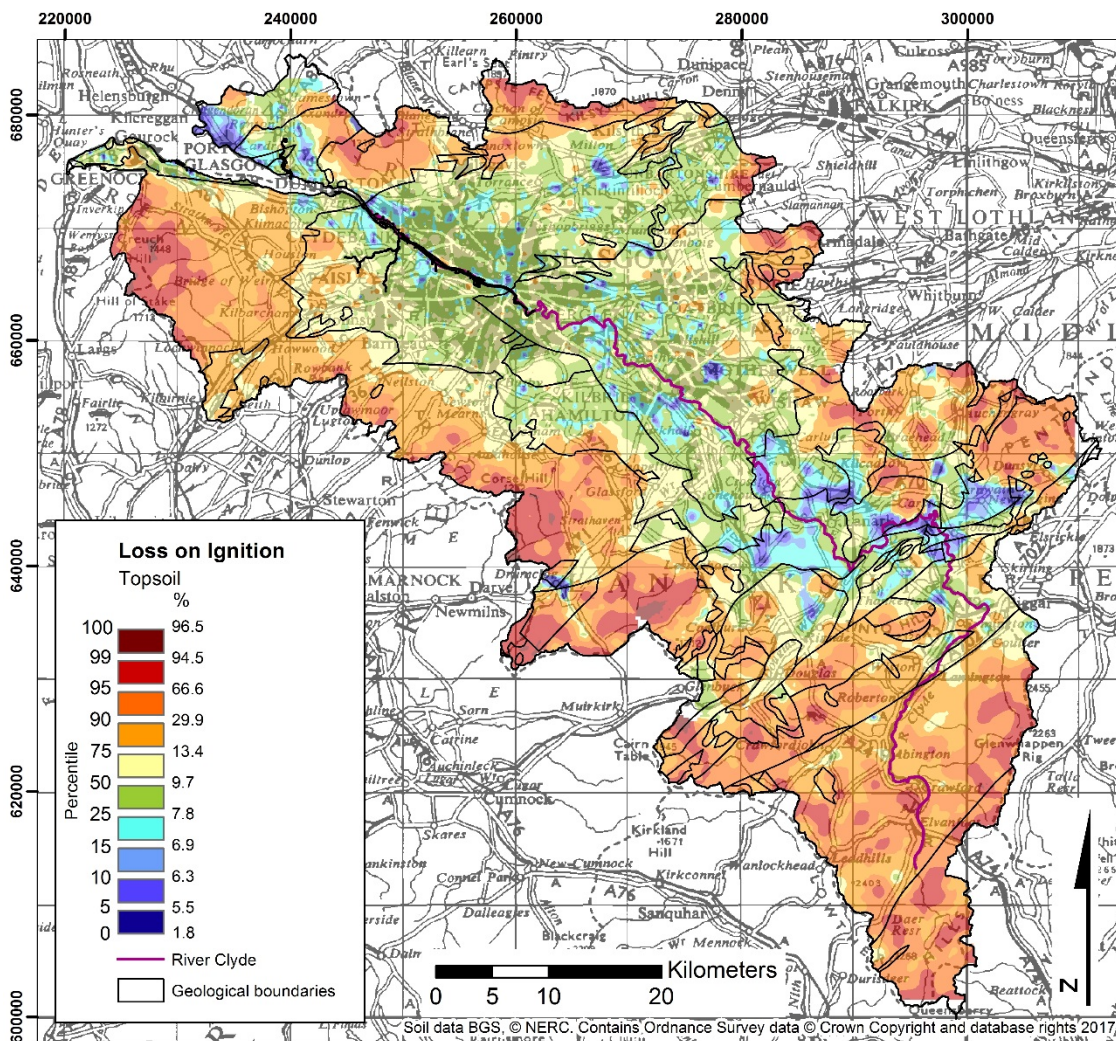
Statistics	pH (deeper soil)		
	Urban	Rural	All
No. of samples	1349	1404	2753
Minimum	2.99	2.67	2.67
Maximum	8.88	7.63	8.88
Standard Deviation	0.90	0.84	1.12
Mean	5.81	4.40	5.09
Median	5.78	4.55	5.03
World soil median			6.3



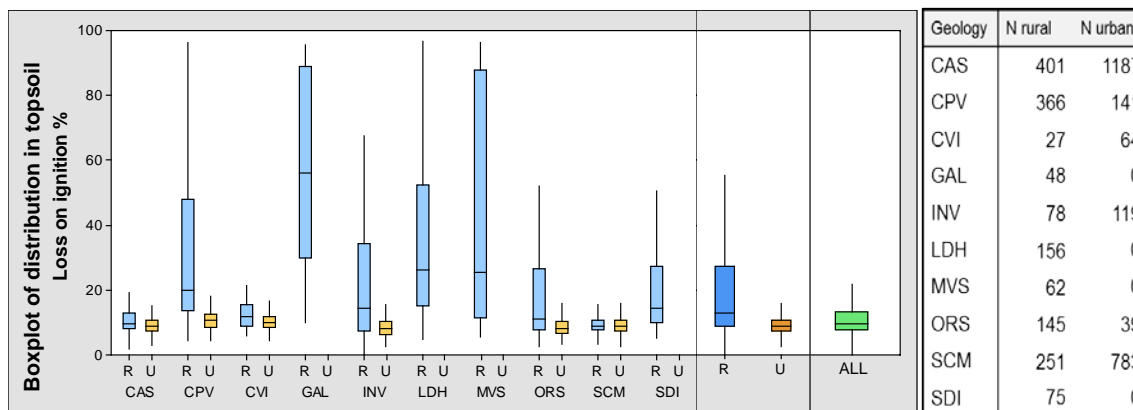
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Loss on ignition (LOI)

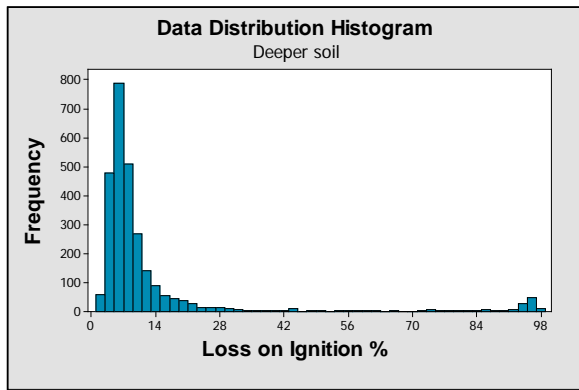
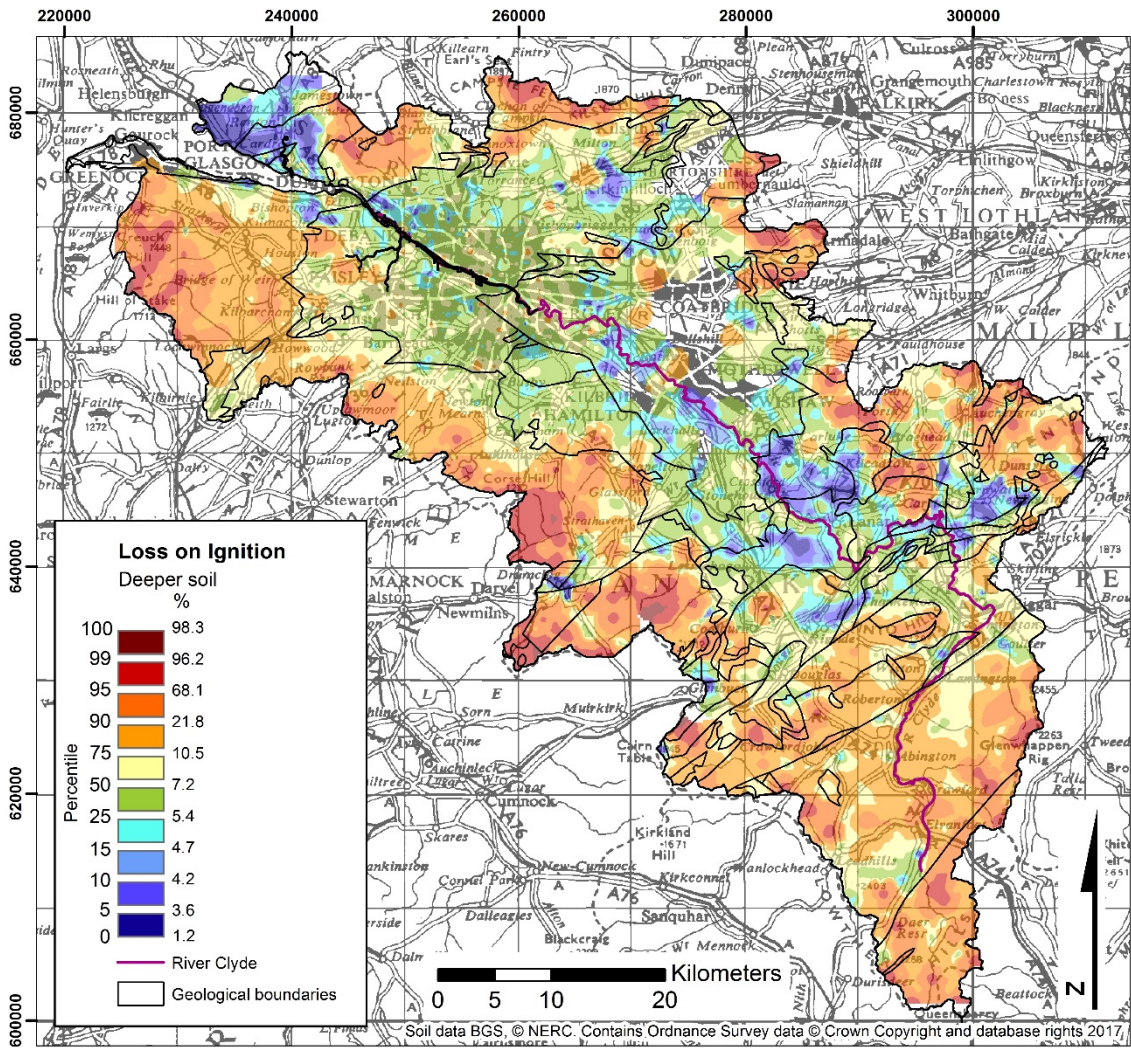
The maps of LOI distribution in topsoil (5 – 20 cm) and deeper soil (35 – 50 cm) are a general indication of soil organic matter content. They reveal that LOI ranges in topsoil (1.8 – 96.5 %) and deeper soil (1.2 – 98.3 %) are similar in the Clyde Basin. The maps show also that organic-rich soil is associated with the upland areas on the periphery of the Clyde Basin over the Southern Uplands, Renfrew Hills and Kilpatrick–Campsie Hills, as well as moorlands in the east of the Basin, as expected. The greywacke rock types underlying much of the Southern Uplands in the south of the area and volcanic rocks of the Renfrew and Kilpatrick–Campsie Hills in the north of the area are harder than other rock types in the region, forming high ground subject to greater rainfall and cooler temperatures. This favours the development of organic-rich and peat soil in these areas (Bown, 1985). By contrast, sandier alluvial soil in the River Clyde Valley has lower organic matter content. Loss on ignition is generally higher in rural than urban soil, as a result of the greater spatial extent of peaty soil in the rural environment.



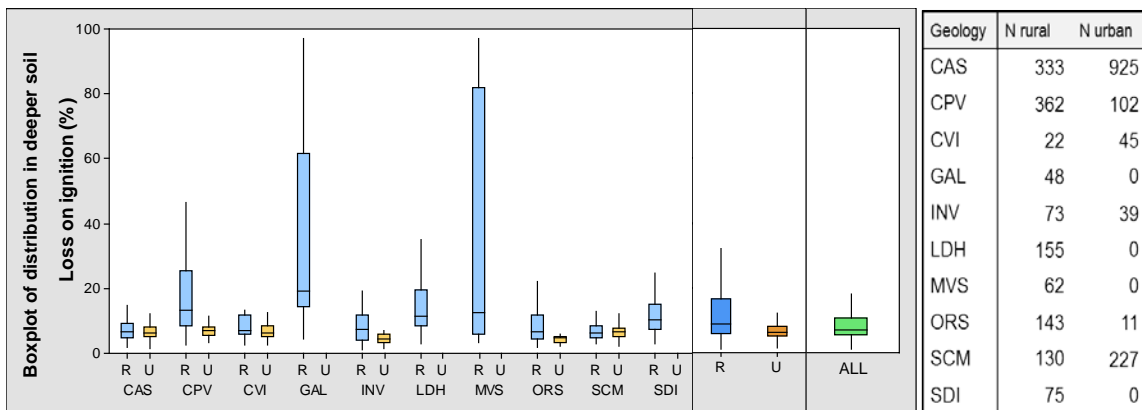
Statistics	Loss on Ignition % (topsoil)		
	Urban	Rural	All
No. of samples	2333	1610	3942
Minimum	2.4	1.8	1.8
Maximum	64.3	96.5	96.5
Standard Deviation	3.8	26.4	18.8
Mean	9.5	25.3	15.9
Median	8.9	12.8	9.7
World soil median			n/a



R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks



Statistics	Loss on Ignition % (deeper soil)		
	Urban	Rural	All
No. of samples	1349	1404	2753
Minimum	1.5	1.2	1.2
Maximum	42.9	98.3	98.3
Standard Deviation	3.5	25.7	19.5
Mean	7.0	19.2	13.3
Median	6.4	8.9	7.2
World soil median	n/a		



R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Aluminium

Al

(Concentrations are expressed in Al₂O₃ wt%)

Environmental behaviour

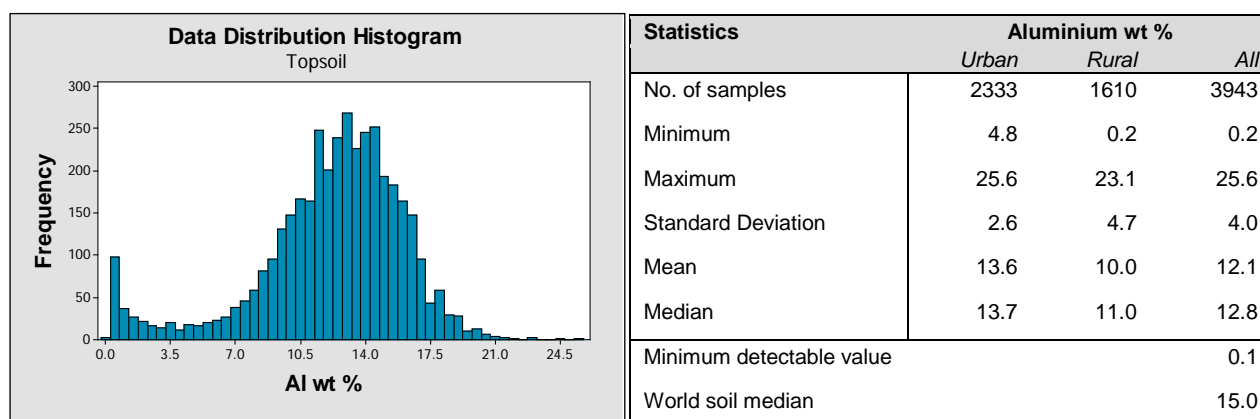
Aluminium (Al) is the most abundant metallic element in the Earth's crust (constituting approximately 8 %). It has one oxidation state (Al³⁺) and is not found in native form, rather it is a constituent of several primary minerals including sillimanite (Al₂SiO₅), corundum (Al₂O₃) and gibbsite (Al(OH)₃). It is also a major component of many rock-forming minerals such as feldspar, mica, amphibole and pyroxene, and is present in clay minerals, such as kaolinite (Al₂Si₂O₅(OH)₄) (Ildefonse, 1999; WHO, 1997). Aluminium is a major constituent of most rock types with contents varying in igneous rocks from 4 wt% (mafic type) to 25 wt% (felsic type). With the exception of shales (15 wt%), sedimentary rocks generally contain < 8 wt% Al₂O₃, whereas metamorphic rocks show a wide range in concentration 1 – 28 wt% (Wedepohl, 1978). As such, Al-bearing minerals are ubiquitous in most soil. Aluminium has poor solubility and low mobility under most environmental conditions. However, below pH 5.5 its solubility increases, as it is released from aluminosilicate minerals in rocks and soil. Aqueous-Al may also be mobilised in anionic form under strongly alkaline conditions above pH 8.0 (Shiller and Frilot, 1996). Under moderate weathering, Al forms intermediate aluminosilicates such as smectite and kaolinite clay minerals. Hence, Al tends to be retained in the soil and contributes to soil acidity. However, under highly reducing conditions in gley soil, it may be leached out in solution (Strawn et al., 2015). Anthropogenic sources of Al include aluminium smelters, cement plants, sewage and anthropogenic dust (Reimann and Caritat, 1998), but natural sources are normally dominant. Aluminium is considered potentially harmful to most organisms. Dissolved cationic Al can be toxic to aquatic life (WHO, 1997).

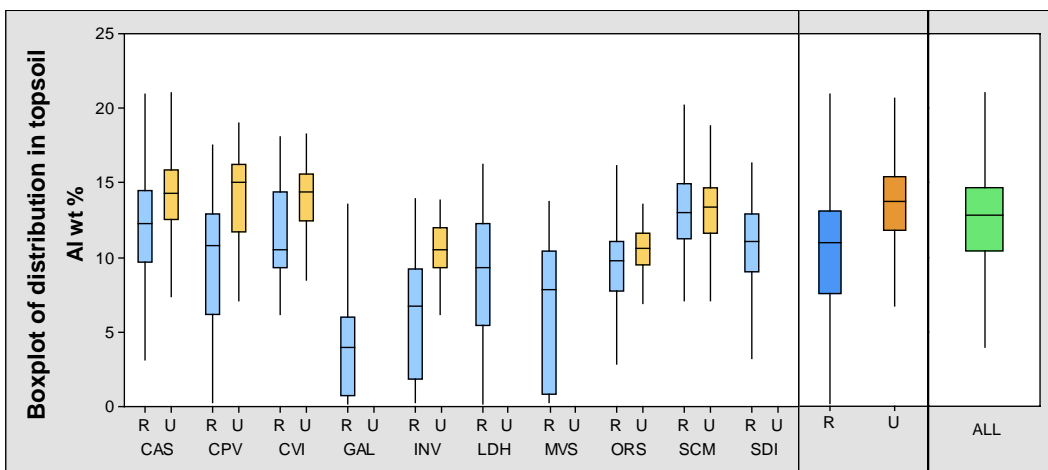
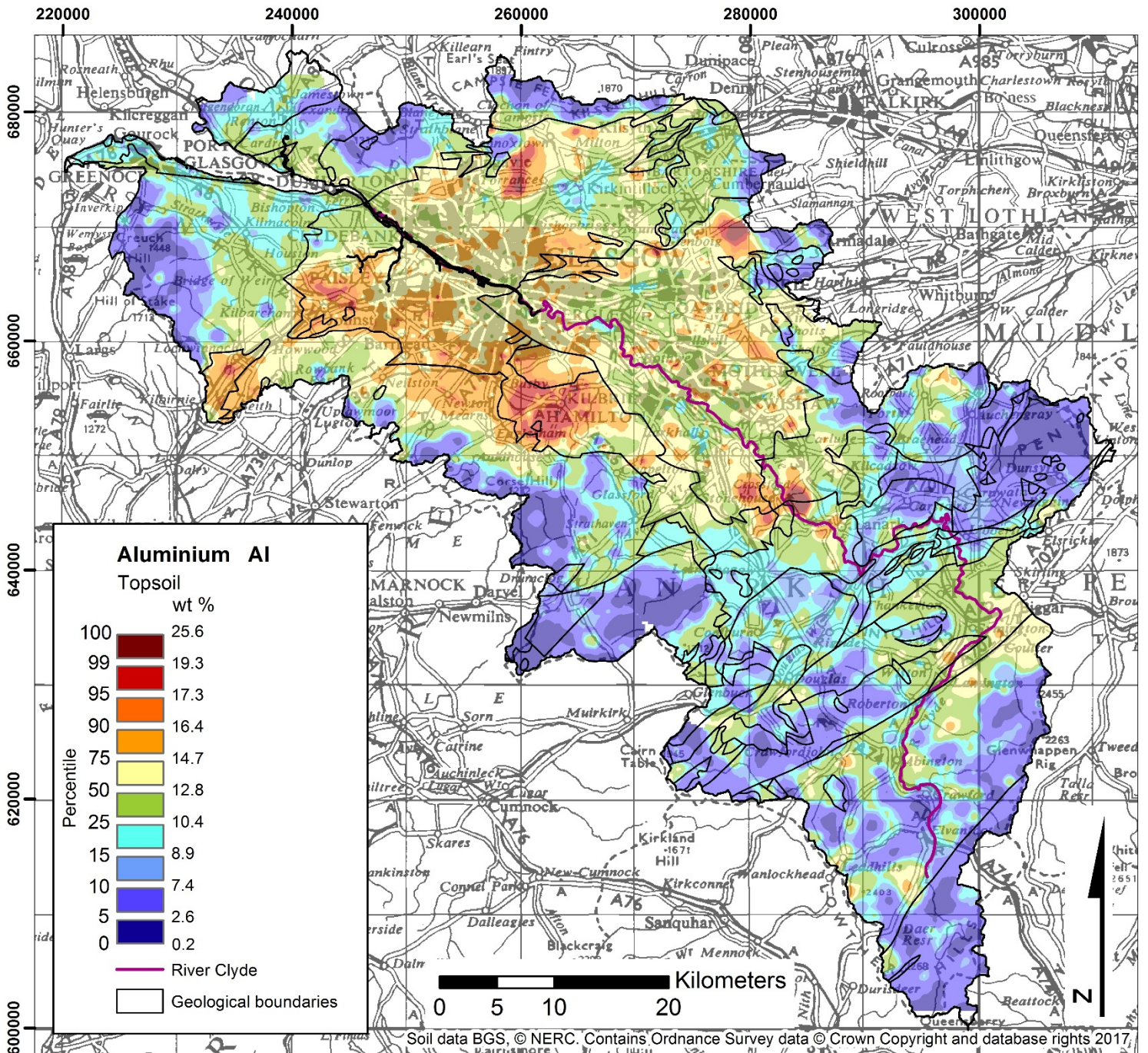
Clyde Basin topsoil

Topsoil Al concentrations range from 0.2 to 25.6 wt% in the area. In the rural parts of the Clyde Basin, the highest concentrations of Al are associated with areas of clayey soil and non-calcareous gley soil overlying the Carboniferous Clackmannan and Strathclyde Groups and Scottish Coal Measures Group in the north of the area. This is likely to relate to the argillaceous lithologies such as clay-rich mudstones and siltstone horizons, which are more abundant in these successions compared to the other, more siliclastic, sedimentary units, which crop out in the region. Lower levels (<10.4 wt%) over mature sandstone bedrock, particularly the Old Red Sandstone Supergroup and Inverclyde Group, reflect the relatively low volumes of feldspar, mica and clays in the soil parent material. A noticeable anomaly around Crossford, south of Carluke in the east of the area (see Figure 3 for locations) is attributed to a number of sites where clay soil was sampled. To a lesser extent, higher Al values (> 12.8 wt%) are observed also in brown-earth soil overlying the Clyde Plateau Volcanic Formation (CPV) and the Silurian to Devonian igneous rocks in the area. This is probably associated with feldspar abundance. However, topsoil Al concentrations are low in organic-rich upland soil over the same units, reflecting the fact that Al tends to be present in the mineral, rather than the organic component of soil. The influence of overlying peat lowers the average topsoil Al concentrations measured over these units.

Similarly, marginally higher concentrations of Al were measured in mineral topsoil overlying the greywackes of the Gala Group and Leadhills Supergroup in the south of the area, than those in peaty soil over the same bedrock. The difference in topsoil Al values between these two units is probably related to greater feldspar and/or clay content in the greywackes of the Leadhills Supergroup compared to the more quartz-rich Gala Group (Stone et al., 2012), and greater coverage of peat over the Gala Group. On average (median values), topsoil-Al concentrations are elevated in urban areas over all bedrock types, suggesting that the presence of artificial ground, building rubble and diffuse anthropogenic pollution has affected its distribution in this environment. An anomaly is seen at Greengairs landfill site in the east of the area (Location 22, Figure 3) (which is lined with clay) where Al was measured at 21.4 wt% in one sample. It is speculated that the relatively higher values in topsoil of the new town of East Kilbride to the south of Glasgow, may reflect glacial reworking of clay material in the underlying till deposits.

The distribution of topsoil-Al in the region is broadly similar to those of gallium (Ga) and scandium (Sc) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Antimony

Sb

Environmental behaviour

Antimony (Sb) is a low-abundance chalcophile element, which forms rare minerals including stibnite (Sb_2S_3), a variety of sulphosalts, valentinite (Sb_2O_3) and kermesite ($2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$). However, it is more usually present at trace levels in minerals such as ilmenite, Mg-olivine, galena, sphalerite and pyrite. It is thus commonly enriched in areas of sulphide mineralisation. It has three main oxidation states of +3, -3, and +5. It has an average crustal abundance of 0.5 mg kg^{-1} and its concentration in mafic to felsic igneous rocks ranges from < 0.1 to 7.8 mg kg^{-1} respectively (Lueth, 1999). Fine-grained, organic-rich and black shale sedimentary rocks are all typically enriched in the element ($> 1 \text{ mg kg}^{-1}$) relative to other sedimentary rock types (Mielke, 1979). In most soil, Sb is present in trace amounts ($< 1 \text{ mg kg}^{-1}$) (Kabata-Pendias, 2001). It adsorbs strongly onto soil organic matter and Fe oxides, especially at low pH. Under neutral–alkaline pH conditions, it adsorbs onto clay minerals also (Boyle and Jonasson, 1984). As such, Sb displays low environmental mobility, especially under reducing conditions (McBride, 1994).

Anthropogenic sources of antimony include metal smelting, coal combustion and car exhaust fumes (Reimann and Caritat, 1998). It can also be dispersed due to metalliferous mining and in urban waste. Its low natural abundance in most circumstances can make it a useful indicator of industrial pollution.

Antimony is a non-essential element for health and has no known function in living organisms. It can be toxic at high concentrations, Sb^{3+} compounds being more toxic than Sb^{5+} compounds, but such exposures are rare in most natural settings (Mertz, 1987).

Clyde Basin topsoil

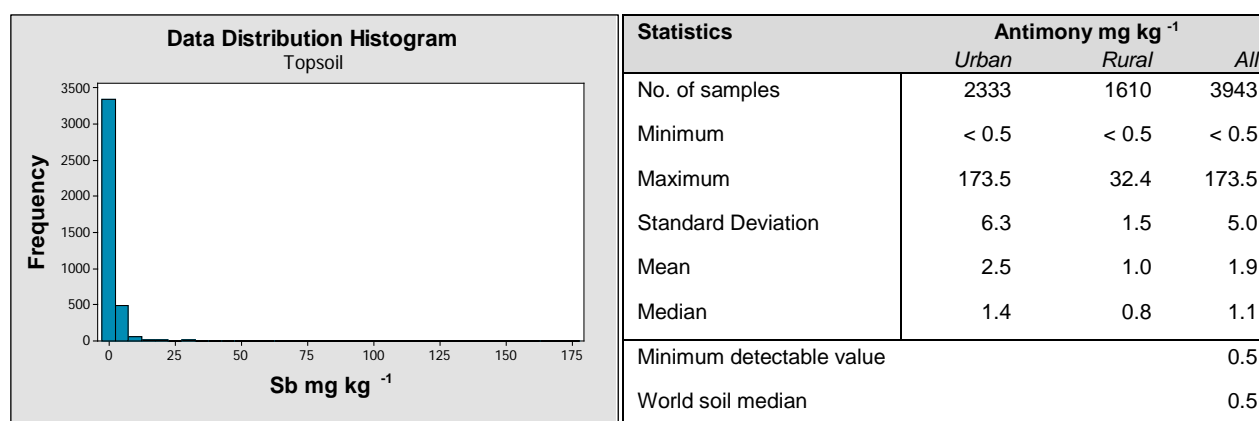
Concentrations of Sb in topsoil range from < 0.5 to 173.5 mg kg^{-1} in the area. In rural parts of the Clyde Basin, the distribution of topsoil Sb is broadly spatially correlated with LOI reflecting an organic matter association. Since Sb can bind to organic matter in soil, concentrations of the element are generally higher ($> 1.1 \text{ mg kg}^{-1}$) in peaty soil in the upland areas on the periphery of the Basin, than over the rest of the rural environment.

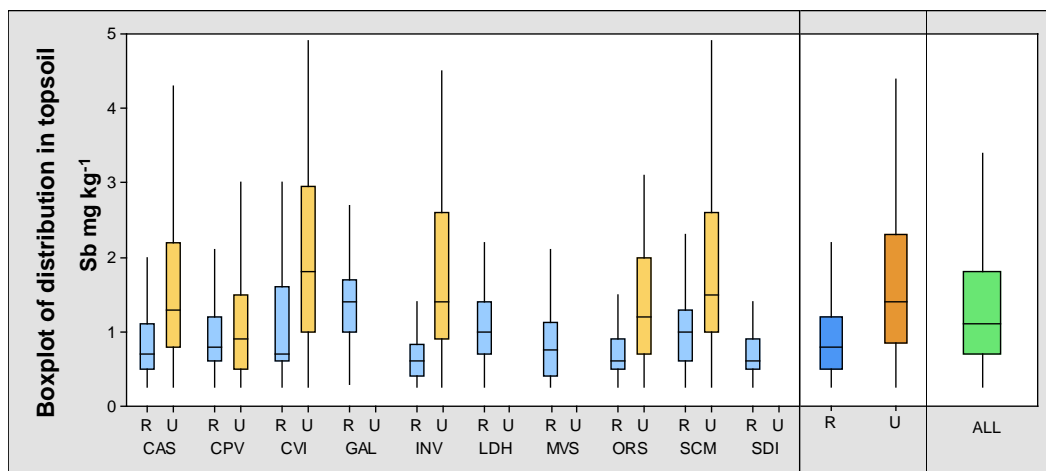
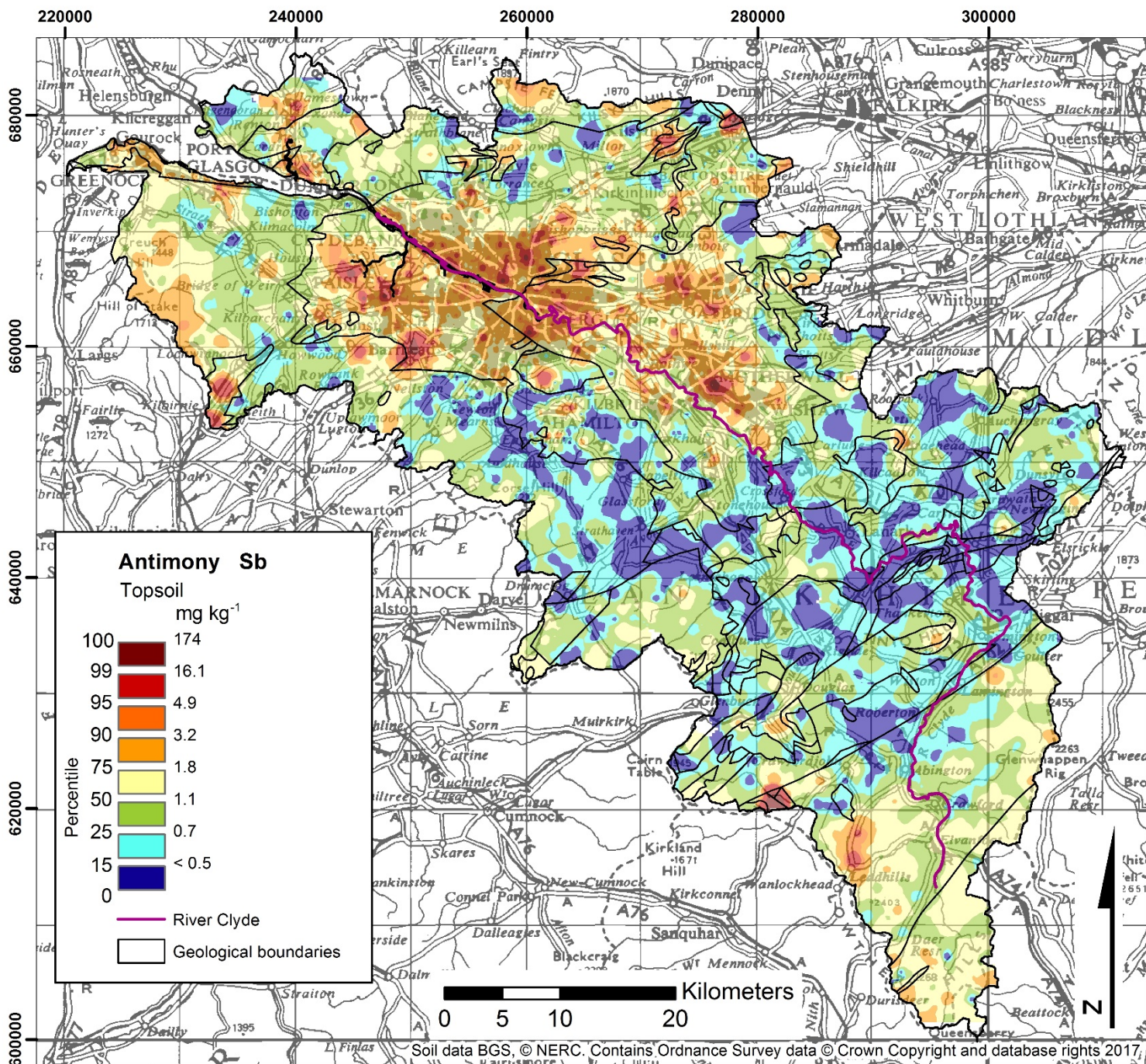
In the south of the area, a high Sb concentration of 32.4 mg kg^{-1} is reported in low pH peaty topsoil to the west of Snar Water (Location 8, Figure 3). Indeed, the extensive peat cover over the Gala Group and Leadhills Supergroup, is likely to contribute to the higher average Sb values measured in soil samples collected over these bedrock units, rather than a geological factor.

Across the region, there is little variation in Sb concentration that can be attributed to the fundamental composition of the bedrock. However, in the south of the area, a high Sb anomaly ($> 1.8 \text{ mg kg}^{-1}$) at Leadhills (Location 11, Figure 3) reflects sulphide mineralisation.

Elevated topsoil concentrations of Sb ($> 1.8 \text{ mg kg}^{-1}$) are widely dispersed over the urban environment regardless of the soil parent material type, indicating the significant influence of diffuse anthropogenic pollution such as fossil fuel combustion and urban waste on soil chemistry. Specific Sb anomalies are associated with topsoil collected from former and current industrial sites. These include the former steel works at Ravenscraig in the east of the area (Location 26, Figure 3); the former metal processing centres of the East End of Glasgow and Airdrie–Coatbridge (in the east of the area) and coach/railway works north of Glasgow city centre.

Elevated Sb concentrations are observed also in samples collected at the former Faskine Iron Pit in Calderbank, Airdrie (Location 24, Figure 3) in the east of the area, and the former ironstone and coal workings and iron foundry at Lochwinnoch and Beith to the southwest of Glasgow (see Figure 3 for locations).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

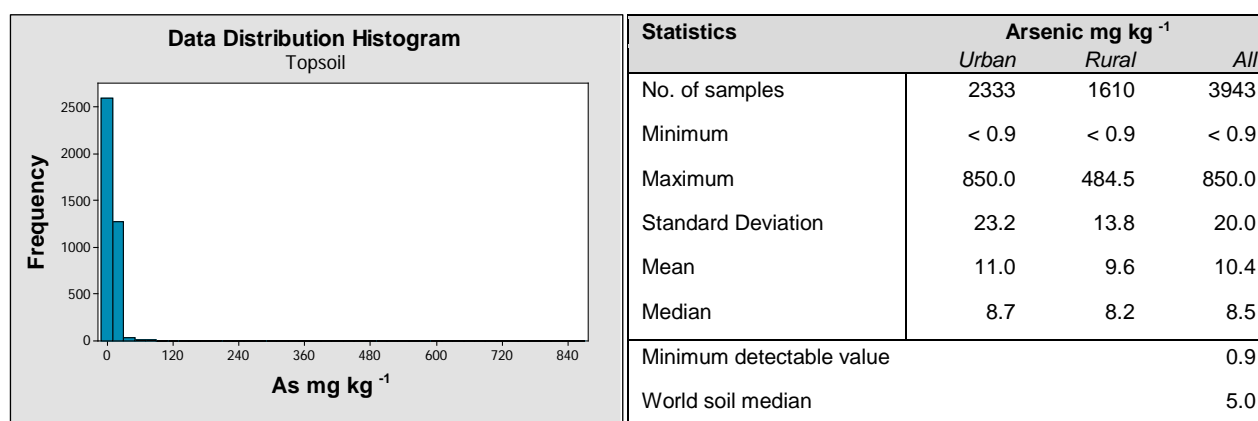
Environmental behaviour

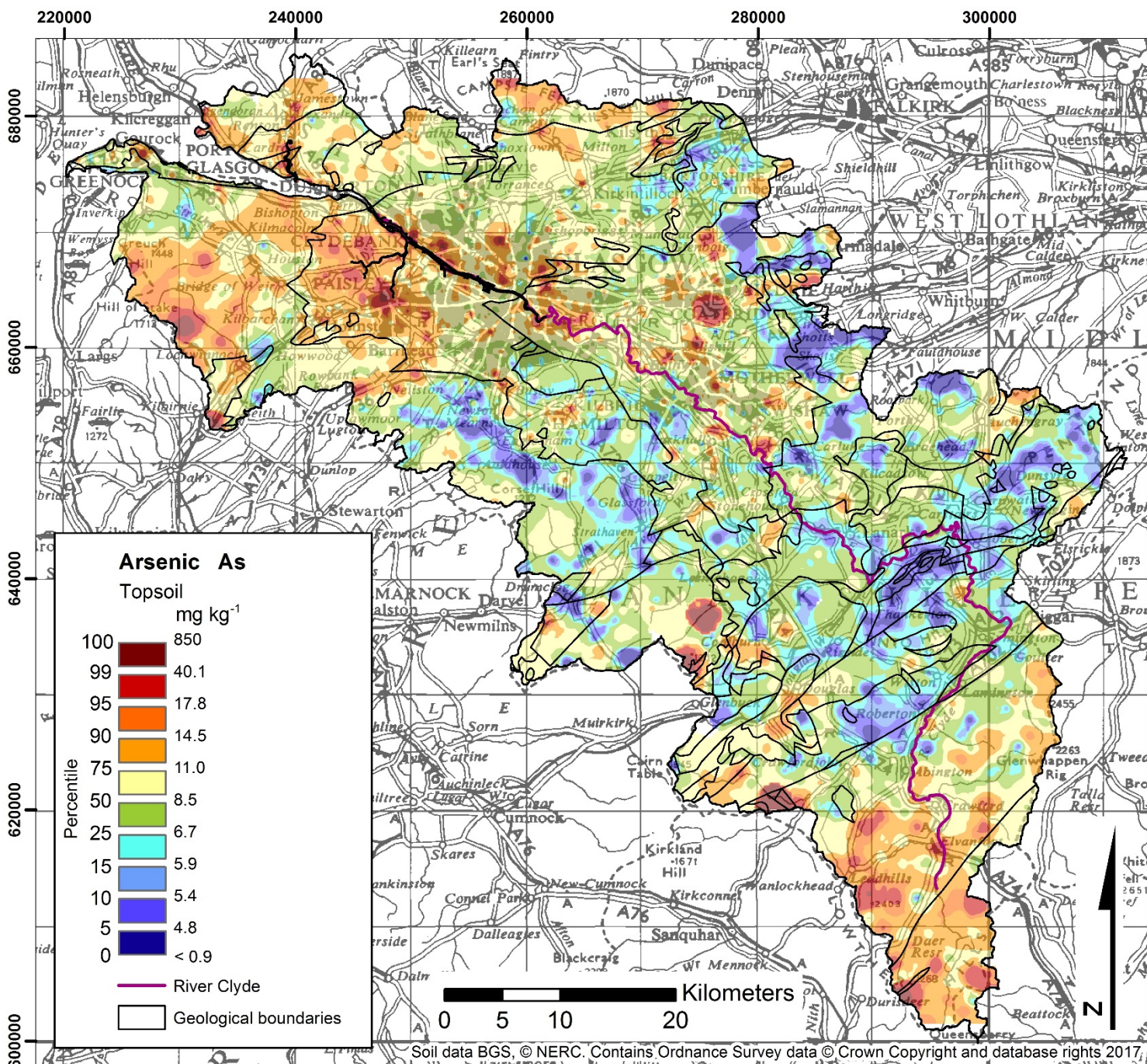
Arsenic (As) has three main oxidation states of -3, +3 and +5 and is a chalcophile element forming several minerals including arsenopyrite (FeSAs), realgar (AsS) and orpiment (As₂S₃), but is more widely present as an accessory element in other sulphide minerals such as pyrite, galena and sphalerite. It has an average crustal abundance of 1.5 mg kg⁻¹ and concentrations range from 1.0 to 10 mg kg⁻¹ in igneous and metamorphic rocks. In sedimentary rocks, highest concentrations (20 – 200 mg kg⁻¹) are generally found in phosphates, coal, shale and ironstone deposits (Plant et al., 2014). The mobility of As is strongly governed by the oxidation state. It is released from arsenopyrite and other sulphides, due to oxidation, which may be microbially mediated (Plant et al., 2014). Arsenic normally has relatively low mobility in soil because of strong adsorption by clays, organic matter and Fe and Mn oxides, particularly in low pH environments (McBride, 1994; Wenzell, 2013). Arsenic can be released from oxide minerals and clays at high pH and upon reduction of soil Fe oxides as a result of flooding or burial (Plant et al., 2014). Anthropogenic sources of As include coal combustion, sulphidic ore roasting and smelting, and pig and poultry sewage (Reimann and Caritat, 1998). Arsenic is generally toxic to most organisms. The toxicity depends on its speciation (As⁵⁺ compounds are less toxic than As³⁺). Chronic exposure increases the risk of cancer and skin pigmentation; however, excess exposure from soil is rare in most natural settings (WHO, 1996).

Clyde Basin topsoil

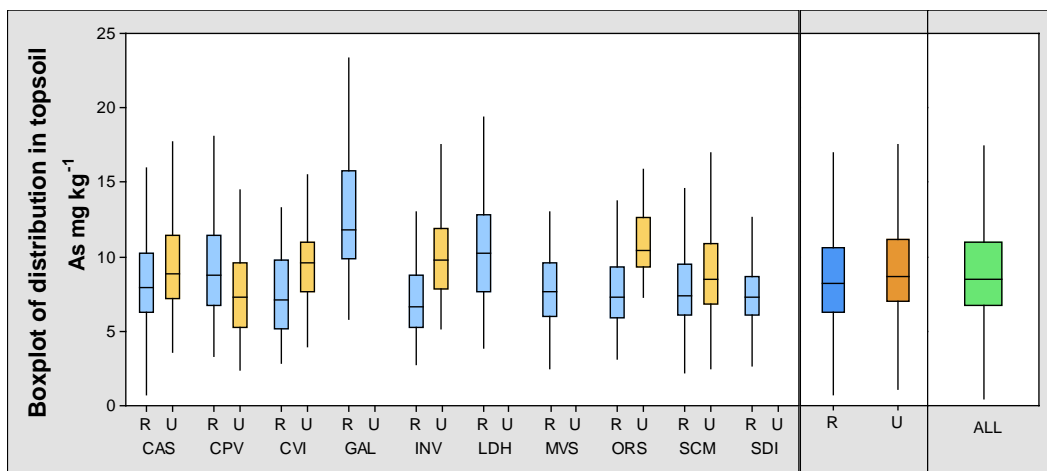
Topsoil As concentrations range from < 0.9 to 850 mg kg⁻¹ in the area. In the rural Clyde Basin, higher As concentrations (> 14.5 mg kg⁻¹) are associated with peaty and upland organic-rich topsoil in the Southern Uplands over the Gala Group and Leadhills Supergroup rock types; and in the Renfrew, Campsie and Kilpatrick Hills around Glasgow, underlain by the Clyde Plateau Volcanic Formation. This may reflect greater atmospheric deposition of As in these higher-rainfall upland areas and trapping of As in these soil types, as the element is readily sorbed to organic matter (Wenzell, 2013). In the south of the region, concentrations of As in rural soil are probably enhanced further by the presence of sulphide mineralisation around Leadhills; and in the Nutberry Hill area (Location 5, Figure 3). The As anomaly at Logan Water (Location 38, Figure 3) may relate to the nearby mineralisation at Nutberry Hill. Similarly, the higher values at Misty Law (Location 14, Figure 3) in the northwest of the region, are possibly influenced by mineralisation in the area. However, these environments, and those at Bishopton and Linwood Moss to the west of Glasgow, and an area south of Glespin (Locations 15, 17 and 44, Figure 3) are characterised by peaty low-pH soil, and the higher As values correspond to Fe and Mn anomalies. This suggests the influence of secondary processes and the mobilisation and then trapping of As in Fe and Mn oxides (Wenzell, 2013).

In the east of the area, elevated topsoil As concentrations (> 14.5 mg kg⁻¹) are associated with former extractive industries such as the oil shale works at Tarbrax (Location 32, Figure 3); the Newmains and Canderigg collieries near Wishaw (Locations 28 and 36, Figure 3) as well as collieries west of Greengairs (Location 22, Figure 3). High topsoil As concentrations in the urban area are located over former Mossend clay and brick pit in Motherwell (Location 25, Figure 3); former ironstone mines in Barrhead and the former Faskine Iron Pit in Calderbank (Location 24, Figure 3), which contains the highest urban topsoil As concentration (850 mg kg⁻¹). Similarly, higher concentrations of As in urban topsoil are associated with the former Ravenscraig steelworks site in Motherwell (Location 26, Figure 3); the former metal processing centres of Rutherglen (Location 19, Figure 3) and Beith; the former Victoria brick works in Paisley; the former Lambhill chemical/engineering and Royston chemical/railway works north of Glasgow city centre; with artificial ground at the former paper mills site at Moffat Mills in Airdrie (Location 23, Figure 3), as well as the shipbuilding centre of Clydebank. In addition to these specific associations, As concentrations are generally marginally elevated in urban compared to rural topsoil regardless of parent material, as a result of diffuse anthropogenic pollution. In summary, the distribution of topsoil-As in the rural environment is predominately controlled by the presence of organic-rich peaty soil and in the urban environment by current/former extractive and metal processing industries.





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Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Barium

Ba

Environmental behaviour

Barium (Ba) has one main oxidation state of +2, it is a lithophile element forming several minerals including barite (BaSO_4) and witherite (BaCO_3), but is widely distributed as an accessory element in such minerals as apatite, K-feldspars, micas and calcite. The principal Ba mineral, barite, is commonly associated with occurrences of metalliferous mineralisation. Barium has an average continental crustal abundance of 584 mg kg^{-1} (Wedepohl, 1995). Its concentrations in igneous rocks range from 0.4 mg kg^{-1} (ultramafic types) to 1600 mg kg^{-1} (syenite types); whereas in sedimentary rocks, highest Ba concentrations are associated with shale (580 mg kg^{-1}), with contents of approximately 10 mg kg^{-1} typical of carbonate and sandstone lithologies (Mielke, 1979).

Barium has low environmental mobility as once weathered from rocks, it is readily precipitated as insoluble carbonate and sulphate salts. Under temperate humid conditions, it is strongly adsorbed by clays and Fe and Mn oxides in soil. However, it may be remobilised in soil under different physico-chemical conditions (Kabata-Pendias, 2001).

Anthropogenic sources of Ba include lead mining, paper and paint manufacturing (Reimann and Caritat, 1998).

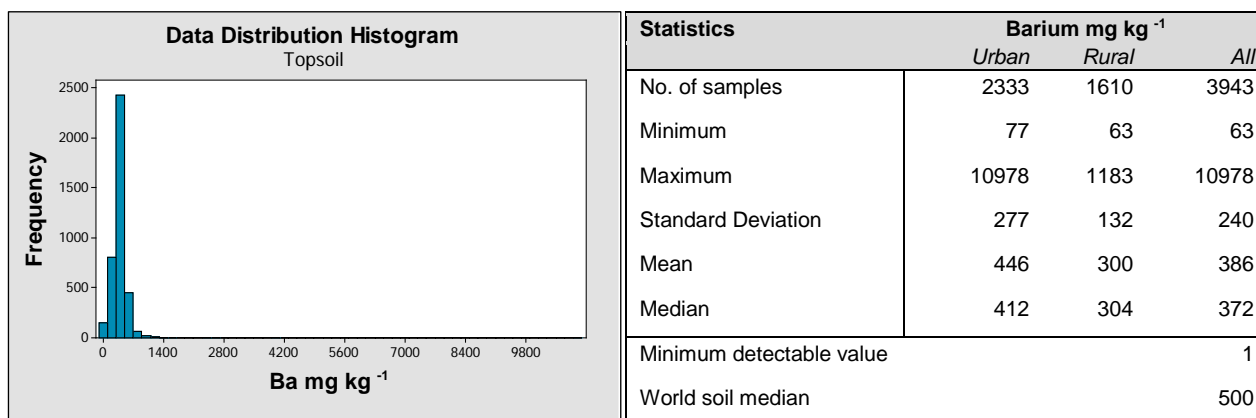
Barium has no known biological role. Its soluble compounds are toxic to humans, animals and plants. However, barium sulphate is insoluble, giving it a low toxicity, and health problems associated with natural environmental exposure are rare (Mertz, 1987).

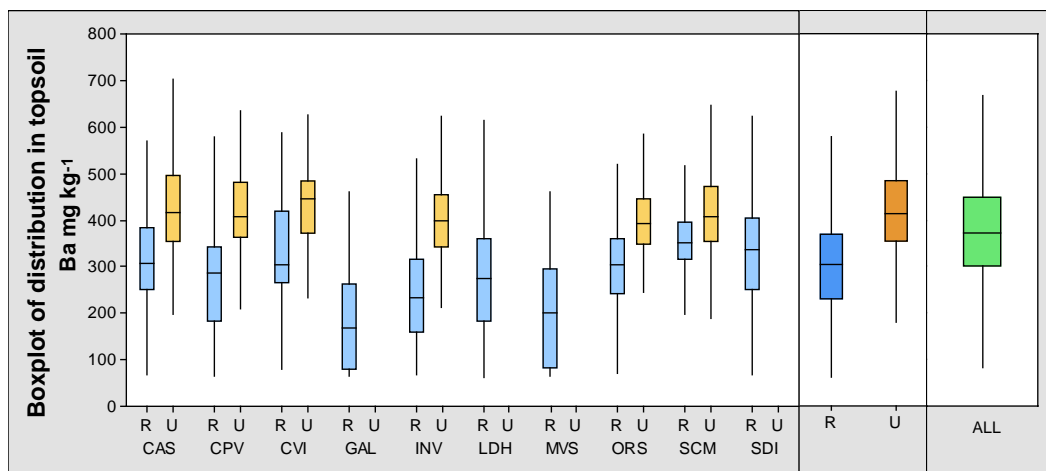
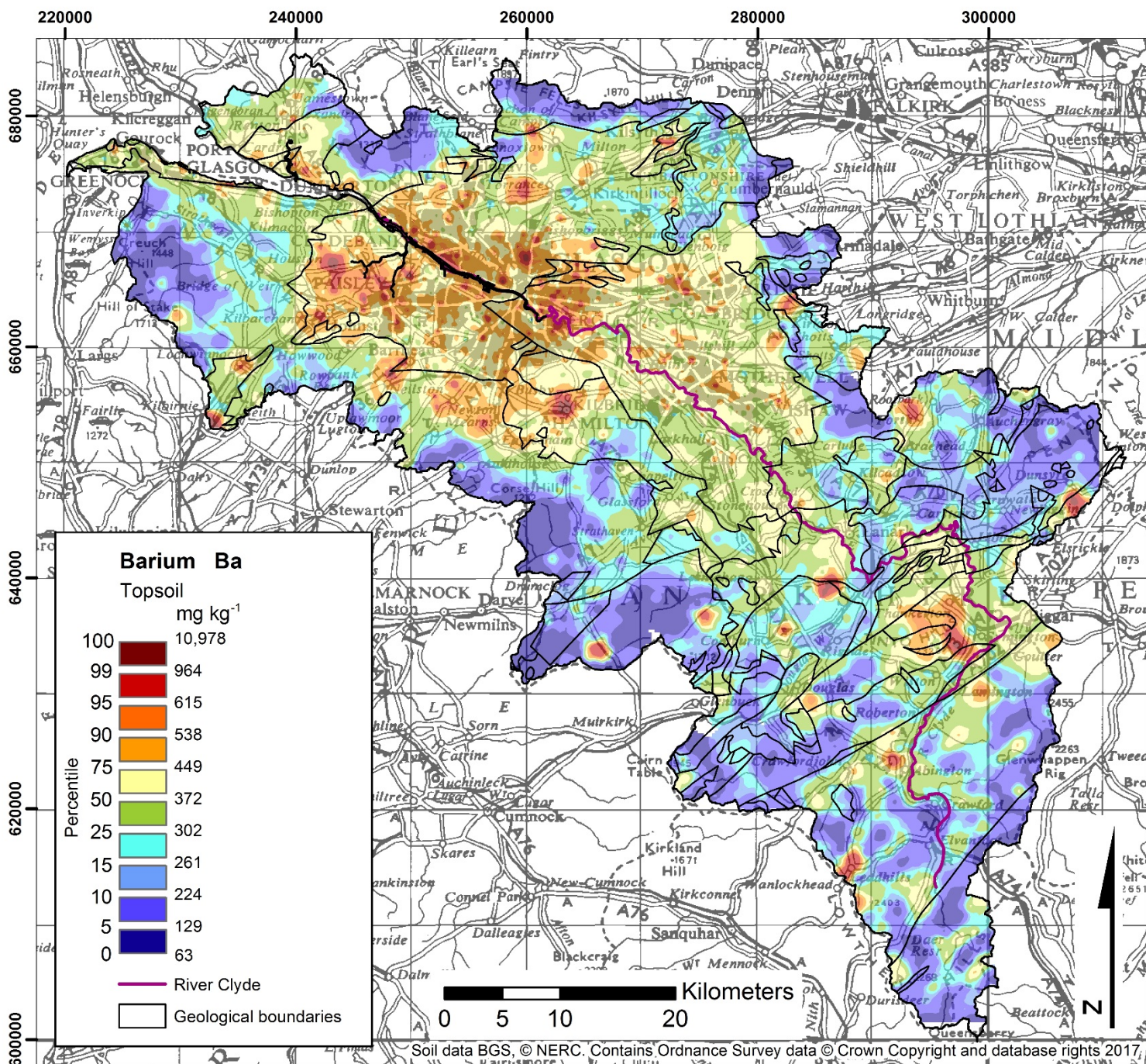
Clyde Basin topsoil

Topsoil Ba concentrations range from 63 to 10978 mg kg^{-1} in the area. Over the majority of the rural Clyde Basin, higher Ba values ($> 302 \text{ mg kg}^{-1}$) are associated with non-calcareous gley, brown-earth and mineral alluvial soil types. The background Ba geochemical distribution is broadly similar to that of K (and Rb). Therefore, Ba concentrations in soil are interpreted to largely reflect variations of K-bearing silicate minerals such as alkali feldspar. As a result, Ba is associated with sandier parent materials and soil types. These minerals are mainly present in the petrogenic component of soil, rather than in the organic component. Correspondingly, Ba values are relatively low over the organic-rich peaty soil of the uplands on the periphery of the Basin and are higher in lower-lying areas and valleys, where sandier material has accumulated. Particularly noticeable elevated values of Ba ($> 615 \text{ mg kg}^{-1}$) are reported around Tinto Hill in the south of the area (Location 40, Figure 3), which represents the largest felsic igneous intrusion in the region (granodiorite-rhyodacite composition). Here again, the association with high levels of K in the same samples suggests that the Ba values are related to K-feldspar, which is abundant in this type of igneous rock. Extensive aggregate extraction occurs in the area, and may have enhanced Ba dispersal in soil of the area.

Elevated concentrations of Ba ($> 538 \text{ mg kg}^{-1}$) in the rural environment are associated also with Ba, Pb and Cu mineralisation, which is known at a number of localities, including Muirshiel and Kaim in the north and Spoutloch Burn and Leadhills in the south of the area (Locations 2, 3, 4, and 11, Figure 3). Whilst Ba mineralisation has been reported in the Carboniferous of the Midland Valley (BGS, 1993), the extraction of other resources is probably responsible for elevated Ba concentrations at a number of other locations such as the former fireclay and opencast coal mine at Newmains Moss in the east of the area (Location 28, Figure 3). Other anomalies nearby Dykehead opencast coal mine and north of Brokencrossmuir coal mine (Locations 27 and 39, Figure 3), also in the east of the area, are attributed to the presence of coal waste, which was recorded in these samples.

In general, Ba concentrations are elevated in urban topsoil, compared to rural, over all bedrock types. This may be due to the legacy of coal and mineral (including ironstone) extraction activities and processing in industrial areas, as well as coal burning and presence of building rubble in urban soil.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Environmental behaviour

Cadmium (Cd) has one main oxidation state of +2. It is a low-abundance chalcophile element forming several minerals including greenockite (CdS) and the rarer octavite (CdCO₃) and monteponite (CdO) (Wedepohl, 1978), but is most commonly found in trace amounts in other sulphides, especially sphalerite where it substitutes for Zn, and silicates such as biotite and amphiboles. It has an average continental crustal abundance of 0.1 mg kg⁻¹ (Wedepohl, 1995). Certain sedimentary rocks such as phosphorites and black shales tend to contain higher Cd contents than other rock types. Cadmium concentrations in natural soil are generally very low (< 1 mg kg⁻¹) except where derived over mineralised or phosphatic/black shale rock types (Alloway, 2013). Cadmium can substitute for Ca in carbonate minerals and for Mn in oxides. It is adsorbed to clay minerals in soil also (Alloway, 2013). However, the organic matter and Fe-Mn oxyhydroxide content exert a greater control on Cd adsorption and distribution in soil than the clay mineral content (Kabata-Pendias, 2001). Cadmium is very soluble at low pH values and is mobile in oxidising conditions over a wide pH range, below pH 8 (Fergusson, 1990). Anthropogenic sources of Cd include Cu and Zn smelters, electroplating, fertilizers and sewage sludge (Reimann and Caritat, 1998). Cadmium is biologically non-essential, and is toxic to humans in high concentration; however, such exposures are rare in the natural environment. Plants can accumulate Cd via their roots, and plants such as mushrooms, spinach and wheat may concentrate Cd (WHO, 1996).

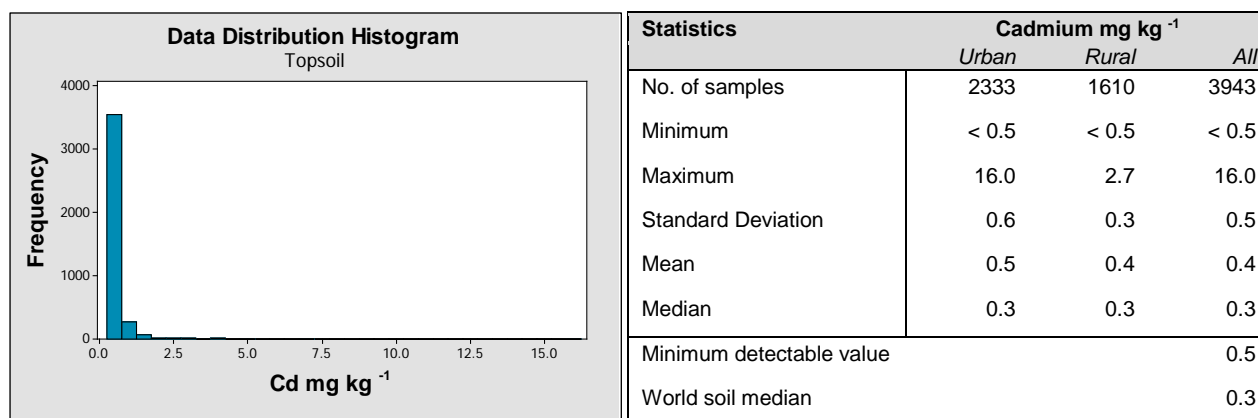
Clyde Basin topsoil

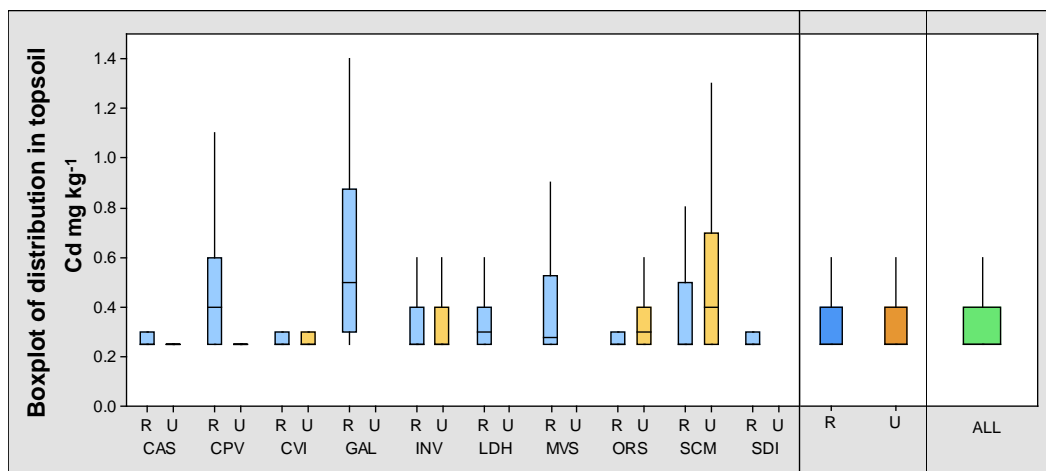
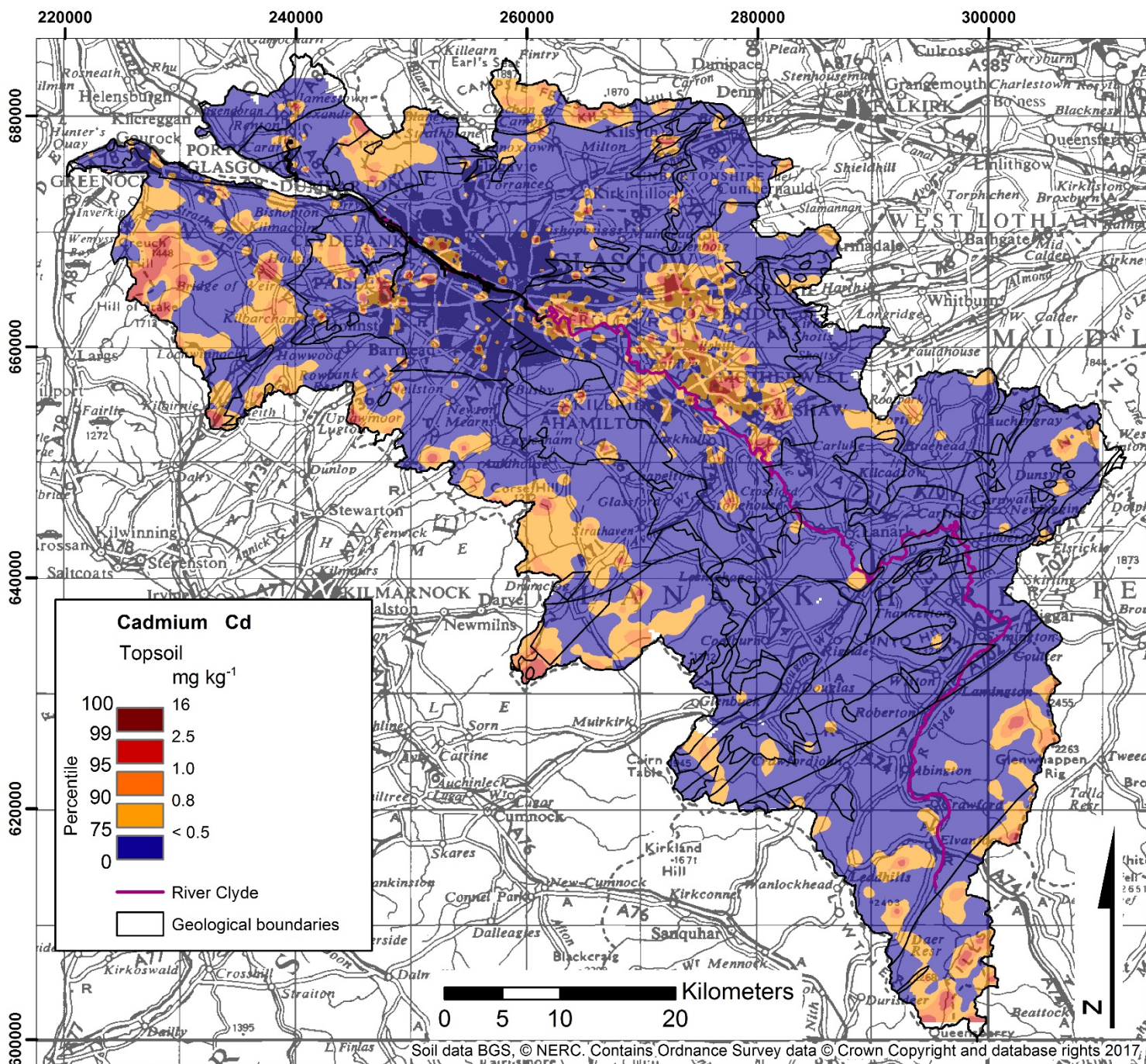
The majority of topsoil in the Clyde Basin contains Cd concentrations below the lower limit of detection (0.5 mg kg⁻¹), as expected, as Cd is generally of very low abundance in most soil (Reimann and Caritat 1998). Where Cd was detected, values range up to 16 mg kg⁻¹.

In the rural environment, higher topsoil Cd concentrations (> 0.5 mg kg⁻¹) are associated with upland organic-rich soil developed over the Gala Group strata in the south of the region, and the Clyde Plateau Volanic Formation in the Renfrew Hills and Kilpatrick-Campsie Hills in the northwest of the area. Similarly, peaty/boggy soil in the vicinity of Linwood Moss to the west of Paisley (Location 17, Figure 3) contains elevated concentrations of Cd, indicating the importance of binding in this organic-rich soil on the distribution of the element in the rural environment. Topsoil collected in the Leadhills former mining area (Location 11, Figure 3) in the south of the region contains higher Cd concentrations (0.5 – 1.1 mg kg⁻¹) relative to most of the rural Clyde Basin reflecting the presence of sulphide mineralisation. In the east of the area, elevated Cd concentrations in rural soil are reported from former coal mining sites west of Greengairs and at Canderigg south of Motherwell (Locations 22 and 36, Figure 3); topsoil from the latter contains the highest Cd concentration in the rural dataset (2.7 mg kg⁻¹).

Topsoil Cd concentrations across much of central Glasgow are low (< 0.5 mg kg⁻¹), but elevated values are associated with the shipbuilding centre at Clydebank in the west, and the former metal processing heartland in the East End of the city (see Figure 3 for locations). Similarly, concentrations are generally higher (> 0.5 mg kg⁻¹) in urban topsoil from Airdrie, Beith, Coatbridge, Motherwell and Wishaw, including at Ravenscraig former steel mill (Location 26, Figure 3), reflecting the history of metal processing, ironstone, coal and fireclay extraction in these urban centres, underlain by the Scottish Coal Measures Group. Higher concentrations in urban soil underlain by the Old Red Sandstone Group are associated with current industrial sites and former quarry and dye works in the Dumbarton area to the northwest of Glasgow. Elevated concentrations are reported from current and former industrial sites in Paisley to the west of Glasgow, including the highest value (16 mg kg⁻¹) in the urban dataset. Higher concentrations reported in the centre of East Kilbride to the south of Glasgow, probably relate to diffuse urban pollution such as bricks and coal waste noted in the samples.

The distribution of topsoil-Cd in the region is broadly similar to that of silver (Ag) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

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Environmental behaviour

Caesium (Cs) is a lithophile element with one oxidation state (+1) it is relatively rare, with an average continental crustal abundance of 3.4 mg kg⁻¹ (Wedepohl, 1995). It can substitute for K in mica and K-feldspar, which are the main sources of Cs in the Earth's crust. It concentrates in igneous rocks that have undergone a greater degree of differentiation, such as granite. Therefore, elevated concentrations can occur in felsic igneous rocks (3 – 12.3 mg kg⁻¹) (Wedepohl, 1978).

Caesium is a relatively immobile element under most environmental conditions; its primary environmental pathways are via rock weathering and geogenic dust. Caesium released by rock weathering processes, is quickly and strongly adsorbed by soil. In particular, it has a high affinity for clays, because their finer grain-size provides more ion-exchange sites (Kabata-Pendias, 2001).

Although Cs can be used as a catalyst, a rocket propellant (CsBH₄), and in photovoltaic cells and atomic clocks, its use in industry is relatively limited; therefore, it is not often encountered as an anthropogenic pollutant. Radiogenic ¹³⁷Cs can be introduced into the environment due to fallout from nuclear explosions; substantial amounts were released into the atmosphere by the Chernobyl nuclear disaster in 1986 (Higgit et al., 1993; Smith and Beresford 2005).

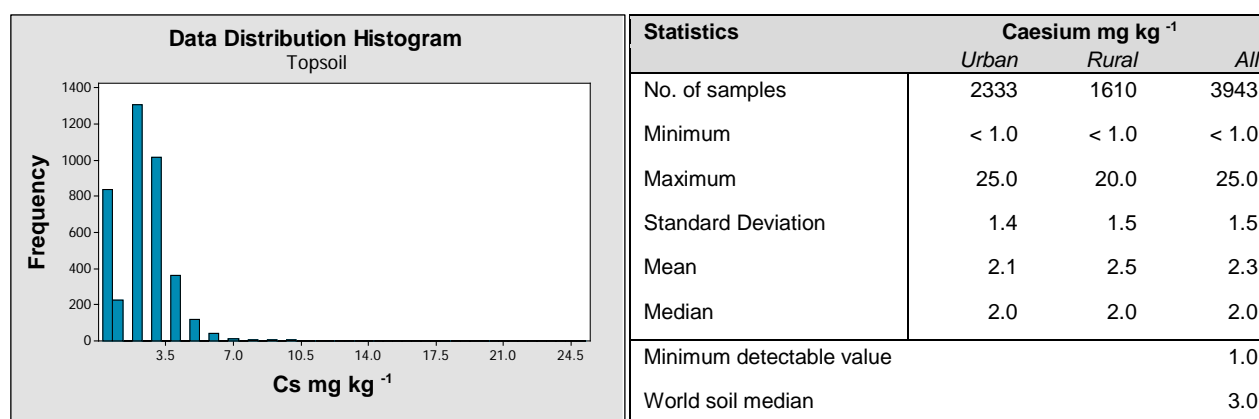
Caesium has no known biological role, and is considered toxic to most organisms; however, health problems related to natural environmental exposure are rare (ATSDR, 2004).

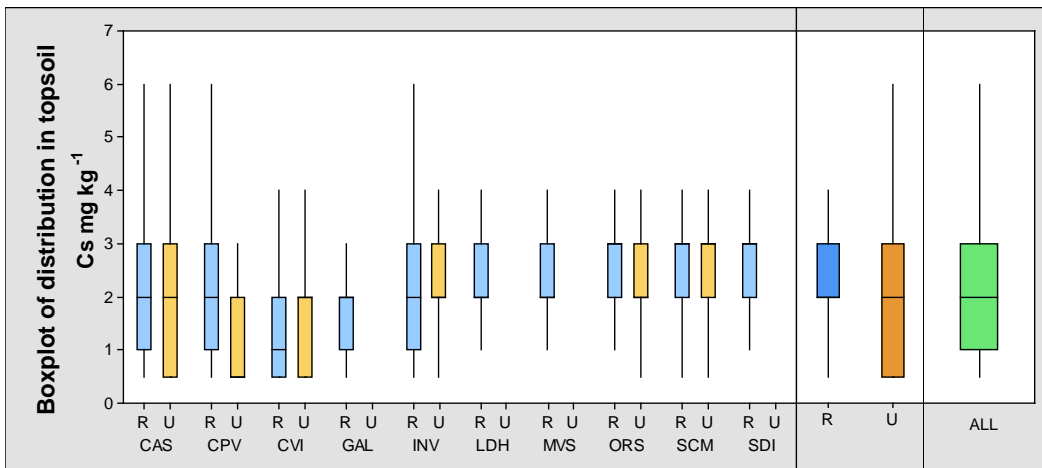
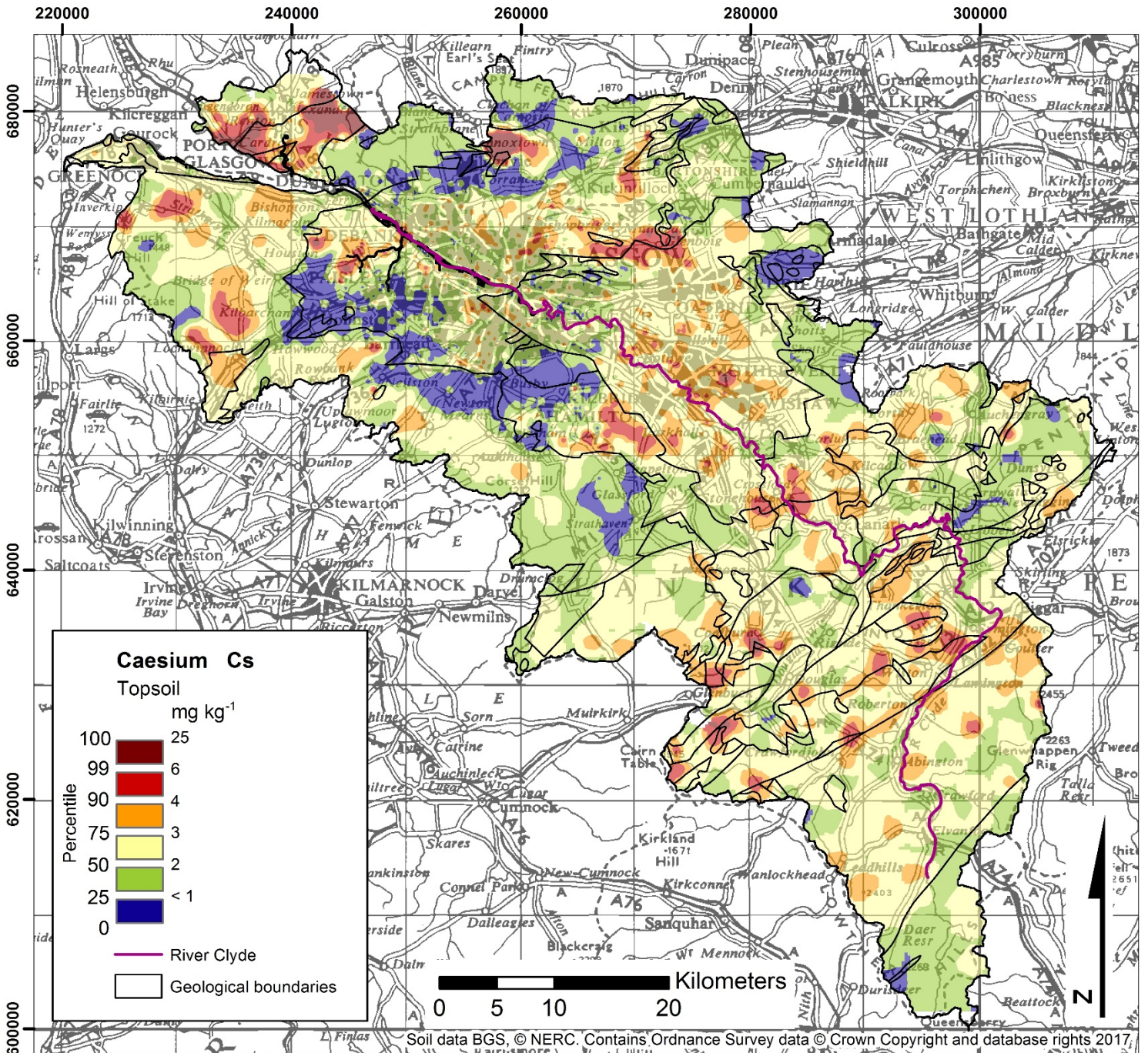
Clyde Basin topsoil

Topsoil Cs concentrations are in the range < 1 – 25 mg kg⁻¹ in the region. In the rural areas, highest Cs concentrations (> 4 mg kg⁻¹) occur in topsoil samples collected over mature sandstone bedrock of the Inverclyde Group in the northwest of the area around Dumbarton. This may be related to greater proportions of minerals that could host Cs in this sedimentary bedrock unit, such as feldspar.

Elevated concentrations of Cs in rural topsoil of the Clyde Basin are somewhat sporadically distributed, and it is difficult to identify any geological or other natural controls. However, some Cs anomalies appear to be related to soil collected in hollows and low-lying areas, most noticeably those immediately to the northwest of Milngavie in the north of the area, and north of Coatbridge in the east of the area. It is speculated that these may be areas where Cs deposited from the atmosphere is able to accumulate. The higher values north of Coatbridge correspond also to former fireclay extraction at Glenboig (Location 21, Figure 3), which may contribute to soil-Cs loadings. A noticeable anomaly in the centre of the area in the Clyde valley is seen around Crossford, south of Carluke, corresponding to clay soil.

Topsoil Cs concentrations in the urban areas are rather similar to those of the surrounding rural soil developed over the same rock types, suggesting that urbanisation has little influence on soil-Cs chemistry. However, a number of localised topsoil Cs anomalies occurring near sites of former and current industrial activity, could suggest the presence of anthropogenic Cs pollution, but it is not widespread. These include the former Ravenscraig steelworks in the east of the area, and the Coalburn opencast coal mine and Longhill Burn limeworks in the south of the region (Locations 26, 41 and 42, Figure 3).





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Calcium

Ca

(Concentrations are expressed in CaO wt%)

Environmental behaviour

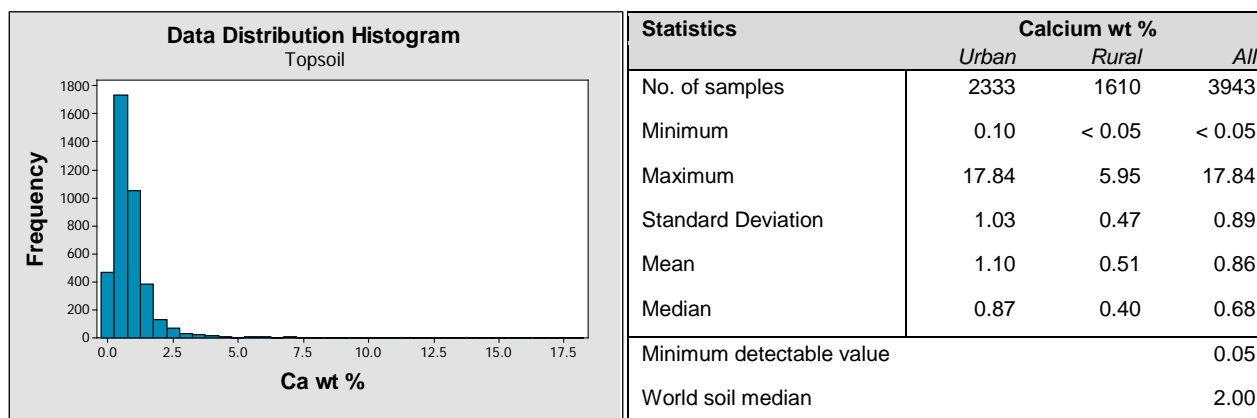
Calcium (Ca) is the fifth most abundant element, constituting 5.29 % of the Earth's continental crust (McLennan and Taylor, 1999). It is a lithophile element with one main oxidation state (+2), and forms several common minerals including calcite (CaCO₃), dolomite (CaMg(CO₃)₂), gypsum (CaSO₄.2H₂O) and anhydrite (CaSO₄). It is widely distributed in other minerals such as feldspar, amphibole and pyroxene. It is also often associated with clay minerals such as illite, chlorite and Ca - montmorillonite (Zupancic and Pirc, 1999). Calcium concentrations in igneous rocks vary widely from 0.7 wt% in low-Ca granites to 10.63 wt% in basalts (Mielke, 1979). In sedimentary rocks, the Ca content reflects the abundance of carbonate minerals and of detrital minerals such as plagioclase. It is a major constituent of limestones and dolomites. Common Ca-bearing minerals such as calcite and dolomite, weather on contact with acid solutions, such as rainwater and soil porewater releasing Ca²⁺. Hence, Ca generally has a high mobility in most environmental conditions, with the Ca²⁺ ion being soluble below pH 7. Calcium is the main cation present in soil, it is held on the surfaces of clay minerals and organic matter, but is released as soil acidity increases (Kabata-Pendias, 2001). Anthropogenic sources of Ca include lime and cement factories, fertilisers and dust. Geogenic sources are more usually important than anthropogenic ones in the environment (Reimann and Caritat, 1998). Calcium is an essential nutrient for plants and animals, for the development of bones, nervous systems and cells (Emsley, 2011).

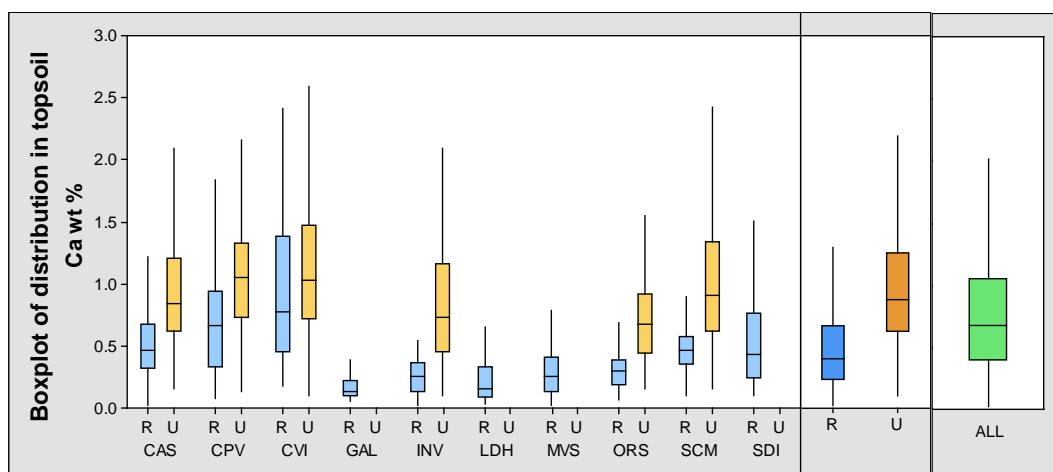
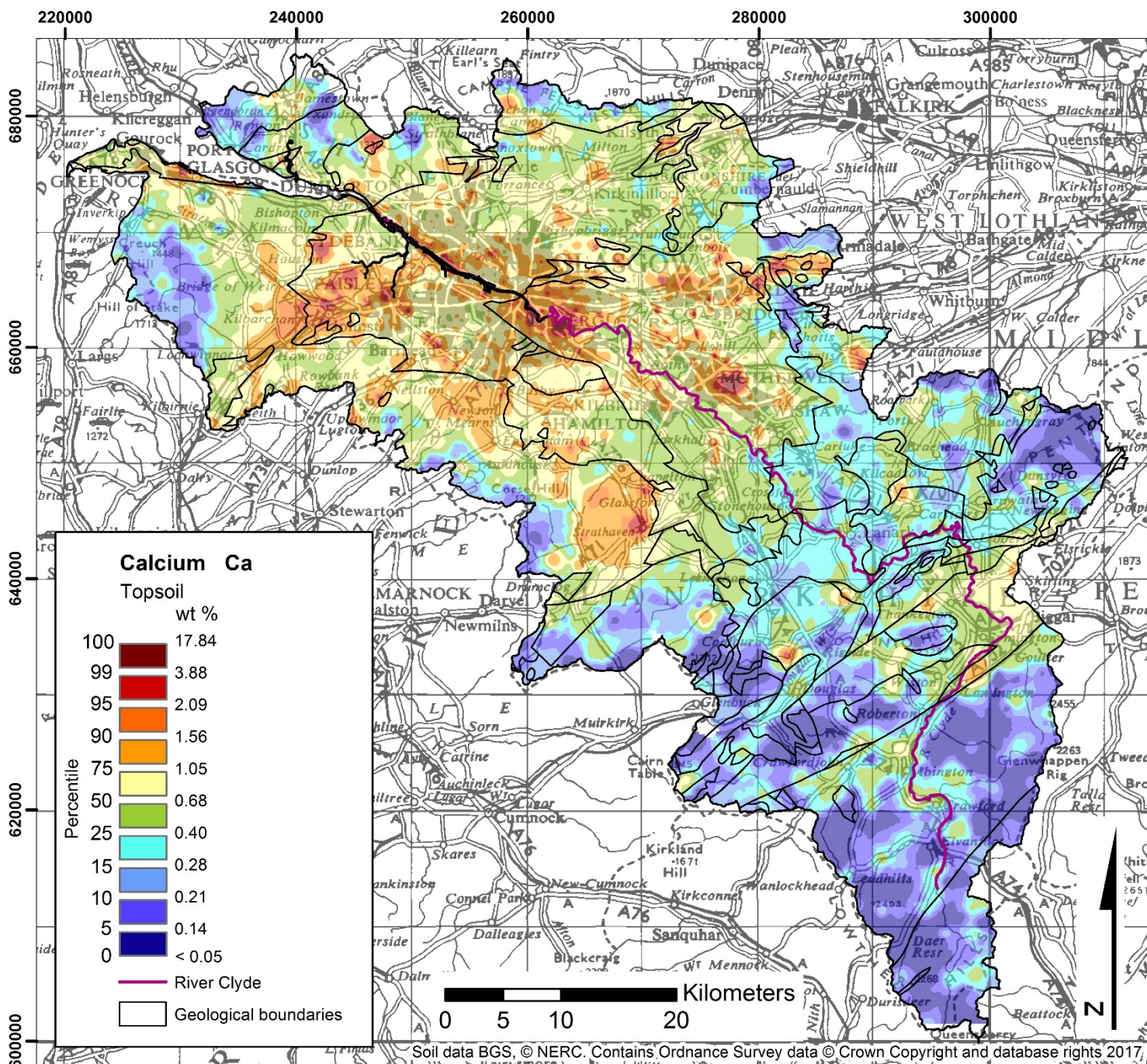
Clyde Basin topsoil

Topsoil Ca concentrations range from < 0.05 to 17.84 wt% in the area. In rural sections of the Clyde Basin, higher concentrations of topsoil Ca (> 1.05 wt%) are observed over the more mafic sections of the Clyde Plateau Volcanic Formation (CPV) and the Silurian to Devonian igneous rocks, reflecting their whole-rock composition. However, the CPV, comprise a range of igneous rock types and lower topsoil Ca values are associated with more evolved andesitic-felsitic components (BGS, 1993). Therefore, Ca is not uniformly high in mineral soil types over the whole CPV outcrop, due to variable parent material chemistry. In upland areas, where peaty soil overlies the CPV, Ca concentrations are lower, reflecting the fact that Ca is contained in the mineral soil rather than the organic component.

A Ca anomaly at the site of the former limeworks at Longhill Burn, Coalburn in the south of the area (Location 42, Figure 3), is due to one sample with Ca concentration of 2.52 wt%. Carboniferous limestone of the Clackmannan and Strathclyde Groups was formerly worked for quicklime at this location.

Topsoil Ca is elevated in the urban relative to the rural areas of the Clyde Basin across all bedrock units, indicating an anthropogenic influence. Demolitions can release dust and fragments of building materials such as concrete and bricks, which contain Ca (as calcium carbonate) to the soil. Building rubble is commonly used as artificial ground fill material also. As a result, within the urban area, some of the highest Ca concentrations (> 3.88 wt%) correspond to sites where soil over artificial ground has been sampled, including anomalies at Johnstone, Paisley, Port Glasgow and Scotstoun in the west, and Airdrie and Rutherglen (Location 19, Figure 3) in the east. Indeed, elevated Ca concentration as a result of the calcareous nature of artificial ground is a typical geochemical signature of urban soil that has been noted in many cities (Fordyce et al., 2005; Birke et al., 2011). High soil-Ca concentrations in Rutherglen and at Ravenscraig in Motherwell (Location 26, Figure 3) reflect the metal processing history of these areas also. Rutherglen was home to the world's largest chrome works until 1968, and highly alkaline chromite-ore processing waste was dispersed in the area (Farmer et al., 1999). Similarly, Ca was used in the steel making process at the Ravenscraig works, and in iron foundries in the East End of Glasgow.





Geology	N rural	N urban
CAS	401	1187
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LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
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R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Chromium

Cr

Environmental behaviour

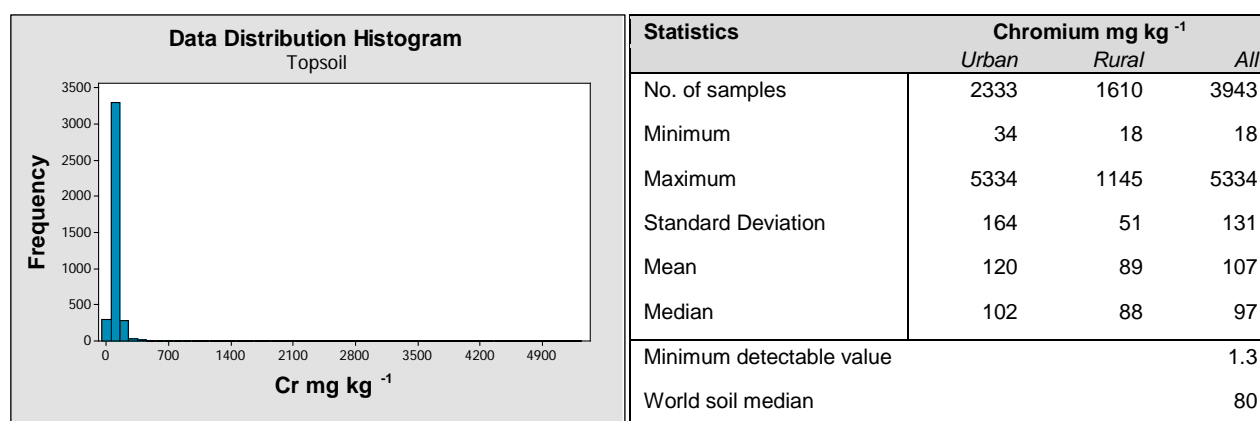
Chromium (Cr) has three main oxidation states (+2, +3, +6) and forms several minerals including chromite and the rare crocoite, and is an accessory element in others e.g. spinels, amphiboles, micas, pyroxenes and garnets. It is a lithophile element with an average continental crustal abundance of 126 mg kg⁻¹ (Wedepohl, 1995). It is more abundant in mafic igneous rocks (1000 – 3000 mg kg⁻¹) than in granitic rocks (10 mg kg⁻¹); and in sedimentary rocks, concentrations are generally higher in shales/mudstones (90 mg kg⁻¹) than in sandstones or limestones (11 – 35 mg kg⁻¹) (Mielke, 1979). Chromium is a low mobility element, especially under moderately oxidising and reducing conditions and near-neutral pH values. In soil, Cr accumulates in Fe and Mn oxides, and is adsorbed onto organic matter and clays, with strong pH and redox control (McBride, 1994). Anthropogenic sources of Cr include Cu smelting, metal electroplating, tanning, the chemical industry, engineering and waste incineration (Reimann and Caritat, 1998). The Cr³⁺ form, which predominates in most natural environments, is considered relatively harmless at levels normally encountered. It is an essential element, needed by the human body in small amounts for insulin action and metabolism of proteins and carbohydrates. However, Cr⁶⁺ (the largely industrial form) is toxic (causing liver and kidney damage) and a carcinogen, but health problems outside of occupational exposure are rare (WHO, 1996).

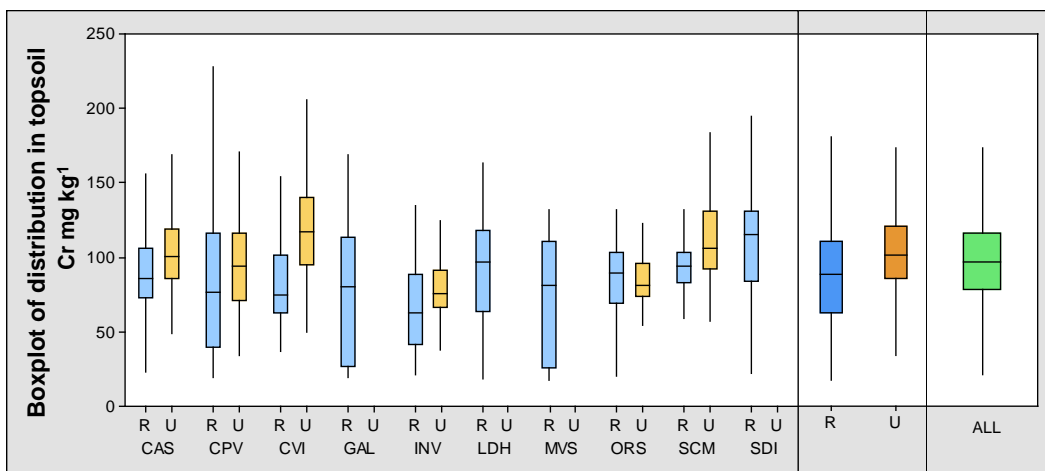
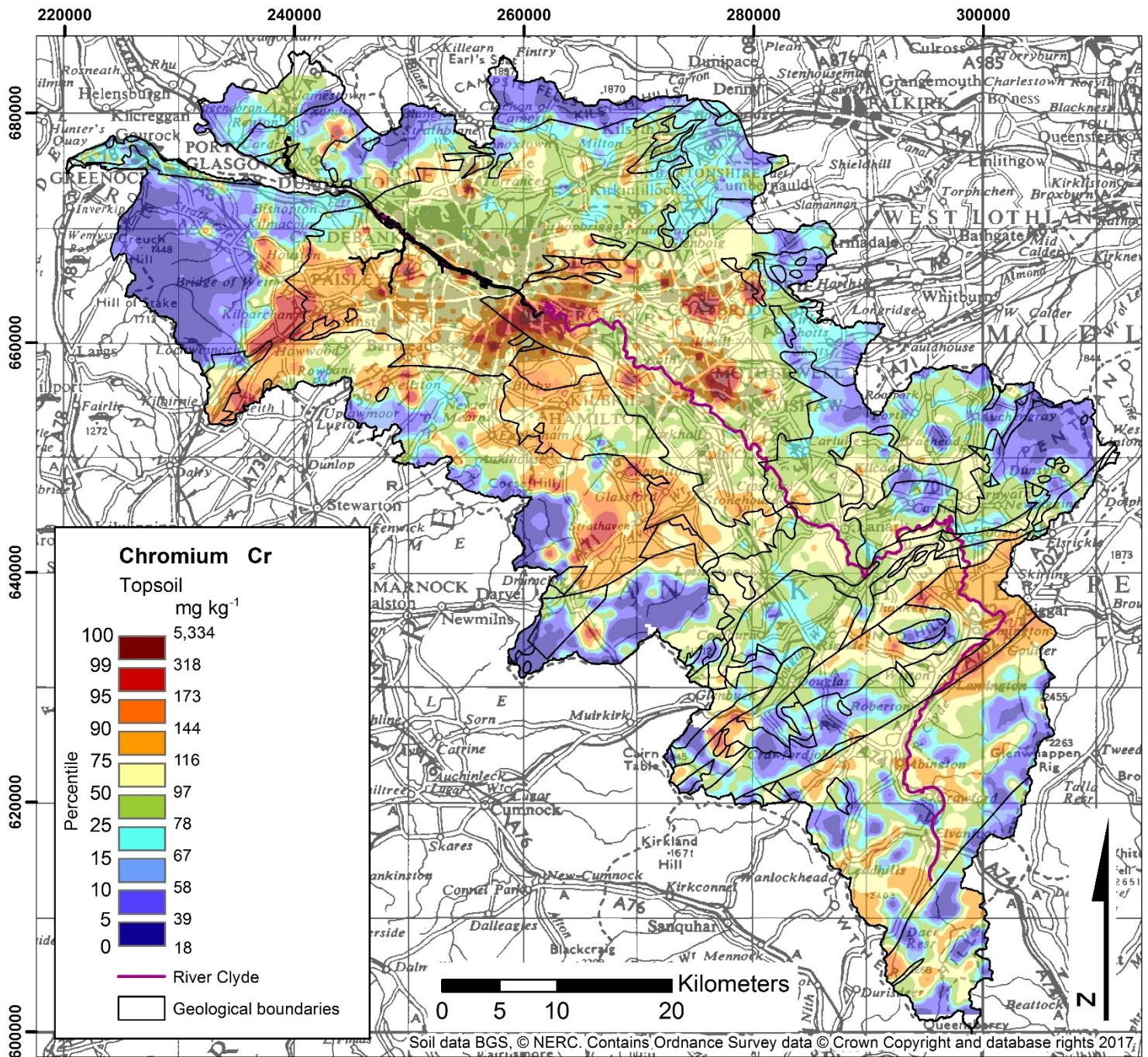
Clyde Basin topsoil

Topsoil Cr concentrations are in the range 18 – 5334 mg kg⁻¹ in the region. Chromium is typically associated with mafic igneous rocks and concentrations are commonly higher in organic-rich rocks such as black shales and coals than in other sedimentary lithologies (Gonnelli and Renella, 2013). As a result, in the rural Clyde Basin, higher topsoil concentrations of Cr (> 116 mg kg⁻¹) are associated with the mafic volcanic components of the Silurian–Devonian igneous rocks in the south of the area and the Clyde Plateau Volcanic Formation (CPV) to the southwest of Glasgow. Topsoil-Cr is generally higher also over the Leadhills Supergroup and Gala Group in the south of the Basin reflecting the mafic source-rocks of these greywacke metasediments (Stone et al. 1997). Lower concentrations of Cr (< 58 mg kg⁻¹) are reported in soil developed over the sandstone-dominated Old Red Sandstone and Inverclyde Groups than the Clackmanan–Strathclyde and Scottish Coal Measures Groups. Upland peaty topsoil on the eastern and western peripheries of the Basin and over the CPV to the west and north of Glasgow have low Cr concentrations, due to their organic, rather than mineral soil composition. Higher soil-Cr values at Glespin (Location 44, Figure 3) in the southwest of the Basin are associated with coniferous forestry and opencast coal mining. They correspond to high-Mn soil suggesting retention of Cr in secondary Mn-oxides in this low-pH environment. Similarly, higher values at the foot of the Campsie Hills to the north of Glasgow correspond to higher Mn-Fe soil.

Anthropogenic activities have a significant influence on the distribution of Cr in urban topsoil. High values (> 173 mg kg⁻¹) are associated with artificial ground in Milngavie (north Glasgow), the Moffat Mills distillery/former paper mill in Airdrie (east of Glasgow) (Location 23, Figure 3), ironworks in Beith and with artificial ground and industrial sites in Renfrew–Paisley–Johnstone (southwest of Glasgow). In the east of the area, high Cr concentrations are reported in soil from the former Ravenscraig steel mill in Motherwell (Location 26, Figure 3) and the former iron pit at Calderbank in Coatbridge (Location 24, Figure 3). Rutherglen in southeast Glasgow (Location 19, Figure 3) was home to the world's largest chromite ore processing plant, during the 19th century, which operated until 1968. Chromite ore processing waste was extensively used as landfill material in southeast Glasgow and it is estimated that 2,500,000 tons (dry weight) were deposited during the lifetime of the factory (Farmer et al., 1999). Consequently, Cr concentrations in topsoil in south and east Glasgow are significantly elevated (> 173 – 4286 mg kg⁻¹). Chromium is enhanced in urban compared to rural soil regardless of parent material type as a result of anthropogenic pollution.

The distribution of topsoil-Cr in the region is broadly similar that of nickel (Ni) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Environmental behaviour

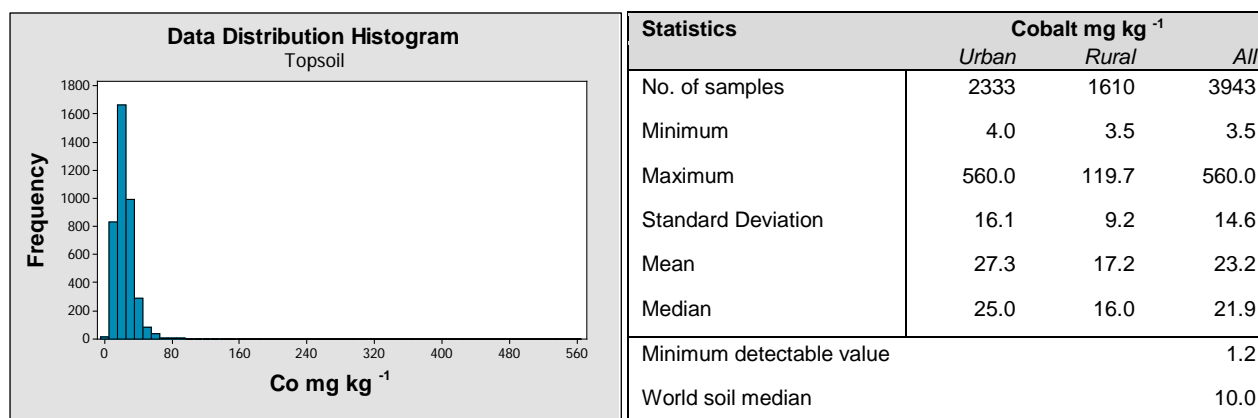
Cobalt (Co) has two main oxidation states (+2, +3) and an average continental crustal abundance of 29 mg kg⁻¹ (McLennan and Taylor, 1999). It is a chalcophile/ siderophile element forming several rather rare minerals including smaltite ((Co,Ni)As_{2-2.5}), cobaltite ((Co,Fe)AsS) and linnaeite ((Co,Ni)₃S₄), though it is present as an accessory element in olivine, pyroxenes, amphiboles, micas, garnets and sphalerite, and in synsedimentary Fe and Mn oxide minerals in sedimentary rocks. Cobalt is generally enriched in ultramafic/mafic (150 mg kg⁻¹) relative to felsic (1 – 7 mg kg⁻¹) igneous rocks and concentrations in shales and mudstones (19 mg kg⁻¹) are typically higher than in sandstone and carbonate sedimentary rocks (< 0.3 mg kg⁻¹) (Mielke 1979; Wedepohl, 1978). It is sometimes associated with Cu, especially in sulphide ore bodies (Erdman and Modreski, 1984). In soil, Co does not form residual silicate minerals, under oxidising near-neutral conditions; it is strongly sorbed to Fe and Mn oxides, by chemisorption and co-precipitation. Manganese oxides have a particular affinity for Co. As the pH value decreases, the solubility of Co increases; hence, it is highly mobile in acidic reducing conditions where the formation of Fe and Mn oxides is inhibited (McBride, 1994). Anthropogenic sources of cobalt include coal combustion, special steels, fertilizers and lead, iron and silver mining and processing (Reimann and Caritat, 1998). Cobalt is a biologically essential element, and is found in vitamin B12. Cobalt can be toxic to humans at high doses. However, problems related to deficiency are more likely than excess dose toxicity. Cobalt has metabolic links with Fe and Cu, which can be depressed at high levels of Co intake, leading to anaemia in animals (Mertz, 1987).

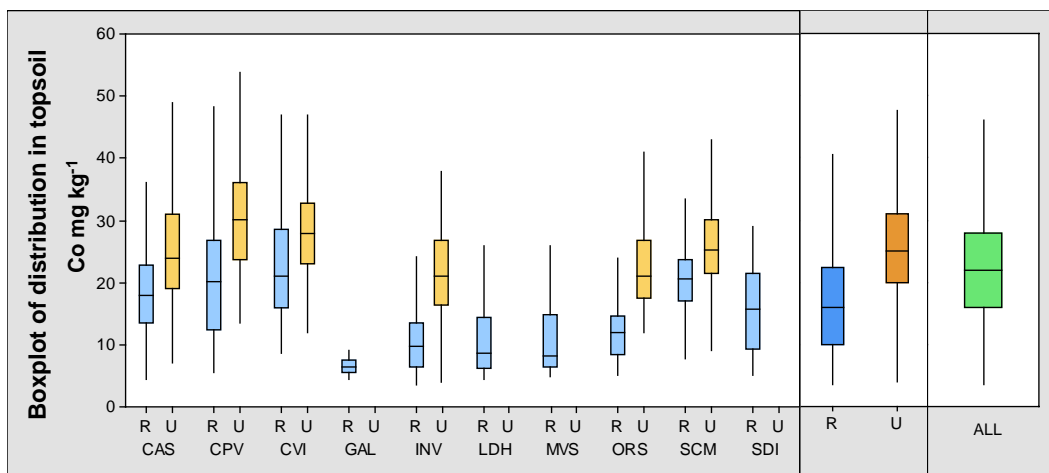
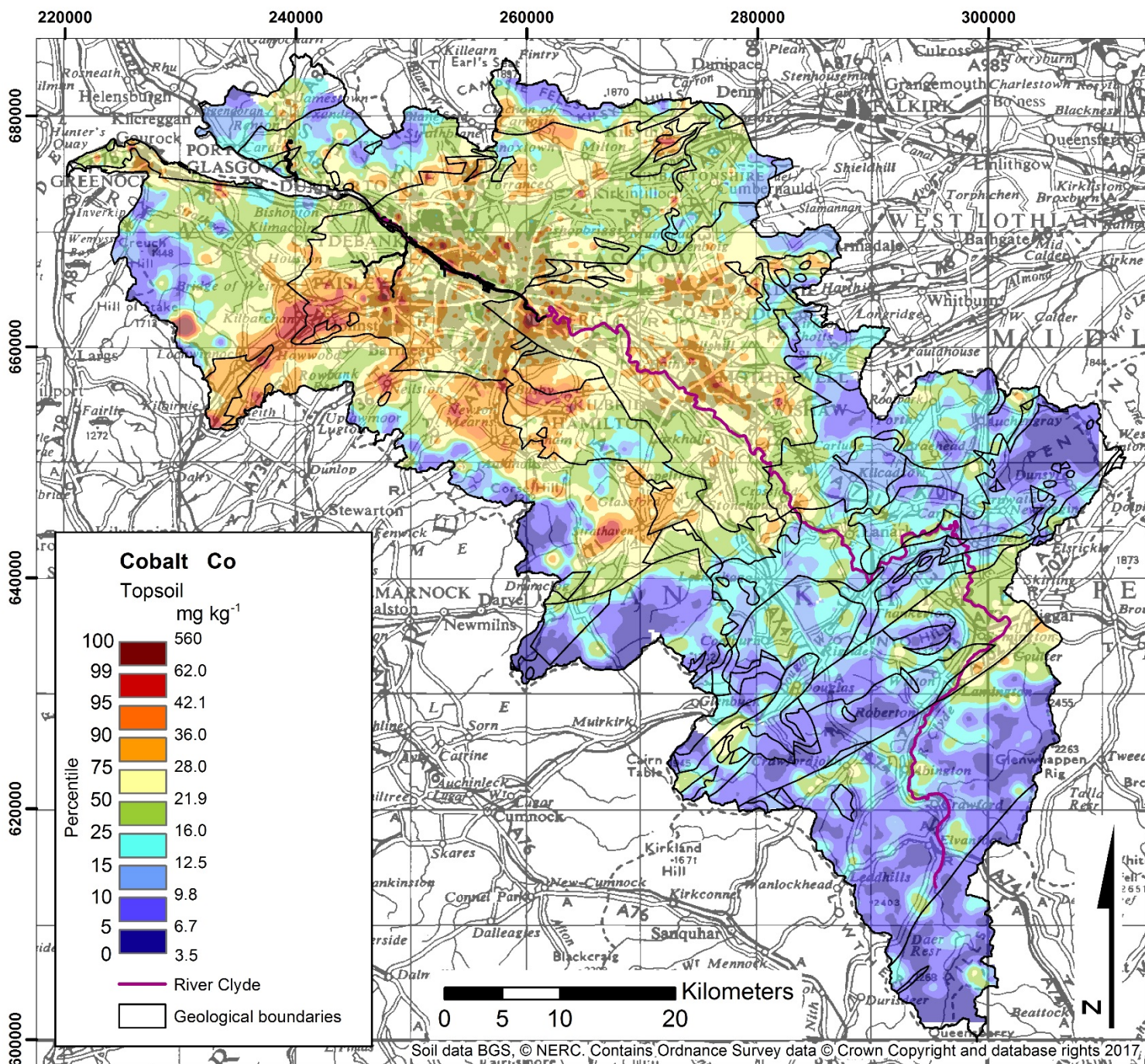
Clyde Basin topsoil

Concentrations of Co in topsoil range from 3.5 to 560 mg kg⁻¹ in the area. In the rural Clyde Basin, higher concentrations of Co (> 21.9 mg kg⁻¹) occur in topsoil samples collected over more mafic components of the Clyde Plateau Volcanic Formation (CPV), Silurian–Devonian igneous rocks and Clyde Volcanics in centre and north of the region, except over areas where peaty soil occurs. Cobalt shows a negative spatial relationship with LOI reflecting its association with the mineral soil component, which has weathered from the underlying igneous bedrock, rather than the organic soil fraction. The CPV consists of a range of igneous rock types in terms of mineral and geochemical composition; therefore, Co concentrations do not appear uniformly high in soil of the same type over the whole outcrop. Cobalt concentrations are generally higher in topsoil over igneous compared to sedimentary bedrock, reflecting whole-rock composition. Cobalt concentrations are typically higher (> 16 mg kg⁻¹) in soil over the Carboniferous sedimentary strata in the north of the Basin, than in soil developed over the greywackes of the Gala Group and Leadhills Supergroup in the south of the area, or over Devonian sandstones in the centre and northwest of the region. A number of topsoil Co anomalies in rural areas correspond to Fe and Mn enrichment, such as those at Misty Law in the northwest of the region (Location 14, Figure 3), and at the foot of the Campsie Hills to the north of Glasgow. This association suggests the influence of secondary processes such as the mobilisation and then trapping of Co in Fe and Mn oxides in a waterlogged, low-pH environment.

In urban topsoil, Co concentrations are broadly elevated compared to rural soil regardless of parent material type, likely due to the influence of diffuse anthropogenic pollution. A number of specific Co anomalies are attributed to former industrial sites. Cobalt is elevated in samples collected from former industrial centres at Rutherglen and the Ravenscraig former steel mill in the east of the area (Locations 19 and 26, Figure 3). High concentrations (> 42.1 mg kg⁻¹) are reported also in topsoil in the centre of Paisley to the west of Glasgow. Similarly, elevated Co concentrations are observed near current and former extractive industrial sites, including Newmains Moss fireclay and coal mines (Location 28, Figure 3) and the former paper mill and aggregate quarry at Moffat Mills in Airdrie, in the east of the area (Location 23, Figure 3).

The distribution of topsoil-Co in the study area is similar to that of vanadium (V) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Copper

Cu

Environmental behaviour

Copper (Cu) has two main oxidation states (+2 and +1) and an average crustal abundance of 68 mg kg⁻¹ (Mielke, 1979). It is a chalcophile element and whilst native Cu occurs rarely in nature, it more typically forms minerals such as chalcopyrite (CuFeS₂), covellite (CuS), and malachite (Cu₂CO₃(OH)₂). However, it is more widely dispersed at trace levels in micas, pyroxenes and amphiboles, thus showing a greater affinity for mafic (40 – 60 mg kg⁻¹) than for felsic igneous rocks (12 mg kg⁻¹) (Wedepohl, 1978). Black shales and coals (40 – 45 mg kg⁻¹) typically contain elevated concentrations of Cu relative to sandstone and carbonate sedimentary rock types (2 – 15 mg kg⁻¹) (Alloway, 2013).

Soil Cu concentrations generally reflect detrital mafic mineral, clay and organic matter content. Many soil minerals including clays and Al and Fe oxides adsorb Cu. The mechanism is dependent on the surface charge, which in turn is controlled by pH. Copper has a strong affinity for organic matter in soil also, and both organic and inorganic processes of adsorption are stronger at higher pH. Therefore, Cu is more mobile under oxidising, acidic conditions (Kabata-Pendias, 2001).

Anthropogenic sources of Cu include Cu mining and smelting, agriculture, sewage sludge and steel works (Reimann and Caritat, 1998).

Copper is an essential trace element for all organisms and is a constituent of a number of key enzymes in the human body; however, it can be toxic at extremely high levels that are not normally encountered in natural settings (WHO, 1996).

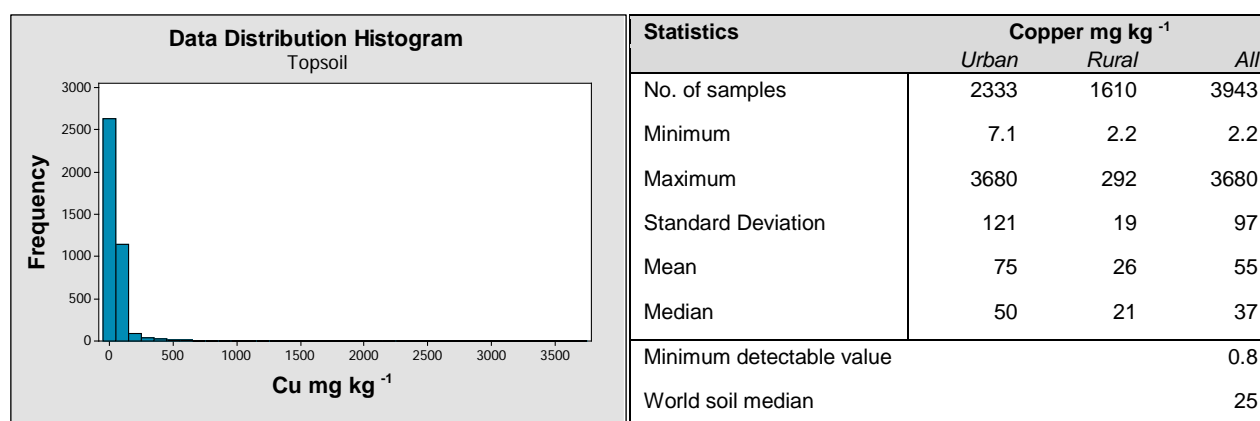
Clyde Basin topsoil

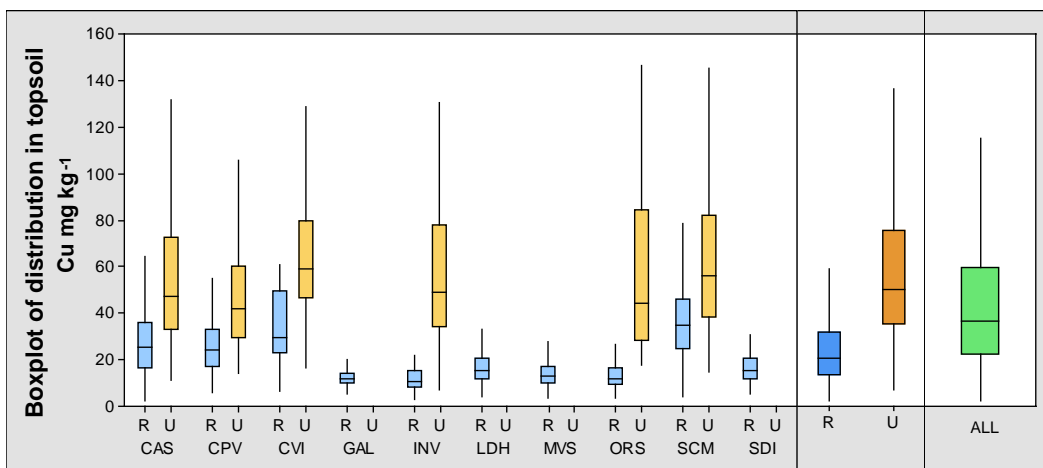
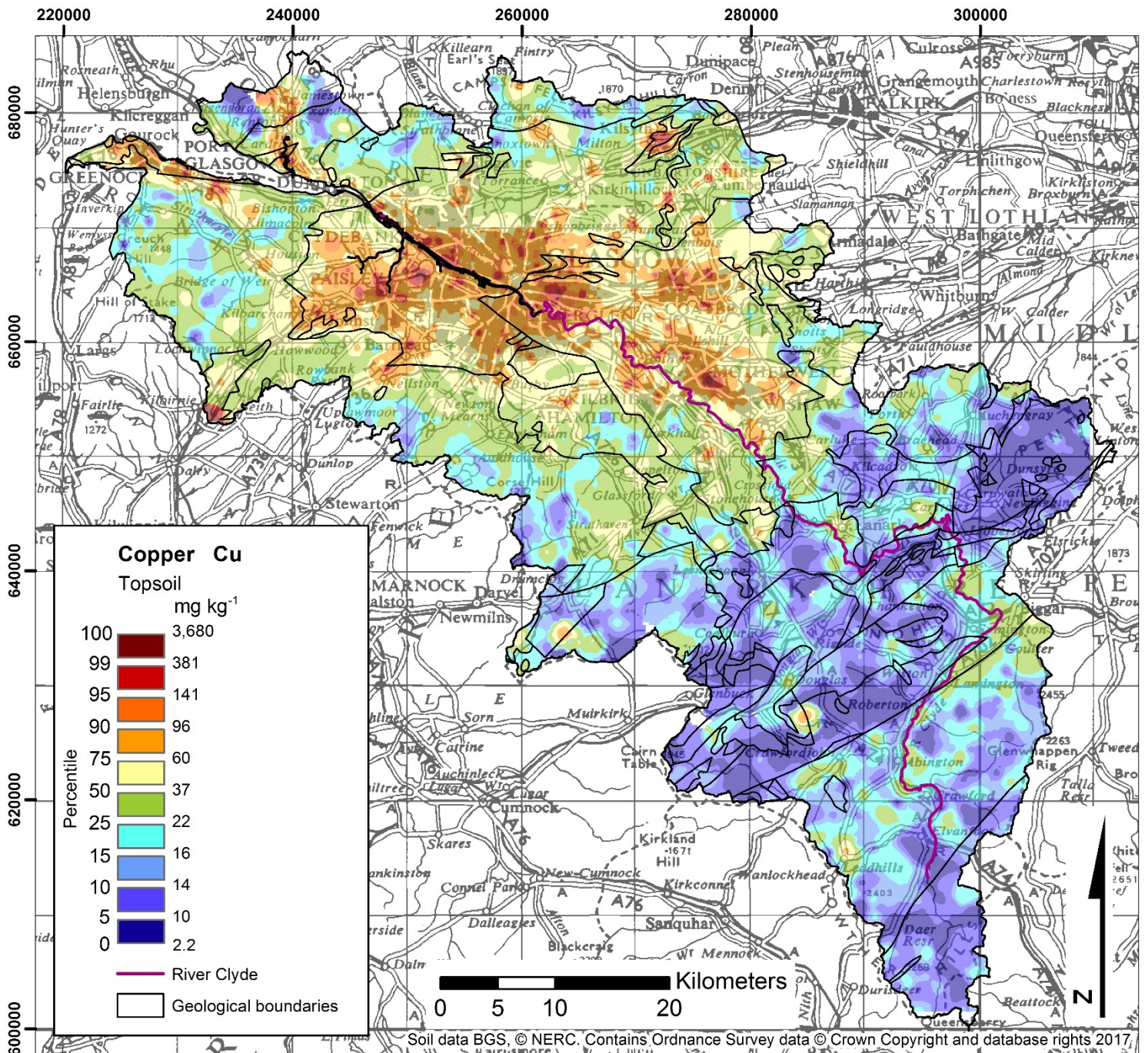
Copper concentrations are in the range 2.2 – 3680 mg kg⁻¹ in Clyde Basin topsoil. In rural areas, Cu is generally higher in topsoil collected over the Clackmannan and Strathclyde Groups and Scottish Coal Measures Group (> 22 mg kg⁻¹) than over the other sedimentary units, probably reflecting a greater proportion of organic-rich coal and shale lithologies. Concentrations of topsoil Cu are marginally higher over igneous rock types (probably related to mafic soil parent material) than over the Proterozoic metasedimentary rocks in the south of the Basin. A number of anomalies are associated with areas of Cu mineralisation, including those at Drumshantie, Gourrock (although the Cu anomaly here is swamped by urban pollution) and Kaim in the northwest of the area, and Leadhills in the south (Locations 1, 3 and 11, Figure 3). Copper-barium mineralization is reported also at Lochwinnoch (BGS, 1993) in the west of the region, which may account for higher Cu in topsoil in this area. However, historic coal and ironstone extraction was once active in the vicinity also.

Concentrations of Cu are elevated in urban relative to rural topsoil in the Clyde Basin regardless of the underlying bedrock type. Indeed, based on median values, the Cu content in urban topsoil (50 mg kg⁻¹) is over twice that of rural soil (21 mg kg⁻¹), indicating that anthropogenic pollution is an important source of Cu.

In addition to widespread topsoil Cu enrichment across the urban environment, a number of specific anomalies are associated with former and current industrial sites. In the east of the area, these include the former Ravenscraig steel mill in Motherwell (Location 26, Figure 3), and the former metal processing centres of the East End of Glasgow and Airdrie–Coatbridge. More generally, higher topsoil-Cu was measured in several urban centres, including those of Paisley and Barrhead southwest of Glasgow and Kilsyth in the north of the area.

The distribution of topsoil-Cu in the region is similar those of both germanium (Ge) and zinc (Zn) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Iodine

I

Environmental behaviour

Iodine (I) has five main oxidation states (-1, +1, +3, +5 and +7) and is the least abundant halogen element, but nevertheless is present throughout the Earth's crust at an average concentration of 0.3 mg kg⁻¹ (Muramatsu and Wedepohl, 1998). Iodine minerals are either soluble iodides e.g. iodemolite Ag(Cl,Br,I), or insoluble iodates e.g. schwartzenbergite Pb₅I₃O₃Cl₃O₃ (Fleischer, 1966). Iodine occurs also in common rock-forming minerals, where it can substitute for anions such as SiO₄⁴⁻, ClO₄⁻ and CO₃²⁻ (Davies, 1980). Low concentrations of the element are reported for igneous and magmatic rocks (<0.02 mg kg⁻¹ to 1.9 mg kg⁻¹) (Fuge and Johnson, 1986). Iodine concentrations in clastic sedimentary rocks are considered to be higher than those of igneous rocks (Butler, 1999), and are highest in organic-rich sedimentary rocks (Cosgrove, 1970). Adsorption of iodine onto clay minerals also enhances I levels in clay-rich sedimentary rocks (Becker et al., 1972).

Iodine is very soluble and mobile under most environmental conditions; weathering processes release approximately half the I present in rocks as water-soluble compounds, mainly iodide (Fuge and Johnson, 1986). In general, soil contains significantly more I than the parent material, as the volatilisation of I from the oceans and terrestrial environments is an important environmental source of the element. This is subsequently deposited in soil by both wet and dry deposition. The ability of soil to retain I is a key control on its distribution. Iodine is strongly sorbed to soil organic matter; hence, peatlands are a major sink for the element. Soil Al and Fe oxides and to a lesser extent clays also adsorb soil-I. Soil developed over carbonate lithologies such as limestone are enriched in the element relative to other rock types, because in circumneutral-alkaline environments, volatilisation of I is restricted as the element is present in IO₃⁻ form (Fuge and Johnson, 2015).

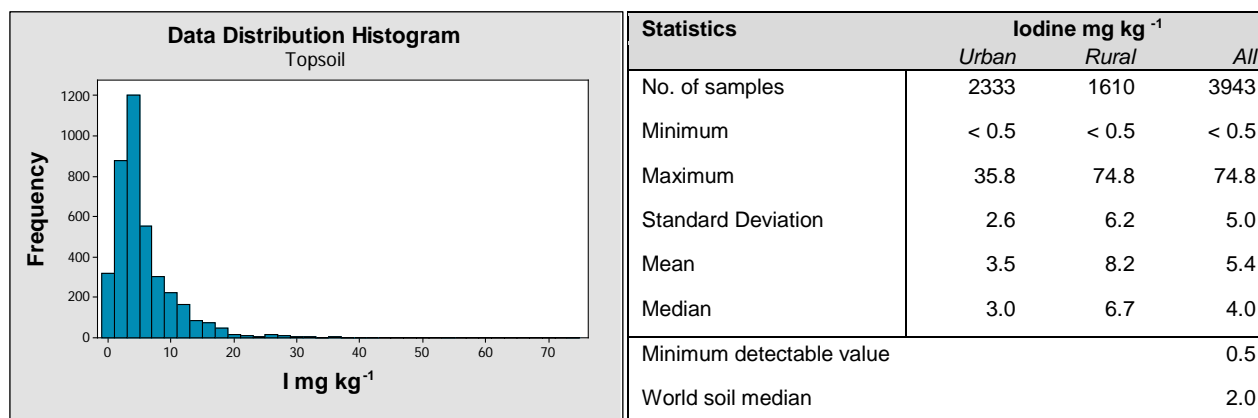
The main anthropogenic source of iodine is nuclear fallout; natural sources are more important (Reimann and Caritat, 1998).

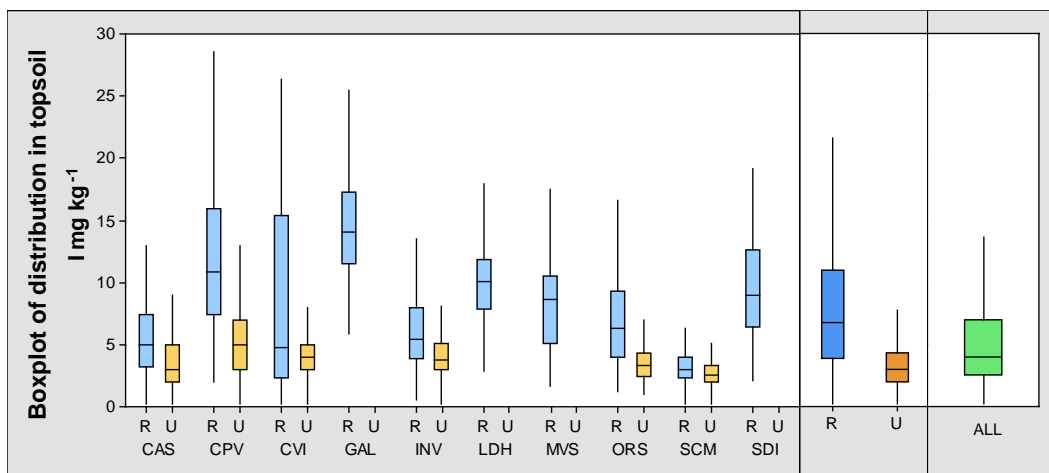
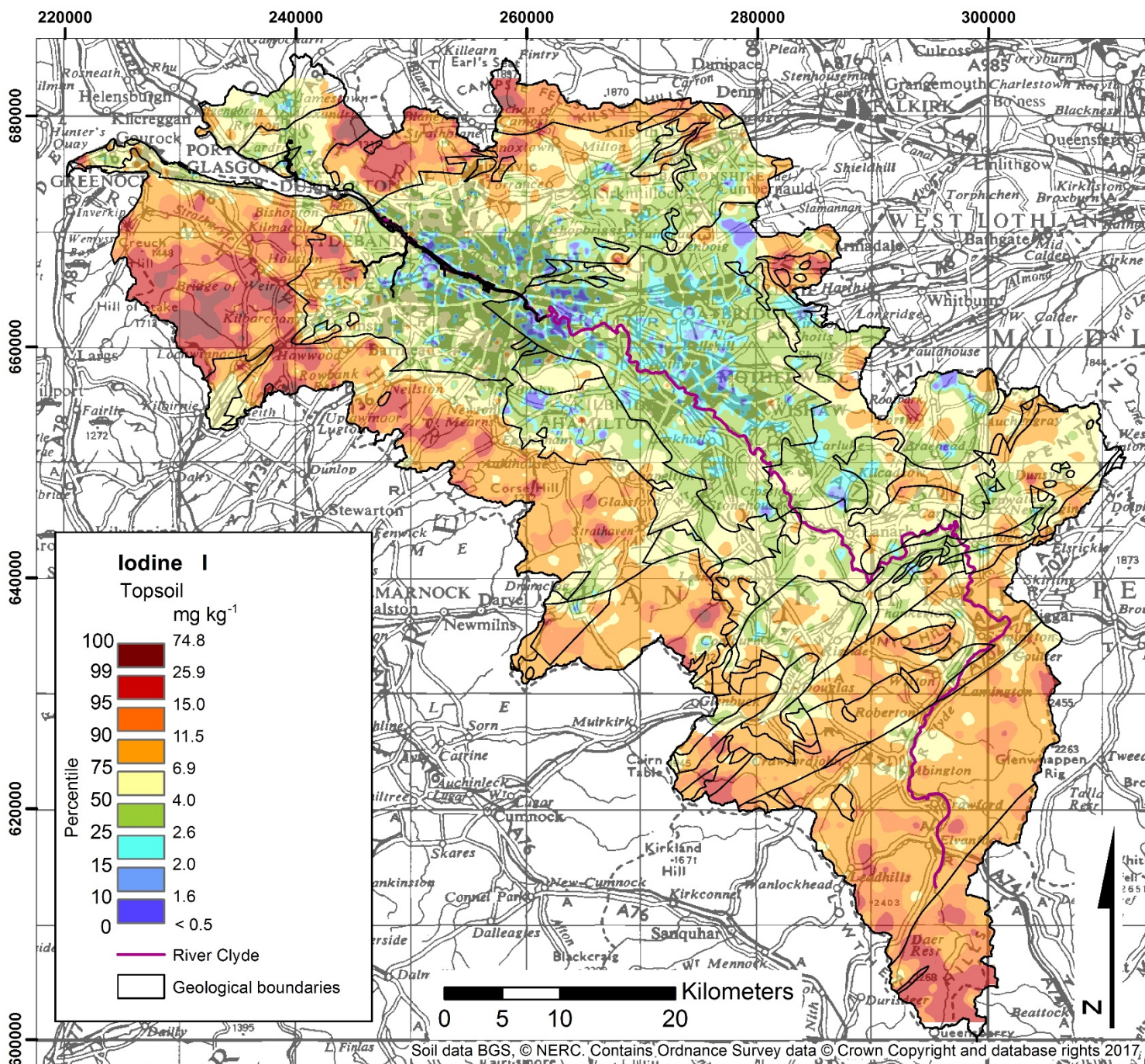
Iodine is an essential trace element for human and animal life. Insufficient dietary I causes several medical conditions known as iodine deficiency disorders (IDDs), which include goitre and mental impairment. Worldwide, IDDs affect over 740 million people (WHO, 1996).

Clyde Basin topsoil

Topsoil iodine contents range from < 0.5 to 74.8 mg kg⁻¹ in the region. In the rural environment, topsoil-I is largely controlled by the presence of organic-rich soil in the upland and peaty areas on the periphery of the Clyde Basin. It shows a strong spatial correlation with LOI in both rural and urban environments, reflecting this organic matter association. The mechanism by which I is drawn-down from the atmosphere and incorporated into organic-rich soil is the main control on I distribution. As a result, I concentrations are lower in urban than rural topsoil reflecting the greater extent of organic-rich soil in the rural environment.

The distribution of topsoil-I in the region is broadly similar those of bromine (Br), chlorine (Cl) and sulphur (S) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Iron

Fe

(Concentrations are expressed in Fe₂O₃ wt%)

Environmental behaviour

Iron (Fe) has two main oxidation states (+2 and +3) and is the fourth most abundant element constituting 5 % of the Earth's crust. With both lithophile and chalcophile properties, it forms several common minerals including pyrite (FeS₂), magnetite (Fe₃O₄), haematite (Fe₂O₃), and siderite (FeCO₃), but is also present in many rock-forming minerals including micas, garnets, amphiboles pyroxenes and olivine. Iron is generally enriched in mafic (9.6 wt%) relative to felsic (2.2 wt%) igneous rocks. In sedimentary rocks, clay, shale and greywacke typically contain higher concentrations (6.7 wt%) than sandstone (1.5 wt%) and carbonate rocks (0.5 wt%). Sedimentary ironstone may contain more than 30 wt% (Williamson, 1999). Iron is a major constituent of soil and is generally present in ferro-magnesium silicate minerals (Fe²⁺) or iron oxides and oxyhydroxides (Fe³⁺). The mobility of Fe is largely controlled by the solubility of Fe oxides, and is dependent on the oxidation state of the compounds present and the pH and redox conditions. Iron oxides are more likely to precipitate and immobilise Fe under oxidising alkaline conditions; hence, Fe is more mobile in acid soil and reducing environments (Kabata-Pendias, 2001).

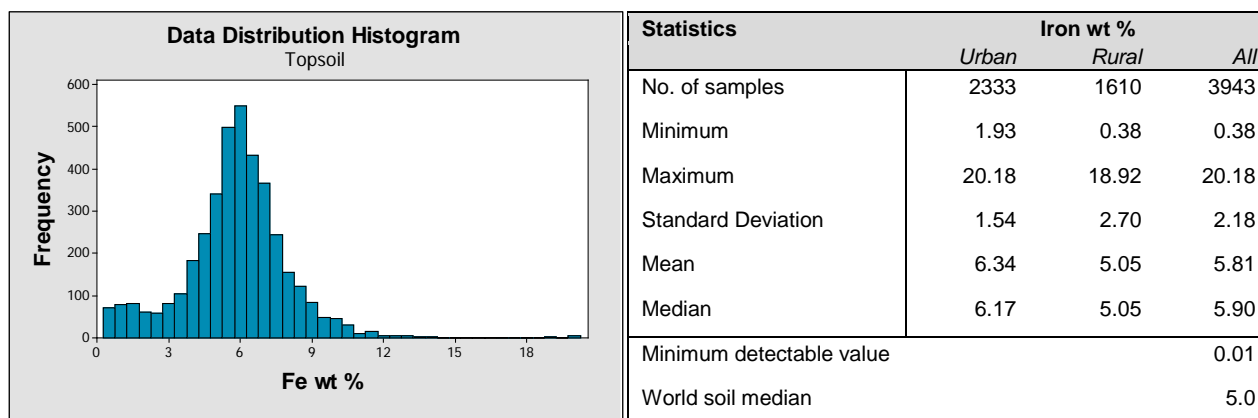
Anthropogenic sources of iron include the iron and steel industry, sewage and iron-mining dust (Reimann and Caritat, 1998). Iron is an essential nutrient for plants and animals and is involved in the production of haemoglobin in red blood cells (WHO, 1996).

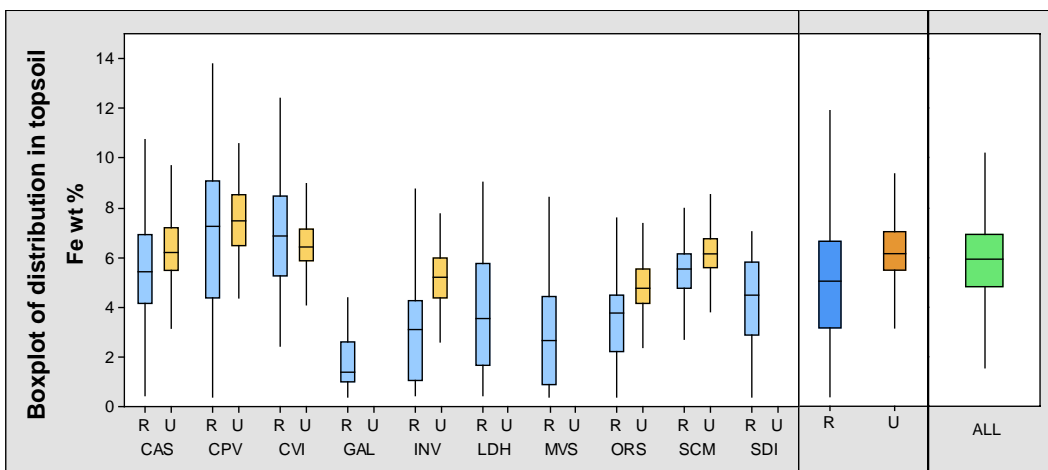
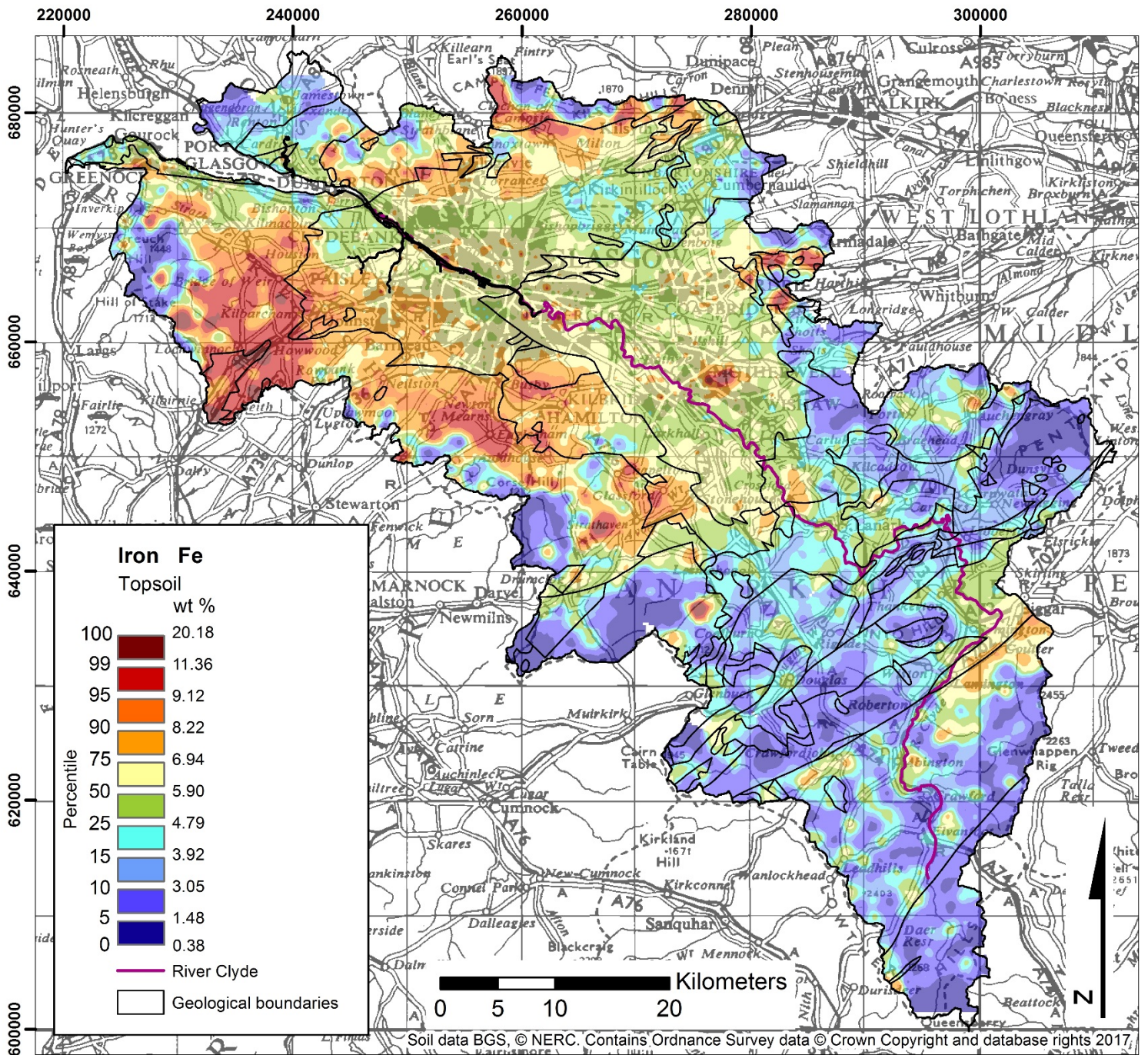
Clyde Basin topsoil

Concentrations of Fe in topsoil range from 0.38 to 20.18 wt% in the region. In the rural areas of the Clyde Basin, the distribution of topsoil Fe is predominantly related to igneous lithologies. Iron is generally higher (> 6.94 wt%) in brown-earth and gleyed soil types overlying the extrusive igneous rocks of the Clyde Plateau Volcanic Formation (CPV). However, Fe content is lower in upland, peaty soil that has formed over the same geology, reflecting mineral versus organic soil composition. As the CPV consists of a range of igneous rock types, Fe concentrations are not uniformly high across the whole outcrop. Topsoil Fe anomalies, related to mafic igneous intrusions of the Clyde Volcanics also occur to the east of Moffat Mills, Airdrie (Location 23, Figure 3). Higher soil-Fe contents proximal to the Southern Upland Fault between Coulter and Lamington correspond to higher Ti and Mn in soil also. This may reflect basalt-dominated detritus in the underlying Marchburn Formation of the Leadhills Supergroup. However, the mobility of Fe may be enhanced by the presence of coniferous forestry in the area. Topsoil Fe concentrations over the Scottish Coal Measures and Clackmannan and Strathclyde Groups are higher (> 5.9 wt%) than over the other sedimentary bedrock units. This is likely to relate to the occurrence of ironstone beds in these geological successions.

Topsoil Fe anomalies at Misty Law and Logan Water (Locations 14 and 38, Figure 3) in the northwest and south of the area respectively, are related to higher levels of Mn, and can be attributed to secondary processes concentrating Fe (and Mn) in a locally acidic, waterlogged surface environment. However, ferruginous mineralisation at Misty Law may influence soil chemistry also (BGS, 1993).

Iron is marginally elevated in the urban relative to the rural topsoil, suggesting the presence of diffuse anthropogenic pollution. In the east of the area, a very noticeable Fe anomaly occurs at the site of the former steelworks at Ravenscraig (Location 26, Figure 3) due to pollution from industrial processes. Smaller Fe anomalies associated with former and current industrial sites are seen at Rutherglen (Location 19, Figure 3), and the former oil shale/coal workings at Tarbrax (Location 32, Figure 3). Higher values are observed also at Lochwinnoch and Beith, southwest of Glasgow, where coal and ironstone were once extracted and processed.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Lanthanum

La

Environmental behaviour

Lanthanum (La) has one main oxidation state of (+3) and an average crustal abundance of 37 mg kg⁻¹ (Mielke, 1979). It is a lithophile element forming several minerals including the relatively common monazite ((Ce, La, Nd, Th, Sm)(PO₄SiO₄)) and rarer cerite ((Ce, La)₉(Mg, Fe)Si₇(O, OH, F)₂₈), though it is widely dispersed at trace levels in several rock-forming minerals such as biotite, apatite, pyroxenes and feldspars. It has an affinity for felsic (45 – 55 mg kg⁻¹) rather than mafic igneous rocks (< 10 mg kg⁻¹), and is held in resistate mineral phases such as monazite, and in feldspars and clays in sedimentary rocks. As such, shale and greywacke tend to contain more of the element (50 mg kg⁻¹) than sandstone and limestone (1 – 30 mg kg⁻¹) (Mielke, 1979).

Lanthanum has very low mobility under most environmental conditions, mainly due to the very low solubility of the phosphate (LaPO₄). As a light rare earth element (REE), it is preferentially adsorbed onto organic matter compared with heavier REEs (Leleyter et al., 1999). All REEs tend to be enriched in alkaline rather than in acid soil; this is likely to be due to the easy removal of their hydroxide complexes (Kabata-Pendias, 2001).

Anthropogenic sources of La include mining and processing of alkaline rock, but natural sources are considered to be more important than anthropogenic ones (Reimann and Caritat, 1998).

Lanthanum is considered biologically inactive and non-essential, and has a low toxicity (Reimann and Caritat, 1998).

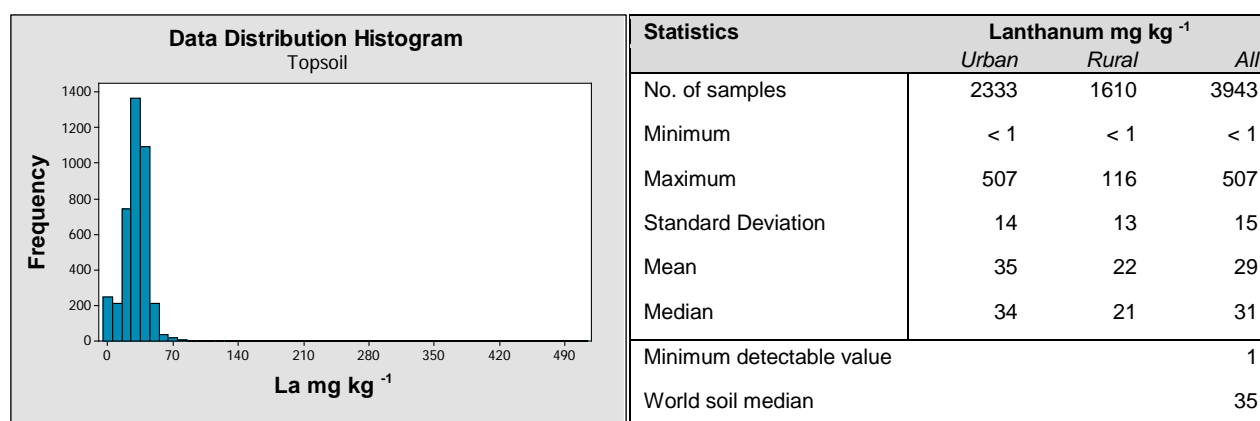
Clyde Basin topsoil

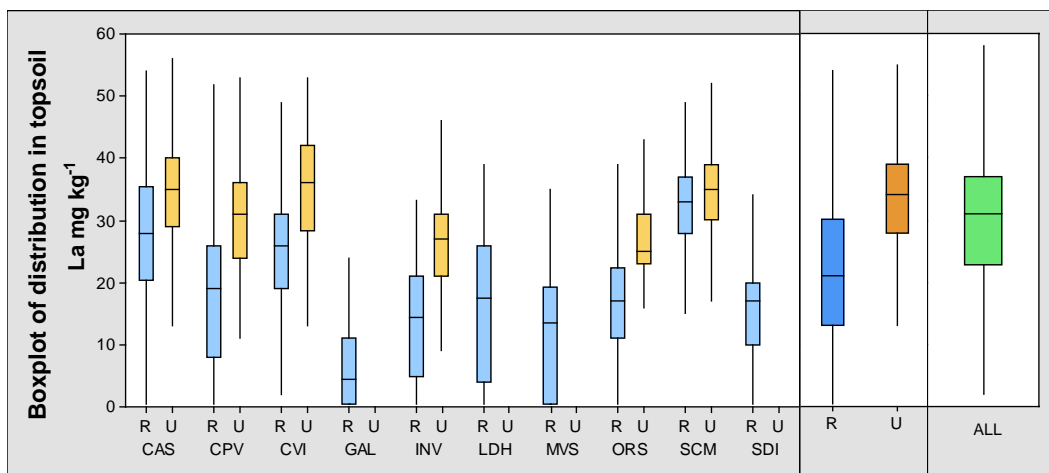
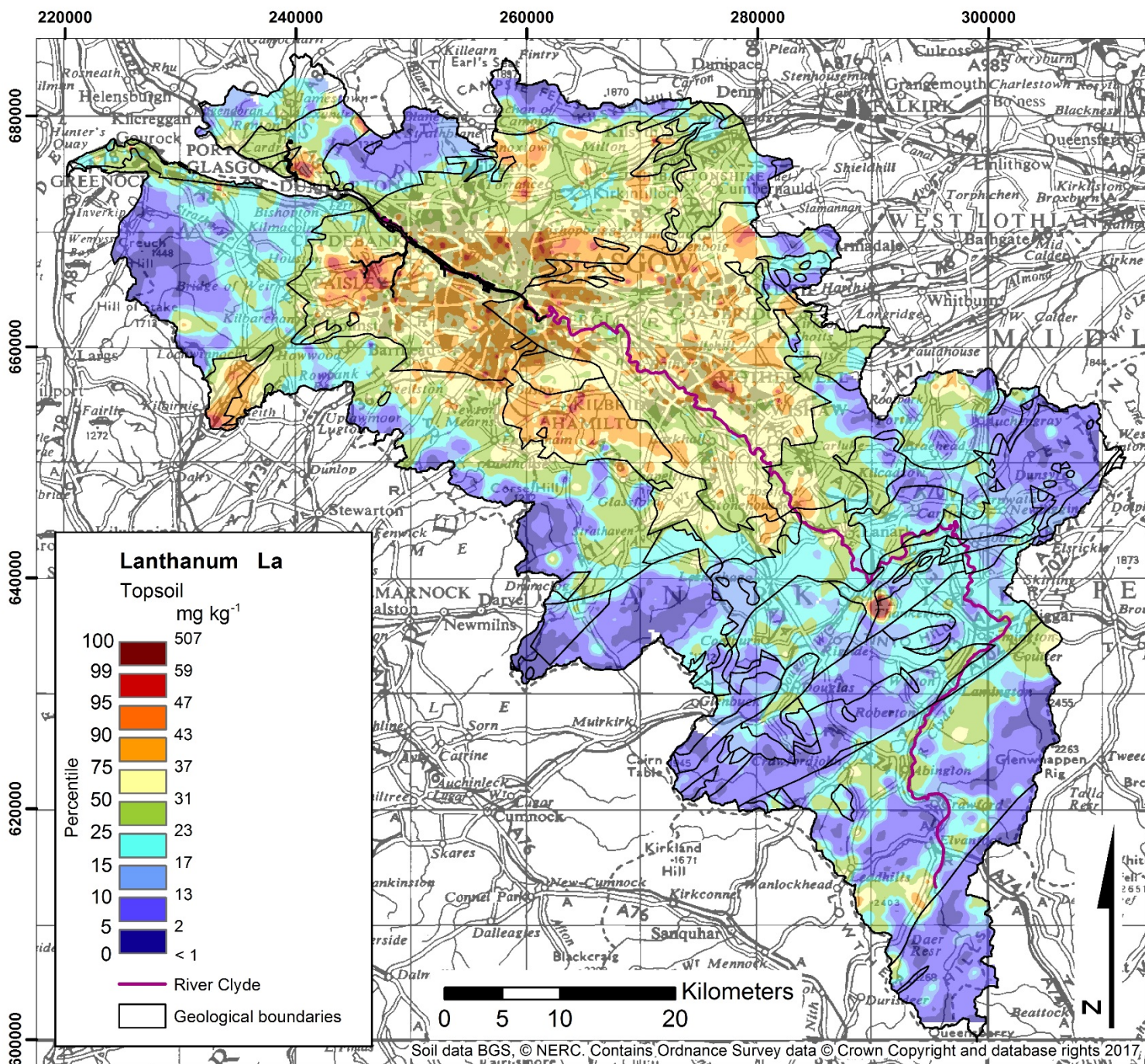
Topsoil La concentrations are in the range < 1 – 507 mg kg⁻¹ in the area. The distribution of topsoil La in the rural parts of the Clyde Basin appears to relate predominately to soil pH and organic matter content (as shown by LOI). Lower values (< 13 mg kg⁻¹) are associated with upland peaty soil on the periphery of the Basin, which is characterized by low pH also. The distribution of lower topsoil La concentrations more closely follows low soil pH than it does high LOI, suggesting that pH is the main controlling factor.

Other natural factors that may influence La distribution include the clay content of soil; a La anomaly, which is not explained by low soil pH, is reported in an area of clay soil at Crossford, south of Carluke in the centre of the area. In urban and rural areas, topsoil over both the Clackmannan and Strathclyde Group (CAS), and the Scottish Coal Measures Group contains higher average La values compared to other sedimentary successions, reflecting the calcareous nature of these units.

On average (median values), La concentration is significantly elevated in urban areas across all rock types, compared to rural topsoil. This largely reflects the CAS parent material underlying the urban areas, but building rubble, slag and artificial ground materials, which are generally calcareous in nature, may also influence its concentration in urban soil. A specific anomaly is seen at Greengairs landfill site (Location 22, Figure 3) in the east of the area, which is lined with clay.

The distribution of topsoil-La in the area is broadly similar to a number of other elements, including other REEs such as cerium (Ce), neodymium (Nd), samarium (Sm), ytterbium (Yb) and yttrium (Y), as well as bismuth (Bi), germanium (Ge) and thorium (Th) (see Appendix 1). Although the majority of topsoil samples did not contain Bi, Sm, and Yb in concentrations above the lower limit of detection, they are considered to have similar controls on their dispersal in Clyde Basin topsoil.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Environmental behaviour

Lead (Pb) has two main oxidation states (+2 and +4) and an average crustal abundance of 13 mg kg⁻¹. It is a chalcophile metallic element forming several important minerals including galena (PbS), anglesite (PbSO₄), cerussite (PbCO₃) and (Pb₃O₄), but is also widely dispersed at trace levels in common minerals, which include K-feldspar, plagioclase, micas, zircon and magnetite, and as such is more abundant in felsic (15 – 19 mg kg⁻¹) rather than mafic (1 – 6 mg kg⁻¹) igneous rocks (Mielke, 1979). Lead has an affinity for organic matter in the environment; hence, concentrations in black shale (up to 100 mg kg⁻¹) are higher than in sandstone and limestone (5 – 10 mg kg⁻¹) sedimentary rocks (Alloway, 2013).

Lead mobility in the soil environment is limited, mainly by the low solubility of its sulphide, sulphate and carbonate compounds. It is limited also by the strong affinity of Pb for sorption by secondary Fe and Mn oxides, Al oxides, clay minerals, carbonate and phosphate particles and organic matter (Kabata-Pendias, 2001). Sulphides such as galena may be oxidised to sulphate at high Eh, but the sulphate produced is itself highly insoluble, and may form a protective crust on the galena grains. Below pH 5.2, it becomes mobile in non-calcareous soil, but is adsorbed preferentially before Cu and Zn on Fe oxides (O'Day et al., 1998); therefore, does not migrate readily (Martinez and Motto, 2000).

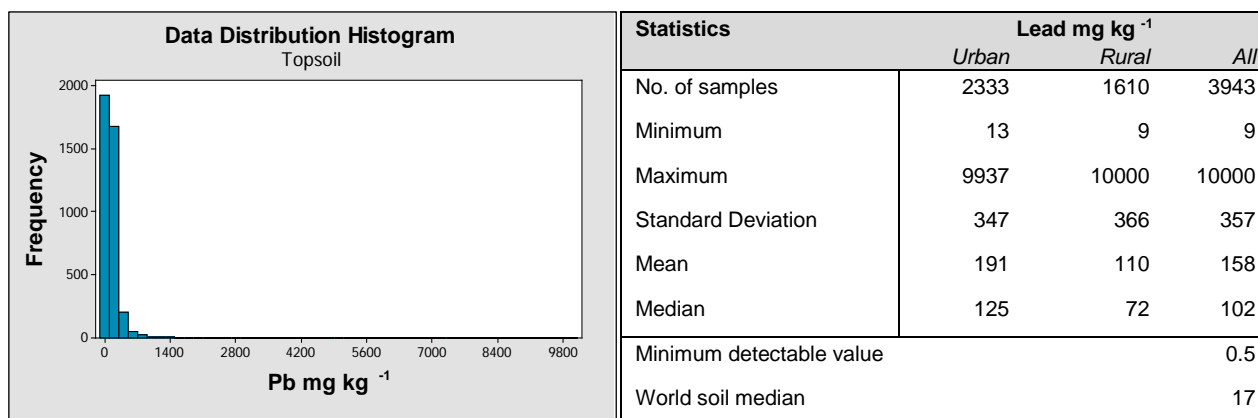
Anthropogenic sources of Pb include aerosols from car exhausts, (this had decreased in recent years with the introduction of Pb-free petrol), old Pb-based paints, pottery glazes, steel works, sewage sludge and smelting (Reimann and Caritat, 1998). Lead is biologically non-essential and is well known for its toxic properties. It can cause mental impairment in young children, and neuropathy and hypertension in adults (WHO, 1996).

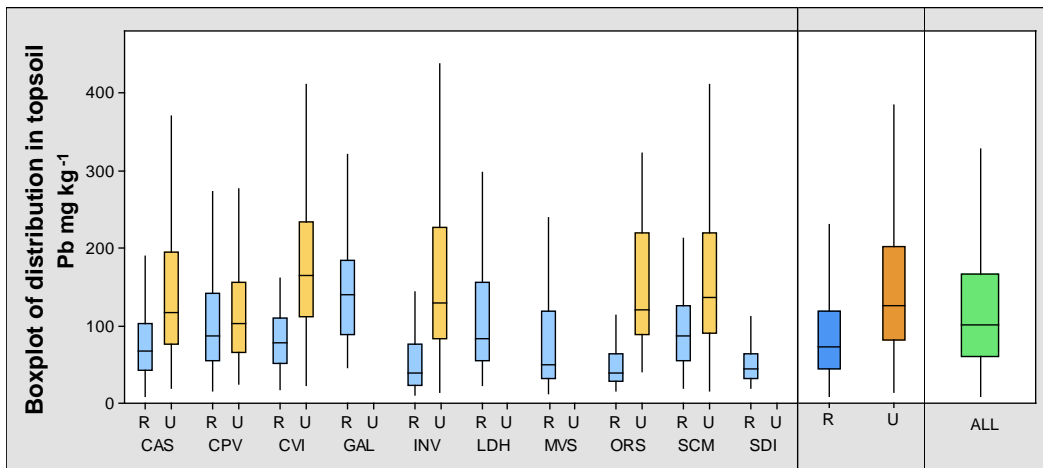
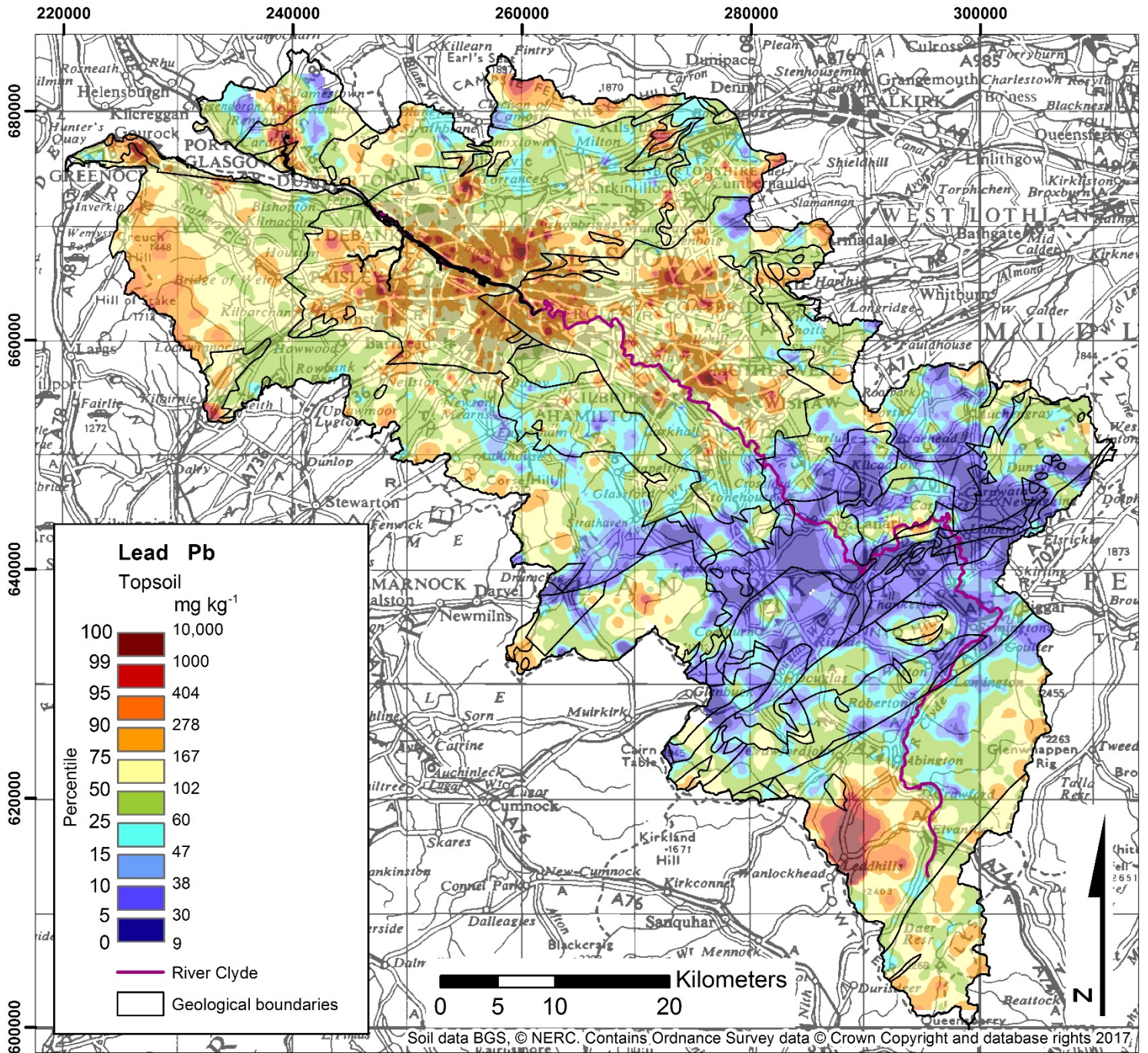
Clyde Basin topsoil

Topsoil Pb concentrations in the area range from 9 to 10,000 mg kg⁻¹. The most notable influence on the distribution of topsoil Pb in the Clyde Basin is the former Leadhills mining area in the south of the region (Location 11, Figure 3). Within the mining district, concentrations range from 74 mg kg⁻¹ to very high values of 10 000 mg kg⁻¹. By contrast, Pb concentrations in non-mineralised/mined Clyde Basin rural soil range between 8 – 758 mg kg⁻¹. Upland peaty areas on the periphery of the Basin contain higher Pb concentrations as a result of atmospheric deposition and trapping of Pb in this organic-rich soil. Indeed, Cloy et al. (2008) have documented the atmospheric deposition of Pb and retention in Scottish peatlands. They demonstrated that it was greatest between the 1880s and 1960s, with annual rates of c. 10 – 40 mg m⁻² per year, declining to c. 0.44 – 5.7 mg m⁻² per year by the 2000s, because of the removal of Pb from petrol and reductions in coal usage and heavy industry. In contrast to the organic-rich soil, concentrations in rural mineral soil over the middle of the Clyde Basin, developed over Devonian and Carboniferous sediments, are notably lower (< 30 mg kg⁻¹).

Lead values in urban topsoil are generally elevated across the whole of the built-up area regardless of parent material, as a result of diffuse pollution. The element is spatially coincident with topsoil Cu and Zn reflecting industrial, transport and energy generation sources. The city centres across the area (Alexandria, Motherwell, Paisley, Milngavie, Kilsyth, Airdrie, Coatbridge and Glasgow city) show elevated topsoil Pb concentrations (> 167 mg kg⁻¹), commensurate with greater traffic densities; and former use of Pb in petrol as well as historic industrial and domestic use of coal and lead-bearing paint. Indeed, investigations using Pb-isotope analysis on a sub-set of the G-BASE soil samples from Glasgow revealed that the Pb is derived from a combination of petrol, coal and paint sources (Farmer et al., 2011).

Point sources of Pb pollution are evident also; higher values are associated with the former iron and steel works at Beith, southwest of Glasgow and Ravenscraig (Location 26, Figure 3) and the former fire clay and coal mines at Newmains in Wishaw (Location 28, Figure 3) in the east of the area.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Manganese

Mn

(Concentrations are expressed in MnO wt%)

Environmental behaviour

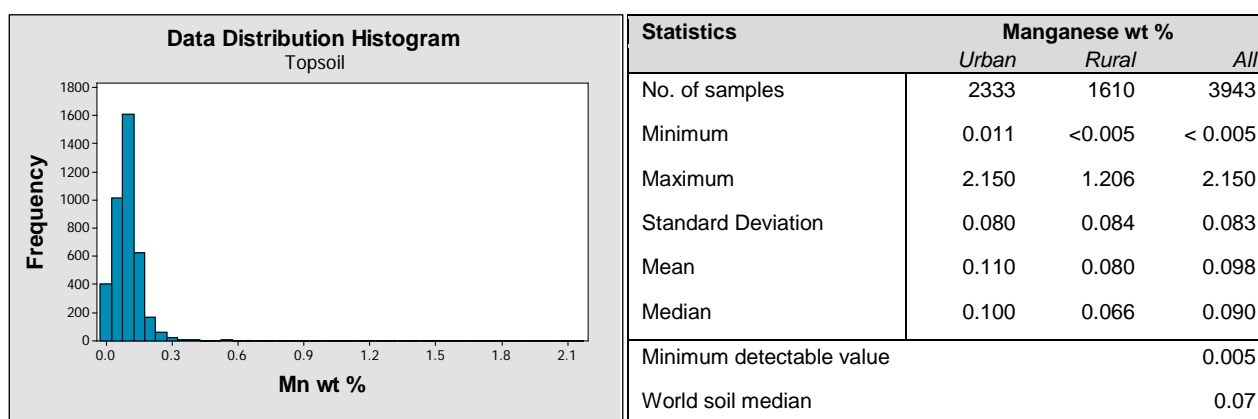
Manganese (Mn) has several oxidation states (+2, +3, +4, +6 and +7) and an average continental crustal abundance of 0.1 wt% (Wedepohl, 1995). It is a common lithophile element forming several minerals including pyrolusite (MnO₂), rhodocrosite (MnCO₃), manganite (MnO(OH)) and several oxides in sedimentary rocks. It is widely distributed as an accessory element in garnets, olivine, pyroxenes, amphiboles and calcite. The element is partitioned into mafic (0.2 wt%) rather than felsic (0.05 - 0.07 wt%) igneous rocks (Mielke, 1979). In sedimentary rocks, Mn concentrations are generally higher in shale, greywacke and limestone (0.07 – 0.09 wt%) than in sandstone (0.02 wt%) (Wedepohl, 1978). Manganese has generally low mobility in the environment, especially under oxidising conditions, as the Mn³⁺ and especially Mn⁴⁺ ions form insoluble oxyhydroxides, which are the main mineral forms found in soil (Uren, 2013). However, Mn is greatly influenced by redox and is easily mobilised as Mn²⁺ in anoxic conditions (Hylander et al., 2000). In temperate acid conditions, Mn is mobilised from soil as bicarbonate or organic complexes. Manganese oxides themselves adsorb many trace metals and bind with organic matter (Kabata-Pendias, 2001). Anthropogenic sources of Mn include mining and smelting, engineering, traffic and agriculture. However, geogenic sources are more important than anthropogenic ones (Reimann and Caritat, 1998). Manganese is biologically active and is an essential trace element for all organisms. Manganese deficiency is more common in humans than toxicity, causing impaired reproduction and growth (Mertz, 1987).

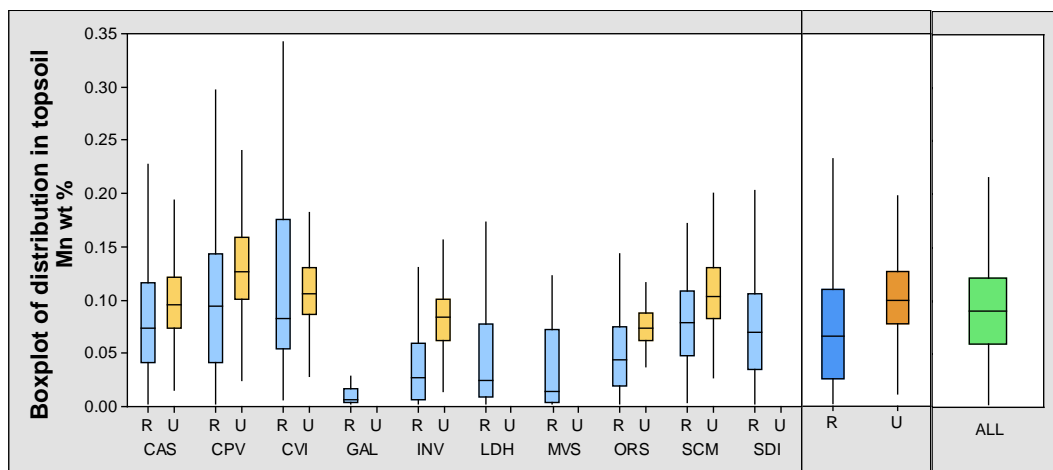
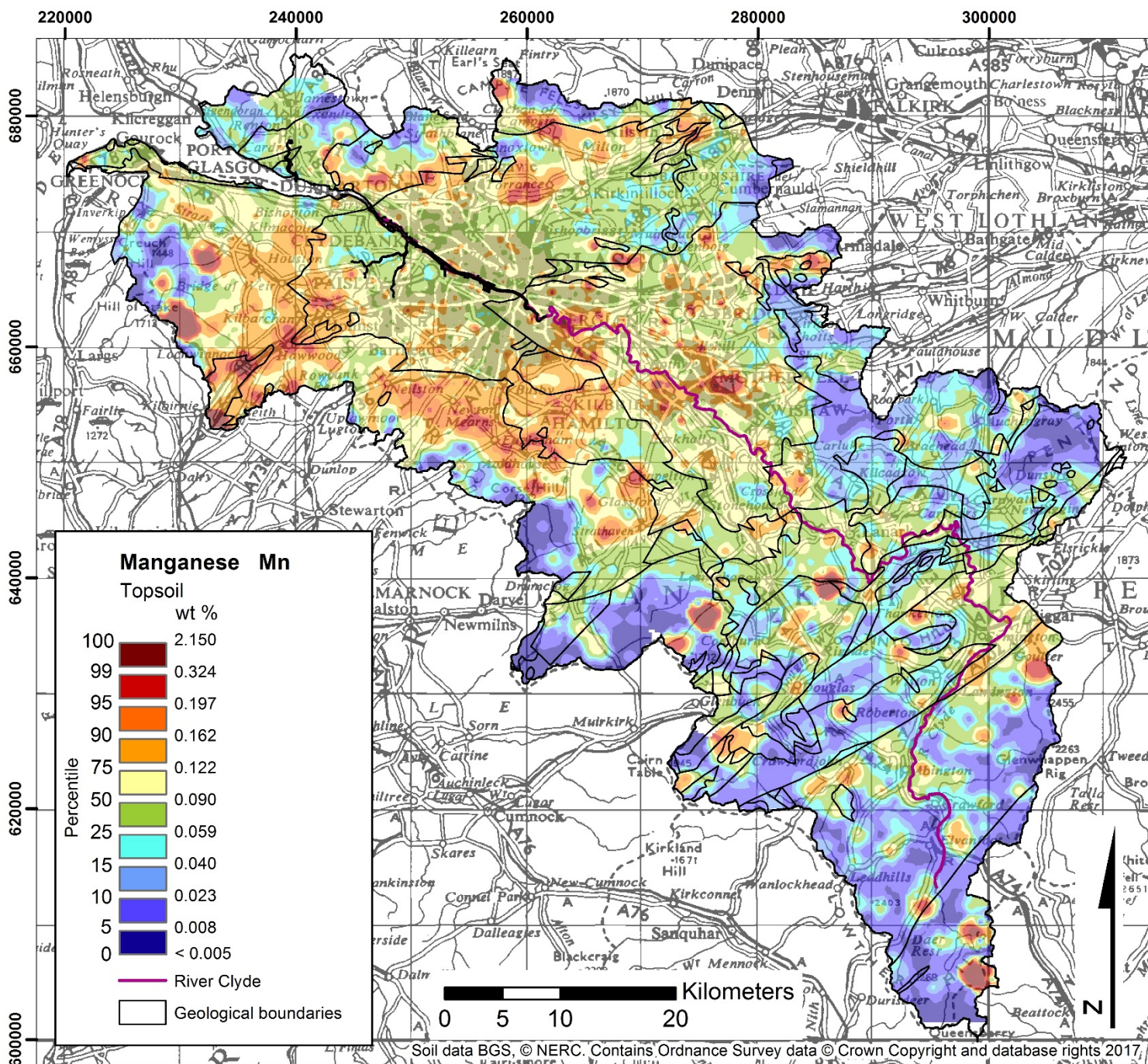
Clyde Basin topsoil

Topsoil Mn concentrations are in the range < 0.005 – 2.15 wt% in the region. In rural areas of the Clyde Basin, the distribution of higher topsoil Mn is mainly influenced by underlying igneous lithologies. Manganese is generally higher (> 0.122 wt%) in brown-earth and gleyed soil overlying the extrusive igneous rocks of the Clyde Plateau Volcanic Formation. It is not uniformly high across the outcrop, reflecting the variable geochemical composition of the lavas comprising this formation. Higher values may be influenced by mineralisation at Misty Law (Location 14, Figure 3) (BGS, 1993) in the northwest of the area. Soil-Mn content may also reflect secondary oxyhydroxide formation in these acidic upland environments. Manganese shows a negative spatial association with peaty soil and LOI in these areas, suggesting that it is hosted in the mineral soil component, which has weathered from the underlying igneous soil parent material, rather than in soil organic matter. High topsoil Mn values (> 0.197 wt%) also correspond to igneous intrusions of the Clyde Volcanics, which outcrop east of Moffat Mills, Airdrie (Location 23, Figure 3). Topsoil Mn concentrations are also higher over the Scottish Coal Measures and Clackmannan and Strathclyde Groups than over the other sedimentary bedrock units in the area. These lithologically controlled concentrations of Mn are closely related to that of Fe over the same bedrock rock and soil types.

Numerous topsoil Mn anomalies correspond to areas of marshy ground and of coniferous forestry across the Basin. Those at Linwood Moss and Logan Water (Locations 17 and 38, Figure 3), in the west and south of the area respectively, are related to high concentrations of Fe also. Whilst these are predominately found in rural soil, high values are associated with an area of low-lying lochs and peat in the north of Glasgow. These enrichments can be attributed to secondary processes concentrating Mn in locally acidic, waterlogged surface environments.

On average (median values), Mn is elevated in urban topsoil regardless of parent material type, suggesting the presence of diffuse anthropogenic pollution. In the east of the area, specific sites where Mn anomalies are related to industrial activity include the former steelworks at Ravenscraig (Location 26, Figure 3), the industrial centre of Rutherglen, and former Tarbrax oil shale/coal works (Locations 19 and 32, Figure 3). Anomalously high values are observed also around Lochwinnoch and Beith, southwest of Glasgow, these may be related to historic coal and ironstone extraction and iron foundry works at Beith.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Molybdenum

Mo

Environmental behaviour

Molybdenum (Mo) has five main oxidation states (+2, +3, +4, +5 and +6) and an average crustal abundance of 1.2 mg kg⁻¹ (Mielke, 1979). It is a chalcophile or siderophile metallic element forming several minerals including molybdenite (MoS₂), wulfenite (PbMoO₄) and powellite (Ca(Mo, W)O₄). However, it is more widely present at trace levels in association with organic matter and sedimentary sulphides, notably in black shales, which typically contain elevated concentrations of the element (70 mg kg⁻¹) relative to other sedimentary rocks (0.2 – 2.6 mg kg⁻¹) (Mielke, 1979; Wedepohl, 1978). It also occurs in the rare tungsten minerals scheelite and wolframite. Molybdenum is able to substitute into a number of sulphide minerals including pyrite, galena and sphalerite, as such it is a frequent accessory component of metal ores (Ure and Berrow, 1982). It behaves incompatibly in the magmatic environment, and does not readily substitute into rock-forming silicate minerals; hence its concentration in igneous rocks is generally low (0.3 – 1.5 mg kg⁻¹) (De Vos and Tarvainen, 2006; Mielke, 1979).

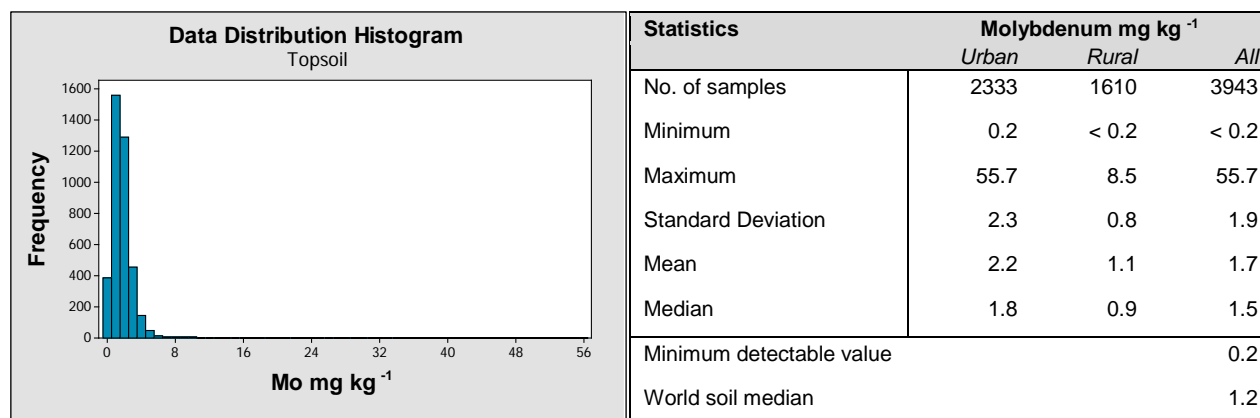
In soil, Mo is typically associated with Fe and Al oxides and is strongly complexed with organic matter. Molybdenum is unusual in that it is present in soil in anionic form and is mobile under oxidising acid to alkaline conditions. During weathering, the oxidation of Mo-minerals releases molybdate anions, which are easily adsorbed by sesquioxides and clays or co-precipitated with organic matter. Fixation to organic matter is greater at lower pH (Alloway, 2013).

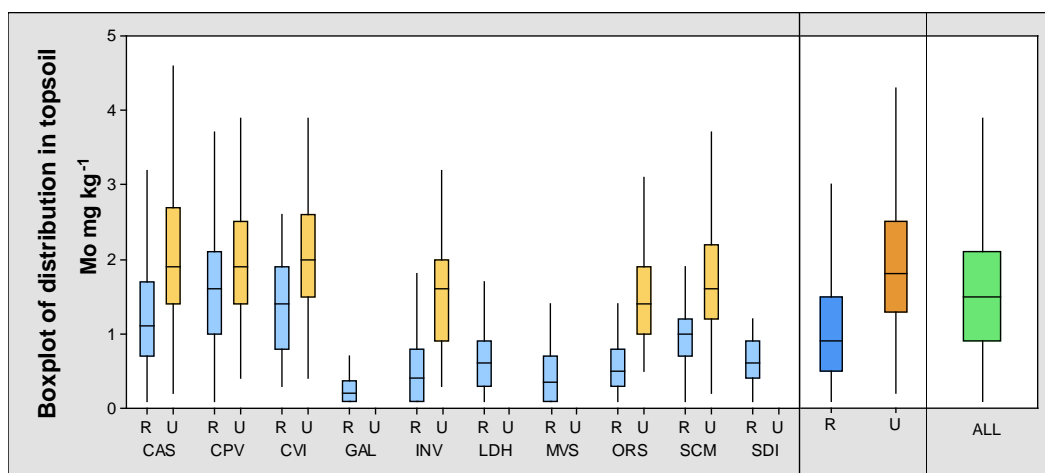
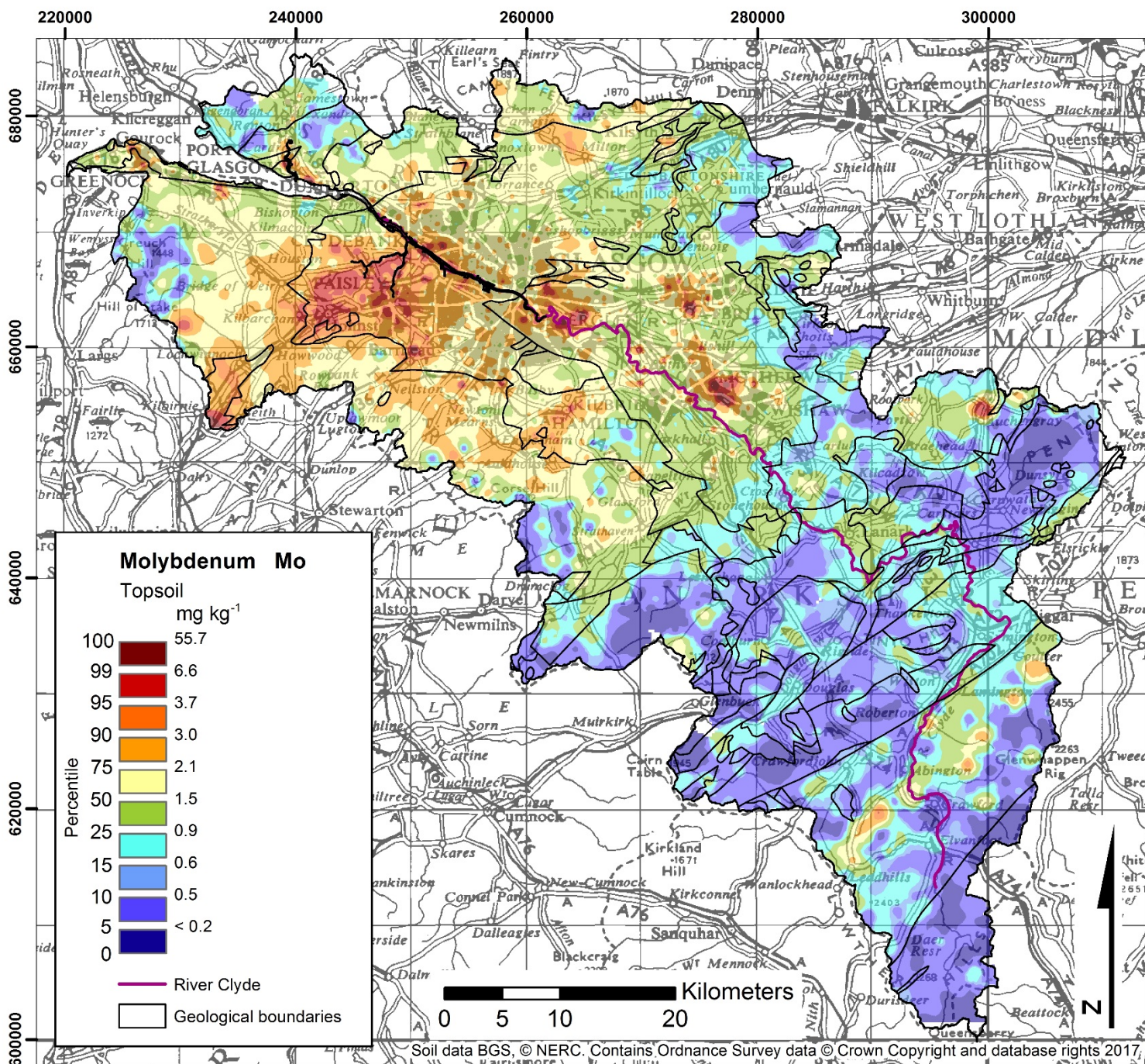
Anthropogenic sources of Mo include Mo-mining and smelting, steel works, oil refining, combustion of fossil fuels, ceramics, phosphate fertilizers and sewage sludge (Reimann and Caritat, 1998). Molybdenum is essential for all organisms; symptoms of deficiency include coma and night blindness. In plants, it has a role in nitrogen fixation. However, it can be toxic at high levels especially to cattle and sheep. Molybdenum intoxication reduces the uptake of Cu in animals, and leads to skeletal deformities (WHO, 1996).

Clyde Basin topsoil

Concentrations of Mo in topsoil range from < 0.2 to 55.7 mg kg⁻¹ in the area. In the rural Clyde Basin, on average (median values) topsoil Mo concentration is higher (> 0.9 mg kg⁻¹) over the Scottish Coal Measures Group, and Clackmannan and Strathclyde Groups than over the other sedimentary rock types. This reflects the greater proportions of coals and shales within these geological units. In the south of the area, a northeast – southwest trending linear set of higher values within the Leadhills Supergroup, stretching approximately from the south of Biggar to north of Wanlockhead, relates to the outcrop of the Moffat Shale Group black shales. Both these enrichments are associated with organic-rich bedrock lithologies; since Mo is strongly complexed by organic matter, particularly in the reducing marine environment in which these shale lithologies were deposited. Topsoil Mo concentrations are higher on average over the Clyde Plateau Volcanic Formation than most other lithologies in the area, reflecting magmatic Mo-enrichment in the more evolved andesitic-felsic and trachyte lavas of the succession (BGS, 1993). In the northwest of the region, higher concentrations at Misty Law (Location 14, Figure 3) and in the Lochwinnoch area may relate to Ba-Cu mineralization. However, coal and ironstone extraction and Fe foundries in Beith may also account for the elevated concentrations in this region.

Molybdenum concentrations are elevated in urban relative to rural topsoil regardless of parent material, indicating anthropogenic sources have affected its distribution in the area. The median Mo concentration in urban topsoil (1.8 mg kg⁻¹) is twice that of rural topsoil (0.9 mg kg⁻¹). It is likely that the distribution of Mo in the urban environment can be attributed to diffuse pollution, probably due to industrial and domestic fossil fuel combustion. In the east of the area, specific anomalies are associated with the Ravenscraig former steel mill (Location 26, Figure 3), the former metal processing centres of the East End of Glasgow and Airdrie–Coatbridge. Similarly, in the west of the area, with shipbuilding in Clydebank and the former industrial centre of Paisley. In rural areas, anomalies at the former Tarbrax coal/oil shale works in the east (Location 32, Figure 3) and the landfill site at Linwood Moss in the west (Location 17, Figure 3) are evident also.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Phosphorus

P

(Concentrations are expressed in P₂O₅ wt%)

Environmental behaviour

Phosphorus (P) has three main oxidation states of (+5, +3 and -3). It is an abundant (0.1 % of the Earth's crust) lithophile/siderophile non-metallic element forming several minerals including apatite (Ca₅(PO₄)₃(F,Cl,OH), monazite ((Ce, La, Nd, Th, Sm)(PO₄SiO₄)) and xenotime (YPO₄). It is widely dispersed at trace levels in minerals such as olivine, pyroxenes, amphiboles and micas. The behaviour of P in igneous rocks is complex, but it shows a tendency to concentrate in basalts (0.25 wt%) rather than granites (0.14 – 0.21 wt%) (Wedepohl, 1978). Levels in shale are reported as 0.16 – 0.18 wt%; sandstones, 0.01 – 0.04 wt%; coals 0.03 wt% and carbonates, 0.09 wt%. High levels occur in rare sedimentary 'bone beds' containing abundant fossil phosphate, and in organic-rich black shales. Some sedimentary ironstones also contain high levels of P, usually strongly bound to the Fe oxides (Miekle, 1979).

Phosphorus is present as inorganic phosphate and in organic matter in soil. In neutral to alkaline conditions, P generally displays low mobility in the environment due to the low solubility of Al, Ca, Fe and Pb phosphates. In acid soil, P is mainly adsorbed to Al and Fe oxides and clays (Strawn et al., 2015). However, in low Ca acid environments, apatite is soluble. Organic matter and peat soil can accelerate the downward movement of P, where it is complexed with organic acids, Fe and Al oxides (Hue, 1991; Taylor and Eggleton, 2001).

Anthropogenic sources of phosphorus include fertilisers, waste water and detergents (Reimann and de Caritat, 1998).

Phosphorus is a key biological element and is essential for all organisms, although it is toxic as the element or oxide at very high doses. It is particularly crucial for plant growth and phosphorus as phosphate is an important fertiliser. However, excessive or improper use can lead to eutrophication in rivers, due to surface run off from fields (Armstrong, 1999).

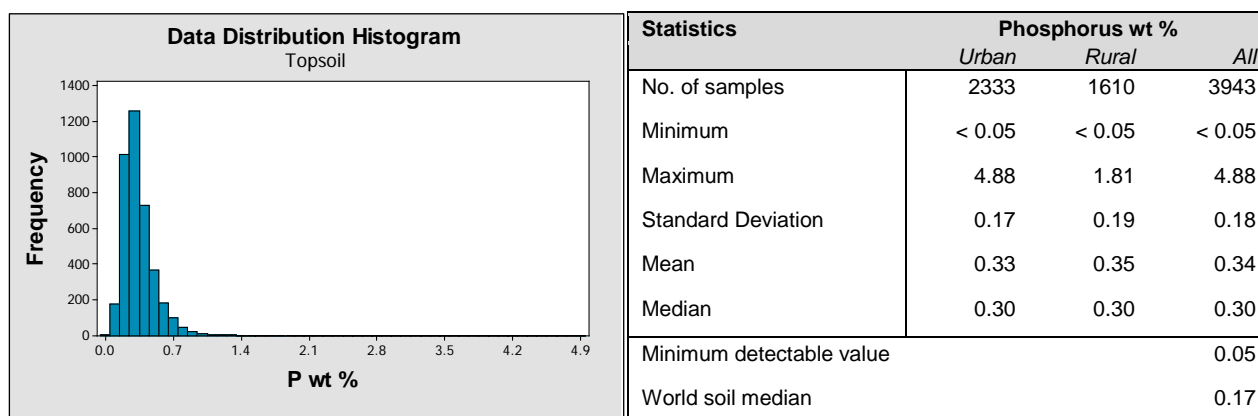
Clyde Basin topsoil

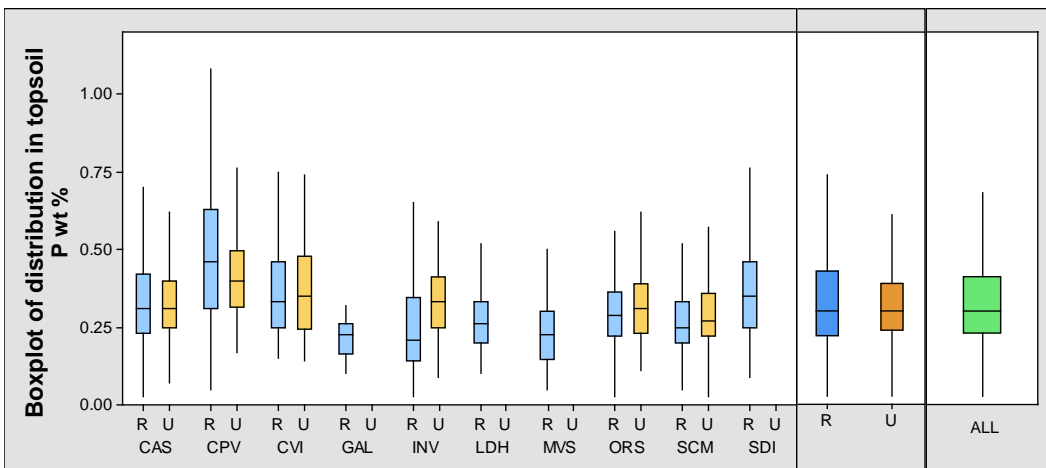
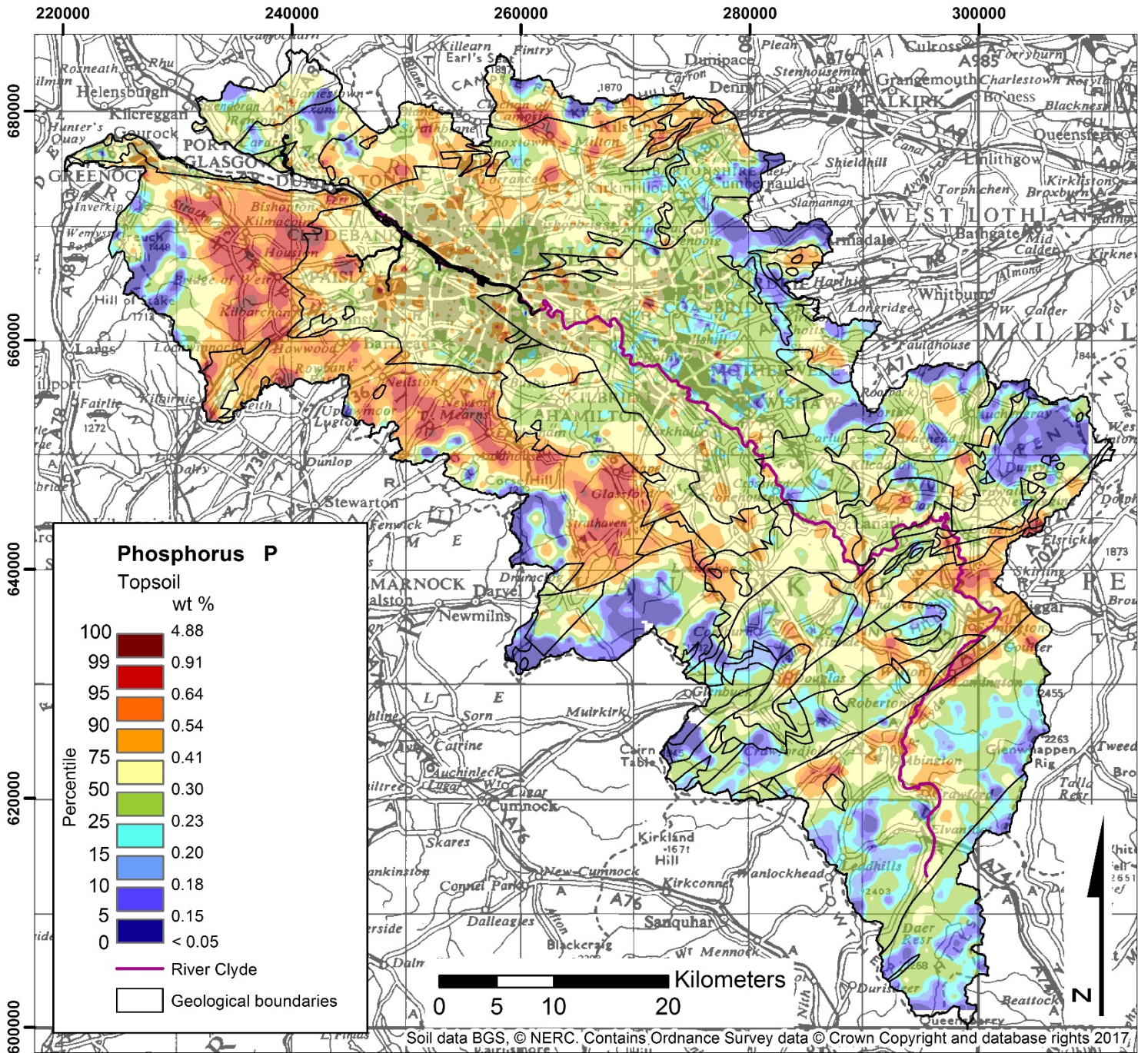
Topsoil P concentrations range from < 0.05 to 4.88 wt% in the region. The highest P concentrations in rural Clyde Basin topsoil (> 0.64 wt%) are associated with igneous bedrock, including parts of the Clyde Plateau Volcanic Formation (CPV) around Glasgow, as well as the Silurian to Devonian igneous rocks, which crop out in the southeast of the area near Biggar. Phosphorus is generally lower in upland, peaty soil over the same geological units and shows a negative spatial association with LOI, indicating that P is hosted in the mineral soil component, rather than organic soil. Phosphorus concentrations are not uniformly high across the whole outcrop of the CPV, reflecting the variable geochemical composition of the underlying bedrock. Concentrations of P are generally elevated over brown-earth soil types also.

Higher P values (> 0.41 wt%) in the valley of the River Kelvin north of Glasgow and in the upper River Clyde valley are possibly attributed to fertiliser runoff and accumulation in river channel/valleys in these agricultural areas.

Topsoil P concentrations are comparable in urban and rural environments underlain by similar rock types, suggesting that the geological background and agricultural inputs are more important than urban sources of soil total-P in the region. However, this does not equate to soluble-P that may be available for plant uptake. Concentrations of P in stream waters collected across the Clyde Basin, suggest mobile P is higher in the lowland and urban areas, than over upland igneous bedrock (Smedley et al., 2017).

The distribution of topsoil-P in the area is broadly similar to those of magnesium (Mg), sodium (Na) and strontium (Sr) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Potassium

K

(Concentrations are expressed in K₂O wt%)

Environmental behaviour

Potassium (K) has one main oxidation state (+1) and is the eighth most abundant element in the Earth's crust (1.84 %) (Fyfe, 1999). It forms several minerals including sylvite (KCl) and carnallite (KMgCl₃·6H₂O), which occur in evaporite deposits; however, it is more widespread in several important rock-forming minerals including feldspars and micas. Potassium is concentrated during magmatic fractionation; hence granites are enriched in the element (2 – 5 wt%) relative to more mafic igneous rock types such as basalt (< 1 wt%). Concentrations of K are higher in clay-rich sedimentary rock types and impure carbonates than in pure carbonates (< 2 wt%) and siliceous sandstone (< 1 wt%) (Wedepohl, 1978).

Potassium has relatively low mobility under most environmental conditions, despite the solubility of the K⁺ ion, due mainly to strong sorption by clay minerals and organic matter, and incorporation into the biosphere via plants. Availability for plant uptake from K-bearing minerals in soil, such as feldspars and micas is low; hence, K-fertiliser is often added to agricultural soil (Strawn et al., 2015). Anthropogenic sources of potassium include fertilisers, but natural sources are more important than anthropogenic ones (Reimann and Caritat, 1998). Potassium is an essential element for all organisms and natural toxic effects are rare. It is important for nervous system and muscle functioning in humans and is crucial for plant growth in agriculture (Armstrong, 1998).

Clyde Basin topsoil

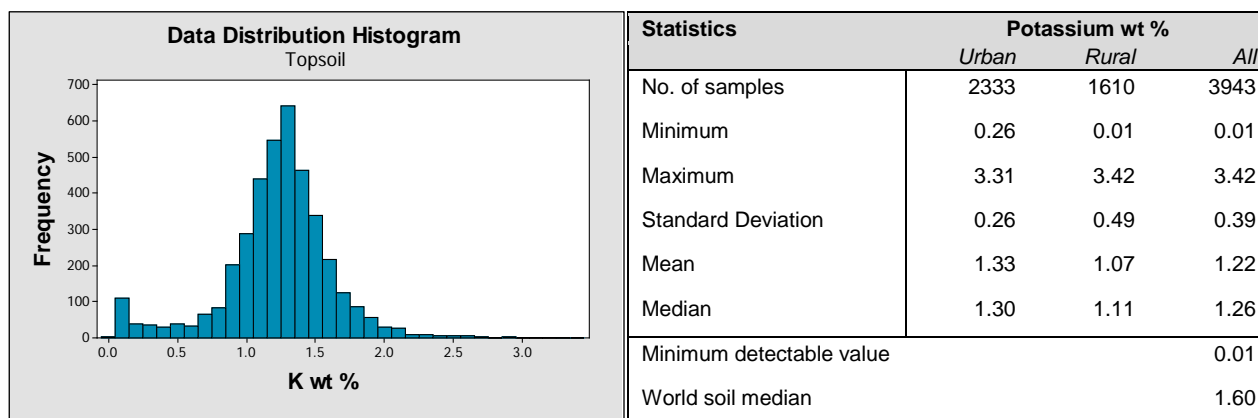
Topsoil K concentrations range from 0.01 to 4.88 wt% in the area. In the rural Clyde Basin, the highest K concentrations (> 1.80 wt%) occur in soil samples collected over mature sandstone bedrock of the Old Red Sandstone and Inverclyde Groups in the north around Dumbarton, as well as over the Leadhills Supergroup in the south, commensurate with greater proportions of K-bearing minerals, such as feldspar, in these lithologies (BGS, 1993).

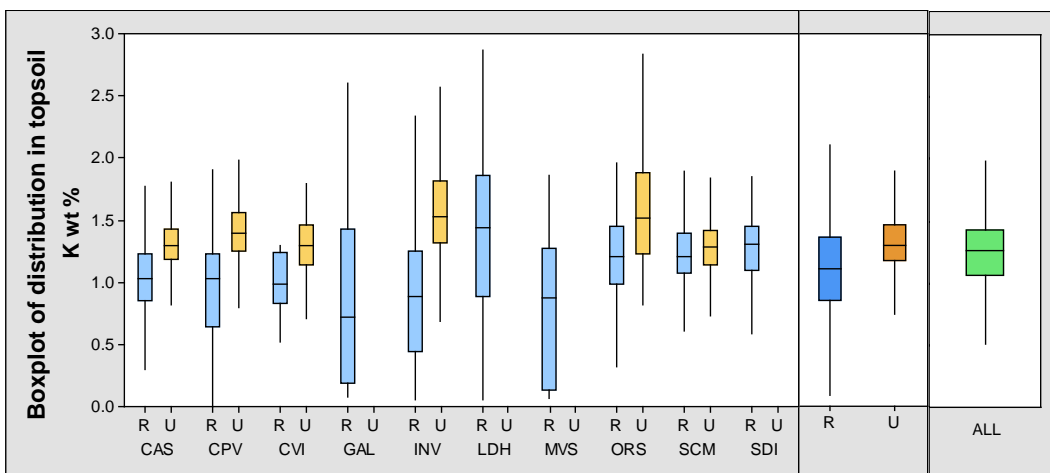
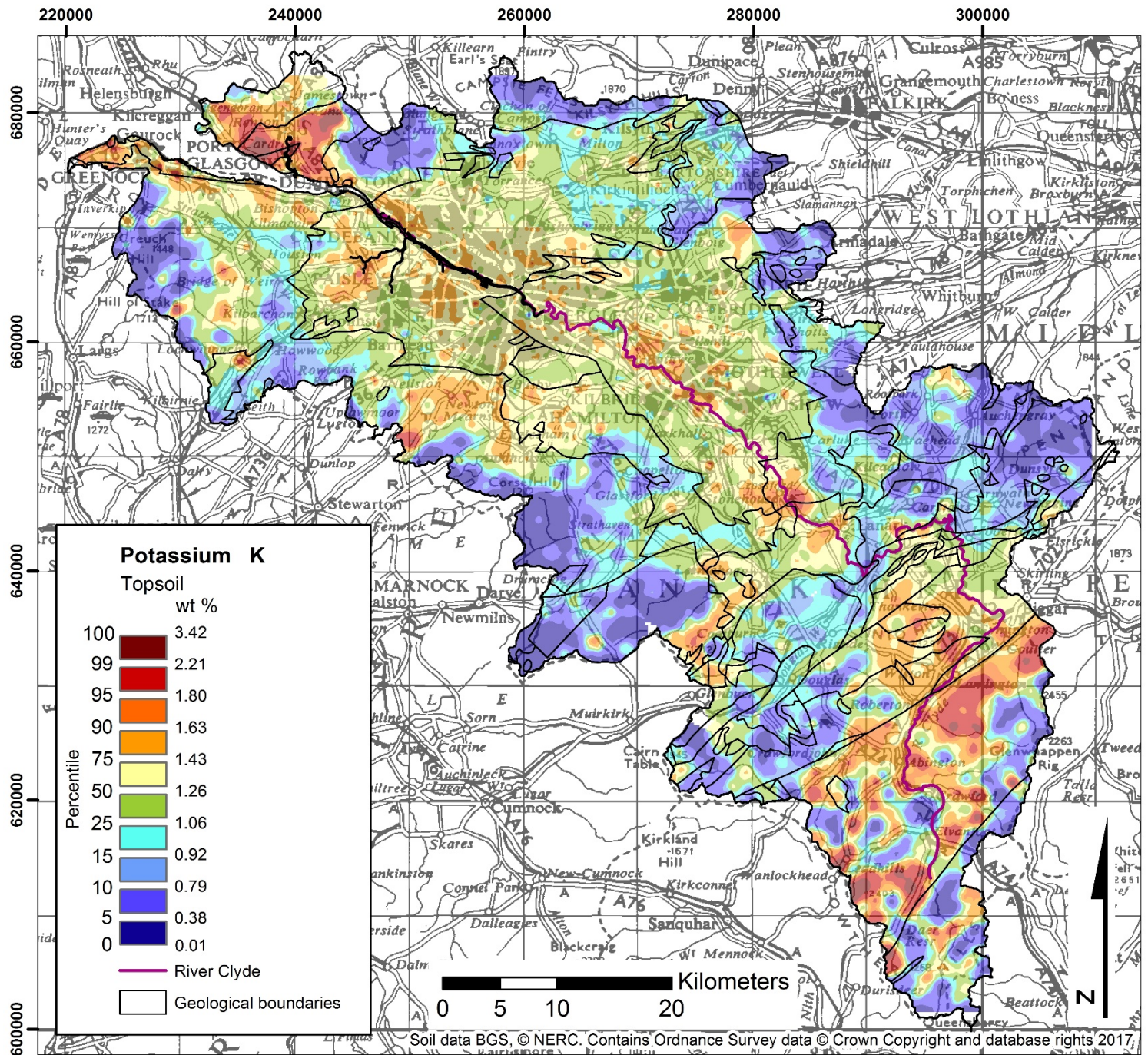
In soil overlying the Leadhills Supergroup, higher K concentrations correspond to samples collected in river valleys, whilst those collected on hill ridges and nearer summits contain lower concentrations. Indeed, across the Basin, in upland areas where organic-rich, peaty soil occurs, concentrations of K are relatively low. Potassium shows a negative spatial association with LOI in both rural and urban soil reflecting the fact that K is present mainly in the mineral component of soil, hosted in clays and feldspar grains, rather than in the organic material. In addition to river valleys in the Leadhills Supergroup, higher K concentrations (> 1.43 wt%) are associated with alluvial soil in the Clyde valley in the centre of the area and in river valleys at Paisley to the southwest of Glasgow. This distribution of higher soil-K in river valleys suggests also an influence from surface weathering processes, whereby feldspar and resistate K-bearing minerals have been eroded from surrounding uplands and concentrated in river valley soil. A noticeable anomaly in the Clyde valley is seen around Crossford, south of Carluke, where clay soil was sampled at a number of sites.

Higher topsoil-K values are associated also with more felsic components of the Silurian to Devonian igneous rocks in the south of the area and the Clyde Plateau Volcanic Formation to the southwest of Glasgow. Similarly, a significant K anomaly at Tinto Hill (Location 40, Figure 3) in the southeast of the area, which represents the largest felsic igneous intrusion (granodiorite-rhyodacite composition) in the Basin, reflects bedrock K-feldspar content. Extensive aggregate extraction occurs in the area, and it is possible this has further elevated K concentrations in topsoil.

On average (median values), K is elevated in urban versus rural topsoil, suggesting that diffuse anthropogenic pollution, possibly with building materials, has affected its distribution in the urban environment. One specific anomaly is seen at Greengairs landfill site (Location 22, Figure 3) in the east of the area, which is lined with clay.

The distribution of topsoil-K in the area is closely similar to that of rubidium (Rb) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Environmental behaviour

Selenium (Se) has four main oxidation states of -2, 0, +4 and +6. It is a chalcophile trace element, with low average crustal abundance (0.05 – 0.09 mg kg⁻¹; Taylor and McLennan, 1985). It forms several rare minerals including crookesite ((Cu, Tl, Ag)₂Se), berzelianite (Cu₂Se) and tiemannite (HgSe). It is more widely present in more common sulphide minerals such as pyrite, chalcopyrite, pyrrhotite and sphalerite, where it substitutes for sulphur. Volcanic tuffs contain higher concentrations of the element (9.15 mg kg⁻¹) than granites (0.01 – 0.05 mg kg⁻¹) or other igneous rocks (0.35 mg kg⁻¹). Selenium is found in greater concentrations in shales (0.06 mg kg⁻¹) than limestones or sandstones (0.01 mg kg⁻¹) and very high Se quantities (>300 mg kg⁻¹) have been reported in some phosphatic rocks. Selenium concentrations in coal and other organic-rich deposits can be high relative to other rock types and typically range from 1 to 20 mg kg⁻¹, although values of over 600 mg kg⁻¹ have been reported in some black shales (Alloway, 2013; Fordyce, 2013; Jacobs, 1989).

In soil, in addition to the composition of the underlying parent material, the Se concentration is heavily influenced by the organic matter content, as organic matter has a propensity to adsorb the element. Selenium mobility is determined by a number of factors, including the prevailing pH and redox conditions, the chemical form of Se, soil texture and mineralogy, and the presence of competitive ions. Selenium is highly mobile under oxidising, acidic, neutral and alkaline conditions. However, in acid and neutral soil, selenite (Se⁴⁺) forms insoluble iron oxide complexes; hence, its mobility decreases with decreasing pH, and it is immobile under reducing conditions (Gondi et al., 1992; Fordyce, 2013).

Selenium is a biologically active element and is essential for human and animal health. It is involved in a number of key enzymes and selenoproteins in the body. Selenium is needed for growth and fertility in animals (Mertz, 1987). It has a narrow optimal intake range and can be toxic at higher levels; excess Se exposure is very rare, but can result in hair and nail loss, skin and neurological disorders (Mertz, 1987; Fordyce, 2013; WHO, 1996). Anthropogenic sources of selenium include coal combustion, smelters, vulcanised rubber, waste water and some phosphate fertilizers (Reimann and Caritat, 1998).

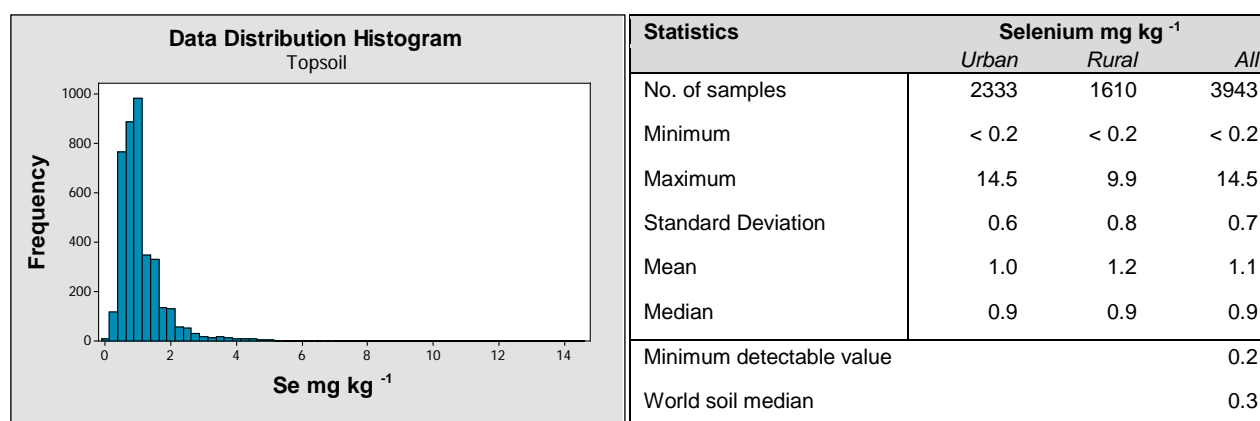
Clyde Basin topsoil

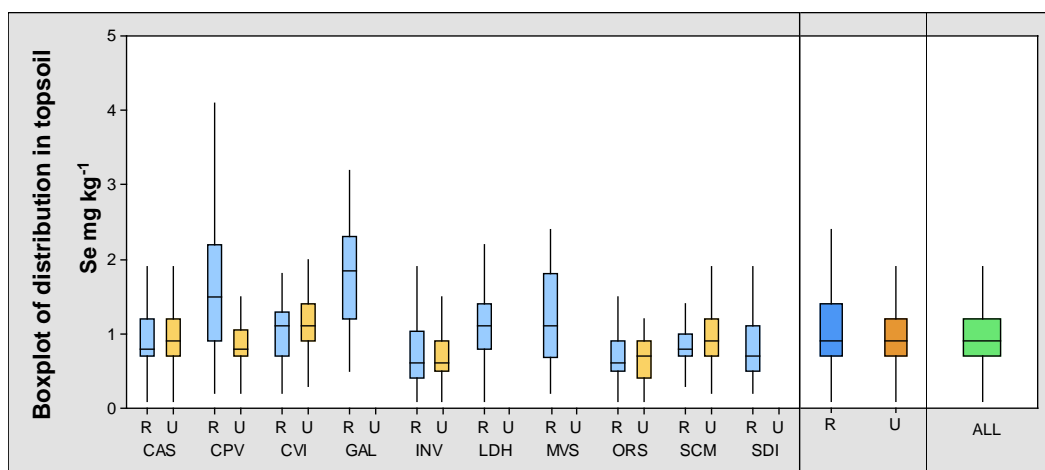
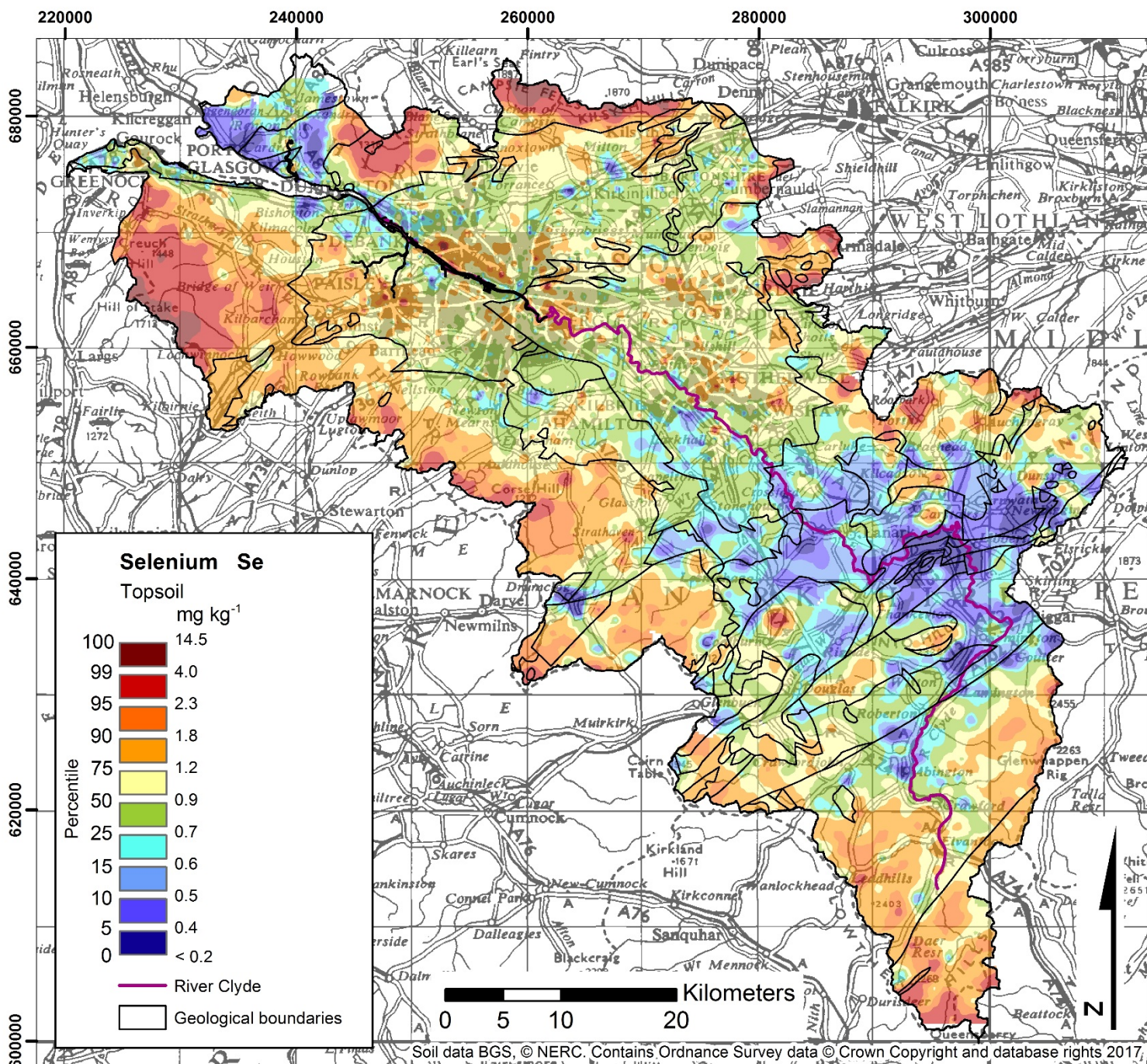
Topsoil Se concentrations in the Clyde Basin range between <0.2 – 14.5 mg kg⁻¹. Its distribution in rural environments is largely controlled by the presence of organic-rich soil in the upland areas on the periphery of the region. It shows a strong spatial association with LOI in both rural and urban soil reflecting this affinity for organic matter. Conversely, lower Se concentrations (< 0.6 mg kg⁻¹) are reported in rural mineral soil developed over the mature sandstone-dominated Old Red Sandstone and Inverclyde Group sediments in the centre of the Basin and around Dumbarton in the northwest of the region. Whilst some rock types, such as black shales and coals, can contain high levels of Se, its concentration in most rock types, and on the soil derived from them, is generally low (< 0.3 mg kg⁻¹). Therefore, in many circumstances its distribution in soil is dominated by the organic matter content, which readily sorbs the element in the soil profile (Fordyce, 2013; Fordyce et al., 2010; Johnson et al., 2000; Shand et al., 2010).

In general, Se concentrations are higher in Clyde Basin rural than urban topsoil. However, specific anomalies in the east of the area are associated with the Ravenscraig former steel mill (Location 26, Figure 3), Newmains former fire clay and coal mines in Wishaw (Location 28, Figure 3), and the former metal processing centres of the East End of Glasgow and Airdrie–Coatbridge. Similarly, with shipbuilding in Clydebank and the former industrial centre of Paisley to the west of Glasgow, indicating the influence of man on the element's distribution in soil across the area.

Elevated values of topsoil-Se occur at Leadhills in the south of the Basin (Location 11, Figure 3) related to the sulphide mineralisation in that area.

The distribution of topsoil-Se in the region is broadly similar to that of thallium (Tl) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Silicon

Si

(Concentrations are expressed in SiO₂ wt%)

Environmental behaviour

Silicon (Si) has three main oxidation states (-4, +2 and +4) and is a lithophile element. It is the second most abundant element in the Earth's crust (30 %) (Wedepohl, 1995), and is mainly present in either silica (SiO₂) or silicate (SiO₄) form. The most common and most stable form of silica is quartz, which is less soluble than other SiO₂ minerals, e.g. opal, chalcedony, cristobalite, and than silicate minerals. Common silicate minerals include olivines, pyroxenes, amphiboles, micas, and feldspars, among others (De Vos and Tarvainen, 2006). Plagioclase feldspar is the most common source of Si in the Earth's crust (Wedepohl, 1978).

Silicon is a major component of nearly all rocks, with the exception of limestone and evaporite deposits. Felsic igneous rocks contain higher quantities (70 wt%) than mafic/ultramafic igneous rocks (35 – 50 wt%). Feldspar, quartz and clay are the most common Si minerals in detrital sedimentary rocks and sandstone typically contains 65 – 75 wt% (Wedepohl, 1978).

Silicon is a low mobility element in most environmental conditions. Due to its low solubility quartz is unreactive, and combined with its high resistance to mechanical weathering, means that it is one of the residual minerals remaining in soil after alteration and dissolution of other minerals (Hinman, 1999).

Anthropogenic sources of silicon include cement factories and Si and ferro-silicon production, although geogenic sources are considered more important (Reimann and Caritat, 1998).

Silicon is essential for vertebrates and insufficient dietary Si can cause bone and cartilage problems. It is generally considered non-toxic; however, exposure to Si-rich dusts in some occupational settings can lead to lung disorders (Carlisle, 1972; Schwartz and Milne, 1972; WHO, 1996).

Clyde Basin topsoil

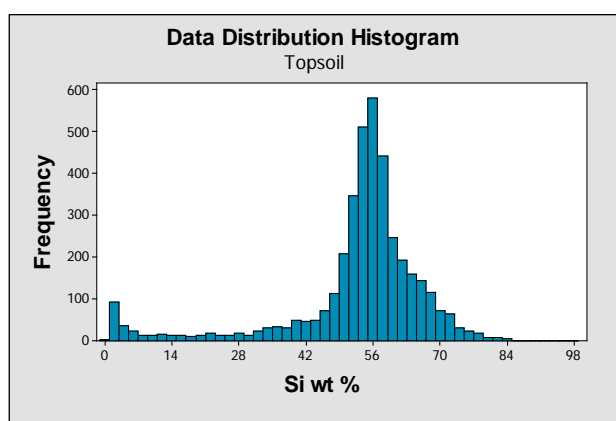
Topsoil Si contents range between 0.8 – 98.7 wt% in the region. In the rural areas of the Clyde Basin, higher concentrations of Si (> 59.7 wt%) occur in brown-earth topsoil overlying the mature sandstones of the Old Red Sandstone Supergroup (ORS) and Inverclyde Group in the northwest and centre of the study area, reflecting the siliciclastic nature of these rock types.

Non-calcareous gley soil and sandy soil, which dominate much of the central Clyde Basin, also show higher concentrations (> 51.0 wt%) relative to peaty and organic-rich soil on the periphery of the region. Topsoil-Si is consistently low (< 45.4 wt%) over the outcrop of the Clyde Plateau Volcanic Formation.

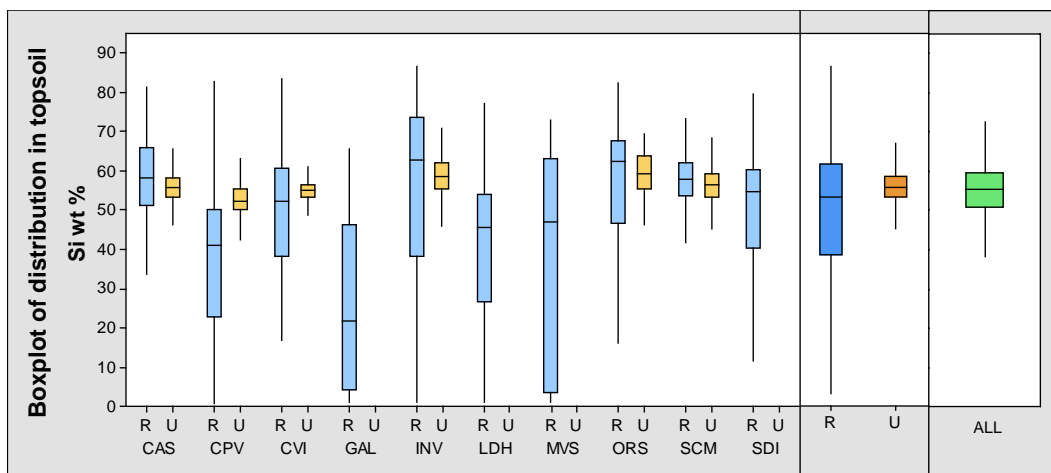
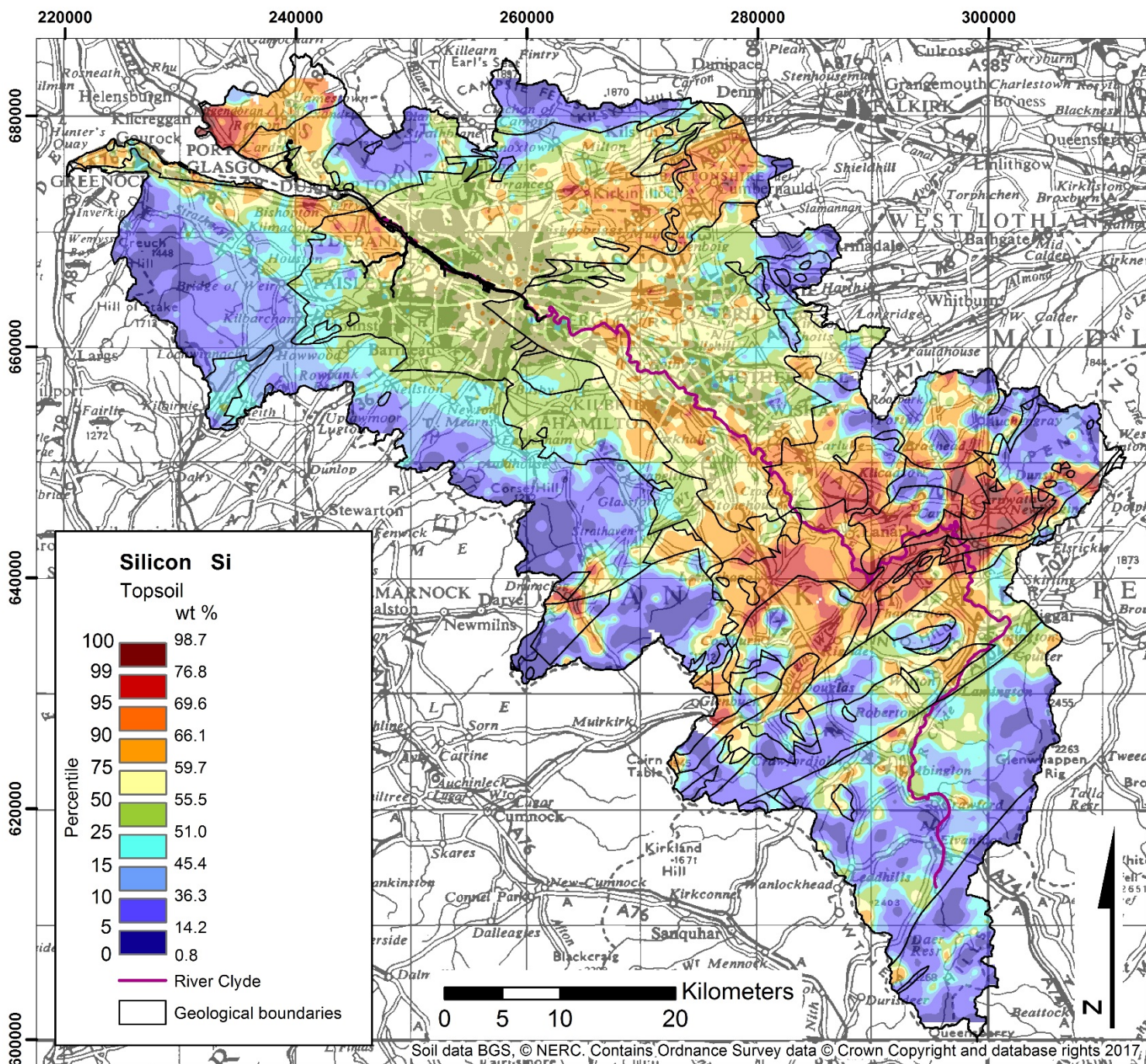
Elevated concentrations of Si are associated with alluvial soil and glacial sands and gravels in the river valleys, which probably contain greater accumulations of coarser-grained quartzo-feldspathic and of weathered resistate minerals, and have experienced more re-working than other soil types. A particularly noticeable feature is that higher concentrations of topsoil-Si occur over a large area in the upper Clyde Basin around Lanark and Carnwath. This appears to be restricted to a zone north of the Southern Upland Fault and may relate to enhanced surface re-working and transport of weathered material into the Clyde valley from the upland areas to the south of the Fault, because of the change in elevation.

Natural processes dominate the distribution of Si in topsoil and anthropogenic sources are not apparent. Specific localised anomalies tend to occur in areas of sandy soil, and are often related to glacial sand and gravel, and to alluvial parent materials. Such locations include; Cumbernauld and Kirkintilloch in the northeast of the area; Coatbridge (east of Glasgow); Paisley (west of Glasgow); Darvel in the west-centre of the area; and in the Clyde Valley around Motherwell (southeast of Glasgow).

Topsoil-Si distribution is broadly similar to those of both hafnium (Hf) and zirconium (Zr) (see Appendix 1).



Statistics	Silicon wt %		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	12.4	0.8	0.8
Maximum	82.3	98.7	98.7
Standard Deviation	6.2	20.7	14.7
Mean	56.4	47.3	52.7
Median	55.9	53.3	55.5
Minimum detectable value			0.1
World soil median			60.0



Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Environmental behaviour

Tin (Sn) has two main oxidation states of +4 and +2. It is a rare siderophile metallic element with an average upper crustal abundance of 2.5 mg kg⁻¹ (Wedepohl, 1995). It forms several minerals including cassiterite (SnO₂) and stannite (Cu₂FeSnS₄), but can be present as an accessory element in more common minerals such as biotite, muscovite, amphiboles, sphene and rutile. Concentrations are enriched in felsic (1.5 – 3 mg kg⁻¹) relative to mafic (0.5 – 1.5 mg kg⁻¹) igneous rocks. Sandstone and carbonate rocks generally contain < 1 mg kg⁻¹ Sn, whereas concentrations in shale are higher (6 mg kg⁻¹) (Mielke, 1979). Tin has a low mobility under most environmental conditions, mainly due to the high stability of the oxide SnO₂ and the insoluble sulphide SnS₂ under reducing conditions (Brookins, 1988). In soil, Sn is readily adsorbed onto Fe and Mn oxides and organic matter, particularly at higher pH (Alloway, 2013).

Anthropogenic sources of tin include coal and wood combustion, waste incineration, biocidal agents and sewage sludge (Reimann and Caritat, 1998). Tin is considered possibly essential for some organisms such as rats, but several of its compounds, particularly organo-tins are toxic to many life forms. Examples being shell abnormalities and imposex in shellfish exposed to tributyltin in anti-fouling paints for ships (De Mora and Phillips, 1997). Inorganic tin toxicity has been demonstrated to cause growth depression and anaemia in rats. Fortunately, it is poorly absorbed by the human body (WHO, 1996).

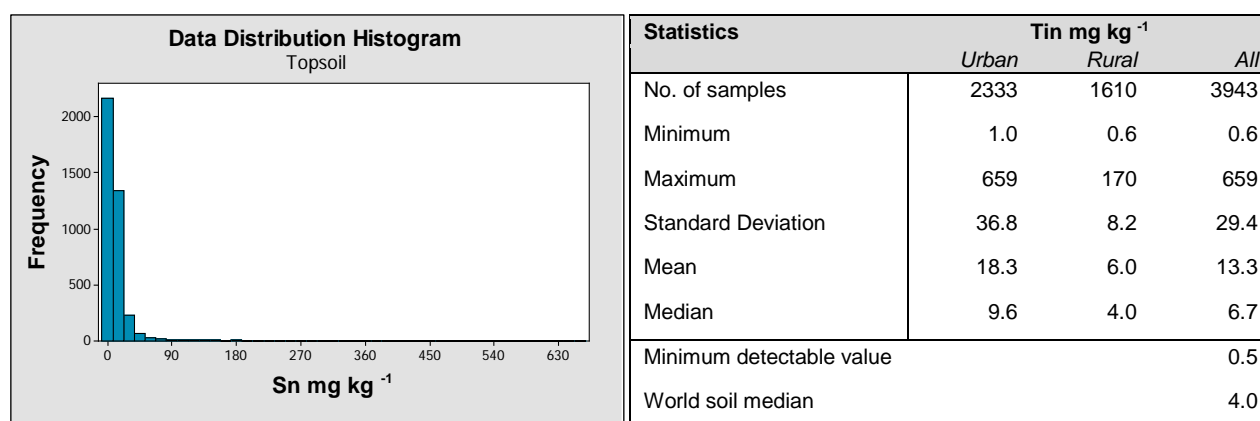
Clyde Basin topsoil

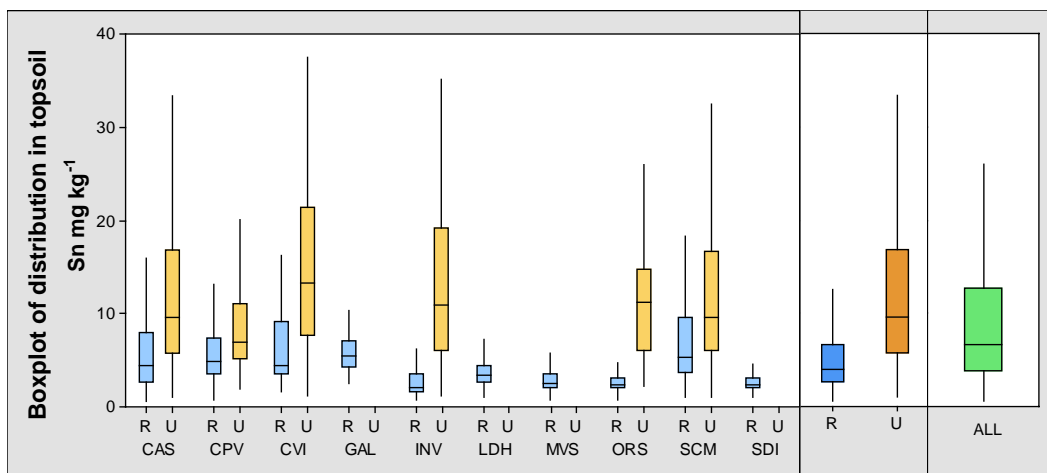
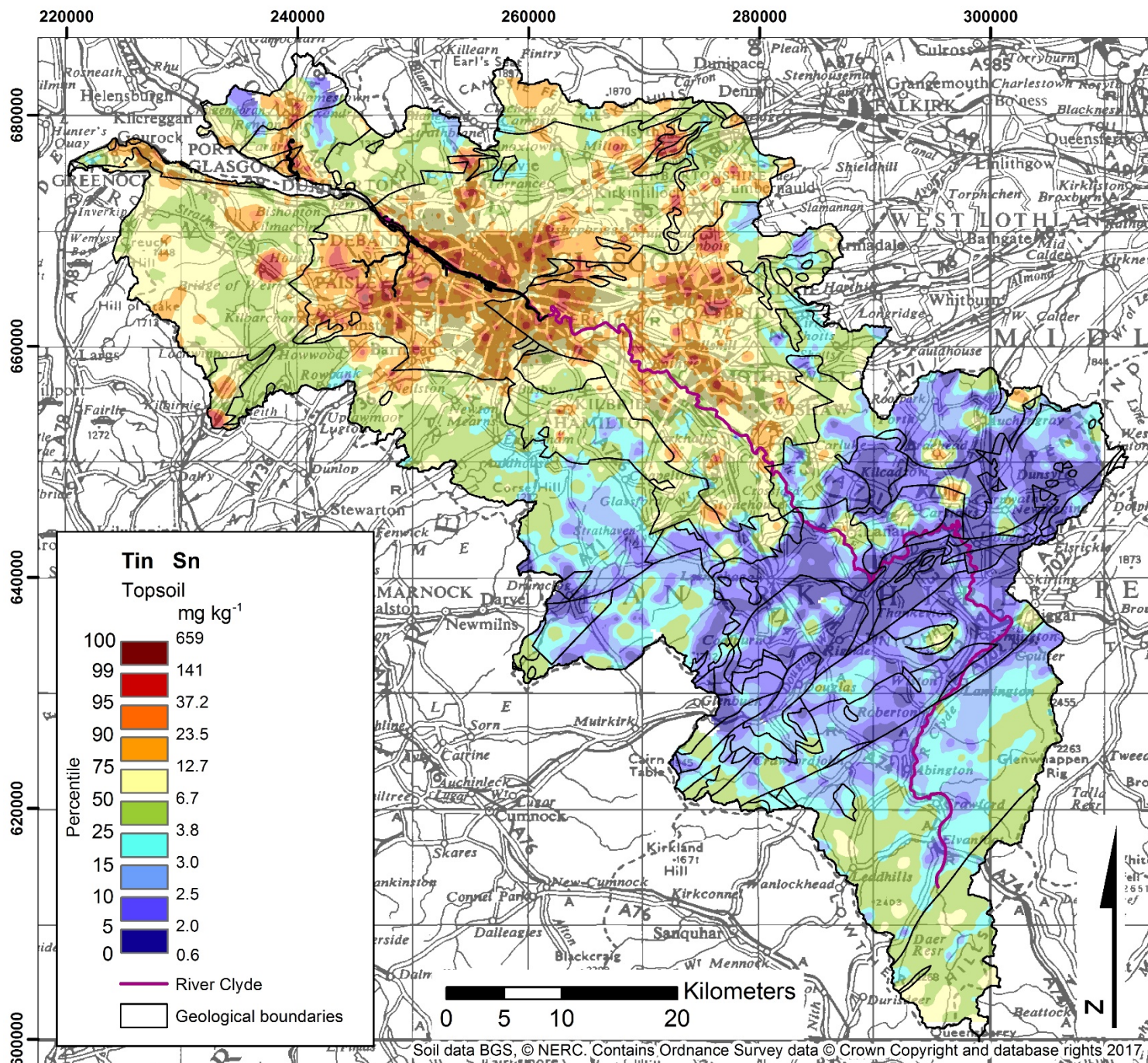
Topsoil Sn concentrations range from 0.6 to 659 mg kg⁻¹ in the region. In the rural areas of the Clyde Basin, moderate topsoil Sn enhancement (> 3.8 mg kg⁻¹), relative to soil over the same rock type, corresponds with upland peaty areas on the periphery of the Basin, reflecting atmospheric deposition and trapping of the element in organic-rich soil. However this association is not as pronounced as it is for other elements such as As, Pb and Se. Across the area, there is little variation in topsoil Sn concentration that can be attributed to the fundamental composition of the underlying bedrock, rather, anthropogenic inputs and point source pollution appear to be the dominant controlling factors on Sn distribution.

Higher concentrations of topsoil Sn (> 12.7 mg kg⁻¹) are observed across most of the urban environment, indicating a significant influence of anthropogenic pollution. Based on median values, Sn concentrations in urban topsoil (9.6 mg kg⁻¹) are more than twice that of rural topsoil (4.0 mg kg⁻¹). Some of the highest Sn topsoil concentrations are reported in the urban centres, including Alexandria, Dumbarton, Motherwell, Kilsyth, Barrhead, Coatbridge, Paisley and Glasgow. This may in part reflect diffuse pollution from fossil fuel combustion and urban waste.

In addition to widespread urban pollution, specific Sn anomalies are associated with former and current industrial sites, including, the former steel works at Ravenscraig (Location 26, Figure 3; southeast of Glasgow), and the former metal processing/working centres of the East End of Glasgow, Airdrie-Coatbridge (east of Glasgow) and Beith (southwest of Glasgow). Tin anomalies also occur at the landfill sites at Linwood moss (now capped) (southwest of Glasgow) and Overwood in the centre of the Basin (Locations 17 and 35, Figure 3).

Elevated Sn concentrations are observed also in topsoil from current and former extractive industrial sites. These include, in the east of the area, the former opencast fireclay and coal mines at Glenboig and Newmains Moss (Locations 21 and 28, Figure 3), the former oil shale/coal workings at Tarbrax (Location 32, Figure 3), the former Faskine Iron Pit in Calderbank, Airdrie (Location 24, Figure 3), and in the west of the area, the former ironstone and coal workings at Lochwinnoch. A number of Sn anomalies in the study area are also attributed to the presence of sporadic contamination in the topsoil samples. An anomaly southeast of Stonehouse in the centre of the area, relates to a sample containing furnace slag, and the two anomalies in proximity to Braehead and Carnwath (in the centre-east of the Basin) to samples containing metal contamination and farm effluent respectively.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Titanium

Ti

(Concentrations are expressed in TiO₂ wt%)

Environmental behaviour

Titanium (Ti) has three main oxidation states of +4, +2 and +3; it is a common lithophile metallic element with an average crustal abundance of 1.05 wt% (Mielke, 1979). It forms several minerals including ilmenite (FeTiO₃), rutile, brookite, anatase (all TiO₂) and sphene (CaTiSiO₅). It is also found as an accessory element in pyroxenes, amphiboles, micas and garnets. Titanium partitions into mafic (2.3 wt%) rather than granitic (0.2 – 0.6 wt%) igneous rocks, and concentrations are typically higher in shale (0.8 wt %) than in sandstone (0.2 wt%) or carbonate (0.1 wt%) sedimentary lithologies (Mielke, 1979).

In soil, Ti is mainly present in detrital resistate minerals, and may be held in association with clay minerals. Many Ti minerals are very resistant to weathering, and any Ti released by the breakdown of minerals such as ilmenite and rutile tends to bind strongly to clays. Hence, Ti has very low mobility under almost all environmental conditions, mainly due to the high stability of the low-solubility oxide (TiO₂) under all but the most acid conditions (pH<2) (Brookins, 1988).

Anthropogenic sources of titanium include paint pigments and alloys, although geogenic sources are more important than anthropogenic ones (Reimann and Caritat, 1998). Titanium is a non-essential and non-toxic element, due to its poor absorption and retention in living organisms. No evidence has been suggested that Ti performs a necessary role in the human body (Mertz, 1987).

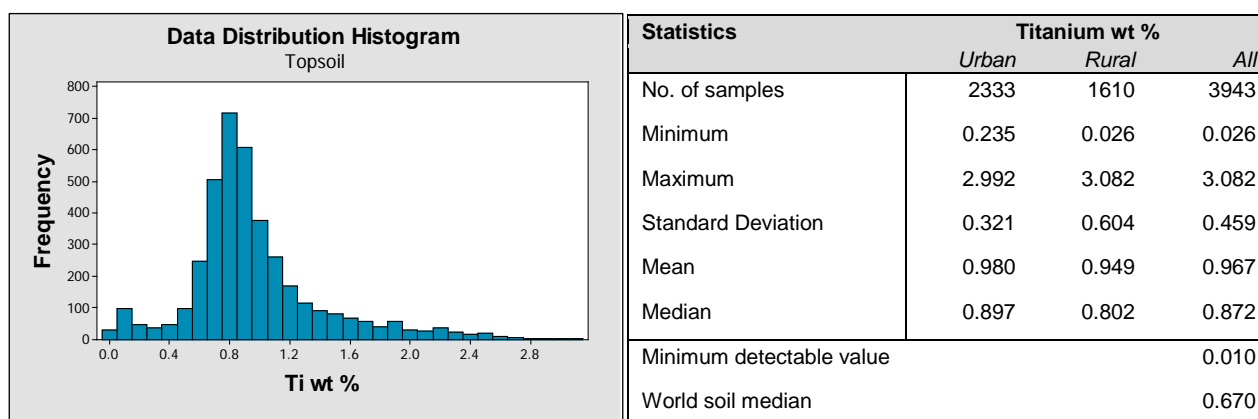
Clyde Basin topsoil

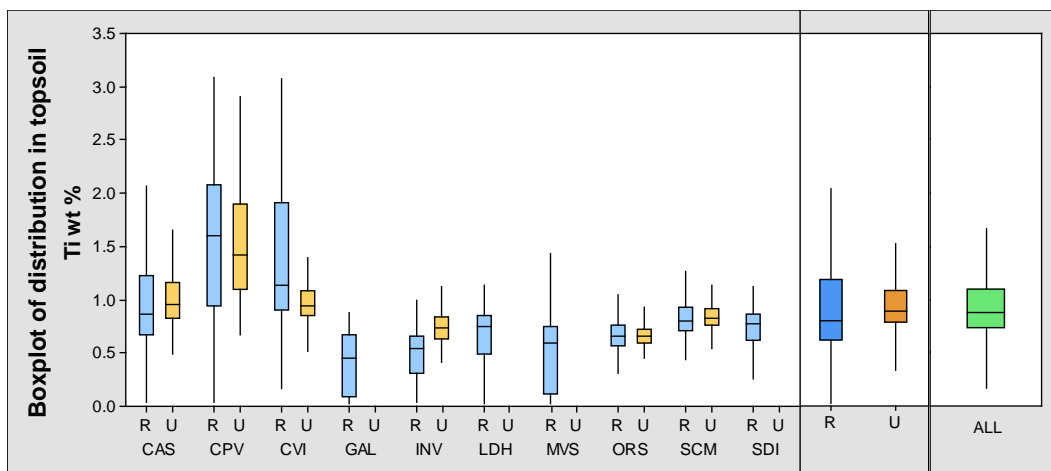
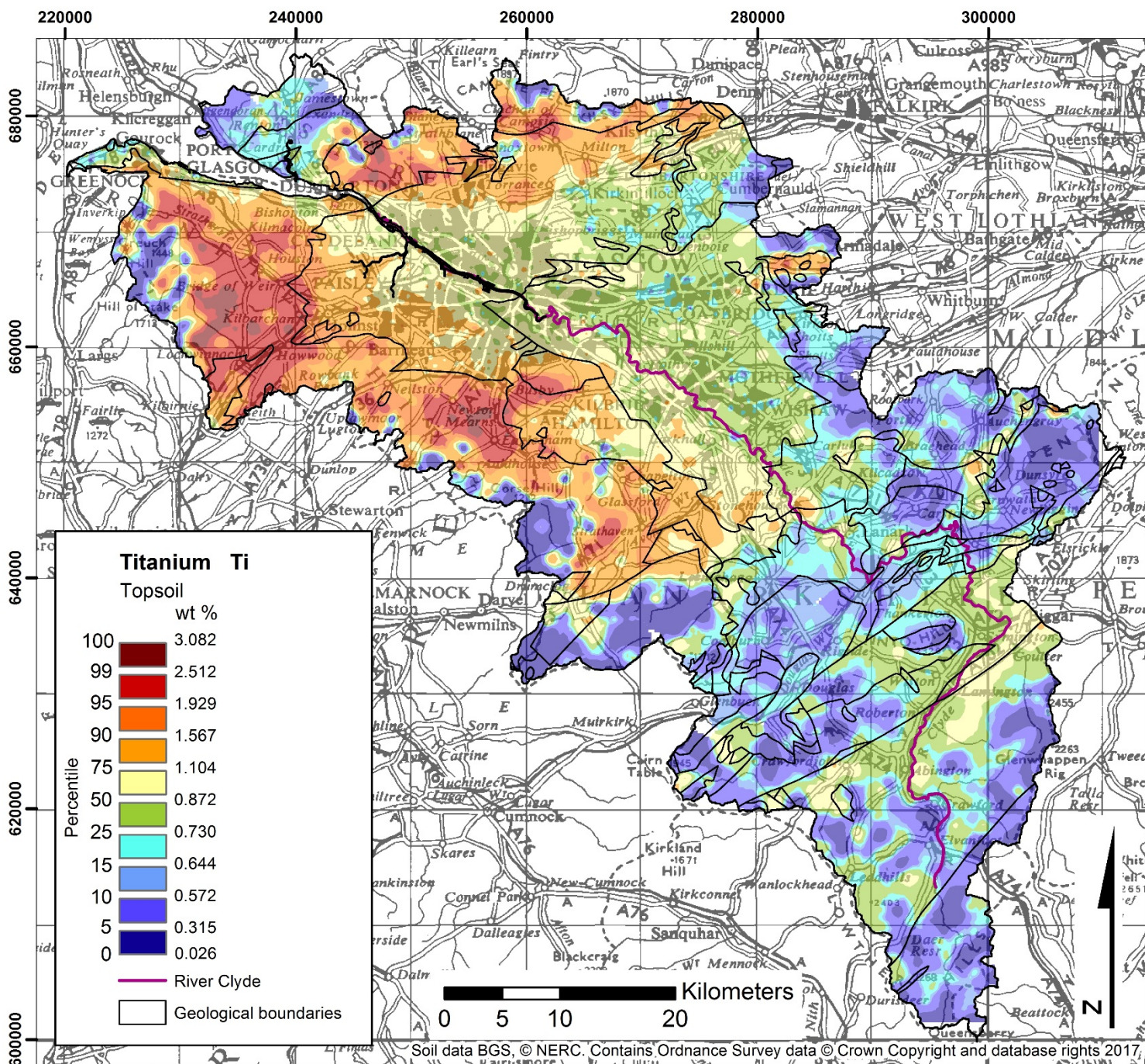
Topsoil Ti concentrations range between 0.026 – 3.082 wt% in the area. In the rural portions of the Clyde Basin, elevated Ti concentrations (> 1.104 wt%) characterise topsoil overlying the Clyde Plateau Volcanic Formation (CPV). High values occur quite consistently across the outcrop, except in organic rich, peaty soil in upland areas. Titanium shows a negative spatial association with LOI in these areas reflecting the fact that it is hosted in the mineral soil component, which has weathered from the underlying igneous soil parent material, rather than the organic soil component. Higher topsoil Ti values are related to the mafic igneous intrusions of the Clyde Volcanics, east of Moffat Mills in the east of the area (Location 23, Figure 3) also. Over the Leadhills Supergroup in the south of the area, soil-Ti concentrations are higher in valleys (>0.730 wt%) compared to the summits of the Lowther Hills, again reflecting mineral versus organic soil dominance in these areas. It is also notable that the distribution of topsoil-Ti is broadly similar to that of Sr and Mg, in terms of an association with igneous parent materials.

Titanium is higher in topsoil covering the outcrop of the Clackmannan and Strathclyde sedimentary groups to the northeast of the CPV, southwest of Glasgow. This may be a result of accumulation in this lower lying area of weathered igneous materials from the adjacent CPV uplands. It also reflects the presence of interbedded volcanics in the Strathclyde Group. The interbedded volcanics may also account for marginally higher Ti values in urban topsoil over the Clackmannan and Strathclyde Groups in the River Clyde valley and in the Glasgow area, than those underlain by urban soil over the Scottish Coal Measures Group to the east of Glasgow.

As a result, concentrations of Ti are, on average (median values), marginally higher in urban topsoil (0.897 wt%) compared to rural (0.802 wt%), but this is likely to represent the influence of geogenic parent material rather than urban pollution.

The distribution of topsoil-Ti in the area is broadly similar to those of niobium (Nb) and tantalum (Ta) (see Appendix 1).





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Environmental behaviour

Tungsten (W), is a trace lithophile and siderophile element, which has two main oxidation states (+4 and +6) and an average crustal abundance of 1.2 mg kg⁻¹ (Mielke, 1979). Whilst it is present in rare sulphide minerals such as tungstenite (WS₂), it is more common in oxide minerals, which include scheelite (CaWO₄), and wolframite ((Fe,Mn)WO₄). Tungsten can also be hosted in muscovite and Mn oxides (De Vos and Tarvainen, 2006). Tungsten is chemically similar to molybdenum and exhibits similar geochemical behaviour; this is reflected in W and Mo minerals such as powellite (CaMoO₄) in which the two elements are interchangeable and can display solid solution between nominal W and Mo end members. The element tends to partition into water-rich magmas; hence, concentrations in granites (1.3 – 2.2 mg kg⁻¹) are higher than in mafic igneous rocks (0.7 mg kg⁻¹). In sedimentary rocks, the W content of carbonates (0.6 mg kg⁻¹) is typically less than that of sandstones and shales (1.6 – 1.8 mg kg⁻¹), but coals and black shales can be enriched in the element (ATSDR, 2005; Mielke, 1979; Wedepohl, 1978).

In soil, the main W-mineral hosts are detrital wolfram and scheelite, but W released by weathering of these minerals may be bound to secondary Fe and Mn oxides, clay minerals and organic matter. Tungsten minerals are poorly soluble; hence, the element has low mobility in most environmental conditions. Although most minerals containing the tungstate WO₄²⁻ anion are generally insoluble, the WO₄²⁻ ion is soluble and stable in oxidising conditions > pH 4, where metal²⁺ cations are absent (Brookins, 1988; Kabata-Pendias, 2001).

Anthropogenic sources include tungsten mining and smelting, coal ash and industrial steel works. However, geogenic sources are more important than anthropogenic ones (Reimann and Caritat, 1998).

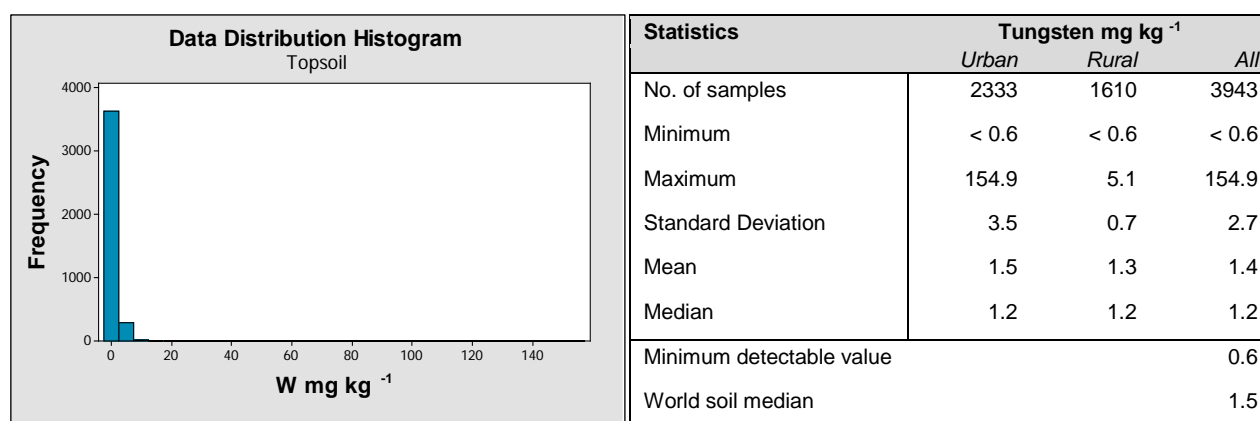
There is little evidence that W plays an important biological role, however, it may be biologically active for some anaerobic bacteria (Frausto da Silva and Williams, 2001). Limited information is available on the toxicity of W, although breathing problems have been noted in laboratory animals exposed to large doses of the element (ATSDR, 2005).

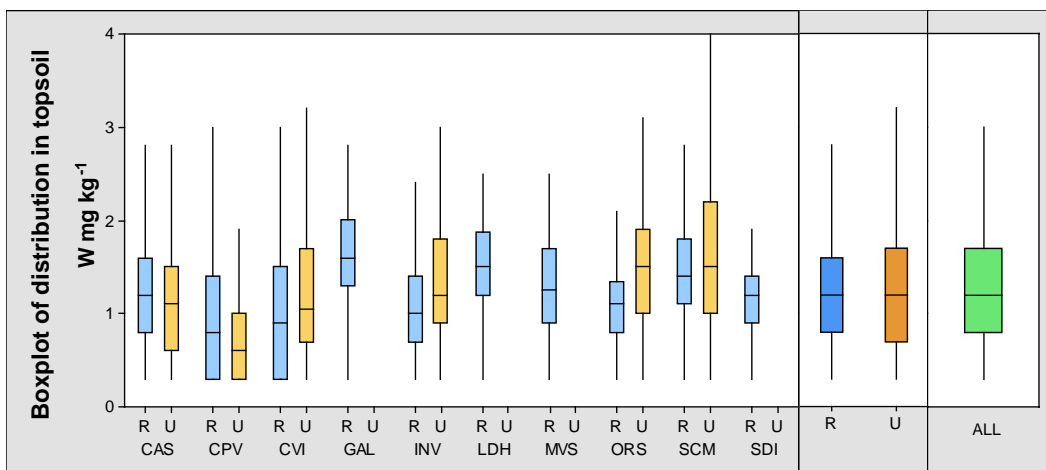
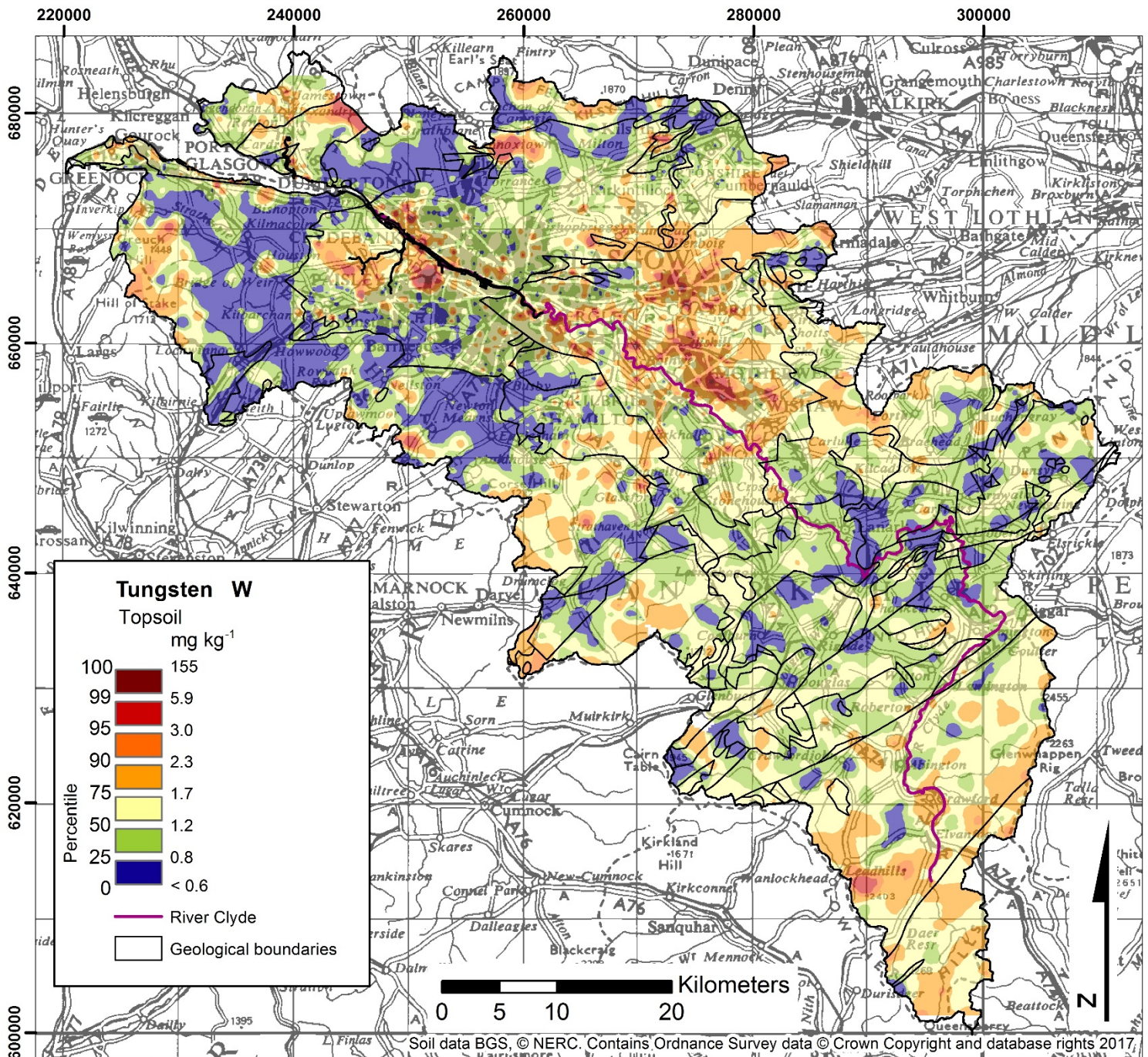
Clyde Basin topsoil

Concentrations of W in topsoil range from < 0.6 to 154.9 mg kg⁻¹ in the area. In rural parts of the Clyde Basin, the distribution of W is largely controlled by the presence of organic-rich soil; it is elevated in the upland areas in the south and on the periphery of the region as a result of atmospheric deposition and trapping in peaty soil. By contrast, mineral soil developed over the Clyde Plateau Volcanic formation to the north and west of Glasgow contains low concentrations of the element (< 0.8 mg kg⁻¹) reflecting bedrock composition. High topsoil W concentrations (> 2.3 mg kg⁻¹), related to mineralisation, are evident at Leadhills in the south of the area (Location 11, Figure 3).

Although topsoil W is not uniformly enhanced across the urban environment, urban pollution is an important control on its distribution and several high W anomalies are reported in urban topsoil. Specific anomalies which relate to areas of former or current heavy industry occur at Paisley and Clydebank (west of Glasgow); and to the east of Glasgow in Rutherglen, the Ravenscraig former steelworks in Motherwell (Locations 17 and 26, Figure 3), and the former metal processing centres of the East End of Glasgow and Airdrie–Coatbridge.

Elevated topsoil W levels are observed also near former and current extractive industrial sites, including the former ironstone and brick pit in Calderbank, Airdrie, and Mossend clay/brick pit in Motherwell (both east of Glasgow) (Locations 24 and 25, Figure 3). Some W anomalies are attributed to the presence of sporadic contamination in the topsoil such as to the north and south of Kilmacollm (west of Glasgow) where furnace slag, bricks, clear glass and ceramics were noted in the samples.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Uranium

U

Environmental behaviour

Uranium (U) has five main oxidation states of +6, +2, +3, +4 and +5. It is a low-abundance lithophile metallic element, with an average crustal content of 2.3 mg kg⁻¹ (Mielke, 1979). It occurs in several minerals including uraninite (UO₂), brannerite ((U, Ca, Ce)(Ti, Fe)₂O₆) and carnotite (K₂(UO₂)₂(VO₄)₂·3H₂O). It is also present as an accessory element in more common minerals such as zircon, apatite, allanite and monazite (Wedepohl, 1978). Uranium behaves incompatibly in magmas; hence concentrations are higher in more evolved granitic rock types (3.0 mg kg⁻¹) than in mafic igneous rocks (0.001 – 1 mg kg⁻¹) (Mielke, 1979). The redox conditions at the time of formation are a major control on U concentrations in sedimentary rocks. Under anoxic conditions, it forms insoluble complexes with organic matter and phosphates. Hence, concentrations in black shales and coals (3 – 1244 mg kg⁻¹) and phosphatic deposits (50 – 300 mg kg⁻¹) are higher than in sandstones, shales and carbonates (0.45 – 3.7 mg kg⁻¹) (Mielke, 1979; Wedepohl, 1978).

Uranium displays moderate mobility under oxidising conditions over a wide pH range; it is largely immobile in reducing conditions (Brookins, 1988; Duff et al., 1997). However, in soil, its mobility can be limited by formation of iron oxides and phosphates and adsorption onto clays and organic matter. Micro-organisms are important in the accumulation of U in soil (Kabata-Pendias, 2001).

Anthropogenic sources of uranium include uranium mining and milling, phosphate fertilizers and coal combustion (Reimann and Caritat, 1998).

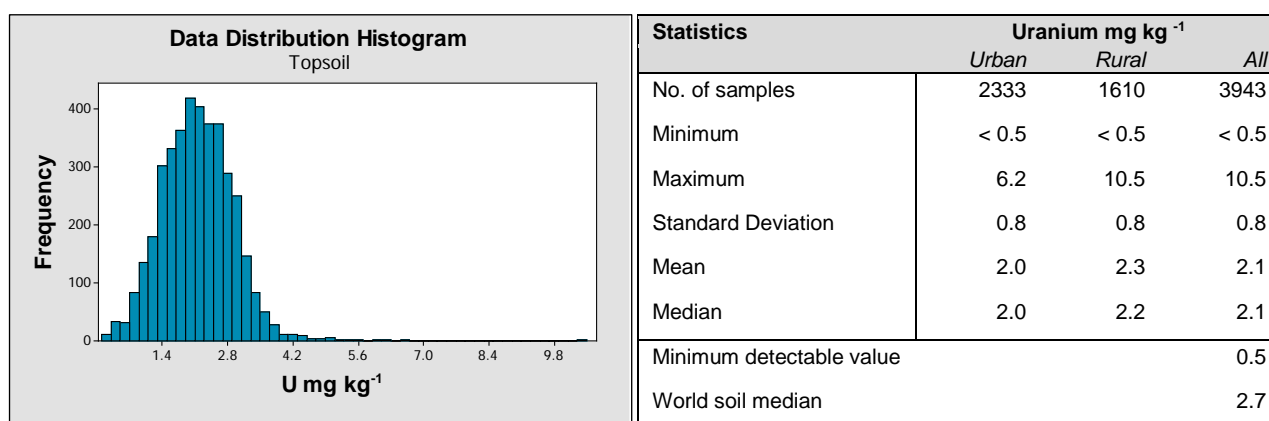
Uranium is a non-essential element, it is chemotoxic and radiotoxic, but environmental exposure to the element is low in most settings. The radioactive decay of U releases radon gas, which is carcinogenic, but is dispersed to low concentrations in the atmosphere in most unconfined environments (ATSDR, 2013).

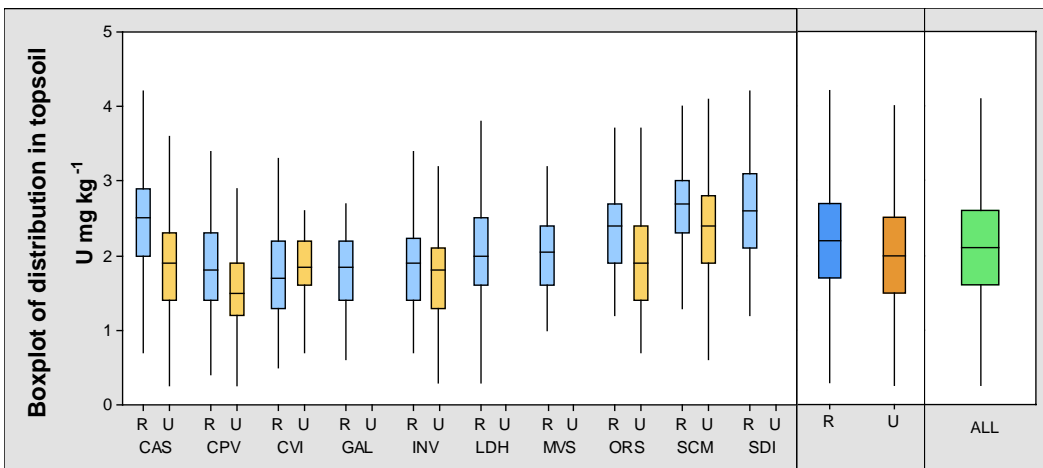
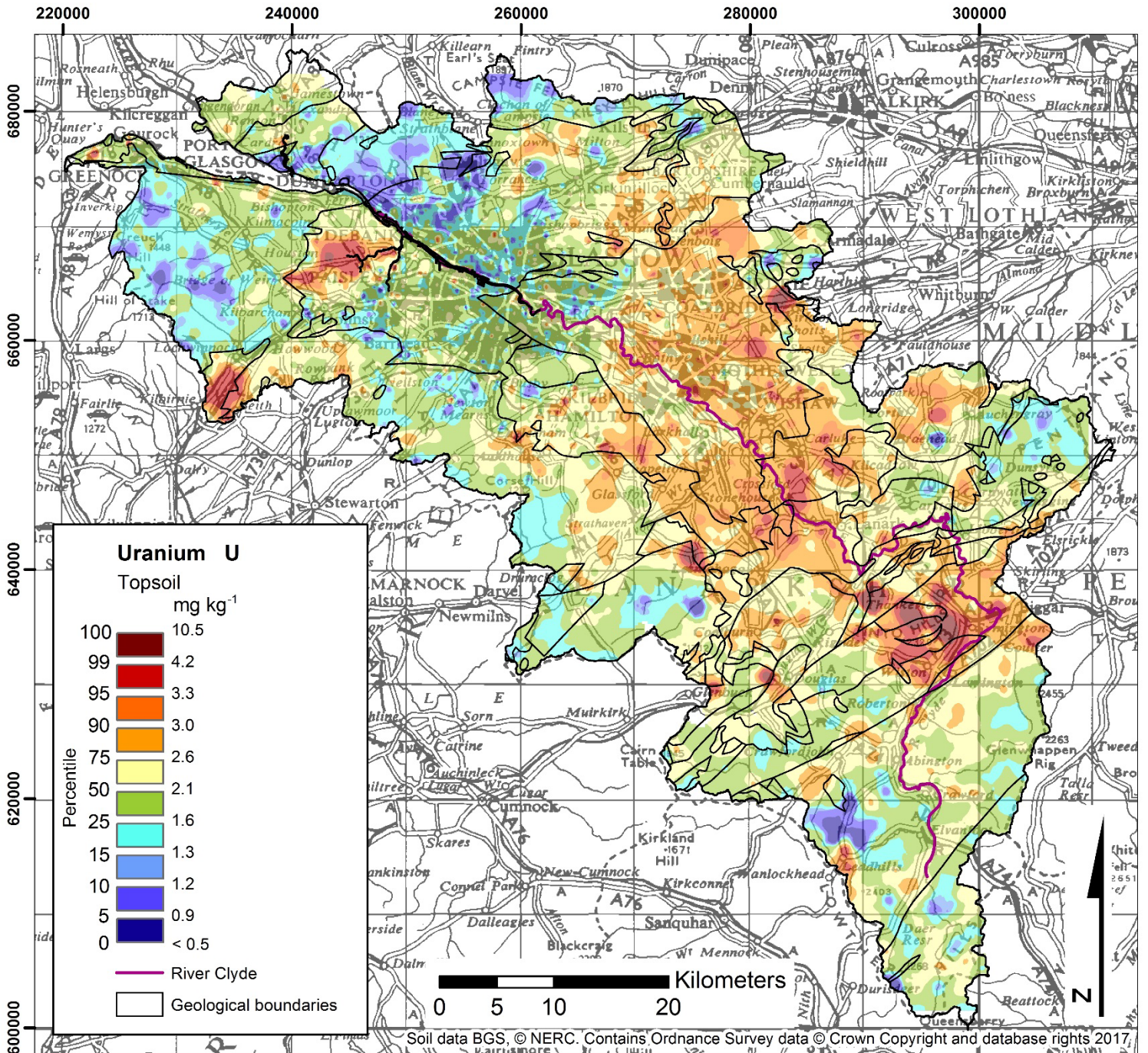
Clyde Basin topsoil

Topsoil-U concentrations are in the range < 0.5 – 10.5 mg kg⁻¹ across the region. In the rural areas of the Clyde Basin, U concentrations appear to be naturally elevated in alluvial and relatively clay-rich, non-calcareous gley soil. In particular, highest topsoil-U (> 3.3 mg kg⁻¹) is in association with alluvial deposits in the area north of Johnstone (west Glasgow), between Beith and Kilbirnie (southwest of Glasgow), and in the River Clyde valley west of Biggar in the southeast of the area. This may reflect a larger proportion of U-bearing resistate minerals in soil containing a significant alluvial component. Uranium levels are also broadly higher (> 2.6 mg kg⁻¹) in soil around Lennoxton (in the north of the region); and in soil to the east of Glasgow, across a wide area encompassing Coatbridge, Wishaw, and Stonehouse. This could reflect U-adsorption onto clay minerals in non-calcareous gley soil, which dominates in this area, but in the Coatbridge–Stonehouse region, may in part be associated with fireclay and shale in the underlying Scottish Coal Measure Group bedrock.

A prominent U anomaly occurs in topsoil around Tinto Hill (Location 40, Figure 3) in the southeast of the region, which represents the largest felsic igneous intrusion in the area (granodiorite-rhyodacite), reflecting bedrock composition. A small U anomaly is evident in topsoil in the Leadhills area in the south of the Basin (Location 11, Figure 3) and is likely to be associated with mineralisation.

On average (median values), U concentrations are marginally higher in rural (2.2 mg kg⁻¹) than urban (2.0 mg kg⁻¹) topsoil; suggesting that geogenic rather than anthropogenic sources are the dominant control on its distribution.





Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Glossary

ANOVA	Analysis of variance
BGS	British Geological Survey
CAS	Clackmannan and Strathclyde Groups
CEH	Centre for Ecology and Hydrology
Chalcophile	Chemical elements having an affinity for sulphur
CPV	Clyde Plateau Volcanic Formation
CRM	Certified reference material
CUSP	Clyde and Glasgow Urban Super Project
CVI	Clyde Volcanics – igneous intrusions
DOL	Depth of organic-rich layer
ED-XRFS	Energy dispersive x-ray fluorescence spectrometry
ESRI	Environmental Systems Research Institute
Felsic	Igneous rocks that are rich in feldspar and silicon
GAL	Gala Group
G-BASE	Geochemical Baseline Survey of the Environment
GCC	Glasgow City Council
GIS	Geographic information system
GPS	Global positioning system
Halogen	Reactive non-metallic elements of Group 17 of the Periodic Table, which form strongly acidic compounds with hydrogen
IDD	Iodine deficiency disorders
IDW	Inverse distance weighting
INV	Inverclyde Group
IQR	Inter-quartile range
LDH	Leadhills Supergroup
Lithophile	Chemical elements that are concentrated in the Earth's crust rather than mantle or core
LLD	Lower limit of detection
LOI	Loss on ignition
Mafic	Igneous rock that is rich in magnesium and iron
MVS	Midland Valley Silurian inliers
NERC	Natural Environment Research Council
NGDC	National Geoscience Data Centre
OPUS	Organic pollutants in urban soil
ORS	Old Red Sandstone
OS	Ordnance Survey
POPs	Persistent organic pollutants
REE	Rare earth elements
SCM	Scottish Coal Measures Group
SDI	Silurian–Devonian intrusive and extrusive igneous rocks

Siderophile	Chemical elements with an affinity for iron
UK	United Kingdom
VW	Voluntary worker
WD-XRFS	Wavelength dispersive x-ray fluorescence spectrometry
XRFS	X-ray fluorescence spectrometry

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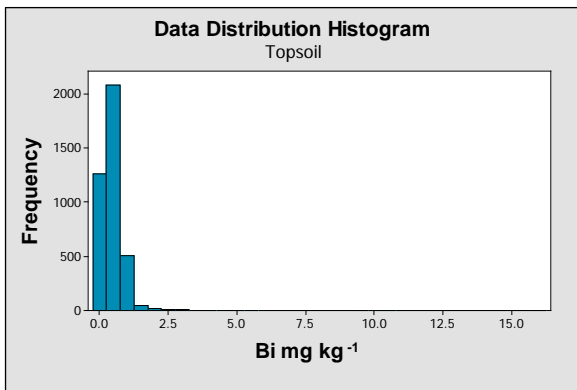
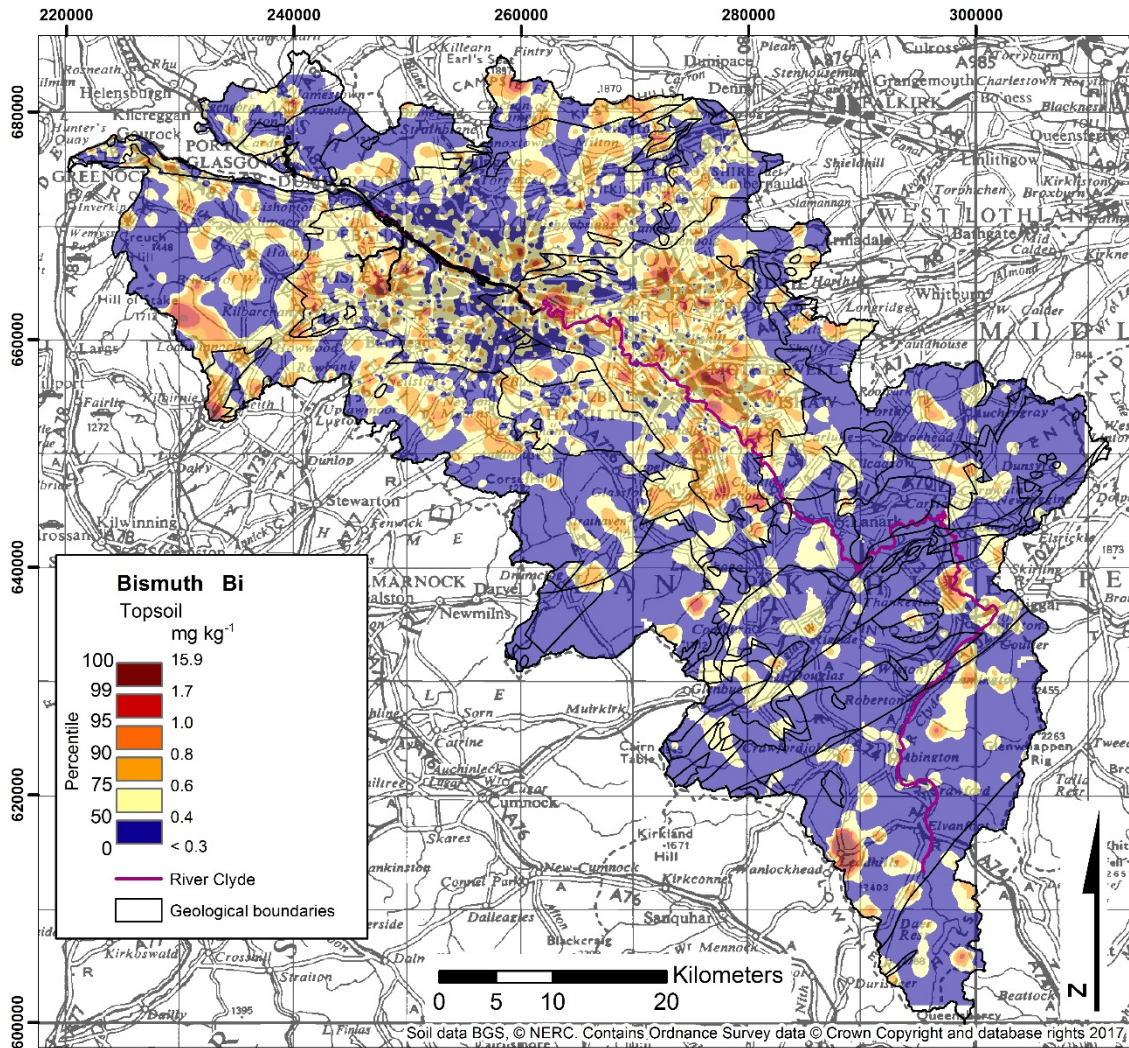
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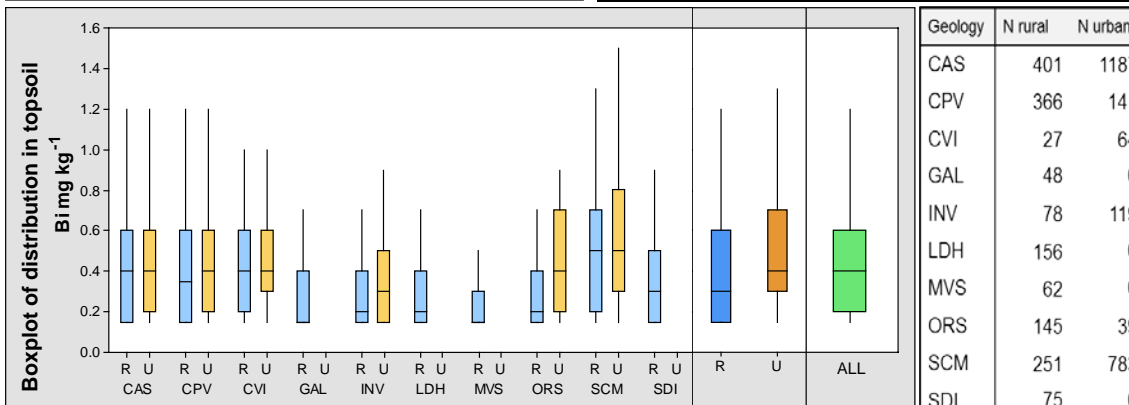
Appendix 1 Additional soil element maps

Bismuth

Bi



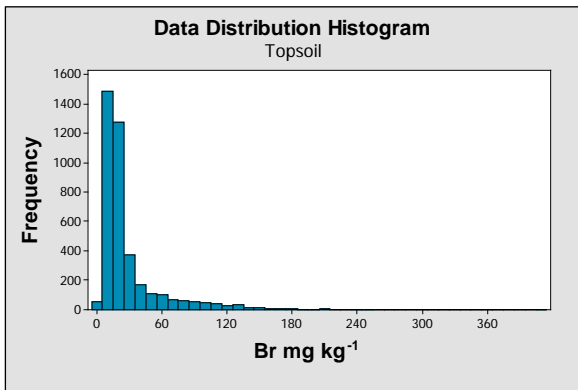
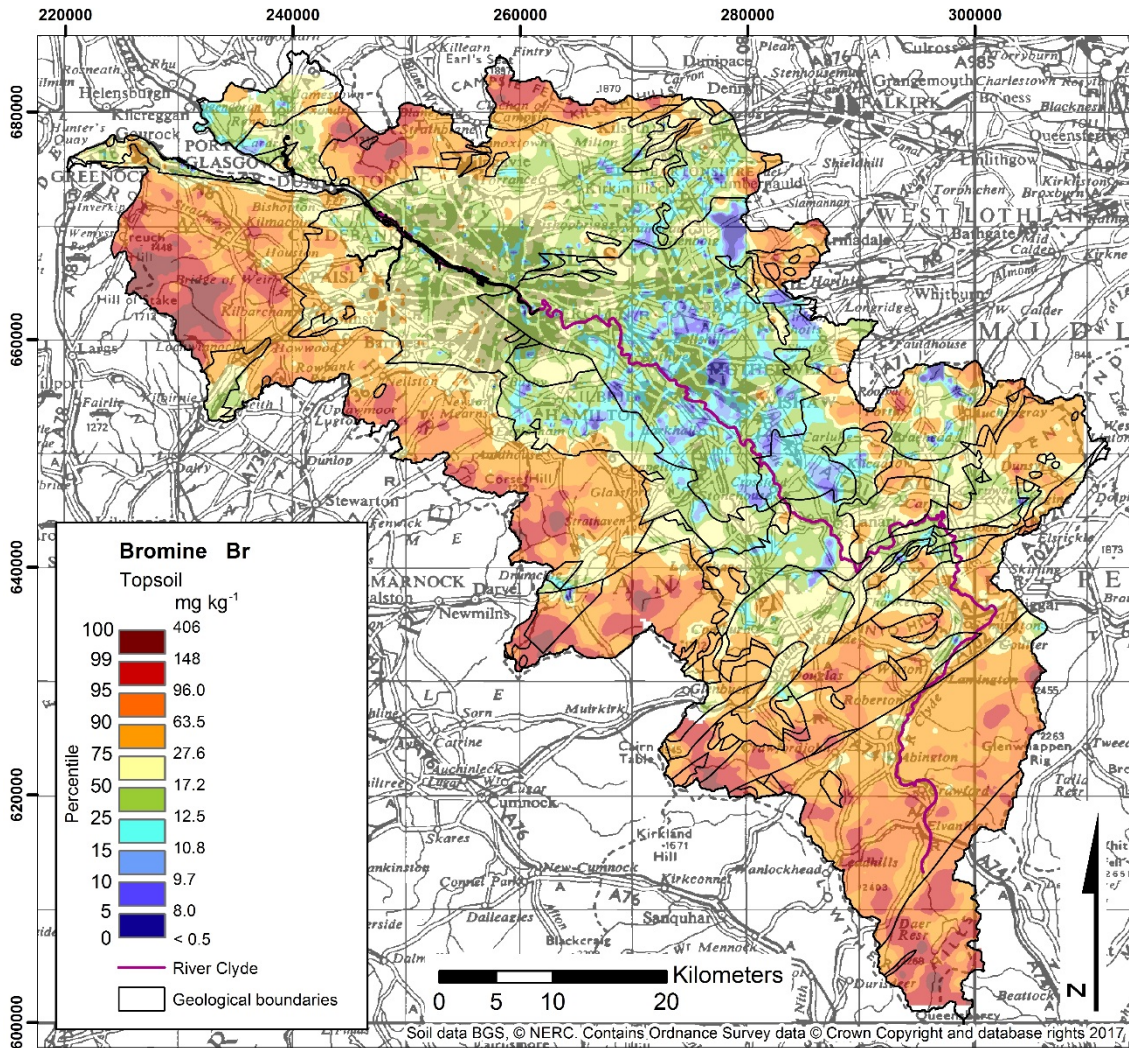
Statistics	Bismuth mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.30	< 0.30	< 0.30
Maximum	15.90	4.80	15.90
Standard Deviation	0.57	0.30	0.48
Mean	0.52	0.39	0.47
Median	0.40	0.30	0.40
Minimum detectable value			0.30
World soil median			0.30



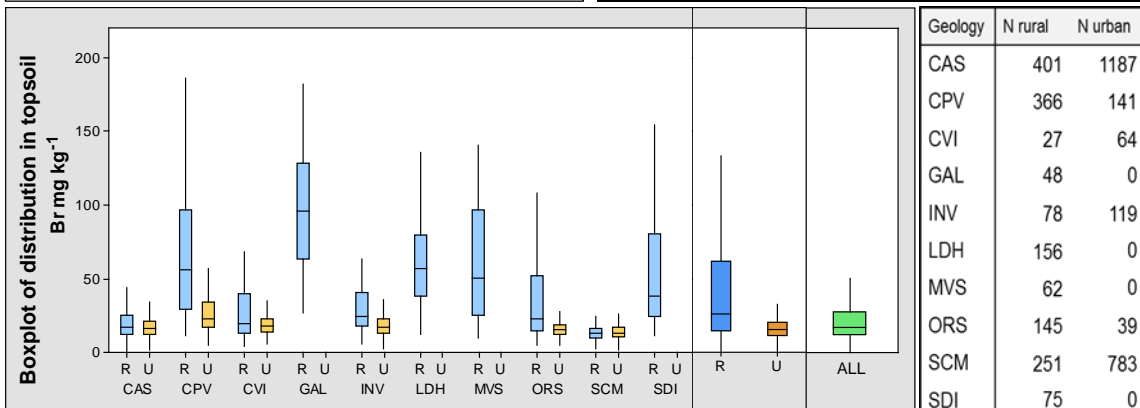
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Bromine

Br



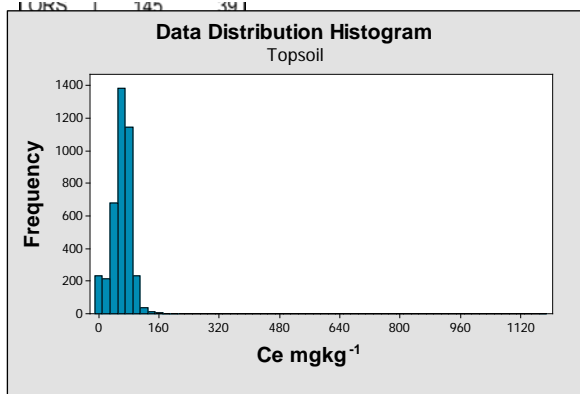
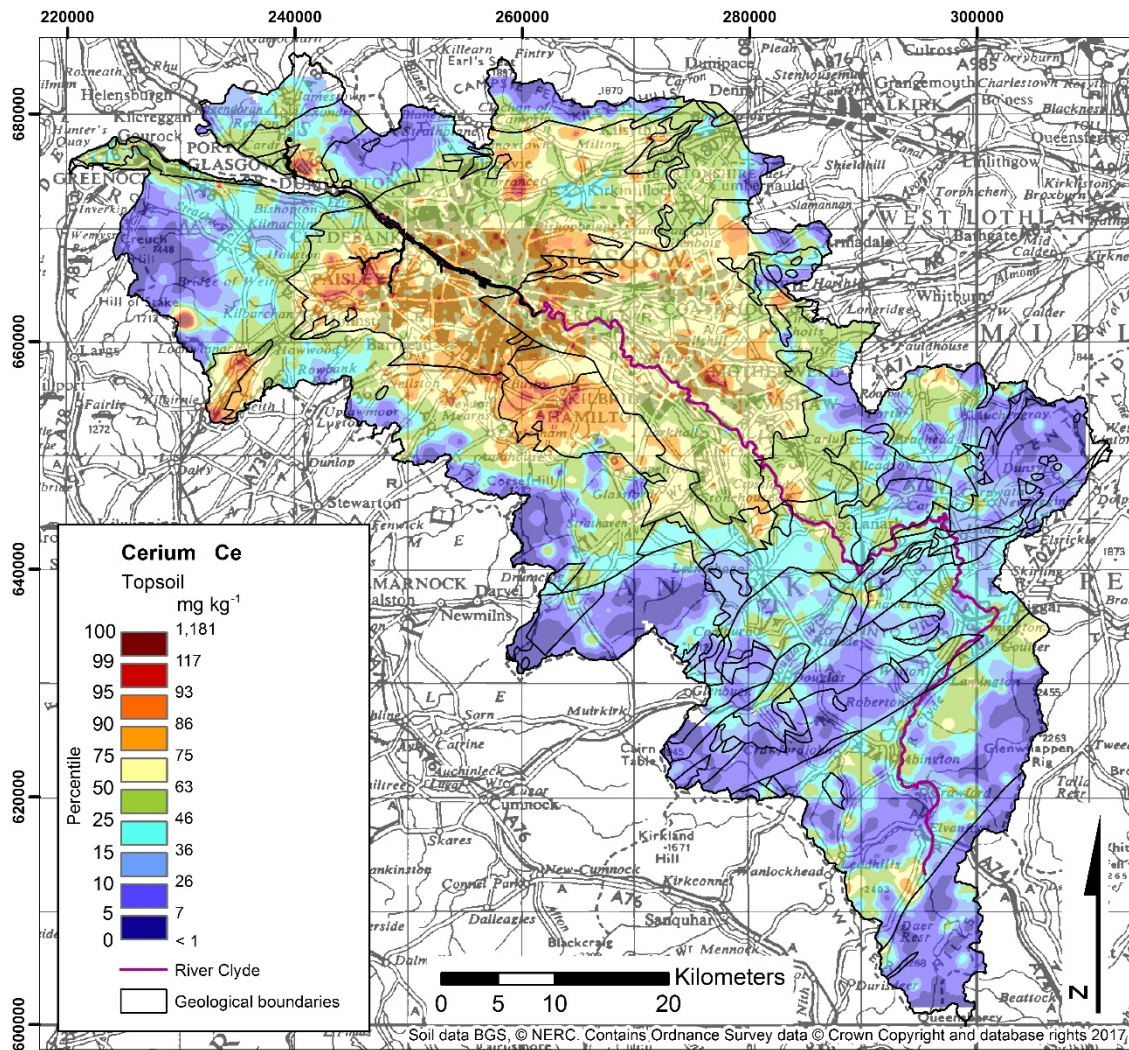
Statistics	Bromine mg kg^{-1}		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.5	< 0.5	< 0.5
Maximum	129.4	406.5	406.5
Standard Deviation	9.0	41.2	30.2
Mean	17.1	43.8	28.0
Median	15.2	26.4	17.2
Minimum detectable value			0.5
World soil median			10.0



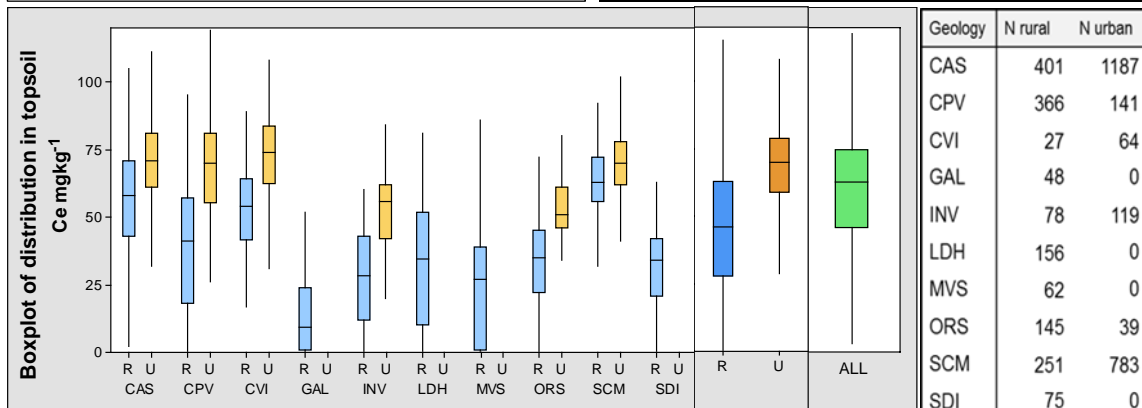
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Cerium

Ce



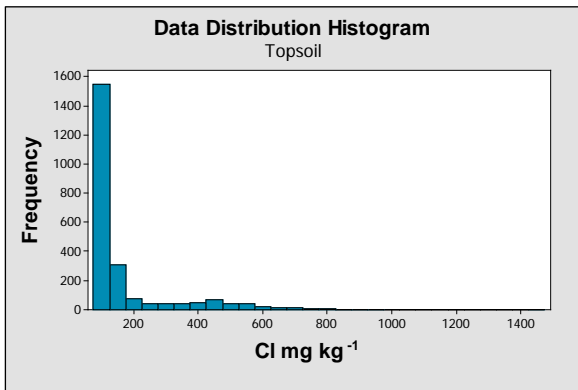
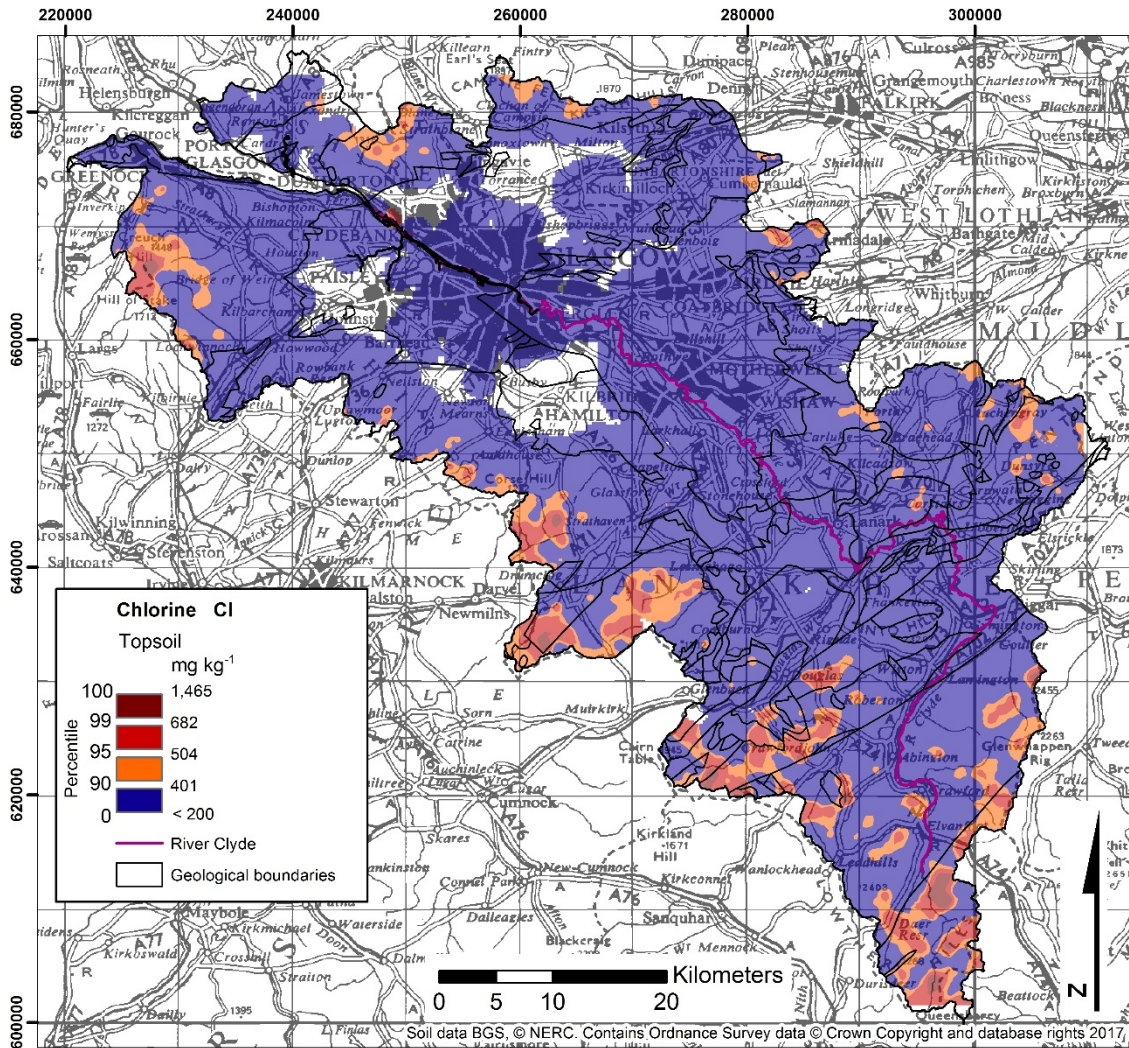
Statistics	Cerium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	11	< 1	< 1
Maximum	1181	146	1181
Standard Deviation	28	25	30
Mean	71	44	60
Median	70	46	63
Minimum detectable value			1
World soil median			65



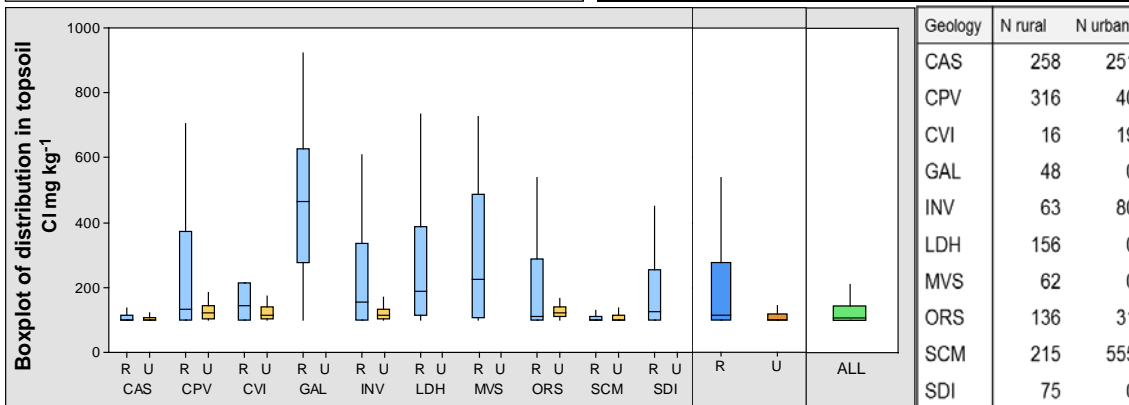
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Chlorine

Cl



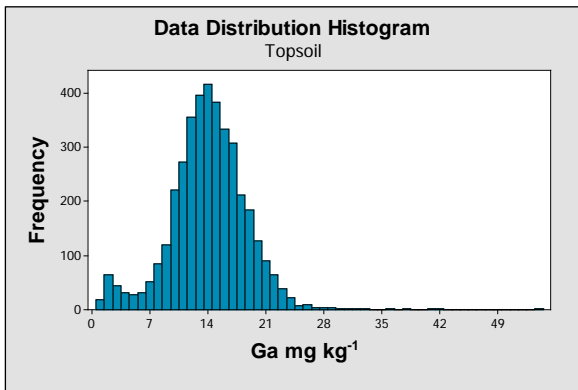
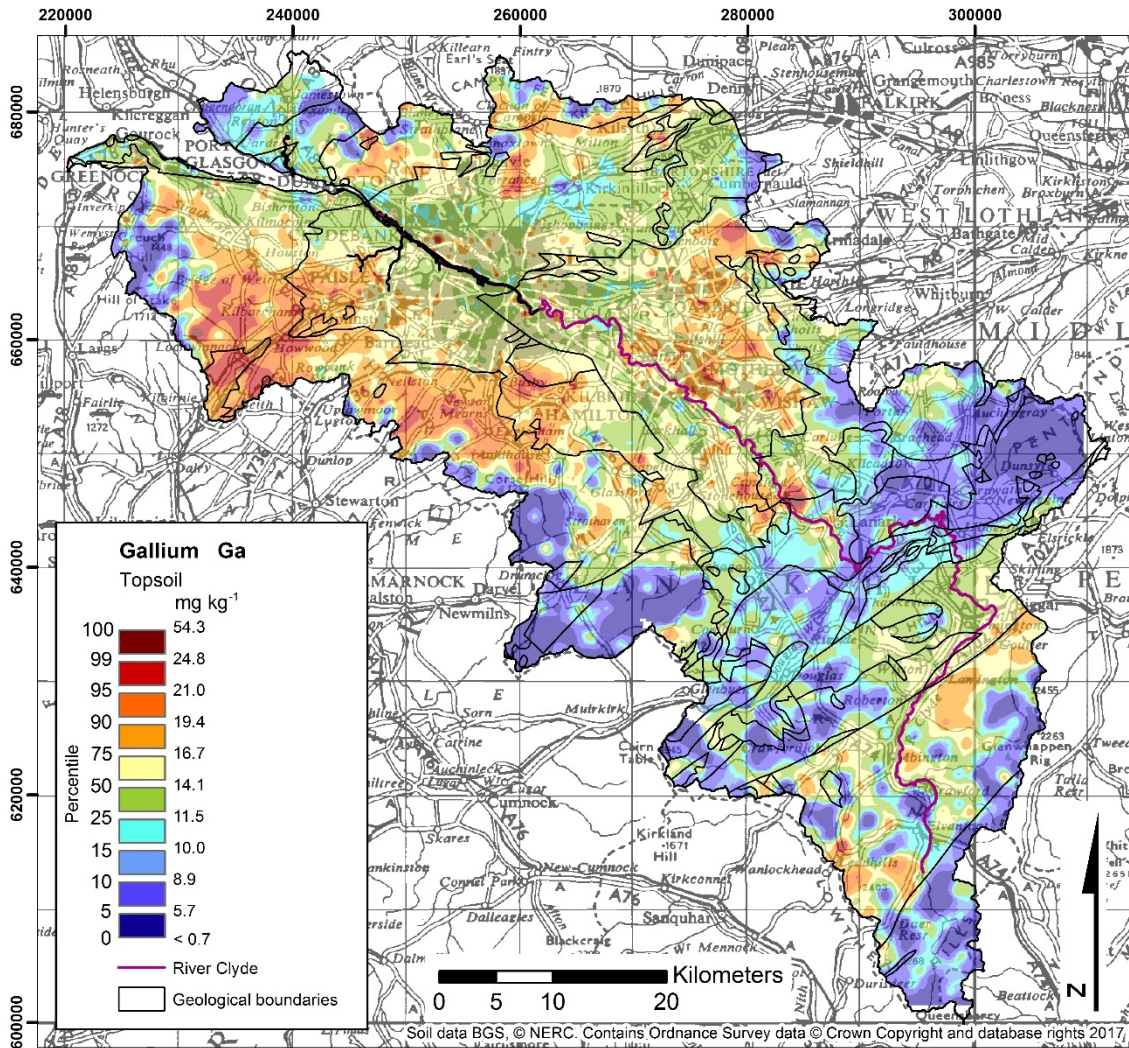
Statistics	Chlorine mg kg ⁻¹		
	Urban	Rural	All
No. of samples	976	1345	2321
Minimum	< 200	< 200	< 200
Maximum	484	1465	1465
Standard Deviation	25	172	140
Mean	113	210	169
Median	101	113	106
Minimum detectable value	200		
World soil median	300		



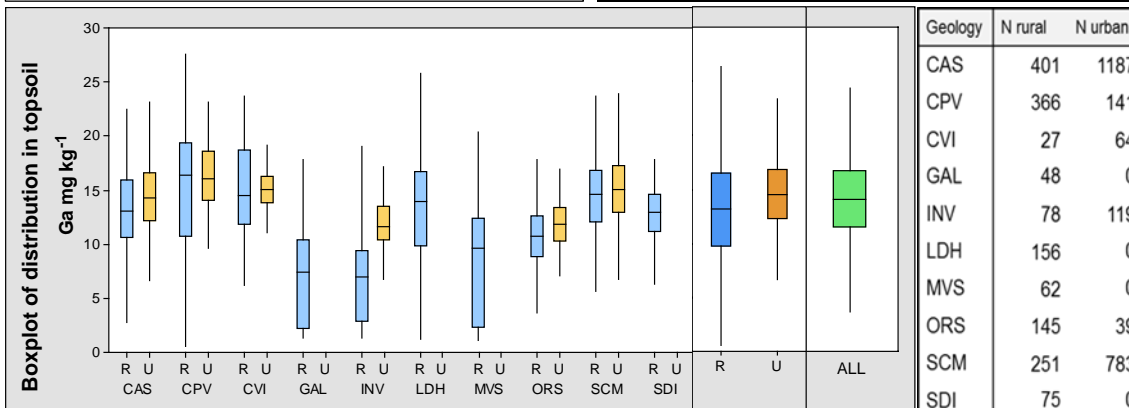
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Gallium

Ga



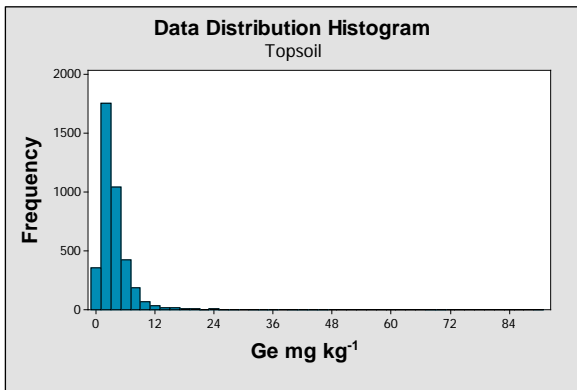
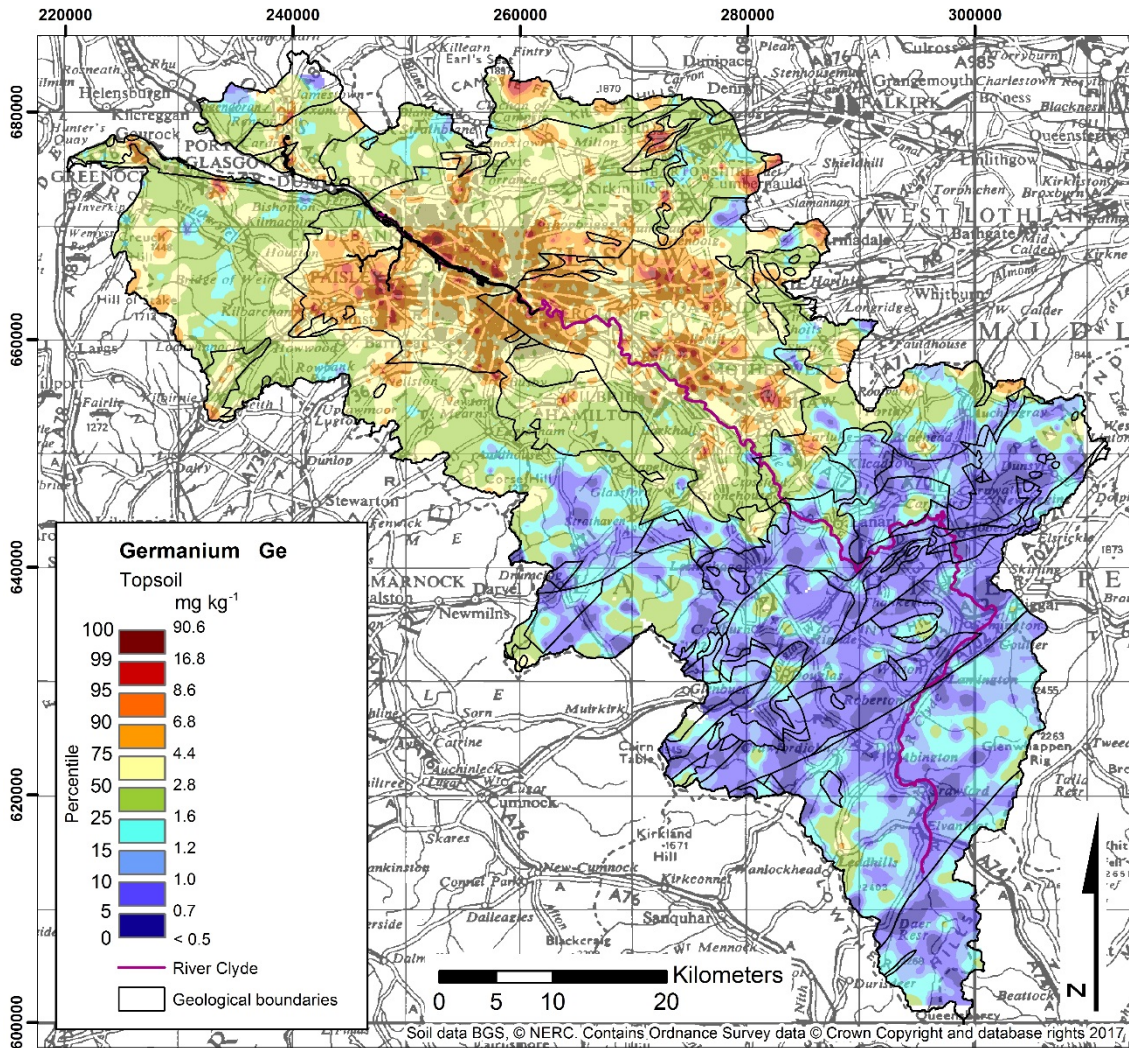
Statistics	Gallium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.7	< 0.7	< 0.7
Maximum	54.3	29.2	54.3
Standard Deviation	3.8	5.3	4.6
Mean	14.9	12.8	14.0
Median	14.5	13.2	14.1
Minimum detectable value	0.7		
World soil median	14.0		



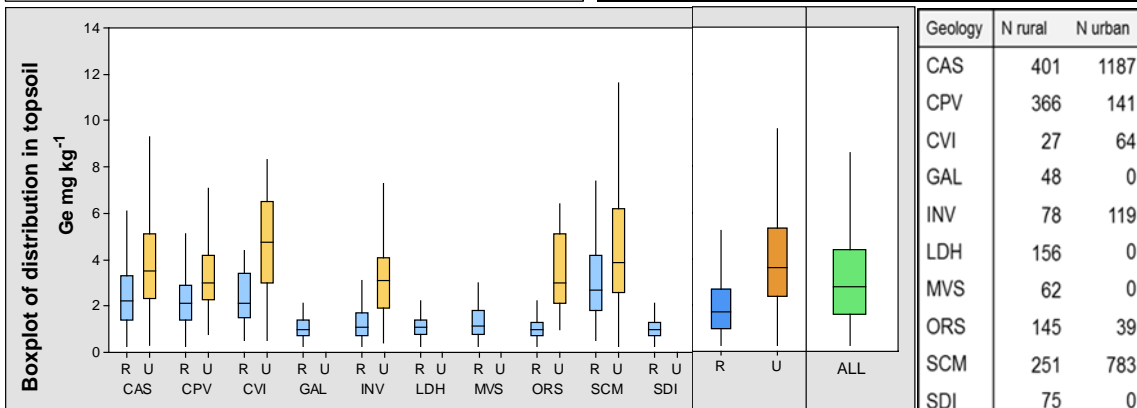
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Germanium

Ge



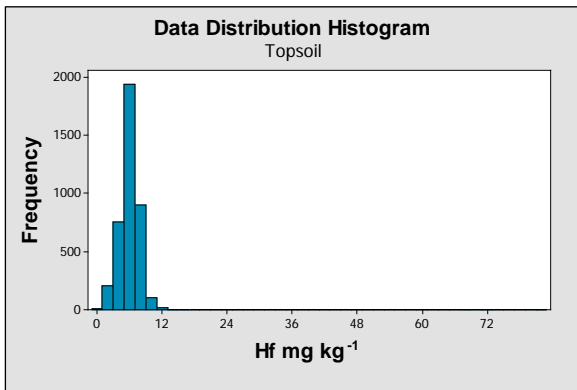
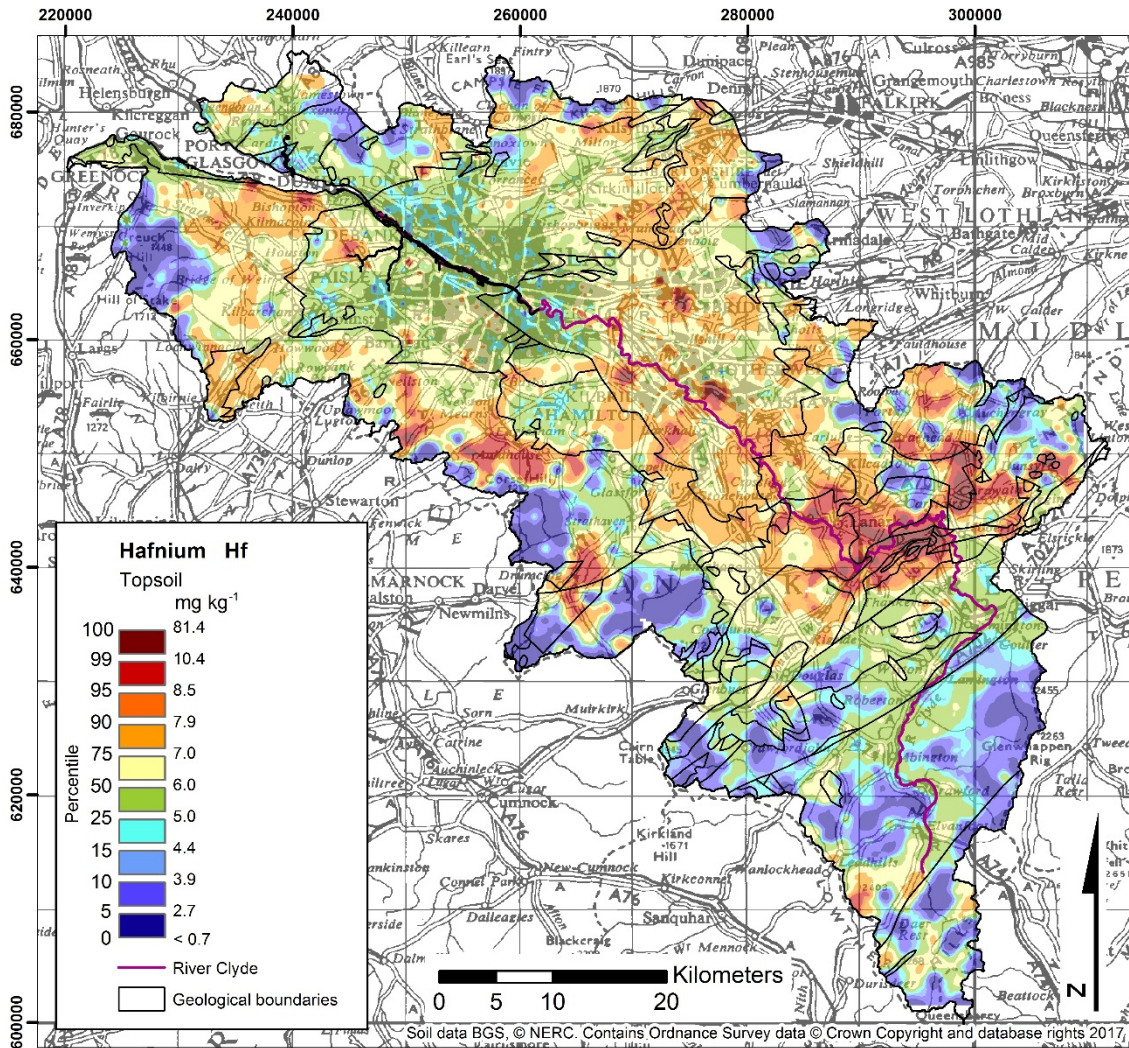
Statistics	Germanium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.5	< 0.5	< 0.5
Maximum	90.6	17.8	90.6
Standard Deviation	4.9	1.7	4.1
Mean	4.6	2.2	3.6
Median	3.6	1.7	2.8
Minimum detectable value	0.5		
World soil median	2.1		



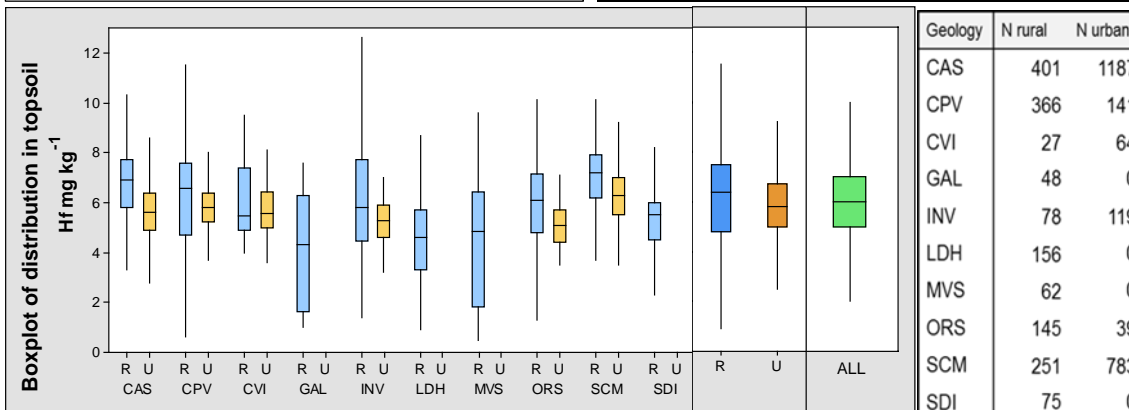
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Hafnium

Hf



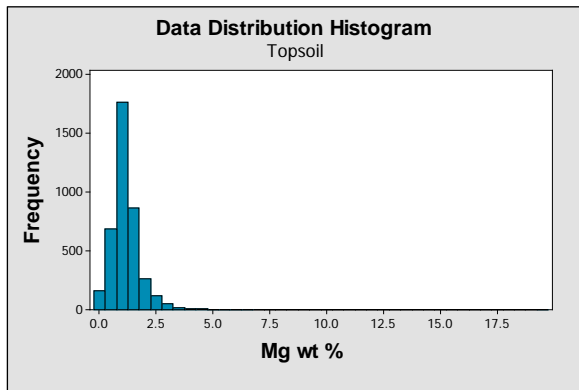
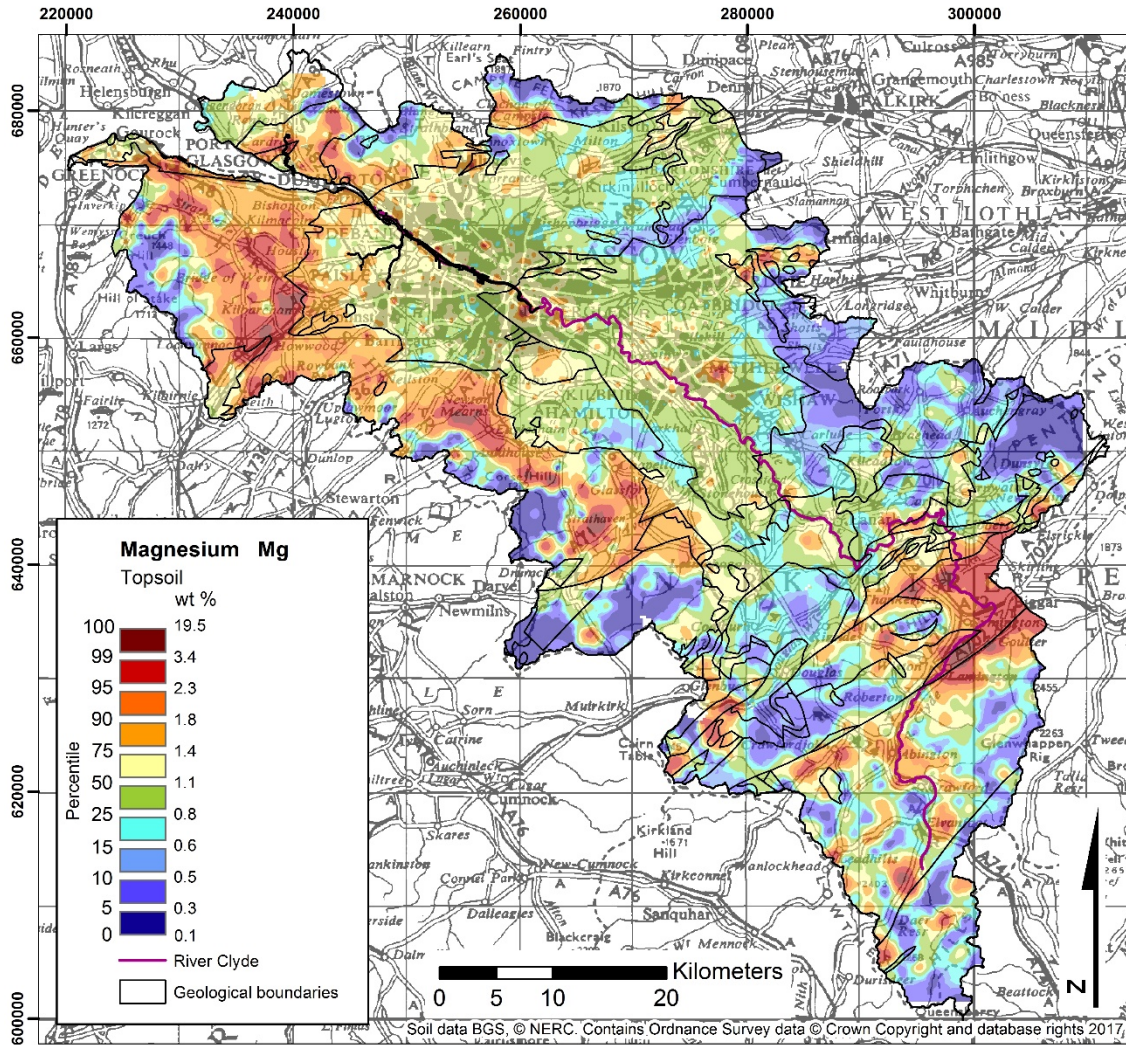
Statistics	Hafnium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.7	< 0.7	< 0.7
Maximum	81.4	13.8	81.4
Standard Deviation	3.1	2.2	2.8
Mean	6.0	6.0	6.0
Median	5.8	6.4	6.0
Minimum detectable value	0.7		
World soil median	5.0		



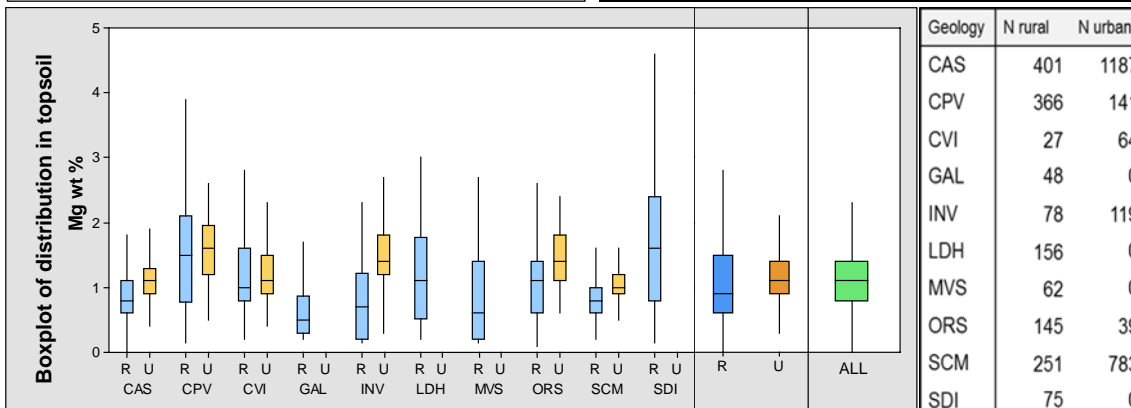
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Magnesium

Mg



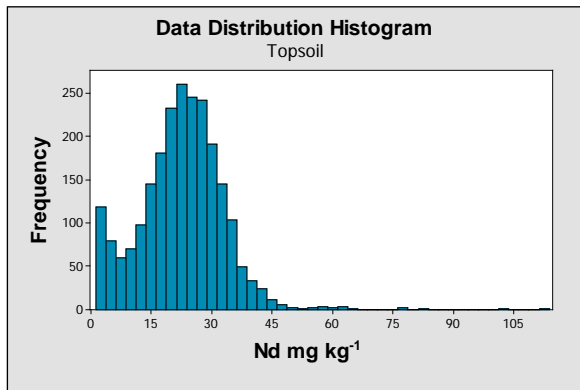
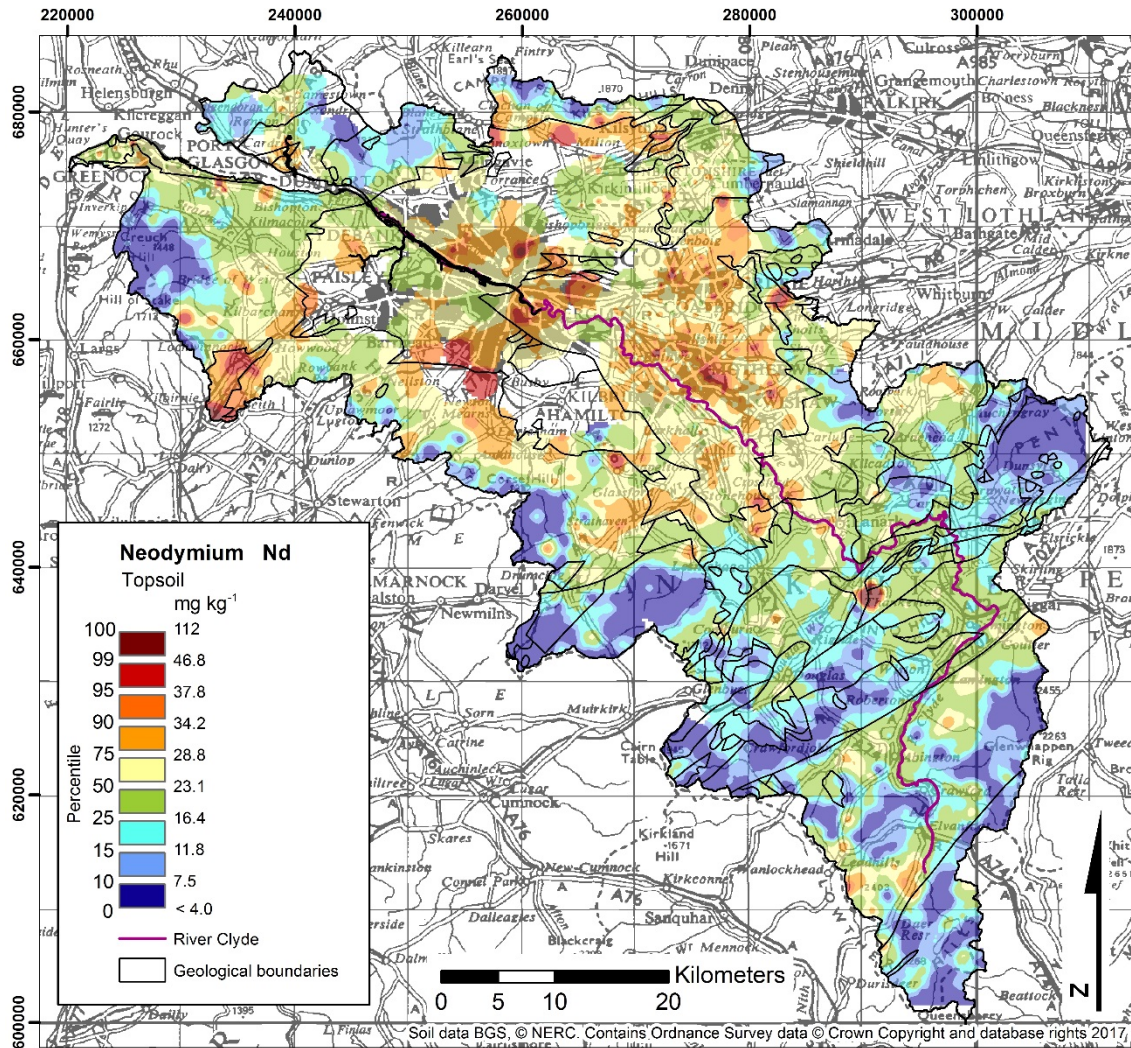
Statistics	Magnesium wt %		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	0.3	0.1	0.1
Maximum	19.5	5.7	19.5
Standard Deviation	0.6	0.8	0.7
Mean	1.2	1.1	1.2
Median	1.1	0.9	1.1
Minimum detectable value	0.1		
World soil median	1.5		



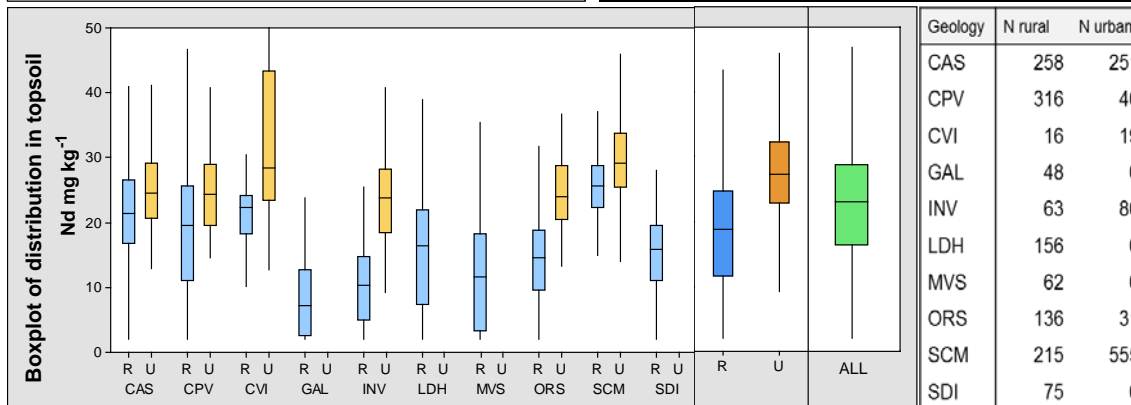
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks. Concentrations are expressed in MgO wt%.

Neodymium

Nd



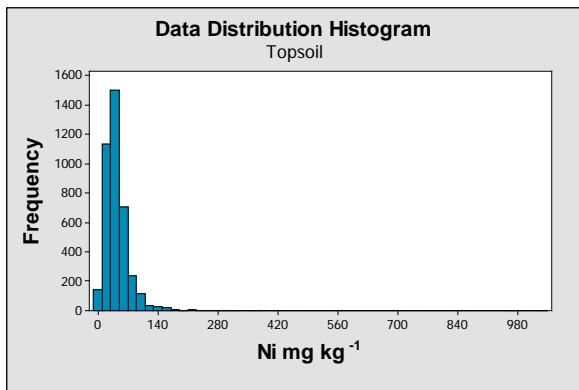
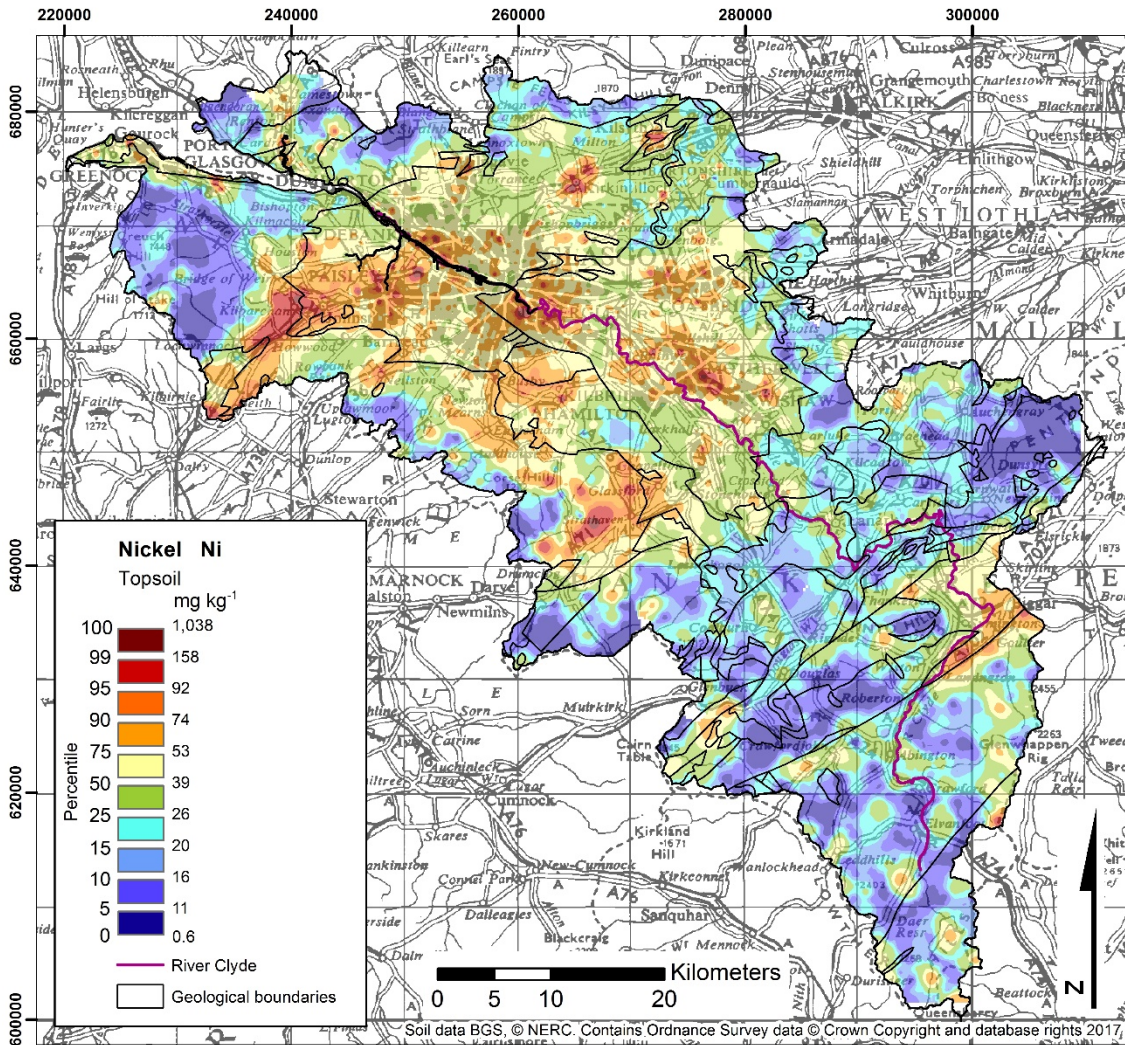
Statistics	Neodymium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	976	1345	2321
Minimum	9.3	< 4.0	< 4.0
Maximum	103.5	112.0	112.0
Standard Deviation	8.4	9.9	10.5
Mean	28.1	18.5	22.5
Median	27.3	18.9	23.1
Minimum detectable value	4.0		
World soil median	n/a		



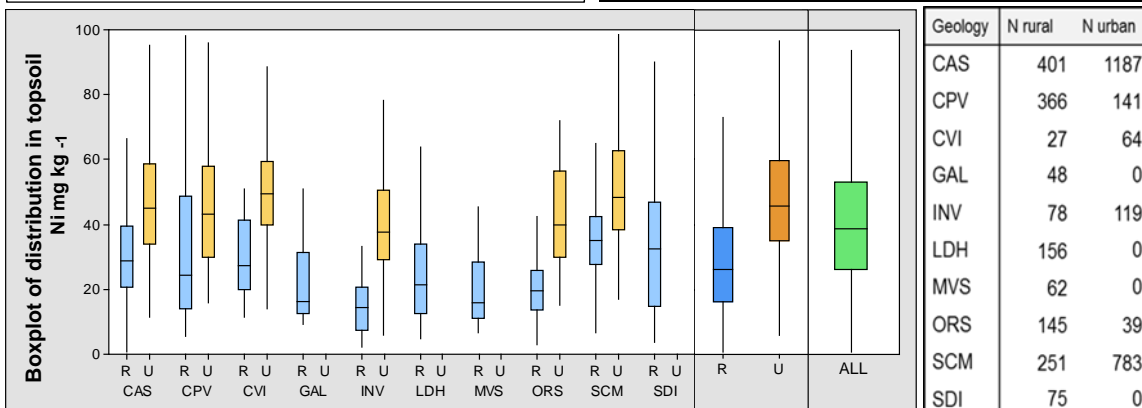
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Nickel

Ni



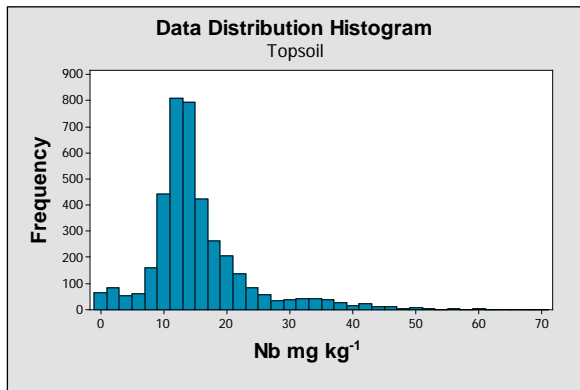
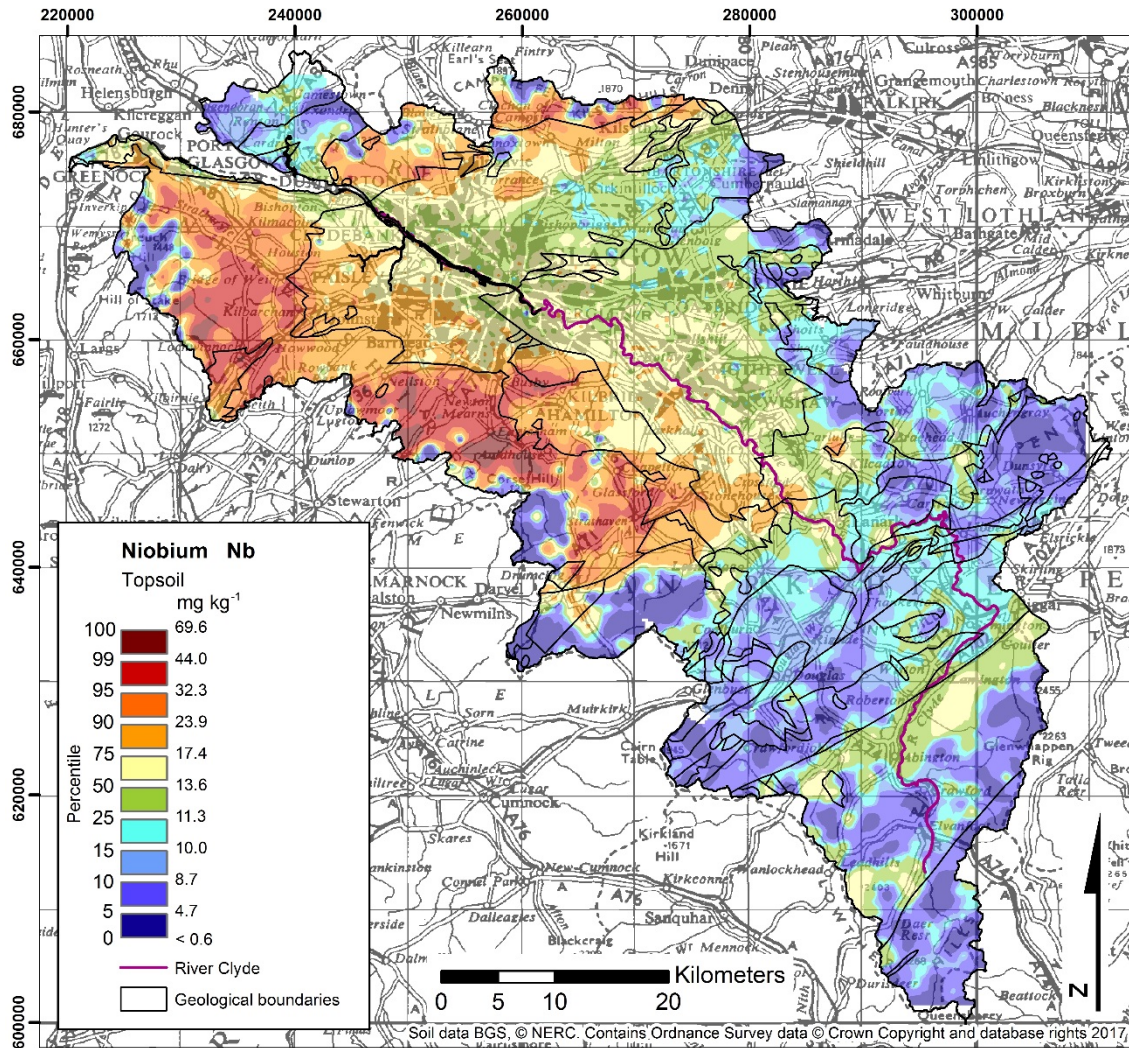
Statistics	Nickel mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	6.00	0.65	0.65
Maximum	1038.10	202.10	1038.10
Standard Deviation	41.80	21.06	36.63
Mean	53.50	30.56	44.13
Median	45.70	26.10	38.60
Minimum detectable value			0.60
World soil median			20.00



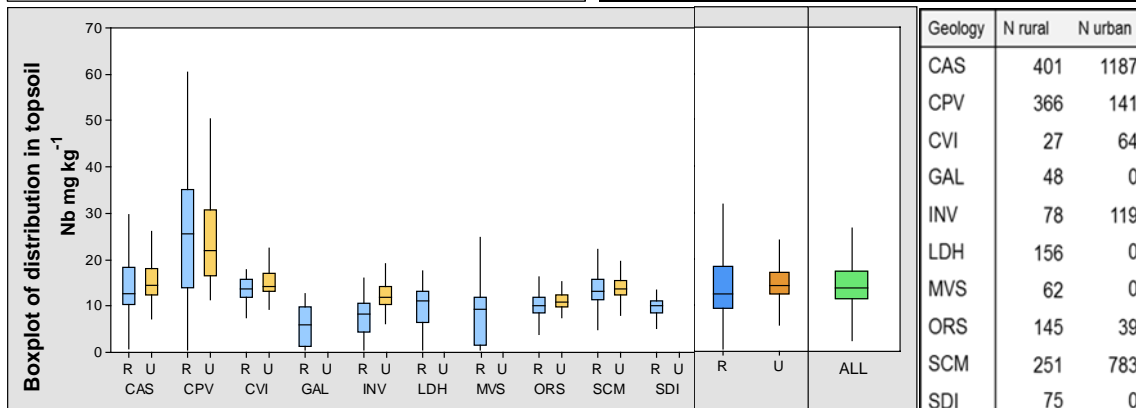
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Niobium

Nb



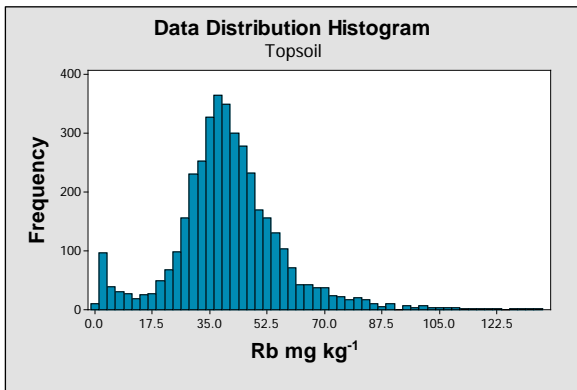
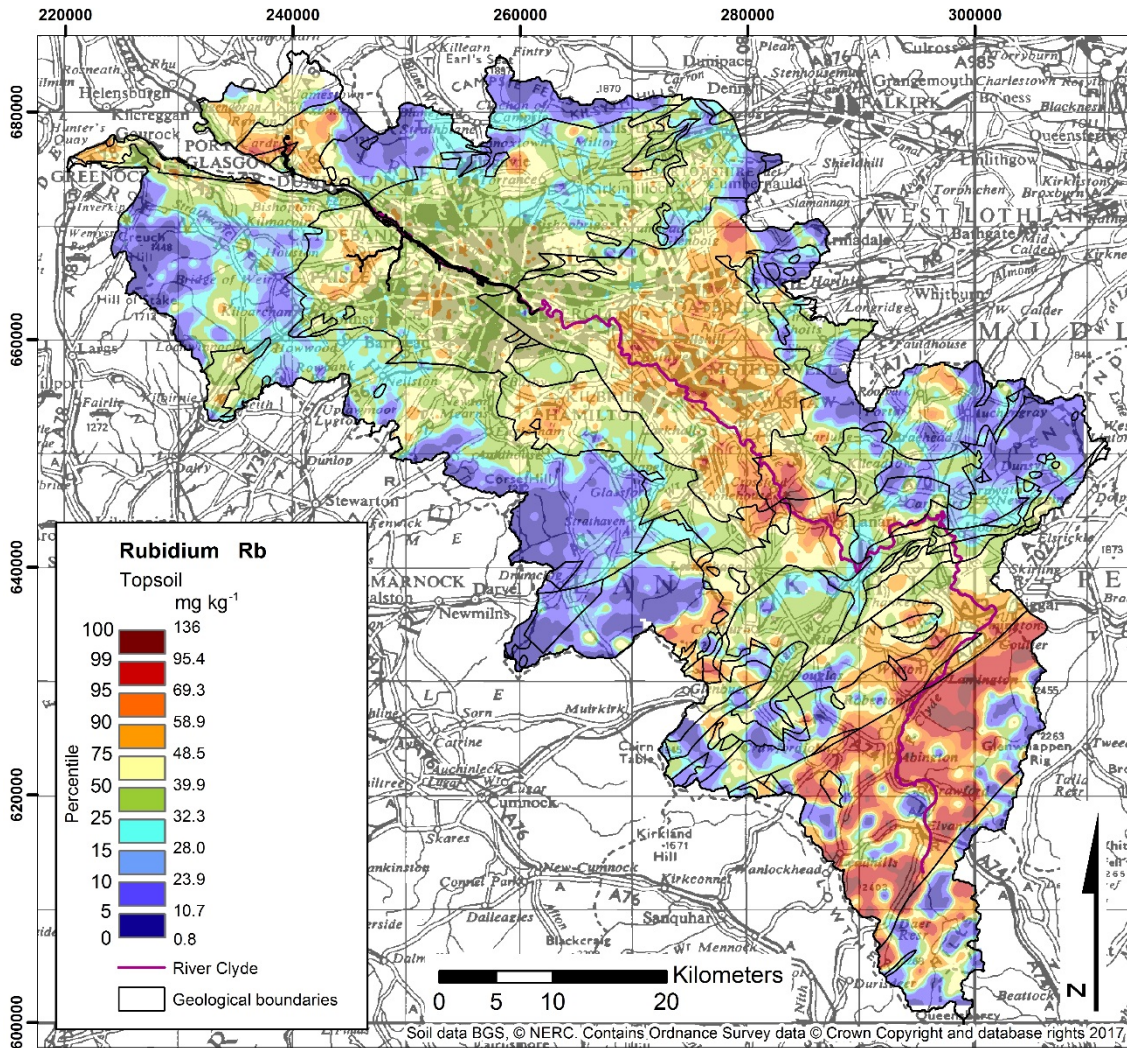
Statistics	Niobium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	0.6	< 0.6	< 0.6
Maximum	61.4	69.6	69.6
Standard Deviation	5.5	10.3	7.9
Mean	15.5	14.9	15.3
Median	14.1	12.3	13.6
Minimum detectable value	0.6		
World soil median	12.0		



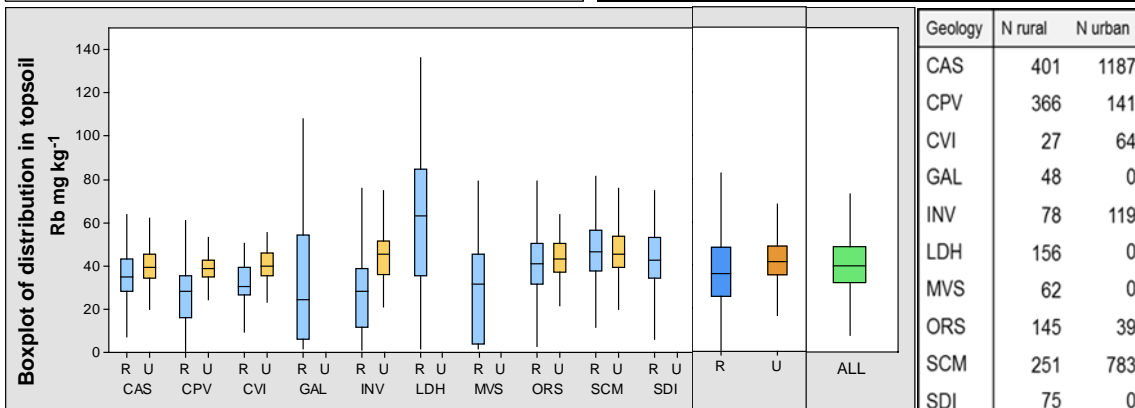
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Rubidium

Rb



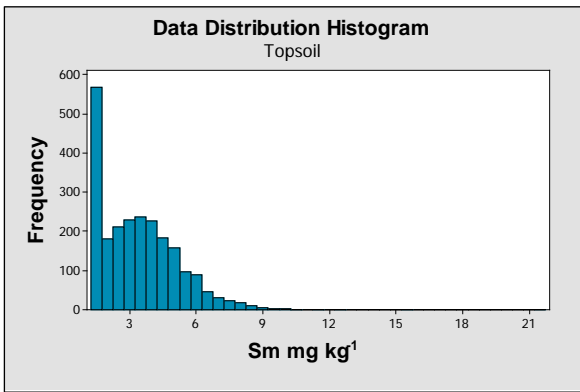
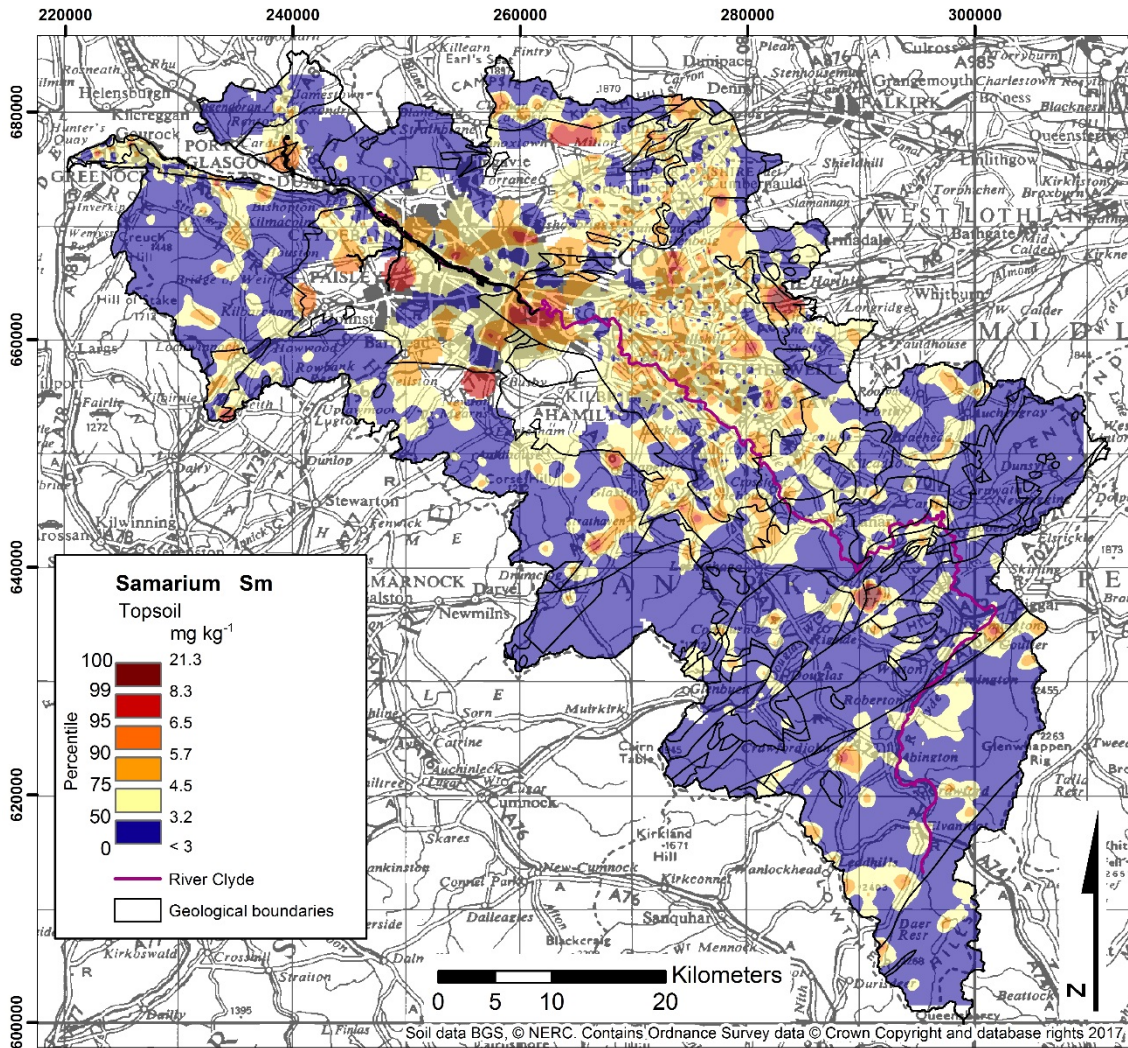
Statistics	Rubidium mg kg^{-1}		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	0.9	0.8	0.8
Maximum	109.3	136.1	136.1
Standard Deviation	11.3	21.8	16.6
Mean	43.1	37.7	40.9
Median	41.3	36.2	39.9
Minimum detectable value			0.5
World soil median			65.0



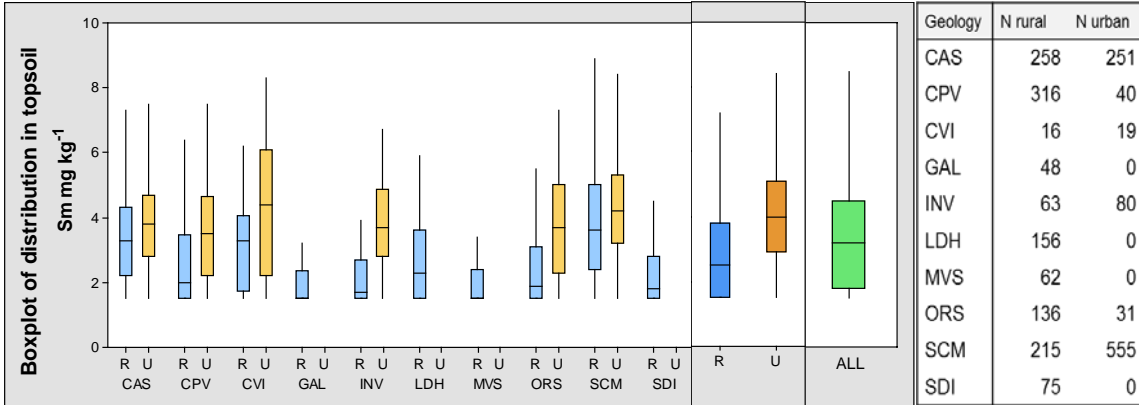
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Samarium

Sm



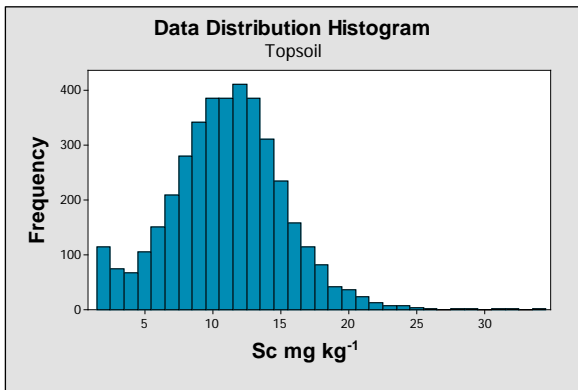
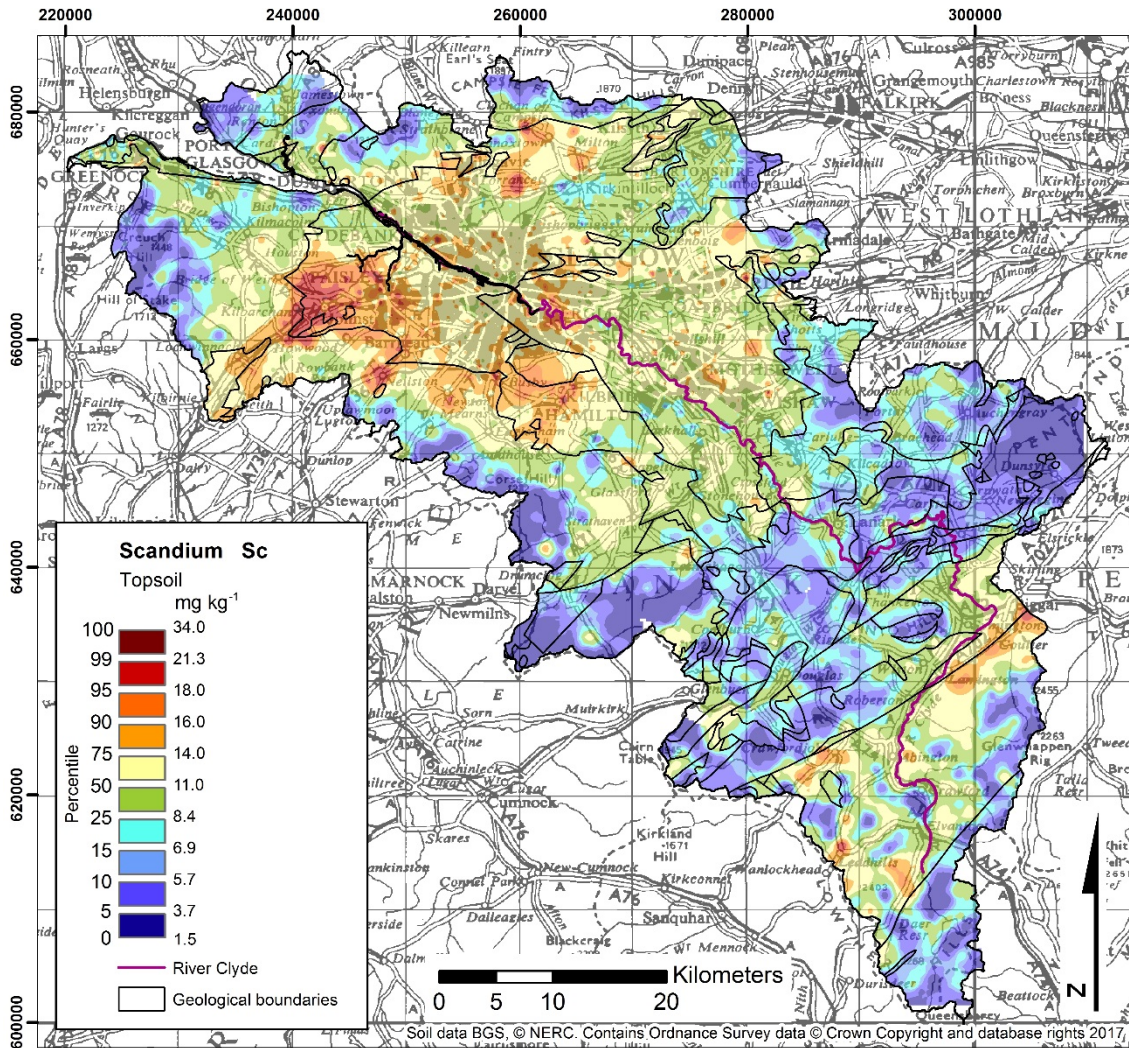
Statistics	Samarium mg kg^{-1}		
	Urban	Rural	All
No. of samples	976	1345	2321
Minimum	< 3.0	< 3.0	< 3.0
Maximum	15.4	21.3	21.3
Standard Deviation	1.7	1.6	1.8
Mean	4.1	2.9	3.4
Median	4.0	2.5	3.2
Minimum detectable value	3.0		
World soil median	6.1		



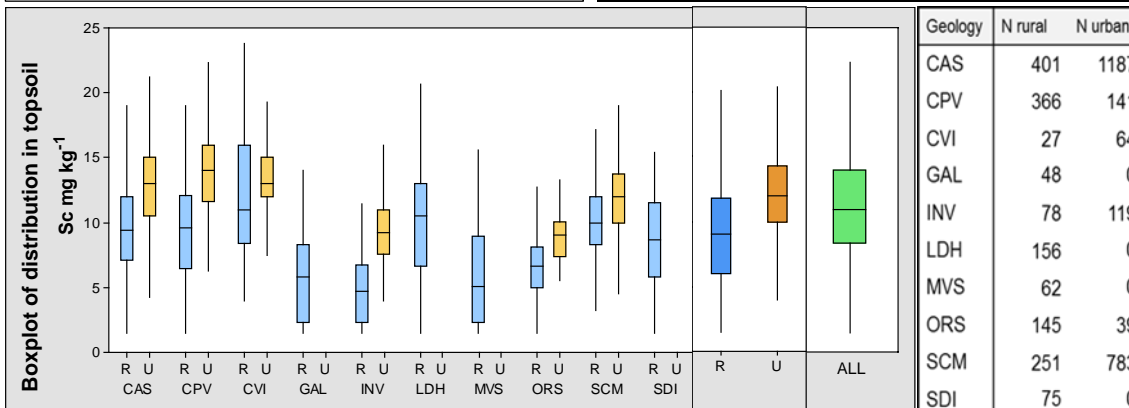
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Scandium

Sc



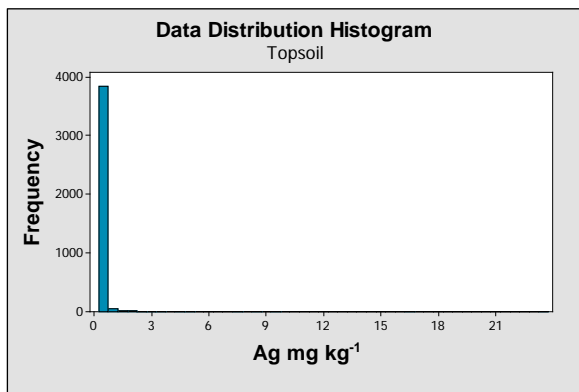
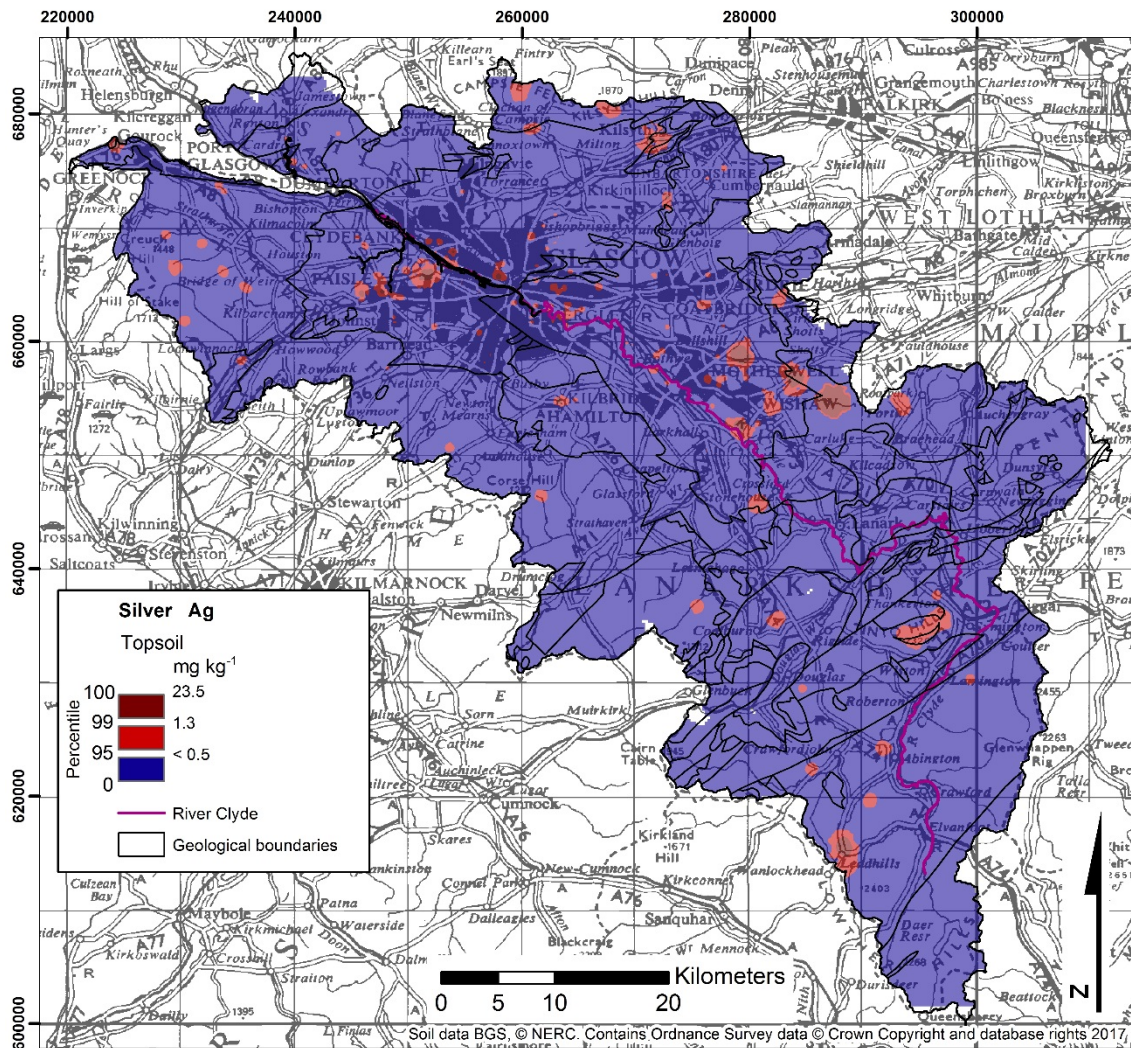
Statistics	Scandium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	4.0	1.5	1.5
Maximum	34.0	24.0	34.0
Standard Deviation	3.5	4.2	4.2
Mean	12.5	9.0	11.0
Median	12.0	9.0	11.0
Minimum detectable value			1.3
World soil median			12.0



R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Silver

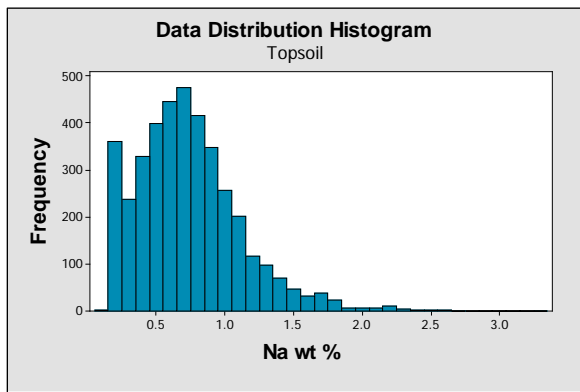
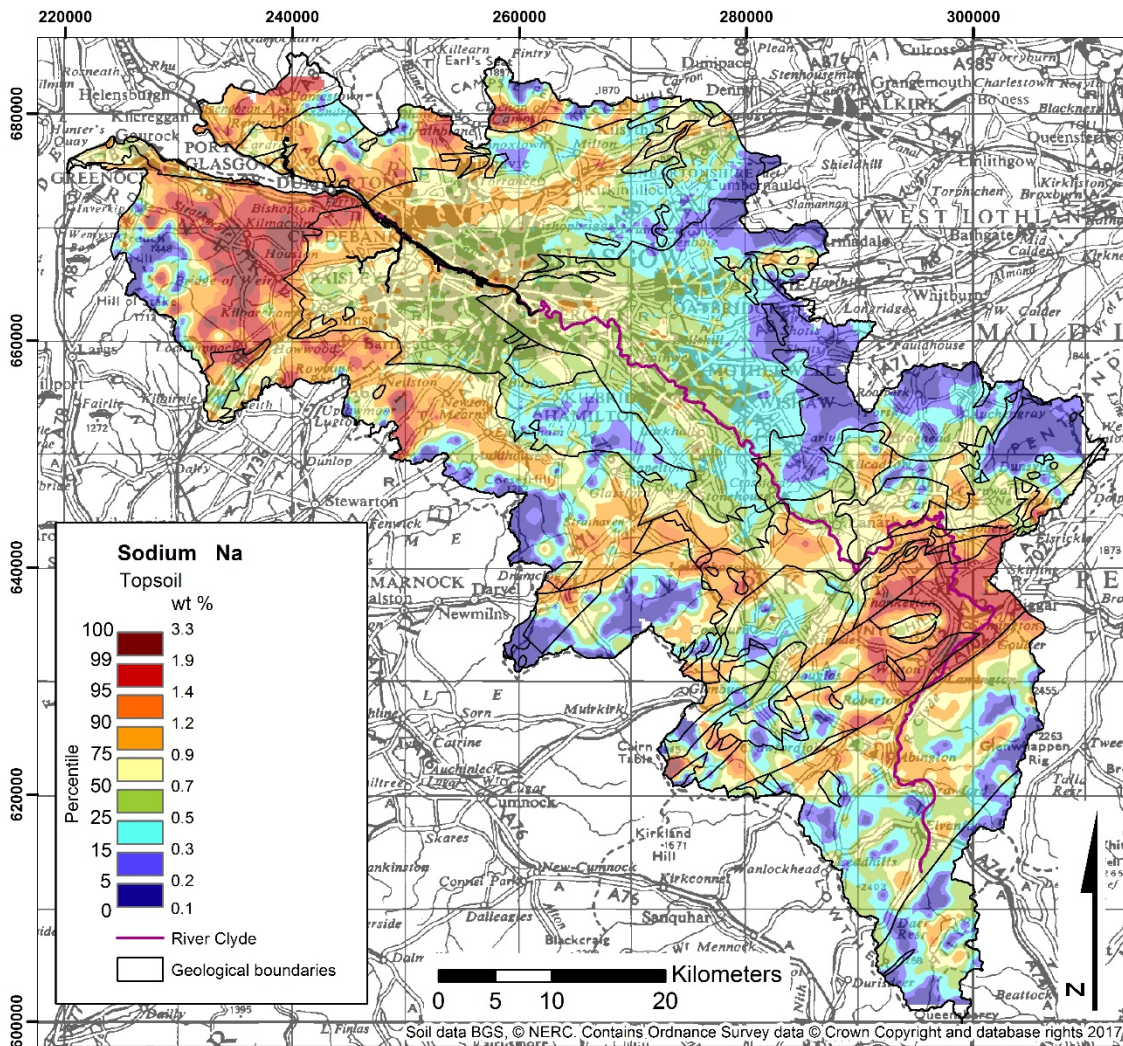
Ag



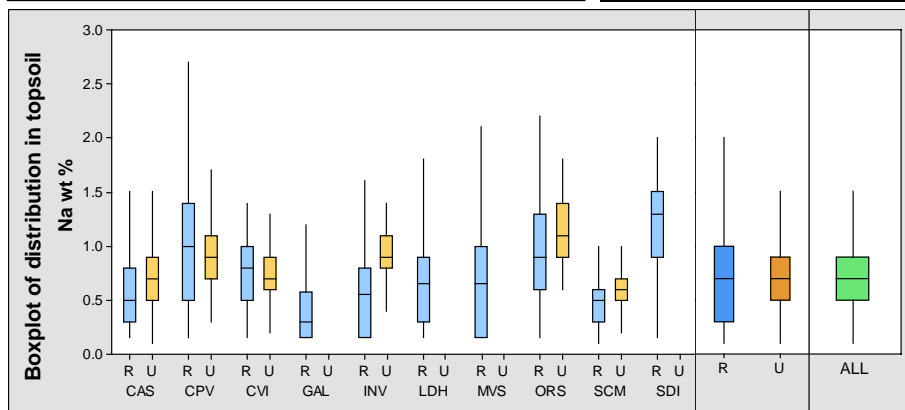
Statistics	Silver mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1609	3942
Minimum	< 0.5	< 0.5	< 0.5
Maximum	23.5	16.4	23.5
Standard Deviation	0.64	0.43	0.56
Mean	0.33	0.29	0.31
Median	0.25	0.25	0.25
Minimum detectable value			0.5
World soil median			0.07

Sodium

Na



Statistics	Sodium wt %		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	0.1	0.2	0.1
Maximum	2.4	3.3	3.3
Standard Deviation	0.3	0.5	0.4
Mean	0.7	0.7	0.7
Median	0.7	0.7	0.7
Minimum detectable value	0.1		
World soil median	1.3		

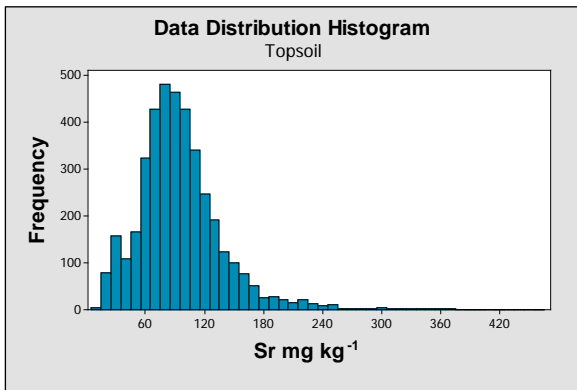
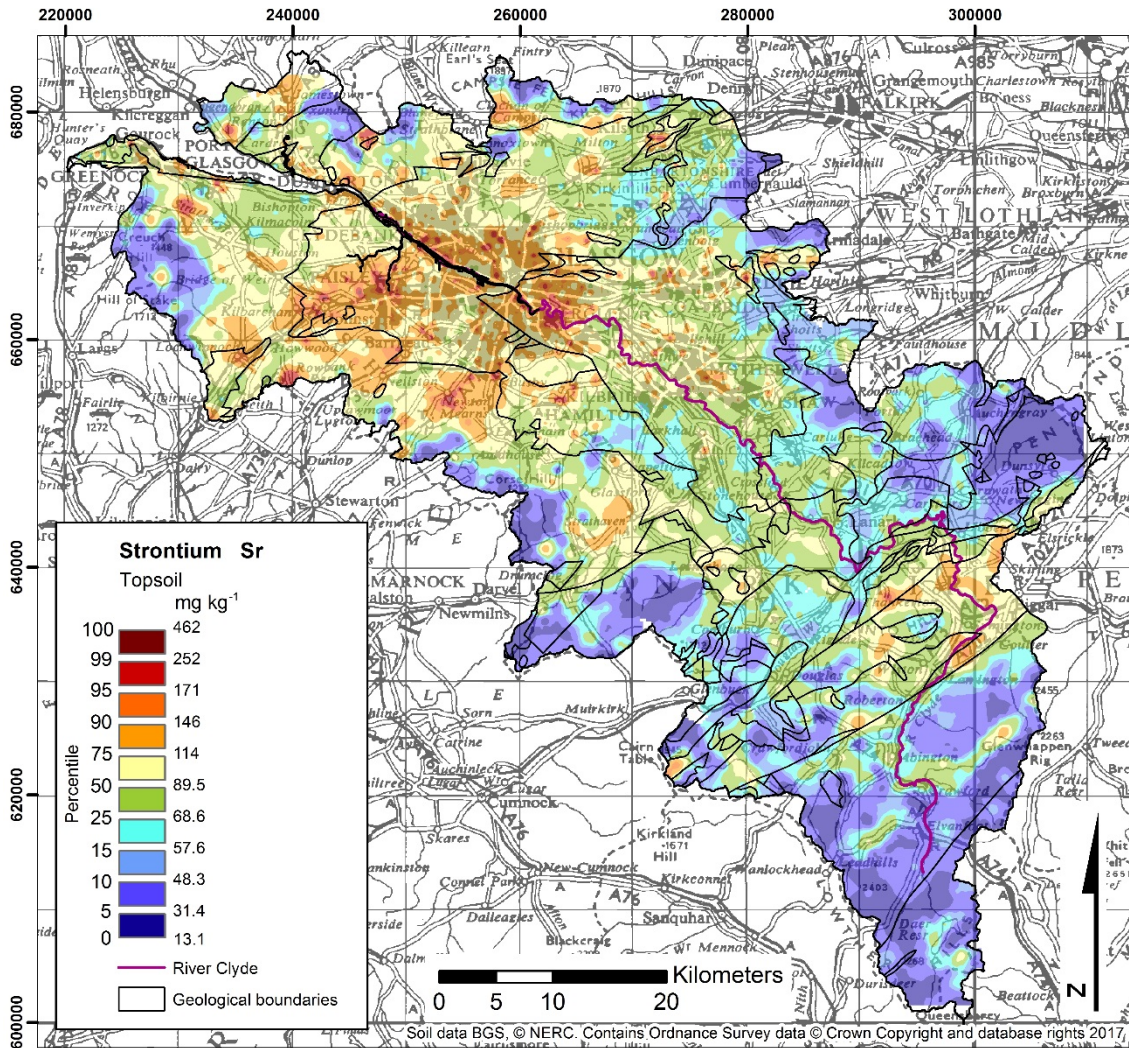


Geology	N rural	N urban
CAS	401	1187
CPV	366	141
CVI	27	64
GAL	48	0
INV	78	119
LDH	156	0
MVS	62	0
ORS	145	39
SCM	251	783
SDI	75	0

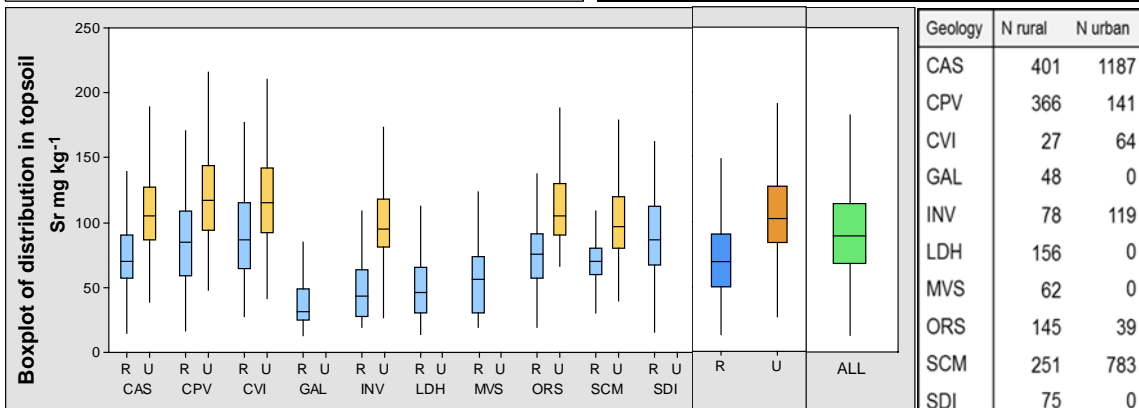
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks. Concentrations are expressed in Na₂O wt%.

Strontium

Sr



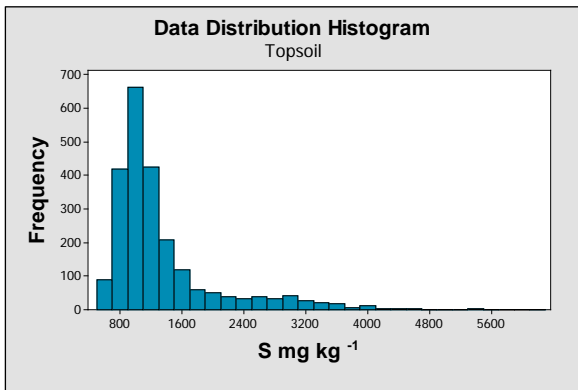
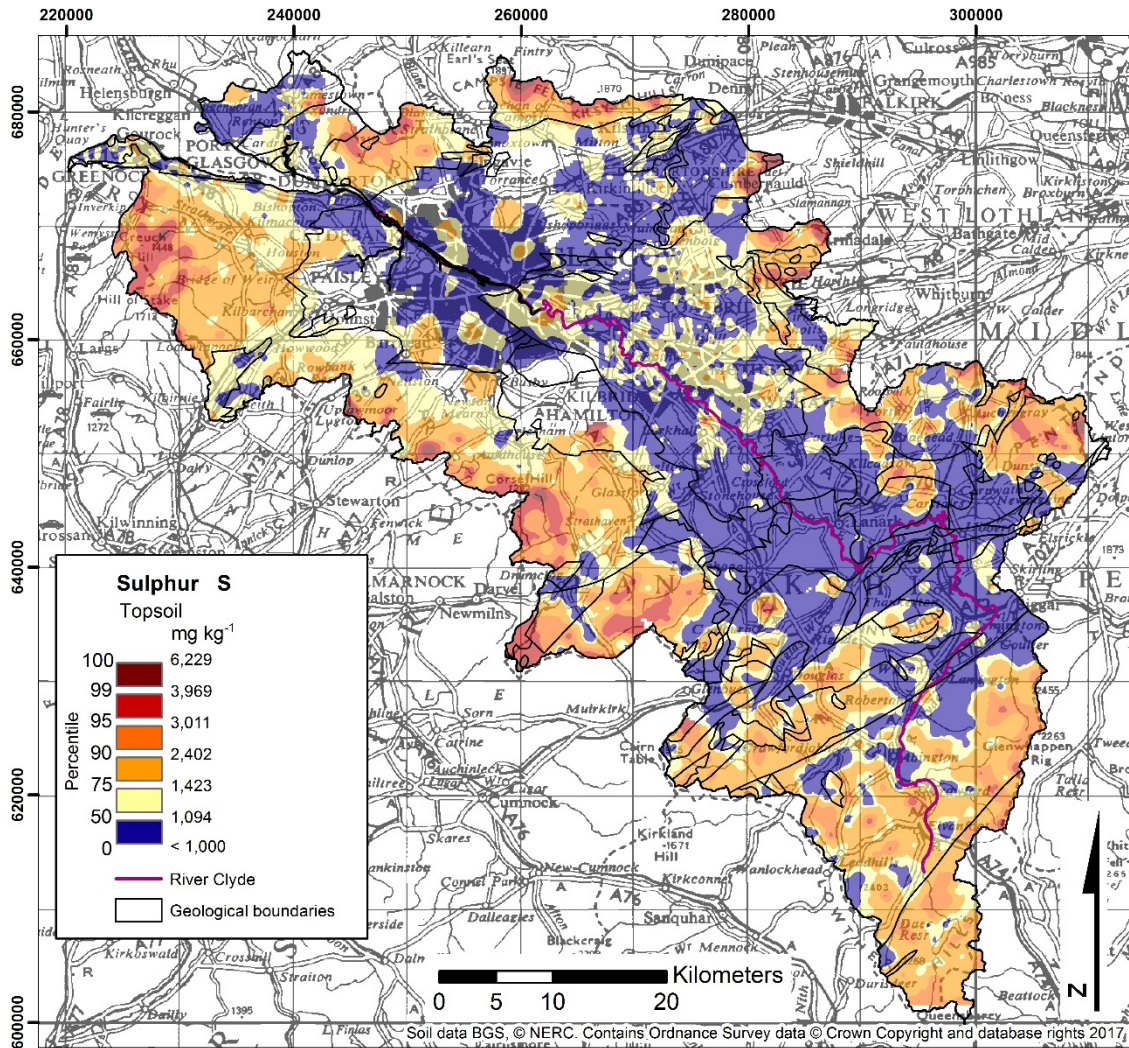
Statistics	Strontium mg kg^{-1}		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	27.1	13.1	13.1
Maximum	462.4	247.3	462.4
Standard Deviation	45.3	33.4	45.3
Mean	111.9	72.3	95.7
Median	102.3	69.4	89.5
Minimum detectable value			0.6
World soil median			240



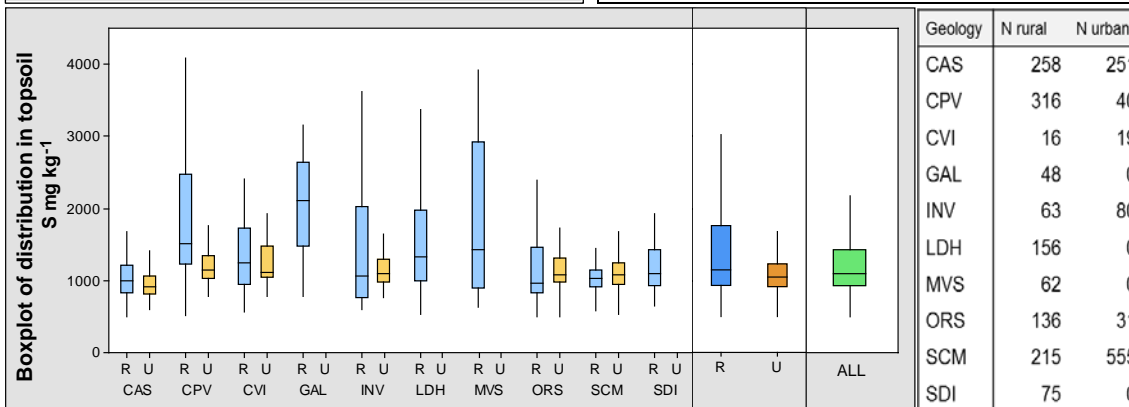
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Sulphur

S



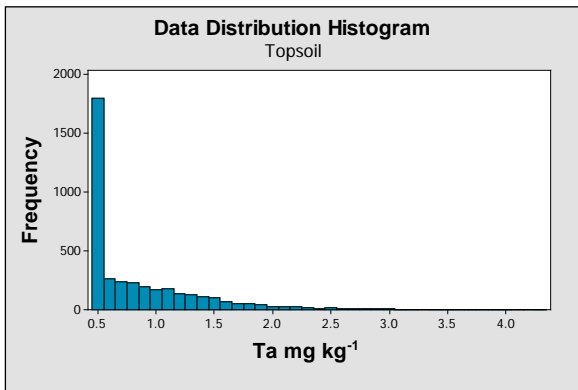
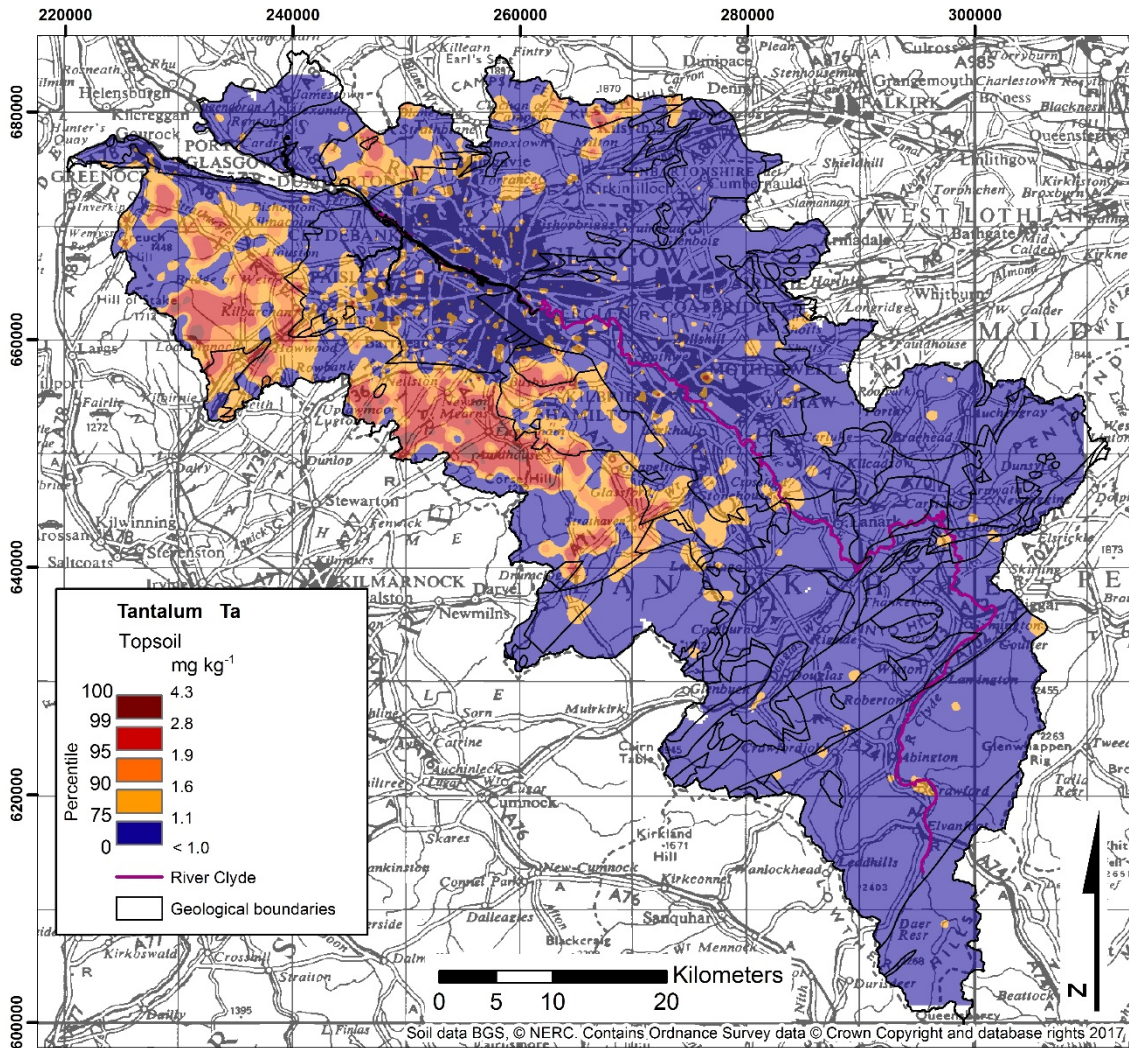
Statistics	Sulphur mg kg ⁻¹		
	Urban	Rural	All
No. of samples	976	1345	2321
Minimum	< 1000	< 1000	< 1000
Maximum	5549	6229	6229
Standard Deviation	334	869	718
Mean	1111	1506	1338
Median	1052	1145	1094
Minimum detectable value	1000		
World soil median	800		



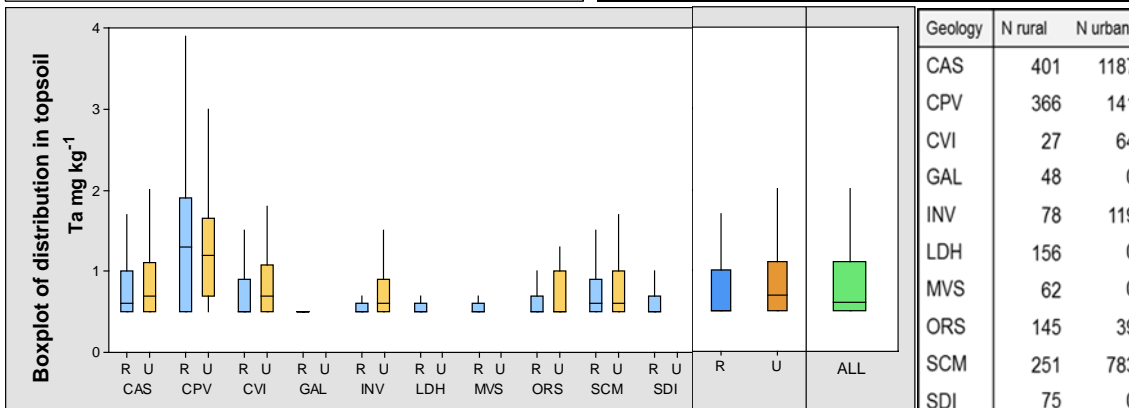
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Tantalum

Ta



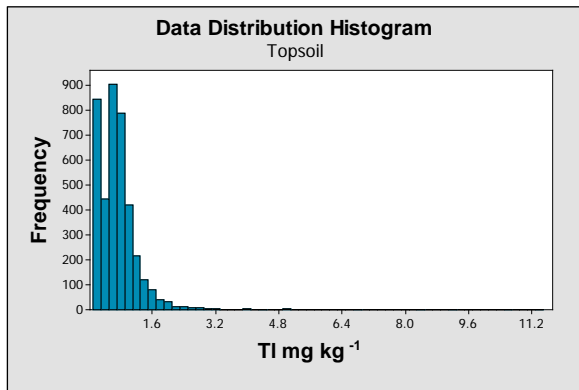
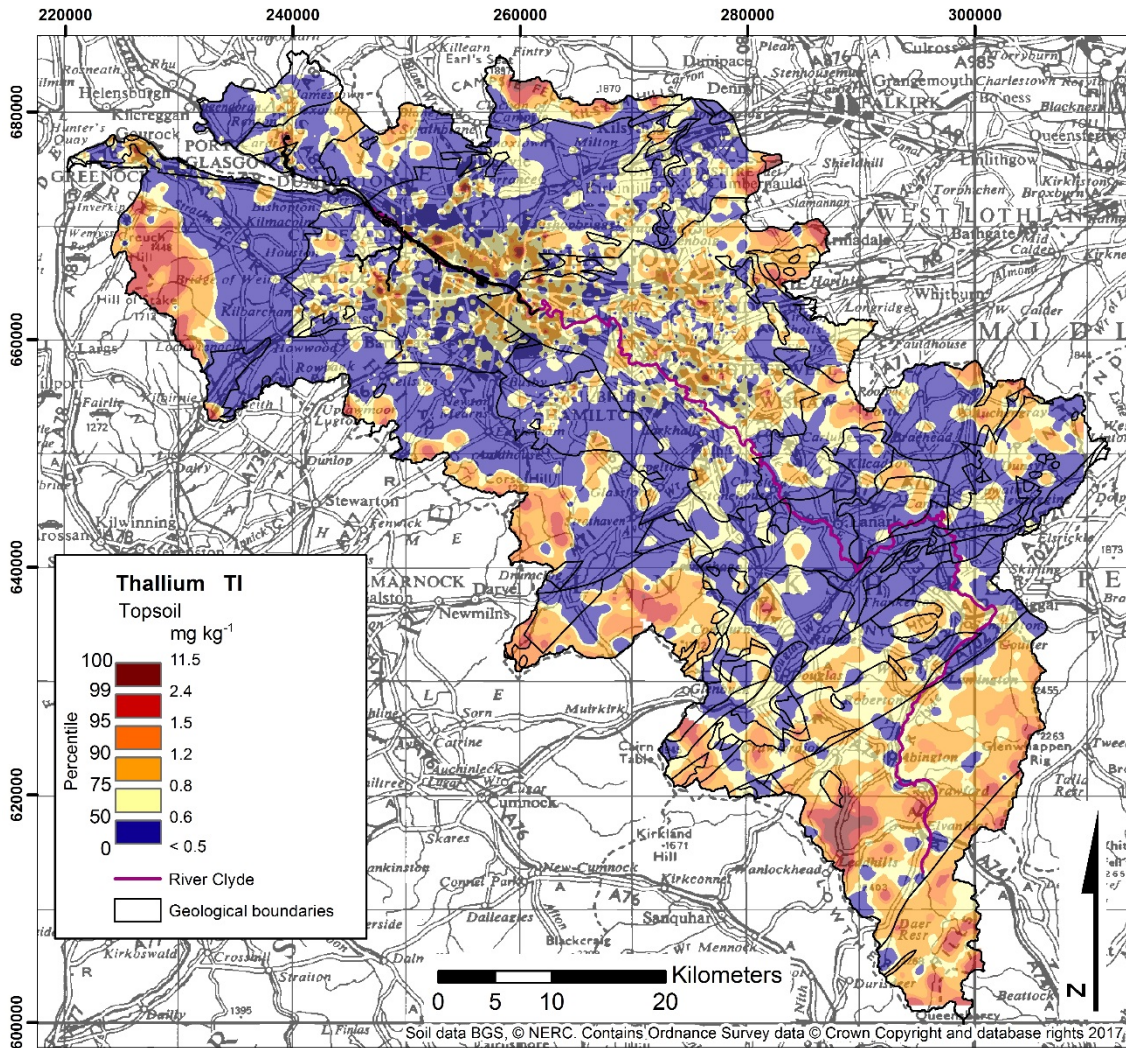
	Tantalum mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 1.0	< 1.0	< 1.0
Maximum	4.0	4.3	4.3
Standard Deviation	0.5	0.6	0.5
Mean	0.9	0.9	0.9
Median	0.7	0.5	0.6
Minimum detectable value	1.0		
World soil median	1.1		



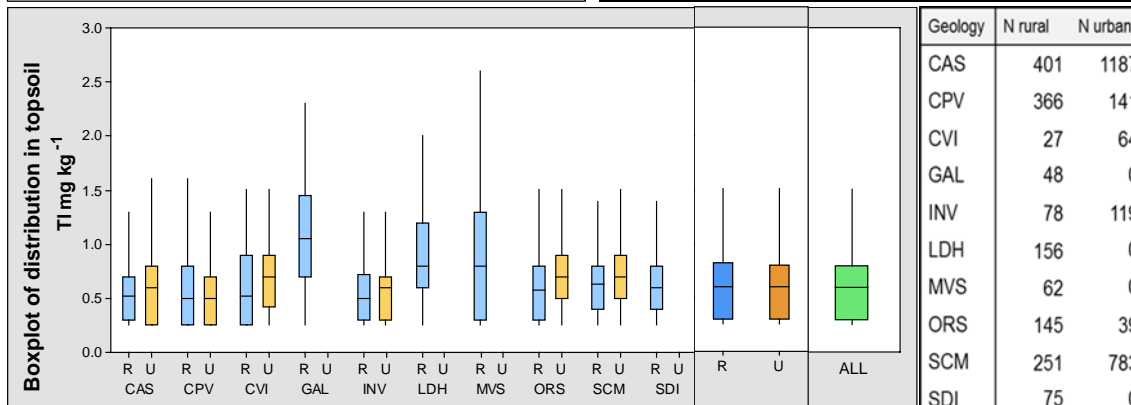
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Thallium

TI



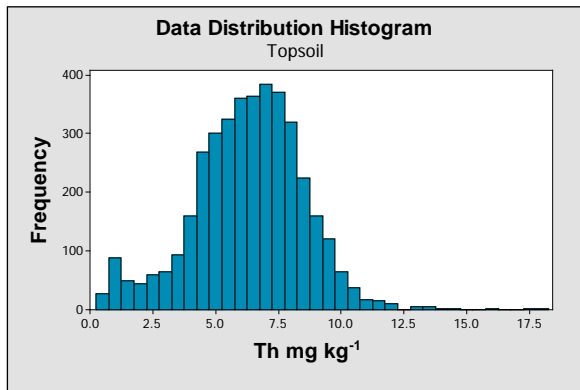
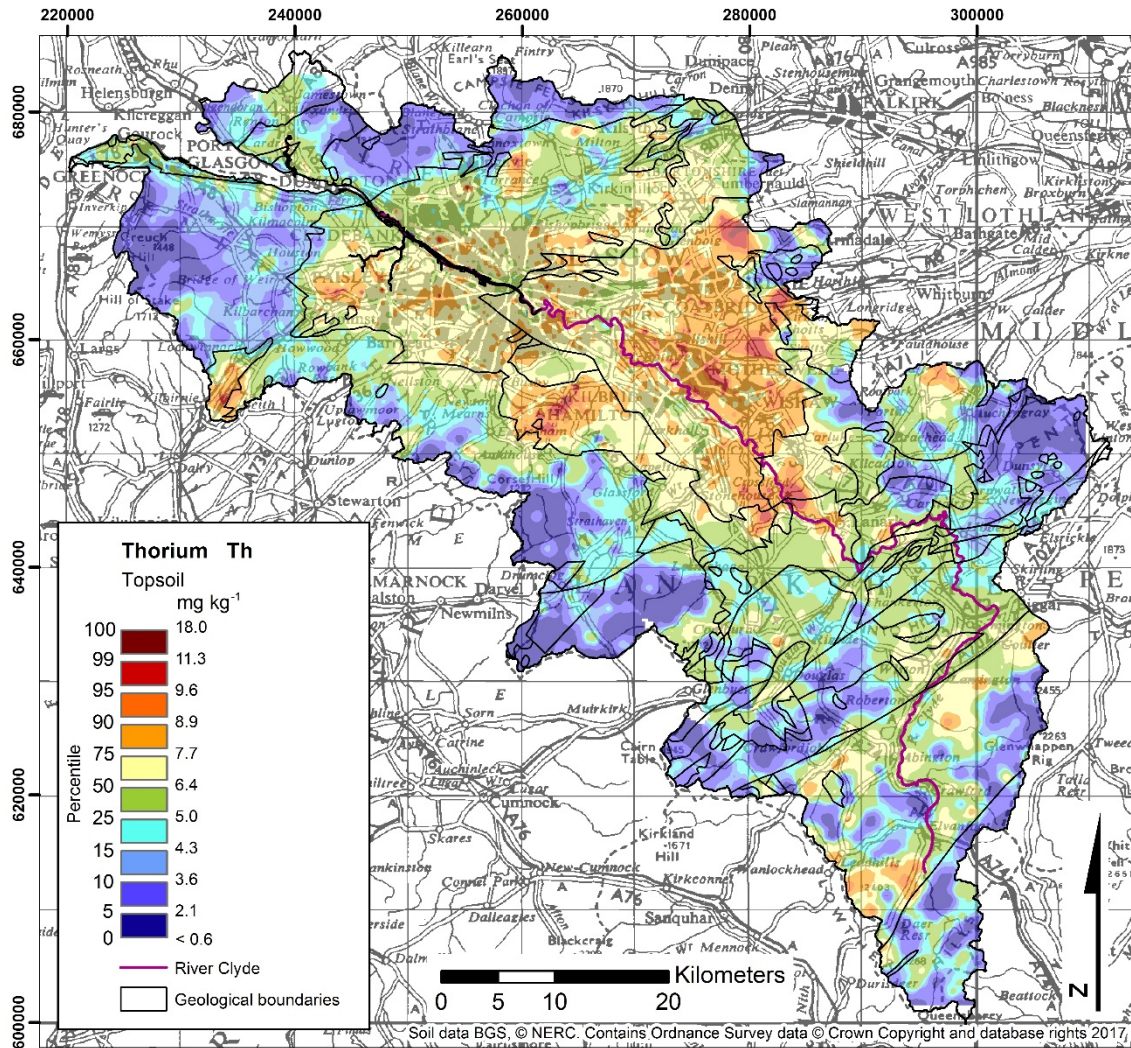
	Thallium mg kg^{-1}		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.50	< 0.50	< 0.50
Maximum	11.50	4.40	11.50
Standard Deviation	0.59	0.46	0.54
Mean	0.69	0.69	0.69
Median	0.60	0.60	0.60
Minimum detectable value	0.50		
World soil median	0.50		



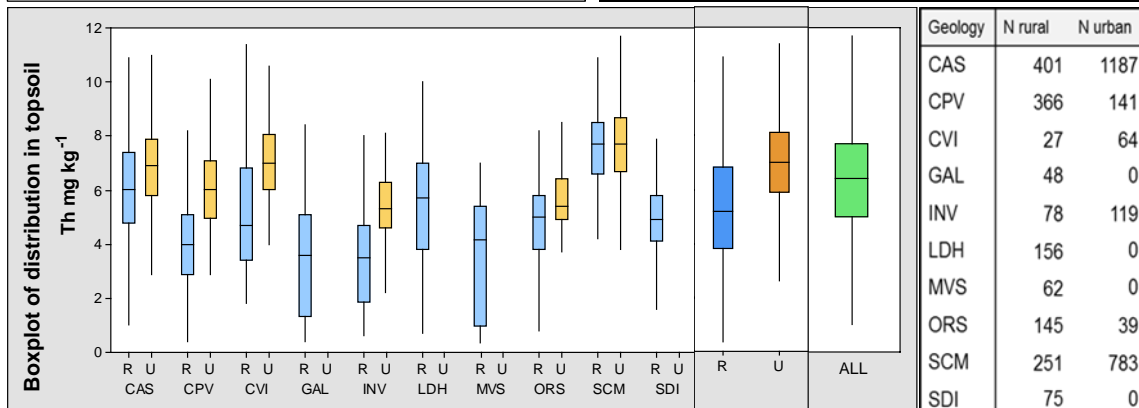
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Thorium

Th



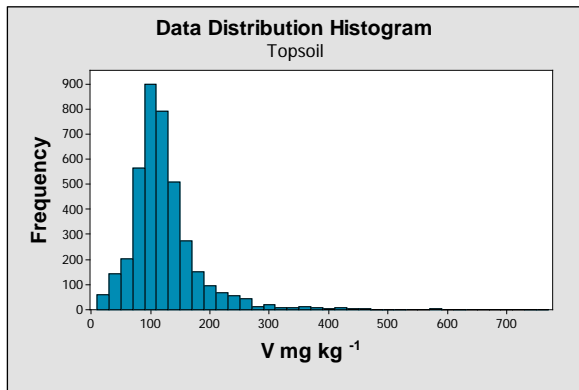
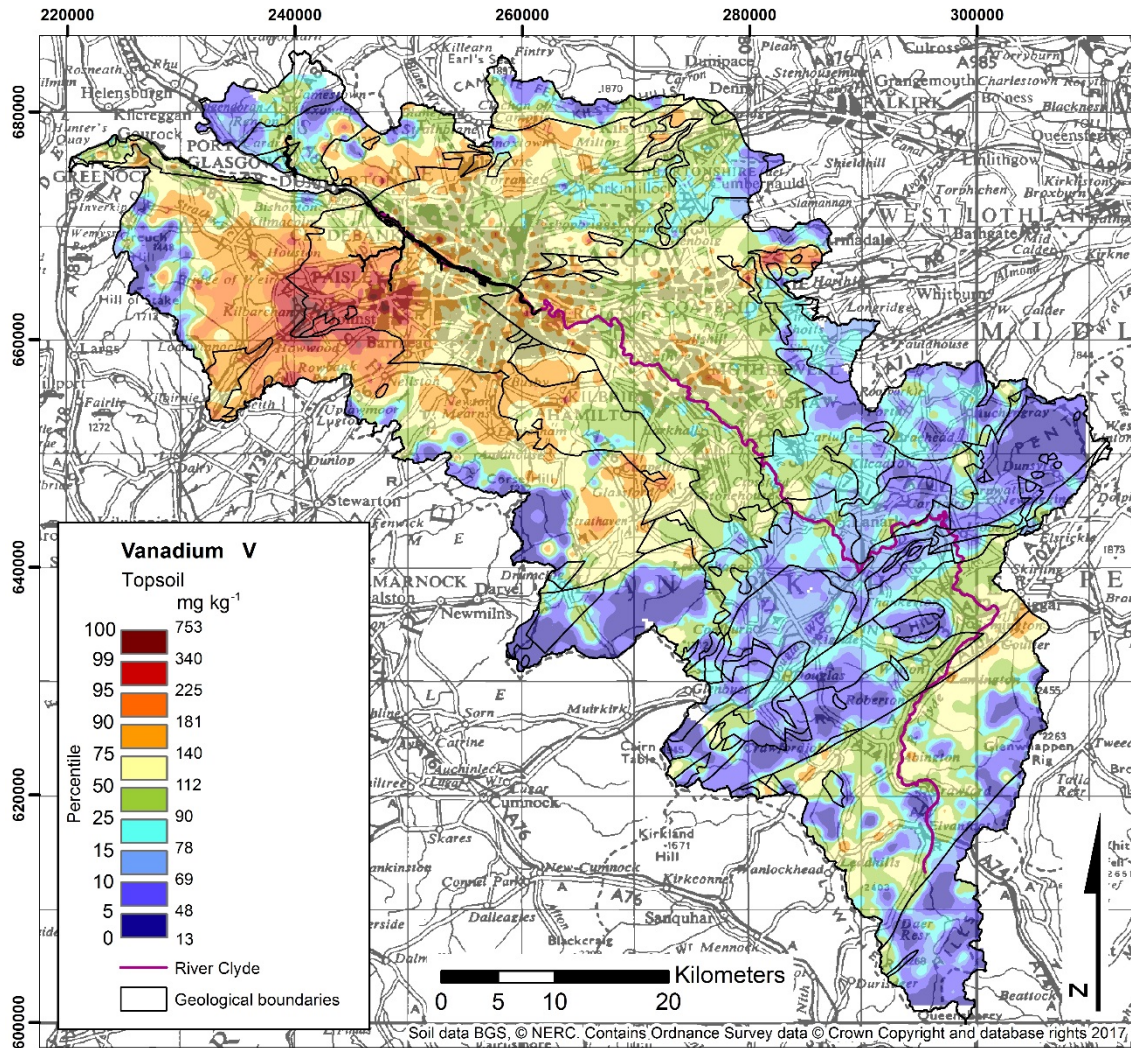
Statistics	Thorium mg kg^{-1}		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	1.0	< 0.6	< 0.6
Maximum	18.0	13.4	18.0
Standard Deviation	1.7	2.3	2.2
Mean	7.1	5.2	6.3
Median	7.0	5.2	6.4
Minimum detectable value	0.6		
World soil median	9.4		



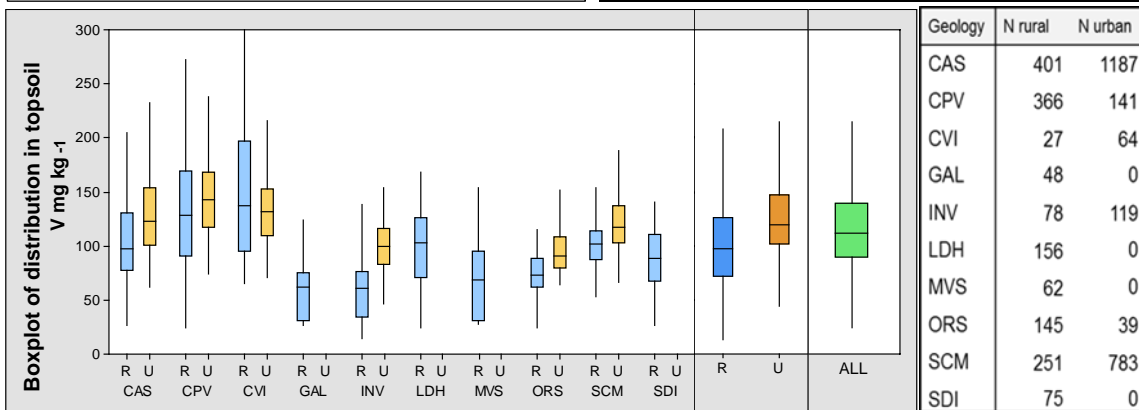
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Vanadium

V



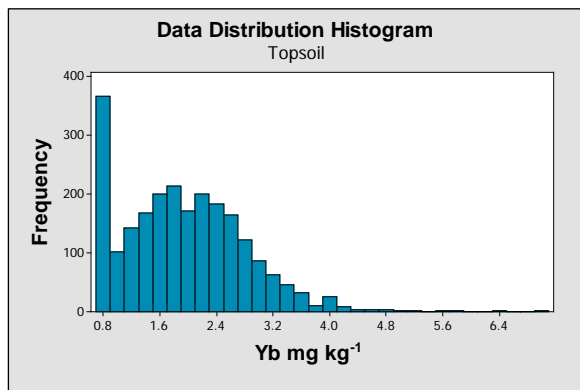
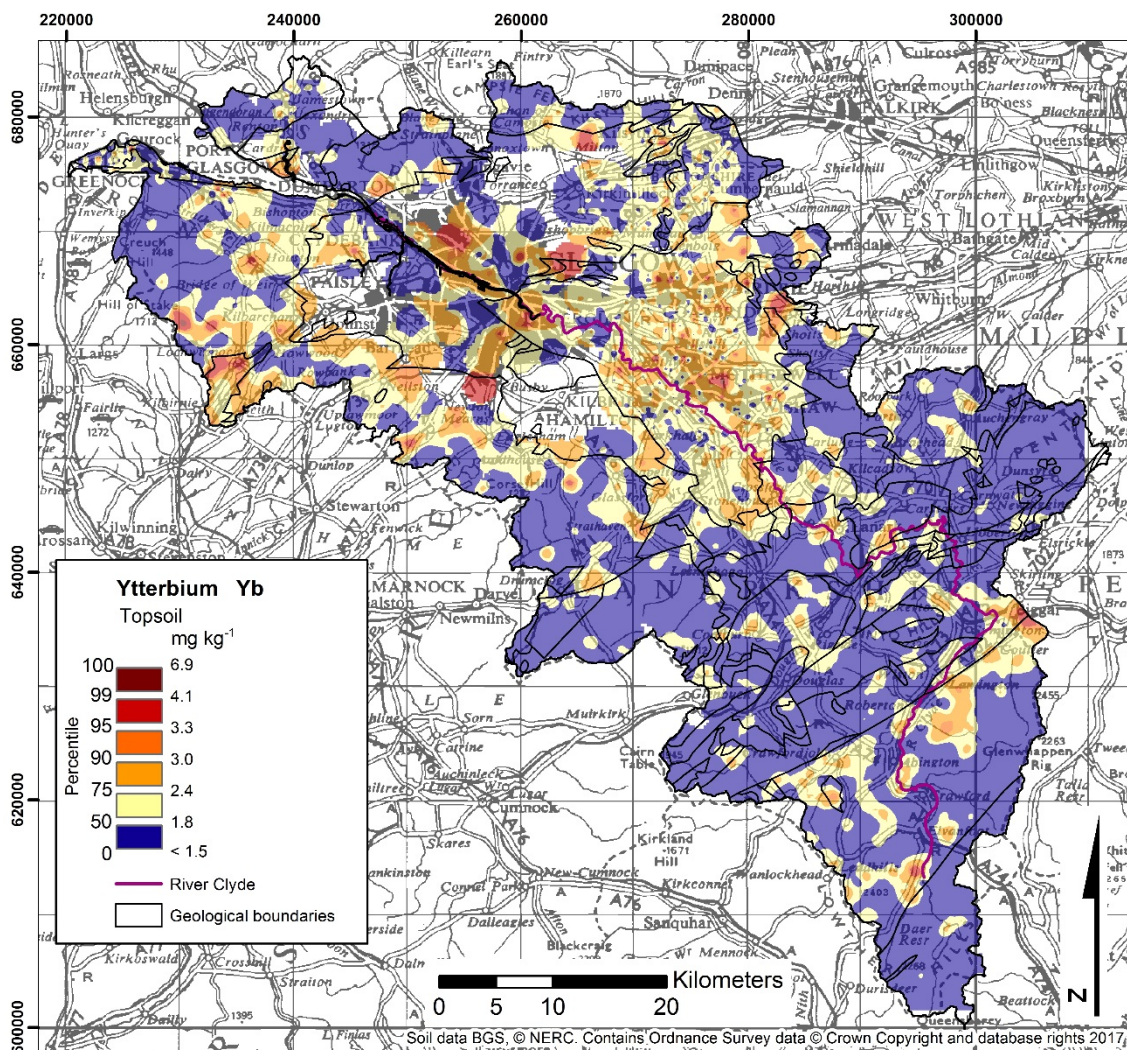
Statistics	Vanadium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	25.0	13.0	13.0
Maximum	737.0	753.0	753.0
Standard Deviation	56.5	54.1	57.4
Mean	133.7	104.0	121.6
Median	119.5	97.3	112.0
Minimum detectable value	1.3		
World soil median	90.0		



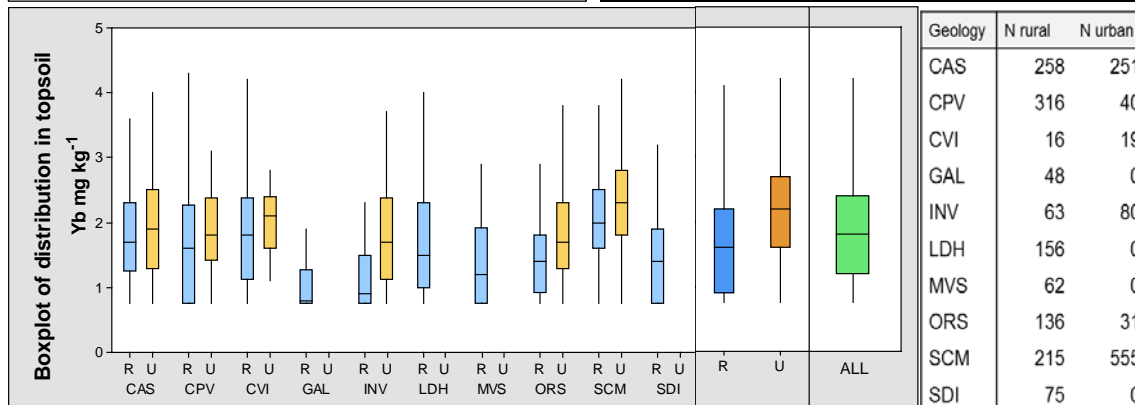
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Ytterbium

Yb



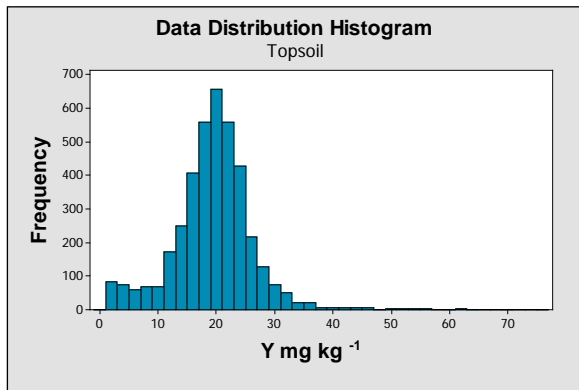
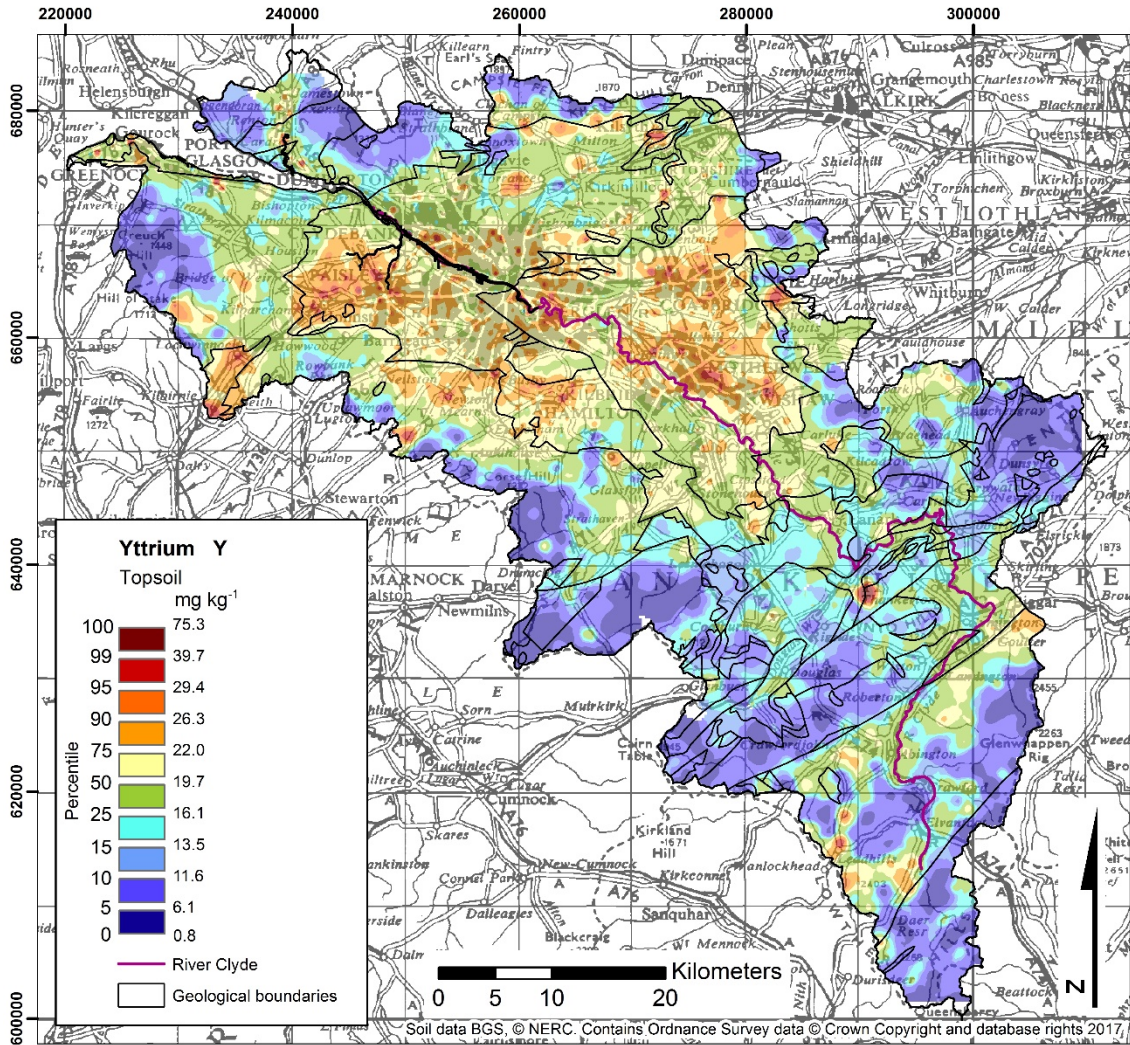
Statistics	Ytterbium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	976	1345	2321
Minimum	< 1.50	< 1.50	< 1.50
Maximum	6.90	4.80	6.90
Standard Deviation	0.87	0.77	0.85
Mean	2.19	1.66	1.89
Median	2.20	1.60	1.80
Minimum detectable value	1.50		
World soil median	3.30		



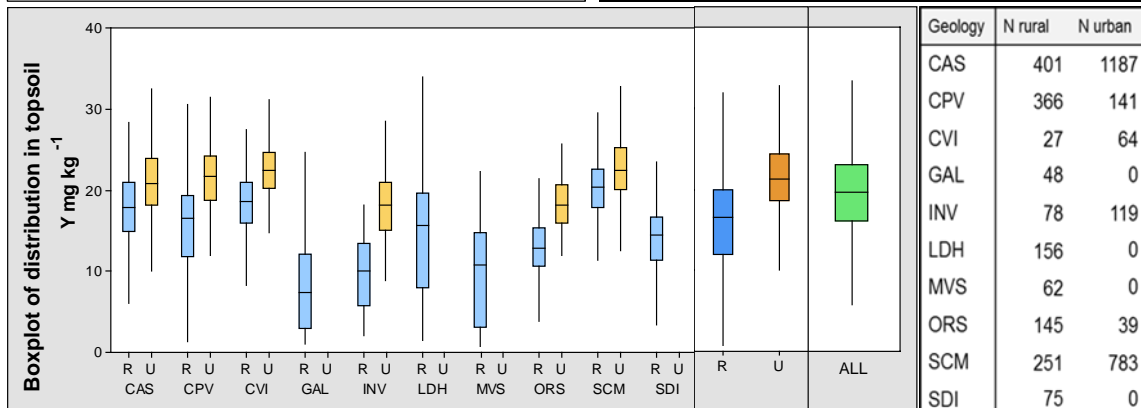
R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks

Yttrium

Y



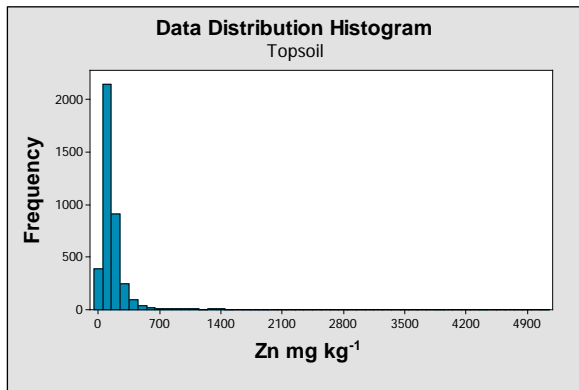
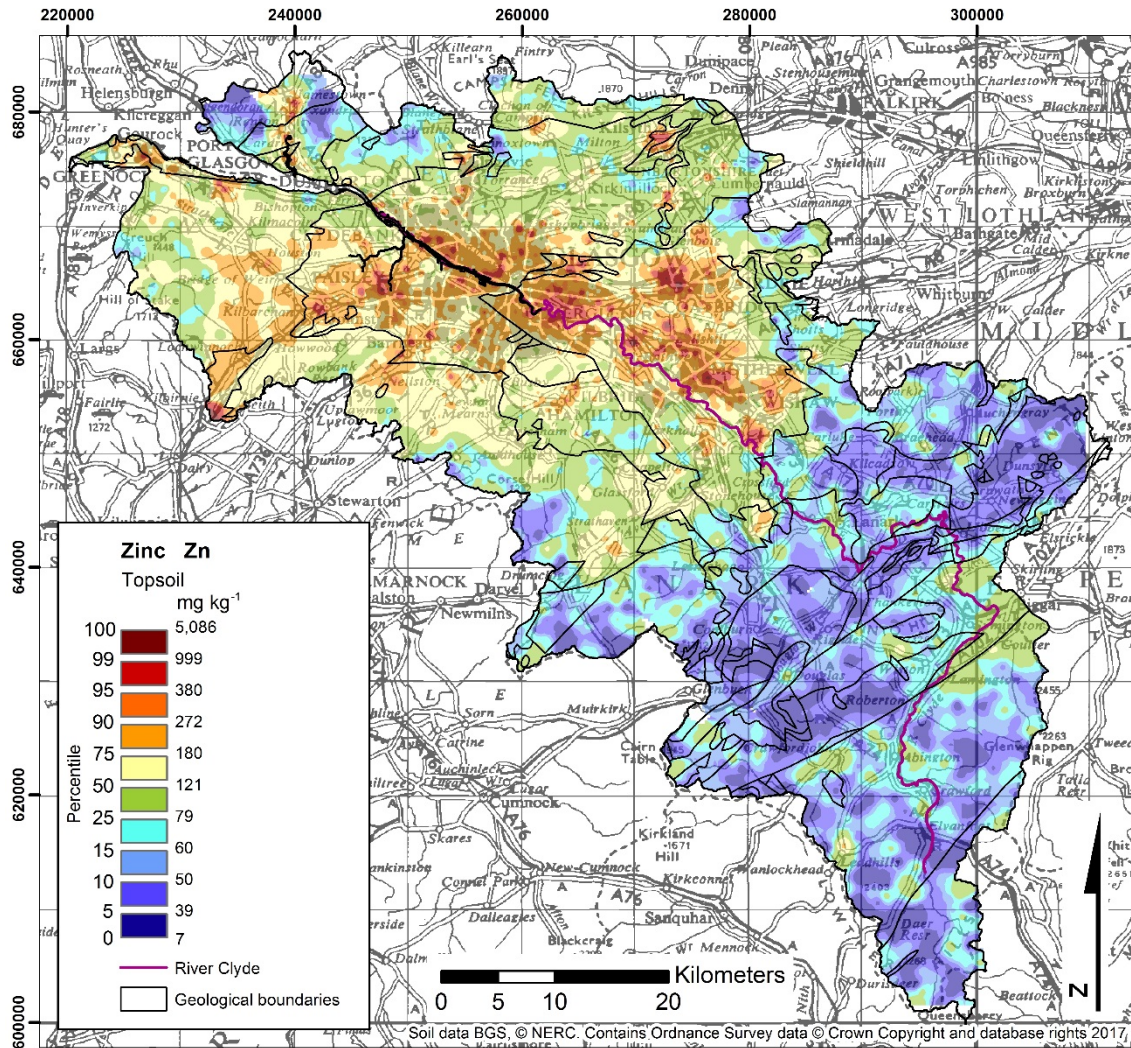
	Yttrium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	2.4	0.8	0.8
Maximum	75.3	55.0	75.3
Standard Deviation	5.8	6.6	6.9
Mean	22.0	15.6	19.4
Median	21.3	16.5	19.7
Minimum detectable value	0.8		
World soil median	20.0		



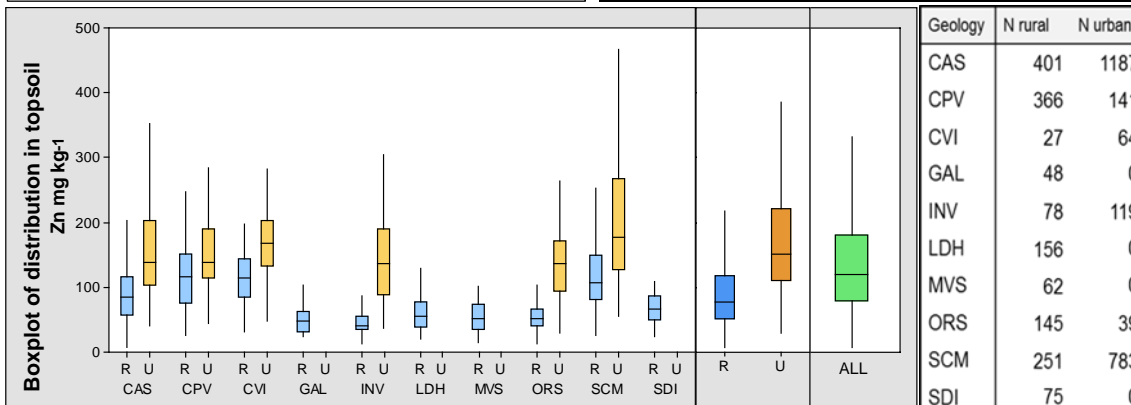
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Zinc

Zn



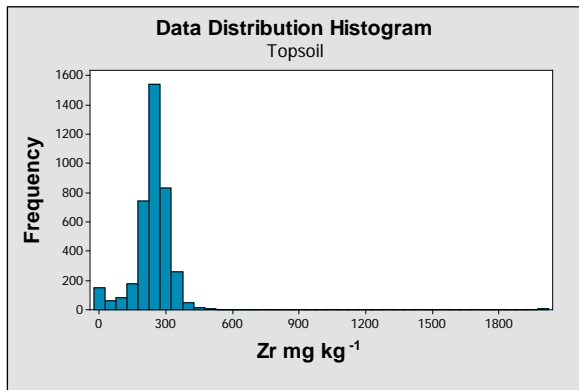
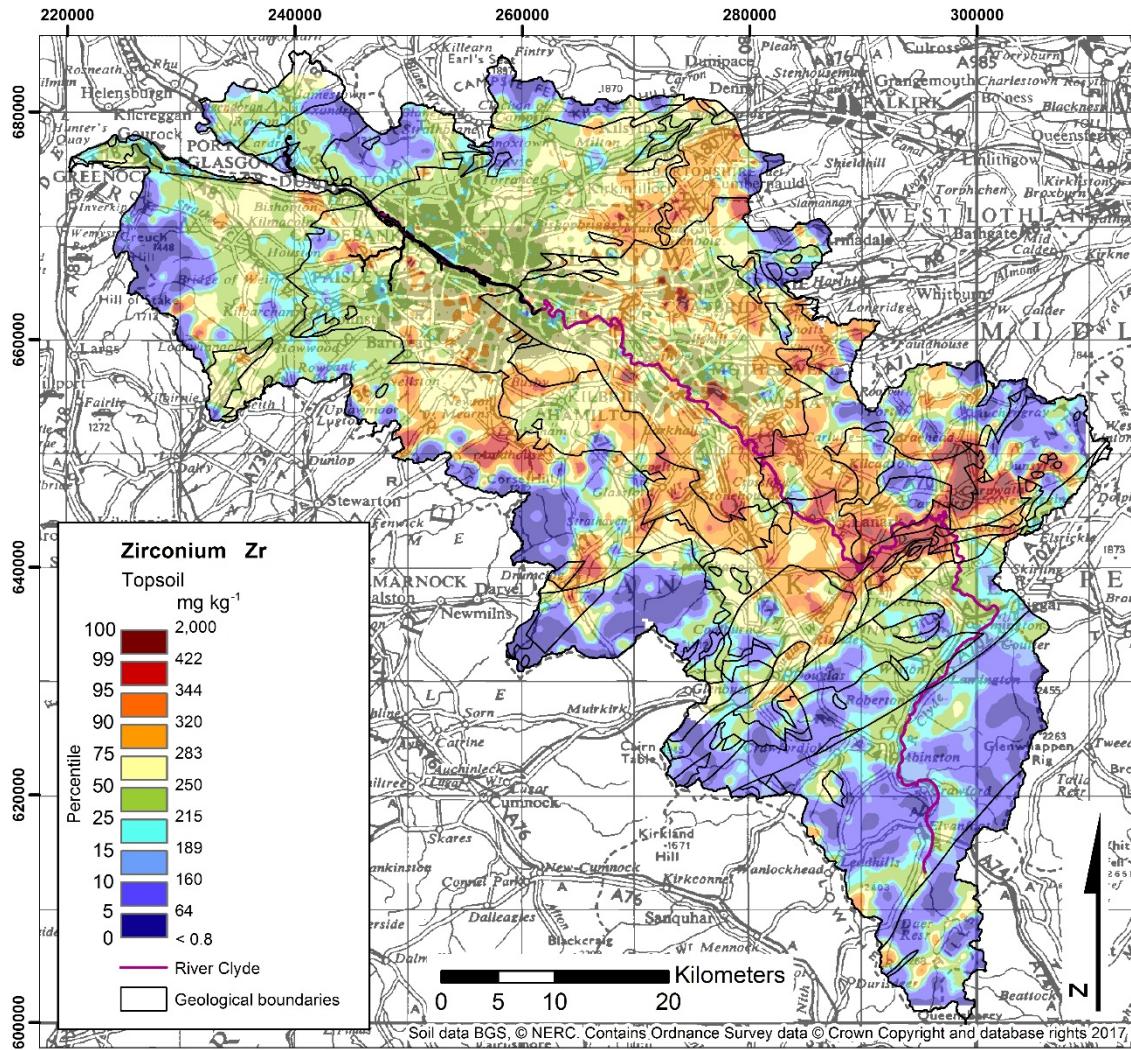
Statistics	Zinc mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	29.4	7.0	7.0
Maximum	5085.9	857.8	5085.9
Standard Deviation	246.3	62.6	201.8
Mean	209.5	93.6	162.2
Median	151.3	78.4	120.7
Minimum detectable value	0.5		
World soil median	70.0		



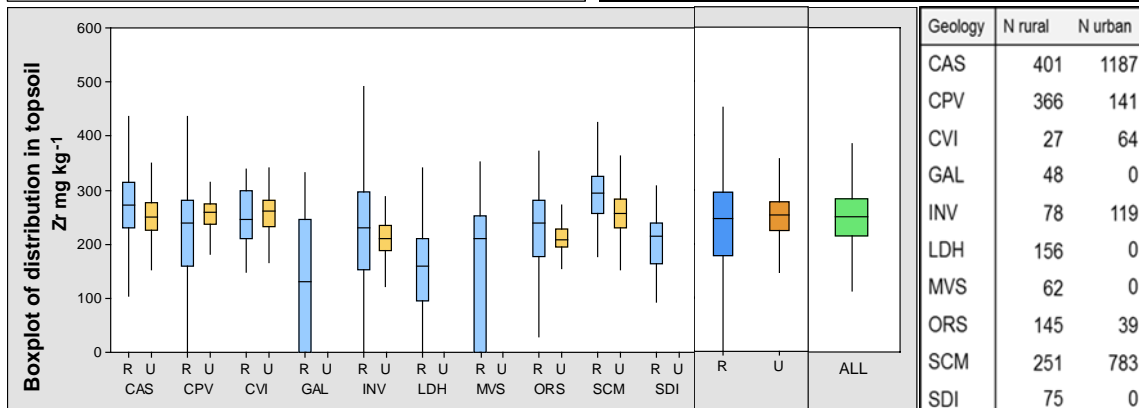
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Zirconium

Zr



Statistics	Zirconium mg kg ⁻¹		
	Urban	Rural	All
No. of samples	2333	1610	3943
Minimum	< 0.8	< 0.8	< 0.8
Maximum	2000.0	641.4	2000.0
Standard Deviation	87.4	106.4	96.8
Mean	255.7	225.0	243.2
Median	251.4	244.8	250.3
Minimum detectable value	0.8		
World soil median	230.0		



R: Rural; U: Urban; *Bedrock Geology Unit*: CAS: Clackmannan and Strathclyde Groups; CPV: Clyde Plateau Volcanic Formation; CVI: Clyde Volcanics – Igneous Intrusions; GAL: Gala Group; INV: Inverclyde Group; LDH: Leadhills Supergroup; MVS: Midland Valley Silurian Inliers; ORS: Old Red Sandstone Supergroup; SCM: Scottish Coal Measures Group; SDI: Intrusive and Extrusive Igneous Rocks