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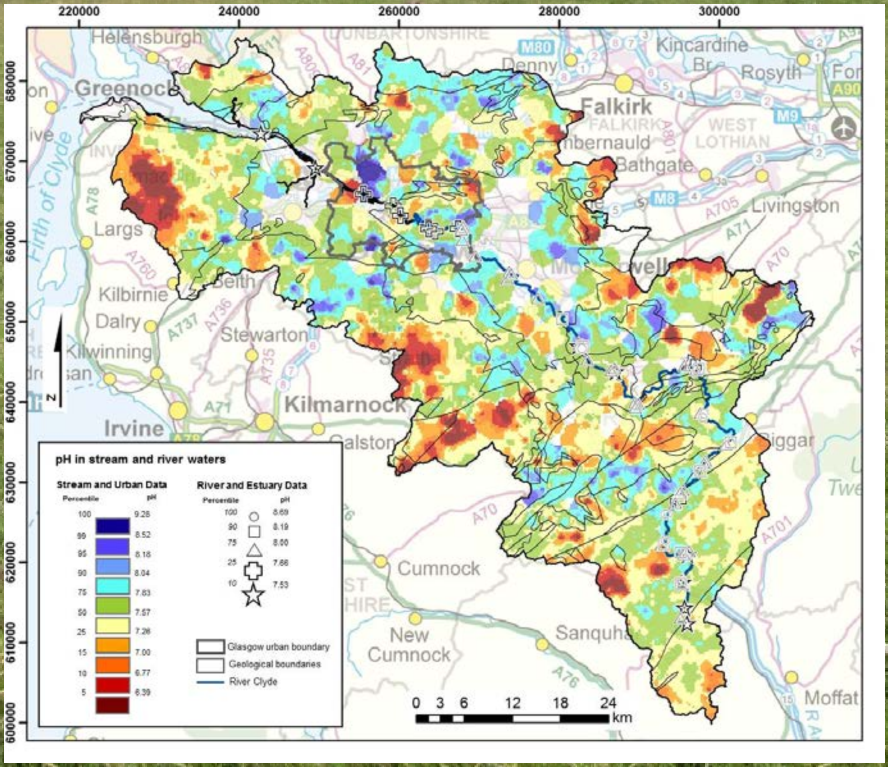
Stream-water geochemical atlas of the Clyde Basin



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River Clyde and map of stream water pH across the Clyde Basin

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Foreword

This report is a published product of the Clyde Urban Super Project (CUSP), a multidisciplinary catchment-based project undertaken by the British Geological Survey in collaboration with Glasgow City Council. The investigation of the chemistry of stream and river waters across the Clyde catchment forms a component of a wider investigation, which includes stream sediment and soil reported as separated atlases in this report series.

The Clyde CUSP project has been undertaken as a component part of the British Geological Survey's G-BASE (Geochemical Baseline Survey of the Environment) programme, and contributes to G-BASE's wider aim to provide state-of-the-art information to characterise the environmental baseline of Great Britain in order to inform policy, aid environmental protection and increase knowledge.

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Contents

FIGURES

TABLES

Summary

Surveys of the inorganic chemical quality of stream water in rural and urban parts of the Clyde Basin, Scotland, have been collated in this investigation in order to characterise the chemical status and its spatial variability. The study has been carried out as part of the wider Clyde and Glasgow Urban Super Project (CUSP), a multidisciplinary collaboration between BGS and Glasgow City Council (GCC), in order to help inform decisions on regional planning and catchment management. Water samples were collected in three phases: from the inner estuary during 2002–2003, from tributaries of the River Clyde in Glasgow during 2003, and from rural parts of the catchment and upper reaches of the River Clyde during 2010. In total, 1892 sample sites were investigated and some 50 elements or compounds analysed by a range of analytical techniques. Maps of spatial distributions, summary statistics, box plots and summary information are presented here to provide an overview of the current status of stream water chemistry and likely controlling factors.

The spatial variation in concentrations of a large number of solutes across the Clyde catchment is striking, with a great many, including most major ions, arsenic (As), boron (B), chromium (Cr), copper (Cu), fluoride (F), lithium (Li), molybdenum (Mo), phosphorus (P), antimony (Sb) and strontium (Sr) showing a clear pattern of highest concentrations in and around the urban centre of Glasgow. This is likely to reflect a combination of lower average rainfall total when compared to the catchment periphery, relatively high base flow index (BFI), geology dominated by argillaceous, sulphide- and organic-enriched Carboniferous sedimentary rocks of the Scottish Coal Measures Group and Strathclyde & Clackmannan formations, and urban and industrial land-use. The relative contributions of each of these are hard to quantify, but geology and land-use probably dominate for most analytes in this category.

Stream water pH also reflects these spatial controls, with acidic waters predominating in the upland areas of heather moor and peat, and neutral to alkaline conditions in the low-lying central part of the Basin, where reactions with argillaceous sedimentary rocks and derivative soils predominate. The pH has an influence on a number of other solutes, including aluminium (Al), cadmium (Cd), iron (Fe), lead (Pb) and rare earth elements, all of which are comparatively mobile in acidic conditions.

For Pb, mining and mineralisation are also locally important to the distributions of dissolved concentrations. High concentrations are a feature in streams around the former mining district of Leadhills in the southern part of the catchment.

For other solutes, different factors appear influential. The distribution of nitrate (NO_3) is patchy, with the highest concentrations occurring sporadically over a wider area of the catchment. The distribution reflects diffuse inputs of nitrate, especially from urban and agricultural sources, and demonstrates the impact of anthropogenic activities on stream water chemistry.

Geology appears to be a strong control on the distributions of Ba and U in the stream waters, with highest concentrations of Ba observed over Inverclyde Group and Old Red Sandstone sedimentary rocks, and Old Red Sandstone also giving rise to the highest concentrations of U.

As a result of this survey, the Clyde Basin is one of the best-characterised catchments in the UK in terms of spatial geochemistry and hydrochemistry. This volume contributes to the wider understanding of the catchment processes and chemical variability in combination with associated databases for stream sediment and soil, which are each reported separately.

1 Introduction

Information on the chemical quality of the environment is important because the 92 naturally occurring elements on Earth that form the various rock, soil, water and gases that are the building blocks of the planet are not distributed evenly across the globe. Concentrations in stream waters at any location are controlled by factors including geology (bedrock and drift), climate, land-use, vegetation, catchment hydrology, mineral weathering, groundwater composition and contribution, and in-stream processes. Of these, the chemical composition of the underlying geology, and its derived soil, and land-use are generally the factors with major influence (BGS, 1999). 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 and humans in high doses (Table 1). The quality of stream water affects the aquatic life that it can support, the mobility of elements being key in any given stretch of stream/river. While the composition of stream water is not necessarily equivalent to that of drinking water, which may undergo treatment before supply to the public, it does provide a useful indicator of the quality of raw surface water within a region.

This volume describes the geochemistry of stream water 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 stream water 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) to characterise the geo-environment of the Clyde Basin and deliver geoscience products to aid sustainable planning and development in Scotland's major conurbation (Campbell et al., 2010).

The stream water survey was carried out in three phases. Samples were collected from the Clyde inner estuary during 2002–2003, from tributaries of the river Clyde within Glasgow during 2003, and during 2010 stream water samples were taken from the rural areas of the Clyde Basin, with a subset of samples taken from River Clyde and its major tributaries upstream of Glasgow . The waters were analysed to determine the concentration of approximately 50 chemical elements and compounds. The results are presented here as a series of interpolated geochemical maps, and statistical summaries, with an overview of the distributions for 28 of the chemicals measured in stream waters.

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)

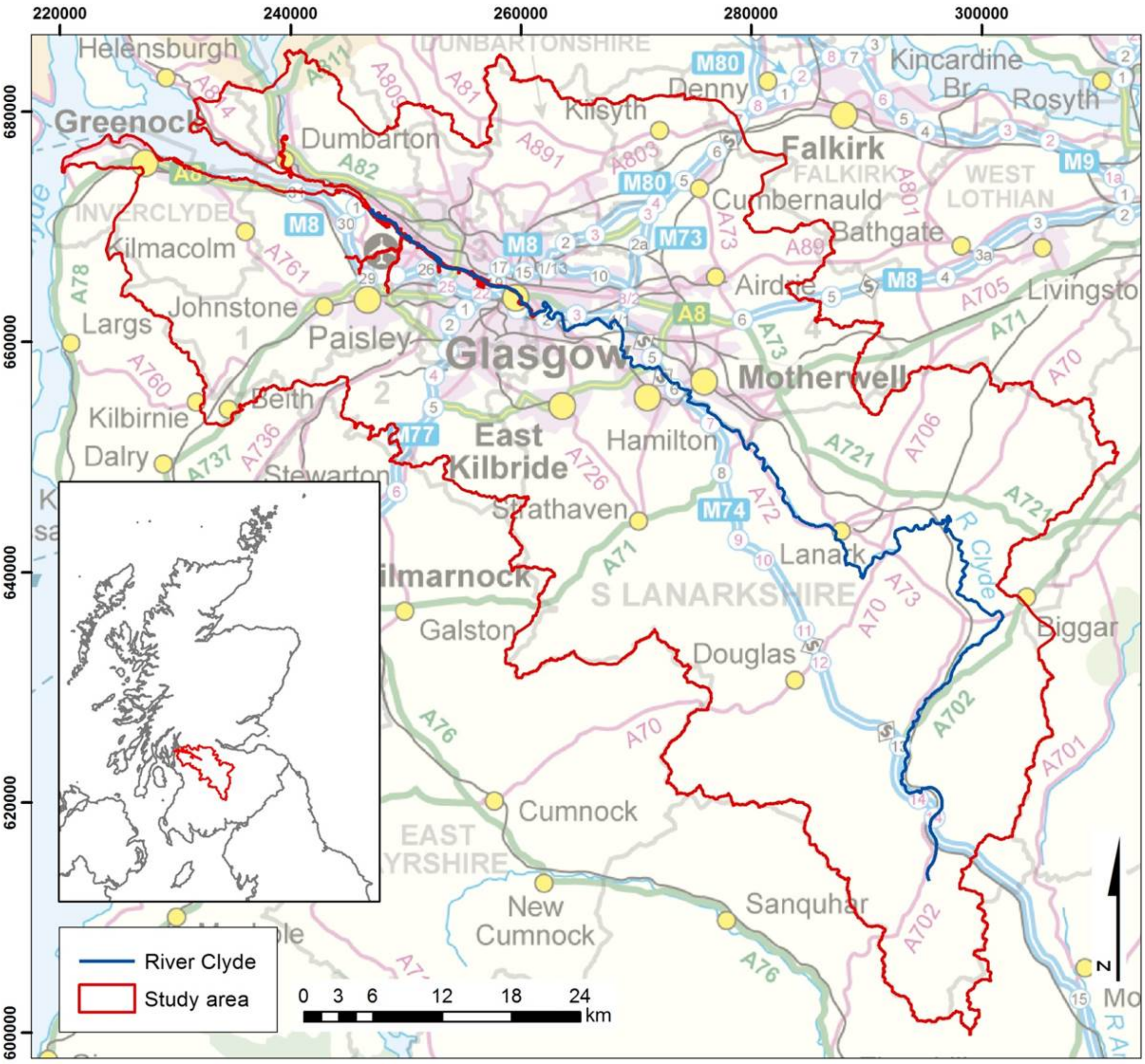

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Figure 1. Location map of the Clyde Basin study area.

1.1 Clyde Basin study area

The CUSP study area covers 3130 km^2, and 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 Gourock. The area includes the settlements of Abington, Leadhills, Lanark, Carluke, Strathaven, Kilmalcolm, 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. By contrast, the south of the area is predominately rural (see Figure 1, Figure 2 and Figure 3 for locations).

The topography of the area ranges from the flat land of the lower River Clyde valley to the upland volcanic-rock plateaux of the Campsie–Kilpatrick Hills to the north of Glasgow and the Renfrewshire Hills to the south-west of Glasgow (Figure 2). In recent times, the upland area of Eaglesham Moor to the south of East Kilbride and Strathaven has become home to the UK's largest wind farm covering 53 km^2 (Location 34, Figure 3). The south of the area is dominated by the rolling hill country of the Southern Uplands. The upland areas of the Campsie–Kilpatrick Hills, Renfrewshire Hills and Southern Uplands 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). A note of land-use was recorded at each site during the course of water sampling. These data are indicated in Figure 5. The observations corroborate land cover indicated in Figure 4.

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. From there, goods still had to be transferred onto smaller shallow-draught boats for the journey into the centre of Glasgow. By 1775 Port Glasgow was the site of the principal Custom's House on the River Clyde. It became a centre for import/export and ship building (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, Gourock was not as industrialised as Greenock or Port Glasgow, but remained a centre of the fishing industry, with some ship building as well as stone quarrying (Milne, 1958). Glasgow became the third most important port in the United Kingdom 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 84 000, 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 south-east 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 north-east 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, 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).

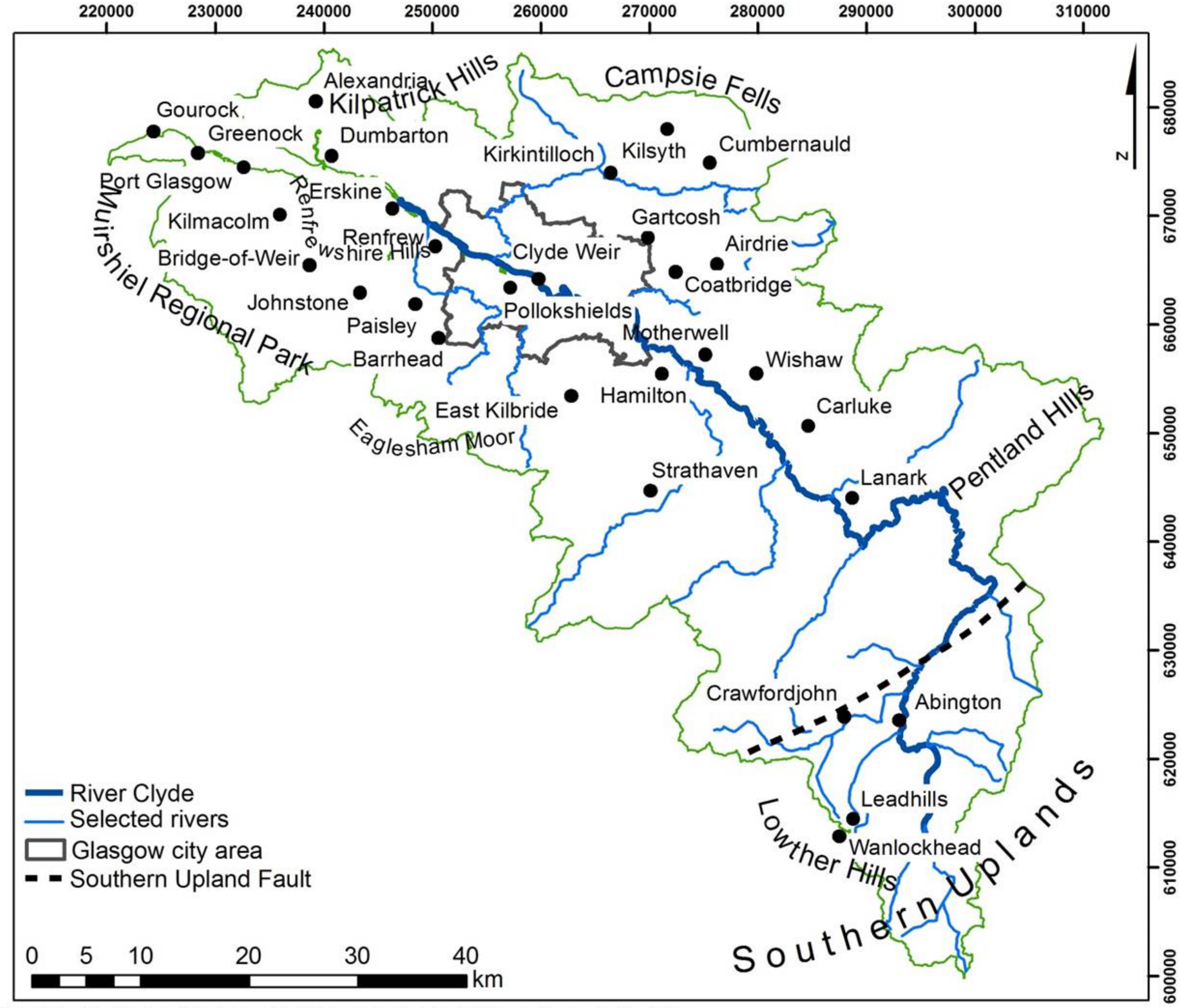

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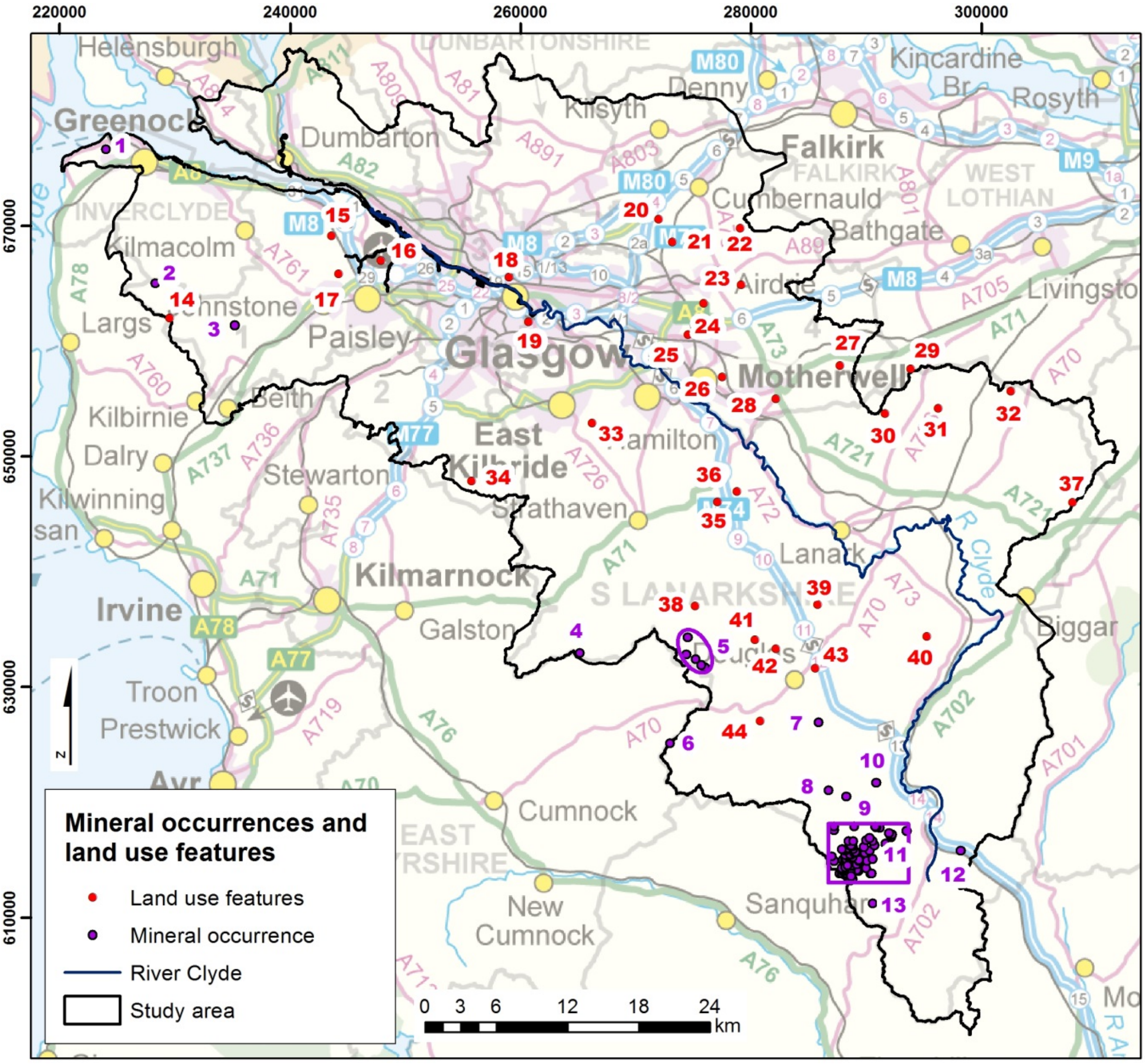
Figure 2. Map indicating places named in the introductory sections of this report.

Across the whole Glasgow conurbation, the trend of increasing population and commercial success continued through the 19th century with the advent of stream 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 (filling cavities) 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).



See Tables 2 and 3 for locations

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

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

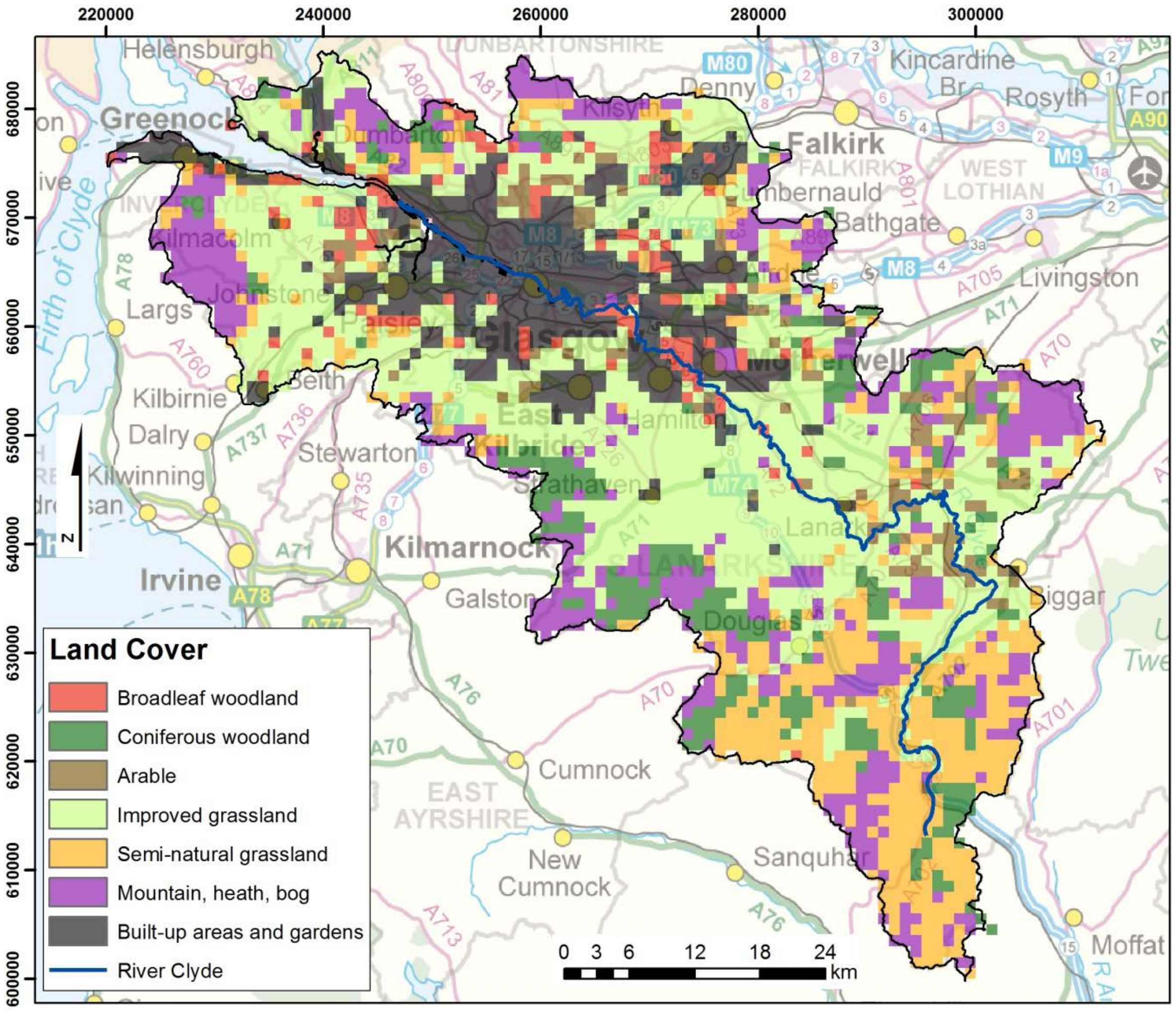
Number	Occurrence name	Mineralisation
1	Drumshantie, Gourock	Cu
2	Muirshiel	Ba
3	Kaim	Ba, Cu
4	Spoutloch Burn	Ba, Pb
5	Nutberry Hill, River Nethan, Cumberhead, Meilke	Ba, Fe, Pb
6	Crossflat Burn	Ba
7	Paige Hill, Auchensaugh Hill	Ba veins
8	Snar Water	Au
9	Glendowran Mine	Pb
10	Drakeslaw Lead Mine	Pb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

From BGS (1993) and the BGS Mineral Occurrences Database

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,
20	Bedlay Colliery	Former deep-shaft coal mining, tips
21	Gartverrie Pit	Former fireclay and silica-sand pit, now
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
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	Wind farm, 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.

In the late 18th and the early 19th centuries, Glasgow became the centre of a cotton spinning region; the number of cotton mills 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 centred 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 print-works partly because of the clean, fast-flowing water (Glasgow City Council, 2014).

Heavy industry, particularly shipbuilding which was focussed at Clydebank, developed along the River Clyde during the 19th and first half of the 20th centuries and Glasgow was renowned 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).

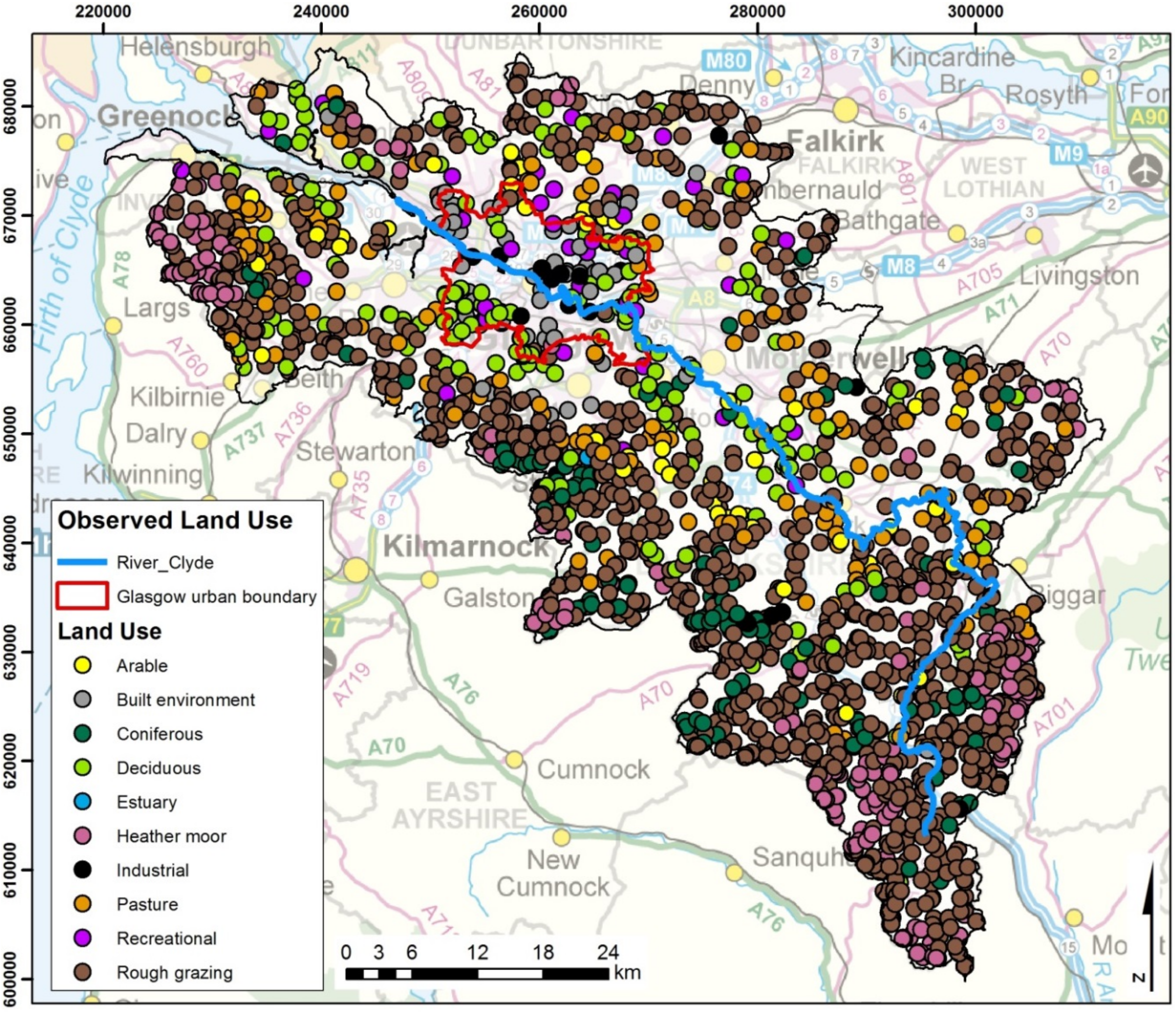


Figure 5. Observed land-use, recorded at the time of water sampling.

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. During the 19th century, the company of JJ Whites in Rutherglen, was the world's largest producer of chrome. The company operated until 1968. Chromite-ore processing residues were extensively used as landfill material around south-east Glasgow and between 1880 and 1968 it is estimated that 2, 500 000 tonnes of chromite waste were dumped (Farmer et al., 1999).

The conurbation, and in particular Clydebank, sustained heavy bombing during the 2nd 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 north-east 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, which 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).

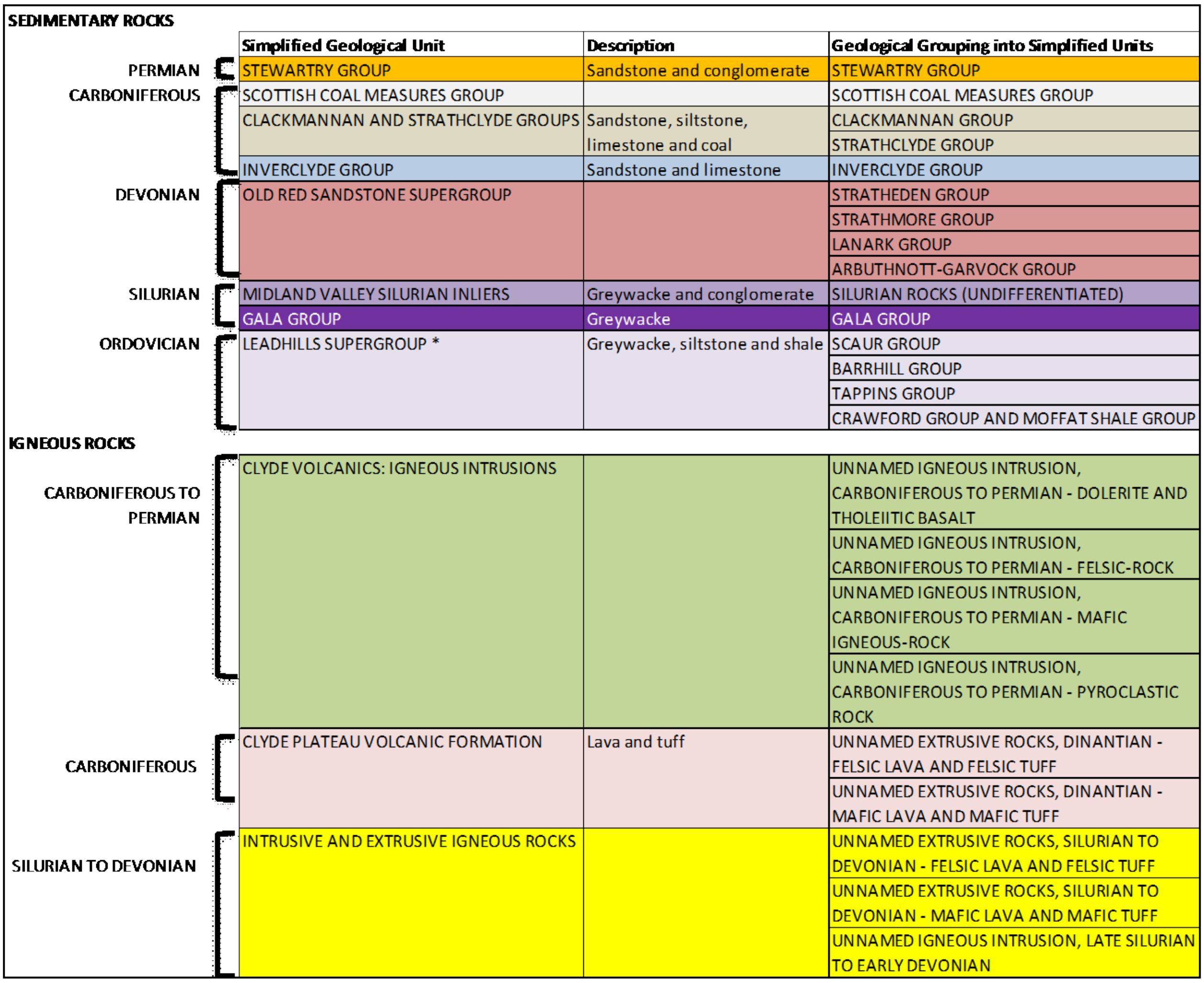
1.2 Bedrock geology

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 Fault and related major faults which trend north-eastwards from south-west 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 (Figure 6).

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 report.

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



	Simplified Geological Unit	Description	Geological Grouping into Simplified Units
SEDIMENTARY ROCKS			
PERMIAN	STEWARTRY GROUP	Sandstone and conglomerate	STEWARTRY GROUP
CARBONIFEROUS	SCOTTISH COAL MEASURES GROUP		SCOTTISH COAL MEASURES GROUP
	CLACKMANNAN AND STRATHCLYDE GROUPS	Sandstone, siltstone, limestone and coal	CLACKMANNAN GROUP
			STRATHCLYDE GROUP
	INVERCLYDE GROUP	Sandstone and limestone	INVERCLYDE GROUP
DEVONIAN	OLD RED SANDSTONE SUPERGROUP		STRATHEDEN GROUP
			STRATHMORE GROUP
			LANARK GROUP
			ARBUTHNOTT-GARVOCK GROUP
SILURIAN	MIDLAND VALLEY SILURIAN INLIERS	Greywacke and conglomerate	SILURIAN ROCKS (UNDIFFERENTIATED)
	GALA GROUP	Greywacke	GALA GROUP
ORDOVICIAN	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 - DOLERITE AND THOLEIITIC BASALT
			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

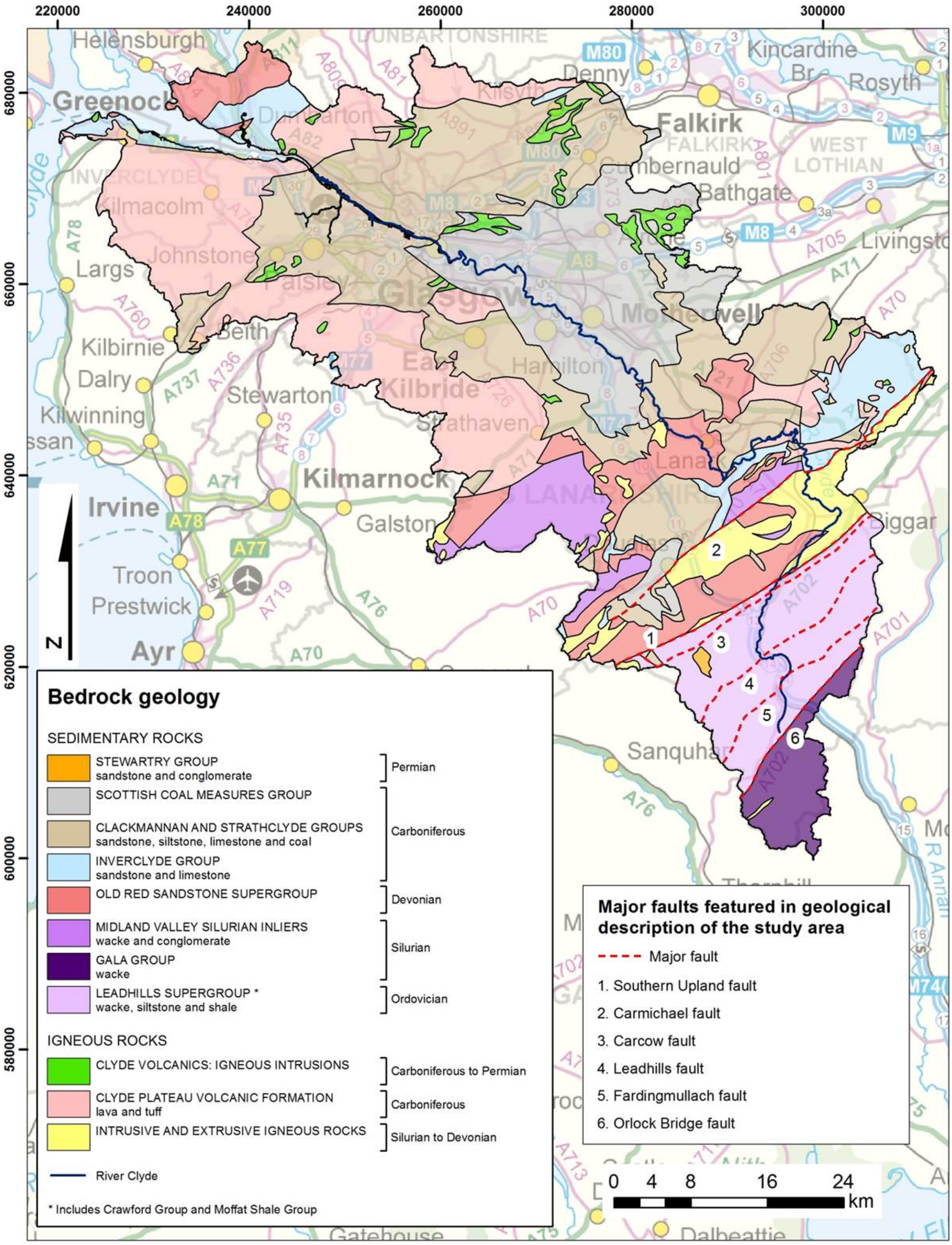


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Figure 6. Simplified bedrock geology map of the Clyde Basin study area.

*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.

1.2.1 Sedimentary rocks

Ordovician–Silurian

Rocks of the Ordovician–Silurian Leadhills Supergroup crop out in the south-east 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 microconglomerates 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 volcaniclastic 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 south-east 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 rocks.

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 fluvio-deltaic 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 fluviodeltaic systems causing 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 south-east 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, north-west 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 subangular 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, feldspar-porphyry, 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 (CPVF) 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 volcaniclastic sedimentary rocks (Cameron and Stephenson, 1985). Tropical weathering between eruptions produced reddened flow tops, or persistent red-brown lateritic boles.

The CPVF 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 north-east to south-west 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.

1.3 Quaternary geology

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 subglacial action into typical glacial landforms such as drumlins, and elsewhere form gently undulating topography (Figure 7).

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).

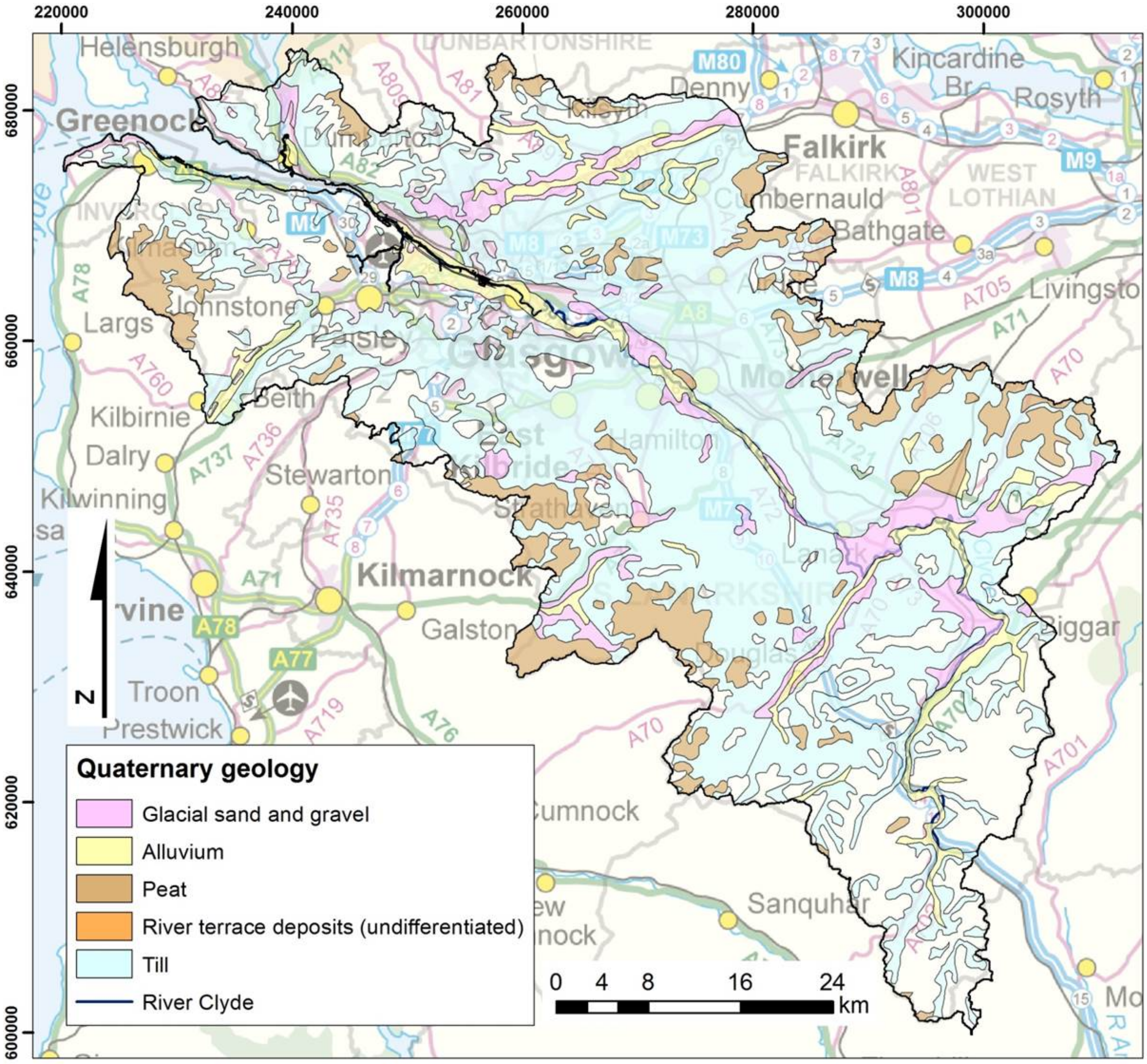

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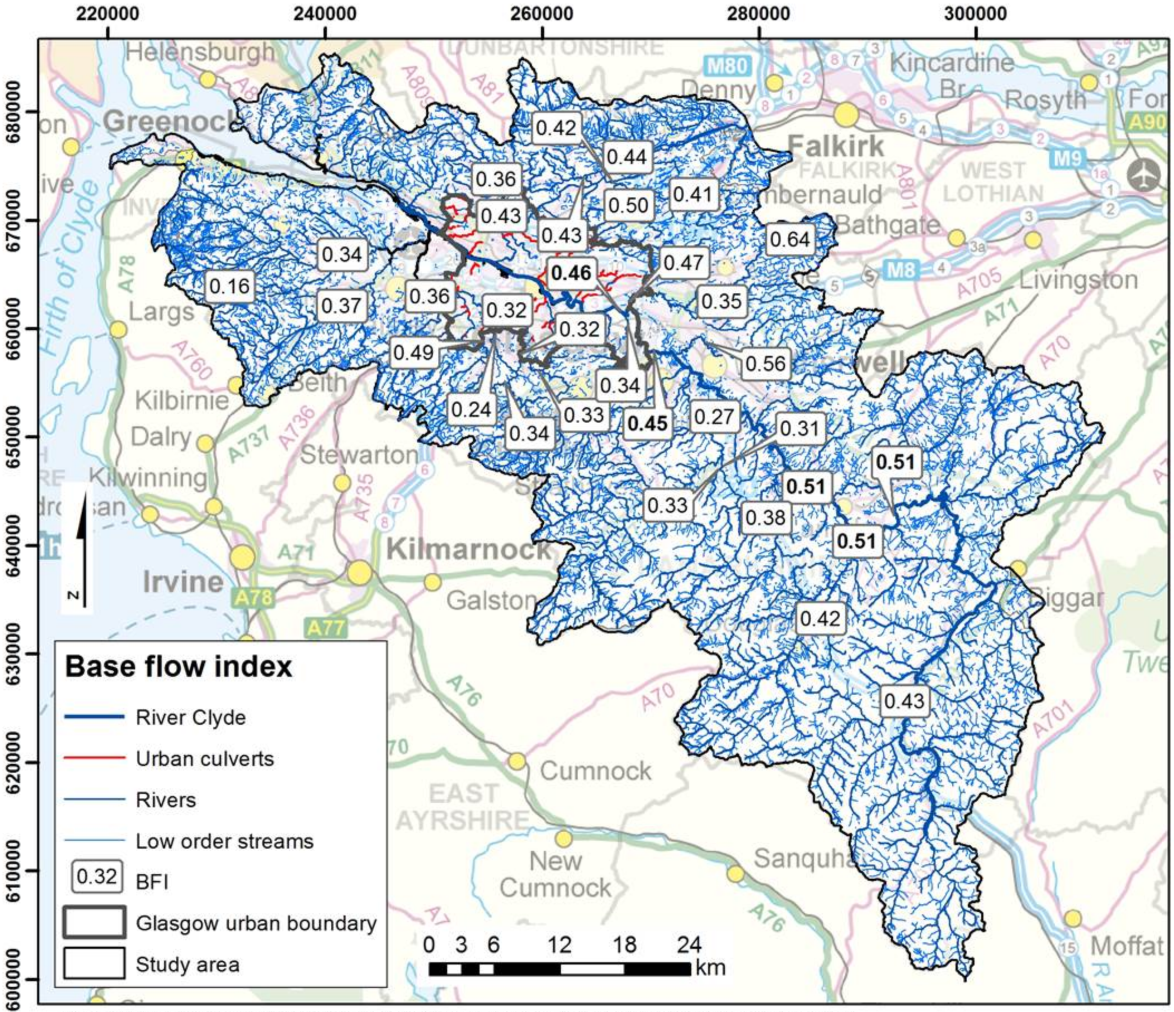
Figure 7. Quaternary geology map of the Clyde Basin study area.

1.4 Base-flow index (BFI)

Distributions of base-flow index (BFI) are shown for the Clyde Basin in Figure 8. The BFI is defined as the ratio of the long-term base flow to total stream flow in a stream or river and is an indication of the contribution, as a fraction, of groundwater to river discharge. Ratios of base flow to streamflow will vary over the year according to seasonal rainfall patterns but over the long term, a high BFI value indicates a relatively large contribution of groundwater to the stream flow.

The spatial variations suggest that groundwater contributes slightly more to the lowland rivers and larger tributaries than to the upland streams, as follows from a greater average rainfall contribution in upland areas. This variation in BFI may have some impact on stream chemical compositions as higher contributions from groundwater will tend, through water–rock reactions, to have a higher concentration of dissolved solids than stream water having had less interaction with the subsurface. As water samples were mostly collected in the summer months, the relative contribution of groundwater across the catchment will likely have been high.



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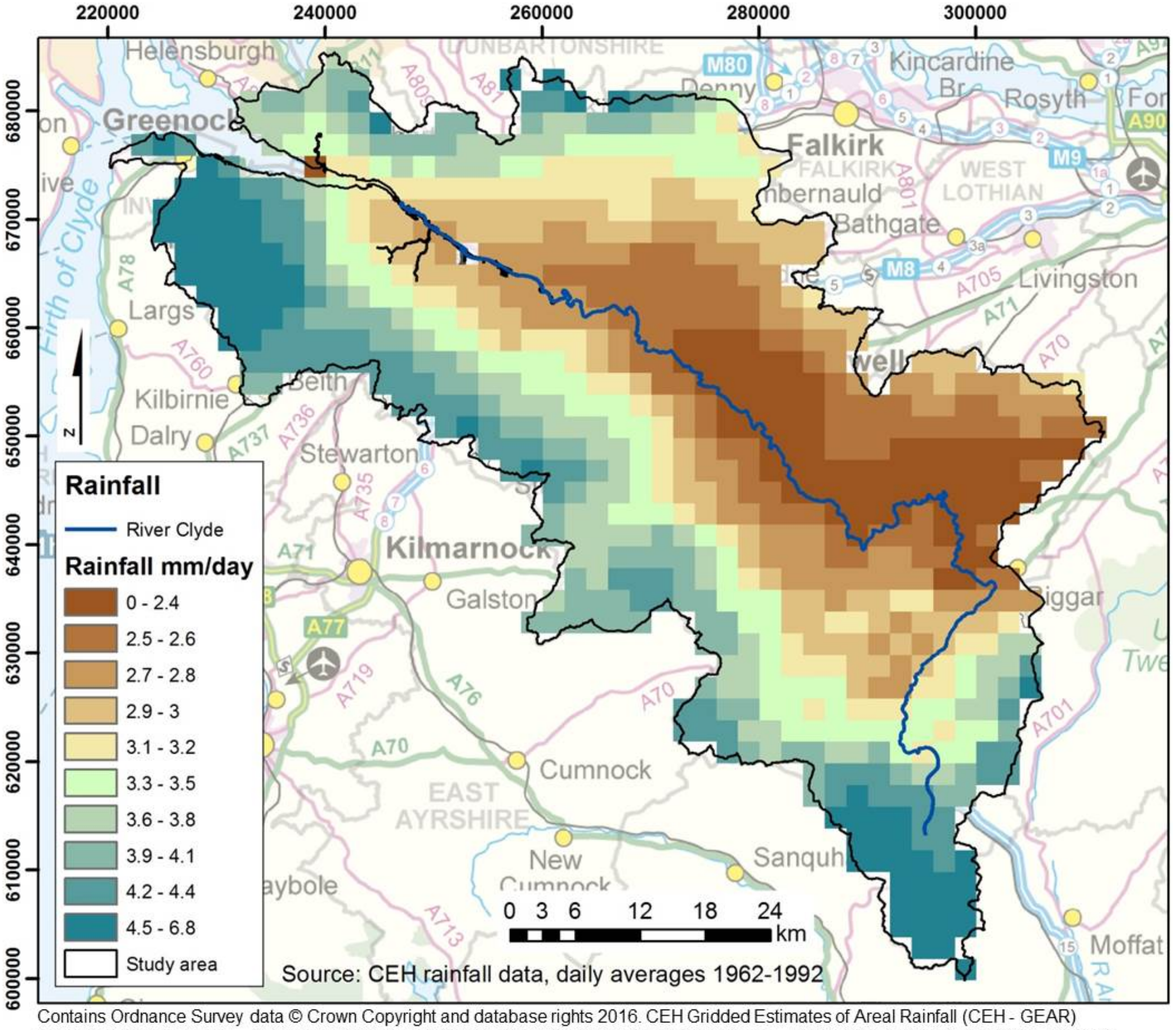
BFI data from Marsh and Hannaford (2008)

Figure 8. Average base-flow index (BFI) for the Clyde Basin (bold text denotes River Clyde values).

1.5 Rainfall

Average rainfall from the CEH GEAR database for the period 1962–1992 (Tanguy et al., 2016) is shown for the Clyde Basin in Figure 9. Average values reach up to 6.8 mm/day. A clear orographic effect is seen, with prevailing westerly winds delivering highest rainfall in the higher ground along the western watershed, and lower values in the lower part of the catchment along the reach of the River Clyde and further east. The impact of rainfall on stream water chemistry is discussed in more detail in Section 2.1 of this report.



Source: CEH rainfall data, daily averages 1962-1992

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Figure 9. Average rainfall for the period 1962–1992 in the Clyde Basin.

1.6 Mineral occurrences and mining

As outlined in Section 1.1 of this volume, much of north-east 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 prominent 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 (BGS, 1993). 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 north-west 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, Lang Cleugh and Snar Water (Locations 4, 6, 7, 8 and 13, Figure 3).

2 Controls on stream-water chemistry

The chemistry of stream water is controlled by numerous often interlinked factors, including rainfall chemistry and pattern, soil type, geology, land cover, groundwater inputs and human influences (Figure 10). As a result, the variations in stream water chemistry across a catchment can be large. The previous sections highlight the significant variations in many of these controlling factors in the Clyde catchment, which influence different chemical elements in stream water to varying degrees.

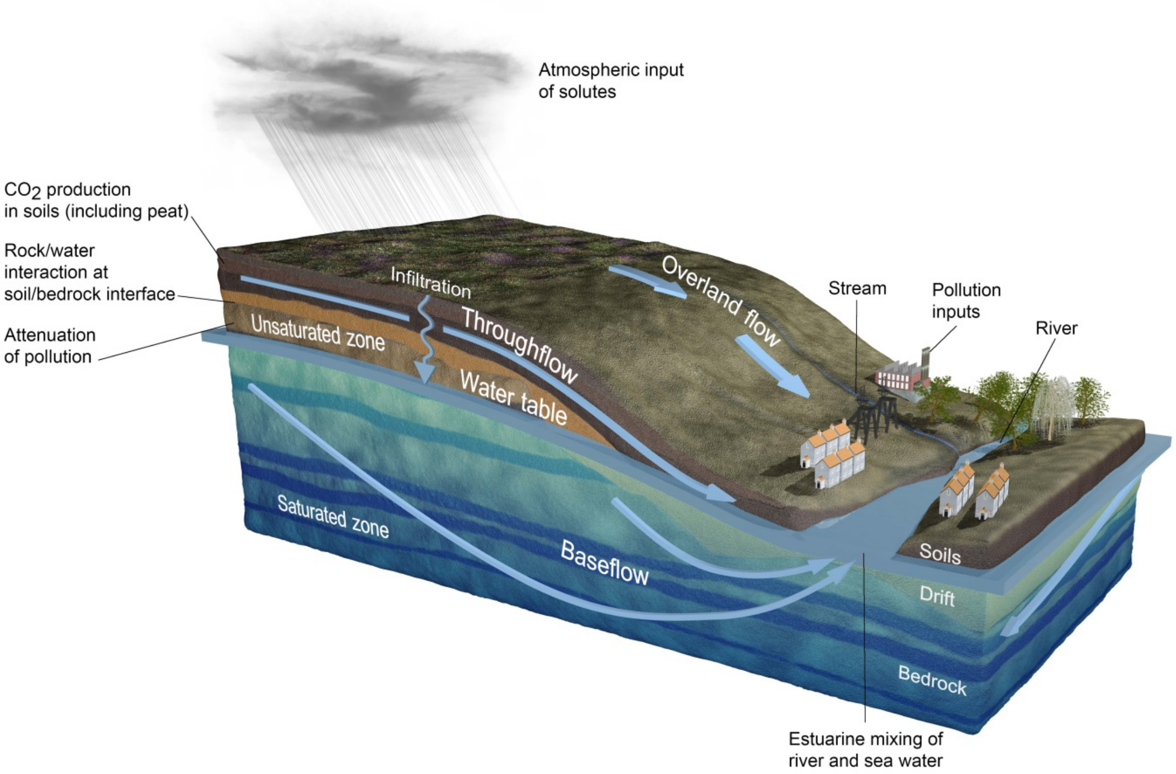


Figure 10. Controls on the chemical composition of stream water.

2.1 Rainfall

Atmospheric deposition consists of a combination of precipitation (rainfall/snowfall) and dry deposition (dust particles and gases). Rainfall chemistry can vary significantly depending on location and inputs. Maritime rainfall carries a strong sea-salt signature with relatively high concentrations of Na, Cl, Mg and SO_4, derived from marine aerosols. The maritime influence diminishes markedly within a short distance inland.

As air masses move over land, continental dust and gases of both natural and anthropogenic origin are picked up and these also modify the composition of rainfall. Atmospheric dusts can contribute a significant amount of Ca, Na and Al to rainfall chemical composition. Dry deposition also contributes NO_3 and nonmarine SO_4 to rainfall chemical compositions, derived via fossil-fuel combustion from sources such as power stations, industrial emissions and car exhausts. Impacts of atmospheric SO_2 on rainwater composition have diminished significantly in recent years following pollution control measures instigated to tackle rainfall acidification (Hand et al., 2012; Lehmann et al., 2008). Measures to tackle N emissions have also been undertaken although vehicle exhausts remain significant sources (Carslaw and Rhys-Tyler, 2013).

Vegetation affects rainfall chemistry by enhancing evapotranspiration and by take-up of nutrients for temporary storage in the biomass. Solute concentration by evapotranspiration is most marked in forested catchments, particularly coniferous forest (Neal et al., 1994).

Agricultural activity can also lead to enrichments in NH_4 in rainfall as a result of animal farming and fertiliser applications. Liming of agricultural land can be an additional source of atmosphere-derived Ca and alkalinity.

In catchments with geology consisting of resistant rock types, rainfall inputs have a relatively large influence on stream-water chemistry. For trace elements where concentrations in bedrock and soil are low, the rainfall component can remain a significant contributor to the stream-water budget. The halogen elements are a particular example (e.g. Edmunds and Smedley, 2013).

Average rainfall in the Clyde catchment varies between <2.4 mm to 7 mm/day, being highest in the upland areas on the north and west margins of the catchment and lowest along the floodplain of the River Clyde (Figure 9). Dilution of stream waters by rainfall should; therefore, be greatest along the upland watershed.

Typical chemical compositions of rainfall are given for Loch Dee [246907, 577768] in the Southern Uplands of Scotland in Table 5. This is a rainfall gauging station in the UKEAP: Precip-Net network (http://uk-air.defra.gov.uk/) that has been monitoring rainfall chemistry fortnightly since 1986. Loch Dee is one of the closest rainfall monitoring stations to the Clyde catchment. The concentrations of solutes in the rainfall provide an insight into the inputs to the local stream network, although concentrations will be modified as a result of evapotranspiration and nutrient uptake by plants. The rainfall data for the Loch Dee site show a mean annual amount of 98.5 mm. Rainfall pH is moderately acidic (mean 5.46) and solutes dominated by Na and Cl, as expected for the site’s location relatively close to the west coast of Scotland. Dissolved SO_4 is also dominated slightly by a marine component (57% of the total SO_4 present; Table 5). Total N in rainfall from the site is 0.60 mg/L.

Table 5. Mean annual rainfall and mean rainfall chemical composition (monthly values) for the year 2014 for the monitoring station at Loch Dee [246907, 577768], Southern Uplands of Scotland**.**

Parameter	Value	Unit
Rainfall	98.5	mm
pH	5.46	
H^+	4.91	µeq/L
SEC	27.0	µS/cm
Ca	0.20	mg/L
Na	3.10	mg/L
K	0.16	mg/L
Cl	5.49	mg/L
SO_4	1.36	mg/L
SO_4-NM	0.582	mg/L
NO_3-N	0.19	mg/L
NH_4-N	0.41	mg/L
PO_4-P	0.04	mg/L

NM: non-marine

Source: (UKEAP: Precip-Net network (http://uk-air.defra.gov.uk/))

2.2 Soil and superficial deposits

The mineralogy and chemical composition of soil is a function of the composition and structure of underlying regolith and bedrock and of vegetation and land-use. Factors such as rainfall and slope also play a role in soil development. The degree of leaching of surface soil varies according to mineralogy and permeability as well as amount of rainfall.

Within the Clyde catchment, superficial deposits and bedrock are dominantly poorly permeable and so the degree of leaching is relatively low. Peat occurs in the upland areas along the catchment boundary, in areas coinciding with highest rainfall and topography (Figure 7). These are also areas with poorly permeable volcanic or metamorphic rocks. Peat consists almost entirely of organic matter. Soil solutions developed within peat in the upland areas are typically acidic as a result of the presence of organic acids and soil CO_2 derived from respiration by vegetation and microorganisms. Peaty soil may also become waterlogged due to poor permeability coupled with high rainfall. Reducing conditions in waterlogged soil can result in redox transformations that mobilise elements such as Fe, Mn and NH_4 and produce reduced sulphide. Following transportation to the stream, such solutions re-oxidise to form Fe and Mn oxides, NO_3 and SO_4.

Mineral soil solutions vary according to soil type but typically have higher concentrations of metal cations (Ca, Mg, Na, K) than organic soils. Solutes accumulate via ion-exchange reactions on clay surfaces and dissolution principally of silicates and carbonates (Clow and Mast, 2010). Solute pH increases correspondingly.

Likewise, superficial drift deposits can variably influence the chemistry of solutes, depending on original bedrock lithology and permeability. Poorly permeable deposits (e.g. till) allow potentially limited infiltration, and decreased flux of oxygen can impose redox changes on redox-influenced solutes. More permeable deposits allow greater infiltration, with redox changes potentially being absent or less significant.

In the Clyde catchment, roughly 10% of the land area lacks a cover of superficial drift deposits. Much of the remaining cover consists of poorly permeable till. Glacial sand and gravel, which although of variable texture tends to be more permeable, is distributed sporadically across the catchment. Alluvium is restricted to the main river channels (Figure 7).

2.3 Land cover

Vegetation cover affects rainfall infiltration and throughfall and; thereby, rates of evapotranspiration. Nutrient uptake by plants also leads to cycling of N, P, K, Ca, Mg, Fe, S and Mo and other essential trace elements with subsequent release via plant decomposition.

As noted above, agricultural practices impact on surface-water chemistry via inputs of e.g. N, P, K, Cl and S from fertilisers, manure and farm slurries. Trace elements may also be enhanced from such sources (e.g. U, B, Zn). Liming contributes Ca and carbonate and potentially increases pH.

Urban land-use affects the chemistry of stream water through inputs from waste water treatment works, soakaways and septic tanks and general urban surface run-off influenced by the build-up of contaminants on hard surfaces and pollution from transport networks etc. Leachates from landfills can also lead to contamination of local water courses with organic and inorganic solutes, as well as a general increase in dissolved solids if landfills are inadequately sealed. This might be the case with older landfills lacking modern liners.

Industrial activities also potentially impact on stream water chemistry. These have particular significance in the Clyde catchment because of the industrial legacy of the Glasgow conurbation and the history of mining in the catchment more widely. In the urban areas, a long history of manufacturing industry has included shipbuilding, iron and steel manufacture and chemicals (e.g. chromite chemical works), with potential impacts on a wide range of contaminants, including chromium and heavy metals. The coal and ironstone mining industries were active during much of the 19th and 20th centuries in areas underlain by Coal Measures deposits. Coal is closely associated with sulphide (pyrite) mineralisation and so water interacting with these clay-rich deposits bearing sulphide minerals can be expected to be impacted through increased concentrations of dissolved solids, trace metals, SO_4 (and possibly acidity in the case of pyrite oxidation). This is likely to be exacerbated by mining activity through opening of fresh reactive mine faces and remobilisation of mine waste as made ground, waste piles and landfill.

In the upper Clyde catchment, historical mining for lead–zinc has been carried out over many decades in zones of metalliferous mineralisation, especially in Leadhills–Wanlockhead (Location 11, Figure 3), Drakeslaw and Glendowran areas (Locations 9 and 10, Figure 3). This may also impact on mobility of SO_4, Pb, Zn and other trace metals through the oxidation of sulphide minerals including galena and sphalerite (PbS, (Zn,Fe)S respectively). However, the mobility of trace metals will ultimately be a function of stability in solution, which is in turn controlled by pH, major-ion content, organic content and occurrence and form of sorbents, rather than simply the availability of primary ore minerals.

3 Methods

3.1 Clyde Basin surveys

The BGS Clyde Basin surface water geochemistry dataset has been compiled from three separate field survey campaigns carried out under the CUSP programme. The first of these was a survey of water and sediment quality in the Inner Estuary of the River Clyde completed by the BGS Estuarine Contamination Project co-sponsored by GCC and supported in-kind with ship-time by the Scottish Environment Protection Agency (SEPA) and Glasgow Humane Society during 2002–2003 (Jones et al., 2004). The second survey assessed urban sediment and water quality in all tributaries of the River Clyde within the GCC area and was carried out by the BGS G-BASE project co-sponsored by GCC during 2003 (Fordyce et al., 2004). In 2010, the G-BASE project extended these surveys to include (i) rural stream waters in the Clyde Basin area and (ii) river water samples from the River Clyde and its junctions with major tributaries upstream of the Glasgow conurbation (Bearcock et al., 2011). The survey strategies are described as follows.

3.1.1 Clyde Estuary Survey

The Clyde Estuarine Contamination Survey and results have been reported in full by Jones et al. (2004). In summary, the water dataset comprises eight samples collected by a team of BGS staff. Five of the samples were collected by boat from the Inner Clyde Estuary between 02/12/02 and 04/12/02. The remaining three samples were taken from locations further upstream on foot on 10/06/03. Four of the samples were collected below the Clyde Weir, which marks the upper tidal limit of the river, and the remaining four samples were taken upstream of this point (Jones et al., 2004) (Figure 11).

3.1.2 Glasgow Urban Clyde Tributaries Survey

The G-BASE–GCC Glasgow Clyde Urban Tributaries project was undertaken between 02/06/03 and 10/06/03 and has been described in detail by Fordyce et al. (2004). In summary, 122 water samples were collected from every 1 km of stream length on all tributaries draining into the River Clyde within the GCC area (Figure 11).

Sampling included culverted as well as open sections of the streams. All samples were collected by BGS staff owing to the increased health and safety risk associated with working in urban drainage sites. Historically the G-BASE project has avoided sampling in urban environments in order to establish the natural geochemical background concentration of elements in stream waters. Consequently, the Glasgow Clyde Urban Tributaries dataset was designed to understand the impact of the urban environment on stream water chemistry (Fordyce et al., 2004).

3.1.3 Clyde Basin Rural Stream Water and River Clyde Survey

Sampling for the Clyde Basin rural and River Clyde surveys was carried out according to standard G-BASE procedures (Johnson, 2005). Samples were collected by a team comprising two members of BGS staff and nine student voluntary workers (VWs). As far as possible, samples were collected upstream of any potential source of contamination, such as habitation, industrial activity or any road or track crossings. For the rural stream survey, 1786 water samples were collected at a sample density of 1 per 1.5 km^2 from small (first to third order) streams across the Clyde Basin, at locations where stream sediment samples had been collected during a previous G-BASE survey of Southern Scotland, carried out between 1977 and 1986 (BGS, 1993).

The G-BASE survey is primarily based upon the collection of surface water samples from small streams only. However, for the Clyde Basin study, 60 water samples were collected along the length of the River Clyde upstream of the Glasgow conurbation to its headwaters in the Southern Uplands. The aim was to integrate these samples with the Clyde Estuary and Glasgow Clyde Urban Tributaries data to provide a complete water dataset for the whole length of the River Clyde. Samples were collected from the Clyde within 500 m upstream and downstream of every junction with a major tributary. In addition samples were collected on each major tributary within 500 m of its junction with the River Clyde.

An area around Leadhills was sampled during a staff training week in May 2010; however, the majority of the stream sampling was carried out between 05/06/10 and 14/08/10, with the remaining stream and river samples taken between 16/10/10 and 30/10/10 (Bearcock et al., 2011).

A summary of the four different sets of data that comprise the Clyde Basin water dataset is given in Table 6.

Table 6. BGS stream and river water datasets for the Clyde Basin.

Dataset name	Abbreviated dataset name	Survey description	Date of survey	Number of samples
Clyde Estuary	Estuary	Samples taken in the inner estuary of the River Clyde	5 samples in 2002 and 3 samples in 2003	8
Glasgow Clyde Urban Tributary	Urban	Samples of every 1 km of stream length on all tributaries of the River Clyde within the Glasgow City Council area	2003	122
Clyde Rural Stream	Stream	Samples taken from rural small streams (1st to 3rd order) across the Clyde Basin at a density of 1 per 1.5 km^2	2010	1770
River Clyde	River	Samples taken from the River Clyde at junctions with its major tributaries upstream of Glasgow	2010	60

Abbreviated dataset names denote how the datasets are referred to in the following chapters

3.2 Sample collection

Whilst the data combined in this atlas are from three 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 it was used to provide the basis of each survey. The procedures for taking water samples are outlined below, and any deviations from standard protocol are identified.

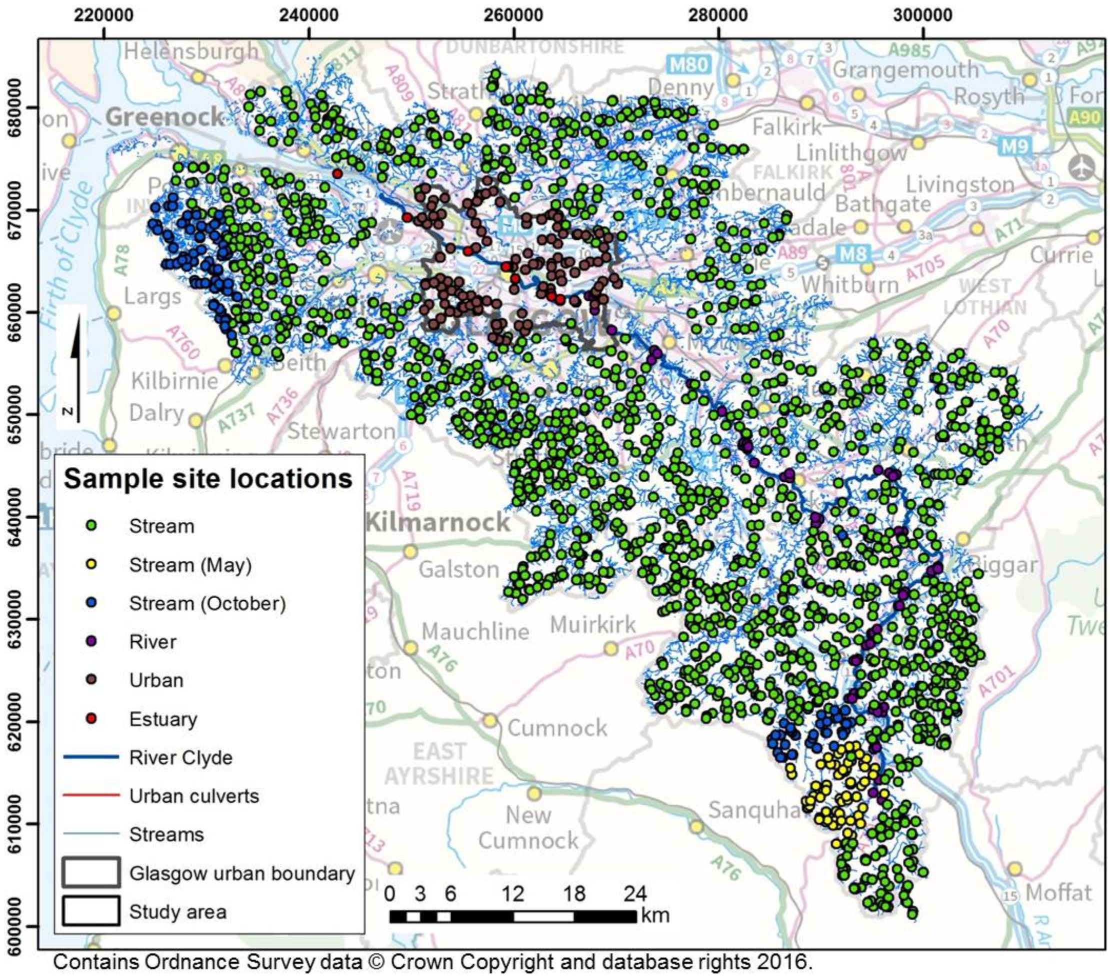
During the surveys, samplers worked in pairs that were interchanged daily to reduce the possibility of sampling bias introduced by the use of individual procedures (Johnson, 2005). All jewellery was removed prior to sampling to avoid possible metal contamination. Filtered water samples were collected at each site for major- and trace-element analysis. In addition, unfiltered water samples were taken for total alkalinity, conductivity and pH measurements. Four water sample bottles were collected at each site as follows:

(i) 60 ml HDPE Nalgene® bottle – 0.45 µm-filtered water, acidified at the field-base with 1% (v/v) nitric acid (HNO_3) for Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) cation analysis;
(ii) 30 ml HDPE Nalgene® bottle – 0.45 µm-filtered water un-acidified for anion analysis by ion chromatography (IC) and dissolved organic carbon determinations by TOC analyser;
(iii) 250 ml Nalgene® bottle – unfiltered water for total alkalinity and conductivity determinations;
(iv) 30 ml polythene bottle – unfiltered water for pH determinations.

Water samples were collected using a 25 mL plastic syringe, and a disposable 0.45 µm cellulose filter. The syringe was reused between sites; therefore, was rinsed prior to sample collection. A new filter was used for each site to avoid any possible cross-contamination between sites. Water was drawn into the syringe, which was rinsed out three times. The syringe was filled with water again and connected to the filter cartridge, which was also rinsed out twice. The syringe was refilled and the sample bottle was rinsed out once with filtered water from the site prior to being filled. The filtered waters were collected in 30 and 60 mL HDPE Nalgene® bottles. The 30 mL bottle was filled to the brim to exclude any air, while the 60 mL bottle was filled to the neck. This allowed space for the addition of 0.6 mL ARISTAR grade nitric acid (HNO_3) on return to the field base. Addition of 1% (v/v) HNO_3 prevents metal precipitation and sorption onto the container walls and minimises post-sampling microbial activity.

Two unfiltered water samples were collected for analyses to be performed at the field base. A 250 mL LDPE Nalgene® bottle for total alkalinity and conductivity determinations; and a 30mL polythene bottle for pH determinations. Both bottles were reused, and so rinsed with sample water three times prior to filling the bottle. The bottles were submerged underwater while the caps were secured to ensure no air was trapped in the sample bottle. This minimises CO_2 degassing, which can affect pH and alkalinity determinations. Upon return to the field base the filtered waters were acidified if required, and refrigerated.

At the time of the Clyde Estuary and Glasgow Clyde Urban Tributaries surveys in 2003, the suite of analytical techniques available included Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), colorimetry, and atomic fluorescence spectrometry (AFS). Therefore, extra samples of filtered water were required to fulfil the analytical sample suite. These samples were collected in the same way as those described above and full methods are given in Jones et al. (2004) and Fordyce et al. (2004).



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Data set types are explained in Table 6

Figure 11. Sample site locations within the Clyde Basin study area.

Additional samples were taken during the Glasgow Clyde Urban Tributaries and Clyde Estuary surveys for determination of analytes that are not considered routinely as part of the G-BASE project, e.g. sulphite, mercury, and in situ dissolved oxygen measurements. Since information for these additional analytes is not available across the whole of the Clyde Basin, they are not included in this atlas. However, the results of the Glasgow Clyde Urban Tributaries and Clyde Estuary surveys have been reported in full by Fordyce et al. (2004) and Jones et al. (2004) respectively.

During the Estuary fieldwork the site locations were recorded on a Garmin® global positioning system (GPS) and a brief description of the site characteristics was made (Jones et al., 2004). For the other surveys, at each sample site, information on the location, contamination, land-use and other features required for data interpretation was entered on a computer-compatible field data card in standard G-BASE format (Johnson, 2005). The field cards were pre-numbered according to a random number system (see Section 3.4). The location was determined using a Garmin® GPS and noted on a field copy of the 1: 25 000 or 1:50 000 Ordnance Survey (OS) map. On completion of each days' fieldwork, the sample locations were plotted on stable-base OS maps using the data cards and the field copies of the OS maps. The field observations were entered into a digital database following collection.

3.2.1 Collecting samples for quality control and quality assurance

Duplicate and replicate samples were collected as part of the error monitoring procedures to establish the validity of variation between samples collected. One site in every batch of 100 stream water sample numbers was designated for the collection of a duplicate field sample. At this site (Duplicate A) the samples for pH and alkalinity were collected as described above. However, rather than the standard set of 60mL and 30mL bottles used for filtered water collection, a single, prelabelled, factory-new 250 mL HDPE Nalgene® sample bottle was filled with filtered water. This sampling procedure was then repeated about 20 m upstream from the original sample site (Duplicate B). Each set of samples was designated a separate sample number. Upon return to the field base, each 250 mL filtered water sample was decanted into two sets of prelabelled 60 mL and 30mL bottles. One of the sets of bottles was labelled with the sample number previously assigned to the duplicate, and one set was labelled with the sample number assigned to the corresponding replicate, i.e. Duplicate A was split to create Duplicate A and Replicate A, while Duplicate B was split to create Duplicate B and Replicate B. These four samples were then treated as normal samples; therefore, acted as "blind" quality control checks within the batch of 100 samples. The duplicates were used to assess sampling variance, while the replicates were used to assess analytical variance (Ander, 2014; Johnson, 2005).

Blank samples were inserted into the analytical run to ensure the cleanliness of the method, equipment, and acids used. In each batch of 100 samples, two sample numbers were reserved for blank waters, one filtered and one unfiltered. These samples were made up in the field using ultra-pure water (18 µΩ Millipore). These samples were then treated like any other sample, and they were not identifiable to the analyst (Johnson, 2005).

3.3 Sample analysis

3.3.1 Field methods

The pH was determined on the day of collection using a temperature compensated glass combination electrode connected to a high performance pH meter (Radiometer Model PHM 80). The following day, conductivity was determined using a Hannah H19033 conductivity meter calibrated to a temperature sensitive standard, and total alkalinity was determined by titration against 0.8 M or 0.08 M sulphuric acid (H_2SO_4) using bromocresol green indicator. Hereafter, total alkalinity is expressed as HCO_3.Total alkalinity was not measured on the estuary water samples.

3.3.2 Laboratory methods

All waters for laboratory analysis were refrigerated after sampling, and delivered to the laboratories as soon as possible.

On return to the laboratory, the Clyde Rural Stream and River Clyde waters collected in 2010 underwent an additional acidification step: 0.3 mL HCl was added to the filtered water samples acidified in the field. Aqua regia (HNO_3 HCl mix, in this case in the ratio 2:1) is not taken into the field because of health and safety implications. Therefore, HCl acidification was carried out in the laboratory.

Analysis of the Clyde Basin water samples was carried out in stages involving a variety of analytical techniques. However, the rigorous quality-control procedures adopted during collection and analysis maximise the consistency of the data produced throughout the surveys. A summary of the analytical methods is presented in Table 7.The five Estuary water samples collected in 2002 were analysed in 2002. However, the remaining three Estuary water samples collected in 2003 were analysed with the Glasgow Clyde Urban Tributaries water samples (Jones et al., 2004). Therefore, for the purposes of this atlas these samples are considered with the Urban Tributary samples in terms of analysis (Table 7), but are interpreted as part of the Estuary dataset. The samples from the Clyde Rural Stream and River Clyde surveys in 2010 were collected and analysed together (Bearcock et al., 2011). The analytical methods adopted for each dataset are as follows.

Table 7. Analytes, methods and lower limits of detection (LLD) for each stage of analysis.

Analyte	Name	Streams and Rivers 2010		Urban (and three Estuary samples) 2003		Estuary 2002	
		Method	LLD	Method	LLD	Method	LLD
Ag**	Silver	ICP-MS	0.01 µg/L	—	—	—	—
Al	Aluminium	ICP-MS	1 µg/L	ICP-MS	1 µg/L	ICP-MS	1 µg/L*
As	Arsenic	ICP-MS	0.01 µg/L	ICP-MS	1 µg/L	ICP-MS	1 µg/L*
B	Boron	ICP-MS	10 µg/L	—	—	ICP-AES	0.04 mg/L
Ba	Barium	ICP-MS	0.1 µg/L	ICP-AES	0.003 mg/L	ICP-MS	0.5 µg/L
Be	Beryllium	ICP-MS	0.005 µg/L	ICP-MS	0.05 µg/L	ICP-MS	0.05 µg/L*
Bi**	Bismuth	ICP-MS	0.01 µg/L	ICP-MS	0.01 µg/L	—	—
Br^-	Bromide	IC	0.02 mg/L	—	—	—	—
C (DOC)	Dissolved Organic Carbon	TOC Analyser	0.5 mg/L	TOC Analyser	1 mg/L	TOC Analyser	1 mg/L
C (TIC)	Total Inorganic Carbon	—	—	TOC Analyser	0.5 mg/L	—	—
Ca	Calcium	ICP-MS	0.3 mg/L	ICP-AES	0.03 mg/L	ICP-AES	0.03 mg/L
Cd	Cadmium	ICP-MS	0.01 µg/L	ICP-MS	0.02 µg/L	ICP-MS	0.02 µg/L*
Ce	Cerium	ICP-MS	0.002 µg/L	ICP-MS	0.01 µg/L	—	—
Cl^-	Chloride	IC	0.05 mg/L	IC	0.05 mg/L	IC	0.05 mg/L
Co	Cobalt	ICP-MS	0.01 µg/L	ICP-MS	0.05 µg/L	ICP-MS	0.05 µg/L*
Cr	Chromium	ICP-MS	0.05 µg/L	ICP-MS	0.5 µg/L	ICP-MS	0.5 µg/L*
Cs	Caesium	ICP-MS	0.01 µg/L	ICP-MS	0.02 µg/L	—	—
Cu	Copper	ICP-MS	0.4 µg/L	ICP-MS	1 µg/L	ICP-MS	1 µg/L*
Dy	Dysprosium	ICP-MS	0.002 µg/L	—	—	—	—
Er	Erbium	ICP-MS	0.002 µg/L	—	—	—	—
Eu	Europium	ICP-MS	0.002 µg/L	—	—	—	—
F^-	Fluoride	IC	0.01 mg/L	IC	0.01 mg/L	IC	5 mg/L

Analyte	Name	Streams and Rivers 2010		Urban (and three Estuary samples) 2003		Estuary 2002	
		Method	LLD	Method	LLD	Method	LLD
Fe	Iron	ICP-MS	1 µg/L	ICP-AES	0.01 mg/L	ICP-AES	0.01 mg/L
Ga**	Gallium	ICP-MS	0.05 µg/L	—	—	—	—
Gd	Gadolinium	ICP-MS	0.002 µg/L	—	—	—	—
Hf	Hafnium	ICP-MS	0.01 µg/L	—	—	—	—
Hg	Mercury			AFS	0.02 µg/L	AFS	0.01 µg/L*
Ho	Holmium	ICP-MS	0.002 µg/L	ICP-MS	0.01 µg/L	—	—
HPO_4**	Phosphate	IC	0.1 mg/L	—	—	—	—
K	Potassium	ICP-MS	0.1 mg/L	ICP-AES	0.1 mg/L	ICP-AES	0.1 mg/L
La	Lanthanum	ICP-MS	0.002 µg/L	ICP-MS	0.01 µg/L	—	—
Li	Lithium	ICP-MS	1 µg/L	ICP-MS	0.1 µg/L	ICP-MS	0.1 µg/L
Lu	Lutetium	ICP-MS	0.002 µg/L	—	—	—	—
Mg	Magnesium	ICP-MS	0.01 mg/L	ICP-AES	0.06 mg/L	ICP-AES	0.06 mg/L
Mn	Manganese	ICP-MS	0.2 µg/L	ICP-AES	0.003 mg/L	ICP-AES	0.003 mg/L
Mo	Molybdenum	ICP-MS	0.02 µg/L	ICP-MS	0.05 µg/L	ICP-MS	0.5 µg/L*
Na	Sodium	ICP-MS	0.1 mg/L	ICP-AES	0.08 mg/L	ICP-AES	0.08 mg/L
Nb**	Niobium	ICP-MS	0.01 µg/L	—	—	—	—
Nd	Neodymium	ICP-MS	0.01 µg/L	—	—	—	—
NH_4	Ammonium	—	—	Colorimetry (s)	0.77 mg/L	—	—
Ni	Nickel	ICP-MS	0.1 µg/L	ICP-MS	1 µg/L	ICP-MS	1 µg/L*
NO_2	Nitrite	IC	0.01 mg/L	IC	0.005 mg/L	—	—
NO_3	Nitrate	IC	0.05 mg/L	IC	0.2 mg/L	IC	4 mg/L
P	Phosphate	ICP-MS	0.01 mg/L	ICP-AES	0.07 mg/L	ICP-AES	0.1 mg/L
Pb	Lead	ICP-MS	0.05 µg/L	ICP-MS	0.2 µg/L	ICP-MS	0.2 µg/L
Pr	Praseodymium	ICP-MS	0.002 µg/L	—	—	—	—
Rb	Rubidium	ICP-MS	—	ICP-MS	0.02 µg/L	—	—
S	Sulphide	ICP-MS	1 mg/L	Hydride gen ICP-AES (s)	0.2 mg/L	Colorimetry (s)	0.2 mg/L
Sb	Antimony	ICP-MS	0.005 µg/L	ICP-MS	0.05 µg/L	ICP-MS	0.05 µg/L
Se	Selenium	ICP-MS	0.05 µg/L	AFS	0.3 µg/L	AFS	0.3 µg/L
Si	Silicon	ICP-MS	50 µg/L	ICP-AES	0.08 mg/L	ICP-AES	0.08 mg/L
Sm	Samarium	ICP-MS	0.002 µg/L	—	—	—	—
Sn**	Tin	ICP-MS	0.1 µg/L	ICP-MS	0.02 µg/L	—	—
SO_4	Sulphate	IC	0.1 mg/L	IC	0.05 mg/L	ICP-AES	0.1 mg/L
Sr	Strontium	ICP-MS	0.2 µg/L	ICP-AES	0.001 mg/L	ICP-AES	0.001 mg/L
Ta**	Tantalum	ICP-MS	0.5 µg/L	—	—	—	—
Tb	Terbium	ICP-MS	0.002 µg/L	—	—	—	—
Th	Thorium	ICP-MS	0.01 µg/L	ICP-MS	0.02 µg/L	—	—
Ti	Titanium	ICP-MS	0.05 µg/L	—	—	—	—
Tl	Thallium	ICP-MS	0.01 µg/L	ICP-MS	0.01 µg/L	—	—
Tm	Thulium	ICP-MS	0.002 µg/L	—	—	—	—
U	Uranium	ICP-MS	0.003 µg/L	ICP-MS	0.02 µg/L	ICP-MS	0.02 µg/L*
V	Vanadium	ICP-MS	0.1 µg/L	ICP-MS	0.5 µg/L	ICP-MS	0.5 µg/L*
W**	Tungsten	ICP-MS	0.2 µg/L	—	—	—	—
Y	Yttrium	ICP-MS	0.005 µg/L	ICP-MS	0.01 µg/L	—	—
Yb	Ytterbium	ICP-MS	0.002 µg/L	—	—	—	—

Analyte	Name	Streams and Rivers 2010		Urban (and three Estuary samples) 2003		Estuary 2002	
		Method	LLD	Method	LLD	Method	LLD
Zn**	Zinc	ICP-MS	0.5 µg/L	ICP-MS	2 µg/L	ICP-AES	7 µg/L*
Zr	Zircon	ICP-MS	0.05 µg/L	ICP-MS	0.01 µg/L	—	—

* denotes lowest LLD reported for data set. Higher LLDs may be relevant where samples have been diluted

** denotes analytes where there may be some limitations on its use (see Ander (2014))
(s) denotes samples were subcontracted to an external laboratory

3.3.2.1 Clyde Estuary 2002 sample analysis

The five samples taken in 2002 from the estuary of the River Clyde were analysed by ICP-AES for 12 major cations and trace elements, and by ICP-MS for 15 trace elements. Dissolved organic carbon (DOC) was analysed by TOC analyser using standard G-BASE methods. These analyses were carried out at the BGS by standard G-BASE methods (Johnson, 2005). The detection limits were based on five times the standard deviation of the blank.

Anions (chloride, nitrate, and fluoride) were determined by ion chromatography and Se was analysed by hydride generation AFS (atomic fluorescence spectrometry), which were not UKAS accredited. Sulphide (S^-) was subcontracted to an external laboratory, who did not hold UKAS accreditation for this method.

3.3.2.2 Glasgow Clyde Urban Tributaries and Clyde Estuary 2003 sample analysis

The urban Clyde tributary samples and remaining three samples taken from the River Clyde estuary were analysed by ICP-AES for 11 major cations and trace elements, by ICP-MS for 26 trace elements, and by TOC analyser for DOC. These analyses were carried out at the BGS by standard UKAS accredited G-BASE methods (BGS, 1999). The detection limits were based on five times the standard deviation of the blank.

Anions (chloride, nitrate, sulphate, and fluoride) were determined by ion chromatography using standard G-BASE methods and Se was analysed by hydride generation AFS, which were not UKAS accredited.

3.3.2.3 Clyde Rural Stream Water and River Clyde water analysis

The determination of 57 major and trace elements in stream and river waters was carried out by ICP-MS. Detection limits were calculated as three times the standard deviation of the blanks inserted at regular intervals during the analysis. As this was a new ICP-MS instrument the method was not accredited at this time.

The DOC samples were analysed using the TOC analyser, carried out at the BGS by standard UKAS accredited G-BASE methods (BGS, 1999).

The anions (chloride, sulphate, nitrate, nitrite, fluoride, bromide and hydrogen phosphate) were determined by ion chromatography using standard G-BASE methods, which were not UKAS accredited.

3.4 Error control and data quality

The following section presents a summary of the quality control (QC) procedures undertaken on the Clyde water data. Full explanations and details can be found in Ander (2014).

3.4.1 Sample numbers

Systematic error in field sampling and 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 analytical instrument drift could be distinguished from genuine geographic variances.

3.4.2 Blank waters

Lower limits of detection (LLD, also referred to as detection limits) were calculated from laboratory blanks inserted throughout the analytical run, using the following equation:

LLD = mean + (3 x Standard Deviation)

The LLDs for each analyte are presented in Table 7.

The field blanks (see Section 3.2.1) were used to identify analytes with artificially increased concentrations. The field blanks were run blind within each batch of samples, and if the measured concentrations were below the laboratory defined LLD, it indicated that post sampling contamination was not an issue. Only Zn data warranted further investigation, three samples exceeded 4 µg/L, which was high in relation to the detection limit, and to the rest of the dataset. Such erroneous values were not reflected in samples run with these blanks, but the random nature of these high concentration blanks does mean isolated high concentrations of Zn within the sample site data should be treated with caution (Ander, 2014).

Where > 80% of the data of an analyte were at or below the detection limit, there was a preliminary inspection of the location of sample sites where the analyte was detectable to check these. No further quality control processes were undertaken. Analytes which were affected by this were: Ga, Nb, Ag, Sn, Ta, W, Bi and HPO_4.

3.4.3 Duplicates and replicates

In the Clyde Basin drainage dataset there were 21 duplicate sample sites, which gave a total of 84 analyses, given that each site produced two pairs of duplicates and replicates (see Section 3.2.1). The data for all analytes were initially plotted using an Excel™ macro (Johnson, 2002), and the resulting graphs permitted a rapid inspection of the dataset to assess if there were any data of a “catastrophic” nature, which could be immediately removed. Data were also removed if most of the duplicate/ replicate data were below the LLD. On this basis, Hf, Tl, Th, Br and NO_2 did not have sufficient samples above the LLD to proceed. The remaining samples were then used within an analysis of variance (ANOVA), processed by the Excel™ macro (Table 8).

It is expected that for data above the LLD, geographical geochemical differences between-site should account for ≥80% of the variance as opposed to < 20% sampling and analytical variance (Ramsay, 1998). However, this was not the case for Zn and Zr. For Zr this was due to low concentrations close to the detection limit. The Zn and Zr data should be considered to have a greater uncertainty than the other analytical data in the Clyde surface water dataset (Ander, 2014).

3.4.4 Reference materials

Primary reference materials and standards were inserted by the laboratories as part of their QC procedures (Table 9). Quality control checks indicated that Li, B, and Al were associated with a higher analytical uncertainty (±20%) than for most of the other elements (±10%). In addition, secondary reference materials (SRMs) and certified reference materials (CRMs) were included within each sample batch to understand any bias in the results, not picked up by the laboratory QC processes. The CRM data allowed for comparison of the measured data with the certified values.

Vanadium, Cu, Be, Zn, P, Ni and Fe had a greater uncertainty than the other analytes, which either had a good precision, low levels of bias, or were so close to the detection limit they could not be assessed satisfactorily (Ander, 2014).

Table 8. ANOVA of geochemical (between site), sampling (between sample) and analytical (residual) variance in the Clyde Basin surface water dataset.

Analyte	Between Site Variance (%)	Between Sample Variance (%)	Residual Variance (%)	No of Duplicates
Al	99	0	0	21
As	99	0	1	21
B	97	-1	4	19
Ba	100	0	0	21
Be	94	1	5	8
Ca	100	0	0	21
Cd	95	1	4	7
Ce	100	0	0	21
Cl	97	0	3	21
Co	99	1	0	21
Cr	97	1	2	21
Cu	80	6	14	13
DOC	99	0	1	20
Dy	99	0	1	21
Er	99	0	1	21
Eu	98	0	2	13
F	96	-1	4	19
Fe	100	0	0	21
Gd	99	0	1	21
Ho	99	0	1	21
K	98	0	2	21
La	100	0	0	21
Li	96	1	3	20
Lu	93	3	4	21
Mg	100	0	0	21
Mn	96	4	0	21
Mo	88	5	7	21
Mo	97	1	2	14
Na	100	0	0	21
Nd	96	0	3	20
Ni	99	0	1	21
NO_3	95	4	1	12
P	95	0	5	18
Pb	91	6	3	20
Pr	99	0	1	21
Rb	99	0	1	21
S	96	3	1	21
Sb	99	0	1	21
Se	94	1	5	21
Si	99	0	1	21
Sm	99	0	1	21
SO_4	97	0	3	21
Sr	100	0	0	21
Tb	98	-1	4	21
Ti	96	1	3	21
Tm	96	0	4	21
U	100	0	0	21
V	98	0	2	14
Y	100	0	0	21
Yb	90	-1	12	21
Zn	**65**	**27**	**8**	**16**
Zr	**47**	**-2**	**55**	**12**
pH	97	3		21
Conductivity	94	6		21
HCO_3	91	9		21

Elements shown in bold have geochemical variance < 80%

Table 9. Results for certified reference material NIST1643e included in the Clyde Basin surface water analysis

Element	Certified Value mg/L	Mean Value mg/L	RSD %	Recovery %	Mean Value mg/L	RSD %	Recovery %	Mean Value mg/L	RSD %	Recovery %	Mean Value mg/L	RSD %	Recovery %
Ca	32.3	30.9	1.4	96	30.3	5.6	94	31.2	2.5	97	31.6	4.3	98
K	2.03	2.1	3.6	103	2	3.9	98	2	2.7	100	2.1	4.7	104
Mg	8.03	8.36	3.4	104	7.9	7	99	8.1	3.2	100	8.4	4.1	104
Na	20.7	21.1	2.1	102	19.8	9.4	95	20.1	4.1	97	21	4.3	101
	µg/L	µg/L	%	%	µg/L	%	%	µg/L	%	%	µg/L	%	%
Ag	1.06	0.74	19.9	69	0.9	7.6	82	0.9	3.3	87	0.9	5	88
Al	141.8	140.9	3.8	99	146.5	5.7	103	151.9	8.9	107	153.1	10.7	108
As	60.4	56.3	2.9	93	55.7	5.2	92	55.6	1.6	92	57.7	4.6	95
B	157.9	164.6	8.6	104	166.7	5	106	164.9	4.2	104	170.2	5.8	108
Ba	544.2	498.9	4.1	92	514.2	3.2	94	515.6	2.1	95	527.9	2.9	97
Be	13.9	13.7	4.8	98	13.6	6.2	97	13.6	2.9	98	13.4	3	94
Bi	13.75	13.98	4.1	102	14.1	4	103	14	1.6	102	14	4.2	105
Cd	6.56	6.29	3.6	96	6.25	5.8	95	6.2	2.4	94	6.5	5.3	99
Co	27	26.5	6.7	98	26.7	4.2	99	26	3.3	96	26	4.1	96
Cr	19.4	20.1	2.8	99	20.9	5.1	103	20.2	2.3	99	20.6	3.4	101
Cu	22.7	21.8	6.9	96	21.9	5.2	96	21.2	3.5	93	21.2	3.5	93
Fe	98.1	101.8	4.6	104	103.7	10.3	106	100.3	2.4	102	103	5.4	105
Li	17.4	18.4	5.4	106	18.3	5.5	105	19	5.3	109	19.2	5.9	110
Mn	38.9	38.3	3.8	98	39.4	5.2	101	37.6	2.3	96	38.2	2.9	98
Mo	121.4	125	4.3	103	120.9	2.1	100	116.2	1.3	96	119.9	2.6	96
Ni	62.4	62	5	99	62.7	4.8	101	60.4	3	97	60.3	5	97
Pb	19.63	18.46	2.4	94	19.4	2.9	99	19.4	1.7	99	19.7	4.2	100
Rb	14.1	13.7	2.5	97	14.3	2.8	101	13.8	2.2	97	14	2.9	99
Sb	58.3	56.44	6	97	58.49	10.1	100	55.7	1.5	96	56	2.7	96
Se	11.9	11.2	7.9	94	11.3	10.9	94	11.8	1.8	98	12.2	5.5	102
Sr	321.1	306.9	3.5	95	315.7	3.5	98	301.9	8.81	93	318.5	5.1	99
Tl	7.44	6.71	2.9	90	6.9	8.9	93	7.1	1.9	95	7.2	3	96
V	37.8	37.3	2.9	98	38.5	3.6	102	37	2.1	98	37.5	3.1	99
Zn	78.5	78.1	2.8	99	77.7	6.9	99	74.5	6.4	95	71.7	7.6	91
		n=17			n=17			n=22			n=22		

3.4.5 Monitor sites

Monitor site streams were selected for sampling once a day, each day of the field campaign. They were representative of the streams being sampled by the field teams. They were chosen to be quick and easy to access; hence, a new monitor site was chosen for each field base. In all other ways the samples were collected and handled following the same protocol as any other sample site. Some systematic temporal changes, which correspond to rainfall events, were identified over the sampling period (Ander, 2014). However, as the data are presented at a regional scale, the temporal variation is usually negligible when compared to the spatial variation (BGS, 1999).

3.4.6 Charge balance

Charge balances were calculated using major ion analyses using the following equation:

Charge balance % = (([sum cations]-[sum anions])/([sum cations]+[sum anions])) x 100 (Appelo and Postma, 2007)

Charge balances could not be calculated for the estuary samples as there were no HCO_3 data. Eight percent of the Urban data, and 16% of the Rivers and Stream data had a charge imbalance ≥10%. Some imbalances were relatively large, which is not unusual for low ionic strength waters. Only 3% of the Rivers and Stream samples with charge imbalances ≥10% were associated with data where the sum of cations and anions was >1 meq/L, the remainder were considered to have such low concentrations that charge balance errors were likely to arise from a cumulative higher uncertainty on each analysis (Ander, 2014).

3.4.7 Analytical cross-check and interference comparisons

As a final check, the geochemical data were graphed to ensure that there were no spatial relationships related to analytical artefacts. Firstly a simple comparison was made between the total dissolved solids (TDS) (derived from simply summing the total major and minor ions), and the conductivity. This is particularly useful to check that the higher conductivity waters data have been correctly transposed from mS/cm into µS/cm. This check highlighted that 34 samples collected on the same day were affected by a fault with the conductivity meter. These samples were all located around the Forth coal mining area (Location 30, Figure 3) and should; therefore, be treated with caution.

3.5 Data presentation

Once full error control and data quality procedures were completed, the Clyde water geochemical results were formally loaded into the BGS Corporate Oracle® Geochemistry Database (Harris and Coates, 1992) where they may be retrieved by means of a database front-end. Where data have higher uncertainty, a qualifier is issued with the data.

To present the data spatially, the Stream and Urban datasets were combined, and interpolated surface geochemical maps were created using the ArcGIS10.1 (ESRI®) geographic information system (GIS) software package. 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, 99, 95, and 99 percentiles of the data distribution for most elements, according to standard G-BASE procedures (Johnson, 2005). The River and Estuary datasets were combined and presented on each interpolated map as graduated symbols. The symbols represent the 10, 25, 75, and 90 percentile boundaries. In addition, geological line work, based on the simplified geological map (Figure 6), was overlain on each geochemical map.

Box plots were created using R (R Development Core Team, 2013) to show data distributions. The boxes are defined as the interquartile range, the horizontal white line depicts the median, whiskers are defined as no more than 1.5 times the interquartile range (Tukey, 1977) and open circles beyond the whiskers are defined as outliers. Boxplot widths are proportional to the square root of the number of observations.

For each parameter, summary statistics were calculated for each dataset (Estuary, Urban, River and Stream) using the NADA package in R (Lee, 2005). These are presented in tables along with data for rainwater and seawater, where available, compiled from various sources (Davies et al., 1964; Hem, 1992; Plant et al., 2004; Smedley and Kinniburgh, 2002).

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.

4 Stream-water chemistry

The following pages provide maps of the spatial distributions of selected solutes in stream and river waters from the Clyde Basin, along with statistical summary data and box plots categorised by water type, land cover and geology. Brief explanations of the distributions are also provided. Maps and statistical summaries of additional trace elements are presented in Appendix 1. On all the maps, the Glasgow urban boundary refers to the area in which samples were taken for the Urban dataset.

Figure 12 shows places named in the following interpretations.

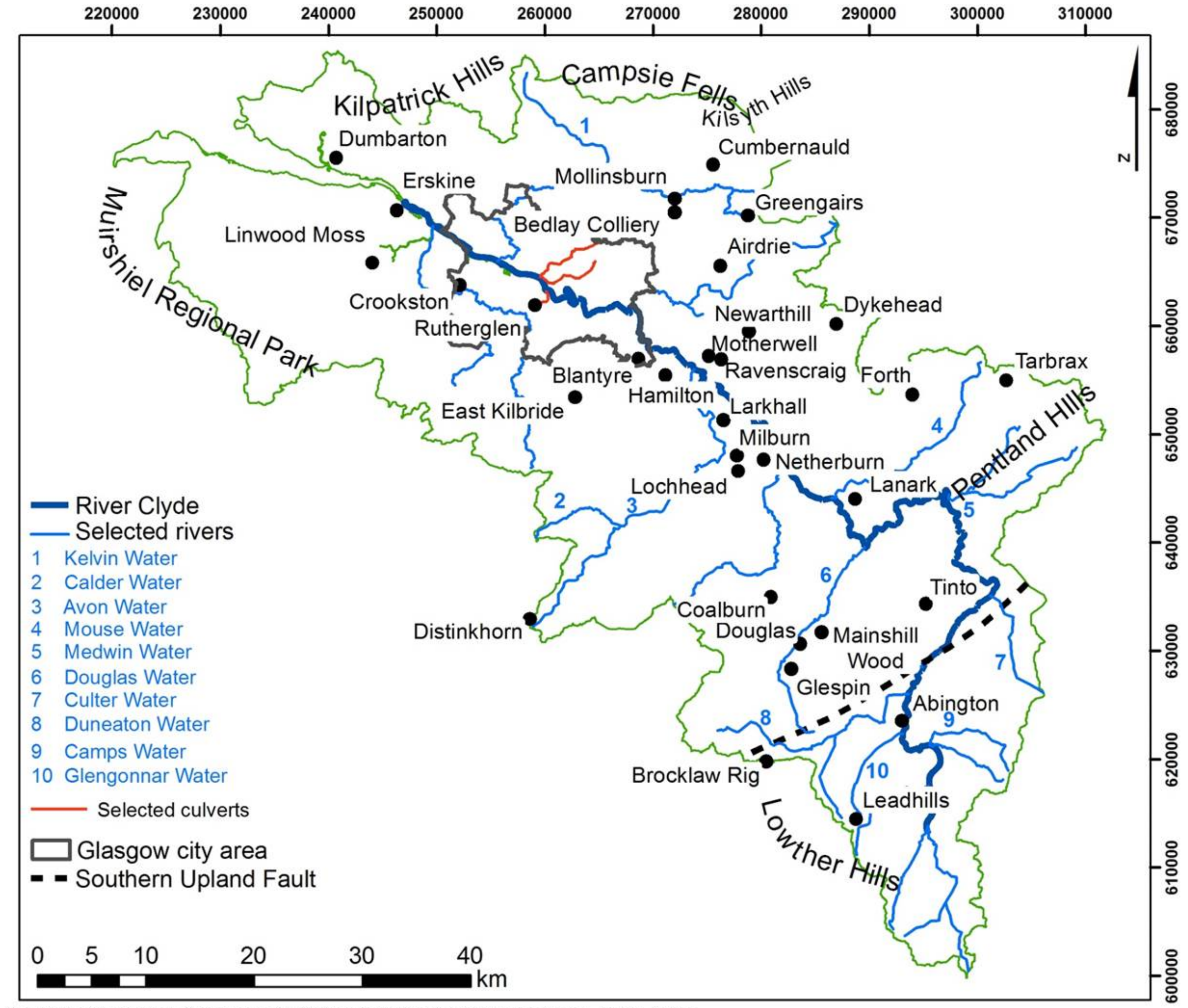

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Figure 12. Location of places named in the descriptive text.

pH pH

The acidity (pH) of water is a function of the activity of hydrogen ions [H^+] (Hem, 1992). The pH of stream water is governed by initial rainfall inputs and by buffering reactions dependent on the abundance of base cations and CO_2 derived from the bedrock and overlying soils (Stumm and Morgan, 1996).

Stream and urban compositions

The pH of stream waters within the Clyde catchment shows no clear spatial trends or relationships with geology; instead soils and land-use appear to play the dominant role. The lowest stream-water pH values are generally located in remote upland areas on the periphery of the catchment. These coincide with mapped occurrences of peat, heather moorland, coniferous forest, or to a lesser extent rough grazing. Low pH values correlate with high concentrations of dissolved organic carbon (DOC), likely to be due to the abundance of organic acids in the stream water, as well as paucity of buffering carbonate minerals. The pH tends to be lower on north-facing slopes. This is particularly evident on the Pentland Hills, Tinto and surrounding hills, and Lowther Hills north of Leadhills, with higher pH evident on the south-facing slopes of the Campsie Fells and the Kilsyth Hills. This does not correspond to measured depth of organic-rich soils (Fordyce et al., 2017), which are generally of comparable depth regardless of slope orientation. Higher rainfall in the western upland parts of the catchment may have had an effect on the stream-water pH by dilution of stream flow with relatively acidic rainwater (pH<6.5).

Low stream-water pH values (<7) are reported in the west of the urban area, sites corresponding to locations of a sewage plant, abandoned factory and hospital within distances of about 500 m.

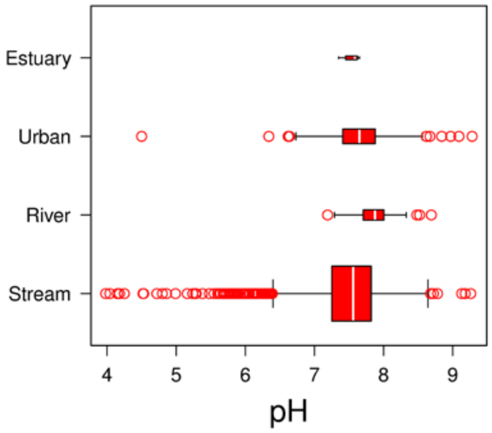
Highest pH values (>8.5) are found within the city of Glasgow. All the samples that contribute to the high pH area around central Glasgow are from the River Kelvin, a major urban tributary of the Clyde. Other areas of high pH (>8) are found around the Glespin, Mainshill Wood, and Coalburn open-cast coal mines, which are all within 5 km of Douglas.

Spatial patterns in stream-water pH distribution are otherwise indistinct. The box plots demonstrate that the medians of each geological class are similar and, with the exception of heather moor and coniferous forest, most land-use types have similar median values.

River and estuary compositions

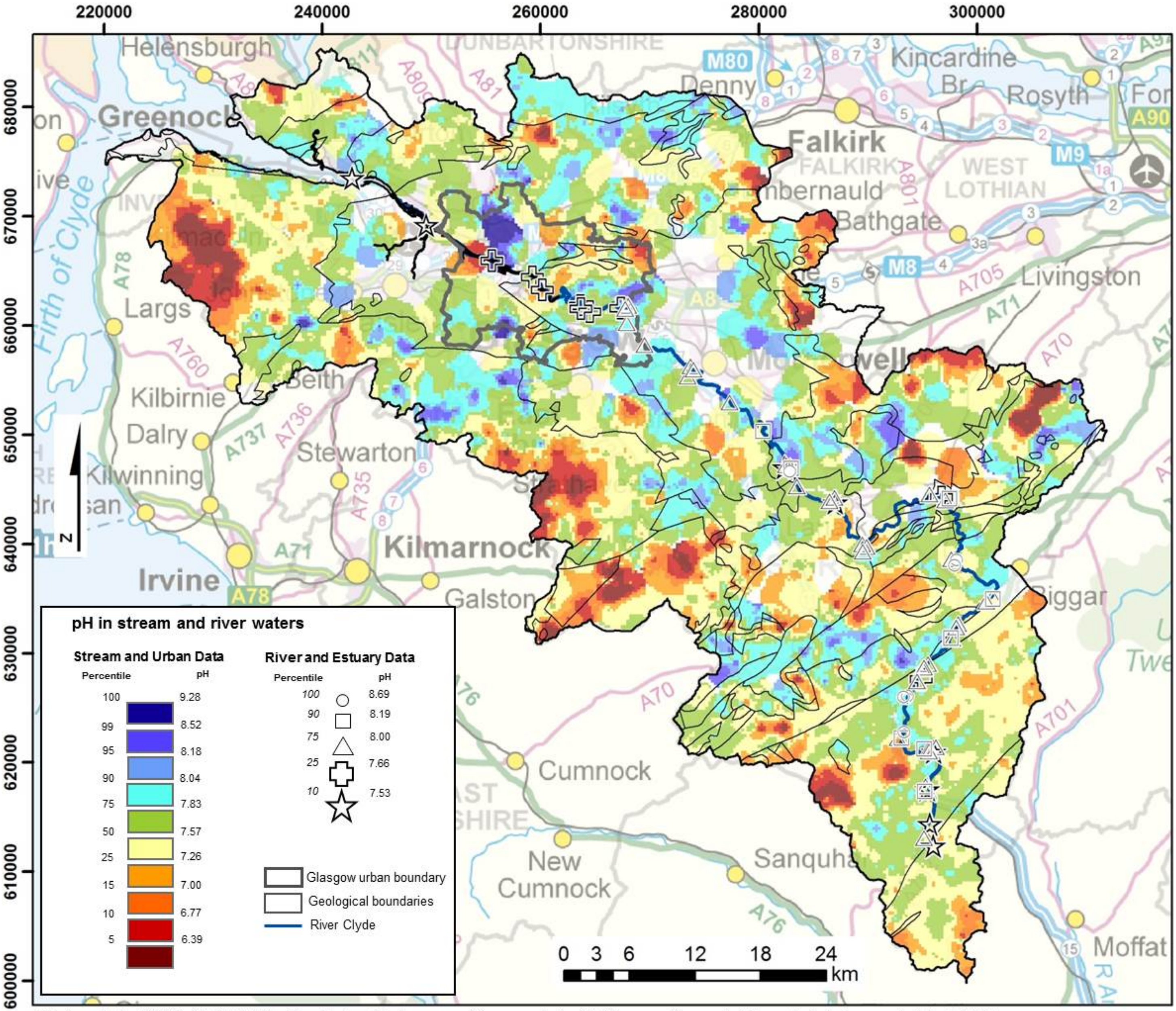
The pH of the river waters is relatively low in the upper reaches of the Clyde Basin. Within the River Clyde, pH tends to increase downstream, although some of the tributaries have lower pH, depending specifically on the area drained. The pH of the Clyde water remains near-neutral until it reaches Glasgow, at which point a decrease is observed as it flows towards the estuary.

	Stream	River	Urban	Estuary
min	3.98	7.19	4.5	7.35
25th %	7.25	7.71	7.41	7.5
50th %	7.56	7.88	7.65	7.58
75th %	7.82	8	7.88	7.62
90th %	8.03	8.22	8.26	7.64
max	9.26	8.69	9.28	7.65
n	1702	60	121	8
n cens	0	0	0	0
rainwater	5.3			
seawater	8.2			



Show location map

pH **pH**



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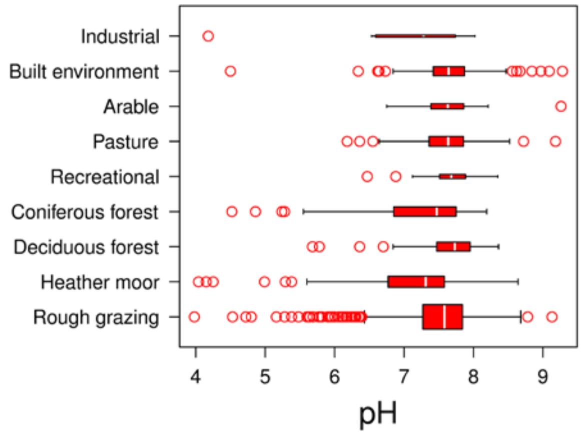
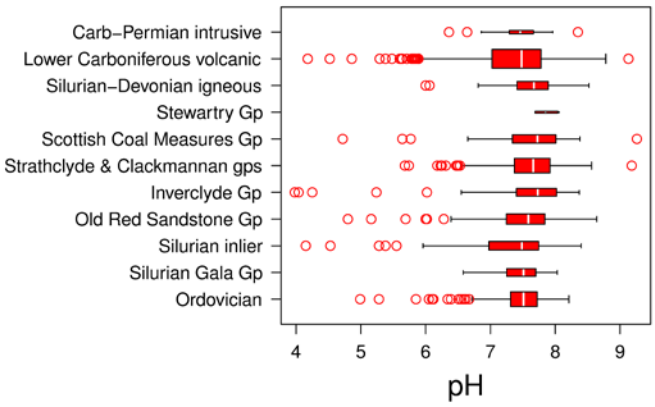




Specific electrical conductance SEC

Specific electrical conductance (SEC) is defined by the concentrations of ions in solution and is; therefore, an indicator of content of total dissolved solids (Drever, 1997).

Stream and urban compositions

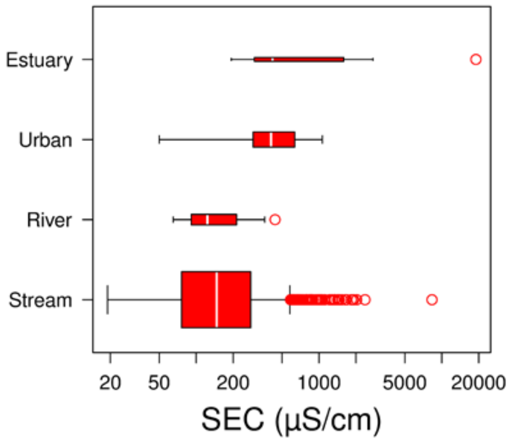
There is a strong spatial and geological dependence of stream-water SEC within the Clyde catchment. Lowest SEC values are found to the south of the Southern Upland Fault and along the western and northern catchment boundaries. These areas are underlain by the Ordovician-Silurian Gala Group and Leadhills Supergroup and the Carboniferous Clyde Plateau Volcanic Formation. On the catchment periphery, low SEC values also correspond to occurrences of peat, which are located in remote upland areas and support heather moorland. As a result, this land-use type has the lowest median stream-water SEC value (57 µS/cm). Streams in these areas are typically more acidic, with limited buffering by carbonate or other mineral reactions, and little impact by human activity. Therefore, SEC values are least modified from rainfall.

Highest stream-water SEC values are reported in the lowland areas of the Clyde Basin and within the urban areas. The spatial variation in BFI may have had some effect on SEC distribution, with a greater groundwater contribution in the low-central part of the catchment. However, the urban areas with high SEC values correspond to occurrences of till or river terrace deposits overlying Carboniferous Clackmannan-Strathclyde Group and the Coal Measure rock types. Highest SEC values are generally recorded where there has been human influence, notably due to mining and landfill. Very high SEC values (>95th percentile of Stream and Urban data) are reported around the Linwood Moss landfill (4 km south of Erskine), close to Ravenscraig disused steel works in east Motherwell, around the Greengairs landfill site (4 km north-west of Airdrie), within the confines of the city of Glasgow, and in the Forth area close to two open-cast coal mines and a landfill site. Whilst it is likely that the land-use in this latter area could give rise to high stream-water conductivity, these conductivity measurements have a greater uncertainty, due to a fault with the equipment, whilst sampling that region (See Section 3.4.7). The highest median stream-water SEC values are within the built environment and recreational land-use classes, which are most common in the city of Glasgow.

River and estuary compositions

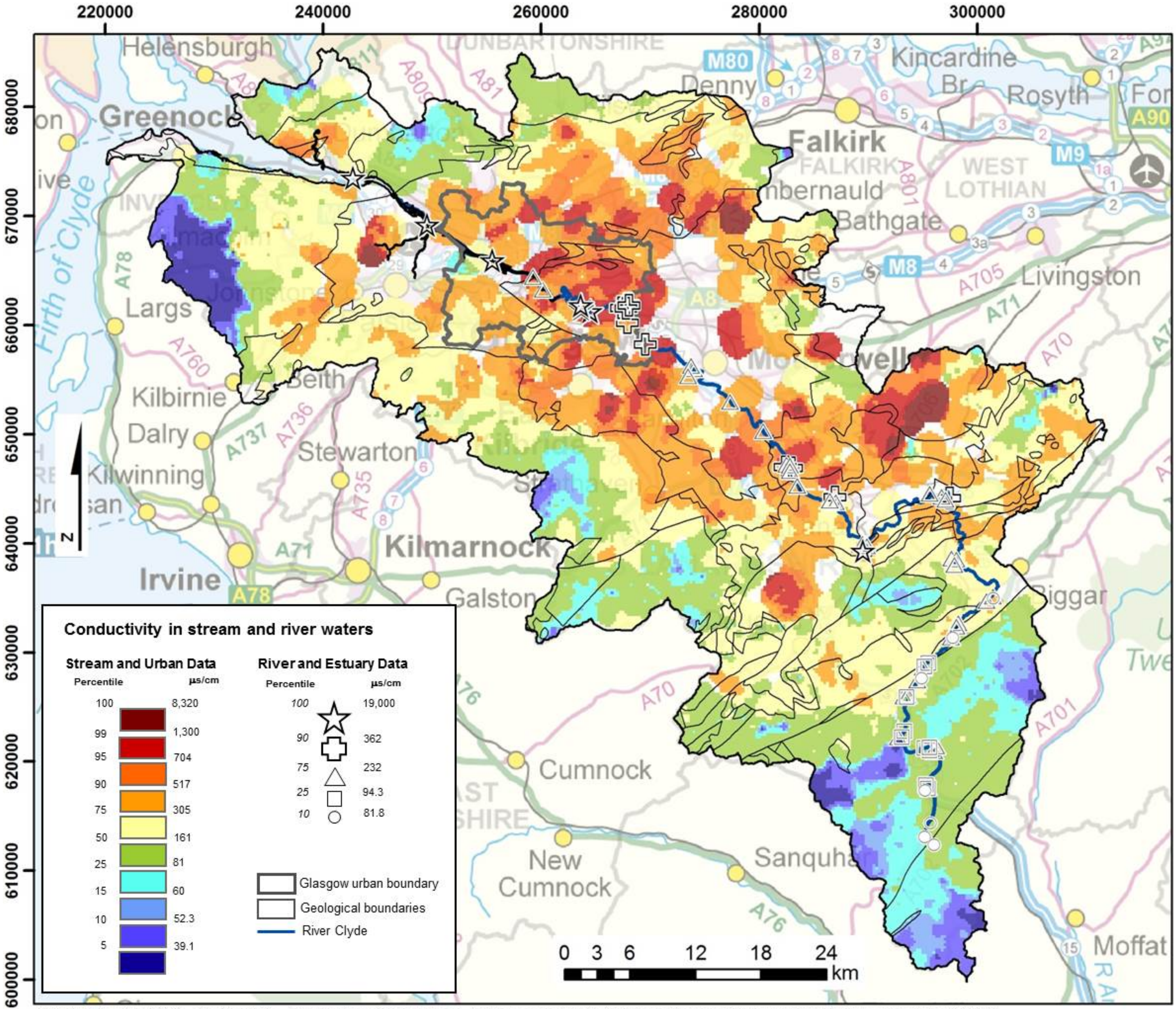
Lowest river water SEC values are found in the headwaters of the Clyde, increasing downstream to a maxima within the estuary. Some of the main tributaries of the River Clyde have higher SEC values, reflecting the local land-use. For example, Douglas Water receives mine drainage from two major coal mines around Coalburn.

	Stream	River	Urban (µS/cm)	Estuary
min	19	65	50	193
25th %	76	91	291	332
50th %	147	124	407	418
75th %	278	213	634	1010
90th %	476	269	887	7610
max	8320	439	1064	19000
n	1702	60	122	8
n cens	0	0	0	0
rainwater	26.7			
seawater	56000			



Show location map

Specific electrical conductance SEC



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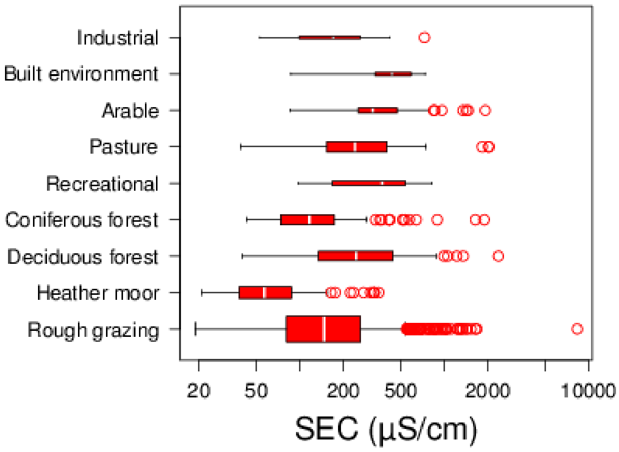
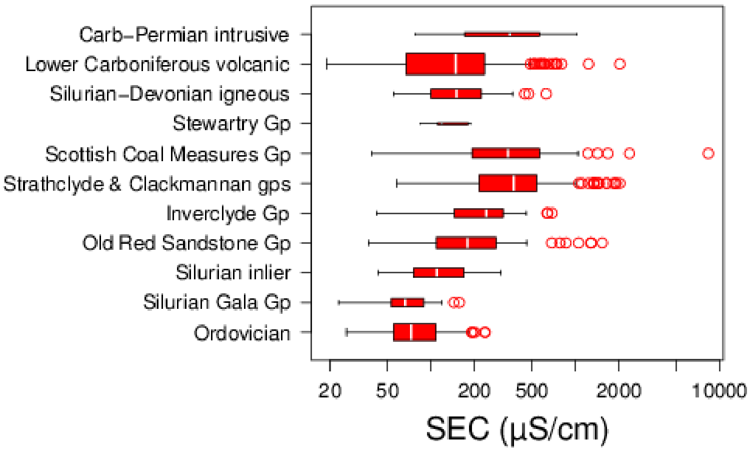




Calcium Ca

The divalent Ca ion (Ca^{2+}) is usually the dominant cation in stream waters (Hem, 2005) and its distribution is therefore usually similar to that of specific electrical conductance (SEC) (e.g. BGS, 1999). Atmospheric deposition provides Ca to stream waters but the main sources are likely to be from dissolution of soluble minerals like calcite and dolomite, with additional inputs possible where present from gypsum and anhydrite. Calcium is also derived from less soluble minerals such as feldspars and from clay minerals by ion exchange (Langmuir, 1997; Shand et al., 2007).

Stream and urban compositions

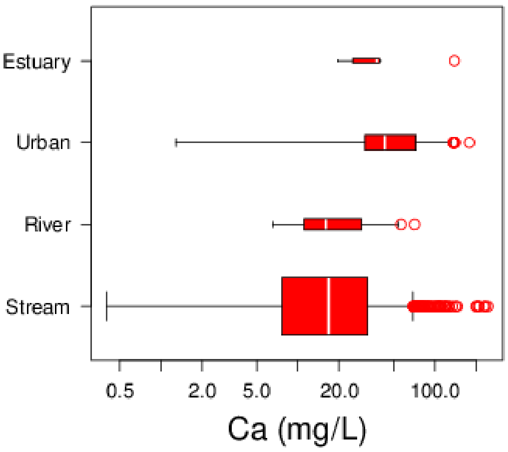
The spatial trend of Clyde Basin stream-water Ca is similar to that of SEC. Lowest concentrations are reported in streams to the south of the Southern Upland Fault and along the western and northern catchment boundaries. These areas are underlain by Ordovician-Silurian Gala Group and Leadhills Supergroup rocks, and by the Carboniferous Clyde Plateau Volcanic Formation. On the upland catchment periphery, lowest Ca concentrations correlate with occurrences of peat, which commonly support heather moorland. These streams have correspondingly high dissolved organic carbon (DOC) concentrations. The uplands are areas of high rainfall, limited buffering of stream compositions by mineral-water reactions, and low impact of anthropogenic activity. Hence, the low Ca concentrations of streams largely reflect rainfall inputs. Areas with lowest stream-water Ca concentrations include Muirshiel Country Park, the Lowther Hills north of Leadhills and the Camps Water and Culter Water catchments.

Higher Ca concentrations (> 34.4 mg/L) are a feature of the lowland streams of the Clyde Basin, which also correspond with the urban areas. High Ca concentrations occur where till and river terrace deposits overlie Carboniferous Clackmannan-Strathclyde groups and Coal Measure rock types. High concentrations are also a feature of streams on the Inverclyde Group (Ballagan Formation) in the northern part of the Basin, likely due to dissolution of gypsum. The highest Ca concentrations are generally found where there has been human influence: downstream of the Coalburn and Dykehead opencast coal-mine sites; around 6 km north-west of Airdrie where there are former coal workings and a former landfilled fireclay mine; around disused coal-mine shafts 4 km south of the Campsie Fells; and at numerous places within the urban area of Glasgow, some of which are also influenced by coal mining. High stream-water Ca concentrations are consistent with neutralisation of acidic mine drainage by dissolution of carbonate minerals in the sedimentary formations and their overlying soils.

River and estuary compositions

Concentrations of Ca in the River Clyde water generally increase downstream. Where tributaries have relatively high concentrations, they influence the composition of the river downstream. For example, Douglas Water contains high Ca concentration (71 mg/L) as it drains the coal mining area around Douglas. The highest concentrations of Ca are found in

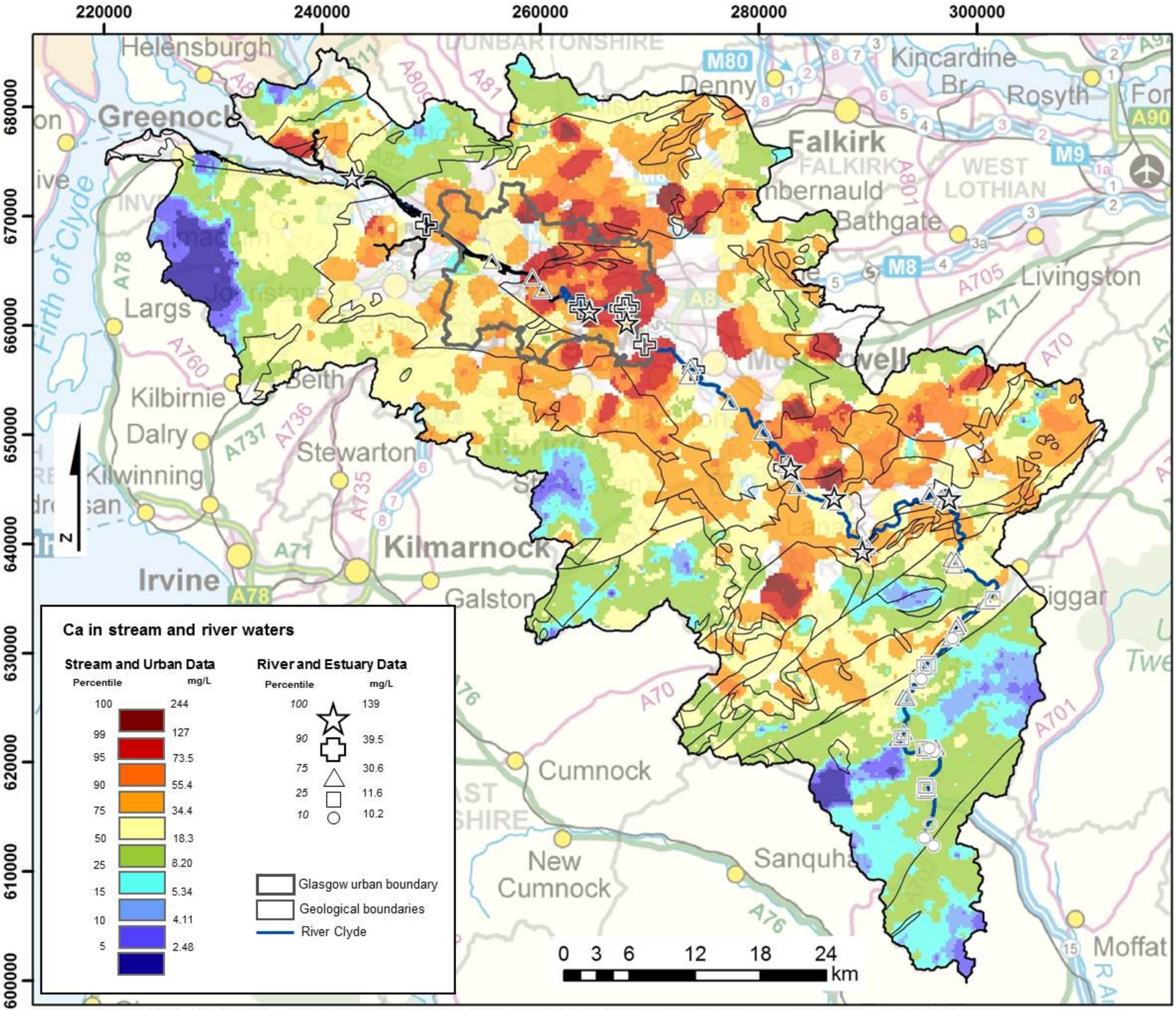
	Stream	River	Urban (mg/L)	Estuary
min	0.402	6.52	1.29	19.6
25th %	7.68	11.1	30.9	26.3
50th %	16.8	16	43.2	37.6
75th %	32.3	29.1	72.5	39.3
90th %	51.7	35	109	69.7
max	244	71.1	179	139
n	1702	60	122	8
n cens	0	0	0	0
rainwater	0.28			
seawater	410			



Show location map

Calcium

Ca



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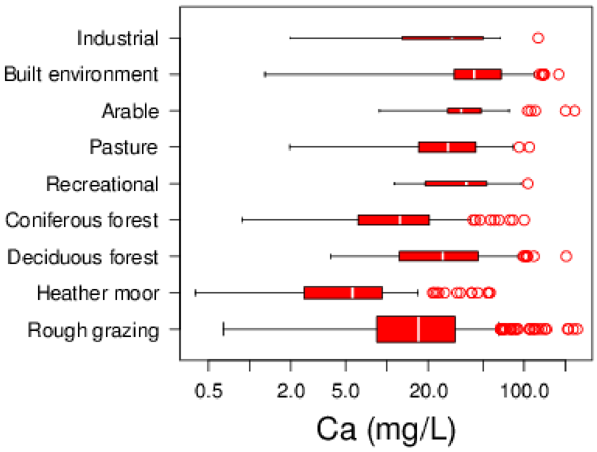
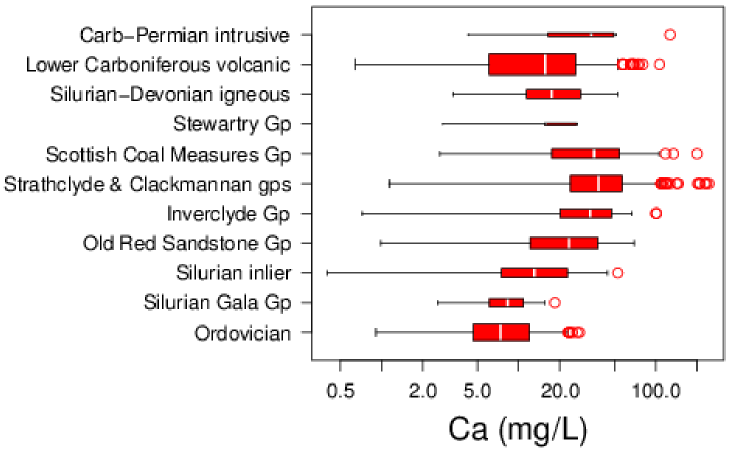




Magnesium Mg

Magnesium (Mg) is one of the major cationic species in stream waters; it is most likely to be present in its free ionic form (Mg^{2+}) (Hem, 2005). The major sources of Mg in natural waters are rainfall, dissolution of dolomite and ferromagnesian minerals, and clay minerals by ion exchange (Langmuir, 1997; Shand et al., 2007).

Stream and urban compositions

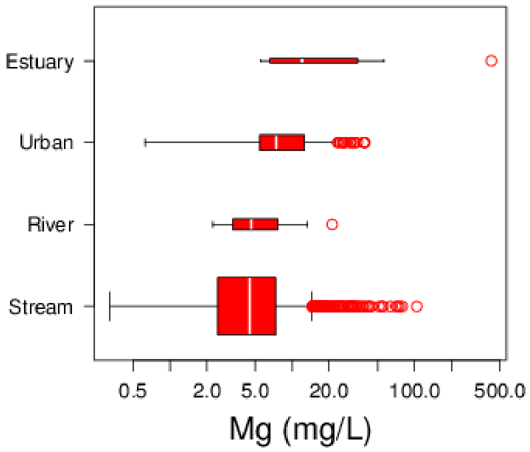
The distribution Mg within the waters of the Clyde Basin is very similar to that of Ca. Lowest Mg concentrations (< 1.05 mg/L) are found south of the Southern Upland Fault and along the western and eastern catchment boundaries. Lowest median values are reported in streams draining the Ordovician-Silurian Gala Group and Leadhills Supergroup and Carboniferous Clyde Plateau Volcanic Formation. Low Mg concentrations occur in streams from the peaty uplands on the catchment boundary, which have correspondingly high concentrations of dissolved organic carbon (DOC), and are characterised by heather moorland. Streams over this land-use type have the lowest median Mg concentration (1.87 mg/L). Paucity of Mg-bearing carbonate minerals, limited water-rock interaction, limited anthropogenic inputs and relatively high rainfall are likely the causes of the low Mg concentrations and, as with Ca, the values observed are likely to be dominated by rainfall inputs. The areas of lowest stream-water Mg concentrations are found in Muirshiel Country Park, on the north-facing slopes of the Pentland Hills, Tinto Hill and the Lowther Hills.

Highest (> 37 mg/L) stream-water Mg concentrations are reported in the lowlands of the Clyde Basin and within the urban areas. These are generally found in human-impacted streams from areas underlain by till and river terrace deposits overlying the Carboniferous Clackmannan-Strathclyde groups, and the Coal Measure rock types. Very high concentrations are found downstream of the Coalburn open-cast coal site, downstream of the Dykehead open-cast coal site (10 km east of Motherwell); around 6 km north-west of Airdrie where there are former coal workings and a former landfilled fireclay mine, around the Greengairs landfill site (4 km north-west of Airdrie), and around the Linwood Moss landfill (4 km south of Erskine).

River and estuary compositions

Concentrations of Mg in the River Clyde water gradually increase downstream. Even large inputs from Douglas Water, which is affected by drainage from Coalburn open-cast coal, and Mouse Water, impacted by drainage from open-cast mining within the Forth area, do not dramatically increase concentrations in the Clyde. The large volume of the Clyde dilutes the more concentrated tributary inputs. Concentrations of Mg in the river waters are generally high over the Coal Measures (> 8.4 mg/L), although they decrease downstream over the Clyde Plateau Volcanic Formation. The highest Mg concentrations are found in the estuary waters.

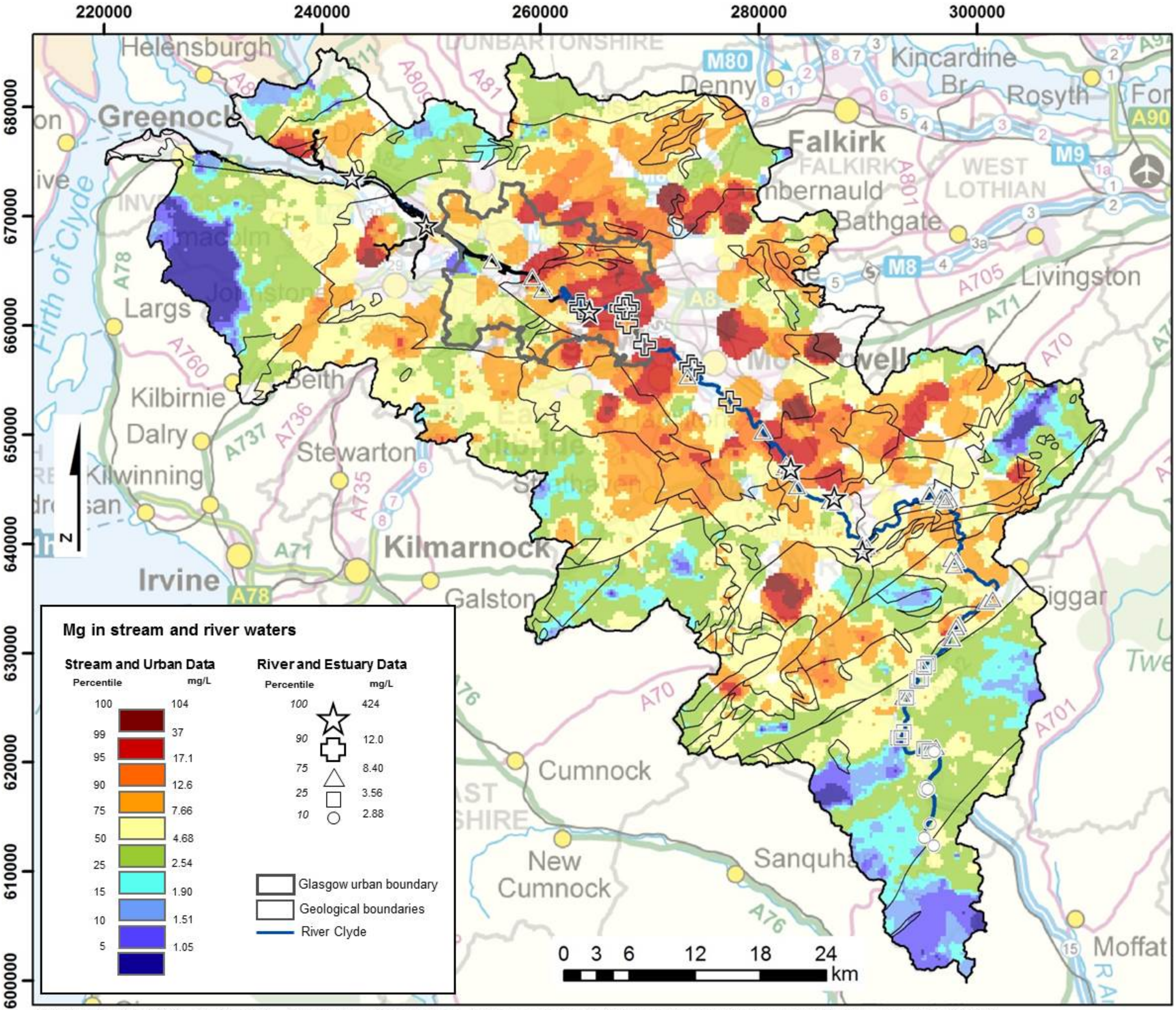
	Stream	River	Urban	Estuary
		(mg/L)		
min	0.323	2.26	0.626	5.54
25th %	2.46	3.27	5.42	6.62
50th %	4.49	4.62	7.35	12
75th %	7.3	7.59	12.5	23.4
90th %	12.3	10.1	26.2	166
max	104	21.2	39.3	424
n	1702	60	122	8
n cens	0	0	0	0
rainwater	0.33			
seawater	1350			



Show location map

Magnesium

Mg



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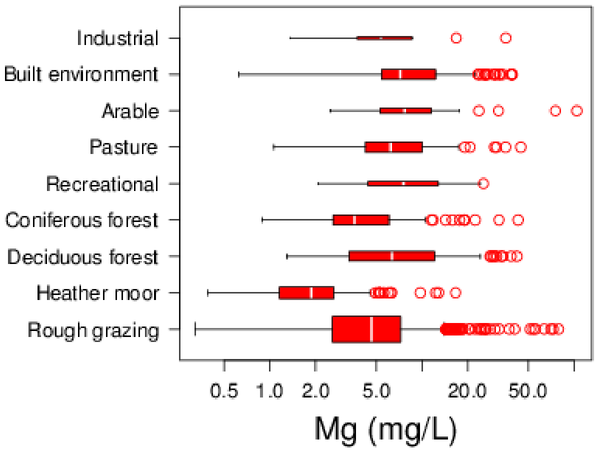
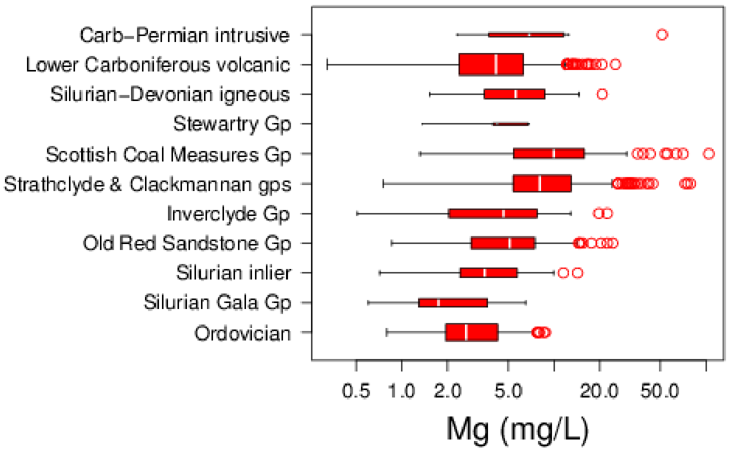




Sodium Na

Sodium has no insoluble salts and so once in solution, tends to remain in the dissolved form, although mobility can be reduced to some extent by adsorption on clays (Hem, 2005). The major natural sources of Na are rainwater, dissolution of evaporites (such as halite), or plagioclase feldspars or clays (Shand et al., 2007). Human activities can also influence the concentration of Na in natural waters (Hem, 2005).

Stream and urban compositions

Within the Clyde Basin, there is a clear spatial trend of stream-water Na concentration, with strong geological and land-use controls. Lowest Na concentrations are found south of the Southern Upland Fault and within the upland areas of the catchment of rough grazing and heather moor. These include Muirshiel Country Park and the Lowther Hills. Indeed, the Ordovician-Silurian Gala Group and Leadhills Supergroup that form the Lowther Hills are the geological classes with lowest median stream-water Na concentrations. In these areas, low concentrations of Na are likely related to relatively high rainfall and limited water-rock interaction such that inputs are likely dominated by rainfall.

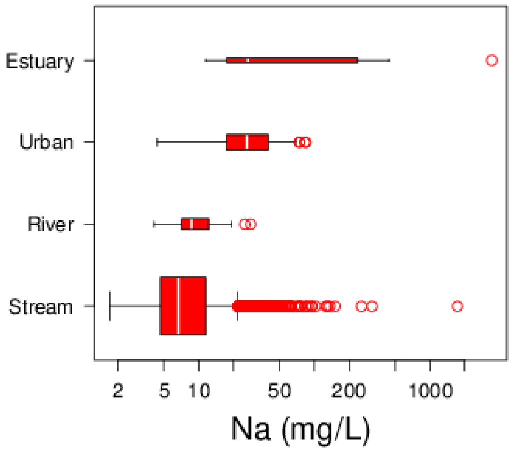
The highest concentrations of stream-water Na are found in the lowland and urban areas in the central part of the catchment (>43 mg/L). Much of this area is underlain by till and river terrace gravels above the Carboniferous Coal Measure and Clackmannan-Strathclyde group lithologies. Land-use in this area is generally built environment, including industry, and wooded and farmed land. The Na may be derived from groundwater baseflow from Carboniferous sediments, which contains relatively high Na concentrations, as well as from pollutant sources. Comparatively low Na concentrations (<7 mg/L) are typical over the Clyde Plateau Volcanic Formation, where the low Na concentrations reflect the low SEC waters, typical of upland areas.

A band of moderately high stream-water Na concentrations coincides with an exposed section of the A74(M) where it emerges from the Clyde valley, north of Abington. This may be caused by the application of road salt for de-icing. Very high concentrations of Na are also found 4 km south of Larkhall: within an area of 10 km^2 there are four former open-cast coal workings, 20 former collieries and a landfill site. Streams with very high Na concentrations occur also around the East Kilbride urban centre and open-cast site, and 4 km south of Erskine around the Linwood Moss landfill. Concentrations are also locally very high around Hamilton. The highest concentrations of stream-water Na in the Clyde catchment are found 4 km north-west of Airdrie, around the Greengairs opencast and landfill site.

River and estuary compositions

Sodium concentration in the river water has a strong correlation with that in stream water and with geology. Concentration increases downstream, with a marked increase in rivers draining the Coal Measures. The Na concentrations in the river waters decrease once they receive inputs from streams over the Clackmannan and Strathclyde groups. Concentrations are highest in the Clyde estuary in response to mixing with estuarine water.

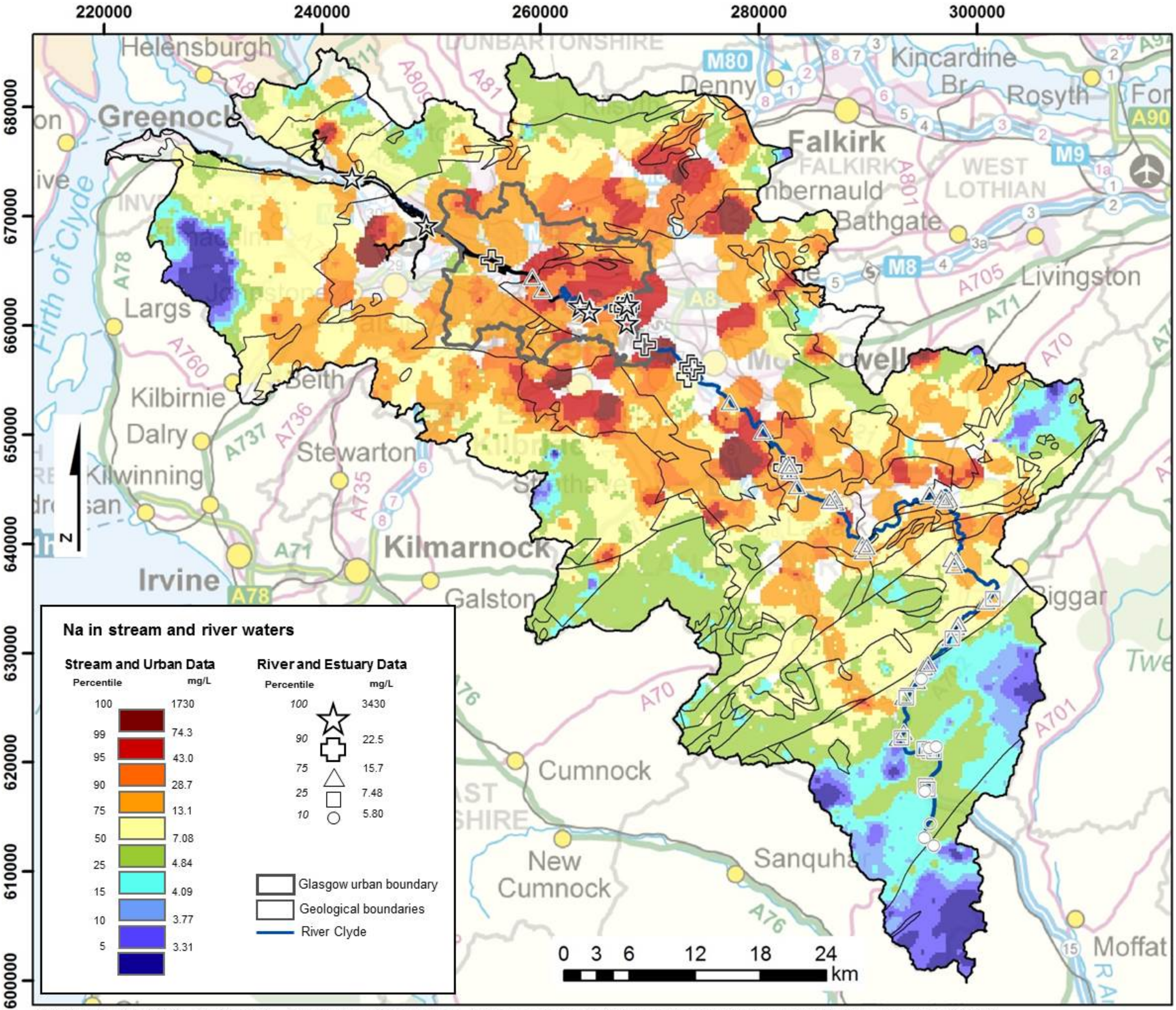
	Stream	River	Urban	Estuary
			(mg/L)	
min	1.71	4.12	4.38	11.5
25th %	4.68	7.2	17.5	19.4
50th %	6.68	8.69	26.1	26.6
75th %	11.5	12.2	39.8	132
90th %	23.9	17.1	61.2	1340
max	1730	28.1	84.7	3430
n	1702	60	122	8
n cens	0	0	0	0
rainwater	2.83			
seawater	10500			



Show location map

Sodium

Na



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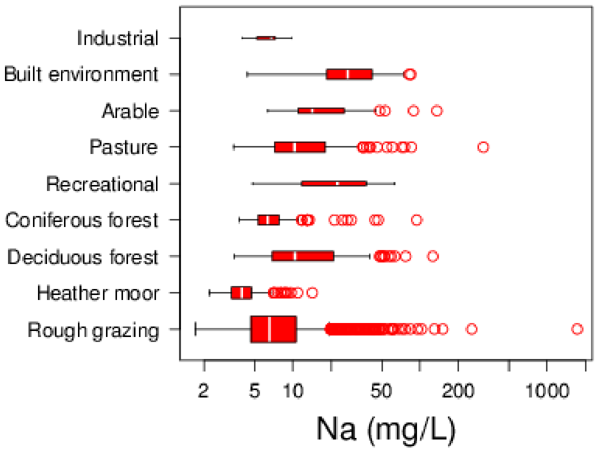
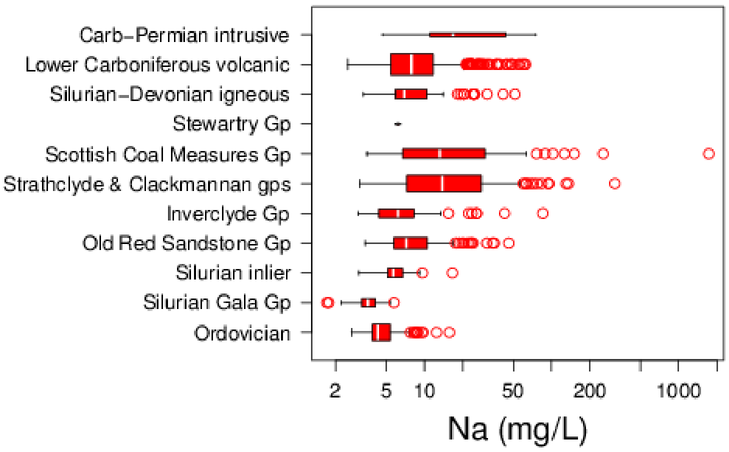




Potassium K

Potassium occurs as K^+ in water though rarely at high concentrations, usually much lower than those observed for Ca or Na. It derives naturally from dissolution of alkali feldspars, micas and clays, and from rainfall. Fertilisers can be important anthropogenic sources of K. The element reincorporates readily into clay minerals and this restricts mobility. Plant uptake is also a major control on mobility.

Stream and urban compositions

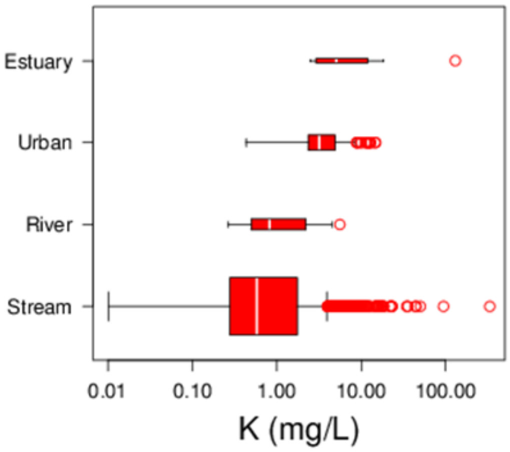
In the Clyde catchment, there is a clear spatial trend of K concentration in stream-water, which is very similar to that of SEC and the other major ions. Low K concentrations (<0.7 mg/L) are found south of the Southern Upland Fault and around the western and northern catchment boundaries. These mainly correspond with areas underlain by the Ordovician-Silurian Gala Group and Leadhills Supergroup as well as the Carboniferous Clyde Plateau Volcanic Formation. The lowest concentrations of stream-water K are found in Muirshiel Country Park, the Kilpatrick Hills, Campsie Fells, within the Avon Water catchment, around the headwaters of Duneaton water and Douglas Water, as well as Leadhills and the Lowther Hills. These areas of low K concentration generally coincide with the heather moorland and coniferous forest land-use types which are typically developed in peaty soils.

High concentrations of K (>2 mg/L) are found within the lowland and urban streams of the Clyde Basin. These correspond with areas of till and terrace deposits overlying Carboniferous Clackmannan-Strathclyde groups and the Coal Measures. Concentrations are also high in streams above the dolomitic and gypsiferous Inverclyde Group Ballagan Formation to the north of the estuary. Groundwater baseflow from these lithologies is a likely contributor to the high K concentrations. Arable farming, pasture, deciduous forest and the built environment are the most common land-use types in these areas and these, along with recreational land-use, have the highest median values of stream-water K. Application of K-bearing fertilisers could account for some contribution of the K in the lower parts of the catchment, although as a diffuse source, this cannot be ascertained directly from the spatial distributions. The highest stream-water K concentrations are found around the Linwood Moss landfill which is 4 km south of Erskine, the Greengairs landfill site 4 km north-west of Airdrie, and around 6 km north-west of Airdrie where there are former underground coal workings with tips. In areas of mine waste, enhanced reaction of clay minerals induced by mine drainage may be a source of the high K values.

River and estuary compositions

The concentrations of K within the Clyde water and its tributaries increase downstream. Within the estuary, K concentration is much higher than at all other sampled sites, as a result of saline mixing.

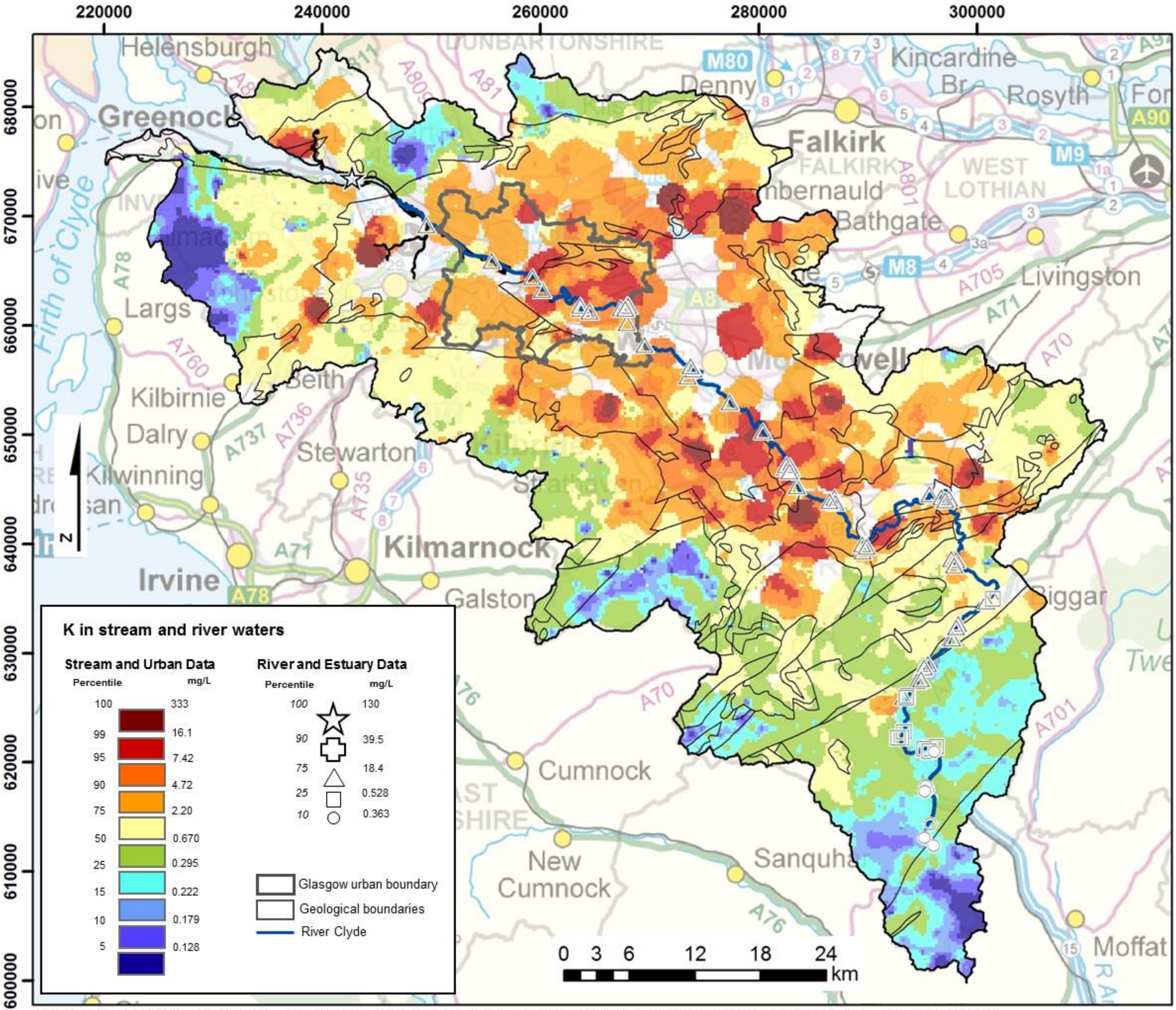
	Stream	River	Urban	Estuary
		(mg/L)		
min	<0.1	0.267	0.432	2.5
25th %	0.28	0.507	2.38	3.1
50th %	0.582	0.826	3.18	5.1
75th %	1.75	2.22	4.87	8.8
90th %	4.31	3.24	9.05	51.9
max	333	5.59	14.9	130
n	1702	60	122	8
n cens	64	0	0	0
rainwater	0.11			
seawater	390			



Show location map

Potassium

K



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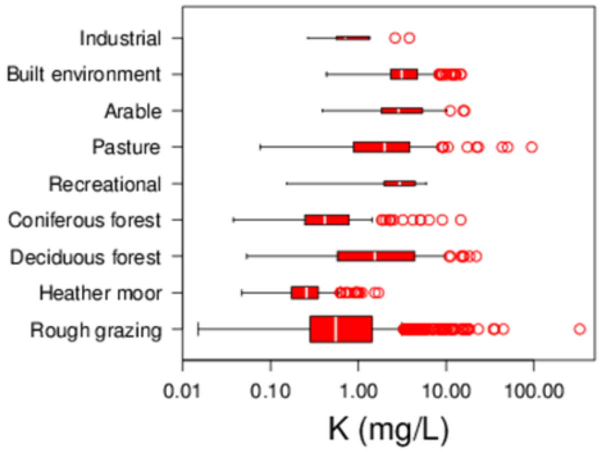
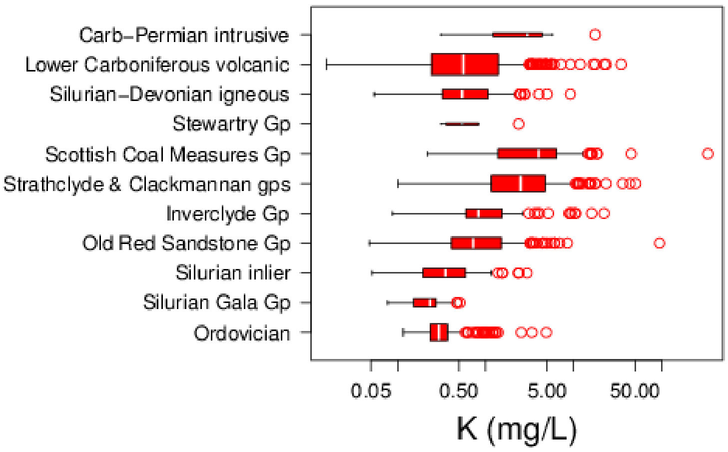




Alkalinity HCO_3

Alkalinity, or the capacity of a solution to neutralise acid, is dominated in natural waters by bicarbonate (HCO_3) and in alkaline solutions (pH>8.3) by carbonate (CO_3). These are derived from CO_2 in the atmosphere and soil, and reaction of carbonate and silicate minerals (Hem, 2005).

Stream and urban compositions

As HCO_3 is the dominant contributor to alkalinity at near-neutral pH, its distribution in the Clyde Basin is very similar to that of Ca and SEC. Low stream-water HCO_3 concentrations (<70 mg/L) are found south of the Southern Upland Fault and along the western and northern catchment boundaries. These areas are underlain by the Ordovician-Silurian Gala Group, Leadhills Supergroup and Midland Valley Silurian inliers and by the Carboniferous Clyde Plateau Volcanic Formation. These geological classes have the lowest median stream-water HCO_3 values. Lowest concentrations are found around Muirshiel Country Park, within the Avon Water catchment, within the upper Calder Water catchment, the Lowther Hills and Tinto Hill.

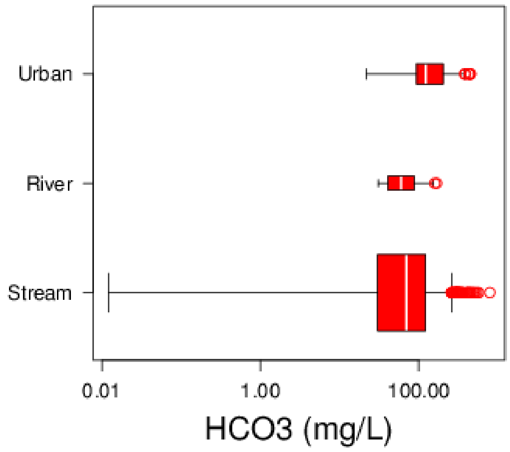
Lowest stream-water HCO_3 concentrations (<11 mg/L) occur in peaty areas, which have correspondingly high concentrations of dissolved organic carbon (DOC), and which commonly support heather moorland. As such, this land-use class has the lowest median stream-water HCO_3 concentration. Relatively high rainfall, and limited concentrations of reactive carbonate minerals in the rock types of these areas, lead to relatively low alkalinity values.

Higher stream-water HCO_3 concentrations (>130 mg/L) are found in the lowland areas of the Clyde Basin and within the urban areas. These correspond to areas of till and terrace deposits overlying Carboniferous Clackmannan-Strathclyde groups and Coal Measures. These formations display the highest median stream water HCO_3 values. Groundwater base flow likely contributes substantially to the increased concentrations in these areas, reactions with carbonate and silicate minerals and with organic matter in sediments and soils being responsible. Highest HCO_3 values are found downstream of the Dykehead open-cast site 10 km east of Motherwell; near the Ravenscraig former steel works in east Motherwell; around the Greengairs landfill site 4 km north-west of Airdrie, and Linwood Moss landfill site 4 km south of Erskine. Numerous locations within the urban area of Glasgow also have relatively high stream-water HCO_3 concentrations. In these areas, neutralisation of mine drainage derived from the Carboniferous coal-bearing sediments is likely responsible for the increased concentrations.

River compositions

Concentrations of HCO_3 in the River Clyde generally increase downstream. Inputs from the Douglas Water, Medwin Water and Mouse Water are high due to the rock types drained in these sub-catchments. Concentration within the Clyde does not increase to a similar order until the section where it drains the Coal Measures. Highest concentrations are found within the tributaries rather than the Clyde, as it contains a large volume of low-alkalinity water from the upper catchment.

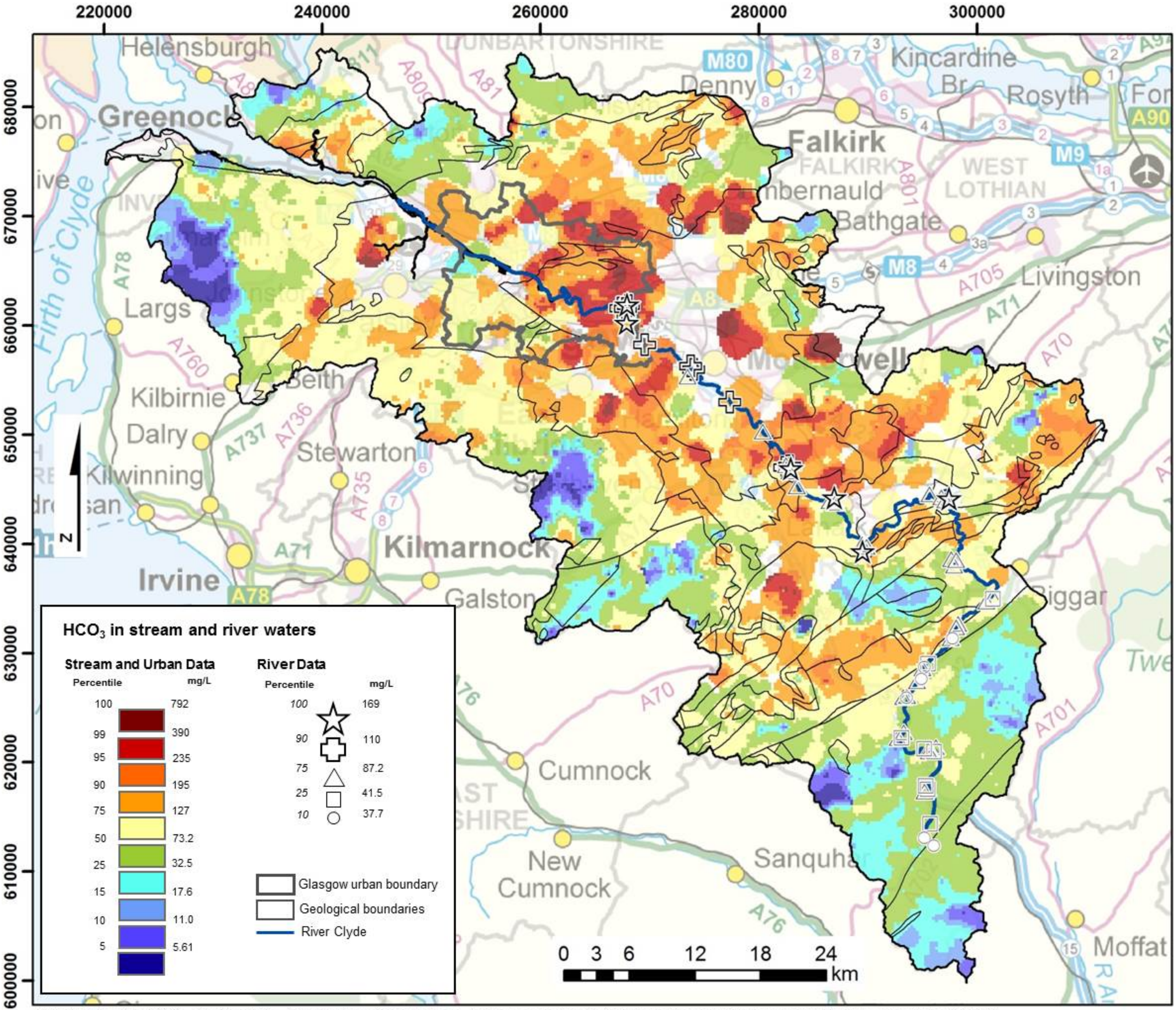
	Stream	River	Urban (mg/L)	Estuary
min	0.0122	30.8	<1	No data
25th %	30.2	41.5	93.9	
50th %	69.5	60.4	123	
75th %	122	87.2	205	
90th %	183	110	308	
max	792	169	451	
n	1702	60	121	
n cens	0	0	1	
rainwater	<1			
seawater	142			



Show location map

Alkalinity

HCO_3



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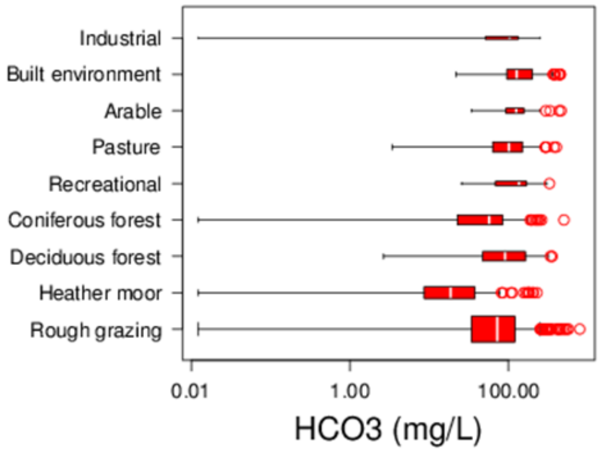
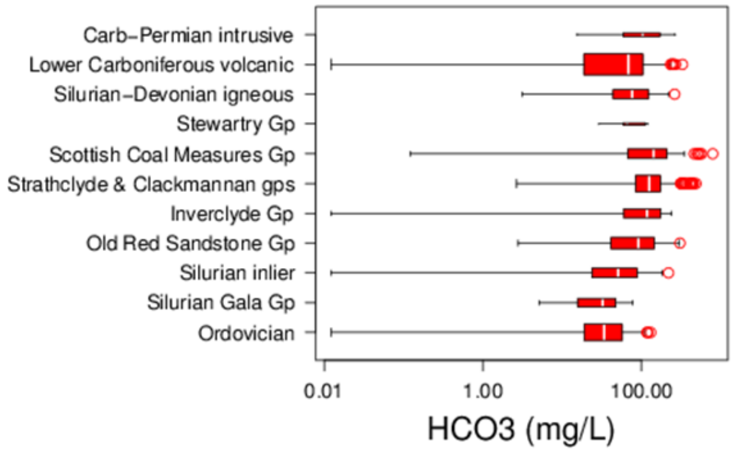




Chloride Cl

Chloride occurs in stream water as the free Cl^- ion (Hem, 2005). The major natural sources of Cl are rainwater, particularly in maritime regions, mixing with seawater in tidal zones and estuaries, inputs from groundwater and, where present, dissolution of evaporite minerals. Minor additional sources potentially include micas and amphiboles. Chloride is also distributed in the environment by human interactions such as use of road salt and fertilisers and from industrial and domestic pollution (Hem, 2005; Shand et al., 2007).

Stream and urban compositions

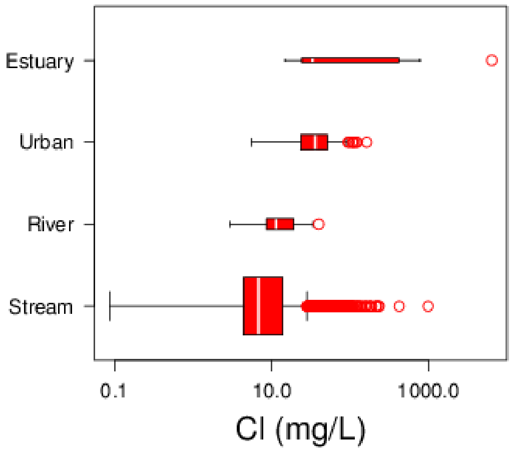
A clear spatial trend of Cl in stream water is apparent in the Clyde Basin, with strong land-use and potentially geological controls. The lowest concentrations of Cl (<7 mg/L) are found south of the Southern Upland Fault and within the upland areas on the periphery of the catchment. Of the geological categories, the Gala Group and Leadhills Supergroup, south of the Southern Upland Fault, have the lowest median stream-water Cl values. The land-use of the areas with low Cl concentrations is dominated by rough grazing and heather moor. Muirshiel Country Park, the Campsie Fells and the Lowther Hills are undeveloped upland areas, partially peaty, with notably low stream-water Cl concentrations. In these areas, Cl is likely to be dominantly of rainfall origin, with little or no additional influence from soil-mineral reactions or pollutant inputs.

Highest stream-water Cl concentrations (>18 mg/L) are found in the lowland and urban areas in the central part of the catchment. Much of this area is underlain by till and terrace deposits above Coal Measures and Clackmannan-Strathclyde group rocks. Natural inputs of baseflow from these units probably contribute to the high concentrations. The land-use in this region mainly comprises built environment, industry, woodland, and farmland. Chloride may derive from pollutant inputs as well as inputs from baseflow. A band of moderately high stream-water Cl concentrations coincides with an exposed section of the A74(M), where it emerges from the Clyde valley, north of Abington. A corresponding zone of high Na concentrations suggests that this may be influenced by the application of road salt. Very high concentrations (>60 mg/L) of stream-water Cl are found 4 km south of Larkhall: within an area of 10 km^2 there are four former open-cast coal workings, 20 former collieries, and a landfill. High Cl concentrations are also seen in streams around East Kilbride town and open-cast site, and 4 km south of Erskine, around the Linwood Moss landfill. Concentrations are also locally high around Hamilton. The highest concentrations (>122 mg/L) of stream-water Cl are found 4 km north-west of Airdrie, around the Greengairs former open-cast and landfill.

River and estuary compositions

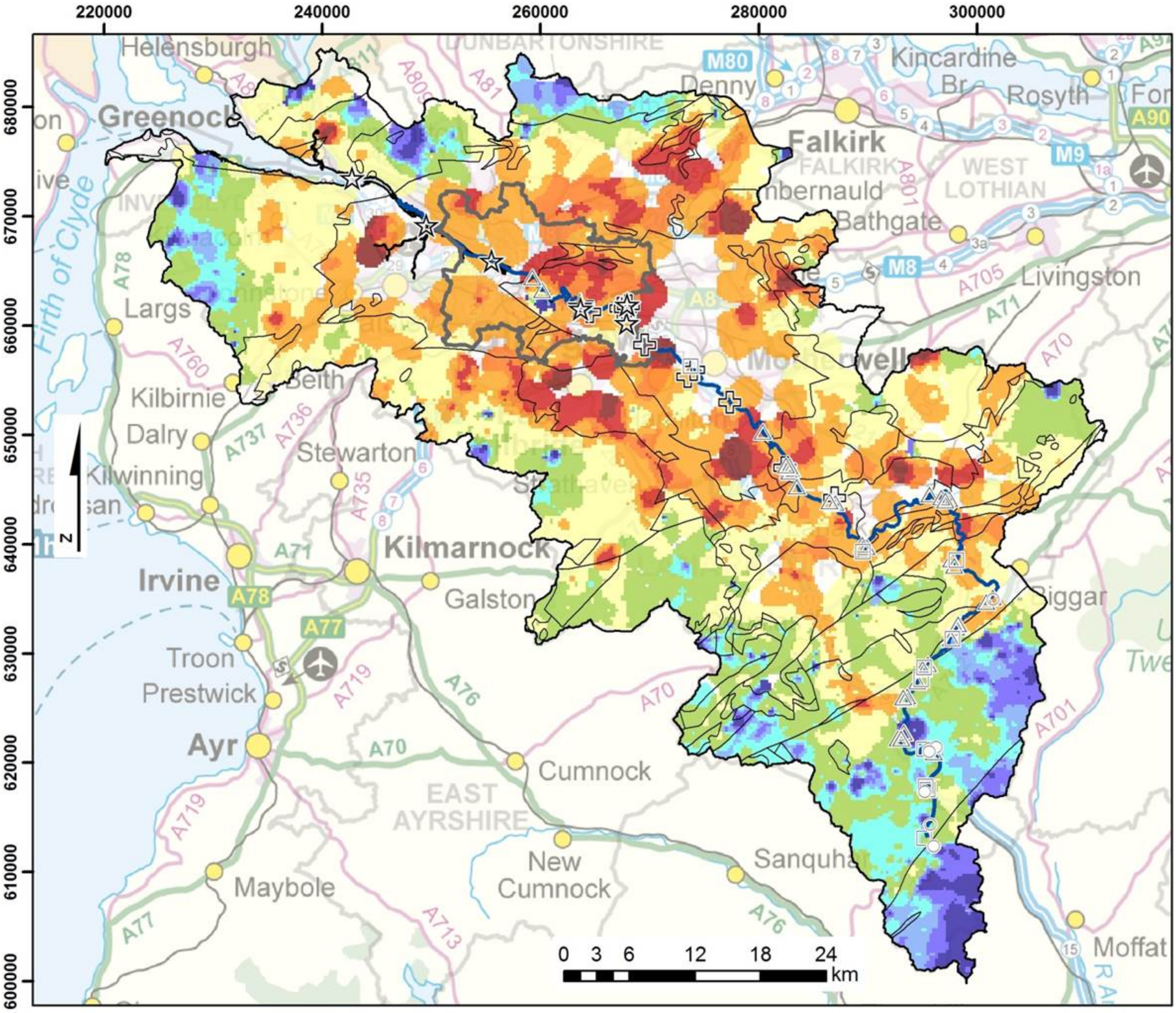
Chloride in the river waters correlates strongly with Cl in contributing streams, and with geology and land-use. Concentrations increase downstream, in particular over the Coal Measures. River Clyde concentrations decrease once they receive inputs from streams draining the Clackmannan-Strathclyde group lithologies. Values are highest in the estuary, where mixed with saline water.

	Stream	River	Urban	Estuary
			(mg/L)	
min	<0.05	2.94	<0.05	14.9
25th %	4.38	8.59	23.8	27.9
50th %	6.77	11.3	36	33.1
75th %	13.9	19	51.2	242
90th %	37.9	24.1	74	2460
max	988	39.9	163	6400
n	1702	60	122	8
n cens	1	0	1	0
rainwater	4.0			
seawater	19000			



Show location map

Chloride Cl


220000
240000
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680000
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Helensburgh
Greenock
Largs
Kilbirnie
Dalry
Kilwinning
Irvine
Troon
Prestwick
Ayr
Maybole
Stewarton
Kilmarnock
Galston
Cumnock
New Cumnock
Sanquhar
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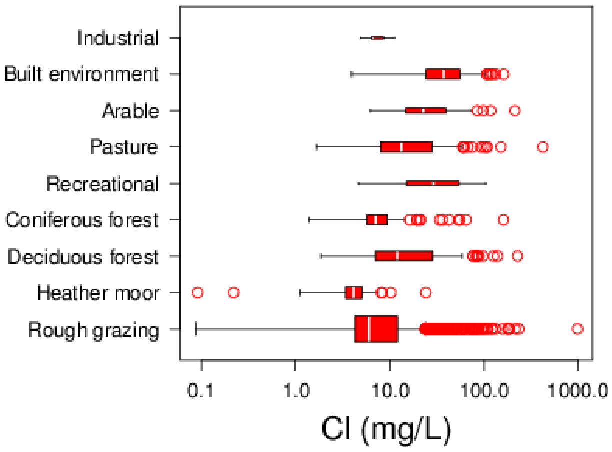
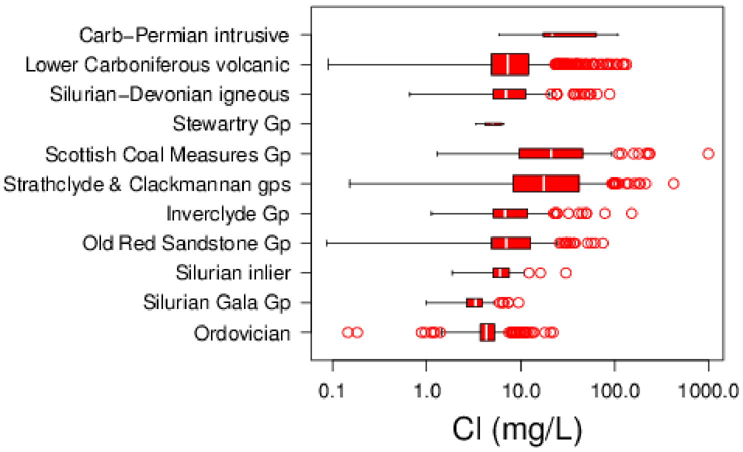
Falkirk
Kincardine
Rosyth
Denny
Bathgate
Livingston
Biggar
Moffat
Firth of Clyde


Industrial
Built environment
Arable
Pasture
Recreational
Coniferous forest
Deciduous forest
Heather moor
Rough grazing
0.1
1.0
10.0
100.0
1000.0
Cl (mg/L)


Carb-Permian intrusive
Lower Carboniferous volcanic
Silurian-Devonian igneous
Stewartry Gp
Scottish Coal Measures Gp
Strathclyde & Clackmannan gps
Inverclyde Gp
Old Red Sandstone Gp
Silurian inlier
Silurian Gala Gp
Ordovician
0.1
1.0
10.0
100.0
1000.0
Cl (mg/L)

Sulphate SO_4

In natural stream waters, dissolved sulphur (S) usually exists as the sulphate (SO_4^{2-}) anion (Hem, 2005). The main sources of sulphate in stream waters include rainfall, particularly in maritime settings. Inputs due to release of SO_2 gases have reduced significantly in recent decades as a result of emissions reductions. Sulphate in stream waters is also derived by release from S-bearing minerals such as gypsum and anhydrite or sulphide minerals or by degradation of organic matter. Sulphate may also be derived from pollutant sources, including industrial effluents, fertilisers or water treatment. It is also concentrated in seawater so increases can be expected in streams affected by estuarine mixing (Hem, 2005; Shand et al., 2007).

Stream and urban compositions

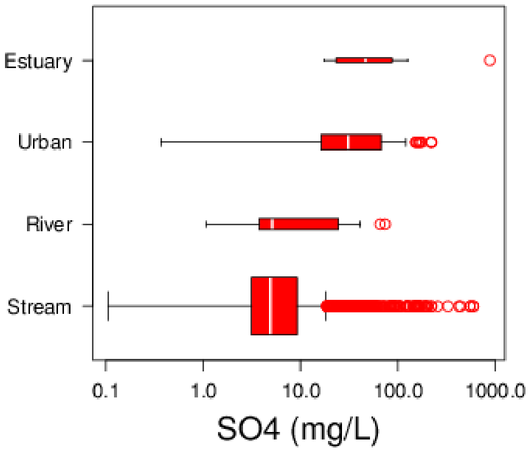
Strong geological and land-use controls on Clyde Basin stream-water SO_4 distribution are apparent. Lowest SO_4 concentrations (<6 mg/L) are found south of the Southern Upland Fault and along the western and northern catchment boundaries. These areas are underlain by the Ordovician-Silurian Gala Group and Leadhills Supergroup and by the Carboniferous Clyde Plateau Volcanic Formation. Streams over peaty upland areas, which commonly support heather moorland, coniferous forest or rough grazing, have some of the lowest SO_4 concentrations. Relatively high rainfall, lack of pollutants and limited water-rock reactions are believed responsible for the low values. Such low SO_4 concentrations are observed particularly in the areas of Muirshiel Country Park, the Lowther Hills north of Leadhills and in the Avon Water catchment.

Higher concentrations of stream-water SO_4 (>6 mg/L) are found in the lowlands of the Clyde Basin and within the urban areas. These correspond with occurrences of till and river terrace deposits above the Carboniferous Clackmannan-Strathclyde groups and the Coal Measures. High concentrations also characterise streams draining the Ballagan Formation (Inverclyde Group) to the north of the estuary. These are gypsiferous deposits, explaining the high stream-water SO_4 concentrations. Sulphate sources across the Basin are a combination of geological and land-use influences. Increased concentrations relate to groundwater baseflow from the Carboniferous formations, as well as point-source inputs from coal workings and landfills. Very high concentrations of SO_4 are found around the Glespin open-cast site (6 km south-west of Douglas); downstream of the Coalburn open-cast site; and within an area 6 km north-west of Airdrie where there are former coal workings and a landfilled fire clay pit. In areas impacted by open-cast and waste sites, oxidation of sulphide minerals is probably the dominant SO_4 source.

River and estuary compositions

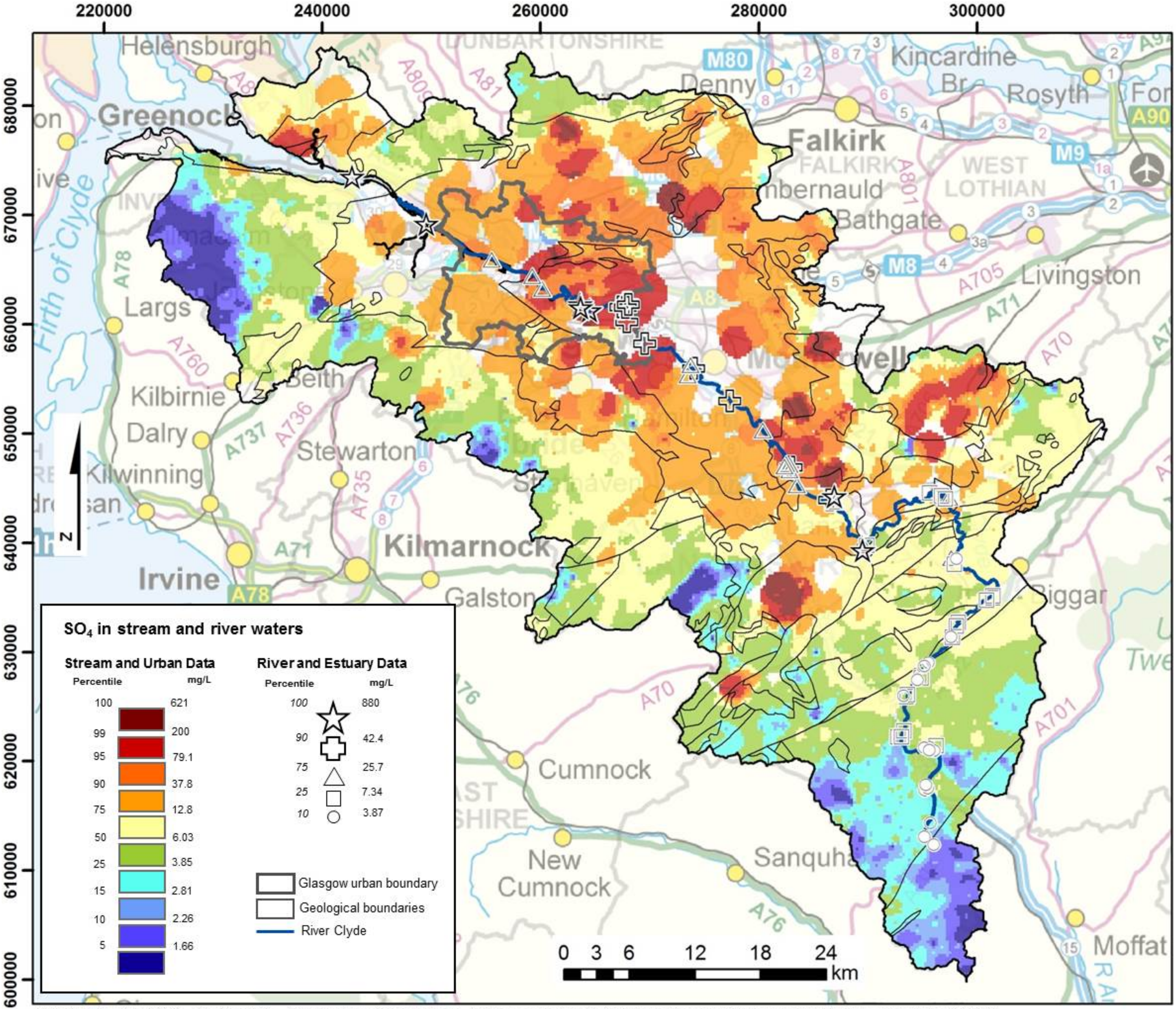
Concentrations of SO_4 in the River Clyde waters generally increase downstream. Tributaries often have higher concentrations than the Clyde, where they are influenced by open-cast coal mining and landfill sites. For example, Douglas Water contains high SO_4 concentrations as it drains the coal-mining area around Douglas. Highest concentrations of SO_4 in the River Clyde are reported in the estuary, in line with estuarine mixing.

	Stream	River	Urban (mg/L)	Estuary
min	<0.1	1.08	0.367	17.6
25th %	3.14	3.75	16.4	24.2
50th %	4.91	5.13	30.8	46.4
75th %	9.24	24.6	66.8	67.4
90th %	24.7	31.2	115	352
max	596	74	222	880
n	1702	60	122	8
n cens	3	0	0	0
rainwater	1.43			
seawater	2700			



Show location map

Sulphate SO_4



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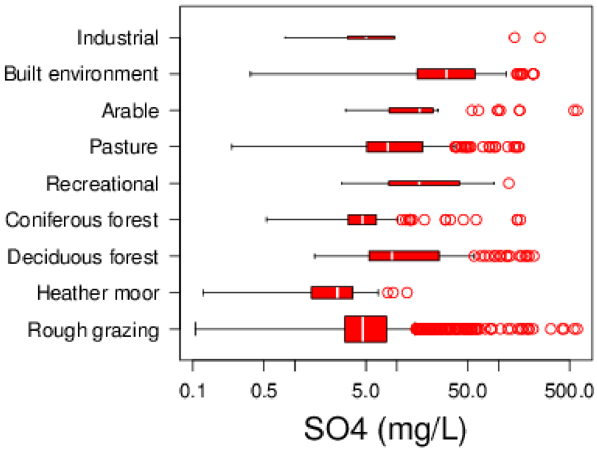
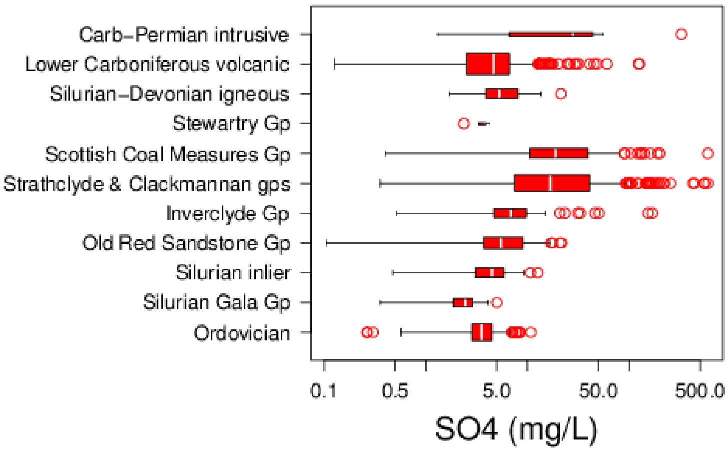




Nitrate NO_3

Nitrate is the dominant form of nitrogen (N) in oxidised stream waters. Nitrogen speciation is controlled by temperature, pH and oxygen availability, as well as by biological cycles (Hem, 2005). Nitrate is not adsorbed to soil and so that present in excess of plant requirements is easily transferred to stream water. The major natural sources of N are soil- and sediment-derived organic matter and rainfall. Pollutant sources include nitrogenous fertilisers, sewage, manure, combustion of fossil fuels from power stations and vehicle emissions (Hem, 2005; Shand et al., 2007).

Streams and urban compositions

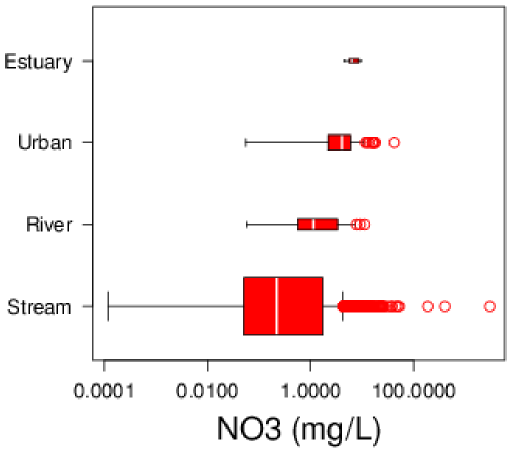
Stream-water NO_3 distribution in the Clyde Basin shows a strong link to land-use, suggesting that the dominant source is anthropogenic. Low concentrations of NO_3 (<0.2 mg/L) are found south of the Southern Upland Fault and along the rural catchment boundaries. Other than the area south of the Southern Upland Fault there is little geological correlation and the NO_3 shows a closer relationship with land-use. Lowest concentrations are found in streams from Muirshiel Country Park, in the Avon Water catchment, and around the upper catchments of Duneaton Water and Douglas Water. In these areas, anthropogenic influences are less significant, and NO_3 is below detection limit. Low-NO_3 areas are generally upland areas of heather moorland or coniferous forest.

Higher concentrations of NO_3 (> 2 mg/L) are found in the lowland areas of the Clyde Basin and within the urban areas. In the lowlands of the Basin, land-use is commonly arable and pasture farming, which can receive NO_3 inputs from diffuse agricultural pollutants. The higher concentrations within the urban areas are also likely to be caused by anthropogenic inputs including industrial and domestic effluents, vehicle emissions and fossil fuels. Of the land-use types, the built environment, arable and pasture land-use have the highest median NO_3 values. In addition, some very high NO_3 concentrations occur in streams around the Greengairs landfill 4 km north-west of Airdrie, and around the Linwood Moss landfill site 4 km south of Erskine.

River and estuary compositions

Concentrations of NO_3 are very low in the headwaters of the River Clyde and its tributaries. The concentrations only begin to increase significantly once the Clyde enters the low-lying areas of the catchment, which are typified by agricultural land-use. The highest concentration in the Clyde occurs in Lanark, downstream of the majority of agricultural activity. The concentrations in the Clyde decrease slightly downstream of this point before increasing again as the river becomes increasingly affected by urbanisation.

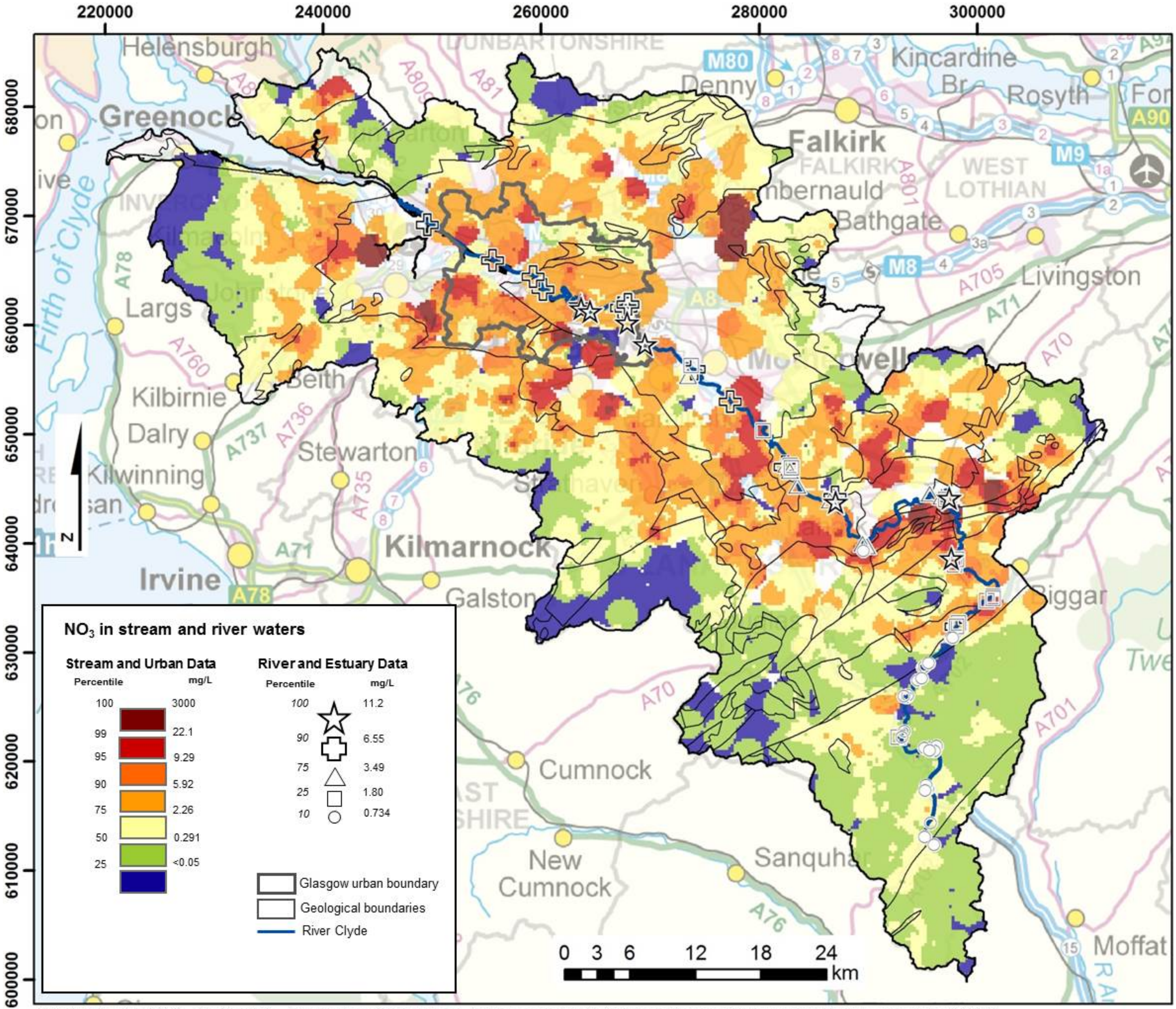
	Stream	River	Urban	Estuary
			(mg/L)	
min	<0.05	<0.05	<0.05	4.49
25th %	0.05	0.565	2.22	5.52
50th %	0.218	1.14	4.1	6.27
75th %	1.74	3.27	5.91	8.7
90th %	5.5	6.35	9.56	9.32
max	3000	11.2	42	9.53
n	1702	60	122	7
n cens	606	1	2	0
rainwater	1.59			
seawater	3.0			



Show location map

Nitrate

NO$_3$



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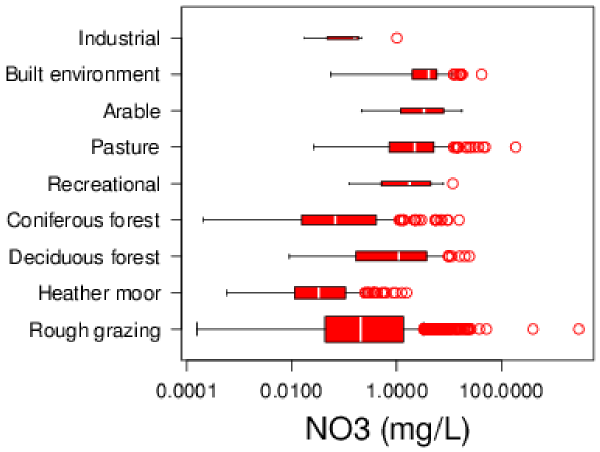
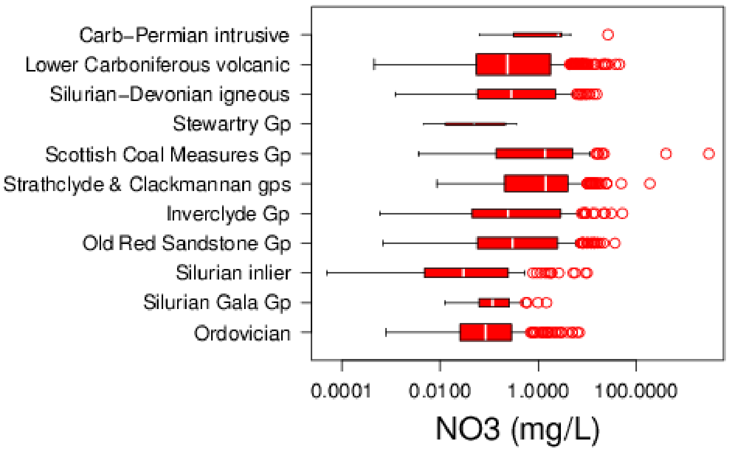




Dissolved organic carbon DOC

Dissolved organic carbon is a general term for the range of organic molecules existing in the aquatic system. Dissolved organic carbon in this study is operationally defined as the organic molecules which pass through the 0.45 µm filter membrane. This may include some colloidal material. The main constituents of DOC are fulvic and humic acids, with minor portions of other organic compounds (Shand et al., 2007). Dissolved organic carbon in surface waters is involved in photochemical reactions. It is also implicated in metal-oxide redox reactions and so can influence the mobility of redox-sensitive elements such as iron or manganese (Drever, 1997). Under stream base-flow conditions, most water in the stream is derived from groundwater and DOC concentrations tend to be low. Concentrations can be much higher when water is entering streams directly via overland flow under storm-flow conditions. Most DOC is derived from decaying vegetation in soils, but stream waters can contain additional DOC derived from pollution sources, such as slurry pits, septic tanks and landfills (Shand et al., 2007).

Stream and urban compositions

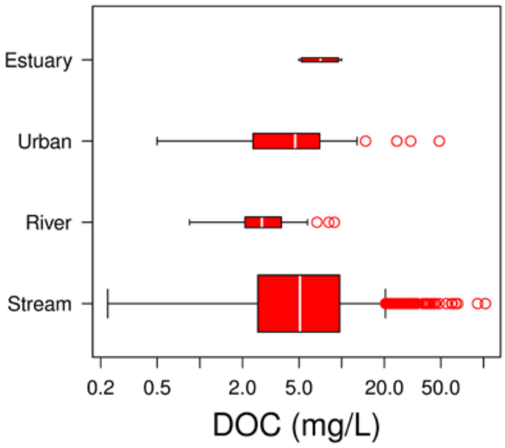
Throughout the Clyde catchment, there is little correlation between DOC in analysed waters and soil depth of organic layer (DOL) or loss on ignition (LOI) (Fordyce et al., 2017). However, there is a strong correlation with mapped peat deposits. Stream water concentrations of DOC are low (< 5 mg/L) to the south of the Southern Uplands Fault, on the south-facing slopes of the Pentland Hills and around the lower-lying northern parts of the catchment. Although an organic-rich soil layer was observed whilst sampling in these areas, they are devoid of mapped peat.

High stream-water concentrations of DOC (> 9 mg/L) are found around the periphery of the central and north-western portions of the catchment. These are all areas with mapped occurrences of peat, which is a rich source of organic matter. The highest DOC concentrations are found 4 km north-west of Airdrie, in streams draining the Greengairs landfill site. These are likely to be influenced by a contribution from organic-rich leachate.

River and estuary compositions

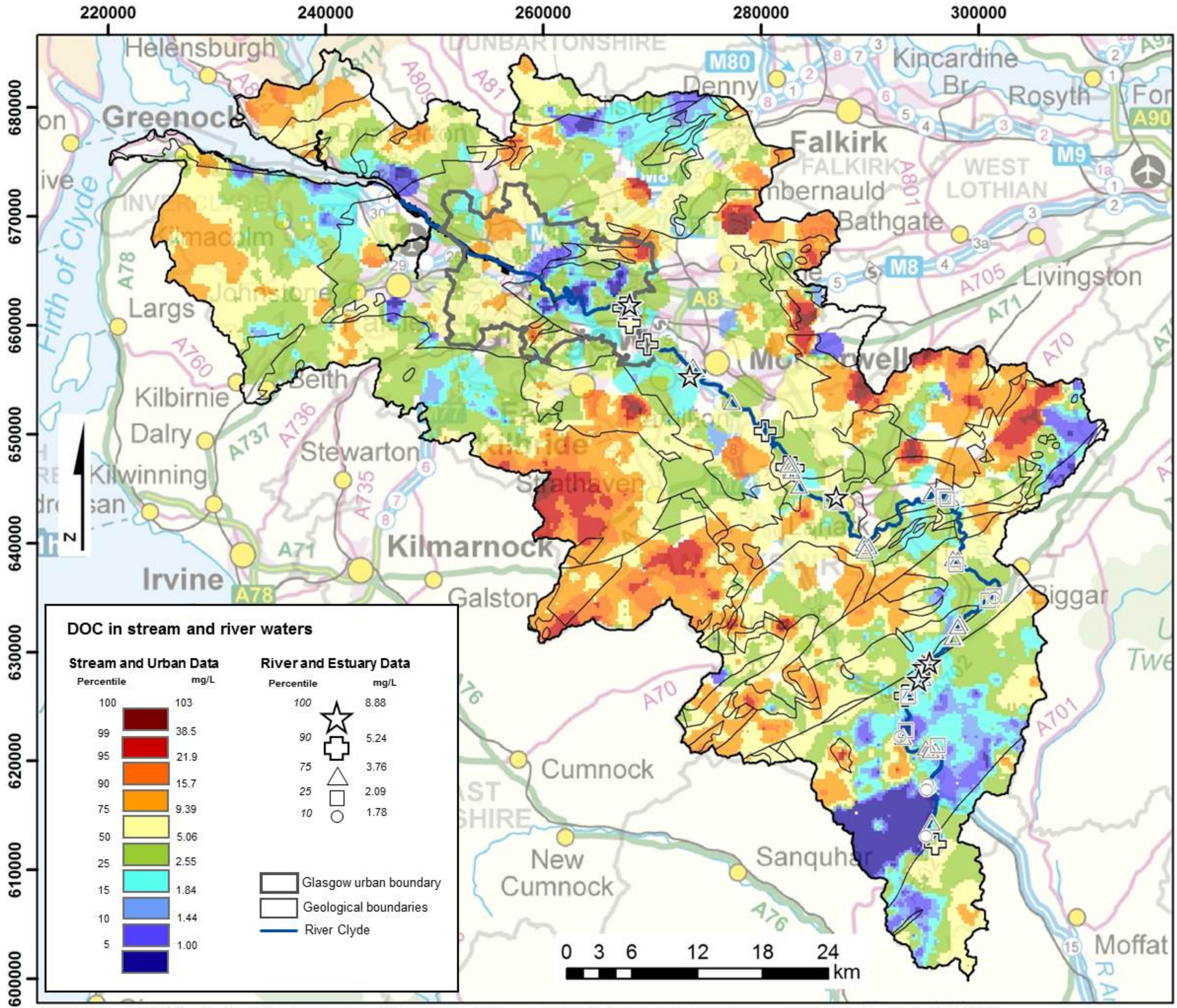
Concentrations of DOC within the River Clyde and its tributaries are highly variable, and do not appear to correlate with location along the river reach. The variability might reflect the variation in BFI across the Basin. The highest concentrations are usually found in tributaries, reflecting more localised inputs from sub-catchments with organic-rich soils. The Clyde DOC values represent a catchment average which includes a large base-flow influence in places.

	Stream	River	Urban	Estuary
		(mg/L)		
min	<0.5	0.845	0.5	4.99
25th %	2.56	2.09	2.41	5.28
50th %	5.08	2.74	4.70	7.09
75th %	9.68	3.76	6.99	9.25
90th %	15.8	5.24	9.67	10.0
max	103	8.88	48.8	10.0
n	1702	60	122	8
n cens	21	0	0	0
rainwater				
seawater	0.1			



Show location map

Dissolved organic carbon DOC



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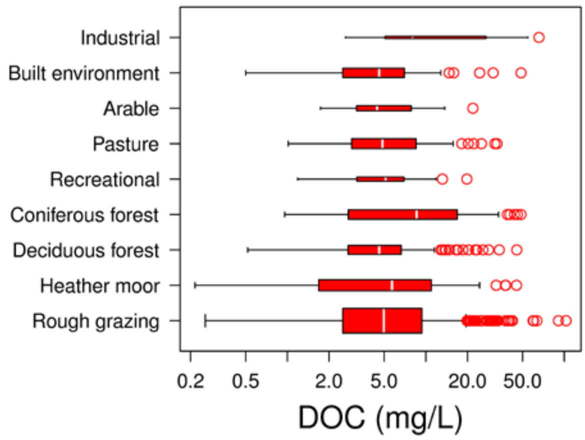
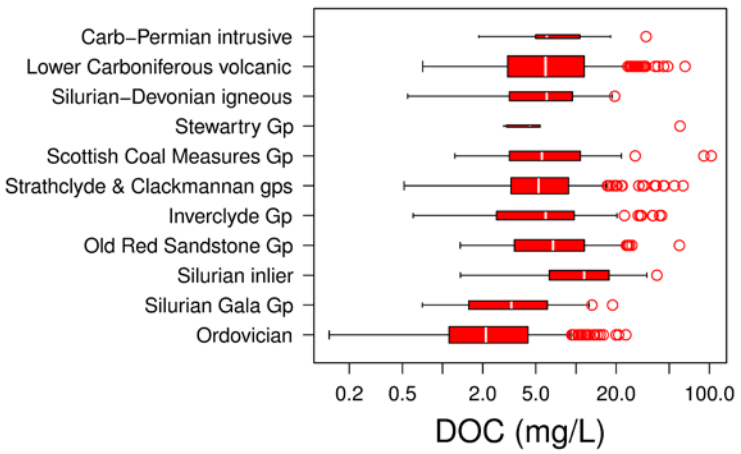




Aluminium Al

Aluminium is the most abundant metal in the lithosphere, but the concentration of dissolved Al in natural waters is generally low because of the low solubility of aluminium minerals under typical pH conditions. The amphoteric nature of Al oxides renders the element more mobile under extremes of pH (<5.5 or >8). The trivalent Al^{3+} ion also forms strong complexes with both inorganic and organic ligands, increasing the activities in solution where these ligands occur in high concentrations (Hem, 2005).

Streams and urban compositions

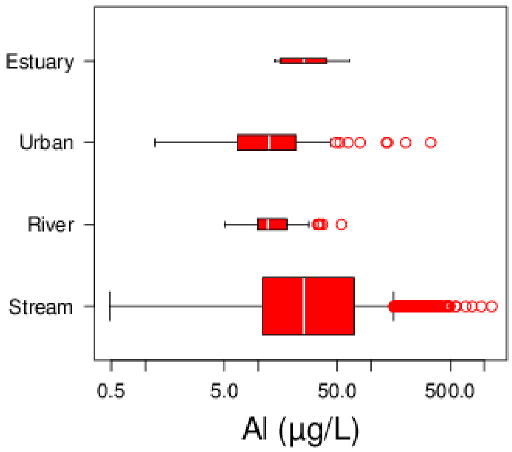
Low concentrations of Al (<20 µg/L) are found within the lowland areas within the central Clyde Basin, throughout the urban areas and extending towards the Kilsyth Hills. These areas generally correspond to the till overlying the Carboniferous Clackmannan-Strathclyde groups and the Coal Measures, which display the lowest median stream-water Al concentrations of the rock types present in the area. Low concentrations are found also on the south-facing slopes of the Pentland Hills, and on the Lowther Hills. The pH of streams in these areas is generally around 7.5 to 8.2.

Areas with higher concentrations of Al (>60 µg/L) are found within the upper reaches of the catchment and along the catchment boundary. These areas correlate well with occurrences of peat and with areas of low stream-water pH. They are usually either areas of heather moorland or coniferous forest. Both these land-use types support formation of acid soil; hence, Al mobility. The largest area of high stream-water Al concentrations is centred over the hills to the west of Tinto Hill. While the recorded land-use of the sample sites includes coniferous forest, deciduous forest and rough grazing, the Ordnance Survey map suggests that in the recent past this entire area was covered by coniferous forest. Coniferous forests scavenge acid species of S and N from the atmosphere, which can lead to soil acidification and could in turn explain the relatively high Al concentrations. Other regions with high concentrations include Muirshiel Country Park, the upper reaches of the Calder water catchment, and the Avon Water catchment. Most of the small areas of high Al concentration are influenced by a single stream within coniferous woodland.

River and estuary compositions

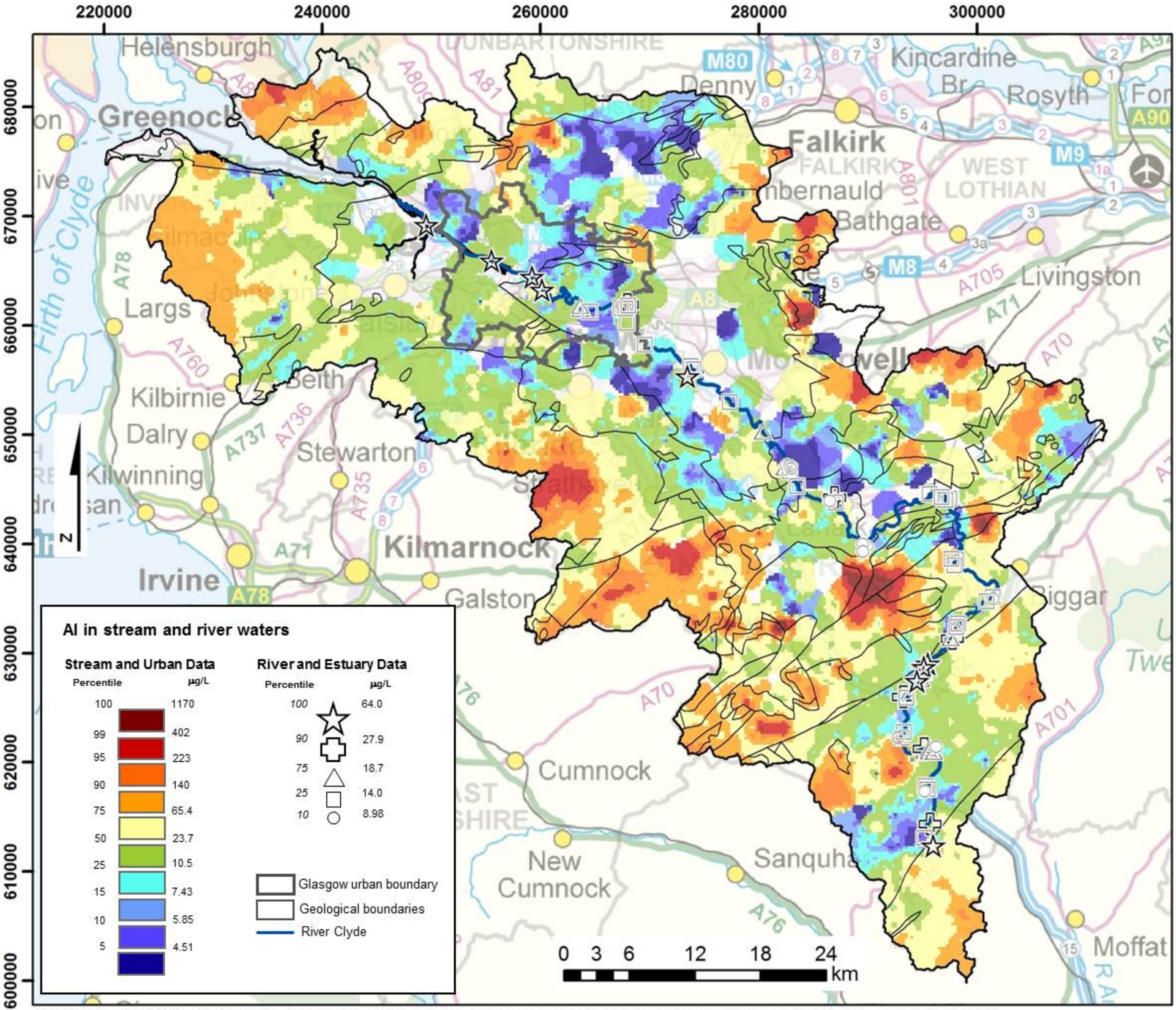
Aluminium concentrations in the River Clyde waters and its tributaries are very variable south of the Southern Upland Fault, reflecting the variability in pH. The concentrations are generally low over the low-lying areas of the catchment, before increasing in the centre of Glasgow and into the estuary.

	Stream	River	Urban (µg/L)	Estuary
min	<1	5.06	1.23	<20
25th %	10.9	9.85	6.56	16.1
50th %	25.3	12.2	12.4	25.7
75th %	70.2	17.6	21.5	38.8
90th %	145	28.4	32.6	50
max	1170	54.6	336	64
n	1702	60	122	8
n cens	4	0	0	1
rainwater	<10			
seawater	1			



Show location map

Aluminium   Al



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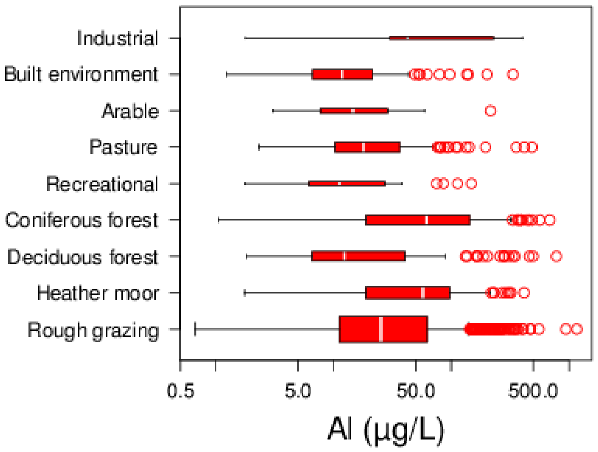
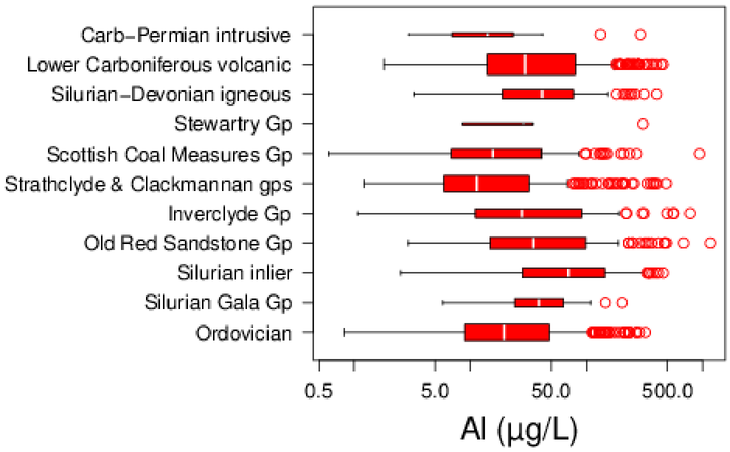




Arsenic As

Arsenic is a metalloid which is toxic to life at trace concentrations in water. It occurs in water predominantly in the inorganic trivalent (arsenite) and pentavalent (arsenate) oxidation states, although in oxic stream waters, the oxidised arsenate form is usually the main form. Organic species may be present in waters affected by industrial pollution or high concentrations of organic matter but are otherwise negligible. Arsenic occurs as a major constituent of a number of metal oxide and sulphide minerals, mostly found in ore deposits. Its mobility in stream waters is strongly controlled by adsorption/desorption reactions involving iron and aluminium oxides. At near-neutral pH in an oxic environment, the strong affinity of these minerals for As sorption renders the element usually immobile, except in proximity to contaminant sources (Hem, 2005).

Streams and urban compositions

In the Clyde Basin, some spatial trend in stream-water As concentration is apparent, with some evidence of associations with bedrock geology and land-use. Concentrations of As are generally low, the lowest (<0.2 µg/L) being found south of the Southern Upland Fault, as well as in the Kilsyth Hills and on the lower slopes of the Kilpatrick Hills. The low concentrations south of the Southern Upland Fault correlate with the outcrop of the Gala Group and the Leadhills Supergroup, which have the lowest median stream-water As values of the geological groups represented in the area. The low values over the Kilsyth and Kilpatrick Hills correlate with occurrences of basaltic volcanic rocks.

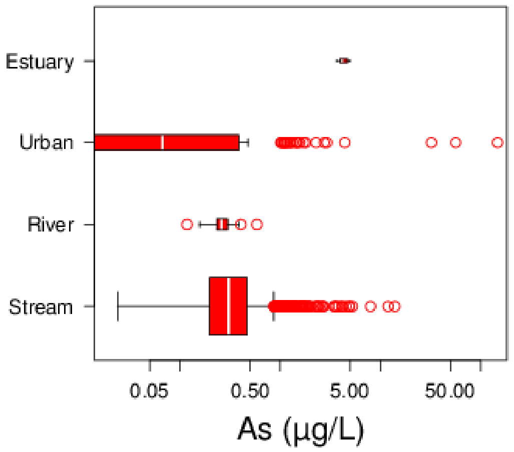
Generally higher concentrations (>0.5 µg/L) are found in the central Basin, including Glasgow city. However, the distribution is uneven and the pattern of high concentrations is patchy. It is likely that the highest concentrations occurring in the city limits are linked to urban and industrial pollution. Other sporadic highs occur; for example, around the Greengairs landfill site 4 km north-west of Airdrie and the Glespin and Forth open-cast coal sites. These likely have been influenced by anthropogenic activities, although this is set in the context of probable naturally high concentrations of As in the argillaceous and coal horizons of the Carboniferous formations in the central part of the Basin.

Two of the most prominent stream-water As anomalies occur along the south-western watershed of the catchment. One in the upper reaches of the Avon Water catchment correlates with the outcrop of the Distinckhorn porphyritic microdiorite pluton. A second occurs downstream of Brocklaw Rig, an outcrop of granodiorite. Arsenic anomalies in these areas may result from weathering of primary minerals and/or hydrothermal mineralisation/alteration associated with these igneous bodies.

River and estuary compositions

Arsenic concentrations in the Clyde waters and its tributaries are very variable over the upper reaches of the Clyde Basin, but are consistent with the distribution in stream waters. Concentrations are consistently high within the urban stretch of the Clyde, reflecting greater inputs of As from the urban tributaries.

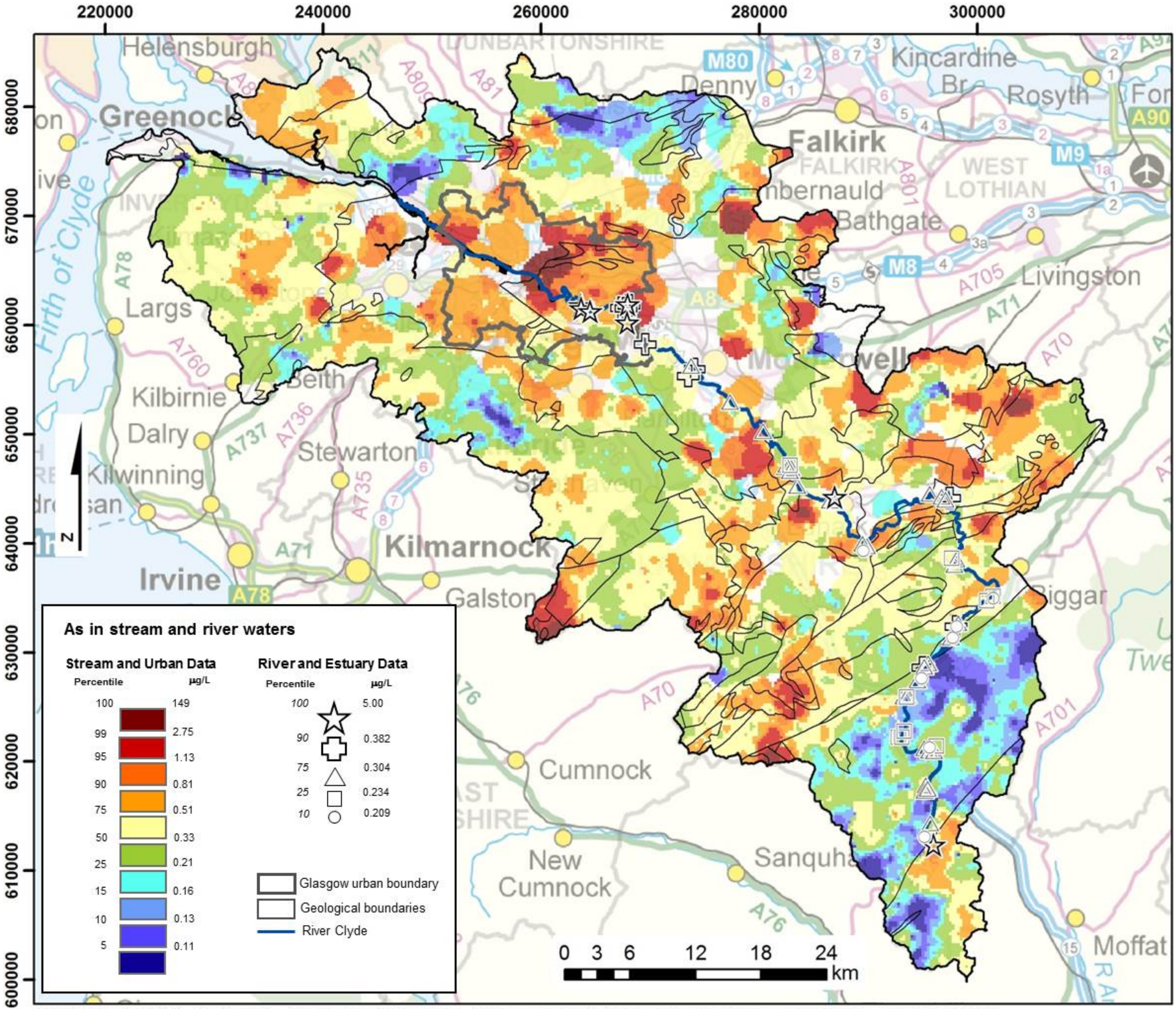
	Stream	River	Urban	Estuary
		(µg/L)		
min	0.024	0.118	<1	<5
25th %	0.198	0.232	0.012	
50th %	0.306	0.261	0.067	
75th %	0.466	0.297	0.382	
90th %	0.735	0.323	1.43	
max	14	0.586	149	5
n	1702	60	122	7
n cens	0	0	95	4
rainwater	0.1			
seawater	1.3			



Show location map

Arsenic

As



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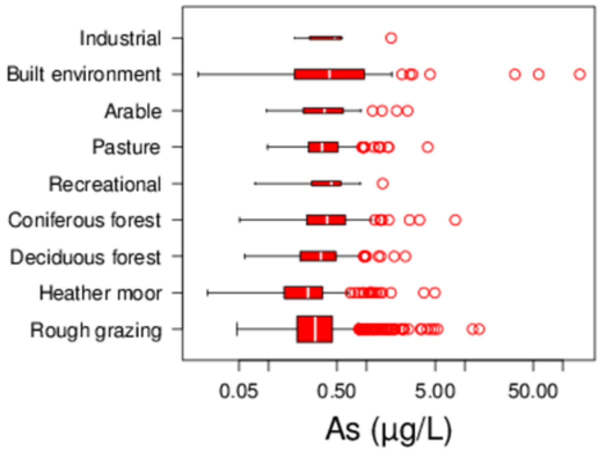
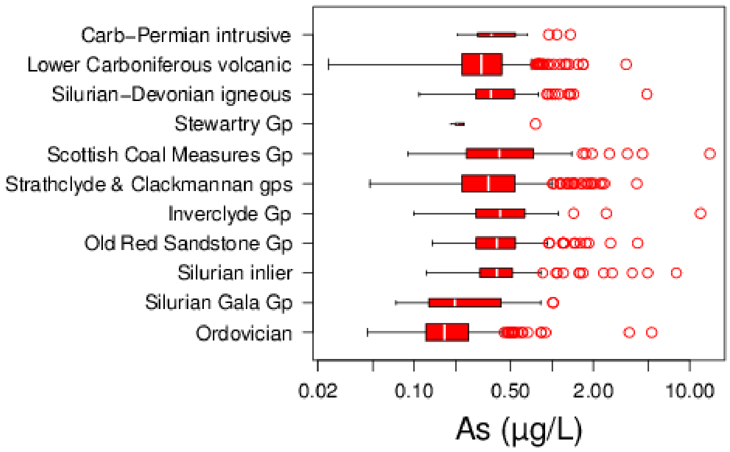




Barium Ba

Barium exists in natural waters as the Ba^{2+} ion. Aqueous pH and Eh conditions do not strongly control Ba mobility. The concentration of Ba in stream waters is mostly controlled by the abundance of Ba in bedrock. However the behaviour of Ba in solution is most likely controlled by the solubility of barite ($BaSO_4$) as the presence of sulphate limits Ba in solution, or by the adsorption to metal oxides and hydroxides (Hem, 2005). As a result stream water concentrations of Ba are typically strongly linked to geology. There are limited anthropogenic sources of Ba. Barite is used as a heavy mud slurry for drilling and within the production of rubber, paper fabrics. Barium compounds are used in the production of glass and enamel. Barium chloride is used as a rat poison and insecticide (BGS, 1999).

Stream and urban compositions

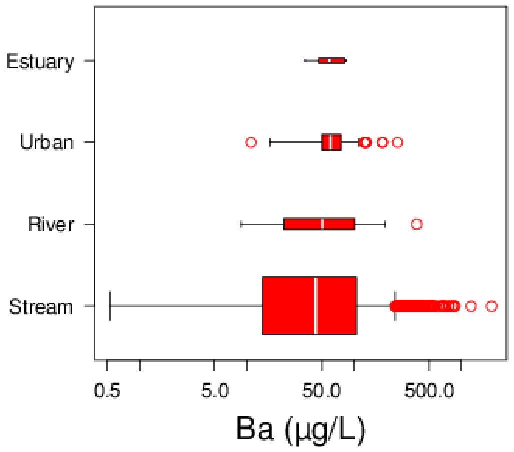
In the Clyde Basin, low concentrations of Ba (<50 µg/L) are found in streams to the south of the Southern Uplands Fault and along the western and northern catchment boundaries. These areas are underlain by Ordovician-Silurian Gala Group and Leadhills Supergroup rocks and by the Carboniferous Clyde Plateau Volcanic Formation. On the upland catchment periphery, lowest stream-water Ba concentrations correlate with occurrences of heather moorland, which is usually found where there are peaty soils. In these areas, low concentrations of Ba are also likely to be related to relatively high rainfall, limited water-rock interaction, and limited impact of anthropogenic activity, such that stream water concentrations are dominated by rainfall. Areas with lowest Ba concentrations include streams flowing via the northern portion of Muirshiel Country Park, the areas within the Lowther Hills, and the Campsie Fells.

Concentrations of stream-water Ba are moderate (~50 – 100 µg/L) around much of the low-lying areas of the catchment, while high Ba concentrations (>100 µg/L) are found in streams in the central area of the catchment. In particular, high Ba concentrations are found in streams draining the area of most complex geology, which is a band of land some 21km wide, north of the Southern Uplands Fault. The Inverclyde Group and Old Red Sandstone Group dominate in this area, and stream-waters over these rock types have the highest median Ba concentrations, which may reflect bedrock composition. The highest Ba stream-water concentrations are found in the area around the Pentland Hills.

River and estuary compositions

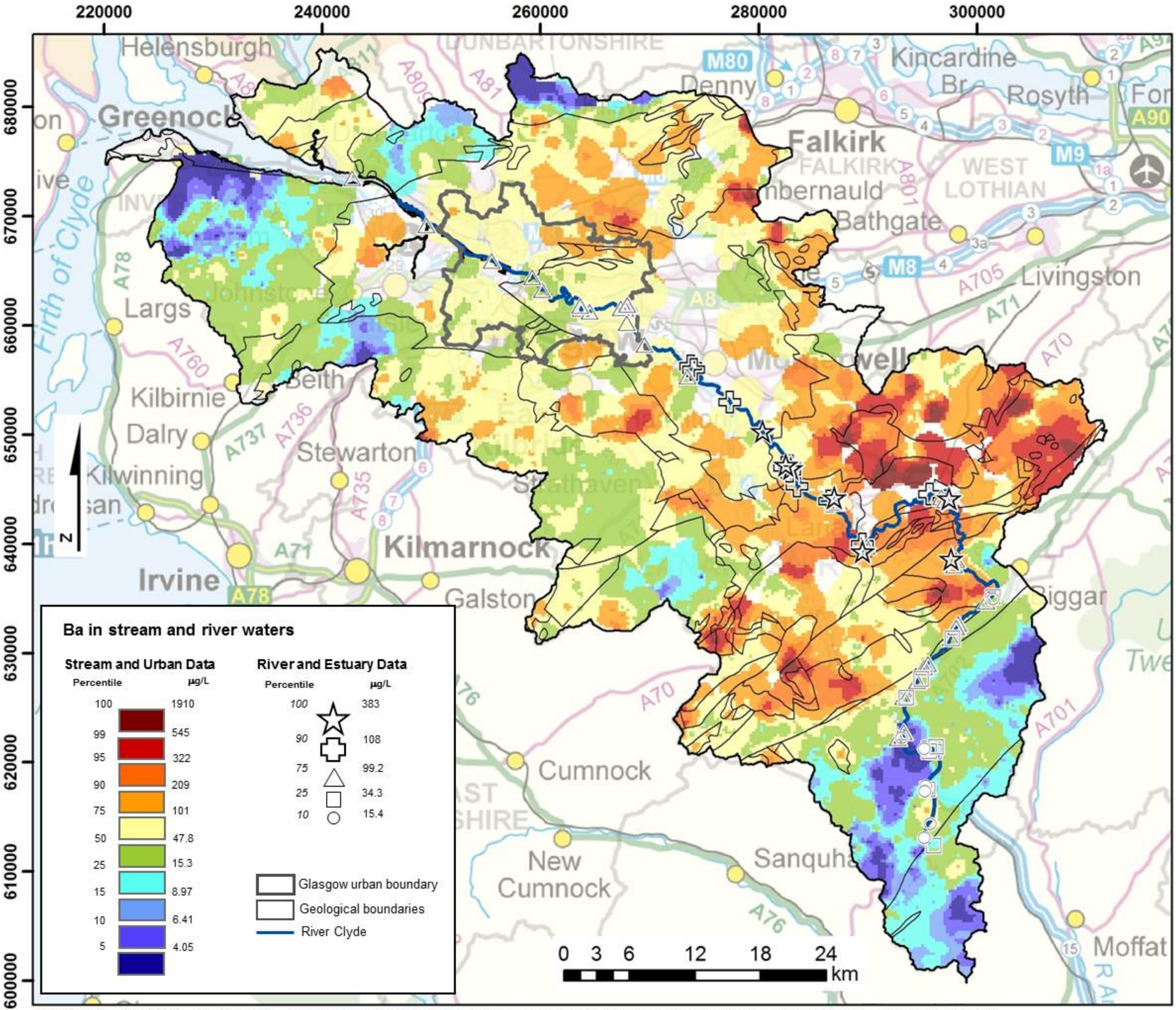
Concentrations of Ba are low in waters of the upper reaches of the River Clyde. Once the Clyde flows north of the Southern Uplands Fault, the concentrations in its main tributaries are high, and consequently, concentrations of Ba within the Clyde increase. Further downstream, as the Clyde drains the Coal Measures, its tributaries contribute less Ba, and as a result of dilution, the concentrations in the Clyde are low as it enters the estuary.

	Stream	River	Urban	Estuary
		(µg/L)		
min	0.531	8.84	10.9	34.8
25th %	14	22.3	50.4	50.7
50th %	43.7	50.5	60.7	58.9
75th %	105	101	75.4	82.3
90th %	220	109	97.6	82.9
max	1910	383	254	84.2
n	1702	60	122	8
n cens	0	0	0	0
rainwater				
seawater	20			



Show location map

Barium Ba



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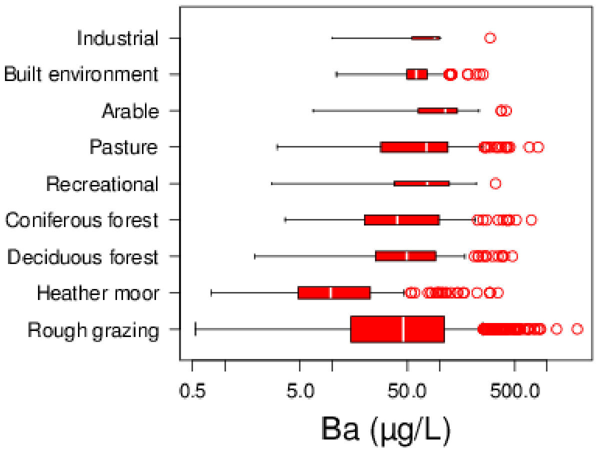
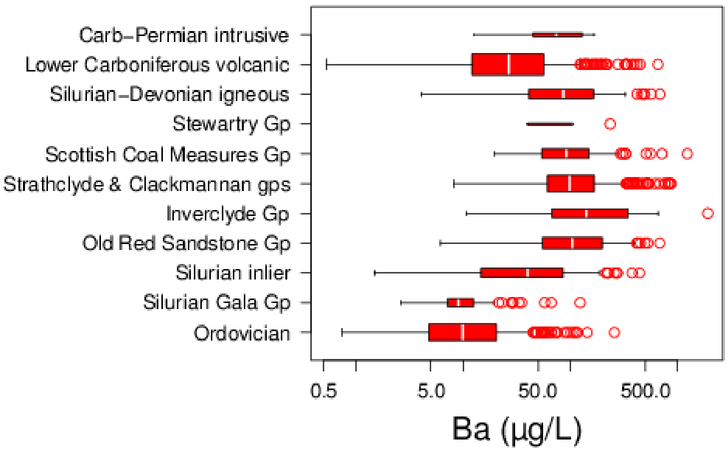




Boron

B

Boron is a non-metallic trace element that occurs in rocks and soils as a minor component of micas, amphiboles, clays and metal oxides and can be introduced from anthropogenic sources such as sewage, wastewater and industrial effluent. Boron occurs in trace quantities in water and the uncharged borate species, H_3BO_3, dominates over the pH range of most natural waters (Hem, 2005; Shand et al., 2007).

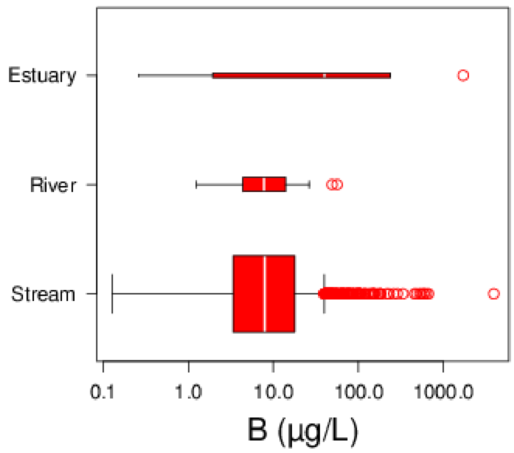
Stream compositions

Data are lacking for boron in the urban waters of the Clyde catchment but from the data available, a strong spatial pattern exists. Concentrations in streams reach up to 3 mg/L but are usually more than an order of magnitude less. Concentrations are highest in the central belt, in waters draining the Carboniferous sedimentary rocks, notably the Scottish Coal Measures and Strathclyde-Clackmannan groups. Origins of B in water in these areas are likely to include clays and metal oxides from the dominantly argillaceous Carboniferous deposits, as well as urban and industrial sources on the periphery of the Glasgow conurbation. Locally high B concentrations are seen in streams close to opencast sites (e.g. Coalburn, Blantyre, Greengairs, Tarbrax) and landfill (Greengairs). Lowest concentrations occur in streams over the western part of the Clyde Plateau, Campsie Fells and Kilsyth Hills which host basaltic lava and tuff, together with those from the Ordovician-Silurian rocks to the south of the Southern Upland Fault. This distribution likely reflects the relative paucity of B in these mafic and metasedimentary rock types, combined with the rural land-use, and the diluting effect from the higher rainfall along the western catchment boundary.

River and estuary compositions

Concentrations in the River Clyde water samples increase downstream from the upper reaches draining Ordovician-Silurian rock types, to the urban and peri-urban areas over Carboniferous sedimentary rocks. The increase is in line with the higher values observed in the contributing tributaries in the central part of the catchment. Relatively high concentrations (up to 1.7 mg/L) are reported in the estuary waters, consistent with increased inputs of B from mixing with seawater.

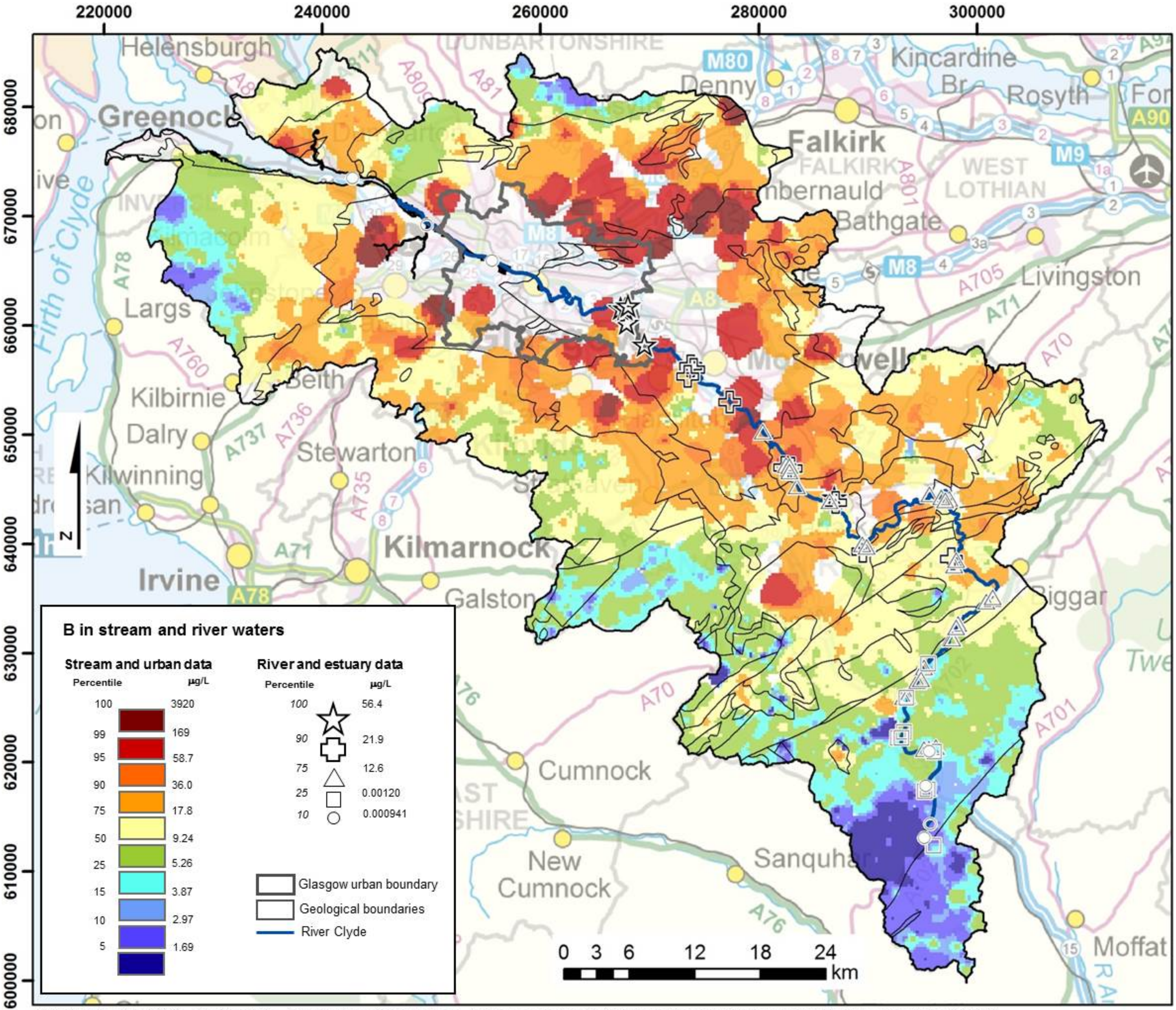
	Stream	River	Urban	Estuary
			(µg/L)	
min	<10	<10	No data	<40
25th %	3.35	4.46		1.95
50th %	7.89	7.77		40
75th %	17.8	13.3		240
90th %	36	22.5		1120
max	3920	56.4		1710
n	1702	60		5
n cens	903	36		2
rainwater				
seawater	4500			



Show location map

Boron

B



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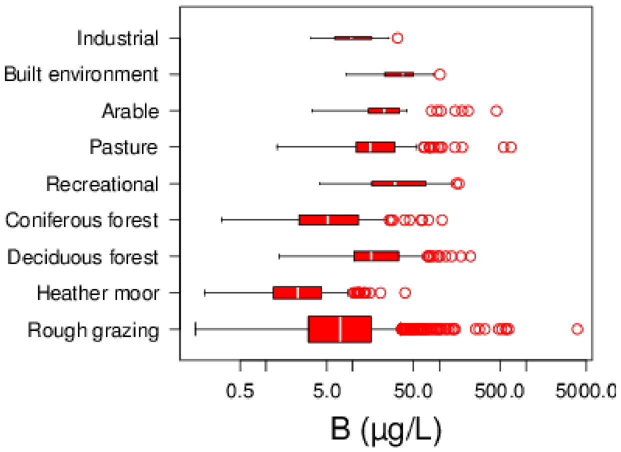
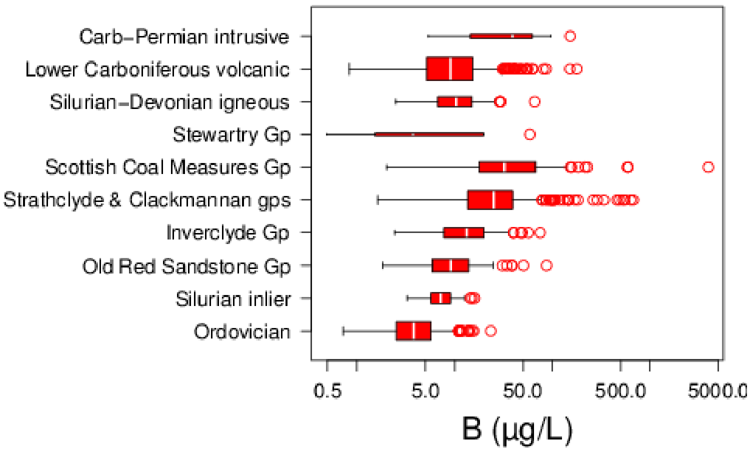




Cadmium Cd

Cadmium is a non-essential element for human health. It tends to accumulate in aquatic animals and plants, leading to acute toxicity. Cadmium is strongly chalcophile and exists solely in the II oxidation state. Its chemistry closely resembles that of Zn, and as a result it is found in minerals such as sphalerite (ZnS), and to a lesser extent smithsonite ($ZnCO_3$). In oxidised surface waters, Cd is most mobile below pH 8. The solubility of Cd carbonates is lower than that of Cd sulphates, and so Cd is less mobile in carbonate-rich environments. Cadmium sorbs to clay minerals, Fe oxides and organic matter or the latter may form complexes with Cd (BGS, 1999; Hem, 2005), thereby affecting mobility in solution. Cadmium has a variety of industrial functions including: welding, photography, production of iron, steel, and cement, as well as Ni-Cd batteries found in mobile phones (Bull, 2010).

Stream and urban compositions

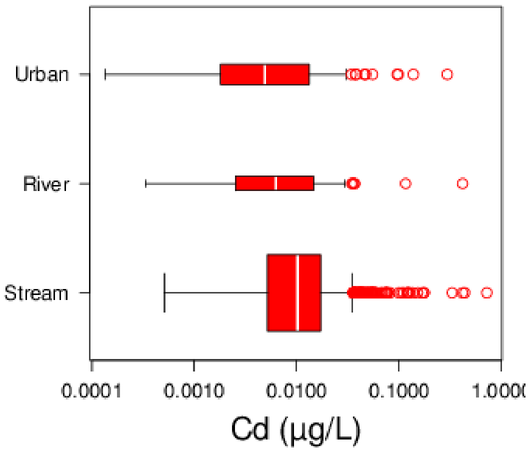
The distribution of stream-water Cd within the Clyde Basin is related to both pH and land-use, but shows no clear spatial trend. The lowest concentrations of Cd (<0.01 µg/L) are generally found in the rural areas of the catchment, where the pH is greater than 7. This tends to be around the Lowther Hills and to the south-east of the River Clyde.

High concentrations of Cd (>0.02) in stream water are generally found where the pH is low, particularly on the periphery of the catchment where there is mapped peat. The highest concentrations tend to be localised, and limited to no more than two adjacent sample sites. Examples include the area around Leadhills, where Cd is likely to exist in sphalerite, which occurs within the local Pb-Zn mineralisation; downstream of coal opencasts, in particular Glespin and Coalburn; downstream of the Greengairs opencast and landfill; and around urban areas of the catchment. Within the urban areas, concentrations of Cd are relatively high regardless of pH, indicating that the mass of Cd derived from made ground, soils, and sediments is relatively high in urban areas.

River and estuary compositions

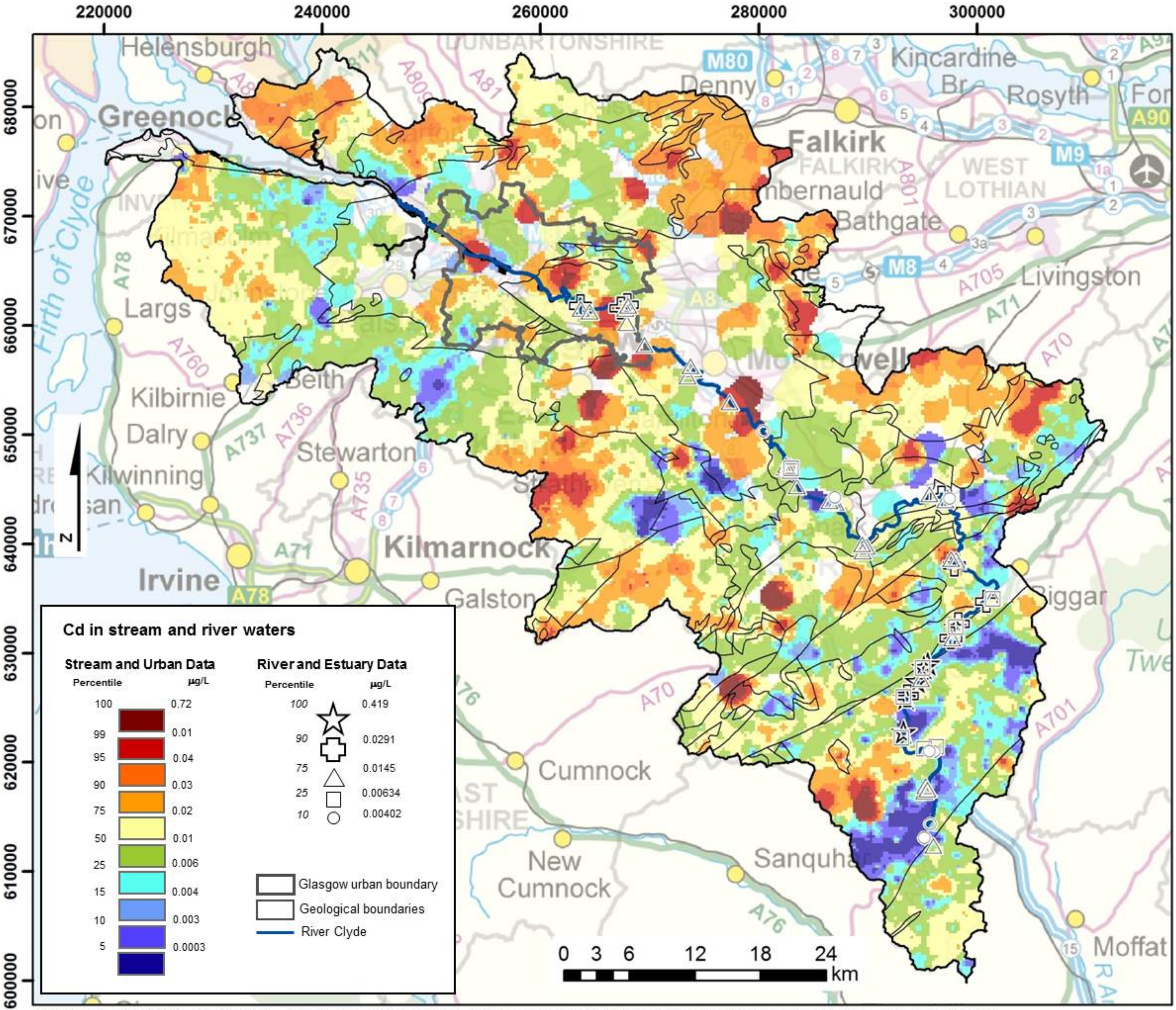
Concentrations of Cd are low in the headwaters and upper reaches of the Clyde. There is a large input of Cd from the Glengonnar Water (0.42 µg/L), which drains the Leadhills mining area. This results in elevated Cd concentrations in the Clyde for almost 20 km downstream. The Cd concentrations remain moderate, until the river enters Glasgow, where the concentrations increase once more. There are no Cd data within the estuary.

	Stream	River	Urban (µg/L)	Estuary
min	<0.01	<0.01	<0.02	<0.05
25th %	0.0052	0.0026	0.0018	
50th %	0.0102	0.0063	0.0049	
75th %	0.0172	0.0144	0.0132	
90th %	0.0283	0.03	0.0301	
max	0.721	0.419	0.296	0.0151
n	1702	60	122	8
n cens	836	32	96	5
rainwater				
seawater	0.11			



Show location map

Cadmium   Cd



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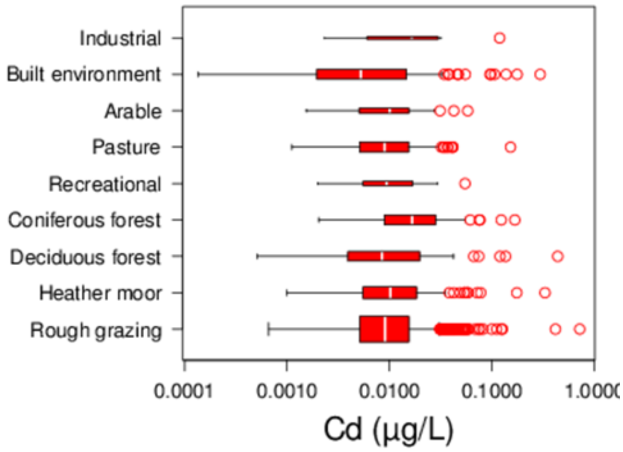
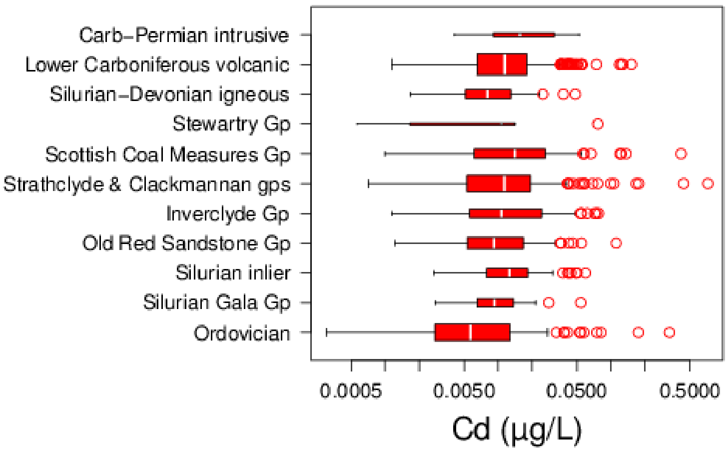




Chromium Cr

Chromium occurs in the environment in both III and VI oxidation states, depending on ambient pH and redox conditions. The two forms have differing toxicity, Cr(III) usually being regarded as essential for human health in small quantities, while Cr(VI) is a known carcinogen (Broadway et al., 2010). Chromium exists predominantly in the trivalent form in primary ore minerals. The main chromium ore mineral is chromite ($FeCr(III)_2O_4$). Hexavalent Cr can be present naturally in the environment but is also produced from industrial processes (Assem and Zhu, 2007).

In Glasgow, the distribution of Cr in the environment is enhanced by the presence in soil of chromite ore processing residue (COPR), produced by a former chromium works over the period 1830–1968. The COPR consists of a mixture of the Cr(III) and Cr(VI) mineral phases (chromite, brownmillerite, ettringite, hydrocalumite and hydrogarnet (Hillier et al., 2003)), which was disposed of at a number of sites around the Cambuslang and Rutherglen areas in south-east Glasgow. COPR was last disposed of over 40 years ago, but its high-pH condition (up to 12.3) has led to the release of Cr(VI) in sufficient quantities to contaminate receiving groundwaters and streams locally (Broadway et al., 2010; Farmer et al., 2006). A significant proportion of the Cr in soils from the affected areas occurs as Cr(VI).

Streams and urban compositions

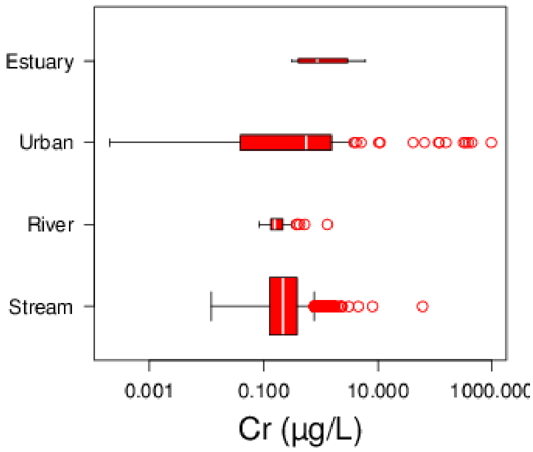
The widest range and highest concentrations of Cr in solution are seen clearly in the urban area of Glasgow, with values up to 971 µg/L. These demonstrate the influence of the industrial COPR legacy. Highest values (>50 µg/L) are almost exclusively from culverted urban streams, many located close to former COPR waste sites. An additional high-Cr stream drains the Greengairs landfill. These locations also correspond with Coal Measures geology. The highest concentrations tend to be present in waters with alkaline pH and demonstrate the mobility, likely in the form of CrO_4^{2-} (chromate).

Rural areas of the catchment have generally low concentrations (97% less than 1 µg/L). Relatively low concentrations are seen to the south of the Southern Uplands Fault, in streams draining Ordovician and Silurian metasedimentary rocks. Lowest concentrations of Cr are reported in streams over the Clyde Plateau Volcanic Formation, where the bedrock is mainly basaltic.

River and estuary compositions

The highest concentrations of Cr in river waters are unsurprisingly found within the urban reaches of the River Clyde. Concentrations increase dramatically as a result of inputs from the Polmadie Burn and the Molendinar Burn. Both these streams are significantly affected upstream by COPR inputs, which remain in solution. Concentrations correlate broadly with the Cr content of the stream sediments in the area (BGS, 1993; Fordyce et al., 2004).

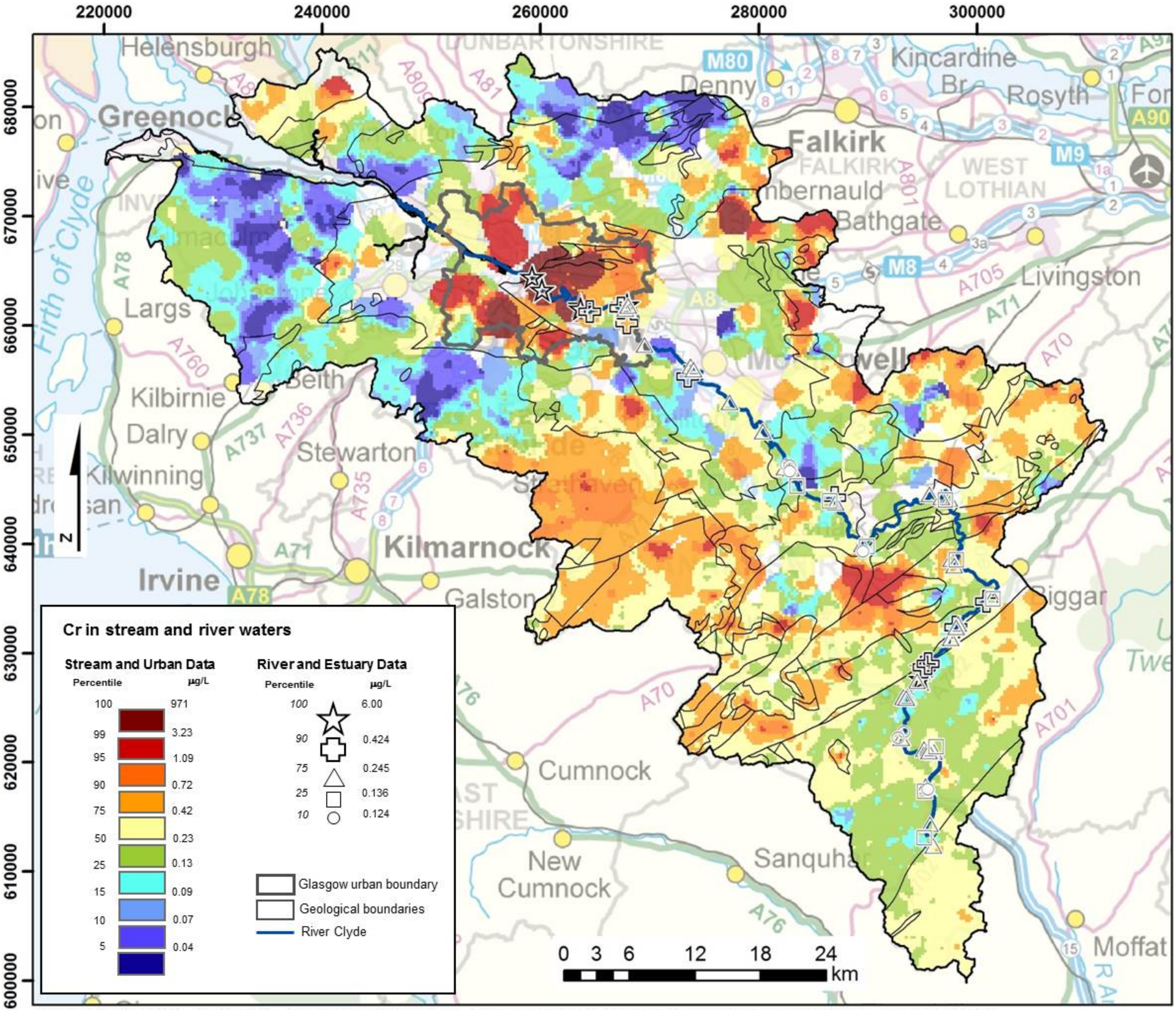
	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.05	0.0824	<0.5	<2.5
25th %	0.129	0.134	0.0403	0.453
50th %	0.218	0.156	0.555	0.5
75th %	0.385	0.213	1.53	2.94
90th %	0.662	0.282	4.98	5.4
max	60.8	1.3	971	6
n	1702	60	122	7
n cens	132	0	54	2
rainwater				
seawater	0.05			



Show location map

Chromium

Cr



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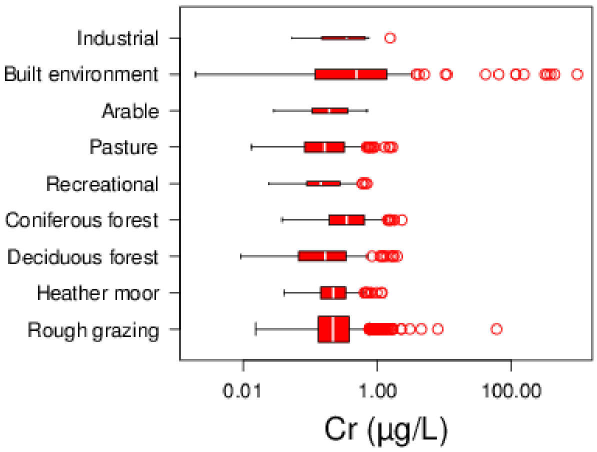
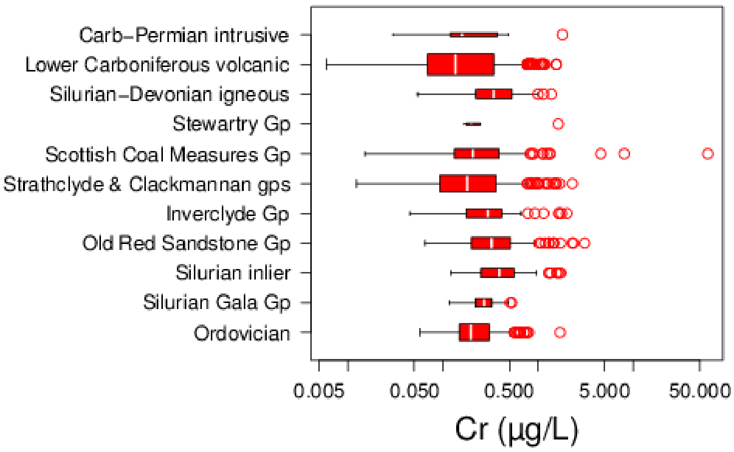




Copper Cu

Copper is an essential trace element in plant and animal metabolism. It occurs in nature as native Cu and in sulphide minerals of ore deposits. In solution, it can occur as either Cu^{2+} or Cu^{+}, but in oxygenated stream water, Cu^{2+} overwhelmingly dominates. Copper forms complexes with a variety of ligands, and sorbs particularly strongly to organic matter. In oxidising stream waters, Cu is mobile where the pH is low. At alkaline pH, Cu may be mobilised as $Cu(OH)_3^-$, although mobility is typically reduced due to the strong binding of Cu to Fe hydroxides or organic matter in neutral or alkaline conditions (Drever, 1997; Hem, 2005). Copper has many applications in modern society, which result in its dispersal in the environment. High Cu concentrations would be expected where there has been most human interaction (Hem, 2005).

Stream and urban compositions

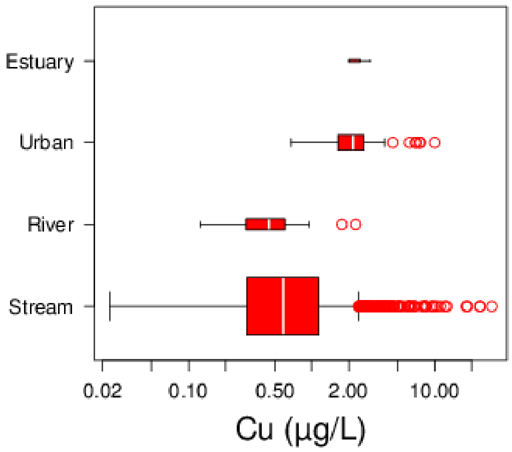
Copper in stream waters in the Clyde Basin has been influenced by geology and land-use. Low concentrations (<0.6 µg/L) are found to the south of northing 63000, and along the catchment boundaries in the most western, north-eastern and eastern edges of the Basin. These areas are predominantly underlain by the Ordovician-Silurian Gala Group, Leadhills Supergroup and the Carboniferous Clyde Plateau Volcanic Formation. Streams over the Gala Group have the lowest median Cu values of the lithologies present in the area. The streams with low Cu concentrations are generally found in areas that have little human influence, where the land-use is typically heather moor, rough grazing, or coniferous forest.

High Cu concentrations (>0.6 µg/L) are found in streams in the lower-lying central areas of the catchment. Concentrations are particularly high in the urban environment and areas underlain by Coal Measures sediments. This reflects the influence of urban and industrial pollution; however, Cu is also potentially derived from sulphide minerals in the Carboniferous rocks that underlie the built-up areas. Very high concentrations are reported from streams in close proximity to motorways around Cumbernauld and Larkhall. Car usage can release Cu to the environment though brake erosion, which will likely drain into adjacent watercourses. Other very high concentrations of Cu are found in streams that drain the area around the Greengairs landfill site some 4 km north-west of Airdrie.

River and estuary compositions

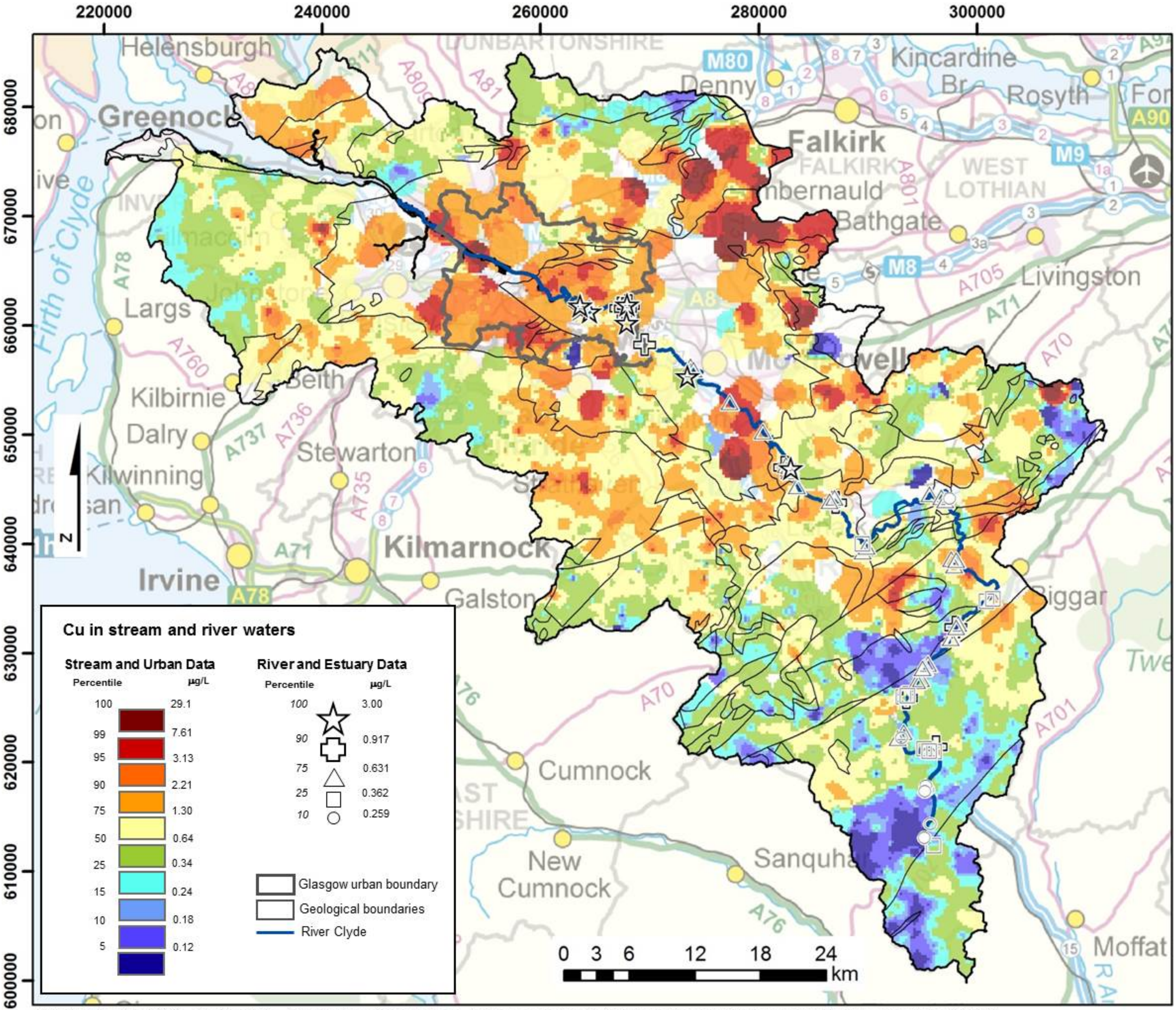
Concentrations of water-Cu are low in the River Clyde and its tributaries within the upper part of the catchment. There are high Cu concentrations in two tributaries north of Lanark and within Avon Water, although concentrations within the Clyde itself remain relatively low until it is downstream of Motherwell. At this point it receives inputs from the urban environment. The large volume of relatively unspoilt water from the upper catchment ensures that concentrations in the Clyde are overall relatively low (<3 µg/L).

	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.4	<0.4	<1	<5
25th %	0.297	0.294	1.64	
50th %	0.589	0.449	2.17	
75th %	1.14	0.6	2.64	
90th %	1.86	0.795	3.52	
max	29.1	2.28	9.99	2.54
n	1702	60	122	7
n cens	574	23	9	4
rainwater				
seawater				



Show location map

Copper Cu



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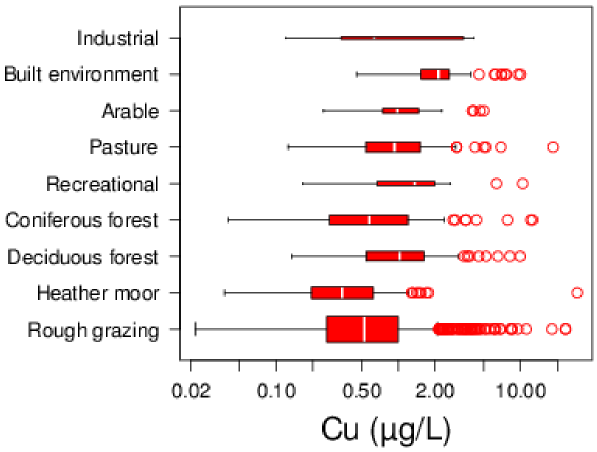
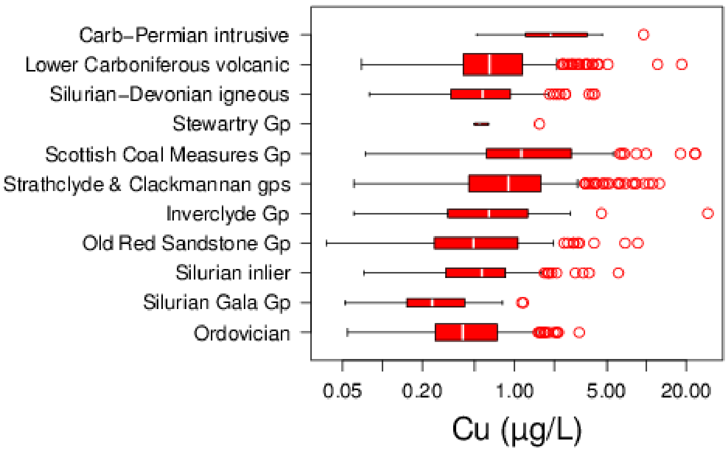




Fluoride F

The element fluorine is a significant constituent of minerals such as biotites, amphiboles and apatite and is a major component of fluorite (CaF_2). Fluorine also adsorbs to Fe and Al oxides and clays. These minerals can; therefore, be important sources and sinks of F in catchments. Granitic rocks, acidic volcanic ashes and mineralised veins have a relative abundance of fluorine, and so weathering of these can give rise to relatively high concentrations of F in solution. Fluorine is the lightest of the halogen elements, and as the most electronegative, has a strong tendency to take on a negative charge. Free F^- is the solute species most favoured over the pH range of most natural waters, although complexation with other ions may occur in acidic conditions. Fluoride has similar properties to OH^- (same charge, similar ionic radius) and so the two can interchange and compete in mineral sorption/weathering reactions. Adsorption of F^- to metal oxides and clays is also pH-dependent, being most favoured in the pH-neutral to acidic range. Therefore, high F concentrations are typically a feature of alkaline aqueous conditions. A solubility limit is imposed by fluorite, precipitation of which restricts the concentrations of F which can be stable in solution (Edmunds and Smedley, 2013). The net effect is that high F concentrations are a feature of Ca-poor water and in particular, of alkaline, Na-HCO_3 dominated water. Sources of F in water may also include airborne contaminants (industrial, marine in the Clyde setting) and inputs from point-source urban and industrial contamination, though mineral reactions probably dominate in all but the most polluted environments.

Streams and urban compositions

Concentrations of F are lowest along the periphery of the Clyde catchment, in association with more acidic stream-waters in heathland and peat uplands. Concentrations are particularly low in the north-western watershed area of the Clyde Plateau and to the south of the Southern Upland Fault in waters draining Ordovician-Silurian Gala and Leadhills Group rocks. These low values are likely a combined function of low-F rock types and more acidic conditions, favouring adsorption to metal oxides and clays.

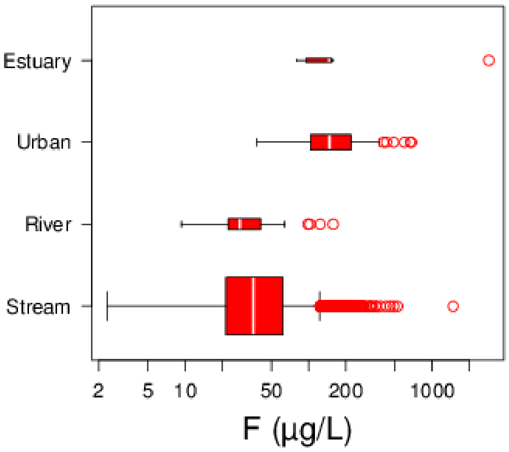
Highest F concentrations are found in the central low-lying, urban part of the catchment around Glasgow. Highest median concentrations are found in streams draining Scottish Coal Measures and Strathclyde-Clackmannan sedimentary rocks. These dominantly argillaceous rock types potentially contain abundant sources of F in the form of clay minerals and metal oxides. Highest median F stream-water values occur where land-use is classified as the built environment, and is generally coincident with the Coal Measure lithology. Concentrations approach 1500 µg/L in the stream water, which is a relatively high value for surface waters, although, for context, it is not in excess of the drinking-water limit for F.

River and estuary compositions

Concentrations in the River Clyde waters show a general downstream increase, mirroring the distribution of F in the rural streams. Increasing concentrations are due to inputs from the urban tributaries.

Concentrations in the estuary samples are generally comparable to those observed from other water types, though one analysis has the highest observed concentration of the dataset (2880 µg/L). This possibly represents a contribution from seawater.

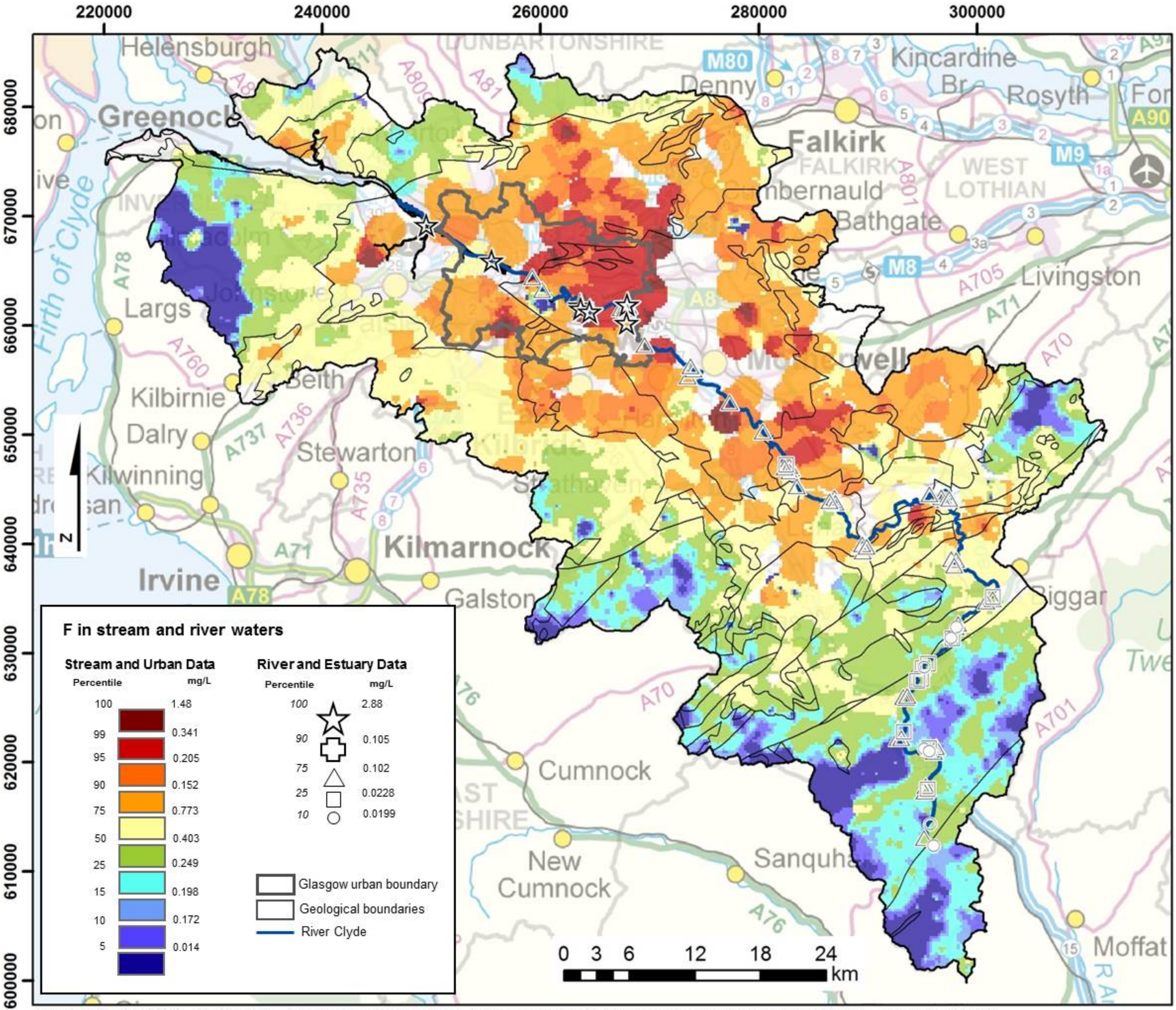
	Stream	River	Urban (µg/L)	Estuary
min	<10	<10	<10	80
25th %	21.5	22.2	104	95
50th %	35.7	27.8	148	147
75th %	62	40.6	218	154
90th %	122	62.1	291	1250
max	1480	158	680	2880
n	1702	60	122	7
n cens	101	1	1	0
rainwater				
seawater	1300			



Show location map

Fluoride

F



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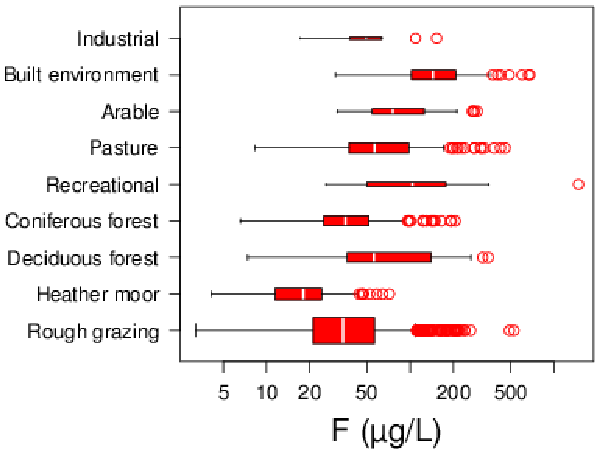
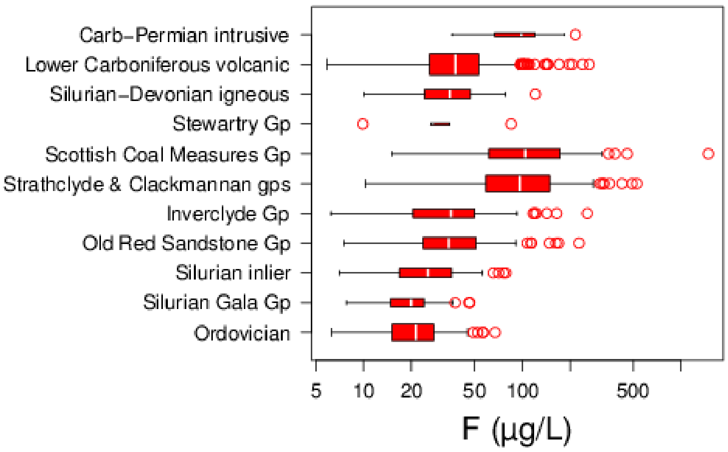




Iron Fe

Iron is the second most abundant metal in the earth's crust, and is a common component of rocks, Quaternary deposits and mineral-rich soils (Hem, 2005). Iron solubility in stream waters is limited by pH and redox conditions. In acidic streams, Fe predominantly occurs as mobile Fe(II) and in circum-neutral oxic stream waters as the less mobile Fe(III). Stream waters are high in dissolved oxygen, so Fe concentrations are normally low under alkaline to neutral conditions, but can be high under strongly acid conditions (Drever, 1997). As 95% of the samples collected within the Clyde Basin have a pH of >6.4, Fe mobility should be limited as streams should be supersaturated with respect to $Fe(OH)_3$ and haematite (after Drever, 1997).

Stream and Urban compositions

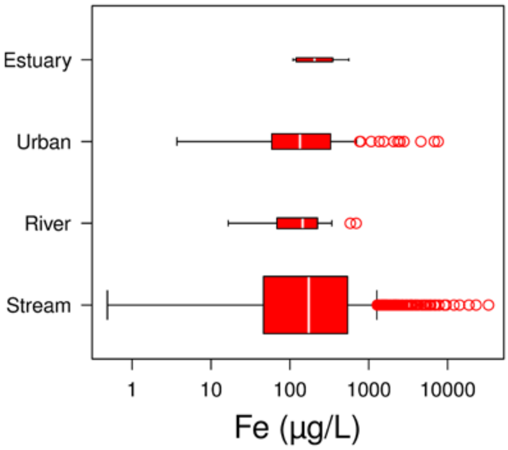
Stream-water Fe concentrations in the Clyde Basin have a spatial trend similar to that of pH, and are linked to geology and land-use type. Many of the high concentrations in the waters may be due to the presence of colloidal Fe. Low concentrations of Fe (<173 µg/L) are found in streams south of the Southern Uplands Fault, which are underlain by Ordovician–Silurian Gala Group and Leadhills Supergroup rocks. These have the lowest stream-water median Fe values of the geological groups within the Clyde Basin. Within this area the higher concentrations of Fe correspond to the areas of lowest pH: heather moor land-use, and peaty soils. Low Fe concentrations are found also over the south-facing slopes of the Pentland Hills, the Kilsyth Hills, around the Clyde Estuary, and around Hamilton. Concentrations of Fe are low also in streams in the lower-lying portion of the catchment. The low Fe concentrations generally correspond to high pH values, suggesting that Fe is immobilised by precipitation of ferric hydroxide.

Areas of high Fe stream-water concentrations (>500 µg/L) are found around the periphery of the catchment, north of the Southern Uplands Fault. These streams have some of the lowest pH values and are commonly underlain by peaty soils, with coniferous forest and heather moor as the dominant land-use types. High Fe concentrations are present also in streams from the coal-mining areas around Douglas and Forth, and around the Bedlay Colliery. Mining activities cause the increased exposure of reactive minerals, particularly pyrite (FeS_2), which can be found within the Coal Measures. Pyrite oxidises readily, mobilising Fe and SO_4 and producing acidity. The land-use type with the highest median stream-water Fe concentration is industrial which, amongst others, represents these sites.

River and estuary compositions

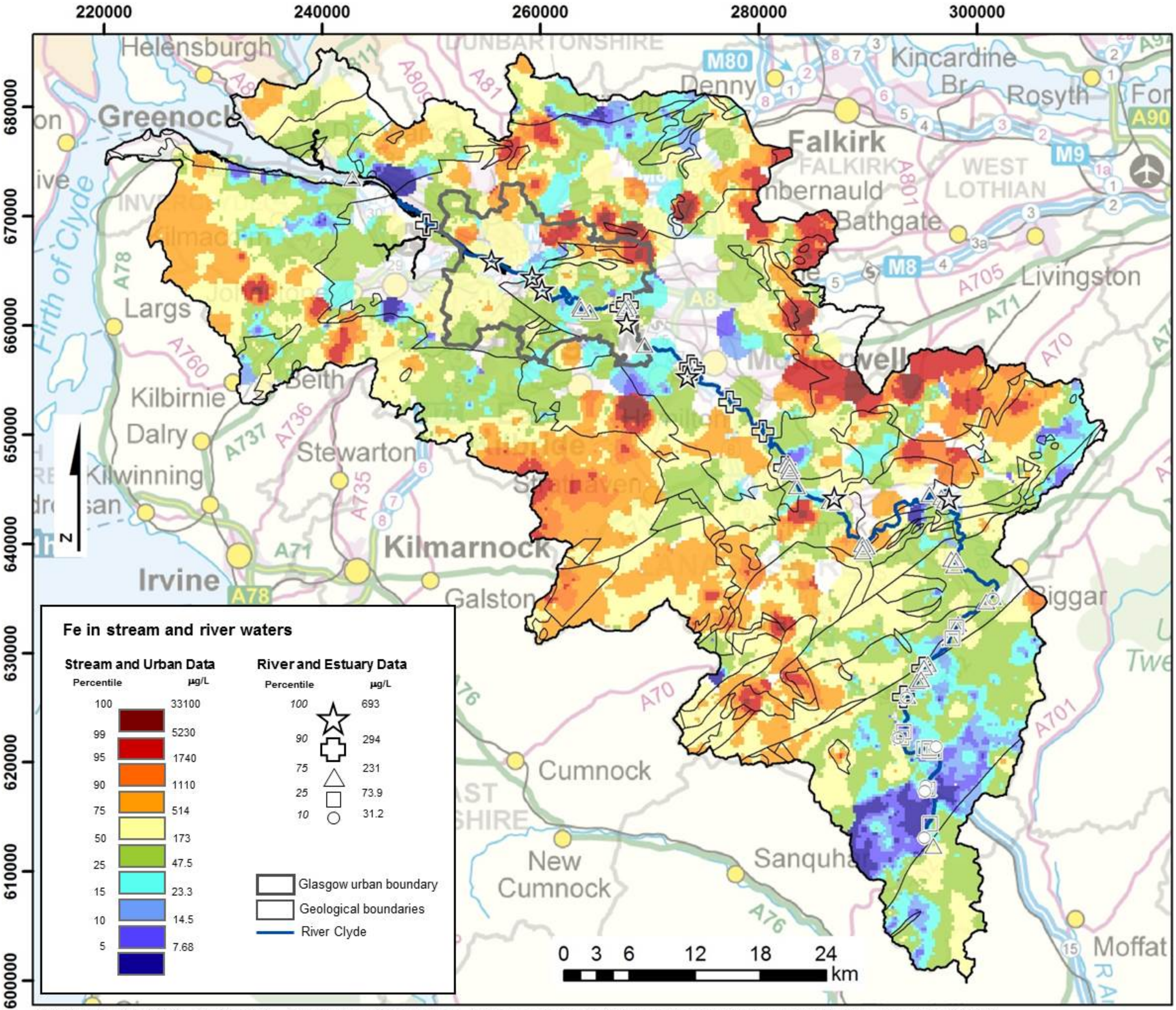
Iron concentrations in the River Clyde waters and its tributaries are generally lower in the upper catchment with an increase downstream. However, there is a lot of local variation reflecting the variability in pH. The highest concentrations are found in Mouse Water, which receives drainage from the mines around Forth.

	Stream	River	Urban	Estuary
			(µg/L)	
min	<1	16.5	<10	110
25th %	46.3	70.2	60.4	120
50th %	174	145	134	205
75th %	539	223	329	345
90th %	1120	262	761	420
max	33100	693	7580	560
n	1702	60	122	8
n cens	3	0	1	0
rainwater	<3			
seawater	3			



Show location map

Iron Fe



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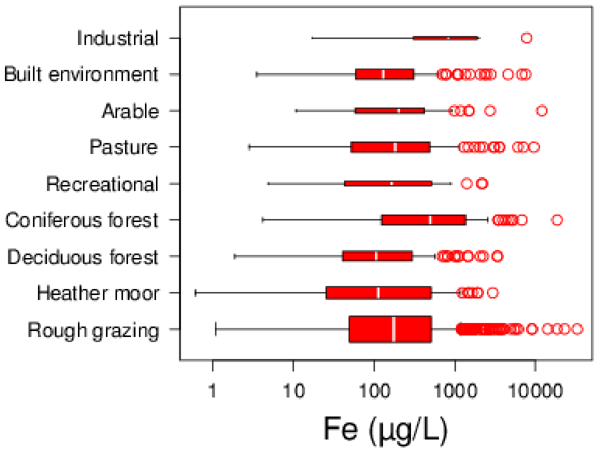
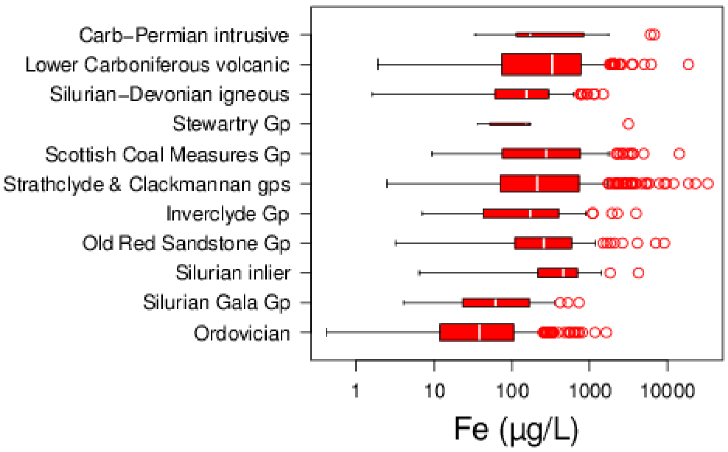




Lithium **Li**

Lithium is a relatively rare alkali metal. Lithium-bearing minerals are found in pegmatites, evaporate deposits and natural brines. Lithium can substitute for Mg in some minerals, and it absorbs weakly to clays. Once Li is in solution it tends to remain so and is relatively mobile in the aqueous environment. Lithium tends to show a relationship with salinity in natural waters (Hem, 2005).

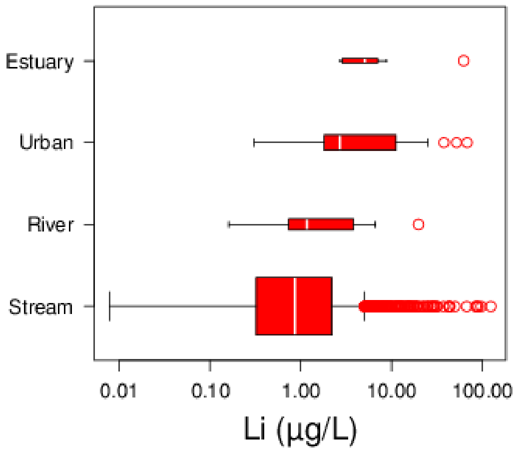
Streams and urban compositions

Concentrations of lithium in stream-water show a relationship with conductivity (SEC), with a clear cluster of high values around the central part of the Clyde Basin. Concentrations are of the order of 100 µg/L or less. The highest median Li stream-water values occur in the built environment land-use type and where the geology consists of Carboniferous sedimentary rocks (Scottish Coal Measures and Strathclyde-Clackmannan groups). Baseflow from these rock types is likely to contain relatively high Li concentrations, alongside other dissolved solids. Anomalous concentrations in stream waters are related to urban industrial centres (e.g. Glasgow city, Rutherglen) and with opencast coal workings (e.g. Coalburn, Tarbrax, Mollinsburn, Castlehill, Greengairs) and the associated landfill at Greengairs. The origin of Li in the stream waters is likely to be a combination of clay minerals in the argillaceous Carboniferous rocks and overlying soils, waste heaps associated with opencast workings and industrial effluents. In general, lowest concentrations occur in streams over the Clyde Plateau Volcanic Formation and the Ordovician-Silurian rock types, where the land-use is classed as heather moor.

River and estuary compositions

Concentrations in the River Clyde water samples increase downstream from the upper reaches underlain by Ordovician-Silurian rock types, to the Carboniferous sedimentary rocks in the central part of the Basin. Concentrations are also relatively high in the estuary waters, with a contribution from seawater likely to be an influence.

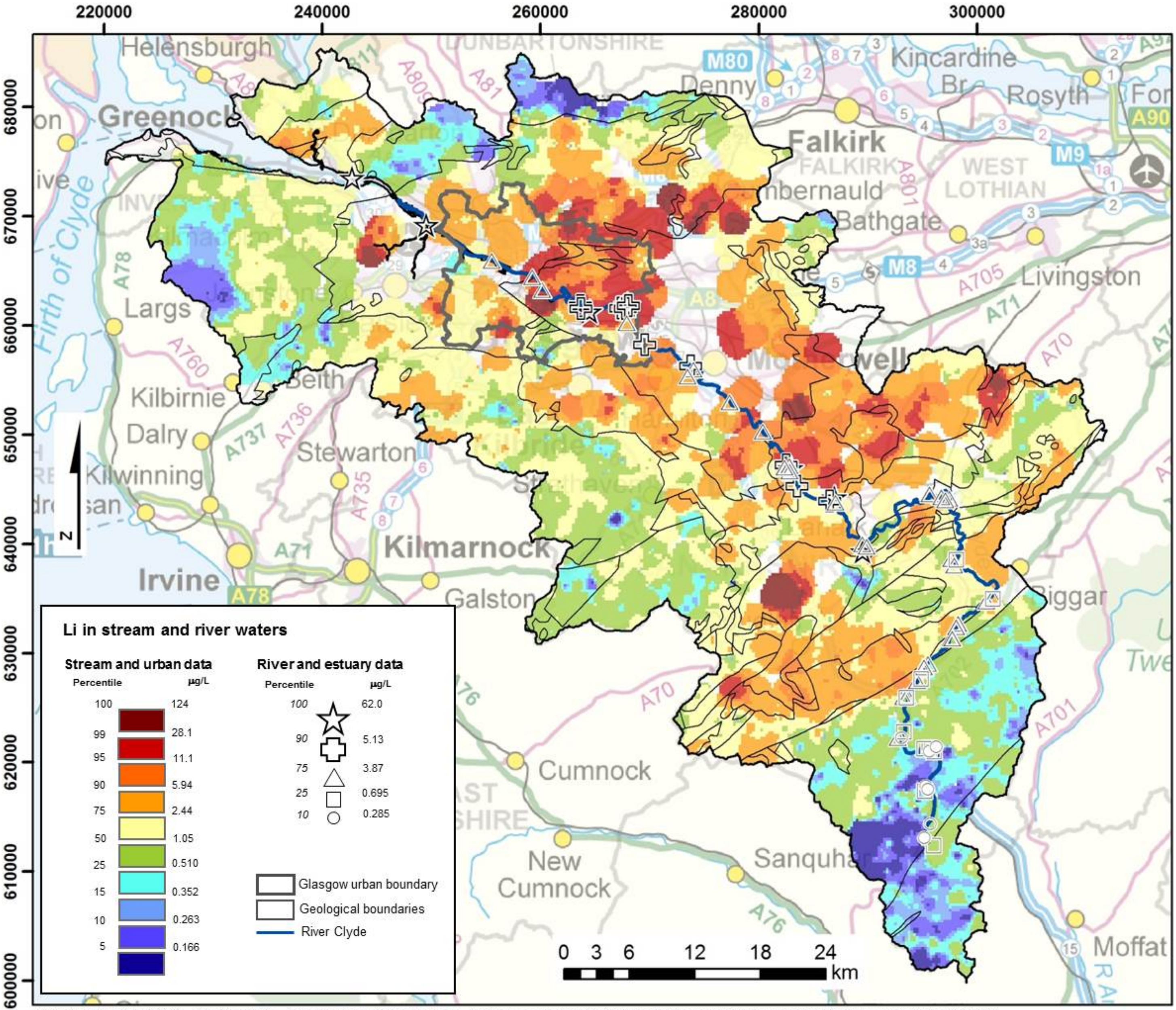
	Stream	River	Urban	Estuary
			(µg/L)	
min	<1	<1	0.307	2.7
25th %	0.323	0.739	1.82	2.88
50th %	0.855	1.16	2.69	5.05
75th %	2.19	3.77	10.3	6.1
90th %	5.42	4.4	18	24.8
max	124	19.7	67.8	62
n	1702	60	122	8
n cens	875	28	0	0
rainwater				
seawater	170			



Show location map

Lithium

Li



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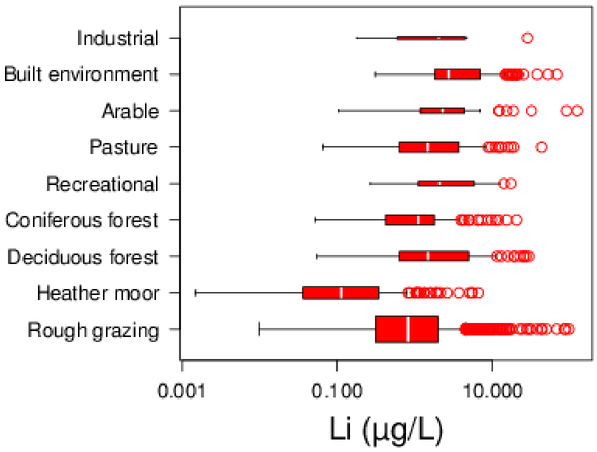
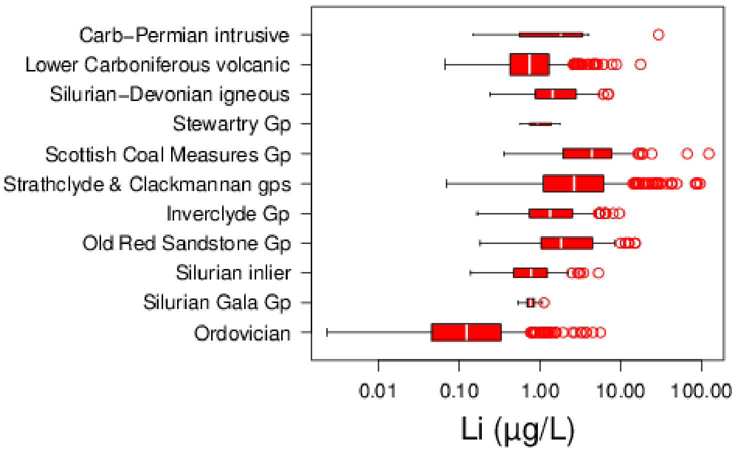




Manganese Mn

Manganese is one of the more abundant metallic elements in the Earth's crust. It has three oxidation states (2^+, 3^+ and 4^+) but in natural waters is most likely to occur in the divalent state. When oxidation occurs, at higher pH and dissolved oxygen content, Mn-oxide coatings can form on stream sediment and can co-precipitate with Fe oxides. Manganese concentrations in stream waters commonly correlate with iron (Fe), which is also a redox-sensitive element. Stream water concentrations are predominantly influenced by variations in pH, supply from soil and bedrock, and attenuation throughout the catchment (Hem, 2005).

Streams and urban compositions

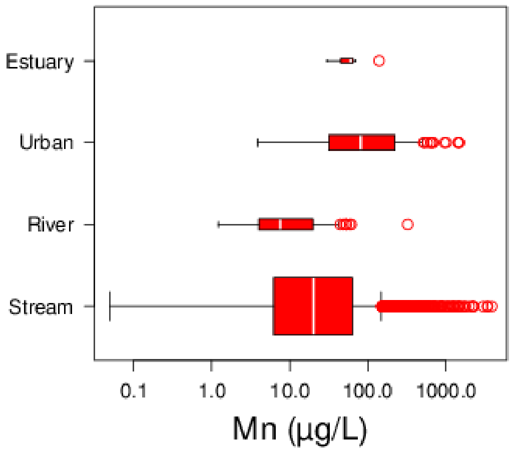
The stream-water Mn concentrations have a strong spatial trend within the Clyde catchment, which is related principally to geology and land-use. Low concentrations of Mn are found in streams south of the Southern Uplands Fault, which are underlain by Ordovician-Silurian Gala Group and Leadhills Supergroup rocks. In contrast to these surrounding rock types, Mn concentration is higher in streams draining the Stewartry Group, which may reflect greater Fe and Mn content in these desert sandstones and conglomerates.

Low Mn stream-water concentrations are found in the north-western part of the catchment, especially around the Campsie Fells and Kilsyth Hills, which form part of the Clyde Plateau Volcanic Formation (CPV). These areas contain mainly basaltic but ranging to more felsic compositions and correspond to higher stream-water pH values, where Mn can be less mobile. Higher concentrations of Mn are recorded in stream-waters within the central portion of the catchment. Some of the highest values are associated with coal workings such as at Coalburn and Forth, and the opencast south-east of East Kilbride, corresponding to elevated Fe concentrations in mining areas. Additionally, the water courses within the Glasgow urban area have very high Mn concentrations. Industrial and built environment land-use types have the highest median stream-water Mn values, and median stream-water Mn values are highest in the urban dataset.

River and estuary compositions

Manganese concentrations in the River Clyde water and its tributaries are generally lower in the upper catchment and increase downstream. The highest concentrations are found within Douglas Water (325 µg/L), which drains the Coalburn coal mining area, and within the urban reaches of the Clyde.

	Stream	River	Urban (µg/L)	Estuary
min	<0.2	1.21	3.91	30
25th %	6.23	4.06	31.9	47.5
50th %	20.2	7.53	81.1	60
75th %	63.6	19.9	217	62.5
90th %	190	44.7	504	91
max	3890	325	1480	140
n	1702	60	122	8
n cens	13	0	0	0
rainwater				
seawater	2			



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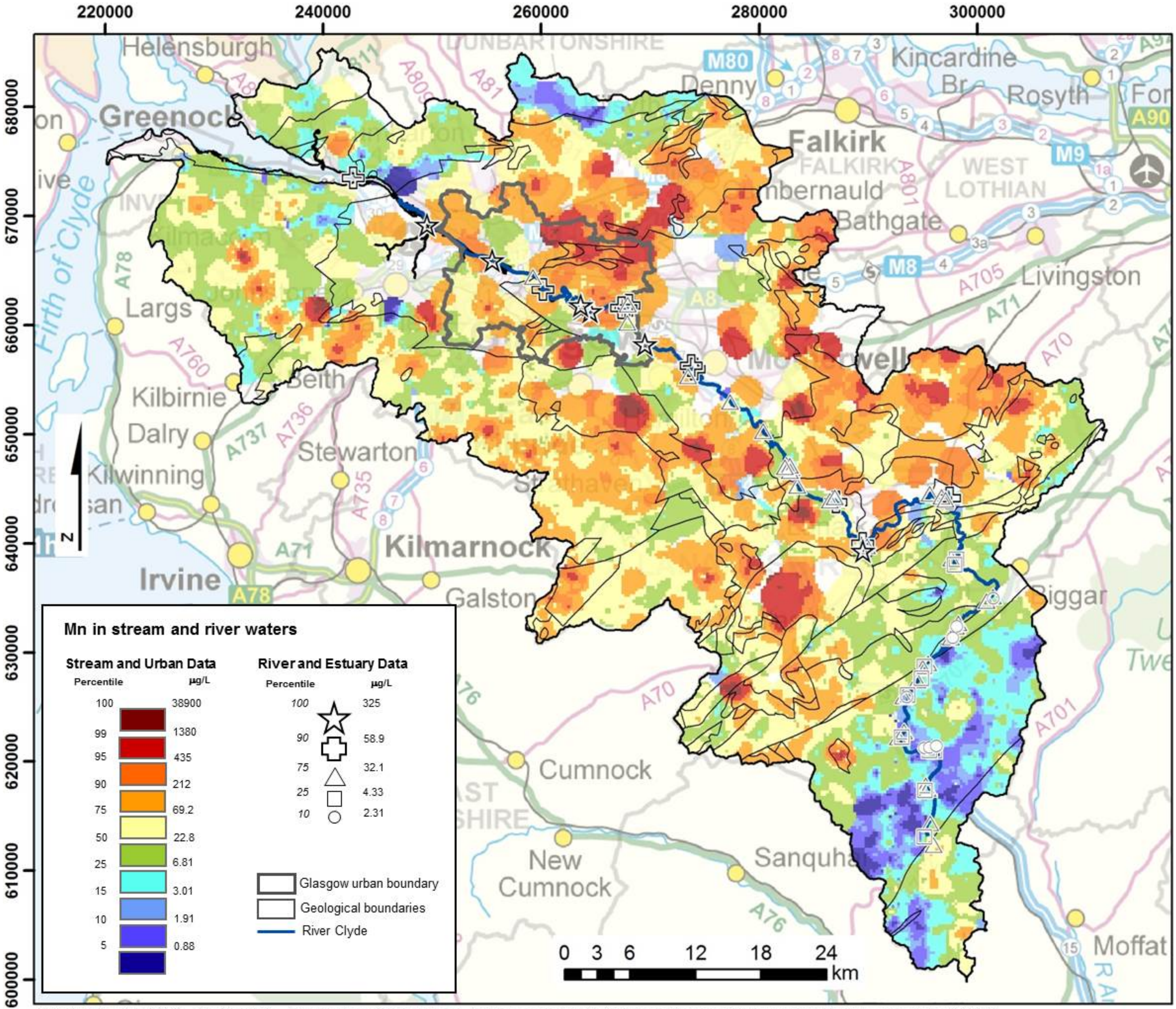
Manganese Mn



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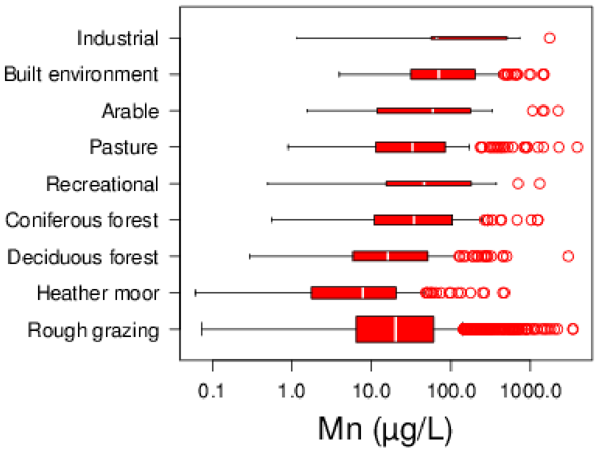
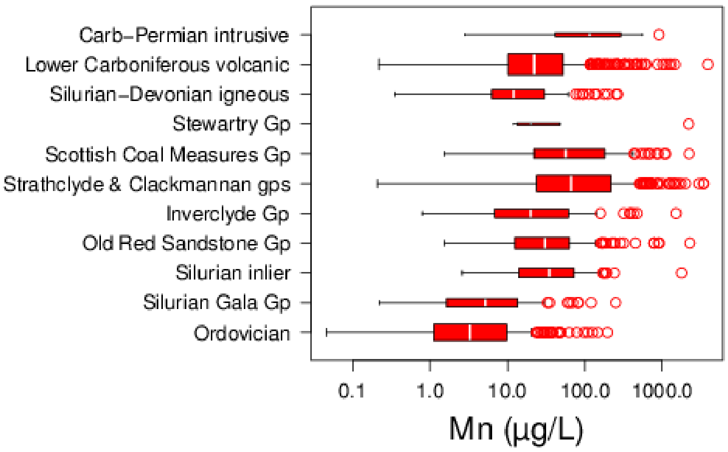




Molybdenum Mo

Molybdenum is a transition metal that occurs in oxidation states from -II to VI, though in nature the predominant forms are Mo(IV) and Mo(VI). Molybdenum occurs as a major constituent in the sulphide mineral molybdenite (MoS_2) and the oxides wulfenite ($PbMoO_4$) and powellite ($Ca(Mo,W)O_4$). It may also be present in other sulphide minerals including the more common pyrite, galena and sphalerite. In sedimentary rocks, molybdenum partitions with organic sulphur and carbon and may thus be relatively abundant in shales and muds. The element has been used as an indicator of sulphidic conditions and organic matter content in sediments. Molybdenum is also a potential contaminant from industry. It is a component of stainless steel, steel alloys, and superalloys and is used in the manufacture of lubricants, corrosion inhibitors, pigments and ceramics. It may also be distributed in the environment as a contaminant from fossil-fuel combustion, fly ash leaching, mine waste and fertilisers (Smedley et al., 2014).

Mobility of molybdenum in the aqueous environment owes much to sorption reactions. It adsorbs readily to iron, manganese and aluminium oxides as well as clays, though the affinity is strongly pH-dependent. Molybdenum is mobile in its oxic form (molybdate) under neutral to alkaline conditions where pH ≥7, but is typically strongly sorbed at pH ≤5 (Smedley et al., 2014).

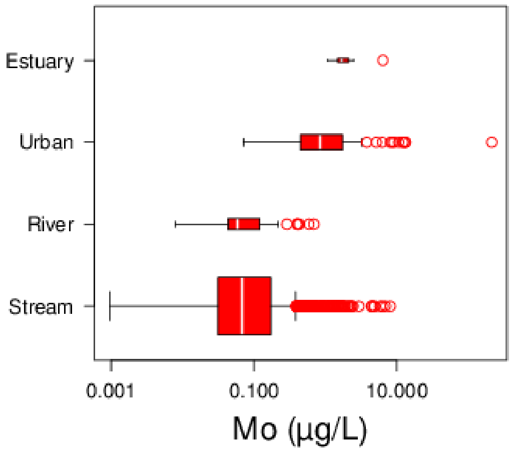
Streams and urban compositions

The distribution of Mo in stream waters of the Clyde Basin is correlated with pH, as well as geology and land-use. The lowest concentrations (< 0.012 µg/L) occur to the south of the Southern Upland Fault and around the catchment boundary, including the Kilsyth and Kilpatrick Hills, Muirshiel, the south-west (Galston) and the Medwin sub-catchment along the north-east boundary. Categorised by geology, highest concentrations occur in streams on till above Scottish Coal Measures and Strathclyde-Clackmannan group sediments. In terms of land-use, highest values occur in streams within the built environment. Relatively high Mo concentrations (> 1.15 µg/L) are found close to the Linwood Moss and Greengairs landfill sites. Highs are also found around Lochhead and Milburn (4 km south of Larkhall) and within Glasgow city centre. The largest range and highest concentrations occur in stream-waters in the pH range 7.0–8.5. Controls on Mo distributions are likely to be a combination of geology (abundance in argillaceous and organic-rich Carboniferous sediments) and urban sources (mining activity, industrial contamination). Relative lows in dissolved Mo around the catchment boundary may be a combination of lower concentrations in component rock types, greater dilution by rainfall and greater influence of sorption at lower pH.

River and estuary compositions

Concentrations of river water Mo increase progressively down-gradient along the Clyde, reaching highest values within the Glasgow urban boundary and the estuary. The pattern correlates well with the spatial trend observed in the stream waters, though the upper limits of observations in the Clyde are much lower (up to 6.4 µg/L) than those observed in the urban streams (up to 214 µg/L).

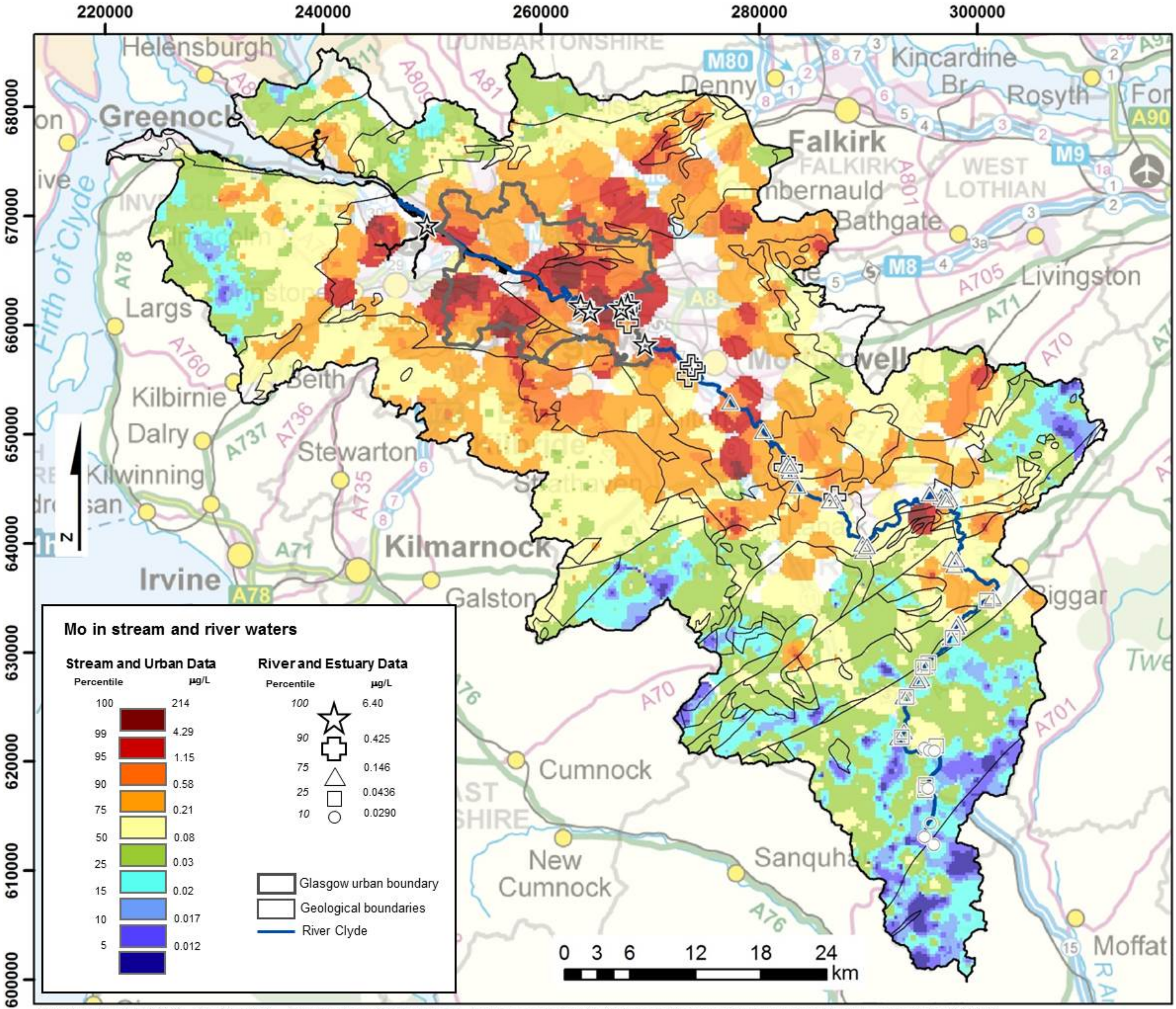
	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.02	<0.02	0.0713	<2.5
25th %	0.0313	0.0433	0.453	1.48
50th %	0.0688	0.059	0.839	1.7
75th %	0.173	0.116	1.71	2.12
90th %	0.403	0.301	3.25	4.05
max	8.1	0.691	214	6.4
n	1702	60	122	7
n cens	227	1	0	3
rainwater	0.2			
seawater	10			



Show location map

Molybdenum

Mo



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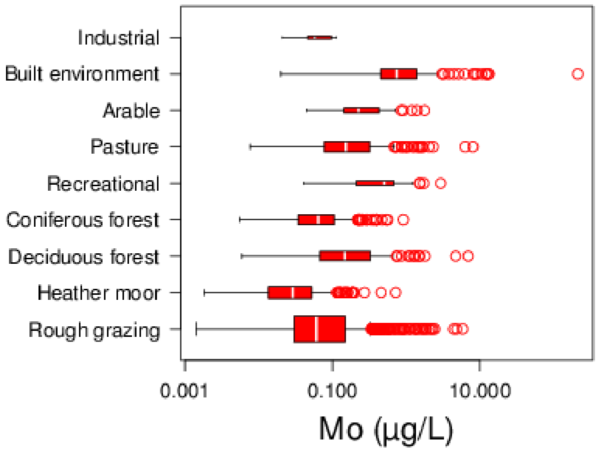
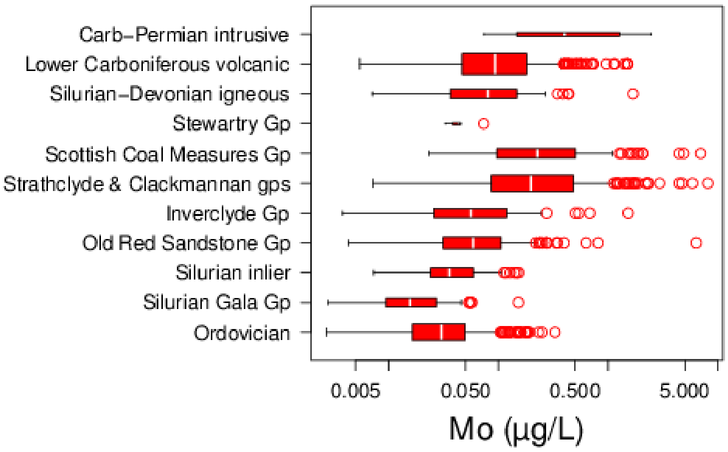




Nickel Ni

Nickel is a metal that is an essential trace element in all organisms. It is widely distributed throughout the Earth's crust. It can form soluble compounds, and in natural stream waters it is usually present as Ni^{2+}. This ion is intermediate in size between Fe^{2+} and Mn $^{2+}$, and so it can readily substitute in minerals rich in Fe or Mn, or co-precipitate with Fe and Mn oxides. Nickel is also commonly enriched in organic matter: there can be more than 50 mg/kg in coal (BGS, 1999; Hem, 2005). Nickel is an important industrial metal, it is used in stainless steel and other alloys, the production of electrical equipment, in jewellery, and in Ni-Cd batteries (PHE, 2009).

Streams and urban compositions

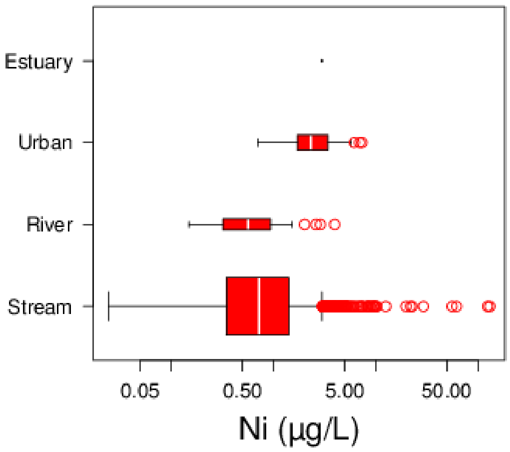
There is a clear spatial trend of Ni in stream waters within the Clyde Basin, which is similar to that of the major elements: the stream water concentrations are low (<0.7 µg/L) south of the Southern Upland fault, and around the northern and western catchment boundaries. These areas are underlain by Ordovician-Silurian Gala Group and Leadhills Supergroup rocks and by the Carboniferous Clyde Plateau Volcanic Formation. Areas with the lowest Ni stream water concentrations include areas within the Lowther hills, Muirshiel Country Park, the campsite Fells and Kilpatrick Hills, and the Pentland Hills. These areas are defined by their unspoilt nature.

Higher Ni concentrations in stream water (>1.5 µg/L) are a feature of the lowland areas of the Clyde catchment, which overlie the Carboniferous Clackmannan-Strathclyde groups and Coal Measures, and include the urban areas. The highest Ni concentrations are generally found where there has been human influence: downstream of the Coalburn and Glespin opencast coal mines; on the catchment boundary, around 15 km south-east from Motherwell, where there is a number of coal opencasts; and downstream of the Greengairs landfill.

River and estuary compositions

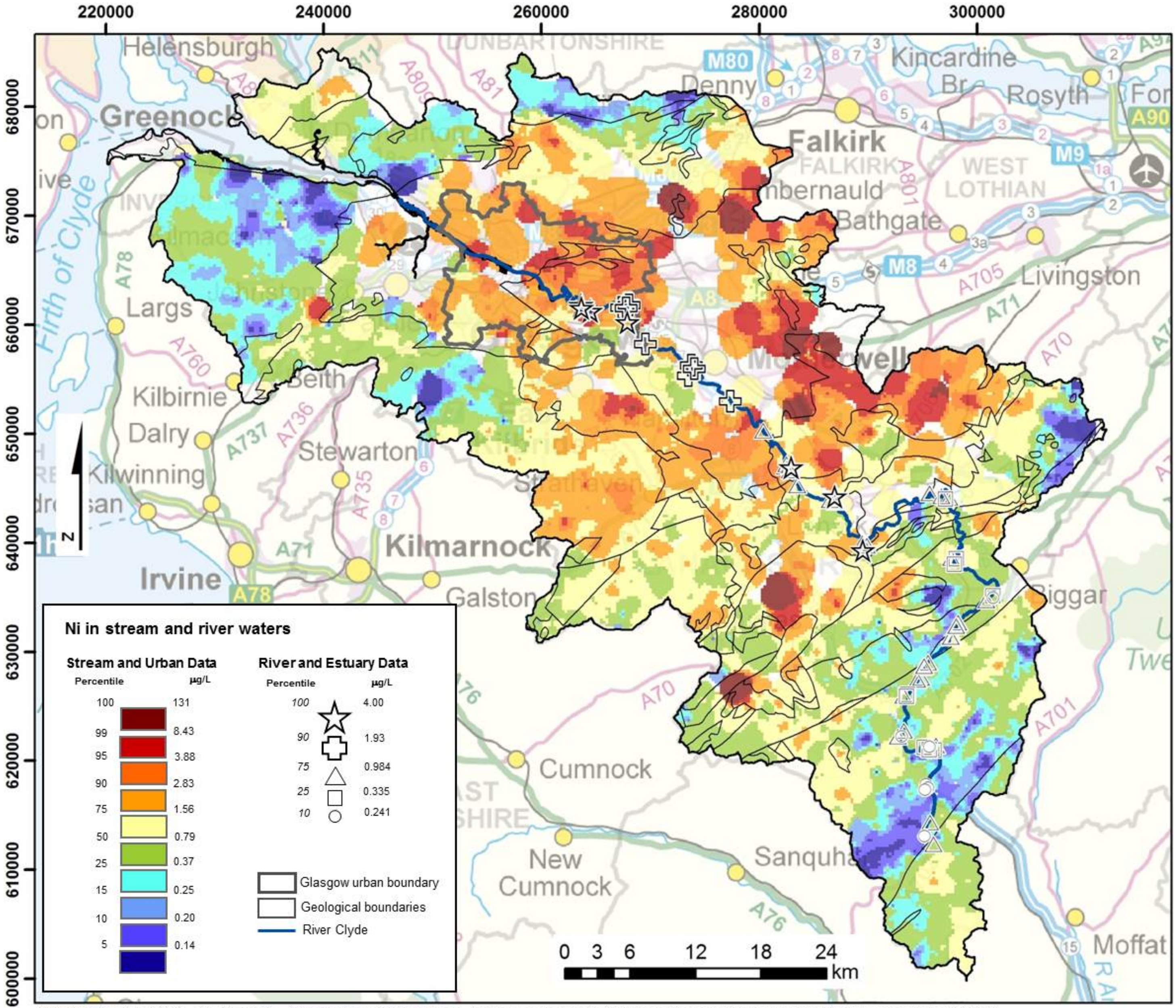
The concentrations of river water Ni in the upper reaches of the Clyde are relatively low (< 0.9 µg/L). Douglas Water, Auchenglen Burn, and Mouse Water, which drain areas affected by opencast coal mining, have high Ni concentrations (> 1.9 µg/L), but the Clyde's concentrations remain moderate until it enters the urban areas. Concentrations within waters of the Clyde and its tributaries are elevated upstream of Glasgow city centre, which are likely influenced by coal mining areas.

	Stream	River	Urban (µg/L)	Estuary
min	<0.1	0.15	<1	<5
25th %	0.349	0.326	1.74	
50th %	0.724	0.567	2.33	
75th %	1.41	0.942	3.43	
90th %	2.5	1.29	4.55	
max	131	4	7.4	3.22
n	1702	60	122	7
n cens	37	0	5	4
rainwater				
seawater	7			



Show location map

Nickel **Ni**



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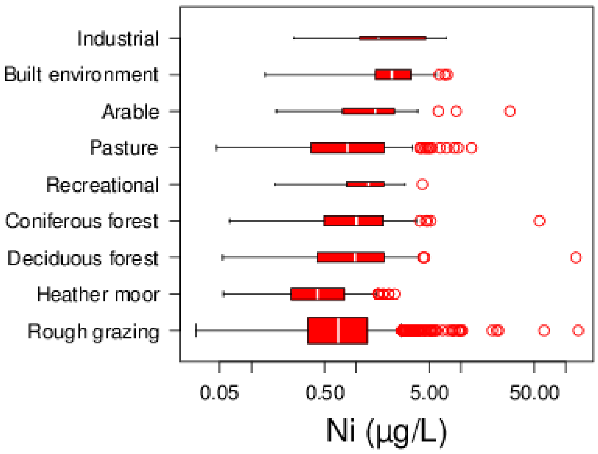
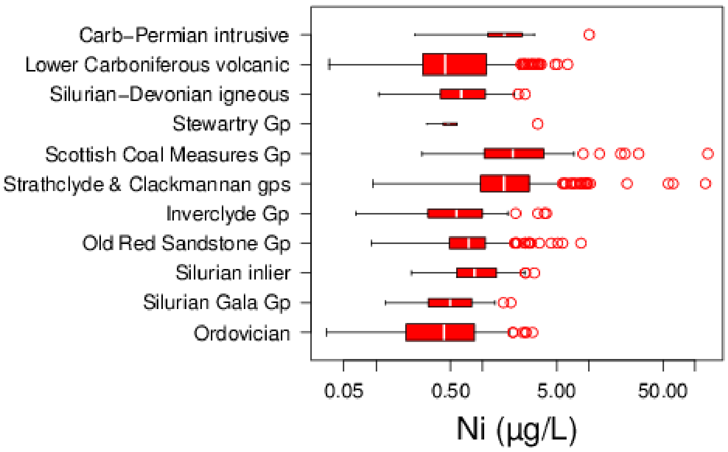




Phosphorus

P

Phosphorus is a non-metal and an important nutrient for plants and animals. Phosphorus occurs naturally in minerals, rocks and soils, but is also a constituent of many agricultural (NPK) fertilisers, manure, sewage, treated wastewater and industrial effluent. As a result, these anthropogenic sources can together contribute significantly to concentrations in the environment. The presence of anthropogenic phosphorus may be an important factor in the eutrophication of surface water.

The main phosphate mineral is apatite, which occurs in igneous and sedimentary rocks. Phosphorus also adsorbs strongly to metal (Fe, Al) oxides and to organic matter. The affinity of metal oxides for phosphate sorption is strongly pH-dependent, being greatest in acidic conditions. Phosphate has low solubility in water as a result of strong binding to minerals, but the principal form of dissolved P is orthophosphate (PO_4^{3-}). Protonated forms are dominated by $H_2PO_4^-$ or HPO_4^{2-}, depending on pH. Organic phosphate may be present either in dissolved or particulate forms.

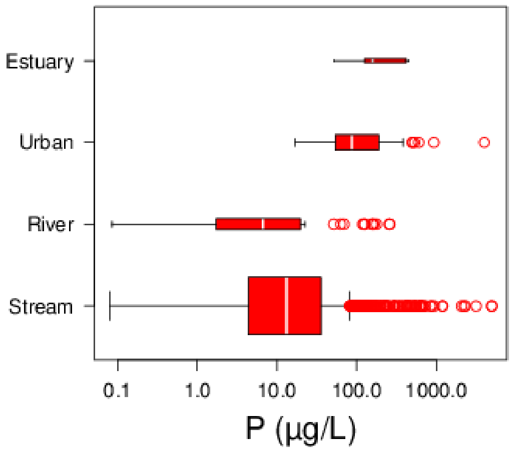
Streams and urban compositions

Distributions of stream-water phosphorus show a strong spatial trend in the Clyde catchment, with high concentrations notably a feature of the urban area of Glasgow. These streams are underlain by Scottish Coal Measure sediments, though some high values are also associated with the Strathclyde-Clackmannan groups, in the low-lying central part of the catchment. Concentrations of total P reach up to 5 mg/L. Many of the high-P occurrences are close to opencast coal works (e.g. Blantyre, Netherburn) and industrial areas (e.g. Rutherglen, Crookston, Kelvin). Anthropogenic sources are strongly implicated in the dissolved P-load of streams in the catchment, although a component of natural origin is also likely. Coal Measures are enriched in clays and organic matter, and likely to be relatively enriched in both organic and inorganic phosphorus. Urban contributions to stream water P concentrations from wastewater, effluent and sewage may be significant. One of the highest P clusters in the catchment occurs in association with the Greengairs landfill, suggesting that landfill leachate may contribute P to the local stream network. The distributions of high-P water may also be influenced by stream pH, as high concentrations tend to be present in areas with alkaline stream water. Lowest P concentrations are seen in streams on the western edge of the Clyde Plateau over rock types dominated by basaltic lava and tuff. Low values are also found in streams draining Ordovician–Silurian rocks to the south of the Southern Upland Fault.

River and estuary compositions

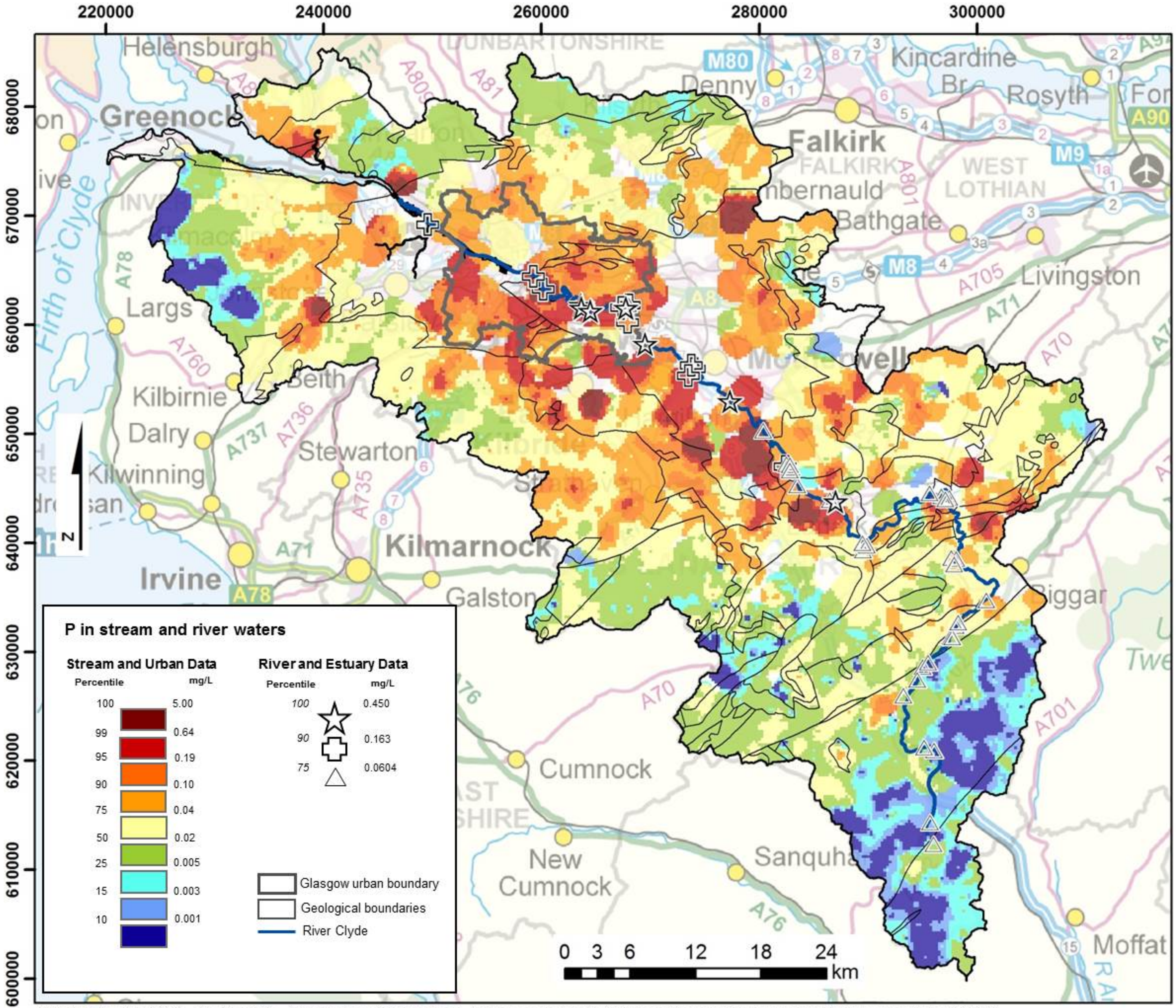
Highest P concentrations in the river waters occur in the estuary and urban stretch of the River Clyde, coincident with high values in the tributaries and contributing small-order streams. In line with stream concentrations, lowest values (< 0.06 µg/L) in the River Clyde are reported in the upland areas in the southern part of the catchment.

	Stream	River	Urban (µg/L)	Estuary
min	<10	<10	17	<70
25th %	4.39	1.77	54.5	125
50th %	13.3	6.63	86.9	160
75th %	35.7	19.8	189	420
90th %	76.9	129	316	438
max	5000	262	4020	450
n	1702	60	122	7
n cens	727	44	0	1
rainwater	12			
seawater	90			



Show location map

Phosphorous **P**



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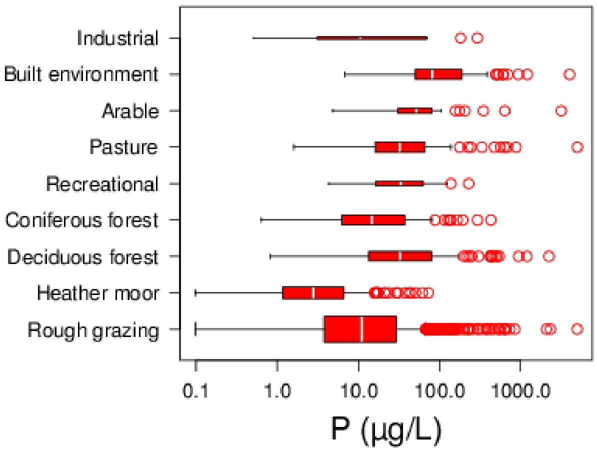
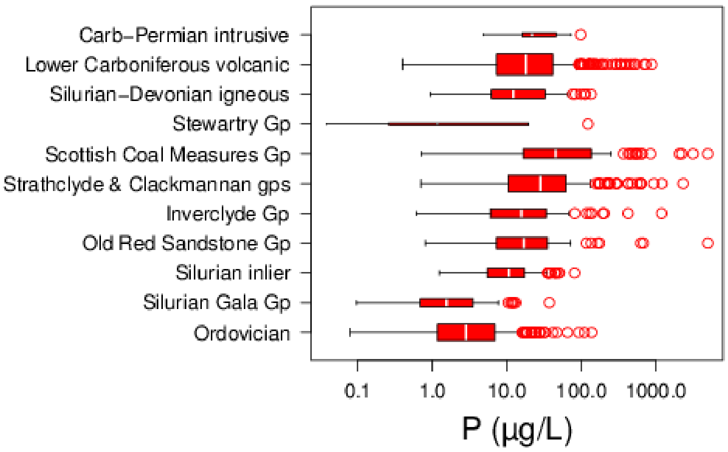




Lead Pb

Lead (Pb) is a toxic element which can affect aquatic organisms at relatively low concentrations. It is commonly found as a trace constituent in rocks, soil, water and air. The natural sources of lead are ore minerals such as galena as well as sulphate, carbonate and chloride minerals. In addition lead is widely dispersed in sedimentary rocks although its natural mobility is low, owing to the low solubility of Pb minerals (Hem, 2005). Lead is most soluble in stream waters at pH values <6. Adsorption to stream sediments, in particular Fe and Mn oxides, tends to maintain low concentrations in surface waters (Drever, 1997). Humans have modified the Pb cycle, most notably with the release of tetraethyl Pb from vehicle exhausts, the release in the smelting of ores, and burning coal. Emissions from these activities have decreased over the last few decades, but human sources of Pb can cause locally enhanced concentrations of stream water Pb (BGS, 1999; MacKinnon et al., 2011).

Streams and urban compositions

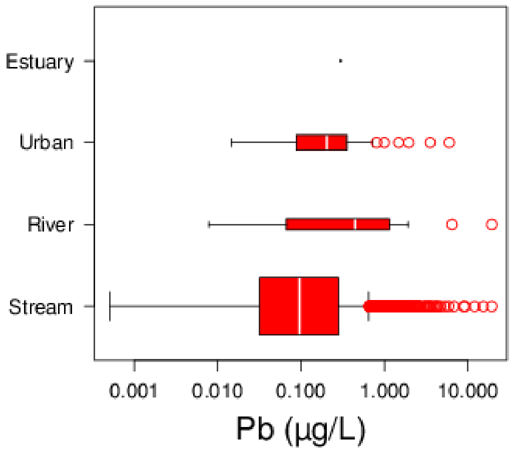
Within the Clyde catchment there is a strong correlation between the spatial distribution of stream-water Pb and pH. The lowest concentrations of Pb in stream waters (< 0.05 µg/L) are generally found in the lower lying rural areas of the catchment, in the south-east of the catchment, on the south-facing slopes of the Pentland Hills and around the Kilsyth Hills. These correspond to areas of high pH, where Pb mobility is low. There is little correlation to geology: the lowest median concentration is within streams draining the Ordovician Leadhills Supergroup. However, the highest concentrations of Pb in stream waters (> 3.4 µg/L) are found in the Leadhills area, which has an abundance of Pb-Zn mineral veins that have been mined in the past. The wealth of reactive Pb-mineral surfaces and low pH of the stream waters, mean that there is a ready source of Pb, and conditions favour the element being kept in solution in its most mobile form: Pb^{2+}.

Higher concentrations of Pb are generally found in streams around the periphery of the catchment, and in the Tinto Hill area. These streams have lower pH and coincide with mapped occurrences of peat, heather moorland, coniferous forest, or to a lesser extent rough grazing. Low pH values correlate with high concentrations of dissolved organic carbon (DOC), reflecting the abundance of organic acids in the stream water, as well as paucity of buffering carbonate minerals in these areas. High Pb concentrations are also present around the city of Glasgow, indicating the influence of anthropogenic Pb sources.

River and estuary compositions

The concentrations of Pb in river water are relatively low in the upper reaches of the Clyde catchment. The highest concentration is reported in Glengonnar Water (19.4 µg/L), which drains the Leadhills mining area. The concentrations of Pb in the Clyde are elevated immediately downstream of the junction with this tributary, and remain high (>75th percentile) for approximately 20 km downstream, until there is sufficient dilution from tributaries with low Pb concentrations. Downstream of Lanark, the concentrations in the Clyde and its tributaries are similar to those upstream of Leadhills.

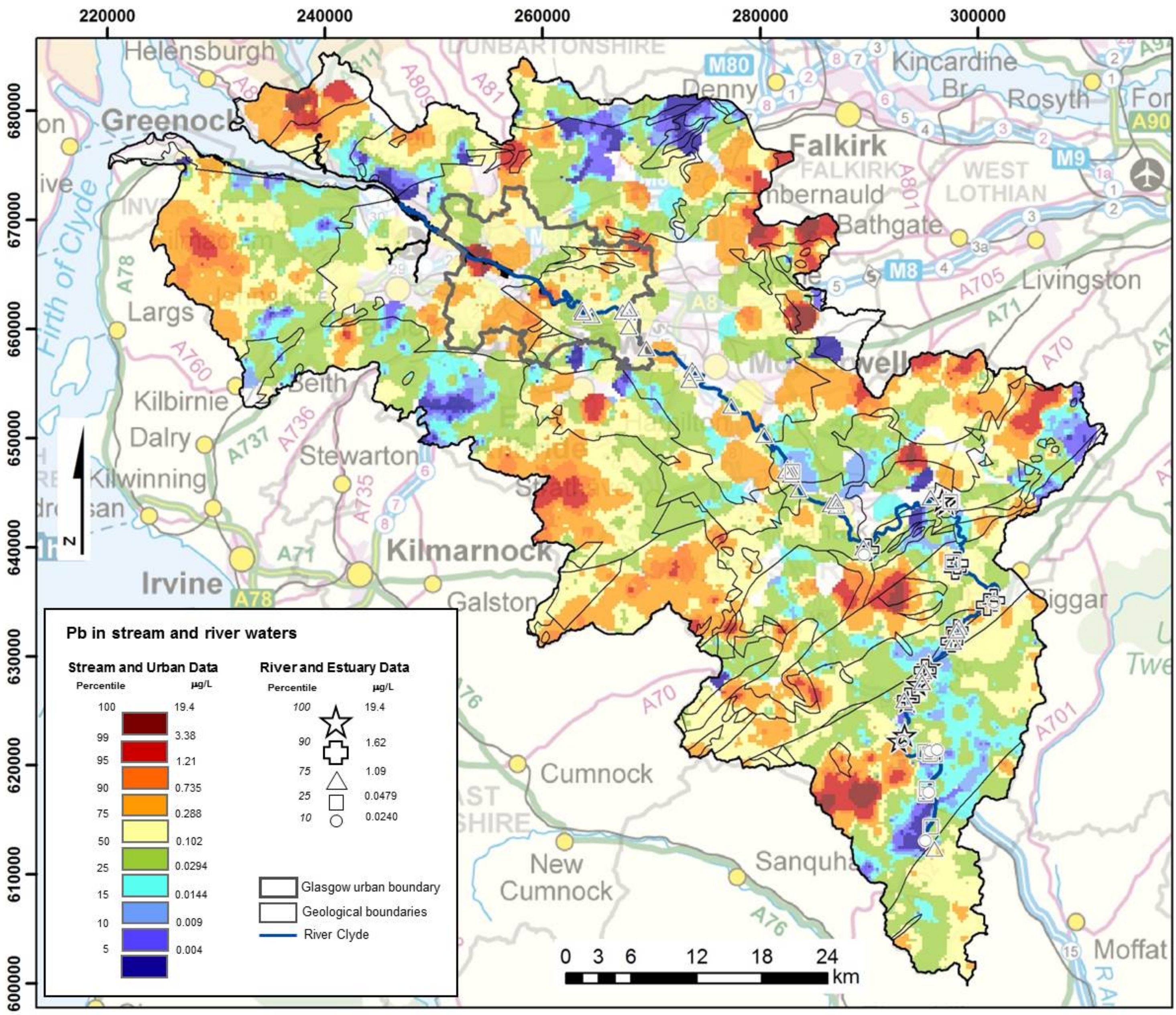
	Stream	River	Urban (µg/L)	Estuary
min	<0.05	<0.05	<0.2	<1
25th %	0.031	0.067	0.089	
50th %	0.096	0.449	0.205	
75th %	0.28	1.15	0.352	
90th %	0.754	1.63	0.507	
max	19.4	19.4	6	0.31
n	1702	60	122	7
n cens	617	16	60	4
rainwater				
seawater	0.03			

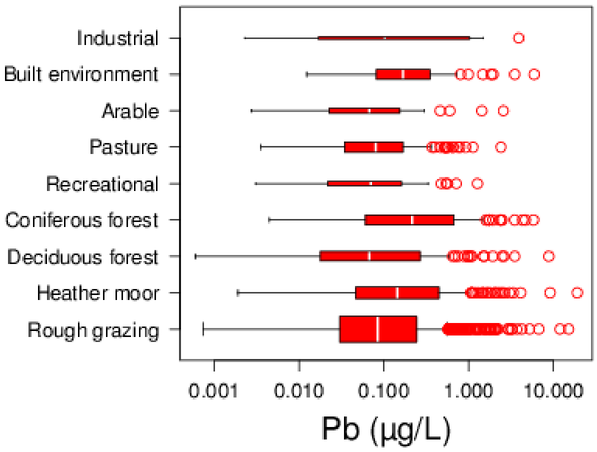


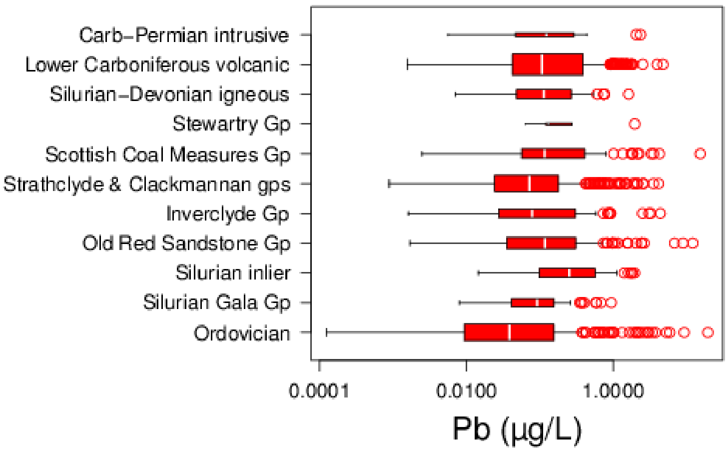
Show location map

Lead

Pb


220000
240000
260000
280000
300000
680000
670000
660000
650000
640000
630000
620000
610000
600000
Pb in stream and river waters
Stream and Urban Data
Percentile
µg/L
100 19.4
99 3.38
95 1.21
90 0.735
75 0.288
50 0.102
25 0.0294
15 0.0144
10 0.009
5 0.004
River and Estuary Data
Percentile
µg/L
100 19.4
90 1.62
75 1.09
25 0.0479
10 0.0240
Glasgow urban boundary
Geological boundaries
River Clyde
0 3 6 12 18 24 km
N
Helensburgh
Greenock
Largs
Kilbirnie
Dalry
Kilwinning
Irvine
Stewarton
Kilmarnock
Galston
Cumnock
New Cumnock
Sanquhar
Moffat
Biggar
Falkirk
Denny
Kincardine Br
Rosyth
Bathgate
Livingston
WEST LOTHIAN
DUNBARTONSHIRE
Firth of Clyde


Industrial
Built environment
Arable
Pasture
Recreational
Coniferous forest
Deciduous forest
Heather moor
Rough grazing
0.001
0.010
0.100
1.000
10.000
Pb (µg/L)


Carb−Permian intrusive
Lower Carboniferous volcanic
Silurian−Devonian igneous
Stewartry Gp
Scottish Coal Measures Gp
Strathclyde & Clackmannan gps
Inverclyde Gp
Old Red Sandstone Gp
Silurian inlier
Silurian Gala Gp
Ordovician
0.0001
0.0100
1.0000
Pb (µg/L)

Strontium Sr

Strontium is an alkaline earth metal that shares several characteristics with Ca and so behaves in a similar way in the environment and natural waters. Strontium is present as a significant trace metal in calcite, dolomite and gypsum. These are present in sedimentary rocks or, in the case of gypsum, can occur as a replacement of oxidised sulphide minerals. The carbonate mineral, strontianite, or the sulphate mineral, celestite may also be present in sediments or sedimentary rocks. Silicate minerals that can contain Sr include calcic plagioclase, pyroxenes and clays. Like Ca, Sr can be involved in ion-exchange and sorption reactions and may be released during weathering and diagenesis. Strontium occurs as the divalent cation (Sr^{2+}) in solution.

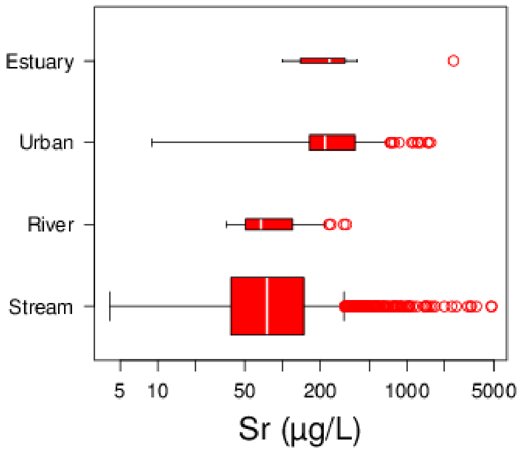
Streams and urban compositions

Concentrations of Sr in stream waters show a similar spatial pattern to that of Ca, with highest values observed in the low-lying central part of the Basin. High concentrations (> 294 µg/L) are a feature of streams draining the Strathclyde-Clackmannan and Scottish Coal Measures sedimentary rocks and thus within land-uses classed as built environment. Stream waters in the urban centre of Glasgow and the industrial area around Rutherglen have high Sr values. Locally high concentrations occur around opencast coal workings at Coalburn, Mollinsburn, Newarthill, Greengairs, Airdrie and Tarbrax. Anomalously high concentrations (up to 4800 µg/L) are also seen in streams draining Inverclyde Group sedimentary rocks north of Dumbarton in the north-western part of the catchment. The mapped geological unit corresponding with this anomaly is specified as the Ballagan Formation, a mudstone unit with ferroan dolomite and gypsum. This unit also accounts for relatively high concentrations of Sr reported in the rough grazing land-use type, which predominates in this area. Relatively low Sr concentrations (< 41 µg/L) are reported in streams draining the Clyde Plateau Volcanic Formation and Ordovician–Silurian rocks to the south of the Southern Upland Fault. These distributions likely represent a combination of dilution by rainfall, reduced mobility of Sr from mafic igneous and metasedimentary rocks and, in the case of the Ordovician-Silurian rocks, smaller solid-phase contents of Sr (reflected by reduced content of Sr in surface soils; Fordyce et al., 2017).

River and estuary compositions

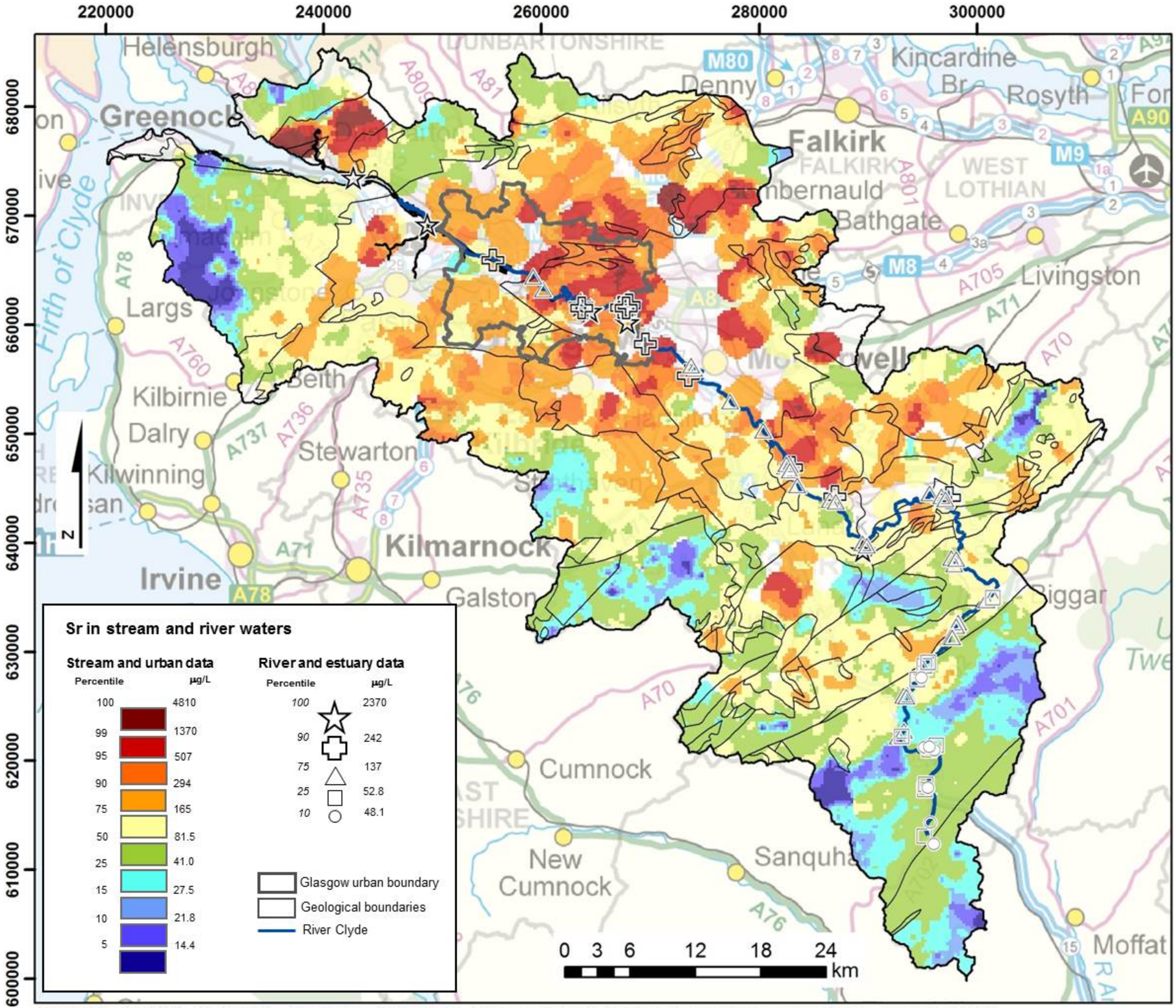
Strontium concentrations in the River Clyde water samples are lowest in the upper, southern part of the catchment (< 53 µg/L), in line with the lower concentrations reported in streams. Concentrations increase downstream as Sr-bearing tributaries enter the main River Clyde channel. Concentrations remain high in the urban conurbation and downstream into the estuary section of the river where they are influenced by mixing with sea water that is naturally enriched in Sr.

	Stream	River	Urban	Estuary
		(µg/L)		
min	4.13	35.8	8.97	100
25th %	38.5	50.9	166	150
50th %	75.7	67.5	220	240
75th %	149	118	381	280
90th %	255	173	731	991
max	4810	326	1550	2370
n	1702	60	122	8
n cens	0	0	0	0
rainwater				
seawater	8000			



Show location map

Strontium Sr



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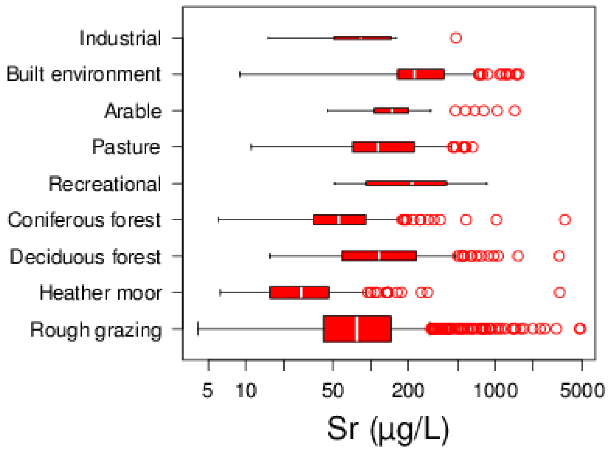
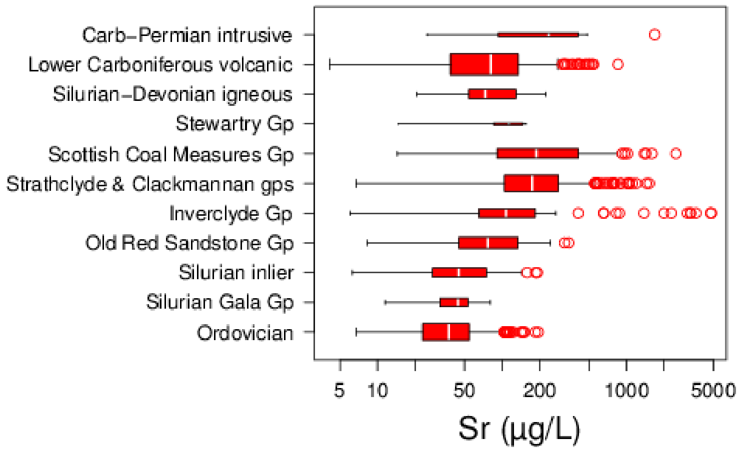




Uranium U

Uranium exists in nature in its VI or IV oxidation states depending on ambient redox conditions. Natural sources of uranium in the environment include U minerals such as uraninite (UO_2), and the partly oxidised pitchblende (U_3O_8), although these are relatively rare in nature and generally restricted to mineralised veins and granitic rocks. Uranium also partitions strongly with phosphate minerals as well as with iron oxides and organic matter. As a result, iron-oxide-rich rocks and mudstones, especially black shales, are also relatively enriched in U. Sorption to iron oxides and phosphate minerals is pH-dependent, and favoured in acidic conditions. Anthropogenic sources of U in the environment include phosphate-bearing fertilisers.

In water, U is mobile in the oxidised U(VI) state, but immobile in the U(IV) state, where it partitions strongly with iron oxides, clays and organic matter. Uranium in water is usually complexed (Langmuir, 1978) and pH and pCO_2 have important controls on its mobility. In oxidising conditions at pH less than around 5, uranyl, UO_2^{2+}, is usually the dominant dissolved form of U(VI). At higher pH, the uranyl ion forms stable complexes with carbonate ions, notably $UO_2(CO_3)_2^{2-}$ and at higher pH, $UO_2(CO_3)_3^{4-}$. Uranium mobility in solution is; therefore, largely a function of pH, redox and dissolved carbonate concentrations, although underlying source U content is important also.

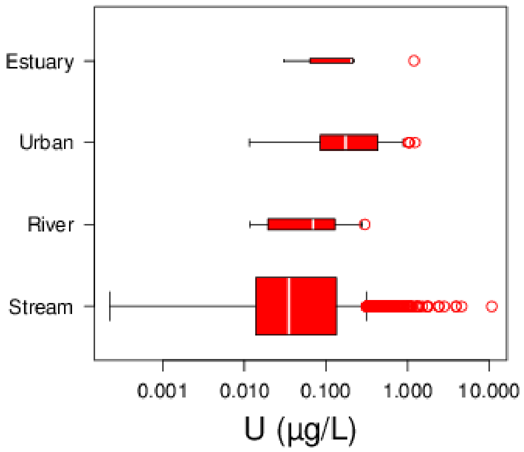
Streams and urban compositions

Stream waters with the notably lowest concentrations of U (< 0.009 µg/L) occur in the upland areas of the north-west and in the northern part of the catchment. These correlate closely with the outcrop of the Clyde Plateau Volcanic Formation, a lithology dominated by basalt, which is generally recognised to have low U contents. These also correspond to areas of peat in the north-west of the Basin, which are also among the most acidic waters, and so U is likely to be immobilised through sorption to mineral surfaces. Some of the lowest concentrations are observed also in streams draining Ordovician–Silurian rock types to the south of the Southern Upland Fault. By contrast, some of the highest dissolved U concentrations (up to 11 µg/L) are observed in streams over Old Red Sandstone rock types. These red beds contain a relative abundance of U in association with phosphate minerals and iron-oxide coatings. Relative highs are also observed in waters draining the Scottish Coal Measures Group. Here, organic-rich and clay-rich deposits occur and dissolved carbonate (alkalinity) is relatively high. Streams overlying the Inverclyde Group (Ballagan Formation) to the north of the Clyde estuary also have high concentrations, likely originating from dolomite or gypsum. Bedrock geology appears to have the strongest control on U distribution in the stream water network.

River and estuary compositions

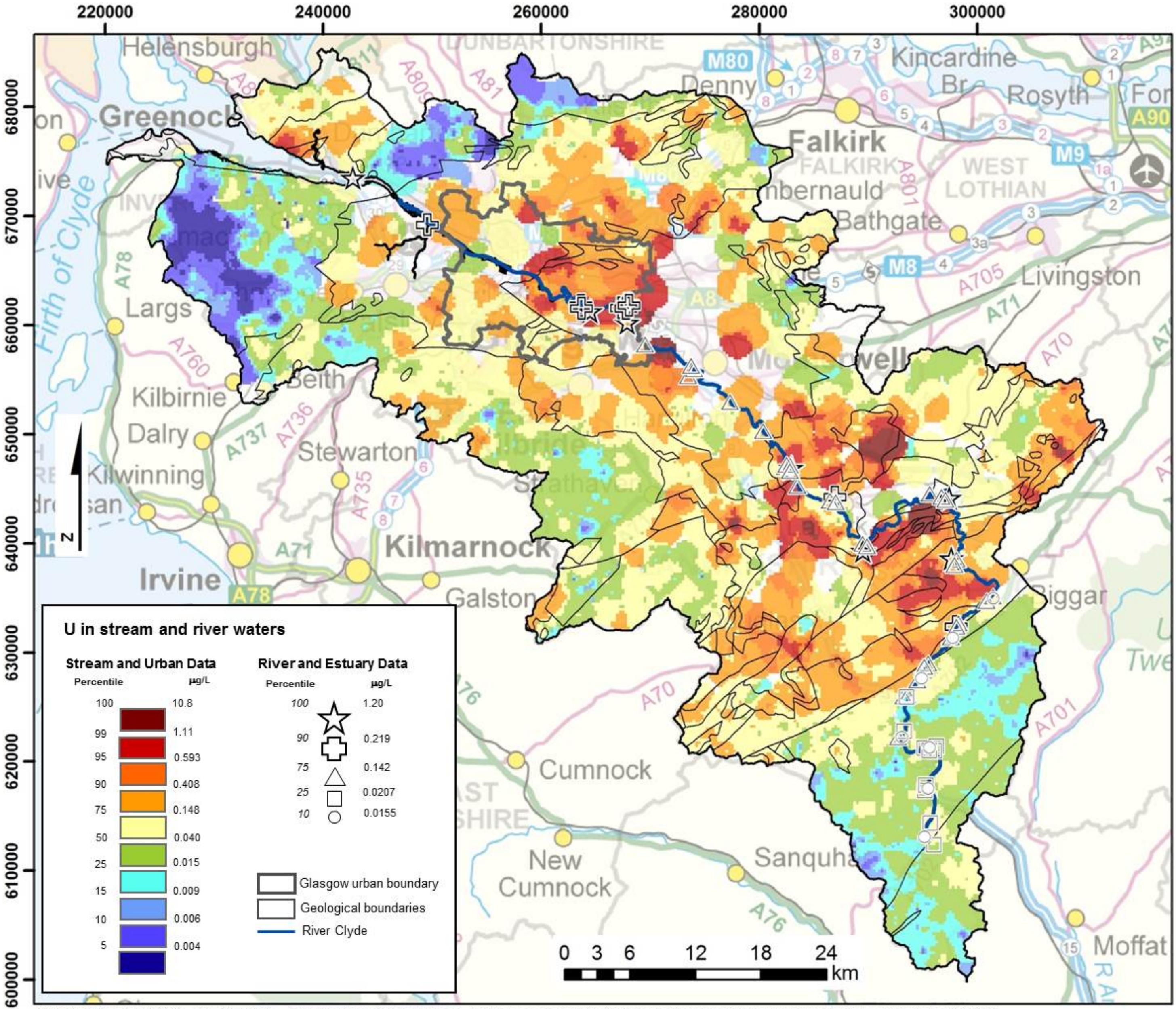
River Clyde water U-composition reflects inputs from contributing tributaries, and is highest in the central part of the catchment where bedrock is dominated by Old Red Sandstone and the Coal Measures. Concentrations are lowest in the upper catchment to the south (usually <0.1 µg/L). Estuary waters display variable concentrations, but typically <0.5 µg/L.

	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.003	0.0118	<0.02	<0.1
25th %	0.0138	0.0196	0.085	0.0694
50th %	0.035	0.0702	0.173	0.205
75th %	0.134	0.128	0.424	0.212
90th %	0.379	0.205	0.696	0.514
max	10.8	0.299	1.24	1.2
n	1702	60	122	8
n cens	75	0	1	3
rainwater				
seawater	3.3			



Show location map

Uranium U



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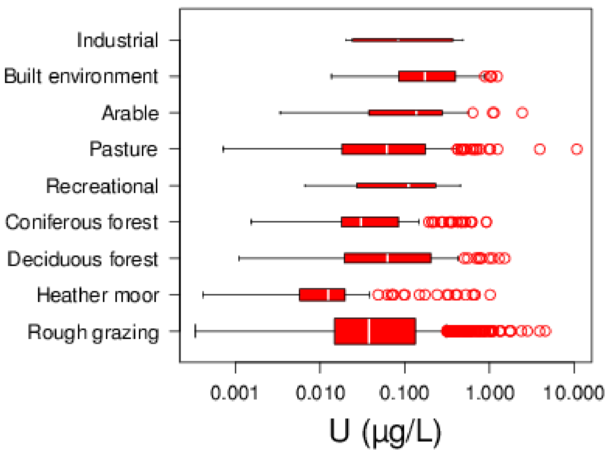
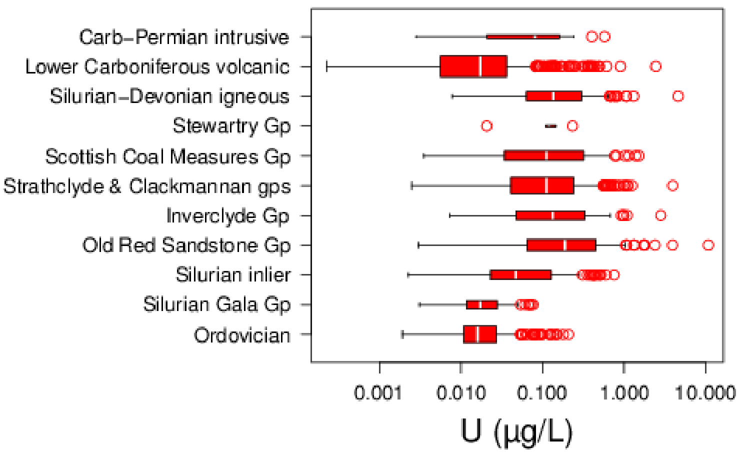




Zinc Zn

Zinc is a chalcophile element, which has one oxidation state, Zn^{2+}; hence, it is insensitive to redox reactions. In stream waters Zn tends to exist as soluble Zn^{2+} below pH 7.5, as insoluble smithsonite ($ZnCO_3$) in the range pH 7.5-8, and as sparingly soluble $Zn(OH)_2$ at pH values >8. Reactions of Zn with mineral surfaces and organic matter may limit Zn stream water concentrations, meaning concentrations can often be lower than predicted by solubility calculations (BGS, 1999). Naturally occurring zinc is found in ore deposits, occurring in sphalerite (ZnS). It is also found in a range of secondary carbonates and oxides, and as a trace constituent in various common minerals including calcite, iron oxides and silicate minerals. Zinc is used as an anticorrosion coating, as a constituent of brass, as a white pigment, and in the manufacture of batteries. As a result, Zn is widely dispersed in the natural environment (Shand et al., 2007).

Streams and urban compositions

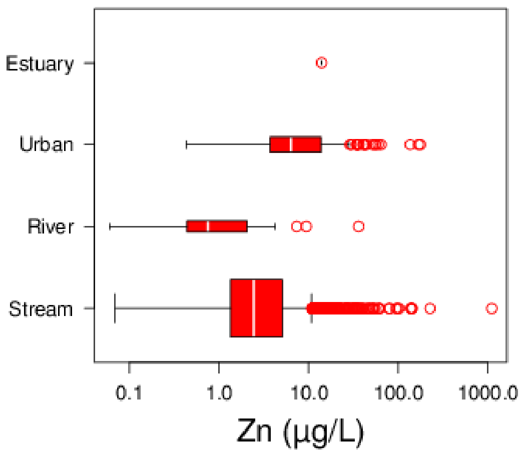
Zinc in Clyde Basin stream water is correlated to pH and land-use. The lowest concentrations of Zn (< 0.7 µg/L) are found in areas where the pH is >7.5. This includes areas within the Lowther Hills south of Leadhills, and around the Kilsyth Hills and Campsie Fells in the north of the catchment. These are remote areas, which would unlikely be affected by anthropogenic Zn, and where the stream water pH limits the mobility of geogenic Zn.

Moderately high concentrations of Zn are found in streams that have relatively low pH (<7), indicating Zn would most likely exist as free Zn^{2+}. These areas are generally on the periphery of the catchment and coincide with mapped occurrences of peat, where heather moorland, coniferous forest, or to a lesser extent, rough grazing predominate. Highest stream-water Zn concentrations (> 59 µg/L) are reported around the city of Glasgow and other urbanised areas, and in proximity to coal mining areas, such as Coalburn, and Larkhall, indicating anthropogenic influences.

River and estuary compositions

The concentrations of river water Zn are relatively low (< 0.5 µg/L) in the upper reaches of the Clyde catchment. The highest concentration is found in Glengonnar Water (36.2 µg/L), which drains the Leadhills Pb-Zn mining area. Former mining activity is likely to have exposed and weathered reactive mineral surfaces, releasing Zn. The concentration of Zn in River Clyde water is elevated immediately downstream of the junction with this tributary. Zinc concentrations within the Clyde remain relatively high for approximately 10 km downstream, until there is sufficient dilution from other tributaries. Between Lanark and Glasgow the concentrations in the Clyde and its tributaries remain relatively low (< 2.10 µg/L). In Glasgow the Zn concentrations in the Clyde increase, owing to the prevalence of Zn in the urban environment.

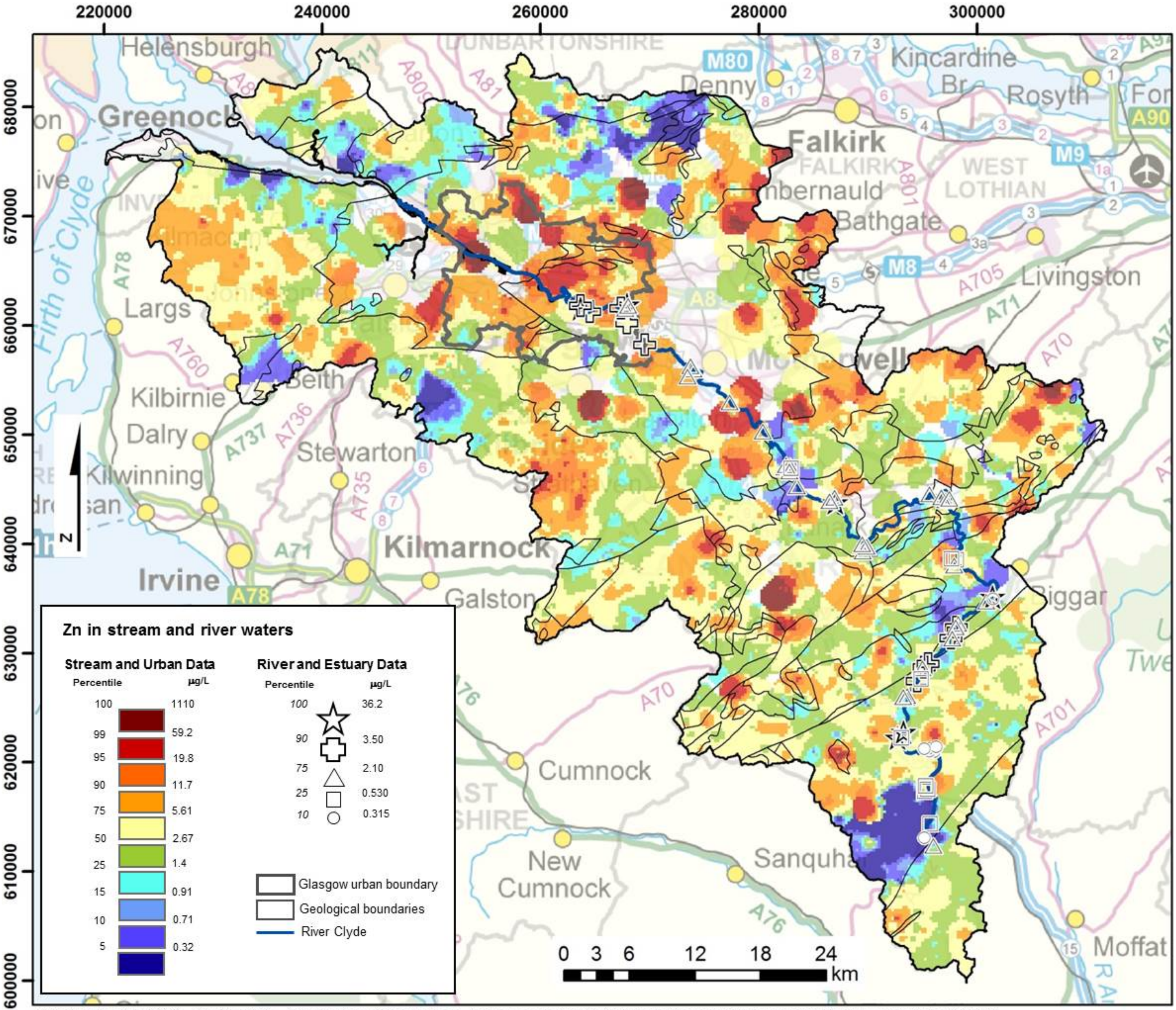
	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.5	<0.5	<2	<7
25th %	1.34	0.483	3.74	
50th %	2.44	0.757	6.33	
75th %	5.13	2.05	13.7	
90th %	10.3	3.01	36.4	
max	1110	36.2	177	14
n	1702	60	122	7
n cens	127	15	9	4
rainwater				
seawater	10			



Show location map

Zinc

Zn



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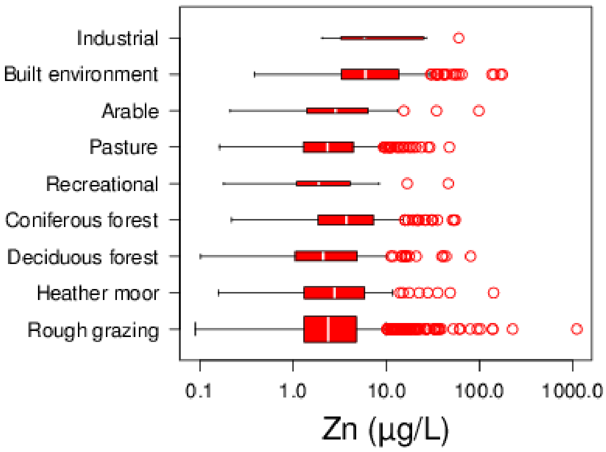
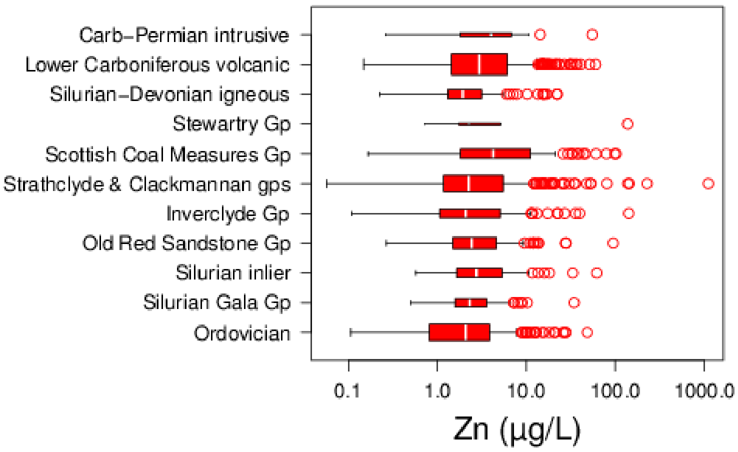
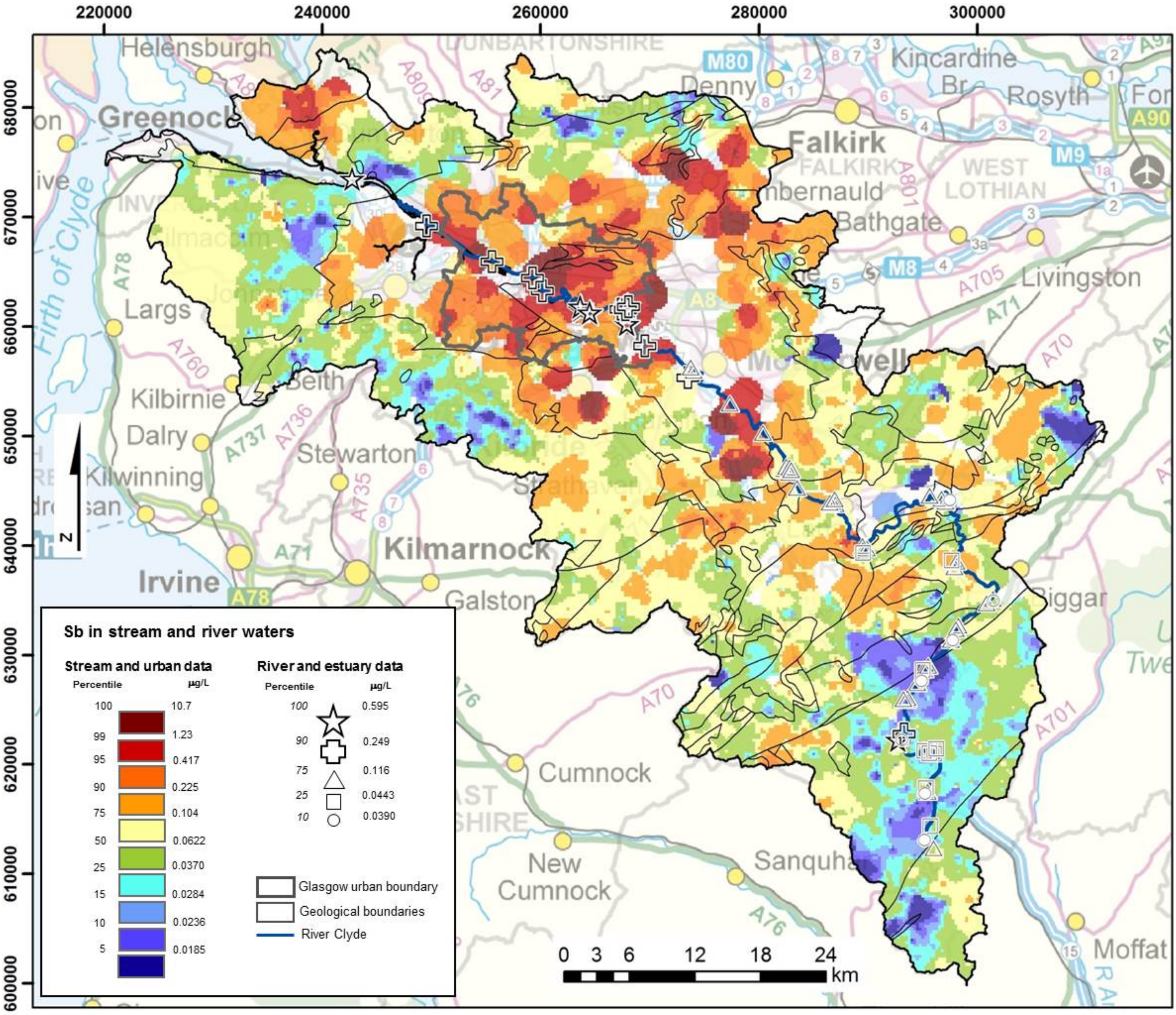




Appendix 1 Other trace-element maps

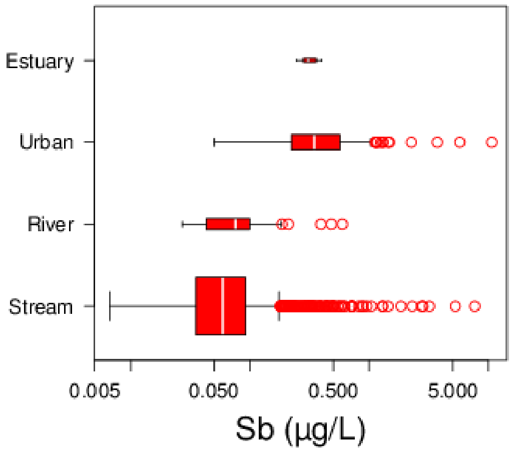
In this section maps, summary statistics and box plots are presented for the remaining elements analysed.

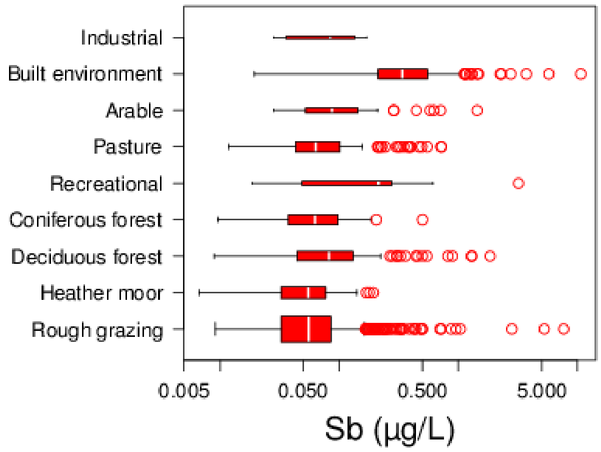
Antimony **Sb**

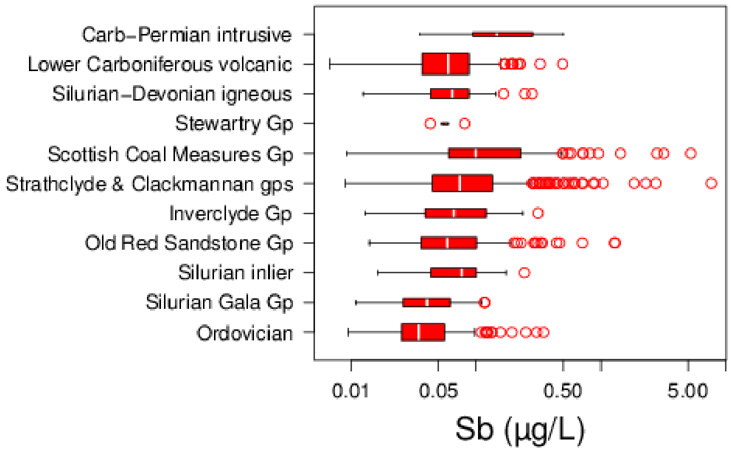

Sb in stream and river waters
Stream and urban data
Percentile µg/L
100 10.7
99 1.23
95 0.417
90 0.225
75 0.104
50 0.0622
25 0.0370
15 0.0284
10 0.0236
5 0.0185
River and estuary data
Percentile µg/L
100 0.595
90 0.249
75 0.116
25 0.0443
10 0.0390
Glasgow urban boundary
Geological boundaries
River Clyde
0 3 6 12 18 24 km
N
220000
240000
260000
280000
300000
680000
670000
660000
650000
640000
630000
620000
610000
600000
Helensburgh
Greenock
Firth of Clyde
Largs
Kilbirnie
Dalry
Kilwinning
Irvine
Stewarton
Kilmarnock
Galston
Cumnock
New Cumnock
Sanquhar
Moffat
Biggar
Falkirk
Cumbernauld
Bathgate
Livingston
Denny
Kincardine
Rosyth
Motherwell
Beith
Strathaven
WEST LOTHIAN
FALKIRK
DUNBARTONSHIRE
M80
M8
M9
A90
A78
A760
A737
A736
A735
A71
A70
A76
A701
A705
A801
A81
A809
A8
A77

Antimony Sb

	Stream	River	Urban (µg/L)	Estuary
min	0.00669	0.0272	0.0503	<0.25
25th %	0.0352	0.043	0.223	0.28
50th %	0.0589	0.0758	0.348	0.308
75th %	0.0918	0.0987	0.567	0.36
90th %	0.147	0.178	1.12	0.388
max	7.68	0.595	10.7	0.4
n	1702	60	122	7
n cens	0	0	0	4
rainwater				
seawater	0.3			

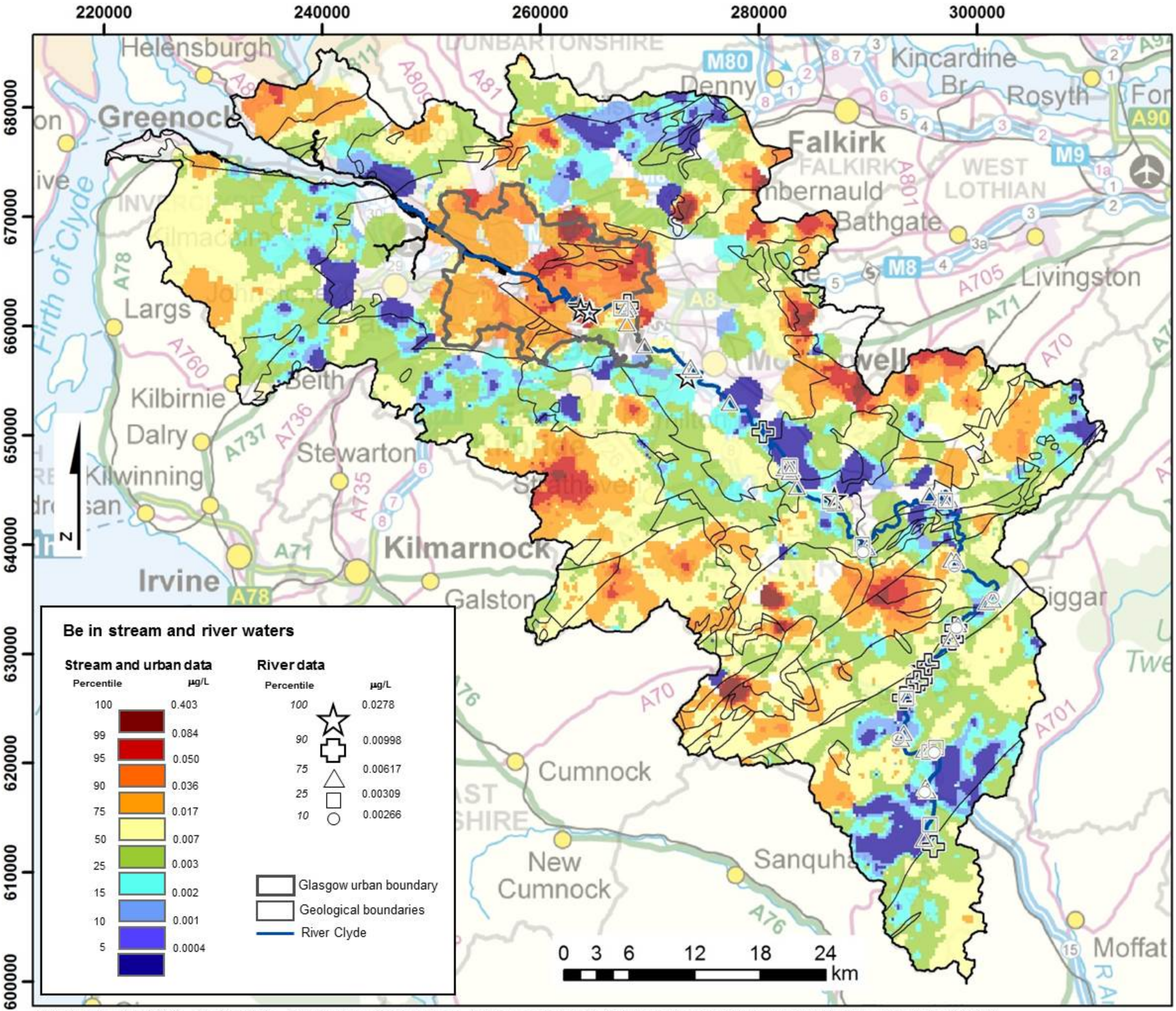






Beryllium

Be



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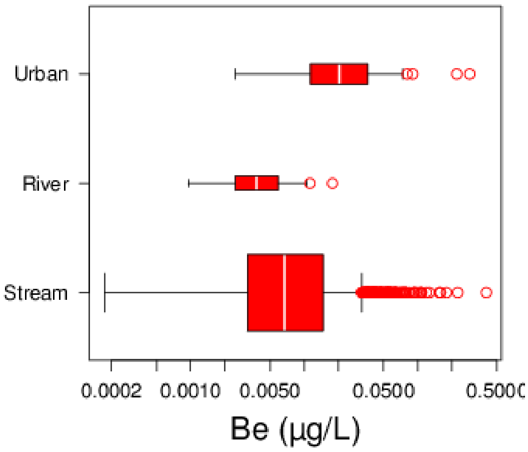
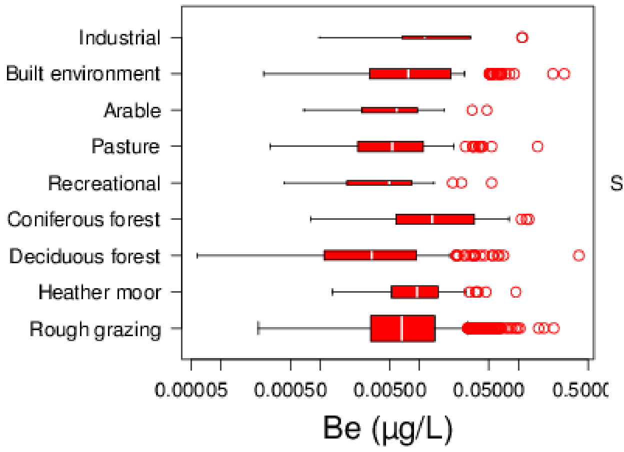
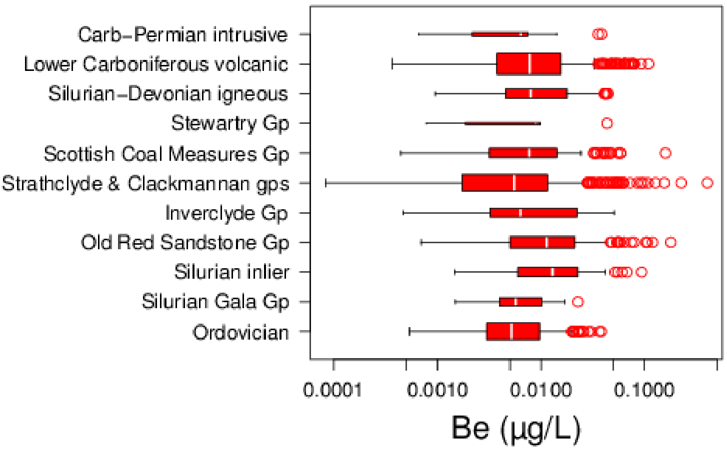
Beryllium

Be

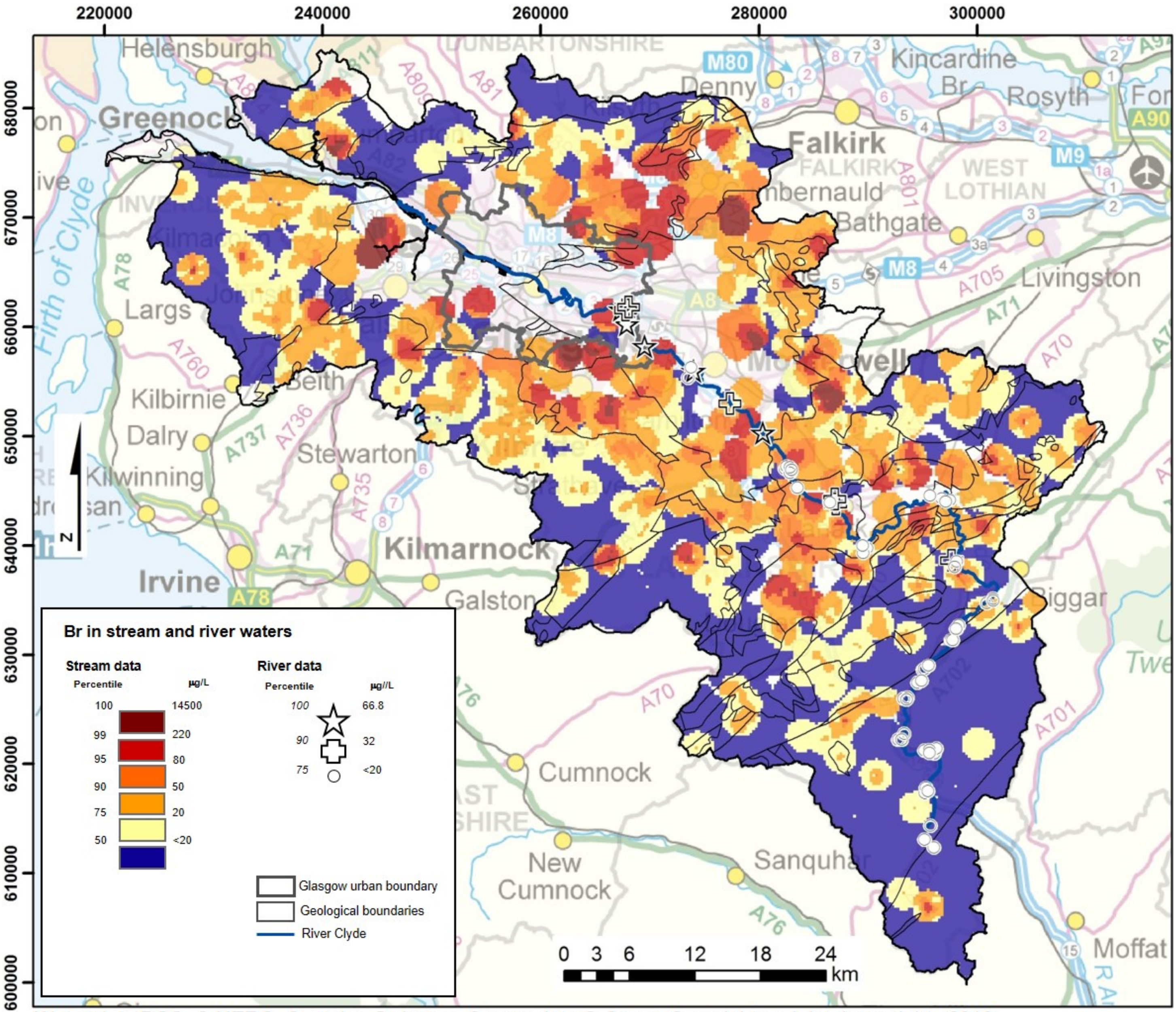
	Stream	River	Urban (µg/L)	Estuary
min	<0.005	<0.005	<0.05	<0.05
25th %	0.00316	0.0025	0.0114	
50th %	0.00666	0.0038	0.0204	
75th %	0.0148	0.00585	0.0363	
90th %	0.0291	0.00869	0.0591	
max	0.403	0.0178	0.287	<0.05
n	1702	60	122	8
n cens	684	40	96	8
rainwater				
seawater				







Bromide **Br**



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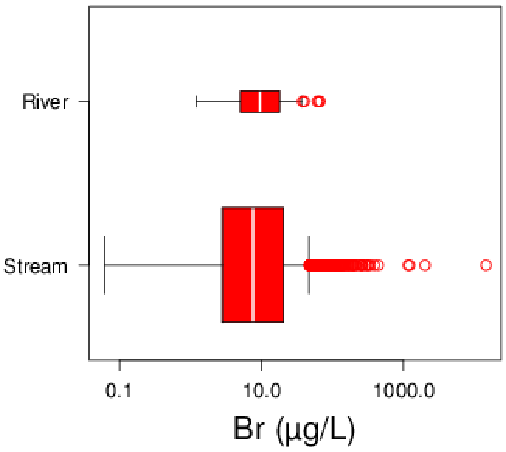
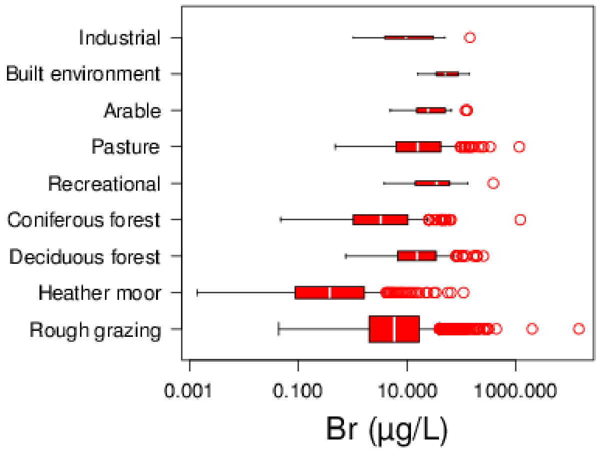
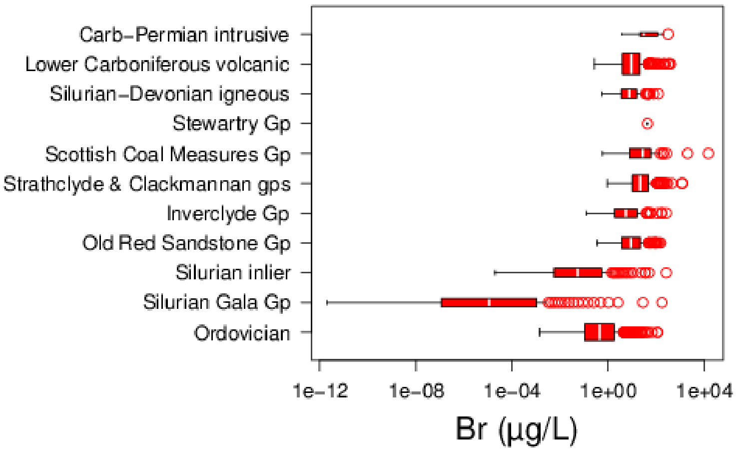
Bromide

Br

	Stream	River	Urban (µg/L)	Estuary
min	<20	<20	No data	No data
25th %	2.81			
50th %	7.63			
75th %	20.4			
90th %	50			
max	14500	66.8		
n	1702	60		
n cens	1286	48		
rainwater				
seawater	67000			

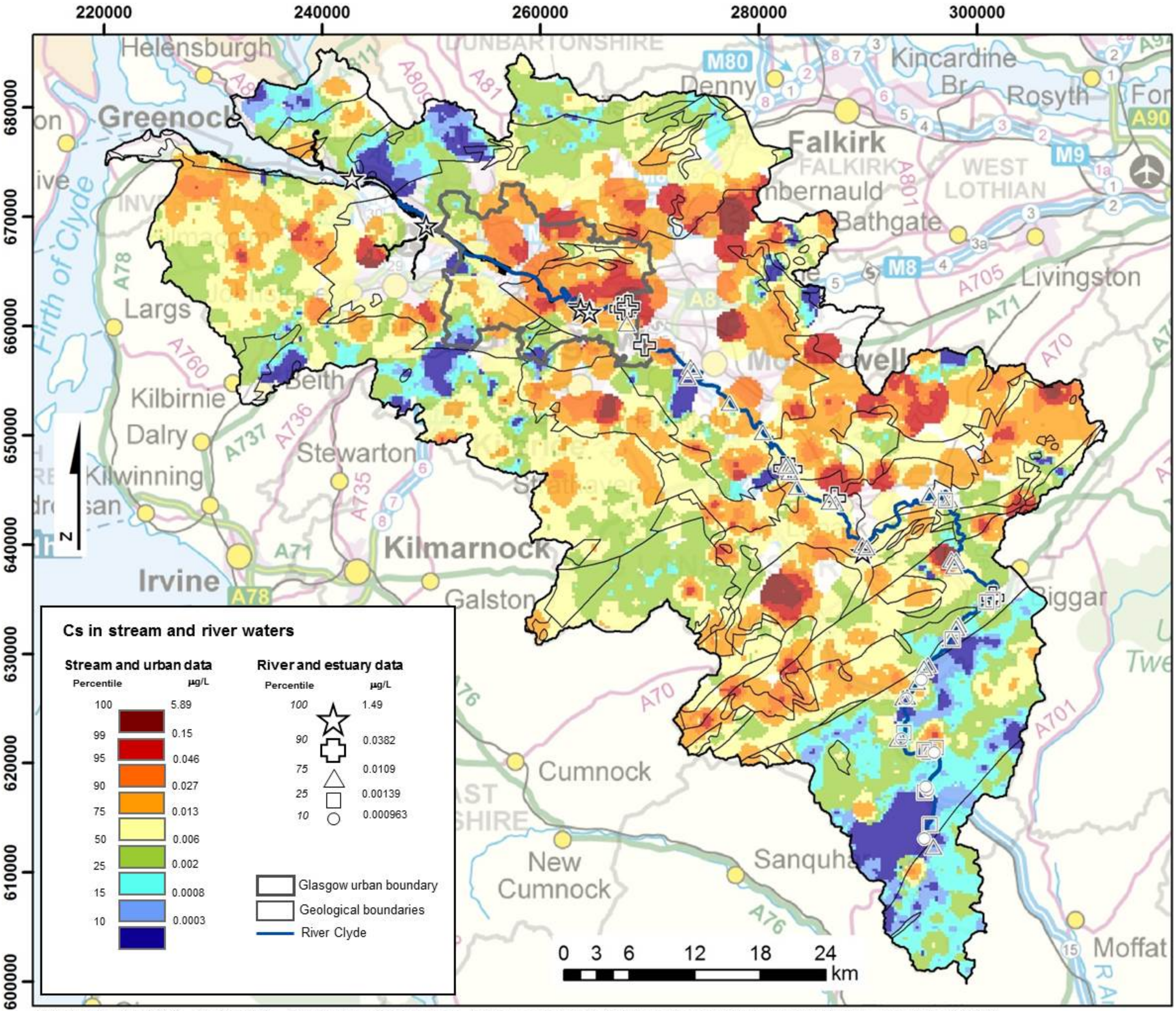






Caesium

Cs



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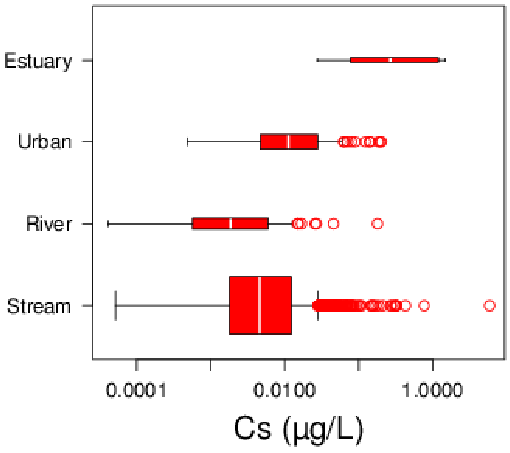
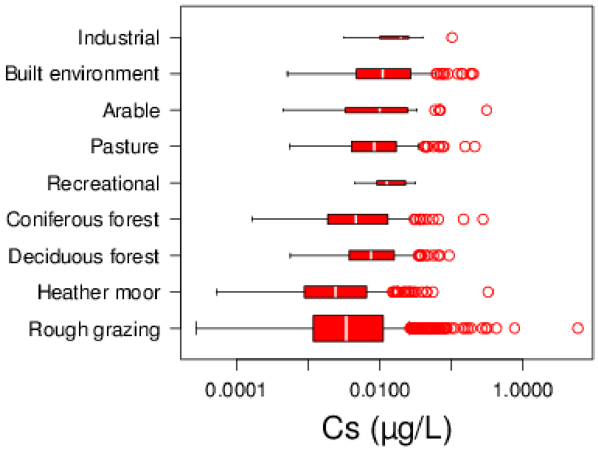
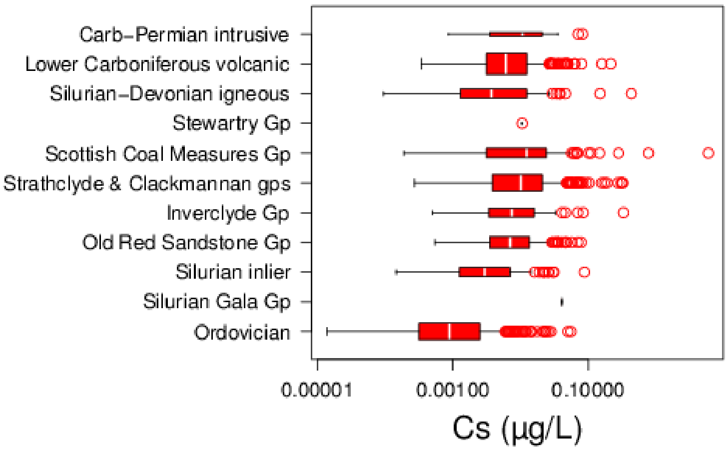
Caesium   Cs

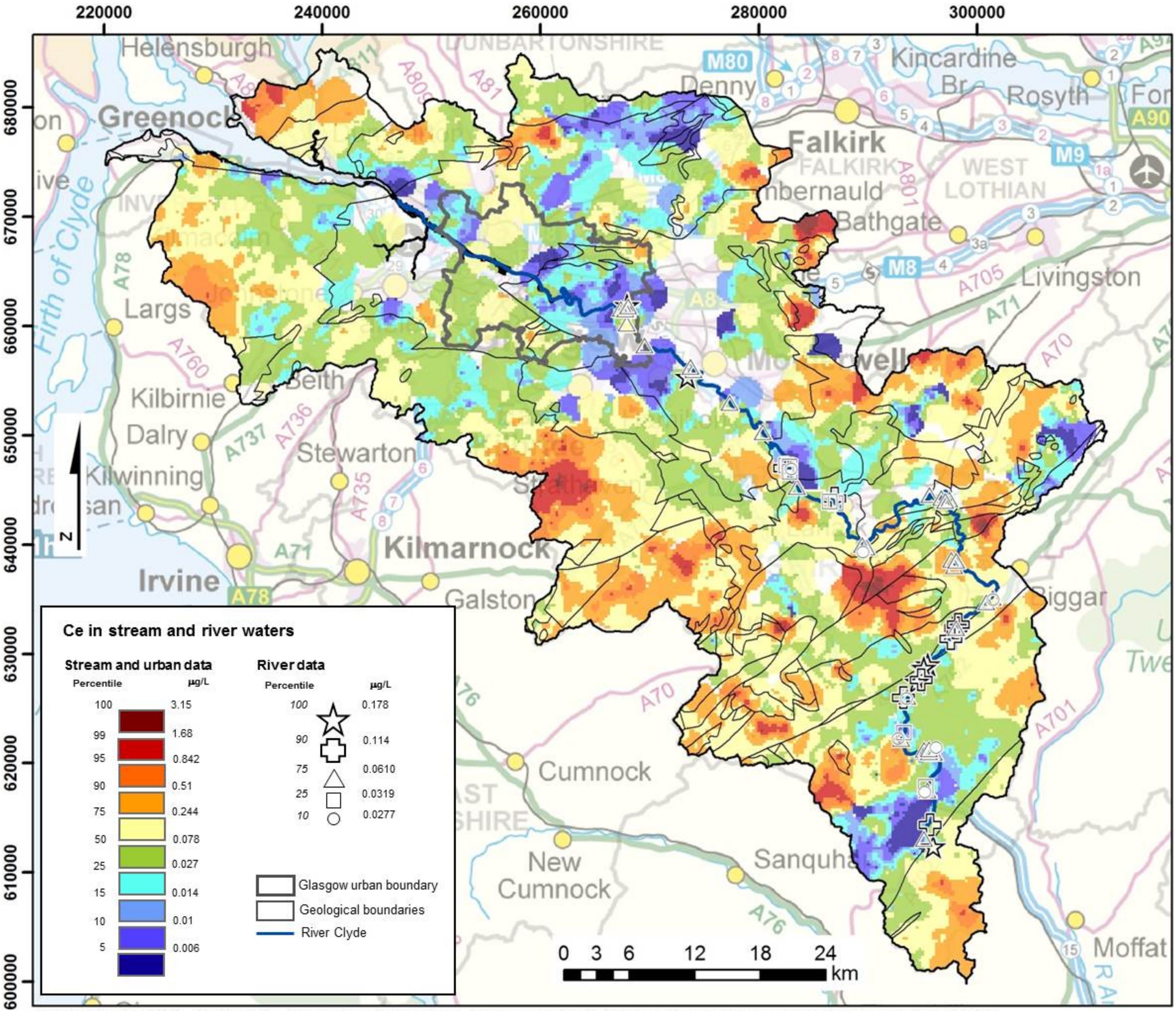
	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.01	<0.01	<0.02	<0.05
25th %	0.0018	0.000582	0.00473	0.0871
50th %	0.00458	0.00185	0.0112	0.27
75th %	0.0123	0.00585	0.0277	1.08
90th %	0.025	0.015	0.0574	1.45
max	5.89	0.18	0.204	1.49
n	1702	60	122	8
n cens	1165	46	82	3
rainwater				
seawater	0.3			







Cerium **Ce**



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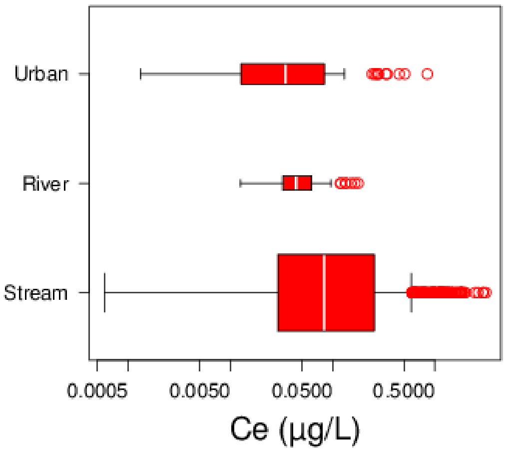
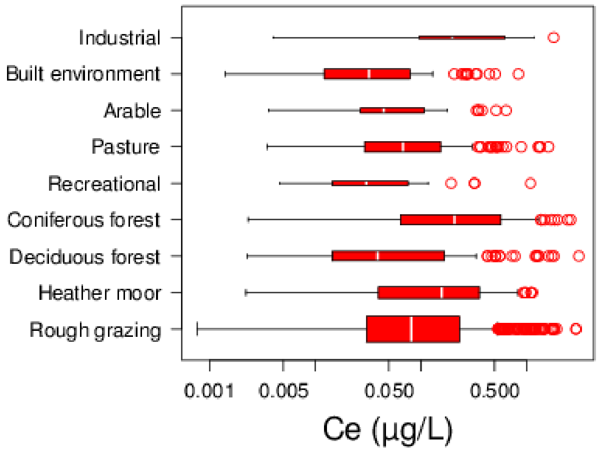
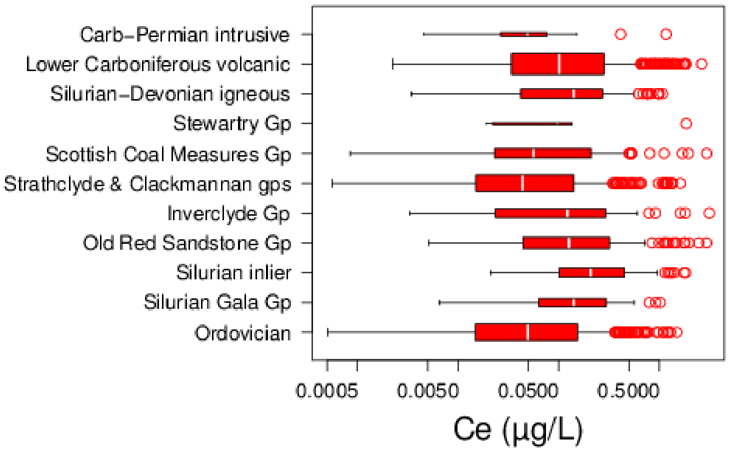
Cerium Ce

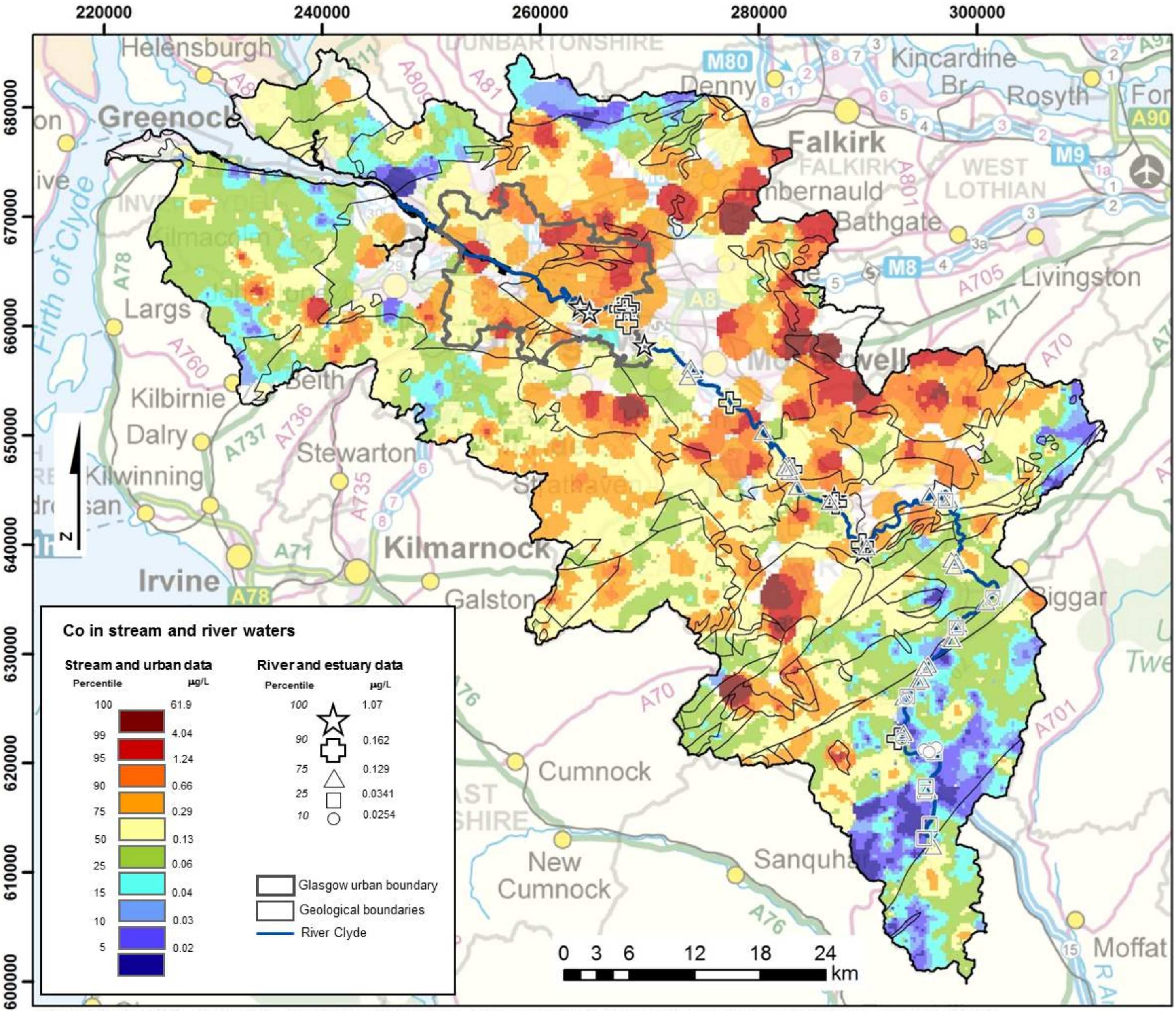
	Stream	River	Urban (µg/L)	Estuary
min	<0.002	0.0126	<0.01	No data
25th %	0.0292	0.0328	0.0127	
50th %	0.083	0.0439	0.0343	
75th %	0.256	0.0615	0.0824	
90th %	0.523	0.119	0.129	
max	3.15	0.178	0.842	
n	1702	60	122	
n cens	7	0	24	
rainwater				
seawater	0.001			







Cobalt **Co**



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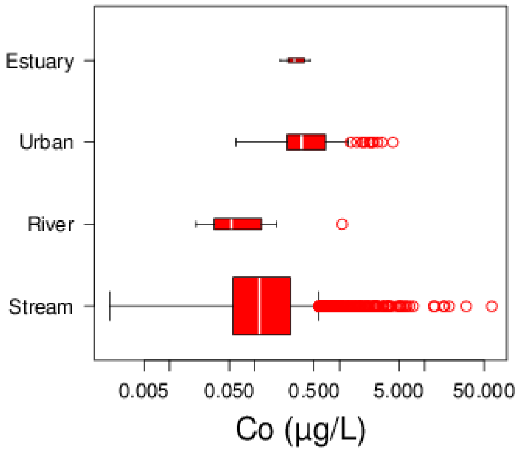
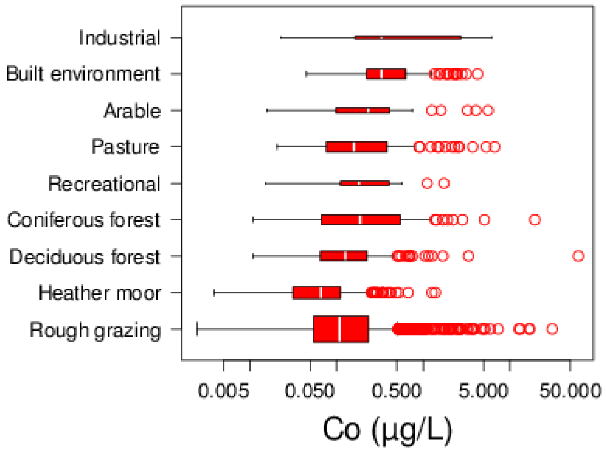
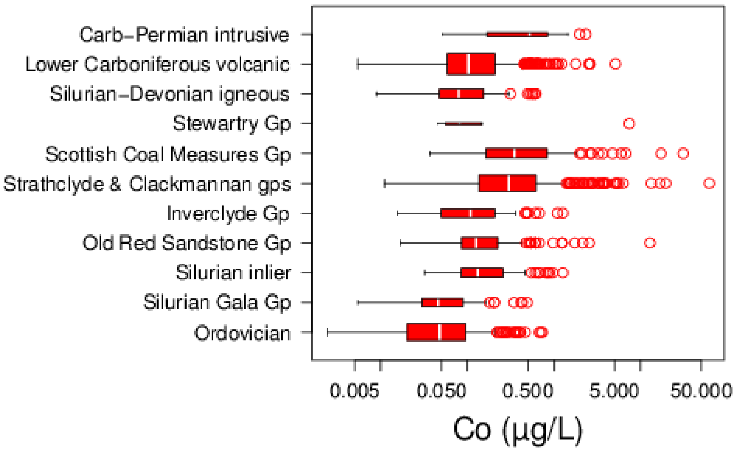
Cobalt Co

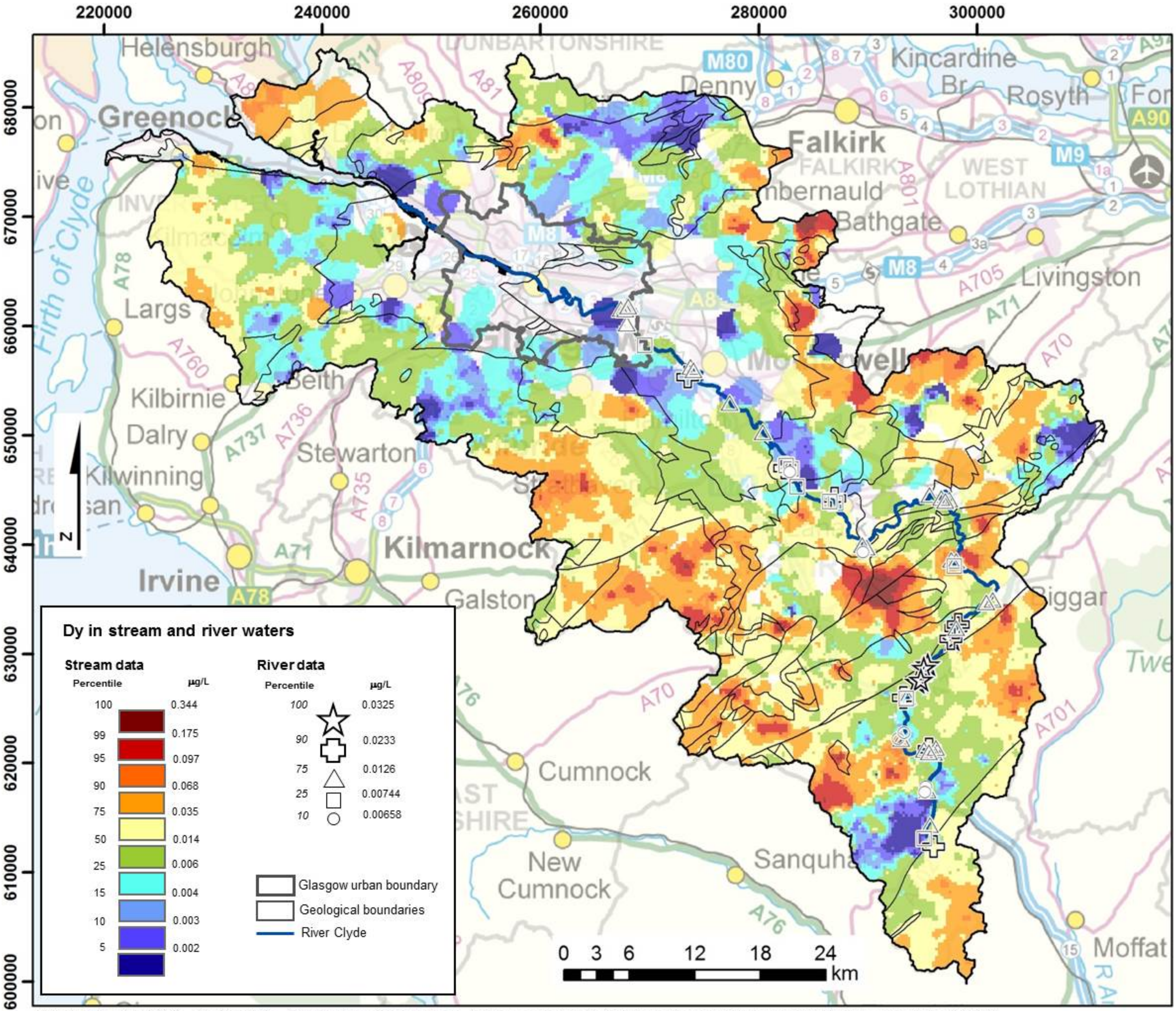
	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.01	0.0205	0.0608	<0.25
25th %	0.0557	0.0338	0.244	0.249
50th %	0.114	0.0532	0.356	0.292
75th %	0.262	0.119	0.677	0.385
90th %	0.608	0.147	1.34	0.438
max	61.9	1.07	4.26	0.45
n	1702	60	122	7
n cens	26	0	0	4
rainwater				
seawater	0.4			







Dysprosium Dy



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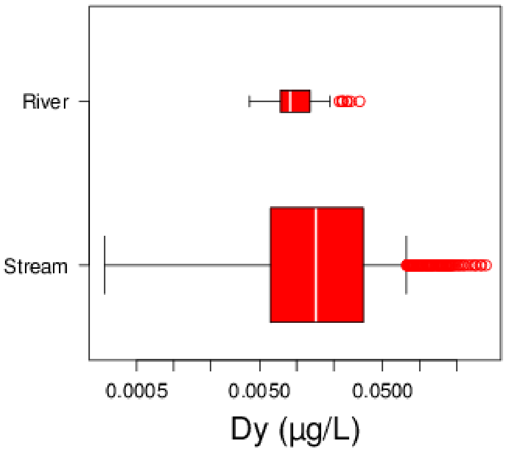
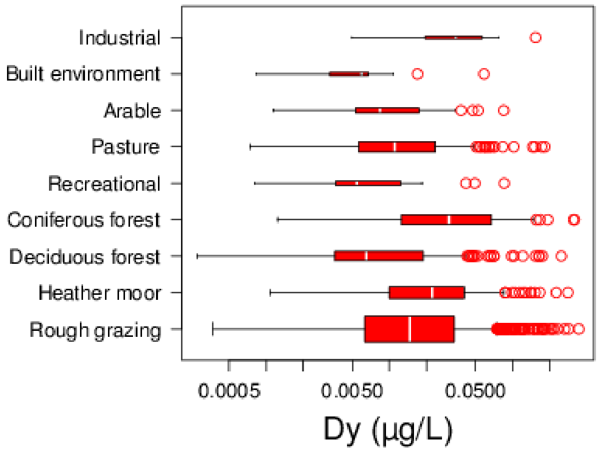
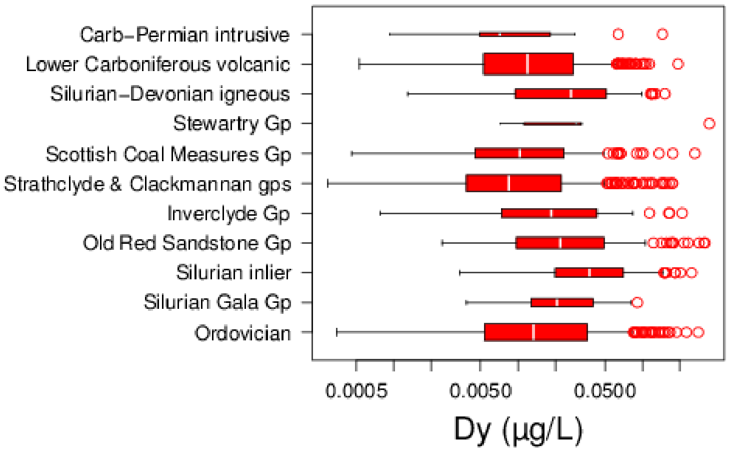
Dysprosium Dy

	Stream	River	Urban (µg/L)	Estuary
min	<0.002	0.00416	No data	No data
25th %	0.0061	0.00744		
50th %	0.0143	0.00885		
75th %	0.0348	0.0126		
90th %	0.0678	0.0233		
max	0.344	0.0325		
n	1702	60		
n cens	81	0		
rainwater				
seawater				

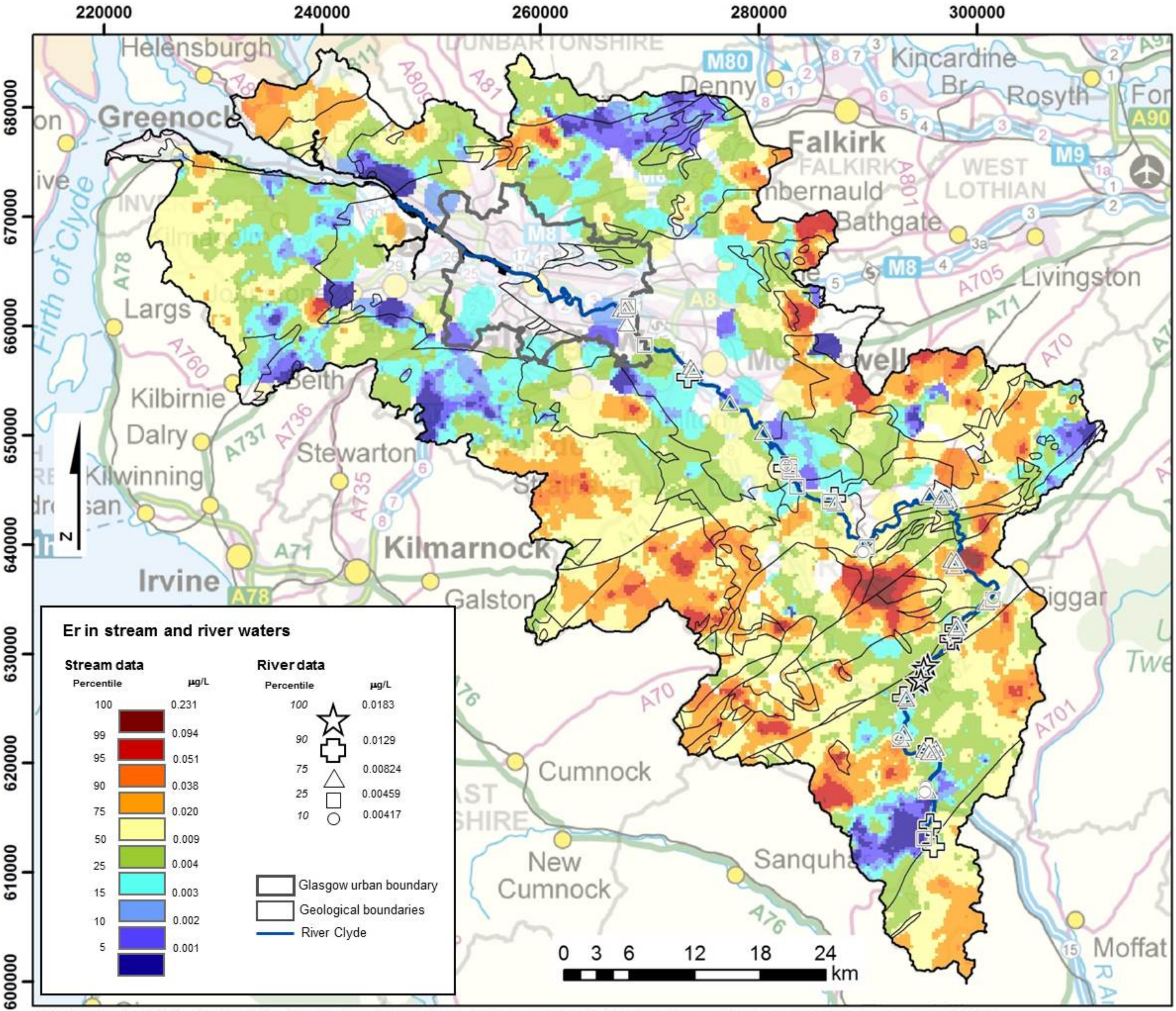






Erbium

Er



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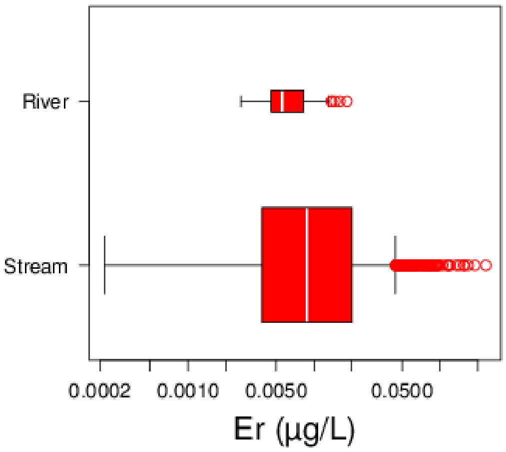
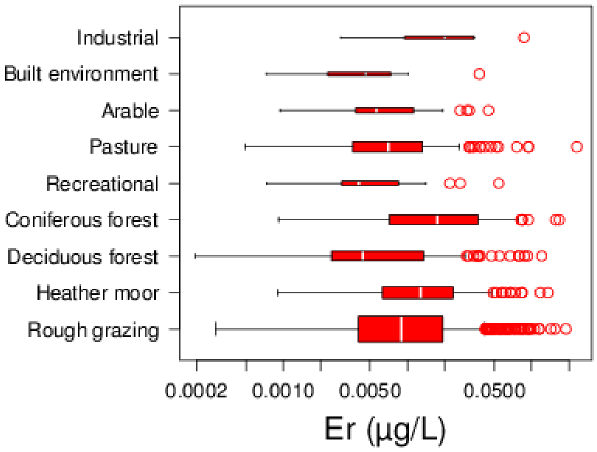
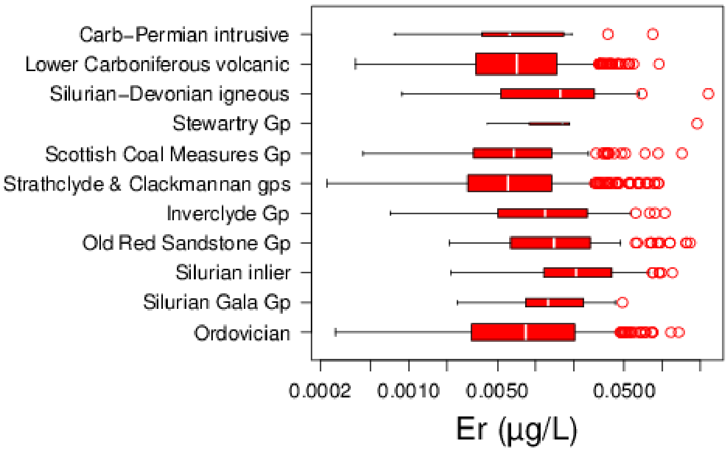
Erbium

Er

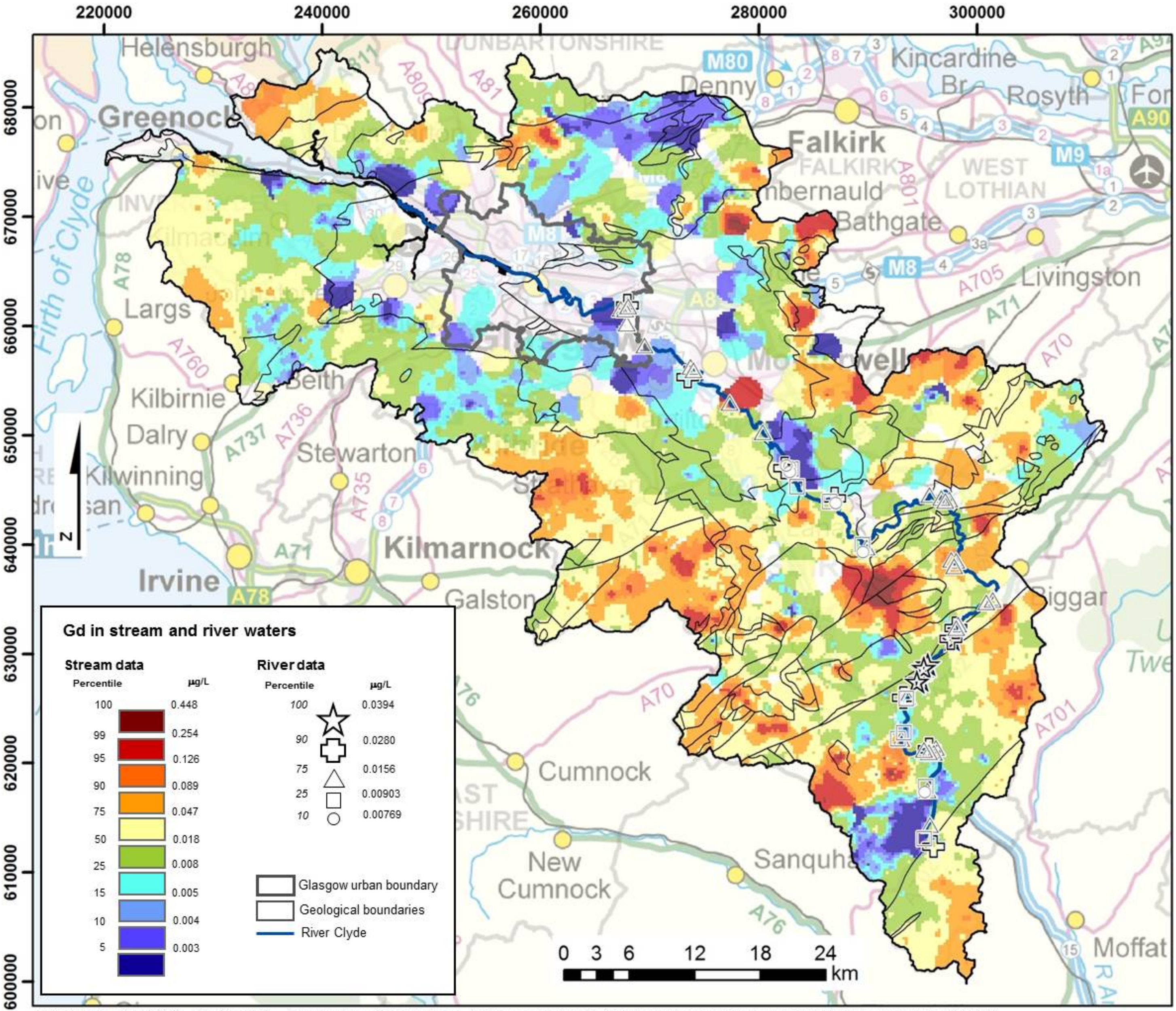
	Stream	River	Urban (µg/L)	Estuary
min	<0.002	0.00263	No data	No data
25th %	0.00387	0.00459		
50th %	0.00879	0.00559		
75th %	0.0201	0.00824		
90th %	0.0376	0.0129		
max	0.231	0.0183		
n	1702	60		
n cens	181	0		
rainwater				
seawater				







Gadolinium Gd



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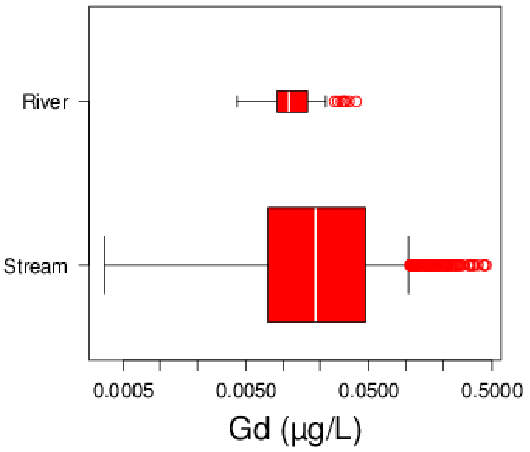
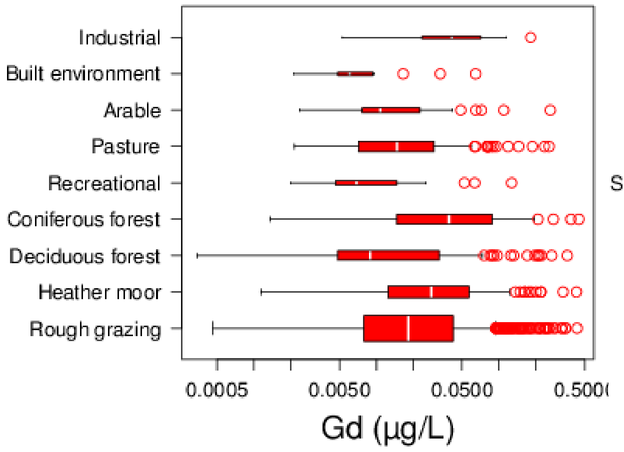
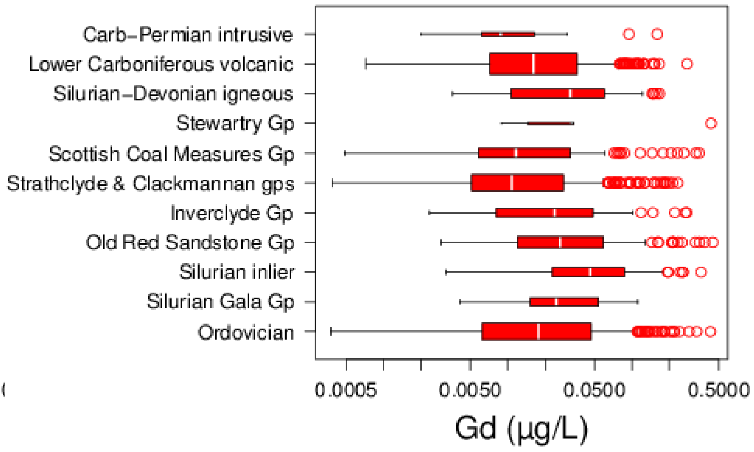
Gadolinium Gd

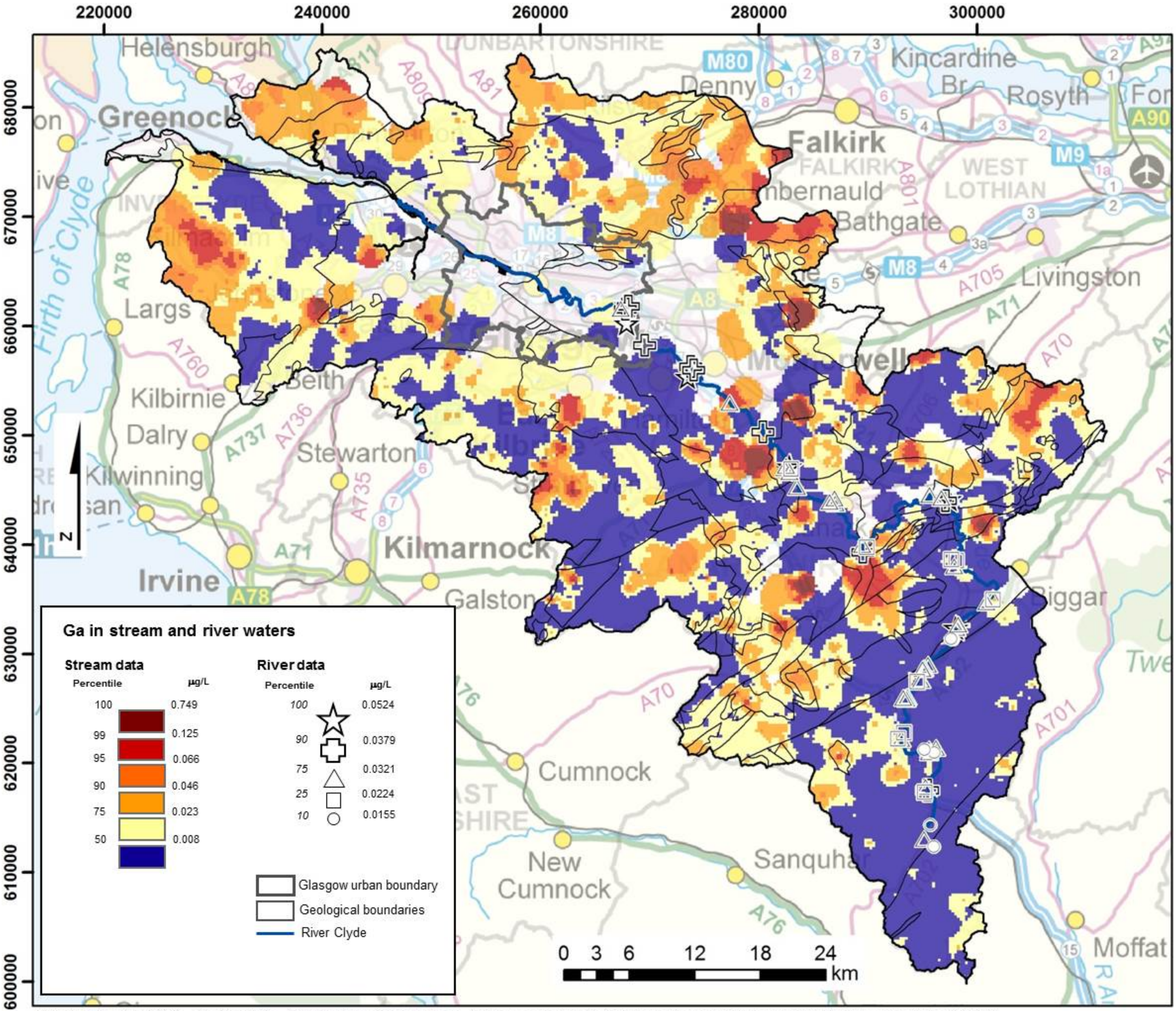
	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.002	0.00424	No data	No data
25th %	0.00754	0.00903		
50th %	0.0183	0.0112		
75th %	0.0468	0.0156		
90th %	0.0892	0.028		
max	0.448	0.0394		
n	1702	60		
n cens	49	0		
rainwater				
seawater				







Gallium Ga



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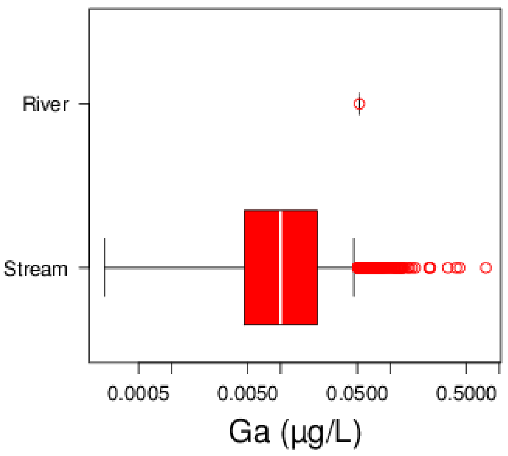
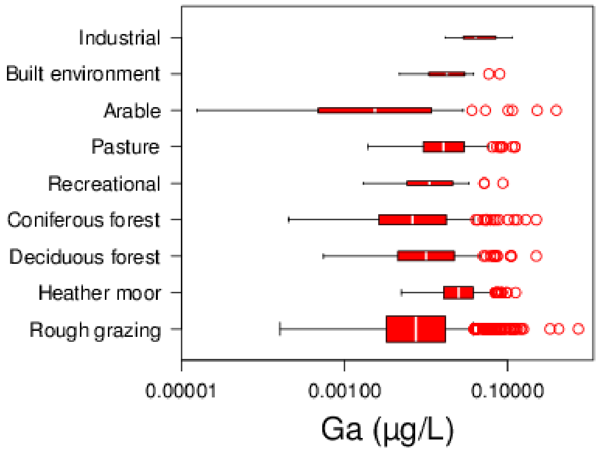
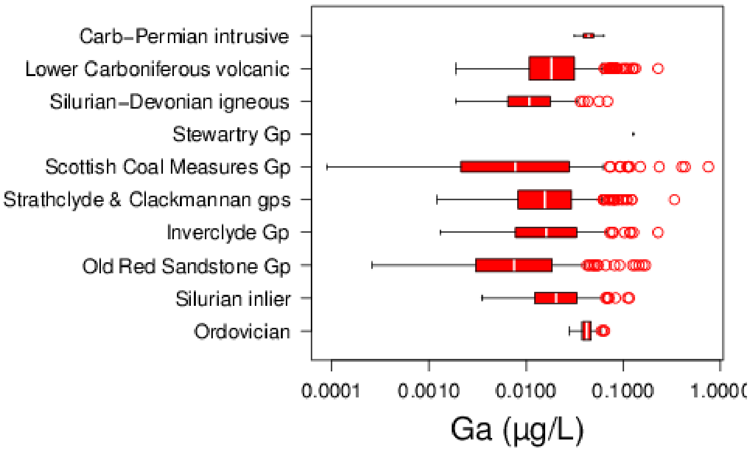
Gallium

Ga

	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.05	<0.05	No data	No data
25th %	NA			
50th %	NA			
75th %	NA			
90th %	NA			
max	0.749	0.0524		
n	1702	60		
n cens	1554	59		
rainwater				
seawater				

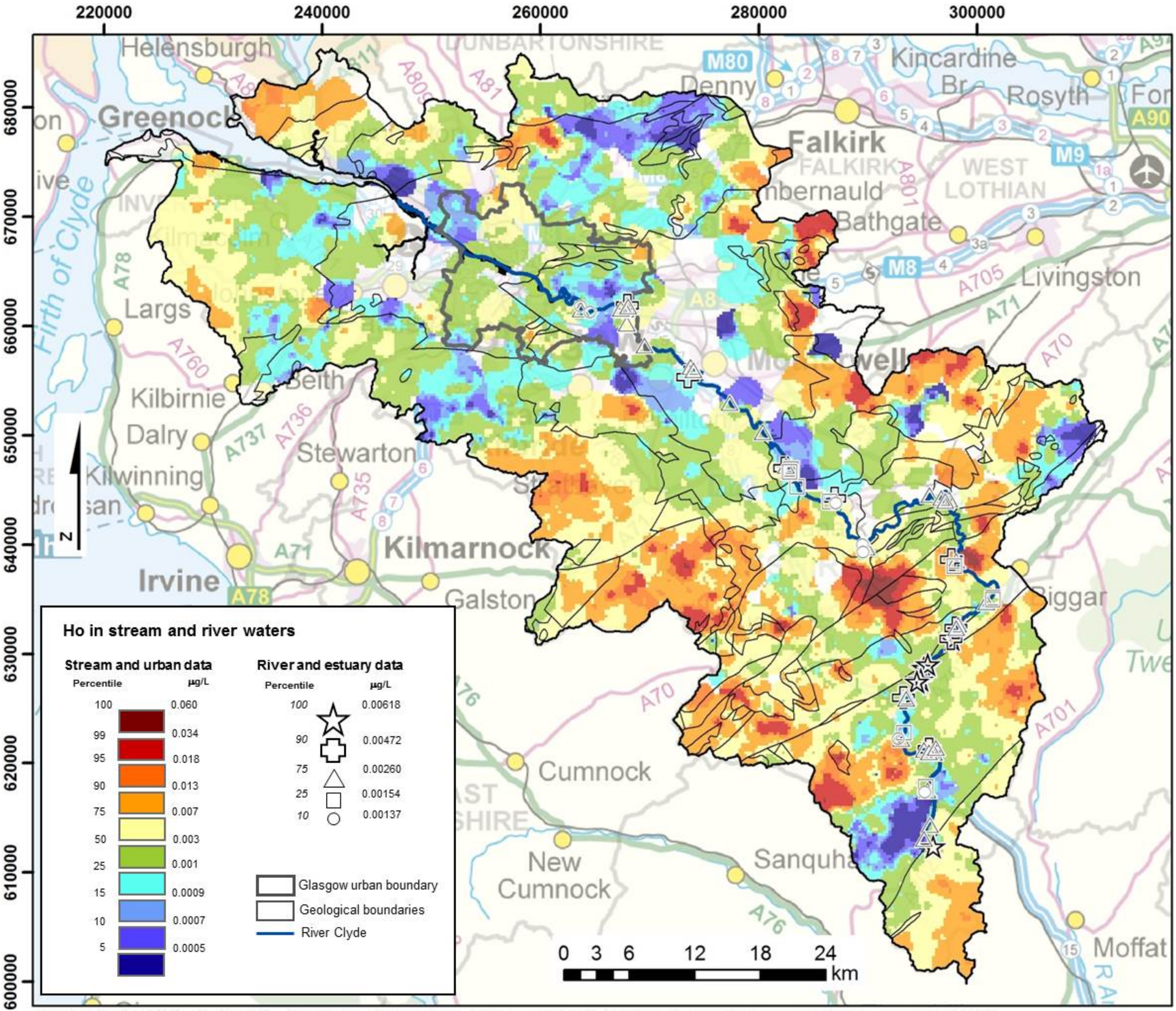






Holmium

Ho



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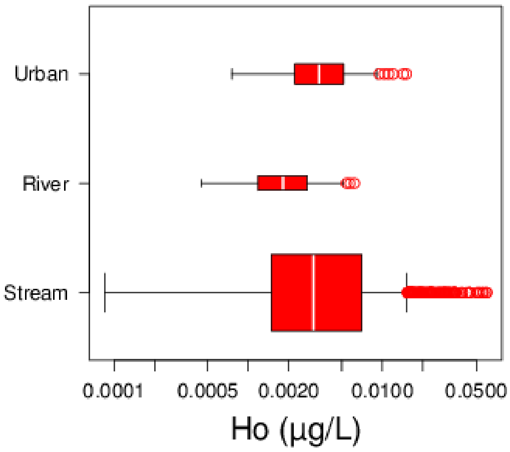
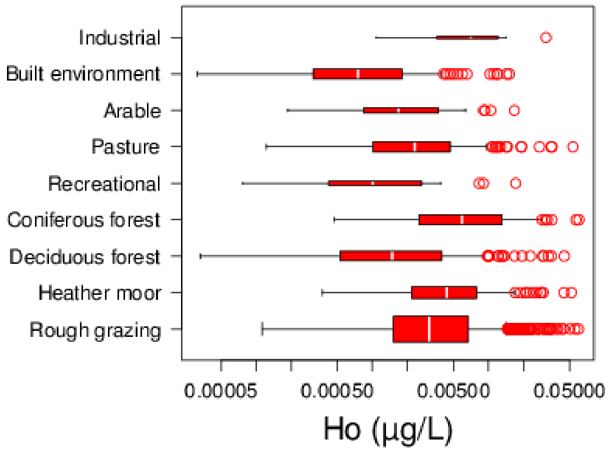
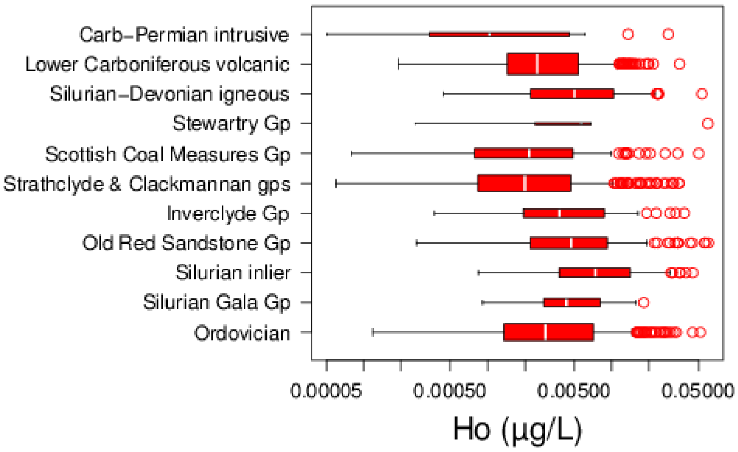
Holmium Ho

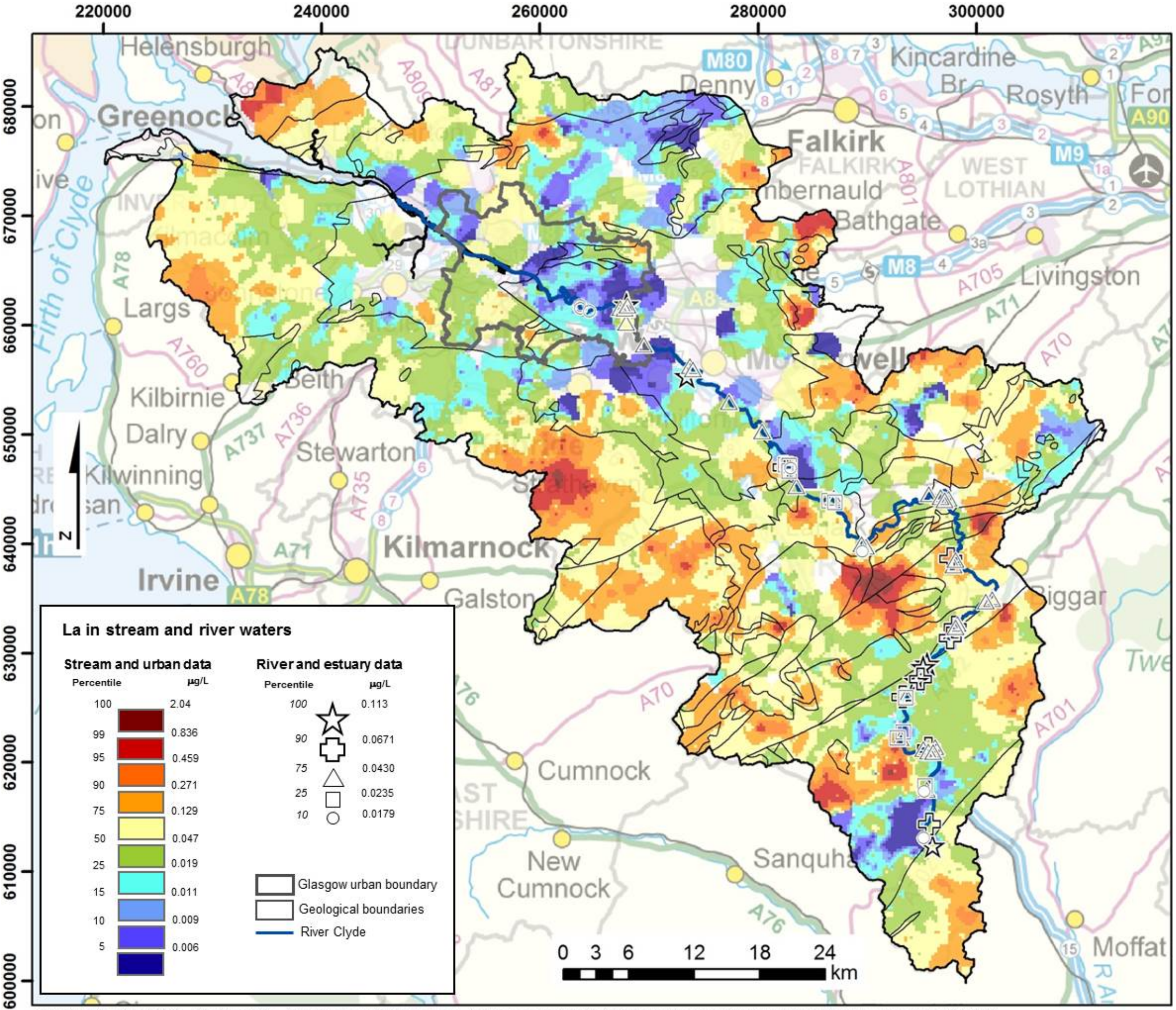
	Stream	River	Urban (µg/L)	Estuary
min	<0.002	<0.002	<0.01	No data
25th %	0.00148	0.00119		
50th %	0.00305	0.00181		
75th %	0.00701	0.00271		
90th %	0.0133	0.00483		
max	0.06	0.00618	0.0151	
n	1702	60	122	
n cens	629	33	117	
rainwater				
seawater				







Lanthanum La



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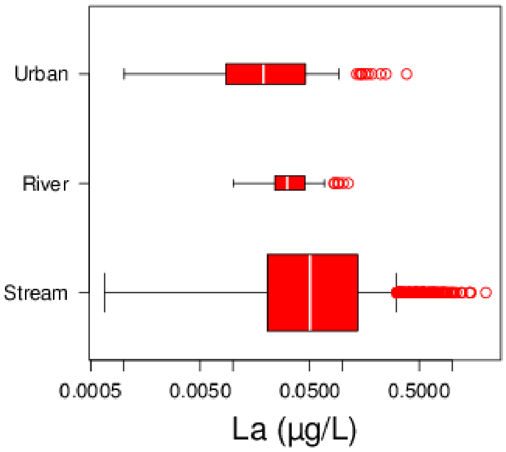
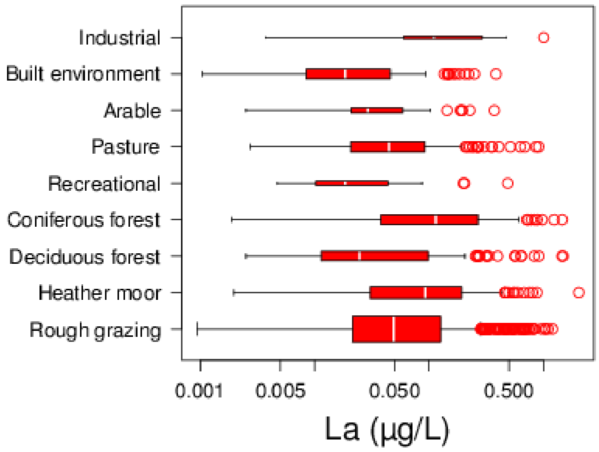
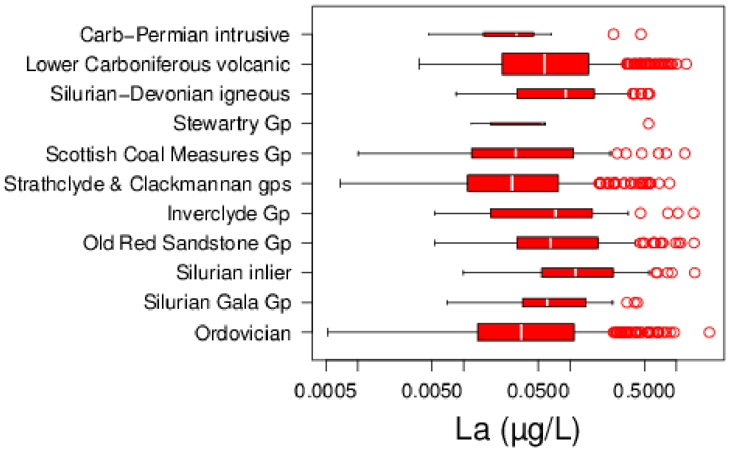
Lanthanum La

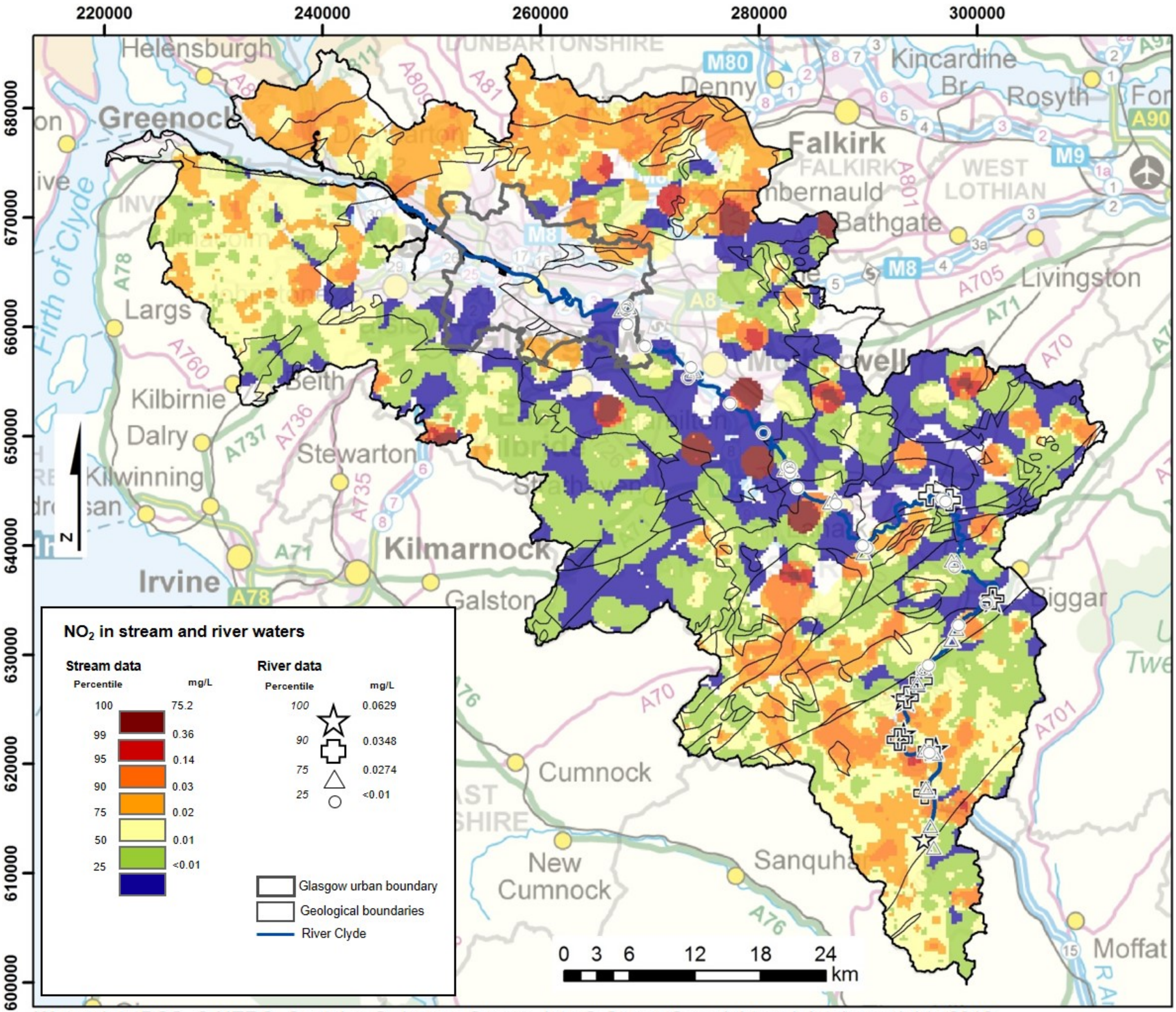
	Stream	River	Urban (µg/L)	Estuary
min	<0.002	0.0101	<0.01	No data
25th %	0.0206	0.0241	0.00863	
50th %	0.0506	0.0311	0.0189	
75th %	0.137	0.0444	0.0459	
90th %	0.28	0.0698	0.0768	
max	2.04	0.113	0.385	
n	1702	60	122	
n cens	9	0	39	
rainwater				
seawater	0.003			







Nitrite NO_2



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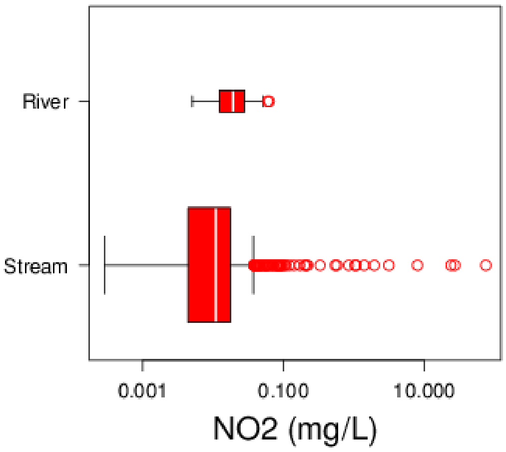
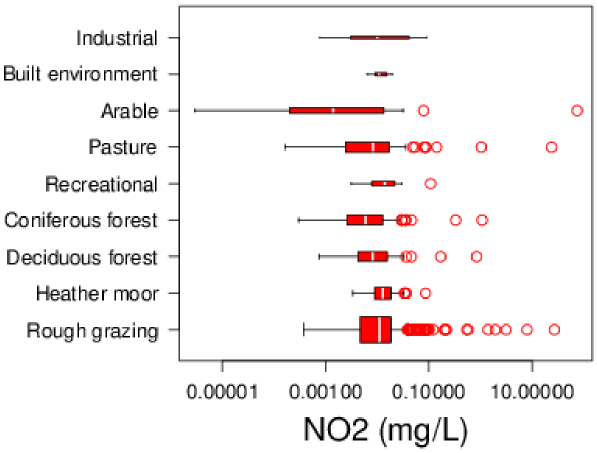
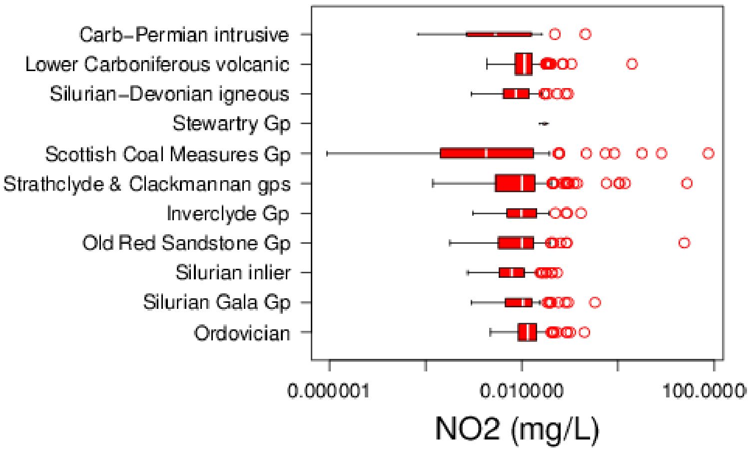
Nitrite NO_2

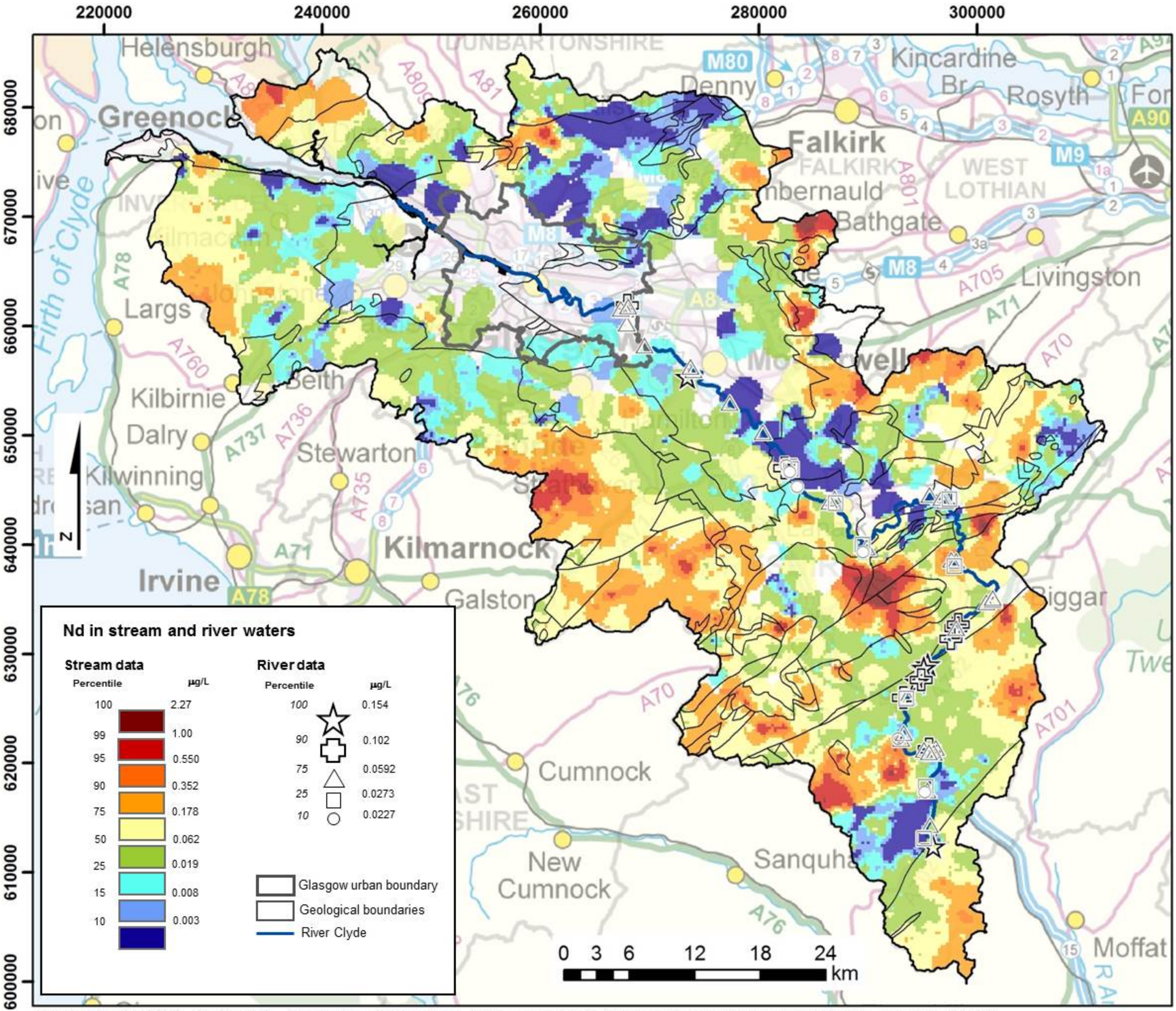
	Stream	River	Urban (mg/L)	Estuary
min	<0.01	<0.01	No data	No data
25th %	0.00443	0.0124		
50th %	0.0109	0.0193		
75th %	0.0177	0.0274		
90th %	0.0265	0.0348		
max	75.2	0.0629		
n	1702	60		
n cens	760	23		
rainwater				
seawater				







Neodymium Nd



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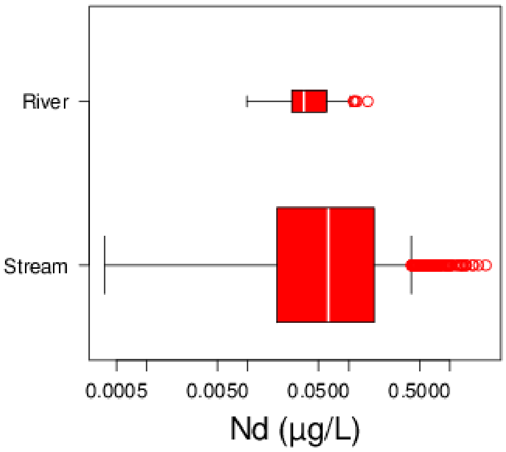
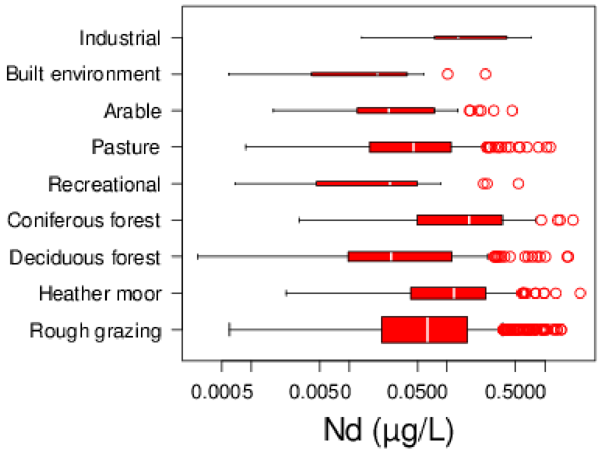
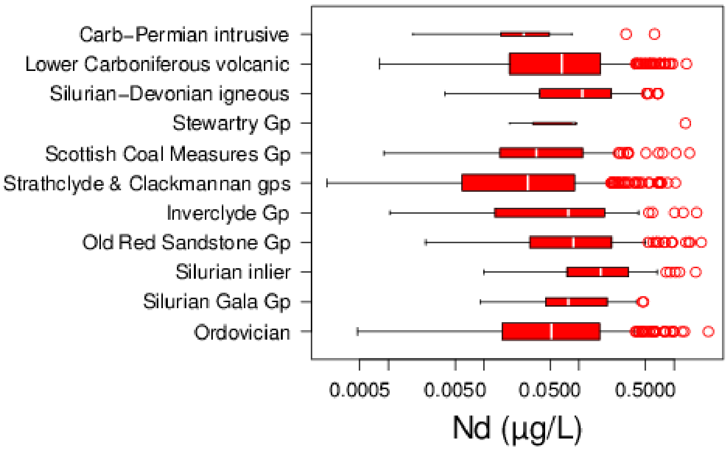
Neodymium Nd

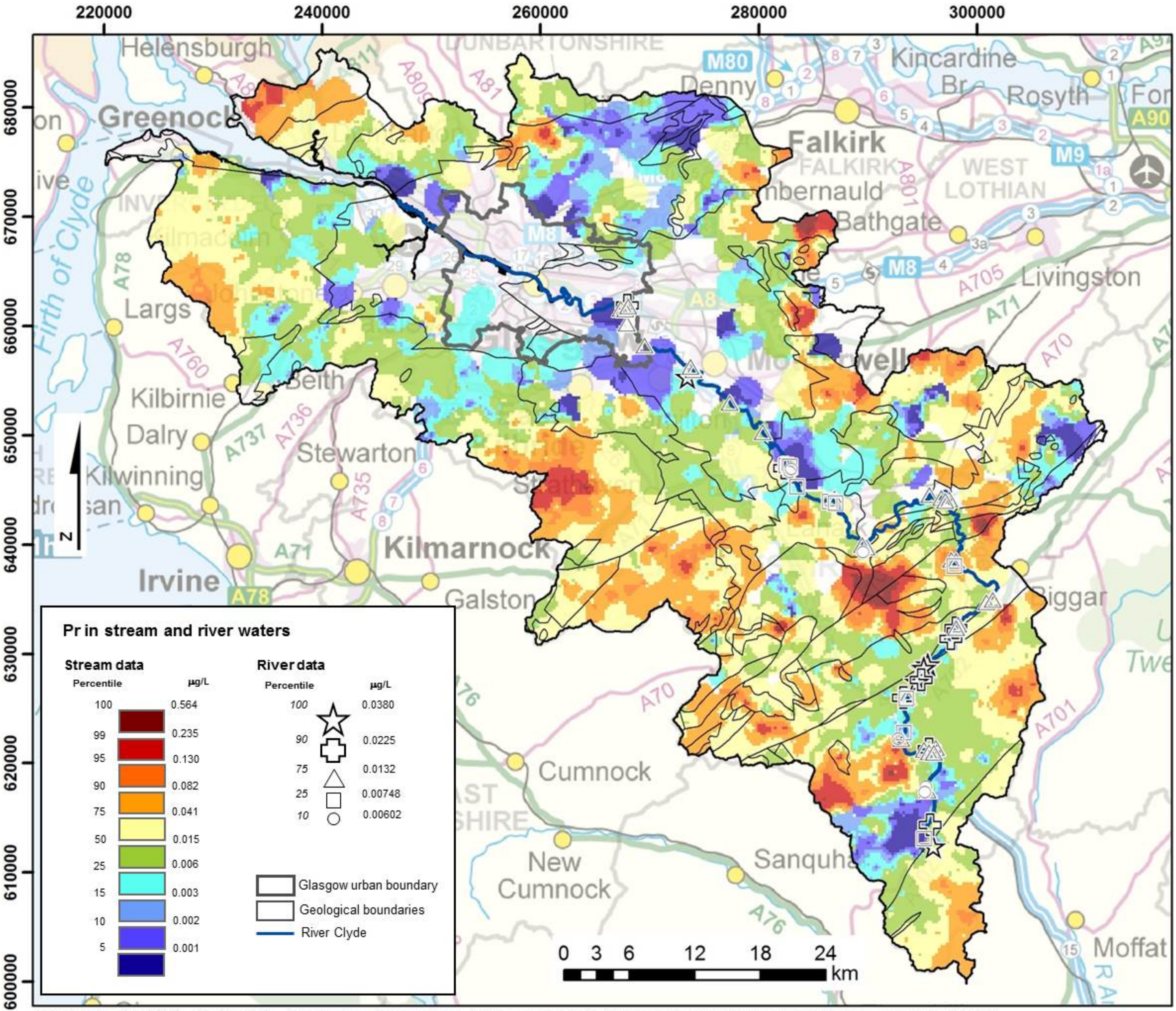
	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.002	0.00982	No data	No data
25th %	0.0194	0.0273		
50th %	0.0624	0.0359		
75th %	0.178	0.0592		
90th %	0.352	0.102		
max	2.27	0.154		
n	1702	60		
n cens	162	0		
rainwater				
seawater				







Praseodymium Pr



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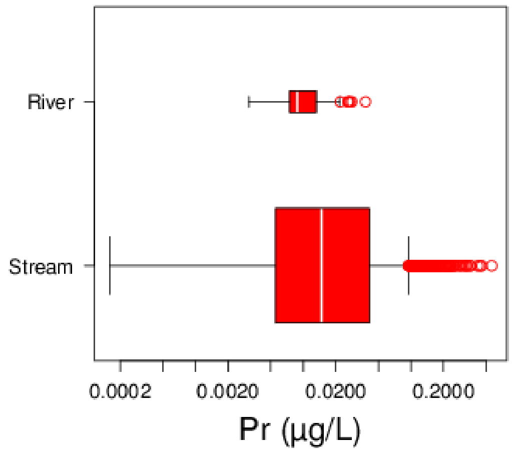
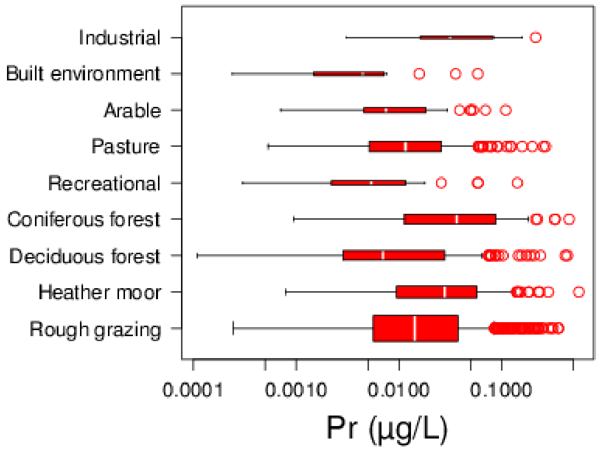
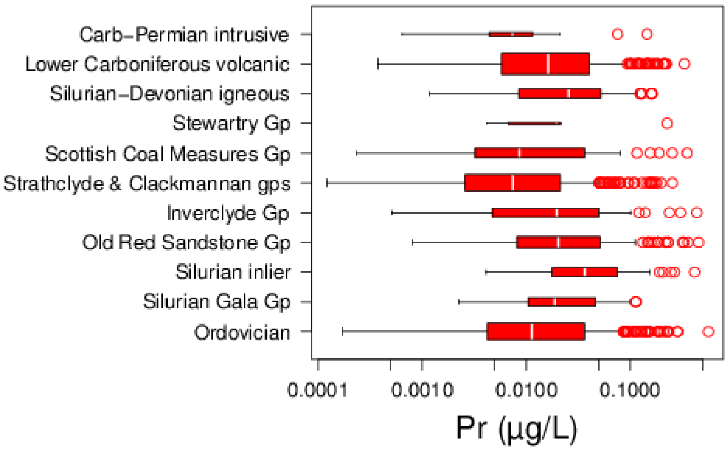
Praseodymium **Pr**

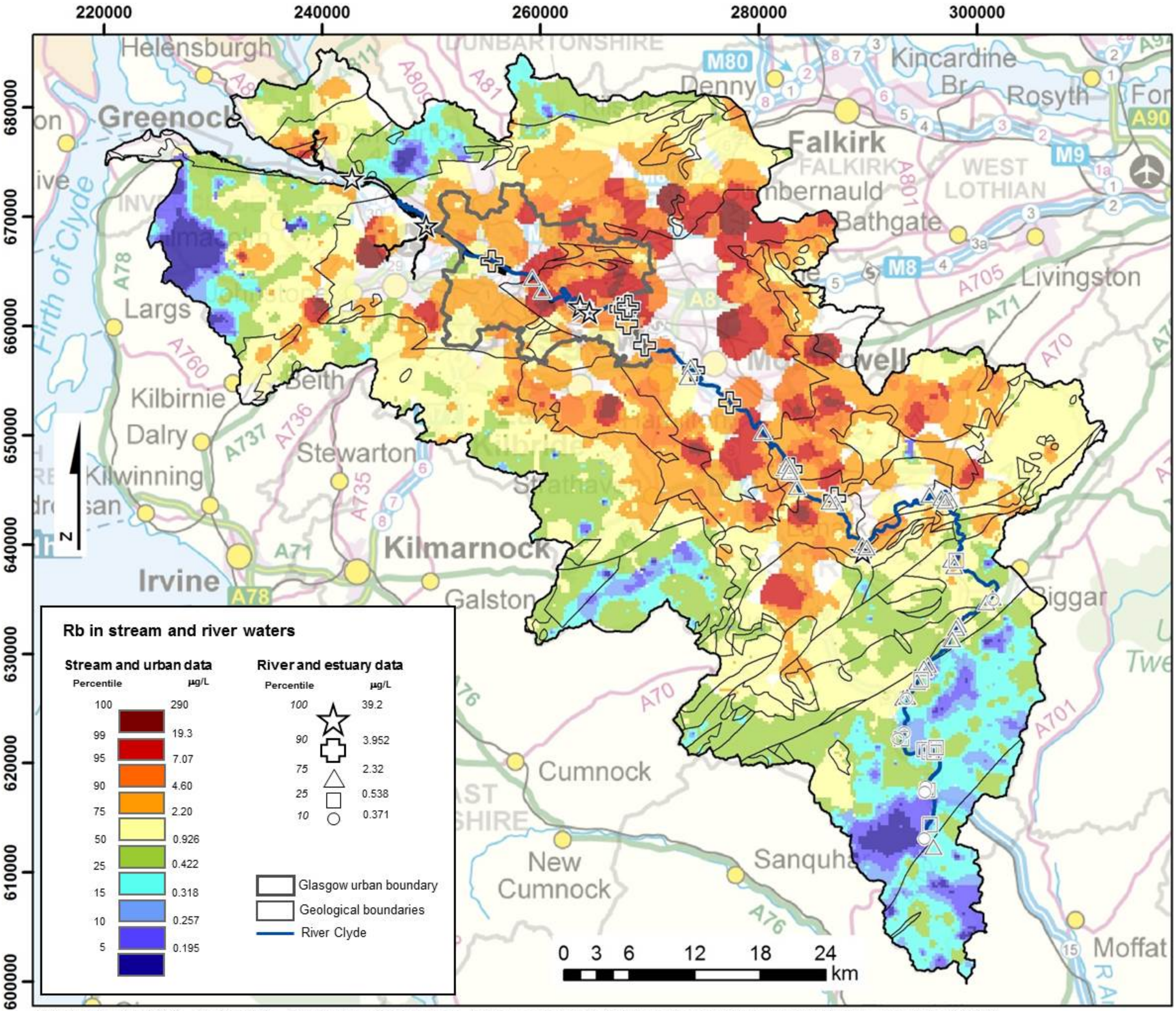
	Stream	River	Urban	Estuary
			(μg/L)	
min	<0.002	0.00313	No data	No data
25th %	0.00551	0.00748		
50th %	0.0147	0.00883		
75th %	0.0411	0.0132		
90th %	0.0823	0.0225		
max	0.564	0.038		
n	1702	60		
n cens	153	0		
rainwater				
seawater				







Rubidium **Rb**



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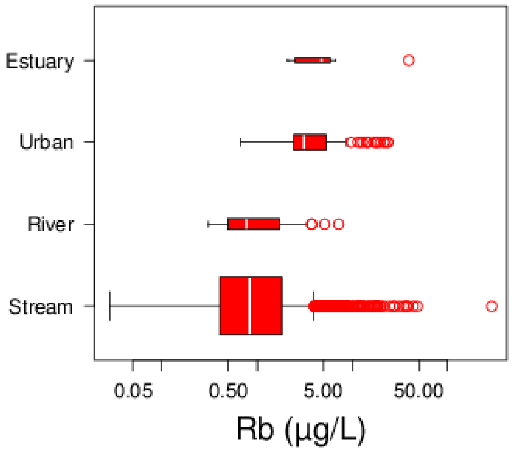
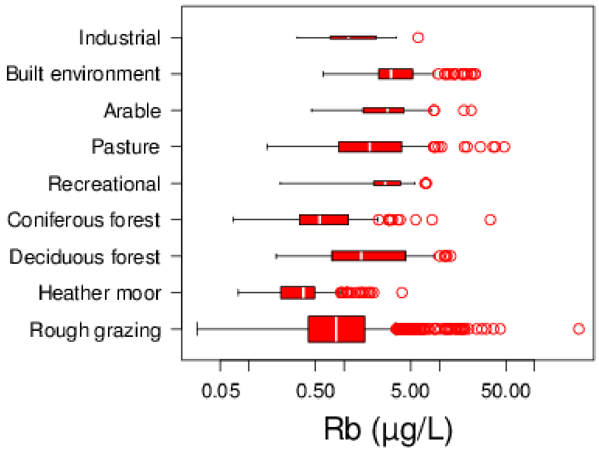
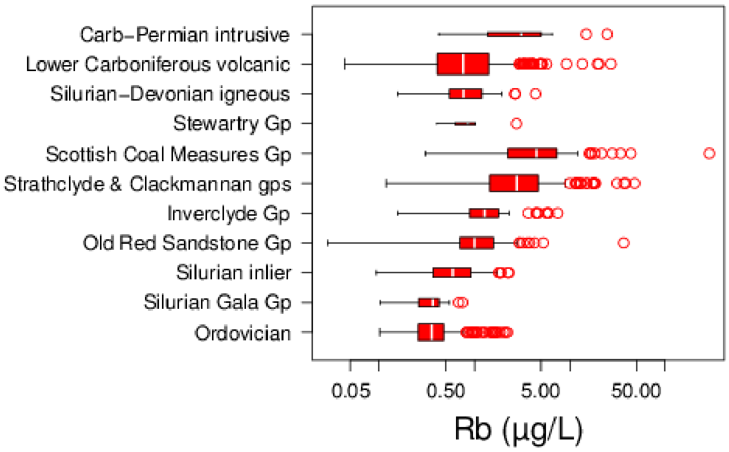
Rubidium

Rb

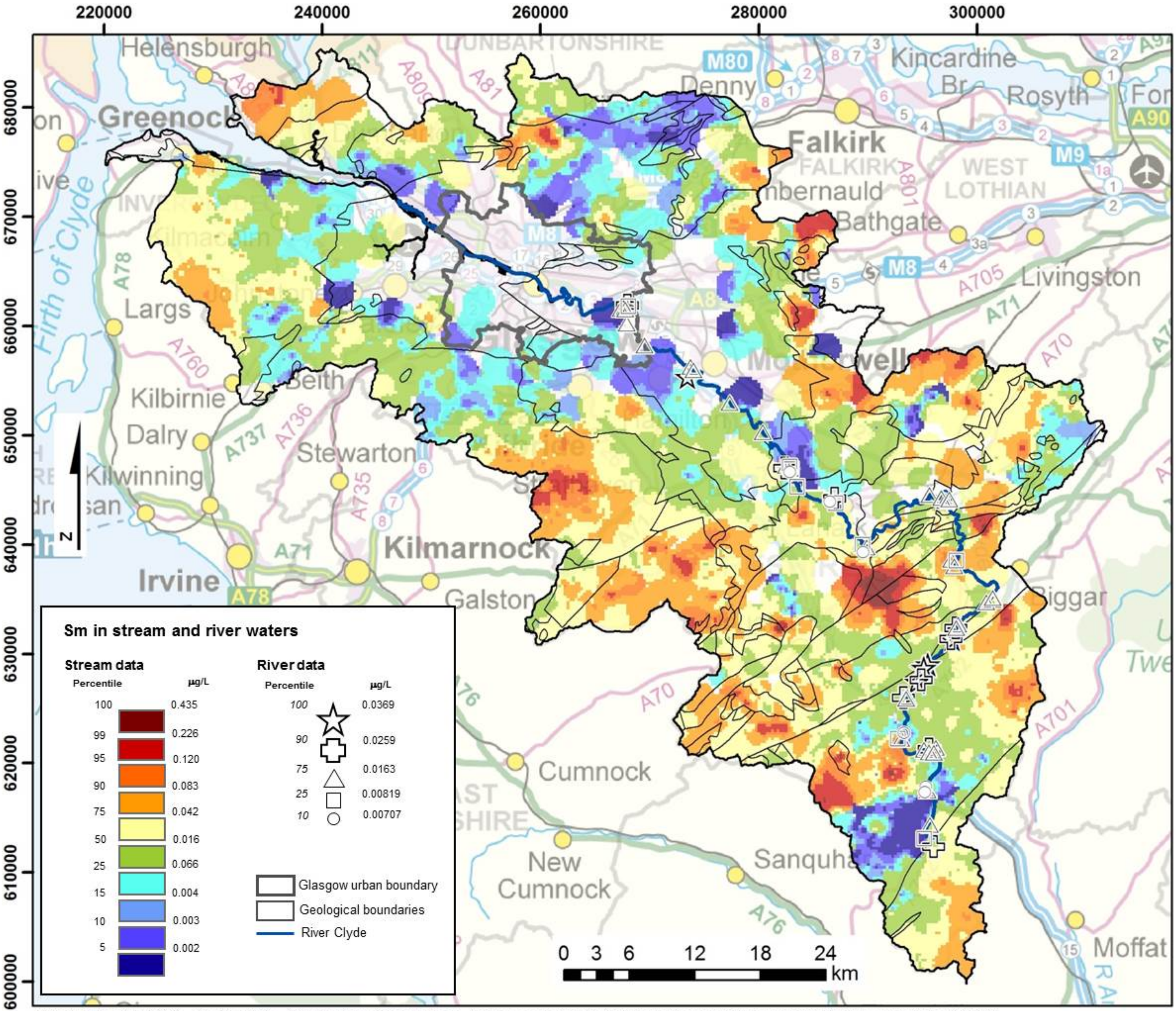
	Stream	River	Urban	Estuary
			(µg/L)	
min	0.0287	0.31	0.674	2.1
25th %	0.406	0.498	2.45	2.65
50th %	0.838	0.766	3.11	4.73
75th %	1.84	1.69	5.27	5.54
90th %	4.24	3.24	12.8	16.4
max	290	7.17	23.7	39.2
n	1702	60	122	8
n cens	0	0	0	0
rainwater				
seawater	120			







Samarium Sm



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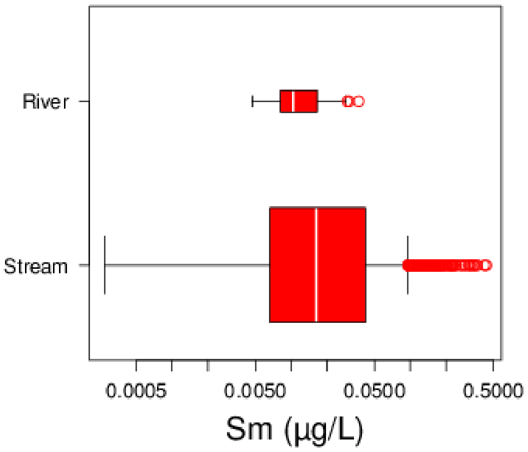
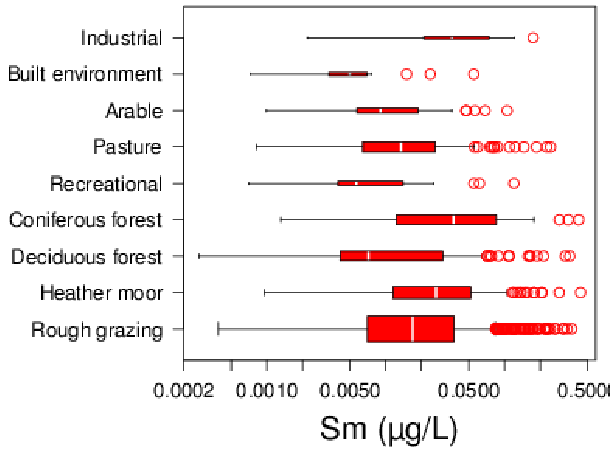
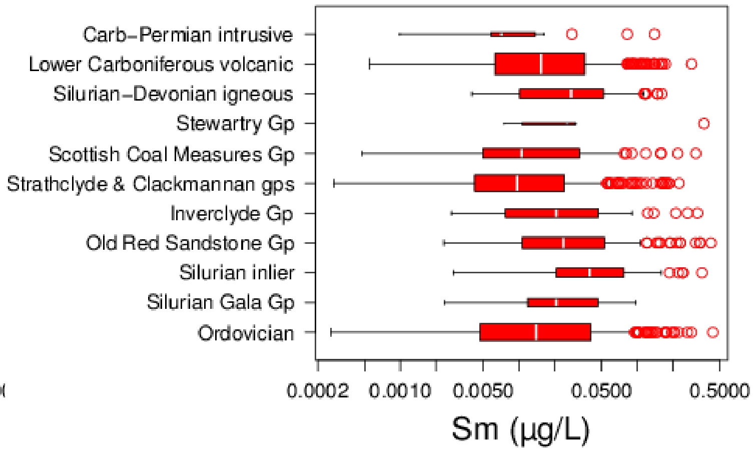
Samarium

Sm

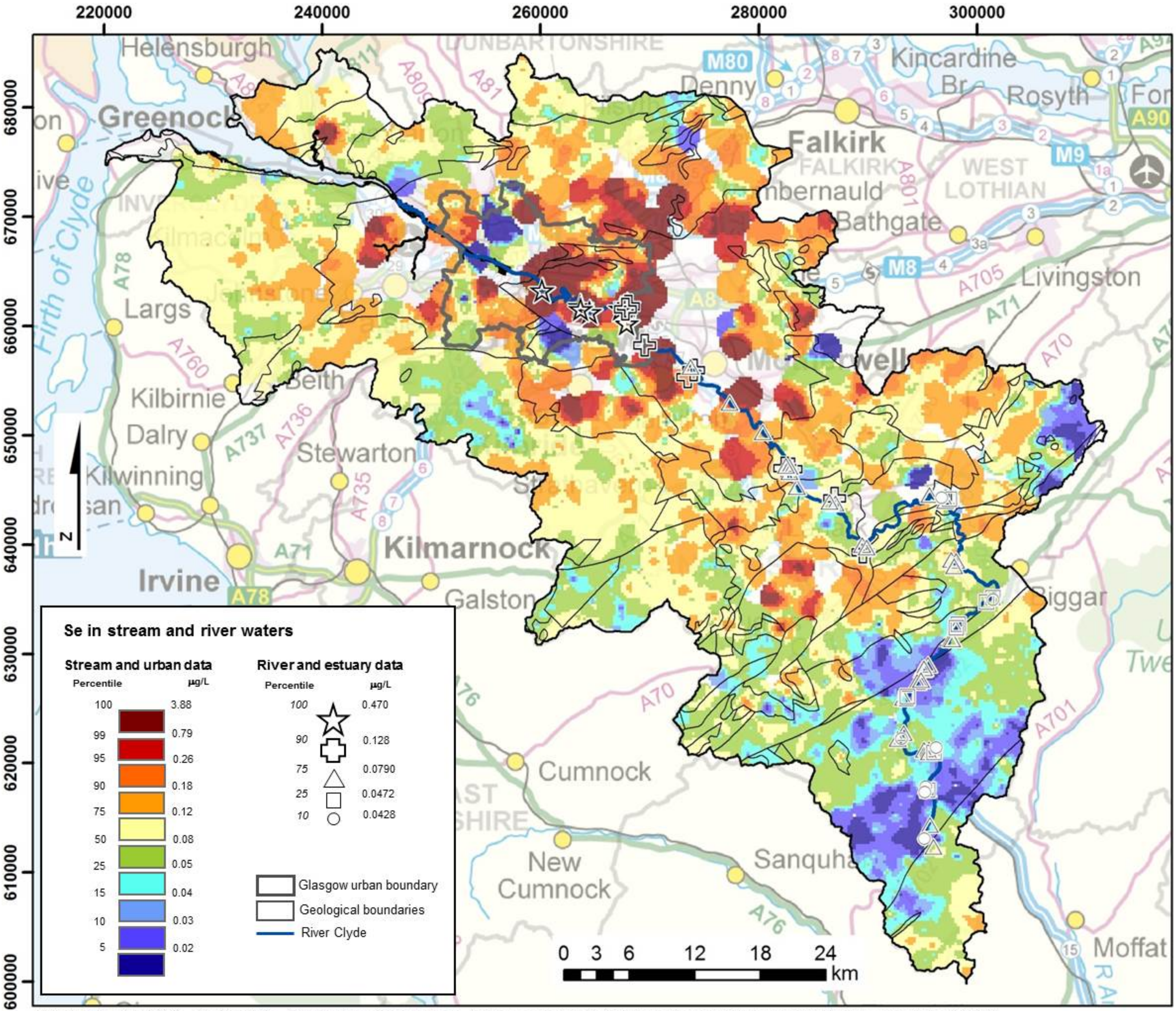
	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.002	0.0047	No data	No data
25th %	0.00661	0.00819		
50th %	0.0163	0.0104		
75th %	0.042	0.0163		
90th %	0.0825	0.0259		
max	0.435	0.0369		
n	1702	60		
n cens	83	0		
rainwater				
seawater				







Selenium **Se**



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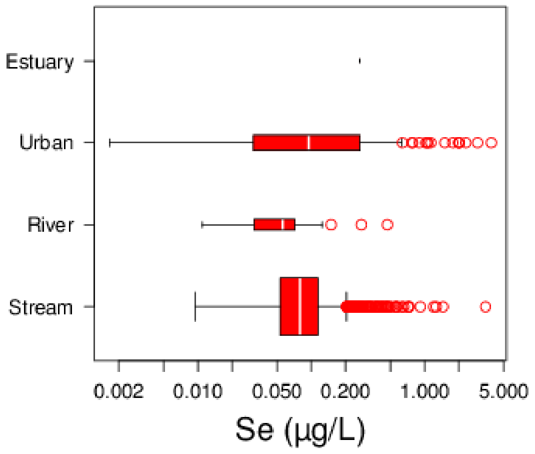
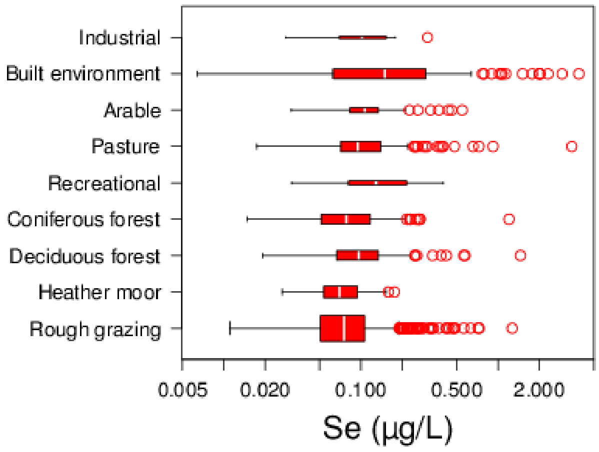
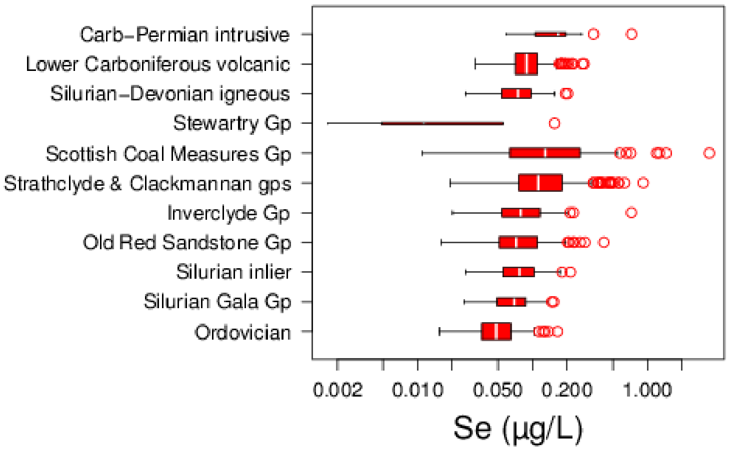
Selenium

Se

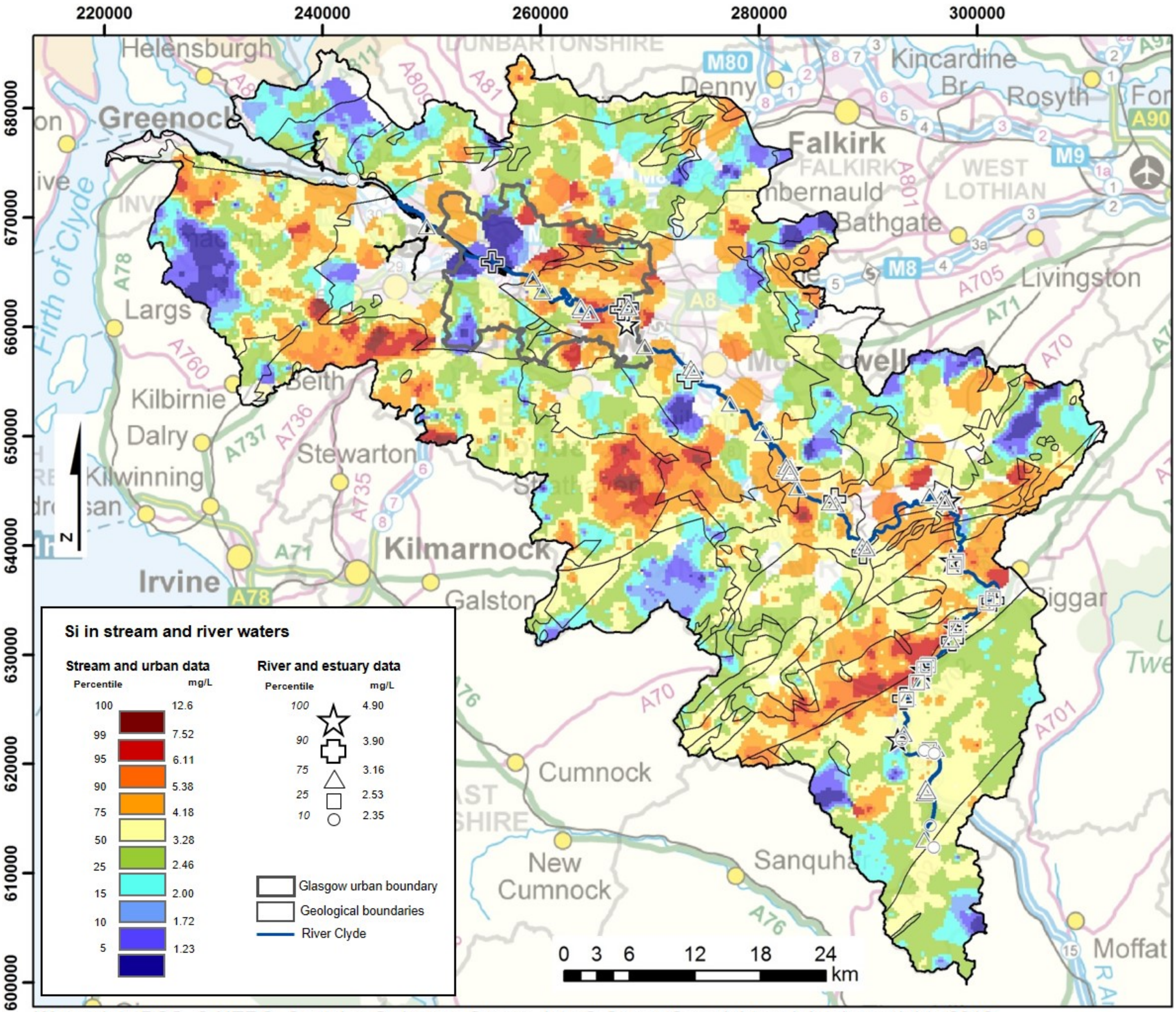
	Stream	River	Urban (µg/L)	Estuary
min	<0.05	<0.05	<0.25	<0.2
25th %	0.0533	0.0317	0.0312	
50th %	0.0801	0.0559	0.0948	
75th %	0.114	0.0709	0.268	
90th %	0.165	0.114	0.889	
max	3.45	0.47	3.88	0.27
n	1702	60	122	8
n cens	364	22	89	7
rainwater	1			
seawater	0.1			







Silicon Si



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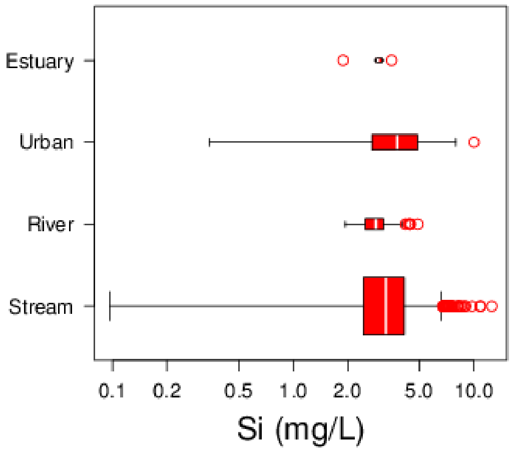
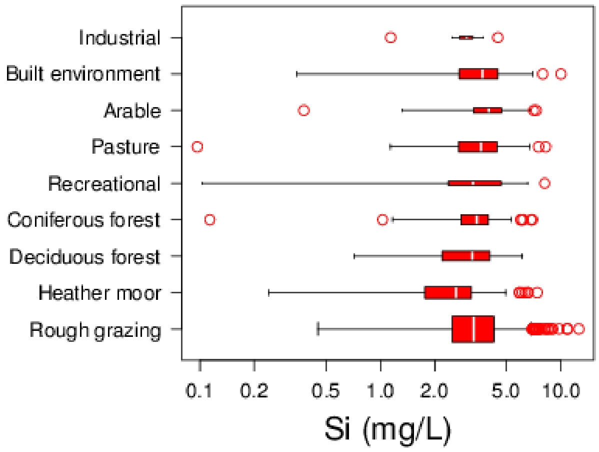
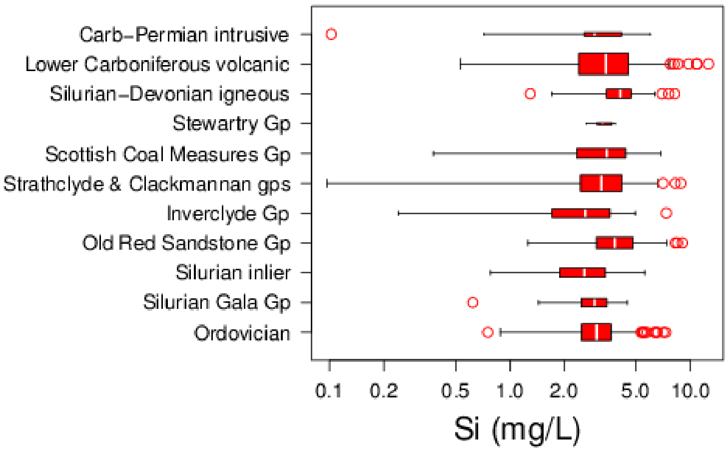
Silicon

Si

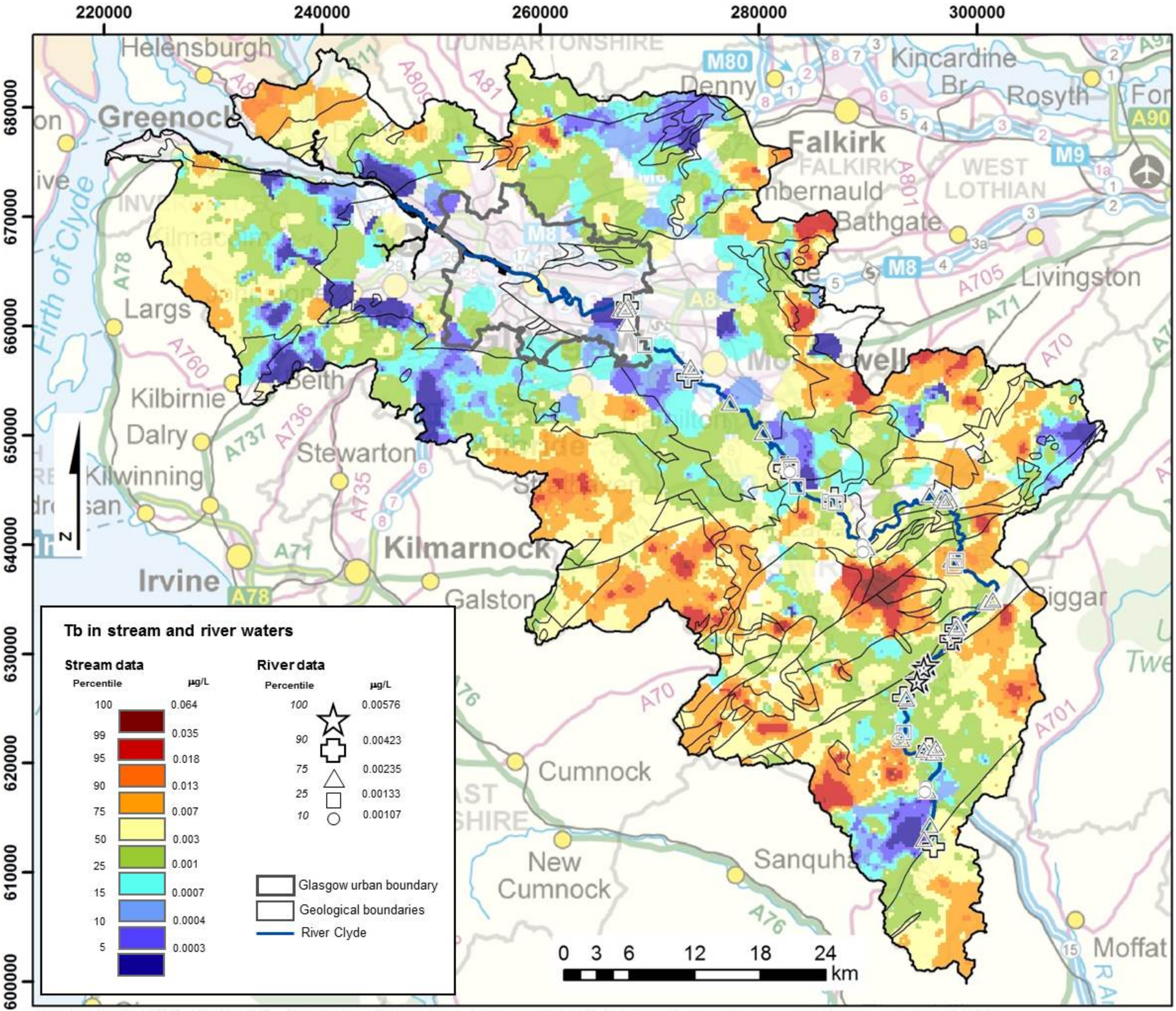
	Stream	River	Urban (mg/L)	Estuary
min	0.0965	1.94	0.346	1.89
25th %	2.44	2.51	2.75	2.89
50th %	3.27	2.87	3.76	2.94
75th %	4.13	3.16	4.83	3.1
90th %	5.29	4.03	6.05	3.26
max	12.6	4.9	10	3.51
n	1702	60	122	8
n cens	0	0	0	0
rainwater				
seawater	3000			







Terbium **Tb**



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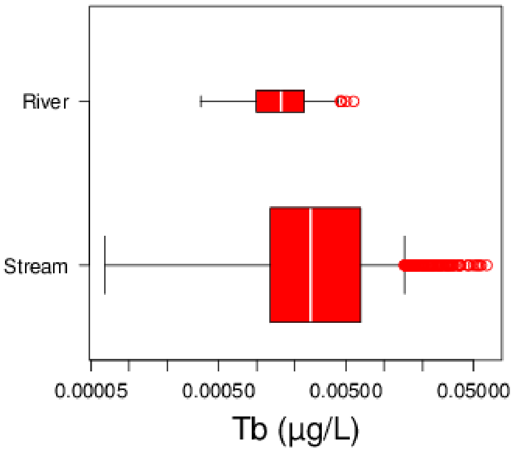
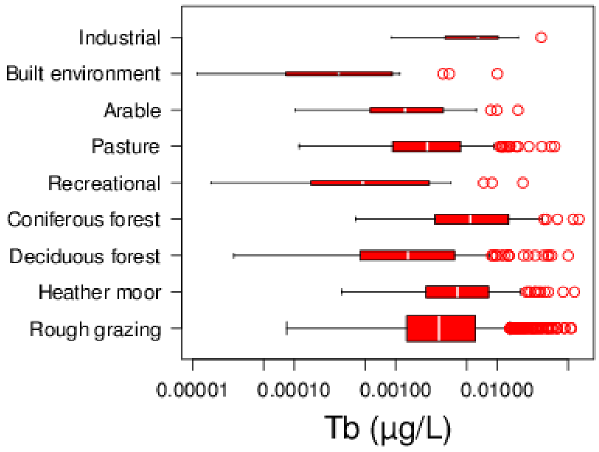
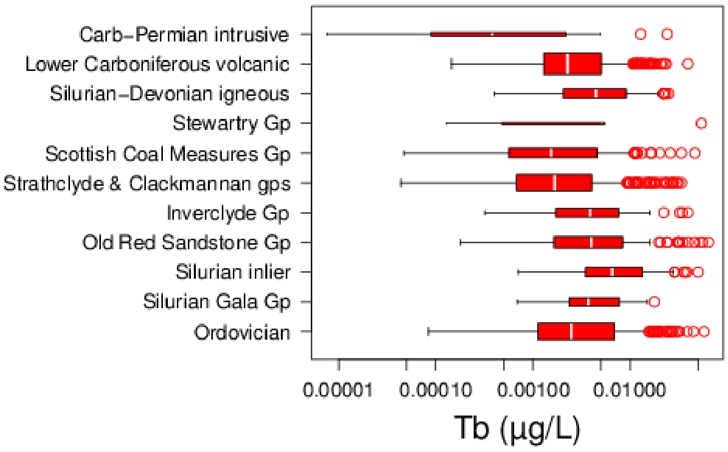
Terbium Tb

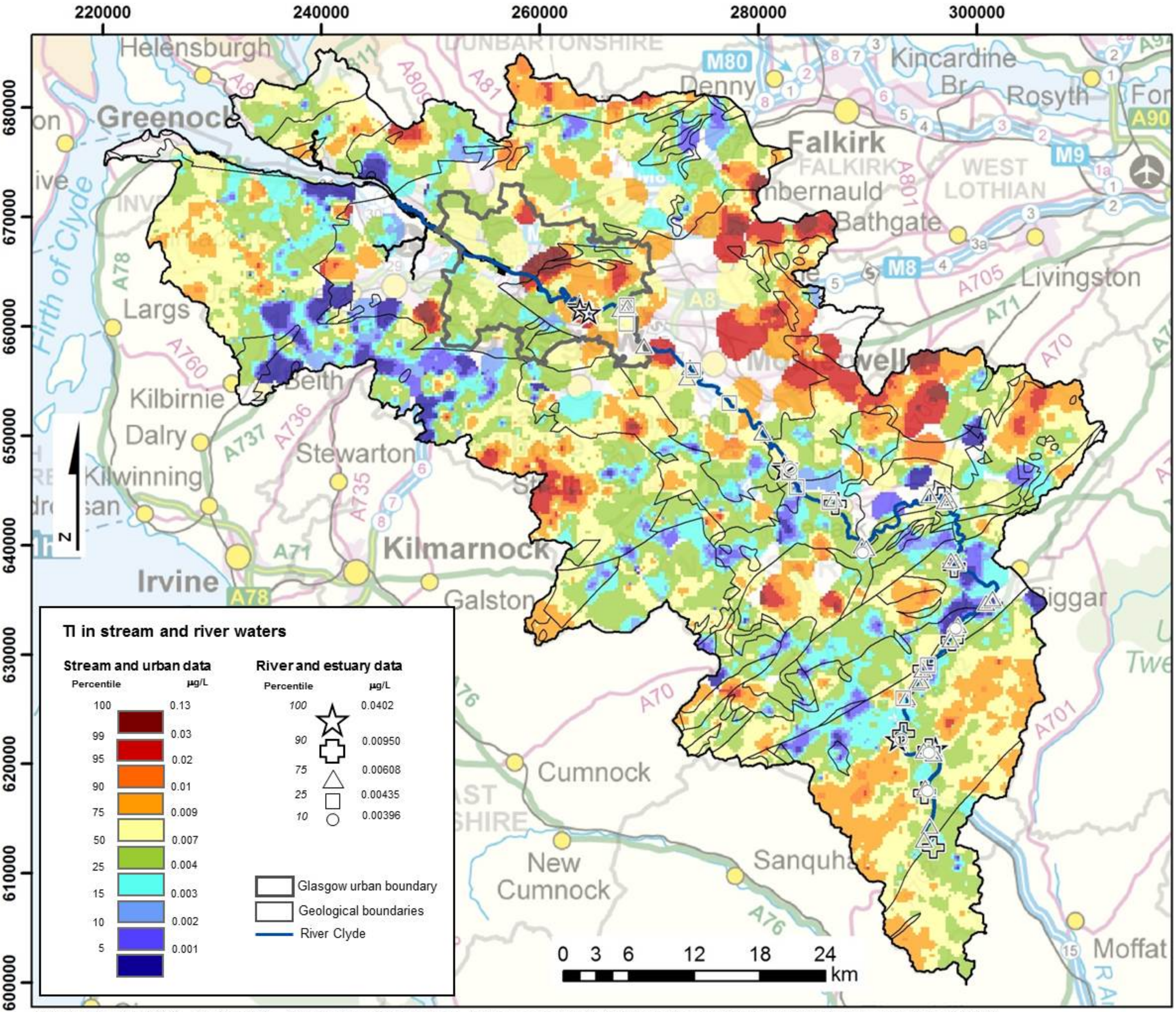
	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.002	<0.002	No data	No data
25th %	0.00128	0.001		
50th %	0.00264	0.00155		
75th %	0.00653	0.00235		
90th %	0.013	0.00423		
max	0.0637	0.00576		
n	1702	60		
n cens	708	38		
rainwater				
seawater				







Thallium Tl



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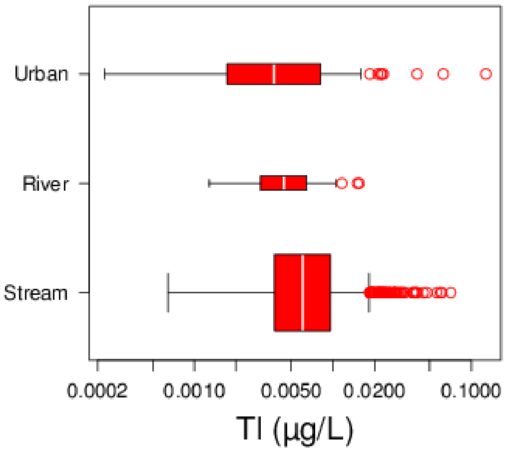
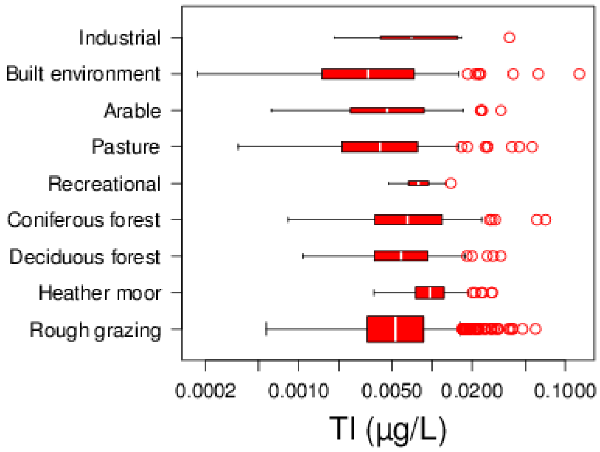
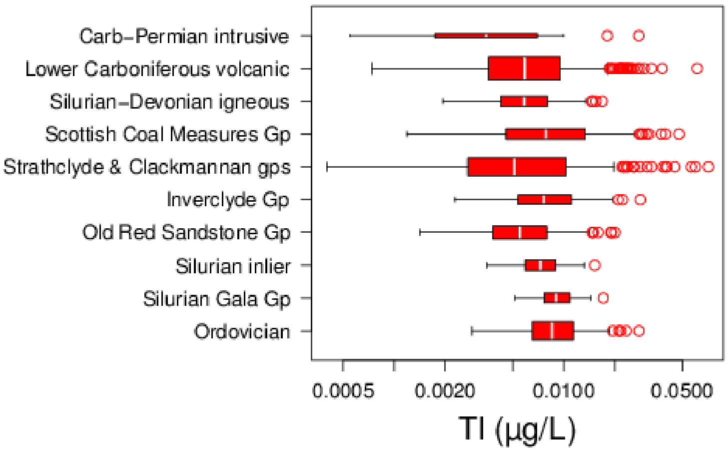
Thallium

Tl

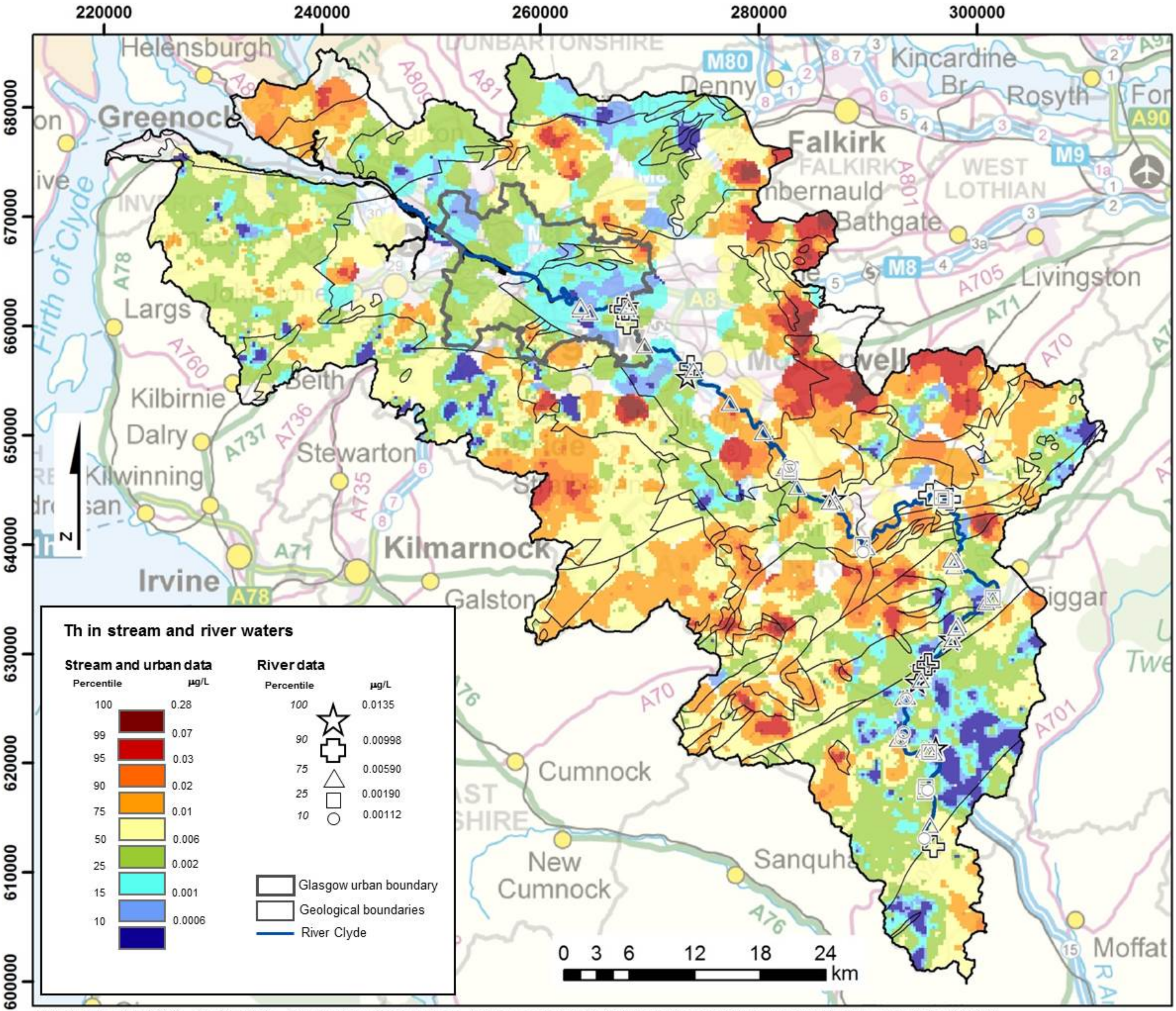
	Stream	River	Urban	Estuary
			(µg/L)	
min	<0.01	<0.01	<0.01	No data
25th %	0.0038		0.00173	
50th %	0.00604		0.00375	
75th %	0.00961		0.00812	
90th %	0.0144		0.0151	
max	0.0712	0.0155	0.127	
n	1702	60	122	
n cens	1278	57	92	
rainwater				
seawater				







Thorium Th



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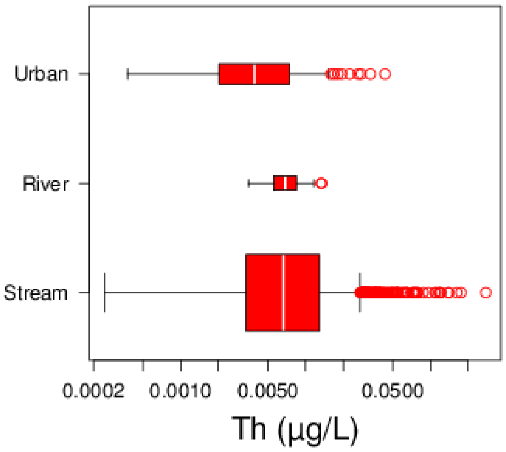
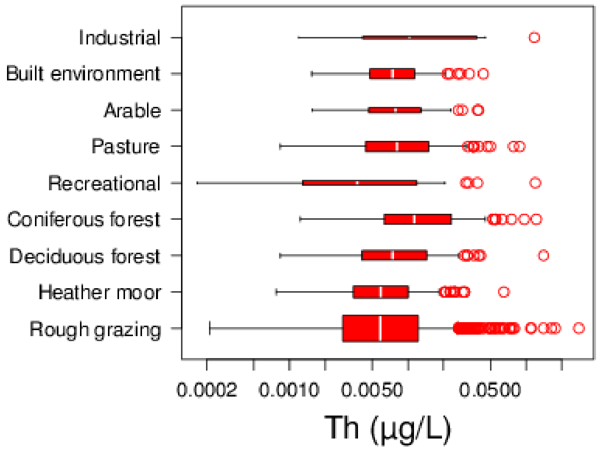
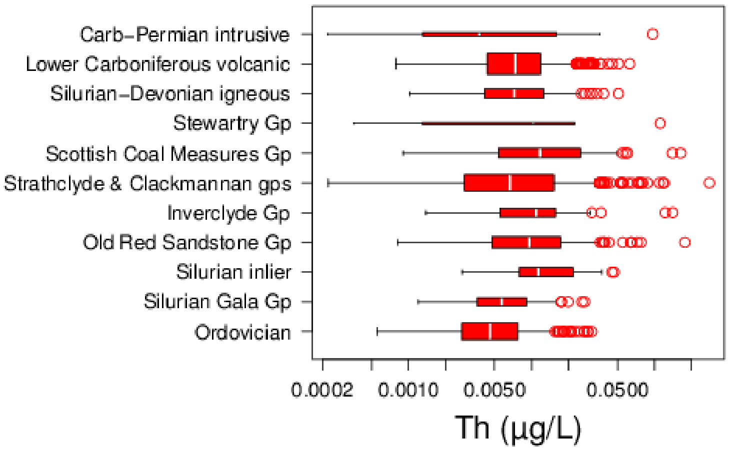
Thorium

Th

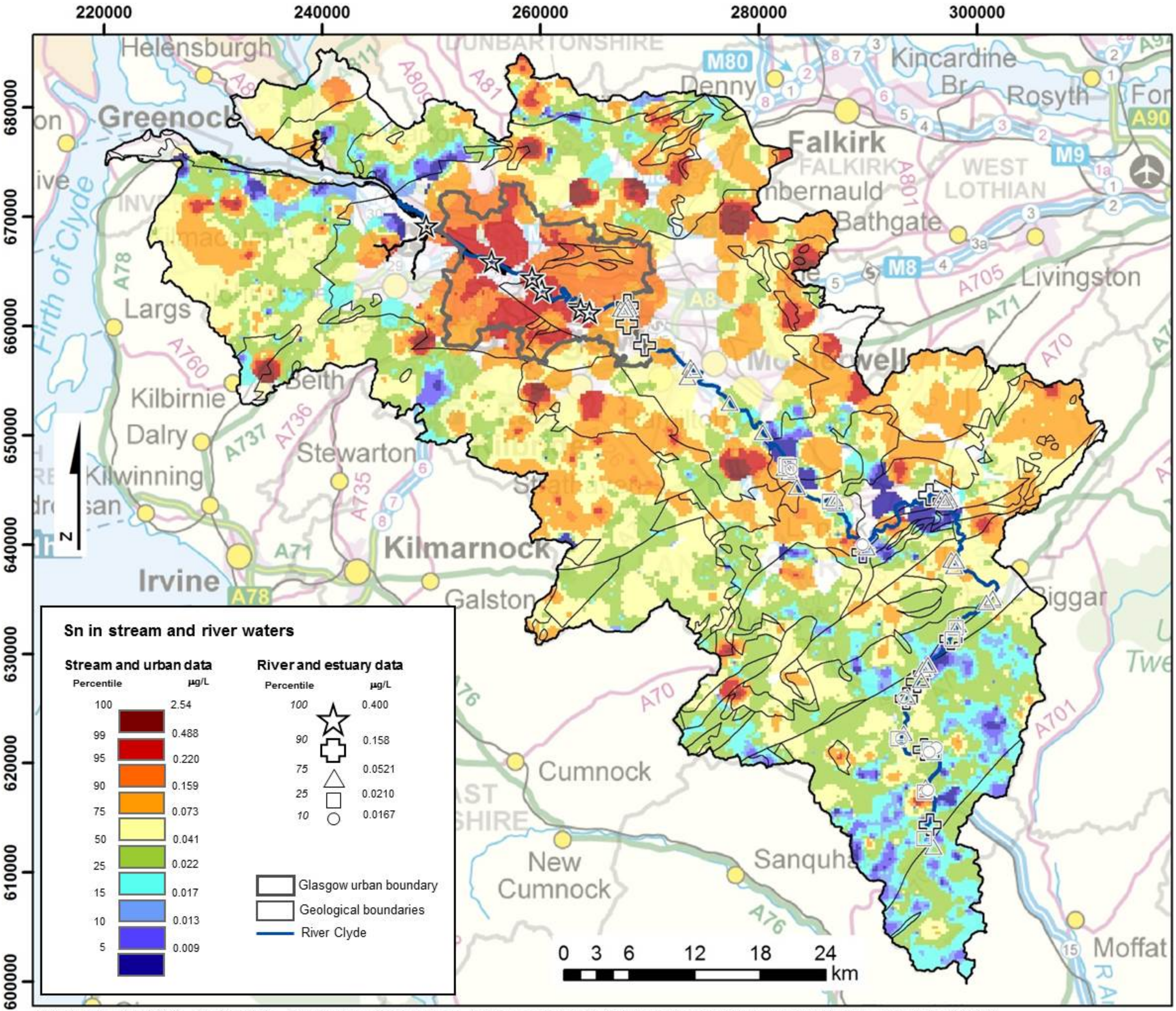
	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.01	<0.01	<0.02	No data
25th %	0.00334			
50th %	0.00662			
75th %	0.013			
90th %	0.0247			
max	0.278	0.0135	0.0434	
n	1702	60	122	
n cens	1128	53	117	
rainwater				
seawater				







Tin Sn



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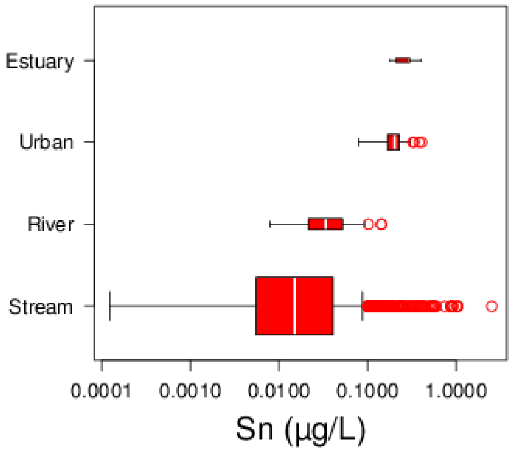
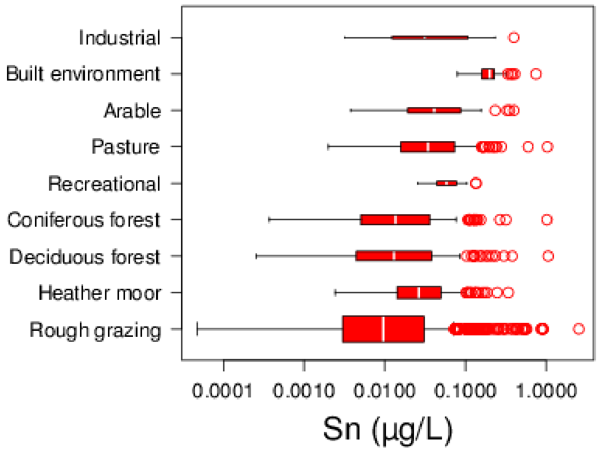
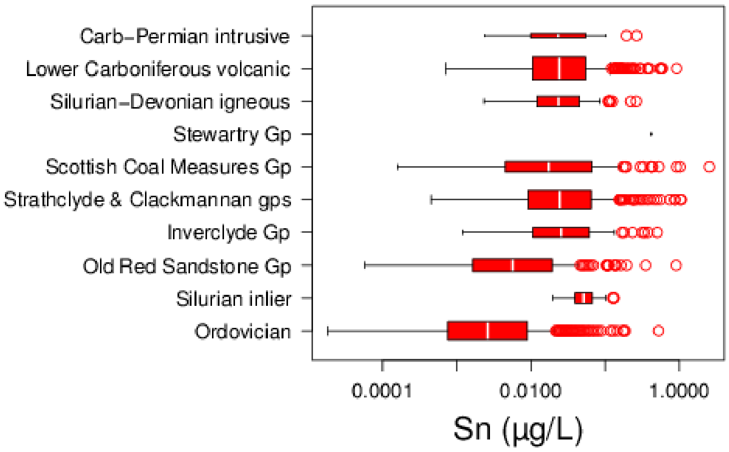
Tin

Sn

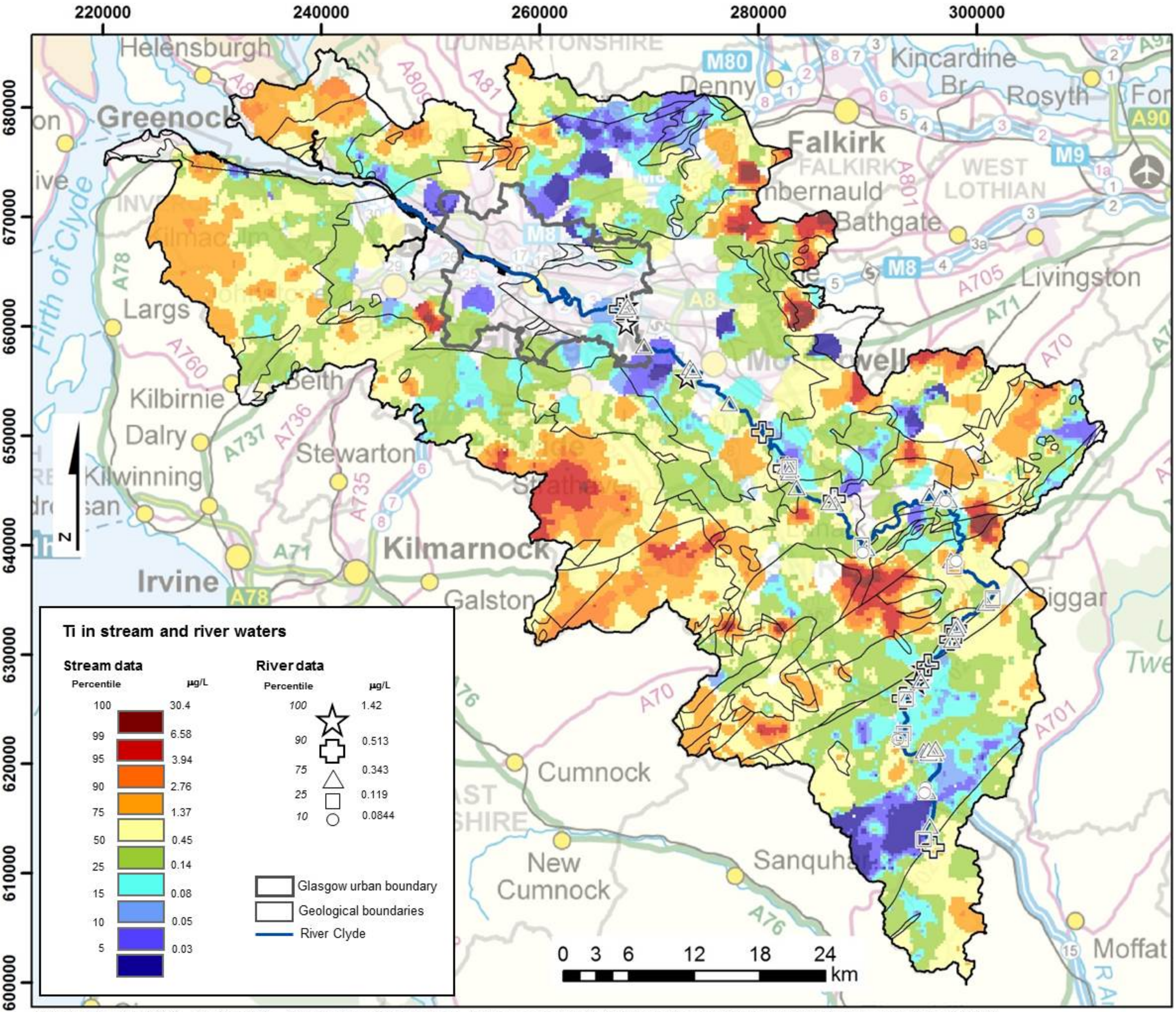
	Stream	River	Urban (µg/L)	Estuary
min	<0.1	<0.1	0.0796	0.18
25th %	NA		0.169	0.21
50th %	NA		0.202	0.3
75th %	NA		0.23	0.3
90th %	NA		0.267	0.34
max	2.54	0.144	0.41	0.4
n	1702	60	122	7
n cens	1504	57	0	0
rainwater				
seawater	0.8			







Titanium Ti



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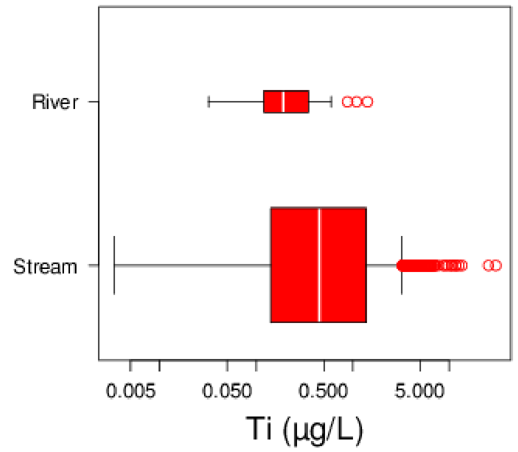
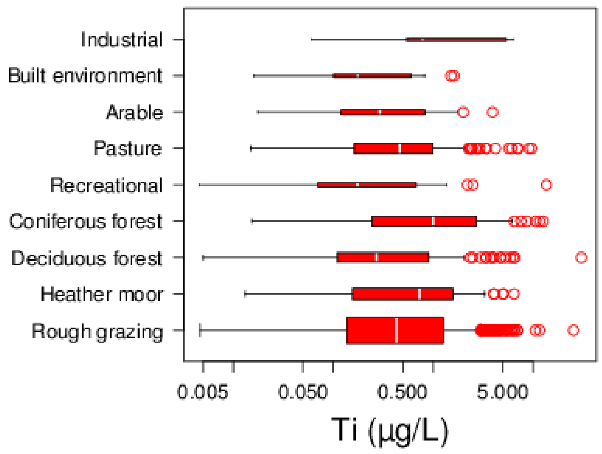
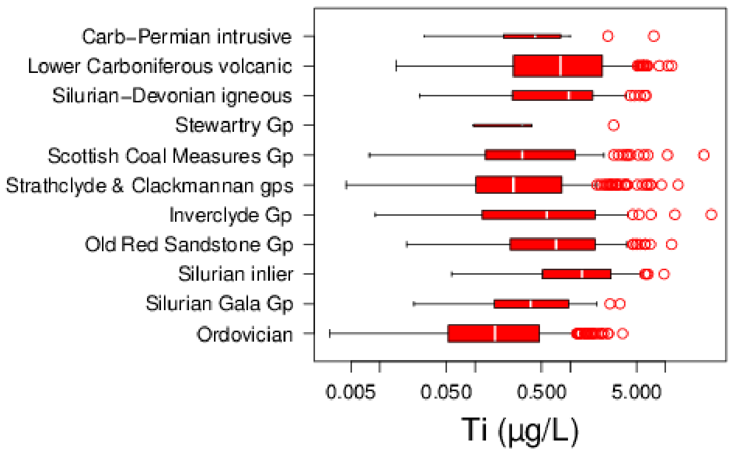
Titanium Ti

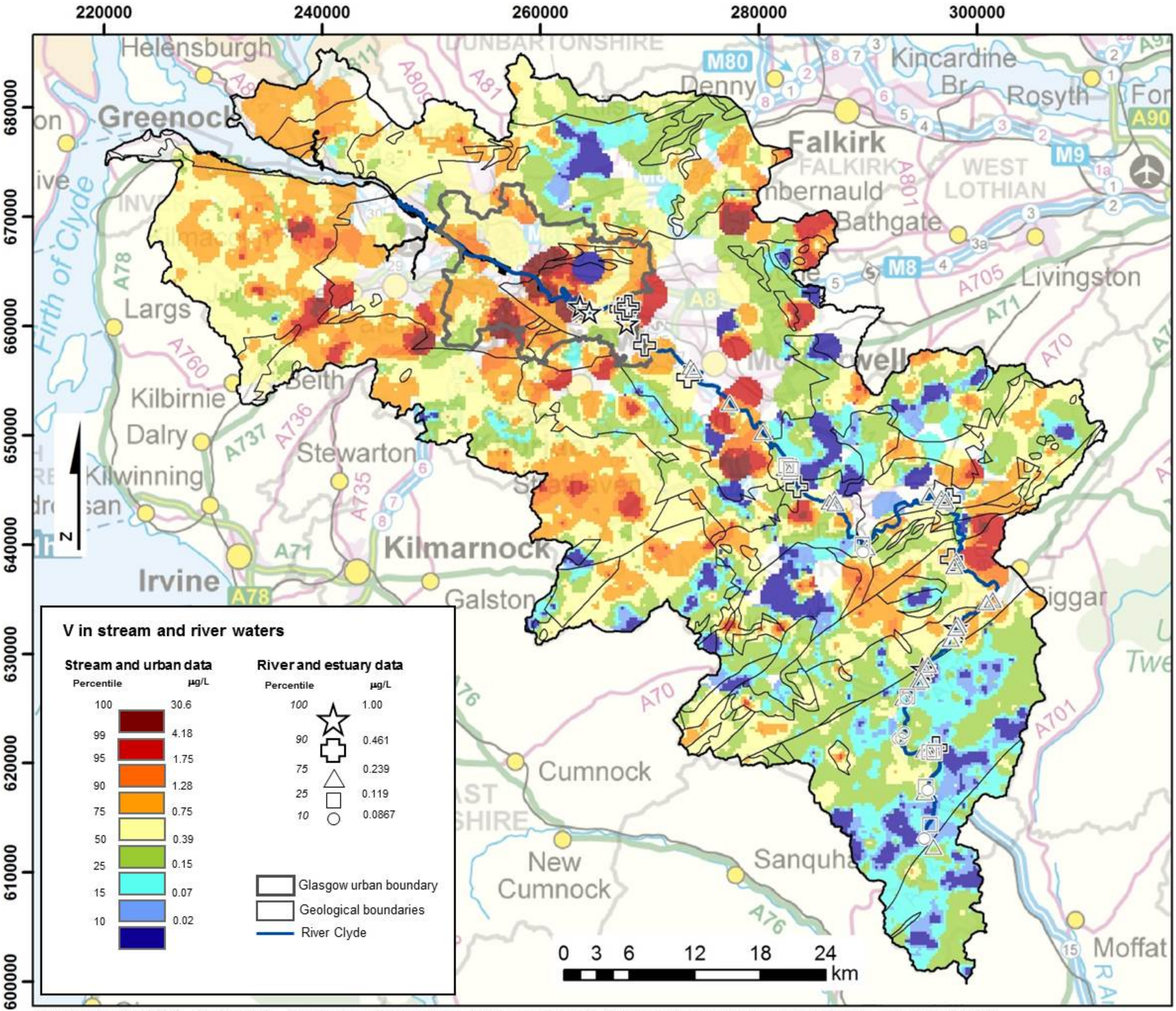
	Stream	River	Urban (µg/L)	Estuary
min	<0.05	<0.05	No data	No data
25th %	0.142	0.119		
50th %	0.45	0.19		
75th %	1.37	0.343		
90th %	2.76	0.513		
max	30.4	1.42		
n	1702	60		
n cens	154	1		
rainwater				
seawater	1			







Vanadium V



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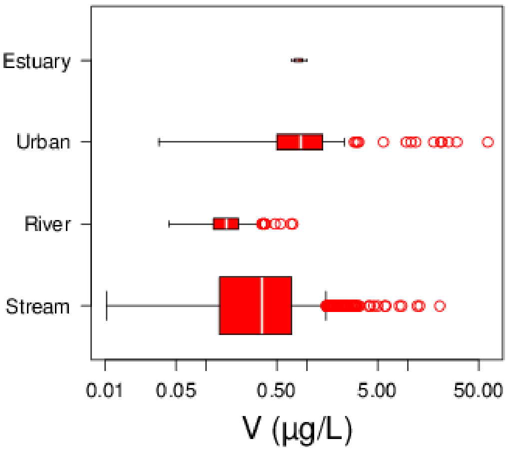
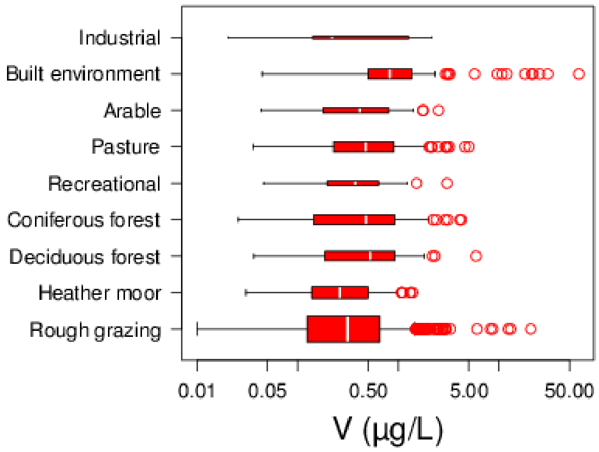
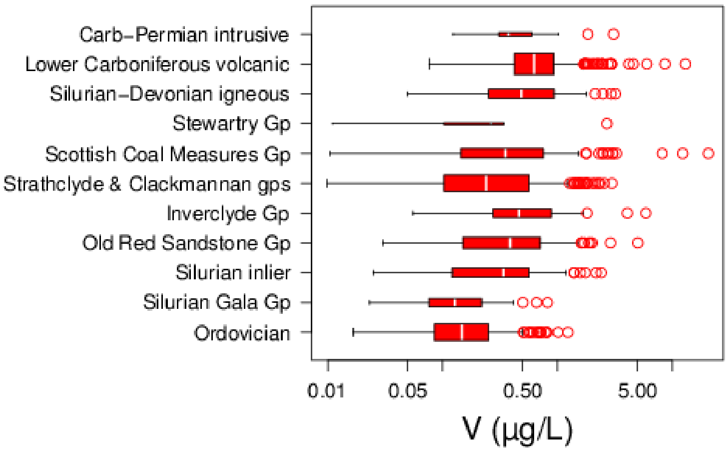
Vanadium

V

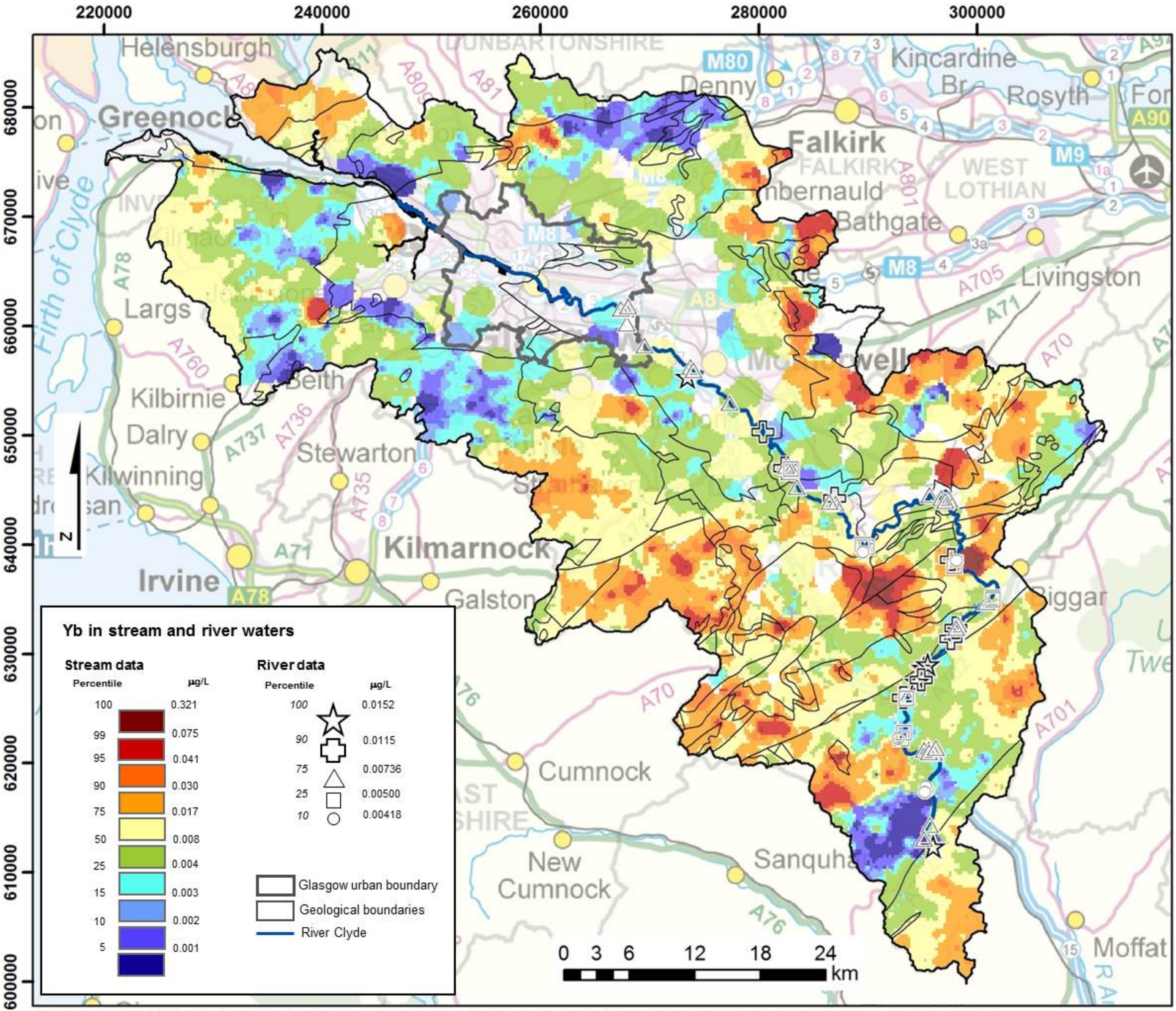
	Stream	River	Urban (µg/L)	Estuary
min	<0.1	<0.1	<0.5	0.7
25th %	0.136	0.118	0.502	0.75
50th %	0.355	0.157	0.865	0.8
75th %	0.699	0.206	1.42	0.9
90th %	1.22	0.372	3.04	0.96
max	20.7	0.723	62.1	1
n	1702	60	122	3
n cens	351	9	29	0
rainwater				
seawater	2			







Ytterbium Yb



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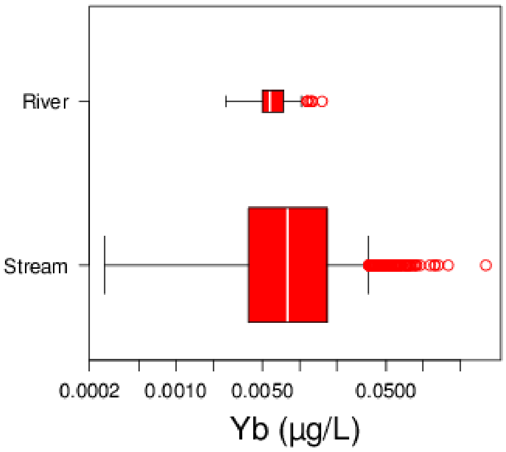
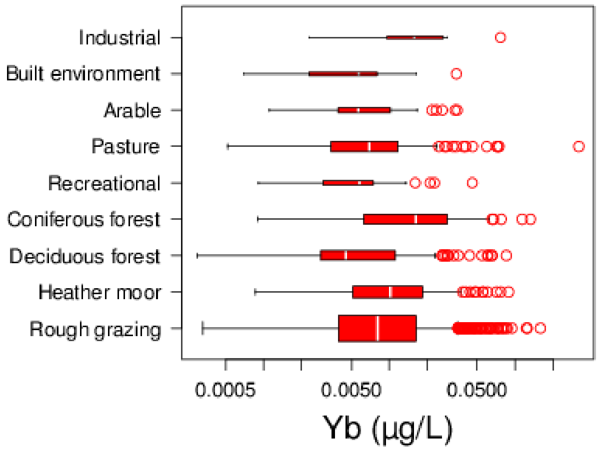
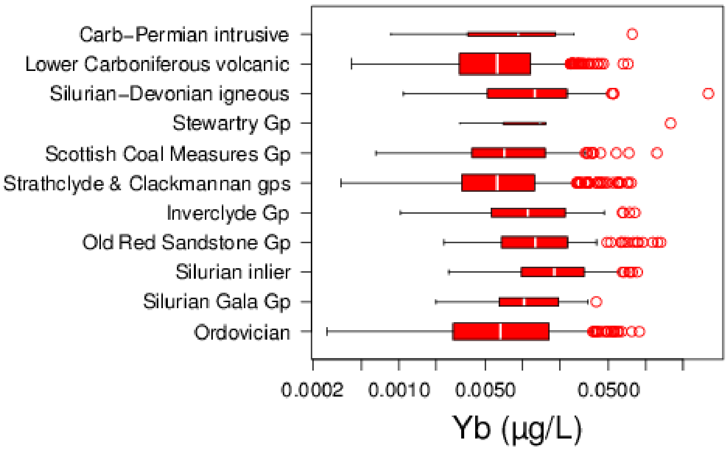
Ytterbium

Yb

	Stream	River	Urban	Estuary
		(µg/L)		
min	<0.002	0.00252	No data	No data
25th %	0.00387	0.005		
50th %	0.00796	0.00572		
75th %	0.0167	0.00736		
90th %	0.0302	0.0115		
max	0.321	0.0152		
n	1702	60		
n cens	171	0		
rainwater				
seawater				

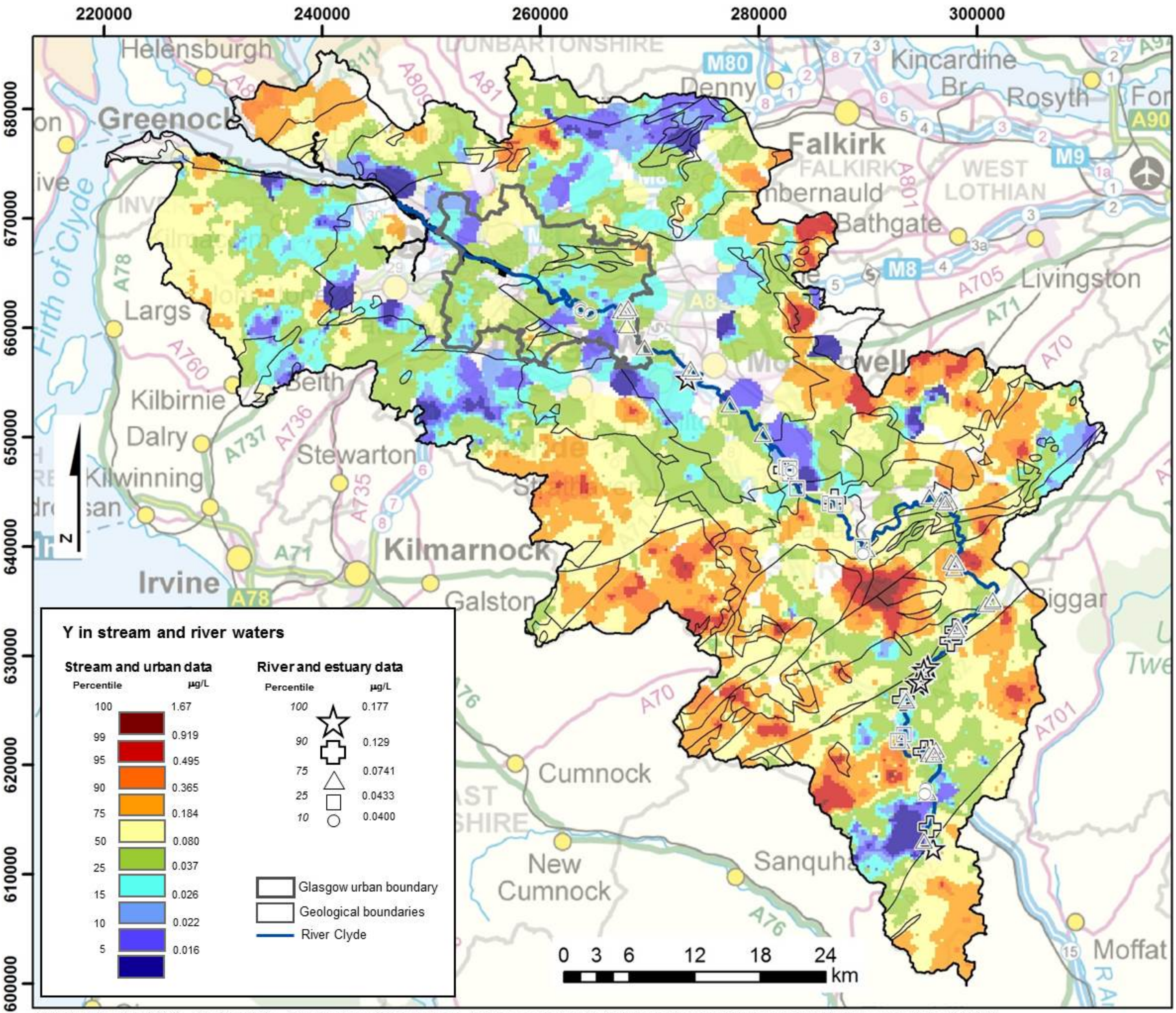






Yttrium

Y



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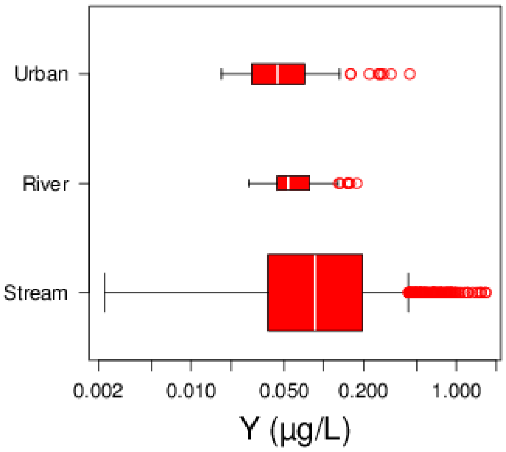
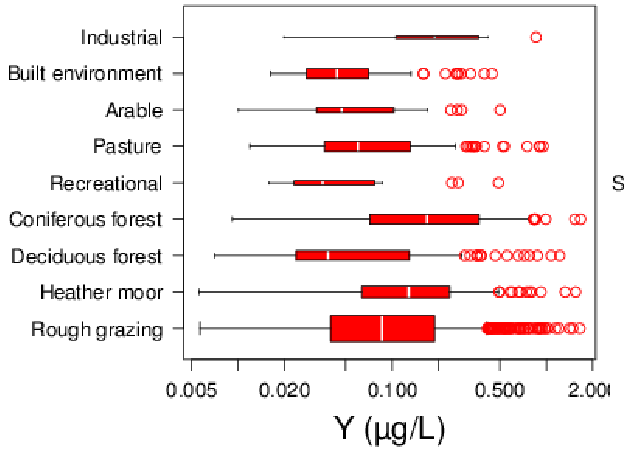
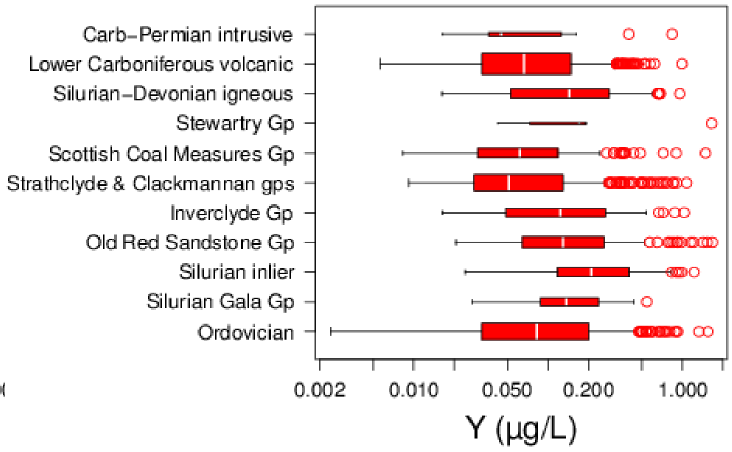
Yttrium

Y

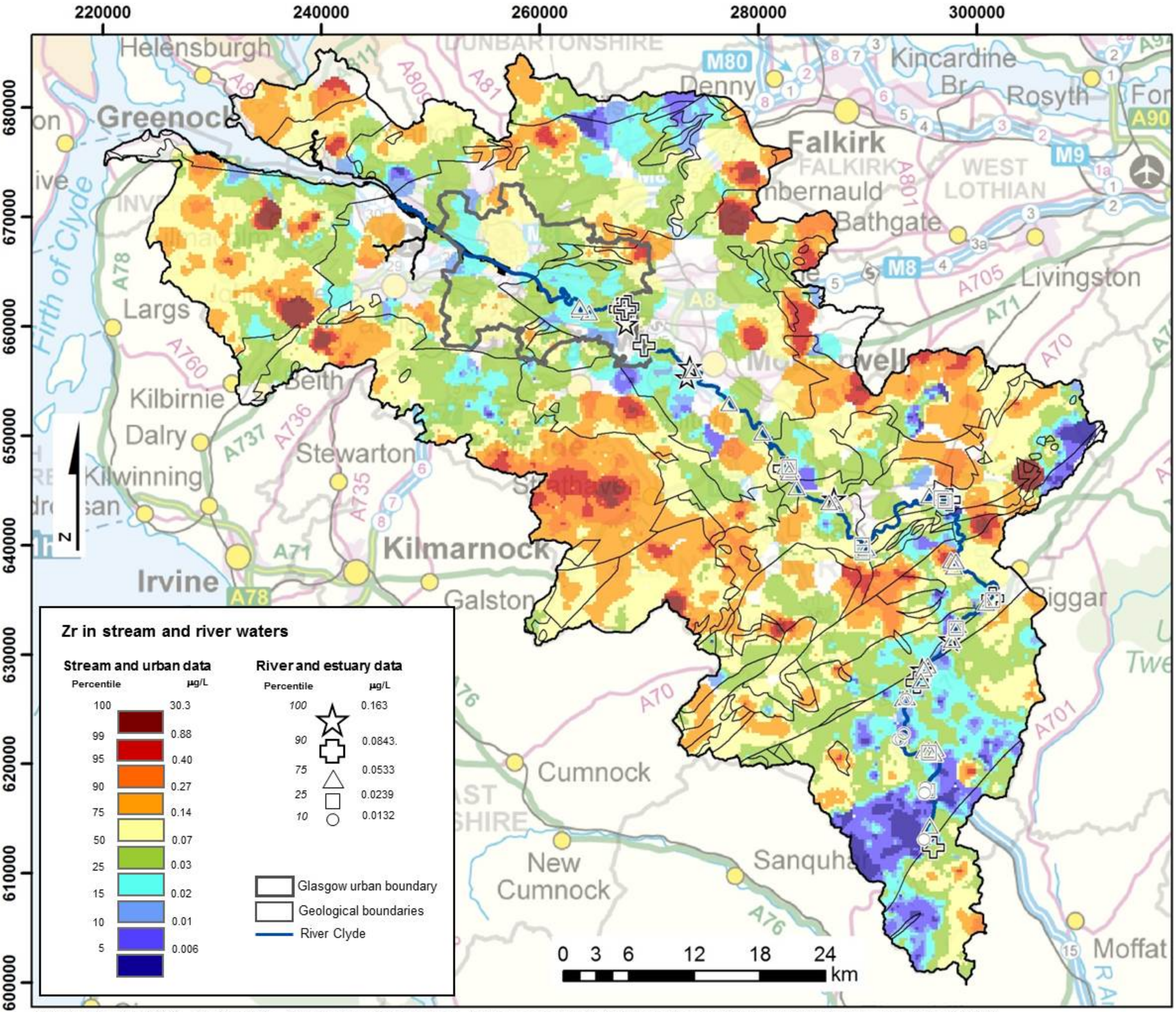
	Stream	River	Urban (µg/L)	Estuary
min	<0.005	0.0273	0.017	No data
25th %	0.038	0.0447	0.0291	
50th %	0.0853	0.0541	0.0452	
75th %	0.196	0.0762	0.0717	
90th %	0.372	0.13	0.108	
max	1.67	0.177	0.444	
n	1702	60	122	
n cens	2	0	0	
rainwater				
seawater	0.003			







Zirconium Zr



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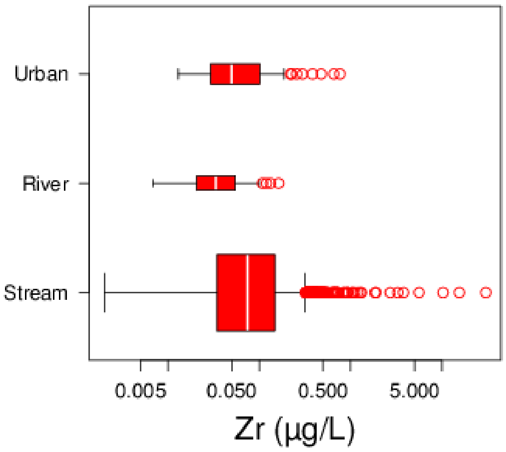
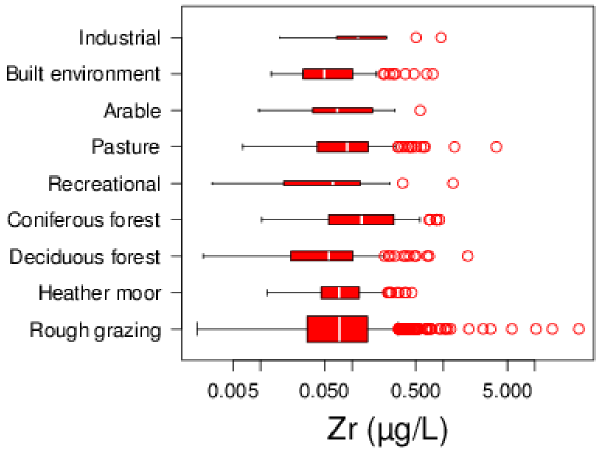
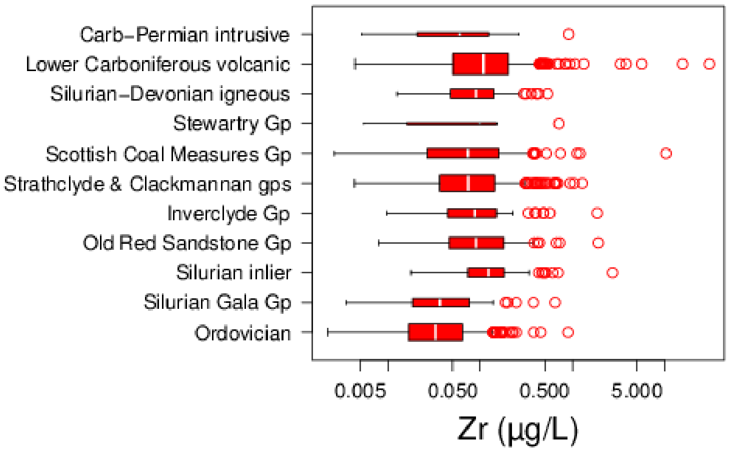
Zirconium Zr

	Stream	River	Urban (µg/L)	Estuary
min	<0.05	<0.05	0.0131	No data
25th %	0.0345	0.0207	0.0292	
50th %	0.0747	0.0335	0.0499	
75th %	0.148	0.0545	0.1	
90th %	0.281	0.087	0.153	
max	30.3	0.163	0.764	
n	1702	60	122	
n cens	623	40	0	
rainwater				
seawater				







Glossary

AFS	Atomic fluorescence spectrometry
ANOVA	Analysis of variance
BGS	British Geological Survey
CEH	Centre for Ecology and Hydrology
CRM	Certified reference material
CUSP	Clyde and Glasgow Urban Super Project
DOC	Dissolved organic carbon
DIC	Dissolved inorganic carbon
EA	Environment Agency (England and Wales)
ESRI	Environmental Systems Research Institute
Estuary	Refers to the samples taken as part of the 2002–2003 survey of the inner Clyde Estuary
G-BASE	Geochemical Baseline Survey of the Environment
GCC	Glasgow City Council
GIS	Geographic information system
Glasgow urban boundary	Refers to the area on the maps in which samples were taken within the area of Glasgow City for the Urban dataset
GPS	Global positioning system
HDPE	High density polyethylene
IC	Ion chromatography
ICP-MS	Inductively coupled -plasma mass spectrometry
ICP-AES	Inductively coupled plasma -atomic emissions spectrometry
IDW	Inverse distance weighted
LDPE	Low density polyethylene
LLD	Lower limit of detection
N cens	Number of samples below detection limit
NERC	Natural Environment Research Council
NPOC	Non purgeable organic carbon
OS	Ordnance Survey
PHE	Potentially harmful element
QC	Quality Control

River	Refers to samples taken from the River Clyde and its major tributaries upstream of Glasgow during 2010
SEPA	Scottish Environment Protection Agency
Stream	Refers to samples taken during 2010 from rural streams across the Clyde Basin at a density of 1 per 1.5km^2
TOC analyser	Total organic carbon analyser
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
UKEAP	United Kingdom Eutrophying and Acidifying Pollutants network
Urban	Refers to Glasgow Clyde Urban Tributary project, samples were taken every 1 km of stream length along tributaries of the river Clyde within the Glasgow City Council area
VWs	Voluntary workers

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