Using geological and geochemical information to estimate the potential distribution of trace elements in Scottish groundwater

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Using geological and geochemical information to estimate the potential distribution of trace elements in Scottish groundwater

Alan M MacDonald, Fiona M Fordyce, Paul Shand and Brighid E Ó Dochartaigh

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British Geological Survey offices

Keyworth, Nottingham NG12 5GG
☎ 0115-936 3241 Fax 0115-936 3488
E-mail: sales@bgs.ac.uk
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Shop online at: www.geologyshop.com

Murchison House, West Mains Road, Edinburgh EH9 3LA
☎ 0131-667 1000 Fax 0131-668 2683
E-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE
☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgslondon@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU
☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF
☎ 028-9038 8462 Fax 028-9066 2835
E-mail: gsn@detini.gov.uk

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB
☎ 01491-838800 Fax 01491-692345
E-mail: hydro@bgs.ac.uk

Sophia House, 28 Cathedral Road, Cardiff, CF11 9LJ
☎ 029–2066 0147 Fax 029–2066 0159

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU
☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk
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Summary

There are currently few reliable data available for the concentrations of trace elements in Scottish groundwaters. A new project Baseline Scotland, jointly funded by the British Geological Survey (BGS) and the Scottish Environment Protection Agency (SEPA), seeks to improve the data availability and general understanding of the chemistry of Scotland’s groundwater. However, this is a major undertaking and these new data will take several years to collect and interpret across the whole of Scotland.

In the interim, SEPA have asked BGS to use their existing knowledge and data to give a rough estimate of where certain elements are more likely to be elevated in groundwater. This information will be used to help focus future monitoring and give background for Baseline Scotland. Predicting trace element concentrations is difficult, in part due to lack of knowledge on the distribution of mineral phases, the reactivity of different minerals and the geochemical environment, particularly the redox status.

This report scopes the potential scale of naturally elevated trace elements in Scottish groundwater, in particular those elements that are potentially harmful to health: e.g. aluminium, arsenic, barium, cadmium, chromium, lead, manganese, nickel, uranium and zinc. The problems and limitations of prediction are discussed in the report and this work does not replace a proper assessment based on actual chemical analyses of groundwater.

The method uses information on the geochemistry of the Scottish environment derived from the most comprehensive geochemical data set for Scotland, the BGS Geochemical Baseline Survey of the Environment (G-BASE), combined with the limited data available on the chemistry of Scottish groundwaters. The conditions under which each of the elements can become elevated in groundwater are discussed and the geological and geochemical information interpreted to produce a series of maps highlighting areas where each trace element may be elevated in groundwater relative to the Scottish average.

The maps are based primarily on the 1:625 000 scale bedrock geology map of Scotland. In order to make the scheme and the maps simple and manageable, we have used the same numbers to describe the individual rock units (1 to 114) that are used on the Geological map of the UK (Solid Geology): North sheet. Some rock units have been subdivided, and other small areas highlighted where additional information is known, either from G-BASE or previous studies.

After assessing the results of the exercise the following conclusions can be drawn:

1. The study has provided a useful summary of geochemical information for trace elements in Scotland, and detail the conditions in which these elements may become elevated in groundwater. This provides essential background to the Baseline Scotland project, which aims to improve the availability of groundwater chemistry data and the general understanding of the chemistry of Scotland’s groundwater.

2. The predictions can be used as a first pass to help focus and prioritise additional monitoring and for helping to interpret groundwater chemistry data from different areas. The predictions are only preliminary and will be modified in the future by detailed groundwater sampling and interpretation.

There are several caveats:

• For all of the trace elements considered, the lack of available groundwater chemistry data with detailed analysis of trace elements, and their restricted spatial distribution,
means that it is not possible to rigorously test whether the groundwater quality predictions are accurate or not.

- More groundwater chemistry data are available for three elements, barium, manganese and zinc, allowing a rudimentary test of the predictive maps. For barium the prediction appears to work well, but there is poor correlation for zinc. For manganese, some correlation is evident, but the complexity and variability of local conditions are such that much variation is observed.

- This approach, using broad, national scale geological and environmental data, cannot account for the complexity of the controls on groundwater chemistry: i.e. the heterogeneous nature of the Scottish environment, not least the aquifer mineralogy and glacial history, and the complex behaviour of trace elements in groundwater, determined by aspects such as flow pathways, residence times, and the geochemical environment (for example, oxidising/reducing or acidic/alkaline conditions).

In summary, this approach appears to be a useful first step in trying to estimate the likely distribution of trace elements in Scottish groundwater, in the absence of much reliable groundwater quality data. However, only by systematically collecting reliable groundwater chemistry data, across different aquifers and regions and from different depths, can the variation in trace elements in groundwater across Scotland be understood. Careful modelling and interpretation of these new data in the context of the geology and environmental conditions will help make future predictions of groundwater quality more reliable and provide reference information for the Water Framework Directive.
1 Introduction

*Baseline Scotland*, jointly funded by BGS and SEPA, aims to improve the data availability and general understanding of the chemistry of Scotland’s groundwater. The project contributes to the aims of both organisations by providing core hydrogeological data and interpretation to help in the implementation of the Water Framework Directive (WFD). The interpretation of the data is focussed to help identify the baseline groundwater chemistry conditions within the aquifer.

There are few data currently available across Scotland on the concentration of trace elements in groundwater. Historically, this is for three reasons: (1) poor coverage of sites across Scotland with reliable groundwater chemistry; (2) routine analysis by Scottish Water or SEPA does not usually include a full suite of trace elements; (3) even where they have been measured, the detection limits can be too high to give detailed information on variations.

This report scopes the potential scale of naturally elevated trace elements in Scottish groundwater, in particular the potentially harmful elements aluminium (Al), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni), uranium (U) and zinc (Zn). This was done by examining the geology, the available geochemistry data, and the limited groundwater quality data for Scotland and making judgements about the conditions in which elements will become soluble in groundwater. Much is speculative due to the limited data, and the resulting maps should be treated only as a broad indication of where certain elements may be more likely to be elevated – locally the conditions may be very different.

The purpose of the exercise is to provide additional information to SEPA to help focus future monitoring for the Water Framework Directive and also to help prioritise new areas to study for *Baseline Scotland*. An accompanying report (MacDonald and Ó Dohartaigh 2005) describes the available groundwater quality data for Scotland in more detail.

The maps in this report are based on the 1:625 000 bedrock geology map for Scotland. Different rock units at this broad scale are attributed as being more, or less, likely to have elevated concentrations of various trace elements. Other areas have been added where additional information is known, either from geochemical data and local knowledge, or the available groundwater data.
An overview of G-BASE for Scotland

2.1 INTRODUCTION

Although data on the quality of Scottish groundwater are rather limited (MacDonald and Ó Dochartaigh 2005), other geochemical datasets exist for Scotland. The most comprehensive is the BGS Geochemical Baseline Survey of the Environment (G-BASE). This chapter introduces the concepts of environmental geochemistry and the G-BASE project before summarising and assessing the data available for selected elements across Scotland. Only arsenic, cadmium, chromium, lead, nickel and uranium are discussed.

High concentrations in stream sediments do not necessarily indicate that concentrations will be high in groundwater. This is discussed in more detail in the next chapter.

2.2 GEOCHEMISTRY

Geochemistry is a useful tool for geologists to help categorise different types of rock as the chemistry can vary according to the mineralogical composition, mode of formation and weathering history. However, rocks do not appear at surface everywhere, but are often covered by superficial deposits. Pioneering work carried out in Russia between the 1930s and 1950s demonstrated that there were strong links between the chemistry of the underlying rocks and that of the weathering products covering them (such as soils, glacial deposits, stream and lake sediments). The main driver behind much of this scientific development was mineral exploration, and the technique was successful because in many cases, the superficial deposits covering mineralised bedrock also have elevated concentrations of metals derived from the bedrock, allowing the underlying mineral deposit to be targeted. Hence, the scientific field of applied geochemical mapping was established.

Over 100 countries around the world have national geochemical mapping programmes as most governments recognise the importance of this information for environmental and mineral resource management. In terms of mineral resource management, high concentrations of the metallic elements are of most interest. However, analytical advances over the last 30 years have allowed the determination of a greater number of parameters at increasingly low concentrations in the Earth’s surface, and many of these mapping programmes that began for mineral exploration are now of prime interest for environmental studies (Darnley et al.1995; Fordyce et al. 1997; Plant et al. 1997).

2.3 THE G-BASE PROJECT

The BGS is responsible for carrying out the national strategic geochemical survey of the UK, known as the Geochemical Baseline Survey of the Environment (G-BASE). The project began in 1970 in the north of Scotland and will eventually provide information for the whole country (Johnson and Breward, 2004). To date, approximately 80% of the UK land area has been sampled (Figure 2.1).

The mapping programme is based primarily on the collection of fine fraction (< 150 µm) rural stream sediments and stream waters from first and second order streams at a sampling density of 1 per 1.5 km². Therefore the drainage network determines the sample distribution in any area (Johnson and Breward, 2004). To date, approximately 100 000 sediment sites have been sampled across the UK.
2.4 G-BASE DATA FOR SCOTLAND

The original driver behind the G-BASE project was uranium exploration, at the time of the oil crisis in the early 1970s when nuclear resources were being sought as an alternative to fossil fuels. The G-BASE project therefore started in the north of Scotland where several granitic bodies and uranium mineralisation provided potential target sources. As a result, Scotland was the first part of the UK to have complete geochemical coverage, and a full set of geochemical atlases was published in 1986 (Appendix 1 has details of the data available for Scotland). However, it should be noted that the Scottish survey focussed on the collection of stream sediments: no regional soils data are available for Scotland, and only a very limited number of parameters were determined in stream water samples (pH, total alkalinity, conductivity, fluoride and uranium). Furthermore, at the start of the programme, stream water samples were only collected at one in every three sites, and therefore the data for the north and west of Scotland are sporadic. It is only in more recent years, when the survey was active in Wales
and Eastern England, that soil sampling and the analysis of a full suite of water chemistry parameters have been added to the project.

The analytical techniques available during the 1970s were not as sensitive as modern methods, and so the limits of detection for elements such as arsenic, cadmium, molybdenum and antimony were not as good as they are at the present day. At the start of the project, the number of elements determined was also restricted by analytical capability. As a result, the number of parameters available for the north and west of Scotland is limited compared to the current suite of G-BASE determinands.

The main G-BASE dataset for Scotland comprises pH, total alkalinity, fluoride (F), uranium (U) and conductivity in stream waters; and total element concentrations in stream sediments for silver (Ag), arsenic (As), boron (B), barium (Ba), beryllium (Be), bismuth (Bi), calcium (CaO), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe₂O₃), gallium (Ga), potassium (K₂O), lanthanum (La), lithium (Li), magnesium oxide (MgO), manganese (MnO), molybdenum (Mo), niobium (Nb), nickel (Ni), phosphorus (P₂O₅), lead (Pb), rubidium (Rb), antimony (Sb), tin (Sn), strontium (Sr), titanium (TiO₂), vanadium (V), yttrium (Y), zinc (Zn) and zirconium (Zr). Full details of the G-BASE survey and the analytical methods used in the project are provided in the series of regional geochemical atlases available for Scotland.

The main focus of the regional G-BASE survey is now to complete coverage of southern England. However, in recent years two projects have been active in Scotland under the urban component of the project.

3. During 2001 and 2002, approximately 1380 urban and 250 peri-urban soil samples were collected across the Glasgow conurbation in collaboration with Glasgow City Council (GCC). These data will be reported and made available under licence from the BGS in 2006 and will represent the first detailed systematic urban soil dataset for Scotland.

4. In addition to land quality, GCC expressed interest in an overview of drainage quality in the Glasgow administrative area to link to on-going investigations into estuarine geochemistry also being carried out by the BGS on the River Clyde (Jones et al. 2004). A systematic survey of urban stream sediments and stream waters from tributaries draining into the River Clyde was carried out during 2003. A total of 118 sediment and 122 water samples were retrieved from every kilometre of stream length across the area. The data were reported in 2004 and are available under licence from the BGS-GCC and represent the first detailed systematic urban stream water chemistry data set for Scotland (Fordyce et al. 2004).

2.5 CONCENTRATIONS OF SELECTED ELEMENTS IN STREAM SEDIMENTS

2.5.1 Scope

It is beyond the scope of this overview of the G-BASE data to retrieve and compile a specific geochemical database for Scotland from the main BGS corporate geochemistry database of the UK, and generate specific individual element maps for the purpose of this study. However, it is recommended that this be carried out in future as part of further investigation into the relationships between geochemistry and groundwater quality. For the purposes of this report, examples of existing interpolated geochemical maps for Scotland, in particular arsenic, cadmium, chromium, nickel, lead and uranium, are compared to geological controls and other factors affecting element distributions. Much of the geochemical information is extracted from the BGS regional atlases that should be referred to for more information regarding localities mentioned in the text (see Appendix 1 for references).
The geochemical maps in this report present data as percentile classes of the data distribution, which is a standard method of representing regional geochemical information. The maps comprise computer-generated surface grids for each element produced by interpolation of the real data using Inverse Distance Weighting (IDW), which calculates a value for each grid cell, whereby each cell represents 250 m on the ground. The calculation is based on data for all samples within a distance of 1500 m (i.e. the sampling density) weighted in accordance with a distance r such that the weighting is proportional to $r^2$. Interpolated areas that fall more than...
1500 m from a sample point (i.e. greater than the normal sample density) are removed from the maps to avoid interpolation into areas of no real data information. The gridded data are then colour classified according to the 5th, 10th, 15th, 25th, 50th, 75th, 90th, 95th and 99th percentiles of the data distribution (BGS 1999).

A map of the geology of Scotland is shown in Figure 2.2 to help interpret the results. The names of various towns, villages or hills are mentioned throughout the text to help locate certain areas. For more detailed information and explanations the individual geochemical atlases should be consulted.

2.5.2 Arsenic (As)

Figure 2.3 shows the distribution of arsenic in stream sediments across Scotland and indicates the scale of the missing data for much of the Highlands.

1. Concentrations of the element are generally low (< 12 mg kg\(^{-1}\)) over much of the country.

2. Isolated anomalies (> 43 mg kg\(^{-1}\)) are associated with various igneous intrusions (Strichen, Aberdeen, Forest of Deer, Grantown-on-Spey, Comrie, Craig Nordie, Glen Gairn, Hill of Fare, Lochnagar and Glen Shee), and generally reflect sulphide mineralisation associated with these granitic bodies. The exception is Grantown, where the high arsenic concentrations may reflect secondary precipitation of iron and manganese oxides, rather than a mineralised source.

3. The Upper Dalradian succession from the Kintyre peninsula to Buchan shows enrichment of arsenic (> 38 mg kg\(^{-1}\)), probably related to the presence of sulphide mineralisation in the succession. Significant anomalies are associated with the Glenn Doll intrusion in Glen Clova, to the north-east of Comrie and Upper Glen Turret and Glen Lednock. Mineralisation in the Loch Etive - Loch Creran and Kilmelford complexes also results in elevated stream sediment concentrations of arsenic (> 70 mg kg\(^{-1}\)). High concentrations are also associated with sulphide mineralisation in the Tyndrum - Loch Lyon fault systems, including Ben More and Cribralrich. Mineralisation in Upper Dalradian quartzites and schists also accounts for high (> 100 mg kg\(^{-1}\)) arsenic concentrations on the southwest coast of Kintyre. Small scale mining activity carried out at numerous locations throughout the Upper Dalradian mineralised sequence may have enhanced the dispersion of arsenic and other metals into the environment, but any impact of these activities above the natural background would have to be investigated in more detail.

4. Extensive high arsenic concentrations (> 85 mg kg\(^{-1}\)) around the Doon and Fleet granites in Dumfries and Galloway and Goat Fell on Arran are related to mineralisation at the margins of these bodies. However, concentrations in stream sediments are also enhanced by the surface pH/Eh conditions whereby As\(^{3+}\) is mobilised under acidic reducing groundwater conditions and subsequently precipitated and adsorbed by iron and manganese oxides in aerobic stream water environments. In Galloway, there is a strong correlation between arsenic, manganese and cobalt, which reflects their high solubility over acid peaty terrain associated with the granites, and precipitation over the more highly buffered metasediments and sediments that make up the surrounding country rock.

5. The Ordovician sediments of the northern Southern Uplands are more enriched in arsenic (18 – 22 mg kg\(^{-1}\)) relative to the Llandovery and Wenlock Siluriangreywackes of the south (10 – 13 mg kg\(^{-1}\)), reflecting differences in mineralogy and provenance of
the sediment. Anomalous concentrations associated with mineralisation occur at, for example, the Fore Burn complex (200 – 840 mg kg\(^{-1}\)), as well as concentrations of up to 600 mg kg\(^{-1}\) at Moorbrook Hill, Glenhead Burn, Glenluce, Silver Ridge, Penhiln Burn Auchenfad, Craigend and Culvennan Fell.

6. Arsenic shows little evidence of enrichment around the peripheries of the urban centres of Scotland. However, high concentrations (> 38 mg kg\(^{-1}\)) at Tentsmuir near St Andrews correspond to reclaimed estuarine land rich in flocculated iron oxides which can act as arsenic scavengers. Streams in the area also contain high organic matter contents on which arsenic may be complexed and absorbed, and these secondary enrichment processes may account for the high concentrations of arsenic reported from this area. Concentrations across the Carboniferous strata of central Scotland are generally low, but may be enhanced locally by coal mining activity.

In summary, over much of the country, arsenic concentrations are low, with sporadic high concentrations associated with mineralised areas. However, concentrations may be enhanced locally by secondary processes, whereby arsenic is more readily soluble under acid reducing conditions, but is precipitated with iron and manganese oxides in oxidized environments. Over the main aquifers in Scotland (Devonian, Carboniferous and Permian sandstones), concentrations are generally low, but localised contamination may occur related to coal mining and urbanisation activities in the Central Belt.

Figure 2.3 Interpolated geochemical map of arsenic concentrations in stream sediments for Scotland. The grey areas have no data. The legend on the bottom indicates the percentile followed by the concentrations (e.g. 75/12 means that the 75% of the land area has less than 12 mg kg\(^{-1}\) As). The outline of the geology of Scotland is in white and can be compared with Figure 2.2.
2.5.3 Cadmium (Cd)
Concentrations of cadmium are generally low in igneous and metamorphic rocks and in sandstones and limestones, but higher in mudstones, organic rich sediments, phosphatic deposits and marine manganese nodules. The element is also strongly partitioned into sulphide minerals and is commonly associated with zinc mineralisation. The G-BASE dataset contains cadmium data for the Southern Scotland and Shetland atlas areas only. Data for Southern Scotland are presented in Figure 2.3.

1. Concentrations of cadmium are generally low (0.5 mg kg\(^{-1}\) or less) in most rock types.
2. The majority of high concentrations of the element (> 1.8 mg kg\(^{-1}\)) are associated with base metal mineralisation in the Upper Dalradian of Kintyre; the granitic plutons on Arran, Loch Doon, Fleet and Crieff in Dumfries and Galloway; around the Leadhills area in the Scottish Borders and at Misty Law in the Clyde Plateau Volcanics to the west of Glasgow.
3. In addition to these ‘natural’ concentrations, cadmium concentrations are elevated (> 0.8 mg kg\(^{-1}\)) relative to the background for Carboniferous sediments (< 0.5 mg kg\(^{-1}\)) in streams on the periphery of Glasgow and Edinburgh, as a result of urban contamination.

![Figure 2.4](Image)

Figure 2.4 Symbol-plot map of cadmium concentrations in stream sediments for Southern Scotland.

2.5.4 Chromium (Cr)
Chromium is commonly enriched in ultrabasic and basic rocks, depleted in acid igneous rocks, and is relatively immobile during metamorphism. In sedimentary rocks, the chromium concentration is determined by the presence of detrital basic minerals and the clay content: hence chromium concentrations are enhanced in clays and fine sediments relative to sandstones and carbonates.

Figure 2.5 shows the distribution of chromium in stream sediments from Scotland and Figure 2.6 for the Glasgow area.

1. Low concentrations (< 52 mg kg\(^{-1}\)) characterise the quartz-rich metasediments of the Lewisian, Moine and Dalradian of northern Scotland; however, concentrations are moderate (72 - 108 mg kg\(^{-1}\)) over the schistose portions of this sequence. Lowest
concentrations are associated with the granitic bodies of the Grampians, Comrie, Glen Coe, Loch Etive and Loch Doon, Fleet and Criffel in Dumfries and Galloway. Low concentrations also occur over the northern extensions of the Clyde Plateau Volcanics to the west of Glasgow in contrast to the southern lavas, reflecting compositional changes and lava evolution.

2. Naturally high baseline concentrations (90 – 744 mg kg⁻¹) are present across the basic and ultrabasic Tertiary Igneous Centres of Skye, Mull and Ardnamurchan and concentrations of 400 –1000 mg kg⁻¹ are associated with the ultramafic Ballantrae Igneous Complex on the coast of Ayrshire. Similarly localised high concentrations occur over the basic igneous intrusions of Aberdeenshire. Concentrations in the Upper Dalradian across mid Scotland from Kintyre to Buchan are moderate (72 – 108 mg kg⁻¹). High concentrations (> 156 mg kg⁻¹) are also associated with the basic components of, and intrusions into, the Lewisian gneiss on Lewis and near Scourie in the northwest Highlands.

3. Samples over the Devonian and Carboniferous lavas of the Lorne area, Strathmore, Fife and the Central Belt have moderately high chromium concentrations (> 500 mg kg⁻¹) in contrast to the sedimentary rocks of the Carboniferous, which generally contain < 200 mg kg⁻¹ of the element. Although concentrations reported over the Devonian of Caithness and the Moray coast are low, relatively high concentrations characterise the Devonian sediments of Strathmore, reflecting the sediment sources. In particular, high concentrations (400 – 2000 mg kg⁻¹) are associated with the sandstones of the Garrock Group between Stirling and Couper Angus.

4. The Silurian-Ordovician succession of the Scottish Borders is relatively enriched in chromium, reflecting mafic igneous provenance for these metasediments. As a result, high chromium concentrations are reported in stream sediments of the area (75 – 1000 mg kg⁻¹).

5. Concentrations of chromium in stream sediments over Permian sandstones are variable, with low concentrations (< 175 mg kg⁻¹) on Arran and much higher values (> 1000 mg kg⁻¹) associated with proximity to the Igneous Ballantrae Complex near Mennane Head on the Ayrshire coast. Similarly, olivine basalts in the Thornhill basin in Dumfries and Galloway account for the high (300 – 1000 mg kg⁻¹) chromium concentrations in the basin.

6. Elevated concentrations of the element on the periphery of Glasgow may reflect contamination. Glasgow was a centre of mineral processing during the 19th century, and the company of JJ Whites in Rutherfden was the world’s largest chrome producer. The plant closed in 1967, but chromite ore processing residues were extensively used as landfill material around southeast Glasgow, and between 1960 and 1966 it is estimated that 60 – 70 tonnes of the waste were dumped daily. The Clyde Tributaries study highlighted the impact of the waste on the quality of sediment in urban streams in Glasgow, where chromium concentrations of up to 3561 mg kg⁻¹ are reported in streams in the east of the city (Figure 2.6, Fordyce et al. 2004).
Figure 2.5 Interpolated geochemical map of chromium concentrations in stream sediments for Scotland.

Figure 2.6 Graduated symbol map of chromium concentrations in stream sediments of the Glasgow area (from Fordyce et al. 2004).
In summary, chromium is concentrated in the basic and ultrabasic igneous rocks of the Inner Hebrides, the Ballantrae Complex in Ayrshire and in intrusions in Aberdeenshire. The element is also found in high concentrations in sedimentary rocks derived from basic igneous sources, including the Devonian of Strathmore and greywackes of the Southern Uplands. Concentrations over the main aquifer units in Scotland are variable, with low concentrations over the Devonian of Caithness and the Moray coast; high concentrations in the Devonian of Strathmore; moderate concentrations over the Carboniferous of Fife and the Central Belt, and moderate to high concentrations over the Permian sandstones of Dumfries and Galloway. High concentrations of chromium in the Glasgow urban environment are associated with the dispersal of chromium waste during the last century.

2.5.5 Lead (Pb)

Lead tends to be enriched in acid igneous rocks, such as granites, relative to basic rocks, but is lost during metamorphic processes. The element is often strongly associated with sulphide mineralisation, and in sedimentary rock concentrations are controlled by the presence of lead bearing detrital minerals, clay minerals, and organic matter. Black shales are therefore often enriched in the element relative to pure sands and limestones. Figure 2.7 shows the distribution of lead in stream sediments for Scotland and northern England.

1. Concentrations are generally low (< 20 mg kg\(^{-1}\)) over the quartz-rich metamorphosed sequences of the Lewisian gneiss, Moine and Dalradian of northern Scotland, although moderate concentrations (20 – 64 mg kg\(^{-1}\)) are associated with the mica-schist portions of the sequence. Low concentrations are also reported over the Tertiary basalts of Skye, Ardnamurchan and Mull and the Ballantrae Igneous Complex on the Ayrshire coast. Moderate concentrations (20 – 65 mg kg\(^{-1}\)) characterise the Jurassic sediments of Skye and Mull and much of the Devonian sandstone outcrop in Caithness, the Moray coast and Strathmore.

2. Concentrations in the Upper Dalradian sequence from the Mull of Kintyre to Buchan are moderate (20 – 65 mg kg\(^{-1}\)), but high concentrations occur locally, associated with mineralisation (such as at Bochancloough, the Strichen granite, Lochnagar-Mount Battock intrusions) and disseminated sulphides (Knapdale area of the Kintyre peninsula). The Ben Eagcach schists in the Upper Dalradian sequence near Foss, Cluinemore and Loch Kander are characterised by lead-barium-zinc mineralisation.

3. Small-scale mining, carried out at numerous locations throughout the Upper Dalradian mineralised sequence, may have enhanced the redistribution of lead and other metals. For example, MacKenzie and Pulford (2002) used lead isotopes to study the dispersion of lead and zinc from the mine at Tyndrum. Lead mining was carried out at Tyndrum between 1741 and 1862, and the original waste dumps were reworked between 1916 and 1925. Little remains of the original buildings and workings, and the contemporary distribution and dispersion pathways of the residual waste are poorly defined. During MacKenzie and Pulford’s 2002 study, the mine and ore processing waste dumps were identified as highly polluted, barren areas, with concentrations of lead and zinc up to 210 000 mg kg\(^{-1}\) and 34 000 mg kg\(^{-1}\) respectively. Significant quantities of waste were also found along riverbanks and in river channel sediments in the vicinity of the mine, with concentrations of up to 52 200 mg kg\(^{-1}\) lead and 23 500 mg kg\(^{-1}\) zinc. The same study also concluded that copper and zinc in Loch Tay sediments had been influenced to a lesser degree by mining activity.

4. High lead values reported on Jura and Islay are probably a result of secondary processes, namely co-precipitation of lead with iron and manganese oxides.
5. The Ordovician strata of the northern Southern Uplands are depleted in lead (< 50 mg kg\(^{-1}\)) relative to the Silurian greywacke sequences to the south (50 – 90 mg kg\(^{-1}\)), reflecting changes in provenance of the sediments. Lead concentrations are enhanced in the Moffat shales relative to other rock types in the area. The Leadhills – Wanlockhead area has been exploited for lead since Roman times, and the ‘natural’ stream sediment signatures for the area are largely masked by the influence of mine-spoil. Lead concentrations up to 10 000 mg kg\(^{-1}\) are reported in the area. Previous investigations into dispersion of lead from the Leadhills mining site have revealed concentrations of 75 000 mg kg\(^{-1}\) in floodplain sediments of the Glengonnar Water (Rowan et al. 1995) and here, as at Tyndrum, the fine particulate matter is most readily dispersed in fluvial systems (Hillier et al. 2001).

6. Elevated concentrations of lead (> 116 mg kg\(^{-1}\)) are also associated with the granites of the Grampians and Aberdeenshire: Etive, Glen Coe, Mull, Goat Fell on Arran, and the Criffel, Loch Doon and Loch Fleet plutons in Dumfries and Galloway. Mineralisation associated with the Loch Doon intrusion results in concentrations of up to 5000 mg kg\(^{-1}\) of the element in the Dundeugh Forest area. In contrast, concentrations over Permian sediments in the region are low to moderate (20 – 70 mg kg\(^{-1}\)), reflecting the dominant quartz lithology of these rock units.

7. The central belt of Scotland is characterised by extensive lead urban and industrial contamination, although background concentrations in the Carboniferous rocks are low. There are many man-made sources of lead in the environment, including deposition.

Figure 2.7 Interpolated geochemical map of lead concentrations in stream sediments for Scotland and northern England.
from power generation, traffic pollution (although it should be noted that there is evidence to suggest that lead concentrations have been falling in urban environments since the phasing out of lead in petrol), piping and paint in homes, and industrial and mineral processing. Widespread dispersal of the element around Glasgow and Edinburgh is evident, where concentrations of up to 3000 mg kg\(^{-1}\) are indicative of pollution. For example, the Clyde Tributaries geochemical survey of Glasgow highlights the marked elevation of lead concentrations in urban streams relative to the rural hinterland. Concentrations of up to 5000 mg kg\(^{-1}\) are reported in the urban environment (Fordyce et al. 2004).

In summary, lead concentrations are low to moderate over most of the major rock types in Scotland, including the Devonian and Permian aquifers. However, elevated concentrations are found in association with granitic bodies, with mineralisation in the Upper Dalradian, and at Leadhills in the Scottish Borders. The ‘natural’ geochemical signature for lead over the Carboniferous aquifer of Central Scotland is low to moderate. However, concentrations of the element in the central belt of Scotland are significantly enhanced by pollution.

2.5.6 Nickel (Ni)

Like copper and chromium, nickel is generally concentrated in basic and ultrabasic rocks, and is relatively depleted in acid igneous rocks and poorly mobilised during metamorphic processes. In sedimentary rocks the main control on the distribution of nickel is the presence of basic detrital minerals, clay, organic matter and iron and manganese oxides. Figure 2.8 shows the distribution of nickel in stream sediments across Scotland.

1. High concentrations (> 96 mg kg\(^{-1}\)) are associated with the ultrabasic and basic rocks of the Lewisian on Lewis and the north-west Highlands around Scourie, the basic and ultrabasic Tertiary Igneous Centres of Skye, Mull and Ardnamurchan, the ultrabasic bodies of Aberdeenshire, and the Ballantrae Igneous Complex on the coast of Ayrshire.

2. Moderate concentrations (24 - 64 mg kg\(^{-1}\)) also characterise much of the Upper Dalradian sequence from the Mull of Kintyre to Buchan. Locally higher concentrations are associated with sulphide mineralisation in the sequence, such as at Glen Doll and Lochnagar and epidiorites and metabasites around Aberfeldy, where concentrations up to 882 mg kg\(^{-1}\) are reported.

3. Low concentrations (< 16 mg kg\(^{-1}\)) characterise the granites of the Grampians, Glen Coe, Glen Etive, Arran, and Dumfries and Galloway. Low concentrations are also associated with the western extensions of the Clyde Plateau lavas around Glasgow. Moine and Lower Dalradian quartzitic metasediments over most of the Northern Highlands and on Islay and Jura also have low nickel concentrations. Schistose rocks in the Moine and Dalradian, however, have moderate concentrations (24 - 40 mg kg\(^{-1}\)).

4. The Devonian sequences of Caithness, the Moray coast, Jedburgh and Strathmore show moderate nickel concentrations in stream sediments, although concentrations in Strathmore are elevated (< 325 mg kg\(^{-1}\)) by the presence of lavas in the sequence. Concentrations over the Carboniferous sediments of the Central Belt and Fife are moderate to high (24 – 96 mg kg\(^{-1}\)), reflecting the influence of volcancis (for example in South Fife and Bathgate) and coals in the sequence. Locally the nickel signature is enhanced by coal mining activities and contamination associated with the urban centres. The high concentrations on the periphery of Glasgow and Edinburgh (> 96 mg kg\(^{-1}\)) are indicative of contamination.
5. The greywackes of the Ordovician and Silurian sequence in the Southern Uplands are characterised by high concentrations (> 75 mg kg\(^{-1}\)) reflecting the basic igneous sources of sediments in the region. In contrast, low to moderate nickel concentrations characterise Permian strata in Dumfries and Galloway and on Arran.

In summary, nickel is concentrated in the basic igneous rocks of the Inner Hebrides, the Ballantrae Complex in Ayrshire, and in basic intrusions in Aberdeenshire. The element is also found in moderate concentrations in sedimentary rocks derived from basic igneous sources, including the Devonian of Strathmore and greywackes of the Southern Uplands. Concentrations over Permian aquifers are generally low, whereas moderate to high concentrations are reported over the Carboniferous of the Central Belt and Fife, where local enhancements above the ‘natural’ background are related to urbanisation and coal mining activities.

2.5.7 Uranium (U)

Granites are generally enriched in uranium relative to basic igneous rocks, as the element is preferentially partitioned into late stage magmas. The element is also commonly associated with zones of hydrothermal alteration and mineralisation during emplacement of acid intrusions and extrusions. In contrast, uranium depletion is common during metamorphic processes. In sedimentary rocks, redox conditions at the time of formation are a major control on uranium concentrations. The element is concentrated in organic-rich facies laid down in

Figure 2.8 Interpolated geochemical map of nickel concentrations in stream sediments for Scotland.
anoxic conditions, and hence particularly high concentrations are associated with black shales, while concentrations in pure sandstones, quartzites and greywackes are generally low. High concentrations are also associated with phosphatic deposits and with lacustrine sediments.

Uranium is the only element for which G-BASE data exist in both stream sediments and stream waters for Scotland. Figure 2.9 shows the distribution in stream sediments over the country. Section 2.6 describes the concentrations in stream water.

1. High concentrations in stream sediments (> 34 mg kg\(^{-1}\)) are associated with the granitic bodies of the Grampians, Aberdeenshire, Dumfries and Galloway, Arran, Loch Etive, Rannoch and Helmsdale. Concentrations in the Helmsdale area are also elevated as a result of uranium-bearing mineralisation.

2. Concentrations are low (< 1 mg kg\(^{-1}\)) over much of the Lewisian, the Tertiary basalts of Skye, Rum, Mull and Ardnamurchan, and the Devonian and Carboniferous lavas of the Lorne area, Central Belt and Fife.

3. Low concentrations (< 3 mg kg\(^{-1}\)) also characterise the western and northern tracts of the Ordovician-Silurian greywacke sequence in the Scottish Borders. Increased uranium concentrations (3 - 6 mg kg\(^{-1}\)) towards the east and south reflect changing provenance from basic source rocks to rocks of more intermediate-felsic composition.

4. Concentrations over the quartzitic Moine and Lower Dalradian rocks of the Northern Highlands are moderate to high (> 6 mg kg\(^{-1}\)) as a result of the acid source rock for

![Uranium mg kg\(^{-1}\) %ile](image)

**Figure 2.9** Interpolated geochemical map of uranium concentrations in stream sediments in Scotland and northern England
much of these sediments. In contrast, low to moderate concentrations (1 - 5 mg kg\(^{-1}\)) characterise the Upper Dalradian metasedimentary sequence between Kintyre and Buchan.

5. Concentrations over the Devonian of Caithness and the Moray coast are high (> 9 mg kg\(^{-1}\)), reflecting the presence of phosphatic sediments or lacustrine deposits. In contrast, concentrations over the Devonian of the Black Isle, Buchan area and Strathmore are moderate (3 - 9 mg kg\(^{-1}\)), although there is enrichment of the element in the mudstone facies of the Devonian in Strathmore.

6. Moderate concentrations (1 - 5 mg kg\(^{-1}\)) are reported over the Carboniferous sequence of the Central Belt and Fife. However, higher concentrations of 6 - 9 mg kg\(^{-1}\) probably result from the presence of organic-rich coal bearing strata in the sequence. Concentrations over Permian rocks are low.

2.6 G-BASE STREAM WATER CHEMISTRY

The stream water dataset for Scotland is very limited, comprising pH, conductivity, alkalinity, fluoride and uranium. For the purposes of this report, only pH and uranium are discussed, since maps are not available for the other parameters.

In undisturbed conditions, the composition of stream sediments changes little over short time scales, whereas stream water chemistry is subject to short term change as variations in rainfall and surface run-off affect the flow conditions. Several of the major cation and anion components of the water chemistry can show marked seasonal changes between winter and summer conditions, and during periods of rainfall. G-BASE stream water sampling is carried out during the summer months when base flow conditions prevail to minimise the impacts of changes in flow on the water chemistry.

Despite the changes in flow conditions, and the long period of time over which samples have been collected (in Scotland between 1970 and 1986), regional geochemical patterns are still evident in the dataset, and allow an overview of water quality at the national scale. This is also borne out by evidence from the full suite of water chemistry data available for Wales (BGS 1999) which suggests that on a regional scale, temporal variability within catchments is a less important influence for most elements than geology and land use.

2.6.1 pH

Most natural waters fall within a pH range of 5 to 9, although drainage from peat bogs may have lower pH. Drainage from mines can also be considerably more acidic. Important controls on stream water pH include the pH of rainwater and the availability of base cations such as Ca and Mg and other buffering components in the bedrock and overburden. Therefore, pH values of 4 – 5 are often associated with poorly buffered granitic rocks, or poorly drained areas over hard crystalline impermeable bedrock where peat bogs commonly accumulate, whereas high pH values (> 8) are associated with carbonate bedrock.

A map of stream water pH over Scotland and northern England is presented in Figure 2.10 and highlights the limited amount of data available for the north of the country.

1. Low pH values (< 5.8) are associated with the granitic bodies of the Grampians, including Lochnagar, Cairngorm, Hill of Fare and Glen Tilt; Goat Fell on Arran; and the Doon, Fleet and Criffel plutons in Galloway, as a result of low weathering rates, poor bedrock buffering capacity, the presence of thick peat and, in the case of the Doon and Fleet granites, extensive coniferous afforestation.
2. Although the data are sparse, low pH values also characterise the Lewisian and quartzitic metasediments of the Moine and Lower Dalradian, again as a consequence of the poor buffering capacity of the bedrock, low weathering rates, and extensive peat cover, such as across southern Islay. Over the Upper Dalradian sequence, neutral-acid conditions (pH 7 - 6) prevail, with the exception of the Kintyre peninsula where low pH values (< 5) reflect peat development and the calcium-poor nature of the bedrock.

3. Concentrations over the Devonian of the Moray Coast, Strathmore, East Lothian and the Borders are neutral to alkaline (pH 7 - 8) with locally high values (pH > 8.1) over Strathmore. Over the Carboniferous of Fife and the Central Belt, and the Ordovician Silurian sequence of the Southern Uplands, pH values strongly reflect the proportions of quartz, feldspar and carbonate in the underlying rocks. Therefore, quartzose units in the Southern Uplands, such as the Shinnel Formation, yield marginally acid waters (pH 7 - 6), whereas alkaline conditions characterise the greywackes of the Hawick and Riccarton Groups (pH 7.5 - 8). Similarly, alkaline conditions dominate over the Carboniferous Limestone sequences of Berwickshire, Ayrshire and Fife whereas waters over the sandstones and coals of the Westphalian to the east of Glasgow are more acid (< pH 6).

4. Localised low pH values in Fife near Kirkcaldy, Dunfermline and Alloa correspond to the weathering of pyrite in spoil materials associated with coal mining. The Devonian and Carboniferous lava sequences of the Central Belt and Strathmore yield near-neutral pH waters, with the exception of Misty Law to the west of Glasgow, which reflects the evolved composition of the underlying lavas and the thick peat cover.

![Interpolated geochemical map of the available G-BASE data for stream water pH in Scotland and northern England.](image)
2.6.2 Uranium (U)

Bedrock sources of uranium were described earlier and shown in Figure 2.9. The element is generally more soluble in oxidizing alkaline and bicarbonate waters than in acid reducing conditions. The element forms strong associations with organic matter and dissolved phosphate in water.

The distribution of uranium in stream waters across Scotland is presented in Figure 2.11.

1. Over most rock types concentrations of uranium in water are low: 98% of the data have concentrations less than 1.5 µg l\(^{-1}\).
2. High concentrations (> 1.5 µg l\(^{-1}\)) are associated with the granitic intrusions of the Grampians, including Lochnagar, Cairngorm, Hill of Fare, and Kemnay, and the Loch Etive area, as well as the plutons of Helmsdale in Sutherland and Fleet, Doon and Criffel in Dumfries and Galloway.
3. Highest concentrations (> 2 µg l\(^{-1}\)) occur in association with the Devonian outcrops of Strathmore, Caithness, the Black Isle, Rhynie and the Moray coast, reflecting the presence of phosphatic deposits in the sequence. A large anomaly at Nairn (> 58 µg l\(^{-1}\)) corresponds to the contact between the Devonian and the Auldearn granite, and

Figure 2.11 Interpolated geochemical map of stream water Uranium concentrations for Scotland
either rock type could be the source. Devonian rocks in Caithness are known to contain uranium mineralisation, explaining the high concentrations reported in the area. Isolated high concentrations over the Carboniferous of Fife, the Central Belt, West and East Lothian probably reflect the presence of coals in the sequence and the greater mobility of uranium under carbonate rich conditions associated with limestones.
3 Indicative maps of selected trace elements in Scottish groundwaters

3.1 GEOLOGY AND GROUNDWATER QUALITY

Groundwater quality is dependent on the characteristics of the aquifer (flow, mineralogy, geochemical environment) and residence time (since most reactions are kinetically controlled). Prediction of the hydrochemical characteristics of groundwater is difficult, due to the lack of detailed knowledge of mineral phases and their distribution, flow pathways, residence times and geochemical environment (for example, oxidising/reducing or acidic/alkaline conditions). Nevertheless, prediction of several major-element concentrations can be attempted with knowledge of the dominant mineral assemblages and some constraints on the residence time of the groundwater. For example, it can often be assumed that carbonate-rich rocks (limestones, calcite-cemented sandstones) will be dominated by calcium- and bicarbonate-type groundwaters if residence times are short.

The ability to predict trace-element concentrations is much more difficult, in part due to lack of understanding of the behaviour of trace elements and also of knowledge on the distribution of mineral phases, the reactivity of different minerals and the geochemical environment, particularly the redox status. The elements iron and manganese are largely controlled by the redox conditions and pH within the aquifer. Hydrous iron and manganese oxides are common in soils and rocks and stable in oxidising environments, occurring as coatings and discrete grains. These minerals can have large surface areas and high adsorption capacities, and form an important control on many trace elements in aquifers including arsenic, cobalt, cadmium, copper, nickel, lead, and zinc. This is because most surfaces of these hydrated oxides have negative surface charges at the pH values typical of groundwaters: at high pH (e.g. >8), cationic metals tend to be more strongly sorbed. If such minerals dissolve under reducing or acidic conditions they can release their adsorbed metals to solution. Arsenic behaves in a different manner and sorption is least at high pH (e.g. >8).

The source of many trace elements, such as barium, strontium and rubidium, is typically major mineral phases including feldspars (and gypsum for strontium), but concentrations are often limited by geochemical processes in the aquifer and difficult to predict. Several other trace elements are sourced from trace mineral phases whose distributions are often localised and heterogeneous. Nevertheless, high concentrations of particular trace elements are associated with specific rock types (as discussed in Chapter 2), and a knowledge of mineralogy and geochemical environment, combined with a knowledge of geochemical processes, can help to highlight potential problem areas.

A full description of the survey and analytical methods and data sets available on Scottish groundwater chemistry is given in MacDonald and Ó Dochartaigh (2005). Data relevant to the current report are included on the maps of each element reviewed in this section.

3.2 SCOPE

The purpose of this summary and the accompanying maps is to highlight areas of bedrock where mobilisation of specific trace elements may occur under different (but natural) environmental conditions. The maps should be used as a basis to help discussions on future groundwater-quality monitoring, or further site investigation for specific problems. Anthropogenic influences may modify the concentrations and distribution of a range of trace elements, and any detailed assessment requires site-specific study. This preliminary assessment includes the elements aluminium (Al), arsenic (As), barium (Ba), cadmium (Cd),
chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni), uranium (U) and zinc (Zn). The problems of prediction discussed above must be borne in mind, and this work cannot substitute for a proper assessment based on actual chemical analyses of groundwater.

The sub-division of rock types is based on the 1:625 000 scale geological map of Scotland. In order to make this simple and manageable, we have used the numbers 1 to 114 for rock units as described on the geological map of the UK (Solid Geology): North sheet (BGS 2002). The numbers in the following sections refer to those on the geology map. The units on the 1:625 000 map group a wide range of rock types (and hence mineralogies) together. Some units have been subdivided, and other small areas have been highlighted where additional information is available.

For each trace element the following is given.

- A brief review of the sources of each of the elements is provided and with the conditions under which increased mobility may occur.
- The 1:625 000 geological map for Scotland has been attributed to identify areas where elevated concentrations of the trace element in groundwater may be more likely to occur. The maps do not indicate what concentrations may be expected, but should be treated only as indicative of areas that may contain concentrations above the Scottish average.
- Some of the rock units have been subdivided, and other small areas highlighted where additional information is available.
- The available groundwater quality data are also shown for comparison (MacDonald and Ó Dochartaigh 2005). These data are skewed to the permeable sandstone aquifers and often do not include a full suite of trace elements. The data were spilt into appropriate bins (e.g. >1, 1-10, >10 μg l\(^{-1}\)) and the EC maximum permissible value (EC 1998), or WHO guideline value identified (WHO 2004).
3.3 TRACE ELEMENTS

3.3.1 Aluminium (Al)

Aluminium can exist in several soluble forms dependent on pH, the most important being Al$^{3+}$ and hydrolysed forms (for example Al(OH)$^{2+}$ and Al(OH)$_3^{-}$). The most toxic form is Al$^{3+}$. The EC maximum permissible value for aluminium in drinking water is 200 µg l$^{-1}$ (EC 1998).

The form Al$^{3+}$ typically occurs in acidic waters, and has a high solubility below pH 4. The solubility of aluminium minerals is low at pH values close to neutral, but because of its amphoteric nature, aluminium concentrations increase at both low and high pH. During weathering, most aluminium-bearing minerals dissolve incongruently, and aluminium is retained in clay secondary minerals.

Aluminium is the third most abundant element in the Earth’s crust, but its low solubility means that it is present in waters as a trace element. It occurs as a major component in most common silicate minerals such as the feldspars, micas and amphiboles. High dissolved concentrations are generally only found in acid waters.

The presence of calcite will buffer pH to circum-neutral values, and high concentrations will therefore generally be found in groundwaters flowing through rocks which are carbonate-free (or devoid of other rapidly reacting silicate minerals). High concentrations will be typical of groundwaters in acidic igneous and metamorphic rocks or beneath areas where peat soils and coniferous forests give rise to low pH. However, any rock type which contains even small amounts of carbonate minerals (in veins or in the matrix) will increase pH and therefore limit the solubility of aluminium minerals. High aluminium concentrations in shallow groundwaters are likely to occur in granites, metamorphic rocks and sedimentary rocks such as shales, mudstones and greywackes devoid of carbonate, due to the slow dissolution kinetics of minerals such as quartz, clays and muscovite mica. Deep groundwaters in such aquifers may, however, contain waters with low aluminium concentrations, due to long residence times (where hydrolysis reactions have increased pH).

In Scotland, shallow groundwater in many of the Caledonian granites is likely to contain elevated aluminium in shallow groundwaters. Individual plutons, however, are complex and can be zoned from basic and ultrabasic margins to granitic centres. Unfortunately, these have all been mapped according to the same unit on the 1:625 000 geology map, so care must be taken to establish the lithology within each pluton.

Figure 3.1 Areas of Scotland where natural groundwater in bedrock may be more likely to have elevated aluminium concentrations (in pink). Red points show measured aluminium concentrations in groundwater that exceed the EC maximum permissible value.
Bearing in mind the above caveats, high aluminium concentrations in groundwater are most likely in areas of poorly buffered groundwater, including rock unit numbers 1, 7, 8-10, 12, 16-21, 34, 37, 46, 51, 54, 57, 58, 61-62, 72-74, 81, 110-114 on the 1:625 000 geology map.

Figure 3.1 shows these areas of possible elevated aluminium concentration, and also areas highlighted as having low pH in the G-BASE stream water data. The map highlights that elevated concentrations can occur in most places in Scotland if the local groundwater conditions are favourable (shallow acidic groundwaters). It also shows the existing data for aluminium concentrations in groundwater, revealing high values in Fife, southwest Scotland and the Borders, Skye and Harris. The high concentrations in southwest Scotland may be related to granite intrusions and acidic sediments, but detailed analysis at this scale is not possible.

3.3.2 Arsenic (As)

Arsenic exists in water in two oxidation states and occurs as anions or neutral species rather than as a cation. Under oxidising conditions arsenic exists in the form of arsenic acid or arsenate in the 5+ oxidation state. As$^{3+}$ can be reduced to As$^{3+}$ under reducing conditions, forming arsenious acid or arsenite. Under even more reducing conditions, arsenic may be incorporated into sulphide minerals, such as arsenopyrite (FeAsS) or pyrite (FeS$_2$), which are commonly present in hydrothermal veins (especially gold-bearing veins); FeS$_2$ can also be found in many reducing environments (e.g. black shales). The EC maximum permissible value for arsenic in drinking water is 10 µg l$^{-1}$ (EC 1998).

In Scotland, sulphide minerals are often associated with acidic igneous rocks such as granites (see earlier); for example, around the Loch Doon and Cairnsmore of Fleet granite in the Southern Uplands and Comrie in Perthshire. In sedimentary aquifers, arsenic can be strongly adsorbed by ferric hydroxide secondary minerals, which may become mobilised under reducing conditions.

Figure 3.2 Areas of Scotland where natural groundwater in bedrock may be more likely to have elevated arsenic concentrations (in pink). Red points show measured arsenic concentrations in groundwater that exceed the EC maximum permissible value.

High concentrations in groundwaters associated with granites (34) may occur locally (especially if reducing conditions exist). Stream sediment data (see section 2.5.2) and knowledge of known arsenic mineralisation have been used to distinguish which granite bodies are likely to have high arsenic (Figure 3.2).
In metamorphic rocks, potential problems are likely to be localised in Upper Dalradian rocks (18, 19 and 20), which are known to host arsenic-rich mineralisation. Again G-BASE data (Section 2.5.2) have been used to highlight specific areas within the Upper Dalradian where mineralisation is more prevalent. Other localised areas highlighted by G-BASE as having arsenic mineralisation have also been added to the map shown in Figure 3.2.

Arsenic can be present in iron oxyhydroxide cements and coatings of sedimentary rocks, and therefore groundwaters in the Devonian sediments (75-78) and Permo-Triassic rocks (89) could locally contain enhanced concentrations of arsenic where the waters are reducing and the iron and arsenic mobilised. However, concentrations in solution may be low precisely because the iron oxy-hydroxides strongly retain the arsenic.

The other main aquifer type where concentrations are likely to be enhanced is sand and gravel deposits (glacio-fluvial or alluvial), which may contain groundwater with enhanced arsenic where the source of sediment is derived from the rocks described above.

Figure 3.2 also shows the existing data for arsenic concentrations in groundwater, highlighting the limited available data: values are available for only a few locations, making it difficult to compare the real and predicted areas of high arsenic concentration.

### 3.3.3 Barium (Ba)

Barium in natural waters occurs predominantly as dissolved Ba\(^{2+}\). Its concentration is limited by barite (BaSO\(_4\)), which is relatively insoluble. Hence high concentrations only occur where sulphate concentrations are low. Barium is also likely to be controlled in aquifers by adsorption onto iron and manganese oxy-hydroxides and clays. The main mineral source of barium is K-feldspar, where it occurs as a minor component. Granitic rocks can contain high concentrations of barium, depending on the type of granite and the nature and type of any mineralisation. However, the relative stability of K-feldspar means that it is released slowly to the environment. The WHO guideline value for drinking water is 700 µg l\(^{-1}\) (WHO 2004).

Scotland has long been recognised as a high barium province, with many of the igneous and metamorphic rocks containing high concentrations. The barium mine at Foss, north of Aberfeldy, is a manifestation of high barium concentrations in Dalradian rocks. The mineral barite is also associated with Devonian sedimentary rocks associated with mineralisation of probable Carboniferous age. Other areas of mineralisation highlighted by the G-BASE atlases are also shown in Figure 3.3. In general, it is probable that localised enhancements will occur over middle...
Dalradian rocks (20-21) which contain barite. Concentrations of barium are known to be high in the Carboniferous Limestone and Millstone Grit of England, and in Scotland these aquifers may also contain groundwaters with high concentrations. Parts of the Torridonian Sandstone in Applecross and Skye may also have elevated barium concentrations.

Figure 3.3 shows the existing data for barium concentrations in groundwater. The available data show elevated groundwater concentrations in the Devonian aquifers; for example in Fife (including two sites that exceed the WHO guideline value), Strathmore and Morayshire, and also of Permo-Triassic aquifers, including the Dumfries Basin. The limited data available for the Highlands means that realistic comparisons between actual barium concentrations and predicted areas of high barium in Dalradian and Torridonian aquifers cannot be made.

### 3.3.4 Cadmium (Cd)

The dominant species of cadmium in solution is as a divalent cation (Cd$^{2+}$). It is mobile under acidic conditions but solubility at higher pH is limited by adsorption and the low solubilities of carbonate or oxide minerals. Under reducing conditions its mobility is limited by the presence of insoluble sulphide minerals.

Cadmium is closely associated with zinc, forming a component of zinc ores such as sphalerite (ZnS). It is also strongly sorbed by manganese and iron oxy-hydroxides. The EC maximum permissible value is 5 µg l$^{-1}$ (EC 1998).

Naturally high concentrations of dissolved cadmium are uncommon, being generally restricted to acidic waters in sulphide-rich environments. Higher than average concentrations are likely to be found in groundwaters in Carboniferous sedimentary rocks (81-83), if the groundwaters are acidic (Figure 3.4). Enhanced concentrations in water may be associated with ore deposits, but are difficult to predict, and likely to be very localised due to the limited mobility of cadmium. Mineralised areas identified from G-BASE have been highlighted in Figure 3.4, along with aureoles around several granitic intrusions. Contamination is likely to be a major control on the element, especially in the Midland Valley.

Figure 3.4 shows the existing data for cadmium concentrations in groundwater and highlights the fact that naturally high cadmium concentrations in groundwater are rare. However, there are few data from the urban areas, where concentrations may be elevated from contamination.
3.3.5 Chromium (Cr)

Chromium exists in nature both in trivalent and hexavalent states. Trivalent chromium is mobilised under acidic and reducing conditions. Under highly oxidising conditions, the hexavalent form (chromate) is stable as an anion at high pH, and since it is not strongly sorbed, is mobile in the environment. The EC maximum permissible value is 50 µg l⁻¹ (EC 1998).

In Scotland, potentially elevated concentrations in groundwater may occur in the vicinity of basic and ultrabasic rocks such as the margins of some plutons (34), and volcanic rocks of Ordovician, Devonian, Carboniferous, Permian and Palaeogene age (42-43, 49, 50, 53 (excluding Greenock), 56, 57). Additionally, high concentrations may occur in basic and ultrabasic rocks, from Precambrian basic dykes to Palaeogene gabbros (5-6, 14-15, 26-27, 31-33, 35-36). Part of the Silurian and Ordovician sedimentary rocks of the Southern Uplands (70-71, 72) contain large amounts of pyroxene and amphibole, which can lead to enhanced concentrations. G-BASE has been used to identify the parts of the Southern Uplands which may be affected.

Figure 3.5 shows the extent of these units across Scotland, with the existing data for chromium concentrations in groundwater. Actual measured natural concentrations in groundwater are generally low. There are no data from Glasgow area where concentrations may be elevated by contamination.

Figure 3.5 Areas of Scotland where natural groundwater in bedrock may be more likely to have elevated chromium concentrations (in pink). No samples exceed the EC maximum permissible value.
3.3.6 Lead (Pb)

The dominant species of lead in solution is as a divalent cation (Pb\(^{2+}\)). It is mobile under acidic conditions, but at higher pH its mobility is limited by adsorption and the low solubilities of carbonate or oxide minerals. Under reducing conditions mobility is also limited by the presence of insoluble sulphide minerals. Lead occurs in the sulphide mineral, galena (PbS) and as a minor constituent in K-feldspars. It is not particularly mobile in most aquifers, except where acidic groundwaters occur. The EC maximum permissible value is 10 µg l\(^{-1}\) (EC 1998).

In Scotland, slightly enhanced levels may be expected in groundwaters of the Millstone Grit (81), but these are unlikely to be more than the EC maximum permissible value. Naturally high concentrations may occur close to areas of lead mineralisation, such as Tyndrum and Comrie in the Dalradian or Leadhills in the Southern Uplands, but may be very localised – mineralised areas, derived from G-BASE data, have been highlighted on Figure 3.6. The limited mobility of lead means that its dispersion in groundwater is likely to be small. The highest concentrations of lead in water are most likely to be present close to urban areas.

Figure 3.6 also shows the existing data for lead concentrations in groundwater. The map indicates that most samples are below the EC maximum permissible value; however, the analytical methods used on the samples are not sufficient to give useful information on the variation of natural lead concentrations in groundwater. The lack of useful data for much of the country make comparisons between predicted and actual areas of high lead concentration difficult.

There are several isolated locations where lead exceeds the EC maximum permissible value (Arran and southwest Scotland). However, the presence of more than one groundwater sample from Devonian aquifers in Strathmore, with lead concentrations above the EC maximum permissible value, warrants further investigation.

Figure 3.6 Areas of Scotland where natural groundwater in bedrock may be more likely to have elevated lead concentrations (in pink). Red points show measured lead concentrations in groundwater that exceed the EC maximum permissible value.
3.3.7 Manganese (Mn)

Manganese is ubiquitous in many rocks and soils, forming an important control on many trace elements through the mechanism of adsorption. Like iron, it is soluble under reducing conditions, as Mn$^{2+}$, but forms an insoluble oxy-hydroxide under oxidising conditions. The stability field of Mn$^{2+}$ is slightly greater than that of Fe$^{2+}$ and it remains soluble under moderately oxidising conditions. Organic complexing is considered to be important, particularly in organic-rich waters and soils. The EC maximum permissible value is 50 µg l$^{-1}$ (EC 1998).

The most important control on manganese is the redox status of the groundwater, and most aquifers therefore have the potential to contain high concentrations of dissolved manganese. Also, manganese, like iron, is mobile under acidic conditions and may be elevated in acidic groundwaters.

In Scotland, aquifers containing high concentrations of iron and manganese oxyhydroxide as cement or grains are potential problem areas. This includes all superficial aquifers (not shown on the Figure 3.7), Devonian (75-78) and Permo-Triassic sandstones (85) and possibly the upper Dalradian (19). Areas indicated by the G-BASE atlases as having low pH in stream water have also been highlighted (Figure 3.7).

Available data for manganese concentrations in groundwater are also shown on Figure 3.7. The data highlight the fact that elevated concentrations can occur in most places in Scotland if the local groundwater conditions are favourable (reducing or acidic groundwaters).

Figure 3.7 also shows the existing data for manganese concentrations in groundwater. There are more data for manganese than for most other trace elements, probably reflecting the fact that elevated manganese concentrations are a well-recognised issue and it is easily measured. Manganese concentrations above the EC maximum permissible value have been found in groundwaters from a variety of aquifer types in Scotland, notably superficial deposits and Devonian and Permo-Triassic sandstones, which are some of the most widely used aquifers in Scotland and for which there are relatively extensive data. However, high manganese concentrations have also been found in groundwaters from Lewisian gneiss and in granite plutons in both southwest Scotland and Sutherland.
3.3.8 Nickel (Ni)

Nickel concentrations in groundwater are strongly influenced by co-precipitation or by adsorption onto secondary mineral phases such as manganese and iron oxy-hydroxides. In solution, nickel generally occurs as Ni²⁺, which is stable at pH values up to about 9.0. The commonest conditions within an aquifer under which high nickel concentrations might be supported are therefore acidic and/or reducing. The EC maximum permissible value for Ni is 20 µg l⁻¹ (EC 1998).

Minerals which contain high concentrations of nickel include olivine, pyroxene, amphibole (to a lesser degree), and nickel-sulphide minerals. In addition, nickel is geochemically strongly associated with manganese and iron oxy-hydroxides, which during reductive dissolution may release nickel to solution. Shales may also contain higher than average concentrations of nickel.

In Scotland, potentially elevated concentrations may occur in the vicinity of basic and ultrabasic rocks, from Precambrian basic dykes to Palaeogene gabbros, and including the margins of some plutons (5-6, 14-15, 26-27, 31-33, 35-36). Volcanic rocks of Ordovician, Devonian, Carboniferous, Permian and Palaeogene age are also potential sources of nickel in groundwater (42-43, 49, 53, 56, 57). This is similar to the potential distribution of chromium. Part of the Silurian and Ordovician sedimentary rocks of the Southern Uplands (70-71, 72) contain large amounts of pyroxene and amphibole, which can lead to enhanced nickel concentrations in groundwater. These areas have been identified using G-BASE data. The association of nickel with sulphide minerals implies that the Coal Measures (82-83) may also produce groundwaters with elevated nickel concentrations.

Figure 3.8 shows the areas of Scotland which may contain groundwater with high nickel concentrations, and also shows the existing data for nickel concentrations in groundwater. The few samples from the available data where nickel exceeds the EC maximum permissible value include one groundwater sample from Lewisian gneiss, one from Carboniferous sedimentary rocks, one from Devonian sandstone, and one from Permo-Triassic sandstone (although this latter is likely to be related to industrial contamination). This pattern indicates the complexities of trying to predict element concentrations in groundwater from the broad geochemical assessments made in this study, and highlights the need for more detailed studies.

![Figure 3.8](image_url)
3.3.9 Uranium (U)

Uranium is typically mobile under oxidising conditions but forms an insoluble oxide under even moderately reducing conditions. Uranium forms complexes with carbonate, which if present, increases its solubility in comparison with carbonate-free waters. An EC maximum permissible value does not exist for uranium, but the WHO provisional guideline value for drinking water is 15 µg l\(^{-1}\) (WHO 2004).

Uranium is typically enriched in acid igneous rocks such as granites and late stage pegmatites associated with granites. It is also commonly associated with phosphate minerals.

The main areas considered at present to be at risk from elevated uranium concentrations in groundwater include granite bodies and acid volcanic rocks (34), as well as the Devonian sequences in Scotland (75-78). Uranium is associated with phosphatic fish remains in Devonian flagstones in Caithness. Although many of the Lewisian (Precambrian) gneisses are acidic in composition, they are depleted in uranium due to the high grade of metamorphism. Permo-Triassic sediments (87-90) may also be at risk where they are close to redox boundaries.

The distribution of these rock types is shown in Figure 3.9, together with the very few measurements of uranium in groundwater in Scotland, all of which are from the Permian aquifer of the Dumfries basin. The lack of groundwater chemistry data makes it impossible to make comparisons with the predicted areas of high uranium, and highlights the need for more groundwater chemistry information.
3.3.10 Zinc (Zn)

The dominant species of zinc in solution is as a divalent cation (Zn$^{2+}$), and it is generally more soluble than the elements nickel and copper, which have a similar abundance in the earth’s crust. Zinc is soluble under acidic conditions, but solubility at higher pH is limited by adsorption and the relatively low solubilities of carbonate and hydroxide species, although these are much higher than other transition elements. Solubility is limited under reducing conditions by the presence of insoluble sulphide minerals, and under oxidising conditions by adsorption onto iron and manganese oxy-hydroxides. The WHO guideline value for zinc in drinking water is 3000 µg l$^{-1}$.

In Scotland, the distribution of zinc in groundwaters is relatively difficult to predict. Elevated concentrations have been found in groundwater in the Carboniferous Limestone of Derbyshire, and may also occur in Scotland (80). Concentrations may also be enhanced where sulphide mineralisation occurs – these have been identified using G-BASE data. The areas where elevated zinc concentrations may occur are shown in Figure 3.10, with the existing data for zinc concentrations in groundwater.

Groundwater chemistry data for zinc are relatively abundant compared to other trace elements, and the map shows that high zinc concentrations in groundwater in Scotland are rare. The only groundwater sample to show a zinc concentration above 1000 µg l$^{-1}$ is from a spring emanating from Devonian sedimentary rocks.

Figure 3.10 Areas of Scotland where natural groundwater in bedrock may be more likely to have elevated zinc concentrations (in pink). There are no measurements of groundwater where zinc exceeds the WHO guideline value.
4 Conclusions

In the absence of a reliable national dataset of trace elements in groundwater, maps have been developed which attempt to predict groundwater quality from geological, geochemical and environmental conditions. The best available data and knowledge have been used to make judgements at a broad national scale for Scotland. The limited groundwater data available for Scotland (reported separately in MacDonald and Ó Dochartaigh 2005) have been compared to the maps showing the areas predicted to have elevated concentrations relative the other areas in Scotland. The following conclusions can be drawn.

1. The study has provided a useful summary of geochemical information for trace elements in Scotland, and also detailed the conditions in which these elements may become elevated in groundwater. This provides essential background to the Baseline Scotland project, which aims to improve the availability of groundwater chemistry data and the general understanding of the chemistry of Scotland’s groundwater.

2. The predictions can be used as a first pass to help focus and prioritise additional monitoring and for helping to interpret groundwater chemistry data from different areas. The predictions are only preliminary and will be modified in the future by detailed groundwater sampling and interpretation.

There are several caveats to the use of the maps of estimated groundwater quality:

- For all of the trace elements considered, the lack of available groundwater chemistry data with detailed analysis of trace elements, and their restricted spatial distribution, means that it is not possible to rigorously test whether the groundwater quality predictions are accurate or not.

- More groundwater chemistry data are available for three elements, barium, manganese and zinc, allowing a rudimentary test of the predictive maps. For barium the prediction appears to work well, but there is poor correlation for zinc. For manganese, some correlation is evident, but the complexity and variability of local conditions are such that much variation is observed.

- This approach, using broad, national scale geological and environmental data, cannot account for the complexity of the controls on groundwater chemistry; i.e. the heterogeneous nature of the Scottish environment, not least the aquifer mineralogy and glacial history, and the complex behaviour of trace elements in groundwater, determined by aspects such as flow pathways, residence times, and the geochemical environment (for example, oxidising/reducing or acidic/alkaline conditions).

In summary, this approach appears to be a useful first step in trying to estimate the likely distribution of trace elements in Scottish groundwater, in the absence of much reliable groundwater quality data. However, only by systematically collecting reliable groundwater chemistry data, across different aquifers and regions and from different depths, can the variation in trace elements in groundwater across Scotland be understood. Careful modelling and interpretation of these new data in the context of the geology and environmental conditions will help make future predictions of groundwater quality more reliable and provide reference information for the Water Framework Directive.
Appendix 1  Summary of the G-BASE geochemical data available for Scotland

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**REPORT:** Shetland Follow-up


**Sampling period:** Summer 1990

**Sampling density:** 1 per 1.2 km²

**No. of sites** 1240

**Sample type** (no. sites sampled)
- Stream sediment (1240 + 124 in pilot study)
- Stream waters (1240 + 124 in pilot study)

**Sample preparation:** The < 150 micron fraction was ground until 95 % was < 53 micron using an agate ball mill.

**Determinands (methods):** Ag, As, Al₂O₃, B, Ba, Be, Bi, Ce, CaO, Cd, Co, Cr, Cu, Fe₂O₃, Ga, K₂O, La, Li, MgO, Mn, Mo, Nb, Nd, Ni, P, Pb, Rb, Sb, SiO₂, Sn, Sr, TiO₂, U, V, W, Y, Zn and Zr (DR-ES and XRF); alkalinity, conductivity, F⁻ (specific ion method); pH; U (laser-induced fluorometry).

**Reported content** Interpolated geochemical maps and accompanying text are presented for As, Ba, Cu and Zn in stream sediments and fluoride in stream water.

**Notes:** Project in collaboration with the Shetlands Islands Council and Highlands and Islands Enterprise.

**ATLAS:** South Orkney and Caithness


**Sheet boundaries:** Min Easting: 281800 Max Easting: 360000 Min Northing: 902700 Max Northing: 1014000

**Sampling period:** July 1969

**Sampling density:** 1 sample per 2.3 km²

**No. of sites** 1287

**Sample type** (no. sites sampled)
- Stream sediment (1287)
- Stream waters (1287)

**Sample preparation:** The < 150 micron fraction ground until 95 % was < 100 micron using a mechanical agate mortar.

**Determinands (methods):** Ba, Be, B, Cr, Co, Fe, Mn, Mo, Ni, Sn, Ti, V and Zr (OES); Cu, Pb and Zn (acid attack (ammonium persulphate with 75% hydrochloric acid) followed by solvent extraction AAS); U (delayed neutron activation analysis). Only 104 sites determined for pH and conductivity of surface water.

**Atlas content** Interpretative maps using proportional vector symbols and accompanying text are presented for 16 elements; Ba, Be, B, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ti, U, V, Zn and Zr in sediment and for pH, conductivity and U in water. Interpreted images for Sn were not presented due to the detection of a significant level of within site variance.
### ATLAS: Southern Scotland

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**Sampling density:**
1 sample per 1.5 km²

**No. of sites**
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**Sample type (no. sites sampled)**
- Stream sediment (19 000)
- Stream waters (4230)

**Sample preparation:**
The < 150 micron fraction was ground until 95% was < 53 micron using an agate ball mill.

**Determinands (methods):**
- Ba, Be, Bi, B, Ca, Cd, Cr, Co, Cu, Ga, Fe, La, Pb, Li, Mg, Mn, Mo, Ni, K, Rb, Ag, Sr, Sn, Ti, V, Y, Zn and Zr (DR-ES); Sb and As (sites to the west of 4°W were analysed by acid attack (ammonium persulphate with 75% hydrochloric acid) followed by solvent extraction AAS). To the east of 4°W Sb and As were analysed by X-ray fluorescence); U (delayed neutron activation analysis)

**Atlas content**
Interpolated geochemical maps and accompanying text are presented for 30 elements; Sb, As, Ba, Be, Bi, B, Ca, Cr, Co, Cu, Ga, Fe, La, Pb, Li, Mg, Mn, Mo, Ni, K, Rb, Ag, Sr, Sn, Ti, U, V, Y, Zn and Zr in sediment and for pH, conductivity, bicarbonate, fluoride and U in water.

### ATLAS: Sutherland

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**No. of sites**
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**Sample type (no. sites sampled)**
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**Sample preparation:**
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**Determinands (methods):**
- Ba, Be, B, Cr, Co, Fe, Mn, Mo, Ni, Sn, V and Zr (OES); Cu, Pb and Zn (acid attack (ammonium persulphate with 75% hydrochloric acid) followed by solvent extraction AAS); U (delayed neutron activation analysis).

**Atlas content**
Interpretative maps using proportional vector symbols and accompanying text are presented for 14 elements; Be, B, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, U, V, Zn and Zr in sediment and for pH, conductivity and U in water (pH and conductivity on only 155 sites). Interpreted images for Sn were not presented due to the detection of a significant level of within site variance and Ba was also omitted due to concern over a change in background level thought to be attributable to analytical error.
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<td><strong>Report content</strong></td>
<td>Graduated symbol maps for determinants in stream sediments and stream waters and accompanying discussion in relation to quality guideline values</td>
</tr>
</tbody>
</table>

**AFS = Atomic Fluorescence Spectrometry**

**GC-MS = Gas Chromatographic Mass Spectrometry**

**PLM = Polarised Light Microscopy**

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<table>
<thead>
<tr>
<th><strong>REPORT:</strong></th>
<th><strong>Glasgow</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>REFERENCE:</strong></td>
<td>In Prep</td>
</tr>
<tr>
<td><strong>Sheet boundaries:</strong></td>
<td>Glasgow Conurbation</td>
</tr>
<tr>
<td><strong>Sampling period:</strong></td>
<td>Summer 2001 and 2002</td>
</tr>
<tr>
<td><strong>Sampling density:</strong></td>
<td>4 sample per 1 km² (urban) 1 per 2 km² (peri-urban)</td>
</tr>
<tr>
<td><strong>No. of sites</strong></td>
<td>122</td>
</tr>
<tr>
<td><strong>Sample type</strong></td>
<td>Urban soil (1380) Top (5 – 20 cm) and deeper (35 – 50 cm) soils Peri-urban soil (250) Top (5 – 20 cm) and deeper (35 – 50 cm) soils</td>
</tr>
<tr>
<td><strong>Sample preparation:</strong></td>
<td>The &lt; 2 mm fractions ground until 95 % was &lt; 53 micron using an agate ball mill</td>
</tr>
<tr>
<td><strong>Determinands (methods):</strong></td>
<td>Ag, Al₂O₃, As, Ba, Bi, Br, CaO, Cd, Ce, Co, Cr, Cs, Cu, Fe₂O₃, Ga, Ge, Hf, I, K₂O, La, MgO, MnO, Mo, Na₂O, Nb, Ni, P₂O₅, Pb, Rb, Sb, Sc, Se, SiO₂, Sm, Sn, Sr, Ta, Te, Th, TiO₂, Ti, U, V, W, Y, Zn, Zr (XRF); pH (CaCl₂ slurry); LOI</td>
</tr>
<tr>
<td><strong>Report content</strong></td>
<td>In Prep</td>
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</tbody>
</table>
References


