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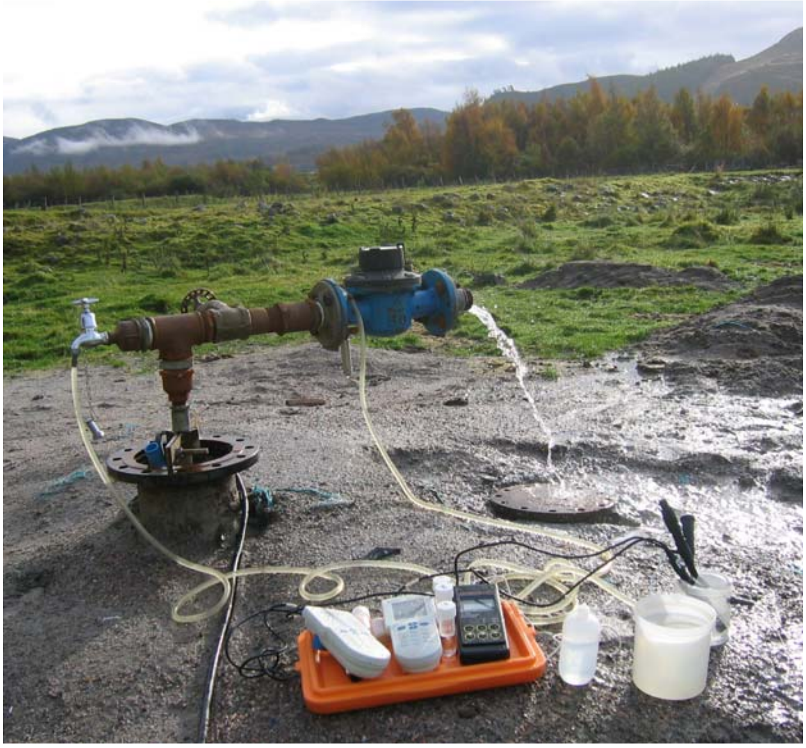

BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME
COMMISSIONED REPORT CR/05/239N

Baseline Scotland: an overview of available groundwater chemistry data for Scotland

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Summary

This report forms a national overview of existing groundwater chemistry data for Scotland, carried out to provide a foundation for the new project *Baseline Scotland*. This project is jointly funded by the British Geological Survey (BGS) and the Scottish Environment Protection Agency (SEPA), and aims to improve data availability and understanding of the chemistry of Scotland's groundwater. Understanding baseline groundwater chemistry is fundamental to helping to implement the Water Framework Directive: it is difficult to determine whether groundwater is polluted unless the baseline is known. Also, the presence or absence of various elements in water can occasionally give rise to health concerns or make the water unacceptable for human use.

Chemistry data from Scottish groundwater samples collected prior to the start of the *Baseline Scotland* project in June 2004 have been collated and described. Many of the data came from previous BGS studies, but data were also available from Scottish Water, councils and SEPA. In total, more than 800 groundwater chemistry analyses were identified.

The data are of variable quality and were subject to a thorough quality-assurance assessment. This involved gathering additional information on sources, checking the units for consistency, removing data from highly contaminated sites and calculating ionic balances. After this process the final dataset was as follows:

- The dataset comprised 428 sites with full major ion chemistry with an error in ionic balance of less than 10%;
- Of these 428 sites, 31 sites had a wellhead measurement of dissolved oxygen, and 103 had a wellhead measurement of the redox potential;
- Information on trace elements was generally limited. Only iron and manganese had more than 200 measurements across Scotland. For arsenic and fluoride (two trace elements generally considered the greatest risk for health in groundwater) data are particularly limited: 65 meaningful measurements for arsenic, and 149 for fluoride. The quality of the data is also variable – samples from Scottish Water and SEPA are generally not filtered at the sample site.

The dataset is highly skewed, with most good quality data being available for the Devonian aquifer in Fife and parts of Morayshire, and the Permian aquifer in Dumfries. There are few data available for Precambrian or Silurian/Ordovician rocks.

The major ion data were used to characterise Scottish groundwaters. Summary statistics have been calculated and the data presented on box plots, cumulative frequency plots and tri-linear diagrams. The data illustrate the variability of Scottish groundwater, reflecting the diverse geology and local environmental conditions.

- The most highly mineralised groundwater is found within the Carboniferous rocks. There is a marked bimodal distribution for chloride and sodium which may indicate mixing with formation water. Sulphate concentrations are considerably higher than for other aquifers which may reflect the oxidisation of sulphide minerals within mudstones and legacy of coal mining.
- Groundwaters from the Permian sedimentary aquifers in Scotland have well-defined chemistry and the least variation in concentrations of major ions of all Scottish groundwaters. Groundwater is of Ca-Mg-HCO_3 type with a narrow range in Mg/Ca ratio, and near-neutral pH.

- Most data are available for the Devonian aquifers in Scotland. Groundwaters tend to be of Ca-HCO_3 to Ca-Mg-HCO_3 type and show a wider range in Mg/Ca ratio than for the Permian rocks, but similar bicarbonate concentrations (median Devonian HCO_3 178 mg/l, median Permian HCO_3 157 mg/l). Median pH from the Devonian groundwaters is 7.5.

- The available data for the superficial deposits, Precambrian rocks and Silurian/Ordovician rocks indicate similar variability of major ion chemistry across the three hydrogeological environments. This may reflect the short residence time of much of the water, and the high proportion of samples from springs and shallow wells. The waters have typically low mineralization and pH less than 7.

- Groundwaters in volcanic aquifers are generally of Ca-HCO_3 type, and similar to the sandstone aquifers, with the exception of potassium which varies considerably across the volcanic aquifers. A small proportion of samples have chloride, sodium, sulphate and calcium concentrations.

- Most of the small island sources have high chloride concentrations, probably as a result of increased chloride concentrations in recharge. Other notable elevated chloride concentrations are observed in the coastal areas of East Lothian, Arbroath, Morayshire and northwest Fife The majority of inland sources have chloride concentrations less than 25 mg/l, and in upland areas concentrations are less than 10 mg/l.

- Nitrate data indicate a clear pattern across Scotland, with concentrations in excess of 25 mg/l as NO_3 across the east and southwest. Concentrations over much of the rest of Scotland are less than 10 mg/l as NO_3. The elevated concentrations of nitrate largely coincide with the agricultural areas of Scotland and are attributable to fertiliser applications and the presence of intensive farming; this is consistent with other recent studies.

There are insufficient reliable data to identify clear trends in the concentration of trace elements in Scottish groundwater. However, the following have been highlighted from the existing data.

- Iron and manganese concentrations greater than the EC maximum permissible value are observed in all hydrogeological units in Scotland. Iron and manganese are ubiquitous in rocks and the dominant controls on their presence in groundwater are the pH and redox status.

- The limited data for aluminium indicate that concentrations approach or exceed the EC maximum permissible value for drinking water in Precambrian and volcanic rocks and granite. This is linked to the acidic conditions of groundwater in these environments.

- The available data indicate that natural chromium concentrations in Scottish groundwater are typically well below the EC maximum permissible value, and usually below detection limit. There are no data from the Glasgow area, where elevated chromium concentrations may be expected due to widespread contamination from the chrome and steel industry.

- Fluoride concentrations greater than 0.5 mg/l have been measured in samples from the Permo-Triassic sandstone in Morayshire and the Permo-Triassic sandstone in Mauchline, southwest Scotland. There are several isolated samples scattered throughout Scotland with fluoride concentrations greater than the EC maximum permissible value of 1.5 mg/l.

In conclusion, there is a lack of systematically collected groundwater quality data for Scotland. Particularly lacking are data on trace elements and pH and redox status. The following recommendations should be implemented to give a reliable national dataset.

1. New data are required that are collected in a consistent, reliable and systematic manner, and analysed to a consistent degree of accuracy.

2. There is not widespread coverage of groundwater chemistry data in Scotland. Certain hydrogeological units have few reliable data and should be targeted for further sampling.
3. Wellhead measurements of redox potential and dissolved oxygen are required in order to understand the groundwater geochemical processes and element distributions.
4. There is evidence that the sampled chemistry is affected by the type of water source (e.g. well, borehole or spring). It is essential that comprehensive data are collected on each sampled source.
5. Routine sampling for age dating would be helpful for understanding residence times of groundwater and interpreting chemical variations – particularly nitrate data.
6. There are insufficient data on many trace elements in Scotland to characterise their occurrence or understand their origin. Comprehensive analysis of groundwater chemistry, including trace elements, should be carried out wherever possible.

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1 Introduction

1.1 SCOTTISH GROUNDWATER

Groundwater is an important, and often undervalued, national resource in Scotland. Groundwater is present both in the bedrock, where much of the flow is through fractures, and in the superficial deposits, where intergranular flow dominates. The most productive bedrock aquifers are the Permian sandstone and breccia in southwest Scotland and the Devonian sandstone in Fife, Strathmore and Morayshire. Alluvium and glaciofluvial sands and gravels can also form important aquifers and provide some of Scotland's most highly yielding boreholes.

There are in excess of 4000 boreholes in Scotland, and over 20 000 springs and wells used for private water supply. There are few available reliable data on the total volumes of groundwater abstracted. However, conservative estimates suggest that the total volume is approximately 330 megalitres per day for public water supply, industry, agriculture and private water supply (MacDonald et al. 2005). The volume of groundwater used in public water supply is growing annually; it is currently 7% of the daily 2400 megalitres per day supplied by Scottish Water.

The environmental importance of groundwater in Scotland is rarely documented or accounted for. Groundwater sustains river flows throughout the year and even in small upland streams may account for 30% of the flow, invaluable for sustaining salmon populations (Soulsby et al. 2000) and keeping streams and rivers viable over dry summers. In addition, groundwater has an important role in sustaining wetlands and fragile ecologies, such as parts of the machair (seasonally waterlogged sandy coastal plains).

The important contribution of groundwater to the health of the Scottish environment and economy is becoming more appreciated, largely driven by European legislation, most notably the Water Framework Directive 2000/60/EC. To help manage groundwater effectively good quality data are required on the status of the groundwater resources. National datasets are required on the chemistry of groundwater, the properties of the aquifers and the quantity of groundwater abstracted.

1.2 BASELINE SCOTLAND

1.2.1 Objectives of Baseline Scotland

Baseline Scotland is a new project, jointly funded by the British Geological Survey (BGS) and the Scottish Environment Protection Agency (SEPA), which seeks 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 to help in the implementation of the Water Framework Directive (WFD).

The overall objectives of *Baseline Scotland* are similar to those of the BASELINE project started in England and Wales in 1996. The BASELINE project has produced reports for 23 areas (e.g. Griffiths et al. 2002, Shand et al. 2003, Smedley et al. 2004) and some of the organising ideas are presented in Shand and Frengstad (2001). The objectives of *Baseline Scotland* are:

1. To characterise the ranges in natural groundwater quality in the main aquifer types in Scotland, by carrying out groundwater sampling surveys that as far as possible incorporate representative areas of each aquifer, allowing extrapolation of the interpreted results to the remaining parts of each aquifer.
2. To provide a scientific foundation to underpin Scottish, UK and European water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

Baseline Scotland represents a major initiative. At proposed funding levels it will take 10 years to collect and interpret the data for the various aquifer types in Scotland.

1.2.2 Scope of this report

This report comprises an overview of the existing groundwater chemistry data for Scotland, prior to the collection of new data for the *Baseline Scotland* project. The specific aims of this study are:

- to collate available *existing* groundwater chemistry data for Scotland;
- to describe the available data and variations in groundwater chemistry across the different aquifers;
- to highlight major gaps in information and/or understanding.

1.3 WHY IS BASELINE CHEMISTRY IMPORTANT?

Groundwater issuing from springs has been regarded since the earliest recorded history as something pure, even sacred. In its natural state, it is generally of excellent quality and an essential natural resource. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to groundwater abstraction and the consequent change in groundwater flow, artificial recharge and direct inputs of anthropogenic substances. A thorough knowledge of the quantity and quality of groundwaters in our aquifers, including a good understanding of the physical and chemical processes that control these, is therefore essential for effective management of this valuable resource.

The properties of groundwater are overwhelmingly determined by geochemical processes taking place as rain or surface water enter the ground and react with rock-forming minerals. This natural baseline quality will vary from one rock type to another, seen at its simplest in the different areas of hard and soft water across the country. Each area will, therefore, be underlain by an almost unique groundwater quality resulting from the influence of the local geology.

It is difficult to distinguish a polluted unless the baseline is known. The baseline chemistry may vary spatially within aquifers due to variations in the original sediments. The chemistry also evolves with time as the water moves along flow lines. A number of geochemical processes may help shape the unique natural characteristics of groundwater. For example oxidation and reduction (controlling natural concentrations of, for example, iron, manganese, arsenic and chromium), mineral solubility (controlling fluoride and barium concentrations, for example), and sorption and exchange with mineral surfaces (affecting the concentrations of many trace elements).

Nine major chemical constituents – sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), bicarbonate (HCO_3), chloride (Cl), sulphate (SO_4), nitrate (NO_3) and silicon (Si) – make up about 99% of the solute content of natural groundwaters. The concentrations of the major ions define the characteristics of the groundwater. However, the presence (or absence) of the remaining 1% (often referred to as the trace elements) can occasionally give rise to health problems or make the water unacceptable for human use.

2 Background

2.1 PREVIOUS STUDIES OF GROUNDWATER CHEMISTRY IN SCOTLAND

A number of previous studies have investigated groundwater chemistry in Scotland, some at a national level and some with a more regional or local focus. Below is a summary of many of the recent studies of groundwater chemistry in Scotland.

1. The first systematic `survey of the groundwater quality of the main aquifers in Scotland was reported by Robins (1986). One hundred groundwater samples were collected from the main aquifers – Permian, Devonian, Carboniferous and superficial deposits and analysed for the major ions plus iron, manganese and fluoride. Robins (1986) concluded that most of the waters were of Ca-Mg-HCO_3 type but required minor element analysis to confirm whether the sources were potable. He described high iron concentrations in the Carboniferous rocks, and sporadic high nitrate concentrations, as being of particular concern. This study was updated by Robins (2002) using additional data. From approximately 300 samples he characterised the major ion groundwater chemistry and again highlighted elevated nitrate concentrations and poor quality water in the Carboniferous rocks of the Midland Valley.
2. As part of a UK-wide survey of minor elements in groundwater, Edmunds et al. (1989) included two aquifers in Scotland: the Permian aquifers of southwest Scotland (as part of a wider study of the Carlisle Basin), and the Devonian aquifer of Morayshire (also reported in Robins et al. 1989). They concluded that the factors controlling the trace element concentrations were the lithology of the aquifers and the aquifer conditions – pH and Eh.
3. Ball (1995) reviewed the occurrence of groundwater pollution in Scotland from existing data (mostly major ion data). He highlighted the general good quality of groundwater in Scotland, but stated the threat posed by rising nitrate concentrations, and the poor-quality water in mining areas.
4. As part of a regional survey of the Fife aquifer Ó Dochartaigh et al. (1999) collected 13 samples and analysed for major elements and some trace elements. Additional work on residence time using tritium was carried out by McNeill et al (2003).
5. A survey of the groundwater chemistry of the Permian sediments of the Dumfries Basin was carried out by MacDonald et al. (1999). Twenty-one boreholes were sampled and analysed for a comprehensive suite of major and trace elements and some for the residence-time indicators CFC and SF6. The data showed a strong correlation between the proportion of modern groundwater and nitrate in a sample and suggested a component of palaeo-water in the basin (MacDonald et al. 2003)
6. The Scottish national groundwater monitoring network was established in 2000 by SEPA and included 150 sites. All were pre-existing water points and most were private supplies. This network was designed to be representative of Scotland's environment: the sample points were spread over 39 biophysical classes based on aquifer permeability, soil leaching potential, and land use (Lilly et al. 2003). The network has expanded to 220 sites (MacDonald et al. 2005) and is monitored specifically for nitrate, but samples are also monitored for other major ions.
7. As part of a study of the quality of water from private water supplies from 1992-98, Reid et al. (2003) analysed nitrate and coliform data from over 1000 sites. They demonstrated that many private supplies failed EC standards during some part of the year. They also demonstrated a positive trend of microbiological failures with rainfall, and inverse trend of nitrate failures with rainfall.

8. As part of the designation of nitrate vulnerable zones in Scotland, nitrate data were collated from a variety of sources including private, public, industrial and agricultural water supplies (Ball and MacDonald 2001). The data clearly showed elevated nitrate concentrations in the east of Scotland where a combined risk/vulnerability methodology had indicated high nitrate concentrations could be expected (Ball et al. 2005). An additional 70 sites in these high-risk areas were identified and sampled to confirm this pattern (Ball and MacDonald 2002).

2.2 GROUNDWATER ENVIRONMENTS IN SCOTLAND

In order to help interpret the groundwater chemistry data for Scotland the hydrogeology was divided into seven units (Figure 1). Robins (1990), Ball (1999) and MacDonald et al. (2005) give more detail about the different aquifers.

Permian sedimentary rocks occur primarily in the southwest of Scotland within small basins. They form some of the most productive aquifers in Scotland, and are widely exploited. The sediments comprise aeolian sandstones, fan breccias and fluviatile sandstones, siltstone and mudstone. Groundwater flow is dominantly through fractures, although the sandstones provide significant intergranular groundwater storage.

Carboniferous sedimentary rocks are present throughout the Midland Valley of Scotland and also in the south of Scotland on the border with England. They comprise rhythmic sequences of sandstone, mudstone, limestone and coal. Groundwater flow is dominantly through fractures, and the sandstone units are moderately permeable. The Passage Sandstone Formation is more permeable than other units within the Carboniferous and has significant intergranular flow. Carboniferous rocks have been extensively mined for coal which has impacted significantly on the groundwater flow and chemistry.

Devonian sedimentary rocks occur widely across the Midland Valley and the northeast of Scotland. They comprise sandstone, siltstone, mudstone and conglomerate. The aquifer is moderately to highly permeable and much of the flow is through fractures, although intergranular permeability and porosity can be important locally. The Devonian sandstone aquifer in Fife is one of Scotland's most productive aquifers and supports several large abstractions for public supply. Elsewhere in Scotland the aquifer is less productive, but is widely developed for agriculture, industry and private supply.

Silurian and Ordovician wackes and siltstones are present throughout southern Scotland. The sediments are hard and well-cemented with negligible primary porosity. Groundwater flow occurs only within fractures, and the rocks are only weakly permeable. The lithology of the sediments is variable and can be calcareous in places. The aquifer is exploited for house and farm supplies.

Much of Scotland is underlain by **Precambrian** rocks. These rocks are highly variable and include metamorphic and igneous rocks. For the purposes of this report, granite of all ages has been put in this category. These rocks are poorly permeable and have negligible intergranular flow. However, there are many private water supplies for individual houses, and some small public water supplies within these rocks.

Volcanic rocks occur throughout Scotland. Groundwater flow occurs within fractures, particularly at the junction between individual lava flows. Some of the volcanic rocks are moderately permeable and can sustain abstractions for public supply and mineral water.

Superficial deposits occur throughout Scotland and form important aquifers. They are not shown on Figure 1 since they are widespread, of limited extent and overlie the bedrock aquifers. Groundwater flow is generally intergranular and flow paths are shallow. High productivity superficial aquifers comprise deposits that have significant sand and gravel content, such as glaciofluvial sand and gravel, and alluvium. Alluvial deposits within valley floodplains, although possibly less than 10 m in thickness, may have the capability to support very large abstraction rates wherever there is good hydraulic contact with adjacent watercourses. Moderate productivity aquifers comprise mainly raised marine deposits. Typically, these contain a high proportion of silt and clay and therefore have lower permeability than the coarser, well-sorted, high productivity deposits. Much of Scotland is covered by till but only thick sandy tills and moraine can be considered as aquifers.

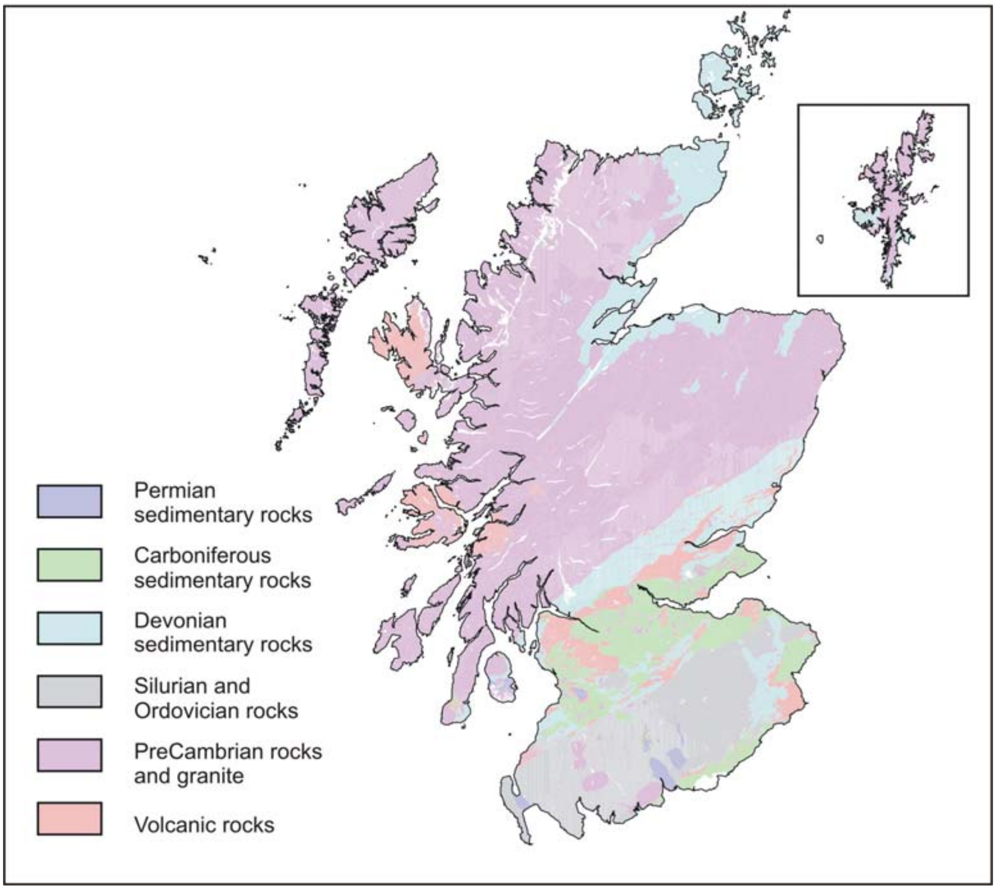


Figure 1 Scottish groundwater units used in this study.

3 Groundwater chemistry data

3.1 DATA SOURCES

The groundwater chemistry data used in this study have been gathered from various existing surveys carried out before June 2004. Many of the data were collected and published by BGS as part of the previous surveys described in Chapter 2, but data have also been collected from Scottish Water and some council datasets. Data from the SEPA groundwater monitoring network have also been included. Table 1 shows the sources of data and the laboratories which undertook the analysis.

Other data exist for a small suite of parameters – for example, nitrate concentrations are measured for private water supplies. However, these data have not been collected, since they do not provide sufficient information to be useful for characterising general baseline groundwater chemistry conditions, and the data can be of poor quality. These data have proved useful for understanding trends in nitrate (Ball and MacDonald 2001)

Table 1 The sources of groundwater chemistry data available before the start of the *Baseline Scotland* project in June 2004.

Dataset	No of samples	Date	Source of data and main reference	Laboratories
Miscellaneous	36	1980-2000	Various BGS reports and projects	Mixture
Strathmore student project	35	1992	Ball 1994	Paisley University
BGS Fife and Dumfries Studies	54	1998-99	MacDonald et al. 1999; Ó Dochartaigh et al. 1999	BGS Wallingford
Trace elements study	32	1983-86	Edmunds et al. 1989	BGS Wallingford
Miscellaneous Scottish Water	98	1995-2004	Various BGS reports and projects	Scottish Water + BGS Wallingford
BGS database	130	1970-89	BGS database	BGS
Scottish overview	138	1984	Robins 1986	The Macaulay Institute
NVZ extra sites	70	2001	Ball & MacDonald 2002	BGS Wallingford
Additional council data	92	1980-97	Robins 2002	Council Laboratories
SEPA	146	2003	SEPA database	SEPA laboratories

3.2 CREATING A USABLE DATASET

The original data gathered from the various sources total approximately 800 groundwater chemistry analyses. These data are of variable quality in terms of the number of determinands reported, the analytical detection limits for trace elements, and the ionic balances of the analyses. To get usable datasets of major ion chemistry and trace elements it was necessary to process the data and carry out quality assurance checks.

1. A thorough assessment of data quality was undertaken to ensure consistency of units (for example to minimise confusion between mgl^{-1} and μgl^{-1}, NO_3-N and NO_3, P and PO_4, Ca and Mg hardness and HCO_3).
2. Information about the samples and the sources was gathered, for example the grid co-ordinates, depth of the source, pumping rate, date of sample etc.
3. Samples that were taken from highly contaminated sites were removed – this included an older set of data from collieries and more recent data from projects targeting contaminated sites. The reason for this was to eliminate bias in the data.
4. To create a dataset of major ions, an ionic balance was calculated for each sample. If the balance between cations and anions differed by more than 10%, the analysis was removed from the dataset.
5. Creating a usable dataset for trace elements was challenging. Often the concentrations of the elements were below the detection limit of the analysis method; also, for each element there were many different detection limits (see Table 2). The data were therefore not of sufficient quality to carry out a detailed statistical analysis, therefore a more robust approach was taken:
    - Where a suite of data was all below detection, and the detection limit was greater than the EC maximum permissible value for drinking water or WHO guideline value, the data were all removed.
    - The detection limits were analysed and a minimum concentration chosen that was equal to or higher than the highest meaningful detection limit.
    - The data were divided into appropriate bins (e.g. >1, 1-10, >10 μgl^{-1}), using the minimum concentration calculated above, and the EC maximum permissible value, or WHO guideline value.
6. For sites with more than one sample, a simple method was used to choose one of the samples. In order of priority this was: most comprehensive analysis; best ionic balance; most recent sample. There were insufficient sites with trend data to make any meaningful observations across Scotland. Previous studies of nitrate trends found only several boreholes in Scotland where sufficient data was available to make meaningful observations (MacDonald et al. 2003, Ball et al. 2005).

These two datasets – the major ion dataset and trace element dataset – were then used to provide the basis for the remainder of this report. The major ion dataset had data for 428 sites across Scotland. The number of samples with trace element data varied from 21 for uranium to 437 for manganese.

Table 2 Detection limits for trace element data.

Element	N° samples	Detection limits (DL)			MPV or GV (μgl^{-1})	N° values > DL	N° values < DL where DL >MPV	N° values > MPV
		Total N° different DLs	Lowest DL (μgl^{-1})	Poorest DL (μgl^{-1})				
Al	186	9	3	100	200[a,d]	109	0	8
As	138	5	1	50	10[a]	40	73	7
Ba	178	2	0.2	2	700[b]	175	0	0
Cd	162	17	0.038	25	5[a]	23	11	1
Cr	164	13	0.38	30	50[a]	39	0	0
F	149	2	30	100	1500[a]	128	0	3
Fe	329	14	0.5	300	200[a,d]	238	1	93
Mn	323	11	0.038	100	50[a,d]	311	6	119
Ni	163	17	0.27	100	20[a]	60	1	5
Pb	182	1	0.042	200	10[a]	49	17	5
U	21	16	none below		15[b]	21	0	0
Zn	187	10	0.45	200	3000[c]	156	0	0

[a] EC maximum permissible value

[b] WHO guideline value

[c] WHO guideline value based on acceptability, rather then health

[d] EC indicator parameter; compliance is less stringent than for other elements

3.3 LIMITATIONS OF THE DATA

Even after carrying out the procedure described above and purging poor-quality data, the dataset is limited.

1. The data are not distributed evenly across Scotland, but are biased towards the more productive aquifers, usually sandstone or superficial deposits (see Figure 2). The Devonian aquifers of Fife, Strathmore and Morayshire and the Permian aquifer in Dumfries are most represented. The data are from a variety of different source types, including springs, boreholes and shallow wells.
2. The groundwater chemistry analyses often do not include a comprehensive suite of determinands. The major ion data are most comprehensive, but even here the full suite of major ions required to carry out an ionic balance was not available for all samples (see earlier). It is important when carrying out any groundwater chemistry sampling to measure all the major ions, not least to allow the ionic balance to be calculated.
3. There is incomplete information about how samples were collected. Of particular concern is that there is little information on whether samples have been filtered at the wellhead. Samples sent to the BGS Wallingford or Macaulay laboratories will have been filtered and acidified; however, those analysed by SEPA, the councils, or Scottish Water, are unlikely to have undergone filtration or acidification. These unfiltered samples are generally analysed

within 24 hours, and only the major ions analysed for, with the addition of iron, manganese and possibly zinc.

4. Many of the analyses contain measurements of a limited number of trace elements, often only those likely to be of high concentration; for example, manganese, iron and zinc. Some elements, such as uranium and arsenic, have been rarely analysed for in Scottish groundwaters. This is a function of the purpose of the study, and the choice of analytical method. However, samples are still not being routinely analysed for a comprehensive suite of trace elements, due partly to cost and sampling protocol but also a lack of awareness of the potential implications of these elements in groundwater.

5. Even where trace elements have been analysed, their concentrations are often lower than the analytical detection limits of the method used, making it impossible to carry out accurate analysis of actual element concentrations. For a number of trace elements, the detection limits from many laboratories are higher than the element concentrations normally seen in Scottish groundwater, and in some cases the detection limits are equal to the maximum concentrations allowed by EC and UK drinking water standards. This is particularly the case for cadmium, chromium, lead and nickel. For some trace elements there are many different detection limits, making analysing the data challenging (see Table 2 above).

6. Wellhead or field-chemistry measurements are not available for many of the samples. Field measurements of pH, temperature, redox potential, dissolved oxygen and alkalinity are useful for helping to characterise the groundwater and interpret the data from the laboratory.

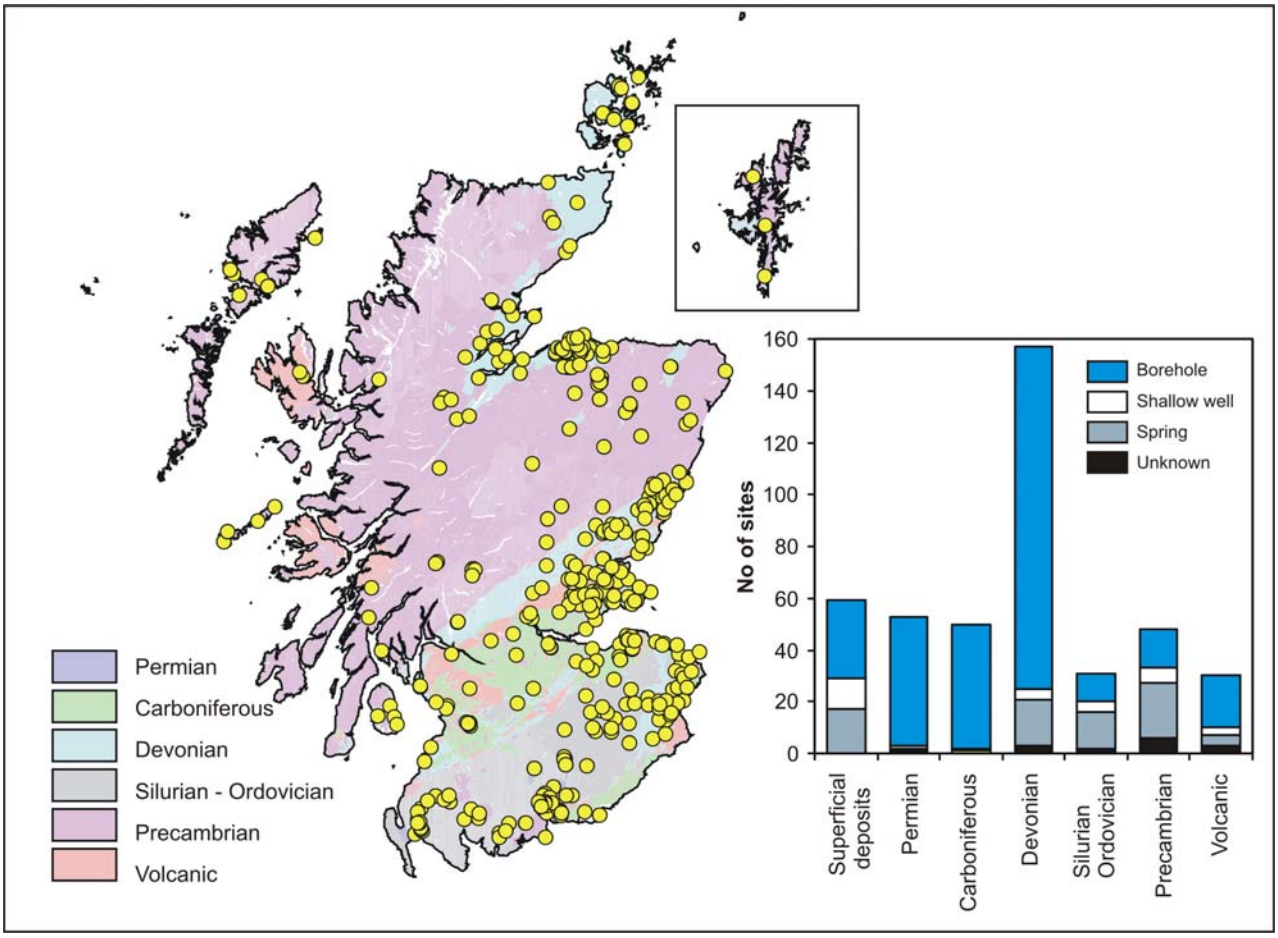


Figure 2 Location of the 428 sites which have complete major ion chemistry data with an error in ionic balance of less than 10%. The graph shows the number of sites in each groundwater unit.

3.4 WELLS, SPRINGS AND BOREHOLES

Data have been gathered from a variety of sources including shallow wells, boreholes and springs (samples from coal mining shafts taken in the 1970s were not considered). Figure 2 indicates the proportion of different sources on each groundwater unit. Springs and wells are most represented in three groundwater units – superficial deposits, Silurian/Ordovician, and Precambrian. Since the major ion chemistry of these three units is similar (see later), it was appropriate to use data from the three units to illustrate the effect of taking samples from different types of groundwater source.

Figure 3 shows the cumulative frequency curves for total dissolved solids (TDS) in wells, springs and boreholes for samples taken from superficial deposits, Precambrian and Silurian/Ordovician rocks. A similarly shaped distribution of TDS is evident for each source type – each approximating to a normal distribution. However, a clear pattern emerges: samples from springs are generally less mineralised than samples from boreholes. Data for shallow wells plot between springs and boreholes.

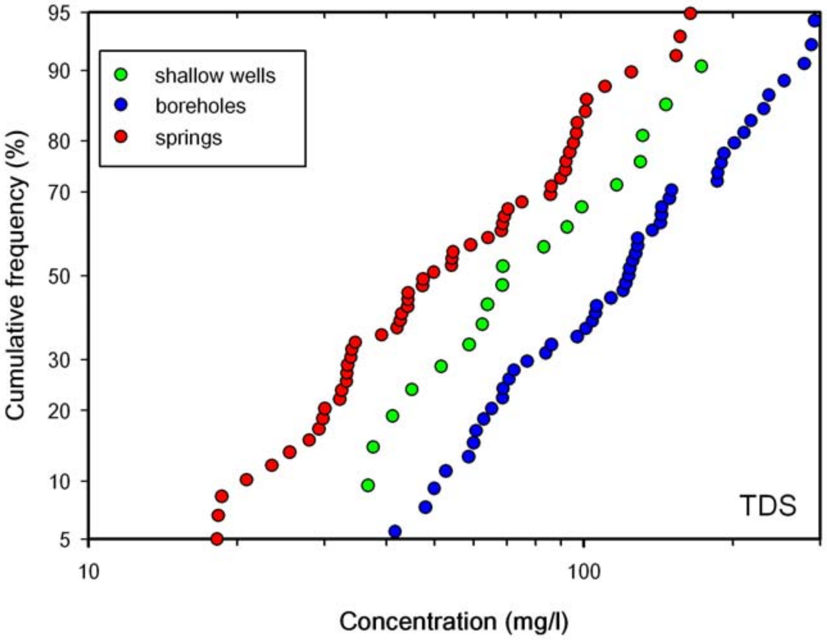


Figure 3 The effect of source type on measured total dissolved solids (TDS) for samples taken from boreholes, wells and springs in the superficial deposits, Precambrian and Silurian/Ordovician aquifers.

4 Major ion chemistry

4.1 AVAILABLE DATA FOR SCOTLAND

Natural groundwater recharge is derived from rainfall. The concentration in rainwater of the major ions sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), bicarbonate (HCO_3), chloride (Cl), sulphate (SO_4), are derived from sea water, and in some locations by contamination (in Scotland sulphate, nitrate and calcium are typically elevated in rainwater). As the rainwater infiltrates through the soil, superficial deposits and bedrock, the chemistry changes due to water-rock interaction. Notable exceptions are chloride and nitrate. Chloride is typically conservative in groundwater and elevated concentrations of nitrate are largely a result of anthropogenic activity.

The degree to which groundwaters become mineralised depends on a number of factors: the aquifer mineralogy, the permeability and nature of groundwater flow; the presence and nature of overlying deposits; the geochemical environment (especially the pH and redox conditions); groundwater flowpaths; and groundwater residence time (since most reactions are kinetically controlled). Anthropogenic influences may also modify the concentrations and distribution of other ions apart from nitrate, in particular potassium, ammonia and sulphate, which can be increased by activities such as fertiliser application.

A statistical summary of the major ion groundwater chemistry data for Scotland is given in Table 3 and is represented in a box plot in Figure 4. Table 4 gives a summary of available wellhead measurements for Scotland. The box plot also gives an indication of the concentrations expected in sea water factorised to the median chloride concentration of the dataset.

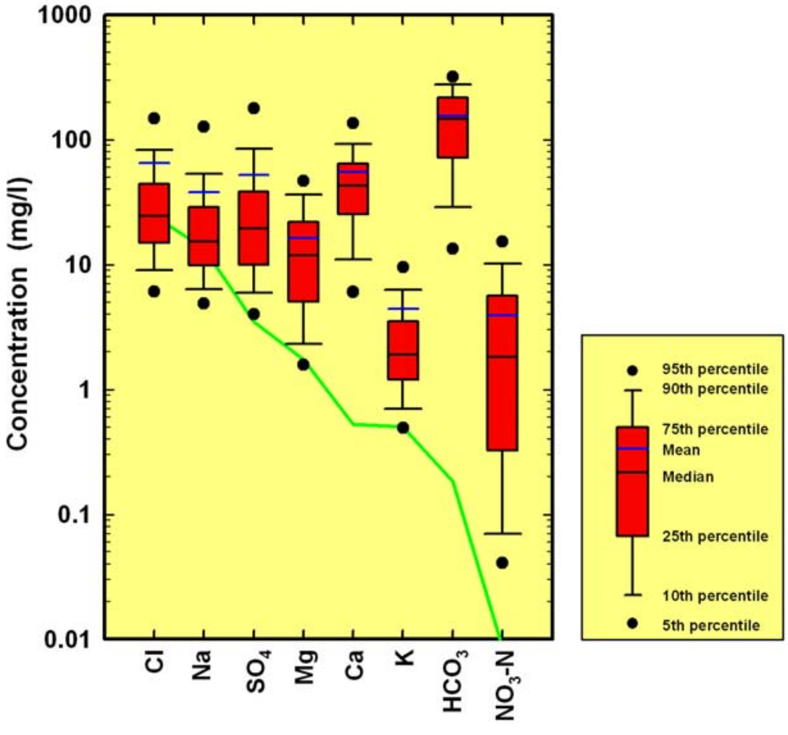


Figure 4 Box plot of major ion groundwater chemistry for Scottish groundwater. The locations of the sites are given in Figure 2. The green line indicates the concentrations expected in sea water factorised to the median chloride concentration of the dataset.

Table 3 Statistical summary of major ion chemistry in Scottish groundwater for all 428 sites.

	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l	NO_3 mg/l
5th percentile	6.18	1.63	5.0	0.49	6.15	4.06	13.5	0.04
25th percentile	25.3	5.10	9.84	1.20	15.0	10.0	71.9	0.33
Median	42.8	11.9	15.2	1.90	24.5	19.6	146	1.81
Mean	55.1	16.4	38.1	4.43	64.6	52.1	155	3.94
75th percentile	64.1	21.9	29.0	3.48	44.0	38.1	218	5.60
95th percentile	132	46.0	121	9.04	142	173	309	15.0

Table 4 Statistical summary of available (pre 2004) wellhead chemistry for Scottish groundwater.

	Temperature	pH	SEC	Eh	DO
Units	°C	pH units	µS/cm@25°C	mV	mg/l
Number of analyses	270	423	367	103	31
5th percentile	6.79	6.2	102	25.5	0
25th percentile	8.5	6.8	266	128	1.9
Median	9.1	7.2	405	306	7.1
Mean	9.35	7.2	522	258	6.1
75th percentile	10	7.6	608	400	10
95th percentile	12.6	8.1	1379	400	11

4.2 OVERVIEW

In general, groundwater in Scotland is dominated by Ca-HCO_3 waters, but with a significant number of Ca-Mg-HCO_3 and weakly mineralised Na-Cl waters. The concentrations of most of the major ions, particularly Ca and HCO_3, but also SO_4, Mg and K, indicate water-rock interaction. There are few data on the redox conditions of the sampled groundwaters. Most of the 31 available measurements of dissolved oxygen have concentrations greater than 1.9 (mg/l). Measurements of redox potential indicate generally oxidising conditions (median of 306 mV) with a significant minority of samples from reducing groundwaters (25 percentile 128 mV). The temperature of the groundwaters does not vary considerably, being typically between 8.5 and 10°C (the interquartile range), with a mean of 9.4°C. Groundwater is typically near-neutral, with a pH between 6.8 and 7.6, and mean of 7.2.

More detailed descriptions of the chemistry are given in Section 4.3 where the data are divided into different hydrogeological units. However, two parameters, nitrate and chloride, are not controlled by water-rock interaction and they are best discussed in a national context.

4.2.1 Chloride

The distribution of chloride across Scotland is given in Figure 5. As discussed above the data are from various years and the samples from different sources – boreholes, springs and wells. With the

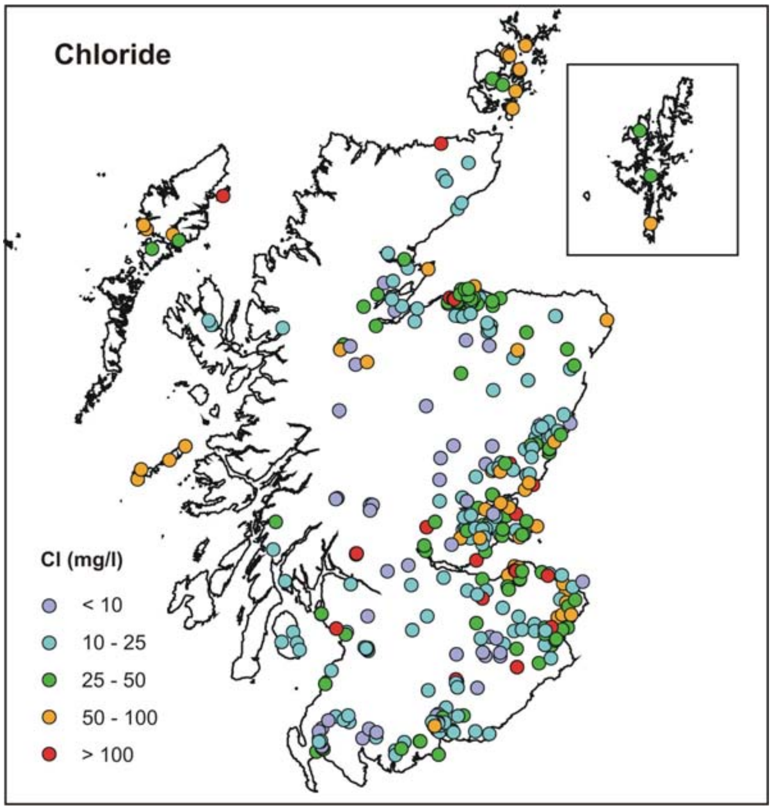


Figure 5 Map of chloride concentrations in Scottish groundwater.

exception of Arran, most of the island sources have high chloride concentrations, probably as a result of increased chloride concentrations in recharge. Other notable elevated chloride concentrations are observed in the coastal areas of East Lothian, Arbroath, Morayshire and northwest Fife – these again are likely to be due to influence from the sea, either as increased chloride in recharge, or in some instances, saline intrusion, or contamination. Another area with high chloride concentrations that merits further investigation is the far west of the Borders between Coldstream and Duns.

The majority of inland sources have chloride concentrations less than 25 mg/l, and in upland areas concentrations are less than 10 mg/l. This reflects the high effective rainfall and therefore the low mineralisation of recharge. There are some isolated non-coastal sources that show chloride in excess of 100 mg/l. These are likely to be due to contamination (including the effect of mining), or the mixing with connate water.

4.2.2 Nitrate

The distribution of nitrate concentrations across Scotland is shown in Figure 6. The data indicate a clear pattern across Scotland, with concentrations in excess of 25 mg/l as NO_3 across the east and southwest (although the data are skewed, with more data available in these areas). Concentrations over much of the rest of Scotland are less than 10 mg/l as NO_3. The elevated concentrations of nitrate largely coincide with the agricultural areas of Scotland and are attributable to fertiliser applications and the presence of intensive farming.

Nitrate concentrations in Scotland have been subject to more rigorous studies, largely driven by the EC Nitrates Directive. A risk/vulnerability method, backed up by data analysis helped to identify 14% of Scotland as nitrate vulnerable (Ball et al. 2005). As part of a project reviewing the SEPA groundwater monitoring network, MacDonald et al. (2005) identified the following trends in nitrate concentrations in groundwater across Scotland (see Figure 7).

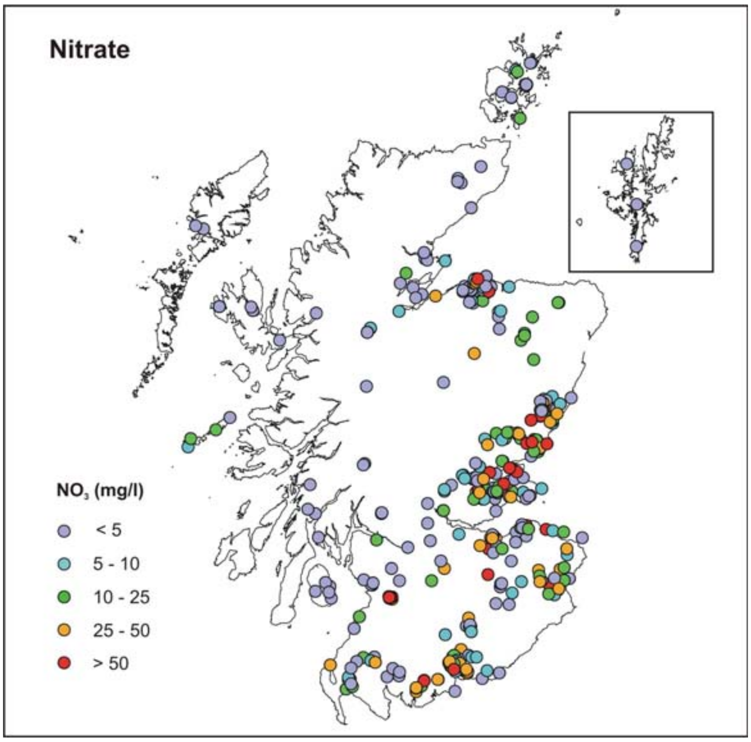


Figure 6 Map of nitrate concentrations in Scottish groundwater.

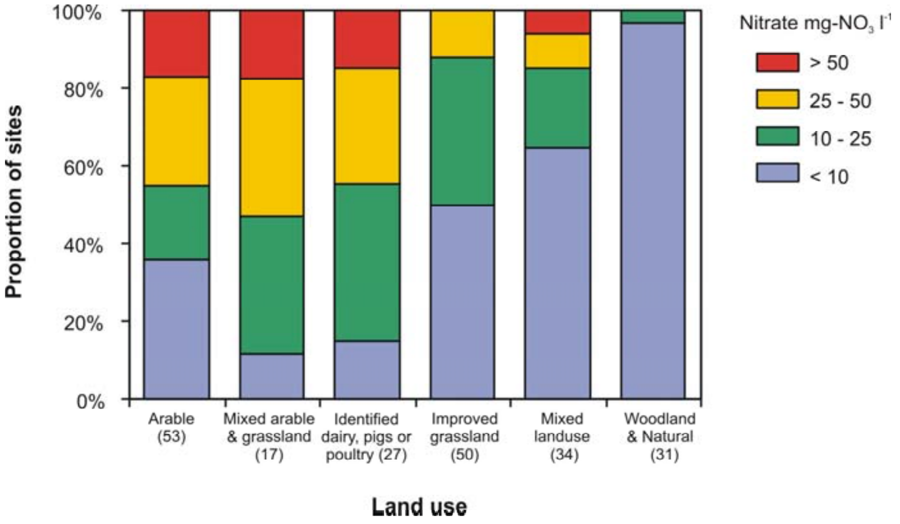


Figure 7 Nitrate concentrations and land use in Scotland (from MacDonald et al. 2005)

- Arable areas, mixed arable and grassland, and land used for dairy, pigs and poultry have the greatest nitrate concentrations.
- Improved grassland by itself (i.e. where not mixed with arable, and with no identifiable pig, poultry or dairy farming) has intermediate nitrate concentrations. This reflects the lower intensity farming methods of cattle production.
- Woodland and semi-natural areas have the lowest nitrate concentrations with virtually all sites below 10 mg/l as NO_3.
- There is still variance that is not explained by the land use which can be explained by denitrification, mixing with older waters, and slow infiltration caused by the geological conditions.

4.3 MAJOR ION CHEMISTRY BY AQUIFER

The major ion data have been subdivided by aquifer in order to show variations in groundwater chemistry between different aquifer types. Box plots for the data are shown in Figure 8, cumulative frequency plots in Figures 9 and 10 and Piper diagrams for four of the aquifers in Figure 11. Summary data are given in Table 5.

The most highly mineralised groundwater is found within the Carboniferous rocks. The median concentrations of all major ions (except nitrate which was discussed previously) are greater for all the other aquifers. There is a marked bimodal distribution for chloride and sodium which may indicate mixing with seawater in coastal areas or formation waters. Sulphate concentrations are considerably higher than for other aquifers which may reflects the mineralogy and legacy of coal mining.

The available data for the superficial deposits, Precambrian rocks and Silurian/Ordovician rocks indicate similar types of water in the three hydrogeological environments. This may reflect the sources for which data are available (mainly springs, and shallow boreholes) and the short residence time of much of the groundwater. The waters have typically low mineralisation, and a wide range in chemical composition. The median pH for the superficial deposits and Precambrian rocks is acidic; for Silurian/Ordovician rocks, however, there is a bimodal distribution for pH (see Figure 10), with one distribution similar to Precambrian and superficial aquifers, and the second distribution more akin to the sandstone aquifers. A similar bimodal distribution is evident for both calcium and magnesium and to a lesser extent bicarbonate (see Figure 9 and 10). The database shows that this is not due to differences in source type and is likely to be due to variations in carbonate within the Silurian and Ordovician rocks.

Groundwaters from the Permian sedimentary aquifers in Scotland have well defined chemistry and little variation in the relative proportions of major ions. Groundwater is of Ca-Mg-HCO_3 type throughout the aquifers with a slightly alkali pH of median 7.3. Sodium and chloride concentrations are particularly low for the aquifer.

More data are available for the Devonian aquifers in Scotland. Groundwater tends to be of Ca-HCO_3 to Ca-Mg-HCO_3 type and shows a narrow range in HCO_3 and Ca concentrations compared to the Permian aquifers. Magnesium concentrations vary considerably, however, reflecting changes in the cement of the Devonian rocks. Median pH is 7.5.

Groundwaters in volcanic aquifers are generally of Ca-HCO_3 type, and similar to the sandstone aquifers, with the exception of potassium which varies considerably across the volcanic aquifers. There are few data available (31 samples) and some of the samples may be from boreholes that penetrate interbedded volcanic and sandstone rocks. A small proportion of samples are highly mineralised, with elevated chloride, sodium, sulphate and calcium (see Figure 8).

The data for the Devonian, Permian, superficial deposits and Carboniferous aquifers are compared on a piper diagram in Figure 11. The area of the diagram in which 75% of the data plot, is shown, along with an indication of the variation of the remaining 25% of the data. The diagram illustrates the differences in groundwater chemistry between the four different aquifers:

- Permian aquifers have well-defined groundwater chemistry and are dominated by Ca-Mg-HCO_3.
- Devonian groundwaters are similar to those from the Permian, except there is a wider range in Mg/Ca ratio.
- Carboniferous groundwaters are generally Ca-Mg-HCO_3 in composition, but a significant minority of the data have elevated sulphate and sodium concentrations.

- Samples from the superficial deposits have a much wider variation in composition, with the groundwater varying from Ca-HCO_3 to Na-Cl. This is attributable to differences in water-rock interaction, with some samples reflecting rainwater composition.

Table 5 Summary statistics for major ion groundwater chemistry for the different hydrogeological environments in Scotland.

		Ca	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**HCO_3**	**NO_3-N**	**pH**
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	pH units
Superficial deposits	25th percentile	11.8	2.79	8.00	0.65	12.8	8.45	28.5	0.64	6.40
	median	22.0	5.10	12.0	1.40	20.0	13.0	47.2	1.21	6.80
n = 59	mean	29.7	7.26	14.8	1.86	26.0	27.2	75.0	2.39	6.82
	75th percentile	35.4	8.10	17.5	2.80	35.0	23.0	105	3.71	7.30
Permian	25th percentile	30.4	11.1	9.32	1.20	14.3	11.3	108	1.43	7.03
	median	37.2	15.8	11.8	1.47	18.0	20.1	157	3.34	7.26
n = 53	mean	42.6	16.9	15.2	1.83	23.1	26.6	155	4.55	7.30
	75th percentile	55.0	20.0	17.9	2.00	23.4	28.9	195	6.30	7.53
Carboniferous	25th percentile	47.8	19.6	14.7	2.21	25.3	35.0	204	0.20	6.78
	median	74.1	29.1	34.1	5.05	40.0	75.7	262	0.30	7.20
n = 50	mean	94.2	35.6	70.7	18.9	111	138	287	2.39	7.13
	75th percentile	105	47.1	52.5	8.58	69.5	128	350	4.38	7.60
Devonian	25th percentile	37.2	7.66	12.0	1.58	19.3	13.4	134	0.76	7.28
	median	51.7	13.0	18.6	2.12	28.6	23.0	178	2.90	7.49
n = 157	mean	56.9	17.1	33.9	3.13	46.5	52.0	179	4.89	7.47
	75th percentile	67.0	22.4	31.8	3.61	48.0	38.4	223	7.34	7.80
Silurian /Ordovician	25th percentile	11.1	3.00	6.63	0.53	7.6	6.92	26.0	0.50	6.42
	median	26.4	7.10	9.94	0.94	14.4	11.1	68.0	2.27	7.07
n = 31	mean	40.0	11.7	40.4	1.92	79.8	30.0	88.3	3.97	6.94
	75th percentile	52.3	17.5	15.6	2.30	27.2	15.7	141	4.30	7.44
PreCambrian	25th percentile	7.79	2.03	4.96	0.78	7.60	5.36	24.4	0.05	6.33
	median	13.3	3.18	11.0	1.40	17.0	7.45	46.0	0.28	6.70
n = 47	mean	22.0	4.28	17.1	1.73	28.4	9.75	71.5	1.30	6.73
	75th percentile	30.0	5.65	21.8	2.35	36.0	11.8	103	1.20	7.20
Volcanics	25th percentile	40.4	10.1	12.4	1.07	21.0	16.1	83.8	0.50	6.98
	median	60.9	19.2	23.6	2.17	32.0	28.4	171	3.20	7.30
n = 31	mean	118	20.7	120	3.43	262	89.6	164	6.73	7.28
	75th percentile	96.1	29.1	46.2	4.75	57.9	47.4	233	11.3	7.60

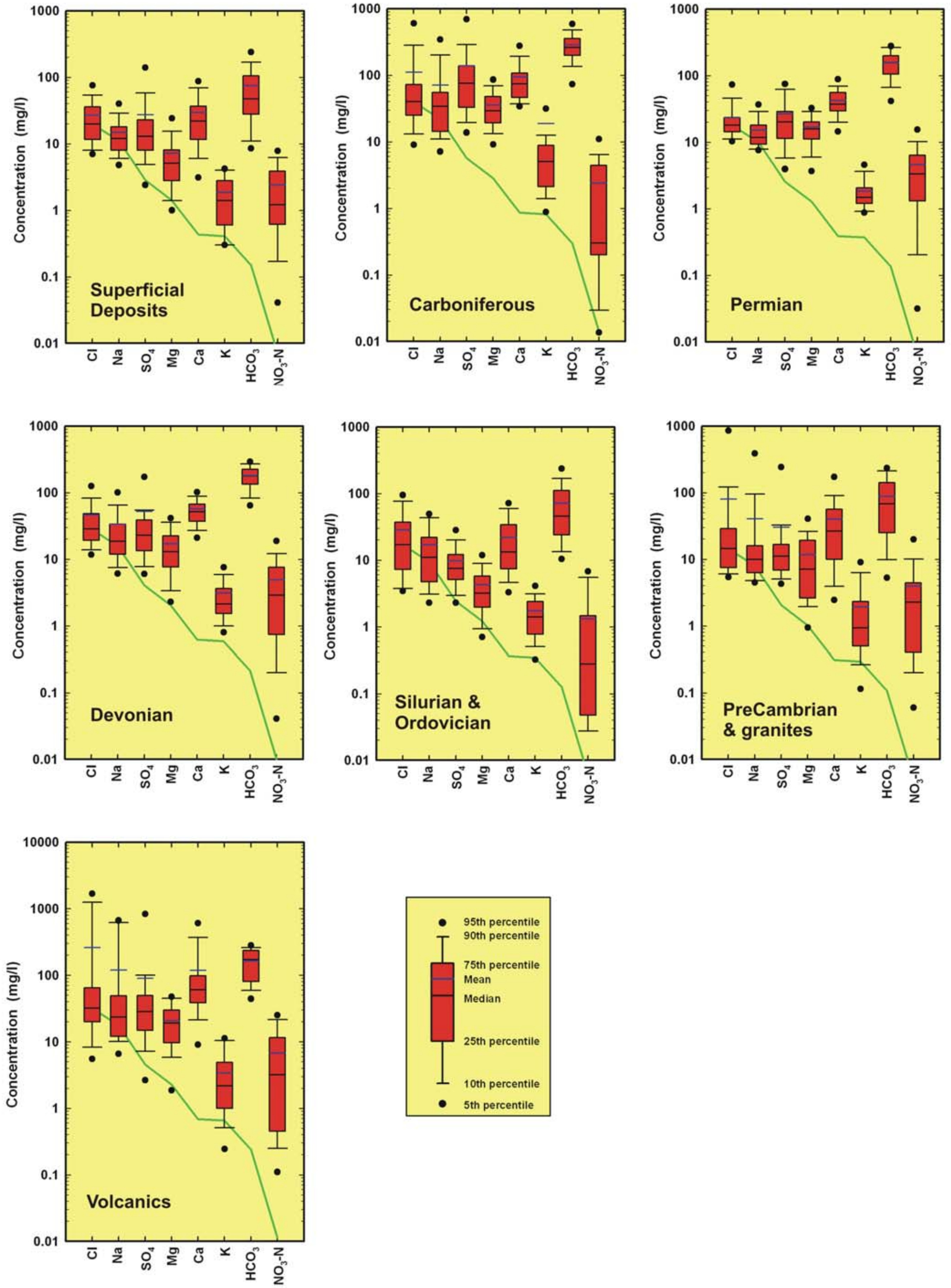


Figure 8 Box plots showing groundwater chemistry data for different hydrogeological environments in Scotland.

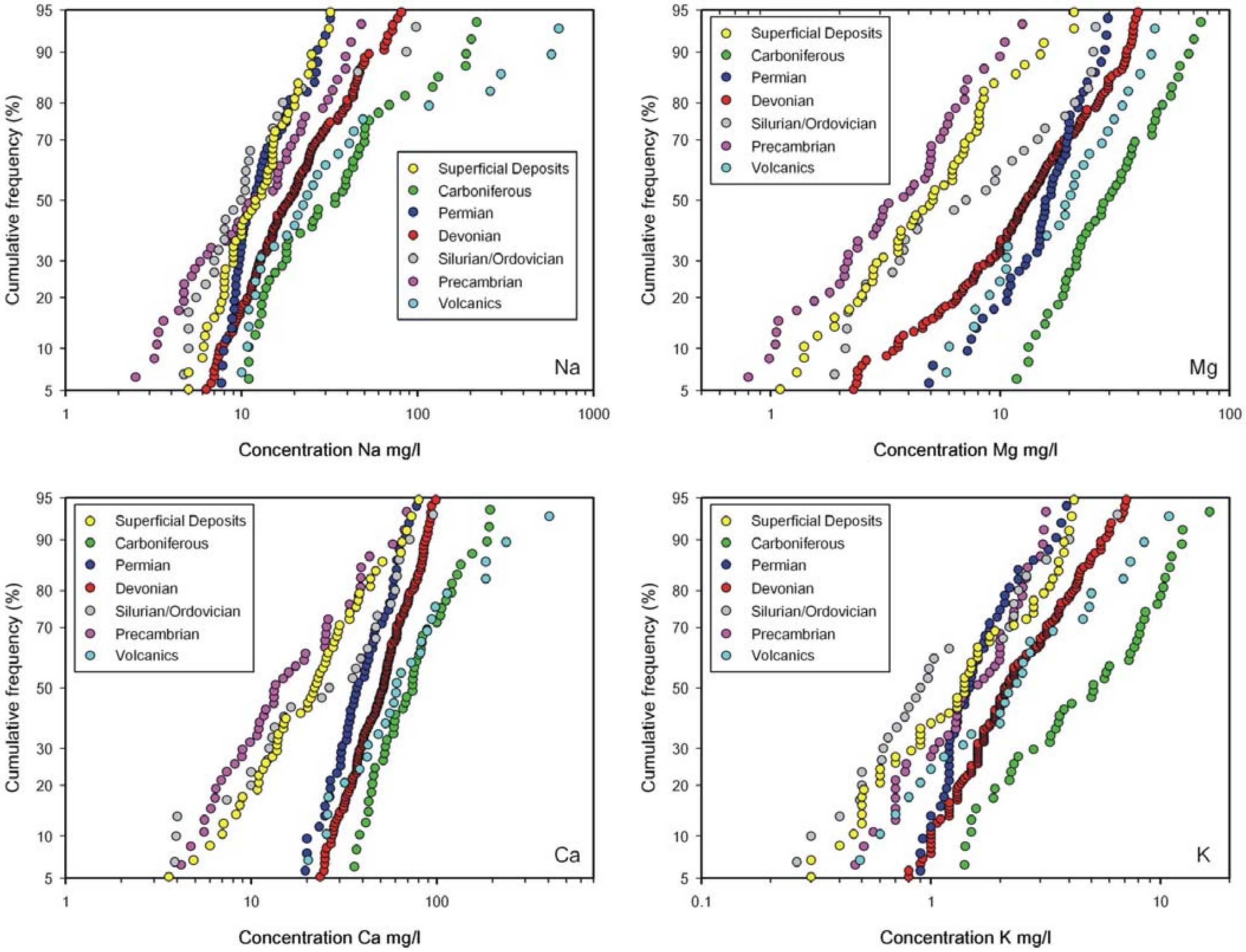


Figure 9 Cumulative frequency plots of major cations for Scotland.

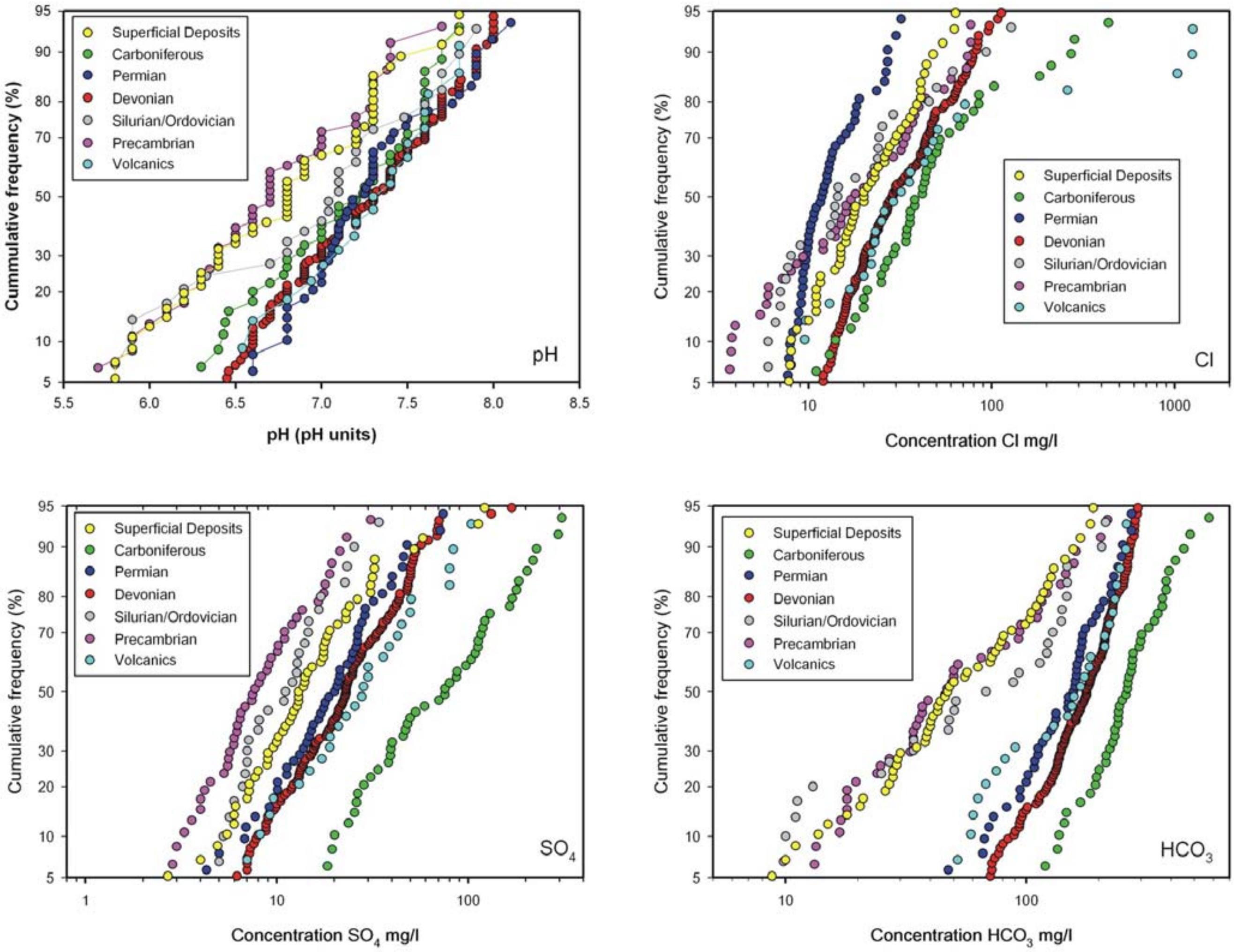
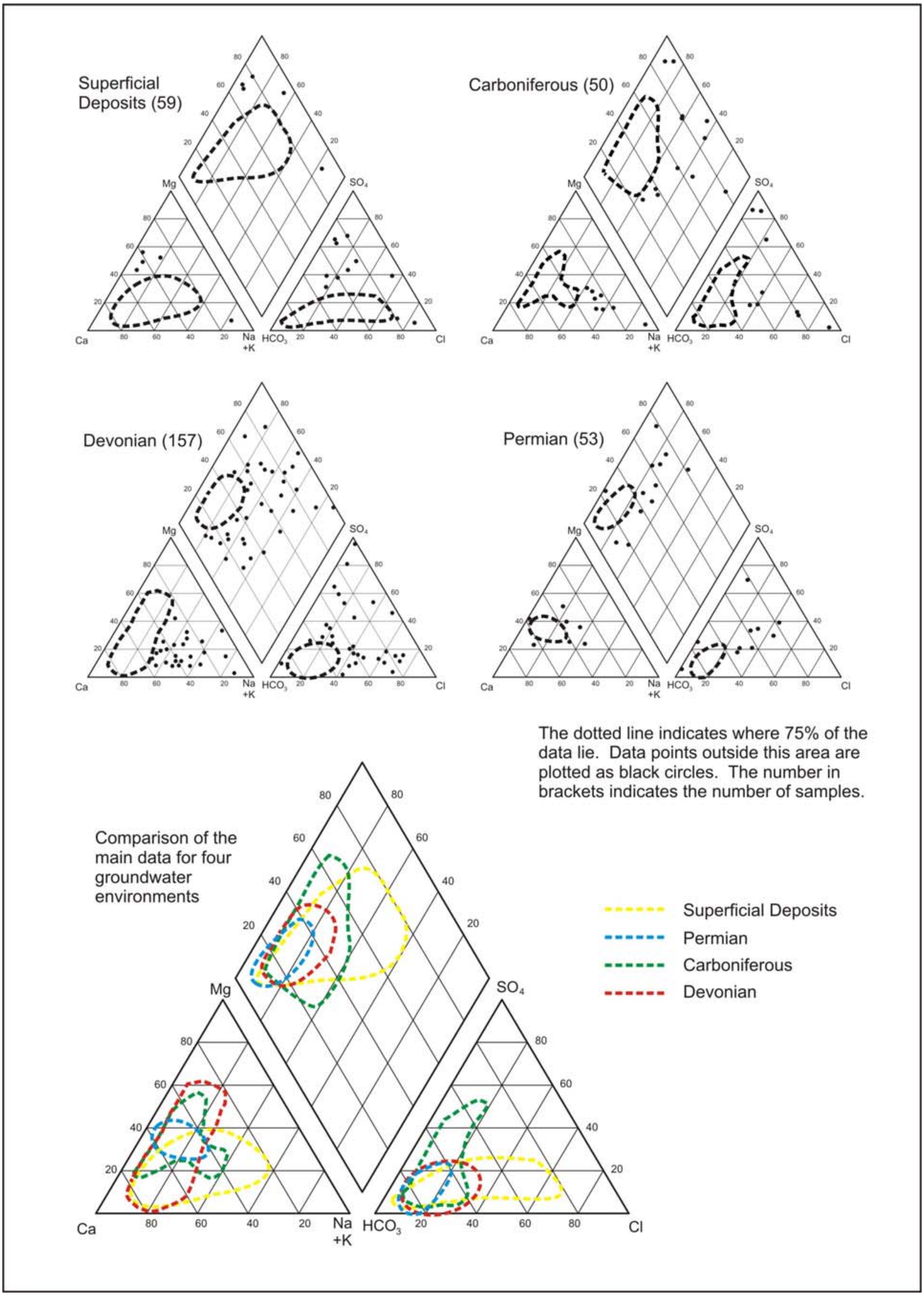


Figure 10 Cumulative frequency plots of major anions for Scotland.


Superficial Deposits (59)

Carboniferous (50)

Devonian (157)

Permian (53)

The dotted line indicates where 75% of the data lie. Data points outside this area are plotted as black circles. The number in brackets indicates the number of samples.

Comparison of the main data for four groundwater environments

Figure 11 Piper diagram for groundwater samples from the superficial deposits, Permian, Carboniferous and Devonian aquifers.

5 Trace element chemistry

Trace element concentrations in groundwater are controlled by a complex range of factors, including the detailed mineralogy of the aquifer rock, and the geochemical environment, particularly the pH and redox status. Anthropogenic influences may also strongly modify the concentrations and distribution of a range of trace ions.

There are few reliable trace element data available for Scottish groundwaters. Chapter 3 discusses the sources and limitations of the available data. There are insufficient good-quality data to give detailed statistics of the occurrence of trace elements. That will only be possible with the systematic collection and analysis of new samples.

In this overview, we focus on the available data for a selection of trace elements: aluminium (Al), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), fluoride (F), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), uranium (U) and zinc (Zn). For each element a map is given of the available data, along with the EC maximum permissible value (EC 1998), or if for a given element no such value exists, the WHO guideline value (WHO 2004). Each map also shows the distribution of the bedrock aquifer types as described in Section 3; the maps do not show superficial deposits.

Elevated concentrations of aluminium can occur in most aquifers in Scotland if the local groundwater conditions are favourable (i.e. acidic pH, or highly alkali pH). Most of the groundwater samples which exceed the EC maximum permissible value (Figure 12) occur in the Precambrian gneiss of Lewis, the volcanic aquifers of Skye and the granites of southwest Scotland. These areas are likely to be peat-covered and comprise shallow groundwater flowpaths in a peaty, acidic environment. Available data indicate that pH is generally acidic in these areas.

The available dataset for arsenic concentration in Scotland is limited, with useful data available for only a few locations, largely in Permian and Devonian aquifers (Figure 12). For many of these, arsenic is below the analytical detection limit, and so detailed analysis of the data is not possible. At least two of the samples, in the Devonian aquifer of Morayshire and the Permian aquifer of the Dumfries basin, contained arsenic concentrations that exceed the EC maximum permissible value of 10 μg/l.

Barium concentrations in groundwater are typically below WHO guideline value of 700 μg/l across Scotland. There is only one exceedance in Scotland, in the Devonian sandstone aquifer of Fife. The data indicate higher concentrations in groundwater from the Devonian, Permian and Carboniferous sandstone aquifers than for other aquifers. Elevated concentrations might also be expected (although there are no data to substantiate) associated with barite mineralisation in igneous and metamorphic rocks.

The available data for cadmium highlight that naturally high cadmium concentrations in groundwater are rare (Figure 12). Cadmium concentrations are elevated relative to the rest of Scotland for several groundwater samples in Carboniferous rocks in East Lothian and Fife and the metamorphic rocks of the highlands. One sample in Strathmore exceeds the EC maximum permissible value of 5 μg/l – the source of the cadmium is unclear.

The available data indicate that natural chromium concentrations in Scottish groundwater are typically low (< 2 μg/l), particularly in the Devonian, Permo-Triassic and Carboniferous aquifers from which most of the data are derived (Figure 13). There are no data from the Glasgow area, where elevated chromium concentrations may be expected due to widespread contamination from chromate waste (Fordyce et al. 2004).

Fluoride concentrations in Scottish groundwater are typically less than 500 µg/l. Lowest concentrations are observed in the two most productive Scottish aquifers – the Dumfries Permian sandstone aquifer and the Fife Devonian sandstone aquifers. Concentrations greater than 500 µg/l have been measured in samples from the Permo-Triassic sandstone in Morayshire and the Permo-Triassic sandstone in Mauchline, southwest Scotland. The elevated concentrations in Morayshire have been attributed to the presence of the mineral fluorite (Edmunds et al. 1999). There are several isolated samples scattered throughout Scotland with fluoride concentrations greater than the EC maximum permissible value of 1500 µg/l.

There are more data for iron than for most other trace elements (Figure 13). Iron concentrations greater than the EC maximum permissible value, 200 µg/l, are observed in all hydrogeological units in Scotland. Iron is ubiquitous in rocks and the dominant control on its presence in groundwater is the redox status and pH.

There is a similar amount of data for manganese as for iron (Figure 13), and the distribution of high manganese concentrations broadly follows the same pattern as iron, reflecting their similar geochemical controls. Therefore manganese concentrations above the EC maximum permissible value can be found in all groundwater units in Scotland.

Nickel concentrations in Scottish groundwater are naturally low and most samples have concentrations below 2 µg/l. Four samples exceed the EC maximum permissible value of 20 µg/l in Scotland (Figure 14) including one groundwater sample from the Precambrian gneiss on Harris, one from the Carboniferous aquifer, one from the Devonian aquifer, and one from the Permian aquifer in the Dumfries basin (although this latter is likely to be related to industrial contamination).

The detection limits are high for many of the available data for lead, which means that the resolution is poor and the only divisions are above or below the EC maximum permissible value of 10 µg/l. Lead concentrations in groundwater are typically low across Scotland; only 3% exceed 10 µg/l (Figure 14). There is a scattering of samples with concentrations above 10 µg/l – the cluster of 3 samples in the Devonian aquifers in Strathmore have concentrations above the EU maximum permissible value warrants further investigation.

Prior to the start of *Baseline Scotland* in the summer of 2004, there were very few measurements of uranium in groundwater in Scotland, all of which were from the Permian aquifer of the Dumfries basin. The data are all below the current WHO (2004) guideline value of 15 µg/l (Figure 14).

Groundwater chemistry data for zinc are relatively abundant compared to other minor ions (Figure 14), and show that concentrations in groundwater in Scotland are low compared to the WHO guideline value of 3000 µg/l (this guideline value is based on acceptability criteria, rather than health concerns). The only sample to show a zinc concentration above 1000 µg/l was from a spring emanating from the Devonian aquifer in Strathmore.

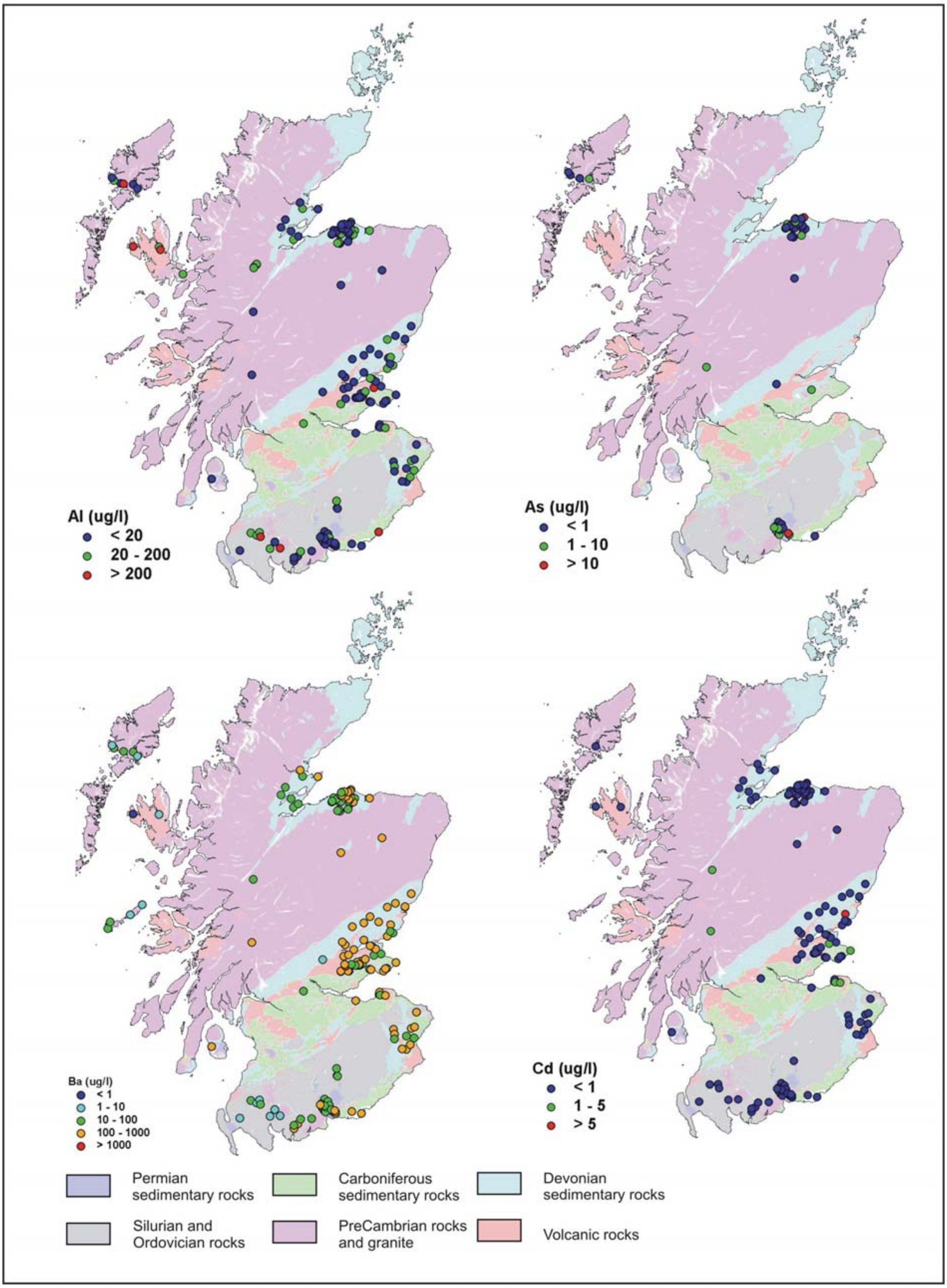


Figure 12 Available groundwater chemistry data in Scotland for aluminium, arsenic, barium and cadmium.

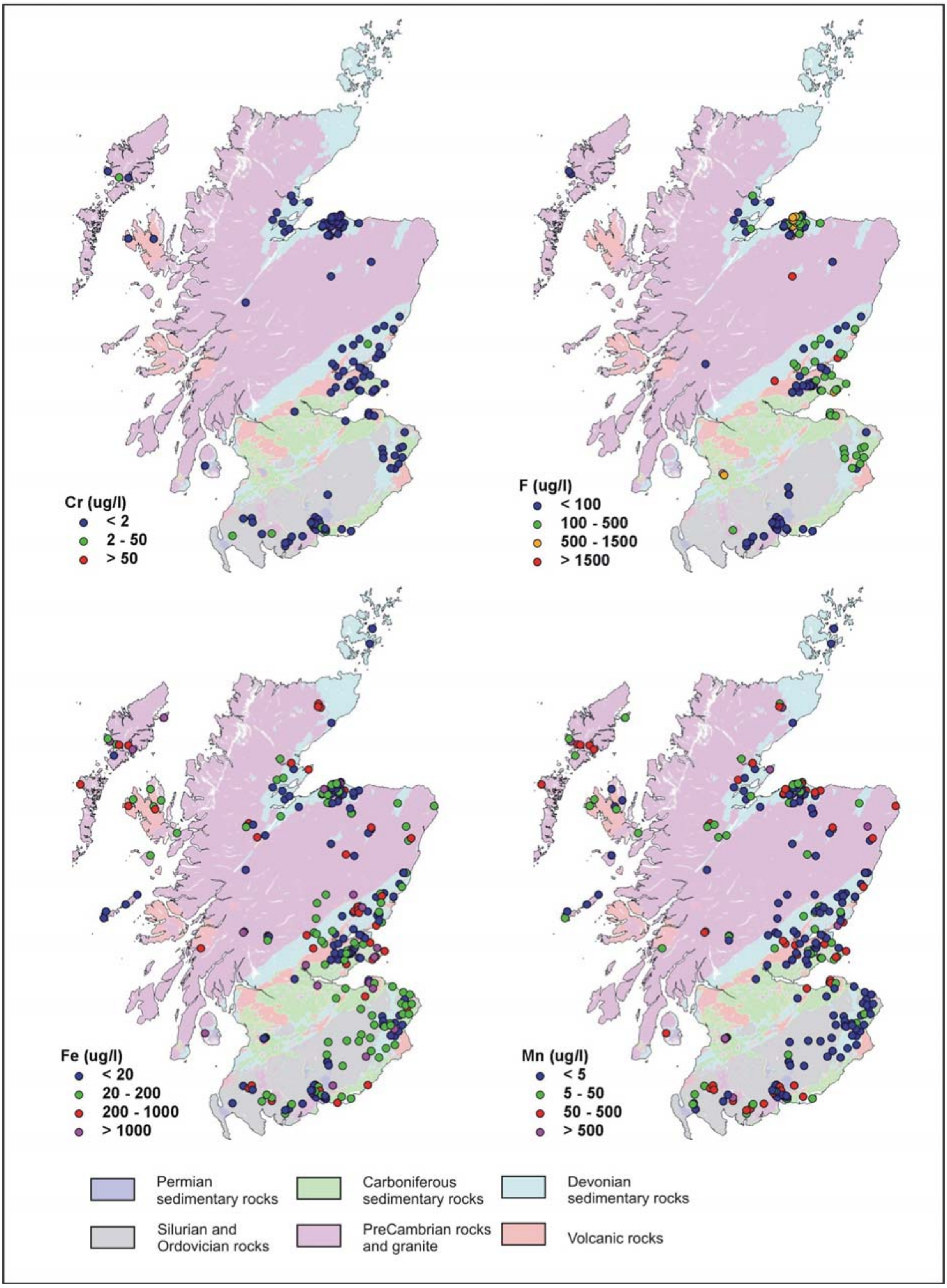


Figure 13 Available groundwater chemistry data in Scotland for chromium, fluoride, iron and manganese.

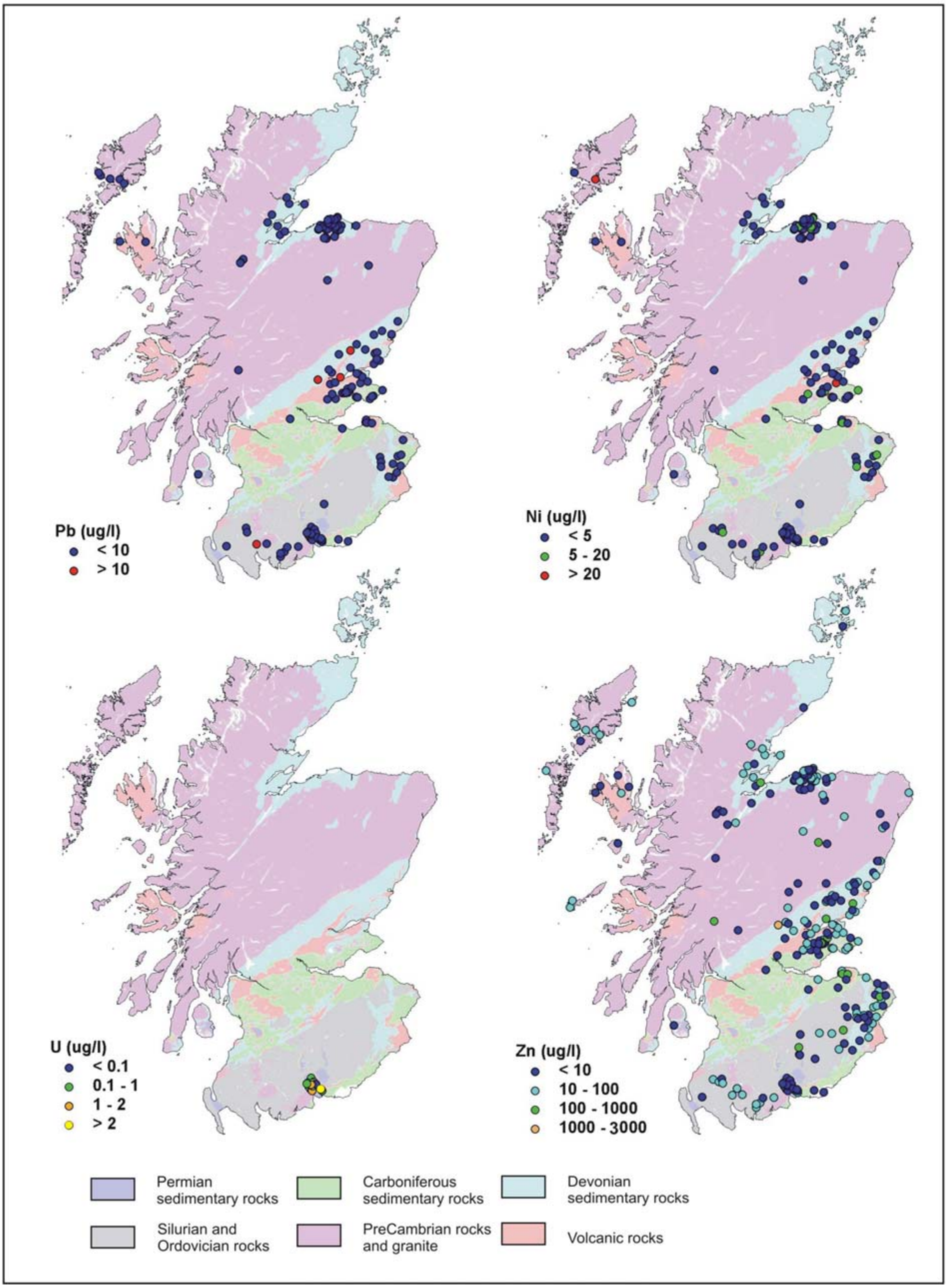


Figure 14 Available groundwater chemistry data in Scotland for the trace elements lead, nickel, uranium and zinc.

6 Summary and recommendations

6.1 AVAILABLE DATA

Chemistry data from Scottish groundwater samples collected prior to the start of the *Baseline Scotland* project in June 2004 have been collated and described. Many of the data came from previous BGS studies, but data were also available from Scottish Water, councils and SEPA. In total, more than 800 groundwater chemistry analyses were identified.

The data are of variable quality and were subject to a thorough quality assurance assessment. This involved gathering additional information on sources, checking the units for consistency and removing data from highly contaminated sites. For major ions the ionic balance was calculated and data with an ionic balance of less than 10% removed. Creating a usable dataset for trace elements was challenging. For many elements concentrations were below the detection limit of the analysis method, and for each element there were many different detection limits. Poor quality data were removed, and the remaining data divided into logical divisions based on concentration categories to help make the interpretation more robust.

After this process the final dataset was as follows:

- 428 sites with full major ion chemistry having charge imbalances of less than 10%;
- of these 428 sites, 423 had a measurement of pH, but only 31 sites with a wellhead measurement of dissolved oxygen, and 103 with a wellhead measurement of the redox potential;
- information on trace elements was highly variable, with only 22 measurements of uranium, but several hundred for iron, manganese and zinc.

The dataset is highly skewed, with most good-quality data being available for the Devonian aquifer in Fife and parts of Morayshire, and the Permian aquifer in Dumfries. There are few data available for the Precambrian rocks or the Silurian/Ordovician rocks.

6.2 SCOTTISH GROUNDWATER

The available major ion data were used to characterise Scottish groundwater. Summary statistics have been calculated and the data presented on box plots, cumulative-frequency plots and piper diagrams. The data illustrate the variability of Scottish groundwater, reflecting the diverse geology and local environmental conditions.

- The most highly mineralised groundwater is found within Carboniferous rocks. There is a marked bimodal distribution for chloride and sodium which may indicate mixing with seawater in coastal areas, and older highly mineralised waters. Sulphate concentrations are considerably higher than for other aquifers which reflects the mineralogy and legacy of coal mining.
- Groundwaters from the Permian sedimentary aquifers in Scotland have well-defined chemistry and the least variation in concentrations of major ions of all Scottish groundwaters. Groundwater is of Ca-Mg-HCO_3 type with a narrow range in Mg/Ca ratio, and near neutral pH.
- Most data were available for the Devonian aquifers in Scotland. Groundwater tends to be of Ca-HCO_3 to Ca-Mg-HCO_3 type and shows a wider range in Mg/Ca ratio than for the Permian rocks; median pH is 7.5.

- The available data for the superficial deposits, Precambrian rocks and Silurian/Ordovician rocks indicate similar variability of major ion chemistry across the three hydrogeological environments. This may reflect the short residence time of much of the water, and the high proportion of samples from springs and shallow wells. The waters have typically low mineralization and pH less than 7.
- Groundwaters in volcanic aquifers are generally of Ca-HCO_3 type, and similar to the sandstone aquifers, with the exception of potassium which varies considerably across the volcanic aquifers. A small proportion of samples contained elevated chloride, sodium, sulphate and calcium concentrations.
- Most of the small island sources have high chloride concentrations, probably as a result of marine-influenced increased chloride concentrations in recharge. Other notable elevated chloride concentrations are observed in the coastal areas of East Lothian, Arbroath, Morayshire and northwest Fife. The majority of inland sources have chloride concentrations less than 25 mg/l, and in upland areas concentrations are less than 10 mg/l.
- Nitrate data indicate a clear pattern across Scotland: elevated concentrations largely coincide with the agricultural areas of Scotland. Concentrations in excess of 25 mg/l as NO_3 are measured in samples from the agricultural areas of the east and southwest. There are fewer data for groundwaters in non-agricultural areas, but th available data indicate concentrations less than 10 mg/l as NO_3.

There are insufficient reliable data to identify clear trends in the concentration of trace elements in Scottish groundwater. However, the following have been highlighted from the existing data.

- Iron and manganese concentrations greater than the EC maximum permissible values, are observed in all hydrogeological units in Scotland. Iron and manganese are ubiquitous in rocks and the dominant controls on its presence in groundwater are the redox status and pH.
- The limited data on aluminium indicate concentrations approaching or exceeding the EC maximum permissible value in Precambrian and volcanic rocks and granite.
- With the existing dataset there are insufficient data to make comments on the distribution of uranium or arsenic in Scottish groundwater.
- The available data indicate that natural chromium concentrations in Scottish groundwater are typically less than 2 µg/l. There are no data from the Glasgow area, where elevated chromium concentrations may be expected due to widespread contamination from chromate waste.
- Fluoride concentrations greater than 0.5 mg/l have been measured in samples from the Permo-Triassic sandstone in Morayshire and the Permo-Triassic sandstone in Mauchline, southwest Scotland. There are several isolated samples scattered throughout Scotland with fluoride concentrations greater than the EC maximum permissible value of1.5 mg/l.

6.3 RECOMMENDATIONS

The existing groundwater chemistry data for Scotland form a diverse dataset, both in the quality of the data and completeness of the analysis. This makes interpretation difficult. New data are required that are collected in a consistent, reliable and systematic manner, and analysed to a consistent degree of accuracy.

There is not widespread coverage of groundwater-chemistry data in Scotland. Certain hydrogeological units have few reliable data and should be targeted for further sampling.

Wellhead measurements of redox potential and dissolved oxygen should be routinely taken in order to determine geochemical processes and explain the reasons for elevated concentrations of both major and trace elements.

There is evidence that the chemistry measured from different types of source (i.e. well, borehole or spring) can vary within the same hydrogeological units. It is essential that comprehensive data are collected on each sampled source.

Routine sampling for age dating of samples would be helpful for understanding residence times of groundwater and interpreting groundwater chemistry, particularly nitrate data.

There are insufficient data on many trace elements in Scotland to characterise their occurrence or understand their origin. Comprehensive analysis of groundwater chemistry, including trace elements, should be carried out wherever possible.

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