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# Baseline groundwater chemistry in Scotland's aquifers

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BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME

OPEN REPORT OR/17/030

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Spray irrigation in Fife using  
groundwater abstracted from the  
Old Red Sandstone South aquifer.  
The Igneous Intrusive Lomond  
Hills form the high ground in the  
distance.

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# Baseline groundwater chemistry in Scotland's aquifers

A M MacDonald, B É Ó Dochartaigh and P L Smedley

Keyworth, Nottingham British Geological Survey 2017

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# Foreword

Scotland's groundwater is a highly valuable resource. The volume of groundwater is greater than the water found in our rivers and lochs, but is hidden from sight beneath our feet. Groundwater underpins Scotland's private drinking water supplies and provides reliable strategic public water supply to many rural towns; it also sustains the bottled water and whisky industries and is relied upon for irrigation by many farmers (DWQR, 2013; Ó Dochartaigh, 2015). Groundwater provides many important environmental functions, providing at least 30% of the flow in most Scottish rivers, and maintaining many precious ecosystems.

In its natural state, groundwater is generally of excellent quality. However, the natural quality of groundwater in aquifers is continually being modified by human influence, through direct and indirect anthropogenic inputs and groundwater abstraction. A thorough knowledge of the quantity and quality of groundwater in our aquifers, and of the processes affecting groundwater, is therefore essential for the effective management of this valuable resource.

Baseline Scotland project has improved the availability of information on, and general understanding of, the chemistry of Scotland's groundwater. The primary aim of the project was to provide core hydrogeological data and interpretation to help in the implementation of the Water Framework Directive. An overview of groundwater chemistry data for Scotland during the inception phase of the project (MacDonald and

Ó Dochartaigh, 2005) highlighted the paucity of reliable data on the natural substances that occur in groundwater. Good quality data that do exist are available for only small areas—but the Water Framework Directive requires an understanding of background levels across a much broader area.

The aims of Baseline Scotland were:

1. To characterise the ranges in natural background groundwater quality in the main aquifers 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.

The data collection phase of Baseline Scotland ran from 2005 to 2011, during which time systematic surveys were undertaken across the different aquifers of Scotland, and several regional-specific reports produced. The work was funded by BGS with specific contributions from SEPA. With the new information generated by the project, Scotland is in a much better position to sustainably develop and manage its groundwater resources.

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# Contents

Foreword	iii	5.12 Halogens	37
Acknowledgements	iv	5.13 Rare earth elements	38
Contents	v	5.14 Uranium	40
Summary	viii	5.15 Summary	41
1 Introduction	1	6 Baseline chemistry of bedrock aquifers in Scotland	43
1.1 Baseline Scotland	1	Appendix 1 Cumulative probability distributions for selected chemical parameters in Scotland's bedrock aquifers	45
1.2 Natural groundwater quality	1	Appendix 2 Statistical summary of baseline groundwater chemistry in Scotland's bedrock aquifers	51
1.3 Groundwater in Scotland	1	Appendix 3 List of previous reports from the Baseline Scotland project	75
1.4 A guide to the report	2	References	76
2 Factors affecting groundwater quality	3	<b>FIGURES</b>	
2.1 Rainwater chemistry	3	Map showing the distribution of pH in groundwaters in Scotland's bedrock aquifers.	ix
2.2 Mineral dissolution and precipitation	3	Groundwater forms an important component of the water cycle.	2
2.3 Redox reactions	4	1 Average concentrations of the most abundant ions in rainfall measured at five sites in Scotland.	3
2.4 Ion exchange and sorption	5	2 The sequence of redox reactions developing as groundwaters move from oxic to reducing conditions.	5
2.5 Natural groundwater quality	6	3 Eh-pH diagram showing stability fields for Mn and data for Scotland.	5
2.6 Geology	7	4 Piper (tri-linear) diagram illustrating how groundwater major ion chemistry can be characterised by where it plots.	6
2.7 Land use	9	5 Periodic table highlighting essential and nonessential elements found in water.	7
3 Bedrock aquifers	10	6 Bedrock geology and (inset) Quaternary (superficial) geology of Scotland at 1:625 000 scale.	8
3.1 Permo-Triassic	11	7 Bedrock aquifer groups used in the Baseline Scotland project.	10
3.2 Carboniferous sedimentary	12	8 Location of Baseline Scotland groundwater samples.	18
3.3 Old Red Sandstone (Devonian) – North and South	13	9 Example of an annotated box plot based on a simulated normal distribution of 2000 values with mean = 100 and standard deviation = 10.	20
3.4 Silurian-Ordovician	13	10 Statistical summary of groundwater temperature in Scotland's bedrock aquifers.	23
3.5 Calcareous	13	11 Statistical summary of groundwater pH in Scotland's bedrock aquifers.	23
3.6 Precambrian North and South	13	12 Statistical summary of groundwater redox potential (Eh) in Scotland's bedrock aquifers.	23
3.7 Igneous Volcanic	15		
3.8 Intrusive Igneous	15		
4 Methodology	18		
4.1 Data collation	18		
4.2 Sample sites and sources	18		
4.3 Sampling and analysis	20		
4.4 Data interpretation and presentation	20		
4.4.1 Summary statistics	20		
4.4.2 Box plots	22		
4.4.3 Maps	22		
4.4.4 Cumulative probability plots	22		
5 Groundwater chemistry	23		
5.1 Physico-chemical characteristics	23		
5.2 Major ions	24		
5.3 Nitrogen species	29		
5.4 Dissolved organic carbon	30		
5.5 Phosphorus	31		
5.6 Silicon and aluminium	31		
5.7 Trace alkali metals	32		
5.8 Alkaline earth elements	34		
5.9 Transition metals	34		
5.10 Metalloids	36		
5.11 Lead	37		

13	Statistical summary of dissolved oxygen (DO) concentrations in groundwater in Scotland's bedrock aquifers.	24	35	Statistical summary of concentrations of Al in groundwater in Scotland's bedrock aquifers.	33
14	Statistical summary of groundwater SEC in Scotland's bedrock aquifers.	24	36	Statistical summary of concentrations of Cs in groundwater in Scotland's bedrock aquifers.	33
15	Map showing the distribution of groundwater SEC in Scotland's bedrock aquifers.	25	37	Statistical summary of concentrations of Li in groundwater in Scotland's bedrock aquifers.	34
16	Piper (tri-linear) diagram illustrating the distribution of major ion compositions of groundwater for each aquifer.	26	38	Statistical summary of concentrations of Rb in groundwater in Scotland's bedrock aquifers.	34
17	Map showing the distribution of groundwater HCO <sub>3</sub> in Scotland's bedrock aquifers.	27	39	Statistical summary of concentrations of Ba in groundwater in Scotland's bedrock aquifers.	34
18	Statistical summary of Ca concentrations in groundwater in Scotland's bedrock aquifers.	28	40	Statistical summary of concentrations of Sr in groundwater in Scotland's bedrock aquifers.	34
19	Statistical summary of Mg concentrations in groundwater in Scotland's bedrock aquifers.	28	41	Statistical summary of concentrations of Fe in groundwater in Scotland's bedrock aquifers.	35
20	Statistical summary of groundwater Na concentrations in Scotland's bedrock aquifers.	28	42	Statistical summary of concentrations of Mn in groundwater in Scotland's bedrock aquifers.	35
21	Statistical summary of K concentrations in groundwater in Scotland's bedrock aquifers.	28	43	Statistical summary of concentrations of Ni in groundwater in Scotland's bedrock aquifers.	35
22	Statistical summary of Cl concentrations in groundwater in Scotland's bedrock aquifers.	29	44	Statistical summary of concentrations of Cr in groundwater in Scotland's bedrock aquifers.	36
23	Statistical summary of SO <sub>4</sub> concentrations in groundwater in Scotland's bedrock aquifers.	29	45	Statistical summary of concentrations of Mo in groundwater in Scotland's bedrock aquifers.	36
24	Statistical summary of HCO <sub>3</sub> concentrations in groundwater in Scotland's bedrock aquifers.	29	46	Statistical summary of concentrations of V in groundwater in Scotland's bedrock aquifers.	36
25	Statistical summary of NO <sub>3</sub> -N concentrations in groundwater in Scotland's bedrock aquifers.	29	47	Statistical summary of concentrations of As in groundwater in Scotland's bedrock aquifers.	36
26	Map showing the distribution of NO <sub>3</sub> -N concentrations in groundwater in Scotland's bedrock aquifers.	30	48	Statistical summary of concentrations of B in groundwater in Scotland's bedrock aquifers.	37
27	Statistical summary of groundwater NO <sub>3</sub> -N concentrations by land use in Scotland.	30	49	Statistical summary of concentrations of Sb in groundwater in Scotland's bedrock aquifers.	37
28	Statistical summary of NH <sub>4</sub> -N concentrations in groundwater by land use in Scotland.	31	50	Statistical summary of concentrations of Br in groundwater in Scotland's bedrock aquifers.	37
29	Map showing the distribution of NH <sub>4</sub> -N concentrations in groundwater in Scotland's bedrock aquifers.	31	51	Statistical summary of concentrations of I in groundwater in Scotland's bedrock aquifers.	38
30	Statistical summary of dissolved organic carbon (DOC) concentrations in groundwater by land use in Scotland.	31	52	Map showing the distribution of F concentrations in groundwater in Scotland's bedrock aquifers.	38
31	Statistical summary of P concentrations in groundwater in Scotland's bedrock aquifers.	32	53	Statistical summary of concentrations of La in groundwater in Scotland's bedrock aquifers.	39
32	Map showing the distribution of P concentrations in groundwater in Scotland's bedrock aquifers.	32	54	Map showing the distribution of La concentrations in groundwater in Scotland's bedrock aquifers.	39
33	Map showing the distribution of Si concentrations in groundwater in Scotland's bedrock aquifers.	33	55	Statistical summary of concentrations of Lu in groundwater in Scotland's bedrock aquifers.	39
34	Statistical summary of concentrations of Si in groundwater in Scotland's bedrock aquifers.	33	56	Shale-normalised REE profiles for groundwaters from Scotland's bedrock aquifers.	40
			57	Map showing the distribution of U concentrations in groundwater in Scotland's bedrock aquifers.	41

58	Cumulative probability distribution of concentrations of the major ions Ca, Mg, Na, K, Cl, SO <sub>4</sub> , HCO <sub>3</sub> and NO <sub>3</sub> -N in groundwater in Scotland's bedrock aquifers.	45	2	Summary of aquifer group characteristics.	16
59	Cumulative probability plots of concentrations of Al, As, B, Ba, Br, Cd, Cr and Cs in groundwater in Scotland's bedrock aquifers.	47	3	Summary of groundwater samples by aquifer group, land use and source type.	21
60	Cumulative probability plots of concentrations of Cu, F, Fe, I, La, Li, Mo and Mn in groundwater in Scotland's bedrock aquifers.	48	4	Summary statistics for elements in all groundwaters sampled for the Baseline Scotland project.	51
61	Cumulative probability plots of Ni, P, Pb, Rb, Sb, Se, Si and Sn concentrations in groundwater in Scotland's bedrock aquifers.	49	5	Summary statistics for elements in groundwaters from Permo-Triassic aquifers in Scotland.	53
62	Cumulative probability plots of Sr, Tb, Tm, U, V, Y, Yb and Zn concentrations in groundwater in Scotland's bedrock aquifers.	50	6	Summary statistics for elements in groundwaters from Carboniferous (not extensively mined) aquifers in Scotland.	55

## PLATES

1	Aeolian dune bedding in Permo-Triassic sandstone exposed in a quarry in Ayrshire, southwest Scotland.	11	7	Summary statistics for elements in groundwaters from Carboniferous Mined aquifers in Scotland.	57
2	Stoop and room (pillar and stall) mining in the Carboniferous Lower Limestone Group in Midlothian.	12	8	Summary statistics for elements in groundwaters from Old Red Sandstone North aquifers in Scotland.	59
3	Gently dipping flagstones of the Middle Old Red Sandstone at Yesnaby, Orkney.	14	9	Summary statistics for elements in groundwaters from Old Red Sandstone South aquifers in Scotland.	61
4	Folded and deformed Silurian greywackes in Wigtownshire, southwest Scotland.	14	10	Summary statistics for elements in groundwaters from Ordovician and Silurian aquifers in Scotland.	63
5	Collecting groundwater samples for the Baseline Scotland project.	19	11	Summary statistics for elements in groundwaters from Calcareous aquifers in Scotland.	65
			12	Summary statistics for elements in groundwaters from Precambrian North aquifers in Scotland.	67
			13	Summary statistics for elements in groundwaters from Precambrian South aquifers in Scotland.	69
			14	Summary statistics for elements in groundwaters from Igneous Intrusive aquifers in Scotland.	71
			15	Summary statistics for elements in groundwaters from Igneous Volcanic aquifers in Scotland.	73

## TABLES

1	Rainfall chemistry at selected monitoring stations, and expected concentration in infiltrating recharge.	4
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# Summary

This report is an output from the Baseline Scotland project, which ran from 2005 to 2014. It provides a summary of data on the chemistry of groundwater from the eleven main bedrock aquifer groups in Scotland.

Groundwater is an important natural resource for Scotland. It provides drinking water, supports agriculture, and is fundamental to the nation's mineral water and whisky industries. Groundwater also plays a vital role in sustaining the flow of rivers and supporting many of Scotland's fragile ecosystems. The naturally high quality of groundwater in Scotland is an important part of why it provides so many benefits. However, groundwater is not invulnerable, and it needs to be protected and managed to preserve it.

This report presents a synthesis of the results of the Baseline Scotland project, which mapped the natural chemistry of groundwater in Scotland's aquifers. The project ran from 2005 to 2014, funded mainly by the British Geological Survey with additional support from the Scottish Environment Protection Agency, and included ten regional surveys that covered much of Scotland. In this overview, the results of the surveys are combined to produce a summary of the baseline chemistry of groundwater in the eleven main bedrock aquifer groups of Scotland.

These aquifer groups represent a range of hydrogeological environments with differing geological controls on both physical aquifer properties and natural groundwater chemistry. They were primarily divided according to rock type: sedimentary (indurated sedimentary or calcareous), metamorphic or igneous; and secondarily according to geological age. The aquifers are: Permo-Triassic; Carboniferous sedimentary rocks (not extensively mined for coal); Carboniferous sedimentary rocks (extensively mined for coal); Old Red Sandstone North; Old Red Sandstone South; Silurian-Ordovician; Precambrian North, Precambrian South; Igneous Volcanics; Igneous Intrusive rocks; and Highland Calcareous rocks.

The chemistry of groundwater in Scotland's bedrock aquifers is highly variable, reflecting a combination of lithology, mineral reactions, redox conditions, groundwater flow paths and residence times. Major ion water types include Ca-HCO<sub>3</sub>, Na-HCO<sub>3</sub>, Na-SO<sub>4</sub> and Na-Cl, with no single type dominating across Scotland. Total dissolved solid (TDS) concentrations in groundwater are typically between 54 and 520 mg/L (10–90th percentile; median 150 mg/L). Some of the highest values of TDS (up to 5000 mg/L) are seen in Carboniferous sedimentary aquifers in central Scotland, particularly where mining has

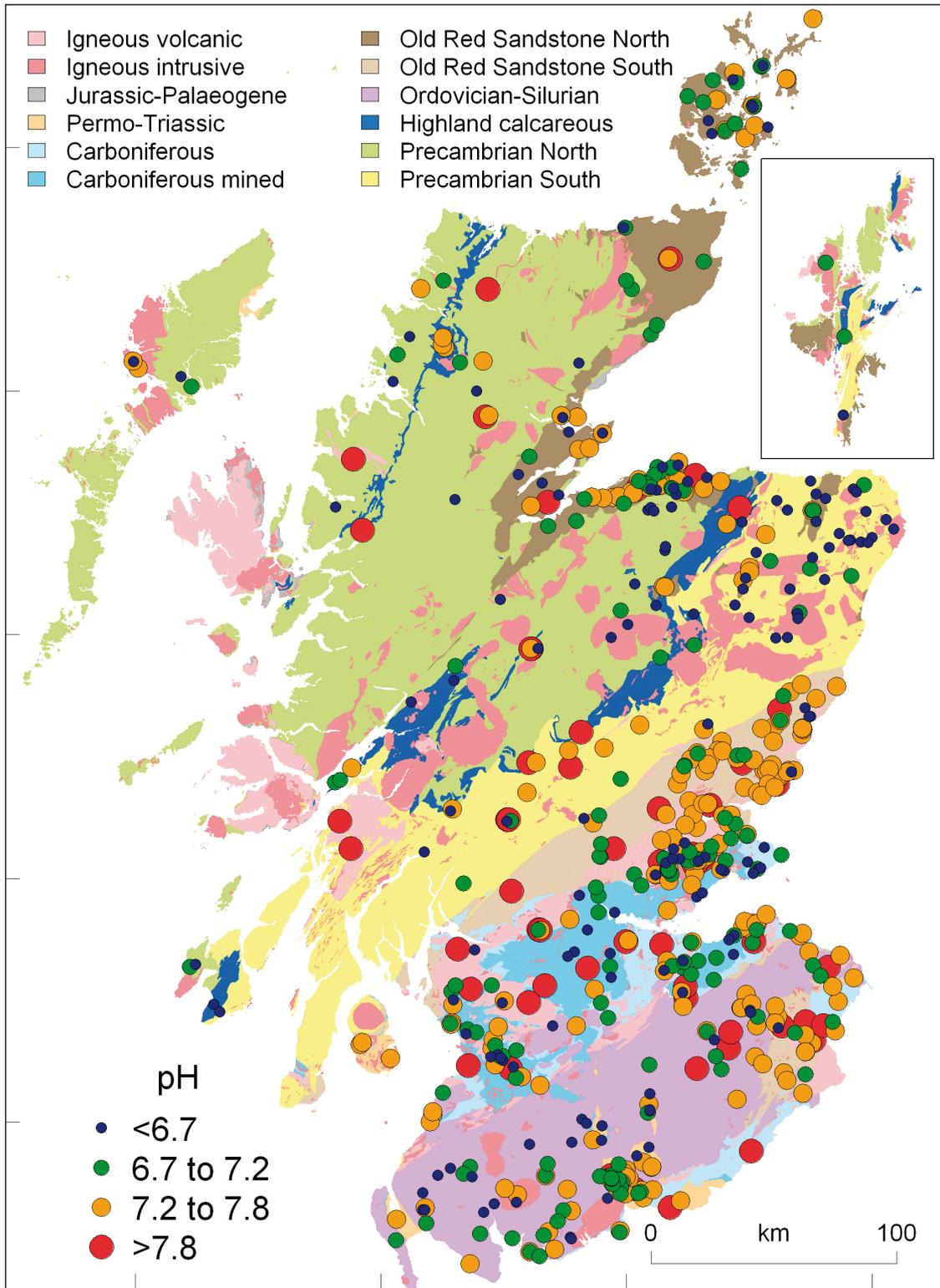
occurred. Elevated TDS also affects some groundwaters in coastal areas. Mineralised springs (e.g. Na-Cl, Na-SO<sub>4</sub> types) occur rarely.

Median pH values for each of the aquifers are near neutral, in the range 6.5 to 7.5 (overall median 7.2). However, acidic groundwater (pH<6) occurs in most of the aquifers, reflecting an absence of carbonate minerals and/or oxidation of pyrite and other metal sulphides. More strongly acidic conditions can give rise to the presence of dissolved Al, Fe, Mn and REE in some groundwaters. Oxic groundwater conditions dominate in most aquifers in Scotland, consistent with dominantly shallow groundwater flowlines in fractured bedrock. Local exceptions occur with mildly reducing zones in several aquifers, but the only regionally extensive reducing conditions are in the Old Red Sandstone North aquifer, particularly in Moray. Within the Carboniferous sedimentary aquifers, and in localised mineralised springs in the Ordovician–Silurian aquifer, conditions can be more strongly reducing, causing SO<sub>4</sub> and NH<sub>4</sub> reduction and even methanogenesis at some locations.

The main impact of land use on groundwater chemistry is the common occurrence of high concentrations of NO<sub>3</sub> in groundwater, which correlate reasonably well with the areal extent of agricultural land use. Occurrences of high P and K are also seen, but are more sporadic in distribution, reflecting the more complex transport properties of these elements in soils and aquifers.

Not all the groundwaters sampled are used for drinking water, and it is not appropriate to assess the state of drinking water quality in Scotland on the basis of the data presented here. These data nonetheless show the typical chemical compositions of raw groundwaters from the sampled aquifers, and indicate the general state of groundwater quality and any potential problems that may be encountered within each aquifer. On this basis, the most frequent exceedances of drinking water limits in the groundwaters are for Fe and Mn (21% and 27% of samples respectively). These elements, together with NH<sub>4</sub> (6.7% exceedance), are largely naturally derived, linked to reducing aquifer conditions. Exceedances for NO<sub>3</sub> (11%) occur in oxic aquifer conditions, and are linked to pollutant inputs, particularly from agriculture. Exceedances for trace elements are less common but do occur locally.

In this report the study methodology is described along with some of the main factors controlling groundwater chemistry. The inorganic chemistry of Scotland's groundwater is then summarised and put in context, before the baseline chemistry for each aquifer is presented.



Map showing the distribution of pH in groundwaters in Scotland's bedrock aquifers.



# 1 Introduction

## 1.1 BASELINE SCOTLAND

This report is a synthesis of the Baseline Scotland project, whose primary aim was to characterise the natural quality of groundwater in the main bedrock aquifers across Scotland. Data collection and analysis for Baseline Scotland ran from 2005 to 2014, with one or two strategic groundwater sampling surveys every year from 2006–2011, each focused on a particular aquifer. New groundwater samples were collected from sites away from any major sources of contamination, and analysed to give detailed information on the natural inorganic groundwater chemistry in bedrock aquifers. This information provides a scientific foundation to underpin Scottish, UK and European water quality policy, most notably the EU Water Framework Directive.

The groundwater sampling surveys provided new analytical data that were added to existing reliable groundwater data identified and collated for each aquifer. These data were systematically analysed and interpreted with the help of additional information on aquifer hydrogeology and geochemistry. The result is a dataset which provides a summary of the inorganic chemistry of groundwater in each of the main bedrock aquifers in Scotland, and of the processes governing variations in the distribution of different hydrochemical parameters.

Prior to this synthesis report, a series of reports presented interim project results, including two scoping reports (MacDonald and Ó Dochartaigh, 2005, MacDonald et al., 2005a) and separate descriptions of the baseline chemistry of five individual regions in Scotland (Ó Dochartaigh et al., 2006, MacDonald et al., 2008, Smedley et al., 2009, Ó Dochartaigh et al., 2010 and Ó Dochartaigh et al., 2011) and a specific study on manganese (Homincik et al., 2010). A list of these reports is provided in Appendix 3. This current synthesis report is the first to provide a national overview for each bedrock aquifer in Scotland. A companion report *Scotland's aquifers and groundwater bodies* (Ó Dochartaigh, 2015), focusing on the physical nature of groundwater in Scotland, is available.

## 1.2 NATURAL GROUNDWATER QUALITY

Groundwater chemistry varies naturally between and within different aquifer types. Many complex and inter-related factors control natural groundwater chemistry, such as the chemistry of infiltrating rainwater, evapotranspiration rates, the type and thickness of soil and superficial deposits, and the geology and geochemistry of the aquifer itself. Groundwater can evolve chemically as it flows through aquifers because it is subject to various geochemical processes such as redox reactions and cation exchange. These processes, are entirely natural and can lead to a wide range in groundwater chemistry without any impact from human activity.

The natural baseline for any given chemical parameter in groundwater therefore varies both between and within aquifers, and is best described by a typical range rather than a single value. The upper limits of natural concentrations can be higher than environmental quality or drinking water standards, because of entirely natural processes. Probably the most well known example is the elevated concentrations of arsenic in groundwater across Bangladesh and parts of India – all as a consequence of natural processes (Fendorf et al., 2010).

For effective management, development, and protection of groundwater, a thorough understanding of natural groundwater chemistry is needed to give the natural baseline against which the impact of human activity and pollution can be assessed.

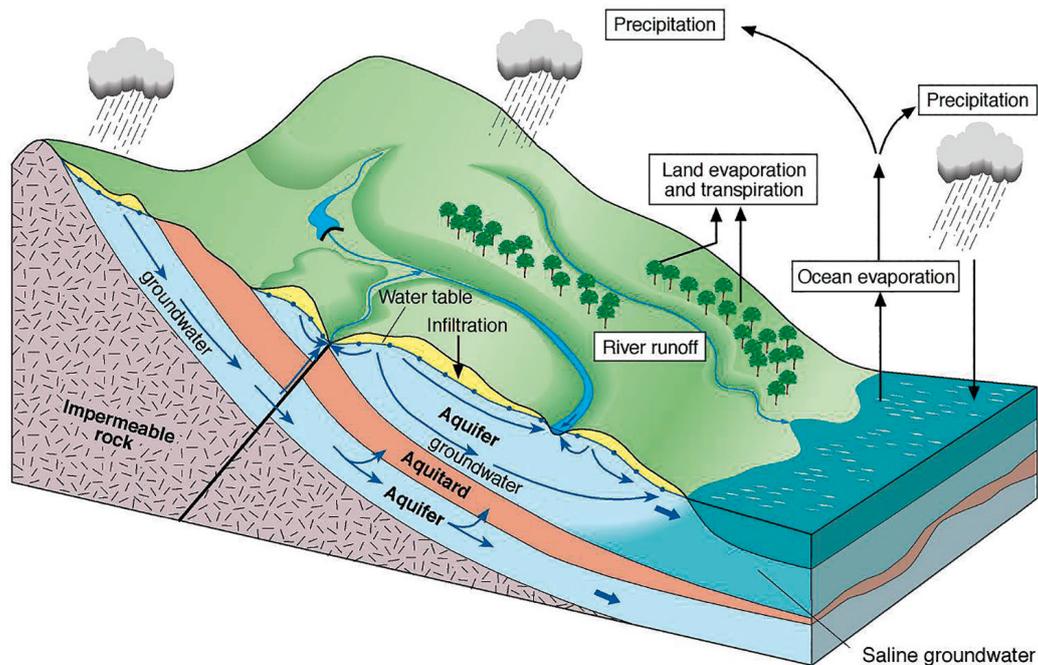
## 1.3 GROUNDWATER IN SCOTLAND

Groundwater is an important natural resource for Scotland. It provides drinking water, sustains agriculture and is fundamental to the nation's mineral water and whisky industries. What is less well known is the vital role that groundwater plays in sustaining the flow of rivers and supporting many of Scotland's fragile ecosystems. The volume of fresh water stored naturally in Scotland's aquifers is more than all the water easily visible in surface reservoirs.

Groundwater directly accounts for approximately 5% of public water supply in Scotland, much of which supports rural towns, such as Dumfries, Moffat, Selkirk, Ullapool, Portree, Fort William, Fochabers, Aviemore and towns on Arran. There are also an estimated 4000 or more boreholes and large springs across Scotland used for agricultural, industrial and large private supplies; and many more (an estimated 20 000) boreholes, small springs and wells providing small private water supplies (MacDonald et al., 2005a; DWQR, 2013).

The environmental use of groundwater, although rarely documented or accounted for, is vital for sustaining baseflow to rivers throughout the year. Even in small upland streams groundwater can account for 30% of flow, and is invaluable for maintaining salmon populations (Soulsby et al., 2000). Groundwater also has an important role in sustaining wetlands and fragile ecosystems, such as parts of the machair (seasonally waterlogged sandy coastal plains); and it has the ability to assimilate, dilute and break down contaminants and waste, such as for infiltration-based sustainable drainage schemes (SuDS).

Groundwater occurs in all the different bedrock environments found across Scotland. The volume of accessible groundwater varies markedly depending on aquifer thickness, lateral extent, and hydraulic characteristics. Groundwater recharges to aquifers by rainfall and, in some cases, by infiltration of



Groundwater forms an important component of the water cycle.

river or other surface water. Groundwater is rarely static, but flows continuously through aquifers, following the hydraulic gradient at a rate controlled by the aquifer permeability and thickness. In unconfined aquifers, groundwater flow follows the topographic gradient, downhill towards valley, plain or coastal areas, where it discharges to rivers or the sea. In deeper confined aquifers, or where the aquifer has been modified by mining, flow paths can be more complex (Ó Dochartaigh et al., 2015). Groundwater residence times can vary greatly, from a few months in upland metamorphic rock aquifers to centuries in the larger sandstone basins.

chemical processes, water rock interaction and rainfall chemistry. Chapter 3 introduces the different bedrock aquifers found within Scotland, and Chapter 4 presents the Baseline Scotland study methodology. Chapter 5 presents the main results from the study, summarising the inorganic groundwater chemistry for each aquifer and placing it in context. Chapter 6 discusses the general conclusions that can be drawn from the study regarding the baseline chemistry of the different bedrock aquifers and links to detailed tables describing the baseline chemistry. A list of all the other reports produced by the Baseline Scotland project is provided in Appendix 3.

## 1.4 A GUIDE TO THE REPORT

Chapter 2 describes the factors controlling groundwater chemistry, including some of the main groundwater

## 2 Factors affecting groundwater quality

The chemistry of groundwater is affected by many interacting processes, which are often difficult to distinguish and quantify. Initial chemical inputs are controlled by rainfall. However, once in the subsurface, groundwater chemistry evolves through biogeochemical reactions within the soil, unsaturated zone, and the saturated aquifer, from where virtually all groundwater ultimately flows back to the earth's surface. The process of groundwater chemical evolution is governed by a complex series of mineral reactions, many of which are aided by microbial activity, gaseous exchange, sorption reactions, mixing and dilution (Appelo and Postma, 2005; Shand et al., 2007). Groundwater flow can also have a significant effect on measured groundwater chemistry, as flow rates and pathways affect solute transport, rates of mixing and dilution, and residence times. In order to understand groundwater chemistry, it is important to understand these controlling processes. This chapter introduces some of the most significant factors and processes involved in controlling the chemistry of groundwater in aquifers. For a more detailed coverage, see Appelo and Postma (2005).

### 2.1 RAINWATER CHEMISTRY

The chemistry of rainfall, which is the source of groundwater, is the natural starting point for understanding groundwater chemistry. While many chemical elements in groundwater are sourced from water-rock interactions, some elements do not form major constituents of rocks and soils, and instead are largely derived from the atmosphere. This is particularly the case for the halogens (Br, I, Cl). Carbon dioxide in the atmosphere also makes rainwater slightly acidic, forming a weak solution of carbonic acid with an equilibrium pH of 5.7 at atmospheric pressure. Rainfall measured over oceans generally resembles dilute sea water. Scotland is subject to a maritime climate with prevailing winds from the southwest, and the chemistry of rainfall largely follows the chemical proportions of sea water, with exceptions due to anthropogenic activity.

The average concentrations of major solutes in rainwater at five rainfall gauging stations in Scotland are shown in Figure 1. Although monitoring periods for each station are slightly different, some general patterns are evident. Concentrations of many elements decrease with increasing distance from the sea – this is most noticeable with Cl, but is also observed with other solutes, such as Na, Mg, and K.

Airborne pollution has a significant impact on rainfall chemistry. The burning of fossil fuels, biomass and other industrial emissions leads to increased concentrations of N oxides and SO<sub>2</sub> in air, which react with other substances to make the rainfall more acidic, and increase the concentrations of NO<sub>3</sub> and SO<sub>4</sub> in rainwater. This can be seen at Whiteadder, which may be influenced both by its position closer to the

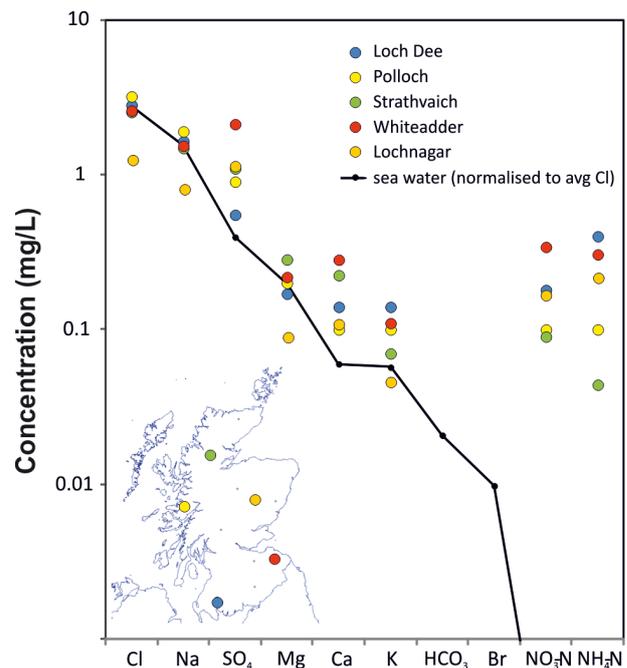


Figure 1 Average concentrations of the most abundant ions in rainfall measured at five sites in Scotland. Data from average concentrations in sea water, normalised to the mean Cl in rainfall, are shown for comparison (Source: AIR: Air Information Resource Data Archive © Crown 2017 copyright Defra via [uk-air.defra.gov.uk](http://uk-air.defra.gov.uk), licenced under the Open Government Licence (OGL)).

major urban-industrial areas in Scotland, and its closer proximity to urban centres in continental Europe. (Figure 1, Table 1). Ammonia derived from agriculture and industry is also readily taken into solution as NH<sub>4(aq)</sub>; and dust and industrial processes (such as cement factories and waste burning) can increase concentrations of dissolved Ca and K in rainwater.

Evapotranspiration leads to a concentration of solutes in water. Since Cl is generally unreactive and therefore conservative, it is often used as an indicator of the magnitude of this concentration effect, so long as there are no immediate sources of contamination. Chloride balances indicate that the concentration factor of evapotranspiration typically ranges from 2–4. Evapotranspiration also further increases the acidity of rainfall, with the result that infiltrating rainwater generally has a pH of less than 5, and is therefore highly reactive.

### 2.2 MINERAL DISSOLUTION AND PRECIPITATION

Reactions between infiltrating groundwater and dissolving rock minerals are key controls on the major ion chemistry of groundwater. Many of these dissolution reactions are

reversible, and the tendency to either dissolve or precipitate is controlled by chemical equilibrium. The rate of these chemical reactions varies considerably for different minerals, so equilibrium can be achieved rapidly for some, but never achieved for others. Four minerals that dissolve rapidly are dolomite, calcite, gypsum and halite. Since many sedimentary rocks contain calcite or dolomite cements, equilibrium reactions with calcite and dolomite are a common control on the concentrations of Ca, HCO<sub>3</sub> and Mg. Gypsum and halite are less common in rocks and tend to occur only in specific environments. However, when they are present, equilibrium reactions with these minerals have a strong impact on groundwater chemistry. Silicate minerals, however, dissolve very slowly: it takes 34 million years for a 1 mm sphere of quartz to dissolve in water of pH 5 (Lasaga, 1984). Hence, although silicon is one of the earth's most ubiquitous minerals, Si concentrations in groundwater are generally low.

Some mineral dissolution reactions are controlled by the water pH, including the dissolution of iron oxides and other trace metals in aquifers. Redox conditions also play a major influence, and therefore pH and redox reactions are often considered together by producing a stability field, or Eh-pH, diagram (Figure 2). Groundwater pH can also control the extent at which these reactions are microbially mediated: e.g., at low pH iron oxides are aggressively dissolved due to microbially mediated reactions.

In natural groundwater systems, equilibrium reactions involving the carbonate minerals calcite and dolomite

are among the most important controls on groundwater chemistry. The production of HCO<sub>3</sub> buffers the pH and naturally neutralizes acidity in groundwater, which in turn reduces the mobilisation of trace metals.

## 2.3 REDOX REACTIONS

Reduction and oxidation processes (redox) exert a significant control on the presence and speciation of a number of key chemical constituents of groundwater, including O<sub>2</sub>, N, Fe, Mn, S and CH<sub>4</sub>. Redox reactions involve the transfer of electrons: oxidation involves the loss of an electron, and subsequent increase in charge; whereas reduction involves gaining an electron and therefore a reduction in charge. The presence of organic matter, either naturally or introduced by contamination, is often a significant driver of redox reactions, providing the electrons to drive consequent reduction. In practice most redox reactions are mediated by microbial activity, which enables the reactions to occur much more rapidly.

Redox reactions in aquifers tend to follow a well established sequence which often coincides with groundwater flowing from unconfined to confined conditions (Figure 2). This begins with the loss of dissolved oxygen, followed by denitrification as NO<sub>3</sub><sup>-</sup> is reduced to NO<sub>2</sub><sup>-</sup> and then to the gases N<sub>2</sub> and N<sub>2</sub>O. As reduction continues, this can be followed by the reduction of Mn oxides to soluble Mn<sup>2+</sup> and of Fe oxides to soluble Fe<sup>2+</sup>. Further reduction occurs in only relatively few

**Table 1** Rainfall chemistry at selected monitoring stations, and expected concentration in infiltrating recharge. Rainfall data from UK-AIR: Air Information Resource Data Archive at <http://uk-air.defra.gov.uk/data/>

	Sites	Loch Dee	Polloch	Strathvaich	Whiteadder	Lochnagar
	units					
NGR		NX 468 779	NM 792 690	NH 348 850	NT 664 633	NO 254 860
Elevation	m OD	230	30	270	250	500
Mean annual rainfall	mm	1633	1836	766	599	1250
Date range for data		2000–2005	2000–2005	1990–1999	1986–2007	1999–2006
		<b>Median concentration in rainfall</b>				
pH	-	5.23	5	5.14	4.66	4.74
SEC	µS cm <sup>-1</sup>	26	21	20	29	17
Ca	mg l <sup>-1</sup>	0.14	0.1	0.224	0.282	0.11
Cl	mg l <sup>-1</sup>	2.81	3.2	2.532	2.5855	1.26
K	mg l <sup>-1</sup>	0.14	0.1	0.07	0.11	0.045
Mg	mg l <sup>-1</sup>	0.17	0.2	0.283	0.218	0.1
NH <sub>4</sub> -N	mg l <sup>-1</sup>	0.4	0.1	0.044	0.305	0.17
NO <sub>3</sub> -N	mg l <sup>-1</sup>	0.18	0.1	0.09	0.341	0.22
Na	mg l <sup>-1</sup>	1.64	1.9	1.483	1.5335	0.72
PO <sub>4</sub> -P	mg l <sup>-1</sup>	-0.01	-0.1	-0.1	-0.05	<0.01
SO <sub>4</sub> -S	mg l <sup>-1</sup>	0.55	0.3	0.365	0.7055	0.366

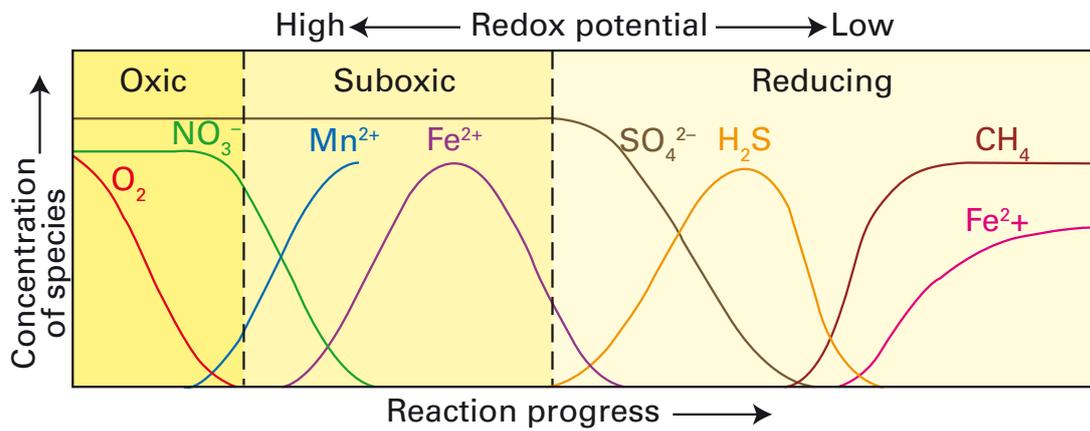


Figure 2 The sequence of redox reactions developing as groundwaters move from oxic to reducing conditions (from Shand et al., 2007).

aquifers, with eventual  $\text{SO}_4^{2-}$  reduction to  $\text{S}^{2-}$ , the production of methane from organic carbon, and  $\text{N}_2$  reduction to  $\text{NH}_4^+$ . Redox reactions also control the mobility of a number of trace elements, some of which have an impact on health, such as As, Cr, Se and U. The likelihood of different redox reactions occurring is generally referred to as the redox potential, and can be estimated using an appropriate electrode.

The oxidation of iron pyrite, where  $\text{FeS}_2$  oxidises to  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$ , causes significant acidity. This is a particular issue in Scotland in areas that have been subject to mining, where the introduction of oxygen to pyrite-rich sediments has led to the mobilisation of Fe and  $\text{SO}_4$ , accompanied by high acidity, which is often buffered by the dissolution of carbonate

material (Younger, 2001; Ó Dochartaigh et al., 2011; Haunch et al., 2013).

Since both redox reactions and pH control the solubility of many minerals, it is useful to construct stability field diagrams, which illustrate the Eh and pH conditions in which different minerals can exist, and different elements can be mobilised. A stability diagram for Mn based on data from the Baseline Scotland project (Figure 3) shows that Mn can be mobilised for much of the groundwater pH-Eh conditions encountered in Scotland, often leading to Mn concentrations exceeding the national drinking water limit of 0.05 mg/L (Homocnik et al., 2010). The stability of Fe is also particularly important, since many trace elements adsorb to Fe(III) oxide. If iron is mobilised to  $\text{Fe}^{2+}$  then the concentrations of these trace elements can increase significantly.

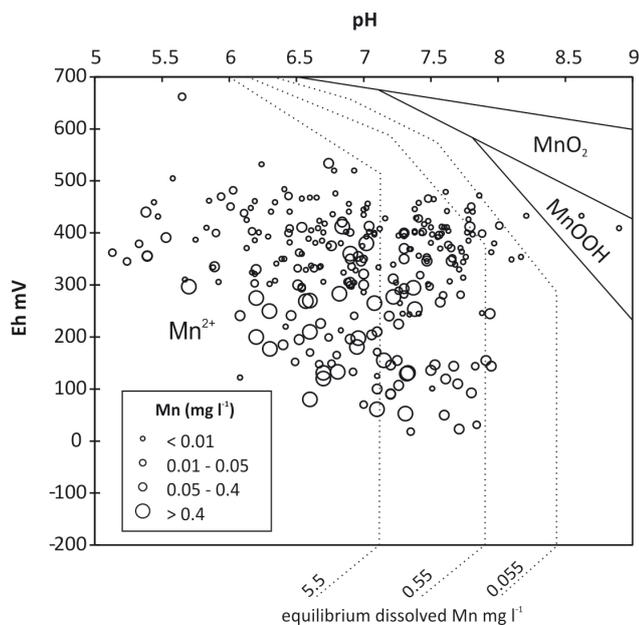


Figure 3 Eh-pH diagram showing stability fields for Mn and data for Scotland (Homocnik et al., 2010). Dissolved Mn concentrations increase with decreasing pH and Eh.

## 2.4 ION EXCHANGE AND SORPTION

Clays, organic matter, and iron oxides all provide large surface areas on which sorption and exchange can occur. Adsorption involves the binding of an ion to a surface, and desorption its release. Ion exchange is the substitution of one bound ion by another. Clay surfaces (particularly from the smectite group), organic material and iron oxides have an excess negative charge, which binds cations. This capacity is known as the cation exchange capacity (CEC) and is measured in meq/L. Divalent cations are bound more strongly than monovalent cations, which means there is a potential for monovalent cations to be exchanged for divalent cations. For cations with similar charge the hydrated radius is important. The general order of cation exchangeability for some of the most common ions in groundwater is:



Ion exchange reactions are particularly important where freshwater is moving through aquifers that previously contained saline water. The  $\text{Ca}^{2+}$  in the freshwater can replace the  $\text{Na}^+$  that is bound to the aquifer rock surfaces, leading to the groundwater evolving from  $\text{Ca-HCO}_3$  to  $\text{Na-HCO}_3$  type waters.

## 2.5 NATURAL GROUNDWATER QUALITY

As a consequence of the processes described above, natural groundwater quality varies widely with variations in the key controlling factors of geology, climate and vegetation. Variations in groundwater quality can occur spatially, with depth, and with time, since many of the reactions are kinetically controlled. However, for most natural groundwater systems in Scotland today, spatial variability due to changes in geological conditions is more significant than temporal changes on scales of several years. Temporal changes become much more important when dealing with pollution. For example, there is clear evidence that nitrate concentrations have increased markedly in Scotland since the middle of the 20th century, when the use of fertilizers increased and farming practices intensified (MacDonald et al., 2003).

Nine major chemical constituents make up approximately 99% of the solute content of natural groundwaters – Na, Ca, Mg, K,  $\text{HCO}_3^-$ , Cl,  $\text{SO}_4$ ,  $\text{NO}_3^-$  and Si. The concentrations and proportions of these constituents characterise the groundwater's hydrochemistry, with many being dominated by Ca and  $\text{HCO}_3^-$ . Classifying groundwaters according to their predominant cations and anions (expressed as meq/L) is a useful approximation, and is often done by means of a piper (tri-linear) plot (Figure 4). However, this type of classification is only a starting point and more detailed quantitative analysis is often done, for example by plotting different chemical ratios, statistics, or geochemical modelling.

The remaining 1% of the chemical constituents in groundwater comprises trace elements, which although small in proportion to the overall major ions present are often of great interest. Some have an impact on human health, by being present either at too high or too low concentrations (Figure 5). Others can impact on ecosystems, and several are useful for unravelling the geochemical evolution of the groundwater, and detecting the presence of pollution.

Determining what is natural groundwater chemistry and what is derived from pollution is not always straightforward. Humans have had a long-term impact on the environment, deforestation, ploughing and mining for millennia; and in the last two centuries intensive industrialisation, urbanisation and the widespread use of chemicals in agriculture. The most reliable way of measuring baseline chemical conditions is to analyse groundwater that is several thousand years old, recharged when human influence was much less. There have been several large projects in Europe that do just this (e.g. Edmunds and Milne, 2001). However, groundwater of >1000 years is rare in Scotland, and most of the shallow groundwater originated as rainfall within the last 100 years. The natural groundwater quality in Scotland must therefore be estimated from measurements of relatively modern groundwater.

Different approaches are taken to defining 'natural' groundwater chemistry – sometimes referred to as baseline or background chemistry, or threshold values. The following

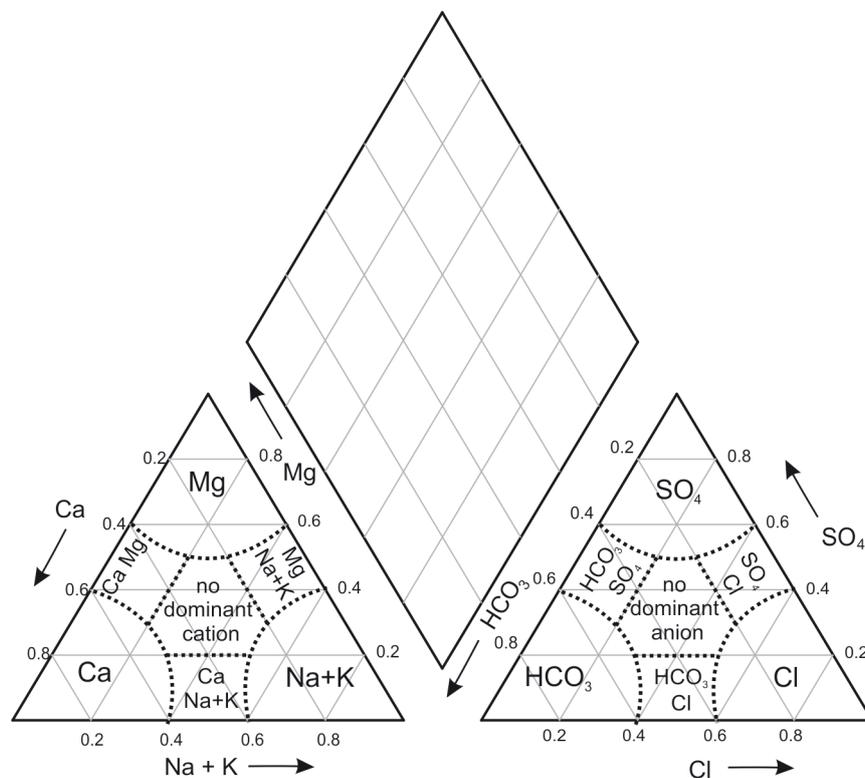
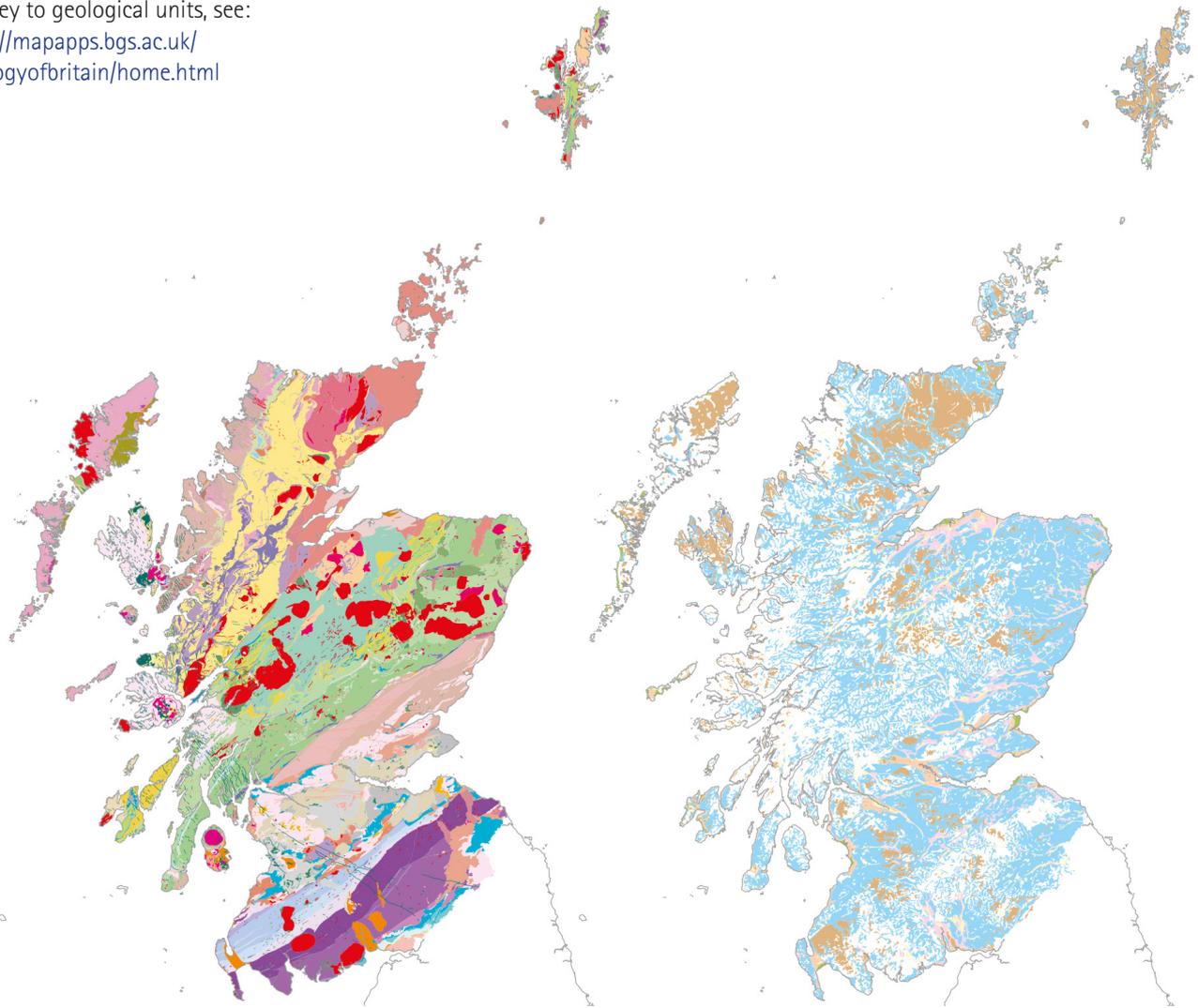


Figure 4 Piper (tri-linear) diagram illustrating how groundwater major ion chemistry can be characterised by where it plots.



For key to geological units, see:  
[http://mapapps.bgs.ac.uk/  
geologyofbritain/home.html](http://mapapps.bgs.ac.uk/geologyofbritain/home.html)



**Figure 6** Bedrock geology and (inset) Quaternary (superficial) geology of Scotland at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

main hydrogeological environments. A brief description of the hydrogeological units is given in Section 3. More information on the geology of Scotland can be found in Trewin, 2002.

Superficial deposits – unconsolidated sediments overlying bedrock – can also play an important role in controlling the chemistry of groundwater in bedrock aquifers. Scotland's superficial deposits (Figure 6) were virtually all deposited during the Quaternary period within the last 20 000 years, and are highly variable in their depositional history and therefore in characteristics including lithology, sediment sorting and 3D geometry. The thickest superficial deposits in Scotland exceed 100 m, where sequences of glaciofluvial and/or marine deposits infill deep valleys eroded by glaciers in bedrock.

Since groundwater infiltrates through the superficial deposits to recharge the bedrock aquifers, the superficial deposits can exert significant control on water chemistry, in particular on pH, organic and inorganic carbon content, and redox

conditions. Their physical properties control the volume of rainfall recharge (or contamination) that can pass through, and the minerals present also enable evolution of the water chemistry en route to the bedrock aquifers. Over much of Scotland, the mineralogy of the superficial deposits largely reflects the mineralogy of the underlying bedrock, which means that the water-rock interaction in the superficial deposits will be similar to those in the underlying bedrock (Griffiths et al., 2011). There are exceptions, such as raised marine deposits and peats. The presence of silts, clays and organic material can lead to reducing conditions in recharging groundwater.

The superficial deposits can also offer some protection for groundwater in underlying bedrock aquifers. The groundwater vulnerability map of Scotland helps classify the protection offered by different deposits (Ó Dochartaigh et al., 2005). Thick sequences of fine-grained, low-permeability superficial

deposits, such as glacial, estuarine and marine silts and clays, or peats, typically provide much greater protection than high-permeability sands and gravels, or thin layers of glacial till.

## 2.7 LAND USE

Land use can have a significant impact on groundwater quality through its influence on pollutant inputs to groundwater. Changes in land use over space and through time can have a significant effect on the baseline chemistry of groundwater. For example, modern agriculture can introduce nutrients (N, P and K) and pesticides into groundwater. Agricultural and domestic wastes can introduce point source

pollutants (such as N, Cl, P, pathogens and organic carbon) from slurry pits and septic tanks. Industries, including mining, can potentially introduce a huge range of inorganic and organic pollutants into groundwater. Fuel filling stations can form point sources of organic pollutants, and transport infrastructure can be a source of inorganic pollutants (such as Na and Cl) and pesticides.

Land use across Scotland has been interpreted through the CEH LCM2007 land cover datasets (Version 1.0), which distinguish 23 land classes (CEH, 2011). Land cover is not always synonymous with land use (e.g. improved grassland land cover may be used for pasture grazing or for recreation, such as for golf courses) but it provides a close proxy in most cases.

### 3 Bedrock aquifers

The bedrock aquifers described here represent hydrogeological environments that exert different geological controls on both physical aquifer properties and natural groundwater chemistry. These aquifer groups form the basis for interpreting the chemistry data collected in the Baseline Scotland project, and much of the data presented

in this report is grouped and analysed according to these aquifer groups. In this chapter we describe the process for subdividing the aquifer groups, and provide a short description of each. More details are available in the report *Scotland's Aquifers and Groundwater Bodies* (Ó Dochartaigh et al., 2015).

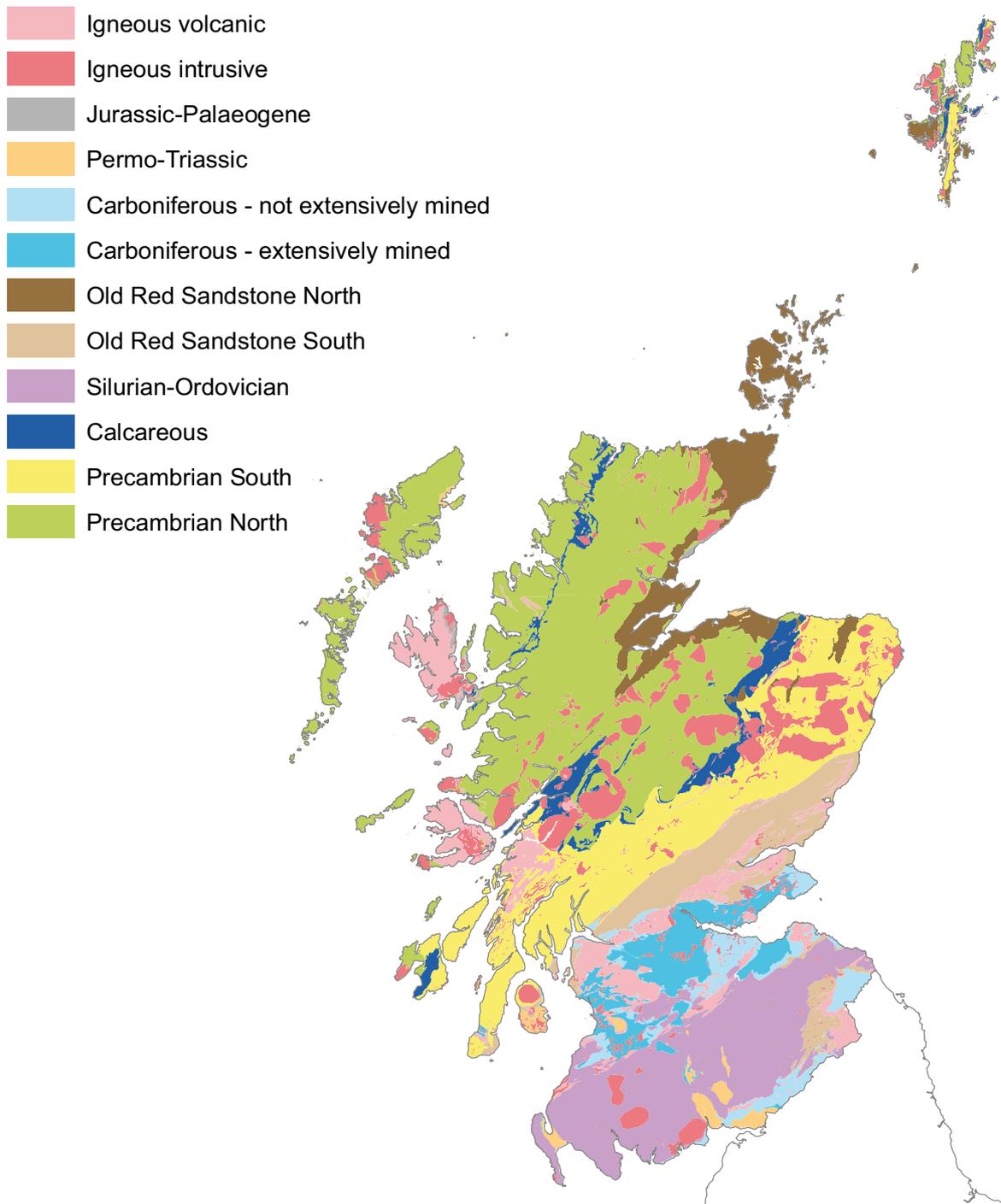


Figure 7 Bedrock aquifer groups used in the Baseline Scotland project. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

The aquifers have been first divided into three categories according to the type of rock they are formed of: sedimentary; metamorphic, igneous or indurated sedimentary; or calcareous. Within these categories, they have been subdivided primarily according to geological age, which itself is a key control on lithology, geological structure and history, and local relationships with other rock types. In some cases, aquifers of the same age have been further subdivided, either because parts of the aquifer have been subject to significant human alteration (such as Carboniferous aquifers which have been extensively mined for coal), or because the rocks in different parts of Scotland, although they have similar physical characteristics, have significantly different effects on groundwater chemistry (such as Old Red Sandstone (predominantly Devonian age) aquifers, which have been divided into a North and a South group).

The aquifer groups are shown in the map in Figure 7; and their key characteristics are described summarised in Table 2. The hydrogeology of the aquifers is summarised in Sections 3.1 to 3.8. More detail on the aquifer hydrogeology can be found in Ó Dochartaigh et al. (2015).

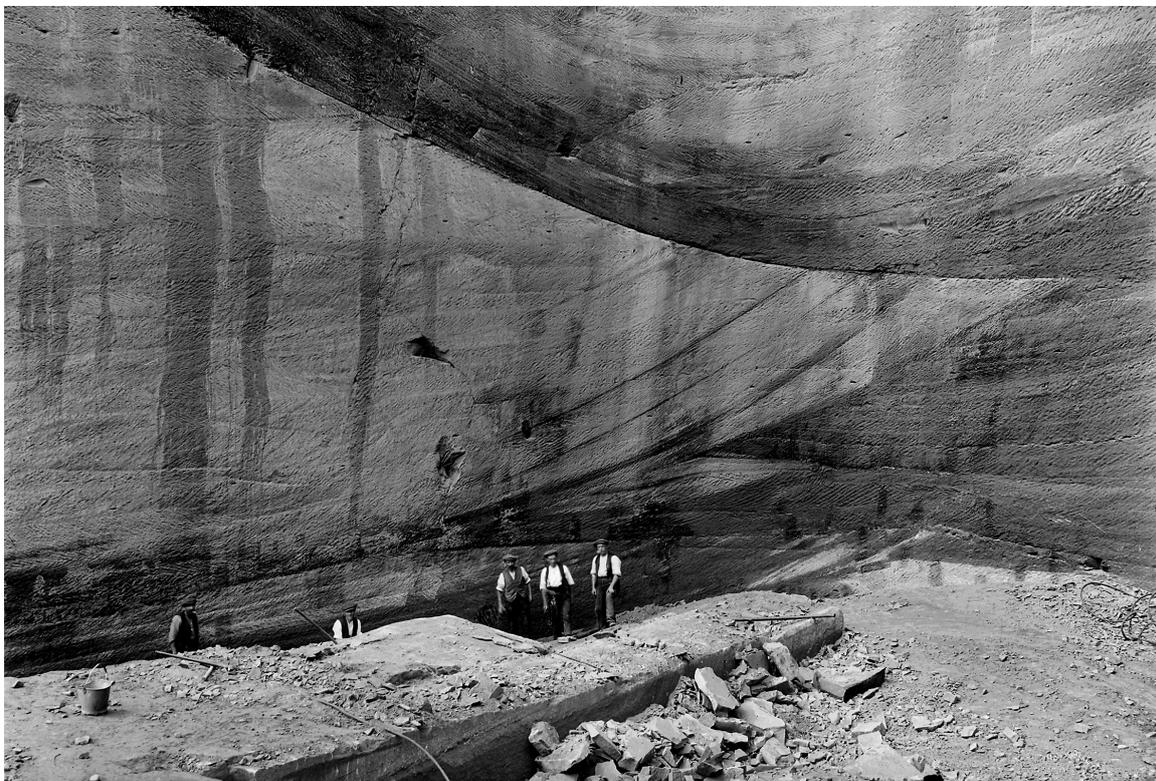
### 3.1 PERMO-TRIASSIC

Permo-Triassic rocks form some of the highest productivity bedrock aquifers in Scotland. They are most significant in southwest Scotland, where they typically form sedimentary

basins, usually many hundreds of metres thick, surrounded by older rocks with lower groundwater potential.

Permo-Triassic aquifers are often characterised by the complex layering of aeolian sandstones (Plate 1) with breccias, creating a dual aquifer system dominated by fracture flow but intergranular storage of groundwater. The breccias have low intergranular porosity but high secondary permeability formed by fractures in the rock; while the sandstones have high intergranular porosity and storage capacity, but relatively low fracture permeability. Subhorizontal fractures along the bedding planes between breccia and sandstone layers form important, fast groundwater flow zones, while intergranular groundwater flow through the sandstones does occur but is slower. Horizontal permeability is therefore usually much greater than vertical permeability, although in some areas there is significant subvertical fracturing associated with faulting, which allows rapid recharge deep into the aquifer. Significant fracture inflows to boreholes occur at up to 100 m below ground level, and smaller inflows have been measured to at least 150 m depth. Groundwater can flow many kilometres laterally along continuous sub-horizontal fracture systems.

Aquifer hydrogeology can be further complicated by the nature and thickness of any overlying Quaternary sediments, which can be a significant control on groundwater-surface water interactions, such as forming a source of delayed recharge, or confining the underlying bedrock aquifer. Multiple groundwater abstractions and discharges in some of the aquifer basins also impact on the local hydrogeology.



**Plate 1** Aeolian dune bedding in Permo-Triassic sandstone exposed in a quarry in Ayrshire, south-west Scotland. BGS Geoscience Imagebase Ref P000072.

### 3.2 CARBONIFEROUS SEDIMENTARY

Carboniferous sedimentary rocks are found mainly in the Midland Valley, with smaller outcrops in southern Scotland (Figure 7), and they vary from less than 500 m thick in the smaller outcrops in southern Scotland, up to 2000–3000 m in the Midland Valley. They tend to form moderately productive aquifers that are dominated by fracture flow.

The rocks comprise repetitive sequences of sandstone and siltstone beds with thinner interbedded mudstones and, more rarely, limestones and coals. The sandstones have the highest aquifer potential, and so the rocks tend to form complex, multilayered aquifers in which groundwater is found preferentially in sandstone layers, separated by lower permeability siltstones, mudstones and coals. Limestone beds have variable permeability, but are generally thin in comparison with the whole aquifer sequence, so their overall impact on groundwater flow is typically only significant on a local scale. The sandstones are typically fine grained and well cemented, with low intergranular porosity and permeability, and so groundwater moves mainly by fracture flow. The exception is the Passage Formation, which has relatively high porosity and intergranular permeability, and is one of the few bedrock aquifers in Scotland which shows significant intergranular groundwater flow.

Groundwater flow paths can be kilometres long, and tend to be complex. This is partly due to the naturally layered nature

of the aquifers, which tends to impart preferential horizontal flow, and the predominance of fracture flow. Faults can also divide the aquifer vertically: some are permeable and act as preferential flow pathways; while others act as barriers to groundwater flow. Unmined coal seams may also restrict groundwater flow between more permeable sandstone beds. Groundwater may be present under unconfined or confined conditions, at various depths, and different groundwater heads are seen in different aquifer layers.

Some of the Carboniferous formations – the Scottish Coal Measures and part of the Clackmannan Group (except the Passage Formation, which does not contain coals) – have been extensively mined for coal (Plate 2). By contrast, the Strathclyde, Inverclyde (both largely in the Midland Valley), Border and Yoredale (both largely in southern Scotland) groups contain few, if any, coal seams. However, these formations have often been subject to generally shallow mining activity, including for oil shale, fireclay and limestone. Mining has had a large impact on the hydrogeology of Carboniferous aquifers. Mine voids (e.g. shafts, tunnels and adits) artificially increase aquifer transmissivity, sometimes across large areas and depths, and can link formerly separate groundwater flow systems, increasing the complexity of groundwater flow paths. Groundwater storage capacity can also be locally increased. Even where mine voids have subsequently collapsed, deformation of the surrounding rock mass is likely to have caused further changes in transmissivity and, to a lesser degree, storage.



Plate 2 Stoop and room (pillar and stall) mining in the Carboniferous Lower Limestone Group in Midlothian.

### 3.3 OLD RED SANDSTONE (DEVONIAN) – NORTH AND SOUTH

Rocks of the Old Red Sandstone sedimentary succession, which are dominantly Devonian in age, occur across large parts of north, north east, central and southeast Scotland, and can be more than 2000 m thick. They form variably productive aquifers, from low to very high depending on their lithology. The sandstones have the highest potential. The youngest sandstones in the group, in Fife, are some of the most highly productive bedrock aquifers in Scotland and form an important resource for public water supply.

Sandstones dominate the sequence, with varying proportions of conglomerate, siltstone, flagstone and mudstone. Volcanic rocks, interbedded with the sedimentary rocks, are significant in some areas. The rocks were formed in two distinct basins: a northern, 'Orcadian', basin, including Shetland, Orkney, Caithness, Morayshire and Aberdeenshire; and a southern basin including Aberdeen itself; the Vale of Strathmore; Loch Lomond to Stonehaven; Fife and the Scottish Borders.

The rocks are typically well cemented, with moderate intergranular porosity and permeability even in sandstones, and groundwater flow is dominantly through fractures. In Caithness and Orkney there are extensive fine grained flagstones, in which groundwater flow is concentrated along bedding planes (Plate 3). Where lower permeability siltstones or mudstones separate sandstone beds, they tend to act as barriers to groundwater flow. Major faults that cut through the rocks may allow groundwater to flow vertically through the aquifer. However, on the whole, groundwater flow paths are likely to follow major surface water catchments.

Overlying superficial deposits can have a significant impact on hydrogeology. For example, in Morayshire low permeability raised marine deposits restrict and alter the chemistry of groundwater recharge; glaciofluvial sands and gravels with high storage capacity in Strathmore augment recharge to the underlying sandstone aquifer; and a thick blanket of peat across Caithness has a widespread impact on the flow and chemistry of underlying groundwater.

### 3.4 SILURIAN-ORDOVICIAN

Rocks of Ordovician and Silurian age dominate southern Scotland (Figure 7), comprising mainly turbiditic sandstones (called greywackes) and siltstones, with variable proportions of conglomerate, mudstone, chert, and volcanic rocks. The rocks are often significantly folded and deformed (Plate 4). The total sequence is many thousands of metres thick. The rocks typically form low productivity aquifers.

The dominantly fine-grained, well-cemented, highly indurated rocks mean that intergranular permeability and porosity are negligible, apart from a sometimes well-developed weathered zone at rockhead, in which permeability is enhanced. Throughout the rest of the aquifer, groundwater storage and

flow are dominated by fractures in the rock. In general, flow paths are likely to be relatively short and localised, but in some cases there may be connectivity over several kilometres from higher ground to valleys.

### 3.5 CALCAREOUS

Most rocks in Scotland are siliceous, but a few – largely in the Highlands – are dominantly calcareous, including Precambrian metalimestones, calcsilicates and calcareous pelites within the Dalradian Supergroup (part of the Precambrian South aquifer group), and Cambro-Ordovician limestones in the north-west Highlands. This has a significant impact on groundwater chemistry and flow. The calcareous rocks have low intergranular porosity and permeability, but dissolution of carbonate by groundwater flowing through fractures in the rock can produce significant karstic permeability, and highly unpredictable groundwater flow paths. In Cambro-Ordovician limestones there is significant karst development, including cave sequences at least 3 km long, through which large flows of 300 l/s discharge (Ball, 1999; Robins, 1990). However, where karst is poorly developed, calcareous aquifers have low productivity, and behave similarly to Precambrian aquifers.

### 3.6 PRECAMBRIAN NORTH AND SOUTH

Precambrian rocks cover most of Scotland north and west of the Highland Boundary Fault. They are subdivided here into two groups. Precambrian North aquifers are typified by massive metamorphic rocks of various grades, including highly metamorphosed Lewisian gneiss, largely un-metamorphosed Torridonian sandstone, Moine and Dalradian (Grampian Group) schists. Precambrian South aquifers largely comprise Dalradian metasedimentary schists of the Southern Highland and Argyll groups, which are typically more layered and less massive than Precambrian North rocks. Precambrian rocks are variously intruded by igneous rocks.

Both Precambrian groups typically form low or very low productivity aquifers, with negligible intergranular porosity and permeability. Weathering of the uppermost few metres of rock, which can be pronounced in areas of intensive faulting, can create a shallow zone of higher intergranular permeability, but away from this, groundwater flow and storage is entirely within fractures. Water-bearing fractures are generally more common at depths of up to approximately 100 m. Often a single fracture, or at most three or four fractures, provide all of the inflow to a borehole, with individual fracture flows up to approximately 0.3 l/s, although typically lower than this. Groundwater flow paths are usually relatively short, less than 1 km, and controlled by local surface water catchments.

Within the Precambrian North group, Torridonian sandstone has the highest aquifer productivity. Within the Precambrian South aquifers, the highest productivity is in parts of Aberdeenshire, where there is often a thick weathered zone, to tens of metres deep, which has enhanced porosity and permeability.



Plate 3 Gently dipping flagstones of the Middle Old Red Sandstone at Yesnaby, Orkney.  
BGS Geoscience Imagebase Ref P000624.



Plate 4 Folded and deformed Silurian greywackes in Wigtownshire, southwest Scotland.  
BGS Geoscience Imagebase Ref P001123.

### 3.7 IGNEOUS VOLCANIC

There are innumerable outcrops of volcanic rocks across Scotland, mostly formed as lava flows. They range from a few centimetres to many kilometres in size. Three geological periods in particular saw large volumes of volcanic rocks formed in Scotland: the Devonian (within the Old Red Sandstone sequence), the Carboniferous and the Tertiary. There can be volcaniclastic and occasionally pyroclastic deposits interbedded within lavas, and volcanic rocks can also be interbedded with sedimentary rocks, forming a mixed aquifer with particular characteristics from both rock types. The volcanic rocks typically form low productivity aquifers, but are occasionally moderately productive. In their unweathered state they have negligible intergranular porosity and permeability, but secondary permeability often develops in thin weathered zones between lava flows, and in fractures throughout the rock, which can connect weathered zones and increase the overall aquifer productivity. However, in general, groundwater flow paths are controlled by local surface water catchments and are usually less than 1 km long. In some areas, such as in Tertiary volcanic rocks on Skye, large springs occur, some of which are used for public water supply; there are also several notable abstractions for mineral water.

### 3.8 INTRUSIVE IGNEOUS

There are many major and innumerable minor igneous intrusions across Scotland, ranging from linear dykes a few millimetres wide to granitic batholiths many tens of kilometres across. Certain geological eras saw major periods of igneous activity, in particular the Caledonian orogeny in Ordovician-Devonian times, which saw the formation of large granite and diorite plutons in the Southern Highlands and southwest Scotland; and opening of the Atlantic Ocean during the Tertiary, which saw substantial igneous intrusions along the west coast of Scotland,

Intrusive igneous rocks typically form low or very low productivity aquifers, with negligible intergranular porosity and permeability. Rock fracturing and weathering, such as at rock head or at the edge of large intrusions, increases local permeability. Groundwater flow paths are generally controlled by local surface water catchments and are usually less than 1 km long.

Table 2 Summary of aquifer group characteristics. For aquifer extents see Figure 7. For more detail see individual descriptions in Sections 3.1 to 3.8. From Ó Dochartaigh et al. (2015).

Aquifer type	Aquifer group	Geological summary	Dominant groundwater flow type	Dominant aquifer productivity	Dominant <sup>1</sup> groundwater flow path length	Typical ground-water flow depth	Dominant groundwater age	
Sedimentary	Permo-Triassic	Sandstone and breccia in small basins	Significantly intergranular (sandstone); Fracture (breccia)	Moderate to Very High	1 km+	100s m	Years to millennia	
	Carboniferous – not extensively mined for coal	Mixed sandstone, siltstone, mudstone and limestone, with some volcanic rock. Some non-coal mining.	Fracture (minor intergranular), except Passage Formation – significantly intergranular	Moderate (except Passage Formation – High)	1–10 km	100s m	Years to millennia	
	Old Red Sandstone North	Mixed sandstone, flagstone, conglomerate and mudstone.	Fracture (minor intergranular)	Low to High	1 km+ Usually follows main river body catchments	10s to 100s m	Decades to centuries	
	Old Red Sandstone South	Mixed sandstone, conglomerate and mudstone, with some flagstone and interbedded volcanic rock.	Fracture (minor intergranular)	Moderate to Very High	1 km + Usually follows main river body catchments	10s to 100s m	Decades to centuries	
Extensively mined for coal	Carboniferous – extensively mined for coal	Same rock types as 'Carboniferous – not extensively mined for coal' but significant deep alterations from coal mining	Fracture (minor intergranular) and through mined voids	Moderate	1–10 km Dominated by impacts of historical mining	100s m+	Months to millennia	
	Metamorphic/Igneous/Indurated Sedimentary	Silurian-Ordovician	Highly indurated greywacke with minor conglomerate, mudstone, chert, and volcanic rock	Fracture	Low	0.1–1 km + Usually follows local surface water catchments	10s m	Years to centuries
		Precambrian North	Ancient, highly metamorphosed gneiss and schist; largely unmetamorphosed Torridonian sandstone	Fracture	Very Low to Low	0.1–1 km Usually follows local surface water catchments	10s m	Years to decades

Table 2 *Continued.*

Aquifer type	Aquifer group	Geological summary	Dominant groundwater flow type	Dominant aquifer productivity	Dominant <sup>1</sup> groundwater flow path length	Typical ground-water flow depth	Dominant groundwater age
Metamorphic/Igneous/Indurated Sedimentary	Precambrian South	Ancient, highly metamorphosed schist	Fracture	Very Low to Low	0.1–1 km Usually follows local surface water catchments	10s m	Years to decades
	Igneous Volcanic	Lava flows with some volcanoclastic and pyroclastic rock. Sometimes interbedded with contemporaneous sedimentary rock	Fracture	Low	0.1–1 km Usually follows local surface water catchments	10s to 100s m	Months to decades
	Igneous Intrusive	Large igneous intrusions, often comprising granite.	Fracture; sometimes weathered intergranular	Low	100s m Usually follows local surface water catchments	10s m	Years to decades
Calcareous	Calcareous	Small outcrops of calcareous meta-sedimentary and sedimentary rocks, mostly Precambrian and Cambro-Ordovician age	Fracture	Low to Moderate	0.1–1 km+ Karstic. Flow paths highly unpredictable	10s to 100s m	Months to decades

<sup>1</sup> Dominant here refers to the typical/modal range of flow path lengths. Shorter and longer outliers also occur.

## 4 Methodology

To characterise Scottish groundwater chemistry new water samples were taken and analysed from existing boreholes and springs, and combined with selected existing data that met quality assurance conditions. Once analysed, the data were interpreted in the main hydrogeological environments identified for Scotland (Section 3) using various statistical methods. This chapter describes the procedures used for data collation and sample collection, how the samples were analysed and the statistical methods used to help interpretation.

### 4.1 DATA COLLATION

A total of 646 chemistry analyses from groundwater chemistry samples across Scotland have been used to interpret the groundwater chemistry of Scotland's bedrock aquifers. The location of these samples is shown in Figure 8.

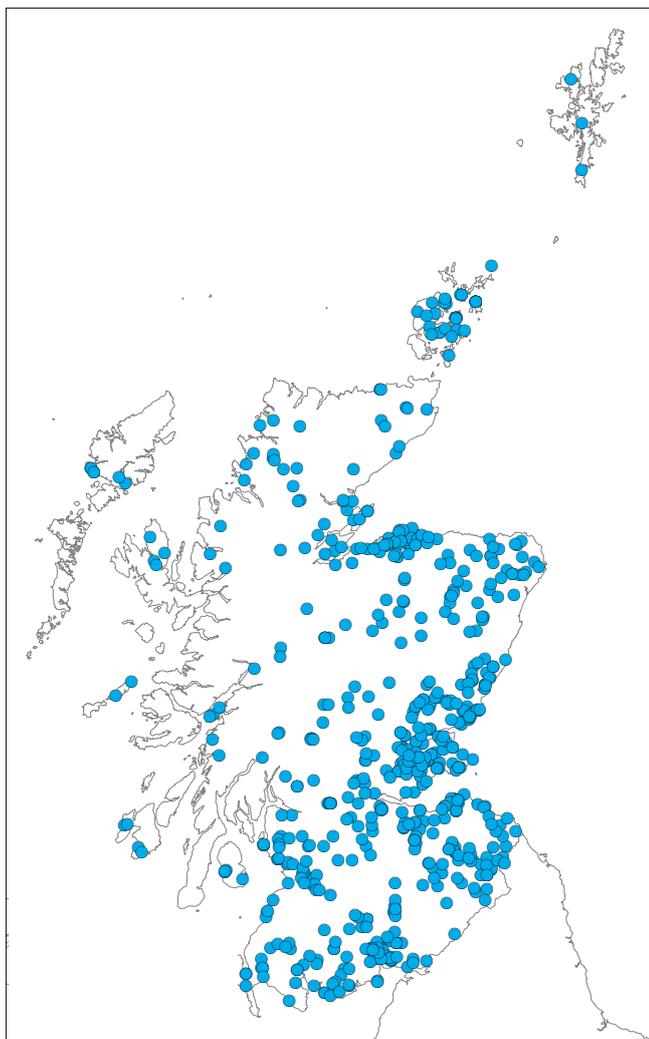


Figure 8 Location of Baseline Scotland groundwater samples.

Of the analyses, 263 were new groundwater samples collected specifically for the Baseline Scotland project between 2004 and 2011. These have been augmented with samples collected during earlier and/or separate projects, largely between 1983 and 2005 (MacDonald et al., 1999; Ó Dochartaigh et al., 1999; MacDonald et al., 2005b; Ball and MacDonald, 2001; MacDonald and Abesser, 2004; Ball et al., 2006 and Ó Dochartaigh, 2006). The oldest samples are four collected and analysed between 1935 and 1955.

The majority of samples, and all samples collected since 1999 (464 in total), were collected and analysed using standardised procedures, described in Sections 4.2 and 4.3. The remainder were mostly collected between 1980 and 1998. All the sample analyses have been subjected to a thorough quality assurance process to ensure the chemistry data are reliable. A high confidence rating was applied to samples collected specifically for the Baseline Scotland project, those collected by BGS for other projects, and non-BGS samples where sampling and analysis procedures were known and the analytical data could be assessed as being of suitable quality. Sample analyses with obviously poor data (ionic imbalances >10%), with largely incomplete data, or where the chemistry data indicate that the groundwater sampled is likely to have been impacted by local contamination, were assigned a lower confidence rating, and removed from the dataset unless there was an overriding reason to retain them – such as incomplete data in some areas being better than having no data at all.

### 4.2 SAMPLE SITES AND SOURCES

The samples were collected from existing groundwater sources across Scotland: largely boreholes but also including springs and a very few shallow wells (Plate 5). None of the samples are believed to be from sources subject to local contamination, although a number are in areas of diffuse groundwater contamination, e.g. by nitrate. For samples collected specifically for the Baseline Scotland project, sample sites were selected so as to be as representative as possible of groundwater in the local area. Groundwater sources that were poorly constructed or close to obvious and significant sources of contamination were avoided. Each sample source and site was assessed at the time of sampling, in particular the source construction and the surrounding land use, to identify any potential sources of contamination that could affect the chemistry of sampled groundwater and the risk of contamination.

When samples were collected for other projects, site selection was not always focused on obtaining groundwater samples that were representative of the surrounding aquifer. However, there is a high degree of confidence that all the samples in the dataset are free from obvious point source contamination. The check of sample chemistry analyses and of any



Plate 5 Collecting groundwater samples for the Baseline Scotland project.

supplementary information was checked rigorously. In many cases, particularly for samples collected since 1999, similarly detailed site assessments were made at the time of sampling. The location of the sampling points is shown in Figure 8. Details of the distribution of samples by source type, aquifer and land use are presented in Table 3.

The majority of samples (500) were collected from boreholes. In most cases, the sampled boreholes had been pumped regularly in the period before sampling, and were pumping at the time of sampling. Hence, groundwater samples were as representative of groundwater in the aquifer as possible. Where boreholes were not pumping on arrival, they were pumped for at least 10 minutes (and usually 30 minutes) before sample collection, allowing for the stabilisation of field physico-chemical parameters. Pumped groundwater samples represent the compositions of water entering the borehole over its open-hole section. As such, each sample may represent a mixture of groundwaters with different chemistry, especially where the borehole screen extends over more than one fracture inflow.

The next most common source type was springs, with 116 samples; and 23 samples were from shallow wells. The large diameter of shallow wells means it can be difficult to ensure that the well is sufficiently purged before sampling to allow stabilisation of field parameters and allow a representative sample to be obtained. However, if the sampled well is in daily use for drinking water supplies, it is regularly pumped and therefore likely to give a representative groundwater sample. Springs are constantly flowing and therefore are naturally purged. Both springs and wells typically tap shallow groundwater and have relatively small catchments, and so are

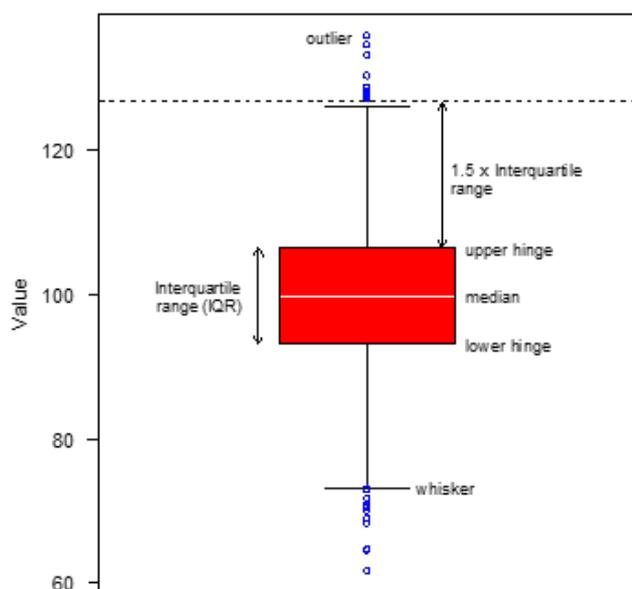


Figure 9 Example of an annotated box plot based on a simulated normal distribution of 2000 values with mean = 100 and standard deviation = 10. In this case, the whiskers are placed at no more than 1.5 x the interquartile range; outliers lie beyond this range.

less likely than boreholes to represent a mixture of groundwaters from different depths. Four samples were collected from shafts or adits directly tapping coal or other mine workings.

### 4.3 SAMPLING AND ANALYSIS

For samples collected specifically for the Baseline Scotland project, the sampling procedure is described below. For previous surveys, sampling methodologies are given in the references cited in Section 4.1. For most of the samples, field measurements were made for pH, dissolved oxygen (DO), redox potential (Eh), water temperature, specific electrical conductance (SEC) and alkalinity. Where possible, pH, DO and Eh were measured in an in-line flow cell to minimise atmospheric contamination and parameters were monitored until stable readings were obtained, which was typically for 10 to 15 minutes. Where not possible, measurements of water direct from the pump outlet were made in a bucket within one to two minutes of water abstraction.

Water samples were collected from each site for subsequent laboratory analysis. Analyses were carried out at BGS laboratories in Keyworth and Wallingford, and for some trace element analysis before 2005, at ACME laboratory in Canada. Samples for major and trace element analysis were filtered through 0.45  $\mu\text{m}$  filters and collected in factory-new polyethylene bottles rinsed with sample water before collection. Three filtered aliquots were collected at each site. Two were acidified to 1% v/v with Aristar  $\text{HNO}_3$ , one for analysis of major cations, total sulphur and Si by ICP-OES (inductively coupled plasma-optical emission spectroscopy), and the other for a large range of trace elements by ICP-MS (inductively coupled plasma-mass spectrometry). A third aliquot was left unacidified for analysis of anions by ion chromatography ( $\text{NO}_3^-$ -N, Cl, Br, F) and automated colorimetry ( $\text{NH}_4^-$ -N, I). Samples were also collected in chromic-acid-washed glass bottles for dissolved organic carbon (DOC) analysis, after filtration using silver-impregnated 0.45  $\mu\text{m}$  filters. DOC was measured by carbon analyser. Additional samples were collected for analysis of the stable-isotopes analyses  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ -DIC), and the dissolved gases CFC,  $\text{SF}_6$ ,  $\text{CO}_2$  and  $\text{CH}_4$  – these are not discussed further in this report. Analyses of total sulphur are hereafter expressed as  $\text{SO}_4$  and alkalinity as  $\text{HCO}_3$ .

BGS laboratories run a series of QA checks, including analysis of certified standards, to ensure integrity of analyses. The mean absolute charge imbalance for all samples in the dataset was 0.55% and the median 0.42%. A total of 82.5% of the whole dataset, and 89% of the samples with the highest confidence rating, have ionic balances of within +/- 5%. Six had ionic balances >10%, most often associated with high iron.

### 4.4 DATA INTERPRETATION AND PRESENTATION

#### 4.4.1 Summary statistics

Summary statistics were calculated for the whole dataset for each of the measured parameters (Table 4 in Appendix 2), and for each of the separate aquifer groups (Table 5 to Table 15

Table 3 Summary of groundwater samples by aquifer group, land use and source type.

Land use	Arable			Improved pasture			Mixed agricultural			Mixed rural land use			Pasture DPP			Recreational			Semi natural			Urban and/or urban industrial			Woodland			Unknown			Total							
	B	S	W	B	S	W	B	S	W	A	B	S	W	B	S	W	B	S	W	A	B	S	W	B	S	W	A	B	S	W		A	B	S	W	U		
Aquifer Group				17			1			5			10													1		19	2	1							62	
Permo-Triassic				4			6			2	1		2	1		5												14	1								55	
Carboniferous	7	1		3			3			1	1		7			1												2	16								56	
Carboniferous mined																																						
Old Red Sandstone North	9			14	2	1	7		1	6	1		7			4												33	8	2							99	
Old Red Sandstone South	23	3	1	8	2		12	1		9	2		3			5												44	3	3							125	
Silurian-Ordovician	2			14	10	1	1						7	1		1												9	8	3	1							73
Calcareous				6						3	1		1																					1	1		18	
Precambrian North				4			1			4	2					1												7	9	1							41	
Precambrian South	2	1		3	4	1	2			7	1		1	1		2												9	1								39	
Igneous volcanic	5			4	3		4			1			2			2												12	3								43	
Igneous intrusive	1			3	2	1	1	1	1	1			4															6	3	1							34	
<b>Total</b>	60	5	2	80	23	4	36	6	2	1	39	9	0	44	2	2	0	0	0	1	25	19	0	22	1	1	1	2	169	39	11	2					645	
	67			107			44			49			48			21			45			24			17			223										

Source type: B – Borehole; S – Spring; W – Well; A – Adit; U – Unknown

in Appendix 2). These provide an indication of the range of values observed, and can be compared with similar tables from other areas.

The median value provides the preferred estimate of the 'central tendency' for a particular dataset since it is less affected by extreme concentrations than the arithmetic mean. Summary statistics have been reported in terms of range and percentiles (minimum, 10th, 25th, 50th, 75th, 90th, 95th and maximum) to provide a non-parametric summary of the chemical distribution (Table 4). Data for many trace elements were close to or below their respective individual detection (or reporting) limits, which can complicate the calculation of summary statistics. The total number of observations and the number of censored (below detection limit) observations are also reported (Table 4 to Table 15 in Appendix 2), to indicate the degree of censoring. Two methods were used to generate summary statistics for datasets with censored data. The non parametric Kaplan-Meier approach was used for most datasets; but where censoring was above 50% we used the 'regression on order' approach (ROS) following the recommendations of Lee and Helsel (2007).

For a discussion on the use of these methods in the Scottish Baseline Scotland project, and a comparison of these and other statistical approaches for dealing with censored data, see MacDonald et al. (2008).

#### 4.4.2 Box plots

Box plots provide a graphical summary of the distribution of data values in a dataset and are an effective way of comparing different distributions. They provide a rapid view of the central location of the distribution (the median), the spread of values (box length is the interquartile range (IQR), i.e. 25th to 75th percentile) and the presence of outliers (open circles beyond the whiskers, which extend to 1.5 times the interquartile range) (Figure 9). Note that the presence of outliers depends to some extent on the number of values summarised, as even perfectly 'normal' distributions can show outliers if there are sufficient values within the distribution. Helsel (2005) discusses how the classical box

plot can be adapted for displaying distributions containing censored data.

#### 4.4.3 Maps

A series of maps displays the spatial distribution of groundwater quality parameters. The chemical parameters are plotted on a base map of the bedrock aquifer groups (Figure 7). In most cases, four classes were used to display each chemical parameter on the maps, with the size and colour of the plotting symbol varying with each class. Class limits were broadly based on the 25th, 50th and 90th percentiles for the determinand range. These were simplified if there were insufficient distinct values to generate reliable percentiles. The maps were generated in R using the PBSmapping package with shapefiles generated by ArcGIS®.

#### 4.4.4 Cumulative probability plots

Cumulative probability plots provide an alternative way of examining variations in groundwater chemistry. They are presented in Appendix 1, in Figures 58 to 62. From the plots it is simple to visualise the variation in median ion concentrations (the points at which the probability is 0.5) in different aquifer groups. The slope of the line is related to the variance of the dataset and the shape of the line the extent to which the distribution conforms to a log-normal distribution. A straight line refers to a log normal distribution. Distinct changes in slope may indicate that the overall distribution is made up of two or more sub-populations with differing statistical properties.

The cumulative probability plots were calculated on an element-by-element basis. The NADA approach was chosen for calculating probabilities, choosing the appropriate method for dealing with censored data according to the criteria outlined in Section 4.4.1: in most cases, this was the Kaplan-Meier method. The x-axis in the plots is the log<sub>10</sub> transformed concentration; the y-axis shows the probability of a value exceeding a given concentration, plotted on a normal probability scale. The cumulative frequency (in percent) is 100 times the probability.

# 5 Groundwater chemistry

From a combined analysis of 646 groundwater samples, summary chemical data are presented in a series of Piper diagrams, maps, box plots, cumulative probability plots, and tables of summary statistical data. These show the enormous variation in inorganic chemistry of Scotland's groundwaters. They also demonstrate the varying controls that geology, groundwater flow regimes, land use and degree of human impact have on the chemical composition of groundwater.

## 5.1 PHYSICO-CHEMICAL CHARACTERISTICS

Groundwater temperature in Scotland averages around 10°C (Figure 10). The lowest median and largest range of temperatures is seen in shallow groundwater from Igneous intrusive aquifers, which tend to be at higher elevations and where near-surface fracture flows are strongly influenced by fluctuations in air temperature. Highest recorded temperatures are seen in groundwaters from Carboniferous mined aquifers, where deeper flows are influenced by the geothermal gradient.

Groundwater pH values are in most cases near neutral, with median values for individual aquifer groups in the 6.5–7.5 range (Figure 11). Some of the most acidic groundwaters are from the Igneous intrusive, Ordovician-Silurian and Permo-Triassic aquifers, although the lowest pH recorded was from a Carboniferous mined aquifer. The pH values reflect the capacity of the aquifers for acid buffering, notably the occurrence of carbonate minerals. Granitic aquifers within Igneous intrusive aquifers, sandstones within Permo-Triassic

aquifers, and Ordovician-Silurian aquifers all appear to lack or to have limited abundance of carbonate minerals, and are least capable of pH-buffering. Carboniferous mined aquifers have the largest observed pH range.

The redox status of the groundwaters is indicated by the redox potential (Eh) and by concentrations of dissolved oxygen (DO), as well as by other redox-sensitive elements. The data indicate

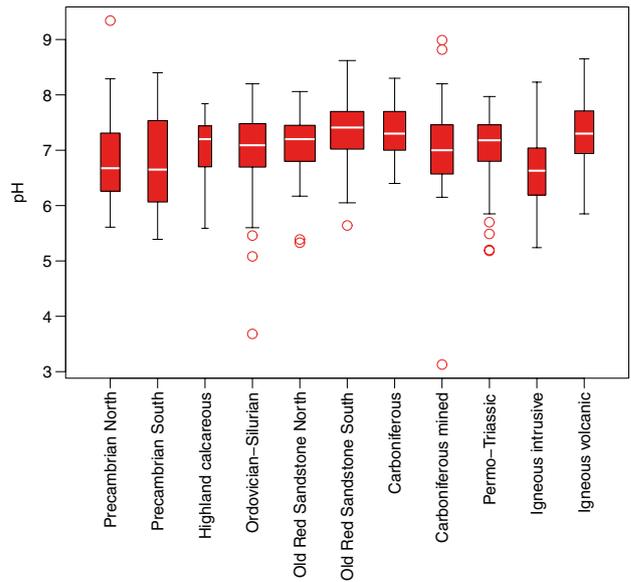


Figure 11 Statistical summary of groundwater pH in Scotland's bedrock aquifers.

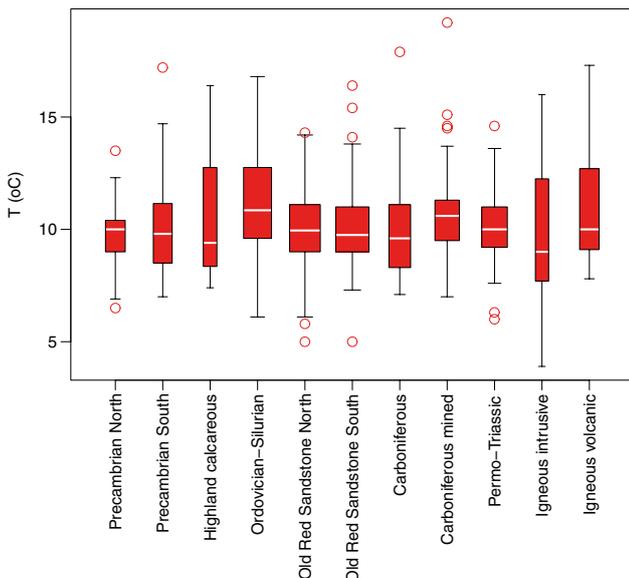


Figure 10 Statistical summary of groundwater temperature in Scotland's bedrock aquifers.

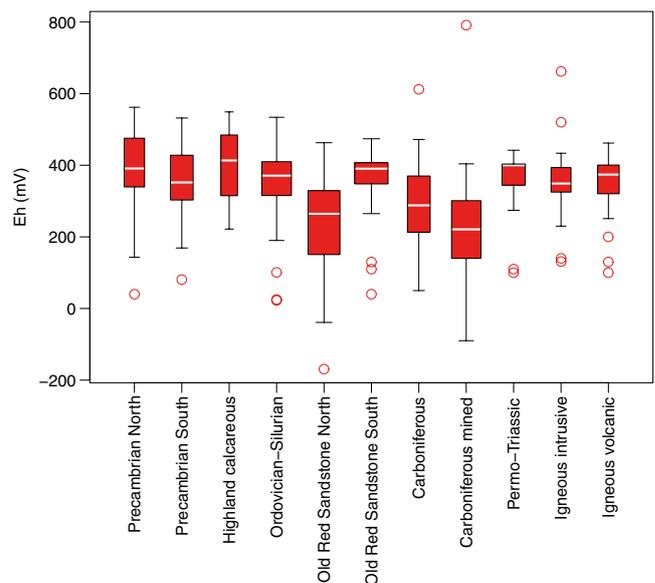


Figure 12 Statistical summary of groundwater redox potential (Eh) in Scotland's bedrock aquifers.

that Scotland's aquifers contain dominantly oxic groundwater, with typical Eh >250 mV (Figure 12) and DO values of >1 mg/L (Figure 13).

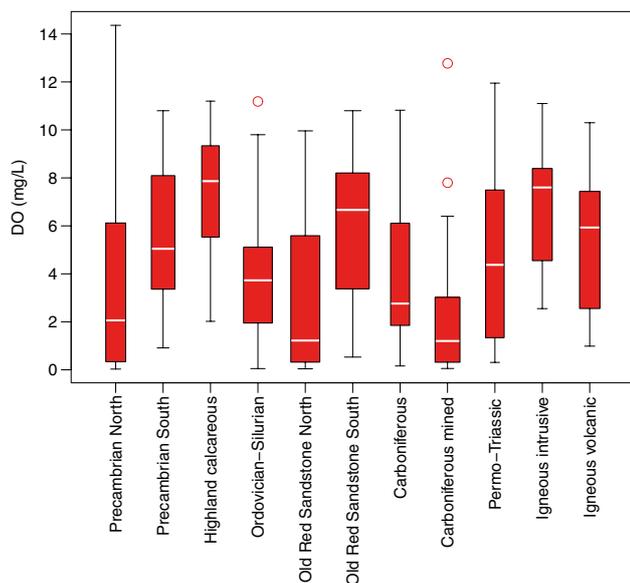


Figure 13 Statistical summary of dissolved oxygen (DO) concentrations in groundwater in Scotland's bedrock aquifers.

Although many of the aquifers showed a few examples of reducing groundwater, controlled by local flow conditions, reducing groundwater only appears dominant in groundwaters from Old Red Sandstone North, Carboniferous, and Carboniferous mined aquifers. In Old Red Sandstone North aquifers, mildly reducing groundwater is linked to the presence of fine-grained superficial deposits that restrict groundwater flows (Ó Dochartaigh et al., 2010). In the Carboniferous aquifers, redox conditions are controlled by the presence of organic matter and sulphide minerals in the sedimentary rocks, particularly in the Coal Measures and Clackmannan groups (Ó Dochartaigh et al., 2011). Groundwaters in Carboniferous as well as the Carboniferous Mined aquifers can be strongly reducing, with methane detectable in some.

Salinity varies within and between different aquifers, with median SEC values for individual aquifer groups typically between 200  $\mu\text{S}/\text{cm}$  and 800  $\mu\text{S}/\text{cm}$  (Figure 14). The highest SEC values tend to be found in Carboniferous mined groundwaters, although outlier saline compositions occur in most of Scotland's aquifers.

Relatively high SEC values reflect mineral reactions in the aquifers, being most pronounced in the Carboniferous sedimentary aquifers. Some saline Na-Cl or Na-SO<sub>4</sub> waters in Ordovician-Silurian aquifers flow from mineral springs (e.g. Moffat Well and St Ronan's Sulphur Spring). These probably reflect both the impact of mineral reactions with shale units within the aquifer and relatively long residence time

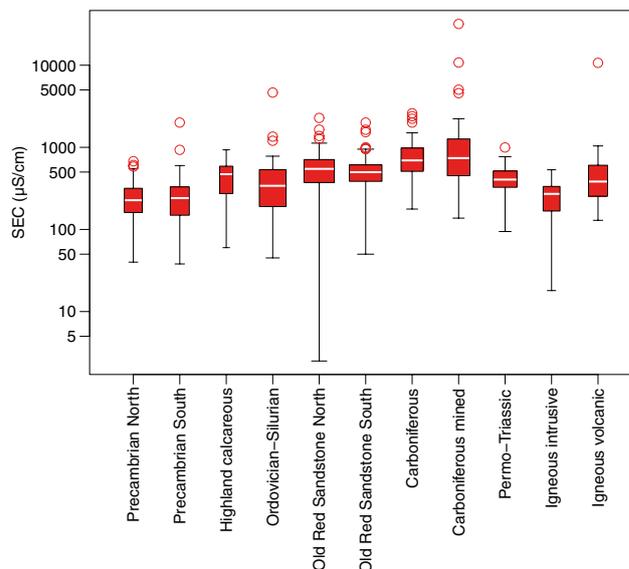


Figure 14 Statistical summary of groundwater SEC in Scotland's bedrock aquifers.

groundwaters flowing from depth via faults (MacDonald et al., 2008). Many high conductivity values in near-coastal settings (Figure 15) are likely to reflect the impact of seawater inflow to the aquifer.

## 5.2 MAJOR IONS

The distribution of major ion compositions in the groundwaters is summarised in a series of Piper diagrams (Figure 16), illustrating the large range and variability within each aquifer group. The major ion compositions observed reflect the combined influence of mineral reactions between groundwater and aquifer rock (dissolution and ion-exchange reactions), groundwater residence time, and saline intrusion. Water types in Scotland's aquifers include Ca-HCO<sub>3</sub>, Na-HCO<sub>3</sub>, Na-Cl and Ca-Mg-SO<sub>4</sub>, as well as mixed compositions. No single water type dominates overall. The Piper diagram also indicates the distribution of more saline waters (SEC > 1000  $\mu\text{S}/\text{cm}$ ). The most extreme variations in chemistry in individual aquifers are seen in Carboniferous and Carboniferous mined groundwaters. Highland calcareous aquifers have the most restricted range of compositions, being mainly of Ca-HCO<sub>3</sub> type, indicating that the dominant control on groundwater chemical composition is reaction with carbonate minerals in the rocks. Igneous intrusive aquifers also show a relatively restricted range in major ion chemistry, but with Ca-HCO<sub>3</sub> less prominent. Relative SO<sub>4</sub> enrichment occurs in several aquifers, especially the Carboniferous and Permo-Triassic aquifers. Across the whole dataset, 2.3% of samples have concentrations of SO<sub>4</sub>, and 3.3% have concentrations of Cl, above the regulatory monitoring limit for drinking water (250 mg/L for each at treatment works). Examples of exceedances of both of these are found in most of the aquifers.

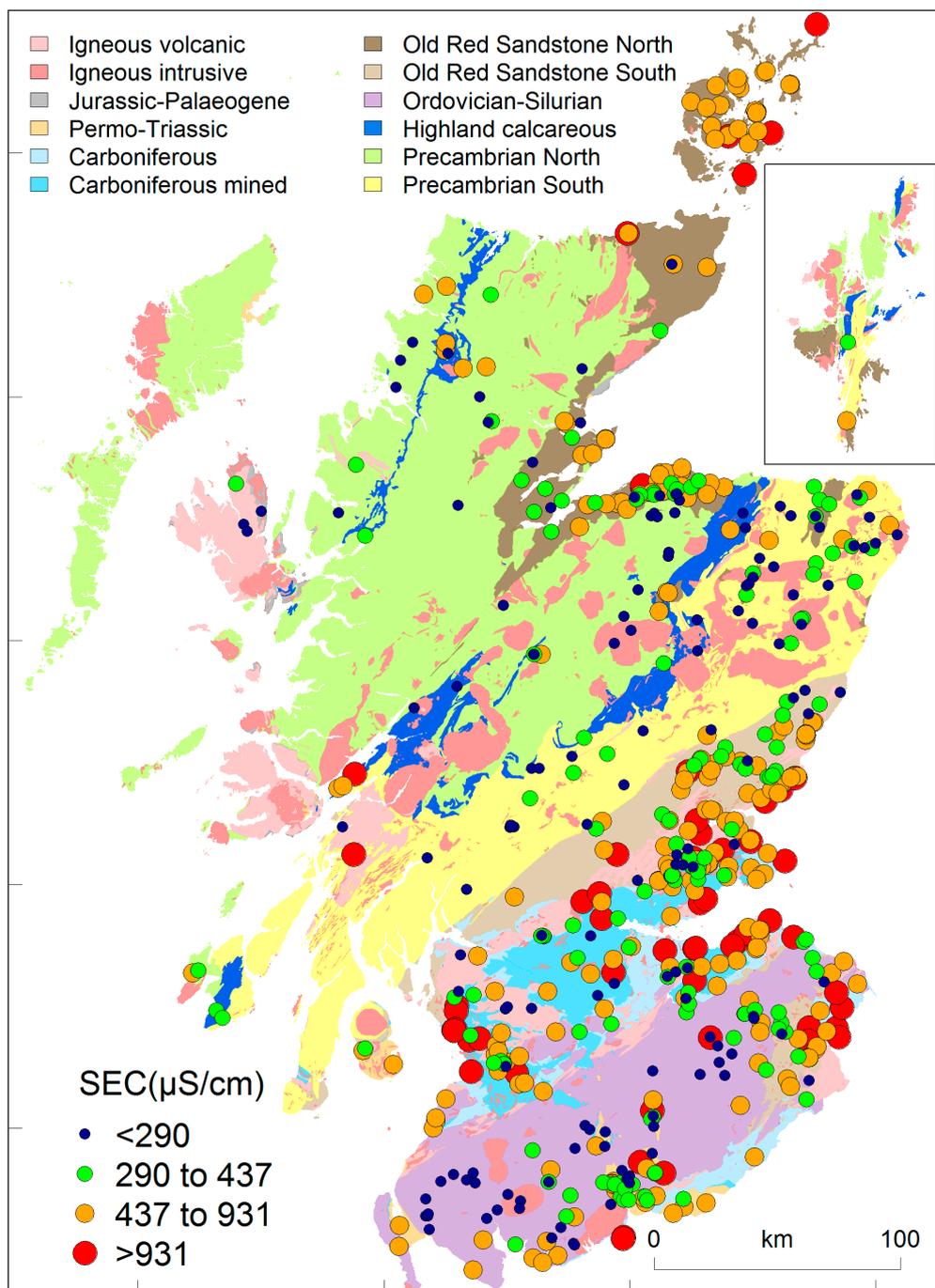


Figure 15 Map showing the distribution of groundwater SEC in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

The concentration ranges of the major ions Ca, Mg, Na, K, Cl,  $\text{SO}_4$  and alkalinity (as  $\text{HCO}_3$ ) all show maximum values within the Carboniferous mined group (Figure 17). Carboniferous aquifers (where not specifically known to be mined) also have relatively high concentrations of these ions, although they lack the extreme outliers present in the mined group (Figure 18, Figure 19, Figure 20, Figure 21, Figure 22, Figure 23, Figure 24). The distribution of major ions in Carboniferous aquifers, both mined and not, reflects the presence of carbonate minerals. Most of the Carboniferous samples are saturated with respect to calcite, and have

near-neutral pH, reflecting the reaction of groundwater with carbonate minerals. Relatively high concentrations of other major ions also reflect interaction with silicate minerals, including clays. Such reactions are enhanced by acidic conditions generated by oxidation of pyrite and other sulphide minerals in the Carboniferous formations. This is particularly so in the Coal Measures and Clackmannan groups (Ó Dochartaigh et al., 2011). Sulphate concentrations reach up to 2100 mg/L in Carboniferous mined aquifers. Concentrations of  $\text{SO}_4$  are also high in a number of groundwaters from Carboniferous aquifers, caused by sulphide oxidation reactions.

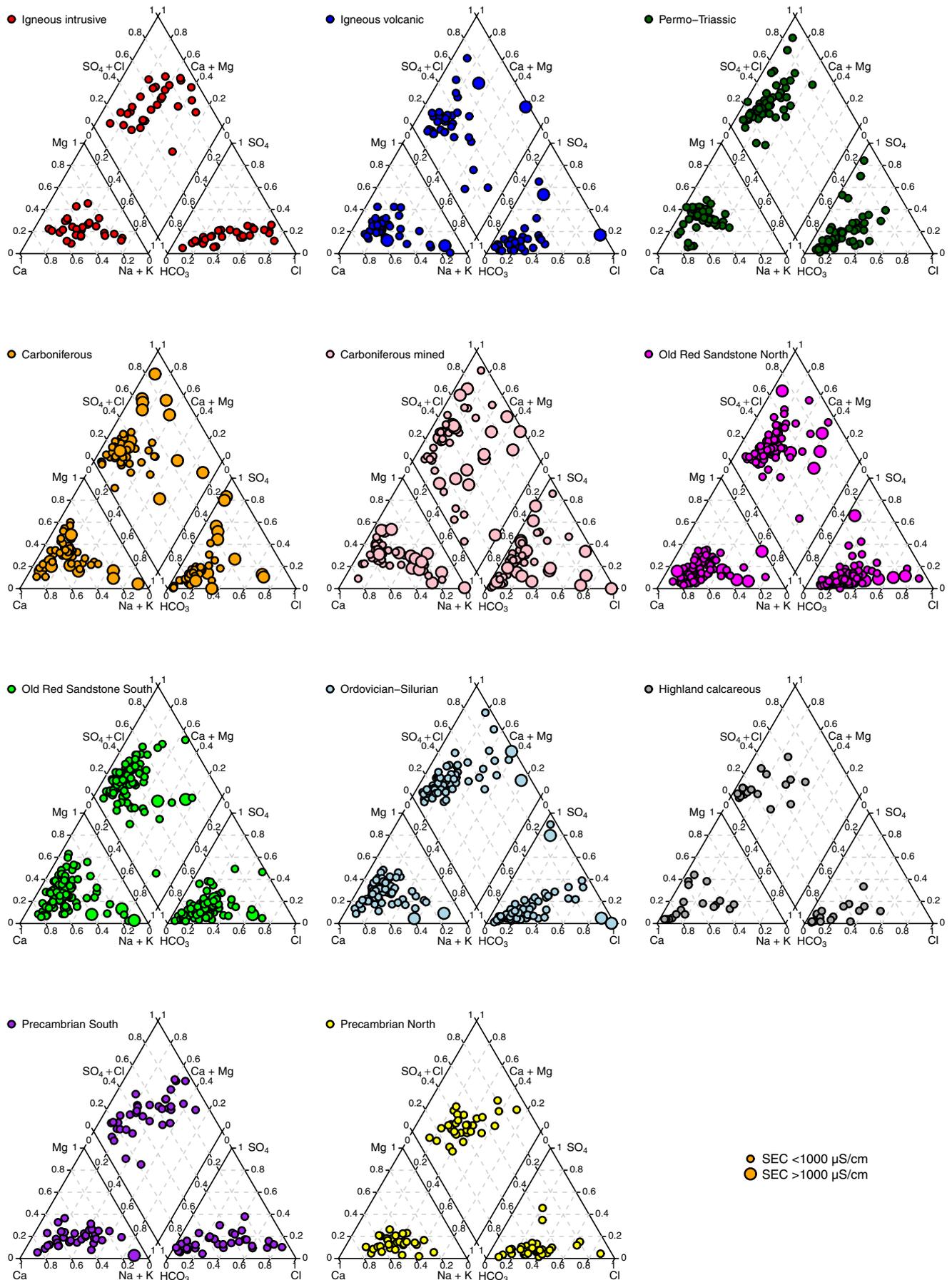


Figure 16 Piper (tri-linear) diagrams illustrating the distribution of major ion compositions of groundwater for each aquifer.

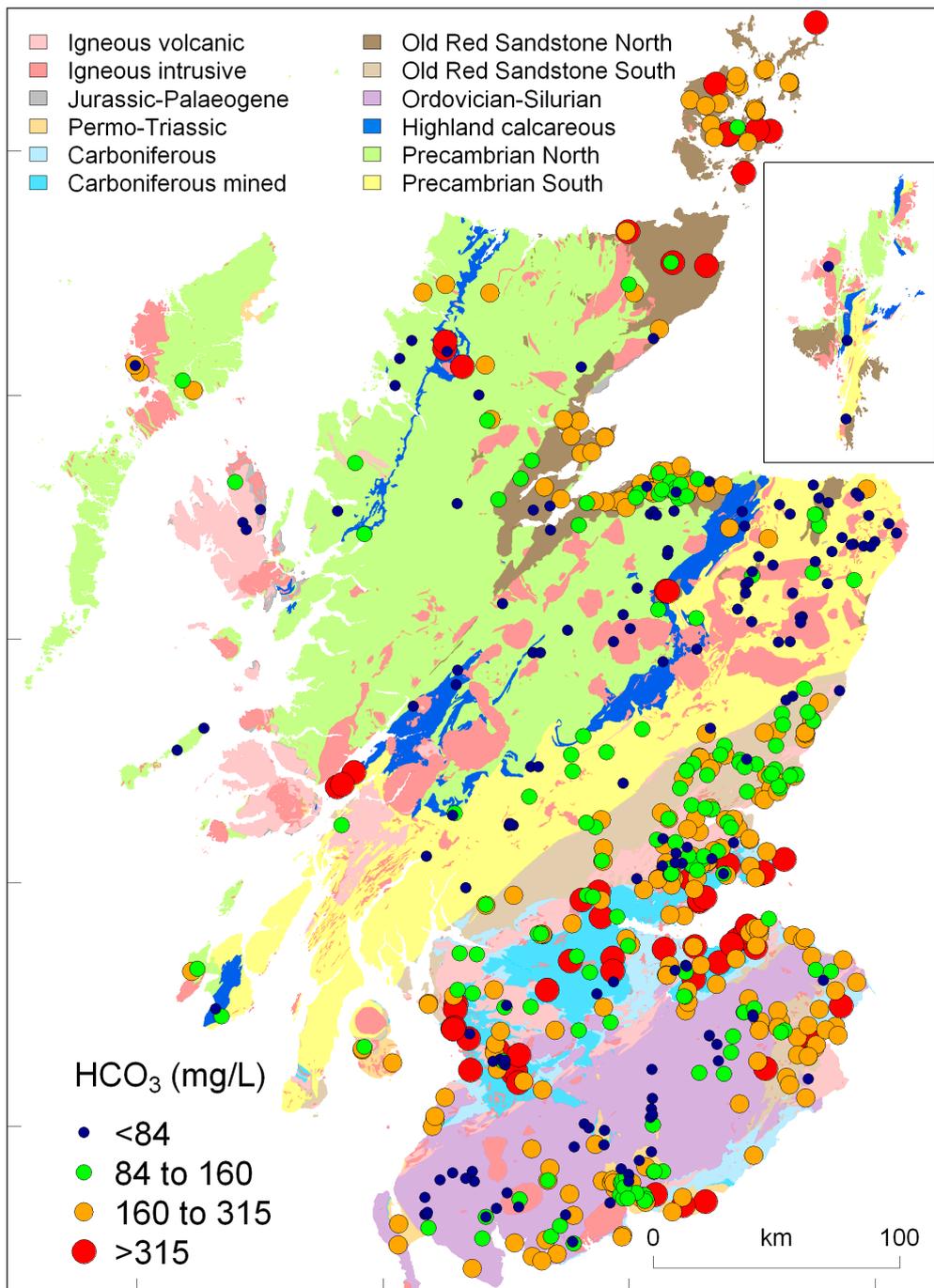


Figure 17 Map showing the distribution of groundwater  $\text{HCO}_3^-$  in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

The high major ion concentrations of groundwaters in Carboniferous aquifers can also be explained in part by residence time, since absolute concentrations in this aquifer correlate to some extent with borehole depth – in general, deeper groundwaters are more likely to have longer residence times. One groundwater sample from a borehole ~1000 m deep in the mined Coal Measures Group had a concentration of Ca of 1640 mg/L; Na of 5360 mg/L; and Cl of 11 500 mg/L, all of which point to water–rock interaction (dissolution and ion exchange) over long periods at depth.

In this case, the concentration of  $\text{SO}_4$  is low (5 mg/L) as a result of sulphate reduction, which is indicative of strongly reducing conditions.

In the dataset overall, only 20% of groundwaters are saturated with respect to calcite, although a larger proportion is close to saturation. The lowest concentrations of Ca and lowest alkalinity values are seen in Igneous intrusive and Igneous volcanic aquifers. This reflects the more indurated nature of the igneous compared to sedimentary rocks in

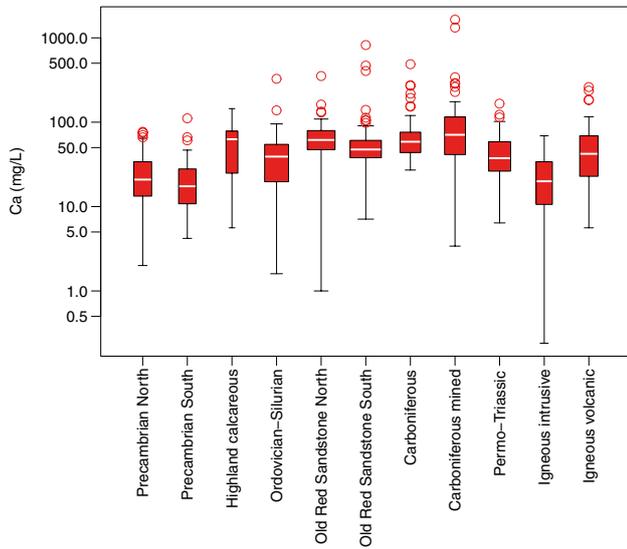


Figure 18 Statistical summary of Ca concentrations in groundwater in Scotland's bedrock aquifers.

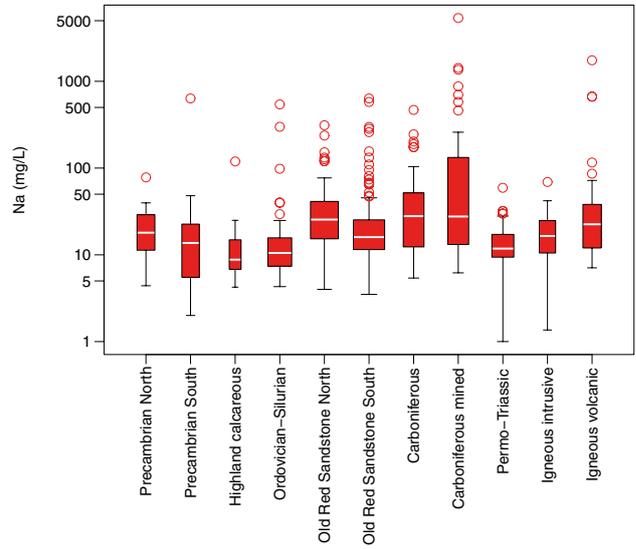


Figure 20 Statistical summary of groundwater Na concentrations in Scotland's bedrock aquifers.

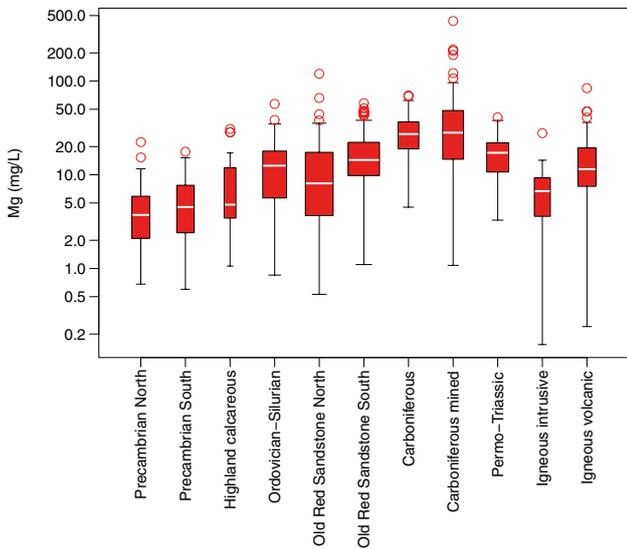


Figure 19 Statistical summary of Mg concentrations in groundwater in Scotland's bedrock aquifers.

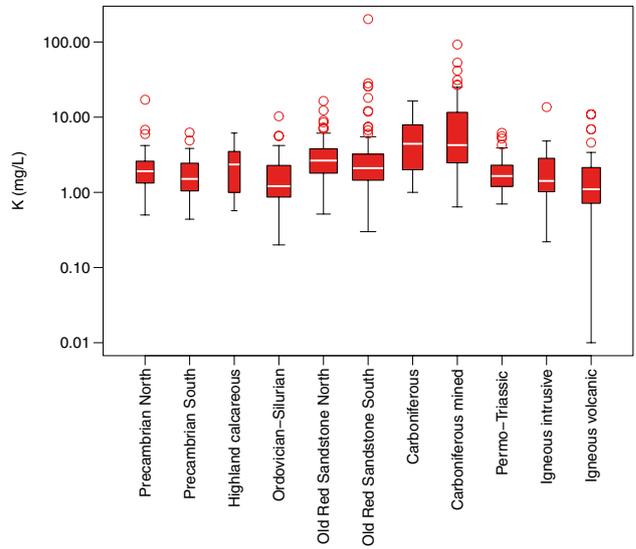


Figure 21 Statistical summary of K concentrations in groundwater in Scotland's bedrock aquifers.

Scotland, and slower reaction of silicates. In the case of the Igneous intrusive rocks, it also reflects the paucity of Ca in the solid phase, as the group is dominated by granitic rock types.

The Old Red Sandstone North aquifer is also characterised by relatively low Ca and alkalinity, with most groundwater samples being undersaturated with calcite.

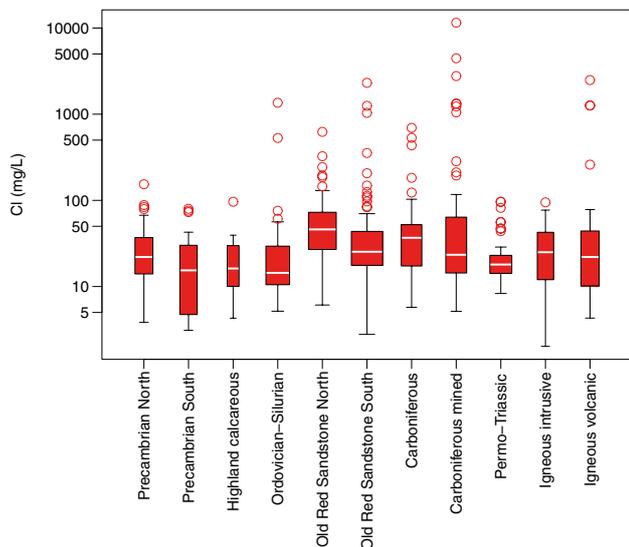


Figure 22 Statistical summary of Cl concentrations in groundwater in Scotland's bedrock aquifers.

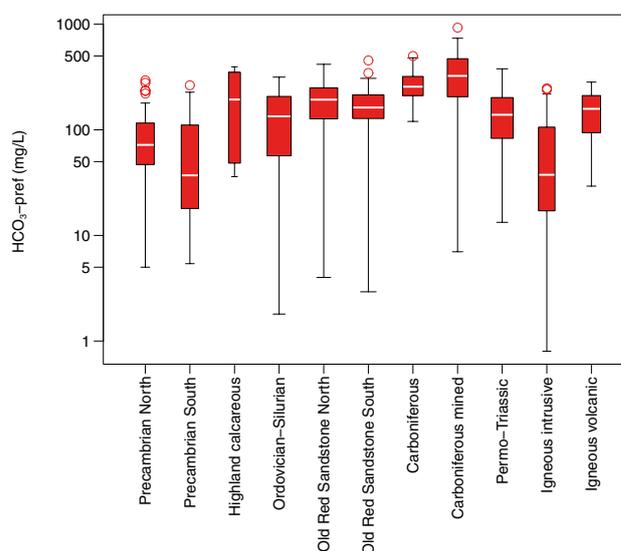


Figure 24 Statistical summary of HCO<sub>3</sub> concentrations in groundwater in Scotland's bedrock aquifers.

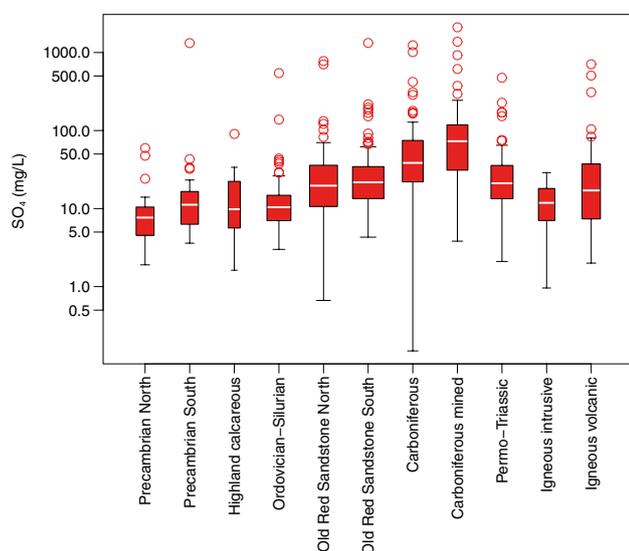


Figure 23 Statistical summary of SO<sub>4</sub> concentrations in groundwater in Scotland's bedrock aquifers.

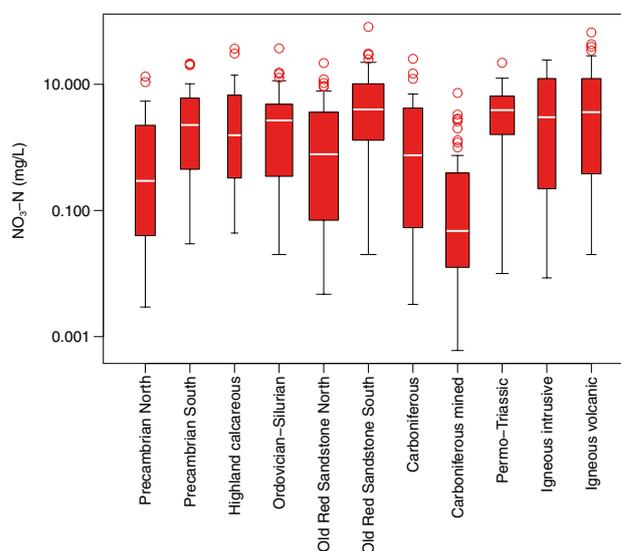


Figure 25 Statistical summary of NO<sub>3</sub>-N concentrations in groundwater in Scotland's bedrock aquifers.

### 5.3 NITROGEN SPECIES

Nitrate (NO<sub>3</sub>) is known to be present in high concentrations in many of Scotland's aquifers, and nitrate vulnerable zones (NVZs) have been designated in several aquifers. Of the samples collected, all aquifers except Carboniferous mined included some instances of groundwaters which exceed the national and EC limit for NO<sub>3</sub> in drinking water of 11.3 mg/L as NO<sub>3</sub>-N (50 mg/L as NO<sub>3</sub>). In the dataset as a whole, 11% of samples were found to be in excess of this limit. The Highland calcareous, Igneous volcanic and Old Red Sandstone South aquifers showed the largest proportion of high nitrate groundwaters (Figure 25). Lower concentrations found in the Carboniferous mined aquifers are related to the prevalence

of reducing conditions and the consequent loss of nitrate through denitrification, and probably also linked to a lower input of pollution-derived nitrate from surface sources, due to the longer groundwater residence times – much of the groundwater in Carboniferous aquifers may have been recharged before the intensification of agriculture since approximately the 1950s (Ó Dochartaigh et al., 2011).

There is a clear spatial trend in nitrate (NO<sub>3</sub>-N) concentration in groundwater in Scotland (Figure 26), with highest concentrations predominating in the east, including parts of the Precambrian South and Old Red Sandstone South aquifers. This distribution corresponds with areas of greatest agricultural activity in Scotland. A box plot of NO<sub>3</sub>-N concentrations

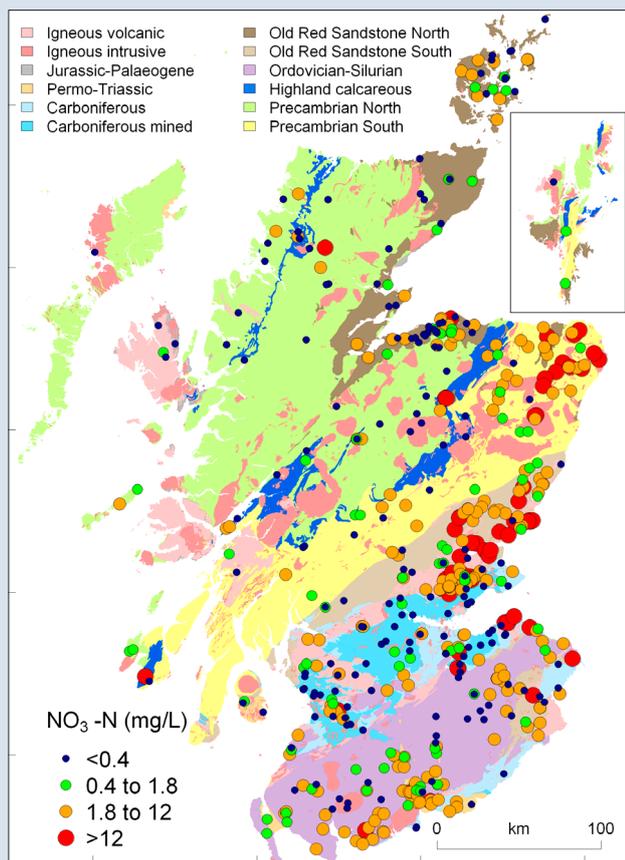


Figure 26 Map showing the distribution of  $\text{NO}_3\text{-N}$  concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

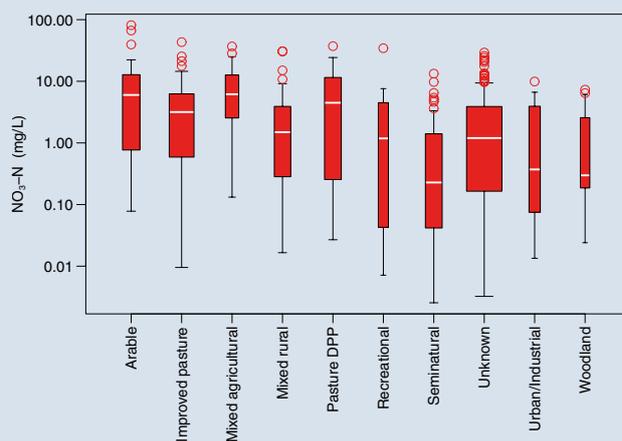


Figure 27 Statistical summary of groundwater  $\text{NO}_3\text{-N}$  concentrations by land use in Scotland.

( $\text{NO}_3\text{-N}$ )

categorised by land use (Figure 27) shows that highest values are observed in groundwaters below arable land. The sample with the highest observed  $\text{NO}_3\text{-N}$  concentration (81 mg/L as N) has correspondingly anomalous concentrations of P and K (41 mg/L and 201 mg/L, respectively), and is most likely to reflect the effect of direct fertilizer contamination. Relatively high  $\text{NO}_3\text{-N}$  concentrations are also a feature of improved pasture and mixed agricultural land (Figure 27). Low  $\text{NO}_3\text{-N}$  concentrations are more typical of semi-natural, urban/industrial and woodland land uses, although there are occasional outliers, such as one sample that exceeded the nitrate limit for drinking water even though the land use was semi-natural.

Concentrations of nitrite ( $\text{NO}_2\text{-N}$ ) are low in most samples, typically <math><0.02</math> mg/L. Two extreme outliers, with concentrations above 1 mg/L (as N), occur in recreational (including golf courses) and urban and/or industrial land use classes. Only 0.8% of analysed samples had concentrations of  $\text{NO}_2\text{-N}$  above the drinking water limit of 0.15 mg/L at consumers' taps.

Highest median values of  $\text{NH}_4\text{-N}$  are also found in groundwaters from recreational and urban/industrial land use classes (Figure 28). Concentrations of  $\text{NH}_4\text{-N}$  are highest overall in Carboniferous, Carboniferous mined and Old Red Sandstone North aquifers (Figure 29). These correspond with

reducing groundwaters, and are likely to have a natural origin from degradation of organic matter. 6.7% of analysed  $\text{NH}_4\text{-N}$  values are above the limit for drinking water (0.39 mg/L).

#### 5.4 DISSOLVED ORGANIC CARBON

Concentrations of dissolved organic carbon (DOC) are typically not more than a few mg/L in most groundwaters in Scotland, with no clear overall spatial pattern. There is no clear relationship with land use, except for two extreme outliers with concentrations of 70.8 mg/L and 47.1 mg/L, in arable and urban/industrial classes, respectively (Figure 30). These anomalous concentrations both occur in groundwaters from the Carboniferous mined aquifer, and may derive from natural oxidation of organic matter in the sediments. There is little evidence to suggest that they are caused by pollution. Relatively high DOC concentrations are also a feature of the Old Red Sandstone North aquifer (median DOC concentration >1 mg/L). Again, this most likely derives from natural degradation of organic matter in the reducing conditions that are widespread in the aquifer. By contrast, the range in DOC concentrations in groundwater from the Permo-Triassic is relatively low, reflecting the paucity of organic matter in these arid red-bed deposits.

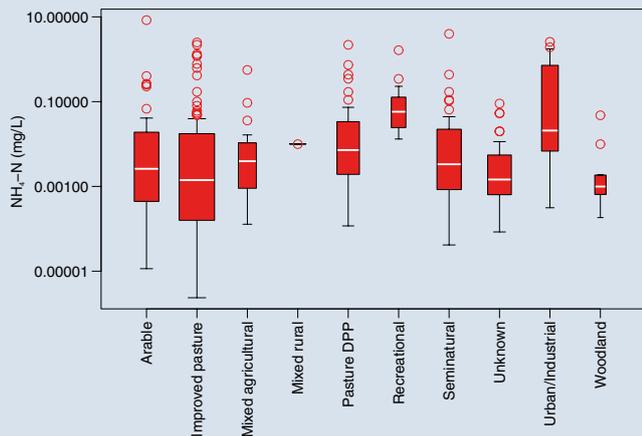


Figure 28 Statistical summary of  $\text{NH}_4\text{-N}$  concentrations in groundwater by land use in Scotland.

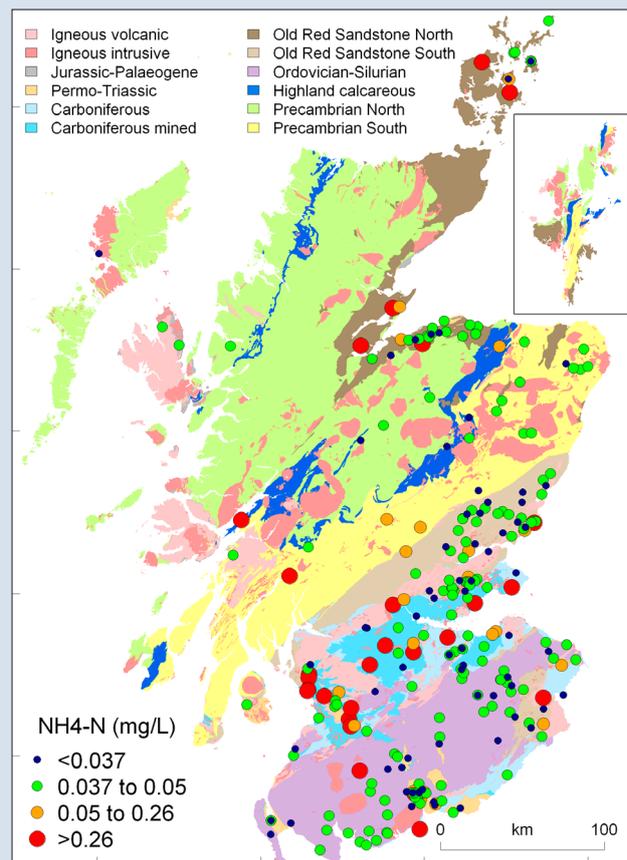


Figure 29 Map showing the distribution of  $\text{NH}_4\text{-N}$  concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

$(\text{NH}_4\text{-N})$

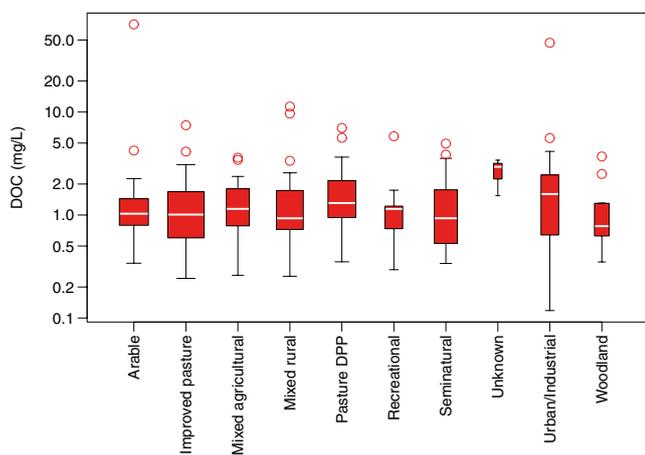


Figure 30 Statistical summary of dissolved organic carbon (DOC) concentrations in groundwater by land use in Scotland.

## 5.5 PHOSPHORUS

A single anomalously high P concentration, of 41 mg/L was mentioned above (in Section 5.3), which coincides with anomalously high  $\text{NO}_3\text{-N}$  and K, and is likely to be due

to agricultural pollution. Two other high P outliers occur within the Old Red Sandstone South aquifer in Strathmore (Figure 31, Figure 32) (Ó Dochartaigh et al., 2006), although for the lower of these outliers (7.8 mg/L) there is less evidence from elevated concentrations of other elements (e.g.  $\text{NO}_3$  or K) of agricultural contamination. Natural phosphate minerals in the red-bed aquifer are possibly responsible.

The Precambrian North aquifer shows consistently low P concentrations (Figure 32). This is likely to reflect the relative paucity of P-bearing minerals in Precambrian metamorphic rocks.

## 5.6 SILICON AND ALUMINIUM

Silicon and aluminium are the dominant chemical constituents of the non-carbonate aquifers in Scotland, but are limited to trace concentrations in the groundwaters because of low mineral solubility. The cumulative probability distribution of Si in groundwaters (Figure 33) show a restricted range due to the solubility limit imposed by quartz: 80% of the sampled groundwaters are saturated with respect to quartz. There is, unsurprisingly therefore, no clear

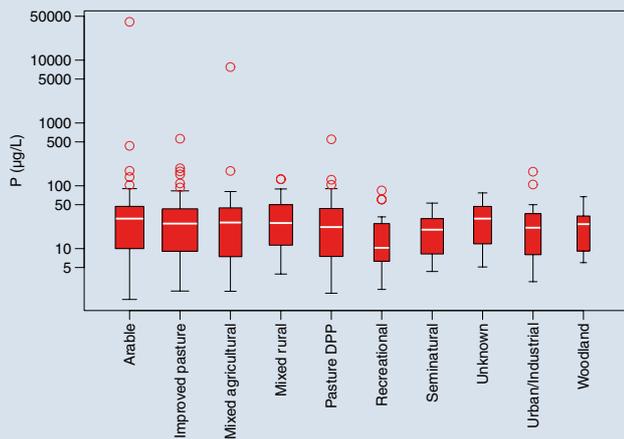


Figure 31 Statistical summary of P concentrations in groundwater in Scotland's bedrock aquifers.

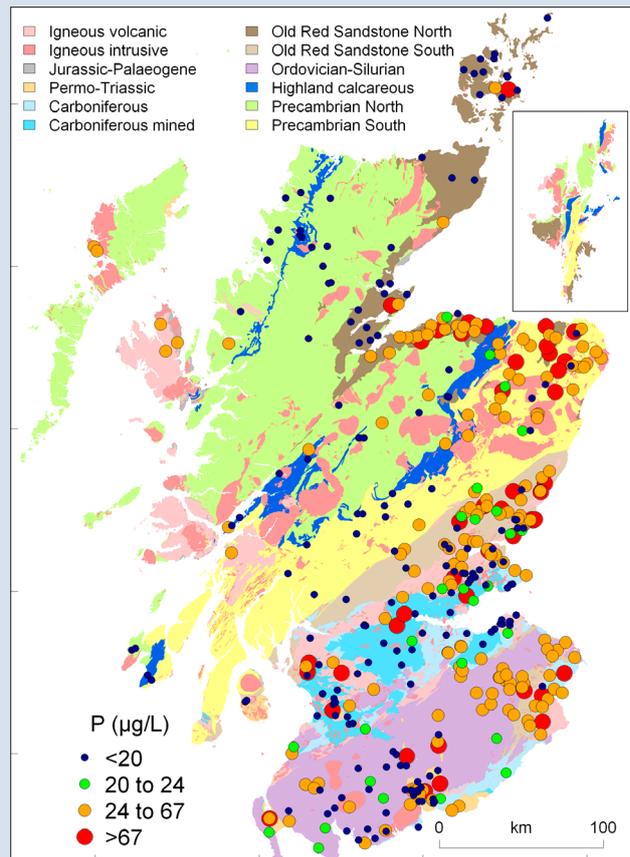


Figure 32 Map showing the distribution of P concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

(P)

spatial trend in Si concentrations (Figure 33), and no strong relationship with aquifer type apart from the volcanic aquifers and Precambrian south which show consistently higher concentrations (Figure 34).

Likewise, few clear spatial trends are seen for Al (Figure 35). Relatively low concentrations appear to be a feature of the Permo-Triassic aquifer, which are likely to be due to the limited presence of feldspars and clays in the quartz-dominated sandstones within this group. Relatively high Al concentrations are common in the Igneous intrusive aquifer, which are likely to be controlled by acidic conditions that are generated in these carbonate-poor, dominantly granitic rocks. A total of 1.3% of the sampled groundwaters had Al concentrations above the national limit for Al in drinking water (200 µg/L).

## 5.7 TRACE ALKALI METALS

Dominant sources of trace alkali metals in groundwater in Scotland are likely to be clay minerals: these metals are well

known to play an active part in cation-exchange reactions with clays. Most of the groundwater samples have Cs concentrations in the range 0.01–10 µg/L, and by far the highest values are seen in the Old Red Sandstone North aquifer (Figure 36), with concentrations up to 19 µg/L. The groundwaters affected are all reducing with respect to Fe and Mn (Edmunds and Smedley, 2000).

Concentrations of Li appear to be relatively high in groundwaters in the Carboniferous and Carboniferous mined aquifers (Figure 37), and may derive in part by mixing with deep saline formation waters in the aquifers. The lowest Li concentrations are seen consistently in the Highland calcareous aquifer, and is likely to reflect the limited availability of Li in carbonate rocks.

Concentrations of Rb are highest in the Carboniferous mined aquifer, but as with Cs, relatively high concentrations are also seen in Old Red Sandstone North groundwaters (Figure 38). The dominant sources of Rb are likely to be clay minerals, with the accumulation of dissolved concentrations related to groundwater residence time.

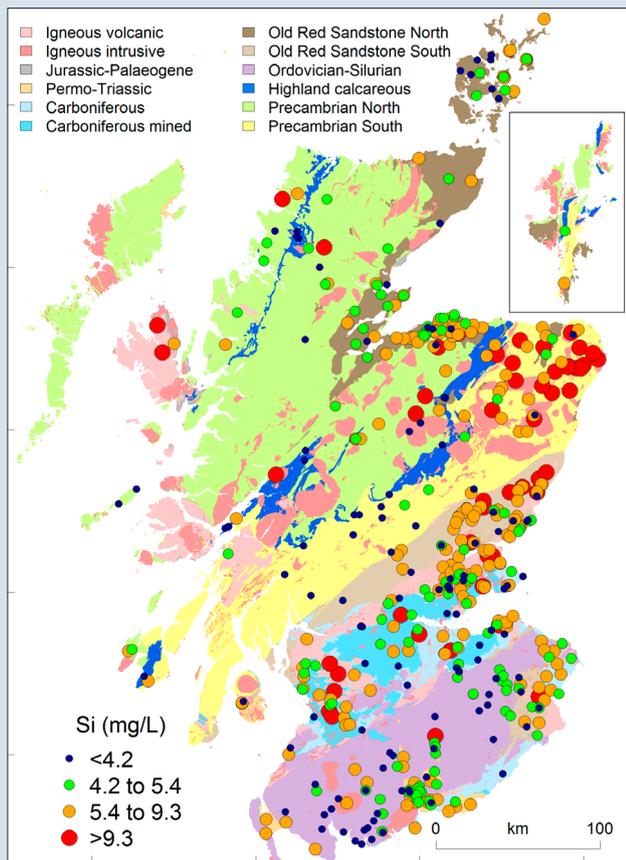


Figure 33 Map showing the distribution of Si concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

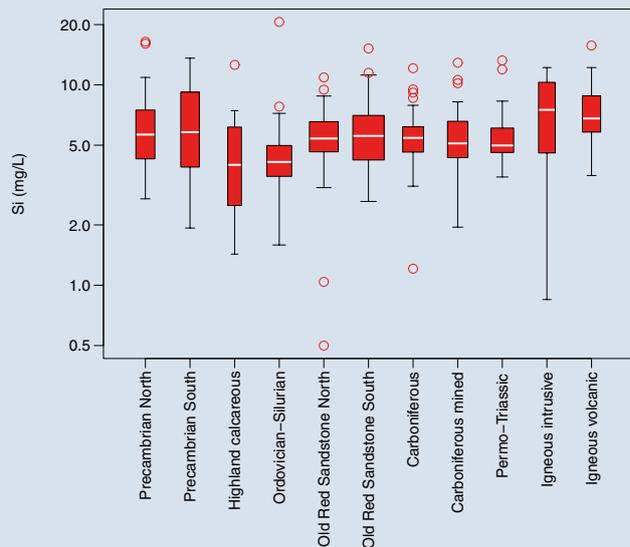


Figure 34 Statistical summary of concentrations of Si in groundwater in Scotland's bedrock aquifers.

(Si)

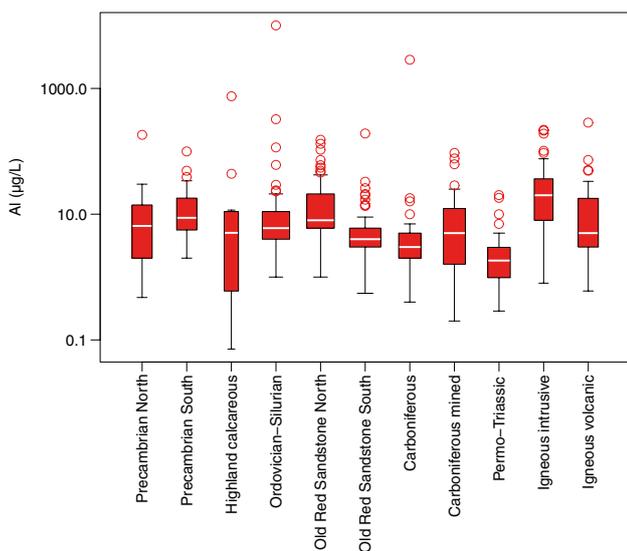


Figure 35 Statistical summary of concentrations of Al in groundwater in Scotland's bedrock aquifers.

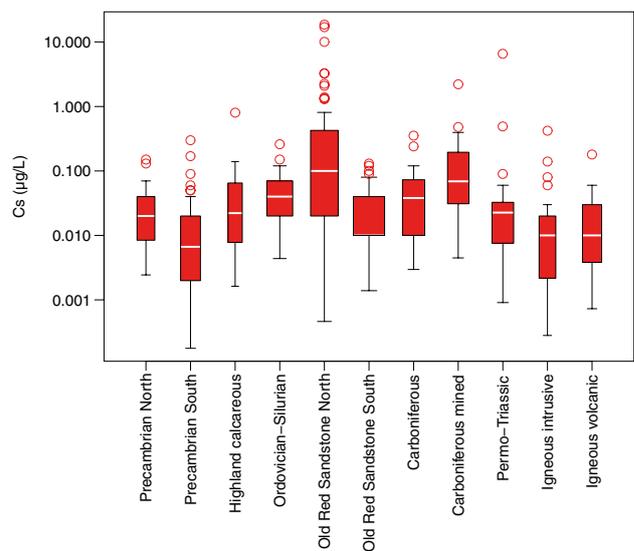


Figure 36 Statistical summary of concentrations of Cs in groundwater in Scotland's bedrock aquifers.

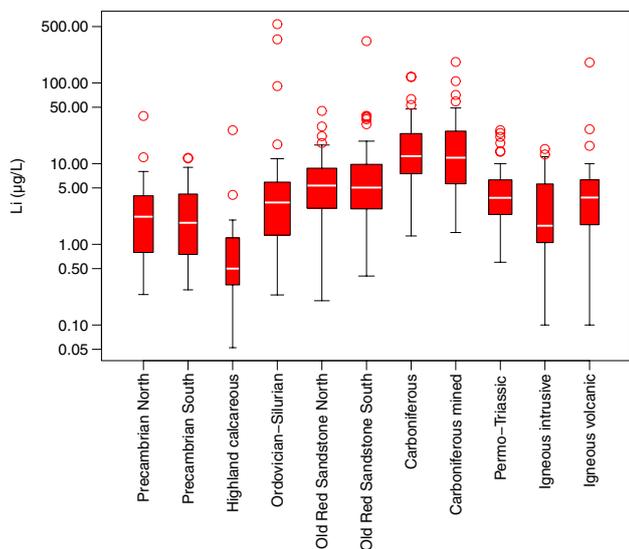


Figure 37 Statistical summary of concentrations of Li in groundwater in Scotland's bedrock aquifers.

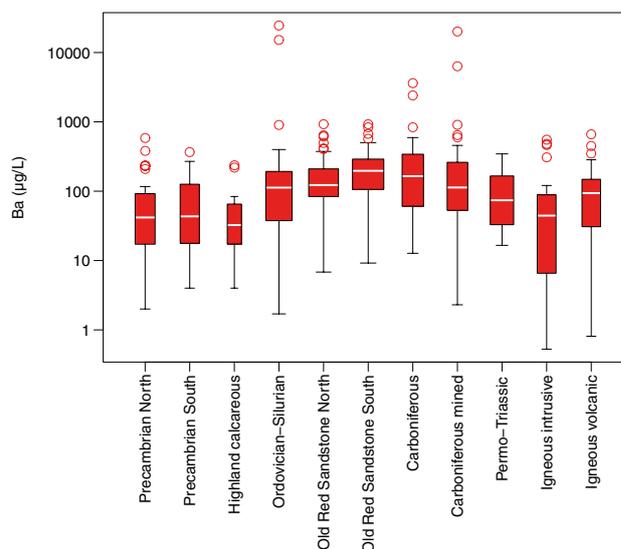


Figure 39 Statistical summary of concentrations of Ba in groundwater in Scotland's bedrock aquifers.

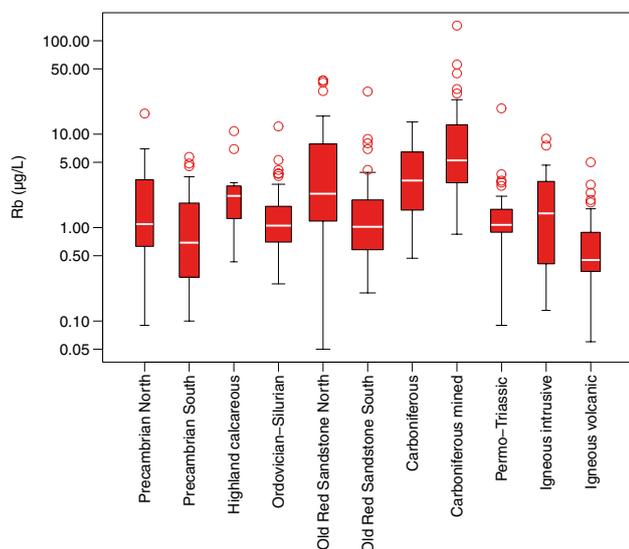


Figure 38 Statistical summary of concentrations of Rb in groundwater in Scotland's bedrock aquifers.

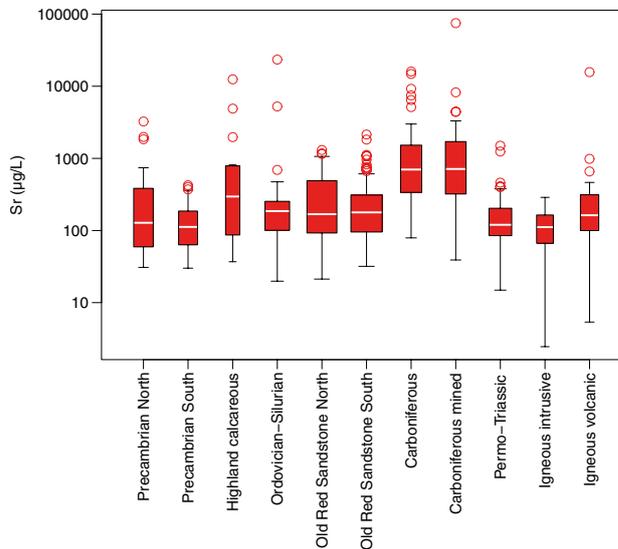


Figure 40 Statistical summary of concentrations of Sr in groundwater in Scotland's bedrock aquifers.

## 5.8 ALKALINE EARTH ELEMENTS

There is a large range in Ba concentrations in the sampled groundwaters, with some extreme outliers (>10 mg/L) in samples from Ordovician-Silurian and Carboniferous mined aquifers (Figure 39). Multimodal populations are seen in the cumulative probability distribution (Figure 59). Concentrations of  $\text{SO}_4$  are an important influence on Ba mobility, due to barite solubility constraints. A total of 52% of samples where there were sufficient data to model the speciation were saturated with respect to Ba.

All analyses of Sr in the sampled groundwaters were above detection limit. As with Ba, extreme outliers with concentrations

>10 mg/L occur, but are uncommon. The highest concentrations occur in Carboniferous and Carboniferous mined aquifers (Figure 40). Strontium shares behavioural traits with Ca, and Sr is enriched in groundwaters from Ca-rich aquifers. Significant mineral sources of Sr are likely to be carbonates, clays and, in the case of basaltic volcanic rocks, calcic plagioclase.

## 5.9 TRANSITION METALS

Concentrations of dissolved Fe and Mn in groundwater are low in most of the sampled groundwaters, related to the oxic conditions of most groundwaters in Scotland. However, where reducing conditions occur, they result in increased solubility of

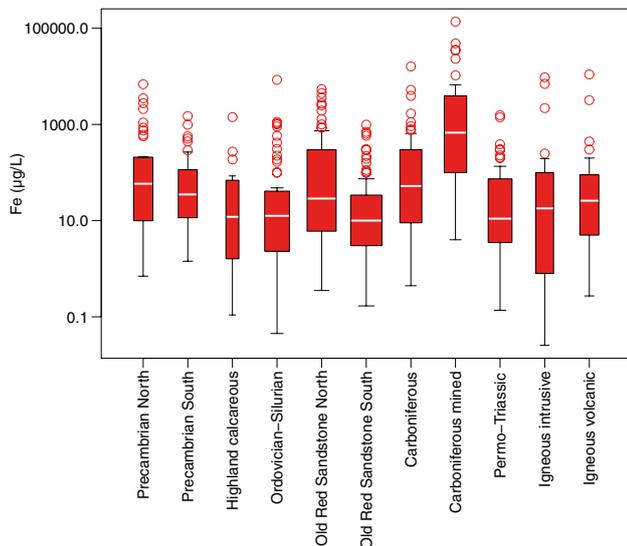


Figure 41 Statistical summary of concentrations of Fe in groundwater in Scotland's bedrock aquifers.

Fe and Mn oxides. A large range, in the concentrations of both metals occurs in several aquifers, with the highest concentrations seen in reducing groundwaters from the Carboniferous mined aquifer (Figure 41, Figure 42). Release from pyrite is also possible. Relatively high concentrations are also observed in groundwaters from the Old Red Sandstone North (Ó Dochartaigh et al., 2010), where reducing conditions are also widespread. The lowest 35 concentrations are seen in the dominantly oxic groundwaters of the Old Red Sandstone South aquifer. Across all the sampled groundwaters, 21% exceed the national drinking water limit for Fe (200 µg/L) and 27% the limit for Mn (50 µg/L).

Concentrations of Co and Ni are also highest in groundwaters from the Carboniferous mined aquifer. A few instances of concentrations above the drinking water limit for Ni (20 µg/L)

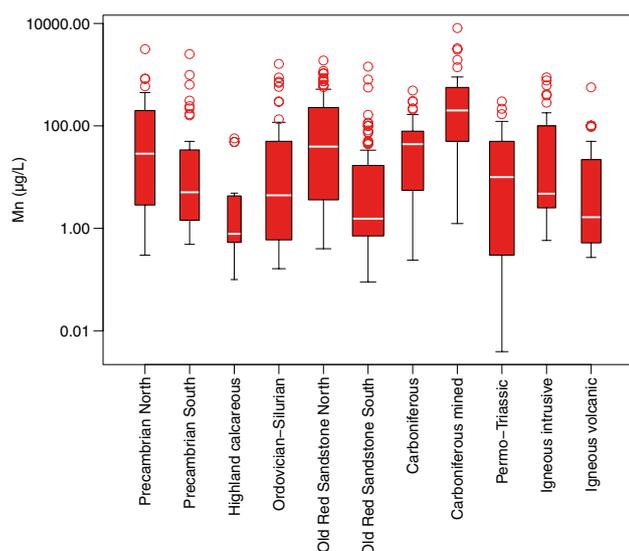


Figure 42 Statistical summary of concentrations of Mn in groundwater in Scotland's bedrock aquifers.

occur in a number of aquifers, but the majority of samples are below this limit (Figure 43). In contrast, concentrations of Cu are relatively low in the Carboniferous mined aquifer compared to other aquifers in Scotland. Concentrations in all samples except one (from the Highland calcareous aquifer) are well below the drinking water limit of 2000 µg/L.

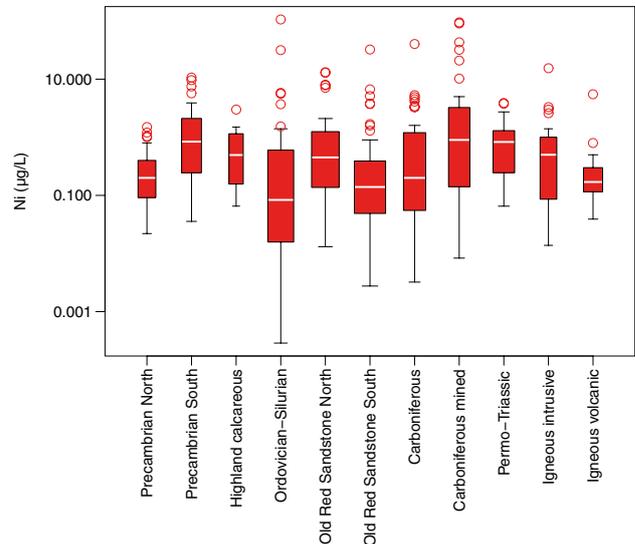


Figure 43 Statistical summary of concentrations of Ni in groundwater in Scotland's bedrock aquifers.

The largest range and lowest median concentrations of both Cr and Mo are seen in the Igneous intrusive aquifer. For Cr in particular (Figure 44), the low median is consistent with low Cr mineral concentrations in granitic rocks, which are the largest single rock type in the Igneous intrusive aquifer group. The high Cr outliers are likely to be related to occurrences of less common intrusive igneous rocks, such as mafic layered intrusions, which can contain significantly higher Cr mineral concentrations. Concentrations of Cr in all the groundwater samples are at least an order of magnitude less than the drinking water limit of 50 µg/L. Molybdenum concentrations are typically in the range <0.1–10 µg/L (Figure 45). There is no limit for Mo in drinking water in Scotland, but the World Health Organisation (WHO) recommends a health based guideline of 70 µg/L. Concentrations in all the groundwater samples from Scotland are lower than this: the maximum observed value is 36 µg/L, and most are at least an order of magnitude less.

Vanadium (V) is notably higher in groundwaters from the Old Red Sandstone South aquifer (Figure 46) than other aquifers. The most likely explanation is desorption of vanadate from iron oxides in the sedimentary rocks under the predominating oxic conditions seen in the aquifer. Some relatively high concentrations are also observed in the Igneous volcanic aquifer, linked to the relative abundance of V in basic igneous rocks. The lowest V concentrations are seen in Carboniferous mined and Highland calcareous aquifers, where limited release

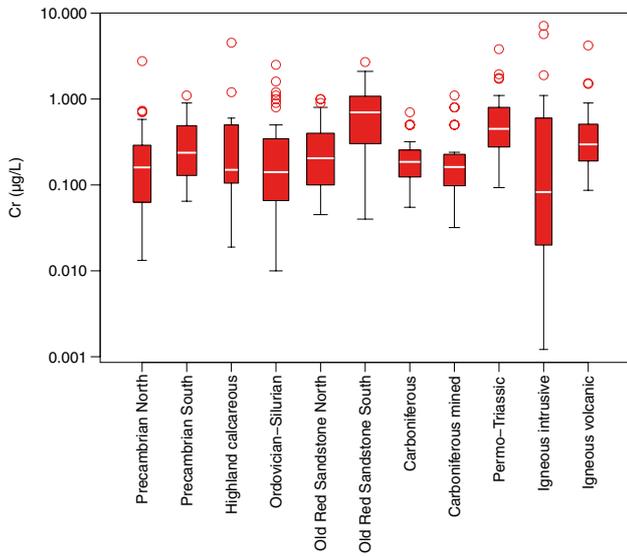


Figure 44 Statistical summary of concentrations of Cr in groundwater in Scotland's bedrock aquifers.

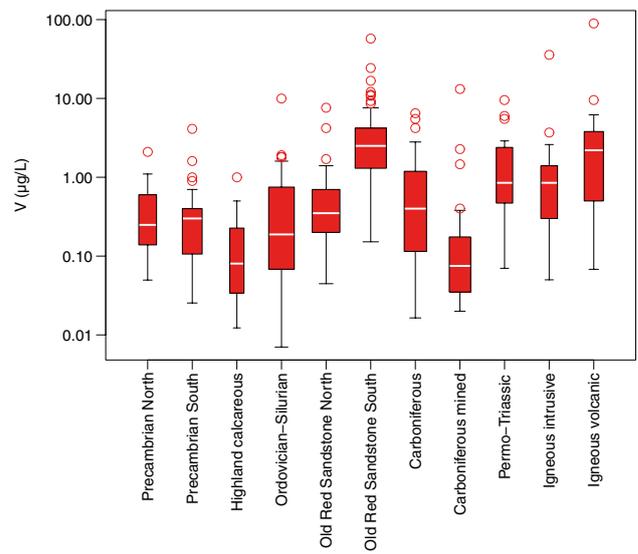


Figure 46 Statistical summary of concentrations of V in groundwater in Scotland's bedrock aquifers.

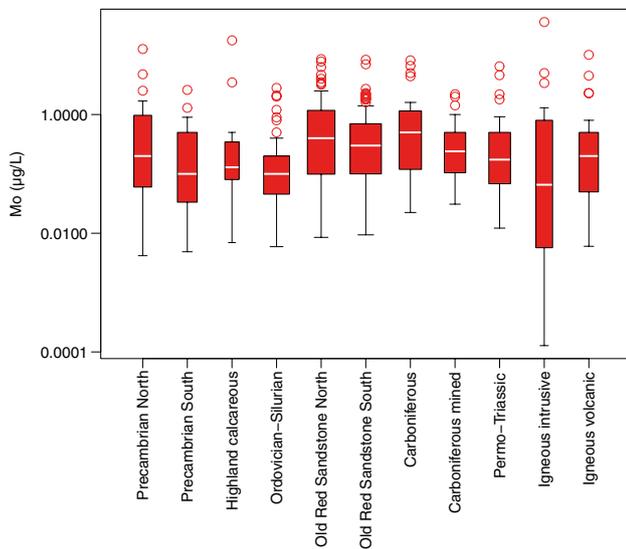


Figure 45 Statistical summary of concentrations of Mo in groundwater in Scotland's bedrock aquifers.

of V is likely to be related to a combination of limited supply from carbonates in the rock, and redox controls.

The Old Red Sandstone South aquifer has some of the highest concentrations of Zn, although the relative difference between these and aquifer types is less pronounced than seen in V concentrations.

Cadmium concentrations are low in all the groundwater samples: mostly in the range 0.01–1 µg/L, and no exceedances of the limit for Cd in drinking water.

Concentrations of Hg are mostly less than the most common detection limit of 0.1 µg/L. Four samples were in excess of the national drinking water limit of 1 µg/L, albeit only just (maximum 2 µg/L). The highest value was seen in the

Carboniferous aquifer. However, the precision of Hg laboratory analyses was low, and more detailed investigation of Hg is needed to investigate this further.

The concentrations of other transition metals (Ag, Au, Hf, Nb, Ta, Ti, W, Sc and Zr) are also universally low in the sampled groundwaters, most being below detection limits.

## 5.10 METALLOIDS

Concentrations of As in groundwaters are usually in the range <0.1–5 µg/L (Figure 47), though in almost all aquifers there are outliers with concentrations >10 µg/L. The two highest concentrations (170 µg/L, 210 µg/L) were from the Precambrian North aquifer. In one of these samples, As is likely to be present

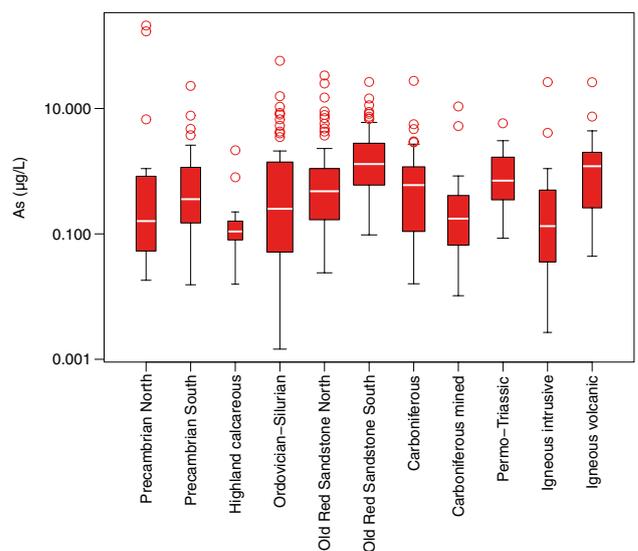


Figure 47 Statistical summary of concentrations of As in groundwater in Scotland's bedrock aquifers.

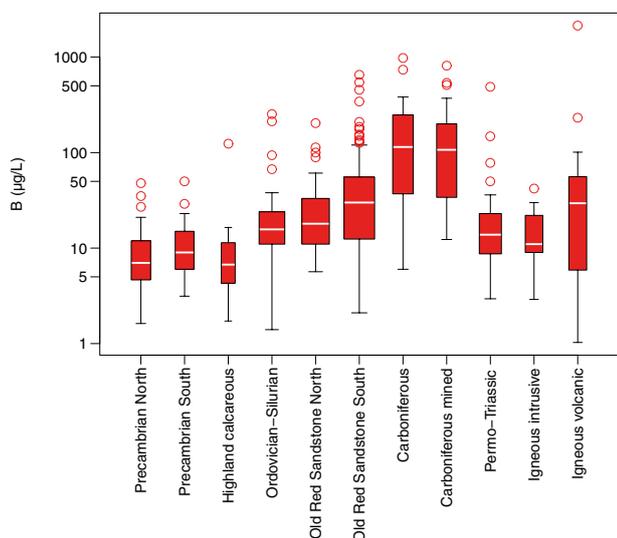


Figure 48 Statistical summary of concentrations of B in groundwater in Scotland's bedrock aquifers.

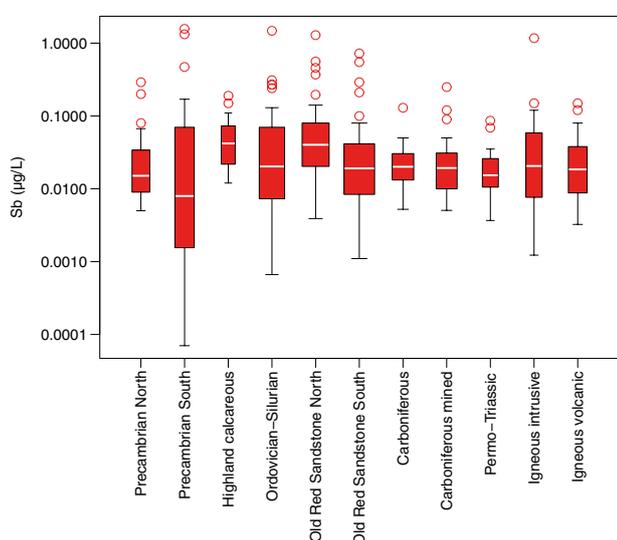


Figure 49 Statistical summary of concentrations of Sb in groundwater in Scotland's bedrock aquifers.

substantially in colloidal form due to the coincidence of high concentrations of Fe, Mn and Si and red discoloration. For the rest of the sampled groundwaters, sources of dissolved As cannot be as confidently assigned, but are likely to be mainly iron oxides and sulphides. A total of 3.8% of analysed samples showed As concentrations above the drinking water limit (of 10 µg/L).

The only sample (0.2%) to contain B at a concentration above the national drinking water limit (1 mg/L) was from the Igneous volcanic aquifer. Apart from this, the highest B concentrations occur in the Carboniferous and Carboniferous mined aquifers (Figure 48). The high concentrations are linked with increased salinity and reflect the component of older, more mineralised water in the Carboniferous aquifers.

There is no obvious spatial trend in Sb concentrations (Figure 49), and they are usually <1 µg/L (maximum observed

1.6 µg/L). None of the samples exceeds the national drinking water limit for Sb (5 µg/L).

There is no obvious spatial trend in the distribution of Ge concentrations, and they are almost exclusively <0.2 µg/L. The highest concentration (4 µg/L) was in a saline sample from a mineralised spring near Moffat (Na 300 mg/L; Cl 530 mg/L).

## 5.11 LEAD

No distinct spatial trend exists in concentrations of Pb, although slightly higher values are found in some of the groundwaters from Old Red Sandstone and Igneous intrusive aquifers. Concentrations are almost all less than the national drinking water limit for Pb (10 µg/L). Only one sample exceeded this (at 13.3 µg/L), from the Carboniferous mined aquifer.

## 5.12 HALOGENS

The variations in salinity and Cl in groundwater across Scotland are reflected by corresponding variations in concentrations of Br and I (Figure 50, Figure 51). Nearly all the aquifers have some samples of high Br, high I groundwater, but the highest values generally occur within the Carboniferous and Carboniferous mined aquifers. Relatively high I concentrations are also found in the Old Red Sandstone North aquifer. These relatively high values coincide with areas impacted by saline intrusion and/or by saline formation water. High I concentrations in groundwater have shown an apparent residence time dependence (Lloyd and Heathcote, 1985; Lloyd and Howard, 1979), and in the case of both Carboniferous and Old Red Sandstone aquifers, high I can be equated with older, deeper groundwaters. In the case of Br, organic matter is a probable additional source (Edmunds, 1996), and derivation from coal and organic-rich mudstones in the Carboniferous rocks explains the relatively high concentrations in groundwater in this aquifer. Edmunds

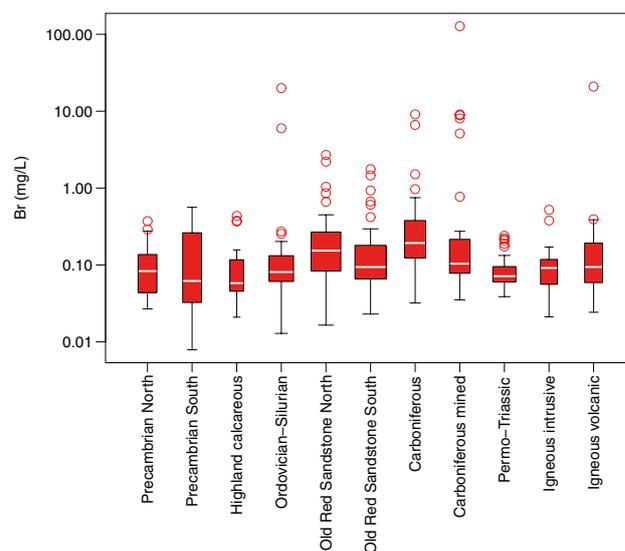


Figure 50 Statistical summary of concentrations of Br in groundwater in Scotland's bedrock aquifers.

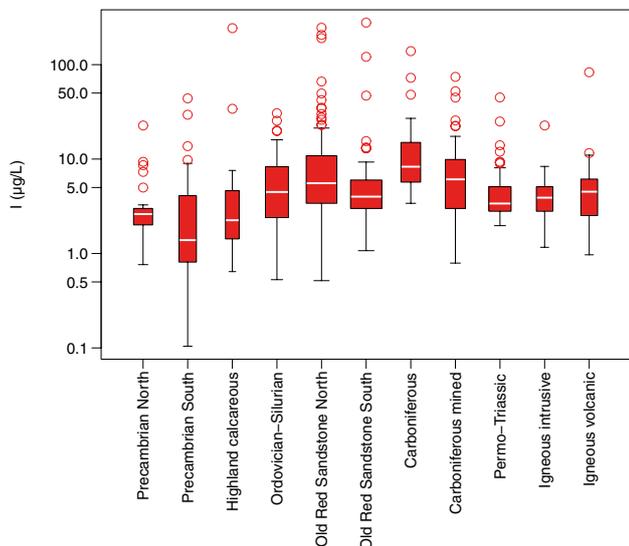


Figure 51 Statistical summary of concentrations of I in groundwater in Scotland's bedrock aquifers.

(1996) found high ratios of Br/Cl in saline groundwaters from the English Coal Measures in comparison to other English aquifers.

There does not appear to be a strong spatial control on F concentrations in groundwater across Scotland (Figure 52). Concentrations reach up to 4.1 mg/L, this in a Na-SO<sub>4</sub> groundwater from the Old Red Sandstone South aquifer (Figure 59). Few samples (0.8%) exceed the drinking water limit for F. In samples where F was measured, all but one were undersaturated with respect to the mineral fluorite.

### 5.13 RARE EARTH ELEMENTS

The lanthanides are here described together because of their similar behaviour in aqueous systems. The greater abundance of light relative to heavy REE is clearly illustrated by the different distributions of La and Lu (Figure 53, Figure 54, Figure 55). REE-rich minerals include micas, apatite, fluorite and monazite as well as the more resistant minerals zircon

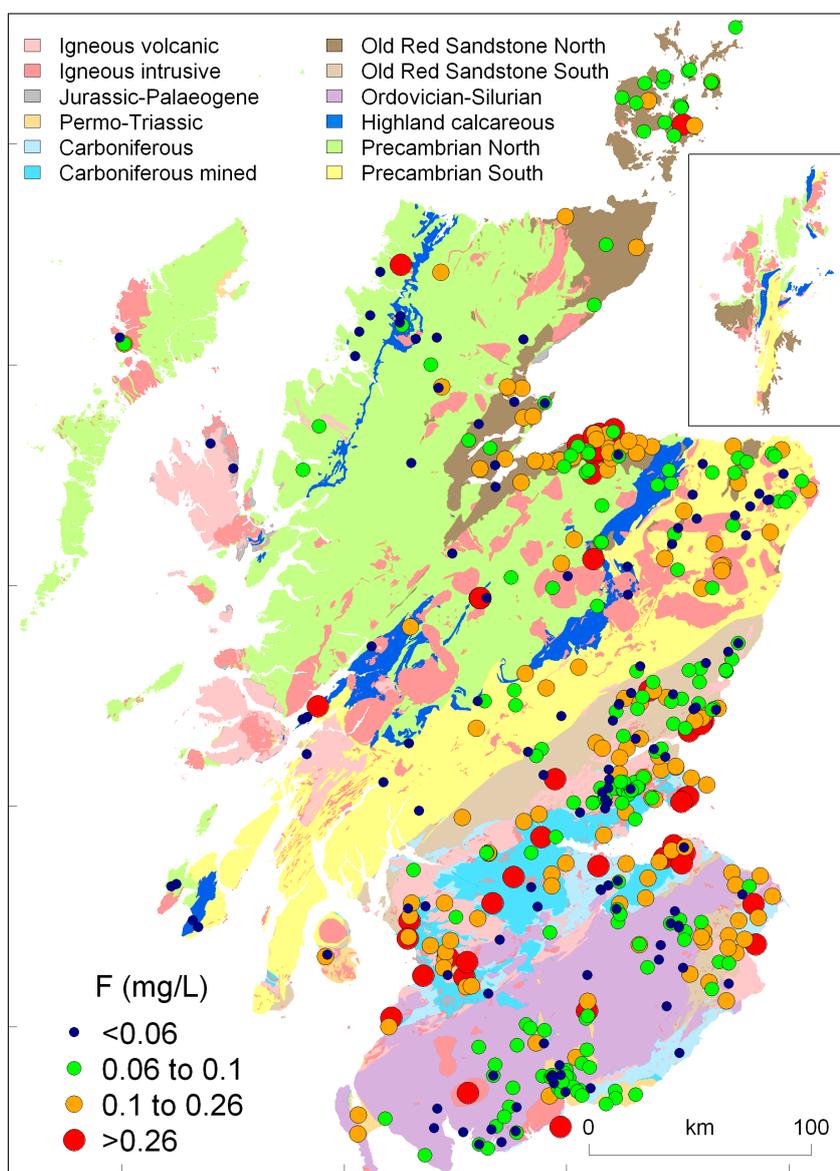


Figure 52 Map showing the distribution of F concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

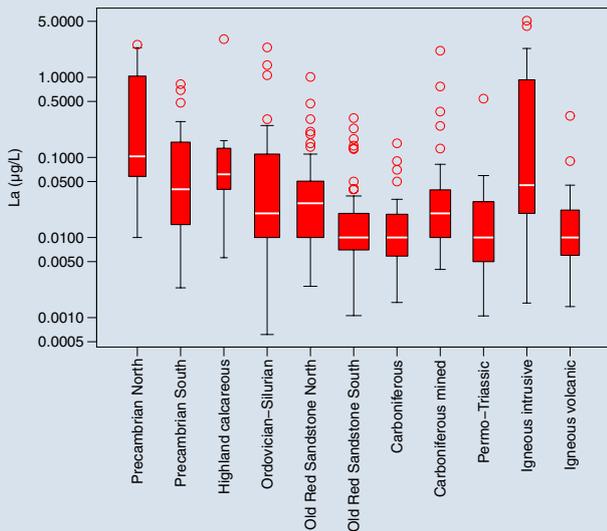


Figure 53 Statistical summary of concentrations of La in groundwater in Scotland's bedrock aquifers.

(La)

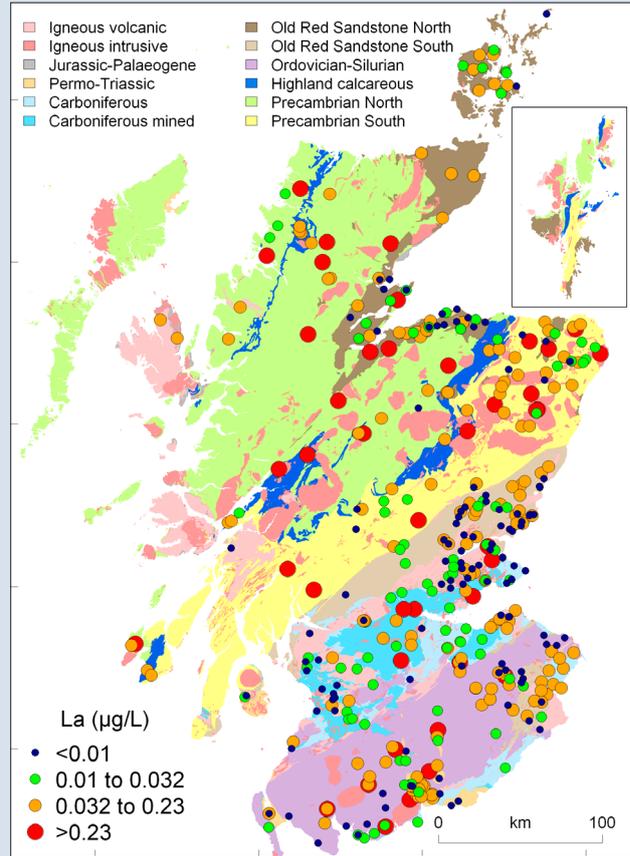


Figure 54 Map showing the distribution of La concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

and sphene. Iron oxides, aluminium oxides and clays also have a strong affinity for REE, and sorption/desorption reactions are likely to be an important control on REE mobility in groundwater. Sorption to metal oxides and clays is strongly pH dependent (Smedley, 1991; Coppin et al., 2002). Most of the REEs form trivalent cations in solution, and as a result REE mobility in groundwater is enhanced in acidic conditions. Exceptions are Eu and Ce, which can form divalent and tetravalent species, respectively, depending on redox conditions, and hence can show different behaviour and compositions from other REEs. The REE compositions of aqueous solutions have been linked to those of their source rocks, and hence may serve as tracers for REE origin and groundwater flow paths (e.g. Johannesson et al., 1997).

The distributions of REEs normalised to shale are shown in Figure 56 (Sholkovitz, 1988). Only non-censored values are plotted. Igneous intrusive and Carboniferous mined aquifers contain some of the most REE-concentrated groundwaters in Scotland. These coincide with more acidic groundwater compositions. In the case of Igneous intrusive aquifers, greater abundance of primary REE-bearing minerals in the aquifer rocks is a likely additional factor in the enhanced REE concentrations in groundwater. Some of the lowest concentrations are seen

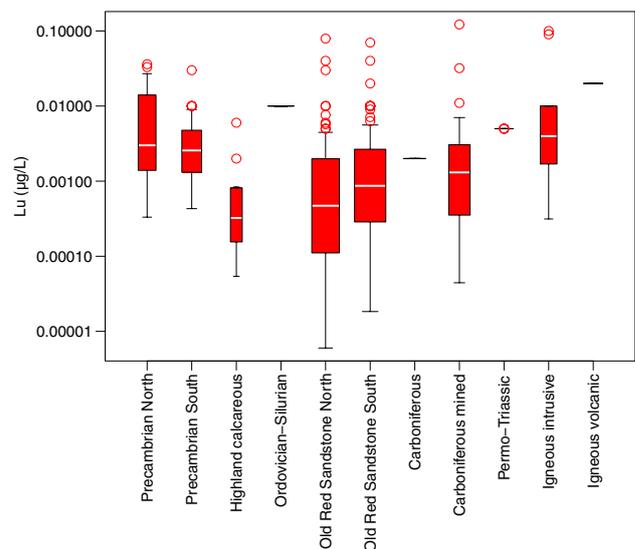


Figure 55 Statistical summary of concentrations of Lu in groundwater in Scotland's bedrock aquifers.

in groundwaters from the Permo-Triassic and Igneous volcanic aquifers. These aquifer rocks are likely to have the lowest contents of REE-rich primary minerals and clays.

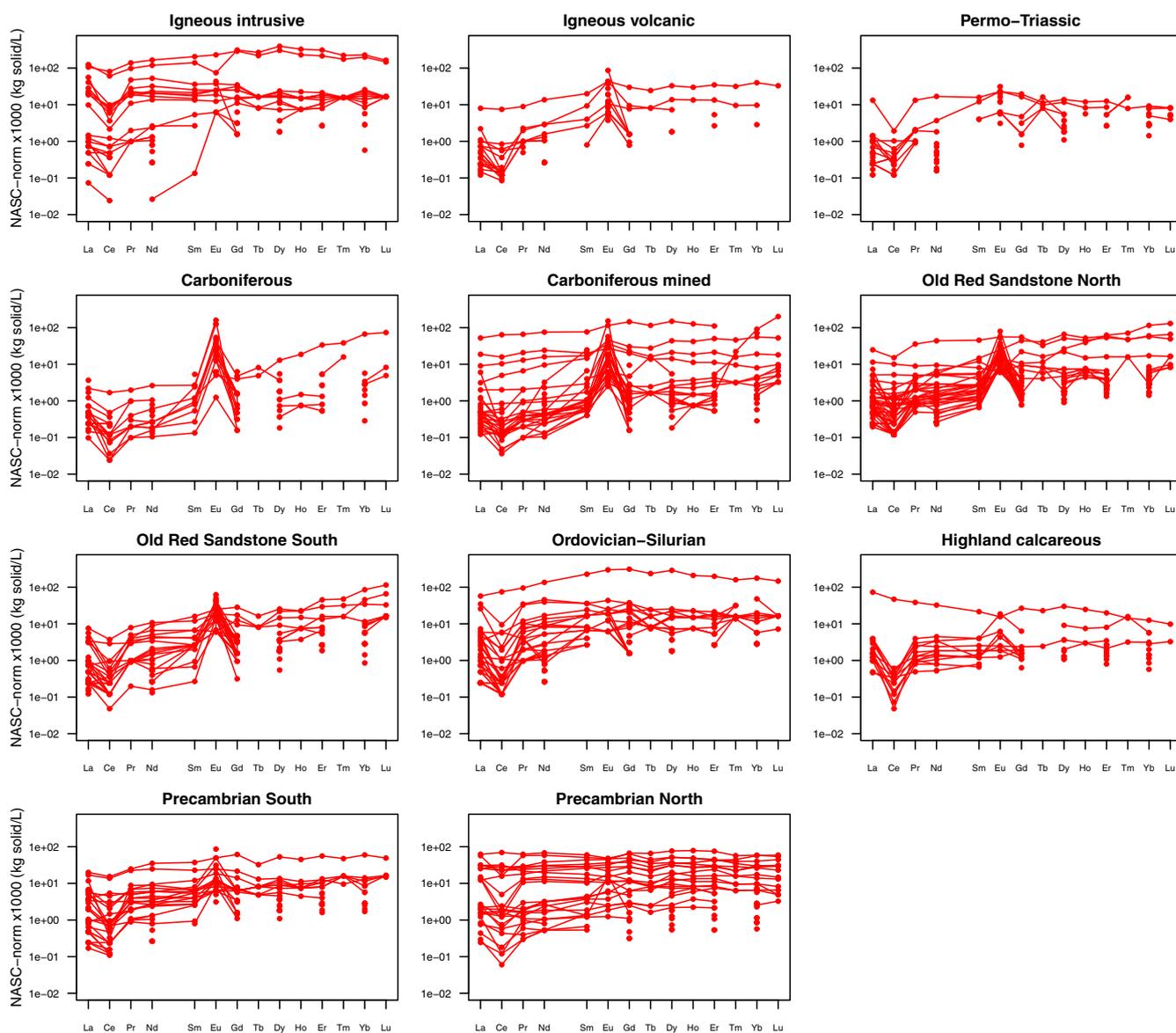


Figure 56 Shale-normalised REE profiles for groundwaters from Scotland's bedrock aquifers.

Most of the groundwaters show flat shale-normalised or light REE-depleted profiles. Slight negative Ce anomalies are seen in many of the groundwaters, generally in samples with lowest concentrations of total REEs. The presence of negative Ce anomalies has been associated with oxidation of Ce to Ce(IV) in oxic, alkaline conditions, resulting in precipitation as CeO<sub>2</sub> or loss by adsorption. Perhaps the most noticeable and consistent negative Ce anomalies are seen in Highland calcareous groundwaters, which are dominantly oxic and have relatively high pH, buffered by carbonate reactions.

Slight positive Eu anomalies are seen particularly in the Carboniferous, Carboniferous mined and Old Red Sandstone aquifers. The ultimate origin of the excess Eu could be from the presence an enriched Eu mineral, for example plagioclase (Weill and Drake, 1973), although the profiles are more likely to have been controlled by reactions with secondary clays and oxides. The precise controls on the individual profiles cannot

be determined without more detailed investigation of the local aquifer geochemistry and mineralogy. Some distinctions in profiles can be seen between groundwaters from the different aquifers, but these are not so clear as to be confident in the use of the REE as flow tracers.

## 5.14 URANIUM

Concentrations of U in groundwater show a patchy regional distribution and no clear geological control (Figure 57), although the highest concentrations occur in the Precambrian North aquifer, where concentrations reach up to 48 µg/L. The highest median value occurs in groundwater from the Old Red Sandstone South aquifer. Sources of U are likely to be localised mineralisation in metamorphic rocks, and/or disseminated phosphate minerals and iron oxides in sedimentary rocks. Both phosphate minerals and iron oxides

are relatively enriched in the sedimentary rocks of the Old Red Sandstone aquifer. The relatively low U concentrations in groundwaters from the Old Red Sandstone North aquifer are likely to reflect the more reducing nature of these groundwaters. Under reducing conditions, U is transformed from U(VI) to U(IV) and is immobilised by co-precipitation or adsorption reactions involving iron oxides (Jeon et al., 2005).

No national drinking water limit exists for U. However, the sample with highest concentration observed has a U

concentration greater than the WHO guideline value for U in drinking water of 30 µg/L (0.2% exceedance).

### 5.15 SUMMARY

The chemistry of groundwater in Scotland's bedrock aquifers is highly variable. Major ion water types include Ca-HCO<sub>3</sub>, Na-HCO<sub>3</sub>, Na-SO<sub>4</sub> and Na-Cl types, with no single type dominating. Mineralised springs (e.g. Na-Cl, Na-SO<sub>4</sub> types) occur rarely in the Ordovician-Silurian aquifer. The chemical

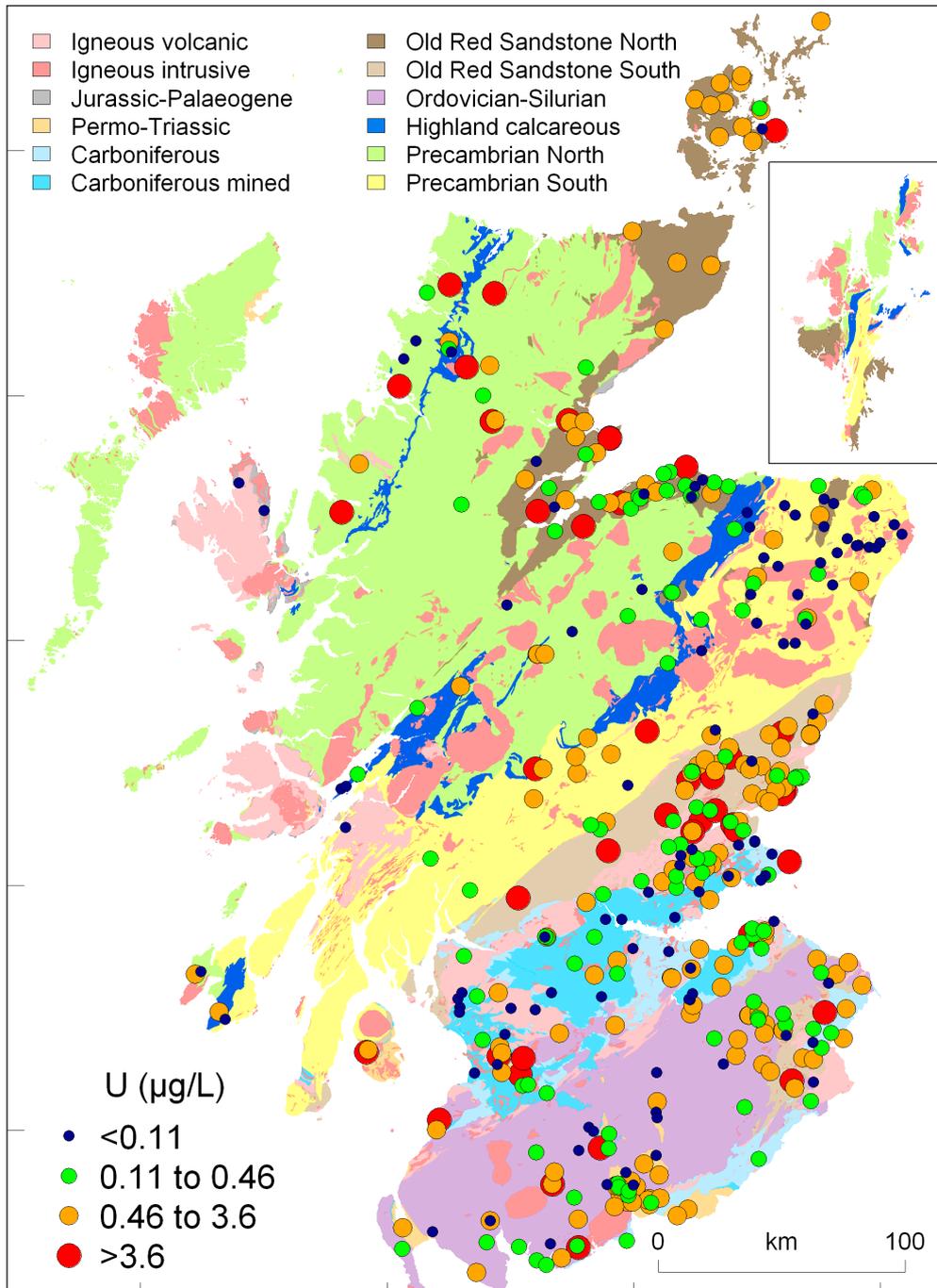


Figure 57 Map showing the distribution of U concentrations in groundwater in Scotland's bedrock aquifers. Bedrock geology linework at 1:625 000 scale (DiGMapGB; British Geological Survey © NERC).

composition of Scotland's groundwaters reflects host aquifer lithology, mineral reactions (e.g. silicate and carbonate dissolution, sulphide oxidations and ion exchange reactions), redox conditions, residence time, and mixing with older formation waters at depth. Some of the highest salinities are seen in the Carboniferous and Carboniferous mined aquifers, and saline intrusion affects some groundwaters in coastal areas.

Acidic groundwaters (pH<6) occur in most aquifer types, although median pH values for all aquifers are in the range 6.5–7.5. Acidic groundwater compositions reflect an absence of carbonate minerals, and/or oxidation of pyrite and other sulphides. More strongly acidic conditions have given rise to higher concentrations of Al, Fe, Mn and REEs in affected groundwaters.

Oxic groundwater dominates most aquifers in Scotland. This is consistent with the most common hydrogeological situation in Scotland of dominantly shallow groundwater flowlines in fracture dominated aquifers. Exceptions occur in mildly reducing sections of several aquifers, but such conditions are only regionally extensive in the Old Red Sandstone North aquifer. Here, conditions are typically reducing with respect to NO<sub>3</sub>-N, Fe and Mn, but not SO<sub>4</sub>. Within the Carboniferous aquifers (and mineralised springs in the Ordovician–Silurian aquifer), conditions become sufficiently strongly reducing for SO<sub>4</sub> reduction to have taken place, and even methane was observed in some boreholes.

Impacts of land use on groundwater chemistry include the common occurrence of high NO<sub>3</sub> groundwaters, which correlate reasonably well with areas of agricultural land use.

Occurrences of high P and K are also seen, but are more sporadic in distribution.

Not all the groundwaters sampled are used for drinking water, and the compositional ranges in groundwater chemistry cannot be used to assess the state of drinking water quality in Scotland. They nonetheless show the typical compositions in raw groundwaters from given aquifers and given hydrogeological conditions, and indicate the scope of the kinds of water quality problems that may be encountered. The most frequent exceedances of drinking water limits in groundwater are for Fe (21% of samples) and Mn (27% of samples) (Homocik et al., 2010), which relate largely to the presence of reducing conditions. Exceedances for NH<sub>4</sub> (6.7%) are also likely to be naturally derived and linked to reducing conditions. A total of 0.8% of samples show NO<sub>2</sub> in excess of the drinking water limit. Exceedances for NO<sub>3</sub> (11%) occur in oxic conditions, and are linked to pollutant inputs, particularly from agriculture. Exceedances for trace elements are less common, but include Al (1.3%), As (3.8%), B (0.2%), Cu (0.2%), F (0.8%), Hg (1.5%), Ni (2.1%) and Pb (0.2%). No exceedances are observed for Cd, Cr, Mo or Sb. No drinking water limit exists for U, but 0.2% of the samples exceed the WHO provisional guideline value.

The new dataset presented here provides an overview of the current state of groundwater chemistry in Scotland with respect to a large number of determinands. On a national scale, processes responsible for groundwater chemistry variations are difficult to determine with precision. More detailed local and site-specific investigations are needed to look at specific relationships between aquifer mineralogy and chemistry, groundwater flow regimes, and human influences.

## 6 Baseline chemistry of bedrock aquifers in Scotland

In this section we provide a summary of the baseline chemistry for each of the bedrock aquifer groups in Scotland (as shown on the map in Figure 7). The baseline chemistry has been defined using a statistical approach, to take account of the natural variation in baseline chemistry in each aquifer. The range in baseline chemistry is defined as being the range between the 10<sup>th</sup> and 90<sup>th</sup> percentile values calculated for each parameter for each aquifer, so that the influence of outliers is reduced. New groundwater samples analysed from a particular aquifer would be expected to plot within this range 80% of the time. Values outside this range can occur naturally, but are less common, and therefore may merit further investigation.

Summary statistics observed concentrations of elements in groundwater in each aquifer are presented in Table 5 to Table 15 in Appendix 2. The major ion distribution for each aquifer is illustrated in the Piper (tri linear) diagrams in Figure 16. Percentile ranges for each element for each aquifer are presented in Figures 57 to 61 (Appendix 1).

Groundwaters within Permo-Triassic sedimentary aquifers in Scotland are typically weakly to moderately mineralised (SEC 196–654  $\mu\text{S}/\text{cm}$ , median 405  $\mu\text{S}/\text{cm}$ ) with near neutral pH (6.2–7.8, median 7.2). Groundwaters are generally of CaMg-HCO<sub>3</sub> type, dominated by the dissolution of carbonate minerals in the sedimentary rocks. Where mudstones are present, SO<sub>4</sub> concentrations can be higher; where aeolian rocks dominate, groundwater mineralisation is generally weaker. Oxic conditions are prevalent and Fe and Mn concentrations are low.

Groundwaters in Carboniferous sedimentary aquifers in Scotland, where not extensively mined, are typically moderately to highly mineralised (SEC 353–1450  $\mu\text{S}/\text{cm}$ , median 694  $\mu\text{S}/\text{cm}$ ) with a slightly alkali pH (6.7–8.0, median 7.3). There is a wide range of chemical types with the most dominant type being Ca (Ca-Mg)-HCO<sub>3</sub>. More highly mineralised groundwaters can be dominated by CaMg(Na)-SO<sub>4</sub> (Cl) with variations linked to depth of sample, residence time and local geology. Redox conditions are variable, and where groundwater is reducing, Fe and Mn concentrations are often elevated.

Where Carboniferous rocks have been extensively mined for coal, groundwater is typically moderately to highly mineralised (SEC 311–1700  $\mu\text{S}/\text{cm}$ , median 740  $\mu\text{S}/\text{cm}$ ) with near neutral pH (6.3–7.7, median 7.0). Groundwaters are generally complex with no particular chemical type dominating. The effects of mining activities, as well as water-rock interactions that take place naturally in sulphide-mineralised environments, can give rise to high concentrations of Fe and SO<sub>4</sub> through pyrite oxidation, and this appears to be the case in the Midland

Valley. No widespread corresponding increases in trace metals such as Ni, Cu, Zn and Pb are seen. Manganese concentrations are often elevated as a result of reducing conditions. Increased mineral content, in particular alkalinity, and the near neutral pH of 'Carboniferous Mined' waters, is attributed to the dissolution of carbonate minerals that buffers the acidity produced by pyrite oxidation.

Groundwaters in the Old Red Sandstone North aquifer, are typically moderately mineralised (SEC, 240–890  $\mu\text{S}/\text{cm}$ , median 547  $\mu\text{S}/\text{cm}$ ) with near neutral pH (6.5–7.7, median 7.2). The dominant water type is Ca-HCO<sub>3</sub>, but a significant proportion of the groundwater samples is not dominated by any cation or anion. There is a high proportion of reducing groundwater samples, with approximately 40% having dissolved oxygen concentrations less than 1 mg/L. Elevated Mn and Fe are common.

Groundwater in Old Red Sandstone South aquifers shows some different characteristics to those in the north. Groundwater is typically moderately mineralised (SEC, 296–821  $\mu\text{S}/\text{cm}$ , median 498  $\mu\text{S}/\text{cm}$ ) with slightly alkaline pH (6.8–7.8, median 7.4). It is dominated by CaMg(Ca)-HCO<sub>3</sub> with a significant minority not dominated by any anion. Groundwater is predominately oxic, and elevated Fe and Mn concentrations are rare.

Groundwater within the Ordovician-Silurian aquifer is typically weakly to moderately mineralised (116–655  $\mu\text{S}/\text{cm}$ , median 340  $\mu\text{S}/\text{cm}$ ) are near neutral pH (6–7.8, median 7.1). Groundwaters are dominated by CaMg (Ca)-HCO<sub>3</sub> with generally low chloride and sulphate concentrations; and are generally oxic with low Fe and Mn concentrations. There are several mineralised springs within the Ordovician-Silurian aquifer that show distinctive highly mineralised local chemistry (MacDonald et al., 2008).

Groundwaters within the basement rocks of the Precambrian North aquifer are generally weakly to moderately mineralised (SEC 110–544  $\mu\text{S}/\text{cm}$ , median 227  $\mu\text{S}/\text{cm}$ ) with variable pH (6.1–8.1, median 6.7). Groundwater is highly variable with bulk chemistry dominated by Ca Na-HCO<sub>3</sub> Cl and sulphate rarely the dominant anion. Redox conditions are also variable with more than 30% of the samples having dissolved oxygen less than 1 mg/L. This impacts on concentrations of Fe, Mn and other trace metals which can be elevated.

Groundwaters from the basement rocks of the Precambrian South and Precambrian North aquifer are similar. They are generally weakly mineralised (SEC 149–449  $\mu\text{S}/\text{cm}$ , median 241  $\mu\text{S}/\text{cm}$ ) with highly variable pH (5.7–8.1, median 6.6). The groundwaters are highly variable in composition, with bulk chemistry generally dominated by Ca Na-HCO<sub>3</sub> Cl, and

sulphate rarely the dominant anion. Groundwater conditions are generally oxic, with less than 10% having dissolved oxygen concentrations of less than 1 mg/L, and concentrations of Fe, Mn and trace metals are generally low.

Groundwaters within Igneous volcanic aquifers vary significantly in mineralisation and composition but are rarely highly mineralised (SEC 178–704, median 383  $\mu\text{S}/\text{cm}$ ). The pH is near neutral with a slight alkali bias (pH 6.6–8.1, median 7.3). Groundwaters are often Ca-HCO<sub>3</sub> dominated, but other chemical types are also encountered. Oxic conditions are prevalent, and Fe and Mn concentrations are rarely elevated.

Igneous Intrusive aquifers occur across Scotland, ranging from linear dykes to large granite batholiths. Groundwater is weakly mineralised (64–430  $\mu\text{S}/\text{cm}$ , median 271  $\mu\text{S}/\text{cm}$ ), often with a slightly acidic bias (5.7–7.3, median 6.6).

Groundwaters do not show a typical water chemistry: there is no dominant cation and anions are dominated by HCO<sub>3</sub> and Cl. All groundwater samples were oxic; and Fe is often low, but other trace metals such as Mn are sometimes elevated due to low pH.

Most rocks in Scotland are dominantly siliceous, but a few, mostly Precambrian and Cambro-Ordovician in age and in the Highlands, are dominantly calcareous. There are relatively few (18) samples from these Highland calcareous aquifers (18). These show weakly to moderately mineralised groundwater (86–656  $\mu\text{S}/\text{cm}$ , median 471  $\mu\text{S}/\text{cm}$ ) with near neutral pH (6.5–7.7, median 7.2). Approximately half the samples are strongly Ca-HCO<sub>3</sub> type, with the remainder showing more variable chemistry. The groundwaters are generally oxic and Fe and Mn concentrations rarely elevated.

# Appendix 1 Cumulative probability distributions for selected chemical parameters in Scotland's bedrock aquifers

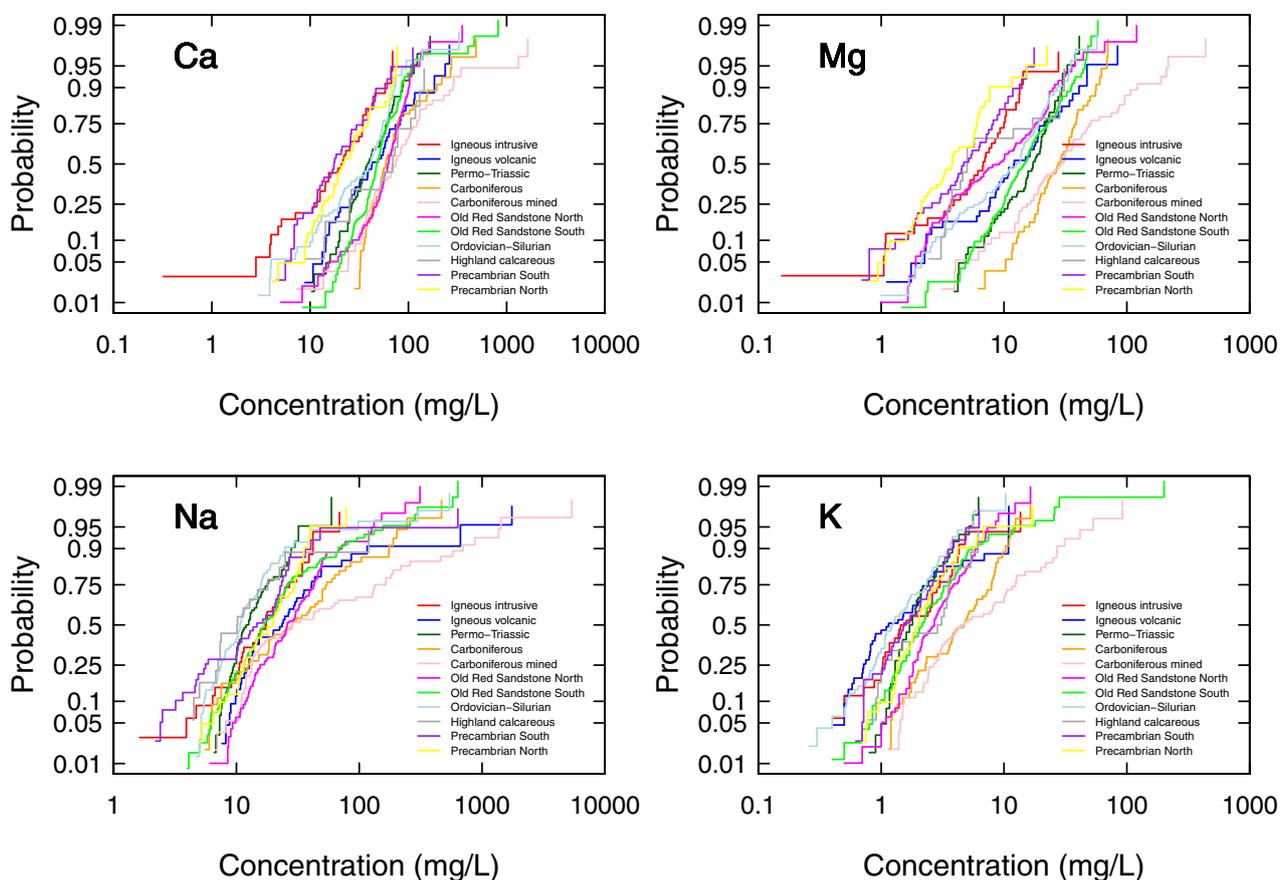


Figure 58 Cumulative probability distribution of concentrations of the major ions Ca, Mg, Na, K, Cl, SO<sub>4</sub>, HCO<sub>3</sub> and NO<sub>3</sub>-N in groundwater in Scotland's bedrock aquifers (*continued overleaf*).

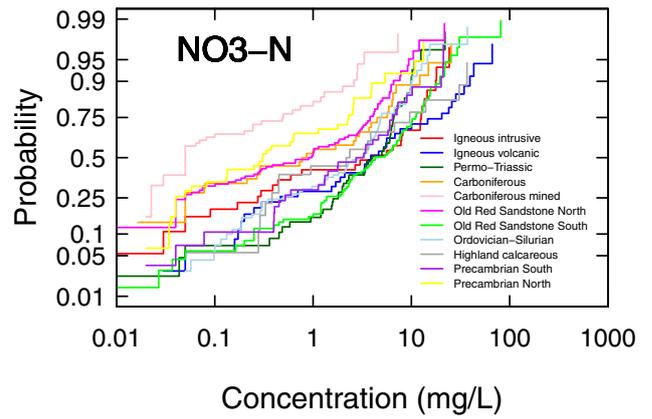
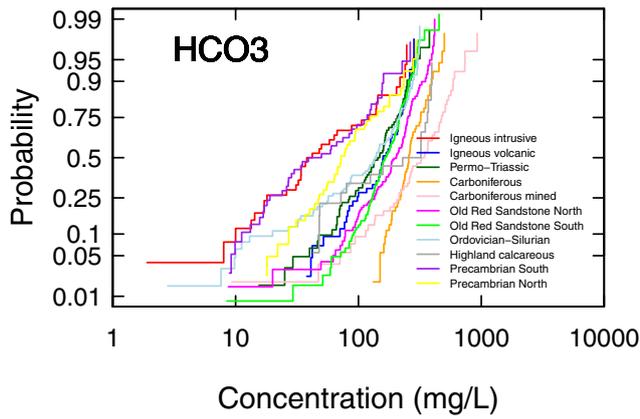
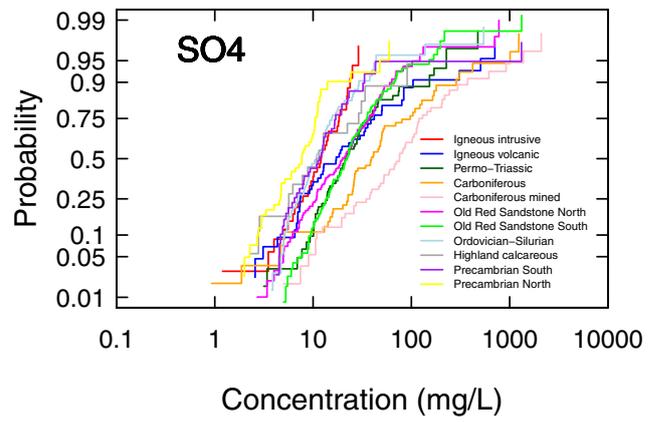
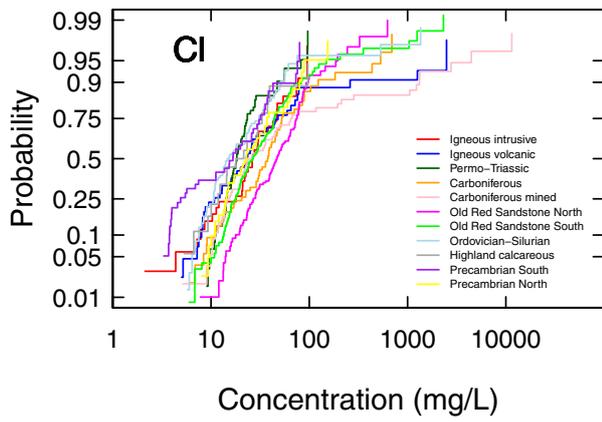


Figure 58 *Continued.*

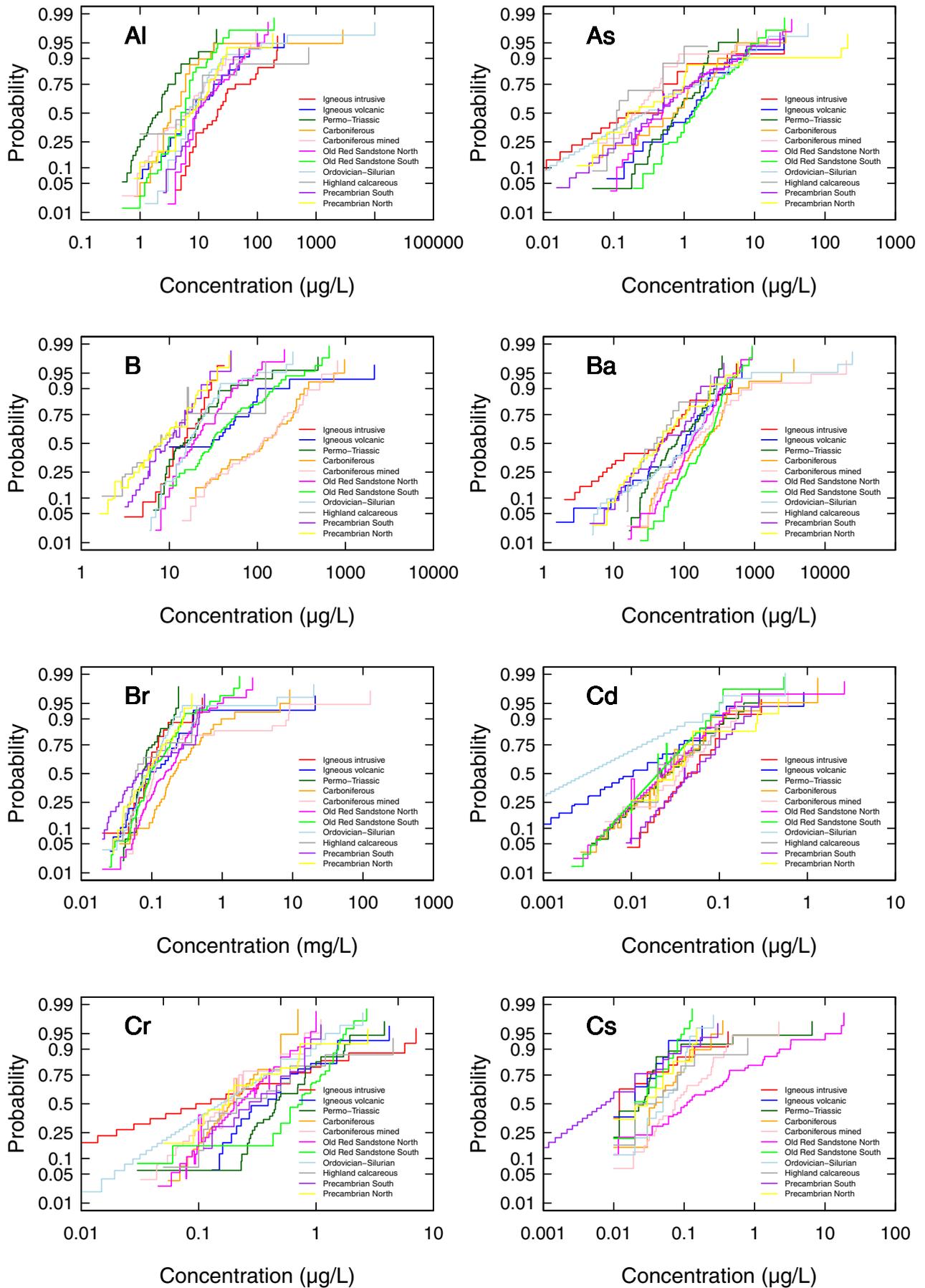


Figure 59 Cumulative probability plots of concentrations of Al, As, B, Ba, Br, Cd, Cr and Cs in groundwater in Scotland's bedrock aquifers.

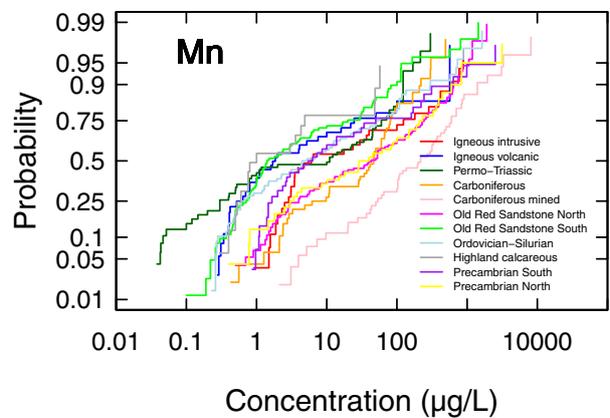
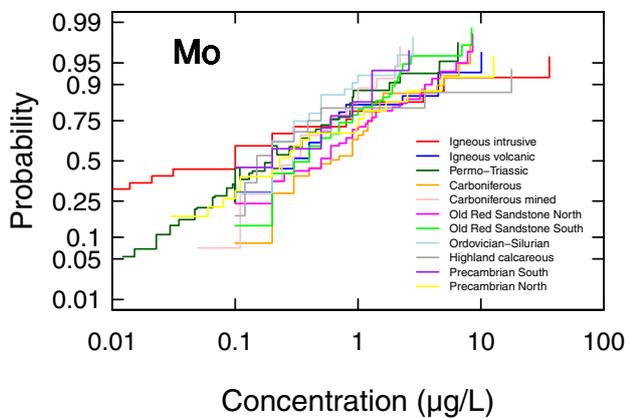
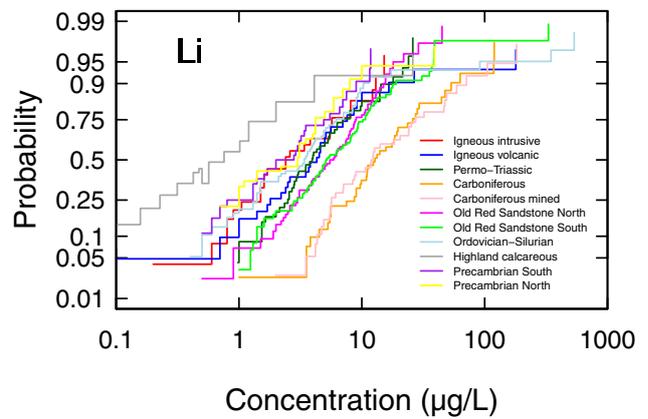
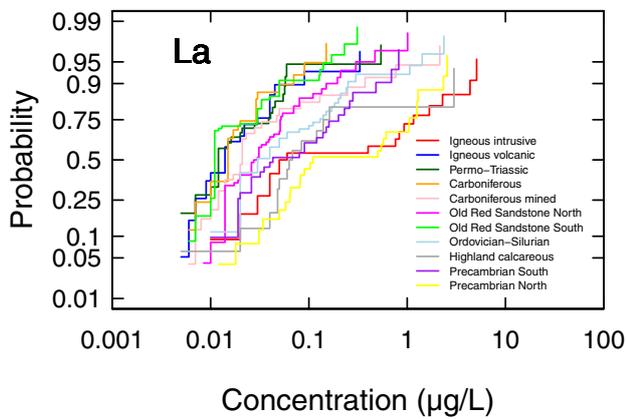
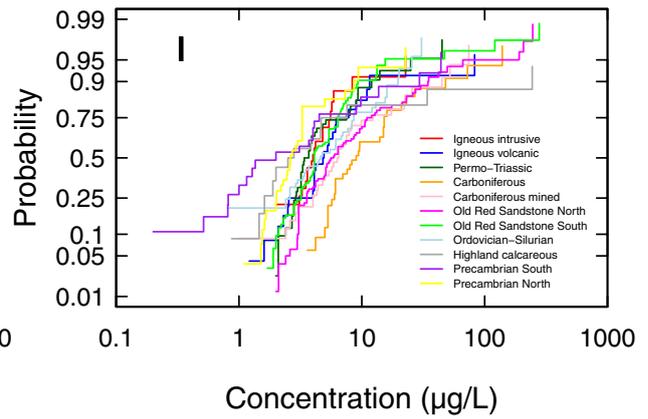
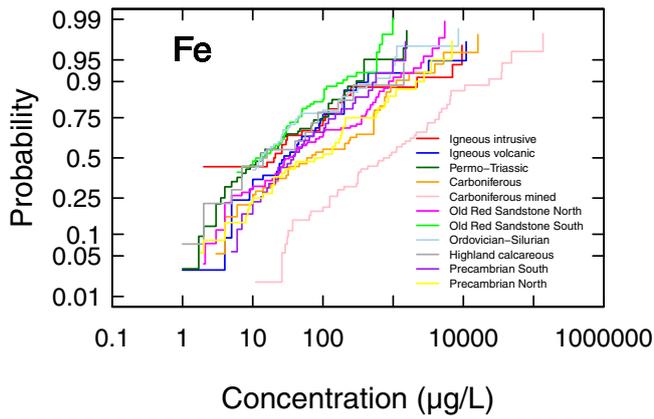
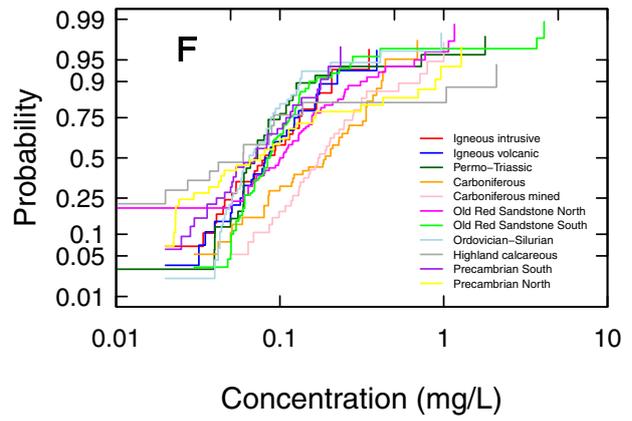
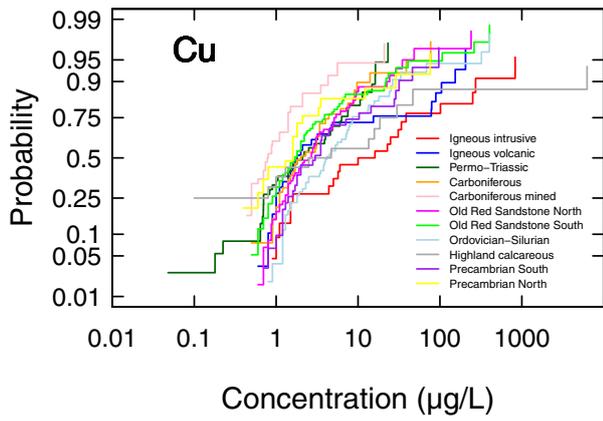


Figure 60 Cumulative probability plots of concentrations of Cu, F, Fe, I, La, Li, Mo and Mn in groundwater in Scotland's bedrock aquifers.

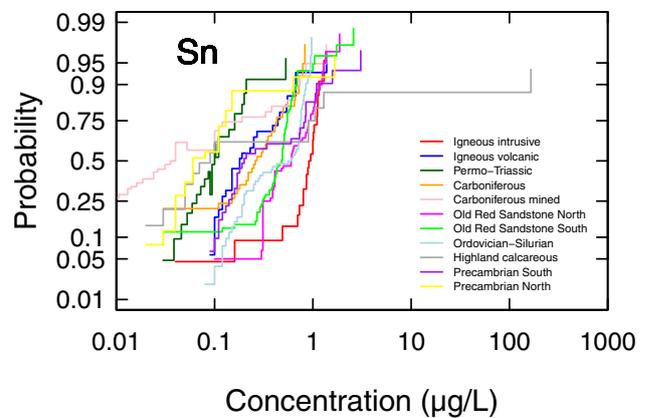
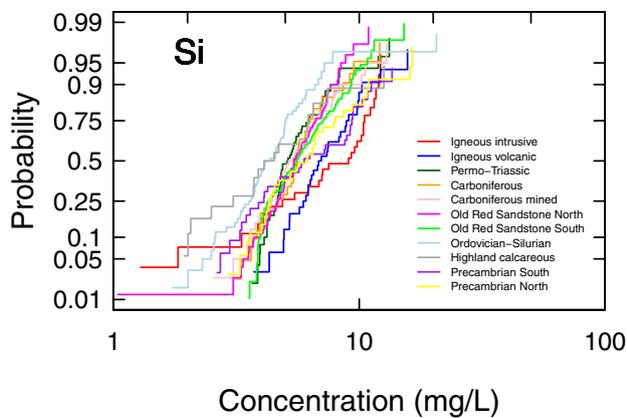
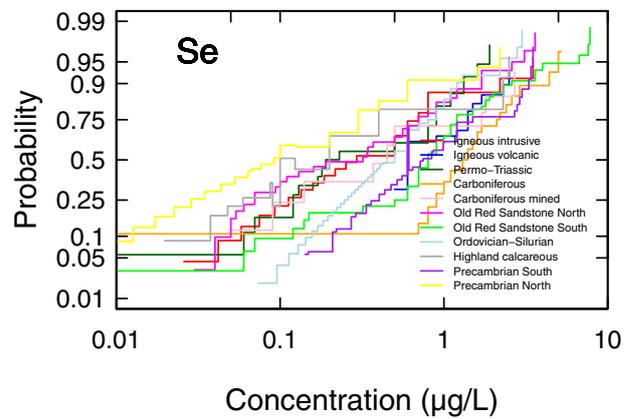
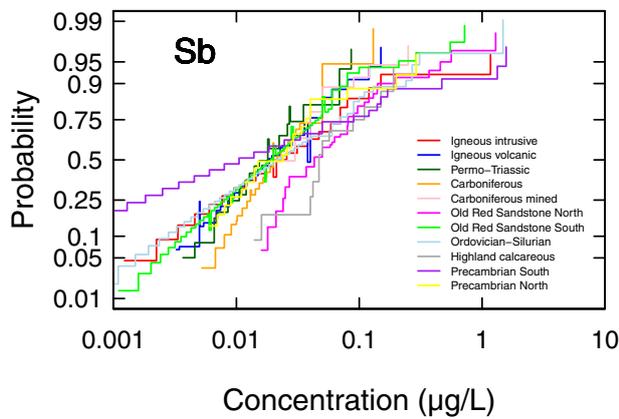
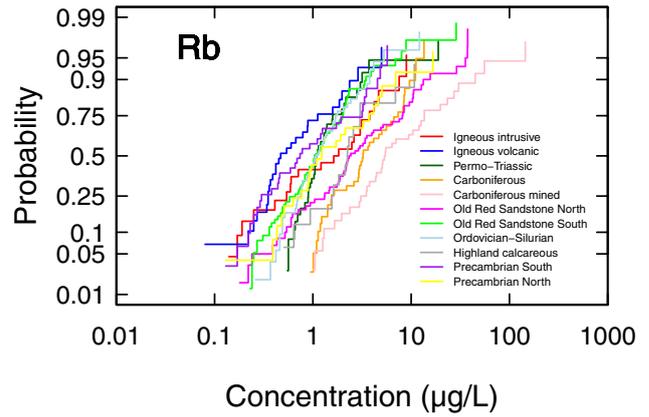
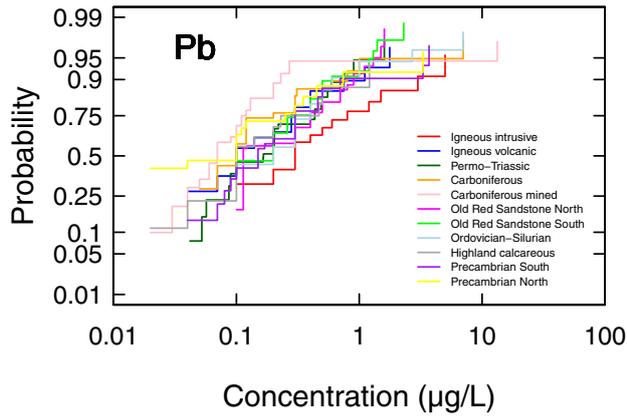
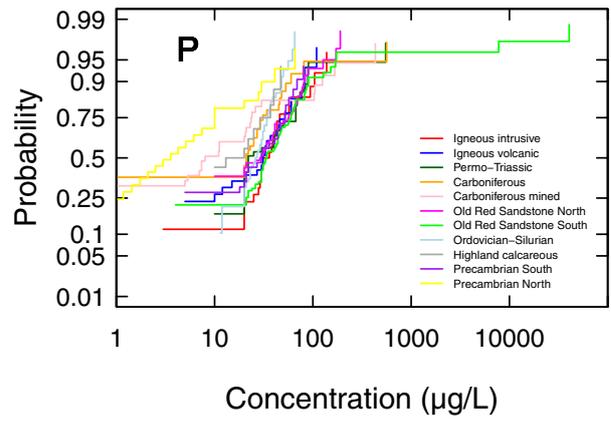
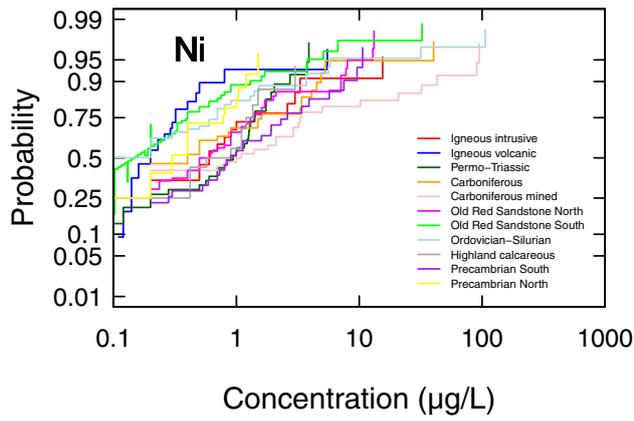


Figure 61 Cumulative probability plots of Ni, P, Pb, Rb, Sb, Se, Si and Sn concentrations in groundwater in Scotland's bedrock aquifers.

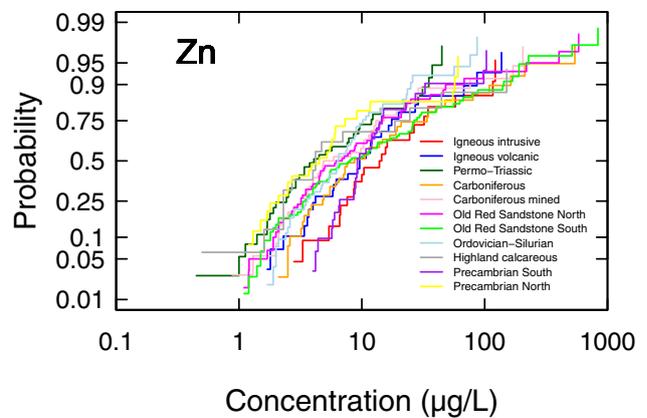
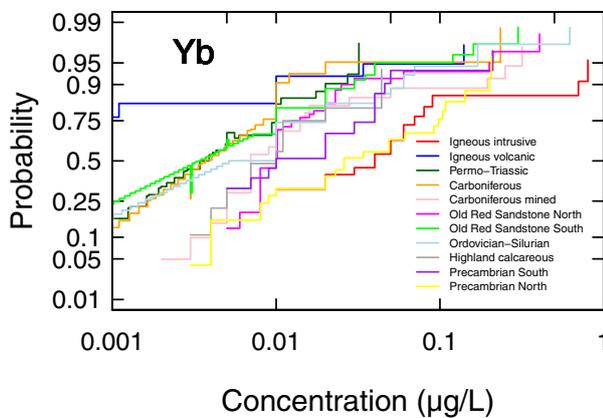
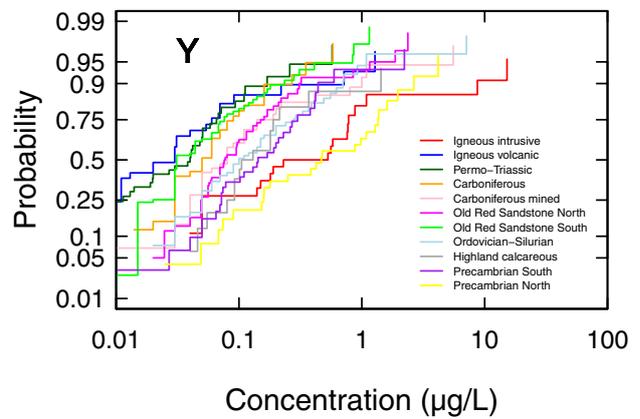
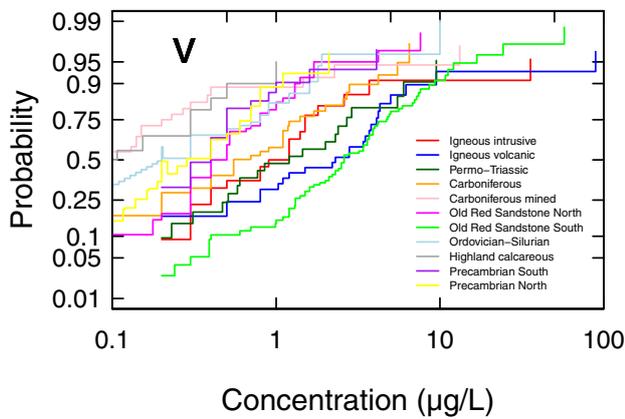
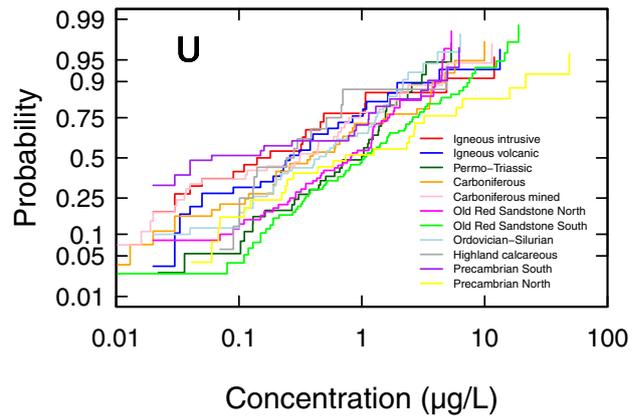
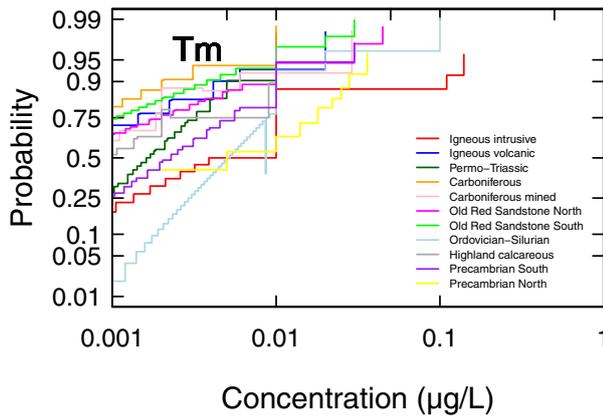
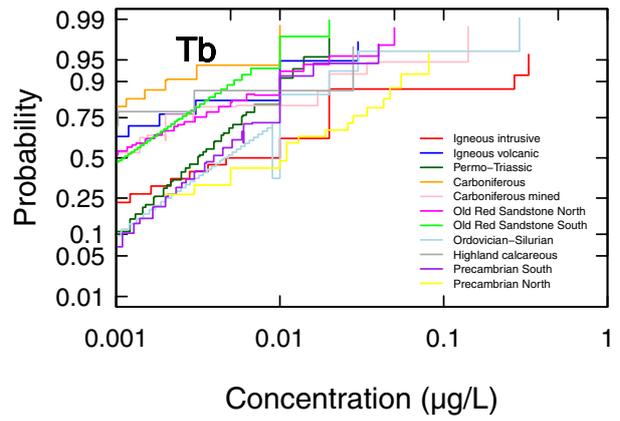
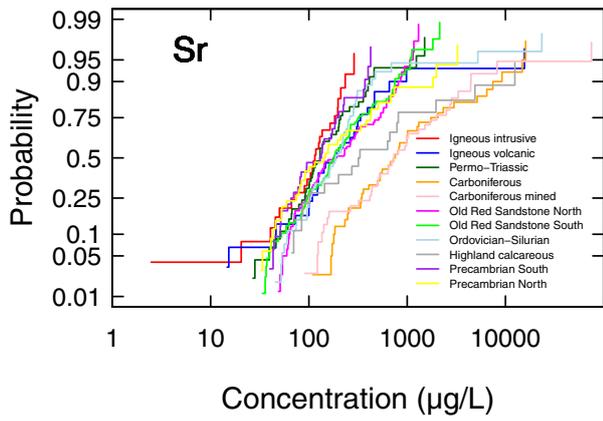


Figure 62 Cumulative probability plots of Sr, Tb, Tm, U, V, Y, Yb and Zn concentrations in groundwater in Scotland's bedrock aquifers.

# Appendix 2 Statistical summary of baseline groundwater chemistry in Scotland's bedrock aquifers

Table 4 Summary statistics for elements in all groundwaters sampled for the Baseline Scotland project.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	526	0	3.9	8	9	10	11.3	13.2	14.1	19.2
pH		607	0	3.13	6.23	6.7	7.2	7.52	7.83	8.07	9.34
DO <sup>1</sup>	mg/L	359	27	<0.1	0.13	1.4	4.17	7.56	9.3	10.2	14.4
Eh <sup>2</sup>	mV	405	0	<169	142.4	265	349	400	442.6	474.8	791
SEC <sup>3</sup>	µS/cm	590	0	2.5	169	290	437	630	931	1290	31800
TDS <sup>4</sup>	mg/L	197	0	15.8	53.5	92.3	152	280	524	882	5340
Ca	mg/L	646	0	0.24	12.8	25.7	45.5	67.4	96.2	130	1640
Mg	mg/L	644	0	0.154	2.5	5.52	12.2	21.6	35.1	46.9	437
Na	mg/L	646	0	1	7	10.5	16.2	30.2	66	148	5360
K	mg/L	641	8	<0.5	0.8	1.26	2.05	3.6	6.7	10.5	201
Cl	mg/L	644	0	2.02	8.93	14.3	23.8	45.2	79.3	143	11500
SO <sub>4</sub>	mg/L	645	0	0.15	5.08	9.3	17.8	35.7	80.8	168	2100
HCO <sub>3</sub>	mg/L	641	3	<10	34	84.5	160	241	315	382	926
NO <sub>3</sub> -N	mg/L	547	68	<0.00452	0.0268	0.185	1.85	6.01	12.2	17.7	81.1
NO <sub>2</sub> -N	µg/L	353	187	<0.3	0.102	0.29	1.1	3.38	8.49	18	6300
NH <sub>4</sub> -N	µg/L	357	231	<0.6	0.0718	0.398	2.71	20.3	115	613	8320
P	µg/L	439	144	<1		3	24	42	69	90	40500
DOC	mg/L	234	10	<0.5	0.474	0.68	1.1	1.74	3	4.15	70.8
F	mg/L	492	63	<0.01	0.028	0.054	0.082	0.133	0.26	0.417	4.1
Br	µg/L	485	9	<20	39.9	61	96	189	375	607	127000
I	µg/L	438	28	<0.2	1.61	2.7	4.15	7.9	17.4	34.1	278
Si	mg/L	512	0	0.5	3.54	4.2	5.4	6.86	9.27	10.7	20.6
Al	µg/L	453	10	<0.5	1.17	3	5	12	29	62.4	10000
As	µg/L	449	147	<0.05	0.05	0.16	0.49	1.4	4.4	7.9	210
B	µg/L	491	132	<10	7	10	19	40.6	136	253	2140
Ba	µg/L	509	3	<2	15.4	42.8	102	212	341	463	24400
Be	µg/L	425	328	<0.001	0.000309	0.001	0.00397	0.0144	0.06	0.108	0.88
Cd	µg/L	425	253	<0.01	0.00332	0.00789	0.0198	0.044	0.1	0.148	2.63
Ce	µg/L	425	120	<0.005	0.003	0.007	0.01	0.04	0.18	0.77	6.67
Co	µg/L	425	96	<0.01	0.009	0.02	0.04	0.12	0.6	1.59	74.9
Cr	µg/L	425	195	<0.03	0.06	0.11	0.24	0.6	1	1.5	7.1
Cs	µg/L	425	104	<0.01	0.005	0.01	0.028	0.07	0.17	0.42	18.6
Cu	µg/L	425	22	<0.0478	0.5	0.9	1.8	5.4	24.1	48.4	6260
Eu	µg/L	363	145	<0.002		0.004	0.01	0.02	0.04	0.05	0.48
Fe	µg/L	600	144	<1	2	4	26	181	906	2760	137000
Gd	µg/L	425	149	<0.001	0.002	0.004	0.01	0.02	0.09	0.18	1.97
Hg	µg/L	272	198	<0.1	0.00441	0.0122	0.0375	0.1	0.49	0.8	2.1
Ho	µg/L	425	318	<0.001	0.000147	0.000445	0.00142	0.00489	0.015	0.03	0.44
La	µg/L	425	64	<0.005	0.006	0.01	0.02	0.05	0.23	0.768	5.09

Table 4 Continued.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Lu	µg/L										
Mn	µg/L	587	29	<0.0382	0.4	1.19	10	100	373	700	8120
Mo	µg/L	425	131	<0.03		0.1	0.2	0.7	1.9	3.49	36.1
Nd	µg/L	425	110	<0.005	0.004	0.009	0.016	0.06	0.33	0.8	6.31
Ni	µg/L	425	170	<0.05	0.06	0.1	0.27	1	3.3	5.7	106
Pb	µg/L	425	154	<0.02	0.01	0.04	0.1	0.23	0.6	1.2	13.3
Pr	µg/L	425	223	<0.001	0.000664	0.00193	0.00528	0.0124	0.0642	0.198	1.4
Rb	µg/L	425	0	0.05	0.364	0.699	1.35	3.23	8.07	12.1	145
Sb	µg/L	426	251	<0.005	0.00602	0.0113	0.0248	0.05	0.11	0.188	1.57
Se	µg/L	389	152	<0.01	0.04	0.09	0.4	0.9	2	2.7	7.8
Sm	µg/L	425	247	<0.004	0.00107	0.00291	0.008	0.02	0.0876	0.158	1.71
Sn	µg/L	408	62	<0.01	0.03	0.1	0.3	0.63	0.91	1.09	165
Sr	µg/L	485	0	2.45	52.8	95.1	181	422	984	1990	74900
Tb	µg/L	425	337	<0.002	0.000101	0.000313	0.00108	0.00376	0.01	0.02	0.33
Ti	µg/L	408	305	<0.01	0.0109	0.0342	0.114	0.501	1.6	2.49	90
Tl	µg/L	425	335	<0.001	0.0000279	0.00013	0.00075	0.00496	0.0196	0.05	4.42
Tm	µg/L										
U	µg/L	425	30	<0.005	0.02	0.111	0.45	1.4	3.66	5.71	48.9
V	µg/L	408	92	<0.02	0.04	0.13	0.4	1.5	4	6.5	89.2
W	µg/L										
Y	µg/L	425	26	<0.00954	0.01	0.02	0.06	0.16	0.56	1.09	15.2
Yb	µg/L	425	216	<0.005	0.00104	0.0025	0.006	0.0104	0.04	0.0968	0.8
Zn	µg/L	425	2	<0.45	1.8	3.3	6.6	14.8	47.7	103	836
Zr	µg/L	408	270	<0.001	0.000764	0.00222	0.00795	0.02	0.0824	0.143	1.15

Table 5 Summary statistics for elements in groundwaters from Permo-Triassic aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	57	0	6	8.9	9.2	10	11	12.1	13	14.6
pH		57	0	5.18	6.18	6.8	7.18	7.46	7.78	7.84	7.97
DO <sup>1</sup>	mg/L	20	2	<0.1		1.22	4.19	7.43	10		12
Eh <sup>2</sup>	mV	31	0	100	313	344	400	404	428	438	442
SEC <sup>3</sup>	µS/cm	58	0	94.3	196	326	405	510	654	757	994
TDS <sup>4</sup>	mg/L	15	0	78.4	93.8	111	132	174	328	366	380
Ca	mg/L	62	0	6.4	19.4	26.4	37.5	58.6	82.2	101	166
Mg	mg/L	62	0	3.28	6.89	10.7	17.2	21.8	29	30	41
Na	mg/L	62	0	1	7.64	9.45	11.8	17	27.5	30	59.4
K	mg/L	62	0	0.7	1.1	1.2	1.65	2.26	3.59	4.28	6.2
Cl	mg/L	62	0	8.3	11	14.2	18	22.9	46.7	56	96.4
SO <sub>4</sub>	mg/L	62	0	2.1	9.38	13.5	21.1	34.8	74.9	169	475
HCO <sub>3</sub>	mg/L	62	0	13.3	48.8	83.4	139	200	241	274	378
NO <sub>3</sub> -N	mg/L	57	2	<0.00452	0.36	1.6	3.9	6.5	9.91	10.7	22
NO <sub>2</sub> -N	µg/L	37	15	<0.3		0.95	1.85	5.8	7.95	9.38	13
NH <sub>4</sub> -N	µg/L	37	25	<3	0.408	1.18	4.39	20	91.6	114	2500
P	µg/L	37	11	<10		10	20	50	80	90	550
DOC	mg/L	11	2	<0.5		0.511	0.6	1.3	2.51		2.7
F	mg/L	48	13	<0.01	0.04	0.06	0.07	0.085	0.126	0.203	1.79
Br	µg/L	48	0	38.7	50	60	71.5	92.7	179	216	240
I	µg/L	42	0	1.97	2.12	2.82	3.38	5.02	9.31	13.9	45
Si	mg/L	50	0	3.47	4.08	4.6	4.98	6.03	7.32	8.27	13.2
Al	µg/L	40	3	<0.5	0.6	1	1.84	2.93	5	9.94	20.1
As	µg/L	41	8	<0.05	0.18	0.33	0.75	1.67	1.9	2.2	5.82
B	µg/L	46	12	<10	6.62	9	13.2	23	36.1	78	488
Ba	µg/L	49	0	16.6	23.7	32.9	74	166	235	291	345
Be											
Cd	µg/L	37	20	<0.01	0.00624	0.0114	0.0222	0.06	0.105	0.17	0.284
Ce	µg/L	37	22	<0.00981	0.000935	0.00213	0.00533	0.0193	0.034	0.0581	0.16
Co	µg/L	37	3	<0.01	0.01	0.02	0.06	0.0899	0.14	0.22	0.236
Cr	µg/L	37	4	<0.03	0.23	0.277	0.45	0.8	1.72	1.94	3.82
Cs	µg/L	37	11	<0.01		0.01	0.0226	0.0326	0.06	0.49	6.55
Cu	µg/L	37	1	<0.0478	0.224	0.7	1.8	6	14.8	16.3	23.2
Dy	µg/L	37	24	<0.005	0.000921	0.00177	0.00434	0.01	0.0243	0.0368	0.076
Er	µg/L										
Eu	µg/L	33	22	<0.005	0.000882	0.00152	0.00344	0.01	0.0172	0.0268	0.037
Fe	µg/L	61	16	<1	1.7	3	11	74	226	300	1560
Gd	µg/L	37	29	<0.005	0.000235	0.000679	0.00203	0.01	0.0223	0.0448	0.124
Hg	µg/L	10	8	<0.1							0.8
Ho	µg/L										
La	µg/L	37	12	<0.005		0.005	0.01	0.028	0.0567	0.0593	0.541
Li	µg/L	49	3	<1	1	2.35	3.77	6.3	14.3	21.5	26
Lu	µg/L										
Mn	µg/L	61	6	<0.0382	0.0433	0.2	10	50	100	123	300

Table 5 Continued.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	37	24	<0.005	0.000424	0.000961	0.00432	0.012	0.0293	0.0834	0.638
Ni	µg/L	37	7	<0.05	0.07	0.12	0.83	1.3	2.04	3.76	3.89
Pb	µg/L	37	12	<0.0418	0.0487	0.0569	0.165	0.4	0.593	0.9	1.6
Pr	µg/L	37	29	<0.005	0.000161	0.000434	0.00141	0.00428	0.0198	0.0202	0.134
Rb	µg/L	37	0	0.09	0.612	0.892	1.07	1.57	2.9	3.28	18.9
Sb	µg/L	37	27	<0.005	0.0066	0.0106	0.0154	0.026	0.0352	0.069	0.086
Se	µg/L	37	18	<0.01	0.03	0.07	0.18	0.8	1.1	1.6	1.9
Sm	µg/L										
Sn	µg/L	21	11	<0.1	0.0459	0.0656	0.0942	0.16	0.2	0.21	0.53
Sr	µg/L	46	0	14.9	48.5	86.4	120	203	389	449	1500
Tb	µg/L										
Ti	µg/L										
Tl	µg/L										
Tm	µg/L										
U	µg/L	37	0	0.013	0.108	0.283	0.697	1.44	2.44	3.13	5.34
V	µg/L	21	1	<0.2	0.2	0.47	0.85	2.39	5.5	6	9.5
W	µg/L										
Y	µg/L	37	8	<0.00954	0.006	0.01	0.0382	0.0582	0.112	0.259	0.573
Yb	µg/L	37	26	<0.005	0.000816	0.00162	0.00342	0.0094	0.0185	0.0282	0.032
Zn	µg/L	37	1	<0.45	1.13	2	3.76	9.6	31.2	37.4	44.8
Zr	µg/L										

Table 6 Summary statistics for elements in groundwaters from Carboniferous (not extensively mined) aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	41	0	7.1	7.9	8.3	9.6	11.1	12.7	14	17.9
pH		50	0	6.4	6.69	7.02	7.3	7.68	8.04	8.16	8.3
DO <sup>1</sup>	mg/L	21	0	0.16	0.8	1.85	2.76	6.11	9.3	10.2	10.8
Eh <sup>2</sup>	mV	30	0	50	167	214	288	370	422	456	612
SEC <sup>3</sup>	µS/cm	50	0	177	353	516	694	976	1450	2130	2600
TDS <sup>4</sup>	mg/L	10	0	65	95.1	128	194	273	348	364	380
Ca	mg/L	55	0	27.1	35.5	43.8	58.7	76.2	154	233	487
Mg	mg/L	55	0	4.51	12.2	18.9	27.2	36.7	53.3	60.8	70
Na	mg/L	55	0	5.4	6.58	12.4	27.9	51.8	146	193	467
K	mg/L	54	0	1	1.4	2.08	4.42	7.75	9.48	11.1	16.4
Cl	mg/L	54	0	5.74	9.67	18.1	36.8	52	98.8	271	692
SO <sub>4</sub>	mg/L	55	0	0.15	5.03	22	38.5	74.6	175	342	1240
HCO <sub>3</sub>	mg/L	54	0	120	166	213	256	318	382	421	500
NO <sub>3</sub> -N	mg/L	36	8	<0.05	0.01	0.0166	0.727	3.9	7.01	14.9	25.4
NO <sub>2</sub> -N	µg/L	23	13	<0.3	0.0236	0.0645	0.251	1.3	6.6	9.58	35.9
NH <sub>4</sub> -N	µg/L	26	14	<3	0.292	0.478	4.99	35	391	1020	1630
P	µg/L	38	16	<1			20	29	53	81	563
DOC	mg/L	11	0	0.56	0.56	0.945	1.14	1.23	1.36	1.39	1.42
F	mg/L	41	3	<0.03	0.042	0.08	0.185	0.32	0.389	0.425	0.69
Br	µg/L	40	0	32	60.7	127	193	371	772	1770	9100
I	µg/L	33	0	3.4	4.36	5.7	8.3	15	26.2	57.8	139
Si	mg/L	42	0	1.21	3.7	4.64	5.44	6.17	7.82	9.12	12.1
Al	µg/L	39	0	0.4	1.4	2	3	5	7.6	16.2	2860
As	µg/L	40	14	<0.05		0.07	0.5	1.13	2.9	4.7	27.6
B	µg/L	40	4	<17	6	36	113	242	304	382	977
Ba	µg/L	41	0	12.7	34.2	60.8	165	341	406	834	3610
Be	µg/L										
Cd	µg/L	39	25	<0.05	0.00689	0.0139	0.0246	0.0492	0.08	0.137	1.31
Ce	µg/L	39	12	<0.01	0.002	0.003	0.01	0.01	0.02	0.04	0.14
Co	µg/L	39	4	<0.02	0.012	0.04	0.09	0.243	0.68	3.35	11.5
Cr	µg/L	39	30	<0.03	0.0898	0.125	0.186	0.251	0.5	0.5	0.9
Cs	µg/L	39	5	<0.01	0.005	0.01	0.038	0.076	0.12	0.24	0.353
Cu	µg/L	39	2	<0.5	0.5	1	1.8	4	9.7	38.8	77
Dy	µg/L	39	23	<0.005	0.00114	0.00196	0.0034	0.0064	0.01	0.0115	0.071
Er	µg/L	39	26	<0.002	0.000686	0.00164	0.00286	0.00585	0.012	0.02	0.126
Eu	µg/L	25	7	<0.01	0.002	0.008	0.01	0.01	0.04	0.04	0.04
Fe	µg/L	52	9	<10	3	6	46	300	921	3930	16100
Gd	µg/L	39	17	<0.005	0.001	0.002	0.004	0.01	0.025	0.03	0.04
Hg	µg/L	30	14	<0.1			0.3	0.9	1.2	1.4	2.1
Ho											
La	µg/L	39	11	<0.01	0.004	0.007	0.01	0.02	0.05	0.09	0.15
Li	µg/L	41	1	<1	3.81	7.5	12.4	23.6	47.6	63.2	120
Lu	µg/L										
Mn	µg/L	48	0	0.24	2.12	5.85	44	78.2	180	272	492

Table 6 Continued.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	39	13	<0.01	0.005	0.006	0.01	0.01	0.023	0.04	0.1
Ni	µg/L	39	19	<0.2			0.2	1.5	4.5	5.3	40.3
Pb	µg/L	39	19	<0.1	0.03	0.03	0.07	0.12	0.6	1.63	7.02
Pr	µg/L	39	28	<0.005	0.00083	0.00111	0.002	0.00344	0.00573	0.01	0.02
Rb	µg/L	39	0	0.47	1.12	1.54	3.19	6.44	8.81	11.1	13.5
Sb	µg/L	39	26	<0.05	0.00973	0.0135	0.0201	0.0299	0.05	0.05	0.18
Se	µg/L	29	4	<0.01		0.8	1.1	1.7	2.9	4.4	5.2
Sm	µg/L	39	28	<0.005	0.00178	0.00274	0.0051	0.00896	0.0154	0.02	0.04
Sn	µg/L	39	9	<0.03		0.11	0.25	0.42	0.72	0.79	0.83
Sr	µg/L	40	0	79	178	339	700	1420	6560	9500	16000
Tb	µg/L										
Ti	µg/L	39	31	<0.01	0.00158	0.00595	0.0213	0.0857	0.241	0.516	13
Tl											
Tm	µg/L										
U	µg/L	39	2	<0.02	0.013	0.112	0.36	1.5	3.75	5.71	9.96
V	µg/L	39	8	<0.02	0.03	0.05	0.4	1.2	2.8	5.5	6.5
W	µg/L										
Y	µg/L	39	3	<0.05	0.01	0.02	0.04	0.08	0.16	0.35	0.58
Yb	µg/L	39	26	<0.005	0.000986	0.00177	0.00349	0.00723	0.01	0.0128	0.234
Zn	µg/L	39	0	1.7	2.58	4.35	7.6	20.2	86.1	168	542
Zr	µg/L	39	17	<0.002	0.002	0.009	0.018	0.034	0.1	0.31	0.51

Table 7 Summary statistics for elements in groundwaters from Carboniferous Mined aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	52	0	7	8.5	9.5	10.6	11.3	13	14.5	19.2
pH		52	0	3.13	6.3	6.58	7	7.46	7.69	8.01	8.99
DO <sup>1</sup>	mg/L	36	4	<0.1		0.3	1.2	2.99	5.96	7.8	12.8
Eh <sup>2</sup>	mV	50	0	<90	109	140	221	301	332	371	791
SEC <sup>3</sup>	µS/cm	52	0	137	311	470	740	1240	1700	4780	31800
TDS <sup>4</sup>	mg/L	16	0	120	139	187	281	549	754	1110	2000
Ca	mg/L	56	0	3.4	30.9	41.5	71	113	245	303	1640
Mg	mg/L	56	0	1.08	7.42	15	28.2	48	102	195	437
Na	mg/L	56	0	6.2	11	13.2	27.6	132	519	995	5360
K	mg/L	54	0	0.64	1.51	2.52	4.26	11.3	26.3	34.7	92.2
Cl	mg/L	56	0	5.14	10.7	14.4	23.4	63.4	1140	1690	11500
SO <sub>4</sub>	mg/L	56	0	3.82	10.8	32.9	73	118	270	692	2100
HCO <sub>3</sub>	mg/L	54	0	7	100	206	324	467	581	651	926
NO <sub>3</sub> -N	mg/L	52	24	<0.0226	0.01	0.02	0.03	0.3	2	2.83	7.29
NO <sub>2</sub> -N	µg/L	36	28	<0.3	0.0000203	0.000264	0.00627	0.246	3.92	42	6300
NH <sub>4</sub> -N	µg/L	35	4	<5	2	15	110	611	781	1930	2570
P	µg/L	36	13	<1			7.36	23	105	167	432
DOC	mg/L	30	0	0.45	0.639	0.972	1.33	1.75	2.62	27.8	70.8
F	mg/L	38	1	<0.05	0.064	0.117	0.17	0.247	0.531	0.793	1
Br	µg/L	38	2	<100	56	81	102	215	8040	9060	127000
I	µg/L	34	3	<1	2.3	3	5.9	9.9	25.6	52.2	74.3
Si	mg/L	40	0	1.95	3.55	4.36	5.11	6.54	7.92	10.2	12.9
Al	µg/L	38	0	0.2	0.97	1.6	5	11.7	26.1	64.6	94
As	µg/L	36	13	<0.05		0.07	0.18	0.37	0.8	5.25	10.8
B	µg/L	38	1	<20	17.5	34	105	200	371	536	814
Ba	µg/L	38	0	2.3	37	55.2	113	260	610	1720	20100
Be	µg/L	36	18	<0.001		0.001	0.006	0.013	0.071	0.232	0.289
Cd	µg/L	36	9	<0.05	0.001	0.008	0.032	0.067	0.135	0.156	0.601
Ce	µg/L	36	5	<0.01	0.004	0.01	0.016	0.04	0.413	1.31	5.29
Co	µg/L	36	3	<0.02	0.008	0.048	0.15	1.32	19.7	56.8	74.9
Cr	µg/L	36	21	<0.05	0.0589	0.1	0.162	0.224	0.65	0.8	1.1
Cs	µg/L	36	4	<0.01	0.01	0.032	0.069	0.176	0.367	0.479	2.21
Cu	µg/L	36	10	<0.5	0.43	0.44	0.74	1.1	3.5	5.6	20.9
Dy	µg/L	36	12	<0.01	0.002	0.005	0.006	0.01	0.078	0.241	0.818
Er	µg/L	36	12	<0.002	0.002	0.002	0.005	0.01	0.042	0.188	0.417
Eu	µg/L	27	6	<0.01	0.005	0.007	0.01	0.025	0.044	0.185	0.245
Fe	µg/L	54	0	4	31.3	106	675	3730	9360	35200	137000
Gd	µg/L	36	8	<0.01	0.001	0.004	0.007	0.012	0.127	0.192	0.918
Hg	µg/L	8	5	<0.1	0.00398	0.00864	0.0251	0.125	0.29	0.395	0.5
Ho	µg/L	36	16	<0.001		0.001	0.001	0.003	0.015	0.056	0.169
La	µg/L	36	6	<0.01	0.006	0.01	0.02	0.033	0.247	0.768	2.15
Li	µg/L	38	0	1.4	4.29	5.64	11.9	25	52	76.2	182
Lu	µg/L	36	24	<0.002	0.00014	0.000362	0.00131	0.00303	0.00651	0.0162	0.122
Mn	µg/L	53	0	1.24	7.76	50	200	563	900	2400	8120

Table 7 Continued.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	36	8	<0.01	0.005	0.009	0.015	0.036	0.365	0.911	2.87
Ni	µg/L	36	14	<0.2	0.14	0.14	0.8	3.2	32.1	90.5	94.9
Pb	µg/L	36	8	<0.05	0.02	0.03	0.06	0.1	0.2	0.27	13.3
Pr	µg/L	36	12	<0.01	0.001	0.002	0.004	0.009	0.067	0.21	0.664
Rb	µg/L	36	0	0.85	1.28	3.04	5.24	12.6	28.8	47.5	145
Sb	µg/L	36	14	<0.05	0.01	0.01	0.02	0.03	0.05	0.12	0.25
Se	µg/L	14	5	<0.05		0.09	0.37	0.5	1.8		2.7
Sm	µg/L	36	11	<0.02	0.004	0.005	0.007	0.018	0.129	0.186	0.576
Sn	µg/L	36	22	<0.01	0.00468	0.00935	0.0288	0.138	0.63	0.76	1.37
Sr	µg/L	38	0	39	132	345	713	1660	3640	5020	74900
Tb	µg/L	36	25	<0.002	0.0000417	0.000138	0.000563	0.002	0.0185	0.0235	0.141
Ti	µg/L	36	9	<0.01	0.01	0.03	0.07	0.27	0.63	0.67	2.15
Tl	µg/L	36	28	<0.001	0.000243	0.000516	0.00142	0.00485	0.0165	0.0222	0.119
Tm	µg/L	36	28	<0.002	0.0000731	0.000183	0.00046	0.00196	0.00216	0.0049	0.029
U	µg/L	36	2	<0.02	0.007	0.031	0.283	0.727	2.38	5.01	11.4
V	µg/L	36	5	<0.05	0.02	0.03	0.07	0.15	0.4	2.27	13.2
W	µg/L										
Y	µg/L	36	10	<0.01	0.01	0.03	0.07	0.11	0.8	1.09	5.55
Yb	µg/L	36	12	<0.01	0.003	0.004	0.005	0.01	0.067	0.25	0.318
Zn	µg/L	36	0	0.8	2.05	3.18	4.84	12.7	28	99.6	204
Zr	µg/L	36	12	<0.002		0.004	0.037	0.065	0.12	0.155	0.392

Table 8 Summary statistics for elements in groundwaters from Old Red Sandstone North aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	82	0	5	8	9.02	9.95	11.1	13.1	13.3	14.3
pH		97	0	5.33	6.5	6.8	7.2	7.45	7.7	7.85	8.06
DO <sup>1</sup>	mg/L	49	14	<0.1			1.22	5.59	8.16	9.8	9.96
Eh <sup>2</sup>	mV	59	0	<169	124	151	264	329	401	409	463
SEC <sup>3</sup>	µS/cm	94	0	2.5	240	374	547	708	890	1040	2280
TDS <sup>4</sup>	mg/L	29	0	35.4	87.1	106	174	289	796	1180	1270
Ca	mg/L	99	0	1	26.6	47.3	61.6	79.5	99.1	108	353
Mg	mg/L	99	0	0.53	2.3	3.67	8.1	17.4	23.8	32	120
Na	mg/L	99	0	4	11.7	15.3	25.5	41.2	56.9	121	312
K	mg/L	98	1	<0.5	1.3	1.8	2.6	3.8	5.8	7.3	16.4
Cl	mg/L	99	0	6.1	17.5	26.9	46	72.7	92.6	149	624
SO <sub>4</sub>	mg/L	99	0	0.665	6.13	10.6	19.6	35.9	54.5	84.5	778
HCO <sub>3</sub>	mg/L	99	1	<20	77	127	193	250	327	380	417
NO <sub>3</sub> -N	mg/L	82	20	<0.00452		0.04	0.66	3.6	6.23	9.15	21.7
NO <sub>2</sub> -N	µg/L	50	27	<0.3	0.0676	0.174	1.02	3.38	15.9	27.1	571
NH <sub>4</sub> -N	µg/L	50	37	<4	0.0447	0.199	1.12	16	125	912	2200
P	µg/L	60	24	<10			26	50	78	89	190
DOC	mg/L	46	0	0.35	0.693	0.965	1.27	2.35	3.77	6.66	11.3
F	mg/L	80	22	<0.01		0.051	0.099	0.15	0.261	0.44	1.16
Br	µg/L	80	1	<20	54	83	152	267	423	663	2700
I	µg/L	80	1	<2	2.98	3.4	5.5	10.7	30.1	49.6	246
Si	mg/L	80	0	0.5	3.72	4.64	5.4	6.53	7.51	8.24	10.9
Al	µg/L	60	0	1	4	6	8	21	49.6	74.6	152
As	µg/L	71	24	<0.5	0.09	0.16	0.479	1.2	4.81	9	33.6
B	µg/L	71	10	<10	8	11	18	33.2	50	89	203
Ba	µg/L	80	0	6.82	45.5	84.3	123	210	308	417	922
Be	µg/L	60	42	<0.005	0.000854	0.00217	0.00541	0.0173	0.045	0.121	0.65
Cd	µg/L	60	31	<0.05	0.00725	0.01	0.0211	0.0485	0.101	0.131	2.63
Ce	µg/L	60	7	<0.01		0.01	0.02	0.06	0.11	0.25	1.26
Co	µg/L	60	10	<0.02		0.04	0.07	0.25	0.88	1.57	10.6
Cr	µg/L	60	30	<0.5	0.0939	0.1	0.2	0.4	0.6	0.8	1
Cs	µg/L	60	7	<0.01		0.02	0.1	0.421	2.09	3.28	18.6
Cu	µg/L	60	0	0.5	0.8	1.2	2.35	4.95	11.3	29.3	240
Dy	µg/L	60	19	<0.005	0.005	0.006	0.01	0.012	0.03	0.12	0.36
Er	µg/L	60	26	<0.005		0.006	0.008	0.01	0.02	0.06	0.234
Eu	µg/L	49	21	<0.005			0.01	0.015	0.025	0.034	0.09
Fe	µg/L	91	19	<5	2.1	4	28.8	300	857	2490	5430
Gd	µg/L	60	15	<0.005		0.007	0.01	0.012	0.045	0.0675	0.35
Hg	µg/L	39	26	<0.1	0.00379	0.0106	0.0351	0.1	0.4	0.81	1
Ho	µg/L	60	46	<0.005	0.000291	0.000665	0.00185	0.006	0.01	0.0216	0.07
La	µg/L	60	3	<0.01	0.01	0.01	0.026	0.05	0.135	0.21	1.01
Li	µg/L	80	7	<2	1.5	2.9	5.2	8.7	14	17	45
Lu	µg/L										
Mn	µg/L	91	3	<2	1.33	3.6	39.4	230	624	867	1900

Table 8 Continued.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	60	5	<0.01	0.00878	0.01	0.0204	0.057	0.19	0.21	1.67
Ni	µg/L	60	17	<0.2	0.059	0.059	0.4	1.2	2.1	7.8	13.2
Pb	µg/L	60	11	<0.1		0.1	0.1	0.3	0.8	1.1	1.6
Pr	µg/L	60	29	<0.005			0.00826	0.012	0.03	0.05	0.36
Rb	µg/L	60	0	0.05	0.511	1.24	2.3	7.71	12.8	29.3	37.6
Sb	µg/L	60	26	<0.05	0.016	0.021	0.037	0.08	0.14	0.37	1.29
Se	µg/L	60	19	<0.5	0.04	0.06	0.19	0.6	1.2	1.7	3.6
Sm	µg/L	60	29	<0.005	0.005	0.008	0.012	0.019	0.0372	0.06	0.34
Sn	µg/L	60	3	<0.1	0.3	0.3	0.5	0.89	1.09	1.25	1.87
Sr	µg/L	80	0	21.2	62.7	93.2	168	479	776	944	1300
Tb	µg/L										
Ti	µg/L	60	37	<10	0.914	1.26	1.76	2.44	3.29	4.13	13
Tl	µg/L	60	39	<0.01	0.000368	0.00159	0.00824	0.05	0.138	0.391	4.42
Tm	µg/L										
U	µg/L	60	4	<0.02	0.06	0.25	0.76	1.45	3.84	4.49	5.36
V	µg/L	60	7	<0.1	0.0679	0.2	0.3	0.7	1.1	1.4	7.6
W	µg/L	60	47	<0.02	0.00148	0.00246	0.00518	0.0113	0.02	0.02	0.16
Y	µg/L	60	0	0.01	0.02	0.0468	0.0755	0.143	0.301	0.865	2.37
Yb	µg/L	60	25	<0.005		0.006	0.008	0.011	0.023	0.06	0.405
Zn	µg/L	60	0	1	1.88	3	6.08	14	46.2	103	582
Zr	µg/L	60	35	<0.02	0.00237	0.00573	0.0168	0.0428	0.1	0.121	0.92

Table 9 Summary statistics for elements in groundwaters from Old Red Sandstone South aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	96	0	5	8.45	9	9.75	11	13	13.6	16.4
pH		113	0	5.64	6.77	7.02	7.41	7.7	7.8	7.98	8.62
DO <sup>1</sup>	mg/L	64	2	<0.1	1.4	3.2	6.64	8.2	9.02	10.1	10.8
Eh <sup>2</sup>	mV	64	0	40	308	349	390	406	445	457	474
SEC <sup>3</sup>	µS/cm	108	0	50	296	386	498	610	821	953	2000
TDS <sup>4</sup>	mg/L	32	0	34.6	85	142	168	267	497	1980	3870
Ca	mg/L	125	0	7.1	25.5	38	47.5	60.9	84.3	104	819
Mg	mg/L	125	0	1.1	5.72	9.82	14.4	22.2	34	43.7	58
Na	mg/L	125	0	3.5	7.48	11.5	16	25.3	66.3	128	634
K	mg/L	125	1	<0.5	0.9	1.45	2.1	3.22	5.1	11.8	201
Cl	mg/L	125	0	2.78	13.3	17.6	25.3	43.6	68.4	123	2320
SO <sub>4</sub>	mg/L	124	0	4.3	9.17	13.5	21.7	34.2	61.9	90	1320
HCO <sub>3</sub>	mg/L	124	0	2.93	89.8	128	162	214	257	290	453
NO <sub>3</sub> -N	mg/L	93	3	<0.00452	0.2	1.3	4	10.2	17.7	22.3	81.1
NO <sub>2</sub> -N	µg/L	58	17	<0.3		1.1	2.59	4.62	18	39.8	194
NH <sub>4</sub> -N	µg/L	62	41	<0.6	0.0426	0.19	1.12	9.42	26.7	67.8	8320
P	µg/L	79	17	<4		20	33	59	86	170	40500
DOC	mg/L	33	0	0.27	0.436	0.57	0.9	1.47	1.94	2.78	5.82
F	mg/L	90	2	<0.03	0.05	0.06	0.08	0.114	0.15	0.269	4.1
Br	µg/L	88	1	<30	49.7	65	94	179	267	607	1760
I	µg/L	83	2	<2	2	3	4	6	9.1	13.3	278
Si	mg/L	94	0	2.62	3.92	4.24	5.56	6.99	9.16	9.82	15.2
Al	µg/L	77	1	<0.5	2	3	4	6	14	21	192
As	µg/L	77	12	<0.5	0.26	0.6	1.3	2.79	6.9	8.8	26.6
B	µg/L	88	21	<10		13	30	55	149	210	654
Ba	µg/L	88	0	9.2	62	107	197	289	376	482	923
Be	µg/L										
Cd	µg/L	77	57	<0.01	0.00568	0.01	0.02	0.0372	0.074	0.1	0.54
Ce	µg/L	77	38	<0.01	0.004	0.004	0.004	0.01	0.03	0.08	0.31
Co	µg/L	77	30	<0.01		0.01	0.02	0.06	0.13	1.09	1.54
Cr	µg/L	77	22	<0.03	0.04	0.43	0.7	1.08	1.5	1.7	2.7
Cs	µg/L	77	16	<0.01		0.01	0.01	0.04	0.07	0.09	0.13
Cu	µg/L	77	0	0.4	0.5	0.8	1.6	3.7	21.1	31.5	403
Dy	µg/L	77	50	<0.005	0.000637	0.00149	0.00353	0.01	0.02	0.034	0.14
Er	µg/L	77	53	<0.002	0.000364	0.000964	0.00258	0.01	0.014	0.034	0.17
Eu	µg/L	63	19	<0.005			0.01	0.02	0.03	0.04	0.05
Fe	µg/L	105	46	<6	2	2	11	44	158	300	987
Gd	µg/L	77	37	<0.005	0.002	0.002	0.006	0.01	0.028	0.06	0.18
Hg	µg/L	68	43	<0.1	0.0104	0.0234	0.0589	0.125	0.43	0.6	0.8
Ho	µg/L										
La	µg/L	77	17	<0.01	0.006	0.007	0.01	0.02	0.04	0.14	0.31
Li	µg/L	88	9	<1	1.3	2.8	5	9.4	17.8	37.1	330
Lu	µg/L										
Mn	µg/L	98	11	<10	0.3	0.64	1.4	16.9	81.7	115	1440

Table 9 Continued.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	77	29	<0.005		0.005	0.01	0.02	0.08	0.19	0.41
Ni	µg/L	77	50	<0.2	0.0171	0.0489	0.139	0.39	1.06	3.74	32.4
Pb	µg/L	77	36	<0.1			0.1	0.26	0.5	1.2	2.3
Pr	µg/L	77	58	<0.005	0.000478	0.00112	0.00264	0.00733	0.01	0.036	0.08
Rb	µg/L	77	0	0.2	0.31	0.58	1.02	1.98	3.32	4.69	28.7
Sb	µg/L	77	58	<0.05	0.00413	0.00839	0.0191	0.0415	0.074	0.122	0.72
Se	µg/L	76	12	<0.01	0.07	0.32	0.7	1.1	2.3	4	7.8
Sm	µg/L	77	60	<0.005	0.000742	0.00169	0.00407	0.0104	0.02	0.0356	0.12
Sn	µg/L	77	9	<0.03		0.3	0.46	0.54	0.67	1	2.59
Sr	µg/L	87	0	31.9	51	95.4	178	310	742	1040	2140
Tb	µg/L										
Ti	µg/L										
Tl	µg/L	77	59	<0.001	0.00219	0.00317	0.00475	0.00713	0.01	0.01	0.09
Tm	µg/L										
U	µg/L	77	2	<0.005	0.13	0.34	1.01	2.57	7.22	12.5	18.9
V	µg/L	77	2	<0.2	0.39	1.3	2.5	4.2	8.6	12.1	57.4
W	µg/L										
Y	µg/L	77	1	<0.05	0.01	0.015	0.03	0.07	0.18	0.41	1.15
Yb	µg/L	77	51	<0.005	0.000399	0.0011	0.00319	0.01	0.024	0.04	0.3
Zn	µg/L	77	0	0.7	1.6	3.3	7.7	26.1	109	190	836
Zr	µg/L	77	60	<0.002	0.00016	0.000516	0.00227	0.00997	0.034	0.092	0.38

Table 10 Summary statistics for elements in groundwaters from Ordovician and Silurian aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	68	0	6.1	8.44	9.65	10.9	12.7	14	15.3	16.8
pH		72	0	3.68	6.04	6.7	7.09	7.48	7.76	7.92	8.2
DO <sup>1</sup>	mg/L	48	1	<0.1	0.14	1.5	3.68	5.1	8.1	8.64	11.2
Eh <sup>2</sup>	mV	51	0	23	265	316	371	410	443	479	534
SEC <sup>3</sup>	µS/cm	73	0	45	116	190	340	536	655	773	4650
TDS <sup>4</sup>	mg/L	11	0	24.3	25.5	41.3	69.9	119	215	221	228
Ca	mg/L	73	0	1.6	10	19.7	39.1	54.6	70	78.6	327
Mg	mg/L	73	0	0.85	2.64	5.66	12.5	17.9	25.1	33.4	57
Na	mg/L	73	0	4.3	5.45	7.4	10.5	15.7	23.9	39.9	543
K	mg/L	72	2	<0.5	0.5	0.86	1.2	2.27	3.4	4.2	10.3
Cl	mg/L	72	0	5.17	7.05	10.5	14.4	28.7	49.6	58.5	1360
SO <sub>4</sub>	mg/L	73	0	3	5.06	7	10.4	14.8	28.3	40.6	544
HCO <sub>3</sub>	mg/L	73	1	<20	13	56.7	134	207	273	300	315
NO <sub>3</sub> -N	mg/L	70	1	<0.05	0.115	0.348	2.51	4.82	9.94	12.7	37.2
NO <sub>2</sub> -N	µg/L	51	19	<0.3			1.2	2.77	3.8	6.06	13
NH <sub>4</sub> -N	µg/L	51	34	<0.6	0.0102	0.0559	0.364	3.7	17.3	35.3	3980
P	µg/L	58	15	<20	10.2	11.9	25	32	47	56	65.3
DOC	mg/L	20	0	0.45	0.576	0.685	1.23	2.15	3.07	3.66	3.86
F	mg/L	55	8	<0.02	0.042	0.049	0.064	0.087	0.13	0.204	0.966
Br	µg/L	54	1	<20	41	61	76	132	199	272	20000
I	µg/L	45	9	<0.8		2.4	4.48	8.31	16	20.1	30.6
Si	mg/L	60	0	1.59	2.58	3.53	4.12	4.98	6.15	7.03	20.6
Al	µg/L	59	0	1	2	4	6	11	23.2	66.4	10000
As	µg/L	53	29	<0.5	0.013	0.0513	0.251	1.4	6.42	9.36	57.5
B	µg/L	62	9	<20	7	11	16	24	36	67	253
Ba	µg/L	62	0	1.7	8.23	38	113	193	288	393	24400
Be	µg/L										
Cd	µg/L										
Ce	µg/L	53	19	<0.00981			0.01	0.03	0.17	0.49	6.22
Co	µg/L	53	28	<0.02	0.000293	0.00152	0.00896	0.06	0.138	0.854	34.7
Cr	µg/L	53	42	<0.5	0.032	0.0671	0.141	0.338	0.89	1.14	2.5
Cs	µg/L	53	7	<0.01		0.02	0.04	0.07	0.105	0.12	0.26
Cu	µg/L	53	0	0.3	0.96	1.5	4	7.9	25	47.3	401
Dy	µg/L	53	19	<0.01			0.01	0.04	0.09	0.12	1.58
Er	µg/L	53	26	<0.01			0.01	0.02	0.06	0.07	0.74
Eu	µg/L	52	33	<0.00781	0.000578	0.00154	0.00429	0.0125	0.039	0.04	0.48
Fe	µg/L	66	27	<10	7.5	7.5	13	41	419	1000	8500
Gd	µg/L	53	13	<0.01		0.01	0.01	0.07	0.17	0.23	1.97
Hg	µg/L										
Ho	µg/L	53	41	<0.01	0.000165	0.000486	0.00159	0.0055	0.02	0.024	0.28
La	µg/L	53	6	<0.01		0.01	0.02	0.11	0.24	1.06	2.36
Li	µg/L	61	4	<0.6	0.4	1.3	3.3	5.9	9.7	17.3	535
Lu	µg/L										
Mn	µg/L	68	0	0.163	0.277	0.597	4.42	50	183	653	1630

Table 10 *Continued.*

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	53	9	<0.01		0.01	0.03	0.1	0.41	1.49	5.17
Ni	µg/L	53	28	<0.2	0.00337	0.0158	0.0836	0.6	1.51	5.68	106
Pb	µg/L	53	24	<0.1			0.1	0.3	0.5	1.2	7
Pr	µg/L	53	26	<0.01			0.01	0.03	0.1	0.33	0.96
Rb	µg/L	53	0	0.25	0.46	0.7	1.05	1.69	3.44	3.93	12.1
Sb	µg/L	53	36	<0.05	0.00289	0.00731	0.0203	0.07	0.126	0.27	1.48
Se	µg/L	51	26	<0.5	0.157	0.253	0.424	0.75	1.1	1.75	3
Sm	µg/L	53	34	<0.02	0.00094	0.0029	0.00984	0.05	0.128	0.216	1.71
Sn	µg/L	52	0	0.07	0.131	0.19	0.495	0.742	0.828	0.912	0.97
Sr	µg/L	54	0	19.8	60.3	101	186	253	355	549	23400
Tb	µg/L	53	38	<0.01	0.0011	0.00217	0.00456	0.01	0.02	0.024	0.29
Ti	µg/L										
Tl	µg/L										
Tm	µg/L	53	41	<0.01	0.00193	0.00305	0.00502	0.0086	0.01	0.014	0.1
U	µg/L	53	6	<0.02	0.03	0.11	0.41	1.28	2.15	3.16	6.33
V	µg/L	52	28	<0.2	0.0287	0.0697	0.188	0.725	1.56	1.8	10
W	µg/L										
Y	µg/L	53	0	0.01	0.02	0.04	0.09	0.24	0.607	0.794	7.11
Yb	µg/L	53	28	<0.01	0.000582	0.00159	0.00473	0.01	0.048	0.064	0.62
Zn	µg/L	53	0	1	2.16	3.5	6.3	9.6	23.4	38.1	86.7
Zr	µg/L										

Table 11 Summary statistics for elements in groundwaters from Calcareous aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	16	0	7.4	7.7	8.38	9.4	12.7	13.8	14.7	16.4
pH		18	0	5.59	6.46	6.7	7.2	7.42	7.72	7.83	7.84
DO <sup>1</sup>	mg/L	18	0	2.02	3.59	5.56	7.86	9.28	10.5	10.9	11.2
Eh <sup>2</sup>	mV	16	0	222	266	320	414	484	528	542	549
SEC <sup>3</sup>	µS/cm	18	0	60	86.1	279	471	576	656	788	932
TDS <sup>4</sup>	mg/L	12	0	56	79.9	190	469	535	621	702	792
Ca	mg/L	18	0	5.6	12.5	25	62.8	78.1	121	132	145
Mg	mg/L	18	0	1.06	2.89	3.51	4.8	10.4	28.4	28.8	30.9
Na	mg/L	18	0	4.24	4.47	6.88	8.8	14.4	23.2	39.1	119
K	mg/L	18	0	0.57	0.877	1.02	2.35	3.48	4.4	5.48	6.15
Cl	mg/L	18	0	4.29	6.27	10.5	16.2	29.8	38.1	48	96.6
SO <sub>4</sub>	mg/L	18	0	1.62	2.64	5.64	9.81	19.9	31.8	42.3	90.6
HCO <sub>3</sub>	mg/L	18	0	36	46.4	54.3	194	344	377	392	395
NO <sub>3</sub> -N	mg/L	18	0	0.0438	0.21	0.341	1.56	6.01	19	31.6	36.8
NO <sub>2</sub> -N	µg/L										
NH <sub>4</sub> -N	µg/L	12	8	<190	12.9	19.6	39.9	126	187	383	620
P	µg/L	16	7	<10			10	25	40		47
DOC	mg/L	12	0	0.26	0.557	0.843	0.949	1.27	2.97	3.3	3.55
F	mg/L	17	4	<0.01		0.014	0.0421	0.089	1.04		2.1
Br	µg/L	17	0	20.9	35.8	45.5	58	117	371	387	435
I	µg/L	16	2	<2	0.871	1.46	2	4.6	34.1		244
Si	mg/L	18	0	1.43	1.99	2.64	3.99	6.16	6.78	8.21	12.6
Al	µg/L	16	4	<1	0.6	0.6	4.1	11	44		748
As	µg/L	17	6	<0.05	0.05	0.08	0.1	0.16	0.8		2.15
B	µg/L	18	14	<10	3.08	4.46	6.72	10.8	16.1	32.6	124
Ba	µg/L	18	0	4	15.7	17.7	32.5	63	124	222	237
Be	µg/L										
Cd	µg/L	16	6	<0.01			0.01	0.03			0.09
Ce	µg/L	16	1	<0.01	0.006	0.01	0.02	0.03	0.051		3.89
Co	µg/L	16	2	<0.02	0.01	0.02	0.03	0.09	0.171		0.19
Cr	µg/L	16	2	<0.05	0.07	0.1	0.15	0.5	1.2		4.53
Cs	µg/L	16	6	<0.01		0.01	0.01	0.05	0.14		0.8
Cu	µg/L	16	4	<0.1			1.3	15.8	46.7		6260
Dy	µg/L	15	2	<0.005	0.006	0.006	0.007	0.02	0.05		0.165
Er	µg/L	16	2	<0.005	0.003	0.005	0.008	0.01	0.03		0.075
Eu	µg/L	16	6	<0.002		0.002	0.004	0.007	0.025		0.03
Fe	µg/L	18	3	<1	1	2	10	69	271		1420
Gd	µg/L	16	1	<0.005	0.004	0.007	0.01	0.012	0.04		0.169
Hg	µg/L										
Ho	µg/L	16	12	<0.002	0.000249	0.000442	0.00108	0.00322	0.007	0.0158	0.033
La	µg/L	16	1	<0.005	0.019	0.04	0.06	0.12	0.162		2.99
Li	µg/L	17	11	<0.7	0.135	0.314	0.5	1.2	2.84	8.48	26
Lu	µg/L										
Mn	µg/L	18	1	<3	0.3	0.53	0.8	4.3	48.8		57.1

Table 11 *Continued.*

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	16	1	<0.005	0.02	0.03	0.054	0.09	0.17		1.23
Ni	µg/L	16	4	<0.1			0.42	1.1	1.5		3
Pb	µg/L	16	5	<0.02		0.04	0.04	0.2	0.5		1.21
Pr	µg/L	16	2	<0.005	0.005	0.009	0.01	0.023	0.04		0.389
Rb	µg/L	16	0	0.43	0.575	1.4	2.18	2.69	4.97	7.88	10.8
Sb	µg/L	16	3	<0.05	0.014	0.016	0.042	0.057	0.15		0.19
Se	µg/L	16	8	<0.1	0.09	0.09	0.1	0.4	2.3		2.5
Sm	µg/L	16	4	<0.005	0.005	0.009	0.011	0.019	0.03		0.161
Sn	µg/L	16	3	<0.02		0.03	0.07	0.13	1.29		165
Sr	µg/L	18	0	36.9	69.1	90.5	296	757	2840	6030	12500
Tb	µg/L										
Ti	µg/L										
Tl	µg/L	16	11	<0.01	0.00306	0.00451	0.00676	0.01	0.02	0.0235	0.03
Tm	µg/L										
U	µg/L	16	0	0.05	0.08	0.0982	0.192	0.418	0.69	1.74	4.88
V	µg/L	16	12	<0.02	0.0231	0.0351	0.0803	0.19	0.45	0.625	1
W	µg/L										
Y	µg/L	16	0	0.009	0.043	0.0738	0.103	0.182	0.292	0.636	1.43
Yb	µg/L	16	3	<0.005	0.002	0.004	0.007	0.01	0.02		0.044
Zn	µg/L	16	1	<0.5	0.8	1.6	4	7	44.5		151
Zr	µg/L	16	12	<0.005	0.00103	0.00241	0.00589	0.0393	0.185	0.348	0.4

Table 12 Summary statistics for elements in groundwaters from Precambrian North aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	34	0	6.5	7.93	9.1	10	10.4	11.4	11.8	13.5
pH		38	0	5.61	6.07	6.27	6.68	7.28	8.09	8.17	9.34
DO <sup>1</sup>	mg/L	23	0	0.03	0.114	0.34	2.06	6.12	9.11	10.5	14.4
Eh <sup>2</sup>	mV	24	0	40	258	342	391	475	490	497	562
SEC <sup>3</sup>	µS/cm	33	0	40	110	161	227	317	544	594	679
TDS <sup>4</sup>	mg/L	32	0	18.3	47	92.2	131	218	337	393	452
Ca	mg/L	41	0	2	9	13.3	20.9	34	64.6	70.5	77
Mg	mg/L	41	0	0.681	1.18	2.1	3.73	5.9	7	11.6	22.4
Na	mg/L	41	0	4.4	7.4	11.3	18	29	35	38.9	78.1
K	mg/L	41	0	0.5	0.95	1.33	1.91	2.6	4.1	5.95	17.1
Cl	mg/L	41	0	3.83	10.1	14	22	37	67.1	83.5	154
SO <sub>4</sub>	mg/L	41	0	1.9	2.7	4.54	7.67	10.5	12	24.1	59.6
HCO <sub>3</sub>	mg/L	41	0	5	27	46.9	72	116	221	234	293
NO <sub>3</sub> -N	mg/L	38	4	<0.02	0.0342	0.04	0.283	2.24	3.95	10.8	13.3
NO <sub>2</sub> -N	µg/L	26	20	<0.3	1.04	1.9	4.04	8.02	14.4	27.5	42.8
NH <sub>4</sub> -N	µg/L										
P	µg/L	26	19	<5	0.499	1.01	2.99	9.36	29	38.2	65.8
DOC	mg/L	22	0	0.243	0.476	0.631	0.859	1.12	2.16	2.49	4.93
F	mg/L	32	3	<0.02	0.0206	0.0242	0.0654	0.126	0.698	0.96	1.28
Br	µg/L	32	0	26.8	33.5	45.9	83.2	135	242	282	371
I	µg/L	31	1	<2	1.51	2	2.62	3	7.31	9.35	22.7
Si	mg/L	35	0	2.7	3.53	4.28	5.65	7.49	10.6	12.4	16.4
Al	µg/L	32	2	<1	0.8	2	6	14	22	30	182
As	µg/L	31	8	<0.08	0.02	0.05	0.15	0.95	1.1	170	210
B	µg/L	35	20	<13	2.58	4.65	7	11.9	20.6	29.4	48
Ba	µg/L	36	0	2	9.46	18.1	41.8	85.5	232	271	583
Be	µg/L	25	12	<0.01			0.01	0.04	0.07	0.07	0.1
Cd	µg/L	25	8	<0.01			0.02	0.03	0.26	0.27	0.47
Ce	µg/L	25	0	0.005	0.012	0.049	0.149	1.33	2.33	2.58	5.75
Co	µg/L	25	3	<0.01		0.02	0.04	0.23	0.88	1.57	1.59
Cr	µg/L	25	6	<0.05		0.06	0.16	0.29	0.72	0.73	2.76
Cs	µg/L	25	11	<0.01			0.02	0.04	0.07	0.13	0.15
Cu	µg/L	25	5	<0.4		0.4	1.3	1.8	12.2	28.8	76
Dy	µg/L	25	0	0.003	0.0048	0.01	0.045	0.172	0.249	0.283	0.421
Er	µg/L	25	2	<0.002	0.002	0.008	0.031	0.106	0.161	0.169	0.282
Eu	µg/L	23	5	<0.002		0.003	0.01	0.035	0.059	0.075	0.078
Fe	µg/L	40	1	<10	2	9	41	208	1100	2760	6870
Gd	µg/L	25	0	0.002	0.0042	0.01	0.04	0.178	0.297	0.386	0.426
Hg	µg/L	4	1	<0.1	0.03	0.03					0.1
Ho	µg/L	25	7	<0.002			0.011	0.036	0.065	0.065	0.105
La	µg/L	25	0	0.01	0.0232	0.058	0.103	1.03	1.28	2.13	2.55
Li	µg/L	35	11	<0.7	0.5	0.7	2.2	4	7	12	39
Lu	µg/L	25	11	<0.002			0.003	0.014	0.027	0.033	0.036
Mn	µg/L	40	3	<0.8	0.78	2.5	28.4	190	447	830	3140

Table 12 *Continued.*

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	25	0	0.02	0.02	0.04	0.12	0.83	1.34	2.07	2.59
Ni	µg/L	25	7	<0.1			0.2	0.4	1.04	1.2	1.5
Pb	µg/L	25	11	<0.02			0.06	0.12	0.45	0.74	3.3
Pr	µg/L	25	0	0.003	0.0048	0.011	0.021	0.215	0.294	0.523	0.632
Rb	µg/L	25	0	0.09	0.406	0.63	1.09	3.25	4.87	6.58	16.6
Sb	µg/L	26	3	<0.04	0.005	0.008	0.015	0.034	0.08	0.2	0.29
Se	µg/L	25	15	<0.1	0.0145	0.0345	0.0764	0.3	0.52	1.4	2.2
Sm	µg/L	25	2	<0.004	0.005	0.01	0.03	0.194	0.327	0.382	0.449
Sn	µg/L	25	2	<0.02	0.02	0.03	0.05	0.11	0.15	0.63	1.66
Sr	µg/L	34	0	30.8	41.9	63	128	372	723	1890	3250
Tb	µg/L	25	8	<0.002			0.01	0.026	0.047	0.055	0.081
Ti	µg/L	25	10	<0.05	0.03	0.03	0.07	0.27	0.57	1.08	1.34
Tl	µg/L										
Tm	µg/L	25	12	<0.002			0.004	0.014	0.025	0.028	0.036
U	µg/L	25	0	0.016	0.0632	0.124	0.585	2.71	12.3	20.5	48.9
V	µg/L	25	13	<0.2	0.0824	0.139	0.249	0.6	0.8	1.04	2.1
W	µg/L										
Y	µg/L	25	0	0.022	0.0566	0.153	0.425	1.28	1.82	2.51	4.18
Yb	µg/L	25	0	0.002	0.003	0.008	0.023	0.092	0.128	0.189	0.206
Zn	µg/L	25	0	0.9	1.24	1.8	3.9	6.1	37.7	56.6	60.6
Zr	µg/L	25	18	<0.005	0.000207	0.000571	0.00516	0.0299	0.264	0.544	1.15

Table 13 Summary statistics for elements in groundwaters from Precambrian South aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	31	0	7	8	8.5	9.8	11.1	12.4	13.6	17.2
pH		39	0	5.39	5.71	6.06	6.65	7.54	8.13	8.2	8.4
DO <sup>1</sup>	mg/L	32	2	<0.1	1.09	3.32	5	7.76	9.78	10.5	10.8
Eh <sup>2</sup>	mV	30	0	81	217	304	352	421	460	468	532
SEC <sup>3</sup>	µS/cm	37	0	38	83.5	149	241	330	449	666	2000
TDS <sup>4</sup>	mg/L	17	0	15.8	17.7	29.9	50.7	100	107	502	2070
Ca	mg/L	39	0	4.2	6.4	10.8	17.4	28	44.3	61.5	111
Mg	mg/L	39	0	0.6	1.2	2.41	4.53	7.72	11	14.1	17.6
Na	mg/L	39	0	2	3.06	5.51	13.7	22.6	28.9	41.1	635
K	mg/L	39	0	0.44	0.7	1.04	1.51	2.45	3.34	3.95	6.27
Cl	mg/L	39	0	3.1	3.76	4.73	15.4	30.1	39.3	73.3	79.6
SO <sub>4</sub>	mg/L	39	0	3.6	4.64	6.29	11.2	16.6	25	34.3	1320
HCO <sub>3</sub>	mg/L	38	0	5.4	10.8	18.2	37	108	155	170	264
NO <sub>3</sub> -N	mg/L	34	2	<0.02	0.04	0.45	1.8	6.04	10.2	21	21.2
NO <sub>2</sub> -N	µg/L	24	15	<0.3	0.164	0.289	0.68	1.68	2.22	2.92	10.5
NH <sub>4</sub> -N	µg/L	24	18	<3	0.203	0.699	3.53	25.5	54.6	204	1330
P	µg/L	32	9	<5			27	47	63		80
DOC	mg/L	18	3	<0.5	0.35	0.522	0.66	1.34	3.35		4.23
F	mg/L	32	2	<0.02	0.025	0.0359	0.0602	0.104	0.169	0.197	0.234
B	µg/L	32	1	<20	21.2	31	60	243	445	476	562
I	µg/L	26	6	<0.2		0.811	1.36	4.1	13.7	29.5	44
Si	mg/L	33	0	1.93	3.03	3.89	5.81	9.2	10.7	12.2	13.6
Al	µg/L	32	0	2	2.92	5.8	8.75	18	33.8	43.5	100
As	µg/L	31	16	<0.08	0.0447	0.149	0.358	1.15	3.74	6.22	23
B	µg/L	33	23	<20	4.27	6	9	15	19.5	25.4	50
Ba	µg/L	33	0	4	10.7	17.7	43.3	126	149	211	365
Be	µg/L	31	24	<0.02	0.00472	0.00814	0.0155	0.0295	0.06	0.085	0.13
Cd	µg/L	31	17	<0.02	0.0145	0.0239	0.0407	0.095	0.15	0.21	0.28
Ce	µg/L	31	3	<0.01	0.009	0.01	0.039	0.121	0.374	1.14	1.27
Co	µg/L	31	5	<0.02	0.01	0.02	0.036	0.22	1.78	2.23	14.3
Cr	µg/L	31	13	<0.5	0.1	0.11	0.22	0.52	0.6	0.9	1.1
Cs	µg/L	31	18	<0.01	0.000713	0.00199	0.00665	0.02	0.06	0.13	0.3
Cu	µg/L	31	0	0.3	1	1.35	2.8	5.9	28.9	38.9	96.8
Dy	µg/L	31	7	<0.005		0.006	0.02	0.04	0.06	0.075	0.29
Er	µg/L	31	8	<0.005		0.006	0.01	0.03	0.04	0.05	0.21
Eu	µg/L	29	8	<0.005		0.005	0.01	0.02	0.05		0.08
Fe	µg/L	39	5	<10	5	10	35	120	508	990	1500
Gd	µg/L	31	7	<0.005		0.009	0.02	0.04	0.05	0.137	0.39
Hg	µg/L										
Ho	µg/L	31	22	<0.005	0.000737	0.0013	0.00283	0.008	0.01	0.014	0.06
La	µg/L	31	2	<0.01	0.01	0.01	0.04	0.16	0.28	0.691	0.82
Li	µg/L	32	3	<0.7	0.3	0.7	1.7	3.5	7.5	11.6	11.8
Lu	µg/L										
Mn	µg/L	38	3	<2	0.97	1.47	4.66	34	311	989	2520

Table 13 *Continued.*

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	31	5	<0.01	0.01	0.01	0.09	0.22	0.34	0.94	1.34
Ni	µg/L	31	6	<0.2	0.06	0.21	0.84	2.3	5.7	9.6	10.6
Pb	µg/L	31	9	<0.04		0.07	0.1	0.2	0.5	3.3	3.7
Pr	µg/L	31	11	<0.005			0.018	0.05	0.07	0.227	0.25
Rb	µg/L	31	0	0.1	0.22	0.295	0.69	1.83	3.5	4.7	5.71
Sb	µg/L	31	22	<0.04	0.00035	0.00156	0.00797	0.07	0.17	0.9	1.57
Se	µg/L	31	21	<0.5	0.22	0.381	0.645	1.35	3	3.35	3.5
Sm	µg/L	31	12	<0.005		0.006	0.02	0.044	0.06	0.171	0.28
Sn	µg/L	31	0	0.08	0.1	0.135	0.19	0.775	1.06	1.34	3.07
Sr	µg/L	32	0	30	44.9	64.5	112	185	347	384	425
Tb	µg/L	31	21	<0.005	0.00128	0.00204	0.00356	0.00639	0.01	0.013	0.04
Ti	µg/L	31	20	<10	0.05	0.085	0.18	0.72	1.22	2	2.79
Tl	µg/L										
Tm	µg/L										
U	µg/L	31	10	<0.02			0.04	1.13	3.03	4.98	6.19
V	µg/L	31	10	<0.2			0.3	0.4	0.9	1.6	4.1
W	µg/L	31	22	<0.005	0.00103	0.00229	0.006	0.0169	0.045	0.0735	0.119
Y	µg/L	31	1	<0.01	0.04	0.07	0.14	0.27	0.42	0.594	2.22
Yb	µg/L	31	13	<0.005			0.009	0.03	0.04	0.05	0.21
Zn	µg/L	31	0	2.9	4.4	6.55	9.1	13.6	27.3	65.4	103
Zr	µg/L	31	21	<0.005	0.00193	0.00371	0.00769	0.0174	0.041	0.046	0.05

Table 14 Summary statistics for elements in groundwaters from Igneous Intrusive aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	15	0	3.9	5.76	7.7	9	12.2	12.9	13.8	16
pH		33	0	5.24	5.69	6.19	6.63	7.04	7.32	7.48	8.23
DO <sup>1</sup>	mg/L	23	0	2.55	3.26	4.55	7.6	8.39	9.7	10	11.1
Eh <sup>2</sup>	mV	23	0	131	245	325	349	394	433	511	662
SEC <sup>3</sup>	µS/cm	29	0	18	63.5	168	271	334	430	476	533
TDS <sup>4</sup>	mg/L										
Ca	mg/L	34	0	0.24	3.93	10.9	20	33.9	45.2	61.1	69
Mg	mg/L	33	0	0.154	1.08	3.6	6.69	9.29	13.1	13.8	27.7
Na	mg/L	34	0	1.36	5.21	10.5	16.5	24.7	37.6	40	69
K	mg/L	34	2	<0.5	0.4	1.02	1.4	2.84	4.19	4.82	13.6
Cl	mg/L	34	0	2.02	7.4	13.5	25	41.4	68.1	77	95
SO <sub>4</sub>	mg/L	34	0	0.96	4.33	7.25	11.8	18	22.3	24.3	28.9
HCO <sub>3</sub>	mg/L	34	1	<10	8	17.1	37	106	204	240	247
NO <sub>3</sub> -N	mg/L	31	3	<0.00682	0.01	0.17	3.01	12.4	14.5	18	24.3
NO <sub>2</sub> -N	µg/L	9	4	<0.3			1.2	1.78			88.8
NH <sub>4</sub> -N	µg/L	10	6	<2	1.26	1.41	4.24	10.7	23	36.4	49.8
P	µg/L	26	5	<3		20	30	43	94	104	138
DOC	mg/L	16	0	0.76	0.925	1.09	1.4	2.5	4.66	6.08	7.44
F	mg/L	29	2	<0.02	0.032	0.046	0.078	0.131	0.17	0.207	0.35
Br	µg/L	26	3	<20	30	56	93	118	171	379	523
I	µg/L	23	4	<2	1.4	2.5	3.9	5.4	5.9	8.36	22.7
Si	mg/L	27	0	0.848	2.72	4.58	7.51	10.3	11.6	11.9	12.2
Al	µg/L	28	0	0.8	5.7	8	20	33.8	129	206	220
As	µg/L	22	12	<0.05	0.0117	0.0357	0.133	0.5	1.07	3.95	26.4
B	µg/L	29	4	<20	5	9	11	22	28	30	42
Ba	µg/L	32	3	<2	2.3	6.12	43.8	84.5	307	481	553
Be	µg/L	22	14	<0.004	0.00307	0.0084	0.0234	0.0775	0.407	0.44	0.6
Cd	µg/L	22	12	<0.05	0.0156	0.0243	0.0417	0.0875	0.1	0.11	0.3
Ce	µg/L	22	2	<0.01	0.002	0.01	0.06	0.56	0.82	5.05	6.67
Co	µg/L	22	6	<0.02			0.03	0.09	0.22	0.235	0.3
Cr	µg/L	22	16	<0.2	0.00596	0.022	0.0827	0.53	1.82	5.51	7.1
Cs	µg/L	22	8	<0.01			0.01	0.02	0.08	0.14	0.42
Cu	µg/L	22	0	0.6	1.01	1.52	8	33.1	236	271	829
Dy	µg/L	22	6	<0.001			0.02	0.1	0.13	1.67	2.16
Er	µg/L	22	6	<0.002			0.03	0.07	0.08	0.81	1.16
Eu	µg/L	22	9	<0.01			0.01	0.04	0.07	0.12	0.37
Fe	µg/L	34	15	<2			16	100	250	7000	9560
Gd	µg/L	22	4	<0.001		0.01	0.02	0.16	0.22	1.84	1.96
Hg	µg/L										
Ho	µg/L	22	10	<0.001			0.01	0.02	0.03	0.31	0.44
La	µg/L	22	1	<0.01	0.01	0.02	0.04	0.93	2.29	4.36	5.09
Li	µg/L	25	0	0.1	0.6	1.05	1.7	5.6	10.6	12.8	15.2
Lu	µg/L	22	12	<0.002	0.000815	0.00169	0.00398	0.01	0.01	0.086	0.1
Mn	µg/L	33	1	<2	1.5	2.51	4.75	100	417	770	884

Table 14 *Continued.*

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	22	0	0.001	0.01	0.0225	0.07	0.795	1.92	4.39	6.31
Ni	µg/L	22	8	<0.2			0.5	1	3	3.3	15.5
Pb	µg/L	22	6	<0.1	0.03	0.03	0.2	0.6	1.5	3	5
Pr	µg/L	22	8	<0.001			0.01	0.2	0.48	0.99	1.4
Rb	µg/L	22	0	0.13	0.172	0.442	1.42	3.1	4.61	7.41	8.94
Sb	µg/L	22	16	<0.05	0.00346	0.00812	0.0206	0.0557	0.116	0.148	1.17
Se	µg/L	21	12	<0.5	0.0579	0.112	0.252	0.6	0.8	2.2	3.5
Sm	µg/L	22	10	<0.02	0.001	0.001	0.001	0.14	0.27	1.05	1.54
Sn	µg/L	22	1	<0.04	0.16	0.73	0.89	1.03	1.12	1.15	1.3
Sr	µg/L	25	0	2.45	28.5	66.5	111	164	206	230	288
Tb	µg/L	22	12	<0.002	0.000427	0.00122	0.00417	0.02	0.02	0.257	0.33
Ti	µg/L										
Tl	µg/L	22	11	<0.004				0.01			0.02
Tm	µg/L	22	12	<0.002	0.000593	0.00135	0.00353	0.01	0.01	0.105	0.14
U	µg/L	22	3	<0.02	0.013	0.02	0.11	0.46	1.07	4.9	12
V	µg/L	22	1	<0.2	0.2	0.3	0.8	1.4	2.6	3.7	35.7
W	µg/L										
Y	µg/L	22	1	<0.05	0.02	0.04	0.19	0.77	1.09	8.72	15.2
Yb	µg/L	22	6	<0.01	0.002	0.002	0.03	0.06	0.09	0.7	0.8
Zn	µg/L	22	0	2.7	3.51	6.93	12.2	26.1	55.5	114	122
Zr	µg/L	22	16	<0.001	0.000037	0.000203	0.00114	0.0167	0.101	0.3	0.34

Table 15 Summary statistics for elements in groundwaters from Igneous Volcanic aquifers in Scotland.

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Temperature	oC	33	0	7.8	8.5	9.1	10	12.7	14.5	14.8	17.3
pH		37	0	5.85	6.62	6.94	7.3	7.71	8.14	8.29	8.65
DO <sup>1</sup>	mg/L	24	1	<0.1	1.48	2.31	5.46	6.9	9.17	9.48	10.3
Eh <sup>2</sup>	mV	27	0	100	231	320	374	400	427	443	462
SEC <sup>3</sup>	µS/cm	37	0	129	178	254	383	605	704	890	10700
TDS <sup>4</sup>	mg/L	20	0	44.4	64	86.1	171	320	760	2400	5340
Ca	mg/L	43	0	5.6	14.4	22.8	42.2	69	116	184	262
Mg	mg/L	42	0	0.24	2.31	7.57	11.5	19.3	36	47	84
Na	mg/L	43	0	7.08	9.17	12	22.5	38.1	83.4	611	1750
K	mg/L	43	2	<0.5	0.51	0.71	1.1	2.18	6.9	10.9	10.9
Cl	mg/L	43	0	4.3	7.59	10.2	22	44.1	77.7	1160	2490
SO <sub>4</sub>	mg/L	43	0	2	4.78	7.37	17.1	37.3	83	288	707
HCO <sub>3</sub>	mg/L	43	0	29.3	55.7	94	158	211	245	261	283
NO <sub>3</sub> -N	mg/L	35	0	0.02	0.164	0.382	3.62	12.4	32	40.5	66.5
NO <sub>2</sub> -N	µg/L	25	18	<0.3	0.0235	0.0553	0.124	0.3	4.17	9.49	15.6
NH <sub>4</sub> -N	µg/L										
P	µg/L	31	8	<5		9	30	46	77	83	109
DOC	mg/L	15	5	<0.5			0.737	1.15	1.3		1.85
F	mg/L	29	2	<0.02	0.032	0.051	0.08	0.122	0.174	0.224	0.39
Br	µg/L	29	0	24.3	34.5	59	94.1	192	373	390	20900
I	µg/L	24	0	0.969	1.74	2.53	4.51	6.12	10.4	11.5	82.8
Si	mg/L	32	0	3.53	4.92	5.87	6.8	8.79	9.97	11.1	15.7
Al	µg/L	32	0	0.6	1.13	3	5	17.8	47.4	60.3	285
As	µg/L	29	5	<0.08	0.11	0.26	1.2	2	4.4	7.46	26.2
B	µg/L	30	14	<10			29	56	99	232	2140
Ba	µg/L	31	0	0.81	9.1	30.8	93.9	148	284	400	661
Be	µg/L										
Cd	µg/L	29	20	<0.01	0.00116	0.00322	0.00806	0.0349	0.08	0.104	0.91
Ce	µg/L	29	11	<0.005			0.01	0.012	0.05	0.07	0.62
Co	µg/L	29	2	<0.01	0.02	0.03	0.039	0.067	0.093	0.11	2
Cr	µg/L	29	9	<0.5	0.13	0.19	0.28	0.51	1.5	1.53	4.2
Cs	µg/L	29	11	<0.01			0.01	0.03	0.05	0.06	0.18
Cu	µg/L	29	0	0.5	0.76	0.9	1.7	4.9	92.1	134	205
Dy	µg/L	29	23	<0.005	0.0000081	0.000046	0.000334	0.00233	0.016	0.0616	0.18
Er	µg/L										
Eu	µg/L	24	9	<0.005			0.009	0.014	0.02		0.07
Fe	µg/L	39	3	<1	4	5	26	92	300	3200	11000
Gd	µg/L	29	18	<0.005	0.00019	0.000497	0.00187	0.01	0.0178	0.0556	0.19
Hg	µg/L	15	10	<0.1	0.00558	0.0128	0.0361	0.15	0.32	0.49	0.7
Ho	µg/L										
La	µg/L	29	5	<0.005	0.005	0.006	0.01	0.022	0.045	0.09	0.33
Li	µg/L	31	2	<0.1	0.9	1.7	3.8	7	10	26.7	179
Lu	µg/L										
Mn	µg/L	38	1	<2	0.31	0.52	1.7	21.9	100	100	566

Table 15 *Continued.*

Element	Units	n	ncens	min	P0.1	P0.25	P0.5	P0.75	P0.9	P0.95	max
Nd	µg/L	29	16	<0.005	0.000989	0.00243	0.01	0.0211	0.07	0.11	0.52
Ni	µg/L	29	10	<0.2	0.11	0.12	0.16	0.3	0.5	0.8	5.5
Pb	µg/L	29	13	<0.04			0.07	0.2	0.75	1.11	1.77
Pr	µg/L	29	20	<0.005	0.000309	0.000676	0.00185	0.007	0.012	0.0218	0.09
Rb	µg/L	29	0	0.06	0.192	0.34	0.45	0.89	2.06	2.67	4.99
Sb	µg/L	29	20	<0.04	0.00504	0.00879	0.0185	0.038	0.064	0.104	0.15
Se	µg/L	29	12	<0.5	0.1	0.1	0.5	1.2	2.3		2.5
Sm	µg/L										
Sn	µg/L	29	2	<0.1	0.09	0.11	0.15	0.39	0.55	0.67	1.38
Sr	µg/L	30	0	5.38	42.8	102	163	312	483	837	15600
Tb	µg/L										
Ti	µg/L	29	17	<0.2	0.0267	0.04	0.086	1	1.37	1.5	1.68
Tl	µg/L										
Tm	µg/L										
U	µg/L	29	1	<0.02	0.02	0.04	0.24	0.642	1.94	4.28	13.3
V	µg/L	29	5	<0.2		0.5	2.2	3.8	6.2	9.5	89.2
W	µg/L	29	20	<0.005	0.00178	0.00286	0.0047	0.00657	0.02	0.02	0.106
Y	µg/L	29	2	<0.01	0.008	0.01	0.02	0.054	0.22	0.716	1.28
Yb	µg/L										
Zn	µg/L	29	0	1.4	2.2	4	9.2	16.5	36.6	79	137
Zr	µg/L	29	16	<0.005	0.00173	0.00401	0.012	0.02	0.044	0.124	0.84

1 DO - Dissolved oxygen

2 Eh - Redox potential

3 SEC - Specific electrical conductivity

4 TDS - Total dissolved solids

## Appendix 3 List of previous reports from the Baseline Scotland project

### In chronological order:

MACDONALD, A M, and Ó DOCHARTAIGH, B É. 2005. Baseline Scotland: an overview of available groundwater chemistry data for Scotland. *British Geological Survey Commissioned Report*, CR/05/239N. <http://nora.nerc.ac.uk/11335/>

MACDONALD A M, FORDYCE F M, SHAND P and Ó DOCHARTAIGH B É. 2005. Using geological and geochemical information to estimate the potential distribution of trace elements in Scottish groundwater. *British Geological Survey Commissioned Report*, CR/05/238N. <http://nora.nerc.ac.uk/11334/>

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