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Baseline Scotland: groundwater chemistry of Aberdeenshire

Groundwater Science Programme

Open Report OR/09/065

BRITISH GEOLOGICAL SURVEY

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Baseline Scotland: groundwater chemistry of Aberdeenshire

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Front cover

Borehole housing in typical rural setting in Aberdeenshire.

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Foreword

Groundwater issuing from springs has been regarded since the earliest recorded history as something pure, even sacred. In its natural state, it is generally of excellent quality and an essential natural resource for Scotland. Groundwater directly accounts for at least 7% of public water supply, as well as sustaining river flows and water to some 30 000 private supplies. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to direct and indirect anthropogenic inputs and to groundwater abstraction. Therefore, a thorough knowledge of the quantity and quality of groundwater in our aquifers, including an understanding of the processes that affect groundwater, is essential for effective management of this valuable resource.

Baseline Scotland, jointly conceived and funded by BGS and SEPA, seeks to improve the data availability and general understanding of the chemistry of Scotland's groundwater. The primary aim of the project is 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 (MacDonald and Ó Dochartaigh 2005) highlighted the paucity of reliable data for natural substances that occur in groundwater. Good quality data that do exist are available for only small areas, e.g. the Dumfries aquifer – but the Water Framework Directive requires an understanding of background levels across a much broader area.

The aims of *Baseline Scotland* are:

1. To characterise the ranges in natural background groundwater quality in the main aquifer types in Scotland, by carrying out groundwater sampling surveys that as far as possible incorporate representative areas of each aquifer, allowing extrapolation of the interpreted results to the remaining parts of each aquifer.

2. To provide a scientific foundation to underpin Scottish, UK and European water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

The project runs from 2005 to 2011, during which time systematic surveys will be undertaken across the different aquifers of Scotland. As we move forward, Scotland will be in a much better position to develop and manage its groundwater resources.

Alan MacDonald BGS

Vincent Fitzsimons SEPA

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Summary

This report describes the baseline groundwater chemistry of Precambrian and igneous bedrock aquifers in northeast Scotland, in an area broadly coincident with the counties of Aberdeen city and Aberdeenshire. For the purposes of this report, this area is referred to as Aberdeenshire. Four aquifer groups have been identified: three divisions of metamorphic aquifers of Dalradian age, the Appin, Argyll and Southern Highland Groups; and a single group incorporating all the intrusive rocks – largely granitic – across the region. The hydrogeochemistry of groundwater from the small Devonian basin outliers in this area will be reported separately.

Groundwater is an important resource in this area, largely for farm use, but also for domestic, public supply, recreation (particularly golf courses) and the food and drink industry, including whisky production.

A total of 23 new samples were collected from the studied aquifers during the project, in November 2006. These have been augmented with 14 samples collected during earlier BGS projects since 2005. Sources were chosen to be representative of groundwater in the area, and sources that were very poorly constructed were avoided.

The hydrochemical data and information on groundwater residence times can help give an insight into groundwater flow in aquifers across Aberdeenshire. In all the aquifers sampled, groundwater flow is largely through fractures, except in certain areas of enhanced, deep weathering where intergranular permeability has been increased. Groundwater is well mixed in the top 50 metres or so. There is no evidence of palaeowater in the area, and all samples recorded some proportion of water less than 50 years old. However, groundwater can be resident for several decades, even in the fractured, low permeability aquifers.

Overview of groundwater chemistry in Aberdeenshire

Most of the groundwater pH values in the region are slightly acidic (5.5 – 7.2) and have relatively low bicarbonate concentrations (10 – 130 mg/L). Groundwaters from the Appin Group tend to have slightly higher pH and bicarbonate than the other aquifer groups. Absolute Cl and SO_4 concentrations are generally low, but because of the relatively low mineralisation of the Aberdeenshire groundwaters, Cl can constitute a large proportion of the total dissolved anions. The most significant source of Cl is likely to be maritime rainfall.

Concentrations of the major cations reflect a combination of rainfall input, mineral weathering, and anthropogenic inputs derived from the use of fertilisers and liming, or from other sources of pollution. Most notable is a relative enrichment in bicarbonate and calcium, and more generally alkaline conditions, in groundwaters from the Appin Group, compared to the other aquifers. All the groundwaters are undersaturated with respect to calcite, reflecting the general lack of calcium carbonate in the bedrock. A few samples came close to saturation, all of which were derived from the Appin and Argyll Groups, which contain occasional calcareous rock bands.

All of the sampled groundwaters are oxic, with dissolved oxygen concentrations generally in the range 3 – 10 mg/L and redox potential greater than 300 mV, reflecting the unconfined nature of the aquifers and the relatively rapid groundwater flow.

Nitrate and phosphorus

The overall median nitrate concentration in groundwaters across Aberdeenshire is 7.15 mg/L as N. Concentrations are related to land use, with groundwaters beneath agricultural land showing higher concentrations than beneath non-agricultural land. The land use class showing

the highest median NO_3 concentration (13.6 mg/L NO_3-N, compared to less than 7.6 mg/L NO_3-N for other land use classes) was land used for rearing dairy, pigs and/or poultry.

The highest groundwater nitrate concentrations were found within the Aberdeenshire nitrate vulnerable zone (NVZ). Only two samples outwith the NVZ had nitrate concentrations of greater than 2.4 mg/L NO_3-N, and the highest of these (5.79 mg/L NO_3-N) is 1 km outside the NVZ boundary.

Phosphorus in groundwater can be an important influence on surface water eutrophication if present in baseflow to streams and rivers. Concentrations in Aberdeenshire range from <20 to 138 µg/L-P, but are mostly in the range 20–80 µg/L. There is little relationship between P and land use, illustrating the complexity of P geochemistry, and the important role that soil geochemistry plays in the mobilisation of P in groundwater.

Baseline

An estimate of the baseline groundwater chemistry conditions for Aberdeenshire is given by the statistical summaries of data collected during this survey, with the exception of NO_3-N and P where the influence of anthropogenic activity is likely to have distorted baseline conditions throughout many of the aquifers. Baseline conditions are broadly represented by data between the 10th and 90th percentiles. To complement this approach, ten of the groundwater samples were chosen, all collected from suitably located and constructed groundwater sources and unlikely to have been impacted by any agricultural contamination. These ten represent the general groundwater conditions in the Precambrian and igneous aquifers in the study area.

1 Introduction

This report describes the baseline groundwater chemistry of Precambrian and igneous bedrock aquifers in the northeast of Scotland. The area of study stretches from the Cairngorm mountains in the south and southwest, to the North Sea in the north and east, and is bounded to the west by the River Spey valley. The area is broadly coincident with the counties of Aberdeen city and Aberdeenshire. Small parts of southeast and southwest Aberdeenshire are not included, and the west of the study area encompasses part of the county of Moray (Figure 1). The boundaries of the study area have been defined on geological not geographical grounds, but for convenience the study area is described in this report as Aberdeenshire.

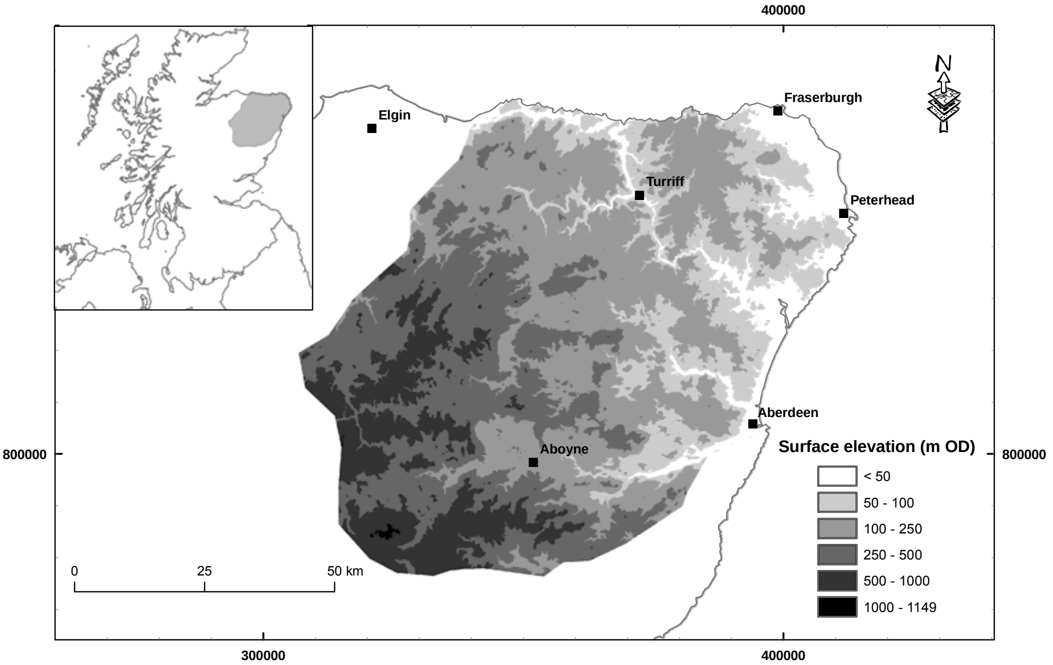


Figure 1 The area of study in Aberdeenshire, showing land surface elevation

Groundwater is an important resource in Aberdeenshire. Existing records indicate more than 300 individual groundwater sources in the study area, although it is likely that the true number of groundwater abstractions is significantly higher than this. The recorded sources are concentrated in the low-lying areas in the northeast of Aberdeenshire, where arable farming is the dominant land use. The vast majority are used for farm or public supply, although there are an increasing number of boreholes being drilled for domestic use, often to replace older shallow, wide-diameter wells which formerly supplied domestic water. Other groundwater abstractors are golf courses and the food and drink industry, including a number of distilleries.

The geology of Aberdeenshire is dominated by metasedimentary rocks of the Dalradian Supergroup, which were formed during the late Neoproterozoic era of the Precambrian period. Across much of southern Aberdeenshire these rocks are intruded by large granite bodies; other smaller bodies of granite occur throughout the study area. Small sedimentary basins also exist, containing predominantly Devonian sandstones and conglomerates, the largest of which lies immediately to the east of the town of Turriff.

Large areas of bedrock in central and northern Aberdeenshire have been subjected to particularly deep weathering. Borehole records show that the weathering commonly extends to depths of 10 to 20 m, and may be more than 50 m thick in places (Merritt et al. 2003).

Superficial deposits in Aberdeenshire mainly comprise glacial till of varying thickness, with alluvial and glaciofluvial deposits over large parts of the major river valleys. Laterally extensive but thin layers of peat cover much of the high ground in the south of the study area.

This study investigated the chemistry of groundwater from the Neoproterozoic and igneous (granitic and basic) aquifers. Groundwater samples were taken from both within and without the mapped extent of deeply weathered bedrock. The hydrogeochemistry of the Devonian basin outlier aquifers will be reported separately, together with the Devonian sedimentary aquifers of Moray and Inverness-shire.

2 Background

In order to understand the chemistry of the groundwater in the area, we need to understand the environmental context. Knowledge of geological, geochemical and hydrogeological parameters is needed to provide a physical framework for the groundwater system. It is also useful to know the chemistry of rainfall in order to define the initial chemical composition of groundwater recharge.

2.1 LAND USE

The southwest of the study area is dominated by the steep slopes of the Cairngorm mountains, where hill and high moorland are the commonest types of land use (Figures 2 and 4). Sheep farming and commercial forestry occur on the lower slopes of the Cairngorms and in the river valleys that cut through the mountains. In lower-lying parts of Aberdeenshire, beef, pig and poultry are the most important types of livestock, and improved pasture is common across much of the study area. Land use of this type is particularly important in the areas to the west of Aberdeen and to the west and southwest of Turriff. Forestry is also an important land use in these areas. The northeast of Aberdeenshire contains large areas of low-lying, fertile land and is dominated by arable farming, with cereals, oilseeds and potatoes the main crops (Figures 2 and 3). Much of this area lies within one of Scotland's four nitrate vulnerable zones (Figure 2).

Many of the major settlements in Aberdeenshire rely heavily on the oil or fishing industries, although there has been considerable recent growth in the service sector.

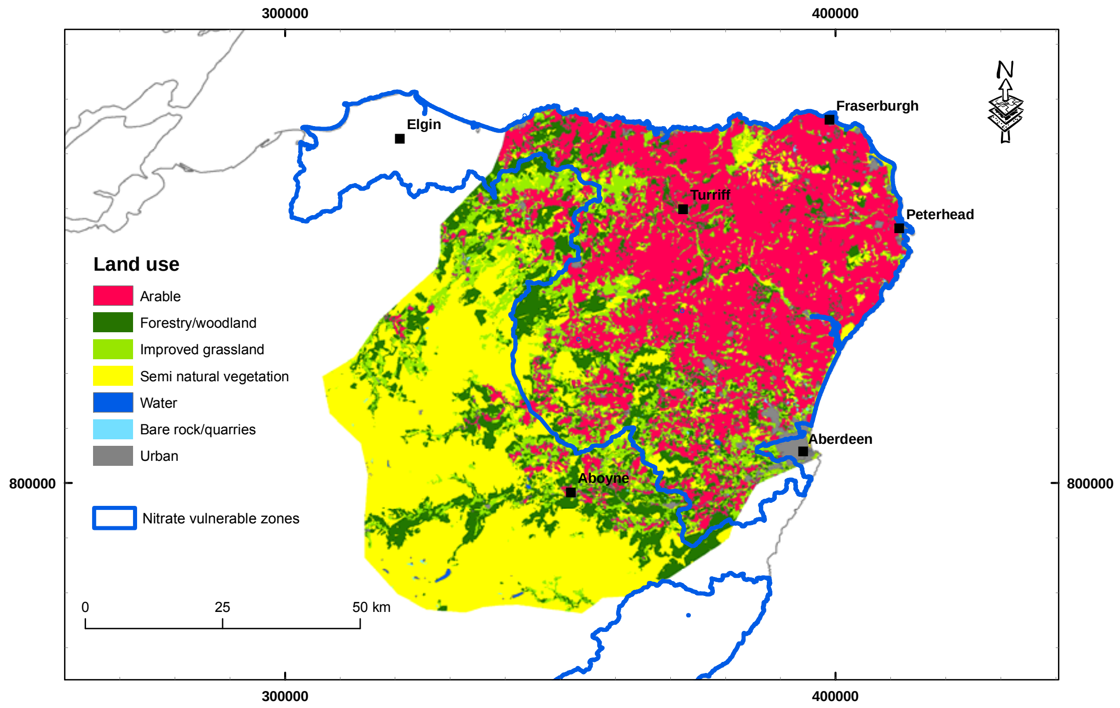


Figure 2 Generalised land use in Aberdeenshire, and nitrate vulnerable zones in the study area.

Figure 3 Arable farmland typical of central and northeast Aberdeenshire

Figure 4 Typical upland area in southwest Aberdeenshire, dominated by high moorland

2.2 BEDROCK GEOLOGY

2.2.1 Introduction

Bedrock geology in Aberdeenshire largely comprises crystalline metamorphic rocks of the Neoproterozoic Dalradian Supergroup and intrusive igneous rocks (Figure 5). Aberdeenshire lies within the Grampian terrane, part of the eroded root zone of the Caledonian mountain belt that developed in late Precambrian to early Palaeozoic times (Strachan et al. 2002, Stephenson and Gould 1994). Major intrusions of granitic and gabbroic rock occur across the south of the study area, forming much of the high ground of the Cairngorm mountains. Smaller igneous intrusions occur across much of northern Aberdeenshire. Three small basins formed within the Dalradian metamorphic rocks in the north and west of the study area are infilled by Devonian sedimentary rocks: these are the Turriff, Rhynie and Tomintoul outliers. Flint and quartzite-rich gravels of Tertiary age are present on isolated hilltops in central Buchan and are some of the few unconsolidated deposits in Scotland that were formed prior to the Quaternary period.

2.2.2 Neoproterozoic

The metamorphic rocks of the **Dalradian Supergroup** were originally deposited as sediments in a major basin, in response to stretching of the lithosphere during the break up of the late Precambrian supercontinent Rodinia and the formation of the Iapetus Ocean (Strachan et al. 2002). A broad change from shallow to deep water deposition has been identified with decreasing age in the Dalradian, along with an increase in volcanism towards the end of the Neoproterozoic era. Although there are few indicators of the precise age of the Dalradian rocks, they are generally thought to have been originally deposited between c. 800 million years ago (Ma) and the early Cambrian to early Ordovician at c. 520 – 500 Ma (Strachan et al. 2002). The sedimentary rocks were then folded and metamorphosed during the Caledonian orogenic period (see Section 2.2.6).

The Dalradian Supergroup is divided, in order of decreasing age, into the Grampian Group, the Appin Group, the Argyll Group and the Southern Highland Group. These are described below.

The oldest rocks in the Dalradian belong to the **Grampian Group**, and record the initiation of the middle to late Neoproterozoic extension and basin development. They are found only in the far west of the study area, and mainly comprise psammites, with pelites and quartzites also common. The base of the group is characterised by deep water turbiditic sedimentation and is overlain by a fluviodeltaic sequence, due to the progressive filling of the Grampian Group basin by sediments derived from the south and west. Rapid variations in thickness and in sedimentary facies (depositional environment) are due to syn-sedimentary faulting (Hambrey et al. 1991, Strachan et al. 2002).

The **Appin Group**, which crops out immediately to the east of the Grampian Group in Aberdeenshire, was laid down following the onset of renewed subsidence at the end of the Riphean Era. There is some evidence to suggest that the true Dalradian Basin began to form around this time. Psammites, quartzites, pelites and metalimestone are all common within the group and represent changing water depths within a tidal shelf environment, due to continued extension of the lithosphere (Hambrey et al. 1991).

The **Argyll Group** covers large areas of southern, western and eastern Aberdeenshire. Its base is marked by the Port Askaig Tillite Formation, indicating the former presence of a large ice sheet. Dolomites overlie this tillite, and are in turn overlain by psammites, quartzites and pelites. Metamorphosed lava and tuff are present near the top of the group, related to extreme local thinning of the crust near the end of the Vendian Era (610 – 570 Ma) (Hambrey et al. 1991).

At the top of the Dalradian succession is the **Southern Highland Group**, which covers much of central and northern Aberdeenshire and is dominated by psammites and semipelites. These were originally laid down as a turbiditic sedimentary and volcaniclastic sequence by density currents in deeper water than the rest of the Dalradian Supergroup, and mark a return to rapid basin deepening (Hambrey et al. 1991).

2.2.3 Devonian

Three small Devonian sedimentary outliers occur within the largely Precambrian and igneous rocks of Aberdeenshire, at Turriff, Rhynie and Tomintoul (Figure 5). They formed as arid, intermontane basins in the Dalradian basement which was deformed during the Caledonian orogeny.

The main outlier is the Turriff basin, in which the oldest rocks form part of the Lower Devonian Crovie Group. This comprises breccias, conglomerates and sandstones with interbedded mudstones, which are highly variable in facies, derivation and thickness. However, the basin is dominated by Middle Devonian sandstones of the Inverness Sandstone Group, largely comprising quartzite-rich conglomerates and locally-derived breccia. The Tomintoul outlier consists of Lower Devonian conglomerates and sandstones. The Rhynie outlier is also of Lower Devonian age, and is represented mainly by sandstones with shales and flagstones (Trewin and Thirlwall 2002).

2.2.4 Tertiary

During the Tertiary period subsidence occurred in the North Sea area, resulting in tilting of the rocks in the study area towards the east (see Section 2.2.6) and sedimentation within the North Sea basin. On the present day land surface, the only Tertiary rocks remaining are flint and quartzite-rich gravels – the Buchan Gravels Formation – that crop out on isolated hilltops in the northeast of the study area. These are some of the few unconsolidated deposits in Scotland that were formed prior to the Quaternary period (Knox 2002, Merritt et al. 2003).

2.2.5 Igneous rocks

Igneous intrusions were emplaced at different times across the northeast of Scotland, and put together cover a large part of the Aberdeenshire study area. The major intrusions are part of the Younger Basic suite, a series of basic and ultrabasic bodies intruded during the late Cambrian or early Ordovician at ca. 490 Ma; large plutons of granitic rocks and associated volcanic rocks and dyke swarms dating from the late Silurian to early Devonian granitoid bodies, intruded between ca. 430 and 398 Ma. Ordovician granitoid bodies also occur, dated to around 470 – 455 Ma. Other igneous rocks present include minor Precambrian granites and various minor metabasic and granitic intrusions, pegmatite veins, metadolerite sheets, various dykes and felsites. Most of the igneous rocks are associated with the Caledonian orogeny, particularly magmatism during and after the late stages of deformation and metamorphism (Stephenson and Gould 1994). Basic igneous intrusions cover large parts of the centre of the study area and are also seen in the north, while granites cover a large part of the south and southeast of the study area as well as smaller areas in the east and northeast (Strachan et al 2002).

2.2.6 Structure

Most of the Precambrian rocks in Aberdeenshire were significantly deformed during the Grampian event of the Caledonian orogeny, associated with the closure of the Iapetus Ocean from the early Ordovician to the late Silurian (approximately 470 to 415 Ma), and by subsequent development of regional folding, shearing and faulting. There is still debate about the detailed structure of this region, and particularly about the timing of the various Caledonian orogenic events. The overall structure is generally held to involve early recumbent nappe folding, probably with an overall direction towards the northwest. The nappe folds were deformed by subsequent folds and thrusts of similar trend and form, and by a series of later, upright folds which trend in a variety of directions (Stephenson and Gould 1994).

During the Tertiary substantial uplift occurred in the west of Scotland and subsidence in the North Sea area, associated with plume development and associated rift tectonics as the North Atlantic Ocean opened (Knox 2002, Boulton et al. 2002). The rocks in the study area were tilted towards the east (Boulton et al. 2002).

2.2.7 Deep weathering

A significant feature of the landscape of the lowland parts of northeast Scotland is the development of in-situ deeply weathered rock (saprolite), to much greater depths and over much greater areal extent than in other parts of Scotland. This weathering is thought to have formed under the humid temperate environments of the Pliocene and warmer periods of the Pleistocene. In Buchan in particular, in the northeast of the study area, it is common to find extensive areas with few, if any, unweathered rock outcrops. The depth of weathering commonly extends to between 10 and 20 m, and can exceed 50 m. Significant variation in weathering thickness occurs laterally (Merritt et al. 2003). The known extent of deep weathering in the study area, based on Merritt et al. (2003) is illustrated in Figure 5, but weathered rock is often wrongly identified as superficial deposits in borehole logs, and its true extent may be much greater.

The saprolites that have formed by deep rock weathering in the study area vary widely in grain size, geochemistry and clay mineralogy, controlled largely by rock type and degree of chemical alteration. Two distinct types are identified. The most common is dominantly sandy, with limited fine-grained material. Clay mineralogy is closely controlled by rock type, with granitic saprolites containing kaolinite-mica mineral assemblages, basic igneous saprolites containing a wide range of clay minerals, acid metamorphic rocks containing kaolinite and mica clays, and metalimestones dominated by smectite. Less common is a more evolved saprolite that has elevated clay content (more than 6 %) with clay mineralogy dominated by kaolinite and haematite (Merritt et al. 2003).

2.3 SUPERFICIAL DEPOSITS

During the Quaternary, the study area was covered by ice sheets on several occasions, but little depositional evidence survives from events that predate the last (Late Devensian) glaciation. The most important site in this respect is at Kirkhill in the northeast corner of the study area, where soils and organic sediments indicative of interglacial conditions are interbedded with glacial deposits of pre-Devensian origin (Merritt et al. 2003).

Most of the superficial deposits in the study area were laid down during the last (Dimlington) stadial of the Late Devensian glacial period, which extended from 28 thousand years ago (ka) to 13 ka. There are several conflicting models of Late Devensian deposition in this area: the model adopted here is that the region was entirely covered by ice in this period, deriving from both the Scottish and Scandinavian ice sheets (Merritt et al. 2003).

The most widely distributed of the Quaternary deposits are tills, which crop out over much of the study area (Figure 6), and also occur beneath younger superficial deposits. The tills are largely composed of diamictons – poorly sorted, unstratified, heterogeneous mixtures of gravel, sand, silt and clay, and were formed from ice- (glacier and ice sheet) transported material.

Hummocky glacial deposits are a distinct sediment-landform association, composed of highly variable sequences of matrix- and clast-supported diamicton, boulder-gravel and lenses of

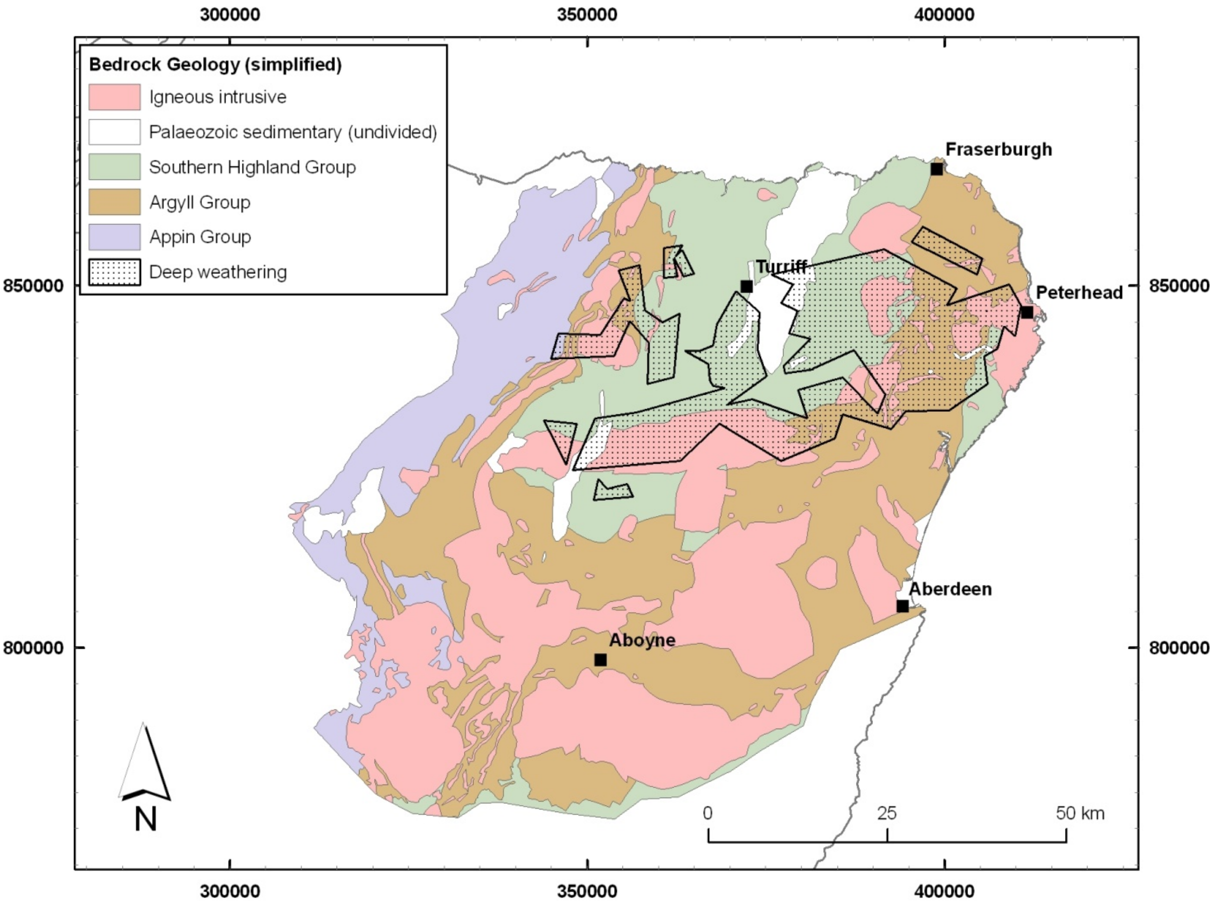


Figure 5 Simplified bedrock geology (from 1:625 000 scale DigMap linework) and extent of known deeply weathered bedrock in Aberdeenshire (after Merritt et al. 2003)

sand, silt and clay. They were formed as material spilled from glacier or ice sheet fronts as mudslides and debris flows.

Outcrops of sand and gravel dominated, variably sorted and stratified glaciofluvial deposits occur across the study area, laid down primarily by melt water flowing from ice sheets and glaciers. Two main categories are distinguished on the most recent maps on the basis of their geomorphology. *Ice-contact deposits* typically form hummocky, moundy topography, although flat-topped plateaux also occur, and include forms such as eskers (steep sided gravel ridges) and kames (rounded hillocks of sand and gravel). They consist mainly of sand and gravel, with subsidiary beds of diamicton, silt and clay. The moundiness of the deposits is mainly the result of post-depositional collapse of the sediment bodies once the ice supporting them had melted. *Sheet deposits* were laid down mainly by braided streams in a proglacial environment, typically forming fan-shaped, elongate terraces and spreads of outwash sand and gravel (Merritt et al. 2003).

Glaciolacustrine deposits, formed of fine-grained sand, silt and clay laid down in standing water, occur in many parts of the study area. They are typically thinly laminated.

Periglacial deposits also occur in the study area. The most common is head, which comprises poorly sorted and poorly stratified sediments formed mainly from the slow viscous downslope movement of waterlogged soils, which were formed most actively during periglacial conditions towards the end of the Late Devensian and during the Loch Lomond Stadial (ca. 12 ka to 9 ka).

During the post-glacial Holocene period, there has been extensive deposition of peat and of alluvial, aeolian, raised marine and present-day marine deposits. Alluvium flanks the courses of rivers in the major valleys, forming low-lying ground and typically consisting of clast-supported gravel (shingle) capped by overbank deposits of laminated silty sand with peat. In smaller basins more heterogeneous and often finer-grained sandy and silty alluvium can occur, and occasionally flat-lying spreads of interbedded humic sand, silt and clay deposits that form lacustrine alluvium. Small alluvial fans of sand, gravel and gravelly diamicton occur where tributary streams with relatively steep gradients discharge into larger river valleys.

Deposits of typically well-sorted, fine to medium grained wind-blown sand occur along the coast, normally next to sandy beaches from which most of the sand has blown, but also locally adjacent to sandy glaciofluvial deposits. Two distinct sets of raised marine deposits are present in the district, formed during periods of relatively high sea level stand in Lateglacial and mid Holocene times, each divided into shoreface and beach deposits – mainly shingle and sand – and tidal-flat, brackish lagoonal and estuarine deposits – mainly fine-grained sand and silt. Present day marine deposits vary considerably but broadly speaking consist of shoreface and beach deposits – mainly sand and shingle – and saltmarsh deposits. Peat occurs partly as basin peat within the sites of former lochans, and most peat mosses are today only a fraction of their original size because of their exploitation for fuel in historical times. It also occurs as extensive spreads of low-lying blanket peat, particularly overlying more clayey and impermeable till deposits. Blanket hill peat also occurs, most extensively on granite outcrops in southern Aberdeenshire, and on the relatively high ground of central Buchan in the northeast of the district (Merritt et al. 2003).

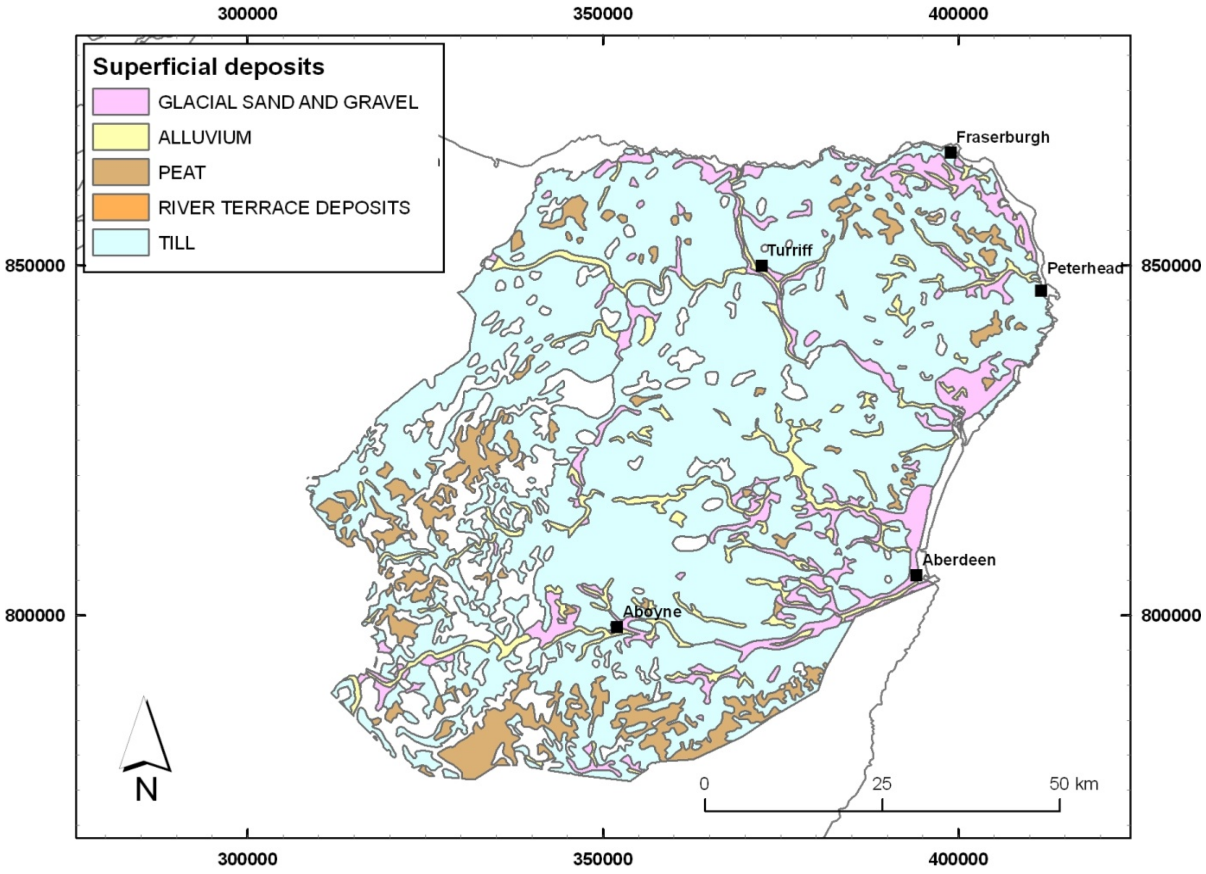


Figure 6 Superficial deposits geology of Aberdeenshire (from 1:625 000 scale DigMap linework)

2.4 HYDROGEOLOGY

2.4.1 Bedrock hydrogeology

The Precambrian and igneous rocks of Aberdeenshire have low permeability in their unweathered state, and typically form low productivity, low storage aquifers (Figure 7). Where they are not significantly weathered, groundwater in these rocks is found only in fractures. Where weathering has occurred in the shallow subsurface, which in this region is often to depths of more than 10 m and occasionally more than 50 m (see Section 2.2.7), the limited permeability of the rocks can be enhanced significantly.

The median yield of boreholes in Dalradian rocks across Scotland is 50.5 m^3/d (based on 88 available records in the Scottish Aquifer Properties Database, most of which are from Aberdeenshire).

The aquifer properties database holds 140 records of groundwater source yields from igneous aquifers across Scotland, although few are from Aberdeenshire. The yields range from less than 1 m^3/d to more than 1300 m^3/d. Much of this range is due to the fractured nature of the aquifers, which is highly variable on a local scale, and can cause boreholes sited close together to have very different yields. Most of the recorded yields are between 10 and 100 m^3/d, and the median yield is 49.6 m^3/d. Yields from extrusive and intrusive igneous rocks are generally similar: the median yield for intrusive rocks is 44.1 m^3/d and for lavas is 54.8 m^3/d.

The heterogeneous nature of fracturing and weathering, including the presence of deep weathered basins that are probably largely unconnected, means that groundwater flowpaths in Precambrian and igneous rocks are often complex and unpredictable, but are generally expected to be relatively short and localised.

2.4.2 Superficial deposits: hydrogeology and groundwater vulnerability

In the main river valleys, especially the Spey and the Dee, the coarse-grained alluvial deposits form permeable local aquifers in which groundwater infiltration and throughflow are often rapid. Shallow water tables in the low-lying deposits adjacent to the rivers mean there can be considerable volumes of groundwater storage in the deposits, and the relatively homogenous alluvial deposits allow lateral continuity, resulting in relatively predictable groundwater flow paths. Recharge potential in these alluvial aquifers is generally high, because their high permeability and location in valleys means they capture a significant proportion of rainfall runoff towards the main surface watercourses. Alluvial aquifers are an important storage sink for groundwater before it discharges as baseflow to rivers, sometimes after several years.

Glaciofluvial sand and gravel deposits are more widespread than alluvium across much of the study area, but are typically more heterogeneous, with finer-grained silts and clays interbedded with the coarser-grained deposits. This means they typically have lower permeability than alluvial deposits, and the restricted lateral continuity in the permeable deposits can lead to more complex groundwater flow paths; for example, along discontinuous gravel-filled channels. The terraces often formed by glaciofluvial sheet deposits on higher ground on valley sides, and the mounded ice-contact deposits, mostly lie above the water table. Although these do not therefore contain significant groundwater storage, their high permeability allows rapid groundwater infiltration and throughflow and they can play an important role in the local groundwater system by providing baseflow to rivers and wetlands.

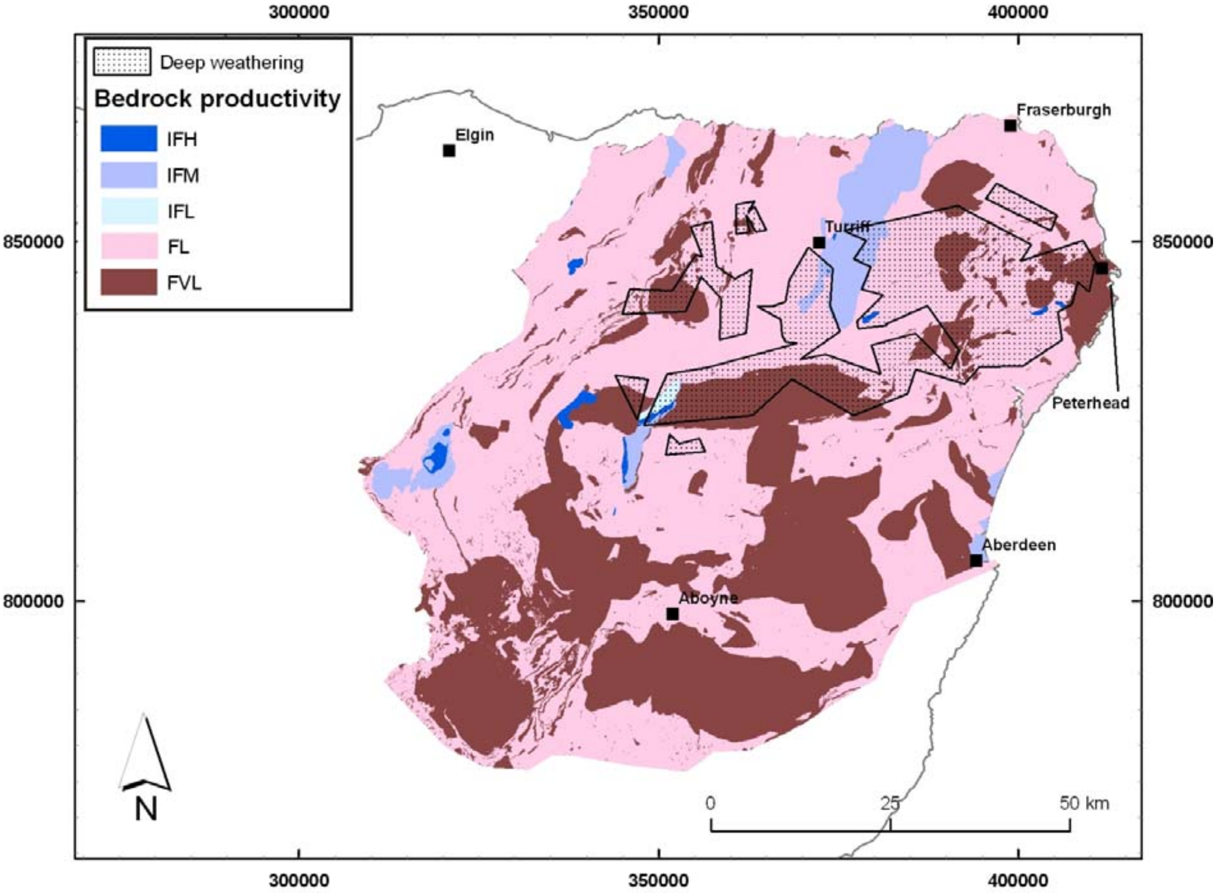


Figure 7 Productivity of bedrock aquifers in Aberdeenshire, also showing the extent of deep bedrock weathering, where aquifer productivity is likely to be increased (after MacDonald et al. 2004)

IFH	intergranular/fracture flow, high productivity	FL	fracture flow, low productivity
IFM	intergranular/fracture flow, moderate productivity	FVL	fracture flow, very low productivity
IFL	intergranular/fracture flow, low productivity		

The widespread till deposits, although sometimes relatively sandy, also typically contain significant amounts of clay and have often been compacted by ice action, and so are generally not highly permeable. However, groundwater seepages and sometimes larger flows are common in the till and many springs occur where sandier and gravellier horizons crop out at the ground surface. Recharge to till deposits can be high, particularly where higher permeability sandy horizons are present.

The characteristic deep bedrock weathering in Aberdeenshire means that there can be a significant thickness of unconsolidated bedrock, which can be misidentified as superficial deposits (Merritt et al. 2003). The weathered bedrock is, however, likely to have similar hydrogeological characteristics to many superficial deposit units in terms of its permeability and the extent to which groundwater infiltration and throughflow can occur.

The generally sandy nature of the tills, which cover most of the study area, and the high permeability of the alluvial and glaciofluvial deposits where these occur, mean that groundwater in both bedrock and superficial aquifers in Aberdeenshire is typically highly vulnerable to pollution from surface and near-surface activities. The only significant area where groundwater vulnerability is likely to be low is along the northeast coast approximately between Ellon and north of Peterhead, where clay-rich till more than 10 m thick is known to occur (Figure 8).

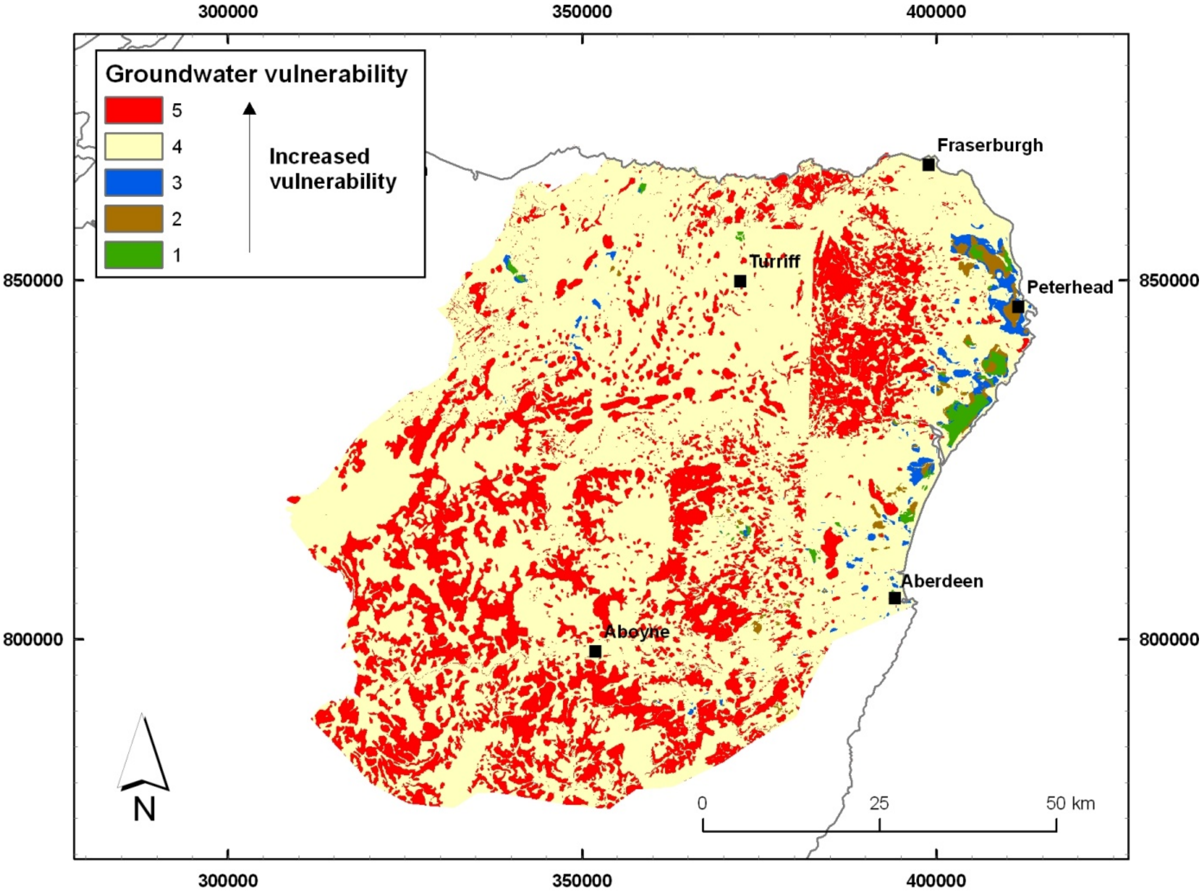


Figure 8 Groundwater vulnerability in Aberdeenshire

2.4.3 Groundwater use

Historically, groundwater has provided a safe, reliable water supply to many communities and individual dwellings across Aberdeenshire. Hundreds, if not thousands, of springs were once used to provide private water supplies for villages, farms and individual dwellings. Larger towns, such as Peterhead and Aberdeen, often relied on groups of springs channelled to a central distribution network. The Peterhead spring supply, from a group of seven springs on the Hill of Longhaven some 5 km southwest of the town, was used until after the Second World War. Where natural springs were absent, shallow wells were dug, usually to depths of between 4 and 10 m. Most farms in particular used private wells, which often exploited sandy or gravelly beds in till, or highly weathered bedrock. In Aberdeen, groundwater in thick coastal glacial sand and gravel deposits was exploited for factory water supplies in the 19th century, although the variable nature and permeability of the glacial deposits and the sometimes poor groundwater quality restricted use, particularly adjacent to the tidal sections of the rivers Dee and Don where groundwater in the superficial deposits is brackish.

The nature of groundwater exploitation in Aberdeenshire began to change towards the end of the 19th century, when boreholes more than 10 m deep were first drilled into bedrock. However, the absence of widespread highly productive bedrock aquifers, and conversely the widespread presence of groundwater at shallow depth in superficial deposits and weathered bedrock, has meant that relatively few very deep boreholes (more than approximately 50 m deep) have been drilled in the district. Most of the deeper boreholes are in the Devonian sandstone outliers, not in the Precambrian and igneous rocks. The only public water supply boreholes in the district abstract from Devonian aquifers, and even industrial boreholes are rare (Merritt et al. 2003). However, groundwater remains an important resource for private water supply. In the absence of public water supply provision in many of the more rural parts of Aberdeenshire, groundwater continues to be used: from springs, shallow wells, and increasingly from drilled boreholes, which are usually less than 50 m deep, but occasionally up to 100 m deep. Most of these groundwater sources, including most of the boreholes, are within the known thickness of the highly weathered zone, and many of the sources are likely to be abstracting groundwater from this zone. Registration of private water supply abstraction has only recently been put in place in Scotland. There is still no comprehensive list of all groundwater abstractions in Aberdeenshire, but the best estimate is that there are at least 400 and probably many more individual abstractions for private water supply in the study area, most of which are for domestic and/or agricultural use.

2.5 AQUIFER GEOCHEMISTRY FROM STREAM SEDIMENT AND STREAM WATER CHEMISTRY DATA

2.5.1 Stream sediment information

An assessment of the mineralogy of the aquifers in the study area has been made based on stream sediment geochemistry collected and analysed as part of the BGS national Geochemical Baseline Survey of the Environment (G-BASE) project, reported for the East Grampians (BGS 1991). The following patterns in selected element distribution have been inferred from the stream sediment geochemistry.

The general distribution of calcium in stream sediments in Aberdeenshire mainly reflects that of plagioclase feldspar, being high (> 6% CaO) over many of the basic igneous intrusions, except where these are covered in thick superficial deposits. By contrast, calcium over many of the major granites is often low (< 1% CaO). Over the Precambrian metasedimentary rocks, the presence of carbonate-rich bands in the Appin and Argyll Groups is reflected in high calcium values (> 7 % CaO); elsewhere, values are variable.

The highest magnesium values (5 – 15% MgO) are associated with ultrabasic igneous intrusions; by contrast, the evolved granites have very low values (0.1 – 0.7 % MgO). Over the quartzo-feldspathic metasediments of the Grampian Group low values are generally seen (<1% MgO); over the Southern Highland Group values are more variable but still generally low (ca. 0.7 – 4% MgO); and over much of the Appin and Argyll groups values are typically ca. 3% MgO.

Only half of the samples analysed showed arsenic concentrations above the detection limit of 5 mg/kg. The dominant feature is an extensive zone of arsenic enrichment associated principally with rocks of the Southern Highland Group, south of Deeside, with values up to ca. 80 mg/kg. Arsenic enrichment also occurs locally over rocks of the Argyll Group, where values can reach 230 mg/kg.

Iron concentrations in stream sediments are highest over the Southern Highland and Argyll groups, and associated with gabbros in some of the basic igneous intrusions (typically 7 – 15% Fe_2O_3). Lower values (< 4% Fe_2O_3) are seen over Grampian Group rocks and most of the granites.

Marked enrichment in lead (> 250 mg/kg) occurs over some of the major granites in the district, in general reflecting the magmatic evolution of the granites with the more evolved plutons showing higher values. Low lead concentrations (< 20 mg/kg) are associated with some diorite bodies, and the major basic igneous intrusions have the lowest values. Over the metasedimentary rocks, lead concentrations are relatively uniform between ca. 20 and 60 mg/kg.

Most of the highest uranium values (> 12 mg/kg) occur over the larger and highly evolved granites. Over large areas of the metasedimentary rocks, concentrations are less than 2 mg/kg, with higher levels over part of the Argyll and Southern Highland groups reflecting granitic veining.

2.5.2 Streamwater information

Limited streamwater chemistry data, including pH, conductivity, alkalinity and fluoride concentrations, were also collected by BGS as part of the G-BASE project.

Areas of markedly low-pH stream waters (pH < 5) in Aberdeenshire are associated with some of the major granitic intrusions, and a group of streamwaters with very low pH values overlies Grampian Group psammites in one area, which is probably associated with the presence of thick blanket peat. Near-neutral pH conditions (pH 6.4 – 7.6) prevail in streams over most of the Precambrian Dalradian rocks, and over the major basic intrusions. Land use can also have an important effect on the pH of surface waters: in agricultural areas the use of lime and other basic fertilisers is likely to contribute to a higher pH, while the planting of coniferous forests may significantly reduce the pH by reducing the acid-neutralising capacity of soils.

Very low conductivities (< 15 µS/cm) occur in streamwaters over many of the major granite intrusions and some Dalradian quartzites, always in association with low pH values. This is consistent with a streamwater source in areas of thick peat and base-deficient glacial deposits. Elsewhere over the Dalradian rocks, conductivities are mostly in the range 30 – 430 µS/cm, with a general decrease towards the northeast that corresponds to a decrease in altitude and rainfall. Near the coast, the influence of sea spray causes some locally high values (>500 µS/cm). Locally higher conductivity values are also associated with the presence of calcareous schists and carbonates in Dalradian rocks in Deeside.

Analyses of bicarbonate in stream water in Aberdeenshire were made at a low sample density of 1 per 15 km^2, which gives only a general picture of the variability in bicarbonate. The lowest concentrations (< 5 mg/L HCO_3) are mainly associated with low-pH and low-salinity waters that occur on the granite intrusions. Higher concentrations (5 – 50 mg/L HCO_3) are found in streamwaters over the metasedimentary rocks, with a trend to values at the higher end of this range towards the northeast coincident with decreasing altitude and rainfall.

The most significant feature of the distribution of fluoride in streamwaters is the association of high levels with many of the major granite intrusions, some of which can be attributed to an unusual fluorite-bearing granite at Glen Gairn, or to lead-fluoride veins. The highly evolved Hill of Fare granite is marked by a group of very low streamwater fluoride values, but apart from this, the only consistently very low fluoride concentrations are associated with low pH and low conductivity and are probably associated with a peat bog source area with minimal mineral input from bedrock. No clear pattern in fluoride distribution is evident over the Dalradian rocks.

Most of the higher uranium concentrations (> 2 µg/L) are in streams over the granites, especially over the more evolved intrusions. Concentrations are generally less than 1.2 µg/L over the metasedimentary rocks.

2.6 RAINFALL CHEMISTRY

Rainfall chemistry data are available from two stations across the study area – at Glen Dye in the southeast and Lochnagar in the southwest (Table 1). The Lochnagar station lies near the

Cairngorm mountains at 785 m OD, where average annual rainfall (for 1999 to 2005) is 1250 mm. The Glen Dye station is at lower elevation nearer the east coast, at 185 m OD, but average annual rainfall (for 1996 to 2005) is still relatively high at 924 mm. The rainfall chemistry is taken as the median for the period 2000 to 2005.

Solutes derived from rainfall typically increase during evapotranspiration. Here, the solute concentration in infiltrating recharge is taken to be roughly three times higher than in rainfall. However, nutrient concentrations (e.g. nitrogen and potassium) may decrease due to biomass uptake, so that infiltrating (recharge) waters may contain lower concentrations of these solutes than the evaporated rainfall. Ammonium would be expected at least partially to oxidise to nitrate on infiltration. An estimate of the likely chemistry of infiltrating recharge water after evapotranspiration, based on a three times concentration of the median 2000–2005 rainfall chemistry, is also presented (Table 1).

Table 1 Rainfall chemistry at monitoring stations in Aberdeenshire, from the UK National Air Quality Information Archive (http://www.airquality.co.uk/archive/index.php)

	Units	**Glen Dye**	**Lochnagar**	**Expected concentration in infiltrating recharge after evapotranspiration**[3]
NGR		NO 642 864	NO 252 859	
Elevation	m OD	185	785	
Annual rainfall	mm	924[1]	1250[2]	
		Median concentration in rainfall 2000–2005	Median concentration in rainfall 2000–2005	
pH		4.70	4.74	-
SEC	µS/cm	24.00	17.00	61.5
Ca	mg/L	0.15	0.11	0.39
Cl	mg/L	1.80	1.26	4.59
K	mg/L	0.09	0.05	0.20
Mg	mg/L	0.15	0.10	0.38
NH_4-N	mg/L	0.25	0.18	-
NO_3-N	mg/L	0.32	0.22	0.82
Na	mg/L	1.09	0.72	2.72
PO_4-P	mg/L	<0.01	<0.01	-
SO_4-S	mg/L	0.48	0.37	1.27

[1] Mean annual rainfall from 1996 to 2005

[2] Mean annual rainfall from 1999 to 2005

[3] Calculated for illustrative purposes as three times the average median rainfall concentration of the two stations, and assuming all NH_4-N oxidises to NO_3-N.

3 Methodology

3.1 INTRODUCTION

A total of 37 samples from Precambrian and igneous aquifers in Aberdeenshire are included in the Baseline dataset. Three of these, all from springs (Samples 4, 12 and 29 – for sample details see Appendix 1) may be derived in part from superficial deposits. Of the dataset of 37, 23 new samples were collected for analysis in November 2006 during the Baseline project. These were augmented with 14 samples collected during earlier projects: five during a project to assess the Scottish Groundwater Nitrate Monitoring Network (MacDonald et al. 2005), and nine during a project investigating the chemistry of spring water (Ball et al. 2006).

3.2 SITES SAMPLED

The sites were chosen to be representative of groundwater in the studied aquifers in the area. Sources that were very poorly constructed, such as open and/or uncased boreholes in leaking chambers, and those which were close to obvious and significant sources of contamination, such as unsecured slurry stores, were avoided.

The criteria for groundwater sample collection were:

- to collect a suitable number of samples from each of the studied aquifer types (the Dalradian metamorphic aquifer, and the igneous (largely granitic) aquifer) according to the distribution and areal extent of the aquifers;
- to collect samples distributed as evenly as possible over each of the aquifer types;
- to collect samples that were as far as possible representative of groundwater in the studied aquifers; and
- to collect samples from areas within and without the mapped extent of deeply weathered bedrock.

Each of the sample sites 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.

The location of the sampling points is shown in Figure 9. Details of the distribution of samples by source type, aquifer and land use are given in Table 2.

The source types from which samples were collected were split almost evenly between boreholes (17 sources) and springs (16 sources). Four samples were also collected from shallow, large diameter wells. In the south of the study area almost all the samples are from springs. Borehole samples dominate in the north, although there are also a few spring samples from this area.

For most of the borehole samples, the boreholes had been pumped regularly in the few weeks leading up to sampling, and were pumping at the time of sampling, ensuring that representative groundwater samples were obtained. Where boreholes were not pumping on arrival, they were pumped for at least 10 minutes to allow purging before sample collection. Pumped groundwater samples represent the compositions of water entering the borehole over its open-hole section. As such, the sample may represent a mixture of waters with different chemistry, especially where the borehole screen extends over more than one fracture inflow. The spring samples are from constantly flowing sources and are therefore naturally purged, and the sampled groundwater is therefore likely to be representative of groundwater in the surrounding aquifer. It is more difficult to ensure that samples from shallow wells are representative, largely because of the difficulty in ensuring that large diameter wells are effectively purged. All of the wells sampled were in daily use for drinking water supplies, and were therefore regularly pumped, and likely to give a representative groundwater sample. Since springs and wells typically tap shallow groundwater and have relatively small catchments, they are less likely than boreholes to represent a mixture of groundwaters from different depths.

3.3 SAMPLING PROCEDURE

At each sample site, field measurements were made of 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 (typically for 10 to 15 minutes) until stable readings were obtained. Where not possible, measurements of water direct from the pump outlet were made in a bucket within one to two minutes of abstraction.

Water samples were collected from each site for subsequent laboratory analysis. Samples for major- and trace-element analysis were filtered through 0.45 μm filters and collected in polyethylene bottles rinsed with sample water before collection. Four filtered aliquots were collected at each site: two were acidified to 1% v/v with Aristar 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 acidified to 1% v/v with Aristar HCl for analysis of As by AFS (atomic fluorescence spectrometry) with hydride generation, to be used if necessary as a check on ICP-MS As analyses. A fourth aliquot was left unacidified for analysis of anions by ion chromatography (NO_3-N, Br, F) and automated colorimetry (Cl, NO_2-N, NH_4-N). Samples were also collected in chromic-acid-washed glass bottles for dissolved organic carbon (DOC) analysis, after filtration using silver-impregnated 0.45 μm filters. DOC was measured by carbon analyser. At 15 of the sample sites, additional samples were collected in glass bottles for stable-isotopic analyses ($\delta^{2}H$, $\delta^{18}O$ and $\delta^{13}C$). At 9 of the sites, a sample was also collected for CFC analysis in a glass bottle, submerged under flowing groundwater to prevent atmospheric contamination. Most analyses were carried out at the BGS laboratories in Wallingford, except for ICP-MS analysis which was carried out by ACME laboratories, Vancouver, Canada.

Analyses of total sulphur are hereafter expressed as SO_4 and alkalinity as HCO_3. Analyses of $\delta^{2}H$, $\delta^{18}O$ are expressed as per mil deviations relative to VSMOW (Vienna Standard Mean Ocean Water) and $\delta^{13}C$ relative to VPDB (Vienna Pee Dee Belemnite).

The average absolute charge imbalance was 1.6% and the maximum imbalance was 6.3%. This gives confidence that the analytical results for the major species of all samples are reliable. The Wallingford laboratories run a series of QA checks, including analysis of certified standards, to ensure that all analyses are within their prescribed limits.

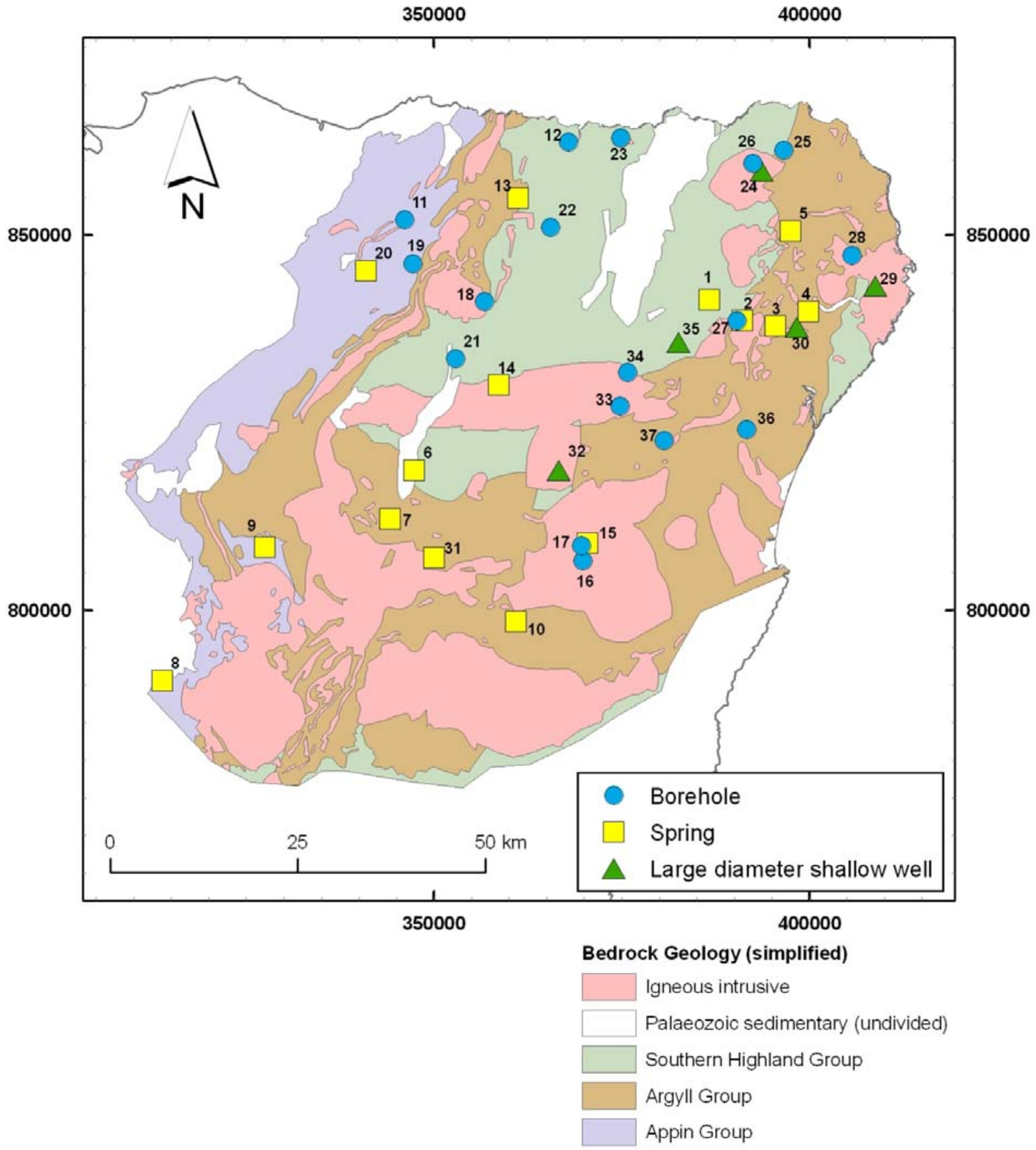


Figure 9 Location and reference numbers of groundwater samples in Aberdeenshire, also showing groundwater source type and bedrock geology. For details of samples see Appendix 1.

Table 2 Summary of samples by geology, surrounding land use and source type

Land use	**Arable**			**Improved grassland**			**Dairy, Pigs and/or Poultry**[1]			**Mixed agricultural**			**Semi natural and woodland**			**Mixed agricultural / non agricultural**			**Total**
Geology	B[2]	S[2]	W[2]	B	S	W	B	S	W	B	S	W	B	S	W	B	S	W	
Dalradian: Appin Group										1	1			2		1			5
Dalradian: Argyll Group	1	1		1	1		1				2			1			2		10
Dalradian: Southern Highland Group					1				1					1		3			6
Igneous: intrusive				1	2	1	4	1		1					1	3	1	1	16
Total	1	1		2	4	1	5	1	1	2	3			4	1	7	3	1	**37**
	2			7			7			5			5			11			

[1] Dairy, Pigs and/or Poultry – Improved grassland positively identified as being used for dairy, pig and/or poultry farming

[2] B – Borehole; S – Spring; W – Well

4 Hydrogeochemistry

4.1 DATA ANALYSIS AND PRESENTATION

4.1.1 Summary statistics

Groundwater quality data are available for a total of 37 sites distributed across the study area. Where these are identified and discussed individually in this report, they are referred to by a numerical ID. Summary details of each of these sample sites, including the IDs used in this report, are provided in Appendix 1. Summary statistics were calculated for each of the measured parameters, both for the whole dataset of samples (Table 3 in Section 5) and for the individual aquifer groups (Appendix 2). These provide an indication of the range of values observed, and can be compared with similar tables from other areas. They are discussed below. The median value provides the preferred estimate of the 'central tendency' for the datasets, since it is unaffected by outliers. Maximum and minimum values are included to show the extreme values in the dataset. The summary statistics have been reported in terms of percentiles to provide a non-parametric summary of the chemical distribution (Table 3 and Appendix 2).

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. Some of the analytes had multiple detection limits and/or a substantial percentage of observations below detection limits. Statistical summary data were therefore calculated using either the Kaplan-Meier non-parametric method or the 'regression-on-order statistics' (ROS) approach (Helsel 2005, Lee and Helsel 2005). Summary data for most elements used the Kaplan-Meier approach, but ROS was used where >50% of the data were below detection limits, following the recommendation of Helsel (2005). The calculations were made using the `NADA` package Version 1.5 in R (Helsel 2005; R Development Core Team 2007).

The total number of observations and the number of censored (below detection limit) observations are also reported to indicate the degree of censoring (Table 3).

4.1.2 Maps

'Bubble' maps were used to display the spatial distribution of the various water quality parameters. These were generated in R using the `PBSmapping` and `maptools` packages and shapefiles generated by ArcGIS®. A simplified geological base map, derived from the BGS 1:625,000 scale bedrock geology map, is presented with the groundwater chemistry information. In most cases, four classes were used to map the chemical parameters, with the size and colour of the plotting symbol varying with the class. Class limits were broadly based on the 25, 50 and 90 percentiles for the determinand range. These were simplified if there were insufficient distinct values to generate reliable percentiles.

4.1.3 Box plots

Box plots provide a quick graphical summary of the distribution of data values in a dataset and give an excellent way of comparing different values. They provide a rapid view of the central location of the distribution (the median), the spread of values (the interquartile range: box length) and the presence of outliers (open circles beyond the whiskers) (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, as in Figure 10.

Helsel (2005) discusses how the classical box plot can be adapted for displaying distributions containing censored data.

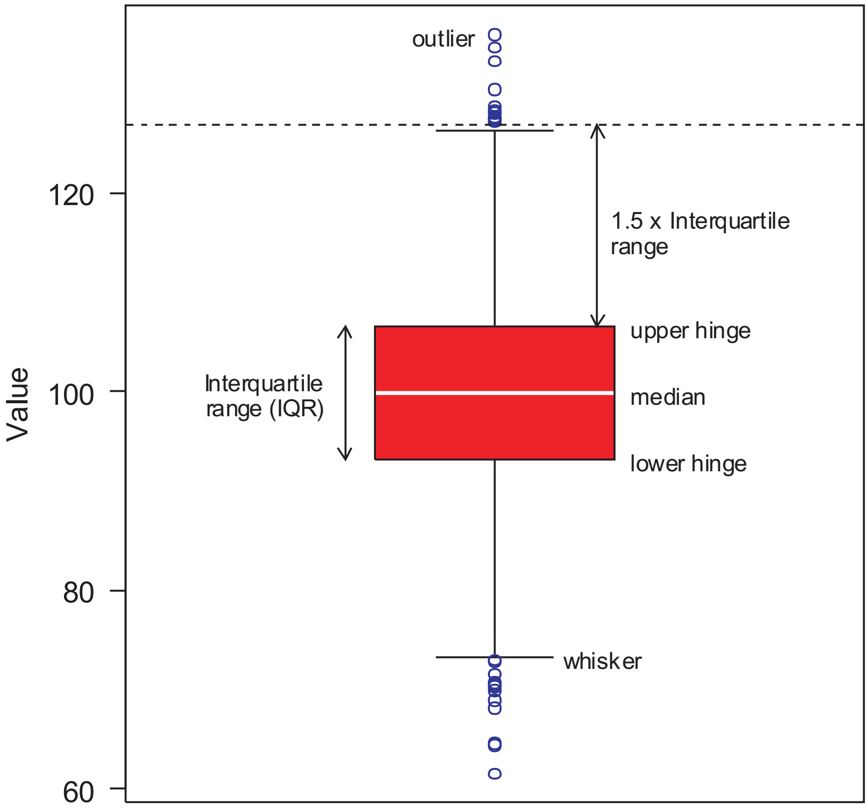


Figure 10 Example of an annotated box plot based on a simulated normal distribution of 2000 values with mean = 100 and standard deviation = 10. In this case, the whiskers are placed at no more than 1.5 × the IQR; outliers lie beyond this range

4.1.4 Classifying the data

The data have been divided based on the bedrock aquifer type from which the sample was taken. There can be other important, and perhaps dominant, factors for specific chemical parameters, but rock type is the single most useful one in the present context.

The samples were classified into four main chronostratigraphic bedrock groups: the Appin Group, Argyll Group and Southern Highland Group (all subdivisions of the Dalradian Supergroup), and a separate group of igneous intrusive rocks of variable composition, including granitic and basic rocks.

The distribution of many elements, especially trace elements, in groundwater is closer to log normal than normal. Many of the elements were therefore plotted on a log scale. This means that the occasional high outlier does not cause the scaling to obscure any low concentration data on the box plots. The pH value is already log-transformed.

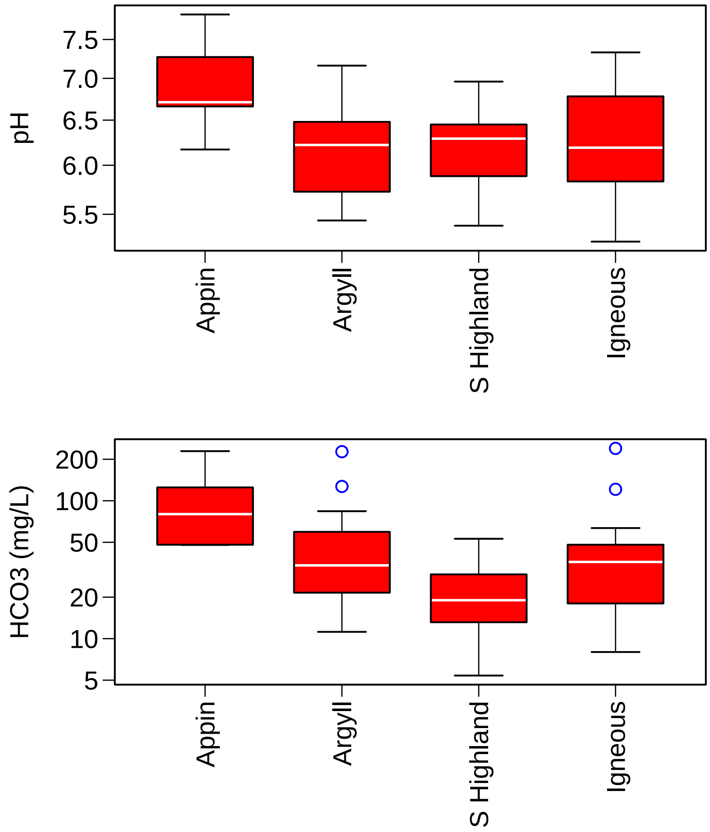
4.2 MAJOR IONS AND PHYSICO-CHEMICAL PARAMETERS

The pH, Eh and the concentrations of the major cations (Na, K, Ca and Mg) and anions (HCO_3, Cl, NO_3, SO_4) together define the basic hydrogeochemical nature of a groundwater. Compositions reflect the chemistry of the rainfall (Section 2.6) and other surface inputs to the aquifer, outputs in the form of evaporation, and subsequent reaction of the groundwater with the aquifer mineral matrix.

In areas where surface inputs are relatively small and nearly constant, the spatial variation in groundwater chemistry will largely reflect variations in rock type. On the other hand, for elements where the contribution from the aquifer rocks is uniformly low, such as is the case with nitrate, variations in groundwater chemistry largely reflect variations in surface inputs – in the case of nitrate, from agriculture.

4.2.1 pH and alkalinity

Most of the Aberdeenshire groundwater samples are slightly acidic, with pH values reaching as low as 5.24. Ranges are comparable in groundwaters from the Argyll, Southern Highland and igneous aquifers. Compositions are typically less acidic in Appin Group groundwaters Figure 11). The generally acidic nature of the groundwater reflects the overall paucity of carbonate minerals in the host aquifer rocks. Alkalinity shows a similar trend, with higher concentrations overall in groundwaters from the Appin Group. There are known carbonate-rich bands in the Appin Group, which are likely to control this alkalinity trend. However, there are also known calcareous bands in the Argyll Group, which do not appear to be sufficiently widespread to have influenced the alkalinity of groundwaters from this group in the same way.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

Figure 11 Box plots showing the distribution of pH and alkalinity (as HCO_3, log scale) in groundwaters in aquifers across Aberdeenshire

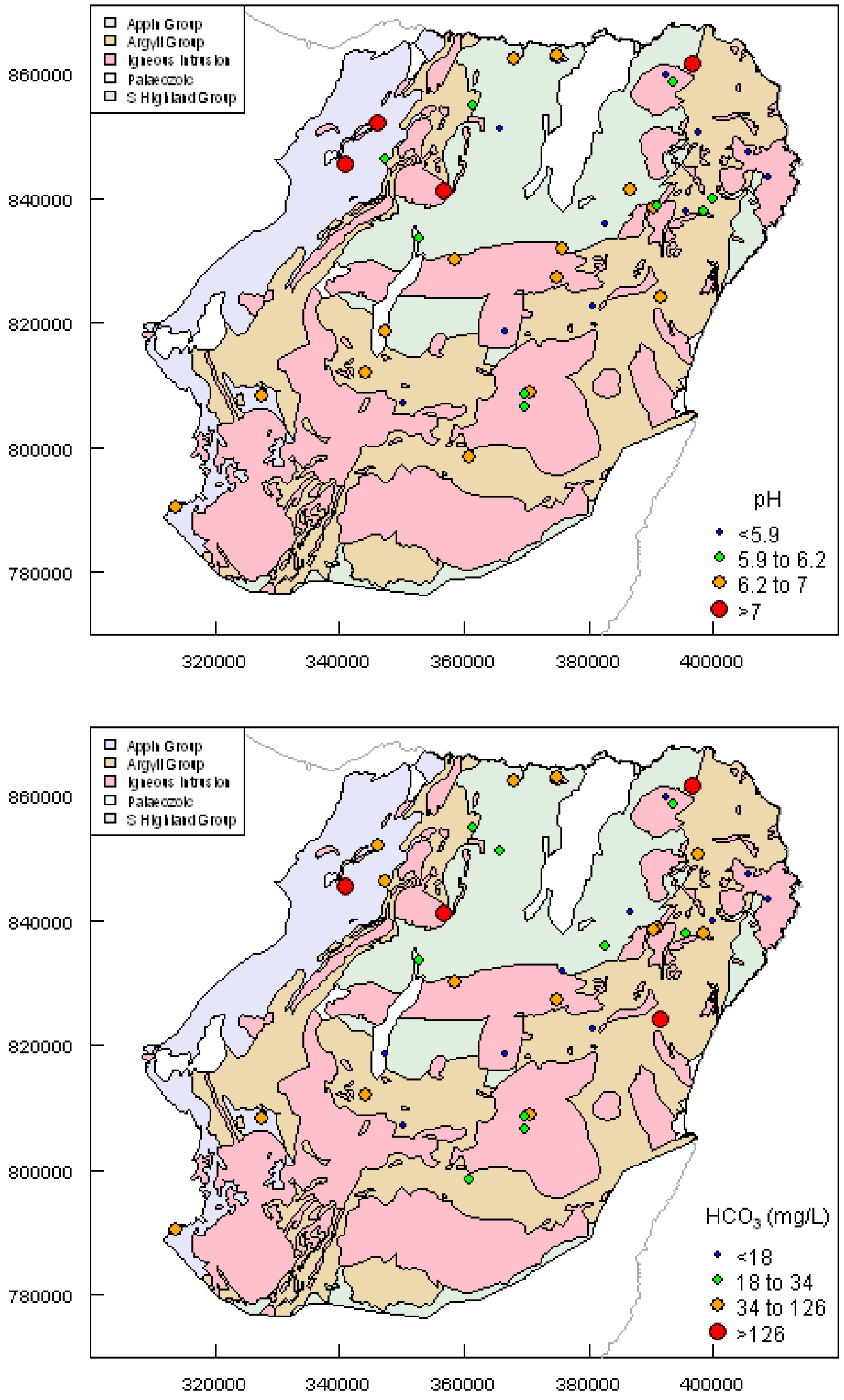
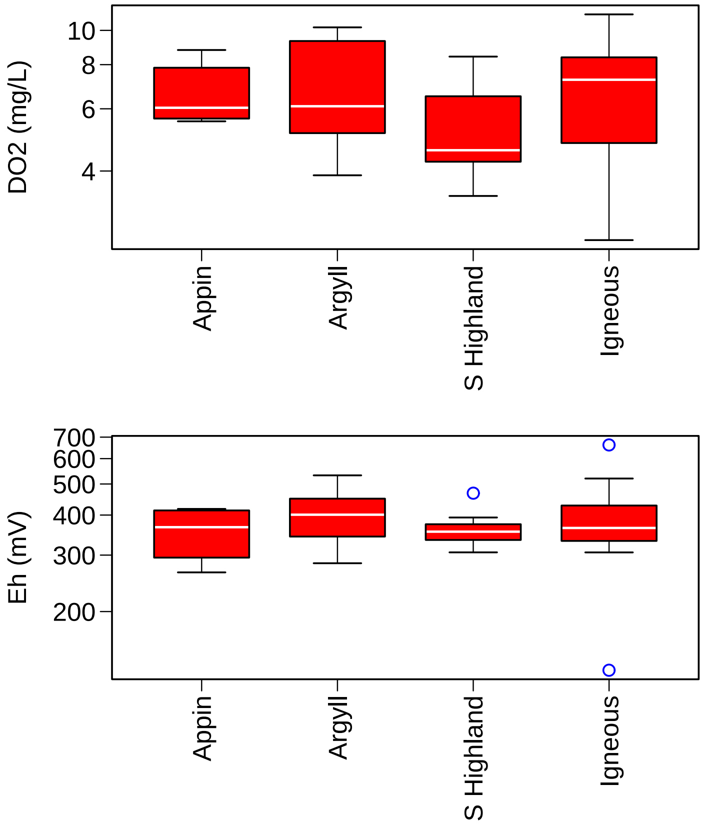


Figure 12 Maps showing the spatial distribution of pH and alkalinity (as HCO_3) in groundwater across Aberdeenshire

4.2.2 Dissolved oxygen and Eh

Almost all samples collected represent oxic groundwater, with (where determined) detectable dissolved oxygen and Eh values of 300 mV or more. Only one sample, from a borehole in granite, had a low Eh value (131 mV). This sample appears to be anoxic.



Number of samples in each category:

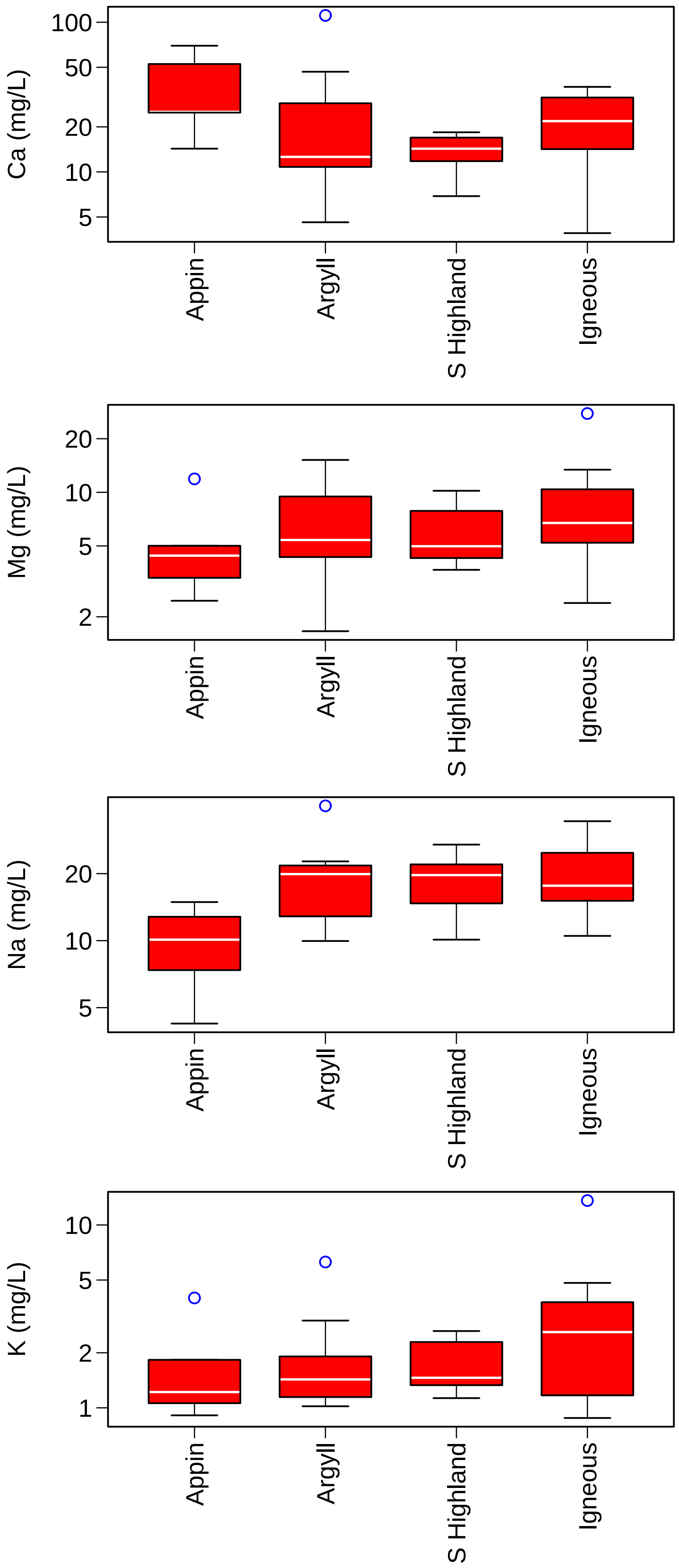
Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

Figure 13 Box plots showing the distribution of dissolved oxygen (DO_2) and redox potential (Eh) in groundwaters in aquifers across Aberdeenshire (log scale)

4.2.3 Major ions

The sampled groundwaters are dominantly poorly mineralised, with SEC values of 500 µS/cm or less, and total dissolved solids (TDS) values that are mostly less than 300 mg/L (ranging up to 540 mg/L). These values are representative of relatively young, shallow groundwater that has had limited chemical interaction with the dominantly silicate aquifer rocks.

Ranges of Ca, Mg, Na and K are illustrated in box plots in Figure 14. There is wide variability in the dominating cations, which is also shown by the varied compositions in the Piper diagram in Figure 44. Some of the most distinctive features include relatively high concentrations of Ca, and low concentrations of Mg and Na, in groundwaters from the Appin Group. This is consistent with the presence of carbonate-rich bands in this rock unit. Concentrations of Na, as with Cl concentrations, are generally highest in the northeast of the study area, adjacent to the sea (see also discussion of Cl, below). The largest range and highest average concentrations of K are seen in groundwaters from igneous rocks. The large range reflects the diversity of igneous rock types. High groundwater K concentrations are likely to reflect reactions with K-bearing minerals such as biotite and perhaps alkali feldspar in the granitic rocks. Concentrations of K in the basaltic rocks from the central part of the study area are among the lowest observed (Figure 17), consistent with the K-poor nature of basic rocks. Agricultural fertilisers may also contribute K to groundwater.

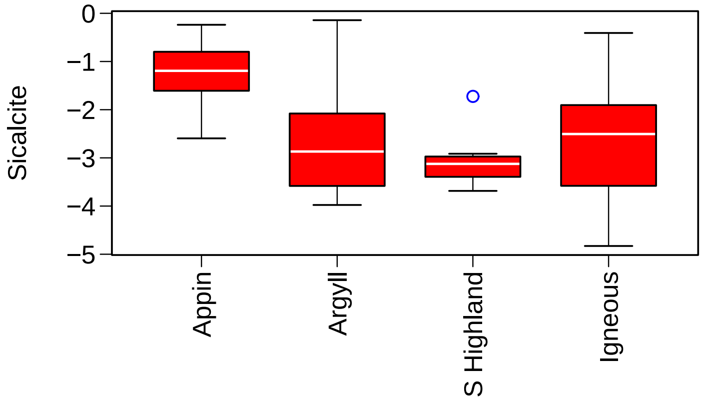


Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

Figure 14 Box plots showing the distribution of major cations (Ca, Mg, Na and K) in groundwaters in aquifers across Aberdeenshire (log scale)

All the samples are undersaturated with respect to calcite (Figure 15). This again reflects the general paucity of carbonate minerals in the bedrock. However, a small number (those with relatively high concentrations of Ca and alkalinity) are close to saturation. These samples are from the Appin and Argyll Groups and are likely to represent local occurrence of, and reaction with, calcite, probably from the calcareous bands that are known to exist in these rock units.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

Figure 15 Box plot showing the distribution of calculated calcite saturation indices ($SI_{calcite}$) in groundwaters in aquifers across Aberdeenshire

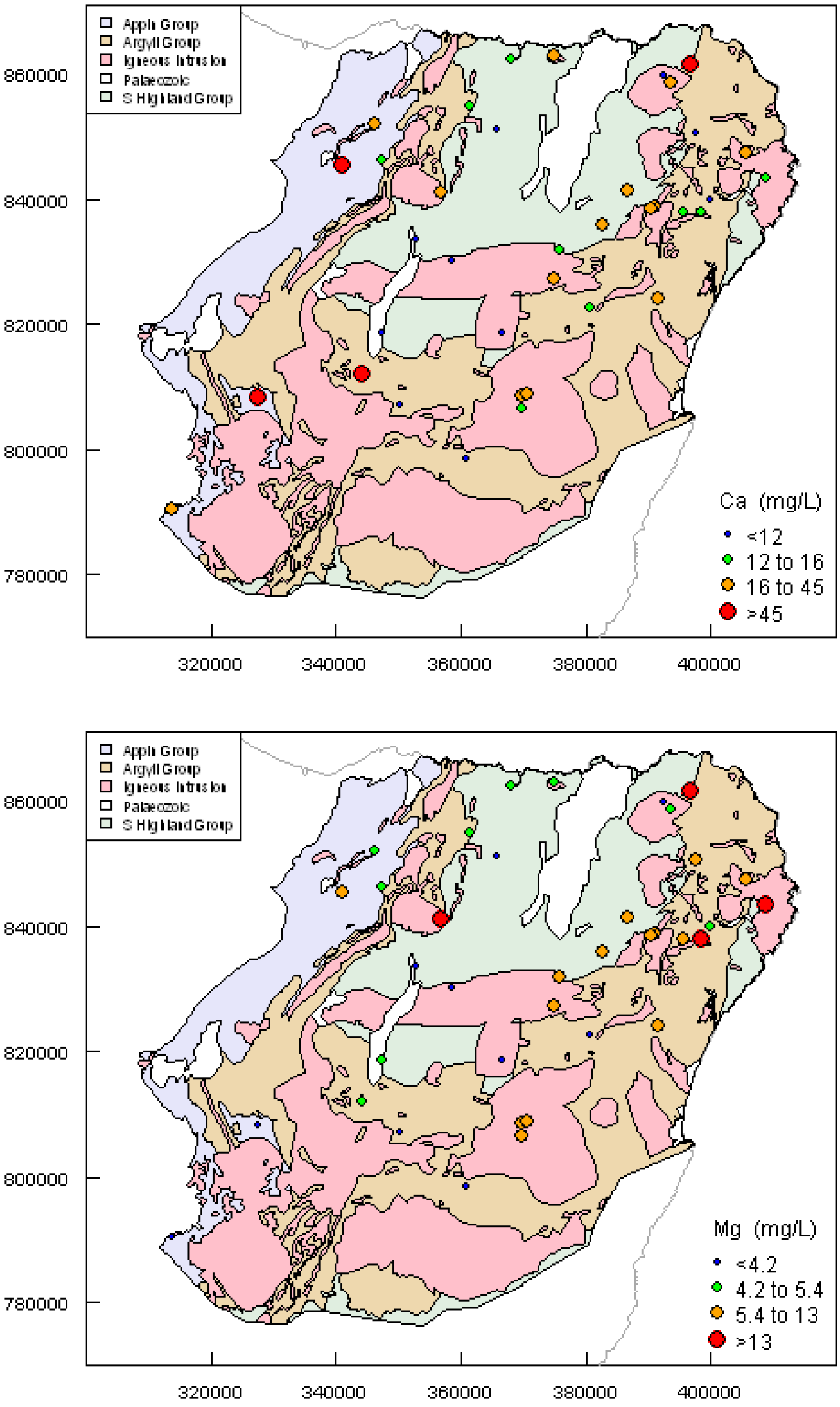


Figure 16 Maps showing the distribution of Ca and Mg in groundwaters in aquifers across Aberdeenshire

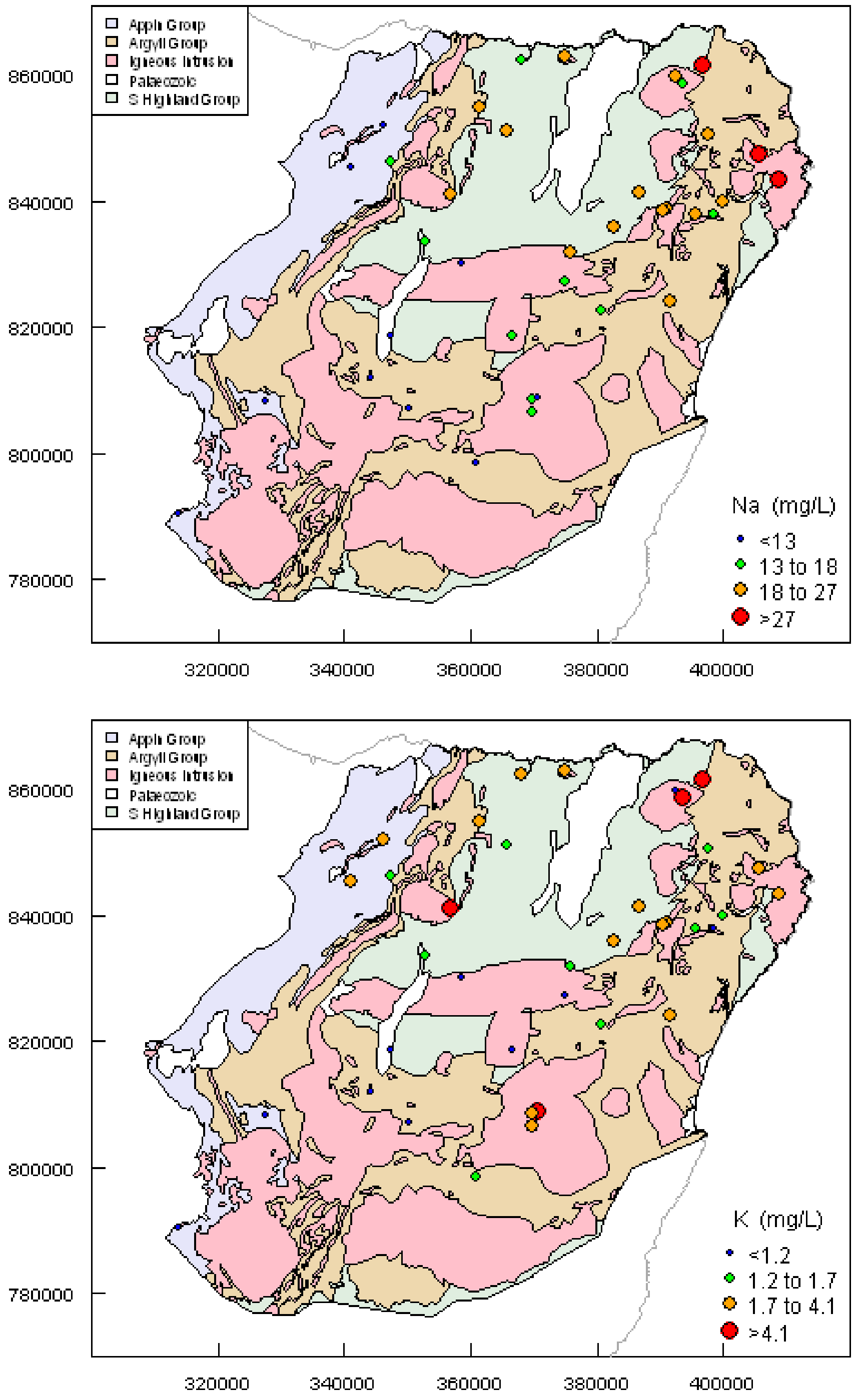
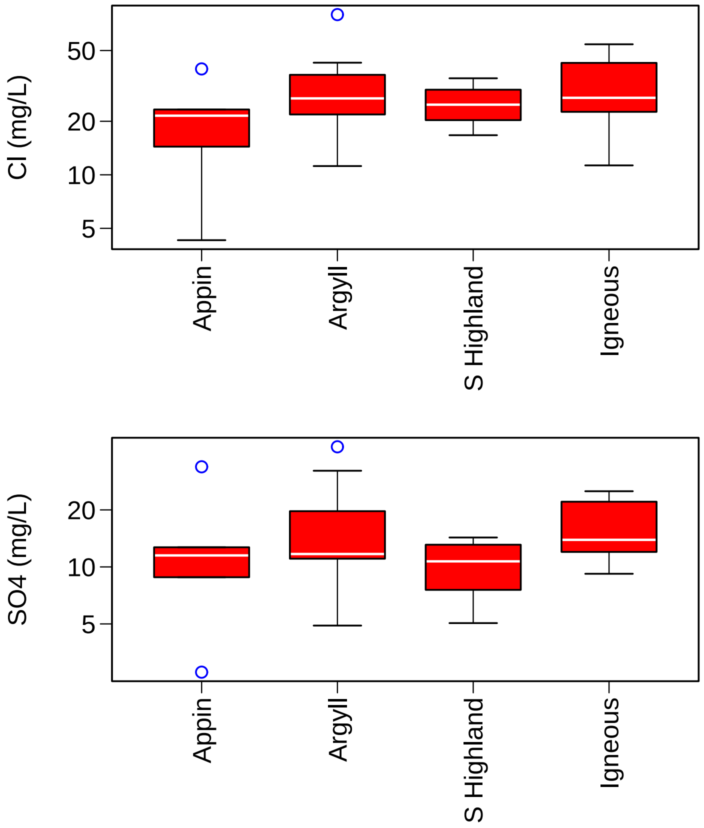


Figure 17 Maps showing the distribution of Na and K in groundwaters in aquifers across Aberdeenshire

Chloride concentrations in the sampled groundwaters reach a maximum of 54 mg/L. While not especially high compared to many other groundwaters, the chloride concentration can constitute a relatively large proportion of the total dissolved anions in the Aberdeenshire groundwaters. Concentrations appear to be highest in the northeast of the study area. The controls on the higher chloride concentrations are unclear, but may be related to the influence of maritime rainfall, agricultural pollutants, or possibly old connate water.

The largest range and highest concentrations of SO_4 occur in groundwaters from the Argyll Group (Figure 18). Potential sources include maritime rainfall (in the northeast); oxidation of sulphide minerals, particularly in argillaceous rock types; and pollutants.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

Figure 18 Box plots showing the distribution of chloride and sulphate concentrations in groundwaters in aquifers across Aberdeenshire

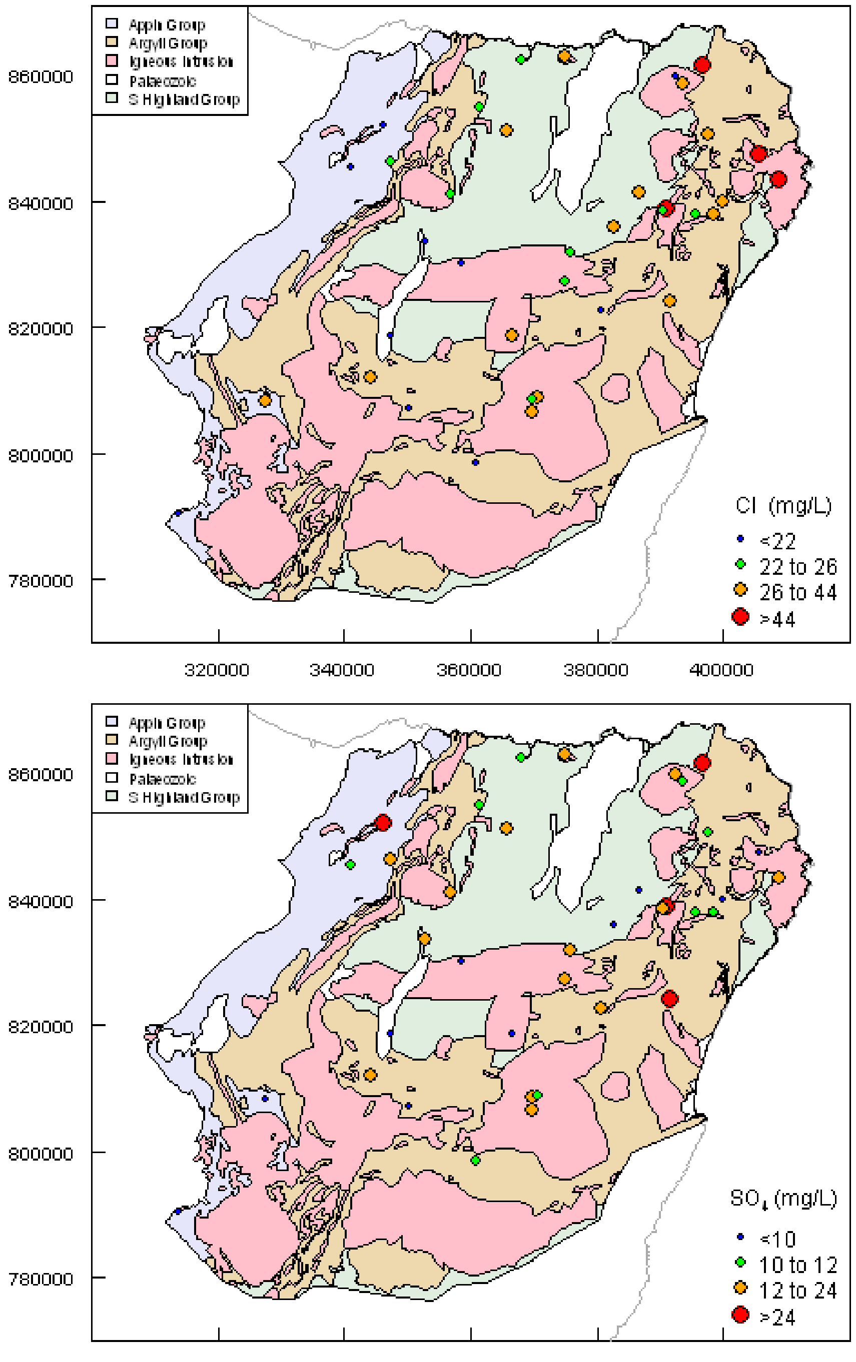
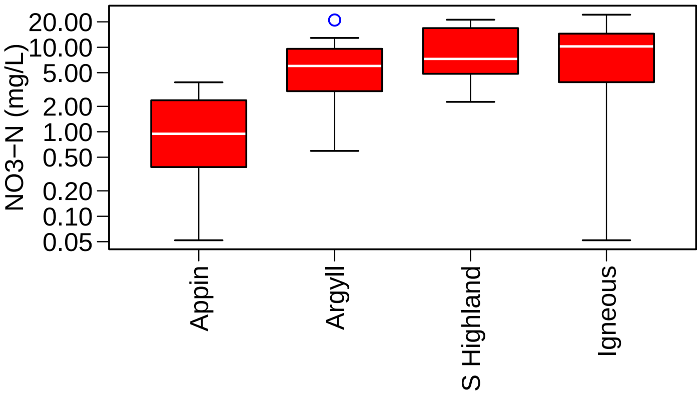


Figure 19 Maps showing the distribution of chloride and sulphate concentrations in groundwaters in aquifers across Aberdeenshire

Distributions of nitrate (as NO_3-N) across the different aquifers are displayed as a box plot and map (Figure 20). Many of the groundwaters have high nitrate concentrations: nearly one third in total (32%) have concentrations higher than the drinking water limit of 11.3 mg/L as N, although the highest median value (10.2 mg/L N) is seen in groundwaters from igneous rocks. Median values for groundwaters from the Argyll Group and Southern Highland Group aquifers are also relatively high, 6.01 mg/L and 7.28 mg/L NO_3-N respectively. By contrast, the median concentration in groundwaters from the Appin Group is low (0.95 mg/L NO_3-N).



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

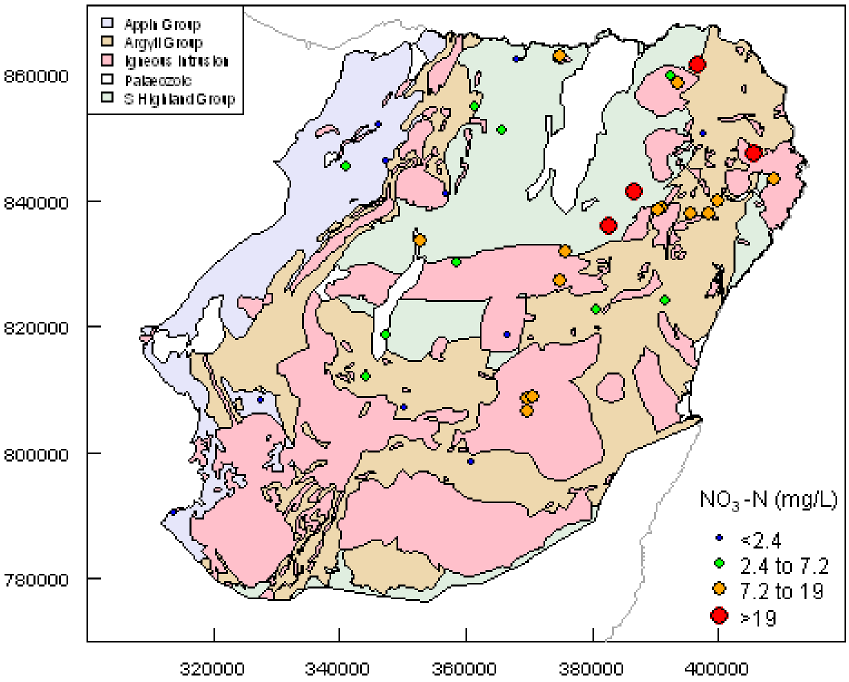


Figure 20 Box plot and map showing the distribution of nitrate concentrations in groundwaters in aquifers across Aberdeenshire

The generally high nitrate concentrations can almost certainly be attributed to pollution from agricultural activities. Further investigation of the data shows that there is a clear relationship between land use and nitrate concentration (Figure 21). Nearly 80% of the samples from areas dominated by woodland and natural (uncultivated) land cover have low nitrate concentrations (less than 2.3 mg/L as N). By contrast, nearly 80% of the samples from land identified as including at least some dairy, pig and/or poultry agricultural activity have high nitrate concentrations (higher than the national drinking water limit of 11.3 mg/L as N; see Figure 46). With decreasing agricultural intensity, the proportion of samples with high nitrate concentrations decreases. Forty percent of samples from land dominated by improved pasture, and only 11% of samples from mixed cultivated land, had high nitrate concentrations; no samples from areas of woodland or natural land cover had high concentrations. The median nitrate concentrations from the different land use classes also show this pattern, with the median value for land identified as being used for dairy, pig or poultry farming at 13.6 mg/L NO_3-N, compared to 7.6 mg/L NO_3-N for improved grassland, 5.8 mg/L NO_3-N for mixed cultivated land, and 0.9 mg/L NO_3-N for non-agricultural (woodland and natural) land uses.

Some of the areas classed as dominantly improved grassland may also include dairy, pig and/or poultry activity which has not been identified explicitly. This may partly explain some of the highest nitrate concentrations seen in areas classed as improved grassland.

There is no relationship between nitrate concentrations and the depth of the sample source (Figure 22).

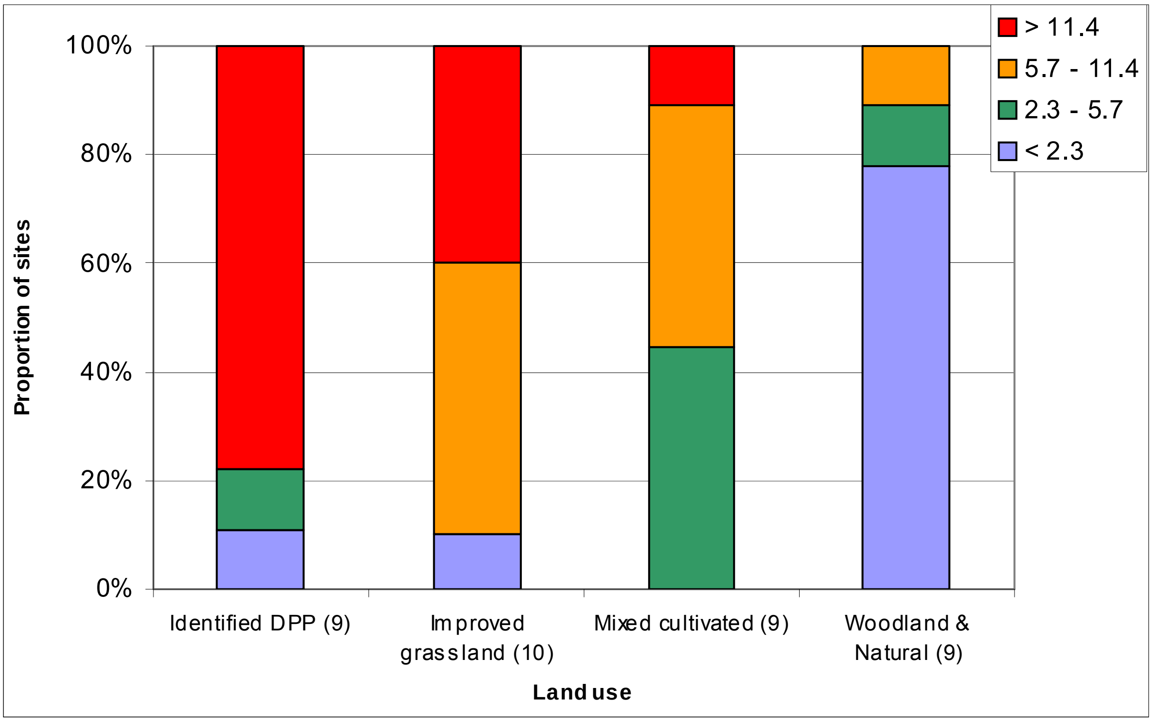


Figure 21 Variations of nitrate concentrations (in mg/L as NO_3-N) in groundwater with land use class, based on land use maps and field observations of the 200 m surrounding the groundwater source. The number of samples in each land use class is shown in brackets. Identified DPP refers to improved grassland positivity identified as being used for dairy, pigs and/or poultry

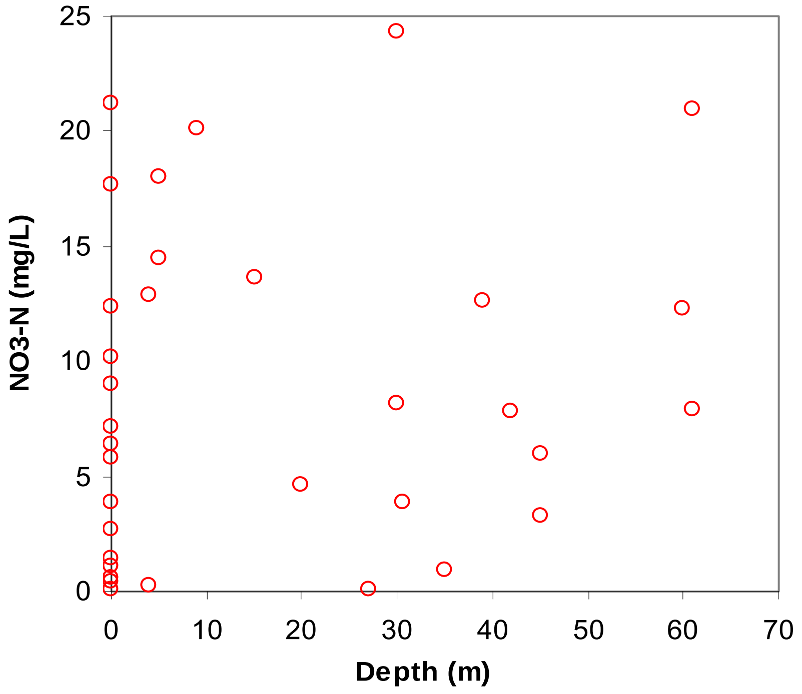
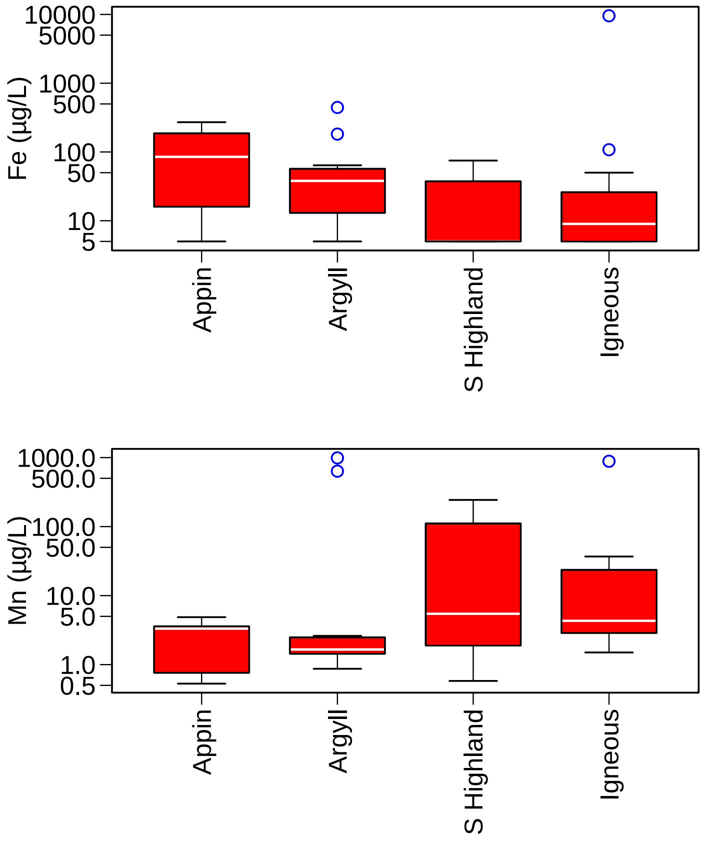


Figure 22 Variation in nitrate concentrations in groundwaters in Aberdeenshire with measured source depth.

4.3 MINOR AND TRACE ELEMENTS

4.3.1 Iron and manganese

Concentrations of Fe and Mn are low in most of the sampled groundwaters. The highest Fe concentration (9560 µg/L) occurs in a groundwater from granite (igneous rocks). This sample also has a high Mn concentration (884 µg/L) and the lowest observed Eh value (131 mV). This groundwater is clearly reducing with respect to Fe and Mn, and these solutes are most likely derived from reductive dissolution of Fe and Mn oxides. None of the other samples is unequivocally reducing, and other occurrences of high Fe and Mn are likely to reflect a combination of mobilisation under acidic conditions, and/or contributions of colloidal material (<0.45 µm) in the samples. The spatial distribution of Fe and Mn concentrations shows no clear pattern (Figure 24).



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

Figure 23 Box plots showing the distribution of iron and manganese concentrations in groundwater in aquifers across Aberdeenshire

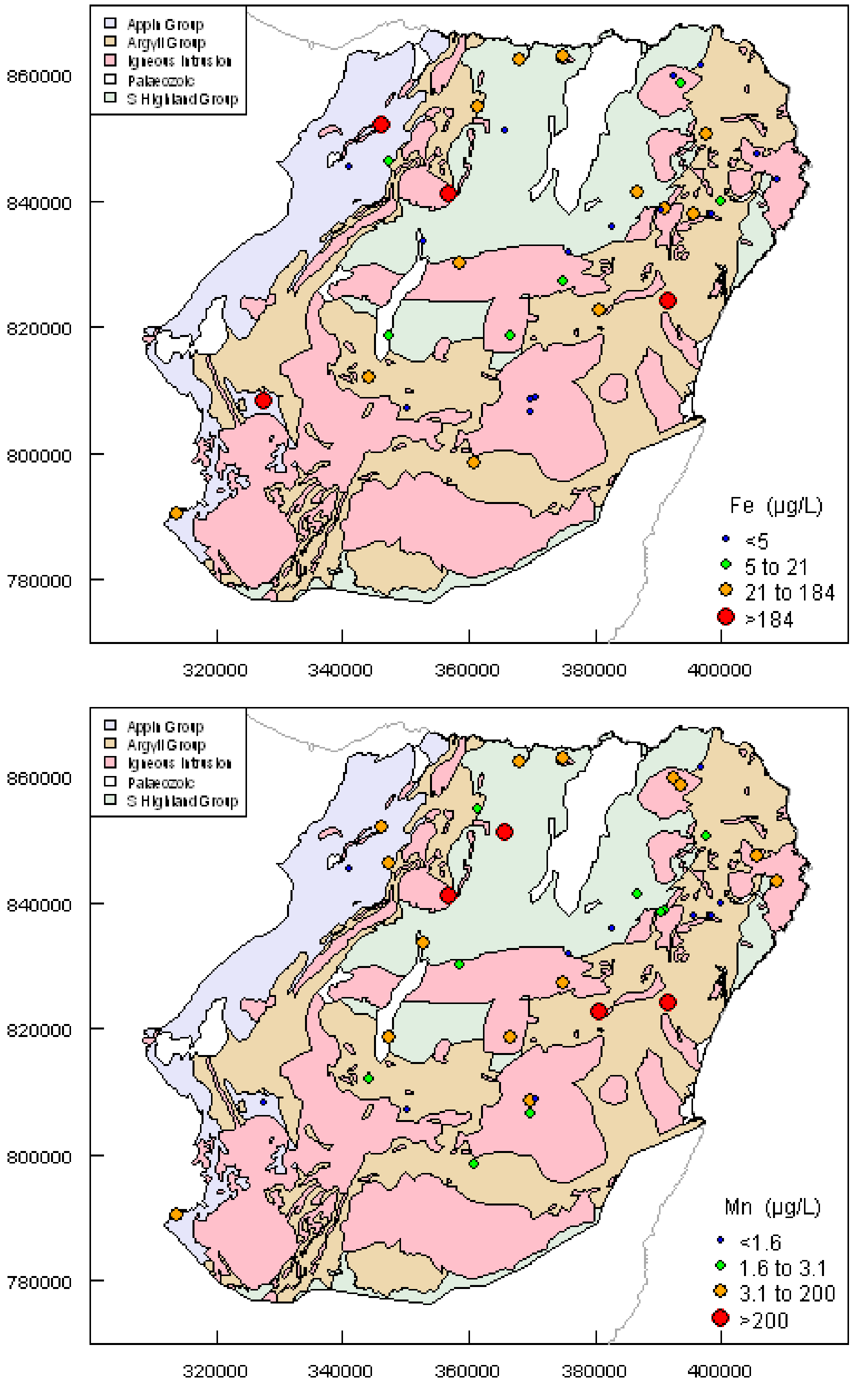
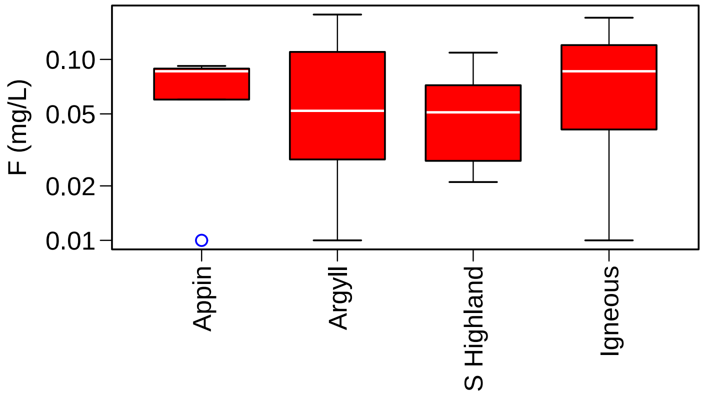


Figure 24 Maps showing the distribution of iron and manganese concentrations in groundwater in aquifers across Aberdeenshire

4.3.2 Fluoride

Concentrations of dissolved F are also low (<0.02–0.14 mg/L). Fluoride is likely to be derived naturally by release from minerals such as fluorite, apatite, biotite and amphibole. Little spatial pattern is apparent (Figure 25), although some of the highest concentrations are found in groundwaters from igneous rocks and the Argyll Group. The granites are expected to have a relative abundance of F-bearing minerals.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

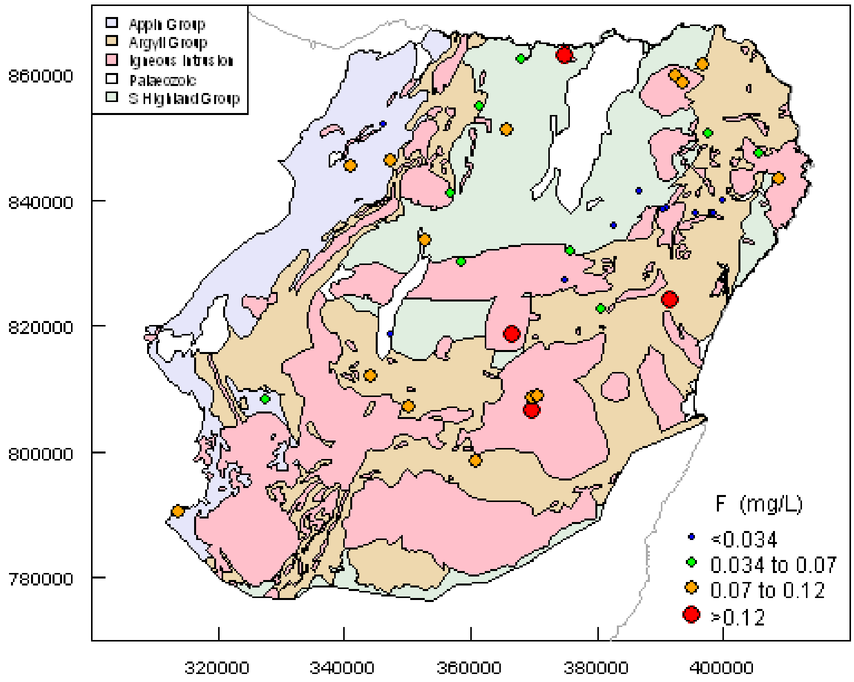
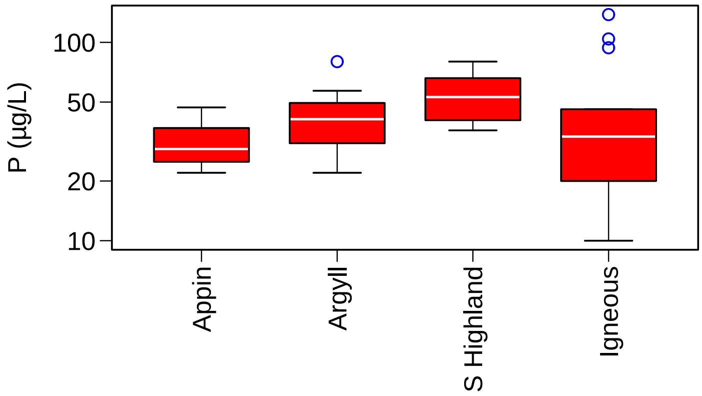


Figure 25 Box plots and map showing the distribution of fluoride in groundwater in aquifers across Aberdeenshire

4.3.3 Phosphorus

Concentrations of dissolved P lie in the range <20 (the detection limit) to 138 µg/L. The largest range and highest concentrations were in the groundwaters from igneous rocks. Relatively high concentrations are also a feature of groundwaters from the Southern Highland Group. Phosphorus may be naturally-derived (e.g. from apatite or Fe oxides), or could be derived from pollutants. Two of the highest concentrations occur in groundwaters from granite (an igneous rock) (Figure 26). There is no clear relationship between P concentration and land use, although a slightly higher proportion of relatively low P concentrations occurs in samples from areas of woodland and natural land use than from agricultural land (Figure 27).



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

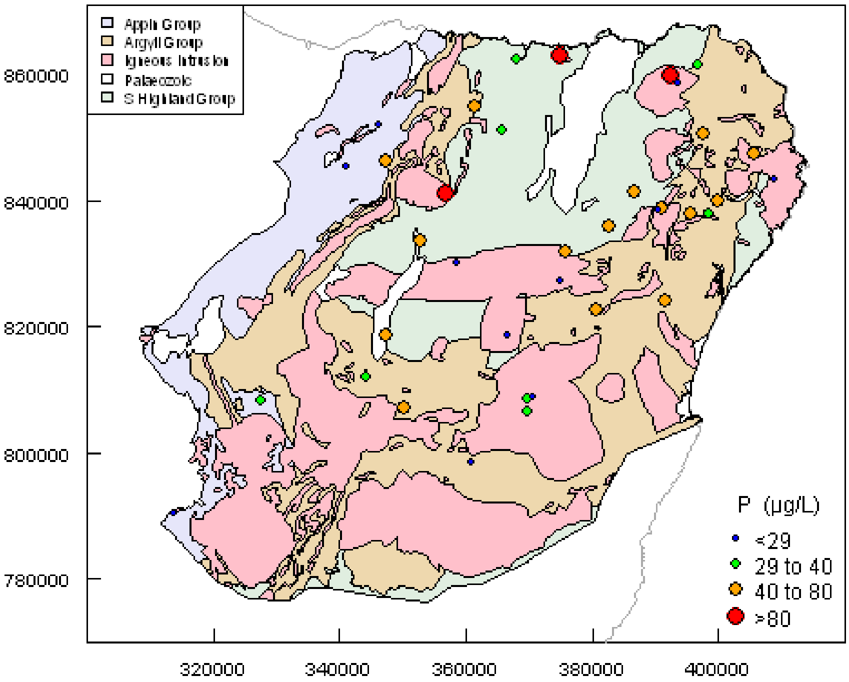


Figure 26 Box plots and map showing the distribution of phosphorus in groundwater in aquifers across Aberdeenshire

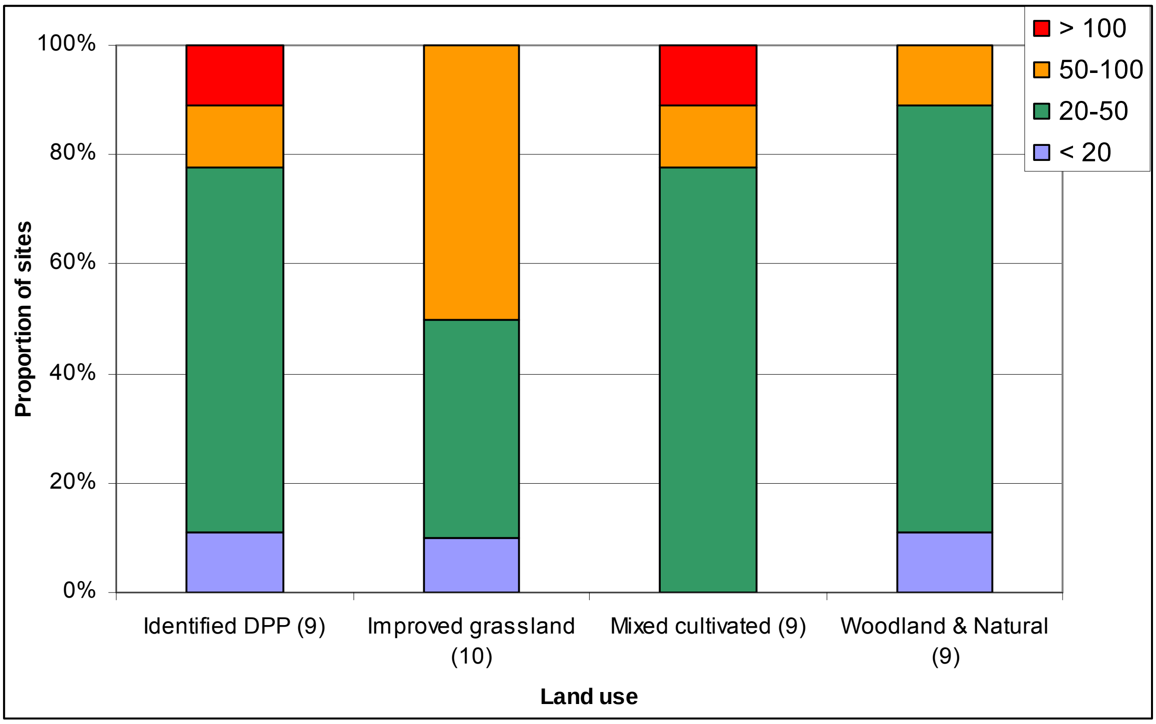


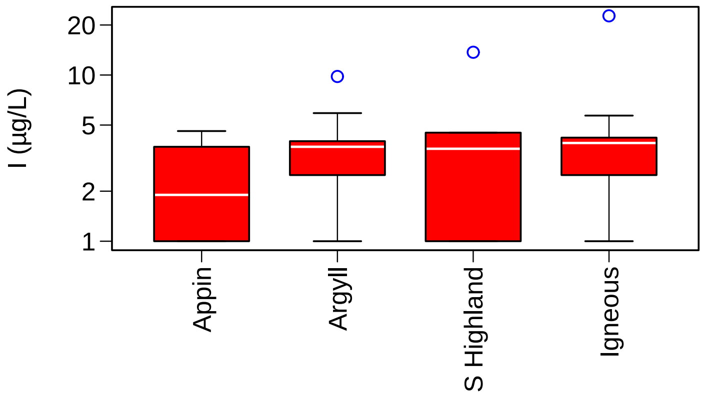
Figure 27 Variation in phosphorus concentrations (as µg P/L) in groundwater with land use type across Aberdeenshire, based on land use maps and field observations of the 200 m diameter area around the groundwater source. Identified DPP refers to improved grassland positivity identified as being used for dairy, pigs and/or poultry

4.3.4 Iodine

Iodine concentrations reach a maximum of 23 µg/L. Potential sources of iodine in groundwater include rainfall, organic matter, and Fe or Al oxides in the soil zone or in bedrock (Whitehead 1985). The highest concentrations in groundwater appear to be mainly located in the northeast of the study area (Figure 28). This may reflect the influence of maritime rainfall. The high concentrations are not aquifer-specific.

4.3.5 Boron

Concentrations of B are universally low (observed maximum 42 µg/L). Relatively high concentrations appear to be a feature of the igneous aquifers (Figure 29). Most likely sources of B in these are biotite and amphiboles in the acidic rock types. In the northeast of the study area, relatively high concentrations could also reflect the influence of maritime rainfall since B concentrations are high in seawater.



Number of samples in each category:			
Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

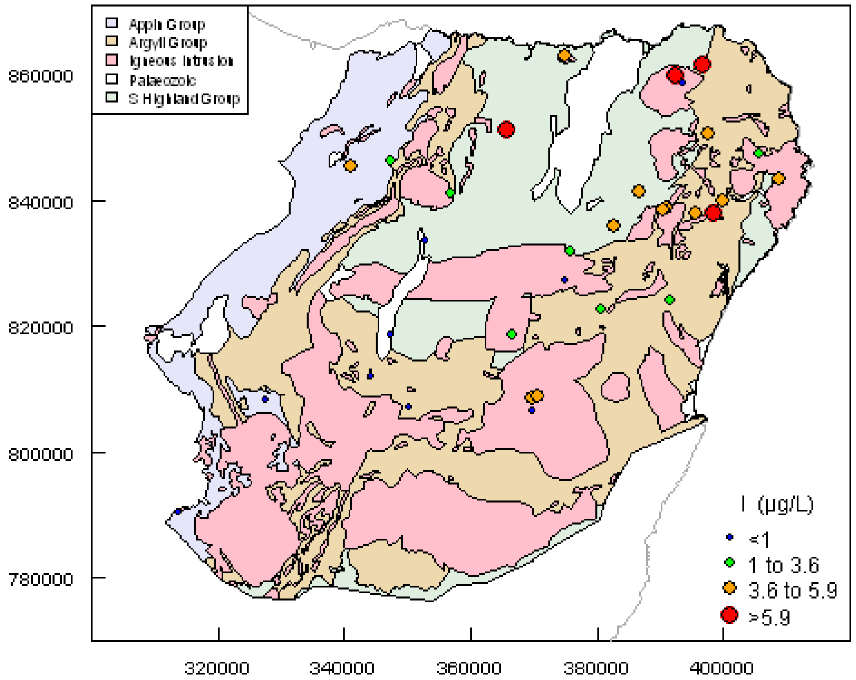
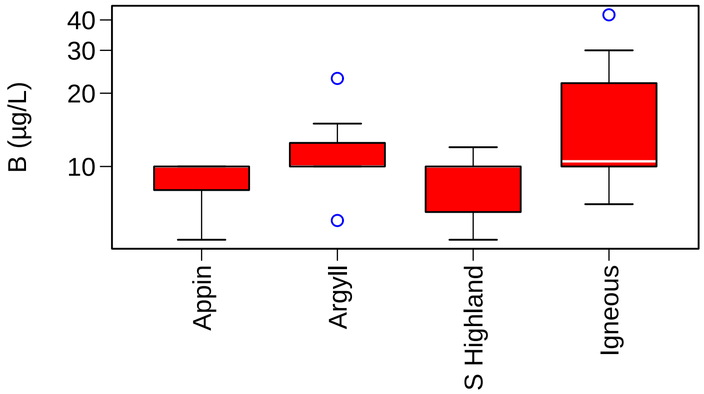


Figure 28 Box plot and map showing the distribution of iodine concentrations in groundwaters in aquifers across Aberdeenshire



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

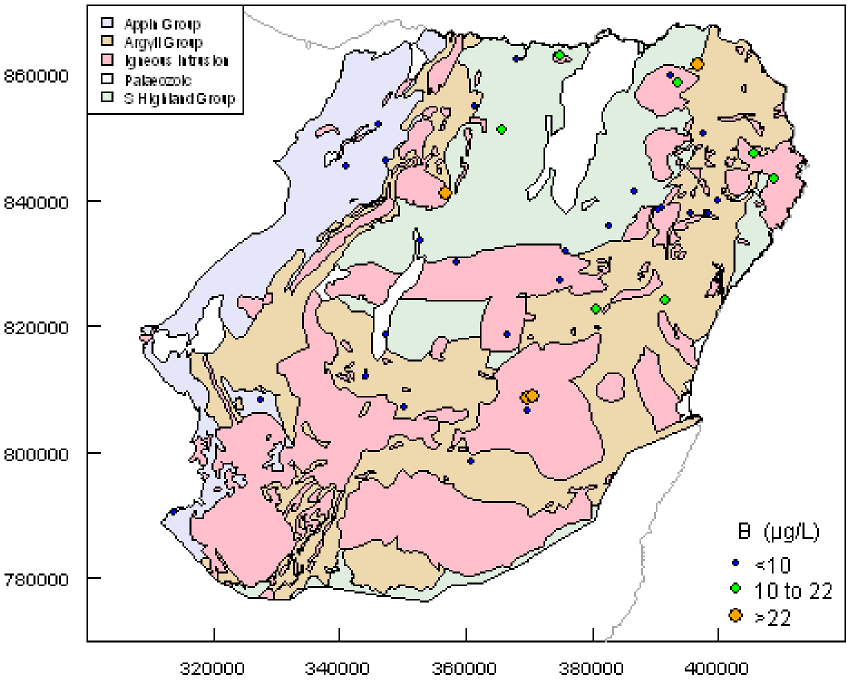
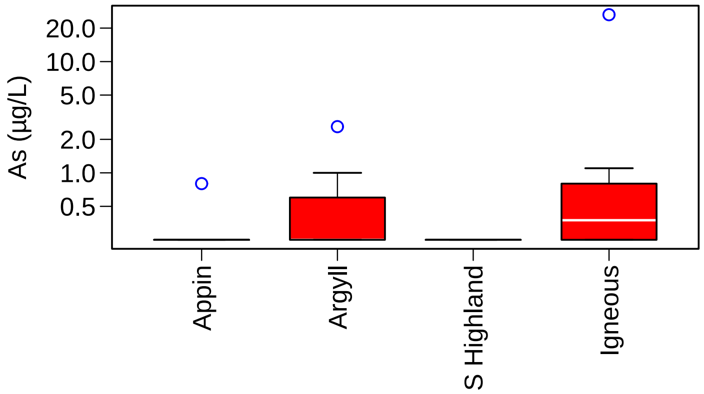


Figure 29 Box plot and map showing the distribution of boron concentrations in groundwaters in aquifers across Aberdeenshire

4.3.6 Arsenic

Most of the analysed samples (68%) had As concentrations below the analytical detection limit of 0.5 µg/L. In all but one of the remaining samples, the As concentration was <3 µg/L. The highest observed value 26 µg/L, was from an igneous aquifer. This was the only sample with a concentration higher than the national drinking water limit for As (10 µg/L). Three samples in the dataset with As concentrations ≥1 µg/L were all from the northeast of the study area, some 10 km southwest of Fraserburgh (Figure 30). These are from different aquifers: two from a felsic igneous intrusion and the third from the Argyll Group, but very close to its boundary with the Southern Highland Group. The sources of dissolved As are unknown, but may be oxidising sulphide minerals, including pyrite.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

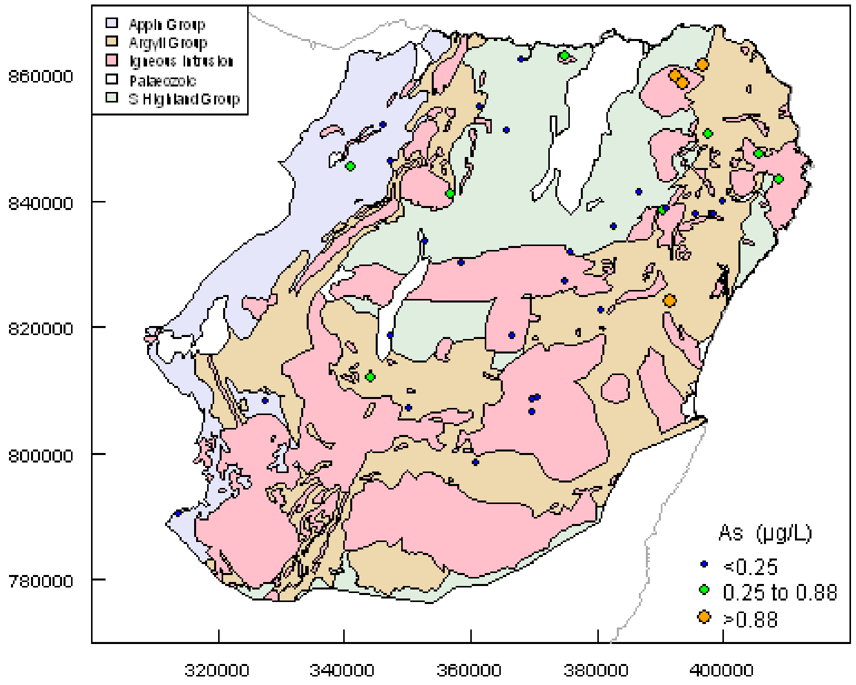
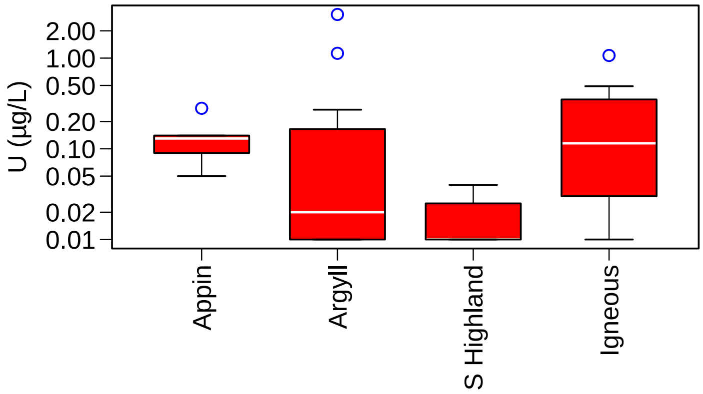


Figure 30 Box plot and map showing the distribution of arsenic concentrations in groundwaters in aquifers across Aberdeenshire

4.3.7 Uranium

Concentrations of U were mostly low, with 30% of analysed samples being below detection limit (<0.02 µg/L). The observed maximum, 3 µg/L, was from a sample from the Argyll Group. Relatively high median values were found in groundwaters from the Appin Group and igneous aquifers (each ca. 0.1 µg/L). There is no obvious spatial or geological pattern to the distribution of the highest concentrations (Figure 31).

Potential sources of U include metal oxides, clays and phosphate minerals. Uranium mineralisation in the granitic rocks in the region is indicated from stream sediment and stream water geochemical data (Section 2.5).



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

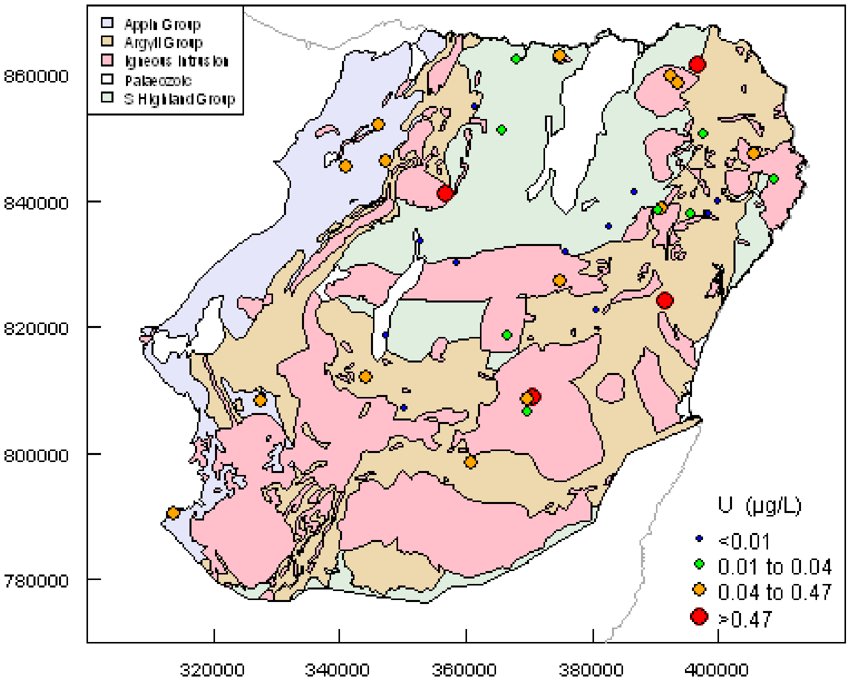
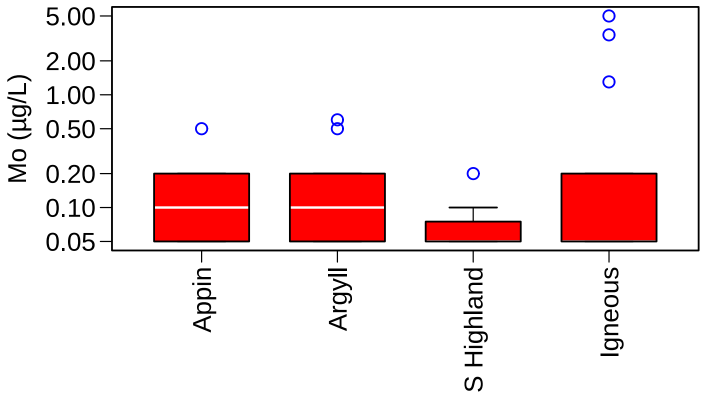


Figure 31 Box plot and map showing the distribution of uranium in groundwaters in aquifers across Aberdeenshire

4.3.8 Molybdenum

Some 51% of the analysed groundwater samples had Mo concentrations below the detection limit of 0.1 µg/L. The median value (0.04 µg/L) for the whole dataset was also very low. The highest observed concentrations, with three samples >1 µg/L, were all from igneous rocks (Figure 32). Potential sources include iron oxides and sulphide minerals. No national drinking water limit exists for Mo, but concentrations in all Aberdeenshire samples are at least an order of magnitude lower than the WHO guideline value for Mo in drinking water.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

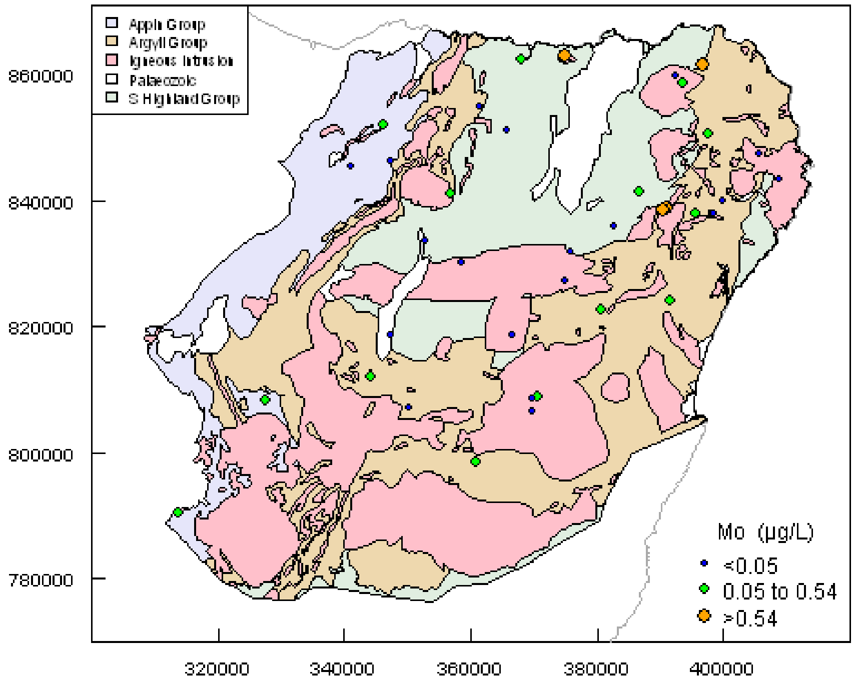
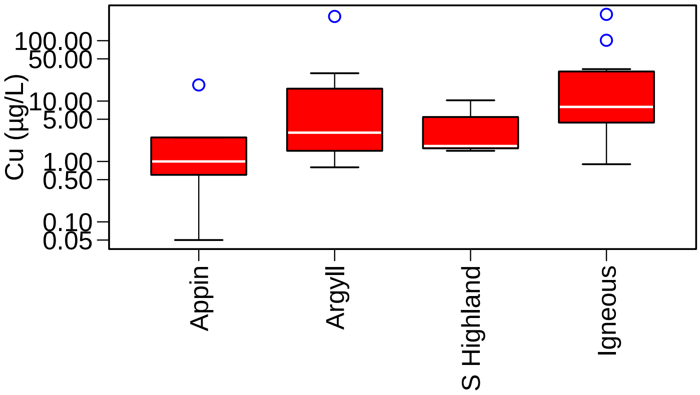


Figure 32 Box plot and map showing the distribution of molybdenum concentrations in groundwaters in aquifers across Aberdeenshire

4.3.9 Copper

Concentrations of Cu have a large range from <0.1 µg/L to 270 µg/L. The highest concentrations and the highest median occur in groundwaters from igneous rocks (Figure 33). Sulphide mineralisation is a likely source of the highest concentrations, although some contamination from metal pipework in boreholes cannot be ruled out.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

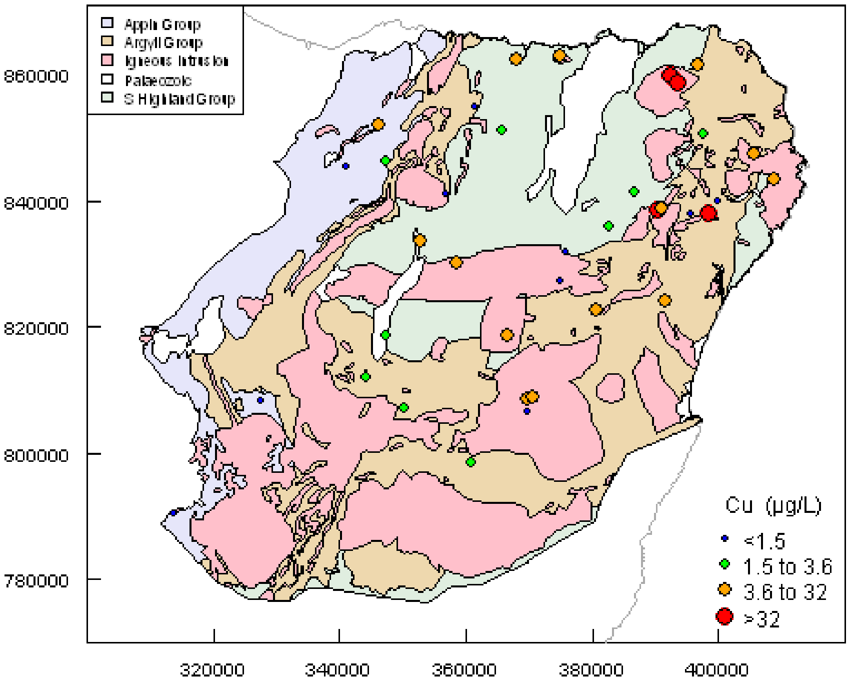
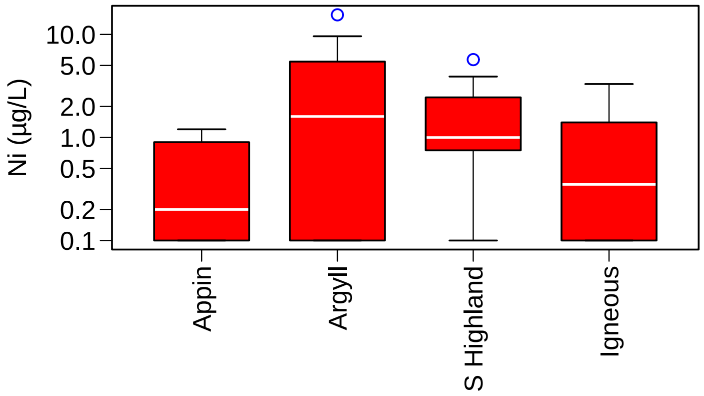


Figure 33 Box plot and map showing the distribution of copper concentrations in groundwaters in aquifers across Aberdeenshire

4.3.10 Nickel

32% of analysed samples had Ni concentrations less than the detection limit of 0.2 µg/L. Relatively high concentrations and the highest maximum observation were from groundwaters from the Argyll Group (Figure 34). Potential sources of Ni include iron oxides and sulphide minerals. Concentrations in groundwaters from granitic rocks are expected to be low because of the correspondingly low Ni concentrations in granitic rocks. All samples had Ni concentrations less than the national limit for Ni in drinking water of 20 µg/L.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

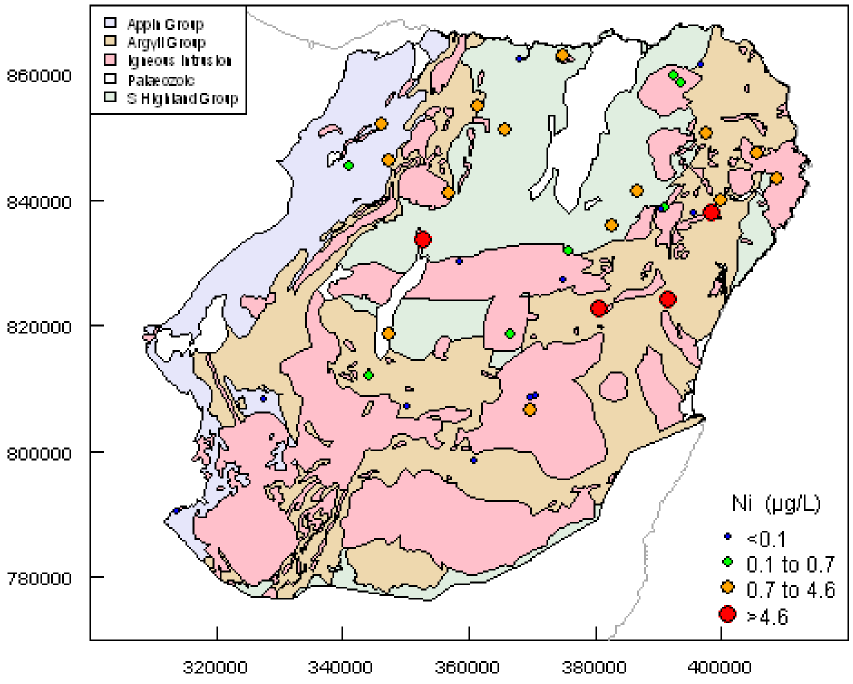
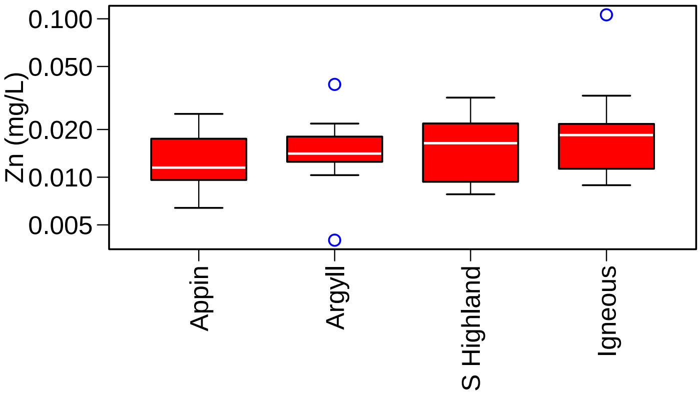


Figure 34 Box plot and map showing the distribution of nickel concentrations in groundwaters in aquifers across Aberdeenshire

4.3.11 Zinc

All samples had detectable Zn, with concentrations ranging up to 106 µg/L. The highest concentration was observed in a groundwater from igneous rocks, although variation between aquifers was relatively small and no notable spatial pattern in concentrations was observed (Figure 35). As with many other transition metals, potential mineral sources include metal oxides and sulphides. Metal pipework in the borehole construction materials could also contribute Zn in some cases. A weak positive correlation exists between Zn and Cu.



Number of samples in each category:

Appin Group	5	Southern Highland Group	6
Argyll Group	10	Igneous	16

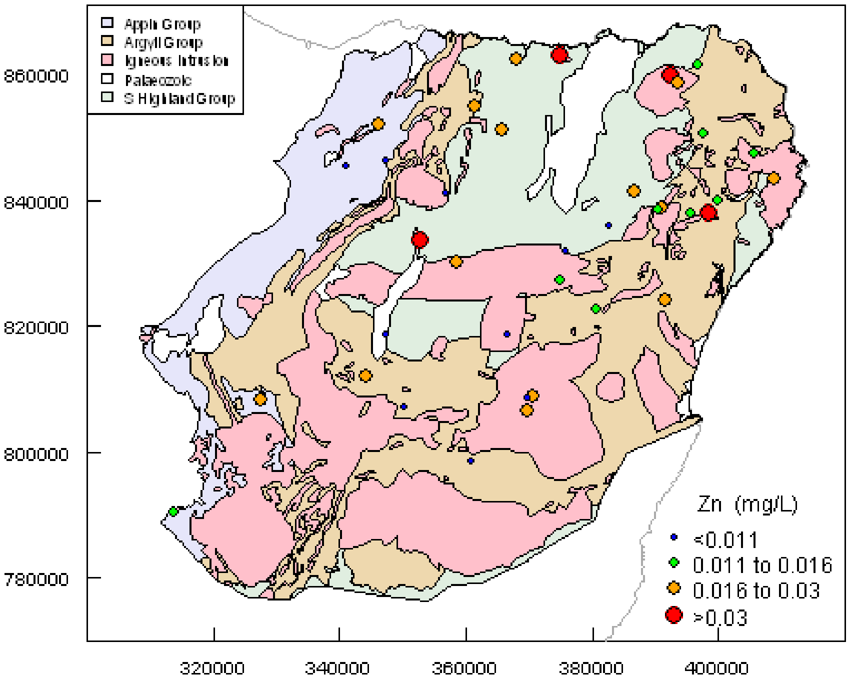


Figure 35 Box plot and map showing the distribution of zinc concentrations in groundwaters in aquifers across Aberdeenshire

4.3.12 Rare earth elements

As expected, rare earth element (REE) concentrations are low for most of the groundwaters, although in most samples, the concentrations of light REE are detectable. Four samples, all from granite aquifers, have notably higher ΣREE concentrations, with, for example, La and Nd concentrations each being >1 µg/L. These high dissolved concentrations in granitic rocks are the reason for the observed La and Lu distributions in groundwaters from igneous aquifers (including granite) (Figure 36). The high-REE samples generally have pH values of <6. Dissolution/desorption from REE-bearing minerals such as amphibole, biotite, muscovite, metal oxides and clays, under slightly acidic conditions, is the most likely mobilisation mechanism for REEs.

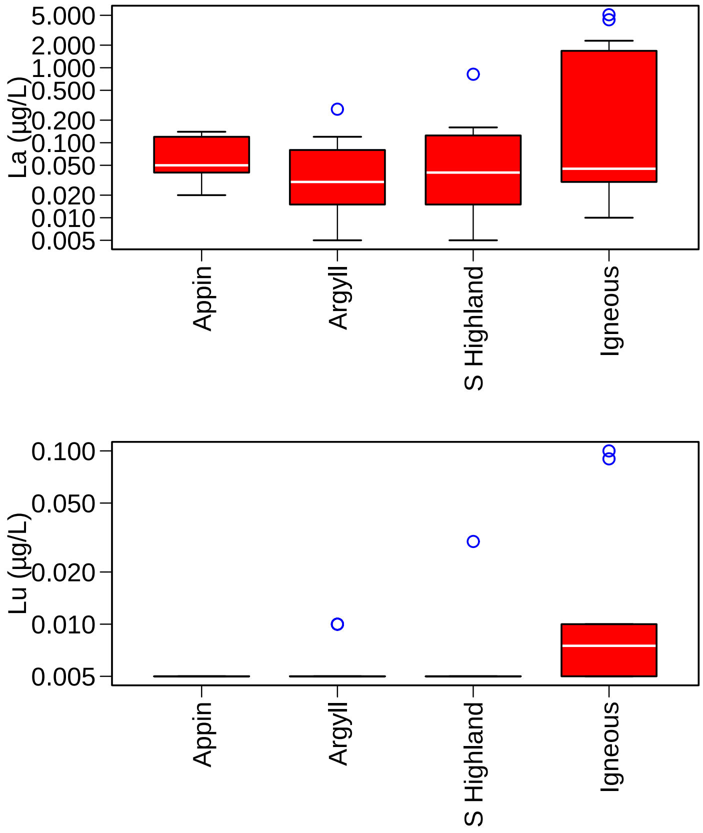


Figure 36 Box plots showing the distributions of La and Lu in groundwaters in aquifers across Aberdeenshire.

Box plots showing the distributions of normalised REE concentrations are shown in Figure 37. The data have been normalised to the 'North Atlantic Shale Composite' (NASC) using data from Sholkovitz (1988). This produces a smoothed distribution by counteracting the typical 'sawtooth' pattern in absolute REE concentrations which occurs when plotted in series (atomic number order). The box plots reveal a large number of upper outliers, largely resulting from the high concentrations in groundwaters from granite aquifers. They also show the relative enrichment in normalised heavy-REEs compared to light-REEs, as is common in groundwaters (e.g. Nelson et al. 2004).

Slight anomalies are apparent for Ce and Eu. The median Ce shows a slight negative anomaly, whereas the median Eu shows a slight positive anomaly (Figure 37). Normalised concentrations of Ce are relatively low compared to the neighbouring REEs. This is most likely to reflect the dominantly oxidising nature of groundwaters in the region. Most REEs in shallow groundwater occur in the 3+ oxidation state, with the potential exception of Ce (e.g. Smedley 1991). Under oxic conditions, stabilisation of Ce in its 4+ state results in removal as ceric oxide or as an adsorbed tetravalent species on clays or metal oxides. This is a likely mechanism for the apparent anomalous behaviour of normalised Ce. In the case of Eu, the slight positive anomaly could be related to the REE compositions of contributing mineral phases. Plagioclase, for example, is well known to contain a relative abundance of Eu in the crystal lattice because of Eu^{2+}/Ca^{2+} substitution during crystallisation (Weill and Drake 1973). This is present in the igneous rocks of the study area. Calcite represents another possible source of enriched Eu. In the heavy REE spectrum, interquartile ranges depicted by the box plots show much greater variability, probably because of the lower absolute abundance and hence increased analytical uncertainty.

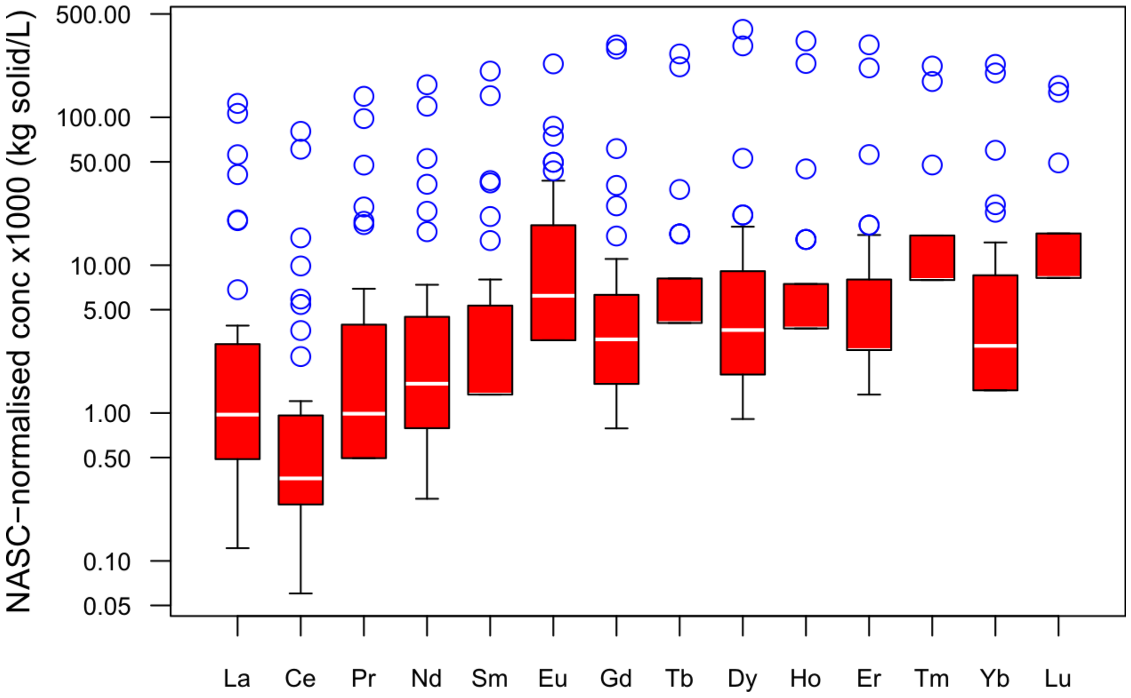


Figure 37 Box plot showing the distribution of the concentrations of REE normalised according to the NASC ‘average shale’.

4.4 CUMULATIVE PROBABILITY PLOTS

Cumulative probability plots provide an alternative way of looking at the distribution of element concentrations. They are complementary to the box plots given above. We use them to provide a way of looking at a group of related elements in a single plot. The x-axis is the $\log_{10}$ transformed concentration (in units of mg/L) while the y-axis gives the probability of a value exceeding a given concentration, plotted on a normal probability scale. The log transform was chosen since many elements, especially the trace elements, show a near log-normal distribution. The cumulative frequency (in percent) is 100 times the probability.

Although cumulative probability plots could be sub-divided usefully by aquifer geology in the same way as the box plots, the limited number of samples in several of the aquifer sub-groups means that the steps in the plotted distributions would be too coarse, and any benefits would be likely outweighed by the increased crowding of the resulting plots. It is therefore assumed that all 37 samples from the study area belong to a single population.

The plots make it easy to see the variation in the median concentrations between different elements (the points at which the probability is 0.5). The slopes of the lines give a measure of the variation (or standard deviation) of the subset of data and the straightness of the lines gives an indication of the extent to which the distribution follows a log-normal distribution. A distinct change in slope may indicate that the overall distribution is made up of two or more sub-populations with differing statistical properties. A tailing at the high concentration end is common, and may indicate a population of contaminated or mineralised sites. However, since there is no mechanism that dictates that a particular distribution should exist, it is not possible to infer the origin or genesis of particular sets of samples purely on the basis of their position within a population. That would require more information, including a model for the processes controlling the concentration of a particular element within the sampled area. Similar reasoning applies to any attempt to distinguish ‘natural’ and ‘contaminated’ samples purely on the position within the overall distribution.

The cumulative probability plots were calculated on an element-by-element basis, with the groups of elements determined by a common theme. Missing data were omitted. The NADA approach was chosen for calculating the probabilities, choosing the appropriate method for dealing with censored data according to the criteria outlined in Section 4.1. In most cases, the Kaplan-Meier method was used.

Cumulative probability plots are shown for the major ions as well as selected minor and trace elements in Figure 38, Figure 39 and Figure 40.

4.4.1 Major elements

Most of the cumulative probability curves for the major ions represent near-linear distributions with no obvious major anomalies. Single analyses are responsible for the slight kinks at the upper end of the ranges for K and Mg. Three samples have anomalously high HCO_3 concentrations. These samples are much closer to saturation with respect to calcite, and are likely to have undergone some calcite reaction.

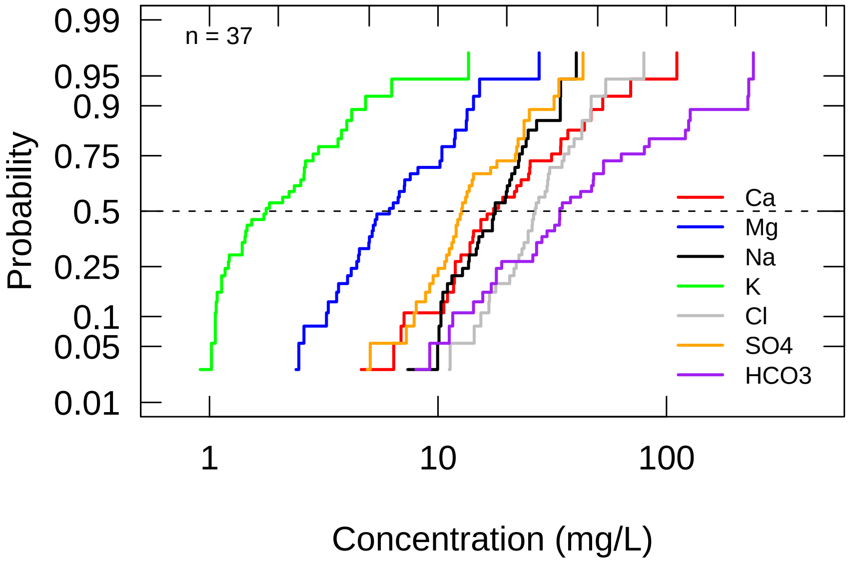


Figure 38 Cumulative probability plots for eight major elements

Minor elements

Cumulative probability plots for Sr, F, and Si show near-linear (log-linear) trends (Figure 39), and lack any evidence for contributions from anomalous sources. The rather narrow range of Si concentrations suggests solubility control by a silicate mineral (amorphous silica or quartz). In the case of Ba and Zn, a single sample has given rise to a tail at the high end of the range. The high-Zn sample also had a high Cu concentration.

Non-linearity in the cumulative probability curves is most extreme for Fe and Mn, which each show large increases at the upper end. A similar, albeit less extreme, rise at the upper end is also evident for Al. As noted earlier, these high concentrations are believed to result from a combination of reducing conditions (which favour release of Fe and Mn) and the presence of colloids in the affected samples (which favour increased concentrations of Fe, Mn and Al).

A distinct offset occurs for Br at a concentration of ca. 110 µg/L. The cause is unclear, but may be due the influence of maritime rainfall (marine aerosol input).

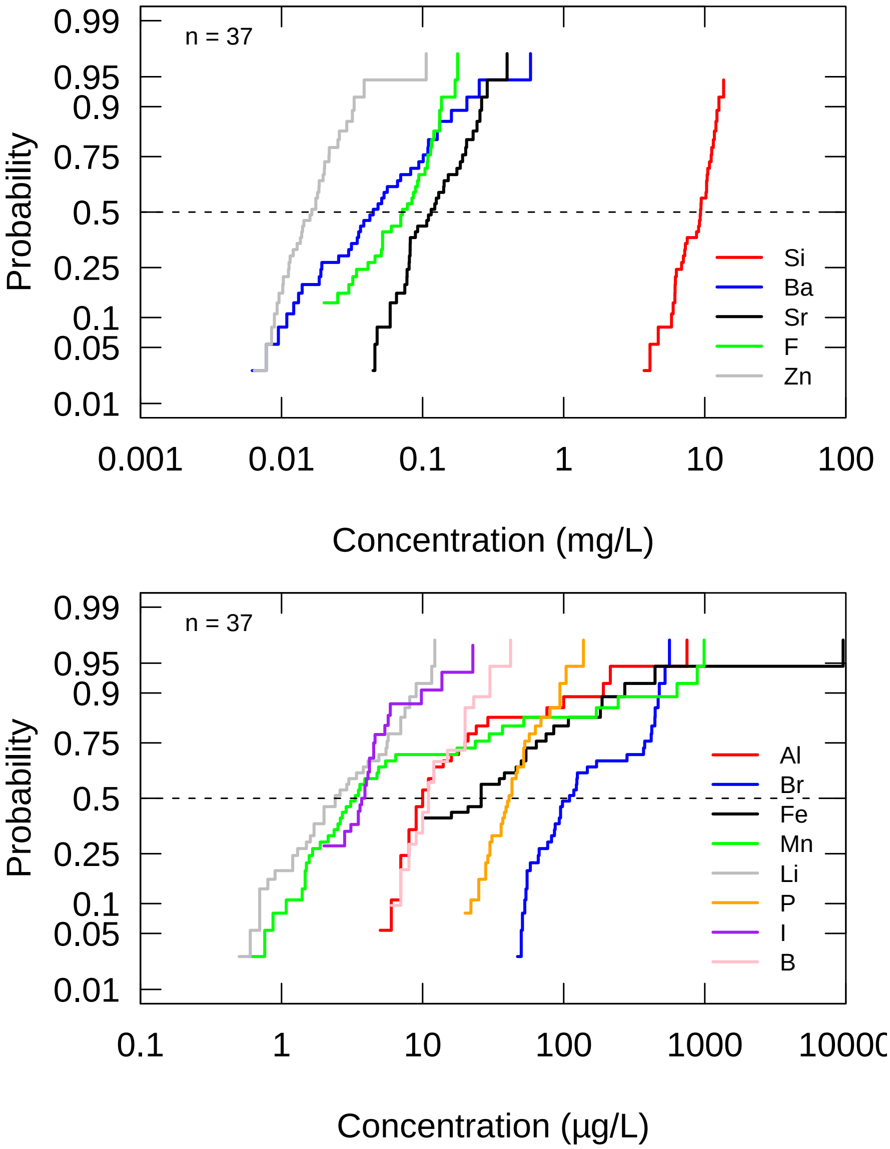


Figure 39 Cumulative probability plots for selected minor elements.

4.4.2 Trace elements

For elements where the number of censored observations was less than ca. 50%, probability distributions have been calculated using Kaplan-Meier. In cases where the degree of censoring was greater than 50%, the data below detection limits have been modelled using the ROS method (Section 4.1). ROS distributions for non-detect data are shown as stepped straight lines on the plots in Figure 40.

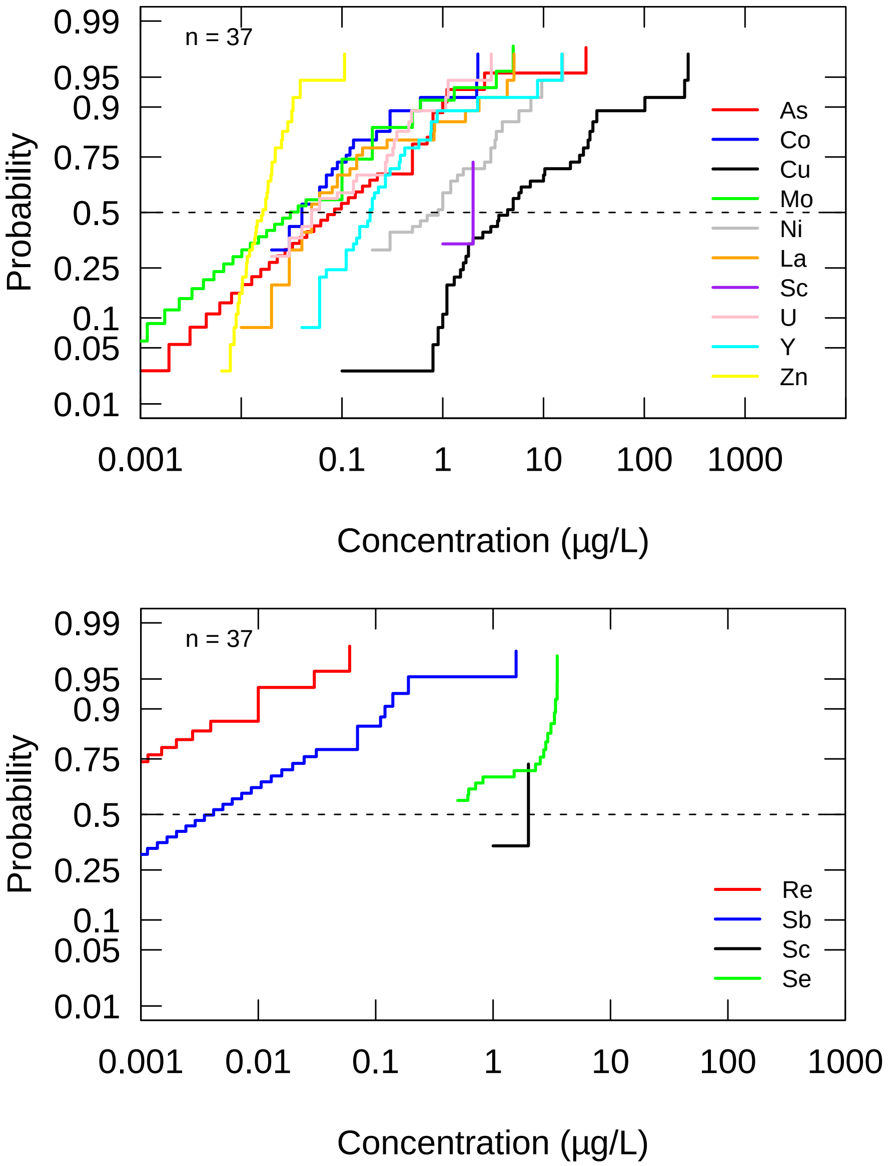


Figure 40 Cumulative probability plots for selected trace elements.

The most obvious deviations at the upper end in the trace-element curves are for As and Sn. As noted above, the origin of the anomalously high As concentration (26 µg/L; Section 4.3.6) responsible for this deviation is uncertain. However, it is likely to derive from localised oxidation of sulphide minerals. The single high Sn sample was from the Appin Group, albeit within close proximity of igneous rocks. Localised Sn mineralisation may be responsible for this anomalous concentration. However, the sample also contained anomalously high concentrations of Fe and Al and may therefore include a component of colloidal material. In this case, the Sn analysis may not represent a truly dissolved concentration.

4.5 ENVIRONMENTAL TRACERS

4.5.1 Stable Isotopes

As is usually found to be the case for groundwaters in temperate climates, $\delta^{18}O$ and $\delta^{2}H$ are well correlated in the Aberdeenshire baseline dataset, so only one of the pair of isotopes needs to be considered further for hydrological purposes: in this case, we have considered $\delta^{18}O$.

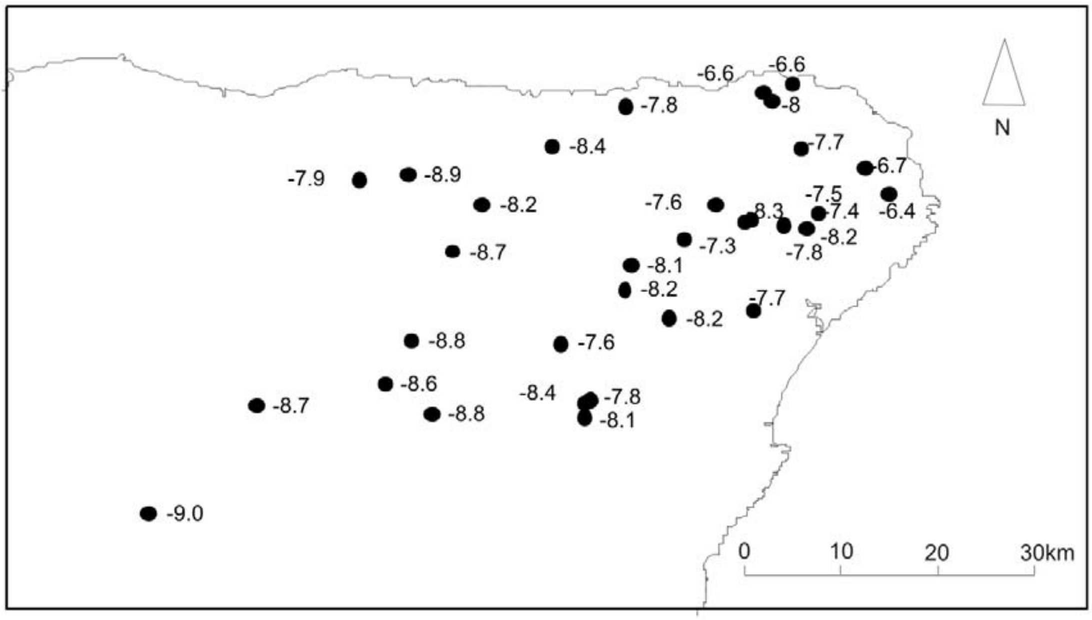


Figure 41 Values of $\delta^{18}O$ in ‰ for selected Aberdeenshire groundwaters

A map of $\delta^{18}O$ values for the Baseline groundwater samples (Figure 41) shows that the most depleted (isotopically negative) groundwater is found in the southwest of the study area, where ground elevation can exceed ~400 m OD. Figure 42 shows $\delta^{18}O$ values in relation to the altitude of the sampling point. Apart from the four most enriched samples in the range (-6.4 to -6.7 ‰), all the other samples tend to become more depleted as altitude increases. This is a normal observation, since the isotopic composition of rainfall becomes more negative as the rain-out altitude increases. However, a typical lapse rate (i.e. depletion in isotopic composition with altitude) for the UK would be -0.3 ‰/100 m (shown on Figure 42). Samples falling on or near this typical depletion line are presumed to be derived mainly from recharge at a similar altitude to the sampling point, and therefore likely to be local in origin. Samples falling well to the left of the line are likely to represent recharge derived from significantly higher elevations.

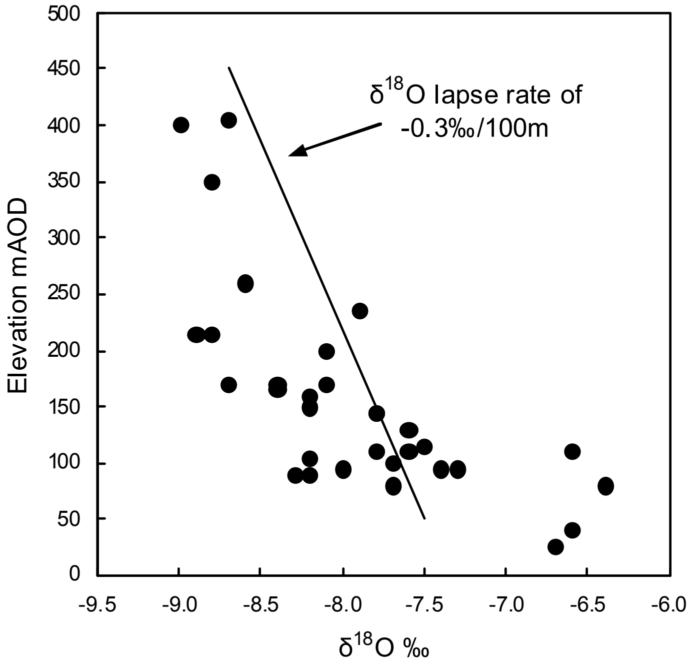


Figure 42 Relationship between $\delta^{18}O$ and sampling altitude for groundwaters in Aberdeenshire. A typical lapse rate for the UK is also shown.

Samples falling to the right of the line (the most isotopically enriched samples) are found near the coast in the northeast of the region (Figure 41). These waters are likely to be well mixed and derived from local recharge, which tends to become less negative along the coastal strip of the UK (Darling et al. 2003). The few examples of more depleted groundwaters found in the immediate vicinity of the coast are likely to be derived from higher elevations inland.

4.5.2 Trace gas residence-time indicators

The dissolved atmospheric trace gases SF_6 (sulphur hexafluoride) and the CFCs (chlorofluorocarbons) were measured on selected samples. The interpretations of age made from such analyses are linked to the increase in concentration of these gases in the atmosphere, and therefore in rainfall, over the past half-century (Darling and Gooddy 2007). However, CFCs can suffer degradation under reducing conditions, and both SF_6 and the CFCs may be subject to local additions from contamination, for example anthropogenic contamination from incorrect disposal of CFC-containing refrigeration units, or SF_6 contamination from fluoride-bearing compounds in the aquifer rock (see below). Care is therefore required in their interpretation. In addition, SF_6 is affected by the 'excess air' usually acquired by recharging waters during passage through the soil. To account for this, raw SF_6 concentration values have been multiplied by a correction factor of 0.75, based on the assumption of a 3 ccSTP/L excess air component (except for the two elevated concentrations referred to below).

Figure 43 shows plots of sample CFC-11 and CFC-12 versus SF_6 concentration. Superimposed on each of the plots is a 'piston flow' curve reflecting the relative inputs of each gas with time, and a binary mixing line between modern and old groundwater. Two sites (Samples 16 and 28) had elevated SF_6 values and do not appear on the plots. Outside urban or industrial areas, elevated SF_6 concentrations are not generally the result of anthropogenic contamination, but have been linked to the presence of igneous rocks, particularly those rich in fluorite (e.g. Busenberg and Plummer 2000). The two cases here are both in groundwaters from granite, which would be consistent with this scenario. However, three of the other SF_6 samples are also derived from granite and do not show elevated SF_6 concentrations, so major SF_6 contamination appears not to be universal in this rock type. Therefore, the variation in SF_6 concentrations from groundwaters in the Aberdeenshire granites may relate to local variation in fluorite concentration in the granites.

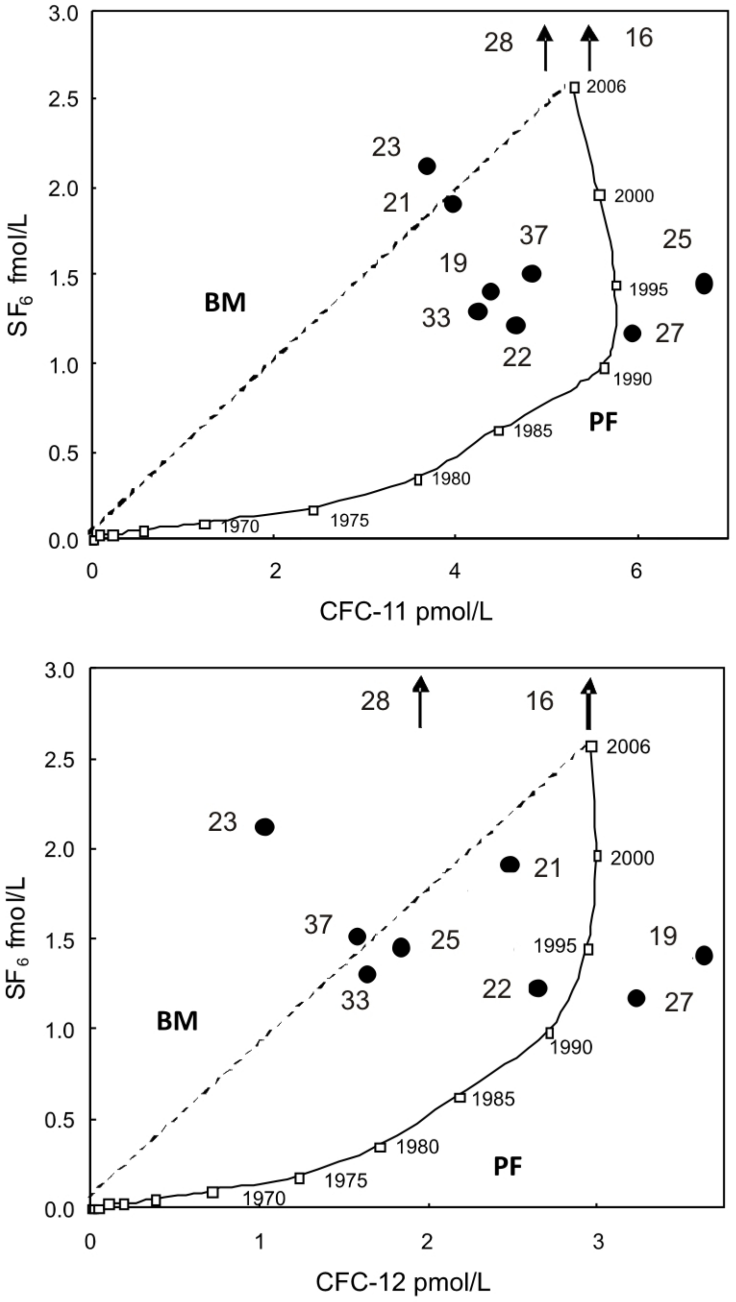


Figure 43 Plots of CFC-11 (top) and CFC-12 (bottom) versus SF_6 concentrations for selected groundwaters from Aberdeenshire. PF: piston flow curve; BM: binary mixing line; both for groundwaters recharged at 10°C

With the exception of these two samples with elevated SF_6 (Samples 16 and 28), all the trace gas data plot within or reasonably close to the piston-flow mixing line field. The simplest form of interpretation is to examine CFC-11 compositions in relation to CFC-12. If CFC-11 is relatively high, then contamination may be suspected. If CFC-11 is relatively low, anoxic breakdown is indicated, which affects CFC-11 more than CFC-12.

The samples can be grouped as follows: samples 25, 37 and 33 are mixed waters with about 50% modern water, but slight CFC-11 contamination, most notably for Sample 25. Sample 22 is a water with an exponential distribution of flowpaths and a mean age of approximately 20 years. Sample 21 is also a mixed and largely young water, with about 80% modern water, and not significantly affected by contamination. Sample 16 and 28 (not on the plots due to excess SF_6) and Sample 27 are piston-flow waters with ages of <5, 25 and 15 years respectively. Sample 19 is lower in CFC-11 than CFC-12, which often indicates anoxic degradation. However, dissolved oxygen is not especially low in this groundwater, so this explanation may not apply. Whatever the reason, this water appears unlikely to be older than about 10 years. Sample 23 is unusual in having an apparently expected CFC-11 but reduced CFC-12 composition. However, this may be an illusion caused by elevated SF_6, since this sample is derived from a granite aquifer, in which fluorite could be present. Assuming this is the case, and using the CFC-12 rather than CFC-11 concentration which may be slightly elevated, the water is either about 30 years old or contains about 30% modern water.

5 Discussion

5.1 BASELINE GROUNDWATER CHEMISTRY

5.1.1 Overall baseline groundwater chemistry

One of the reasons for undertaking this survey was to determine the baseline groundwater chemistry conditions for the different aquifers in Aberdeenshire. Baseline chemistry can incorporate a range of chemical concentrations in groundwater in any one aquifer, influenced by natural processes, such as oxidation state and residence time. However, many of the samples have been influenced by human activity, particularly related to agricultural practices. To try and define the natural baseline chemistry of groundwater unaffected by human activity, two approaches have been taken, as for previous Baseline Scotland reports (Ó Dochartaigh et al. 2006, MacDonald et al 2008). The first is statistical; a secondary approach involves selecting individual samples from each aquifer group which are judged to be representative of baseline conditions.

The main approach to defining baseline groundwater chemistry is statistical, and assesses the natural variation in baseline chemistry that can occur. Under this approach, the data between the 10th and 90th percentiles are examined for each element or ion (Table 3 for all groundwaters sampled in Aberdeenshire; Appendix 2 for the statistical distribution of chemistry in each aquifer group). Using only data between the 10th and 90th percentiles allows the influence of outliers to be minimised. New groundwater chemistry data from the same aquifers would be expected to plot within this range 80% of the time. Data outwith this range can still occur naturally, but are less common, and therefore may merit some further investigation.

The baseline statistics are presented first for all the groundwaters sampled in Aberdeenshire (Table 3). The overall major ion distribution in the groundwaters is illustrated in a Piper diagram (Figure 44). Summary statistics are also presented for the four individual aquifer groups (Appendix 2), and the overall chemistry of groundwater from each aquifer group is summarised briefly (Section 5.1.2).

Two parameters for which concentrations cannot be regarded as ‘baseline’ are nitrate and phosphorus. In the study area, these appear to have been modified substantially by anthropogenic (mainly agricultural) activity. These parameters are discussed in more detail in Section 5.3.

As a secondary approach to identifying baseline groundwater chemistry, ten groundwater samples from across the region have been selected as representative both of the likely natural groundwater chemistry and of the general observed range in chemical variation. All were sampled from sources where there is little or no indication of direct contamination. These can be used as reference groundwaters for management purposes. The chemistry of each sample broadly falls within the 10th to 90th percentile ranges for each aquifer, as presented in Appendix 2, and the sources from which the samples were collected show no evidence of direct contamination. Samples where NO_3-N is below 4 mg/L were preferred (taken as the upper limit of naturally occurring nitrate in the region), but four of the baseline samples have higher nitrate concentrations than this, of up to 8.17 mg/L as N.

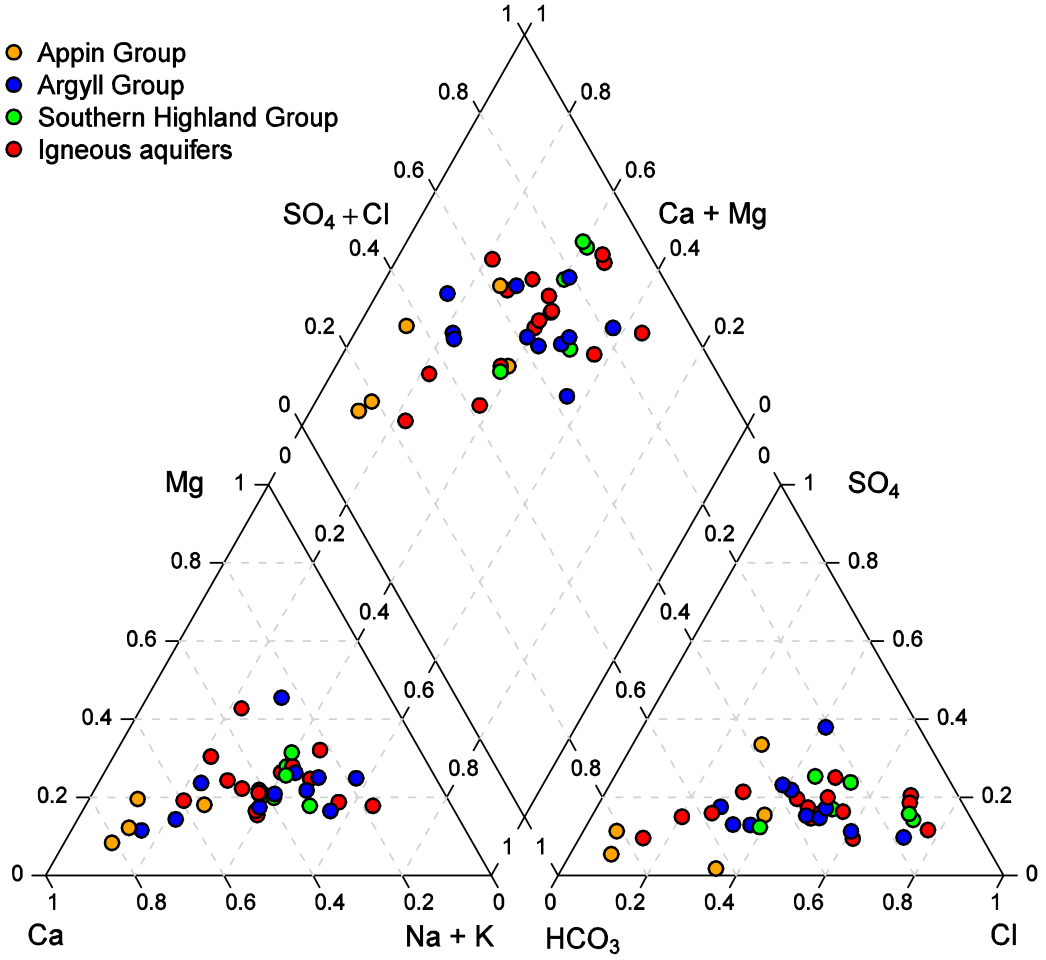


Figure 44 Piper diagram showing the compositions of groundwater from different formations in Aberdeenshire

At least two samples were chosen from each aquifer: two from the Argyll Group; two from the Appin Group; three from the Southern Highland Group; and three from igneous aquifers. The samples represent a range of land uses from woodland and semi natural to pasture. None was from land used for dairy, pigs or poultry, as nitrate concentrations in groundwater from such areas tends to be significantly elevated. Five of the samples were collected from springs, four from boreholes. The location of the baseline samples related to the aquifer distribution is shown in Figure 45, and the samples are highlighted in Appendix 1.

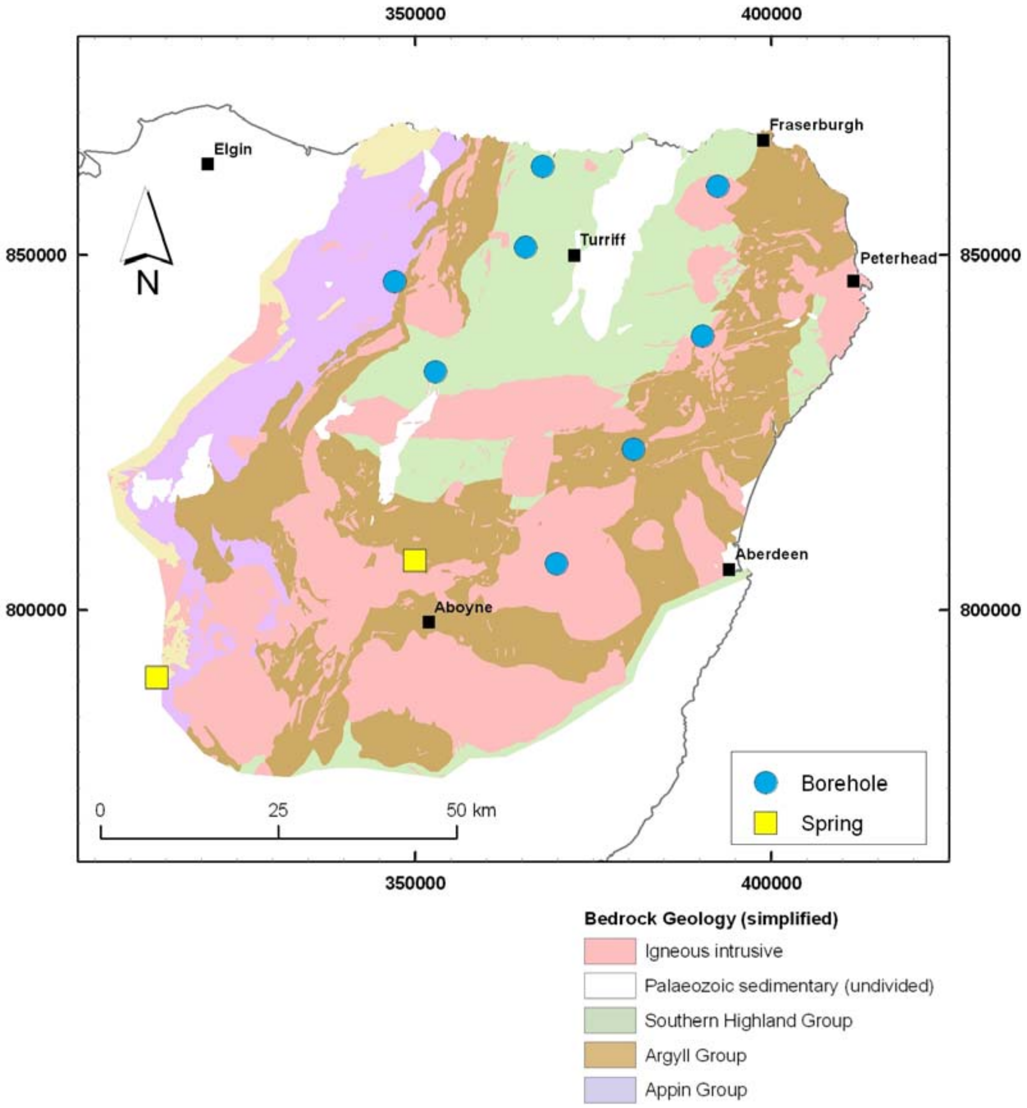


Figure 45 Location of the ten representative baseline groundwater samples across Aberdeenshire

5.1.2 Baseline groundwater chemistry by aquifer

A summary of the overall chemistry of groundwater from each of the four aquifer groups in Aberdeenshire is presented here. The data presented in Section 4 indicate that systematic variations in groundwater chemistry with geology across Aberdeenshire are slight. However, some do exist, particularly related to bicarbonate, and are summarised here.

Summary statistics for chemical elements in groundwater from each of the aquifer groups are presented in Appendix 2.

APPIN GROUP

Groundwaters from the Appin Group are generally of Ca-HCO_3 type, with low concentrations of Mg, Na-K and SO_4 (Figure 44). They are typically oxic and slightly acidic (pH generally between 6.17 and 7.27; median 6.71). SEC typically ranges between 60 and 349 µS/cm, with a median of 274 µS/cm. They have significantly higher HCO_3 (generally between 47.8 and 125 mg/L; median 80 mg/L) and Ca concentrations, and lower Mg, and are generally more alkaline than groundwaters from the other three aquifer groups. The known presence of calcareous bands in the Appin Group is likely to be the main control on this alkalinity trend.

Of the few Aberdeenshire groundwater samples which were close to saturation with respect to calcite, most were from the Appin Group.

Iron concentrations vary from less than the detection limit to just above the national drinking water limit, at 271 µg/L, with a median of 85 ug/L. Mn concentrations are low, always less than 5 µg/L.

ARGYLL GROUP

Most groundwater samples from the Argyll Group are fairly balanced with regards to the major ions, with a slight cationic dominance by Ca and a slightly anionic dominance by Cl, and generally low SO_4 (Figure 44) They are typically oxidising and more acidic than groundwaters from the Appin Group (pH range 5.67 – 6.82, with a median of 6.22). SEC generally ranges between 93.1 and 434 µS/cm, with a median of 238 µS/cm. HCO_3 ranges between 15.7 and 127 mg/L, with a median of 34 mg/L.

Although there are also known calcareous bands in the Argyll Group, these do not appear to influence the chemistry of groundwaters to the same degree as in the Appin Group. However, some of the few samples that were close to saturation with respect to calcite are from the Argyll Group.

Iron and Mn concentrations range from low (below or near detection limit) to high, in both cases significantly higher than the drinking water quality limits, at 444 µg/L (Fe) and 636 µg/L (Mn). However, both show a relatively low median value, at 38 µg/L (Fe) and 1.66 µg/L (Mn).

SOUTHERN HIGHLAND GROUP

Groundwaters from the Southern Highland Group are typically balanced between the major cations, but show an anionic bias toward Cl, and like the other groundwaters have low SO_4. They are typically oxic with similar pH to the Argyll Group (general pH range from 5.39 to 6.6; median 6.29). Their bicarbonate concentrations, however, tend to be lower, with a general range in HCO_3 between 5.4 and 30 mg/L, and a median of 19 mg/L. The waters are slightly more mineralised on average, with SEC generally ranging from 200 to 352 µS/cm, with a median of 292 µS/cm. Although represented by fewer sampled, these groundwaters show the smallest major ion variation between samples of all the four aquifer groups.

Iron concentrations are typically low, with a median of 9.95 µg/L and a maximum of 75 µg/L. The median Mn concentration is relatively low, at 5.46 µg/L, but Mn ranges up to significantly above the drinking water limit, at 243 µg/L.

IGNEOUS AQUIFERS

Groundwaters from igneous aquifers are generally balanced between the major cations, but their anionic type ranges from Cl to HCO_3, with similarly low SO_4 to the other Aberdeenshire groundwaters. They are typically oxic with similar pH to the Argyll and Southern Highland groups (general pH range from 5.47 to 6.94, with a median of 6.19). Bicarbonate concentrations are relatively low, similar to waters from the Southern Highland Group, with an observed range from 11.6 to 121 mg/L and a median concentration of 34 mg/L. These groundwaters showed the greatest chemical variation between samples of all the four aquifer groups. Overall, they are slightly more mineralised than groundwaters from the metamorphic aquifers, with SEC ranging from 152 to 448 µS/cm and a median of 314 µS/cm.

Iron and Mn concentrations are highly variable, with low median values (7.29 µg/L for Fe and 3.89 µg/L for Mn) and high maxima (9560 µg/L for Fe and 884 µg/L for Mn).

Table 3 Summary statistics for chemical elements in groundwater in all aquifers across Aberdeenshire. Summary statistics for the individual aquifers are presented in Appendix 2.

Elem	Units	No.	No. censored	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	36	0	7.4	7.6	8.4	9	10.1	10.8	11.7	13.7	KM
pH		37	0	5.24	5.47	5.88	6.24	6.71	7.16	7.33	7.84	KM
Eh	mV	36	0	131	297	324	371	428	468	532	662	KM
DO	mg/L	36	0	2.55	3.89	4.58	6.04	8.39	9.56	10.2	11.1	KM
SEC	µS/cm	37	0	60	119	200	258	349	463	533	931	KM
Ca	mg/L	37	0	3.9	6.89	11.8	16.4	25.3	46.7	69.7	111	KM
Mg	mg/L	37	0	1.66	2.59	4.17	5.4	10.2	13.4	15.2	27.7	KM
Na	mg/L	37	0	4.24	10.1	12.8	17.5	22.5	27	34.4	40.3	KM
K	mg/L	37	0	0.88	1.02	1.17	1.73	2.63	4.19	6.27	13.6	KM
Cl	mg/L	37	0	4.29	14.4	21.5	26.2	34.9	46.5	54.2	79.6	KM
SO_4	mg/L	37	0	2.78	7.27	10	12.5	18.1	25.1	33.8	43.1	KM
HCO_3	mg/L	37	0	5.4	11.2	18	34	53	127	229	240	KM
NO_3-N	mg/L	37	0	0.052	0.382	2.36	7.15	12.6	20.1	21.2	24.3	KM
NO_2-N	mg/L	14	2	<0.0003	NA	0.001	0.002	0.002	0.003	NA	0.009	KM
NH_4-N	mg/L	14	8	<0.01	0.001	0.002	0.006	0.022	0.049	0.092	0.17	ROS
P	µg/L	37	3	<20	20	29	40	52	80	104	138	KM
DOC	mg/L	23	0	0.26	0.76	1.03	1.34	2.13	4.23	5.62	7.44	KM
F	mg/L	37	5	<0.02	NA	0.034	0.07	0.108	0.132	0.17	0.177	KM
Br	µg/L	37	0	39	51	66	98	368	467	523	562	KM
I	µg/L	32	9	<2	NA	NA	3.6	4.2	5.9	13.7	22.7	KM
Si	mg/L	37	0	3.32	4.68	6.29	9.28	10.8	12.2	NA	13.6	KM
Al	µg/L	37	0	4	5	7	9	18	100	214	748	KM
As	µg/L	37	25	<0.5	0.006	0.019	0.084	0.5	0.88	1.4	26.4	ROS
Au	µg/L	37	35	<0.05	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS
B	µg/L	37	14	<20	6	7	10	15	23	30	42	KM
Ba	mg/L	37	0	0.0031	0.009	0.019	0.042	0.094	0.16	0.252	0.582	KM
Be	µg/L	37	27	<0.05	0.001	0.004	0.013	0.06	0.182	0.432	0.60	ROS
Cd	µg/L	37	18	<0.05	NA	NA	0.06	0.09	0.15	0.23	0.28	KM
Ce	µg/L	37	3	<0.01	0.01	0.02	0.03	0.08	0.82	5.05	6.67	KM
Co	µg/L	37	12	<0.02	NA	NA	0.03	0.09	0.3	2.17	2.23	KM
Cr	µg/L	37	24	<0.5	0.033	0.074	0.193	0.6	0.98	1.34	7.1	ROS
Cs	µg/L	37	21	<0.01	0.0002	0.0007	0.003	0.01	0.034	0.052	0.8	ROS
Cu	µg/L	37	1	<0.1	0.9	1.5	3.6	18.5	33.8	251	272	KM
Dy	µg/L	37	8	<0.01	NA	0.01	0.02	0.05	0.12	1.67	2.16	KM
Er	µg/L	37	8	<0.01	NA	0.01	0.01	0.03	0.07	0.81	1.16	KM
Eu	µg/L	37	17	<0.01	NA	NA	0.01	0.03	0.08	0.14	0.37	KM
Fe	µg/L	37	15	<10	NA	NA	21	54	187	444	9560	KM
Ga	µg/L	37	35	<0.05							0.14	ROS
Gd	µg/L	37	5	<0.01	NA	0.01	0.02	0.04	0.22	1.84	1.96	KM
Ge	µg/L	37	36	<0.05							0.23	ROS
Hf	µg/L	37	36	<0.02	0.02						0.02	ROS
Hg	µg/L	37	36	<0.1							0.1	ROS
Ho	µg/L	37	23	<0.01	6E-05	0.0002	0.002	0.01	0.02	0.11	0.44	ROS
La	µg/L	37	3	<0.01	0.01	0.02	0.04	0.12	1.68	4.36	5.09	KM

Table 3 cont'd

Elem	units	No.	No. censored	min	10%	25%	50%	75%	90%	95%	max	method[1]
Li	µg/L	37	0	0.1	0.6	1.2	2	5.5	8.1	11.6	12.2	KM
Lu	µg/L	37	27	<0.01	9E-05	0.0003	0.001	0.01	0.01	0.042	0.1	ROS
Mn	µg/L	37	0	0.53	0.87	1.57	3.09	17.5	243	884	989	KM
Mo	µg/L	37	19	<0.1	0.002	0.008	0.044	0.2	0.54	1.72	5	ROS
Nb	µg/L	37	35	<0.01							0.01	ROS
Nd	µg/L	37	0	0.01	0.01	0.03	0.06	0.17	1.34	4.52	6.31	KM
Ni	µg/L	37	12	<0.2	NA	NA	0.7	2.6	5.7	9.6	15.5	KM
Pb	µg/L	37	10	<0.1	NA	NA	0.2	0.3	0.8	1.5	3.7	KM
Pr	µg/L	37	12	<0.01	NA	NA	0.01	0.04	0.25	0.99	1.4	KM
Rb	µg/L	37	0	0.1	0.14	0.25	0.6	1.83	4.2	8.94	10.8	KM
Re	µg/L	37	33	<0.01							0.06	ROS
Rh	µg/L	37	32	<0.01							0.01	ROS
Sb	µg/L	37	30	<0.05							1.57	ROS
Sc	µg/L	37	13	<1	NA	NA	1	NA	NA	NA	2	KM
Se	µg/L	37	21	<0.5	0.145	0.277	0.592	2.3	3.12	3.42	3.5	ROS
Sm	µg/L	37	19	<0.02	0.0004	0.0016	0.0091	0.04	0.204	0.434	1.54	ROS
Sn	µg/L	37	0	0.11	0.13	0.18	0.86	1.09	1.3	2.25	165	KM
Sr	mg/L	37	0	0.034	0.0476	0.0776	0.11	0.185	0.255	0.287	0.397	KM
Tb	µg/L	37	26	<0.01	3-05	0.0001	0.0009	0.01	0.02	0.086	0.33	ROS
Tl	µg/L	37	24	<0.01	0.003	0.004	0.006	0.01	0.01	0.02	0.02	ROS
Tm	µg/L	37	26	<0.01	9E-05	0.0003	0.001	0.01	0.01	0.046	0.14	ROS
U	µg/L	37	11	<0.02	NA	NA	0.04	0.27	0.49	1.13	3.03	KM
V	µg/L	37	5	<0.2	NA	0.2	0.4	1	2.6	4.1	35.7	KM
W	µg/L	37	33	<0.02							0.17	ROS
Y	µg/L	37	0	0.02	0.04	0.07	0.18	0.37	0.88	8.72	15.2	KM
Yb	µg/L	37	14	<0.01	NA	NA	0.01	0.03	0.09	0.7	0.8	KM
Zn	mg/L	37	0	0.004	0.0085	0.0112	0.016	0.020	0.032	0.039	0.106	KM
Zr	µg/L	37	29	<0.02	0.0001	0.0004	0.0022	0.011	0.04	0.102	0.34	ROS

[1] Statistical method (for more details see Section 4.1.1). Where >80% of samples were non-detects, ranges only are quoted.

KM: Kaplan-Meier

ROS: Regression on Order Statistics

NA: not available

5.2 EXCEEDANCES ABOVE DRINKING WATER STANDARDS

The Baseline Scotland survey is not intended to provide an assessment of drinking water quality in the study area. Many of the samples collected are not used for drinking waters; where they are, the samples collected were usually not collected from drinking water taps. The analyses are therefore not necessarily representative of the quality of water used for drinking. However, a significant proportion of the sample sources are private supplies which are at least in part used for drinking water supply. The Baseline Scotland samples were collected from raw water as close to the wellhead as possible. Water supplied from these sources to normal drinking water supply points (usually kitchen taps) may subsequently undergo some form of treatment or storage (e.g. aeration, chlorination, UV filtration or settling) which could change the chemistry of the raw water sampled here. The Baseline Scotland data can therefore provide an overall indication of drinking water quality, but are no substitute for specific water supply testing.

The results indicate that few of the inorganic parameters tested are present at concentrations in excess of national drinking water quality limits. Concentrations of B, Cd, Cr, Cu, Hg, NH_4, NO_2, Pb, Sb, Se and SO_4 were all well below the specified drinking water quality limits. The maximum observed Pb concentration was 3.7 µg/L – significantly below even the new, lower 2013 limit of 10 µg/L. SEC values were also within prescribed limits. Although no UK drinking water limits exist for Mo or U, observed concentrations in the Baseline samples were below the respective WHO guideline values for these elements, with observed maxima of 5 µg/L and 3 µg/L respectively.

Exceedances were found for NO_3, Fe, Mn, Al and As. Twelve samples (32%) had NO_3-N concentrations greater than 11.3 mg/L, which is the maximum limit for drinking water. This distribution reflects the oxic nature of most of the groundwaters and the likely impact of agricultural and domestic pollutants. Three samples (8%) exceeded the drinking water limit for Fe, and six samples (16%) exceeded the limit for Mn. At least one sample was clearly reducing with respect to Fe and Mn, which increases the probability of high Fe and Mn concentrations occurring in the groundwaters. Other factors which can increase the incidence of high Fe and Mn in groundwater are acidic pH and, in some cases, the likely presence of colloidal particles (< 0.45µm). Concentrations of Fe and Mn may not be representative of water quality from drinking water taps, because of the likely mitigating effects of aeration and settling subsequent to the point of sampling for Baseline Scotland.

Two samples (5.4%) had Al concentrations in excess of the drinking water limit. As with Fe and Mn, Al concentrations in groundwater are related to acidic pH and/or the presence of colloids. Colloids are likely to be especially significant in samples from springs or shallow wells. The sample with the highest Al concentration (748 µg/L) had a relatively low pH of 5.9.

One sample (2.7%) had a concentration of As of 26.4 µg/L, which is in excess of the national drinking water limit of 10 µg/L.

The most frequent contravention of Scottish drinking water limits was for pH. In total, 23 samples (62%) had pH values that were less than the minimum prescribed value of 6.5. No exceedances of the maximum (pH 9) were observed.

5.3 NITRATE AND PHOSPHORUS

The overall median nitrate concentration in the sampled groundwaters from Aberdeenshire is 7.15 mg/L NO_3-N. Median concentrations in three of the aquifer groups (the Argyll and Southern Highland groups and the igneous aquifers) are also high, between 6.01 and 10.24 mg/L NO_3-N, but are low in the Appin Group (< 1 mg/L NO_3-N). Concentrations are often well above that which would be expected from local recharge (< 2 mg/L NO_3-N). Nitrate concentrations in groundwater are strongly related to land use. Using the same methodology as in previous Baseline surveys (e.g. MacDonald et al. 2008) and as followed by MacDonald et al. (2005) to characterise sample sites into different land use classes, groundwater beneath agricultural land is shown to have higher nitrate concentrations than that beneath non-agricultural land (Figure 20). The highest median groundwater nitrate concentration in Aberdeenshire is from groundwater in areas of improved pasture grassland used for rearing dairy cattle, pigs and/or poultry, as has been shown is the case for other parts of Scotland (MacDonald et al. 2005).

All of the north and east of Aberdeenshire lies within a nitrate vulnerable zone (NVZ). Only the higher ground in the west and southwest is excluded. All of the highest groundwater nitrate concentrations were found within the NVZ (Figure 46). Only two samples outwith the

NVZ had nitrate concentrations of greater than 2.4 mg/L NO_3-N, and the highest of these (5.79 mg/L NO_3-N) is only 1 km outside the NVZ boundary.

There appears to be some relationship between nitrate concentrations and areas of deep weathering. Most of the samples with the highest nitrate concentrations are within known areas of deep weathering (Figure 46). However, this may be largely or wholly because most of the samples were collected in these areas, which in turn may be related to the increased aquifer permeability and productivity caused by deep weathering, and a corresponding increase in the number of groundwater abstractions.

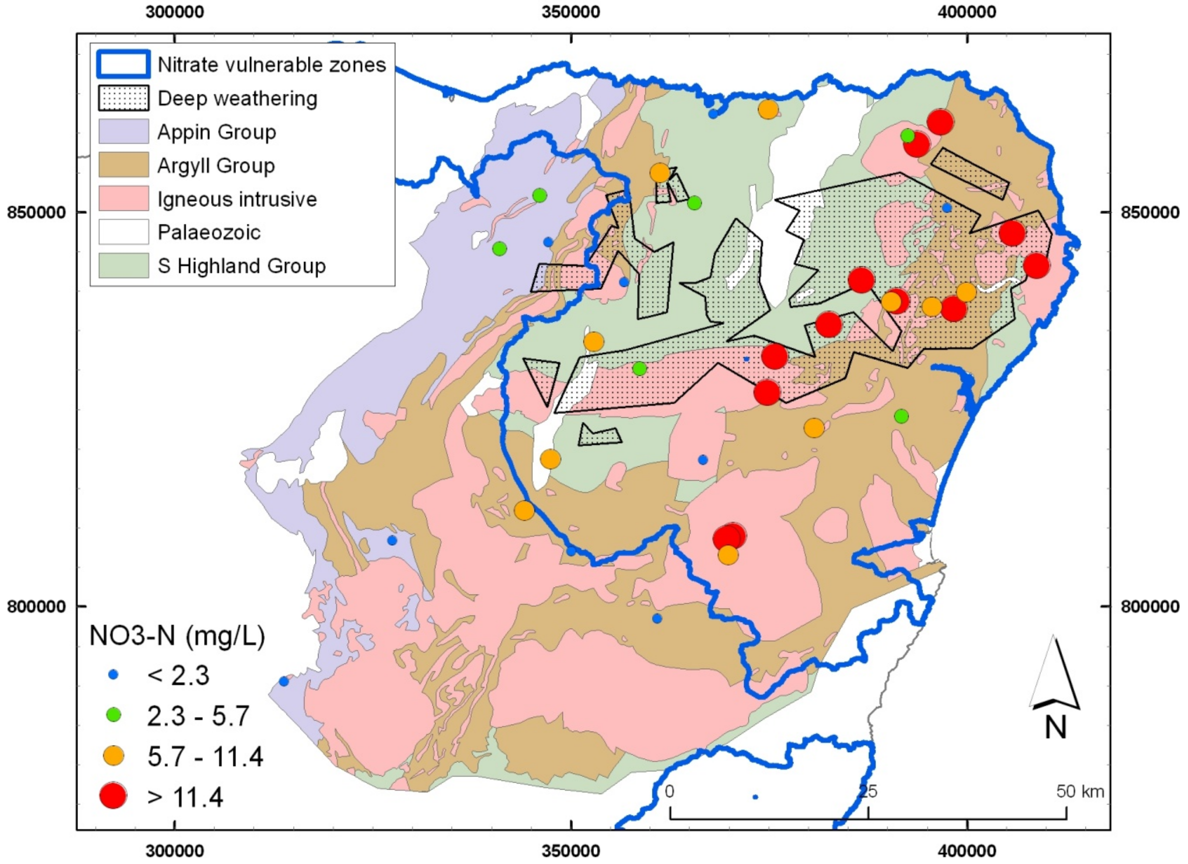
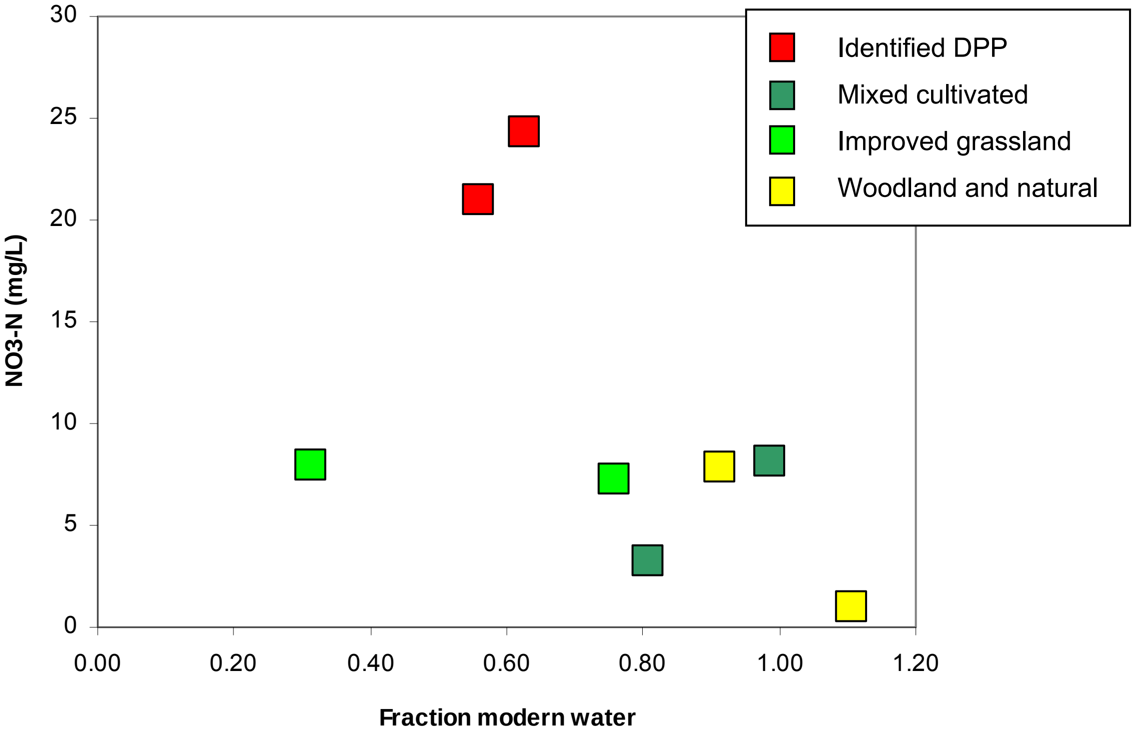


Figure 46 Nitrate concentrations, areas of deep weathering and NVZ boundaries in Aberdeenshire



n = 37

Figure 47 Nitrate concentrations plotted against fraction of modern water, based on CFC-12 concentrations. Identified DPP refers to improved grassland positivity identified as being used for dairy, pigs and/or poultry

Phosphorus in groundwater can be an important influence on surface water eutrophication by providing baseflow to streams and rivers. SEPA have set limits of 8 µg P/L for oligotrophic surface waters, 25 µg P/L for mesotrophic waters and 80 µg P/L for eutrophic surface waters, based on annual geometric mean concentrations. The distribution of phosphorus concentrations in the Aberdeenshire groundwaters gave an overall median concentration of 40 µg P/L. Maximum observed concentrations for groundwaters from the individual aquifers were variable, from 47 µg P/L in the Appin Group, to 80 µg P/L in the Argyll and Southern Highland groups, to 138 µg P/L in igneous aquifers. Median P concentrations in groundwater were between 29 and 41 µg P/L for three of the aquifers, and 53 µg P/L for the Southern Highland Group. This is in the mesotrophic range for surface waters. Concentrations are often much higher than expected from local rainfall inputs (< 30 µg P/L).

There is no clear relationship between P concentration and land use (Figure 27), although there is a slightly higher proportion of relatively low P concentrations from areas of woodland and natural land use.

5.4 GROUNDWATER FLOW IN ABERDEENSHIRE

The hydrochemistry data and information on groundwater residence times help give an insight into groundwater flow in the aquifers of Aberdeenshire. The most likely interpretation of the groundwater flow system is that groundwater flow occurs both through fractures and, where weathering is most developed, through the more permeable weathered zone. The groundwaters are generally well mixed throughout the sampled aquifer depths; i.e., at least within the top 50 m or so of the aquifers. This is supported by the lack of correlation of nitrate with groundwater source depth across the region, and by the evidence from CFC and SF_6 concentrations, which in most cases indicate piston flow, rather than mixing models.

Where CFC and SF_6 were measured, all the samples recorded at least some proportion of water less than 50 years old, with most being largely or wholly younger than 50 years. However, groundwater in at least the Argyll and Southern Highlands groups and in igneous aquifers can be resident for several decades, and in at least some cases longer than 50 years. The only residence time sample taken from the Appin Group appears to be a young water of less than 10 years, but it is likely that overall this aquifer shows a similar groundwater residence pattern to the others, with older water mixed with younger water in some areas.

6 Conclusions

The groundwater chemistry of bedrock aquifers in Aberdeenshire has been investigated using new chemistry analyses, generated during the Baseline Scotland project, combined with existing analyses from earlier projects. The chemistry of groundwater from four aquifer groups has been examined: three divisions of metamorphic aquifers of Dalradian age, the Appin, Argyll and Southern Highland groups, and a single group incorporating all the intrusive igneous rocks – largely granitic – across the region.

A total of 37 groundwater sample analyses were interpreted for the purposes of this study. Of these, 23 were collected in November 2006 specifically for the Baseline Scotland project. These were augmented with a further 14 samples collected during separate BGS projects since 2004. The sites were chosen to be representative of groundwater in the area, and sources that were very poorly constructed were avoided.

An estimate of the baseline groundwater chemistry conditions in Aberdeenshire aquifers has been presented, based on a statistical summary of the chemical data. This represents data between the 10th and 90th percentiles, with the exception of NO_3-N and P, where the influence of anthropogenic activity is likely to have distorted baseline conditions throughout much of the study area.

This statistical approach to estimating baseline was complemented by selecting ten analyses of groundwater samples collected from high quality groundwater sources, which are unlikely to have been impacted by any agricultural contamination, and which represent the general the groundwater conditions in the four aquifer groups in Aberdeenshire.

A summary of the conclusions arising from this study follows.

1. Groundwater flow in Aberdeenshire is likely to be largely through fractures, except in areas of enhanced, deep weathering (Figures 7 and 46), where intergranular permeability is likely to have been enhanced and intergranular groundwater flow may dominate. Groundwater is well mixed in the top 50 metres or so. There is no evidence of palaeowater in the area, and all samples recorded some proportion of water less than 50 years old. However, groundwater can be resident for several decades, even in the fractured, low permeability aquifers.
2. Groundwaters are generally similar across the four different aquifer types. The main differences are related to bicarbonate.
3. Most of the groundwater pH values are slightly acidic, between approximately 5.5 and 7.2 (10th – 90th percentile range), with a median of 6.2. Groundwaters from the Appin Group tend to have slightly higher pH (median pH 6.7) than those from the other aquifer groups (median pH values 6.2 – 6.3).
4. Most groundwaters have relatively low bicarbonate concentrations, with a range from 11 to 127 mg/L (10th to 90th percentiles), and a median of 34 mg/L. Similar patterns to pH are observed between the aquifer groups, with HCO_3 generally higher (median 80 mg/L) in Appin Group groundwaters, than in the others (medians 19 to 34 mg/L). Absolute Cl concentrations are relatively low compared to many other groundwaters, but because of the relatively low mineralisation of the Aberdeenshire groundwaters, Cl can constitute a relatively large proportion of the total dissolved anions, particularly in the Argyll and Southern Highland groups and in the igneous aquifers. The most significant source of Cl is likely to be maritime rainfall. SO_4 concentrations are generally low.

5. Concentrations of the major cations reflect a combination of rainfall input, mineral weathering, and anthropogenic inputs derived from the use of fertilisers and liming, or from other sources of pollution. Most notable is a relative enrichment in bicarbonate and calcium, and more generally alkaline conditions, in groundwaters from the Appin Group compared to the other aquifer groups. All the groundwaters are undersaturated with respect to calcite, reflecting the general lack of carbonate minerals in the bedrock. The few samples close to saturation were derived from the Appin and Argyll Groups, which both contain calcareous rock bands.
6. All of the groundwaters in the study area are oxic, with dissolved oxygen concentrations generally in the range 3.9–9.6 mg/L and redox potential (Eh) generally greater than 300 mV. This reflects the unconfined nature of the aquifers and the generally relatively rapid groundwater flow.
7. The overall median nitrate concentration in groundwaters across Aberdeenshire is 7.15 mg/L (as N). Concentrations are related to land use, with groundwaters beneath agricultural land showing higher concentrations than beneath non-agricultural land. The land use class showing the highest median NO_3 concentration (13.6 mg/L NO_3-N, compared to less than 7.6 mg/L NO_3-N for other land use classes) was land used for rearing dairy, pigs and/or poultry, as has been found in other parts of Scotland (MacDonald et al. 2008, MacDonald et al. 2005).
8. All of the highest groundwater nitrate concentrations were found within the Aberdeenshire nitrate vulnerable zone (NVZ). Only two samples outwith the NVZ had nitrate concentrations of greater than 2.4 mg/L NO_3-N, and the highest of these (5.79 mg/L NO_3-N) is 1 km outside the NVZ boundary.
9. Phosphorus in groundwater can be an important influence on surface water eutrophication if present in baseflow to streams and rivers. Concentrations in Aberdeenshire generally range from 20 to 80 mg/L-P. Although a slightly higher proportion of relatively low P concentrations occur in samples from areas of woodland and natural land use than from agricultural land, there isn't a strong relationship between P and land use, illustrating the complexity of P geochemistry, and the important role that soil geochemistry plays in the mobilisation of P into groundwater.

References

Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

BALL D F, ABESSER C AND GRIFFITHS K. 2006. Selected spring sources in Scotland. British Geological Survey Commissioned Report CR/06/005N.

BOULTON G S, PEACOCK J D AND SUTHERLAND D G. 2002. Quaternary. In *The Geology of Scotland*. TREWIN N H (editor). The Geological Society, London, 409-430.

BUSENBERG E, PLUMMER LN. 2000. Dating young groundwater with sulfur hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. Water Resources Research 36, 3011–3030.

DARLING W G AND GOODDY D C. 2007. Assessing the applicability of global CFC and SF_6 input functions to groundwater dating in the UK. Science of the Total Environment 387, 353–362.

DARLING W G, BATH A H AND TALBOT J C. 2003. The O & H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater. Hydrology & Earth System Sciences 7, 183–195.

HAMBREY M J, FAIRCHILD I J, GLOVER B W, STEWART A D, TREAGUS J E AND WINCHESTER J A. 1991. The Late Precambrian Geology of the Scottish Highlands and Islands. *Geologists' Association Guide 44.* The Geologists' Association, London.

HELSEL D R. 2005. Nondetects and Data Analysis: Statistics for censored environmental data. *John Wiley and Sons*, USA, NJ.

KNOX R W O'B. 2002. Tertiary sedimentation. In *The Geology of Scotland*. TREWIN N H (editor). The Geological Society, London, 361-370.

LEE L AND HELSEL D R. 2005. Baseline models of trace elements in major aquifers of the United States. Applied Geochemistry **20**, 1560-1570.

MACDONALD A M , BALL D F AND Ó DOCHARTAIGH B É. 2004. A GIS of aquifer productivity in Scotland: explanatory notes. British Geological Survey Commissioned Report CR/04/047N.

MACDONALD A M, GRIFFITHS K J, Ó DOCHARTAIGH B É, LILLY A AND CHILTON P J. 2005. Scotland's groundwater monitoring network: its effectiveness for monitoring nitrate. British Geological Survey Commissioned Report CR/05/205N.

MACDONALD A M, Ó DOCHARTAIGH B É,KINNEBURGH D G AND DARLING W G. 2008. Baseline Scotland: groundwater chemistry of southern Scotland. British Geological Survey Open Report OR/08/62.

MERRITT J W, AUTON C A, CONNELL E R, HALL A M AND PEACOCK J D. 2003. Cainozoic geology and landscape evolution of north-east Scotland. *Memoir of the British Geological Survey*, Sheets 66E, 67, 76E, 77, 86E, 87W, 87E, 95, 96W, 96E and 97 (Scotland).

NELSON B J, WOOD S A, and OSIENSKY J L. 2004. Rare earth element geochemistry of groundwater in the Palouse Basin, northern Idaho-eastern Washington. *Geochemistry: Exploration, Environment, Analysis*, Vol. 4, 227-241.

Ó DOCHARTAIGH B É, SMEDLEY P L, MACDONALD A M AND DARLING W G. 2006. Baseline Scotland: the Lower Devonian aquifer of Strathmore. British Geological Survey Commissioned Report CR/06/250N.

R DEVELOPMENT CORE TEAM. 2007. R: A language and environment for statistical computing. Version 2.5. *R Foundation for Statistical Computing, Vienna, Austria*. URL http://www.R-project.org

SHOLKOVITZ E R. 1988. Rare earth elements in the sediments of the North Atlantic Ocean, Amazon delta, and East China Sea: reinterpretation of terrigenous input patterns to the oceans. *American Journal of Science*, Vol. 288, 236-281.

SMEDLEY P L. 1991. The geochemistry of rare-earth elements in groundwater from the Carnmenellis Area, Southwest England. *Geochimica et Cosmochimica Acta*, Vol. 55, 2767-2779.

WEILL, D F, and DRAKE, M J. 1973. Europium Anomaly in Plagioclase Feldspar: Experimental Results and Semiquantitative Model. *Science*, Vol. 180, 1059-1060.

STEPHENSON D AND GOULD D. 1994. The Grampian Highlands. British Geological Survey. Fourth Edition.

STRACHAN R A, SMITH M, HARRIS A L AND FETTES D J. 2002. The Northern Highlands and Grampian terranes. In *The Geology of Scotland*. TREWIN N H (editor). The Geological Society, London, 81-148.

TREWIN N H AND THIRLWALL M F. 2002. Old Red Sandstone. In *The Geology of Scotland*. TREWIN N H (editor). The Geological Society, London, 213-249.

WHITEHEAD D C. 1985. The distribution and transformations of iodine in the environment. *Environment International*, Vol. 10, 321-339.

Appendix 1 Description of sampling sites

ID	Lab Sample ID	Project	Aquifer	Source type	Depth (m)	Land use
1	S04-01103	Springs		Spring	0	Improved grassland
2	S04-01104	Springs		Spring	0	Improved grassland
3	S04-01105	Springs		Spring	0	Mixed cultivated
4	S04-01106	Springs		Spring	0	Mixed cultivated
5	S04-01107	Springs		Spring	0	Improved grassland
6	S04-01108	Springs		Spring	0	Improved grassland
7	S04-01109	Springs		Spring	0	Mixed cultivated
8	**S04-01111**	**Springs**		**Spring**	**0**	**Woodland and natural**
9	S04-01112	Springs		Spring	0	Woodland and natural
10	S05-00291	SGMN [1]		Spring	0	Woodland and natural
11	S05-00293	SGMN		Borehole	unknown	Identified DPP[2]
12	**S05-00294**	**SGMN**		**Borehole**	**unknown**	**Woodland and natural**
13	S05-00295	SGMN		Spring	0	Improved grassland
14	S05-00296	SGMN		Spring	0	Woodland and grassland
15	S06-01080	Baseline		Spring	0	Mixed cultivated
16	**S06-01081**	**Baseline**		**Borehole**	**30-100 m**	**Woodland and natural**
17	S06-01082	Baseline		Borehole	30-100 m	Improved grassland
18	S06-01083	Baseline		Borehole	30-100 m	Identified DPP
19	**S06-01084**	**Baseline**		**Borehole**	**30-100 m**	**Woodland and natural**
20	S06-01085	Baseline		Spring	0	Mixed cultivated
21	**S06-01086**	**Baseline**		**Borehole**	**30-100 m**	**Improved grassland**
22	**S06-01088**	**Baseline**		**Borehole**	**30-100 m**	**Mixed cultivated**
23	S06-01091	Baseline		Borehole	30-100 m	Improved grassland
24	S06-01094	Baseline		Shallow well	30-100 m	Improved grassland
25	S06-01095	Baseline		Borehole	30-100 m	Identified DPP
26	**S06-01096**	**Baseline**		**Borehole**	**30-100 m**	**Mixed cultivated**
27	**S06-01097**	**Baseline**		**Borehole**	**30-100 m**	**Mixed cultivated**
28	S06-01098	Baseline		Borehole	30-100 m	Identified DPP
29	S06-01099	Baseline		Shallow well	5-30 m	Identified DPP
30	S06-01100	Baseline		Shallow well	<5 m	Identified DPP
31	**S06-01101**	**Baseline**		**Spring**	**0**	**Woodland and natural**
32	S06-01102	Baseline		Shallow well	<5 m	Woodland and natural
33	S06-01103	Baseline		Borehole	30-100 m	Identified DPP
34	S06-01104	Baseline		Borehole	5-30 m	Identified DPP
35	S06-01105	Baseline		Shallow well	5-30 m	Identified DPP
36	S06-01106	Baseline		Borehole	5-30 m	Mixed cultivated
37	**S06-01107**	**Baseline**		**Borehole**	**30-100 m**	**Improved grassland**

[1] SGMN – Scottish Groundwater Monitoring Network [2] DPP – Dairy, Pigs and Poultry

The ten selected baseline samples are highlighted in bold.
The ID numbers in the left hand column are used to refer to the samples throughout the report. For sample locations see Figure 9.

Summary statistics for chemical elements in groundwaters from individual aquifers in Aberdeenshire

Table A2.1 Summary statistics for chemical elements in groundwaters from the Appin Group aquifer in Aberdeenshire

Param	units	no.	no. cens'd	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	5	0	7.4	7.4	7.4	7.9	8.3	NA	NA	9.3	KM
pH		5	0	6.17	6.17	6.66	6.71	7.27	NA	NA	7.84	KM
Eh	mV	4	0	265	265	265	324	NA	NA	NA	418	KM
DO	mg/L	5	0	5.53	5.53	5.63	6.04	7.84	NA	NA	8.8	KM
SEC	µS/cm	5	0	60	60	220	274	349	NA	NA	492	KM
Ca	mg/L	5	0	14.3	14.3	24.9	25.2	52.6	NA	NA	69.7	KM
Mg	mg/L	5	0	2.46	2.46	3.31	4.41	5.01	NA	NA	11.9	KM
Na	mg/L	5	0	4.24	4.24	7.37	10.1	12.8	NA	NA	14.9	KM
K	mg/L	5	0	0.91	0.91	1.06	1.22	1.83	NA	NA	3.99	KM
Cl	mg/L	5	0	4.29	4.29	14.4	21.5	23.3	NA	NA	39.4	KM
SO_4	mg/L	5	0	2.78	2.78	8.82	11.5	12.7	NA	NA	33.8	KM
HCO_3	mg/L	5	0	47.8	47.8	48	80	125	NA	NA	229	KM
NO_3-N	mg/L	5	0	0.052	0.052	0.382	0.947	2.36	NA	NA	3.85	KM
NO_2-N	mg/L	3	0	0.001	0.001	0.001	0.002	NA	NA	NA	0.009	KM
NH_4-N	mg/L	3	0	0.016	0.016	0.016	0.023	NA	NA	NA	0.169	KM
P	µg/L	5	0	22	22	25	29	37	NA	NA	47	KM
F	mg/L	5	1	<0.02	NA	0.06	0.086	0.089	NA	NA	0.092	KM
Br	µg/L	5	0	50	50	54	58	368	NA	NA	375	KM
I	µg/L	4	2	<2	0.916	1.14	2.03	3.25	4.06	4.33	4.6	ROS
Si	mg/L	5	0	3.71	3.71	6.14	6.16	6.19	NA	NA	12.6	KM
Al	µg/L	5	0	6	6	6	8	11	NA	NA	748	KM
As	µg/L	5	4	<0.5	0.8	0.8	0.8	0.8	0.8	0.8	0.8	ROS
B	µg/L	5	3	<20	5.3	5.75	6.5	7.25	7.7	7.85	8	ROS
Ba	mg/L	5	0	0.013	0.013	0.019	0.025	0.034	NA	NA	0.045	KM
Cd	µg/L	5	3	<0.05	0.056	0.061	0.067	0.08	0.086	0.088	0.09	ROS
Ce	µg/L	5	0	0.01	0.01	0.02	NA	NA	NA	NA	0.03	KM
Co	µg/L	5	2	<0.02	NA	NA	0.03	0.04	NA	NA	0.11	KM
Cr	µg/L	5	1	<0.5	NA	0.5	0.5	0.6	NA	NA	1.2	KM
Cs	µg/L	5	1	<0.01	NA	0.01	0.03	0.05	NA	NA	0.8	KM
Cu	µg/L	5	1	<0.1	NA	0.6	1.0	2.5	NA	NA	18.5	KM
Dy	µg/L	5	1	<0.01	NA	0.01	0.01	0.02	NA	NA	0.05	KM
Er	µg/L	5	1	<0.01	NA	0.01	0.01	0.01	NA	NA	0.03	KM
Eu	µg/L	5	3	<0.01	0.0003	0.0006	0.002	0.012	0.022	0.026	0.03	ROS
Fe	µg/L	5	1	<10	NA	16	85	187	NA	NA	271	KM
Ga	µg/L	5	4	<0.05	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS
Gd	µg/L	5	0	0.01	0.01	0.01	0.01	0.01	NA	NA	0.04	KM
Ho	µg/L	5	4	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
La	µg/L	5	0	0.02	0.02	0.04	0.05	0.12	NA	NA	0.14	KM
Li	µg/L	5	0	0.5	0.5	1.2	2	2	NA	NA	4.1	KM
Mn	µg/L	5	0	0.53	0.53	0.76	3.33	3.59	NA	NA	4.87	KM
Mo	µg/L	5	2	<0.1	NA	NA	0.1	0.2	NA	NA	0.5	KM
Nd	µg/L	5	0	0.02	0.02	0.03	0.06	0.13	NA	NA	0.17	KM
Ni	µg/L	5	2	<0.2	NA	NA	0.2	0.9	NA	NA	1.2	KM
Pb	µg/L	5	2	<0.1	NA	NA	0.1	0.2	NA	NA	0.5	KM
Pr	µg/L	5	1	<0.01	NA	0.01	0.01	0.03	NA	NA	0.04	KM
Rb	µg/L	5	0	0.43	0.43	1.83	2.25	2.33	NA	NA	10.8	KM

Param	units	no.	no. cens'd	min	10%	25%	50%	75%	90%	95%	max	method[1]
Rh	µg/L	5	4	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Sb	µg/L	5	3	<0.05	0.023	0.030	0.048	0.11	0.158	0.174	0.19	ROS
Sc	µg/L	5	2	<1	NA	NA	1	1	NA	NA	2	KM
Se	µg/L	5	3	<0.5	1.8	1.89	2.02	2.3	2.42	2.46	2.5	ROS
Sm	µg/L	5	3	<0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	ROS
Sn	µg/L	5	0	0.13	0.13	0.13	1.05	1.29	NA	NA	165	KM
Sr	mg/L	5	0	0.075	0.075	0.082	0.089	0.152	NA	NA	0.287	KM
Tl	µg/L	5	3	<0.01	0.001	0.002	0.003	0.010	0.016	0.018	0.02	ROS
Tm	µg/L	5	4	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
U	µg/L	5	0	0.05	0.05	0.09	0.13	0.14	NA	NA	0.28	KM
V	µg/L	5	2	<0.2	NA	NA	0.3	0.4	NA	NA	0.5	KM
Y	µg/L	5	0	0.04	0.04	0.13	0.18	0.19	NA	NA	0.37	KM
Yb	µg/L	5	2	<0.01	NA	NA	0.01	NA	NA	NA	0.02	KM
Zn	mg/L	5	0	0.006	0.006	0.010	0.012	0.018	NA	NA	0.025	KM
Zr	µg/L	5	4	<0.02	0.04	0.04	0.04	0.04	0.04	0.04	0.04	ROS

[1] Statistical method (for more details see Section 4.1.1):

KM – Kaplan-Meier

ROS – Regression on Order Statistics

Table A2.2 Summary statistics for chemical elements in groundwaters from the Argyll Group aquifer in Aberdeenshire

Param	units	no.	no. cens'd	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	11	0	7.6	8.4	8.4	9.4	10.6	11.4	NA	11.7	KM
pH		11	0	5.44	5.67	5.7	6.22	6.65	6.82	NA	7.16	KM
Eh	mV	11	0	283	297	314	401	459	468	NA	532	KM
DO	mg/L	11	0	3.89	4.09	5.09	6.1	9.56	9.78	NA	10.2	KM
SEC	µS/cm	11	0	69	93.1	149	238	315	434	NA	931	KM
Ca	mg/L	11	0	4.61	6.4	10.6	12.6	43.7	46.7	NA	111	KM
Mg	mg/L	11	0	1.66	2.59	4.17	5.4	11.8	14.3	NA	15.2	KM
Na	mg/L	11	0	9.96	10.3	11	19.9	22.5	22.7	NA	40.3	KM
K	mg/L	11	0	1.02	1.07	1.08	1.43	2.09	3	NA	6.27	KM
Cl	mg/L	11	0	11.2	15.4	17.9	26.9	37.4	42.7	NA	79.6	KM
SO_4	mg/L	11	0	4.9	8.03	10.9	11.7	22.4	32.2	NA	43.1	KM
HCO_3	mg/L	11	0	11.2	15.7	17.1	34	84	127	NA	227	KM
NO_3-N	mg/L	11	0	0.594	1.13	1.42	6.01	10.2	12.9	NA	21	KM
NO_2-N	mg/L	6	1	<0.0003	NA	0.0004	0.001	0.002	NA	NA	0.0019	KM
P	µg/L	11	0	22	30	31	41	52	57	NA	80	KM
DOC	mg/L	5	0	1.23	1.23	1.34	1.49	2.88	NA	NA	4.23	KM
F	mg/L	11	3	<0.02	NA	NA	0.052	0.116	0.12	NA	0.177	KM
Br	µg/L	11	0	39	55	77	110	445	476	NA	562	KM
I	µg/L	9	2	<2	NA	2.5	3.7	4	NA	NA	9.8	KM
Si	mg/L	11	0	5.81	7.21	7.29	9.44	12	NA	NA	13.6	KM
Al	µg/L	11	0	4	5	6	9	10	16	NA	18	KM
As	µg/L	11	7	<0.5	0.024	0.054	0.147	0.6	1	1.8	2.6	ROS
Au	µg/L	11	10	<0.05	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS
B	µg/L	11	6	<20	6.49	9.0	11.5	15	16.3	19.6	23	ROS
Ba	mg/L	11	0	0.010	0.011	0.014	0.030	0.109	0.160	NA	0.252	KM
Be	µg/L	11	8	<0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.06	ROS
Cd	µg/L	11	4	<0.05	NA	NA	0.08	0.1	0.12	NA	0.28	KM
Ce	µg/L	11	1	<0.01	0.01	0.01	0.02	0.05	0.08	NA	0.2	KM
Co	µg/L	11	3	<0.02	NA	NA	0.03	0.22	2.17	NA	2.23	KM
Cr	µg/L	11	6	<0.5	0.024	0.057	0.166	0.6	0.8	3.95	7.1	ROS
Cs	µg/L	11	6	<0.01	0.003	0.004	0.008	0.02	0.03	0.035	0.04	ROS
Cu	µg/L	11	0	0.8	1.0	1.3	3	27.7	28.9	NA	251	KM
Dy	µg/L	11	1	<0.01	0.01	0.01	0.02	0.04	0.04	NA	0.05	KM
Er	µg/L	11	2	<0.01	NA	0.01	0.01	0.02	0.03	NA	0.04	KM
Eu	µg/L	11	5	<0.01	NA	NA	0.01	0.02	0.02	NA	0.14	KM
Fe	µg/L	11	3	<10	NA	NA	38	64	182	NA	444	KM
Gd	µg/L	11	2	<0.01	NA	0.01	0.02	NA	NA	NA	0.04	KM
Hg	µg/L	11	10	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	ROS
Ho	µg/L	11	9	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
La	µg/L	11	2	<0.01	NA	0.01	0.03	0.08	0.12	NA	0.28	KM
Li	µg/L	11	0	0.6	0.7	0.8	3	7.5	9	NA	11.6	KM
Lu	µg/L	11	9	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Mn	µg/L	11	0	0.87	1.4	1.4	1.66	2.61	636	NA	989	KM
Mo	µg/L	11	4	<0.1	NA	NA	0.1	0.2	0.5	NA	0.6	KM
Nd	µg/L	11	0	0.01	0.01	0.02	0.05	0.1	0.17	NA	0.28	KM
Ni	µg/L	11	4	<0.2	NA	NA	1.6	7.5	9.6	NA	15.5	KM
Pb	µg/L	11	3	<0.1	NA	NA	0.2	0.3	1.2	NA	3.7	KM

Param	**units**	**no.**	**no. cens'd**	**min**	**10%**	**25%**	**50%**	**75%**	**90%**	**95%**	**max**	**method[1]**
Pr	µg/L	11	3	<0.01	NA	NA	0.01	0.03	0.04	NA	0.07	KM
Rb	µg/L	11	0	0.1	0.17	0.22	0.27	0.78	0.93	NA	2.49	KM
Re	µg/L	11	10	<0.01	0.06	0.06	0.06	0.06	0.06	0.06	0.06	ROS
Rh	µg/L	11	9	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Sb	µg/L	11	9	<0.05	2E-07	3E-06	7E-05	0.0028	0.14	0.855	1.57	ROS
Sc	µg/L	11	6	<1	0.278	0.401	0.652	1	2	2	2	ROS
Se	µg/L	11	5	<0.5	NA	NA	0.6	3.3	3.4	NA	3.5	KM
Sm	µg/L	11	6	<0.02	0.006	0.008	0.013	0.025	0.03	0.04	0.05	ROS
Sn	µg/L	11	0	0.11	0.12	0.15	0.74	0.84	0.95	NA	1.06	KM
Sr	mg/L	11	0	0.048	0.048	0.059	0.080	0.192	0.243	NA	0.397	KM
Tb	µg/L	11	9	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Tl	µg/L	11	7	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Tm	µg/L	11	9	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
U	µg/L	11	5	<0.02	NA	NA	0.02	0.27	1.13	NA	3.03	KM
V	µg/L	11	1	<0.2	0.2	0.3	0.4	1	1.2	NA	4.1	KM
W	µg/L	11	9	<0.02	6E-06	3E-05	0.0002	0.002	0.02	0.05	0.08	ROS
Y	µg/L	11	0	0.04	0.04	0.07	0.15	0.23	0.30	NA	0.42	KM
Yb	µg/L	11	6	<0.01	0.004	0.007	0.01	0.03	0.03	0.035	0.04	ROS
Zn	mg/L	11	0	0.004	0.010	0.012	0.014	0.020	0.022	NA	0.039	KM
Zr	µg/L	11	9	<0.02	0.011	0.015	0.020	0.027	0.04	0.045	0.05	ROS

[1] Statistical method (for more details see Section 4.1.1):

KM – Kaplan-Meier

ROS – Regression on Order Statistics

Table A2.3 Summary statistics for chemical elements in groundwaters from the Southern Highland Group aquifer in Aberdeenshire

Param	**units**	**no.**	**no. cens'd**	**min**	**10%**	**25%**	**50%**	**75%**	**90%**	**95%**	**max**	**method**[1]
T	°C	7	0	7.6	7.6	8.2	8.6	9	NA	NA	9.8	KM
pH		7	0	5.39	5.39	5.88	6.29	6.6	NA	NA	6.96	KM
Eh	mV	7	0	306	306	334	355	393	NA	NA	468	KM
DO	mg/L	7	0	3.4	3.4	4.09	4.58	7.6	NA	NA	8.43	KM
SEC	µS/cm	7	0	200	200	226	292	352	NA	NA	463	KM
Ca	mg/L	7	0	6.89	6.89	11.8	14.3	17.5	NA	NA	18.4	KM
Mg	mg/L	7	0	3.67	3.67	4.02	4.98	8.17	NA	NA	10.2	KM
Na	mg/L	7	0	10.1	10.1	13.7	19.7	23.4	NA	NA	27	KM
K	mg/L	7	0	1.13	1.13	1.22	1.46	2.35	NA	NA	2.63	KM
Cl	mg/L	7	0	16.7	16.7	16.8	24.8	30.8	NA	NA	34.9	KM
SO_4	mg/L	7	0	5.05	5.05	7.27	10.7	13.4	NA	NA	14.3	KM
HCO_3	mg/L	7	0	5.4	5.4	9.2	19	30	NA	NA	53	KM
NO_3-N	mg/L	7	0	2.26	2.26	3.28	7.28	20.1	NA	NA	21.2	KM
NO_2-N	mg/L	3	0	0.002	0.002	0.002	0.002	NA	NA	NA	0.002	KM
NH_4-N	mg/L	3	1	<0.003	NA	NA	0.016	NA	NA	NA	0.047	KM
P	µg/L	7	0	36	36	40	53	69	NA	NA	80	KM
DOC	mg/L	4	0	0.35	0.35	0.35	1.16	NA	NA	NA	1.73	KM
F	mg/L	7	0	0.021	0.021	0.025	0.051	0.084	NA	NA	0.109	KM
Br	µg/L	7	0	53	53	67	123	421	NA	NA	467	KM
I	µg/L	6	2	<2	NA	NA	3.1	4.5	NA	NA	13.7	KM
Si	mg/L	7	0	4.68	4.68	5.97	8.74	9.17	NA	NA	10.3	KM
Al	µg/L	7	0	4	4	7	10	14	NA	NA	100	KM
B	µg/L	7	3	<20	5	5	6	7	12	12	12	KM
Ba	mg/L	7	0	0.008	0.008	0.031	0.048	0.132	NA	NA	0.206	KM
Be	µg/L	7	5	<0.05	0.034	0.043	0.057	0.084	0.112	0.121	0.13	ROS
Cd	µg/L	7	3	<0.05	NA	NA	0.1	0.19	NA	NA	0.23	KM
Ce	µg/L	7	1	<0.01	NA	0.02	0.06	0.45	NA	NA	1.27	KM
Co	µg/L	7	3	<0.02	NA	NA	0.02	0.22	NA	NA	0.6	KM
Cr	µg/L	7	6	<0.5	0.8	0.8	0.8	0.8	0.8	0.8	0.8	ROS
Cu	µg/L	7	0	1.5	1.5	1.6	1.8	7.4	NA	NA	10.3	KM
Dy	µg/L	7	2	<0.01	NA	NA	0.01	0.06	NA	NA	0.29	KM
Er	µg/L	7	2	<0.01	NA	NA	0.01	0.03	NA	NA	0.21	KM
Eu	µg/L	7	3	<0.01	NA	NA	0.01	NA	NA	NA	0.08	KM
Fe	µg/L	7	4	<10	2.89	4.93	9.95	37.5	62.4	68.7	75	ROS
Gd	µg/L	7	1	<0.01	NA	0.01	0.01	0.04	NA	NA	0.39	KM
Ho	µg/L	7	4	<0.01	0.0002	0.0004	0.002	0.01	0.03	0.045	0.06	ROS
La	µg/L	7	1	<0.01	NA	0.01	0.04	0.16	NA	NA	0.82	KM
Li	µg/L	7	0	0.6	0.6	0.9	1.7	5.5	NA	NA	7	KM
Lu	µg/L	7	6	<0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.03	ROS
Mn	µg/L	7	0	0.58	0.58	1.08	5.46	170	NA	NA	243	KM
Mo	µg/L	7	5	<0.1	0.005	0.009	0.020	0.067	0.14	0.17	0.2	ROS
Nd	µg/L	7	0	0.01	0.01	0.01	0.07	0.22	NA	NA	1.34	KM
Ni	µg/L	7	1	<0.2	NA	0.6	1	3.9	NA	NA	5.7	KM
Pb	µg/L	7	2	<0.1	NA	NA	0.1	0.2	NA	NA	0.7	KM
Pr	µg/L	7	3	<0.01	NA	NA	0.01	0.05	NA	NA	0.25	KM
Rb	µg/L	7	0	0.13	0.13	0.17	0.59	0.98	NA	NA	1.2	KM
Re	µg/L	7	6	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Rh	µg/L	7	6	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Sb	µg/L	7	6	<0.05	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS

Param	**units**	**no.**	**no. cens'd**	**min**	**10%**	**25%**	**50%**	**75%**	**90%**	**95%**	**max**	**method**[1]
Sc	µg/L	7	3	<1	NA	NA	1	1	NA	NA	2	KM
Se	µg/L	7	4	<0.5	0.523	0.702	1.03	2.1	2.82	2.91	3	ROS
Sm	µg/L	7	3	<0.02	NA	NA	0.02	0.06	NA	NA	0.28	KM
Sn	µg/L	7	0	0.13	0.13	0.16	0.73	1.58	NA	NA	2.25	KM
Sr	mg/L	7	0	0.065	0.065	0.081	0.092	0.175	NA	NA	0.255	KM
Tb	µg/L	7	4	<0.01	0.0004	0.0009	0.002	0.010	0.022	0.031	0.04	ROS
Tl	µg/L	7	6	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Tm	µg/L	7	5	<0.01	9E-5	0.0002	0.0008	0.006	0.018	0.024	0.03	ROS
U	µg/L	7	5	<0.02	0.04	0.04	0.04	0.04	0.04	0.04	0.04	ROS
V	µg/L	7	1	<0.2	NA	0.2	0.2	0.3	NA	NA	0.4	KM
Y	µg/L	7	0	0.02	0.02	0.04	0.07	0.38	NA	NA	2.22	KM
Yb	µg/L	7	1	<0.01	NA	0.01	0.01	0.02	NA	NA	0.21	KM
Zn	mg/L	7	0	0.008	0.008	0.008	0.016	0.026	NA	NA	0.032	KM
Zr	µg/L	7	5	<0.02	0.04	0.04	0.04	0.04	0.04	0.04	0.04	ROS

[1] Statistical method (for more details see Section 4.1.1):

KM – Kaplan-Meier

ROS – Regression on Order Statistics

Table A2.4 Summary statistics for chemical elements in groundwaters from igneous aquifers in Aberdeenshire

Param	units	number	no. cens'd	min	10%	25%	50%	75%	90%	95%	max	method[1]
T	°C	13	0	8.4	8.5	8.8	9.8	10.6	10.8	NA	13.7	KM
pH		14	0	5.24	5.47	5.83	6.19	6.78	6.94	NA	7.33	KM
Eh	mV	14	0	131	306	332	349	428	520	NA	662	KM
DO	mg/L	13	0	2.55	3.2	4.8	7.25	8.39	9.14	NA	11.1	KM
SEC	µS/cm	14	0	119	152	177	314	357	448	NA	533	KM
Ca	mg/L	14	0	3.9	7.1	14.2	21.6	31.4	34.5	NA	37	KM
Mg	mg/L	14	0	2.39	3.25	5.21	6.69	10.4	13.4	NA	27.7	KM
Na	mg/L	14	0	10.5	11.5	15.1	17.5	24.8	34.3	NA	34.4	KM
K	mg/L	14	0	0.88	1.02	1.17	2.59	3.78	4.82	NA	13.6	KM
Cl	mg/L	14	0	11.3	20.6	22.6	26.6	42.6	46.8	NA	54.2	KM
SO_4	mg/L	14	0	9.2	9.52	12	13.7	22.1	23.8	NA	25.1	KM
HCO_3	mg/L	14	0	8	11.6	18	34	48	121	NA	240	KM
NO_3-N	mg/L	14	0	0.052	0.274	3.86	8.17	14.5	18	NA	24.3	KM
P	µg/L	14	3	<20	NA	20	29	46	104	NA	138	KM
DOC	mg/L	12	0	0.76	0.86	1.03	1.3	2.13	5.62	NA	7.44	KM
F	mg/L	14	1	<0.02	0.032	0.041	0.078	0.12	0.136	NA	0.17	KM
Br	µg/L	14	0	47	51	66	95	125	171	NA	523	KM
I	µg/L	13	3	<2	NA	2.5	3.9	4.2	5.7	NA	22.7	KM
Si	mg/L	14	0	3.32	4.09	7.05	10.2	11.1	11.7	NA	12.2	KM
Al	µg/L	14	0	5	6	8	12	29	191	NA	214	KM
As	µg/L	14	7	<0.5	0.00797	0.0278	0.306	0.725	1.01	9.95	26.4	ROS
Au	µg/L	14	13	<0.05	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS
B	µg/L	14	2	<20	9	9	11	22	30	NA	42	KM
Ba	mg/L	14	0	0.0031	0.0062	0.0383	0.0664	0.101	0.127	NA	0.582	KM
Be	µg/L	14	9	<0.05	0.0258	0.045	0.091	0.193	0.437	0.496	0.6	ROS
Cd	µg/L	14	8	<0.05	0.0383	0.0463	0.0583	0.0875	0.097	0.104	0.11	ROS
Ce	µg/L	14	1	<0.01	0.01	0.03	0.06	0.49	5.05	NA	6.67	KM
Co	µg/L	14	4	<0.02	NA	NA	0.03	0.09	0.13	NA	0.3	KM
Cr	µg/L	14	11	<0.5	0.0723	0.125	0.251	0.498	1.04	1.38	1.9	ROS
Cs	µg/L	14	7	<0.01	0.00109	0.00211	0.00726	0.01	0.017	0.034	0.06	ROS
Cu	µg/L	14	0	0.9	1	4.4	6	30.9	101	NA	272	KM
Dy	µg/L	14	4	<0.01	NA	NA	0.02	0.12	1.67	NA	2.16	KM
Er	µg/L	14	3	<0.01	NA	0.01	0.03	0.07	0.81	NA	1.16	KM
Eu	µg/L	14	6	<0.01	NA	NA	0.01	0.06	0.12	NA	0.37	KM
Fe	µg/L	14	7	<10	0.040	0.234	7.29	24.8	90.6	3420	9560	ROS
Ga	µg/L	14	13	<0.05	0.14	0.14	0.14	0.14	0.14	0.14	0.14	ROS
Gd	µg/L	14	2	<0.01	NA	0.01	0.02	0.16	1.84	NA	1.96	KM
Ge	µg/L	14	13	<0.05	0.23	0.23	0.23	0.23	0.23	0.23	0.23	ROS
Hf	µg/L	14	13	<0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	ROS
Ho	µg/L	14	6	<0.01	NA	NA	0.01	0.02	0.31	NA	0.44	KM
La	µg/L	14	0	0.01	0.01	0.03	0.04	1.68	4.36	NA	5.09	KM
Li	µg/L	14	0	0.1	0.6	1.5	1.7	5.7	8.1	NA	12.2	KM
Lu	µg/L	14	7	<0.01	0.0003	0.0009	0.007	0.01	0.066	0.094	0.1	ROS
Mn	µg/L	14	0	1.5	1.88	2.87	3.89	23.6	36.8	NA	884	KM
Mo	µg/L	14	8	<0.1	0.0003	0.002	0.017	0.175	2.77	3.96	5.0	ROS
Nb	µg/L	14	12	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS

Param	units	number	no. cens'd	min	10%	25%	50%	75%	90%	95%	max	method[1]
Nd	µg/L	14	0	0.01	0.01	0.03	0.05	0.88	4.52	NA	6.31	KM
Ni	µg/L	14	5	<0.2	NA	NA	0.2	1.4	3	NA	3.3	KM
Pb	µg/L	14	3	<0.1	NA	0.1	0.2	0.5	0.8	NA	1.5	KM
Pr	µg/L	14	5	<0.01	NA	NA	0.01	0.2	0.99	NA	1.4	KM
Rb	µg/L	14	0	0.13	0.14	0.25	0.6	3.77	4.66	NA	8.94	KM
Re	µg/L	14	12	<0.01	7E-7	6E-6	0.0002	0.0009	0.008	0.017	0.03	ROS
Rh	µg/L	14	13	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Sb	µg/L	14	12	<0.05	0.002	0.004	0.010	0.023	0.059	0.088	0.12	ROS
Sc	µg/L	14	2	<1	NA	1	1	NA	NA	NA	2	KM
Se	µg/L	14	9	<0.5	0.034	0.07	0.175	0.6	0.77	1.74	3.5	ROS
Sm	µg/L	14	7	<0.02	0.0005	0.002	0.015	0.147	0.816	1.22	1.54	ROS
Sn	µg/L	14	0	0.16	0.49	0.86	1	1.11	1.15	NA	1.3	KM
Sr	mg/L	14	0	0.034	0.045	0.107	0.122	0.202	0.228	NA	0.262	KM
Tb	µg/L	14	8	<0.01	0.00009	0.00044	0.002	0.020	0.195	0.291	0.33	ROS
Tl	µg/L	14	8	<0.01	0.003	0.004	0.006	0.010	0.017	0.02	0.02	ROS
Tm	µg/L	14	8	<0.01	0.00009	0.0003	0.002	0.010	0.08	0.12	0.14	ROS
U	µg/L	14	1	<0.02	0.02	0.03	0.09	0.35	0.49	NA	1.07	KM
V	µg/L	14	1	<0.2	0.2	0.5	0.9	1.8	3.7	NA	35.7	KM
W	µg/L	14	12	<0.02	1.5E-08	2E-7	6E-6	0.0002	0.014	0.073	0.17	ROS
Y	µg/L	14	0	0.02	0.02	0.06	0.19	0.77	8.72	NA	15.2	KM
Yb	µg/L	14	5	<0.01	NA	NA	0.03	0.08	0.7	NA	0.8	KM
Zn	mg/L	14	0	0.009	0.009	0.011	0.018	0.022	0.033	NA	0.106	KM
Zr	µg/L	14	11	<0.02	6E-6	4E-5	0.0005	0.005	0.223	0.321	0.34	ROS

[1] Statistical method (for more details see Section 4.1.1):

KM – Kaplan-Meier

ROS – Regression on Order Statistics