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Baseline Scotland: groundwater chemistry of the Old Red Sandstone aquifers of the Moray Firth area

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Front cover

Looking south across typical coastal plain landscape, underlain by Old Red Sandstone aquifers, in the Moray Firth area. The higher ground in the background is formed of Precambrian rocks. Land use is typified by arable fields and small towns such as here, as well as livestock (especially pigs and dairy) agriculture.

Bibliographical reference

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Baseline Scotland: groundwater chemistry of the Old Red Sandstone aquifers of the Moray Firth area

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Keyworth, Nottingham British Geological Survey 2010

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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 (MacDonald et al., 2005b). 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

The groundwater chemistry of Old Red Sandstone aquifers in the Moray Firth area has been characterised based on new chemistry analyses generated during the Baseline Scotland project, combined with existing analyses from earlier projects. A total of 39 groundwater sample analyses were interpreted for the purposes of this study. Of these, 17 were collected in 2007 specifically for the Baseline Scotland project. These were augmented with a further 22 samples collected during separate BGS projects since 2001. The sites were chosen to be representative of groundwater in the area, and sources that were poorly constructed were avoided.

A summary of the conclusions arising from this study follows.

1. Groundwater in the Old Red Sandstone aquifers of the Moray Firth is generally moderately mineralised, with a median SEC of 469 µS/cm (interquartile range 341–591 µS/cm). The pH is variable: median pH is slightly alkaline (7.31), but values range from 5.33 to 8.06. The major ion chemistry appears to be dominated by the dissolution of carbonate cements within the aquifer and overlying deposits, and the variable influence of seawater (either directly as saline intrusion or as aerosols).
2. The dominant cation is Ca, with a median concentration of 54.8 mg/L (interquartile range 42.5 – 74 mg/L). Mg and K concentrations are generally low (median 4.21 and 3.7 mg/L respectively). The median Na is 20.6 mg/L (interquartile range 12.6–28 mg/L); however, a few samples have been affected by proximity to the sea and have much higher concentrations, as illustrated by the 95th percentile (68 mg/L) and maximum concentration (153 mg/L).
3. The dominant anion is bicarbonate, with a median concentration of 183 mg/L (interquartile range 183–230 mg/L). Around one third of the samples are saturated with respect to calcite. Sulphate concentrations are generally low (median 14.6 mg/L, interquartile range 7.7–36.4 mg/L), although higher concentrations are encountered in samples affected by seawater, and/or possibly by gypsum bands within the aquifer. Chloride concentrations follow broadly the same distribution as Na and have a median of 38.8 mg/L and interquartile range of 19.5–49.5 mg/L; the same few samples show high Cl concentrations as do Na.
4. Concentrations of minor and trace elements in the groundwater are dominated by the redox conditions. Measured values of dissolved oxygen indicate a large range in redox conditions across the aquifer. Concentrations of DO close to 10 mg/L indicate fully oxic conditions. By contrast, groundwaters with DO concentrations <1 mg/L are indicative of sub-oxic or mildly reducing conditions, and appear to be prevalent in much of the Upper Old Red Sandstone outcrop, and parts of the Middle Old Red Sandstone. Reducing conditions may reflect the presence of low permeability layers (often marine in origin) within the thick superficial deposits overlying the Old Red Sandstone aquifer. The effect of reducing conditions is to increase concentrations of Fe and Mn, which show median concentrations of 38 and 43 µg/L respectively, and 75th percentile values of 354 and 227 µg/L respectively.
5. The majority of samples (21) were collected from the Upper Old Red Sandstone aquifer; 14 samples were collected from the Middle Old Red Sandstone and only 4 samples from the Lower Old Red Sandstone. The samples show broadly similar chemistry across the three aquifer units; however, there are several notable differences. Samples from the Upper Old Sandstone aquifer show very similar cation distribution, dominated by Ca, while the Lower and Middle Old Red Sandstone aquifers show a wider cation distribution and appear less affected by calcite dissolution. The pH of the Lower and Middle Old Red Sandstone aquifers is slightly lower (more acidic), generally less than 7.0. Groundwaters

within the Upper Old Red Sandstone aquifer are generally more reducing, probably reflecting their location close to the coast and hence the influence of the sea and/or overlying marine superficial deposits.

6. Nitrate concentrations are variable across the aquifer units, although median concentrations are low (1.45 mg/L TON-N or less in each aquifer). The prevalence of low oxygen conditions in the sampled groundwaters has led to denitrification, which means the relationship between land use and nitrate concentrations is less obvious than for other parts of Scotland (MacDonald et al., 2005a). However, there is a clear relationship between nitrate concentrations and the Nitrate Vulnerable Zone (NVZ) that covers much of the study area, with the seven highest groundwater nitrate concentrations, ranging from 5.98 to 22.1 mg/L TON-N, all from samples taken within the NVZ. The highest median concentrations were from samples collected on land known to be used for dairy, pig or poultry farming.

7. Phosphorus concentrations in Moray Firth groundwaters range from less than detection limit up to 172 µg P/L, with an overall median of 36 µg P/L, which is in the eutrophic range for surface waters. Concentrations are generally low in the western part of the study area, and an observed relationship with the spatial pattern of F suggests that both elements may be in part derived from the dissolution of phosphate minerals, such as apatite, from the aquifer rocks. Concentrations in the eastern part of the study area are generally higher, usually in the mesotrophic or eutrophic range for surface waters. The higher values may be related to land use, with P inputs from agricultural activity.

8. An estimate of the baseline groundwater chemistry conditions in the Old Red Sandstone 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 Old Red Sandstone aquifers in the Moray Firth area.

1 Introduction

This report describes the baseline groundwater chemistry of the Old Red Sandstone sedimentary aquifers of the Moray Firth area and of outliers in Aberdeenshire (Figure 1). Groundwater is an important resource in the Moray Firth area. Although comprehensive groundwater abstraction records do not exist, there are at least 60 significant (abstraction greater than 10 m^3/day) groundwater sources in the study area, and probably many tens of additional smaller abstractions. The majority of abstractions are for agricultural use, both for irrigation or livestock, but there are also a significant number of industrial (largely food and drink producing) and private domestic abstractions.

The Old Red Sandstone rocks range from Silurian to Carboniferous in age, and occur across Scotland. In the Moray Firth area, they crop out along the largely flat coastal strip, usually between 10 and 20 km wide. Occasional outliers also occur, the largest of which is further east along the coast (the Turriff basin), and the rest of which are inland (Figure 1). Much of the aquifer is covered by superficial deposits, largely glacial till and glaciofluvial sand and gravel.

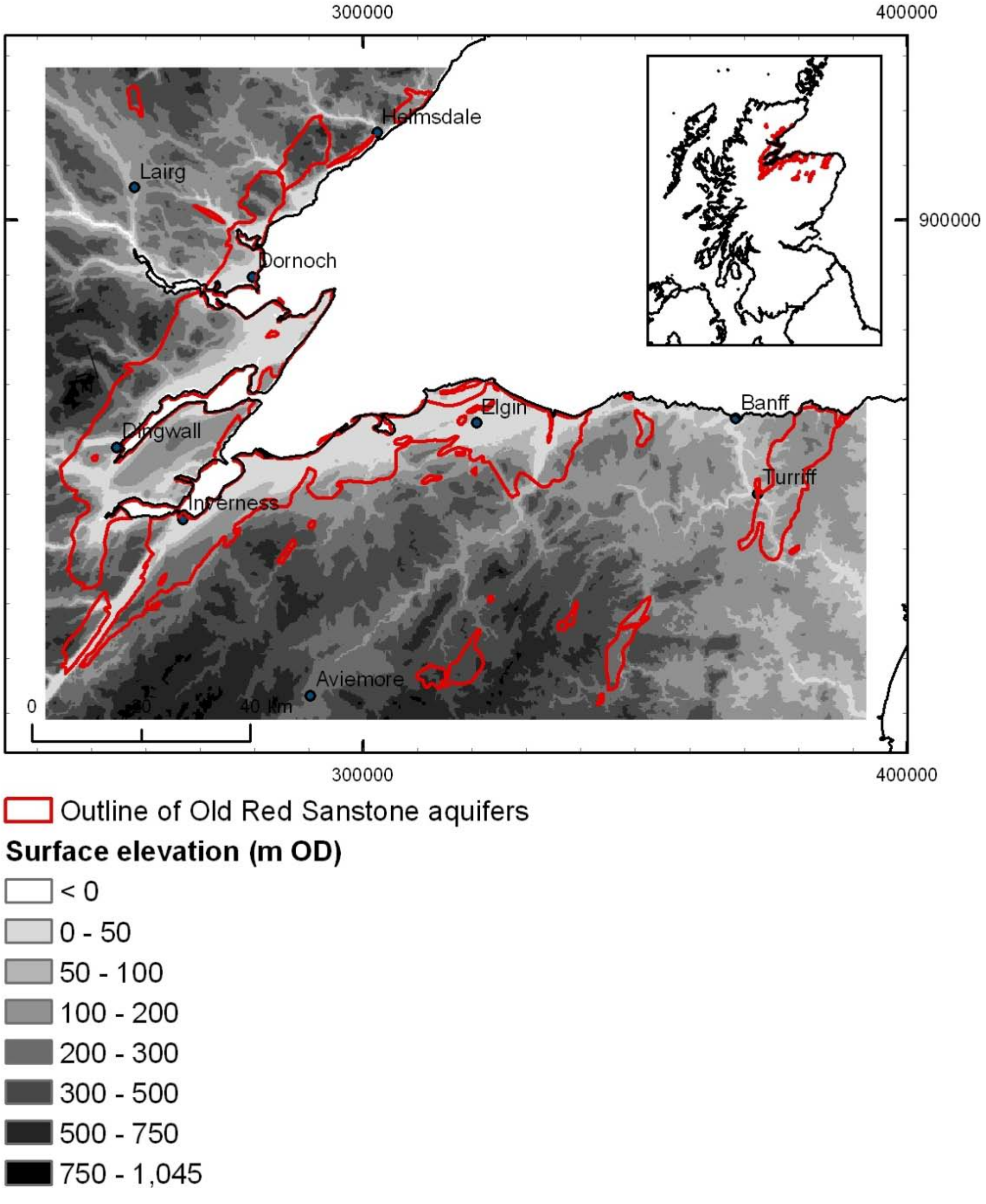


Figure 1 The Moray Firth study area, showing the outline of the Old Red Sandstone aquifers, land surface elevation, and major towns

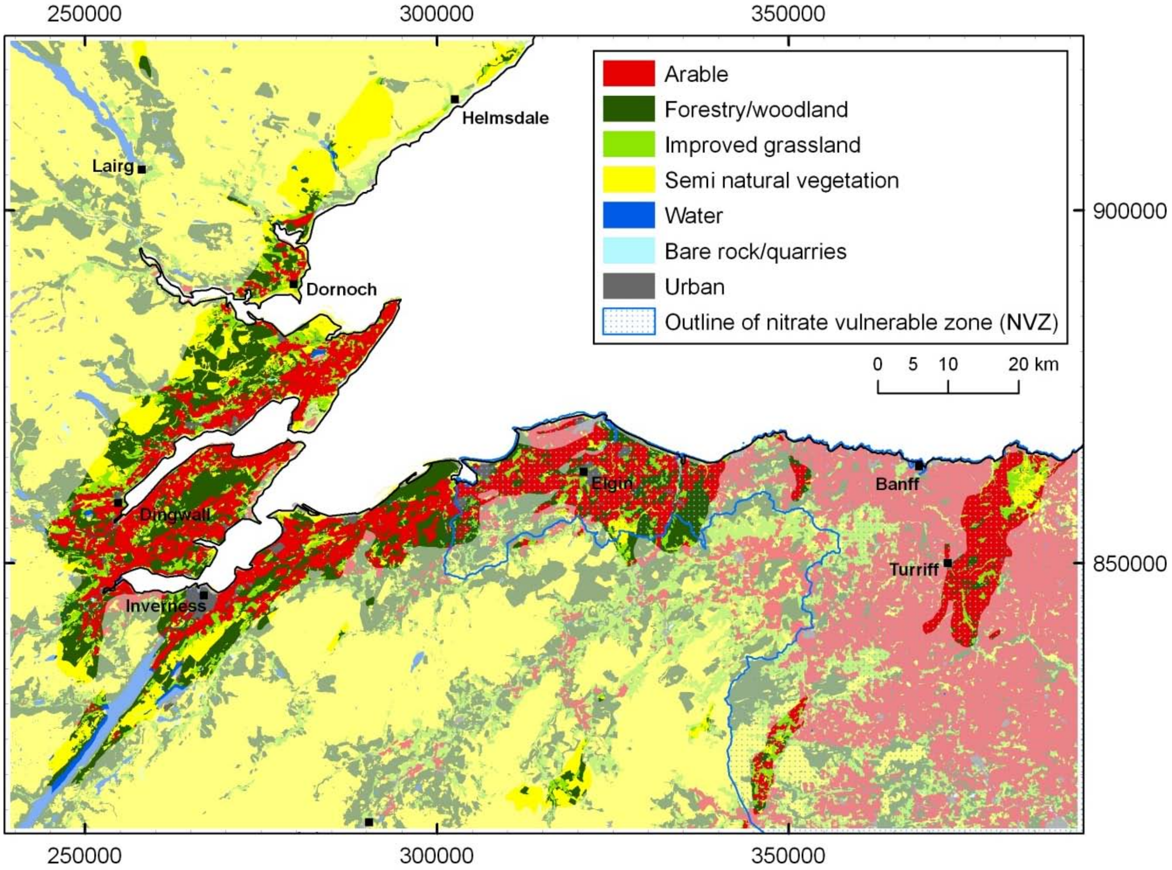
2 Background

In order to understand the chemistry of the groundwater in the area, it is important to understand the environmental context. This chapter sets out the geology, landuse and hydrogeology of the area, and also discusses the available rainfall chemistry data.

2.1 LAND USE

Most the study area is dominated by arable agriculture, including barley and wheat (Figure 2 and Macaulay Land Use Research Institute, 1993). In the northwest and southwest of the outcrop of the Old Red Sandstone aquifer, arable land is largely replaced by semi natural vegetation and woodland (mostly coniferous forest). Significant areas of woodland also occur in other parts of the study area, including Millbuie Forest on the Black Isle north of Inverness, Culbin Forest near Forres to the west of Elgin, and the Wood of Ordiequiesh at Fochabers. There are also smaller but widespread areas of improved grassland given over to pastoral agriculture, largely pig and cattle.

To the east of Forres most of the Old Red Sandstone aquifer outcrop lies within the Aberdeenshire nitrate vulnerable zone (Figure 2).



The area outside the Old Red Sandstone outcrop is faded out.

Land use data from the Macaulay Land Use Research Institute; © Crown Copyright 1992. All rights reserved. British Geological Survey User Licence Number MI/2007/246.

Figure 2 Generalised land use in the Moray Firth area, with the outline of the Old Red Sandstone aquifer highlighted, and showing nitrate vulnerable zones.

2.2 BEDROCK GEOLOGY

The bedrock geology of the study area is dominated by sedimentary rocks of the Old Red Sandstone system. Old Red Sandstone is now used as a facies term: the rocks are largely of Devonian age, but the oldest are thought to be as old as the Middle Silurian, and the youngest of Carboniferous age (Trewin and Thirlwall, 2002). The Old Red Sandstone rocks of the Moray Firth were originally laid down in the southern part of a large depositional basin known as the Orcadian Basin. They now occur onshore as disconnected outcrops between Helmsdale and Inverness, and an elongated strip along the coast from Inverness to the east of Elgin (Figure 3). To the east and southeast of the main outcrops, in Aberdeenshire, are three outliers, at Turriff, Rhynie and Tomintoul. The rocks in the study area belong largely to the Middle Old Red Sandstone, but also include rocks of the Lower and Upper Old Red Sandstone.

The Old Red Sandstone rocks represent cycles of sedimentation, with the thickness of the cycles ranging from about 6.5 m to 12 m. The southern part of the Orcadian Basin at this time was an alluvial plain periodically transgressed by the major lake that occupied the basin. The rocks are dominantly fluvial sandstones and alluvial fan conglomerates, with thin but extensive lacustrine units, which largely represent southward extensions of the main Orcadian lake to the north (Trewin and Thirlwall, 2002).

The oldest rocks, Lower to Middle Old Red Sandstone, are conglomerates, deposited along the northwest and southern edges of the former Orcadian Basin. Active fault scarps controlled the northwest margin of the depositional area, shedding material to alluvial fans building to the southeast. Clasts are dominantly of Moine derivation, but also include Torridonian and Cambrian rocks (Trewin and Thirlwall, 2002). To the south and southeast of the area, alluvial fans built to the north and northwest, deposited by rivers draining the Grampian area. Formations include the Cnoc Fyrish Conglomerate Formation, the Braemore Mudstone Formation, and the Daviot Conglomerate Formation. The conglomerates in the Dornoch area are up to 500 m thick (Trewin and Thirlwall, 2002).

The rocks of the Middle Old Red Sandstone are generally of fluvial origin, deposited by rivers draining northeast, with subordinate, largely fine-grained, lacustrine sediments. Clasts of andesitic lava are common in the sandstones. There is a marked cyclicity that was controlled by transgression of the alluvial plains by lakes: fluvial cycles commencing with erosively-based channel sandstones and conglomerates fine upwards into finer-grained lacustrine sandstones and shales with carbonate concretions, or limestones. Coarsening up sequences represent progradation of alluvial deposits into the lake (Trewin and Thirlwall, 2002). The dominant groups are the Sarclet Sandstone Group and the Black Isle Sandstone Group (which date from the Early Devonian), and the Inverness Sandstone Group, which includes formations such as the Hillhead Sandstone Formation, the Inshes Flagstone Formation, the Kilmuir Conglomerate Formation and the Spey Conglomerate Formation. The thickness of the rocks in the Elgin area is estimated to be 300 to 600 m (Trewin and Thirlwall, 2002).

The youngest rocks, the Upper Old Red Sandstone, are dominated by fluvial sandstones with subordinate conglomerates and fine-grained lithologies. The sandstones and conglomerates are typically channel deposits, containing mudstone clasts. Palaeoflow directions are generally northwards. There are associated caliche profiles (Trewin and Thirlwall, 2002). The main stratigraphical unit is the Forres Sandstone Group, which includes the Alves Beds, the Rosebrae Beds, the Scaat Craig Beds and the Kingsteps Sandstone Formation. The total thickness of the Upper Old Red Sandstone in this area is difficult to estimate but is thought to be around 450 m in the River Findhorn near the eastern edge of the outcrop east of Elgin, and up to 1200 m east of the Rothes Fault, which runs below Elgin; in the Dornoch area the rocks are up to 1000 m (Trewin and Thirlwall, 2002).

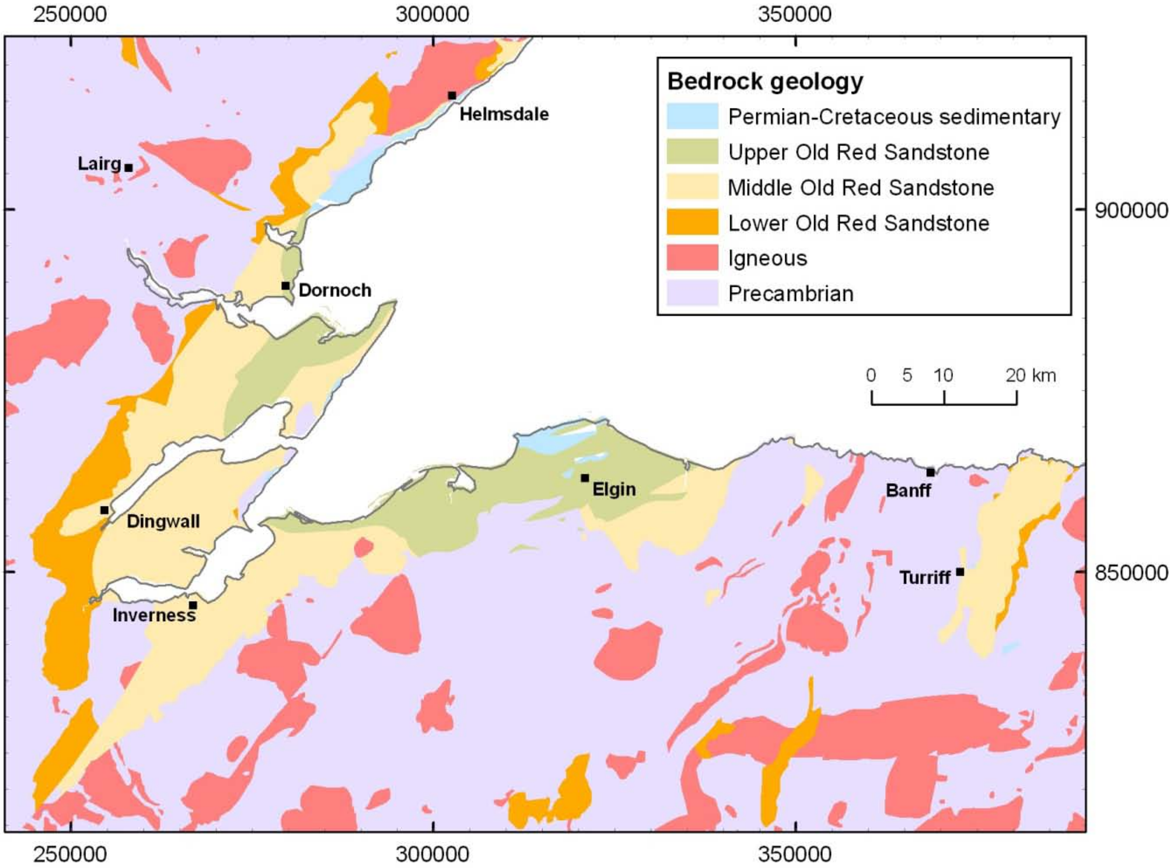


Figure 3 Bedrock geology (from 1:625 000 scale DigMap linework) of the Moray Firth area

The oldest rocks in the Turriff basin – largely sandstones with interbedded mudstones – are part of the Lower Old Red Sandstone, but this outlier basin is dominated by Middle Old Red Sandstone rocks of the Inverness Sandstone Group. The Tomintoul outlier comprises conglomerates and sandstones of the Lower Old Red Sandstone. The Rhynie outlier also belongs to the Lower Old Red Sandstone, and consists mainly of sandstones with shales and flagstones.

Underlying the low ground of Easter Ross is the Black Isle Syncline, which trends northeast from Beauly to Inver on the Dornoch Firth. Along the belt of Devonian rocks southwest of Inverness along the Great Glen, the rocks have been tightly folded and affected by localised low-angle thrusting.

2.3 SUPERFICIAL DEPOSITS GEOLOGY

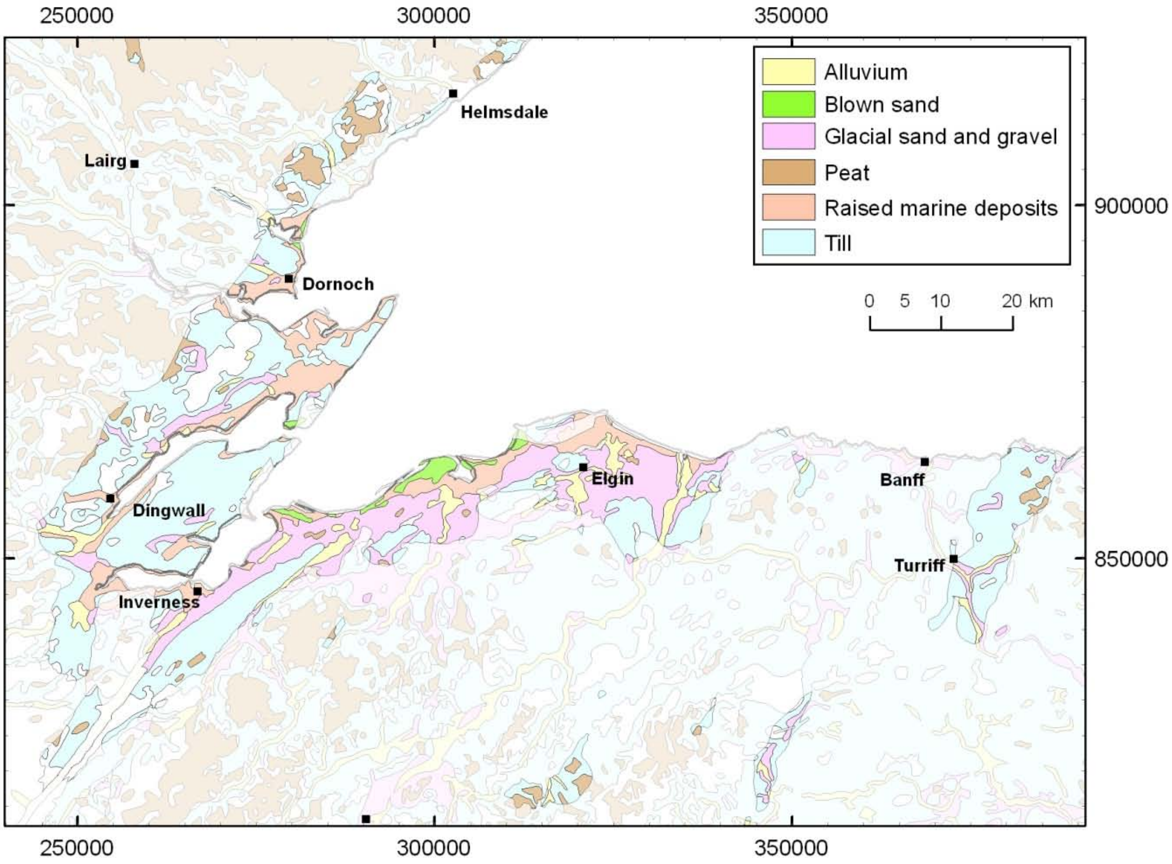
There is little evidence of Quaternary deposition in the area before the last, Late Devensian, glaciation. The pattern of ice cover during the Late Devensian across the area is still debated. Most models show a very restricted extent of ice over the Moray Firth, and much of the eastern part of the area is likely to have been ice-free for much of the period (Boulton et al., 2002, Merritt et al., 2003).

Along the west of the Moray Firth, through the Black Isle, Cromarty and Dornoch areas, glacial till is the most widely distributed superficial deposit, cropping out across most of the area, particularly across the Black Isle (Figure 4). Till is also the most common deposit in more inland (and therefore upland) areas, and across the Turriff Basin. In general, tills tend to occur in areas of poorly drained ground of low relief and smooth slopes. The tills are composed mainly of ice-transported *diamicton*, a poorly sorted mixture of rock fragments, gravel, sand, silt and clay, although they vary considerably in lithology and in thickness across the area (Merritt et al., 2003).

Along the south of the Moray Firth, between Inverness and Buckie, the most common deposits are glaciofluvial sediments, laid down primarily by meltwaters from ice sheets and glaciers. Two main categories are distinguished: moundy *ice-contact deposits* and terraced spreads called *sheet deposits* (Merritt et al, 2003). Ice-contact deposits consist mainly of sand and gravel, with subsidiary beds of diamicton, silt and clay. They typically form hummocky topography, including eskers and kames, and occasionally also flat-topped plateaus. Sheet deposits were laid down mainly by braided streams in a pro-glacial environment, forming fan-shaped bodies and spreads of outwash sand and gravel, and sometimes distinct terraces. The deposits are dominantly sand and gravel, generally becoming less coarse and more sandy downstream from the ice margin, although many of them coarsen upwards, indicating that they accumulated during glacial still-stands or minor readvances (Merritt et al, 2003).

Thin outcrops of alluvium occur along the course of the major rivers in the area: the Conon, Ness, Nairn, Findhorn, Lossie and Spey, typically forming low-lying ground potentially liable to flooding. The alluvium commonly comprises clast-supported, reasonably well-sorted gravel (shingle) capped by one to two metres of overbank deposits: fine grained, humic, laminated silty sand, locally intercalated with peat. Along the River Spey downstream of Fochabers there are particularly high-energy, coarse-grained bars of cobble shingle (Merritt et al, 2003). Thicknesses vary depending on the size of the valley, but along the River Spey around Fochabers range from less than 6 to approximately 20 m.

Deposits of peat occur mainly on more upland areas to the west of the Moray Firth and in the outliers at Turriff and Tomintoul. Most areas of basin peat (deposited mainly within the sites of former lochans) have been heavily exploited for fuel and are a fraction of their original size and thickness, generally not exceeding 1 m in thickness, but remain waterlogged (Merritt et al., 2003).



The area outside the Old Red Sandstone outcrop is faded out.

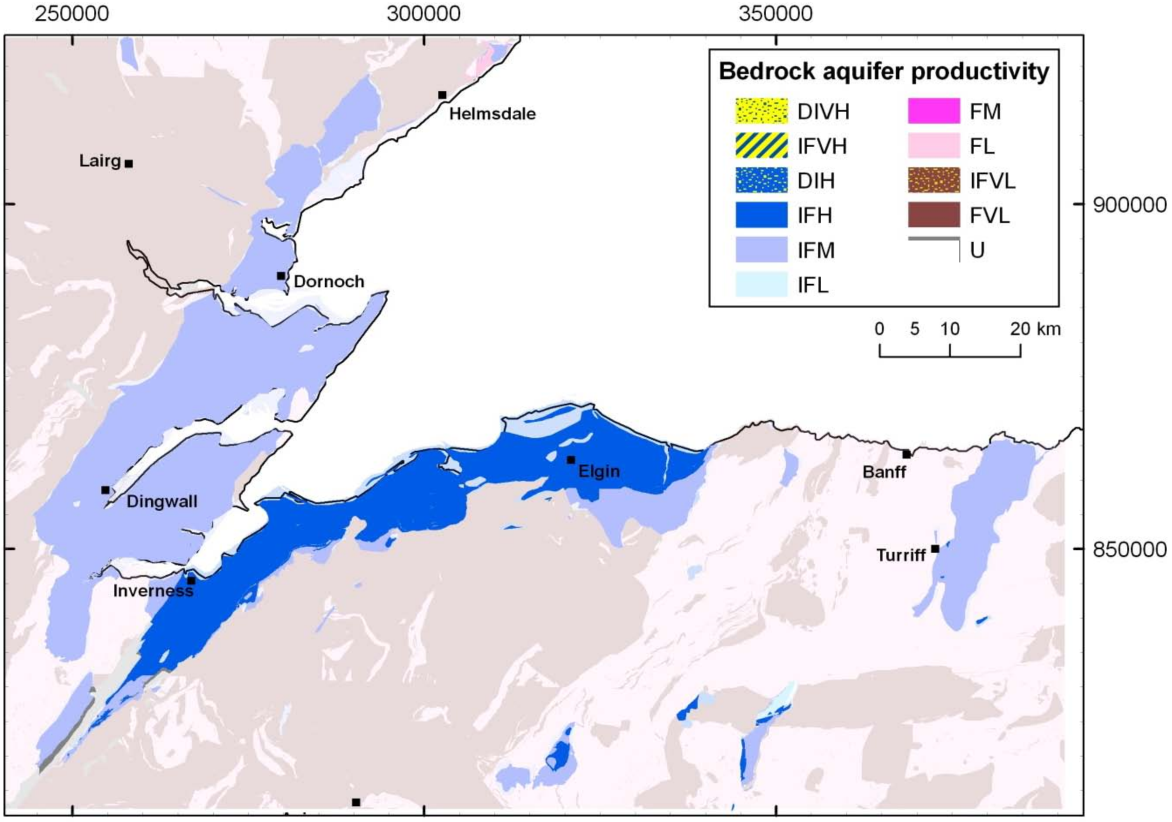
Figure 4 Superficial deposits (from 1:625 000 scale DigMap linework) in the Moray Firth area

2.4 HYDROGEOLOGY

2.4.1 Bedrock hydrogeology

The relatively limited available hydrogeological information indicates that the Old Red Sandstone rocks form moderately to highly productive aquifers (Figure 5). Groundwater flow is almost entirely via fractures (Robins, 1989). Even the dominantly sandstone formations are interbedded with finer grained horizons, which restrict intergranular groundwater flow.

Most available information is for the Moray coastal area. Most of the sandstones from the Upper Old Red Sandstone and some from the Middle Old Red Sandstone in this area are classed as highly productive aquifers. Recorded borehole yields range from 163 to 2160 m^3/d, with a mean value of 970 and a median value of 880 m^3/d (information from the Scottish Aquifer Properties Database). In the area between Inverness and Dornoch there is particularly limited information. Limited data from boreholes west of Inverness indicate that hydraulic conductivity is variable over short distances, with borehole yields generally ranging from poor to moderate (Ball, 1999). In occasional cases, relatively high yields have been reported anecdotally.



The area outside the Old Red Sandstone aquifer outcrop is greyed out.

DIVH	dominantly intergranular flow, very high productivity	FM	fracture flow, moderate productivity
IFVH	intergranular/fracture flow, very high productivity	FL	fracture flow, low productivity
DIH	dominantly intergranular flow, high productivity	IFVL	intergranular/fracture flow, very low productivity
IFH	intergranular/fracture flow, high productivity	FVL	fracture flow, very low productivity
IFM	intergranular/fracture flow, moderate productivity	U	unknown aquifer productivity
IFL	intergranular/fracture flow, low productivity		

Figure 5 Productivity of the Old Red Sandstone aquifers in the Moray Firth study area (after MacDonald et al., 2004).

Limited aquifer properties data are available from the Scottish Aquifer Properties Database. Twelve transmissivity values range from 10 to 608 m^2/d, with an arithmetic mean of 198 m^2/d and a median of 80 m^2/d. Thirteen specific capacity values range from 4 to 770 m^3/d/m, with an arithmetic mean of 119 m^3/d/m and a median of 41 m^3/d/m. Ten of these values are from sandstones of the Upper Old Red Sandstone, and range from 28 to 222 m^3/d/m. The smallest two values, at 4 and 5 m^3/d/m, are from sandstones of the Lower and Middle Old Red Sandstone to the west of Inverness. The largest value, which at 770 m^3/d/m is significantly larger than the next largest of 222 m^3/d/m, is from a borehole abstracting from sandstones of the Middle Old Red Sandstone. Core porosity and hydraulic conductivity data are available for only one borehole, in the Turriff Basin in conglomerate of the Middle Old Red Sandstone. Porosity ranged from 8.3 % to 12.4 %, and hydraulic conductivity from 0.00002 to 0.0001 m/d.

2.4.2 Superficial deposits hydrogeology and groundwater vulnerability

The deposits with the largest storage and highest permeability are the coarse alluvial gravels along the main rivers, in particular the River Spey and the River Lossie, where there are significant volumes of saturated gravels beneath the shallow water tables. The alluvial gravels have greater lateral continuity than the more heterogeneous glaciofluvial sand and gravel deposits. Recharge potential to the alluvial aquifers is high, because of their high permeability and location in valley floors, where they can intercept run-off towards rivers. There is also strong hydraulic connection between groundwater in the alluvial aquifers and the adjacent rivers, with rivers both losing to, and gaining from, groundwater, depending on the seasonal water level conditions in the aquifer and rivers. Alluvial aquifers act as an important storage medium for groundwater before it discharges (sometimes after several years) to rivers. Glaciofluvial sand and gravel deposits tend to have lower permeability than alluvium, although it is still relatively high, and their heterogeneous nature also results in more complex groundwater flow paths, for example via discontinuous gravel-filled channels. Terraces within sheet deposits often flank alluvium on valley sides, and mostly lie above the water table. Moundy ice-contact deposits are also often above the local water table. Recharge potential to the deposits is high, and the deposits tend to play an important role as a temporary groundwater store and a conduit for groundwater flow to adjacent valley alluvium and/or rivers (Merritt et al., 2003).

Where alluvium and/or glaciofluvial deposits directly overlie the Devonian bedrock aquifer, there may also be a strong hydraulic connection between the two, with groundwater in the superficial deposits infiltrating to the underlying bedrock, and/or an upward gradient from the bedrock to the superficials, depending on the relative hydraulic heads (which could change seasonally).

The widespread till deposits, although they can be relatively sandy, also typically contain significant amounts of clay, and have often been compacted by ice action, and so generally show significantly lower permeability than glaciofluvial or alluvial deposits. Small groundwater seepages are common, and larger flows can occur along sandier horizons and gravelly beds, and on a regional scale, there is likely to be a significant amount of groundwater movement through till deposits. Recharge to till can be relatively high where sandy horizons are present.

Across most of the study area, groundwater in both superficial deposits and bedrock aquifers is highly vulnerable to contamination from surface activities (Figure 6). This is partly due to the generally thin superficial deposits cover across much of the area, and to the fact that much of the thicker superficial deposits are highly permeable and do not provide significant protection. It also reflects the dominance of fracture permeability in the bedrock aquifers, which can lead to rapid transport of contaminants from the ground surface to the water table. Most of the arable land in the east of the study area lies within a nitrate vulnerable zone, designated on the basis of the high risk land use and on known nitrate concentrations in groundwater (Figure 2).

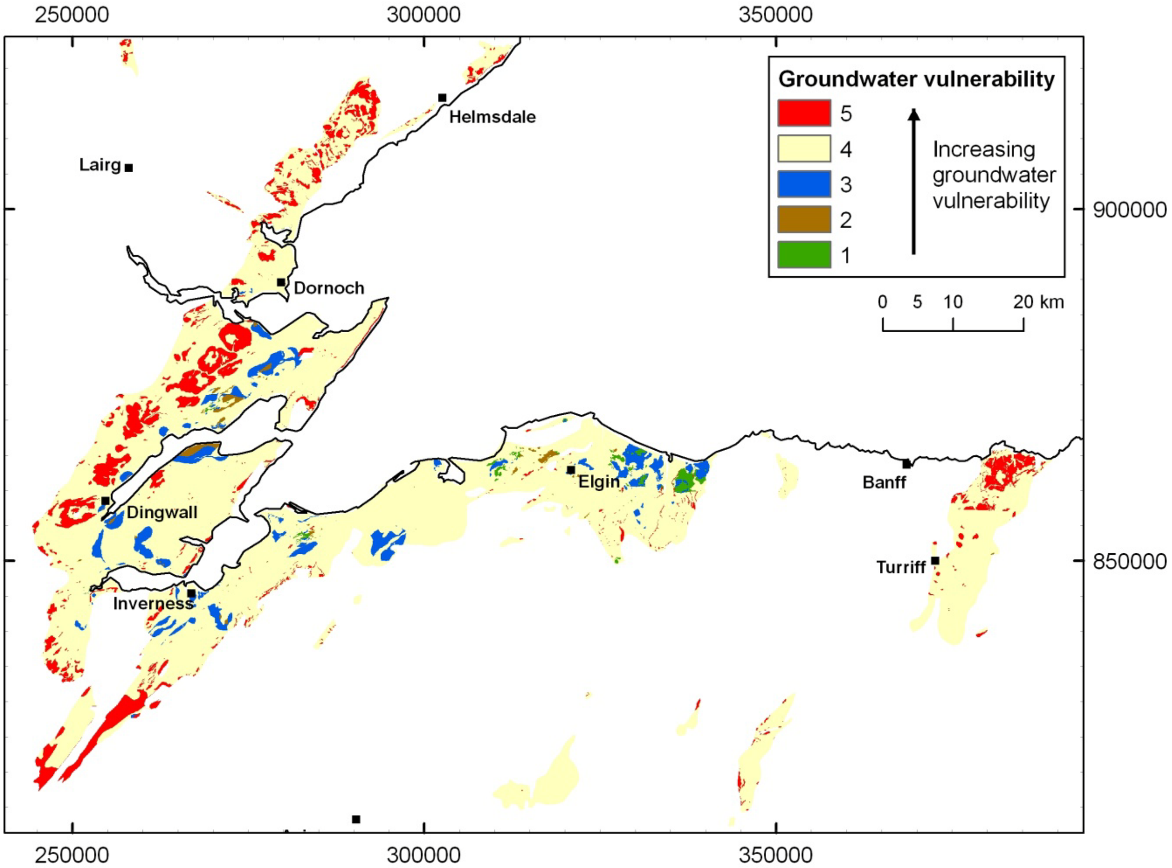


Figure 6 Groundwater vulnerability across the Old Red Sandstone aquifer outcrop in the Moray Firth area

2.4.3 Groundwater use

There are a number of groundwater abstractions from the Old Red Sandstone aquifer in the Moray Firth area, particularly in the area to the west of Elgin. These are mainly used for industry (food and drink), agriculture (irrigation, livestock and market gardening), and recreation (largely golf course) use. Middle Old Red Sandstone conglomerates of the Turriff Basin outlier support a public supply borehole yielding up to 2100 m^3/d. Trial boreholes indicate that the Turriff Basin aquifer has the potential to support further abstraction (Ball, 1999).

The superficial deposits also form an important aquifer across the area, and provide groundwater for large public water supply schemes, industry and agriculture. The presence of usable groundwater within the superficial deposits has probably reduced the amount of groundwater development within the Old Red Sandstone aquifers.

2.5 AQUIFER GEOCHEMISTRY FROM STREAM SEDIMENT AND STREAM WATER 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 (BGS, 1987, BGS, 1991). The following patterns in selected element distribution have been inferred from the stream sediment geochemistry:

- Over most of the Old Red Sandstone aquifer outcrop, calcium in stream sediments is low (0.6–2% CaO) and does not vary much. Over a small area north of Elgin, values reach 3.6% CaO. The Turriff basin outlier appears to have lower calcium concentrations than the rest of the Old Red Sandstone (0.04–0.6% CaO).

- Magnesium is low (generally <0.9% MgO) across the whole of the Old Red Sandstone aquifer in the study area.
- Potassium is generally moderate (2–3.2% K2O) across the study area, with an area of higher values (up to 5.4% K2O) over Middle and Upper Old Red Sandstone rocks south of Elgin.
- Iron concentrations in stream sediments are generally low (<5% Fe2O3), with two small areas of higher iron (up to 18.7% Fe2O3) over Upper Old Red Sandstone rocks near the Moray coast around Lossiemouth, on the coast north of Elgin.
- There is a small area of marked lead enrichment (up to 167 mg/kg) in the area immediately south of Findhorn Bay (approximately halfway between Inverness and Elgin) on Upper Old Red Sandstone rocks. Elsewhere, lead concentrations are generally low (<30 mg/kg).

2.5.2 Streamwater information

Limited stream water chemistry information (pH, conductivity, alkalinity and fluoride concentrations) was also collected by BGS as part of the G-BASE project (BGS, 1987, BGS, 1991).

Values of pH in stream waters draining the Old Red Sandstone aquifer, and particularly over arable land, are typically high (>7.0). The use of lime and other basic fertilisers may contribute to a higher pH. Values of less than 7.0 are mainly seen in areas of coniferous forest, which can reduce the soil's acid-neutralising buffering capacity – such as in woodland southeast of Elgin, where some samples showed pH <5.0 and in one case as low as 4.1.

Conductivity in stream waters over the Old Red Sandstone aquifer is generally high (mean >200 µS/cm) and over 500 µS/cm in the area immediately west of Elgin and parts of the Black Isle between Inverness and Dingwall, and in Easter Ross between Dingwall and Dornoch. The highest values may be enhanced by contamination from fertiliser in areas of intensive farming or could also indicate a high proportion of baseflow from groundwater. Lower conductivity values (<200 µS/cm) are generally found in association with Lower Old Red Sandstone rocks, but also with the southern and western edges of the study area adjacent to Precambrian rocks. It is therefore unclear if this is due to different geochemistry in Lower Old Red Sandstone rocks, or to the effects of Precambrian geologies on stream water.

There are only 13 bicarbonate analyses for stream waters in the study area, all either within about 25 km of Elgin, or in the Turriff basin outlier. Most are between 20 and 80 mg/L HCO_3. There is no obvious pattern to the distribution of the concentrations. The sample with the lowest concentration (6 mg/L HCO_3) lies on the southern edge of the Old Red Sandstone outcrop and is likely to reflect the geochemistry of the Precambrian rocks to the south.

There are no fluoride measurements in stream waters in the west of the study area (from just east of Inverness). Across the rest of the Old Red Sandstone, values range from 0.04 to 0.43 mg/L. The highest values (>0.1 mg/L) are mainly associated with the Upper Old Red Sandstone; concentrations <0.1 mg/L are generally associated with the Lower and Middle Old Red Sandstone.

Most of the stream water samples analysed showed uranium below the detection limit of 0.01 µg/L. Of the twelve higher than the detection limit, all but one is less than 0.1 µg/L, and all are on Middle or Upper Old Red Sandstone rocks. The highest value measured was 0.23 µg/L (on sandstones from the Middle Old Red Sandstone between Dingwall and Dornoch.

2.6 RAINFALL CHEMISTRY

There are no stations with rainfall chemistry data in the study area itself, but there are three in the surrounding region, within 20 to 45 km. Achanarras (to the north of the study area in Caithness) and Strathvaich Dam (to the west of the study area, approximately 25 km west of Dingwall) are likely to be closest in topography, environment and rainfall volume to the study area, particularly Achanarras which is more coastal and at a lower elevation. Allt a Mharcaigh (to the south of the study area in the Cairngorm mountains) is more inland and subject to much higher rainfall.

Average annual rainfall at Achanarras is 714 mm and at Strathvaich Dam is 766 mm (data for the 1990s).

Solutes derived from rainfall typically increase during evapotranspiration, such that the solute concentration in infiltrating recharge is expected 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 to oxidise to nitrate on infiltration. An estimate of the likely chemistry of infiltrating recharge water in the study area after evapotranspiration, based on a three times concentration of the median 1990-1999 (or 1995 for Allt a Mharcaigh) rainfall chemistry, is also presented (Table 1).

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

	Units	Allt a Mharcaigh	Strathvaich Dam	Achanarras	Expected concentration in infiltrating recharge after evapotranspiration[4]
NGR		NH 876 052	NH 347 750	ND 151 550	
Elevation	m OD	274	270	98	
Annual rainfall	mm	2061[1]	766[2]	714[3]	
		Median concentration in rainfall 1990-1995	Median concentration in rainfall 1990-1999	Median concentration in rainfall 1990-1999	
pH	-	5.02	5.14	5.00	5.05
SEC	µS/cm	18.00	20.00	32.00	70
Ca	mg/l	0.179	0.224	0.402	0.805
Cl	mg/l	1.628	2.532	5.902	10.06
K	mg/l	0.067	0.070	0.201	0.338
Mg	mg/l	0.153	0.283	0.557	0.993
NH_4-N	mg/l	0.067	0.044	0.308	-
NO_3-N	mg/l	0.136	0.090	0.238	0.464
Na	mg/l	0.997	1.483	3.326	5.81
PO_4-P	mg/l	<0.05	<0.10	-	-
SO_4-S	mg/l	0.361	0.365	2.031	2.76

[1] Mean annual rainfall from 1990 to 1995

[2] Mean annual rainfall from 1990 to 1999

[3] Mean annual rainfall from 1990 to 1999

[4] Calculated for illustrative purposes as three times the average median concentration of the three stations, except pH and NH_4-N are given as the average median concentration of the three stations.

3 Methodology

3.1 INTRODUCTION

A total of 39 detailed groundwater chemistry analyses are available for the Old Red Sandstone aquifers in the study area. Of these, 17 were from samples collected from the main aquifer outcrop in September 2007 specifically for the Baseline Scotland project. These were collected mostly from the area east of Inverness. A further five were from samples collected in November 2006, also for the Baseline Scotland project, from Old Red Sandstone outliers of Turriff and Rhynie (Smedley et al., 2009). Fifteen samples were collected between November and December 2001 as part of a project to assess nitrate conditions in Scottish groundwater (Ball and MacDonald, 2002). Two samples were collected in 2007 as part of a project in Forres investigating groundwater flooding (MacDonald et al., 2007; 2008a).

3.2 SITES SAMPLED

The sites were chosen to be representative of groundwater in the Old Red Sandstone aquifer in the study area. Sources that were very poorly constructed (e.g. open and/or uncased boreholes in leaking chambers) and which were close to obvious and significant sources of contamination (e.g., unsecured slurry stores) were avoided.

The criteria for sample site selection were:

- to collect a suitable number of samples from the Old Red Sandstone aquifer across the study area, including the outliers;
- to collect samples distributed as evenly as possible over the study area; and
- to collect samples which were as far as possible representative of groundwater in the Devonian aquifer.

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 locations of the sampling points are shown in Figure 7. Most of the samples were collected from boreholes; one from a spring, and one from a shallow large diameter well. Details of the distribution of samples across source type, aquifer and land use are given in Table 2.

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. 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. The only shallow well sampled for this study was used daily for domestic and livestock supplies, and was therefore likely to be sampling fresh groundwater. Because 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.

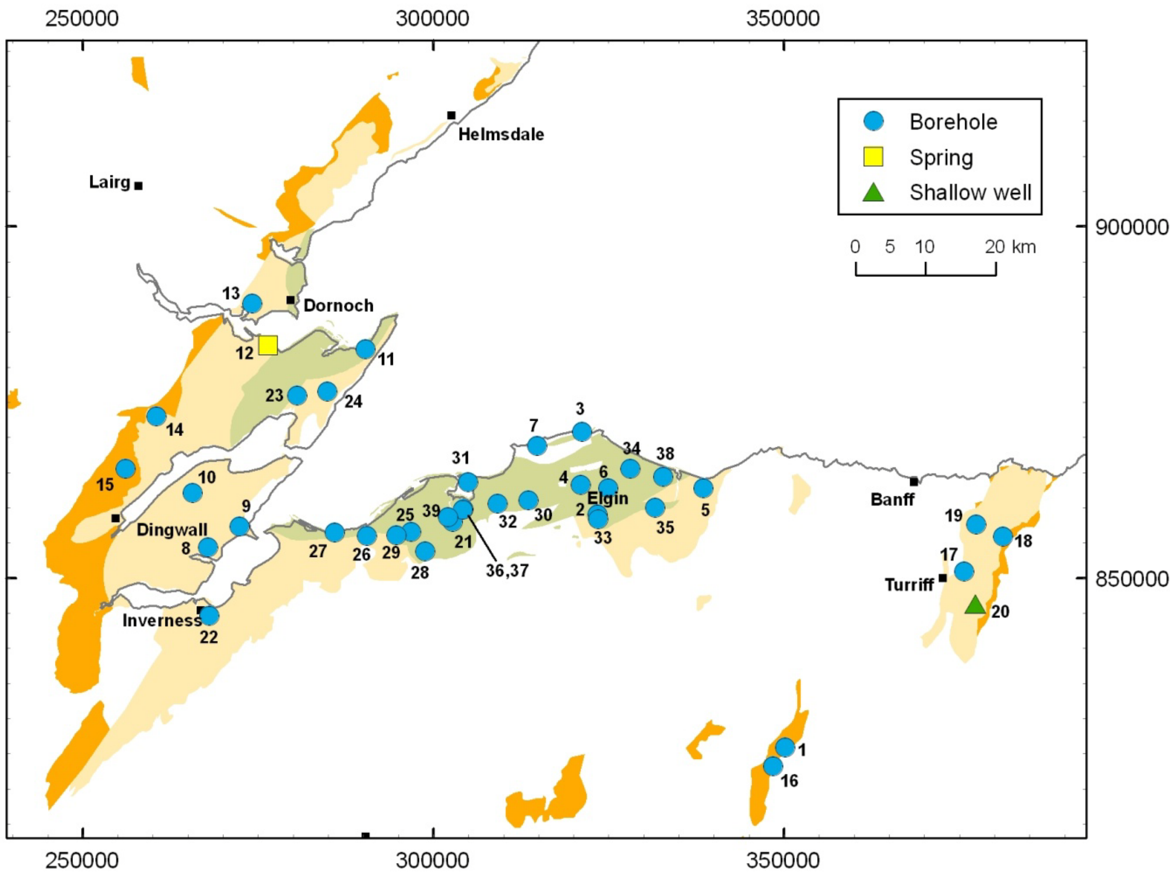
3.3 SAMPLING PROCEDURE

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 for 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 for 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 for 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 (δ^2H, $\delta^{18}O$ 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 δ^2H, $\delta^{18}O$ 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.



For key to geology see Figure 3.

For details of samples see Appendix 1.

Figure 7 Location and reference numbers of groundwater samples in the Old Red Sandstone aquifers of the Moray Firth area

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

Land use	Arable			Identified DPP[1]			Improved grassland / mixed cultivated			Non-agricultural			Total
Geology	B[2]	S[2]	W[2]	B	S	W	B	S	W	B	S	W	
Lower Old Red Sandstone							3			1			4
Middle Old Red Sandstone	4		1	1			3			4	1		14
Upper Old Red Sandstone	9			7						5			21
Total	13		1	8			6			10	1		**39**

[1] DPP – Dairy, Pigs and Poultry

[2] Non-agricultural includes recreational, residential, rural industrial and semi natural

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

4 Hydrogeochemistry

4.1 DATA ANALYSIS AND PRESENTATION

4.1.1 Summary statistics

Groundwater chemistry data are available for a total of 39 sites distributed across the Old Red Sandstone aquifers in the Moray Firth area. Where these are identified and discussed individually in this report, they are referred to by a numerical ID. Summary details of each of the sample sites are provided in Appendix 1. Summary statistics were calculated for the whole dataset for each of the measured parameters (Table 5 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. Maximum and minimum values show the extreme values in the dataset. The median value, rather than the mean, has been chosen as the preferred estimate of the central tendency for a particular data distribution, as it is unaffected by outliers. The total number of observations and the number of censored (non-detect) observations are also reported, and give an indication of the degree of censoring for each element.

Many trace elements had concentrations close to or below their respective individual detection (or reporting) limits. For some elements, the data distributions had multiple detection limits. This complicates the calculation of summary statistics significantly. For most elements considered in this study, the summary statistics were calculated using the non-parametric Kaplan-Meier method (Lee and Helsel, 2007). Exceptions were for elements where >50% of the data were below detection limits, in which case the ROS (regression-on-order statistics) method was used. Data for percentiles and median values have been calculated using these methods and are given in Table 3. The Kaplan-Meier method does not allow calculation of percentiles at concentrations below the maximum detection limit. The ROS method provides estimates of distributions below the detection limits (Lee and Helsel, 2007).

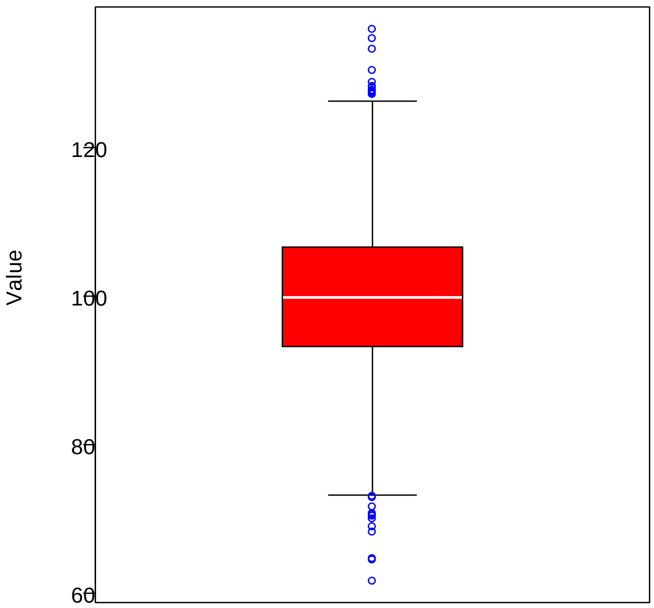
4.1.2 Maps

Maps are used to display the spatial distribution of the various inorganic chemical constituents of the groundwaters. 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

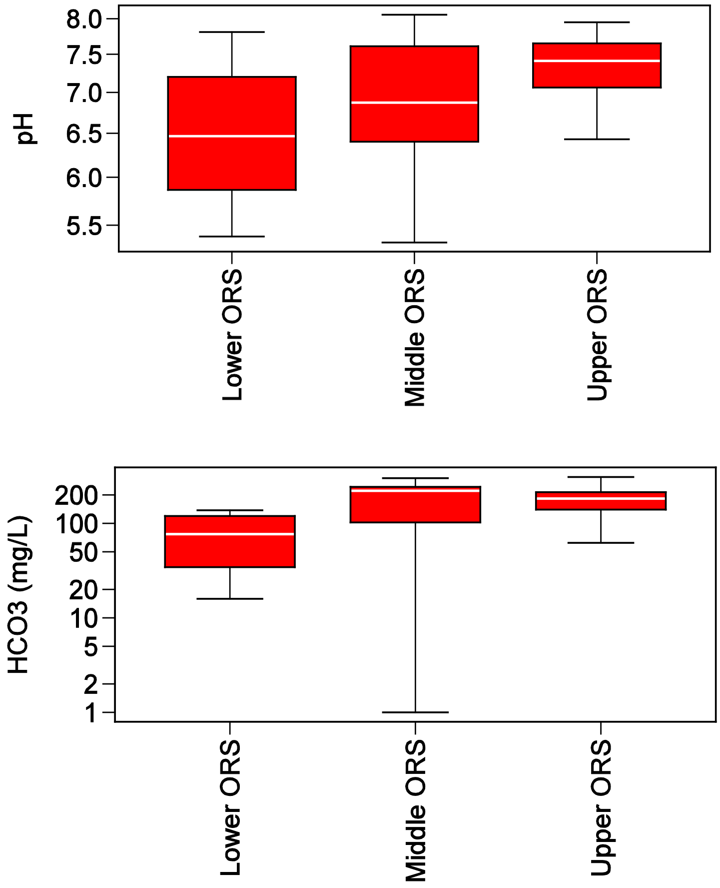
Box plots provide a quick graphical summary of the distribution of data values in a dataset and give an excellent way of comparing different values. They provide a rapid view of the central location of the distribution (the median), the spread of values (the interquartile range: box length) and the presence of outliers (open circles beyond the whiskers) (Figure 8). Note that the presence of outliers depends to some extent on the number of values summarised, as perfectly ‘normal’ distributions can show outliers if there are sufficient values within the distribution, as in Figure 9.

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


Value
120
100
80
60

4.2.1 pH and alkalinity

Groundwaters from the Middle Old Red Sandstone aquifer tend to have near-neutral pH; those from the Upper Old Red Sandstone aquifer tend to have slightly above-neutral pH. In both aquifers, bicarbonate concentrations tend to be around 100–200 mg/L (Figures 9 and 10). The four samples from the Lower Old Red Sandstone have more variable (particularly compared to the Upper Old Red Sandstone waters) and lower median pH values and bicarbonate concentrations. No strong spatial or geological pattern emerges from the data distribution (Figure 10): low pH values of less than 6.6 are seen in all three aquifer categories and all parts of the study area. Controls on pH and bicarbonate are likely to involve local variations in carbonate mineral content, and potentially the flow of groundwater through non-Devonian strata, particularly in areas close to the aquifer margins. Value of pH, and bicarbonate concentrations, are relatively high in reducing groundwaters (Section 4.2.2).



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 9 Box plots showing the distribution of pH and bicarbonate concentration (as log scale) in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

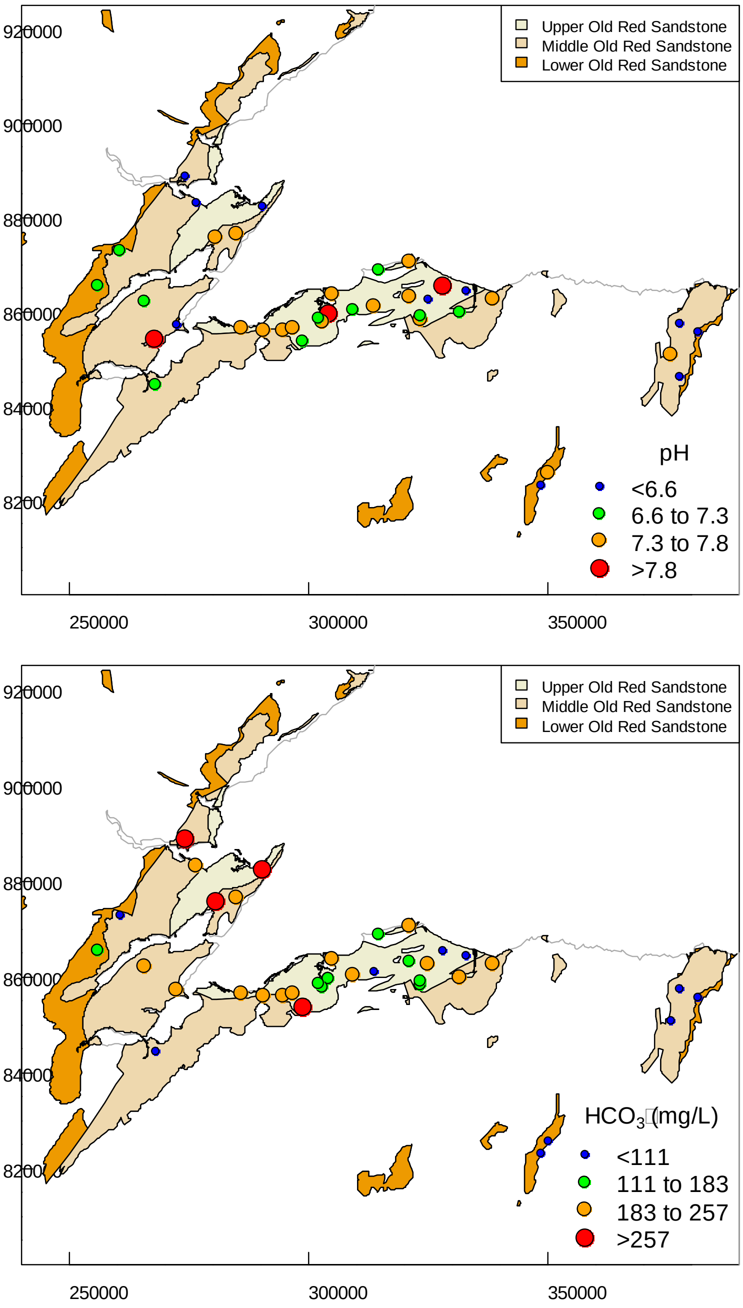
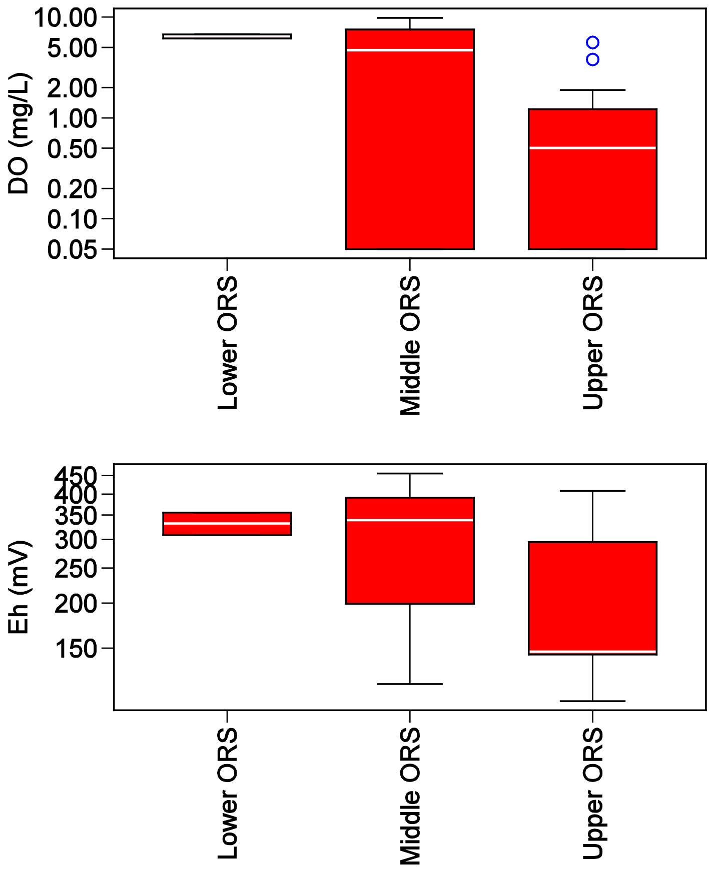


Figure 10 Maps showing the spatial distribution of pH and bicarbonate in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.2.2 Dissolved oxygen and Eh

Measured values of dissolved oxygen (DO) and Eh (Figure 11) indicate a large range in redox conditions across the aquifers. Concentrations of DO close to 10 mg/L (Eh above ~350 mV) indicate fully oxic conditions. By contrast, groundwaters with DO concentrations <1 mg/L and Eh values <250 mV are indicative of sub-oxic or mildly reducing conditions. These appear to be prevalent in much of the Upper Old Red Sandstone outcrop, and parts of the Middle Old Red Sandstone. The presence of reducing conditions may reflect the presence of low permeability layers (often marine) within the thick superficial deposits overlying the Old Red Sandstone strata; the mineralogy of the superficial and bedrock aquifers may also have an influence.

Data for DO and Eh are only available for two out of the four analysed samples from the Lower Old Red Sandstone. These samples are oxic (DO ~6 mg/L; Eh 300–360 mV) (Figure 11).



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

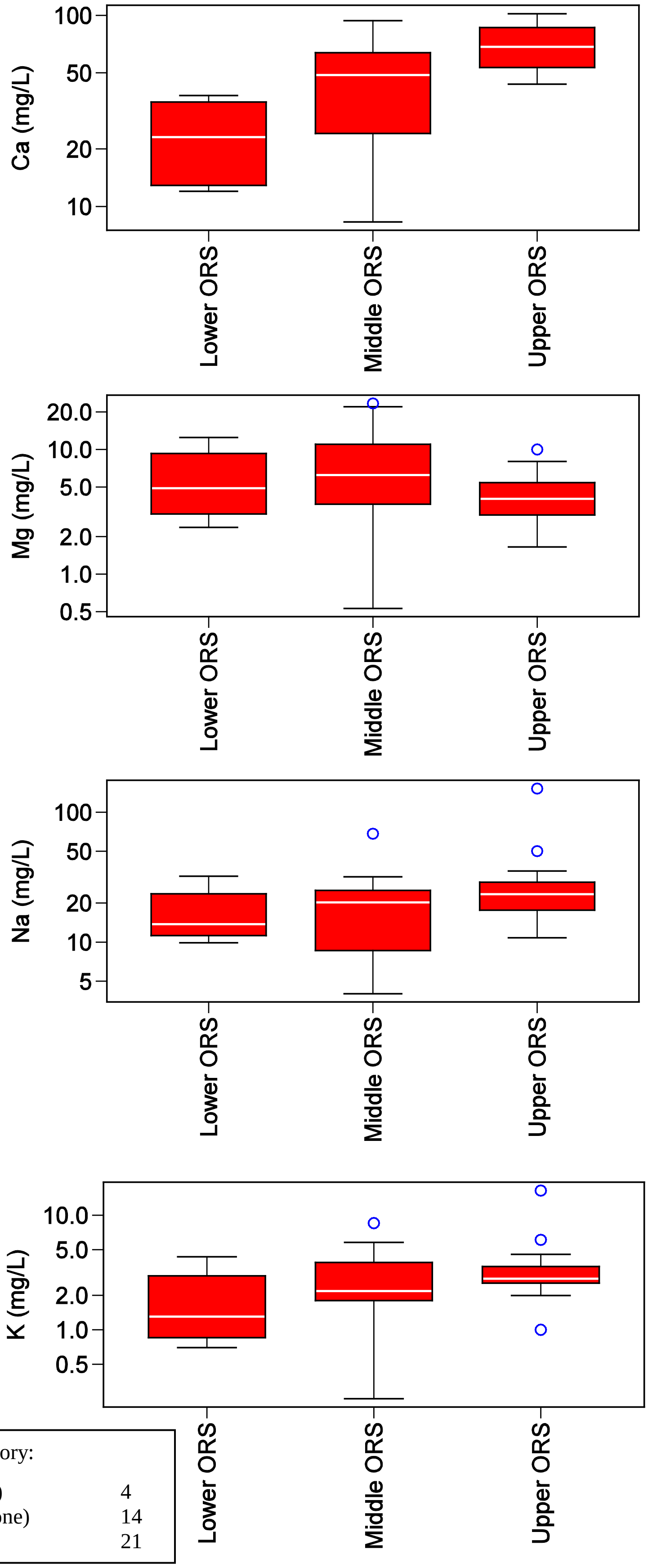
Figure 11 Box plots showing the distribution of dissolved oxygen (DO) and redox potential (Eh) in groundwaters from Old Red Sandstone aquifers in the Moray Firth area (log scale)

4.2.3 Major ions (other than bicarbonate)

Box plots for major cations (Figure 12) indicate that groundwaters from the Lower Old Red Sandstone have lower average Ca, Na and K concentrations than those from the younger two aquifers, but that average Mg concentrations are comparable across all three aquifer groups. Highest values of Mg (outliers) occur in groundwaters from the Middle Old Red Sandstone, and outliers of Na and K occur in groundwaters from the Upper Old Red Sandstone. The relatively low Ca concentrations in the Lower Old Red Sandstone groundwaters coincide with lower average pH values, and probably result from a paucity of carbonate minerals, which is also reflected in the lower $SI_{calcite}$ values for these groundwaters. All except one of the groundwater samples from the Lower Old Red Sandstone were strongly undersaturated with respect to calcite (Figure 13).

The spatial distribution of major cations is illustrated Figures 14 and 15. The spatial distribution in Na concentrations reveals some relationship with proximity to the coast. Concentrations above 33 mg/L are seen mostly in near-coastal sites (Figure 15). Contributions from marine aerosols or saline intrusion could be responsible for these relatively high concentrations, although the highest concentration observed was only 152 mg/L (sample 31). This would imply a relatively small seawater component in the groundwater, of the order of 1%. In a study of groundwater from superficial aquifers in the area MacDonald et al. (2007) found saline intrusion to the aquifer unlikely due to low ratios of Br/Cl that are inconsistent with widespread seawater intrusion.

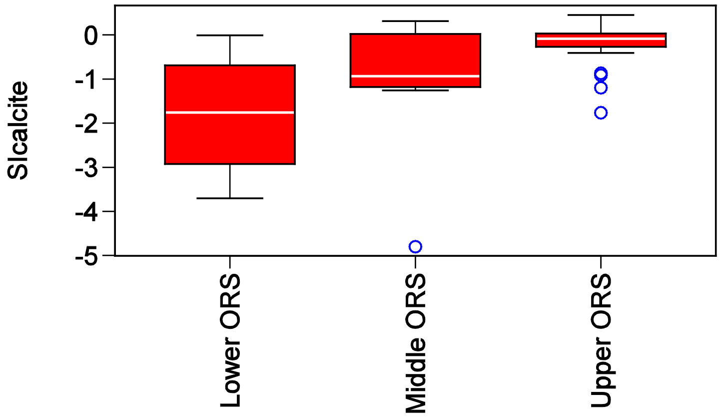
K concentration shows no clear spatial trend (Figure 15). Potential sources of K include clay minerals, feldspars and seawater, as well as pollutants such as NPK fertilisers.



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 12 Box plots showing the distribution of major cations (Ca, Mg, Na and K) in groundwaters from Old Red Sandstone aquifers in the Moray Firth area (log scale).



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 13 Box plot showing the distribution of calculated calcite saturation indices ($SI_{calcite}$) in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

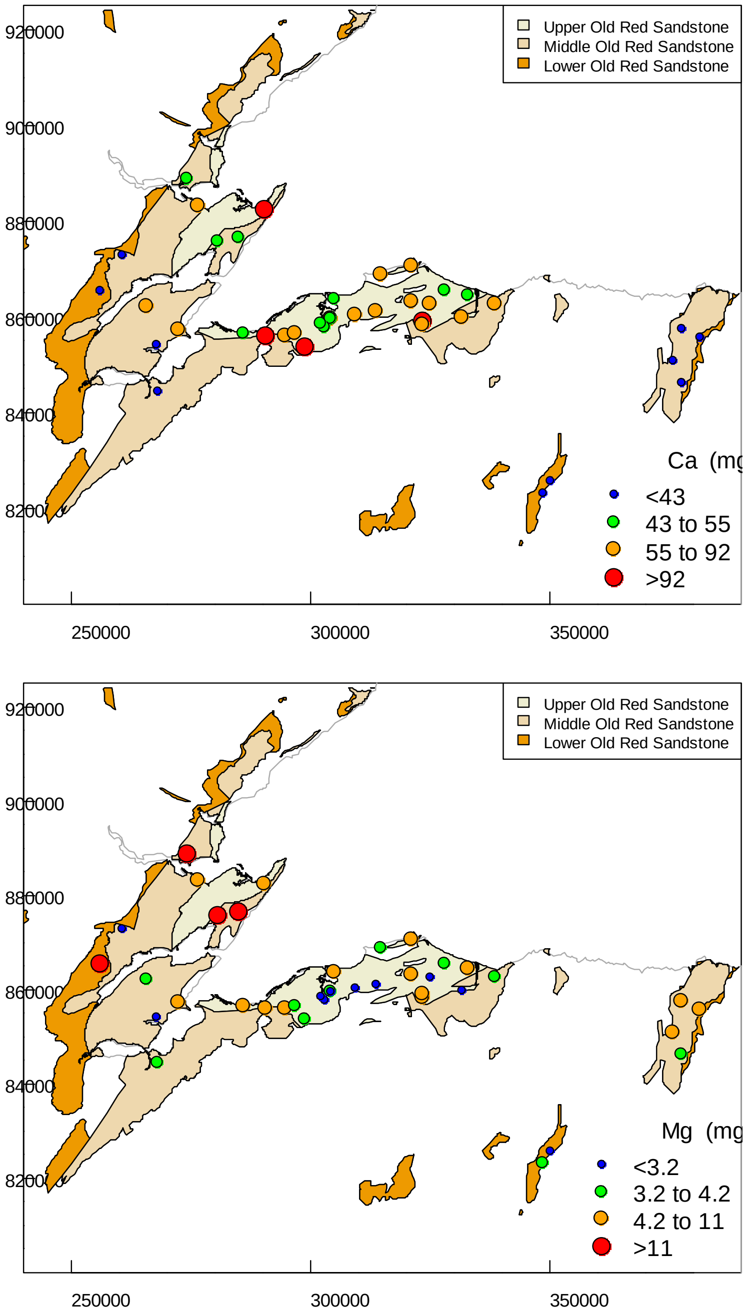


Figure 14 Maps showing the distribution of Ca and Mg in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

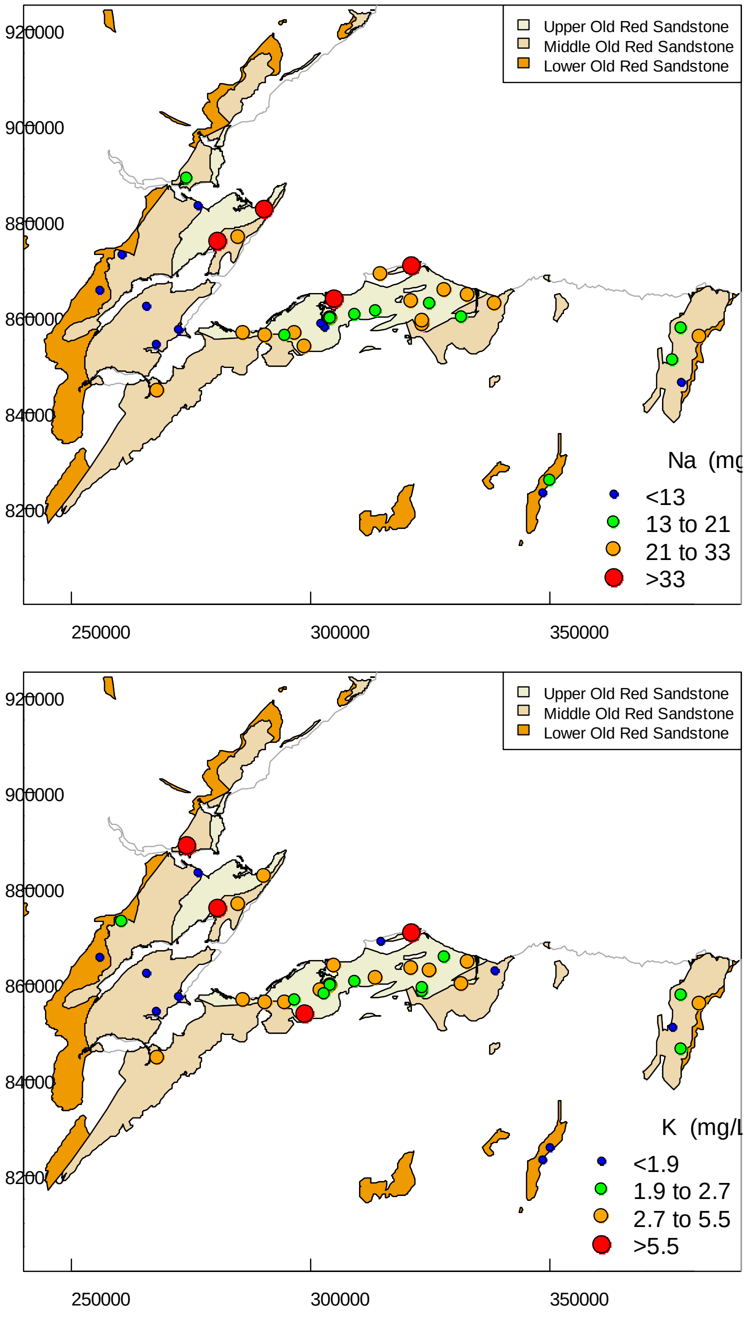
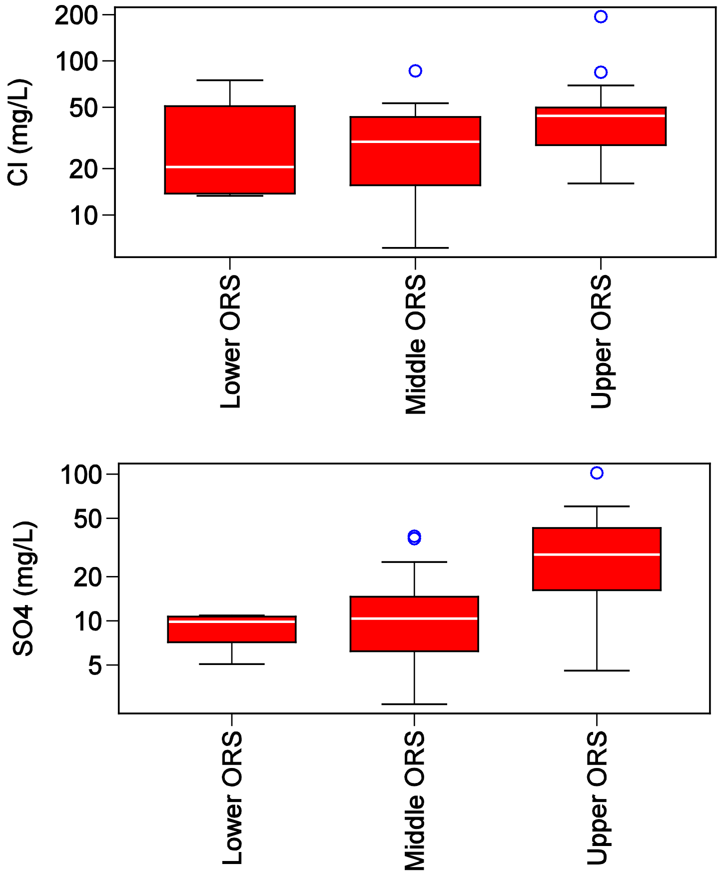


Figure 15 Maps showing the distribution of Na and K in groundwaters from Old Red Sandstone aquifers in the Moray Firth area



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 16 Box plots showing the distribution of chloride and sulphate concentrations in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

The highest observed Cl concentration (194 mg/L) occurs in the sample with the correspondingly highest Na concentration (sample 31), and is within a few hundred metres of the coast (Figure 17). The Cl concentration in this sample is also consistent with a minor seawater component (<1%). Groundwaters from the Upper Old Red Sandstone groundwaters show the highest median Cl (Figure 16).

Likewise, the highest concentrations and highest median value of SO_4 occur in groundwaters from the Upper Old Red Sandstone (Figure 16, Figure 17). A positive but weak correlation (r^2 = 0.2) exists between Cl and SO_4, although the sample with the highest concentration of SO_4 (102 mg/L; sample 30) is more than 5 km from the coast, and does not have the highest concentration of Cl. This suggests that a source or sources other than seawater are also contributing SO_4 to groundwater. Possible sources include sulphide minerals, gypsum and agricultural fertilisers.

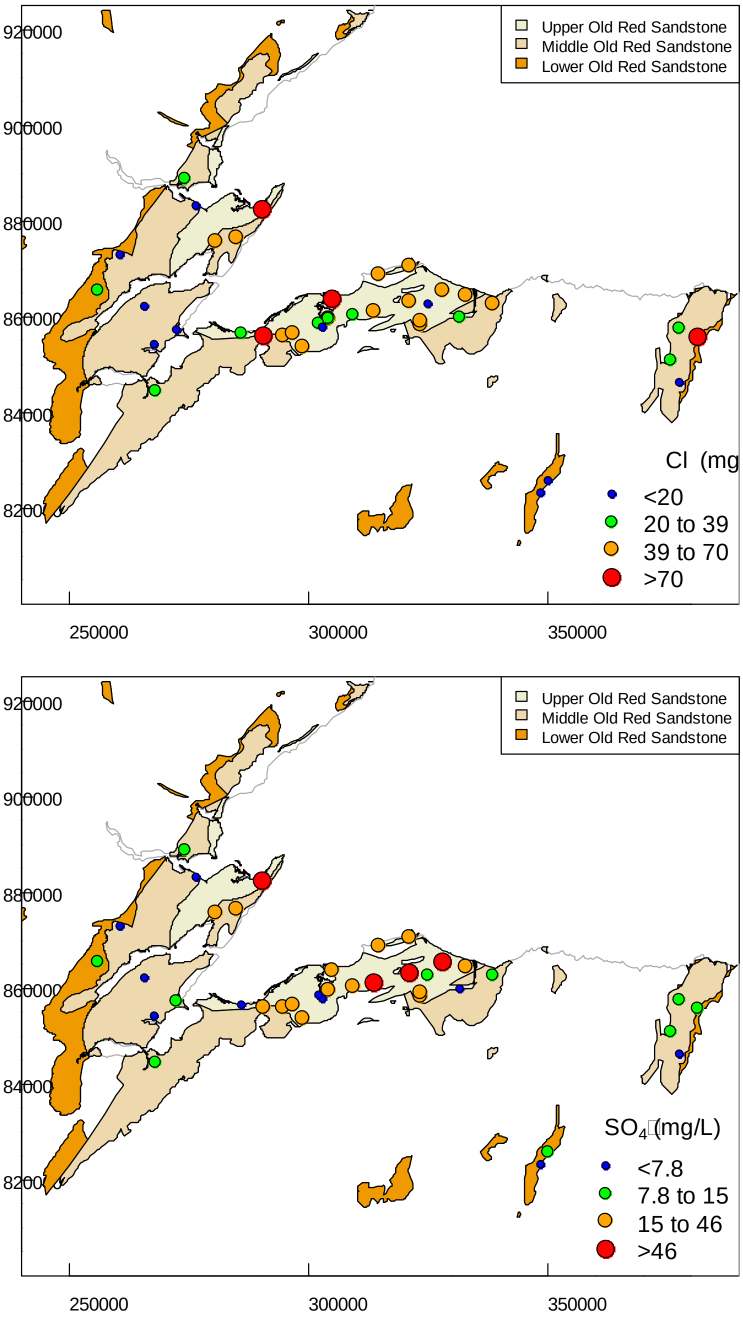
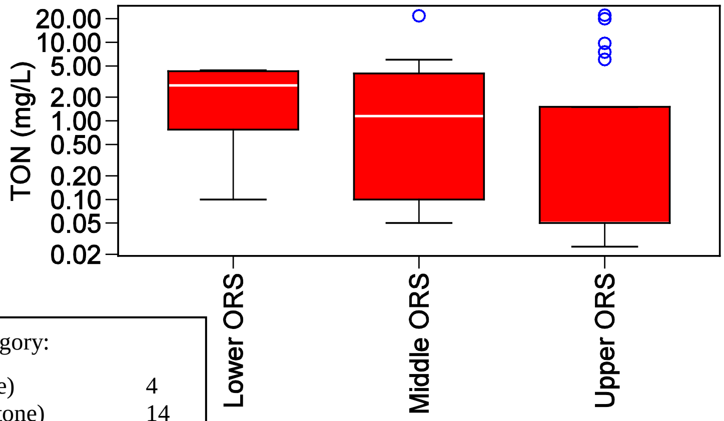


Figure 17 Maps showing the distribution of chloride and sulphate concentrations in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

There is a large range in observed nitrate concentrations, spanning four orders of magnitude (Figure 18). The highest median value occurs in groundwaters from the Lower Old Red Sandstone, consistent with the occurrence of oxic conditions in groundwaters from this unit. Some outlying high concentrations, up to 22.1 mg/L TON-N, also occur in groundwaters from the Upper and Middle Old Red Sandstone units (Figure 18). Such high concentrations are unlikely to be naturally derived, and most likely reflect inputs from nitrogenous fertilisers or slurry spreading. The distribution of nitrate by land use indicates that slurry spreading related to dairy, pig and poultry farming is a key input (Figure 19).

By contrast, a large proportion of analysed groundwaters have low concentrations, and the overall median is 0.3 mg/L TON-N. Low concentrations generally occur in the reducing groundwaters (evidenced by low DO and Eh values), and reflect the impact of denitrification and also possibly the influence of overlying Quaternary superficial deposits protecting the deeper groundwater from nitrate contamination.

In one sample, the concentration of NH_4-N is as high as 2.2 mg/L. This value is consistent with the local occurrence of more strongly reducing conditions. The NH_4 is most likely to be derived from degradation of organic matter, but there is no evidence whether this is from pollution or naturally derived.



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

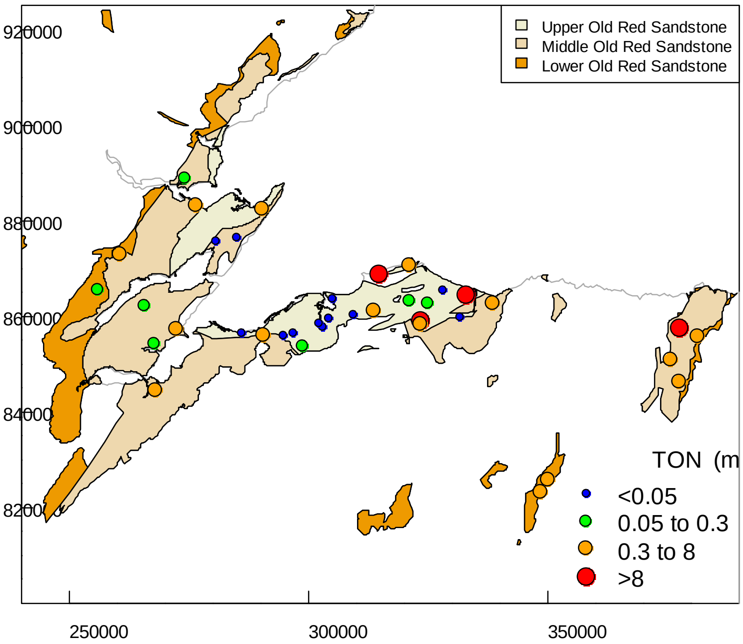
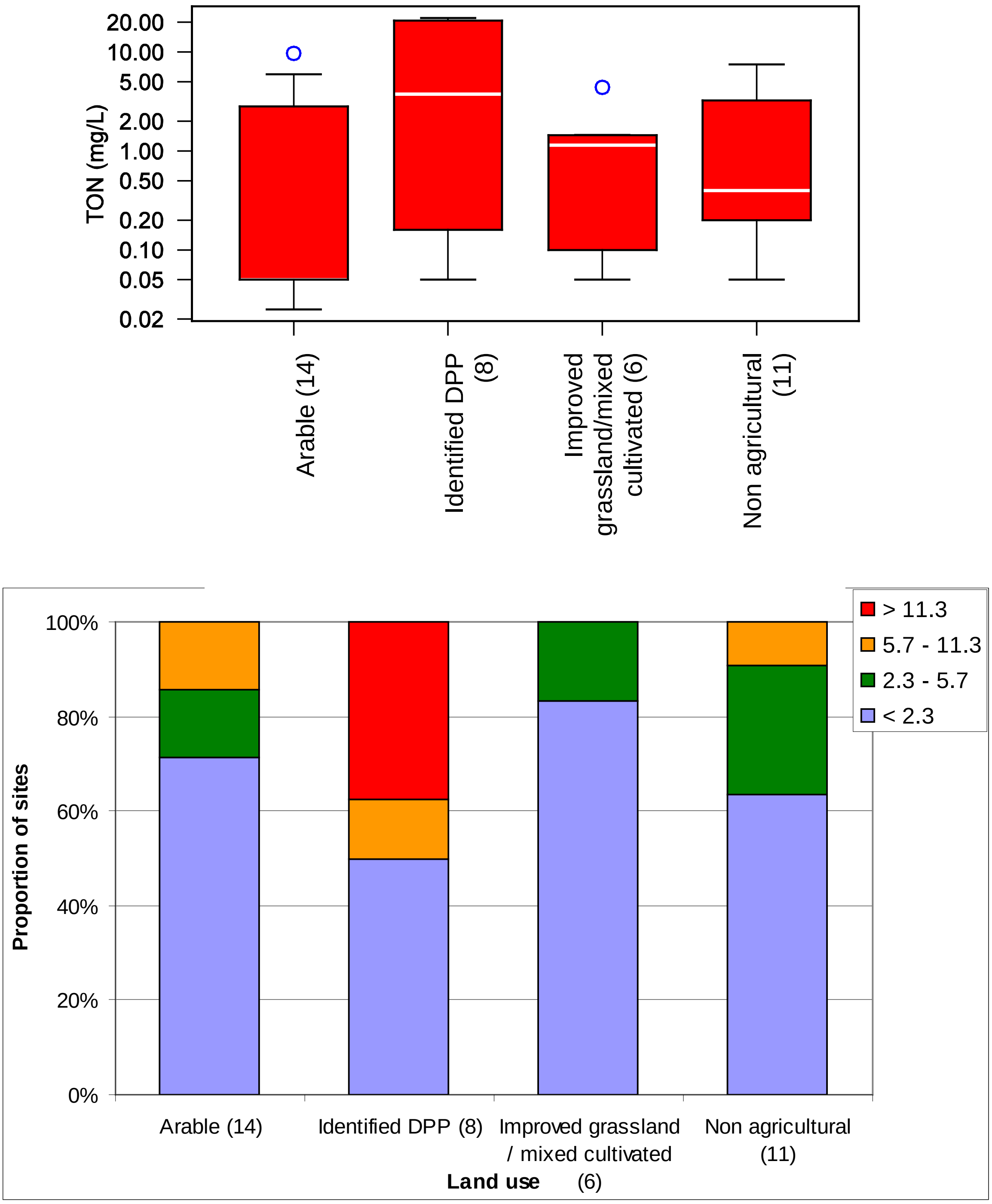


Figure 18 Box plot and map showing the distribution of nitrate (as TON-N: total oxidised nitrogen given as N) in groundwaters from Old Red Sandstone aquifers in the Moray Firth area



The number of samples in each land use class is shown in brackets.

Figure 19 Box plot and chart illustrating the variation in nitrate concentrations (as mg/L TON-N) in groundwater across land use classes, based on land use maps and field observations of the 200 m surrounding the groundwater source

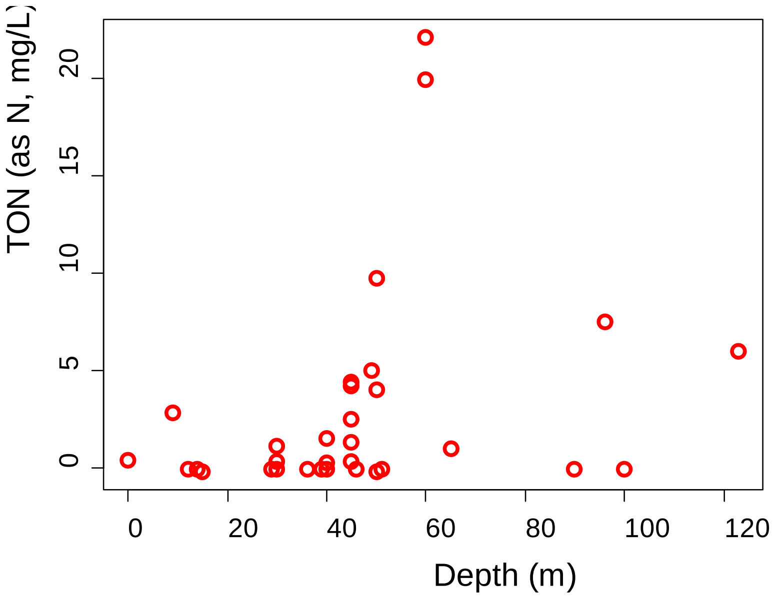


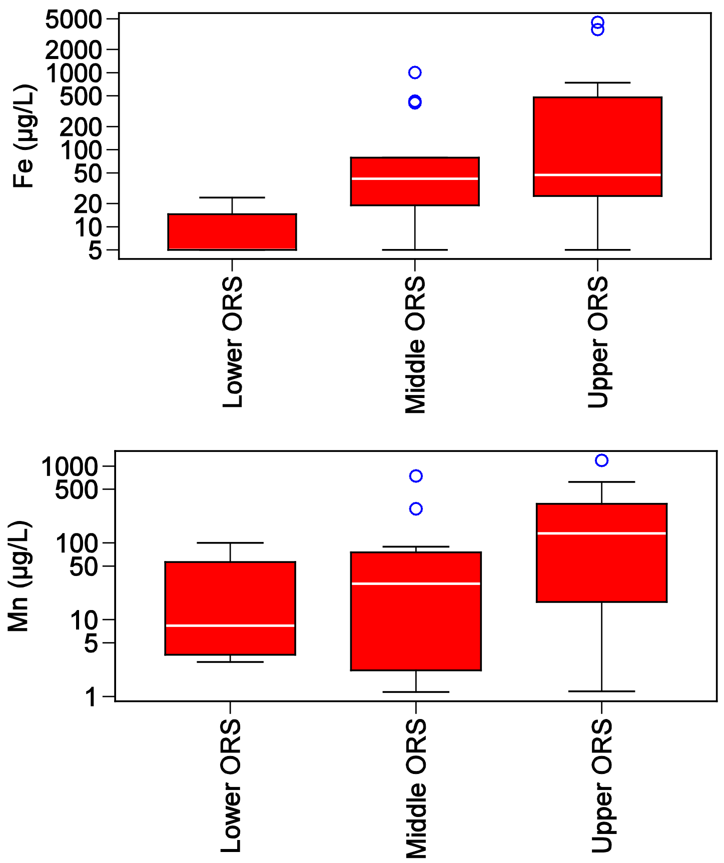
Figure 20 Variation in nitrate (TON) concentrations with measured source depth of groundwaters from Old Red Sandstone aquifers in the Moray Firth area.

The relationship between nitrate (measured as TON) concentration and borehole depth is variable, although relatively low concentrations (<4 mg/L TON-N) appear to be most common in shallow groundwaters (from groundwater sources less than 40 m deep) (Figure 20). The highest concentrations were seen in groundwaters from boreholes between 50 and 60 m deep. In common with much of the rest of Scotland, highest TON concentrations are found in areas with slurry spreading from dairy, pigs or poultry (Figure 19). However, the general correlation with land use is poor, and much weaker than found in other areas (MacDonald , 2005a). This is most likely explained by denitrification occurring in the groundwater which is much more likely to occur in the low oxygen conditions found throughout much of the area.

4.3 MINOR AND TRACE ELEMENTS

4.3.1 Iron and manganese

Concentrations of Fe and Mn also have a large range, each spanning four orders of magnitude (Figure 21). This reflects the large range in redox conditions across the aquifers. Under oxic conditions at near-neutral pH, the solubility of Fe and Mn oxides is low, and concentrations of dissolved Fe(II) and Mn(II) should be correspondingly low. Most of the groundwaters have near-neutral pH values and even those with the lowest pH values (5.3–5.4) have Fe concentrations below detection limits and relatively low Mn concentrations. Samples with the highest concentrations of dissolved Fe (>1000 µg/L) all occur in groundwaters with DO concentrations <1 mg/L (some substantially less) and Eh values <150 mV, indicating that the concentrations are strongly redox-controlled. Although concentrations of dissolved Mn are variable in the reducing groundwaters, high values (>400 µg/L) occur in groundwater samples with Eh <300 mV. Box plots show that concentrations of Fe are notably lower in the four groundwater samples from the Lower Old Red Sandstone aquifer, where conditions are oxic (Figure 21, Figure 11). The spatial distribution of Fe and Mn shown in Figure 22 indicates particularly high values in the Upper Old Red Sandstone between Inverness and Elgin and, for Fe, in Middle and Upper Old Red Sandstone in Easter Ross between Dingwall and Dornoch (for place names referred to in text see Figure 1).



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 21 Box plots showing the distribution of iron and manganese concentrations in groundwaters from Old Red Sandstone aquifers in the Moray Firth area. Concentrations are related to the redox conditions of the groundwater

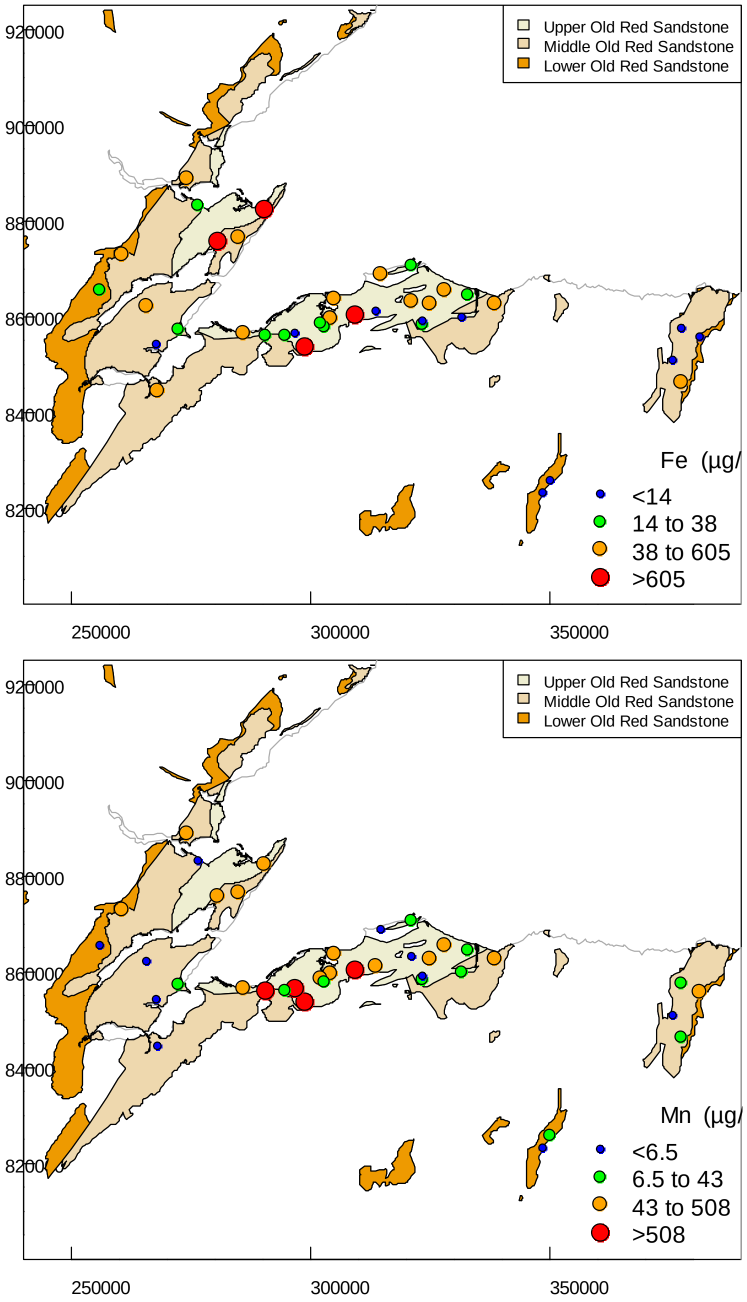
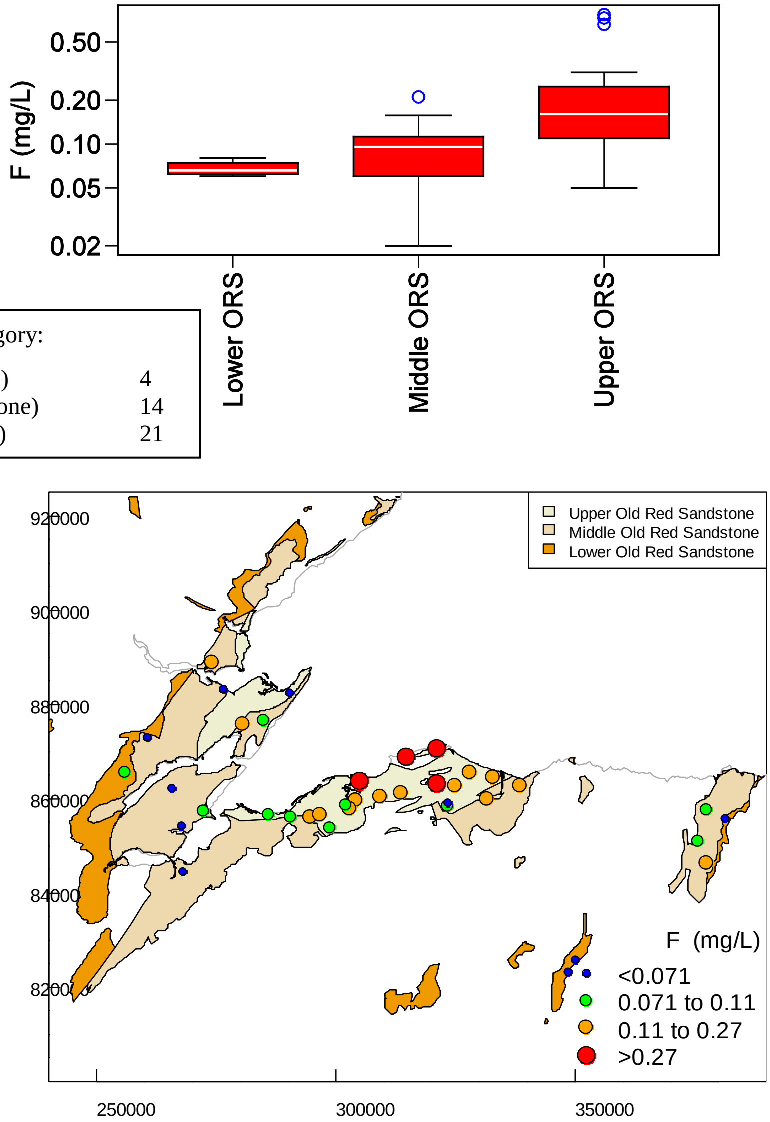


Figure 22 Maps showing the distribution of iron and manganese concentrations in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.2 Fluoride

Concentrations of dissolved F are universally low, the highest observation being 0.8 mg/L. Most samples have concentrations of less than 0.2 mg/L, and groundwaters from the Lower Old Red Sandstone have a particularly small range, with a median of 0.07 mg/L (Figure 23). Much of the solute F content is likely to be derived from mineral dissolution, with potential mineral sources including and detrital apatite and silicate minerals (pyroxene, amphibole, biotite). However, seawater is a potential additional source, either from saline intrusion or maritime rainfall, and relatively high F concentrations do appear in groundwater sources close to the Moray coast (Figure 23). All the groundwater samples are strongly undersaturated with respect to fluorite.



Number of samples in each category:

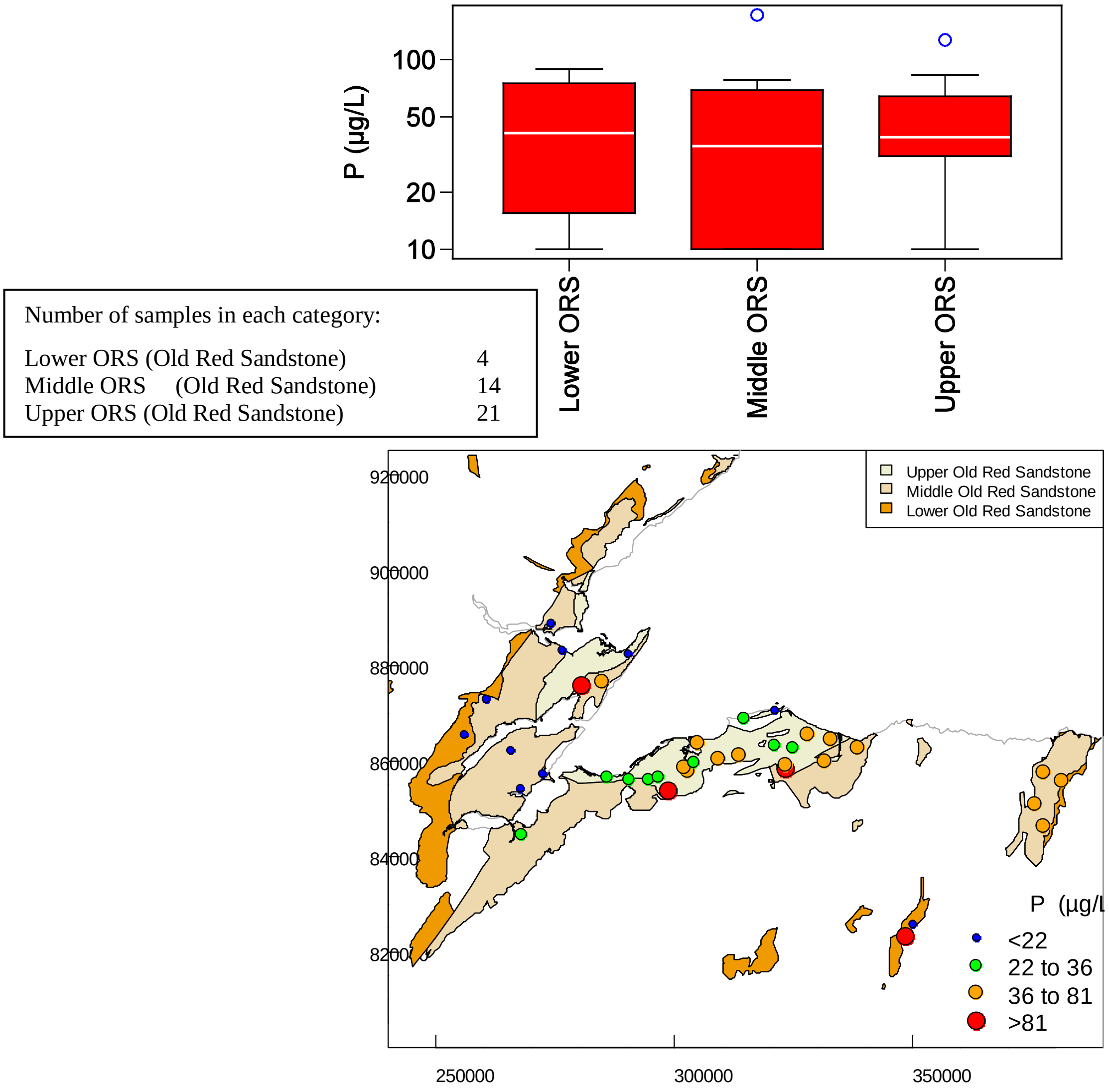
Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 23 Box plots and map showing the distribution of fluoride in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.3 Phosphorus

Concentrations of P are in most cases less than 100 µg/L (Table 5). Concentrations appear to be relatively low in the western part of the study area, apart from two outliers on agricultural land, and the spatial variation shows some relationship with that for F (Figures 23 and 24). Derivation of both elements from the dissolution of phosphate minerals in the aquifer rocks (e.g. apatite) may be partially responsible.

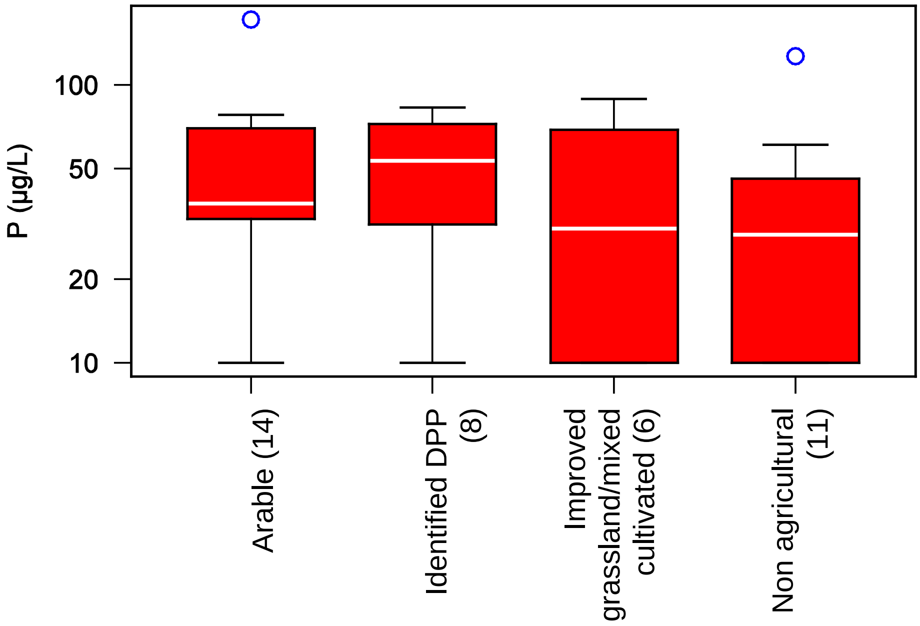
There is some evidence of a link between land use and P concentration, with the highest median P concentration seen in groundwaters from land identified as used for dairy, pig or poultry farming, and the highest outlier seen in a sample from arable land. The lowest median concentration is seen in groundwater from non-agricultural land. However, the pattern is complex and groundwater from non-agricultural land shows a wide range in P concentrations, and the second highest outlying value (Figure 25).



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 24 Box plots and map showing the distribution of phosphorus in groundwaters from Old Red Sandstone aquifers in the Moray Firth area



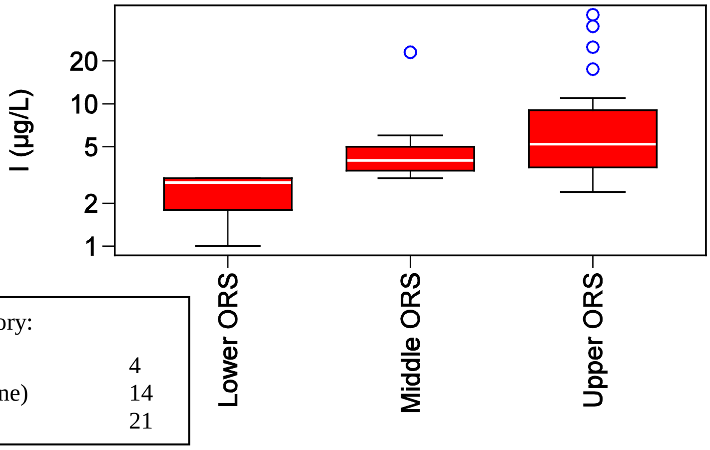
Data based on land-use maps and field observations within a 200 m diameter of the groundwater source.

The number of samples in each land use category is shown in brackets.

Figure 25 Variation in phosphorus concentrations (as µg/L-P) with land use in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.4 Iodine

Iodine concentrations are generally highest in the reducing groundwaters. The highest concentration observed (42 µg/L) occurs in the sample with the highest concentration of dissolved Fe (sample 28), and there is a broad though weak negative correlation between I and Eh. There is some evidence of a relationship between I and Cl, which suggests that a proportion of the total I is likely to be derived from maritime rainfall. Nonetheless, there is no clear spatial relationship between groundwater I concentrations and proximity to the coast (Figure 26). Potential mineral sources of I include clays and organic matter.



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

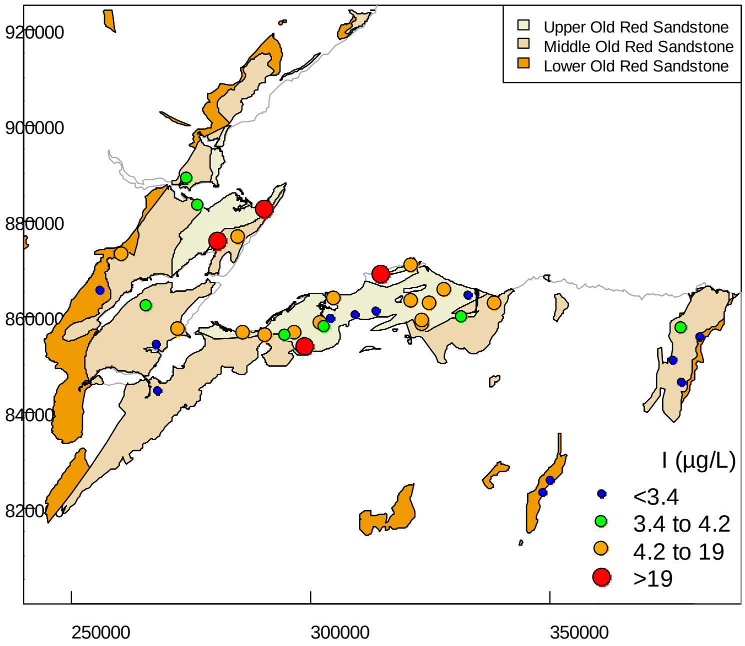
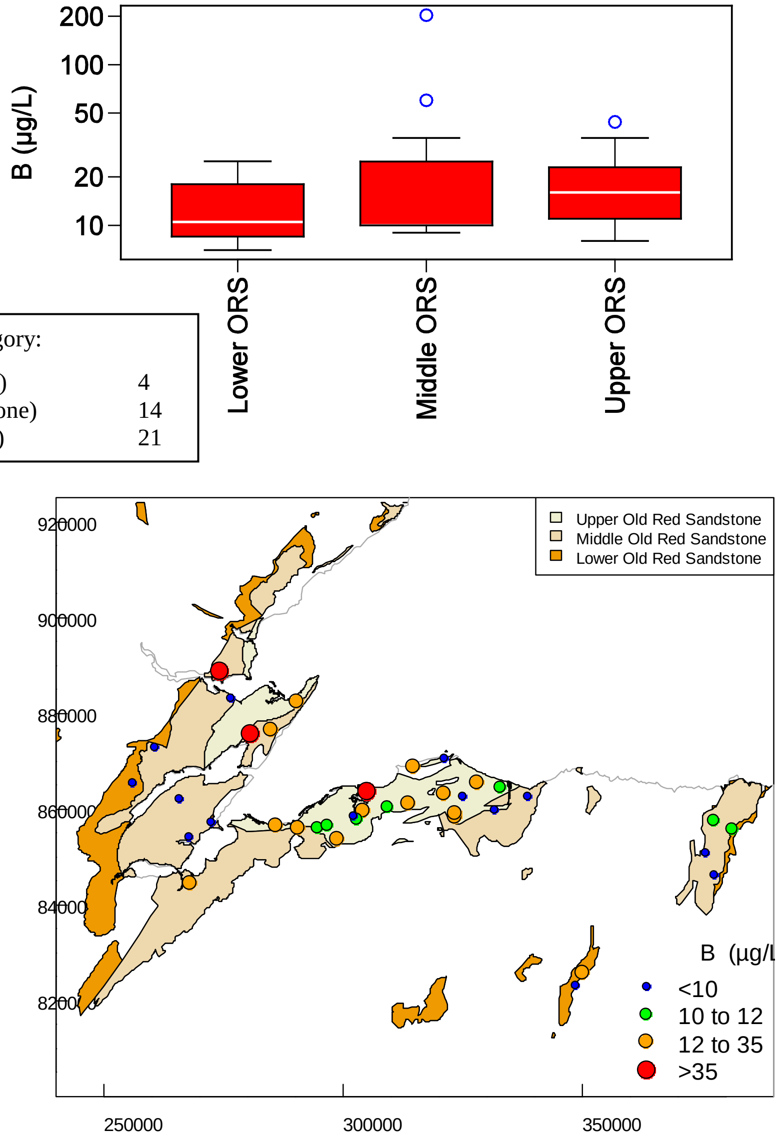


Figure 26 Box plot and map showing the distribution of iodine in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.5 Boron

With one exception (the maximum of 203 µg/L), concentrations of B are low, being usually in the range <20–30 µg/L. There appears to be little spatial trend (Figure 27). The highest concentration occurs in a sample with relatively high concentrations of Li, Sr and Rb (sample 13). Potential sources of B include clay minerals, although seawater also has relatively high B concentrations and some of the coastal sites could have a contribution from seawater. However, the correlation between B and indicators of salinity is poor.



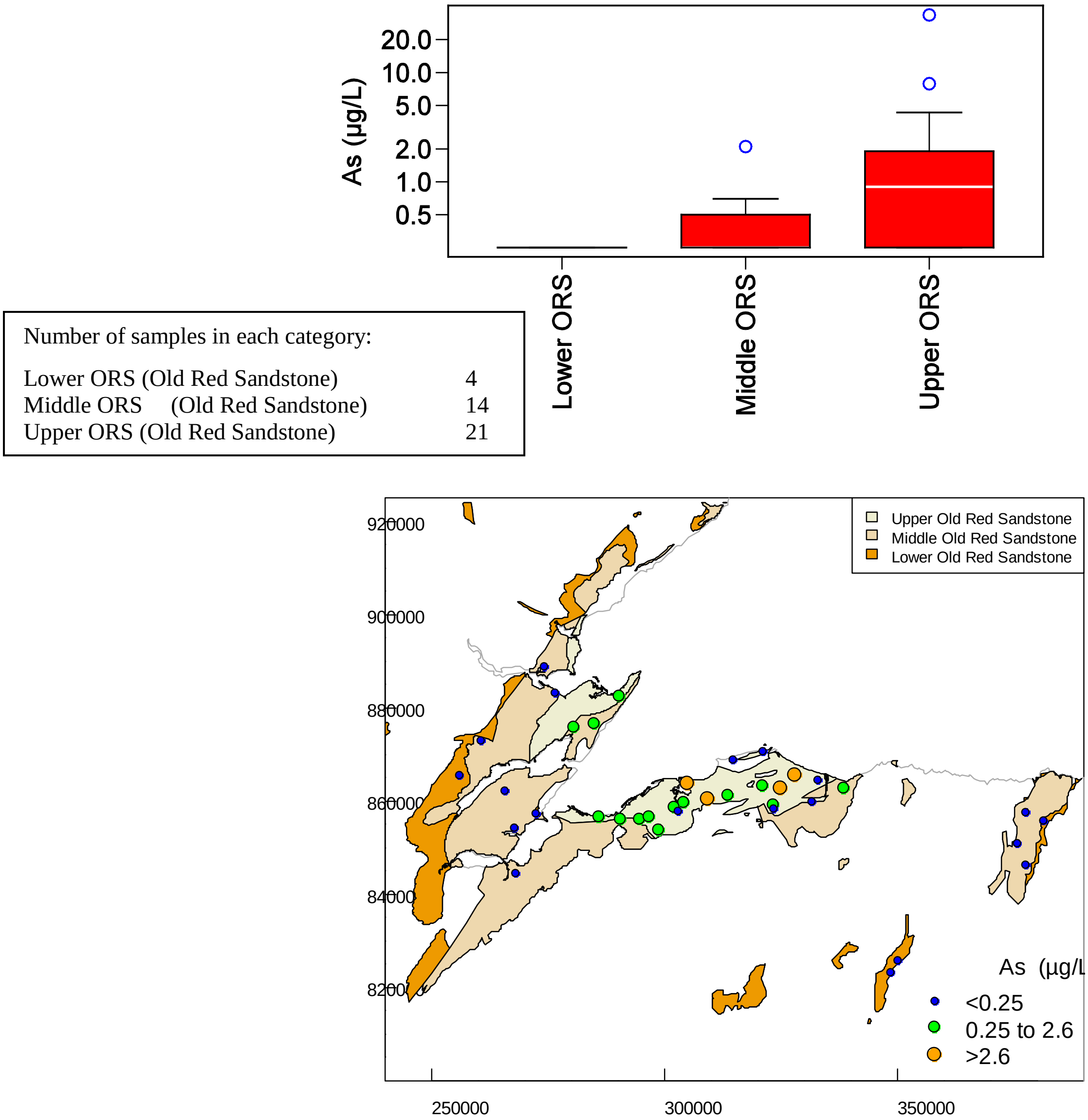
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 27 Box plot and map showing the distribution of boron in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.6 Arsenic

Most of the groundwater samples have As concentrations below detection limit (<0.5 µg/L). The highest observed concentration (33.6 µg/L) occurs in a reducing, high-Fe groundwater from the Upper Old Red Sandstone (sample 32). The most likely source of As in the groundwaters is from Fe oxides, with release occurring preferentially under reducing conditions. Concentrations in the Lower Old Red Sandstone are universally low (Figure 28), in line with the oxic conditions in this aquifer. Concentrations appear relatively high in the central part of the study area in groundwaters from the Upper Old Red Sandstone aquifer (Figure 28).



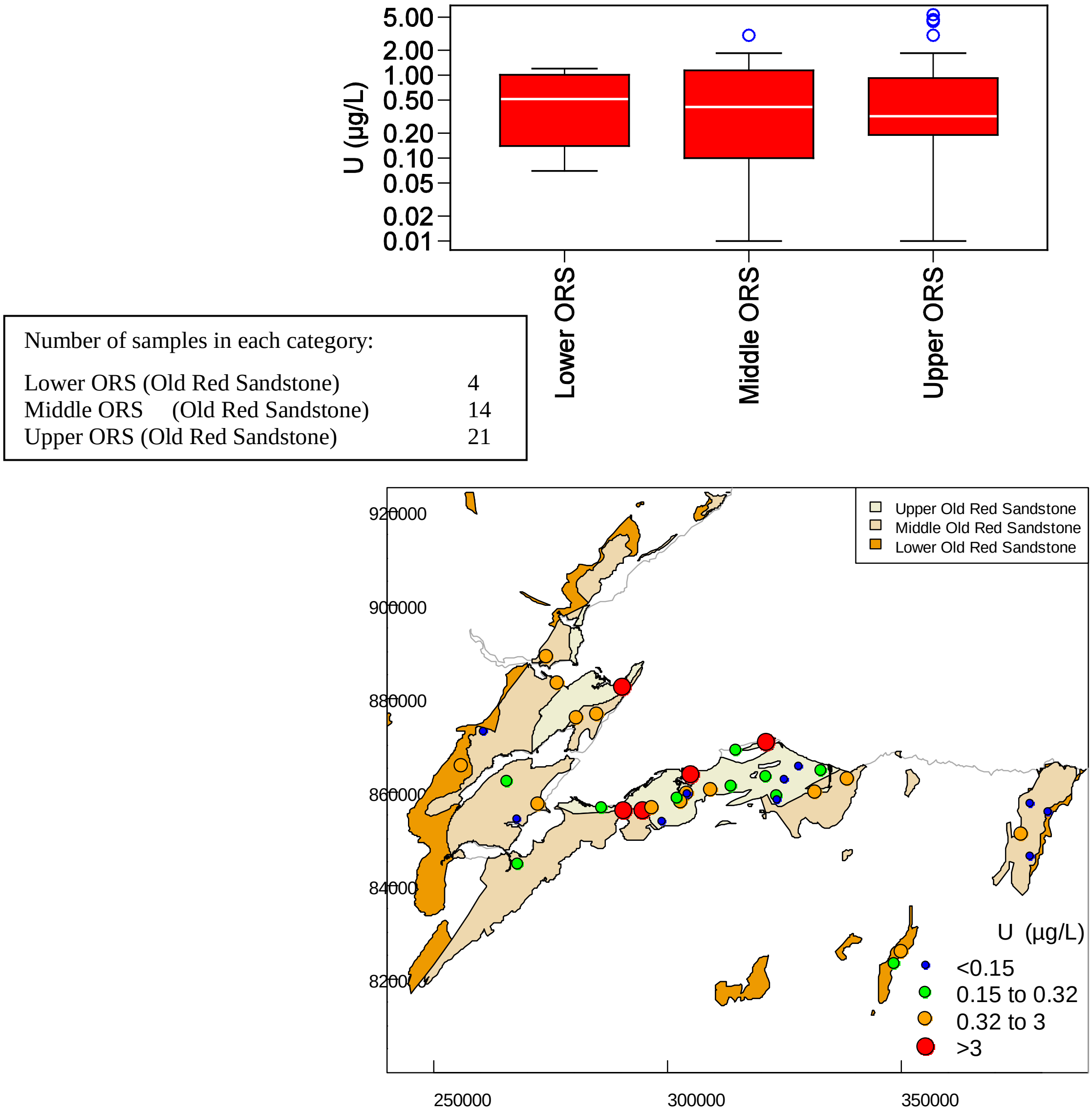
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 28 Box plot and map showing the distribution of arsenic in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.7 Uranium

Concentrations of U lie in the range <0.02 to 5.4 µg/L, with an overall median value of 0.32 µg/L (Table 3). High concentrations are most prevalent in groundwaters from the Upper Old Red Sandstone in the central part of the study area (Figure 29). A weak correlation exists between U and HCO_3 (and to some extent pH), indicating that U is preferentially mobilised in alkaline conditions. Dissolved U is likely to be stabilised in the groundwaters as U-carbonate complexes. Potential mineral sources of U include Fe oxides, clays and phosphate minerals.



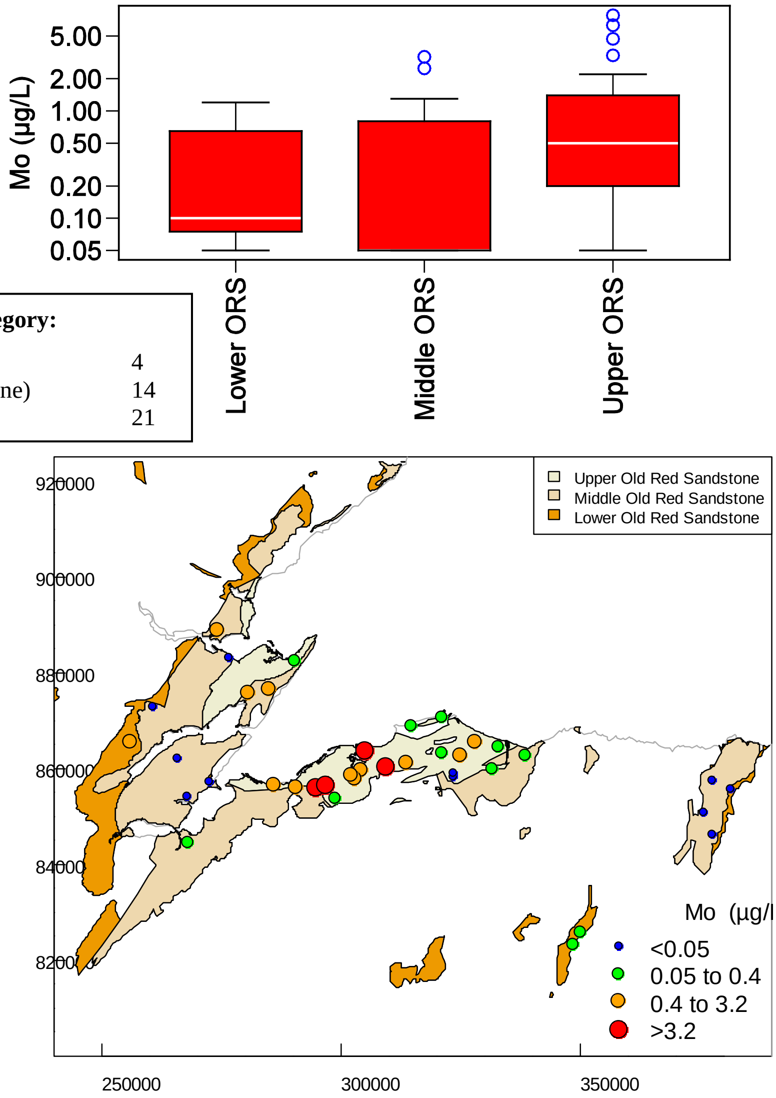
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 29 Box plot and map showing the distribution of uranium in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.8 Molybdenum

As with U, concentrations of Mo appear highest in groundwaters from the Upper Old Red Sandstone, and concentrations above 3 µg/L are located in groundwaters from this aquifer in the central part of the study area (Figure 30). A relationship also exists between Mo concentrations, pH and HCO_3. Concentrations of Mo above 3 µg/L occur in groundwaters with pH values above 7.2 and HCO_3 above 150 mg/L. The Mo is likely to be mainly derived by desorption from Fe oxides and clays in the aquifer rocks.



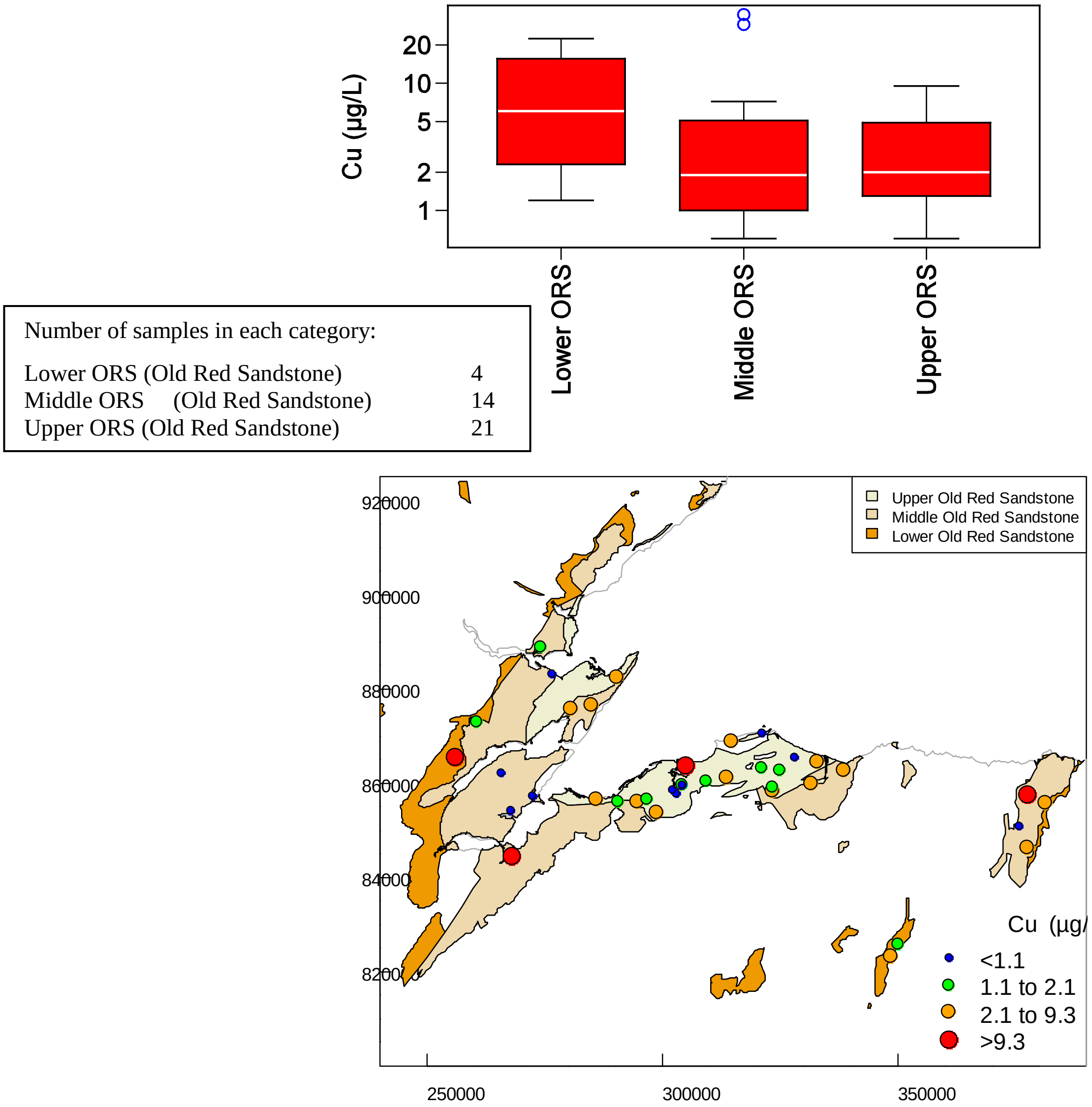
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 30 Box plot and map showing the distribution of molybdenum concentrations in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.9 Copper

Copper is detectable in all samples and concentrations vary from 0.6 to 35 µg/L. Relatively high concentrations, and the highest median value, are found in the groundwaters from the Lower Old Red Sandstone, although the highest outliers are seen in samples from the Middle Old Red Sandstone (Figure 31). Poor correlations exist with most other solutes, although high Cu values (>10 µg/L) are found in groundwaters with pH values ≤7 and low bicarbonate concentrations (<150 mg/L). Mobilisation of Cu is most favourable under acidic conditions, particularly through desorption from metal oxides.



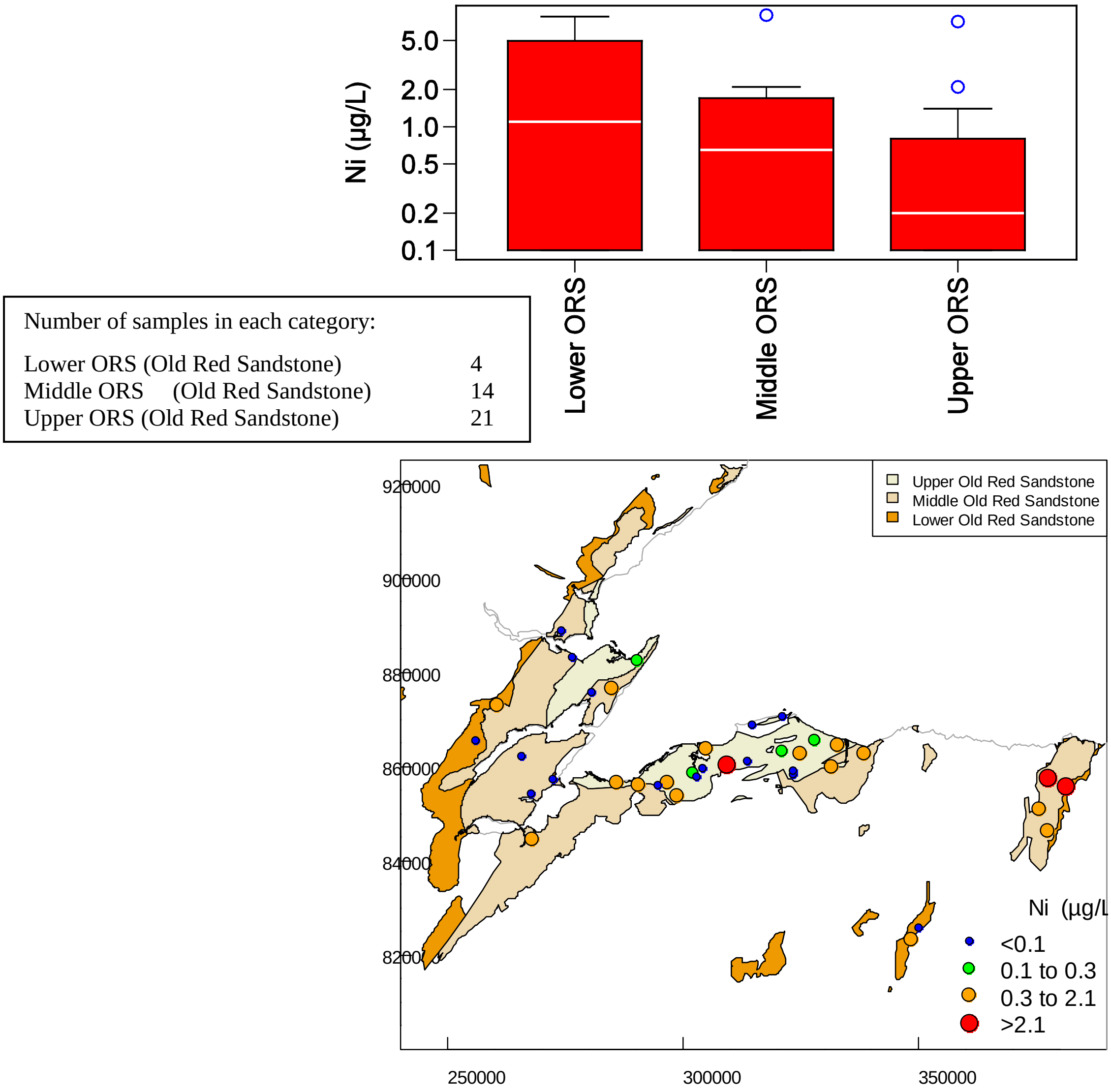
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 31 Box plot and map showing the distribution of copper concentrations in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.10 Nickel

Nickel varies from <0.2 to 8 µg/L. The highest median concentration is in groundwaters from the Lower Old Red Sandstone, but high outliers also occur in the other two aquifer categories (Figure 32). Potential sources of Ni include dissolution from iron oxides and sulphide minerals. The correlation between Ni and Cu is poor.



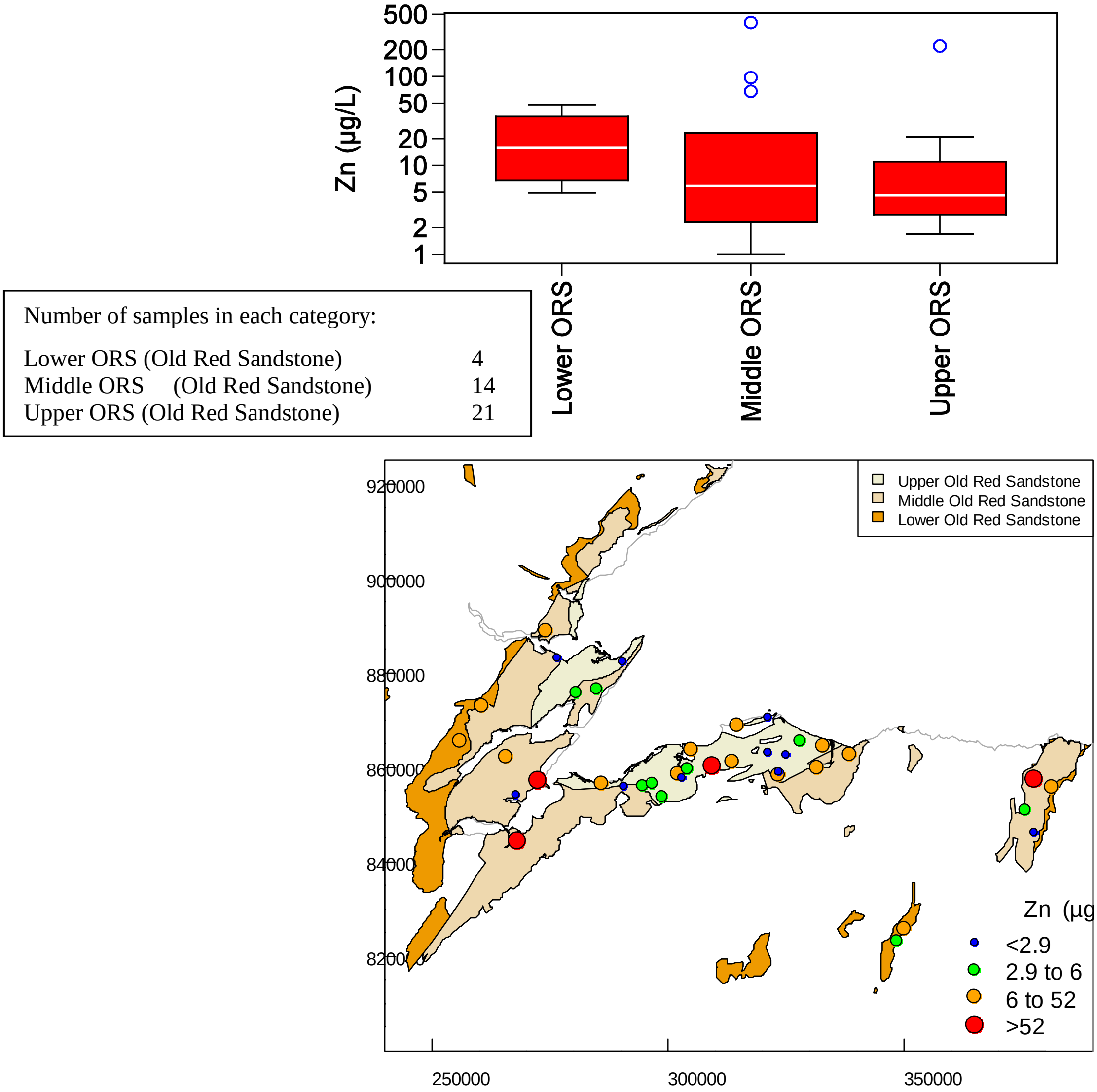
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 32 Box plot and map showing the distribution of nickel in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.11 Zinc

Zinc varies from 1 to 403 µg/L. The highest median Zn concentrations are seen in Lower Old Red Sandstone groundwaters, as for Cu and Ni, although the correlations between Zn and these metals is poor. High concentration outliers are also seen in Middle and Upper Old Red Sandstone groundwaters. No clear correlation exists with pH, although where pH values are greater than 7.4, Zn concentrations are universally <25 µg/L. It is likely that pH-dependent sorption plays a role in Zn mobility in these aquifers.



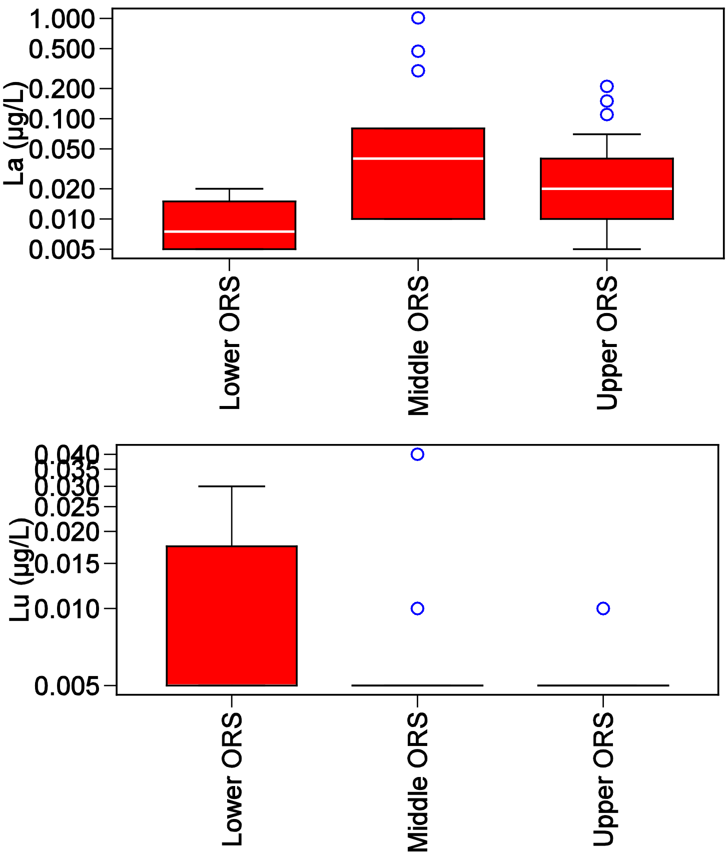
Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 33 Box plot and map showing the distribution of zinc in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.3.12 Rare earth elements

Concentrations of the rare earth elements (REE) are usually low and, especially the heavy REE, are often below detection limits. Concentrations of ∑REE range from <0.08 to 5.9 µg/L, although all except one sample has a concentration of <2 µg/L. Some relationship exists between REE concentrations and pH. For the heavy REE, highest concentrations occur in groundwaters with pH values <6.2. Correlations for the lighter REE are less clear. Box plots (Figure 34) show the variability in absolute concentrations of La (light REE) and Lu (heavy REE). Groundwaters from the Middle Old Red Sandstone show the highest median and maximum La concentrations (Figure 35).



Number of samples in each category:

Lower ORS (Old Red Sandstone)	4
Middle ORS (Old Red Sandstone)	14
Upper ORS (Old Red Sandstone)	21

Figure 34 Box plots showing the distributions of La and Lu in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

Box plots showing the distributions of normalised REE concentrations are shown in Figure 35. The data have been normalised to the ‘North Atlantic Shale Composite’ (NASC) using original data from Sholkovitz (1988). Normalisation counteracts the uneven distributions of absolute concentrations of neighbouring REE (odd/even atomic numbers) and produces a smoothed pattern. The box plots show the frequency of non-detect data, especially for the elements Tb, Ho, Tm and Lu. The plots also show a number of upper outliers with anomalous REE concentrations. These are typically the low-pH (pH <6.2) samples. The distributions indicate a relative enrichment in normalised heavy REE concentrations compared to light REEs, as is common in groundwaters (e.g. Nelson et al., 2004). Interquartile ranges for the light REE are particularly variable although there is a slight indication of a positive Eu anomaly in the data distribution. Primary source minerals are likely to include silicates such as micas and amphiboles as well as apatite. Excess Eu may have been derived from feldspar. Secondary sources likely include Fe oxides, either by desorption or reductive dissolution depending on ambient redox conditions.

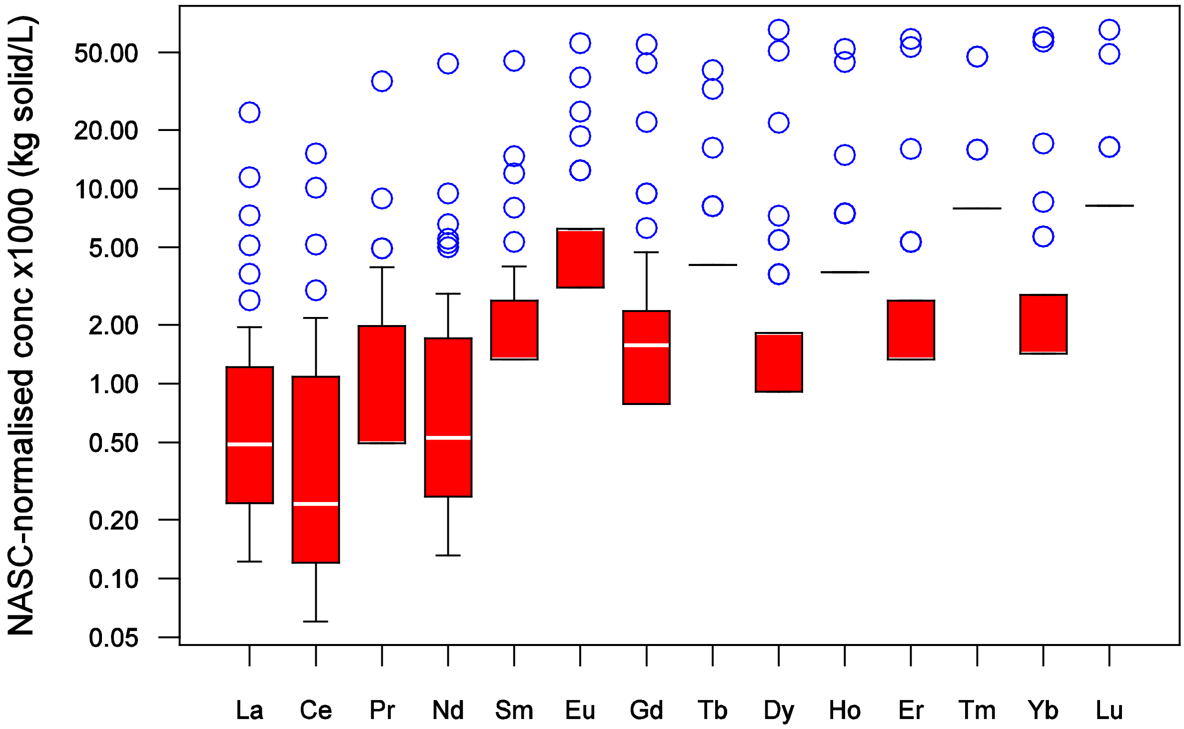


Figure 35 Box plot showing the distribution of the concentrations of REEs normalised according to the NASC ‘average shale’. Non-detects have been plotted as half-detection-limit values.

4.4 CUMULATIVE PROBABILITY PLOTS

Cumulative probability plots provide an additional view of the distribution of a range of element concentrations in groundwaters in the Moray Firth area (Figures 36–38). The x-axis is the $\log_{10}$ transformed concentration and the y-axis gives the probability of a value exceeding a given concentration, plotted on a normal probability scale. The log transform is used 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 subdivided into the three aquifer groups, the limited number of samples for the Lower Old Red Sandstone in particular (4 samples) means that the steps in the plotted distributions would be coarse. The data for all 39 samples have therefore been plotted as a single population.

The plots clearly show the variation in the median concentrations (the points at which the probability is 0.5) between different elements. The slopes of the lines give a measure of the variation (or standard deviation) of the subset of data. Steep slopes may, for instance, indicate a mineral solubility limit on the dissolved concentrations. The straightness of the lines gives an indication of the extent to which the distribution conforms to being log-normal. In addition, 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 samples. Since there is no law of nature 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 probability distribution. This would require more information, including a model for what controls 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 concentration range. 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. However, in all cases, the distributions of data below the analytical detection limits have been modelled using the 'regression on order' statistics (ROS) method.

4.4.1 Major elements

Probability plots for most of the major ions (Figure 36) show nearly parallel distributions, but with a slightly gentler slope and an inflexion close to the median value for SO_4, possibly reflecting multiple sources for this ion. Most ions have near-linear distributions, but high-concentration tails are seen in the curves for K, Mg, SO_4, Na and Cl. This is likely to be due to inputs of saline water from saline intrusion or marine aerosols. One sample with low bicarbonate concentration (and a pH of 5.3) is clearly seen in the data distribution for HCO_3.

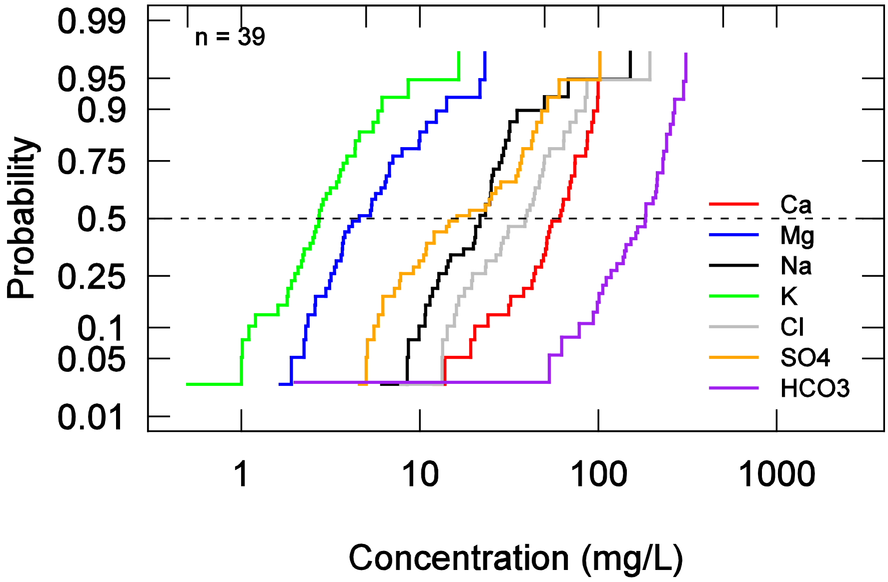


Figure 36 Cumulative probability plots for eight major elements in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.4.2 Minor elements

Cumulative probability plots for a number of minor elements are presented in Figure 37. The particularly large range observed for NH_4-N is attributed to multiple detection limits, and one high-N sample (NH_4-N of 2.2. mg/L). Most samples have concentrations below the detection limit, but high concentrations are observed in some of the reducing groundwaters. The range of Si concentrations is comparatively small, as shown by the steep slope of the line. Most of the samples are saturated with respect to quartz, and this is probably the main control on dissolved Si concentrations.

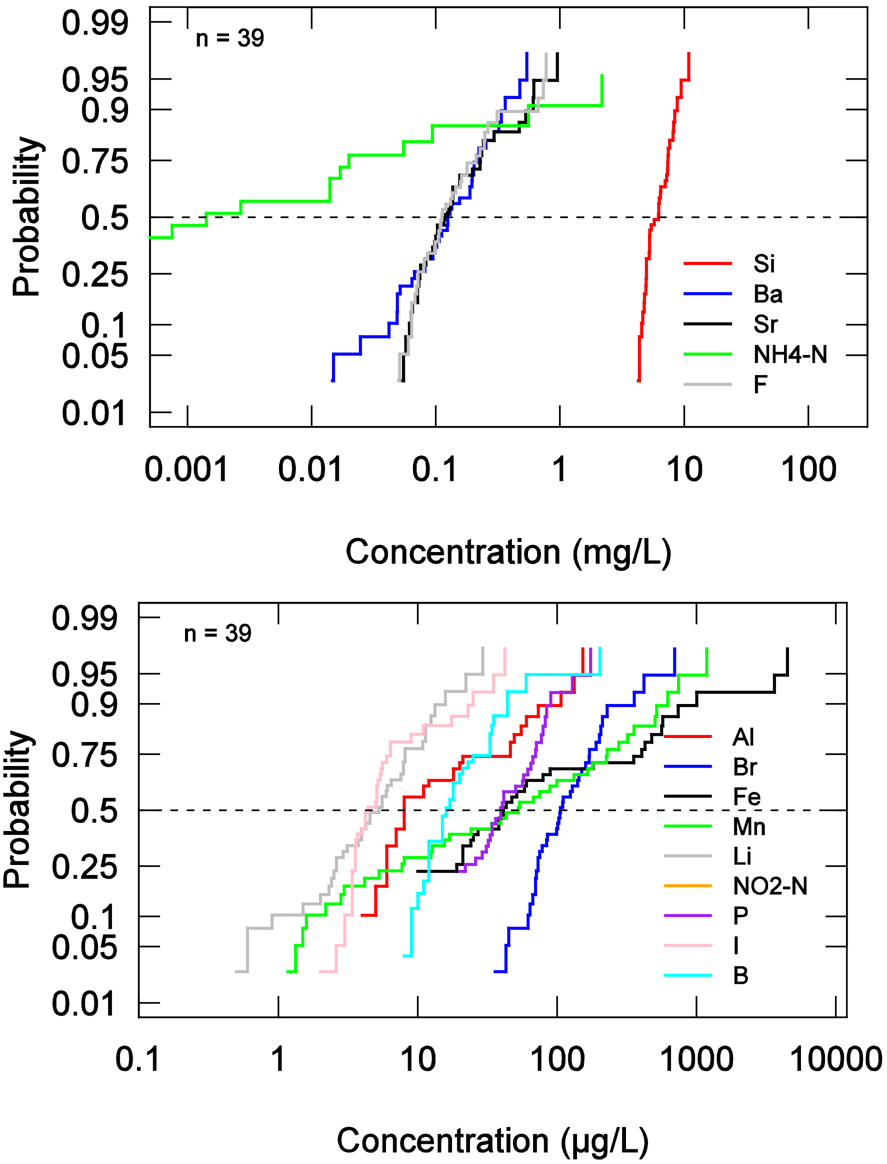
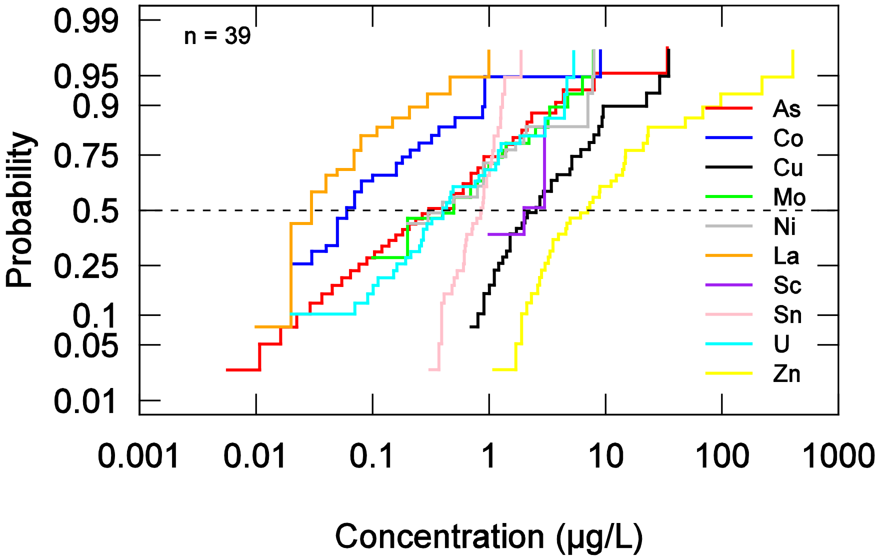


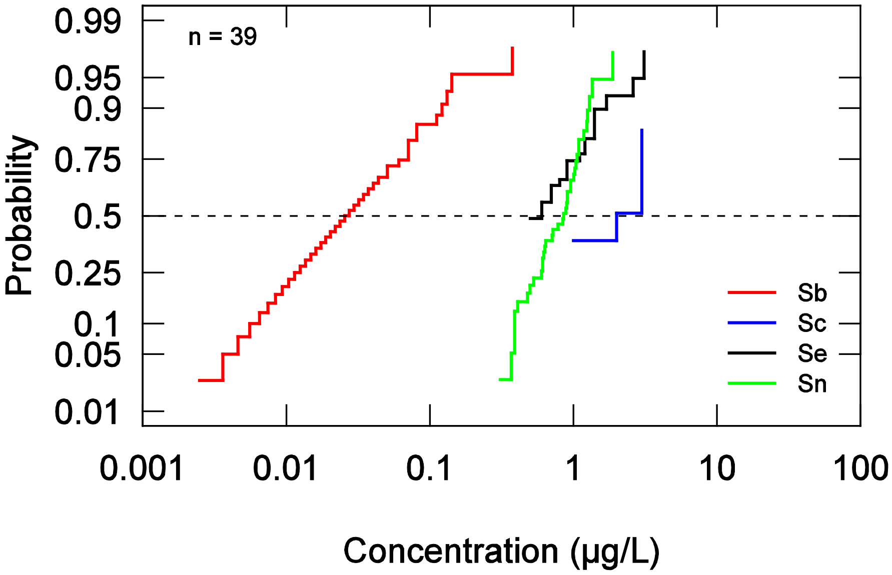
Figure 37 Cumulative probability plots for selected minor elements in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

The probability plots for Fe and Mn (Figure 37) show a comparatively large range, which is in response to the variable redox conditions across the aquifers. A few samples have very high concentrations of Fe, up to a maximum of 4.5 mg/L. Boron shows a pronounced tail at the high-concentration end, which is also likely to be in response to inputs of saline water in some near-coastal samples.

4.4.3 Trace elements

The non-linear trends for Zn, La and Y, and to some extent Cu (Figure 38) reflect the influence of a few high concentrations of these elements, probably due to increased solubility in low-pH samples. Most samples have As concentrations below detection limit (for this, the low concentration distribution has been estimated using the ROS method). One high-As sample has created in a distinct step at the high-concentration tail of the plot. The ROS linear regression method has also been used to estimate distributions at low concentrations for Sb W, and Tl, creating the linear stepped pattern.





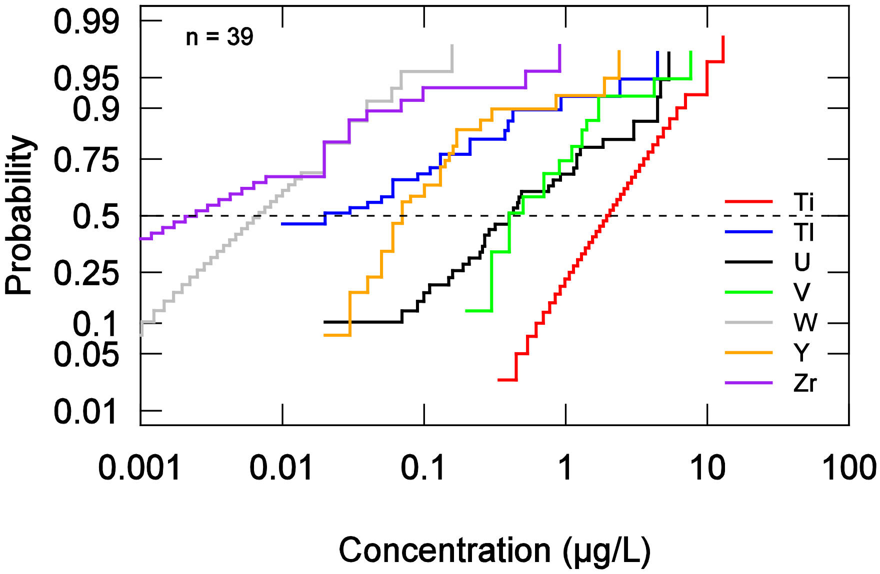


Figure 38 Cumulative probability plots for selected trace elements in groundwaters from Old Red Sandstone aquifers in the Moray Firth area

4.5 ENVIRONMENTAL TRACERS

4.5.1 Stable Isotopes

The fairly depleted (negative) isotopic compositions of the Moray Firth groundwaters (Figure 39) are largely as would be expected for this part of Scotland (Darling , 2003). Most of the samples are derived from sources at less than 50 m elevation (AOD) (Figure 40), and have a relatively restricted range of isotopic composition. The typical UK lapse (depletion) rate of around –0.3‰ $\delta^{18}O$ per 100 m rise in elevation is also shown in Figure 40. Samples falling on or near this assumed depletion line are assumed to consist mainly of recharge at a similar elevation to the sampling point, and are therefore likely to be local in origin. Samples falling to the left of the line are likely to represent recharge derived from higher elevations than the sampling point. Two sites from the Turriff outlier do not conform to either scenario, being significantly less negative (Figures 40 and 41). In their case, it is likely that the sampled groundwater is derived from poorly-mixed, probably very recent recharge.

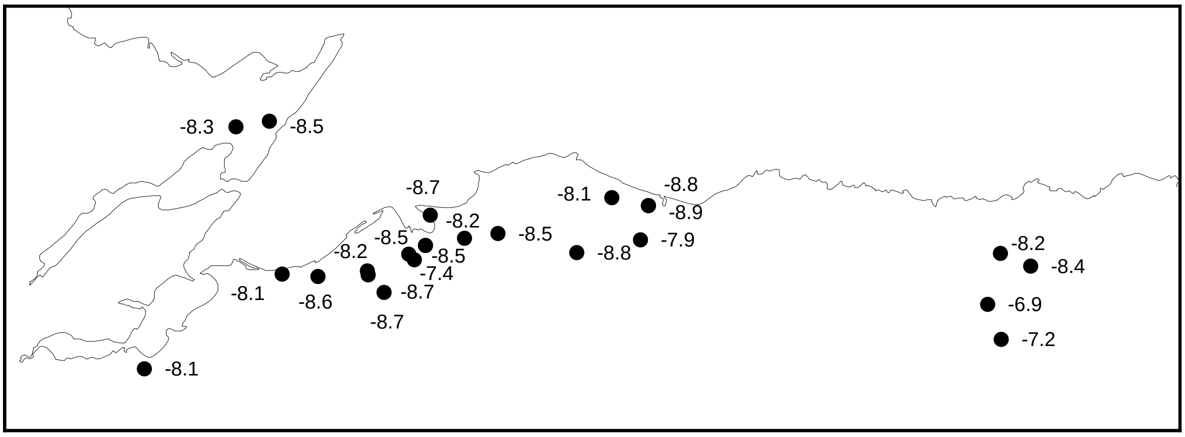


Figure 39 Values of $\delta^{18}O$ for groundwaters in Old Red Sandstone aquifers in the Moray Firth area

The co-plot of $\delta^{18}O$ against $\delta^{2}H$ (Figure 41) shows a large range of compositions for the groundwaters from the Middle Old Red Sandstone. This is consistent with the larger range of major ion concentrations in these samples, with higher concentrations of Na, Mg, Cl, and SO_4 indicating a small contribution from saline water. The Old Red Sandstone groundwaters lie on a mixing line towards a seawater isotopic composition, reflecting inputs from saline intrusion and/or marine aerosols. The samples plot close to, but mostly above, the World Meteoric Water Line (MWL), with slightly enriched $\delta^{2}H$ compositions relative to $\delta^{18}O$. The freshwater end-member is likely to be local rainfall recharge (meteoric water).

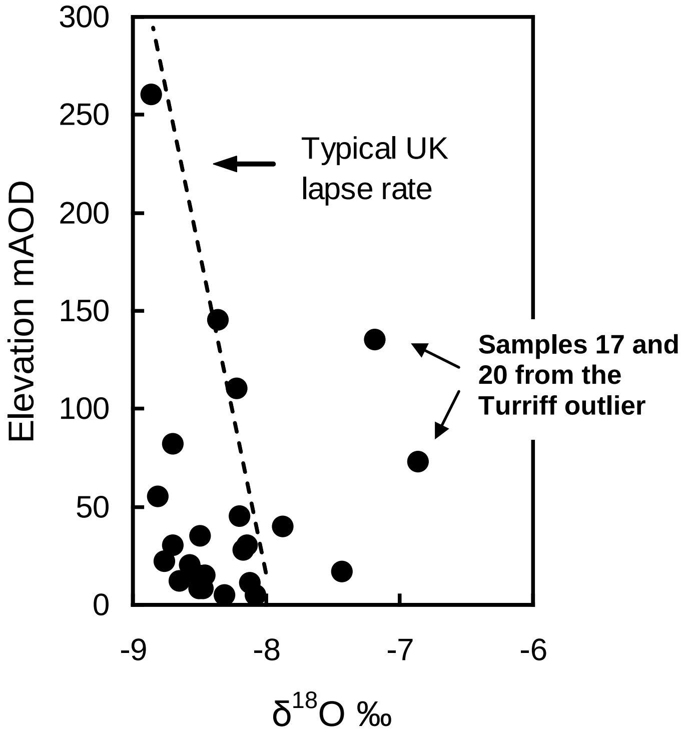


Figure 40 The relationship between δ^{18}O and sample elevation for groundwaters in Old Red Sandstone aquifers in the Moray Firth area

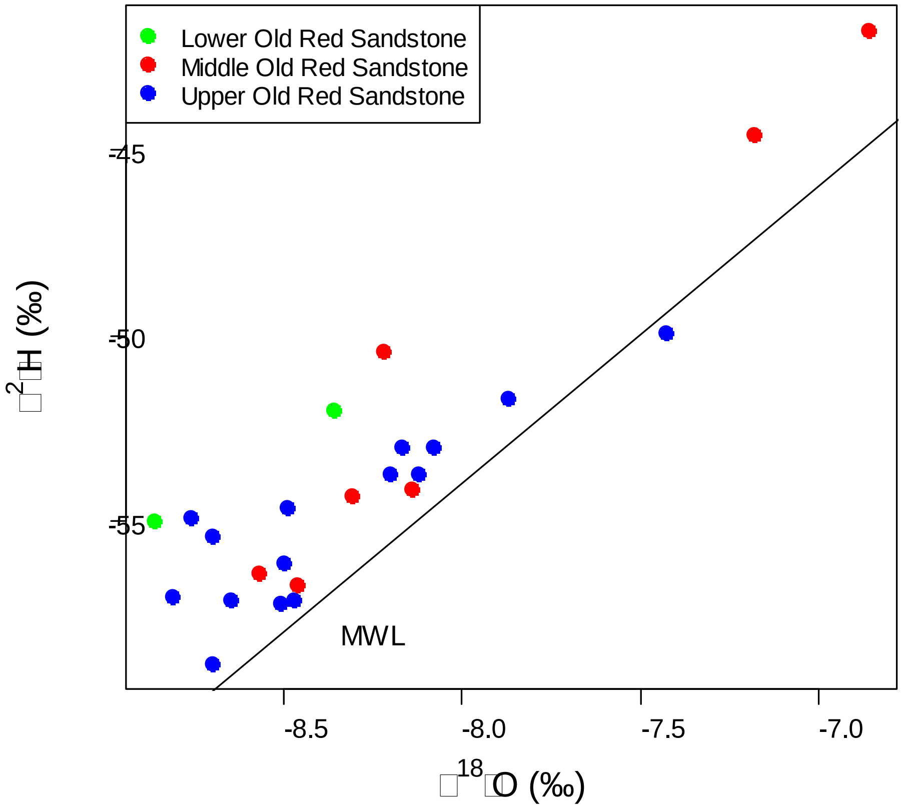


Figure 41 Isotopic co-plot (δ^{18}O against δ^{2}H) showing the disposition of groundwater samples relative to the World Meteoric Water Line (MWL)

Values of δ^{13}C-DIC appear to be related to the lithology of (and particularly the source of bicarbonate in) the superficial deposits overlying the Old Red Sandstone aquifer, through which recharge infiltrates, with a division at around –15.5‰ (Table 3). Values more negative than this are largely associated with groundwaters from beneath glaciofluvial deposits, while more positive values are mainly associated with those beneath marine or beach deposits. This is most likely to indicate two sources of bicarbonate: silicate hydrolysis (bicarbonate is released as carbonic acid is consumed) in recharge infiltrating through glaciofluvial deposits, and shell carbonate dissolution in recharge infiltrating through marine or beach deposits.

Table 3 Values of δ^{13}C-DIC for selected groundwaters from Old Red Sandstone aquifers in the Moray Firth area

Lab No	Bedrock geology	Superficial geology	δ^{13}C-DIC ‰
S07-00961	Alves Beds	Glaciofluvial ice-contact deposits	-18.39
S07-00957	Forres Sandstone Group	Glaciofluvial ice-contact deposits	-17.79
S07-00959	Alves Beds	Glaciofluvial ice-contact deposits	-17.61
S07-00963	Scaat Craig Beds	Glaciofluvial ice-contact deposits	-17.45
S07-00954	Inverness Sandstone Group	Glaciofluvial ice-contact deposits	-17.39
S07-00953	Forres Sandstone Group	Glaciofluvial ice-contact deposits	-16.59
S07-00955	Forres Sandstone Group	Blcwn sand	-16.08
S07-00964	Elgin Calcrete Formation	Glaciofluvial ice-contact deposits	-15.92
S07-00956	Forres Sandstone Group	Glaciofluvial ice-contact deposits	-15.84
S07-00949	Hillhead Sandstone Formation	Glaciofluvial sheet deposits	-15.79
S07-00951	Raddery Sandstone Formation	Raised marine deposits	-15.13
S07-00952	Raddery Sandstone Formation	Raised marine deposits	-14.68
S07-00960	Forres Sandstone Group	Blown sand	-13.58
S07-00966	Forres Sandstone Group	Raised marine deposits	-13.54
S07-00967	Forres Sandstone Group	Raised marine deposits	-13.40
S07-00965	Scaat Craig Beds	Glaciofluvial ice-contact deposits	-12.79

4.5.2 Residence time indicators

The dissolved atmospheric trace gases SF_6 (sulphur hexafluoride), CFC-12 and CFC-11 (chlorofluorocarbons) were measured on selected samples. The interpretations of groundwater residence time made from these analyses are linked to the rise of these gases in the atmosphere, and therefore rainfall, over the past half-century (Darling and Gooddy, 2007). However, CFC gases can suffer breakdown under reducing conditions, and both SF_6 and CFCs may be subject to local non-atmospheric additions, for example from contamination from discarded refrigeration units or aerosols. Therefore, a certain amount of care is required in their interpretation. In addition, SF_6 is affected by the 'excess air' usually acquired by recharging waters during infiltration 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. Results are presented in Table 4.

Table 4 **Chlorofluorocarbon and sulphur hexafluoride concentrations in groundwaters from the Moray Firth area. Also shown are SF_6 values corrected for likely excess air inputs, dissolved oxygen and nitrate concentrations, and SF_6-based ages assuming piston flow.**

Lab No	CFC-11 pmol/L	CFC-12 pmol/L	SF_6 raw fmol/L	SF_6 corr fmol/L	Diss O_2 mg/L	NO_3-N mg/L	SF_6 age yrs
S07-01142			0.72	0.54	0.81	<0.05	24
S06-01087	4.62	2.56	1.34	1.01	6.14	1.45	17
S06-01090	4.40	2.64	1.30	0.98	6.75	4.18	17
S07-00318	0.10	0.11	1.22	0.92	<0.10	<0.05	18
S07-00951	0.57	0.38	0.65	0.49	<0.10	0.185	24
S07-00952	0.43	0.25	0.52	0.39	<0.10	<0.05	25
S07-00953	0.57	0.39	2.17	1.63	<0.10	<0.05	10
S07-00954	2.26	1.71	1.07	0.80	<0.10	6.0	19
S07-00955	0.12	0.03	0.95	0.71	<0.10	<0.05	21
S07-00956	0.17	0.64	0.74	0.56	0.91	0.334	24
S07-00960	0.10	0.08	1.02	0.77	<0.10	<0.05	20
S07-00961	0.08	0.15	0.45	0.34	0.43	<0.05	27
S07-00964	0.24	-0.01	0.23	0.17	<0.10	<0.05	32
S07-00965	0.25	0.17	1.50	1.13	<0.10	0.06	15

Figure 42 shows a plot of CFC-12 versus SF_6 concentrations. Superimposed on the plot is a curved ‘piston flow’ line reflecting the relative inputs of each gas with time, and a dashed mixing line between modern (2007) and old groundwater. Only two of the samples plot on the piston flow line. All the samples have concentrations below the natural maxima, suggesting that additions, anthropogenic or natural, are not an issue. However, many of the samples have very low CFC concentrations in relation to their SF_6 values (Figure 42, Table 4). The reason for this is likely to be the decay of the CFCs due to low oxygen conditions: dissolved oxygen is below 1 mg/L (and usually <0.1 mg/L) for 85% of the samples (Table 4). The only two exceptions, with relatively high dissolved oxygen, plot on the piston flow line. In the absence of other evidence to the contrary, it is assumed that all the other samples would originally have plotted close to this line, and that the CFCs have been degraded in low oxygen conditions and cannot be used to estimate age. The samples have therefore been assigned a piston flow age on the basis of their SF_6 concentration (Table 4 and Figure 42). Residence times range from approximately 10 to 30 years, and do not appear to be controlled by any particular combination of bedrock and cover type, or geographical location. There is also no relationship with sample depth (Figure 43, inset): groundwater from the deepest borehole (over 90 m deep) has an intermediate age, while some of the oldest groundwaters were sampled from shallow boreholes less than 30 m deep.

Just as the CFCs can be degraded by low oxygen conditions, nitrate concentrations (Table 4) can reduce due to denitrification. It is therefore not possible to test this dataset for a meaningful correlation between nitrate concentration and groundwater age, as has been done elsewhere in Scotland (e.g. MacDonald et al., 2003).

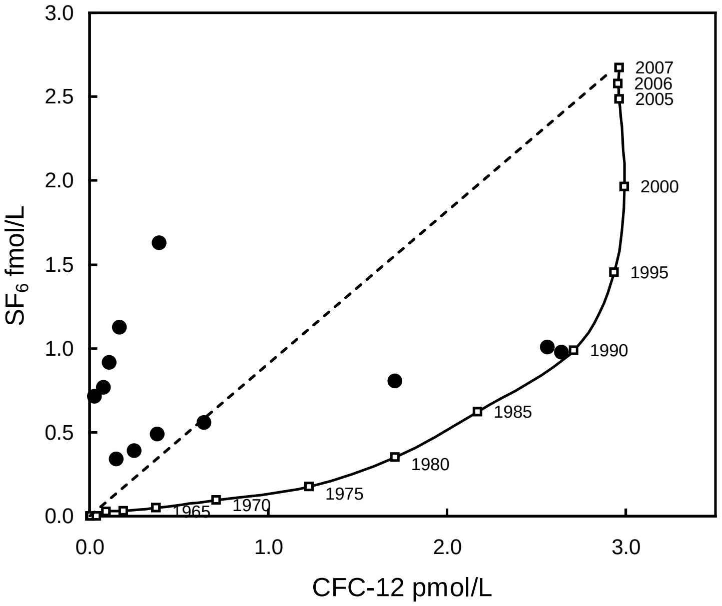


Figure 42 Plot of CFC-12 versus SF_6 concentration for groundwaters from the Moray Firth area. Also shown are the piston flow curve (labelled by year) and binary mixing line (dashed) for groundwaters recharged at 10°C

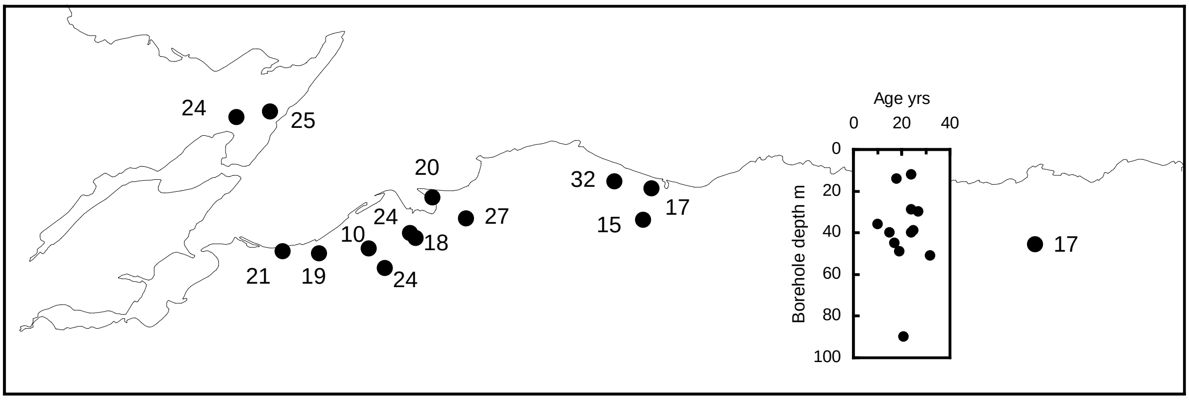


Figure 43 Map showing groundwater ages (in years) in the Moray Firth area based on SF_6 concentrations. Inset: plot of groundwater age versus borehole depth, showing no obvious correlation

5 Discussion

5.1 BASELINE GROUNDWATER CHEMISTRY

5.1.1 Defining baseline groundwater chemistry

One of the reasons for this study was to determine the baseline groundwater chemistry conditions for Old Red Sandstone aquifers in the Moray Firth area. 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., 2008b, Smedley et al., 2009). The first is statistical; the second involves selecting individual boreholes from each aquifer which are judged to generally represent baseline conditions.

Baseline groundwater chemistry does not relate to nitrate and phosphorus in the groundwater, which have generally been modified from natural conditions due to anthropogenic (mainly agricultural) activity. These are discussed in more detail in Section 5.3.

The main approach to defining baseline groundwater chemistry is statistical, and allows for the natural variation in baseline chemistry that can occur. Using this approach, the data between the 10th and 90th percentiles are examined for each element or ion (Table 5 for the dataset of all the sampled groundwaters; Appendix 2 for each aquifer group separately). 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 overall major ion distribution of groundwaters in the Old Red Sandstone aquifer in the Moray Firth area is illustrated in a Piper diagram (Figure 44). The baseline statistics are presented first for all the sampled groundwaters (Table 5). 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).

As a secondary approach to identify 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 natural chemical variation. All were sampled from sources where there is little or no indication of direct contamination. The location of the baseline samples is shown in Figure 45, and the samples are highlighted in Appendix 1. 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. In other Baseline studies, we have used the sample nitrate concentration as an indicator of whether groundwater has been impacted by human activity or not, but the evidence for denitrification in the Moray Firth area means this approach is less useful here. All but one of the baseline samples has a nitrate concentration of less than 3 mg/L TON-N (3 to 4 mg/L TON-N is taken as the upper limit of naturally occurring nitrate in the region), with the exception being a single concentration of 5.98 mg/L TON-N. However, some of the low nitrate concentrations in the baseline samples could be due to denitrification. All but one of the samples is from a borehole, the final one being from a large spring. The samples are distributed across the study area and across the different land uses: four are from non-agricultural areas; two from improved grassland or areas of mixed cultivation; three and from arable land; and one from an area known to be used for dairy, pig or poultry farming.

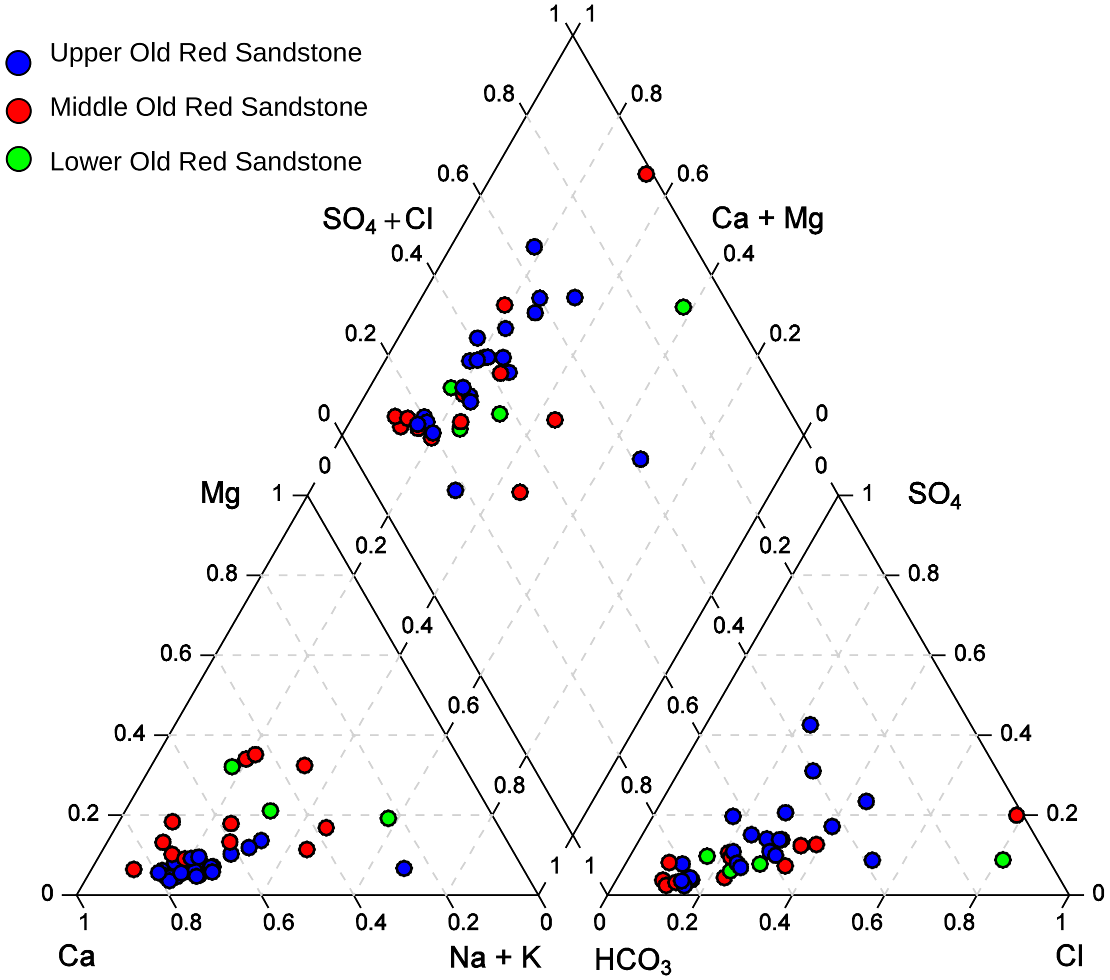


Figure 44 Piper plot of major ion composition of groundwaters from Old Red Sandstone aquifers in the Moray Firth area

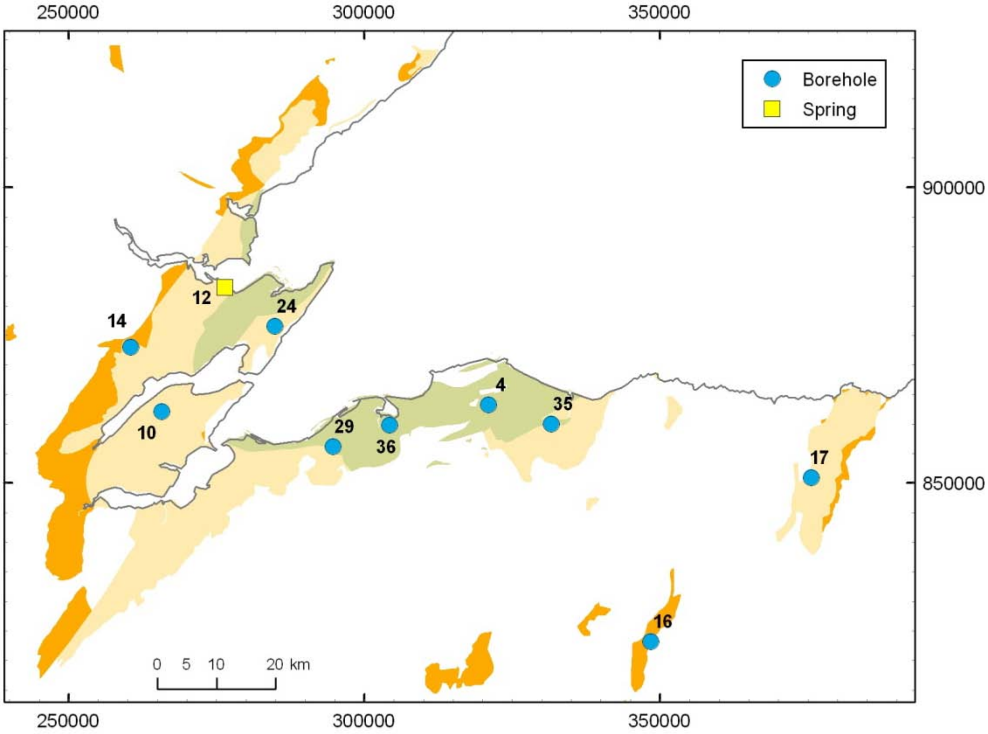


Figure 45 Location of the ten representative baseline groundwater samples from the Old Red Sandstone aquifer in the Moray Firth area

5.1.2 Baseline groundwater chemistry by aquifer

Many more groundwater samples from the Upper Old Red Sandstone aquifer were available for this study than for the other two aquifer divisions, particularly the Lower Old Red Sandstone, for which only four samples were analysed. This reflects the geological outcrop pattern: the Upper Old Red Sandstone occurs across a larger area, and most often in the coastal plain, where agriculture and population centres are concentrated and more groundwater sources exist. It means that the interpretation of the baseline chemistry of groundwater from the Upper Old Red Sandstone is more likely to reflect the actual range in chemical variation seen in the aquifer than that of the baseline chemistry of groundwater from the Lower Old Red Sandstone. With only four analyses, it is more likely that the natural range in groundwater chemistry in the Lower Old Red Sandstone aquifer will not be adequately represented. This is illustrated by the fact that the groundwaters from the Lower Old Red Sandstone show a statistically different major ion chemistry to those from the other two aquifer groups, in particular the Upper Old Red Sandstone (Table 5, Appendix 2), although the maximum range in major ion concentrations indicated by the Piper diagram (Figure 45) is similar for all three groups. There are unlikely to be enough samples from the Lower Old Red Sandstone to a rigorous statistical interpretation.

LOWER OLD RED SANDSTONE

The four Lower Old Red Sandstone groundwaters showed a range in cation dominance from Ca to Na-K. All but one are dominated by HCO_3 anions, with the remaining sample strongly dominated by Cl. Dissolved oxygen and redox (Eh) values are only available for two of the samples, which were oxic. The four samples have a range of pH values from 5.39 to 7.81, but three of the four had below-neutral pH values, and the median was 6.34, lower than the median for the whole Old Red Sandstone dataset. Concentrations of most major ions are lower on average than in Middle and Upper Old Red Sandstone groundwaters, except Mg which is similar. Median values are: HCO_3 (53 mg/L), Ca (13.8 mg/L), Na (12.6 mg/L), Cl (14.2 mg/L), Mg (3.7 mg/L), SO_4 (9.2 mg/L) and K (1.01 mg/L). The relatively low Ca concentrations and pH values probably result from a lack of carbonate minerals in the aquifer or overlying superficial deposits, which is also reflected in the lower calcite saturation values for these groundwaters (all but one of the samples was strongly undersaturated with respect to calcite). Iron concentrations are typically low (median 24 µg/L). Manganese concentrations show a larger range, with a low median (4.17 µg/L).

MIDDLE OLD RED SANDSTONE

Groundwaters from the Middle Old Red Sandstone aquifer show an overall cationic dominance by Ca, but a relatively wide spread, trending towards no dominant cation. Their anionic distribution is more restricted, strongly dominated by $HCO\text{-}_3$, apart from a single Cl-dominated water. They show very little SO_4 influence. Most of the samples are undersaturated with respect to calcite, but less strongly so than the Lower Old Red Sandstone waters.

Dissolved oxygen and Eh measurements are available for only seven of the fourteen Middle Old Red Sandstone samples, of which four are oxic and three are anoxic. The groundwaters have a higher median pH (6.7) than the Lower Old Red Sandstone waters, and the highest median HCO_3 concentration (212 mg/L) of the three aquifers. SEC (median 405 µS/cm) and median Ca (48.1 mg/L), Na (20 mg/L), K (median 2.16 mg/L) and Cl (median 28.6 mg/L) concentrations are in between the average values for the Lower and the Upper Old Red Sandstone groundwaters. Concentrations of SO_4 (median 9.9 mg/L) are, as for the Lower Old Red Sandstone, relatively low. Magnesium concentrations (median 5.7 mg/L) are comparable to the other two aquifers.

Iron and Mn concentrations are highly variable, from low (less than the detection limit for Fe) to high (maximum 1000 µg/L for Fe and 744 µg/L for Mn), although both show low median concentrations (41 µg/L for Fe and 15.5 µg/L for Mn). The main control on the presence of high

Fe and Mn is likely to be the presence of anoxic conditions within the aquifer (Homoncik , 2010).

UPPER OLD RED SANDSTONE

Groundwaters from the Upper Old Red Sandstone aquifer typically show very similar cation distribution, dominated by Ca in all but one case, and closely grouped. They show a wider anionic range, from HCO_3 towards Cl and SO_4.

Most of the samples for which DO and Eh measurements are available are anoxic; only three of fourteen samples showed clearly oxic conditions. The groundwaters have the highest median pH value of the three aquifers, and a median HCO_3 concentration of 183 mg/L, slightly lower than that of the Middle Old Red Sandstone waters. The median SEC value (510 µS/cm) and median concentrations of all of the major ions except Mg are also the highest of the three aquifers: Ca (median 68.5 mg/L), Na (median 23.4 mg/L), K (median 2.79 mg/L), and Cl (median 44 mg/L). SO_4 concentrations in particular are noticeably higher than the other two aquifers, with a median of 28.3 mg/L.

Iron and Mn concentrations are also highly variable, from low (less than the detection limit for Fe) to very high (maximum 4500 µg/L for Fe and 1190 µg/L for Mn). The median Fe concentration is not especially high at 47 µg/L, but the median Mn concentration (133 µg/L) is more than twice the drinking water limit. The high concentrations of both of these parameters are linked to the prevalence of anoxic conditions across much of the aquifer (Homoncik et al., 2010).

5.2 GROUNDWATER CHEMISTRY AND 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. The groundwaters sampled are from sources with a range of uses, including agricultural, industrial, recreational and domestic. Some are used for drinking water supply, though not necessarily without prior treatment (the Baseline Scotland samples were collected from raw water as close to the wellhead as possible). However, it is useful to examine the inorganic chemical quality of groundwaters from the Old Red Sandstone aquifers in the study area to give an indication of their suitability for potable supply.

Considering the inorganic parameters that are measured in relation to The Water Supply (Water Quality) Regulations (Scotland) (2001), the main inhibitors to water use for potable supply are likely to be Fe, Mn and nitrogen species. Concentrations of all these parameters vary across the study area depending on local redox conditions in the aquifers, but where the groundwater is reducing (anoxic), concentrations of Fe and Mn can be high, and there is a high probability of them exceeding the respective drinking water limits of 200 µg/L and 50 µg/L. The concentration of NH_4-N was also above the drinking water limit (0.39 mg/L as N) in two analysed samples, in one case significantly so (2.2 mg/L). In the oxic groundwaters, the concentrations of NO_3-N were comparatively high, and three analysed samples had concentrations above the drinking water limit (11.3 mg/L as N).

Salinity is unlikely to be a significant problem in terms of potable supply, although this will be dependent to a large extent on proximity to the coast. Concentrations of parameters such as Na, Cl, SO_4 and B, and levels of SEC, were well within drinking water limits. Groundwater pH values were also mostly within the allowable ranges for drinking water (6.5–9.5), although a few showed relatively low values. Some young (short residence time) waters could have too low pH values to be suitable for drinking water without treatment.

Table 5 Summary statistics for chemical elements in groundwater in all Old Red Sandstone aquifers in the Moray Firth area

Element	Units	Number[1]	No. censored[2]	Min	10%	25%	50%	75%	90%	95%	Max	Method[3]
pH	-	39	0	5.33	6.34	6.53	7.32	7.65	7.91	7.95	8.06	KM
Eh	mV	18	0	107	119	144	254	377	409	NA[4]	456	KM
DO	mg/L	23	9	-0.1	NA	NA	0.81	5.59	6.75	9.4	9.8	KM
SEC	µS/cm	39	0	138	241	341	469	591	752	778	1120	KM
Ca	mg/L	39	0	8.3	19.3	42.5	54.8	74	93.9	99.7	102	KM
Mg	mg/L	39	0	0.53	2.25	3.13	4.21	6.8	12.5	22	23.4	KM
Na	mg/L	39	0	4	8.62	12.6	20.6	28	35.3	68.3	152	KM
K	mg/L	39	1	<0.5	1.01	1.9	2.7	3.7	5.8	8.54	16.4	KM
Cl	mg/L	39	0	6.1	13.4	19.5	38.8	49.5	74.9	86.2	194	KM
SO_4	mg/L	39	0	2.7	5.08	7.7	14.6	36.4	48.1	60.3	102	KM
HCO_3	mg/L	37	1	<2	62.2	111	183	230	263	301	310	KM
NO_3-N	mg/L	24	11	<0.05	NA	NA	0.058	4.54	9.15	12	21.7	KM
NO_2-N	mg/L	19	11	<0.001	1.86E-05	6.84E-05	0.000314	0.00239	0.0102	0.0337	0.052	ROS
NH_4-N	mg/L	19	12	<0.01	1.58E-05	0.000121	0.00075	0.0185	0.187	0.722	2.18	ROS
P	µg/L	39	9	<20	NA	21	36	66	83	127	172	KM
DOC	mg/L	24	0	0.44	0.53	0.85	1.26	1.97	7.01	9.65	11.3	KM
F	mg/L	39	0	0.02	0.06	0.07	0.11	0.178	0.31	0.73	0.77	KM
Br	µg/L	39	0	27	45	71	105	171	231	423	702	KM
I	µg/L	39	1	<2	2.6	3.4	4.2	6	23	35	42.2	KM
Si	mg/L	39	0	1.04	4.36	4.93	5.73	7.4	8.42	9.47	10.9	KM
Ag	µg/L	39	36	<0.05	0.00176	0.00337	0.00724	0.0156	0.03	0.051	0.09	ROS
Al	µg/L	39	0	3	3	5	7	21	73	132	152	KM
As	µg/L	39	20	<0.5	0.0278	0.0831	0.304	1.1	2.58	4.66	33.6	ROS
Au	µg/L	39	34	<0.05	0.00149	0.00334	0.00865	0.0225	0.056	0.085	0.17	ROS
B	µg/L	39	9	<20	8	11	15	25	35	60	203	KM
Ba	mg/L	39	0	0.01	0.0247	0.064	0.123	0.202	0.335	0.474	0.541	KM
Be	µg/L	39	33	<0.05	0.000186	0.000712	0.00344	0.0167	0.08	0.152	0.65	ROS
Bi	µg/L	39	38	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Cd	µg/L	39	30	<0.05	0.00999	0.0166	0.0303	0.0516	0.102	0.132	0.18	ROS
Ce	µg/L	39	7	<0.01	NA	0.01	0.02	0.09	0.25	0.84	1.26	KM
Co	µg/L	39	10	<0.02	NA	NA	0.05	0.18	0.88	0.92	9.08	KM
Cs	µg/L	39	7	<0.01	NA	0.01	0.13	1.3	3.28	17.1	18.6	KM
Cu	µg/L	39	0	0.6	0.7	1.1	2.1	5.1	9.5	29	34.7	KM

Element	Units	Number[1]	No. censored[2]	Min	10%	25%	50%	75%	90%	95%	Max	Method[3]
Dy	µg/L	39	18	<0.01	NA	NA	0.01	0.01	0.04	0.28	0.36	KM
Er	µg/L	39	23	<0.01	0.00021	0.000679	0.00285	0.01	0.02	0.074	0.22	ROS
Eu	µg/L	39	19	<0.01	NA	NA	0.01	0.01	0.03	0.06	0.09	KM
Fe	µg/L	39	9	<10	NA	10	38	354	739	3620	4500	KM
Ga	µg/L	39	38	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Gd	µg/L	39	11	<0.01	NA	NA	0.01	0.02	0.06	0.28	0.35	KM
Ge	µg/L	39	31	<0.05	0.00229	0.00519	0.0136	0.0358	0.09	0.115	0.35	ROS
Hf	µg/L	39	37	<0.02	1.67E-05	5.95E-05	0.000266	0.00119	0.00428	0.00911	0.04	ROS
Hg	µg/L	39	25	<0.1	0.00429	0.0121	0.0418	0.15	0.8	0.81	1	ROS
Ho	µg/L	39	31	<0.01	6.88E-05	0.000222	0.000892	0.00372	0.01	0.024	0.07	ROS
Ir	µg/L	39	38	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
La	µg/L	39	3	<0.01	0.01	0.01	0.02	0.05	0.21	0.47	1.01	KM
Li	µg/L	39	0	0.2	0.6	2.5	4.5	7.8	13.1	21.9	28.9	KM
Lu	µg/L	39	35	<0.01	1.75E-05	6.47E-05	0.000302	0.00143	0.00601	0.012	0.04	ROS
Mn	µg/L	39	0	1.14	1.5	5.28	43.1	227	519	744	1190	KM
Mo	µg/L	39	11	<0.1	NA	NA	0.4	1.2	3.3	6.3	7.8	KM
Nb	µg/L	39	9	<0.01	NA	0.01	0.01	0.01	0.02	0.03	0.04	KM
Nd	µg/L	39	5	<0.01	NA	0.01	0.02	0.07	0.21	0.36	1.67	KM
Ni	µg/L	39	17	<0.2	NA	NA	0.3	1.2	2.1	7.8	8	KM
Os	µg/L	39	38	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Pb	µg/L	39	8	<0.1	NA	0.1	0.1	0.5	0.9	1.3	1.6	KM
Pd	µg/L	39	38	<0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	ROS
Pr	µg/L	39	24	<0.01	0.000313	0.000962	0.00367	0.02	0.042	0.054	0.36	ROS
Pt	µg/L	39	38	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Rb	µg/L	39	0	0.05	0.24	0.85	2.69	9.6	28.9	37.4	37.6	KM
Re	µg/L	39	27	<0.01	0.005	0.00596	0.00737	0.01	0.01	0.01	0.02	ROS
Rh	µg/L	39	37	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Ru	µg/L	39	38	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Sb	µg/L	39	27	<0.05	0.0063	0.0119	0.0253	0.065	0.112	0.131	0.37	ROS
Sc	µg/L	39	15	<1	NA	NA	1	2	NA	NA	3	KM
Se	µg/L	39	19	<0.5	NA	NA	0.5	0.9	1.4	2.6	3.1	KM
Sm	µg/L	39	28	<0.02	0.000195	0.000669	0.0029	0.02	0.044	0.092	0.34	ROS
Sn	µg/L	39	0	0.22	0.37	0.53	0.84	1.04	1.25	1.35	1.87	KM
Sr	mg/L	39	0	0.0216	0.0572	0.0727	0.116	0.227	0.531	0.617	0.954	KM

Element	Units	Number[1]	No. censored[2]	Min	10%	25%	50%	75%	90%	95%	Max	Method[3]
Ta	µg/L	39	38	<0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	ROS
Tb	µg/L	39	33	<0.01	5.53E-05	0.000177	0.000703	0.00284	0.01	0.022	0.05	ROS
Te	µg/L	39	38	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Th	µg/L	39	31	<0.05	0.00701	0.0116	0.021	0.038	0.06	0.093	0.13	ROS
Ti	µg/L	39	37	<10	0.683	1.11	1.95	3.44	5.57	7.33	13	ROS
Tl	µg/L	39	18	<0.01	NA	NA	0.01	0.11	0.42	2.4	4.42	KM
Tm	µg/L	39	35	<0.01	5.85E-05	0.00017	0.000599	0.00213	0.00675	0.012	0.03	ROS
TON	mg/L	39	17	-0.2	NA	NA	0.3	4.18	9.7	21.7	22.1	KM
U	µg/L	39	4	<0.02	NA	0.15	0.32	1.14	3.03	4.68	5.36	KM
V	µg/L	39	5	<0.2	NA	0.2	0.3	0.9	1.4	4.2	7.6	KM
W	µg/L	39	27	<0.02	0.0012	0.00266	0.00688	0.02	0.04	0.061	0.16	ROS
Y	µg/L	39	0	0.01	0.02	0.04	0.06	0.14	0.3	1.87	2.37	KM
Yb	µg/L	39	24	<0.01	0.00014	0.000488	0.00224	0.01	0.022	0.074	0.21	ROS
Zn	µg/L	39	0	1	1.7	2.8	6	14.6	68	219	403	KM
Zr	µg/L	39	26	<0.02	8.79E-05	0.000403	0.00248	0.02	0.046	0.143	0.92	ROS

[1] Number: number of samples

[2] No. censored: number of samples below detection limit

[3] Method: method (for more details see Section 4.1.1). KM – Kapler-Meier; ROS – Regression On Order

[4] NA: not available

Few of the trace elements were present in excess of drinking water limits. Arsenic concentrations exceeded 10 µg/L in one analysed groundwater sample, which was a reducing, high-Fe groundwater. Apart from this, the reducing groundwaters sampled in this study had As concentrations that were mostly <3 µg/L. However, concentrations of As could potentially be high in some reducing groundwaters in the region. Concentrations of F (maximum observed 0.8 mg/L) were universally well below the limit of 1.5 mg/L.

No national drinking water limit exists for U, but all the Moray Firth groundwaters had U concentrations that were well below the WHO provisional guideline value of 15 µg/L. However, concentrations in the Moray Firth groundwaters were generally relatively high compared to other UK groundwaters (Shand et al., 2007). Eleven samples had U concentrations of >1 µg/L, with a maximum observed value of 5.4 µg/L.

No determinations were made of bacterial counts or of organic compounds in the groundwaters.

5.3 NITRATE AND PHOSPHORUS

Nitrate concentrations are variable across the aquifers, although median concentrations are low (1.45 mg/L TON-N or less in each of the aquifers). In the Lower Old Red Sandstone, the maximum concentration is 4.4 mg/L TON-N, probably reflecting both the few samples in this group and the aquifer outcrop pattern: the Lower Old Red Sandstone tends to underlie the more inland, upland areas with less intensive agriculture. The maximum nitrate concentration in the Middle (21.7 mg/L TON-N) and Upper Old Red Sandstone (22.1 mg/L TON-N) aquifers is significantly higher, again probably reflecting the more widespread arable land, in particular, overlying the outcrops of these two aquifers (Figure 2).

The eastern part of the study area lies within a nitrate vulnerable zone (NVZ) (Figure 2). There is a clear relationship between nitrate concentrations and the NVZ boundary, with the seven highest groundwater nitrate concentrations, ranging from 5.98 to 22.1 mg/L TON-N, all from samples taken within the NVZ. The highest nitrate concentration of any of the samples from outside the NVZ was 5.01 mg/L TON-N.

The relationship between nitrate (measured as TON) concentration and borehole depth is variable, although relatively low concentrations (<4 mg/L TON-N) appear to be most common in shallow groundwaters, from boreholes less than 40 m deep (Figure 21). The highest concentrations were seen in groundwaters from boreholes between 50 and 60 m deep.

The prevalence of low oxygen conditions in the sampled groundwaters, combined with the low average nitrate (as TON) concentrations, suggests that denitrification is occurring in the groundwater. This may explain the large number of low nitrate concentrations in samples from shallow sources.

Because of the likelihood of denitrification, it is not possible to test this dataset for a meaningful correlation between nitrate concentrations and groundwater age, as has been done elsewhere in Scotland (e.g. MacDonald et al., 2003). It also means that it is difficult to test the dataset for a relationship between nitrate concentrations and land use, although there is some evidence of a positive correlation between land used for intensive agriculture (Figure 20). The only nitrate concentrations above the drinking water limit of 11.3 mg/L, and the highest median concentrations, were from land known to be used for dairy, pig or poultry farming. Samples from both arable and dairy, pig and poultry land uses show a wide variation in nitrate concentration; samples from improved grassland, land used for mixed cultivation and non-agricultural land show a slightly smaller range in nitrate concentration.

Phosphorus in groundwater can be an important influence on surface water eutrophication by increasing nutrient concentrations in baseflow to streams and rivers. SEPA have set upper limits for total phosphorus of 8 µg P/L for oligotrophic surface waters, 25 µg P/L for mesotrophic surface waters and 80 µg P/L for eutrophic surface waters, based on annual geometric mean concentrations. Phosphorus concentrations in the Moray Firth groundwaters range from less than detection limit up to 172 µg P/L, with an overall median of 36 µg P/L (Table 5), which is in the eutrophic range for surface waters. Concentrations are generally low in the western part of the study area (Figure 25), and an observed relationship with the spatial pattern of F (Figure 24) suggests that both elements may be in part derived from the dissolution of phosphate minerals, such as apatite, from the aquifer rocks. Concentrations in the eastern part of the study area are generally higher, usually in the mesotrophic or eutrophic range for surface waters. The higher values may be related to land use, with P inputs from agricultural activity. The highest median P concentration is for samples from land known to be used for dairy, pig or poultry farming, although high concentration outliers also occur in samples from arable and non agricultural land uses (Figure 26). Samples from improved grassland, land used for mixed cultivation and non-agricultural land show the widest range in P concentrations.

5.4 GROUNDWATER FLOW IN THE OLD RED SANDSTONE AQUIFERS IN THE MORAY FIRTH AREA

The hydrochemistry data and information on groundwater residence times help give some insight into groundwater flow in the Old Red Sandstone aquifers of the Moray Firth area. Firstly, there is no evidence of palaeowater in the samples taken from the area; most of the groundwater are interpreted as being less than 50 years old using the SF_6 data. The reducing nature of the groundwaters make it difficult to interpret the CFC data (since both CFC11 and CFC-12 have been reduced) and get a reliable estimate of whether flow is predominately fracture dominated or piston intergranular flow. Two samples that were not reducing appear to show piston flow; however, groundwater chemistry (in particularly nitrate) show no significant depth correlations, implying that groundwater is well mixed. A possible explanation is that piston flow occurs in the thick overlying superficial deposits, but within the sandstones fracture flow may dominate.

Carbon isotope evidence indicates the significant role of the nature of the superficial cover in impacting the groundwater chemistry, showing differences between groundwaters recharged through glaciofluvial deposits, which are likely to derive bicarbonate from silicate hydrolysis, and those recharged through marine or beach deposits, in which bicarbonate is likely to derive from dissolution of shell carbonate.

6 Conclusions

The groundwater chemistry of Old Red Sandstone aquifers in the Moray Firth area has been characterised based on new chemistry analyses generated during the Baseline Scotland project, combined with existing analyses from earlier projects. A total of 39 groundwater sample analyses were interpreted for the purposes of this study. Of these, 17 were collected in 2007 specifically for the Baseline Scotland project. These were augmented with a further 22 samples collected during separate BGS projects since 2001. The sites were chosen to be representative of groundwater in the area, and sources that were poorly constructed were avoided.

A summary of the conclusions arising from this study follows:

1. Groundwater in the Old Red Sandstone aquifers of the Moray Firth is generally moderately mineralised, with a median SEC of 469 µS/cm (interquartile range 341–591 µS/cm). The pH is variable: median pH is slightly alkaline (7.31), but values range from 5.33 to 8.06. The major ion chemistry appears to be dominated by the dissolution of carbonate cements within the aquifer and overlying deposits, and the variable influence of seawater (either directly as saline intrusion or as aerosols).
2. The dominant cation is Ca, with a median concentration of 54.8 mg/L (interquartile range 42.5–74 mg/L). Mg and K concentrations are generally low (median 4.21 and 3.7 mg/L respectively). The median Na is 20.6 mg/L (interquartile range 12.6–28 mg/L); however, a few samples have been affected by proximity to the sea and have much higher concentrations, as illustrated by the 95th percentile (68 mg/L) and maximum concentration (153 mg/L).
3. The dominant anion is bicarbonate, with a median concentration of 183 mg/L (interquartile range 183–230 mg/L). Around one third of the samples are saturated with respect to calcite. Sulphate concentrations are generally low (median 14.6 mg/L, interquartile range 7.7–36.4 mg/L), although higher concentrations are encountered in samples affected by seawater, and/or possibly by gypsum bands within the aquifer. Chloride concentrations follow broadly the same distribution as Na and have a median of 38.8 mg/L and interquartile range of 19.5–49.5 mg/L; the same few samples show high Cl concentrations as do Na.
4. Concentrations of minor and trace elements in the groundwater are dominated by the redox conditions. Measured values of dissolved oxygen indicate a large range in redox conditions across the aquifer. Concentrations of DO close to 10 mg/L indicate fully oxic conditions. By contrast, groundwaters with DO concentrations <1 mg/L are indicative of sub-oxic or mildly reducing conditions, and appear to be prevalent in much of the Upper Old Red Sandstone outcrop, and parts of the Middle Old Red Sandstone. Reducing conditions may reflect the presence of low permeability layers (often marine in origin) within the thick superficial deposits overlying the Old Red Sandstone aquifer. The effect of reducing conditions is to increase concentrations of Fe and Mn, which show median concentrations of 38 and 43 µg/L respectively, and 75th percentile values of 354 and 227 µg/L respectively.
5. The majority of samples (21) were collected from the Upper Old Red Sandstone aquifer; 14 samples were collected from the Middle Old Red Sandstone and only 4 samples from the Lower Old Red Sandstone. The samples show broadly similar chemistry across the three aquifer units; however, there are several notable differences. Samples from the Upper Old Sandstone aquifer show very similar cation distribution, dominated by Ca, while the Lower and Middle Old Red Sandstone aquifers show a wider cation distribution and appear less affected by calcite dissolution. The pH of the Lower and Middle Old Red Sandstone aquifers is slightly lower (more acidic), generally less than 7.0. Groundwaters

within the Upper Old Red Sandstone aquifer are generally more reducing, probably reflecting their location close to the coast and hence the influence of the sea and/or overlying marine superficial deposits.

6. Nitrate concentrations are variable across the aquifer units, although median concentrations are low (1.45 mg/L TON-N or less in each aquifer). The prevalence of low oxygen conditions in the sampled groundwaters has led to denitrification, which means the relationship between land use and nitrate concentrations is less obvious than for other parts of Scotland (MacDonald et al., 2005a). However, there is a clear relationship between nitrate concentrations and the Nitrate Vulnerable Zone (NVZ) that covers much of the study area, with the seven highest groundwater nitrate concentrations, ranging from 5.98 to 22.1 mg/L TON-N, all from samples taken within the NVZ. The highest median concentrations were from samples collected on land known to be used for dairy, pig or poultry farming.

7. Phosphorus concentrations in Moray Firth groundwaters range from less than detection limit up to 172 µg P/L, with an overall median of 36 µg P/L, which is in the eutrophic range for surface waters. Concentrations are generally low in the western part of the study area, and an observed relationship with the spatial pattern of F suggests that both elements may be in part derived from the dissolution of phosphate minerals, such as apatite, from the aquifer rocks. Concentrations in the eastern part of the study area are generally higher, usually in the mesotrophic or eutrophic range for surface waters. The higher values may be related to land use, with P inputs from agricultural activity.

8. An estimate of the baseline groundwater chemistry conditions in the Old Red Sandstone 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 Old Red Sandstone aquifers in the Moray Firth area.

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Appendix 1 Description of sampling sites

ID	Lab Sample ID	Project	Source type	Aquifer	Depth (m)	Land use
1	S02-00248	Orig. NO_3[1]	Borehole	Lower ORS[3]	45	Improved grassland / mixed cultivated
2	S02-00249	Orig. NO_3	Borehole	Upper ORS	60	Identified DPP
3	S02-00250	Orig. NO_3	Borehole	Upper ORS	30	Non agricultural
4	S02-00251	Orig. NO_3	Borehole	Upper ORS	45	Non agricultural
5	S02-00252	Orig. NO_3	Borehole	Middle ORS	45	Improved grassland / mixed cultivated
6	S02-00253	Orig. NO_3	Borehole	Upper ORS	50	Arable
7	S02-00254	Orig. NO_3	Borehole	Upper ORS	60	Identified DPP
8	S02-00255	Orig. NO_3	Borehole	Middle ORS		Arable
9	S02-00256	Orig. NO_3	Borehole	Middle ORS	65	Improved grassland / mixed cultivated
10	S02-00257	Orig. NO_3	Borehole	Middle ORS	30	Non agricultural
11	S02-00258	Orig. NO_3	Borehole	Upper ORS	40	Identified DPP
12	S02-00259	Orig. NO_3	Spring	Middle ORS	0	Non agricultural
13	S02-00260	Orig. NO_3	Borehole	Middle ORS		Non agricultural
14	S02-00261	Orig. NO_3	Borehole	Middle ORS	45	Non agricultural
15	S02-00262	Orig. NO_3	Borehole	Lower ORS	15	Improved grassland / mixed cultivated
16	S06-01087	Baseline Abd[2]	Borehole	Lower ORS	30-100	Improved grassland / mixed cultivated
17	S06-01089	Baseline Abd	Borehole	Middle ORS	123	Arable
18	S06-01090	Baseline Abd	Borehole	Lower ORS	45	Non agricultural
19	S06-01092	Baseline Abd	Borehole	Middle ORS		Identified DPP
20	S06-01093	Baseline Abd	Shallow well	Middle ORS	9	Arable
21	S07-00318	Pilmuir (1)	Borehole	Upper ORS	14	Arable
22	S07-00949	Baseline Mry	Borehole	Middle ORS	50	Non agricultural
23	S07-00951	Baseline Mry	Borehole	Middle ORS	29	Arable
24	S07-00952	Baseline Mry	Borehole	Middle ORS	39	Improved grassland / mixed cultivated
25	S07-00953	Baseline Mry	Borehole	Upper ORS	36	Arable
26	S07-00954	Baseline Mry	Borehole	Middle ORS	49	Arable
27	S07-00955	Baseline Mry	Borehole	Upper ORS	90	Non agricultural
28	S07-00956	Baseline Mry	Borehole	Upper ORS	40	Identified DPP
29	S07-00957	Baseline Mry	Borehole	Upper ORS	100	Arable
30	S07-00959	Baseline Mry	Borehole	Upper ORS		Identified DPP
31	S07-00960	Baseline Mry	Borehole	Upper ORS	30-100	Non agricultural
32	S07-00961	Baseline Mry	Borehole	Upper ORS	30	Arable
33	S07-00963	Baseline Mry	Borehole	Upper ORS	96	Non agricultural
34	S07-00964	Baseline Mry	Borehole	Upper ORS	51	Identified DPP
35	S07-00965	Baseline Mry	Borehole	Upper ORS	40	Identified DPP
36	S07-00966	Baseline Mry	Borehole	Upper ORS	46	Arable
37	S07-00967	Baseline Mry	Borehole	Upper ORS	30-100	Arable
38	S07-01076	Baseline Mry	Borehole	Upper ORS	50	Arable
39	S07-01142	Pilmuir (2)	Borehole	Upper ORS	12	Arable

[1] Original Nitrate (Ball and MacDonald 2002) [2] Baseline Aberdeenshire (Smedley et al., 2009)

[3] ORS – Old Red Sandstone

The ID numbers here are used throughout this report. For sample locations see Figure 8.

Appendix 2 Summary statistics for chemical elements in groundwaters from individual aquifers in Aberdeenshire

Table A2.1 Summary statistics for chemical elements in groundwaters from the Lower Old Red Sandstone aquifer in the Moray Firth area

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
pH	-	4	0	5.39	5.39	5.39	6.34	NA[2]	NA	NA	7.81	KM
Eh	mV	2	0	308	NA	NA	NA	NA	NA	NA	355	KM
DO	mg/L	2	0	6.14	NA	NA	NA	NA	NA	NA	6.75	KM
SEC	µS/cm	4	0	172	172	172	250	NA	NA	NA	351	KM
Ca	mg/L	4	0	12	12	12	13.8	NA	NA	NA	38.1	KM
Mg	mg/L	4	0	2.37	2.37	2.37	3.7	NA	NA	NA	12.5	KM
Na	mg/L	4	0	9.88	9.88	9.88	12.6	NA	NA	NA	32.2	KM
K	mg/L	4	0	0.7	0.7	0.7	1.01	NA	NA	NA	4.33	KM
Cl	mg/L	4	0	13.3	13.3	13.3	14.2	NA	NA	NA	74.9	KM
SO_4	mg/L	4	0	5.08	5.08	5.08	9.2	NA	NA	NA	10.9	KM
HCO_3	mg/L	4	0	15.9	15.9	15.9	53	NA	NA	NA	138	KM
NO_3-N	mg/L	2	0	1.45	NA	NA	NA	NA	NA	NA	4.18	KM
P	µg/L	4	1	<20	NA	NA	21	NA	NA	NA	89	KM
F	mg/L	4	0	0.06	0.06	0.06	0.064	NA	NA	NA	0.08	KM
Br	µg/L	4	0	36	36	36	64	NA	NA	NA	99	KM
I	µg/L	4	1	<2	NA	NA	NA	NA	NA	NA	3	KM
Si	mg/L	4	0	4.77	4.77	4.77	6.23	NA	NA	NA	7.07	KM
Al	µg/L	4	0	5	5	5	5	NA	NA	NA	106	KM
Au	µg/L	4	3	<0.05	0.08	0.08	0.08	0.08	0.08	0.08	0.08	ROS
B	µg/L	4	1	<20	7	7	11	NA	NA	NA	25	KM
Ba	mg/L	4	0	0.0812	0.0812	0.0812	0.098	NA	NA	NA	0.187	KM
Be	µg/L	4	3	<0.05	0.65	0.65	0.65	0.65	0.65	0.65	0.65	ROS
Cd	µg/L	4	3	<0.05	0.13	0.13	0.13	0.13	0.13	0.13	0.13	ROS
Ce	µg/L	4	2	<0.01	0.000358	0.000661	0.00541	0.0175	0.031	0.0355	0.04	ROS
Co	µg/L	4	2	<0.02	0.00135	0.00227	0.0114	0.03	0.048	0.054	0.06	ROS
Cs	µg/L	4	2	<0.01	0.00267	0.00391	0.0123	0.0275	0.041	0.0455	0.05	ROS
Cu	µg/L	4	0	1.2	1.2	1.2	3.4	NA	NA	NA	22.4	KM

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
Dy	µg/L	4	3	<0.01	0.36	0.36	0.36	0.36	0.36	0.36	0.36	ROS
Er	µg/L	4	3	<0.01	0.22	0.22	0.22	0.22	0.22	0.22	0.22	ROS
Eu	µg/L	4	1	<0.01	NA	NA	0.01	NA	NA	NA	0.04	KM
Fe	µg/L	4	3	<10	24	24	24	24	24	24	24	ROS
Gd	µg/L	4	1	<0.01	NA	NA	0.01	NA	NA	NA	0.28	KM
Ge	µg/L	4	3	<0.05	0.11	0.11	0.11	0.11	0.11	0.11	0.11	ROS
Hg	µg/L	4	3	<0.1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	ROS
Ho	µg/L	4	3	<0.01	0.07	0.07	0.07	0.07	0.07	0.07	0.07	ROS
La	µg/L	4	2	<0.01	0.00174	0.00247	0.00644	0.0125	0.017	0.0185	0.02	ROS
Li	µg/L	4	0	3.1	3.1	3.1	7.5	NA	NA	NA	10.7	KM
Lu	µg/L	4	3	<0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.03	ROS
Mn	µg/L	4	0	2.81	2.81	2.81	4.17	NA	NA	NA	99.9	KM
Mo	µg/L	4	1	<0.1	NA	NA	0.1	NA	NA	NA	1.2	KM
Nb	µg/L	4	3	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Nd	µg/L	4	0	0.01	0.01	0.01	0.01	NA	NA	NA	0.21	KM
Ni	µg/L	4	2	<0.2	0.125	0.209	1.18	3.53	6.09	6.94	7.8	ROS
Pb	µg/L	4	1	<0.1	NA	NA	0.1	NA	NA	NA	0.8	KM
Pr	µg/L	4	3	<0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	ROS
Rb	µg/L	4	0	0.22	0.22	0.22	1.04	NA	NA	NA	6.44	KM
Re	µg/L	4	3	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Rh	µg/L	4	3	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Sb	µg/L	4	3	<0.05	0.14	0.14	0.14	0.14	0.14	0.14	0.14	ROS
Sc	µg/L	4	2	<1	1	1	1	1	1	1	1	ROS
Se	µg/L	4	3	<0.5	0.7	0.7	0.7	0.7	0.7	0.7	0.7	ROS
Sm	µg/L	4	3	<0.02	0.11	0.11	0.11	0.11	0.11	0.11	0.11	ROS
Sn	µg/L	4	0	0.37	0.37	0.37	0.78	NA	NA	NA	1.25	KM
Sr	mg/L	4	0	0.0572	0.0572	0.0572	0.071	NA	NA	NA	0.617	KM
Tb	µg/L	4	3	<0.01	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Tm	µg/L	4	3	<0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.03	ROS
TON	mg/L	4	1	<0.2	NA	NA	1.45	NA	NA	NA	4.4	KM
U	µg/L	4	0	0.07	0.07	0.07	0.21	NA	NA	NA	1.2	KM
V	µg/L	4	1	<0.2	NA	NA	0.4	NA	NA	NA	1.4	KM
W	µg/L	4	3	<0.02	0.16	0.16	0.16	0.16	0.16	0.16	0.16	ROS
Y	µg/L	4	0	0.02	0.02	0.02	0.05	NA	NA	NA	2.37	KM

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
Yb	µg/L	4	3	<0.01	0.2	0.2	0.2	0.2	0.2	0.2	0.2	ROS
Zn	µg/L	4	0	4.9	4.9	4.9	8.7	NA	NA	NA	48.1	KM

[1] Method: Statistical method (for more details see Section 4.1.1). KM – Kapler-Meier; ROS – Regression On Order

[2] NA: not available

Table A2.2 Summary statistics for chemical elements in groundwaters from the Middle Old Red Sandstone aquifer in the Moray Firth area

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
pH	-	14	0	5.33	6.17	6.4	6.71	7.61	7.68	NA[2]	8.06	KM
Eh	mV	7	0	119	119	144	339	403	NA	NA	456	KM
DO	mg/L	7	3	<0.1	NA	NA	4.7	9.4	NA	NA	9.8	KM
SEC	µS/cm	14	0	138	214	313	405	510	726	NA	752	KM
Ca	mg/L	14	0	8.3	19.3	24.1	48.1	63.8	85	NA	93.9	KM
Mg	mg/L	14	0	0.53	2.61	3.64	5.68	11	22	NA	23.4	KM
Na	mg/L	14	0	4	6.1	8.62	20	25	31.8	NA	68.3	KM
K	mg/L	14	1	<0.5	1.1	1.8	2.16	3.88	5.8	NA	8.54	KM
Cl	mg/L	14	0	6.1	7.8	15.6	28.6	43.3	53.2	NA	86.2	KM
SO_4	mg/L	14	0	2.7	5	6.2	9.9	14.6	36.4	NA	37.8	KM
HCO_3	mg/L	12	1	<2	78.1	93.7	212	233	263	NA	301	KM
NO_3-N	mg/L	7	1	<0.05	NA	0.185	4.54	6	NA	NA	21.7	KM
NO_2-N	mg/L	4	0	0.00165	0.00165	0.00165	0.00485	NA	NA	NA	0.052	KM
NH_4-N	mg/L	4	2	<0.01	0.00224	0.00424	0.0497	0.211	0.42	0.49	0.56	ROS
P	µg/L	14	6	<20	NA	NA	34	69	78	NA	172	KM
DOC	mg/L	7	0	0.53	0.53	0.72	1.44	2.37	NA	NA	9.65	KM
F	mg/L	14	0	0.02	0.051	0.06	0.086	0.112	0.157	NA	0.21	KM
Br	µg/L	14	0	27	43	70	84	144	192	NA	231	KM
I	µg/L	14	0	3	3	3.4	4	5	6	NA	23	KM
Si	mg/L	14	0	1.04	4.35	4.54	4.96	8.23	8.8	NA	9.47	KM
Ag	µg/L	14	13	<0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.06	ROS
Al	µg/L	14	0	3	3	5	7	55	132	NA	152	KM
As	µg/L	14	10	<0.5	0.0189	0.0409	0.111	0.433	0.67	1.19	2.1	ROS
Au	µg/L	14	11	<0.05	0.00789	0.0134	0.0261	0.0505	0.115	0.144	0.17	ROS
B	µg/L	14	6	<20	9	10	12	25	60	NA	203	KM
Ba	mg/L	14	0	0.01	0.015	0.0487	0.083	0.202	0.474	NA	0.541	KM
Be	µg/L	14	12	<0.05	0.028	0.0371	0.0528	0.075	0.11	0.13	0.15	ROS
Cd	µg/L	14	12	<0.05	0.00715	0.0119	0.0226	0.0427	0.0871	0.117	0.15	ROS
Ce	µg/L	14	2	<0.01	NA	0.01	0.03	0.1	0.84	NA	1.26	KM
Co	µg/L	14	2	<0.02	NA	0.03	0.06	0.16	0.32	NA	0.92	KM
Cs	µg/L	14	4	<0.01	NA	NA	0.01	0.05	0.32	NA	0.81	KM
Cu	µg/L	14	0	0.6	0.6	1	1.7	5.1	29	NA	34.7	KM

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
Dy	µg/L	14	5	<0.01	NA	NA	0.01	0.03	0.12	NA	0.28	KM
Er	µg/L	14	6	<0.01	NA	NA	0.01	0.02	0.06	NA	0.2	KM
Eu	µg/L	14	5	<0.01	NA	NA	0.01	0.01	0.06	NA	0.09	KM
Fe	µg/L	14	3	<10	NA	19	41	79	427	NA	1000	KM
Gd	µg/L	14	4	<0.01	NA	NA	0.01	0.06	0.14	NA	0.35	KM
Ge	µg/L	14	13	<0.05	0.09	0.09	0.09	0.09	0.09	0.09	0.09	ROS
Hf	µg/L	14	13	<0.02	0.04	0.04	0.04	0.04	0.04	0.04	0.04	ROS
Hg	µg/L	14	8	<0.1	0.008	0.017	0.0454	0.175	0.2	0.41	0.8	ROS
Ho	µg/L	14	10	<0.01	0.000103	0.000298	0.00119	0.00833	0.017	0.034	0.06	ROS
La	µg/L	14	0	0.01	0.01	0.01	0.03	0.08	0.47	NA	1.01	KM
Li	µg/L	14	0	0.2	0.5	0.9	2.5	5.9	13.1	NA	28.9	KM
Lu	µg/L	14	12	<0.01	1.02E-06	5.66E-06	5.36E-05	0.000507	0.00741	0.0205	0.04	ROS
Mn	µg/L	14	0	1.14	1.33	2.19	15.5	75.2	278	NA	744	KM
Mo	µg/L	14	8	<0.1	0.00109	0.00484	0.0346	0.625	2.14	2.75	3.2	ROS
Nb	µg/L	14	4	<0.01	NA	NA	0.01	0.01	0.03	NA	0.04	KM
Nd	µg/L	14	2	<0.01	NA	0.02	0.02	0.19	0.36	NA	1.67	KM
Ni	µg/L	14	6	<0.2	NA	NA	0.5	1.7	2.1	NA	8	KM
Pb	µg/L	14	2	<0.1	NA	0.1	0.1	0.7	0.9	NA	1.1	KM
Pr	µg/L	14	6	<0.01	NA	NA	0.01	0.04	0.09	NA	0.36	KM
Rb	µg/L	14	0	0.05	0.18	0.39	0.94	2.33	5.19	NA	15.6	KM
Re	µg/L	14	12	<0.01	9.76E-05	0.000234	0.000722	0.00223	0.00811	0.0135	0.02	ROS
Sb	µg/L	14	11	<0.05	0.0117	0.0178	0.0303	0.0513	0.105	0.123	0.13	ROS
Sc	µg/L	14	7	<1	0.426	0.607	0.947	2	2	2.35	3	ROS
Se	µg/L	14	7	<0.5	0.242	0.319	0.466	0.75	0.87	1	1.2	ROS
Sm	µg/L	14	9	<0.02	0.00031	0.001	0.00459	0.035	0.081	0.177	0.34	ROS
Sn	µg/L	14	0	0.22	0.37	0.6	0.64	1.09	1.29	NA	1.35	KM
Sr	mg/L	14	0	0.0216	0.055	0.0633	0.0903	0.242	0.531	NA	0.954	KM
Tb	µg/L	14	10	<0.01	0.000277	0.000643	0.00191	0.00858	0.017	0.027	0.04	ROS
Th	µg/L	14	10	<0.05	0.0111	0.0166	0.0278	0.0551	0.081	0.1	0.12	ROS
Ti	µg/L	14	13	<10	13	13	13	13	13	13	13	ROS
Tl	µg/L	14	12	<0.01	1.48E-09	2.63E-08	1.25E-06	6.01E-05	0.0071	0.045	0.11	ROS
Tm	µg/L	14	12	<0.01	6.72E-06	2.64E-05	0.000157	0.000934	0.00762	0.017	0.03	ROS
TON	mg/L	14	4	<0.2	NA	NA	1	4.01	5.98	NA	21.7	KM
U	µg/L	14	2	<0.02	NA	0.1	0.4	1.14	1.84	NA	3.03	KM

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
V	µg/L	14	3	<0.2	NA	0.2	0.2	0.5	1.4	NA	1.7	KM
W	µg/L	14	11	<0.02	0.00618	0.00817	0.0116	0.0166	0.027	0.03	0.03	ROS
Y	µg/L	14	0	0.02	0.03	0.04	0.1	0.25	0.85	NA	1.87	KM
Yb	µg/L	14	8	<0.01	8.96E-05	0.000341	0.00202	0.01	0.051	0.112	0.21	ROS
Zn	µg/L	14	0	1	1.1	2.3	4.5	23.1	97	NA	403	KM
Zr	µg/L	14	9	<0.02	4.33E-05	0.000213	0.00172	0.0275	0.061	0.367	0.92	ROS

[1] Method: Statistical method (for more details see Section 4.1.1). KM – Kapler-Meier; ROS – Regression On Order

[2] NA: not available

Table A2.3 Summary statistics for chemical elements in groundwaters from the Upper Old Red Sandstone aquifer in the Moray Firth area

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
pH		21	0	6.43	6.46	7.06	7.41	7.65	7.91	7.94	7.95	KM
Eh	mV	9	0	107	107	144	147	295	NA[2]	NA	409	KM
DO	mg/L	14	6	<0.1	NA	NA	0.43	1.22	3.79	NA	5.59	KM
SEC	µS/cm	21	0	241	341	437	510	601	760	778	1120	KM
Ca	mg/L	21	0	43.7	50.7	53.4	68.5	86.5	99	99.7	102	KM
Mg	mg/L	21	0	1.65	2.25	2.98	4.02	5.42	6.8	8.03	10	KM
Na	mg/L	21	0	10.8	12.8	17.6	23.4	28.9	35.3	50.2	152	KM
K	mg/L	21	0	1	2.07	2.55	2.79	3.56	4.56	6.1	16.4	KM
Cl	mg/L	21	0	16	19.7	28.4	44	49.8	69.3	84.4	194	KM
SO_4	mg/L	21	0	4.58	6.21	16.2	28.3	43	52	60.3	102	KM
HCO_3	mg/L	21	0	62.2	106	140	183	214	242	268	310	KM
NO_3-N	mg/L	15	10	<0.05	3.94E-05	0.000383	0.00671	0.196	8.55	10	12	ROS
NO_2-N	mg/L	15	11	<0.001	0.000149	0.000269	0.000465	0.00107	0.0025	0.0031	0.00354	ROS
NH_4-N	mg/L	15	10	<0.01	4.75E-06	3.54E-05	0.000184	0.0155	0.041	0.692	2.18	ROS
P	µg/L	21	2	<20	22	31	39	64	81	83	127	KM
DOC	mg/L	15	0	0.73	0.85	1.03	1.27	2.04	7.01	NA	11.3	KM
F	mg/L	21	0	0.05	0.081	0.109	0.16	0.247	0.661	0.73	0.77	KM
Br	µg/L	21	0	45	67	85	129	203	361	423	702	KM
I	µg/L	21	0	2.4	3.4	3.57	5.2	9	25	35	42.2	KM
Si	mg/L	21	0	4.27	4.91	5.23	5.73	7.36	7.67	8.15	10.9	KM
Ag	µg/L	21	19	<0.05	0.000427	0.00104	0.00308	0.00913	0.0221	0.05	0.09	ROS
Al	µg/L	21	0	3	4	6	7	18	21	46	73	KM
As	µg/L	21	6	<0.5	NA	NA	0.9	1.9	4.3	7.9	33.6	KM
Au	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
B	µg/L	21	2	<20	8	11	16	23	34	35	44	KM
Ba	mg/L	21	0	0.0147	0.049	0.0943	0.133	0.214	0.292	0.319	0.335	KM
Be	µg/L	21	18	<0.05	0.000603	0.00155	0.0049	0.0154	0.06	0.07	0.17	ROS
Bi	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Cd	µg/L	21	15	<0.05	0.00774	0.0133	0.0258	0.05	0.1	0.11	0.18	ROS
Ce	µg/L	21	3	<0.01	NA	0.02	0.02	0.06	0.13	0.25	0.43	KM
Co	µg/L	21	6	<0.02	NA	NA	0.05	0.25	0.88	0.88	9.08	KM
Cs	µg/L	21	1	<0.01	0.08	0.4	0.73	2.25	10.1	17.1	18.6	KM

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
Cu	µg/L	21	0	0.6	0.8	1.3	2	4.9	7.9	9.3	9.5	KM
Dy	µg/L	21	10	<0.01	NA	NA	0.01	0.01	0.01	0.02	0.03	KM
Er	µg/L	21	14	<0.01	0.00358	0.00463	0.00639	0.01	0.01	0.01	0.02	ROS
Eu	µg/L	21	13	<0.01	0.00262	0.00384	0.00622	0.01	0.02	0.02	0.02	ROS
Fe	µg/L	21	3	<10	NA	25	47	477	739	3620	4500	KM
Ga	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Gd	µg/L	21	6	<0.01	NA	NA	0.01	0.01	0.02	0.03	0.04	KM
Ge	µg/L	21	15	<0.05	0.00212	0.005	0.0143	0.05	0.09	0.16	0.35	ROS
Hf	µg/L	21	20	<0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	ROS
Hg	µg/L	21	14	<0.1	0.0036	0.0105	0.0397	0.1	0.8	0.9	1	ROS
Ho	µg/L	21	18	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Ir	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
La	µg/L	21	1	<0.01	0.01	0.01	0.02	0.04	0.11	0.15	0.21	KM
Li	µg/L	21	0	0.6	2.4	2.9	5.2	7.8	12.3	15.6	21.9	KM
Lu	µg/L	21	20	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Mn	µg/L	21	0	1.17	2.97	17	133	322	519	624	1190	KM
Mo	µg/L	21	2	<0.1	0.1	0.2	0.5	1.4	4.7	6.3	7.8	KM
Nb	µg/L	21	2	<0.01	0.01	0.01	0.01	0.01	0.01	NA	0.02	KM
Nd	µg/L	21	3	<0.01	NA	0.01	0.01	0.03	0.11	0.11	0.2	KM
Ni	µg/L	21	9	<0.2	NA	NA	0.2	0.8	1.4	2.1	7.1	KM
Os	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Pb	µg/L	21	5	<0.1	NA	0.1	0.1	0.3	0.9	1.3	1.6	KM
Pd	µg/L	21	20	<0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	ROS
Pr	µg/L	21	15	<0.01	0.00116	0.0022	0.00486	0.01	0.02	0.03	0.05	ROS
Pt	µg/L	21	20	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Rb	µg/L	21	0	0.43	0.71	2.9	8.47	12.7	35.6	37.4	37.6	KM
Re	µg/L	21	12	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Rh	µg/L	21	20	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Ru	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Sb	µg/L	21	13	<0.05	0.00606	0.0114	0.0249	0.07	0.08	0.11	0.37	ROS
Sc	µg/L	21	6	<1	NA	NA	2	2	NA	NA	3	KM
Se	µg/L	21	9	<0.5	NA	NA	0.5	1.2	1.7	2.6	3.1	KM
Sm	µg/L	21	16	<0.02	0.00765	0.00949	0.0124	0.0163	0.02	0.02	0.03	ROS
Sn	µg/L	21	0	0.31	0.39	0.53	0.88	0.95	1.06	1.18	1.87	KM

Element	Units	Number	No. censored	Min.	10%	25%	50%	75%	90%	95%	Max.	Method[1]
Sr	mg/L	21	0	0.0534	0.0727	0.0947	0.118	0.156	0.228	0.234	0.472	KM
Ta	µg/L	21	20	<0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	ROS
Tb	µg/L	21	20	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
Te	µg/L	21	20	<0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	ROS
Th	µg/L	21	17	<0.05	0.00322	0.00593	0.0125	0.0265	0.06	0.06	0.13	ROS
Ti	µg/L	21	20	<10	10	10	10	10	10	10	10	ROS
Tl	µg/L	21	2	<0.01	0.01	0.04	0.09	0.37	0.92	2.4	4.42	KM
Tm	µg/L	21	20	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	ROS
TON	mg/L	21	12	<0.2	0.00564	0.0251	0.127	1.5	9.7	19.9	22.1	ROS
U	µg/L	21	2	<0.02	0.09	0.19	0.32	0.92	4.45	4.68	5.36	KM
V	µg/L	21	1	<0.2	0.2	0.3	0.4	0.9	1.3	4.2	7.6	KM
W	µg/L	21	13	<0.02	0.00301	0.00534	0.0109	0.02	0.04	0.06	0.07	ROS
Y	µg/L	21	0	0.01	0.01	0.03	0.06	0.08	0.16	0.16	0.17	KM
Yb	µg/L	21	13	<0.01	0.0029	0.00406	0.00623	0.01	0.01	0.02	0.02	ROS
Zn	µg/L	21	0	1.7	2.1	2.8	4.6	11	14.2	20.9	219	KM
Zr	µg/L	21	13	<0.02	0.000185	0.000668	0.00335	0.02	0.03	0.1	0.53	ROS

[1] Method: Statistical method (for more details see Section 4.1.1). KM – Kapler-Meier; ROS – Regression On Order

[2] NA: not available