Baseline Scotland: the Lower Devonian aquifer of Strathmore

Groundwater Management Programme

Commissioned Report CR/06/250N

BRITISH GEOLOGICAL SURVEY

GROUNDWATER MANAGEMENT PROGRAMME

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Baseline Scotland: the Lower Devonian aquifer of Strathmore

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Keywords

Chemistry, baseline, groundwater, Scotland.

Front cover

View northeast across Strathmore towards the Grampian hills, showing the typical landuse of arable agriculture and golf courses, with commercial forestry on higher ground.

Bibliographical reference

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Foreword

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

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

The aims of *Baseline Scotland* are:

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

The project runs from 2005 to 2010, 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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Executive Summary

This report presents a summary of the groundwater chemistry of the Devonian sedimentary aquifer in Strathmore, eastern Scotland. The area covered by this study extends from Perth in the southwest to Stonehaven in the northeast. The survey forms part of the ongoing Baseline Scotland project.

The Devonian sedimentary rocks of Strathmore form an important regional aquifer in an area of some of the most fertile agricultural land in Scotland, with a number of major urban settlements. The aquifer provides water for agriculture, industry, recreation and domestic use. The aquifer can be divided into six main geological units, largely sandstones but with significant conglomerates and, less commonly, mudstones. All of these units are classed as moderately or highly productive aquifers, but too few data are available to allow a detailed analysis of the hydrogeological variations between the formations.

A total of 35 new groundwater samples were collected during this project, and the resulting chemistry data combined with data from 13 additional samples collected during a BGS sampling programme in 2001. The samples were analysed at BGS laboratories for a wide range of chemical constituents.

The collection and interpretation of new groundwater chemistry data for the Strathmore area has led to the following conclusions.

- The groundwaters of the Devonian aquifer in Strathmore are mainly weakly mineralised, with TDS concentrations mostly less than 400 mg l^{-1}. Groundwaters have near-neutral to slightly alkaline pH values and are for the most part oxygenated, with detectable dissolved oxygen and high redox potentials. As a result, dissolved iron, manganese and ammonium (NH_4-N) concentrations are usually low. Water from shallow boreholes and springs is often undersaturated with calcite, but in deeper boreholes, reaction with carbonate minerals in the aquifer is more usual and most of these are saturated with respect to calcite.
- Nitrate concentrations are often high, with an interquartile range of 2.6 mg l^{-1} to 11.7 mg l^{-1} as NO_3-N. Nearly one third of the samples exceeded the EC drinking-water limit for nitrate of 11.4 mg l^{-1} as NO_3-N. An anomalously high nitrate concentration of 81 mg l^{-1} as NO_3-N was observed in one sample, and appears to result from direct downhole contamination by nitrogen fertiliser. Under the oxidising conditions, nitrate is a stable solute species across the aquifer and is found at depths in excess of 100 m.
- Concentrations of phosphorous in groundwater across the aquifer are typically less than 0.1 mg l^{-1} (the 90th percentile), with a median of 0.03 mg l^{-1}. Given the importance of P in controlling eutrophication in surface water, these concentrations in groundwater may be significant.
- Increased salinity occurs in groundwater in some near-coastal boreholes, most likely as a result of mixing with seawater.
- Most cationic trace elements have low concentrations, in accordance with the neutral-pH groundwater conditions. Concentrations of arsenic are relatively high in some groundwaters (up to 8.8 µg l^{-1}) though none exceeds the EC maximum permissible value for drinking water of 10 µg l^{-1}. Concentrations of uranium reach up to 15.4 µg l^{-1}, with the highest concentration just exceeding the WHO provisional guideline value for drinking water of 15 µg l^{-1}. Two other exceedances above maximum permissible values for drinking were observed, for nitrite (highest concentration 0.194 mg l^{-1}) and fluoride (highest concentration 3.7 mg l^{-1}).

- The chemistry and residence time indicators (CFC and stable isotopes) indicate that the groundwaters are largely of young age, being mostly recharged within the last 40 years, with mixing throughout the top 100 m of the aqufier. The samples show little evidence of the presence of palaeowaters. The young age of the groundwaters means they are vulnerable to contamination.
- A first estimate of the baseline groundwater chemistry conditions in the Strathmore Lower Devonian aquifer can be given by the statistical summary of the data collected in this study (with the exception of nitrogen (N) and phosphorous (P), where the influence of anthropogenic activity is likely to have affected concentrations across the aquifer). To compliment this approach, six good quality sites have been chosen which represent the majority of groundwaters found in Strathmore.
- The most significant groundwater-quality problems identified by this survey are:
    - the widespread presence of elevated nitrate concentrations in groundwater, which is strongly linked to agricultural activity;
    - elevated phosphate concentrations which may affect the quality of surface water when discharged to rivers as baseflow.
    - the presence of saline water in some near-coastal boreholes, indicating localised saline intrusion. It is not clear to what degree the saline intrusion is natural and to what degree it has been enhanced by over-pumping.

1 Introduction

The Strathmore region runs from southwest to northeast between Perth and Stonehaven, a distance of approximately 120 km (Figure 1). Strathmore itself forms a broad valley bounded to the north by the rugged Grampian hills and to the south by the Sidlaw Hills. Also included in the study area is the coastal plain which lies to the south of the valley, south of the Sidlaw Hills, and runs along the northern edge of the Firth of Tay and the North Sea.

The largely flat, broad valley and the coastal plain, underlain dominantly by red Devonian sandstones, boasts some of Scotland's most productive farmland. Landuse in Strathmore is dominated by arable agriculture, producing soft fruits, vegetables and cereals such as oats, barley and hay. In the Sidlaw Hills and the northeast of Strathmore, around Glen Esk, the land is higher and less fertile, and landuse is dominated by pastoral agriculture, typically cattle, and by commercial coniferous forestry. Recreational landuse includes many golf courses.

The main urban areas are along the southern boundary of Strathmore, with Perth at the western edge; Dundee, the largest urban centre in the region; Arbroath and Montrose. Elsewhere the land is dominantly rural with small market towns such as Coupar Angus, Kirriemuir, Forfar and Brechin.

The main rivers in the region are the River Tay, which runs into the Firth of Tay, the River North Esk, which reaches the sea just north of Montrose, and the River South Esk, which flows into the Montrose basin. All of these have tributaries to the north of Strathmore in the Grampian hills. A number of other, smaller rivers have shorter courses, rising in the Sidlaw Hills.

The two main commercial activities of arable agriculture and golf courses are water-intensive, and irrigation demand in the region is high. Much of this water demand is met by groundwater from the Devonian sandstone aquifer. There are also groundwater abstractions for domestic and industrial supplies, including a mineral water bottling plant, some of which are derived from volcanic rocks and superficial deposits. There are no operational public water supply groundwater sources in the region, although there is a standby public water borehole near Montrose.

Currently, interest in groundwater in Strathmore remains high, driven by the new legislative requirements of the Water Framework Directive. These include groundwater abstraction licensing, for which the Scottish Environment Protection Agency (SEPA) requires a better understanding of the aquifer system, and increasing pressure on public water supplies, which has led Scottish Water to look again at the feasibility of groundwater supplies.

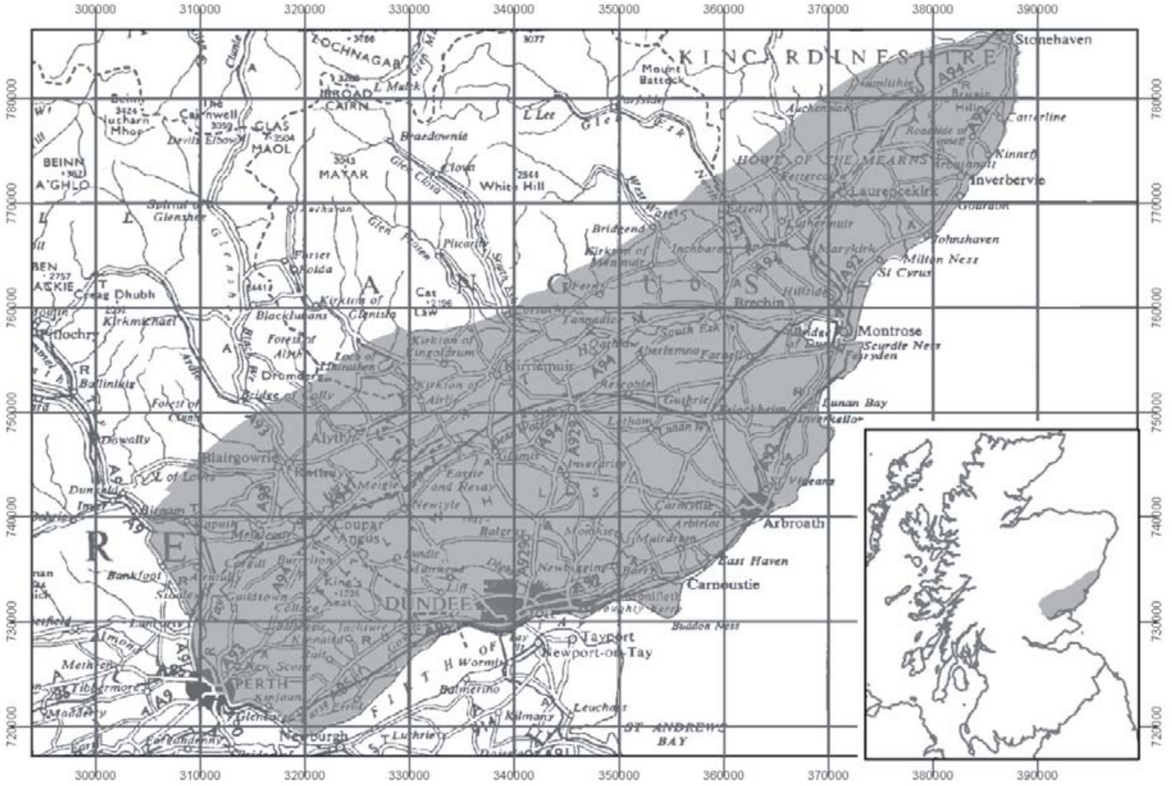


Figure 1 The area of study in Strathmore

2 Background to understanding groundwater chemistry

2.1 GENERAL

In order to understand the groundwater chemistry of the aquifer, it is necessary to understand the groundwater system. This requires a knowledge of the geological and hydrogeological properties to provide a physical framework for the system. Knowledge of the mineralogy and geochemistry of the aquifer minerals is also needed to explain the observed groundwater chemistry. Finally, the initial input to the groundwater system – rainfall – needs to be known in order to define the initial composition of groundwater recharge.

2.2 BEDROCK GEOLOGY

The geology in Strathmore dates predominantly from the Lower Devonian: the oldest formations may date from late Silurian, but the bulk of the succession is early Devonian in age. The rocks are principally composed of sandstones, with notable successions of conglomerates, shales and mudstones, and volcanic rocks. They were deposited within the Strathmore basin, an elongate trough that extended across the northern Midland Valley of Scotland. The largely sedimentary Devonian sequence is bounded to the northwest by the Highland Boundary Fault. The area of study is bounded to the southeast by the Firth of Tay (Figure 2).

Strathmore is crossed by a number of faults, mainly with northwest to southeast and northeast to southwest trends. The Devonian sedimentary rocks have been folded into the asymmetrical Strathmore Syncline and the parallel Sidlaw Anticline (Figure 2). The northwestern limb of the syncline steepens towards the Highland Boundary Fault zone and becomes vertical and locally overturned along the fault. The southeastern limb is gently inclined. The Sidlaw Anticline is roughly symmetrical and the axis extends from Montrose to the Ochil Hills. Rocks of the Ochil Volcanic Formation form the Sidlaw Hills.

The current lithostratigraphical classification for Lower Devonian strata at group level includes, from oldest to youngest, the Stonehaven Group, the Dunnottar-Crawton Group, the Arbuthnott-Garvock Group and the Strathmore Group. The lithological groups are described in detail in Browne et al. (2001). The youngest rocks in Strathmore are part of the Stratheden (Upper Devonian) and Inverclyde (Lower Carboniferous) groups. The spatial distribution of these lithological groups is illustrated in Figure 2. The formations making up each of these groups across the region are summarised in Table 1.

The oldest rocks, of the Stonehaven and Dunnottar-Crawton groups, are restricted to the Stonehaven area with minor outcrops largely adjacent to the Highland Boundary Fault. There are no known groundwater abstraction boreholes in these rocks and they were not considered in detail in this study.

The Arbuthnott-Garvock Group (Figure 2) is between 2400 and 4000 m thick and consists mainly of sandstones, dominantly the Scone Sandstone Formation, with some clast-supported conglomerates, and siltstone and mudstone in some areas. A calcrete limestone occurs near the top of the group in many areas. There are significant thick intercalations of lava flows, small outcrops of volcanic detrital sedimentary rocks (tuff). Within the group, the Dundee Flagstone Formation contains many intercalations of upward-coarsening lacustrine cycles (commonly more than 30 m thick) consisting of mudstone, siltstone and flaggy sandstone. The Scone Sandstone Formation contains common pebbles of limestone and calcareous mudstone.

The Strathmore Group (Figure 2) is approximately 1800 m thick, and crops out largely along the axis of the Strathmore Syncline. It consists largely of medium-grained sandstones, dominantly the Teith Sandstone Formation, with important developments of clast-supported conglomerates, with the Cromlix Mudstone Formation in the lower part of the succession containing characteristic thick developments of red siltstone and silty mudstone.

Upper Devonian to Lower Carboniferous rocks are rare in Strathmore, cropping out over small areas along the coast, to the west of Dundee, at Arbroath and at Montrose. The rocks largely comprise sandstones of the Glenvale Sandstone Formation, part of the Stratheden Group, which are typically fine- to coarse-grained with pebbles of largely silty mudstone. There are also small outcrops of the Ballagan Formation, of the Inverclyde Group, which typically comprise mudstones and siltstones with variable thicknesses of interbedded sandstones.

The Devonian rocks are folded along regional fold axes: the Strathmore Syncline and the Sidlaw Anticline, the approximate positions of which are shown as solid lines on Figure 2.

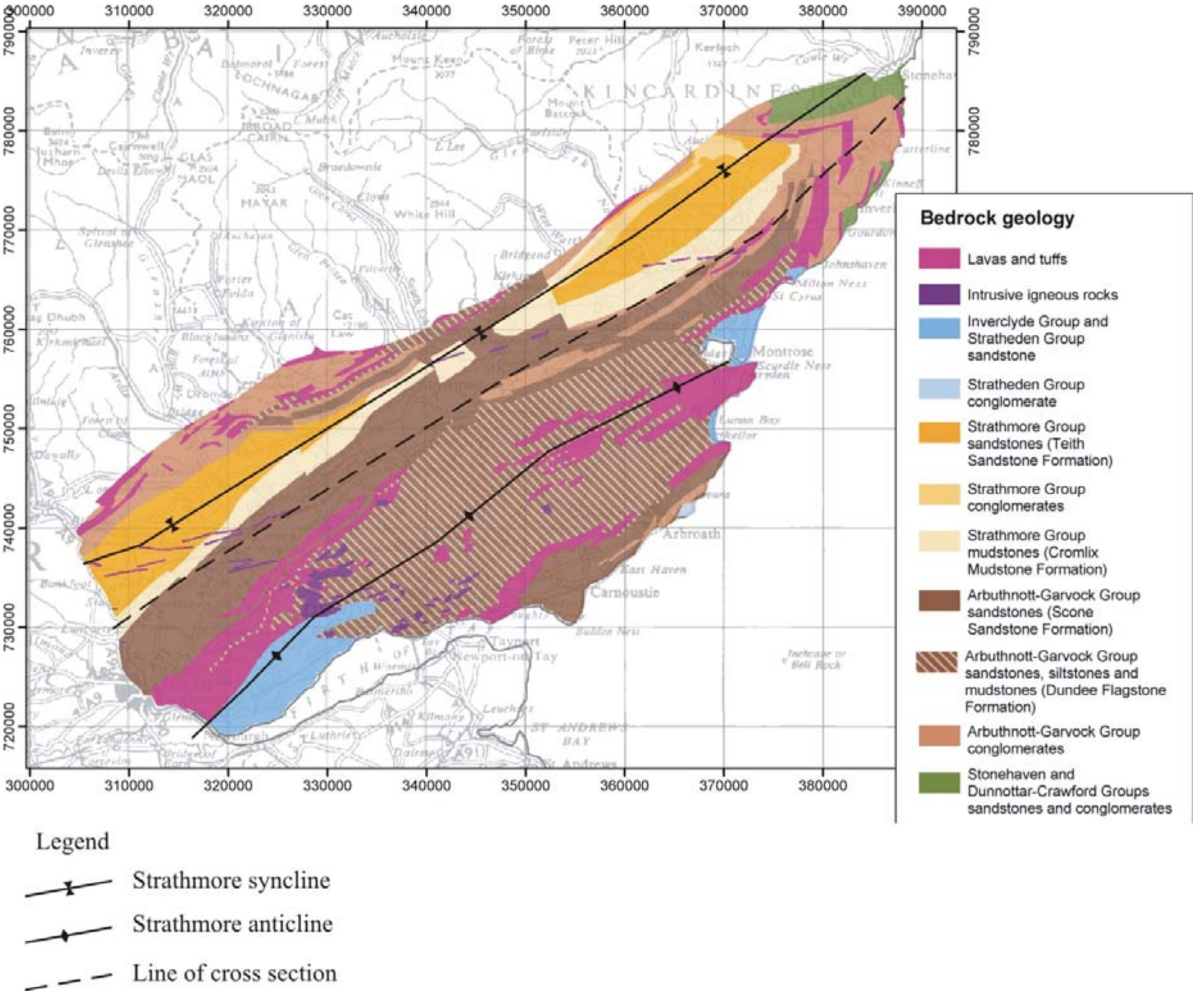


Figure 2 Geology of Strathmore, based on 1:250 000 linework. Individual formation names mentioned extensively in the text (based on 1:50 000 scale mapping) are given in brackets in the legend.

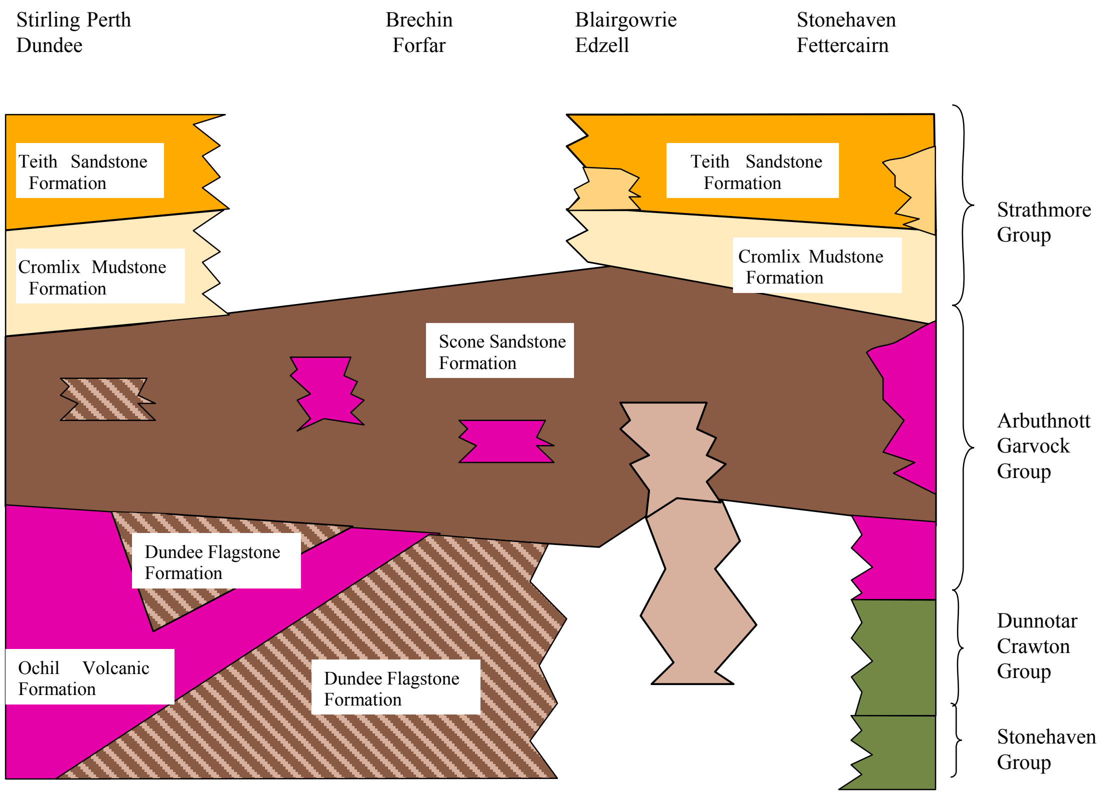
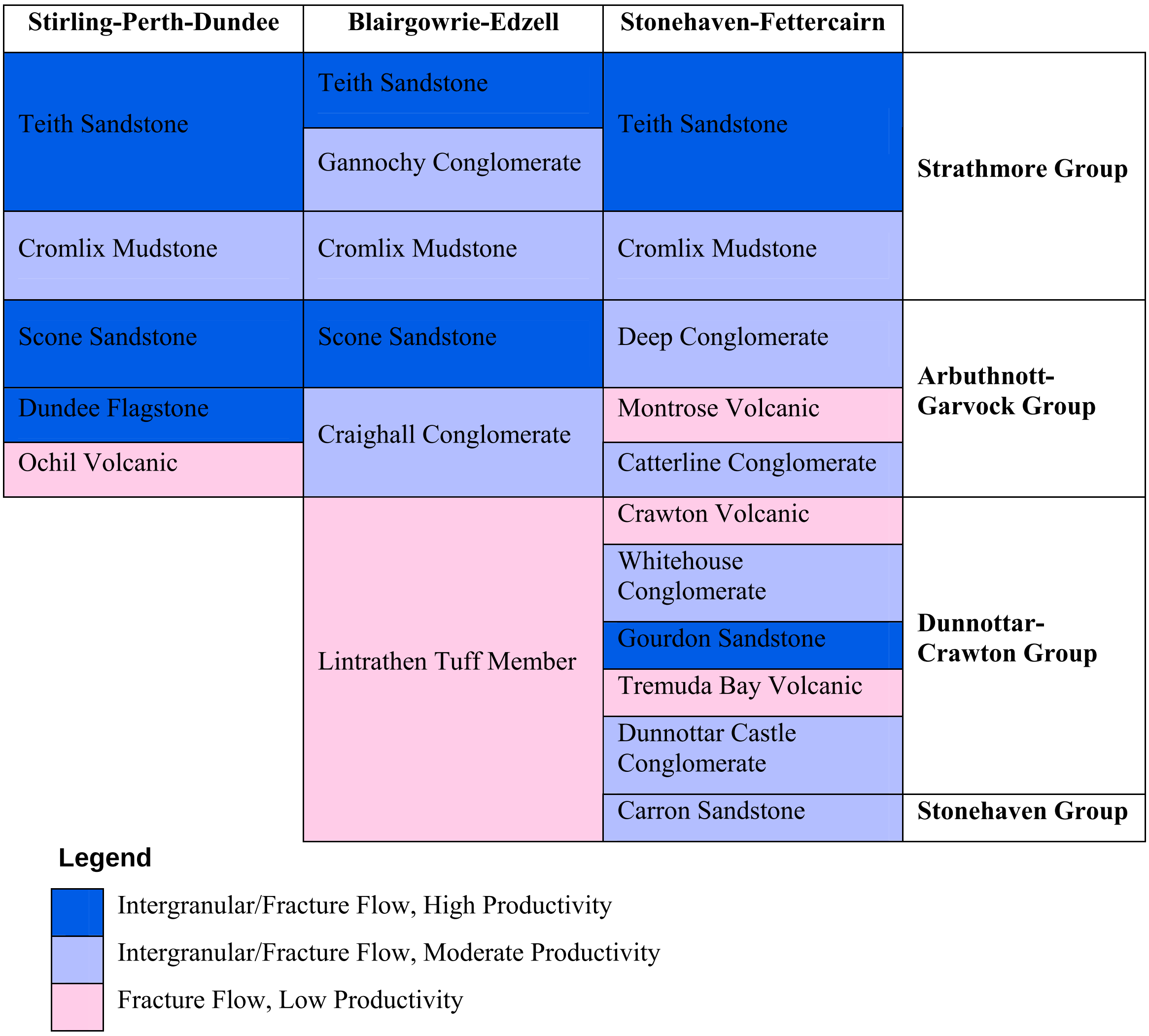


Figure 3 Schematic cross section of the Strathmore rocks from southwest to northeast, along the line shown in Figure 2 (after Armstrong and Paterson, 1970). Colour legend as for Figure 2.

Table 1 Late Silurian to Lower Devonian formations in Strathmore (from Browne *et al.* 2001), classified by aquifer productivity (see also Figure 5, based on MacDonald *et al.* 2004)



Stirling-Perth-Dundee	Blairgowrie-Edzell	Stonehaven-Fettercairn	
Teith Sandstone	Teith Sandstone	Teith Sandstone	**Strathmore Group**
	Gannochy Conglomerate		
Cromlix Mudstone	Cromlix Mudstone	Cromlix Mudstone	
Scone Sandstone	Scone Sandstone	Deep Conglomerate	**Arbuthnott-Garvock Group**
Dundee Flagstone	Craighall Conglomerate	Montrose Volcanic	
Ochil Volcanic		Catterline Conglomerate	
	Lintrathen Tuff Member	Crawton Volcanic	**Dunnottar-Crawton Group**
		Whitehouse Conglomerate	
		Gourdon Sandstone	
		Tremuda Bay Volcanic	
		Dunnottar Castle Conglomerate	
		Carron Sandstone	**Stonehaven Group**

Legend

- 🟦 Intergranular/Fracture Flow, High Productivity
- ▨ Intergranular/Fracture Flow, Moderate Productivity
- □ Fracture Flow, Low Productivity

2.3 SUPERFICIAL DEPOSITS GEOLOGY

The distribution of superficial deposits across Strathmore is shown in Figure 4. Most of the area is covered by glacial till, which is typically dominated by granular rather than clayey deposits. Much of the low lying areas are dominated by well developed spreads of glaciofluvial sand and gravel, associated with large meltwater rivers that drained Highlands areas during the last period of retreat of glacial ice. These deposits are generally less than 10 m thick, but in places up to 30 m have accumulated. In the major valleys, alluvial deposits often overlie the glaciofluvial sand and gravel. Granular raised beach deposits are not widespread, but in places they are of significant thickness, such as at Montrose, where they are up to 30 m thick in places. Along the coast between Dundee and Arbroath are fine-grained blown sands and fine- to moderate-grained raised granular marine deposits, commonly to a depth of 6 m or more. Under the Carse of Gowrie, between Dundee and Perth, beds of marine and estuarine clay overlie the Devonian sandstone, which can be more than 30 m thick.

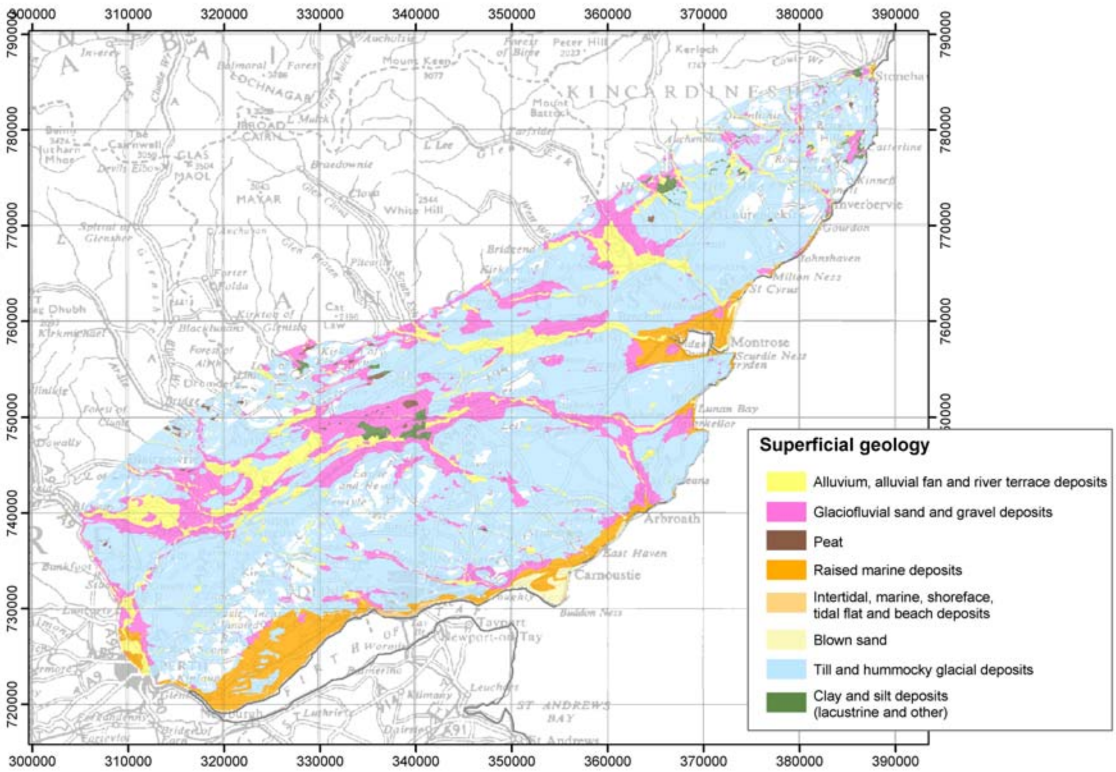


Figure 4 Superficial deposits in Strathmore

2.4 HYDROGEOLOGY

2.4.1 Bedrock hydrogeology

The Lower Devonian strata in Strathmore form an important regional aquifer. The hydrogeology and aquifer properties of the aquifer are described in Ó Dochartaigh (2004), and are summarised here. Upper Devonian to Lower Carboniferous rocks occur only in small areas in Strathmore, so that although in other parts of Scotland they form highly productive aquifers, they are not significant aquifer units in Strathmore.

The Lower Devonian sedimentary rocks can be divided into a number of aquifer units, of which the major ones are the:

- Teith Sandstone Formation (Strathmore Group) – dominantly sandstone
- Cromlix Mudstone Group (Strathmore Group) – dominantly siltstone and mudstone
- Strathmore Group undivided – dominantly conglomerate
- Scone Sandstone Formation (Arbuthnott-Garvock Group) – dominantly sandstone
- Dundee Flagstone Formation (Arbuthnott-Garvock Group) – dominantly sandstone
- Arbuthnott-Garvock Group undivided – dominantly conglomerate

Most if not all of these units, in particular those of the Arbuthnott-Garvock Group, also contain intercalations of volcanic rocks in varying proportions.

Most of the water boreholes for which data are available do not have good geological logs to show the actual rock sequence intercepted, and the aquifer tapped by each borehole generally has to be inferred from its depth and the mapped geology. The limited available data allows some distinction to be made between the aquifer units in terms of their hydrogeological properties, but there is no clear overall pattern of variation, which reflects the complexity of the geology and the paucity of data.

AQUIFER PROPERTIES

The sandstone-dominated formations, the Scone Sandstone, Teith Sandstone, and Dundee Flagstone formations, are all classed as highly productive (MacDonald *et al.* 2004, Table 1, Figure 5). The conglomerate- and mudstone-dominated formations, the Strathmore and the Arbuthnott-Garvock groups and the Cromlix Mudstone Group, are classed by BGS as moderately productive aquifers (MacDonald *et al.* 2004, Table 1, Figure 5).

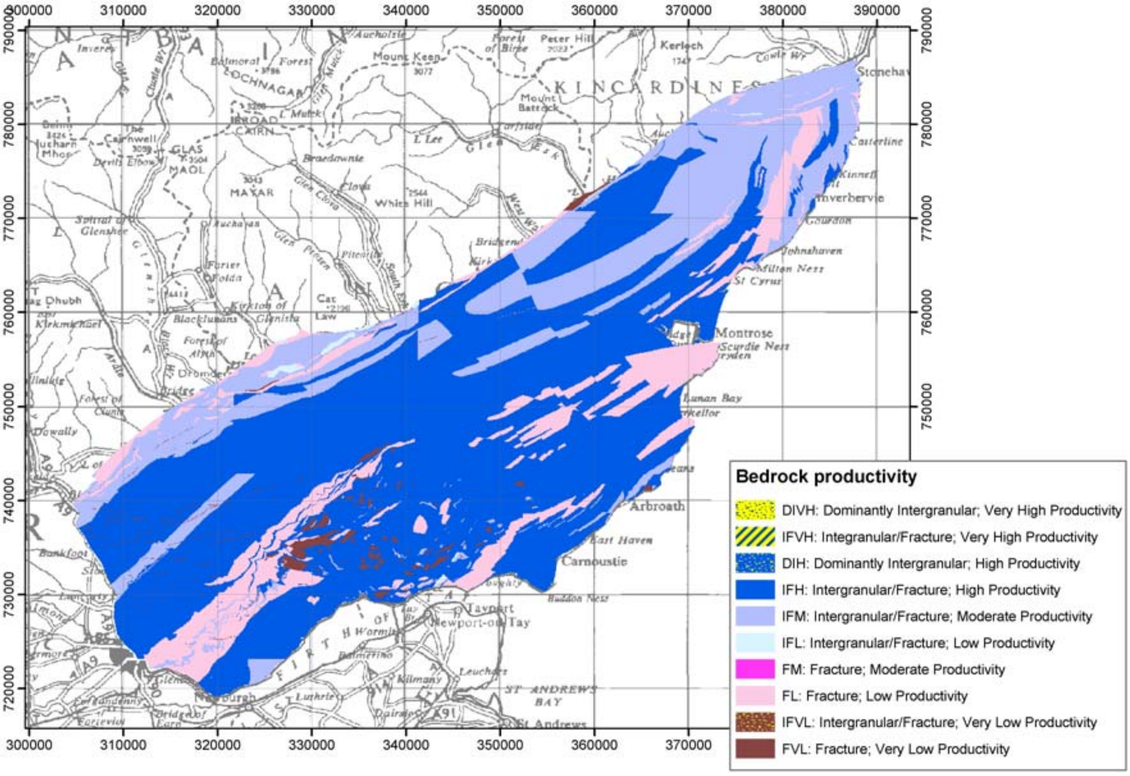


Figure 5 Productivity of the bedrock aquifers in Strathmore

The available aquifer properties data, from laboratory analyses, test pumping and geophysical logging, are largely for a small area in the centre of Strathmore, with no data for the western part of the aquifer. Data on borehole yields are available for a number of boreholes across Strathmore. The following is a summary of the available information.

- The sandstone-dominated formations typically comprise a largely uniform sandstone succession, with occasional coarser (conglomerate) and finer (silty) beds. Individual beds vary in terms of the degree of cementation.
- Normal operating yields of boreholes in the Devonian sedimentary rocks are in the range 5 to 15 l s^{-1}, with maximum recorded yields of up to 28 l s^{-1}. Little is known about the groundwater potential of the Devonian volcanic rocks.
- Measurements of the intergranular porosity and permeability of Lower Devonian sedimentary rocks in Strathmore are available from only one borehole near Forfar, with a total of 14 analyses of rock core samples at depths of between 7 and 147 m below ground level. Median porosity is 14 %, which is similar to the median porosity (15%) of the Lower Devonian Glenvale Sandstone Formation in Fife (Ó Dochartaigh

2004). Median permeability from the one Lower Devonian borehole in Strathmore is 0.0014 m d^{-1}.

- Measurements of the intergranular porosity and permeability of are available for one borehole in Strathmore, at Borrowfield, with samples from two depths at 97 and 140 m below ground level. The data indicate that the median porosity of the Upper Devonian samples is 27 %, with an interquartile range of 26 to 31 % and the median permeability of the Upper Devonian samples is 0.0353 m d^{-1}, with an interquartile range of 0.0173 to 0.318 m d^{-1} (Ó Dochartaigh 2004).
- Only 12 values for the transmissivity of the Lower Devonian aquifer are available, most of which are for the Teith Sandstone Formation (Strathmore Group) and the Arbuthnott-Garvock Group (undivided). Summary statistics are presented in Table 2, and indicate that the Teith Sandstone Formation, with a median transmissivity of 100 m2 d^{-1}, is generally more productive than the Arbuthnott-Garvock Group, with a median value of 34 m2 d^{-1}.
- A total of 43 values for the specific capacity of the aquifer are available, which can be divided between the Strathmore Group (undivided) and the Arbuthnott-Garvock Group (undivided), with the remainder from the undivided Lower Devonian aquifer. Summary statistics are presented in Table 2, and also indicate that the Stathmore Group, with a median specific capacity of 161 m^3 d^{-1} m^{-1}, is more productive than the Arbuthnott-Garvock Group, with a median value of 25 m^3 d^{-1} m^{-1}.
- Calculated values for storage in the Lower Devonian aquifer are available from only five boreholes, with an interquartile range from 0.0002 (25th percentile) to 0.03 (75th percentile) and a median value of 0.002.

Table 2 Summary statistics of transmissivity and specific capacity measurements for the Lower Devonian aquifer

	Transmissivity $m^2 d^{-1}$			**Specific Capacity $m^3 d^{-1} m^{-1}$**		
	Teith Sandstone Formation (Strathmore Group)	Arbuthnott-Garvock Group undivided	Lower Devonian undivided	Strathmore Group undivided	Arbuthnott-Garvock Group undivided	Lower Devonian undivided
Count	6	6	2	17	7	20
Minimum	51	4	164	17	2	1
25th percentile	100	24	-	118	14	47
Median	100	34	-	161	25	91
75th percentile	151	50	-	173	47	124
Maximum	200	290	174	770	258	605

GROUNDWATER FLOW

Downhole geophysical logging indicates that fracture permeability dominates groundwater flow in the Lower Devonian aquifer, even in the sandstone formations where intergranular permeability is relatively high and anisotropic, suggesting there may be preferential horizontal flow along bedding planes. Calliper logging has identified numerous enlargements in borehole walls, many of which correspond with discontinuities in water temperature and/or specific electrical conductivity (SEC) observed during flow logging. These are interpreted as individual fractures or occasionally zones of fractured rock, which form discrete groundwater inflow points. Such inflows have been inferred at depths of between 13 and 156 m. The little available information from mudstone and conglomerate formations indicates that they too show discrete fracture inflows.

Little is known directly about groundwater flow in the Devonian volcanic rocks, although fracture flow is likely to dominate, except along the boundaries of individual lava flows which may be preferentially weathered, increasing the local intergranular permeability. Intercalations of volcanic rocks within the sedimentary sequence are likely to restrict groundwater flow both vertically and laterally.

GROUNDWATER LEVELS

The limited available data show that groundwater levels across the low-lying parts of Strathmore are typically less than 10 m below ground level. The shallowest groundwater levels – typically less than 5 m below ground level – are found close to the major rivers, in valleys and on lower ground adjacent to the coast. Beneath the higher ground in the north, groundwater levels are often between 20 and 35 m below ground level. Measured annual water level fluctuations are on the order of 1 to 3 m, with a gradual recession from late spring to early autumn, followed by the onset of recharge and water level rebound in October or November. During the low rainfall year of 2003-04, initial water level recovery was slow, but increased rapidly during early January 2004 and reached a peak in mid to late January, although these data may not be representative of long term average patterns.

2.4.2 Superficial deposits hydrogeology

The till that covers most of the Strathmore area is thin and typically contains little usable groundwater. In some areas, often along the Highland Boundary Fault, the till is known to be more granular and therefore more permeable, and it may form a low productivity local aquifer, suitable for small groundwater supplies, at least seasonally. The blown sand and raised marine deposits along the coast is likely to form moderately permeable local aquifer. The highest permeability superficial deposits are the glaciofluvial and alluvial sands and gravels that infill the major valleys, and these typically form highly productive aquifers (Figure 6).

2.4.3 Groundwater vulnerability

Across most of Strathmore, groundwater is highly vulnerable to contamination from surface activities (Figure 7). This is partly due to the dominance of fracture permeability, which can lead to rapid transport of contaminants from the ground surface to the water table; and partly to the often thin and moderately to highly permeable overlying superficial deposits, which provide little protection from infiltrating contaminants. Most of Strathmore lies within a nitrate vulnerable zone, designated on the basis of high risk landuse (largely intensive fruit and vegetable farming) and on known high nitrate concentrations in groundwater.

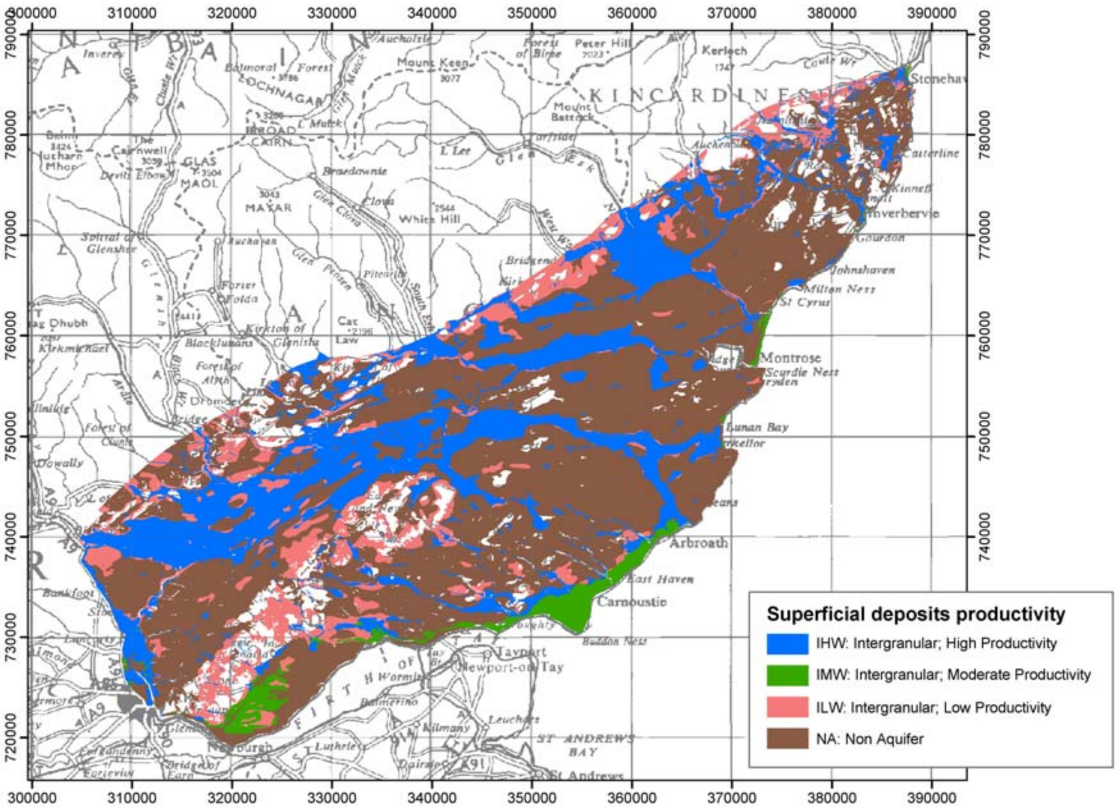


Figure 6 Productivity of the superficial deposits aquifers in Strathmore

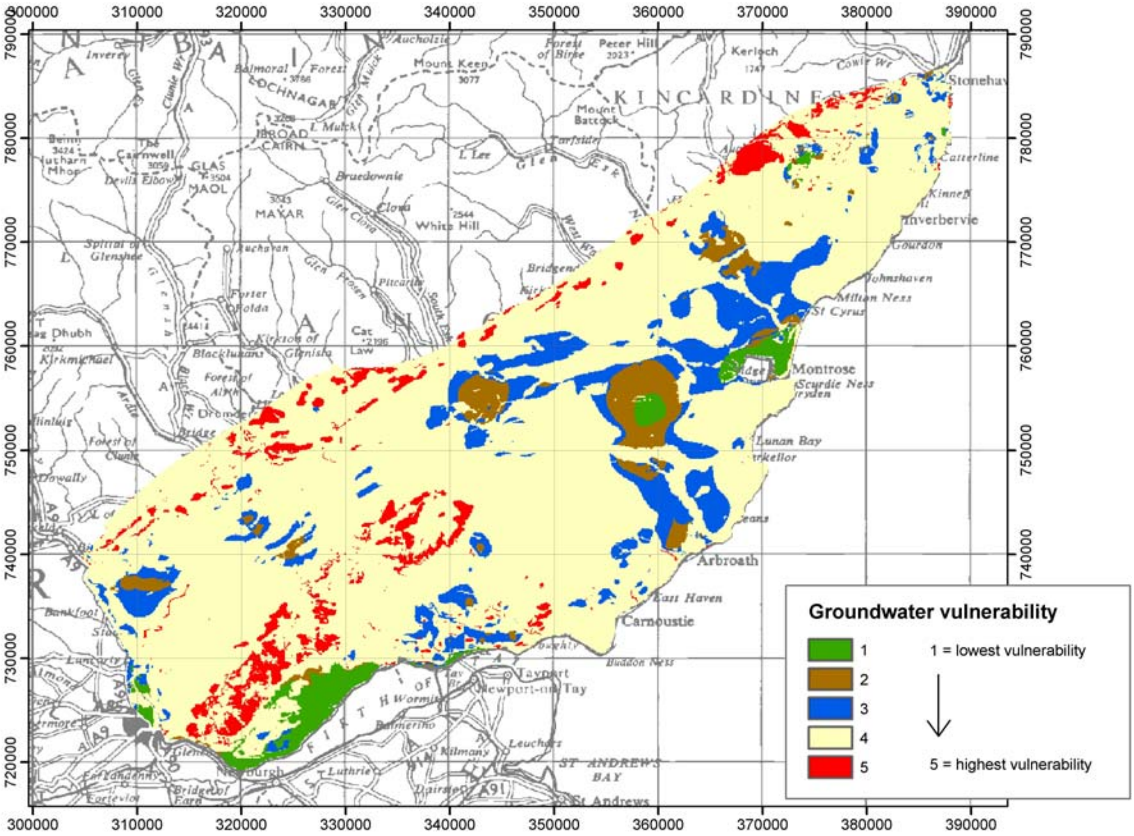


Figure 7 Groundwater vulnerability in Strathmore

Box 1 Summary of the hydrogeology of the Lower Devonian aquifer in Strathmore

- Fracture flow dominates groundwater movement through the aquifer.
- Median intergranular porosity is 14 %.
- Intergranular permeability is low, with a median of 0.0014 m d^{-1}
- Measured aquifer transmissivity and specific capacity are highly variable. Transmissivity ranges from 4 to 290 m^2 d^{-1}, and specific capacity from 1 to 770 m^3 d^{-1} m^{-1}.
- From the available data it appears there is more variability within aquifer units than between units, but in general the Strathmore Group, and in particular the Teith Sandstone Formation, appears to be the most productive aquifer formation.
- The variability within aquifer units is related to the geological complexity, in that most of the units comprise cyclical sedimentary sequences that include sandstone, conglomerate and mudstone, as well as intercalated volcanic rocks.

2.5 AQUIFER GEOCHEMISTRY AND MINERALOGY

There is little published information on the mineralogy of the Lower Devonian sedimentary rocks in Strathmore. Preliminary studies of the petrology and mineralogy of the Devonian sedimentary rocks in parts of the Strathmore area are reported by Phillips (2004, 2006). The formations are dominantly quartzose to quartzofeldspathic with varying proportions of lithic clasts, generally quartzose and feldspathic.

The Dundee Flagstone and the Scone Sandstone formations typically show the poorest development of carbonate cements, with only traces seen in occasional samples. The Teith Sandstone Formation shows varying amount of carbonate cement with some samples showing well developed carbonate, such as Edzell (Phillips 2004). The fine-grained rocks of the Cromlix Mudstone Formation all show some replacement of clay grade material by fine-grained granular carbonate. The sandstones of the Glenvale Sandstone Formation are typically calcareous, characterised by a well-developed carbonate cement (Phillips 2004). Dolomitic cement has not been specifically tested for, but may be present anywhere in the aquifer in varying proportions, as occurs in other Devonian sandstones in the UK.

A preliminary report on the regional geochemistry of Strathmore, based on stream sediment geochemistry (Breward 2004), identified a number of regional-scale variations and more localised anomalies. The most evident, and those which may have most impact on groundwater chemistry, are described briefly here.

- An ultrabasic anomaly, with high chromium, nickel and magnesium, and also high tin and cobalt, occurs at Alyth. This is possibly related to the presence of ophiolitic ancient Highland Border Complex rocks, or to granite clasts in conglomerates. Very high chromium concentrations of up to 1960 mg kg^{-1} have been measured.
- The sandstones and conglomerates of the Arbuthnott-Garvock Group are marked by a broad area, especially north of Perth, of high chromium concentrations (up to 800 mg kg^{-1}). By contrast, relatively low chromium concentrations predominates over the sandstones of the Strathmore Group, with a major break between the two units, implying a major change in sediment provenance.

- High iron concentrations, combined with high gallium, occur in a broad southeasterly trending band over the Arbuthnott-Garvock Group between Dundee and Montrose. Elsewhere there are generally very low iron concentrations in stream sediments over the sandstone and conglomerate units.
- High calcium concentrations are associated with lavas in the western part of Strathmore.
- Higher than average concentrations of uranium appear to be associated with the sedimentary rocks of the Strathmore Group, although the sediments of the Arbuthnott-Garvock Group may also show elevated values. The origin of this is uncertain, but may be related to the presence of granitic clasts derived from north of the Highland Boundary Fault or to relative abundance of phosphate minerals or iron oxides.
- There is a marked urban-industrial ‘halo’ of anthropogenic copper around Dundee. Elsewhere, copper concentrations are generally relatively low, with generally higher concentrations over volcanic rocks, but there are isolated areas of high copper in stream sediments (mostly around 100 mg kg^{-1}) over parts of the Strathmore and Arbuthnott-Garvock groups.

2.6 RAINFALL CHEMISTRY

Rainfall chemistry is available from a station at Glen Dye [NGR 364200 786400], which lies approximately 10 km north of the aquifer outcrop, to the north of Edzell and Laurencekirk. The station is also north of the Highland Boundary Fault in a mountainous area, at an altitude of 185 m above Ordnance Datum (OD), which is higher than much of the area of aquifer outcrop in Strathmore.

The average annual rainfall at the Glen Dye station (based on the mean of all years from 1987 to 2003) is 873 mm, with a range from 568 to 1253 mm. The average rainfall chemistry for the period 1987 to 2003, based on 685 samples collected over that period, and the average rainfall chemistry for the period January to December 2003, based on 25 samples collected between January and December 2003, is shown in Table 3.

Solutes derived from rainfall typically increase during evapotranspiration, such that the solute concentration in infiltrating recharge is expected to be roughly three times higher. However, nutrient concentrations (e.g. nitrogen and potassium) may decrease by biomass uptake, so that 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 after evapotranspiration, based on a three times concentration of the median 1987-2003 rainfall chemistry, is also presented in Table 3.

Table 3 Rainfall chemistry at Glen Dye [NGR 364200 786400], taken from the UK National Air Quality Information Archive (http://www.airquality.co.uk/archive/index.php).

Solute	**Units**	**Mean 1987-2003**	**Median 1987-2003**	**Mean 2003**	**Median 2003**	**Expected chemistry of infiltrating water after evapotranspiration**[1]
pH		4.65	4.61	4.65	4.49	3.73
SEC	µS cm^{-1}	35.60	28.00	37.33	28.5	84
Ca	mg l^{-1}	0.30	0.19	0.33	0.26	0.57
Cl	mg l^{-1}	3.91	2.09	4.00	3.13	6.27
K	mg l^{-1}	0.14	0.10	0.15	0.10	0.30
Mg	mg l^{-1}	0.30	0.17	0.32	0.18	0.51
Na	mg l^{-1}	2.21	1.23	2.57	1.34	3.69
NO_3-N	mg l^{-1}	0.50	0.324	0.77	0.46	1.75
NH_4-N	mg l^{-1}	0.43	0.26	0.64	0.40	–
SO_4-S	mg l^{-1}	0.87	0.64	0.76	0.62	1.92

[1] Calculated for illustrative purposes as three times the median 1987–2003 rainfall concentration

3 Methodology

3.1.1 Sampling and chemical analysis

A total of 35 new samples were collected from a series of boreholes, springs and shallow wells in Strathmore in July 2004. Most of the boreholes investigated 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. There are no data available to identify where this is the case, although deeper boreholes are likely to have broader input zones than shallow boreholes. Although construction details are lacking for most of the boreholes sampled, where they do exist they show that boreholes are generally uncased in the bedrock, so that there may be inflows throughout the length of the borehole. The data provided from pumped samples do not give information about fine resolution of groundwater-quality variations, but they do provide useful depth-integrated compositions that are of value in regional assessments.

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 0.22 µm filters and collected in polyethylene bottles rinsed with sample water before collection. Four filtered aliquots were collected at each site: two were acidified to 1% v/v with Aristar HNO_3, one for analysis of major cations, total sulphur and Si by ICP-OES (inductively coupled plasma-optical emission spectroscopy), and the other for a large range of trace elements by ICP-MS (inductively coupled plasma-mass spectrometry). A third aliquot was acidified to 1% v/v with Aristar HCl for analysis of As by AFS (atomic fluorescence spectrometry) with hydride generation, to be used if necessary as a check on ICP-MS As analyses. A fourth aliquot was left unacidified for analysis of anions by ion chromatography (NO_3-N, Br, F) and automated colorimetry (Cl, NO_2-N, NH_4-N). Samples were also collected in chromic-acid-washed glass bottles for dissolved organic carbon (DOC) analysis, after filtration using silver-impregnated 0.45 µm filters. DOC was measured by carbon analyser. At 15 of the sample sites, additional samples were collected in glass bottles for stable-isotopic analyses (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 samples from the 2004 survey were augmented with data from 13 sites in the Lower Devonian Strathmore aquifer sampled in November and December 2001 as part of a project to identify suitable points for groundwater sampling from areas proposed as nitrate-vulnerable zones (NVZs). Field measurements for these samples were taken of pH, SEC, water temperature and alkalinity (Ball and MacDonald 2002). Supplementary analyses by ICP-OES, colorimetry and ion chromatography were also carried out at the BGS laboratories; no ICP-MS or isotopic measurements were made on these earlier samples.

Ionic charge imbalances are less than 5% for all 48 samples incorporated in the dataset. The locations of all 48 samples are shown in **Figure 8**.

3.1.2 Sample sources and aquifer units

The groundwater samples were obtained from a range of different source types, including springs, shallow wells and boreholes of different depths. A summary of the distribution of groundwater samples from the different source types, aquifer units and landuse types is given in Figures 9 and 10. A large majority of the groundwater samples are from the Arbuthnott-Garvock Group **(**Figure 9), which includes the Scone Sandstone Formation and the Dundee Flagstone Formation (Figure 3 and Table 1). Most of the samples were taken from areas of dominantly arable agriculture, reflecting the main landuse in Strathmore, but there are a significant number from areas of mixed cultivated land and mixed landuse (including areas of mixed golf course and arable land use) (Figure 10).

The majority (31) of the samples were collected from groundwater sources sited on largely sedimentary bedrock units, although as described above (Section 2.4.1), may also intercept volcanic rocks in varying proportions. Three of the samples were collected from boreholes sited on volcanic rocks of the Arbuthnott-Garvock Group. One sample was collected from a high yielding shallow borehole where there may be a large component of flow from glaciofluvial sand and gravel deposits overlying the Teith Sandstone Formation.

3.1.3 Statistical handling

The groundwater chemistry data from all 48 samples were amalgamated into a single database. Statistical summaries of the groundwater chemistry data were calculated using R (R Development Core Team 2005). These included observed minima and maxima, median and selected quantiles. Statistical distributions were calculated using the non-parametric Kaplan-Meier method to handle data below detection limit (Helsel 2004) and quantile values together with cumulative-frequency diagrams were produced using the NADA package in R (Lee 2005). This approach could deal with multiple detection limits, a common feature of geochemical data sets. Box-and-whiskers plots were also produced using R, but here the distributions were calculated by substituting non-detects with values of half the detection limit. This approach is somewhat arbitrary, but is a standard approach in groundwater chemistry analysis (e.g. Shand *et al.* 2003). Limitations of the calculated graphical distributions must however be borne in mind for trace elements where a significant number of samples lie below the detection limit (or limits).

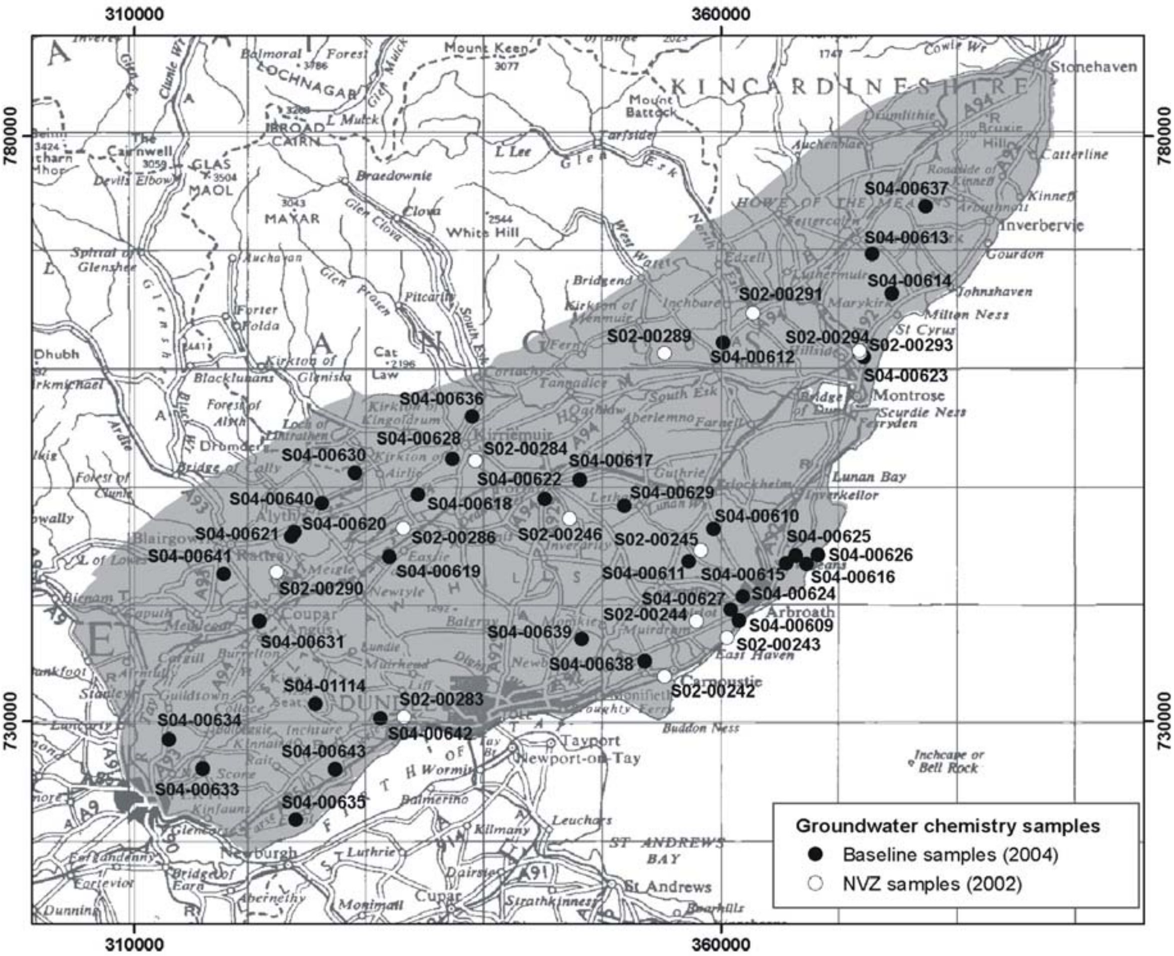


Figure 8 Locations and reference numbers of groundwater samples in Strathmore

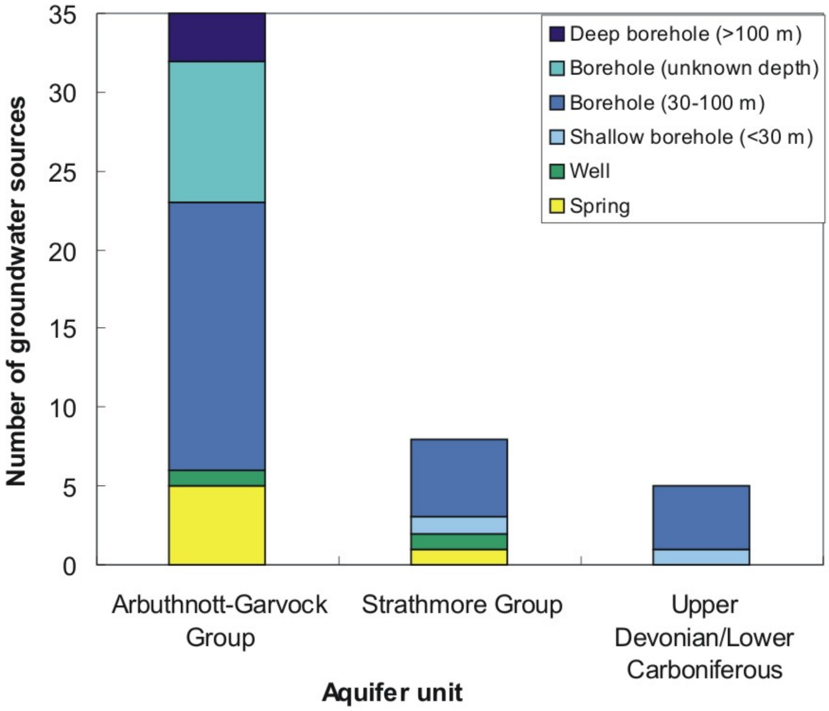


Figure 9 Distribution of groundwater samples by source type and aquifer unit

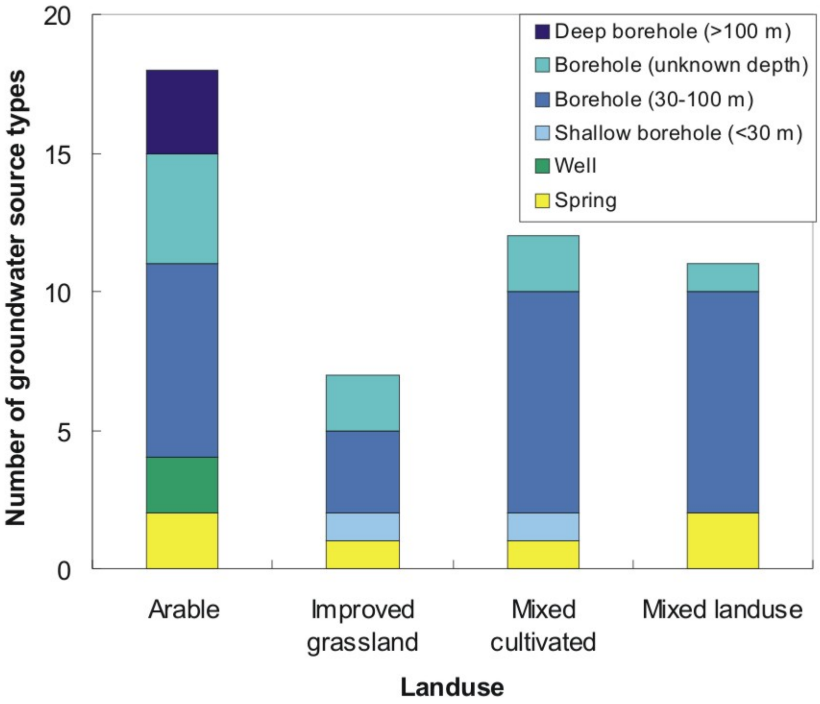


Figure 10 Distribution of groundwater samples by source type and landuse

4 Hydrogeochemistry

4.1 DATA PRESENTATION

Summary hydrogeochemical data for the Strathmore groundwaters are presented in graphical form as a Piper diagram (Figure 11), as box-and-whiskers plots for selected major and trace elements (Figure 12) and as cumulative-frequency diagrams (Figure 13). Box-and-whisker plots provide graphical summaries of the sample population median (white line) and inter-quartile range (box margins); brackets indicate a range of 1.5 times the inter-quartile range, positioned on the nearest actual observation and outliers are shown as individual lines. Box widths are directly proportional to the number of samples. In the cumulative-frequency diagrams, no data are plotted for values below the lowest detection limit, although the data are accounted for. A statistical summary of the data is also given in Table 4.

Table 4 Statistical summary of groundwater chemistry data for the Strathmore aquifer.

Parameter	Units	min	10%	25%	median	75%	90%	max	n
Temp	°C	7.4	8.7	9.3	10.2	11.1	12.8	14.1	43
pH		6.54	6.89	7.32	7.48	7.62	7.81	8.62	48
Eh	mV	281	342	380	404	441	459	481	34
DO	mg l^{-1}	<0.1	1.65	3.88	7.21	8.3	9.1	10.4	35
SEC	µS cm^{-1}	273	320	420	508	607	938	1528	38
δ^{2}H	‰	-59.5	-59.1	-57.9	-56.5	-52.7	-50.5	-50.3	14
δ^{18}O	‰	-8.78	-8.71	-8.57	-8.15	-7.76	-7.64	-7.13	14
δ^{13}C	‰	-19.1	-18.8	-18.1	-16.0	-15.0	-8.5	-7.1	14
Ca	mg l^{-1}	24.7	28.9	39.7	52.4	60.6	89.1	140	48
Mg	mg l^{-1}	3.89	5.1	8	11.7	15.5	18.9	32.4	48
Na	mg l^{-1}	8.17	11.9	14.3	20.9	26.3	67.1	284	48
K	mg l^{-1}	<0.5	0.85	1.47	2.13	3.2	4.5	201	48
Cl	mg l^{-1}	6.83	13.5	18.6	29.3	43.3	78.1	354	48
SO_4	mg l^{-1}	4.3	10.5	15.4	22.4	29.6	66.7	169	48
HCO_3	mg l^{-1}	84.2	98	132	158	211	219	293	48
NO_3-N	mg l^{-1}	0.2	1.3	2.6	6.7	11.7	15.7	81	48
NO_2-N	mg l^{-1}	<0.0003	0.00072	0.00132	0.0029	0.00587	0.018	0.194	35
NH_4-N	mg l^{-1}	<0.004	<0.004	<0.004	<0.004	0.005	0.0255	8.32	35
P	mg l^{-1}	<0.02	<0.02	<0.02	0.03	0.07	0.10	40.5	37
DOC	mg l^{-1}	0.38	0.43	0.48	0.88	1.24	1.9	5.82	23
F	mg l^{-1}	0.028	0.05	0.061	0.088	0.124	0.23	3.7	47
Br	mg l^{-1}	<0.03	0.05	0.08	0.095	0.186	0.243	1.76	47
I	mg l^{-1}	0.0005	0.0024	0.0034	0.0042	0.0071	0.0093	0.278	47
Si	mg l^{-1}	3.98	4.18	5.03	6.56	8.12	9.67	15.2	48
Ag	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	35
Al	µg l^{-1}	2	3	4	5	6	6	26	35
As	µg l^{-1}	<0.5	0.6	0.8	1.5	3.7	6.9	8.8	35
Au	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	35
B	µg l^{-1}	<10	<10	<10	30	46	84	343	35
Ba	µg l^{-1}	30	65	85	227	300	372	570	35
Be	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	0.15	35
Bi	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	35
Cd	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	0.07	0.1	0.12	35
Ce	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.24	35
Co	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	0.03	0.03	0.070	35
Cr	µg l^{-1}	<0.5	<0.5	<0.5	0.6	1	1.3	2.10	35
Cs	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.03	0.07	0.12	35
Cu	µg l^{-1}	0.5	0.6	0.8	1.2	1.8	7	40.7	35
Dy	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.12	35
Er	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.17	35
Eu	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.03	35

Parameter	Units	min	10%	25%	median	75%	90%	max	n
Fe	µg l^{-1}	<6	<6	<6	<6	26	100	547	40
Ga	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	35
Gd	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.08	35
Ge	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	0.09	35
Hf	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	35
Hg	µg l^{-1}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	35
Ho	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	35
In	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	35
Ir	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	35
La	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.02	0.045	0.23	35
Li	µg l^{-1}	1.1	1.3	3.8	6.3	10.2	17.3	39	35
Lu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	35
Mn	µg l^{-1}	0.1	0.29	0.52	1.43	19	47	528	42
Mo	µg l^{-1}	<0.1	0.1	0.1	0.2	0.7	1.4	8.4	35
Nb	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	35
Nd	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.02	0.075	0.25	35
Ni	µg l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	0.4	0.9	35
Os	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	35
Pb	µg l^{-1}	<0.1	<0.1	<0.1	0.1	0.2	0.4	1.3	35
Pd	µg l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	35
Pr	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.05	35
Pt	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	35
Rb	µg l^{-1}	0.08	0.27	0.42	0.87	1.29	1.88	28.7	35
Re	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	35
Rh	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	35
Ru	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	35
Sb	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	0.55	35
Sc	µg l^{-1}	<1	<1	<1	<1	<1	<1	1	35
Se	µg l^{-1}	<0.5	<0.5	<0.5	0.6	1.0	1.2	2.3	33
Sm	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.05	35
Sn	µg l^{-1}	0.23	0.42	0.46	0.49	0.51	0.54	1.74	35
Sr	µg l^{-1}	71.8	85.5	119	183	293	756	1120	35
Ta	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	35
Tb	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	35
Te	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	35
Th	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	35
Ti	µg l^{-1}	<10	<10	<10	<10	<10	<10	90	35
Tl	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.02	35
Tm	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	35
U	µg l^{-1}	0.08	0.13	0.32	1.32	2.9	6.71	15.4	35
V	µg l^{-1}	<0.2	1.3	1.7	3.2	4.8	7.2	24.3	35
W	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	35
Y	µg l^{-1}	0.01	0.01	0.02	0.04	0.07	0.14	0.84	35
Yb	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.30	35
Zn	µg l^{-1}	0.7	1.6	3.3	9.2	55.9	139.9	836	35
Zr	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.09	35

DO: dissolved oxygen; SEC: specific electrical conductance; DOC: dissolved organic carbon

4.2 MAJOR IONS

The results of the hydrogeochemical investigation indicate that groundwater in the Devonian sedimentary aquifer of Strathmore is for the most part weakly mineralised, with total dissolved solids (TDS) typically less than 400 mg l^{-1} and in some cases less than 200 mg l^{-1}. Nonetheless, the concentrations of solutes are normally higher than likely concentrations in recharge water (rainwater subject to evaporation, Section 2.6) and imply that solutes have accumulated in the groundwaters by water-rock interaction since recharge.

Calcium and HCO_3 are usually the dominant ions. A few more saline groundwaters occur in coastal areas. These have TDS concentrations up to more than 1000 mg l^{-1} and trend to Na-Cl compositions. The distributions of major ions are illustrated in the Piper diagram in Figure 11. The trend to increasing Na-Cl compositions suggests that these groundwaters can be explained by simple mixing between fresh groundwater and seawater. One sample approximately 3 km from the coast (S02-00244) has a slightly more sodic composition than implied from simple linear mixing and may have an increased Na concentration through ion exchange. Magnesium concentrations and Ca-Mg ratios vary considerably, indicating that dolomitic cement does occur in a number of locations across the aquifer and that groundwater evolution reflects this.

Groundwater pH is typically neutral to slightly alkaline with a range of 6.5 to 8.6. Higher pH values are generally associated with low pCO_2 values. Many samples, especially the low-TDS, low pH waters from shallow boreholes and springs, are undersaturated with respect to calcite ($CaCO_3$) and indicate a lack of equilibration with calcite and/or paucity of calcite at shallow levels in the aquifer matrix. Most of the samples with higher pH are saturated with respect to calcite. Almost all are undersaturated with respect to dolomite ($Ca,Mg(CO_3)_2$).

The box-and-whiskers (Figure 12) and cumulative frequency diagrams (Figure 13) also demonstrate the dominance of Ca and HCO_3 ions and the appearance of outliers of more saline composition. In the cumulative-frequency trends these are demonstrated by a break of slope at the high end of the distribution.

The groundwaters of the region are almost invariably oxygenated with detectable concentrations of dissolved oxygen (DO) and high Eh values. This is consistent with the generally unconfined condition of the aquifer and paucity of clay-rich superficial deposits. Where measured, DO was only undetected (less than 0.1 mg l^{-1}) at one sampling site and concentrations ranged up to 10.4 mg l^{-1}, approximating saturation at the ambient temperatures of the groundwaters. The Eh range of all the samples was 281 to 481 mV. Values in excess of around 300 mV are typically indicative of oxygenated conditions.

The unconfined and oxygenated conditions of the Strathmore aquifer mean that the groundwaters are vulnerable to contamination by nitrate from agricultural and domestic sources. Infiltrating recharge might be expected to contain of the order of 2 mg l^{-1} NO_3-N or less (Section 2.6). Concentrations of NO_3-N in the groundwaters range between 0.2 mg l^{-1} and 81 mg l^{-1}, though the maximum is an extreme and the next highest concentration is 22 mg l^{-1} (Figure 12). This latter value is twice the EC maximum permissible value for NO_3-N in drinking water. In total, 29% of analysed samples exceed the EC maximum of 11.3 mg l^{-1}. The sample with the highest NO_3-N concentration of 81 mg l^{-1} (S04-00616) also had a K concentration of 201 mg l^{-1}, P of 40.5 mg l^{-1}, NH_4-N concentration of 8.3 mg l^{-1} and TDS of 755 mg l^{-1}, as well as relatively high concentrations of B, Cu, Fe, Mn, Mo, Rb and Ti. It is suspected that this sample has suffered from the effects of direct contamination by fertiliser in the vicinity of the borehole. Despite the obvious contamination in the sample of the chemical parameters named above, many other parameters appear unaffected by the pollutant inputs, as concentrations lie within the ranges of other samples from the Strathmore aquifer. Figure 12 and Figure 13 show that nitrate is one of the more variable parameters in the groundwaters, with one of the largest observed inter-quartile ranges (standard deviations). The controls on nitrate concentrations in groundwater in Strathmore are discussed in Section 5.5.

Phosphorous in the samples is typically less than 0.1 mg l^{-1} (the 90th percentile), with a median of 0.03 mg l^{-1}. The highest P concentration is 40.5 mg l^{-1} (S04-00616), in a sample that has clearly suffered from extreme agricultural pollution and also shows anomalously high concentrations of nitrate and other nutrients of agricultural origin (see above). The next highest concentration is 7.2 mg l^{-1} (S02-00290), from a borehole on agricultural land, but which does not show anomalously high nitrate, and the source of the high phosphate is not clear. All other samples show less than 0.2 mg l^{-1} PO_4-P.

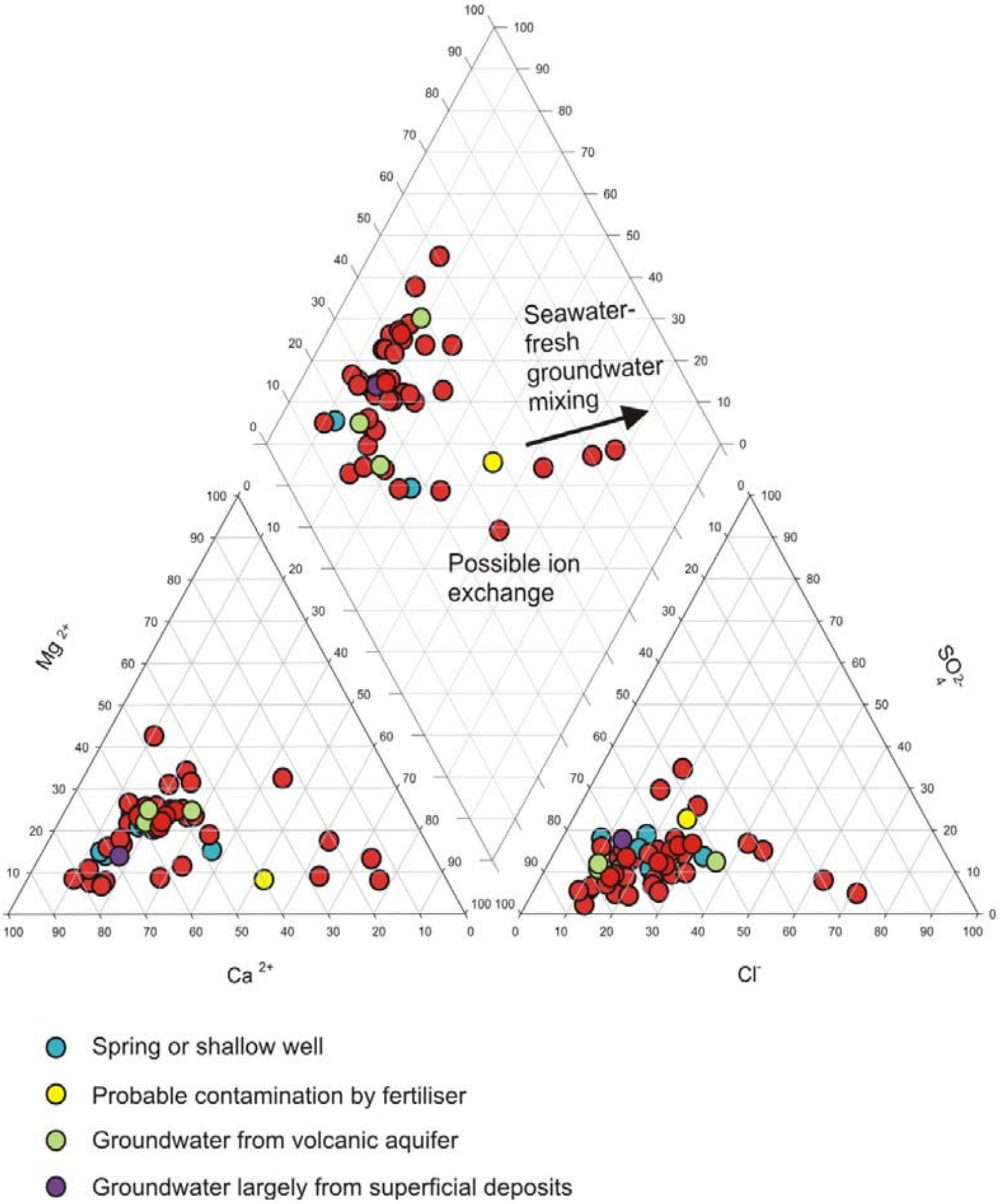


Figure 11 Piper diagram showing the distribution of major ions for the 48 groundwater samples.

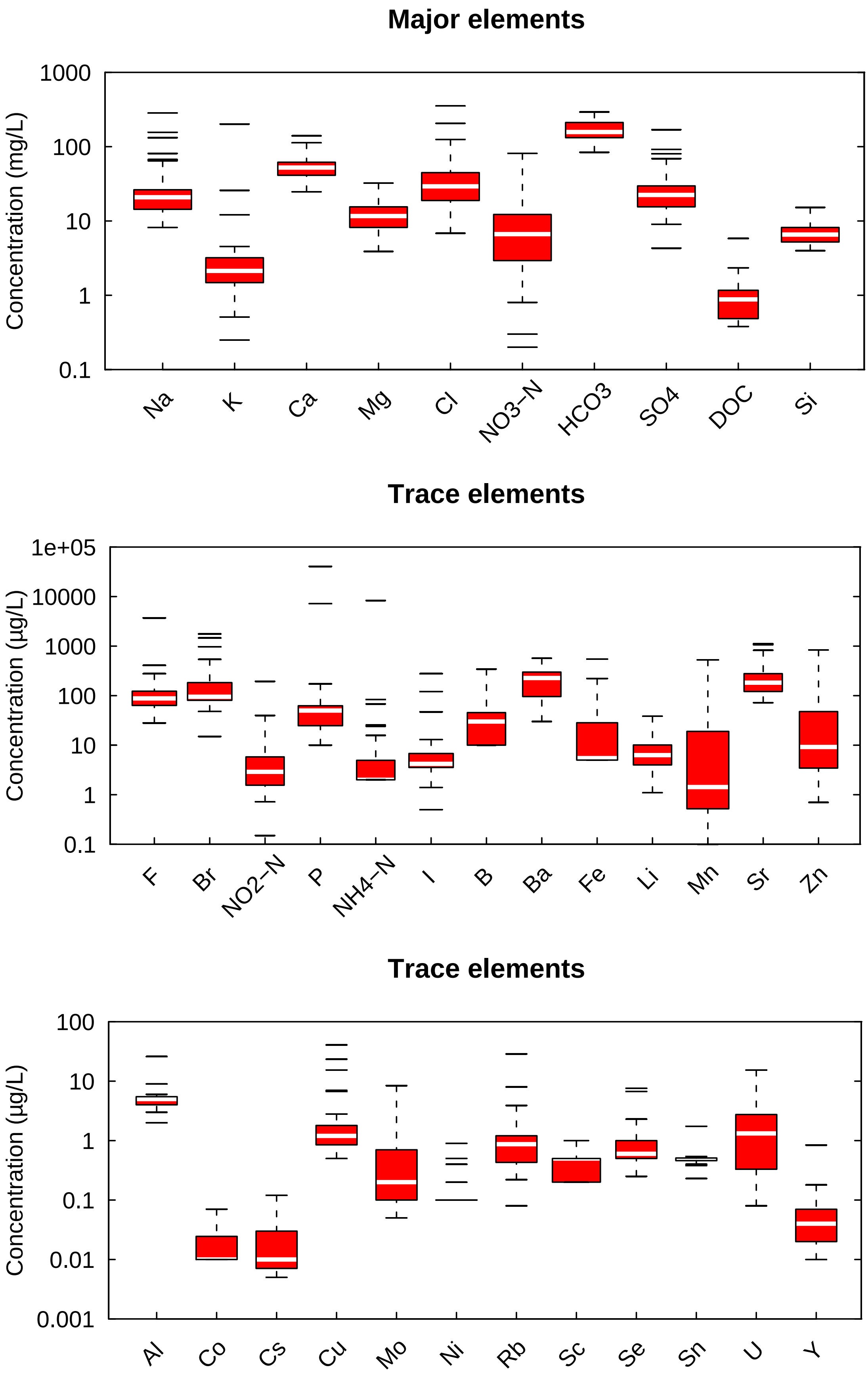


Figure 12 Box-and-whiskers plots for major ions and selected trace elements in the Strathmore groundwaters.

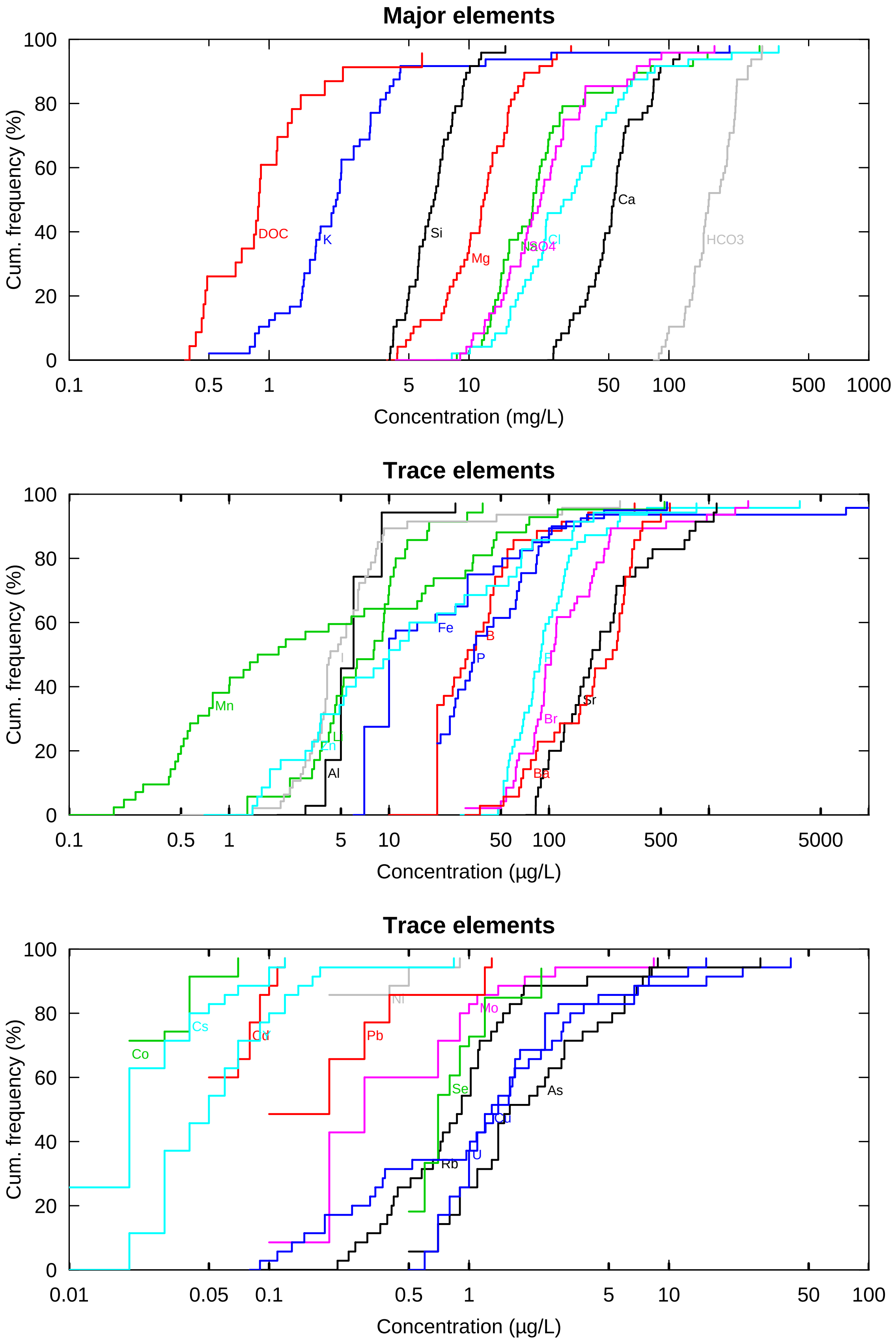


Figure 13 Cumulative-frequency diagrams for selected major and trace elements in the Strathmore groundwaters. Data below detection limits are not plotted here, but are accounted for in the analysis.

4.3 TRACE ELEMENTS

As a result of the generally oxygenated nature of the groundwaters, concentrations of NO_2-N and NH_4-N are generally low: most NO_2-N concentrations are less than 0.04 mg l^{-1} and most NH_4-N concentrations less than 0.08 mg l^{-1}. Only one sample (NO_2-N of 0.194 mg l^{-1}) exceeded the EC maximum permissible value for NO_2-N in drinking water of 0.15 mg l^{-1}. Concentrations of DOC reach up to 5.8 mg l^{-1} but most are around 1 mg l^{-1} or less, as is common for oxygenated groundwaters in the UK (Figure 12).

Concentrations of Fe and Mn are also typically low because of the low solubility of iron and manganese oxide minerals in oxygenated environments. The concentrations of Fe are usually less than 100 µg l^{-1}, though they range up to 547 µg l^{-1}, and concentrations of Mn are usually less than 50 µg l^{-1}, though they show a large range (Figure 12 and Table 4) from 0.1 µg l^{-1} to 528 µg l^{-1}. The highest recorded Fe and Mn concentrations were in a sample less than 1 km from the coast near Carnoustie (S02-00242). No DO or Eh measurements were made at this site. Though chemical data for the sample are limited, the groundwater from this borehole appears to be unusual. The sample has much higher concentrations of Ca and SO_4 than other groundwaters in the area, without having exceptionally high salinity (SEC 950 µS cm^{-1}). The high Ca and SO_4 concentrations suggest that the composition of the water has evolved by dissolution of some gypsum although the sample is still undersaturated with respect to this mineral. The sample also has an unusually high concentration of F (3.7 mg l^{-1}; Table 4) and its chemical composition indicates saturation with respect to the mineral fluorite (CaF_2). It is concluded that this source is tapping relatively old groundwater that has had a comparatively long residence time in the aquifer and hence has equilibrated with fluorite and dissolved some gypsum (or anhydrite). It may also be relatively reducing compared to other borehole waters in the area.

This sample is also the only one that has a F concentration in excess of the EC maximum permissible value for F in drinking water of 1.5 mg l^{-1}. Concentrations in most analysed samples are low (90th percentile 0.23 mg l^{-1}; Table 4) and reflect a general paucity of F-bearing minerals in the aquifer. All samples other than this one are strongly undersaturated with respect to fluorite.

Barium and Sr concentrations reach up to 570 µg l^{-1} and 1120 µg l^{-1} respectively. Feldspars are likely to be an important source of both elements in the groundwaters, although additional Sr could be derived from calcite and Ba from barite ($BaSO_4$). Most of the groundwaters are saturated with respect to barite.

Concentrations of As range from less than 0.5 to 8.8 µg l^{-1}. All are below the EC limit for As in drinking water of 10 µg l^{-1}, though a number of samples have concentrations approaching this value. The source of the As is considered most likely to be iron oxides which are present in the cement and as grain coatings in the sandstones. The cause of the spatial variability in As concentrations is unclear as the element correlates poorly with most other analysed chemical parameters.

Under the near-neutral groundwater conditions typical of the aquifer, most trace elements that form cationic species have low concentrations. Concentrations of Co are all less than or equal to 0.07 µg l^{-1}; Ni concentrations are universally less than 1 µg l^{-1} and Pb concentrations are less than or equal to 1.3 µg l^{-1}. Zinc concentrations reach up to 836 µg l^{-1}, though most are less than 120 µg l^{-1}. The concentrations of Al reach up to 26 µg l^{-1}; though most are less than 6 µg l^{-1}, reflecting the low solubility of aluminosilicate minerals at neutral pH. The highest observed Al concentration (sample S04-00619) may be due to a small contribution from colloidal particles (less than 0.22 µm), as the sample also had an anomalously high Fe concentration (100 µg l^{-1}) given the sample pH of 7.49 and the oxygenated condition of the water (DO was 6.7 mg l^{-1}).

Concentrations of most rare-earth elements (REE) are also low, and typically below analytical detection limits. Some are detectable however, with ∑REE concentrations up to 1.75 µg l^{-1} (sample S04-00617). Shale-normalised profiles (normalised to NASC, "North Atlantic Shale Composite" of Sholkovitz 1988) are shown in Figure 13 for the samples where a substantial number of REE were detectable by ICP-MS. The shale-normalised profiles most often show enrichment of the heavy REE relative to the light REE and a negative Ce anomaly is common. It is well-established that heavy REE form more stable complexes with carbonate ligands than light REE (e.g. Goldstein and Jacobsen 1988, Smedley 1991) and given the dominance of the HCO_3 anion in the groundwaters, this is the most likely control on the relative REE distributions. The negative Ce anomaly most likely reflects the oxygenated nature of the groundwaters. Under oxygenated conditions, Ce is stabilised in its Ce(IV) oxidation state and forms insoluble Ce(IV) oxides. The normalised Ce concentration is therefore much lower than the concentrations of the neighbouring trivalent REE.

Sample S04-00619 has a distinct normalised REE profile, being flatter with no negative Ce anomaly and a small positive Eu anomaly. As this sample is believed to contain a component of colloidal material (see above), it is speculated that the profile reflects the inputs of a contribution of colloidal REE which would explain the closer correspondence of the profile to a "shale" composition. The positive Eu anomaly may reflect higher inputs from a Eu-rich mineral (such as alkali feldspar) in the sandstone source rocks than are found in the shale composite. The origin of the REE in the Strathmore samples is uncertain, but is most likely to be by desorption from iron oxides (haematite, goethite) that occur as grain coatings and cement in the sandstone.

Concentrations of U in the groundwater samples reach up to 15.4 µg l^{-1}, although 75% are less than 2.9 µg l^{-1}. The highest concentration observed exceeds the WHO (2004) provisional guideline value for U in drinking water of 15 µg l^{-1}, although this source is not used for potable supply. The concentrations of U in the groundwaters are relatively high compared to groundwaters in other British aquifers, although they are in line with concentrations found in groundwater from red-bed sandstones (Smedley *et al.* 2006). The U concentrations show a weak positive correlation with pH (Figure 15) and suggest that mobilisation is favoured under alkaline conditions, probably stabilised as aqueous U-carbonate species. Highest concentrations appear to be present where dissolved-oxygen concentrations are lowest (Figure 15). This is likely to be a function of groundwater residence time, dissolved U concentrations being lowest in young shallow groundwaters but higher where water-rock interactions have been more prolonged. Positive correlations between U and both Li and B (Figure 15), are also believed to be related to time-dependent water-rock interaction.

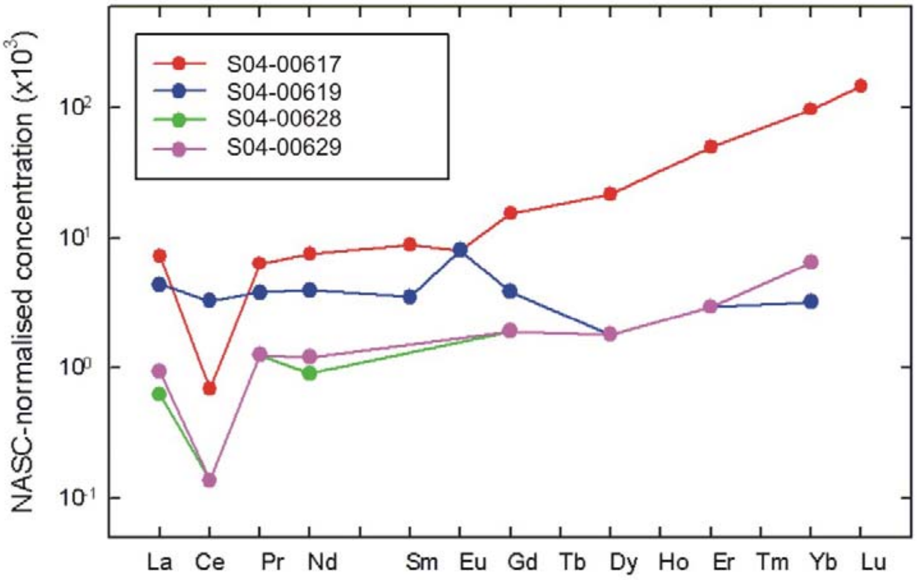


Figure 14 Rare-earth element profiles (normalised to North Atlantic Shale Composite used by Sholkovitz, 1988) for selected groundwater samples from the Strathmore aquifer.

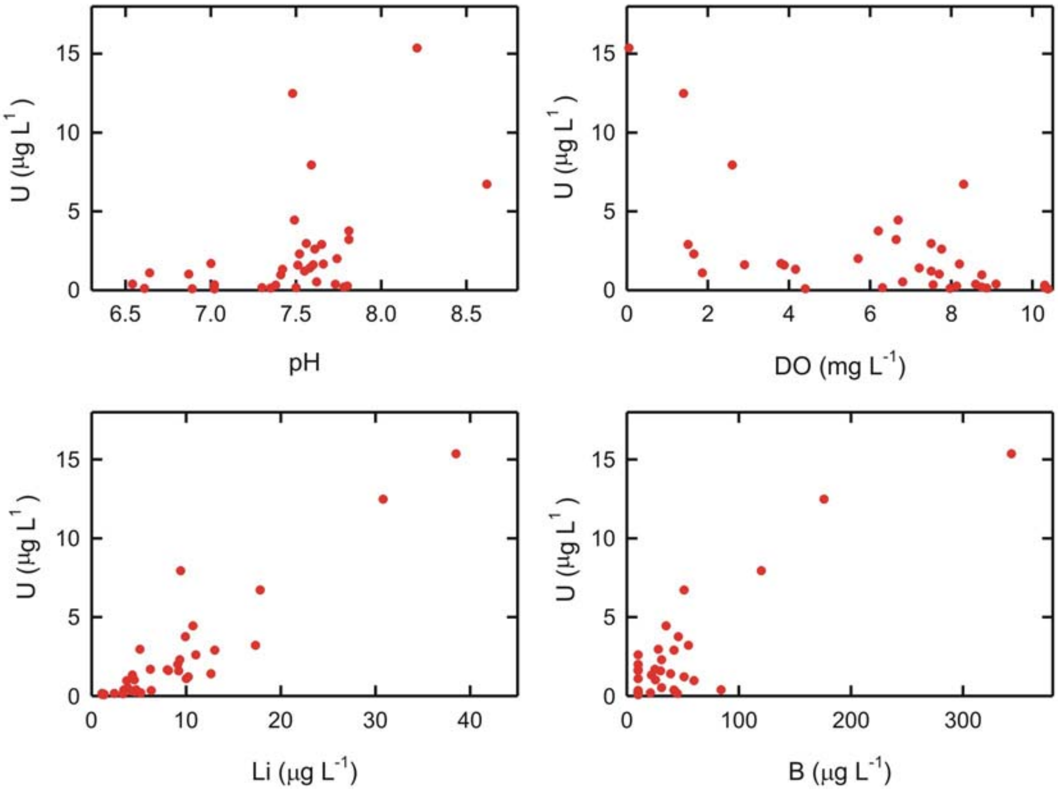


Figure 15 Variation of uranium with other parameters in the Strathmore groundwaters.

4.4 STABLE-ISOTOPIC COMPOSITIONS

4.4.1 δ^{18}O and δ^{2}H

A plot of δ^{18}O vs δ^{2}H for the Strathmore groundwaters (Figure 16) indicates that the samples are disposed around the World Meteoric Line (WML) and that they are predominantly the product of normal meteoric infiltration. The range of values appears to be linked to geographical position, with samples near the coast being isotopically more enriched than those inland (Figure 16). The more depleted samples are likely to reflect some recharge at or from higher elevations: an 'altitude effect' of approximately 0.3 ‰ in δ^{18}O per 100 m in recharge altitude would be expected in Scotland (Darling and Talbot 2003). This higher-altitude recharge could be derived directly by groundwater flow or via leakage from rivers or streams. There is no evidence for the kind of isotope depletions (~2 ‰ in δ^{18}O) expected for Pleistocene (more than 10 000 years old) water, though mixing between remnants of such waters and modern water has been proposed for other basins in Scotland (MacDonald *et al.* 2003) and cannot be wholly ruled out for Strathmore in the absence of radiocarbon data.

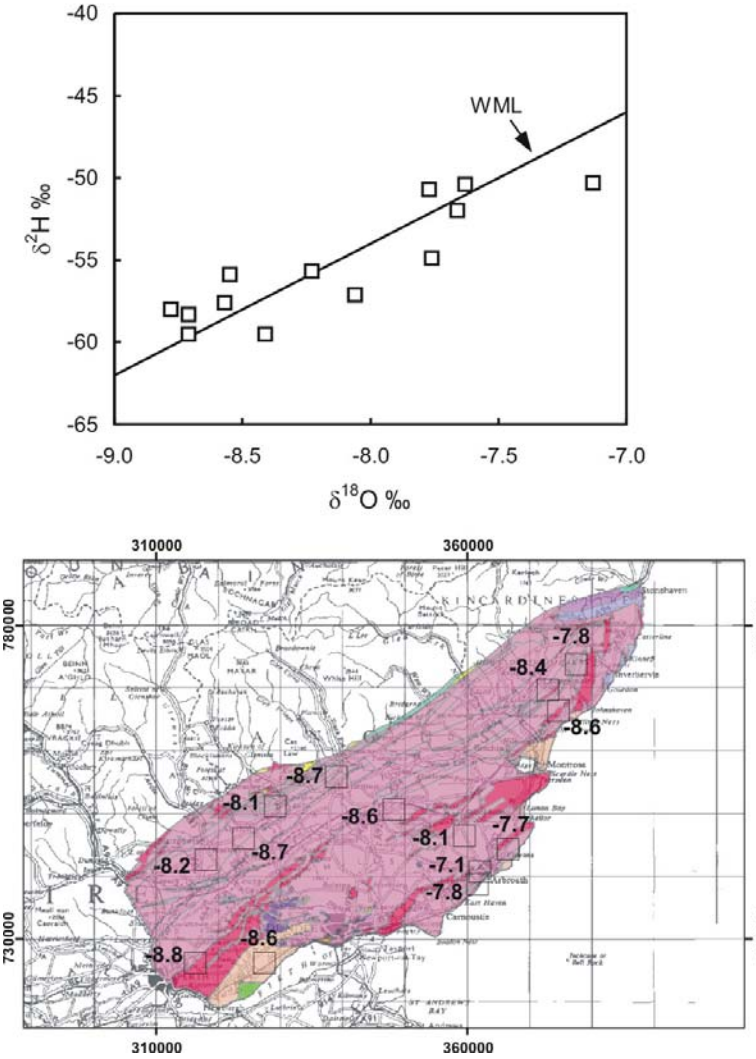


Figure 16 Plot of variation of δ^{18}O with δ^2H and spatial variations in selected Strathmore groundwater samples. MWL: World Meteoric Line.

4.4.2 Stable C isotopes

Most sampled groundwaters have δ^{13}C-DIC values ranging from approximately -15 to -19 ‰ and averaging -17 ‰. However, three sites have relatively enriched δ^{13}C compositions (S04-00617, S04-00620 and S04-00630). The more negative results are typical of sandstone aquifers: groundwaters in these tend to show little evolution towards more enriched compositions over time because of the paucity of carbonate and low carbonate/water ratio. Accordingly they give little information about residence time, even qualitatively. Values of δ^{13}C-DIC in the three more enriched samples may be due to several processes. Sample S04-00617 has evidence of contamination in the form of over-modern CFC values: low TDS means the water is rather poorly-buffered against sources of C contamination. The borehole from which sample S04-00620 was taken was only pumped for 5 minutes prior to sampling and there may therefore have been some isotopic equilibration between atmospheric CO_2 and DIC. The borehole from which sample S04-00630 was taken is also a recent borehole (completed 2003) and might not have settled down at the time of sampling. There is no reason to believe that any of these three waters is especially old. This is supported by the fact that the groundwater from the three sites contains dissolved oxygen and nitrate.

Apart from the three anomalous sites, values of δ^{13}C-DIC are most likely the result of 1:1 dissolution of carbonate cement by soil CO_2, supplemented by silicate weathering. Thus as Si concentrations increase, δ^{13}C-DIC tends to become more depleted (Figure 17), because silicate-associated DIC derives exclusively from soil CO_2 (with a composition of approximately -26 ‰).

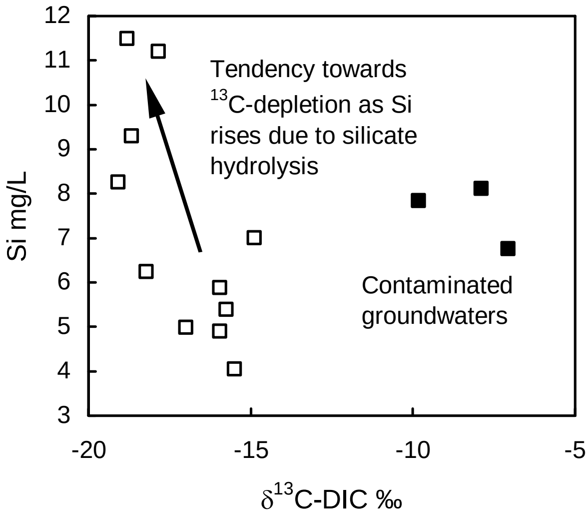


Figure 17 Variation of Si with δ^{13}C in the groundwaters.

4.5 CHLOROFLUOROCARBONS (CFCs)

Based on recharge at 10°C and sea level, four out of the nine sites sampled for CFCs showed evidence of slight CFC contamination. Any corrections for likely reductions in recharge temperature away from the coast would be small and would not affect the interpretation.

In aquifers such as Strathmore where groundwater flow is dominantly through fractures, CFCs are commonly interpreted in terms of mixing between modern infiltration water and CFC-free water less than 50 years old (Macdonald *et al.* 2003). This can be expressed as 'modern fraction' (MF), i.e., the measured concentration divided by the maximum concentration for the CFC. CFC-11 peaked at 5.6 pmol l^{-1} in the mid 1990s, while CFC-12 peaked at 3 pmol l^{-1} in 2000. These values have been used in the calculations. Results for the samples are shown in Table 5.

Table 5 Concentrations, calculated fractions and estimated dates of groundwater from CFC-11 and CFC-12 data.

Sample	**CFC-12**	**CFC-11**	**CFC-12**	**CFC-11**	**CFC-12**	**CFC-11**
	pmol l^{-1}		**Modern Fraction (MF)**		**Year of recharge**	
S04-00610	1.25	2.78	0.42	0.51	1975	1976
S04-00614	2.86	2.26	0.95	0.41	1993	1974
S04-00616	4.75	11.43	1.59	2.09	>modern	>modern
S04-00617	9.21	19.95	3.08	3.65	>modern	>modern
S04-00636	4.39	8.56	1.47	1.56	>modern	>modern
S04-00637	0.25	0.68	0.08	0.12	1962	1966
S04-00641	2.33	4.54	0.78	0.83	1986	1985
S04-00643	0.29	0.85	0.10	0.15	1963	1967
S04-01114	3.93	6.78	1.31	1.21	>modern	>modern

For the below-modern samples, the modern fractions calculated from CFC-11 and CFC-12 concentrations are in generally good agreement, with the calculated modern fraction values ranging between averages of 10% and 80%. Only sample S04-00614 showed divergence (Table 5). Water from this site shows no indications of reducing conditions so there is no reason to believe that CFC-11 has suffered the degradation observed in anoxic environments (e.g. Plummer and Busenberg 1999). The CFC-11 modern fraction of 40% is therefore likely to be correct, while the CFC-12 value may have been affected by contamination.

There is no indication that the old water component of these samples is of particularly long residence: neither O and H stable isotopes nor δ^{13}C-DIC show evidence of a relationship with modern fraction. The former tends to argue against the existence of a relict Pleistocene (palaeo) groundwater in the basin, while the latter confirms that δ^{13}C-DIC in this aquifer is controlled by factors other than residence time.

Since their atmospheric input curves are proportionally similar, CFC-11 and CFC-12 are relatively poor at distinguishing between groundwater mixing and plug, or piston, flow (the additional use of a new tracer, SF_6, can help to resolve this). Although as outlined above there are good reasons to believe the mixing model is most likely, if the piston flow model is preferred then residence times range from modern to 40 years (Table 5). The sites with over-modern CFC values, while not 'datable', clearly have at least some water derived from recharge in the last 50 years.

5 Discussion

5.1 DEPTH TRENDS

There are few data available to enable the identification of depth variations in groundwater chemistry in the Strathmore aquifer. No groundwater depth sampling in individual boreholes is known to have been carried out. Downhole geophysical logging data show changes in water temperature and SEC with depth that imply vertical variations in water chemistry and residence time, likely to be due to inflow of water from discrete horizons with differing water chemistry and residence times. Logging has also shown that vertical groundwater flow, both upwards and downwards in the borehole, occurs (Clark 1981, Cripps and Buckley 1990). In one trial borehole near Forfar, drilled on a boundary between the Scone Sandstone and the Dundee Flagstone formations, SEC increased from 400 µS cm^{-1} to 1500 µS cm^{-1} between 130 m and 156 m depth, indicating the presence of deep saline water. Further work is needed to establish whether significant variations in water chemistry with depth exist and whether they are of regional extent.

The water chemistry in the samples from this regional study shows no discernible trends with borehole depth, although this is unsurprising given the large spatial coverage of the samples, and the limited number of samples where borehole depths are known. Specifically, no notable changes in groundwater salinity were noted with increasing borehole depth, although the boreholes including in the dataset did not extend to the depths (more than 130 m) where salinity increases were observed from geophysical logging.

One feature of note in the depth variations is the persistence of nitrate in the groundwaters even in boreholes up to 120 m deep (Figure 18): nitrate appears to be well mixed throughout the aquifer to at least these depths, with similar concentrations in deep and shallow boreholes. The depth of inflow zones that contribute groundwater to the individual boreholes is unknown, but the implication is that the aquifer remains largely oxygenated throughout its fractured productive zone, and that even deep boreholes are therefore vulnerable to nitrate pollution.

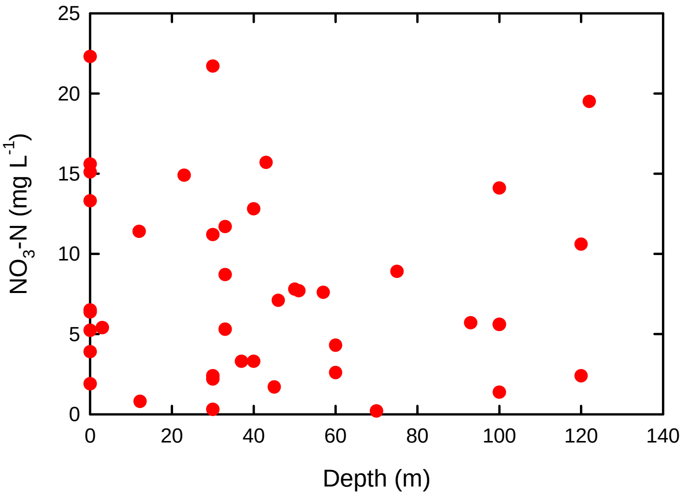


Figure 18 Variation in NO_3-N concentration with borehole depth in the Strathmore groundwaters.

5.2 TEMPORAL VARIATIONS

There are no long-term groundwater chemistry records for any boreholes in the study area. SEPA currently monitor groundwater quality in 27 boreholes in Strathmore as part of their national groundwater quality monitoring network. Most of these have been monitored since the start of 2003. All but two of the boreholes are monitored four times a year for major ions, including nitrate; five of the boreholes are monitored for chemicals associated with sheep dip; and three are monitored for agricultural chemicals (e.g. pesticides). There are no clear seasonal trends in any major ion concentrations at the monitored sites, although there are slight variations in SEC at a small number of sites. There is similarly no clear evidence of a rising trend of any major ion, including nitrate.

For a small number of sites there are earlier limited chemical analyses, generally including only major ions, made between 1978 and 1994. There are six sites with more than one chemical analysis before 2001, of which three were re-sampled for the current study. The data indicate no consistent trend.

5.3 REGIONAL VARIATIONS

The concentrations of selected parameters across the Devonian aquifer are illustrated against a backdrop of the major geological divisions in a series of maps in Appendix 1. Key maps are reproduced in this section.

There are few distinctive spatial trends in groundwater chemistry. One of the most notable features is the increase in salinity (dissolved solids content) in groundwaters close to the coast, demonstrated by the maps of Cl, SEC, Na and SO_4 in particular (e.g. **Figure 19**). The chemistry data suggest that the increased salinity of groundwater in the coastal areas results from simple mixing between fresh groundwater and recent seawater, which would be caused by saline intrusion, perhaps enhanced by over-pumping.

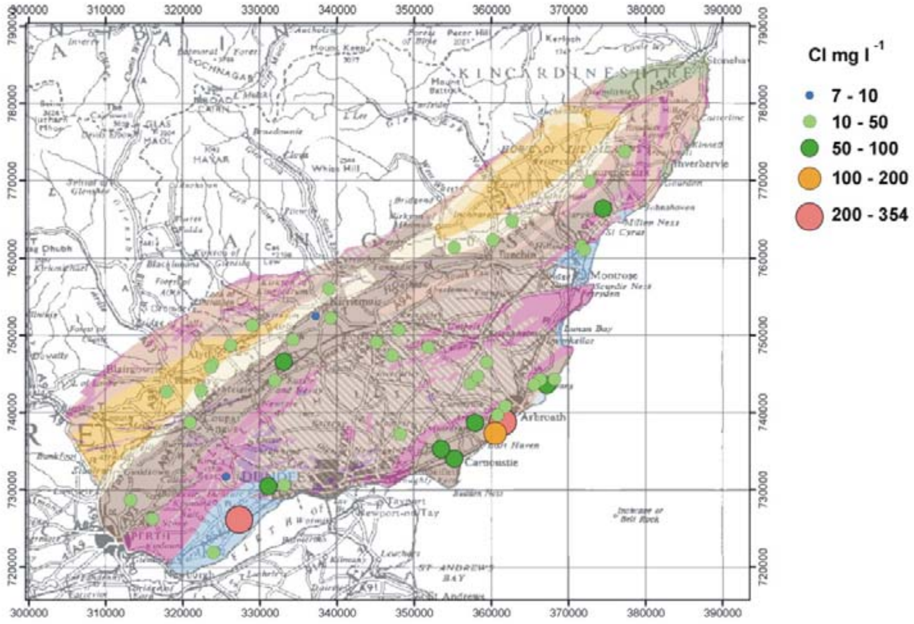


Figure 19 Concentrations of Cl across the Devonian aquifer. Geological legend as for Figure 2.

There is little evidence for the existence of palaeowaters in the aquifer across the region, save for one groundwater sample (S02-00242) near the coast at Carnoustie. The chemistry was unusual at this site, with evidence of reduction and dissolution with gypsum. As this site had been sampled in a previous project, there were no stable isotope or CFC data available.

Nitrate shows one of the most variable distributions across the aquifer (Figure 20). Its distribution is controlled by landuse as well as by geology. Because of the distinctive nature of its provenance and the degree of interest in nitrate as an environmental pollutant, it is dealt separately in the next section (Section 5.4).

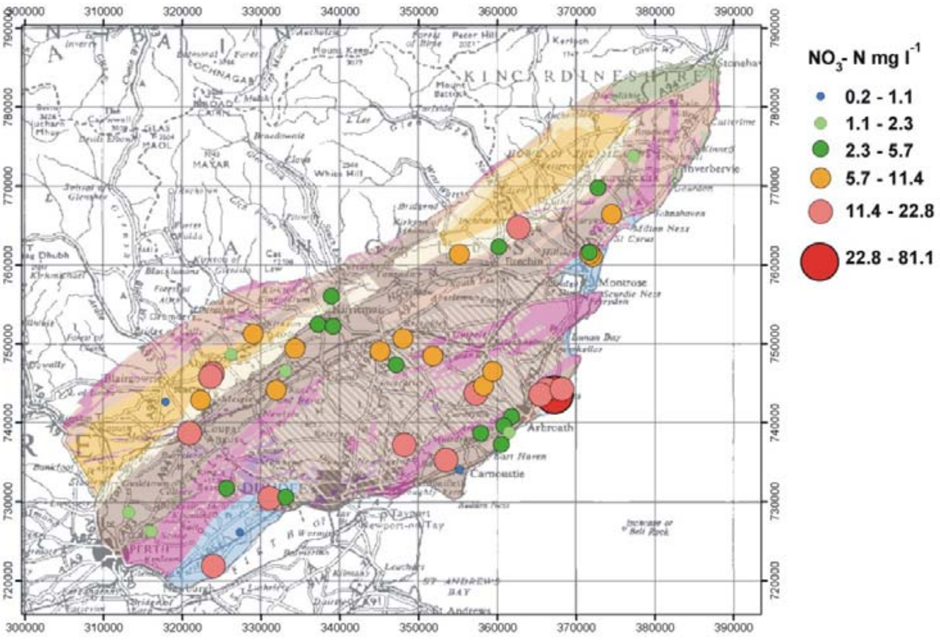


Figure 20 Concentrations of NO_3-N across the Devonian aquifer. Geological legend as for Figure 2.

5.4 NITRATE

Almost all Strathmore groundwaters appear to have been impacted to some extent by nitrate pollution, of agricultural or domestic origin or both. There is a very large range in the concentrations of NO_3-N in the Strathmore groundwaters, from less than 0.2 mg l^{-1} to 81 mg l^{-1} (S04-00616). The sample with the highest concentration has obviously suffered from extreme pollution, seen both in the high nitrate concentration and the presence of anomalous concentrations of other nutrients of agricultural origin.

Nitrate concentrations in groundwater are closely related to aquifer type and landuse. Across eastern Scotland, a previous study demonstrated that high nitrate concentrations largely coincide with moderate- and high-productivity aquifers and areas of high leaching potential over intensively farmed ground (Ball and MacDonald 2001). This is supported by the data from this study (Figure 21), which show that most of the groundwater samples with low nitrate concentrations are in areas of moderate leaching potential, while most of the samples with high concentrations are in areas of high leaching potential.

Further investigations showed that areas of arable land, mixed cultivation of both arable land and grassland, and areas where dairy, pigs or poultry are reared are generally associated with the highest nitrate concentrations in groundwater (MacDonald et al. 2005). This is supported by the data from the current study (Figure 22), which show the highest nitrate concentrations occur in aquifers below arable land.

The earlier investigations also indicated a number of potential effects that can lead to lower than expected nitrate concentrations in groundwater, including dilution from rainfall, mixing with older, low-nitrate waters, denitrification in anoxic conditions, or the presence of low permeability soil and superficial deposits which slow the downward movement of high nitrate water and therefore reduce the vulnerability of the underlying aquifers to nitrate (MacDonald *et al.* 2005).

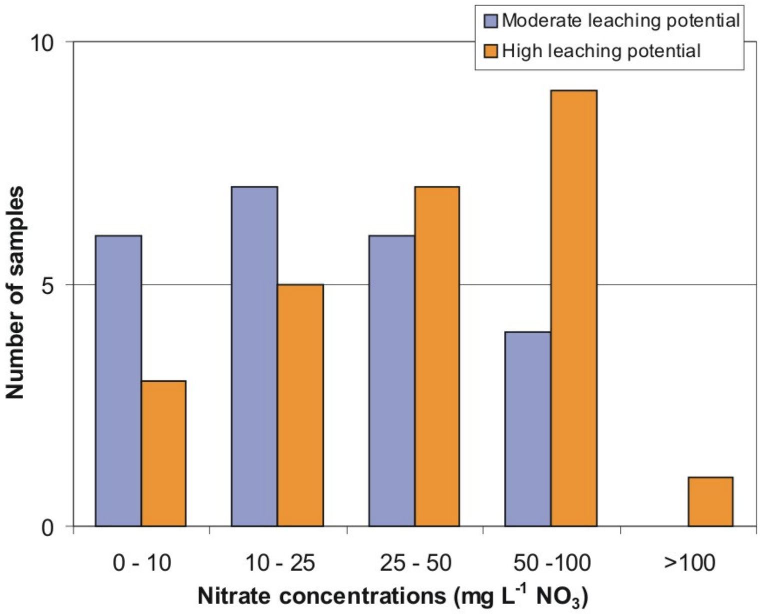


Figure 21 The variation in nitrate concentration across areas of moderate and high soil leaching potential (information from MLURI)

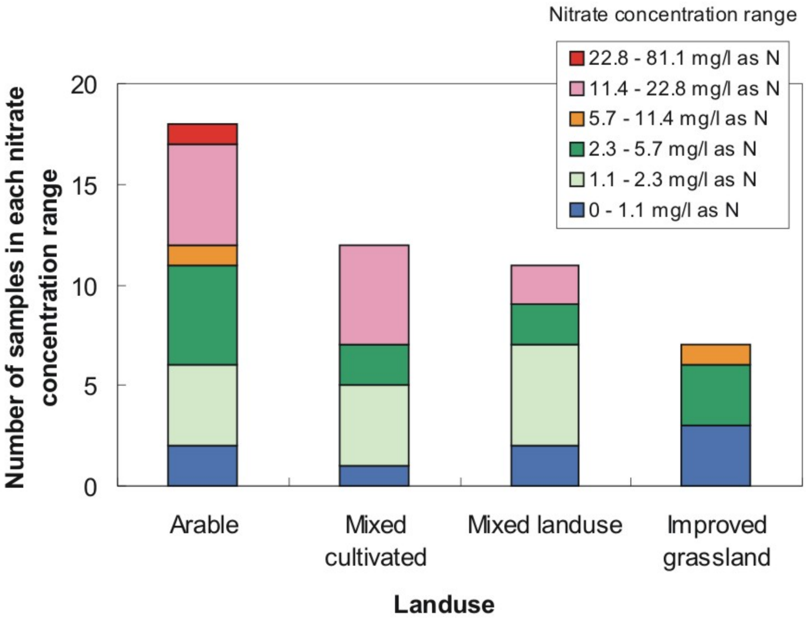


Figure 22 The distribution of nitrate concentration by land use type across the Strathmore aquifer

Rainfall chemistry data indicate that recharge inputs to the aquifer could introduce a concentration of around 2 mg l^{-1} (2.5 mg l^{-1} if the median rainfall NO_3-N for 2003 is taken; Section 2.6) and this is a useful starting point for assessing the likely baseline concentration of nitrate in the groundwaters. However, nitrate concentrations are strongly controlled by the complexity of the natural nitrogen cycle in the soil zone, even in the absence of agricultural impacts.

The groundwaters in Strathmore are for the most part oxygenated, and the lower nitrate concentrations observed are therefore unlikely to reflect significant influence of denitrification, but reflect generally lower nitrate inputs to the aquifer. Nitrate occurs even in boreholes up to 120 m deep (Figure 18): although the depth of the inflow zones to these boreholes is unknown, the implication is that the largely oxygenated nature of the aquifer throughout its fractured productive zone means that even deep boreholes are vulnerable to nitrate pollution.

5.5 PHOSPHOROUS

Phosphorous is naturally found in water, and is an essential nutrient for plant life. Elevated levels of phosphorus in water can lead to eutrophication and excessive algal growth. Elevated concentrations in groundwater are a concern primarily because of the contribution of groundwater to rivers as baseflow. SEPA have adopted Water Quality Standards for P for Scottish freshwater lochs that vary from <0.0025 mg l^{-1} for ultra-oligotropic lochs to 0.08 mg l^{-1} for eutropic lochs (SEPA 2002). Concentrations of P across Strathmore are shown in Figure 23. Concentrations are typically less than 0.1 mg l^{-1} (the 90th percentile), with a median of 0.03 mg l^{-1}. The maximum concentration is 40.5 mg l^{-1} (S04-00616), in a sample that has clearly suffered from extreme agricultural pollution and also shows anomalously high concentrations of nitrate and other nutrients of agricultural origin (Section 5.4). The next highest value is 7.2 mg l^{-1} (S02-00290), from a borehole on agricultural land, but which does not show anomalously high nitrate.

Therefore, concentrations of phosphorous in groundwater across the aquifer clearly will have an impact on surface water quality. Not only from the few sites where there is evidence of contamination from P, but across much of the northern section of the aquifer, where concentrations approach 0.1 mg l^{-1}.

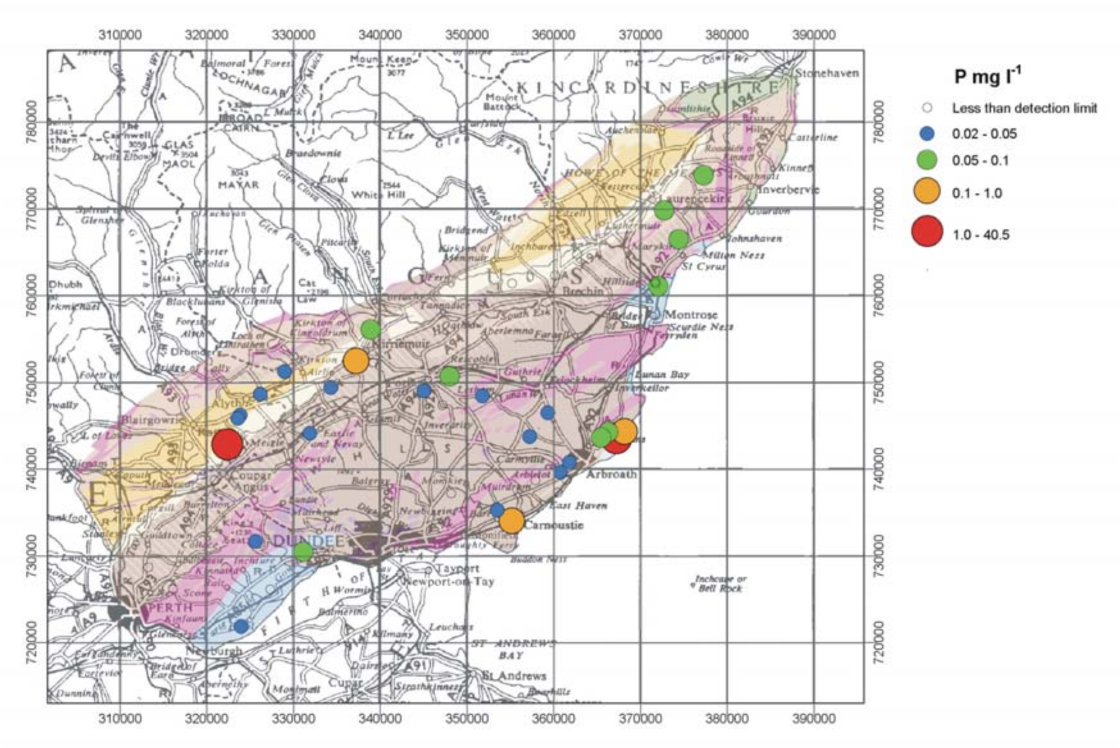


Figure 23 Phosphorous concentrations in groundwater in Strathmore.

5.6 SALINE INTRUSION

Most of the groundwaters in Strathmore have low chloride concentrations. The bromide/chloride ratio of all the samples is similar to the standard bromide/chloride ratio of seawater (Hem 1985) (Figure 24), implying that the dominant control on the groundwater bromide and chloride concentrations is seawater, by means of the effects of marine aerosols on rainfall recharge. The few groundwaters sampled with high TDS concentrations (up to more than 1000 mg l^{-1}) all occur along the coast. These trend to Na-Cl compositions, indicating that the salinity can be explained by simple mixing between fresh groundwater and seawater. Apart from sample S02-00244, which has a slightly more sodic composition than would be implied from simple linear mixing, and may have an increased Na concentration through ion exchange, there is no evidence of causes of salinity other than a sea water source, either from marine aerosols or saline intrusion.

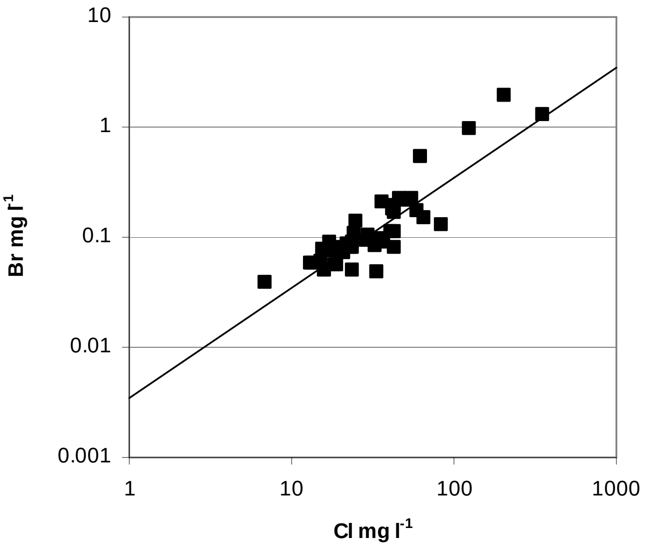


Figure 24 Bromide/chloride ratios for the Strathmore groundwater samples, with trend line showing the theoretical bromide/chloride ratio in seawater based on chloride and bromide concentrations in Hem (1985)

5.7 RELATIONSHIP WITH AQUIFER MINERALOGY AND GEOCHEMISTRY

There is little detailed information on aquifer mineralogy that would allow mineralogical controls on groundwater chemistry to be examined. However, the dominance of calcium ions in the sampled groundwaters, and the calcite saturation of most of the samples from deeper boreholes, is explained by the common presence of carbonate cement in most of the aquifer units (Section 2.5). Although there has been no specific testing for dolomitic cements in the aquifer units, the wide variation in Mg concentrations and Ca-Mg ratios indicates that such cements are present in a number of areas across Strathmore.

The groundwater trace element data do not reflect the patterns observed in stream sediment geochemistry across Strathmore (Section 2.5). There is little evidence in the groundwater chemistry of the ultrabasic anomaly identified from stream sediment geochemistry at Alyth. The chromium concentrations in all the samples are relatively low, all less than 2.1 µg l^{-1} (compared to the WHO guideline value of 50 µg l^{-1}). Although the second highest chromium concentration of the samples was from a borehole abstracting from the Teith Sandstone Formation of the Strathmore Group at Alyth, there are a number of other samples from the area surrounding Alyth of which none are elevated (Figure 25).

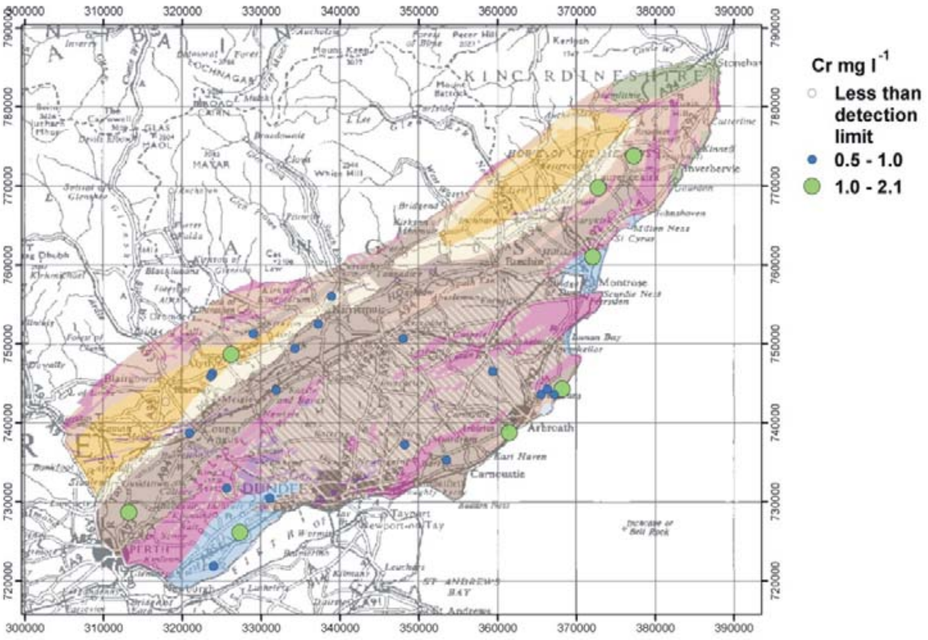


Figure 25 Concentrations of Cr across the Devonian aquifer. Geological legend as for Figure 2.

The lack of correspondence between stream sediment geochemistry and groundwater, in terms of elements such as chromium and copper, may also be partly due to the limited number of groundwater samples. For example, the absence of samples from the Dundee area means that any parallel in groundwater of the elevated copper concentrations observed in stream sediments around the urban-industrial centre of Dundee would not be observed. No samples were taken from within Dundee itself, and the closest samples – some 4 to 7 km distant – had low copper concentrations. The highest copper concentrations were seen at Auchteralyth and Windyhills Farm, both from boreholes in the Arbuthnott-Garvock Group. The borehole at Windyhills Farm also appears to be subject to severe contamination from fertiliser.

Uranium concentrations in groundwater are similar to that measured in stream water where concentrations can be in excess of 2 µg l^{-1} (see MacDonald *et al.* 2005 for more details). The uranium concentrations in Strathmore groundwater are elevated compared with other UK groundwaters, but similar to other UK red-bed sandstones (Smedley et al. 2006).

5.8 CHEMISTRY AND GROUNDWATER FLOW

The groundwater chemistry data also help improve understanding of groundwater flow in the Strathmore aquifer. The groundwater is generally young, with no evidence of palaeo-waters (Section 4.5). Groundwater flow paths are therefore likely to be relatively short: certainly much of the groundwater flow is likely to occur on the scale of decades. This largely reflects the dominance of fracture flow in the aquifer.

The similarity of nitrate concentrations in deep and shallow boreholes, with no obvious trend to lower nitrate with depth, is also likely to reflect the dominance of fracture flow, as rapid groundwater flow through fractures in the aquifer has allowed nitrate-enriched recent recharge to reach the deep aquifer. This is supported by the CFC data, which indicate modern fraction values of between 10% and 80% (Section 4.5).

5.9 WATER SUPPLY

The Lower Devonian rocks in Strathmore form an important regional aquifer containing a large groundwater resource. A crude estimate of the total volume of groundwater stored in the aquifer, based on a probable aquifer thickness of 100 m and an average porosity of 14 %, is over 45 million megalitres.

For water supply, of the chemical constituents measured, nitrate represents the most problematic constituent in the Strathmore groundwaters. It exceeds EC drinking-water limits more than any other parameter. It also shows the greatest variability in spatial distribution, linked dominantly to agricultural practices, although factors such as aquifer vulnerability are also important. A new action programme to address nitrate contamination from agricultural activities within Nitrate Vulnerable Zones was initiated in 2003 (Scottish Executive 2003), and may eventually cause nitrate concentrations in groundwater in Strathmore to stop rising and even fall.

Other elements that occasionally exceed EC or WHO limits or guideline values are nitrite, fluoride and uranium, with one exceedance of each element. A further sample had a uranium concentration that approaches the guideline value. Although there is one exceedance of fluoride, the fluoride concentrations are generally low across the aquifer. The concentrations of arsenic, although all less than the drinking-water limit of 10 $\mu g\ L^{-1}$, do approach this limit in some cases, making it worthy of monitoring.

It is stressed that not all chemical parameters for which drinking-water guidelines or regulations exist have been investigated in this study and no assessment of the concentrations of these unstudied parameters should be implied from this report.

5.10 BASELINE

5.10.1 Baseline statistics

Assessment of the baseline compositions of the different chemical parameters in the groundwaters is difficult for two main reasons. First, the concept of baseline for any groundwater constituent also represents a range of concentrations, rather than a single value. Concentrations vary according to the local mineralogy of the aquifer (which is highly variable in Strathmore), groundwater flow conditions and residence time, mixing between freshwater and saline water bodies, and, not least, redox processes. These variations are quite apart from those imposed by inputs from pollution sources.

Secondly, each parameter is impacted to different degrees by pollution inputs, and it is difficult to assess the scale of these impacts from statistical distributions and limited geochemical information. Some parameters, such as nitrate, show clear evidence of increased concentrations due to pollution (Section 5.4). Others, such as many of the trace elements, are likely to be little affected and many of the observed concentrations can be the result of entirely natural geochemical processes. Multimodal distributions of elements have been used by some as evidence of pollution inputs (e.g. Kunkel *et al.* 2004). However, such distributions can occur for a number of reasons, not all of which may be induced by man. In the Strathmore groundwaters, for example, there is a distinct set of higher-salinity waters, all near-coastal samples, which are likely to reveal the effects of seawater intrusion. Whether the saline intrusion is natural, or has been induced by pumping and therefore constitutes a human influence, and departure from baseline conditions, is debatable.

Despite these caveats, the statistical summaries given in Table 4 and represented in Figures 11 and 13 can be a useful first step in assessing whether a groundwater is typical of other groundwaters in Strathmore. With the exception of nitrate and phosphorous, where concentrations are likely to have been elevated across much of the area by anthropogenic activity, the majority of samples show little evidence of gross contamination. Variations in concentrations are therefore largely due to natural processes. The interquartile range, and 10th and 90th percentiles given in Table 4 can therefore be used with confidence to as a guide to typical groundwater in Strathmore. Concentrations that lie well outside these ranges are not necessarily due to contamination, but may also be explained by changes in mineralogy, redox conditions and residence time.

5.10.2 Representative sites

In addition to the statistical summaries, six sites have been chosen from the 48 sampled that are broadly representative of conditions in the aquifer. The locations of these samples are shown in Figure 26. All are good quality, reliable sites, where there was no obvious point source contamination, and from sources which are regularly flushed (either regularly pumped boreholes or a constantly flowing spring). None of the samples show evidence of contamination from over-modern CFC. The samples are spread across the aquifer and are broadly representative of the median groundwater major ion chemistry, except where samples have been selected to reflect particular trends in groundwater chemistry – in particular, the trend towards Na-Cl waters along the coast, and reflecting the natural variations in Mg concentration.

The major ion chemistry of the 'baseline' subset is shown in Figure 27.

- Four of the samples, including the spring water, are strongly Ca-HCO_3 waters, and represent the bulk of the groundwaters sampled across the Strathmore aquifer.
- The sample from furthest northeast in the aquifer (S04-00637) shows elevated Mg and a distinctly different Ca-Mg ratio to the other samples, This sample has been chosen to represent the groundwaters in Strathmore that show the effect of dolomitic cement in the Devonian rock.
- The coastal sample shows the effect of saline intrusion, which is relatively common along the Strathmore coast. It is a strongly Na-Cl type water and, unlike most of the other samples, is anoxic.

The most obvious departure from baseline concentrations in the Strathmore groundwaters occurs with nitrate. In the 'baseline' subset, nitrate varies from 1.4 mg l^{-1} NO_3-N to 13.3 mg l^{-1} NO_3-N, with a median concentration of 5.25 mg l^{-1} NO_3-N. This compares closely with the 10th to 90th percentiles and median for the Strathmore dataset as a whole. An estimate of the probable upper limit for the true 'baseline' concentration for NO_3-N in the generally unconfined, aerobic aquifer conditions is some 1.75 mg l^{-1} (Table 3). This in itself is likely to represent recharge that has been modified to some extent by anthropogenic inputs to rainfall.

Phosphorous in the 'baseline' subset varies from less than 0.02 mg l^{-1} (the detection limit) to 0.06 mg l^{-1}, with a median (taking half the value of the detection limit for those below the limit) of 0.02 mg l^{-1}. This compares closely with the median concentration for the whole dataset.

Iron and manganese concentrations in the 'baseline' subset are low, as in groundwaters across Strathmore; so are those of most trace ions. The most notable exception is As, which shows high variability across the aquifer, reflected in As concentrations in the 'baseline' subset, which vary from 0.6 to 8.8 µg l^{-1} – this is from the 10th percentile to the maximum of the whole sample set.

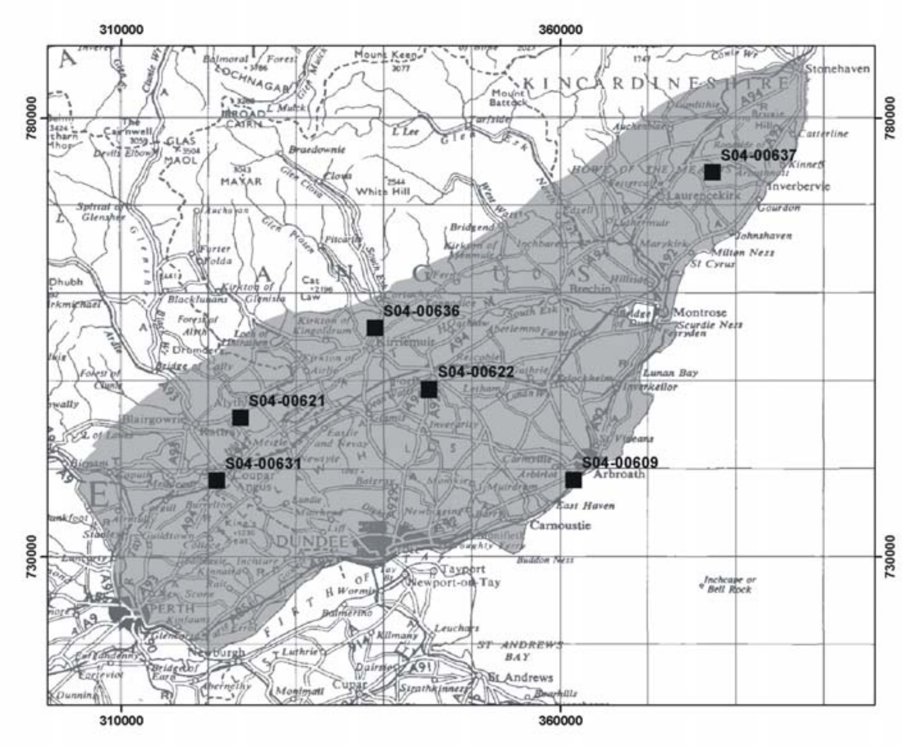


Figure 26 Location of selected 'baseline' samples

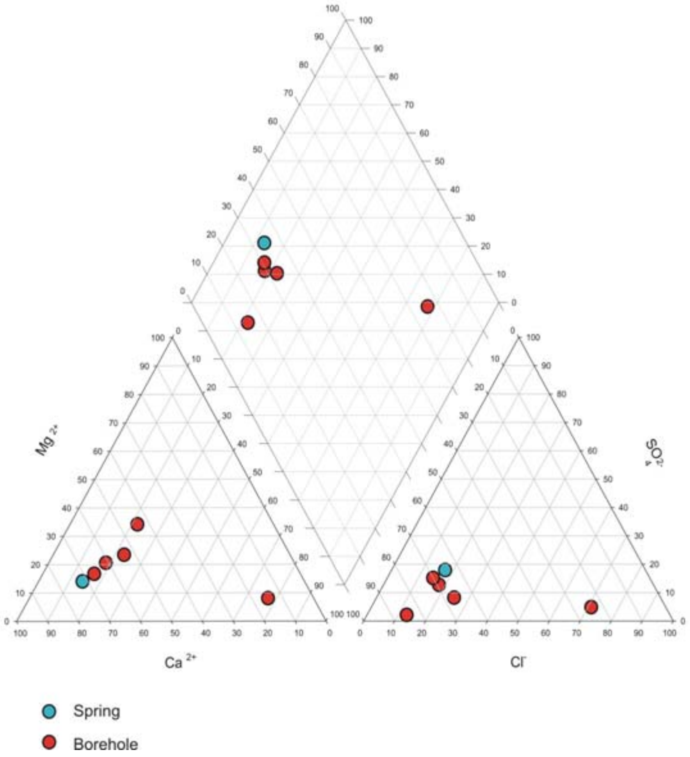


Figure 27 Piper diagram showing the distribution of major ions for the subset of six 'baseline' samples

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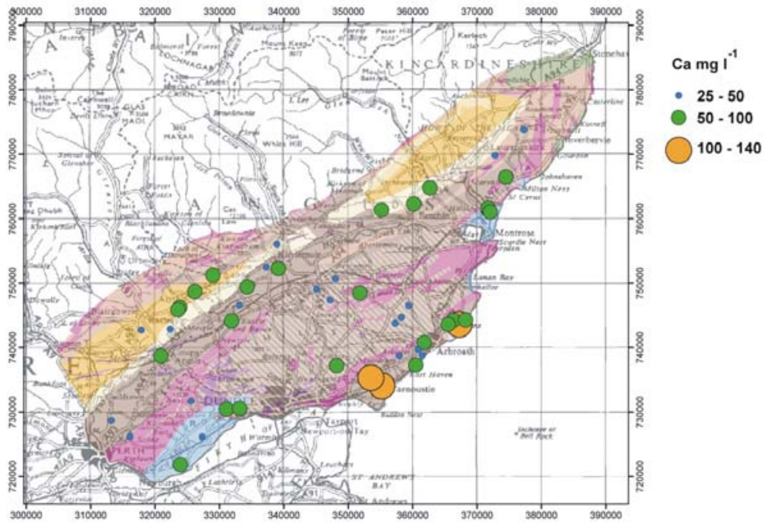
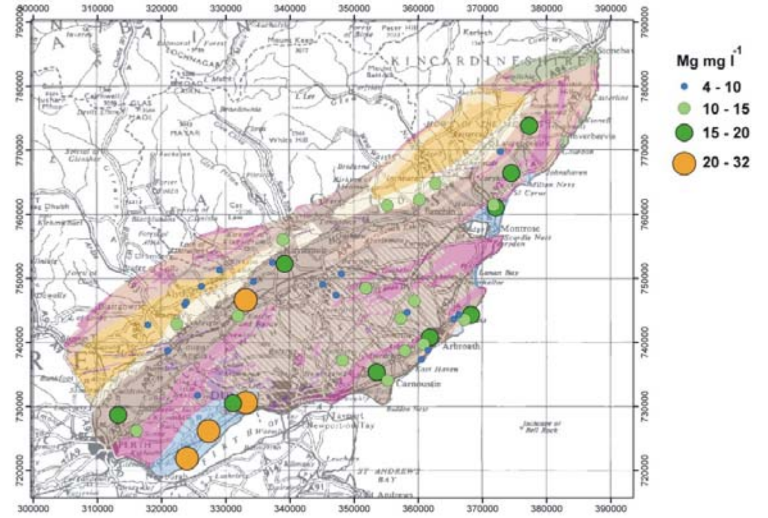
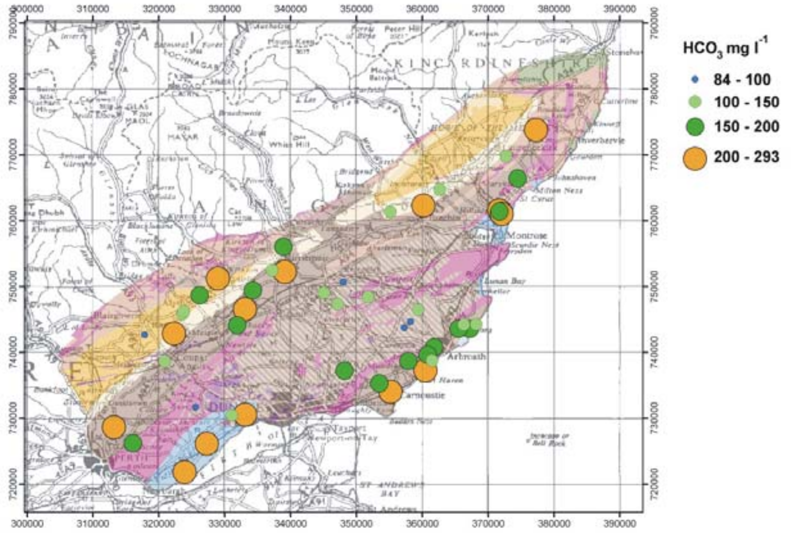
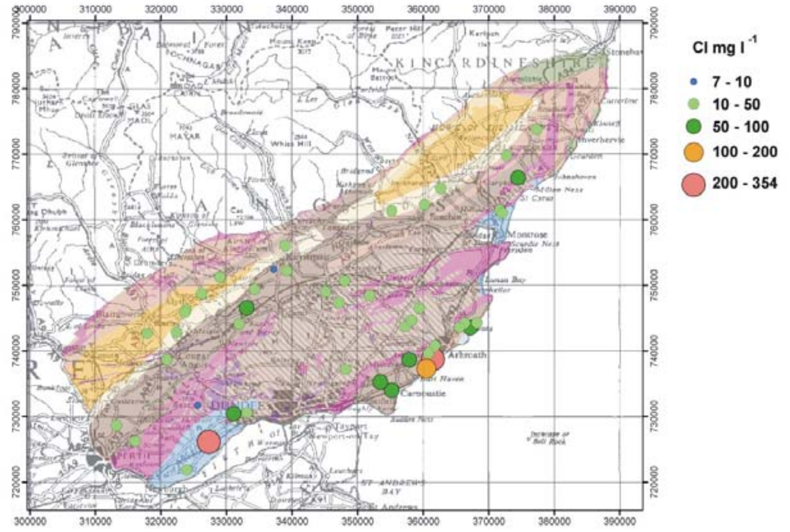
Appendix 1 Regional concentrations in selected ions








Cl mg l -1
7 - 10
10 - 50
50 - 100
100 - 200
200 - 354
300000
310000
320000
330000
340000
350000
360000
370000
380000
390000
720000
730000
740000
750000
760000
770000
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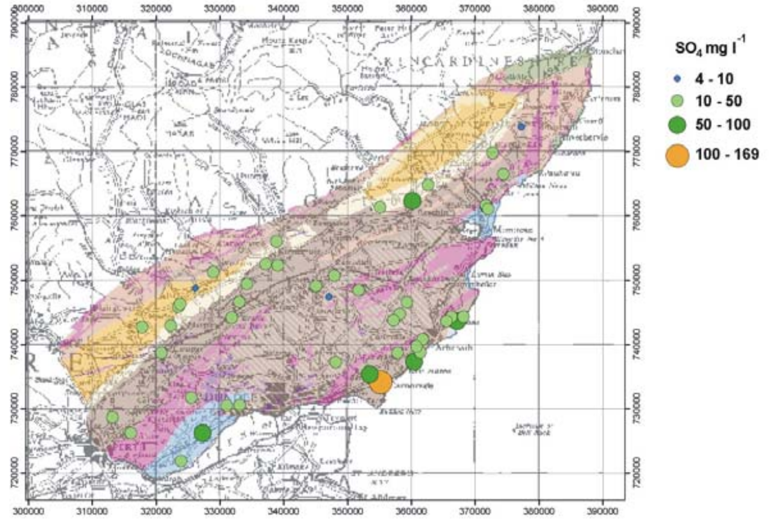
790000
KINCARDINESHIRE
Montrose
Arbroath
Carnoustie
DUNDEE
PERTH


SO4 mg l -1
4 - 10
10 - 50
50 - 100
100 - 169
300000
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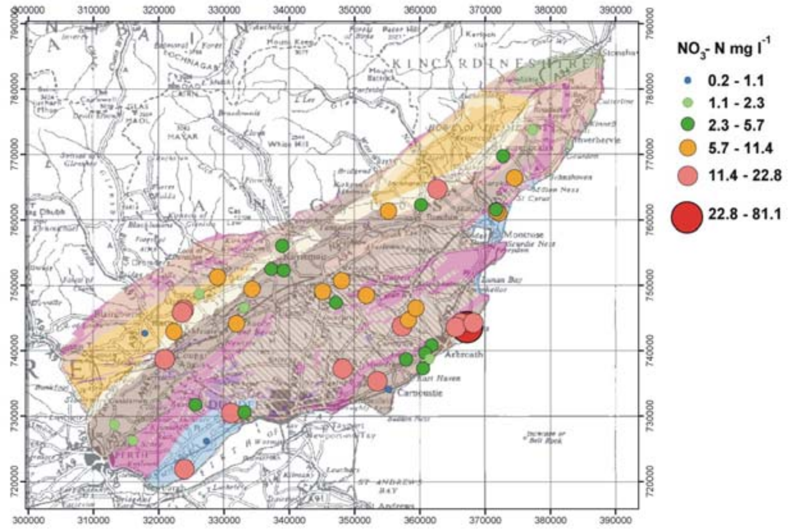
NO3- N mg l -1
0.2 - 1.1
1.1 - 2.3
2.3 - 5.7
5.7 - 11.4
11.4 - 22.8
22.8 - 81.1
300000
310000
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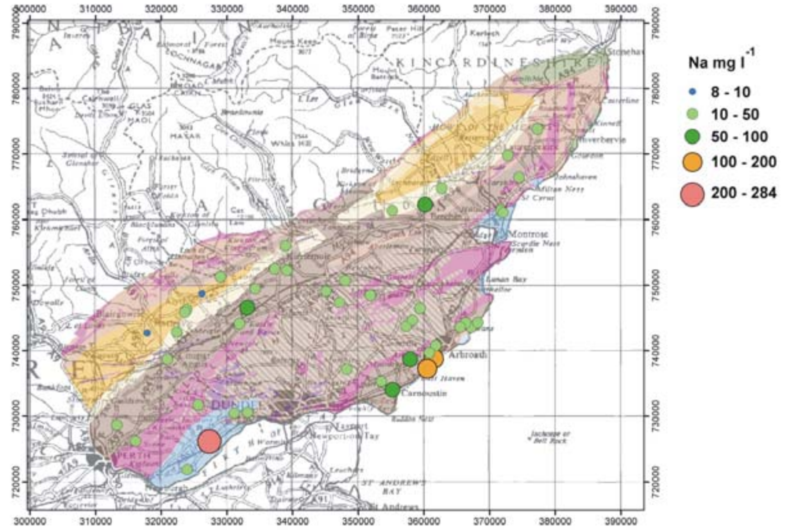
Na mg l^{-1}
8 - 10
10 - 50
50 - 100
100 - 200
200 - 284
KINCARDINESHIRE
Montrose
Arbroath
Carnoustie
DUNDEE
PERTH
Newport-on-Tay
ST ANDREWS BAY
300000
310000
320000
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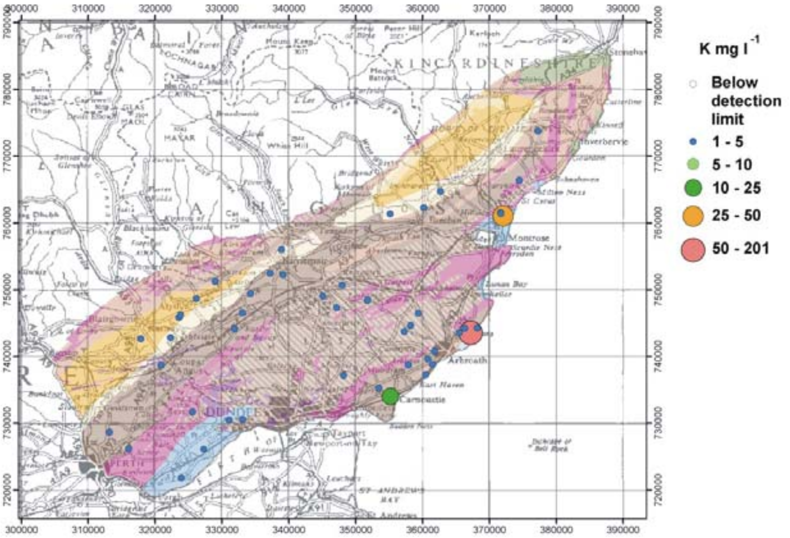
K mg l^{-1}
Below detection limit
1 - 5
5 - 10
10 - 25
25 - 50
50 - 201
KINCARDINESHIRE
Montrose
Arbroath
Carnoustie
DUNDEE
PERTH
Newport-on-Tay
300000
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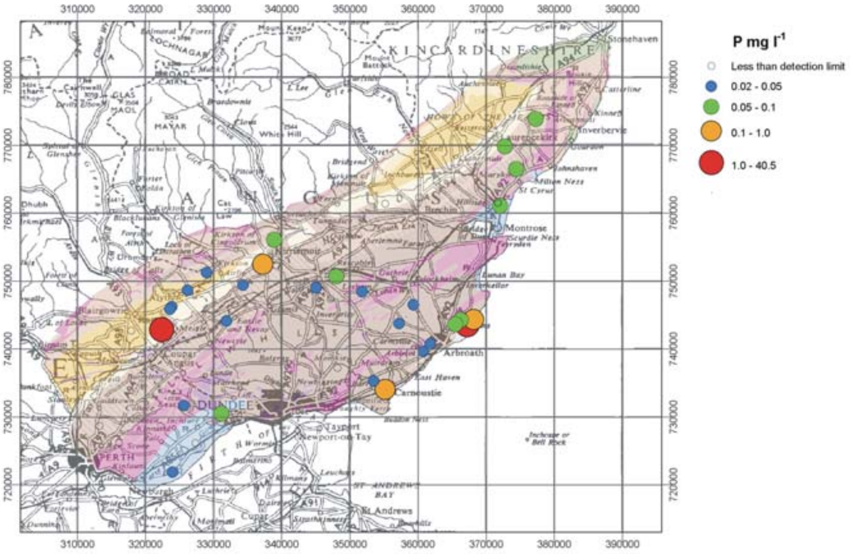
P mg l^{-1}
Less than detection limit
0.02 - 0.05
0.05 - 0.1
0.1 - 1.0
1.0 - 40.5
KINCARDINESHIRE
Stonehaven
Inverbervie
Montrose
Arbroath
Carnoustie
DUNDEE
PERTH
Newport-on-Tay
St Andrews
310000
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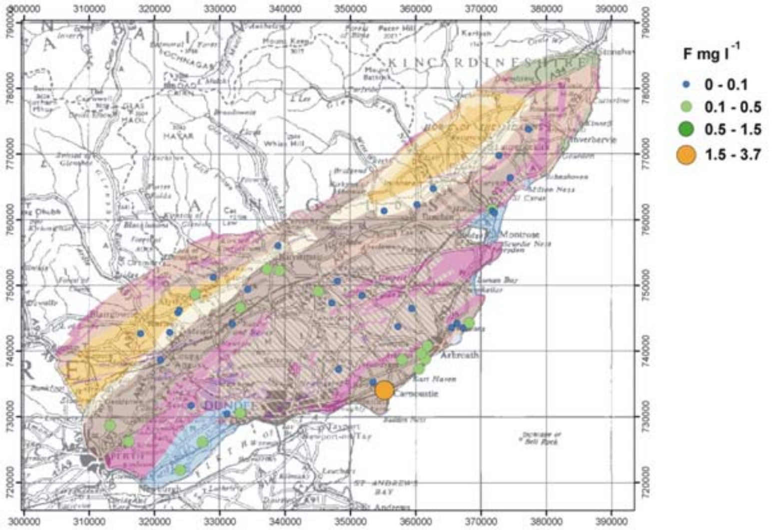
F mg l^{-1}
0 - 0.1
0.1 - 0.5
0.5 - 1.5
1.5 - 3.7
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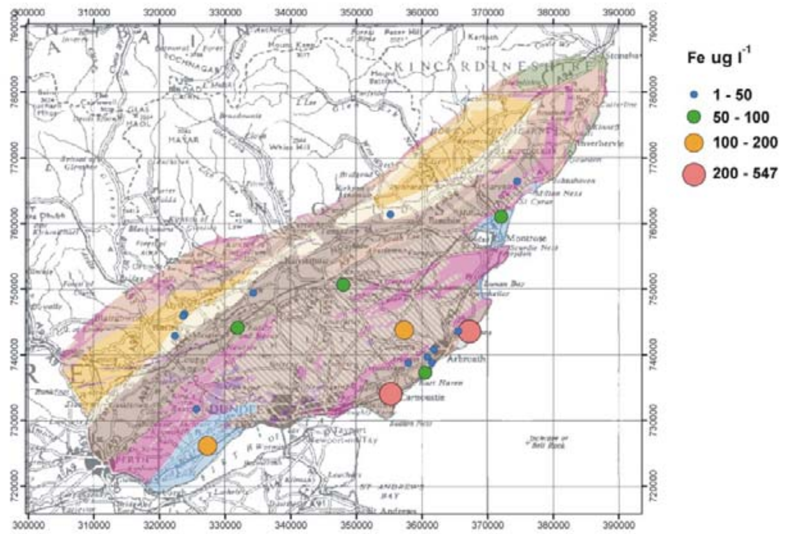
PERTH
Arbroath
Montrose
Carnoustie
KINCARDINESHIRE


Fe ug l^{-1}
1 - 50
50 - 100
100 - 200
200 - 547
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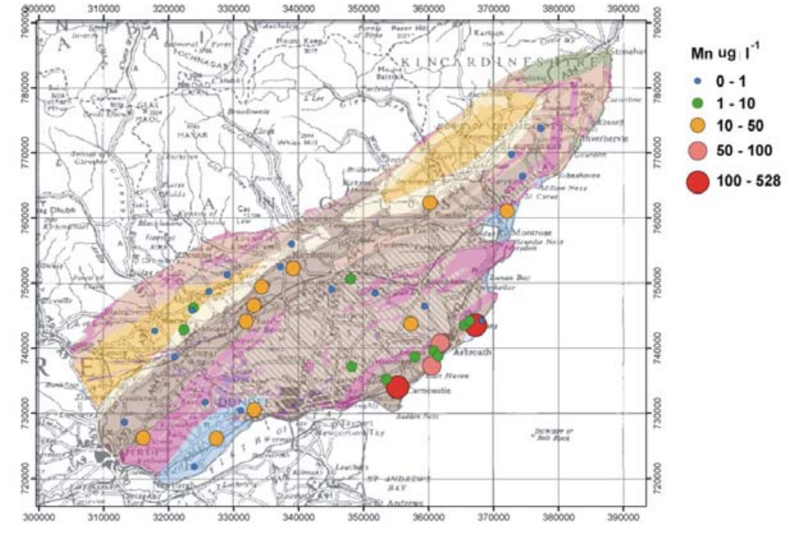
Mn ug l^{-1}
0 - 1
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10 - 50
50 - 100
100 - 528
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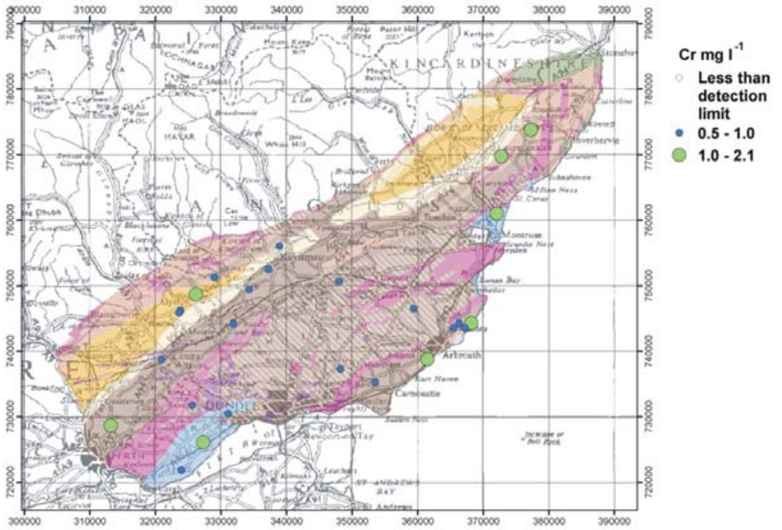
Cr mg l^{-1}
○ Less than detection limit
● 0.5 - 1.0
● 1.0 - 2.1
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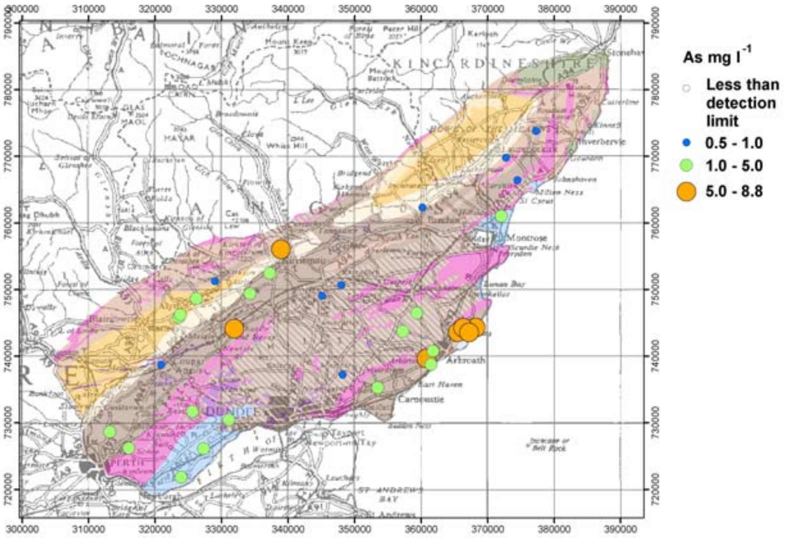
As mg l^{-1}
○ Less than detection limit
● 0.5 - 1.0
● 1.0 - 5.0
● 5.0 - 8.8
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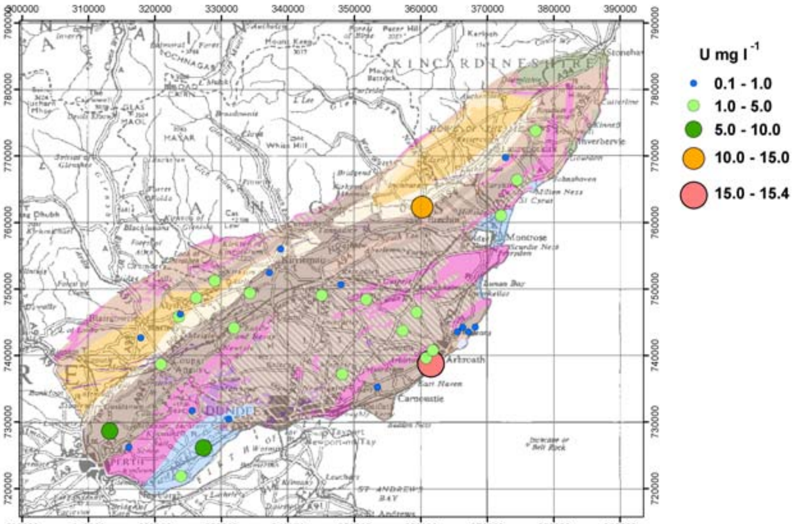
U mg l^{-1}
● 0.1 - 1.0
● 1.0 - 5.0
● 5.0 - 10.0
● 10.0 - 15.0
● 15.0 - 15.4
300000
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320000
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Arbroath
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Kincardineshire