Baseline groundwater chemistry: the Carboniferous Limestone aquifer of the Derbyshire Dome

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Foreword

Although groundwater has long been seen as a relatively pure natural resource stored in subsurface aquifers, its quality is under an ever-increasing threat from human influences. Changes in chemical quality occur through direct inputs of anthropogenic substances, through groundwater abstraction and resultant change in groundwater flow regimes and through artificial recharge. Groundwater is an important resource for drinking, agricultural, industrial and domestic supply. About 35 per cent of public water supply in England and Wales and more than 70% in south and east England is provided by groundwater resources. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater. Monitoring, management and protection of groundwater quantity and quality are therefore important economic and environmental priorities.

Characterisation and monitoring of groundwater chemistry is a critical component of management and protection. This provides the basis for defining the suitability of groundwater for its intended purpose, identifying pollution inputs and assessing any temporal change. The main European driver for the characterisation and monitoring of groundwater quality is European Union legislation in the form of the Water Framework Directive, Groundwater Directive, EC drinking-water regulations and environmental-quality standards. A key starting point for aquifer protection is defining the natural or 'baseline' chemistry of the groundwater body concerned. This sets the framework against which anthropogenic impacts and trends can be measured.

The concept of 'baseline' in the context of groundwater quality is difficult to define in detail and opinions differ on the meaning and application of the term. The presence of purely anthropogenic substances such as pesticides or CFCs indicates a departure from the natural condition, but for many solutes which can be derived either from pollution or natural sources, for example nitrate, phosphorus or arsenic, the distinction is less clear-cut. In addition, specific chemical constituents in a given groundwater body may be identified as pollutants while other component solutes may be entirely naturally-derived. For the purposes of this study, baseline is defined as:

> "*the range in concentration (within a specified system) of an element, species or chemical substance present in solution which is derived by natural processes from natural geological, biological, or atmospheric sources*".

The baseline chemistry of groundwater varies widely as a function of the many complex geological, geochemical, hydrogeological and climatic factors. These give rise to large spatial and temporal variations in chemical quality, at a range of scales. Hence, the baseline for a given element or compound will vary significantly both between and within aquifers. It is, therefore, scale-dependent and should be considered as a range rather than a single value.

Attempting to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England and Wales has been the objective of the project 'Baseline'. The project involves the characterisation of spatial and temporal variations in groundwater chemistry and interpretation of the dominant controlling processes within a given area, aquifer or aquifer block. For each study area, this has been achieved through collation of existing reliable groundwater, rainfall, land-use and host-aquifer mineralogical and geochemical data, as well as new strategic sampling of around 25–30 groundwater sources for a comprehensive suite of inorganic constituents. Selected analysis of stable isotopic compositions (e.g. O, H, C) and atmospheric tracers (CFCs, SF_6) has also been undertaken where appropriate. Statistical methods, including statistical summaries (medians,

means, percentiles), together with box plots and cumulative-frequency diagrams, provide some of the most valuable analytical tools for the assessment of chemical data and have been used in the Baseline report series. The Baseline reports provide a summary of the inorganic chemical status of groundwaters in a given study area and key pressures on water quality which should provide useful background information of value to water regulators and managers, environmental scientists and water users.

The current series of Baseline reports has been produced by the British Geological Survey with funding from the Natural Environment Research Council. This follows on from a previous series which was produced in collaboration with, and with co-funding from, the Environment Agency.

Previous published reports in the Baseline Series (British Geological Survey – Environment Agency):

1. The Triassic Sandstone of the Vale of York
2. The Permo-Triassic Sandstones of West Cheshire and the Wirral
3. The Permo-Triassic Sandstones of South Staffordshire and North Worcestershire
4. The Chalk of Dorset
5. The Chalk of the North Downs
6. The Chalk of the Colne and Lee River Catchments
7. The Great and Inferior Oolite of the Cotswolds District
8. The Permo-Triassic Sandstones of Manchester and East Cheshire
9. The Lower Greensand of southern England
10. The Chalk of Yorkshire and North Humberside
11. The Bridport Sands of Dorset and Somerset
12. The Devonian aquifer of South Wales and Herefordshire
13. The Great Ouse Chalk aquifer
14. The Corallian of Oxfordshire and Wiltshire
15. The Palaeogene of the Wessex Basin
16. The Granites of South-West England
17. The Ordovician and Silurian meta-sedimentary aquifers of central and south-west Wales
18. The Millstone Grit of Northern England
19. The Permo-Triassic Sandstones of Liverpool and Rufford
20. The Permo-Triassic Sandstone Aquifer of Shropshire
21. The Chalk and Crag of North Norfolk and the Waveney Catchment
22. The Carboniferous Limestone of Northern England
23. The Lincolnshire Limestone

Acknowledgements

Contents

FIGURES

PLATES

TABLES

Summary

This report characterises the spatial and temporal variations in groundwater chemistry in the Carboniferous Limestone aquifer of the Derbyshire Dome. The report incorporates results from available archive groundwater-chemistry data, together with rainfall and host-aquifer mineralogical and geochemical data and the results from strategic sampling and analysis of new samples from 31 groundwater sources.

The Derbyshire Dome is an anticlinal structure which consists of marine Carboniferous (Dinantian) Limestone flanked by shales and sandstones of the Millstone Grit (Namurian). The Limestone is extensively mineralised in some parts, in particular in the east of the study area. The mineralised areas display a distinct zonation in mineralogy with a west-east progression from calcite to barite to fluorite as the dominant gangue minerals.

The Carboniferous Limestone forms a regionally significant aquifer for potable and industrial use. The hydrogeology of the area is dominated by natural karstic features but even more by the 'anthropogenic karst' which has developed as a result of the extensive historic mining activities. This has created a network of mine passages and drainage adits ('soughs'), some of which are now used for public water supply.

The results from this study suggest that the natural baseline chemistry of the groundwater is largely controlled by differences in bedrock lithology and by the extensive mineralisation that occurs in the study area. The latter is responsible for the increased concentrations of trace elements including F, Ba, Ni, Pb, Zn, Mo and U in the groundwaters, although their mobility is also controlled by mineral solubility and/or redox conditions within the aquifer. The influence of bedrock lithology on the groundwater composition is obvious from the dominance of $Ca-Mg-HCO_3$ waters, reflecting the prevalence of limestone. The influence of Millstone Grit can be inferred in many groundwaters (especially near the Dinantian/Namurian interface) from the occurrence of increased concentrations of Fe, Mn and Si which result from varying lithologies and redox conditions.

The presence of thermal waters which contain varying proportions of long-residence-time groundwater, has also affected the regional groundwater baseline as these are enriched in a number of solutes, particularly Sr, SO_4 and Cl. Anthropogenic influences on the groundwater chemistry appear to be minor compared with natural processes, although one of the solutes most significantly impacted is nitrate. Comparison with a previous survey in 1967/8 suggests that nitrate concentrations in the groundwater have increased two-fold during the last 40 years and locally exceed the NO_3-N drinking-water limit of 11.3 mg L^{-1}.

Extensive mining activities have also impacted on the groundwater chemistry, firstly by lowering the base drainage level and promoting the upconing of thermal/deeper waters in parts of the aquifer, and secondly, by providing artificially high surface areas for enhanced bedrock weathering. The impact of mining on the baseline concentrations of solutes is difficult to quantify.

1   Introduction

The Derbyshire Dome, located in the Peak District National Park, is an anticlinal structure of Dinantian marine limestones surrounded by gritstones, sandstones and black shales of the Namurian Millstone Grit. The area is generally referred to as the 'White Peak' because of the pale colour of the limestone outcrops. The terrain is well-drained and dissected by both dry valleys and river valleys. The soils are calcareous and generally poor, creating grazing land for both sheep and cattle. The excavation of limestone is widespread in the White Peak and quarries (operational and historic) occur at various locations throughout the area.

The Derbyshire Dome is renowned for its thermal springs and their alleged curative properties which are celebrated by the many spas and baths that are found in the area. Examples include Buxton Spa and Matlock Bath. The Limestone forms a regionally significant aquifer for potable and industrial use and groundwater discharges from powerful springs to feed the main streams and rivers.
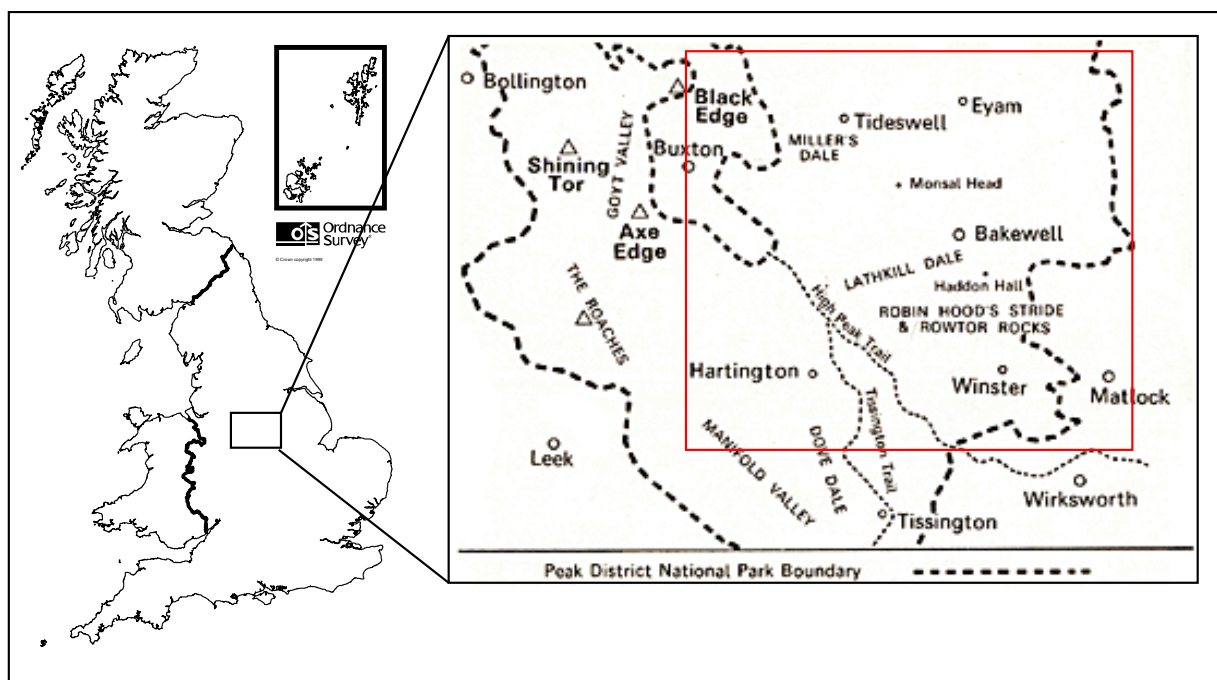
Figure 1.1   Location of the study area

The Limestone exhibits karstic features, but its hydrogeology is dominated by the 'anthropogenic karst' formed by the extensive mining of galena, fluorite (fluorspar) and accessory minerals. This has created a network of mine passages and drainage adits ('soughs') which honeycomb the hills of the Derbyshire Dome (Edmunds, 1971). When active, the mines were typically dewatered by pumping from shafts or by draining adits ('soughs'). Some of these soughs and shafts are now used for public water supply (e.g. Meerbrook Sough). As pointed out by Banks (Banks, 1997a), 'one might query the suitability of lead-mine drainage for public consumption', but the quality of the water is surprisingly good (Edmunds, 1971; Abesser and Smedley, 2006).

There is concern that radon concentrations in dwellings on the Derbyshire Dome may exceed the action levels of 200 Bq m^{-3} (Miles et al., 2007). Concentrations in excess of this value have been reported in soil gases (Ball et al., 1991; 1992) as well as in some of the limestone caves in the area (Gunn et al., 1991; Middleton et al., 1991). The high radon concentrations in soil gases have been linked ultimately to the concentrations of uranium in the underlying

bedrock (Peacock and Taylor, 1966; Ball et al., 1991; Hyslop, 1993; CEFAS, 2004) and various potential uranium sources have been identified within the Carboniferous bedrock (Hyslop, 1993; Abesser and Smedley, 2006). However, concentrations of uranium in the groundwater are generally low and during a recent survey did not exceed the WHO provisional guideline value for drinking water of 15 μg L^{-1} (Abesser and Smedley, 2006).

Historically, the area was known for a prevalence of goitre (swelling of the thyroid gland), known locally as 'Derbyshire neck', which declined from the 1930s when salt manufactures started to add small amounts of iodine to salt. Endemicity of goitre was generally higher in the Carboniferous limestone areas (Turton, 1933) and was believed to be associated with iodine deficiency in soils and groundwater. However, recent studied could not identify a clear link between endemic goitre and the distribution of environmental iodine in Derbyshire and suggest that additional factors (e.g., calcium and fluoride content in soils and water) may have contributed to the prevalence of goitre in the area (Saikat et al., 2004).

Agricultural activity is dominated by sheep and cattle grazing with some arable agriculture. The application of fertilisers to grassland provides a potential source of pollution of the groundwater. Pollution incidents have occurred in the groundwaters around Castleton, including the dispersal of fertiliser leachate (Gunn et al., 2000). However, groundwater and sediment studies have suggested that the composition in these groundwaters is dominated by water-rock interactions (Bottrell et al., 2000) and less affected by agricultural inputs.

2   Geographical setting

2.1   STUDY LOCATION

The study area is situated in the Peak District National Park in Derbyshire (Figure 1.1), mostly in the area of the White Peak. The sampling locations extend over an area of around 900 km^2 spanning the areas from Castleton (north-west of Eyam) in the north, Buxton and Leek in the west and Matlock in the south-east.

2.2   LAND-USE

A map of land-use is given in Figure 2.1. Usage is dominated by improved grassland and calcareous grass. Shrub heath, setaside grass and rough grass as well as 'acid' grass also occur but are more common where rocks of the Millstone Grit Series dominate the underlying geology. The most common agricultural activity is dairy and livestock farming as well as some cultivation of crops (Peak District National Park Authority, 2008). The excavation of limestone is widespread in the White Peak and quarries occur at various locations throughout the study area. A number of smaller settlements occur but urban areas of considerable size are outside or at the periphery of the study area. The locations of individual sampling sites are also given in Figure 2.1.

2.3   METEOROLOGY AND HYDROLOGY

Average annual rainfall over the area varies between 850-1600 mm/year (1961-1990) (NRFA, 2008), the greatest rainfall occurring in the north-west. Between 30 and 100% of the total is available as effective precipitation to infiltrate into the aquifer (Edmunds, 1971). In terms of hydrochemistry, this means that local rainfall may provide an important source of solute inputs into the groundwater, in particular when concentrations are enriched due to evapotranspiration effects. Table 2.1 gives the volume-weighted annual average of the major-element composition of rainfall (1994-2003) at the Drayton ECN terrestrial site [4162 2551], located approximately 100km south of the study area. The data were multiplied by a factor of three to account for the effect of evapotranspiration, which is assumed to result in a threefold concentration under the prevailing climatic conditions (Appelo and Postma, 1993).

The intermediate concentrations of Na, Cl and SO_4 suggest some inputs from maritime sources. This maritime influence may be larger closer to the study area as indicated by the data quoted by Gunn et al. (2006) for rain water collected near Castleton (Cl=11.9 mg L^{-1}, SO_4=11.1 mg L^{-1}). In any case, these concentrations are likely to include some contributions from anthropogenic emission sources as indicated by the presence of comparatively high concentrations of N. The pH of the rain water is acidic (5.8), despite being relatively well-buffered (alkalinity 5.8 mg L^{-1}). This reflects the effect that the presence of atmospheric pollutants (NO$_3$-N, NH$_4$-N, SO_4) has on lowering rain water pH (in addition to that produced by atmospheric CO_2).

Surface water drainage of Derbyshire Dome is south-eastwards via the rivers Wye, Bradford and Lathkill to the River Derwent (Figure 2.1). In the west and south-west, the rivers Dove, Hamps and Manifold drain the area, while Bradwell Brook and Peakshole Water drain the north.
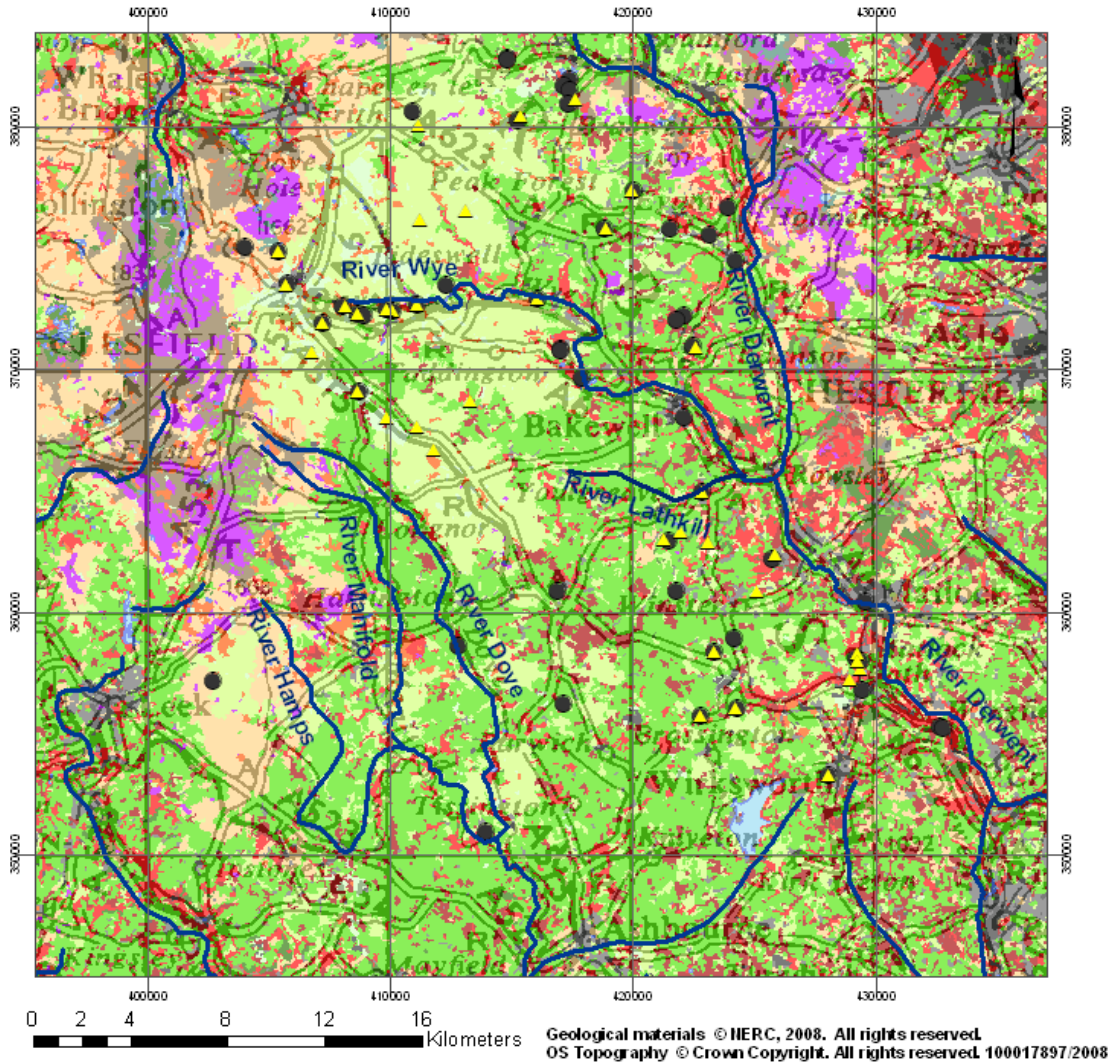
Legend

△ Sampling sites - previous surveys

● Sampling sites - Baseline survey

━━━ Rivers

Landuse

- ■ Broad-leaved/ mixed woodland
- ■ Coniferous woodland
- ■ Crops
- ■ Improved Grassland
- ■ Setaside grass & Rough grass
- ■ Calcareous grass
- ■ Acid grass
- ■ Bracken
- ■ Shrub heath
- ■ Fen, marsh, swamp
- ■ Bog
- ■ Water
- ■ Inland bare ground
- ■ Suburban/ rural development
- ■ Urban

Figure 2.1   Land cover in the study area and distribution of groundwater sampling sites of previous and current (Baseline) groundwater surveys (data from CEH Land Cover map, 2000; River data from National River Flow Archive (NRFA))

River flows in the limestone area are mostly groundwater-fed (Edmunds, 1971), in particular in the lower reaches of the rivers. The flat gradient of the flow duration curves (Figure 2.2 and Figure 2.3) illustrates that moderate and low flows are sustained by groundwater inputs. A high groundwater contribution is also implied from the low Q_{25}/Q_{75} ratios of 2.4 (River Derwent at St Mary's Bridge) and 2.5 (River Dove at Isaac Walton). Low values of these ratios (i.e. $1 < Q_{25}/Q_{75} < 2$) are typical of catchments in which almost all the flow is supplied by groundwater discharge, whereas increasingly high values indicate an increasing influence of surface runoff (Younger, 2007). The absolute groundwater contributions at these two gauging stations, as estimated from the Q_{95} values, are 5.0 m^3/s and 0.6 m^3/s, respectively. Some of the rivers are winterbourne and river stretches (e.g., the Lathkill at Lathkill Dale) are dry for variable periods and lengths each year. During periods of low flows, the River Hamps and stretches of the River Manifold disappear completely underground, flowing through a series of caves and subterranean passages before re-emerging after a few miles at the 'boil-holes' in the grounds of Ilam Hall in the Manifold Valley. Much of the river flow is derived from discrete springs, but Edmunds (1971) points out that a considerable volume of flow must also be gained from effluent inputs directly into the river channel. Along a 7-km stretch of the River Dove, for example, he observed a considerable increase in flow but found only four small springs over that distance.

Table 2.1   Rainfall chemistry at the ECN terrestrial site at Drayton [4162 2551] and surface water chemistry of the River Lathkill at the ECN freshwater site [4220 3647] for the period (1994-2003), averages were calculated from annual averages provided by the ECN (ECN, 2008)

		Average annual rainfall composition (1994-2003)	Concentrated rainfall (enrichment by evapotranspiration)	Average annual river composition (1994-2003)
T	°C	8.5*		9.8
pH		5.8	5.8	8.2
Alkalinity	mg L^{-1}	5.8	17	
Conductivity	µs cm^{-1}	35	105	524
Ca	mg L^{-1}	1.02	3.07	103
Mg	mg L^{-1}	0.22	0.66	5.6
Cl	mg L^{-1}	2.17	6.50	29.1
Na	mg L^{-1}	1.4	4.2	12
K	mg L^{-1}	0.3	0.97	1.4
SO$_4$	mg L^{-1}	2.9	8.8	64
SiO$_2$	mg L^{-1}			4.4
NO$_3$-N	mg L^{-1}	0.6	1.9	4.9
NO$_2$-N	mg L^{-1}			0.01
NH$_4$-N	mg L^{-1}	1.18	3.6	0.02
PO$_4$-P	mg L^{-1}	0.05	0.16	0.08
rainfall amount	mg L^{-1}	619		
discharge	m^3 s^{-1}			1.36

average annual (wet) air temperature
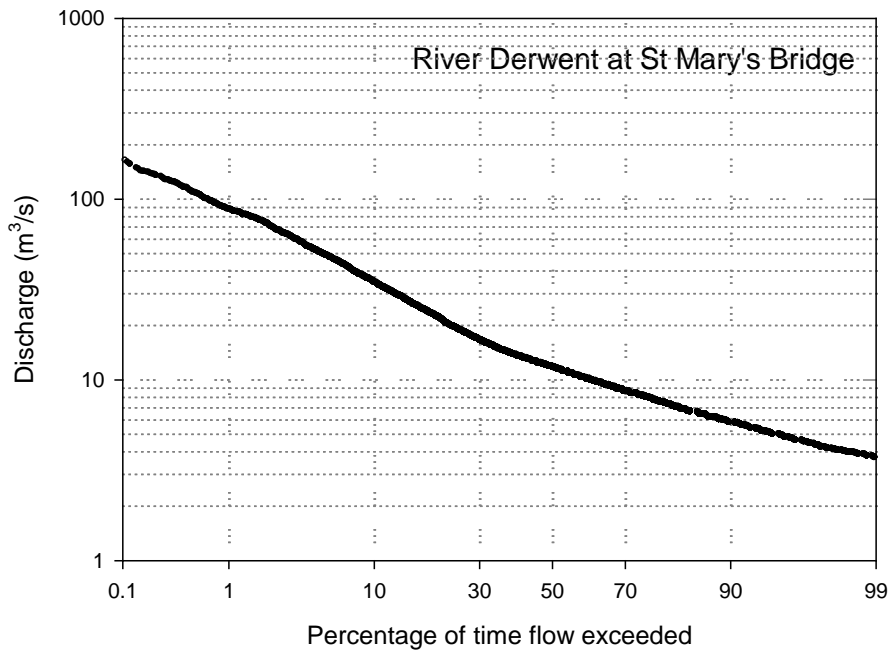
Figure 2.2 Flow duration curve of the River Derwent at St Mary's Bridge [4356 3363], Q_{95}=5.0 m^3/s , Q_{25}/Q_{75}=2.4 (Curves and ratios were calculated from average daily discharge for the period of 1938-79, data provided by NRFA, 2008)
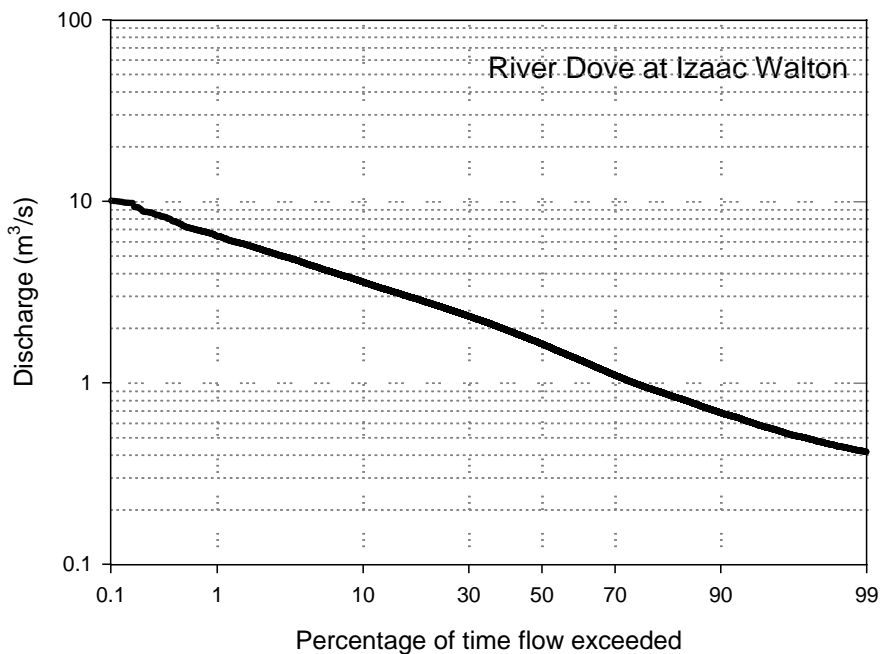
Figure 2.3 Flow duration curve of the River Dove at Izaac Walton [4164 3509], Q_{95}=0.6 m^3/s , Q_{25}/Q_{75}=2.5 (Curves and ratios were calculated from average daily discharge for the period of 1986-2006, data provided by NRFA, 2008)

River chemistry data are available for the River Lathkill, measured at the ECN Freshwater site [4220 3647]. The mean annual discharge at this site is 1.36 m^3/s and annual average concentrations[1] of selected elements are summarised in Table 2.1 (ECN, 2008). Major ion concentrations in the river lie well within the range observed in local (non-thermal) groundwaters (Edmunds, 1971; Gunn et al., 2006) confirming its groundwater-fed nature. Nitrate and nitrite concentrations are also similar to those observed in the groundwater although concentrations may increase as a result of pollution from the Knotlow cave system which has recently been contaminated with sewage effluent (ECN, 2008).

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[1] Calculated from annual average concentrations between 1994-2003

3   Regional geology and hydrogeology

3.1   REGIONAL GEOLOGY

The geology of the study area is illustrated in Figure 3.1. Geology is dominated by the Derbyshire Dome, an anticlinal structure that mainly consists of marine limestones of Dinantian age (Carboniferous Limestone Series). Overlying the limestones are shales and sandstones of Namurian Millstone Grit Series.

The limestones have a maximum thickness of 1900 m in the north-eastern part of the dome, but are much thinner in the west and south-west, reaching a minimum thickness of only 660 m at Buxton (Aitkenhead et al., 1985). The succession was formed from a variety of carbonate sediments deposited in diverse marine environments. Two contrasting lithofacies can be distinguished (Aitkenhead et al., 2002): the carbonate-platform facies (previously described as shelf facies), consisting of mainly shallow water deposits and the carbonate-ramp facies (previously described as off-shelf facies), which is dominated by deep-water deposits. A third lithofacies, the 'reef' facies occurs between the shelf margins and deeper water basins, and is composed of poorly bedded micritic limestone, often containing coral reef material and varied amounts of bioclasts.

The northern, central and eastern areas of the dome consist of limestones of the platform facies, typically comprising thick to very thick, uniform and extensive beds of bioclastic and peloidal grainstones and packstones. In the south and south-west, thinly bedded bioclastic packstones of the ramp environment predominate, interbedded with shales of varying thickness. Limestones of the reef facies developed along much of the northern, western and southern rims of the Derbyshire Dome (Aitkenhead et al., 2002).

Basaltic lavas, pyroclastic rocks and intrusive rocks are interbedded with the limestone in one or two horizons, primarily in the platform facies. However, the most widespread volcanic deposits in this succession are thin beds of varicoloured clays which are derived from fine volcanic ash and are locally known as 'clay wayboards'.

The Dinantian outcrop of the Derbyshire Dome is flanked by the Millstone Grit of Namurian age (Figure 3.1), except in the south where Triassic deposits overlap onto the limestone. Millstone Grit deposits include the Edale Shales which are composed of turbiditic, calcareous mudstones and siltstones and include numerous marine bands of several metres thickness. Protoquartzitic siltstones and sandstones occur in parts of the formation, interbedded with various proportions of dark fissile mudstone (Aitkenhead et al., 2002). The formation is overlain by the coarse-grained sandstones of the Millstone Grit, which can be distinguished easily from those of the Edale Shales by their feldspar-rich composition.

Drift deposits are rare as much of the higher ground remained ice-free during the last glacial period. Some deposits of 'Older Drift' are found in the form of erratics scattered along the eastern and western flanks of the dome (Burek, 1977). Isolated occurrences of boulder clay have also been reported in the Wye Valley between Bakewell and Rowsley, on the south side of the Lathkill Valley and in the western part of the district between Leek and The Roaches (Aitkenhead et al., 1985). Considerable erosion occurred throughout the Tertiary and Quaternary, exposing the underlying Carboniferous deposits and thereby promoting karstification and cave development in the limestone. Sediment derived by weathering of the overlying younger formations (Carboniferous to Pliocene) was deposited in the caves or in other karst features such as fissures, sinkholes or collapse depressions, the most spectacular of which are the so-called 'pocket deposits' in the south-west of the limestone outcrop.

Figure 3.1 Geology of the study area and distribution of groundwater sampling sites of previous and the current (Baseline) surveys

3.2   REGIONAL HYDROGEOLOGY

The Carboniferous Limestone of the Derbyshire Dome is hydrogeologically distinguished from other British limestone karst. Firstly, the sequence is very thick with resultant great depths to the base of the formation (100 m to over 1800 m). Secondly, the formation is surrounded by less-permeable strata, namely Namurian rocks, which support surface drainage. This combination has resulted in the development of a ponded karst system, which is characterised by a phreatic water table at depth (Gunn, 1992).

Groundwater flow in the Carboniferous Limestone is controlled by topography, the physical properties of the rocks, geological structure and lithology as well as by anthropogenic activities related to mining (Edmunds, 1971; Gunn, 1992). Primary porosity (0.001–1.0%) and intergranular hydraulic conductivity (0.001–0.01 m d^{-1}) of the limestone are generally very low (Gunn, 1992) and groundwater movement is almost entirely along solution-enlarged joints, fractures and bedding planes. Underground flow velocities through the conduits are generally rapid (100–500 m hr^{-1}) (Gunn, 1992) but vary significantly throughout the year depending on the hydrological conditions. The direction of groundwater flow varies largely throughout the Derbyshire Dome and is locally controlled by sub-catchment hydrology and morphology, i.e. directed towards valley bottoms. In places, deeper flow occurs along extended flowpaths (BGS, unpublished data). Edmunds (1971) presented tentative groundwater contours for the limestone area based on available water-level data. The resulting map suggests that groundwater flow is dominantly towards the east and this is supported by a more recent analysis of flow data (Shepley, 2007). In places, the surfaces of the igneous strata have weathered to clays and act as aquitards, giving rise to perched water tables (and associated groundwater springs) that can be in excess of 100 m above the position of the main water table (Shepley, 2007).

Extensive mining activity, which has taken place over the last 2000 years, has influenced flow directions and water levels in the northern and eastern part of the study area. The excavation of large quantities of ore and gangue minerals has emphasised the strong west-east drainage pattern while the construction of drainage tunnels ('soughs') has lowered the water table in many parts of the aquifer by creating new groundwater outlets. The Derbyshire lead industry declined after the late-eighteenth century, mostly because of worked-out veins, increased production costs and the discovery of much cheaper foreign sources. Henry VIII's dissolution of the monasteries has also been blamed for the collapse of lead mining due to the recycling of lead from the monasteries' roofs (Peak District Info, 2008). The last lead mine (Millclose Mine) was finally closed in 1940 and limestone quarrying took over as the main local industry.

Hydrogeologically, the limestones of the Derbyshire Dome and their different facies can be considered as a single lithological unit (Edmunds, 1971). Their different lithological composition, however, may affect the geochemistry of the groundwaters, especially on the local scale.

The Carboniferous Limestone exerts an important control on the groundwater chemistry, with previous studies showing that Ca-(Mg)-bicarbonate groundwaters predominate throughout the study area. Some variations in SO_4^{2-} and Cl^- concentrations occur, often associated with (less mineralised) Millstone Grit groundwaters and/or (more mineralised) thermal waters (Edmunds, 1971). Sulphate- and chloride-groundwaters are more common to the east of the Derbyshire Dome and have been associated with the presence of more evolved and/or connate groundwaters (Downing, 1967). Recent studies concluded that evaporite dissolution is the main source of SO_4 and Cl in these waters (Gunn et al., 2006).

Thermal waters[2] discharge from the Carboniferous Limestone at various localities including springs, boreholes and several mines and soughs (Stephens, 1929; Edmunds, 1971; Banks, 1997a; Gunn et al., 2006). The source of these thermal waters is debated. They are possibly related to a thermal anomaly below the Peak District which allows the rapid, cross-stratum upward migration of deep, warm groundwater along transmissive fracture zones (Banks, 1997a). Along the eastern side of the Dome, the locations of these thermal waters are believed to be structure-controlled with thermal fluxes, originating at ca. 800 m depth, being focussed by plunging anticlinal structures that have been truncated by the incision of a surface valley (e.g. the Derwent valley) (Gunn et al., 2006). At Buxton, however, karstic permeability is providing a hydraulic pathway for thermal discharge from the deeper (sandstone) aquifer (ca. 1000–1500 m) to a discharge point at a topographic low (Gunn et al., 2006). A different hypothesis was favoured by Brassington (2007) who suggested that thermal groundwater flow in the Derbyshire Dome results from the formation of convection cells which were induced by the combination of a large thermal gradient (30°C) between the top and the bottom of the Dinantian limestone and the significant variations in bedrock thermal properties and permeabilities of the Dome. He assumed that these thermal cells are located within the Dinantian aquifer with their upward limbs being located along the periphery of the Limestone Dome, matching the present distribution of thermal springs along its edges.

Based on hydrogeochemical investigations, eight centres of thermal water are recognised in the study area (Edmunds, 1971), the best known being the Buxton and Matlock Bath springs. Previous studies undertaken in 1967/68 suggested, based on tritium measurements, that many of these thermal waters were more than 15 years old and originate from local meteoric waters that have circulated to considerable depths (Edmunds, 1971). Subsequent radiocarbon dating showed that at least some of the thermal waters had bulk ages of up to several thousand years (Evans et al., 1979). For example, Barker et al. (2000) reported a bulk age of 5000 years for the Buxton thermal water. That study also found tritium contents between 0.8 and 4.5 TU in the Buxton water, confirming the old age of the groundwater but also implying some recent recharge. In addition, a more recent investigation which included CFC dating techniques (BGS, unpublished data), also indicated the existence of a minor modern recharge component in the thermal waters at Buxton. This is presumably due to the fracture permeability of the limestone which allows the mixing of waters of different ages. This is, to a greater or lesser extent, a feature of all Carboniferous thermal sources (Evans et al., 1979).

There are significant differences between the water chemistry at the different thermal centres, but separate springs within each centre are of the same chemical type. This finding has been used to support the idea that each centre originates from a separate flow cell with chemical differences reflecting variations in flow characteristics (depths of circulation, interaction with deep brine) at each thermal flow system and in the surrounding geology/mineralogy (Brassington, 2007). While most thermal waters are believed to originate within the Carboniferous Limestone sequence, there is some debate about the origin of the Buxton source (Bottrell et al., 2008). Based on the chemical and isotopic composition of the Buxton thermal water, Gunn et al. (2006) concluded that a significant component of flow has

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[2] The term 'thermal water' is not well defined (Pentecost et al., 2003) and is generally used to refer to groundwaters whose temperature is (significantly) higher than the annual mean air temperature (Edmunds, 1971; Albu et al., 1997). To derive a more qualitative distinction between thermal and non-thermal groundwaters and considering that annual groundwater temperatures vary by less than 5°C (Freeze and Cherry, 1979; Lee, 2006) we define thermal waters as those having a temperature more than 5°C higher than the local mean annual temperature of 10.3°C (estimated from monthly average of dry temperatures from ECN data at Drayton; Section 4.1). Groundwaters with temperatures of more than 2°C above the annual average are considered to contain at least a thermal component.

interacted with non-limestone lithologies, implying an ultimate source in the deeply-buried, locally confined Namurian sandstone aquifer to the west of Buxton (Goyt Syncline). In contrast, Brassington (2007) maintained that Buxton waters are derived from a thermal cell within the Dinantian aquifer with only a minor component of flow from the Goyt Syncline (Brassington, 2007; Bottrell et al., 2008).

3.3   AQUIFER MINERALOGY AND CHEMISTRY

The Carboniferous Limestone is a limestone of varying chemical purity, including formations with a $CaCO_3$ content of over 98.5% (Aitkenhead et al., 2002). Dolomitisation is widespread in the south and south-east area of the dome (Parsons, 1922). This is believed to be due to magnesium-rich downward-percolating groundwaters during Permian and Triassic times (Aitkenhead et al., 2002), although Ford (1999) raised the possibility of it being an early phase of mineralisation. A second type of dolomitisation, which affected older limestones between Buxton and Eyam, may have resulted from the action of hypersaline brines during periods of restricted circulation and intensive evaporation in the late-Dinantian shelf sea. Alternatively, this type of dolomitisation could be related to the action of magnesium- and iron-rich fluids migrating upwards from underlying volcanic rocks or surrounding basinal sequences during deep burial in late Carboniferous times (Aitkenhead et al., 2002). Beside its effect on the groundwater's geochemical characteristics, dolomitisation may also influence the hydrogeological characteristics of the aquifer by creating secondary porosity (Machel, 1999) and hence increasing the specific yield of (and storage within) the dolomitised limestone areas. This mechanism was suggested by Shepley (2007), who analysed discharges from mine shafts and groundwater hydrographs in the catchment of the Meerbrook Sough/Wirksworth area, to explain the higher than expected storage (and hence porosity) in parts of the aquifer.

Silica is common in some limestone formations of the Derbyshire Dome, but is absent in others, e.g., in the reef-facies formation (Ford, 1999). Where present, silica occurs in the form of chert nodules, authigenic quartz or silicified fossils or as quartz rock (Sylvester-Bradley and Ford, 1968).

The Carboniferous Limestone is extensively mineralised, in particular in the eastern part of the dome. The mineralisation is concentrated in veins and 'rakes' and includes the metallic ores galena and sphalerite as well as the gangue minerals fluorite, barite and calcite. Minor occurrences of manganese and iron ores have also been noted and an isolated complex of copper-zinc-lead mineralisation occurs around Ecton (Ford, 1968b). The mineralisation has been sub-divided into different zones according to the occurrence of the various gangue minerals, reflecting the west-east progression from calcite to barite to fluorite as the dominant gangue mineral. Mineralisation is less important in the Namurian deposits, although phosphatic nodules at the base of the Edale Shales around Matlock, Calver and Eyam have yielded an appreciable proportion of uranium oxide (Ford, 1968a).

4 Data availability and analytical methodology

4.1 DATA SOURCES

Historic data for the Derbyshire Dome were available from previous surveys carried out by BGS in 1967/68 (Edmunds, 1971) and in 2005 (Abesser and Smedley, 2006). Both surveys cover the Carboniferous Limestone aquifer but also contain some groundwater samples from the adjacent Millstone Grit.

The data collected in 1967/68 comprised a wide range of determinands, including field measurements of pH, temperature and alkalinity as well as major ions and selected trace elements. For all but four samples, the cation-anion balance of the analysis was <10%, reflecting the limited accuracy of the measuring technology at the time. Tritium analyses were carried out on a limited number of thermal waters. The complete list of determinands as well as details of sampling and analytical techniques are given in Edmunds (1971). Since the data are not available in digital format (at the time of writing), they were not included in the statistical data analysis presented here. Instead, the results were used for comparison with the recently collected data and references to the earlier findings are made where relevant.

For the survey undertaken in 2005, sample collection and analysis followed the procedures described in Section 4.2. The suite of chemical determinands was identical to the current study, except for stable isotopes and CFCs and SF_6 which were not done in the original study.

Additional data are available from a recent publication by Gunn et al. (2006) including sulphate ($^{34}S/^{32}S$, $^{18}O/^{16}O$) and Sr ($^{87}Sr/^{86}Sr$) isotopic analysis. Reference to these data has been made where appropriate.

Some early analyses are also available from Stephens (1929) for selected wells and springs in Derbyshire. These include analyses of the thermal waters at Buxton and Matlock Bath as well as of various non-thermal springs (e.g. Russett Well) and have been used for comparison.

Chemical data for precipitation as well as for the River Lathkill were available from the Environmental Change Network (ECN) website at http://www.ecn.ac.uk/index.html as well as from Gunn et al. (2006).

4.2 SAMPLING AND ANALYSIS

A total of 31 samples were collected by BGS in March 2006 from natural springs, decommissioned mines and soughs as well as from industrial and farm boreholes, in the area spanning between Castleton in the north, Buxton and Leek in the west and Matlock in the south east. The sampling locations are given in Figure 2.1 and Table 4.1.

The sampling sites were selected to include groundwaters from mineralised and non-mineralised bedrock, mine drainage and thermal waters. Samples were mostly collected from permanently operating boreholes and/or after a minimum pumping of an estimated two well bore volumes, prior to sampling. However, where this was not possible owing to a large borehole volume, samples were collected after on-site readings of e.g. temperature had stabilised. Efforts were made to sample groundwater as close to the discharge point as possible. Sampling from storage tanks was generally avoided unless a representative sample of groundwater was considered to be obtainable. At two sites, however, passage through the tanks has brought the (reducing) groundwater in contact with atmospheric O_2. This may have resulted in some Fe precipitation within the tanks prior to sampling.

Table 4.1   Sampling locations (S=spring, MD=mine drainage/adit/sough, BH=borehole)

No	Locality	Easting	Northing	Source	Thermal
1	Russet Well	414830	382830	S	
2	Slop Moll (Sough)	414813	382761	MD	
3	Bradwell Caravan Park	417416	381997	S	x
4	Michlow Well	417155	381724	MD	
5	Bradwell Springs	417417	381552	S	
6	Bagshave Rising (Sough)	417370	380980	MD	
7	Penny Dale	410919	380649	BH	
8	Moss Rake	415245	380283	BH	
9	Shepherds Flatt	420060	377387	BH	
10	Stoke Sough at 'Roman Bath'	423956	376667	MD	x
11	Hawkenedge Sough	421561	375822	MD	
12	Water Grove Mineshaft / Cavendish Mill	418845	375815	MD	
13	Stoney Middleton Sough	423194	375537	MD	x
14	Brookfield Hall	404045	375073	BH	
15	Lightwood Borehole	405418	374881	BH	
16	Brightside Sough Calver	424268	374474	MD	
17	St Anne's Well	405787	373556	S	x
18	Wormhill Spring	412323	373522	S	
19	Litton Mill Spring	416068	372940	S	
20	Blackmill Well	411150	372690	S	
21	Ashwood Dale	408075	372617	BH	
22	Woodale Borehole	409860	372480	BH	
23	Topley Pike	410130	372440	BH	x
24	Rockhead Spring	408660	372317	S	
25	Hassop Spring - Wood Supply	422084	372255	MD	
26	Sally Spring Roadside A6	408938	372242	S	
27	Hassop Springs - Lower Spring	421799	372061	S	
28	Staden	407255	371933	BH	
29	Birchill	422497	370955	BH	
30	Lower Dimmindale S-bank Wye - Upper Spring	417023	370833	S	
31	Lower Dimindale S-bank Wye - Lower Spring	417049	370781	S	
32	Magpie Sough	417935	369635	MD	
33	Brierlow	408733	369074	BH	
34	Holywell, Bakewell	422098	368042	S	x
35	Shining Bank	422846	364938	BH	
36	Mawstone Spring	421480	362973	S	
37	Mill Close Mine (Darley Dale Smelter)	425771	362166	MD	
38	Friden Borehole	416900	360900	BH	
39	Oddo House	421780	360900	BH	
40	Snitterton Sough	628167	360820	MD	
41	Allenhill Spaer (Matlock East Bank)	429612	360427	MD	
42	Shothouse Spring	424176	358924	S	
43	Beresford Dale Spring	412793	358621	S	x
44	Ivonbrook	423395	358333	BH	
45	Matlock Bath, Royal Well	429220	358080	S	x
46	Matlock Bath, West Bank -Fountain	429404	358007	S	x
47	Dunlea	402719	357199	BH	
48	Cromford Sough	429480	356790	MD	
49	Hawkslow	417169	356232	BH	
50	Griffe Walk	424300	356047	BH	
51	Longcliffe	422795	355708	BH	
52	Meerbrook Sough at Homeford	432644	355266	MD	x
53	Meerbrook Sough	432800	355200	MD	x
54	Ladyflatte Mine	428072	353277	MD	
55	Ilam Spring	413944	350967	S	

Sampling included on-site measurements of temperature, specific electrical conductance (SEC) and alkalinity (by titration against H_2SO_4) as well as pH, dissolved oxygen (DO) and redox potential (Eh). Where possible, the latter three parameters were measured in an anaerobic flow cell. At each site, samples for the analysis of major and trace elements were collected in polyethylene (Nalgene®) bottles. All samples were filtered through a 0.45 μm filter and aliquots for cation and trace-element analysis, were acidified to 1% v/v HNO_3 to prevent metal precipitation and to minimise adsorption onto container walls. Samples for dissolved organic carbon (DOC) were filtered through a 0.45 μm silver-impregnated filter and collected in chromic-acid-washed glass vials. Samples for the determination of stable isotopes (O, H, C) were collected unfiltered into glass bottles. At suitable sites, samples for the measurement of atmospheric trace gases CFCs and SF_6 were collected following the displacement method described in Oster et al. (1996). Samples were collected unfiltered, into glass bottles contained within metal cans in order to avoid atmospheric contact and to ensure that the sample was protected from atmospheric contamination by a jacket of the same water.

Analysis of major cations and sulphate was carried out by inductively-coupled plasma optical-emission spectrometry (ICP-OES) and of anion species (Cl, Br, I, F) by ion chromatography at the BGS laboratory in Wallingford. A wide range of trace elements was analysed by inductively-coupled plasma mass spectrometry (ICP-MS) at the Acme Laboratory, Canada.

Ionic charge imbalances were less than 5%, except for three samples which had imbalances of 5.4%, 5.9% and 6.4%. The precision of the trace-element data was verified by determining the relative standard deviation (rsd) of replicate analyses. The median rsd for all elements was <1% although somewhat higher rsd values (max 35%) were observed where elemental concentrations were near the detection limit.

4.3 DATA HANDLING

For the data analysis, the data collected during this sampling survey and data collected during a previous BGS survey (2005) were combined into one data set. For a number of elements, concentrations were below the reporting limit of the laboratory. This meant that special statistical analysis methods were required for computing the summary statistics for the data set in order to account for the censoring.

Summary statistics were calculated for the combined dataset using the NADA package for the R statistical computing environment (Venables et al., 2008). The package is designed for the statistical treatment of censored data and contains the analysis methods described in Helsel (2005; 2005). Calculations of summary statistics were based on a combination of the Kaplan-Meier method and the robust 'Regression on order statistics' (ROS) method. The Kaplan-Meier method is widely applied in the medical sciences (survival analysis) but also recommended for environmental data (Helsel, 2005). This is particularly useful for summarising censored data as it does not make/require an assumption about the underlying distribution of the data, and it does not require estimates of the unknown distance between non-detects and detected values, only their relative order. The method calculates the relative position (rank) of the observed data and estimates the summary statistics, including percentiles, mean and standard deviation based on the empirical cumulative distribution function (ECDF) of the ranked data.

The Kaplan-Meier method only accepts right-censored (above detection) data and is suitable for small and large data sets provided less than 50% of the data are censored.

The ROS method used in the NADA package is based on the Multiple-limit Regression (MR) by Helsel and Cohn (1988). It is best used for small data sets (n<30) where maximum

likelihood estimations (MLE) of statistical parameters become inaccurate (Helsel, 2005) and it is also one of the most reliable procedures for estimating summary statistics of multiply-censored data (Shumway et al., 2002). The method is a probability-plotting and regression procedure that models censored data distributions using a linear regression of the observed concentrations versus their normal quantiles. The procedure first computes the Weibull-type plotting positions of the combined uncensored and censored observations using a formula designed for multiply-censored data. A linear regression is formed using the plotting positions of the uncensored observations and their normal quantiles. This model is then used to estimate the concentration of the censored observations as a function of their normal quantiles. Finally, the observed uncensored values are combined with modelled censored values to estimate summary statistics of the entire population. By combining the uncensored values with modelled censored values, this method is more resistant to any non-normality of errors, and reduces any transformation errors that may be incurred. This method has been used to calculate summary statistics where the number of non-detects lies between 50-80%.

Summary statistics for individual determinands were calculated separately using one of the above methods. The selection of the most suitable method for each determinand was based on the proportion of censored data in the dataset and followed the recommendations by Helsel (2005) as given below:

Non-detects <50%	Kaplan-Meier method
Non-detects >50% and <80%	ROS method (log-transformed data)
Non-detects >80%	Ranges only quoted

Consequently, different procedures were used for calculating the summary statistics of the different parameters and the methods applied for each determinand. The statistical parameters derived by each method also differed as is summarised in Table 4.2. Calculation of the boxplots included in this report (Figure 5.1 and Figure 5.9) is based on statistics using the ROS method.

In this study, minima and maxima are used to determine the concentration range of individual parameters in the groundwater, while the 95th percentile is used as the overall cut-off for upper outliers. This threshold has been used in this report as an appropriate indicator of 'upper baseline' concentrations. The choice of percentile is somewhat arbitrary and various other percentiles have been used elsewhere, e.g. 90th–95th (Lee and Helsel, 2005) or 97.7th

Table 4.2 Statistical parameters calculated by the different methods

Method	N	N (c)	Minimum	Mean	Maximum	0th percentile	25th percentile	50th percentile	75th percentile	90th percentile	95th percentile	100th percentile
<50% non-detects (K-M)	✓	✓	✓	✓	✓	✗	✓	✓	✓	✓	✓	✗
>50<80% non-detects (ROS)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
>80% non-detects	✓	✓	✓	✗	✓	✗	✗	✗	✗	✗	✗	✗

N= number of samples, N(c) = number of censored data

(Langmuir, 1997) to remove outlying data/extremes. However, the applicability of percentiles as an upper threshold for baseline conditions is limited. For example, most aquifers in the UK are impacted by nitrate inputs from agricultural practices and, thus, values below the 95% threshold do not necessarily represent baseline conditions. Similarly, data above this threshold can in some cases represent baseline conditions as anomalous, and background concentrations often show significant overlap (Sinclair, 1974). Nevertheless, the 95th percentile, by definition, presents the concentrations that are exceeded by only 5% of samples. It, therefore, defines concentrations that are unlikely to be exceeded in subsequently analysed samples unless the conditions in the aquifer have changed. The 95th percentile can also be readily calculated for small data sets (n<50) and is used in this study to define the upper limits to 'baseline' concentrations.

The data have been summarised in the form of tables (Table 5.1, Table 5.2), boxplots (Figure 5.1, Figure 5.9) and cumulative probability curves (Figure 5.3, Figure 5.8). Background information on the application and interpretation of cumulative probability diagrams is given in Shand et al. (2007) and Reimann et al. (2008).

5 Regional hydrogeochemistry

5.1 MAJOR CONSTITUENTS

The sampled groundwaters display a wide range of physico-chemical characteristics and element concentrations. Data for major ions and field-determined parameters are summarised in Table 5.1 and boxplots, a Piper diagram and cumulative probability distributions of major ions are illustrated in Figure 5.1, Figure 5.2 and Figure 5.3 respectively.

Table 5.1   Statistical summary of field-determined parameters, major constituents and isotopic compositions of groundwaters from the Carboniferous Limestone aquifer

Parameter	Units	N	N (c)	min	mean	max	P0	P25	P50	P75	P90	P95	P100
T	°C	57	0	4.6	10.5	25.1		8.6	9.7	11.7	15	17.4	
pH		57	0	5.94	7.37	9.17		7.21	7.34	7.48	7.75	8.1	
Eh	mV	57	0	112	444	691	112	396	463	524	551	559	691
DO	mg L^{-1}	53	0	0	6.1	16.1		4.5	6.7	8.1	10	10.7	
SEC	µS cm^{-1}	57	0	221	648	1650		560	623	697	865	981	
$\delta^{13}C$		31	0	-19.4	-15	-10.1	-19.4	-15.7	-15.1	-13.9	-13.3	-12.6	-10.1
$\delta^{18}O$		31	0	-8.14	-7.76	-6.93	-8.14	-7.92	-7.77	-7.66	-7.46	-7.28	-6.93
δ^2H		31	0	-54.9	-51.2	-44.8	-54.9	-52.8	-51.5	-49.7	-48.8	-47.3	-44.8
Ca	mg L^{-1}	57	0	2.36	96.1	171		93.8	104	109	125	135	
Mg	mg L^{-1}	57	0	0.269	10.9	36.3		2.41	7.9	19.9	24.7	29	
Na	mg L^{-1}	57	0	3.89	23.7	192		8.78	12	22.4	45.5	126	
K	mg L^{-1}	57	8	<0.5	1.74	13.5		0.89	1.21	1.63	3.43	4.56	
Cl	mg L^{-1}	57	0	7.32	34.3	266		16.7	21.5	32.3	77.8	106	
SO$_4$	mg L^{-1}	57	0	4.96	47	311		21.2	27.8	46.3	117	144	
HCO$_3$	mg L^{-1}	57	0	21	263	367		244	268	293	328	346	
NO$_3$-N	mg L^{-1}	57	8	<0.05	3.22	12.6		0.878	3.06	4.13	6.03	8.5	
NO2-N	mg L^{-1}	57	30	<0.0007	0.00232	0.0872	<0.0007	<0.0007	0.0004	0.0012	0.0017	0.0026	0.0872
NH$_4$-N	mg L^{-1}	57	33	<0.006	0.0311	0.434	<0.006	0.0006	0.0030	0.0136	0.1108	0.163	0.434
TDN	mg L^{-1}	57	9	<0.05	2.99	11.9		0.824	2.84	3.93	5.89	8.32	
TON	mg L^{-1}	30	0	0.24	4	13.4		1.03	3.67	4.67	5.75	13.2	
P	mg L^{-1}	57	3	<0.02	0.037	0.16		0.025	0.031	0.041	0.057	0.074	
DOC	mg L^{-1}	56	0	0.4	1.4	8.6		0.69	1	1.6	2.9	3.8	
F	µg L^{-1}	57	0	25	598	1780		170	505	969	1420	1490	
Br	µg L^{-1}	57	5	<20	100	804		49	67	93	182	274	
I	µg L^{-1}	31	2	<0.9	3.75	18.1		1.99	2.84	4.4	6.9	9.4	
Si	µg L^{-1}	57	0	1590	4120	13600		2390	2960	4440	8200	12800	

P: percentile; N (c): number censored; TON: total oxidised N; TDN: total dissolved N

Most noticeable is the wide range of temperatures observed in the groundwaters (4.6 to 25.1°C with a median of 9.7°C). The lowest temperatures were measured at a spring site, indicating that the groundwater flow to the spring must be relatively shallow, and/or contains a component of surface water. High groundwater temperatures were observed in boreholes, springs and wells and are associated with the occurrence of thermal waters. They appear mostly in springs and soughs along the fringes of the Derbyshire Dome (Appendix 1, Plate 1), near the interface between the Carboniferous Limestone and the overlying Millstone Grit. Banks (1997a) suggested that these springs represent discharge points for long, deep flow paths through the Limestone, the location of which is controlled by fault structures. The origin

of the thermal water at Buxton however, is still debated (Bottrell et al., 2008). Gunn et al. (2006) suggested that much of the Buxton thermal water has migrated from the Namurian sandstone of the Goyt syncline (north-west of Buxton) before discharging through the fissured limestone at the head of the Wye valley. Brassington (2007), however, maintained that Buxton waters are derived from within the Dinantian aquifer with only a minor component of flow from the Goyt Syncline (Bottrell et al., 2008).

The groundwaters are well buffered at circum-neutral pH (median pH 7.34) although somewhat lower pH values occur in groundwaters that discharge directly from the Millstone Grit (e.g., Mawstone Spring, Shepherds Flatt, Allen Hill Spaw) and/or that contain a significant proportion of Millstone Grit groundwater (e.g. Meerbrook Sough) (Appendix 1, Plate 1). The exceptionally high pH of the groundwater from a sample at Shining Bank is attributed to the groundwater system being closed with respect to CO_2 as it is confined by the Conksbury Bridge Lavas. The evolution of the groundwater appears to be dominated by plagioclase hydrolysis, calcite saturation and precipitation and/or ion exchange (Abesser and Smedley, 2006). This has resulted in the Na-rich, alkaline composition of the groundwater as discussed in the following section.
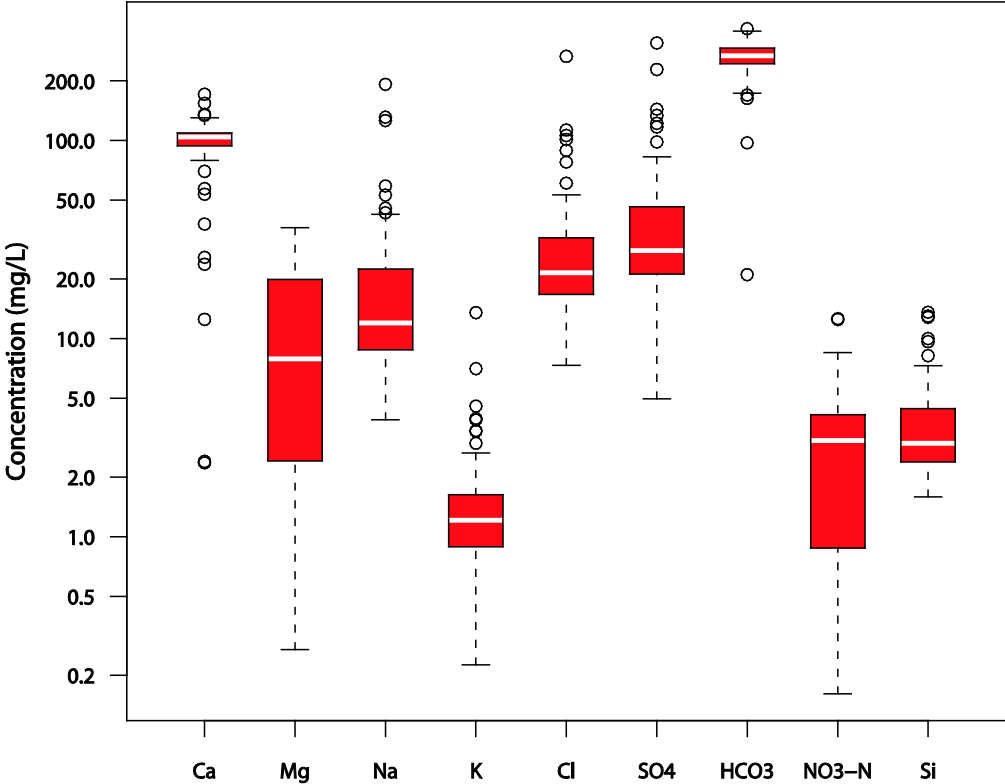
Figure 5.1   Elemental range of major elements in the groundwaters of the Derbyshire Dome

20
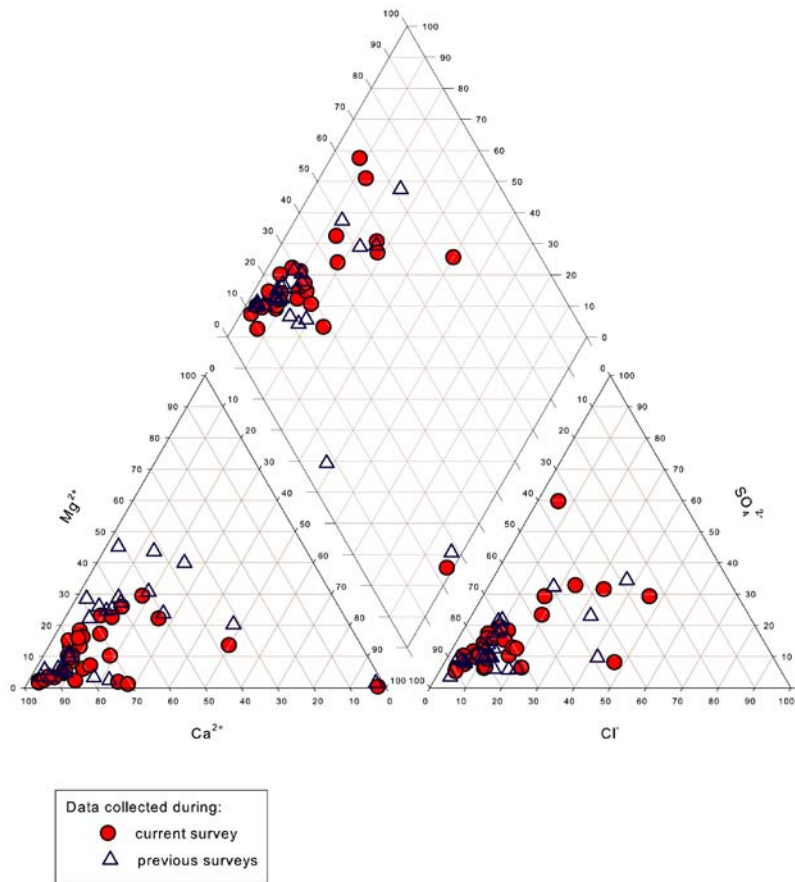
Figure 5.2 Piper plot of Derbyshire Dome groundwaters

The Piper plot (Figure 5.2) illustrates that most groundwaters are of Ca-Mg-HCO$_3$ type, with some variations in Mg, Na and Cl.

A small number of groundwaters show a tendency towards Ca-SO$_4$-Cl type. All but three of these are of thermal origin and issue from the mineralised eastern part of the Derbyshire Dome. They are characterised by increased salinity and SO$_4$ concentrations and have probably interacted with Lower Carboniferous evaporite deposits (Gunn et al., 2006) and/or with the adjoining Namurian strata. Of the three remaining Ca-SO$_4$-Cl groundwater samples, one spring issues from the Millstone Grit. Mineralisation of this groundwater is generally much lower than in the limestone groundwaters due to the carbonate-poor lithology. Consequently, SO$_4$ and Cl are the major anions although their total concentrations are low.

The groundwater composition from a borehole at Brierlow [408731 369079] near Buxton, tends more towards a Ca-Cl water. Details of the depth of this borehole are not available, but the groundwater has a comparatively high salinity and a Br/Cl ratio (1.3×10^{-3}) which is slightly below that of seawater (3.45×10^{-3}). The ratios for Na/Cl, SO$_4$/Cl and Ca/Cl are also very similar to seawater composition, suggesting that mixing with residual, more mineralised (connate) waters may have occurred (Downing, 1967). The Carboniferous Limestone (as well as the early phase of Millstone Grit) formed in a marine environment and pores of the rock matrix must initially have contained seawater. Hence, it is likely that some saline waters have been retained in the limestone, in particular at depths where circulation (and hence flushing) is restricted or absent due to the low intrinsic permeability. This interpretation assumes that
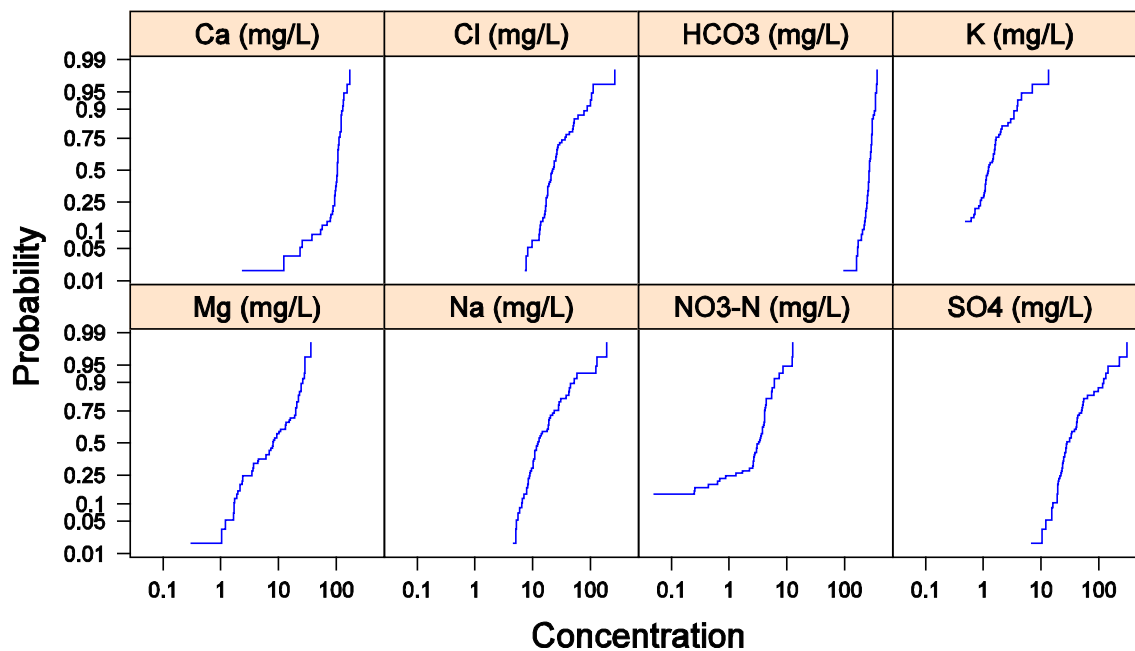
Figure 5.3 Cumulative-frequency distributions of major elements in the Derbyshire Dome groundwaters

the source at Brierlow Quarry abstracts from considerable depths within the aquifer. A deep source is also implied by the relatively enriched $\delta^{13}C$ signature (-14.3 ‰) of the groundwater, although a recent recharge component is present, as indicated by the presence of NO_3 (3.5 mg L^{-1} NO_3-N). It is possible that on-site production of Sorbacal®, a patented hydrated lime product, has contributed to the increased salinity in the groundwater. However, without further details on the on-site production processes and chemicals involved (e.g. accelerators, additives) this remains hypothetical.

Groundwaters of Na-HCO_3 type occur in deeper groundwaters near Youlgreave, for example at Shining Bank [422857 364938] and near Buxton (Lightwood borehole [405418 374881]). The aquifer in these areas is locally confined respectively by the Conksbury Bridge Lavas and Namurian shales and mudstones. Both groundwaters are characterised by considerably lower concentrations of Ca, Mg and Ba, while Na, Li and Rb are enriched. These relationships suggest that ion exchange between Na on clay minerals and Mg and Ca from the infiltrating meteoric waters has occurred. Such processes have been observed in a number of aquifers as a result of aquifer freshening following saline water ingress. Examples can be seen in parts of the Carboniferous Limestone of North Yorkshire (Abesser et al., 2005b), the Lincolnshire Limestone (Edmunds, 1981), the Millstone Grit (Abesser et al., 2005a) and the Coal Measures (Banks, 1997b). Weathering of plagioclase in conjunction with carbonate precipitation may have further contributed to the formation of these Ca-poor, Na-HCO_3-rich waters. However, such processes are probably more important in the groundwater at Shining Bank where the aquifer is overlain by plagioclase-rich basaltic lava deposits (Abesser and Smedley, 2006).

The spatial variation in groundwater chemistry clearly reflects the distribution of bedrock geology and mineralisation. Groundwaters from the Carboniferous Limestone aquifer are characterised by high Ca and HCO_3 and these groundwaters are saturated or oversaturated with respect to calcite. The Ca concentrations are therefore strongly controlled by calcite solubility as indicated from the steep gradient in the upper part of cumulative-probability curve (Figure 5.3).

22

Calcium concentrations are much lower in the Millstone Grit groundwaters (Appendix 1, Plate 1) which are undersaturated with respect to calcite. Calcite undersaturation is also common near the Carboniferous Limestone/Millstone Grit interface where mixing between the different groundwaters occurs (e.g. Russett Well, Meerbrook Sough). In these 'mixed' waters, Ca concentrations are comparatively high (ca. 100 mg L^{-1}) compared to the Millstone Grit groundwaters (median 47 mg L^{-1}).

Silica concentrations show an opposite trend to those of Ca (Appendix 1, Plate 2). In the Carboniferous Limestone groundwaters, concentrations are generally low (median 2.96 mg L^{-1}), mostly due to the limited availability of SiO_2 in the bedrock and/or short groundwater residence times. Concentrations are higher in the Millstone Grit groundwaters as well as in the mixed groundwaters near the interface. Most Limestone groundwaters are near-saturated with respect to quartz. Only the groundwaters in the north-east (along the Wye Valley) are undersaturated with quartz. In contrast, groundwaters from the Millstone Grit are typically oversaturated with respect to quartz, but remain undersaturated with respect to the more soluble amorphous silica.

Magnesium concentrations are generally low (median 7.90 mg L^{-1}) but tend to be higher in some thermal waters (e.g. Bradwell, Stoke Sough, Stoney Middleton Sough) as well as in the Millstone Grit groundwaters (Appendix 1, Plate 1). The latter are characterised by higher Mg/Ca (molar) ratios (0.6–1.1 compared to median ratio (all groundwaters) of 0.2) (Figure 5.4), probably reflecting the proportionally higher Mg availability in the bedrock. High Mg concentrations also occur in the south-east of the Derbyshire Dome, where bedrock dolomitisation has been widespread and saturation of the groundwaters with respect to dolomite is common. Dissolution of dolomite is probably responsible for the highest observed Mg concentrations (36.6 mg L^{-1}) in the groundwaters. These maximum concentrations occurred in the borehole at Oddo House, which penetrates secondary dolomites and abstracts from a perched water table above an igneous horizon (Shepley, 2007).

Sulphate is present in the groundwater of the Derbyshire Dome at concentrations ranging
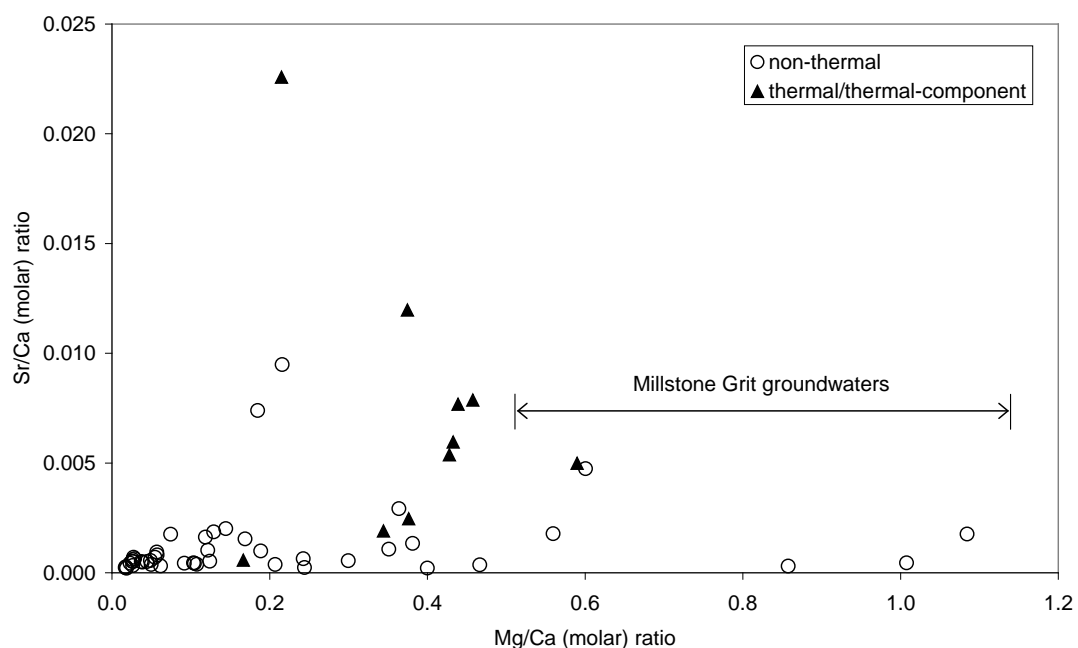
Figure 5.4   Molar ratios of Mg/Ca and Sr/Ca of the Derbyshire Dome groundwaters (thermal and non-thermal)

between 4.96 and 311 mg L^{-1}, with higher concentrations occurring in the eastern part of the area (Appendix 1, Plate 2). Figure 5.5 shows that many of the thermal and thermally-influenced groundwaters (i.e. those with temperatures >15°C and >12°C) have higher SO$_4$ concentrations, often in excess of 100 mg L^{-1}. Enrichment of SO$_4$ in the thermal groundwaters compared to non-thermal groundwaters was previously observed by Edmunds (1971) who also noted a general east-west trend in SO$_4$ distribution, as seen in this study. The high SO$_4$ concentrations in the waters of the mineralised eastern part were attributed by Edmunds (1971) to the dissolution of barite as well as to the oxidation of sulphide minerals such as galena (PbS), sphalerite (ZnS) or pyrite (FeS$_2$) (Banks, 1997a) during the passage of groundwater through mineralised fractures and mineral-vein "rakes". These processes are likely to control compositions of the shallow groundwaters but a different mechanism is required to explain the high SO$_4$ concentrations in the deep, thermal groundwaters, e.g., at Holywell (Bakewell), Bradwell, Stoke Sough and Matlock Bath which also show the highest saturation with respect to gypsum (SI$_{gyp}$ -1.4 to -0.9) and anhydrite (SI$_{anh}$ -1.6 to -1.1).

Worthington and Ford (1995) concluded that the high SO$_4$ concentrations in the thermal springs at Matlock are derived from the dissolution of highly soluble sulphate minerals (gypsum or anhydrite) which are known to be present at depths around 700 m, toward the base of the Dinantian sequence (Bottrell et al., 2008). Such evaporite dissolution is considered to be critical to the early development of deep flow paths within this part of the aquifer. This hypothesis is supported by recent findings by Gunn et al. (2006) who showed that the δ^{34}S
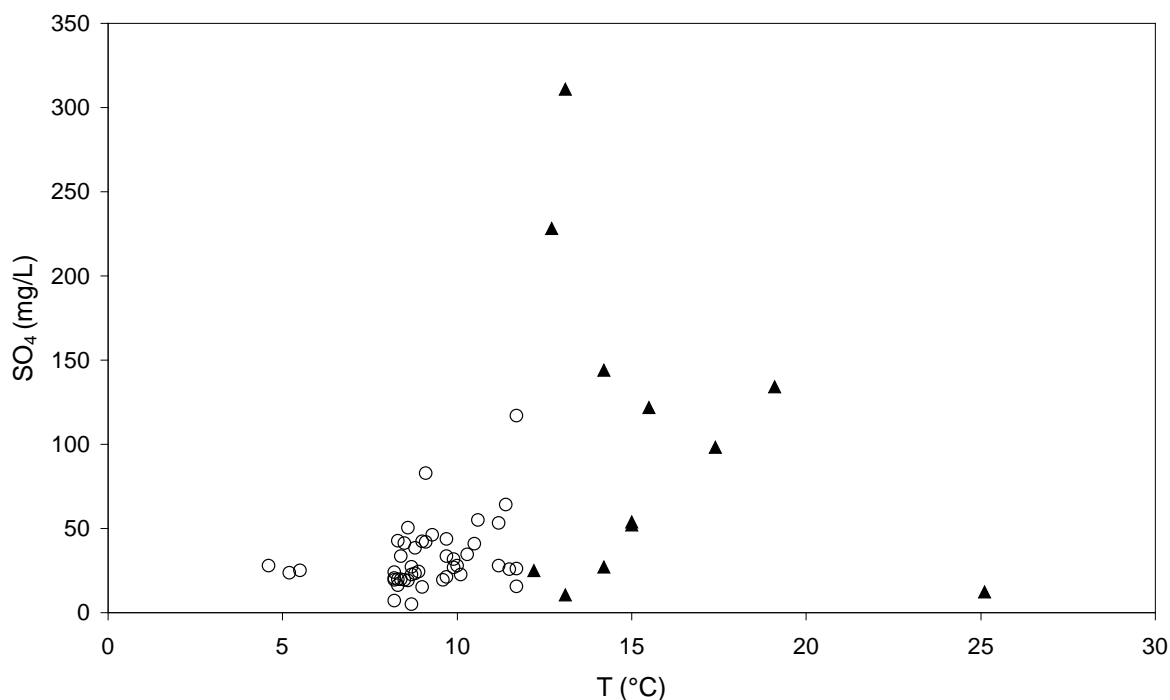
Figure 5.5   Relationship between dissolved sulphate and temperature (open circles=non-thermal groundwater, triangles=thermal/thermally influenced groundwater)

and δ^{18}O signatures of dissolved sulphate in these thermal groundwaters is very similar to that of Lower Carboniferous evaporate sulphate. Evaporite dissolution would also explain the high Cl levels observed in these thermal waters, which cannot be derived from barite dissolution and/or from other mineralised vein assemblages.

By contrast, concentrations of both SO_4 and Cl in the St Anne's Well (Buxton) sample are relatively low (12.2 mg L^{-1} and 37.9 mg L^{-1} respectively). These concentrations, together with observed $^{87}Sr/^{86}Sr$ ratios, suggest that the Buxton thermal waters are associated with a different thermal source which originates from deep sandstone aquifers. The waters rise via permeable zones in the limestone (Gunn et al., 2006). In parts of the (sandstone and/or limestone) aquifer, reducing conditions at depth may have led to reduction of SO_4 in the groundwater. The presence of H_2S in thermal waters of the area has been described previously by Short (in Stephens, 1929) who reported the occurrence of sulphur waters at Wirksworth [4289 3540] and Kedleston Park (north-east of Derby, [4312 3403]) which 'stink intolerably'. In the Buxton thermal waters, however, bacterial SO_4 reduction is unlikely to be important as indicated by the lack of enrichment in sulphate isotopic composition ($\delta^{34}S$ around +6 ‰ and $\delta^{18}O$ around +10 ‰) (Gunn et al., 2006).

Nitrate is present in most groundwaters (<0.05–12.6 mg L^{-1} as N) (Figure 5.6) and is probably derived from agricultural inputs. Concentrations are mostly low (median 3.06 mg L^{-1}) but are generally higher in the groundwaters on the Carboniferous Limestone outcrop than on the Millstone Grit (except for one very young groundwater) as fractures in the limestone provide pathways of rapid transport to the water tables. Concentrations are generally highest in oxic groundwaters (Eh >350mV)(Figure 5.6). Nitrate is also detectable in most thermal waters (except for St Anne's Well), indicating the presence of a component of recent recharge. Denitrification may have lowered NO_3-N concentrations in some groundwaters, as indicated in Figure 5.6 as well as by the negative skew in the cumulative-probability curve (Figure 5.3). These processes are particularly important in the groundwaters of the Millstone Grit (e.g. Dunlea, Shepherds Flatt) and/or in deeper (confined or thermal) sources (e.g. Shining Bank, Bradwell) where reducing conditions prevail (Figure 5.6).

At low redox, NH_4-N is the more stable N-species and concentrations in the reducing groundwaters reach up to 0.43 mg L^{-1} (Figure 5.6). Elevated NH_4-N concentrations in oxidising groundwaters were observed at two sites, Allenhill Spaw and Friden. The groundwater at Allenhill Spaw is also high in NO_2-N (an intermediate metastable N-species that is produced during denitrification) and other elements that are mobilised at low redox (Fe, Mn). This suggests that mixing with waters from more reducing groundwater environments has occurred at the sampling site. In contrast, the groundwater at Friden, has very high NO_3-N concentrations (12.6 mg L^{-1}). It contains a relatively high proportion of recent recharge, compared to other deep groundwaters (Table 5.3), and is probably affected by anthropogenic pollution.

Dissolved phosphorus concentrations are low (median 31.5 µg L^{-1}). The occurrence of phosphate could be due to anthropogenic inputs of fertilisers or other agricultural chemicals. However, concentrations are generally higher near the Carboniferous Limestone/ Millstone Grit interface and in the Millstone Grit groundwaters. This suggests instead that mineral sources may be important. Phosphate-rich limestones, for example, are present in the area around Castleton (Peacock and Taylor, 1966) and P is also likely to be enriched in the organic-rich Namurian Shales.
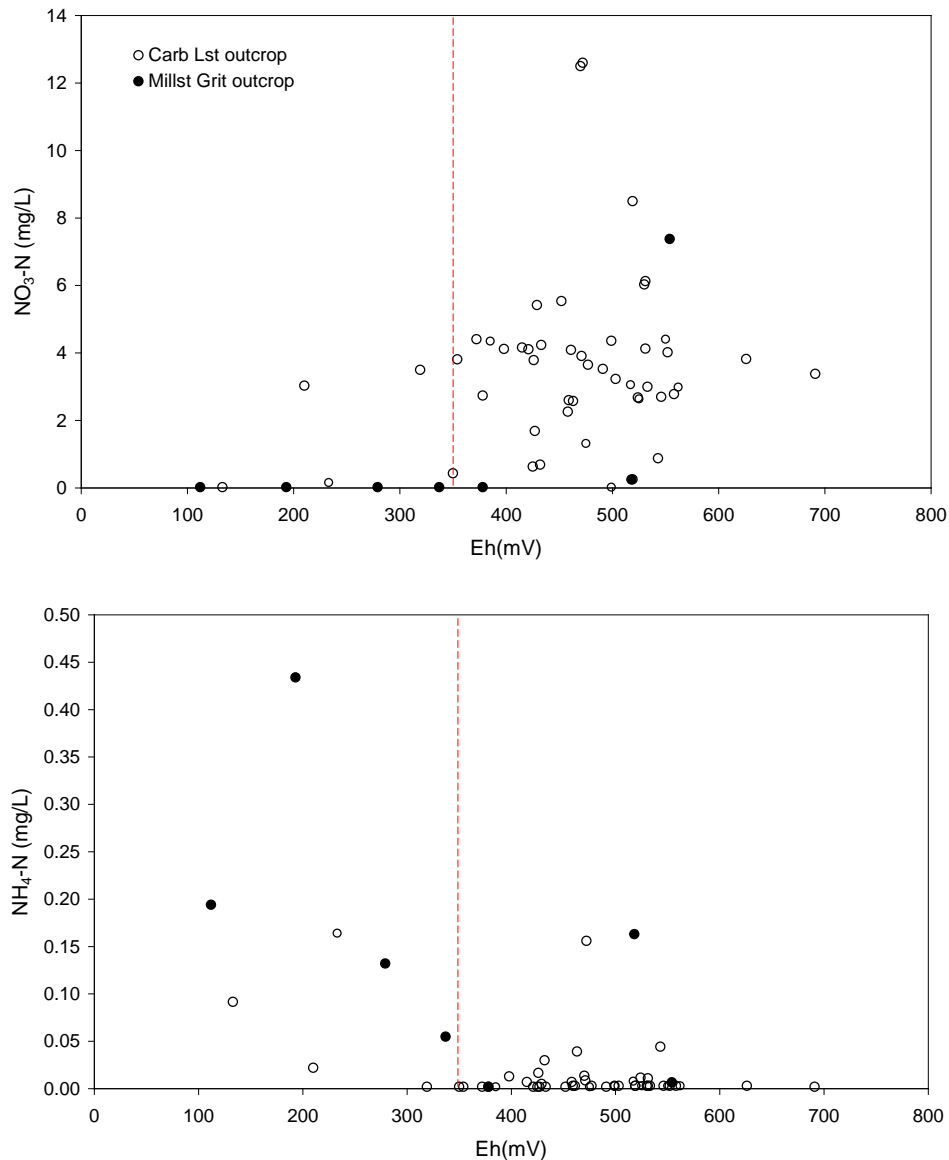
Figure 5.6   Relationship between redox (Eh), NO_3 and NH_4 in the groundwaters (open circles= Carboniferous Limestone + mixed gw, closed circles= Millstone Grit + confined gw, red line= Eh below which NO_3 is reduced to NH_4)

5.2   TRACE ELEMENTS

Summary data for trace elements are given in Table 5.2. There appears to be little systematic pattern in the distribution of most investigated trace metals, although Ni, Pb and Zn concentrations are generally highest in the groundwaters of the eastern, mineralised part of the Derbyshire Dome (Appendix 1, Plate 3). This corresponds with the main area of Pb-Zn mineralisation.

Lithium concentrations tend to be highest in the thermal waters and in groundwaters from the Millstone Grit (Appendix 1, Plate 2). Lithium shows a good correlation with other alkali metals (K, Rb, Cs). While higher concentrations in the thermal waters are likely to reflect the longer contact times of these groundwaters with the bedrock, there may also be a geological control, such as a more Li-rich composition of the Namurian Shales/ Millstone Grit Series.

26

However, this assumption needs further verification, in particular since it disagrees with findings from previous studies in the area which did not observe a relationship with lithology (Edmunds, 1971; Edmunds et al., 1989).
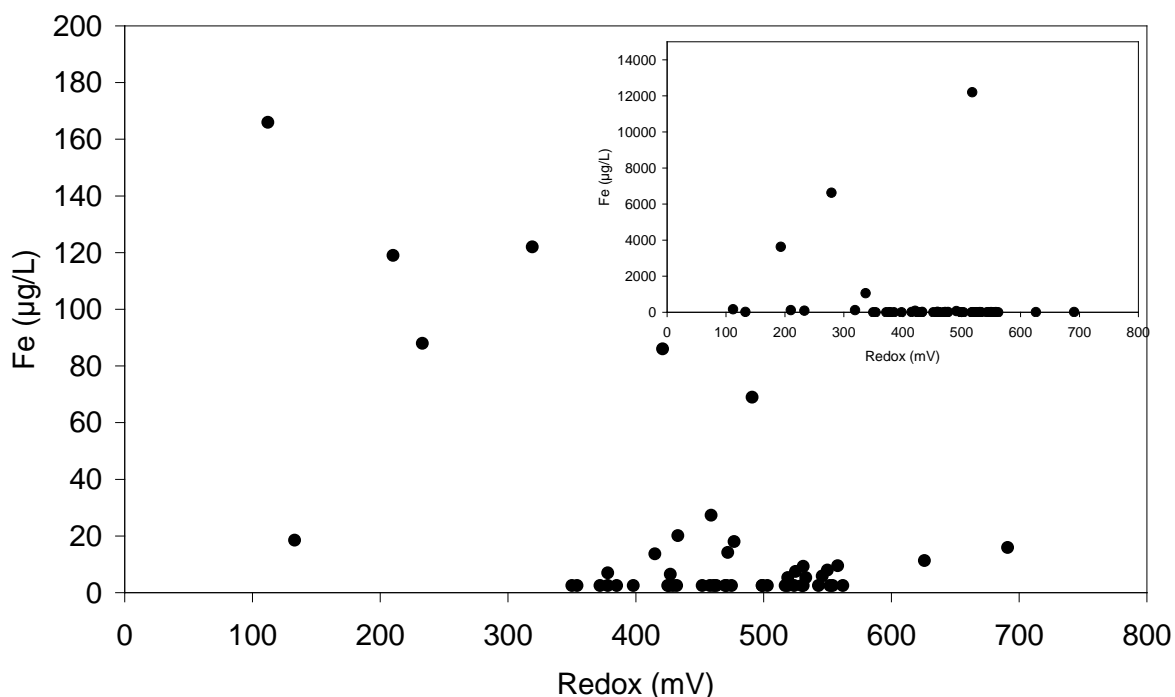
Figure 5.7 Relationship between Eh and Fe in the groundwaters of the Derbyshire Dome (main diagram shows only samples with Fe <200 $\mu g\,L^{-1}$)

Dissolved Fe concentrations are mostly low (median 5 $\mu g\,L^{-1}$) and strongly controlled by the redox conditions within the aquifer (Figure **5.7**). Reducing conditions with respect to Fe mainly occur in groundwaters from the Namurian Shales (Millstone Grit Series) but also in Carboniferous Limestone groundwaters which are confined by Namurian Shales (Appendix 1, Plate 3). These groundwaters also have the highest Fe concentrations, exceeding the EC drinking-water limit of 200 $\mu g\,L^{-1}$ (European Commission, 1998) at four of the sampled groundwater sites (concentrations up to 12 $mg\,L^{-1}$). Considering the intensive bedrock mineralisation and the recognised presence of pyritic horizons in the Namurian strata (Banks, 1997b), the very high concentrations of dissolved Fe are likely to be due to a combination of Fe hydroxide reduction and pyrite dissolution. The influence of differing processes on the groundwater composition is highlighted by the multimodal Fe distribution in Figure 5.8. Highest concentrations of dissolved Fe are observed at Allenhill Spaw (12 $mg\,L^{-1}$) which is the oldest spa feature in Matlock and is thought to be a mine sough driven into the Namurian Shales. The low pH and high SO_4 concentration (117 $mg\,L^{-1}$) of the groundwater suggest that Fe is derived from pyrite oxidation within the black shales (Banks, 1997a). Under natural conditions, pyrite oxidation is often incomplete, in particular in groundwater where oxygen supply is limited, resulting in solutions rich in dissolved ferrous Fe and SO_4 (Appelo and Postma, 2005). However, most of the other high-Fe groundwaters in the study area have near-neutral pH (due to carbonate buffering) and the Fe/SO_4 weight ratios of around 0.1 are smaller than would be expected for pyrite oxidation (ca. 0.3). Assuming that no additional SO_4 source is present, this suggests that dissolved Fe concentrations in these waters are diminished, probably by precipitation of iron oxides. Certainly, iron oxides have been observed along fractures in the shales/gritstones (Hyslop, 1993) and/or in the more oxidising environments of

the Carboniferous Limestone aquifer. At two sites, samples were collected from storage tank outlets and although residence time in the tanks was very short, it is possible that some Fe oxidation occurred during this period. This would imply that the actual concentrations within the aquifer at these sites are even higher than those reported here.
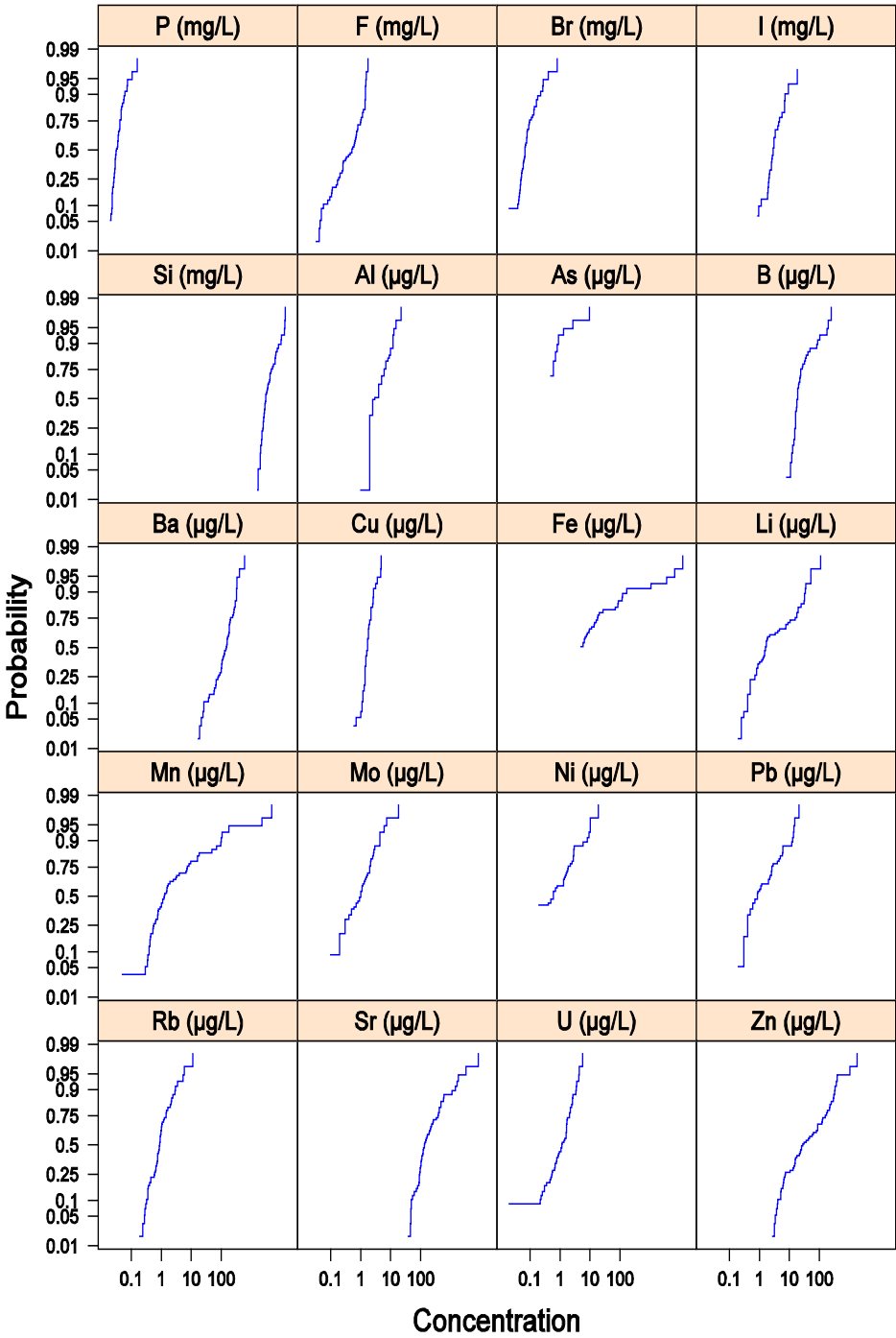
Figure 5.8   Cumulative-frequency distributions of minor and trace elements in the Derbyshire Dome groundwaters

Chalybeate groundwaters[3] are common in Derbyshire (Stephens, 1929), although their occurrence is limited to locations near the interface of the Carboniferous Limestone and the

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[3] Waters containing iron (usually in large quantities)

Millstone Grit and/or to the Millstone Grit itself. A (cold) chalybeate spring used to occur at Buxton (Stephens, 1929) and the high concentrations of Fe (23 mg L^{-1}) and SO_4 (158 mg L^{-1}) are believed to have arisen from a (probably pyritic) shale horizon at the Carboniferous Limestone/Millstone Grit interface (Stephens, 1929; Langham and Wells, 1986; Banks, 1997a). This hypothesis is supported by findings from Gunn et al. (2006). Based on sulphur-isotopic data for the nearby St Anne's Well, they concluded that part of the SO_4 in the spring was derived from sulphide oxidation.

Manganese is detectable in most of the groundwaters and, as with Fe, concentrations are controlled mainly by redox conditions and bedrock lithology. Concentrations tend to be higher in the groundwaters of the Millstone Grit and near the Carboniferous Limestone/ Millstone Grit interface (Appendix, Plate 3). At a few sites, concentrations exceed the EC drinking-water limit of 50 µg L^{-1} (European Commission, 1998). Some thermal waters are also enriched in Mn. Examples are Bradwell (99.5 µg L^{-1}) and St Anne's Well (48.6 µg L^{-1}). These may contain a component of Millstone Grit water. It is possible that the concentrations observed at the sampling point at St Anne's Well are somewhat lower than those actually present in the groundwaters due to precipitation of Mn oxide in the spring reservoir, as was reported by Thresh (in Stephens, 1929).

Figure 5.9   Elemental range of selected trace elements in the groundwaters of the Derbyshire Dome

Table 5.2 Statistical summary of trace elements in groundwaters from the Carboniferous Limestone

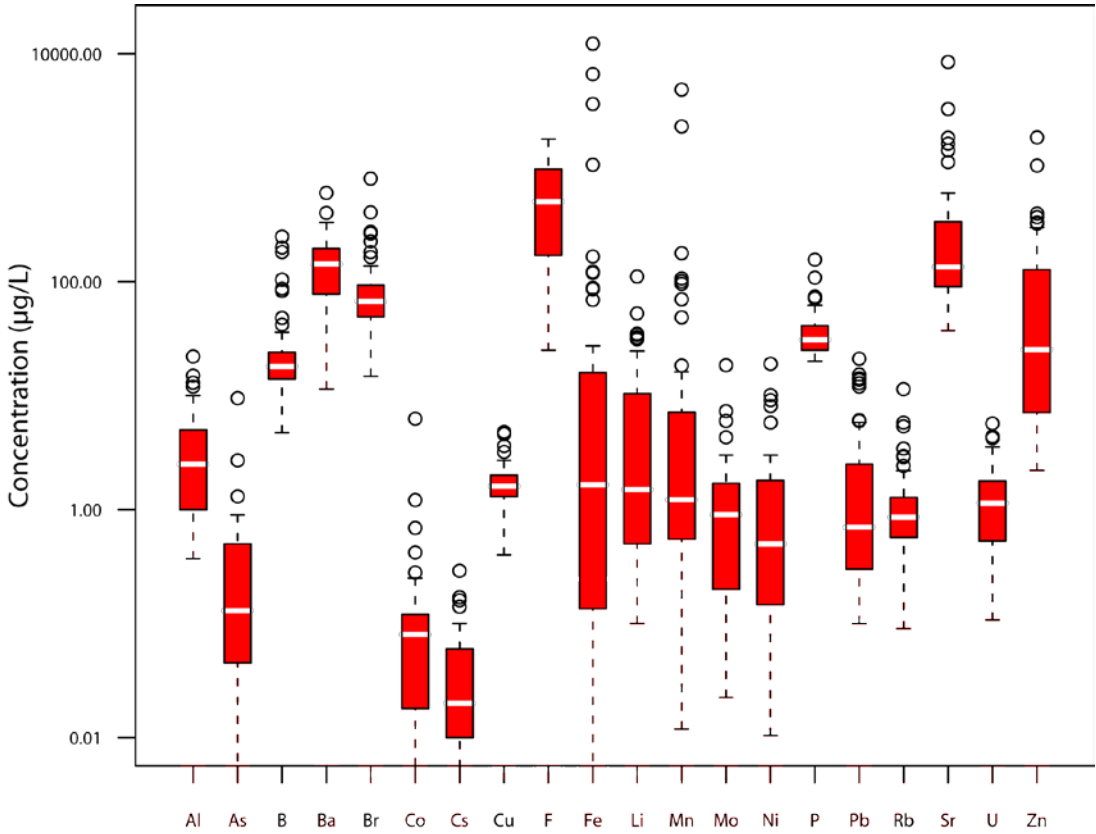| Element	Units	N	N (c)	min	mean	max	P0	P25	P50	P75	P90	P95	P100
Ag	µg L^{-1}	57	55	<0.05		0.14							
Al	µg L^{-1}	57	1	<1	4.1	22		1	2.5	5	10	13	
As	µg L^{-1}	57	40	<0.5	0.46	9.5	<0.5	<0.5	<0.5	0.5	0.74	0.98	9.5
Au	µg L^{-1}	57	54	<0.05		0.14							
B	µg L^{-1}	57	18	<20	32.4	248		15	18	23	83	182	
Ba	µg L^{-1}	57	0	11.4	158	600		77.5	142	195	321	331	
Be	µg L^{-1}	57	54	<0.05		0.07							
Bi	µg L^{-1}	57	57	<0.05		<0.05							
Cd	µg L^{-1}	57	10	<0.05	0.937	13.5		0.07	0.17	0.69	1.85	6.97	
Ce	µg L^{-1}	57	34	<0.01	0.009	0.06	<0.01	<0.01	<0.01	0.01	0.02	0.03	0.06
Co	µg L^{-1}	57	17	<0.02	0.219	6.25		0.08	0.12	0.25	0.69		
Cr	µg L^{-1}	57	34	<0.5	0.55	2.0	<0.5	<0.5	<0.5	0.7	1.2	1.4	2
Cs	µg L^{-1}	57	7	<0.01	0.044	0.29		0.01	0.02	0.06	0.1	0.16	
Cu	µg L^{-1}	57	0	0.4	1.7	4.8		1.3	1.6	2	2.6	3.6	
Dy	µg L^{-1}	57	53	<0.01		0.02							
Er	µg L^{-1}	57	53	<0.01		0.01							
Eu	µg L^{-1}	57	33	<0.01	0.014	0.13	<0.01	<0.01	<0.01	0.02	0.032	0.042	0.13
Fe	µg L^{-1}	57	29	<5	428	12200	<5	<5	<5	15.9	120.2	1570	12200
Ga	µg L^{-1}	57	55	<0.05		0.07							
Gd	µg L^{-1}	57	32	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	0.01	0.01	0.012	0.02
Ge	µg L^{-1}	57	50	<0.05		0.13							
Hf	µg L^{-1}	57	57	<0.02		<0.02							
Hg	µg L^{-1}	57	57	<0.1		<0.1							
Ho	µg L^{-1}	57	57	<0.01		<0.01							
In	µg L^{-1}	57	56	<0.01		0.01							
Ir	µg L^{-1}	57	57	<0.05		<0.05							
La	µg L^{-1}	57	24	<0.01	0.011	0.03			0.01	0.01	0.01	0.02	
Li	µg L^{-1}	57	0	0.1	9.7	111		0.5	1.5	10.4	32.4	34.8	
Lu	µg L^{-1}	57	57	<0.01		<0.01							
Mn	µg L^{-1}	57	2	<0.05	138	4840		0.55	1.22	7.15	95.4	178	
Mo	µg L^{-1}	57	5	<0.1	1.55	18.5		0.2	0.9	1.7	3	6	
Nb	µg L^{-1}	57	30	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.02
Nd	µg L^{-1}	57	20	<0.01	0.012	0.04			0.01	0.01	0.02	0.03	
Ni	µg L^{-1}	57	24	<0.2	1.85	19			0.5	1.8	5.8	9.1	
Os	µg L^{-1}	57	57	<0.05		<0.05							
Pb	µg L^{-1}	57	0	0.1	2.8	21		0.3	0.7	2.5	12	14	
Pd	µg L^{-1}	57	57	<0.2		<0.2							
Pr	µg L^{-1}	57	53	<0.01		0.01							
Pt	µg L^{-1}	57	57	<0.01		<0.01							
Rb	µg L^{-1}	57	0	0.09	1.33	11.4		0.57	0.86	1.28	2.89	5.38	
Re	µg L^{-1}	57	9	<0.01	0.025	0.16		0.01	0.01	0.03	0.05	0.08	
Rh	µg L^{-1}	57	46	<0.01		0.09							
Ru	µg L^{-1}	57	57	<0.05		<0.05							
Sb	µg L^{-1}	57	14	<0.05	0.096	0.5		0.025	0.06	0.12	0.22	0.35	
Sc	µg L^{-1}	57	17	<1	1.1	3		1	1	1	2		
Se	µg L^{-1}	57	3	<0.5	1.41	7.9		0.7	1.1	1.9	2.6	3.4	
Sm	µg L^{-1}	57	57	<0.02		<0.02							
Sn	µg L^{-1}	57	21	<0.05	0.085	0.17			0.08	0.11	0.12	0.14	
Sr	µg L^{-1}	57	0	37.1	469	8440		90.24	134.6	336.2	1118	1830	
Ta	µg L^{-1}	57	57	<0.02		<0.02							
Tb	µg L^{-1}	57	57	<0.01		<0.01							
Te	µg L^{-1}	57	57	<0.05		<0.05							
Th	µg L^{-1}	57	55	<0.05		0.23							
Ti	µg L^{-1}	57	57	<10		<10							
Tl	µg L^{-1}	57	17	<0.01	0.042	0.28			0.02	0.05	0.12	0.16	
Tm	µg L^{-1}	57	57	<0.01		<0.01							
U	µg L^{-1}	57	5	<0.02	1.41	5.68		0.53	1.14	1.78	3.4	4.23	
V	µg L^{-1}	57	13	<0.2	0.62	3.1		0.2	0.4	0.7	1.5	1.9	
W	µg L^{-1}	57	44	<0.02	<0.02	0.11	<0.02	<0.02	<0.02	<0.02	0.02	0.04	0.11
Y	µg L^{-1}	57	0	0.01	0.035	0.13		0.02	0.03	0.04	0.06	0.09	
Yb	µg L^{-1}	57	54	<0.01		0.02							
Zn	µg L^{-1}	57	0	2.2	130	1840		7.1	25.4	127	324	396	
Zr	µg L^{-1}	57	42	<0.02	<0.02	0.04	<0.02	<0.02	<0.02	0.02	0.02	0.03	0.04

Concentrations of As are generally low, being mostly <1 µg L^{-1} (Appendix 1, Plate 3), although concentrations up to 9.5 µg L^{-1} are observed. The sample with the highest concentration is from the western confined Carboniferous Limestone aquifer. The presence of dissolved As may be related to sulphide oxidation in pyritic horizons in the shales and/or in the mineralised bedrock or to the reduction of iron oxides. Anomalously high As concentrations were also observed in the stream sediments from this area (>30 mg kg^{-1}) which likely reflect the concentrations in the Namurian Shales (Nichol et al., 1970) and/or local bedrock mineralisation.

It is interesting to note that As was not detected in the groundwaters at Buxton (St Anne's Well) or at Stoney Middleton, which were previously found to have high As concentrations of 15 µg L^{-1} and 20 µg L^{-1} (as AsO_4^{3-}) (Edmunds, 1971). In the current survey, samples at both sites were not collected directly from the spring reservoirs, but from the public fountain (St Anne's Well) and from an outflow behind the Bath House (Stoney Middleton). It is therefore possible that precipitation of iron oxide in the spring reservoir itself and/or during passage to the sampling point has removed As from the water.

Molybdenum is present in detectable concentrations in the groundwaters of the mineralised eastern part of the Carboniferous Limestone outcrop but also occurs in considerable concentrations in some thermal water including that from St Anne's Well. The presence of Mo at St Anne's Well was previously reported by Thresh and Hart (in Stephens, 1929) and it was suggested that the elevated concentrations are derived from lead molybdate occurrences in Carboniferous Limestone cavities (Stephens, 1929). A similar source may be responsible for the anomalous concentrations at Topley Pike (18.5 µg L^{-1}), which were also observed in a previous study by Edmunds (1971). Molybdenum induces a Cu deficiency in many animal species (Wennig and Kirsch, 1988) and Mo anomalies in stream sediments in Derbyshire have been linked to the occurrence of hypocupremia (abnormally low levels of blood copper) in cattle (Thornton et al., 1972). Molybdenum shows a good correlation with U. This is probably due to the similar behaviour of these two elements (formation of oxyanion, complexation) but could also indicate a common source. The high Mo concentrations in the groundwaters at Dunlea (7.3 µg L^{-1}) are associated with high concentrations of As, Cu, Fe and Ni concentrations and stream-sediment studies in this area suggest that concentrations of these elements are also high in the Namurian Shales (Nichol et al., 1970). They are likely to be related to the local mineralisation in the area around Mixon.
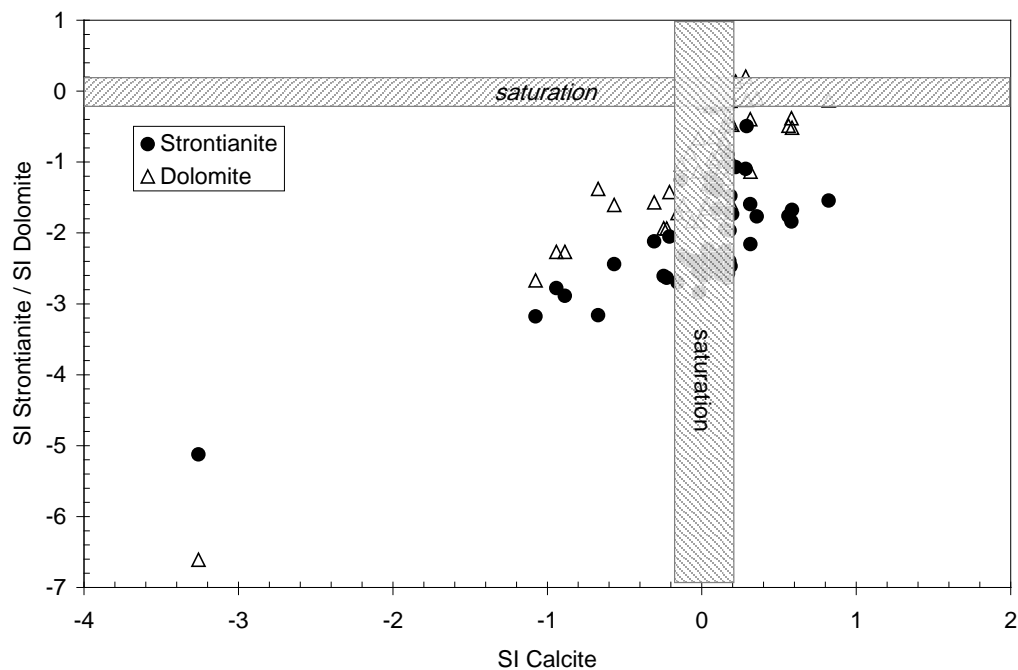
Figure 5.10   Comparison between calcite saturation and strontianite/dolomite saturation in the groundwaters of the Derbyshire Dome

Strontium concentrations in the Derbyshire Dome groundwaters range between 37.1 and 8440 $\mu g\,L^{-1}$ and are highest in the thermal groundwaters. Non-thermal groundwaters have relatively constant Sr/Ca ratios (Figure 5.4) suggesting that Sr is mostly derived from congruent dissolution of calcite. The Sr/Ca ratio is considerably higher in the thermal waters. This reflects the longer residence times of these groundwaters and the increased interactions between the groundwater and the bedrock material. Recurring carbonate dissolution-precipitation reactions concentrate Sr in the aqueous phase (incongruent dissolution) as calcite saturation (and precipitation) is achieved more rapidly than saturation with respect to Sr (and Mg) minerals. Most waters are undersaturated with respect to strontianite (and dolomite) while saturated with respect to calcite (Figure 5.10).

In addition to the distinct enrichment in the thermal waters, there is also a clear difference in Sr concentration in the groundwaters from the non-mineralised western part and the mineralised eastern part of the Derbyshire Dome (Appendix 1, Plate 2). Strontium occurs naturally as a minor constituent of barite, and Edmunds (1971) suggested that barite gangue minerals may constitute a Sr source in the mineralised zone (although barite solubility is low and no clear relationship was found between Ba and Sr). Enrichment in Sr in the mineralised areas may be enhanced by the increased contact of the groundwater with mineral veins which is amplified by the artificial drainage. Alternatively, mixing with uprising, deeper thermal waters induced by falling heads due to mine pumping has been suggested to contribute to elevated Sr concentrations in mine waters (Gunn et al., 2006).

The distribution of fluoride in the groundwater of the Derbyshire Dome reflects a clear lithological control. Concentrations in the groundwater are comparatively low (median 0.51 mg L^{-1}) but increase to >1 mg L^{-1} along the eastern edge of the Carboniferous Limestone outcrop, corresponding approximately with the occurrence of fluorite mineralisation (Appendix, Plate 2). The relatively high concentrations in the thermal waters, (Bradwell: 1.8 mg L^{-1}, Stoke Sough: 1.5 mg L^{-1} and Holywell at Bakewell: 1.4 mg L^{-1}) suggest that long residence times and/or increased temperatures have promoted the F accumulation in these

groundwaters. Fluorite solubility appears to be of minor importance in determining/limiting F concentrations in the groundwaters as is indicated by the consistent undersaturation with respect to CaF_2. The absence of a CaF_2 solubility control is also reflected in the log-normal frequency distributions of F concentrations (Figure 5.8) and their poor correlation with Ca (Figure 5.11).
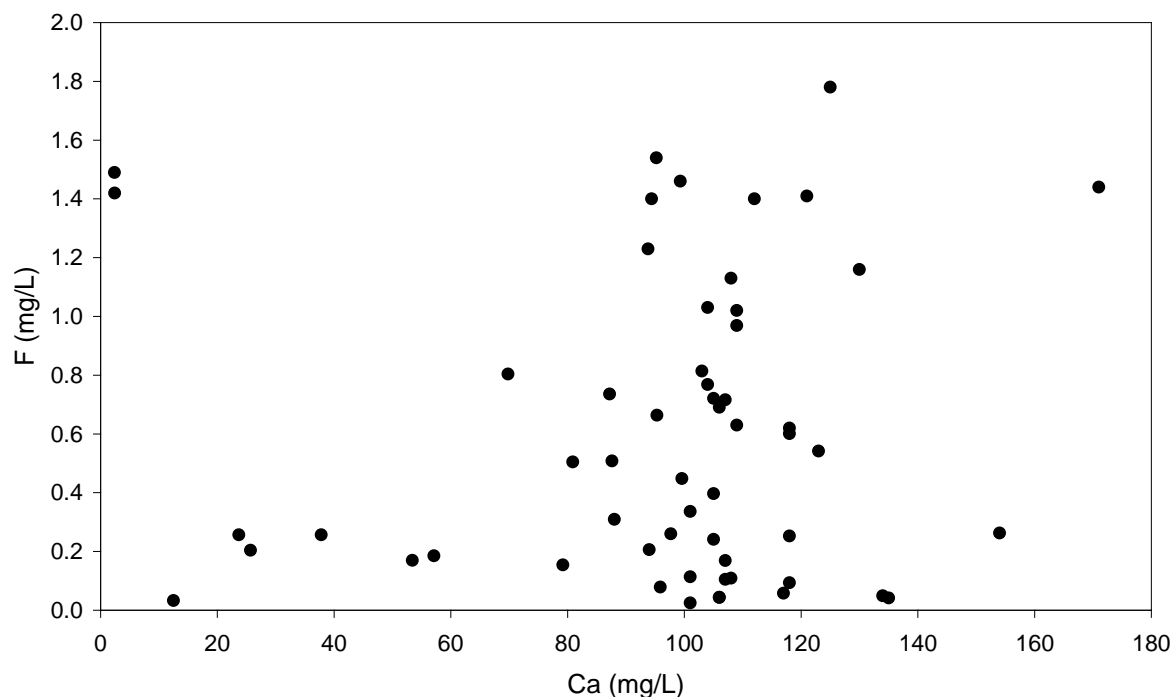

Figure 5.11   Relationship between calcium and fluoride in the groundwaters of the Derbyshire Dome

Westwards of this zone, high-Ba groundwaters occur (Appendix 1, Plate 2), probably related to the barite gangue mineralisation. However, elevated Ba levels are also observed in the groundwaters near Buxton, in particular along the Wye Valley. These are probably related to local bedrock mineralisation and hydrothermal mineral veins (rakes) that occur in the area (Ford, 1968b). The Ba concentrations in the groundwater are strongly controlled by SO_4 concentrations (Figure 5.12) and limited by barite solubility; most of the groundwaters are saturated with respect to barite. Where SO_4 concentrations are low ($<50\ mg\ L^{-1}$), Ba concentrations can be in excess of the EC drinking-water limit for Ba of $100\ \mu g\ L^{-1}$ (Figure 5.12).

Uranium concentrations range between 0.01 and $5.68\ \mu g\ L^{-1}$. The median concentration ($1.14\ \mu g\ L^{-1}$) is slightly higher than that in groundwater from other British aquifers of similar lithology (Smedley et al., 2006). The median concentration in groundwater from samples in the Carboniferous Limestone of North Yorkshire was $0.31\ \mu g\ L^{-1}$ (Abesser et al., 2005b) while that in groundwater from the Mendip Hills was $0.86\ \mu g\ L^{-1}$ (Bonotto and Andrews, 2000). Uranium concentrations are commonly higher in groundwaters from the eastern mineralised part of the outcropping Carboniferous Limestone (Appendix, Plate 3) and are mostly associated with drainage from mines and soughs and/or with thermal waters. High U concentrations are also observed in the thermal groundwaters on the western edge of the outcrop, at Beresford Springs and at St Anne's Well. The latter has long been recognised as

being somewhat radioactive (Stephens, 1929), containing 0.034 Bq L^{-1} radium, 77 Bq L^{-1} radon and 2.78 µg L^{-1} uranium (Andrews, 1991 in Banks, 1997a). The source of U in the Derbyshire groundwater is uncertain but most is likely associated with bedrock mineralisation and/or the Namurian Shales of the Millstone Grit Series (Abesser and Smedley, 2006). Agricultural applications of U-rich phosphate fertiliser may also contribute some U to the groundwater, although these anthropogenic inputs are probably insignificant compared to the geological sources.

Selenium is present in most groundwaters of the study area. Edmunds (1971) found that Se was highest in hybrid waters[4], implying a Se source in the Millstone Grit. In this study, however, Se is low (<1 µg L^{-1}) in most Millstone Grit and hybrid groundwaters. High Se concentrations are present in the groundwaters at Hassop Spring: 7.3 µg L^{-1}, Stoney Middleton: 3.4 µg L^{-1}, Stoke Sough: 2.6 µg L^{-1}, Bradwell: 4.1 µg L^{-1} and Topley Pike (3 µg L^{-1}) and appear to be associated with bedrock mineralisation, e.g., the presence of lead and copper sulfidic ores (Committee on Medical and Biological Effects on Environmental
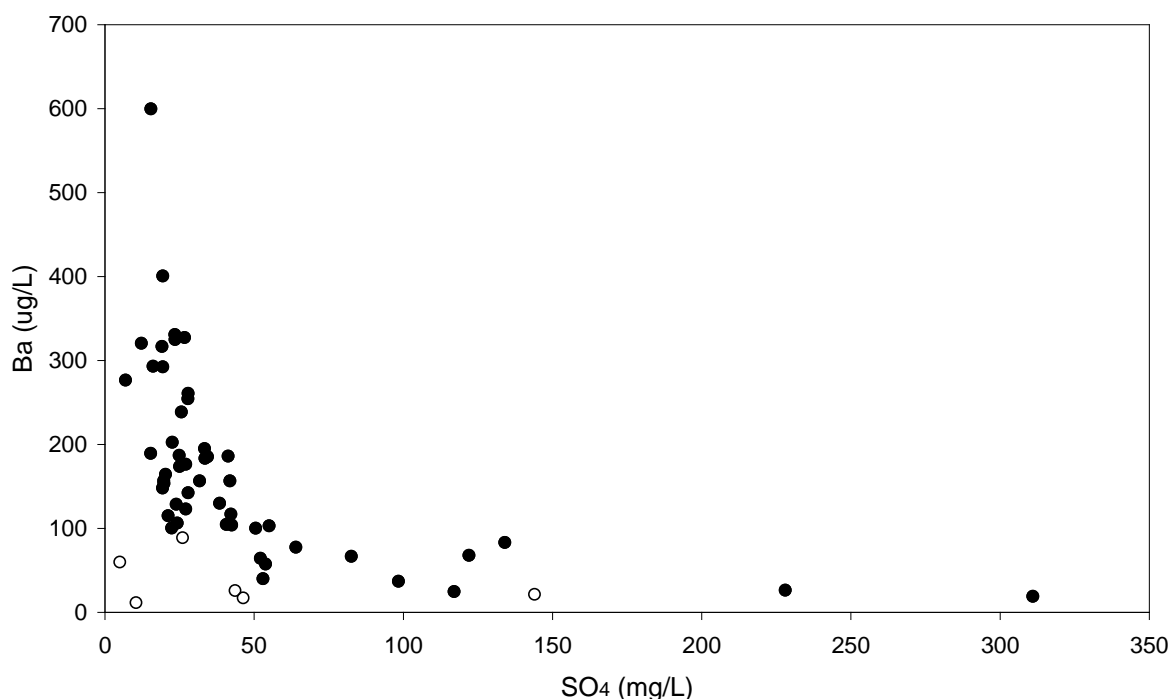

Figure 5.12 Relationship between sulphate and barium in the groundwaters of the Derbyshire Dome (open circles=unsaturated /closed circles =saturated with respect to barite)

Pollutants, 1976), rather than with the Namurian Shales. Selenium is redox-sensitive and concentrations in the groundwater also depend on the pH (Basu et al., 2007). The mobility of Se in groundwater systems is lowest under reducing conditions due to the rapid reduction of selenate (Se(VI)) to less soluble selenite (Se(IV)) and/or insoluble elemental selenium (Se(0)). In acidic waters and in the presence of Fe, Se mobility is further reduced as Se(IV) is strongly adsorbed onto ferric oxides and also forms insoluble ferric selenite or iron serenide (Committee on Medical and Biological Effects on Environmental Pollutants, 1976). The relationships between Se and Fe as well as pH are illustrated in Figure 5.13 and Figure 5.14.

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[4] Hybrid water = mixed groundwaters from the Carboniferous Limestone aquifer and the Millstone Grit aquifer

The plots show that at Fe>30 $\mu g\,L^{-1}$ and pH<7, Se concentrations remain low (<2 $\mu g\,L^{-1}$). This reflects the increased adsorption of Se(VI) onto Fe oxides, although the inverse relation to Fe is also related to Eh. At pH>7, Se mobility increases due to diminished adsorption to Fe oxides and Se accumulates in the groundwater, e.g., at Hassop Spring (Se: 7.3 $\mu g\,L^{-1}$, pH 7.8, Fe<0.5 $\mu g\,L^{-1}$).
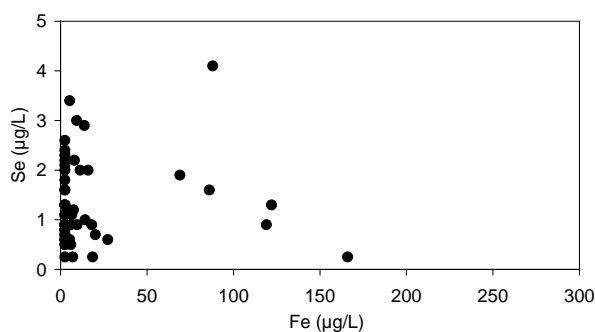

Figure 5.13   Inverse relationship between Fe and Se concentrations
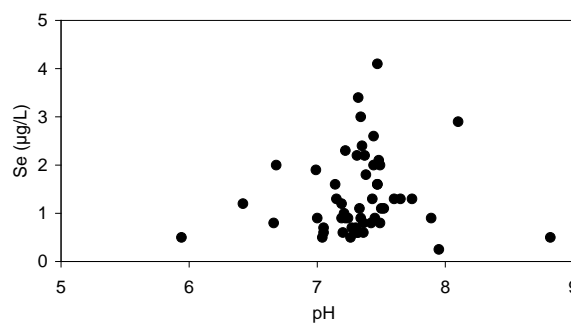
Figure 5.14   Positive relationship between pH and Se concentrations

5.3   ISOTOPIC COMPOSITIONS AND TRACERS

5.3.1   Isotopes

The carbon isotope ^{13}C, in conjunction with groundwater chemical data, can help to characterise chemical reactions, evolution and groundwater residence time. Groundwater from the Carboniferous Limestone is often enriched in ^{13}C as a result of marine calcite dissolution. In the groundwaters of the Derbyshire Dome, $\delta^{13}C$ compositions range between –19.4 ‰ and -10.1 ‰. The more depleted $\delta^{13}C$ signatures (-17.0 ‰ or less; from Shothouse Spring, Blackmill Well, Brighside Sough (Calver) and Snitterton Sough) suggest relatively short groundwater residence times, although at Snitterton Sough the depleted signature is partly due to mixing with groundwaters from non-carbonate Millstone Grit.

In contrast, the enriched $\delta^{13}C$ composition of the Bradwell thermal water (–10.1 ‰) indicates more significant carbonate reaction, which was also inferred from the high Sr/Ca ratios. Similar enrichment in $\delta^{13}C$ is found in other thermal groundwaters, for example at St Anne's Well (around –9 ‰, unpublished BGS data, Evans et al., 1979; Gunn et al., 2006), Stoney Middleton (–8.1 ‰, Gunn et al., 2006), Stoke Sough (–9.0 ‰, Gunn et al., 2006) and Matlock (–10 ‰ to –12 ‰, Gunn et al., 2006). For the Stoke Sough and Matlock locations, the $\delta^{13}C$ signatures obtained in this study are somewhat less enriched than those quoted by Gunn et al. (2006). However, the samples were collected at slightly different locations. Furthermore, data presented by Gunn et al. (2006) represent an annual (volume-weighted) average compared to point samples used in this study. Although many of the thermal waters have enriched $\delta^{13}C$ compositions, that from a sample taken at the thermal Bradwell springs (–15.8 ‰) is distinctly more depleted. This suggests that mixing with more recent recharge (sources dominated by soil CO_2) and/or with Millstone Grit groundwater must have occurred at this site.

The slightly enriched $\delta^{13}C$ value of –14.3 ‰ in a sample from Shining Bank Quarry with associated high pH (8.8–9.2) indicates that closed-system conditions prevailed during much of the groundwater evolution in this part of the aquifer. The $\delta^{13}C$ signature also suggests the presence of an older (long-residence-time) groundwater component. However, the composition may have been depleted by silicate hydrolysis which contributes soil gas CO_2 ($\delta^{13}C$ = –25‰) to the groundwater DIC pool. Nonetheless, silicate weathering is generally slow and the actual contribution of this source of CO_2 to the groundwater carbon inventory is probably small (Mook, 2006). An intermediate value of –13.6 ‰ is observed in the groundwater at Brookfield Hall.
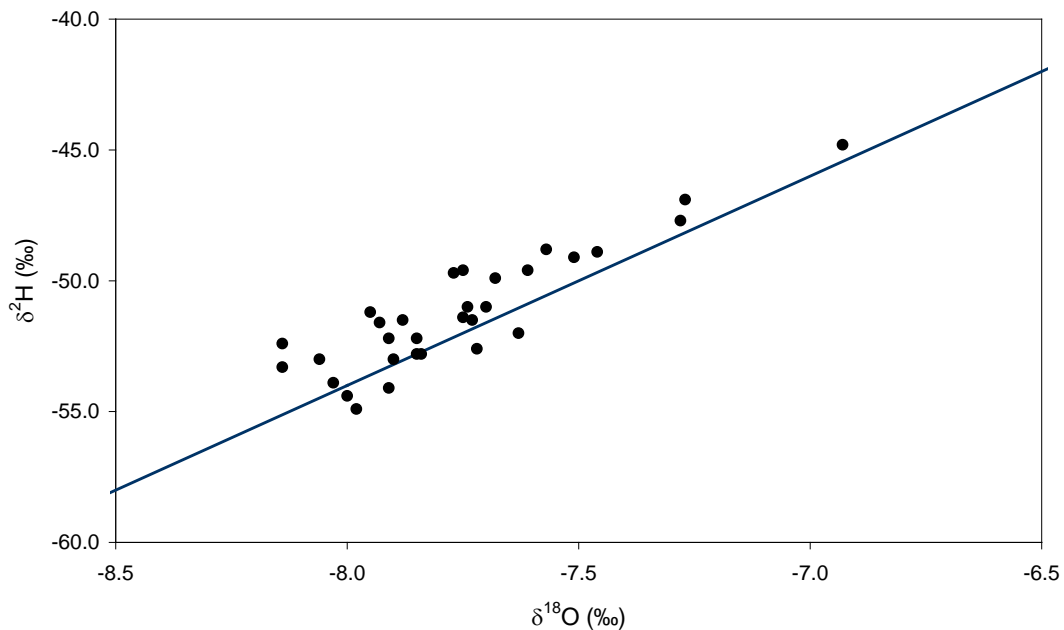

Figure 5.15   O and H stable-isotopic composition of the groundwaters of the Derbyshire Dome (World Meteoric Line calculated as $\delta^2H=8\delta^{18}O+10‰$; (Craig, 1961))

Observed O and H stable-isotopic compositions lie in the range -8.1 ‰ to -6.9 ‰ for $\delta^{18}O$ and -44.8 ‰ to -54.9 ‰ for δ^2H. These values are consistent with compositions of 'recent' groundwaters (0–10 ka) analysed in the Derbyshire area (Darling et al., 2003). A plot of $\delta^{18}O$ against δ^2H (Figure 5.15) shows that all groundwaters lie on the World Meteoric Line and the values are also in reasonable agreement with those for the average yearly rainfall in the area (Darling and Talbot, 2003). This suggests that no significant isotopic exchange with the carbonate bedrock has occurred (even in the thermal waters) and that the O and H isotopic signatures have undergone little or no alteration during passage of the groundwater through the aquifer.

5.3.2   Tracers

Results for analysis of CFC and SF_6 on selected groundwaters are given in Table 5.3 for the two models that are commonly used for interpreting such data. The mixing model assumes mixing of waters of different ages within the aquifer and estimates the proportion of modern recharge in each sample based on its CFC content. The piston flow model assumes that the concentration of CFC's was not altered by transport processes from the point of entry to the

36

measurement point in the aquifer and estimates the 'apparent' groundwater age or year of recharge by comparing the observed concentrations in the water with atmospheric mixing ratios of the past 50 or so years.

The data in Table 5.3 indicate that the groundwater at Shining Bank is contaminated with SF_6 and CFC-12. The CFC-11 dates suggest a relatively old groundwater component with less than 3% modern[5] recharge. However, concentrations may be affected by the reducing conditions in the groundwater which favour microbial degradation of CFC-11. CFC-12 and SF_6 are generally less affected by microbial degradation (Plummer and Busenberg, 1999; Busenberg and Plummer, 2000). CFC degradation is usually not detected in groundwater until conditions in an aquifer are sufficiently reducing to achieve SO_4 reduction (Plummer and Busenberg, 1999), although the process may begin when denitrification is complete (Semprini et al., 1992). Denitrification is likely to take place in the Shining Bank groundwater as indicated by the low NO_3 concentrations and by the presence of NO_2; SO_4 reduction is not likely to be important as the SO_4 concentration is 46 mg L^{-1}. The presence of long-residence time groundwater at Shining Bank has been confirmed by the relatively enriched $\delta^{13}C$ signature. However, a small modern component must also be present, as indicated by the observed SF_6 and CFC-12 contamination.

Table 5.3   Results of CFC and SF_6 analysis on selected groundwaters (c=contaminated)

	Mixing model % modern		Piston flow Year of recharge		
	CFC-11	CFC-12	CFC-11	CFC-12	SF_6
Meerbrook Sough	58.7	c	1978	c	2003
Friden Brickworks	51.0	34.4	1976	1973	1970
Shining Bank Quarry	2.7	c	1958	c	c
Brookfield Hall	0.4	0.7	1951	1947	<1970

Using the piston flow model, the three tracers show good agreement in piston-flow age for the groundwater samples from Friden and Brookfield Hall, giving 'apparent'[6] groundwater ages of around 30 years and 55 years, respectively.

At Meerbrook Sough, the groundwater is known to consist of a mix of waters of different ages and provenances (Shepley, 2007). This implies that the piston flow model does not apply, hence the mixing model is used for interpreting the SF_6 and CFC data. The CFC-11 signature suggests that 59 % of the groundwater originates from modern recharge, although

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[5] 'modern' refers to waters that were recharged during the last 60 years.

[6] The term 'apparent' is used to indicate that CFC-based groundwater ages are not necessarily equal to the transit time of water in the aquifer as transport and/or chemical processes that have affected CFC concentrations in the water are not accounted for when calculating the 'apparent' age.

this proportion is likely to be higher as degradation of CFC-11 may have occurred in the more reducing environments of flooded mines. A higher proportion of modern groundwater in the Meerbrook Sough discharge is also indicated by the findings from Steele (1995) (as quoted by Shepley 2007) who estimated that only 5% of the Meerbrook Sough groundwater are of hydrothermal (i.e., old) origin.

5.4   CHEMICAL VARIATIONS WITH DEPTH

At the time of writing, no data could be found on groundwater chemical variations with depth.

5.5   TEMPORAL VARIATIONS

Likewise, only limited data are available on chemical variations with time. Data from a survey undertaken in 1967/68 by Edmunds (1971) are plotted against those from this study for selected sites and parameters in Figure 5.16. The data do not show significant changes in the general chemical composition of the groundwater between 1967/68 and 2005/06, although concentrations of NO_3-N appear to have increased by a factor of two (or more) at all but two sites. This is probably due to increased inputs from agricultural sources. An overall increase in groundwater NO_3 between 1967/68 and 2005/06 is also suggested by the summary statistics, which show an increase in NO_3-N range and median concentration between the two surveys. In 1967/68, NO_3-N range and median concentration were <0.02–3.1 mg L^{-1} and 0.40 mg L^{-1} (35 samples) compared to <0.05–12.6 mg L^{-1} and 3.06 mg L^{-1} (57 samples) in the more recent survey. Overall phosphorus concentrations in the groundwater remained fairly constant ranging between 0.02–0.2 mg L^{-1} (median=0.04 mg L^{-1}) in 1967/68 and between <0.02–0.16 mg L^{-1} (median=0.03 mg L^{-1}). Site-to-site comparison shows a reduction in P at almost all sites, most obvious being the 10-fold decrease at the Matlock Bath Fountain.

Some variations are observed in temperature and pH and this is not surprising considering the dynamic nature of these parameters. Variations in these parameters are less obvious in the thermal groundwaters (e.g. at Holywell, Matlock Bath, Beresford Dale Springs, St Anne's Well); differences in pH and temperature in these are <0.05 and <0.7ºC, respectively. It needs to be stressed that data in Figure 5.16 represent a comparison of only two sets of samples. Much more frequent monitoring is required to establish whether significant temporal trends in groundwater composition exist.

More comprehensive information on the temporal variability in groundwater composition is available from a detailed study at Rockhead Spring (Gunn et al., 2002). The study was carried out over two two-year periods, i.e. 1977–1979 and 1986–1988, and the results indicate that the hydrogeochemistry of the spring is remarkably stable. It was concluded that the observed variations can be attributed to random error and do not imply changes in the geochemical composition of the groundwater (Gunn et al., 2002).
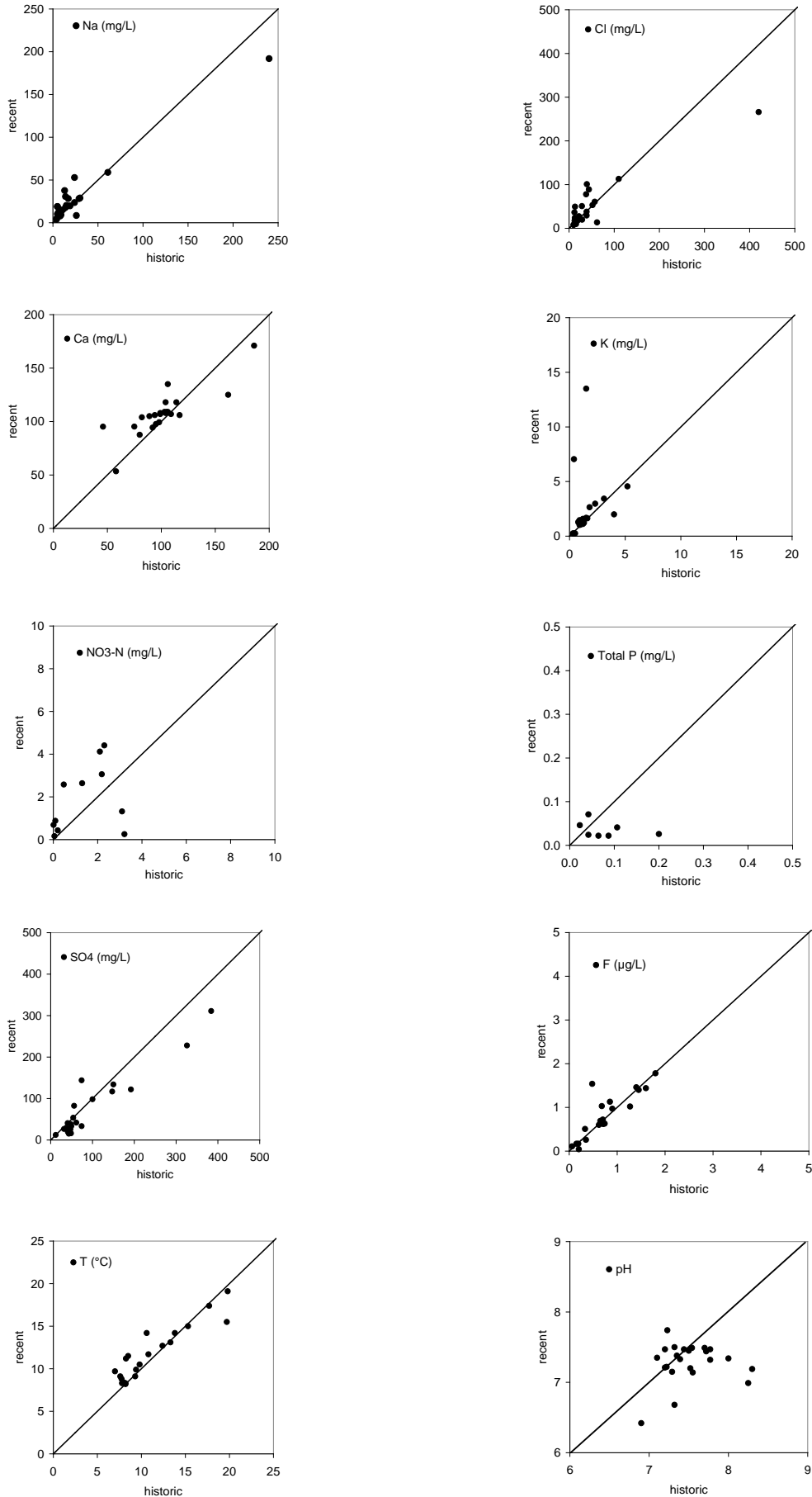
Figure 5.16   Comparison of selected water-chemistry parameters from historic (1968) and recent (2005–2006) water-quality surveys (solid line = unity, gradient 1)

39

6 Baseline groundwater chemistry

6.1 EXTENT OF ANTHROPOGENIC INFLUENCES

The concentrations of most elements in the groundwater of the study area are controlled by natural processes associated with water-rock interactions and related to solubility-controlled dissolution and precipitation of minerals or redox-controlled processes. However, there are a number of elements that are influenced by anthropogenic activities. These influences are most obvious for NO_3-N which shows a distinct bi-modal distribution. While the median concentration of 3 mg L^{-1} NO_3-N is near that expected for pristine conditions (1–3 mg L^{-1}), higher concentrations (> 5 mg L^{-1}) occur in the southern part of the Carboniferous Limestone outcrop, as well as in parts of the north, suggesting that pollution, probably of agricultural origin, has affected the baseline conditions of the groundwater. Where reducing conditions occur, as in the Namurian Shales, groundwater NO_3-N concentrations are low and denitrification may have been a factor in controlling the concentrations.

Other pollution incidents associated with agricultural activities have been reported in the groundwaters around Castleton, in the north of the limestone outcrop (Gunn et al., 2000). Here, the general deterioration of cave water quality resulting from agricultural activities has been inferred from the presence of faecal coliforms and faecal streptococci in sinking streams (Hunter et al., 1999) and in groundwater springs (Gunn et al., 1998).

Inputs from U-rich phosphate fertilizers were previously suggested to have contributed to elevated concentrations of groundwater U and PO_4 in this part of the study area (Abesser and Smedley, 2006), although a U isotope study did not provide evidence to support this hypothesis (Abesser, unpublished data). Bottrell (1996) and Bottrell et al. (2000) concluded from carbon and sulphur-isotopic data that natural processes (e.g., water-rock interactions) dominate the composition of groundwaters and cave sediments in the Castleton area while agricultural inputs are of minor importance.

It is likely that other anthropogenic activities, such as mining, have indirectly contributed to the elevated trace-metal concentrations in the mine drainage groundwaters by creating larger cavities and rock debris and hence providing artificially high surface areas for enhanced bedrock weathering and oxidation. Such inputs are corroborated by the non-linearity of cumulative-probability plots for a number of the trace elements. However, considering that most of the groundwaters were collected from mine adits and shafts, their quality is surprisingly good and today, some of these former mining structures even serve as sources for public water supply (e.g. Meerbrook Sough, Ladyflatte Mine). Possible reasons why toxic metals are not present in excessive concentrations in these groundwaters are discussed in Banks (1997a) and Abesser and Smedley (2006). Most relevant in the context of 'baseline' are the following considerations:

- the solubility of the metals being limited by the high alkalinity and pH of the waters as well as by mineral solubility controls (e.g., fluorite, barite);

- groundwater flow through the mine conduits being fast relative to the slow rate of sulphide oxidation (hence groundwater residence times may be too short to build up high metal concentrations);

- the hydraulic equilibrium in the aquifer being long-established with limited water-table fluctuations, it is possible that most of the metals have been removed from the aquifer by prolonged weathering under oxidising conditions, in particular in the zone

of active groundwater flow. However, in stagnant groundwater zones, oxygen flux may be limited, thereby limiting processes of sulphide oxidation.

The mining activities, in particular the driving of adits (soughs), have also altered the hydrodynamics of the aquifer by lowering the groundwater head. Gunn et al. (2006) concluded that this has caused the upconing of deeper, thermal groundwater in the Matlock area resulting in the discharge of Matlock-type thermal water from mine adits, such as the Meerbrook Sough. It is not possible to establish to what degree this has affected the overall baseline composition of the groundwater in the study area.

6.2   REGIONAL BASELINE CHARACTERISTICS

For many solutes, the 'baseline' concentrations of groundwaters in the study region embrace a wide range. This reflects the varying sources and pathways (residence times) of the groundwaters and illustrates the effect of different bedrock lithologies (limestone, shales, gritstone) as well as the extensive bedrock mineralisation on their chemical composition.

Groundwater baseline concentrations have been defined using the 95th percentile (P_{95}) value, which, although somewhat arbitrary, approximates an upper limit to the range of natural baseline concentrations for many elements (Section 4.3). For some elements, associated with bedrock mineralisation, it is a not certain whether the upper limit actually represents baseline composition, as mining activities may have enhanced their concentrations in the groundwater by artificially enhancing natural processes of bedrock weathering and oxidation (Section 6.1).

Bedrock lithology and mineralisation are the dominant controls on groundwater composition. They are responsible for the wide concentration ranges and the high upper baseline limits (taken as the 95th percentile (P_{95}), Section 4.3) in F (25–1780 $\mu g\ L^{-1}$, P_{95}=1490 $\mu g\ L^{-1}$), Ba (11.4–600 $\mu g\ L^{-1}$, P_{95}= 331 $\mu g\ L^{-1}$) and Zn (2.2–1840 $\mu g\ L^{-1}$, P_{95}=396 $\mu g\ L^{-1}$). Mineralisation has also affected the concentrations of other trace elements in the groundwater including Cd (<0.05–13.5 $\mu g\ L^{-1}$, P_{95}=6.97 $\mu g\ l^{-1}$), Ni (<0.2–19 $\mu g\ L^{-1}$, P_{95}=9.1 $\mu g\ L^{-1}$) and Pb (0.1–21 $\mu g\ L^{-1}$, P_{95}=14 $\mu g\ L^{-1}$). In fact, the occurrence of metal-enriched groundwaters mirrors the distribution of bedrock mineralisation in the study area. The mineralisation is concentrated along the eastern flank of the Derbyshire Dome, although minor occurrences of bedrock mineralisation are present throughout the study area.

The occurrence of thermal groundwaters, containing varying proportions of long-residence-time groundwater, also has a strong influence on the baseline concentrations of the study area. Thermal waters are enriched in most elements, compared to the (non-mineralised) limestone waters, but in particular in Sr, Cl and SO_4. These waters contribute to the naturally high baseline ranges (min-P_{95}) of 37–1830$\mu g\ L^{-1}$ (Sr), 7–106 mg L^{-1} (Cl) and 5–144 mg L^{-1} (SO_4), respectively. The source of sulphate in the thermal waters is still debated. Early studies concluded that SO_4 originated from pyrite (sulphide) oxidation and/or barite dissolution (Edmunds, 1971, Downing, 1967). Recent findings by Gunn et al. (2006) from a S-isotope study concluded that dissolution of evaporites at depth within the Limestone provides most of the SO_4 present in the thermal waters, in particular in the eastern part of the Derbyshire Dome. A different source, however, namely pyrite dissolution, was identified for SO_4 in the thermal water at St Anne's Well (Buxton), leading to the conclusion that most of the thermal water at Buxton is derived from the Millstone Grit Series (underlying the Goyt Syncline) rather than from the Carboniferous Limestone itself. The influence of Millstone Grit groundwaters on the natural baseline concentrations of the Derbyshire Dome groundwaters is also observed in other parts of the study area, in particular along the periphery of the Carboniferous Limestone outcrop and where the Carboniferous Limestone aquifer is confined

by Namurian Shales. The effect on the baseline concentration is most obvious from the large concentration ranges (min–P_{95}) for elements like Fe (<5–1570μg L^{-1}), Mn (<0.05–178μg L^{-1}) and Si (1.6–13 mg L^{-1}), which are generally more abundant in the bedrock and groundwaters of the Millstone Grit (Banks, 1997b; Abesser et al., 2005a) compared to (non-mineralised) Carboniferous Limestone (Bonotto and Andrews, 2000; Abesser et al., 2005b).

7 Conclusions

The baseline concentrations of the studied groundwaters embrace a wide range for many elements, reflecting the varying sources and pathways (residence times) of these groundwaters as well as the influence of different bedrock lithologies and extensive bedrock mineralisation on their chemical composition. The natural baseline compositions of the groundwaters is defined using the 95th percentile (P_{95}) value, which for most elements approximates an upper limit to the range of natural baseline concentrations. For elements associated with bedrock mineralisation, however, it is possible that the actual baseline concentrations are somewhat lower than those estimated from P_{95}. This is due to extensive mining activities (dating back to prehistoric times) which may have enhanced their concentrations in the groundwater by artificially enhancing natural processes of bedrock weathering and oxidation.

Most groundwaters in the study area are of Ca-Mg-HCO$_3$ type, reflecting the prevalence of limestone lithologies, and are relatively constant in their chemical composition. A number of groundwaters of Ca-SO$_4$-Cl type occur in the study area and these are probably directly derived from, or have interacted with, Namurian strata and/or with Lower Carboniferous evaporite deposits. Groundwaters of Na-HCO$_3$ type are also present and must have formed as a result of ion-exchange processes in confined parts of the aquifer.

A number of different factors control the groundwater chemical composition, the most important controls being bedrock lithology and mineralisation. In the absence of mineralisation, calcite dissolution dominates the groundwater chemistry, resulting in Ca-HCO$_3$ waters. These have uniform major-element chemistry and no distinct regional changes, except for locally increased Mg concentration in areas of dolomitisation.

Bedrock mineralisation occurs at different locations throughout the study area but is most significant in the eastern part of the Derbyshire Dome. This mineralisation is responsible for the enrichment of Ni, Pb, Zn, Mo and U in the groundwater as well as for the observed east-west zonation with respect to F and Ba concentrations. Many of these groundwaters are mine-drainage waters. Trace-element concentrations are likely to be enhanced as a result of the increased water-rock interactions promoted by the larger contact area between groundwater and bedrock as well as by the direct contact between groundwater and mineralised bedrock, including the freshly excavated (non-weathered) surfaces. At the periphery of the Carboniferous Limestone outcrop, and where the limestone is confined by the Namurian Shales, groundwater chemistry is strongly influenced by the chemical composition of the shales. Features include increased concentrations of dissolved Si, Fe, Mn and As as a result of silicate-mineral dissolution and pyrite oxidation.

Thermal groundwaters (with elevated temperatures) are present in the study area and these are also an important influence on the regional groundwater chemical composition. Thermal waters occur along the periphery of the limestone outcrop and are enriched in most constituents compared to the non-thermal limestone waters. Most noticeable are the high Sr concentrations, as well as the high Sr/Ca ratios of these waters which together with the enriched δ^{13}C signatures indicate enhanced water-rock interactions and prolonged residence times.

The extent to which thermal waters affect the groundwater signatures (and baseline concentrations) in the study area is difficult to estimate as the local lowering of groundwater heads by mine drainage has induced uprising of deeper (thermal) waters (Gunn et al., 2006) in areas where the thermal influence would otherwise be minimal. Some regional differences in

43

groundwater chemistry can be discerned between the thermal waters, in particular with respect to their SO_4, Cl and trace-element contents. These differences were attributed to the presence of distinct thermal centres (Edmunds, 1971), although the sources and pathways of the Derbyshire Dome thermal waters are still subject of debate (Bottrell et al., 2008; Brassington, 2008).

A number of geochemical controls including mineral solubility and redox potential also exert a considerable influence on the elemental (and baseline) compositions of the Derbyshire Dome groundwaters. Mineral solubility has a strong control on distributions of Ba, F, Ca, Mg, Si and HCO_3, as can be inferred from the steep gradients in the upper part of their cumulative-frequency curves (Figure 5.3 and Figure 5.8) as well as from the fact that groundwaters are generally saturated with respect to the associated solid phases (barite, fluorite, calcite, quartz (chalcedony, amorphous silica) and dolomite). Redox processes are likely to have a strong control on the concentrations of NO_3, Fe, Mn and As. Contributory processes include pyrite oxidation, reduction of Fe/Mn oxides and denitrification.

Anthropogenic inputs have also influenced the groundwater compositions in the study area and the effects of agricultural inputs are most obvious from the presence of NO_3 in the groundwater. At two sites, concentrations exceed the drinking-water limit of 11.3 mg L^{-1} (as N), probably reflecting the intensification of agriculture in the study area during the last decades.

The very limited available temporal information indicates that the major-ion compositions have been relatively stable over time, except for a two-fold increase in NO_3 since 1968. More comprehensive chemical data from regular monitoring is required for an adequate assessment of temporal trends in groundwater composition.

8   References

ABESSER, C, SHAND, P, and INGRAM, J. 2005a. Baseline Report Series 18: The Millstone Grit of Northern England. *British Geological Survey Commissioned Report*, British Geological Survey Commissioned Report, CR/05/015N.

ABESSER, C, SHAND, P, and INGRAM, J. 2005b. Baseline Report Series 22: The Carboniferous Limestone of Northern England. *British Geological Survey Commissioned Report*, British Geological Survey Commissioned Report, CR/05/076N.

ABESSER, C, and SMEDLEY, P. 2006. Uranium concentrations in the groundwaters of the Derbyshire Dome. *British Geological Survey Internal report*, IR/06/072.

AITKENHEAD, N, BARCLAY, W J, BRANDON, A, CHADWICK, R A, CHISHOLM, J I, COOPER, A H, and JOHNSON, E W. 2002. *British Regional Geology: The Pennines and Adjacent Areas* (4th edition edition). (Nottingham: British Geological Survey.)

AITKENHEAD, N, CHISHOLM, J I, and STEVENSON, I P. 1985. *Geology of the Country around Buxton, Leek and Bakewell.* Memoir of the 1:50 000 Geological Sheet 111 (England and Wales). (London: British Geological Survey.)

ALBU, M, BANKS, D, and NASH, H. 1997. Hydrogeochemistry and origin of mineral waters. 48-100 in *Mineral and Thermal Groundwater Resources.* ALBU, M, BANKS, D, and NASH (editors). (London: Chapman & Hall.)

ANDREWS, J N. 1991. Radioactivity and dissolved gases in the thermal waters of Bath. 157-170 in *Hot Springs of Bath.* KELLAWAY, G A (editor). (Bath: Bath City Council.)

APPELO, C A J, and POSTMA, D. 1993. *Geochemistry, Groundwater and Pollution* (1 edition). (Rotterdam: Balkema.)

APPELO, C A J, and POSTMA, D. 2005. *Geochemistry, Groundwater and Pollution* (2 edition). (Leiden: Balkema.)

BALL, T K, CAMERON, D G, and COLMAN, T B. 1992. Aspects of Rn potential mapping in Britain. *Radiation Protection Dosimetry*, Vol. 45, 211-214.

BALL, T K, CAMERON, D G, COLMAN, T B, and ROBERTS, T B. 1991. Behaviour of Rn in the geological environment - a review. *Quarterly Journal of Engineering Geology*, Vol. 24, 169-189.

BANKS, D. 1997a. Spas of England. 235-280 in *Mineral and Thermal Groundwater Resources.* ALBU, M, BANKS, D, and NASH, H (editors). (London: Chapman & Hall.)

BANKS, D. 1997b. Hydrogeochemistry of Millstone Grit and Coal Measures groundwaters, south Yorkshire and north Derbyshire, UK. *Quarterly Journal of Engineering Geology*, Vol. 30, 237-256.

BARKER, J A, DOWNING, R A, GRAY, D A, FINDLAY, J, KELLAWAY, G A, PARKER, R H, and ROLLIN, K E. 2000. Hydrogeothermal studies in the United Kingdom. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 33, 41-58.

BASU, R, HAQUE, S E, TANG, J, JI, J, and JOHANNESSON, K H. 2007. Evolution of selenium concentrations and speciation in groundwater flow systems: Upper Floridan (Florida) and Carrizo Sand (Texas) aquifers. *Chemical Geology*, Vol. 246, 147-169.

BONOTTO, D M, and ANDREWS, J N. 2000. The transfer of uranium isotopes ^{234}U and ^{238}U to the waters interacting with carbonates from Mendip Hills area (England). *Applied Radiation and Isotopes*, Vol. 52, 965-983.

BOTTRELL, S, LOWE, D, GUNN, J, WORTHINGTON, S, and BRASSINGTON, F C. 2008. Discussion of 'A proposed conceptual model for the genesis of the Derbyshire thermal springs' by F. C. Brassington, Quarterly Journal of Engineering Geology and Hydrogeology, 40, 35-46. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 41, 119-120.

BOTTRELL, S H. 1996. Organic carbon concentration profiles in recent cave sediments: Records of agricultural pollution or diagenesis? *Environmental Pollution*, Vol. 91, 325-332.

BOTTRELL, S H, WEBBER, N, GUNN, J, and WORTHINGTON, S R H. 2000. The geochemistry of sulphur in a mixed allogenic-autogenic karst catchment, Castleton, Derbyshire, UK. *Earth Surfaces Processes and Landforms*, Vol. 25, 155-165.

BRASSINGTON, F C. 2007. A proposed conceptual model for the genesis of the Derbyshire thermal springs. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 40, 35-46.

BRASSINGTON, F C. 2008. Discussion of 'Analysis of flows from a large Carboniferous Limestone drainage adit, Derbyshire England' by M.G. Shepley Quarterly Journal of Engineering Geology and Hydrogeology, 40, 123-135. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 41, 121-122.

BUREK, C. 1977. The Pleistocene ice age and after. 87-128 in *Limestones and Caves of the Peak District*. FORD, T D (editor). (Norwich: GeoAbstracts.)

BUSENBERG, E, and PLUMMER, L N. 2000. Dating young groundwater with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. *Water Resources Research*, Vol. 36, 3011-3030.

CEFAS. 2004. Radioactivity in Food and the Environment, 2003. *The Centre for Environment, Fisheries and Aquaculture Science, on behalf of the Environment Agency, Environment and Heritage Service, Food Standards Agency and the Scottish Environment Protection Agency.*

COMMITTEE ON MEDICAL AND BIOLOGICAL EFFECTS ON ENVIRONMENTAL POLLUTANTS. 1976. *Selenium*. Medical and Biologic Effects of Environmental Pollutants. (Washington, D.C.: National Academy of Sciences.)

CRAIG, H. 1961. Isotopic variations in natural waters. *Science*, Vol. 133, 1702-1703.

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

DARLING, W G, and TALBOT, J C. 2003. The O & H stable isotope composition of fresh waters in the British Isles. 1. Rainfall. *Hydrology and Earth System Sciences*, Vol. 7, 163-181.

DOWNING, R A. 1967. The geochemistry of groundwaters in the Carboniferous Limestone in Derbyshire and the East Midlands. *Bulletin of the Geological Survey of Britain*, Vol. 27, 289-307.

ECN. 2008. Environmental Change Network. http://www.ecn.ac.uk, accessed on 16 September 2008.

EDMUNDS, W M. 1971. Hydrogeochemistry of groundwaters in the Derbyshire Dome with special reference to trace constituents. *Institute of Geological Sciences*, Report 71/7.

EDMUNDS, W M. 1981. Hydrogeochemical investigations. 87-112 in *Case Studies in Groundwater Resource Evaluation.* LLOYD, J W (editor). (Oxford: Oxford Science Publications.)

EDMUNDS, W M, COOK, J M, KINNIBURGH, D G, MILES, D L, and TRAFFORD, J M. 1989. Trace-element occurrence in British groundwaters. *British Geological Survey Hydrogeological Series Research Report*, SD/89/3.

EUROPEAN COMMISSION. 1998. Directive 1998/83/EC of the European Parlament and of the Council. *Official Journal of the European Communities*, 32-54.

EVANS, G V, OTLET, R L, DOWNING, R A, MONKHOUSE, R A, and RAE, G. 1979. Some problems in the interpretation of isotope measurements in United Kingdom aquifers. 679-708 in *Isotope Hydrology 1978, Vol. II.* (Vienna: International Atomic Energy Agency.)

FORD, T D. 1968a. The Millstone Grit. 83-94 in *The Geology of the East Midlands.* SYLVESTER-BRADLEY, P C, and FORD, T D (editors). (Bath: Leicester University Press.)

FORD, T D. 1968b. Epigenetic mineralisation of the Carboniferous Limestone. 117-123 in *The Geology of the East Midlands.* SYLVESTER-BRADLEY, P C, and FORD, T D (editors). (Bath: Leiceister University Press.)

FORD, T D. 1999. The growth of geological knowledge in the Peak District. *Mercian Geologist*, Vol. 14, 161-190.

FREEZE, R A, and CHERRY, J A. 1979. *Groundwater.* (Englewood Cliffs, NJ: Prentice-Hall, Inc.)

GUNN, J. 1992. Hydrogeological contrasts between British Carboniferous Limestone Aquifers. *International Contributions to Hydrogeology*, Vol. 13, 25-41.

GUNN, J, BOTTRELL, S H, LOWE, D J, and WORTHINGTON, S R H. 2006. Deep groundwater flow and geochemical processes in limestone aquifers: evidence from thermal waters in Derbyshire, England, Uk. *Hydrogeology Journal*, Vol. 14, 868-881.

GUNN, J, FLETCHER, S, and PRIME, D. 1991. Research on radon in British caves and mines. *Cave Science*, Vol. 18, 63-82.

GUNN, J, HARDWICK, P, and WOOD, P J. 2000. The invertebrate community of the Peak-Speedwell cave system, Derbyshire, England - pressures and considerations for conservation management. *Aquatic Conservation: Marine and Freshwater Ecosystems*, Vol. 10, 353-369.

GUNN, J, LOWE, D, and BOTTRELL, S. 2002. Comparative hydrogeology and geochemistry of two potable water springs at Buxton, England. *The XVIIIth International Symposium on Theoretical and Applied Karstology*, 24-28 May 2002, Baile Herculane, Romania.

GUNN, J, TRANTER, J, PERKINS, J, and HUNTER, C. 1998. Sanitary bacterial dynamics in a mixed karst aquifer. 61-70 in *Karst Hydrology*. LEIBUNDGUT, C, GUNN, J, and DASSARGUES, A (editors). No 247. (Wallingford: IAHS Publication.)

HELSEL, D R. 2005. *Nondetects And Data Analysis: Statistics for censored environmental data*. (New York: Wiley.)

HELSEL, D R, and COHN, T A. 1988. Estimation of Descriptive Statistics for Multiply Censored Water Quality Data. *Water Resources Research*, Vol. 24, 1997-2004.

HUNTER, C, PERKINS, J, TRANTER, J, and GUNN, J. 1999. Agricultural land-use effects on the indicator bacterial quality of an upland stream in the Derbyshire peak district in the U.K. *Water Research*, Vol. 33, 3577-3586.

HYSLOP, E K. 1993. Uranium distribution studies of potential radon source rocks from the Ashover area, Derbyshire UK. *British Geological Survey*, BGS Report, WG/93/04.

LANGHAM, M, and WELLS, C. 1986. *Buxton Waters- A history of Buxton the Spa*. (Derby, UK: J.H. Hall & Sons.)

LANGMUIR, D. 1997. *Aqueous Environmental Geochemistry*. (New Jersey: Prentice Hall.)

LEE, J-Y. 2006. Characteristics of ground and groundwater temperatures in a metropolitan city, Korea: considerations for geothermal heat pumps. *Geosciences Journal*, Vol. 10, 165-175.

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

MACHEL, H G. 1999. Effects of groundwater flow on mineral diagenesis, with emphasis on carbonate aquifers. *Hydrogeology Journal*, Vol. 7, 94-107.

MIDDLETON, T, GUNN, J, FLETCHER, S, and PRIME, D. 1991. Radon daughter concentrations in Giants Hole, Derbyshire. *Cave Science*, Vol. 18, 67-70.

MILES, J C H, APPLETON, J D, REES, D M, GREEN, B M R, ADLAM, K A M, and MYERS, A H. 2007. Indicative Atlas of Radon in England and Wales. *Health Protection Agency*, HPA-RPD-033.

MOOK, W G. 2006. *Introduction to Isotope Hydrology*. International Contributions to Hydrogeology. No. 25. (London: Taylor & Francis.)

NICHOL, I, THORNTON, I, WEBB, J S, FLETCHER, W K, HORSNAIL, R F, HKHALEELEE, J, and TAYLOR, D. 1970. Regional reconnaissance of the Derbyshire area. *Institute of Geological Sciences*, Report 70/2.

NRFA. 2008. National River Flow Archive. http://www.nwl.ac.uk/ih/nrfa/station_summaries/op/EA-Midlands_map.html, accessed on 16 September 2008.

OSTER, H, SONNTAG, C, and MÜNNICH, K O. 1996. Groundwater age dating with chlorofluorocarbons. *Water Resources Research*, Vol. 32, 2989-3001.

PARSONS, L M. 1922. Dolomitisation in the Carboniferous Limestone of the Midlands. *Geological Magazin*, Vol. 80, 104-117.

PEACOCK, J D, and TAYLOR, K. 1966. Uraniferous collophane in the Carboniferous Limestone of Derbyshire and Yorkshire. *Bulletin of the Geological Survey of Britain*, Vol. 25, 19-32.

PEAK DISTRICT INFO. 2008. http://www.thepeakdistrict.info/peak-district-mining.php, accessed on 27-08-08.

PEAK DISTRICT NATIONAL PARK AUTHORITY. 2008. http://www.peakdistrict-education.gov.uk/Fact%20Sheets/factshframe.html, accessed on 12 February 2008.

PENTECOST, A, JONES, B, and RENAUT, R W. 2003. What is a hot spring? *Canadian Journal of Earth Sciences*, Vol. 40, 1443-1446.

PLUMMER, L N, and BUSENBERG, E. 1999. Chlorofluorocarbons. 441-478 in *Environmental Tracers in Subsurface Hydrology*. COOK, P, and HERCZEG, A (editors). (Amsterdam: Kluwer Academic Press.)

REIMANN, C, FILZMOSER, P, GARRETT, R, and DUTTER, R. 2008. *Statistical data Analysis Explained*. (Chichester, UK: Wiley.)

SAIKAT, S, CARTER, J, MEHRA, A, SMITH, B, and STEWART, A. 2004. Goitre and environmental iodine deficiency in the UK--Derbyshire: a review. *Environmental Geochemistry and Health*, Vol. 26, 395-401.

SEMPRINI, L, HOPKINS, G D, MCCARTHY, P L, and ROBERTS, P V. 1992. In-situ transformation of carbon tetrachloride and other halogenated compounds resulting from biostimulation under anoxic conditions *Environmental Science and Technology*, Vol. 26, 2454-2461.

SHAND, P, EDMUNDS, W M, LAWRENCE, A R, SMEDLEY, P L, and BURKE, S P. 2007. The natural (baseline) quality of Groundwater in England and Wales. *British Geological Survey Brirish Geological Survey Research Report*, No RR\07\06.

SHEPLEY, M G. 2007. Analysis of flows from a large Carboniferous Limestone drainage adit, Derbyshire, England. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 40, 123-135.

SHUMWAY, R H, AZARI, R S, and KAYHANIAN, M. 2002. Statistical Approaches to Estimating Mean Water Quality Concentrations with Detection Limits. *Environ. Sci. Technol.*, Vol. 36, 3345-3353.

SINCLAIR, A J. 1974. Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Exploration*, Vol. 3, 129-149.

SMEDLEY, P L, SMITH, B, ABESSER, C, and LAPWORTH, D. 2006. Uranium occurrence and behaviour in British groundwater. *British Geological Survey Commissioned Report*, CR/06/050N.

STEELE, A. 1995. A catchment delineation and hydrogeological study of the Meerbrook Sough, Derbyshire. MSc thesis, University of Birmingham.

STEPHENS, J V. 1929. *Wells and Springs of Derbyshire*. Memoirs of the Geological Survey of England and Wales. (London: Her Majesty's Stationary Office.)

SYLVESTER-BRADLEY, P C, and FORD, T D. 1968. *The Geology of the East Midlands*. (Bath: Leicester University Press.)

THORNTON, I, KERSHAW, G F, and DAVIES, M K. 1972. An investigation into copper deficiency in cattle in the Southern Pennines. I. Identification of suspect areas using geochemical reconnaissance followed by blood copper surveys. II. Response to copper supplementation. *Journal of Agricultural Sciences*, Vol. 78, 157-171.

TURTON, P H J. 1933. The distribution of simple goitre in Derbyshire. *Proceedings of The Royal Society of Medicine*, Vol. 26, 1223–1266.

VENABLES, W N, SMITH, D M, and R DEVELOPMENT CORE TEAM. 2008. *An introduction to R (version 2.7.2)*.

WENNIG, R, and KIRSCH, N. 1988. Molybdenum. 437-452 in *Handbook on Toxicity of Inorganic Compounds*. SEILER, H G, SIGEL, H, and SIGEL, A (editors). (New York: Marcel Dekker.)

WORTHINGTON, S R H, and FORD. 1995. High sulfate concentrations in limestone springs: An important factor in conduit initiation? *Environmental Geology*, Vol. 25, 9-15.

YOUNGER, P L. 2007. *Groundwater in the environment: An introduction*. (Blackwell Publishing.)

Appendix 1 Spatial distribution of elemental concentrations in the groundwaters of the Derbyshire Dome
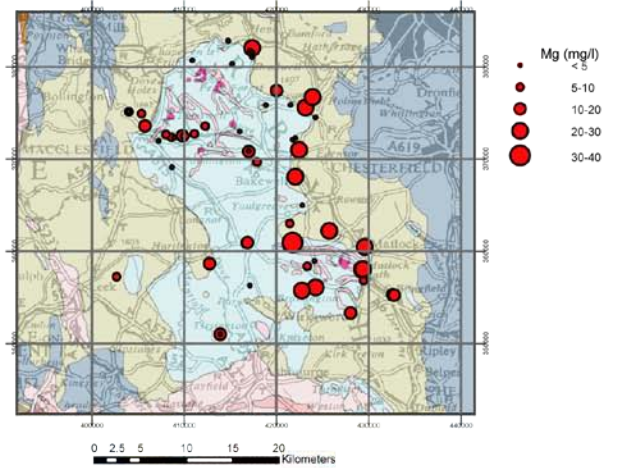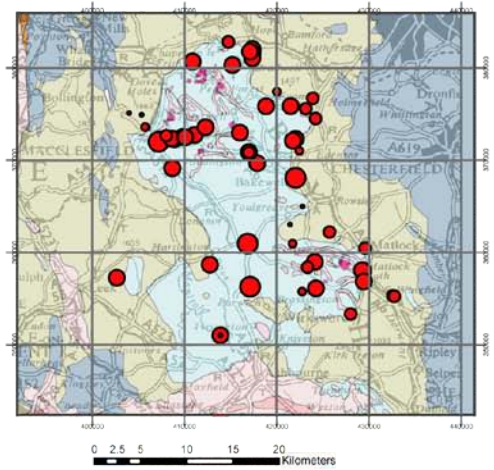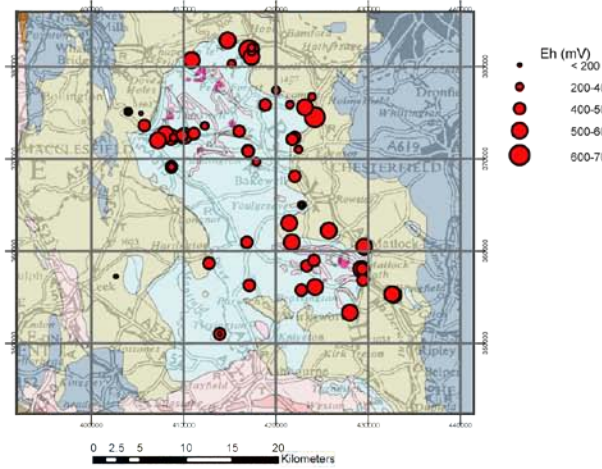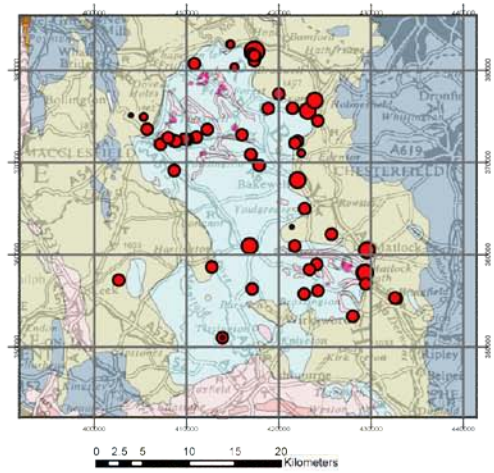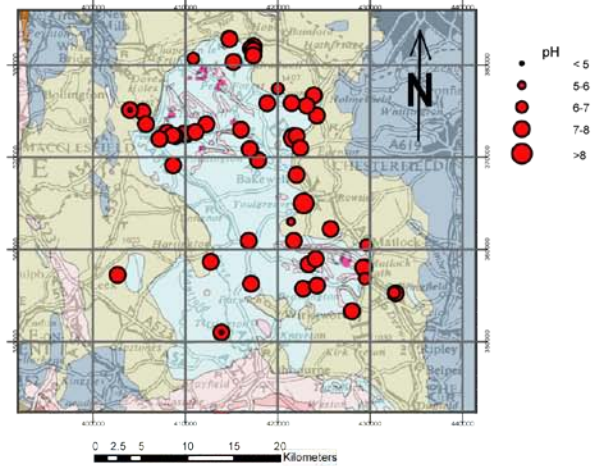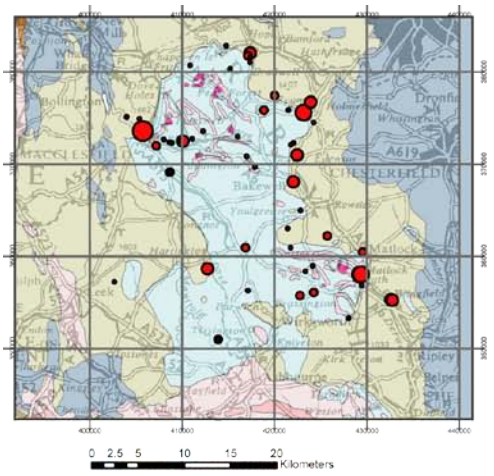
Plate 1 Distribution of temperature, pH, Eh, SEC, Ca and Mg in the study area
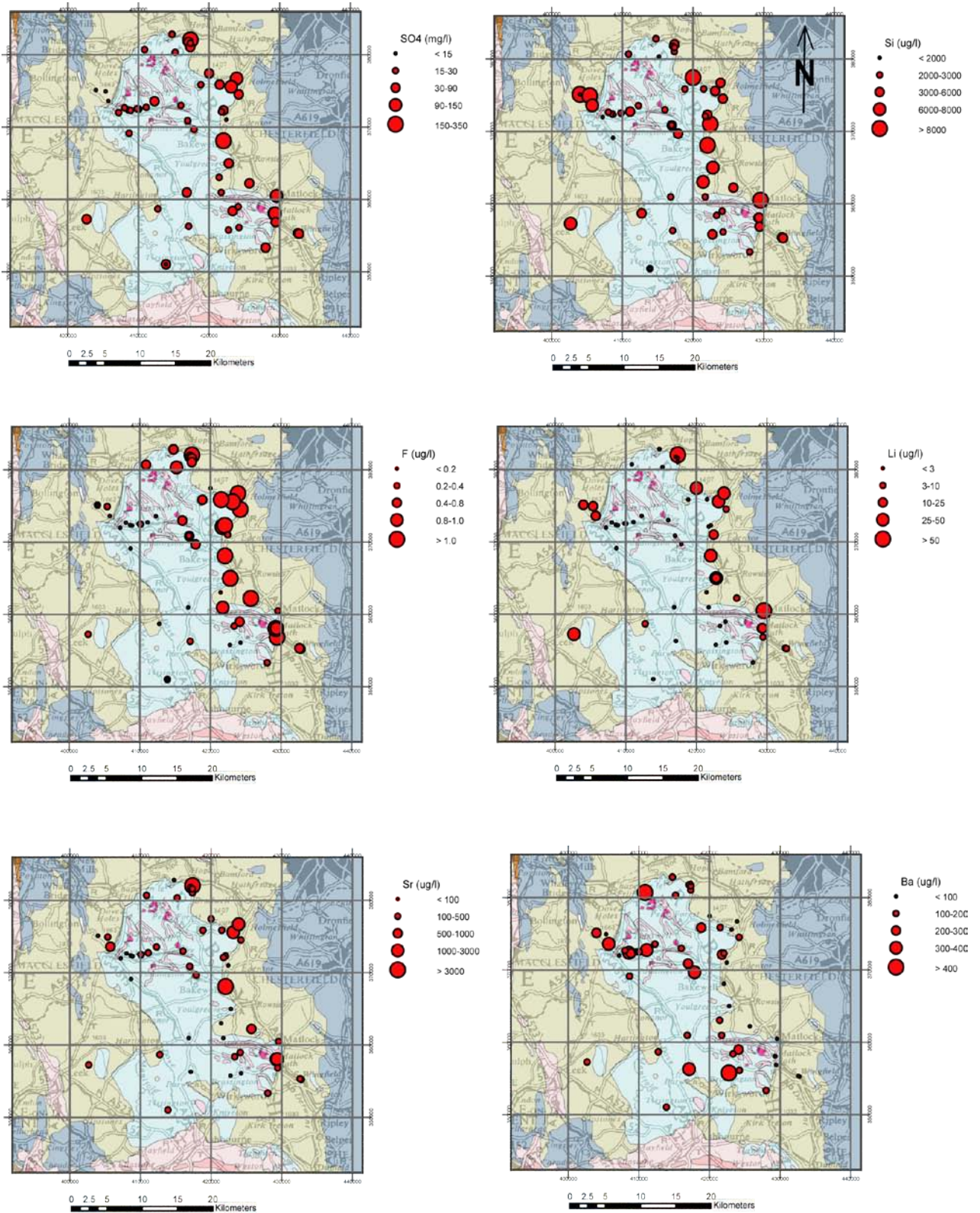
52

Plate 2 Distribution of SO$_4$, Si, F, Li, Sr and Ba in the study area

53

Plate 3 Distribution of Fe, Mn, As, U, Pb and Ni in the study area

54