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Uranium concentrations in the groundwaters of the Derbyshire Dome

Groundwater Management Programme

Internal Report IR/06/072



BRITISH GEOLOGICAL SURVEY

GROUNDWATER MANAGEMENT PROGRAMME

INTERNAL REPORT IR/06/072

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C Abesser and P Smedley

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Summary

This report describes the concentrations and distribution of uranium (U) in the groundwater of the Derbyshire Dome and discusses potential sources and controls on U mobility within the aquifer. The Derbyshire Dome is an anticlinal structure which consists of marine Carboniferous Limestone (Dinantian), 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 and different zones of mineralisation are distinguished, reflecting the west-east progression from calcite to barite to fluorite as the dominant gangue minerals.

The hydrogeology of the study area is dominated by natural karstic features but even more by the ‘anthropogenic karst’ which has developed as a result of the extensive mining activities that have created a network of mine passages and drainage adits (“soughs”). Water movement through the aquifer is generally very rapid, but varies temporally as well as spatially. Thermal springs issue from a number of locations, some of which are known or believed to have bulk ages of up to several thousand years.

Uranium is present in the bedrock as well as in the groundwater of the study area. The mineralogy and precise nature of U in the bedrock(s) is not known but a number of potential sources within the Dinantian and Namurian have been identified. These include organic matter fragments and hydrocarbon globules within the matrix of the Carboniferous Limestone, the organic-rich shales of the Namurian (Millstone Grit Series) and bedrock mineralization.

A total of 26 groundwater samples were collected in July 2005 and analysed for a comprehensive suite of major, minor and trace elements, including U. Samples were collected from various sources including natural springs, decommissioned mines and soughs as well as from industrial and farm boreholes. The results show that aquifer lithology is the dominant control on the groundwater chemistry in the study area, hence Ca-(Mg)-bicarbonate waters are the most common groundwater type. Some groundwaters of Ca-(SO₄)-Cl type and Na-HCO₃ type are also present in the study area and they are due to different thermal sources, mixing with deep (connate) waters as well as ion exchange and mineral dissolution processes.

Uranium concentrations in the groundwaters range between < 0.2 and $4.23 \mu\text{g l}^{-1}$, and do not exceed the WHO provisional guideline value for U in drinking water of $15 \mu\text{g l}^{-1}$. The concentrations of U in the groundwaters are strongly controlled by pH, redox conditions and the presence of complexing agents such as carbonate or phosphate. Bedrock mineralization appears to be a major control on U concentrations in the groundwater as indicated by the spatial distribution of dissolved U in the study area as well as by the relatively high concentration associated with drainage from soughs and mines. The observed U concentrations are low compared with U-mineralised areas worldwide. This could be due to the limited solubility of uranyl minerals at $\text{pH} > 7$ and increased adsorption of U onto hydrous ferrous oxide (Hfo) surfaces. Alternatively, uranyl carbonate solubility controls or the ‘exhaustion’ of easily leachable U source may have contributed to the low U concentrations.

While U concentrations are well below the WHO provisional guideline value for U concentrations in drinking water, it is possible that U activities (^{234}U and ^{238}U) in some of the sampled groundwaters exceed the WHO screening value for total alpha emissions in drinking water, in particular where ^{234}U dominates over ^{238}U .

This study has shown that the highest observed U concentrations in the groundwater of the Derbyshire Dome are largely associated with bedrock mineralisation, probably due to (1) the abundance of U-bearing minerals in mineral veins and secondary iron deposits and (2) the

high surface area provided by cavities and rock debris resulting in enhanced bedrock weathering. High U concentrations are also present in the geochemically more evolved thermal waters and U enrichment is likely to result from prolonged water-rock interactions and increased mineral solubility at higher temperatures.

1 Introduction

In view of the potential health risks associated with uranium (U), it is essential to gain a better understanding of the behaviour of U in areas of bedrock mineralization, such as the Derbyshire Dome, and to establish the range of natural background concentrations that occur in the groundwater. Such knowledge is imperative for local authorities, water industry and regulators, in particular since the inclusion of a U limit in future EC drinking water regulations is likely.

This study has been undertaken by the British Geological Survey (BGS) as part of BGS' Groundwater and Health Project with the aim to establish the natural concentrations of U that occur in the groundwaters of the Derbyshire Dome. The main focus of the study was on the spatial distribution of U in the groundwaters as well as on the identification of potential U sources. Based on the results, the implications for the use of these groundwaters as drinking water supplies can be considered in relation to the existing WHO (provisional) guideline value for U in drinking water.

The distribution and mineralogy of U in Derbyshire has been of great interest due to the direct link to radon (Rn) production. High Rn concentrations ($100\text{--}300\text{ Bq l}^{-1}$) in soil gases over limestone have been reported (Ball, *et al.*, 1991, 1992) and these levels are exceeded in some of the limestone caves in the Derbyshire area (Gunn, *et al.*, 1991, Middleton, *et al.*, 1991). The high Rn levels in soil gases have ultimately been linked to the concentrations of U in the underlying bedrock (Ball, *et al.*, 1991, CEFAS, 2004, Hyslop, 1993, Peacock and Taylor, 1966) and various potential U sources within the Carboniferous bedrock have been identified. As a result, the relationship between bedrock U concentrations and Rn emanation in the Derbyshire Dome has been relatively well described. Yet, little is known about how these high bedrock U concentrations impact on the groundwater quality in the area, although an early study by Peacock (1961) found U concentrations between 2 and $15\text{ }\mu\text{g l}^{-1}$ in the Derbyshire groundwaters. Various other groundwater geochemical studies have been conducted in the area (Downing, 1967, Edmunds, 1971, Edmunds, *et al.*, 1989), but these did not include U.

Uranium is considered a potential chemical hazard and when ingested can cause a number of health problems including damage to kidneys (nephritis) (Hursh and Spoor, 1973, Zamora, *et al.*, 1998), reproductive organs and other internal organs (Pavlakis, *et al.*, 1996). Uranium is weakly radioactive but its radiological toxicity is hypothetical and currently, there are no unequivocal studies that show that intake of uranium induces radiation effects in humans or animals (ATSDR, 1999). Although little information is available on the carcinogenicity of U and/or on the chronic health effects of exposure to environmental U in humans, a provisional guideline value of $15\text{ }\mu\text{g l}^{-1}$ has been established by the WHO (WHO, 2004). This guideline value may actually be exceeded in some Derbyshire groundwaters as indicated by Peacock (1966). The potential for increased groundwater U is also indicated by the fact that groundwaters from the Carboniferous Limestone in Derbyshire was the only groundwater source (out of ~30 monitored network sites) in which consistently detectable U radionuclide activities were observed during the nationwide CEFAS RIFE monitoring programme (CEFAS, 2005). In 2003, groundwater radioactivity even exceeded the WHO screening values of 0.1 Bq l^{-1} for total alpha emissions in drinking waters (CEFAS, 2003). The authors concluded that these high total alpha levels are "due to high concentrations of natural uranium (in the groundwater) arising from local geology".

2 Behaviour of uranium in groundwater

Uranium occurs naturally in several oxidation states, including U(III), U(IV), U(V) and U(VI). In aqueous solutions, U(III) and U(IV) exist as the aqua ions U^{3+} and U^{4+} whereas U(V) and U(VI) form the oxyanions UO_2^+ and UO_2^{2+} (uranyl ions). However, in natural weathering systems, only the (tetravalent) U(IV) and the (hexavalent) U(VI) species are believed to be important while U(III) and U(VI) are not expected to exist in these conditions (Langmuir, 1997, Shock, *et al.*, 1997).

The presence and mobility of the two main U species, U(IV) and U(VI) in natural groundwater systems is controlled by various factors, in particular the groundwater redox status (pe) and pH as well as its solute chemistry. Under oxidizing conditions, U(VI) predominates in the groundwater and is present as the highly soluble uranyl ion UO_2^{2+} and its hydroxyl complexes (Figure 2.1a). Under reducing conditions, U is present as the uranous ion (U^{4+}) and its aqueous complexes. The tetravalent form U(IV) is also the major oxidation state in the most common uranium ore minerals (e.g., uraninite- $UO_2(c)$, pitchblende- $UO_2(am)$, coffinite- $USiO_4$). Aqueous concentrations of the U(IV) species are usually extremely low (Langmuir, 1997), in particular at $pH > 4$, due to the low solubility of the solid uranium phase. As a consequence, in most natural waters ($6 < pH < 9$), the concentrations of U(VI) species are about four orders of magnitude greater than that of U(IV) due to the low mobility of U(IV) above pH 4. A pe–pH diagram for the system U- O_2 - CO_2 - H_2O and a typical groundwater U concentration of $1e^{-9}$ mol kgw^{-1} is given in Figure 2.1a. The plot illustrates the predominance of aqueous uranyl complexes under oxidising as well as the large size of the stability field of uraninite at low pe. Uranium concentrations are usually higher in groundwaters compared to surface waters due to the greater extent of water-rock-interaction associated with the longer contact (residence) times of groundwaters with the rock matrix.

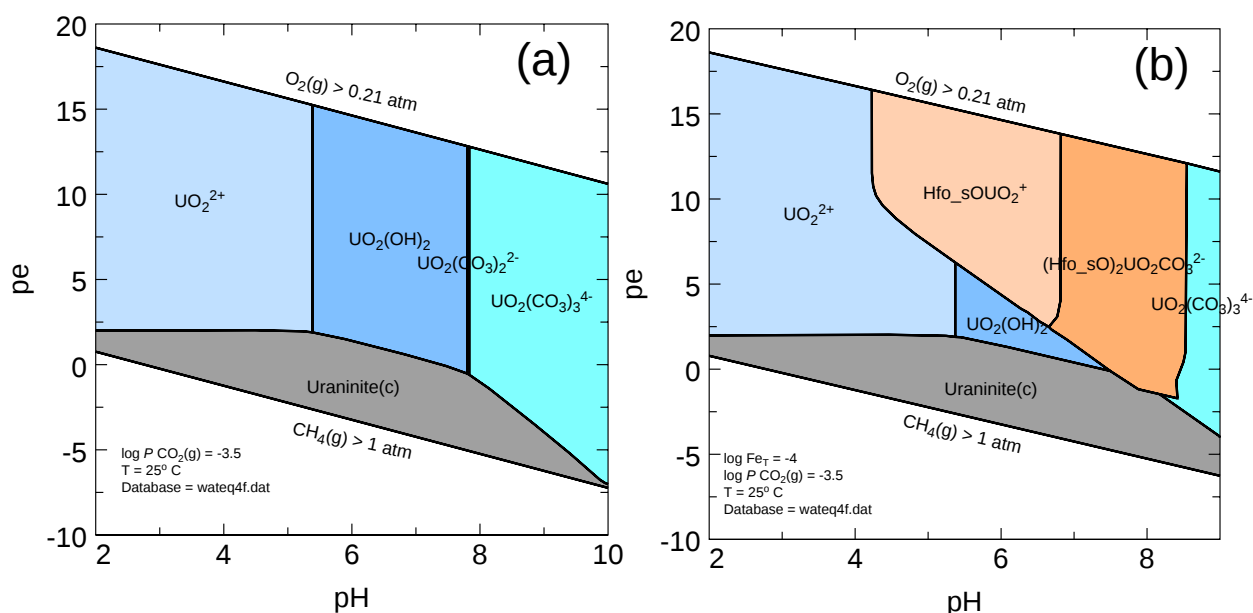


Figure 2.1 pe–pH diagram for aqueous species in the U- O_2 - CO_2 - H_2O system in water at 25°C and 1 bar total pressure for (a) $U = 1e^{-9}$ mol/kgw and (b) $U = 1e^{-9}$ mol/kgw and $FeT = 1e^{-4}$ mol/kgw. Database = wateq4f.dat with surface U species by Waite *et al.* (1994) as given by Weber. [Note: $pe \approx Eh \text{ (Volts)}/0.05916$]

Uranium is usually complexed in solution and its mobility is strongly controlled by the pH and $p\text{CO}_2$ of the solution. In the presence of carbonate, U carbonate complexes form, dominating U speciation at higher pH, as is illustrated in Figure 2.1a. These complexes are extremely important because they greatly increase the solubility of U minerals, facilitate U(IV) oxidation and also increase U mobility by limiting U adsorption in oxidising waters (Langmuir, 1997). Other important complexes are formed with phosphate (Sandino and Bruno, 1992), fluoride (Romberger, 1984), chloride (Kominou and Sverjenski, 1996), sulphate (Grenthe, *et al.*, 1992) and organic ligands (Plater, *et al.*, 1992, Singhal, *et al.*, 2005), which also enhance the mobility of U in the groundwater system under certain conditions.

As U moves through porous and fractured media, it is partitioned between water and the surfaces of solids in soils, sediments and rocks. In typical groundwaters (pH >5), more than 99% of the total U may, in fact, be associated with solid surfaces and only 1% dissolved (Langmuir, 1997). Hence, the migration of U during groundwater movement may be strongly retarded by sorption processes. The most important potential sorbents for U are probably Fe(III) oxyhydroxides (Gomez, *et al.*, 2005, Langmuir, 1978, Villalobos, *et al.*, 2001) due to their common occurrence in the natural environment and their strong sorptive behaviour towards U(VI). The effectiveness of Fe (hydr)oxides in removing U from the aqueous solution is illustrated in Figure 2.1b, which shows that at intermediate pH and under oxidising conditions, most U is adsorbed onto Fe (hydr)oxide surfaces. Other important sorbents include organic matter (Van der Weijden and Van Leuwen, 1985), oxy(hydr)oxides and clay minerals (Langmuir, 1978). The degree to which these surfaces interact with U in the groundwater largely depends on the aqueous U speciation and complexation and also on the pH of the groundwater. Sorption of U (VI) onto mineral surfaces is generally greatest in the near-neutral pH range which is also the range of minimum solubility of uranyl minerals (Langmuir, 1978). Hence, in the oxidising environment and in most natural groundwaters ($6 < \text{pH} < 9$), concentrations of U may be low, controlled by the solubility of uranyl as well as by adsorption processes.

3 Study area

3.1 GEOLOGY AND MINERALISATION OF THE STUDY AREA

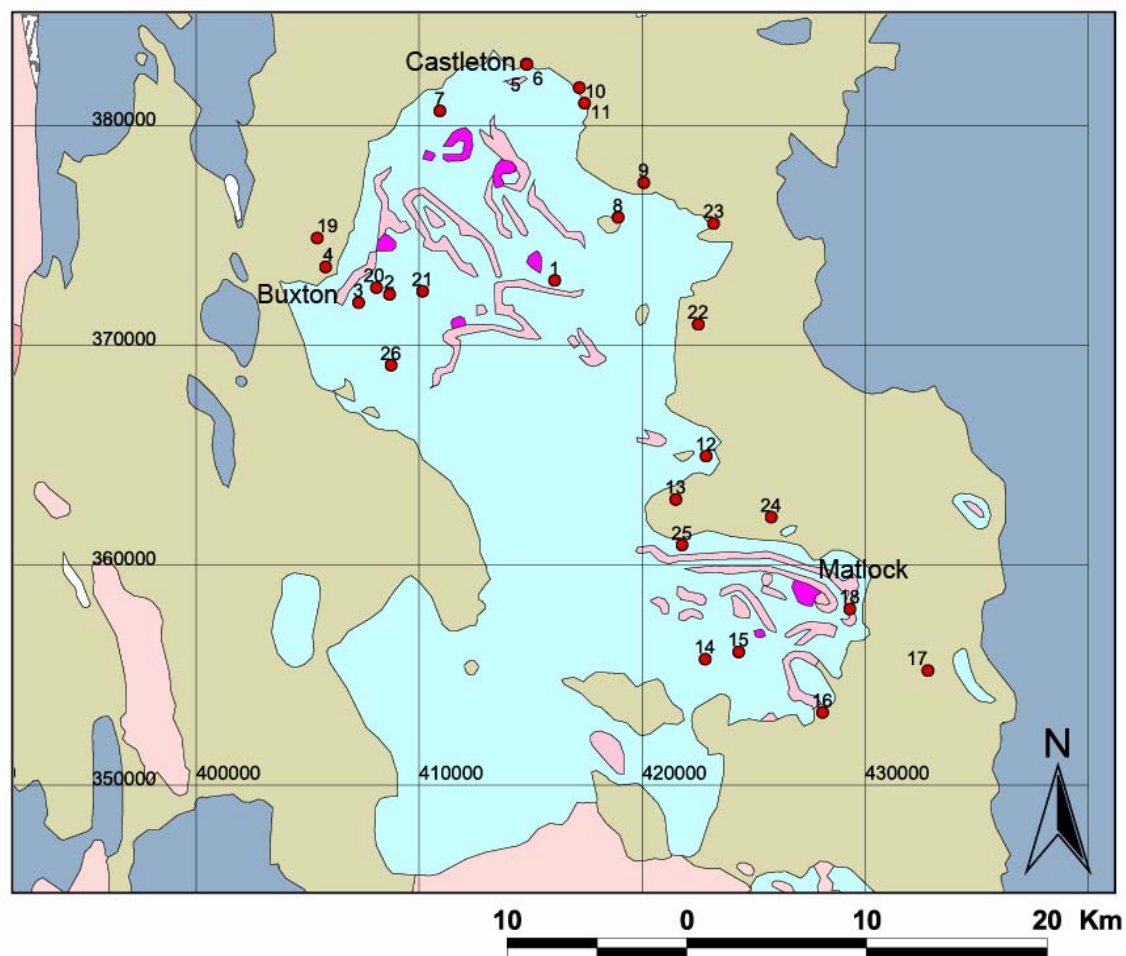
The geology of the study area is illustrated in Figure 3.1. It is dominated by the Derbyshire Dome - an anticlinal structure which mainly consists of marine limestones of Dinantian age (Carboniferous Limestone Series). Overlying the limestones are shales and sandstones of Namurian age (Millstone Grit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

The limestones have a maximum thickness of 1900 m in the north-east of the dome, but are much thinner in the west and southwest, reaching a minimum total thickness of only 660 m at Buxton (Aitkenhead, *et al.*, 1985). The succession was formed from a variety of carbonate sediments deposited in a number of different 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), 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 southwest, 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) and, today, form some of the most spectacular scenery of the area.

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

Silica is common in some limestone formations, while others, particularly the reef-facies formations, are almost devoid of silica (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). 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) raises the possibility of it being an early phase of mineralisation. A second type of dolomitisation, which affected older limestones in the area 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).



Legend

- | | |
|---|--|
| Triassic mudstones | Groundwater sampling location |
| Permian and Triassic sandstones | |
| Coal Measures (Westphalian) | |
| Millstone Grit Series (Namurian) | |
| Carboniferous Limestone Series (Dinantian) | |
| Basalt and spilite | |
| Basalt dolerite | |

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Figure 3.1 Geology of the study area and distribution of groundwater sampling sites

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 easily distinguished from those of the Edale Shales owing to their feldspar-rich composition.

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, baryte and calcite. Minor occurrences of zinc, 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).

Drift deposits are rare, as much of the higher ground remained ice-free during the most recent glaciation. Some deposits of ‘Older Drift’ are found in the form of erratics scattered along the eastern and western flanks of the dome (Burek, 1977) and isolated occurrences of boulder clay have been reported in the Wye Valley between Bakewell and Rowsley, and on the south side of the Lathkill Valley as well as 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 themselves or in 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.

3.2 HYDROGEOLOGY AND GEOCHEMISTRY OF THE STUDY AREA

The Carboniferous Limestone (Dinantian) of the Derbyshire Dome is hydrogeologically distinguished from other British limestone karst; firstly, by the thickness of the limestone strata and the resultant great depths to the basal rocks (100 m to over 1800 m) and, secondly, in that it is surrounded by less permeable strata, namely Namurian rocks and Triassic sandstones, 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 depths (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 ($0.001\text{--}0.01\text{ m d}^{-1}$) 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 ($100\text{--}500\text{ m hr}^{-1}$) (Gunn, 1992) but vary largely throughout the year depending on the hydrological conditions. The direction of groundwater flow is locally very

varied and mostly of catchment scale, i.e. directed towards valley bottoms. In places, deeper flow along extended flowpath occurs (BGS, unpublished data). Tentative groundwater contours have been drawn for the limestone area based on available water level data (Edmunds, 1971), but given the uncertainty inherent in the data, the contours should be regarded cautiously. In places, the surfaces of the basaltic lavas have weathered to clays and act as aquitards giving rise to perched water tables or groundwater springlines.

Extensive mining activities, which have taken place over the last 2000 years, have largely 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.

However, for hydrogeological purposes, the limestones of the Derbyshire Dome can be considered as a single lithological unit (Edmunds, 1971), although the different facies and their different lithological composition may affect the geochemistry of the groundwaters.

Thermal waters (i.e. those with temperatures higher than the mean annual air temperatures of $\sim 10^{\circ}\text{C}$) issue from the Carboniferous Limestone at various localities in the study area, including springs and boreholes, as well as several mines and soughs. The occurrence of these thermal waters is fracture controlled, possibly related to a thermal anomaly below the Peak District which allows the rapid upward migration of deep, warm groundwater along transmissive fracture zones (Banks, 1997b). Eight centres of thermal waters were recognised by Edmunds (1971), the best known being the Buxton and Matlock springs. Previous studies undertaken in 1968/69 suggested, based on tritium measurements, that many of these thermal waters are more than 15 years old and originate from local meteoric waters that have circulated to considerable depths (Edmunds, 1971). Subsequent work using radiocarbon showed that at least some of the thermal waters had bulk ages of up to several thousand years (Evans, *et al.*, 1979). However, both this and a more recent study which included CFC dating techniques (BGS, unpublished data), 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 allowing the mixing of waters of different ages which, to a greater or lesser extent, is a feature of all Carboniferous thermal sources (Evans, *et al.*, 1979).

The Carboniferous Limestone is an important control on the groundwater chemistry, with previous studies showing that Ca-(Mg)-bicarbonate type groundwaters predominate throughout the study area. Some variations in SO_4^{2-} and Cl^- contents 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). In this area the Limestone aquifer is overlain by younger Carboniferous rocks of the Millstone Grit Series.

3.3 NATURAL SOURCES OF URANIUM IN THE STUDY AREA

The mineralogy and precise nature of U in the bedrock(s) of the study area are not known but a number of potential sources within the Carboniferous bedrock have been suggested (Table 3.1).

The micritic limestone matrix generally contains only low to moderate concentrations of U (typically $2\text{--}40\text{ mg kg}^{-1}$) which appear to be controlled by the amount of kerogen matter present in the limestone. Higher U contents occur in association with organic fragments (150 mg kg^{-1}) or in organic accumulations along stylolitic boundaries (several tens of

mg kg⁻¹) (Hyslop, 1993). The latter have large surface areas and are often laterally extensive and, hence, may provide an easily leachable source for further mobilisation of U and a possible pathway into the groundwater. In the north of the study area, high U concentrations (5–830 mg kg⁻¹) are associated with the presence of collophane (Peacock and Taylor, 1966), a fine-grained apatite variety, and/or uraninite (Parnell, 1988) which have replaced the micritic matrix and are frequently impregnated with hydrocarbons. Such small hydrocarbon globules appear to be present throughout the bedrock and contain considerable amounts of U (>500 mg kg⁻¹) (Hyslop, 1993). However, due to the rare occurrence and the small surface area of these globules it seems unlikely that they present an important source for U in the groundwater, although they may make some contribution.

Mineralised bedrock was found to be a major source of U (Hyslop, 1993). While U is generally not present within the mineral structure of vein minerals (calcite, fluorite, sulphides), it is more commonly associated with secondary oxides in late fractures and grain boundaries (Hyslop, 1993). These may provide an easily leachable source for further U mobilisation into the groundwater owing to their large surface area.

Table 3.1 Concentrations of U in the bedrock and sediments of the study area

Lithology/ Source	U concentration range (mg kg⁻¹)	Reference
Carboniferous Limestone	5- 830	Peacock and Taylor (1966)
Carboniferous Limestone	1-10	Ball et al. (1992)
Carboniferous Limestone (non-mineralised)	2- 40	Hyslop (1993)
Carboniferous Limestone (organic matter as fragments / in stylolithes)	5 - 150	Hyslop (1993)
Carboniferous Limestone (hydro-carbon inclusions)	> 500	Hyslop (1993)
Carboniferous Limestone (mineralised)	low to several hundred	Hyslop (1993)
Millstone Grit - gritstones	< 5	Hyslop (1993)
Millstone Grit – Edale Shales	20-60	Hyslop (1993)
Millstone Grit - Edale Shales	10 - 60	Ball et al. (1992)
Clay-rich deposits in karst cavities	15-24	Bottrell (1993)
Stream sediments (at Crich)	3-6	(Chenery, <i>et al.</i> , 2002)

Other potential sources of U in the study area are provided by the overlying Millstone Grit Series, which is composed of Namurian shales and gritstones. While low in the gritstones

(<5 mg kg⁻¹), the U content of the basal shales (Edale shales) is relatively high, varying between 4–35 mg kg⁻¹ (Ball, *et al.*, 1992, Hyslop, 1993), depending on the organic content of the rock. The distribution of U is generally very uniform throughout the groundmass, although secondary mobilisation has led to local enrichment of U in the shales. Erosion (transport and re-deposition) of these U-rich shales (and sediments) during the Tertiary and Quaternary may have created a secondary U source in the underlying karstified limestone, forming the U-rich fine-grained, clay deposits observed by Bottrell *et al.* (1999) and Gunn *et al.* (1991).

4 Methodology

A total of 26 samples were collected by BGS in July 2005 from natural springs, decommissioned mines and soughs and 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 3.1 as well as in Table 4.1. Table 4.1 also provides details on the type of source and the (predominant) lithology from which the groundwater originates.

Table 4.1 List of sampling sites

Site Number	Site Name	Easting	Northing	Type	Lithology
1	Litton Mill Spring	416068	372940	Sp	CL
2	Rockhead Spring	408660	372317	Sp	CL
3	Staden	407255	371933	Bh	CL
4	St Anne's Well	405787	373556	Sp, Th	CL
5	Russet Well	414800	382800	Sp	CL
6	Slop Moll (Sough)	414813	382761	S	CL
7	Penny Dale Farm	410919	380649	Bh	CL
8	Cavendish Mill (Water Grove Mine)	418900	375800	M	CL
9	Shepherds Flatt Farm	420060	377387	Bh	MG/CL
10	Michlow Well	417155	381724	M (?)	CL
11	Bagshave Rising	417400	381000	S	CL
12	Shining Bank Quarry	422857	364938	Bh	CL
13	Mawstone Spring	421480	362973	Sp	MG
14	Longcliffe Quarry	422795	355708	Bh	CL
15	Griffe Walk Farm	424300	356047	Bh	CL
16	Ladyflatte Mine	428072	353277	M	CL
17	Meerbrook Sough	432800	355200	S, Th	CL
18	Matlock Bath Grotto	429300	358000	Sp, Th	CL
19	Lightwood Borehole	405418	374881	Bh	CL /MG
20	Ashwood Dale Quarry	408075	372617	Bh	CL
21	Topley Pike Quarry	410130	372440	Bh	CL
22	Birchill Farm	422497	370955	Bh	MG/CL
23	Stoney Middleton Sough	423194	375537	S, Th	CL
24	Darley Dale Smelter	425771	362166	M	CL
25	Oddo House Farm	421780	360900	Bh	CL
26	Hindlow Quarry	408731	369079	Bh	CL

Legend:

<i>Bh</i> - Borehole	<i>CL</i> - Carboniferous Limestone
<i>M</i> - Mine shaft (disused)	<i>MG</i> - Millstone Grit
<i>S</i> - Sough	
<i>Sp</i> - Spring	
<i>Th</i> - Thermal	

The sampling sites were selected to include groundwaters from the Carboniferous Limestone aquifer as well as from the Millstone Grit aquifer, from mineralised and non-mineralised bedrock, mine drainage as well as 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 the large borehole volume (e.g., at Shining Bank Quarry and Lightwood), samples were collected after on-site readings of temperature, etc. had stabilised. Efforts were made to sample groundwater as close to the discharge as possible. Sampling from storage tanks was generally avoided unless a representative sample of groundwater was considered to be obtainable.

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 (Nalgen®) bottles. All samples were filtered through a $0.45\mu\text{m}$ filter and aliquots for cation and trace element analysis, including U, 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 $0.45\mu\text{m}$ silver-impregnated filter and collected in chromic-acid-washed glass vials.

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

5 Results

5.1 GENERAL GROUNDWATER CHEMISTRY

5.1.1 Major ions

Groundwaters from the study area display a wide range of physio-chemical characteristics and element concentrations. Groundwater chemistry data are summarised in Table 5.1 and Table 5.2. and probability distributions of selected elements are given in Figure 5.1 and Figure 5.2.

Most groundwaters are well buffered at circumneutral pH but some lower pH values are observed in the groundwaters of the Millstone Grit/Namurian shales at Mawstone Spring (BNG 421480 362973) and Shepherds Flatt Farm (BNG 420060 377387). The groundwaters are only weakly mineralised (SEC 229-981 $\mu\text{g l}^{-1}$) and higher conductivities are mostly associated with the geochemically more evolved thermal waters. Groundwater temperatures in the study area average around 10.2 °C, but are generally higher where thermal groundwaters occur, e.g. at St Anne's Well in Buxton (BNG 405787 373556) where temperatures of 25.1°C were observed.

Table 5.1 Concentrations of major elements in the groundwaters of the study area

Element	Units	Minimum	Mean	Median	Maximum	N° samples
T	°C	8.2	11.4	10.2	25.1	26
pH		5.94	7.31	7.33	8.82	26
Eh	mV	112	489	525	626	26
DO	mg l^{-1}	0.0	5.4	5.6	12.3	26
SEC	$\mu\text{S cm}^{-1}$	229	617	632	981	26
Ca	mg l^{-1}	2.4	83.6	94.1	134.0	26
Mg	mg l^{-1}	0.31	11.99	8.06	36.30	26
Na	mg l^{-1}	4.7	21.0	11.0	126.0	26
K	mg l^{-1}	< 0.5	1.3	1.1	4.0	26
Cl	mg l^{-1}	7.5	29.6	21.3	113.0	26
SO ₄	mg l^{-1}	5.0	34.0	24.6	134.0	26
HCO ₃	mg l^{-1}	21	258	266	356	26
NO ₃ as N	mg l^{-1}	< 0.05	3.09	3.00	8.50	26
NO ₂ as N	mg l^{-1}	< 0.0007	0.0007	0.0004	0.0025	26
NH ₄ as N	mg l^{-1}	< 0.006	0.023	0.003	0.194	26
TON	mg l^{-1}	< 0.01	2.96	2.84	8.32	26
P	$\mu\text{g l}^{-1}$	< 20	33	25	156	26
DOC	mg l^{-1}	0.40	1.12	0.86	3.77	26
F	$\mu\text{g l}^{-1}$	25	496	407	1490	26
Br	$\mu\text{g l}^{-1}$	< 20	81	57	405	26
Si	$\mu\text{g l}^{-1}$	1650	3970	2745	12800	26

Table 5.2 Concentrations of minor and trace elements in the studied groundwaters

Element	Units	Minimum	Mean	Median	Maximum	N° samples
Ag	µg l ⁻¹	< 0.05	0.03	0.03	0.14	26
Al	µg l ⁻¹	1	4	3	13	26
As	µg l ⁻¹	< 0.5	0.3	0.3	0.8	26
Au	µg l ⁻¹	< 0.05	0.03	0.03	0.14	26
B	µg l ⁻¹	< 20	27	10	199	26
Ba	µg l ⁻¹	11.44	163.7	145.3	599.8	26
Be	µg l ⁻¹	< 0.05	0.03	0.03	0.07	26
Bi	µg l ⁻¹	< 0.05	0.03	0.03	0.03	26
Cd	µg l ⁻¹	< 0.05	0.90	0.15	10.8	26
Ce	µg l ⁻¹	< 0.01	0.01	0.01	0.03	26
Co	µg l ⁻¹	0.02	0.11	0.09	0.28	26
Cr	µg l ⁻¹	< 0.5	0.5	0.3	1.3	26
Cs	µg l ⁻¹	< 0.01	0.04	0.01	0.17	26
Cu	µg l ⁻¹	0.4	1.8	1.5	4.8	26
Dy	µg l ⁻¹	< 0.01	0.01	0.01	0.01	26
Er	µg l ⁻¹	< 0.01	0.01	0.01	0.01	26
Eu	µg l ⁻¹	< 0.01	0.03	0.02	0.13	26
Fe	µg l ⁻¹	<5	307	5	6630	26
Ga	µg l ⁻¹	< 0.05	0.03	0.03	0.07	26
Gd	µg l ⁻¹	< 0.01	0.01	0.01	0.02	26
Ge	µg l ⁻¹	< 0.05	0.03	0.03	0.13	26
Hf	µg l ⁻¹	< 0.02	0.01	0.01	0.01	26
Hg	µg l ⁻¹	< 0.1	0.1	0.1	0.1	26
Ho	µg l ⁻¹	< 0.01	0.01	0.01	0.01	26
In	µg l ⁻¹	< 0.01	0.01	0.01	0.01	26
Ir	µg l ⁻¹	< 0.05	0.03	0.03	0.03	26
La	µg l ⁻¹	< 0.01	0.01	0.01	0.03	26
Li	µg l ⁻¹	0.1	6.7	1.5	35	26
Lu	µg l ⁻¹	< 0.01	0.01	0.01	0.01	26
Mn	µg l ⁻¹	< 0.05	186	1.28	4840	26
Mo	µg l ⁻¹	< 0.1	1.7	0.8	19	26
Nb	µg l ⁻¹	< 0.01	0.01	0.01	0.02	26
Nd	µg l ⁻¹	< 0.01	0.01	0.01	0.04	26
Ni	µg l ⁻¹	< 0.2	1.2	0.6	10.1	26
Os	µg l ⁻¹	< 0.05	0.03	0.03	0.03	26
Pb	µg l ⁻¹	0.1	3.0	0.8	15	26
Pd	µg l ⁻¹	< 0.2	< 0.2	< 0.2	< 0.2	26
Pr	µg l ⁻¹	< 0.01	< 0.01	< 0.01	0.01	26
Pt	µg l ⁻¹	< 0.01	< 0.01	< 0.01	< 0.01	26
Rb	µg l ⁻¹	0.24	1.03	0.86	3.43	26
Re	µg l ⁻¹	< 0.01	0.02	0.01	0.05	26
Rh	µg l ⁻¹	< 0.01	0.01	< 0.01	0.03	26
Ru	µg l ⁻¹	< 0.05	< 0.05	< 0.05	< 0.05	26
Sb	µg l ⁻¹	3	12	9	49	26
Sc	µg l ⁻¹	< 0.05	0.10	0.05	0.50	26
Se	µg l ⁻¹	< 1	1	< 1	1	26
Sm	µg l ⁻¹	< 0.5	1.2	0.9	3.4	26
Sn	µg l ⁻¹	0.08	0.11	0.11	0.17	26
Sr	µg l ⁻¹	37.12	278.5	103.8	1830	26
Ta	µg l ⁻¹	< 0.02	< 0.02	< 0.02	< 0.02	26
Tb	µg l ⁻¹	< 0.01	< 0.01	< 0.01	< 0.01	26
Te	µg l ⁻¹	< 0.05	< 0.05	< 0.05	< 0.05	26
Th	µg l ⁻¹	< 0.05	< 0.05	< 0.05	0.23	26
Ti	µg l ⁻¹	<10	<10	<10	<10	26
Tl	µg l ⁻¹	< 0.01	0.03	0.01	0.24	26
Tm	µg l ⁻¹	< 0.01	< 0.01	< 0.01	< 0.01	26
U	µg l ⁻¹	< 0.02	1.36	1.10	4.23	26
V	µg l ⁻¹	< 0.2	0.3	0.2	1.3	26
W	µg l ⁻¹	< 0.02	< 0.02	< 0.02	0.07	26

Element	Units	Minimum	Mean	Median	Maximum	N° samples
Y	$\mu\text{g l}^{-1}$	0.01	0.03	0.03	0.09	26
Yb	$\mu\text{g l}^{-1}$	< 0.01	< 0.01	< 0.01	0.02	26
Zn	$\mu\text{g l}^{-1}$	2.2	140	61	1050	26
Zr	$\mu\text{g l}^{-1}$	< 0.02	< 0.02	< 0.02	0.04	26

Most groundwaters are oxidising ($E_{h_{\text{median}}} = 525 \text{ mV}$) but low DO concentrations and Eh values occur at a number of sites indicating that reducing conditions prevail locally, in particular where the aquifer is confined by basaltic lava or Namurian shales.

The variations in major-ion composition of the sampled groundwaters are illustrated in the Piper plot in Figure 5.3. Different symbols have been used to distinguish between thermal waters, mine/sough waters and groundwaters from the Carboniferous Limestone and Millstone Grit aquifers. The plot illustrates that the groundwaters in the study area can be separated into three groups of different chemical composition: (1) Ca-Mg- HCO_3 type, (2) Ca- SO_4 -Cl type waters and (3) Na- HCO_3 type groundwaters.

The majority of groundwaters are of Ca-Mg- HCO_3 type and include thermal waters, mine drainage as well as groundwaters from the Dinantian and Namurian strata. They are relatively constant in their chemical composition except for slight variations in Mg, Na and Cl contents.

Four samples show a tendency towards Ca-(SO_4)-Cl type waters including one sample from the Millstone Grit aquifer collected at Mawstone spring (NGR 421480 362973). Mineralisation in the Millstone Grit groundwater is generally much lower than in the limestone groundwaters due to the carbonate-poor lithology and Cl and SO_4 are the major anions although the total concentrations of these anions are low. The two thermal waters of Ca- SO_4 -Cl type are characterised by increased salinity and SO_4 content and were collected from the mineralised eastern part of the study area at Matlock Bath (BNG 429300 358000) and Stoney Middleton (NGR 423194 375537). They differ in composition from the thermal waters from the western, non-mineralised part of the study area (near Buxton), and are probably derived from a different thermal centre (Edmunds, 1971). The groundwater composition at Brierlow Quarry (NGR 408731 369079), near Buxton, tends more towards a Ca-Cl type water. The sample was collected from one of the deepest boreholes in the study area (213.5m) and the increased salinity is probably due to mixing with deeper, more mineralised (connate) waters (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.

Groundwaters of Na- HCO_3 type occur in the deeper groundwaters near Youlgreave (at Shining Bank Quarry (NGR 422857 364938)) and near Buxton (in the Lightwood borehole (NGR 405418 374881)). The aquifer in both areas is locally confined, by the Conksbury Bridge Lavas and by Namurian shales and mudstones, respectively. Both groundwaters are characterised by considerably lower concentrations of Ca, Mg and Ba while Na, Li and Rb are enriched. The low Cl levels indicate that the aquifer has generally been well flushed of original formation waters, so that high Na concentrations are more likely to be the result of ion exchange of Na on clay minerals for Mg and Ca from the infiltrating groundwaters. Ion exchange processes occur in a wide range of aquifers where Na-charged cation exchange media are present (e.g., as a result of post-glacial seawater incursions), such as in the Carboniferous Limestone of North Yorkshire (Abesser, *et al.*, 2005a), the Lincolnshire Limestone (Edmunds, 1981) and other lithologies such as the Millstone Grit (Abesser, *et al.*, 2005b) and the Coal Measures (Banks, 1997a). Plagioclase weathering may have contributed

to the formation of Na-HCO₃-type waters and such processes were found to be responsible for the wide occurrence of Na-HCO₃-type waters in the Norwegian crystalline bedrock aquifers (Banks and Frengstad, 2006). Such processes are probably more important at Shining Bank Quarry where the aquifer is overlain by plagioclase-rich basaltic lava deposits and where elevated Si (6.3 mg l⁻¹) and Al concentrations (10 µg l⁻¹) in the groundwater occur. However, even if plagioclase dissolution is important, it must be followed by calcite precipitation and/or cation exchange, to remove the Ca, released during plagioclase hydrolysis and carbonate dissolution, from the system.

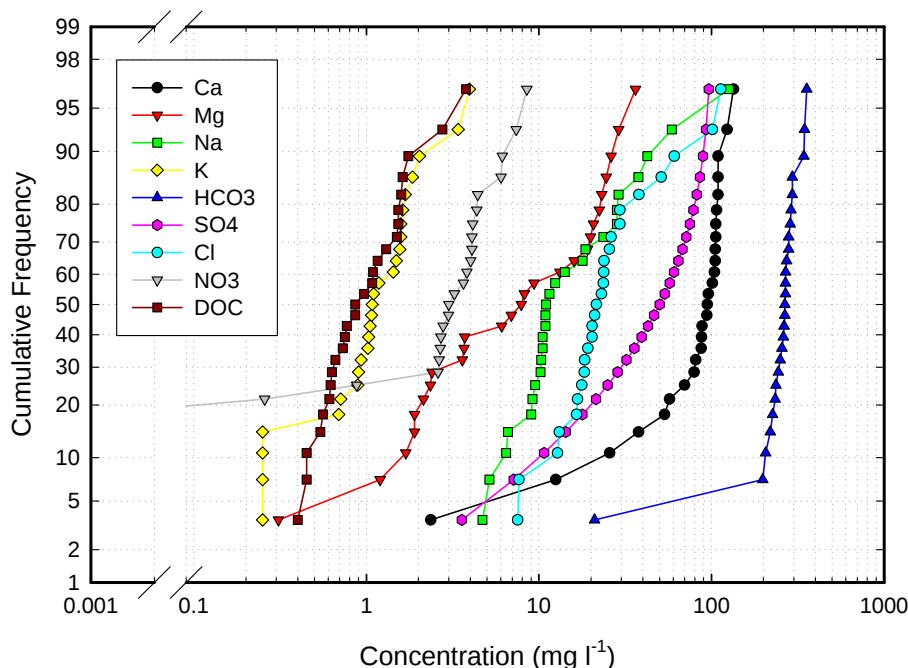


Figure 5.1 Probability plots of main element distribution in the groundwaters of the study area

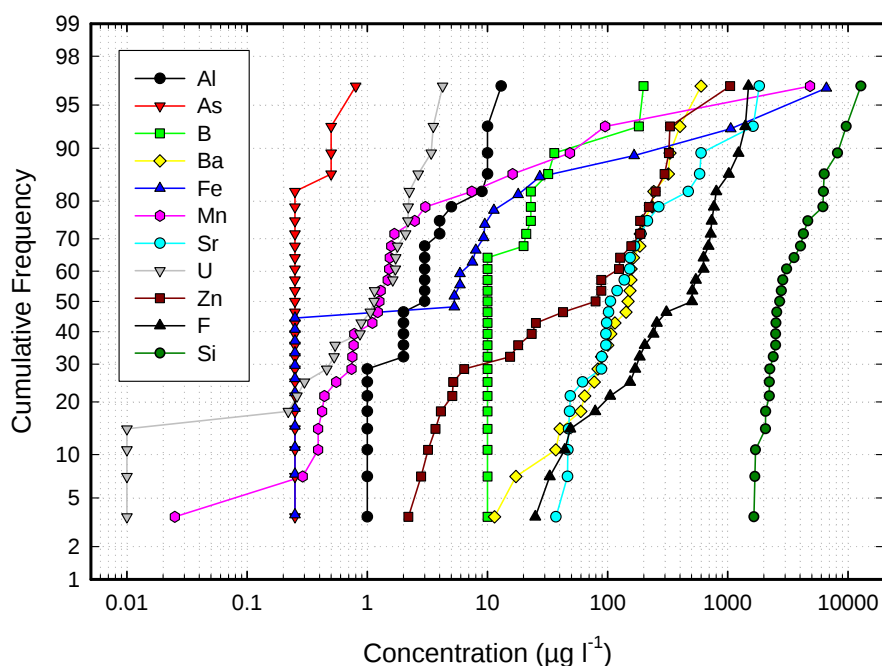


Figure 5.2 Probability plots of minor and trace element distribution in the groundwater of the study area

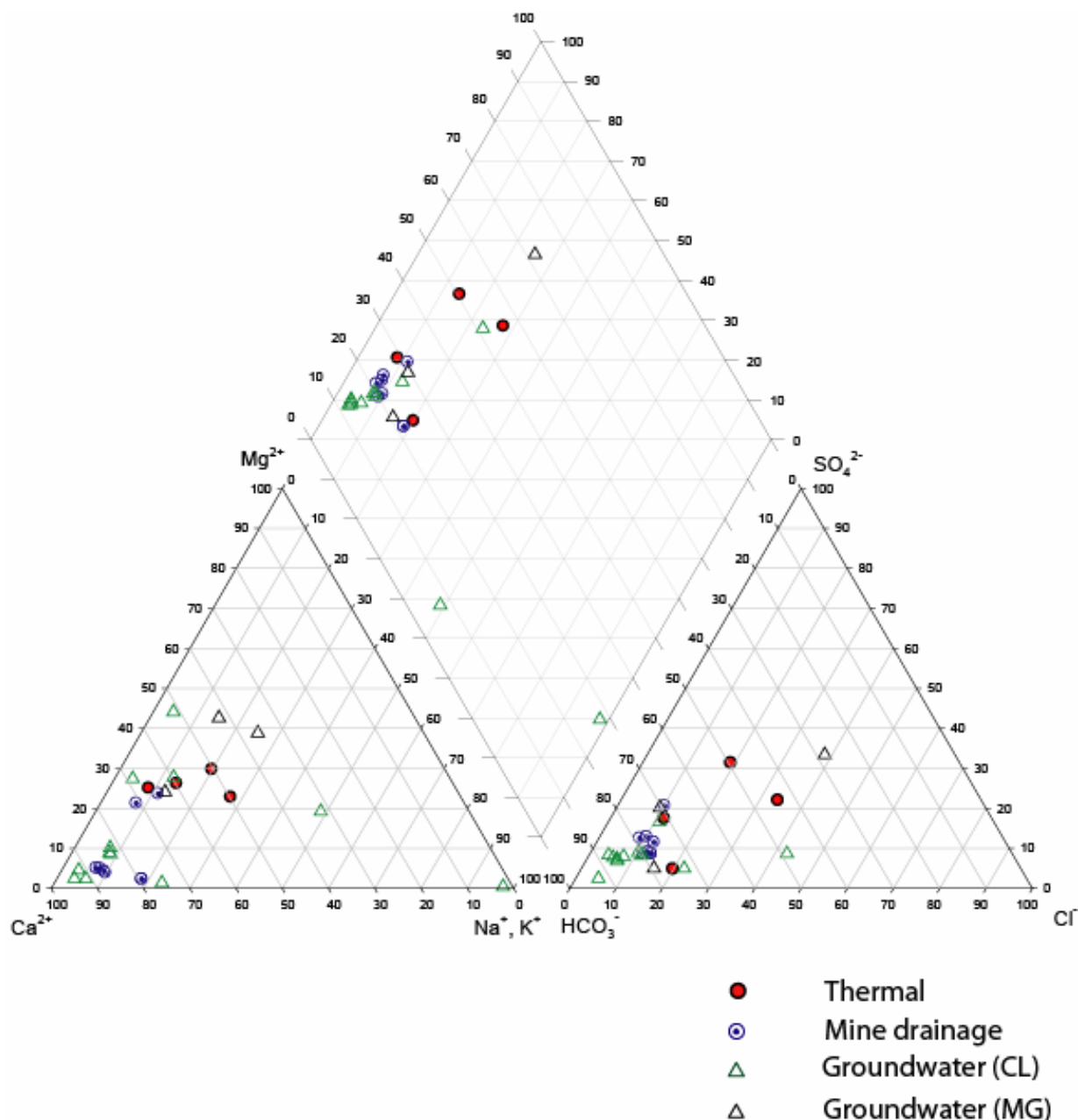


Figure 5.3 Piper Plot showing relative concentrations of major cations and anions in the groundwaters of the study area, including thermal waters, mine drainage waters and groundwaters from the Carboniferous Limestone (CL) and the Millstone Grit (MG) aquifers

The spatial variations in the groundwater chemistry clearly reflect the distribution of bedrock geology and mineralisation. Groundwaters of the Carboniferous Limestone aquifer are characterised by high Ca and HCO_3 content and, except for three groundwaters, are either saturated or over-saturated with respect to calcite (Figure 5.4). Since equilibrium with calcite is rapidly achieved, the presence of undersaturated groundwaters in the limestone implies that (1) mixing of different groundwaters, (2) degassing of saturated waters during turbulent flow or (3) mixing of CO_2 -rich soil air with atmospheric air in the cavern system has occurred. The three samples were collected near the northern edge of the outcrop and it is likely that mixing with Millstone Grit groundwaters has taken place, resulting in undersaturation.

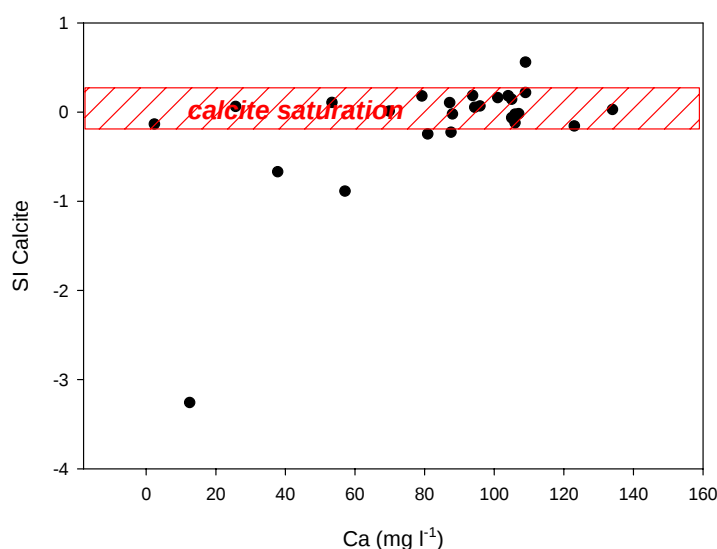


Figure 5.4 Relationship between calcite saturation and Ca in the groundwaters

Magnesium contents in the groundwaters are relatively low but tend to be higher in the south-east of the study area (around Matlock), where bedrock dolomitisation is widespread and dolomite saturation in the groundwaters is common. In the Millstone Grit aquifer, Ca and HCO_3 concentrations are low and groundwaters remain unsaturated with respect to calcite and dolomite, (due to the base poor nature of the bedrock) while saturated with respect to quartz.

5.1.2 Trace elements

High fluoride concentrations are found in the groundwaters from the eastern edge of the Carboniferous Limestone outcrop and correspond approximately with the occurrence of fluorite mineralisation but also with low Ca contents which favour the accumulation of F in the groundwater (CaF_2 solubility control). Westwards of this zone, high Ba groundwaters occur, probably related to the barite gangue mineralisation, although elevated Ba levels are also observed in the groundwaters near Buxton. There is a clear difference in Sr distribution between groundwaters from the west and from the east. Concentrations are generally higher on the eastern edge of the outcrop, probably related to the presence of barite mineralisation which has been linked to groundwater Sr concentrations higher than $100 \mu\text{g l}^{-1}$ (Edmunds, 1971). Strontium is also distinctly enriched in the thermal waters, including those from the Buxton area. Such enrichment may, in fact, be diagnostic for thermal waters in which high concentrations of Sr can accumulate due to the increased mineral solubility at high temperatures, the long water-rock contact times and the absence of a strontianite (SrCO_3) solubility control (Banks, 1997a).

Lead is present in mine drainage waters, but is also commonly detected in groundwaters at the eastern edge of the Carboniferous Limestone outcrop. In the area around Matlock, high Pb concentrations in the groundwater are often associated with high Zn corresponding to the main area of Pb-Zn mineralisation (Aitkenhead, *et al.*, 2002, Frost and Smart, 1979). Nickel concentrations are also highest in the south-east of the study area with highest concentrations being found at the Darley Dale Smelter, which abstracts water from the former Millclose (Lead) Mine. Copper is present throughout the study area but concentrations in the soughs and mine shafts are low. There is no clear pattern in the distribution of Cu, suggesting that Cu mineralisation is very localised.

Molybdenum is found in all mine drainage and thermal waters but also occurs in the groundwater at Topley Pike Quarry (NGR 410130 372440), near Buxton. Concentrations in this groundwater are $18.5 \mu\text{g l}^{-1}$ —the highest in the study area—and agree with anomalous concentrations ($16 \mu\text{g l}^{-1}$) observed during a previous study by Edmunds *et al.*, (1989). Molybdenum induces a Cu deficiency in many animal species (Wennig and Kirsch, 1988) and Mo anomalies in stream sediments in Derbyshire were linked to the occurrence of hypocupremia (abnormally low levels of copper in the blood) 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.

Sulphate is higher in the groundwaters of the mineralised areas, and probably originates from the oxidation of sulphide minerals such as galena (PbS), sphalerite (ZnS) or pyrite (FeS) in the mineral-vein “rakes” and leaching into the groundwater during its passage through mineralised fractures.

5.2 URANIUM IN GROUNDWATERS OF THE STUDY AREA

Uranium concentrations in the study area range between <0.02 and $4.23 \mu\text{g l}^{-1}$ (median $1.14 \mu\text{g l}^{-1}$) (Table 5.2.). These concentrations are relatively low compared with high U-groundwaters worldwide (Banks, *et al.*, 1995, Langmuir, 1997, Ragnarsdottir and Charlet, 2000, Smedley, *et al.*, 2006) and do not exceed the WHO (provisional) guideline level for drinking water of $15 \mu\text{g l}^{-1}$. However, median concentrations in the Derbyshire groundwater are considerably higher than those observed in most other UK aquifers of similar lithology (Smedley, *et al.*, 2006). In the Carboniferous Limestone of North Yorkshire, for example, median groundwater U concentrations were $0.31 \mu\text{g l}^{-1}$ (N=24) (Abesser, *et al.*, 2005a, Smedley, *et al.*, 2006) while average (mean) values in the Carboniferous Limestone of the Mendip Hills were $0.86 \mu\text{g l}^{-1}$ (N=12) (Bonotto and Andrews, 2000).

Uranium concentrations in the groundwaters are commonly higher in the eastern, mineralised part of the study area (Figure 5.5), along the limestone-shale boundary, and high concentrations are mostly associated with drainage from mines or soughs and/or with thermal waters. In the western part of the study area, around Buxton, U concentrations in the groundwater are low ($<1 \mu\text{g l}^{-1}$), except for the thermal water at Buxton (St Anne’s Well (NGR 405787 373556)) and the groundwater at Topley Pike Quarry (NGR 410130 372440) which have the highest U contents ($3.54 \mu\text{g l}^{-1}$ and $4.34 \mu\text{g l}^{-1}$, respectively) in the study area. In the groundwaters of the Millstone Grit, U concentrations are generally low, in most cases below the detection limit of $0.02 \mu\text{g l}^{-1}$. Equally low concentrations were observed by other geochemical studies in the Millstone Grit groundwaters in Yorkshire (Abesser, *et al.*, 2005b) and in Derbyshire (Banks, 1997a).

Figure 5.5 illustrates that the distribution of U in groundwaters of the study varies spatially. Since most groundwaters were derived from the Carboniferous Limestone, except for the three Millstone Grit groundwaters, factors other than bedrock lithology must control the concentrations and spatial distribution of U in the groundwaters of the study area, and U may actually be derived from different sources.

The mobilisation of U in water has been described in Section 2. Redox conditions, pH and solution chemistry were identified as the most important controls on U concentrations in groundwaters. The influence of these parameters on groundwater U in the study area is illustrated in Figure 5.6. The graph shows that high U concentrations are limited to oxidising groundwaters with Eh $> 450\text{mV}$ where U is likely to be present as the highly soluble U(VI)

form. Where reducing conditions prevail, e.g., as in the groundwaters of the Millstone Grit/Namurian Shales, U concentrations are low due to the low mobility of U(IV) which is the dominant U species in such reducing environments.

There is also a weak relationship with pH (Figure 5.6b). Below pH 7, U concentrations are usually low, due to lack of aqueous carbonate which is the most important U complexing agent in most natural waters. Above pH 7, U concentrations are generally higher. The relationship between groundwater U and alkalinity is less well defined (Figure 5.6c) probably because alkalinity in the sampled groundwaters is generally high ($\text{HCO}_3^- > 200 \text{ mg l}^{-1}$) and U carbonate complexation is only limited below pH 7 where U(VI) hydroxyl complexes predominate (Langmuir, 1997).

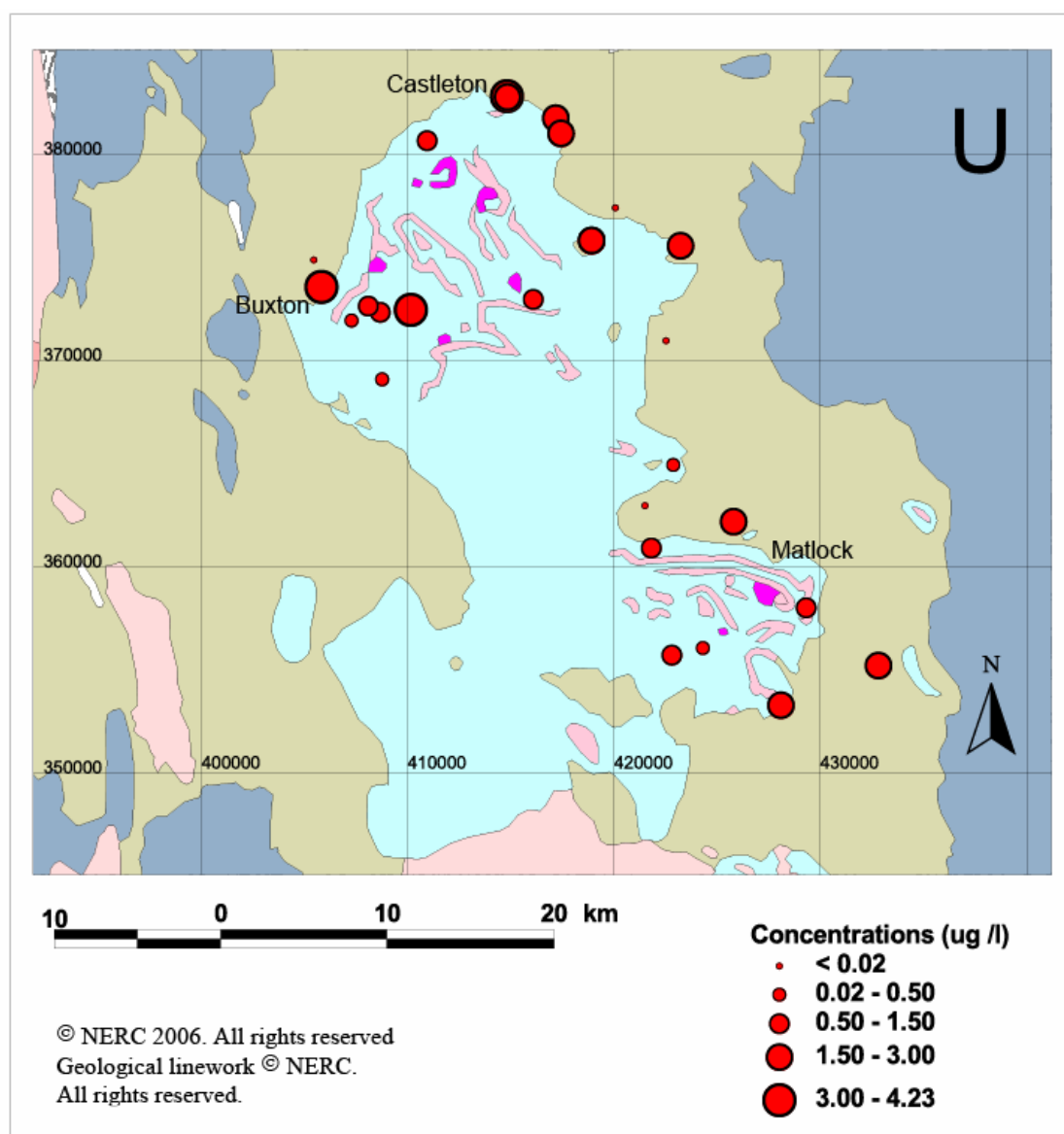


Figure 5.5 Distribution of U ($\mu\text{g l}^{-1}$) in the groundwaters of the study area

The relationships between U and the elements F, Ba, Fe and Mo are illustrated in Figure 5.7. Different symbols have been used to distinguish between thermal waters, waters from mines and soughs (mine drainage) and spring/borehole waters. The plots show that high U concentrations are generally associated with groundwaters from mines and soughs or with

thermal waters, although the highest observed U concentrations were found in the groundwater at Topley Pike Quarry (NGR 410130 372440), which was collected from a borehole.

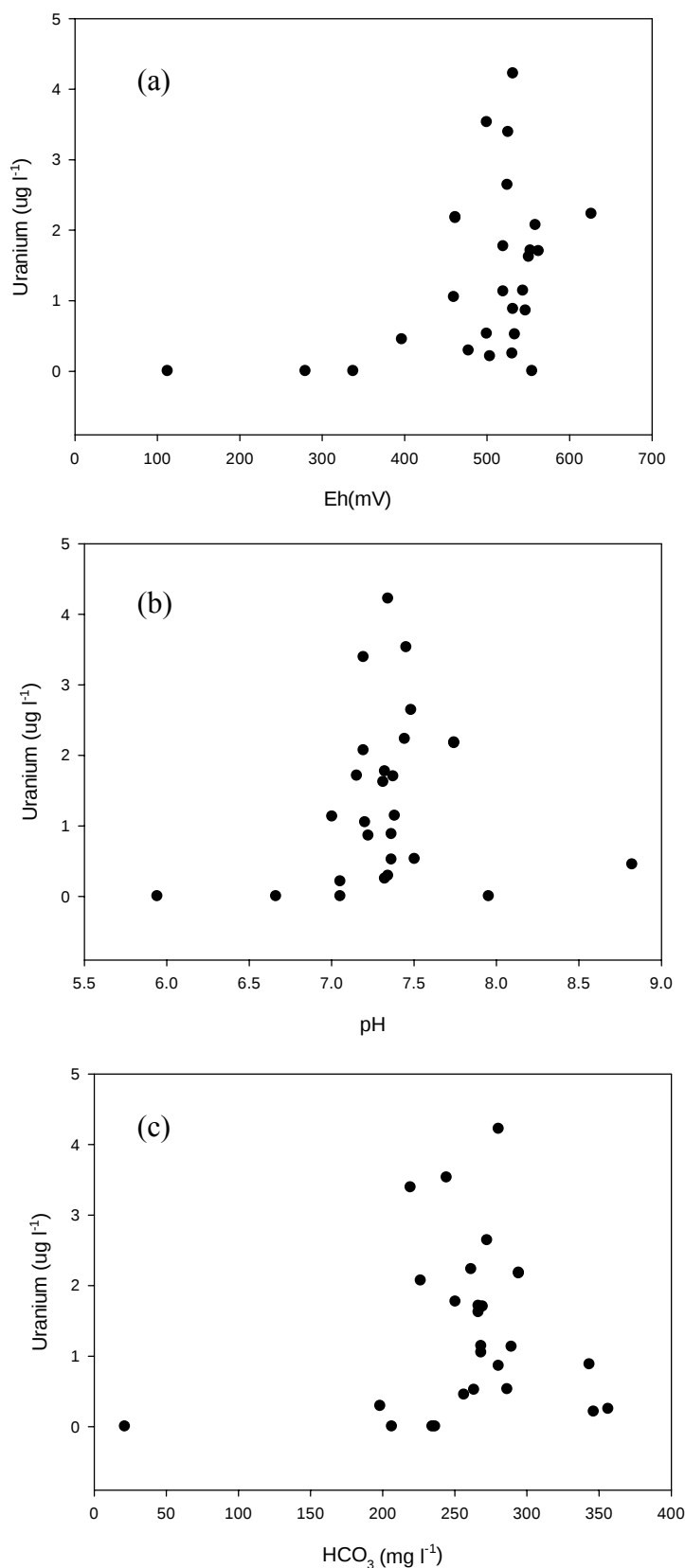


Figure 5.6 Relationship between U and (a) redox (as Eh), (b) pH and (c) alkalinity (as HCO_3)

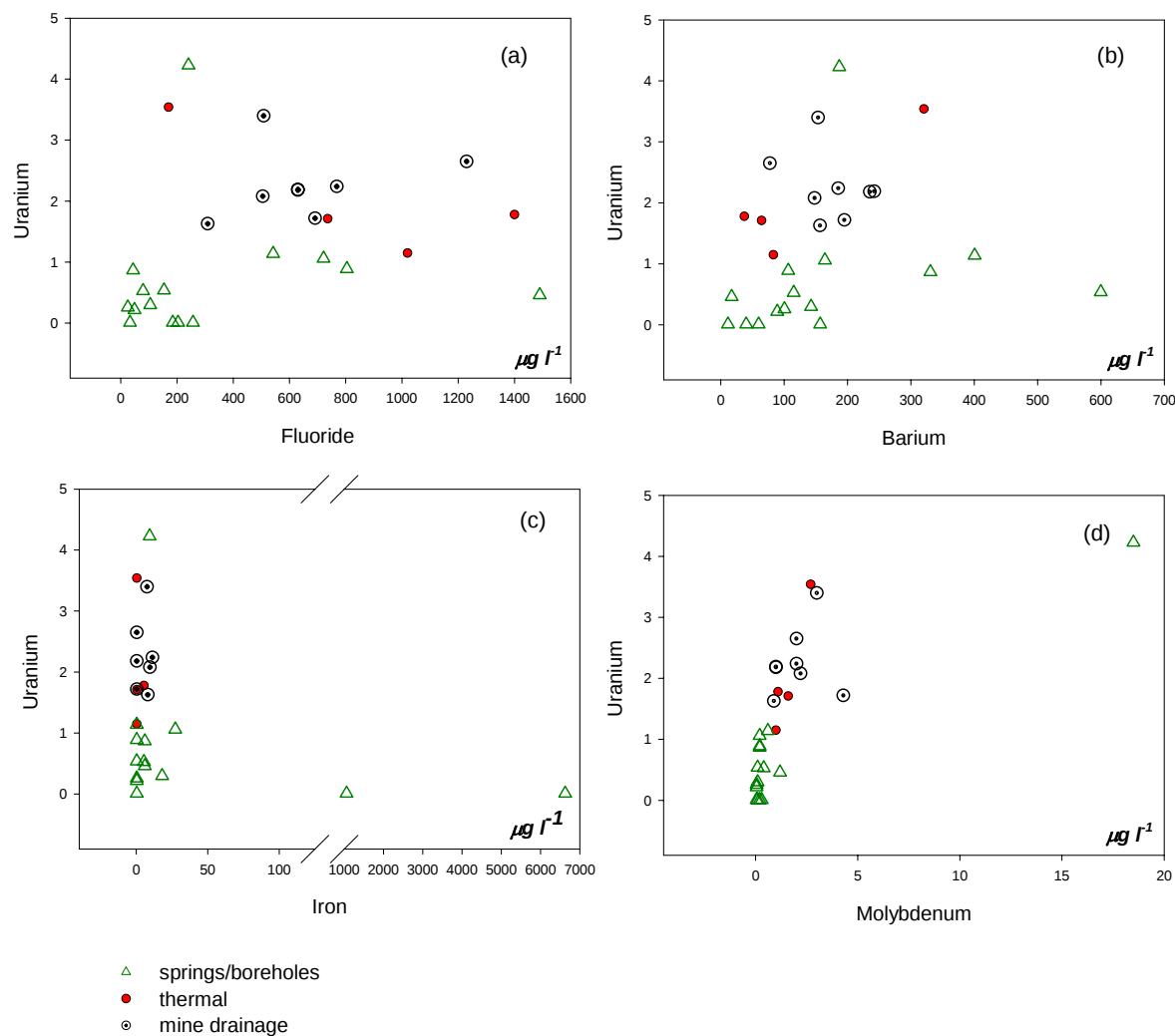


Figure 5.7 Relationship between uranium and (a) fluoride, (b) barium, (c) iron and (d) molybdenum (all concentrations in $\mu\text{g l}^{-1}$)

Uranium shows no clear relationship with F (Figure 5.7a), which is indicative of gangue mineralisation (see section 3.1), although in the thermal and mine drainage waters from the mineralised, eastern part of the study area, high U groundwaters are generally also enriched in F. Many of these waters also contain increased levels of Pb and/or Zn, indicating that dissolution of mineral veins and oxidative alteration of secondary oxides have significantly modified the groundwater chemical signature and may have contributed to the U enhancement. A positive correlation exists between U and Ba, which is also an important element in gangue mineralisation (e.g., barite veins). It is interesting to note that high concentrations of both, F and Ba, as well as U are generally associated with thermal waters and/or mine drainage. This suggests that groundwater residence times as well as bedrock mineralisation control/influence the presence/concentrations of these elements in the groundwater.

There is no clear trend between U and most other redox elements such as Fe (and Mn), except for Mo, although groundwaters with high Fe (and Mn) concentrations are generally low in U. This would be expected owing to the contrasting redox behaviour of these elements.

However, the co-occurrence of both, elevated U and Fe concentrations is possible and has been observed in the groundwaters at Litton Mill Spring (NGR 416068 372940) and at Topley Pike Quarry (NGR 410130 372440). At Topley Pike Quarry, the groundwater is clearly enriched in U, Fe and Mo, and also has increased levels of trace elements such as Cd, Co, Cr, Ni, Se, Sm. The borehole is located near the hydrothermal mineral veins (rakes) which stretch from Chelmorton north-westwards (Edmunds, 1971, Ford, 1968b) and metal enrichment in the groundwater is probably related to local bedrock mineralisation. Iron oxides are present near the western end of the vein system (Strahan and Carruthers, 1923; Wilson, 1922 in Ford (1968a)) and dissolution of these may have contributed towards enhanced U concentrations. The slightly elevated groundwater temperature of 12.2°C suggests that a thermal component may also be present.

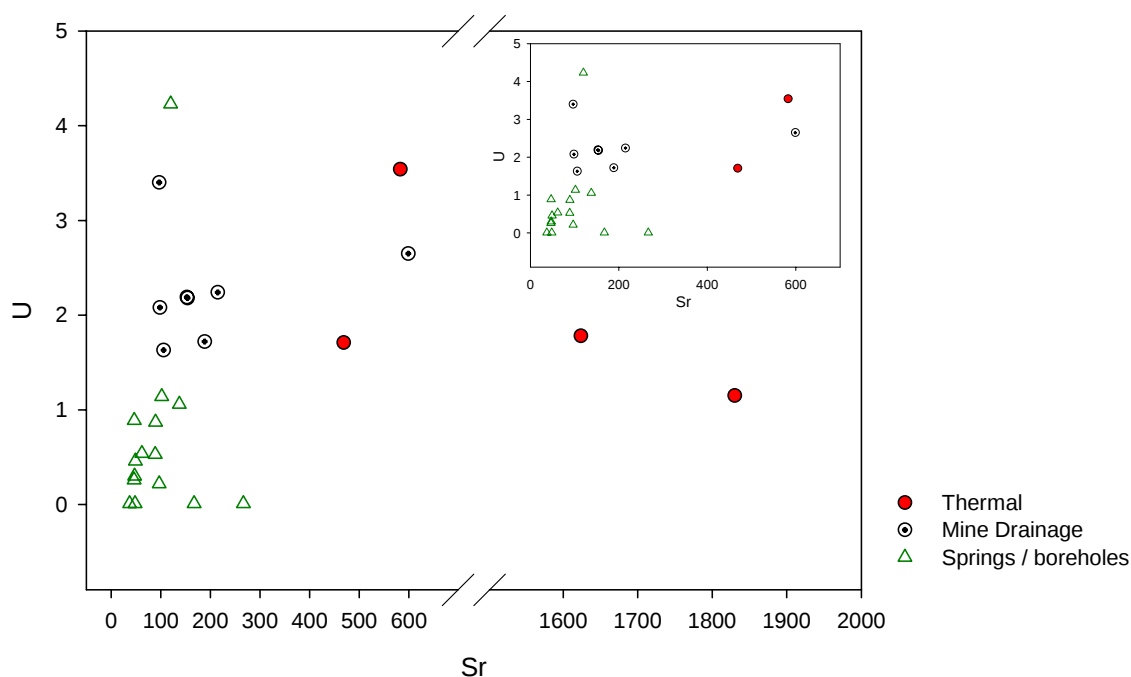


Figure 5.8 Relationship between U and Sr in the groundwaters of the study area (concentrations in $\mu\text{g l}^{-1}$).

A reasonably good correlation exists with Sr (Figure 5.8) which, in the Carboniferous Limestone, is principally derived from congruent or incongruent solution of carbonate or from barite (Edmunds, *et al.*, 1989). The trend is less obvious in the thermal waters from Stoney Middleton and Matlock Bath where Sr concentrations are significantly higher probably due to the presence of barite mineralisation.

The best elemental correlation in the groundwaters is observed for U and Mo. Molybdenum often occurs together with Pb (and Cu) ores, although it is also used as a micronutrient in agricultural applications (Wennig and Kirsch, 1988).

There is no clear relationship between U and DOC in the groundwaters of the study area (Figure 5.9), although increased DOC concentrations are found in the U-rich mine-drainage groundwaters around Castleton and Bradwell. While DOC may originate from bedrock weathering of Carboniferous Limestone and/or organic-rich Namurian shales, other sources such as organic-rich runoff from the Moors and Dales, situated North of the study area, as well as anthropogenic sources need to be considered. The somewhat increased NO_3 concentrations ($\sim 4 \text{ mg l}^{-1}$ as N) in some of these groundwaters (e.g., at Bagshave Rising

(NGR 417400 381000) and Michlow Well (NGR 417155 381724)) suggest that contributions from anthropogenic DOC sources are possible. Pollution incidents from point-sources as well as from diffuse agricultural inputs have been reported in the Peak-Speedwell Cavern system (which feeds the springs at Slop Moll and Russet Well) (Gunn, *et al.*, 2000) as well as in a sinking stream in the area (Hunter, *et al.*, 1999). In contrast, studies on cave sediments using stable isotopes ($^{13}\text{C}/^{12}\text{C}$ ratio) concluded that most DOC is derived from natural sources, e.g., C_3 plants, rather than from agricultural pollution (Bottrell, 1996).

No clear trend is observed between P and U in the groundwaters (Figure 5.9), except for the groundwaters in the Castleton/Bradwell area which have slightly higher P concentrations ($>40 \mu\text{g l}^{-1}$) compared to most other groundwaters in the study area. While anthropogenic sources are possible (see discussion above), the occurrence of phosphate in the Carboniferous Limestone of the Castleton area (close to the outcrop of the Edale Shales) has been established by Peacock and Taylor (1966). These phosphate-rich limestones often contain high levels of U_3O_8 ($5\text{--}660 \text{ mg kg}^{-1}$) and leaching of uraniferous phosphate has been considered to cause high U concentrations ($13\text{--}15 \mu\text{g l}^{-1}$) in spring waters at the limestone/shale contact in the Castleton area (Peacock and Taylor, 1966). The high bicarbonate concentrations have probably increased the solubility of U in the spring water, although in the presence of phosphate, uranyl ions also form strong complexes with phosphate. Speciation calculations using PHREEQC indicate that phosphate complexes (in the form of $\text{UO}_2(\text{HPO}_4)_2^{2-}$) dominate in the groundwaters around Castleton and while there is no relation between P and U in the groundwaters of the study area, a significant positive correlation exists between U and $\text{UO}_2(\text{HPO}_4)_2^{2-}$ (Figure 5.9). Hence, complexation with phosphate rather than with carbonate may be important in the Castleton groundwater; the dominance of phosphate complexation over carbonate complexation has also been observed in laboratory studies (Sandino and Bruno, 1992) although the validity of including $\text{UO}_2(\text{HPO}_4)_2^{2-}$ in geochemical models has been debated.

Similarly, the presence of naturally-derived organic matter has probably also affected the U speciation and stability, increasing the residence time of dissolved U in the groundwater through the formation of stable complexes of uranyl with organic ligands (fulvic and humic acids) (Singhal, *et al.*, 2005).

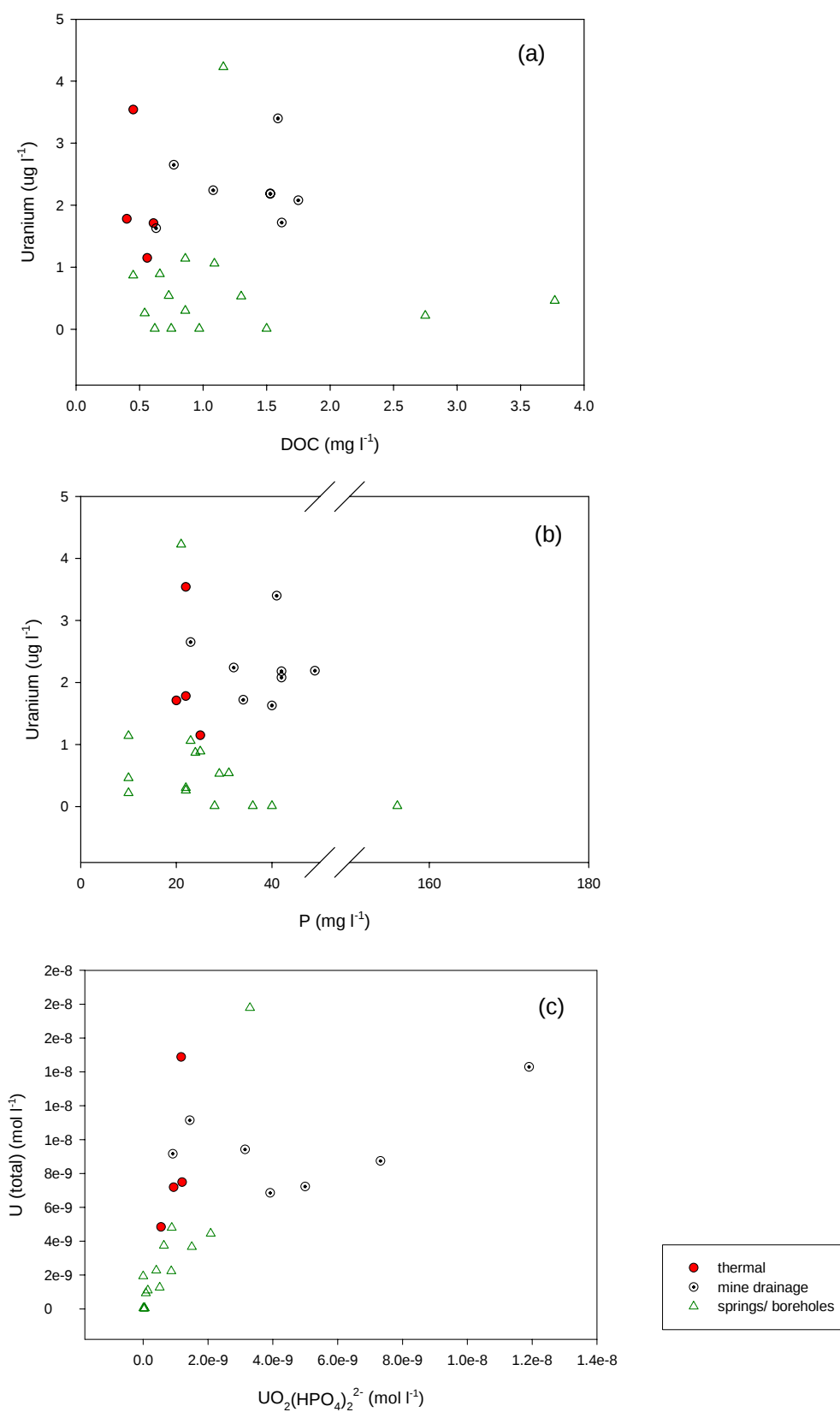


Figure 5.9 Relationship between U and (a) DOC, (b) phosphorus and (c) U phosphate complexes ($\text{UO}_2(\text{HPO}_4)_2^{2-}$).

6 Discussion

6.1 CONTROLS AND POTENTIAL SOURCES OF URANIUM

Uranium concentrations in the groundwater of the study area are largely controlled by hydrochemical factors, such as pH and redox condition in the groundwater as well as by complexation with carbonates (Figure 5.6). Complexation with phosphate and/or organic matter may also play a role in increasing the mobility of dissolved U in the groundwater, at least in parts of the aquifer. However, based on the available data this can only be hypothesized.

Bedrock mineralisation appears to be a major control on U in the groundwater as indicated by the spatial distribution of U in the study area (Figure 5.5) and by the high concentration associated with drainage from soughs and mines (Figure 5.7). Uranium in the mineralised bedrock is commonly associated with secondary Fe oxides in late fractures, grain boundaries and stained wall rocks (Hyslop, 1993). Enriched U concentrations are also present in the thermal groundwaters, which originate from old, deep waters (Edmunds, 1971) and are probably to some extent due to greater contact times of the water with uranium-bearing bedrock. However, the U content of non-mineralised limestone is typically low (Hyslop, 1993), which may explain why U concentrations in the thermal waters do not usually exceed those in the groundwater of the mineralised part, despite their more evolved nature. It has been suggested that reducing conditions are present at depths within the aquifer (Downing, 1967) and reducing conditions have also been encountered in the thermal waters at St Anne's well (BGS, unpublished data). Hence, this could limit the U solubility in the deeper (thermal) groundwaters and/or promote precipitation of U from these waters prior to their 'ascent' and mixing with more recent, oxidising recharge waters.

It is likely that anthropogenic activities, such as mining, have indirectly contributed to the elevated U concentrations in the mine drainage groundwaters by creating larger cavities and rock debris and hence providing artificially high surface areas for enhanced bedrock weathering. Agricultural inputs, in particular from PO_4 based fertilizers, may also have added some U to the groundwaters. Uranium concentrations in such fertilizers can be very high (up to 221 mg kg^{-1}) (Hamamo, *et al.*, 1995) and prolonged agricultural application was found to increase U concentrations in rivers and runoff waters (Conceicao and Bonotto, 2003, Zielinski, *et al.*, 2000). Pollution incidents have occurred in the groundwaters around Castleton, including fertilizer leachate (Gunn, *et al.*, 2000), but groundwater and sediment studies have suggested that composition in these groundwaters is dominated by water-rock interactions (Bottrell, *et al.*, 2000) and less affected by agricultural inputs. The contribution from phosphate-derived U is, therefore, believed to be minimal although relative increases may occur during storm events when inputs from direct surface runoff into the groundwater system increase.

Other potential U sources exist in the study area (see section 3.3), such as the shales of the Millstone Grit strata which are enriched in U (Hyslop, 1993). Most groundwaters from springs, mine drainage and probably some thermal waters contain varying proportions of water derived from the Namurian shales. It is possible that some of the U in these groundwaters originates from Namurian bedrock rather than from the limestone and/or mineralisation. This may be particularly important in areas where the limestone aquifer is directly recharged by run-off from the Millstone Grit Series and where a high proportion (e.g., up to 37% in the Peak-Speedwell Cavern system) of the allogenic (i.e. originating outside the karst system) water is derived from Namurian strata (Bottrell, *et al.*, 2000). However, groundwater circulation in the Namurian shales is probably limited and mobility of U is

restricted by reducing conditions. Hence, in-situ mobilisation and direct release of U from the Namurian shales into the groundwater is probably of minor importance. A more likely source are the clay-rich deposits which originate from the weathering and re-deposition of Namurian sediments and are a common feature in the limestone karst near the limestone-shale interface (Bottrell, 1993). The deposits are characterised by high U levels and high surface areas (small grain size) and when in contact with the groundwater, they could be potentially important in terms of U release.

6.2 POTENTIAL FACTORS LIMITING URANIUM CONCENTRATIONS IN THE GROUNDWATER

The observed U concentrations in the groundwaters are less than would be expected given the results from previous groundwater surveys (Peacock and Taylor, 1966) and considering the relative abundance of U in bedrock and mineralisation (Hyslop, 1993, Parnell, 1988, Peacock and Taylor, 1966) as well as the high Rn levels observed in soil gas (Ball, *et al.*, 1991, Ball, *et al.*, 1992), dwellings and limestone caverns (Gunn, *et al.*, 1991) of the study area. A number of possible explanations for these relatively low U concentrations are discussed in the following section.

1. Many of the groundwaters in the area are derived from springs and mines/soughs and contain a proportion of allogenic water with residence times of as little as 50 h (Gunn, 1991). Such short residence times and the generally rapid flows of limestone groundwaters through the karst and mine conduits compared with the relatively slow kinetic rate of dissolution and oxidation of metal oxides may have limited the U concentrations in the groundwaters. Inputs of such allogenic waters may also have diluted the U concentrations in the more evolved, U-enriched groundwaters.
2. The rather low enrichment (compared to other mineralised areas worldwide) may also be due to the buffering effect of the limestone which maintains groundwater pH of greater than 7, restricting the mobility and solubility of uranyl minerals. Uranium retention in oxidising, near-neutral groundwaters is further enhanced in the presence of iron owing to adsorption of U onto hydrous ferrous oxides (Hfo) and the formation of Hfo-U complexes. However, U adsorption and complexation is pH dependent and will be less at high pH.
3. Banks (1997b) suggested that groundwater in the vicinity of ore bodies is saturated with respect to heavy metal carbonates, thus limiting the solubility and mobilisation of these elements. The water is then being diluted by limestone water from non-mineralised parts during its passage through the aquifer.
4. Given that a hydraulic equilibrium in the aquifer has long been established with limited water table fluctuations, it is possible that easily leachable U has been removed from the aquifer by prolonged weathering under oxidising conditions, in particular in the zone of active groundwater flow. Alternatively, stable water table conditions may have limited the oxygen flux in parts of the aquifer, thereby limiting U mobility.

6.3 IMPLICATIONS FOR USE AS DRINKING WATER SOURCE

Uranium in the groundwaters of the study area is present in moderate concentrations (Table 5.2) and the maximum U concentration of $4.23 \mu\text{g l}^{-1}$ is well below the WHO (provisional) guideline level for drinking water of $15 \mu\text{g l}^{-1}$ (WHO, 2004). Increased concentrations are present in groundwaters from mines and soughs, some of which are now used as a source for public water supply (e.g., Meerbrook Sough, Ladyflatte Mine). While chemical guideline

levels for U are not exceeded in these waters, CEFAS RIFE reports have shown that concentrations of alpha emitting radionuclides (including U) in the groundwater at Meerbrook Sough regularly exceed the WHO screening values of 0.1 Bq l^{-1} (CEFAS, 2003). Measurements of groundwater radioactivity have not been included in this study, but U activities can be estimated from the observed mass concentrations. Assuming secular equilibrium between ^{234}U and ^{238}U in the groundwater and applying the commonly used conversion factor of $1 \mu\text{g} = 2.5 \times 10^{-2} \text{ Bq } (^{234}\text{U} + ^{238}\text{U})$ (Milvy and Cothorn, 1990), a value of 0.11 Bq l^{-1} for ^{234}U and ^{238}U radioactivity is calculated for the groundwater at Topley Pike Quarry which contains the highest observed U concentration. Here the alpha emission level is likely to exceed the statutory radioactivity limits for drinking water (WHO, 2004). Estimates for the groundwaters at St Anne's Well, Meerbrook Sough and Ladyflatte Mine give U activity values of 0.09 Bq l^{-1} , 0.04 Bq l^{-1} and 0.04 Bq l^{-1} , respectively, which fall below the given limit. However, the assumption of secular equilibrium may not be valid and, in terms of activity, the shorter-lived ^{234}U is often dominant over ^{238}U in groundwater (Elliot, *et al.*, 1999, Milvy and Cothorn, 1990). For 2003, CEFAS data for Meerbrook Sough reported ^{234}U activity of 0.043 Bq l^{-1} , ^{235}U activity of $<0.01 \text{ Bq l}^{-1}$ and ^{238}U activity of 0.023 Bq l^{-1} (CEFAS, 2004). Here, the $^{234}\text{U}/^{238}\text{U}$ activity ratio equals 1.87 rather than 1 (=secular equilibrium), hence the U activities in the groundwater are probably underestimated by the above calculations. Consequently, it is possible that while U concentrations are low in terms of mass, activities may still exceed total alpha emission levels set for drinking water (WHO, 2004) as was experienced in the groundwaters of Meerbrook Sough.

7 Summary and Conclusions

The observed U concentrations in the groundwaters of the study area range between < 0.2 and $4.23 \mu\text{g l}^{-1}$ and lie below the (provisional) WHO guideline value for U in drinking water. Most U is derived from bedrock sources and higher concentrations are generally associated with drainage from mines and soughs as well as with thermal groundwaters where prolonged contact times favoured U mobilisation and release into the groundwater. Additional inputs may be derived from fertilizer applications, although the contribution from such sources is believed to be low. Concentrations are strongly controlled by pH, redox conditions and solute chemistry of the groundwater. Complexation with carbonates and also with phosphates is likely to increase the concentrations of dissolved U in the groundwater.

Highest concentrations of U in the groundwaters are associated with areas of bedrock mineralisation and this is probably due to two factors: (1) the abundance of U-bearing minerals in mineral veins and secondary iron deposits and (2) the high surface area provided by cavities and rock debris resulting in enhanced bedrock weathering. Some U may be derived from deposits of Namurian age, in particular the Edale Shales. While direct U mobilisation in the shales is limited because of the reducing conditions, the U-rich and clay-rich deposits of weathered Namurian sediments which have accumulated in the limestone caves near the shale-limestone interface (e.g., around Castleton) may provide a source for U release into the groundwater.

Generally, the observed U concentrations in the groundwater are lower than would be expected from previous surveys on bedrock and groundwater composition as well as from radioactivity surveys. The relatively low U concentrations in the groundwaters are, in the first instance, attributed to the flashy nature of the groundwater system and the associated short groundwater residence times. Other factors, such as limited mobility and solubility of uranyl minerals at $\text{pH} > 7$, adsorption of U onto hydrous ferrous oxide (Hfo) surfaces, U solubility controls as well as 'exhaustion' of easily leachable U source may also have contributed to low U in the groundwaters.

However, despite the low U (mass) concentrations found in the groundwater, it is still possible that the activities of ^{234}U and ^{238}U in some of the sampled groundwaters exceed the WHO screening values for total alpha emission in drinking water of 0.1 Bq l^{-1} , in particular where ^{234}U dominates over ^{238}U . However, given the available information this can only be hypothesised and more detailed investigation of the radioactive isotope composition of the groundwaters is required to test the above assumption.

Within the scope of this study, it was not possible to observe the temporal distribution of U in the groundwater. Some temporal variations may occur, and U concentrations in the groundwater may increase during low-recharge periods and prolonged groundwater-rock contact times and decrease during storm-events where higher proportion of short-residence time waters enter the aquifer.

References

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

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

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

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). British Geological Survey, London.

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. British Geological Survey, Nottingham.

ATSDR, 1999. Toxicological profile for uranium. PB/99/163362, U.S. Department of Health and Human Services, Atlanta.

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*, 24: 169-189.

BALL, T. K., CAMERON, D. G. and COLMAN, T. B., 1992. Aspects of Rn potential mapping in Britain. *Radiation Protection Dosimetry*, 45(1-4): 211-214.

BANKS, D., REIMANN, C., ROYSET, O., SKARPHAGEN, H. and SAETHER, O. M., 1995. Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters. *Applied Geochemistry*, 10(1): 1-16.

BANKS, D., 1997a. The spas of England. In: ALBU, M., BANKS, D. and NASH, H. (Editors), *Mineral and Thermal Groundwater Resources*. Chapman & Hall, London, pp. 235-280.

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

BANKS, D. and FRENGSTAD, B., 2006. Evolution of groundwater chemical composition by plagioclase hydrolysis in Norwegian anorthosites. *Geochimica et Cosmochimica Acta*, 70: 1337-1355.

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*, 52: 965-983.

BOTTRELL, S. H., 1993. Redistribution of uranium by physical processes during weathering and implications for radon production. *Environmental Geochemistry and Health*, 15(1): 21-25.

BOTTRELL, S. H., 1996. Organic carbon concentration profiles in recent cave sediments: Records of agricultural pollution or diagenesis? *Environmental Pollution*, 91(3): 325-332.

BOTTRELL, S. H., HARDWICK, P. and GUNN, J., 1999. Sediment dynamics in the Castleton karst, Derbyshire. *Earth Surface Processes and Landforms*, 24: 745-759.

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*, 25: 155-165.

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

CEFAS, 2003. Radioactivity in Food and the Environment, 2002., 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.

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.

CEFAS, 2005. Radioactivity in Food and the Environment, 2004., 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.

CHENERY, S. R. N., ANDER, E. L., PERKINS, K. M. and SMITH, B., 2002. Uranium anomalies identified using G-Base data - Natural or anthropogenic? A uranium isotope pilot study. Internal report, IR/02/001, British Geological Survey, Keyworth.

CONCEICAO, F. T. and BONOTTO, D. M., 2003. Use of U-isotope disequilibrium to evaluate the weathering rate and fertilizer-derived uranium in São Paulo state, Brazil. *Environmental Geology*, 44(4): 408-418.

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*, 27: 289-307.

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

- EDMUNDS, W. M., 1981. Hydrogeochemical investigations. In: LLOYD, J. W. (Editor) *Case Studies in Groundwater Resource Evaluation*. Oxford Science Publications, Oxford, pp. 87-112.
- EDMUNDS, W. M., COOK, J. M., KINNIBURGH, D. G., MILES, D. L. and TRAFFORD, J. M., 1989. Trace-element occurrence in British groundwaters. Hydrogeological Series Research Report, SD/89/3, British Geological Survey, Wallingford.
- ELLIOT, T., ANDREWS, J. N. and EDMUNDS, W. M., 1999. Hydrochemical trends, paleorecharge and groundwater ages in the fissured Chalk aquifer of the London and Berkshire Basins, UK. *Applied Geochemistry*, 14: 333-363.
- 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. In: *Isotope Hydrology 1978, Vol. II*. International Atomic Energy Agency, Vienna, pp. 679-708.
- FORD, T. D., 1968a. The Millstone Grit. In: SYLVESTER-BRADLEY, P. C. and FORD, T. D. (Editors), *The Geology of the East Midlands*. Leicester University Press, Bath, pp. 83-94.
- FORD, T. D., 1968b. Epigenetic mineralisation of the Carboniferous Limestone. In: SYLVESTER-BRADLEY, P. C. and FORD, T. D. (Editors), *The Geology of the East Midlands*. Leicester University Press, Bath, pp. 117-123.
- FORD, T. D., 1999. The growth of geological knowledge in the Peak District. *Mercian Geologist*, 14(4): 161-190.
- FROST, D. V. and SMART, J. G. O., 1979. Geology of the Country North of Derby. Memoirs for 1:50 00 Geological Sheet 125. Her Majesty's Stationery Office, London, 199 pp.
- GOMEZ, P., GARRALON, A., BUIL, B., TURRERO, M. J., SANCHEZ, L. and DE LA CRUZ, B., 2005. Modelling of geochemical processes related to uranium mobilization in the groundwater of a uranium mine. *Science of the Total Environment*, 366(1): 295-309.
- GRENTHE, I., FUGER, J., KONINGS, R. J. M., LEMIRE, R. J., MULLER, A. B., NGUYEN-TRUNG, C. and WANNER, H., 1992. Chemical Thermodynamics of Uranium. North Holland, Amsterdam.
- GUNN, J., 1991. Water tracing experiments in the Castleton karst. *Cave Science*, 18: 43-46.
- GUNN, J., FLETCHER, S. and PRIME, D., 1991. Research on radon in British caves and mines. *Cave Science*, 18(2): 63-82.
- GUNN, J., 1992. Hydrogeological contrasts between British Carboniferous Limestone Aquifers. *International Contributions to Hydrogeology*, 13: 25-41.
- 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*, 10: 353-369.

- HAMAMO, H., LANDSBERGER, S., HARBOTTLE, G. and PANNO, S., 1995. Studies of radioactivity and heavy metals in phosphate fertilizer. *Journal of Radioanalytical and Nuclear Chemistry*, 194(2): 331-336.
- 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 UK. *Water Research*, 33: 3577-3586.
- HURSH, J. B. and SPOOR, N. L., 1973. Data on man. In: HODGE, H. (Editor) *Handbook of Experimental Pharmacology: Uranium, Plutonium, Transplutonic Elements*. Springer Verlag, Berlin, pp. 197-240.
- HYSLOP, E. K., 1993. Uranium distribution studies of potential radon source rocks from the Ashover area, Derbyshire UK. BGS Report, WG/93/04, British Geological Survey, Keyworth.
- KOMNINOU, A. and SVERJENSKI, D. A., 1996. Geochemical modelling of the formation of an unconformity-type uranium deposit. *Economic Geology*, 91: 590-606.
- LANGMUIR, D., 1978. Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits. *Geochimica et Cosmochimica Acta*, 42(6): 547-569.
- LANGMUIR, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-Hall, New Jersey.
- MIDDLETON, T., GUNN, J., FLETCHER, S. and PRIME, D., 1991. Radon daughter concentrations in Giants Hole, Derbyshire. *Cave Science*, 18(2): 67-70.
- MILVY, P. and COTHERN, C. R., 1990. Scientific background for the development of regulations for radionuclides in drinking water. In: COTHERN, C. and REBERS, P. (Editors), *Radon, Radium and Uranium in Drinking Water*. Lewis Publishers, Inc.
- PARNELL, J., 1988. Mineralogy of uraniferous hydrocarbons in carboniferous-hosted mineral deposits, Great Britain. *Uranium*, 4: 197-218.
- PARSONS, L. M., 1922. Dolomitisation in the Carboniferous Limestone of the Midlands. *Geological Magazine*, 80: 104-117.
- PAVLAKIS, N., POLLOCK, C. A., MCLEAN, G. and BARTROP, R., 1996. Deliberate overdose of uranium: toxicity and treatment. *Nephron*, 72: 313-317.
- PEACOCK, J. D. and TAYLOR, K., 1966. Uraniferous collophane in the Carboniferous Limestone of Derbyshire and Yorkshire. *Bulletin of the Geological Survey of Britain*, 25: 19-32.
- PLATER, A. J., IVANOVICH, M. and DUGDALE, R. E., 1992. Uranium series disequilibrium in river sediments and water - the significance of anomalous activity ratios. *Applied Geochemistry*, 7: 101-110.
- RAGNARSDOTTIR, K. V. and CHARLET, L., 2000. Uranium behaviour in natural environments. In: COTTER-HOWELLS, J. D., CAMPBELL, L. S., VALSAMI-JONES, E. and BATCHFELDER, M. (Editors), *Environmental Mineralogy: Microbial Interactions, Anthropogenic Influences*,

Contaminated Land and Waste Management. Mineralogical Society Series. 9. Mineralogical Society of Great Britain and Ireland, London, pp. 245-289.

ROMBERGER, S. B., 1984. Transport and deposition of uranium in hydrothermal systems at temperatures up to 300°C: geological implications. In: DE VIVO, B., IPPOLITO, F., CAPALDI, G. and SIMPSON, P. R. (Editors), *Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources*. Institution of Mining and Technology, London.

SANDINO, A. and BRUNO, J., 1992. The solubility of $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ and the formation of U(VI) phosphate complexes: Their influence in uranium speciation in natural waters. *Geochimica et Cosmochimica Acta*, 56(12): 4135-4145.

SHOCK, E. L., SASSANI, D. C. and BETZ, H., 1997. Uranium in geologic fluids: Estimates of standard partial molal properties, oxidation potentials, and hydrolysis constants at high temperatures and pressures. *Geochimica et Cosmochimica Acta*, 61(20): 4245-4266.

SINGHAL, R. K., KUMAR, A., KARPE, P. J. R., DATTA, M. and HEGDE, A. G., 2005. Association of uranium with colloids of natural organic matter in subsurface aquatic environment. *Journal of Radioanalytical and Nuclear Chemistry*, 265(3): 405-408.

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

SYLVESTER-BRADLEY, P. C. and FORD, T. D., 1968. The Geology of the East Midlands. Leicester University Press, Bath, 400 pp.

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*, 78: 157-171.

VAN DER WEIJDEN, C. H. and VAN LEUWEN, H. P., 1985. The effect of the pH on the adsorption of uranyl onto peat. *Uranium*, 2(1): 59-66.

VILLALOBOS, M., TROTZ, M. A. and LECKIE, J. O., 2001. Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II), and U(VI) on Goethite. *Environ. Sci. Technol.*, 35(19): 3849-3856.

WAITE, T. D., DAVIS, J. A., PAYNE, T. E., WAYCHUNAS, G. A. and XU, N., 1994. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochimica et Cosmochimica Acta*, 58(24): 5465-5478.

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

WHO, 2004. Guidelines for Drinking-Water Quality. 3rd edition. World Health Organisation, Geneva, Switzerland.

ZAMORA, M. L., TRAVY, B. L., ZIELINSKI, J. M., MEYERHOF, D. P. and MOSS, M., 1998. Chronic ingestion of uranium in drinking water: a study of kidney bio-effects in humans. *Toxicological Sciences*, 43: 68-77.

ZIELINSKI, R. A., SIMMONS, K. R. and OREM, W. H., 2000. Use of ^{234}U and ^{238}U isotopes to identify fertilizer-derived uranium in the Florida Everglades. *Applied Geochemistry*, 15: 369-383.