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Uranium occurrence and behaviour in British groundwater

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Uranium occurrence and behaviour in British groundwater

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Permo-Triassic red-bed sandstones, Shropshire (from Smedley et al., 2005b).

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Foreword

This report has been produced by the British Geological Survey (BGS) and represents the final report resulting from a study of uranium in groundwater in Great Britain. This was carried out under contract DWI 70/2/180 funded by the Department for Environment, Food and Rural Affairs (DEFRA) and managed by the Drinking Water Inspectorate (DWI). The report concentrates mainly on groundwater quality in England & Wales in line with DWI responsibilities but includes available data from Scotland as well as other parts of the world in order to provide a broader context for the England & Wales data. The project has been undertaken during the period January 2005 to March 2006. A variation of contract involving an expanded groundwater sampling and analysis programme was agreed with DWI in December 2005 and has resulted in a two-month extension to the original contract period.

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Summary

This report describes the concentrations and distributions of uranium (U) in groundwater from aquifers in Great Britain and discusses the most likely sources and controls on U mobility. The report also reviews the ranges of U observed in groundwater worldwide in order to place the British data within a wider context. Groundwater-chemistry results are presented from 116 samples of raw groundwater taken from 101 operational boreholes and springs across England & Wales. The samples are from a selection of public and private water sources. Twelve of the sources were sampled twice, once in the spring of 2005 and once in autumn 2005 in order to provide some limited assessment of the temporal variation in U concentrations. The report also describes the results from 1556 analyses of groundwater U collated from the BGS groundwater-chemistry database and various published accounts. This provides a basis for assessing the implications to the water industry and regulators of U in groundwaters in England & Wales in the event that a new European drinking-water limit for the element is introduced in the coming years.

The mobility of U in water is controlled by a number of factors, among the most important being pH, redox status and concentrations of coexisting dissolved ions. Uranium is a redox-sensitive heavy metal that occurs in water principally under oxic conditions in its hexavalent (U(VI)) form. It is usually complexed in solution, especially with carbonate ligands, but also less significantly with phosphate, fluoride or sulphate depending on their respective dissolved concentrations and ambient pH. Under anoxic conditions, U is reduced to its tetravalent U(IV) state and its concentration in water is usually low as a result of stabilisation of the sparingly soluble mineral, uraninite.

Groundwaters often have higher concentrations of U than surface waters because of the large solid/solution ratios in aquifers and the greater influence of water-rock interactions. Uranium occurs as a major constituent of minerals such as uraninite, coffinite and autunite. These can be significant localised sources of U in some groundwaters, especially those in mineralised areas and some granitic terrains. Uranium is also closely associated with iron oxides, phosphates, clays and organic matter and these minerals can be important sources, as well as sinks, of U. The abundance of phosphates in aquifers is usually limited but iron oxides and clays are common rock-forming minerals and are particularly important in iron-rich and argillaceous sediments and metasediments. The concentrations of U in abundant silicate minerals such as quartz and feldspar and carbonate minerals are usually low.

Results from the 101 groundwater sources analysed in England & Wales indicate a range in U concentrations of <0.02–48.0 µg L^{-1} (median 0.39 µg L^{-1}). The vast majority of samples had U concentrations well below the WHO provisional guideline value for U in drinking water of 15 µg L^{-1}, with concentrations in only two samples exceeding it. Both these were from private supplies. The observed range compares reasonably with that from the collated database of 1556 groundwater samples from Great Britain, which was <0.01–67.2 µg L^{-1} (median 0.29 µg L^{-1}). Of the latter dataset, 0.71% (11 samples) exceeded the WHO provisional guideline value for U in drinking water of 15 µg L^{-1}, while 0.45% (7 samples) exceeded 20 µg L^{-1} (the Canadian standard) and 0.26% (4 samples) exceeded 30 µg L^{-1} (the US-EPA maximum contaminant level). A large majority, 78.1% (1216 samples), had U concentrations less than 1 µg L^{-1}. This indicates that most British groundwaters have concentrations well below those that would become problematic if a European drinking-water limit comparable to the WHO provisional guideline value or current American regulations were to be imposed.

The distribution of U in the groundwaters has strong links with aquifer geology. Highest concentrations in the collated groundwater dataset (1556 samples) occur in borehole sources

in the Old Red Sandstone and Permo-Triassic Sandstone aquifers (up to 48 µg L^{-1} and 67 µg L^{-1} respectively). A single borehole sample from the Torridonian Sandstone of Scotland also had a relatively high concentration (6.6 µg L^{-1}). These aquifers are all red-bed sandstones, their most characteristic unifying feature being the abundance of Fe(III) oxides which occur as grain coatings and cements. The dissolved U in these aquifers is thought to be derived principally by desorption from iron oxides, facilitated by complexation with dissolved carbonate species at alkaline pH. The high U concentrations tend to be limited to the unconfined portions of these aquifers where oxidising conditions prevail, allowing the predominance of the oxidised U(VI)-carbonate complexes. In reducing confined aquifers, groundwater U concentrations tend to be low (<1 µg L^{-1}).

Concentrations were variable and occasionally high in groundwater from other aquifers, although none exceeded 15 µg L^{-1}. Most carbonate aquifers had low groundwater U concentrations, with median values typically of 0.2–0.3 µg L^{-1} although values ranged up to 7.8 µg L^{-1} in the Carboniferous Limestone and 7.6 µg L^{-1} in the Chalk. These occasional high values may be linked to local U-mineralisation, and in the case of the Chalk to interaction of groundwater with phosphate horizons.

Concentrations in groundwaters from granites of south-west England were generally low (up to 3.6 µg L^{-1}) in our study, despite the known U mineralisation in the rocks of the region and the observation of groundwater U concentrations up to 11.6 µg L^{-1} by other researchers. High-U groundwaters appear not to be a widespread feature of the granites of the region, perhaps because of the short residence times of the groundwaters and their slightly acidic, low-alkalinity compositions. The sporadic nature of the U mineralisation may also be a factor.

Of the 12 sources that were sampled and analysed more than once during the study period, all but four had differences in dissolved U concentration of less than 15%. The variations in the remainder are difficult to interpret from the limited numbers of samples, particularly in the most extreme case which had concentrations varying between 3.48 µg L^{-1} and 48 µg L^{-1}. However, the results suggest that at least a few sites can experience significant time variations in groundwater U concentrations. The causes are unknown but seasonal variations in groundwater level and pumping rates leading to differing flow patterns are possibilities.

The observed concentration ranges of U in British groundwater are relatively narrow compared to those in groundwaters from other parts of the world where concentrations can span some six orders of magnitude (<0.01–8000 µg L^{-1}). The higher concentrations tend to be found in U-mineralised areas and U-rich granitic terrains (e.g. western USA, Scandinavia), which are of relatively limited extent in Britain.

1 Introduction

1.1 HEALTH EFFECTS OF URANIUM IN DRINKING WATER

Uranium is a heavy metal that although commonly thought of as rare, is more common in nature than many other trace elements such as cadmium, selenium and some of the rare earth elements (Kay and Laby, 1995). Uranium occurs naturally in variable concentrations in all soils, minerals, rocks and waters. It can also be derived from several anthropogenic sources.

Uranium is weakly radioactive and human exposure to the element has long been considered to pose a radiological hazard. However, there are few if any epidemiological studies that have been able to demonstrate any resultant harm, even in occupational contexts (The Royal Society, 2001). In recent years, there has been increasing concern that the chemical effects of uranium may also pose a potential hazard to exposed populations. Toxic effects of exposure include nephritis (kidney disease), and possible changes to bone structure (Milvy and Cothern, 1990; Kurttio et al., 2005). Toxic effects have been found in animal species, including death at high exposures (LD_{50} 100–200 mg kg^{-1} body weight). However, so far evidence of chemical toxicity in humans is limited (Kurttio et al., 2002; The Royal Society, 2002; WHO, 2004). There is no evidence that U is essential to man.

1.2 DRINKING-WATER GUIDELINES AND REGULATIONS

Exposure of humans to U from drinking water is usually minor but where concentrations are high, drinking water can constitute an important and possibly dominant pathway of non-occupational exposure to U. The WHO (1993) guidelines for drinking-water quality recognised uranium as a potential chemical risk but concluded that insufficient data were available to derive a realistic guideline value at the time. The WHO (1998) addendum to the guidelines incorporated a provisional value of 2 µg L^{-1} based on a tolerable daily intake by ingestion of 0.5 µg per kg body weight (soluble uranium). Since the publication of this provisional guideline value, it has become increasingly clear that concentrations can often exceed 2 µg L^{-1} in groundwater and that the value may therefore be impractical. On the basis of currently-available data for sources of uranium in the human diet, WHO has recently reapportioned the tolerable daily intake from drinking water and food and has consequently revised the guideline value for drinking water. As a result, the WHO (2004) guidelines specify a provisional guideline value of 15 µg L^{-1}.

Whilst this value is based on the chemical rather than radiological toxicity of U, it should be noted that the WHO radiological screening level for gross alpha activity in drinking water of 0.5 Bq L^{-1} would be breached by a water containing in excess of 19 µg L^{-1} U (assuming activity is due only to uranium and that ^{238}U and ^{234}U are in secular equilibrium with an aggregate activity of 0.684 pCi $µg^{-1}$). Calculations of radiological dose using actual dose conversion factors for uranium indicate that the 0.1 mSv yr^{-1} excess dose assumption (WHO, 2004) would only be breached at a U concentration exceeding 100 µg L^{-1}.

Uranium is a list II substance within the context of the EC Groundwater Directive (1998) and hence legislation already exists to minimise inputs to the groundwater environment from anthropogenic sources. These sources potentially include mineral mining operations, the nuclear industry (waste and fuel fabrication), fertiliser manufacture and use, and industrial activities (Jackson, 2001). However, to date no European statutory limits have been imposed for U in drinking water.

The recent changes to the WHO drinking-water guidelines mean that addition of U to future EC drinking-water regulations is a possibility. The likely limit for U adopted into any future regulation is uncertain. Traditionally, drinking-water standards have tended to follow WHO guidelines and a value of 15 µg L^{-1} therefore seems likely. However, for comparison, the US-EPA in 2000 introduced a maximum contaminant level (MCL) for U in drinking water of 30 µg L^{-1}. This is applicable to public supplies in the USA. The level set followed an initial proposal of 20 µg L^{-1} in 1991. The drinking-water standard in Canada is 20 µg L^{-1}.

The UK Committee on Toxicology of Chemicals in Food, Consumer Products and the Environment (COT) is considering the health implications for bottle-fed infants of consuming formula reconstituted with water containing uranium at the WHO provisional guideline value. The views of the COT on whether the provisional guideline value offers adequate protection will be relevant to any further UK and EU discussion on advisory or regulatory limits.

1.3 STUDY OBJECTIVES

The recent WHO promulgation of a provisional guideline value for U has brought the element into focus as a potential drinking-water health hazard. Groundwater is particularly vulnerable to accumulation of dissolved U because of the mineral-water reactions that can take place and the large solid/solution ratios that exist in aquifers. Groundwater is also an important source of drinking-water supply in Britain and elsewhere. A number of studies of U abundance, mobilisation and transport in the environment have been carried out in connection with radioactive waste disposal and contaminated sites and uranium mineral exploration. Some localised studies of natural groundwaters have also been carried out. However, U is generally not analysed routinely in groundwater and most water-quality investigations exclude it. In Britain, there has until now not been a concerted attempt to collate available groundwater U data and to assess the occurrence and distribution of U in different aquifers on a national scale.

This study attempts to provide the requisite background information to establish the observed ranges of concentrations and distributions of U in groundwater in England & Wales as well as Scotland and to place them in an international context. This information will provide the water industry and regulators with a better understanding of the practical implications of any new EC drinking-water limit, in the event that one is imposed in the coming years.

The main objectives of this study, as defined by DEFRA, were to:

1. identify relevant studies that provide data on the concentrations of uranium in groundwater in the UK and worldwide;
2. assess the quality of the studies identified, in terms of the scope of study and performance of the analytical methods used;
3. summarise the findings of the studies and identify any geological characteristics that may be associated with high uranium concentrations and critically assess the relevance of the studies and any geological features identified to England & Wales;
4. carry out a representative survey of public and private groundwater sources in England & Wales and collate with existing data to establish the range of uranium concentrations in groundwater;
5. resample groundwater at up to 12 sites (during the spring and autumn) in order to investigate potential seasonal variations;
6. conduct the survey in accordance with best practice in terms of sampling and analysis, including appropriate quality control;

7. report the findings of the survey, identifying possible implications for water supplies should a standard be set at a range of different likely values.

These objectives have been achieved and the results of the investigation are described in this report.

2 Geochemistry of uranium

2.1 PHYSICAL AND CHEMICAL PROPERTIES

Uranium is a dense silver-grey metallic element of the actinide group. Elemental uranium has an atomic number of 92 and a relative atomic mass of 238.03.

The element is weakly radioactive and contributes to natural background environmental radiation. Natural uranium comprises three radioactive isotopes: ^{234}U, ^{235}U and ^{238}U. The percentage of each by weight is respectively about 0.0054%, 0.72% and 99.27%. Some 48.9% of the radioactivity is associated with ^{234}U, 2.2% with ^{235}U and 48.9% with ^{238}U. The half-lives (time for the radioactivity to decay to half its original value) of the uranium radioisotopes are very long: 244,000 years for ^{234}U, 710 million years for ^{235}U and 4500 million years (or about the age of the Earth) for ^{238}U. The original uranium atoms of ^{238}U and ^{235}U decay to many other radioisotopes, ending in the decay chain as stable (non-radioactive) isotopes of lead. As a result of its long radioactive half-life in comparison to the age of the solar system, uranium is considered to be a naturally-occurring primordial radioelement.

In the majority of situations, natural ^{238}U and ^{235}U occur with the relative mass abundances given above. However, in natural waters, soils and atmospheric dusts these ratios may be influenced by natural nuclear and chemical processes that have led to the enrichment or depletion of ^{234}U relative to ^{238}U. For example the theoretical mass ratio of $^{234}U/^{238}U$ (0.0000554) has been observed to range from 0.00005 to 0.0004 in atmospheric dusts (US-EPA, 1994) and 0.00003 to 0.0014 in natural waters (Ivanovich and Harmon, 1982). Anthropogenically-produced uranium can have variable isotopic ratios (either enhanced or depleted in ^{238}U, ^{235}U and ^{234}U relative to natural abundances) and may also include the anthropogenic nuclide ^{236}U (The Royal Society, 2001).

All isotopes of uranium undergo the same chemical reactions in nature and possess almost identical physical properties such as melting point, boiling point and volatility. The radioactive properties (half-life, specific activity, decay mode) differ.

2.2 URANIUM SOURCES

2.2.1 Uranium minerals

Uranium occurs in nature in two main oxidation states: the hexavalent form, U(VI), and the tetravalent form, U(IV). In most U minerals, the metal occurs as U(IV). Approximately 5% of all known minerals contain U as an essential structural constituent (Mandarino, 1999). The principal U minerals include uraninite (UO_2) and its oxidised or partly oxidised massive form, pitchblende (U_3O_8), as well as coffinite ($(USiO_4)_{1-x}(OH_{4x})$), autunite ($Ca(UO_2)_2(PO_4)_2 10–12H_2O$) and uranophane ($Ca(UO_2)_2SiO_3(OH)_2 \cdot 5(H_2O)$). These contain high concentrations of U but most are comparatively rare minerals, generally being restricted to U-mineralised zones. Such uranium mineralisation typically occurs along fractures and the distribution can therefore be highly heterogeneous. The vast majority of these mineral zones do not form deposits of economic proportions.

Redistribution of U in mineralised zones and dispersed deposits can occur as a result of hydrothermal alteration, weathering and erosion (Porcelli and Swarzenski, 2003). Redistribution is of particular importance in the development of sandstone-hosted U deposits formed by the oxidation of primary U(IV) minerals and redistribution by groundwater. So-called 'roll-front uranium deposits' are produced as a result of flow of oxygenated groundwater through an aquifer where conditions are initially reducing (e.g. bearing iron

Figure 2.1 Map showing the locations of recognised zones of sub-economic U mineralisation in Britain (from BGS, 2005).

sulphide minerals and organic matter and with disseminated U(IV)). As the oxygenated groundwater permeates the aquifer, a redox front is created between the oxidising and reducing zones. Uranium dissolves in the oxidising zone but is immobilised at the redox front and so precipitates as uraninite (or in some cases coffinite). The U front moves in the direction of groundwater flow, but at a much slower rate than the water itself. The accumulation of U at the front can lead to the development of economic deposits (Drever, 1997; Plant et al., 1999). High concentrations of dissolved V, Mo and Se can accompany U at the roll front (Nash et al., 1981).

In Britain, occurrences of U mineralisation are relatively rare and usually below economic grade. The locations of recognised U mineral zones are shown in Figure 2.1 (BGS, 2005). Pitchblende-bearing mineral veins occur alongside Cu-Sn and Pb-Zn-Ni mineralisation associated with the Cornubian granite in south-west England. In Scotland, U mineralisation occurs in U-Pb mineral veins as well as phosphatic and carbonaceous horizons of the middle Devonian (Old Red Sandstone) of Caithness and Orkney. It also occurs in veins along the margins of the Helmsdale granite (Ousdale) and the Criffel-Dalbeattie granodiorite (Figure 2.1). Other occurrences in England & Wales noted in Figure 2.1 are mainly associated with black shale deposits.

2.2.2 Rock-forming and accessory minerals

Uranium(VI) partitions strongly with phosphate and so can occur in high concentrations not only in U-phosphate minerals (such as autunite) (Cothern and Lappenbusch, 1983; Jerden et al., 2003) but also as adsorbed species to minerals such as hydroxyapatite (Murray et al., 1983; Arey et al., 1999). Concentrations of U in the range 20–300 mg kg^{-1} have been reported for phosphate ores from the USA (EPA, 1993). Smith et al. (1996) found concentrations of 75–200 mg kg^{-1} in phosphate ores of Jordan.

Studies of alteration zones above primary uranium deposits have found strong associations between U and phosphate minerals. In the weathered zone overlying the Koongara uranium deposit in north central Australia, U appears to have been fixed as magnesium uranyl phosphate, formed by alteration of primary uraninite (Murakami et al., 1997). Studies of weathered saprolite overlying the Coles Hill uranium deposit in Virginia, USA have also indicated that U is associated with U(VI) phosphate minerals (barium meta-autunite) in oxidising environments (Jerden et al., 2003). The primary ore body contains coffinite, and minor uraninite with abundant fluorapatite and chlorite. U concentrations up to 1300 mg kg^{-1} were found in the lower part of the weathering profile, indicating enrichment in U relative to the unaltered primary ore deposit. The enrichment zone coincides with a redox front characterised by oxidation of iron. Above the water table, U(VI) meta-autunite minerals of the type found in the saprolite were absent and U concentrations in the solid were around 250 mg kg^{-1}. In this zone, U was found to be mainly associated with Al phosphate minerals and adsorbed to ferric oxides (Jerden et al., 2003). Similar associations between U and phosphate have also been found in the Southern Karoo province of South Africa and the Northwestern province of Zambia (Sandino and Bruno, 1992).

Various workers have suggested that phosphate minerals offer potential in the containment of U-contaminated groundwaters. Krestou et al. (2004) for example demonstrated from experimental and theoretical studies that hydroxyapatite had a very strong capacity to remove U(VI) from solution. Stable precipitates of $Ca(UO_2)(PO_4)_2$ or $Ca(UO_2)_2(PO_4)_2$ were produced at near-neutral to acidic pH with total P concentrations of 10^{-3} M, although the removal of U was found to be much less efficient under alkaline conditions (pH >9).

High concentrations of U have also been found in some zircons, sphenes and monazites. These minerals occur in granitic rocks and, as late-formed minerals, they tend to accumulate U and other ‘incompatible’ elements from magmas in the late stages of crystallisation (Porcelli and Swarzenski, 2003). They are however, relatively insoluble and unlikely to contribute significant U to groundwater.

The strong affinity of iron oxides, including goethite, haematite, ferrihydrite and magnetite, for U is well known (Hsi and Langmuir, 1985; Bianconi and Kögler, 1992; Scott et al., 2005). This is commonly attributed to surface adsorption of the $U(VI)O_2^{2+}$ uranyl ion, although there is also evidence that U(VI) can be incorporated within the structure of haematite and other iron oxides (Duff et al., 2002). Concentrations in secondary iron oxides downgradient of the Koongarra uranium deposit in Australia for example were noted to have total U concentrations in the range 773–4540 mg kg^{-1} (up to 8 weight % UO_3) (Sato et al., 1997). Similarly, concentrations in excess of 1500 mg kg^{-1} U have been found in iron precipitates on wellhead structures from an area of U-rich groundwater in Jordan (Smith et al., 2000).

Uranium has also been associated, albeit to a lesser degree, with carbonate minerals such as calcite and dolomite, being substituted for Ca^{2+} in structural sites. It may also be adsorbed to clay minerals (Bonotto and Andrews, 2000).

2.2.3 Anthropogenic sources

Man’s activities have potential to influence the distribution and concentrations of U in the environment. Uranium is used in the ceramics, chemicals, photographic chemicals and lighting industries. It can also occur at high concentrations (around 20–200 mg kg^{-1}) in phosphate fertilisers (Hess et al., 1985; Zielinski et al., 1997) and may therefore be introduced to soils by agricultural activities. Uranium is processed to produce enriched uranium (enriched in ^{235}U) which is used in nuclear power plants and nuclear weapons. Its by-product, depleted uranium (relatively enriched in ^{238}U), is used in military operations as armour for tanks and as penetrators in bullets and missiles. It has also been used in the aircraft industry. Virtually all uranium currently used in industry is depleted uranium which, as a by-product, has relatively low cost.

Several studies have reported the effects of industrial activities on distributions of U in the environment. These effects can be significant, at least locally. Uranium can be redistributed in the environment by mining activities and U hotspots around mining sites have been well-documented (e.g. Langmuir and Chatham, 1980; Colon et al., 2001). In the UK, historical uranium mining probably represents the most significant source of anthropogenic remobilised U. Mining has been carried out in the past in a few locations in south-west England and mining-related contamination has been reported, particularly around spoil heaps (DETR, 2001). Studies of disturbed areas associated with such mining were used extensively during the 1980s and 1990s as natural analogues for the investigation of radioactive-waste disposal (Hooker et al., 1989). Processing of phosphate minerals was also important in the UK during the 20th century, with more than 1 million tons of phosphate rock being produced annually in the 1950s (Binks et al., 1959). Historical discharges to the Irish Sea from this industry have been documented (Poole et al., 1995). Anthropogenic activities including authorised discharges of U isotopes into the environment have resulted in measurable changes to the natural abundance of ^{235}U, ^{238}U and ^{234}U (Chenery et al., 2002).

The effect of phosphate fertilisers on concentrations of U in groundwater and soils is so far poorly constrained in the UK although some studies have been carried out elsewhere. Popit et al. (2004) carried out a survey of Ra and U in groundwater from springs on agricultural (subjected to fertiliser application) and non-agricultural land in Slovenia. Average concentrations of U in the groundwaters were respectively 0.5 µg L^{-1} and 0.3 µg L^{-1}. Although the average concentration in springs from agricultural land was higher, the difference was not significant and did not demonstrate any appreciable effect from fertiliser use. Likewise, Zielinski et al. (1997) using U concentrations and isotopic ratios found little effect from PO_4-based fertilisers on U in waters below agricultural land in Colorado, USA. Mobility was limited by the formation of Ca-P-U precipitates. However, Zielinski et al. (2000) found that surface waters draining agricultural land in the Floridan Everglades had small but significant increases in dissolved U (0.3–2.4 µg L^{-1} compared to background concentrations of <0.1 µg L^{-1}) that could be attributed to phosphate fertiliser use. Further downstream in peat wetlands, dissolved U concentrations were low but concentrations in peat were relatively high (>1 mg kg^{-1} dry weight), suggesting that fertilizer-derived U in this area was mainly bound to the soil. The impact of fertiliser-derived U on soils and waters is likely to be dependent on several factors, including fertiliser composition, water chemistry and soil properties (pH, moisture content, mineralogy and texture) (Zielinski et al., 1997) and is therefore likely to be spatially variable.

2.2.4 Uranium in rocks

Uranium concentrations in rocks are typically around 1–4 mg kg^{-1} (Hess et al., 1985; Taylor and McLennan, 1985; Drever, 1997). Relatively high concentrations occur in granitic rocks (Voronov, 2004), argillaceous sediments (clays, shales) and Fe-rich rocks and metamorphic rocks derived from them. Langmuir (1978) noted concentrations in granite of 2.2–15 mg kg^{-1}. However, much higher concentrations (20–54 mg kg^{-1}) have been found in samples from the Stripa granite in Sweden (Table 2.1). The uranium in the Stripa granite was found as uraninite concentrated in microfractures in feldspars (Andrews et al., 1989) and is readily leachable. Uraninite is a common accessory mineral in many granitic rocks and pegmatites and is probably the most important source of dissolved U in groundwaters from such lithologies.

Bromley (1989) reported a range of U concentrations in the granites of south-west England of <1–20 mg kg^{-1} (Table 2.1). Poole (2001) also reported variable though often high U concentrations for the Carnmenellis and Land's End granites (1.4–19 mg kg^{-1}; average 7.2 mg kg^{-1}). The U in these is concentrated in primary accessory minerals such as monazite, zircon and uraninite, as well as iron oxides (Heath, 1982; Poole, 2001). Popit et al. (2004) noted that U concentrations in acidic igneous rocks were in the range 3–4 mg kg^{-1}, while concentrations in intermediate igneous rocks were typically around 1.5 mg kg^{-1}, basic igneous rocks were around 0.6 mg kg^{-1} and ultrabasic types around 0.03 mg kg^{-1}.

High U concentrations have also been found in phosphate-bearing rocks. In Britain, phosphate-rich horizons occur in several sedimentary rocks, but are particularly abundant in fine-grained Mesozoic (Jurassic, Cretaceous) strata. Phosphorite horizons in Mesozoic rocks of Cambridgeshire, Lincolnshire and Yorkshire have U concentrations of 30–119 mg kg^{-1} U (Sutherland, 1991). Roessler et al. (1979) found concentrations up to 120 mg kg^{-1} in phosphate rocks from Florida, USA (Table 2.1). Ilani et al. (2006) found concentrations of 100–150 mg kg^{-1} in Senonian phosphorites of the Negev desert in Israel. Jordanian phosphorites also have relatively high concentrations (Khaled and Abed, 1981).

Deposits rich in organic matter can also often have high U concentrations, presumably because reducing conditions favour the stabilisation of U(IV) in the solid phase and the strong binding of U by humic substances. A number of studies of black shales have found relatively high concentrations. Bottrell (1993) found concentrations in the Edale Shales of Derbyshire of 5–10 mg kg^{-1} while those in the Chapel en le Frith area had 10–60 mg kg^{-1} U (Ball et al., 1992). In south-west England, Carboniferous black shales have concentrations of 5–21 mg kg^{-1} (Ball and Miles, 1993). Lee et al. (2001) reported an average U concentration in Cambro-Ordovician black shales from the Okchun area of Korea of 250 mg kg^{-1} (Table 2.1).

Table 2.1 Typical U concentrations (mg kg^{-1}) in selected rocks

Rock/sediment	Range	Reference
Average upper crust	2.8	Taylor and McLennan (1985)
Granite	2.2–15	Langmuir (1978)
Granite, south-west England	<1–20	Bromley (1989); Poole (2001), Hussain (1997)
Granite, Stripa, Sweden	20.2–53.7	Andrews et al. (1989)
Acid igneous rocks	3–4	Eisenbud (1987); Popit et al. (2004)
Intermediate igneous rocks	1.5	Popit et al. (2004)
Basic igneous rocks	0.6	Popit et al. (2004)
Ultrabasic igneous rocks	0.03	Popit et al. (2004)
Ophiolite, Troodos, Cyprus	0.17	Tzortzis and Tsertos (2005)
Limestone	1.3	Eisenbud and Gesell (1997)
Phosphate rocks, USA	up to 120	Roessler et al. (1979); Eisenbud (1987)
Cretaceous phosphorite, Israel	100–150	Ilani et al. (2006)
Chalk, southern England	0.05–6.3	Murphy (1998)
Sherwood Sandstone, England	0.5–5.1 (up to 14)	Andrews and Lee (1979); Haslam and Sandon (1991); Cuttell et al. (1988)
Black shales, UK	5–60	Ball et al. (1992); Ball and Miles (1993); Bottrell (1993)
Black shale, Korea	250	Lee et al. (2001)
Cretaceous oil shale, Negev, Israel	10–56	Ilani et al. (2006) and references therein
Cretaceous oil shale, Mount Arbel, Israel	3.3–24	Ilani et al. (2006)
Tidal flats, iron-oxide-rich alluvial fan deposits, Baja California	2.0–4.3	Zielinski et al. (1983)
Quaternary loess silts, Argentina	0.9–5.1	Smedley et al. (2005a)
Continental margin sediments, off California, USA	2–8	McManus et al. (2005)
U-contaminated alluvial aquifer sediments, Naturita, Colorado, USA	2.3–11.9	Kohler et al. (2004)
Soils, Troodos Ophiolite Complex, Cyprus	0.0008–0.6	Tzortzis and Tsertos (2005)

Leventhal and Daws (1986) found a concentration of 56 mg kg^{-1} in a black shale from Kentucky, USA. These authors also reported a large range of concentrations in other organic-rich deposits, ranging up to 120,000 mg kg^{-1} for a uraninite-bearing organic-rich Proterozoic metasediments from Canada. Concentrations of 10–56 mg kg^{-1} U (average 23 mg kg^{-1}) have also been found in oil shale deposits from the Cretaceous Ghareb Formation of northern Negev in Israel (Ilani et al., 2006). Holocene peat deposits in Caithness have been found with concentrations in excess of 200 mg kg^{-1} (Read et al., 1993). Concentrations in coal vary but an average for U in coal from the USA is a low value of 2 mg kg^{-1} (EPA, 1993).

In fine-grained sediments, a range of U concentrations occurs in relation to texture, mineralogy and provenance. McManus et al. (2005) found concentrations in the range 2–8 mg kg^{-1} in continental shelf deposits off the coast of California (Table 2.1). Smedley et al. (2005a) found 0.9–5.1 mg kg^{-1} in Quaternary silty loess deposits from Argentina. Ivanovich and Alexander (1985) found concentrations typically averaging 2–3 mg kg^{-1} for argillaceous deposits from southern England (2.71 mg kg^{-1} for Gault Clay; 2.2 mg kg^{-1} for Kimmeridge Clay; 2.52 mg kg^{-1} for Lias Clay).

Red-bed sandstones can have relatively high U concentrations. In the Triassic Sandstone aquifer of the UK, concentrations have been reported in the range 0.5–5.1 mg kg^{-1} (Table 2.1), although values up to 14 mg kg^{-1} have been determined (BGS, unpublished data). Highest concentrations tend to be found in the finer-grained horizons (Cuttell et al., 1988). Much of the U in this aquifer is likely to be associated with iron oxides (goethite, haematite), which are abundant as grain coatings and cements in the formation. Uranium-rich bleached spheroids have also been described in the Triassic Sandstone which are of debatable origin but likely to be localised reduction zones perhaps linked to the presence of organic matter (Metcalfe et al., 1999). High U concentrations can also be present in refractory minerals such as zircon and sphene, but these are relatively rare in the Sherwood Sandstone and are poorly soluble. In the Old Red Sandstone of Scotland, locally high concentrations of U have been found in phosphate horizons (Michie, 1970).

Red-bed tidal-flat and alluvial-fan deposits from Baja California (Zielinski et al., 1983) were found to have U concentrations in the range 1.8–4.2 mg kg^{-1} (27 samples). The U was concentrated either in the rare refractory minerals, or at lower concentrations but more widely-disseminated on the surfaces of detrital magnetite grains or in the red surface coatings of minerals. Very little U was present in the unstained cores of quartz or feldspar grains which formed the bulk of the rocks (Zielinski et al., 1983). Weibel and Friis (2004) observed phosphatic coffinite in the mineralised cores of reduction spots in the Triassic (Bunter) Sandstone of Germany. As is likely in parts of the British Triassic Sandstone, this accumulation of U probably formed as a result of reduction of uranyl in the vicinity of pockets of organic matter.

By contrast, limestones typically contain relatively low concentrations of U; an average of around 1.3 mg kg^{-1} was quoted by Eisenbud and Gesell (1997). Ivanovich and Alexander (1985) determined average concentrations in the Chalk of southern England of 2.03 mg kg^{-1}. Concentrations in the range 0.05–6.3 mg kg^{-1} were quoted for the Chalk by Murphy (1998), but pure chalk samples were usually found to have <1 mg kg^{-1} with the higher concentrations occurring in marl horizons and hardgrounds. These are likely to have had higher concentrations of U-bearing phosphate.

2.3 URANIUM IN WATER

2.3.1 Units of measurement

Units of concentration used to describe the abundance of uranium in water are diverse and often complicate the comparison of data from different databases. The concentrations of individual isotopes of uranium are usually recorded as the radiochemical activity present per unit volume of substance, for example pCi L^{-1} (picoCuries per litre) or Bq L^{-1} (Bequerels per litre) or alternatively pCi kg^{-1} or Bq kg^{-1}. The use of picoCuries is still common in the literature even though this has been superseded by the Bequerel as the SI unit for radioactivity. One Bq is defined as one disintegration per second. One Bq is equal to approximately 27 pCi.

It is also common practice to measure and report natural uranium concentration in mass units, i.e. µg L^{-1} or occasionally µg kg^{-1} (1 µg L^{-1} is equal to 0.02528 Bq L^{-1} assuming secular equilibrium between ^{238}U and ^{234}U, natural ^{235}U and a specific activity of 25,280 Bq g^{-1}). Mass units (µg L^{-1}) are used in this study.

2.3.2 Concentration ranges

A large range of U concentrations, spanning several orders of magnitude, are observed in natural waters. Concentrations in surface waters are usually low. Surveys of stream waters in Britain carried out by BGS over the last few years have shown concentrations mostly less than 1 µg L^{-1} although some samples with concentrations exceeding 15 µg L^{-1} have been found (BGS, 2004). Of survey results obtained by 2005, only 38 out of 57,911 water analyses (0.07%) stored in the BGS surface-water (GBASE) database for Great Britain exceeded 15 µg L^{-1}. Many of the higher concentrations occur in streams overlying the Permo-Triassic sediments of the East Midlands and Yorkshire and Scottish Devonian strata (Figure 2.2). Some relatively high concentrations (>3 µg L^{-1}) also occur in areas underlain by granitic rock types such as in north-east Scotland and the Cheviot Hills. The GBASE streamwater database does not yet cover southern England (sampling of central England and East Anglia has recently been completed and reporting is in progress). A local stream survey in Devon carried out by Heath (1991) found U concentrations greater than 13 µg L^{-1} in a small number of samples from the north-eastern part of the Dartmoor granite. Heath (1991) speculated that this may be due to higher fracture density in this part of the granite.

The GBASE data shown in Figure 2.2 are mainly for samples from first- or second-order streams and how well these would compare with concentrations in higher-order streams that may be used as abstraction points for drinking water is not known. Higher-order streams are likely to have U concentrations that reflect an average streamwater composition integrated over the catchment.

Concentrations of U in the range 1–2 µg L^{-1} have been found in some rivers in Texas, USA although concentrations in other USA rivers are usually much lower (Cothern and Lappenbusch, 1983). The high values have been attributed the use of phosphate fertilisers. Surface waters from 68 stations in Canada were found to have U in the range 0.1–4.3 µg L^{-1} but usually <1 µg L^{-1} (Cothern and Lappenbusch, 1983).

Uranium concentrations in most groundwaters are also usually low, typically in the range 0.1–1 µg L^{-1}, but can reach several tens to hundreds of µg L^{-1} as a result of reactions with minerals in aquifers. Concentrations up to 1000 µg L^{-1} are comparatively rare.

2.3.3 Uranium isotopes and radioactive decay

As noted in Section 2.1, U has three isotopes in nature, ^{238}U being overwhelmingly the dominant form (99%). Radioactive (secular) equilibrium is established throughout the ^{238}U decay series within 1.25 x 10^6 years in closed systems containing ^{238}U. Activities of ^{234}U and ^{238}U are equal at equilibrium (Andrews, 1991). However, a number of studies have shown that the U isotopes are often not in secular equilibrium in water and that the activity of dissolved ^{234}U commonly exceeds that of ^{238}U. Activity ratios in the range 1–3 are typical (Lee et al., 2001; Cizdziel et al., 2005) but can be as high as 28 (Hess et al., 1985). This has been attributed to the selective mobilisation of ^{234}U in aqueous solution as a result of preferential leaching or alpha recoil during radioactive decay resulting in damage to the crystal structure of minerals (Andrews, 1991; Ivanovich, 1994). Enhanced alpha recoil rates and generation of disequilibrium (giving high ^{234}U/^{238}U activity ratios) have been linked to reduction and precipitation of U close to redox boundaries (Bonotto and Andrews, 2000). Disequilibrium has also been associated with increased groundwater residence time (Andrews, 1991; Lee et al., 2001; Yamamoto et al., 2003).

Radioactive decay of U produces a number of daughter products, including radium (^{226}Ra) and radon (^{222}Rn). Radon gas has been found in association with U-rich rocks, notably granites and U-mineralised limestones, both in the air in restricted spaces and dissolved in groundwater. The concentrations of Rn in groundwater are typically some hundreds of Bq L^{-1} but can vary from around 3 Bq L^{-1} to 80,000 Bq L^{-1} (Appleton, 2005). Although associated, the properties of Rn and U differ significantly, Rn being a dissolved inert gas and U a redox-sensitive solute with strong adsorption and complexation controls. Hence, although the two elements can be derived from a common source and can occur together in groundwaters, they have very different transport behaviour and may therefore become separated. Indeed, several studies have shown a poor correlation between dissolved U and Rn in groundwater (e.g. Virk et al., 2001; Ilani et al., 2006). The concentrations of U in a groundwater cannot therefore be used as a reliable indicator of the concentrations of Rn or other associated radionuclides, or vice versa.

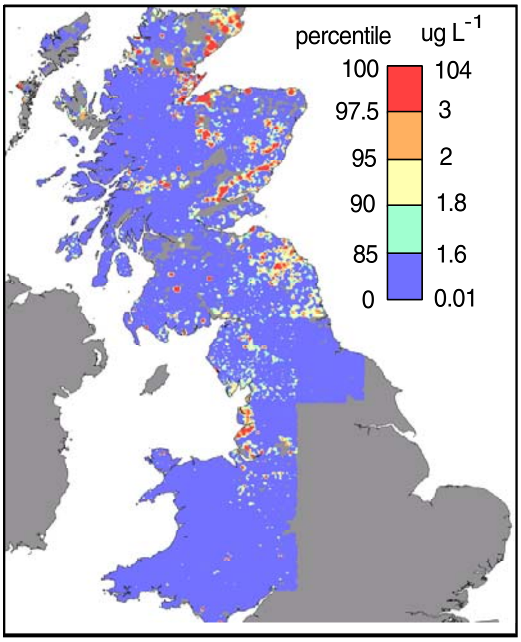

Figure 2.2 Map of U concentrations in streamwaters from the BGS-GBASE survey programme (BGS, 2004). The data indicate a concentration maximum of 104 µg L^{-1}, with 85% of samples analysed having concentrations less than 1.6 µg L^{-1}.

2.4 URANIUM MOBILISATION AND SORPTION

The mobilisation of U in the environment is strongly controlled by its redox state. It is generally only the oxidised hexavalent form, U(VI), that occurs significantly in solution. Under reducing conditions, dissolved concentrations are kept low because of the very low solubility of uraninite. Equilibrium with this mineral limits U concentrations to less than 0.06 µg L^{-1} (Langmuir, 1978; Gascoyne, 1992). In a typical redox sequence (Berner, 1981), reduction of U occurs concurrently with iron reduction (reduction of Fe(III) to Fe(II)) and before sulphate reduction (Finneran et al., 2002). The reduction of U(VI) is facilitated significantly by microbial activity (Lovley et al., 1991); laboratory experiments suggest that abiotic reduction reactions (e.g. by Fe(II) or sulphide) are ineffective (Finneran et al., 2002).

Uranium in water is usually complexed (Langmuir, 1978) and pH and pCO_2 have important controls on its mobility. In oxidising conditions (high Eh or pe) at pH less than around 5, uranyl, UO_2^{2+}, is the dominant dissolved form of U(VI) although uranyl fluoride complexes can occur where F concentrations are sufficiently high. At higher pH, the uranyl ion forms stable complexes with carbonate ions, notably $UO_2(CO_3)_2^{2-}$ and at higher pH, $UO_2(CO_3)_3^{4-}$ (Figure 2.3a). Complexes with phosphate can also occur at near-neutral pH. Drever (1997) concluded that the aqueous species $UO_2(HPO_4)_2^{2-}$ could be important in neutral-pH waters. Sandino and Bruno (1992) found that at pH 6–9, aqueous phosphate complexes could dominate when the total concentration ratio of PO_4^{3-}/CO_3^{2-} was greater than 10^{-1}. The dominant species were concluded to be UO_2HPO_4(aq) and $UO_2PO_4^-$. Complexation with sulphide and fluoride can occur under acidic conditions (Langmuir, 1978; Drever, 1997) and chloride and sulphate may become important ligands in saline waters (Porcelli and Swarzenski, 2003). Uranium(VI) also forms stable complexes with dissolved organic carbon (Cothern and Lappenbusch, 1983; Higgo et al., 1993; Arey et al., 1999). Uranium mobility can therefore be significantly enhanced in organic-rich waters.

The mobility of U(VI) can also be restricted in the approximate pH range 4–8 in the presence of high concentrations of vanadium (around 100 µg L^{-1} or more) as a result of stabilisation of the mineral carnotite ($K_2(UO_2)_2(VO_4)_2$ (Drever, 1997). However, high concentrations of V in water are uncommon, except in some U-V mineralised areas and some alkaline groundwaters (e.g. Smedley et al., 2002).

The redox and carbonate complexation controls on dissolved U are exploited to effect in the uranium mining industry. The technique of in-situ extraction involves the pumping of hydrogen peroxide (oxidising agent) and ammonium carbonate/bicarbonate (complexing agent) into an aquifer that contains U minerals. The U-bearing minerals dissolve and the solution is pumped out for U processing above ground. On the other hand, the biological reduction of U(VI) to U(IV) by dissimilatory metal-reducing bacteria in the presence of Fe(III) oxides has been recognised as a promising strategy for bioremediation of U-contaminated sites (Lovley et al., 1991; Anderson et al., 2003; Cheng et al., 2004; Jeon et al., 2004).

Despite the relative mobility of U(VI) in the aqueous environment, the concentrations of U under oxidising conditions can be limited by adsorption onto phosphate minerals and iron oxides, as well as organic matter and clay minerals (Ivanovich, 1994). These minerals can therefore act as important sinks as well as potential sources. Sorption of U onto minerals is greatest in the near-neutral pH range (Langmuir, 1978; Prikryl et al., 2001).

The importance of iron oxides as U sorbents has been known for a long time (e.g. Payne et al., 1994; Villalobos et al., 2001). Iron oxides have highly reactive surfaces and hence a strong affinity for U. As these are more abundant than phosphate minerals, they have an important control on U mobility in the environment. Ferrihydrite has been found to have a stronger affinity for U on a weight by weight basis than more crystalline forms of iron oxide such as goethite and haematite (Payne et al., 1994). Evidence suggests that adsorbed U is also incorporated into more stable oxide sites during ageing and crystallisation (Payne et al., 1994).

Adsorption of U(VI) on iron oxides is dependent on groundwater pH and dissolved carbonate concentration (Kohler et al., 2004). As many of the uranyl-carbonate complexes are anionic, sorption is generally less strong at high pH, >7–8 (Figure 2.3b). The desorption results from competition for the uranyl ion between mineral surface sites and carbonate ligands (Villalobos et al., 2001). The presence of dissolved phosphate can also strongly affect the adsorption of U(VI) on iron oxides, although the relationships are complex. Cheng et al. found that at low pH (e.g. pH 6 or less), U(VI) adsorption on goethite increased in the presence of phosphate. They attributed this to the formation of ternary surface complexes involving both phosphate and U(VI), of the form $FePO_4UO_2$. At high pH (>7), adsorption was found to decrease in the presence of phosphate. This they attributed to the formation of soluble U(VI)-phosphate complexes.

2.5 URANIUM REMOVAL FROM WATER

Uranium can be removed from groundwater by a number of processes though there appear to be relatively few groundwater treatment plants that operate for this purpose. Methods include anion exchange or reverse osmosis, use of sorbents such as zeolites or activated carbon, removal by zero-valent iron (Noubactep et al., 2003), lime softening or coagulation using iron

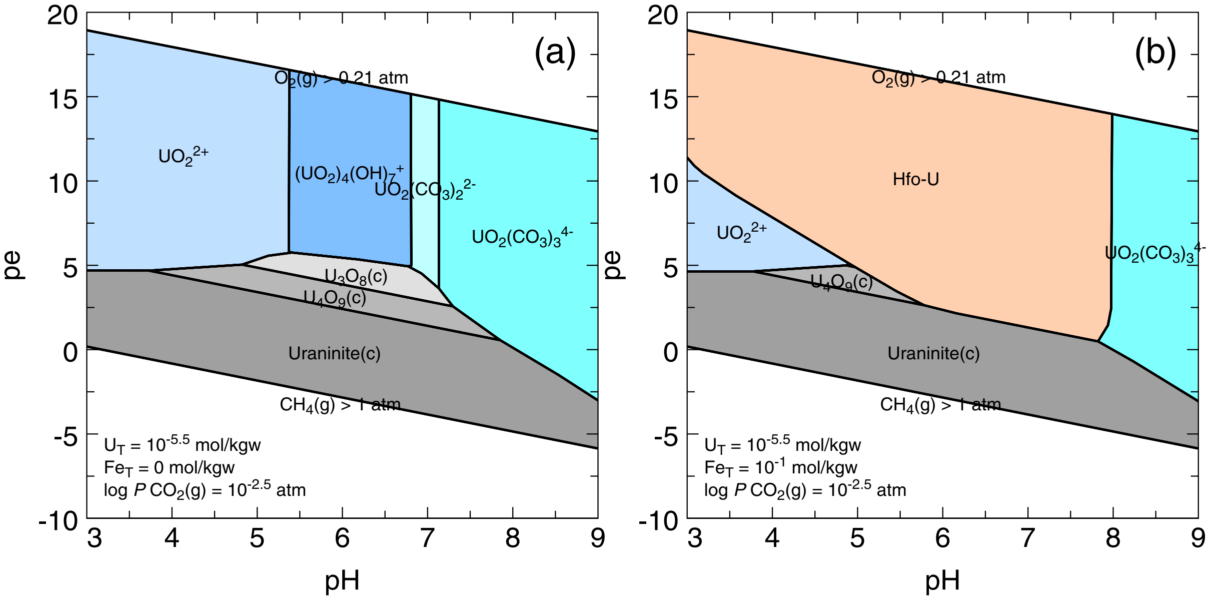

Figure 2.3 pe-pH predominance diagrams at 10ºC for uranium in (a) the absence and (b) the presence of iron. Under oxidising conditions the iron in (b) precipitates as hydrous ferric oxide (Hfo) which strongly adsorbs uranium species, making Hfo-U the predominant species over much of the diagram. A fixed partial pressure of CO_2(g) of $10^{-2.5}$ atm was imposed in both cases leading to uranyl carbonate species becoming predominant at high pH. The diagrams were prepared using the full chemical speciation method of Kinniburgh and Cooper (2004). Speciation calculations were carried out using PHREEQC (Parkhurst and Appelo, 1999) and the `wateq4f.dat` database.

(ferrous, ferric sulphate) or aluminium (alum) salts (Sorg, 1990). Many of these methods are technically demanding and expensive but conventional coagulation-filtration has been found to have a removal efficiency of 80–98% and ion exchange about 90–100% (WS Atkins, 2001). WHO also state that a uranium concentration of around 1 µg L^{-1} ought to be achievable using coagulation or ion-exchange methods. Removal efficiency varies according to factors such as pH and uranium speciation and in the case of coagulation, to coagulant dose (Sorg, 1990). Methods used for the removal of arsenic or phosphate from water should be effective for the removal of U.

As noted in Section 2.4, in-situ bioremediation of contaminated groundwaters in U-mineralised or industrial sites has been advocated by means of microbially-mediated reduction of soluble U(VI) to insoluble U(IV) (Lovley et al., 1991; Finneran et al., 2002). Remediation of U-contaminated soils has also been proposed by leaching with alkaline sodium carbonate/bicarbonate solutions (Mason et al., 1997) or a combination of bicarbonate leaching and microbial reduction (Phillips et al., 1995).

3 Groundwater data compilation

3.1 GROUNDWATER SAMPLING AND ANALYSIS FOR THIS STUDY

A set of groundwater samples has been collected for this study from 101 sources from sites distributed across England & Wales. These were taken mainly from areas where little information was available from previous studies and were from a range of aquifer types and hydrogeological conditions. All were from either boreholes in regular use or flowing springs.

Samples were collected in three campaigns during the periods March 2005, October 2005 and December 2005–January 2006. During the March 2005 campaign, samples were collected from 18 sources from 16 geographically-dispersed sites and included a selection of both public and private sources. During the October 2005 campaign, 12 of these sources were resampled in order to compare analytical results and investigate whether significant variations existed in water quality between the spring and autumn. Sampling during the third campaign included 83 new sites, all from public-supply sources, plus three additional samples from three sources originally sampled in March 2005. The resampling of these three sources was to verify the U concentrations determined from the earlier samples. It is stressed that all samples are of raw groundwater taken directly from wellheads and therefore represent in-situ groundwater compositions rather than the compositions of drinking water at domestic taps or put into public supply.

Where boreholes were sampled, care was taken to ensure that the borehole had been adequately purged before samples and measurements were taken. Sampling involved on-site analysis of groundwater temperature, alkalinity, specific electrical conductance (SEC), pH, Eh and dissolved oxygen. Where possible, the latter three determinands were measured in an in-line flow cell to exclude air and maintain the redox condition of the groundwater during monitoring. Monitoring was continued until stable readings were obtained. Alkalinity was measured by titrating against H_2SO_4 and is quoted as HCO_3.

Water samples were also collected at each source for subsequent laboratory analysis. Three aliquots of filtered (0.45 µm) water were collected in polyethylene bottles for analysis of major ions and trace elements, including U. Aliquots were filtered to remove particulate matter. Although it is possible that some colloidal material of <0.45 µm size can get through the filter, this is considered to be negligible except in cases where waters are turbid. Two of the filtered aliquots were acidified with 1% Aristar® HNO_3, one for the analysis of cations, SO_4 and selected trace elements by inductively-coupled plasma optical-emission spectrometry (ICP-OES) and the second for trace elements including U by inductively-coupled plasma mass spectrometry (ICP-MS). The third was left unacidified for the analysis of anions by either automated colorimetry (N species) or ion chromatography (NO_3-N, Cl). In addition, aliquots of unfiltered water were collected for analysis of total U (particulate and dissolved), also by ICP-MS. All samples in the March and October 2005 campaigns were sampled and analysed for unfiltered U. As these showed little difference in U concentration between filtered and unfiltered aliquots, 30 of the unfiltered samples in the December 2005–January 2006 campaign were selected at random from the available samples and analysed for U.

ICP-OES, automated colorimetry and ion chromatography analyses were carried out at the BGS laboratories in Wallingford. Electrical charge imbalances were in all cases less than 5%.

Uranium analysis was carried out on all water samples collected in the three campaigns by ICP-MS at the BGS analytical laboratory in Keyworth. The laboratory holds ISO 17025 accreditation as testing laboratory 1816 from the UK Accreditation Service (UKAS). Although not specifically included in the list of elements accredited in the analytical method, U was analysed along with other elements which are accredited and with the same attention to quality assurance. Samples were regularly interspersed with standards and blanks; raw data were corrected using Re as an internal standard. Typical detection limits during the analytical runs were 0.02 µg L^{-1}. Six replicate analyses of NIST (USA) standard 1640 carried out during the analysis of the March and October 2005 sample set gave an average U concentration of 0.76 ± 0.04 µg L^{-1}, relative to a long-term BGS mean analysis for this standard of 0.79 µg L^{-1} (no NIST-certified U value is given for this standard). Four replicate analyses of NWRI (Canada) standard TM23 analysed at the same time as the samples collected during December 2005–January 2006 gave a mean U concentration of 5.41 ± 0.03 µg L^{-1}, compared to a certified value of 5.1 µg L^{-1}.

3.2 COLLATED GROUNDWATER DATASET

Published reports describing the distribution and concentrations of U in groundwater in England & Wales are relatively scarce but available and accessible data have been assessed and collated. No data have been found from UK water companies or the Environment Agency.

The collated dataset comprises 1556 analyses from groundwaters across England, Wales and Scotland. Most of the data used in the compilation are from the BGS groundwater-chemistry database, which includes samples collected from the late 1980s onwards (most dating from the late 1990s). BGS analyses are all from filtered samples (mostly 0.45 µm but some 0.22 µm), preserved by acidification with 1% HNO_3 Aristar® acid. All analyses were carried out by ICP-MS, either in BGS laboratories or by a commercial laboratory in Canada. The samples were for the most part taken to be a ‘random’ selection of groundwaters, that is they were collected with no prior knowledge of U concentrations, but within the constraints of accessible and operational sampling points. Samples are from a large range of aquifer types from a range of hydrogeological settings. Samples are also from sources with a range of uses (industrial, agricultural, domestic and public supply).

Limited analyses, with reported georeferences, are also available from a report on the trace-element geochemistry of groundwaters in Britain (Edmunds et al., 1989). These have been incorporated into the collated dataset.

Groundwater U data are also available in the open literature from a small number of studies in England. These include an investigation by Ivanovich et al. (1992) of the U concentrations and isotopic ratios in groundwater from 5 boreholes in the Permo-Triassic Sandstone of the lower Mersey Basin. Uranium concentrations were determined by isotope dilution/alpha spectrometry and the study reports ancillary water-quality data and sample grid references. These data have also been included in the collated database.

The CEFAS RIFE reports (e.g. CEFAS, 2003, 2004), give data on U radionuclide activities in various environmental media in the UK, but give few analyses of groundwaters. Of those quoted, activities of ^{234}U, ^{235}U and ^{238}U are almost always below analytical detection limits and no data are given for total U concentrations in water samples. The only groundwater source in the monitored network with consistently detectable U radionuclide activities was Meerbrook Sough in Derbyshire. For example, 2002 data which are reasonably representative of data given at other times for this source, had a ^{234}U activity of 0.041 Bq L^{-1}, ^{235}U activity of <0.01 Bq L^{-1} and ^{238}U activity of 0.021 Bq L^{-1} (CEFAS, 2003). Taking a specific activity for ^{234}U of 0.33 pCi µg^{-1}, for ^{235}U of 2.2 pCi µg^{-1} and ^{238}U of 6.2x10^3 pCi µg^{-1}, this equates to an upper estimate for U concentration of 1.7 µg L^{-1}. The CEFAS data for this source have not been incorporated into the dataset as a more recent sample has been collected and analysed by BGS (observed concentration 1.71 µg L^{-1}).

Other published studies include the radioactivity of private groundwater supplies in west Devon by Talbot et al. (2001), the Jurassic Lincolnshire Limestone of eastern England by Andrews and Kay (1982), the hot springs of Bath by Andrews et al. (1991), groundwaters from the Carboniferous Limestone of the Mendip Hills (Bonotto and Andrews, 2000) and groundwaters from the Millstone Grit and Coal Measures of Derbyshire and Yorkshire (Banks, 1997). Results and conclusions from these studies have been summarised in Section 4.3, but the data have not been incorporated into the database for mapping and statistical handling as either grid references were not reported or detection limits were high or only ranges or average values were quoted. Data given by Andrews and Kay (1983) for groundwater from the Triassic Sandstone are also not included as more recent BGS data are available in the database for the sites investigated in their study.

4 Uranium in groundwater in Britain

4.1 CONCENTRATIONS IN SAMPLED GROUNDWATERS

Groundwater-chemistry results for the sites sampled during the March 2005 and October 2005 campaigns are shown in Table 4.1. Those from the December 2005–January 2006 sampling campaign are given in Table 4.2. Summary U statistics for the groundwater samples collected in this study are also given in Table 4.3. Where sources were analysed more than once, only the first determined result was included for the statistical calculations.

Of the 101 groundwater sources investigated, the observed range in U concentration was <0.02–48 µg L^{-1} with a median of 0.39 µg L^{-1} and a mean of 1.58 µg L^{-1}. Two samples (2%) had concentrations above the WHO provisional guideline value for U in drinking water of 15 µg L^{-1}; 1 sample had more than 30 µg L^{-1}. By contrast, 74 samples (73%) had concentrations <1 µg L^{-1} (Table 4.3). The highest concentration (48 µg L^{-1}) was found in a groundwater sample from a private borehole in the Old Red Sandstone aquifer of Herefordshire. The high concentration is most likely linked to natural water-rock reaction processes; there is no evidence that the groundwater has been affected by pollution.

Private groundwater sources had a range of U concentrations of <0.02–48.0 µg L^{-1}, median 0.98 µg L^{-1} (13 samples). Public raw water sources (from water companies) had a range of <0.02–6.45 µg L^{-1}, median 0.36 µg L^{-1} (88 samples).

At all sources sampled in March and October 2005, U analysis was carried out on both filtered (0.45 µm) and unfiltered samples. Thirty selected sources from the December 2005–January 2006 campaign were also analysed for both filtered and unfiltered U. Comparisons of the results indicated that all agreed within 15% and all but one within 5%. This indicates that in the samples investigated, U was overwhelmingly present in dissolved rather than particulate form. This is expected since the sampled groundwaters were generally clear with no visible particulate matter.

4.2 GROUNDWATER MONITORING SITES

Groundwater data for the sources monitored more than once in this study are also shown in Table 4.1. These include the March 2005 and October 2005 samples as well as the three further samples collected in January 2006 for sites 5, 6 and 7.

Comparison of major-ion and U data for the sources that were sampled more than once indicates in most cases good agreement, the majority of samples having differences of less than 15% (see Table 4.1, Figure 4.1). Although little can be deduced concerning temporal variation from just two or three analyses for any given groundwater source, the limited data suggest that most of the sampled groundwaters have relatively stable U concentrations. However, there are some notable exceptions. Sources 2 and 7 had very different U concentrations in the March and October samples and source 5 had very different concentrations in March 2005 compared to January 2006 (Table 4.1).

Source 2 abstracts groundwater from the Carboniferous Limestone in North Wales. Although not appreciated during sampling in March 2005, the site has two boreholes each of which are pumped regularly and discharge to a single large storage tank. Sampling upstream of the tank is not possible and so at both times a sample from the tank was taken. It is possible that differing pumping regimes were operating at the times the two samples were collected and this could explain the differences in chemical composition. The two boreholes have depths of 52 m and 76 m and groundwater abstracted from them may be from different depth zones or

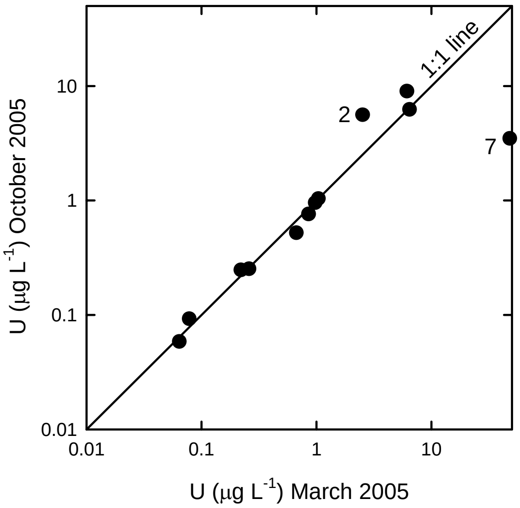

Figure 4.1 Variation in groundwater uranium concentration between samples collected in March 2005 and October 2005. Results show close comparison for most sources. The two sources with the greatest discrepancies (sources 2 and 7) are also shown.

fractures. This raises the possibility of vertical stratification in dissolved U concentrations in the groundwater at this location.

The other sources with significant temporal variations, sources 5 and 7, are from an industrial site in Herefordshire which abstracts groundwater from the Old Red Sandstone aquifer. The site has three operational water-supply boreholes (sources 5, 6 and 7), all of which are pumped regularly. Borehole source 5 has a total depth of 55 m and source 6 a depth of 40 m; the depth of source 7 is unknown. Source 5 had a U concentration of 28.8 µg L^{-1} in March 2005 but this reduced to 7.22 µg L^{-1} in January 2006. Source 6 had comparable concentrations in March 2005 and January 2006 (3.99 µg L^{-1} and 4.15 µg L^{-1} respectively). Source 7 had concentrations of 48.0 µg L^{-1} in March 2005, 3.48 µg L^{-1} in October 2005 and 9.56 µg L^{-1} in January 2006 (Table 4.1). The resampling in January 2006 confirmed that no errors in source labelling had been made in the previous campaigns and that the temporal variations in U concentration therefore appeared to be real. The observed data suggest that significant spatial and temporal variations occur at this site. More monitoring of the site would be required to ascertain the causes of the variations but seasonal variations in groundwater level and hence inflow zones are a possibility. Variable pumping rate or duration leading to changing flow patterns may also be factors.

A further source, source 8, had U concentrations which were around 38% different between the March and October samples. The difference is relatively small in absolute terms but larger than observed at most other sites. The samples were from a shallow borehole (9.14 m depth) in the Quaternary Yazor River Terrace Gravels in Hereford. The concentrations are relatively high (6.1 µg L^{-1} and 9.0 µg L^{-1} for dissolved U in the March and October samples respectively; Table 4.1). It is not clear whether the differences represent real temporal variations, but this is a possibility as the groundwater is abstracted from a shallow aquifer likely to be affected by large seasonal variations in both groundwater and river flow.

Table 4.1 Field-determined parameters, major-ion and uranium concentrations in groundwaters sampled in England & Wales during March and October 2005 (data from resampling of sources 5, 6 and 7 in January 2006 are also given)

Field no.	Sample number	Sampling date	Aquifer	Region	Source type	pH	Eh mV	DO mg L^{-1}	Ca Mg L^{-1}	Mg mg L^{-1}	Na mg L^{-1}	K mg L^{-1}	Cl mg L^{-1}	HCO$_3$ mg L^{-1}	SO$_4$ mg L^{-1}	NO$_3$-N mg L^{-1}	U$_{filt}$ µg L^{-1}	U$_{unfilt}$ µg L^{-1}
1A	S05-00213	08-Mar-05	Triassic Sandstone	Denbigh, Wales	Public	7.44		10.6	61.1	7.07	11.2	1.96	17.5	194	8.6	2.61	0.52	0.50
2A	S05-00214	08-Mar-05	Triassic Sandstone	Denbigh, Wales	Private	7.00		10.1	96.6	11.5	19.2	2.45	37.6	252	31.3	10.5	2.52	2.49
2B	S05-00626	11-Oct-05	Triassic Sandstone	Denbigh, Wales	Private	7.16	479	8.9	123	11.0	17.8	1.99	36.5	286	37.7	13.3	5.60	5.76
3A	S05-00215	08-Mar-05	Carb. Limestone	Henllan, near Denbigh	Private	6.82		6.1	134	12.4	27.5	2.96	62.5	345	24.7	15.4	0.98	0.96
3B	S05-00627	11-Oct-05	Carb. Limestone	Henllan, near Denbigh	Private	7.00		5.2	143	12.3	27.6	2.93	63.8	355	26.5	15.0	0.96	0.93
4A	S05-00216	09-Mar-05	Triassic Sandstone	St Austells, Denbighshire	Private	7.03			98.9	18.6	21.5	1.77	31.2	359	26.3	1.76	1.86	1.87
5A	S05-00217	10-Mar-05	Old Red Sandstone	Leominster, Herefordshire	Private	7.25		8.1	71	8.77	95.2	2.94	59.9	374	17.6	6.38	28.8	28.5
5C	S06-00014	10-Jan-06	Old Red Sandstone	Leominster, Herefordshire	Private				116	8.80	32.2	2.61		356	22.7		7.22	
6A	S05-00218	10-Mar-05	Old Red Sandstone	Leominster, Herefordshire	Private	6.94		6.7	127	9.50	20.4	2.29	38.0	375	21.2	8.94	3.99	3.93
6C	S06-00013	10-Jan-06	Old Red Sandstone	Leominster, Herefordshire	Private				132	8.99	22.7	2.36	32.8	384	22.0	8.73	4.15	
7A	S05-00219	10-Mar-05	Old Red Sandstone	Leominster, Herefordshire	Private	7.35		9.2	57.5	9.91	112	2.92	63.9	388	12.0	7.24	48.0	48.5
7B	S05-00628	12-Oct-05	Old Red Sandstone	Leominster, Herefordshire	Private	6.94	457	7.3	136	9.50	23.9	2.51	35.4	381	23.0	8.52	3.48	3.98
7C	S06-00012	10-Jan-06	Old Red Sandstone	Leominster, Herefordshire	Private				124	11.0	27.8	2.25	33.7	380	20.4	8.81	9.56	
8A	S05-00220	10-Mar-05	Yazor River-Terrace Gravels	Hereford	Private	7.09		6.3	124	7.62	17.3	3.18	37.3	321	28.5	15.4	6.11	6.00
8B	S05-00629	12-Oct-05	Yazor River-Terrace Gravels	Hereford	Private	7.11	409	6.8	137	8.6	19.0	3.01	41.5	346	31.3	14.1	9.01	8.66
9A	S05-00221	11-Mar-05	Permo-Triassic Sst	Ottery St Mary, Devon	Public	7.47		4.0	46.3	18.7	10.4	2.53	17.8	216	10.0	1.70	6.45	6.31
9B	S05-00631	13-Oct-05	Permo-Triassic Sst	Ottery St Mary, Devon	Public	7.64		4.3	47.1	19.2	10.8	2.59	19.1	227	11.2	1.78	6.25	6.44
10A	S05-00222	11-Mar-05	Permo-Triassic Sst	Harpford, Devon	Public	6.70		3.9	69	10.2	12.5	4.78	25.9	192	36.0	5.48	0.67	0.59
10B	S05-00630	13-Oct-05	Permo-Triassic Sst	Harpford, Devon	Public	6.79	463	6.1	70.8	10.2	12.9	4.60	27.2	193	40.9	4.87	0.52	0.53
11A	S05-00223	11-Mar-05	Carb. Limestone	Barton, nr Wells, Somerset	Private	6.90		7.7	114	32.5	10.5	2.25	12.9	457	17.4	4.62	0.87	0.85
12A	S05-00224	15-Mar-05	Corallian Limestone	Pickering, Yorks	Private	7.21	513	9.0	140	4.9	8.27	4.31	23.3	298	40.2	14.6	0.26	0.24
12B	S05-00623	10-Oct-05	Corallian Limestone	Pickering, Yorks	Private	7.17	462	4.0	130	9.2	9.31	2.71	27.1	307	50.3	12.6	0.25	0.30

Field no.	Sample number	Sampling date	Aquifer	Region	Source type	pH	Eh	DO	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3-N	U_{filt}	U_{unfilt}
							mV	mg L^{-1}	Mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	μg L^{-1}
13A	S05-00225	16-Mar-05	Magnesian Lst	Thornton Watlass, Yorks	Private	7.19	516	9.5	107	38.1	20.1	1.98	50.5	362	39.4	11.4	0.85	0.83
13B	S05-00624	10-Oct-05	Magnesian Lst	Thornton Watlass, Yorks	Private	7.19	469	9.6	106	35.3	13.3	0.90	42.1	345	43.0	12.4	0.76	0.76
14A	S05-00226	16-Mar-05	Millstone Grit	Ramsgill, Pateley Bridge	Private	7.46	290	0.2	52.6	11.4	19.6	5.26	12.5	237	17.2	<0.05	0.08	0.09
14B	S05-00625	11-Oct-05	Millstone Grit	Ramsgill, Pateley Bridge	Private	7.41	242	0.6	53	11.6	19.3	5.16	13.9	238	18.2	<0.05	0.09	0.08
15A	S05-00242	17-Mar-05	Triassic Sandstone	Lambley, Notts	Public	8.26	496	9.6	17.6	17.7	4.68	1.68	8.03	112	4.6	3.06	1.04	1.01
15B	S05-00622	10-Oct-05	Triassic Sandstone	Lambley, Notts	Public	8.26	434	8.7	18.3	18.0	4.79	1.73	9.37	127	5.5	2.94	1.04	1.05
16A	S05-00243	17-Mar-05	Triassic Sandstone	Bestwood, Notts	Public	7.87	503	11.5	56.5	24.1	15.5	2.73	48.4	115	58.9	17.2	0.06	0.06
16B	S05-00621	10-Oct-05	Triassic Sandstone	Bestwood, Notts	Public	7.87	402	9.5	57.8	24.4	15.0	2.66	47.1	118	59.7	17.3	0.06	0.05
17A	S05-00244	18-Mar-05	L. Cretaceous Ashdown/Hastings Beds	Bodiam, East Sussex	Private	6.31	308	0.7	51.6	11.9	27.5	2.55	37.1	155	69.0	0.06	<0.02	<0.02
18A	S05-00245	23-Mar-05	Chalk	Lambourn, Berkshire	Private	7.21	520	10.0	109	1.32	7.29	0.99	18.0	215	22.7	8.74	0.22	0.22
18B	S05-00632	14-Oct-05	Chalk	Lambourn, Berkshire	Private	7.03	504	8.5	117	1.55	6.35	1.12	21.9	249	27.7	10.2	0.25	0.25

Eh: redox potential, DO: dissolved oxygen
U_{filt}: U filtered (0.45 μm); U_{unfilt}: U unfiltered

Table 4.2 Field-determined parameters, major-ion and uranium concentrations in groundwaters (public sources) sampled in England & Wales during December 2005 and January 2006

Field number	Sample number	Sampling date	Aquifer	Region	pH	Eh	DO	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3-N	U_{filt}	U_{unfilt}
						mV	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}
19	S05-00759	12-Dec-05	Magnesian Limestone	Teeside	7.12	349	2.52	157	61.8	75.9	3.03		274	348	0.71	1.89	
20	S05-00760	12-Dec-05	Magnesian Limestone	Teeside	7.47	333	7.05	70.7	41	144	3.91		251	53	1.66	0.81	0.79
21	S05-00761	12-Dec-05	Magnesian Limestone	Teeside	7.29	349	3	78.0	43.9	30.2	2.31	35.1	334	78.4	3.51	1.26	1.24
22	S05-00762	12-Dec-05	Magnesian Limestone	Teeside	7.46	370	1.6	58.7	32.4	38.2	2.81	33.9	271	69.7	0.959	1.02	
23	S05-00763	12-Dec-05	Magnesian Limestone	Teeside	7.64	381	5.3	58.7	29.8	31.3	2.33	30.7	236	73.1	0.346	1.02	
24	S05-00764	12-Dec-05	Magnesian Limestone	County Durham	7.42	332	0.0	68.2	34.3	21.6	2.62	23.5	310	45.6	0.614	1.13	1.14
25	S05-00765	12-Dec-05	Magnesian Limestone	County Durham	7.27	385	0.0	97.3	42.2	37.8	2.96	24.5	365	120	0.608	1.68	
26	S05-00766	13-Dec-05	Carb Limestone	Northumberland	7.00	224	0.0	117	12.6	13.1	3.37	15.3	366	35.4	< 0.05	0.03	
27	S05-00767	13-Dec-05	Carb Lst/Millstone Grit	Northumberland	6.83	414	4.81	40.5	6.06	8.39	1.15	10.0	126	15.4	0.53	0.08	0.08
28	S05-00768	12-Dec-05	Millstone Grit	Northumberland	6.38	443	6.3	19.2	3.45	5.89	0.74	13.4	48	10.6	1.07	<0.02	<0.02
29	S05-00769	13-Dec-05	Millstone Grit	Northumberland	7.05	450	10.86	14.0	4.95	3.5	0.95	5.26	52	9.38	< 0.05	<0.02	<0.02
30	S05-00770	13-Dec-05	Carb Lst/Millstone Grit	Northumberland	5.08	531	7.54	1.08	1.31	3.4	< 0.5	5.18	5.0	4.09	0.296	<0.02	
31	S05-00771	13-Dec-05	Carb Lst/Millstone Grit	Northumberland	6.37	490	7.78	20.6	8.02	4.03	1.07	5.57	97	12.4	< 0.05	<0.02	
32	S05-00772	14-Dec-05	Fell Sst/Carb Limestone	Northumberland	7.20	400	9.52	21.4	10.7	6.66	1.15	15.1	98	6.65	0.593	0.06	0.06
33	S05-00773	14-Dec-05	Fell Sst/Carb Limestone	Northumberland	7.05	442	8.2	16.8	6.46	6.79	1.16	13.3	72	5.06	0.687	<0.02	
34	S05-00774	14-Dec-05	Fell Sst/Carb Limestone	Northumberland	6.02	499	7.69	10.4	4.52	13.9	1.86	22.1	22	16.6	2.59	0.04	0.05
35	S05-00775	14-Dec-05	Fell Sst/Carb Limestone	Northumberland	6.87	478	4.89	53.2	25	14.7	3.53	30.5	185	46.6	5.41	3.21	3.09
36	S05-00776	14-Dec-05	Fell Sst/Carb Limestone	Northumberland	6.27	440	6.75	24	11	15.2	3.69	30.5	63	25.6	6.64	0.04	
37	S05-00777	15-Dec-05	Millstone Grit	North Yorkshire	7.15	498	5.88	55.2	8.03	7.76	0.89	14.4	161	14.1	1.05	0.30	
38	S05-00778	15-Nov-05	Carb Lst/Millstone Grit	North Yorkshire	7.65	482	10.9	69.4	8.61	6.53	1.1	12.1	205	14.8	2.25	0.34	
39	S05-00779	15-Dec-05	Carb Limestone	North Yorkshire	7.46	480	5.32	40.2	6.78	6.72	1.22	11.2	185	11.6	1.5	0.24	
40	S05-00780	15-Dec-05	Millstone Grit	North Yorkshire	7.52	485	8.37	43.2	5.0	5.30	1.57	9.07	137	11.7	0.596	0.19	0.19
41	S05-00781	15-Dec-05	Millstone Grit	North Yorkshire	7.67	479	8.67	80.7	7.22	4.30	0.53	7.46	222	10.5	1.63	0.42	
42	S06-00001	09-Jan-06	Great Oolite	Gloucestershire	7.20	474	0.19	107	6.69	15.8	2.02	20.5	266	54	0.638	0.36	0.36
43	S06-00002	09-Jan-06	Great Oolite	Gloucestershire	7.21	301	0.0	96.1	8.14	43.4	3	40.9	302	54.7	< 0.05	0.20	
44	S06-00003	09-Jan-06	Carb Limestone	Somerset	7.57	415	10.08	105	4.74	7.33	1.57	15.4	291	11	5.62	0.33	0.33
45	S06-00004	09-Jan-06	Carb Limestone	Glamorgan	7.15	406	5.25	77.1	8.37	14.2	2.39	27.6	241	21	3.79	0.45	
46	S06-00005	10-Jan-06	Permo-Triassic Sandstone	Welsh Border	6.64	460	9.1	69.0	7.67	17.2	2.11	39.4	134	31.5	15.2	0.08	
47	S06-00006	10-Jan-06	Permo-Triassic Sandstone	Welsh Border	6.77	461	8.23	73.6	8.3	14.6	2.43	40.5	172	24.9	12.5	0.21	
48	S06-00007	10-Jan-06	Permo-Triassic Sandstone	Welsh Border	6.95	460	8.19	74.8	10.1	12.9	3.07	30.5	215	17.8	10.7	0.39	0.38
49	S06-00008	10-Jan-06	Permo-Triassic Sandstone	Welsh Border	7.35	441	5.65	91.4	32	173	7.63	175	293	210	5.49	2.59	2.56

Field number	Sample number	Sampling date	Aquifer	Region	pH	Eh	DO	Ca	Mg	Na	K	Cl	HCO$_3$	SO$_4$	NO$_3$-N	U$_{\text{filt}}$	U$_{\text{unfilt}}$
						mV	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}
50	S06-00009	10-Jan-06	Permo-Triassic Sandstone	Welsh Border	7.30	425	8.41	83.1	30.7	14.6	4.77	28.9	287	41	14.5	1.57	1.53
51	S06-00010	10-Jan-06	Old Red Sandstone	South Wales	7.24	435	7.25	93.9	37.8	12.4	3.49	26.9	351	61.2	8.1	3.27	
52	S06-00011	10-Jan-06	Carb Limestone	Gloucestershire	7.37	440	6.5	60.7	33.3	8.56	1.6	20.1	297	29.5	4.28	0.61	0.58
53	S06-00015	11-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.39	501	7.21	73.8	13.3	52.4	3.03	101	201	47.3		0.40	
54	S06-00016	11-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.36	831	9.51	67.1	20.0	7.34	4.83		251	21.6		1.07	
55	S06-00017	11-Jan-06	Permo-Triassic Sandstone	Leicestershire	7.37	231	0.0	78.3	28.5	27.8	7.89		310	91.2		2.54	
56	S06-00018	11-Jan-06	Permo-Triassic Sandstone	Leicestershire	7.32	206	0.0	111	35.5	60.1	10.5		279	184		2.89	
57	S06-00019	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.47	410	8.11	51.0	25.9	7.92	2.15		211	15.2		0.36	0.35
58	S06-00020	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.62	433	7.49	57.4	16.4	9.42	2.62		169	22.2		0.28	
59	S06-00021	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.56	444	7.89	71.7	16.5	10.2	3.24	28.7	183	25.2	15.1	0.21	
60	S06-00022	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.32	461	5.65	79.9	13.9	11.4	4.45	31.2	217	29.5	11.7	0.57	
61	S06-00023	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.47	440	4.7	69.3	24.7	12.1	3.17	26.6	212	71.2	5.81	1.51	1.47
62	S06-00024	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.56	406	6.01	64.5	17	9.96	2.86	27.2	230	29.1	5.5	1.42	
63	S06-00025	12-Jan-06	Permo-Triassic Sandstone	Staffordshire	7.52	447	7.31	85.0	2.65	11.9	2.51	29.9	195	22.5	5.79	0.20	0.17
64	S06-00026	13-Jan-06	Inferior Oolite	Lincolnshire	7.08	570	9.12	134	4.87	18.7	5.75	58.4	241	69.2	15.4	0.35	
65	S06-00027	13-Jan-06	Inferior Oolite	Lincolnshire	7.87	541		129	6.31	14.4	1.01	42.4	200	67.3	18.8	0.32	0.33
66	S06-00028	13-Jan-06	Great Oolite	Lincolnshire	7.28	540	1.36	149	5.75	13.8	2.16	35.2	258	113	5.66	3.43	
67	S06-00029	13-Jan-06	Great Oolite	Lincolnshire	7.27	547	1.18	145	9.07	14.8	3.32	32.5	284	117	3.57	2.19	
68	S06-00040	16-Jan-06	Chalk	Wiltshire	7.10	359	8.05	126	2.32	8.83	2.45	20	309	24.7	7.66	0.27	
69	S06-00041	16-Jan-06	Chalk	Wiltshire	7.23	481	8.71	110	1.45	5.04	0.8	14.9	265	14.2	6.05	0.25	0.24
70	S06-00042	16-Jan-06	Permo-Triassic Sandstone	Devon	7.00	582	4.43	59.1	9.1	13.9	4.95	25.5	168	23.1	7.04	0.26	
71	S06-00043	16-Jan-06	Permo-Triassic Sandstone	Devon	7.49	561	6.57	81.4	12.5	15	4.76	31.4	219	24	10.7	0.20	
72	S06-00044	16-Jan-06	Permo-Triassic Sandstone	Devon	6.75	566	6.8	54.2	4.97	14.6	4.83	26.8	127	16.8	10.5	0.60	
73	S06-00045	16-Jan-06	Permo-Triassic Sandstone	Devon	5.74	561	7.43	23	7.79	14.5	6.65	30.3	30	16.1	13.8	0.03	0.03
74	S06-00046	16-Jan-06	Permo-Triassic Sandstone	Devon	7.56	302	2.08	59.7	17.3	15.4	3.5	30.4	220	17.7	5.49	1.64	
75	S06-00047	16-Jan-06	Permo-Triassic Sandstone	Budleigh Salterton, Devon	6.92	427	5.17	48.2	6.44	15.7	5.11	29.1	135	15.9	5.42	0.19	
76	S06-00048	16-Jan-06	Permo-Triassic Sandstone	Devon	6.96	473	1.92	70.1	10.2	12.8	4.56	26.8	181	40	4.94	0.55	0.56
77	S06-00049	17-Jan-06	Chalk	Wiltshire	7.27	417	9.04	98.8	1.47	7.32	< 0.5	17	226	16	8.57	0.16	
78	S06-00050	17-Jan-06	Chalk	Wiltshire	7.30	449	8.88	98.7	1.02	7.37	< 0.5	17.1	242	7.94	6.18	0.14	
79	S06-00051	17-Jan-06	Chalk	Wiltshire	7.28	473	3.53	98.6	1.91	6.12	1.26	11.4	256	21	1.48	0.36	
80	S06-00052	17-Jan-06	Chalk	Wiltshire	7.03	474	2.59	151	1.88	5.89	1.43	21	334	46.6	6.04	0.57	
81	S06-00053	18-Jan-06	Chalk	West London	7.19	419	0.77	117	4.48	32.3	5.98	53.3	272	55.4	3.51	0.67	
82	S06-00054	18-Jan-06	Chalk	West London	7.31	367	4.48	106	4.75	30.6	3.94	50.4	243	55.7	4.01	0.50	

Field number	Sample number	Sampling date	Aquifer	Region	pH	Eh	DO	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3-N	U_{filt}	U_{unfilt}
						mV	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}
83	S06-00055	18-Jan-06	Chalk	West London	7.32	454	3.2	108	4.55	30.3	4.9	48	251	50.2	7.04	0.53	0.54
84	S06-00056	18-Jan-06	Chalk	West London	7.23		0.75	112	4.12	27.3	4.29	44.3	272	45.4	5.05	0.65	
85	S06-00057	18-Jan-06	Chalk	West London	7.25	406	1.06	112	4.46	29.8	4.58	46.5	263	48.9	5.71	0.75	
86	S06-00058	18-Jan-06	Chalk	Chilterns	7.15	474	8.22	118	1.53	9	1.42	20.6	288	12.7	6.41	0.21	
87	S06-00059	18-Jan-06	Chalk	Chilterns	7.08	462	7.33	127	1.41	7.24	1.12	12.3	333	2.55	4.17	0.25	0.25
88	S06-00060	18-Jan-06	Chalk	Chilterns	7.23	450	4.75	112	2.05	17.2	1.74	24.6	275	24.6	6.83	0.29	
89	S06-00061	19-Jan-06	Thames Gravels	Surrey	7.22	356	1.45	115	5.72	38.2	6.18	63.1	255	72.3	2.12	0.97	
90	S06-00062	19-Jan-06	Thames Gravels	Surrey	7.52	348	3.25	118	5.24	38.8	6.39	59.6	254	59.8	7.25	0.82	
91	S06-00063	19-Jan-06	Thames Gravels	West London	7.20	403	1.72	123	4.91	35.4	5.45	57	294	60.9	4.56	1.07	
92	S06-00064	19-Jan-06	Chalk	West London	7.15	409	3.13	123	3.92	18.3	3.08	35.9	285	35.8	9.76	0.51	0.49
93	S06-00065	19-Jan-06	Chalk	Chilterns	7.13	793	7.45	111	1.41	9.5	1.11	18.1	309	7.44	5.71	0.16	0.17
94	S06-00066	19-Jan-06	Chalk	Luton, Beds	7.09	654	7.09	142	2.58	22.3	2.39	44.6	282	69.3	11	0.31	0.30
95	S06-00067	19-Jan-06	Chalk	Hertfordshire	6.60	803	6.5	120	2.93	11.9	1.71	23.7	261	16.4	5.65	0.49	
96	S06-00068	23-Jan-06	Chalk	Hampshire	7.36	483	8.35	92.7	1.70	7.18	0.54	16.7	237	12.6	7.25	0.19	0.19
97	S06-00069	23-Jan-06	Chalk	Hampshire	7.28	489	8.02	101	1.69	7.97	0.83	18.3	267	8.95	6.38	0.18	0.19
98	S06-00090	23-Jan-06	Chalk	Hampshire	7.28	496	8.59	107	1.78	6.66	0.76	16.6	279	14.3	8.31	0.25	
99	S06-00091	23-Jan-06	Chalk	Hampshire	7.25	507	6.5	98.5	1.65	6.76	1	15.7	275	7.51	6.35	0.22	
100	S06-00092	23-Jan-06	Chalk	Hampshire	7.26	523	7.48	114	2.37	7.21	1.2	14.8	349	7.45	3.87	0.25	
101	S06-00117	23-Jan-06	Chalk	Hampshire	7.16	485	5.79	99.7	1.4	5.49	1.05	11.8	284	9.2	5.6	0.17	

Eh: redox potential, DO: dissolved oxygen
U_{filt}: U filtered (0.45 µm); U_{unfilt}: U unfiltered

4.3 COLLATED GROUNDWATER DATA

4.3.1 Statistical summary

A statistical summary of the samples from the collated database is given along with that for the newly sampled groundwaters in Table 4.3. From the database of 1556 British groundwater analyses (which includes the 101 newly sampled sources), 0.71% (11 samples) had concentrations greater than 15 µg L^{-1} (the WHO provisional guideline value), while 0.45% (7 samples) had concentrations greater than 20 µg L^{-1} and 0.26% (4 samples) had concentrations greater than 30 µg L^{-1}. This contrasts with 78% (1216 samples) having concentrations less than 1 µg L^{-1} and 96% (1501 samples) less than 5 µg L^{-1}. The overall median was 0.29 µg L^{-1} and the mean 1.03 µg L^{-1} (Table 4.3). Means were calculated using the non-parametric Kaplan-Meier method to handle non-detect data (Helsel, 2004) and using the NADA package in the statistical program R (Lee, 2005). Although means are included, median values are considered better indicators of central tendency as they are less influenced by outlier concentrations and uncertainties associated with left-censored data.

It was not possible from the database to provide statistical summaries on the basis of source ownership (private/public) or groundwater use as this information is not routinely recorded.

The results for the collated data compare reasonably with those for the 101 newly sampled groundwater sources but the concentration range from the former is larger, the median and mean values are slightly lower and the percentages of exceedances above the defined values (15 µg L^{-1}, 20µg L^{-1} and 30 µg L^{-1}) are also lower. The larger database is considered most representative of the distribution of U in groundwaters in Great Britain.

4.3.2 Spatial and lithological distributions

The distributions of U in groundwater in Great Britain are shown on a geological map in Figure 4.2. The distribution is relatively patchy and availability of data sparse in some areas but the greatest densities of samples are typically found in the most important water-supply aquifers. The distribution of dissolved U is highly spatially variable but shows a marked relationship with geology.

Summary statistics for groundwater U classified by aquifer geology are shown in Table 4.4. Both median and mean values are given for each subdivided lithology. Table 4.4 also shows summary statistics for some other published groundwater U studies from England. Depending

Table 4.3 Statistical summary of groundwater U data (all as µg L^{-1}) for sources sampled in this study and all available data in the collated database (percentages in parentheses)

	This study	Collated dataset
N	101	1556
Min	<0.02	<0.01
10th percentile	0.059	0.01
Median	0.39	0.29
Mean	1.58	1.03
90th percentile	2.54	2.18
Max	48.0	67.2
<1 µg L^{-1}	74 (73.3)	1216 (78.1)
>2 µg L^{-1}	13 (12.9)	168 (10.8)
>4 µg L^{-1}	4 (4.0)	70 (4.50)
>15 µg L^{-1}	2 (2.0)	11 (0.71)
>20 µg L^{-1}	2 (2.0)	7 (0.45)
>30 µg L^{-1}	1 (1.0)	4 (0.26)

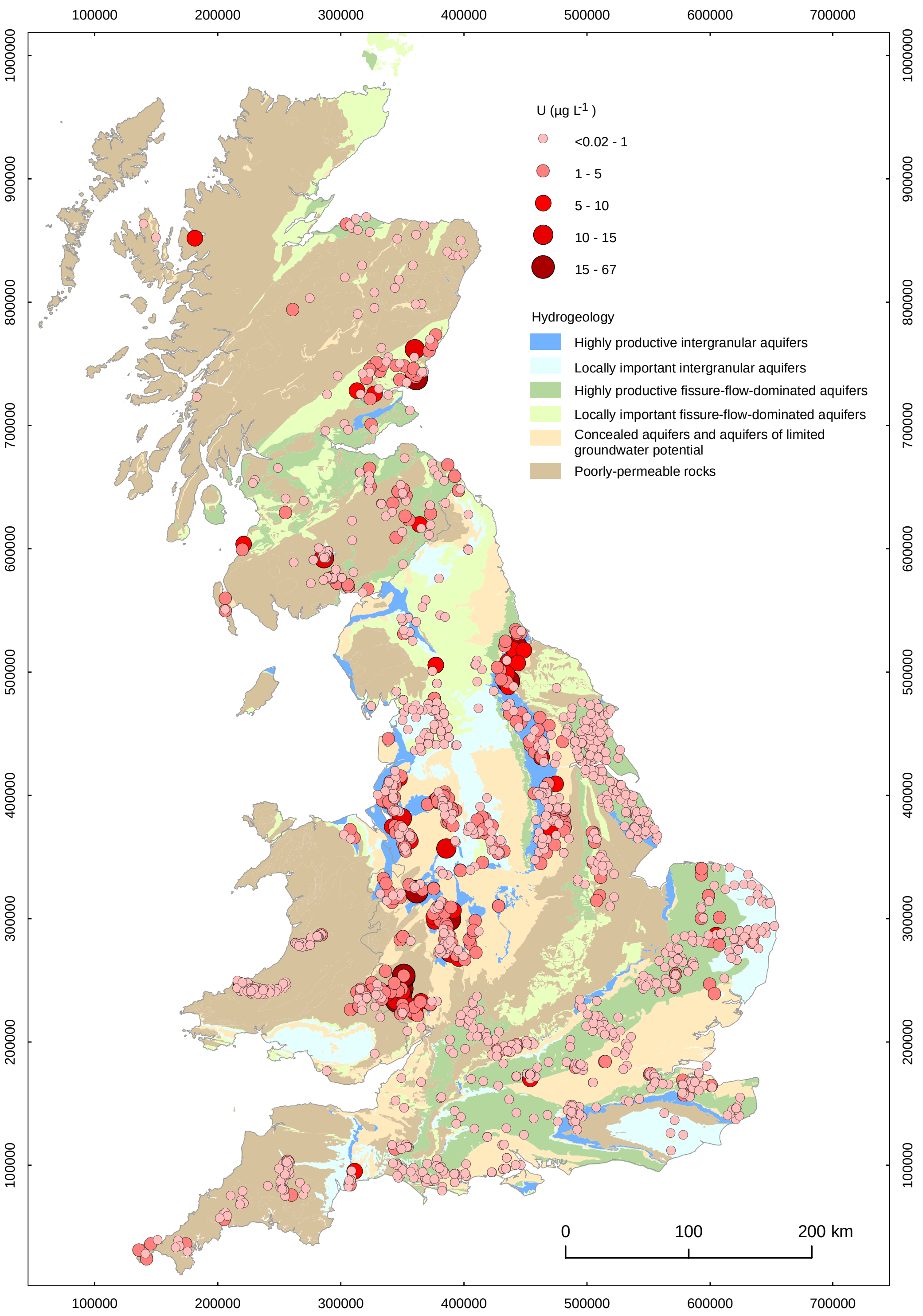

Figure 4.2 Geological map of Great Britain showing the distributions of U in groundwater. The dataset includes samples collected for this study.

on reporting, mean and median values are not always available for these studies. The data are also represented in box plots (Figure 4.3) and cumulative-frequency diagrams (Figure 4.4).

Figure 4.2, Figure 4.3, Figure 4.4 and Table 4.4 together indicate that from the collated dataset the highest U concentrations are found in groundwaters from the Old Red Sandstone and Permo-Triassic Sandstone aquifers. All sources with concentrations >15 µg L^{-1} were from these aquifers. The Old Red Sandstone crops out in a large tract of land from Shropshire, Herefordshire and Gloucestershire through south-central Wales and although not used significantly for public supply has a large number of private licensed abstractions in this region.

In Scotland, major outcrops occur in the Midland Valley including a broad continuous outcrop from the northern side of the River Clyde in the west to Aberdeenshire and Angus in

Table 4.4 Statistical summary of U concentrations (μg L^{-1}) in British groundwater, classed by geology. The collated dataset includes data for sources sampled in this study (d.l.: detection limit)

Aquifer	Min	Median	Mean	Max	n°. sources	n°. below d.l.
Collated data (this study)						
Yazor Gravels (Quaternary)	6.11	6.11	6.11	6.11	1	0
Thames Gravels	0.82	0.97	0.96	1.07	3	0
Gravels (various)	<0.02	0.06	0.16	1.12	14	6
Quaternary (unspecified)	<0.02	<0.02	<0.02	<0.02	1	1
Palaeogene	<0.02	0.02	0.07	0.77	23	10
Chalk & Crag	<0.02	0.06	0.39	4.22	56	20
Chalk	<0.02	0.26	0.35	7.63	396	28
Carstone (L. Cretaceous)	<0.05	<0.05	0.08	0.17	7	5
Lower Greensand (L. Cret)	<0.01	<0.01	0.11	1.30	58	44
Wealden (L. Cretaceous)	<0.02	<0.1	<0.1	<0.1	5	5
Spilsby Sst (U. Jur/L. Cret)	<0.05	<0.05	0.09	0.65	24	18
Bridport Sands (Jurassic)	<0.05	0.43	0.46	1.06	21	2
Corallian (Jurassic)	<0.02	0.15	0.38	1.51	25	8
Lincs Limestone (Jurassic)	<0.02	0.28	0.68	3.70	23	8
Great/Inferior Oolite (Jurassic)	<0.05	0.31	0.51	3.43	29	2
Permo-Triassic Sandstone	<0.02	0.93	2.08	67.2	333	16
Permian (various)	0.06	0.82	2.46	11.4	6	0
Magnesian Lst (Permian)	0.81	1.07	1.21	1.89	8	0
Millstone Grit (Carboniferous)	<0.02	0.05	0.18	1.87	34	16
Carb Limestone/Millstone Grit	<0.02	0.21	0.49	1.63	8	2
Fell Sst/Carb Limestone	<0.02	0.04	0.67	3.21	5	1
Carboniferous Limestone	<0.02	0.45	0.87	7.84	92	10
Carboniferous (Devon)	<0.01	<0.02	0.15	1.50	37	19
Old Red Sandstone (Devonian)	<0.1	1.39	3.89	48.0	110	5
Ordovician/Silurian	<0.02	0.11	0.46	2.38	45	14
Granite	0.02	0.55	0.98	3.57	25	0
Palaeozoic (various)	<0.02	0.04	0.22	7.93	72	23
Dalradian	2.45	2.45	2.45	2.45	1	0
Torridonian	6.61	6.61	6.61	6.61	1	0
Unspecified	<0.02	0.14	0.64	6.29	93	21
Overall	<0.01	0.29	1.03	67.2	1556	284
Other studies						
Palaeozoic sediments and intrusive rocks, west Devon; tapwaters (Talbot et al., 2001)	<0.007	0.08	0.6	11.6	127	19
Millstone Grit & Coal Measures, Derbys/Yorks (Banks, 1997)	<2			13	20	
Lincolnshire Limestone (Andrews and Kay, 1982)	<0.04			3.4		
Hot springs, Bath (Andrews, 1991)	0.025			0.055	31	
Carboniferous Limestone, Mendips (Bonotto and Andrews, 2000)	0.09		0.86	4.56	12	

the north-east. More sporadic outcrops also exist on the south side of the Midland Valley and in the Scottish Borders. The Old Red Sandstone also crops out along the Moray and Cromarty Firths as well as in Caithness and Orkney.

The Permo-Triassic Sandstone is one of the most important water-supply aquifers in Britain and has a large number of both public and private licensed abstraction sources. The aquifer is present under either confined or unconfined conditions in large areas of England & Wales, including the Welsh Borders, Cheshire Basin and in the outcrop which extends from the East Midlands via the Vale of York as far as Hartlepool in the north-east (Figure 4.2). In Scotland, the Permo-Triassic Sandstone is of more restricted extent but outcrops occur in the Dumfries Basin in the Scottish Borders.

Groundwaters from the Old Red Sandstone of Wales have U concentrations up to 39 µg L^{-1}; those of Strathmore, east-central Scotland have concentrations up to 15 µg L^{-1}. The Permo-Triassic Sandstone of Scotland (Dumfries Basin) has groundwater with up to 11 µg L^{-1} U, while Permo-Triassic Sandstone groundwater in England has concentrations up to 67 µg L^{-1}. Strata classed as Permian also have concentrations up to 11 µg L^{-1} (Table 4.4; Figure 4.3). The concentrations for the Old Red Sandstone groundwaters are much higher than the range of 0.09–0.46 µg L^{-1} (mean 0.22 µg L^{-1}, 4 samples) reported for this aquifer in the Mendips area by Bonotto and Andrews (2000). A relatively high U concentration (6.61 µg L^{-1}) is also found in the only sample in the dataset from the Torridonian Sandstone of north-west Scotland (Figure 4.2; Table 4.4).

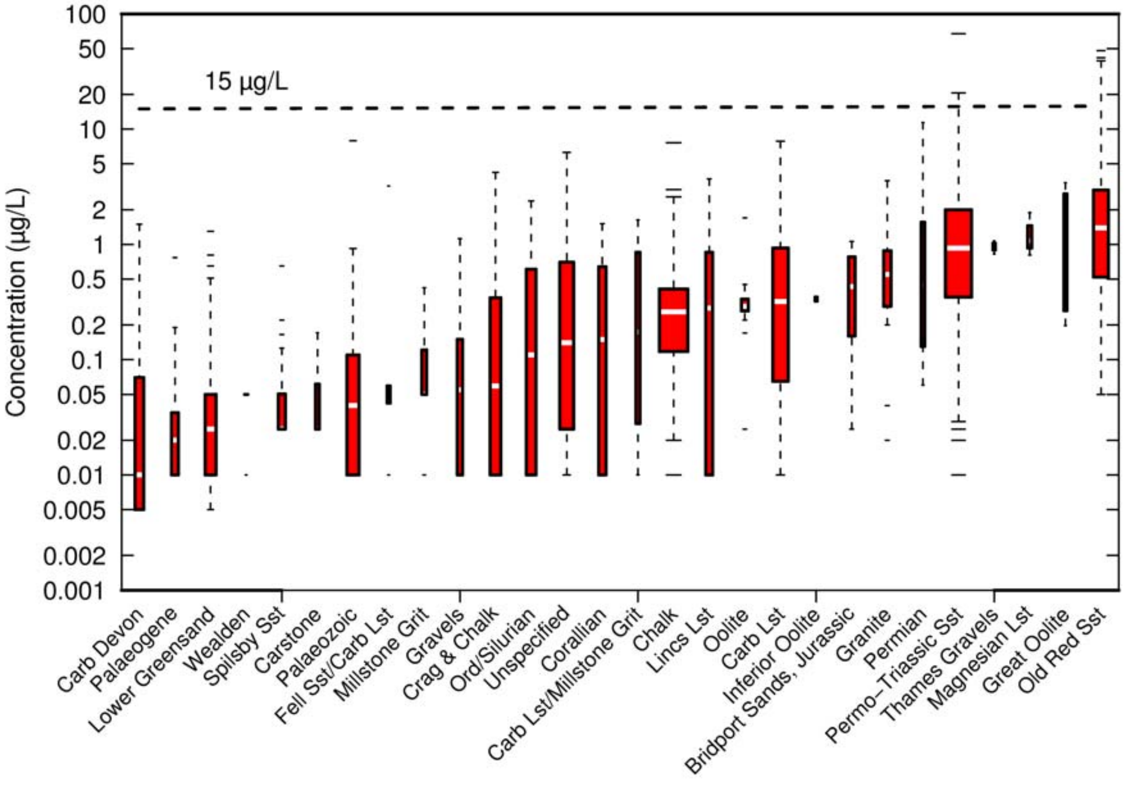

Figure 4.3 Box plots showing summary statistics for groundwater U concentrations in British aquifers, ordered approximately in terms of medians. Box upper and lower margins indicate the interquartile range and medians are indicated by horizontal white lines. Whiskers represent 1.5 times the interquartile range and outliers are also shown as separate horizontal lines. Box widths are proportional to the square root of the numbers of samples in each class. Classes with only single values are not plotted. The WHO provisional guideline value of 15 µg L^{-1} is also shown for reference.

The highest U concentration observed in the dataset overall (67 µg L^{-1}) is from a borehole groundwater in the Permo-Triassic Sandstone of Shropshire. Whilst this was not a drinking-water supply borehole, the groundwater from it is believed to be representative of that in the aquifer of the region and the sample was collected following standard sampling protocols. It is noteworthy that the Old Red Sandstone, Permo-Triassic Sandstone and Torridonian aquifers are all red-bed sandstone aquifers. These typically contain relatively high concentrations of Fe(III) oxides as grain coatings, fracture fills and cements. The iron oxides are likely important sources of U. This close link with aquifer geology strongly points to water-rock reaction as the cause of the high U concentrations rather than pollution from agricultural or industrial sources.

Other aquifers had variable U concentrations but with occasional high values. One sample from the Yazor Gravels had a concentration of 6.11 µg L^{-1}.

Generally lower concentrations are observed in groundwater from the limestone aquifers (Chalk, Lincolnshire Limestone, Great/Inferior Oolite, Carboniferous Limestone, Magnesian Limestone) although these too have sporadic high values. Maximum concentrations in these aquifers are respectively 7.6 µg L^{-1}, 3.7 µg L^{-1}, 3.4 µg L^{-1}, 7.8 µg L^{-1} and 1.9 µg L^{-1} (Table 4.4) although median concentrations are typically in the range 0.2–0.3 µg L^{-1} (note the Magnesian Limestone median of 1.07 µg L^{-1}). None of the groundwater samples analysed from the limestone aquifers contained U at concentrations greater than 15 µg L^{-1} (Table 4.4). Bonotto and Andrews (2000) also found mostly low concentrations in groundwaters from the Carboniferous Limestone of the Mendip Hills of south-west England. Concentrations were in the range 0.09–4.56 µg L^{-1} (mean 0.86 µg L^{-1}, no median quoted; 12 samples; Table 4.4).

Other sandstone aquifers also have generally low concentrations. The Lower Greensand has a maximum concentration of 1.3 µg L^{-1} with a median 0.03 µg L^{-1}; the Spilsby Sandstone maximum is 0.65 µg L^{-1} with a median of 0.03 µg L^{-1}. This may partly reflect the abundance

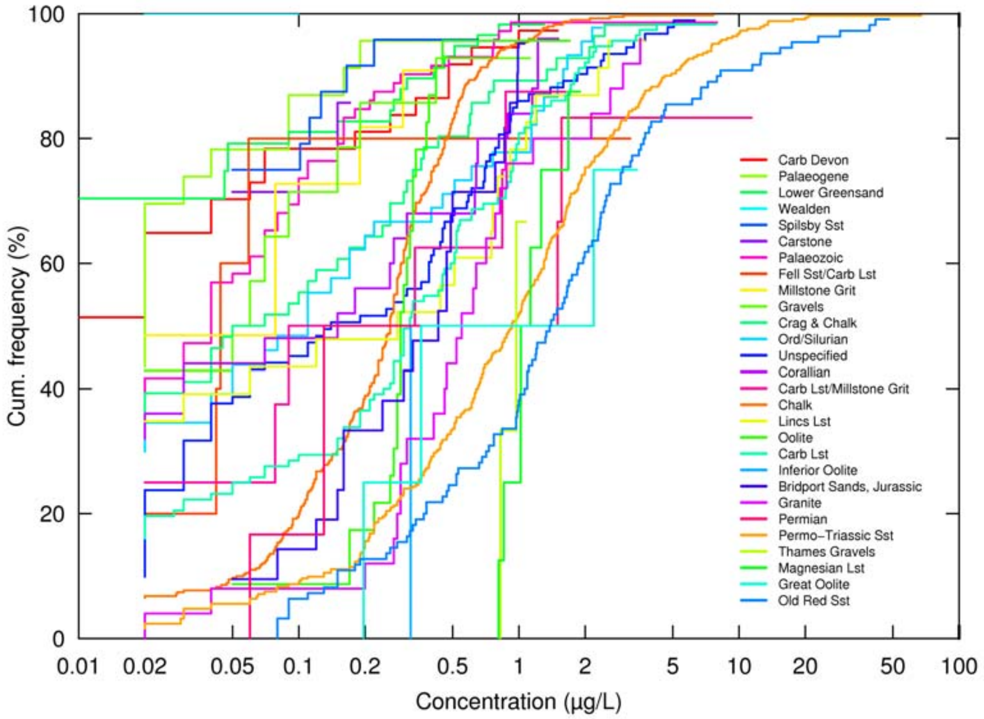

Figure 4.4 Cumulative-frequency plots for U in groundwater in British aquifers. The legend is ordered approximately in terms of increasing median value. Classes with one sample are not plotted.

and speciation of U in the solid minerals of these sandstones, but is in no small part linked to the dominance of confined abstraction boreholes and hence reducing conditions in these aquifers. The redox control on U mobilisation in groundwater is discussed further in Section 4.3.5.

Samples of granite groundwater from south-west England also have mostly low U concentrations (range 0.02–3.6 µg L^{-1}, median 0.55 µg L^{-1}; Table 4.4). This is perhaps surprising given the regionally high U concentrations in the granite itself (e.g. Bromley, 1989). However, the groundwaters from the region typically have very low concentrations of dissolved solids and they are moderately acidic (pH 4–6) with low alkalinity values (<30 mg L^{-1} as HCO_3). They are also usually young shallow groundwaters that are unlikely to have had significant interaction with the aquifer rock.

A recent DETR report (Talbot et al., 2001) characterised the natural radioactivity and U concentrations in private water supplies in the Tavistock area of west Devon. This is a heavily mineralised area, just to the west of the Dartmoor granite. The study showed that groundwater supplies from private wells, springs and boreholes had U concentrations in the range <0.007–11.6 µg L^{-1}, with a median of 0.08 µg L^{-1} (127 samples). The analysis was carried out by ICP-MS with good quality-control measures. The samples in the dataset were mostly collected from consumers' taps rather than directly from groundwater sources. Some changes to the water chemistry may have occurred in the distribution system since abstraction from the aquifer (e.g. by settling in tanks or mixing). However, unless abstracted groundwater has a high particulate load, settling is likely to have a minor effect and the range observed is therefore probably representative of the groundwater from the aquifer. As most of the shallow groundwaters from the granite are oxic, tank storage is also not likely to result in significant aeration and iron-oxide precipitation.

Only 4 of the samples in the Talbot et al. (2001) study were collected directly from the groundwater sources. These had universally low concentrations of <0.03–0.89 µg L^{-1} with a median of 0.08 µg L^{-1}. The sample size was small however, and the representativeness of the data is therefore uncertain. Of the 127 tapwater samples collected, 3 (2.4%) had concentrations above 5 µg L^{-1}, though none exceeded the WHO guideline value for U in drinking water of 15 µg L^{-1}. The highest concentration observed in the study (11.6 µg L^{-1}; Table 4.4), was from a borehole source in the Dartmoor granite. This sample also had the highest Rn concentration (5300 Bq L^{-1}). 9% of samples taken directly from groundwater sources had Rn concentrations which exceeded the draft European Commission action level of 1000 Bq L^{-1} (Talbot et al., 2001). The results from groundwater samples taken from the granite of south-west England clearly have a large range and although concentrations of U are mostly low (<4 µg L^{-1}), occasional higher concentrations are possible.

Banks (1997) also carried out a survey of groundwater from springs and boreholes from the Millstone Grit and Coal Measures in Derbyshire and Yorkshire. The U analyses were determined by ICP-MS but the reported detection limit was relatively high: 2 µg L^{-1}. Of 20

Table 4.5 Statistical summary of U concentrations (µg L^{-1}) in groundwater from Great Britain, classed by sample source

Aquifer	Min	Median	Mean	Max	n^o. samples
Springs	<0.02	0.17	0.41	7.93	253
Boreholes	<0.02	0.31	1.19	67.2	1234
Wells	<0.02	0.08	0.40	3.54	48
Mine drainage	1.63	1.75	1.85	2.18	6
Unspecified	0.06	0.27	0.25	0.39	15

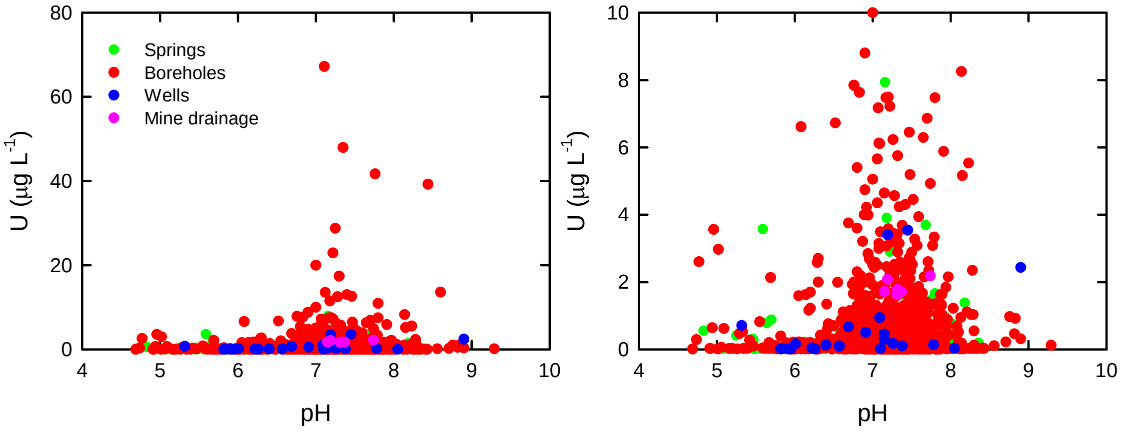

Figure 4.5 Variation of U with pH in the groundwater from the collated dataset (expanded y-scale on right-hand diagram).

samples reported from the study, all but one had concentrations <2 µg L^{-1}. One sample from a shallow spring in the Millstone Grit had a concentration of 13 µg L^{-1}, although this showed the extreme effects of pyrite oxidation, being saline (electrical conductance 2200 µS cm^{-1}), acidic (pH 3.08), and highly enriched in iron (Fe 27 mg L^{-1}) and other trace elements. It is therefore atypical.

Andrews (1991) reported concentrations of U in the range 0.025–0.055 µg L^{-1} (Table 4.4) in hot springs discharging from Mesozoic strata in Bath. These are thought to have been derived by geothermal heating in the deeper Carboniferous Limestone. Andrews (1991) concluded that the low observed concentrations in the hot springs were due to the reducing conditions of the artesian waters.

4.3.3 Variations with water source type

The distribution of U in groundwater from the collated data, divided on the basis of source type (springs, wells, boreholes), is shown in Table 4.5. The largest range, with the highest median and maximum values, occurs in the groundwaters from boreholes. Lowest concentrations are seen in water from wells. Springs also have a relatively low median but range up to 7.9 µg L^{-1}. The higher concentrations in the boreholes are expected if the main source of the U is taken to be the aquifer minerals. Groundwater residence time is likely to be

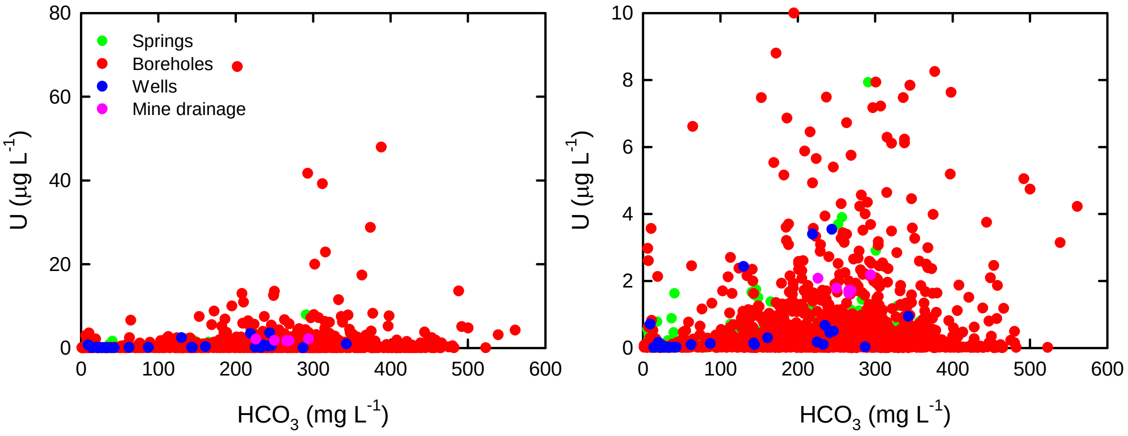

Figure 4.6 Variation of U with HCO$_3$ in the groundwater from the collated dataset (expanded y-scale on the right-hand diagram).

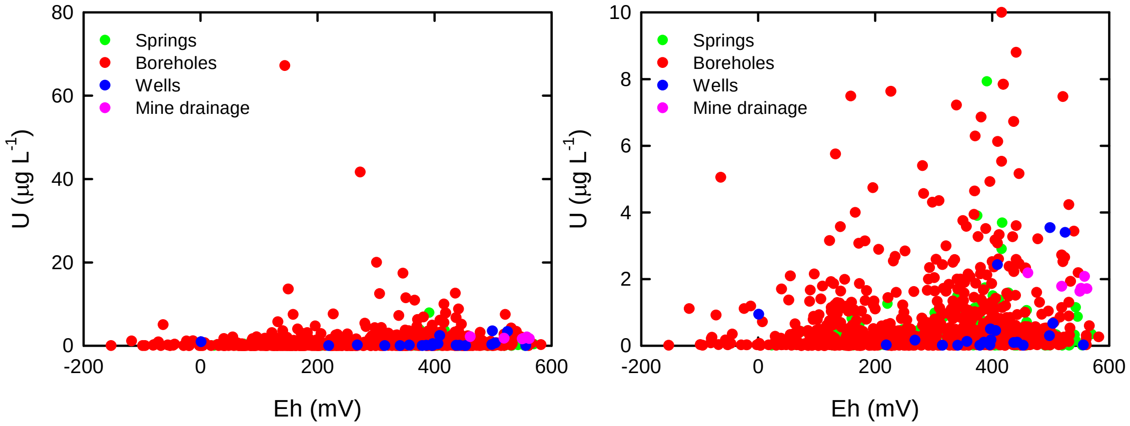

Figure 4.7 Variation of U with redox potential (Eh) in groundwaters from the collated dataset (expanded y-scale on the right-hand diagram).

more prolonged in groundwaters abstracted from boreholes than those from shallower wells or springs and water-rock interaction is therefore likely to be correspondingly more significant. This provides further support for the conclusion that the U is not significantly of pollutant origin.

A few samples of groundwater classed as mine drainage have a relatively small range of concentrations (1.6–2.2 µg L^{-1}; Table 4.5). This slightly higher range compared to those in the other classes likely reflects the flow of mine drainage waters in mineralised zones where U among other metals are likely to be more concentrated.

4.3.4 Variations linked to water chemistry

The mobilisation of U in water has been described in Section 2.4. Among the most important controls identified are solution pH, redox and solute chemistry. Under oxidising conditions at neutral and alkaline pH, dissolved U(VI) is stabilised as uranyl carbonate species. The concentrations of U in the British groundwaters appear to have a broad positive correlation with groundwater pH (Figure 4.5). At pH values less than 7, U concentrations are usually low. Under alkaline conditions (pH >7), concentrations are higher and more variable. This can be attributed to the formation of soluble U-carbonate complexes at high pH. The influence of inorganic carbon species as U complexing agents is also shown by the relationship between U in groundwater and HCO_3 concentrations, albeit with a less strong correlation (Figure 4.6). Uranium mobility therefore appears to be most favoured in neutral-high pH groundwaters with high alkalinity. Groundwaters with alkalinity values less than around 150 mg L^{-1} as HCO_3 typically have low U concentrations (Figure 4.6).

4.3.5 Variations with redox status

Redox conditions have a major significance in controlling the concentrations of U in groundwater. Large differences are often apparent in groundwater U concentrations under confined compared to unconfined conditions. This results from the large solubility differences between U(VI) and U(IV) species (Section 2.4). The redox influence is shown broadly by the relationship between U concentration and redox potential (Eh) in the groundwaters in the collated dataset (Figure 4.7). Not all samples have recorded Eh values but of those that do, highly variable and sometimes high U concentrations are observed at Eh greater than around 100–200 mV. Above 100 mV the median observed U concentration in the dataset is 0.27 µg L^{-1} (566 samples). Below 100 mV (i.e. under reducing conditions), the number of samples is much more limited but concentrations are usually lower, with a median of 0.04 µg L^{-1} (maximum of 2.1 µg L^{-1}; 50 samples).

More analyses are available within the collated dataset for groundwaters from the Chalk and Permo-Triassic Sandstone than for other aquifers. In the Chalk groundwaters, samples with Eh values >100 mV have a range of U concentrations of <0.02–1.26 µg L^{-1} (median 0.20 µg L^{-1}, 140 samples). At Eh less than 100 mV, concentrations are in a similar range, <0.02–1.19 µg L^{-1}, but the median is lower at 0.054 µg L^{-1} (14 samples).

In the Permo-Triassic Sandstone, groundwaters with Eh values <100 mV have a U range of 0.030–2.15 µg L^{-1} with a median of 0.37 µg L^{-1} (16 samples); those with Eh >100 mV have a range of 0.029–13.6 µg L^{-1} with a median of 0.51 µg L^{-1} (70 samples).

The redox control on groundwater U concentrations is well-illustrated by the example of the Triassic Sherwood Sandstone aquifer of the English East Midlands. The groundwater chemistry of the aquifer has been characterised from various studies (e.g. Edmunds et al., 1982; Smedley and Edmunds, 2002). The East Midlands aquifer can be clearly distinguished into an unconfined, aerobic, aquifer in the west and a confined (by Mercia Mudstone), anaerobic section down the groundwater flow gradient further east (Figure 4.8). Close to the unconfined/confined interface, a distinct redox boundary exists, denoted by a drop in redox potential (Eh) of some 300 mV and loss of dissolved oxygen. Several other redox-sensitive species, including nitrate, Fe, Mn and U are also significantly changed.

Figure 4.9 shows the change in U concentrations down the groundwater flow gradient (groundwater temperature is here used as a proxy for groundwater depth and residence time in

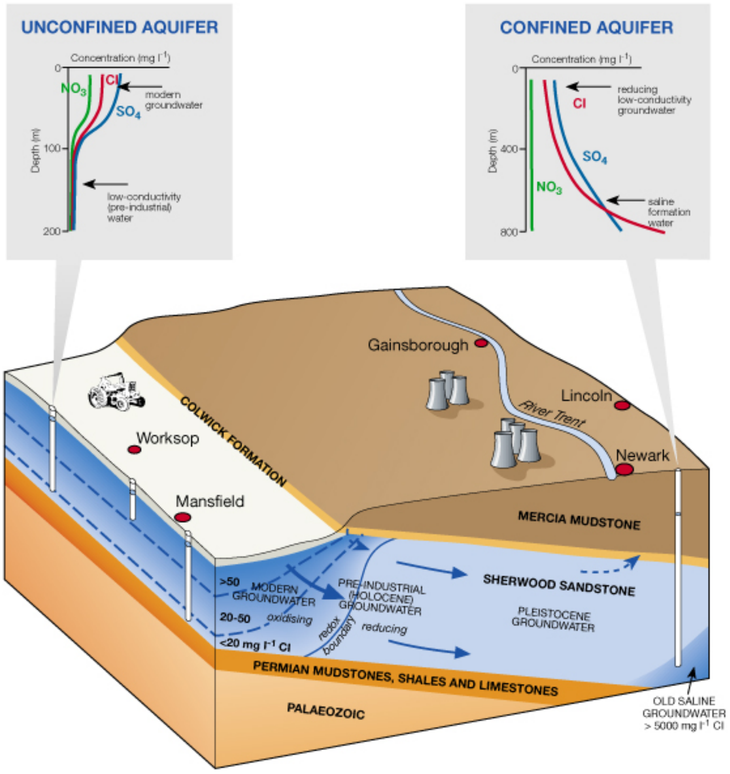

Figure 4.8 Model of groundwater flow in the Triassic Sherwood Sandstone aquifer of the English East Midlands, showing distribution of modern (aerobic) groundwater in the unconfined part and progressively older groundwater down the flow gradient in the confined aquifer (from Smedley and Brewerton, 1998). The interface between the two is defined by a 'redox boundary' where the chemistry of the groundwater changes significantly and the groundwaters become anaerobic.

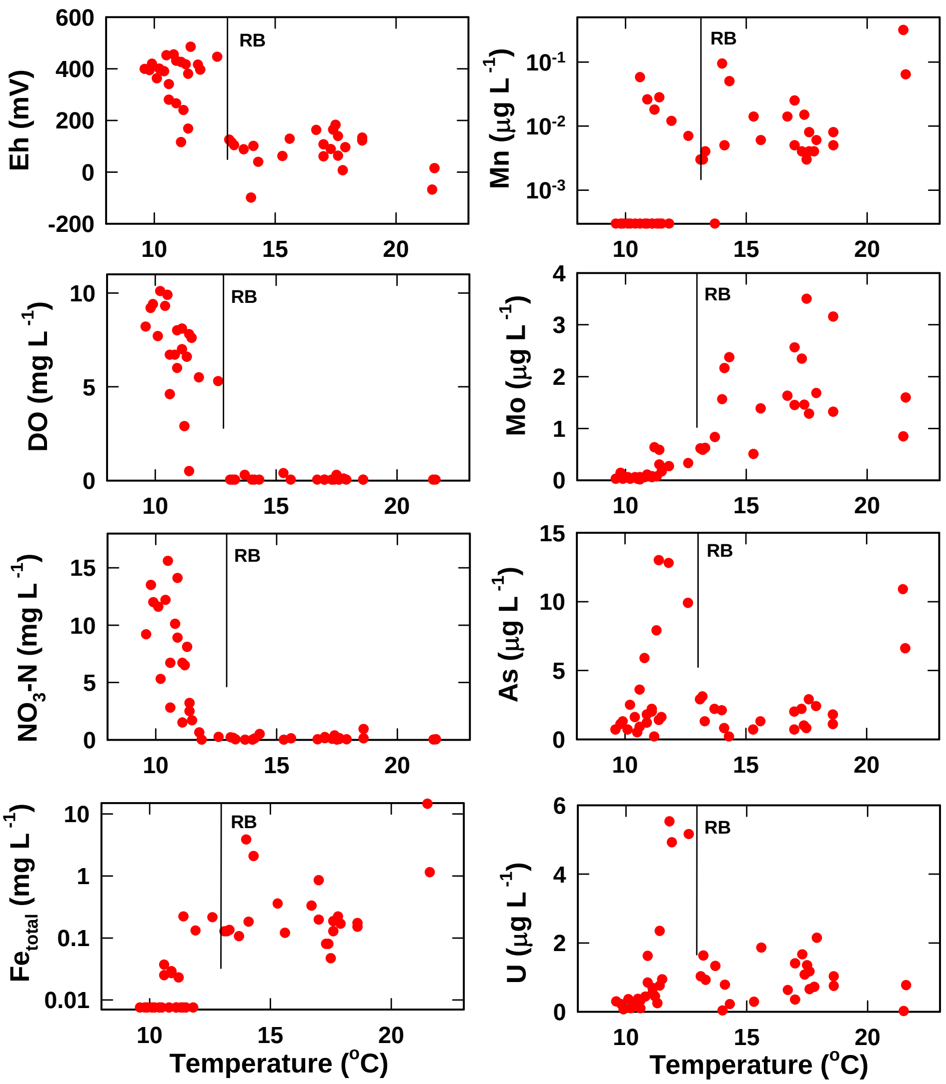

Figure 4.9 Variation in groundwater chemistry along the flow gradient of the East Midlands Triassic Sandstone aquifer, showing the important effect of the redox boundary (RB) on element concentrations. Groundwater temperature increases with borehole depth in response to the geothermal gradient and is here taken as a proxy measure of groundwater depth and residence time. Higher temperatures are from older, deeper groundwaters in the confined aquifer (from Smedley and Edmunds, 2002).

the aquifer). In the unconfined (aerobic) aquifer, concentrations build up to around 5.5 µg L^{-1}, the higher concentrations in the groundwaters with the longest residence times. These also have high relatively pH values (pH 8.6) (Smedley and Edmunds, 2002). At the redox boundary, U concentrations diminish sharply (to <2 µg L^{-1}) as a function of reduction of U(VI) to U(IV) and likely precipitation as uraninite or adsorption to iron oxides (Smedley and Edmunds, 2002).

In the Sherwood Sandstone in other areas, the spatial variations in U concentrations are less clear because of the variable influence of superficial drift deposits, some of which can act as local confining layers. Redox-influenced variations in U concentration are also apparent in other aquifer lithologies in England & Wales, with anaerobic groundwaters typically having U concentrations less than around 2 µg L^{-1} and often much less.

Changes in groundwater U concentration with redox status were also documented in the Lincolnshire Limestone aquifer of eastern England by Andrews and Kay (1982). They described concentrations in the range 0.7–3.4 µg L^{-1} (mean 1.3 µg L^{-1}) in the unconfined part of the aquifer in its westerly outcrop area but observed an abrupt decrease in concentrations at the redox boundary where the limestone becomes confined by overlying clay-rich deposits. Beyond the redox boundary under reducing conditions, the concentrations of U were 0.1 µg L^{-1} or less with a mean of 0.04 µg L^{-1}. Corresponding changes in $^{234}U/^{238}U$ activity ratios were also observed in response to increased residence time downgradient.

4.3.6 Bottled mineral water survey

A recent survey of the natural radioactivity of bottled mineral water samples collected from various retail outlets in the UK was carried out on behalf of the Food Standards Agency (FSA, 2004). The survey found that concentrations of U were less than the current WHO provisional guideline value of 15 µg L^{-1} in all samples tested (170 samples) but a relatively large range was observed. Concentrations were in the range <0.01–13 µg L^{-1}. The highest concentrations were found in two samples of Caffe Nero water (12 and 13 µg L^{-1}). The next highest concentrations were found in mineral water samples from the Radnor Hills in mid Wales. Two samples from this source had concentrations of 11 and 7.8 µg L^{-1}. The underlying geology of the groundwater source is believed to be Old Red Sandstone, but Silurian rocks also outcrop in the area. Relatively high concentrations of U were also found in samples of San Pellegrino water (7.0–8.6 µg L^{-1}, 6 samples), Rocwell water (5.5 µg L^{-1}, one sample), and St Yorre water (6.1–10 µg L^{-1}), all of which are from groundwater sources outside the UK. Buxton Spring water had concentrations of 3.2–3.9 µg L^{-1} (6 samples). All other samples tested had concentrations of 2 µg L^{-1} or less.

5 Uranium in groundwater worldwide

5.1 CONCENTRATION RANGES

Many studies of U concentrations and radioactivity have been carried out in groundwaters from aquifers overseas and a relatively large literature exists on total concentrations and isotopic activity ratios. Concentrations span a large range with greater extremes than are found in the data from Great Britain. The following review gives an account of the observed

Table 5.1 Summary of U concentrations (µg L^{-1}) in groundwaters from other parts of the world

Aquifer/Region	Range (median)	n°. samples	Reference
U mineralised areas			
Okélobondo uraninite deposit, Gabon, west Africa	0.25–260	15	Salas and Ayora (2004)
Coles Hill uranium deposit, Virginia, USA	3.2–13.6		Jerden et al. (2003)
Los Ratones uranium mine, Spain	<1–104	48	Gómez et al. (2006)
Sedimentary aquifers			
Phosphate-mineralised limestone, Jordan	0.04–1400 (2.4)	168	Smith et al. (1996; 2000)
Shale overlain by alluvium, Colorado, USA	40–69	2	Zielinski et al. (1997)
Mixed sand & gravel, limestone, chalk, Cyprus	0.005–38 (0.86)	215	Smith et al. (2000)
Pampean (Quaternary) loess sediments, Argentina	6.2–248 (30.6)	107	Smedley et al. (2002)
Bangladesh Quaternary alluvial and deltaic sediments	<0.01–47 (0.45)	245	BGS and DPHE (2001)
Quaternary alluvial and lake sediments, Huhhot Basin, Inner Mongolia, China	<0.01–52.8 (1.24)	73	Smedley et al. (2003)
Sediments (unspecified), Norway	0.003–15 (0.1)	172	Reimann et al. (2005)
Mixed sediments, Carson Desert, USA	1–1000	73	Welch and Lico (1998)
Hardrock and mixed aquifers			
Granitic basement, Finland	1–1920 (28)	325	Kurrtio et al. (2002)
Lac du Bonnet Granite, Canadian Shield, Manitoba	<1–893	74	Gascoyne (2004)
Stripa Granite, Sweden	0.05–90.2	100	Andrews et al. (1989)
Mixed granite, schist, greenstone, Singida, Tanzania	0.1–647 (5.5)	82	BGS (unpublished data)
Granite, charnockite, quartzite, Sri Lanka	0.017–6.4 (0.3)	123	BGS (unpublished data)
Granite and weathered granite, Uganda	<0.05–17	139	BGS (unpublished data)
Carbonates, valley-fill, volcanics, Nevada, USA	0.01–14.0	41	Farnham et al. (2003)
Tertiary volcanics and alluvium, southern Nevada, USA	0.17–9.87 (2.7)	49	Cizdziel et al. (2005)
Granite, metamorphic and volcanic rocks, Korea	<0.012–402	498	Kim et al. (2004)
Hot springs in Cambro-Ordovician Okchun black shale, Korea	10–263	19	Lee et al. (2001)
Cold springs, Okchun black shale, Korea	0.54–49	14	Lee et al. (2001)
Basement, Bergen & Oslo, Norway	<0.01–2020 (ca. 5)	150	Reimann et al. (2005)
Basement, Norway	<0.001–1000 (ca. 2)	480	Reimann et al. (2005)

concentrations and distributions of U in groundwater from uranium mineralised areas as well as hard-rock aquifers and unconsolidated sediments and sedimentary rocks. Many occurrences of high-U groundwater worldwide are associated with U-rich rock types (e.g. U mineral deposits, granitic rocks). However, others are associated with sedimentary aquifers, including both consolidated (e.g. sandstones, limestones) and unconsolidated types. In some arid regions, high U concentrations have been associated with evaporation.

5.1.1 Groundwater in uranium mineralised areas

High concentrations of dissolved U can occur in U-mineralised areas, although the observed concentrations depend strongly on local redox conditions, mineralogy and solute compositions. Salas and Ayora (2004) found a large range of U concentrations (0.25–260 µg L^{-1}) in groundwaters close to a 300 m deep buried uraninite deposit in Gabon, west Africa. Low concentrations were found in groundwaters from shallow pelites overlying the deposit, but the higher concentrations were found in more oxic groundwaters from deep boreholes abstracting water from close to the deposit. Under reducing conditions at shallow depth, the groundwaters were saturated with respect to uraninite; the deeper groundwaters were undersaturated.

In a study of U mobilisation in the Coles Hill uranium deposit of Virginia, USA, Jerden et al. (2003) found U concentrations in the range 3.2–13.6 µg L^{-1} in groundwater from the weathered U-bearing saprolite. The relatively low dissolved concentrations were taken to be due to the low solubility of U(VI) phosphate minerals in the deposit.

Gómez et al. (2006) reported concentrations of dissolved U up to 104 µg L^{-1} in groundwater close to a uranium mine in the Variscan Massif of western Spain. The highest concentrations were found in groundwaters which were hydraulically linked to pitchblende-bearing granitic dykes within the granite country rocks, whilst lowest U concentrations were found in reducing groundwater more remote from the mineralised zone. Low concentrations were also linked to co-precipitation of UO_2 with newly-formed iron oxides.

5.1.2 Groundwater in hard-rock aquifers

High U concentrations have often been reported in groundwater in granitic terrains. A large range of U concentrations was observed in groundwaters from the Lac du Bonnet Granite of the Canadian Shield. Gascoyne (2004) reported concentrations of <1–893 µg L^{-1} (Table 5.1). The U concentrations were found to be generally highest at shallow depths (<60 m; depth range of boreholes up to 1000 m) in oxic groundwaters showing evidence of active groundwater circulation. The dominant controls on U concentration were redox potential and the formation of soluble anionic U-carbonate species. The concentration of HCO_3 was highly positively correlated with the dissolved U concentrations suggesting that the high concentrations and increased mobility were the result of complexation with HCO_3.

High uranium concentrations have also been found in both surface waters and groundwaters from the Leinster Granite in south-east Ireland. A tributary of the River Slaney had concentrations of 30–60 µg L^{-1}, presumably reflecting a high groundwater component. Groundwater from a well in the same area had a U concentration of 300 µg L^{-1} (Cullen, 2005).

Several occurrences of high-U groundwater have been reported in granitic and other hard-rock aquifers in Scandinavia. Kurrtio et al. (2002) found concentrations ranging up to 1920 µg L^{-1} in groundwater from hard-rock aquifers including granites in Finland. They recorded an average value of 131 µg L^{-1} and a median of 28 µg L^{-1}. Similarly, Reimann et al. (2005) found U concentrations up to 2020 µg L^{-1} in groundwater from hard-rock aquifers of

Norway. Andrews et al. (1989) found concentrations of 0.05–90.2 µg L^{-1} in groundwaters from the Stripa granite of Sweden. Highest concentrations (10–90 µg L^{-1}) were found in oxic shallow groundwaters (<80 m) and minewaters (<410 m) from the granite whilst lower concentrations occurred in deeper groundwaters under more reducing conditions.

Some high concentrations have also been found in groundwater from central Tanzania (0.1–647 µg L^{-1}; Table 5.1). The highest concentration was found in groundwater associated with tuff deposits. Some granites also occur in the area. Concentrations in hard-rock aquifers in north-central Sri Lanka, including some granitic rocks, appear to be mostly low (0.017–6.4 µg L^{-1}) (BGS, unpublished data; Table 5.1).

Uranium concentrations in groundwater from Precambrian granitic and meta-igneous rocks from Brazil were given by Almeida et al. (2004), although the concentration range is unclear as the units quoted are dubious and contradictory. The values are said however to be lower than the national standard for U in drinking water of 20 µg L^{-1}. In these groundwaters, U was found to correlate with electrical conductivity and major-ion concentrations.

In Korea, Kim et al. (2004) found concentrations in the range <0.012–402 µg L^{-1} in groundwater from aquifers with variable lithologies. The observed geometric mean was a low value of 0.17 µg L^{-1}. Concentrations were noted to be highest in the groundwaters from granite and metamorphic rock types. Lee et al. (2001) also found high U in some spring waters from the Cambro-Ordovician Okchun U-rich black shale deposit of Korea. Highest concentrations (up to 263 µg L^{-1}) were found in hot springs (temperatures ca. 40–50ºC) and were concluded to result from enhanced leaching of U from local organic-rich rocks by the hydrothermal fluids.

Farnham et al. (2003) reported the concentrations of U in groundwater from mixed Palaeozoic carbonates, valley-fill deposits and volcanic rocks in Nye County, Nevada. Observed concentrations were in the range 0.01–14.0 µg L^{-1} (14 samples).

In the USA, groundwater U concentrations vary significantly. Longtin (1988) reported an average U concentration of 1.9 µg L^{-1} in a US national survey of groundwater, with 3% of samples exceeding 10 µg L^{-1}. More recent sampling by the USGS NAWQA program (National Water-Quality Assessment Program) has found a range of 0–1235 µg L^{-1} in groundwaters. The highest concentration was in California but high values were also found in the Rocky Mountain region (Colorado, New Mexico), North Dakota, New York State and Florida. Hess et al. (1985) also observed relatively high U concentrations in groundwaters from the Colorado Plateau, Western Central Plateau, Basin & Range and Pacific Mountain System as well as the Rocky Mountains. Numerous uranium mineral deposits exist in these areas.

Some high concentrations have also been found in parts of the eastern USA (e.g. South Carolina, Connecticut; Orloff et al., 2004). Orloff et al. (2004) reported concentrations in the range 1.8–7780 µg L^{-1} with a median of 157 µg L^{-1} in groundwater from 35 private wells in South Carolina. The U was concluded to be of natural origin, supported by the wide geographical extent of the high concentrations and the large depth range of affected wells (30–260 m). However, the study was mainly an investigation of community health in relation to U concentrations in drinking water and so the sample selection may have been biased towards high concentrations. Certainly the median concentration reported was significantly higher than has been found in studies elsewhere.

Misund et al. (1999) carried out a survey of trace elements in bottled mineral waters from across Europe. These were groundwaters from unspecified aquifers but likely to include a large range of rock types. Uranium concentrations were determined by ICP-MS in the Federal

Institute for Geosciences & Natural Resources (BGR), Hannover, Germany. Concentrations of U in the range <0.001–9.5 µg L^{-1} were reported with a median of 0.1 µg L^{-1} (56 samples).

5.1.3 Groundwater in sedimentary aquifers

Groundwater can have high U concentrations in some sedimentary aquifers, particularly in areas where the sediments themselves have high concentrations. Examples include deposits rich in clay minerals, iron oxides and phosphate minerals as well as sediments derived from granitic precursors.

Smith et al. (1996) found concentrations of U ranging up to 1400 µg L^{-1} in groundwater from a fractured limestone aquifer in Jordan. The U was considered to have derived ultimately from phosphate-bearing horizons higher in the stratigraphic sequence and the high concentrations in the limestone related to mobilisation of U along fractures.

Zielinski et al. (1997) found concentrations of 40–69 µg L^{-1} in springs from shale in Colorado, USA. Some young sediments can also contain groundwater with appreciable concentrations of U. Groundwaters from Holocene and Pleistocene alluvial aquifers (typically some tens to hundreds of thousands of years in age) in Bangladesh have concentrations up to 47 µg L^{-1} (Table 5.1). Many of the groundwaters in Bangladesh are anaerobic and have low U concentrations as a result of the reduction of U to U(IV). Highest concentrations were found in groundwaters from shallow hand-dug wells that are more oxic than the groundwater from boreholes in the area. Desorption of U from iron oxides under the oxic conditions is the likely release mechanism (BGS and DPHE, 2001). Similarly high concentrations have been found in some groundwaters from Holocene alluvial and lake sediments in the Huhhot Basin of Inner Mongolia, China (Table 5.1). Smedley et al. (2003) reported concentrations in the range <0.01–53 µg L^{-1}, the highest concentrations being from oxic groundwaters from the margins of the basin.

Concentrations are also high in many groundwaters from Quaternary loess (aeolian) deposits in La Pampa, central Argentina. Smedley et al. (2002) reported a range of 6.2–248 µg L^{-1}. The high concentrations were associated with oxic, high-pH, high-alkalinity groundwaters and are also believed to be linked with desorption of U(VI) from iron oxides. Although the concentrations of U in the groundwaters from La Pampa are extremely high, they are anomalous as they also contain high concentrations of numerous other trace elements, including As, V and F (Smedley et al., 2002). They cannot therefore be considered analogous to the sedimentary aquifers of Great Britain.

Some high concentrations of U were also reported by Welch and Lico (1998) for Pleistocene mixed alluvial, aeolian and lake sediments form the arid Carson Desert of Nevada, USA. Concentrations in the range 1–1000 µg L^{-1} were attributed to a number of processes, including evaporation in areas of shallow upward-flowing groundwater and desorption from iron oxides.

Clearly, U concentrations in several groundwater sources worldwide are high, although the range observed is large, spanning around six orders of magnitude. The maximum concentrations in many areas are much higher than have been observed to date in British groundwaters. The most analogous situations in Britain where high groundwater U concentrations (>15 µg L^{-1}) might be expected are areas with granitic rocks, areas of uranium mineralisation and sedimentary aquifers with substantial concentrations of iron oxides.

6 Implications of the findings for the water industry

The surveys of U in groundwater in Great Britain indicate that concentrations range between <0.01 µg L^{-1} and 67 µg L^{-1}, some four orders of magnitude. The highest recorded value in the dataset is four times the WHO provisional guideline value of 15 µg L^{-1}. Despite the relatively large range of concentrations, very few of the observed data (11 samples from the collated dataset; 0.7%) exceed the WHO provisional guideline value. Even fewer exceed the Canadian national standard or US-EPA maximum contaminant level of 20 µg L^{-1} and 30 µg L^{-1} respectively. Hence, for the large majority of samples, U concentrations are well below the values that would become problematic if a new EC regulation for U of 15–30 µg L^{-1} were to be introduced.

The largest ranges and highest concentrations of U concentrations are typically found in unconfined (oxic) red-bed sandstone aquifers such as the Permo-Triassic Sandstone and Old Red Sandstone. Concentrations in some borehole sources in these aquifers exceed 15 µg L^{-1}. Outcrops of the Permo-Triassic Sandstone are widespread, particularly in England. The Old Red Sandstone crops out over a large part of south-central Wales and the Welsh Border as well as in the Scottish Midland Valley, Scottish Borders and north-eastern Scotland.

The Permo-Triassic Sandstone is the second most important aquifer in Britain in terms of public water supply. The Old Red Sandstone is not a major source of groundwater for public supply but there are nonetheless numerous private abstractions from it. Uranium could become a water-quality issue for operators abstracting groundwater from the Permo-Triassic Sandstone if a new limit were to be introduced in future European and national drinking-water regulations. It is unlikely that significant numbers of sources in this aquifer would exceed 15 µg L^{-1} but the introduction of regulation would at least require testing of U in those intended for public supply. The observed temporal variations in some sources in our study also suggest a need for monitoring of vulnerable sources with time. As the observed ranges of U are variable in all aquifer types, there is also a case for screening of all public-supply sources to establish the U concentrations. Analysis of U can be achieved relatively easily and cheaply by the ICP-MS technique which is now quite widely available and well-suited for detecting U within the concentration range of interest.

It must be emphasised that the data described in this study are all for raw groundwaters and are not necessarily representative of the water quality at consumers' taps. Public-water supplies are often subjected to treatment before distribution to consumers. Uranium concentrations could be modified significantly by for example water blending (depending on the end-member U concentrations), or by ion exchange or coagulation methods. Aeration and settling should have minimal effect since this is principally for the treatment of high-iron waters which by their reducing nature are not likely to have high U concentrations. Chlorination should also not substantially affect dissolved U concentrations.

7 Conclusions

From analyses of samples from 101 raw groundwater sources in England & Wales, determined for this study from a range of aquifers with varying hydrogeological conditions, two (2%) had U concentrations exceeding 15 µg L^{-1}, the current provisional WHO guideline value for U in drinking water. From the database of 1556 groundwater analyses collated from across Britain, 0.71% (11 samples) had U concentrations in excess of 15 µg L^{-1}. Assuming that the larger database is representative of groundwater compositions in Great Britain as a whole, the number of raw groundwaters breaching a new EC drinking-water limit would be minor if 15 µg L^{-1} were the chosen limit. The value chosen for any new EC limit is unclear but it is unlikely to be less than 15 µg L^{-1} in view of the limited evidence for human health effects at such concentrations and the current US-EPA and Canadian national U standards for drinking water (30 µg L^{-1} and 20 µg L^{-1} respectively). The observed ranges are much smaller than those reported in other aquifers across the world. These span some six orders of magnitude with values ranging up to 8000 µg L^{-1}. Most of the extremely high concentrations are found in areas of U-mineralisation and granitic terrains. These occur widely throughout other parts of the world but are of relatively limited extent in Britain.

Studies in Britain have shown that measured groundwater U concentrations can vary by up to five orders of magnitude within a given aquifer. This indicates a need for caution in relying on low-density groundwater surveys in vulnerable aquifers and a need for systematic testing for U during groundwater resource development.

The concentrations of U in the groundwaters have a close link with aquifer geology and associated geochemistry. The largest ranges and highest concentrations of U are found in groundwater from red-bed sandstone aquifers such as the Old Red Sandstone and Permo-Triassic Sandstone; one relatively high U concentration (6.6 µg L^{-1}) was also found in a groundwater from the Scottish Torridonian Sandstone. The mostly likely cause of the U mobilisation in these aquifers is desorption from iron-oxide minerals at neutral to alkaline pH and higher alkalinity, the soluble U being stabilised as U(VI)-carbonate complexes.

Occasional high U concentrations were also found in groundwater from a number of other aquifers, though none exceeded 15 µg L^{-1}. Groundwaters from granites in south-west England were found surprisingly to have usually low concentrations (up to 3.6 µg L^{-1}), although values up to 11.6 µg L^{-1} have been found in groundwater from this region by other workers. This is despite the relatively high U concentrations of the granites of the region and the high regional heat flow. The generally low concentrations are attributed to short residence times of shallow groundwaters in the granites and the dominance of moderately acidic, low-alkalinity groundwaters. Uranium concentrations were also mostly low in groundwaters from the carbonate aquifers, although maxima of 7.8 µg L^{-1} were found in the Carboniferous Limestone and 7.6 µg L^{-1} in the Chalk.

Redox conditions in the aquifers have an additional strong influence on groundwater U concentrations, with higher concentrations in a given aquifer occurring under oxic conditions (Eh>100–200 mV) compared to those in reducing conditions (Eh<100–200 mV). Aquifers that have both confined and unconfined sections can have large differences in U concentrations that significantly affect the statistical distributions of U concentration. This applies notably to the Chalk and Permo-Triassic Sandstone aquifers. The statistical distributions of U in groundwater from several other aquifers such as the Palaeogene, Carstone, Lower Greensand, Spilsby Sandstone, Corallian Limestone, Lincolnshire Limestone and Great & Inferior Oolite are also affected by the prevalence of borehole sources in the confined sections of these aquifers.

The collated groundwater U data indicated broadly that the highest U concentrations were found in borehole sources rather than groundwaters from shallower wells or springs. This suggests that source depth has an influence on U concentration and that time-dependent water-rock interaction (i.e. groundwater residence time) may play an additional part in determining groundwater U concentrations. It was not possible to investigate the detailed relationships between groundwater U concentration and source depth in the samples incorporated in this study so the vertical variations in dissolved U for any given aquifer remain largely unknown.

Most of the sources sampled twice during this study did not show significant temporal variation in U concentration. However, the observations of significant temporal changes at a small number of sites in our monitoring survey suggest that, even some sources that have concentrations of U exceeding the WHO guideline value for U in drinking water, may not do so at all times of year. This is most likely due to changes in flow rather than geochemical reaction. The observed variations highlight the need for more detailed groundwater monitoring of such sources in order to identify the causes and representativeness of the temporal changes.

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