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Groundwater Systems and Water Quality
Commissioned Report CR/04/255

Environment Agency Science Group
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The Natural Quality of Groundwater in England and Wales

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and the Environment Agency

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Cliffs of jointed granite at Pordenack Point, near Land's End (photography: C J Jeffery).

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Baseline Report Series: 16. The Granites of South-West England

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Contents

FOREWORD	v
BACKGROUND TO THE BASELINE PROJECT	vii
1. EXECUTIVE SUMMARY	1
2. PERSPECTIVE	2
2.1 Study area	2
2.2 Current issues in groundwater quality	4
3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY	6
3.1 Introduction	6
3.2 Geology	8
3.3 Hydrogeology	12
3.4 Mineralogy and mineral chemistry	14
3.5 Rainfall chemistry	16
3.6 Land use	18
4. DATA AND INTERPRETATION	19
4.1 Data sources	19
4.2 Data quality and handling	19
5. HYDROCHEMICAL CHARACTERISTICS	21
5.1 Introduction	21
5.2 Major constituents	23
5.3 Trace elements	25
5.4 Organic compounds	26
6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS	28
6.1 Introduction	28
6.2 Regional variations and controls	28
6.3 Temporal variations	38
6.4 Depth variations	38
6.5 Groundwater residence time	39
7. BASELINE CHEMISTRY OF THE AQUIFER	40
8. SUMMARY AND CONCLUSIONS	41
9. REFERENCES	43
ACKNOWLEDGEMENTS	47

List of Figures

Figure 2.1.	Geographical setting of south-west England showing generalised topography, rivers, rainfall-gauging stations and the location of the Cornubian granites; these are from west to east: Land's End, Godolphin, Carnmenellis, St Austell, Bodmin Moor and Dartmoor (smaller plutons are not marked).....	2
Figure 2.2.	Land's End, Cornwall [SW 342 253] from the South West Coast Path.	3
Figure 2.3.	Sandy beaches and tourism in St Ives, Land's End granite [SW 520 403].....	3
Figure 2.4.	Granite tor, Heltor Rock, Dartmoor [SX 7997 8703] (photography: T. Cullen).	4
Figure 3.1.	View of the East Dart River and granite landscape, Bellever, Dartmoor [SX 658 773].	6
Figure 3.2.	Legacy of the Cornish tin-mining history, St Just, Land's End granite [SW 388 312].	7
Figure 3.3	Geological map of south-west England showing the locations of the Cornubian granite outcrops and locations of groundwater samples included in this study.....	8
Figure 3.4	Map of the distribution of drift deposits on the granites of south-west England.	11
Figure 3.5.	Kaolin extraction, Greensplat quarry in the St Austell granite [SX 000 555].	11
Figure 3.6.	Typical biotite granite, Trevone Quarry [SW 7473 3235], Carnmenellis granite (photography: J.M. Pulsford).....	14
Figure 3.7.	Map of land use in the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology & Hydrology, ©NERC.	17
Figure 5.1.	Piper diagram for groundwater samples from the granites of south-west England investigated in this study.....	23
Figure 5.2.	Box-and-whiskers plots showing the ranges of minor constituents in groundwaters from the granites of south-west England. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration); grey line: typical detection limits. Legend as in Figure 5.3.....	24
Figure 5.3.	Box-and-whiskers plots showing the ranges of major constituents in groundwaters from the granites of south-west England. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration).....	24
Figure 5.4.	Cumulative-frequency plots for the major constituents in groundwaters from the granites of south-west England.....	25
Figure 5.5.	Cumulative-frequency plots for the minor constituents in groundwaters from the granites of south-west England.....	26
Figure 6.1.	Regional variation of pH in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	29
Figure 6.2.	Variation in SO ₄ and Na with Cl in groundwaters from the granites of south-west England. Concentration curves for evaporated average rainfall from Goonhilly and	

	Yarner Wood are given for comparison.....	29
Figure 6.3.	Regional variation of Na in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	30
Figure 6.4.	Regional variations in Ca in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	31
Figure 6.5.	Regional variations of SEC (specific electrical conductance) in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	32
Figure 6.6.	Regional variations in Cl in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	33
Figure 6.7.	Regional variations in NO ₃ -N in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	34
Figure 6.8.	Regional variations in Cu in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.	35
Figure 6.9.	Granite-normalised REE profiles for groundwaters (µg l ⁻¹) from the granites of south-west England (2003 collected samples only). Granite compositions used to normalise the data are averages (mg kg ⁻¹) from data presented by Alderton et al. (1980), Charoy (1986) and Stone (1992).	36
Figure 6.10.	Variation in δ ¹⁸ O and δ ² H in the groundwaters from the Granites, compared with the best-fit line for rainfall from Valentia gauging station, Ireland (51.93°N –10.25°W) (rainfall data from IAEA/WMO, 2004).	38

List of Tables

Table 3.1.	Average chemical compositions of granites from the Carnmenellis and St Austell plutons (as weight %; from a compilation by Selwood et al., 1998).	15
Table 3.2.	Weighted mean annual solute concentrations in rainfall for 2000 at Goonhilly [SW 723 214] and Yarner Wood [SX 786 789] rainfall gauging stations (data from AEA, 2004) and compositions of estimated recharge (3 times concentration).....	16
Table 5.1.	Statistical summary of major and trace constituents and stable isotopic compositions of groundwaters from the granites.	21
Table 5.2.	Summary statistics for selected parameters from the five major granite plutons.	23

FOREWORD

Groundwater issuing from springs has been regarded since the earliest recorded history as something pure, even sacred. In its natural state, it is generally of excellent quality and an essential natural resource. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to groundwater abstraction and the consequent change in groundwater flow, artificial recharge and direct inputs of anthropogenic substances. A thorough knowledge of the quantity and quality of groundwaters in our aquifers, including a good understanding of the physical and chemical processes that control these, is therefore essential for effective management of this valuable resource.

About 35 per cent of public water supply in England and Wales is provided by groundwater resources, this figure being higher in the south and east of England where the figure exceeds 70 per cent. Groundwater is also extremely important for private water supplies and in some areas, often those with the highest concentration of private abstractions, alternative supplies are generally not available. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater, especially in eastern and southern England. The quantity and quality of groundwater is therefore extremely important to sustain both water supply and sensitive ecosystems.

Until now there has not been a common approach, either in the UK or across Europe, to define the natural “baseline” quality of groundwater. Such a standard is needed as the scientific basis for defining natural variations in groundwater quality and whether or not anthropogenic pollution is taking place. It is not uncommon for existing limits for drinking water quality to be breached by entirely natural processes. This means that it is essential to understand the natural quality of groundwater to enable the necessary protection, management and restoration measures for groundwater to be adopted.

One of the main problems pertinent to groundwater remediation issues concerns the background or baseline to which remedial measures must, or can, be taken. Naturally high concentrations of some elements in particular areas may make it impossible or uneconomic to remediate to levels below the natural background which may already breach certain environmental standards. The Baseline Reports Series assesses the controls on water quality which are responsible for causing the natural variations seen in groundwater and provides a background for assessing the likely outcomes and timescales for restoration.

This report builds on a scoping study of England and Wales, carried out in 1996 by the British Geological Survey for the Environment Agency, which reviewed the approach to be adopted in producing a series of reports on the principal aquifers in England and Wales. The initial phase of this work was completed in 1998 and comprised reports on seven aquifers. This report forms part of the second phase of the work that will extend coverage to all the important aquifers in England and Wales. The Baseline reports will be of use not only to regulatory agencies but also to all users of groundwater, including water companies, industry and agriculture, and all those involved in the protection and remediation of groundwater.

BACKGROUND TO THE BASELINE PROJECT

The **baseline** concentration of a substance in groundwater may be defined in several different ways. For the purpose of the project, the definition is given as

“the range in concentration (within a specified system) of a given element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources”

Terms such as **background** or **threshold** can have a similar meaning and have often been used to identify “anomalous” concentrations relative to typical values e.g. in mineral exploration. There may be additional definitions required for regulation purposes, for example when changes from the **present-day conditions** in groundwater may represent the starting point of monitoring. This may be defined as background and such an initial condition may include some anthropogenic component in the water quality.

In order to interpret the water quality variations in terms of the baseline, some knowledge of the residence times of groundwater is required. For this purpose both inert and reactive chemical and isotopic tracers are essential. Measurement of the absolute age of groundwater presents many difficulties and radiocarbon dating is the most widely used technique. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water may also provide indirect evidence of residence time. The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium (^3H), dissolved greenhouse gases – chlorofluorocarbons (CFCs) – and certain micro-organic pollutants may provide evidence of a recent component in the groundwater. The baseline has been modified by man since earliest times due to settlement and agricultural practices. However, for practical purposes, it is convenient to be able to distinguish water of different ‘ages’: (i) palaeowater – recharge originating during or before the last glacial era i.e. older than c.10 ka (ii) pre-industrial water (pre 1800s), (iii) water predating modern agricultural practices (pre 1940s) and (iv) modern post-nuclear-testing era (post 1963).

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer’s physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use historical records and the application of graphical procedures such as probability plots to discriminate different populations (Shand and Frengstad, 2001; Edmunds et al., 2003). The “baseline” refers to a *specified system* (e.g. aquifer, groundwater body or formation) and is represented by a range of concentrations within that system. This range can then be specified by the median and lower and upper limits of concentration.

The BASELINE objectives are:

1. to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound

geochemical principles, as a basis for defining water quality status and standards in England and Wales (in the context of UK and Europe); also to assess anomalies due to geological conditions and to formulate a quantitative basis for the definition of groundwater pollution;

2. to characterise a series of reference aquifers across England and Wales that can be used to illustrate the ranges in natural groundwater quality. The baseline conditions will be investigated as far as possible by cross-sections along the hydraulic gradient, in well characterised aquifers. Sequential changes in water-rock interaction (redox, dissolution-precipitation, surface reactions) as well as mixing, will be investigated. These results will then be extrapolated to the region surrounding each reference area. Lithofacies and mineralogical controls will also be taken into account. A wide range of inorganic constituents as well as organic carbon will be analysed to a common standard within the project. Although the focus will be on pristine groundwaters, the interface zone between uncontaminated and contaminated groundwaters will be investigated; this is because, even in contaminated systems, the main constituents of the water are also controlled by geological factors, amount of recharge and natural climate variation;
3. to establish long term trends in water quality at representative localities in the selected reference aquifers and to interpret these in relation to past changes due to natural geochemical as well as hydrogeological responses or anthropogenic effects;
4. to provide a scientific foundation to underpin UK and EU water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high-quality groundwater.

1. EXECUTIVE SUMMARY

This report describes the regional geochemistry of groundwater from the Cornubian granites of south-west England. The study area covers some 150×50 km, though the granites outcrop as five major and discrete plutons from Land's End (Cornwall) in the west to the uplands of Dartmoor (Devon) in the east, rather than as one continuous body. The report considers data for up to 195 samples, taken from a combination of boreholes, springs, adits and wells from each of the major plutons.

The groundwaters of the region are mainly shallow, circulating within thin soils, weathered near-surface bedrock and granite fractures. Most boreholes from which samples were taken in this study had total depths of around 30 m or less and water from wells and springs is likely to have circulated at even shallower levels. As a result, the groundwaters are predominantly oxidic, acidic, soft and unmineralised, and most appear to show evidence of having been recently recharged from local rainfall.

The chemistry of the groundwaters from the granites appears to be strongly controlled by initial rainfall compositions, which themselves show a strong maritime signature, with additional inputs resulting from rock weathering. Key mineral dissolution reactions involve plagioclase and biotite and to a lesser extent alkali feldspars. Clay minerals are also important controls on hydrogeochemistry, particularly on trace-element compositions. Some evidence of oxidation of sulphide minerals is observed, especially in groundwater discharging from some of the adits. However, this is not thought to be of widespread regional significance.

As the groundwaters are mostly from shallow depths, they are particularly vulnerable to surface-derived pollution. The area is not significantly affected by modern heavy industry and although historic mining activity leads to environmental problems in some places, it is not of widespread occurrence across the region. Nor is the study area intensively farmed for arable crops. Hence, dominant pollutant inputs are likely to be from agricultural (pastoral) and domestic sources. High concentrations of $\text{NO}_3\text{-N}$ (up to 33 mg l^{-1}) are observed in some groundwaters, along with often high concentrations of dissolved K (up to 67 mg l^{-1}), P (up to 0.9 mg l^{-1}), SO_4 (up to 53 mg l^{-1}) and organic carbon (TOC up to 8.8 mg l^{-1}), as well as higher than average SEC values (up to $713 \mu\text{S cm}^{-1}$). Groundwaters from the Bodmin Moor and Dartmoor plutons appear to be the least contaminated. These have the highest elevations and are the most remote and least populated of the granite masses.

Groundwater yields from the granites are small (typical boreholes yields being $30\text{--}50 \text{ m}^3 \text{ day}^{-1}$) and very few boreholes are licensed for public drinking-water supply. Nonetheless, many rural communities rely on the groundwaters for private supply for agricultural, domestic and potable use. Most require pH regulation for use as drinking water and to reduce their corrosive effects on metal pipework.

2. PERSPECTIVE

2.1 Study area

The study area incorporates the Cornubian granites of Cornwall and Devon (Figure 2.1). These comprise the five major plutons: Land's End, Carnmenellis, St Austell, Bodmin Moor and Dartmoor as well as the smaller Godolphin granite (Figure 2.1), the Carn Brea and Carn Marth granites situated close to the Carnmenellis pluton and the Gunnislake and Kitt Hill granites west of Dartmoor (not shown).

The region is a major tourist centre in the summer months by virtue of its warm climate and attractive scenery which includes rocky cliffs (Figure 2.2), long beaches (Figure 2.3) and wild upland moor (Figure 2.4), many of which are formed as a result of the granite. Dartmoor is a national park.

The region is famous for its history of metal mining, which has had a significant economic as well as environmental impact over the last few centuries. Extraction of tin from alluvial deposits and surface lodes began in the Bronze Age and the first known underground mining was initiated in the 14th century. Early mining for lead and silver also took place on a small scale. Mining for tin and copper increased in the 17th century, and during the 18th and 19th centuries deep mines were developed with pioneering steam-driven mechanical pumps to extract groundwater. These greatly increased the commercial importance of the region's mining industry. During the 19th century, mining activity was mostly concentrated in Cornwall (St Just, Camborne–Redruth) but the Devon Great Consols Mine (Gunnislake area) for a time was the largest producer of copper (and arsenic) in the world. The region was also a world leader in production of arsenic, and tungsten was also mined successfully during the

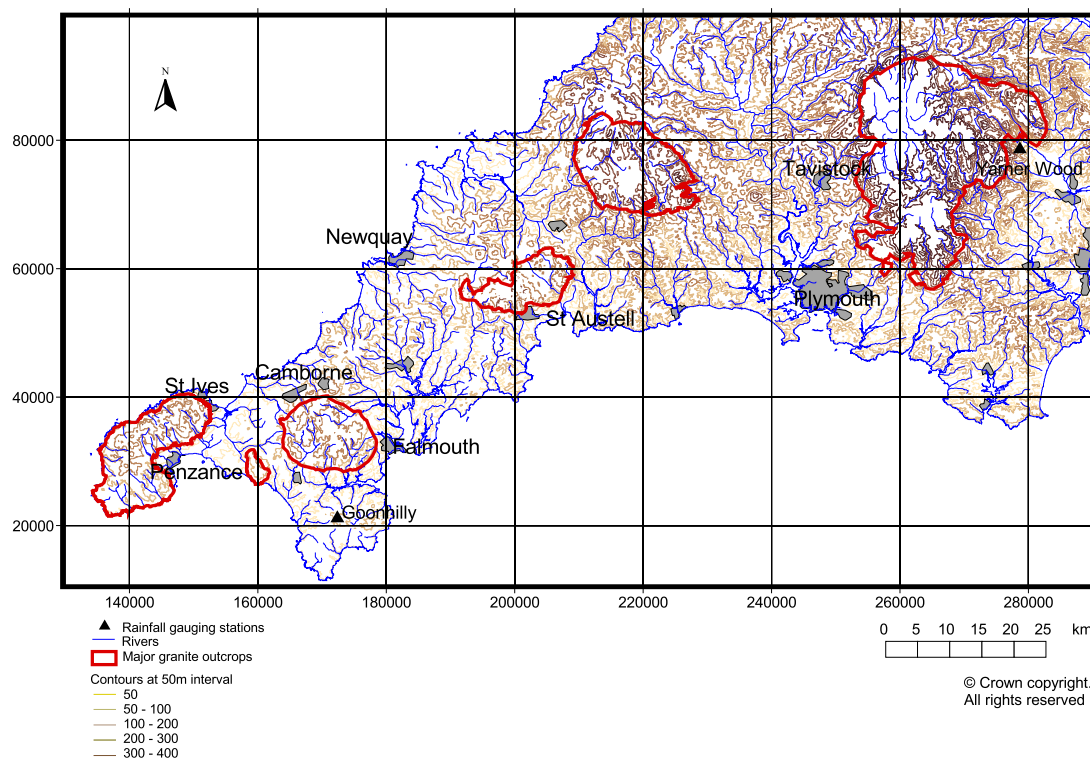


Figure 2.1. Geographical setting of south-west England showing generalised topography, rivers, rainfall-gauging stations and the location of the Cornubian granites; these are from west to east: Land's End, Godolphin, Carnmenellis, St Austell, Bodmin Moor and Dartmoor (smaller plutons are not marked).



Figure 2.2. Land's End, Cornwall [SW 342 253] from the South West Coast Path.

late 19th century, albeit on a comparatively small scale. Although the range of metals mined was large, copper and tin were the dominant mined resources. At its peak, the mining industry of Cornwall and Devon constituted several thousand mines and produced more than 40% of the world's copper and around 50% of the world's tin. Production of copper and tin reached peaks in 1860 and 1870 respectively (Dines, 1956).

The dominance of the English metal-mining industry was not to last however. Competition from cheaper foreign imports caused the demise of the copper and tin industries in turn. The local copper industry collapsed in 1866. The introduction of the rock drill in 1881 improved the commercial success of the tin-mining industry but this too declined over the following years as a result of cheaper



Figure 2.3. Sandy beaches and tourism in St Ives, Land's End granite [SW 520 403].



Figure 2.4. Granite tor, Heltor Rock, Dartmoor [SX 7997 8703] (photography: T. Cullen).

imports from newly discovered reserves in Australia, Malaya and Bolivia. Limited mining continued into the 20th century as a result of fluctuating tin prices, improved technology and an increased demand for tin during the two world wars. However, the last remaining tin mine in Europe, South Crofty in Camborne, finally closed in 1998. There are currently discussions about reopening the mine due to increasingly favourable economic conditions, but the land is also being considered for development and no decision on the site's future has yet been made. Today, many of the mine buildings of the region have been preserved as museums and a bid has been made to preserve parts of the industrial area as a world heritage site.

2.2 Current issues in groundwater quality

The granites of south-west England are not major aquifers and the groundwater stored within them is dominantly shallow and within fractures. Water supply for the region is predominantly from surface sources. Nonetheless, the groundwaters provide small-scale private supplies for domestic and agricultural use across much of the area. As the groundwaters are mostly shallow, they are potentially vulnerable to inputs from surface pollutants. The open moorland areas are generally given over to sheep farming and hence pollution from nitrogenous fertilisers is not likely to be a major problem. However, in some rural areas pollution from slurry, septic tanks and soakaways and highways may have an effect on local groundwater quality.

Mining activity has a potentially major impact on groundwater quality in the mineralised areas, as well as an impact on surface waters in the areas of mine discharges. Acid mine drainage, produced by the oxidation of sulphide ore minerals, can have high concentrations of iron, sulphate and a number of potentially toxic trace metals, as well as being of acidic composition. South Crofty mine used to discharge mine drainage directly into the Red River with a resultant plume of red iron-oxide-rich water which flowed downstream towards St Ives Bay. In 1992, the closure of Wheal Jane mine led to rising groundwater levels and the discharge of red ochreous acid mine drainage from an adit which caused major contamination of the Carnon River and Fal Estuary (NRA, 1994). Subsequent remediation measures have reduced concentrations of toxic trace elements, including Cd down to pre-mine-closure concentrations.

High Rn concentrations have been found in some shallow groundwaters from the granites. Selwood et al. (1998) quoted a typical value of 1 MBq m^{-3} . Talbot et al. (2000) reported some high concentrations in groundwaters from the Dartmoor granite of west Devon. From 38 analysed groundwaters from private-supply sources, they found a range in Rn concentrations of $<1\text{--}2780 \text{ Bq l}^{-1}$ with an average of 775 Bq l^{-1} . Groundwater from several rock types was sampled, the granite having the highest average concentration. A small number of groundwater sources exceeded the EC recommended action level of 1000 Bq l^{-1} for Rn in individual and public-water supplies (Talbot et al., 2000). Unfortunately, due to budget constraints Rn has not been investigated in this study.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

This section provides an overview of the geography, geology, hydrogeology and environmental conditions in the study area. Understanding of these factors is a prerequisite for the characterisation and definition of the natural (baseline) quality of the groundwater in the granites.

The south-west peninsula has a temperate maritime climate with average annual rainfall of around 900–1100 mm in most areas and up to 1800 mm at the highest elevations. Annual potential evapotranspiration for the Carnmenellis area is around 530 mm but effective infiltration is dependent on local soils and vegetation (Smedley et al., 1989) and is typically in the range 500–700 mm per year (SWWA, 1979).

The granites form large areas of upland moor with sporadic rocky tors. The most extensive and highest moorland occurs on Dartmoor. The highest point is High Willhays (621 m) on the north-west margin of the Dartmoor intrusion and the highest elevations are generally in the north-central part. The highest point on Bodmin Moor is Brown Willy (420 m). Moors on the Land's End, Carnmenellis and St Austell plutons generally have altitudes up to 300 m. Natural vegetation is dominated by species which can tolerate acidic soils, with the moorland species being dominantly heather, gorse, bracken and grasses. Mosses dominate in areas of peat bog.

Rivers typically flow radially away from the granitic high ground and follow deeply incised channels. On the Carnmenellis granite south of Camborne, the main rivers are the Red, Carnon and Cober rivers. The rivers Fowey, Lynher and Inny are the main drainage for the Bodmin Moor granite, while the rivers Dart, Teign, Okement, Tavy, Meavy, Erme and Avon radially drain Dartmoor (e.g. Figure 3.1). Many stream courses have a structural control and therefore have north-north-west or north-north-east orientations. Smedley et al. (1989) reported high baseflow components for rivers draining the Carnmenellis granite. Base flow indices were 0.68 for the Kennal at Ponsanooth and 0.73 for the Cober at Helston. The high values indicate a significant groundwater storage in the Carnmenellis



Figure 3.1. View of the East Dart River, Bellever, Dartmoor [SX 658 773].



Figure 3.2. Legacy of the Cornish tin-mining history, St Just, Land's End granite [SW 388 312].

granite. Lower average values are reported for gauged rivers on the Bodmin Moor granite (0.57) and Dartmoor (0.48).

Mining has had a major impact on the economic and demographic development of the region. Penzance and Truro largely developed as a result of the mining activity, as did many other urban centres. The Camborne–Redruth area is one of the most densely populated parts of the region.

The long history of metal mining in the region has also left its legacy in the environment (Figure 3.2). Most noticeable of the environmental impacts are the piles of waste spoil that remain. Many of these are contaminated, with high concentrations of toxic trace metals, especially Cu, Pb and Zn, as well as As. Soils on some of the mineralised areas are also noted to have high concentrations of these elements (Rawlins et al., 2003). The impacts on regional surface-water quality have already been discussed in Section 2.1.

Today the only major mineral extraction that takes place in and around the granites is of kaolin, or china clay. This is a product of the intense alteration of the granites and quarrying operations are dominantly around St Austell, though Stannon is a current working clay pit in the Bodmin Moor pluton and past smaller-scale extractions have taken place in other areas. Two major companies extract the china clay, producing 3.4 million tonnes annually, some 3 million from the St Austell area (Cornwall County Council, 2001). Most is exported to Europe. The industry produces some 22 million tonnes of waste annually and the waste piles produced are unsightly and of environmental concern, though some have been reclaimed by landscaping. Backfilling of quarries has generally not been carried out as it would render future reserves at depth inaccessible.

Granite is also quarried in some areas for aggregate, including quarries at Hingston Down [SX 409 720], Luxulyan [SX 053 592], Carnsew Quarry [SW 764 355] and Castle-an-Dinas [SW 489 341]. Granite is also quarried in some places for ornamental stone (Selwood et al., 1998).

3.2 Geology

3.2.1 The granites

The five major granite plutons of south-west England, together with the Isles of Scilly, are the surface expressions of a major Cornubian batholith which is identified by a regional negative gravity anomaly and appears to be over 200 km long and 50 km wide. The batholith was intruded at the close of the Hercynian orogeny and the rocks date back to the late Carboniferous and early Permian. The Carnmenellis granite has been established as the oldest pluton (ca. 290 Ma based on Sr-isotopic data) and the youngest the Land's End pluton (268 Ma; Darbyshire and Shepherd, 1985). A later magmatic event at around 280–268 Ma produced a series of quartz-feldspar porphyry dyke swarms (Darbyshire and Shepherd, 1985; 1987).

The granite plutons are peraluminous with strong S-type affinities (Chappell and White, 1974), considered to have been produced by partial melting of lower crustal materials or with a substantial component of lower crustal materials (Durrance and Laming, 1982). Most of the plutons are composed of biotite granite, with less common tourmaline granite and topaz granite (Selwood et al., 1998).

The Cornubian batholith contains high concentrations of the heat-producing elements K, U and Th and the regional heat flow is therefore high. Heat flows of more than 100 mW m² occur in some areas (Wheildon et al., 1980), which is around twice the global average. The average geothermal gradient of the granites is around 35°C km⁻¹. The area has been investigated for its commercial geothermal potential but is not deemed at present to be economically viable (Box 3.1). A related feature is the comparatively high radon content of the granites. Radon is a radioactive gas produced by U and Ra decay and can accumulate in poorly-ventilated buildings. Heath (1982) concluded that the Rn distribution in streams is in large part controlled by groundwater movement and fracture permeability. The Rn contents of streams appeared to be highest in areas of groundwater discharge, particularly

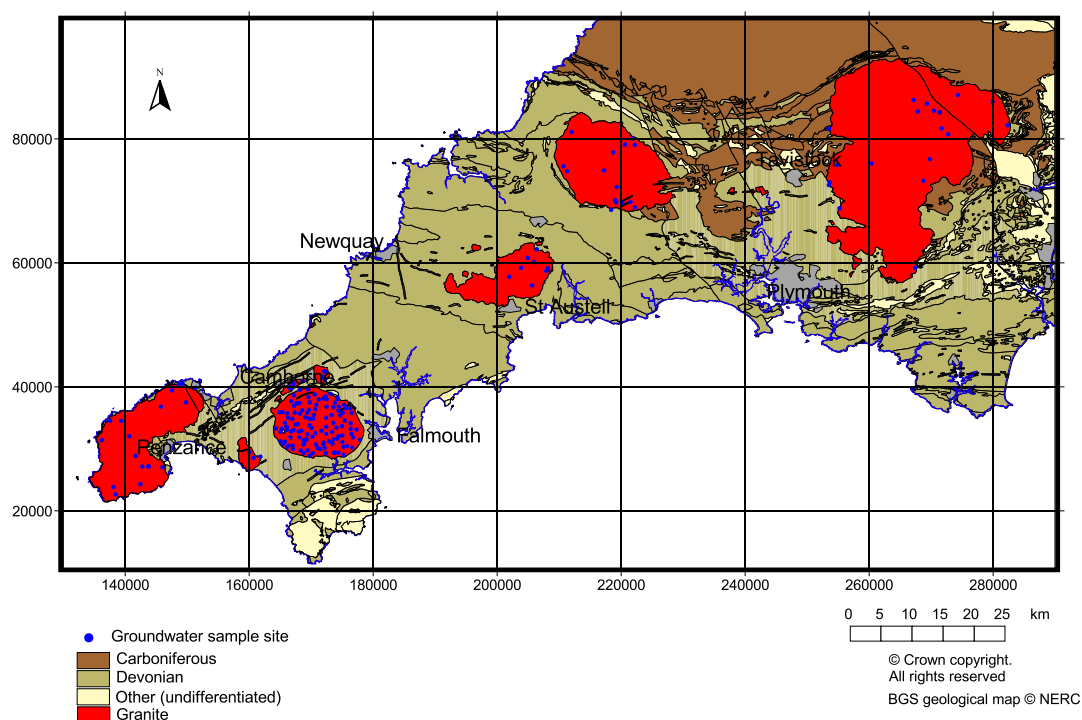


Figure 3.3 Geological map of south-west England showing the locations of the Cornubian granite outcrops and locations of groundwater samples included in this study.

where upwelling springs occurred. Poole (2001) also found that high Rn concentrations were associated with areas of U mineralisation.

The granites intrude into Devonian and Carboniferous metasediments with well-developed thermal aureoles. These are narrow (<1 km wide) around the Carnmenellis and Bodmin Moor granites and widest (up to 7 km wide), around the St Austell pluton. The width of the aureoles is considered to be related to the position of the granite outcrop with respect to the roof of the intrusion. Field relations of the outcropping St Austell granite suggest that the present erosion surface is close to the original roof of the pluton whereas the other granites have been eroded to deeper levels. These therefore have steeper sides and the width of the contact aureole is narrower (Bromley, 1989; Selwood et al., 1998).

3.2.2 *Hydrothermal mineralisation*

Hydrothermal activity was prevalent during and after the regional magmatism and produced widespread mineralisation with copper, zinc, tin, lead and arsenic ores. Mineralised zones occur both within the granite bodies and in the surrounding country rocks. Heavily mineralised areas include the Camborne–Redruth area north of the Carnmenellis granite, St Just–Botallack areas of the Land’s End granite and the Gunnislake–Tavistock area of Devon. Mining has excavated many of the metalliferous lodes in the region, with depths in the Dolcoath Mine in the Camborne–Redruth area excavated to more than 1000 m below surface and the Devon Great Consols lode mined to depths of around 550 m. Most were shallower than this, however.

The hydrothermal fluids circulated preferentially along existing fractures and other planes of weakness and the mineral veins produced have two main orientations. A roughly east-north-east–west-south-west (or east–west) set of lodes contains Sn, Cu, As and W minerals. Later veins (so-called ‘cross-courses’) trend north-north-west–south-south-east or north–south and carry Pb, Zn and Ag ores (Bromley, 1989; Selwood et al., 1998). Mineral veins (lodes) have variable dimensions but workable veins usually exceed 200 m in length, are commonly 1 km or so long and in the case of the Devon Great Consols Main Lode, reach almost 4 km long (Selwood et al., 1998). Worked veins are typically 1 or 2 m thick and are usually steeply-dipping.

The hydrothermal solutions responsible for the mineralisation are thought to have been derived in the earlier stages by separation of hydrous saline fluids from the crystallising magma, and later from circulation and interaction of meteoric fluids. They have given rise to a stratigraphically complex array of mineral veins which have been described in detail by Bromley (1989) and Selwood et al. (1998).

The early magmatic fluids produced two different styles of mineralisation: first a phase of greisen mineralisation, involving alteration of granite to an assemblage of quartz, muscovite and topaz with associated wolframite (FeMnWO_4), lollingite (FeAs_2), cassiterite (SnO_2) and native bismuth. The age of this phase probably differs in each intrusion as the date of magma emplacement varied. In the Carnmenellis granite, the greisen mineralisation is thought to date around 285 Ma, approximately coincident with emplacement of the pluton (Bromley, 1989). A subsequent phase of tourmalinite-breccia mineralisation was much more extensive and produced an assemblage of quartz, tourmaline, cassiterite and minor rutile. Sulphide minerals are rare. Chlorite, fluorite and quartz constitute the main gangue minerals in this phase (Bromley, 1989).

Box 3.1: Hot Dry Rocks – geothermal energy from granite

The fuel crisis of the early 1970s led to an increased focus on alternative, renewable forms of energy in the UK and elsewhere, including that from geothermal sources. The Cornubian granite of south-west England has a high regional heat flow, in places over 100 mW m^{-2} (up to 120 mW m^{-2}). Such areas have considerable potential for development of so-called ‘Hot-Dry-Rock’ (HDR) geothermal energy. During the 1970s and 1980s, experiments were carried out at the Camborne School of Mines’ Rosemanowes Quarry site [SW 735 346] in the Carnmenellis granite to investigate the feasibility of developing a geothermal power plant in Cornwall. The project involved pilot-scale studies with boreholes to 300 m depth which were subsequently deepened to 2.5 km (ambient temperature 80°C). Coupled injection-production boreholes were installed with inclined sections at depth (around 300 m apart) in order to intersect as many fractures as possible. Fractures were stimulated further by hydraulic fracturing to create a larger surface area for heat exchange. A heat exchanger was installed at the surface to harness the heat produced from the abstracted water. Site investigations including numerous pump tests were carried out at the site over its 12-year history to investigate the feasibility of commercialising the resource.



*Rosemanowes Quarry,
Carnmenellis granite,
during the 1980s*

In 1989, initial plans to instigate a commercial HDR plant with boreholes at depths of 6–7 km were shelved because it was concluded that such a system at the location would not be economically feasible using the currently-available technology. Difficulties in predicting geological conditions at such depths were also instrumental in the decision. The Rosemanowes HDR project therefore terminated. Since 1989, British expertise in HDR technology has been channelled elsewhere in Europe and geothermal energy has had a low priority in Britain.

These phases of mineralisation were later overprinted by the so-called ‘main-stage mineralisation’ (Selwood et al., 1998) which is responsible for the main economic concentrations of Sn, Cu and As in the region. This stage involved multiple episodes of replacement of earlier lode assemblages. Early minerals included cassiterite, wolframite and arsenopyrite with tourmaline and quartz. Later assemblages were dominated by Cu, Zn, Fe, As, Sn and Pb sulphides. Quartz, chlorite and fluorite constitute the main gangue minerals. Evidence suggests that fluid temperatures gradually diminished during the evolutionary history of this mineralisation. Early Sn-W temperatures were around $250\text{--}450^\circ\text{C}$, later Cu-Fe-As-Sn phases were around $200\text{--}350^\circ\text{C}$ and late-stage Pb-Zn mineralisation was emplaced at around $200\text{--}250^\circ\text{C}$ (Selwood et al., 1998). These later overprints of the greisen and tourmalinite phases are thought to have been derived from fluids of mixed magmatic and meteoric origin.

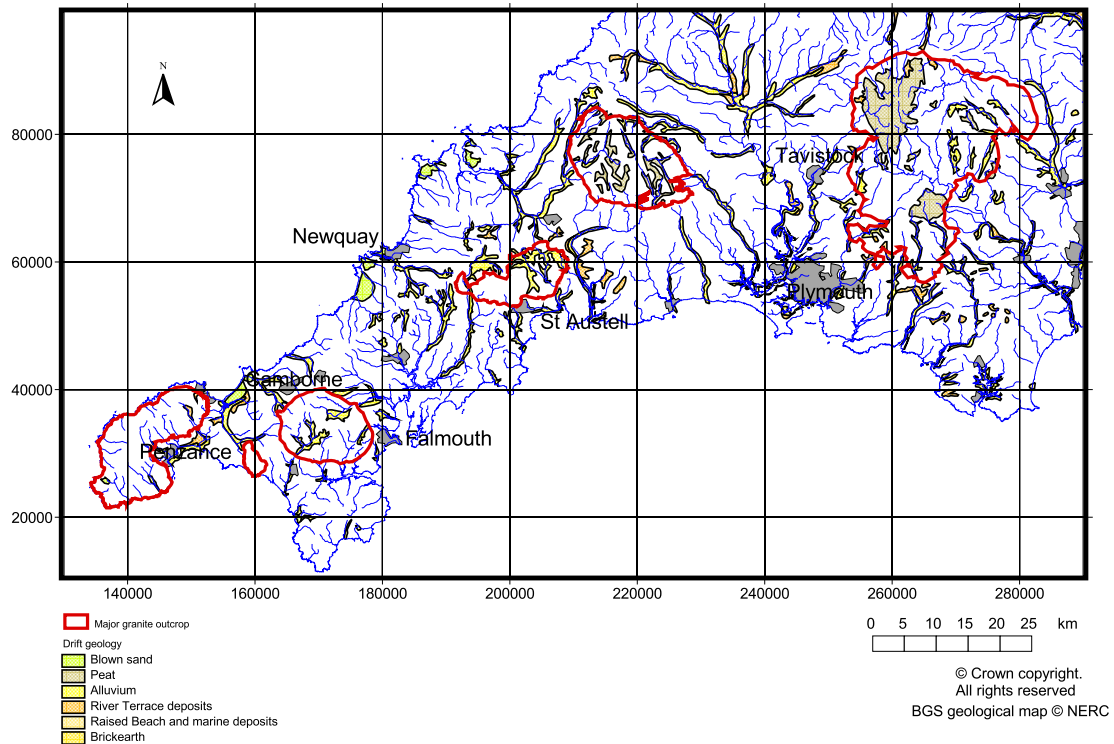


Figure 3.4 Map of the distribution of drift deposits on the granites of south-west England.

Near-surface sulphide-rich ore bodies have typically been weathered by circulating groundwaters and the sulphides have been oxidised and removed, giving rise to weathered surface ‘gossans’ which consist mainly of residual quartz and iron oxides. Weathering and deposition of ores in alluvial (placer) deposits has also taken place.

The later north-north-west–south-south-east and north–south cross-courses are post-granite phases of mineralisation with mainly quartz, Pb-Ag-Zn sulphides, fluorite and siderite assemblages (Durrance



Figure 3.5. Kaolin extraction, Greensplat quarry in the St Austell granite [SX 000 555].

and Laming, 1982). These were a response to changing regional stress fields and the onset of extensional faulting. The minerals were emplaced from fluids with temperatures of around 80–180°C or less. The cross-course fluids contained a dominant meteoric-water component. The cross-courses are generally more abundant in the country rocks than the granite (Selwood et al., 1998) and have been well-documented in the Camborne–Redruth mining area (Bromley, 1989). In Devon, the most mineralised cross-courses occur across the Tamar Valley, Mary Tavy and the Teign Valley. Dating of Pb-Ag-Zn cross-course veins in the Tamar Valley revealed a mid to late Triassic age of 236 Ma, coincident with regional rifting (Scrivener et al., 1994).

One of the latest stages of alteration of the granites has been kaolinisation (Figure 3.5). This began in the Mesozoic era but recurred at other intervals subsequently. In places the kaolinisation has produced china clay of economic proportions, especially in the western part of the St Austell granite. Evidence suggests that the kaolinisation also occurred by alteration of bedrocks by circulating meteoric fluids. Fluid-inclusion studies suggest that they were formed at temperatures in the region of 70–160°C, too high for weathering. This is supported by their often funnel- or pipe-like shapes which are more consistent with hydrothermal alteration than low-temperature weathering. Recent consensus considers that probably both hydrothermal and low-temperature weathering processes were involved (Bristow and Exley, 1994). Uranium mineralisation has also been found on the southern margin of the St Austell granite and its metamorphic aureole and on the northern margin of the Land's End pluton. The close spatial association with kaolinisation suggests a causal link.

3.2.3 *Superficial deposits*

The region was not impacted directly by glaciation during the Quaternary climatic variations. The most southerly of the glacial advances was during the Wolstonian event when glacier ice extended to the present northern coastal areas of Devon and Cornwall (Durrance and Laming, 1982). Nonetheless, periglacial conditions during the Devensian cold period obliterated earlier geomorphological features and a number of periglacial features, including patterned ground, solifluxion deposits and head deposits were produced. Drift deposits are localised, with alluvium mainly being confined to the river valleys (Figure 3.4).

Soils are generally thin with compositions reflecting the bedrock lithology. Most are well-drained gritty loamy soils with a surface humic-rich horizon in places and sometimes well-developed thin iron pans. Some upland areas have slowly permeable acidic wet or peaty surface soils (Soil Survey, 1983). The uplands of west Dartmoor have the largest area of perennially wet blanket peat (Figure 3.4). The depth of weathering of the granites is variable, ranging from very thin on hill tops to several metres in some of the valleys (Buckley and Cripps, 1989).

3.3 **Hydrogeology**

Probably the best-documented of the granites in terms of hydrogeology is the Carnmenellis granite, as a result of its past exploration for HDR geothermal potential. A hydrogeological map of the Carnmenellis granite was produced by BGS in 1989. This summarised the hydrogeological features of the granite, many of which can be applied to the other plutons of the region, although the impact of mining is probably greater in and around the Carnmenellis pluton than elsewhere.

As with the main rivers, regional groundwater flow in the granites is typically radially away from the high ground, although local deviations occur as stream baseflow and springs. Perched water tables occur in some areas though hydraulic connection between the solid bedrock and weathered regolith is often good (Smedley et al., 1989). Hydraulic gradients are often steep and indicative of low aquifer permeability (BGS, 1989).

Box 3.2: Carnmenellis thermal brines

During the 1980s and 1990s when several of the deep tin mines in Cornwall were still operating, thermal brines were reportedly discharging into mine cavities from fractures and lodes in the Camborne–Redruth mining area on the northern edge of the Carnmenellis granite. In South Crofty mine, brines discharged from the east-north-easterly lode structures and north-westerly cross-courses in both the granites and country rocks at depths up to 820 m below ground level (Bromley and Thomas, 1987). Observed TDS concentrations for brines from South Crofty were in the range 9–14 g l⁻¹ with temperatures of 35–42°C (Smedley et al., 1989). TDS concentrations up to 32 g l⁻¹ and temperatures up to 55°C have been observed in other thermal brines in the area. The geothermal discharges continued (at rates of 1–10 l s⁻¹) over several decades while the mines were actively pumped, and implied that a significant body of saline water exists at depth in these areas.

The origin of the waters is uncertain but stable-isotopic evidence suggests that they are meteoric rather than seawater-derived. It has been suggested that they evolved from meteoric waters by prolonged water-rock reaction involving weathering of plagioclase and biotite in the granite (Edmunds et al., 1984; 1985). Reaction of fluids with the surrounding metasediments has also been implicated in evolution of the salinity (Edmunds et al., 1987). Brine temperatures are controlled by ambient rock temperature, although common observations of brine temperature exceeding surrounding rock temperature by a few degrees suggests equilibration at deeper levels. Estimates of brine age are difficult as they are of mixed origin. Enhanced ⁴He values and U series geochemistry of the brines suggest that they may have components with ages of the order of 10⁴–10⁶ years. However, the presence of tritium in some reveals that they contain a substantial component of modern recharge water which may have circulated to great depths in the mineralised areas via fractures and lodes. Although present at depth in the Camborne–Redruth area and potentially affecting shallow groundwaters and surface mine discharges locally, they are not likely to have a major effect on shallow systems on a regional scale.

The granites have low primary permeability but groundwater flow is significantly enhanced by fractures and joints as well as mine workings. The granites are well-jointed in places with dominant planes being near-horizontal and near-vertical. These largely control the shapes and dimensions of tors. Jointing is most pronounced in the upper sections of quarry faces and tors in response to release of overburden stresses. Fractures have numerous orientations in the granites, but the most prominent correspond to the regional east-north-east–west-south-west lodes and north-north-west–south-south-east cross-courses. On Dartmoor, a major fracture with granite displacement extends south-eastwards from Sticklepath via Chagford and controls part of the course of the River Bovey (Figure 3.3). Another major fault with the same orientation extends along a line through Callisham Down and Cornwood in south-west Dartmoor (Durrance and Laming, 1982).

Mining has also had a major impact on hydrogeology in parts of the Carnmenellis and Land's End plutons: adits, shafts, lode structures and mine workings all act as conduits and storage zones for groundwater. Over 3000 mine shafts have been mapped in the Camborne–Redruth area alone. Most of these are in the metamorphic country rocks but some extend into the granite. During active mining, the mine pumps dewatered large areas. The South Crofty and Wheal Jane mines dewatered areas down to 200 m below sea level over a lateral distance of around 5 km (Smedley et al., 1989). This would have had a major impact on regional groundwater flow, creating artificial hydraulic gradients and inducing flow towards the mines. The mine drainage would have also been a major component of river baseflow.

In the Mount Wellington–Wheal Jane area, the County Adit is the most important drainage system. This is an almost horizontal drain on the western side of the Carnon River and drains into the river. In

1980, it was estimated that this adit intercepted and drained at least 15% of the estimated infiltration in the area (WLP, 1980). Post-mining groundwater rebound can also significantly impact on local groundwater quality as rising waters dissolve the reaction products of sulphide-mineral oxidation and produce acid mine drainage.

In the Carnmenellis granite, the major north-west–south-east cross-courses are important features for groundwater flow and have been found to be major flow paths for deep thermal fluids which issue in the mines on the northern margin of the granite at depths up to 820 m (Box 3.2; Edmunds et al., 1984; Bromley and Thomas, 1987). Isotopic evidence suggests that these brines are of meteoric origin and tritium in many suggests that they contain a substantial component of recent shallow groundwater. This implies that recent shallow groundwaters can circulate to great depths in the areas of mining activity. By contrast, locally high ^4He and ^{222}Rn concentrations of some surface waters and soils implies upwelling of deep groundwater along major joints and cross-courses (Gregory and Durrance, 1987a, b).

Borehole yields from the granites are typically about $30\text{--}50\text{ m}^3\text{ day}^{-1}$ and rarely exceed $100\text{ m}^3\text{ day}^{-1}$ (BGS, 1989). They may be reduced in areas affected by mine dewatering. Yields are generally only sufficient for private water supply and groundwater abstraction licences for the granites are mainly for private agricultural and domestic use.

3.4 Mineralogy and mineral chemistry

The granites of Devon and Cornwall can be classified as K-rich adamellites and have a fairly limited range of compositions. More than 90% of the outcropping areas are composed of biotite granite (Figure 3.6). This mineral type is also seen in the Carnmenellis pluton down to its maximum explored depth at 2.5 km. The biotite granites vary in grainsize but are generally rich in alkali feldspar megacrysts, which themselves vary in size from 2–20 cm long (Selwood et al., 1998). The largest megacrysts are generally seen in the St Austell, Land's End and Dartmoor plutons, perhaps because the outcrops in these areas are closer to the roofs of the intrusions. Plagioclase (albite-oligoclase) is abundant in the matrix. The granites have a total feldspar content of around 65%, along with around 30% quartz and typically 5–7% biotite. Accessory phases include muscovite, tourmaline and chlorite

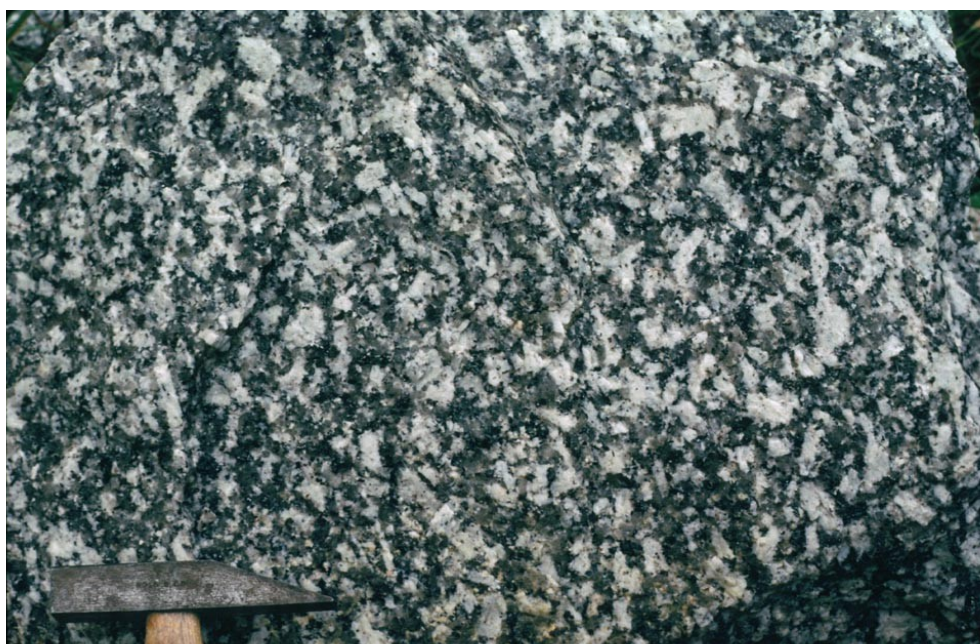


Figure 3.6. Typical biotite granite, Trevone Quarry [SW 7473 3235], Carnmenellis granite (photography: J.M. Pulsford).

Table 3.1. Average chemical compositions of granites from the Carnmenellis and St Austell plutons (as weight %; from a compilation by Selwood et al., 1998).

	Biotite granite Carnmenellis	Biotite granite St Austell	Tourmaline granite St Austell	Topaz granite St Austell
No. analyses	7	6	25	9
SiO ₂	72.26	71.62	75.05	73.26
TiO ₂	0.26	0.33	0.08	0.04
Al ₂ O ₃	14.80	14.59	13.67	13.06
Fe ₂ O ₃	1.80	2.55	1.36	0.83
MgO	0.36	0.50	0.15	0.08
CaO	0.69	1.06	0.54	0.49
Na ₂ O	3.11	3.39	2.81	3.70
K ₂ O	5.02	5.00	4.71	4.46
P ₂ O ₅	0.28	0.23	0.34	0.46
Li ₂ O	0.082	0.07	0.15	0.42
F	0.244	0.24	0.68	1.16
B ₂ O ₃	0.066	0.09	0.41	0.10
Total	98.97	99.67	99.95	98.06

Original data sources: Harding and Hawkes (1971), Darbyshire and Shepherd (1985), Charoy (1986) and Hill (1988).

and less common apatite, monazite, zircon, fluorite, ilmenite, magnetite, rutile and topaz. Some apatite, zircon and monazite occurs as inclusions within the biotites. Accessory phases account for mostly less than 1% of the total (Durrance and Laming, 1982).

Other granite types include tourmaline granite which accounts for around 5% of the outcropping areas and topaz granites which account for around 1% of outcrops (Selwood et al., 1998). The tourmaline granites typically occur as minor veins of leucogranite, with tourmaline crystals up to 8 mm long and occasional alkali feldspar phenocrysts. They are best exposed in the St Austell granite, especially close to china clay workings. They contain Li-mica and are equivalent to the Li-mica granites described by Exley et al. (1983). The topaz granites are equigranular with subhedral topaz (around 3%). The plagioclases are of albite composition and Li-mica, along with accessory rutile, ilmenorutile and tourmaline are also present. The topaz granites occur in the St Austell and Tregonning plutons but have not been observed elsewhere (Durrance and Laming, 1982).

Many of the granites have been altered since emplacement with resultant widespread kaolinisation, haematisation and chloritisation. Partial alteration of biotite to muscovite, chlorite and iron oxide is common, particularly close to areas of veining. Sericitisation of feldspars is also widespread. Kaolinisation is often patchy but is well-developed in the St Austell granite and is responsible for the major china clay workings in that area. Kaolinised patches in the St Austell granite are of the order of 250 m wide. In the Dartmoor granite, a 1–3-km-wide band of kaolinisation corresponds with the Calisham Down–Cornwood Fault (Durrance and Laming, 1982). The alteration has involved conversion of plagioclase and some alkali feldspar to secondary mica and kaolinite-mica aggregates.

Typical chemical compositions of the granites are shown in Table 3.1. The data indicate a limited range of major-element compositions but generally high K₂O concentrations, reflected by the abundance of alkali feldspar. The tourmaline and topaz granites have much higher concentrations of Li, B, F and P compared to the more abundant biotite granites. The topaz granites are also apparently enriched in Rb and Cs. Darbyshire and Shepherd (1985) reported Rb concentrations of 423–481 mg kg⁻¹ in the biotite granites of the Carnmenellis pluton. By contrast, concentrations in the approximate range 600–1100 mg kg⁻¹ were given by Selwood et al. (1998) for the tourmaline granites, and 1500–2000 mg kg⁻¹ for the topaz granites. Sr concentrations of biotite granites are

Table 3.2. Weighted mean annual solute concentrations in rainfall for 2000 at Goonhilly [SW 723 214] and Yarner Wood [SX 786 789] rainfall gauging stations (data from AEA, 2004) and compositions of estimated recharge (3 times concentration).

Determinand		Goonhilly		Yarner Wood	
		Concentration	Concentrated rainfall	Concentration	Concentrated rainfall
Annual rainfall	mm	934		1315	
SEC	$\mu\text{S cm}^{-1}$	60.2		25.9	
pH		4.70	3.86*	4.77	3.97*
Ca	mg l^{-1}	0.40	1.19	0.20	0.60
Mg	mg l^{-1}	0.88	2.65	0.29	0.86
Na	mg l^{-1}	6.88	20.6	2.38	7.15
K	mg l^{-1}	0.30	0.89	0.11	0.34
Cl	mg l^{-1}	12.5	37.5	4.41	13.2
SO ₄	mg l^{-1}	2.67	8.00	1.27	3.82
NO ₃ -N	mg l^{-1}	0.24	1.26*	0.16	0.87*
NH ₄ -N	mg l^{-1}	0.18	—	0.13	—

*Assuming all NH₄-N is oxidised to NO₃-N on infiltration

typically 74–97 mg kg⁻¹ (Darbyshire and Shepherd, 1985) while tourmaline granites have typically <60 mg kg⁻¹ and topaz granites have more variable concentrations, in the range 20–200 mg kg⁻¹ (Selwood et al., 1998).

Arsenic concentrations are often high in the granites (5–100 mg kg⁻¹; Darbyshire and Shepherd, 1985). Arsenic may be present in biotite, apatite and iron oxides as well as sulphides in mineral veins. Concentrations of U (12–17 mg kg⁻¹) and Th (12–23 mg kg⁻¹) are also unusually high (Bromley, 1989). Poole (2001) 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 and Th are concentrated in primary accessory minerals such as monazite, zircon and uraninite as well as iron oxides (Heath, 1982; Poole, 2001). The high concentrations of U and Th in the granites are consistent with their high heat-flow values.

Hall (1988) found that concentrations of NH₄ were high in the Cornubian granites compared to many other granitic rocks. Concentrations in fresh rock samples ranged between 2.3–125 mg kg⁻¹ (as N) with an average of 28 mg kg⁻¹. Concentrations were significantly higher in hydrothermally altered granites (greisenised, tourmalinised and kaolinised) with observed values up to 264 mg kg⁻¹ (as N). Hall (1988) concluded that the N had its origin in sedimentary rocks, either through partial melting of metasedimentary lower crustal material or crustal contamination of upwelling granite magma. The observation is in accord with the strongly S-type, peraluminous and K-rich nature of the granites.

The granites are typically LREE- (light-rare-earth-element) enriched relative to chondrite, with negative Eu anomalies (Jefferies, 1985; Charoy, 1986). The patterns reflect their evolved character and the presence of LREE-enriched accessory minerals such as monazite. Relative Eu depletion is controlled by fractional crystallisation of feldspars. The rarer tourmaline and topaz granites are less LREE-enriched with less marked Eu anomalies (Manning and Hill, 1990; Stone, 1992).

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharging water and may be considered as approximating minimum baseline concentrations of solutes, except where severely impacted by atmospheric pollution, particularly in urban areas affected by smelting and combustion of fossil fuels.

Chemical compositions of rainfall in the region have been assessed from weighted-mean annual concentrations for the latest available year, 2000, for gauging stations at Goonhilly on the Lizard [SW 723 214] and Yarner Wood in eastern Dartmoor [SX 786 789] (from AEA, 2004). Concentrations in the rainfall are given in Table 3.2, along with values for ‘concentrated rainfall’ calculated as three times the weighted-mean values, and approximating the enrichment expected due to evapotranspiration. Such enriched concentrations are those likely to be infiltrating the aquifers of the region. The rainfall totals for 2000 are 934 mm at Goonhilly and 1315 mm at Yarner Wood (cf. Section 3.1).

The volume-weighted mean concentrations of solutes in rainfall at the Goonhilly site are two to four times more concentrated than those at Yarner Wood, with the greatest relative increases in Na, Mg and Cl. This reflects the coastal position of the Goonhilly site and the increased proportions of marine-derived solutes in the rainwater. At Goonhilly, the average non sea-salt SO_4 as a proportion of the total for 2000 was 35% whilst at Yarner Wood, the proportion was higher at 53%. This reflects the larger input of marine-derived SO_4 in rainfall in the extreme south-west. If these compositions are representative of infiltrating recharge, higher concentrations of seawater-derived solutes are expected in the south-westerly parts of the Cornish peninsula.

For elements such as Cl, little interaction with soils and vegetation is expected on recharge and baseline concentrations of modern recharge are therefore likely to be of the order of 13 mg l^{-1} in inland areas but up to 38 mg l^{-1} in near-coastal areas (especially the Land’s End pluton). For other elements, especially K, some changes are likely on infiltration as a result of the weathering of feldspars and clays which should involve initial release of K, as well as uptake by plants and clay minerals in soils with resultant removal from solution.

Assuming that all NH_4 in rainfall oxidises to NO_3 on infiltration to groundwater, modern baseline concentrations of dissolved $\text{NO}_3\text{-N}$ derived from rainfall ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ combined) are likely to be of the order of 1.3 mg l^{-1} or less (Table 3.2), with relatively low concentrations in the Dartmoor

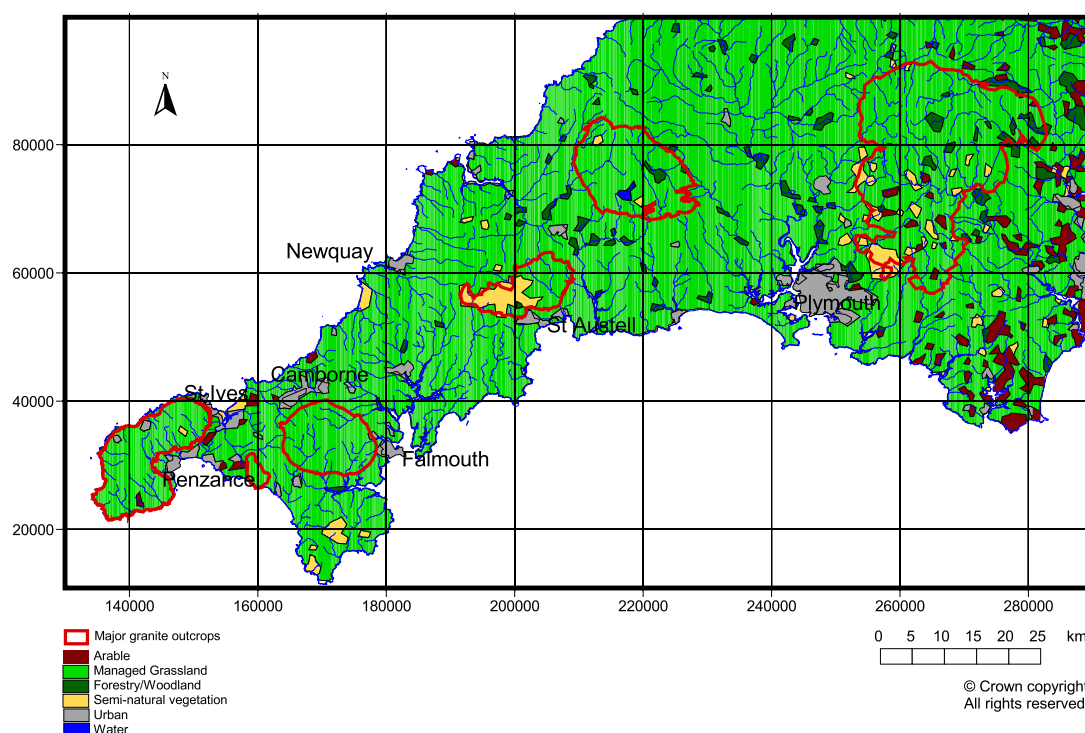


Figure 3.7. Map of land use in the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology & Hydrology, ©NERC.

groundwaters. The presence of dissolved NH_4^+ ions in local rainfall suggests that the pH of recharge may be even lower than that indicated from the rain compositions as a result of oxidation to NO_3^- , which results in the release of protons (H^+ ions). Recharge is therefore likely to have pH values close to or less than 4.

3.6 Land use

Land use on the granites is almost entirely classified as managed grassland (Figure 3.7). The dominant agricultural activity is stock rearing and dairying, though acid upland and peaty soils tend to have poor to moderate grazing value. Some land use is classified as semi-natural vegetation (heather moorland). Arable farming is minor but early potatoes and broccoli are grown in some areas of west Cornwall. Coniferous woodland occupies about 2–3% of the area of granite outcrop. Urban areas are scattered, though the largest centre of the region (Plymouth) is not located on the granite.

4. DATA AND INTERPRETATION

4.1 Data sources

The data used to compile this report are from three datasets originating from both BGS and the EA. The earliest dataset is from a BGS survey of shallow groundwater chemistry in the Carnmenellis area of Cornwall, carried out in 1990 as part of a wider investigation into the geothermal potential of the UK granites ('Hot Dry Rock' project). This survey involved analysis of major constituents and a limited number of trace elements but no isotopic analyses. Data from two groundwater surveys carried out by Geotechnics on behalf of the NRA, (now EA) during 1992 (Phase I) and 1993 (Phase II) are also included. In each case, only the data for groundwater from granites has been incorporated. This comprises 121 groundwater samples from the 1988 BGS survey (excludes streamwater samples) and 52 samples from each of the two Geotechnics surveys (Geotechnics 1993; 1994). One of the samples from the Geotechnics 1992 survey was excluded as it showed strong evidence of contamination. The sample had an $\text{NH}_4\text{-N}$ concentration of 15 mg l^{-1} , organic carbon of 36 mg l^{-1} and K concentration of 48 mg l^{-1} and was probably contaminated with farm slurry. The two Geotechnics surveys included analysis of several organic compounds including polycyclic aromatic hydrocarbons (PAHs) and some pesticides. These have been discussed briefly in this report but have not been summarised statistically.

In addition to the archive data from these surveys, a new set of groundwater samples was collected by BGS specifically for this project during a sampling campaign in September 2003. This set comprises 25 groundwater samples, mostly from EA licensed abstraction sources, collected with a spatial spread across the region. Five samples were collected from each of the main granite plutons of south-west England, i.e. the Land's End, Carnmenellis, St Austell, Bodmin Moor and Dartmoor granites (Figure 3.3). Samples were from 14 pumped boreholes, 1 pumped well and 10 flowing springs. In each case, efforts were made to sample groundwater as close to the aquifer outlet as possible. Sampling downstream of storage tanks was generally avoided unless a representative sample of groundwater was considered to be obtainable. Sampling involved on-site analysis of water 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. Alkalinity was measured by titrating against H_2SO_4 and is quoted as HCO_3 . Filtered ($0.2 \mu\text{m}$) samples were also collected for subsequent laboratory analysis of major and trace elements as well as $\delta^{18}\text{O}$ and $\delta^2\text{H}$. At each site, five aliquots were collected in polyethylene bottles. Two were acidified subsequently with 1% HNO_3 for analysis of cations, SO_4 and trace elements by ICP-OES and ICP-MS. A third was acidified with 1% HCl for analysis of As by hydride-generation-AFS. Two further aliquots were left unacidified for analysis of anions by automated colorimetry (Cl, I) and ion chromatography (N species, Br, F). Further unfiltered samples were collected in glass bottles for the analysis of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ by mass spectrometry. All analyses were carried out at the BGS laboratory in Wallingford, except N species (EA laboratory) and ICP-MS (Acme laboratory, Canada). Results of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ have been calculated as ‰ deviations relative to SMOW.

As a result of the input from the BGS 1988 data, the majority of samples from these combined datasets are from the Carnmenellis granite and the geographical coverage is therefore non-uniform. In total, the database comprises 195 samples, 18 of which are from the Land's End granite, 133 from Carnmenellis and its satellite plutons (Carn Brea, Carn Marth and Tregonning), 11 from St Austell, 12 from Bodmin Moor and 21 from the Dartmoor granite.

4.2 Data quality and handling

For the 1988 BGS survey samples from the Carnmenellis area, most had analytical charge imbalances less than 5% although around 9% of samples had higher imbalances (worst value 11%; Smedley et al., 1989). The EA data quality were more difficult to assess because many did not have recorded

alkalinity values. Of those with complete major-element analyses, most had charge imbalances less than 5% (and often much less), although a few had imbalances up to 10%. It is worthy of note that obtaining good charge balances is particularly difficult in low-TDS waters. No data were excluded from this study on the basis of charge balances. However, one outlying pH value was excluded from the EA dataset (pH 10) and all the EA dissolved-oxygen measurements were excluded as improbable concentrations up to 21 mg l⁻¹ had been recorded.

Analytical charge imbalances for the 25 newly-collected groundwater samples were generally small, all being <4.6% with 84% being <3%. Duplicate analysis of some elements by ICP-OES and ICP-MS also showed good overall agreement: Ba and Mn for example mostly agreed to much better than 10%. For these two elements, the ICP-MS analyses were taken for interpretation and statistical handling. ICP-MS analyses of P (as total P) were also used as the detection limit is better than by ICP-OES.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section describes the main characteristics and regional variations in groundwater chemistry observed in the granites and presents data in the form of statistical summaries and in graphical form (as a Piper diagram, box plots and cumulative-frequency diagrams). Summary statistical data for a large range of chemical determinands are given in Table 5.1. For each of the classes, minima, maxima, median and mean values are given, together with the 97.7th percentile, equivalent to the mean + 2 σ value on a log-normalised data set. The dataset incorporates data with widely differing detection limits for some elements and this is in some cases reflected by differences between the minimum and 5th percentile values (Table 5.1). Median values are useful indicators of approximate average baseline concentrations, but the mean + 2 σ values are given as representative of approximate upper baseline concentrations for most solutes.

Table 5.1. Statistical summary of major and trace constituents and stable isotopic compositions of groundwaters from the granites.

Parameter	Units	Min	5 centile	Median	Mean	97.7 centile	Max	n
Depth	m	0	0	10.1	16.5	62	100	150
Temperature	°C	9.0	10.6	12.5	12.7	16.3	18.5	194
pH		4.26	4.94	5.64	5.69	6.81	7.20	192
Eh	mV	261	274	380	374	476	495	25
DO	mg l ⁻¹	0.3	3.5	6.8	6.3	8.1	8.2	25
SEC	$\mu\text{S cm}^{-1}$	14.0	68.8	206	225	496	713	192
$\delta^2\text{H}$	‰	-37	-37	-31	-32	-30	-30	12
$\delta^{18}\text{O}$	‰	-6.0	-5.8	-5.0	-5.1	-4.8	-4.8	12
Ca	mg l ⁻¹	<2.0	2.74	12.2	14.0	40.2	66.2	195
Mg	mg l ⁻¹	0.80	1.03	3.40	3.99	12.5	22.7	195
Na	mg l ⁻¹	4.00	7.00	15.6	16.8	35.1	56.0	195
K	mg l ⁻¹	<0.5	0.70	2.50	4.44	19.5	66.8	195
Cl	mg l ⁻¹	4.70	10.9	27.0	29.2	66.9	105	195
SO ₄	mg l ⁻¹	<5.0	5.24	14.3	16.2	39.0	52.6	195
HCO ₃	mg l ⁻¹	<10	<10	10.5	16.8	81.1	203	177
NO ₃ -N	mg l ⁻¹	<0.8	0.59	5.35	6.35	16.7	33.3	194
NO ₂ -N	mg l ⁻¹	<0.0006	<0.01	<0.01	<0.01	0.010	0.085	75
NH ₄ -N	mg l ⁻¹	<0.02	<0.03	<0.03	0.015	0.049	0.21	51
P	mg l ⁻¹	<0.02	<0.1	<0.1	0.090	0.47	0.90	144
TOC	mg l ⁻¹	<0.2	<0.5	1.0	1.4	5.9	8.8	50
DOC	mg l ⁻¹	0.30	0.32	0.90	1.3	4.2	5.8	25
F	$\mu\text{g l}^{-1}$	<50	<100	<100	142	467	1500	75
Br	$\mu\text{g l}^{-1}$	<30	<30	60	92	287	320	25
I	$\mu\text{g l}^{-1}$	1.0	1.0	4.0	7.4	31	34	25
Si	$\mu\text{g l}^{-1}$	701	1680	2900	3260	7290	12600	194
Ag	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Al	$\mu\text{g l}^{-1}$	<30	<100	150	234	855	1270	195
As	$\mu\text{g l}^{-1}$	<0.1	<0.5	0.2	0.8	4.8	5.8	76
Au	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
B	$\mu\text{g l}^{-1}$	<5	<20	8.5	22	60	190	194
Ba	$\mu\text{g l}^{-1}$	<1	<4	8.0	10.3	30.1	56	194
Be	$\mu\text{g l}^{-1}$	<0.05	<1	<1	<1	1.8	4.0	75
Bi	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Cd	$\mu\text{g l}^{-1}$	<0.2	<0.2	<0.2	0.14	0.31	0.37	76
Ce	$\mu\text{g l}^{-1}$	<0.03	0.064	0.80	1.5	4.8	5.1	56
Co	$\mu\text{g l}^{-1}$	<0.02	<1	<1	<1	0.31	1.0	75

Parameter	Units	Min	5 centile	Median	Mean	97.7 centile	Max	n
Cr	$\mu\text{g l}^{-1}$	<0.5	<1	<1	<1	2.0	2.0	76
Cs	$\mu\text{g l}^{-1}$	0.06	0.11	0.58	0.79	3.4	3.8	56
Cu	$\mu\text{g l}^{-1}$	<1	<1	7.45	31.2	250	520	76
Dy	$\mu\text{g l}^{-1}$	<0.08	<0.08	0.14	0.17	0.44	0.62	56
Er	$\mu\text{g l}^{-1}$	<0.01	<0.08	0.08	0.10	0.22	0.28	56
Eu	$\mu\text{g l}^{-1}$	<0.01	<0.06	<0.06	0.04	0.13	0.22	56
Fe	$\mu\text{g l}^{-1}$	<5	<50	10	198	749	21800	194
Ga	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Gd	$\mu\text{g l}^{-1}$	<0.05	<0.09	0.16	0.24	0.66	0.68	56
Ge	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Hf	$\mu\text{g l}^{-1}$	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	25
Hg	$\mu\text{g l}^{-1}$	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1	76
Ho	$\mu\text{g l}^{-1}$	<0.01	<0.05	0.020	0.034	0.074	0.11	56
In	$\mu\text{g l}^{-1}$	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	25
Ir	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
La	$\mu\text{g l}^{-1}$	<0.05	0.03	0.49	0.72	2.60	3.07	56
Li	$\mu\text{g l}^{-1}$	0.4	0.48	2.8	4.5	28	46	56
Lu	$\mu\text{g l}^{-1}$	<0.01	<0.01	0.010	0.010	0.024	0.030	25
Mn	$\mu\text{g l}^{-1}$	<1	2.0	14.5	58.3	224	5960	195
Mo	$\mu\text{g l}^{-1}$	<0.1	<0.1	<0.1	0.08	0.30	0.30	25
Nb	$\mu\text{g l}^{-1}$	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	25
Nd	$\mu\text{g l}^{-1}$	<0.1	<0.2	0.62	0.91	2.90	3.01	56
Ni	$\mu\text{g l}^{-1}$	<0.2	<1	<1	0.84	5.6	10.0	75
Os	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Pb	$\mu\text{g l}^{-1}$	<1	<1	<1	2.4	7.6	110	76
Pd	$\mu\text{g l}^{-1}$	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	25
Pr	$\mu\text{g l}^{-1}$	<0.04	<0.08	0.15	0.22	0.69	0.72	56
Pt	$\mu\text{g l}^{-1}$	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	25
Rb	$\mu\text{g l}^{-1}$	1.3	2.5	9.5	11.7	37	60	56
Re	$\mu\text{g l}^{-1}$	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	25
Rh	$\mu\text{g l}^{-1}$	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	25
Ru	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Sb	$\mu\text{g l}^{-1}$	<0.05	<1	<1	0.35	0.16	0.29	75
Sc	$\mu\text{g l}^{-1}$	<1	<1	<1	<1	1.0	1.0	25
Se	$\mu\text{g l}^{-1}$	<0.2	<0.5	<0.5	0.24	1.1	1.9	74
Sm	$\mu\text{g l}^{-1}$	<0.02	<0.09	0.12	0.20	0.67	0.69	56
Sn	$\mu\text{g l}^{-1}$	0.06	0.07	0.09	0.09	0.14	0.16	25
Sr	$\mu\text{g l}^{-1}$	6.9	18.8	58	70	173	418	144
Ta	$\mu\text{g l}^{-1}$	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	25
Tb	$\mu\text{g l}^{-1}$	<0.01	<0.01	0.01	0.02	0.07	0.10	25
Te	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	25
Th	$\mu\text{g l}^{-1}$	<0.05	<0.05	<0.05	0.035	0.098	0.28	25
Ti	$\mu\text{g l}^{-1}$	<10	<10	<10	<10	<10	<10	25
Tl	$\mu\text{g l}^{-1}$	<0.01	<0.01	0.020	0.033	0.089	0.10	25
Tm	$\mu\text{g l}^{-1}$	<0.01	<0.01	0.010	0.012	0.029	0.040	25
U	$\mu\text{g l}^{-1}$	0.02	0.072	0.55	0.98	3.56	3.57	25
V	$\mu\text{g l}^{-1}$	<0.2	<0.2	<0.2	0.2	0.53	0.70	25
W	$\mu\text{g l}^{-1}$	<0.02	<0.02	<0.02	<0.02	0.044	0.05	25
Y	$\mu\text{g l}^{-1}$	0.040	0.098	0.69	0.94	2.85	3.66	25
Yb	$\mu\text{g l}^{-1}$	<0.01	<0.07	0.03	0.07	0.21	0.26	56
Zn	$\mu\text{g l}^{-1}$	<2	<2	8.4	50	274	1600	75
Zr	$\mu\text{g l}^{-1}$	<0.02	<0.02	0.02	0.09	0.57	1.02	25

SEC at 25°C; HCO_3^- are alkalinity as HCO_3^- , almost all as field measurements; TOC/DOC: total and dissolved organic carbon respectively

Table 5.2. Summary statistics for selected parameters from the five major granite plutons.

Pluton		pH	SEC	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	NO ₃ -N	NH ₄ -N
Land's End	min	4.8	96	3.0	0.8	4.0	1.0	4.7	3.8	5.0	0.68	0.01
	max	6.8	713	66.2	22.7	56.0	8.5	105	47.1	81.0	33.3	0.21
	median	5.8	341	19.3	6.2	27.0	2.9	54	13.1	17.0	10.2	0.01
Carnm'llis	min	4.3	14	2.8	0.9	8.5	0.4	13	7.8	2.1	0.4	0.01
	max	7.2	570	44.0	18.8	36.4	66.8	61	52.6	203	20	0.015
	median	5.6	217	13.3	3.5	16.1	2.8	28	16.7	9.5	6.1	0.01
St Austell	min	5.0	119	4.4	1.5	8.8	1.0	12	5.8	7.3	1.9	0.004
	max	6.4	418	31.3	8.3	19.0	8.5	32	15.0	36.9	21.3	0.02
	median	5.6	176	9.0	2.3	13.0	2.0	23	11.0	12.1	3.27	0.015
Bodmin M.	min	4.7	80	3.0	0.8	6.8	0.3	10	5.0	5.0	0.59	0.01
	max	6.3	278	15.0	20.2	21.0	10.5	26	17.0	26.0	6.99	0.056
	median	5.6	120	8.8	1.4	9.0	1.1	15	6.3	17.3	2.04	0.01
Dartmoor	min	4.9	63	1.0	0.8	5.2	0.4	7.1	2.5	5.0	0.13	0.01
	max	7.2	491	42.0	11.6	28.0	10.5	53	27.0	42.0	14.0	0.112
	median	5.7	85	3.0	1.6	7.0	0.9	12	6.0	8.7	1.29	0.01

All concentrations in mg l⁻¹ except SEC (μS cm⁻¹) and pH

5.2 Major constituents

The sampled groundwaters from the granites are from shallow boreholes, wells, adits and springs. Recorded borehole depths were up to 100 m but most were lower than 30 m with a median of just 10 m. As the groundwaters are generally shallow, they typically show the characteristics of young, freshly recharged water. Those sampled are universally oxidic, with dissolved-oxygen concentrations in the range 0.3–8.2 mg l⁻¹ and with generally high redox potentials (Eh 261–495 mV, median 380 mV;

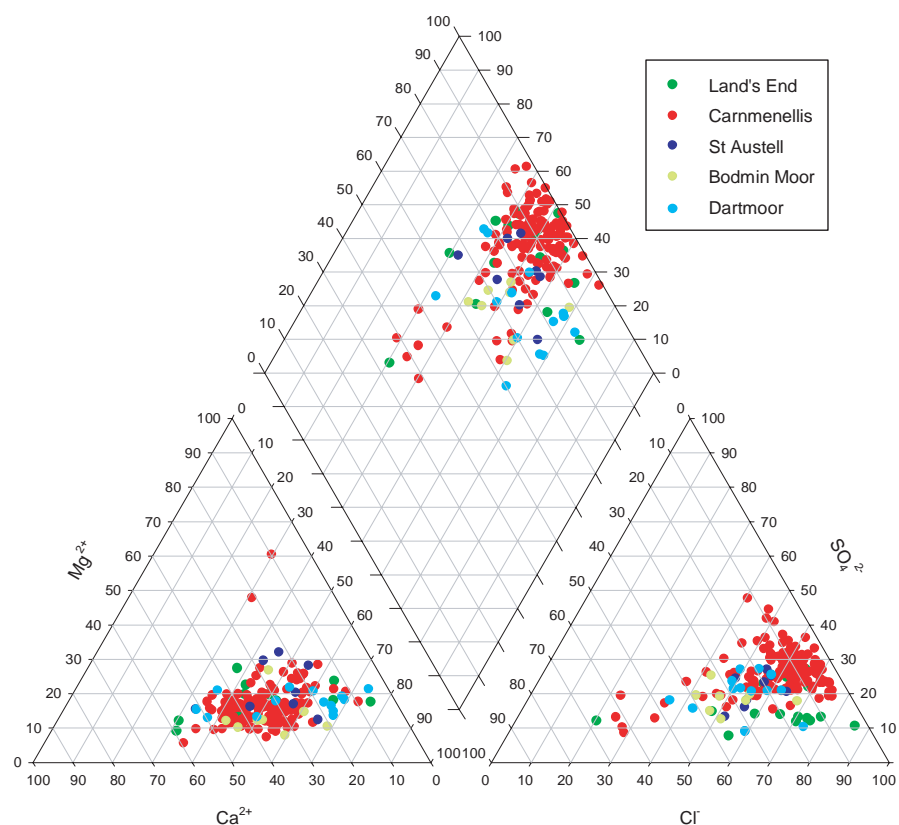


Figure 5.1. Piper diagram for groundwater samples from the granites of south-west England investigated in this study.

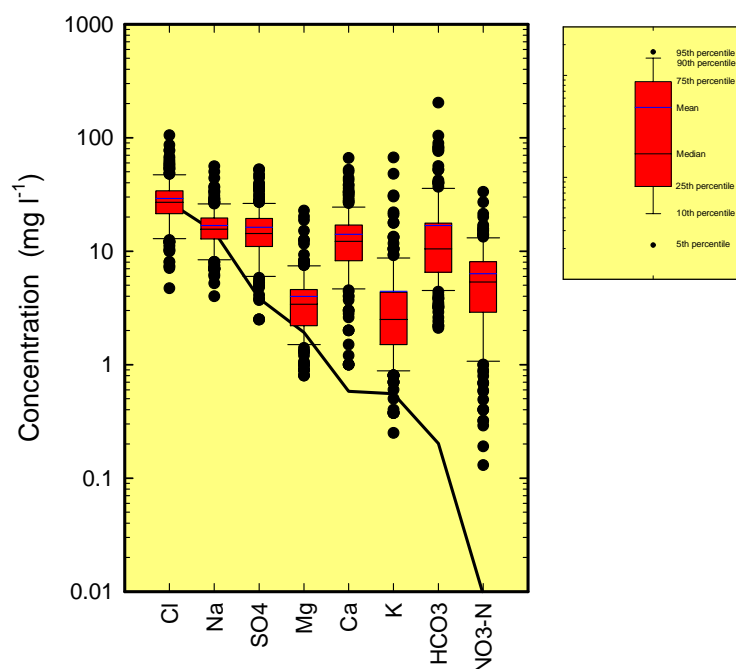


Figure 5.3. Box-and-whiskers plots showing the ranges of major constituents in groundwaters from the granites of south-west England. Black line: concentrations of ‘diluted’ seawater (normalised to median Cl concentration).

Table 5.1). The groundwaters are weakly mineralised, with low concentrations of dissolved solids. SEC values have a large range (14–713 $\mu\text{S cm}^{-1}$) but the median is low, just 206 $\mu\text{S cm}^{-1}$. The groundwaters are typically acidic with pH values in the range 4.3–7.2. Ranges and medians of pH, SEC and major ions are given for the individual major plutons in Table 5.2.

The Piper diagram (Figure 5.1) indicates that the cations are Na-dominant or mixed Na-Ca dominant,

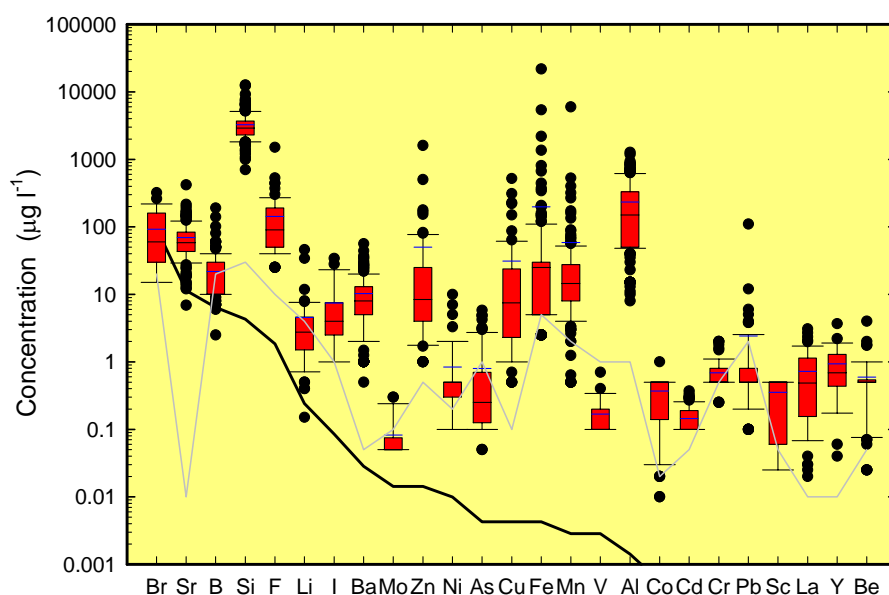


Figure 5.2. Box-and-whiskers plots showing the ranges of minor constituents in groundwaters from the granites of south-west England. Black line: concentrations of ‘diluted’ seawater (normalised to median Cl concentration); grey line: typical detection limits. Legend as in Figure 5.3.

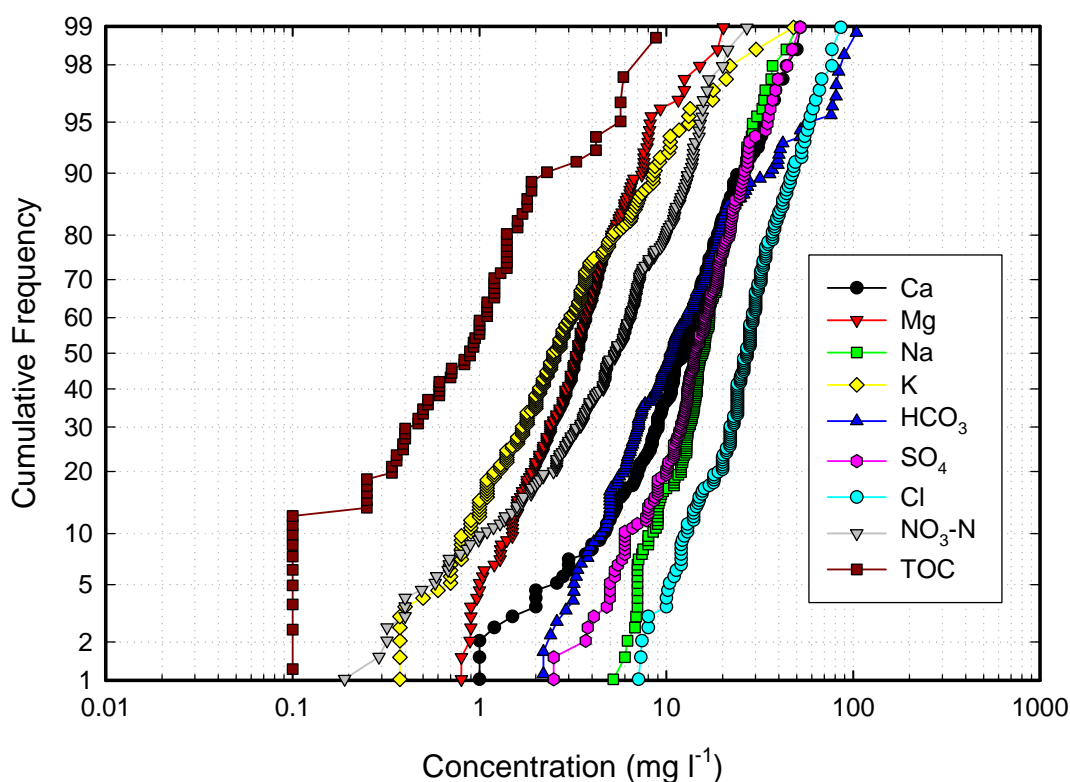


Figure 5.4. Cumulative-frequency plots for the major constituents in groundwaters from the granites of south-west England.

although two samples (from the Carnmenellis granite) have relatively high proportions of Mg. Anions are mostly dominated by Cl, but a trend to samples with higher HCO₃ concentrations is also observed. No major differences can be seen between the compositions of groundwaters from the different plutons, except that the Land's End granite samples appear to have relatively low proportions of SO₄ (higher Cl) compared to the other granites.

As expected for granitic areas, the groundwaters are mostly soft with low overall concentrations of Ca and Mg (up to 66 mg l⁻¹ and 23 mg l⁻¹ respectively). Hardness values for the samples from the Geotechnics datasets are in the range 8–223 mg l⁻¹ as CaCO₃. Hardness was not measured in the BGS samples. Sodium concentrations are in the range 4–56 mg l⁻¹. Alkalinity values are mostly very low but range between <10 and 203 mg l⁻¹.

Concentrations of NO₃-N have a relatively large range of <0.8–33 mg l⁻¹. The median is 5.4 mg l⁻¹. A few have concentrations in excess of the EC maximum permissible value for NO₃-N in drinking water of 11.3 mg l⁻¹. Concentrations of other nitrogen species (NO₂-N, NH₄-N) are generally low (Table 5.1) but NH₄-N reaches 0.21 mg l⁻¹ in one sample. Concentrations of total and dissolved organic carbon (TOC, DOC) are comparable and in the range <0.5–8.8 mg l⁻¹ and 0.3–5.8 mg l⁻¹ respectively. In the cumulative-frequency plot (Figure 5.4), a distinct change of slope occurs at around 2 mg l⁻¹ TOC, suggesting that the dataset contains two different sample populations.

5.3 Trace elements

The concentrations of many trace elements are low, in line with the young, freshly recharged character of the groundwaters. Concentrations of P are mostly less than 0.1 mg l⁻¹ although they reach up to 0.9 mg l⁻¹. Likewise, F concentrations are mostly less than 100 µg l⁻¹, although they reach 1500 µg l⁻¹ in one sample. Silicon ranges between 701–12600 µg l⁻¹ with a median of just 2900 µg l⁻¹.

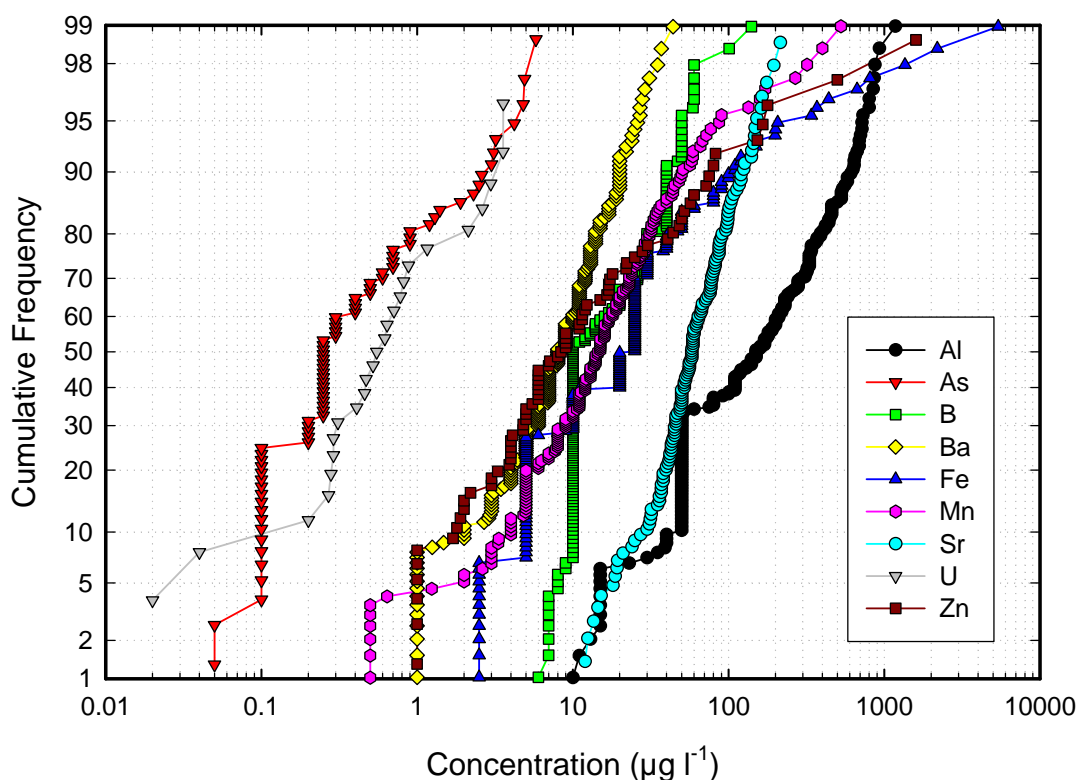


Figure 5.5. Cumulative-frequency plots for the minor constituents in groundwaters from the granites of south-west England.

However, the acidic conditions of the groundwaters have given rise to high concentrations of some trace elements, notably Al (up to $1270 \mu\text{g l}^{-1}$), Cu (up to $520 \mu\text{g l}^{-1}$), Zn (up to $1600 \mu\text{g l}^{-1}$), Pb (up to $110 \mu\text{g l}^{-1}$), Y (up to $3.66 \mu\text{g l}^{-1}$) and REE (e.g. La and Ce up to $3.07 \mu\text{g l}^{-1}$ and $5.1 \mu\text{g l}^{-1}$ respectively). Concentrations of Fe and Mn are also high in a few of the groundwater samples (up to 21.8 mg l^{-1} and 5.96 mg l^{-1} respectively) though this is not simply a function of acidity.

The high regional concentrations in the granites of some of the incompatible elements which concentrate in late-stage melts are also reflected in relatively high concentrations in the groundwaters. Lithium reaches concentrations up to $46 \mu\text{g l}^{-1}$, B up to $190 \mu\text{g l}^{-1}$, Cs up to $3.8 \mu\text{g l}^{-1}$ and Rb up to $60 \mu\text{g l}^{-1}$. Barium concentrations are usually low, reaching up to $56 \mu\text{g l}^{-1}$.

Despite the high concentrations of As in the solid phase in some of the mineralised areas, concentrations in the sampled groundwaters are mostly low, values being up to $5.8 \mu\text{g l}^{-1}$. Uranium concentrations were up to $3.6 \mu\text{g l}^{-1}$.

In terms of drinking-water quality, only a few of the samples included in this study have concentrations of individual solutes above acceptable limits. These include Pb and Mn. Fluoride is present at a concentration equivalent to the EC drinking-water limit of $1500 \mu\text{g l}^{-1}$ in one sample. In some instances, Al concentrations exceed the EC limit of $200 \mu\text{g l}^{-1}$. However, it is stressed that the waters included in this study are raw groundwaters and the drinking-water limits are given for comparative purposes only.

5.4 Organic compounds

The shallow depth of weathering and fractured nature of the granite aquifer means that the groundwater may also be susceptible to pollution from organic compounds released at the land surface. Few data currently exist for the organic compounds in the groundwaters, but sampling campaigns carried out for the NRA in 1992 and 1993 included analysis of a limited number of

compounds (Geotechnics, 1993; 1994). Results indicated that some of the more commonly detected compounds were the polycyclic aromatic hydrocarbons (PAHs), including fluoranthene, benzo[b]fluoranthene, chrysene, pyrene, indeno[1,2,3]pyrene and benzo[g,h,i]perylene. Concentrations were mostly low, but fluoranthene reached up to $3.6 \mu\text{g l}^{-1}$, benzo[b]fluoranthene up to $0.056 \mu\text{g l}^{-1}$, chrysene up to $0.008 \mu\text{g l}^{-1}$, pyrene up to $0.012 \mu\text{g l}^{-1}$, indeno[1,2,3]pyrene up to $0.14 \mu\text{g l}^{-1}$ and benzo[g,h,i]perylene up to $0.006 \mu\text{g l}^{-1}$. The maximum observed concentrations of indeno[1,2,3]pyrene and fluoranthene are in excess of the EC maximum permissible value for specific PAHs of $0.1 \mu\text{g l}^{-1}$. The PAH compounds may be introduced to the groundwater by anthropogenic activity either indirectly through fossil-fuel burning or directly via oil spills, waste water or landfill leachate, although they may also be derived from natural sources such as degradation of organic matter.

Few other analysed compounds were found to be significant on a regional scale. The pesticide atrazine was detected at a concentration of $0.3 \mu\text{g l}^{-1}$ in one sample although most were below the detection limit of around $0.01 \mu\text{g l}^{-1}$. The same sample contained $0.26 \mu\text{g l}^{-1}$ of the breakdown product deethylatrazine. Simazine concentrations were up to $0.064 \mu\text{g l}^{-1}$ but most were below detection limit of $0.005 \mu\text{g l}^{-1}$. Analysis of a number of chlorinated solvents also showed mostly low concentrations. One sample contained 1,1,1-trichloroethane at a concentration of $2.6 \mu\text{g l}^{-1}$ but concentrations were below detection limit in all other samples. The compounds trichloroethene, 1,2-dichloroethene, carbon tetrachloride and trichloromethane were also all below analytical detection limits. The generally low concentrations of these compounds are in line with the dominantly rural land use of the region.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

This section describes the spatial variation in groundwater chemistry in the granites of south-west England and the main processes controlling them. The spatial variation is highlighted by a number of regional groundwater-quality maps. Identifying the main processes is an important prerequisite for defining likely baseline compositions of groundwaters in a given aquifer (Box 6.1). The groundwaters have chemical compositions which have evolved from local rainfall (recharge) compositions by mineral dissolution (and precipitation) reactions in the soils and bedrocks. A paucity of carbonate minerals in the rocks and soils has had a marked effect on regional water quality. Some show evidence of additional inputs of surface pollutants.

6.2 Regional variations and controls

6.2.1 Major-element compositions

The most notable features of the quality of groundwater from the granites are its softness and acidity. Most users of pumped groundwater supplies install pH regulators (lime or calcium carbonate) in order to increase the hardness and reduce the aggressiveness of the water to metal pipework. Acid attack of pipework can cause long-term damage, as well as increasing the concentrations of dissolved metals (particularly Cu and Zn) in water used for drinking. As noted in Section 5, the median pH of the groundwaters of the region is 5.7. The regional distribution of pH values in the groundwaters is shown in Figure 6.1.

The acidic compositions result from the generally poor acid-buffering capacity of the soils and bedrocks. Soils on the granites are typically thin, sandy, acidic and in some places peaty. Granite and

Box 6.1 How can we distinguish pristine waters from polluted groundwater?

Groundwater prior to the industrial era (before ca. 1800) emerged as springs or was taken from shallow wells. The water would have had compositions largely reflecting true baseline, determined by natural geological and geochemical processes. Today, the influences of modern anthropogenic activities mean that only rarely is it possible to find such waters, particularly in shallow aquifers which are most vulnerable to contamination. The problem in defining baseline conditions for a given aquifer or region is to recognise the impact of any human activities over and above the natural baseline in the data sets used.

The logical approach adopted is threefold:

- (i) to have evidence of groundwater age;
- (ii) where available, to extrapolate data back to a pre-industrial time;
- (iii) to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced organic carbon and N species, especially NO_3 . These indicate the presence of foreign substances such as agricultural or industrial chemicals. The sets of data are examined for these substances to identify the presence of “contamination”, although it is stressed that it is impossible to quantify this. Although contaminants may be identifiable, traces of such contaminants may have little impact on the overall chemistry of the groundwater.

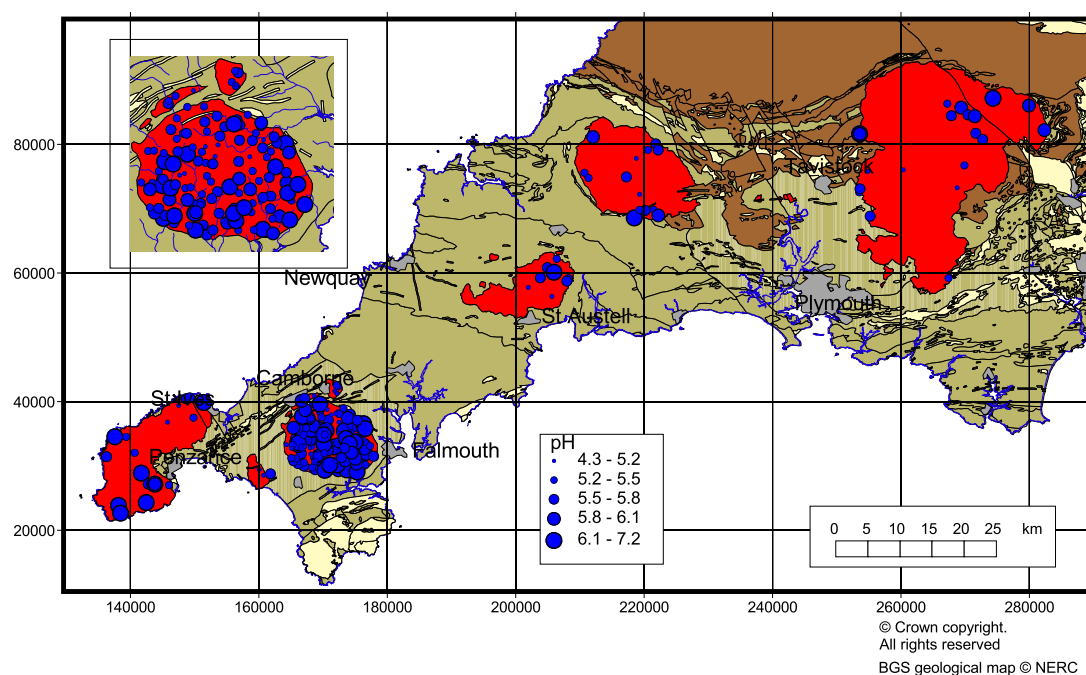


Figure 6.1. Regional variation of pH in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

weathered bedrock is silicic, Na-rich and with a lack of carbonate minerals. Infiltrating rainfall is already acidic with pH values likely to be <4 (Section 3.5). Although silicate weathering reactions can increase the pH of infiltrating groundwaters, the acid-buffering capacity of the bedrocks is poor compared to those containing carbonate minerals such as calcite and dolomite. Alkalinity is generated to some extent by weathering of silicate rocks (by reaction of silicates with carbonic acid from the soil) but the low acid-buffering capacity of the groundwaters is reflected in the low alkalinity values (median $10.5 \text{ mg l}^{-1} \text{ HCO}_3$). As expected, all the groundwaters are significantly undersaturated with respect to calcite and dolomite. Groundwater pCO_2 values are usually high (average $10^{-1.7} \text{ atm}$).

Acidity can also be generated by the oxidation of Fe sulphides (pyrite, arsenopyrite) in mineral veins. This has been observed in mine drainage issuing from the mines in the Camborne–Redruth area, for example, and could be an additional source of protons in the mineralised areas. Acid mine drainage

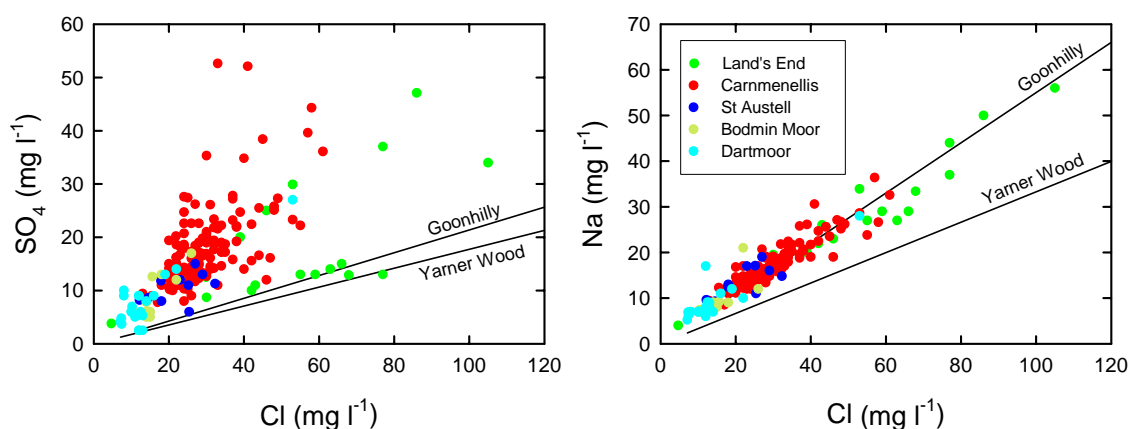


Figure 6.2. Variation in SO_4 and Na with Cl in groundwaters from the granites of south-west England. Concentration curves for evaporated average rainfall from Goonhilly and Yarnier Wood are given for comparison.

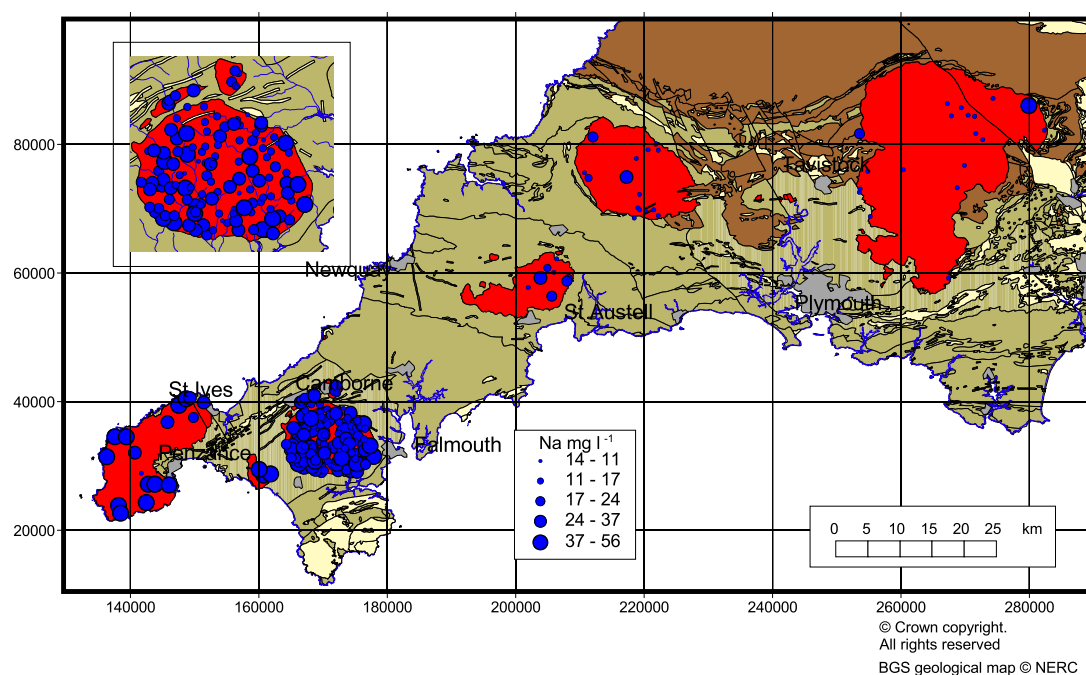


Figure 6.3. Regional variation of Na in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

typically has associated high SO_4 concentrations resulting from the oxidation. For example, a sample from Geevor adit in the Land's End granite has a SO_4 concentration of 34 mg l^{-1} , likely to be largely from the oxidation of sulphide minerals. Although important in mineralised areas, sulphide oxidation probably has less significance on a regional scale in generating the acidic groundwater conditions. Sulphide minerals are not abundant secondary minerals in the granites away from the major mineral veins (Section 3.2.2).

Sources of dissolved SO_4 in groundwater also include rainfall (from both industrial emissions and evaporated seawater) and agricultural pollutants. Figure 6.2 shows the relationship between SO_4 and Cl in the groundwaters. Some samples lie close to the curves for evaporated local rainfall. Samples with SO_4 concentrations up to around 15 mg l^{-1} in the Land's End granite appear to be linked to rainfall composition. This is slightly higher than the estimate of 8 mg l^{-1} expected from rainfall having undergone evapotranspiration in Section 3.5, although additional inputs from marine aerosols may be contributing in coastal areas. Most sample compositions lie above the rainfall curves, which indicates additional inputs of SO_4 . Concentrations of SO_4 reach up to 53 mg l^{-1} in the groundwaters from the Carnmenellis granite. As suggested above, some of this excess SO_4 may be derived from the oxidation of sulphide minerals. However, many samples with high SO_4 concentrations have associated high concentrations of K, $\text{NO}_3\text{-N}$ and P. For example, the sample with the highest observed SO_4 concentration, also has a K concentration of 18 mg l^{-1} , $\text{NO}_3\text{-N}$ concentration of 11 mg l^{-1} and P concentration of 0.5 mg l^{-1} (no data for $\text{NH}_4\text{-N}$ or TOC in this sample). These parameters together suggest that the groundwater has been affected by agricultural pollution, probably from slurry. The sample was from a shallow well on a farm site.

Granitic rocks and the soils produced from them generally lack the main elements which generate water hardness: Ca and Mg. The dominance of Na-rich rocks (the plagioclase is dominantly albite or oligoclase) together with the lack of secondary carbonate minerals accounts for the major-element compositions of the groundwaters of the region. The sodic compositions of the granites explain the tendency for Na to be often the dominant cation in the groundwaters, with relatively low Ca concentrations. The regional distributions of Na and Ca are shown in Figure 6.3 and Figure 6.4 respectively.

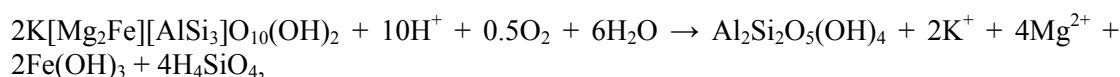
The most easily weathered of the minerals in the granites are likely to be the plagioclase feldspars and biotites. The feldspars alter to clay minerals; biotite weathers to clay including chlorite, and iron oxides. Alkali feldspar and muscovite are less reactive and quartz is typically the least reactive of all the constituent minerals. The accessory minerals (e.g. apatite, sphene, zircon, monazite, topaz, tourmaline) have variable resistance to weathering. Compared to plagioclase and biotite, most are likely to be unreactive, but as they contain high concentrations of many trace elements, they can contribute a relatively high proportion of these to the groundwaters. Alteration of sodic plagioclase (albite) to kaolinite can be described as:



a process which reduces acidity and generates dissolved Na and dissolved silicate. Gibbsite rather than kaolinite may be a reaction product of albite weathering. Weathering of alkali feldspar follows a similar reaction to that of albite, but with the release of dissolved K:



Weathering of biotite can be described by the reaction:



which contributes dissolved K, Mg and silicate to solution.

Some weathering of these minerals to produce enhanced dissolved concentrations of Na, Mg, K and Si (for example) may occur, but the ratio of Na to Cl in the groundwaters is very similar to that in local rainfall (Figure 6.2). This suggests that Na accumulation in the groundwater by water-rock interaction has been relatively small.

This limited degree of rock weathering is also manifested by low overall concentrations of dissolved

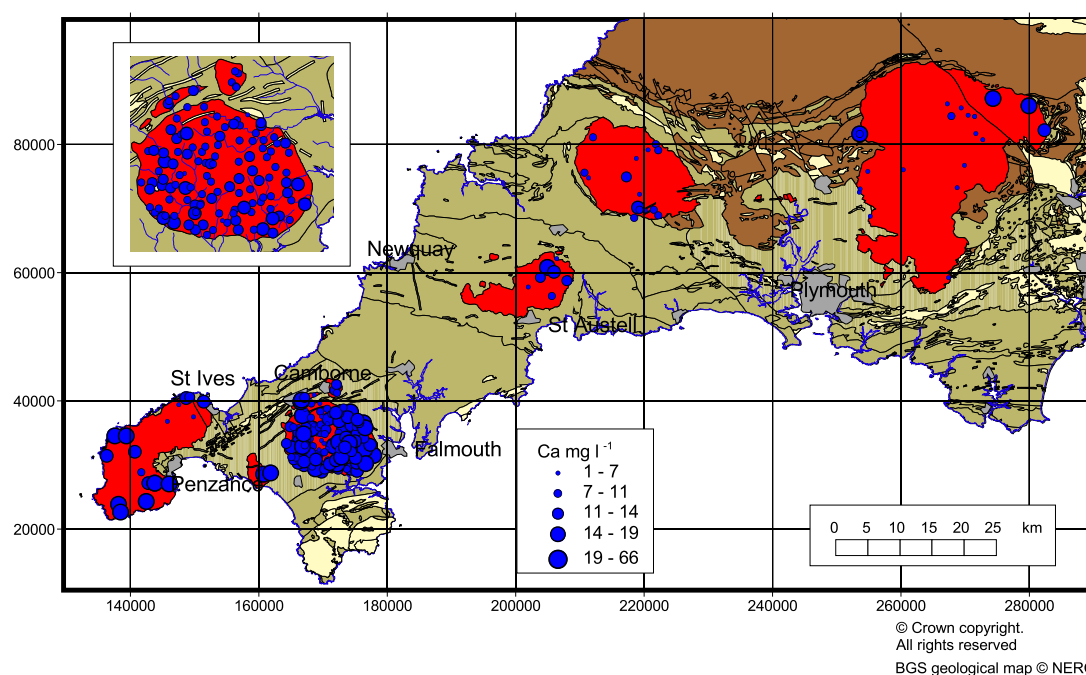


Figure 6.4. Regional variations in Ca in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

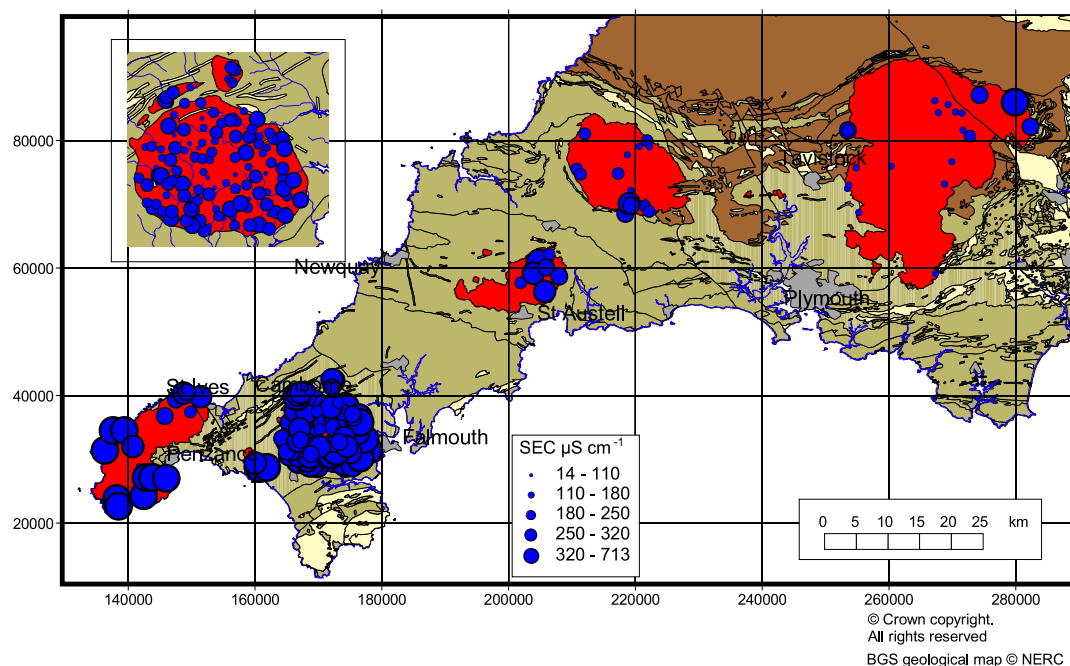


Figure 6.5. Regional variations of SEC (specific electrical conductance) in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

solids. Low salinity values are a typical feature of groundwater from silicate rocks and are a reflection of the comparatively slow reaction kinetics of silicate minerals. Fracture flow also leads to limited contact between bedrock and groundwater due to the relatively small surface area exposed to water. Smedley et al. (1989) noted that groundwaters from the Carnmenellis granite had lower salinity values overall than those from the surrounding metasediments despite the fact that both are shallow groundwater systems with likely comparable residence times. Smedley et al. (1989) concluded that the differing salinities related to the low reactivity of the granites compared to the clay-rich country rocks.

A map of the regional distribution of SEC is shown in Figure 6.5. The SEC values are generally higher in the groundwaters of the Land's End and Carnmenellis granites than in the other three plutons. The variations are believed to reflect largely the influence of marine-derived rainfall, although as noted earlier, higher SO_4 concentrations may be related to additional sulphide oxidation and some local pollutant inputs may affect the values. Saline intrusion is not evident in the coastal part of the Land's End granite, probably because of the elevated topography of most of the granite outcrop and the high resulting hydraulic gradients. Two samples with relatively high SEC values are seen in the north-east of the Dartmoor granite. Higher concentrations of many solutes (Ca, K, Cl, HCO_3 , $\text{NO}_3\text{-N}$) are also observed in these two samples. The reasons for these concentrations are unclear but as elsewhere may relate to local pollutant inputs or geochemical reactions from mineralised zones.

As groundwater salinity is low, the compositions of infiltrating recharge have a relatively large impact on the overall compositions of the groundwaters. As described in Section 3.5, the rainfall of the region is affected by marine inputs, especially in the extreme south-west coastal area. Regional variations in salinity are therefore to be expected as a result of variations in rainfall composition. Concentrations of Cl in the groundwater are likely to be dominated by atmospheric inputs. The range in Cl concentrations described in Section 0 ($4.7\text{--}105\text{ mg l}^{-1}$) is relatively large. Chloride concentrations in recharge are considered likely to range between about 38 mg l^{-1} in the extreme south-west and 13 mg l^{-1} further inland (Section 3.5). Many sites fall within this range, although a few higher

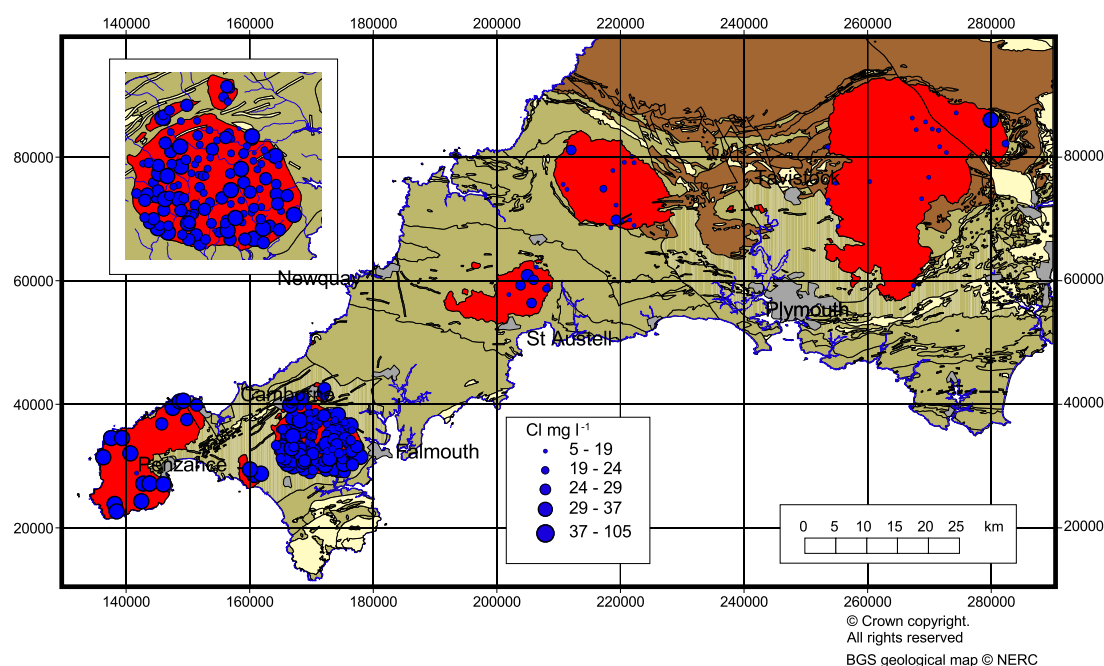


Figure 6.6. Regional variations in Cl in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

concentrations are in excess. Some extra Cl could be derived from marine aerosols (seaspray) in the immediate coastal areas. Derivation of Cl (and other solutes) by saline intrusion is not considered a likely process as the granites tend to have a large topographic elevation with typically large hydraulic gradients. Increases in groundwater Cl concentrations in saline groundwaters from the Cornish granites were attributed by Edmunds et al. (1984) to the weathering of biotites containing Cl-rich fluid inclusions. This may be an additional source of Cl but its influence on the shallow groundwaters is unquantified. The regional variations in groundwater Cl concentration are shown in Figure 6.6. The distributions clearly show the relatively high concentrations in groundwaters from the Land's End and Carnmenellis granites.

Potassium concentrations are controlled by both mineral reaction, including weathering of biotite, alkali feldspar and secondary clays, as well as pollution. Arable agriculture is relatively minor in the granite areas of south-west England, but application of NPK fertilisers to areas of arable land may be one source of K, as may the application of fertiliser or slurry to managed grassland. Inputs of K from point sources such as landfills, septic tanks, highways and domestic soakaways may also occur.

Concentrations of $\text{NO}_3\text{-N}$ are in many places higher than the predicted concentrations for recharge based on the local rainfall data. A maximum of $33 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ was observed. Sources include N from the soil zone and from reaction of granite (which has been found to contain up to $125 \text{ mg kg}^{-1} \text{ NH}_4\text{-N}$; Hall, 1988) but much of the excess must represent pollutant inputs. The groundwater with the highest $\text{NO}_3\text{-N}$ concentration was from a farm on the Land's End granite and had an unusually high SEC value ($693 \mu\text{S cm}^{-1}$, also the highest observed value). Contamination with farm slurry locally around the borehole is possible. The regional distribution of $\text{NO}_3\text{-N}$ in groundwater is shown in Figure 6.7. The distribution shows that much lower concentrations occur in samples from the Bodmin Moor and Dartmoor granites (except the two samples from the north-eastern part of the pluton). The regional variation in rainfall nitrogen content will have some effect on the regional variations in groundwater compositions, but this is small in relation to the variations caused by post-infiltration processes and surface pollution. The lower concentrations on groundwaters from Bodmin Moor and Dartmoor coincide with more remote areas of open moorland. They are therefore less populated and

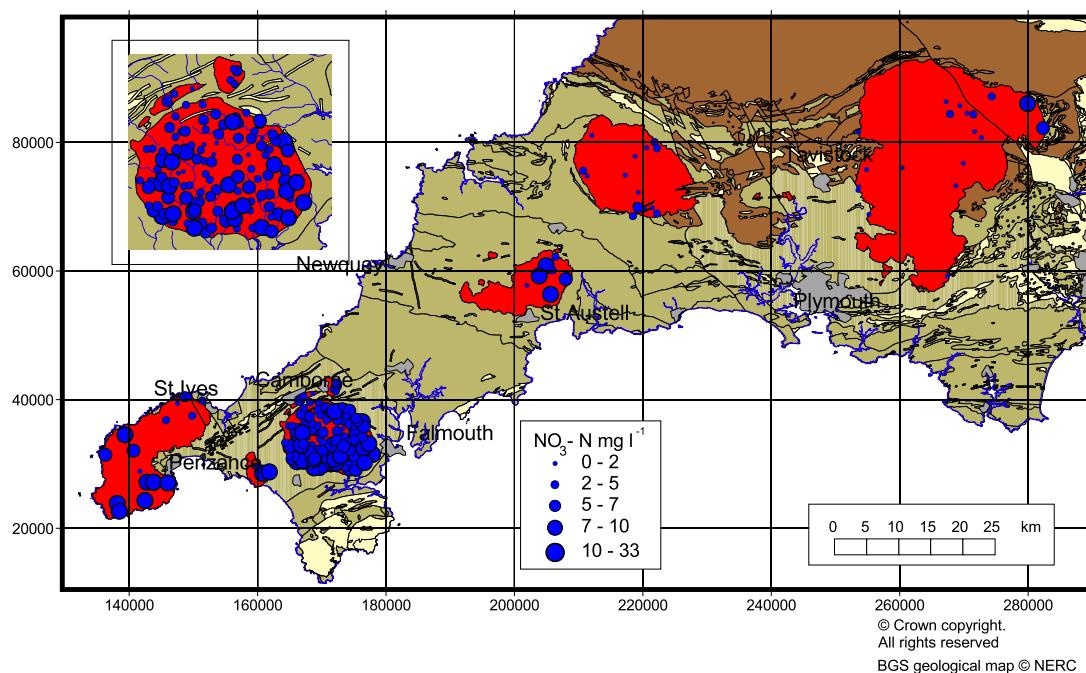


Figure 6.7. Regional variations in $\text{NO}_3\text{-N}$ in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

less affected by agricultural activities. The $\text{NO}_3\text{-N}$ concentrations of the Bodmin Moor and Dartmoor groundwaters are likely to be more representative of baseline compositions.

6.2.2 Trace-element compositions

Given the low salinities of the groundwaters of the region, the concentrations of dissolved Si are relatively high and reflect the dissolution of silicate minerals. Many of the groundwaters are saturated with respect to quartz and this may be a control on the Si concentrations. Silica solubility is also temperature-dependent. Some localised high concentrations of Si were observed by Smedley et al. (1989) in groundwaters from the Carnmenellis granite in the north-east–south-west tract to the east of the River Cober. The area is noted to be heavily dissected by adits and mine shafts and the locally high Si concentrations (associated with high Mg/Ca ratios) were attributed to deeper circulation of groundwaters through mine workings or mixing of young shallow recharge waters with deeper minewaters.

Concentrations of dissolved Al are high compared to most groundwaters. The activity of Al in water is strongly pH-dependent. Initial weathering of silicate minerals and weathering of secondary clays and/or gibbsite ($\text{Al}(\text{OH})_3$) is likely to be responsible for the high dissolved concentrations. Most groundwaters are saturated with respect to gibbsite. Weathering of clay minerals is also likely to have a major effect on many of the other trace elements (e.g. alkali and alkaline earth metals) that these minerals contain.

Phosphorus concentrations are low, although the analytical methods used (ICP-OES in most cases) are rather insensitive to P; detection limits are typically $100 \mu\text{g l}^{-1}$. Where detectable concentrations occur, they may be due to dissolution of apatite, the dominant P-bearing mineral phase in the granites. Many of the groundwaters with high concentrations of $\text{NO}_3\text{-N}$, K and SEC also appear to have comparatively high concentrations of P. This suggests that some of the P has been derived from pollutant sources.

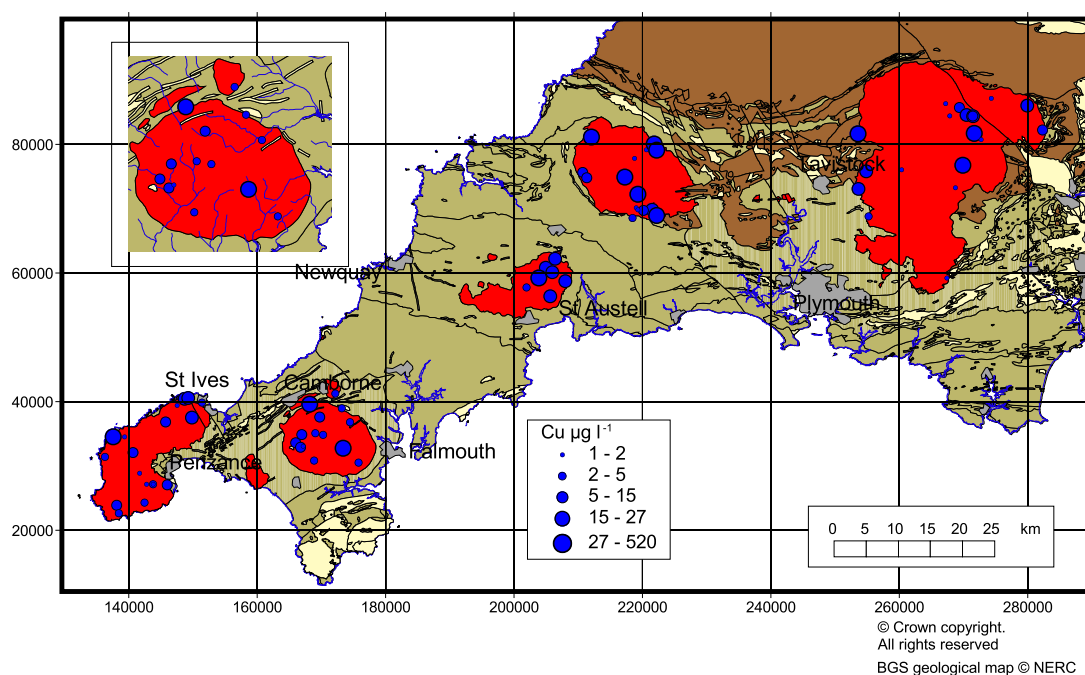


Figure 6.8. Regional variations in Cu in groundwaters from the granites of south-west England. The inset map shows more detail of the Carnmenellis granite.

Iron and manganese have a large range of compositions, between <0.05 – 21.8 mg l^{-1} and <1 – 5960 µg l^{-1} respectively. The median value for Fe is less than the highest detection limit of 50 µg l^{-1} and that for Mn is 15 µg l^{-1} . These concentrations are low as a result of the oxidising conditions of the groundwaters and the low solubility of Fe and Mn oxides under such conditions. The sample with the highest concentrations of each also had relatively high concentrations of K (22 mg l^{-1}), P (0.3 mg l^{-1}), HCO_3 (203 mg l^{-1}) and high SEC (480 µS cm^{-1}). This sample was from a borehole with a depth of 26 m and is likely to have been contaminated by farm slurry. The high Fe and Mn concentrations were probably produced by locally reducing conditions generated by the introduction of the contaminant. A second sample with an Fe concentration of 2.2 mg l^{-1} was a shallow sample from a dug well, had very low concentrations of total dissolved solids, a low Mn concentration of 24 µg l^{-1} and an $\text{NO}_3\text{-N}$ concentration of 10 mg l^{-1} . From this evidence the groundwater in the well is likely to be oxic and with a pH of 5.8, it was also not unusually acidic, hence it is probable that the Fe present was colloidal rather than dissolved. It is therefore not representative of the regional groundwater Fe concentrations.

Concentrations of dissolved Cu (Figure 6.8) are generally high in the groundwaters (range <1 – 520 µg l^{-1} ; median 7.5 µg l^{-1}) as a result of the acidic conditions. Zinc concentrations are also high in some groundwaters (range <2 – 1600 µg l^{-1} ; median 8.4 µg l^{-1}). These may be partly derived from dissolution of minor minerals (e.g. sulphide phases) in the granites, but they may equally be from metal pipework where it exists in the boreholes. It is difficult to distinguish between the two sources. No correlations are discernible in the groundwaters between SO_4 and dissolved Cu or Zn which may have indicated a dominant sulphide source.

The concentrations of F in the groundwaters are usually low and all samples where F data are available are significantly undersaturated with respect to the mineral fluorite (CaF_2). Although the groundwaters are mostly Ca-deficient, and should favour dissolution of fluorite, the mineral appears to be generally concentrated in the mineralised zones rather than as a widespread accessory phase in the granite. Low F concentrations in the groundwaters therefore reflect this overall paucity of fluorite and the mineral's slow reaction kinetics. They are also related to the short residence times of the groundwaters in the aquifers. One sample had an unusually high concentration of 1500 µg l^{-1} F. This also had a high concentration of Si (12.6 mg l^{-1}) and relatively high B (101 µg l^{-1}) and As (4.2 µg l^{-1}).

The sample was taken from the extreme westerly edge of the Dartmoor pluton and may have been affected by local mineralisation.

Arsenic concentrations are mostly low, the highest observed value being $5.8 \mu\text{g l}^{-1}$. Although As concentrations in the Cornubian granites are typically high relative to many other rock types (Section 3.4), these are not reflected in the groundwaters because of their acidic and oxic nature. Under such conditions, As is largely immobile as a result of its tendency to adsorb onto metal oxides (Smedley and Kinniburgh, 2002). Arsenic-bearing sulphide minerals are also restricted to the mineralised areas rather than being of widespread occurrence.

Barium concentrations are also usually low, reaching up to only $56 \mu\text{g l}^{-1}$. The groundwaters are undersaturated with respect to barite. The origin of the Ba present is likely to be mainly from dissolution of alkali feldspar. This mineral, along with biotite, is also likely to be a major source of Rb (Edmunds et al., 1987; Smedley et al., 1989). Concentrations of dissolved Rb are high, reaching up to $60 \mu\text{g l}^{-1}$ and reflect the high concentrations in the granites themselves.

Lithium and Cs are considered to be derived mainly from the reaction of biotite (Edmunds et al., 1984; 1987). The Cs concentrations in particular are high compared to groundwaters in most other rock types. It was noted that in saline groundwaters from the Carnmenellis granite, Cs concentrations were often double those of Rb despite much higher Rb concentrations in the granite itself. This implies non-stoichiometric dissolution and/or preferential removal of Rb in secondary phases (especially clays).

Strontium concentrations are generally higher in groundwaters from the Land's End and Carnmenellis plutons. This is in line with their higher Cl concentrations and reflects a greater marine influence. However, the concentrations of Sr in these are significantly higher than would be expected simply

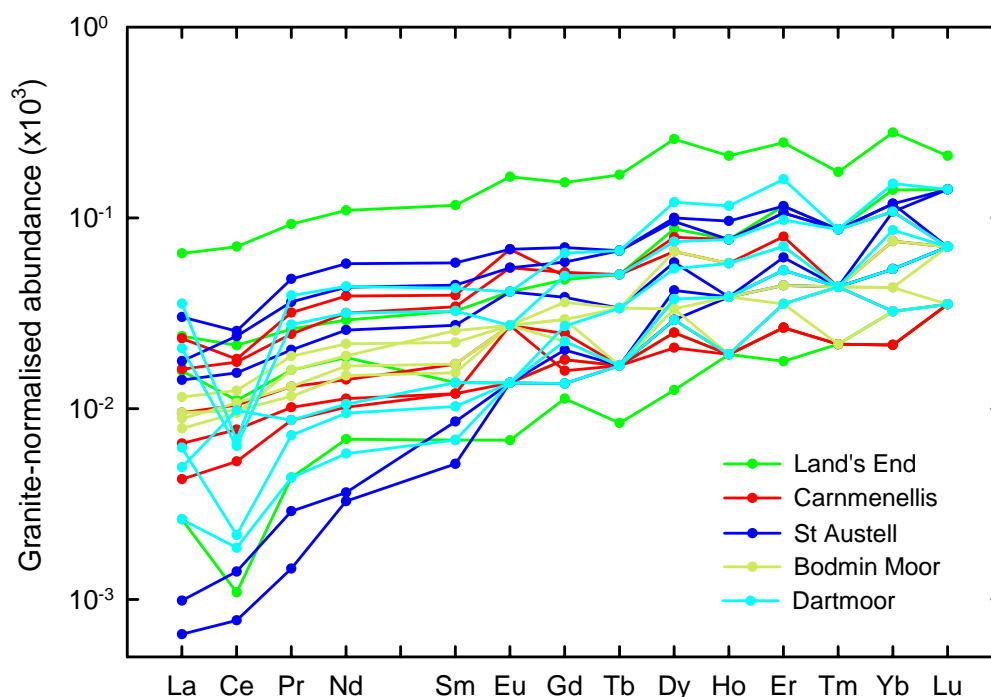


Figure 6.9. Granite-normalised REE profiles for groundwaters ($\mu\text{g l}^{-1}$) from the granites of south-west England (2003 collected samples only). Granite compositions used to normalise the data are averages (mg kg^{-1}) from data presented by Alderton et al. (1980), Charoy (1986) and Stone (1992).

from a seawater influence (either saline intrusion or maritime rainfall). The average Sr/Cl weight ratio of the groundwaters is 0.002 compared to a weight ratio in seawater of 0.0004. This implies enrichment in Sr as a result of water-rock interaction. Edmunds et al. (1987) concluded from $^{87}\text{Sr}/^{86}\text{Sr}$ data that weathering of plagioclase feldspar, which had observed ratios around 0.73, could account for much of the Sr in saline thermal groundwaters from the Carnmenellis granite. However, they found that shallow groundwaters had relatively depleted isotopic compositions (around 0.715) and considered that initial accumulation of Sr in fresh recharge may be due to dissolution of fluorite (containing possibly 0.05–0.5% Sr) rather than plagioclase. This neglects the fact that initial Sr in recharge would have had $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to seawater (ca. 0.708). Hence, the observed ratios in shallow groundwaters could simply represent a mixture between seawater-derived and plagioclase-derived Sr. Plagioclase is also more abundant in the system and much more reactive than fluorite. Whatever the origin of the Sr, some enhancement in concentration due to mineral weathering in the granite is indicated.

The highest observed U concentrations ($3.6 \mu\text{g l}^{-1}$) are relatively low considering the U-rich nature of the granites of the region. The low values are a result of the acidic conditions of the groundwaters, the short residence times and the paucity of dissolved carbonate: U mobilisation is known to be favoured by the formation of uranyl carbonate complexes ($\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$).

Concentrations of REE are very high in the groundwaters as a result of the acidic conditions. This was noted for groundwaters from the Carnmenellis granite by Smedley (1991), with correlations observed between pH and the concentrations of individual elements. The concentrations of LREE are generally higher than the HREE, with Ce and Nd having the highest absolute concentrations (with maxima of $5.1 \mu\text{g l}^{-1}$ and $3.0 \mu\text{g l}^{-1}$ respectively). The main mineral sources of the REE are likely to be biotite and muscovite as well as the accessory phases monazite and apatite. REE also occur in high concentrations in zircon, though this is highly resistant to weathering and is unlikely to have contributed REE to the groundwaters.

The data for groundwater samples collected during the 2003 sampling campaign have been normalised to ‘average Cornubian granite’, the likely source of the REE in the groundwaters (Figure 6.9). The average compositions were calculated from analyses of fresh granite given by Alderton et al. (1980), Charoy (1986) and Stone (1992). Two groundwater samples with low overall REE concentrations are excluded from the figure as they have concentrations close to analytical detection limits and therefore have ‘noisy’ normalised profiles. The trends in Figure 6.9 indicate a slight to notable LREE depletion relative to the HREE. This is commonly observed in surface waters and groundwaters and has been associated with the greater stability of HREE-carbonate complexes compared to LREE-carbonate complexes (Elderfield et al., 1990; Smedley 1992). Whether this is true for the groundwaters of south-west England is not certain as carbonate is a minor dissolved constituent compared to that in most groundwaters. Speciation modelling by Smedley (1991) suggested that the REE in solution were dominated by the free Ln^{3+} species. Preferential release of HREE from minerals (such as apatite) and/or preferential incorporation of LREE into secondary minerals may also be responsible for the fractionation between the LREE and HREE. The compositions from the five major plutons do not show major differences in groundwater REE profiles, except that two samples from the St Austell granite are especially LREE-depleted. No other distinguishing feature could be found for these two samples and without knowing the detailed local geology, the reason for the more marked depletion is unclear.

One other notable feature of the REE profiles is the lack of negative Ce anomalies in most samples. Where they occur, they are more commonly in the groundwaters from the Dartmoor granite (Figure 6.9). The fact that Ce behaves in a similar way to the neighbouring REE in most samples suggests that it is present as a trivalent ion in solution, favoured by the acidic conditions. In higher-pH conditions, oxidation to Ce(IV) can take place with resultant loss of Ce from solution (as CeO_2 or $\text{Ce}(\text{OH})_4$) and resultant development of a negative Ce anomaly (Smedley, 1992).

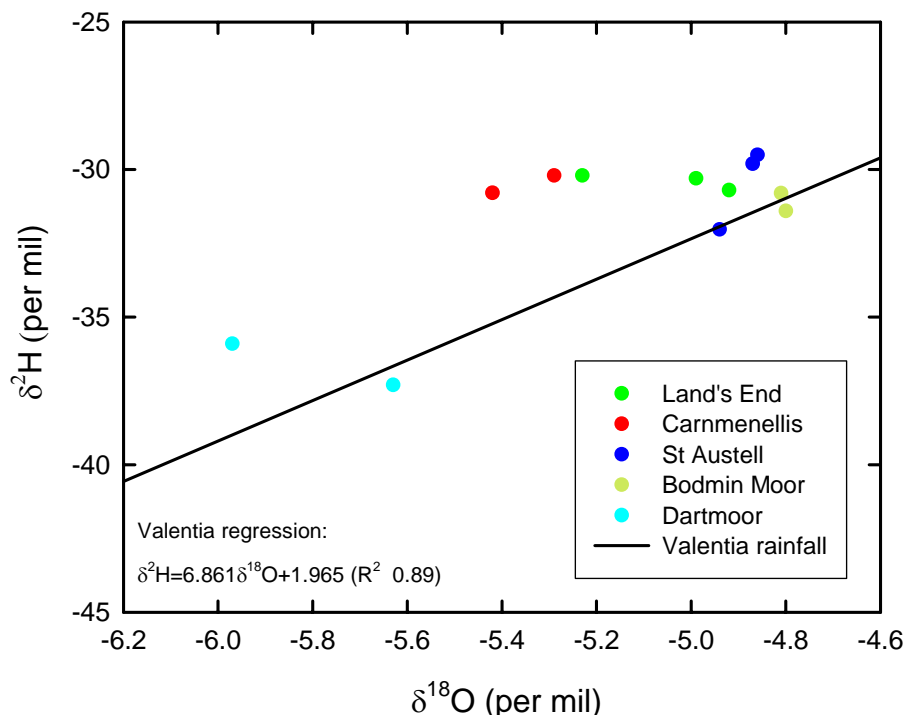


Figure 6.10. Variation in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the groundwaters from the Granites, compared with the best-fit line for rainfall from Valentia gauging station, Ireland (51.93°N –10.25°W) (rainfall data from IAEA/WMO, 2004).

6.2.3 Isotopic compositions

Few data are available to assess the stable-isotopic compositions of the groundwaters of the region but those available are shown in Figure 6.10. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ trend line for the samples compares reasonably well with that for modern rainfall from Valentia monitoring station in western Ireland, which supports the view that the groundwaters are the product of local recharge from marine-influenced rain. The ranges of isotopic compositions in the groundwaters are quite large (e.g. $\delta^{18}\text{O}$ -4.8 to -6.9 ‰) and samples from the Dartmoor granite are clearly more depleted than those from the other plutons. A much smaller influence of maritime rainfall is indicated for the Dartmoor samples, consistent with the more ‘continental’ chemical compositions of rainfall from Dartmoor (Yarner Wood, Section 3.5). The isotopic compositions reflect modern recharge.

6.3 Temporal variations

It has not been possible to assess the temporal variations in chemistry of the groundwaters of south-west England as the amounts of data are too limited. Very few samples in the database have been analysed more than once and those that have, have not been analysed sufficiently often to obtain statistically useful results. It is therefore not possible at the time of writing to provide an assessment of the baseline chemistry of the groundwaters based on temporal changes.

6.4 Depth variations

As noted earlier, the groundwaters from the granites of south-west England are mainly from shallow depths. Recorded well depths are up to 100 m, with most being around 30 m deep or less. Many are shallow springs. To the best of our knowledge, no studies on the relationship between groundwater chemistry and well depth have been carried out in the granites and it is therefore difficult to assess vertical variations in groundwater quality except in areas of mining activity which represent special

and probably unrepresentative cases. Many of the samples collected also have no recorded depth data which makes interpretation yet more difficult.

Only three samples in the database used in this study were from boreholes with recorded depths greater than 80 m. These had comparatively low, though still detectable, $\text{NO}_3\text{-N}$ concentrations (around 5 mg l^{-1} or less). The values indicate that at these depths, the groundwaters are still oxidic with respect to nitrate but that they are probably less prone to contamination from surface pollutants. At the shallowest depths, a large range of $\text{NO}_3\text{-N}$ concentrations is observed with no discernible depth trend, a fact which is not surprising given the large spatial spread of collected data.

Concentrations of Si show some depth variation, with samples from wells of 20 m deep or less having concentrations of $<6 \text{ mg l}^{-1}$ and a number of samples from greater depths having concentrations up to 12 mg l^{-1} . However, no clear relationship with groundwater temperature is discernible. The higher concentrations suggest increased reaction of groundwaters with silicate minerals at greater depths and hence longer residence times. Nonetheless, the time scales involved are not discernible from the Si data alone.

Geophysical logging of five boreholes in the Carnmenellis granite was carried out by Buckley and Cripps (1989). This study included downhole SEC measurements but no groundwater chemistry investigations. The boreholes were logged to depths up to 240 m below surface (most to around 100 m depth). As with regional groundwater chemistry data reported earlier, fluid SEC values were low at all sites, reaching up to $310 \mu\text{S cm}^{-1}$ but with most being $<200 \mu\text{S cm}^{-1}$. No notable variations with depth were observed. The results suggest that there is no discernible stratification in water quality in the boreholes studied. The logging results indicated that groundwater movement was limited in all the boreholes and that no major regolith horizons were visible in the uppermost parts of the granite. Buckley and Cripps (1989) concluded that this was due to most of the boreholes being at high elevations and that weathered regolith layers may be better developed in the granite in valley locations.

6.5 Groundwater residence time

Few lines of direct evidence are available from which to ascertain the residence times of groundwaters in the granites with certainty. No systematic radiometric dating (e.g. tritium or ^{14}C) has been carried out for the shallow groundwaters of the region. However, combined chemical and stable-isotopic evidence suggests that the majority of groundwaters included in this study represent relatively recent recharge with short residence time in the aquifers. Groundwater flow in the granites is mainly shallow, being restricted to weathered regolith and fractures within the granite.

Some exceptions to the shallow groundwater circulation occur, such as where mining operations have developed deeper cavities. Such cavities allow penetration of groundwater to deeper levels. Indeed, isotopic and trace-element studies of thermal brines in the Camborne–Redruth area have pointed towards interaction between shallow groundwaters and deeper, older, circulation cells (Edmunds et al., 1984; Smedley et al., 1989). However, these appear to be exceptional and given that the mines are no longer actively pumped, they are probably more historical than a reflection of modern flow regimes. Also as noted in Section 6.4, a few groundwater samples from this study were from deeper boreholes with depths up to 100 m. These do not show markedly different chemistry from the shallower samples, although slightly higher Si concentrations suggest longer silicate reaction times.

The shallow depths of most groundwaters, together with oxidic conditions, low salinity and stable-isotopic compositions comparable to modern rainfall, suggest that they mostly represent modern recharge. The presence of PAHs was also noted in some of the groundwaters. These do not unequivocally indicate a pollution origin as the compounds may have been derived by natural organic degradation processes. However, their detection in the groundwaters is not inconsistent with derivation from modern industrial atmospheric inputs.

7. BASELINE CHEMISTRY OF THE AQUIFER

In some respects, the compositions of the groundwaters from the granites of south-west England are less variable than in many other aquifers in the UK as the conditions are overwhelmingly oxic and therefore redox processes appear not to have played a major role in generating compositional diversity. In most cases, the groundwaters contain measurable dissolved oxygen, have high redox potentials (ca. 300 mV and higher), detectable NO_3 and low concentrations of many of the elements that are preferentially mobilised under reducing conditions such as Fe, Mn, NH_4 and As.

Some regional variations in composition are visible as a result of varying rainfall compositions and therefore geographical location. Hence, the baseline concentrations of major and trace constituents in groundwater from the granites are represented by ranges rather than a set of discrete values.

Superimposed on these baseline compositions are the contributions from surface pollutants. The shallow groundwaters are vulnerable to such inputs and in the study area, potential sources are likely to be dominantly agricultural and domestic rather than industrial. Regional groundwater chemistry suggests that farm slurry may be a significant source of contamination in the groundwaters, often (though not always) resulting in increased concentrations of $\text{NO}_3\text{-N}$, as well as organic carbon, K, and P and increased SEC values. Of the groundwaters studied, those from the Dartmoor and Bodmin Moor plutons appear to be the least polluted. It is a moot point whether the contribution made to groundwater chemistry from water-rock interaction in hydrothermal mineral veins represents a natural phenomenon, and hence merely expands the range of 'baseline' concentrations of affected elements, or whether in mining areas these should be considered as contaminants.

Without long-term temporal trends in groundwater quality from which to assess pre-anthropogenic chemical compositions, it is difficult to define the ranges of element concentrations that can be considered as baseline. In the absence of more definitive data, it seems reasonable to suggest that, for most chemical constituents of the groundwaters of the region, compositions within the 5th and 97.7th percentiles (i.e. excluding outliers) represent likely ranges of baseline compositions. For some of the more easily recognised pollutants such as $\text{NO}_3\text{-N}$, K, P, organic carbon and SO_4 the upper bounds of these ranges are probably too high. From the cumulative-frequency distribution of TOC concentrations (Figure 5.4), a break of slope at a concentration of around 2 mg l⁻¹ suggests that this is an approximate cut-off value between natural concentrations and higher values resulting from pollution. From the rainfall data (Section 3.5), recharge inputs for $\text{NO}_3\text{-N}$ up to the order of 1.3 mg l⁻¹ were considered likely. These are enhanced naturally by inputs of soil N and possible mobilisation of NH_4 from the minerals in the granites. Lowest overall concentrations are seen in the groundwaters from the Dartmoor and Bodmin Moor granites. These mostly have $\text{NO}_3\text{-N}$ concentrations of around 4 mg l⁻¹ or less and this is considered a likely estimate of upper baseline concentration. Such a concentration is in line with the conclusions from baseline groundwater studies in other UK aquifers (e.g. Shand et al., 2002; Smedley et al., 2004).

Removing all samples arbitrarily with concentrations of $\text{NO}_3\text{-N}$ greater than 4 mg l⁻¹ and SEC values greater than 400 $\mu\text{S cm}^{-1}$ gave maximum values in the remaining dataset (74 samples) of 25 mg l⁻¹ for SO_4 , 53 mg l⁻¹ for Cl, 12 mg l⁻¹ for K, 0.7 mg l⁻¹ for P and 8.8 mg l⁻¹ for TOC. The value for TOC is also probably too high but those for the other constituents could be taken as upper baseline estimates: they are mostly lower than the 97.7th percentile values in the complete dataset. This censoring approach fails to take into consideration concentrations of $\text{NO}_3\text{-N}$ that might have been reduced as a result of redox reactions driven by local inputs of reducing pollutants (e.g. slurry), but this effect is observed to be minor.

8. SUMMARY AND CONCLUSIONS

The groundwaters from the granites of south-west England are typically acidic and oxic with low concentrations of dissolved solids. The groundwaters circulate in shallow flow cells within soils, weathered granite and fractures and their compositions show the strong signatures of local rainfall with a superimposed limited degree of water-rock reaction. Their major-element, trace-element and isotopic compositions suggest that they are dominantly young recharge waters having had short residence times in the subsurface. The shallow circulation and young age of the groundwaters means they are vulnerable to surface pollution, particularly from agricultural and domestic sources. Pollutant inputs to the groundwaters from such sources can be detected especially by high concentrations of K, P and in some cases organic carbon and electrical conductance. Most, though not all polluted samples also contain high concentrations of $\text{NO}_3\text{-N}$ (up to 33 mg l^{-1}). Past pumping of deep minewaters in the Camborne–Redruth mining area has been shown by other workers to result in the circulation of some shallow groundwaters down to deeper levels, though this has not been demonstrated to be a widespread phenomenon elsewhere.

Infiltrating recharge waters are likely to have a strong regional compositional variation related to the proximity to the coast and the prevailing winds, as evidenced by variations in local rainfall composition. Indeed, the Lands' End and Carnmenellis granites have groundwaters with the highest concentrations of marine-derived solutes (notably Na, Cl, Mg, Sr). Concentrations of these elements are appreciably lower in the groundwaters from the Bodmin Moor and Dartmoor plutons. The acidic soils and granitic bedrocks lack carbonate minerals and have little acid-buffering capacity for the infiltrating recharge waters, which are themselves already acidic. Groundwater pH values of around 5.6 are therefore typical and the waters are soft with low concentrations of dissolved Ca and Mg and low alkalinity (usually less than $20 \text{ mg l}^{-1} \text{ HCO}_3$). The groundwaters are typically aggressive to metal pipework and private abstractions used for drinking water usually require pH regulation before use.

The groundwaters have mostly had limited opportunity for water-rock interaction since being recharged but some accumulation of solutes is apparent as a result of silicate reactions. The dominant processes appear to have been weathering of plagioclase and to a lesser degree alkali feldspar (generating dissolved Na, Ca, K, HCO_3 , Sr, Ba). Biotite is also a likely source of some weathering products (e.g. Mg, Li, Cs, Rb, F), as is the continued weathering of clay minerals generated by reaction of primary silicates. Oxidation of sulphide minerals in mineralised areas is also implied and increased concentrations of SO_4 in groundwaters from the Carnmenellis and Land's End plutons in particular suggest that this has occurred to a greater extent in these areas than in the other granites. Oxidation of iron sulphides has the capacity to generate additional acid and may have had some effect on groundwater pH values in some areas. Correlations with $\text{NO}_3\text{-N}$, K and P in some groundwaters suggest that some SO_4 may also have been derived from surface pollution. Quantifying the relative contributions is difficult.

Groundwaters with the highest concentrations of $\text{NO}_3\text{-N}$ show a clear influence of pollution, likely to be mainly from agricultural sources. Arable farming is not practised widely on the granites and so the pollutant inputs are probably mainly from sources such as slurry. The concentrations of nitrate in the groundwaters vary significantly across the region, with appreciably lower concentrations in the remote uplands of Bodmin Moor and Dartmoor. Groundwaters from these areas have nitrate compositions close to 'baseline', although the inputs of nitrogen from rainfall are themselves likely to be affected by anthropogenic inputs.

A number of the trace elements are present in relatively high concentrations as a result of the acidic conditions. Notable among these are Al with concentrations up to $1270 \text{ } \mu\text{g l}^{-1}$, Pb up to $110 \mu\text{g l}^{-1}$, Cu up to $520 \text{ } \mu\text{g l}^{-1}$, Zn up to $1600 \text{ } \mu\text{g l}^{-1}$ and REE (Ce up to $5.1 \text{ } \mu\text{g l}^{-1}$; Nd up to $3 \text{ } \mu\text{g l}^{-1}$). These are largely derived from rock weathering reactions. Aluminium is likely to be mostly from feldspars and

clays, Pb, Cu and Zn from sulphide minerals and REE from accessory minerals and biotite. Additional Cu and Zn from metal pipework is probable.

Groundwaters from the Bodmin Moor and Dartmoor plutons are likely to have compositions closest to baseline for a wide range of major and trace constituents, though the large variations in recharge compositions likely from rainfall variations mean that the compositional range observed cannot simply be related to variable inputs of pollutants.

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