Baseline groundwater chemistry: the Sherwood Sandstone of Devon and Somerset

Groundwater Programme

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J M Bearcock, P L Smedley

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British Geological Survey offices

BGS Central Enquiries Desk

Tel 0115 936 3143   Fax 0115 936 3276
email enquiries@bgs.ac.uk

Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241   Fax 0115 936 3488
email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

Tel 0131 667 1000   Fax 0131 668 2683
email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090   Fax 020 7584 8270
Tel 020 7942 5344/45   email bgslondon@bgs.ac.uk

Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

Tel 029 2052 1962   Fax 029 2052 1963

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800   Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

Tel 028 9038 8462   Fax 028 9038 8461

www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500   Fax 01793 411501
www.nerc.ac.uk

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Foreword

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

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

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

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

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

Attempting to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England and Wales has been the objective of the project 'Baseline'. The project involves the characterisation of spatial and temporal variations in groundwater chemistry and interpretation of the dominant controlling processes within a given area, aquifer or aquifer block. For each study area, this has been achieved through collation of existing reliable groundwater, rainfall, land-use and host-aquifer mineralogical and geochemical data, as well as new strategic sampling of typically 25–30 groundwater sources for a comprehensive suite of inorganic constituents. Selected analysis of stable-isotopic compositions (e.g. O, H, C) and atmospheric tracers (CFCs, SF_6) has also been undertaken where appropriate. Statistical methods, including statistical summaries (medians, arithmetic means, percentiles), together with box plots and cumulative-probability diagrams, provide some of the most valuable analytical tools for the assessment of chemical data and have been used in the Baseline report series. The Baseline reports provide a summary of the inorganic chemical status of groundwaters in a given

study area and key pressures on water quality which should provide useful background information of value to water regulators and managers, environmental scientists and water users.

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

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

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

Reports in the current series:

The Carboniferous Limestone aquifer of the Derbyshire Dome
The Chalk aquifer of Hampshire
The Magnesian Limestone of County Durham and north Yorkshire
The Palaeogene of the Thames Basin

Acknowledgements

Contents

FIGURES

TABLES

Summary

This report describes the regional geochemistry of groundwater from the Sherwood Sandstone aquifer of Devon and Somerset. In order to assess the likely natural baseline chemistry of the groundwater in the area, information has been gathered from the strategic collection of 21 new groundwater samples, and from collation of existing groundwater, rainfall, mineralogical and geochemical data.

The Sherwood Sandstone aquifer results from continental deposition during the early Triassic period. The deposition comprised thick clastic deposits in basins created during the late Permian. There are two distinct units: the Otter Sandstone Formation and the underlying Budleigh Salterton Pebble Beds Formation. These units form the most important aquifer in south-west England.

The main chemical properties of the groundwater are determined by rainwater recharge reacting with the aquifer minerals. Of these minerals carbonates are the dominant influence on the water chemistry. While Ca is dominant in groundwaters from both aquifer units, the water types from the two units can be distinguished: the Otter Sandstone Formation aquifer has mainly $Ca-HCO_3$ type waters, with some mixing towards Mg, and the groundwaters in the Budleigh Salterton Pebble Beds Formation aquifer are of $Ca-HCO_3$ type to $Na+K-Cl$ type. There is little variation in the major ion proportion of the groundwaters from the Otter Sandstone Formation, most likely as these represent groundwater in equilibrium with the minerals which give it this character. There is greater variation in the Budleigh Salterton Pebble Beds Formation groundwaters. Besides the difference in groundwater types, the groundwater from the Budleigh Salterton Pebble Beds Formation is more acidic, more oxic, has lower SEC values, and HCO_3, Cr, U and Mg concentrations, and higher concentrations of Al, Be, Cd, Cr, Co, Tl and REE than the groundwater from the Otter Sandstone Formation.

Human impacts on the water quality are evident. These are mainly visible in the presence of indicator contaminants, such as nitrate. The widespread presence and changes of nitrate concentrations over time indicate the extent to which the unconfined aquifer is influenced by modern farming practices or urban pollution. Concentrations of NO_3-N exceeded the current drinking water limit of 11.3 mg L^{-1} in 25% of the sampled groundwaters, which probably reflects the intensification of agriculture in the study area over the last few decades. Indeed, the dominant land uses of the area are agriculture and grassland. However, recent legislation and the drive towards intelligent farming have meant that in some groundwaters the concentrations of nitrate are decreasing.

While many of the groundwaters investigated in this study are of good inorganic quality there are some notable exceptions which contain elevated concentrations of Fe, SO_4, Ni, Co and NO_3. The distribution of the poor-quality is generally so sporadic that water quality would be difficult to predict prior to drilling a borehole.

For many analytes, the 95th percentile of the distributions has been taken as a first approximation of an upper limit of baseline concentrations as this serves to eliminate the most extreme outlier concentrations that likely represent a distinct population.

1 Introduction

This study concerns the Sherwood Sandstone aquifer of south-west England. This aquifer occupies a narrow north-south trending outcrop between Budleigh Salterton in the south, and Minehead in the north. This aquifer represents the major water supply source in East Devon, and. is important for both public and private water supply, as well as industrial and agricultural use. The importance for public supply decreases northwards, and there are limited abstractions in the Somerset portion of the aquifer.

This report characterises the groundwater chemistry in the Sherwood Sandstone of Devon and Somerset, outlining spatial and temporal variability. The likely main controls and likely ranges of baseline concentrations are assessed.

2   Geographical setting

2.1   STUDY LOCATION

The Sherwood Sandstone aquifer of Devon and Somerset comprises the Budleigh Salterton Pebble Beds Formation and the Otter Sandstone Formation (Figure 2.1). These formations create a predominantly north-south trending outcrop, which extends between Budleigh Salterton in the south and the Quantock Hills in the north. These aquifer units represent a major groundwater resource in south-west England. The study area of this report extends from Somerset to Devon and the sample sites extend over an area of approximately 200 km^2.

2.2   LAND USE AND PHYSICAL FEATURES

Differences in land use often relate to variations in topography, climate, soil fertility, and geology (Kelly and Panno, 2008), which in turn can have important implications for groundwater quality. The topography and land use in the area around the Sherwood Sandstone outcrop generally reflects the underlying geology. The area surrounding and including the outcrop area
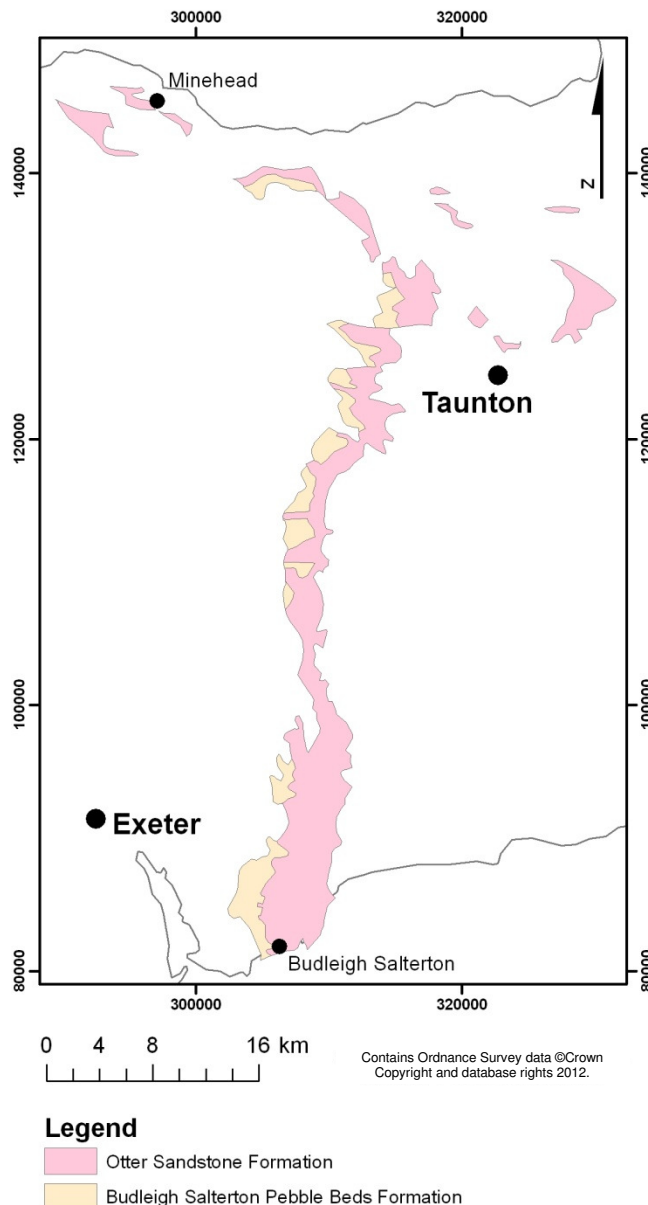
Figure 2.1 Location of Sherwood Sandstone strata in south-west England

of the Sherwood Sandstone aquifer depicted in Figure 2.2 is underlain by sedimentary strata, which get progressively younger towards the east. The region predominantly supports grassland and arable farming, which are found over most of the area. Grassland dominates in the north-west of the region depicted in Figure 2.2. This is an area underlain by siliciclastic argillaceous rocks, contrasting with the typically arenaceous nature of the rest of the region. Wooded areas are generally scarce: the largest areas occur in the north and are underlain by Devonian Hangman Sandstone formation. Bare ground within the study area is generally found along the coast.

In terms of its landuse the area underlain by Sherwood Sandstone is generally indistinguishable from adjacent areas underlain by the Aylesbeare Mudstone Group (to the west) or the Mercia Mudstone Group (to the east). However, on the south-west of the outcrop the Budleigh Salterton Pebble Beds Formation gives rise to an escarpment. This escarpment is identified by bog and

Legend

- Extent of Sherwood Sandstone outcrop
- Arable
- Bare Ground
- Bog and Shrub
- Grassland
- Urban
- Water
- Woodland

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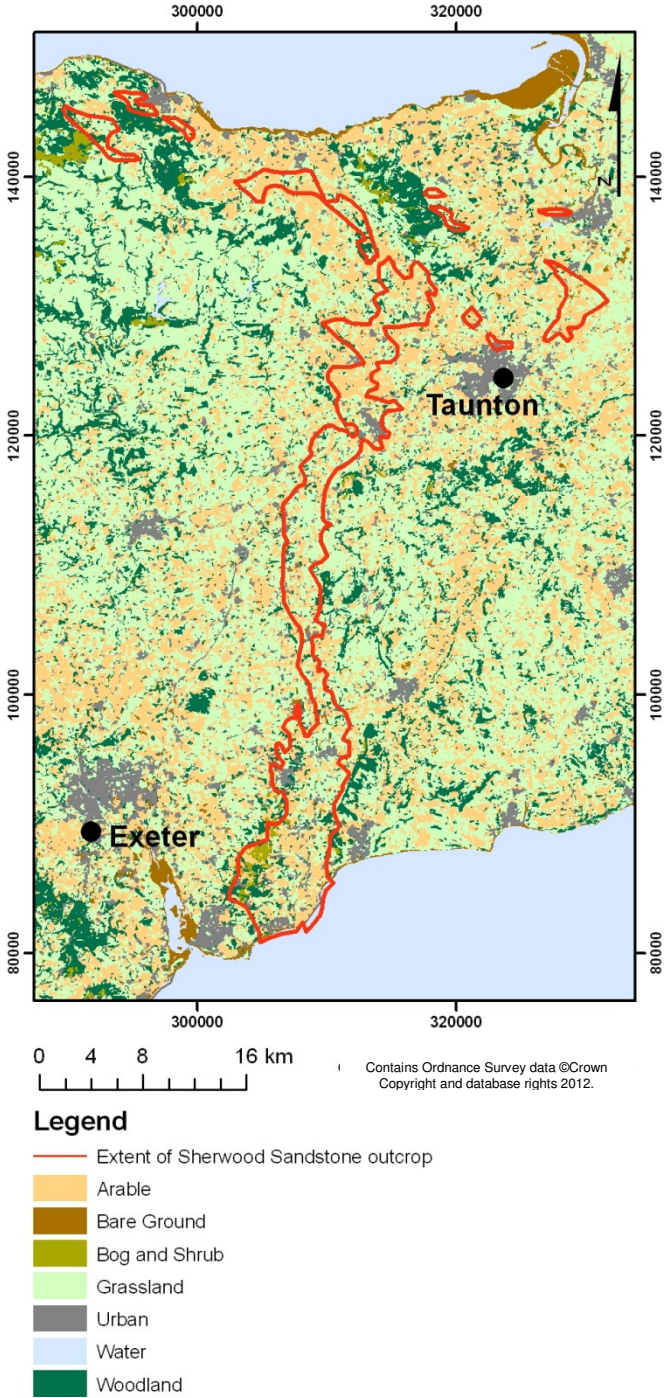
Figure 2.2 Landuse of the study area based on digital spatial data licensed from the Centre for Ecology & Hydrology, © NERC (CEH) (Fuller et al., 2002)

shrub, which is common on higher ground, and mostly absent from the rest of the region (Figure **2.2**).

Urban land cover is limited; the two main urban centres are Exeter and Taunton and these are outside the aquifer outcrop. The other built-up areas are found along the coast, or adjacent to the major rivers (Figure 2.3). The southerly section of the Sherwood Sandstone aquifer forms the Otter Valley. The River Otter is the main river in the area occupied by the Sherwood Sandstone aquifer; its flow is generally southwards draining to the English Channel at Budleigh Salterton. All surface runoff within the southerly portion of the Sherwood Sandstone aquifer unit drains towards the River Otter (EA, 2004). The other significant rivers in the area are the Halse Water and Rivers Culm and Tone, which are present in the northern part of the Sherwood Sandstone aquifer. The River Culm drains south-west, across the Sherwood Sandstone aquifer, to join the River Exe before entering the English Channel at Exmouth (Figure 2.3). Halse Water and the River Tone drain eastwards, into the River Parrett, which enters the Bristol Channel at Burnham on Sea.
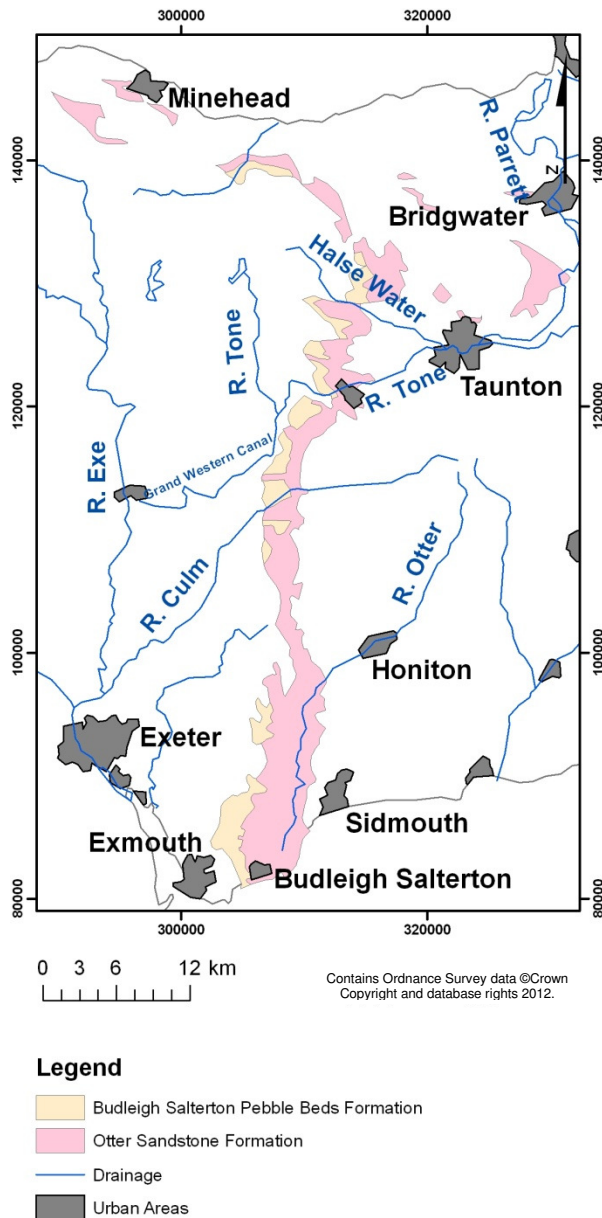
Figure 2.3 Physical features of the area around the Sherwood Sandstone outcrop of south-west England

The sample sites used in this study are shown in Figure 2.4, which also shows the data source (discussed in Section 4.1), and the aquifer source unit. Figure 2.5 shows the major urban areas and places named in this report.
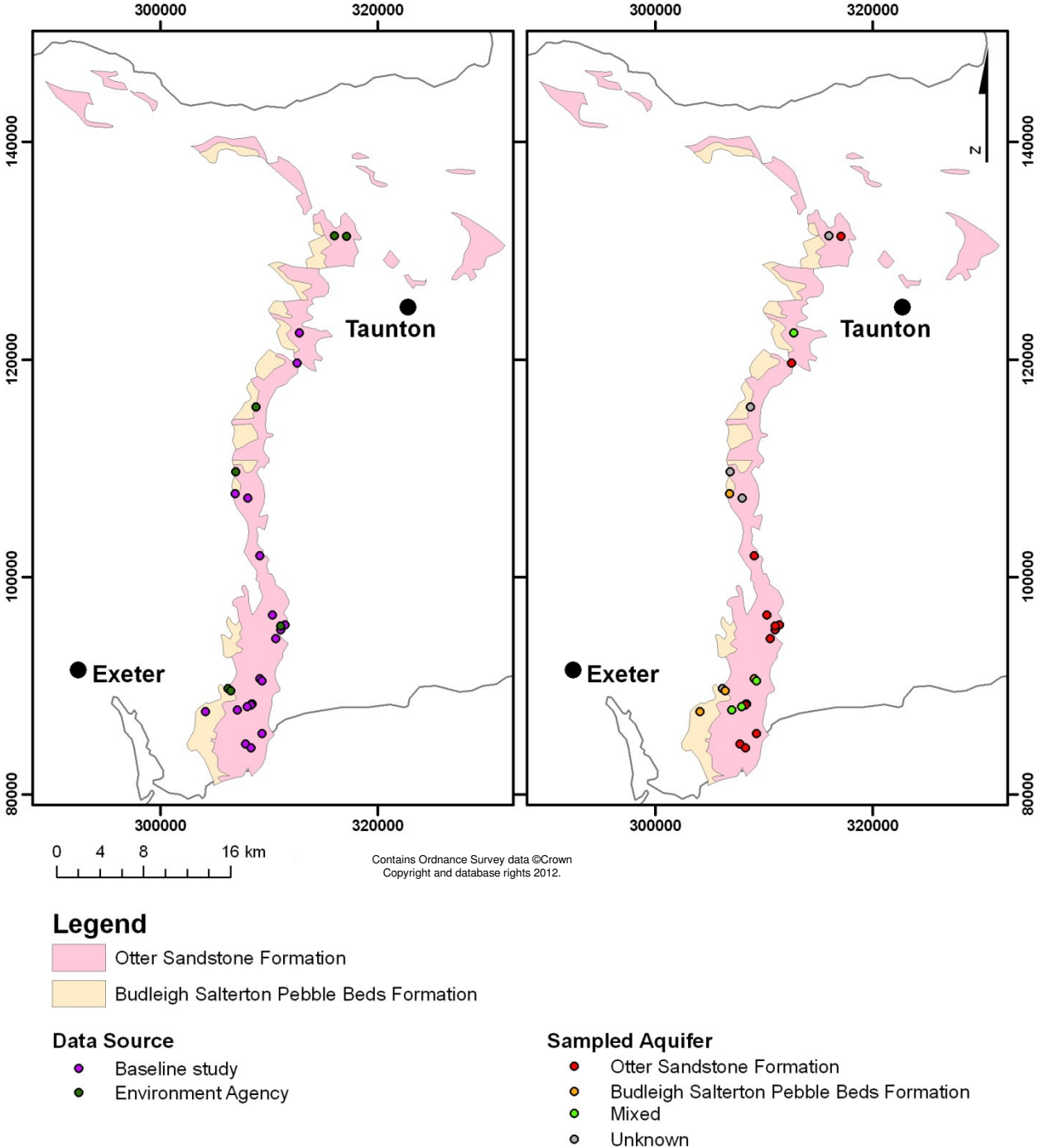
Figure 2.4 Location, data source, and sampled aquifer of sample sites
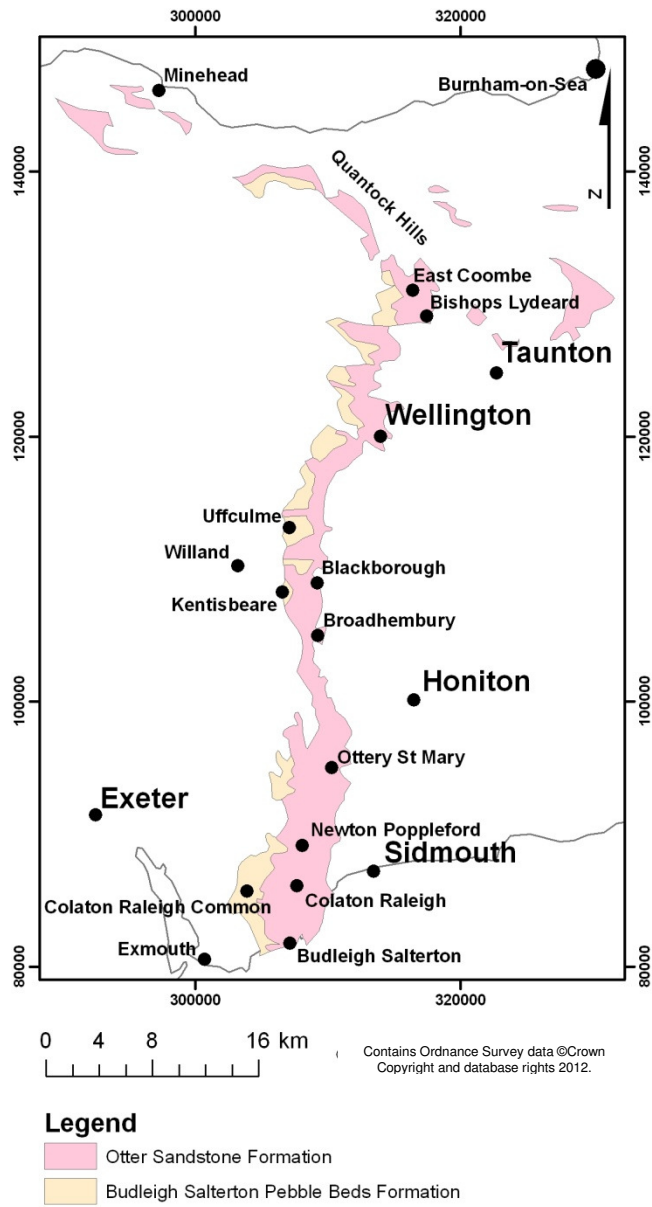
Figure 2.5 Major urban areas and places named in this report

3 Regional geology and hydrogeology

3.1 REGIONAL GEOLOGY

3.1.1 Geological setting

The Permo-Triassic boundary (251 Ma) represents the start a new era of geological time, the Mesozoic. This boundary represents a large extinction event, thought to be caused by the major continental collision completing the formation of the super continent Pangaea (Hounslow and Ruffell, 2006).

During the Triassic (251-199 Ma) Britain, as part of Pangea, lay within northern tropical latitudes (McLeish, 1992). During this interval the landmass comprising what is now Britain drifted northwards from ca. 16ºN-34 ºN (Hounslow and Ruffell, 2006). Triassic deposition in Britain represents largely continental sedimentation from seasonal rivers, deserts and saline lakes (Hounslow and Ruffell, 2006; McLeish, 1992).

The end of the Permian was characterised by the recession of shallow seas, causing a return of continental conditions in the Triassic. The basins initiated in the Permian continued to subside meaning that thick clastic deposits could accumulate. These deposits make up the Sherwood Sandstone Group. The deposits are mostly fluvial in origin, thought to have been deposited by a major braided river system. There are local windblown deposits, marls and breccias, which are thought to represent local variations in deposition, and are typical of contemporary desert basins. Subsequent deposits of partly marine red mudstone and siltstone of the Mercia Mudstone Group covered the Sherwood Sandstone Group (Allen et al., 1997).

The nomenclature of Triassic strata in the onshore areas of south-west Britain has been formalised relatively recently (after Allen et al., 1997). In much of the literature the old terminology is used. Table 3.1 presents the correlation of the Triassic units in the area of the Sherwood Sandstone aquifer. The geology of these strata is discussed below, and a map of the geology of the area is presented in Figure 3.1.

3.1.2 Aylesbeare Mudstone Group

The Aylesbeare Mudstone Group is the oldest member of the Triassic succession. It can be differentiated into two formations: the Littleham Mudstone and the Exmouth Mudstone and Sandstone. The group is typically ca. 300 m thick, but can vary locally between 70 and 530 m thick. The Aylesbeare Mudstone Group is composed of red-brown mudstones, with beds containing variable quantities of sand and silt (Allen et al., 1997). The group is thought to have been deposited in a sabkha-playa environment with periodical evaporite precipitation (Edwards

Table 3.1 Correlation of the local groups and formations (after Allen et al., 1997). Old terminology is stated in parentheses.

Era	Period	Group	Formations
Mesozoic	Triassic	Mercia Mudstone (Keuper Marl)	
		Sherwood Sandstone (Bunter Sandstone)	Otter Sandstone (Upper Sandstone)
			Budleigh Salterton Pebble Bed (Pebble Beds)
		Aylesbeare Mudstone (Lower Marls)	Littleham Mudstone
			Exmouth Mudstone and Sandstone
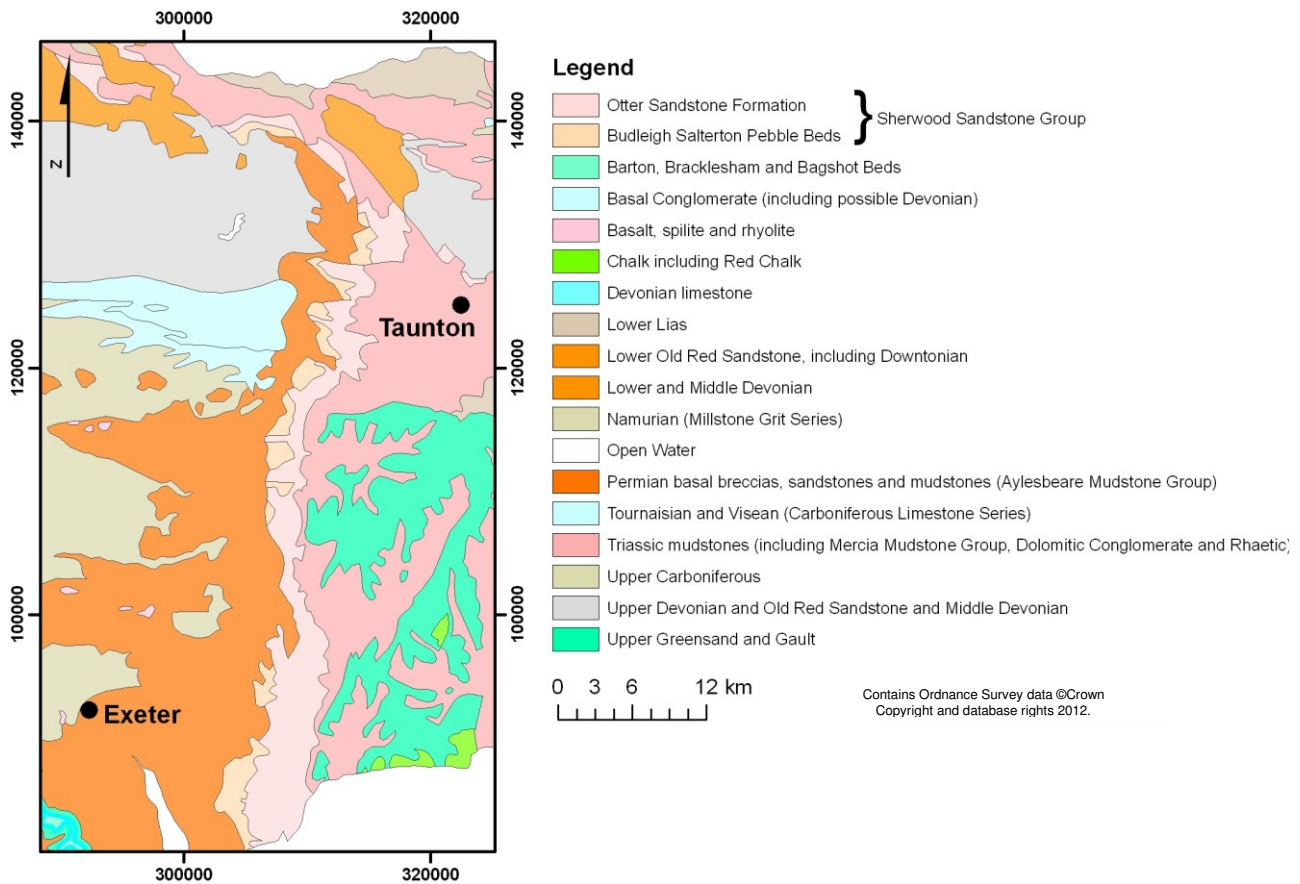
Figure 3.1 Geological map of the area surrounding the Sherwood Sandstone outcrop

and Gallois, 2004). There is a lack of palaeontological evidence to define the Permian-Triassic boundary, but it is thought that it may lie within this group (Edwards and Gallois, 2004).

3.1.3 Budleigh Salterton Pebble Beds Formation

The Budleigh Salterton Pebble Beds Formation is the lower formation within the Sherwood Sandstone Group. It lies conformably on the Aylesbeare Mudstone Group and forms disconnected, partly fault-bounded outcrops along the western edge of the overlying Otter Sandstone Formation. The Budleigh Salterton Pebble Beds Formation is typically 20 to 30 m thick, and it mainly consists of conglomerates containing rounded metaquartzite clasts in a matrix of medium- to coarse-grained red-brown sand. The sandy matrix composes ca. 20% of the formation. In addition the formation contains lenses of silt, and strongly micaceous current-bedded sands. The formation generally dips gently to the east, at a dip of about 5º (Allen et al., 1997; Edwards, 1997; Edwards and Gallois, 2004; Ussher et al., 1913; Walton, 1982).

The Budleigh Salterton Pebble Beds Formation varies in nature from north to south. North of Uffculme it consists of breccio-conglomerate, containing sub angular grits, small pebbles of quartz and chert, limestone clasts and occasional decomposed material of igneous origin with a strongly calcareous cement. A large proportion of the clasts in the pebble beds are locally derived. These are set within a matrix of medium grained, red, micaceous sandstone, which is very similar to coarser parts of the overlying Otter Sandstone Formation. The topography, land use and vegetation are indistinct from that covering the overlying Otter Sandstone Formation because the bulk mineralogy and lithology of the rocks are broadly similar. The degree of cementation increases northwards and the pebble bed is a massive and very tough calcareously cemented conglomerate in the Halse aquifer block in Somerset. In addition there is local ferruginous cementation (Allen et al., 1997; Edmonds and Williams, 1985; Ussher et al., 1906; Walton, 1982).

15

In the south of the study area, the Budleigh Salterton Pebble Beds Formation forms the top of a 160 m high ridge of heath land, distinct from the Otter Sandstone Formation by the elevation and vegetation type (see Figure 2.2) (Ussher et al., 1913; Walton, 1982). South of Uffculme the nature of the formation changes considerably. Locally derived limestone clasts are replaced by quartzite, and the formation becomes unconsolidated and uncemented (Allen et al., 1997; Walton, 1982). In the south the formation consists of brown gravel with subordinate beds of sand. The gravel comprises well-rounded pebbles, cobbles and boulders contained within a coarse to fine gravel and a silty sand matrix. Up to 90% of the clasts are metaquartzite with some composed of porphyry, vein quartz, tourmaline and feldspathic conglomerate (Edwards, 1997). There is a lack of carbonate cement, and only localised patches of iron minerals are found. This southern portion of the Budleigh Salterton Pebble Beds Formation has therefore been worked for aggregates over the years. The type locality for the formation is found in the coastal cliffs, west of Budleigh Salterton (Allen et al., 1997; Walton, 1982).

The pebbles and cobbles decrease markedly in size northwards, along the strike. This is inferred to indicate deposition in a high-energy braided river system that generally flowed northwards. Heavy mineral analysis has indicated that a minor flow from the east joined the main northerly deposition current close to Wellington. The first appearance of the carbonate cement is also found around Wellington and is probably derived from the Carboniferous limestones which crop out about 1 km west of the Sherwood Sandstone aquifer. These limestones are the source for many of the grits and clastic material within the Budleigh Salterton Pebble Beds Formation (Walton, 1982).

3.1.4   Otter Sandstone Formation

The Otter Sandstone Formation forms the younger portion of the Sherwood Sandstone Group. It lies unconformably on the Budleigh Salterton Pebble Beds Formation. The Otter Sandstone Formation is typically 120 m thick, although it reaches a maximum thickness of around 170 m on the southern coast, and thins to about 30 m northwards. The Otter Sandstone Formation mainly consists of soft, reddish orange-brown, weakly to moderately cemented, cross-bedded, fine- and medium-grained sandstone with minor units of conglomerates (about 20%) silts and mudstone (about 5%), which occur as discontinuous lenses and sheets. The conglomerates within the formation are mostly intraformational, less than 0.5 m thick, well-cemented with calcite, and can be found at regular intervals (1-6 m) throughout the sequence. The mudstones form lenses, are usually red-brown and up to 2 m thick. The formation dips gently to the east (ca. 5°) (Allen et al., 1997; Edwards, 1997; Edwards and Gallois, 2004; Ussher et al., 1906; Walton, 1982).

As with the Budleigh Salterton Pebble Beds Formation, the Otter Sandstone Formation becomes increasingly cemented to the north. There is extensive calcite cementation north of Bishop's Lydeard, where the rocks may be considered to be sandy limestones, and consequently have been burnt for lime. Unlike the Budleigh Salterton Pebble Beds Formation, there is otherwise little lithological separation between the north and the south (Edmonds and Williams, 1985; Edwards, 1997; Walton, 1982).

The sand grains within the formation are well-rounded and have an average size of 0.3 mm. They are dominated by quartz, with 10 to 25% of the formation comprising orthoclase feldspar. The formation is therefore sub-arkosic. The bedding planes are frequently well developed, and cross bedding is common throughout. Tabular cross-bedded sandstones are the most abundant facies, comprising 49% of the total formation; the remaining formation is made up of trough cross-bedded sandstones, plane bedded sandstones, and ripple cross-laminated sandstones (Edwards, 1997; Walton, 1982).

Calcareous concretions are locally important. In the southern part of the outcrop (especially in the Otter Valley) the sands typically contain about 1-4% carbonate as calcite, with minor dolomite; locally this can reach 10-20%. In contrast, much of the northern portion of the outcrop

has strongly indurated sands with carbonate cements and the formation can contain as much calcite as quartz (ca. 45% calcite) (Edwards, 1997; Walton, 1982).

This formation takes on a deep red-brown colour owing to a haematite cement forming a thin coating around individual sand grains, although there are local areas of reduced green, yellow-orange and white sands. Reduced bands are more common in the south in coarse beds, underlain by thin marl bands. The most prominent example of this is at the boundary between the Budleigh Salterton Pebble Beds Formation and the Otter Sandstone Formation at outcrop, west of Budleigh Salterton. At the boundary between the formations there are 20 cm thick yellow-orange and green sandstone bands, thought to be caused by groundwater reduction (Walton, 1982). In other places the base of the formation is considered to be arbitrary, and is generally to be taken to be between predominantly conglomeratic and predominantly sandstone successions (Edmonds and Williams, 1985).

Sedimentary structures indicate that the lowest part of the Otter Sandstone Formation at Budleigh Salterton was deposited as windblown sand. The remaining Otter Sandstone Formation beds are thought to be deposited in braided, meandering stream channels, flowing from the south and west, to the north and east (Allen et al., 1997; Edwards and Gallois, 2004).

3.1.5 Mercia Mudstone Group

The Mercia Mudstone Group overlies the Otter Sandstone Formation. It is around 360 m thick, and forms the lowlands extending 20 km east from the Otter Sandstone Formation. The group is relatively homogeneous and mainly comprises red silty mudstones, although there are subordinate beds of sandstone, gypsum, and halite.

3.1.6 Quaternary Deposits

In the outcrop area the superficial deposits are scarce, limited to riverine alluvial deposits and sporadic river terrace deposits. The nature and thickness of these are variable over the Sherwood Sandstone outcrop (Perl et al., 2004).

3.2 REGIONAL HYDROGEOLOGY

The Budleigh Salterton Pebble Beds Formation and the Otter Sandstone Formation together form a major aquifer. In the south of the outcrop area these formations form the most important aquifer in the south-west of England (Allen et al., 1997). Table 3.2 shows the hydrogeological significance of the Triassic formations in south-west England.

Table 3.2 Hydrogeological significance of Triassic formations in south-west England (after Allen et al., 1997 and Perl et al., 2004)

Group	Formation	Hydrogeological Significance	Classification
Mercia Mudstone		Aquitard	Locally classed as a minor aquifer
Sherwood Sandstone	Otter Sandstone	Aquifer	Major aquifer
	Budleigh Salterton Pebble Bed	Aquifer	Major aquifer
Aylesbeare Mudstone	Littleham Mudstone	Aquitard	Locally classed as a minor aquifer
	Exmouth Mudstone and Sandstone		

3.2.1 Aquifer properties

The Aylesbeare Mudstone Group aquitard underlies the Budleigh Salterton Pebble Beds, separating the Sherwood Sandstone aquifer from the underlying Permian sandstone aquifers. The Aylesbeare Mudstone Group corresponds to Permian marls separating the Triassic and Permian sandstones found elsewhere in the UK (Allen et al., 1997). While it is relatively impermeable and generally considered an aquitard, limited fracture flow and local sandy horizons may supply a limited quantity of water. This allows numerous supplies for small domestic requirements, and locally the Aylesbeare Mudstone Group is classified as a minor aquifer (Perl et al., 2004).

The Budleigh Salterton Pebble Beds Formation and Otter Sandstone Formation are generally taken to be in hydraulic continuity, and considered together as the Sherwood Sandstone aquifer hydrogeological unit. Groundwater flow within the aquifer comprises matrix and fracture flow. The fractures, which are commonly sub vertical, allow an increase in the overall permeability. The aquifer resources are used for public water supply, agricultural and commercial purposes. (Allen et al., 1997; Perl et al., 2004).

The Mercia Mudstone Group overlies the Otter Sandstone Formation. This unit is characterised by a low permeability. Locally this aquitard is used as a source of supply and is classed as a minor aquifer (Perl et al., 2004).

The aquifer unit comprising the Otter Sandstone Formation and Budleigh Salterton Pebble Beds Formation is restricted by thinning out to the west, a saltwater interface to the south, and increasing cementation to the north. The eastern limit of the aquifer is considered to be 5 km down dip, beneath the Mercia Mudstone Group, where high dissolved solids concentrations mean that the water is non-potable (Allen et al., 1997; Perl et al., 2004). Where there is a lack of cement (e.g. the southern portion of the Budleigh Salterton Pebble Beds Formation) the aquifer has an increased importance for groundwater supply (Allen et al., 1997; Walton, 1982).

The hydraulic continuity of the Budleigh Salterton Pebble Beds Formation and Otter Sandstone Formation is evident in the northern portion of the outcrop, where both formations are lithologically similar. However, towards the east of the outcrop an iron pan reduces flow between the formations, and in the southern part of the outcrop there is evidence for discontinuous mudstone-ironstone beds between the Budleigh Salterton Pebble Beds and the Otter Sandstone. This creates a significant degree of hydraulic discontinuity between the two units (Walton, 1982).

In the Otter Valley, the River Otter is partially in hydraulic continuity with the aquifer. Under natural conditions the river gains water from the groundwater system. However, under the normal pumping regime, the drawdown is such that the situation is reversed and the river loses water to the aquifer (Walton, 1982). In some boreholes located close to the river there is a contribution of up to 50% river water in groundwater abstractions (Allen et al., 1997).

Allen et al. (1997) presented hydraulic conductivity values for 228 BGS core samples from the Sherwood Sandstone Group in the area, mainly from the Otter Valley. These data were shown to have a fairly uniform scatter, ranging from 10^{-6} to 6 m day^{-1}. The data do not follow a normal distribution and are truncated at the lower end owing to limitations of the equipment. The horizontal hydraulic conductivities are generally 3 times larger than vertical values (Allen et al., 1997). Intergranular permeabilities are generally 1 to 3 m day^{-1} in the south of the outcrop area. Increased cementation in the north means that intergranular permeabilities are usually 1 to 2 orders of magnitude lower. The Budleigh Salterton Pebble Beds Formation has a much greater permeability than the Otter Sandstone Formation (Allen et al., 1997).

Allen et al. (1997) presented BGS core porosity data for the Sherwood Sandstone aquifer. Half of the samples tested have a porosity between 9.9 and 19.5%, and the median porosity is 14.8%. This compares to porosity values ranging from 16-33% in outcrop samples. A general decrease in porosity is seen northwards. Allen et al. (1997) suggested that the wide variation in

permeability and porosity, particularly the northwards decreases, may be a result of the variable cementation in the sandstone.

Transmissivity values from pumping tests are variable across the Otter Valley. The aquifer has generally high transmissivity values, which decrease northwards. However, north of Ottery St Mary limited pumping test data exist. Transmissivity values range from tens to >1000 m^2 day^{-1}. Transmissivity variations at individual sites can be broadly explained in terms of aquifer thickness and borehole penetration. As the aquifer thickens, and consequently boreholes are deeper, to the south and east, the transmissivity generally increases. Boreholes which penetrate beneath the Otter Sandstone Formation and into the Budleigh Salterton Pebble Beds Formation generally have enhanced transmissivities owing to the higher intergranular permeabilities in the Budleigh Salterton Pebble Beds Formation (Allen et al., 1997).

Despite local variations detailed above, modelling studies and pumping tests have indicated that the Otter Sandstone Formation and Budleigh Salterton Pebble Beds Formation respond as one aquifer (Allen et al., 1997).

3.2.2 Conceptual Flow Model

Perl et al. (2004) outlined the following conceptual groundwater flow model within the Otter Valley. They concluded that rainfall provides most of the recharge to the Sherwood Sandstone groundwater unit, and that the effective precipitation calculated by MORECS[1] is 427 mm a^{-1}. Rain which falls onto high ground to the west and east of the River Otter percolates into exposed Budleigh Salterton Pebble Beds and Otter Sandstone horizons. Further east, where the Sherwood Sandstone aquifer is confined, there is potential for recharge to the aquifer by leakage from the overlying mudstones.

Groundwater levels in the Otter Sandstone Formation have a response time to rainfall of two to twelve weeks. Where the unsaturated zone is thin this is reduced to two to eight weeks. In the Otter Sandstone Formation annual potentiometric surface fluctuation averages 0.7 m. In the Budleigh Salterton Pebble Beds Formation there is a larger average annual fluctuation of 1.4 m.

Within the Otter Valley the groundwater flows towards the River Otter, and groundwater in the unconfined aquifer has a relatively short residence time. West of the river the groundwater flow follows the dip. However, east of the river the flow is against the dip of the rocks, but with the topographic slope. Under natural flow conditions the Sherwood Sandstone aquifer discharges into the River Otter, but local groundwater abstraction reverses this, and locally the river water infiltrates into the Sherwood Sandstone aquifer.

There are few boreholes and observation points into the confined portion of the aquifer to the east of the River Otter. This means that there is scarce information on the mechanisms of groundwater flow outside of the River Otter discharge zone. It is thought that flow occurs at depth and there is discharge to sea via freshwater springs. The Sherwood Sandstone aquifer is in continuity with the sea, meaning there is potential for saline intrusion along the coast. The quantity of water abstracted by public supply boreholes is controlled by trigger levels designed to prevent saline intrusion by maintaining a positive hydraulic head between the Sherwood Sandstone aquifer and the sea.

3.2.3 Aquifer resources

The Otter Valley aquifer has been developed for public water supply, and many boreholes penetrate into the Sherwood Sandstone aquifer. The effective thickness is thought to be the entire aquifer, even if only the top portion is penetrated, as there is upwards leakage from beneath the base of the borehole. In 1997 abstraction from the Sherwood Sandstone aquifer in south east

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[1] MORECS is the generic name for the Met Office services involving the routine calculation of evaporation and soil moisture throughout Great Britain.

Devon was around 25,000 m^3 day^{-1}; which equates to half the estimated rainfall recharge resources in the Otter Valley outcrop, not including any river recharge (Allen et al., 1997).

The importance of the Sherwood Sandstone aquifer as a water resource is highlighted by the fact that of all the licensed water abstractions south of Broadhembury, 80% are groundwater, and only 20% are surface water. Around two thirds of the licensed abstractions from groundwater are used for agriculture, about 28% are used for public water supply and the remaining licensed groundwater abstractions are used for industrial and private water supplies (Perl et al., 2004).

North of Ottery St Mary the Sherwood Sandstone aquifer is not developed for public water supply. The Budleigh Salterton Pebble Beds Formation and Otter Sandstone Formation form a local water resource at outcrop. The yields within this portion vary greatly owing to the local importance of cementation and fractures. Continuing northwards, beyond the Otter Valley the aquifer is divided into compartments by faulting, meaning there is less potential for groundwater development (Allen et al., 1997).

In 2004, Perl et al. (2004) indicated that the current "Resource Availability" status of the Otter Valley groundwater monitoring unit at that time was "No Water Available". This is based on all licences pumping to their maximum authorised quantity.

3.3   AQUIFER MINERALOGY AND CHEMISTRY

The Sherwood Sandstone aquifer is dominated by silicate minerals, meaning that it is relatively inert. Only fine grained interstitial materials and cements have much of an influence on the chemistry of percolating groundwater.

3.3.1   Budleigh Salterton Pebble Beds Formation

The clasts within the Budleigh Salterton Pebble Beds Formation are primarily composed of metaquartzite (up to 90% of the clasts in the south of the region), which are >95% quartz. Of the 20% of the total formation that is matrix, a quarter is K-feldspar, some of which has altered to kaolinite. The remaining three quarters of the matrix is composed of equal proportions of quartz and metaquartzite grains (Walton, 1982). North of Uffculme the formation is strongly cemented with a calcareous cement. Sediment in the south is less cemented, but there are localised patches of amorphous iron oxides, and cements comprising poorly crystalline goethite or lepidocrocite throughout the formation (Walton, 1982). Flakes of mica, small crystals of feldspar, occasional pyrite nodules and iron oxide coatings have been observed in the south west (Ussher et al., 1913).

Heavy minerals from the southern part of the Budleigh Salterton Pebble Beds Formation contain staurolite, kyanite and sillimanite, which appear to indicate an origin from a southern metamorphic terrain. Tourmaline, zircon, staurolite and titanium minerals, with garnet, cassiterite, monazite, apatite, allanite, andalusite, calcic amphibole, topaz, anatase, rutile and brookite have been found in cored material from a borehole west of Ottery St Mary. This second assemblage is indicative of an origin in Cornwall (Edwards, 1997).

3.3.2   Otter Sandstone Formation

The sandstones of the Otter Sandstone Formation are generally mostly of quartz, metaquartzite and 20 – 25% orthoclase feldspar grains with flakes of muscovite (Edwards, 1997; Walton, 1982). This means that the Otter Sandstone Formation is mainly classified as a sub-arkose. Holloway et al. (1989) identified a widespread occurrence of anhydrite. The matrix comprises haematite-stained silt, which accounts for 10% of the formation by weight, and clay, which is predominantly illite. The haematite and secondary precipitates of amorphous and poorly crystalline iron oxides, especially goethite, give the Otter Sandstone Formation its red colour. There is a band of cementation at the Budleigh Salterton Pebble Beds Formation and Otter

Sandstone Formation junction, which is thought to comprise Fe and Mn (Edwards, 1997; Walton, 1982).

In the southern part of the Otter Sandstone outcrop the sands typically contain 1-4% carbonate, present mainly as calcite, with some dolomite. Locally there may be up to 20 wt% carbonate. In contrast, in much of the northern portion of the outcrop the sands are strongly indurated with carbonate cement, and there is regularly as much calcite as there is quartz (up to 45% calcite). In the south Devon portion of the outcrop cements have been dissolved, and the sandstones are now loosely cemented with calcite, ferric oxide and kaolinite (Edwards, 1997; Walton, 1982).

Heavy mineral assemblages are not markedly different from those found in the Budleigh Salterton Pebble Beds Formation; but staurolite is less abundant in the Otter Sandstone Formation (Edwards, 1997).

3.4   RAINFALL CHEMISTRY

Recharge to the Sherwood Sandstone aquifer is predominantly rainfall. The scarcity of superficial deposits means that recharge can readily take place over the outcrop area. In the south east of the aquifer direct recharge is limited by the overlying Mercia Mudstone (Perl et al., 2004). Where rainwater can readily infiltrate into the aquifer, it may provide an important source of solutes to the groundwater, especially if the concentrations are enriched because of evaporation and canopy-rain interactions (Kinniburgh and Edmunds, 1986). Table 3.3 shows the chemical composition of rainfall in the area from the North Wyke monitoring site [SX 649 998], which is located approximately 45 km west north west of Ottery St Mary (www.ecn.ac.uk).

The concentrations of Na and Cl, as well as SEC, are fairly high in the North Wyke rainwater, suggesting that there are local maritime influences at this site. The Sherwood Sandstone aquifer extends from the south coast to the Bristol Channel, meaning there would be a range of solute inputs along the outcrop. It is likely that the maritime contribution to groundwater recharge would be greatest along the south coast owing to the influence of the prevailing south westerly winds. In addition the location of the North Wyke monitoring station is relatively remote; the presence of major roads and town centres along the Sherwood Sandstone outcrop would suggest

Table 3.3 Rainfall chemistry from the North Wyke monitoring site [SX 649 998]. The mean annual rainfall at this site is 1052mm. The average rainfall composition was calculated from the data provided by the Environmental Change Network (ECN) (www.ecn.ac.uk)

Parameter	Units	Average rainfall composition (2009)	Concentrated rainfall composition (3× enrichment by evapotranspiration)
pH		5.4	4.0
SEC	$\mu S\ cm^{-1}$	25	76
Ca	$mg\ L^{-1}$	0.28	0.84
Mg	$mg\ L^{-1}$	0.36	1.1
Na	$mg\ L^{-1}$	3.1	9.4
K	$mg\ L^{-1}$	0.22	0.65
Cl	$mg\ L^{-1}$	5.1	15
SO_4-S	$mg\ L^{-1}$	0.45	1.3
NO_3-N	$mg\ L^{-1}$	0.31	1.78*
NH_4-N	$mg\ L^{-1}$	0.28	

*Assuming all NH_4-N is oxidised to NO_3 on infiltration

that the solute inputs may be higher in these areas (e.g. NO_x, SO_x species).

Rainwater is naturally acidic owing to the dissolution of atmospheric CO_2, which forms a weak solution of carbonic acid with an equilibrium pH of around 5.7. The North Wyke rain water has an average pH of 5.4 indicating there are likely to be few airborne pollutants present that are capable of further acidification, such as NO_x and SO_x. Areas closer to industrial atmospheric sources are likely to have rainfall with higher concentrations of S and N species and to have a lower pH. With the exception of the M5, which, until north of Wellington is within 10 km of the Sherwood Sandstone outcrop, there is little evidence of industrial atmospheric sources of solutes. The area is mostly covered by small towns, minor roads, and farm land.

If it is assumed that all the NH_4 in rainfall oxidises to NO_3 on infiltration to groundwater, baseline concentrations of dissolved NO_3-N derived from rainfall alone are likely to be in the order of 1.78 mg L^{-1} or less. The pH of recharge may be even lower than that measured in the rainfall owing to the oxidation of NH_4^+ ions to NO_3 which results in the release of H^+ ions and concentration by evapotranspiration. The pH of recharge is typically in the range 3–5 (Shand et al., 2007; Smedley and Allen, 2004).

3.5 CURRENT PRESSURES ON GROUNDWATER QUALITY

The main aim of the Environment Agency's (EA) Water Framework Directive (WFD) is to ensure that waters should attain good chemical status by 2015. The EA, tasked with planning and delivering better water environments, defined the 11 river basin districts for which management plans were created to identify the current status of groundwater. The Sherwood Sandstone aquifer is within the South-west River Basin District. This aquifer is divided into two groundwater bodies[2]. In the upper Otter catchment the chemical status is assessed as good while in the lower Otter catchment the status is assessed as poor. It is predicted that the chemical status in the poor area will remain poor in 2015, owing to the disproportionate expense associated with achieving good status. It is anticipated, however, that good status will be achieved by 2027 (EA, 2009).

The groundwaters are monitored to assess the risks of not meeting water-quality standards. The main risks to the inorganic water quality in the Sherwood Sandstone aquifer are the presence of nutrients (namely nitrate and phosphate), hazardous substances or other pollutants introduced as a result of abstraction and other artificial flow pressures (EA, 2009). The groundwater bodies are all classified as drinking water protection areas, which mean they need to be managed for this use, and are protected by WFD legislation. In particular action needs to be taken to prevent or limit the inputs of NO_3 to the groundwater. This will safeguard against future deterioration of groundwater quality, and ensure that increasing NO_3 trends can be reversedand is being done by a combination of regulatory and voluntary measures. Nitrate vulnerable zones (NVZs) were first designated by the EA in 1996, and then updated in 2002 and 2008. Currently almost 70% of England is designated as an NVZ. Farms within NVZs have to comply with rules affecting the careful planning, storage and usage of NO_3 rich substances. Almost all of the Sherwood Sandstone aquifer at outcrop in this region is located within a NVZ (DEFRA, 2010). Voluntary measures, such as catchment sensitive farming (CSF), are also encouraged in order to protect the groundwater from NO_3 contamination (DEFRA, 2010). While potential for saline intrusion exists along the coast (Allen et al., 1997) there is a high confidence that the aquifer is currently considered to be of good condition with regards to saline intrusion. It is predicted that this status will remain in 2015 (EA, 2009).

Source protection zones (SPZs) around boreholes have been identified by the EA. These show the risk of contamination from activities which may cause pollution. They are zoned according to the risk in terms of time for the pollution to travel to the borehole and extent of the

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[2] Groundwater bodies are the management units defined for the purposes of the Water Framework Directive.

contamination risk. Large areas of the Otter Valley are classified as SPZs, especially in the south of the valley (Perl et al., 2004).

4 Data availability and analytical methods

4.1 DATA SOURCES

Groundwater chemical data were acquired for the area by collection of 21 new groundwater samples and collation of available data from the Environment Agency (EA) database (7 sites). The EA data include analyses of the major elements and selected trace elements and field-determined parameters. These data comprise time-series analyses, generally from 2000 to 2010. These time-series data are discussed separately in Section 5.5. The most recent EA data (7 sites) were added to the 21 new groundwater samples to expand the spatial coverage, and create a data set of 28 sites (see Figure 2.4). These samples are summarised in Table 4.1

Table 4.1 Summary of groundwater sources used in this report

Number	Study*	Source	Groundwater unit	Land use+
1	BGS	Borehole	Budleigh Salterton Pebble Beds	Agricultural
2	BGS	Borehole	Otter Sandstone	Horticultural
3	BGS	Borehole	Otter Sandstone	PWS/ Agricultural
4	BGS	Borehole	Otter Sandstone	PWS/ Agricultural
5	BGS	Borehole	Budleigh Salterton Pebble Beds	PWS/Village/minor road side
6	BGS	Borehole	Mixed	PWS/Village/minor road side
7	BGS	Borehole	Otter Sandstone	PWS/ Agricultural
8	BGS	Borehole	Mixed	PWS/ Agricultural
9	BGS	Borehole	Otter Sandstone	PWS/ Agricultural
10	BGS	Borehole	Mixed	PWS/ Agricultural
11	BGS	Borehole	Budleigh Salterton Pebble Beds	PWS/ Agricultural
12	BGS	Borehole	Otter Sandstone	PWS/ Agricultural
13	BGS	Borehole	Otter Sandstone	PWS/ Agricultural
14	BGS	Borehole	Mixed	PWS/ Agricultural
15	BGS	Borehole	Otter Sandstone	Agricultural
16	BGS	Borehole	Otter Sandstone	Horticultural
17	BGS	Borehole	Unknown	Agricultural
18	BGS	Borehole	Otter Sandstone	Recreational
19	BGS	Borehole	Mixed	Horticultural
20	BGS	Spring	Budleigh Salterton Pebble Beds	Recreational
21	BGS	Borehole	Otter Sandstone	Agricultural
22	EA	Well	Unknown	Agricultural
23	EA	Borehole	Unknown	Agricultural
24	EA	Borehole	Otter Sandstone	PWS/Village/minor road side
25	EA	Borehole	Unknown	Agricultural/ major road side
26	EA	Borehole	Budleigh Salterton Pebble Beds	Agricultural/ major road side
27	EA	Borehole	Unknown	Industrial
28	EA	Borehole	Otter Sandstone	Horticultural

*"BGS" refers to samples taken for this study; "EA" refers to samples from the Environment Agency monitoring network. +Land use refers to the local area surrounding the borehole headworks, PWS = public water supply

4.2   SAMPLING AND ANALYSIS

The 21 new groundwater samples were collected by BGS between 27th and 30th September 2010 from commercial abstraction and private boreholes exploiting groundwaters from the Sherwood Sandstone aquifer. The sample locations are shown in Figure 2.4.

Samples were mostly collected from pumping boreholes. Where practical, the pumps at private sources were switched on at least 10 minutes prior to samples being taken. Efforts were made to sample the groundwater as close to the borehole as possible and with minimum transport through pipes or hoses. Sampling from storage tanks was avoided. All efforts were made to ensure collection of a representative groundwater sample.

At each site, measurements were made of temperature, specific electrical conductance (SEC), alkalinity (by titration against H_2SO_4), pH, dissolved oxygen (DO) and redox potential (Eh). Where possible the latter three parameters were measured in an anaerobic flow cell to prevent contact with the atmosphere and parameters were monitored until stable readings were obtained. In a few cases, use of a flow cell was not possible and on-site parameters were measured rapidly in a bucket. In each case a note was made of the sampling conditions.

Groundwater samples were also taken at each site for laboratory analysis. Samples for major- and trace element analysis were collected in factory-new rinsed polyethylene bottles and filtered to <0.45 µm. Filtration was performed using a disposable filter and syringe. Those required for cation and trace element analysis were acidified to 1% (v/v) HNO_3 to prevent metal precipitation and minimise sorption onto the container walls.

Samples for dissolved organic carbon (DOC) analysis were filtered through a 0.45 µm silver-impregnated filter and collected in glass vials pre-cleaned with chromic acid. Samples for the determination of stable isotopes (^{18}O and ^2H in water and ^{13}C in dissolved inorganic carbon) were collected unfiltered in rinsed glass bottles.

Analysis of major and trace cations, and I was carried out by inductively-coupled plasma mass spectrometry (ICP-MS). Anions (Cl, NO_3, NO_2, Br and F) were determined by ion chromatography (IC), NH_4 by automated colorimetry (AC), and any titrations repeated in the laboratory were determined by potentiometric titration. Samples for DOC were analysed using a TOC analyser.

Samples analysed in the BGS laboratories had an ionic charge imbalance of <2.4%, with one exception: a sample with a very low dissolved solids concentration (specific electrical conductance = 139 µs cm^{-1}). This had an imbalance of 8.25%. The EA samples generally had an ionic imbalance of <10%.

4.3   DATA HANDLING

The data collected as a result of the sampling campaign and the archive EA data were combined into one set for determining summary statistics and for interpretation. For many of the trace elements, the concentrations were below the detection limits of the analytical techniques used.

Summary statistics were calculated using R (R Development Core Team, 2005) using the NADA package. This package is used to perform statistical analysis on censored data and uses the methods described in Helsel (2005). Summary statistical data for the combined BGS-EA dataset were computed using the Kaplan-Meier (K-M) and the robust "regression on order statistics" (ROS) methods. These can both be used to summarise multiply-censored data sets (Lee and Helsel, 2005b, 2007).

The K-M method is commonly used in the medical sciences and is the standard method for estimating summary statistics of survival data. It is also recommended for environmental data (Lee and Helsel, 2007). The K-M method neither needs, nor makes, any assumptions about the distribution of the data, making it suitable for summarising censored data (Helsel, 2005). It only accepts right-censored data but the method can be equally valid for left-censored detection-limit

data if they are flipped. The K-M method calculates the rank of the flipped data, placing each non-detect at its detection limit prior to ranking. The method thus accounts for the censored data between the detected observations. The summary statistics are estimated using the empirical cumulative distribution function of the ranked data. Typically this method produces a small positive bias in the mean produced for environmental data. However the method is considered to be suitable for datasets where fewer than 50% of the data are censored (Abesser et al., 2005; Helsel, 2005).

The ROS method used in the NADA package is a "robust" semi-parametric method which has been evaluated as one of the most reliable methods for producing summary statistics of multiply-censored data (Shumway et al., 2002). The method is particularly useful for small data sets (n<30) where other methods may become inaccurate. It is also particularly useful where the non-detects comprise up to 80% of the data set. Regression-on-order statistics is a probability-plotting and regression approach that models censored distributions using a linear regression of observed concentrations against their normal quantiles (or "order statistics") (Lee and Helsel, 2005a). The method firstly computes Weibull-type probability distributions of the data set, which includes both the censored and non-censored data. The formula used is designed to account for multiply-censored data. The plotting positions of the uncensored observations and their normal quantiles define a linear regression. This regression model can then be used to estimate the concentrations of the censored observations as a function of their normal quantiles (Lee and Helsel, 2005a). The last stage in the algorithm is to combine the observed uncensored values with the modelled censored values to produce estimations of the summary statistics. This combination of observed and modelled censored values creates a method that is more resistant to non-normality of errors and also reduces any transform biases that occur (Lee and Helsel, 2005a).

As noted by Lee and Helsel (2005a, b), where the data set has greater than 80% non-detects, the estimated summary statistics are very tenuous. They suggest that in such cases the data can only be summarised by presenting minimum and maximum values (Lee and Helsel, 2005a). The summary statistics in this report were calculated using each of the above methods. The most appropriate method for each analyte was taken following the recommendations of Helsel (2005), as given below:

<50% non-detects	K-M method
50% to 80% non-detects	ROS method
>80% non-detects	ranges only quoted.

The summary statistics reported are therefore derived from a range of methods and do not all present the same parameters. To produce the box plots in this report (Figure 5.4 and Figure 5.12), ROS statistics have been applied using functions available in the NADA package.

In the Baseline report series, the 95th percentile of a data distribution has typically been used as an upper cut-off for outlier compositions. The choice of percentile is somewhat arbitrary and other percentiles have been used elsewhere. The 90–95th percentile was used by Lee and Helsel (2005a) and the 97.7[th] percentile was used by Langmuir (1997). While using percentiles as an upper limit provides a simple definition of outliers, the method clearly has its limitations. For example, many UK groundwaters are contaminated by nitrate derived from long-term use of nitrogenous fertilisers in agriculture. Nitrate concentrations are therefore variable and the 95% threshold in unconfined aquifers rarely represents a cut-off between natural and anthropogenically-influenced compositions. Likewise, for some elements, data presented above a given threshold are presented as anomalous, when they can in fact represent baseline concentrations. However, the 95th percentile represents a simplification to exclude the upper 5% of the data distribution and has been used in the Baseline report series as one measure for estimating likely upper limits to baseline concentrations. Concentrations above this threshold are unlikely to be exceeded in future samples unless conditions within the aquifer have changed. It

should be emphasised that this is not the only factor used when attempting to characterise the baseline groundwater compositions. A combination of understanding of the hydrogeological and geochemical processes, rainfall compositions, land use and residence times, together with temporal variability observed through time-series data are also taken into consideration. These are discussed later in Section 5.

In addition to the statistical analysis, saturation indices were calculated for the newly collected groundwater samples using PHREEQCi with the `wateq4f.dat` database. Saturation indices will be discussed where appropriate in Section 5.

Box plots are used to show data ranges of a population and identify outliers. They are hence useful indicators of baseline ranges. Cumulative-probability plots are an efficient way of identifying distinct populations and defining anomalies. If the x axis (concentration) is logarithmic, a log normal distribution will plot as a straight line, and bimodal, or multimodal distributions will plot as curves (see Shand et al., 2007 for more details). In cumulative-probability plots, flexure may be used to discriminate baseline concentrations from anomalous populations. However, when interpreting cumulative-probability plots, care must be taken as natural reactions, such as redox reactions, sorption and denitrification can introduce anomalous concentrations, which are of entirely natural origin (Shand et al., 2007).

5 Regional hydrochemistry

Sandstones can form good aquifers. As a whole the Permo-Triassic Sandstones form the second most important aquifer in the UK. These sandstones supply approximately 25% of licensed groundwater abstractions in England and Wales (Allen et al., 1997). The relatively small outcrop of Sherwood Sandstone in Somerset and Devon provides a useful local resource. Although the Sherwood Sandstone is a silicate aquifer it is likely that the groundwater chemical composition will be dominated by the interaction with fine-grained interstitial minerals and cements, which are commonly non-siliceous.

The groundwater chemistry data set for the Sherwood Sandstone aquifer of Devon and Somerset is discussed below in terms of data distribution i.e., summary statistics, as well as spatial distribution. The nature of the narrow north-south trending outcrop means it can be difficult to highlight west-east trends in the data set. In the south of the region the groundwater flows into the River Otter, and the detail and resolution of the sample distribution means that trends following flowlines (west to east, and east to west towards the centre of the Otter Valley), or trends following down dip (west to east) are unlikely to be evident.

5.1 MAJOR CONSTITUENTS

Statistical data for major ions, field determined parameters, and stable isotopes are summarised in Table 5.1, Figure 5.1, Figure 5.4 and Figure 5.5. Additionally spatial variations are presented in Figure 5.2, Figure 5.3, and Figure 5.6 to Figure 5.11. It should be noted that where an element or parameter was not included in the EA data set, only data from the 21 new BGS analyses are presented.

Table 5.1 Statistical summary of field-determined parameters, major ions, stable isotope compositions and nitrogen species

	units	n	n(c)	min	Mean	max	P5	P25	P50	P75	P90	P95
Temp	ºC	28	0	4.3	11.6	16.2	9.1	11.2	11.7	12.1	13	13.9
pH		28	0	5.14	6.75	7.7	5.2	6.53	6.91	7.21	7.32	7.33
Eh	mV	21	0	273	405	490	371	390	407	416	446	469
DO	mg L^{-1}	28	0	2.31	5.66	10.6	2.35	3.78	5.03	7.3	9.2	9.49
SEC	µs/cm	28	0	114.1	540	936	119	426	542	665	825	907
δ^{2}H	‰	21	0	-43.9	-39.8	-36	-43.5	-41	-39.6	-39	-38	-37
δ^{18}O	‰	21	0	-6.65	-6.3	-5.8	-6.61	-6.47	-6.36	-6.1	-5.98	-5.87
δ^{13}C	‰	21	0	-18.2	-15.5	-13	-17.2	-16.3	-15.6	-14	-13.9	-13.4
Ca	mg L^{-1}	28	0	1.6	74.6	196	4.9	48.5	72.2	95.3	134	143
Mg	mg L^{-1}	28	0	2.62	12.2	36.2	2.66	4.78	10.4	18.6	21.2	27.2
Na	mg L^{-1}	28	0	7.4	14.5	27.7	8.57	11.9	14.5	15.5	18.7	23.3
K	mg L^{-1}	28	0	1.47	5.1	22.7	2.08	3.15	4.74	5.34	6.98	9.75
Cl	mg L^{-1}	28	0	14.2	28.5	71.8	18.9	21.9	26.7	31.2	38.4	42.8
SO$_4$	mg L^{-1}	28	2	<10	33.8	407	4.00	13.7	19.2	23.8	40.1	52.4
HCO$_3$	mg L^{-1}	28	2	<1	195	372		101	226	268	315	321
NO$_3$-N	mg L^{-1}	28	0	1.58	9.55	29.5	1.194	5.92	7.88	10.8	18.5	21.2
NO$_2$-N	mg L^{-1}	28	24	<0.003		0.00448						
NH$_4$-N	mg L^{-1}	28	14	<0.003	0.118	0.19			0.00312	0.01	0.009	0.018
DOC	mg L^{-1}	21	6	<0.5	1.16	6.48			0.594	0.88	1.8	3.7
Si	mg L^{-1}	28	0	3.01	5.08	7.32	3.13	4.06	5.16	5.75	6.54	6.59

DO: dissolved oxygen; SEC: specific electrical conductance; DOC: dissolved organic carbon; P: percentile; n: number of samples; n(c): number of censored samples; min and max are observed values

The Sherwood Sandstone aquifer is largely composed of quartz (see Section 3.3), but the reaction of silicate minerals is minor compared to carbonate dissolution. When calcium carbonate minerals are present in rocks and soils at a level of 1% or more they will tend to dominate the aqueous chemistry (Faure, 1998; Hem, 1992; Langmuir, 1997). This is demonstrated by Table 5.1 and Figure 5.1, which show that, despite Ca only comprising a minor portion of the Sherwood Sandstone aquifer in cements and grain coatings, it dominates the aqueous chemistry of many samples, especially those from the Otter Sandstone Formation.

Figure 5.1 demonstrates the variation in major ion chemistry, and highlights the differences between the two units of the Sherwood Sandstone aquifer. The groundwaters sampled from the Otter Sandstone Formation are mainly Ca-HCO_3 type, with some mixing towards Mg. These samples form a tight group in the central quadrilateral of the Piper diagram.

In contrast, the Budleigh Salterton Pebble Beds Formation groundwaters plot along a continuum between Ca-HCO_3 type, and Na-Cl type. This is similar to a seawater mixing line, although it is unlikely seawater is the cause of this relationship, given the distance of many of the sites from the sea. The groundwaters from Permo-Triassic sandstones elsewhere in the UK are affected by mixing with older, more saline formation waters still present in the aquifers, or locally from
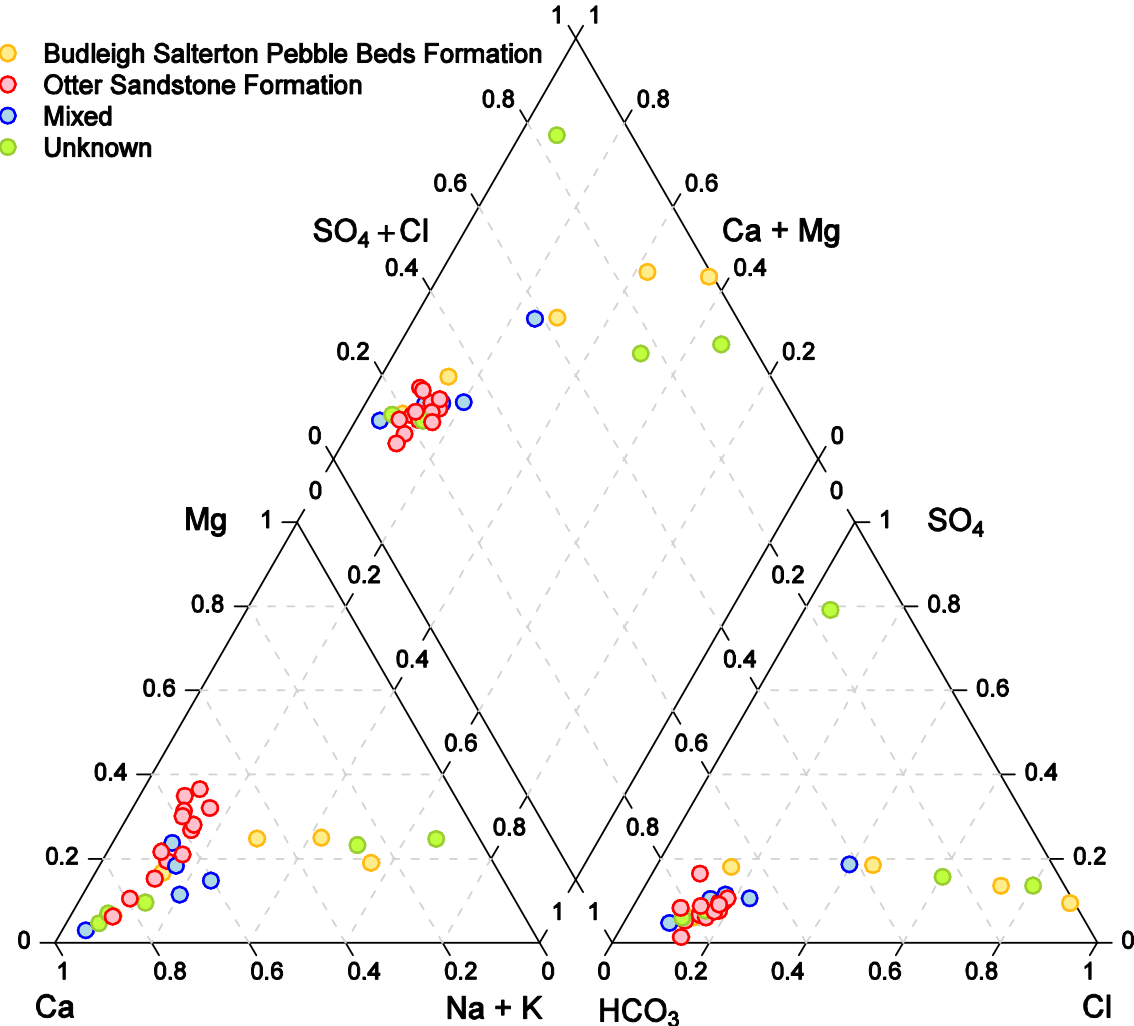

Figure 5.1 Piper diagram of the chemistry of the Sherwood Sandstone groundwaters

29

underlying aquifers. It is likely that, as the underlying unit, the Budleigh Salterton Pebble Beds Formation contains groundwater which is influenced by formation waters (Shand et al., 2007). In addition a possible source of K is the feldspars, which make up a quarter of the matrix of the Budleigh Salterton Pebble Beds Formation. One site of unknown groundwater origin is of Ca-SO_4 type. It is possible that this is taken from the Otter Sandstone Formation aquifer, where anhydrite is known to occur (Section 3.3.2).

The temperatures of the groundwaters range from 4.3 to 16.2°C, with a median of 11.7°C (Table 5.1). The 5th to 95th percentile range is 9.1 to 13.9°C (Table 5.1). The coldest temperature was recorded in the EA data set, and is from a well sampled during December 2010. This was a particularly cold period, and the sample may represent a shallow, young groundwater, which reflects surface temperatures. As this was a sample from the EA monitoring network it is not known how much this sample was purged prior to collection. If the sample was not freshly drawn from the aquifer the temperature of the groundwater will reflect the air temperature. Other than the maximum temperature, which may be an artefact caused by water warming in the tubes connecting the tap to the flow cell, the remainder are consistent with values for modern recharge. Although there are no real spatial trends, the coldest samples are generally found along the south western edge of the outcrop (Figure 5.2).

The pH of the groundwaters ranges from 5.14 to 7.7, with a 5th to 95th percentile range of 5.2 to 7.3, and a median of 6.9 (Table 5.1). These waters are weakly acidic to circum-neutral. The pH of the groundwaters is very strongly linked to the aquifer source unit (see Figure 2.4 and Figure 5.2). Groundwaters sourced from the Budleigh Salterton Pebble Beds Formation have pH values that range from 5.14 to 6.89; groundwaters sourced from the Otter Sandstone Formation have pH values that range from 6.89 to 7.7. The mixed groundwaters from both aquifer sources have pH values that range from 6.01-7.12. It is therefore possible to suggest which aquifer source provides the major groundwater portion of the mixed groundwaters and those from unknown sources. Those with pH values <6.89 are most likely to be dominated by groundwaters from the Budleigh Salterton Pebble Beds Formation, whereas those with pH values >6.89 are most likely to be dominated by groundwaters from the Otter Sandstone Formation.

The spatial variation of pH is presented in Figure 5.2, which shows the lowest pH values are found in groundwaters sampled towards the west of the outcrop. Here the Budleigh Salterton Pebble Beds Formation is present either at outcrop, or at relatively shallow depths. The boreholes in these areas therefore exploit either groundwaters from the Budleigh Salterton Pebble Beds Formation or a mixed source. Groundwaters exploiting the Otter Sandstone Formation are most likely to be found towards the east of the area.

The measured dissolved oxygen content ranges from 2.31 to 10.6 mg L^{-1}, with a 5th to 95th percentile range of 2.35 to 9.45 mg L^{-1}; and a median of 5.03 mg L^{-1}. The Eh ranges from 273 to 490 mV, with a 5th to 95th percentile range of 371 to 469 mV, and a median of 407 mV (Table 5.1). This represents a relatively small range, indicating that all the groundwaters analysed are oxidised. The most oxidising waters tend to be found along the western edge of the outcrop (Figure 5.3). Eh values of BGS groundwater samples known to be taken from the Budleigh Salterton Pebble Beds Formation range between 419 and 490 mV, and groundwater samples known to be sampled from the Otter Sandstone Formation range from 273 to 427 mV. The interdependence of pH and Eh are the critical factors determining the stability of minerals present, and controlling solubility and speciation (Levinson, 1974). This will be discussed further, where relevant, when describing elemental concentrations.
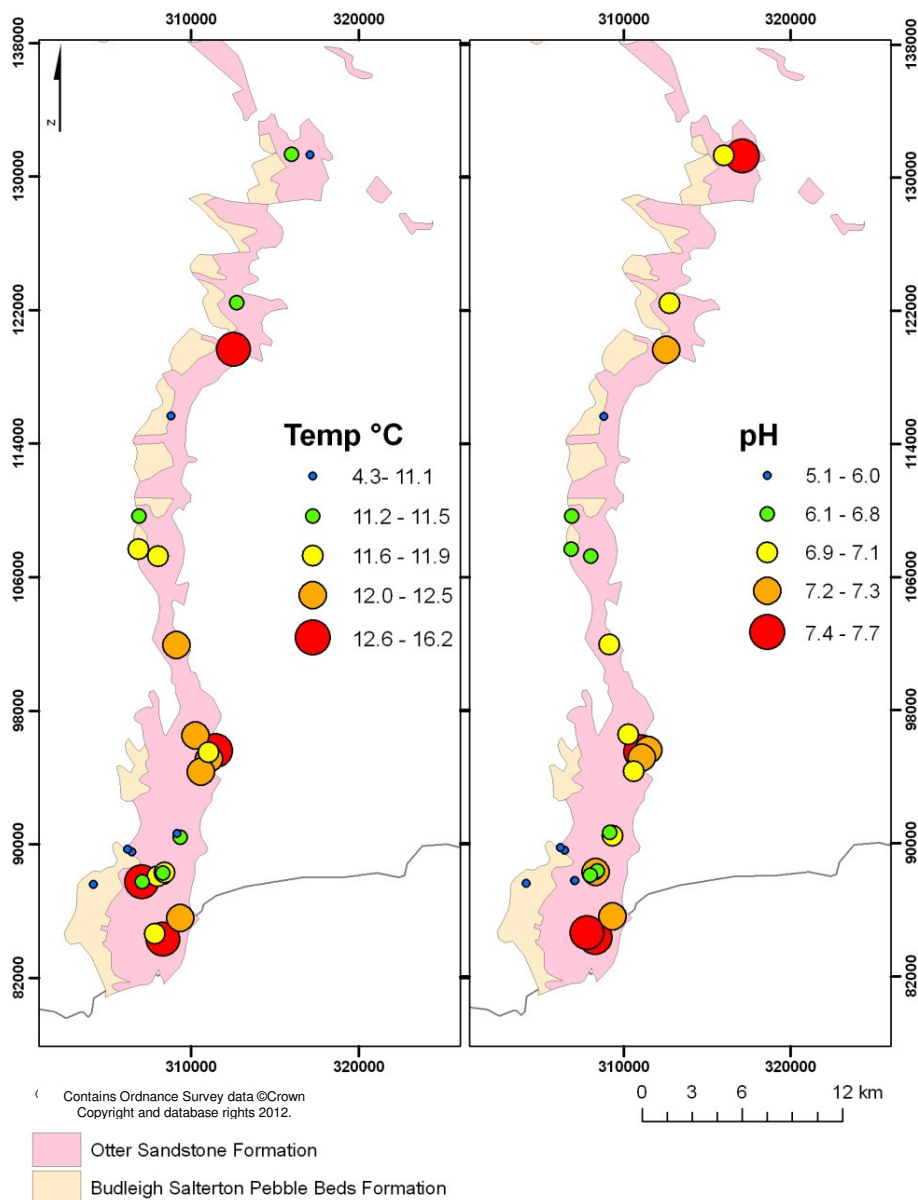
Figure 5.2 Regional variation of temperature and pH within the
Sherwood Sandstone aquifer

The range in specific electrical conductance (SEC) spans from 114 – 936 µS cm^{-1}. The 5th to 95th percentile range is 119-907 µS cm^{-1}, and the median is 542 µS cm^{-1} (Table 5.1). These values are generally comparable with other Permo-Triassic sandstones around the UK (Shand et al., 2007). The groundwaters that are known to originate from the Budleigh Salterton Pebble Beds Formation generally have lower SEC values, ranging from 139 to 568 µS cm^{-1}, whereas the groundwaters from the Otter Sandstone Formation have SEC values ranging from 443-825 µS cm^{-1}. The highest SEC values (907, 936 µS cm^{-1}) and lowest SEC values (114, 119 µS cm^{-1}) are all from boreholes with undefined geology. The samples with the lowest SEC values have pH values of 5.2 and 5.7 (although no available Eh values), which suggest a Budleigh Salterton Pebble Beds Formation source. This is consistent with the observation that the Budleigh Salterton Pebble Beds Formation has the lowest SEC values. The samples with the highest SEC values have pH values of 6.8 and 6.86, and one has an Eh value of 384 mV. It is possible that these samples derive from either unit, or be a mixture of Budleigh Salterton Pebble Beds Formation and Otter Sandstone Formation groundwaters.

The relationship with the source aquifer means that the lowest SEC values are found in the south and west of the area, where the Budleigh Salterton Pebble Beds Formation is at or near the
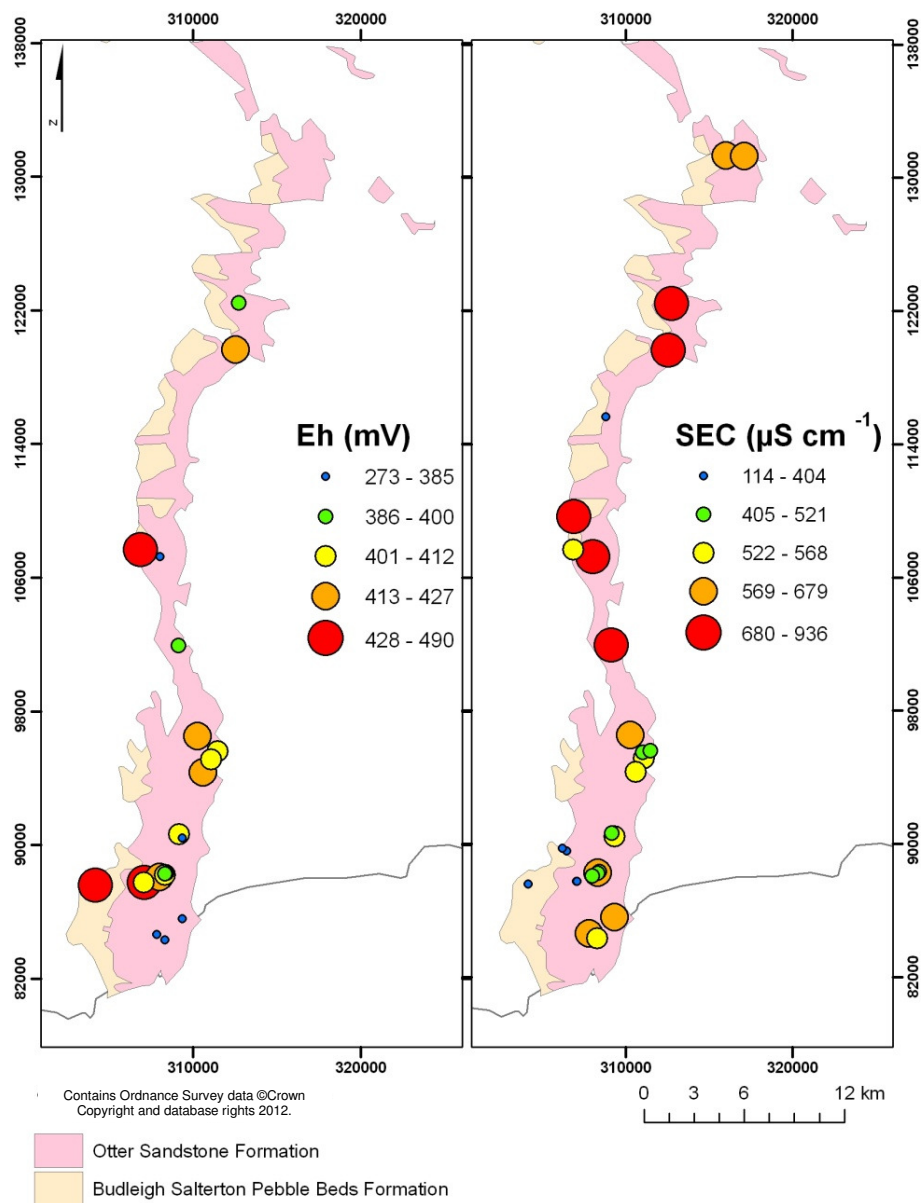
Figure 5.3 Regional variation of Eh and SEC within the Sherwood
Sandstone aquifer

surface. The higher values are found to the north and east of the region, where the Otter Sandstone Formation is exploited, and where carbonate cements are common (Figure 5.3).

The major-ion data are presented as box plots in Figure 5.4, and cumulative probability distribution plots in Figure 5.5. Both provide a useful graphical method for summarising and characterising geochemical data distributions (Shand et al., 2007). These plots are used in this report to present the range of results from the combined data sets comprising the new BGS data and the EA data sets.
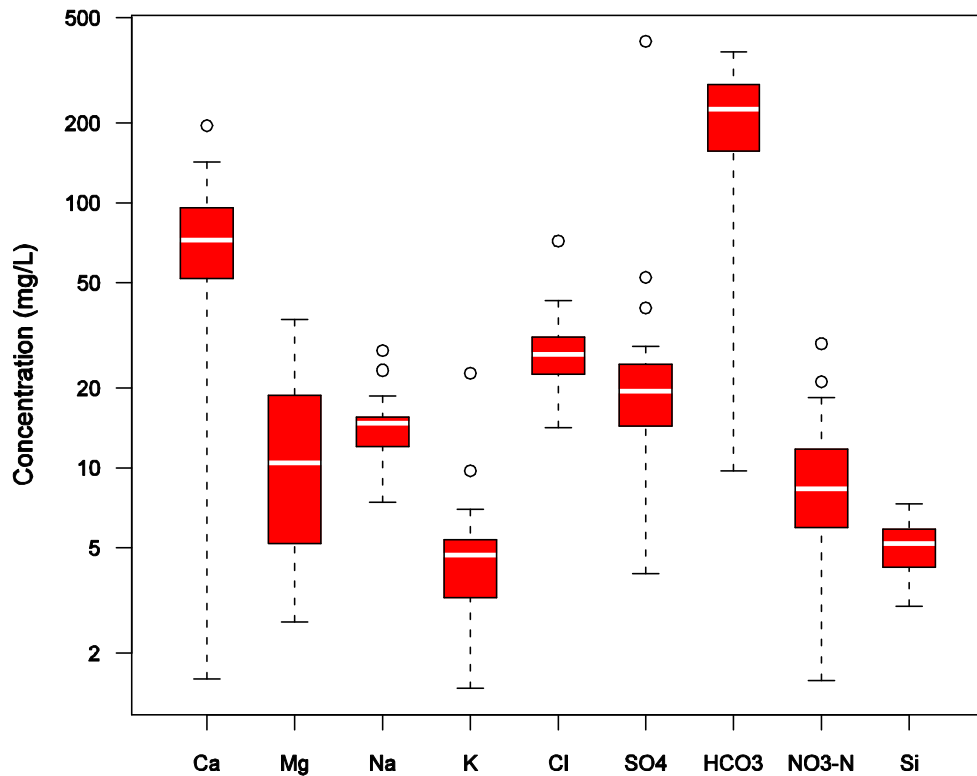
Figure 5.4 Box plots for the major ions in the Sherwood Sandstone aquifer. For an explanation of the box plots see Section 4.3
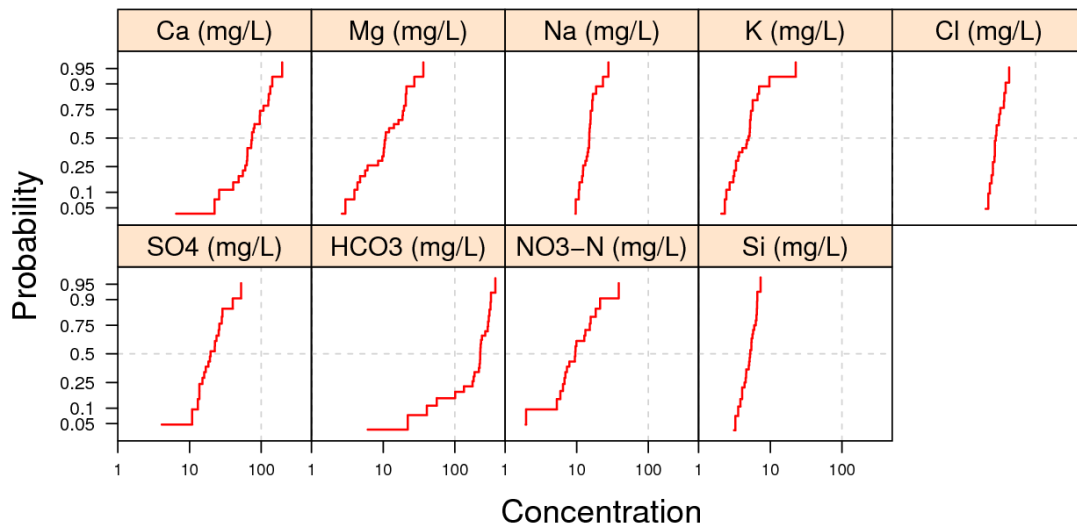
Figure 5.5 Cumulative-probability plots for the major ions in the Sherwood Sandstone aquifer

Figure 5.4 and Figure 5.5 present the ranges and outliers for the major ions. The range of concentrations for each element span up to two orders of magnitude. Of particular note are the groundwater concentrations of NO_3-N. The concentration range supports the evidence that the groundwaters are oxic. The cumulative-probability plots (Figure 5.5) show that most of the major elements present a distribution which is moderately linear. Bicarbonate alkalinity and Ca are negatively skewed indicating there are some very soft waters. This may be in areas where a carbonate cement is absent.

Calcium has a concentration range of 1.6 to 196 mg L^{-1}, a 5th to 95th percentile range of 4.9-143 mg L^{-1}, and a median of 72.2 mg L^{-1} (Table 5.1). The concentration range covers 2 orders of magnitude, and presents a similar distribution, and median (<85 mg L^{-1}) to other groundwaters from the Permo-Triassic Sandstones in the UK (Shand et al., 2007). In the Permo-Triassic Sandstone aquifers already examined in Baseline groundwater studies the Ca concentrations were mainly attributed to gypsum dissolution and mixing with formation waters or seawater. It is likely that the concentrations in the Sherwood Sandstone aquifer of the current study reflect dissolution of $CaCO_3$ grain coatings, which are common, especially in the Otter Sandstone Formation. The correlation of Ca to HCO_3 is moderate (r^2=0.46) indicating that $CaCO_3$ is likely to be the dominant source of Ca.

The spatial variation of Ca in groundwaters is quite striking (Figure 5.6). Highest concentrations are found north of the Otter Valley, where the rapid equilibration with calcite is the likely cause of the high observed Ca concentrations. In the south of the region, carbonate cements are rare, and this is reflected in the relatively low Ca concentrations. A secondary trend is that Ca concentrations in groundwaters from the Budleigh Salterton Pebble Beds Formation are lower than those in groundwaters from the Otter Sandstone Formation.

Interestingly, the trend of the modelled saturation indices of calcite do not follow a north-south pattern like Ca; instead groundwater samples from the Otter Sandstone Formation are at or near equilibrium, and samples from the Budleigh Salterton Pebble Beds Formation are undersaturated, following the less dominant spatial trend. This may be because the groundwaters of the Budleigh Salterton Pebble Beds Formation have a lower pH, meaning the $CaCO_3$ solubility is higher. The abundance of Ca is therefore primarily controlled by the abundance of carbonate cements, and a secondary control is the solubility of $CaCO_3$.

Magnesium has a range of 2.62 to 36.2 mg L^{-1}, a 5th to 95th percentile range of 2.66 to 27.2 mg L^{-1} and a median of 10.4 mg L^{-1} (Table 5.1). These are relatively low concentrations, in a narrow range, when compared to other groundwaters from Permo-Triassic Sandstone aquifers in the UK (Shand et al., 2007). There are accounts of minor occurrences of dolomite within the southern area of the Sherwood Sandstone aquifer. All the waters are undersaturated with respect to dolomite reflecting the limited occurrence and solubility of dolomite, which is lower than that of calcite. Secondary sources of Mg in this aquifer are likely to be rainfall, or mixing with formation water.

Figure 5.6 shows the spatial variation of Mg concentrations in the Sherwood Sandstone aquifer. The highest concentrations are generally found in the south and west. There is a strong correlation with source aquifer, supporting the evidence of dolomite occurring within the aquifer. As dolomite is a soluble mineral only a very small amount would need to be present to give the low Mg concentrations observed within the Sherwood Sandstone aquifer.

Sodium has a range of 7.4 to 27.7 mg L^{-1}, a 5th to 95th percentile range of 8.57 to 23.3 mg L^{-1}, and a median of 14.5 mg L^{-1} (Table 5.1). This is a relatively narrow range when compared to other Permo-Triassic Sandstone aquifers in the UK. The lowest Na concentrations (up to the 25th percentile) in the Budleigh Salterton Pebble Beds Formation and Otter Sandstone Formation groundwaters are comparable with that of local rainfall (see Table 3.3). In other UK Permo-Triassic Sandstone aquifers the minimum concentration is comparable to those found in the Sherwood Sandstone aquifer in Devon and Somerset, but maximum concentrations elsewhere range to much higher values (up to 10 g L^{-1}). These have been interpreted as mixing with saline formation waters (Shand et al., 2007). This appears not to be an influence on the Sherwood Sandstone aquifer of Devon and Somerset. The steep gradient of the cumulative-probability curve (Figure 5.5) also does not imply a separate population of groundwaters influenced by mixing with formation waters.
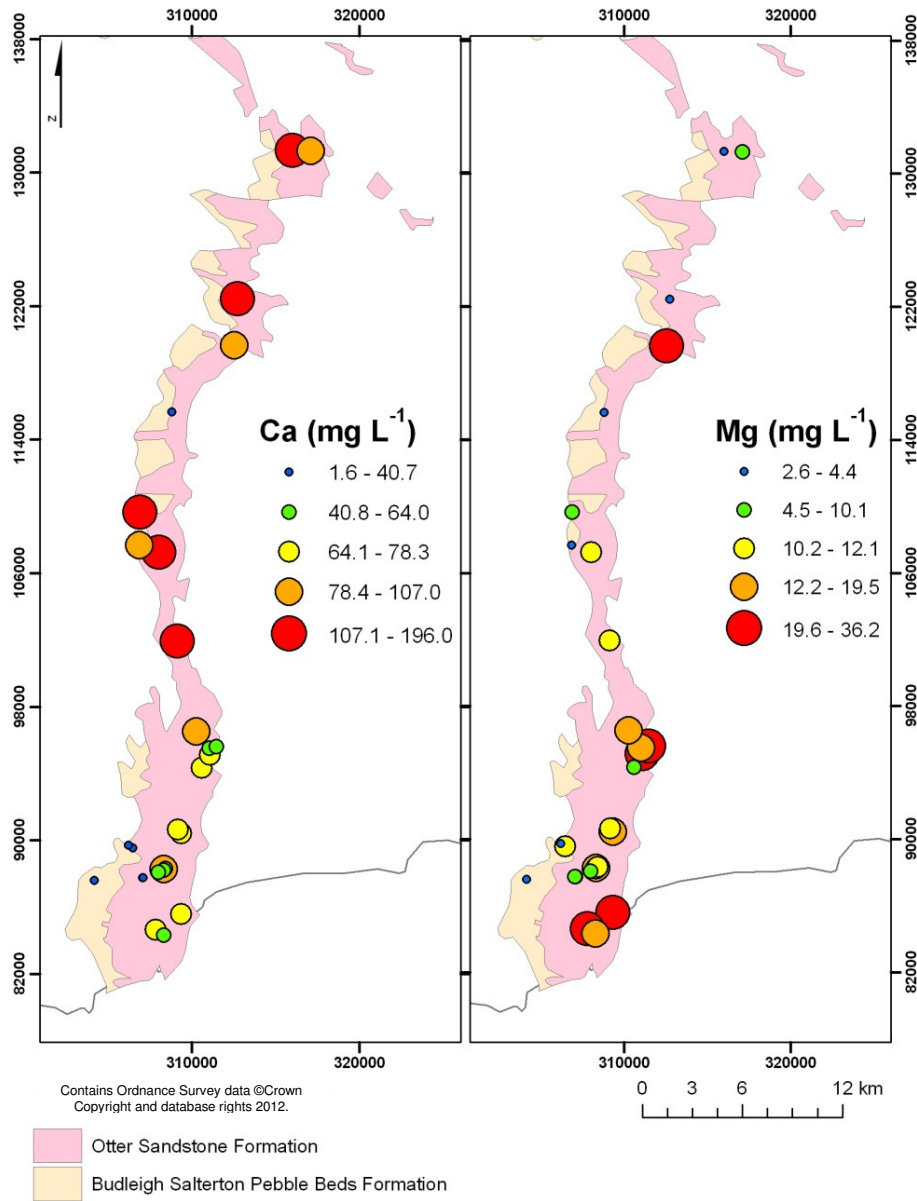
Figure 5.6 Regional variation of Ca and Mg within the Sherwood
Sandstone aquifer

There is no correlation of Na concentration with source aquifer unit, although there is a spatial trend evident (Figure 5.7). The lowest concentrations are generally found in groundwaters in the north of the region and some of the highest concentrations of Na are found in the groundwaters closest to the south coast, which may be a function of the coastal location and prevailing wind. There are other isolated samples of groundwater with high Na concentrations, which may be caused by localised dissolution of feldspars.

Potassium has a range of 1.47 to 22.7 mg L^{-1}, a 5th to 95th percentile range of 2.08 to 9.75 mg L^{-1} and a median of 4.64 mg L^{-1} (Table 5.1). This distribution is fairly typical of other Permo-Triassic Sandstone aquifers in the UK (Shand et al., 2007), which are thought largely to reflect the dissolution of K feldspar. Potassium feldspar is common in the Sherwood Sandstone aquifer of Devon and Somerset, and it is likely that these data also represent K feldspar dissolution. The cumulative probablility graph (Figure 5.5) shows a slight upper tail, which represents one site where the K concentration is double the next highest value. The land use of this site was farming, which could imply that there is some contamination from fertilizers or farm waste, yet concentrations of other elements associated with such contamination (P, N, DOC) are not
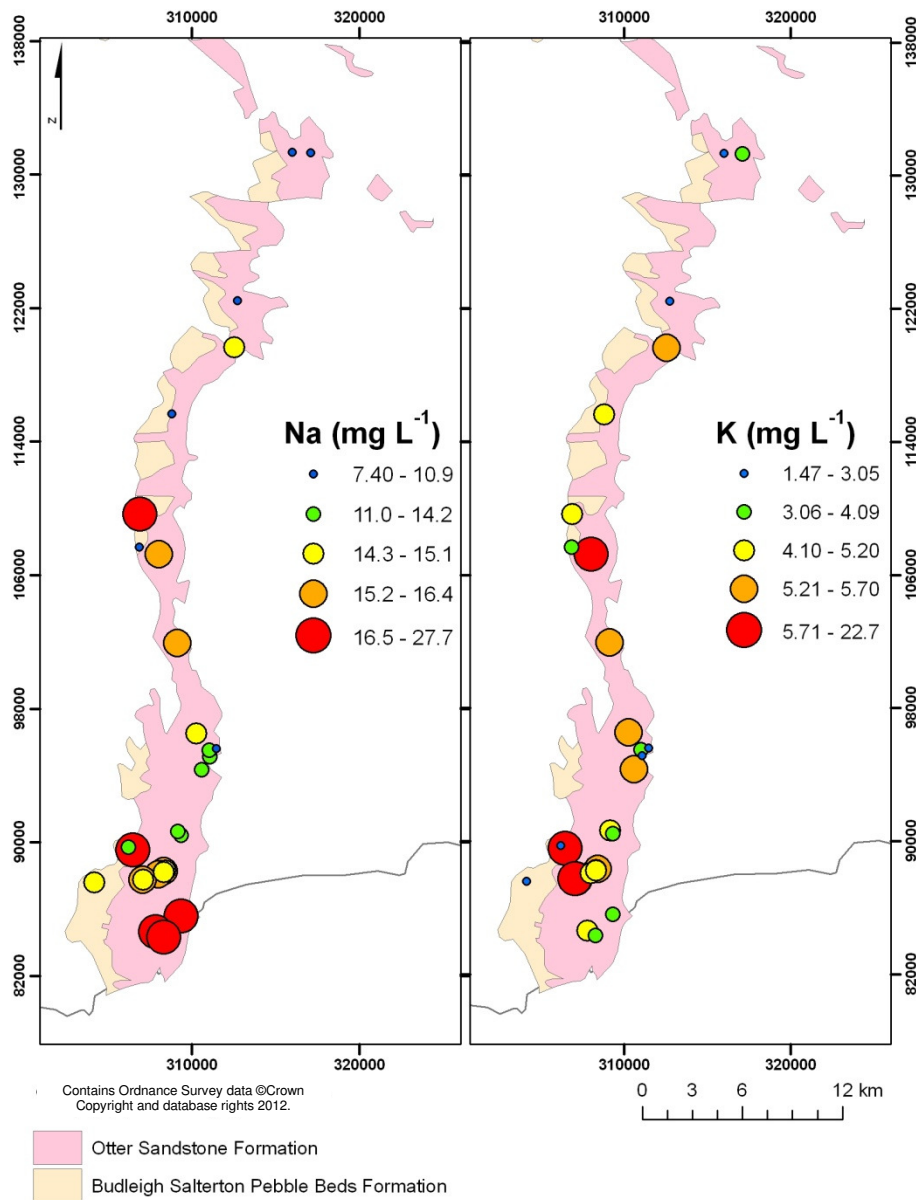
Figure 5.7 Regional variation of Na and K within the Sherwood
Sandstone aquifer

particularly elevated. There is no relationship of K with aquifer source unit, although concentrations of K are generally higher in the south (Figure 5.7).

Chloride has a range of 14.2 to 71.8 mg L^{-1}, a 5th to 95th percentile range of 18.9 to 42.8 mg L^{-1}, and a median of 26.7 mg L^{-1} (Table 5.1). The lowest Cl concentrations are comparable to those found in local rainfall (see Table 3.3). The lowest observed concentrations are consistent with the lower concentrations found in other UK Permo-Triassic Sandstone aquifers, but the range for the Devon and Somerset aquifer is much more restricted. The higher concentrations found elsewhere (up to 10 g L^{-1}) represent mixing with formation water(Shand et al., 2007). There is no relationship between Cl concentration and aquifer source unit, but the spatial variation (Figure 5.8) is very similar to that of Na (see Figure 5.7). The highest values are generally found near the south coast, and the loweset values are found in the north of the region. The correlation between Na and Cl is good (r^2= 0.73). Given the spatial trends it is likely that this is derived from the sea. As the concentrations of Na and Cl are moderate it is most likely these concentrations are derived from marine aerosols, rather than saline intrusion.

Sulphate has a range of <10 to 407 mg L^{-1}, a 5th to 95th percentile range of 4.00 to 52.4 mg L^{-1}, and a median of 19.2 mg L^{-1} (Table 5.1). This distribution is fairly typical of Permo-Triassic Sandstone aquifers in the UK. It is unusual that two values are below detection limit, although 10 mg L^{-1} is a high detection limit, as the lowest measured value is 3.83 mg L^{-1}. These censored data probably represent values that are similar to local rainfall (see Table 3.3), although the high detection limit makes comparison difficult The groundwater concentrations of SO$_4$ do not correlate with source aquifer unit, and there appears to be a lack of obvious spatial trend within the dataset (Figure 5.8).The largest concentration (407 mg L^{-1}) exceeds the drinking-water standard of 250 mg L^{-1}. If this water were to be used for drinking, treatment would be required before it would be considered suitable. The sample in which the maximum concentration occurs also has the highest Ca concentration, suggesting that the high SO$_4$ concentration could be due to the presence of anhydrite, which has been reported in the Otter Sandstone Formation (Holloway et al., 1989).

Bicarbonate (alkalinity) has a range of <1 to 372 mg L^{-1}, a 95th percentile of 321 mg L^{-1}, and a median of 226 mg L^{-1} (Table 5.1). This distribution is similar to that found in other Permo-
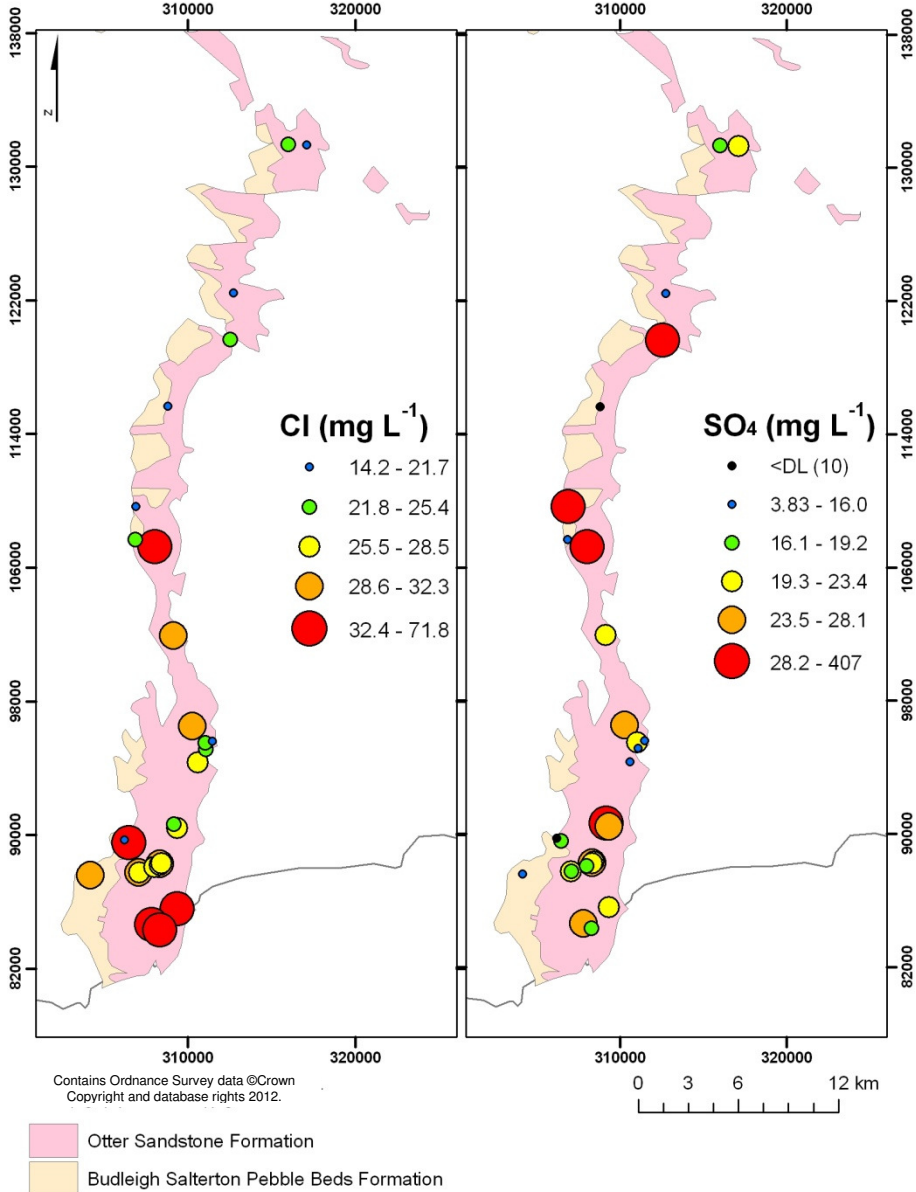

Figure 5.8 Regional variation of Cl and SO$_4$ within the Sherwood Sandstone aquifer

Triassic Sandstone aquifers within the UK. There are two unusual values that are below detection limits (one <1 mg L^{-1}, and one <6 mg L^{-1}), which represent very soft waters with no buffering capacity (the ability to withstand changes in pH, e.g. by acid rain). The first site (with an HCO$_3$ concentration of <1 mg L^{-1}) was sampled from a spring collect, and has a pH of 5.14 and SEC of 139 µS cm^{-1}. This site has very low concentrations of all the major ions except Na and Cl, which are probably elevated due to proximity to the sea. The second site (with a HCO$_3$ concentration of <6 mg L^{-1}) has a pH of 5.2 and SEC of 114 µS cm^{-1}. This site has very low concentrations for all ions. Both of these sites therefore likely represent very young groundwater.

There is some correlation between HCO$_3$ and source aquifer unit. Groundwaters from the Budleigh Salterton Pebble Beds Formation have HCO$_3$ concentrations which range between <1 and 224 mg L^{-1}, while those exploited from the Otter Sandstone Formation range between 185 and 307 mg L^{-1}, groundwater from mixed sources range between 41 and 321 mg L^{-1}, and groundwaters from undefined sources have a HCO$_3$ concentration that ranges between <6.1 and 372 mg L^{-1}.

There are also spatial trends evident, in that the highest concentrations are found in the north of the region (Figure 5.9). This spatial distribution appears very similar to the Ca distribution. Bicarbonate is correlated with the Ca concentration ($r^2 = 0.46$). There is one outlier, which represents a sample taken from an undefined aquifer source unit, which is located in the centre of the study area. It has the highest Ca value, but a HCO$_3$ concentration that represents the 25th percentile of the data, suggesting that there must be another source of Ca at this site. The highest SO$_4$ concentration is found at this site and the sample plots as Ca-SO$_4$ type on the Piper diagram, (Figure 5.1) which indicates that there is localised anhydrite within this aquifer. While the dissolution of anhydrite has dominated the chemistry of this sample, modelled saturation indices indicate that this site (like all the other sites) is undersaturated with respect to anhydrite. This reflects the highly soluble nature of anhydrite. The outlier was removed from the correlation of Ca and HCO$_3$. With this one sample removed there was a strong correlation of HCO$_3$ with Ca ($r^2 = 0.84$), suggesting that calcite is probably the dominant source of Ca and HCO$_3$ in these groundwater samples.

Dissolved organic carbon (DOC) concentration ranges from <0.5 to 6.48 mg L^{-1}, with a 95th percentile of 3.7 mg L^{-1}, and a median of 0.59 mg L^{-1} (Table 5.1). Concentrations are variable in other Permo-Triassic Sandstone aquifers in the UK, although the distribution presented here represents a relatively large range. Compared to the other areas investigated by Shand et al. (2007), minimum, maximum and median concentrations are low. These may be due to the lack of organic-rich superficial deposits (e.g. peat). The DOC that is present will have entered the groundwater system via percolation through overlying soils, and it is likely that the DOC data presented here represent baseline concentrations. The DOC concentrations are generally higher near to the south coast (Figure 5.9), which may be indicative of deeper soil profiles in the lowest lying areas of the study.

Nitrate as N ranges in concentration from 1.58 to 29.5 mg L^{-1}, with a 5th to 95th percentile range of 1.94 to 21.2 mg L^{-1}, and a median of 7.88 mg L^{-1} (Table 5.1) The data form a near straight line on the cumulative-probability graph (Figure 5.5). This reflects the oxidised nature of all the samples. There is, however a small break of slope at 2 mg L^{-1} NO$_3$-N (Figure 5.5). It is possible that values below 2 mg L^{-1} are naturally occurring, but those above 5 mg L^{-1} have been affected by human activities. The concentration of NO$_3$-N in local recharge waters is 1.78 mg L^{-1} (see Table 3.3), indicating that the groundwaters with NO$_3$-N concentrations <2 mg L^{-1} may represent scarcely altered rainfall.
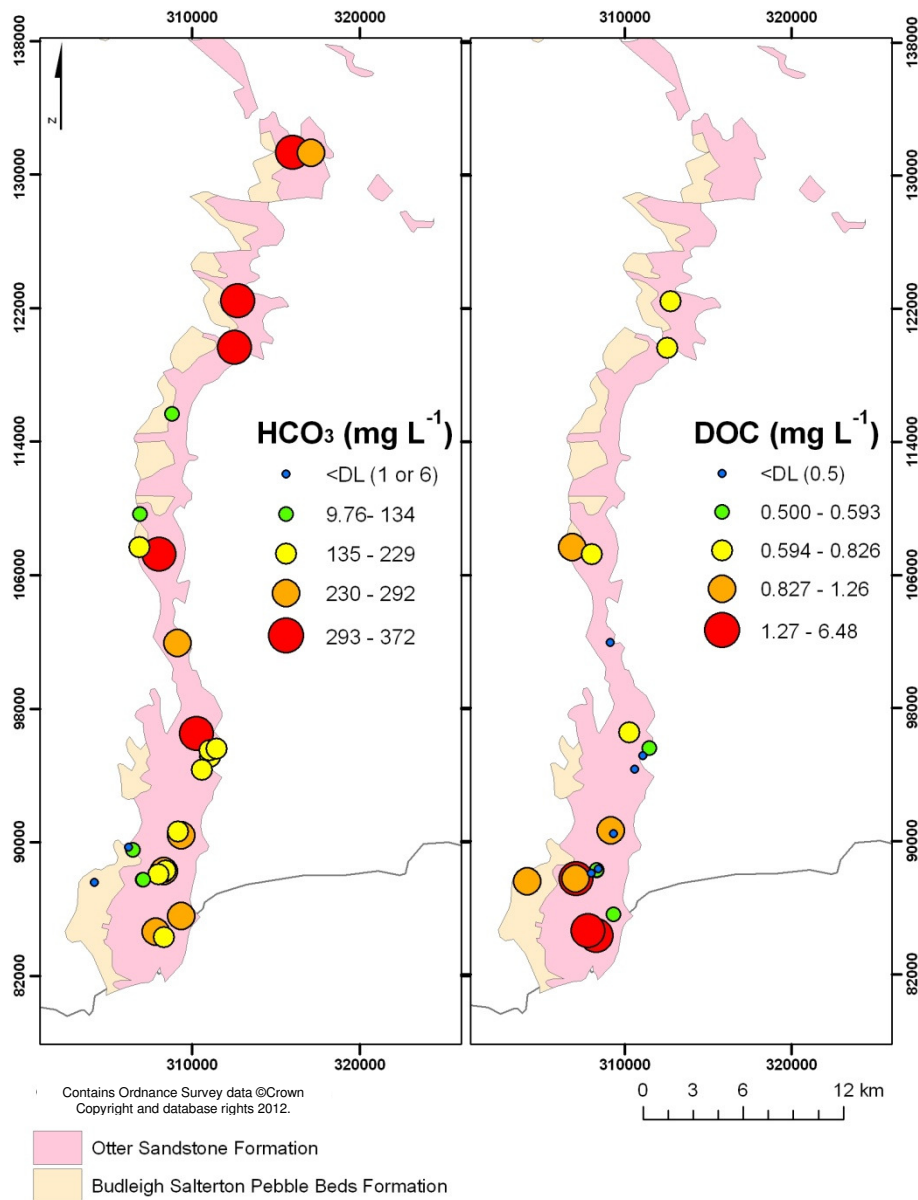
Figure 5.9 Regional variation of HCO_3 and DOC within the Sherwood Sandstone aquifer

There is no relationship of NO_3-N with aquifer source unit and there is no clear spatial trend (Figure 5.10). Of the 28 samples, seven had NO_3-N concentrations above the drinking water limit of 11.3 mg L^{-1} (OPSI, 2010). Of the seven samples above the drinking water limit, five were from farms or nurseries, and two were taken from public supply boreholes which were adjacent to farm land. It seems that the strongest relationship is to local land use, and this also implies the NO_3-N concentrations are impacted by human activity.

Nitrite as N ranges in concentration from <0.003 to 0.00448 mg L^{-1} (Table 5.1). Twenty four of the 28 analyses are non-detects, meaning only minimum and maximum observed concentrations can be quoted. Three of the sites at which NO_2-N was measurable are of agricultural or horticultural land use, and have groundwater concentrations of NO_3-N >11.3 mg L^{-1}, as described above. The measurable NO_2-N concentrations do not correlate with Eh: the largest NO_2-N concentration is in the groundwater at a site with a measured Eh of 400 mV, and the highest NO_3-N concentration. There is no clear spatial trend given the number of censored data (Figure 5.10).

Ammonium as N has a range of <0.003 to 0.192 mg L^{-1}, a 95th percentile of 0.018 mg L^{-1}, and a median of 0.00312 mg L^{-1} (Table 5.1). Ammonium is strongly sorbed onto mineral surfaces and is stable in reducing conditions. Where concentrations are high it is often associated with pollution. In half the samples (14) NH$_4$-N is above the detection limit, although one detection limit is ten times higher than the other. There is no relationship of NH$_4$-N with aquifer source unit. There are no obvious spatial trends in the NH$_4$-N concentration (Figure 5.10). The concentrations are relatively low, which reflects the oxidising nature of the waters. While the maximum concentration may represent contamination (it is over 10 times greater than the next highest concentration, and appears to be located on farmed land), it is unlikely that the remaining samples do. The second highest concentration is found in a sample which was taken from a spring collect in an area surrounded by open heath. The area is used for recreation, although it is surrounded by MOD training land.

Silicon has a concentration range of 3.01 to 7.32 mg L^{-1}, a 5th to 95th percentile range of 3.13 to 6.59 mg L^{-1} and a median of 5.16 mg L^{-1} (Table 5.1). This distribution is typical of Permo-Triassic Sandstone aquifers in UK groundwaters, and represents a rapid attainment of SiO$_2$
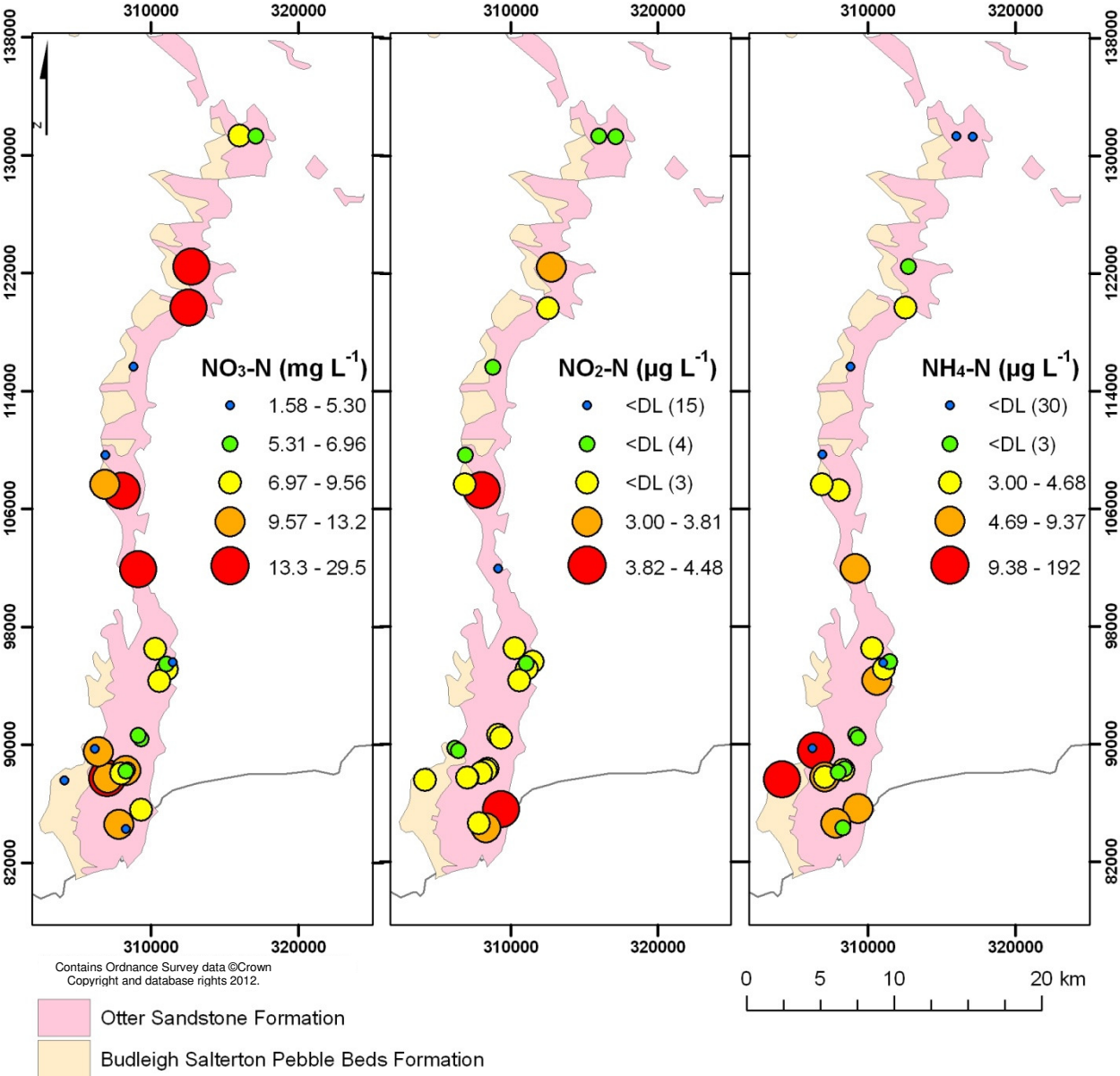
Figure 5.10 Regional variation of N species within the Sherwood Sandstone aquifer

saturation. Despite the abundance of Si in the Earth's crust (it is the second most abundant element) the concentrations of Si are relatively low, owing to low solubility (Hem, 1992). The most soluble of the SiO_2 polymorphs is amorphous SiO_2 and the least soluble is quartz. From modelled saturation indices, quartz is generally close to equilibrium, with a few sites being supersaturated. In contrast, all sites were undersaturated with respect to amorphous SiO_2. There was no correlation of Si groundwater concentration to aquifer source unit, and no particular spatial trend (Figure 5.11). This is likely to be a reflection of the dominance of silicate minerals throughout both aquifer units.

5.2   MINOR AND TRACE CONSITUENTS

Summary statistical data for minor and trace constituents are presented in Table 5.2, Figure 5.12 and Figure 5.13. In addition spatial variations are presented in Figure 5.14 to Figure 5.25. Where all the determinations are below the detection limit the element is not discussed here (see Table 5.2).

Figure 5.11 Regional variation of Si and P within the Sherwood Sandstone aquifer

5.2.1   Phosphorus

Phosphorus has a concentration range of <0.01 to 0.3 mg L^{-1}, a 95th percentile of 0.24 mg L^{-1} and a median of 0.02 mg L^{-1} (Table 5.2). Out of 21 analyses there were six below the detection limit so a 5$^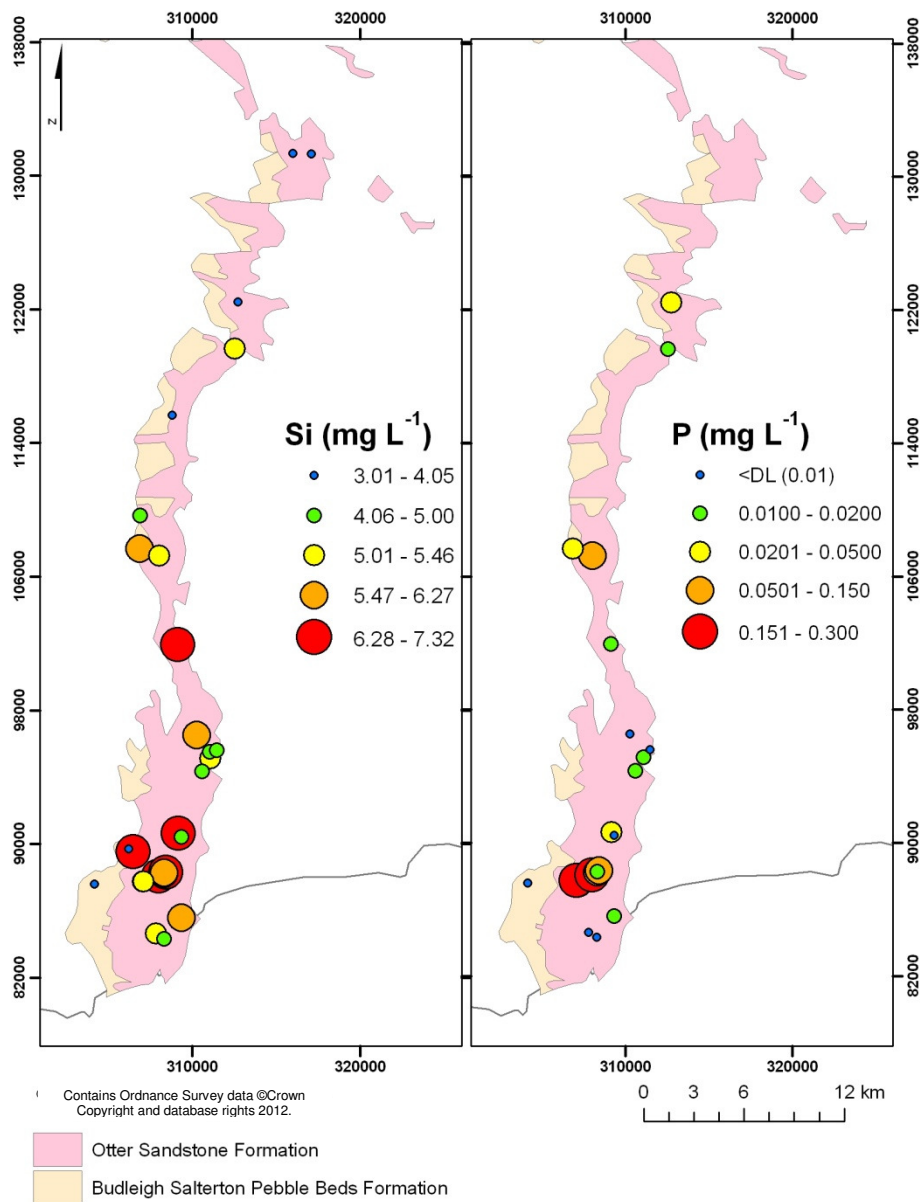{th}$ percentile could not be calculated. When compared to other Permo-Triassic Sandstone aquifers in the UK, this represents a similar distribution, but with a relatively low median (Shand et al., 2007). High concentrations of P are sometimes found in old groundwaters, which can imply that these are relatively young groundwaters. Groundwaters from the Otter Sandstone Formation generally contained P below, or close to, the detection limit. There is one exception to this, where a sample from the Otter Sandstone Formation contained 0.15 mg L^{-1}. In contrast samples from the Budleigh Salterton Pebble Beds Formation were measured in the range 0.03 to 0.3 mg L^{-1}, again with one exception: the site which was a spring collect which probably represented very new groundwater. The highest concentrations are clustered around the area between Colaton Raleigh and Newton Poppleford, although there is no obvious reason why this should be the case.

5.2.2   Halogen elements

The distribution of the data is very similar for all the minor halogen elements (F, Br, I) (Figure 5.12 and Figure 5.13). The cumulative-probability distributions (Figure 5.13) show a small range of concentrations.

Fluoride has a concentration range of <0.05 to 0.156 mg L^{-1}, a 5th to 95th percentile range of 0.0143 to 0.147 mg L^{-1}, and a median of 0.077 mg L^{-1} (Table 5.2). All these values are well within the drinking water limit of 1.5 mg L^{-1} (OPSI, 2010). This is a narrow range, and the median of the distribution is low. When compared to concentrations found in groundwaters in other Permo- Triassic Sandstone aquifers in the UK these data are fairly typical. It is most likely that the source of F is from minor minerals within the aquifer matrix. Fluorite is the most common mineral containing F as a major component, but minerals such as apatite, amphiboles and micas can contain appreciable F concentrations. In most waters the F concentrations are controlled by fluorite saturation as this mineral is relatively insoluble. The modelled saturation indices show that all the waters are undersaturated with respect to fluorite, showing that this mineral must form a very minor part of the mineral matrix, and this is reflected in the low F concentrations of these groundwaters. The highest values of F in the Sherwood Sandstone aquifer groundwaters are generally found in a band between Ottery St Mary and Colaton Raleigh (Figure 5.14). There is no obvious reason for this.
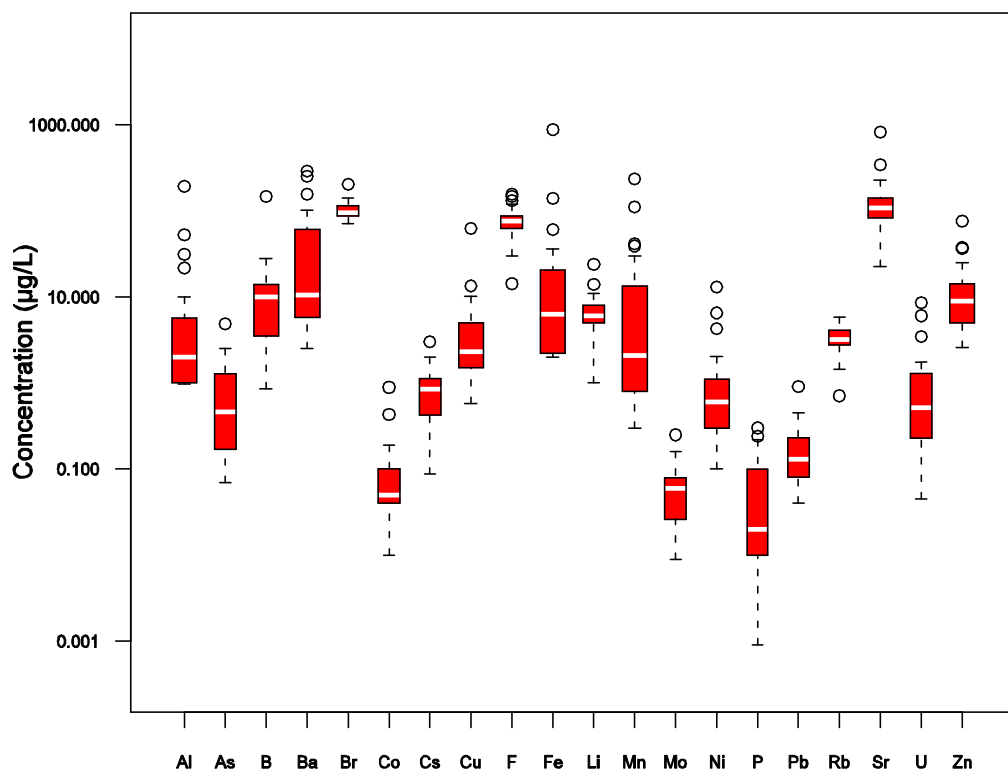
Figure 5.12 Box plot for the minor and trace elements in the Sherwood Sandstone aquifer. For an explanation of the box plots see Section 4.3

Bromide has a concentration range of 0.0707 to 0.205 mg L^{-1}, a 5th to 95th percentile range of 0.0712 to 0.141 mg L^{-1}, and a median of 0.0956 mg L^{-1} (Table 5.2). The geochemistry of Br is similar to that of Cl, and these two elements are generally highly correlated. The data presented here show a weak correlation (r^2=0.12). Edmunds et al (1989) identified that because of the similar geochemical behaviour of Cl and Br the ratio Cl/Br is usually very similar to that of sea water (Cl/Br = 288). They suggested that deviation from this ratio would have diagnostic value in interpreting the origin of Br. The Cl/Br ratios of 21 samples in this study range from 112 to 357. There is no clear relationship of Cl/Br, either spatially, with aquifer source unit, or by land use type. It is likely there are a range of processes causing deviation from the seawater ratio. Most calculated ratios (n=13) are less than the seawater value of 288, which indicates Br enrichment. This may be caused by influences from organic sources, or water vapour enriched in Br owing to its high volatility. This latter effect is evident in rainfall (after Edmunds, W.M. et al., 1989). Seven ratios are greater than 288. If Cl/Br values far exceed 288, which indicate Br depletion, it is likely that there has been a dilution effect from a halite source; either a natural geological source or from agriculture or industry (Edmunds, W.M. et al., 1989). The Cl/Br values are moderately higher than that of sea water, which is most likely caused naturally on infiltration (Edmunds, W. M., 1996).

While there is no conclusive spatial trend in Br concentrations, many of the highest values are found in groundwaters in the south of the study area (Figure 5.14). As with Cl there may be a maritime input of Br at these sites. Where there are high concentrations of Br in groundwaters in the north of the region there may be inputs from organic contamination, as these sites are either agricultural or horticultural.

Table 5.2 Statistical summary of data for minor and trace elements

	units	n	n(c)	min	mean	max	P5	P25	P50	P75	P90	P95
Ag	µg L^{-1}	21	21	<0.05		<0.05						
Al	µg L^{-1}	27	3	<10	13.4	194	1	1	2	7	31.3	53
As	µg L^{-1}	21	0	0.07	0.97	4.87	0.09	0.17	0.46	1.28	2.13	2.52
B	µg L^{-1}	27	15	<10	14.5	147	1.47	3.54	10	14	21.2	26.5
Ba	µg L^{-1}	27	0	2.5	49.6	289	2.8	5.3	10.5	64.3	155	252
Be	µg L^{-1}	21	14	<0.001	0.013	0.09	8.84×10^{-5}	0.000472	0.00187	0.01	0.03	0.09
Br	mg L^{-1}	21	0	0.071	0.105	0.205	0.0712	0.087	0.0956	0.114	0.129	0.141
Cd	µg L^{-1}	27	5	<0.01	0.022	0.154	0.01	0.01	0.01	0.02	0.04	0.104
Ce	µg L^{-1}	21	5	<0.002	0.016	0.226		0.002	0.003	0.009	0.017	0.019
Co	µg L^{-1}	21	0	0.01	0.118	0.89	0.01	0.04	0.05	0.1	0.19	0.43
Cr	µg L^{-1}	27	6	<0.5	0.353	3.36	0.06	0.17	0.21	0.28	0.53	0.56
Cs	µg L^{-1}	21	0	0.088	0.947	3	0.172	0.425	0.851	1.12	1.71	1.99
Cu	µg L^{-1}	27	2	<1	5.74	62.2	0.8	1.5	2.2	5.3	10.1	13.5
Dy	µg L^{-1}	21	13	<0.002	0.005	0.06	4.44×10^{-6}	4.05×10^{-5}	0.000264	0.002	0.004	0.025
Er	µg L^{-1}	21	12	<0.002	0.003	0.031	1.89×10^{-5}	0.000109	0.000502	0.002	0.004	0.022
Eu	µg L^{-1}	21	12	<0.002	0.004	0.024	4.87×10^{-5}	0.00024	0.000915	0.003	0.016	0.023
F	mg L^{-1}	21	1	<0.05	0.080	0.156	0.0143	0.0625	0.0765	0.0881	0.132	0.147
Fe	µg L^{-1}	27	3	<30	48.7	880	2	2	5	22	61	140
Ga	µg L^{-1}	21	21	<0.03		<0.03						
Gd	µg L^{-1}	21	13	<0.002	0.006	0.068	8.47×10^{-6}	6.72×10^{-5}	0.000378	0.003	0.005	0.025
Hf	µg L^{-1}	21	15	<0.01	0.006	0.02	0.00147	0.00274	0.00464	0.01	0.01	0.02
Ho	µg L^{-1}	21	19	<0.002		0.012						
I	mg L^{-1}	21	0	0.006	0.009	0.016	0.00659	0.008	0.0086	0.0101	0.011	0.012
La	µg L^{-1}	21	2	<0.002	0.015	0.214		0.002	0.003	0.006	0.012	0.013
Li	µg L^{-1}	27	6	<100	7.05	24	1	5	6	8	11	14
Lu	µg L^{-1}	21	19	<0.002		0.003						
Mn	µg L^{-1}	27	1	<10	19.9	234	0.4	0.8	2.1	19	41.3	111
Mo	µg L^{-1}	21	6	<0.03	0.071	0.25			0.06	0.08	0.15	0.16
Nb	µg L^{-1}	21	21	<0.02		<0.02						
Nd	µg L^{-1}	21	15	<0.01	0.017	0.28	8.79×10^{-6}	8.61×10^{-5}	0.000581	0.01	0.02	0.02
Ni	µg L^{-1}	27	2	<1	1.47	13	0.2	0.3	0.7	1.14	4.3	6.5
P	µg L^{-1}	21	6	<0.01	0.065	0.3			0.02	0.06	0.22	0.24
Pb	µg L^{-1}	27	6	<2	0.206	0.91	0.04	0.08	0.13	0.23	0.43	0.45
Pr	µg L^{-1}	21	16	<0.002	0.004	0.067	1.75×10^{-7}	2.97×10^{-6}	3.15×10^{-5}	0.0004	0.002	0.003
Rb	µg L^{-1}	21	0	0.71	3.24	5.82	1.44	2.77	3.2	4.14	4.59	5.41
Sb	µg L^{-1}	21	0	0.017	0.094	0.209	0.023	0.04	0.076	0.146	0.182	0.199
Se	µg L^{-1}	21	1	<0.1	0.548	1.3	0.2	0.3	0.4	0.7	1.2	1.2
Sm	µg L^{-1}	21	14	<0.002	0.004	0.059	4.71×10^{-6}	3.96×10^{-5}	0.000234	0.002	0.004	0.012
Sn	µg L^{-1}	21	3	<0.02	0.071	1.04		0.02	0.02	0.03	0.03	0.03
Sr	µg L^{-1}	27	0	22.5	147	827	23	81.2	109	145	229	344
Ta	µg L^{-1}	21	21	<0.02		<0.02						
Tb	µg L^{-1}	21	19	<0.002		0.011						
Th	µg L^{-1}	21	18	<0.02		0.03						
Ti	µg L^{-1}	21	9	<0.05	0.075	0.19			0.05	0.07	0.14	0.14
Tl	µg L^{-1}	21	11	<0.01	0.01	0.04	0.00123	0.00291	0.00617	0.01	0.02	0.03
Tm	µg L^{-1}	21	19	<0.002	NA	0.004						
U	µg L^{-1}	21	0	0.045	1.37	8.53	0.065	0.227	0.519	1.29	3.47	6.05
V	µg L^{-1}	21	5	<0.1	0.519	3.7		0.1	0.3	0.6	0.9	1.1
W	µg L^{-1}	21	21	<0.01		<0.01						
Y	µg L^{-1}	21	1	<0.005	0.046	0.385	0.006	0.01	0.014	0.019	0.063	0.275
Yb	µg L^{-1}	21	11	<0.002	0.003	0.026	8.16×10^{-5}	0.000313	0.000981	0.003	0.004	0.018
Zn	µg L^{-1}	27	4	<5	14.1	76.4	4.3	4.7	8.9	14.2	36.5	37.4
Zr	µg L^{-1}	21	21	<0.05		<0.05						

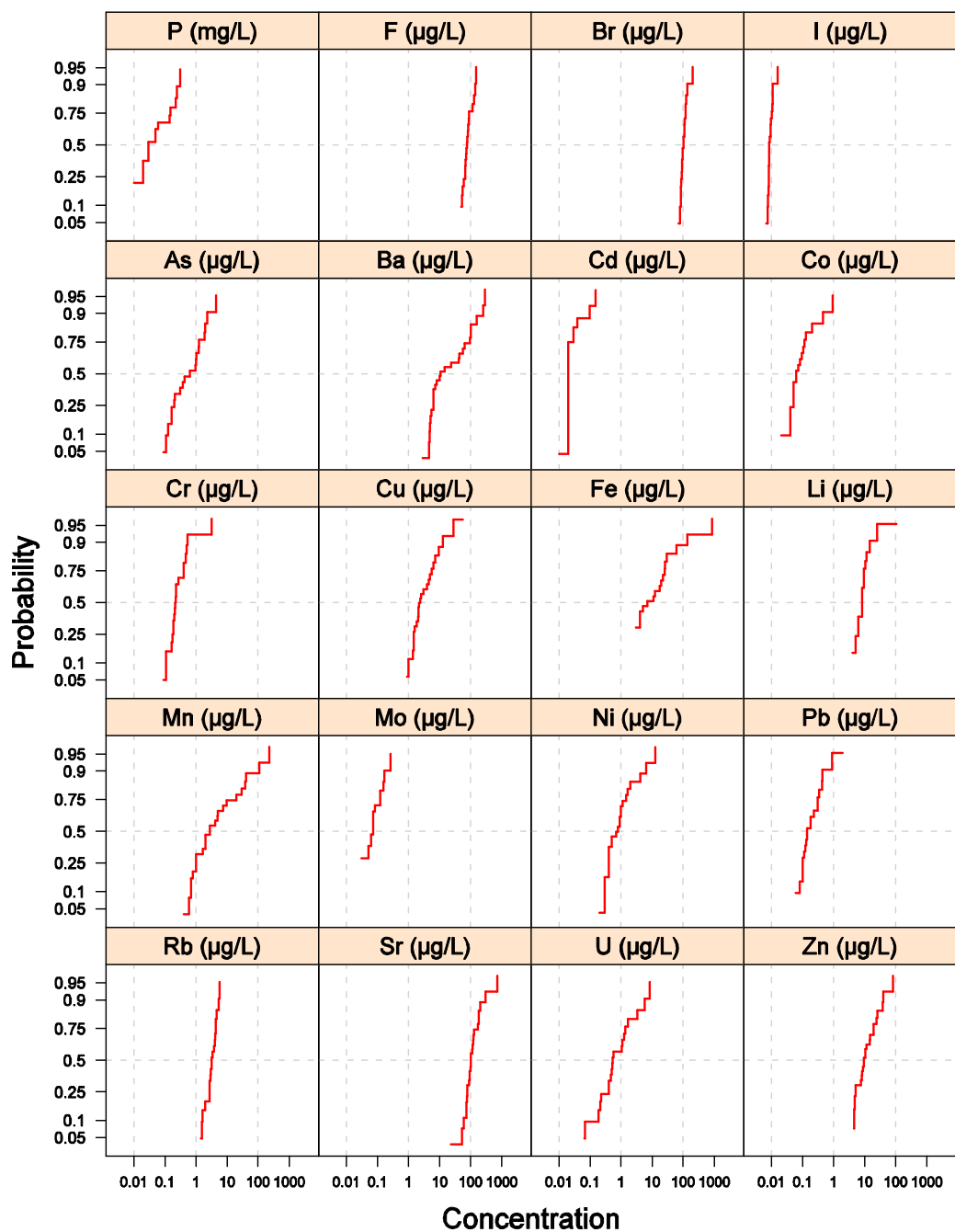P= percentile; n(c) = number censored; min and max are observed values

Figure 5.13 Cumulative probability plots for selected trace elements in the groundwater from the Sherwood Sandstone aquifer

Iodine has a concentration range of 5.5 to 16.4 μg L^{-1}, a 5th to 95th percentile range of 6.6 to 11.5 μg L^{-1} and a median of 8.6 μg L^{-1} (Table 5.2). This distribution is fairly typical of Permo-Triassic Sandstone aquifers in the UK. Iodine generally behaves conservatively like Br and Cl. However, the ratio of I/Cl is generally higher in rainfall than sea water because iodine is strongly fractionated. The main sources of I in groundwaters are rainfall and organic material. The regional variation of I is very similar to that of Br, especially in the north of the study area (Figure 5.14). Of the six samples with the highest I concentrations, five were taken from sites where the land use was associated with horticulture or agriculture. These groundwaters may be affected by interaction with organic material from the activities undertaken at these sites.
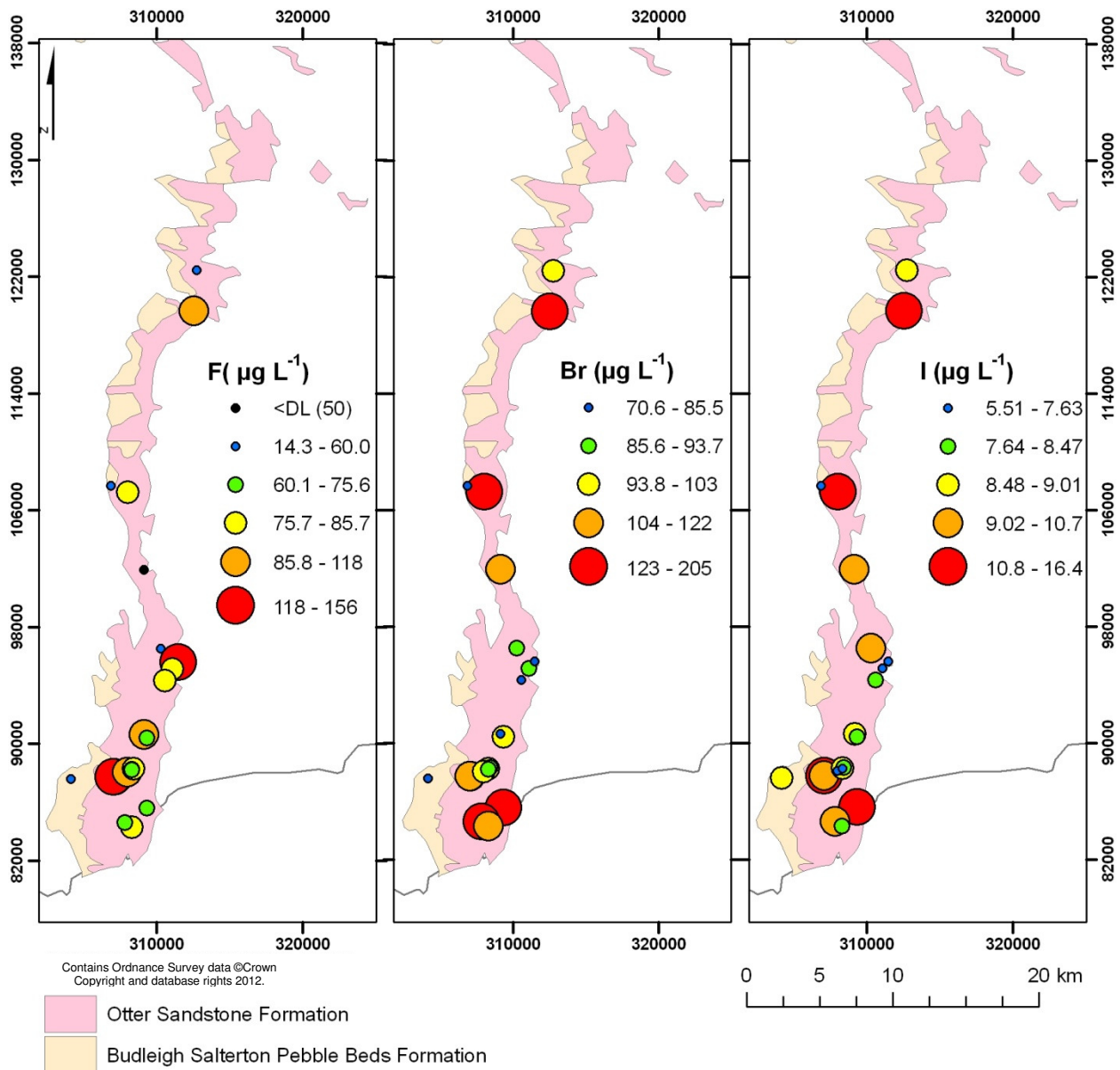
Figure 5.14 Regional variation of halogen elements within the Sherwood Sandstone aquifer. The black circle indicate a detection limit (stated in parenthesis) which exceed measured analyses

5.2.3 Alkaline earth elements

Barium has a concentration range of 2.5 to 289 µg L^{-1}, a 5th to 95th percentile range of 2.8 to 252 µg L^{-1} and a median of 10.5 µg L^{-1} (Table 5.2). The Ba data are spread across a similar range to other Permo-Triassic Sandstone aquifers in the UK, but the median is lower. Barium concentrations in groundwaters are mostly controlled by barite ($BaSO_4$) saturation (Hem, 1992). North of Kentisbeare the groundwaters were generally saturated with respect to barite, but south of this the waters were undersaturated. Sulphate concentrations of 10 or 100 mg L^{-1} should limit Ba concentration in solution to 140 µg L^{-1} or 14 µg L^{-1} respectively (Hem, 1992). However in one sample the SO_4 concentration was 407 mg L^{-1}, yet the Ba concentration was 103 µg L^{-1}; likewise in a sample with a SO_4 concentration of 52 mg L^{-1} the Ba was present at 155 mg L^{-1}. Both these samples were super saturated with respect to barite, while most other samples were undersaturated. The highest concentrations were found in the north and west of the study area (Figure 5.15). There is no relationship between Ba and aquifer source type, indicating a mineralogical control over solubility. In the Otter Valley the Ba concentrations have a negative correlation to the SO_4 concentrations, highlighting the barite control. The small range is typical

46

of elements controlled by solubility, and the lack of obvious sources of local contaminants suggests that the observed Ba range represents baseline compositions.

Strontium has a concentration range of 22.5 to 827 µg L^{-1}, a 5th to 95th percentile range of 23 to 344 µg L^{-1} and a median of 109 µg L^{-1} (Table 5.2). When compared to other Permo-Triassic Sandstone aquifers in the UK this is a relatively narrow range with a low median. Strontium is a fairly common trace element in groundwater, and it has a similar chemistry to Ca owing to its similar ionic radius (Hem, 1992). It is often present in high concentrations in Ca-bearing minerals. The spatial distribution is very similar to that of Ca (Figure 5.15 and see also Figure 5.6), being more concentrated in the north of the region. It is therefore likely that Sr is derived from the calcite cements, which are more common in the north of the study area. Sr concentrations are generally higher in Otter Sandstone Formation groundwaters (77 to 229 µg L^{-1}) than in Budleigh Salterton Pebble Beds Formation groundwaters (22.5 to 139 µg L^{-1}). The fact that Ca-bearing minerals are relatively minor in the Sherwood Sandstone aquifer probably accounts for the relatively low Sr concentrations.
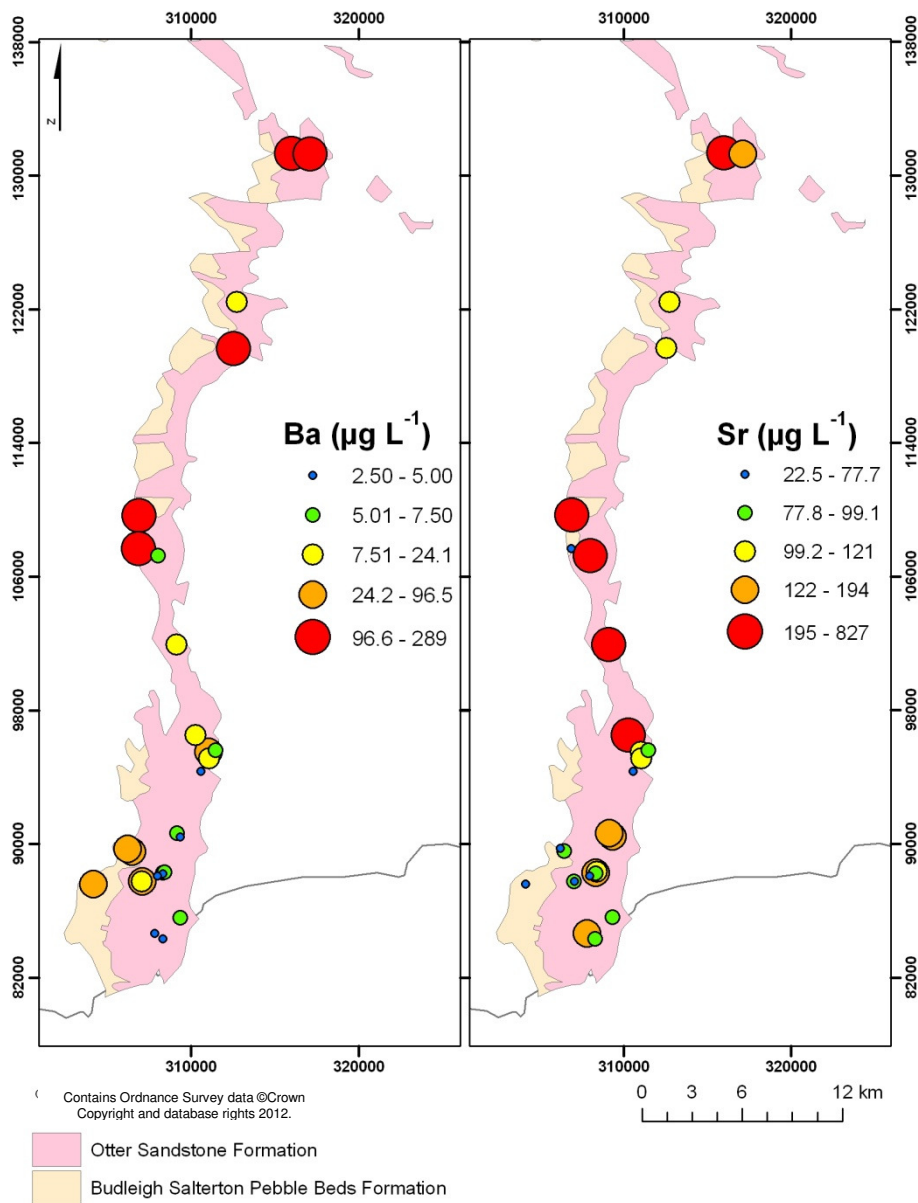

Figure 5.15 Regional variation of Ba and Sr within the Sherwood Sandstone aquifer

5.2.4 Alkali metals

Lithium has a concentration range of <100 to 24 µg L^{-1}, a 5th to 95th percentile range of 1 to 14 µg L^{-1} and a median of 6 µg L^{-1} (Table 5.2). While six values are below the detection limit, it is difficult to interpret these as the detection limit is four times higher than the maximum concentration. These non-detect data are therefore ignored in the discussion below. When compared to other Permo-Triassic Sandstone aquifers in the UK the range presented here is relatively narrow with a fairly low median. The likely source of Li is as a trace constituent in silicate minerals (e.g. the metaquartzite that makes up most of the formation) or where it substitutes for Mg in clays. Lithium often shows an increased concentration with increasing residence times (Shand et al., 2007). Figure 5.16 shows that the highest concentrations are found to the east of the study area. The lowest concentrations are generally found in groundwaters from the Budleigh Salterton Pebble Beds Formation and mixed sources (1 to 8 µg L^{-1}), and higher concentrations are found in groundwaters from the Otter Sandstone Formation (6 to 24 µg L^{-1}, and one sample with a concentration of 4 µg L^{-1}).
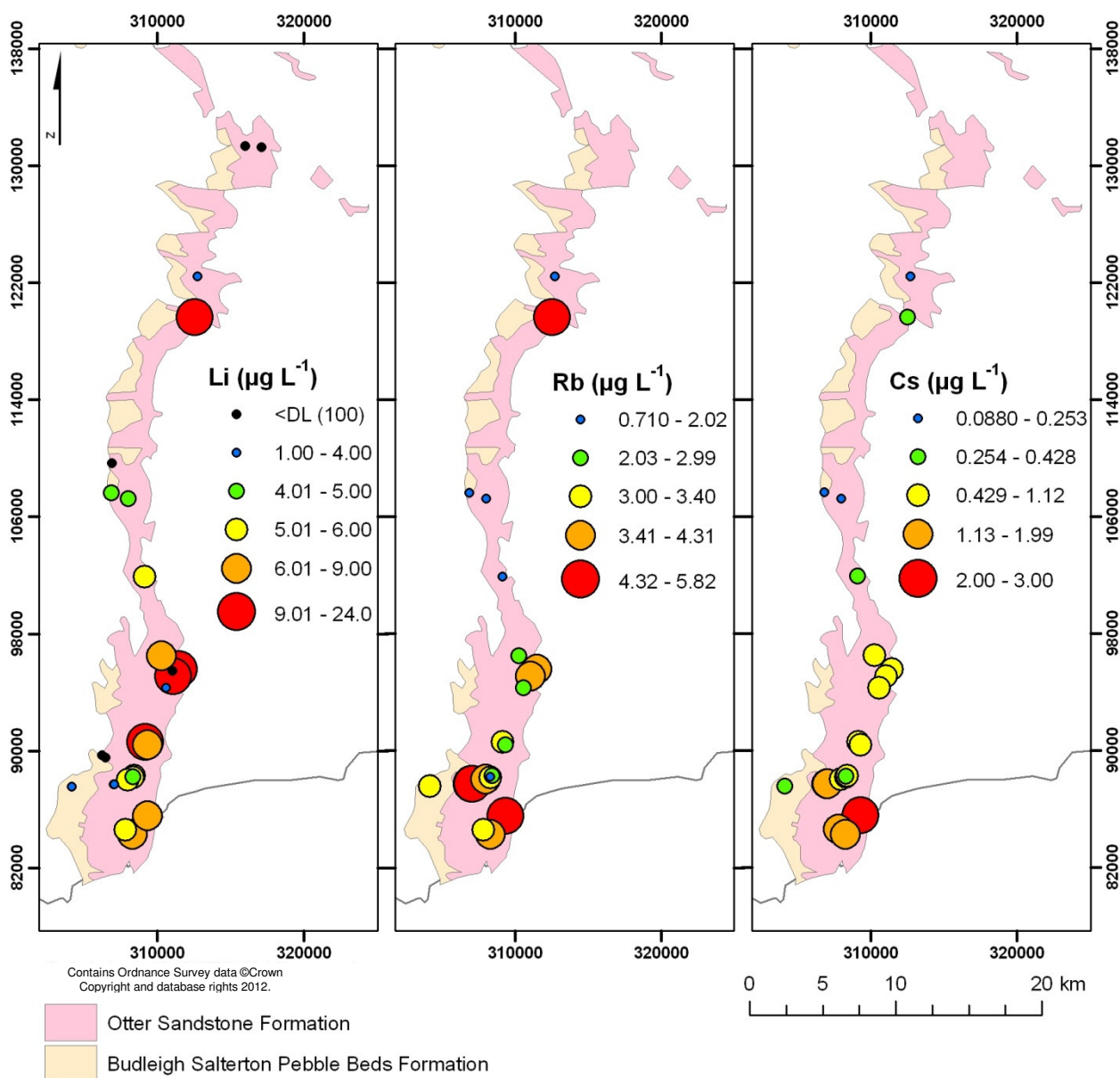

Figure 5.16 Regional variation of the alkali metals within the Sherwood Sandstone aquifer. Black circles for Li indicate a detection limit (stated in parenthesis) which exceed measured analyses

Rubidium has a concentration range of 0.71 to 5.82 μg L^{-1}, a 5th to 95th percentile range of 1.44 to 5.41 μg L^{-1} and a median of 3.2 μg L^{-1} (Table 5.2). The distribution is typical of other Permo-Triassic Sandstone aquifers in the UK. Rubidium often displays similar geochemical behaviour to K, as it has a similar ionic radius. There is a weak correlation between groundwater concentrations of these two elements (r^2=0.104), although there are few similarities between the spatial variations (Figure 5.16 and Figure 5.7). There is also no relationship between source aquifer unit and Rb concentration. It has been suggested that the source of Rb in other Permo-Triassic Sandstone aquifers is dissolution of K-feldspars (Shand et al., 2007), but it is possible that desorption from clay minerals is responsible.

Caesium has a concentration range of 0.088 to 3 μg L^{-1}, a 5th to 95th percentile range of 0.172 to 1.99 μg L^{-1} and a median of 0.85 μg L^{-1} (Table 5.2). The range is relatively large when compared to other Permo-Triassic Sandstone aquifers in the UK (Shand et al., 2007). The highest concentrations are found in the south of the study area, and there appears to be a strong north-south trend (Figure 5.16). There is no relationship between source aquifer unit and Cs concentration. There is also little similarity to the distributions of Rb and K, despite the geochemical similarities, and enrichment of Cs in K-feldspars and K-micas. It is likely that the K-feldspars found in the Sherwood Sandstone matrix are the most likely source of Cs in the groundwaterand that the concentrations presented here represent baseline compositions.

5.2.5 Iron and manganese

Iron and Mn are both redox- and pH-sensitive. Iron oxides are soluble and Fe is mobilised as Fe(II) under moderately reducing and acidic conditions. Under oxidising conditions Fe(III) prevails. This forms insoluble Fe oxyhydroxides at circum-neutral pH (Drever, 1997).

Iron has a concentration range of <30 to 880 μg L^{-1}, a 5th to 95th percentile range of 2 to 140 μg L^{-1} and a median of 5 μg L^{-1} (Table 5.2). The range is fairly small when compared other Permo-Triassic Sandstone aquifers in the UK. Where both Fe and Eh data are available the highest Fe concentration (61 μg L^{-1}) is found in the groundwater with the lowest Eh value (273 mV). The remaining data have relatively low Fe values (2-26 μg L^{-1}) and are oxidising waters (Eh = 371 to 490 mV). There is little relationship between source aquifer unit and Fe concentration, and the spatial variation is indistinct (Figure 5.17). It is difficult to see spatial similarities to the Eh values because, with the exception of a few outliers, the variations are quite small. The maximum observation exceeds the drinking water standard of 200 μg L^{-1} (OPSI, 2010), this water would require treatment if used for potable supply. There are no Eh data available for this source.

Manganese has a concentration range of <10 to 234 μg L^{-1}, a 5th to 95th percentile range of 0.4 to 111 μg L^{-1} and a median of 2.1 μg L^{-1} (Table 5.2). The range is fairly small when compared to other Permo-Triassic Sandstone aquifers in the UK. There is a strong relationship between the groundwater concentrations of Mn and those of Fe, although the relationship with Eh is weak (r^2=0.103). Like Fe, as discussed above, where Eh and Mn are available the highest Mn concentration relates to the lowest Eh, and most of the remaining data form a cluster of low Mn concentrations in oxidising waters, meaning there are no spatial trends in the data (Figure 5.17). Two samples contained Mn in excess of the drinking water limit of 50 μg L^{-1} (OPSI, 2010). One of these is from the sample that contained 880 μg L^{-1} Fe.

The limited ranges and low medians of Mn and Fe reflect the oxidising nature of the Sherwood Sandstone aquifer. The Fe is likely to be derived from oxidised coatings and rock cements, and the Mn is likely to be associated with Fe. The concentrations of Fe and Mn presented here most likely represent baseline compositions up to the 95th percentile at least.
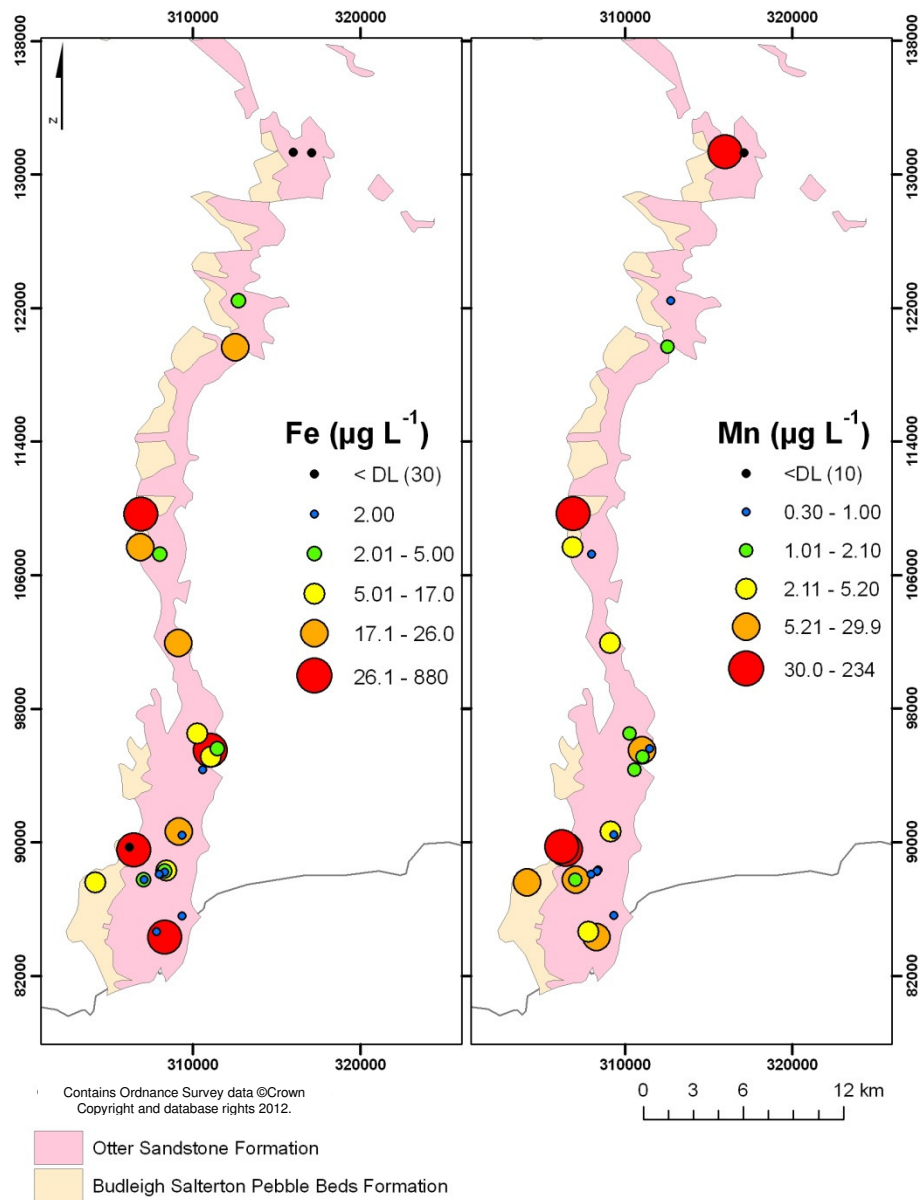
Figure 5.17 Regional variation of Fe and Mn within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

5.2.6   Rare earth elements

The rare earth elements (REE) are here, as commonly, considered as a group along with Yttrium due to their similar behaviour in the environment (Cornell, 1993). The REEs are most commonly below detection limits in groundwaters in the UK (Shand et al., 2007). Yttrium, La and Ce are found in this study to be detectable in most groundwaters analysed. The remaining REEs are detectable in 10 to 50% of the samples collected. The maximum REE concentration is 0.28 µg L^{-1} (Nd) and Y has a concentration of 0.385 µg L^{-1} (Table 5.2).

The highest concentration of each REE, except Eu, is found in the same sample from a site about 3 km west of Colaton Raleigh, taken from the Budleigh Salterton Pebble Beds Formation. Most of the next highest concentrations of the REEs are found at a site near Colaton Raleigh, also taken from the Budleigh Salterton Pebble Beds Formation aquifer. These two sites are the only sites where Tb, Ho, Tm and Lu are above detection limits in the groundwater. Aside from these two sites, most other values are below, or close to, detection limits, so spatial comparison is difficult. Figure 5.18 presents examples of REE distribution, showing an example of a REE
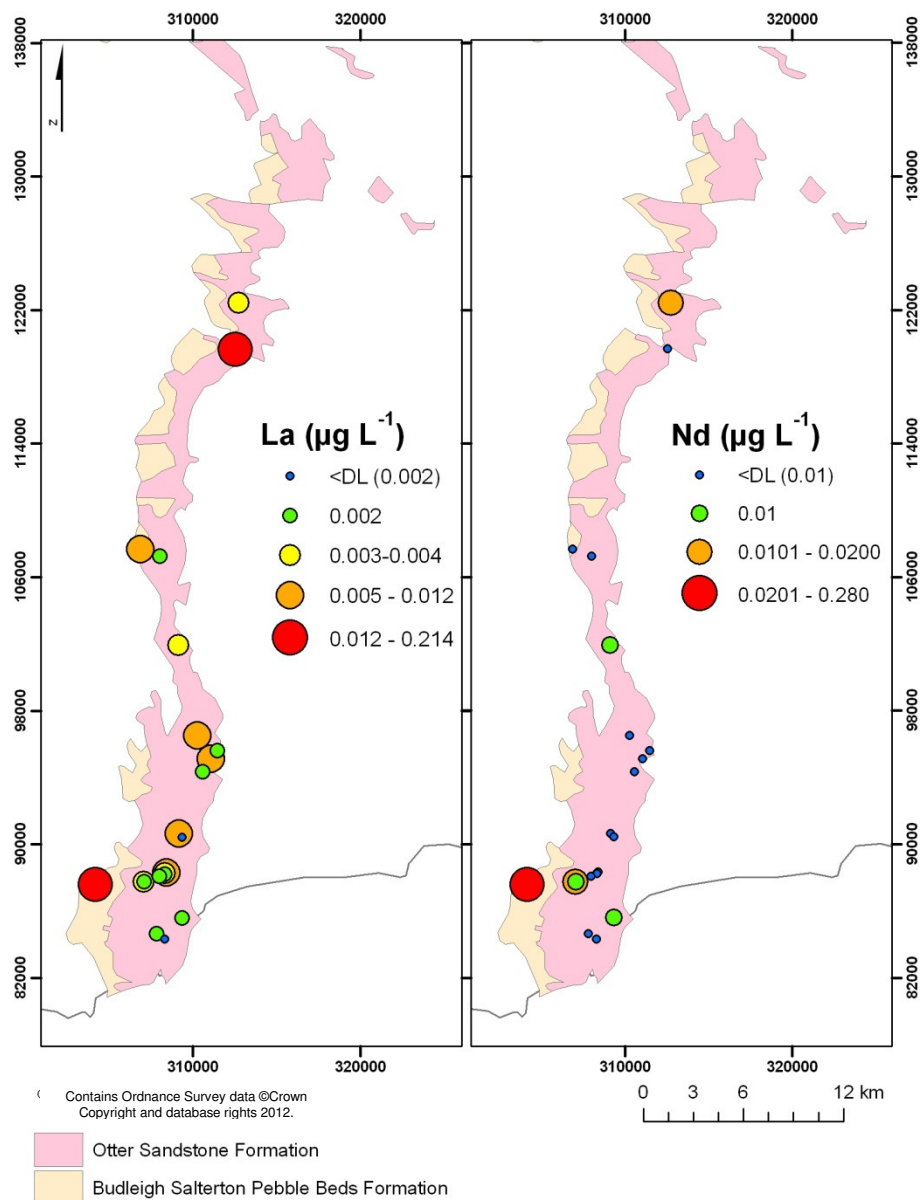
Figure 5.18 Regional variation of La and Nd within the Sherwood
Sandstone aquifer, presented to exemplify REE distribution

where most sites contain measurable concentrations (La), and an example where most measurements are below the detection limit (Nd).

5.2.7 Other trace elements

Aluminium has a concentration range of <10 to 194 µg L^{-1}, a 5th to 95th percentile range of 1 to 53 µg L^{-1} and a median of 2 µg L^{-1} (Table 5.2). This distribution is fairly typical of groundwater concentrations in Permo-Triassic Sandstone aquifers. The highest groundwater concentrations are generally found in the Budleigh Salterton Pebble Beds Formation, where the Al concentration ranges from 2 to 53 µg L^{-1}. In comparison the Al concentrations in Otter Sandstone Formation groundwaters range from 1 to 7 µg L^{-1}, with 3 samples <10 µg L^{-1}. The highest concentration of Al was from a sample of undefined source and is close to the drinking water standard of 200 µg L^{-1} (OPSI, 2010). The spatial distribution reflects this relationship with source aquifer: the highest concentrations of Al are found in groundwaters to the west of the study area (Figure 5.19). The distribution is most likely to be linked to pH. While Al is one of the most abundant elements on Earth, with an average crustal and soil abundance of 6 to 7 wt%, it is classed as a trace element in natural waters because its solubility is limited at circum-neutral
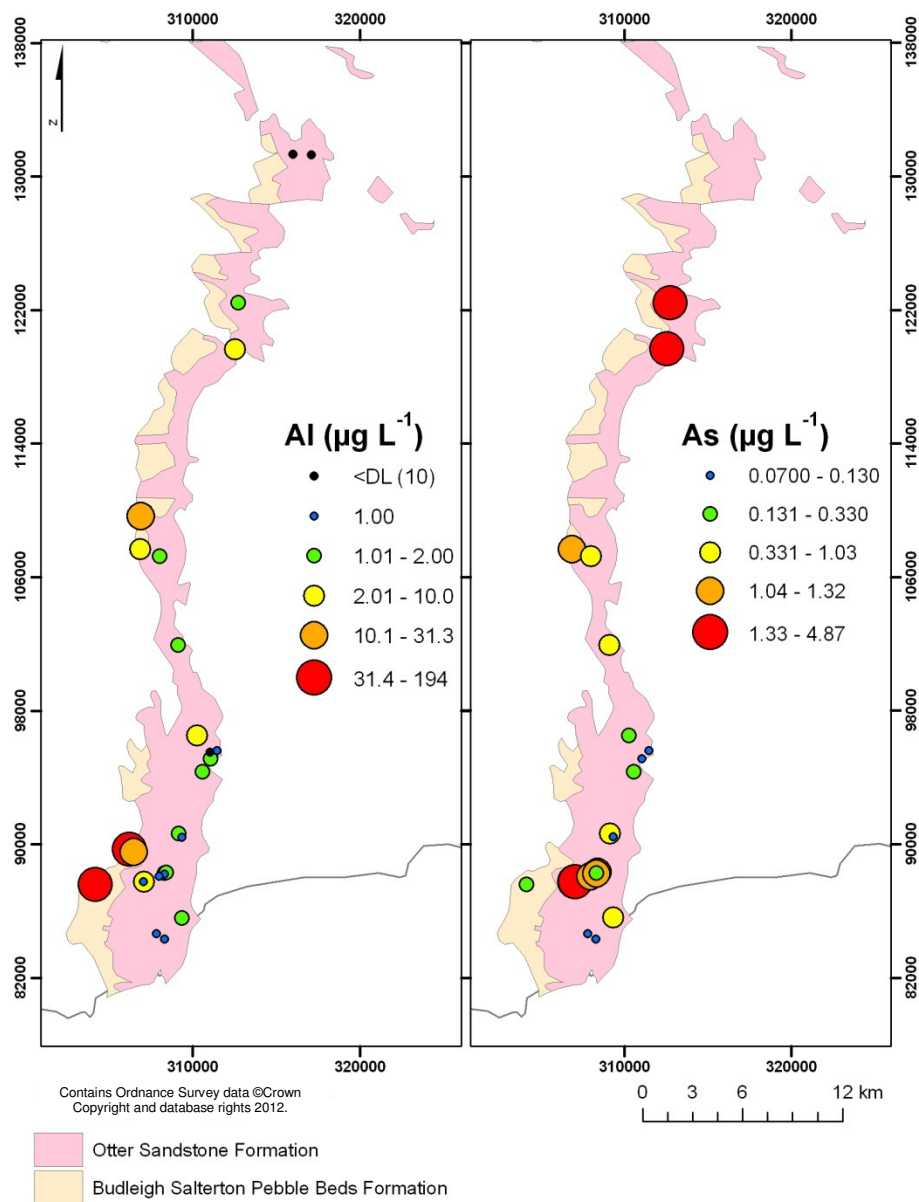
51

Figure 5.19 Regional variation of Al and As within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

pH values (pH 6-8). Such pH values are typical of ground and surface waters, and hence Al concentrations are generally limited. The Budleigh Salterton Pebble Beds Formation groundwaters are more acidic than most groundwaters (pH values in the range of 5.1 to 6.9), and this will allow higher concentrations of Al. Where the pH is >6 the Al ranges from <10 to 31 μg L^{-1}, and these data have a 5th to 95th percentile range of <10 to 9.7 μg L^{-1}. However, where the pH is <6 the Al ranges from 10 to 194 μg L^{-1}. The original source of Al is most likely to be from the K-feldspars, common within the matrix of the Sherwood Sandstone aquifer, or traces of clays and micas (after Shand et al., 2007). There is no evidence that the Al concentrations in the groundwaters are of anthropogenic origin and so the range is taken to represent baseline compositions.

Arsenic has a concentration range of 0.07 to 4.87 μg L^{-1}, a 5th to 95th percentile range of 0.09 to 2.52 μg L^{-1} and a median of 0.46 μg L^{-1} (Table 5.2). When compared to other UK Permo-Triassic Sandstone aquifers this range is low. All waters are well below the 10 μg L^{-1} limit for drinking water (OPSI, 2010). Arsenic has two main oxidation states in groundwater, As(III) and As(V). The As(III) form is typically the dominant form in Fe reducing conditions. As(V) is

strongly sorbed to metal oxides at near-neutral and acidic pH values, and hence under oxidising conditions the concentrations of dissolved As are expected to be low (Shand et al., 2007). It is interesting to note therefore, that while there is little clear spatial distribution, the highest As concentrations are found in oxidising and circum-neutral groundwaters (Figure 5.19).

Boron has a concentration range of <10 to 147 µg L^{-1}, a 5th to 95th percentile range of 1.47 to 26.5 µg L^{-1} and a median of 10 µg L^{-1} (Table 5.2). In over half the samples B was below the detection limit. The range is typical of groundwaters from Permo-Triassic Sandstone aquifers in the UK. Low concentrations are indicative of a source mainly derived from rainwater, and typical of aquifers with a short residence time (Shand et al., 2007). There is no relationship of B with aquifer source type and no spatial trends are evident (Figure 5.20). Boron in these groundwaters is most likely sourced from clays and Fe oxides within the Sherwood Sandstone aquifer cement.

Beryllium has a concentration range of <0.001 to 0.09 µg L^{-1}, a 5th to 95th percentile range of 8.84×10^{-5} to 0.09 µg L^{-1} and a median of 0.00187 µg L^{-1} (Table 5.2). This distribution is typical
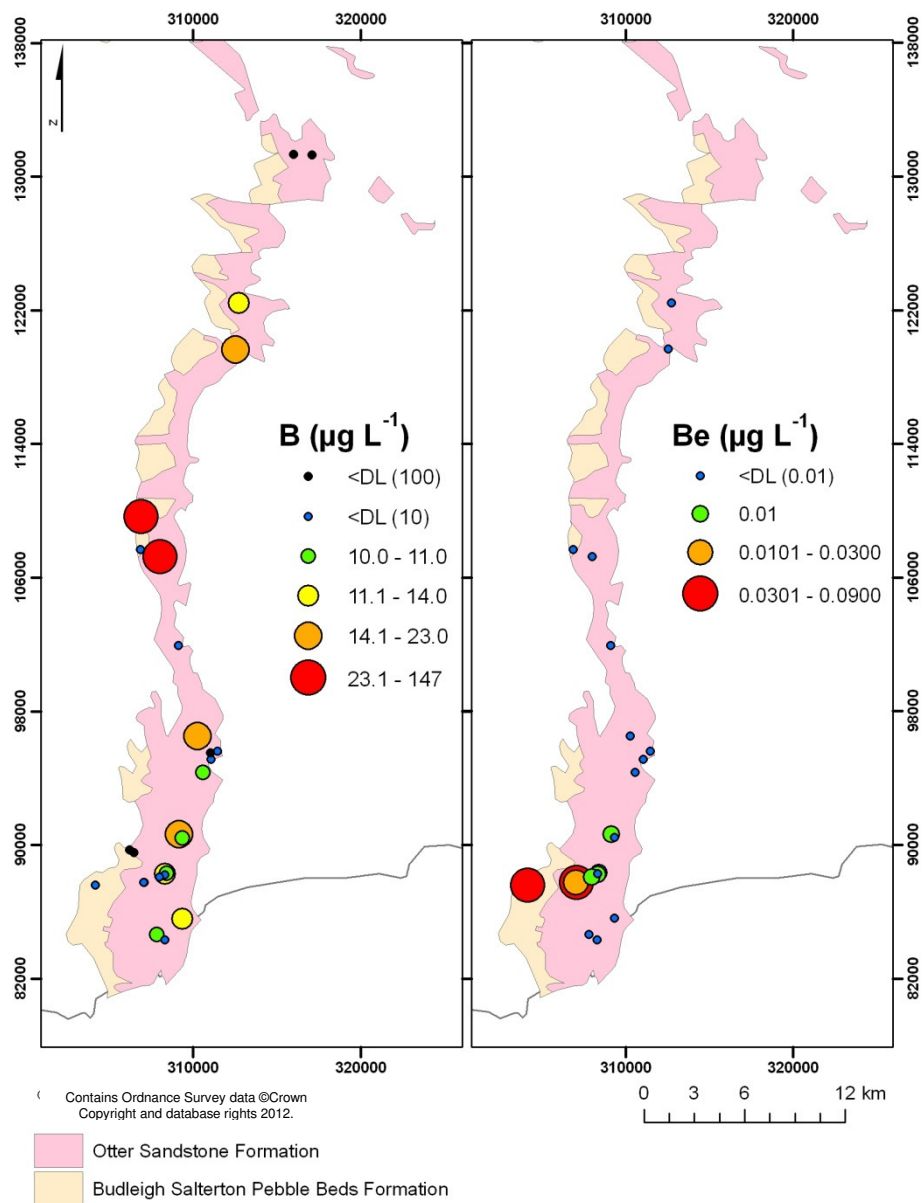

Figure 5.20 Regional variation of B and Be within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

of most UK groundwaters. In two thirds of the Sherwood Sandstone groundwater samples Be was below the detection limit. All the samples with detectable Be are clustered around Newton Poppleford, Colaton Raleigh and Colaton Raleigh Common (Figure 5.20). Of the 21 Be analyses only one sample taken from the Otter Sandstone Formation had detectable Be, while only one sample from the Budleigh Salterton Pebble Beds Formation did not contain detectable Be. Berylium has been found in enhanced concentrations (up to 10 μg L^{-1}) in low-pH waters (Shand et al., 2007), and the detectable Be here is found in groundwaters with pH <6.8. Beryllium occurs in silicate minerals, substituting for Al or Si. It is likely that the Be source is naturally occurring aquifer minerals, and the low pH values mobilise Be. These concentrations probably represent baseline compositions.

Cadmium has a concentration range of <0.01 to 0.154 μg L^{-1}, a 5th to 95th percentile range of 0.01 to 0.104 μg L^{-1} and a median of 0.01 μg L^{-1} (Table 5.2). Most of the samples contain Cd at, or close to, the detection limit. Only two samples contain Cd at a concentration >0.04 μg L^{-1} (0.104, and 0.154 μg L^{-1}). This kind of distribution is fairly typical of groundwaters in the Permo-Triassic Sandstone aquifers (Shand et al., 2007), although it is difficult to compare directly as the detection limit for the data presented in this study appears to be lower than for the Cd data presented by Shand et al. (2007). The lowest concentrations of Cd are found in Otter Sandstone Formation groundwaters (<0.1 to 0.1 μg L^{-1}), and Cd is found in Budleigh Salterton Pebble Beds Formation groundwaters at concentrations of 0.01 to 0.104 μg L^{-1}. This is reflected in the spatial distribution (Figure 5.21) where the highest concentrations are found along the western edge of the Sherwood Sandstone aquifer. Cadmium displays chalcophile behaviour and is therefore commonly associated with sulphide ore deposits. It can also be adsorbed to the surfaces of, or become incorporated into, calcite; which is the most likely source of Cd in these groundwaters.

Cobalt has a range of 0.01 to 0.89 μg L^{-1}, a 5th to 95th percentile range of 0.01 to 0.43 μg L^{-1} and a median of 0.05 μg L^{-1} (Table 5.2). This range is fairly typical of Permo-Triassic Sandstone groundwaters in the UK. The lowest concentrations of Co are generally found in the Otter Sandstone Formation groundwaters, ranging from 0.01 to 0.1 μg L^{-1}. The higher concentrations are found in Budleigh Salterton Pebble Beds Formation groundwaters, with four measured values: 0.02, 0.12, 0.19 and 0.89 μg L^{-1}. Spatially the highest concentrations are found in the south of the region, not just in the west, as mixed and unknown groundwater sources also contain higher concentrations of Co (Figure 5.21). Cobalt is usually derived from ferromagnesian minerals, and contaminant sources are often limited by natural attenuation in the soil zone. It is likely that Co is found in the coatings of grains or cements within the aquifer, and the range presented here probably represents a baseline concentration range.

Chromium has a range of <0.5 to 3.36 μg L^{-1}, a 5th to 95th percentile range of 0.06 to 0.56 μg L^{-1} and a median of 0.21 μg L^{-1} (Table 5.2). This range is typical of other Permo-Triassic Sandstone aquifers in the UK. Of the values above the detection limit (which was greater than many of the measurable analyses owing to the inclusion of two datasets) there is a striking difference between Cr concentrations in the Otter Sandstone Formation and the Budleigh Salterton Pebble Beds Formation, which is also evident from the spatial distribution. Concentrations of Cr measured in Budleigh Salterton Pebble Beds Formation groundwaters range from 0.06 to 0.11 μg L^{-1}, whereas Cr concentrations in groundwaters from the Otter Sandstone Formation range from 0.17 to 0.56 μg L^{-1}. Mixed sources have Cr concentrations which range from 0.18 to 3.36 μg L^{-1}. Chromium is generally more mobile under alkaline oxidising conditions. Chromium in groundwater tends to occur from the weathering of ferromagnesian minerals, shales, and argillaceous rocks. If the values with the high detection limits are ignored there is a clear distinction between Cr concentrations in the Otter Sandstone Formation and Budleigh Salterton Pebble Beds Formation.
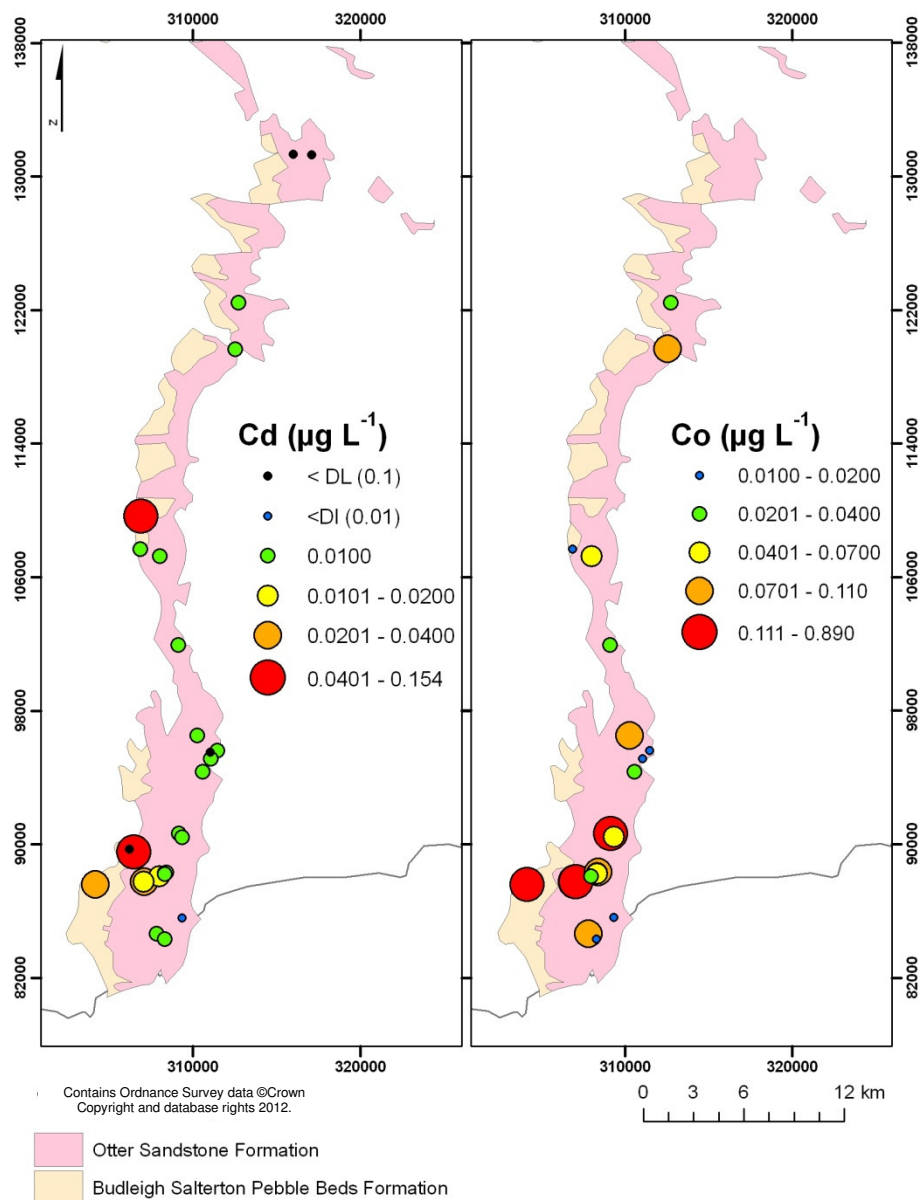
Figure 5.21 Regional variation of Cd and Co within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

Copper has a range of <1 to 62.2 μg L^{-1}, a 5th to 95th percentile range of 0.8 to 13.5 μg L^{-1} and a median of 2.2 μg L^{-1} (Table 5.2). This distribution is similar to other Permo-Triassic Sandstone aquifers in the UK. Copper occurs naturally as native metal, or in sulphide ore deposits, but is also a very commonly used metal in industrialised countries, and in pipwork in the water supply infrastructure. Anthropogenic inputs are to be expected in young groundwaters (Shand et al., 2007). Where the groundwater is oxidising, Cu is most soluble under acidic conditions. As the pH increases, Cu can adsorb to organic matter or Fe and Mn oxyhydroxides (Shand et al., 2007). There is no correlation of Cu concentration with aquifer source unit, and the spatial distribution is similarly indistinct. There is a cluster of higher values, however, around Colaton Raleigh and Newton Poppleford, with intermediate values around Ottery St Mary. There is a poor correlation between pH and Cu (r^2=0.02). This could indicate local contamination derived from various anthropogenic activities.

Hafnium has a range of <0.01 to 0.02 μg L^{-1}, a 5th to 95th percentile range of 0.0015 to 0.02 μg L^{-1}, and a median of 0.0045 μg L^{-1} (Table 5.2). Fifteen of the 21 Hf determinations are
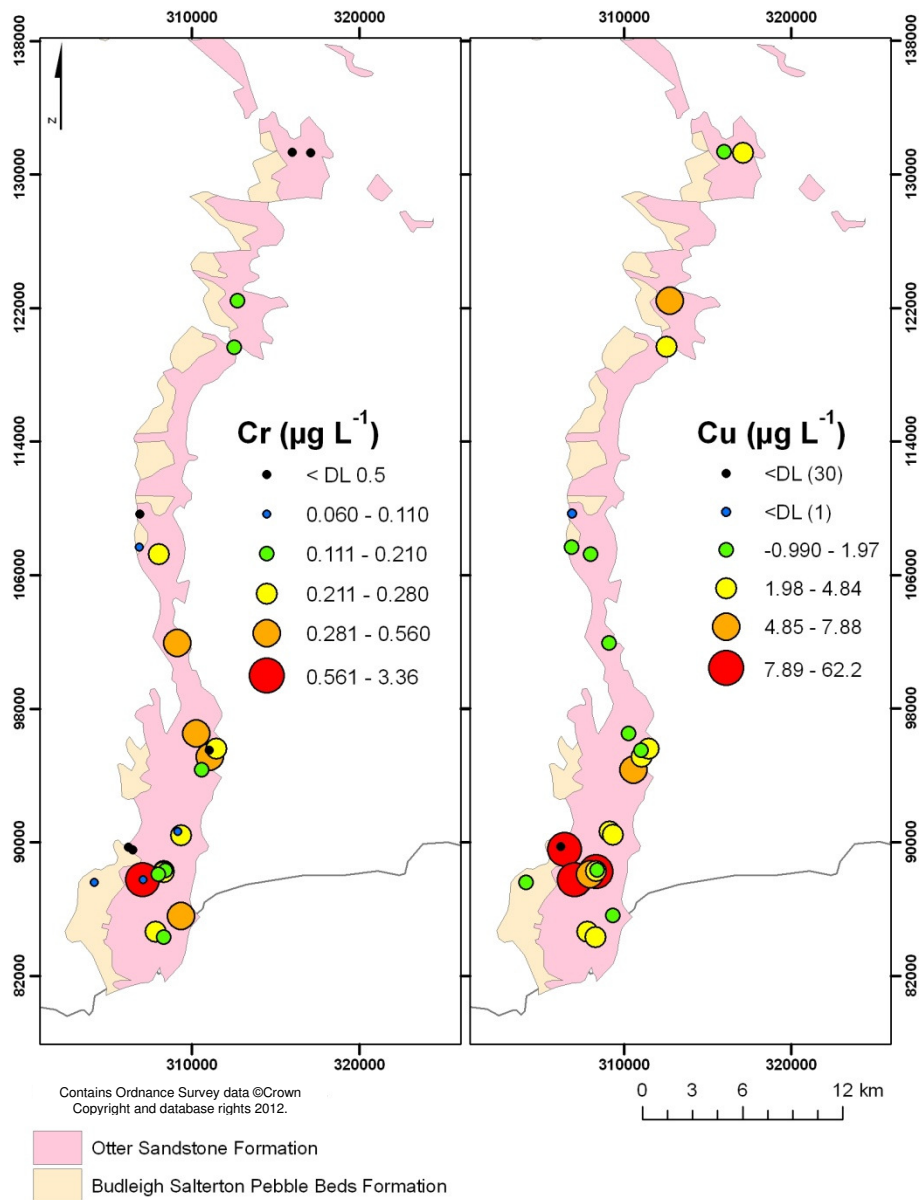
Figure 5.22 Regional variation of Cr and Cu within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

below the detection limit. Hafnium is generally not detectable in groundwaters, for instance Shand et al. (2007) reported that the 97th percentile of 727 waters was <0.02 μg L^{-1}

Molybdenum has a range of <0.03 to 0.25 μg L^{-1}, and a median of 0.06 μg L^{-1} (Table 5.2). Mo is relatively rare, occurring as the mineral molybdenite (MoS$_2$). Under oxidising conditions the dominant species are pH-dependent, although at the range of pH values present in the Sherwood Sandstone aquifer (above 5) the molybdate ion will dominate (after Shand et al., 2007). The range of concentrations presented here is relatively small when compared to other Permo-Triassic Sandstone aquifers in the UK. The maximum concentration of each of the six Permo-Triassic Sandstone aquifers studied as part of the Baseline report series (see Shand et al., 2007) exceeds 1 μg L^{-1}, and it was concluded that the maximum baseline in UK Permo-Triassic Sandstone aquifers is 10 μg L^{-1}. It is therefore likely that the concentrations presented in this report represent baseline concentrations. There is no correlation of the data presented here with the aquifer source unit or pH, and there are no spatial trends evident.

56

Nickel has a range of <1 to 13 µg L^{-1}, a 5th to 95th percentile range of 0.2 to 6.5 µg L^{-1}, and a median of 0.7 µg L^{-1} (Table 5.2). The range presented here is fairly typical of groundwaters from Permo-Triassic Sandstone aquifers in the UK. In the environment Ni behaves in a similar way to Co, which in turn associates with Fe and Mn (Shand et al., 2007). There is only a weak correlation of Ni with Co (r^2=0.12). This is reflected in the poor spatial correlation between Ni and Co (Figure 5.23 and Figure 5.21). There is also a weak correlation with Mn (r^2= 0.15), which does show a similar spatial distribution (Figure 5.17). There is some relationship between Ni and aquifer source unit: the lowest concentrations are found within the Otter Sandstone Formation aquifer (measurable Ni = 0.1 to 0.9 µg L^{-1}), and the highest values are found within groundwaters from the Budleigh Salterton Pebble Beds Formation (Ni = 0.3 to 13 µg L^{-1}). Concentrations of Ni in the Sherwood Sandstone aquifer do not exceed the drinking water limit of 20 µg L^{-1} (OPSI, 2010).

Lead has a range of <2 to 0.91 µg L^{-1}, a 5th to 95th percentile range of 0.04 to 0.45 µg L^{-1}, and a median of 0.13 µg L^{-1} (Table 5.2). The detection limit, which is higher than all the measurable determinations, means the data distribution (Figure 5.13) is of limited value. The measurable
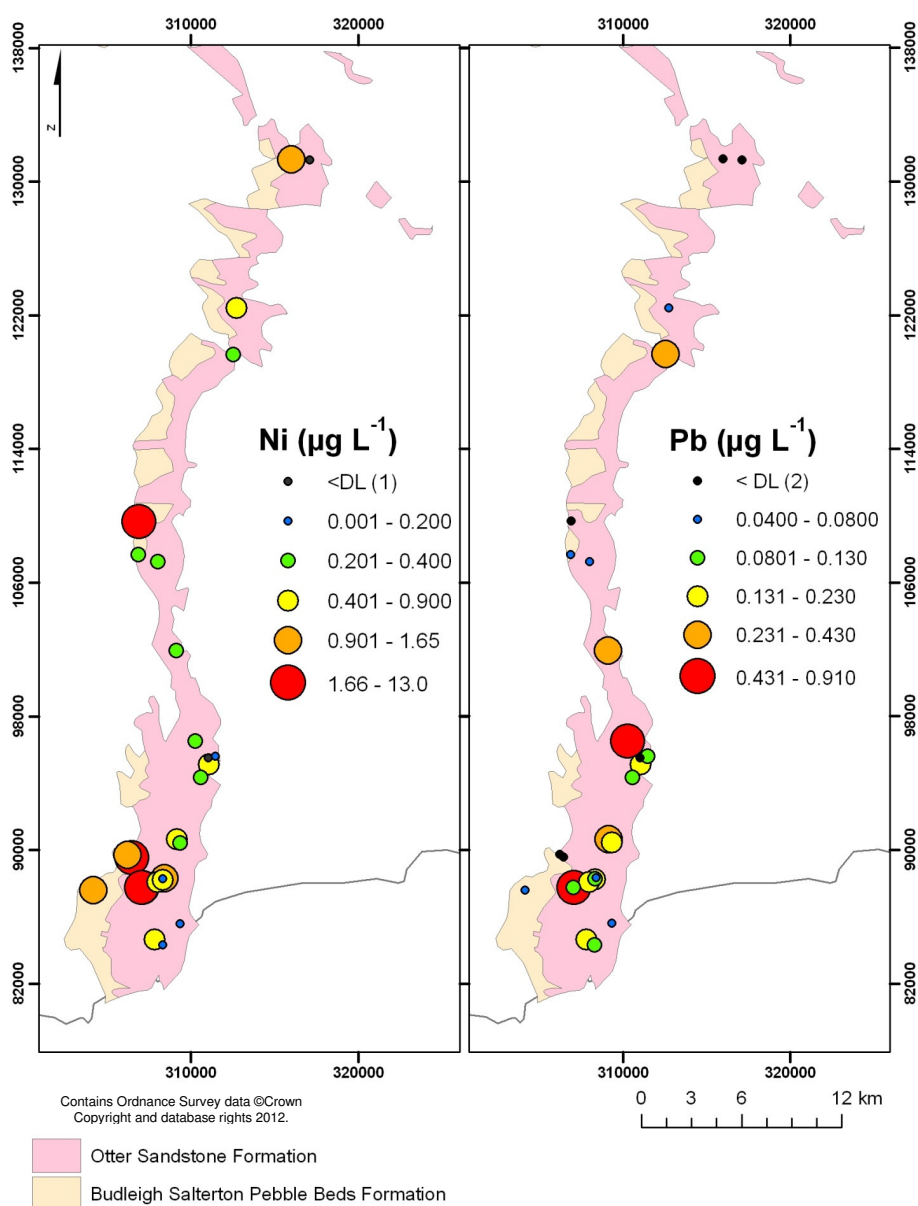

Figure 5.23 Regional variation of Ni and Pb within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

57

concentrations are fairly low, and have a narrow range when compared to other Permo-Triassic Sandstone aquifers in the UK, which are variable between each aquifer (Shand et al., 2007). Lead can be present as a trace constituent in K feldspars (Shand et al., 2007). This is the most likely natural source of Pb in the groundwaters of the Sherwood Sandstone aquifer, as K feldspars are abundant in the Sherwood Sandstone aquifer matrix. There are no distinct spatial trends (Figure 5.23), and there is no correlation of Pb concentration with aquifer unit. The natural baseline of Pb is likely to be anthropogenically influenced by built up and industrial areas, and major roads. There are no large built up areas or roads within the study area, and so Pb concentrations are relatively low. Nonetheless it is very unlikely that these groundwaters are pristine with respect to Pb, as the anthropogenic use of Pb has been so widespread. In this case the arbitrary value of the 95th percentile should be taken to define the upper baseline value (0.45 μg L^{-1}). It is worth noting that all the measured values are well below the current drinking water limit of 25 μg L^{-1}, and the new December 2013 limit of 10 μg L^{-1}(OPSI, 2010).

Antimony has a range of 0.017 to 0.209 μg L^{-1}, a 5th to 95th percentile range of 0.023 to 0.199 μg L^{-1} and a median of 0.076 μg L^{-1} (Table 5.2). The range is smaller than that found in Permo-Triassic Sandstone aquifers elsewhere in the UK where the highest concentrations are around 1 μg L^{-1}, The spatial variation of Sb is similar to that of As (Figure 5.24 and Figure 5.19). Antimony is expected to occur at concentrations less than 1 μg L^{-1} in unpolluted waters, and it is expected that the range of concentrations presented here represents baseline concentrations.

Selenium has a range of <0.1 to 1.3 μg L^{-1}, a 5th to 95th percentile range of 0.2 to 1.2 μg L^{-1}, and a median of 0.4 μg L^{-1} (Table 5.2). Selenium is mobilised in oxidising waters, but under reducing conditions it is reduced to elemental, relatively insoluble Se. Where Fe is present Se may be co-precipitated or sorbed (Hem, 1992). Three of the 21 samples analysed had concentrations exceeding 1 μg L^{-1}. The highest concentration was found at a site close to the coast. However, there are no other spatial trends (Figure 5.24), relationships to source aquifer or pH. The 95th percentile is interpreted as an approximate upper limit for the baseline range of this aquifer.

Tin has a range of <0.02 to 1.04 μg L^{-1}, a 5th to 95th percentile range of 0.02 to 0.03, and a median of 0.02 μg L^{-1} (Table 5.2). This range is typical of groundwaters from Permo-Triassic Sandstone aquifers in the UK, where concentrations rarely exceed 1 μg L^{-1} (Shand et al., 2007). Only the maximum value (1.04 μg L^{-1}) is significantly above the detection limit (0.02 μg L^{-1}); the second highest concentration of Sn measured in these waters is 0.03 μg L^{-1}. The highest value may therefore represent contamination, and the 95th percentile value can be considered an upper baseline estimate.

Thorium has a range of <0.02 to 0.03 μg L^{-1} (Table 5.2). Eighteen of the 21 analyses are below detection limits. These values are likely to represent baseline concentrations.

Titanium has a range of <0.05 to 0.19 μg L^{-1}, a 95th percentile of 0.14 μg L^{-1}, and a median of 0.05 μg L^{-1} (Table 5.2). Nine of the 21 determinations are below detection limits. While Ti is relatively abundant in crustal rocks, it is usually found in resistant minerals, which means its abundance tends to be low in natural waters. Titanium concentrations can range up to a few tens of μg L^{-1}, and averages around 3 μg L^{-1} in stream waters (Hem, 1992). All analyses in this study are below 0.2 μg L^{-1}, and it is suggested that this represents an approximate baseline range.

Thallium has a range of <0.01 to 0.04, a 5th to 95th percentile range of 0.0012 to 0.03, and a median of 0.006 µg L^{-1} (Table 5.2). Eleven of the 21 analyses are below detection limits. Lower concentrations are generally found in the groundwaters from the Otter Sandstone Formation. These range from <0.01 to 0.01 µg L^{-1}. With the exception of one site, at which Tl in the groundwater was below the detection limit, the concentrations are higher in the Budleigh Salterton Pebble Beds Formation. The concentrations in these groundwaters range from 0.02 to 0.04 µg L^{-1}. It is likely that the range of data presented here represents baseline compositions.

Uranium has a range of 0.045 to 8.53 µg L^{-1}, a 5th to 95th percentile range of 0.065 to 6.05 µg L^{-1}, and a median of 0.519 µg L^{-1} (Table 5.2). This range is similar to that recorded in the groundwaters of other Permo-Triassic Sandstone aquifers in the UK (Shand et al., 2007). Uranium occurs naturally in soils and rock-forming minerals, and it has a strong affinity for iron oxides. It is thought that much of the U in the Triassic sandstone aquifer of the UK is derived from iron oxide grain coatings or cements (Smedley et al., 2006) However there is no relationship of the U data with Fe concentration (r^2=0.03) because of the oxic nature of the analysed groundwaters. Desorption of U from oxide and possibly carbonate surfaces seems a likely origin. There is a weak correlation of U with pH (r^2=0.14). Hence, the lower values are
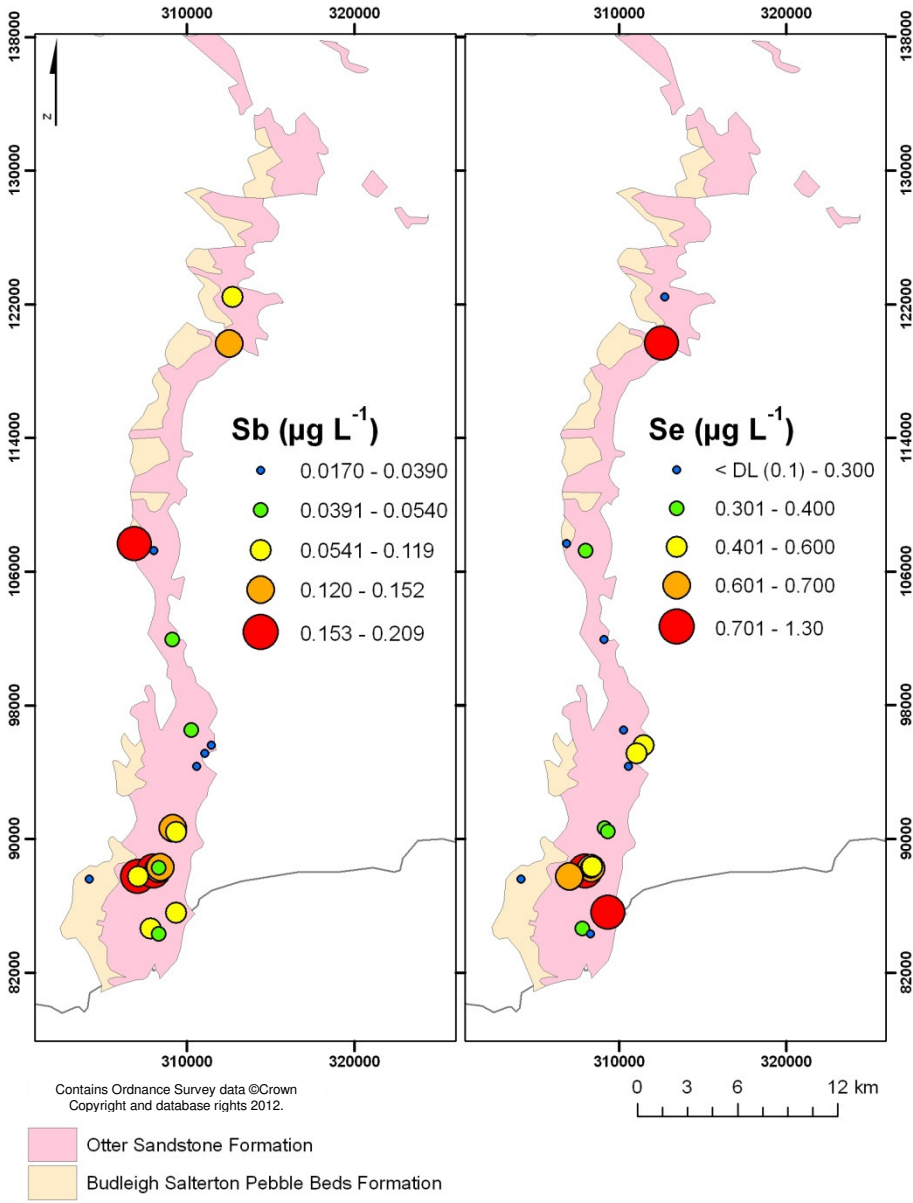

Figure 5.24 Regional variation of Sb and Se within the Sherwood Sandstone aquifer.

found in groundwaters within the Budleigh Salterton Pebble Beds Formation (0.045 to 0.47 µg L^{-1}) and the higher values are found in groundwaters from the Otter Sandstone Formation (0.22 to 8.53 µg L^{-1}). This is also reflected in the spatial distribution, as the higher values are generally found in groundwaters extracted from boreholes to the east of the study area (Figure 5.25). All of the determinations are well within the WHO provisional drinking water guideline value of 30 µg L^{-1}, and is unlikely that the observed concentrations of U are impacted significantly by anthropogenic inputs.

Vanadium has a range of <0.1 to 3.7 µg L^{-1}, a 95th percentile of 1.1 µg L^{-1}, and a median of 0.3 µg L^{-1} (Table 5.2). This distribution is typical when compared to other Permo-Triassic Sandstone aquifers in the UK. Vanadium is highly mobile under oxidising and alkaline conditions, and while the highest values are found under these conditions there are no relationships between the V data and pH or Eh. In addition there is no correlation with the aquifer source rock, and no spatial trends. It is likely therefore that the sources of V are minerals within the aquifer rocks, especially Fe oxides.
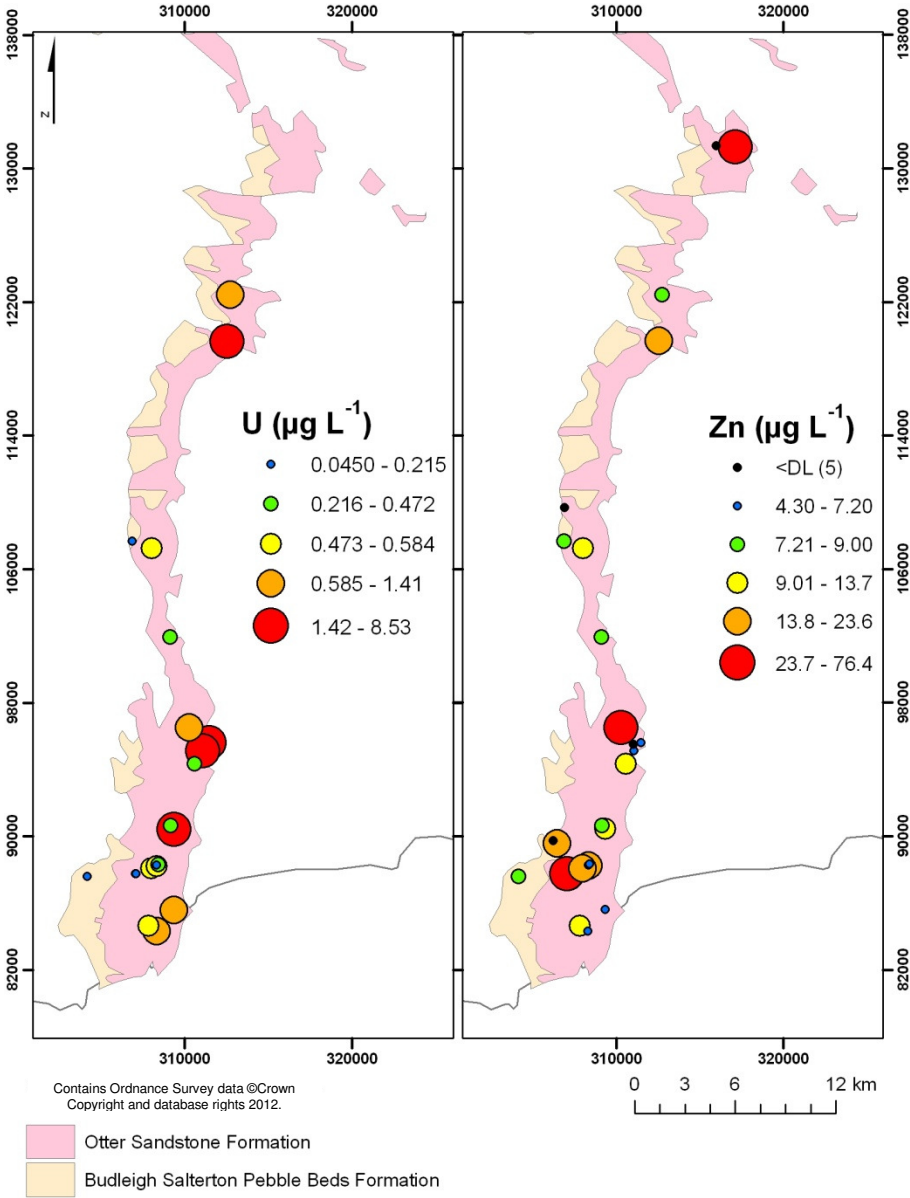

Figure 5.25 Regional variation of U and Zn within the Sherwood Sandstone aquifer. Black circles indicate a detection limit (stated in parenthesis) which exceed measured analyses

Zinc has a range of <5 to 76.4 µg L^{-1}, a 5th to 95th percentile range of 4.3 to 37.4 µg L^{-1}, and a median of 8.9 µg L^{-1} (Table 5.2). This data range is smaller than that analysed in other groundwaters from other Permo-Triassic Sandstone aquifers in the UK: the maximum values of Zn in these groundwaters range from ca. 100 to 10,000 µg L^{-1}. The solubilities of many common Zn minerals are high, and it is most mobile at acidic pH values (Shand et al., 2007). However, there is no relationship of the Zn data presented here with aquifer source unit or pH. The higher concentrations are generally found in the south of the study area, but this is a tenuous trend (Figure 5.25). Zinc is a common industrial metal and contamination can derive from road dust, landfill leachate, or other urban contamination sources. The relatively rural nature of the area means that contamination from urban or industrial sources is unlikely, although contamination from borehole pipework is a possibility. It is unlikely that the waters are pristine with respect to anthropogenic Zn. It is likely that the 95th percentile represents an estimate of the upper baseline value for Zn.

5.3   ISOTOPIC COMPOSITION

Measured compositions of δ^{18}O lie in the range -6.65 to -5.79 ‰, with a median of -6.36 ‰. The δ^2H has a range of -43.9 to -35.8 ‰ with a median of -39.6 ‰. This represents rainfall relatively enriched in the heavier isotopes when compared to that in the east of the country, likely because of the Rayleigh fractionation effect (Darling and Talbot, 2003). However, the interquartile ranges of δ^{18}O and δ^2H, are generally consistent with compositions of recently recharged (Holocene) groundwaters analysed from south-west England (Darling et al., 2003).

The complete range of compositions is relatively large, given the restricted size of the study area. Values within the upper and lower 25th percentiles of the δ^{18}O and δ^2H data are outside of the range of values expected for local Holocene groundwaters, and more negative values may represent older groundwaters (Darling et al., 2003). However, the relationship between δ^{18}O and δ^2H (Figure 5.26) shows a general correspondence with the world meteoric water line, indicating that the groundwaters represent recharged local modern rainfall.

The δ^{18}O and δ^2H data are distinguished in Figure 5.26 by the aquifer unit from which the samples were taken. Groundwaters sampled from the Budleigh Salterton Pebble Beds Formation are relatively enriched in terms of δ^{18}O and δ^2H values. As all the samples were collected from
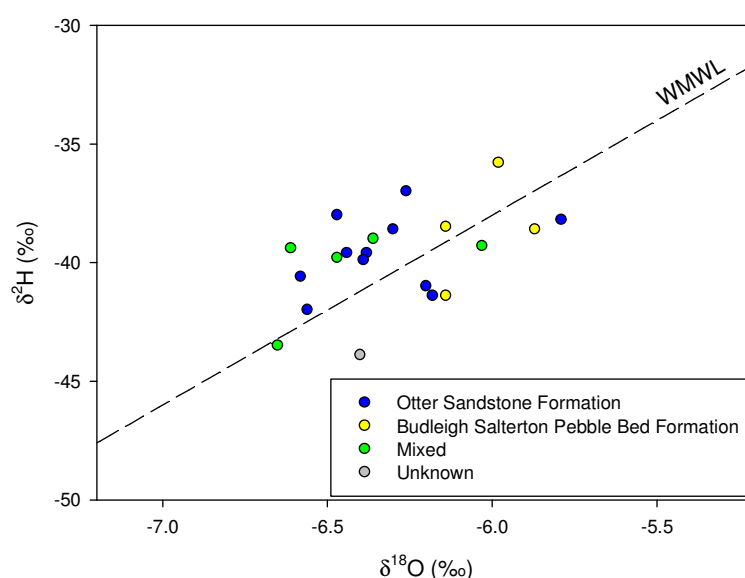

Figure 5.26 O and H stable isotopic composition of the
Sherwood Sandstone aquifer of Devon and Somerset. WMWL =
world meteoric water line.

the unconfined aquifer, and all the boreholes are assumed to be shallow, these data are unsuitable to date the aquifer. The relatively small outcrop area means that the spatial variation of $\delta^{18}O$ and δ^2H is difficult to identify. There only trend is that the more enriched samples tend to be located near to the coast (Figure 5.27), and therefore affected by marine aerosols.

The spatial distribution of ^{13}C in DIC can be an effective tracer of carbonate evolution (Clark and Fritz, 1997; Darling et al., 2005). Groundwater acquires dissolved inorganic carbon (DIC) through reaction with carbonate minerals, and with CO_2 derived from the overlying soil. The resulting C isotopic composition of the DIC represents a mixture of that of the soil (generally around -23 ‰) and that of a carbonate mineral source (ca. 0 ‰). Over time, excess CO_2 is consumed and solution precipitation reactions fractionate the $\delta^{13}C$ value towards the isotopic composition of the rock. Hence, more depleted values represent compositions less impacted by carbonate reaction. The more enriched values suggest longer residence times.

The compositions of $\delta^{13}C$ in the Sherwood Sandstone aquifer of Devon and Somerset range between -18.21 and -12.84 ‰, with a median of -15.63 ‰. There is an unclear spatial trend (Figure 5.27) which may be due to a combination of residence times and varying amounts of
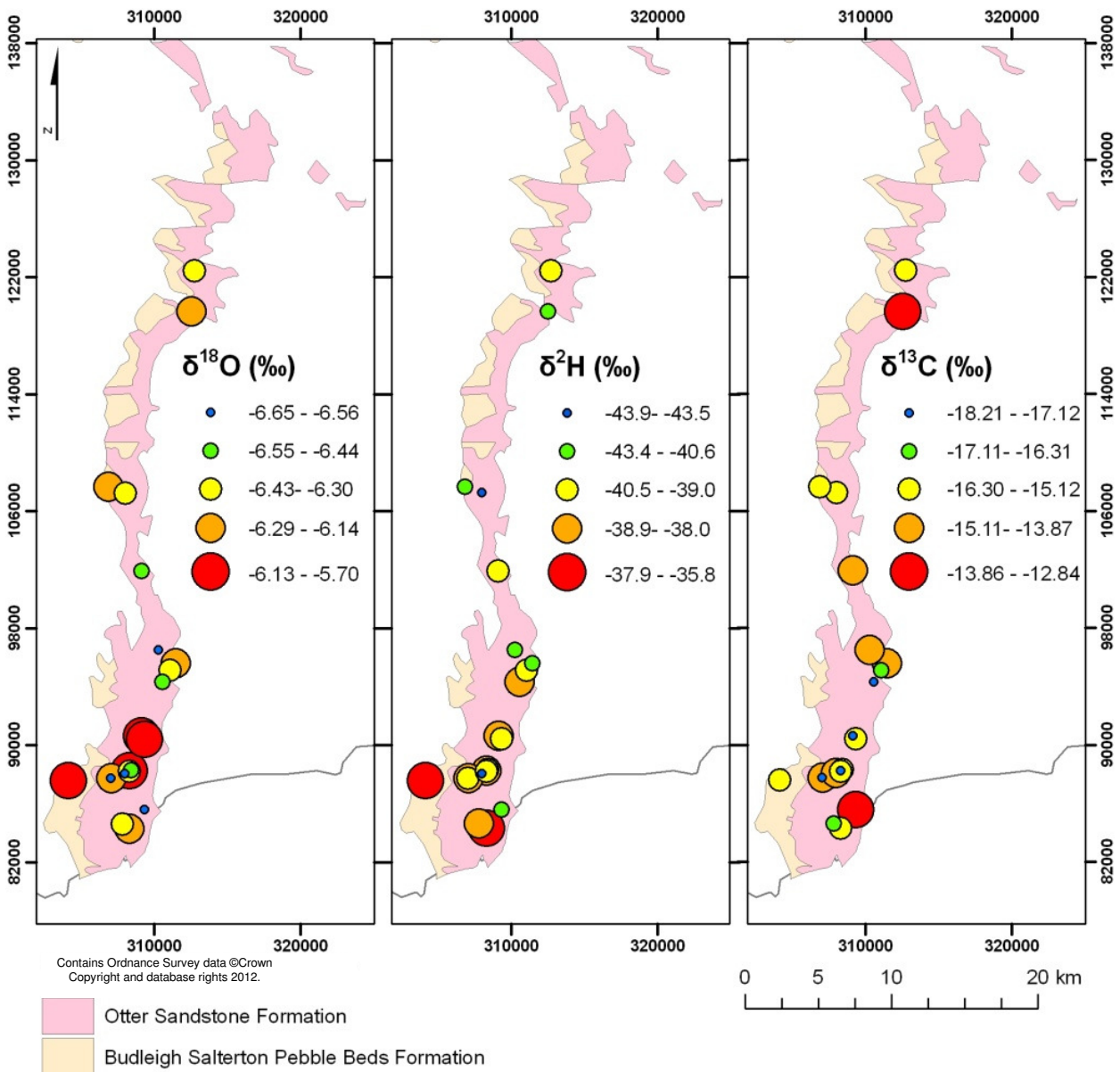

Figure 5.27 Regional variation of $\delta^{18}O$, δ^2H, and $\delta^{13}C$ within the Sherwood Sandstone aquifer

carbonate cement. However, the most negative values are found in the southern portion of the outcrop in an area where there is less carbonate cement. A value for $\delta^{13}C$ close to that of soil CO_2 would be expected. It is interesting to note that the highest $\delta^{13}C$ values (-14 to -12.84 ‰) are similar to those found in groundwaters from a carbonate aquifer (Bearcock and Smedley, 2009).

5.4   CHEMICAL VARIATIONS WITH DEPTH

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

5.5   TEMPORAL VARIATIONS

Data for 12 sites are available from the EA database with up to ca. 10 years of analytical results, at a sampling frequency of around twice per year. All 12 sites were not used in the main baseline data set as some of the sites had been more recently sampled for the purposes of this baseline study. The majority of the analyses are for unfiltered water. For some elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Na, Ni, Pb, Sr, Zn) data for filtered waters are also available, but there are rarely sufficient data (generally ca. 3 analyses), to enable interpretation of temporal trends. Therefore the majority of the following discussion relates to unfiltered water, and should be treated with some caution.

The concentration of Fe in filtered and unfiltered water samples from a site near the hamlet of East Coombe exemplifies the need to treat this discussion with caution. Sufficient data were available for this site to compare the Fe concentration in filtered and unfiltered samples (Figure 5.28). The Fe concentration over time follows different trends in the filtered and unfiltered samples. In the filtered samples the concentration of Fe was ca. 60 µg L^{-1} during the interval 2003 to 2008, but after 2008 the concentration fell below the detection limit. The detection limit is 30 µg L^{-1}, and the points are marked on Figure 5.28 as half the detection limit (15 µg L^{-1}). In contrast the concentration of Fe in the unfiltered samples increases from 500 µg L^{-1} in 2003 to a peak of 14500 µg L^{-1} in 2008 and decreases to 3500 µg L^{-1} subsequently. Figure 5.28 shows that the trends of Fe in the filtered and unfiltered samples are broadly the same, but the concentration of Fe in the unfiltered sample far exceeds the concentration in the filtered samples owing to the
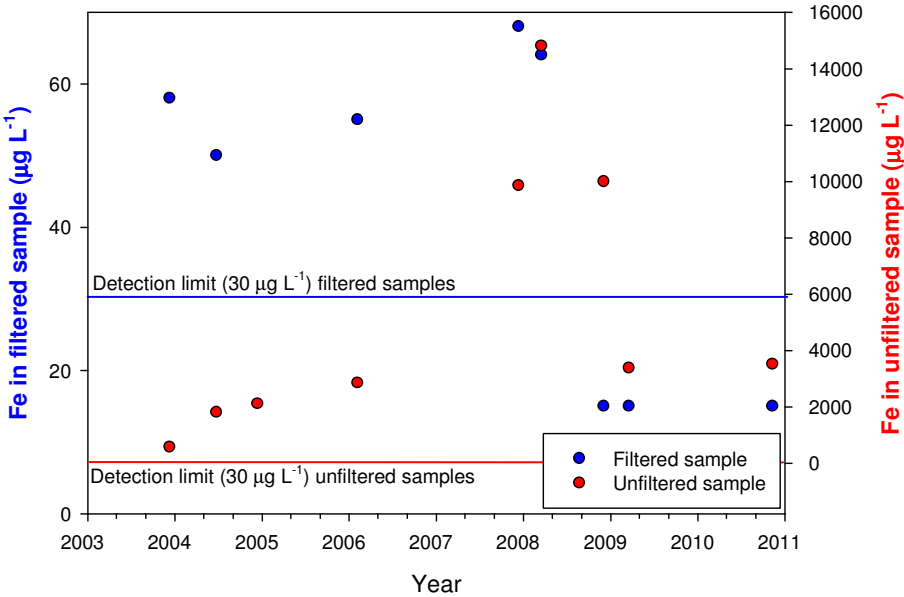

Figure 5.28 Iron concentration over time in samples of filtered and unfiltered water from a site near East Coombe

presence of Fe-rich particulate matter. A change in the system is likely to have taken place in 2008 which caused such a reduction in concentrations.

The temporal variation of NO_3-N in EA samples is also of interest, as discussed in Chapter 3.5. Four of the EA sites show a decrease in NO_3-N concentrations with time, while three sites show an increase. Figure 5.29 shows NO_3-N concentrations in groundwaters from a site near Newton Poppleford. At this site there is a steady decline over 10 years, from >8.5 mg L^{-1} NO_3-N in 2001 to ca. 6.5 mg L^{-1} NO_3-N in 2010. This may be caused by an increased awareness of NO_3-N as a diffuse pollutant in response to the designation of the area as a NVZ (see Section 3.5). At two of the sites, there was a decrease in NO_3-N concentrations values from near the drinking-water limit (11.3 mg L^{-1}) to concentrations of 8 and 6 mg L^{-1}. However, at one site, about 2.5 km south west of Blackborough, the concentration reduced steadily from ca. 18 mg L^{-1} to 17 mg L^{-1} over a five-year period between 2005 and 2010. Despite the slight downwards trend in NO_3-N concentration the drinking water limit was still far exceeded in 2010.

Three sites within the EA monitoring network have shown an increase in NO_3-N concentrations. Of these three sites, two have concentrations which remain within the drinking-water limit. The groundwater at a site near Collaton Raleigh, had NO_3-N concentrations above the drinking-water limit (>12 mg L^{-1}) in 2000, rose to a peak of 15 mg L^{-1} in 2003, and has declined steadily since. Despite this decline, the most recent analyses of NO_3-N, in 2010 show that the NO_3-N concentration is still greater than both the drinking-water limit and the 2000 concentration (Figure 5.30a) Such changes may be caused by changes in farming practices, especially as there is a definite reversal of trend around 2003.

The EA temporal data show that trends in NO_3-N concentrations over time are similar to those of the other major ions (especially Cl and K, but excluding Mg). As an example Figure 5.30b shows the concentrations of Cl and K in the groundwater at the site discussed above near Collaton Raleigh. The concentration of these elements increased between 2000 and 2003; and then declined up to the 2010 sample. These are both elements that have been associated with diffuse agricultural inputs, and are probably linked to the changing NO_3-N concentrations. The concentration changes at this site may be due to updated NVZ guidelines which came into force in 2002 (DEFRA, 2010).

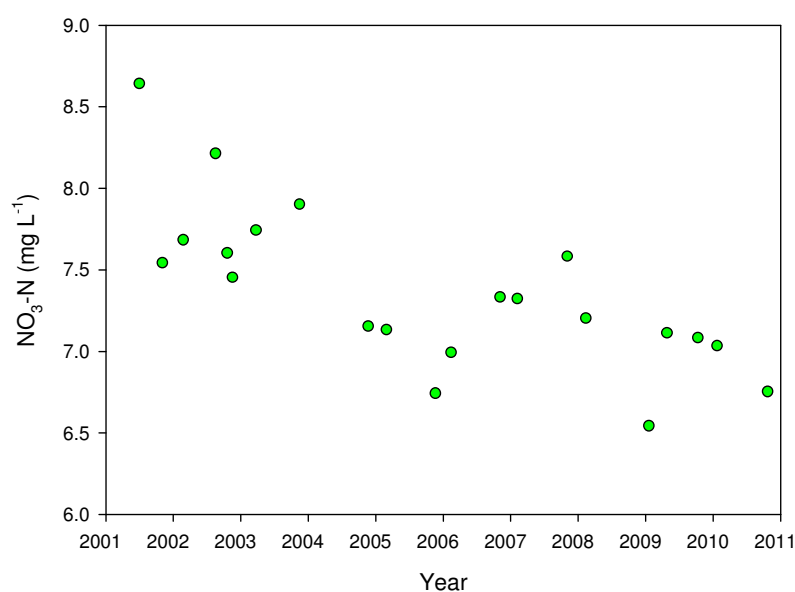At the same site, near Collaton Raleigh, the concentration of Zn in the groundwater increased

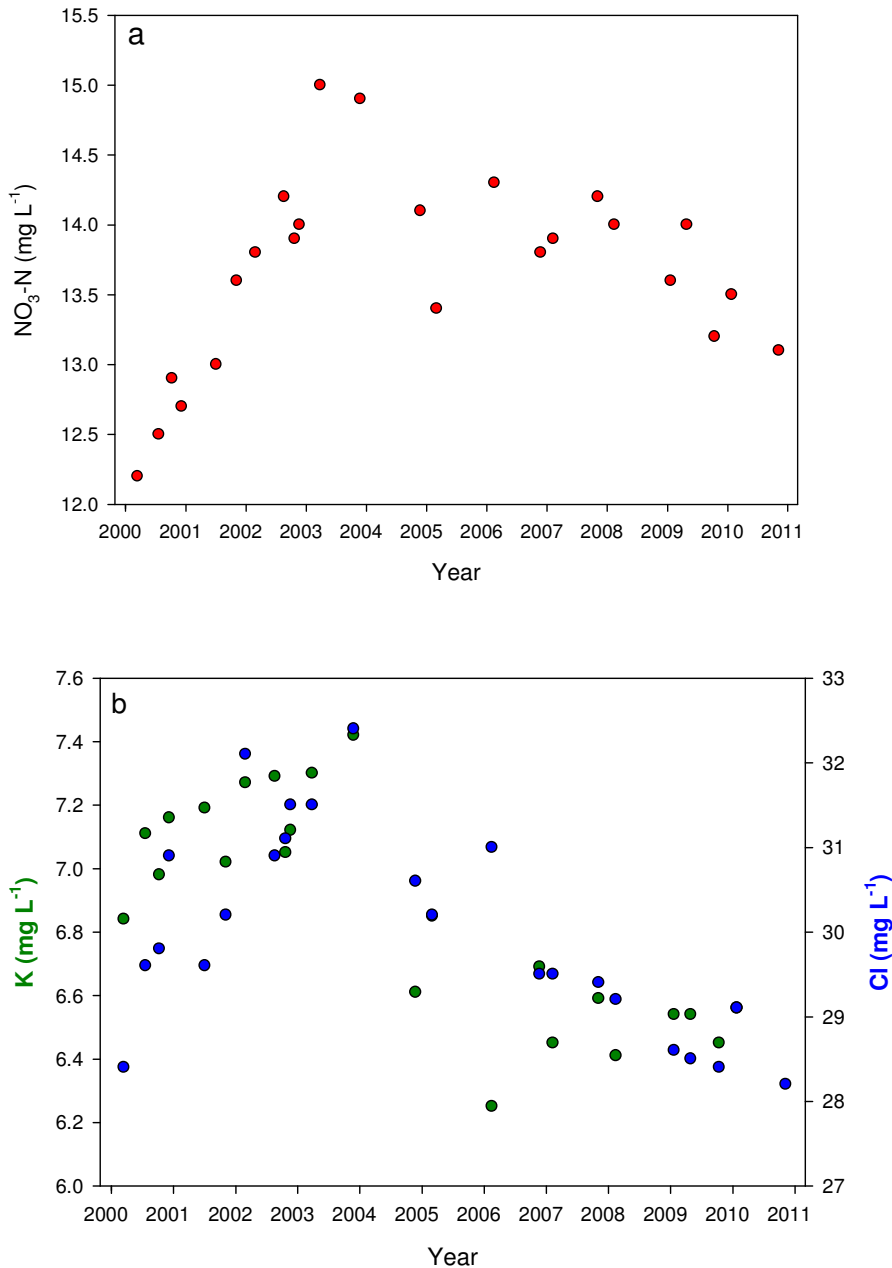Figure 5.29 NO_3-N over time at a monitoring site near Newton Poppleford

Figure 5.30 a) NO$_3$-N, and b) K and Cl concentrations over time at a monitoring site near Collaton Raleigh

between 2004 and 2007. Prior to this the concentration was relatively stable, and after this period of increase the concentrations started to decline (Figure 5.31). The cause of the Zn trend is unclear, though pollution is a possibility. The proximity of the borehole to the River Otter suggests there may be some influence from the river, but this does not provide a clear explanation for these increases.

Strontium and Ba both increase in concentration at two groundwater sites; at a further two sites either Sr or Ba increase in concentrations. Three of these sites are south of Ottery St Mary, but one is in the far north of the study area, near Bishops Lydeard. Barium is commonly present in K-feldspars (Shand et al., 2007), which account for a quarter of the Budleigh Salterton Pebble Beds Formation matrix, and about 5% of the total formation.
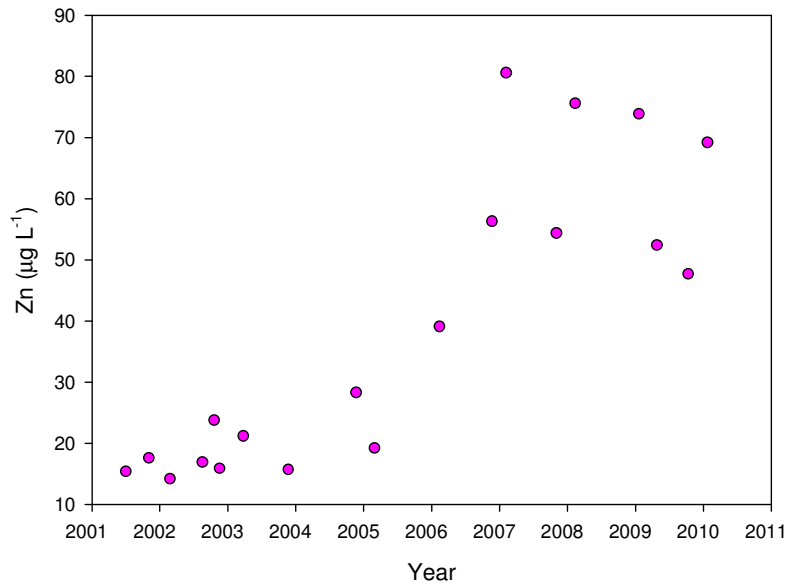
Figure 5.31 Groundwater Zn concentrations at a site near Collaton Raleigh

As noted in Section 5.2.3 Sr is commonly present in high concentrations in Ca-bearing minerals such as calcite. Calcite within the Otter Sandstone Formation cement could be the source of Sr in the groundwaters. Dissolution of this cement may cause increases in groundwater concentrations. The largest increase in Sr occurs at the site near Bishops Lydeard, which is in the more cemented portion of the Otter Sandstone Formation outcrop. Figure 5.32 shows Sr concentrations in the groundwaters of sites near Bishops Lydeard and Ottery St Mary. The latter site is representative of those with Sr increases in the southern part of the Sherwood Sandstone outcrop. At this site the concentration of Sr increases from ca. 110 μg L^{-1} to ca. 122 μg L^{-1} over a ten year period. At the site near Bishops Lydeard the Sr increases from ca. 170 μg L^{-1} to ca. 210 μg L^{-1} over a seven year period.
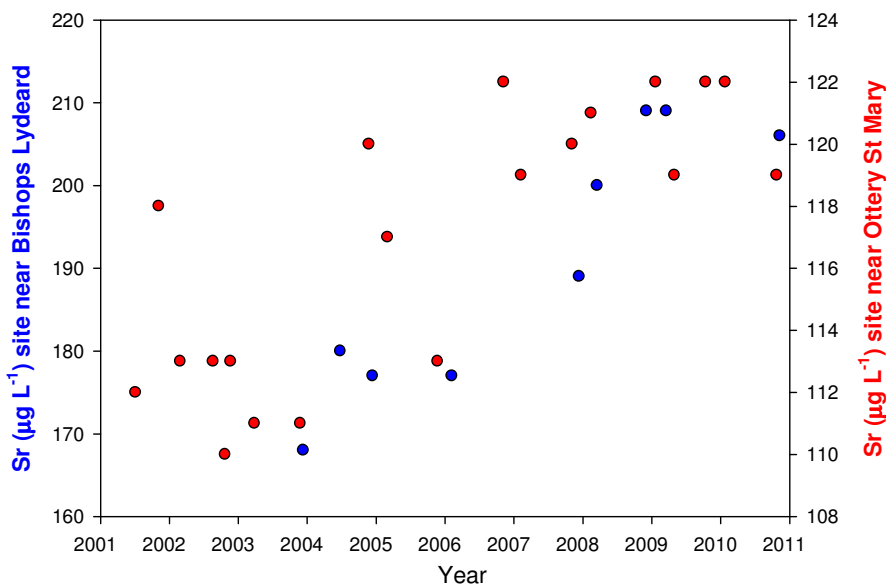

Figure 5.32 Groundwater Sr concentrations at sites near Bishops Lydeard and Ottery St Mary

66

5.6   GENERAL DISCUSSION AND SITES OF PARTICULAR INTEREST

The above discussion has highlighted that the groundwaters of each source aquifer (Otter Sandstone Formation and Budleigh Salterton Pebble Beds Formation) can be distinguished by their chemistry. The best indicators are pH, Eh and HCO_3, although other components are distinctively different between aquifer units. As discussed above, the groundwaters from the Budleigh Salterton Pebble Beds Formation are more acidic, more oxic, and have lower SEC values, HCO_3 and Mg concentrations than the groundwaters from the Otter Sandstone Formation. In addition the concentrations of Al, Be, Cd, Cr, Co, Tl and REE are higher, and the Cr and U concentrations are lower in groundwaters from the Budleigh Salterton Pebble Beds than those from the Otter Sandstone.

The distinction between the aquifer source units is such that it is possible to suggest which unit the groundwaters of unknown source unit derive from. Two of the groundwaters from unknown source units have chemistries which suggest a source in the Budleigh Salterton Pebble Beds Formation aquifer. Two of the groundwaters from unknown sources have chemistries consistent with an Otter Sandstone Formation origin. These conclusions are supported by their plotted positions on the piper diagram (Figure 5.1) and the sample site locations: those thought to be from the Budleigh Salterton Pebble Beds Formation are located on the eastern edge, and those thought to be from the Otter Sandstone Formation are found more centrally (Figure 2.4). The chemistry of the final groundwater sample derived from an unknown source is not typical of groundwaters derived from Budleigh Salterton Pebble Beds Formation or Otter Sandstone Formation aquifers. It is most likely that this represents a mixed source. This is the sample which has a high SO_4 concentration (Figure 5.1). In addition it is located close to the outcrop boundary of the Budleigh Salterton Pebble Beds Formation (ca. 3km WSW of Willand).

The discussion above indicates that the aquifer source unit is the largest influence on the groundwater chemistry. However, a few individual sites are worthy of extra note.

The sample taken from a spring collect (located on Colaton Raleigh Common) was the most acidic, with the lowest alkalinity and in this respect closely resembled fresh rainwater. It contained relatively high concentrations of Co, and REE, which were similar to concentrations found in other samples from the Budleigh Salterton Pebble Beds Formation aquifer. It seems likely that this is a very young groundwater, although the acidic nature has given rise to the preferred release of some solutes.

In an area between Colaton Raleigh and Ottery St Mary, high concentrations of trace metals were observed. One site in particular near Colaton Raleigh had groundwater with elevated concentrations of Co, Cu, Cr, Ni, Pb (all at or above the 95th percentile), and Zn (90th percentile). Furthermore, some of the concentrations have been increasing over time (Section 5.5). This suite of elements is indicative of metallic contamination, probably derived from the borehole headworks. This site is the only one to have an elevated concentration of such a suite of elements, and so the significance of metallic contamination is likely to be very limited.

6 Baseline groundwater chemistry

6.1 REGIONAL BASELINE CHARACTERISTICS

The groundwaters in this study of the Sherwood Sandstone aquifer of Devon and Somerset derive from the Otter Sandstone Formation, the Budleigh Salterton Pebble Beds Formation, or a mixture of the two. The study area is relatively small and there are limited lithological variations between each aquifer unit. Hydraulic conductivity between the two appears to be limited largely to the northern part of the aquifer. The unconfined portion of the aquifer was examined in this study. There are few boreholes exploiting the Otter Sandstone Formation confined by the Mercia Mudstone Group to the east of the study area, and it is likely the chemistry here would be very different.

The major source of most groundwater in the study area is rainfall. There may be some inputs from mudstones underlying the Budleigh Salterton Pebble Beds Formation or from the River Otter. During recharge a series of chemical reactions takes place, the most important of which are mineral dissolution and precipitation. In this aquifer there are also likely to be mixing and sorption/ desorption reactions. However, redox reactions and ion-exchange are likely to be limited owing to the nature of the oxidising unconfined aquifer and the scarcity of exchange sites. Once the Sherwood Sandstone aquifer becomes confined, down dip, it is likely that redox reactions would have greater importance.

The groundwaters in this study were sampled from two units which make up the Sherwood Sandstone aquifer in Devon and Somerset. The water types were distinctly different between these units to the extent that groundwaters of unknown source could be identified. The groundwaters sampled from the Otter Sandstone Formation are mainly Ca-HCO_3 type, with some mixing towards Mg, and the groundwaters sampled from the Budleigh Salterton Pebble Beds Formation range from Ca-HCO_3 type to Na-Cl type. In addition the groundwaters from the Budleigh Salterton Pebble Beds Formation are more acidic, more oxic, have lower SECs, and HCO_3, Cr, U and Mg concentrations, and higher concentrations of Al, Be, Cd, Cr, Co, Tl and REEs than the groundwaters from the Otter Sandstone Formation.

The concentrations of solutes in the groundwaters in the Sherwood Sandstone aquifer can span many orders of magnitude. The observed ranges result from a number of factors, and natural geochemical reactions can account for the bulk of the observed variation. For most determinands the 95th percentile can be taken as a first approximation of the upper limit of the baseline range. This removes any obvious upper outliers for most determinands.

A notable exception to this is NO_3-N, for which the 95th percentile is 21.2 mg L^{-1}, and the 90th percentile is 18.5 mg L^{-1}. These values are in excess of the drinking-water limit (11.3 mg L^{-1}), and are unlikely to be naturally derived. Out of 28 analyses, seven were in excess of this limit. While NO_3-N concentrations in some groundwaters were seen to increase over time, it is evident that the increase of more sensitive farming methods has led to some decrease in the groundwater concentrations of NO_3-N.

Rainfall is an important control on the groundwater chemistry of conservative elements such as Cl. Most of the groundwater Cl concentrations are much higher than the concentrated rainfall concentrations shown in Table 3.3. This suggests additional inputs of solutes, or more pronounced evapotranspiration than is typical in UK groundwaters. The highest values are generally found near to the south coast, and the Cl data correlate well with the Na data, indicating that marine NaCl provides additional inputs of these major elements.

Trace elements mainly derive naturally from the varied geological strata, their distribution being dependent on abundance as well as speciation and local aquifer conditions, including Eh and pH. Observed concentrations in many cases represent baseline compositions but some anomalous concentrations have been linked to contamination of the groundwater by anthropogenic

activities. The source of any contamination has been interpreted from geographic location, concentrations of accompanying solutes, local land-use and temporal variability.

6.2   EXTENT OF ANTHROPOGENIC INFLUENCES

Superimposed on natural baseline compositions are anthropogenic influences. Anthropogenic influences can directly affect the groundwater chemistry via point sources or diffuse pollution. Additionally, anthropogenic influences can indirectly affect the groundwater chemistry, for example by physical processes such as abstraction.

Abstraction from boreholes near to the River Otter has been is thought to cause infiltration from the river into the aquifer (Perl et al., 2004). The limited area of aquifer which crosses the flow lines meant it was difficult to identify any lateral trends, and so any effect on the groundwater quality is difficult to identify from spatial distributions.

Nitrate pollution is one of the largest problems facing unconfined groundwater in the UK: 60% of groundwater bodies in England may fail to meet the Water Framework Directive requirement of 'good' status by 2015 because of high NO_3 concentrations (Rivett et al., 2007). The main cause of these high concentrations is the development of intensive agriculture, which uses NO_3-rich fertilisers. Nitrate is extremely mobile and, while there are relatively few sites in the study area whose NO_3 concentrations exceed the drinking-water limit, there are signs that concentrations are increasing locally, and could exceed this limit in the future.

Anomalous concentrations of a suite of trace elements such as Zn, Cu, Cr, Mo, Mn and Ni can represent contamination from the wellhead pipework. However, only one sample contains particularly elevated concentrations of more than two of these elements. This indicates that metallic contamination is relatively minor in these groundwater samples, and the 95th percentile is a good first approximation for baseline ranges of these elements.

7 Conclusions

The Sherwood Sandstone aquifer is comprised of two distinct geological units, and the groundwater in these units is consequently variable in its natural character. The chemical compositions of the groundwaters have been characterised by investigation of the statistical distributions, mapping of the spatial variability, assessment of temporal changes, and interpretation of the predominant geochemical processes. For many analytes, the 95th percentile of the distributions has been taken as a first approximation of an upper limit of baseline concentrations as this serves to eliminate the most extreme outlier concentrations that likely represent a distinct population.

The main properties of the groundwater are determined by rainwater recharge reacting with the aquifer minerals. Of these minerals carbonates are the dominant influence on the water chemistry, giving mainly Ca-HCO_3 type waters in the Otter Sandstone Formation aquifer, and Ca-HCO_3 type to Na+K-Cl type in the Budleigh Salterton Pebble Beds Formation aquifer. There is little variation in the major ion proportion of the groundwaters from the Otter Sandstone Formation, most likely as these represent groundwater in equilibrium with the minerals which give it this character. There is greater variation in the Budleigh Salterton Pebble Beds Formation groundwaters.

The most obvious impacts of anthropogenic inputs are seen in the spatial and temporal variations in NO_3 derived mainly from modern intensive farming practices. Concentrations exceed the current drinking-water limit of 11.3 mg L^{-1} (as NO_3-N) at seven of the sites. This is a large proportion (25%) of the sampled groundwaters. This probably reflects the intensification of agriculture in the study area over the last few decades. Indeed, the dominant landuses of the area are agriculture and grassland.

There was no evidence for widespread contamination by potentially harmful trace elements. For most trace elements, any elevated concentrations tend to be localised, and probably represent either localised pollution, contamination of the sample from the head workings of the borehole, or are a natural localised anomaly.

The waters were generally of good inorganic quality, but the high concentrations of nitrate mean that there are some waters of poor quality within this aquifer.

References

ABESSER, C, SHAND, P, and INGRAM, J. 2005. The Carboniferous Limestone of Northern England. *British Geological Survey and Environment Agency*, BGS Report CR/05/076N; Environment Agency Report NC/99/74/22 (Keyworth and Solihull).

ALLEN, D J, BREWERTON, L M, COLEBY, L M, GIBBS, B R, LEWIS, M A, MACDONALD, A M, WAGSTAFF, S, and WILLIAMS, A T. 1997. The physical properties of major aquifers in England and Wales. *British Geological Survey*, WD/97/34 (Keyworth).

BEARCOCK, J, and SMEDLEY, P L. 2009. Baseline groundwater chemistry: the Magnesian Limestone of County Durham and North Yorkshire. *British Geological Survey* BGS Report OR/09/030 (Keyworth).

CLARK, I, and FRITZ, P. 1997. *Environmental Isotopes in Hydrogeology*. (Boca Raton, USA: Lewise Publishers.)

CORNELL, D H. 1993. Rare-earths from supernova to superconductor. *Pure and Applied Chemistry*, Vol. 65, 2453-2464.

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

DARLING, W G, MORRIS, B L, STUART, M E, and GOODDY, D C. 2005. Groundwater indicators from public supplies tapping the Chalk aquifer of southern England. *Journal of the Chartered Institution of Water and Environmental Management*, Vol. 19, 30-40.

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

DEFRA. 2010. Department for Environment Food and Rural Affairs. http://ww2.defra.gov.uk/food-farm/land-manage/nitrates/ Accessed 11/1/11. [cited 11/1/11].

DREVER, J I. 1997. *The Geochemistry of Natural Waters: Surface and Groundwater Environments, 3rd Edition*. (Upper Saddle River: Prentice-Hall, Inc.)

EA. 2004. Groundwater Quality Review: Otter Sandstone. *Environment Agency*, BGS Report OR/09/030 (Bristol).

EA. 2009. River Basin Management Plan South West River Basin District, Environment Agency.

EDMONDS, E A, and WILLIAMS, B J. 1985. *Geology of the country around Taunton and the Quantock HIlls*. (London: HMSO.)

EDMUNDS, W M. 1996. Bromine geochemistry of British groundwaters. *Mineralogical Magazine*, Vol. 60, 275-284.

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

EDWARDS, R A. 1997. Geology of the Budleigh Salterton District. British Geological Survey technical report WA/97/50.

EDWARDS, R A, and GALLOIS, R W. 2004. *Geology of the Sidmouth district - a brief explanation of the geological map* . Sheet Explanation of the British Geological Survey. 1:50 000 Sheets 326 and 340 Sidmouth (England and Wales).

FAURE, G. 1998. *Principles and Applications of Geochemistry*. (New Jersey: Prentice Hall.)

FULLER, R M, SMITH, G M, SANDERSON, J M, HILL, R A, and THOMSON, A G. 2002. The UK Land Cover Map 2000: construction of a parcel-based vector map from satellite images. *Cartographic Journal*, Vol. 39, 15-25.

HELSEL, D. 2005. *Nondetects and Data Analysis: Statistics for Censored Environmental Data*. (New York: Wiley & Sons.)

HEM, J D. 1992. *Study and Interpretation of the Chemical Characteristics of Natural Water* (Third Edition edition). US Geological Survey Water-Supply Paper 2254. (Washington: United StatesGovernment Printing Office.)

HOLLOWAY, S, MILODOWSKI, A E, STRONG, G E, and WARRINGTON, G. 1989. The Sherwood Sandstone Group (Triassic) of the Wessex Basin, southern England. *Proceedings of the Geologists' Association*, Vol. 100, 383-394.

HOUNSLOW, M W, and RUFFELL, A H. 2006. Triassic: seasonal rivers, dusty deserts and saline lakes. 559 in *The Geology of England and Wales*. BRENCHLEY, P J, and RAWSON, P F (editors). (London: The Geological Society.)

KELLY, W R, and PANNO, S V. 2008. Some considerations in applying background concentrations to ground water studies. *Ground Water*, Vol. 46, 790-792.

KINNIBURGH, D G, and EDMUNDS, W M. 1986. The susceptibility of UK groundwaters to acid deposition. Hydrogeological Report, British Geological Survey No. 86/3.

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

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

LEE, L, and HELSEL, D. 2005b. Statistical analysis of water-quality data containing multiple detection limits: S-language software for regression on order statistics. *Computers & Geosciences*, Vol. 31, 1241-1248.

LEE, L, and HELSEL, D. 2007. Statistical analysis of water-quality data containing multiple detection limits II: S-language software for nonparametric distribution modeling and hypothesis testing. *Computers & Geosciences*, Vol. 33, 696-704.

LEVINSON, A A. 1974. *Introduction to Exploration Geochemistry*. (Calgary: Applied Publishing Ltd.)

MCLEISH, A. 1992. *Geological Science*. (Cheltenham: Nelson Thornes Ltd.)

OPSI. 2010. The Water Supply (Water Quality) Regulations 2010. <u>Welsh Statutory Instruments 2010 No. 994 (W.99)</u>.

PERL, T, ROY, S, THOMSON, P, and LEES, J. 2004. Groundwater Quality Review: Otter Sandstone. Analysis of the Otter Sandstone Groundwater Chemistry. Environment Agency Report GWQR019.

R DEVELOPMENT CORE TEAM. 2005. R: a language and environment for statistical computing. *R Foundation for Statistical Computing* (Vienna, Austria).

RIVETT, M O, SMITH, J W N, BUSS, S R, and MORGAN, P. 2007. Nitrate occurence and attenuation in the major aquifers of England and Wales. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol. 40, 335-352.

SHAND, P, EDMUNDS, W M, LAWRENCE, A R, SMEDLEY, P L, and BURKE, S. 2007. The natural (baseline) quality of groundwater in England and Wales. *British Geological Survey & Environment Agency*, RR/07/06 & NC/99/74/24 (Keyworth and Solihull).

SHUMWAY, R H, AZARI, R S, and KAYHANIAN, M. 2002. Statistical approaches to estimating mean water quality concentrations with detection limits. *Environmental Science & Technology*, Vol. 36, 3345-3353.

SMEDLEY, P L, and ALLEN, D. 2004. The Granites of south-west England. *British Geological Survey and Environment Agency*, BGS Report CR/04/255; Environment Agency Report NC/99/74/16 (Keyworth and Solihull).

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

USSHER, W A E, REID, C, FLETT, J S, and MACALISTER, D A. 1913. *Geology of the country around newton Abbot*. (London: HMSO.)

USSHER, W A E, WOODWARD, H B, and JUKES-BROWN, A J. 1906. *The Geology of the country between Wellington and Chard*. (London: HMSO.)

WALTON, N R G. 1982. A detailed hydrogeochemical study of groundwaters from the triassic sandstone aquifer of south-west England. Institute of Geological Sciences Report 81/5.