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14. The Corallian of Oxfordshire and Wiltshire

Groundwater Systems and Water Quality
Commissioned Report CR/04/262N

Science Group: Air, Land & Water
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The Natural Quality of Groundwater in England and Wales
A joint programme of research by the British Geological Survey and the Environment Agency

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Cover illustration

Shelly, oolitic Corallian limestone near Baulking, Vale of White Horse.

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Baseline Report Series: **14. The Corallian of Oxfordshire and Wiltshire**

J Cobbing, M Moreau, P Shand, A Lancaster

Contributors

R Hargreaves (GIS)

Environment Agency Project Manager:

Dr Rob Ward / Jonathan Smith
Science Group: Air, Land & Water

British Geological Survey Project Manager:

Dr Paul Shand
Groundwater Systems & Water Quality Programme

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Keyworth, Nottingham NG12 5GG

0115 936 3100 Telex 378173 BGSKEY G
 Fax 0115 936 3200
e-mail: sales@bgs.ac.uk www.bgs.ac.uk

Murchison House, West Mains Road, Edinburgh, EH9 3LA

0131 667 1000 Telex 727343 SEISED G
 Fax 0131 668 2683

London Information Office at the Natural History Museum, Earth Galleries, Exhibition Road, South Kensington, London, SW7 2DE

0207 589 4090 Fax 0207 584 8270
 0207 938 9056/57

St Just, 30 Pennsylvania Road, Exeter EX4 6BX
 01392 278312 Fax 01392 437505

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

01232 666595 Fax 01232 662835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

01491 838800 Fax 01491 692345
email: hydro@bgs.ac.uk

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

01793 411500 Telex 444293 ENVRE G
 Fax 01793 411501

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Environment Agency, Rio House, Waterside Drive, Aztec West Almondsbury, Bristol, BS32 4UD

Tel: 01454 624400 Fax: 01454 624409
www.environment-agency.gov.uk

Further copies of this report are available from the Environment Agency's National Customer Contact Centre by emailing: enquiries@environment-agency.gov.uk or by telephoning 08708 506506.

Environment Agency Regional Offices

Anglian
Kingfisher House,
Goldhay Way, Orton Goldhay, Peterborough PE2 5ZR
Tel 01733 371811 Fax 01733 231840

Midlands
Sapphire East, 550 Streetsbrook Road, Solihull, West Midlands B91 1QT
Tel 0121 711 2324 Fax 0121 711 5824

North East
Rivers House, 21 Park Square South, Leeds LS1 2QG
Tel 0113 244 0191 Fax 0113 246 1889

North West
Richard Fairclough House, Knutsford Road, Warrington WA4 1HG
Tel 01925 653999 Fax 01925 415961

South West
Manley House, Kestrel Way, Exeter EX2 7LQ
Tel 01392 444000 Fax 01392 444238

Southern
Guildbourne House, Chatsworth Rd, Worthing, Sussex BN11 1LD
Tel 01903 832000 Fax 01903 821832

Thames
Kings Meadow House, Kings Meadow Road, Reading RG1 8DQ
Tel 0118 953 5000 Fax 0118 950 0388

Environment Agency Wales
29 Newport Road, Cardiff CF24 0TP
Tel 01222 770088 Fax 01222 798555

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FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

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

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer's physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use historical records and the application of graphical procedures such as probability plots to discriminate different populations (Shand and Frengstad, 2001; Edmunds et al., 2002). The “baseline” refers to a *specified system* (e.g. aquifer, groundwater body or formation) and is represented by a range of concentrations within that system. This range can then be specified by the median and lower and upper limits of concentration.

The BASELINE objectives are:

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

1. EXECUTIVE SUMMARY

The Corallian Group of southern England is composed of discontinuous, interlayered carbonate and clastic rocks of Jurassic age deposited in shallow marine conditions, which dip to the southeast and are bounded above and below by clay lithologies. The Corallian is commonly regarded as a minor aquifer, although it is locally important. The study area of this report extends from approximately Swindon in the southwest to Oxford in the northeast, although the Corallian Group as a whole stretches from Dorset to the north of England. The aquifer can be considered as a series of layers that are frequently hydraulically separate, and which can have markedly different chemical characteristics. Faulting further complicates flow patterns. Yields from boreholes in the Corallian are moderate, typically between 25 and 85 m³ d⁻¹. Groundwater flow is both intergranular and via fissures, with the latter considered to be important in sustaining larger yields. The Corallian aquifer in the study area supported several large abstractions in the past, including a public water supply for the town of Abingdon, whilst today it still supplies many farms, nurseries, market gardens, golf courses and domestic users.

The present study used a combination of existing data from the Environment Agency together with 24 new samples collected from boreholes across the study area in August 2003 to draw conclusions about the chemistry of the Corallian groundwater. Relatively little prior research on the hydrogeochemistry of Corallian groundwaters has been carried out. Groundwater in the Corallian is usually of good quality in terms of inorganic constituents where the aquifer outcrops, although salinity increases rapidly down dip of the outcrop area. Iron concentrations can be high, in a number of cases exceeding the CEC drinking water limit (0.2 mg/l), particularly where reducing conditions are present. This is thought to be due to dissolution of iron oxyhydroxides from the aquifer matrix. The carbonate matrix of the aquifer tends to buffer infiltrating acidic waters, and also gives rise to the typical Ca-HCO₃ water types. Concentrations of metals such as aluminium, mobile in more acidic waters, are consequently low. The dominant influence on the groundwater chemistry is considered to be interaction of the water with the aquifer material (mineral dissolution), together with mixing with connate palaeowaters in certain places. There is a large range in concentration for most of the major elements. There is evidence for ion exchange reactions as groundwater moves from the recharge area at outcrop to the part of the aquifer overlain by clays, with exchange of dissolved Ca for sorbed Na giving rise to waters of Na-HCO₃ type.

Pollution of groundwater by nitrate is a known problem in some areas, although concentrations in most boreholes sampled in this study were low. Groundwater sampling was not carried out in urban areas such as Abingdon where it is possible that evidence of pollution, possibly from former industrial activity, would be found. The presence of clay layers in the aquifer probably provides some protection from surface pollution. However, the fractured nature of the limestones that constitute the important permeable units within the Corallian implies potentially rapid transport of contaminants with little attenuation.

2. PERSPECTIVE

The Corallian aquifer, of Jurassic age, forms an important minor aquifer in southern England. The area of this study extends from Wheatley near Oxford in the northeast, to Calne (southwest of Swindon) in Wiltshire in the southwest (Figure 2.1). This strip of Corallian rocks is on average about 4 km wide, but varies in width up to about 8 km (Arkell, 1927). The Corallian rocks form a range of low hills, such as those to the south and west of Oxford, which contrast with the surrounding lower lying and less competent clay formations above and below. This ridge of Corallian hills separates the Thames (or Isis) Valley from the Vale of the White Horse (Sumbler, 1996). The area is drained eastwards by the River Thames (flowing from north of Swindon to Oxford and then southwards) and its tributaries, in particular the River Ock flowing roughly west to east in the Vale of the White Horse (Swindon to Abingdon). In former times, salt marshes existed around Abingdon and Harwell, probably as a result of up-welling saline groundwaters. These marshes have now been drained.

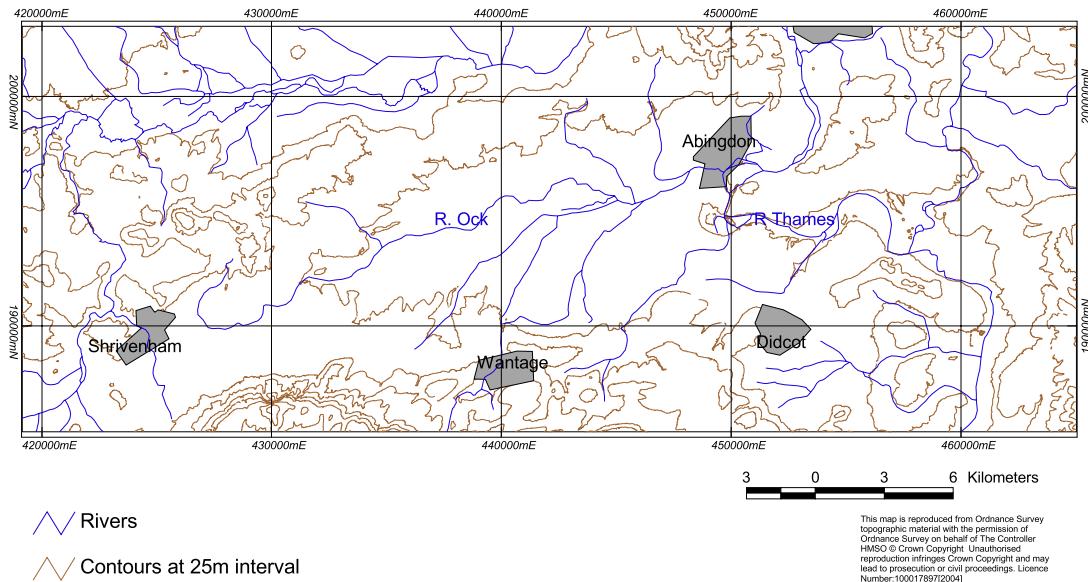


Figure 2.1 Topographic Map of the study area showing the main towns.

There is an even distribution and widespread coverage of licensed boreholes across the Corallian outcrop, and a similar distribution of monitoring boreholes. However, due to the proximity of the Chalk, most of the water supplies in the Thames Region, including public water supplies, tend to draw groundwater from the higher yielding Chalk rather than the Corallian. There are no major supplies used for public consumption in the Corallian, and therefore there are no published source protection zones. Previously the town of Abingdon, together with several of the smaller towns situated on or near the Corallian outcrop, relied on groundwater from the aquifer for public supply. Today water supplies are more integrated and this is no longer the case. Nonetheless, the Corallian constitutes a locally important aquifer and supplies farms, golf courses, houses and other private users.

There is currently an investigation being undertaken to assess the impact of abstractions from the Corallian aquifer on groundwater-dependent wetland sites. Calcareous fens near the Corallian springs on the dip slope are designated as Sites of Special Scientific Interest (SSSIs). In order to protect the springs issuing from the Corallian, abstractions are no longer permitted from the Coral Rag near Swindon so significant degradation of these SSSIs is not expected.

The Corallian Group has been extensively quarried for both sand and building stone, and many of the ancient buildings in Oxford as well as parts of Windsor Castle are built from the Coral Rag and

Wheatley Limestones (Sumbler, 1996). The group is still quarried in the study area as a source of building sand, gravels and aggregates.

Aquifers are variably vulnerable to urban, agricultural and industrial pollution. The local vulnerability map (NRA, 1995) classifies soils in the outcrop area as mainly H1 and I1, which means that many areas have soils with high or intermediate soil leaching potential which provide little protection against either diffuse or point source pollution from the ground surface. The main urban developments in the area of study include Oxford, Swindon and Faringdon. The town of Abingdon is located on the edge of the outcrop. Most of the rest of the outcrop area is used as managed grassland, or for growing crops. Agricultural practice in the area includes mixed crops and livestock, including dairying. These are potentially sources of nitrate, phosphate, sulphate and fertilizer pollution. The designation of this area as a Nitrate Vulnerable Zone is primarily designed to protect surface water (which has nitrate concentrations exceeding thresholds set out in the EC Nitrate Directive), however the Corallian aquifer may also benefit from these control measures.

Proposals for a reservoir near Abingdon (at approximately SU 4450 9400), with a surface area of roughly 6 km², are being discussed at present. If constructed, a possible impact on the aquifer could be leakage through the partially excavated Kimmeridge Clay at the base of the reservoir into the Corallian, due to the increase in hydraulic head (about 20 m). The location and extent of discontinuities within the Kimmeridge Clay would require further investigation. The Corallian aquifer provides baseflow to the River Ock. Leakage from the Kimmeridge Clay could force saline porewaters in the clay into the underlying Corallian aquifer that could lead to higher mineral concentrations in the Corallian groundwater, and possibly affect the River Ock.

The focus of this report is on the variations in the water quality related to natural geochemical processes and how these vary within the aquifer. This will be presented in relation to current understanding of the hydrogeology of the aquifer. Hydrochemical data will also be used to estimate relative groundwater ages and temporal variations.



Figure 2.2 A view north across the Corallian outcrop from the Chalk scarp at Whitehorse Hill (from approximately SU 297 865).

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

In order to assess the baseline groundwater quality of the aquifer, it is necessary to understand the groundwater system. This requires information on the geological and hydrogeological setting and the groundwater flow regime. Knowledge of the mineralogy and geochemistry of the component minerals, and of rainfall as the initial source term, is also required to explain the characteristic groundwater chemistry.

3.2 Geology

The Jurassic rocks in the study area (Figure 3.1) comprise Oxford Clay (of Callovian age), overlain by the Corallian and related strata, which are in turn overlain by the Kimmeridge Clay (Table 3.1). These are overlain in turn by Cretaceous rocks of the Lower Greensand, Gault, Upper Greensand and Chalk Formations. The Corallian rocks are therefore bounded above and below by low-permeability clays. The Corallian strata dip gently to the southeast beneath the Kimmeridge Clay Formation, hence the northern limit of the Corallian is at the edge of the outcrop, where the formation is replaced by the underlying Ancholme Group. The southern limit of the Corallian as an aquifer is more difficult to assess, since groundwater quality deteriorates fairly rapidly down dip and is consequently rarely used. The Group is not thought to extend far down dip of its outcrop however. The Corallian thins in the southwest and the northeast, where it is replaced by the West Walton Formation, interdigitated in places with the Corallian. The Corallian consists of a varied sequence of calcareous sandstones, clays and shallow marine limestones with local developments of coral (Jones et al., 2000). The nature of the deposits suggests that they formed relatively close to a shoreline. The local coral growth and carbonate deposition that formed the Corallian on the margins of the London platform occurred in Late Oxfordian times, during a short-lived change to shallower water, high-energy conditions (Sumbler, 1996). This is thought to have been accompanied by a warmer and drier climate. Much of the Corallian Group is richly fossiliferous, containing corals, gastropods, bivalves, echinoids, ammonites and other fossils (Sumbler, 1996). Superimposed on the general dip of the strata are local changes in stratigraphy and topography due to lateral changes in composition and the effects of faulting and flexuring (Paterson, 1979). The rocks are affected by major faults and periclinal structures east of Oxford.

The thickness of the Corallian in the study area is usually estimated to be about 35 m, although it thins to the northeast and southwest. A 78 m thick sequence of Corallian strata was recorded at Harwell (Alexander and Brightman, 1985). The Corallian rocks are not thought to extend far down dip of the outcrop area (Jones et al., 2000). Boreholes at Ware, Slough, Winkfield (near Bracknell) and London indicate that the Corallian is not present at these locations some distance down dip of the outcrop (Arkell, 1927).

The complexity and relatively rapid lateral changes in the lithology have led to a variety of local names being applied to the strata. Locally one or more units may be absent due to its laterally discontinuous nature. Uncertainties in correlation remain to this day. The Corallian has been broadly divided into the Lower Corallian and the Upper Corallian divisions (Richardson et al., 1946). The Lower Corallian is represented by the sands and concretionary calcareous sandstones of the Lower Calcareous Grit Formation. This formation consists of yellow and white sands and sandstones, containing bands of hard spheroidal concretionary masses or doggers. The doggers are thought to have formed as a result of secondary processes, since false bedding passes through them (Arkell, 1933). Numerous small pebbles of white vein quartz and hard black lydite, a dense black variety of chert, (formerly used as a ‘touchstone’ for determining the purity of gold and silver) occur. These are derived presumably from Palaeozoic rocks. Fossilised wood, vertebrae of Teleosaurus (a Jurassic crocodilian reptile), and other plant and animal fossils have also been found. The Lower Calcareous Grit varies from 3.5 m to 24 m thick, but is usually 9-12 m thick (Arkell, 1933).

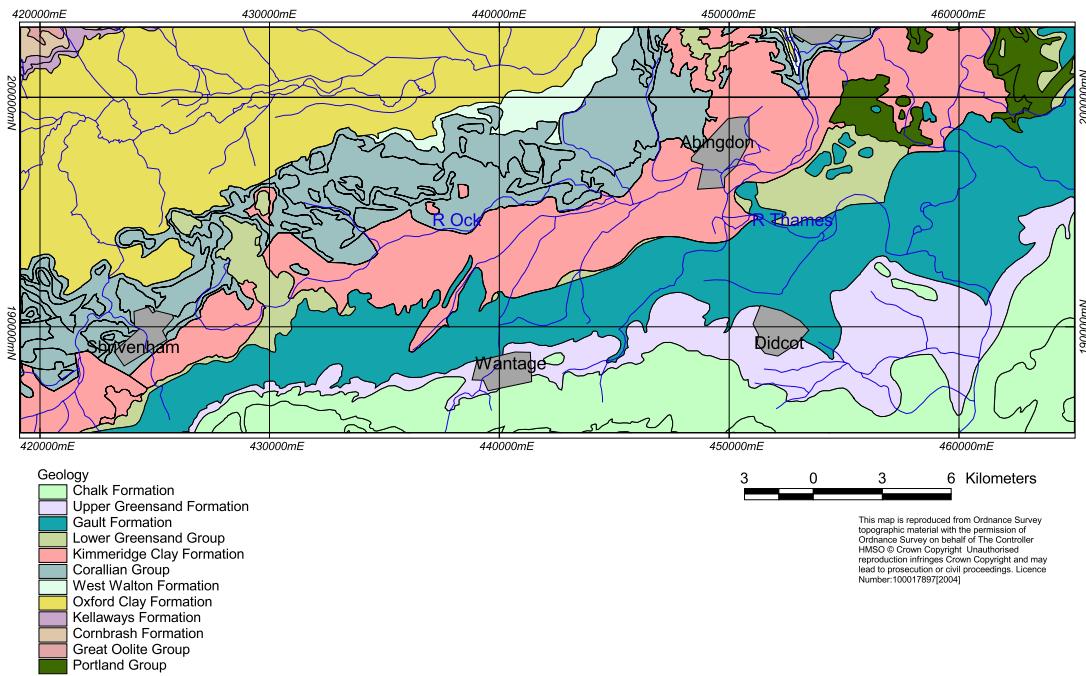


Figure 3.1 Solid geology of the study area.

The Lower Corallian is succeeded unconformably by a sequence of shelly fragmented limestones, which include coral debris, sandstones and mudstones, and which together comprise the Upper Corallian division. The presence of sand in all of the layers above the Lower Calcareous Grit can make it difficult to distinguish the top of the Lower Corallian, although a pebble bed generally marks the bottom of the Upper Corallian. Some of these pebbles consist of well-rounded, indurated Lower Calcareous Grit, proving that a considerable period of erosion took place after the latter was deposited (Arkell, 1927). Other pebbles in this lower layer consist of chert and quartz, together with characteristic non-oolitic grey limestone pebbles up to 10 cm in diameter, thought to be derived from the Oxford Clay. The lowermost of the Upper Corallian layers is the Highworth Limestone Formation, which is overlain by thin grey oolitic marls up to 1.5 m thick. The marls are overlain by the Highworth Clay and the Highworth Grit. It is recorded that the water supply of the town of Highworth near Swindon was historically obtained from the Highworth Grit, by means of numerous shallow wells sunk through the overlying formations (Arkell, 1933). At this location the Highworth Grit and the Highworth Clay together are between 3 m and 3.5 m thick. These strata are absent in the area immediately around Faringdon.

The top of the Upper Corallian is known as the Coral Rag Formation, and contains reef-building corals that in places form irregular blocks a metre or more in diameter (Richardson et al, 1946). The Coral Rag was deposited unconformably onto a variety of underlying Corallian strata, depending on the location. In some locations, the formation was deposited directly onto the eroded surface of the Lower Calcareous Grit (Arkell, 1927). The corals are thought to have formed coastal reefs and islands, and the Coral Rag Formation terminates abruptly near Wheatley where the sea became deeper. Near Highworth, and again from Faringdon to Kingston Bagpuize, the Coral Rag is underlain by false bedded, fissile, sandy oolites known as the Pusey Flags, which reach a maximum thickness of about 3 m (Arkell, 1933). The Coral Rag is replaced in some locations by greyish white limestones of the Wheatley Limestone Formation, so called because they are particularly thick near the town of Wheatley, just to the east of Oxford. This formation consists of alternating softer and harder bands, is usually non-oolitic and is composed of finely ground fragments of corals and shells. A detrital “brash” (broken or rubbly) facies may also be present in this upper part. The Corallian limestones generally tend to be soft, poorly cemented and porous (Jones et al., 2000).

Table 3.1 summarises the principal formations (after Powell et al, 1998).

Table 3.1 Principal lithologies of the Corallian

Unit	Description
Coral Rag Formation/Wheatley Limestone Formation	Shelly, locally coral-rich limestone
Calne Formation and Osmington Oolite Formation	Limestone, ooidal in part
Highworth Grit Formation/Beckley Sand Formation	Calcareous sandstone
Highworth Clay Formation	Mudstone
Highworth Limestone Formation	Limestone
Lower Calcareous Grit Formation	Calcareous sandstone, spiculitic sandstone and sand

Drift deposits in the study area consist mainly of Pleistocene alluvium and river terrace deposits associated with the Rivers Thames and Ock (Figure 3.2). The river terrace deposits are mainly sands and gravels, and have become isolated as the river has cut downwards. The upper terraces are therefore the oldest. Terrace formation is considered to be related to climatic fluctuations in the Pleistocene, with most deposits thought to have been formed during cold climate stages (Sumbler, 1996). However, small amounts of material from warmer periods have been recognised. The higher-level terraces are relatively poorly preserved, and may contain pebbly clays with pebbles of quartzite, quartz and other rocks derived from Triassic lithologies in the Midlands.

It is difficult to predict the precise nature of the rocks that will be encountered by a borehole prior to drilling, since many layers in the Corallian are discontinuous and vary in thickness over relatively short distances. The classification of the strata after drilling is also often difficult.

Geophysical logging of boreholes can provide a way of resolving the different Corallian strata at a local scale. There are relatively few geophysical logs currently available for the Corallian aquifer in the study area, although the technique lends itself to the delineation of clay rich layers. The geophysical logs presented in Figure 3.3 are from a site at Kingston Hill Farm (NWI No: SP40/75; SP 4080 0000). They show the changes in the natural gamma ray (track 3, pink) and resistivity (track 4, blue) logs that are related to changes in mineralogy and aquifer properties. In particular, the proportion of clay minerals in the rock determines the natural gamma ray activity, and also has an effect on the resistivity. Gamma ray and resistivity logs such as these, showing significant variation, confirm that the relative proportions of clay and limestone change over relatively short intervals in the Corallian, and are probably the easiest way to discern the discontinuous limestone bands that exert a large control over the hydrogeological properties. The fluid temperature (track 1) and fluid conductivity (track 2) logs can be used to infer flow horizons. For example, the temperature and conductivity anomaly at about 7 m below ground level correlates with a resistivity “low”, implying a limestone layer at this point that is more permeable than other parts of the sequence.

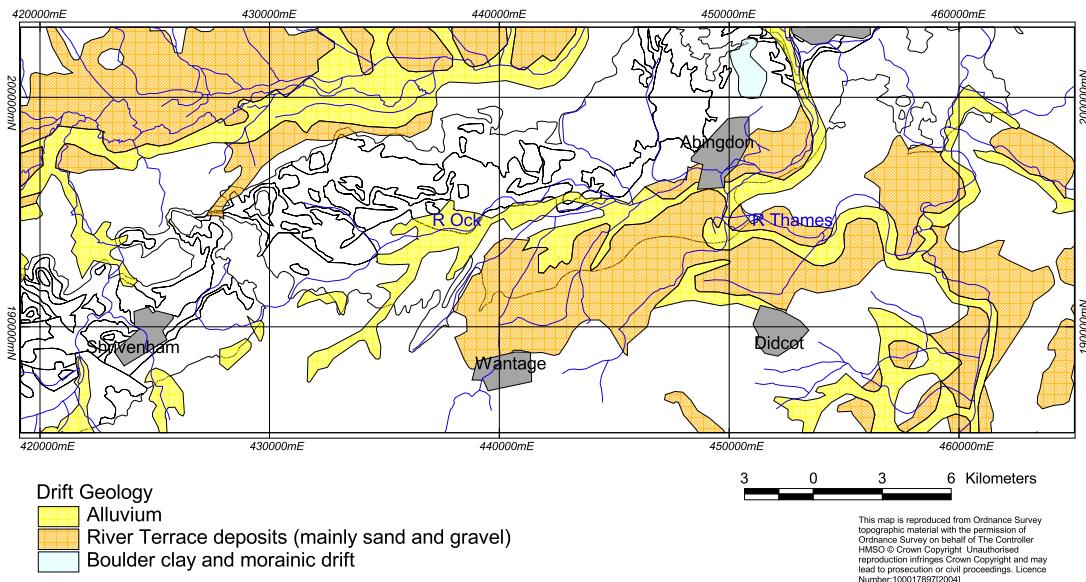


Figure 3.2 Drift geology of the study area.

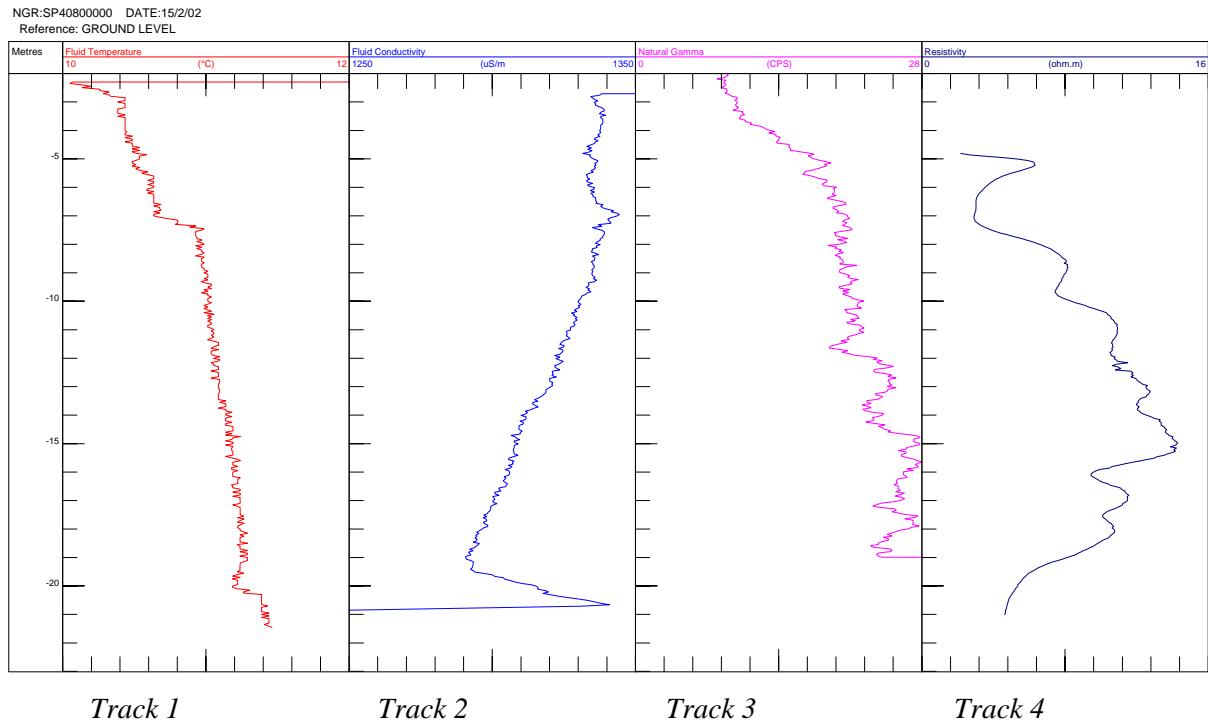


Figure 3.3 Geophysical Logs at Kingston Hill Farm.

3.3 Hydrogeology

The limestones and calcareous sandstones of the Corallian Group in the study area are usually grouped together as a “Minor Aquifer” (Jones et al, 2000), although they are of considerable local importance. The aquifer is particularly productive in the Abingdon area, where several important industrial and public water supply abstractions were formerly sited (Alexander and Brightman, 1985). Examples of former industrial abstractions in the area include the Vineyards Maltings and the Pavlova Leather Works boreholes, although both sites have now been redeveloped. The changes in industry that have taken place in Abingdon, such as the closure of the MG automotive works in 1980 and the Morlands Brewery in 1999, together with the centralisation of water supplies, have meant that several

large sources in the town are no longer used. However, numerous smaller supplies for farms, nurseries, golf courses and households continue to draw water from the Corallian. Where clays overlie the aquifer groundwaters generally have high hardness but are potable, and dissolved iron concentrations are raised. Most sources are situated either on or very close to the outcrop of the aquifer, because salinity increases quite rapidly down dip of the outcrop.

The Corallian Group may be better described as a sequence of minor aquifers, rather than as a single aquifer, because the different layers can have very different hydraulic and chemical characteristics. The total thickness of the group in the study area is normally around 35 m, although around Oxford the basal part of the group is very silty and the usable aquifer here is probably only about 20 m thick (Jones et al., 2000). Considerable variations in thickness are found. The Coral Rag in the upper part of the sequence is the most permeable of the aquifer units in the study area. The variation in properties between the different aquifer units can lead to fresh and saline waters being in close vertical proximity, such as is found at Harwell (Alexander and Brightman, 1985). Faulting is known to affect groundwater flow in the various units, either by restricting flow to discrete hydraulic "blocks", or by enabling flow between units that would otherwise be hydraulically separate. Since the aquifer units are relatively thin, even faults with fairly small displacements have this potential. Assigning hydraulic characteristics to the aquifer group as a whole is complicated by the fact that boreholes rarely penetrate the full thickness of the Group.

Springs occur on the scarp slope close to the Corallian and Oxford Clay junction, and on the dip slope at the junction of the Coral Rag with the overlying Kimmeridge Clay (Jones et al., 2000). These latter springs are supersaturated with calcium carbonate and deposit tufa, producing calcareous fens (e.g. Marcham Fen at SU 467 797). Spring waters from the Corallian have generally high hardness, and the relative stability of the spring water temperature indicates generally slow movement of groundwater (Paterson, 1979).

The general flow direction in the Corallian is towards the south to southeast, following the dip of the strata. However, recharge percolating downwards through the overlying strata down dip of the aquifer is thought to contribute to another element or sub-system of flow in a northwesterly direction. This sub-system is driven by the elevated topography of the Chalk Downs to the south of the Corallian outcrop. The two flow systems meet in a region of low hydraulic head centred around Abingdon and extending in a westerly direction along the Ock Valley, where a zone of mixing is thought to exist just under the edge of the Kimmeridge Clay (the area was once a salt-marsh). The position of the mixing zone can change with time in response to recharge and abstractions (Alexander and Brightman, 1985). The fact that both saline and fresh waters exist in juxtaposition in this locality is attributed to the laterally variable nature of the Coral Rag, which results in interdigitation (Alexander and Brightman, 1985). There may be a component of groundwater derived from the underlying Oxford Clay, but this is not proven.

Down dip, the aquifer is confined and overflowing artesian conditions are found, especially to the south and southeast of Abingdon. However, as the water quality deteriorates rapidly with distance from outcrop (including increases in chloride and sodium concentrations associated with mixing with connate waters) this water is little used (Jones et al., 2000). Highly mineralised, non-potable water is found at distances of between 5 and 6 km down dip of the Corallian outcrop (Alexander and Brightman, 1985). The age of groundwater increases quite rapidly down dip, based on ^{14}C dating, and it is estimated that no modern water is present at distances of 3 km or more from the edge of the outcrop (Alexander and Andrews, 1984).

Yields from boreholes in the Corallian aquifer are typically between 25 and 85 $\text{m}^3 \text{ d}^{-1}$ (0.3 to 1 1 s^{-1}), but are less when the aquifer is not fully saturated. A maximum yield of 1425 $\text{m}^3 \text{ d}^{-1}$ (16.5 1 s^{-1}) was obtained at Cowley (SP 5513 0311) from a 250 mm diameter borehole, for a drawdown of 2.2 m (Jones et al., 2000). Near Abingdon, sustainable yields of up to 800 $\text{m}^3 \text{ d}^{-1}$ (9 1 s^{-1}) have been obtained (Sumbler, 1996). At Wootton (SP 4811 0063) the Corallian yields 660 $\text{m}^3 \text{ d}^{-1}$ (7.6 1 s^{-1}) and was used for public supply (Richardson et al., 1946). The borehole at Peach Croft Farm (SU 5120 9910, sampled in this study) yielded 11.3 1 s^{-1} during a 48 hour long pumping test for a drawdown of 27.6 m.

Solution enhanced fractures in the limestone units are likely to contribute significantly to borehole yields where they are present. The final yield of a borehole will depend on the number and connectivity of the fractures that it intersects.

The porosity of the Corallian limestones appears to be highly variable. Reported values range from 6.0 % to 39.3 %, with a mean value of 23.7 %, obtained from a set of 11 analyses from a single borehole at Harwell (Jones et al., 2000). This is thought to be due to variations in clay content and the degree of cementation. Hydraulic conductivity is also variable, values from ten boreholes ranged from $2.5 \times 10^{-5} \text{ m d}^{-1}$ to $1.4 \times 10^{-2} \text{ m d}^{-1}$, with a geometric mean of $2.3 \times 10^{-4} \text{ m d}^{-1}$. However, a pumping test at Marcham (near Abingdon, at SU 4626 9736) on a borehole penetrating 12 m of Corallian sandstone and limestone was analysed to give a storage coefficient of 6×10^{-4} , and a transmissivity of $700 \text{ m}^2 \text{ d}^{-1}$. Data for the specific capacities of boreholes in the Corallian range from $4 \text{ m}^3 \text{ d}^{-1} \text{ m}^{-1}$ to $2200 \text{ m}^3 \text{ d}^{-1} \text{ m}^{-1}$, with a geometric mean of $54 \text{ m}^3 \text{ d}^{-1} \text{ m}^{-1}$. Groundwater flow in the Corallian is thought to be a combination of fissure and intergranular flow, with the fissure component being important in the higher yielding boreholes.

3.4 Aquifer mineralogy

In general terms, shallow carbonate facies predominate in the study area, together with a suite of clay minerals. The Lower Calcareous Grit consists of calcareous sands, pebbles of black lydite and white vein quartz (of Palaeozoic origin). Accessory minerals in the sands include kyanite, staurolite, tourmaline, rutile, zircon, garnet and sphene (Arkell, 1927). Fossils such as the gastropod "*Natica*" are found, and are sometimes replaced by crystalline calcite. Silicified wood is also common. The overlying Highworth Limestone Formation consists mainly of tough grey limestone with shells, pebbles of lydite and vein quartz, pebbles of phosphatic mudstone and other more distant pebbles (e.g. a rhyolite pebble has been recorded). Pebbles at the base of the Upper Corallian consist of chert, quartz, and grey non-oolitic limestone. The Coral Rag is composed of fossil corals with a large proportion of clay and with numerous shell fragments. Scattered ooliths are found. Tuffaceous material may be present (Richardson, 1946).

3.5 Rainfall chemistry

Table 3.2 presents a chemical analysis for local rainfall, collected at Compton (SU 512 804). The site is situated at an elevation of approximately 149 m above Ordnance Datum.

The solutes derived from rainfall typically increase during evapotranspiration and the data have been multiplied by three in the table, to approximate the enrichment expected in infiltrating waters. However, nutrient (e.g. N, K) concentrations may be used during biomass uptake and recharge waters may contain lower concentrations than rainfall. The relatively high concentration of non-marine sulphate is possibly derived from local pollution sources, such as the large power station at Didcot about ten kilometres to the north of the site.

Table 3.2 Rainfall Chemistry from the site at Compton, to the southeast of the aquifer outcrop (SU 512 804). The data are for January 2003 and were obtained from the UK National Air Quality Information Archive website at: <http://www.airquality.co.uk/archive/index.php>

Parameter	Units	Concentration	Concentration x 3
Calcium	mg/l	0.07	0.21
Chloride	mg/l	0.895	2.685
Potassium	mg/l	0.04	0.12
Magnesium	mg/l	0.055	0.165
Ammonium as N	mg/l	0.195	0.585
Nitrate as N	mg/l	0.17	0.51
Sodium	mg/l	0.47	1.41
Phosphate as P	mg/l	<0.01	<0.03
Sulphate as S	mg/l	0.283	0.849
Non-marine sulphate as S	mg/l	15.2	45.6
Conductivity (μ S/cm)	μ S/cm	13	39
pH		4.62	

3.6 Land use

The major urban centres in the study area are Abingdon, Didcot, Wantage and Shrivenham, with Oxford and Swindon lying just outside of the area studied. Most of the land in the study area is classified as arable, with a smaller proportion being managed as grassland. Common crops include wheat, barley, vegetables, linseed, fruit orchards and oil seed rape. Potatoes grow well in the sandier soils. A few small areas of forestry or woodland exist (Figure 3.4). There are a small number of quarries that are still active in the area (Figure 3.5).

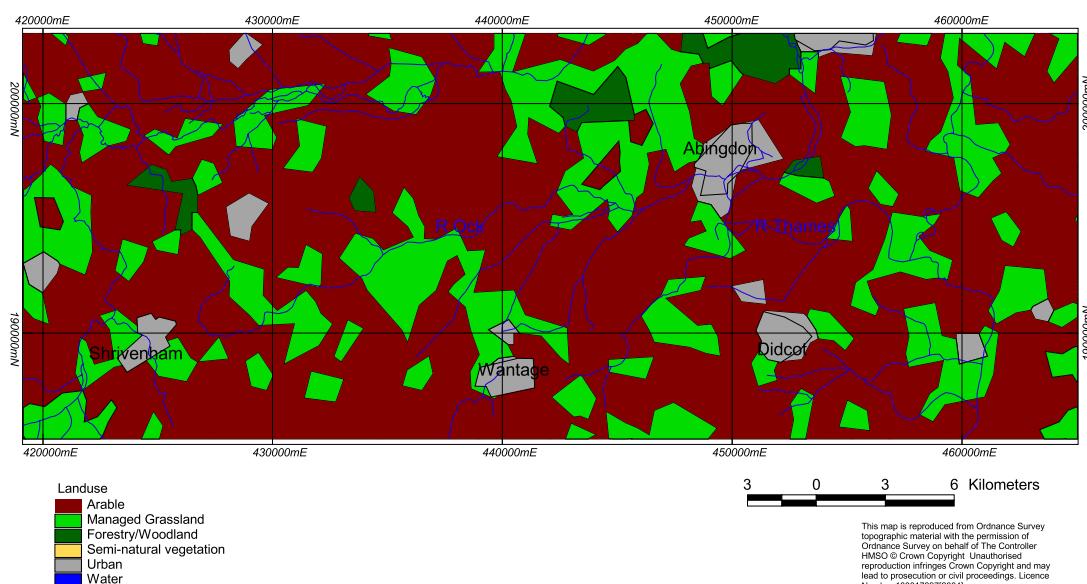


Figure 3.4 Generalised land use map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology. ©NERC.



Figure 3.5 Sand and aggregate quarrying operations near Shellingford (SU 329 938).



Figure 3.6 Former Corallian limestone quarry near Stanford in the Vale (SU 326 943).

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 24 samples were collected during August 2003 by the authors. Of these, 22 samples were taken from private boreholes and 2 samples from springs. The sample sites were selected, where possible, to provide a reasonable coverage over the Corallian aquifer at outcrop and where it is confined, although the number of boreholes available for sampling was limited. All of the boreholes sampled were in regular use, and during sampling it was requested that the system be allowed to flow for a minimum of about 15 minutes prior to monitoring and sampling. Pumped groundwater samples represent water entering the borehole over the entire length of the screened interval. The sample may therefore represent a mixture of waters with different chemistries, especially if the aquifer is vertically stratified in terms of water quality, which is known to occur in the Corallian. Despite this problem, the results can be useful in interpreting regional variations that exist within the aquifer.

Where possible pH, dissolved oxygen (DO) and redox potential (Eh) were measured using an in-line flow-through cell to avoid contact with the air. Other on-site measurements included temperature, specific electrical conductance (SEC) and bicarbonate alkalinity by titration. Samples were collected for chemical analysis in polyethylene bottles. Those for analysis of major and trace elements were filtered through 0.45 µm filters and an aliquot for cation and trace elements was acidified to 1% v/v HNO₃ to preserve the chemical composition and prevent precipitation. Selected samples were collected in glass bottles for stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$). Samples for dissolved organic carbon (DOC) were collected in chromic acid-washed glass bottles using a 0.45µm silver-membrane filter.

Major cations, sulphate and selected trace elements were analysed by ICP-AES and a wide range of trace elements were analysed by ICP-MS. Nitrogen species and other anion species (Cl, Br, I, F) were measured using automated colorimetry (SKALAR). Stable isotope analyses were measured by mass spectrometry and the results reported relative to Standard Mean Ocean Water (VSMOW) for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and Pee Dee Belemnite (VPDB) for $\delta^{13}\text{C}$.

4.2 Previous data

Data for 14 groundwater monitoring network sites were provided by the Environment Agency (EA Thames Region). Some historical water-quality data records (seven sites) were available for the Corallian aquifer from the Environment Agency. Five of the new sites sampled in 2003 are part of the Environment Agency's current groundwater monitoring network of 14 sites, and it was possible to compare the BGS results with historical analyses from these sites. The dates of analyses obtained from the EA monitoring network range from 1993 to 2002 (one site runs only to 1998). It has unfortunately not been possible to obtain analyses of waters from previous abstractors of large water supplies from the aquifer, such as the Morlands Brewery or the MG automotive works borehole, both formerly in Abingdon.

4.3 Interpretation of pumped groundwater samples

When interpreting trends in regional water quality data it is important to bear in mind the variations in water quality that may arise between sampling boreholes due to differences in borehole design and construction, different stratigraphic horizons being tapped and different pumping histories.

4.3.1 Different borehole designs

The Corallian is a diverse succession of limestone and calcareous sandstone showing rapid lateral facies changes, and the water quality within each stratigraphic formation may vary. As a consequence, differences in borehole design, in particular depth of borehole and depth of casing, may produce differences in water quality not related to geochemical reactions along a flow path. Differences in

fracture geometry in boreholes of similar design may produce waters of different chemical compositions.

4.3.2 Different pumping histories

In areas where the Corallian aquifer is overlain by permeable drift deposits, the pumping history of an individual borehole may have a significant impact on water quality. For instance, abstraction boreholes where large volumes of water have been pumped historically are likely to have induced significant recharge through the permeable drift deposits. Thus the proportion of modern, high nitrate water in the pumped sample may be relatively high, compared with a borehole where only small volumes have been pumped.

It has not been possible, within the resources available to this project, to evaluate which factors may be influencing water quality for each of the water sampling boreholes. Instead, this report presents a broad assessment of the water quality variations observed across the aquifer and the controlling geochemical processes. It is accepted that some water quality variation may be due to the factors described above.

4.4 Data handling

The plots and tables of geochemical data are based on both the new sampling programme and historical data (one analysis per site, usually the more recent analyses containing the maximum of information for samples from 1993 to 2002). Historical data with an ionic charge balance greater than 10% were rejected. For samples collected within the project, the maximum ionic balance accepted was also 10%, although most were below 5 %.

For statistical purposes, analyses that fell below detection limits were dealt with by substitution of half of the detection limit. However, changes in the detection limits both with time and between laboratories proved problematical in calculation of the average results. The median is least affected by outlying data compared to mean, and is therefore used, together with the minimum, maximum and 97.7th percentile (mean plus two standard deviations) to describe the average and ranges of data. The 97.7th percentile for each baseline determinand has been taken as an estimate of the upper limit of the concentration range, to remove outlying data.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

A summary of the chemical data for the Corallian groundwaters is shown in Tables 5.1 and 5.2 for the study area. The BGS data have been used instead of the EA data for the five sites where data from both sources exist, since more determinands were covered by the BGS data set. The tables show the ranges and averages of data as well as an upper concentration (defined as mean + 2 σ or 97.7th percentile), which is used as a cut-off to distinguish outlying data. The median is preferred to the mean as an expression of the average since it is less affected by the extreme values in any given dataset.

Table 5.1 Summary of field parameters, isotope data and minor element concentrations.

Parameter	units	min.	max.	median	mean	97.7th percentile	Upper baseline*	N
T	°C	9.00	17.2	12.6	13.0	17.2		33
pH		6.63	8.62	7.32	7.35	8.25		33
Eh	mV	81.0	323.7	230.0	225.0	321.9		24
DO	mg l ⁻¹	-0.55	10.2	2.73	3.44	9.7		31
SEC	µS cm ⁻¹	456.0	1808	787.7	813.7	1438.4		33
δ ² H	‰	-51.50	-41.50	-48.10	-47.07	-41.75		6
δ ¹⁸ O	‰	-7.91	-6.27	-7.48	-7.19	-6.29		6
δ ¹³ C	‰	-15.82	-4.46	-14.37	-13.01	-5.47		6
Ca	mg l ⁻¹	2.50	179.0	103.0	99.3	169.4		33
Mg	mg l ⁻¹	0.92	20.2	7.51	7.95	17.3		33
Na	mg l ⁻¹	6.60	406.0	21.7	76.8	327.3		33
K	mg l ⁻¹	0.53	80.4	3.76	7.80	42.1		33
Cl	mg l ⁻¹	6.62	181.0	33.6	45.4	139.8		33
SO ₄	mg l ⁻¹	15.6	270.0	62.0	75.0	221.4		33
HCO ₃	mg l ⁻¹	68.9	539.2	341.7	340.2	498.1		32
NO ₃ -N	mg l ⁻¹	0.1	29.5	0.25	4.47	22.1		33
NO ₂ -N	mg l ⁻¹	0	0.53	0	0.04	0.42		33
NH ₄ -N	mg l ⁻¹	0.02	0.80	0.07	0.19	0.70		33
P	mg l ⁻¹	0.01	0.10	0.02	0.02	0.08		33
DOC	mg l ⁻¹	0.40	8.70	1.20	1.78	5.84		24
F	mg l ⁻¹	0.05	1.98	0.20	0.29	1.62		33
Br	mg l ⁻¹	0	0.71	0.05	0.11	0.55		33
I	mg l ⁻¹	0	0.12	0.01	0.02	0.08		24
Si	mg l ⁻¹	3.51	13.4	5.52	5.99	12.66		24

* estimated upper baseline for elements modified by anthropogenic influences

Concentrations may be enhanced above local baseline but less than regional baseline

Table 5.2 Summary of concentrations of trace elements

Parameter	units	min.	max.	median	mean	97.7th percentile	N
Ag	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Al	µg l-1	< 1	84.0	2.00	8.35	66.0	24
As	µg l-1	< 0.5	1.90	0.50	0.63	1.85	24
Au	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
B	µg l-1	10.0	1772.0	87.0	234.15	1623.3	33
Ba	µg l-1	3.23	50.19	10.48	12.69	34.84	24
Be	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Bi	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Cd	µg l-1	< 0.05	0.15	0.038	0.04	0.11	32
Ce	µg l-1	< 0.01	0.27	0.02	0.04	0.23	24
Co	µg l-1	< 0.02	1.96	< 0.02	0.15	1.18	24
Cr	µg l-1	< 0.5	1.40	< 0.5	0.38	1.19	32
Cs	µg l-1	< 0.01	0.04	0.01	0.01	0.03	24
Cu	µg l-1	0.50	304.0	1.38	16.5	143.8	32
Dy	µg l-1	< 0.01	0.03	0.01	0.01	0.02	24
Er	µg l-1	< 0.01	0.02	0.01	0.01	0.01	24
Eu	µg l-1	< 0.01	0.01	0.01	0.01	0.01	24
Fe	µg l-1	< 5	1770.0	137.0	333.8	1152.5	33
Ga	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Gd	µg l-1	< 0.01	0.05	< 0.01	< 0.01	0.04	24
Ge	µg l-1	< 0.05	0.10	< 0.05	< 0.05	0.09	24
Hf	µg l-1	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	24
Hg	µg l-1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	31
Ho	µg l-1	< 0.01	0.01	< 0.1	< 0.1	0.01	24
In	µg l-1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	24
Ir	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
La	µg l-1	< 0.01	0.14	0.01	0.02	0.12	24
Li	µg l-1	1.20	78.3	12.8	20.4	66.7	24
Lu	µg l-1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	24
Mn	µg l-1	< 2	466.0	17.0	58.7	391.0	33
Mo	µg l-1	< 0.1	5.20	0.10	0.40	2.82	24
Nb	µg l-1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	24
Nd	µg l-1	< 0.01	0.21	0.01	0.03	0.18	24
Ni	µg l-1	< 0.2	8.90	0.25	1.33	7.19	32
Os	µg l-1	< .05	< 0.05	< 0.05	< 0.05	< 0.05	24
Pb	µg l-1	< 0.1	3.90	0.35	0.57	2.19	32
Pd	µg l-1	< 0.2	0.20	< 0.2	< 0.2	0.15	24
Pr	µg l-1	< 0.01	0.04	< 0.01	< 0.01	0.03	24
Pt	µg l-1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	24
Rb	µg l-1	0.22	23.40	1.91	2.79	12.84	24
Re	µg l-1	< 0.01	0.02	< 0.01	< 0.01	0.02	24
Rh	µg l-1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	24
Ru	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Sb	µg l-1	< 1	1.00	< 1	0.6	1.00	24
Sc	µg l-1	< 0.06	0.48	< 0.06	0.05	0.31	24
Se	µg l-1	< 0.5	1.50	0.60	0.66	1.39	24
Sm	µg l-1	< 0.02	0.04	< 0.02	< 0.02	0.03	24
Sn	µg l-1	< 0.05	0.64	0.08	0.09	0.39	24
Sr	µg l-1	88.60	1860.0	359.6	648.4	1856.6	32
Ta	µg l-1	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	24
Tb	µg l-1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	24
Te	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Th	µg l-1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24
Ti	µg l-1	< 10	< 10	< 10	< 10	< 10	24
Tl	µg l-1	< 0.01	0.03	< 0.01	< 0.01	0.02	24
Tm	µg l-1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	24
U	µg l-1	< 0.02	1.51	0.11	0.38	1.36	24
V	µg l-1	< 0.2	1.40	0.30	0.49	1.40	24
W	µg l-1	< 0.02	0.12	< 0.02	0.02	0.11	24
Y	µg l-1	< 0.01	0.18	0.01	0.03	0.14	24
Yb	µg l-1	< 0.01	0.01	0.01	0.01	0.01	24
Zn	µg l-1	1.00	288.9	11.40	39.95	167.26	32
Zr	µg l-1	< 0.02	0.14	< 0.02	0.03	0.11	24

The summary data are shown graphically on a Piper Plot, box plots and cumulative frequency plots (Figures 5.1-5.5). The box plots (or box and whisker plots) display the ranges of data and are designed to highlight the percentile distribution of data (the boxes show the range between the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles and the dots the 5th and 95th percentiles). In addition, the median is shown as a horizontal black line and the mean as a blue line within the box. The solid black line on the graph represents a diluted seawater curve that has been normalised to the median chloride concentration of the samples. This provides a general indication, in most aquifers, of inputs from water-rock interaction above the marine-derived (rainfall or connate) input. The solid grey line on Figure 5.3 shows typical detection limits for each element. Cumulative frequency plots are useful in visualising the distribution of data and may be of use in determining outlying data or discerning pollution. Geochemical processes may alter the distribution of populations in several different ways giving rise to complex distributions.

5.2 Water types and physicochemical characteristics

The major-ion chemistry is summarised on the Piper diagram (Figure 5.1). The analyses show that the Corallian groundwaters range in composition mainly from the Ca-HCO₃ type to the Na-HCO₃ type. The dominant cations are always Ca or Na, with the proportion of Mg usually below 10% and never exceeding 20% on the Piper plot. The dominant anion is almost always HCO₃.

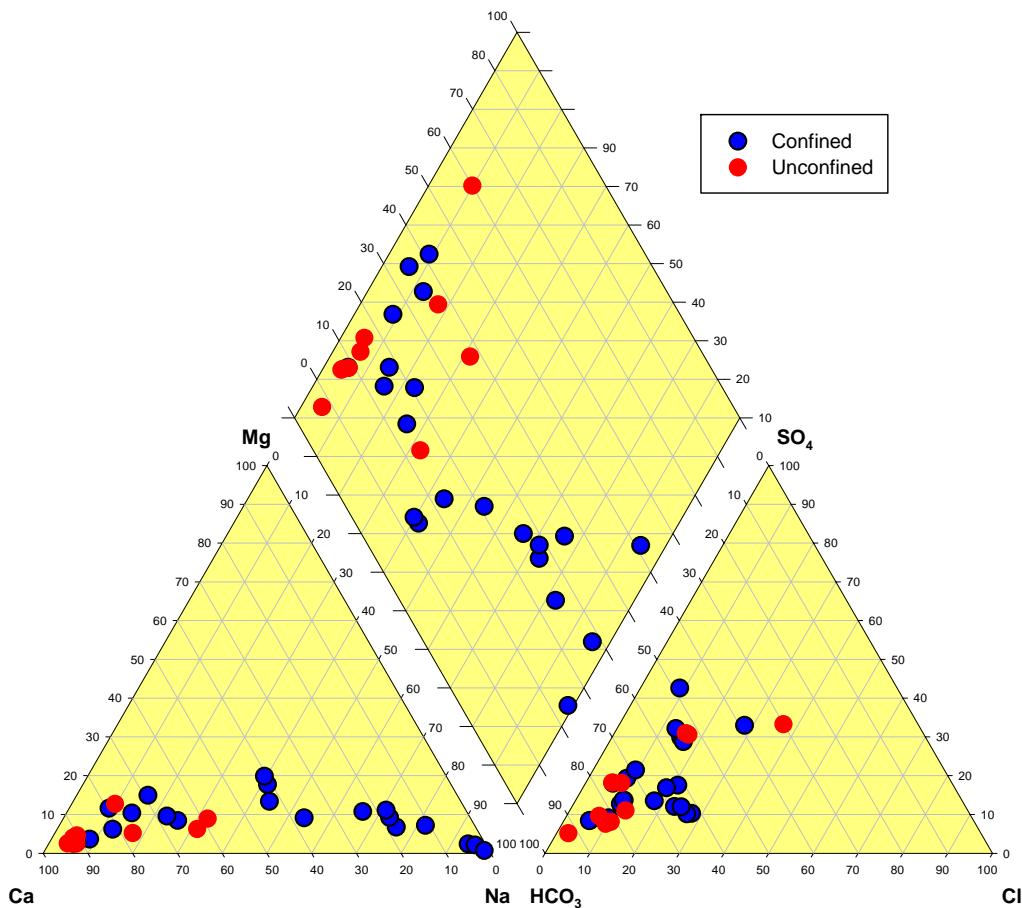


Figure 5.1 PIPER plot showing the relative concentrations of major elements.

The samples have been divided into “confined” and “unconfined” sets, depending on whether they were collected from sites on the Corallian outcrop or from sites where the Corallian is overlain by clays. (21 of the total of 33 samples were classed as “confined”.) It is acknowledged that these terms are not necessarily exact, in that confined conditions can occur within the Corallian even where clays

do not overlie it, due to clay-rich layers within the aquifer. Conversely, Corallian groundwater may be unconfined down dip of the feather edge of the Kimmeridge Clay. The terms have been retained for the sake of convenience and the distinction has proved to be a useful way of distinguishing some of the differences in the groundwater chemistry. Most of the unconfined samples were of Ca-HCO₃ type whereas the confined samples varied from Ca-HCO₃ to Na-HCO₃ type. A few of the samples had high proportions of sulphate and chloride, and there are three sites with compositions that are markedly different to the others (Nineveh Farm, Baldons Farm and Steeds Spring, with Ca-HCO₃-SO₄, Na-HCO₃-SO₄ and Ca-SO₄-HCO₃ compositions respectively). There is a clear distinction between confined and unconfined samples, with all of the unconfined samples having Ca as the dominant cation, whilst the confined samples have both Ca and Na as the dominant cation.

Corallian groundwaters are moderately mineralised. The median specific electrical conductance (SEC) is 788 µS cm⁻¹, and only four samples have SEC values less than 600 µS cm⁻¹. The maximum value is 1808 µS cm⁻¹. It is known that more highly mineralised waters exist in the Corallian (see for instance Alexander and Brightman, 1985), particularly at depth and where clays overlie the aquifer. The sources available for sampling were biased towards the more potable end of the spectrum since these were in continual use. The data presented here therefore represent the baseline “system” (see baseline definition page v) comprising the shallowest part of the aquifer where abstraction is greatest. The range of SEC in the outcrop part of the aquifer is small, varying from 621–857 µS cm⁻¹, with a median of 791 µS cm⁻¹. In the confined part of the aquifer the median is very similar (780 µS cm⁻¹), but the range is much larger, varying from 456–1808 µS cm⁻¹.

The groundwaters are well buffered, with a mean and median pH of 7.35 and 7.32 respectively. The lowest value is 6.6, and only 7 groundwaters out of the set of 33 have pH values lower than 7. There appears to be little difference between the pH of the confined and unconfined subsets.

Groundwater temperatures in the Corallian range from 9 °C to 17.2 °C, with a median of 12.6 °C. The spring and catch pit samples were removed from the dataset for this calculation because the temperatures of these sources are known to show large seasonal fluctuations. The difference in temperature between confined and unconfined sources is small: medians of 12.6 °C and 13.1 °C respectively. It is possible that the unconfined sources would have been cooler than the confined sources had the sampling been carried out in winter.

Dissolved oxygen concentrations range from less than 0.1 mg l⁻¹ to just over 10 mg l⁻¹, close to saturation with oxygen. The accuracy of this measurement depends partly on being able to sample groundwater before it has come into contact with the atmosphere using a flow cell, and this was not always possible because some sources were pumped first to a storage tank from where the sample was taken. Eleven of the BGS samples were taken using a flow cell. The median dissolved oxygen content of the confined samples was 1.3 mg l⁻¹ as opposed to 4.4 mg l⁻¹ for the unconfined samples. The redox potential of all of the samples ranged from 81 to 324 mV, with a median value of 230 mV. The confined samples had a median redox potential of 164 mV, compared with 298 mV for the unconfined samples.

5.3 Major elements

There is a large range in the concentrations of most major elements, typically over at least an order of magnitude, except for HCO₃, which shows a more limited range (Figures 5.2 and 5.3). Although the highest median cation concentration in equivalents is for Ca, Na dominates in approximately a third of the samples (Figure 5.1). These elements show contrasting characteristics between the unconfined and confined parts of the aquifer: the unconfined groundwaters had median concentrations of Ca and Na of 144 mg l⁻¹ and 13.8 mg l⁻¹ respectively, whilst the confined groundwaters had median concentrations of 60 mg l⁻¹ and 70 mg l⁻¹. Sodium displayed the widest range of cation concentrations (Figure 5.2), varying from 6.6 mg l⁻¹ (similar to rainfall) up to 406 mg l⁻¹. Chloride concentrations range from 6.6 to 181 mg l⁻¹, with a median of 33.6 mg l⁻¹. There is little difference between the confined and unconfined subsets.

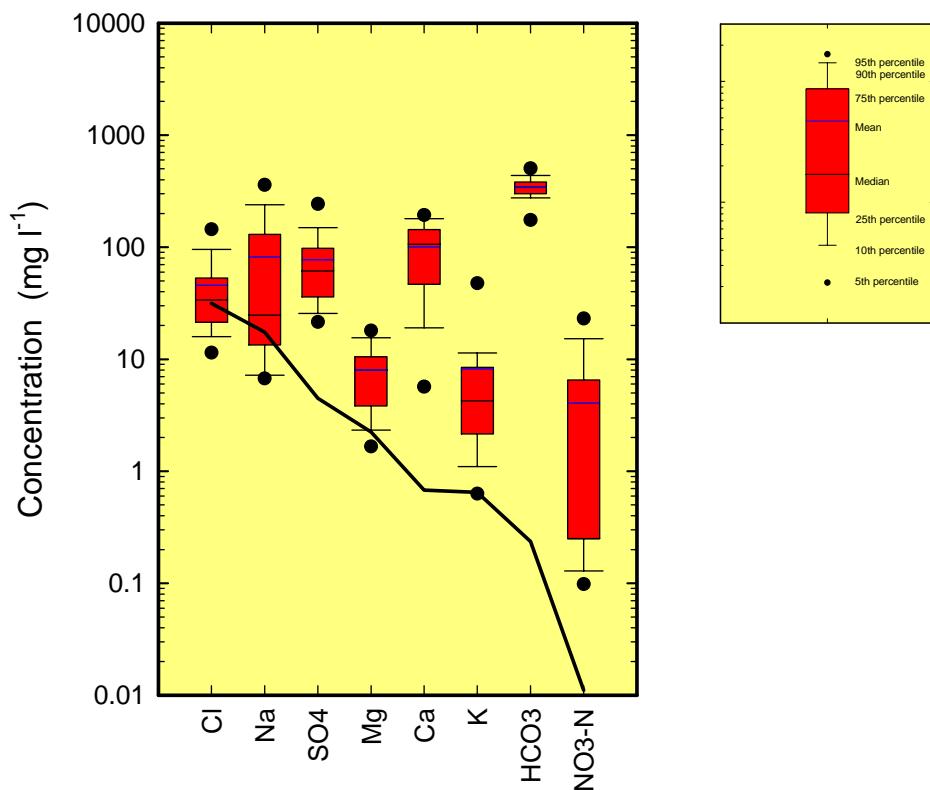


Figure 5.2 Box plot showing the ranges of major element concentrations.

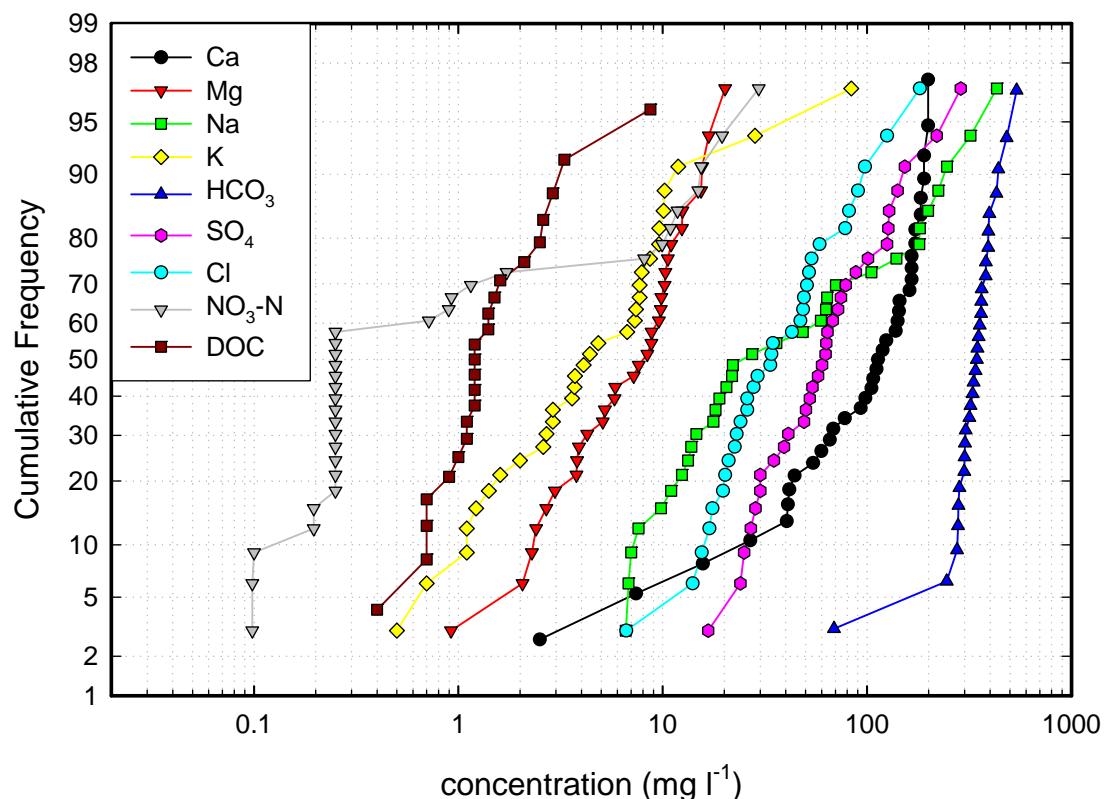


Figure 5.3 Cumulative probability plot of major elements.

Sulphate is elevated well above the dilute seawater line, indicating that there is an additional source of sulphate in the aquifer. The median sulphate concentration is 62 mg l^{-1} , and is similar for confined and unconfined samples. Magnesium concentrations are relatively low, with most values below 10 mg l^{-1} . The median concentration for confined samples was 9.8 mg l^{-1} compared with 4.3 mg l^{-1} for the unconfined samples.

The median potassium concentration is 3.8 mg l^{-1} . Concentrations were generally low, although the highest is 80.4 mg l^{-1} (Wickwood Farm), which is more than three times the next highest value. Only three groundwaters had K concentrations greater than 10 mg l^{-1} . However, there is a definite distinction between the confined and unconfined subsets with median concentrations of 7.3 mg l^{-1} and 2 mg l^{-1} respectively.

There was a large range in nitrate concentrations, from below detection limit to $29.5 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. The higher concentrations ($\text{NO}_3\text{-N}$ concentrations $>10 \text{ mg l}^{-1}$ from six unconfined sources) are probably due to the anthropogenic pollution, probably in the form of agricultural fertilisers. A total of 14 of the 24 new samples had nitrate concentrations below the detection limit of the analytical equipment used ($<0.5 \text{ mg l}^{-1}$). 10 out of 33 samples had nitrate concentrations above 1 mg/l (as $\text{NO}_3\text{-N}$). Shallow groundwater sources are most seriously affected, and all three spring sources had nitrate values above the Council of the European Communities Directive 80/778 (CEC) maximum admissible concentration (MAC) of $11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ for drinking water. The median nitrate concentration for the unconfined samples was $8.1 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ compared to a median of $< 0.5 \text{ mg l}^{-1}$ (i.e. below the detection limit) for the confined samples, which is consistent with denitrification occurring in the reducing environment of the confined aquifer, or alternatively the samples were older water.

5.4 Minor and trace elements

Many of the minor and trace elements in the Corallian groundwaters have a range of concentrations that vary over two or more orders of magnitude (Figures 5.4 and 5.5). The box and cumulative frequency plots are particularly useful since they show the ranges of the data.

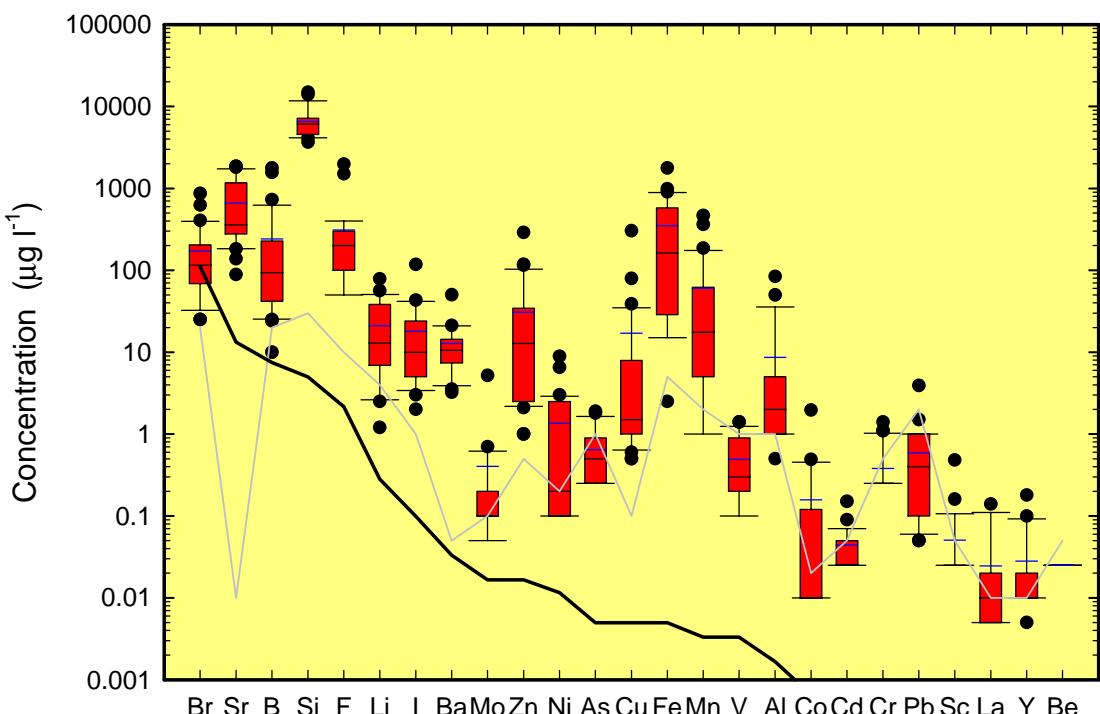


Figure 5.4 Box plot showing the ranges of minor and trace element concentrations.

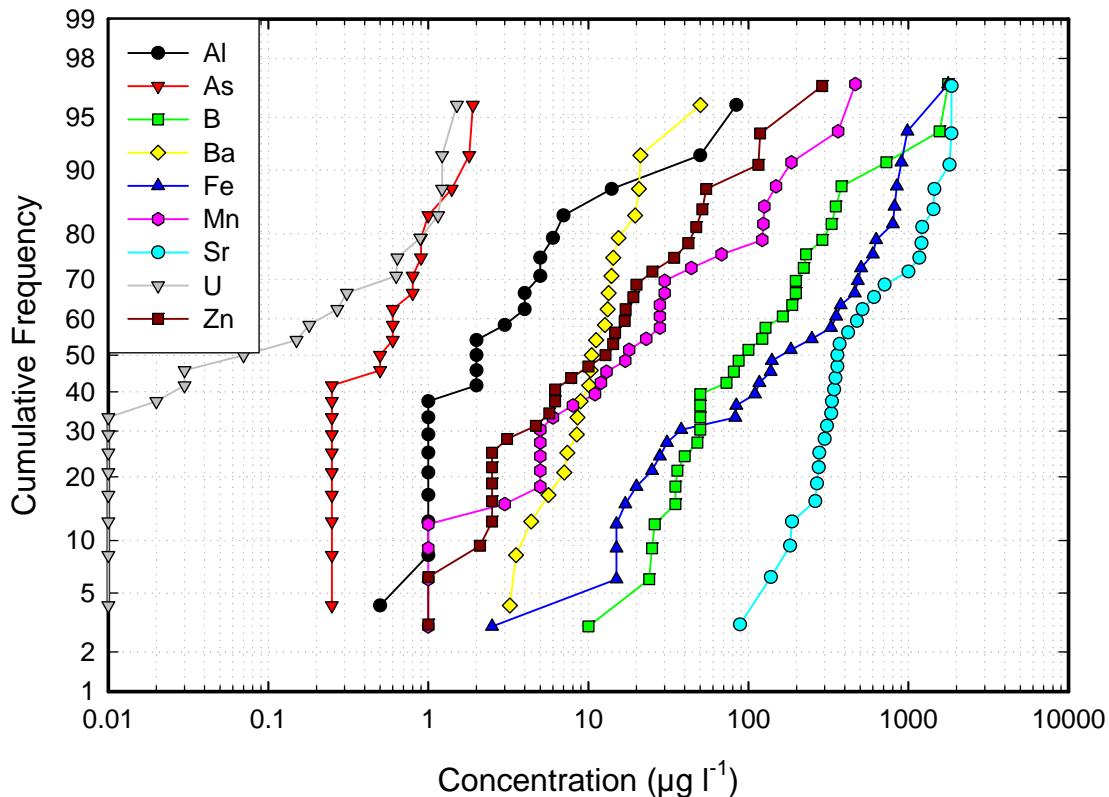


Figure 5.5 Cumulative probability plot of selected minor and trace elements.

Iron and manganese show large variations in concentration, which may be related to the differences in redox potential across the aquifer. More than half of the samples taken have iron concentrations higher than the CEC MAC of $200 \mu\text{g l}^{-1}$. The median iron concentration in the confined samples is $354 \mu\text{g l}^{-1}$ compared with $84 \mu\text{g l}^{-1}$ for the unconfined samples, which is expected given that iron is more mobile in reducing environments. The median concentration of Mn is however similar in the unconfined and confined groundwaters (28 and $17 \mu\text{g l}^{-1}$ respectively). Zinc also shows a large range in concentration with medians of 7.8 and $18.5 \mu\text{g l}^{-1}$ for the confined and unconfined subsets respectively.

The median bromide concentration sits on the dilute seawater line reflecting the similar behaviour of Br to Cl. Fluoride concentrations are moderate, and are also distributed over a relatively narrow range. The median fluoride ion concentration is $200 \mu\text{g l}^{-1}$. The maximum concentration is $1979 \mu\text{g l}^{-1}$, which is higher than the CEC MAC for drinking water of $1500 \mu\text{g l}^{-1}$. However, most fluoride concentrations are lower than $400 \mu\text{g l}^{-1}$. The high concentrations are found in the Na-HCO₃ waters with very low Ca concentrations. Silicon concentrations are fairly high (median of 5.52 mg l^{-1}), but show a narrow range in concentration, which is probably a result of the element reaching saturation in most of the waters.

The concentrations of many of the other trace elements are low. The heavy metals in particular are either very low or are below the detection limits of the analytical technique, which is to be expected at the relatively neutral pH ranges of these waters. Mercury, cadmium and lead median concentrations are < 0.1 , 0.038 and $0.35 \mu\text{g l}^{-1}$ respectively. The maximum measured concentrations are < 0.1 , 0.15 and $3.9 \mu\text{g l}^{-1}$ respectively. Concentrations of both arsenic and uranium (medians of 0.5 and $0.11 \mu\text{g l}^{-1}$ respectively, and maxima of 1.9 and $1.51 \mu\text{g l}^{-1}$ respectively) are also low. Copper is generally present at low concentrations (median of $1.38 \mu\text{g l}^{-1}$), but one sample had a relatively high concentration of $304 \mu\text{g l}^{-1}$. This is thought to be due to copper piping rather than a reflection of natural conditions in the aquifer. The next highest copper concentration recorded was $79 \mu\text{g l}^{-1}$. Concentrations of

aluminium are almost always low, and all but three of the samples have concentrations lower than $10 \mu\text{g l}^{-1}$. The highest measured aluminium concentration was $84 \mu\text{g l}^{-1}$.

5.5 Pollution indicators

The most obvious indicator of diffuse pollution is the presence of high nitrate concentrations, usually related to agricultural activities. Nitrate concentrations are low to moderately high throughout the aquifer. The highest nitrate concentration was 29.5 mg l^{-1} (as N), however the median was low at 0.25 mg l^{-1} , reflecting the reducing conditions in many of the groundwaters. Concentrations of the agricultural triazine pesticides atrazine and simazine were found to be below the detection limit of the analytical equipment used. However, point source agricultural pollution may occur away from the monitoring boreholes and concentrations of these pollutants may well be higher in shallow groundwaters, which were not sampled. No groundwater samples from the main urban areas overlying the aquifer were taken, due to a lack of available boreholes. Given the industrial past of centres such as Abingdon (where a leather works and a motor works, amongst other industries, were formerly situated) it would be surprising if no evidence of pollutants such as hydrocarbons and chlorinated solvents were to be found there. The layered nature of the aquifer is likely to retard the downward migration of surface pollutants, and also complicate the assessment of pollutant migration once in the aquifer.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

This chapter presents a summary of the main factors that control the chemistry of the Corallian groundwaters sampled in this study. The dominant geochemical processes involved in determining groundwater chemistry in many aquifers include:

- Mineral dissolution and precipitation
- Redox reactions
- Ion exchange and sorption reactions
- Mixing of recent recharge with formation or connate water

A fifth process can be added to this list, namely the influence on groundwater chemistry by human activities. The application of fertiliser to farmlands, the disposal of wastes, the pumping of groundwater and various other activities change groundwater chemistry. This chapter will end with a brief assessment of whether activities such as these have influenced the Corallian groundwaters. Chemical evolution of groundwaters can sometimes be discerned by sampling of groundwater along a flow line. However, it is often difficult to establish flow lines in aquifers, especially where the geology is complex. Nevertheless, a set of six sample points have been selected which are situated along the regional flow direction and these will be compared in a later section.

6.2 Mineral Dissolution Reactions

Dissolution reactions involving mineral phases in the aquifer rock matrix generally constitute a very important influence on the chemistry of the groundwater. In particular, the reaction kinetics (rate of reaction) for carbonate and evaporite minerals are rapid, and these minerals may dominate groundwater chemistry even if present in small quantities. The carbonate rich nature of the Corallian aquifer ensures that the solutes Ca, Mg and HCO₃ are dominant in the groundwaters. This can be clearly seen on the Piper plot, and can be regarded as the most important general influence on Corallian hydrogeochemistry. The relevant reactions can be summarised as follows:



The dissolution of calcite also results in the buffering of acidic infiltrating waters, and explains the generally neutral pH values found. High partial pressures of CO₂ in the soil zone can lower the pH of infiltrating rainfall to values of between 4 and 5, but such acidic pH values have not been recorded in the groundwater. The buffering of infiltrating waters also has the effect of limiting the concentrations of elements such as aluminium and heavy metals such as lead and cadmium, which are mobile at low pH values, and this partly explains the uniformly low concentrations of these elements in the Corallian. Most of the groundwaters are at saturation or slightly oversaturated with respect to calcite, whereas most are undersaturated with respect to dolomite. Once saturation is reached, calcite may continue to dissolve through incongruent dissolution. However, in order to maintain equilibrium, an equivalent amount of calcite must precipitate. The re-precipitated calcite is purer than the original calcite (due to the freshwater environment), hence the impurities are released to solution and increase as the reaction progresses. This leads to an increase in Sr/Ca and Mg/Ca ratios in the groundwaters with time. The Sr/Ca ratio of the Corallian groundwaters correlates with the Mg/Ca ratio ($r^2=0.92$) and is generally much higher in the confined aquifer. The relative enrichment of Sr and Mg in relation to Ca may indicate that the confined groundwaters are much older than the unconfined groundwaters. Both ratios also increase with Na concentration indicating that the incongruent dissolution may be linked to the increase in Na (this will be further discussed in section 6.4).

The presence of relatively high concentrations of sulphate in most of the groundwaters, well above the expected input from rainwater, and the predominance of the sulphate anion in certain samples, suggests that there is a source of sulphate in the aquifer. It is unlikely to be gypsum. The highest sulphate concentrations are present in the confined groundwaters where Cl is high and are thought to be related to mixing (Section 6.5). However, many groundwaters have SO_4/Cl ratios that are too high to be explained by mixing alone. A likely source of the additional sulphate is the oxidation of sulphide minerals such as pyrite. The highest ratios are also found in the unconfined aquifer, and it is likely that anthropogenic inputs are an additional source.

Amorphous silicate dissolution reactions are much slower than carbonate dissolution. Silicon concentrations are moderately high, reaching concentrations of 13.4 mg l^{-1} , and all groundwaters are saturated with respect to the silica polymorph chalcedony. The source of Si is likely to be from silicate minerals rather than quartz due to the stability and slow kinetics of quartz dissolution. Silicate dissolution of any feldspars or alteration of clay minerals is the likely source of the Si as well as cations such as K, Ca and Na.

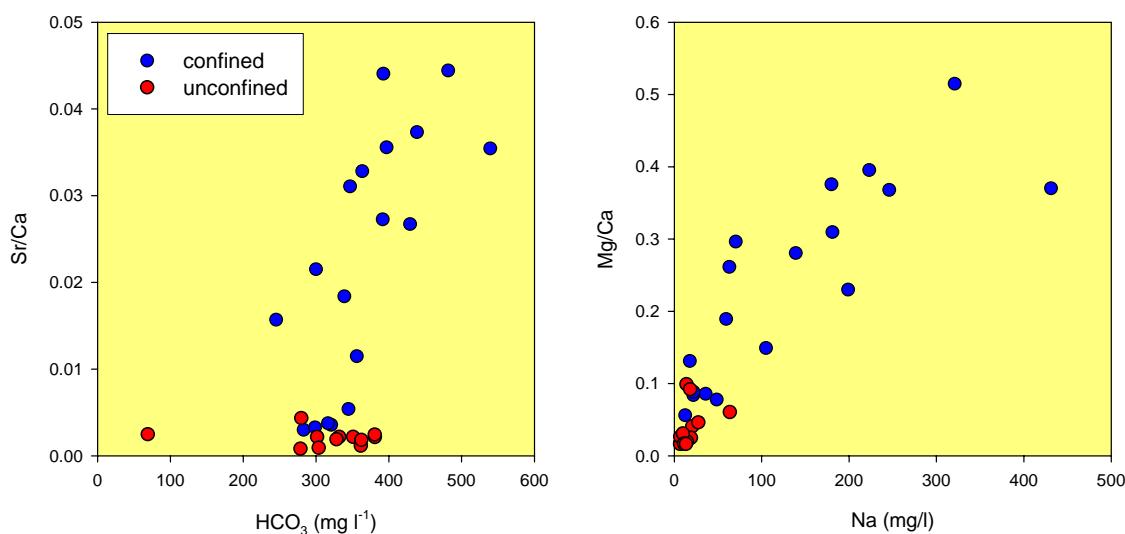


Figure 6.1 Plots of Sr/Ca ratio against HCO_3 concentration, and Mg/Ca ratio against Na concentration.

6.3 Redox reactions

The redox potential (Eh) and dissolved oxygen (DO) concentration provide the primary indicators of the redox status of natural groundwaters. It is generally expected that as groundwaters become more confined, concentrations of dissolved oxygen and redox potentials fall. (The loss of oxygen leads to a rapid decrease in Eh). The situation is likely to be more complex in the Corallian, since redox potentials may change with depth due to the layering in the aquifer. Semi-confining clay units overlying more permeable limestones are likely to lead to low dissolved oxygen concentrations due to increased residence time. It is therefore thought unlikely that a single redox boundary will be present at or near the line where the aquifer becomes confined by the overlying clays. Furthermore, these parameters are unstable and extremely sensitive to changes caused by contact with the atmosphere and, therefore, should be monitored in a flow-through cell where the water is pumped directly from the borehole. This was not always possible during sampling, and the following analysis only considers the eleven samples that were monitored using a flow cell.

The concentrations of iron, manganese, arsenic and uranium (amongst others) are particularly sensitive to redox conditions in the aquifer. The concentrations of these ions have been plotted against redox potential (Eh) on Figure 6.2. The concentration of dissolved oxygen correlates with redox potential, as expected. Iron is mobile as Fe^{2+} under reducing conditions but forms insoluble Fe^{3+} hydroxides in oxidising environments at the neutral pH typical of the Corallian groundwaters. The

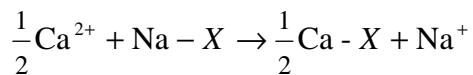
highest Fe concentrations are found in the low-Eh reducing groundwaters (Figure 6.2). Manganese is more soluble over a wider range of pH-Eh conditions than Fe. The low concentrations in the reducing groundwaters may be related to lower concentrations in the aquifer matrix, but there are no geochemical data with which to assess this. Arsenic is often more mobile under anoxic conditions. This is consistent with a general decline in arsenic concentration with increasing redox potential, apart from one anomalous high-Eh site (Chandlings Manor School) where the arsenic concentration is relatively high (1.8 µg/l). Concentrations of arsenic are generally low, ranging from below the analytical detection limit to 1.9 µg/l. Uranium is typically more mobile in oxidising environments, and the highest observed concentrations of uranium that occur in the unconfined aquifer reach up to 1.51 µg/l.

Dissolved nitrogen species are also redox controlled, and nitrate is only stable in the presence of oxygen. The high nitrate groundwaters are from the oxidising part of the aquifer and concentrations in excess of a few mg l⁻¹ probably reflect anthropogenic inputs. Ammonium is stable under reducing conditions and shows an increase in the confined groundwaters. The ammonium may be derived by desorption reactions from clay minerals, or from the decomposition of organic matter.

The redox conditions may also affect other trace elements that are not redox-sensitive, such as Ni or Co. These elements are commonly adsorbed on ferric hydroxides and dissolution of these phases under reducing conditions may release them to solution. These elements are present in low concentrations and do not show a relationship with Eh or Fe concentration. In most cases these elements are higher in oxidising groundwaters and may be derived from the oxidation of sulphide minerals or from anthropogenic inputs.

6.4 Ion exchange reactions

It is known that the freshening of aquifers that originally contained seawater can lead to significant chemical changes in groundwater as it flows through and displaces the original ‘connate’ or modified formation water. Any clays present will initially have Na as the dominant sorbed cation, and freshening by a typical Ca-HCO₃ type recharge groundwater will change the composition of this groundwater to attain equilibrium with the clays. In the case of a typical recharge water of Ca-HCO₃ type, the Ca in the groundwater will exchange for Na on the clays leading to groundwaters of Na-HCO₃ type:



The Corallian aquifer was deposited under shallow marine conditions, and it is likely that the first groundwaters present were of marine composition. There are also abundant clay layers in the aquifer that provide ready sites for ion exchange processes to take place. The Piper plot (Figure 5.1) suggests that there is an evolutionary trend in the Corallian groundwaters from calcium as the dominant cation to sodium as the dominant cation. A plot of calcium ion concentration versus sodium concentration (Figure 6.3) shows that an inverse relationship exists between the two elements i.e. as calcium decreases so the sodium ion concentration increases. The Na/Cl ratio is high in the groundwaters with high Na concentration indicating that mixing with connate (marine-derived) water cannot be the only source of Na. The Na from connate or formation water can be estimated and deducted from each sample (using Cl as conservative parameter and deducting Na in proportion to seawater). These ion exchange reactions are most important in the confined parts of the aquifer where residence times are likely to be greatest. It was noted earlier that there is a correlation between Na concentration and the Sr/Ca and Mg/Ca ratios, implying that the geochemical processes responsible might be related. This will be discussed in the next section, which assesses the likelihood of mixing with formation water because the processes of carbonate dissolution, ion exchange and mixing may be linked.

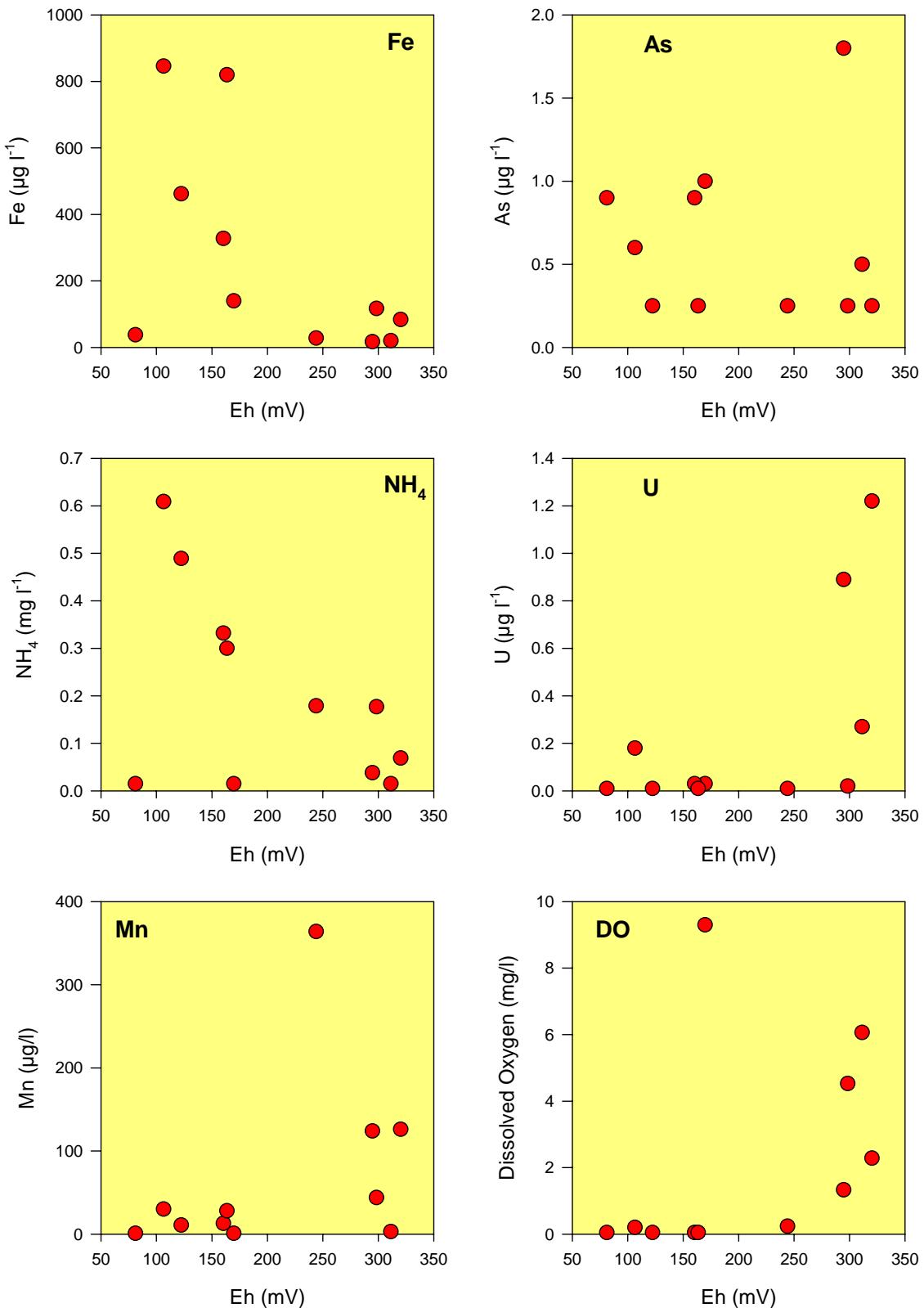


Figure 6.2 Plots of selected element concentrations against Eh (mV).

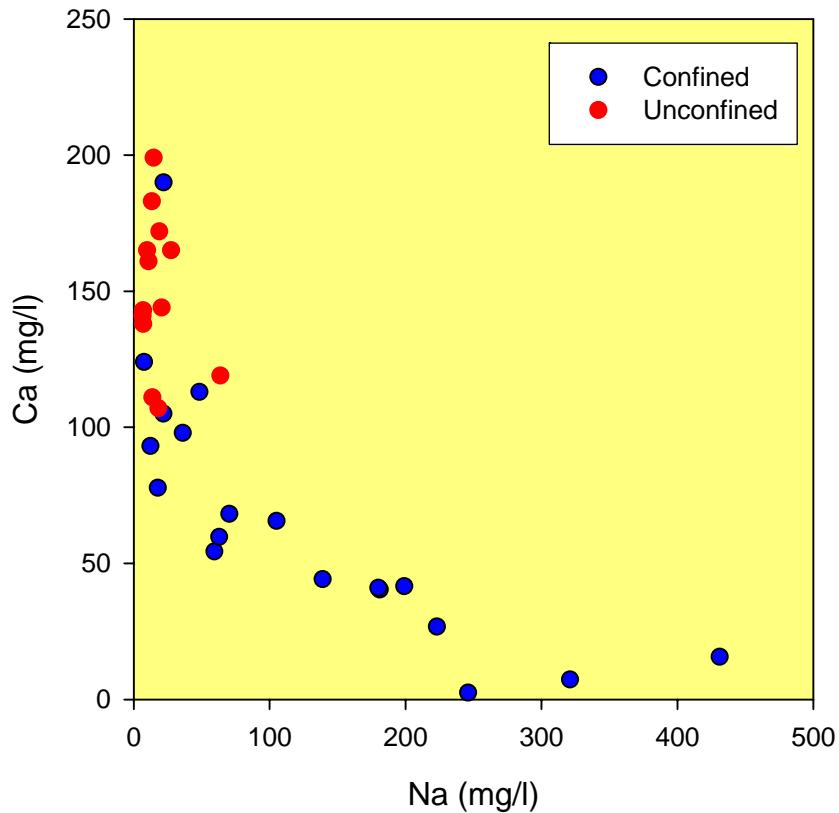


Figure 6.3 Ca concentration plotted against Na concentration for confined and unconfined groundwaters.

6.5 Mixing with connate waters

It is likely that the full extent of mixing with older formation waters (i.e. of marine origin) is not shown by the present data set, since the available sample points are located predominantly in those parts of the aquifer that are relatively fresh, representing more recent groundwater. However, the generally higher chloride and sodium ion concentrations of some of the confined groundwaters a short distance from outcrop, and the correlation between sodium and chloride concentrations (Figure 6.4) suggest that mixing processes are taking place and contribute to the composition of Corallian groundwaters. The groundwaters in the confined aquifer plot well above the dilute seawater curve due to the importance of ion exchange as discussed in section 6.3. The Br/Cl ratio is similar to that of seawater but diverges at higher Cl concentrations. Sulphate and boron concentrations are much higher than expected in comparison to dilute seawater indicating that mixing between recharge water and a modified connate water is the dominant mixing process in most groundwaters. The high Br/Cl ratios in two unconfined groundwaters are from farm boreholes and it is likely that these have been influenced by anthropogenic inputs. This is certainly consistent with the very high DOC (8.7 mg l^{-1}) in one of the groundwaters.

Mixing becomes much more important some distance from outcrop, where the groundwater is generally not potable due to high salinity. Alexander and Brightman (1985) provided evidence of groundwater mixing at the Harwell research site, about 10 km from the Corallian outcrop. The chloride ion concentration sampled at this site was up to 7500 mg l^{-1} , and there was a similar increase in sodium concentration. It is thought that there is a zone of mixing, which moves depending on regional head variations, where recent, potable Corallian groundwaters come into contact with interstitial connate waters of marine origin. Alexander and Brightman (1985) calculated that groundwaters at the Harwell site have a 40% marine composition, although the marine component diminished rapidly up-dip.

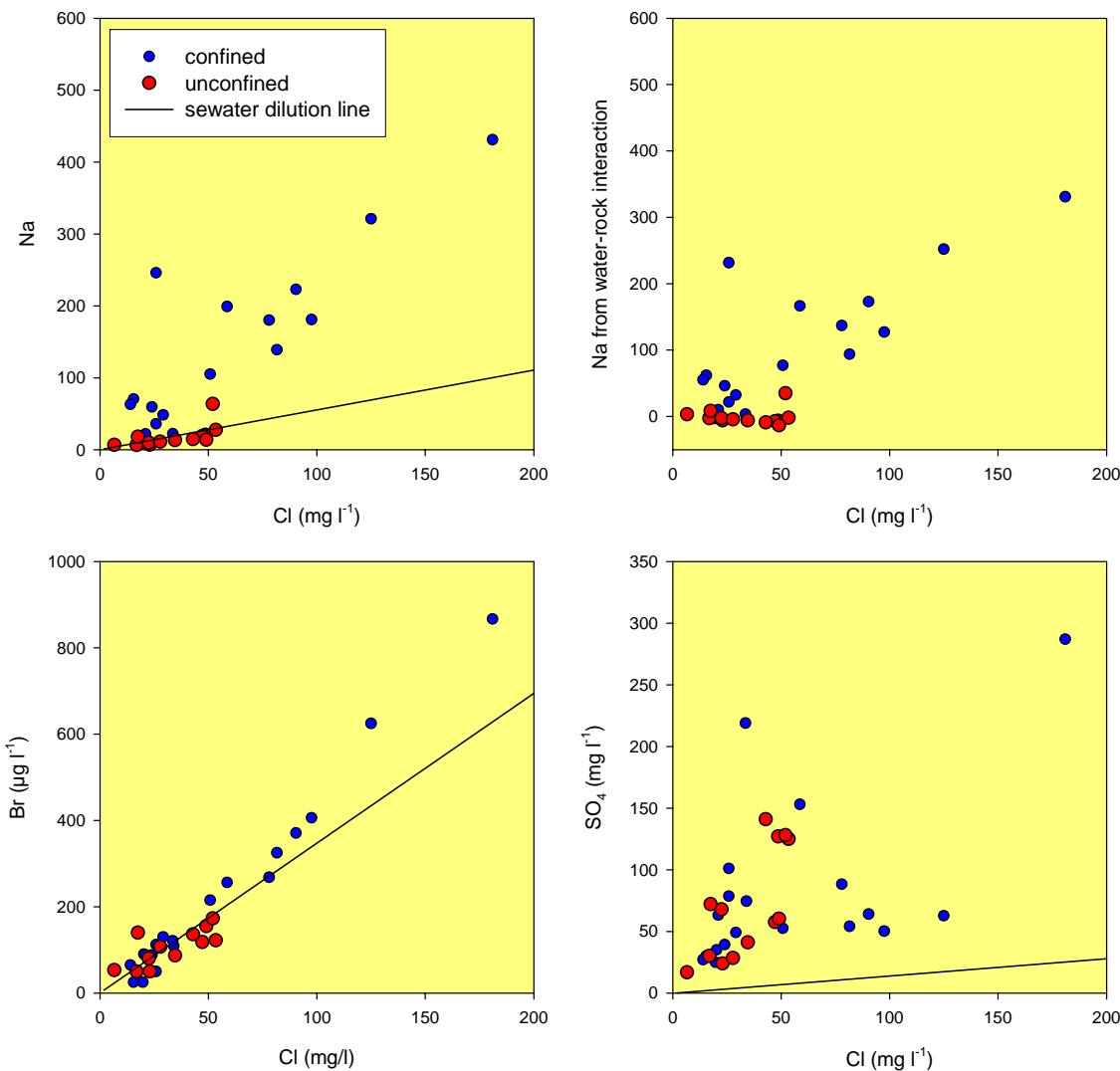


Figure 6.4 Selected parameters plotted in relation to a seawater dilution line.

It is concluded that the increase in Na is partly due to mixing with formation water and partly due to ion exchange. The amount of Na derived from this mixing can be subtracted from the total Na in proportion to the Cl in the sample (assuming the same Na/Cl as in seawater). Interestingly, the excess Na also correlates with Cl implying that waters with greater salinity have undergone a greater amount of ion exchange (Figure 6.4). In addition, the groundwaters with high Cl also have high Sr/Ca and Mg/Ca ratios suggesting a link between the three processes of incongruent dissolution, ion exchange and mixing with formation water. Although it is possible that these processes are independent and the correlations are related to residence time, they can be related geochemically. The parts of the aquifer that contain the highest proportion of (Na-Cl type) formation water, hence more adsorbed Na, will undergo ion exchange (for dissolved Ca) to a greater degree, hence the correlation between ion-exchange derived Na and Cl. The reduction in dissolved Ca due to ion exchange may lead to undersaturation with respect to calcite, promoting further dissolution, hence the increase in Sr/Ca by incongruent dissolution.

Alexander and Andrews (1984) concluded on the basis of isotopic, radioelement and inert gas studies that variations in chemistry can be attributed to cross-formational flow e.g. from the Lias. Although this is possible, especially in the deeper parts of the aquifer around Harwell (not sampled in the present study), it is difficult to accept for many of the shallower confined groundwaters that have

undergone significant ion exchange. Further detailed work on both the hydrochemistry and hydraulic properties of the aquifer would help to assess the validity of such models. Nevertheless, the chemical processes which have given rise to the Na-HCO₃ type waters (ion exchange, incongruent dissolution, mixing) are still valid.

6.6 Chemical evolution along flowlines

Six sample sites were selected to represent a section of the aquifer north to south along the regional flow direction in the aquifer (Figure 6.5). The three most northerly sites are located on the outcrop of the aquifer, whilst the other three are sited on varying thicknesses of the overlying clay. The names and locations of the six sites are given in Table 6.1. The distance in metres from the first site (Well House) to each site was measured along a south-southwest trending section. Since most of the sample sites are spread out along the strike of the Corallian, and the groundwater flow is perpendicular to this (roughly in the direction of the dip), it was not possible to select a flow line with more sample sites.

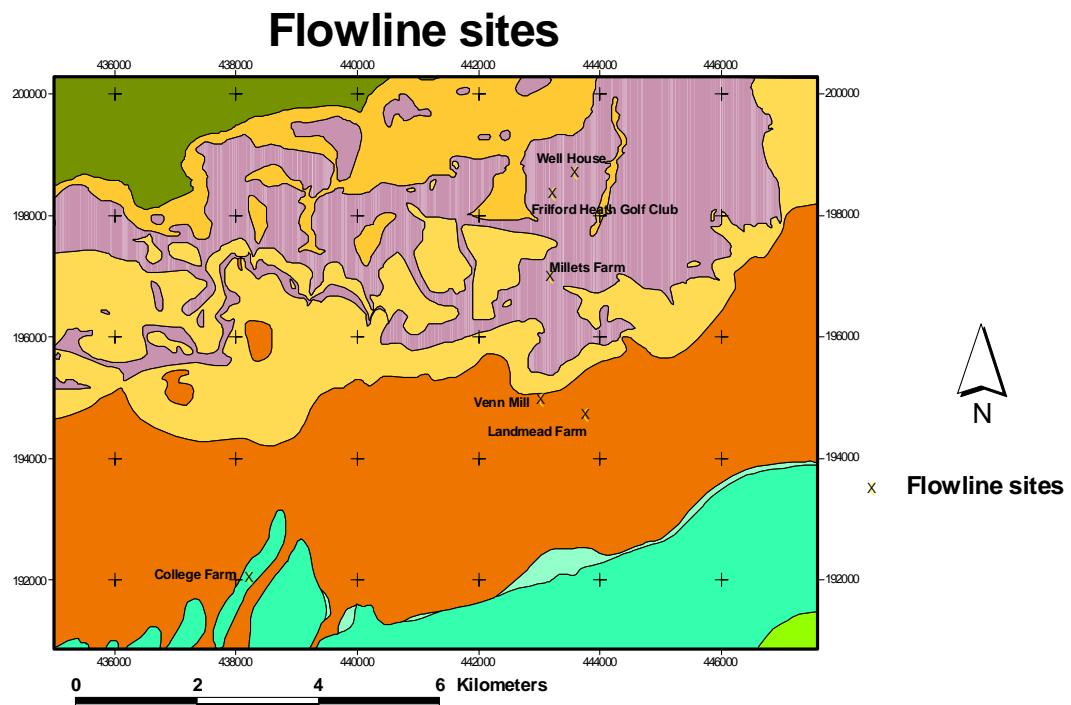


Figure 6.5 Sites along a transect representing a possible flowline.

Table 6.1 Sites chosen to represent a flowline in the Corallian

Site Name	Easting	Northing
Well House	443599	198698
Frilford Heath Golf Club	443228	198368
Millets Farm	443185	196996
Venn Mill	443021	194960
Landmead Farm	443763	194714
College Farm	438230	192051

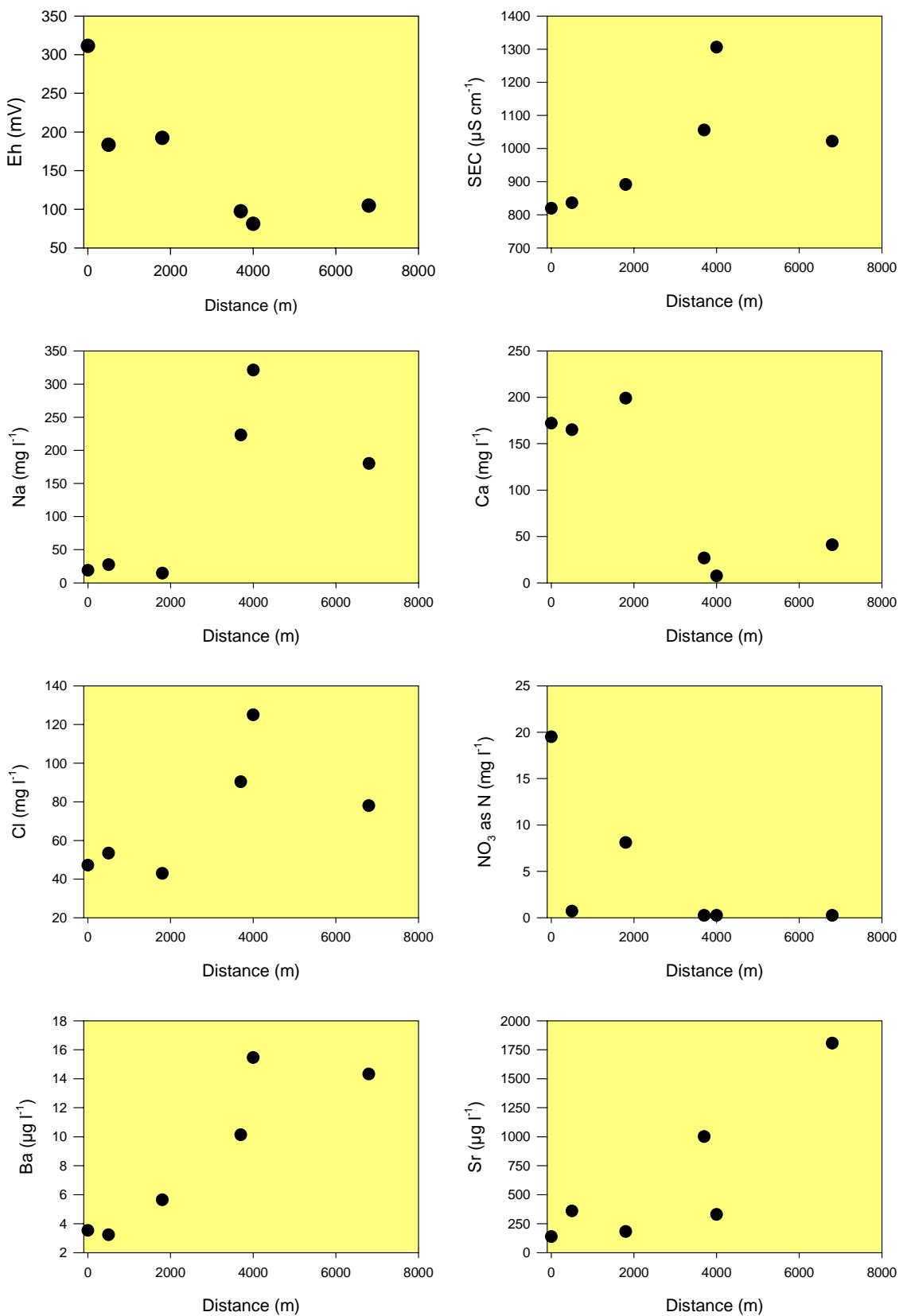


Figure 6.6 Selected parameters plotted against distance along a transect.

An examination of the data from each site along the flow line (Figure 6.6) serves to illustrate some of the observations made earlier in the chapter, highlighting the differences between groundwaters in outcrop areas and those in the confined parts of the aquifer. As expected, both redox potential (Eh) and dissolved oxygen concentrations decline where the aquifer becomes confined. As groundwater moves from the recharge area on the Corallian outcrop to the confined part of the aquifer, the waters become progressively more mineralised, shown by increasing SEC measurements along the flow line. This is probably mainly a result of increased dissolution of the aquifer matrix due to increased residence times, although mixing has also occurred with more saline formation waters as they move deeper into the aquifer. This is indicated by the increase in Cl concentration. Nitrate concentrations are markedly higher in the three unconfined sites, and decline once the aquifer becomes confined. The decrease in NO₃-N follows the removal of oxygen from the groundwater, and may be associated with the oxidation of organic carbon using NO₃ as the terminal electron acceptor (i.e. denitrification). Mixing with older (pre-agricultural and low nitrate) water in the confined zone may also play a part.

There is a decline in calcium ion concentration, and a rise in sodium ion concentration, as the groundwaters become confined. This is consistent with the process of ion exchange, which causes the geochemical evolution of the water. Increases also occur in several trace elements such as Sr and Ba due to water-rock interaction.

6.7 Temporal variations

The Environment Agency has recently added sites to its water-quality monitoring network in the Corallian, and therefore long-term records are not yet established for these sites. Eight of the monitoring sites have been monitored since 1993, although samples were not taken every year for all of these sites. Two of these sites are classified as unconfined, the rest confined. The depths are not known. It is not possible to provide an accurate picture of the changes in chemical composition with time across the Corallian aquifer with this limited dataset. A more comprehensive dataset is ideally needed. However, the eight sites that are available have been examined for obvious trends.

Major-element concentrations seem to be fairly stable, as expected for waters that are thought to have had time to reach equilibrium. Agricultural chemicals are probably most likely to show changes in concentration with time in this area, due to widespread farming activities in the study area, although this is likely to apply mainly to the unconfined boreholes. Nitrate values are low (generally lower than 0.1 mg l⁻¹ as N) for four of the eight samples for which time series data are available. No common trend in the concentration of nitrate is discernable for the remaining four sites. At one of the sites (PGWU0672, classified as confined) nitrate concentrations show a definite increase since the beginning of 2000, but this trend is not common to the other samples, which show if anything a slight decrease in nitrate concentration with time. Concentrations of sulphate do not show a common, identifiable trend with time for the eight samples.

Concentrations of the pesticides atrazine and simazine do not show a clear trend with time in the available samples. Most of the concentrations of these chemicals were below the detection limit of the available analytical equipment, and this may reflect the restrictions that have been placed on their use since the early 1990s.

6.8 Depth variations

The highly stratified nature of the Corallian aquifer together with the discontinuous nature of confining layers makes it unlikely that gradual changes in groundwater chemistry with depth occur uniformly across the aquifer. It is more likely that each borehole that is drilled will encounter relatively large changes in groundwater chemistry with depth (particularly if a series of permeable units separated by clays are encountered). This pattern will not necessarily be repeated at another site hundreds or even tens of metres away. Increasing depth would be expected to have a similar effect on groundwater chemistry as increasing distance from outcrop in the confined part of the aquifer. For instance, it would be expected that the concentrations of many dissolved species would increase, since

increasing depth implies longer residence times. Dissolved oxygen and redox potentials might be expected to decline. Concentrations of pollutants such as nitrate would naturally be expected to be most elevated in the uppermost layers of the aquifer.

It was possible to ascertain the depths of 13 of the boreholes that were sampled, together with the two springs that were assigned a depth of zero metres. Depth information for the remaining boreholes was not available. Very little information regarding screen and casing details was available, although it is the construction of the borehole that controls the exact horizons from which groundwater is derived. However, selected data have been plotted against borehole depth (where known) in order to determine if any general trends can be seen (Figure 6.7).

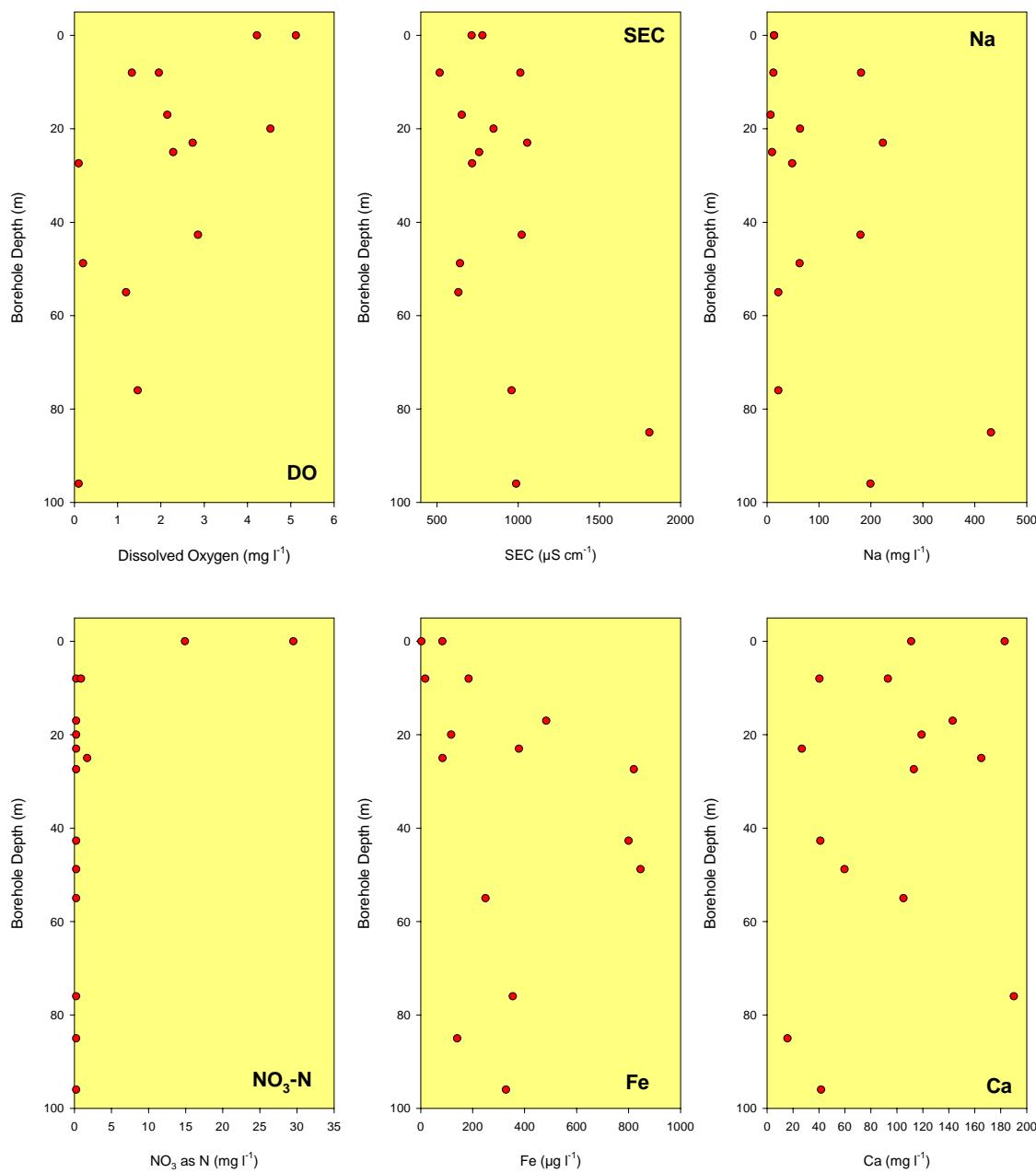


Figure 6.7 Selected parameters plotted against borehole depth.

The plots show a general decline in dissolved oxygen (DO) with depth, although it should be remembered that it was not possible to use a flow cell for each of these samples (only seven of the fifteen samples for which depths are known were sampled using the flow cell). A slight smell of

hydrogen sulphide was noted at some of the deeper boreholes during sampling, confirming the reducing (low oxygen) conditions present at depth in the aquifer. The concentration of dissolved iron increases with depth, and this is due to the dominance of Fe^{2+} in the deeper reducing environments. There is a slight rise in SEC with depth, which may be indicative of the longer residence times of deeper groundwater, as well as the possible presence of connate waters. Nitrate is found only at shallow depths – most notably at the two spring sources. The calcium concentration appears to decline with depth, and the sodium concentration increases. This is likely to be due to ion-exchange reactions as water (Ca-saturated) passes through the various (Na-rich) clay layers, and Ca substitutes for Na on the clay minerals. However, there is much scatter in these plots that may indicate that depth is not a good indicator of residence time or geochemical processes due to the large variations in hydrogeology and mineralogy of the aquifer.

6.9 Age of the groundwater

The study of the Corallian by Alexander and Brightman (1985) indicates that outcrop waters are essentially modern in age (<1000 years old), whilst ages increase rapidly down dip of the outcrop. This was based on tritium analyses (45 TU at outcrop, declining to less than 1.5 TU at the confined Harwell site). Alexander and Andrews (1984) showed that there was no significant contribution from modern waters at distances greater than 3 km from outcrop, based on tritium results. The same study calculated groundwater ages based on radiogenic helium concentrations, and these proved to be two orders of magnitude greater than the tritium ages. This was attributed to assumptions made in calculating the helium ages, but may also be due to complications arising from diffusional exchange between sandstones and impermeable clays in the aquifer. Both methods do, however, confirm that Corallian groundwaters increase in age with distance down dip. Calculated ^{14}C ages for groundwaters from the Corallian aquifer varied from 1000 to 17000 years old (Alexander and Andrews, 1984), but there is no direct age information on the age of younger groundwaters.

Selected samples were analysed for the stable isotopes $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Figure 6.8). On a $\delta^2\text{H}$ - $\delta^{18}\text{O}$ plot, the waters lie along the World Meteoric Water Line showing the waters are predominantly of meteoric origin and have been little modified by other processes. The samples with the most enriched (more positive) signatures are from the southwest of the study area, and the more depleted samples are from the northeast of the area, and the range may be related to rainfall inputs that vary across the country (Darling et al., 1997). These ratios are consistent with a Holocene or modern age. However, one of the samples (Baldons Farm) has a relatively depleted $\delta^2\text{H}$ - $\delta^{18}\text{O}$ signature, implying that a component of palaeowater (i.e. water recharged in the Pleistocene when temperatures were colder) is present. The borehole from which this sample was collected is one of the deepest (85 m) in the study area. This sample also has a very heavy ^{13}C signature that implies extensive carbonate reaction and the highest SEC. It is therefore likely that a component of groundwater > 10 000 years BP is present in the deeper parts of the aquifer in this area.

6.10 Spatial variations

Variations in the spatial distribution of ions are illustrated in Figures 6.9 to 6.14. The diverse nature of the Corallian and the fact that the depths of the sampling points are not known with certainty makes it difficult to draw conclusions from the dataset. However, the spatial variations confirm the general conclusions found along the regional flow line (Section 6.5). SEC tends to increase in concentration moving from the outcrop of the aquifer to those sites overlain by Kimmeridge Clay. This is consistent with what is known of the aquifer in terms of flow direction, in that waters with longer residence times are more highly mineralised. Waters in the confined part of the aquifer are also more likely to mix with more mineralised palaeowaters.

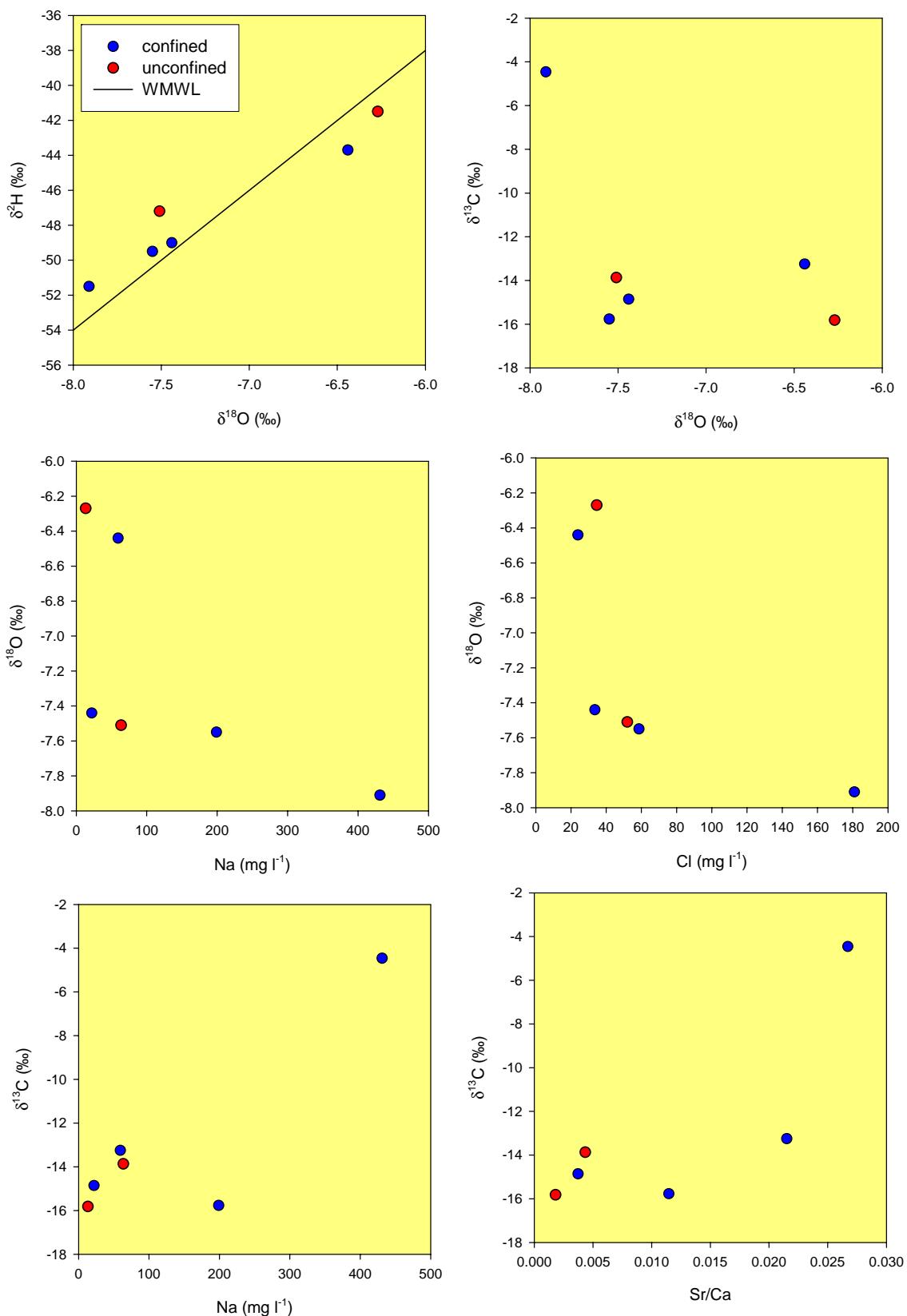


Figure 6.8 Plots of isotope ratios against selected parameters.

The calcium ion concentration is generally higher at outcrop (in the north of the study area) than at those locations where the aquifer is overlain by clays. In contrast, Na concentrations are generally higher in the south of the study area. Some of the samples with higher Na also have higher Cl

implying some of the Na increase is related to mixing with remnants of palaeowater. However, Na/Cl ratios increase significantly along the strike of the outcrop where the aquifer is confined, and where a decrease in Ca occurs, it is concluded that ion exchange of Na for Ca is the dominant geochemical control. Sulphate concentrations tend to increase towards the east of the study area, both in the unconfined and confined aquifer, although the reasons for this are not clear. Mg concentrations are highest in confined waters and the higher Mg/Ca ratios imply that incongruent dissolution of carbonate minerals is occurring.

The outcrop groundwaters are mostly oxidising with high concentrations of dissolved oxygen – nitrate is also higher but decreases in the southerly confined area, which is more reducing. Iron and manganese increase in the confined part of the aquifer, which is expected since these elements are more mobile under reducing conditions. Uranium in contrast is more mobile under oxidising conditions and this is reflected in the regional plots, with higher uranium concentrations in the north. Arsenic concentrations are generally low (median and maximum concentrations of 0.5 and 1.9 $\mu\text{g l}^{-1}$ respectively). Although the highest As concentrations were found in reducing waters, the concentrations are variable spatially. Ammonium concentrations are higher in the reducing waters, and this is probably due to desorption from clay minerals, or the decomposition of organic matter.

It is likely that the groundwaters in the confined part of the aquifer are older. This is confirmed by an increase in the concentrations of minor and trace elements, which typically increase with residence time. Fluoride and strontium ion concentrations both show large increases in the confined zone.

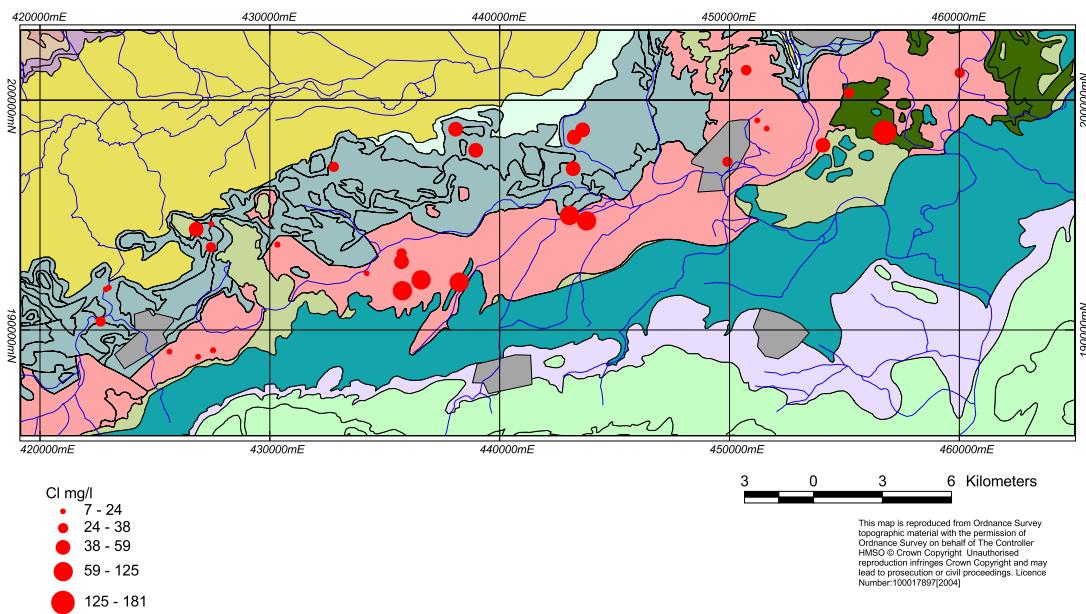
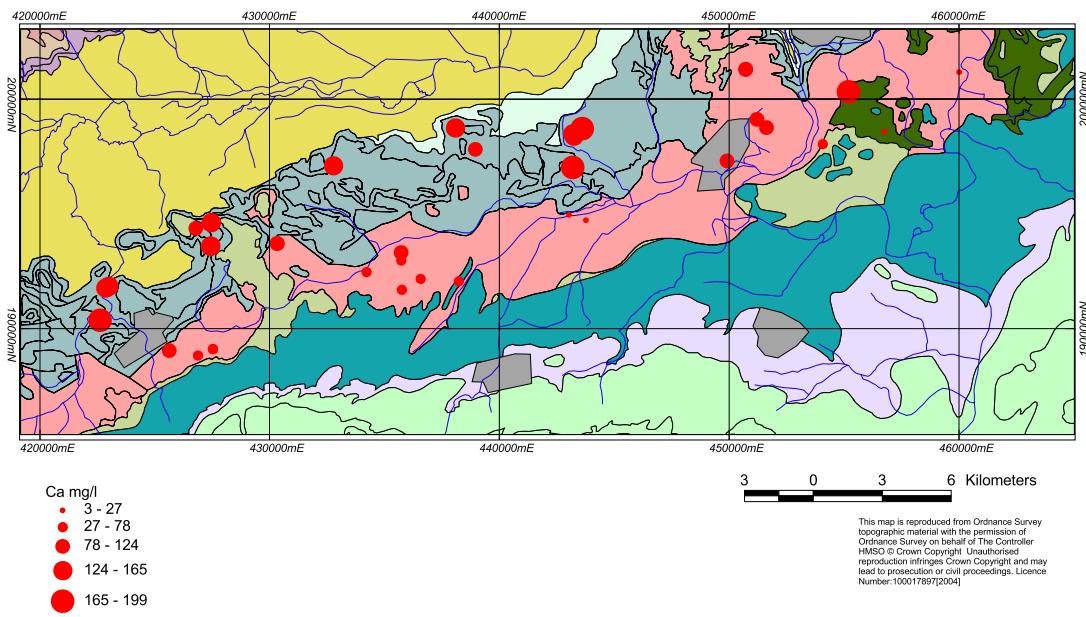


Figure 6.9 Regional variations in Ca and Cl concentrations in the Corallian groundwaters.

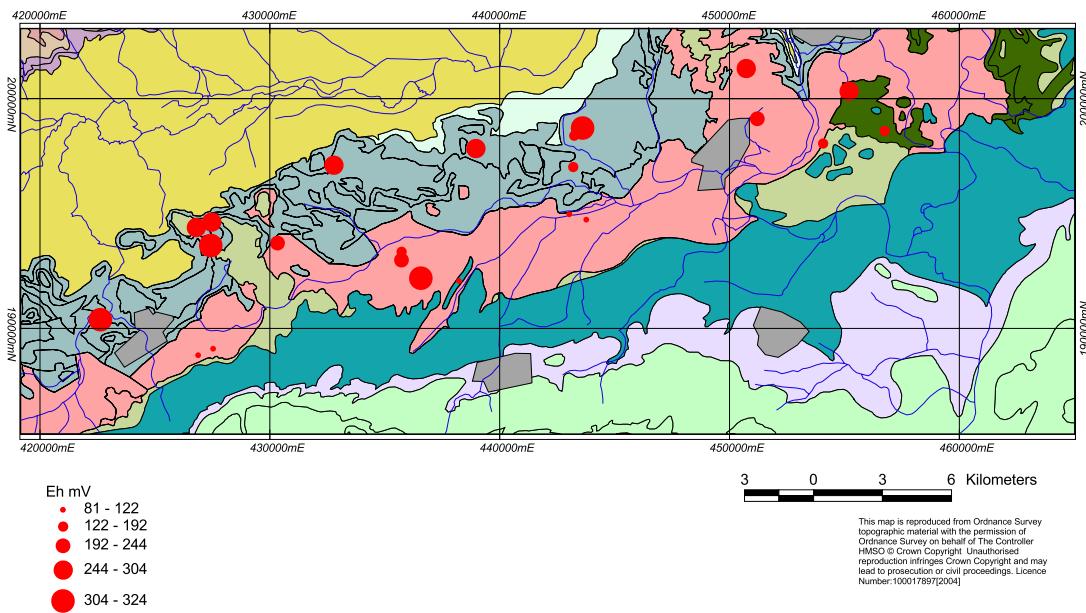
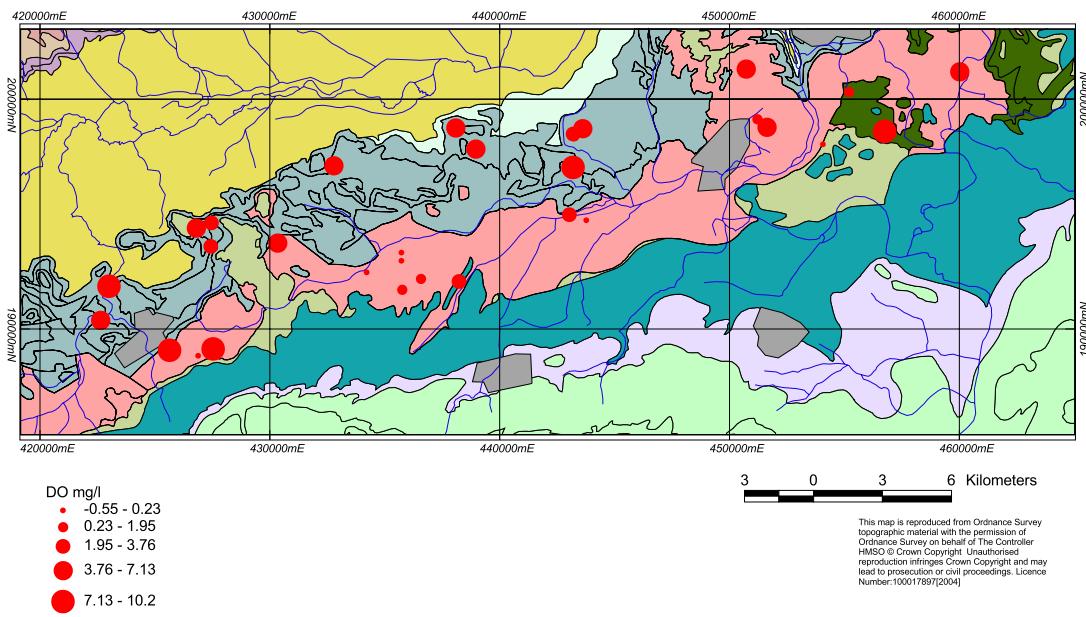


Figure 6.10 Regional variations in dissolved oxygen concentrations and Eh in the Corallian groundwaters.

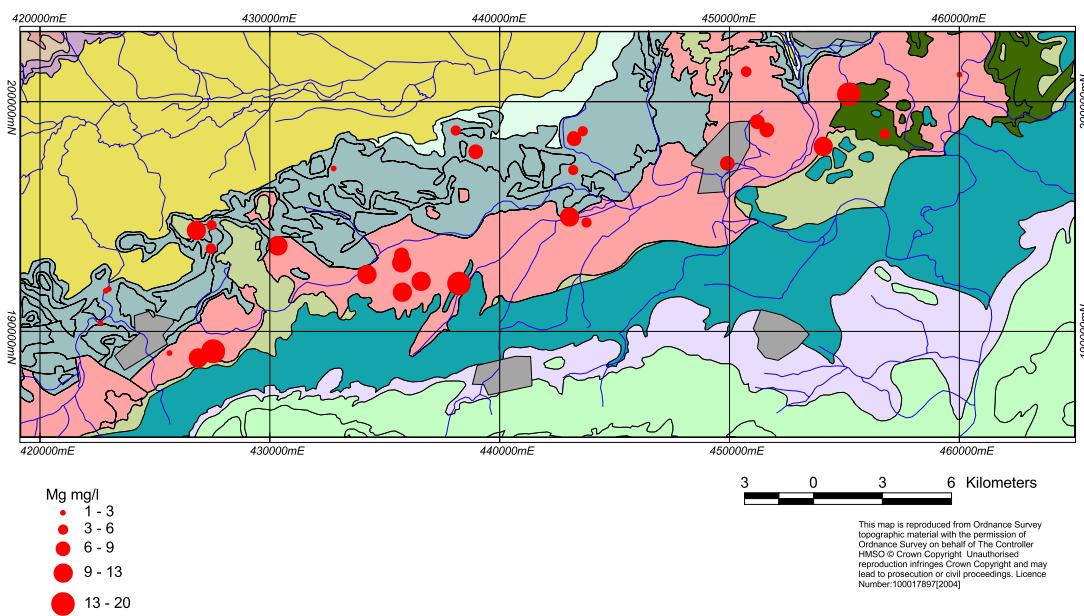
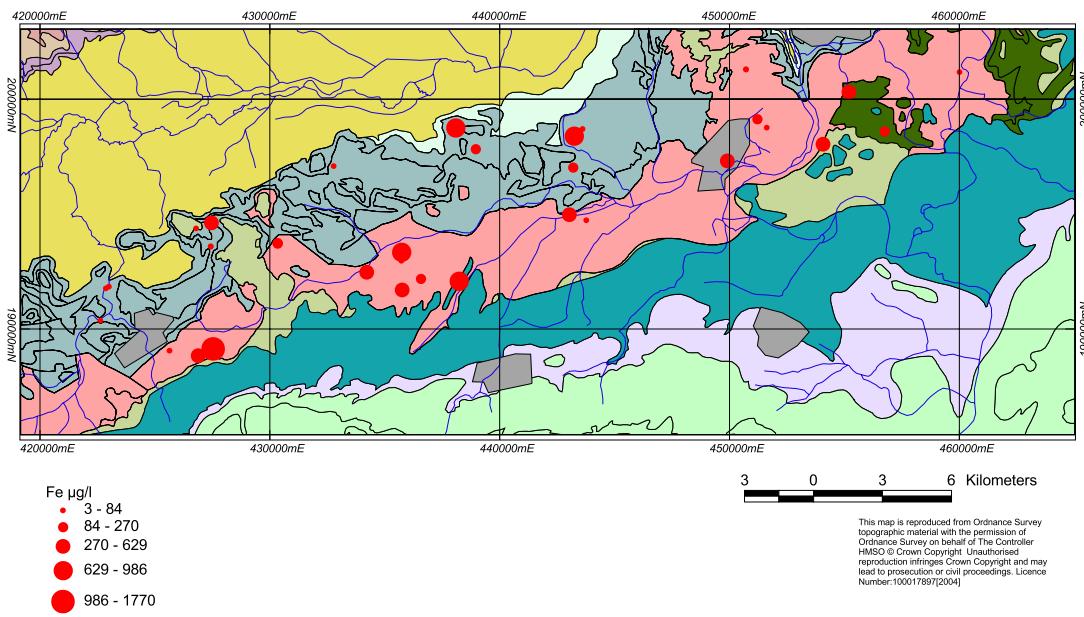


Figure 6.11 Regional variations in Fe and Mg concentrations in the Corallian groundwaters.

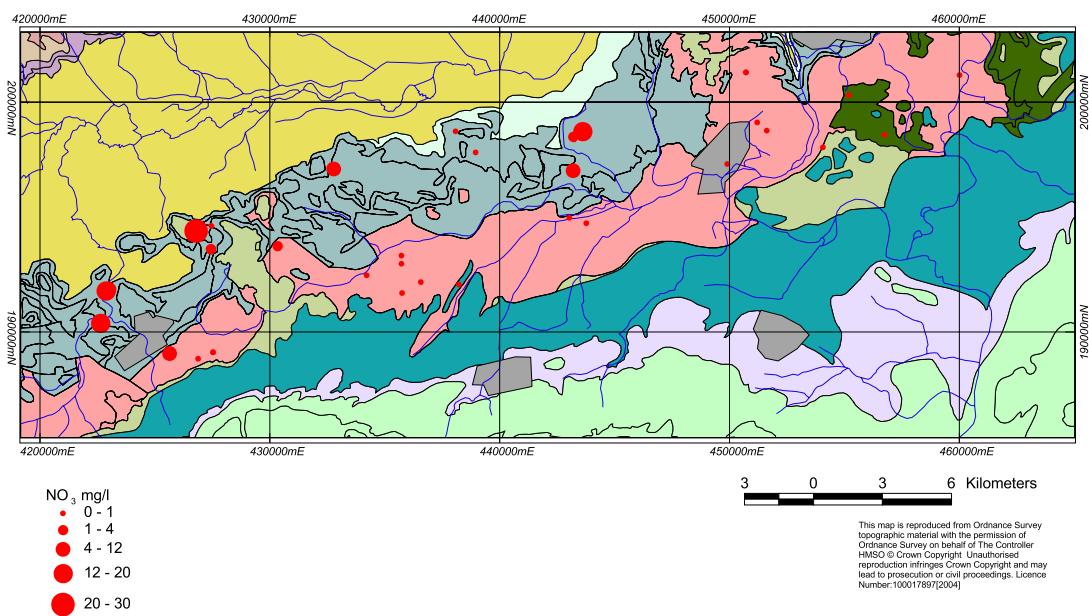
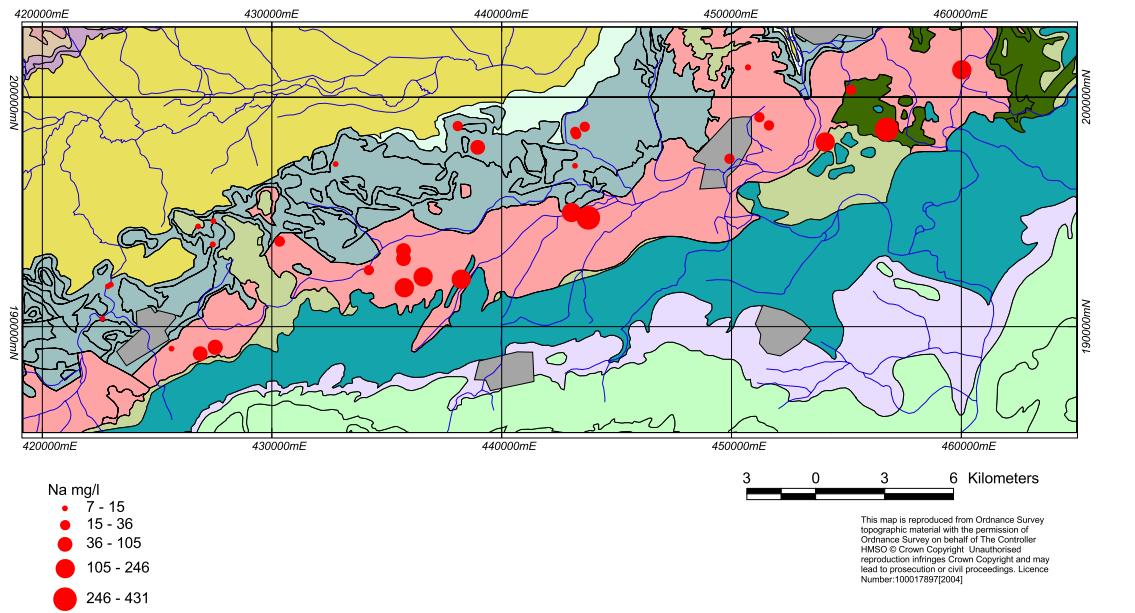


Figure 6.12 Regional variations in Na and NO₃ concentrations in the Corallian groundwaters.

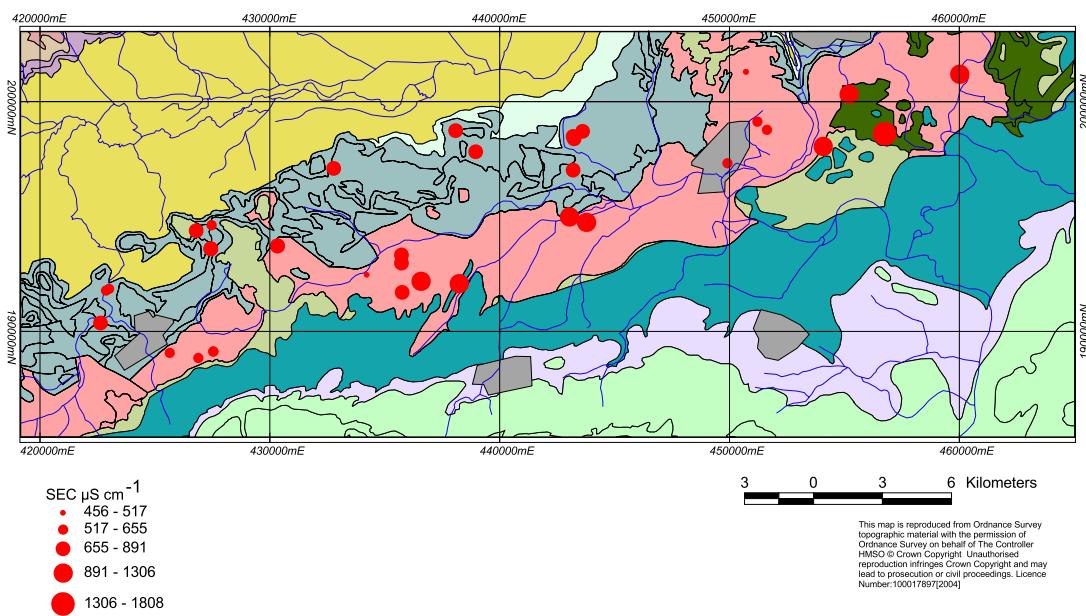
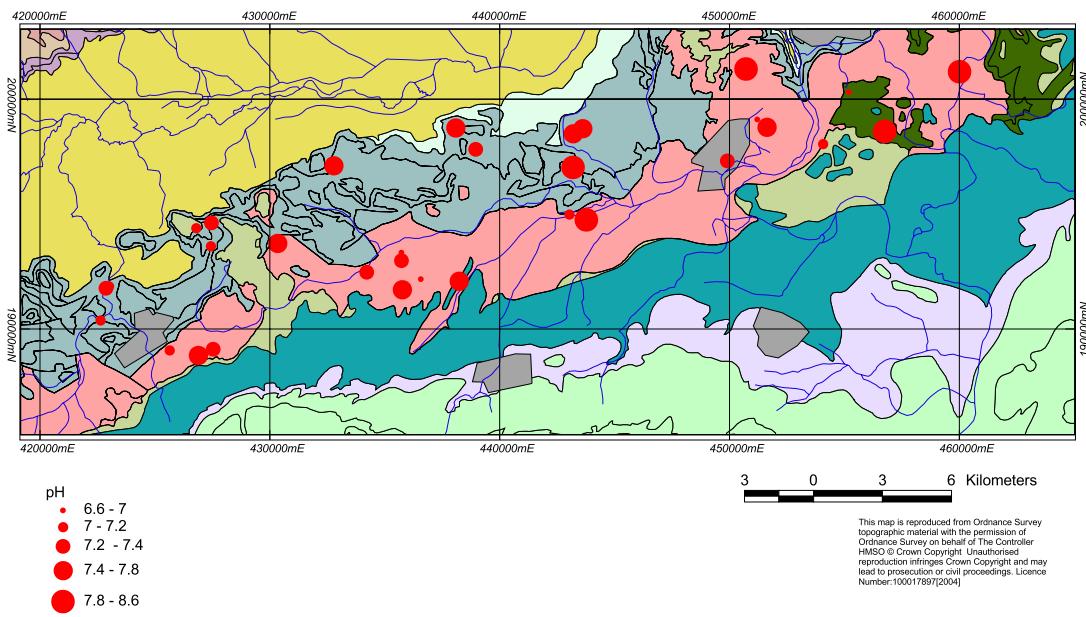


Figure 6.13 Regional variations in pH and SEC in the Corallian groundwaters.

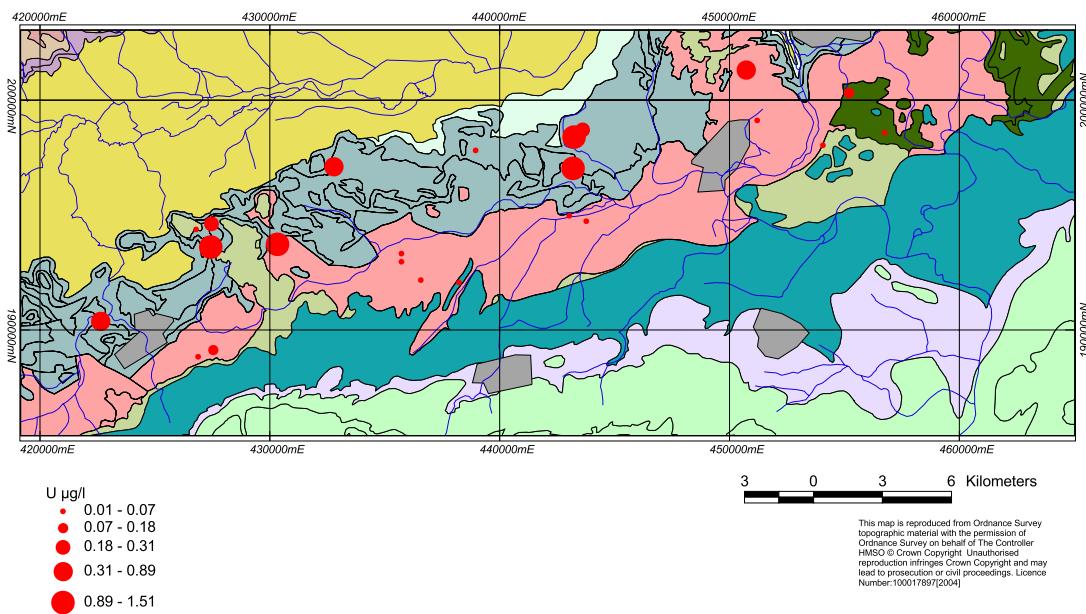
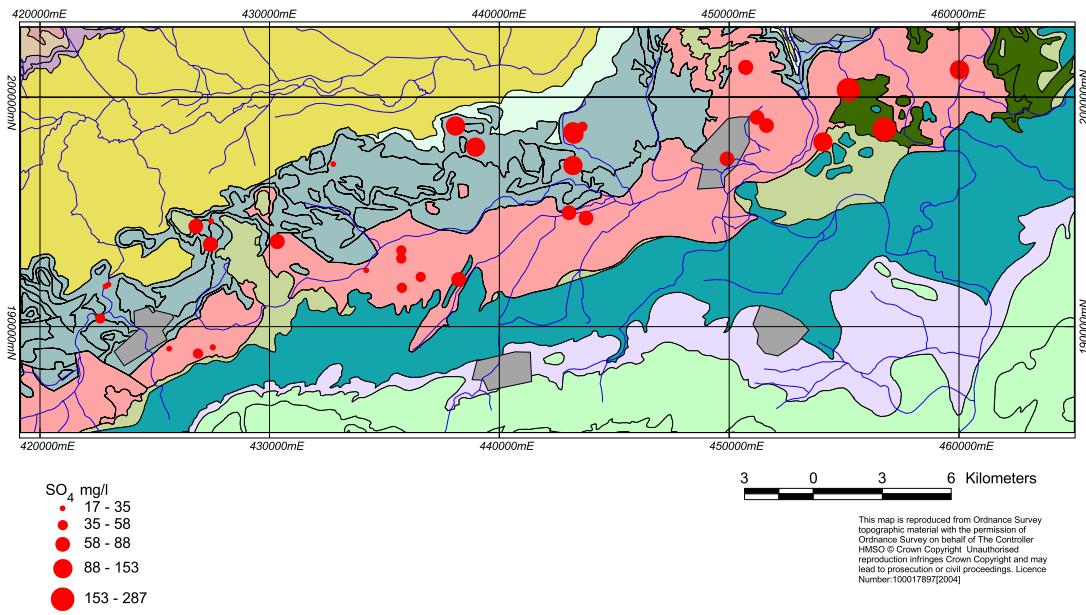


Figure 6.14 Regional variations in SO₄ and U concentrations in the Corallian groundwaters.

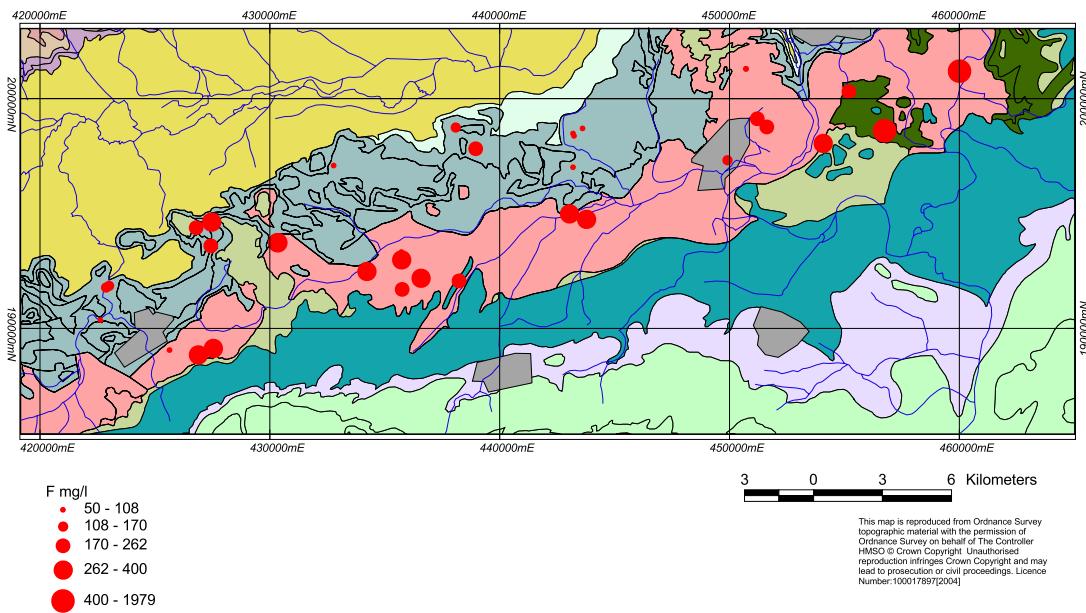
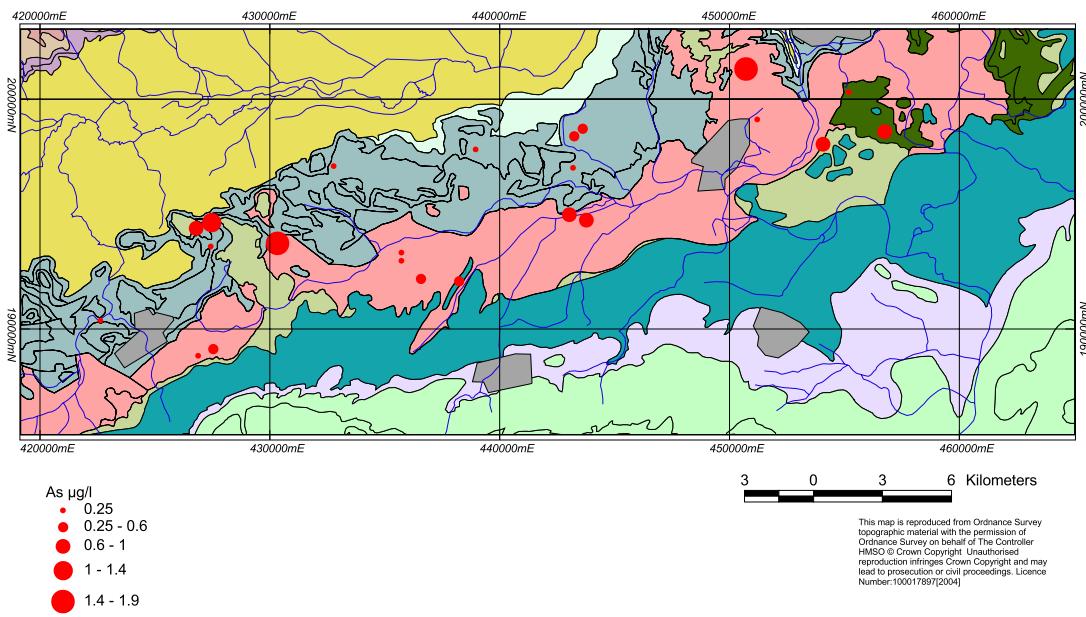


Figure 6.15 Regional variations in As and F concentrations in the Corallian groundwaters.

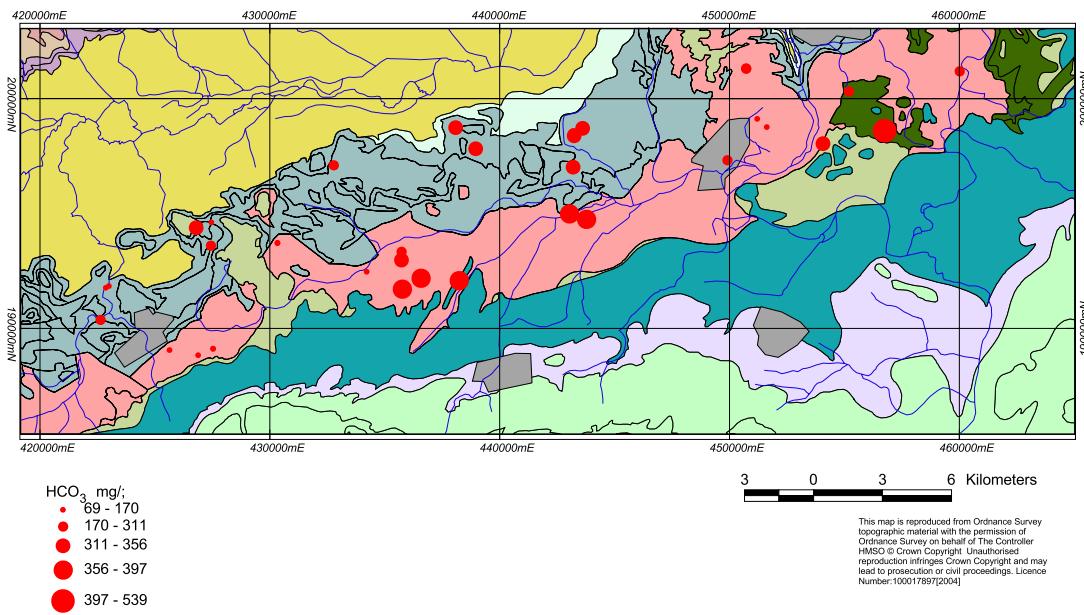
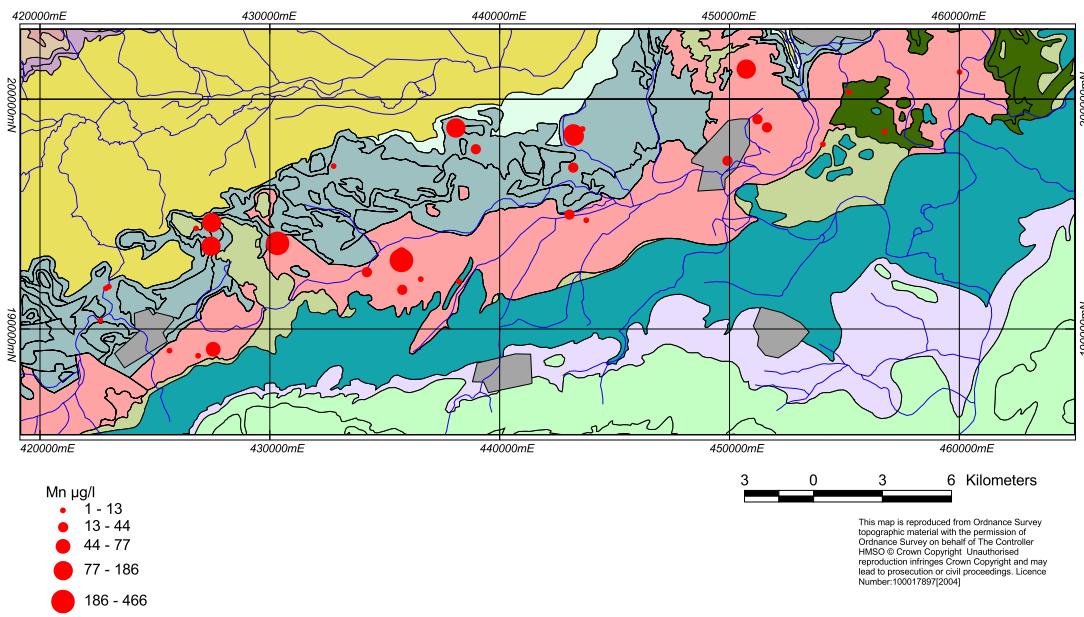


Figure 6.16 Regional variations in Mn and HCO₃ concentrations in the Corallian groundwaters.

7. BASELINE CHEMISTRY OF THE AQUIFER

A wide range of physical and chemical processes determine the baseline groundwater chemistry of any aquifer. The primary input to most major aquifers is rainfall although connate or formation water may be present in parts of the aquifer where flushing has not been complete. In addition, leakage from underlying or overlying aquifer units may modify the groundwater chemistry either locally or regionally. A series of chemical reactions take place during recharge and groundwater flow, the most important being mineral dissolution and precipitation, ion exchange, mixing, redox reactions, and sorption/desorption reactions. Many of the above-mentioned reactions are also time-dependent and this gives rise to a range in baseline chemistry as the groundwaters move from areas of recharge to discharge. Superimposed on this “natural” baseline are anthropogenic influences. These include point source and diffuse pollution, which directly modify the baseline chemistry.

In the present study, boreholes that are known to be affected by point-source pollution have been excluded from the database. However, many groundwaters in major aquifers, especially where unconfined, show signs of diffuse pollution, dominantly from urban or agricultural activities and these have been included. The determination of baseline in such cases can be determined from historical records, where these exist, by comparing with pristine areas, applying statistical techniques or modelling. Most of these have limitations and should be used together to provide a reasonable estimate of the baseline (Shand and Frengstad, 2001).

The geochemical data suggest that the composition of Corallian groundwaters can be ascribed largely to natural processes of water-rock interaction. The upper baseline can thus be represented by the 97.7th percentile concentration in Tables 5.1 and 5.2. The carbonate composition of the most permeable parts of the aquifer is responsible for the predominantly Ca-HCO₃ type waters found. This also serves to buffer the pH of infiltrating water, which lowers the solubility of certain trace metals. Ion exchange reactions were important in modifying the groundwater chemistry and this is responsible for the higher sodium concentrations found in the more evolved waters, and the coincident drop in calcium concentration. Mixing with remnants of formation water has occurred, mainly in the deeper part of the aquifer, reflected by an increase in Na, Cl and other “marine-derived” components.

The Corallian has a heterogeneous geology, which means that from a hydraulic point of view it can be considered as a series of discontinuous permeable layers rather than a single, uniform aquifer. This has implications for the groundwater chemistry, which varies depending on the lithology at a particular location together with the governing hydraulic conditions. More generally however, Corallian groundwater is only potable at or near the outcrop of the aquifer. The quality declines rapidly away from the outcrop towards a saline and non-potable composition. At Harwell, a few kilometres down dip of the outcrop, the water is thought to be composed of about 40% connate water, which is likely to have been present since the strata were deposited (Alexander and Brightman, 1985). The flow regime described by Alexander and Brightman (1985) shows that there is very little through-flow of groundwater in the deep confined aquifer, and in the past part of the area around Harwell was a salt marsh.

Corallian groundwaters often have moderate to high iron concentrations, primarily as a result of iron oxide cements in the aquifer matrix combined with the redox conditions. Iron concentrations increase where redox potentials drop, since iron is more mobile under these conditions. In the Corallian, this is generally where the aquifer is overlain or confined by clays, or at depth. High iron concentrations can present a problem to users of the groundwater, mainly causing iron staining of fittings and an unpleasant taste to the water. More than half of the samples taken had iron concentrations higher than the CEC maximum admissible concentration (MAC) of 200 µg l⁻¹, and fewer than a third were within the CEC Guide Level (GL) of 50 µg/l. One of the sources sampled had a fluoride concentration in excess of the CEC MAC of 1500 µg/l, but the rest were within this limit. Three of the samples had boron concentrations higher than 500 µg/l. Concentrations of uranium, lead, cadmium, aluminium and nickel were generally within acceptable ranges.

Anthropogenic influences on the groundwater quality include raised concentrations of nitrate, particularly at shallow depths. Records of groundwater chemistry are only available going back ten or fifteen years, and are therefore probably too short to provide an idea of changes in the concentrations of baseline constituents likely to be affected by human activities with time. The baseline concentration of nitrate in the confined parts of the aquifer is typically less than detection limit due to denitrification, and it is not possible to use such older waters to assess the baseline concentration of outcrop areas. The baseline concentration of nitrate in the aquifer would be expected to be low. Significant concentrations of nitrate in the groundwater are very likely to be a result of pollution. It is possible that pesticides and other toxic compounds used in agriculture are present in these waters, but for the most part these have not been tested for. A few data were available concerning concentrations of atrazine and simazine, and were found to be very low. Groundwater samples were not taken from the urban area of Abingdon, where industrial activities including the use of chlorinated organic compounds took place. Industrial contamination of these waters is therefore a possibility.

Finally, all of the boreholes and wells suitable for sampling are in use, generally for a purpose requiring the water to be potable or at least relatively fresh. This naturally biases all of the samples towards the potable end of the spectrum for the aquifer as a whole. Boreholes drilled in the aquifer that encounter poor quality water tend not to be used, or have been filled in, and few boreholes are drilled where poor quality water is expected. The study by Alexander and Brightman (1985), as well as other evidence, points to large parts of the aquifer where the groundwater is not potable (i.e. the confined areas south of the outcrop), and it is possible that water quality in other parts of the aquifer not sampled are of poor quality.

8. SUMMARY AND CONCLUSIONS

The Corallian rocks of Oxfordshire and Wiltshire form a minor aquifer that supports a number of small to moderate groundwater abstractions. Most of the sources are within the unconfined part of the aquifer, since groundwater quality declines down dip where the Corallian rocks are confined by clays. The hydrogeology and hydrogeochemistry of the aquifer is complicated by the fact that it is composed of discontinuous layers of limestone which are easily disrupted by faulting. Investigations at Harwell have shown that different layers in relatively close proximity can vary significantly in groundwater chemistry (Alexander and Holmes, 1983).

The dominant control on groundwater chemistry in the Corallian aquifer was found to be the interaction of infiltrating water with the aquifer material. The carbonate nature of the Corallian aquifer matrix ensures that infiltrating waters are well buffered, and leads to HCO_3^- being the dominant anion in nearly all cases. Ion exchange reactions are important in the confined parts of the aquifer, with Ca in groundwater being replaced by desorption of Na from clays in the aquifer matrix. These two processes together lead to the typical Ca-HCO₃ and Na-HCO₃ groundwater types. The absence of low pH groundwaters was also thought to be partly responsible for the generally low concentrations of metals such as Pb, Al and Cd in solution, since these species are mobile mainly in acidic waters. Mixing with more saline formation waters is important down dip in the deeper parts of the aquifer, where water quality is poor, and consequently most abstractions are situated on the outcrop strip. There is inevitably a sample bias towards the more potable end of the spectrum, since this is where most accessible abstractions are located.

Natural dissolved iron concentrations were found to be generally high in Corallian groundwaters, in some cases exceeding drinking water standards. Superimposed on the natural chemistry of the aquifer are the effects of humans. Nitrate concentrations were relatively high locally, indicating anthropogenic pollution, probably due to fertiliser application. Concentrations of other measured pollutants were low in those boreholes that were sampled.

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