



# Baseline Report Series:7. The Great and Inferior Oolite of the Cotswolds District

Groundwater Systems and Water Quality Commissioned Report CR/03/202N

National Groundwater & Contaminated Land Centre Technical Report NC/99/74/7



**The Natural Quality of Groundwater in England and Wales** A joint programme of research by the British Geological Survey and the Environment Agency

#### BRITISH GEOLOGICAL SURVEY Commissioned Report CR/03/202N

ENVIRONMENT AGENCY National Groundwater & Contaminated Land Centre Technical Report NC/99/74/7

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## Baseline Report Series:7. The Great and Inferior Oolite of the Cotswolds District

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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 <u>baseline</u> 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 <u>background</u> or <u>threshold</u> 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 <u>present</u> <u>day status</u> 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 (<sup>3</sup>H), 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) Pre-War (1940) and (iv) modern 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 & 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 Great and Inferior Oolite limestones form important aquifers in the Cotswolds. The groundwater abstracted is used mainly for public supply, with small but important fractions serving agricultural and private needs. The area covered in this study extends from Broadway in the north towards Cricklade in the South including the Cotswold Hills. The report describes the regional variations in the baseline hydrochemistry of groundwaters and the dominant geochemical processes taking place in the limestone aquifers.

The limestones crop out in the north-west of the study area, but dip gently south-eastwards where they are covered progressively by younger deposits, resulting in aquifer confinement. Numerous spring lines are present in the area, the majority occurring along the northern limestone escarpment.

The most important factor affecting the chemical composition of the limestone groundwaters in the region is carbonate reaction. Close to the recharge area, waters are oxidising and strongly pH-buffered with Ca and HCO<sub>3</sub> as the dominant dissolved ions. Distinct hydrochemical changes are observed downgradient as the aquifer becomes progressively more confined. Ion-exchange processes become significant and a change to a Na-HCO<sub>3</sub> water occurs. Redox-sensitive elements document the onset of reducing conditions. Further along the flowline, deep within the confined limestone, mixing with old formation waters influences the water chemistry, resulting in a Na-Cl type groundwater. Distinct stable-isotopic compositions suggest long residence times in the order of several thousands of years of age for these waters.

The majority of unconfined groundwaters, and in particular, spring waters in the region are affected by agricultural pollution, showing high nitrate concentrations. In confined groundwaters, where dissolved oxygen is reduced or absent, nitrate concentrations are lower indicating that denitrification is likely to have occurred. Some of these waters may even be of sufficient age to represent pre-modern water.

It is concluded that the hydrochemical properties of the groundwaters in the Great and Inferior Oolite limestone are mainly determined by natural reactions between the recharged water and the limestone rock. Natural baseline concentrations for some elements can range over several orders of magnitude.

## 2. PERSPECTIVE

The study area is situated mainly in the eastern part of Gloucestershire. It extends from Broadway in the north to Cricklade in the south, Gloucester in the west to Carterton in the east and encompasses the greater part of the Cotswold Hills (Figure 2-1). The geological strata cropping out vary from mudstones and siltstones of the Lower Jurassic in the far north-west through to the predominantly limestone sequences of the Inferior and Great Oolite Groups of the Middle Jurassic, to the Kellaways and Oxford Clay formations of the Upper Jurassic in the south-east corner (Figure 3-3).

The topography generally reflects the underlying geology. The Inferior and Great Oolite limestones occupy the majority of the area, forming a broad plateau that dominates the landscape and slopes from its escarpment in the north-west at just under 300 m above sea level to about 80 m in the south-east (Figure 2-2). The escarpment itself forms a surface water divide between the River Thames and the River Severn catchments. The area is drained by rivers rising close to the escarpment. Towards the south-east, these are mainly the Windrush, Coln and Churn draining eventually into the River Thames. Towards the north-west, springs act as headwaters and small streams drain into the River Severn, either directly or via the River Avon and River Chelt.



Figure 2-1 Location map of the Cotswold study area



#### Figure 2-2 Topographical map of the Cotswolds study area

The highly permeable limestones of the Inferior Oolite and Great Oolite Groups form major aquifers in the study area. The two formations are partly separated by the mudstones of the Fullers Earth Formation.

Jurassic limestones are the third most important source of groundwater in the United Kingdom. Groundwater abstraction is used for public supply, with a small quantity serving agricultural and private needs. Major pumping stations for public water supply include Baunton [SP 0195 0484], Bibury [SP 1123 0712], Ashton Keynes [SU 042 941], Latton [SU 081 968] and Meysey Hampton [SU 1130 9880], all operated by Thames Water plc. Taking these sources into account, the total quantity of licensed abstraction from the Inferior Oolite is about  $13.5 \times 10^6$  m<sup>3</sup>y<sup>-1</sup> and from the Great Oolite it is about  $3.5 \times 10^7$  m<sup>3</sup>y<sup>-1</sup> (Sumbler et al. 2000). However, discharge from pumped wells and boreholes accounts for only a small proportion of the total discharge from the aquifer. The vast majority of the discharge occurs in the form of springs mainly along the north facing limestone escarpment, of which the most important are Chalford [SO 8915 0243], Cleeve Hill [SP 0064 2638], Northfield [SO 9844 2217], Stanton [SP 0752 3392], Stanway [SP 0745 3237] and Winchcombe [SP 0375 2785], all sources operated by Severn Trent Water plc (Figure 3-3).

The area receives annual precipitation of about 650 mm in the north and north-east increasing to 800 mm in the south-west. Due to the faulted and fissured nature of the Great and Inferior Oolite Group, the aquifer responds quickly to rainfall events resulting in rapid changes in groundwater level. As a

result, the upper reaches of many rivers become dry each year. Thus drought conditions can occur within a few months, with low groundwater levels and river flows in summer and autumn being a common and natural occurrence within the study area.

The land is predominantly used for arable farming, with minor areas of managed grassland present, particularly along the Cotswolds escarpment. Only small patches of woodland exist along the escarpment in the north-west. Larger urban areas are only present to the north-west of the study area. Smaller villages are found throughout the region, with houses often built out of the honey-coloured Oolitic limestones (Figure 2-3).



#### Figure 2-3 View of Broadway, with houses using honey-coloured Oolitic limestone

There are a number of potential pollution sources and these can result in anthropogenic impacts on groundwater chemistry. The greatest current impact is from diffuse pollution sources, predominantly agriculture. The impact is observed by high nitrate concentrations and by increasing levels of pesticides in some sources of groundwater. Several waste disposal sites exist within the study area, of which the majority are situated on the Kellaways and Oxford Clay formation (see Table 3.1). Additionally, various consented discharges into the rivers Coln, Cole and Leach exist. These point sources of pollution, together with possible spills and industrial activities, could potentially have a adverse effect on individual abstractions.

Current issues in the study area relate to:

• alleviation of low river flows in the summer and autumn months. The drought of 1989-1992 and the dry summers of 1995 and 1996 exacerbated public concern about river flows, levels, water quality and stream ecology in the groundwater-fed watercourses in the study area. Subsequently, schemes for the alleviation of low flows in the River Churn and Ampney Brook have been introduced. As a result, abstractions are subject to substantial reduction at several public water supply sources at times of normal summer low-flow (LEAP, 2001). In future, abstraction licences will be tied in with the low-flow alleviation of the Churn and Ampney Brook;

- *nitrate from arable land in recharge areas.* Statutory measures to reduce the leaching of nitrate from farmland to groundwater and surface water have been introduced by the government in the form of Nitrate Vulnerable Zones (NVZs). Farmers are required to comply with restrictions on the spreading of fertilisers onto their land in order to protect water quality and maintain efficient agriculture;
- *the need to understand surface-water groundwater interaction* and the links to environmental requirements;
- *the need to understand the Cotswolds groundwater system* in particular variations in groundwater quality, to identify groundwater resources at risk of pollution;
- *use of the aquifer for Aquifer Storage and Recovery (ASR) schemes.* To address the problem of river low flows during summer and autumn, ASR could provide a future option for additional water resources in the study area by injecting treated water from surplus river flows in the winter via boreholes into the confined aquifer.

The focus of this report is on the variations in groundwater quality related to natural geochemical processes and how these vary spatially across the aquifer. Attempts are also be made to ascertain relative groundwater ages and to describe temporal variations.

## 3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

#### 3.1 Introduction

In order to assess the baseline groundwater quality, it is necessary to understand the system within which the groundwater is contained. This requires information on the geological and hydrogeological properties to provide the physical framework of the system; knowledge of the mineralogy and geochemistry of the component minerals to explain the characteristic groundwater chemistry, and the initial water input to the system, principally rainfall chemistry.

#### 3.2 Geology

The geological succession in the research area ranges in age from Lower Jurassic to Quaternary (Table 3.1).

The Jurassic rocks of Britain were deposited under tropical climatic conditions in a marine environment. The sedimentation was affected by a series of sea transgressions and regressions resulting in various facies changes. These range from the mudstones and siltstones of the Lias Group, through predominantly limestone sequences of the Inferior and Great Oolite groups to the mudstones and sandstone beds of the Kellaways Sands and Oxford Clay formations.

The first transgression was in early Jurassic times. Predominantly fine-grained sediments were deposited, represented by the clays of the Lias Group, which form the lower part of the escarpment (Figure 3-3). At first, these were marine mudstones, with interbedded limestones at the base (Blue Lias and Charmouth Mudstone Formation). Later, increased terrigenous sediment supply, possibly accompanied by slight transgression, added silt and fine sand to the mud being deposited, forming the Dyrham Formation. Following this, rapid regression led to the formation of continental shelves across the region, in which iron-rich ooids were deposited with sand, silt and shell debris to form the Marlstone Rock Formation, a ferrugineous limestone. The ooids are made of concentric calcite layers around a nucleus and are formed by chemical precipitation of calcium carbonate under warm climates in shallow waters (Figure 3-11). With a renewed deepening of the sea, mud deposition resumed to form the Whitby Mudstone Formation. Once again, at the end of the Lower Jurassic, a regression generated coarser sediment forming the Bridport Sand Formation, previously known as the Cotteswold Sand.

The clays of the Lias Group are several hundred metres thick and are incompetent under pressure. Hence, cambering and landslipping has occurred widely throughout the study area wherever the limestones of the Inferior and Great Oolite overlie these mudstones on valley slopes or escarpments, displacing limestone strata downhill, as can be seen in Figure 3-1.



#### Figure 3-1 View of the Cotswolds escarpment near Barrow Wake [SO 9312 1539]. Landslides have protruded the scarp locally towards the north-west.

By the early Mid Jurassic, a shallow shelf sea was established across the Cotswold region, producing widespread carbonate deposits. During the deposition of the Inferior Oolite Group, made up of the Birdlip, Aston and Salperton Limestone Formations and the Great Oolite Group, made up of the Fuller's Earth, Taynton Limestone, Hampen, White Limestone, Forest Marble and Cornbrash formations, high-energy, open-water environments predominated, depositing ooid and bioclastic limestones. The formations also contain numerous invertebrate marine fossils, notably ammonites and bivalves (Figure 3-2).



Figure 3-2 Great Oolite limestone rock sample with bivalves. Farmington Quarry [SP 1305 1686]

Periodically, more protected, lagoonal conditions were established and marl and mudstone horizons deposited. The most substantial units of mudstone occur in the lower and upper parts of the Great Oolite Group, namely the Fuller's Earth Formation and the Forest Marble Formation.

The Inferior Oolite Group forms a broad plateau that ends at the Cotswold escarpment. Its thickness increases from 15 metres in the south-east to over 100 metres at Cleeve Hill in the north-west. The Great Oolite Group forms a broad tract trending from west-south-west to east-north-east across the research area, with scattered outliers to the north. It forms the dip-slope side of the Cotswold escarpment to the south-east. The thickness of the Great Oolite Group increases from about 60 m in the east to about 100 m in the west. The Fullers Earth Formation, a mudstone with thin limestone beds, separates the Great and Inferior Oolite. Its thickness varies from less than 10 m in the north-east to over 30 m in the south-west of the area, but can be locally absent.

Both the Inferior and Great Oolite have been used extensively for building material and many villages within the region have been built from the honey coloured limestone rock (Figure 2-3). Nowadays, 'acid rain' threatens some of the older buildings by dissolving the carbonate rock.

The overlying Upper Jurassic sediments mark the establishment of relatively quiet offshore conditions (Horton & Cornwell, 1982). At the base, the Kellaways Clay is a grey mudstone. It is overlain by the Kellaways Sands, a fine-grained, silty sand with interbedded mudstone horizons. This is followed by a thick sequence of mudstones of the Oxford Clay Formation, which accumulated in an open, fully marine environment.

The study area is free of drift deposits with recent deposits comprising river terraces and floodplain deposits along all principal rivers and streams.

In general, the Jurassic rocks in the study area dip in a predominantly south to south-easterly direction at angles between 0.5 and 1.5°. Locally, however, faults have distorted the geological succession. Predominant fault trends in the area are north to south and west-north-west to east-south-east. Throws are reported to be up to 50 m.

Age	Lithostratigraphy	Rock type	Thickness	
ry T	Alluvium; Peat; Tufa; Head variable limestone gravel, loam and clay		up to 2m	
River Terrace Deposits		mainly limestone gravel	up to 6m	
	Oxford Clay Formation	grey mudstone	up to 30 m	
	Kellaways Formation	grey mudstone overlain by fine-grained sand	10 to 13 m	
	Great Oolite Group:			
	Cornbrash Formation	rubbly, shell-detrital limestone	3 to 4.5 m	
fiddle Jurassic	Forest Marble Formation	mudstone with beds of shell-detrital, ooidal limestone	10 to 30 m	
	White Limestone Formation (passes westwards into the Athelstan Oolite Formation)	limestone with clay beds	15 to 39 m	
	Hampen Formation (passes westwards into the Dodington Ash Rock Formation)	sandy and ooidal limestone with clay and marl beds	4 to 11 m	
	Taynton Limestone Formation	shell-detrital, ooidal limestone	0 to 11 m	
2	Fuller's Earth Formation	grey mudstone with limestone beds	0 to 41 m	
	Chipping Norton Limestone Fm	sandy, ooidal limestone	0 to 6 m	
	Inferior Oolite Group:			
	Salperton Limestone Formation	shelly, ooidal limestone	7 to 21 m	
	Aston Limestone Formation	shelly, sandy limestone	0 to 21 m	
	Birdlip Limestone Formation	ooidal, sometimes sandy limestone with sandy clay layers	0 to 90 m	
	Lias Group:			
sic	Bridport Sand Formation	sandy mudstone and fine-grained sandstone	0 to 10 m	
rase	Whitby Mudstone Formation	mudstone with limestone beds at base	12 to 98 m	
Ju	Marlstone Rock Formation	ferruginous, ooidal limestone and sandstone	0 to 5 m	
wer	Dyrham Formation	silty mudstone and siltstone	15 to 54 m	
Lo	Charmouth Mudstone Formation	mudstone with thin beds and nodules of limestone	120 to 284 m	
	Blue Lias Formation	mudstone with thin beds of limestone	8 to 58 m	

## Table 3.1Geological succession of the Jurassic in the study area (after Sumbler et al. 2000)



Figure 3-3 Geological map of the Cotswolds study area with location of main pumping stations and spring sources.



#### Figure 3-4 Cross section through the geological sequence from NNW to SSE.

#### 3.3 Hydrogeology

The hydrogeology and aquifer properties of the area have been described by Allen et al. (1997) and the reader is referred to this text for a more detailed description. In the study area, two relatively thick aquifers occur: the Inferior Oolite aquifer and the Great Oolite aquifer. Towards the north, these are exposed and unconfined. However, the south-east dip of the strata results in confinement of the aquifers beneath younger formations in the south. Where the Great and Inferior Oolite are separated by the Fuller's Earth, a clay formation acting as an aquiclude, they are essentially separate aquifer systems, with the underlying Inferior Oolite being confined. The separation is most effective in the west, where the formation is at its thickest, while it is of variable efficiency towards the north-east where the mudstones thin out. In areas where the Fuller's Earth is absent, the two aquifers are in direct hydraulic contact. Faulting occurs in the study area, resulting in the Inferior and Great Oolite being locally connected hydraulically.

The Inferior Oolite aquifer comprises mainly limestones of the Inferior Oolite Group. Additionally, the Bridport Sand Formation of the Lias Group, as well as the Chipping Norton Limestone at the base of the overlying Great Oolite Group in the north-eastern part of the area is in hydraulic continuity and considered part of the Inferior Oolite aquifer (Allen et al., 1997). Transmissivities obtained from pumping tests vary greatly from 3 to 11 000 m<sup>2</sup>/d with a geometric mean of 139 m<sup>2</sup>/day. Hydraulic conductivities obtained from core analysis range from 2.6x10<sup>-6</sup> m/d to 0.5m/d with a geometric mean of  $5x10^{-4}$ m/d. The bulk of porosity values vary between 12 to 24% (Allen et al., 1997). Pumping test results suggest storage coefficients to be between  $7x10^{-5}$  and  $1x10^{-4}$  for the confined aquifer and around  $8x10^{-2}$  for the unconfined aquifer (Allen et al., 1997).

The Great Oolite aquifer comprises limestones of the Great Oolite Group. These limestones are brittle and fractured and contain numerous fissured horizons (Figure 3-5). The fissures provide preferential pathways of high transmissivity but low storage, resulting in a very rapid response of water levels in the aquifer to recharge events. Morgan-Jones and Eggboro (1981) quote transmissivities of  $1500 \text{ m}^2\text{d}^{-1}$  and a storage coefficient of  $1.3 \times 10^{-4}$ . Rushton et al. (1992) gave a range of transmissivities between 300 to  $1500 \text{ m}^2\text{d}^{-1}$  and a storage coefficient varying between  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$ . Core analysis on 96 samples from three locations in the Great Oolite indicated a mean hydraulic conductivity of  $9.8 \times 10^{-5} \text{ m/d}$  (Allen et al., 1997).

Both aquifers are characterised by low intergranular permeability and low storage potential. Groundwater flow predominantly takes place along preferential flowpaths such as fissures, faults and fracture zones. Geophysical logging in a number of boreholes in the confined Inferior Oolite showed that zones of groundwater flow were not necessarily related to stratigraphy, but that structural features were an important influencing factor (Morgan-Jones & Eggboro, 1981).



#### Figure 3-5 Well developed fractures and fissures in a Great Oolite limestone road cutting on A417 [SP 0162 0522]

The aquifers offer large areas for recharge, being exposed over a wide region. The Inferior Oolite is additionally recharged by seepage from the Great Oolite Group across the Fuller's Earth Formation and by downward flow along fractures and faults. Morgan-Jones and Eggboro (1981) estimated recharge to be 370 mm  $a^{-1}$  for the limestone aquifers, whereas Rushton et al. (1992) gave a figure of 380 mm  $a^{-1}$ .

Numerous spring lines are present in the study area. Along the Cotswold escarpment, several springs issue at the base of the Inferior Oolite aquifer. These discharge at the junction with the underlying impermeable clays of the Upper Lias. A second spring line forms at the junction between the Great Oolite aquifer and the Fuller's Earth Formation on the dip slope plateau. Other springs may be associated with hardbands within the aquifer or are structurally controlled. Many springs have an intermittent character, depending on the time of year and water levels in the aquifer (Boak and Grapes, 1996).

The groundwater piezometric surface has a generally south-easterly dip, following that of the geological formations. The piezometric contours in the Great Oolite aquifer are locally up to several

tens of meters higher than those in the Inferior Oolite and exhibit large seasonal changes. They are generally much more uniform than those in the Inferior Oolite aquifer, as the land surface formed by the Great Oolite limestone is less dissected by valleys (Boak and Grapes, 1996). Groundwater flow is locally controlled by topography with the deeply incised valleys having a strong influence on hydraulic gradients, especially in the Inferior Oolite. Maximum groundwater levels depend on the elevation of springs in valleys, so that some boreholes in the area display flat-topped hydrographs (Sumbler et al., 2000). An example for a flat-bottomed well hydrograph is shown in Figure 3-6 and caused by the aquifer draining to its base during the summer months. A well hydrograph for the Inferior Oolite is shown in Figure 3-7.



Figure 3-6 Typical flat-bottomed well hydrograph in the unconfined Great Oolite aquifer. Sheep Farm Observation Borehole [SP 0564 0548]



Figure 3-7 Well hydrograph in the Inferior Oolite aquifer. Edge Observation Borehole [SO 8490 0970]

A conceptual model of the groundwater regime in the study area is shown in Figure 3-8, while a hydrogeological map showing sampling points and groundwater contours is presented in Figure 3-10. Within the groundwater regime, three distinct subdivisions may be identified:

Zone 1: In the north-north-west the Inferior and Great Oolite are unconfined and direct recharge from precipitation is occurring. Groundwater flows generally north west and south east from either side of the groundwater divide. The groundwater flowing to the north west discharges via springs rising at the junction of the underlying Lias Clays. Most of the groundwater flowing to the south discharges via springs controlled by hardgrounds, faults or the Lias Clays exposed within deeply incised valleys. Some groundwater flow recharges the confined aquifer to the south. Groundwater in these unconfined aquifers tends to have a relatively short residence time.

Zone 2: Further towards the south, the limestone aquifers are confined and recharge to the Great Oolite aquifer through the overlying younger low permeability deposits is minimal. The Inferior Oolite receives small amounts of recharge via the Great Oolite aquifer. Residence times of groundwater are prolonged with some groundwater recharging the deeper confined parts of the aquifer and some groundwater discharging via spring sources along river valleys or fault zones.

Zone 3: Where the Inferior and Great Oolite limestone aquifers are deeply confined in the southsouth-east, recharge is minimal. Groundwater residence times are prolonged and flow occurs to deeper confined parts of the aquifer and possibly by upward leakage to overlying formations. Mixing with old formation water is proposed just under the edge of the Oxford Clay. On a regional scale this mixing zone coincides with a hydraulic low proposed by Alexander & Andrews (1984), to which water is drawn from the north as seen in the study area but also from the south. Water flowing from the south originates from the elevated Cretaceous aquifers on the northern flank of the London Basin syncline and moves up-dip under artesian conditions (Figure 3-9).

Both aquifers are moderately used for public and private water supplies. There are five major public water supply abstractions in the study area. These are Ashton Keynes [SU 042 941], Latton [SU 081 968], Meysey Hampton [SU 1130 9880], Baunton [SP 0195 0484] and Bibury [SP 1123 0712] and they abstract from the confined portions of both the Inferior and Great Oolite aquifers (Figure 3.3). It has been found, that these abstractions have a significant effect on river flows, especially the main Inferior Oolite water supply sources can cause a reduction in river flows (Allen et al., 1997). Within the unconfined aquifer, spring sources are used for public water supply, with the most important sources being Chalford [SO 8915 0243], Cleeve Hill [SP 0064 2638], Northfield [SO 9844 2217], Stanton [SP 0752 3392], Stanway [SP 0745 3237] and Winchcombe [SP 0375 2785] (Figure 3.3). There are a number of smaller public water supply abstractions as well as a significant number of domestic, industrial and farm supplies in the oolite aquifers.

Where boreholes penetrate the Great and Inferior Oolite, they are not permitted by the Environment Agency to connect the two aquifers hydraulically and have to be constructed accordingly (Sumbler et al. 2000). However, artificial discharge via boreholes only accounts for a small proportion of the total discharge from the aquifer. Most discharge takes place via springs located at the top and bottom of the aquifers, at the junctions with the overlying and underlying aquitards.







Figure 3-9 Groundwater movement in the study area and towards the SSE (after Alexander and Andrews, 1984)



Figure 3-10 Hydrogeological map of the Cotswolds study area with sampling points and groundwater contours

#### **BOX 3-1 GROUNDWATER VULNERABILITY**

The Cotswold aquifers are highly vulnerable to contamination from human activities associated with agricultural practices, urbanisation, industrial processes, disposal of wastes and spillage of chemicals such as solvents and fuel oils.

The vulnerability of an aquifer can be assessed from the nature and thickness of the unsaturated zone and overlying deposits (soil and drift), the depth of the water table and the speed with which water flows through this zone. The Environment Agency has therefore prepared groundwater vulnerability maps covering the UK (Refer to Policy and Practice for the Protection of Groundwater, 1998 for more detailed information). These maps utilise soil property information to predict leaching characteristics of the soil. The soil leaching information is combined with the aquifer classification to provide an overall assessment of vulnerability. Planning authorities, consultants, water companies, waste management companies and industry use these maps to help them assess groundwater vulnerability. They are also useful for emergency planning especially where chemical spillages have occurred.

The Cotswold aquifers are classified with a high risk vulnerability, designated as purple on the map below, because the overlying soils have little ability to attenuate pollutants. The Great and Inferior limestones also contain fissures and fractures, which provide pollutant with a fast pathway into the saturated zone. This combined with a shallow water table and a thin soil cover makes the aquifer highly susceptible to pollution.



#### **3.4** Aquifer mineralogy

The Upper Lias Formation is characterized by bluish-grey mudstones. These are succeeded by the Bridport Sand Formation, previously known as the Cotteswold Sands. This formation is a yellowish micaceous fine grained sand or silt, weakly cemented by calcite. The formation is succeeded by the Inferior Oolite Group, which in its basal unit comprises grey, rubbly, ferruginous, sandy, argillaceous, shelly ooidal limestone with thin marl beds. It resembles, at outcrop, the Bridport Sand, as it weathers and decalcifies to a yellow and reddish sand. The Inferior Oolite Limestone is made up predominantly of ooidal and shell-detrital limestones, with thin mudstones, marl and sandstone beds. Some beds are appreciably sandy and in parts ferruginous.

The Inferior Oolite is succeeded by the Fuller's Earth Formation throughout the study area, except where the Chipping Norton Limestone is developed in the north-east. The Fuller's Earth is dominated by grey mudstones of marine origin, but contains sporadic thin beds and lenses of calcareous sandstone or sandy limestone. The clay fractions of the Fuller's Earth contain up to 90% smectite. The Chipping Norton Limestone is characterized by a pale yellowish, medium- to fine-grained, well-sorted ooidal limestone.

The overlying part of the Great Oolite Group is made up largely of marine carbonate rocks. A study into the mineralogy of the Great Oolite limestones was carried out by Milodowski & George (1985) at the Harwell research site just to the south of Oxford. Petrographic studies were conducted using scanning electron microscopy (SEM) and thin section optical petrography (Figure 3-11 to Figure 3-13). It was found, that the mineralogy of the Great Oolite limestones are dominated by calcite but detrital quartz, clay minerals and pyrite may be found in some rocks. In its upper parts, within the Forest Marble Formation (Figure 3-13), substantial units of mudstones are present. They are generally greenish grey with calcareous concretions. The clay mineralogy is dominated by illite and kaolinite, although minor chlorite is also present (Milodowski & George, 1985). Throughout the Great Oolite limestones, pyrite is common, especially within clay-rich matrix, but may also occur within ooids and other carbonate detritus (Figure 3-11). The Great Oolite Group is overlain by the Kellaways and Oxford Clay formations, thick mainly clayey formations with scattered traces of pyrite.



Figure 3-11 Backscattered scanning electron microscope image of a typical well-cemented oolitic grainstone from the White Limestone Formation (Great Oolite Group). The calcitic grains are tightly cemented by weakly ferroan calcite (light grey). No significant matrix porosity is visible. [Taken from Milodowski and George, 1985, Harwell Borehole No. 3, 362.4 m].



Figure 3-12 Backscattered scanning electron microscope image of a very porous oolitic grainstone from the Taynton Stone Formation (Great Oolite Group). The grains are composed of calcite but they are coated with a tangential film of illitic or illite-smectite mixed-layer clay. The intergranular pores are lined by weakly ferroan calcite. Very fine pyrite (white) is present within the oolitic grains but is largely isolated from contact with groundwater flowing through the intergranular pores. [Taken from Milodowski and George, 1985, Harwell Borehole No. 3, 378.6 m].



Figure 3-13 Backscattered scanning electron microscope image of a rock sample from the Forest Marble Formation (Great Oolite Group). It comprises sub-rounded worn shell fragments composed of calcite (grey) with a matrix of fine microporous micritic calcite. Fine grained authigenic pyrite (white) is disseminated within the microporous matric. [Taken from Milodowski and George, 1985, Harwell Borehole No. 3, 342.7 m].

#### 3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharge waters and should be considered as representing minimum baseline concentrations. The median rainfall chemistry for 1993 to 2001 for Wytham precipitation station [SP 459 094] and for 1993 to 1998 for Drayton station [SP 162 551] is shown in Table 3.2. The data have been multiplied by 3 in the last column in order to estimate the approximate enrichment due to evaporation. Although Cl may be assumed to behave conservatively during most recharge conditions, this is not the case for other elements e.g. K and N-species which may be taken up by vegetation, and concentrations may therefore be less in recharge waters than rainfall. Nevertheless, the table indicates the order of magnitude of concentrations expected in young waters, which have not reacted with vegetation, soils or aquifer minerals.

		Wytham		Dra	yton
Parameters	Units	Median rainfall	Median rainfall	Median rainfall	Median rainfall
			(x3)		(x3)
pН		4.86		5.80	
Na	mg l <sup>-1</sup>	0.76	2.28	1.09	3.27
K	mg l <sup>-1</sup>	0.06	0.18	0.20	0.60
Ca	mg l <sup>-1</sup>	0.51	1.53	0.63	1.89
Mg	mg l <sup>-1</sup>	0.12	0.36	0.16	0.48
Cl	mg l <sup>-1</sup>	1.80	5.40	1.70	5.10
$SO_4$	mg l <sup>-1</sup>	0.68	2.04	0.90	2.70
NO <sub>3</sub> -N	mg l <sup>-1</sup>	0.34	1.02	0.43	1.29
NH <sub>4</sub> -N	mg l <sup>-1</sup>	0.49	1.47	0.83	2.49
SEC	$\mu S cm^{-1}$	23.9	71.7	29.5	88.5

Table 3.2Rainfall chemistry from Wytham and Drayton (data obtained from Centre of<br/>Ecology and Hydrology, Environment Change website)

#### 3.6 Landuse

Arable farming is the dominant land use on the unconfined aquifers but some minor areas of managed grassland are also present. Cereals and oilseed rape are the main cultivated crops whilst steeper slopes are often under permanent grass and valley floors under meadow for sheep and cattle grazing (LEAP, 2000). The area is mainly rural with the larger urban areas of Gloucester and Cheltenham found to the north west. Smaller villages are found throughout the region, including Cirencester, Broadway, Stanton and Bourton-On-The-Water (Figure 3-14).

Numerous quarries exist in the Cotswolds where the limestone is still excavated for building material. Additionally, river gravel extraction takes place in the water meadows of the Thames Valley in the south of the study area. Groundwater levels are generally shallow and the majority of extractions are facilitated by abstraction from shallow boreholes to lower the water table locally. On completion and with the cessation of abstraction, these gravel pits fill with water. The most extensive man-made lake area in the Cotswolds is the Cotswolds Water Park (SU 0488 9529), covering some 19 km<sup>2</sup> with 132 lakes, to the south-east of Cirencester.



The grid on this map is the National Grid taken from the Ordnance Survey with permission of the Controller H.M.S.O

Figure 3-14 Generalised landuse map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology © NERC.

#### **BOX 3-2 SPRINGS OF THE COTSWOLDS**

Many of the villages and settlements in the Cotswolds owe their origin not only to the geology of the area, but also to the hydrogeological setting of their location. A reliable, good quality water source was always sought and many settlements were founded in close proximity to spring and river sources not only for drinking, washing and cooking but also for water power and industrial use. The Saxons preferred to site settlements above springs on drier land whereas the Romans constructed villas below so that spring waters would feed into their baths and washhouses by gravity. So the origin of the settlements today is a direct result of our ancestors.

Compton Abdale near the town of Northleach (SP 0605 1657), still has a particularly reliable perennial spring where copious water issues from a crocodile mouth carved from the Great Oolite Limestone and flows into the nearby River Coln.

There many 'dry valleys' are or 'Winterbournes' in the Cotswolds that are without rivers and streams and yet further down the valley slope there is a gushing stream issuing from a spring. During periods of high rainfall in the winter, springs can re-emerge up slope in the valleys and streams start to flow once again as groundwater levels rise. Dry valleys are relic features from the end of the last Ice Age when the climate was much wetter with higher rainfall producing a much higher water table and hence springs flowed from the head of the valley. Today, the water table is much lower, causing springs to emerge much further down slope. They do however, still fluctuate with rainfall particularly in the winter months.



**Compton Abdale Spring** 'Reproduced with the permission of the UK Groundwater Forum'

## 4. DATA AND INTERPRETATION

#### 4.1 **Project sampling programme**

A total of 29 samples were collected during November 2001 and March 2002 from private supplies and Severn Trent Water spring supplies situated between Broadway in the North and Cricklade in the South (Figure 3-10). The sampling points were chosen to provide a good regional coverage of the Great and Inferior Oolite aquifers along the general groundwater flow direction incorporating the spring line along the escarpment and the groundwaters from both the unconfined and confined parts of the aquifers in the central and southern parts of the area. Information on the aquifer being tapped was available for all sampled boreholes. However, no details of screened intervals were known. The majority of samples were from the Inferior and Great Oolite outcrop area, including 16 spring samples. Eight sample sources were obtained from the confined aquifers.

Boreholes were pumped prior to sampling in order to flush at least three borehole volumes. Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured on site in a flow-through cell. Additionally, temperature, electrical conductivity (SEC) and alkalinity were measured on-site. On site measurements are necessary for the above mentioned determinants, as their concentration might undergo changes once the groundwater sample is brought to the surface. For example degassing of  $CO_2$  may occur, causing changes in pH and alkalinity. Samples were filtered through 0.45 µm filters and collected for major- and minor-ion chemistry in polyethylene bottles. Samples for major cations and SO<sub>4</sub> were acidified to 1% v/v HNO<sub>3</sub>. In addition, eight samples were collected in glass bottles for analysis of the isotopes  $\delta^{18}O$ ,  $\delta^{2}H$  and  $\delta^{13}C$ .

Analysis of major ions, Fe, Mn and isotopes was undertaken by BGS, while nitrogen species were analysed at the Environment Agency laboratories in Nottingham. The remaining minor ions were analysed at ACME, Analytical Laboratories Ltd., Canada.

#### 4.2 Historical data

The longest digital records of water chemistry data in the study area are from the Severn Trent Water public supply sources at Stanton [SP 0752 3392], Northfield [SO 9844 2217] and Cleeve Hill [SP 0064 2638], which date from 1974. Data exist for these sites for  $NO_3$ -N, Cl,  $SO_4$  and other major-ion concentrations.

In the Thames Region in the Environment Agency, digital data exist as far back as 1985. An exception is Old Chalford [SP 3445 2544], a public water supply source just to the east of the study area, monitored regularly by Thames Water since 1976.

In 1978, Morgan-Jones and Eggboro (1981) collected 77 spring and borehole samples across the Inferior and Great Oolite aquifers between Cheltenham in the north-west and Lechlade in the southeast. This study was duplicated and extended in 1986 to deduce whether significant water quality changes had occurred at individual sources over the intervening eight years. Both data sets provide a regional comparison of changes in the overall geochemistry over the last two decades.

#### 4.3 Data handling

The data used in the study include all that collected from the sampling programme carried out during this project and 16 analyses from privately owned abstraction boreholes and springs supplied by the Environment Agency (Thames Region and Midlands Region), as well as six spring sources owned by Severn Trent Water plc. Where duplicate sets of data were available for given sites, BGS analyses were used in preference because of the larger number of analysed determinands and the lower detection limit for trace elements. Throughout the report, plots or tables showing the distribution or
concentration of major ions were based on all data available, while plots or tables showing minor ions or field parameters have been generated using the data from the new sampling programme only, as it offers lower detections limits. Where data were below the detection limit of analysis, a concentration equal to half the detection limit has been substituted for statistical purposes. Where chemical data were examined on the basis of their location along a flowline, the distance used was calculated by setting the limestone escarpment in the north to zero metres and referencing all subsequent sample locations accordingly.

# 5. HYDROCHEMICAL CHARACTERISTICS

# 5.1 Introduction

Summary statistics for major and minor ion concentrations are given in Table 5.1 and Table 5.2. Median, mean, minimum and maximum concentrations are given. The major-ion data are presented graphically on a Piper plot (Figure 5-1), boxplots (Figure 5-2) and cumulative frequency plots (Figure 5-3). The boxplots display the ranges of data and are designed to highlight the distribution of data on a percentile basis (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 within the box and the mean as a blue line. The solid black line on the graph represents a diluted seawater curve, which has been normalised to the median Cl concentration of the samples. This provides a general indication of a more saline formation water. Cumulative probability plots are useful in visualising the distribution of data and may be of use in determining outlying data or discriminating pollution.



i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.

ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.

iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).

iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO3 by in situ denitrification).

v) A narrow range in concentration at the upper limit may indicate a mineral solubility control (e.g. F by fluorite)

vi) A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of natural higher salinity.

	Units	Min	Max	Median	Mean	97.7th	Ν
Temp.	°C	5.20	11.7	10.0	9.80	11.5	43
рН		6.40	8.00	7.20	7.18	7.86	43
Redox- potential	mV	234	474	377	375	460	29
Diss. Oxygen	mg l <sup>-1</sup>	0.00	10.8	8.90	7.16	10.7	29
SEC	$\mu S \text{ cm}^{-1}$	290	1508	534	524	726	42
δ²H	‰	-51.6	-46.9	-49.6	-49.2	-47.0	8
δ <sup>18</sup> Ο	‰	-7.71	-7.12	-7.44	-7.43	-7.13	8
δ <sup>13</sup> C	‰	-15.6	-5.68	-13.2	-12.4	-6.40	8
Ca	mg l <sup>-1</sup>	14.4	138	96.9	93.3	122	50
Mg	mg l <sup>-1</sup>	1.80	14.2	4.71	5.12	13.5	50
Na	mg l <sup>-1</sup>	4.00	345	7.45	18.0	110	50
К	mg l <sup>-1</sup>	0.20	7.60	1.10	1.44	4.05	50
Cl	mg l <sup>-1</sup>	7.90	286	16.2	23.2	50.7	50
SO <sub>4</sub>	mg l <sup>-1</sup>	19.1	79.4	33.3	35.7	67.9	50
HCO <sub>3</sub>	mg l <sup>-1</sup>	128	400	242	239	331	50
NO <sub>3</sub> -N	mg l <sup>-1</sup>	< 0.004	18.2	8.16	8.27	16.8	50
NO <sub>2</sub> -N	mg l <sup>-1</sup>	< 0.002	0.02	< 0.002	< 0.002	0.01	43
NH <sub>4</sub> -N	mg l <sup>-1</sup>	< 0.004	0.61	< 0.004	0.03	0.26	43
Р	mg l <sup>-1</sup>	< 0.02	0.12	0.02	0.02	0.1	42
ТОС	mg l <sup>-1</sup>	<1.00	2.19	0.85	1.08	2.12	20
DOC	mg l <sup>-1</sup>	<1.00	5.40	2.10	2.52	5.21	29
F	μg l <sup>-1</sup>	<50.0	4800	90.0	253	926	49
Br	μg l <sup>-1</sup>	19.0	1595	65.5	115	580	34
Ι	μg l <sup>-1</sup>	<1.00	148	6.00	18.6	122	29
Si	μg l <sup>-1</sup>	1100	4930	1950	2290	4190	29

Table 5.1Field parameters, isotope data and range of major and minor element<br/>concentrations in groundwaters of the Great and Inferior Oolite in the<br/>Cotswolds

	Units	Min	Max	Median	Mean	97.7th	Ν
Ag	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29
Al	μg l <sup>-1</sup>	<1.00	26.0	1.00	2.21	13.1	29
As	μg l <sup>-1</sup>	<1.00	1.00	<1.00	<1.00	1.00	29
Au	μg l <sup>-1</sup>	< 0.05	0.17	< 0.05	< 0.05	0.14	29
В	μg l <sup>-1</sup>	<20.0	1467	23.0	89.7	728	29
Ba	μg l <sup>-1</sup>	3.46	14.0	8.20	8.36	13.8	29
Be	μg l <sup>-1</sup>	< 0.05	0.11	< 0.05	< 0.05	0.08	29
Bi	μg l <sup>-1</sup>	< 0.05	0.15	< 0.05	< 0.05	0.10	29
Cd	μg l <sup>-1</sup>	< 0.05	0.07	< 0.05	< 0.05	0.06	29
Ce	μg l <sup>-1</sup>	< 0.01	0.15	0.01	0.01	0.10	29
Со	μg l <sup>-1</sup>	< 0.01	0.10	0.03	0.03	0.09	29
Cr	μg l <sup>-1</sup>	< 0.50	0.50	< 0.50	< 0.50	0.50	29
Cs	μg 1 <sup>-1</sup>	< 0.01	0.02	0.01	0.01	0.01	29
Cu	μg 1 <sup>-1</sup>	0.10	115	1.00	7.01	62.8	29
Dy	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Er	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Eu	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Fe	μg l <sup>-1</sup>	< 5.00	1260	23.0	109	1144	29
Ga	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29
Gd	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Ge	μg l <sup>-1</sup>	< 0.05	0.07	< 0.05	< 0.05	< 0.05	29
Hf	μg l <sup>-1</sup>	< 0.02	0.03	< 0.02	< 0.02	0.02	29
Hg	μg Γ΄	< 0.10	0.20	< 0.10	< 0.10	0.20	29
Ho	μg Ι <sup>-1</sup>	< 0.01	< 0.01	<0.01	< 0.01	< 0.01	29
ln	μg Ι <sup>-1</sup>	< 0.01	< 0.01	< 0.01	<0.01	< 0.01	29
lr •	μg Γ'	< 0.05	< 0.05	<0.05	< 0.05	< 0.05	29
La	μg Ι '	< 0.01	0.03	0.01	0.01	0.02	29
L1 1	μg Ι <sup>-</sup>	<4.00	48.0	<4.00	5.62	50.0 <0.01	29
Lu M	μg I	< 0.01	< 0.01	< 2.00	< 2.00	12.0	29
NIN Ma	μg 1	<2.00	180	<2.00 0.10	<2.00 0.27	12.9	29
NIO Nh	μg 1	<0.10	0.02	0.01	0.01	0.01	29
Nd	μg 1	<0.01	0.02	0.01	0.01	0.01	29
Ni	μg 1 μg 1 <sup>-1</sup>	<0.01	7 30	<0.01	0.36	2 73	29
Os	μg 1 <sup>-1</sup>	<0.20	<0.05	<0.20	<0.05	<0.05	29
Ph	μg 1 <sup>-1</sup>	<0.10	5 40	0.10	0.69	5.21	29
Pd	µg 1 <sup>-1</sup>	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	29
Pr	ug 1 <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Pt	ug 1 <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Rb	μg l <sup>-1</sup>	0.15	2.39	0.55	0.71	2.05	29
Re	ug 1 <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Rh	$\mu g l^{-1}$	< 0.01	0.02	0.01	0.01	0.02	29
Ru	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29
Sb	μg l <sup>-1</sup>	< 0.05	0.08	< 0.05	< 0.05	0.07	29
Sc	μg l <sup>-1</sup>	0.75	5.94	1.41	1.86	5.79	29
Se	μg l <sup>-1</sup>	0.50	9.80	1.00	1.23	4.26	29
Sm	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29
Sn	μg l <sup>-1</sup>	< 0.05	0.67	0.08	0.13	0.55	29
Sr	μg l <sup>-1</sup>	128	659	213	272	573	29
Та	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29
Tb	$\mu g l^{-1}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Те	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29
Th	μg l <sup>-1</sup>	< 0.05	0.11	0.03	0.03	0.10	29
Ti	μg l <sup>-1</sup>	<10.0	<10.0	<10.0	<10.0	<10.0	29
Tl	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Tm	μg l <sup>-1</sup> .	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
U	μg 1 <sup>-1</sup> .	< 0.05	1.70	0.30	0.35	1.02	29
V	μg l <sup>-1</sup>	<1.00	5.00	0.50	0.88	4.36	29
W	μg l <sup>-1</sup> .	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	29
Y	μg l <sup>-1</sup> .	< 0.01	0.03	0.01	0.01	0.02	29
Yb	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	29
Zn	μg l <sup>-1</sup>	< 0.50	133	47.2	41.6	108	29
Zr	μg l <sup>-1</sup>	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	29

Table 5.2Trace element concentrations in groundwaters of the Great and Inferior Oolite<br/>in the Cotswolds

#### 5.2 Water types and physicochemical characteristics

Groundwaters of three different types have been sampled: (i) unconfined aquifer – spring sources, (ii) unconfined aquifer – borehole sources, (iii) confined aquifer – boreholes sources. Summary statistics of their major-ion chemistry are given in Table 5.3. Spring waters and groundwaters derived from boreholes in the unconfined aquifers are fresh with temperatures generally between 9 and 12°C and are well buffered with a median pH of 7.0. The median concentration of dissolved oxygen in spring waters is 9.6 mg l<sup>-1</sup> and the redox potential is high, indicating oxidizing conditions. The electrical conductivity (SEC) is comparatively low with a median concentration of 498  $\mu$ S cm<sup>-1</sup>. Groundwater derived from boreholes in the unconfined aquifers show enhanced mineralisation (median SEC of 618  $\mu$ S cm<sup>-1</sup>) and lower dissolved oxygen concentrations and redox potentials (median of 5.7 mg l<sup>-1</sup> and 342 mV respectively), indicating oxidising to weakly reducing conditions. Bicarbonate is the dominant anion in all these waters and the Piper diagram reveals that the spring waters and unconfined groundwaters derived from borehole sources are of Ca-HCO<sub>3</sub> type.

Where the limestone aquifers become increasingly confined, the groundwater changes to a Na-HCO<sub>3</sub> type water. Mineralisation increases and SEC reaches 1508  $\mu$ S cm<sup>-1</sup>. Dissolved oxygen concentration is generally low and Eh values decrease to a minimum of 234 mV, indicating slightly more reducing conditions. One sample from deep within the confined Great Oolite aquifer shows elevated Na and Cl concentrations and a shift towards a Na-Cl-HCO<sub>3</sub> type water.

		Confiı (Boreh	ied groundv ole sources,	vaters N = 8)	Unconfi (Boreh	ned ground	lwaters N = 5)	Unconfined groundwaters (Spring sources, N =16)			
		Median	Min	Max	Median	Min	Max	Median	Min	Max	
Eh	mV	318	234	377	342	308	371	424	328	474	
DO	mg l <sup>-1</sup>	5.50	0.00	7.50	5.70	0.70	7.80	9.59	6.1	10.8	
SEC	$\mu S cm^{-1}$	602	573	1508	618	445	679	498	386	608	
Ca	mg l <sup>-1</sup>	98.1	14.4	117	115	82.6	138	93.8	63.9	119	
Mg	mg l <sup>-1</sup>	9.35	5.03	14.2	7.27	4.88	10.1	2.94	2.18	7.57	
Na	mg l <sup>-1</sup>	17.4	7.70	345	7.80	7.3	8.6	6.25	4.2	17.2	
Κ	mg l <sup>-1</sup>	2.05	1.30	7.60	1.70	1.3	2.8	0.95	0.25	2.8	
Cl	mg l <sup>-1</sup>	18.1	14.0	286	13.2	11.7	16.4	14.8	7.9	38.2	
$SO_4$	mg l <sup>-1</sup>	49.4	25.3	79.4	42.0	32.9	63.2	28.8	19.1	46.2	
HCO <sub>3</sub>	mg l <sup>-1</sup>	315	288	400	289	248	316	184	141	282	
NO <sub>3</sub> -N	mg l <sup>-1</sup>	0.10	< 0.003	9.79	8.19	1.28	11.8	10.7	4.32	16.8	
Si	μg 1 <sup>-1</sup>	2937	1439	4926	2710	1474	3342	1763	1101	3372	

Table 5.3Summary statistics of major ion concentrations in confined and unconfined<br/>groundwaters and spring sources of the Great and Inferior Oolite of the<br/>Cotswolds (based on the sampling programme carried out during this study<br/>only)

From the groundwater chemistry, there is no evidence, that changes in the geological nature of the aquifers themselves influence the concentration of major and minor ions significantly, hence no major differences in the chemistry between the Great and Inferior Oolite groundwaters can be observed. Table 5.4, based on BGS analyses, summarises median concentrations of some major and minor ions for the Inferior and Great Oolite for comparison. The Great Oolite groundwaters are slightly more enriched in Mg and  $SO_4$  compared to the Inferior Oolite waters, however in general the major ion chemistry is similar in both aquifers. Variations in chemistry appear instead to be related to the aquifer confinement. This also accounts for the minor ion concentrations, with differences pronounced between confined and unconfined sources but no significant differences between the Great and Inferior Oolite aquifers.

Table 5.4Comparison between median major and minor ion concentrations in<br/>groundwaters of the Great and Inferior Oolite aquifers of the Cotswolds (based<br/>on the sampling programme carried out during this study only)

		DO	Ca	Mg	Na	K	Cl	<b>SO4</b>	NO <sub>3</sub> as	F	Br	Si	Ba	Fe	Rb	Sr	U	Zn
		mg l <sup>-1</sup>	mg l⁻¹	mg l <sup>-1</sup>	mg l <sup>-1</sup>	mg l⁻¹	mg l <sup>-1</sup>	mg l <sup>-1</sup>	N mg l <sup>-1</sup>	μg Ι <sup>-1</sup>	μg l <sup>-1</sup>	μg Ι <sup>-1</sup>	μg l⁻¹	μg l <sup>-1</sup>	μg Γ¹	μg Γ <sup>1</sup>	μg l⁻¹	μg l⁻¹
	confined	5.7	98.5	12	16.4	2.1	17.4	63.9	0.03	470	94	3390	9.36	62	1.08	496	0.22	65.3
Great Oolite	unconf., BHs	5.7	115	7.27	7.8	1.7	13.2	42	8.2	150	71	2710	8.33	23	0.89	247	0.33	49.2
ound	unconf., spring	9.63	107	2.24	5	0.9	13.4	20.4	12.6	70	66	1465	7.98	2.5	0.44	184	0.27	0.25
	confined	5.4	97.6	6.3	18.4	1.6	18.8	41	0.18	440	100	2330	6.66	15	1.01	439	0.29	10.6
Inf. Oolite	unconf., BHs	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
	unconf., spring	9.48	83.4	3.53	6.5	1.1	15.5	35.4	9.45	80	63	1827	7.08	24	0.23	182	0.34	54.6

#### 5.3 Major elements

Major element concentrations are shown in boxplots in Figure 5-2. The median chloride concentration of 16.2 mg  $l^{-1}$  is about three times the concentration of the estimated bulk precipitation. All other major ions, except Na, plot above the diluted seawater curve, indicating that solutes have been accumulated in the groundwaters as a result of extensive water-rock interaction. All but NO<sub>3</sub>-N show a relatively narrow range of concentrations. The wide range of NO<sub>3</sub>-N concentrations reflects its redox-controlled occurrence and possibly variations in amount of pollution.

The majority of the cumulative frequency plots of the major ions show a relatively narrow range and some approach log-normal distribution with relatively steep gradients (Figure 5-3). For HCO<sub>3</sub> and Ca, the narrow ranges of concentrations shown in the cumulative frequency plots indicate saturation with calcite in groundwaters with the upper limit being controlled by carbonate mineral solubility.

Na and Cl concentrations are variable. The cumulative frequency plots indicate a positive skew within the upper 10 % of the data, particularly for Na, which reaches concentrations up to 345 mg  $l^{-1}$ , higher than the EC MPV (EC maximum permissible value for drinking water) of 150 mg  $l^{-1}$ .

The strong negative skew in the cumulative frequency plot for NO<sub>3</sub> indicates the presence of reducing waters and the removal of nitrate by in-situ denitrification. Additionally, old formation waters will exhibit low nitrate concentrations, being recharged before agricultural pollution occurred, while some groundwaters, e.g in woodland areas might be generally unaffected by agricultural pollution. The most notable break of slope occurs at approximately 6 mg  $l^{-1}$ . Many waters exhibit NO<sub>3</sub>-N concentrations above the EC MPV (maximum permissible value for drinking water) of 11.3 mg  $l^{-1}$ .



Figure 5-1 Piper plot showing the relative concentrations of major cations and anions in the limestone aquifers of the Cotswolds. (Blue = unconfined, spring sources; green = unconfined, borehole sources; red = confined)





Figure 5-2 Range of major and minor ion concentrations in the limestone aquifers in the Cotswolds. Black lines represent the element concentrations in diluted seawater at the median Cl concentration of the groundwater datasets.



Figure 5-3 Cumulative probability plots for groundwaters from the limestone aquifers in the Cotswolds

### 5.4 Minor and trace elements

Minor and trace element concentrations are shown in boxplots and cumulative frequency plots in Figure 5-2 and Figure 5-3. Most elements plot above the seawater line, determined using median Cl, indicating inputs through water-rock interaction. In general, the minor and trace elements show a wide range of concentrations and generally more complex distributions than the major elements.

The cumulative probability plots show a log-normal distribution for Ba and Si. Maximum concentrations for both remain below the EC MPV, with Ba up to 14.3  $\mu$ g l<sup>-1</sup> and Si up to 4926  $\mu$ g l<sup>-1</sup>. In contrast, B varies over a wide range of concentrations (up to 1467  $\mu$ g l<sup>-1</sup>) with a median value of 23  $\mu$ g l<sup>-1</sup>.

Iron also shows a broad range of concentrations (Figure 5-3). Many samples are below the detection limit, indicated by a vertical line at low concentrations, but concentrations may reach up to 1260  $\mu$ gl<sup>-1</sup>. Manganese remains below detection limit in most of the groundwaters, but concentrations reach up to 18  $\mu$ g l<sup>-1</sup>. Other redox-sensitive elements include NH<sub>4</sub> and NO<sub>2</sub> and these show a similarly wide range of concentrations, reflecting their redox-controlled occurrence. Ammonium as N reaches up to 0.6 mg l<sup>-1</sup>, exceeding the EC MP concentration of 0.5 mg l<sup>-1</sup> in one groundwater sample.

A positive skew in the upper 10 % to 20 % of the data is observed on the frequency probability plots for U, Sr, Al, B and F, with the latter reaching up to a maximum of 4800  $\mu$ g l<sup>-1</sup> in one analysis, hence exceeding the EC MP concentration of 1500  $\mu$ g l<sup>-1</sup>.

Concentrations of many trace metals are low under the neutral pH conditions and many samples show concentrations below the detection limit, indicated by the vertical line at low concentrations in the cumulative probability plots and less than values in Table 5.2. Median concentrations of Cd are  $< 0.025 \ \mu g \ l^{-1}$ , Al = 1  $\mu g \ l^{-1}$ , As  $< 0.5 \ \mu g \ l^{-1}$  and Pb = 0.1  $\mu g \ l^{-1}$ . Zinc concentrations vary over 3 orders of magnitude with maximum concentrations over 100  $\mu g \ l^{-1}$  and Co, Mo and Ni are locally high.

# 5.5 **Pollution indicators**

In order to determine baseline concentrations, it is desirable to study only pristine waters and to define and exclude polluted waters. Pollution may alter baseline concentrations, either directly, by adding solutes, or indirectly by promoting chemical reactions in the aquifer.

It is generally difficult to find and sample pristine waters, in part because waters may be sampled over a large screened interval where polluted waters are present at shallow depth, or because diffuse pollution (especially agricultural pollution) is present in large parts of the unconfined aquifer. Boreholes obviously affected by point-source pollution have been excluded from the dataset but most groundwaters in unconfined aquifers show the effects of agricultural pollution indicated by high nitrate concentrations.

#### Box 5.2 How can we distinguish pristine waters from polluted groundwater?

Groundwater prior to the industrial era (before c. 1800) emerged as springs or was taken from shallow wells, whilst the deeper reserves were in a pristine condition. The water first encountered using modern drilling practices would have had compositions reflecting true baseline determined only by geological and geochemical processes. Only rarely is it possible to find such waters because the majority of groundwaters sampled in the present study are derived from aquifers which have been developed for decades. The challenge is to recognise the impact of any of human activities over and above the natural baseline in the data sets used.

The approach adopted is threefold:

- (i) to have evidence of groundwater age
- (ii)to extrapolate data series back to an initial time
- (iii)to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced TOC and N species especially  $NO_3$  the presence of substances such as agro-chemicals or industrial chemicals. The sets of data are examined for these substances as a clue to the presence of "contamination", although it is difficult to quantify this. Even where traces of contamination are present, this may have little impact on the overall chemistry of the groundwater.

Nitrate concentrations in the unconfined Great and Inferior Oolite aquifers are very variable ranging from <0.004 mg  $\Gamma^1$  to 18.2 mg  $\Gamma^1$  NO<sub>3</sub>-N, with a median concentration of 8.16 mg  $\Gamma^1$  NO<sub>3</sub>-N. Approximately 30% of all groundwater samples in the study area showed NO<sub>3</sub>-N concentrations in excess of the EC MPV (maximum permissible values) of 11.3 mg  $\Gamma^1$ . However, this figure rises to 50% if only spring waters are considered. There does not appear to be a measurable difference between nitrate concentrations from sources in arable areas compared to those in grassland areas. The lowest nitrate concentration in the unconfined groundwater (4.3 mg  $\Gamma^1$  NO<sub>3</sub>-N) is obtained from a source located in woodlands. In the reducing confined groundwaters might even be of sufficient age to have been recharged with pre-modern water.

No clear correlation exists between nitrate concentrations and other common indicators of pollution such as Cl,  $SO_4$  or K. This indicates that their distribution is not dominated by pollution from fertilisers, but mainly derived from geochemical controls. This is highlighted further in Chapter 6. However, several spring waters exhibit higher concentrations of Cl,  $SO_4$ ,  $NO_3$  and K than unconfined groundwaters obtained from borehole sources further along the flowline, suggesting that some of the shallow spring water sources may be influenced by agricultural pollution.

Information on pesticide concentrations in groundwaters is available for sources analysed by the Environment Agency and Severn Trent Water plc from 1993 onwards. Most pesticide concentrations were below the detection limit in all samples investigated. However, low concentrations of atrazine and simazine have been detected sporadically in the Slacksbarn [SO 9679 1661], Chalford [SO 8915 0243] and Fossbridge [SP 0768 1125] spring sources and in the Dean Farm [SP 1656 0798] and Homeleaze Farm [SP 1744 0410] boreholes. In addition to atrazine and simazine, detectable levels of isoproturon (maximum 0.11  $\mu$ g l<sup>-1</sup>) were present at Cleeve Hill spring source [SP 0064 2638]. Since 1994, Trowel Covert spring source [SP 1332 1158] has exhibited permanently elevated concentrations of atrazine, with maxima of 0.037  $\mu$ g l<sup>-1</sup> for Simazine and 0.39  $\mu$ g l<sup>-1</sup> for Atrazine, the latter being above EC MPV of 0.1  $\mu$ g l<sup>-1</sup>.

Analyses for chlorinated solvents are available since 1985 within the study area. However, only a limited number of sources have been analysed. Concentrations remain below detection limit in the majority of the analysed sources. Only the Northfield spring source [SO 9844 2217] showed very sporadically Chloroform and Chlorodibromomethane concentrations above the detection limit and might, due to its proximity to Cheltenham, be influenced by anthropogenic sources of pollution, originating from the urban area.

Previous work on trace organic compounds in major British aquifers by Clark and Kenrick (1986) found high concentrations of a complex suite of unusual organic compounds in groundwaters from Sheephouse Farm. However, publications about the work carried out supplied no details.

Locally high concentrations of Al, Cd, Cu, Pb and Zn are present within the spring water sources along the Cotswold escarpment; the regional distributions of Al and Zn are shown in Figure 6-11. The relative proximity of these sources to urban areas like Cheltenham towards the north might suggest that these elevated concentrations are due to anthropogenic impacts. However, concentrations remain well below the EC MP values.

#### **BOX 5-3 SOURCE PROTECTION ZONES**

As all groundwater sources, including springs, boreholes and wells, have the potential to become contaminated by pollutants, Source Protection Zones or SPZs around groundwater sources have been defined (Refer to Policy Practice for the and Protection of Groundwater, 1998 for more information). The zones vary in size and shape as they are determined by the local hydrogeological characteristics of the strata including the geology of the direction aquifer, of groundwater flow, effective rainfall, permeability and volume of water abstracted.



Although non-statutory, SPZs do provide a useful tool for the Environment Agency, Planning Authorities Industry, Water Companies, Consultants and Waste Management companies to help protect groundwater from pollution.

#### BOX 5-2 NITRATE VULNERABLE ZONES

Historically, the Cotswold aquifers have been used to support a number of important local groundwater abstractions for both public and private supplies. However, pollution of these supplies by nitrate from agricultural sources is becoming an increasing problem. During and after the Second World War, farming practices became more intensive in order to increase crop productivity. Modern farming methods use manures, sewage sludge and chemical fertilisers to achieve this, but over application and surplus nitrogen can lead to environmental problems. Agricultural fertilisers and organic wastes from sewage farm spreading are diffuse sources of nitrate. Excess nitrate can leach into groundwater with infiltrating rainwater and potentially pollute natural groundwater resources such as springs and boreholes. Rainwater recharging the aquifer can pass quickly through the fractured Cotswold Limestone making the aquifer highly vulnerable to pollution. Resultant high nitrate concentrations in groundwater sources have been dealt with in recent years by blending with low-nitrate water sources.

The Ministry of Agriculture, Fisheries and Food (MAFF – responsibilities now within the Department of Rural Affairs, DEFRA) established Nitrate Sensitive Areas (NSAs) in the late 1980s to address the nitrate problem, as laid down under the 1989 Water Act. NSAs are selected catchments where nitrate concentrations in sources of public drinking water exceeded, or were at risk of exceeding, the 11.3 mg  $l^{-1}$  NO<sub>3</sub>-N limit in drinking water.

Voluntary, compensated agricultural management measures were introduced with the aim of reducing nitrate concentrations. By 2003, all existing NSA agreements will have expired but nitrate leaching will still be restricted as all NSAs will be within areas designated under the EC Nitrates Directive as Nitrate Vulnerable Zones (NVZs). In December 2002, the new NVZ designations came into effect with surface and groundwater zones now covering the whole of the Cotswolds area.



# 6 GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

# 6.1 Introduction

The following sections outline some of the key factors involved in generating the regional variations in groundwater chemistry across the Great and Inferior Oolite aquifers in the Cotswolds. Major, minor and trace-element data and isotopic compositions are discussed in relation to:

- Mineral dissolution reactions
- Redox reactions
- Ion exchange reactions
- Mixing with older formation water
- Groundwater residence time

It is important to bear in mind that some variations in chemical composition are due to differences in borehole design and construction, different stratigraphic horizons being tapped and different pumping histories. Differences in borehole design, including variations in casing and well depth may lead to localised water-quality variations. Differences in aquifer lithology may include changes in facies and variations in type and degree of cementation. Variations in pumping history may also have resulted in differences in water quality as differing pumping rates may affect the degree of flushing of solutes from parts of the aquifer. Pumping may also have induced vertical or lateral flow from overlying formations where present. Such chemical variations are quite different from the variations observed along groundwater flow lines that result from progressive water-rock interaction processes with increased residence time in aquifers. It is beyond the scope and resources of this project to assess in detail the factors influencing water quality for each of the boreholes in the data set. The report presents a broad assessment of the groundwater-quality variations observed across the aquifers and the main geochemical processes that are likely to control them. It is accepted that some water-quality variation may be due to the artificial influences described above.

# 6.2 Chemical evolution along flowlines

The flowline studied extends from the limestone escarpment in the north and north-west to Cricklade in the south (Figure 3-10). The main lithological change at outcrop within this stretch is the transition from the Inferior Oolite to the Great Oolite Group, intersecting the Fuller's Earth Formation. There are no drift deposits, but Oxford Clay overlies the limestone aquifers in the south (Figure 3-3). Recharge to the Inferior Oolite aquifer occurs along its north-western outcrop area and possibly by leakage from the Great Oolite aquifer, while the Great Oolite aquifer is recharged from its outcrop area further to the south.

To illustrate the hydrochemical changes, relevant parameters have been plotted against distance along the flowline in Figure 6-1 to Figure 6-5. To distinguish between the Great and Inferior Oolite aquifers in these plots, green and red symbols have been used respectively. Large symbols refer thereby to confined sources, whereby small symbols represent unconfined groundwater sources.

# 6.2.1 Mineral dissolution reactions

Figure 6-1 demonstrates that one of the most important factors affecting the chemical compositions of the limestone groundwaters of the region is carbonate dissolution reaction. Close to the recharge area, bicarbonate concentrations are relatively low with values around 150 mg l<sup>-1</sup>, but increase two, to threefold towards the confined part of the aquifer. Equilibrium with respect to calcite occurs rapidly,

leading to strongly buffered and carbonate-dominated groundwaters, acquiring Ca-HCO<sub>3</sub> composition. Saturation with respect to dolomite increases along the flow line. However the groundwater remains mainly undersaturated, indicating that the Great and Inferior Oolite limestones contain low Mg-calcite. This is also reflected in the generally low Mg/Ca ratios (up to 0.47) (Figure 6-4). Whilst the Mg content increases along the flowpath, most of the groundwater along the flowpath is saturated or near saturated with calcite. Hence, evolution from initially very low Mg/Ca ratios towards slightly higher ratios is observed as the waters move downgradient into the confined aquifer.

While the dissolution of calcite provides the dominant control on water chemistry in the unconfined part of the aquifer, in the confined part of the aquifer a decrease in Ca, mirrored by an increase in Na, indicates that ion-exchange processes become significant. This is discussed in further detail in section 6.2.3. Consequently, a change from a Ca-HCO<sub>3</sub> type water to a Na-HCO<sub>3</sub> water occurs. Further down the flowline, deep within the confined limestone, Na concentrations appear to be above values expected from simple ion-exchange with Ca. A similar increase in Cl concentrations is observed and mixing with older formation water is regarded to be the mechanism influencing the water chemistry in this part of the aquifer and is discussed in further detail in section 6.2.4.

#### 6.2.2 Redox Reactions

The distribution of redox-controlled species is shown in Figure 6-3.

Dissolved oxygen (DO) and redox potential (Eh) provide the primary indicators of the redox status of natural groundwaters. The DO concentrations are at saturation in the majority of the unconfined groundwaters, but decrease along the flow line. In the confined aquifers, groundwaters have low or no detectable dissolved oxygen and low redox potentials. The approximate location of the redox boundaries for the Inferior and Great Oolite aquifers are shown on Figure 6-10 together with the regional variations of dissolved oxygen concentrations.

In the Great Oolite limestone, the onset of reducing conditions at depths occurs before the aquifer becomes confined. The shallowest borehole penetrating the unconfined Great Oolite aquifer showing signs of reducing conditions with low DO and Eh is Foxbury Farm [SP 2880 0878], which draws water from 32 m depth. However, nitrate values above 8 mg  $\Gamma^1$  indicate, that removal of NO<sub>3</sub>-N through denitrification has not occurred appreciably. An 80 m deep borehole in the unconfined aquifer at Sheephouse Barn Farm [SP 0560 0495] yields more strongly reducing waters with DO concentrations of 0.7 mg  $\Gamma^1$ , low Eh and NO<sub>3</sub>-N of 1.28 mg  $\Gamma^1$ .

Within the Inferior Oolite aquifer, all unconfined groundwaters appear to be oxidising. The redox boundary lies within the confined part of the Inferior Oolite aquifer. All groundwater samples obtained from the confined Inferior Oolite show reducing conditions, however, sample points are 7 km and more down gradient from confinement. Due to lack of boreholes penetrating the confined Inferior Oolite aquifer between the onset of the confinement and the first sampled borehole ca. 7 km down-gradient, only a very approximate redox boundary location can be drawn (Figure 6-10). Previous studies by Morgan-Jones and Eggboro (1981) and Morgan-Jones (1986), concluded on the basis of a similar sample point distribution in the Inferior Oolite, that the redox-boundary occurs some 7-8 km down gradient of nominal confinement.

However, the redox boundary within the Great Oolite aquifer was believed to occur within 1-2 km after confinement. These findings were based on DO, Eh and major ion profiles and are in contrast to the findings in this study. The apparent difference in the findings might be related to different sample densities in both studies.

The difference between the onset of reducing conditions in the Great and Inferior Oolite aquifer in the study area is possibly due to the influence of fresh water from the Great Oolite leaking downwards into the Inferior Oolite aquifer, delaying the attainment of reducing conditions. Flow vertically

downwards is likely to occur due to the fissuring in the Great Oolite limestone. Additionally, groundwater within the Great Oolite might move at a slower rate, resulting in more rapid attainment of reducing conditions.

The redox boundary is also apparent when considering redox-sensitive species such as NO<sub>3</sub>, Fe, Mn, NO<sub>2</sub> and NH<sub>4</sub>. In the aerobic unconfined aquifer, nitrate is a stable species in solution. Baseline concentrations of NO<sub>3</sub>-N from rainfall inputs (Table 3.2) would be expected to be around 1-2 mg  $\Gamma^1$ , allowing for addition or removal from the soil zone. However, unconfined groundwaters in the area show a wide distribution of nitrate concentrations with the majority of samples exhibiting concentrations above likely baseline concentrations, reflecting the influence of agricultural pollution sources (Figure 6-3). Under anaerobic conditions, nitrate concentrations generally decrease and many confined groundwaters in the area exhibit values close to detection limit. However, it is not clear in all cases whether confined groundwaters have ever contained appreciable nitrate concentrations because of their possible pre-modern age (see Section 6.4). Where nitrate concentrations decrease due to denitrification, concentrations of the reduced nitrogen species NO<sub>2</sub> and NH<sub>4</sub> would be expected to increase. There is evidence for this in several sources drawing water from the confined aquifer. In the case of Dudgrove Farm [SU 1888 9835], the EC MPV for NH<sub>4</sub>-N in drinking water of 0.5 mg  $\Gamma^1$  is exceeded.

Iron concentrations increase in groundwaters beyond the redox boundary, reaching up to  $1260 \ \mu g \ l^{-1}$  towards the end of the flow line (Figure 6-3). Manganese concentrations are also high in some confined groundwater samples. Both elements are likely to be derived mainly by natural dissolution of Fe and Mn oxides under reducing conditions.

Sulphate reduction is believed to have occurred in two boreholes drawing water from the confined limestone aquifers. Troutbeck [SP 1899 0453] and Dudgrove Farm [SU 1888 9835] exhibit low concentrations of  $SO_4$  together with elevated Mn, Fe and low DO concentrations. However, no notable smell of sulphide (H<sub>2</sub>S) was recorded and the process, if occurring, is not considered to be quantitatively important.

The redox-sensitive trace element Sn shows a very subtle increase in concentration beyond the redox boundary, while U concentrations decrease, consistent with the low mobility of U under anaerobic conditions.



Water, when recharged, is generally saturated with dissolved oxygen at the partial pressure of the atmosphere (10-12 mg  $l^{-1}$  depending upon barometric conditions). Passing through the soil and the unsaturated zone some of this O<sub>2</sub> will react as a result of microbiological processes and oxidation-reduction reactions. However, almost all water reaching the water table still contains several mg  $l^{-1}$  O<sub>2</sub>. Geochemical reactions (oxidation of traces of pyrite, organic matter and Fe<sup>2+</sup> present in minerals) progressively remove the O<sub>2</sub> along flow lines. Once all the oxygen has reacted an abrupt change of water chemistry takes place (redox boundary). Other changes may occur at, and down-gradient, of the redox boundary, especially denitrification and the total dissolved iron (Fe<sup>2+</sup>) concentrations are likely to increase. Sulphate reduction and the production of sulphide (H<sub>2</sub>S as HS<sup>-</sup> in solution) may also occur at greater depths.

### 6.2.3 Ion exchange reactions

As groundwater flows along the transect through the limestone aquifer, freshening, i.e more recently recharged water comes in contact with parts of the aquifer containing older formation water, may cause cation exchange of Ca for Na according to equation:

$$Ca^{2+} + 2Na_{(adsorbed)} = 2Na^{+} + Ca_{(adsorbed)}$$

 $Ca^{2+}$  is taken up from water, in return for Na<sup>+</sup>, with a Na-HCO<sub>3</sub> type water as result. The effect of ion exchange in the aquifer is illustrated in Figure 6-4. The Ca/Cl ratio increases along the flowpath in the unconfined aquifer with increasing water-rock interaction. Once confined conditions are reached, the ratio decreases due to the loss of Ca, with further decreases for groundwaters influenced by mixing with old formation water. This is matched by an increase in the Na/Cl ratio. Clay minerals with exchangeable Na within the limestones and the Fuller's Earth Formation are regarded to be the source of Na for the exchange process. Various other trace elements are also subject to ion exchange, including K, Rb and Li, which increase in the confined aquifer, as they are released from clay minerals.

#### 6.2.4 Mixing with older formation water

It is generally considered that chloride behaves conservatively (i.e. non-reactively) in groundwater systems and therefore may provide a good indicator that mixing processes are taking place between recharge and formation waters. The chloride concentrations are generally low within both aquifers (median concentration of 16.2 mg  $\Gamma^1$ ), but are significantly elevated in waters from the Troutbeck [SP 1899 0453] and Dudgrove Farm [SU 1888 9835] boreholes (up to 286 mg  $\Gamma^1$ ). A similar increase is observed in Na concentrations. Both boreholes draw water from deep within the confined parts of the Great and Inferior Oolite aquifers and the increase in Cl suggests that some mixing may be taking place. Further support for this is evidenced in the increase in Na/Cl ratios, which for the majority of the groundwaters remain similar to the seawater ratio of 0.55. The increase in the confined aquifer is initially likely to reflect ion exchange but later may reflect mixing with old formation water. Potassium also shows elevated concentrations for groundwaters affected by mixing, while Mg and SO<sub>4</sub> concentrations remain low in those waters. Besides high Na, K and Cl concentrations, the groundwaters affected by mixing show elevated concentrations of several minor and trace elements, such as NH<sub>4</sub>, F, Br, B and Li.

The above findings are consistent with a study by Alexander and Andrews (1984), investigating environmental isotopes and inert gas content in aquifers along a transect from the Inferior Oolite escarpment in the north-west to the Chalk of the Berkshire Downs in the south-east. It was concluded that the groundwater flow pattern in the Great and Inferior Oolite Group involves two sub-systems. In the north-west, the present study area, water flows from outcrop towards a region of low hydraulic potential, while in the south-east, water moves up-dip towards this regional low under artesian conditions. A zone of mixing is proposed just under the edge of the confining Oxford Clay (Figure 3-9).

# 6.2.5 Trace elements

Concentrations of several trace elements are shown in Figure 6-2. A regional trend can be observed with increasing concentrations along the flowline for Rb, Sr, Li, B, F and Si.

Strontium concentrations are controlled by carbonate reactions, with Sr commonly found as a substitute for Ca in the calcite structure and is therefore often found in high concentrations in chalk and limestones. Concentrations in the unconfined groundwaters show median concentrations of 190  $\mu$ g l<sup>-1</sup>, whereas concentrations increase in the confined groundwaters with values up to 659  $\mu$ g l<sup>-1</sup> and a median concentration of 495  $\mu$ g l<sup>-1</sup>. The increasing Sr concentrations along the flowpath imply

prolonged groundwater residence time. A very similar distribution is found for Rb in the study area, although with much lower concentrations of between 0.15 and 2.4  $\mu$ g l<sup>-1</sup>. A similar strong correlation is found between Rb and bicarbonate, with highest concentrations being found in older groundwaters (Figure 6-4).

Fluoride concentrations are generally low in the outcrop groundwaters as residence times of groundwaters are relatively short and Ca concentrations are high. Concentrations of F increase in the reducing groundwaters as ion-exchange reactions and mixing produce groundwaters with high Na and lower Ca concentrations. The dominant source of fluoride is likely to be fluorapatite in the limestone. Fluoride concentrations reach up to 4800  $\mu$ g l<sup>-1</sup> in confined groundwaters, exceeding the EC MPV of 1500  $\mu$ g l<sup>-1</sup> and are here close to saturation (Figure 6-5).

Silicon in outcrop waters has a median concentration of 1793  $\mu$ g l<sup>-1</sup>, increasing in the confined groundwaters to 2.9 mg l<sup>-1</sup>. It is proposed that the increase in concentration is due to the dissolution of silica during percolation, and thereafter due to the reaction of groundwater with clay minerals (Edmunds, 1997). A strong correlation exists between Si and Sr, both believed to reflect groundwater residence time in the study area. The highest concentrations occur in the confined part of the aquifers, where saturation in respect to quartz is achieved. Concentrations in the limestone aquifer are low compared to Chalk aquifers investigated by Edmunds (1989) in Berkshire (median Si concentration of 8.1 mg l<sup>-1</sup>) and in the Central London Basin (median Si concentration of 6.24 mg l<sup>-1</sup>).

Boron varies in the groundwaters between 10 and 1467  $\mu$ g l<sup>-1</sup>, with a median of 23  $\mu$ g l<sup>-1</sup>. The increase in B along the flowpath parallels that of Li, varying between 2 and 48  $\mu$ g l<sup>-1</sup>. Concentrations in the majority of the samples do not correlate with Cl, suggesting that their increase is derived mainly by water-rock interaction and is indicative of prolonged residence time. Both elements occur mainly in clay minerals. However, in the deeper confined aquifer, a strong enrichment in Li and B occurs, which is in accordance with Cl, suggesting mixing with old formation water.

Bromide concentrations (median of 65.5  $\mu$ g l<sup>-1</sup>) do not exhibit any trend in the majority of the groundwater samples, except in the deepest confined groundwaters, where Br increases in line with Cl, due to mixing with older formation waters. In the majority of groundwater samples, the Br/Cl ratio remains above the ratio of sea water of 0.00347, indicating that uptake of Br has occurred in the aquifer, probably from organic sources (Figure 6-4).

Concentrations of Ba (median of 8.2  $\mu$ g l<sup>-1</sup>) are very variable and no distinct trend can be observed. The groundwaters are generally undersaturated with respect to barite.

Copper and Zn show locally high concentrations in spring sources while the remaining samples indicate a general increase along the flowpath. It is possible that Cu and Zn are derived from trace amounts of sulphide minerals present in the limestone matrix, while the elevated concentrations in some spring sources might be pollution derived (see Chapter 5.5). However, all sources remain at all times well below the EC MP values.

# 6.3 Temporal variations

Temporal variations in water chemistry in the area were studied using data from Stanton [SP 076 339], Northfield [SO 979 222] and Cleeve Hill [SP 007 264] public supply sources, which have measurements reaching back as far as 1974. Nitrate has been one of the most frequently measured determinands, as it is the most likely to exceed existing drinking-water standards. Variations in NO<sub>3</sub>-N concentration with time are shown in Figure 6-8, while changes over time in other major ions are illustrated in Figure 6-6 and Figure 6-7 for Northfield and Cleeve Hill.

The concentrations of Cl, Na and  $SO_4$  in Northfield spring exhibit a slight increasing trend between 1974 and 1983. However, concentrations of K remain constant over the same interval. The Cleeve

Hill spring source exhibits a slight decrease during the period 1976 to 1993 in Cl, Na and  $SO_4$  concentrations, however, K concentrations increase with time. In general, the data suggest that for many solutes no significant trend is apparent.

A distinct trend is observed in the nitrate concentrations in Northfield, with slight trends also in Cleeve Hill and Stanton. In all three spring sources, concentrations have increased steadily from 1973 to 1989. This background trend is of the order of 0.5 mg  $l^{-1}$  NO<sub>3</sub>-N per year for Northfield and 0.1 mg $l^{-1}$  NO<sub>3</sub>-N per year for Cleeve Hill and Stanton, and is likely to reflect the increased nitrate loading over the previous decades (Figure 6-8).

Seasonal variations in the nitrate concentration are apparent in all three sources and can be visualized by decomposing the nitrate time series into two components: a long term component and one reflecting hydrological changes and scatter. The long term component was obtained through linear regression and can be seen in Figure 6-8. This long term trend is then abstracted from the data series (Figure 6-9) so that the data set only reflects natural scatter and the response to changing hydro(geo)logical conditions. The data were normalised, so the mean becomes zero and the standard deviation becomes one. Where data have been collected frequently (period 1974 to 1976) strong seasonality of nitrate concentrations is visible. Generally high nitrate concentrations coincide with late winter and early spring periods where water levels are expected to be high, suggesting that these spring sources are part of a shallow hydrological flow system, which reacts more rapidly to hydrological changes.

Locality	Year sampled	Easting	Northing	Т	pН	Eh <sub>(25C)</sub>	DO	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	NO <sub>3</sub> -N	Fe
				°C		mV					1	mg l <sup>-1</sup>				
	2001	418878	198347	11.5	7.9	272	< 0.004	14.4	6.8	345	7.6	286	25.3	400	< 0.004	0.062
Dudgrove Farm	1986	418890	198330	15.0	8.2	115	0.4	11.0	7.0	400	5.0	358	10.0	410	0.7	0.020
r ai 111	1978	418890	198330	15.3	8.1		0.4	15.0	6.2	382	5.5	295	25.0	411	0.2	< 0.01
Chalk Hill	2001	413049	226005	10.7	7.5	328	9.0	110	2.7	10.8	2.8	14.8	30.9	282	7.8	0.290
Spring	1978	413040	226000	10.5	7.5		9.9	90.0	1.7	7.5	2.5	18.0	43.0	166	12.5	< 0.01
Lyefield	2001	402576	225384	10.0	7.2	453	9.6	74.4	7.6	8.8	0.6	20.0	38.1	141	9.9	0.003
Spring	1978	402600	225360	10.2	7.7		9.4	66.0	7.3	9.6	0.5	22.0	32.0	168	4.5	< 0.01
Woodbridge	2001	403618	214461	10.0	7.1	429	9.5	63.9	2.4	4.6	0.3	10.0	19.2	167	4.3	0.003
Spring	1978	403600	214450	10.5	7.7		9.3	79.0	2.3	4.6	0.2	11.0	16.0	156	1.8	< 0.01
Pinnock	2001	407970	227148	10.0	6.6	432	6.1	102	5.7	7.9	1.1	14.8	35.4	211	7.7	0.044
	1978	408070	227020	10.5	7.7		9.9	78.0	2.9	5.7	0.3	15.0	25.0	176	8.4	< 0.01
Cobblers Hill	2001	406265	216775	10.6	7.1	437	9.6	94.8	2.4	5.0	0.9	7.9	20.8	241	9.0	0.003
	1978	406150	216700	13.7	7.9		8.1	106	3.3	7.8	1.3	19.0	44.0	215	11.6	0.010
Fossbridge	2001	407685	211245	11.2	7.0	411	10.8	107	2.2	5.0	0.7	13.6	19.1	256	14.9	0.003
	1978	407710	211210	10.9	7.7		9.4	117	2.3	5.2	0.9	15.0	37.0	232	9.5	< 0.01
Trowel	2001	413326	211597	10.6	7.3	349	10.1	119	2.5	5.7	1.2	13.4	20.3	277	16.8	0.023
	1978	413320	211580	9.50	7.3		9.9	126	2.8	1.9	0.7	17.0	18.0	264	15.9	< 0.01
Doon Form	2001	416558	207984	10.8	7.1	342	7.1	117	7.3	7.3	2.0	11.7	35.5	312	10.5	0.025
Dean rarm	1986	416560	207960	12.0	7.3	350	4.9	114	7.7	14.0	3.1	16.0	51.0	293	7.5	< 0.01

Table 6.1	Major ion chemistry of boreholes sampled during multiple research studies
	(2001: this study; Year 1986: Morgan-Jones, (1986); Year 1978: Morgan-Jones
	and Eggboro (1981))

In the late 1970s, Morgan-Jones and Eggboro (1981) undertook an investigation into the hydrochemistry of the Great and Inferior Oolite Group in the study area. This was succeeded by a follow-up study in 1986 by Morgan-Jones, which concluded that no major chemical trends could be identified in the eight intervening years. Comparing the results from the present study with the major-

ion concentrations in 1978 and 1986 for the area, it appears that no significant change in the hydrochemistry has occurred. Table 6.1 lists all boreholes, which have been sampled a number of times. The majority show no significant trends, except for the nitrate concentrations, which are generally increasing.

#### BOX 6-2 NITRATE SENSITIVE AREA AT OLD CHALFORD, WEST OXFORDSHIRE [SP 3445 2544]

A total of 32 Nitrate Sensitive Areas (NSAs) were set up in England, ten of which formed the Pilot NSA Scheme areas launched in 1990. These included Old Chalford. The remaining 22 areas were introduced in 1994, as part of the EC Agri-Environment Regulation. At Old Chalford, the majority of the land under agreement was effectively farmed and managed under a nitrate friendly system for 10 years.

Throughout the duration of the NSA scheme, intensive monitoring of nitrate in groundwater, surface water and soil leachate nitrate concentrations has taken place. Nitrate concentrations in both surface water and groundwater within the Old Chalford catchment have displayed a marked seasonality, which appears to be controlled principally by catchment hydrology. The data also show that groundwater nitrate concentrations have declined throughout the 1990s. This decline has been attributed to a combination of reduced nitrate leaching and fluctuating groundwater levels. Although over a quarter of the arable land within the catchment was converted to no or low nitrogen input grassland and the catchment has a rapid relative response time, the decline in nitrate concentrations has been variable. A significant decrease in nitrate concentration was noted at the public water supply spring, but smaller decreases and several increases have been noted elsewhere in the catchment.



These results for Old Chalford demonstrate that nitrate concentrations in groundwater can be reduced if there are major long-term changes in farming practices, but that the beneficial effects take time to be noticeable.

#### 6.4 Age of the groundwater

Increasing concentrations of determinands such as  $HCO_3$ , Sr or Rb along the flowline as described in Section 6.2 suggest an increasing groundwater residence time. However, this does not provide any quantitative information on groundwater age. To determine groundwater age stable isotopic

measurements can be used (Figure 6-5). The stable isotopes  $\delta^{18}$ O,  $\delta^{2}$ H and  $\delta^{13}$ C have been analysed in eight groundwater samples; 4 taken from unconfined aquifers and 4 from the confined. Unlike most chemical species in water, stable isotopes of O and H behave conservatively in groundwater systems as they are an integral part of the water molecule, while carbon stable isotope ratios in waters are a function of interactions between water, rock and gases. During infiltration, soil carbon dioxide reacts with rock carbonate to form dissolved inorganic carbon with a  $\delta^{13}$ C value intermediate between the two reactants. Subsequent to this, the  $\delta^{13}$ C values may become more depleted (more negative) by further exchange with soil CO<sub>2</sub>, or more enriched by carbonate dissolution-reprecipitation reactions. Hence, the  $\delta^{13}$ C values give some idea of a relative age, whereby increasing  $\delta^{13}$ C values suggest increased residence time of the water.

 $\delta^{13}$ C values in the groundwaters of the study area cover a range of approximately 10 ‰ with generally more enriched composition in the confined limestone aquifers. Groundwater obtained from Dudgrove Farm shows the strongest enrichment with a value of -5.7 ‰. Compared to data from other British aquifers this suggests that this groundwater is of the order of several thousands of years old. Unconfined groundwaters have variable compositions, generally in the range -11 ‰ to -16 ‰. A plot of  $\delta^{13}$ C versus HCO<sub>3</sub> confirms that the least 'mature' waters are springs within the Inferior Oolite (Figure 6-5).

The stable isotopes of O and H do not show a distinct trend between spring waters and confined groundwater sources. The lack of depleted groundwater compositions suggest that no samples investigated are the product of recharge during past cold periods during the Quaternary. Hence, the isotopic composition suggests, that all waters are of Holocene age (<10,000 years).

The above findings are in accordance with a study carried out by Alexander and Andrews (1984). Ten groundwater samples from the Great and Inferior Oolite were analysed for their environmental isotope and inert gas content. These authors found a general trend of increasing age in the downdip direction in the Great Oolite. Tritium contents confirmed that no significant contribution from modern water occurred at distances greater then 3 km from outcrop.

Other studies by Morgan-Jones and Eggboro (1981) using tritium have confirmed, that a large proportion of groundwater close to the recharge area has been derived from rainfall dating from post 1953. However, a study by Morgan-Jones in 1986 using tritium noted that all groundwaters, including confined sources in the study area, have some component of post 1953 water.

# 6.5 Regional variations

The regional chemical variations across the study area are shown for selected elements in Figure 6-11. The geochemical controls discussed in the preceding sections can be applied to the chemical changes present in the study area.

Groundwater obtained from spring sources is fresh, oxygenated and young, having been recharged from the Great and Inferior Oolite limestone cropping out in an area from south-west to north-east. Low SEC values indicate the low degree of mineralization of these waters. They appear to be the least evolved waters observed. Nitrate concentrations are typically high, as are other ions related to anthropogenic inputs (Figure 6-11).

Towards the south-east, the data indicate that the groundwaters become progressively more evolved due to increased water-rock interactions, ion-exchange and redox reactions. SEC values increase where water is drawn from deeper parts of the unconfined Great Oolite aquifer and the confined limestone aquifers. Where SEC values are high, the dominant ions which have elevated concentrations are HCO<sub>3</sub>, K, SO<sub>4</sub> and Na. Groundwaters become progressively more reducing with low or no detectable dissolved oxygen and low redox potentials. The onset of reducing conditions in the Great Oolite aquifer occurs within the unconfined aquifer at depth. Within the Inferior Oolite

aquifer, the redox boundary occurs approximately 8 km after the onset of confinement. Groundwaters show elevated concentrations of F, Sr, Rb, Si, Br and B, indicating prolonged residence time in the aquifer.

Further south-east, deep within the confined part of the Great Oolite aquifer, a further change in the water composition takes place. Combined major, trace-element and isotopic investigations of the groundwater from the Dudgrove Farm [SU1888 9835] borehole suggest the presence of older water in this part of the aquifer. High SEC values are associated with high Na and Cl concentrations and groundwaters are possibly influenced by old formation water of Na-Cl type.

There is no evidence from the regional distribution of major ions, that concentration variability is associated with the changing nature of the aquifer host rock. No significant differences in the chemistry of the Great and Inferior Oolite groundwaters can be observed. Variations in chemistry along the flowpath in the study area are a function of residence time, ion-exchange and redox reaction together with mixing, rather than changes in the geological nature of the aquifers themselves.



Figure 6-1 Major element characteristics of the groundwaters along the flowline. (Green: Great Oolite, Red: Inferior Oolite, Large dot: confined, Small Dot: unconfined, black Circle: spring sources)



Figure 6-2 Minor element characteristics of the groundwaters along the flowline. (Green: Great Oolite, Red: Inferior Oolite, Large dot: confined, Small Dot: unconfined, black Circle: spring sources)



Figure 6-3 Redox parameters and redox sensitive species along the flowline. (Green: Great Oolite, Red: Inferior Oolite, Large dot: confined, Small Dot: unconfined, black Circle: spring sources)



Figure 6-4 Elemental ratios along the flowline. (Green: Great Oolite, Red: Inferior Oolite, Large dot: confined, Small Dot: unconfined, black Circle: spring sources)



Figure 6-5 Saturation indices and isotopic composition along the flowline. (Green: Great Oolite, Red: Inferior Oolite, Large dot: confined, Small Dot: unconfined, black Circle: spring sources)



Figure 6-6 Variations in major ion concentration over time in the Northfield public water supply source



Figure 6-7 Variations in major ion concentration over time in the Cleeve Hill public water supply source



Figure 6-8 Variations in NO<sub>3</sub>-N concentration with time in the Northfield, Stanton and Cleeve Hill public water supply source



May-73 May-75 May-77 May-79 May-81 May-83 May-85 May-87 May-89 May-91



May-73 May-75 May-77 May-79 May-81 May-83 May-85 May-87 May-89 May-91



May-73 May-75 May-77 May-79 May-81 May-83 May-85 May-87 May-89 May-91



Figure 6-9 Seasonal variations in NO<sub>3</sub>-N concentration in the Northfield public water supply source



Figure 6-10 Regional variations of dissolved oxygen concentrations in the Cotswolds study area and approximate position of redox boundaries within the Inferior and Great Oolite aquifers













Figure 6-11 Regional variations in selected elements in the Cotswolds study area plotted on solid geology map

# 7 **BASELINE GEOCHEMISTRY**

The groundwater chemical data show that the most important influence on water chemistry is carbonate dissolution reaction. This has resulted in relatively high natural concentrations of Ca and HCO<sub>3</sub>. Magnesium, even though increasing along the flow path, remains relatively low, suggesting the Great and Inferior Oolite limestone to contain low Mg-calcite. While the dissolution of calcite provides the dominant control on water chemistry in the unconfined aquifers, ion-exchange becomes significant in the confined part, resulting in increasing Na and decreasing Ca concentrations. In addition, mixing with old formation water contributes to high Cl, Na and K concentrations in the south-easterly part of the confined aquifers. Redox-reactions are important for many species due to the confined nature of the aquifers in the south-east. Anthropogenic inputs are most noticeable in form of elevated NO<sub>3</sub>-N concentrations in the unconfined part of the aquifer, while overlying younger deposits towards the south minimise any impact on the confined aquifer. Therefore, for most elements, the concentrations measured and the ranges found can be taken as representative of natural baseline.

The data have been presented in Table 5.1 and Table 5.2 and the median value and 97.7 percentile provide a good estimate of the average and upper baseline concentrations in the limestone aquifers. However, the study showed that concentrations vary spatially in the study area and baseline chemistry changes from north-west to south-east in relation to the extent of water-rock interaction and hence residence time and local geochemical controls, e.g. oxidation-reduction controls. As a result, three regimes with different baseline concentrations can be identified: the unconfined north-western area, the confined south-easterly region and the extreme south, which is influenced by old formation water. These regional variations must be taken into account when defining the local baseline for the aquifers. There is no evidence from the regional distribution of major ions that changes in the geological nature of the aquifers themselves influence baseline concentrations. No significant differences in the chemistry between the Great and Inferior Oolite groundwaters can be observed.

Although most groundwaters are dominated by baseline concentrations of solutes, concentrations of N-species are influenced by anthropogenic inputs. Agricultural practices have resulted in elevated NO<sub>3</sub> and pesticide concentrations in the unconfined part of the aquifers. Baseline nitrate concentrations are most likely to be around a few mg  $\Gamma^1$  in the unconfined aquifer, while concentrations of up to 18.2 mg  $\Gamma^1$  NO<sub>3</sub>-N have been recorded in the study area. Within the confined part of the aquifers nitrate concentrations are lower. In some boreholes this is due to denitrification or nitrate reduction, while other groundwaters might be of sufficient age to have been recharged prior to anthropogenic impacts. However a historic baseline for nitrate cannot be derived from these data as many of the original nitrate concentrations will have been reduced by denitrification. Unfortunately, there are also insufficient historical data available to estimate such a baseline from historical records. Cl, K and SO<sub>4</sub> are other solutes often influenced by urban, agricultural or industrial pollution. However, within the study area, although individual water samples may have been affected by such inputs, concentrations are generally within the range of baseline concentrations produced through natural processes.

Some concentrations of trace elements such as Al and Zn are relatively high in some spring sources and might be derived from anthropogenic inputs. Zn shows distinct baseline concentrations in the unconfined part and the confined part of the aquifer, with higher concentrations in the latter. However, individual spring sources show equally high concentrations and this might represent urban or industrial input rather than natural baseline concentrations (Figure 6-11).

# 8 SUMMARY AND CONCLUSIONS

The Great and Inferior Oolite limestones form important aquifers in the Cotswolds district of England. Groundwater abstraction from these aquifers is used for public supply, with a smaller fraction serving agricultural and private needs.

The limestones crop out in the north-west of the study area, but dip gently south-eastwards where they are covered progressively by younger deposits, resulting in aquifer confinement. Numerous spring lines have evolved in the area, the majority occurring along the northern limestone escarpment, where springs emerge at geological contacts with the Lias clays.

The most important factor affecting the chemical composition of the limestone groundwaters in the region is carbonate reaction. Close to the recharge area in the north and north-west, waters are oxidising and strongly pH-buffered with Ca and HCO<sub>3</sub> as the dominant dissolved ions. Distinct hydrochemical changes are observed down gradient as the aquifer becomes progressively more confined. Ion-exchange processes become significant and a change to a Na-HCO<sub>3</sub> water occurs. Redox-sensitive elements document the onset of reducing conditions. Further down the flowline towards the south-east, deep within the confined limestone aquifer, mixing with old formation waters influences the water chemistry, resulting in a Na-Cl type groundwater. Stable-isotopic compositions suggest long residence times.

The natural baseline concentrations for some elements can range over several orders of magnitude within the limestone aquifers. In the unconfined groundwaters, baseline concentrations are partly influenced by anthropogenic input, which is difficult to quantify. In confined aquifers, concentrations of many elements appear to be elevated, but these represent naturally derived baseline concentrations.

The majority of unconfined groundwaters and, in particular, spring waters in the region are influenced by agricultural activities, showing elevated nitrate concentrations. In confined groundwaters, where a redox-boundary is formed, nitrate concentrations are reduced, possibly due to denitrification. However, some confined groundwaters might even be of sufficient age to have been recharged with pre-modern water. Most pesticide concentrations remain below the detection limit. However, atrazine and simazine have been detected sporadically in several groundwater sources, with one source exhibiting permanently elevated concentrations, partly above the EC MPV. Locally elevated concentrations of trace metals occur in spring waters and are probably anthropogenic derived, but are currently well below EC maximum permissible values for drinking water (MPVs).

It is concluded, that the hydrochemical properties of the groundwaters in the Great and Inferior Oolite limestone are mainly determined by natural reactions between the recharged water and the limestone rock.
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