



## Baseline Report Series: 4. The Chalk of Dorset

Groundwater Systems and Water Quality Commissioned Report CR/02/268N

National Groundwater & Contaminated Land Centre Technical Report NC/99/74/4



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

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ENVIRONMENT AGENCY National Groundwater & Contaminated Land Centre Technical Report NC/99/74/4

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## **Baseline Report Series: 4. The Chalk of Dorset**

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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 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's) 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 from boreholes that may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that very often 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 aguifers, 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 of 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 unpolluted and polluted 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 Dorset Chalk contains groundwater predominantly of very high quality. However, much of the area is given over to farming, the long term effects of which have impacted on the natural groundwater quality. The main observed effect of agricultural activity has been the increase in nitrate, over several decades, from a baseline value of around 1 mg  $\Gamma^1$  in the early 20<sup>th</sup> century to concentrations up to the maximum acceptable concentrations for drinking water. A rise in potassium from agricultural sources above the natural background is also demonstrated. The impacts of less mobile contaminants such as micro-organics are restricted, in the data examined, to shallow spring sources. Apart from these examples of diffuse pollution, there is no evidence for widespread contamination from urban and rural wastes or other point sources of pollution in the data examined.

The natural baseline is expressed as a range of values which is controlled by rainfall inputs and by the hydrogeology of the area. There are only subtle changes in this baseline in the main body of the groundwater in the unconfined aquifer; for example, the Cl concentrations vary with distance from the coast. Oxidising conditions predominantly found in the unconfined Chalk aquifer give way rapidly to a reducing environment as the aquifer becomes confined beneath Palaeogene deposits. Increases in elements such as F, Fe and Mn are noted, but this environment also allows natural denitrification with possible benefits for abstraction in these areas. Details of the natural variations and the overall statistical data for approximately 90 constituents in the groundwaters of the area are presented. These are inorganic ions which are the focus of this project. The many possible micro-organic substances that are often sought in monitoring are by definition introduced substances.

It is concluded that the properties of groundwater in the Dorset Chalk are overwhelmingly determined by natural reactions, especially in the topmost few metres. It is generally of high quality but is being progressively impacted by agrochemicals in unconfined areas, the evidence of which is found even in deeper groundwaters. Waters of pristine pre-industrial quality are rare in the basin and restricted essentially to the confined aquifer.

## 2. PERSPECTIVE

The Dorset Chalk area lies at the western end of the Wessex Basin and is centred on the town of Dorchester (Figure 2.1). The basin is a synclinal structure whose northern limb forms the high ground overlooking the Vale of Pewsey and its southern limb forming the high ground of the Purbeck monocline overlooking the coast near Lulworth. The river catchments of the Frome and the Piddle drain the centre of the syncline. The Chalk outcrop area is of typical Chalk downland, common to much of southern England. In the east, towards Poole Harbour, the Chalk is overlain by younger Palaeogene sediments (sands, gravels and clays) which provide the contrasting heathland scenery.

The area of Chalk downland forms the core for evaluating the regional baseline groundwater quality. Selected data for groundwater derived from springs and boreholes from the region have been used to provide areal coverage and to investigate trends in quality over recent decades. The geochemical properties of the Chalk are relatively uniform and results from the Dorset Chalk may be used for comparison with other regions of the Chalk of southern Britain.



#### Figure 2.1 Topographic map of Dorset showing surface drainage and main settlements.

The Chalk aquifer is classified as a Major Aquifer by the Environment Agency and contains large volumes of high quality potable water. It also provides an essential source of baseflow to maintain river quantity and quality. Its principal economic uses are its important role in providing high quality

drinking water for both public and private water supplies, agricultural use, such as watercress and fish farming, and for industry. Specialised local users include hospitals, breweries and food processing factories.

The focus of this study is on the natural spatial and temporal variations in the groundwater chemistry of the Chalk aquifer. The study is limited by the availability of data both areally and in the depth dimension. Conclusions concerning trends in groundwater chemistry are limited by the restricted amount of time series data that has been accessible. Nevertheless the clear definition of the ranges in baseline quality are required to provide comparative data to establish changes in this groundwater quality. Only with such information can managerial decisions be taken to mitigate or remediate these anthropogenic effects.

Current issues in the area relate mainly to groundwater abstraction close to the rivers and streams of the basin, which may lead to unacceptable low stream baseflow which impacts on the sensitive Chalk stream ecology (riparian, instream and wetlands).

Although the Dorset Chalk contains very high quality groundwater much of the area is given over to farming and the impacts on quality of long term farming which poses a threat to this high quality water. Increases in fertiliser application since the end of the second world war have resulted in high nitrate loadings in recharge. The impact of pesticide application is less well known! As well as diffuse pollution, there is the potential for point source pollution derived from urban and rural wastes, including landfills, industry, farm sources and sewage effluent. Spatial variations in groundwater occur due to changes in rock type, hydrogeological characteristics affecting flow rates, rainfall/recharge inputs through different soils types and differing land use. While some of these processes take place on a geological timescale, others, reflecting climatic variations, land use change, and abstraction may induce changes in decades, years or even seasonally.

The approach adopted has been to build upon previous reviews of the hydrochemistry and hydrogeology of the aquifers in the area. These are taken mainly from published and unpublished BGS and Environment Agency sources, which are listed in the reference section. Existing groundwater quality data in BGS and Environment Agency archives have been supplemented by the analysis of samples taken specifically for the purpose of the study.

## 3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

#### 3.1 Introduction

An essential first step for assessing the natural (baseline) groundwater quality is an understanding of the system through or in which the groundwater flows or is contained. This requires information on the geological and hydrogeological properties to provide the physical framework of the system being studied, definition of the mineralogy and geochemistry of the component minerals to explain the characteristic groundwater chemistries; and finally the initial input(s) to the system, principally rainfall chemistry, but also interaction with the soil zone and other groundwater/surface water interactions, for instance in the hyporheic zone beneath streams.

The Chalk is composed of fine-grained, highly porous soft limestone that contains large volumes of groundwater. Movement of groundwater through the rock from areas of recharge to discharge is principally along fractures that are present as a result of induration, mass movement or deformation of the rock, for instance through the folding or faulting that has taken place. The flow of water along the fractures leads to their widening through dissolution of the rock. Groundwater flow is further controlled by changes in climatic conditions that have taken place affecting base levels as well as weathering of the chalk at the near surface. The result of all these factors is to produce the variable landscape and hydrogeological conditions that are now encountered. The proximity of the aquifer to the sea also has an influence on the chemistry of the rainfall and hence the baseline groundwater quality.

## 3.2 Geology

*Stratigraphy.* Although the Chalk stratigraphy of the Wessex Basin has been revised (Newell et al, 2002), for the purpose of this report the old classifications of Upper, Middle and Lower have also been used. The Upper Chalk forms the main outcrop over most of the area (Figure 3.1). Thin outcrops of Middle and Lower Chalk are also present in the upper valleys and along scarp edges. Thin hill-top deposits of Pleistocene and Recent material occur, most notably clay-with-flints, on the interfluves. To the east, the Chalk is progressively confined by Palaeogene sand and clay deposits (Figure 3.1). Alluvium and Head deposits are found within the valleys (Newell et al, 2002). Across the region, the thickness of the Upper Chalk in Dorset can be up to 260 m, the Middle Chalk 26 to 41 m and the Lower Chalk 22 to 57 m (Rawson et al., 1978). The Upper Greensand is between 16 and 57 m thick. The Palaeogene sediments may reach a thickness of more than 100 m in the east of the area. The thickness of these overlying strata limit the extent that the confined Chalk is economically developed for potable supply.

*Structure.* The Wessex basin Chalk lies in a broad syncline which has suffered particularly intense deformation in the South Dorset area. Here the syncline is truncated by a faulted monocline which is associated with the so-called Purbeck disturbance. Clearly such faulting has a distinct effect on groundwater flow in this area. Significantly many of the river, stream and dry valley drainage systems appear to be fault controlled. The complex Chalk stratigraphy and the intercalated sands and clays of the Palaeogene together with the structure result in a potentially very complex hydrogeological flow regime.

*Pleistocene events.* Until around 8000 years ago sea levels were much lower than those of today and the coastline of Dorset lay at least 50 km to the south of the present day coast. This situation which had lasted for over 80 000 years beforehand was the result of a smaller ocean volume due to the extensive ice caps. The lowered sea levels would have resulted in development of new base levels for surface and groundwater flow. The Purbeck anticline was breached during this time and the groundwater flow regime in the confined aquifer is likely to have been changed allowing fresher water to flow towards Poole Harbour (Veligrakis et al., 1999).

The land area shallow subsurface was affected by the periglacial climate for much of the Pleistocene. These cold conditions with permafrost accelerated chalk weathering and enhanced the near-surface permeability. Solution features (dolines) also abound near the junction between the Chalk and Tertiary strata (e.g. Culpepper Dish), where the acidic waters in the Palaeogene strata have dissolved underlying Chalk strata causing collapse.



# Figure 3.1 Geological map of the study area showing main towns and rivers (Line of section shown on Figure 3.2).

#### 3.3 Hydrogeology

It is important to state at this point that the hydrogeology of the Dorset chalk catchments is highly complex and poorly understood. The aquifer system is complicated by acute heterogeneity in the Chalk at various scales (karst, vertical variations due to lithology, structure). This is further complicated by the surface water/groundwater interactions and interaction with other geological

formations which contain extensive lithologies that can be regarded as aquifers (Palaeogene deposits, and upper Greensand).

The hydrogeology of the aquifer can be considered in three areas; the *southern Chalk* outcrop of the Purbeck Hills and Lulworth, the *northern Chalk* outcrop and the valleys of the Frome and Piddle and finally the *confined Chalk* in the Wareham and Poole Harbour areas (Figure 3.1). The Chalk is underlain by the Upper Greensand which is in hydraulic continuity with the overlying Chalk. The effective base of the aquifer is defined as the top of the well-cemented, low permeability Exogra Sandstone within the Upper Greensand (Alexander, 1981; Allen et al., 1997). Chalk hardgrounds (such as the Melbourne Rock and the Chalk Rock) have a reduced porosity, typically 10 to 20 %, but where they are fractured they can provide productive flow zones. The transmissivity of the Chalk ranges from 500 to 1000 m<sup>2</sup>/d and storage coefficients are between 5 x 10<sup>-4</sup> and 3.5 x 10<sup>-2</sup>. Pump tests conducted on interfluve locations indicate typical transmissivity values to be much lower at less than 50 m<sup>2</sup> d<sup>-1</sup> (Allen et al, 1997).

The overlying Palaeogene beds comprise the Poole Formation which consists of an alternating sequence of sands and clays; groundwater within the Poole Formation forms an important minor aquifer. Underlying the Poole Formation is a variable thickness of London Clay. The London Clay has a sandy unit, the West Park Farm Member, at its base in contact with the Chalk. It is likely that this unit is therefore in hydraulic connection with the underlying Chalk and that some upward leakage could occur from the Chalk to the Palaeogene deposits, although there is little geochemical evidence to suggest this.

In *southern Dorset* the highly folded chalk typically has a lower porosity and intergranular permeability than less-deformed chalk. The tectonically hardened chalk, most notably in the Lulworth area, has reduced transmissivity and lower storage which indicates that fracture distribution has been altered by chemical or mechanical diagenetic processes (Allen et al., 1997). However, faulting appears to have increased transmissivity locally, for example at Lulworth. Groundwater flow divides are discordant with the surface water drainage pattern in the southern part of the basin. In the vicinity of Lulworth, this discordance is the product of coastal breaching of the aquifer resulting in reversal of flow i.e. the direction of groundwater flow is towards the coast rather than towards the River Frome (Houston et al., 1986; Allen et al., 1997). Significant groundwater discharges at the coast therefore occur in the form of springs located e.g. at Lulworth Cove and Arish Mell.



Geological cross section (north-south) through the southern Wessex Basin (line of section shown as line 2 on Figure 3.1). UGS=Upper Greensand; ZCk=Zig Zag Chalk; HCk-NCk=Holywell Nodular Chalk to Newhaven Chalk; TCk+SpCk=Tarrant Chalk and Spetisbury Chalk; PCk=Portsdown Chalk; LC=London Clay; Poole=Poole Formation Figure 3.2

In the *North Dorset Downs* groundwater flow paths are likely to be dominated by the interplay of flow along bedding features (such as the Melbourne and Chalk Rocks) and the river system development along, often faulted, planes of weakness. The unsaturated zone is often very thick in the high interfluves and the development of permeability poor. Between the Rivers Frome and Piddle the interfluve has a partial covering of Palaeogene sands and the area is characterised by the largest concentration of karst (dolines) features on the chalk of southern England. In the upper catchments of the Frome and Piddle the streams flow over Gault clay and receive flow from the Upper Greensand. Here the Chalk forms – capping to the hills and perched water tables occur providing high level springs of Chalk groundwater which subsequently flow across Gault and Upper Greensand before reaching the Chalk once again. The variability of spring occurrences and baseflows in the streams indicate a complicated hydrogeology, as yet, poorly understood.

In the *Wareham and Poole Harbour* area the Chalk is confined beneath Palaeogene strata. In the vicinity of Empool (NGR 374 087), values of transmissivity range from 2000 to 15 000  $\text{m}^2/\text{d}$ , apparently caused by solution enhancement (Allen et al., 1997). At greater depths however, in the vicinity of Wareham and Poole Harbour, the Chalk is confined by more than 100 m of Palaeogene deposits and most boreholes are artesian with piezometric heads of more than 20 m above ground level. (Buckley, 1996).

Fluid logging in the confined Chalk (Buckley, 1996; Buckley et al., 1998) indicates that the main water bearing horizons within the Chalk are in the uppermost 50 m. Most of the groundwater movement is restricted to the Upper Chalk (notably the part classified as Portsdown Chalk under the modern nomenclature), although minor geophysically logged temperature changes may be detected at greater depths, indicating possible flow horizons up to -300 m OD. The groundwater at these depths is relatively fresh although transmissivities are low. The piezometric surface from the edge of the Palaeogene outcrop to the centre of the basin falls by about 10 m which is taken as an indication that the aquifer cannot readily discharge to the Palaeogene deposits above the London Clay or across the Purbeck structure (Buckley, 1996). Water levels often fluctuate seasonally being highest in the winter and lowest during the summer months (Figure 3.3).



Figure 3.3 Groundwater level fluctuations in a chalk borehole at Ashton Farm.

Recharge to the Portsdown Chalk (top of upper Chalk) appears to occur at its outcrop to the north between Winterbourne Kingston and the Palaeogene cover. Recharge to the underlying Chalk formations further to the north appears to flow at a gradient less steep than the inclination of the bedding and transfer takes place to younger horizons as it flows south. Minor recharge contributions may be coming from the Chalk outcrop to the south-west although this water may be diverted offshore by the Purbeck structure (Buckley, 1996).

### 3.4 Chalk mineralogy and geochemistry

Chalk is a marine sediment which accumulated slowly on the sea bed from plankton microfossils (coccoliths) as well as from the remains of other creatures with carbonate skeletons. Some silica skeletons also contributed and these have undergone diagenesis to form flint bands in the Upper and Middle Chalk. The microscopic texture of local chalk, illustrated here (Figure 3.4) shows that the microfossil remains are well preserved. The high intergranular porosity (between 20-45%) is also apparent with the diameter of the pores around one micron in size. This provides a large and reactive surface area for chemical processes to take place and this interaction between water and rock largely controls the baseline chemistry.

The Upper and Middle Chalk microfossil debris consists of relatively pure calcite (calcium carbonate). However, small amounts of other elements (Mg, Sr, Mn, Fe) are present in the calcite structure, which helped to stabilise the carbonate in the marine environment. These impurities in the carbonate lattice play an important role in the evolution of the groundwater chemistry, since they are slowly released to the groundwater as the chalk recrystallises under freshwater conditions.

The Upper and Middle Chalk also contain between a 1-5% non-carbonate fraction, although this increases to 5-12% in the Lower Chalk. This fraction consists of quartz, clay minerals (montmorillonite, white mica and, in the Lower Chalk, kaolinite), as well as phosphate minerals (francolite, fluorapatite).

Groundwater in the Chalk occurs in the pore spaces of the matrix and also in fractures, where most of the flow takes place. Water in the pore spaces remains relatively immobile because of the very low matrix permeability. The relationship between fracture and pore waters can be seen on Figure 3.5. Water moving rapidly along the fractures brings in new (reactive) water which dissolves fresh chalk, but also may lead to new minerals precipitating on the Chalk surface. There is an exchange and diffusion between the water in the matrix and water in the fractures which has a strong influence on the resulting groundwater chemistry with time as water moves through the aquifer.

#### 3.5 Rainfall chemistry

Rainfall chemistry can be regarded as the primary input contributing to the baseline quality. For some elements it may well be the major source of solutes with very little being added during infiltration and saturated flow. For this area no rainfall stations which routinely measure rainfall chemistry were found and therefore a station in Sussex (Barcombe Mills) is used. This is in a similar geographic position relative to the coastline and with a similar rainfall amount to Dorset.

The analyses for this station are given in Table 3.1 for the major elements. In addition these have been multiplied by a factor of 3 which roughly accounts for the likely concentration due to evaporation under the prevailing climatic conditions. These values may be used as a guide for comparison with groundwaters. It is important to note that Cl is regarded as a conservative ion and groundwater concentrations may be largely rainfall derived. The Mg concentrations exceed Ca and reflect the higher ratios in sea water aerosols. Ammonium is the main N source being mainly derived from agricultural sources. The background concentrations (as N) at the present day, after allowing for evapotranspiration, may be as high as 4 mg  $l^{-1}$ .



Figure 3.4a. SEM photomicrographs Lulworth and Shapwick: 1) Lulworth 93.8m. Magnetite and pyrite vein filling with large crystal of sphalerite (ZnS). Open and recrystallised chalk fabric, slightly different on either side of fracture 2) Intergrowths of pyrite and recrystallised pyrite (Lulworth 93.8m). 3) Lulworth (93.8m) Newly crystallised calcite rhombohedra on a matrix of microfossil fragments (some coccoliths still recognisable).4) Lulworth (47.9m) Sugary fabric with recrystallising chalk debris – high porosity retained. 5) Lulworth 47.9. Foraminifera with late crystal of magnetite growing inside recrystallised skeleton. 6) Lulworth 47.9. Overall texture of the chalk at Lulworth at magnification of x450 with a phosphatic fragment of fish scale (?).



Figure 3.4b. SEM photomicrographs Lulworth and Shapwick: 1) Shapwick. Texture of chalk at magnification of x784 showing high porosity and preserved chambered formainifera. 2) Back-scattered electron image of chalk texture – mainly open structure with only slight recrystallisation (Shapwick). 3) Lulworth 93.8m. Recrystallisation of foraminifera showing the overgrowth of calcites on skeleton. However some coccoliths are still well preserved in this tectonised zone of the Chalk. 4) Lulworth 47.9m Intergrowth of clays (smectite) and gypsum on surface of a fracture. 5) Shapwick. High magnification view (x7600) of the chalk matrix at Shapwick. 6) Detail of slide no 3.

#### Figure 3.4 SEM photomicrographs



Figure 3.5 Model of water-rock interactions in the chalk at the microscopic scale. Interstitial water (stippled) exchanges with fracture water.

Table 3.1	<b>Rainfall chemistry</b>	for Barcombe	Mills. Average	of three years	1996-1998.
	•/			•/	

	Units	Rainfall	Rainfall x3
PH	pH value	4.9	
Na	$mg l^{-1}$	7.44	22.3
K	mg $l^{-1}$	0.24	0.73
Ca	mg $l^{-1}$	1.84	5.5
Mg	mg $l^{-1}$	4.21	12.7
Cl	mg $l^{-1}$	5.61	16.8
SO <sub>4</sub>	mg l <sup>-1</sup>	1.07	3.2
NO <sub>3</sub>	mg $l^{-1}$	0.38	1.15
$NH_4$	mg $l^{-1}$	1.34	4.01
Total N	mg $l^{-1}$	1.13	3.85
Rainfall	mm	678	

### 3.6 Landuse in the area

The dominant land use over the aquifer comprises managed grassland and to a lesser degree arable land and forestry (Figure 3.6). The main urban areas are present mainly in the coastal areas, although many smaller towns and villages are found throughout the region.



Figure 3.6 Generalised landuse map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology © NERC.

## 4. DATA AND INTERPRETATION

## 4.1 Historical Data

Few chemical analyses carried out on public or private water supplies during much of the 20<sup>th</sup> century have been found. Extensive searches as part of the present programme have failed to locate significant material of value to the present studies, although occasional analyses have been found in BGS memoirs and records. Information on trends comes mainly from the records of the Environment Agency collected in the last two decades.

Data are also available from a number of published and unpublished investigations relating to water quality in the area and these are used in parts of the report. These include analyses of interstitial water from core material derived from drilling at Lulworth (Buckley et al., 1998; Shand, 1999, Gaus et al., 2001). Investigations of the hydrochemistry of the confined Chalk beneath the Poole area have been carried out in collaboration with Wessex Water (Edmunds, 1996a).

## 4.2 Current Era

Data are available from the Environment Agency's network for strategic groundwater quality monitoring network. However, the data are incomplete and often only comprise partial time series and a limited range of determinands. Data used here are from 26 selected sites (analyses from the mid 1990s) from the Environment Agency's monitoring network and are shown on Figure 4.1. These have been used i) for statistical purposes to supplement new sample data and ii) to determine trends at the decadal scale that may aid interpretation of trends away from baseline conditions.

## 4.3 New sampling programme

Thirty samples were collected during late autumn 2000 from sites in the Dorset area shown in Figure 4.1. These form the main set of data used for deriving baseline conditions. They have been analysed for a range of inorganic species and in addition field measurements (Eh, DO, pH, temperature and SEC) are used in the interpretation. All samples were filtered in the field and acidified with nitric acid (1% v/v) to stabilise trace elements.

## 4.4 Data handling

All plots and tables showing statistical information have used data from the new sampling programme plus the selected Agency monitoring sites and four analyses from earlier BGS records for confined groundwaters in the Wareham area. Where data are below detection limits, a value of half the detection limit has been used for statistical purposes only.

Major cations and sulphate were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry and a wide range of trace elements by Inductively Coupled Plasma Mass Spectrometry. Nitrogen species were analysed by colorimetry at the Environment Agency laboratories in Nottingham and other anion species (Cl, Br, I, F) by automated colorimetry at the BGS laboratory in Wallingford. Stable isotope analyses were completed in the BGS laboratory by mass spectrometry and the results reported relative to the standards SMOW for  $\delta^2$ H and  $\delta^{18}$ O and PDB for  $\delta^{13}$ C.



Figure 4.1 Geological map showing boreholes and spring sampled during November 2000.

## 5. HYDROCHEMICAL CHARACTERISTICS

#### 5.1 Introduction

The summary statistics for Dorset are given in Table 5.1. A total of 88 field, chemical and isotopic parameters are shown with maxima and minima and median values calculated from all data (using half detection limit values where necessary). A total of up to 59 analyses were available using both BGS and Agency datasets and up to 30 samples were analysed from new sites.

Summary data are shown graphically on a PIPER plot (Figure 5.1) and for the most important elements in the box plots and cumulative probability plots (Figures 5.2 and 5.3) where the ranges of data are shown at a log scale for both major and minor elements. This plot gives an indication of the range of data about the median for any given species or element. It also allows the spread of the data population to be visualised (see Box 5.1) and it is intended that these two diagrams provide a diagrammatic representation to the data shown in Table 5.1.

Parameter	units	Minimum	Maximum	Median	97.7th percentile	Upper baseline	Ν
T	<sup>0</sup> C	0	17.0	11.4	16.4		50
	°C	9	1/.2	11.4	16.4		58 22
рн Бр	mV	0.94	7.38 552	7.215	1.52 549		32 12
	111  v m $\approx 1^{-1}$	199 <0.1	11.01	JI/ 7.61	10.5		15
DU	ing i	<0.1	11.01	/.01 596	10.5		21
SEC S <sup>2</sup> II	μS cm	545	20	200	857		31 1(
0 H S <sup>18</sup> O	%00 0∕	-45	-30	-39	-30		10
$\begin{array}{c} 0  \mathbf{U} \\ \mathbf{S}^{13} \mathbf{C} \end{array}$	%00 0/	-6.8	-5.82	-0.30	-3.8		10
0 °C	%0 1-1	-15.7	-5.6	-14.3/	-/.8		16
Ca	mg l <sup>1</sup>	50	125	105	120		34
Mg	mg l <sup>-1</sup>	1.7	19.4	2.5	18.1		34
Na	mg l <sup>-1</sup>	6	155	10.6	85.2		34
K	mg $l^{-1}$	0.9	7	2.3	6.6		8
Cl	mg l <sup>-1</sup>	14	223	21	83.3		59
$SO_4$	mg l <sup>-1</sup>	2.5	43	13	32.8		35
HCO <sub>3</sub>	mg l <sup>-1</sup>	107	324	269	313		30
NO3-N	mg l <sup>-1</sup>	0.05	12.00	6.20	11.2	3-4	34
NO <sub>2</sub> -N	mg l <sup>-1</sup>	< 0.001	0.0569	< 0.001	0.043		58
NH <sub>4</sub> -N	mg l <sup>-1</sup>	< 0.003	0.310	0.011	0.131		58
Р	mg l <sup>-1</sup>	10	163	44	118		30
ТОС	mg l <sup>-1</sup>	0.49	5.78	1.18	5.3		30
DOC	mg l <sup>-1</sup>	0.25	4.16	0.75	3.8		56
F	$mg l^{-1}$	0.048	4.3	0.08	1.7		31
Br	mg l <sup>-1</sup>	0.057	0.289	0.084	0.222		31
Ι	$\mu g l^{-1}$	2	20.1	3	18.7		31
Si	$mg l^{-1}$	3.3	12.2	4.7	11.6		56

# Table 5.1aField parameters, isotope data and range of major and minor element<br/>concentrations in groundwaters of the Dorset Chalk.

\* estimated upper baseline for elements modified by anthropogenic influences. N = number of sample analyses

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

#### 5.2 Water types and physicochemical characteristics

The groundwaters of the Dorset Chalk display a narrow range in pH (6.9 to 7.6) are have moderate TDS (median SEC of 586  $\mu$ S cm<sup>-1</sup>). Although the range of Eh values is over 300 mV the majority of samples are relatively oxidising in the unconfined part of the aquifer but the deeper confined groundwaters are relatively reducing.

The boxplot and cumulative probability plot (Figures 5.2a and 5.3a) show that Ca and  $HCO_3$  are the major constituents of the Dorset Chalk groundwaters and the majority are of Ca-HCO<sub>3</sub> type (Figure 5.1). The Piper diagram indicates a possible trend towards Na-HCO<sub>3</sub> and one sample has a relatively high SO<sub>4</sub>.



Figure 5.1 PIPER plot showing the relative concentrations of major cations and anions in groundwaters of the Dorset Chalk

#### 5.3 Major elements

An upper limit is apparent for the concentrations of Ca and  $HCO_3$  (Figure 5.3a) imposed by the maximum solubility of the CaCO<sub>3</sub>. The fact that all the waters have high bicarbonate concentrations shows that solution must be rapid. These two ions totally dominate the chemistry, followed by Na and Cl. The behaviour of the latter elements is similar as a result of being derived principally from rainwater. Some10% of the groundwaters contain slightly greater salinity than derived from rainfall,

the salinity being derived from other sources as discussed later. Most other ions (see Figure 5.3a) show distributions approaching log-normal.

Representative analyses of waters from the Chalk of the area for key parameters are shown in Table 5.2. They include samples of spring water, unconfined groundwater, groundwater confined beneath the Tertiary and deeper confined water from beneath Wareham.

Paramo	eter units	Minimum	Maximum	Median	97.7th	Ν
					percentile	
Ag	μg l <sup>-1</sup>	< 0.05	0.16	< 0.05	0.07	30
Al	μg l <sup>-1</sup>	<1.0	2.0	1.0	2.0	30
As	μg l <sup>-1</sup>	<1	1.60	<1	1.24	56
Au	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
В	μg l <sup>-1</sup>	<20	<21	<22	74.8	31
Ba	μg l <sup>-1</sup>	5.00	99.0	12.0	40.5	57
Be	μg l <sup>-1</sup>	< 0.05	0.25	0.03	0.10	30
Bi	μg l <sup>-1</sup>	< 0.05	0.07	0.03	0.06	30
Cd	μg l <sup>-1</sup>	< 0.05	0.06	< 0.05	< 0.05	30
Ce	μg l <sup>-1</sup>	< 0.01	0.010	< 0.01	0.010	30
Со	μg l <sup>-1</sup>	< 0.01	14.5	0.02	8.08	30
Cr	μg l <sup>-1</sup>	< 0.5	< 0.5	< 0.5	< 0.5	30
Cs	μg l <sup>-1</sup>	< 0.01	0.020	< 0.01	0.013	30
Cu	μg l <sup>-1</sup>	0.2	13.7	2.20	11.2	30
Dy	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Er	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Eu	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Fe	μg l <sup>-1</sup>	<5	20007	2.50	4901	35
Ga	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
Gd	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Ge	μg l <sup>-1</sup>	< 0.05	0.08	< 0.05	0.08	30
Hf	μg l <sup>-1</sup>	< 0.02	< 0.02	< 0.02	< 0.02	30
Hg	μg l <sup>-1</sup>	< 0.1	< 0.1	<0.1	< 0.1	56
Но	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
In	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Ir	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
La	μg l <sup>-1</sup>	< 0.01	0.02	< 0.01	0.01	30
Li	μg l <sup>-1</sup>	0.20	20.00	0.85	14.0	31
Lu	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Mn	μg l <sup>-1</sup>	< 0.04	555	< 0.04	150	33
Мо	μg l <sup>-1</sup>	< 0.1	2.50	< 0.1	1.17	30
Nb	μg l <sup>-1</sup>	< 0.01	0.01	< 0.01	0.01	30
Nd	μg l <sup>-1</sup>	< 0.01	0.02	< 0.01	0.01	30
Ni	μg l <sup>-1</sup>	< 0.2	20.3	0.35	16.2	30
Os	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
Pb	μg l <sup>-1</sup>	<2.0	<2.0	<2.0	<2.0	30
Pd	μg l <sup>-1</sup>	< 0.2	< 0.2	< 0.2	< 0.2	30
Pr	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30

 Table 5.1b
 Trace element concentrations in groundwaters of the Dorset Chalk.

Param	eter units	Minimum	Maximum	Median	97.7th	Ν
					percentile	
Pt	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Rb	μg l <sup>-1</sup>	0.71	1.96	1.31	1.84	30
Re	μg l <sup>-1</sup>	< 0.01	0.01	< 0.01	0.01	30
Rh	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Ru	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
Sb	μg l <sup>-1</sup>	< 0.05	0.98	< 0.05	0.47	30
Sc	μg l <sup>-1</sup>	1.19	2.99	1.58	2.50	30
Se	μg l <sup>-1</sup>	0.5	2.50	0.65	1.87	56
Sm	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
Sn	μg l <sup>-1</sup>	< 0.05	0.21	0.07	0.18	30
Sr	μg l <sup>-1</sup>	142	2680	233	1407	31
Та	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
Tb	μg l <sup>-1</sup>	< 0.01	< 0.01	< 0.01	< 0.01	30
Те	μg l <sup>-1</sup>	< 0.05	0.10	< 0.05	< 0.05	30
Th	μg l <sup>-1</sup>	< 0.05	< 0.05	< 0.05	< 0.05	30
Ti	μg l <sup>-1</sup>	<10	<10	<10	<10	30
TI	μg l <sup>-1</sup>	< 0.01	0.04	0.01	0.03	30
Tm	μg l <sup>-1</sup>	< 0.02	< 0.02	< 0.02	< 0.02	30
U	μg l <sup>-1</sup>	< 0.05	0.50	0.24	0.43	30
V	μg l <sup>-1</sup>	<1	<1	<1	<1	30
W	μg l <sup>-1</sup>	< 0.1	<0.1	< 0.1	<0.1	30
Y	μg l <sup>-1</sup>	< 0.01	0.06	< 0.01	0.05	30
Yb	μg l <sup>-1</sup>	< 0.01	0.01	< 0.01	< 0.01	30
Zn	μg l <sup>-1</sup>	0.8	145	6.40	80.5	30
Zr	μg l <sup>-1</sup>	< 0.5	< 0.5	< 0.5	< 0.5	30

#### 5.4 Minor and trace elements

A combination of circum-neutral pH and oxidising conditions means that the solubilities of many trace metals are limited in the groundwaters of the Dorset Chalk. Iron and Mn are in most cases below detection limit. The trace metals Ni, Zn and Cu are important trace elements in the Chalk and are present at concentrations roughly one order of magnitude higher than Mn and Co. In the confined part of the aquifer concentrations of Fe and Mn are relatively high and exceed 100 and  $1\mu g l^{-1}$  respectively in the deeper confined groundwaters.

#### 5.5 **Pollution indicators**

Three indicator organics (atrazine, chloroform and trichloroethylene) are used here to indicate the scale of any unequivocal modern contamination. Atrazine was detected at two sites (both springs) at approximately twice the detection limit. Chloroform was detected in three different springs at up to 8 times the detection limit and in one borehole at twice the detection limit. Trichloroethylene was detected at one site (same as the chloroform) at just above the detection limit. Nitrate median concentrations are high (6.65 mg  $l^{-1}$ ) and indicate human influence from agriculture.

	Units	Bulbarrow Farm	Winterbourne Abbas	Lulworth Spring	Eagle Lodge BH2a	Woodsford Farm	Stoborough
Locality		Farm borehole	Public supply raw water	Spring	Public supply	Farm borehole	Deep borehole
Т	°C		11.6	11.4		11.4	15
pН		7.38	7.23	7.42	7.13	7.02	7.5
DO	mg l <sup>-1</sup>	5.3	9.6	6.5	5.7	0	0
SEC	μS cm <sup>-1</sup>	492	558	584	586	343	683
Ca	mg l <sup>-1</sup>	87.8	110	94	114	23	60
Mg	mg l <sup>-1</sup>	1.73	2.28	3.82	2.57	2.24	17.2
Na	mg l <sup>-1</sup>	8.4	12.1	23	13.3	9.3	63
K	mg l <sup>-1</sup>	0.9	1.8	1.9	2.3	0.25	3.3
Cl	mg l <sup>-1</sup>	15.2	20.3	36.6	22.2	22.7	85
SO <sub>4</sub>	mg l <sup>-1</sup>	12.3	13.5	13.3	15.3	32.4	8
HCO <sub>3</sub>	mg l <sup>-1</sup>	214	249		271	107	277
NO3-N	mg l <sup>-1</sup>	3.31	7.9	6.31	7.64	< 0.1	< 0.1
NH <sub>4</sub>	mg l <sup>-1</sup>	0.0047	< 0.003	0.0045	0.0072	0.0063	0.14
DOC	mg l <sup>-1</sup>	0.5	0.91	1.44	0.94	0.87	1.95
F	mg l <sup>-1</sup>	0.064	0.08	0.087	0.07	0.09	
Si	mg l <sup>-1</sup>	6.8	4.22	4.38	4.69	3.3	
Ba	μg l <sup>-1</sup>	5.5	7.4	8.2	11.9	11.7	
Fe	mg l <sup>-1</sup>	< 0.005	< 0.005	< 0.005	< 0.005	20	0.25
Li	μg l <sup>-1</sup>	3.0	0.8	0.7	0.8	11.1	
Mn	μg l <sup>-1</sup>	1.94	< 0.04	< 0.04	< 0.04	555	< 0.04

Table 5.2Representative analyses of groundwater from Dorset. The locations are shown in<br/>Figure 4.1 (Woodsford Farm and Stoborough are confined).



Figure 5.2a Boxplot for major elements in the Chalk aquifer of Dorset. Black line within box represents the median and the blue line is the mean.



Figure 5.2b Boxplot of minor and trace elements in the Chalk aquifer of Dorset. Grey line is the detection limit for samples collected during the study.



Figure 5.3a Cumulative probability plots for major elements in Dorset Chalk groundwaters.



Figure 5.3b Cumulative probability plots for selected minor and trace elements in Dorset Chalk groundwaters.



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. NO<sub>3</sub> 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.

#### 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 problem in baseline 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 foreign 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 stressed that it is impossible to quantify this. However, traces of contamination may have little impact on the overall chemistry of the groundwater.

# 6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

#### 6.1 Introduction and major element controls

The natural baseline characteristics of the Dorset groundwaters can be further explained with reference to the trilinear diagram (Figure 6.1) and with reference to two cross sections through the area (Figures 6.2 - 6.3), one from Powerstock in the west to Wareham in the east and the second from Wool and, to the north of Bulbarrow Down, to Lulworth.

Two trilinear diagrams have been shown. First as a plot of the Dorset data (Figure 5.1) used in the report and then a cation diagram in which all other data from Dorset (as well as Berkshire for reference) are plotted (Figure 6.1). These data are taken from additional sources obtained from work carried out by BGS. Almost all groundwaters have a similar cation composition dominated by calcium. This is clear evidence that the main control is the initial (congruent) solution of chalk as recharge enters the soil zone and unsaturated zone since values are only slightly enriched in Mg compared with the chalk itself. Some slight increase in Mg in dilute groundwaters may be due to the influence of the rainfall (Table 3.1). As the groundwaters evolve with depth an increase in Na is seen as well as an increase in Mg due to incongruent solution.

The cation trilinear plot (Figure 6.1) shows how the samples in the present survey relate to waters at depth. The increase in Mg (and Mg/Ca ratio) is indicative of increasing residence time as observed in Berkshire (Edmunds et al., 1987) and can be explained by continuous reaction between groundwater and the rock (Box 6.1). Thus the groundwater beneath Wareham (and Stoborough) are the oldest groundwaters in the area on the basis of their Mg/Ca ratio.



Figure 6.1 Trilinear cation plot showing the relative proportions of major cations in Chalk groundwaters.

#### 6.2 Downgradient evolution

Downgradient trends, which help to illustrate some of the controls, are shown for two lines of crosssection (Figures 6.2 and 6.3) for selected parameters. Groundwater chemistry evolution within the chalk aquifer is a function of 3D spatial and temporal distribution as well the geological variations such as changes in lithological facies. These plots show the changes down hydraulic gradient towards the coast (Poole Harbour and Lulworth) from the upland areas of outcrop. Some of the distance (and time) variations will be complicated as a result of differences in sample depth, which are not shown. The lines of section commence in unconfined Chalk but show the evolution towards the deeper confined aquifer. Most boreholes are in the range of 30 - 100 m in depth and some springs are also included. On the diagram the springs (s) are indicated, as are the two deepest boreholes at Dorchester Hospital (DH) and Eldridge Pope Brewery (EP). The latter might be expected to be the most "evolved" of the unconfined set of groundwaters.

Chloride is inert and is likely to have its source in rainfall, ancient formation waters (old sea water for example) or from contaminant sources. The section from Woolland to Lulworth spring clearly shows an increase towards the coast from 16 to about 40 mg l<sup>-1</sup> Cl. Although no local values exist for rainfall chemistry these trends are consistent with a source from water infiltrating from evaporated rainfall (Table 3.1). The same background values are seen in the west-east section, but slightly higher Cl is seen in the deepest samples from Dorchester (Eldridge Pope) which suggests that a small component of deeper, older water is incorporated. Some of the groundwater in the confined aquifer also has higher Cl, indicating that the older water contains traces of salinity derived from the chalk formation waters. Further evidence of the sources of the Cl is given by the Br/Cl ratios. The low Cl waters all have ratios slightly above those for sea water, which is a feature of rainwater (Edmunds, 1997). A source other than rainfall for Cl is suggested by the Br/Cl from the deeper two waters in Dorchester which have higher Br (one with higher I also). This enrichment normally suggests an organic rich source. However the origin of this Cl is not clear. The confined groundwaters have relatively high Cl with depleted Br/Cl ratios suggesting a residual formation water.

#### Box 6.1 Reaction of Carbonate Minerals in Chalk

The concentrations of  $H^+$  (pH), HCO<sub>3</sub>, Ca and Mg in Chalk groundwaters are all closely related by the following reaction which represents how rainwater, assisted by CO<sub>2</sub> produced microbiologically in the soil reacts with (impure) chalk. Although the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in the atmosphere is quite low it may increase by up to 100 passing through the soil; variable soil types may yield different pCO<sub>2</sub> values and HCO<sub>3</sub> concentrations in recharging water.

$$Ca(Mg)CO_3 + H_2O + CO_2 = Ca^{2+} + (Mg^{2+}) + 2HCO_3$$

The above reaction (congruent dissolution) is rapid, taking place in the top few metres of the Chalk. Once saturation with respect to calcite is reached no further calcite will dissolve rapidly. Congruent dissolution yields Ca and Mg concentrations which are identical to those in the dissolving chalk. However with passage of time, in waters which are in equilibrium with the chalk, a second process (incongruent dissolution) may occur where the impurities (e.g. Mg) in the Chalk are slowly released and a purer calcite left behind. In this process the Mg/Ca ratio in groundwater progressively increases with time.

The concentrations of sulphate (median 14 mg  $l^{-1}$ ) are in excess of those from rainfall (c. 3 - 4 mg  $l^{-1}$ ) and are likely to represent an increase from a geological or pollution source. It is apparent that the two deepest groundwaters at Dorchester also have high SO<sub>4</sub> and so a geological origin is suggested. The SEM sections (Figure 3.3) indicate that gypsum derived from the oxidation of pyrite may be present

in the aquifer at intermediate depths. Sulphate in the deeper confined groundwaters does not increase (in fact a slight decrease in the older waters may be due to sulphate reduction).

Dissolved oxygen and nitrate are used here to illustrate the redox (oxidation – reduction; Box 6.2) characteristics of the groundwaters. Dissolved oxygen concentrations are uniformly high in the unconfined groundwaters (overall median value of 7.6 mg  $\Gamma^1$ ). These values represent a loss of only 30-40% of oxygen from atmospheric values. Slightly lower concentrations are found in one of the Dorchester deep groundwaters (3 mg  $\Gamma^1$  DO). There is a distinct change in the oxygen concentrations near the unconfined/confined contact. To the east of this point, termed a "redox boundary", the groundwaters are reducing as they become confined. Once the oxygen has been consumed, the nitrate is then reduced very quickly. The nitrate concentrations are uniformly high across the unconfined aquifer, even at two deeper sites near Dorchester. This suggests that contamination from agricultural sources is universal. It is of interest that the lowest NO<sub>3</sub> value is from the area of Bulbarrow Down where the catchment is mainly unfertilised grassland.



The Mg/Ca ratio (see also the trilinear diagram Figure 6.1) and fluoride concentrations can also be used to interpret the hydrogeochemical evolution across the aquifer. Low values of Mg/Ca and fluoride concentrations at or below 100  $\mu$ g l<sup>-1</sup> characterise the unconfined groundwaters. Slightly

higher Mg/Ca and also F from one site are found for the deeper Dorchester boreholes, supporting the idea that the deeper waters are more evolved and therefore older. A slight increase in both Mg/Ca and F can be detected along the lines of flow being a sign that slightly older water is being entrained during down-gradient flow. This effect is then shown very clearly in the deeper confined (although still fresh) groundwaters beneath Wareham. These indicators provide clear distinction, here as elsewhere in the UK, of modern Chalk groundwater.

As an example of trace element behaviour, uranium concentrations are shown for both lines of section. Uniform concentrations are found between 0.1 and 0.4  $\mu$ g l<sup>-1</sup> in the oxidising (unconfined) groundwaters and are believed to represent a true baseline concentration resulting from reaction with the chalk matrix. In contrast the U concentrations are below detection limit in the reducing groundwaters.

The variations, and geochemical processes operating along the general flow direction need to be considered at a more regional scale. The spatial distribution of selected elements is shown on Figure 6.4 which highlights the redox control of species such as NO<sub>3</sub>, and provides an indication of the scale of heterogeneity within the aquifer.

## 6.3 Depth Profiles

The samples obtained from pumping boreholes and springs are typically mixtures of water from different flow lines and depths and represent the average chemical composition of the groundwater in large volumes of the aquifer. It is possible to obtain improved information on any stratification in chemistry or age from samples taken either from interstitial waters (waters contained in the rock pores) or from depth samples taken from the borehole water column. Interstitial waters are obtained by high-speed centrifugation (either gravity drainage or displacement by an immiscible heavy liquid) and allow continuous detailed chemical profiles to be built up. Examples are available from Dorset of interstitial water profiles taken from both the unsaturated and saturated zones as well as borehole depth profiles of conductivity and temperature which have provided the basis for depth sampling for chemistry.

#### 6.3.1 Interstitial waters in the unsaturated zone

Interstitial water samples are available (Geake and Foster, 1989) for a borehole drilled beneath rough grassland at Gussage (SY 9938 1094). This was drilled in 1977 and 1979 at a site previously cored in 1970 to provide an indication of the rate of movement of water through the unsaturated zone (Figure 6.5). The radioactive isotope tritium which was produced during the thermonuclear (hydrogen bomb) testing in the 1960s acts as a tracer for the water molecule, with a maximum concentration occurring in 1963. The three peaks illustrate how the 1963 tritium "peak" (which undergoes radioactive decay) has moved down the profile and in turn how both water and solutes may move towards the water table. The preservation of the peak, although decreasing by radioactive decay with time, indicates that the bulk of the water moves downwards in a piston movement although undergoing some dispersion. The displacement of the peak with time indicates that the bulk of the water table at approximately 1 m yr<sup>-1</sup>. Nevertheless it has also been shown that at some locations where larger fractures occur, some by-pass flow takes place allowing a fraction of the water to move more rapidly. No chemical data are available for the Gussage site, but elsewhere in southern England, the slow transfer of nitrate together with sulphate beneath agricultural land has been shown (Foster et al., 1982).



Figure 6.2a Major and minor element characteristics of the Chalk groundwaters along a line of flow from Powerstock to Wareham (line 1 on Figure 3.1).



Figure 6.2b Major and minor element characteristics of the Chalk groundwaters along a line of flow from Powerstock to Wareham (line 1 on Figure 3.1).



Figure 6.3a Major and minor element characteristics of the Chalk groundwaters along a line of flow from Woodland to Lulworth (line 2 on Figure 3.1).



Figure 6.3b Major and minor element characteristics of the Chalk groundwaters along a line of flow from Woodland to Lulworth (line 2 on Figure 3.1).







# Figure 6.5 Sequential tritium profiles from the unsaturated zone of the Dorset Chalk (from Geake & Foster, 1989).

#### 6.3.2 Interstitial waters in the saturated zone

Interstitial waters from a research borehole at West Lulworth, drilled during the late 1970s to a depth of -170 m OD provide a very detailed profile of the changes in the water quality with depth (Figure 6.6). Temperature and electrical conductivity (SEC) logs subsequently carried out in 1997 provide an additional control on the groundwater flow and chemistry at this site. It can be seen that the base of the present-day flow system is at approximately –65 m OD as defined by the temperature profiles. Below this depth, the temperature increases linearly in line with the geothermal gradient; above this water temperature is disturbed by flow. A slight decrease in fluid conductivity is recorded with depth below -65 m OD indicating that the Chalk contains freshwater to its total depth. This is in line with deeper penetration of freshwater found elsewhere near the coastline of southern England (see below).



Figure 6.6 Interstitial water chemistry, temperature and SEC profiles from the research borehole at West Lulworth.

Higher nitrate concentrations between 5 and 15 mg  $l^{-1}$  NO<sub>3</sub>-N are found above -65 m confirming the penetration depth of modern groundwater. Below this depth, nitrate concentrations are detectable and are in the range 0 to 2 mg  $l^{-1}$ . No radiocarbon data are available for this water, but stable isotope results indicate a modern signature. Some suggestion of a more mature water is indicated by higher Sr and Na in the pore water profile at a depth below -140 m. It is probable that groundwater below – 65 m OD to the total depth (-170 m) represents slower moving water of early Holocene age, (some 8-10 000 yr before present (BP)), comparable to that found in the South Downs and which remains separate from the main groundwater circulation of the present day. This water represents a good reference for the baseline composition for some elements for the Chalk of the area. Summary analyses of interstitial groundwater from the deeper section (uncontaminated by modern circulation) are given in Table 6.1.

Confined groundwater in the Chalk aquifer beneath Poole Harbour is relatively fresh (<1000  $\mu$ S cm<sup>-1</sup> down to a depth of at least -240 m OD in the Stoborough borehole). Fluid temperature logging in the basin suggests that present day groundwater circulation in the Chalk aquifer exists down to a depth of -170 to -180 m OD. This is considerably deeper than elsewhere along the South Coast and is believed to be controlled by the local geological structure. Interstitial waters from terminal cores taken from

Stoborough and Wareham boreholes indicate that fresh water occurs to depths of -250 m OD and with only minor evidence of any salinity derived from the sea or from residual saline formation water. The original saline formation water could have been expelled from the sediment during the Alpine folding, which affected this part of Britain 20–40 million years ago. However detectable radiocarbon of 1-2 pmc (per-cent modern carbon) in these samples implies that some of the freshwater is late Pleistocene in age.

Representative analyses of the groundwater from beneath Wareham are shown in Table 3 (Stoborough borehole). The evolved geochemical characteristics of the water (high F, Sr and enriched <sup>13</sup>C) confirm that despite the freshness, the water is of considerable age.

Parameter	Depth (m bgl)				
	69.6	104.9	125.1		
рН	7.40	7.84	7.58		
<b>Ca</b> (mg l <sup>-1</sup> )	67	70	68		
Mg (mg l <sup>-1</sup> )	2.1	1.8	2.0		
Na (mg l <sup>-1</sup> )	23	22	21		
$K (mg l^{-1})$	2.7	1.0	1.3		
$HCO_3 (mg l^{-1})$	179				
Cl (mg l <sup>-1</sup> )	27	34	35		
$NO_3-N (mg l^{-1})$	1.2	7.1	3.6		
<b>Sr</b> (mg l <sup>-1</sup> )	0.30	0.24	0.25		

Table 6.1	Representative	analyses	of	interstitial	groundwater	from	the	West	Lulworth
	borehole.								

#### 6.4 Age of the groundwater

Several indicators are available to help understand the residence time of water in the Chalk: the seasonality of springs, records of tritium, the presence of contaminants introduced by man since the industrial era, as well as radiocarbon dating for the older groundwaters. The ratios and absolute concentrations of major or trace elements also gives an indication. The groundwater originally had a natural age distribution but this has inevitably been disturbed by pumping with water moving preferentially towards abstraction areas, distorting the age structure.

Most spring waters are likely to contain a mixture of age components. The oscillations at Litton Cheney (Figure 6.7) illustrate that some short-term component (residence time of weeks or months) contributes to flows. Tritium measured in the unsaturated zone suggests that groundwater moves toward the water table at approximately 1 m yr<sup>-1</sup> and that water at the immediate water table will therefore have an age proportional to the depth of the unsaturated zone typically measured in decades. In areas of the Chalk with strong fracture systems, for example along valleys, preferential, more rapid, flow may occur. The presence of high nitrate concentrations in most of the Chalk outcrop areas (and the rising concentrations in springs and boreholes) supports these observations and the influence of agricultural practices over the past 40-50 years, involving high rates of agrochemical application, is observed.



# Figure 6.7 Temporal variations in hydrochemical parameters in the Litton Cheney Spring (NGR 355000 090800).

Older, fresh groundwater is found in the confined aquifer which contains traces of radiocarbon. There are problems in assigning an age to this groundwater, but the indications are that beneath Wareham the bulk of the Chalk waters to a depth of -300 m OD are of Holocene age.

#### 6.5 Temporal variations

Long term data sets are not widely available from the region in general and it is feared that much of the time series data from public supply wells prior to the 1980s has not survived. However, some records have been identified from the Sutton Poyntz spring dating back to the late 19<sup>th</sup> century as well as from the breweries in Dorchester and Blandford Forum. Data used here are taken for selected parameters over the past two decades from two sites Litton Cheney and West Houghton (Figures 6.6 and 6.7).



Figure 6.8 Temporal variations in hydrochemical parameters from West Houghton (NGR 382300 045000).

The Litton Cheney spring lies at the western end of the region and has been monitored at least monthly since 1992, although with lesser frequency since mid 1996. The specific electrical conductance (SEC) is a sensitive indicator of the overall change in the total mineralisation of the spring. Two observations may be made. Firstly, there is a seasonality in the conductivity with higher values (up to 100  $\mu$ S cm<sup>-1</sup> higher) in the summer than in the winter months. This reflects the relatively short residence time of the water (probably weeks or months) and the influence of more dilute water (with shorter residence time) coming through at times of higher rainfall and also showing that evapotranspiration has the effect of concentrating the water composition. It is then apparent that there is no perceptible overall trend in SEC over the seven year period. Seasonality may also be detectable in the Cl data and this also suggests that the extent of evaporative effects are higher in summer, the Cl being derived from rainfall. There is also a small but significant increase in Cl over the time period. Sulphate also follows the same subdued seasonal pattern but with no overall increase with time. Nitrate in contrast shows both a strong seasonality as well as an increase from 4 to just below 6 mg  $l^{-1}$ NO<sub>3</sub>-N over the measurement period, most probably linked to the increase in arable farming activity and nitrate loading. The seasonality seen here is likely to be related to water level variation, the highest NO<sub>3</sub>-N occurring at time of highest water level. The lowest values probably do not represent the lowest (baseline) values for the Chalk and records back to pre-war time would be needed to investigate this. The DOC (dissolved organic carbon) concentrations remain relatively constant over the measurement period at about  $0.6 \text{ mg l}^{-1}$ . It is interesting that a spike in both DOC and NO<sub>3</sub>-N occurs in late 1994. This may indicate a pollution incident.

A 17-year record is available for a limited number of parameters for a shallow borehole at West Houghton fish farm (Figure 6.8). The Cl record here shows no significant increase over the measurement period. The initial data seem rather noisy and this is attributed to analytical problems. The mean value for this inland site (16 mg l<sup>-1</sup> Cl) is about 5 mg l<sup>-1</sup> lower than for Litton Cheney reflecting the decrease in maritime influence. Nitrate also increases at this location from around 2.5 to 5 mg l<sup>-1</sup> over the measurement period, although for this borehole no clear seasonality is seen. For this site there is also a record of dissolved oxygen which shows some oscillation with time. This has no obvious explanation but strongly aerobic conditions are maintained over the whole period.

Miscellaneous records are available in BGS files dating back to the immediate post-war period. Of relevance is analysis of nitrate (1.5 mg  $l^{-1}$  NO<sub>3</sub>-N) at Alton Pancras new borehole (1946). Further data are available back to the early 20<sup>th</sup> century (Whitaker and Edwards, 1926) and a summary of these is given in Table 6.2.

Site	Date	Nitrate NO3-N (mg l <sup>-1</sup> )	Cl (mg/l)
Corfe Mullen well	1908	1.0	30
Durweston	1911	1.3	17
Upwey	1910	0.88	23
Sutton Poyntz	1913	0.73	19

 Table 6.2
 Summary information from archive data taken from BGS records

## 7. BASELINE CHEMISTRY OF THE AQUIFER

Dorset is a type location for demonstrating groundwater quality evolution in the UK Chalk in the context of the present baseline studies. It is exposed to the influence of the prevailing westerly winds and rainfall recharge, and it lies in an area mainly free of any major urban or industrial influences. It is however an area which contains a high proportion of arable farmland. A high proportion of water supply is derived from groundwater, although compared to other regions of the UK the demands on the aquifer are not stressed (i.e. abstraction does not exceed recharge), although in the River Piddle catchment there is evidence of abstraction adversely affecting spring flows.

The main aspects of baseline quality can be summarised with reference to the cross section (Figure 7.1). Rainfall chemistry influences are apparent in generating the chemical background of inert constituents such as Cl; this influence is apparent in the groundwater as a gradual reduction in Cl concentrations away from the coast. The baseline quality for several other elements such as F is also likely to be influenced by rainfall after allowing for evapotranspiration. The main control on the baseline quality is the geochemistry of the chalk sediment. Water interacting with the chalk produces a hard water where Ca predominates over all other cations, HCO<sub>3</sub> being the main anion. Variations in the natural chemistry also take place with increasing residence time and due to redox changes as groundwater moves beneath the Tertiary cover. High natural concentrations of Fe, Mn and F may be found in the deeper freshwaters, not currently used for water supply purposes. In general, the residence time of groundwaters in the Dorset Chalk can be measured in decades, although this is of the order of several months for flow to springs. Nevertheless Fresh groundwater occurs at depth in the Chalk beneath the Palaeogene sediments extending beneath Poole harbour with a residence time of thousands of years.



# Figure 7.1 Conceptual diagram of the Chalk aquifer of Dorset highlighting the main geochemical processes controlling water quality.

The natural baseline is represented by a range of values for any given element, these being controlled by climatic and geological factors. Human impacts are mainly visible in the presence of indicator contaminants such as nitrate and artificial organic chemicals and it is very difficult to discern any effects of human activity in other compounds. As far as nitrate is concerned, evidence from pore waters at depth (Lulworth borehole) and from the inspection of old records, indicates that baseline concentrations were below 2 mg  $l^{-1}$  NO<sub>3</sub>-N and most probably around 1 mg  $l^{-1}$ , before the onset of intensive farming in the latter half of the 20<sup>th</sup> century. Nitrate is highly mobile and its widespread

presence at concentrations well above the baseline value, increasing progressively over the past two decades, indicates the extent to which the aquifer is now influenced by farming practices. Trace organic compounds are only detected locally in spring samples and are likely to be less mobile than nitrate, having undergone degradation or adsorption. The effect on the overall chemical quality is more difficult to demonstrate, although the increase in potassium concentrations (and K/Na ratios, Figure 7.2) may be shown to relate to agricultural inputs rather than to natural geochemistry. Some increase in sulphate may also be due to human impacts although in Dorset no clear evidence is available to support this.

The summary table and the different plots included in the report show ranges and values for the wide range of chemical elements and constituents considered in the study. These may be used for reference purposes in different applications. The report includes all the common elements plus most of those ranked as potentially hazardous by water quality (EC) guidelines. In addition data are summarised for a wide range of potential contaminants which may be of natural or introduced origin. The median value may be used as a reference value for purposes of comparison, but it is stressed that the baseline range may extend within the 5 to 97.7 percentile range, over an order of magnitude for some elements, as a result of purely natural geochemical processes. It is found that individual values for NO<sub>3</sub>, F, Fe, Mn may exceed the maximum permissible concentrations for drinking water in some waters. Of these, F, Fe and Mn are generally of natural origin. The estimation of "baseline" concentrations is of considerable strategic importance as it provides a value against which quality problems and associated remedial measures may be assessed. Several elements in this category are highly toxic (e.g. Ti, Be) but their natural abundance and mobility is very low.



Figure 7.2 Plot of Na vs. K in Dorset Chalk groundwaters showing the increase in K and K/Na ratio due to pollution.

In conclusion, it is confirmed that the groundwater quality in Dorset is overwhelmingly controlled by natural reactions between rainwater and the Chalk, following which further geochemical evolution takes place along flow pathways. It is also clear, however, that the influence of diffuse pollution from agriculture is widespread, especially in the build up of nitrate above a low baseline of around 1 mg  $l^{-1}$ .

## 8. SUMMARY AND CONCLUSIONS

- The Chalk aquifer of Dorset contains predominantly very high quality groundwater. The main properties are determined by natural reactions between rainwater reacting with the carbonate rock.
- Nevertheless, the impact of agricultural activities are widely observed on the groundwater quality. The main impact is the rise in nitrate concentrations to values exceeding 5 mgl<sup>-1</sup>, above a baseline value of approx. 1 mg l<sup>-1</sup>, before the modern intensive farming commenced after the second world war. The impacts of farming are also seen in the potassium concentrations in groundwater.
- No evidence has been found of widespread contamination from point sources or urban environments affecting the regional water quality.
- Within the unconfined aquifer the conditions are aerobic. Reducing conditions are found beneath the confining Tertiary cover. The confined groundwaters are typically fresh and of pristine quality.
- The study provides baseline information of a strategic value for around 90 parameters, mainly inorganic constituents as an aid to future water quality management of the aquifer.

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