Baseline Report Series:
10. The Chalk Aquifer of Yorkshire and North Humberside

Groundwater Systems and Water Quality
Commissioned Report CR/04/128

Environment Agency Science Group
Technical Report NC/99/74/10

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/04/128

ENVIRONMENT AGENCY
Science Group: Air, Land & Water
Technical Report NC/99/74/10

Baseline Report Series: 10. The Chalk Aquifer of Yorkshire and North Humberside

P L Smedley, I Neumann and R Farrell*

Contributors
R Hargreaves, C J Milne, D Chadha* and M Morton*

Environment Agency Dissemination status
Internal: Release to Regions
External: Public Domain
ISBN: 978-1-84432-635-8
Product code: SCHO0207BLYH-E-P

Statement of use
This document forms one of a series of reports describing the baseline chemistry of selected reference aquifers in England and Wales.

Cover illustration
Upper Chalk exposure on Flamborough Head, Yorkshire coast, with cliffs of Selwicks Bay in the background (©NERC 2004).

Key words
Baseline, Chalk, Yorkshire, Humberside, water quality, hydrogeochemistry, UK aquifer.

Bibliographic Reference
Smedley, P.L., Neumann I. and Farrell, R. 2004 Baseline Report Series 10: The Chalk aquifer of Yorkshire and North Humberside
British Geological Survey Commissioned Report No. CR/04/128

Environment Agency Project Manager:

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

British Geological Survey Project Manager:

Dr Paul Shand
Groundwater Systems & Water Quality Programme

Environment Agency Science Group, Solihull 2004
British Geological Survey, Keyworth, Nottingham 2004

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from BGS Sales Desk at the Survey headquarters, Keyworth, Nottingham. The more popular maps and books may be purchased from BGS-approved stockists and agents and over the counter at the Bookshop, Gallert 37, Natural History Museum, (Earth Galleries), Cromwell Road, London. Sales Desks are also located at the BGS London Information Office, and at Murchison House, Edinburgh. The London Information Office maintains a reference collection of the BGS publications including maps for consultation. Some BGS books and reports may also be obtained from the Stationery Office Publications Centre or from the Stationery Office bookshops and agents.

The Survey publishes an annual catalogue of maps, which lists published material and contains index maps for several of the BGS series.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG
☎ 0115 936 3100 Telex 378173 BGSKEY G
Fax 0115 936 3200
e-mail: sales@bgs.ac.uk www.bgs.ac.uk

Murchison House, West Mains Road, Edinburgh, EH9 3LA
☎ 0131 667 1000 Telex 727343 SEISED G
Fax 0131 668 2683

London Information Office at the Natural History Museum, Earth Galleries, Exhibition Road, South Kensington, London, SW7 2DE
☎ 0207 589 4090 Fax 0207 584 8270
☎ 0207 938 9056/57

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

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS
☎ 01232 666595 Fax 01232 662835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB
☎ 01491 838800 Fax 01491 692345
email: hydro@bgs.ac.uk

Parent Body
Natural Environment Research Council
Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU
☎ 01793 411500 Telex 444293 ENVRE G
Fax 01793 411501

ENVIRONMENT AGENCY

The Environment Agency is the leading public body protecting and improving the environment in England and Wales.

It's our job to make sure that air, land and water are looked after by everyone in today's society, so that tomorrow's generations inherit a cleaner, healthier world.

Our work includes tackling flooding and pollution incidents, reducing industry's impacts on the environment, cleaning up rivers, coastal waters and contaminated land, and improving wildlife habitats.

Environment Agency, Rio House, Waterside Drive, Aztec West
Almondsbury, Bristol, BS32 4UD
Tel: 01454 624400 Fax: 01454 624409
www.environment-agency.gov.uk

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

Environment Agency Regional Offices

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

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

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

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

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

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

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

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

Contents

FOREWORD v

BACKGROUND TO THE BASELINE PROJECT vii

1. EXECUTIVE SUMMARY 1

2. PERSPECTIVE 2
    - 2.1 Study area 2
    - 2.2 Current issues in groundwater quality 3

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY 4
    - 3.1 Introduction 4
    - 3.2 Regional geography 4
    - 3.3 Geology 5
    - 3.4 Hydrogeology 9
    - 3.5 Aquifer mineralogy 11
    - 3.6 Rainfall chemistry 12
    - 3.7 Land use 13

4. DATA AND INTERPRETATION 15
    - 4.1 Data sources 15
    - 4.2 Data quality and handling 16

5. HYDROCHEMICAL CHARACTERISTICS 17
    - 5.1 Introduction 17
    - 5.2 Major constituents 19
    - 5.3 Trace elements 21

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS 25
    - 6.1 Introduction 25
    - 6.2 Regional variations and controls 26
    - 6.3 Transect across the aquifer 36
    - 6.4 Temporal variations 39
    - 6.5 Depth variations 40
    - 6.6 Age of the groundwater 41

7. BASELINE CHEMISTRY OF THE AQUIFER 44

8. SUMMARY AND CONCLUSIONS 45

9. REFERENCES 47

ACKNOWLEDGEMENTS 50

List of Figures

Figure 2.1. Map of the study area showing principal rivers and towns and the regional extent of the Chalk aquifer. 2
Figure 3.1 View south-east to Flamborough Head, Yorkshire, showing sea stacks and landslips of Selwick's Bay (photography: K E Thornton). 4
Figure 3.2 Geological map of Yorkshire and North Humberside showing the Chalk outcrop and distribution of superficial Drift deposits. 6
Figure 3.3 Geological cross section through the Chalk and superficial sediments of Yorkshire. The line of section runs approximately east-west. 8
Figure 3.4. Artesian spring on the margins of the Drift deposits [TA 030 461], close to Scorborough. The spring was sampled by BGS in December 2002. 10
Figure 3.5. Map of land use in the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology & Hydrology, ©NERC. 13
Figure 5.1. Piper diagram for the groundwater samples investigated in this study. Red circles: oxidising groundwaters, blue circles: reducing groundwaters. 19
Figure 5.2. Box-and-whiskers plots showing the ranges of major constituents in (a) oxidising and (b) reducing groundwaters of the Yorkshire Chalk. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration). 20
Figure 5.3. Box-and-whiskers plots showing the ranges of minor constituents in (a) oxidising and (b) reducing groundwaters of the Yorkshire Chalk. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration); grey line: typical detection limits. Legend as in Figure 5.2. 21
Figure 5.4. Cumulative-frequency plots for the major constituents in the oxidising groundwaters of the Yorkshire Chalk. 23
Figure 5.5. Cumulative-frequency plots for the major constituents in the reducing groundwaters of the Yorkshire Chalk. 23
Figure 5.6. Cumulative frequency plots for the minor constituents in the oxidising groundwaters of the Yorkshire Chalk. 24
Figure 5.7. Cumulative frequency plots for the minor constituents in the reducing groundwaters of the Yorkshire Chalk. 24
Figure 6.1. Regional variation in pH of groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 27
Figure 6.2. Regional variation in Cl in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 28
Figure 6.3. Regional variations in SO_4 in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 29
Figure 6.4. Regional variation in NO_3-N in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 30
Figure 6.5. Variation of Cl and SO_4 with NO_3-N in aerobic (unconfined and semi-confined) groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 31
Figure 6.6. Regional variations in K in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 31
Figure 6.7. Regional variations in Fe in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 32
Figure 6.8. Regional variations in As in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 33
Figure 6.9. Regional variations in P in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 34
Figure 6.10. Regional variations in U in groundwaters from the Chalk aquifer of Yorkshire and North Humberside. 35
Figure 6.11. Variation in major ions in groundwater in a west-east transect across the Chalk aquifer (Etton to Hornsea). Vertical line marks the redox boundary. 37
Figure 6.12. Variation in trace elements in groundwater in a west-east transect across the Chalk

aquifer (Etton to Hornsea). Vertical line marks the redox boundary. 38
Figure 6.13. Variation in stable isotopic compositions in groundwater in a west-east transect across the Chalk aquifer (Etton to Hornsea). Vertical line marks the redox boundary. 39
Figure 6.14. Variation in NO_3-N, Cl and SO_4 in depth samples (mbgl) from Etton boreholes. Etton C is an observation borehole; only Etton 4 was pumping at the time of sampling. The water table during sampling was ca. 29 m below ground level. 41
Figure 6.15. Variation in $\delta^{18}O$ with Cl in the Chalk groundwaters. The freshwater-seawater mixing line is shown for comparison. Samples in green are from the eastern part of the confined aquifer (Holderness and Brandesburton areas) and probably represent older groundwaters. 42

List of Tables

Table 3.1. Lithostratigraphy of the Northern Province (English) Chalk (from Mortimore et al., 2001). 5
Table 3.2. Weighted mean annual solute concentrations in rainfall for 1999 at High Muffles rainfall gauging station, North Yorkshire [4776 4939] (data from AEA, 2003). 12
Table 3.3. Agricultural land use in the study area (data from ADAS and reported by Smedley et al., 1996). 14
Table 5.1. Statistical summary of major constituents in, and isotopic compositions of, groundwaters from the Yorkshire and North Humberside Chalk, divided into oxidising (unconfined and semi-confined) and reducing sections. 17
Table 5.2. Statistical summary of trace elements in groundwaters from the Yorkshire and North Humberside Chalk, divided into oxidising (unconfined and semi-confined) and reducing sections........ 18

FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

In order to interpret the water quality variations in terms of the baseline, some knowledge of the residence times of groundwater is required. For this purpose both inert and reactive chemical and isotopic tracers are essential. Measurement of the absolute age of groundwater presents many difficulties and radiocarbon dating is the most widely used technique. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water may also provide indirect evidence of residence time. The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium (^{3}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) water predating modern agricultural practices (pre 1940s) and (iv) modern post-nuclear-testing era (post 1963).

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

The BASELINE objectives are:

1. to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound geochemical principles, as a basis for defining water quality status and standards in England and Wales (in the context of UK and Europe); also to assess anomalies due to geological

conditions and to formulate a quantitative basis for the definition of groundwater pollution;

2. to characterise a series of reference aquifers across England and Wales that can be used to illustrate the ranges in natural groundwater quality. The baseline conditions will be investigated as far as possible by cross-sections along the hydraulic gradient, in well characterised aquifers. Sequential changes in water-rock interaction (redox, dissolution-precipitation, surface reactions) as well as mixing, will be investigated. These results will then be extrapolated to the region surrounding each reference area. Lithofacies and mineralogical controls will also be taken into account. A wide range of inorganic constituents as well as organic carbon will be analysed to a common standard within the project. Although the focus will be on pristine groundwaters, the interface zone between uncontaminated and contaminated groundwaters will be investigated; this is because, even in contaminated systems, the main constituents of the water are also controlled by geological factors, amount of recharge and natural climate variation;

3. to establish long term trends in water quality at representative localities in the selected reference aquifers and to interpret these in relation to past changes due to natural geochemical as well as hydrogeological responses or anthropogenic effects;

4. to provide a scientific foundation to underpin UK and EU water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high-quality groundwater.

1. EXECUTIVE SUMMARY

Groundwater from the Chalk aquifer of Yorkshire and North Humberside is an important resource for public supply, agriculture and industry. The water chemistry shows some important regional variations, with the main controlling factors being carbonate dissolution/precipitation reactions, redox reactions and in the coastal areas, saline intrusion. Pollutant inputs are also evident in the unconfined aquifer. The Chalk groundwater is generally hard, with Ca and HCO_3 as the dominant ions and pH usually buffered around 7.0 to 7.5 as a result of reaction with the chalk matrix. In the east of the region, variable thicknesses of Drift deposits cover the Chalk. In the Beverley to Driffield area, these are discontinuous and moderately permeable with the result that the underlying Chalk aquifer is semi-confined. Further east of this zone, a fossil Ipswichian cliffline running from Sewerby via Driffield and Beverley to Hessle marks the limit of a much thicker sequence of poorly permeable Drift deposits which confine the Chalk. Both the fossil cliffline and the covering clayey Drift deposits have a major impact on regional groundwater quality. Groundwater in the western unconfined part of the aquifer is aerobic and shows evidence of inputs of pollutants, likely to be principally from agricultural sources. The effects are seen particularly from relatively high concentrations of NO_3-N, Cl and SO_4 and good correlations occur between these three constituents. The highest concentrations are seen in the scarp-slope spring waters which are likely to be in response to rapid shallow flow along fissures. Dip-slope unconfined groundwaters also show evidence of anthropogenic inputs of these compounds but the effects are less extreme. Monitoring of groundwater from the unconfined aquifer over the last few decades indicates that NO_3-N concentrations have been increasing in some sources. In many supply sources, nitrate increases to maximum concentrations during spring when groundwater levels are at their highest following winter recharge. Concentrations of NO_3-N, Cl and SO_4 in the semi-confined groundwaters from the Beverley to Driffield area are low compared to those further west and are believed to reflect more closely natural baseline values for the aerobic sections of the aquifer. South of Beverley however, increased concentrations of NO_3-N (around 9 mg l^{-1}) probably reflect inputs from urban and domestic sources (e.g. septic tanks and leaking sewers).

The fossil cliffline marks the approximate location of a notable redox boundary, beyond which groundwater becomes progressively more reducing with distinct changes in redox-sensitive elements. In the reducing groundwaters, concentrations of NO_3-N diminish significantly whereas Fe, Mn, NH_4-N and As increase. Related increases in P and Mo also occur in the reducing groundwater.

In the low-lying near-coastal parts of the confined aquifer, the groundwater becomes increasingly saline as a result of mixing with seawater. The highest electrical conductivity (SEC) values are found in groundwater from the Holderness peninsula (up to 17 mS cm^{-1}). The age of the seawater end member is unknown but sluggish groundwater movement in the region and combined trace-element and stable-isotopic evidence suggest that it is unlikely to be modern. Saline infiltration in the Holderness peninsula may have occurred at some point during the Holocene when sea level was higher than at the present day.

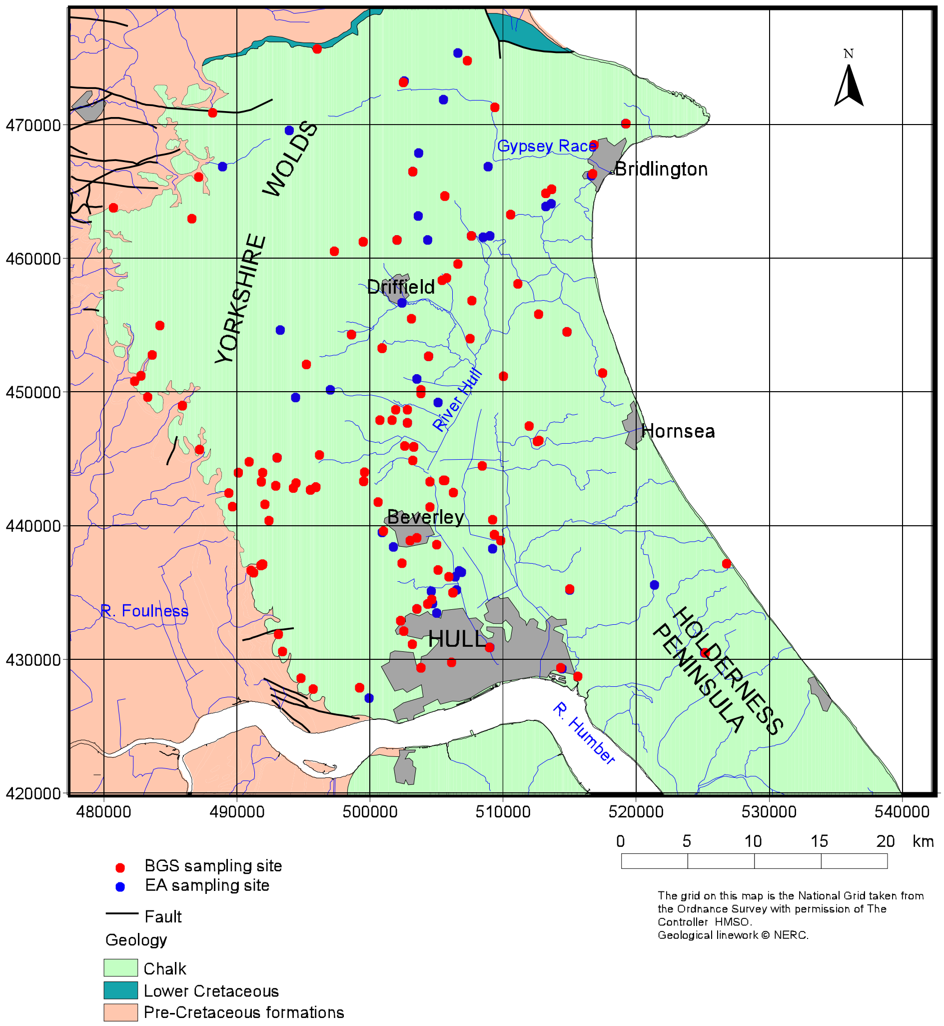
2. PERSPECTIVE

2.1 Study area

This report describes the body of information currently available on the quality of groundwater in the Chalk aquifer of Yorkshire and North Humberside. It has been compiled from BGS databases that result from a number of projects carried out in the region since the 1970s, as well as from Environment Agency data and additional information provided by academic studies (e.g. Elliot et al., 2001).

The region under investigation is the Chalk aquifer to the north of the Humber Estuary which extends between Flamborough Head in the north-east and Spurn Head in the south-east and inland as far as Welton [496 427] and Millington [483 452] (Figure 2.1). The area investigated includes both the unconfined Chalk of the Yorkshire Wolds in the west and the part of the aquifer confined by Drift in the east (Section 3.3).

The Chalk is the most important aquifer for water supply in Britain, and groundwater resources in the region are heavily licensed. At present, the entire public water supply of the region is derived from the aquifer. Significant abstraction occurs from both the confined and unconfined sections of the aquifer. Most abstraction boreholes are concentrated in a north-south line through Driffield and Beverley



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

Figure 2.1. **Map of the study area showing principal rivers and towns and the regional extent of the Chalk aquifer.**

(Figure 2.1) where the population is greatest, though abstraction from parts of the unconfined aquifer is also significant. The Hull area is particularly heavily licensed, Yorkshire Water being licensed to abstract 65 Ml day^{-1} from the aquifer. Groundwater abstraction in the area is potentially close to the sustainable limit at low-flow periods. Droughts in recent years have caused increased drawdown and influx of deeper, more saline water in the boreholes around Hull.

2.2 Current issues in groundwater quality

Probably the principal issue affecting groundwater quality in the Yorkshire and North Humberside Chalk to date has been the impact of pollution, especially from agricultural chemicals, in the western unconfined section of the aquifer. This has resulted in a tangible rise in concentrations of nitrate in several unconfined water sources over the last few years or decades, in some cases to concentrations in excess of drinking-water standards. Indeed, the Yorkshire Chalk was the first area in England where a growing groundwater nitrate problem was recognised (Foster and Crease, 1974). Increases in the concentrations of other constituents such as Cl, SO_4 and Ca have also been observed. Organic compounds have also been detected, albeit at low concentrations, in a number of unconfined borehole sources. To date, much of the research carried out on the quality of water resources in the aquifer has been directed towards nitrate occurrence and distribution.

In the near-coastal sections of the confined aquifer, problems with pumping-induced saline intrusion are also experienced, particularly in the Hull area (e.g. Chadha, 1986).

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

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

3.2 Regional geography

The Chalk crops out in the west and north of the study area, where the undulating Yorkshire Wolds reach an elevation of up to 200 m AOD and form a characteristic west-facing escarpment and east-facing dip slope. In east Yorkshire, the Chalk forms steep and often inaccessible sea cliffs. These have been often severely affected by coastal erosion and large landslips have occurred in some areas. Further south and eastwards, the Chalk is covered by glacial Drift deposits and the topography becomes a flat and low-lying coastal plain. The Holderness Peninsula has an elevation of only a few metres above sea level.

The Wolds Chalk outcrop consists of treeless rolling hills, with little surface drainage. The area is crossed by a series of dry valleys. The only significant surface flow occurs in the Gypsey Race [TA 17 67] which flows eastwards towards Bridlington. Flow in the Gypsey Race may become intermittent at times of low water table and ceases altogether during drought periods. Springs occur just to the south of the northerly Chalk outcrop. Some of these flow southwards over the Drift deposits and form tributaries of the River Hull. The most important in terms of flow volume are the West Beck and Kelk Beck tributaries which join the River Hull near North Frodingham [TA 08 53]. The River Hull flows south to Hull to join the Humber (Figure 2.1) and is tidal below Hempholme Lock [TA 080 498]. Other streams flow southwards into the Holderness Drain and also drain into the Humber, or flow directly to the North Sea.

Mean annual rainfall ranges from more than 700 mm in the Wolds uplands to as low as 600 mm over the Holderness Peninsula.

The main urban centre of the area is Hull on the Humber Estuary. Beverley and Driffield are also

Figure 3.1 View south-east to Flamborough Head, Yorkshire, showing sea stacks and landslips of Selwick's Bay (photography: K E Thornton).

important towns. Bridlington, on the Yorkshire coast, is a tourist centre.

3.3 Geology

3.3.1 Chalk

The Chalk in Yorkshire has a total thickness over 430 m and dips gently eastwards at an angle of about 1–2°. In places, it is more heavily contorted with occasional minor faulting. The Hunmanby Monocline [510 472] has a north-south axis and acts as a hydraulic barrier, deflecting the course of the Gypsey Race southwards. The Chalk is exposed in a number of working quarries. A small former quarry at Rifle Butts near Goodmanham [SE 897 427] has been preserved as an SSSI on the basis of its geological interest.

Sedimentation patterns during the Cretaceous were controlled strongly by regional structure and topography. The Market Weighton structure, a topographic high during Jurassic and Cretaceous times, caused considerable variations in sedimentation and sediment thickness. The structure represented a hinge with a more rapidly subsiding area to the north and an area of less rapid subsidence to the south.

The Yorkshire and Humberside Chalk has been classified as part of the ‘Northern Province Chalk’ which is more indurated than its equivalent from the ‘Southern Province’ of southern England and has notable sedimentological, faunal and lithological differences (Mortimore et al., 2001). The Northern Province Chalk has been divided into four lithostratigraphical units. In ascending order these are the Ferriby Chalk, Welton Chalk, Burnham Chalk and Flamborough Chalk formations (Table 3.1; Wood and Smith, 1978; Mortimore et al., 2001). Nodular chalks and flint horizons are only weakly developed and glauconitised and phosphatised hardgrounds are much less well-developed than in the Southern Province. These features have been interpreted to indicate deposition of the chalk strata in a deeper-water environment than further south (Mortimore et al., 2001).

The lowermost unit of the Chalk sequence comprises the Red Chalk of Albian age. This is a distinct brick-red marker horizon, unique to the Northern Province. The Red Chalk is much less important than further south in Lincolnshire, being only a few metres thick and at a minimum close to the Market Weighton structure. Estimated thickness of the Red Chalk in the Winestead borehole [TA 2741 2433] near Patrington is 12.8 m, though this is unusually thick and may be a suspect value (Berridge and Pattison, 1994). Some workers have included the Red Chalk within the Ferriby Chalk Formation (Wood and Smith, 1978) although more recent literature treats it as a separate formation (Mortimore et al., 2001).

The overlying Ferriby Chalk Formation of Cenomanian age is typically 20–30 m thick. It is generally a soft, white, flintless marly chalk, but includes the Totternhoe Stone, a thin layer of hard shelly

Table 3.1. Lithostratigraphy of the Northern Province (English) Chalk (from Mortimore et al., 2001).

Old units	Formations	Local formal names	Local informal names
Upper Chalk	Flamborough Chalk Fm Burnham Chalk Fm		Flamborough Sponge Bed
Middle Chalk	Welton Chalk Fm	Plenus Marls Member	Black Band
Lower Chalk	Ferriby Chalk Fm		Nettleton Stone Totternhoe Stone
	Red Chalk Fm		

limestone. The Ferriby Chalk Formation crops out in the north-western part of the Wolds and along Wolds valley sides and bottoms.

The Welton Chalk of Upper Cenomanian to Upper Turonian age is typically 44–53 m thick and some 47 m thick in the Winestead borehole. It is mostly composed of massive white chalk but has distinct marl bands, notably the Black Band at its base (thought to be equivalent to the Plenus Marls), as well as the Grasby Marl and the Barton Group. Discontinuous flint bands also occur within the sequence.

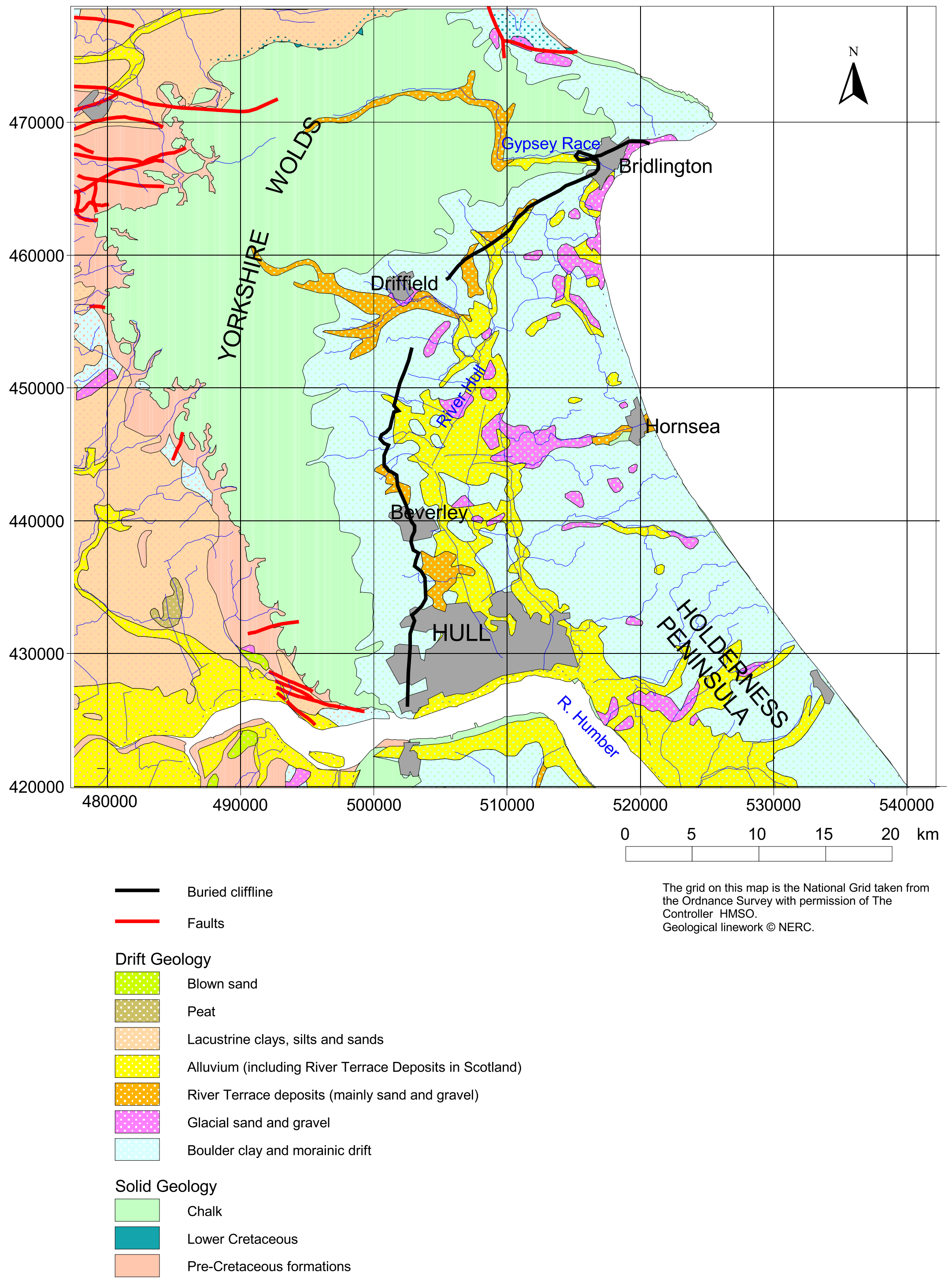


Figure 3.2 Geological map of Yorkshire and North Humberside showing the Chalk outcrop and distribution of superficial Drift deposits.

The Turonian–Coniacian Burnham Chalk is around 130–150 m thick and consists largely of hard white chalk with thin marl bands, some greenish-grey and of volcanogenic origin. It is distinguished from the other Formations by its abundant tabular flint beds. The top of the Formation is marked by a distinct flint horizon in the BGS Humberside No. 3 borehole [TA 2756 1677] (Berridge and Pattison, 1994). Marl seams are also present throughout.

The topmost part of the sequence, the Flamborough Chalk, reaches about 260–280 m thick. It crops out at Flamborough Head and in the northern part of the Yorkshire Wolds (Figure 3.2). The basal part, 120 m thick, is proved in the Humberside No. 3 borehole where macrofaunal evidence indicates a Santonian–Campanian age. Only 100 m of Flamborough Chalk are found in the Winestead borehole, suggesting that part of the sequence may have been faulted out in this area (Berridge and Pattison, 1994). The Formation is composed of typically flintless, well-bedded and marly chalk with numerous marl seams.

3.3.2 Other formations

The Chalk is underlain in the south and along its northern edge by Lower-Cretaceous sediments. These consist of a sequence of marine clays, the Speeton Clay, which is typically around 60 m thick in Yorkshire but up to 175 m thick offshore. Elsewhere in Yorkshire, it is underlain by Jurassic strata including the Inferior Oolite, Cornbrash, Kellaways Beds or Corallian Limestone.

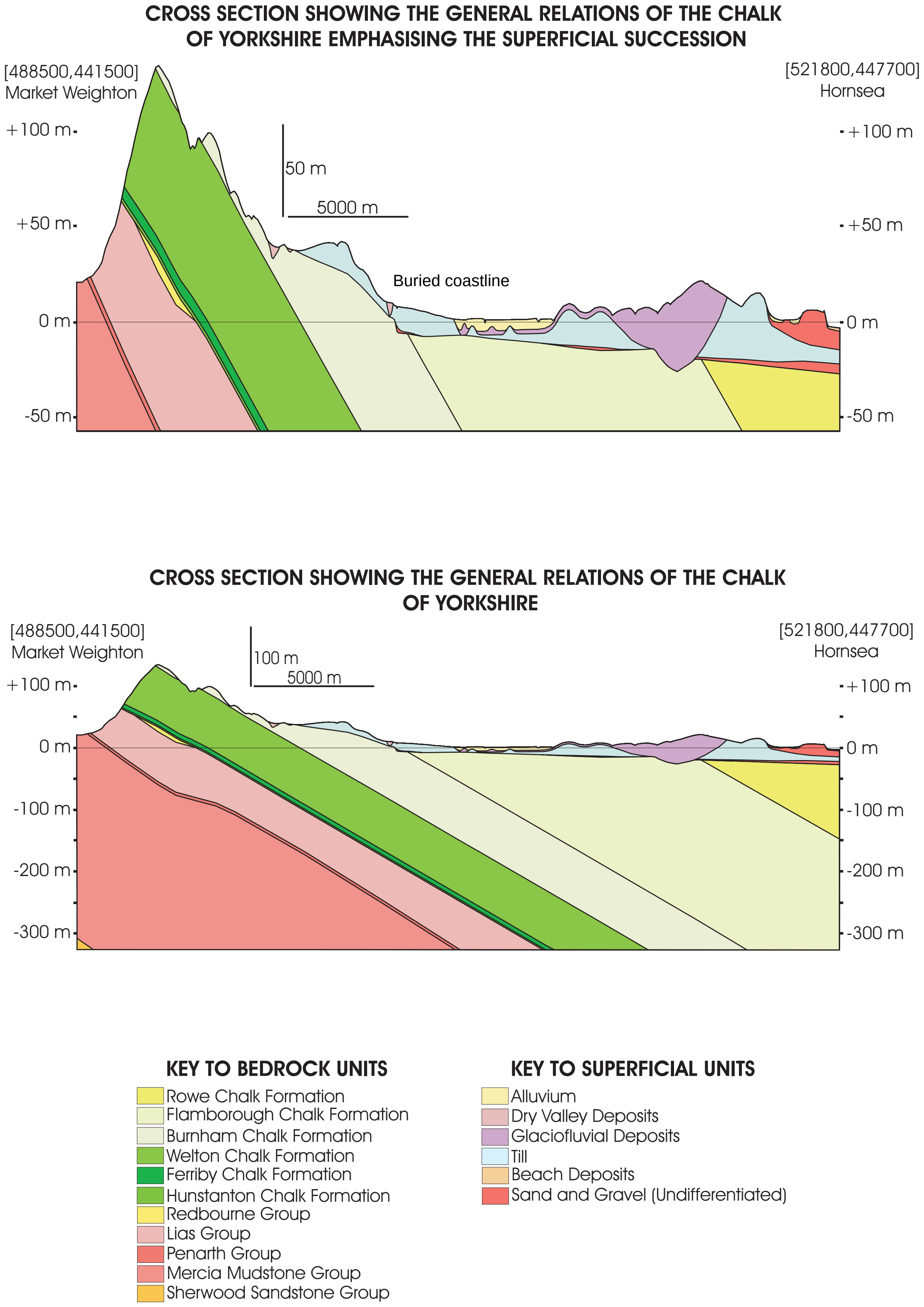
To the south and east of the Wolds outcrop, the Chalk is overlain by Quaternary Drift deposits which are variable in thickness and lateral extent but generally increase in thickness eastwards, reaching up to 45 m in the Holderness Peninsula. The distribution of Drift deposits (Figure 3.2, Figure 3.3) is strongly influenced by the occurrence of a fossil coastline which extends north-south from Sewerby [TA 20 69] via Driffield and Beverley to Hessle [TA 04 26] and continues southwards into Lincolnshire. This was generated as a result of sea-level rise during the Ipswichian Interglacial. The fossil coastline has little topographical expression in the Humber area but reaches the dimensions of a cliff further north. It is everywhere buried by Drift.

Deposits of Anglian age have not been proved in the area, but analogues of the Kirmington Buried Channel in south Humberside are found in the Holderness area and are thought to date from the Anglian glacial period. In the Winestead borehole, 17.3 m of laminated silt and clay, thought to be Anglian glacial sediments, overlie the Chalk. Around 12 m of similar material, possibly deposited around the same time, have been found at Salt End near Hull.

Hoxnian Interglacial sediments are relatively minor but occur in the Hull area. They consist of estuarine silt and clay overlain by gravel (Gaunt et al., 1992; Berridge and Pattison, 1994).

Traditionally, the oldest till of the Quaternary sequence in the region has been taken as the Basement Till complex, assigned a Wolstonian age (Catt and Digby, 1988), but recently disputed as a younger deformation till possibly of late Devensian age (Eyles et al., 1994). The deposit comprises dark-grey chalk-bearing silty clay with up to 10% cobbles. These include Caledonoid igneous rocks, flint, Chalk and Magnesian Limestone. The Till also contains marine fossils. The complex comprises pre-existing till and glacio-marine sediment, deposited by an advancing ice sheet (Berridge and Pattison, 1994). Outcrops are visible in the Bridlington area.

The Ipswichian Interglacial is associated with sea level rise (ca. 1.5 m above OD; Aspinwall, 1995) and resultant generation of the buried fossil coastline. Ipswichian sediments consist mainly of shoreline deposits, in places banked up against the cliffline. Sands and gravels in south Humberside are considered to be of Ipswichian age.



CROSS SECTION SHOWING THE GENERAL RELATIONS OF THE CHALK OF YORKSHIRE EMPHASISING THE SUPERFICIAL SUCCESSION

CROSS SECTION SHOWING THE GENERAL RELATIONS OF THE CHALK OF YORKSHIRE

Figure 3.3 Geological cross section through the Chalk and superficial sediments of Yorkshire. The line of section runs approximately east-west.

Devensian ice cover in the area extended between ca. 18,500 and 13,000 years BP. Devensian sediments include glacial and fluvio-glacial sands and gravels and argillaceous till, deposited during a major southwards ice-sheet advance. In the Holderness area where the sequence is well-developed, the Formation includes the Dimlington Silts, Skipsea Till, Withernsea Till, Glacial Sand and Gravel, Glacial Silt and Clay and Kelsey Hill Gravels. The blanket of sediment is thick where backed up against the buried cliffline, and is commonly 30 m thick north of the Humber. Sediment thickness is nonetheless variable: Chalk occurs at relatively shallow levels at Pulfin Bog on the River Hull [TA 050 442] for example. In addition to the glacial deposits, head was deposited widely during periglacial conditions.

Holocene deposits record the post-glacial rise in sea level as a result of melting of the Devensian ice sheet. Seawater re-entered the region around 7,500 years BP. Holocene sediments comprise mainly fluvial and lacustrine alluvium, blown sand, storm-beach and head deposits. Post-glacial peat deposits have also been recorded at Salt End and Paull (Hull area). By the end of the Devensian, the River Humber and its tributaries had cut a deeply incised channel into the glacial deposits. Post-glacial transgression may have initially flooded the valley and produced a ria (Berridge and Pattison, 1994). Alluvium is prevalent along the valley of the River Hull, predominantly filling a buried channel which largely follows the course of the present river (alluvial infill in Figure 3.3).

3.3.3 Soil

The Chalk is overlain by generally shallow, well-drained calcareous soils. Soil thickness varies from about 0.2–1 m (Foster and Crease, 1974). Two soil types are predominant in the region. Lithomorphic soils (brown silty rendzinas) are characteristic of the higher and steeper parts of the Wolds. Brown calcareous soils with clearly developed top soil and subsoil horizons form the major soil type on the lower, more gentle, eastern side of the Wolds. The presence of clay and sand deposits in the deeper soils along the dip-slope causes some drainage problems and seasonal waterlogging. Heavy clay loams predominate above the Drift deposits.

3.4 Hydrogeology

Potential evapotranspiration averages 425 mm yr^{-1} but infiltration of rainfall varies according to permeability of surface strata (Berridge and Pattison, 1994). The long-term average infiltration in the Yorkshire Wolds has been estimated at about 300 mm yr^{-1} and is usually concentrated in the months October to March (Foster, 1974; Foster and Crease, 1974). Infiltration decreases markedly to around 180 mm yr^{-1} further east (Environment Agency, unpublished).

The Chalk aquifer is unconfined in the upland Wolds, but becomes semi-confined on the lower-lying parts of the dip slope where it is covered by variably permeable thin Drift deposits. Such conditions exist in the north-south tract of land between Driffield and Hull (Figure 3.2), referred to by some workers as the artesian overflow zone (e.g. Elliot et al., 2001). Historically, eastward-flowing water from the recharge area discharged via springs and blow wells along the Drift margins in this area. While some springs still flow (e.g. north of Beverley, Figure 3.4), urbanisation has led to changes in the natural groundwater flow conditions. More than a century ago, deep shafts and an adit system around 1.5 km long were built in the Cottingham area to supply water to the city of Hull (Chadha et al., 1997). Today, Cottingham pumping station has a licensed abstraction of about 68,000 m^3 day^{-1} and actual average abstraction of some 24,000 m^3 day^{-1} (Zang and Lerner, 2002). As a result of heavy groundwater abstraction, particularly from Cottingham pumping station, most springs between Beverley and Hull have dried up over the last century (Chadha, 1986). Many former artesian boreholes in this southern zone now require pumping. To the east of the buried Ipswichian coastline, the thick cover of impermeable Drifts deposits render the Chalk confined. Clay bands within the Chalk may also act as locally confining layers (Barker et al., 1984). Little recharge to the Chalk is therefore likely from these areas.

In the semi-confined aquifer west of the buried cliffline, observations from groundwater recessions suggest that there is a relatively high degree of connection between the Drift deposits and the Chalk. This is probably the case in areas where the Drift is dominated by glacial sand and gravel and where boulder clay is thin or absent (Chadha et al., 1997). Hence in the area north of Hull (Dunswell, Cottingham), Drift may be contributing a significant amount of water to supply boreholes.

Groundwater recharge occurs throughout the unconfined Chalk and flow in the unsaturated zone is thought to take place by a combination of matrix and by-pass flow. Response times of groundwater levels are typically 2.5–7 hours per metre of unsaturated zone (Foster and Crease, 1974). Much flow is concentrated along fissures (Ward et al., 1997), principally along bedding planes and joints, which have been preferentially widened by solution. Chadha et al. (1997) concluded from tracer experiments that groundwater flow velocities towards Dunswell and Cottingham pumping station could be as much as 160 m day^{-1}. Tracer tests around Kilham pumping station found velocities around 130–475 m day^{-1}, suggesting that the aquifer is karstic in some places.

Groundwater flow directions are variable because of variations in topography and groundwater abstraction. Predominant natural flow is eastwards along the dip slope and westwards along the escarpment, although flow is northwards off the northern edge of the Chalk. Dip-slope flow to the north of Hempholme Lock tends to be towards Driffield in response to pumping. In the Humber area, pumping-induced flow is concentrated southwards towards Hull. The hydraulic gradient in the Chalk follows the regional topography and is shallow in most places, but steeper in the Wolds. Groundwater levels range between about 10 m below surface in the Wolds valleys to around 100 m below surface in the upland areas (Robertson, 1984). In the Holderness Peninsula, groundwater levels are normally near ground level and may be artesian in places. Groundwater flow is minimal beneath the till of the Holderness Peninsula.

Along the Wolds escarpment, a pronounced spring line occurs at the margin of the Chalk and the underlying impermeable Jurassic strata. Studies during the 1970s found higher tritium counts as well as higher nitrate concentrations in the spring waters from the escarpment than in unconfined dip-slope groundwaters (e.g. Foster and Crease, 1974). This suggests that infiltration to the water table is more rapid in the escarpment area, either as a result of the relative importance of rapid by-pass flow along

Figure 3.4. **Artesian spring on the margins of the Drift deposits [TA 030 461], close to Scorborough. The spring was sampled by BGS in December 2002.**

fissures or a reduced thickness of the unsaturated zone, or both.

Seasonal head variations are low in the confined aquifer, but may be as much as 30 m in the unconfined aquifer (Berridge and Pattison, 1994). Long-term falling head levels have resulted in saline intrusion from the Humber Estuary around the city of Hull in particular (Foster et al., 1976).

Groundwater flow is largely restricted to the upper 50–100 m of the Chalk where fissuring is best-developed. In the unconfined aquifer, major fissure systems occur in the zones of present and past water-table fluctuation. Chalk transmissivity is variable as a result such variations in fissuring and rock jointing. Pump tests can reveal very different results therefore depend on ambient groundwater levels. Foster and Milton (1976) found a fissure system some 7 m thick in the zone of fluctuation at Etton pumping station [SE 958 428]. Calculated transmissivity at the site varied between 2200 m^2 day^{-1} at high water tables and 1000 m^2 day $^{-1}$ at low levels, the increased transmissivity resulting from the high fissure density. Buckley and Talbot (1994) identified major active solution-enhanced fissures in the Chalk of the Kilham area from geophysical borehole logging. They found that fissures tended to be parallel to bedding and often occurred immediately above marl bands which act as hydraulic barriers and hence concentrate groundwater flow.

Observed transmissivity values quoted by Allen et al. (1997) are in the range <1–10,000 m^2 day^{-1} with a geometric mean of 1258 m^2 day^{-1}. Berridge and Pattison (1994) noted values of typically 1000–5000 m^2 day^{-1}. Transmissivities >10,000 m^2 day^{-1} have been noted near the buried cliffline, reflecting concentration of water flow in the area immediately west of the historic springline (Elliot et al., 2001). Values around 6000 m^2 day^{-1} were also noted around Haisthorpe, to the west of the buried cliffline (Foster and Milton, 1976), attributed to solution enhancement of fissures by invading seawater during periods of higher sea level or concentrated flow of groundwater along spring lines which emerge at the buried cliffline. High transmissivities have also been recorded for boreholes located in dry valleys. These may be partly attributable to the contribution from Chalk bearings, a coarse breccia-like chalk deposit formed through periglacial processes (Younger et al., 1997).

Transmissivities are much lower in the Holderness Peninsula (less than 50 m^2 day^{-1}) as there is less scope for enlargement of fissures by dissolution. Values are also low around the Hunmanby Monocline (ca. 350 m^2 day^{-1}; Chadha and Courchee, 1978). Typical yields from large-diameter boreholes in the Chalk are 4000–7000 Ml day^{-1}, depending on fissure density and connectivity.

Chalk porosity is variable. Foster and Milton (1976) suggested low values for the Yorkshire Chalk of around 0.14–0.20, resulting from a high degree of post-depositional cementation. However, Lawrence et al. (1983) found some areas with higher porosities of 0.36–0.42. The Burnham Chalk Formation is thought to have higher porosity than the underlying strata at ca. 0.30 (University of Birmingham, 1978). However, effective porosity is much smaller than these actual total porosity values, probably approximating the fissure porosity at around 0.01 (University of Birmingham, 1978).

Minor downward leakage of groundwater from the Chalk into underlying Jurassic strata may occur, but the small size of spring flows from the Jurassic outcrop suggests that this is minor. Where it underlies the Chalk, the poorly permeable Lower Cretaceous Speeton Clay forms an effective base of the aquifer and its presence determines the location of several spring flows along its boundary with the Chalk.

3.5 Aquifer mineralogy

The Chalk is a soft, relatively pure micritic limestone. In the Northern Province, the Chalk has undergone a degree of diagenetic alteration and recrystallisation. As a result, it is more indurated than its counterpart in southern England (Berridge and Pattison, 1994). The Chalk comprises about 98% calcite. This usually has a low Mg concentration (ca. 1 mol %; Pitman, 1986). Minor impurities in the chalk are mainly clay (chiefly illite and smectite, Hancock, 1975), iron oxide, flint bands and fragments of clastic limestone. Phosphate minerals (collophane) occur sporadically as concretions in hardgrounds or, less commonly, as disseminated grains (Hancock, 1993). Minor occurrences of pyrite have also been reported (Hancock, 1975). The Chalk has a low concentration of organic matter. Chalk from eastern England typically has organic carbon in the range 0.01–0.1%, the highest values being associated with phosphorite horizons in hardgrounds (Pacey, 1989).

The Ferriby Chalk at the base of the sequence is a relatively impure limestone compared to the overlying formations, with a higher component of clay, clastic limestone and ferruginous sediment. The beds immediately overlying the basal Red Chalk comprise soft nodular chalk with marl partings. The top of the Ferriby Chalk Formation consists of hard grey-white chalk with pink clay bands. The overlying Welton Chalk consists of mainly massive, indurated chalk, although the basal few metres are lithologically similar to the Ferriby Chalk, being soft, argillaceous and flint-free (Berridge and Pattison, 1994). The topmost part of the sequence, the Flamborough Chalk, is composed of soft, less indurated white chalk, more akin to the Chalk of southern England. Thin marl bands are prevalent in the formation and minor discontinuous flint bands also occur.

3.6 Rainfall chemistry

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

Table 3.2 shows the volume-weighted mean annual concentrations of major ions in rainfall from High Muffles gauging station in North Yorkshire for the latest available year (1999, total annual rainfall 936 mm). Values are also given for 'concentrated rainfall' which are three times the weighted mean values, approximating the enrichment expected due to evapotranspiration. Such enriched concentrations are those likely to be infiltrating the aquifers of the region. Ammonium in rainfall is assumed to fully oxidise to nitrate before infiltration to soils and so the nitrogen is given all as NO_3-N in the concentrated values. Oxidation of NH_4-N also reduces the pH of the rainfall as the reaction releases protons (H^+ ions).

For elements such as Cl, little interaction with soils and vegetation is expected on recharge and baseline concentrations of modern recharge are therefore likely to be of the order of 10 mg l^{-1} or less. For other elements, especially K, some uptake by plants and clay minerals in soils is expected and so the values outlined in Table 3.2 are an upper estimate of recharge compositions. Modern baseline concentrations of dissolved nitrogen (NO_3-N and NH_4-N combined) from rainfall evidence are likely to be of the order of 3 mg l^{-1}.

Table 3.2. Weighted mean annual solute concentrations in rainfall for 1999 at High Muffles rainfall gauging station, North Yorkshire [4776 4939] (data from AEA, 2003). 'Concentrated rainfall' represents values 3x the rainfall concentration.

Determinand	Units	Concentration	Concentrated rainfall
pH		4.65	3.54*
Ca	mg l^{-1}	0.56	1.68
Mg	mg l^{-1}	0.32	0.96
Na	mg l^{-1}	1.74	5.22
K	mg l^{-1}	0.094	0.28
Cl	mg l^{-1}	3.13	9.39
SO_4	mg l^{-1}	2.20	6.60
NO_3-N	mg l^{-1}	0.44	2.88
NH_4-N	mg l^{-1}	0.52	–

*Assuming all NH_4-N is oxidised to NO_3-N on or before filtration

3.7 Land use

Land use of the area is overwhelmingly dominated by arable farming (Figure 3.5). Cereal crops (mainly wheat and barley) predominate (ADAS, 1993; Table 3.3) but other crops include sugar beet, potato, vegetables, peas, beans and oil-seed rape. In recent years, set-aside has also become a more important use of land, amounting to some 10% of arable landuse in the Etton and North Newbald catchments (Chilton et al., 1997). Animal farming is dominated by pigs and poultry (much being free-range) and sheep are also important, particularly in parts of the upland Wolds where the terrain is steeper. Dairy and beef production is important along the Hull valley. Glasshouse horticulture is important in the Hull–Beverley–Driffield area.

Manufacturing industry is relatively minor and is concentrated around the urban centres, particularly Hull (Figure 3.5). Industrial activities are dominated by food processing.

The dominant fertilisers in use over the Chalk aquifer over the last decade have been NH_4NO_3 and urea. A survey of overall fertiliser use on the whole Yorkshire–Humberside Chalk in the 1990s concluded that coverage was 151 kg ha^{-1} on tillage (i.e. everything except grasses), of which 130 kg ha^{-1} was applied as these compounds. The remainder comprised mixed NPK fertilisers (British Survey of Fertiliser Practice, 1995). Foster and Crease (1974) noted a progressive replacement of $(NH_4)_2SO_4$-based fertilisers by NH_4NO_3-based fertilisers in the Etton, Cherry Burton and Goodmanham catchments during the 1970s. Application rates of nitrogenous fertiliser were noted to increase from estimates of <10 kg N ha^{-1} yr^{-1} in the 1940s to around 95 kg N ha^{-1} yr^{-1} in 1971.

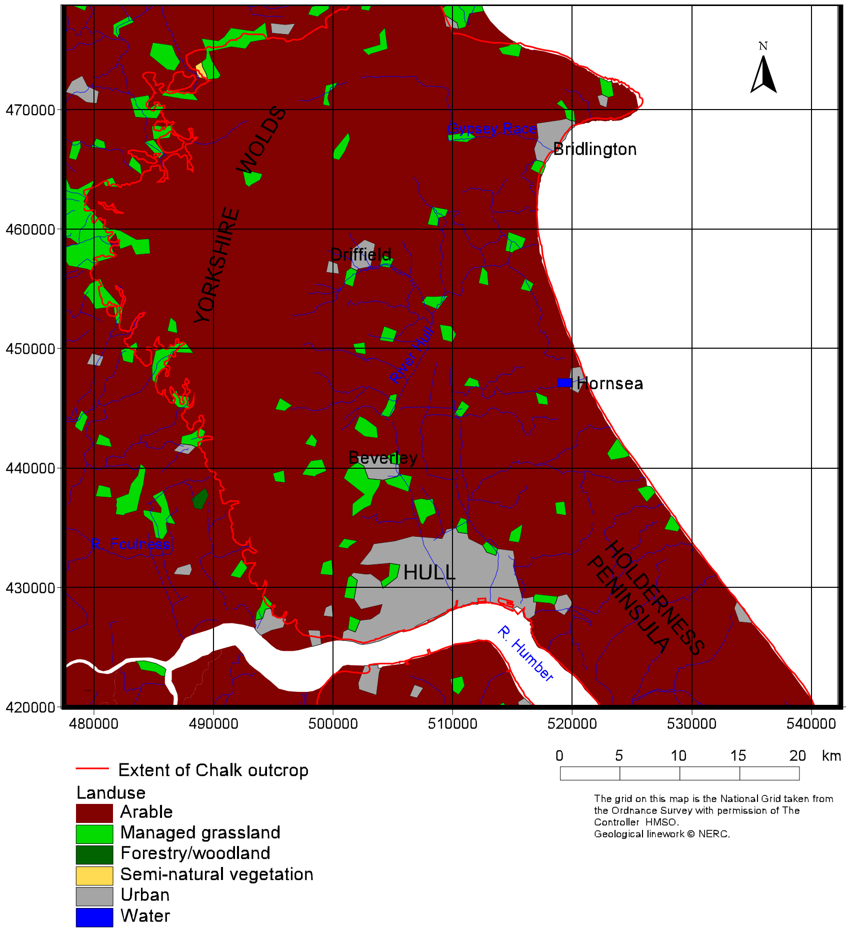


Figure 3.5. Map of land use in the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology & Hydrology, ©NERC.

Table 3.3. **Agricultural land use in the study area (data from ADAS and reported by Smedley et al., 1996).**

Crop	**Western area (W of Easting 500)** **Hectares**	**Eastern area (E of Easting 500)** **Hectares**	**Total area** **Hectares**
Permanent grassland	3505.7	4328.5	6847.7
Grassland excluding rough grazing	8593.7	9779.7	16235.6
Set aside	7745.9	10956.1	16699.3
Wheat	28846.1	44812.9	65624.7
Winter barley	11967.6	15775.1	25078.5
Spring barley	3352.3	3123.4	5726.8
Oats	485.7	836.7	1200.1
Rye	46.3	0	46.3
Triticale	77.0	31.6	93.9
Maize (threshing/stockfeeding)	64.6	131.6	182.2
Potatoes (early and main crop)	2213.4	2225.7	3954.6
Sugar beet (not stockfeed)	1969.8	1204.2	2824.3
Winter oilseed rape	4136.6	7240.4	10182.3
Spring oilseed rape	566.8	608.5	1020.0
Flax	117.8	13.4	127.8
Peas (dry harvest)	1779.0	1701.0	2984.1
Vining peas	3448.8	2770.5	5161.1
Field beans	496.7	1012.7	1341.6
Linseed	329.4	213.6	475.0
Total	**79743.2**	**106765.6**	**165805.9**

Sulphate-based fertilisers are applied to oilseed rape crops and some other cereals, but not to sugar beet or potatoes. Salt (NaCl) is also applied to sugar beet in the area at a rate of 400 kg ha^{-1} (British Survey of Fertiliser Practice, 1995).

Pesticide and herbicide use in northern Britain (including Humberside and Yorkshire) in 1995, ranked by area, was dominated by isoproturon (408 t, over 414 kha), chlormequat (448 t, over 377 kha) and fenpropimorph (66 t, over 260 kha). Mecoprop usage amounted to 162 t over 100 kha and simazine to 39 t over 14 kha. Ranked in order of weight, the most important compound used in the same area was sulphuric acid (594 t, over 5 kha). This is used in spray form to kill potato haulms and as a desiccant for onion and linseed crops. Elemental sulphur is also applied to sugar beet as a fungicide. Such applications therefore represent a potentially important source of extra SO_4 to groundwater.

4. DATA AND INTERPRETATION

4.1 Data sources

4.1.1 Historical data

Groundwater-quality data used in this report have been collated from BGS and Environment Agency databases. BGS archive data have been produced as a result of a number of previous hydrogeochemistry projects carried out in the region, the largest being a regional survey of groundwater quality in the aquifer in April 1996 (Smedley et al., 1996). That investigation involved the collection of groundwater samples from 84 borehole and spring sites across the aquifer. During the 1996 sampling campaign, attempts were made to collect a representative set of samples spread over the aquifer, although in practice sampling density was greater in some areas than others due to variations in density of licensed-abstraction sites. A large number of abstraction boreholes are sited in the Driffield–Beverley areas due to higher population density. Fewer samples were collected from parts of the unconfined aquifer, particularly the Yorkshire Wolds as a result of the paucity of abstraction boreholes in that area.

During the 1996 BGS sampling campaign, field analysis of groundwaters included pH, temperature, and alkalinity and where possible, Eh (redox potential) and dissolved oxygen. No field measurements were carried out at the public-water supply sites investigated for the study as field sampling was carried out by Yorkshire Water staff. At each site, separate water samples were collected for subsequent laboratory analysis. Filtered (0.45 µm) and unfiltered aliquots were collected in plastic bottles for analysis of metals and anions respectively. Samples for purgeable and other organic compounds were also collected. Analysis of these determinands was carried out at the Environment Agency laboratories in Leeds. A more detailed account of these determinands is given by Smedley et al., (1996).

Filtered samples collected in the 1996 survey by BGS staff were for analysis of selected major and extra trace elements at the BGS laboratories. Three aliquots were collected in acid-washed polyethylene bottles, one unacidified for anion analysis, one acidified with 1% v/v HNO_3 for trace-metal analysis and one acidified with ca. 0.1% HCl for As(III) (and subsequently to 2% v/v HCl for total As).

Most of the laboratory analysis was carried out at the Environment Agency laboratories. Calcium, Mg, Na, K, Sr and B were analysed by ICP-OES and the remaining metals by ICP-MS. Sulphate was analysed by ion chromatography, F by ion-selective electrode and alkalinity, Cl and nutrients by automated colorimetry. Nitrate determinations are strictly measured as total-oxidised nitrogen (TON) which includes nitrite, NO_2-N. However, nitrite concentrations were found to be very low in all but one sample (which had an NO_2-N concentration of $1.0\ \mathrm{mg\ L^{-1}}$). Concentrations of TON have therefore been taken as nitrate, except in the one high-NO_2 sample for which nitrate has been calculated by subtraction of the NO_2-N species.

Additional chemical analysis carried out by BGS included major and selected trace elements by ICP-OES and ICP-MS. Iodine was also analysed by automated colorimetry. Arsenic(III) and total As were measured by hydride-generation ICP-OES.

Additional groundwater chemistry data in this report have been collated from a separate BGS survey of Yorkshire Chalk groundwater carried out during February–March 1996, and from a BGS study of groundwater nitrate concentrations at Etton pumping station (Chilton et al., 1997). Sampling and analytical methods for these campaigns were as described in the larger BGS April 1996 survey.

Groundwater chemistry data for 33 selected sites from Environment Agency records have also been included in the evaluation. Although Environment Agency data are available for more than 33 sites, those sites covered in BGS sampling campaigns were excluded as the latter usually contain a greater number of determinands with overall lower detection limits.

4.1.2 Project sampling programme

In addition to the archived BGS and Environment Agency groundwater chemistry data described above, a new groundwater sampling campaign of groundwaters from the Yorkshire Chalk was carried out by BGS in December 2002. In this, a total of 18 samples were taken from boreholes in a transect across the aquifer from Etton to Warne, representing an approximate east-west groundwater flow line. These sources were sampled using similar protocols to the BGS April 1996 regional groundwater survey, with on-site analysis of water temperature, alkalinity, specific electrical conductance (SEC), pH and where possible Eh and dissolved oxygen (the latter three determinands measured in an in-line flow cell to exclude contamination from atmospheric oxygen). Filtered (0.45 µm) samples were collected for subsequent laboratory analysis by ICP-OES, ICP-MS and automated colorimetry. ICP-OES analysis included major cations, SO_4 and selected trace elements (P, Si, Ba, Fe, Sr). Colorimetric analysis was for anions and ICP-MS analysis for remaining trace elements. Selected unfiltered samples were also collected for stable-isotopic analysis ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$). Results of $\delta^{18}O$ and $\delta^{2}H$ have been calculated as per mil deviations relative to SMOW and $\delta^{13}C$ relative to PDB.

4.2 Data quality and handling

The new BGS data collected for this study had analytical charge imbalances in most cases of less than 4% (the worst being 5.3%). In the previous BGS surveys and the Environment Agency data sets, imbalances were in most cases also less than 5%.

Where concentrations of determinands were below the analytical detection limit, a value of half the detection limit has been used for the calculation of arithmetic mean vales and for plotting purposes.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

The regional variation in Chalk-groundwater chemistry is influenced most strongly by carbonate reaction, redox processes, saline intrusion and pollution. Most of the elements considered are affected by more than one of these processes so the regional trends in chemical composition are necessarily somewhat complex. This section describes the main characteristics and regional variations in groundwater chemistry observed in the Chalk and presents data in the form of statistical summaries and in graphical form (as a Piper diagram, box plots and cumulative-frequency diagrams).

Summary statistical data for a large range of chemical determinands are given in Table 5.1 and Table 5.2. The data throughout this report have been divided into oxidising and reducing categories as the compositions of a number of solutes are distinctive in these two classes. The classification was made of the basis of presence or absence (<0.2 mg l^{-1}) of dissolved oxygen where data were available and on geographical location relative to the position of the fossil coastline. For each of the classes, minima, maxima, median and mean values are given, together with the 97.7th percentile, equivalent to the mean + 2σ value on a log-normalised data set. Median values are useful indicators of approximate average baseline concentrations, but the mean + 2σ values are given as representative of approximate upper baseline concentrations for most solutes.

Most of the groundwaters included in this study are oxidising because of the larger number of boreholes in the unconfined and semi-confined sections of the aquifer. The statistical data and regional maps therefore reflect the relative paucity of information from the reducing confined aquifer.

Table 5.1. Statistical summary of major constituents in, and isotopic compositions of, groundwaters from the Yorkshire and North Humberside Chalk, divided into oxidising (unconfined and semi-confined) and reducing (confined) sections.

	Units	Min	Median	Mean	97.7th centile	Max	n	Min	Median	Mean	97.7th centile	Max	n
				Oxidising						Reducing			
Temp	ºC	6.1	9.8	9.9	12.6	17.4	98	9.2	10.8	10.8	12.3	12.4	19
pH		6.34	7.28	7.26	7.74	7.80	119	6.62	7.22	7.20	7.50	7.55	22
Eh	mV	165	398	389	464	474	53	36	133	138	240	245	13
DO	mg L^{-1}	2.3	8.7	8.3	12.1	12.8	54	<0.1	<0.1	0.4	3.9	5.7	15
SEC	µS cm^{-1}	389	581	592	897	1170	115	448	2210	3106	12421	17200	21
Ca	mg L^{-1}	62.4	106	108	150	218	127	60.8	98.1	108	218	252	22
Mg	mg L^{-1}	0.83	2.98	3.83	11.8	23.0	127	5.64	47.0	77.7	411	626	22
Na	mg L^{-1}	4.7	11.1	12.4	30.7	41.1	127	13.9	304	587	3263	4910	22
K	mg L^{-1}	0.26	1.27	1.59	4.53	7.60	126	1.97	10.1	24.0	104	155	22
Cl	mg L^{-1}	11.2	25.8	28.6	71.8	87.6	127	14.9	421	948	5895	8890	22
SO_4	mg L^{-1}	<5	26.7	34.2	97.7	324	127	6.1	135	203	994	1287	22
HCO_3 field	mg L^{-1}	130	241	240	323	347	97	269	395	381	460	464	19
HCO_3 lab	mg L^{-1}	120	213	213	282	288	29	238	273	290	355	359	3
NO_3-N	mg L^{-1}	<0.5	8.81	9.5	20.1	33.2	127	<0.2	<0.5	0.20	0.7	1.2	22
NO_2-N	µg L^{-1}	<1	<10	6	20	270	127	<3	<10	54	560	1010	22
NH_4-N	µg L^{-1}	<3	<30	20	90	550	127	<30	880	1450	6840	10600	22
P	mg L^{-1}	<0.02	<0.1	0.062	0.13	0.87	97	<0.1	0.20	0.22	0.70	0.82	19
TOC	mg L^{-1}	<1	1.1	1.3	3.5	9.4	65	0.73	2.7	3.4	6.1	6.1	11
DOC	mg L^{-1}	2.5	4.4	4.8	8.2	8.6	14	6.1	7.3	8.1	11.4	11.6	4
δ^2H	‰	-56.0	-52.0	-52.2	-49.0	-48.0	45	-59.0	-50.1	-51.7	-47.0	-47.0	15
$\delta^{18}O$	‰	-8.4	-8.1	-8.0	-7.5	-7.3	45	-8.4	-8.0	-7.9	-7.1	-7.0	15
$\delta^{13}C$	‰	-17.0	-13.8	-12.9	-7.4	-7.0	45	-14.0	-9.1	-9.2	-2.7	-2.4	15

Temp: temperature; SEC: specific electrical conductance (25ºC); TOC/DOC: total/dissolved organic carbon

Table 5.2. Statistical summary of trace elements in groundwaters from the Yorkshire and North Humberside Chalk, divided into oxidising (unconfined and semi-confined) and reducing (confined) sections.

	Min	Median	Mean	97.7th centile	Max	n	Min	Median	Mean	97.7th centile	Max	n
	Oxidising						Reducing					
Si	1750	3130	3210	4510	6400	114	2310	4580	4960	7620	8010	21
Ag	<0.05	<0.05	0.03	<0.05	<0.05	14	<0.05	<0.05	0.08	0.22	0.24	4
Al	<1	<1	3	21	33	84	<1	3	16	97	110	19
As	<1	<1	0.6	1.2	1.3	106	<1	3.7	6.3	56	63	20
Au	<0.05	<0.05	<0.05	<0.05	<0.05	14	<0.05	<0.05	0.04	0.09	0.10	4
B	<10	10.2	25	58	344	117	<100	267	436	1656	2220	21
Ba	12	67	64	128	148	95	12	59	73	218	258	19
Be	<0.03	<0.05	0.02	<0.05	<0.05	84	<0.03	<0.05	0.05	0.20	0.21	19
Bi	<0.05	<0.05	0.03	<0.1	<0.05	14	<0.05	<0.05	0.04	0.08	0.09	4
Br	41.4	86.1	90.6	164	164	33	136	2565	4832	24011	29000	12
Cd	<0.05	<0.1	0.04	0.10	0.44	106	<0.05	<0.1	0.04	0.12	0.13	21
Ce	<0.01	<0.01	0.03	0.16	0.21	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Co	<0.02	0.1	0.2	0.7	2.8	84	0.03	0.67	1.6	7.0	8.9	19
Cr	<0.2	<0.5	0.3	1.6	3.4	106	<0.20	0.39	0.73	3.1	4.1	21
Cs	<0.01	<0.04	0.02	<0.04	<0.04	84	<0.01	<0.04	0.02	0.054	0.064	19
Cu	<0.5	1.8	2.8	11	33	102	<0.5	<1	1.3	5.6	7.2	18
Dy	<0.01	<0.01	0.005	0.004	0.010	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Er	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Eu	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
F	<250	140	191	421	3150	107	230	650	969	3340	3800	21
Fe	<3	<30	19	75	870	123	373	2270	2192	4769	4860	22
Ga	<0.05	<0.05	0.025	<0.05	<0.05	14	<0.05	<0.05	0.025	<0.05	<0.05	4
Gd	<0.01	<0.01	0.006	0.011	0.020	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Ge	<0.05	<0.05	0.025	<0.05	<0.05	14	<0.05	<0.05	0.05	0.12	0.13	4
Hf	<0.02	<0.02	0.01	<0.02	<0.02	14	<0.02	<0.02	0.01	<0.02	<0.02	4
Hg	<0.1	<0.1	0.05	<0.1	<0.1	14	<0.1	<0.1	0.05	<0.1	<0.1	4
Ho	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
I	0.63	2.00	2.72	5.87	7.22	33	17.5	164	189	476	508	12
In	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Ir	<0.05	<0.05	0.025	<0.05	<0.05	14	<0.05	<0.05	0.025	<0.05	<0.05	4
La	<0.01	<0.04	0.019	0.03	0.12	84	<0.01	<0.04	0.017	<0.040	<0.04	19
Li	0.29	1.3	1.9	6.7	12.1	84	3.1	14.0	20.2	87	116	19
Lu	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Mn	<0.2	<10	2.9	17	57	124	7.0	100	119	318	372	22
Mo	<0.1	<0.1	0.08	0.31	0.39	84	<0.10	0.85	1.2	4.3	4.5	19
Nb	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Nd	<0.01	<0.01	0.02	0.12	0.15	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Ni	<0.2	2.2	3.8	8.5	17	117	<0.2	2.2	4.4	16	16	21
Os	<0.05	<0.05	<0.05	<0.05	<0.05	14	<0.05	<0.05	<0.05	<0.05	<0.05	4
Pb	<0.1	<1	0.3	2.5	3.0	107	<0.1	<0.4	0.52	5.0	9.1	21
Pd	<0.2	<0.2	0.1	<0.2	<0.2	14	<0.2	<0.2	0.1	0.2	0.2	4
Pr	<0.01	<0.01	0.006	0.01	0.02	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Pt	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Rb	0.08	0.67	0.77	2.1	2.5	84	0.71	3.8	5.6	29	43	19
Re	<0.01	<0.01	<0.01	<0.01	<0.01	14	<0.01	<0.01	<0.01	<0.01	<0.01	4
Rh	<0.01	<0.01	<0.01	<0.01	<0.01	14	<0.01	<0.01	<0.01	<0.01	<0.01	4
Ru	<0.05	<0.05	<0.05	<0.05	<0.05	14	<0.05	<0.05	<0.05	<0.05	<0.05	4
Sb	<0.05	<0.08	0.05	0.14	0.41	84	<0.05	<0.08	0.094	0.60	0.89	19
Sc	0.74	0.85	0.86	1.0	1.0	14	1.2	1.5	1.5	1.8	1.8	4
Se	<0.5	<1	0.5	1.1	1.1	36	<0.5	<1.0	1.1	3.8	4.2	6
Sm	<0.02	<0.02	0.01	0.02	0.03	14	<0.02	<0.02	0.01	<0.02	<0.02	4
Sn	0.09	0.17	0.16	0.20	0.21	14	0.17	0.17	0.19	0.23	0.23	4
Sr	164	297	323	644	1657	116	655	2118	4117	19515	27200	21
Ta	<0.02	<0.02	<0.02	<0.02	<0.02	14	<0.02	<0.02	<0.02	<0.02	<0.02	4
Tb	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
Te	<0.05	<0.05	<0.05	<0.05	<0.05	14	<0.05	<0.05	0.05	0.10	0.11	4
Th	<0.05	<0.05	<0.05	<0.05	<0.05	14	<0.05	<0.05	0.036	0.06	0.07	4
Ti	<10	<10	<10	<10	<10	14	<10	<10	<10	<10	<10	4
Tl	<0.01	<0.01	0.007	0.01	0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4

Tm	<0.01	<0.01	0.005	<0.01	<0.01	14	<0.01	<0.01	0.005	<0.01	<0.01	4
U	<0.05	0.12	0.17	0.64	0.82	84	<0.02	<0.05	0.18	0.99	1.1	19
V	<0.2	<0.2	0.19	0.6	0.7	14	<0.2	0.7	0.9	2.1	2.2	4
W	<0.02	<0.02	0.01	0.04	0.06	14	<0.02	<0.02	0.015	0.03	0.03	4
Y	<0.01	<0.01	0.01	0.05	0.14	84	<0.01	<0.01	0.026	0.12	0.15	19
Yb	<0.01	<0.01	<0.01	<0.01	<0.01	14	<0.01	<0.01	<0.01	<0.01	<0.01	4
Zn	<2	7.2	97	669	3750	105	<2	8.6	351	3726	6074	18
Zr	<0.01	<0.02	0.06	0.50	0.71	25	<0.02	<0.02	0.01	0.02	0.02	4

All concentrations in µg L^{-1}

5.2 Major constituents

The chemistry of the groundwater of the region is largely typical of groundwater seen elsewhere in the English Chalk. Compositions are largely near-neutral with pH values buffered in the range 6.3–7.8 (and mostly between 7.0 and 7.5). Fresh groundwater from the unconfined aquifer in the west has generally high hardness values and is mostly of Ca-HCO_3 type, though some groundwaters range towards more SO_4-rich compositions. Calcium concentrations in the unconfined (Yorkshire Wolds) and semi-confined groundwaters (beneath permeable Drift, west of the buried coastline) lie in the range 62–218 mg l^{-1} and HCO_3 concentrations in the range 130–347 mg l^{-1} (Table 5.1). Chloride and SO_4 concentrations in excess of 30 mg l^{-1} and 50 mg l^{-1} respectively are also common with values up to 88 mg l^{-1} and 324 mg l^{-1} respectively (Table 5.1). Concentrations of Na are typically low (4.7–41 mg l^{-1}).

Distinct differences are seen in the compositions of groundwaters from the unconfined/semi-confined sections and the confined (reducing) sections of the aquifer. These are illustrated clearly by the Piper diagram in Figure 5.1. Groundwaters from the confined aquifer in the east of the region range to much more saline compositions, especially close to the coast (Holderness Peninsula, Brandesburton–Hornsea and along the Humber Estuary). Here compositions become Na-Cl-HCO_3 and ultimately Na-Cl-dominant. The compositional range in the confined groundwaters shows evidence of mixing between fresh Chalk groundwater and seawater (Figure 5.1). A maximum Cl concentration of 8890 mg l^{-1} (SEC 17 mS cm^{-1}; TDS 16.6 g l^{-1}), roughly half that of modern seawater, has been found

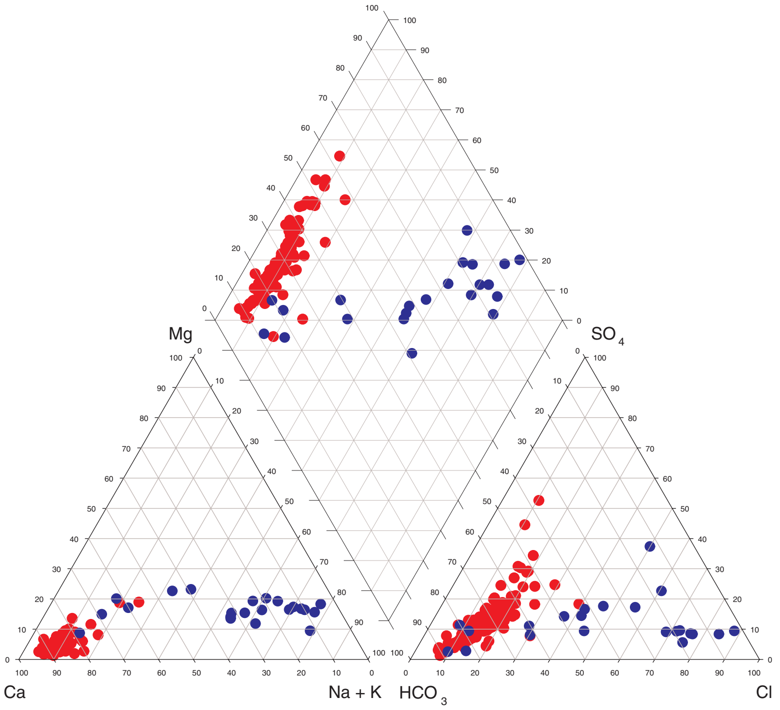


Figure 5.1. Piper diagram for the groundwater samples investigated in this study. Red circles: oxidising groundwaters, blue circles: reducing groundwaters.

in groundwater from Holderness (Table 5.1). Higher concentrations of Na, HCO_3, Mg and SO_4 are also present in the confined aquifer, particularly samples from the Holderness and Brandesburton [TA 12 47] areas.

The unconfined and semi-confined groundwaters are oxidising with Eh values >300 mV and dissolved-oxygen concentrations varying between 2.3 and 12.8 mg l^{-1}. They also have relatively high concentrations of NO_3-N, often in excess of 10 mg l^{-1}. As noted in Section 2.2, nitrate pollution is a major management problem in this section of the aquifer.

The poorly permeable Drift cover has a profound impact on the mobility of redox-sensitive elements in the Chalk groundwaters. A distinct redox boundary exists some 5–10 km east of the westerly edge of the Drift deposits, roughly corresponding with the location of the buried coastline. Eastwards of this, the Drift cover is thickest and dominated by clay. Downgradient of the boundary, the groundwaters become more reducing with significantly lower Eh values and dissolved-oxygen concentrations below detection limit. The lowest Eh value measured in the confined aquifer was -36 mV. As noted above, the reducing groundwaters from the confined aquifer are generally those with higher salinity.

The reducing groundwaters from the confined aquifer have much lower concentrations of NO_3-N (<1.2 mg l^{-1}; Table 5.1) than those further west. Chloride and SO_4 have a large range in both the oxidising and reducing groundwaters but are highest in groundwaters from the coastal areas where they are affected by seawater intrusion.

The ranges of both TOC and DOC are relatively large in both the oxidising and reducing sections of the aquifer. Concentrations of TOC reach up to 9.4 and 6.1 mg l^{-1} in these sections respectively (Table 5.1).

Box-and-whiskers plots for the major ions in both the oxidising and reducing groundwaters from the aquifer are given in Figure 5.3 and Figure 5.2 respectively. The plots reveal the higher concentrations of most major and trace constituents above a 'diluted' seawater composition (normalised to the median Cl concentration for the respective oxidising and reducing categories of groundwaters).

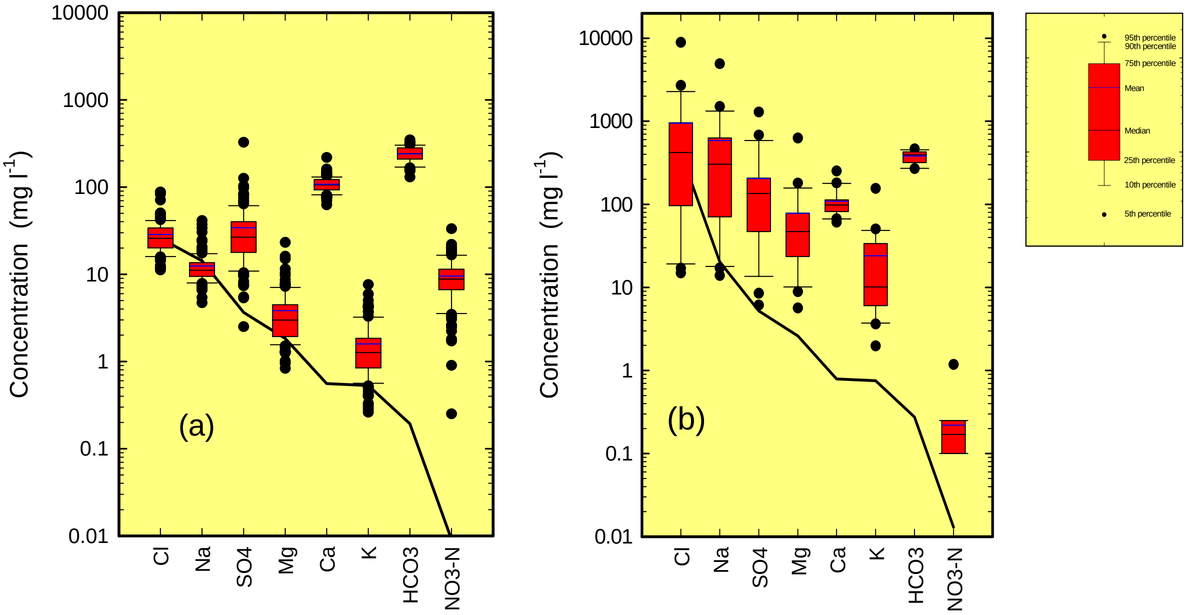


Figure 5.2. **Box-and-whiskers plots showing the ranges of major constituents in (a) oxidising and (b) reducing groundwaters of the Yorkshire Chalk. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration).**

5.3 Trace elements

Box-and-whiskers plots for trace elements are given for the oxidising and reducing groundwaters in Figure 5.3. As with the major ions, the concentrations of a 'diluted' seawater are given for comparison as are the typical detection limits for the trace elements included in the study.

The principle behind the value of cumulative-frequency plots as a tool for hydrogeochemical interpretation is demonstrated in Box 5.1 and cumulative-frequency distributions for selected major and trace constituents in the Chalk groundwaters are given in Figure 5.4, 5.5, 5.6 and 5.7.

As with the major constituents, trace elements show a large variation between the oxidising and reducing sections of the aquifer and in relation to groundwater salinity. In the oxidising groundwaters, dominant trace elements include Si (range 1.75–6.4 mg l^{-1}), B (<10–344 µg l^{-1}), Ba (12–148 µg l^{-1}), Br (41–164 µg l^{-1}), Sr (164–1660 µg l^{-1}) and F (<250–3150 µg l^{-1}). The highest observed F concentration in the oxidising sample group is unusual however, as most samples have less than 400 µg L^{-1} F. Maxima for Fe and Mn are 870 µg l^{-1} and Mn 57 µg l^{-1} respectively. Arsenic concentrations are universally low in the oxidising groundwaters, the maximum observed being

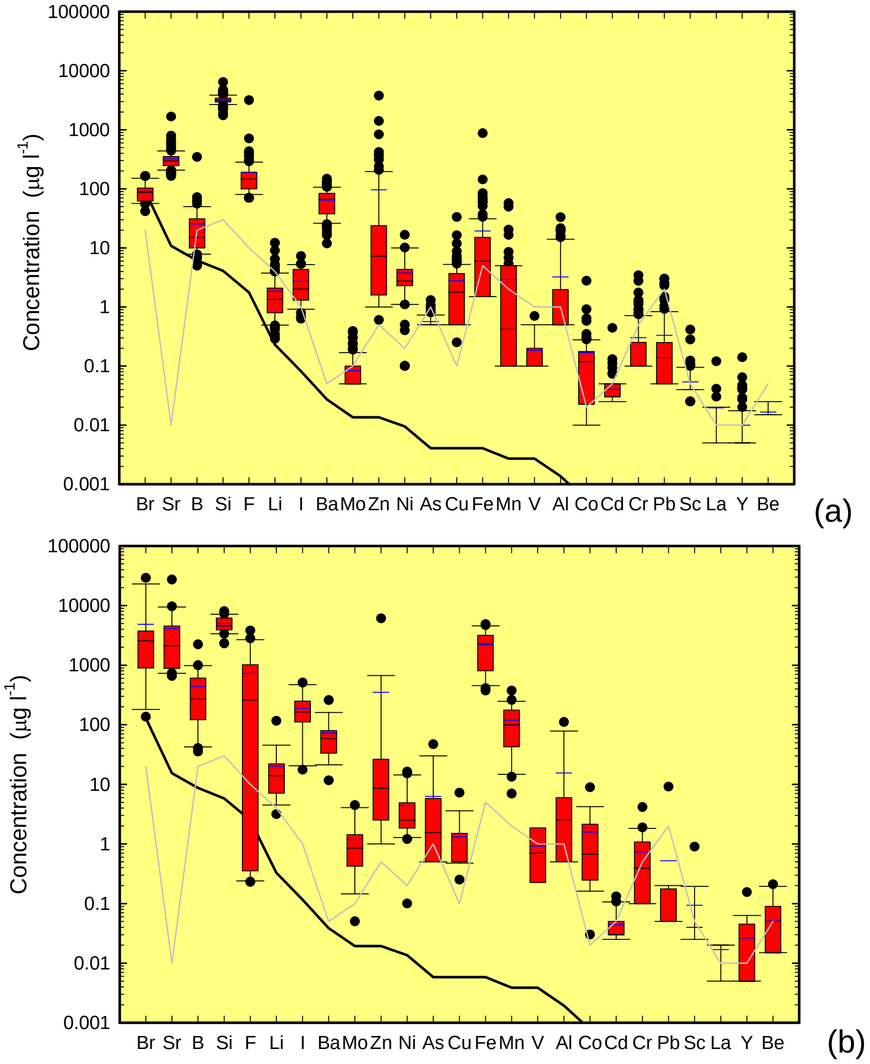
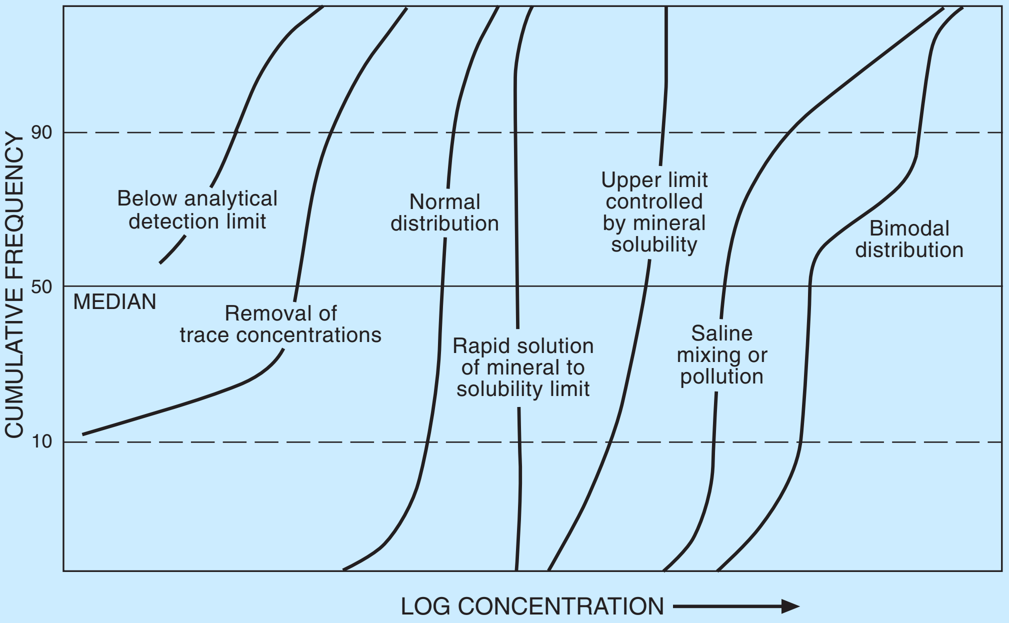


Figure 5.3. Box-and-whiskers plots showing the ranges of minor constituents in (a) oxidising and (b) reducing groundwaters of the Yorkshire Chalk. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration); grey line: typical detection limits. Legend as in Figure 5.2.

Box 5.1. Use of cumulative-frequency diagrams to indicate baseline characteristics of 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_3 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.

1.3 µg l^{-1}. Maximum concentrations for Cr (3.4 µg l^{-1}) Co (2.8 µg l^{-1}), Cd (0.44 µg l^{-1}) and V (0.7 µg l^{-1}) are also very low. Concentrations of Pb reach 3 µg l^{-1}. Relatively high maxima are observed for Cu (33 µg l^{-1}), Ni (17 µg l^{-1}), and Zn (3.75 mg l^{-1}). As a guide, none of the trace elements investigated exceeds current European drinking-water limits, although concentrations of Ni approach them. The EC maximum permissible value for Ni is 20 µg l^{-1}.

In the reducing groundwaters, the same suite of trace elements generally dominates but many of the elements have much larger range of concentrations, reflecting distinct geochemical processes, particularly enhanced residence time, redox-driven processes and saline intrusion. Concentrations of Si and Ba are broadly similar to those in the oxidising groundwaters (2.3–8.1 mg l^{-1} and 12–258 µg l^{-1} respectively), but a number of elements have much higher average and maximum concentrations (notably B, Br, F, Fe, I, Li, Mn, Mo, Rb and Sr; Table 5.2). A number of the higher concentrations of F and B in the reducing groundwaters exceed the current EC drinking-water maximum permissible values of 1.5 mg l^{-1} and 1 mg l^{-1} respectively and the highest Pb concentration observed, 9 µg l^{-1}, is just below the maximum permissible value of 10 µg l^{-1}. Concentrations of Fe reach up to 4.9 mg l^{-1} and Mn up to 0.37 mg l^{-1}. Much higher concentrations are also observed for As in the reducing groundwaters, with the maximum being 63 µg l^{-1}, again in excess of the EC drinking-water limit of 10 µg l^{-1}.

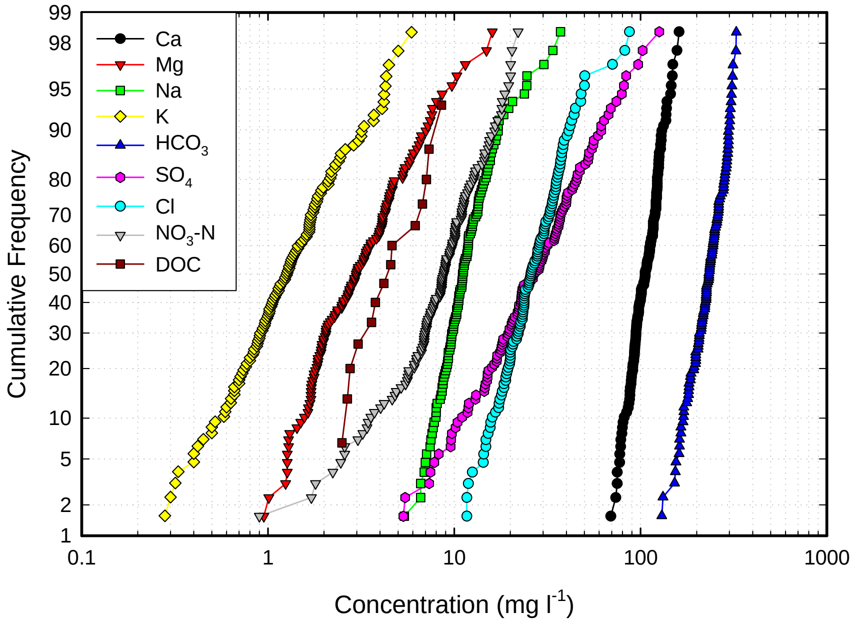


Figure 5.4. **Cumulative-frequency plots for the major constituents in the oxidising groundwaters of the Yorkshire Chalk.**

Median values for P are higher in the reducing groundwaters than in the oxidising aquifer, though observed maxima are comparable (0.8–0.9 mg l^{-1}). These values are relatively high for UK groundwaters. Uranium concentrations are less than 1 µg l^{-1} in all groundwaters investigated. Most other trace elements analysed have very low concentrations (Table 5.2).

The diagrams show the relatively narrow range of Ca and HCO$_3$ concentrations in groundwaters from both oxidising and reducing sections of the aquifers, consistent with solubility controls imposed by calcite equilibrium. A larger spread is observed in concentrations of K, Mg, Cl, NO$_3$-N, DOC and SO$_4$. Inflections at the upper ends of the ranges of Na, Mg and Cl may reflect inputs from anthropogenic sources. In the reducing groundwaters, inflections at the upper ends of ranges for K,

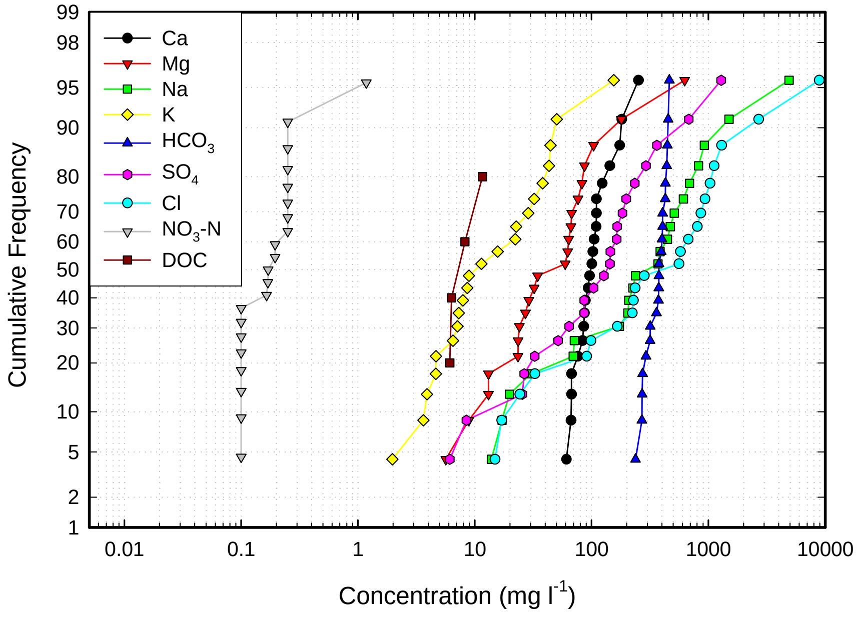


Figure 5.5. **Cumulative-frequency plots for the major constituents in the reducing groundwaters of the Yorkshire Chalk.**

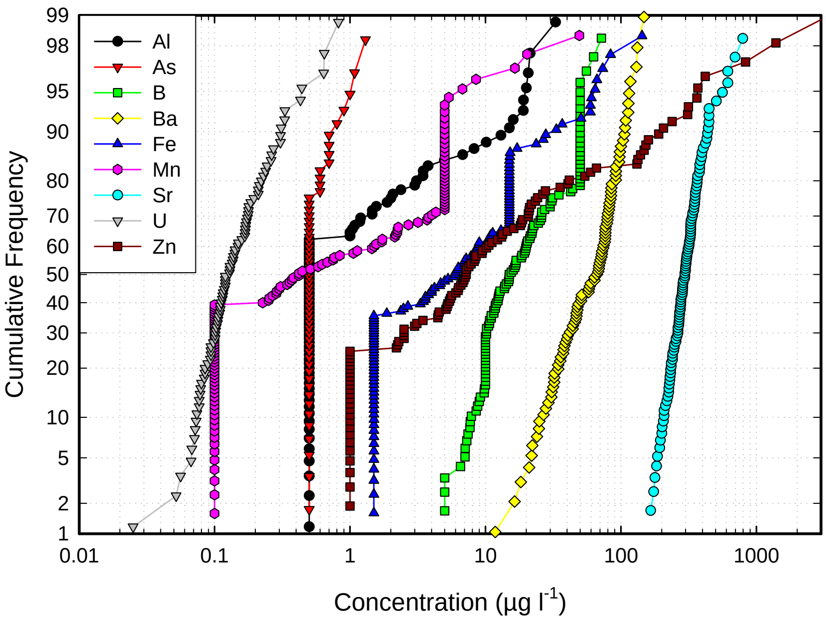


Figure 5.6. **Cumulative-frequency plots for the minor constituents in the oxidising groundwaters of the Yorkshire Chalk.**

Mg, Na, SO_4 and Cl probably reflect influence of seawater intrusion into the aquifers in coastal areas.

Cumulative-frequency plots for selected trace elements (Figure 5.6 and Figure 5.7) show the relatively narrow range for Sr in oxidising compared to reducing groundwaters. The higher concentrations of Fe and Mn are also demonstrated. Many of the elements plotted have significant numbers of samples below the analytical detection limits and hence plot as vertical lines in the figures.

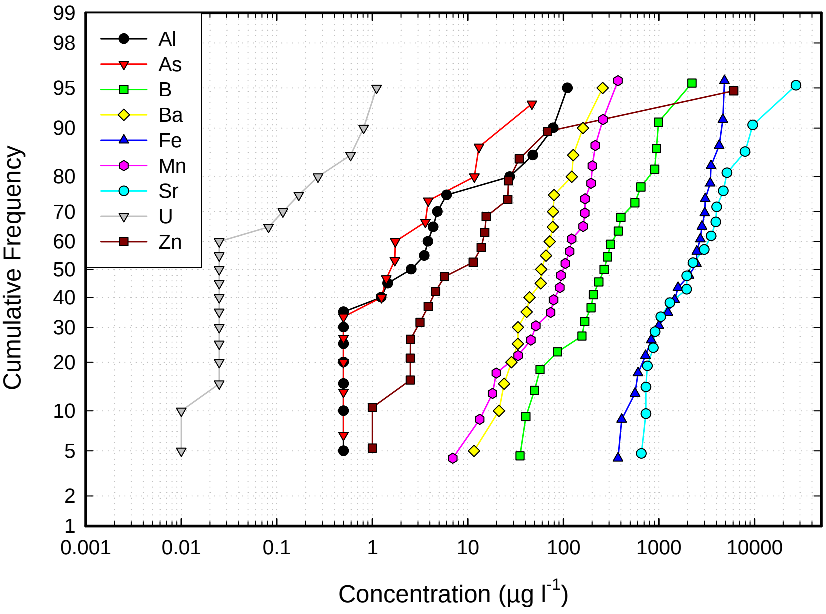


Figure 5.7. **Cumulative-frequency plots for the minor constituents in the reducing groundwaters of the Yorkshire Chalk.**

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

This section describes the spatial variations in groundwater chemistry in the Yorkshire Chalk aquifer, both laterally and with depth, and gives an account of the main processes believed to be controlling the distributions. These processes include mineral dissolution and precipitation reactions, redox reactions, pollution, and mixing of waters with distinctive chemistries. Identifying such processes is an important prerequisite for defining likely baseline compositions of groundwaters in a given aquifer (Box 6.1). The section includes maps of selected chemical determinands to show the spatial variations. In addition, a profile across the aquifer from Etton to Hornsea has been described to highlight some of the chemical variations that occur along an approximate groundwater flow line from the unconfined aquifer in the west, to that buried below poorly-permeable Drift deposits in the east.

Many of the observed spatial chemical variations can result from evolution of groundwater along flow lines. However, when interpreting spatial variations in water-quality data, it is important to bear in mind that compositions can be complicated by factors such as differences in borehole design and construction, tapping of different stratigraphic horizons in a given aquifer, and differing borehole pumping histories. Differences in borehole design, including variations in casing and well depth may lead to apparent localised water-quality variations. Differences in aquifer lithology may include facies changes and variations in type and degree of cementation. Variations in pumping history may also have imposed 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 Quaternary sediments where present, or of more saline pockets of groundwater in coastal areas. Such chemical variations are quite apart 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 sample set. The report presents a broad assessment of

Box 6.1 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 agricultural 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.

the groundwater-quality variations observed across the aquifer and the main controlling geochemical processes. It must be borne in mind that some additional water-quality variation may be due to the factors described above.

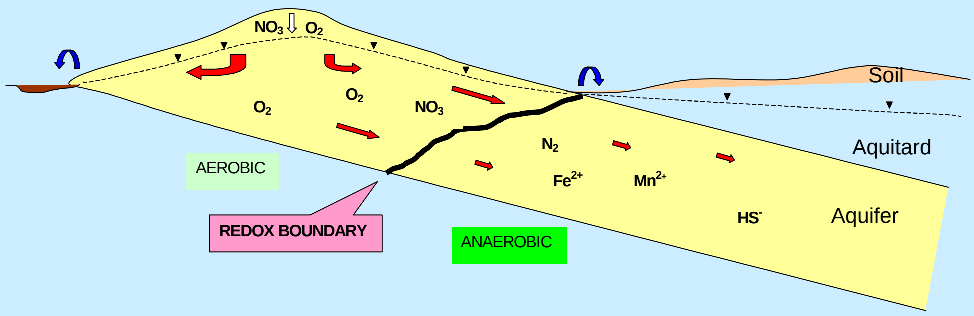
One of the most important factors controlling the chemistry of the groundwaters of the region is reaction with the carbonate minerals that compose the rock. This gives rise to a characteristic groundwater chemical composition with similarities to many other Chalk groundwaters (e.g. Smedley et al., 2003). In the west where the aquifer is unconfined, the effects of pollution, particularly from diffuse agricultural sources, are discernible in the groundwater compositions and can pose a water-supply problem in some areas. The presence of nitrate at concentrations greater than the EC maximum permissible value (11.3 mg l^{-1}) in some groundwater sources is one of the most significant of these problems although traces of some organic compounds have been found in some of the unconfined groundwaters (Smedley et al., 1996). Further east where the Chalk is covered by thick Drift deposits, the aquifer becomes confined. Here, redox processes exert an important influence, with the redox boundary (Box 6.2) marking a zone of significant change in the concentrations of a number of elements. In near-coastal areas, especially where the land is low-lying such as the Holderness Peninsula, saline intrusion becomes an additional control. There is evidence that the saline groundwaters may comprise different generations with different emplacement histories.

6.2 Regional variations and controls

6.2.1 Major-element compositions

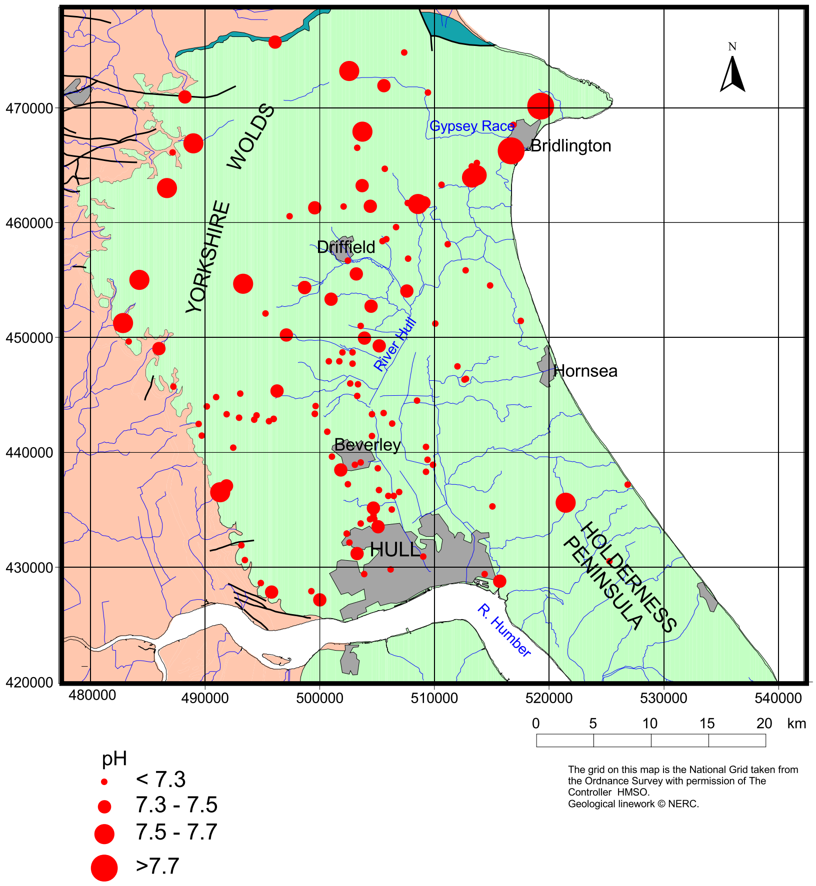
Maps of the distributions of the major constituents of the groundwaters reveal that available data are sparse for part of the Yorkshire Wolds due to lack of licensed abstraction sites in this area (Section 3). Coverage in the confined aquifer of Holderness is also poor due to a paucity of available boreholes for sampling. Many groundwater-abstraction sites in the confined aquifer have been abandoned due to high salinity and poor yield. Better coverage has been possible over the rest of the aquifer.

Box 6.2 Redox boundary (schematic)



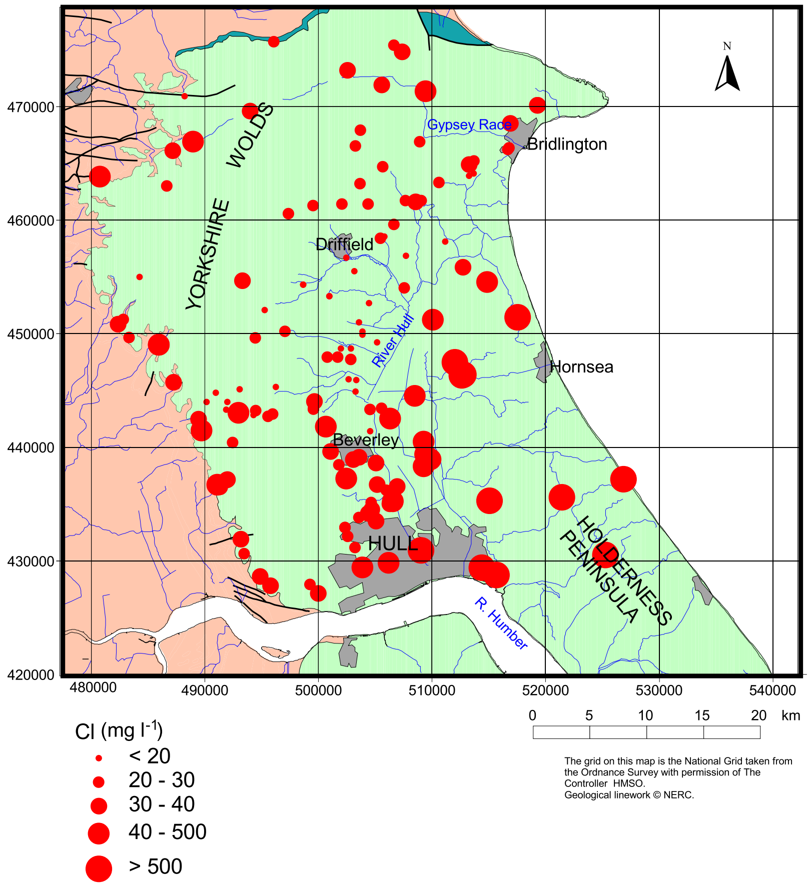
Recharging water is generally saturated with dissolved oxygen at the partial pressure of the atmosphere (10–12 mg l^{-1} depending upon barometric conditions). Passing through the soil and the unsaturated zone some of this O_2 will react as a result of microbiological processes and oxidation-reduction reactions. However, almost all water reaching the water table still contains several mg l^{-1} dissolved O_2. Geochemical reactions (oxidation of traces of pyrite, organic matter and Fe^{2+} present in minerals) progressively remove the O_2 along flow lines. Once all the oxygen has reacted, an abrupt change of water chemistry takes place. This zone is known as the redox boundary. Other changes may occur at and further down-gradient of the redox boundary, especially denitrification and increased concentrations of dissolved iron (Fe^{2+}) concentrations. Sulphate reduction and the production of sulphide (H_2S as HS^- in solution) may also occur at greater depths.

Reaction of groundwater with calcium carbonate is a dominant control on groundwater chemistry and exerts a strong influence on pH, Ca, Mg, HCO_3 (and Sr) in particular. Rapid equilibration with chalk gives rise to strongly buffered groundwaters (pH mostly 7.0–7.5) with Ca and HCO_3 being the dominant ions, although exceptions occur in the coastal areas where groundwaters become more saline and Na and Cl become more dominant. Smedley et al. (1996) discussed the spatial variations in pH in the Chalk groundwaters and noted that they were generally higher in scarp-slope groundwaters from springs than in unconfined groundwaters from dip-slope sites as well as Drift-confined groundwaters. The variation is linked to groundwater pCO_2 values and may reflect variations in land use and depth of the unsaturated zone. Parts of the western escarpment have steep slopes and are likely to have thin soil cover, low organic-matter content and a relatively thick unsaturated zone. This regional variation in pH is also shown in Figure 6.1. With the exception of the scarp-slope springs, most groundwater samples investigated are saturated or nearly saturated with respect to calcite, reflecting rapid equilibration with the rock matrix. Variations in calcite saturation were also observed by Pitman (1978) for springs in the Givendale escarpment area north-west of Beverley. Here also, escarpment springs were noted to be significantly undersaturated with calcite in contrast to dip-slope sites. Seasonal variations in pCO_2 were noted as a result of temperature-related soil CO_2 compositions. Maximum pCO_2 values were found in September and October and minima in winter and early spring. Pitman (1978) concluded that dip-slope groundwaters evolved by open-system evolution with respect to CO_2 while scarp-slope groundwaters evolved under a closed system. The depth of the unsaturated zone was seen as a critical factor in determining the two paths of groundwater evolution.



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

Figure 6.1. Regional variation in pH of groundwaters from the Chalk aquifer of Yorkshire and North Humberside.



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

Figure 6.2. **Regional variation in Cl in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**

Concentrations of Mg are mostly low (0.8–23 mg l^{-1} in the oxidising low-salinity groundwaters), reflecting the reaction with low-Mg calcite in the chalk (Section 3.5). Concentrations increase in the more saline waters from the confined aquifer. This is mainly linked to mixing with seawater in the saline parts of the aquifer but may also have been affected in part by enhanced diagenetic reactions resulting from prolonged groundwater residence time in the Chalk. Groundwaters from the unconfined aquifer are significantly undersaturated with respect to dolomite. Only a few samples from the confined saline aquifer approach or exceed saturation. However even here, dolomite is unlikely to be a precipitating mineral phase because of kinetic constraints on formation.

Concentrations of HCO_3 lie in the range 130–347 mg l^{-1} in the unconfined and semi-confined (oxidising) aquifer but reach up to 464 mg l^{-1} in the confined aquifer. The increased concentrations are believed to be linked with seawater mixing although the highest observed concentration is far in excess of that present in modern seawater (140 mg l^{-1}; Hem, 1992). Salinity-induced carbonate reaction is probably controlling the increased concentrations of HCO_3 and enhanced groundwater residence time is also a likely factor. In the reducing part of the aquifer, some increase is also likely to be linked to the oxidation of organic matter.

The distribution of Cl is shown in Figure 6.2. These are usually lowest (often <20 mg l^{-1}) in the semi-confined aquifer between Beverley and Driffield and some of the unconfined dip-slope groundwaters (Goodmanham area) but are higher in the escarpment springs (typically 20–50 mg l^{-1}) and much higher (up to 8890 mg l^{-1}) in the confined aquifer. The lowest concentrations observed are believed to equate to background values. Those in the escarpment areas reflect rapid transit times of pollutants to the water table and are likely to derive from sources such as animal wastes and road salting (Smedley et al., 1996). Some additional Cl may derive from increased concentrations in modern (polluted) rainfall. In the confined aquifer, the much higher observed concentrations relate to mixing with a seawater.

As with Cl, SO_4 (Figure 6.3) is present at lowest concentrations in the central area (Beverley–Driffield–Goodmanham). The concentrations are typically <20 mg l^{-1} which are also likely to represent baseline concentrations for fresh groundwaters. The occurrence of lowest SO_4 concentrations in an area covered by relatively permeable and pyrite-bearing Drift deposits suggests that leakage of SO_4-rich groundwater from the Drift has not taken place. This is supported by the spring flows in this area which suggest that groundwater flow is upwards in this part of the Chalk aquifer.

Sulphate can also potentially derive by dissolution (oxidation) of pyrite. This is present as a minor phase in parts of the Chalk, especially within impure zones (hardgrounds) and is also likely to be present in the overlying Drift deposits. Likewise oxidation of pyrite in the confined aquifer is unlikely to be an important cause of the increased concentrations of SO_4 as the potential for oxidation will be limited in the reducing conditions prevalent in this part of the aquifer.

In the confined near-coastal aquifer, concentrations reach up to 1290 mg l^{-1} in response to saline intrusion. Pitman (1986) claimed that SO_4 reduction is important in the confined aquifer, although this was based on analysis of only one sample. To the best of our knowledge, no analysis of dissolved sulphide has been carried out in the Chalk groundwaters. A few sites from the confined aquifer in the Holderness and Hull areas have a detectable smell of H_2S, although this could still involve low concentrations (H_2S is generally unstable at near-neutral pH). Also, the redox status of the aquifer is unlikely to be sufficiently low for sulphate reduction to occur. Concentrations of SO_4 generally

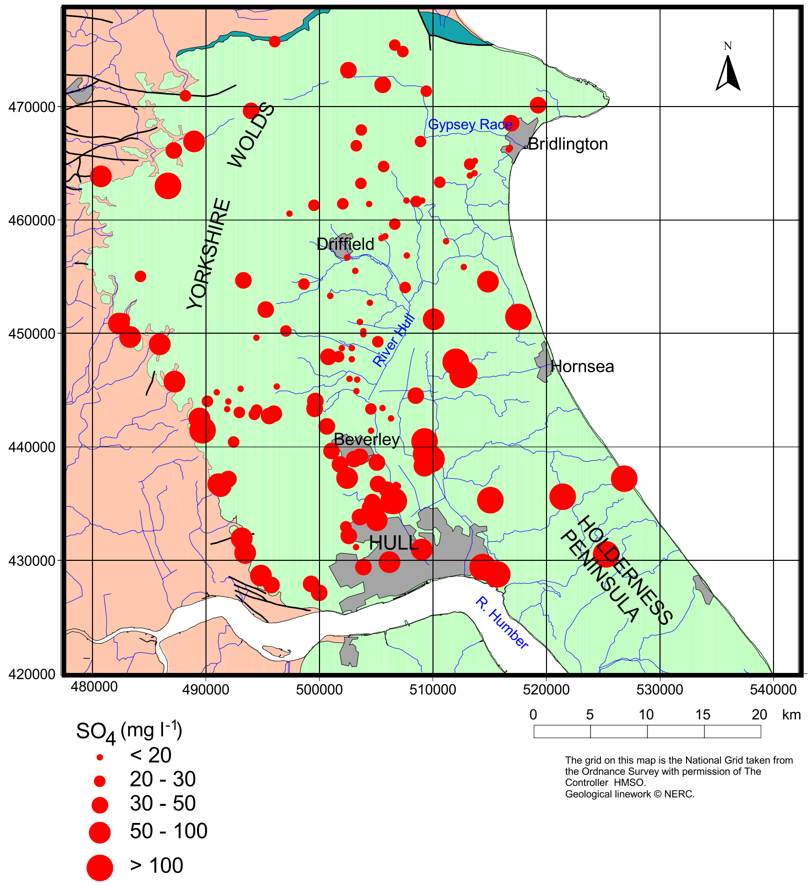


Figure 6.3. **Regional variations in SO_4 in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**

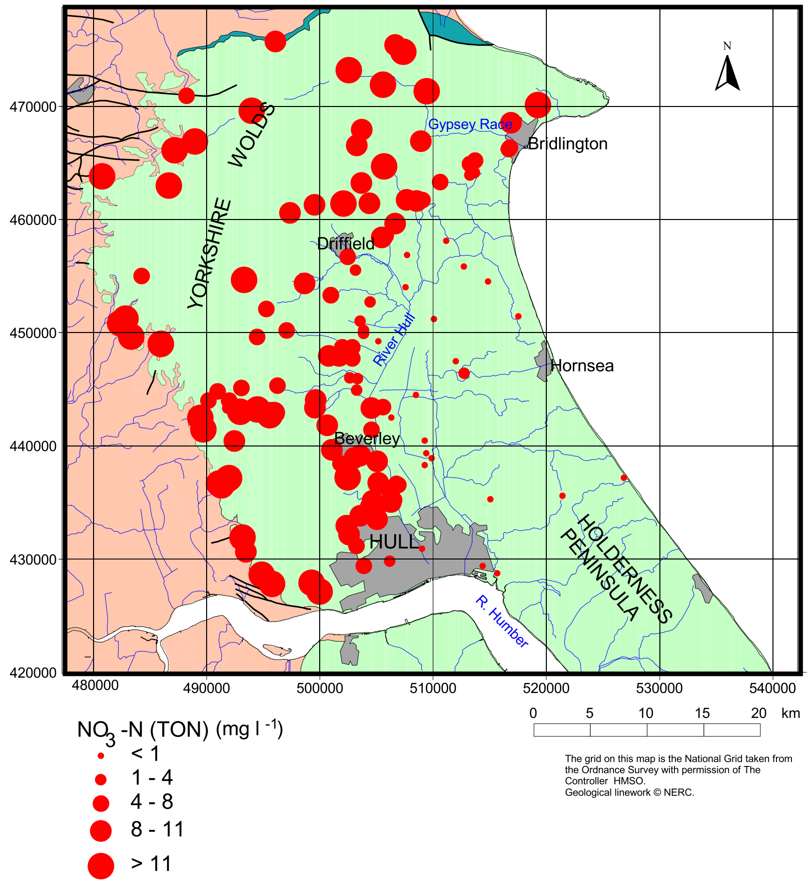


Figure 6.4. **Regional variation in NO_3-N in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**

increase in the confined aquifer, rather than decrease, and any decrease related to SO_4 reduction will be greatly outweighed by increases related to saline mixing.

Nitrate also displays a pronounced regional variation. Highest observed concentrations of NO_3-N are ca. 20 mg l^{-1}. The sources of the nitrate are mainly agricultural fertilisers and increased soil nitrogen loads due to intensive crop production, as well as effluents from animal farming. Highest concentrations are generally found in the escarpment springs (Figure 6.4) whilst dip-slope unconfined groundwaters have lower concentrations more typically in the range 6–10 mg l^{-1}. This may be due to relatively rapid by-pass flow in the escarpment areas or a relatively thin unsaturated zone (Section 3.4). In the semi-confined dip-slope groundwaters of the Beverley–Driffield area, where Drift cover is largely arenaceous, NO_3-N concentrations are generally in the range 2–10 mg l^{-1}. These regional trends were also noted by Smedley et al. (1996). Concentrations in the confined aquifer are low (usually <1 mg l^{-1} and often much lower), either as a result of denitrification or recharge of the groundwaters at a time before the use of modern agricultural chemicals. Since the NO_3-N concentrations in pre-pollution recharge are likely to have been of the order of 3–4 mg l^{-1} (Section 7), this implies that some degree of denitrification has taken place in the confined aquifer.

Chadha et al. (1997) found that groundwater from urban sites north of Hull (Dunswell, Cottingham) in the semi-confined aquifer contained NO_3-N believed to be derived principally from septic tanks. Concentrations from these sites in this study were around 9 mg l^{-1} and confirm that some anthropogenic inputs are likely to be present in these groundwaters.

In the aerobic groundwaters, there is a good positive correlation between NO_3-N concentrations and those of Cl and SO_4 (Figure 6.5), as observed by Smedley et al. (1996). This suggests that each was

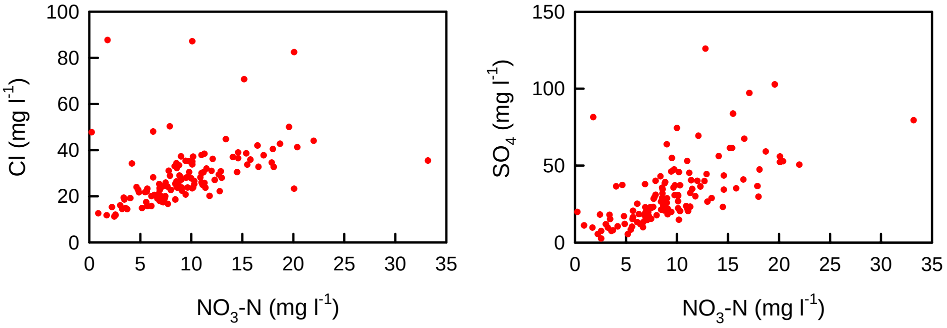
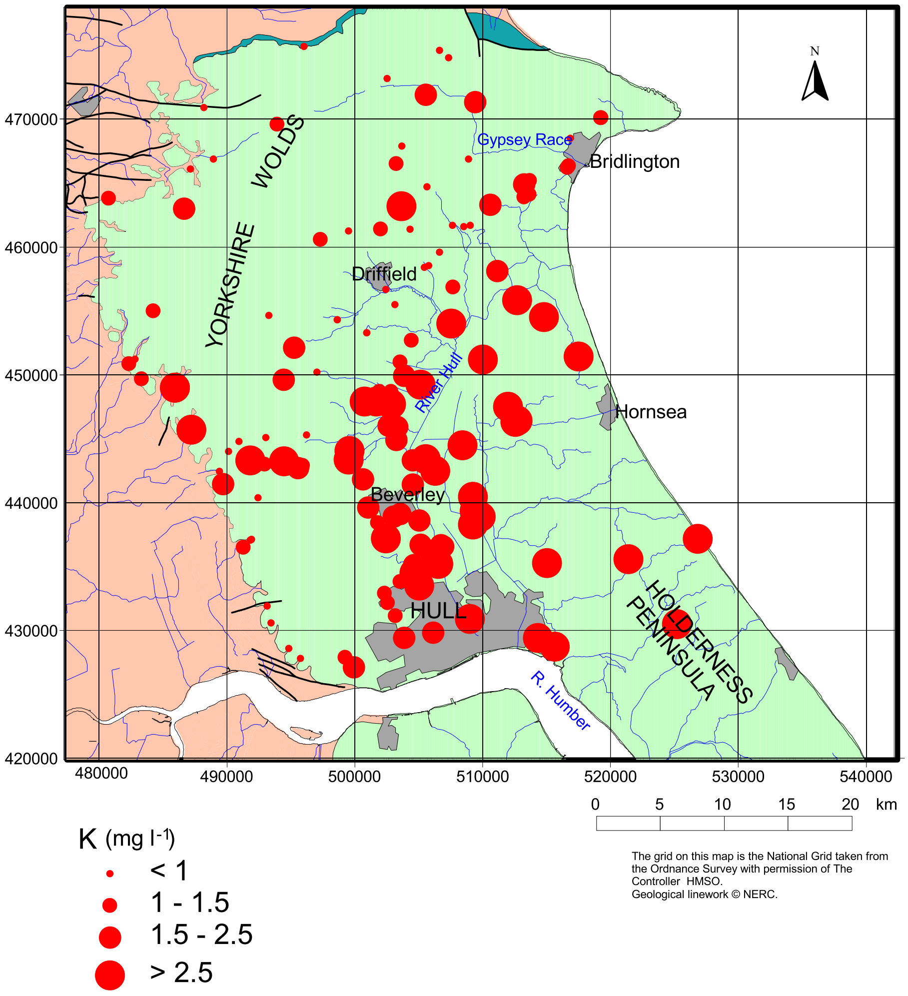


Figure 6.5. **Variation of Cl and SO_4 with NO_3-N in aerobic (unconfined and semi-confined) groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**

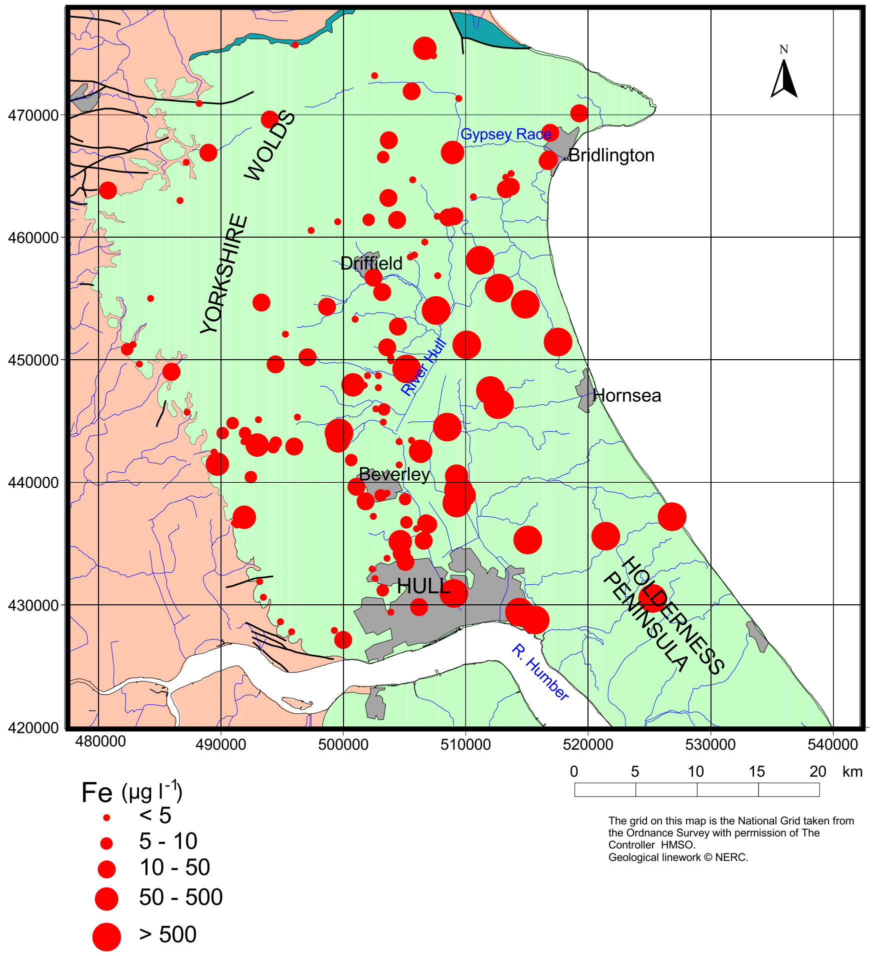
derived substantially from the same pollutant sources as NO_3-N. As noted above, these are considered to be agricultural fertiliser but may also be derived from the effluent from pig, poultry, cattle and sheep farming. Application of sulphuric acid to potato crops may be an additional SO_4 source, though this is restricted to the dip-slope areas.

Concentrations of organic carbon are around 0.5–3 mg l^{-1} in the aerobic groundwaters from the Chalk.



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

Figure 6.6. **Regional variations in K in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

Figure 6.7. Regional variations in Fe in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.

Some organic-carbon analyses for groundwaters in the confined Chalk aquifer are apparently up to 6 mg l^{-1}. The concentration of organic matter in the solid chalk ranges from 0.01–0.1% (Pacey, 1989), although this is not likely to be completely labile and reactive. Such sources of organic carbon are potentially important in supporting microbial populations which catalyse the denitrification reactions.

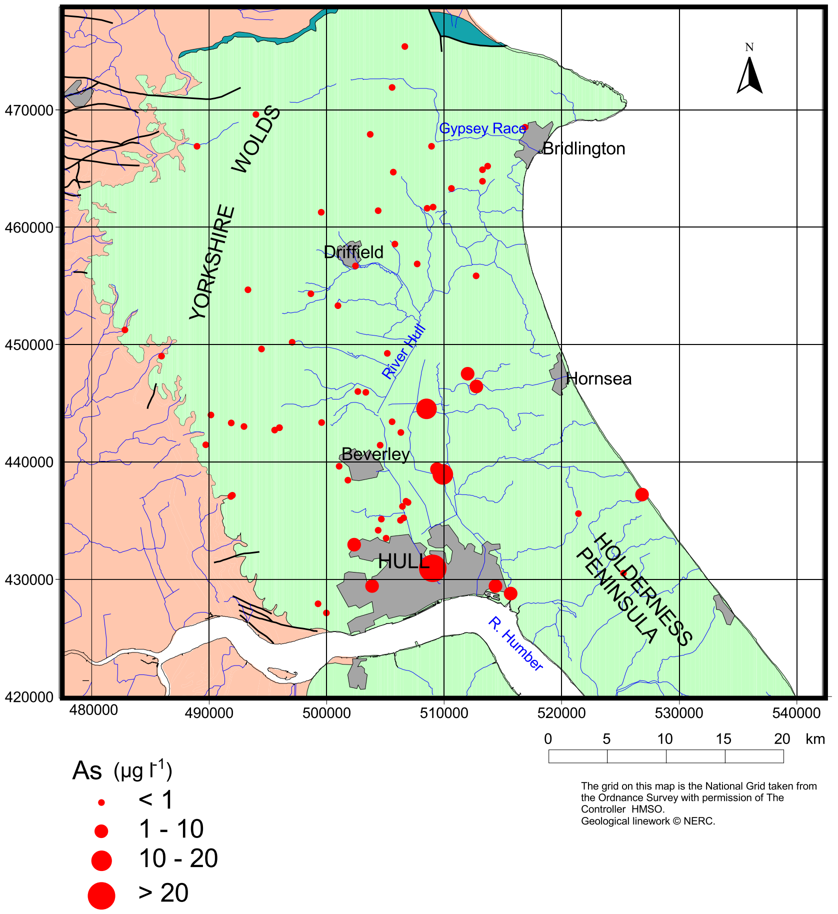
The regional distribution of K (Figure 6.6) shows a strong influence from both interaction with clay minerals, and saline intrusion. Clay minerals, present in higher concentrations in the chalk marls, are potentially important sources of K and other alkali and alkaline-earth metals. In the saline groundwaters from the confined aquifer, mixing with a seawater end member is likely to be a dominant control (modern seawater has a K concentration of around 390 mg l^{-1}; Hem, 1992).

6.2.2 *Trace-element compositions*

Strontium is present at concentrations typically of the order of 800 mg kg^{-1} in chalk (Edmunds et al., 1992) and reaction of groundwater with chalk can increase the concentrations in groundwater significantly. Increased concentrations can also arise due to mixing with seawater since concentrations in modern seawater are typically around 8 mg l^{-1} (Hem, 1992). There is evidence that both these controls are important in the Chalk groundwaters of the region. Strontium concentrations in the oxidising groundwaters from the unconfined and semi-confined aquifer lie in the range 0.16–1.7 mg l^{-1} (Table 5.2) but are much higher in the groundwaters from the confined aquifer, the highest observed concentration being 27 mg l^{-1}. Although some of this increase can be linked to mixing with seawater in the near-coastal parts of the aquifer, the highest concentrations are observed to be far in excess of the modern seawater value and the excess must have been derived by dissolution from the chalk. In the confined aquifer, this implies a prolonged groundwater residence time. From Sr data alone, the timescale involved is not quantifiable. Bath and Edmunds (1981) found high Sr concentrations (up to 37 mg l^{-1}) in deep porewaters from the Chalk of Norfolk. These were also linked to long residence times and the authors concluded that the high Sr concentrations derived from the presence of a connate water component that had undergone significant diagenesis since entrapment in the chalk matrices.

As with K, trace alkali metals and alkaline-earth metals (Li, Rb, Sr, Ba) are likely to derive dominantly from reaction of groundwater with clay minerals, which are especially concentrated in the marls. Mixing with saline water will also have had an influence on these elements, with many observed increases in the near-coastal low-lying areas.

Although the concentrations of oxide minerals (iron oxide and to a lesser extent manganese oxide) are generally low in the Chalk, they are likely to be the dominant control on the distribution of dissolved Fe and Mn. In the oxidising sections of the aquifer, iron and manganese oxides are stable phases and largely insoluble. Dissolved concentrations of Fe and Mn are usually low (typically <30 µg l^{-1} and <10 µg l^{-1} respectively). By contrast, reductive dissolution of iron and manganese oxides in the reducing sections of the aquifer results in release of both trace elements with consequently much higher dissolved concentrations. Calcite is a potential additional source of Mn, but significant release of this is only likely on calcite dissolution and the dissolved Mn concentrations produced from this process will be controlled subsequently by Mn-oxide solubility.



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

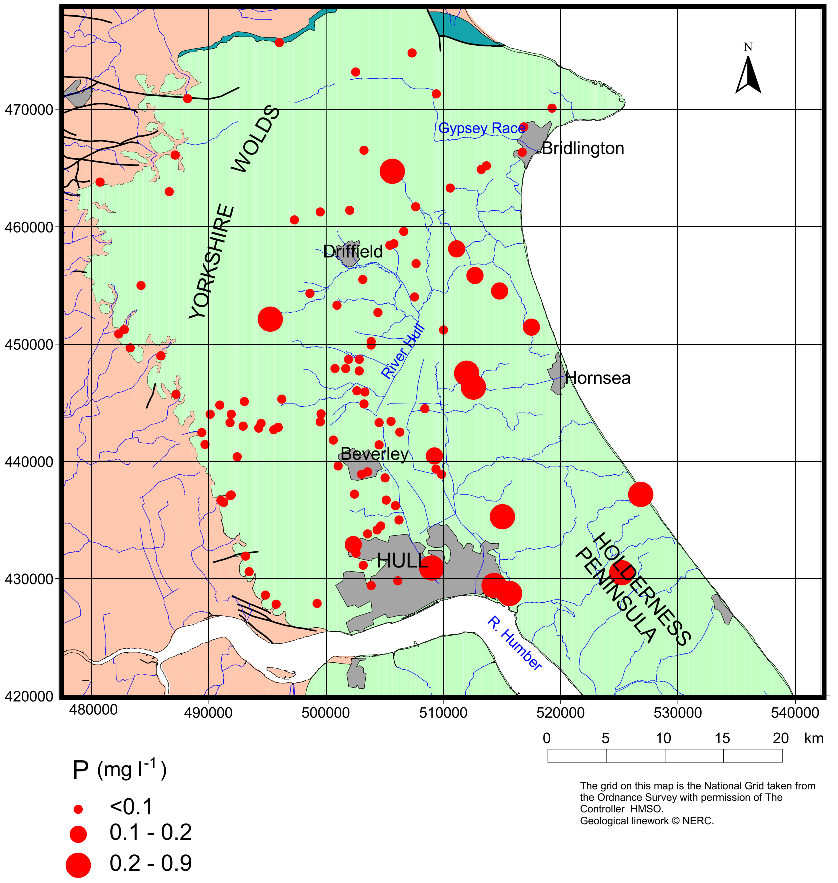
Figure 6.8. **Regional variations in As in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**

A map of the regional distribution of Fe is shown in Figure 6.7. The map shows the generally low concentrations in the unconfined aquifer. Even groundwaters in the semi-confined aquifer between Beverley and Driffield have low concentrations. These are below Drift (Figure 3.2) but in this region the Drift is mostly of arenaceous composition and hence diffusion of atmospheric oxygen to the aquifer has not been significantly restricted. In the section of the aquifer east of the buried cliffline, concentrations of Fe are mostly higher. One or two samples with low concentrations in this zone (Figure 6.7) may be due to variations in thickness (and permeability) of the overlying Drift deposits.

Adsorption or coprecipitation of a number of trace elements to the iron and manganese oxides can also affect their speciation and distribution in the groundwaters. Transition metals such as Co, Cu, Zn and Ni are often associated with iron oxides in particular, although the differences in concentrations of these elements between the oxidising and reducing sections of the aquifer are not notable.

By contrast, As shows a significant difference in concentration between the oxidising and reducing groundwaters (Figure 6.8), being 1.3 µg l^{-1} or less in the former but reaching up to 63 µg l^{-1} in the latter. The distribution is believed to be caused by the release of As by dissolution of, or desorption from, the iron oxides under reducing conditions. Pyrite is well known to be a potential source of As in groundwater as it can contain very high concentrations. However, the association of highest dissolved As concentrations in reducing conditions means that pyrite oxidation is an unlikely control on As mobility.

The concentrations of Mo and P also increase substantially in the reducing part of the aquifer. As with a number of other trace elements, this may be due to release from iron oxides under reducing conditions as well as release form organic matter. Phosphorite, which is present in disseminated



The grid on this map is the National Grid taken from the Ordnance Survey with permission of The Controller HMSO.
Geological linework © NERC.

Figure 6.9. Regional variations in P in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.

grains in the Chalk and particularly in hardgrounds, is a potentially important additional source of dissolved P. Most groundwaters in the oxidising aquifer have low concentrations. Two high-P samples from the unconfined aquifer (Kilham and Westfield Spring; BGS data) (Figure 6.9) may have been polluted by inputs of phosphate in agricultural (NPK) fertiliser but the impacts of pollution on P concentrations in the unconfined aquifer appear to be generally small, probably because inputs will tend to have been mitigated by the strong sorption capacity of soils as well as uptake by plants.

Figure 6.10 shows the regional distribution of U in the groundwaters. Uranium is commonly found in small concentrations in carbonate minerals and iron oxides and also in association with phosphorite (Edmunds et al., 1992; Smedley and Edmunds, 2002). The element is strongly redox-controlled, being more mobile in solution in its oxidised, hexavalent (VI) state. Uranium mobility is also enhanced by formation of carbonate complexes. Under reducing conditions, as a tetravalent (IV) form, it is much less mobile as a result of its strong tendency to adsorb onto iron oxide. Concentrations of U in the Chalk groundwaters are low, being in all cases 1 µg l^{-1} or less. Highest concentrations are found just upgradient of the redox boundary, in oxidising waters from the Hull–Beverley area and just downgradient in the westerly part of the confined aquifer (Figure 6.10). Concentrations are low in reducing groundwaters from the Holderness Peninsula, reflecting the reduced mobility of the U(IV) species. Concentrations are also low in the oxidising, unconfined aquifer in the Wolds area, including the escarpment springs. Although the regional pattern of U concentrations reflects a redox control, it is also likely that the regional distribution is influenced by the residence time of groundwaters in the Chalk. Springs from the westerly escarpment have travelled along shallow flow lines in the Chalk and

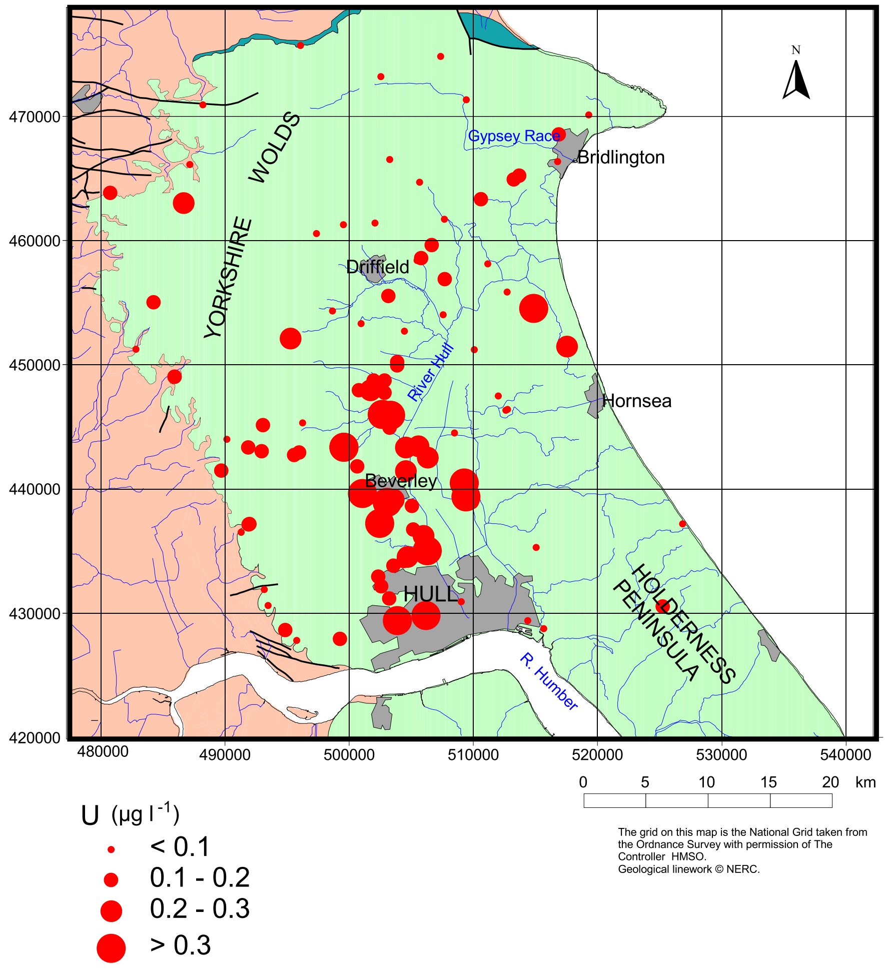


Figure 6.10. **Regional variations in U in groundwaters from the Chalk aquifer of Yorkshire and North Humberside.**

have short residence times in the aquifer. Groundwaters from boreholes further east have longer flow paths and a greater degree of matrix reaction and equilibration has been possible. The U trends therefore reflect increasing residence time along the flow path, followed by reduction to U(IV) and loss by adsorption beyond the redox boundary.

The regional variation in NH_4-N concentration in the Chalk groundwaters appears to be largely redox-controlled. Applications of ammonium-based fertilisers are known to have been made on the land in the area investigated and NH_4 is known to be an important component of manure. Small amounts of NH_4 are also derived from atmospheric deposition. Despite this, the concentrations of NH_4-N in groundwaters from the unconfined aquifer are low and usually below detection limits. Escarpment-spring sources with the highest pollution component, evidenced by high NO_3, Cl and SO_4 concentrations, also have low NH_4-N concentrations. It is considered that any excess NH_4 leaching from the soil zone is oxidised rapidly to NO_3 in the aerobic aquifer. Further downgradient in the confined aquifer, NH_4 concentrations are much higher, reaching up to 11 mg l^{-1}. (Table 5.2) These are not believed to be pollution-derived because of the confined nature of the groundwaters. The high concentrations are more likely to derive by decomposition (oxidation) of organic matter. Ammonium ions are also known to adsorb readily to clay-mineral surfaces (e.g. Appelo and Postma, 1993). Other cations, having increased activity in the saline waters, may be additionally responsible for the high dissolved concentrations of NH_4, due to increased competition for binding sites on clay surfaces. Such high NH_4-N concentrations are often a feature of reducing groundwaters, including those from the Chalk (e.g. Smedley et al., 1993).

6.2.3 Organic compounds

A detailed assessment of the distribution, source and behaviour of organic compounds in the Yorkshire Chalk groundwaters is beyond the scope of this project. However, an overview of their occurrence is of relevance to the assessment of pollution impacts and, by inference, baseline conditions in groundwater and so a short summary of the findings of previous projects is given here. Most of the organic compounds investigated in the April 1996 BGS regional survey were found to be below analytical detection limits (Smedley et al., 1996). Of the compounds investigated, only atrazine, DCM (dichloromethane) and some of the trihalomethanes were present at elevated concentrations. Atrazine was detected in 4 samples (out of 50) from the unconfined and semi-confined aquifer; simazine at 2 of these sites. The chlorinated solvent DCE (*t*-1,2,-dichloroethene) was detected in 5 groundwater samples from the semi-confined and confined aquifer at concentrations >0.2 µg l^{-1}. All were substantially below 1 µg l^{-1}. A number of the detectable trihalomethane compounds were found in raw water supplies from pumping stations. Their origin is uncertain, but local spillage of water disinfection products is a possibility. These are routinely used for treatment of public water supplies but much less commonly at private sites. The results suggest that organic pollutants have reached some groundwaters but the proportions are in most cases minor (see Smedley et al., 1996). None of the samples collected in the 1996 survey has been excluded from the dataset compiled for this report on the basis of their organic compound content.

6.3 Transect across the aquifer

Variations in chemical composition of groundwaters in a transect across the aquifer from the Etton area in the west to Hornsea in the east (plotted against easting) are shown in Figure 6.11 (Eh and major constituents), Figure 6.12 (selected trace elements) and Figure 6.13 ($\delta^{18}O$ and $\delta^{13}C$). Major constituents (Figure 6.11) demonstrate the change in compositions from oxidising (high Eh, high dissolved-oxygen) conditions in the western unconfined and semi-confined parts of the aquifer and the contrasting reducing conditions in the confined aquifer further east. As demonstrated in previous sections, salinity also increases markedly in the confined aquifer as a result of saline intrusion. This is shown clearly by variations in Mg, Cl and SO_4. Under the reducing conditions in the confined aquifer, concentrations of NO_3-N diminish significantly while NH_4-N increases. The variation in DOC shows that concentrations are relatively high compared to many groundwaters in both the confined and unconfined aquifers but are highest in the confined section. The DOC in the unconfined aquifer may reflect a combination of natural and pollutant inputs of organic carbon to the aquifer, but the high concentrations in the confined aquifer are believed to be natural. Concentrations of dissolved P are also higher in the confined aquifer suggesting a natural origin. The P is thought to be derived mainly from collophane minerals in the chalk.

Trace-element variations also display the range of processes that are active in the aquifer. Strontium, F, Mo and B for example clearly display the effects of saline intrusion, although some influence of groundwater residence time is also implied. This is seen especially for the F trend, where concentrations increase steadily eastwards, even in the semi-confined (oxidising) groundwaters in the

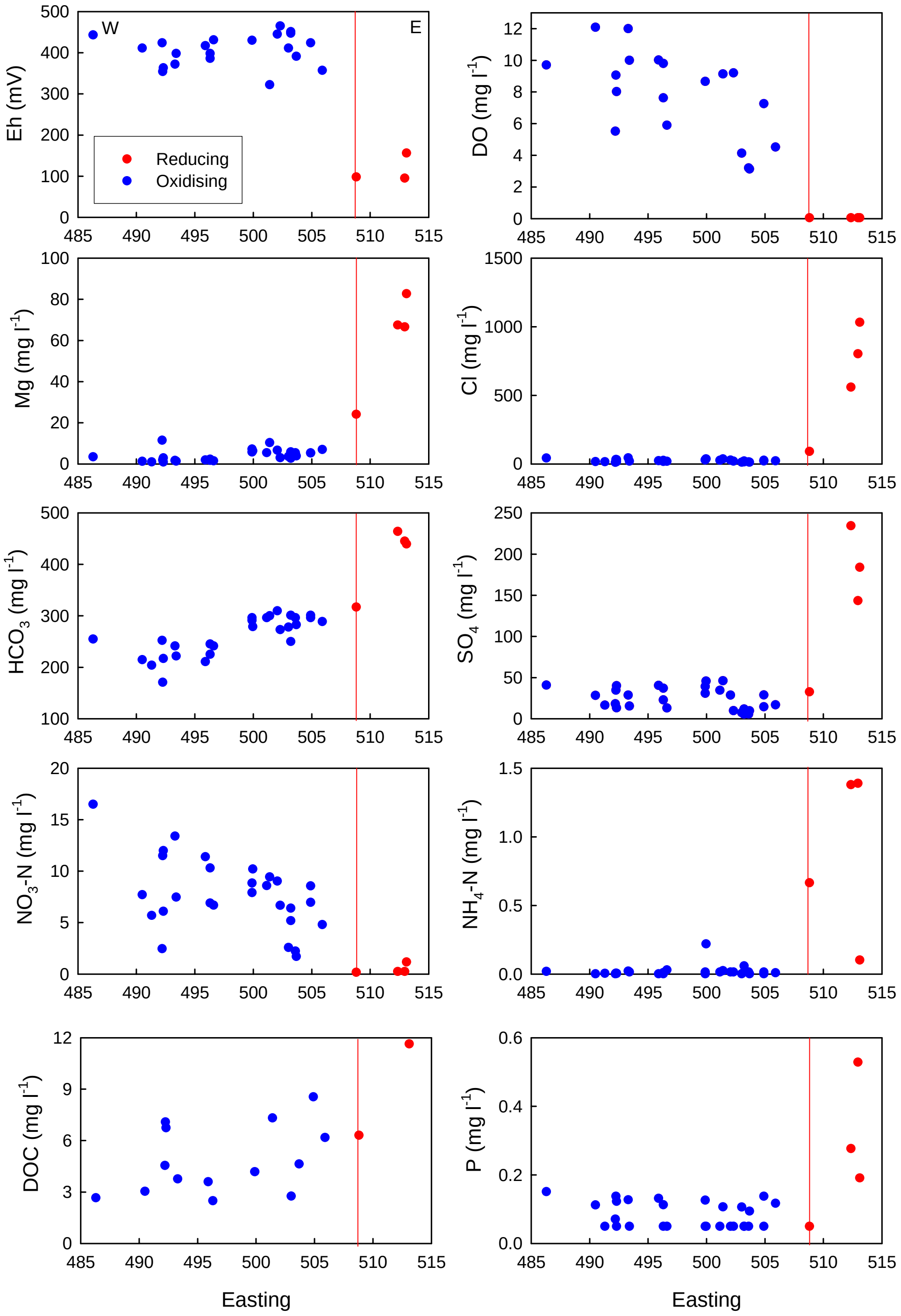


Figure 6.11. **Variation in major ions in groundwater in a west-east transect across the Chalk aquifer (Etton to Hornsea). Vertical line marks the redox boundary.**

central part of the transect. These are not influenced by saline intrusion and so the increase must be related to water-rock reaction processes. The F is probably from dissolution of phosphate minerals.

By contrast, Fe, Mn, As, and U show the effects of redox changes across the aquifer. Iron, Mn and As increase under reducing conditions as a result of iron- and manganese-oxide dissolution, while U decreases in the reducing aquifer, probably as a result of reduction to U(IV) and immobilisation by adsorption. Interestingly, Ni and Zn have generally higher concentrations in the unconfined

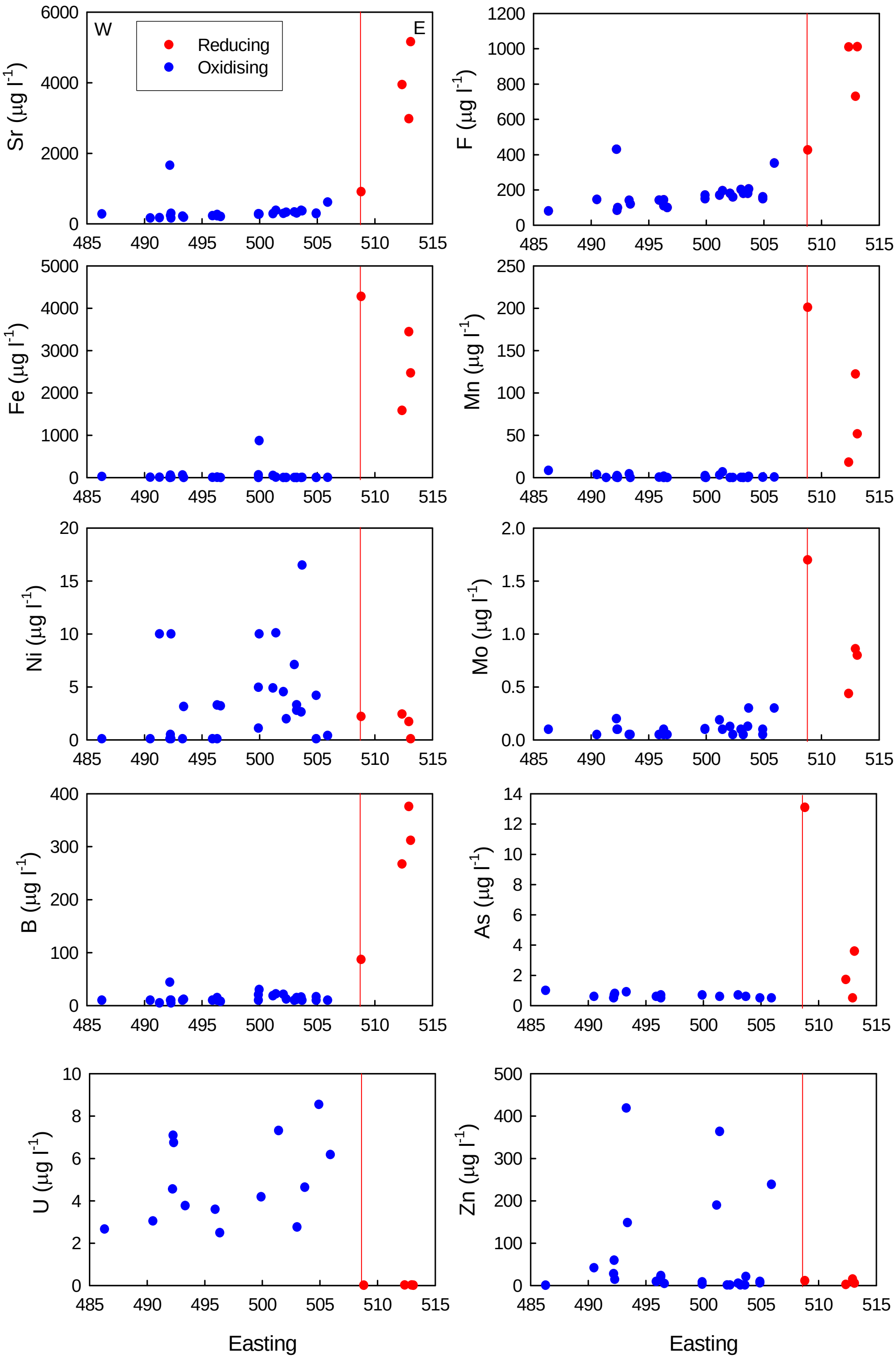


Figure 6.12. **Variation in trace elements in groundwater in a west-east transect across the Chalk aquifer (Etton to Hornsea). Vertical line marks the redox boundary.**

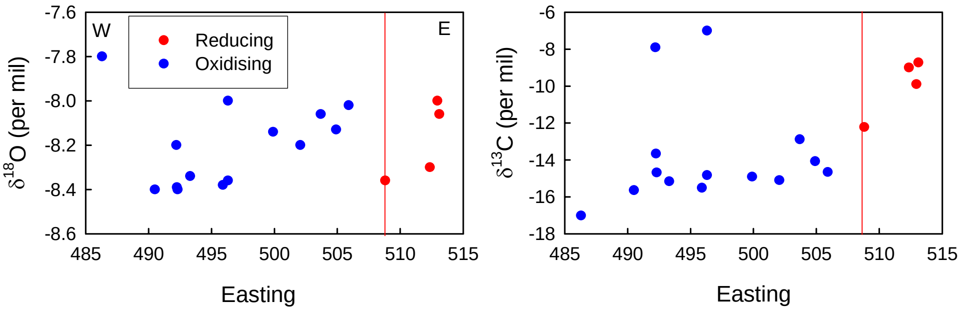


Figure 6.13. **Variation in stable isotopic compositions in groundwater in a west-east transect across the Chalk aquifer (Etton to Hornsea). Vertical line marks the redox boundary.**

groundwaters than in the confined groundwaters. The reason for this is less clear, pollution (e.g. from landfills) is unlikely since the sample locations do not correspond closely with landfill sites. Agricultural fertilisers are also not thought to be likely sources. It is possible that the relatively high concentrations have been derived naturally by the oxidation of minor amounts of pyrite in the chalk under oxidising (but not reducing) conditions.

Variations in $\delta^{18}O$ (Figure 6.13) show little spatial trend and cover a range of -8.4 to -7.8 ‰. However, those from the confined aquifer are more saline than the unconfined groundwaters. Since these are considered to be a mixture between seawater and fresh groundwater, this implies that the fresh groundwater end member was more depleted in its $\delta^{18}O$ than equivalents in the unconfined aquifer. A more depleted composition implies an older groundwater. Compositions of $\delta^{13}C$ in dissolved inorganic carbon have a range of -17 to -7 ‰. The more depleted compositions in the unconfined groundwater indicate the presence of recent recharge with carbon being derived from a combination of soil CO_2 ($\delta^{13}C$ -25 ‰) and calcite ($\delta^{13}C$ 0 ‰). Compositions are more enriched in the confined groundwaters. This is likely to be due to a combination of greater reaction of carbonate (producing a trend towards zero) and mixing with seawater (also producing a trend toward zero). Greater reaction of carbonate implies longer residence times of groundwater in the confined aquifer. Groundwater residence time is discussed further in Section 6.6.

6.4 Temporal variations

Few long-term data are available for groundwaters from the study area. Monitoring data from the confined aquifer is particularly scarce. Trends for nitrate in the unconfined Chalk groundwater have been monitored at some vulnerable sites since the 1970s. Concentrations have been rising steadily in some boreholes since this period. Predictions made by Lawrence et al. (1983) that concentrations at some sites would exceed the EC limit for drinking water of 11.3 mg l^{-1} during the 1990s have in some cases been realised. Market Weighton (Springwells) pumping station has been taken out of service for this reason. The dominant source of the nitrate is probably agricultural fertiliser and increased soil nitrogen brought about by agricultural practices but pig, poultry and cattle farming is also common on the Chalk outcrop and this constitutes a likely additional diffuse source.

Lawrence et al. (1983) observed from groundwater-quality monitoring during the 1970s that nitrate concentrations varied between pumping sites in dip-slope and escarpment locations. The Market Weighton (Springwells) source on the Chalk escarpment had higher nitrate, Cl and SO_4 concentrations throughout the year, with peak concentrations generally later in the year (April-May) and not coincident with the peak groundwater level. Lawrence et al. (1983) also found no obvious correlation between nitrate and rainfall intensity and observed frequent nitrate lows during mid-winter, perhaps due to dilution after the major autumn leaching episode. It was suggested that this relates to increased influence of rapid by-pass flow through the unsaturated zone (pumped groundwaters from the site had higher tritium concentrations than the Etton dip-slope site, suggesting rapid flow of recent water to the water table).

Nitrate and Cl concentrations in groundwaters from a typical dip-slope site at Etton were noted by Lawrence et al. (1983) to increase with rising groundwater levels during the early part of the winter and to peak simultaneously (to within a few days) with peak groundwater level. They also found that the magnitude of the nitrate increase was directly proportional to the water-level rise.

Trends for nitrate concentrations in groundwater from sources at Millington Springs, North Newbald and Etton pumping stations over about a decade from the 1980s were given by Smedley et al. (1996). Increasing concentrations were seen in boreholes from Millington Springs and North Newbald over the period of monitoring. These are both escarpment sites. Rates of nitrate increase varied from source to source, but were generally around 0.2 mg l^{-1} NO_3-N per year. Annual average concentrations of some of these sources now exceed the EC maximum permissible value. The period of monitoring of these sites given by Smedley et al. (1996) showed near-linear increases in nitrate concentrations with no evidence that the earlier data provided represented pre-pollution compositions. Minimum concentrations in the early 1980s at these sites were around 6–8 mg l^{-1}. These are believed to be above 'baseline' concentrations.

At Etton, data from Lawrence et al. (1983) indicated that NO_3-N concentrations increased steadily during the 1970s. Concentrations during 1970 were around 3 mg l^{-1} but by 1980 had risen to 8 mg l^{-1} (borehole number unknown). Trends since 1980 did not appear to show any increase. Concentrations varied between about 6.5 mg l^{-1} and 11 mg l^{-1} between 1980 and 1996 but average annual concentrations are apparently little different today from their values during the 1980s. More detailed investigations of the relationships between groundwater levels and NO_3-N concentrations at Etton (Chilton et al., 1997) suggest that there has still been a slight increase in concentrations since 1980, but that this is only around 0.05 mg l^{-1} per year and much lower than at the escarpment sites. A lack of distinct rises in groundwater NO_3-N at Etton since the late 1970s is likely due to the fact that pumping rates increased significantly in the Etton sources at that time. This would have resulted in a lowering of the groundwater table and the introduction of a larger unsaturated zone. It is therefore likely that there would be an increased time lag in groundwater responses to surface nitrate inputs (Foster, pers. comm., 2002).

Sources at North Newbald and Etton pumping stations also show some seasonal trends in NO_3-N concentration. Trends at Etton typically correlate well with groundwater level with a time lag of a few days (Chilton et al., 1997). This is consistent with the earlier observations of Lawrence et al. (1983) for this site. There is not such a good correlation between groundwater levels and NO_3-N concentrations at the Millington Springs and North Newbald sites (Chilton et al., 1997). It is also less clear whether seasonal variations are occurring in the sources at Millington Springs as sampling intervals have been greater than at North Newbald and Etton and resolution is therefore poorer. For the Etton site in particular, and probably other dip-slope slopes in general, sampling during spring when groundwater levels are at a maximum following winter recharge is likely to have given an indication of the regional quality of the aquifer at its worst with respect to nitrate and other pollutants.

6.5 Depth variations

Few data are available to assess the depth variation in groundwater quality across the aquifer. The only studies carried out involve the assessment of pollutant transport through the unsaturated zone and particularly the fate of nitrate as it infiltrates to the water table in the unconfined aquifer.

In the unsaturated zone of the unconfined Chalk, Lawrence et al. (1983) found that concentrations of NO_3-N as well as SO_4 and Cl reached much higher values than those in the saturated zone. Peak NO_3-N concentrations in the range 20–40 mg l^{-1} were observed in unsaturated-zone porewaters from the Etton catchment area. Concentrations in the zone of water-level fluctuation were in the range 5–15 mg l^{-1}. High values have also been found in porewaters from the unsaturated zone in the Etton catchment by Chilton et al. (1997). Their study has shown that NO_3-N, Cl and SO_4 concentrations peak in the top 10 m of Chalk, reaching up to 48 mg l^{-1}, 70 mg l^{-1} and 85 mg l^{-1} respectively in porewaters from three cored boreholes. In the zone of water-table fluctuation, concentrations were

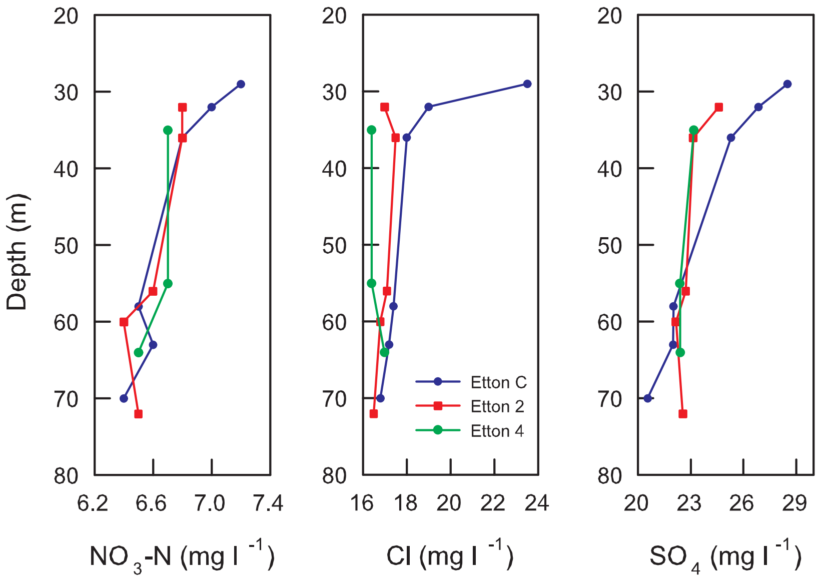


Figure 6.14. **Variation in NO_3-N, Cl and SO_4 in depth samples (mbgl) from Etton boreholes. Etton C is an observation borehole; only Etton 4 was pumping at the time of sampling. The water table during sampling was ca. 29 m below ground level.**

much lower at ≤10 mg l^{-1}, ca. 20 mg l^{-1} and ca. 20 mg l^{-1} respectively, most likely as a result of dilution by groundwater of better inorganic quality from below. The implication of the recent unsaturated-zone study by Chilton et al. (1997) is that concentrations of nitrate, Cl and SO_4 have not yet reached a peak and groundwater quality is likely to deteriorate still further as the poor-quality porewater infiltrates downwards towards the water table.

Depth samples from the shallow part of the saturated zone at Etton pumping station (Etton 2, 4 and Etton C observation borehole, Figure 6.14) indicate that concentrations of NO_3-N, Cl and SO_4 also diminish with depth below the water table, again presumably as a result of dilution of solute loads picked up from the unsaturated zone by groundwater of better quality. Highest concentrations of these determinands were present in the samples from Etton C observation borehole. Heat-pulse flow logging of Etton C whilst pumping Etton 4 indicated that groundwater flows downwards in the borehole from the water table to ca. 38 m depth and upwards from 72 m depth towards 38 m depth (Chilton et al., 1997). Groundwater close to the water table is therefore of poorer inorganic quality than that deeper in the unconfined aquifer.

6.6 Age of the groundwater

It is reasonable to conclude that the groundwater from the unconfined aquifer is dominantly young recharge (years or decades in age) as it has abundant evidence of the impacts of modern pollution and stable isotopic compositions ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$) largely typical of young recharge waters found elsewhere in the UK. Conclusions concerning the age of groundwaters in the confined and semi-confined parts of the aquifer are less clear, but several studies have concluded that the confined aquifer in the Holderness Peninsula contains palaeowater which possibly dates from the Ipswichian Interglacial (University of Birmingham, 1978). Seawater would have covered the wave-cut platform of the Chalk as far inland as the buried cliffline during the Ipswichian and increased concentrations of Sr and I and high I/Cl ratios have particularly been used as evidence that the Holderness groundwater represents trapped seawater dating from this period (e.g. Pitman, 1986; Elliot et al., 2001). Lack of enhanced Li concentrations was used by Elliot et al. (2001) to suggest that the Holderness groundwater is unlikely to be connate. The evidence for existence of old groundwater suggests that there is minimal groundwater flow in this low-lying part of the Chalk.

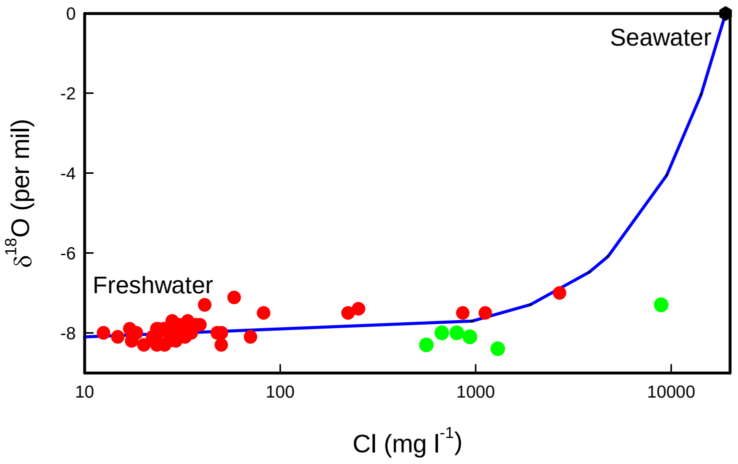


Figure 6.15. **Variation in $\delta^{18}O$ with Cl in the Chalk groundwaters. The freshwater-seawater mixing line is shown for comparison. Samples in green are from the eastern part of the confined aquifer (Holderness and Brandesburton areas) and probably represent older groundwaters.**

By contrast, studies of saline groundwater in the Hull area suggest that intrusion of relatively recent seawater from the Humber Estuary is occurring as a result of groundwater pumping in the urban areas (Foster et al., 1976). This is supported by evidence of increasing Cl concentrations in pumped groundwaters from this area over the last few decades. Saline intrusion became a recognised problem in the Hull area in the early 20th century and has been monitored regularly over a number of decades. However, the seawater component cannot be strictly modern as tritium concentrations of most groundwater samples investigated in the 1970s were low (mostly <2 TU, Foster et al., 1976) and a period of residence in the aquifer is necessary to reduce dissolved-oxygen concentrations from saturated values to the low values observed in the aquifer of the Hull area. This is supported by monitoring evidence from the 1970s which indicated that no further saline intrusion had taken place over that period despite rapidly fluctuating water levels, a long-time low water level (>10 m below sea level) and temporary reversal of hydraulic gradients from river to aquifer (Chadha, 1986). This suggests limited hydraulic connection between the surface and the Chalk in the area (Elliot et al., 2001). Management of groundwater abstraction rates in recent times means that the saline front in Hull is today reasonably stable (Chadha, 1986). Elliot et al. (2001) considered that the saline groundwater of the Hull area is possibly of Holocene age.

The variations in groundwater ages are demonstrated to some extent by the variations in stable isotopic compositions and Cl concentrations. Ratios of $\delta^{18}O$ in groundwaters from the Chalk range between -8.4 ‰ and -7.0 ‰ and $\delta^{2}H$ between -59 ‰ and -47 ‰. Groundwater samples from the shallow escarpment springs cover almost the whole compositional range ($\delta^{18}O$ -8.3 to -7.3 ‰). This is considered to reflect the range of composition of local modern recharge. The most depleted isotopic signature observed is from a sample in the Holderness part of the confined aquifer ($\delta^{18}O$ -8.4 ‰, $\delta^{2}H$ -59 ‰). With a Cl concentration of 1300 mg l^{-1}, this represents a mixture between freshwater and a minor proportion of seawater. The fresh end member is likely to have had an even lighter $\delta^{18}O$ composition since seawater has a $\delta^{18}O$ composition at or close to zero. The fresh end member may therefore represent a relatively old water having recharged under an earlier, cooler climate than present climatic conditions would generate.

Figure 6.15 shows the variation of $\delta^{18}O$ with Cl in the Chalk groundwaters. A theoretical mixing line between fresh groundwater and modern seawater is given for reference. Most of the groundwater samples fall close to this theoretical curve, including brackish samples from the Hull area, north of the Humber Estuary. Most sample compositions can therefore be explained by mixing between relatively recent recharge and modern seawater, although without independent isotopic-dating evidence, the relative ages of these end members remain uncertain.

A few saline groundwaters from the confined aquifer have isotopic compositions which are slightly more depleted than the seawater mixing line. These are shown in green in Figure 6.15. The samples are from the eastern part of the confined aquifer in the Holderness and Brandesburton areas. It is likely that these groundwaters represent mixtures between slightly more depleted (older) recharge water and seawater and hence fall on a more depleted mixing line than that shown in Figure 6.15. The fact that these samples are from the same part of the confined aquifer lends some support to this view.

The Chalk groundwaters from Yorkshire and North Humberside do not share the isotopic depletions characteristic of the Triassic Sandstone aquifer of the English East Midlands, where $\delta^{18}O$ compositions more negative than -9 ‰ for instance have been reported (e.g. Edmunds et al., 1982; Smedley et al., 1993). This suggests that Chalk groundwaters are not as old as those from the deep confined Sherwood Sandstone and perhaps relates to the nature of groundwater flow in the Chalk. Flow in the Chalk is strongly controlled by fissures whereas matrix flow has a much greater importance in the Sherwood Sandstone. Groundwater in the British Chalk is known to represent a much poorer record of palaeoenvironmental conditions during the Quaternary than the Sandstones because of the relative importance of rapid by-pass flow and consequent obliteration of evidence for pre-existing palaeowaters (Darling et al., 1997).

7. BASELINE CHEMISTRY OF THE AQUIFER

Attempting to define the range of groundwater compositions that can be considered as natural baseline compositions is difficult, not least in a regionally extensive aquifer with such a large range of geochemical controls as observed in Yorkshire and North Humberside. In the unconfined aquifer in the west of the study area, the effects of pollution from agricultural sources are clear to see and are best demonstrated by concentrations of NO_3, Cl and SO_4. Baseline concentrations are not found in the escarpment springs and some of the dip-slope unconfined groundwaters. Pre-pollution recharge would be expected to have low, though still detectable NO_3-N concentrations as N would be derived from atmospheric inputs and natural soil-microbiological processes. Concentrations would probably have been <5 mg l^{-1}. Indeed, NO_3-N concentrations in the unconfined Chalk groundwaters during the 1960s were relatively constant and in the range 3–4 mg l^{-1} (Foster and Crease, 1974). Baseline concentrations of Cl and SO_4 in the aerobic Chalk groundwaters are probably both 20 mg l^{-1} or less.

Pollution is likely to have affected other elements to some extent (e.g. K, Ca, P, NH_4) although the effects are less extreme. Many will have been altered by other processes such as adsorption, and pollution components are therefore difficult to quantify. Other elements in the unconfined aquifer are likely to have been less impacted and can be considered largely as baseline compositions. For many of the trace elements, the 97.7 percentile values given in Table 5.2 are useful indicators of upper baseline values in the absence of more definitive information.

Groundwaters from the semi-confined aquifer are offered a degree of protection from the effects of pollution and indeed, in the Beverley–Driffield section, many of the determinands known to be affected by pollution (NO_3-N, Cl, SO_4) are present at relatively low concentrations. In the oxidising sections of the aquifer therefore, the semi-confined groundwaters north of Beverley are taken to be more representative of aerobic groundwater baseline compositions.

In the confined aquifer, groundwater is to a large extent protected from the effects of modern pollution and so the observed concentrations are closer to baseline compositions. These are nonetheless highly variable compositions because they include groundwaters having undergone various degrees of mixing with seawater. In the Holderness Peninsula, the salinity variations are naturally derived. In the Hull area, the determination of baseline compositional ranges is more difficult as the groundwaters are likely to have higher salinity as a result of modern groundwater pumping than would occur under natural and historic conditions. It is therefore a moot point whether or not these represent baseline compositions.

8. SUMMARY AND CONCLUSIONS

The Chalk aquifer of Yorkshire and North Humberside probably displays as well as any other aquifer the large diversity in compositions of groundwaters that can occur as a result of an array of geochemical processes and that can be considered as baseline. Unconfined, oxidising conditions give rise to a characteristic set of compositions defined by Ca-HCO_3 dominance, strongly buffered pH and low or very low concentrations of most trace elements. Confined, anaerobic conditions give rise groundwaters with higher concentrations of Fe, Mn, NH_4-N and As and lower NO_3-N. Prolonged residence times of groundwater in the unconfined aquifer give rise to slight though detectable increases in concentrations of U. In the confined aquifer, prolonged residence allows concentrations of many of the major and trace elements including Li, K, Sr and Mo to increase. Seawater intrusion adds yet another complication to the characterisation of baseline compositions, with resultant development of groundwaters with very variable salinity. All these processes can be considered as entirely natural and representative of 'baseline' compositions. Added to this are the obvious effects of human activities such as pollution from agricultural and other activities (demonstrated best by spatial and temporal variations in groundwater NO_3-N concentrations), and pumping-induced saline intrusion.

Nitrate (NO_3-N) concentrations are high in groundwaters throughout the unconfined aquifer and attest to the relatively poor quality and vulnerability of the resource. The escarpment springs have the highest concentrations, some as high as 20 mg l^{-1}. Concentrations of Cl and SO_4 are also elevated in these samples. The increased concentrations are likely to relate to rapid responses of springs to surface-pollution inputs as a result of preferential by-pass flow through fissures, shallow flow through the Chalk and the relative thinness of the unsaturated zone at these sites.

Nitrate trends in many groundwaters from the unconfined aquifer have shown approximately linear increases over the last few decades as a result of changing and intensifying agricultural practices. Increases in NO_3-N concentrations in the groundwaters from escarpment springs are particularly marked and have been of the order of 0.2 mg l^{-1} yr^{-1} over the last decade or so. Concentrations of NO_3-N in porewaters from the unsaturated zone in the Etton catchment are in places even higher at up to 48 mg l^{-1}. In studies of the quality stratification of groundwaters from Etton, concentrations of NO_3-N as well as Cl and SO_4 are highest close to the water table, diminishing at greater depths due to dilution by longer-residence-time groundwater of better quality. The peaks at the water table are likely the result of pollutant leaching within the unsaturated zone at times of rising groundwater level and from rapidly-infiltrating fissure water derived from the soil zone.

Groundwater quality in the semi-confined aquifer of the Beverley to Driffield area have much lower concentrations of NO_3-N, Cl and SO_4 than further west. These are afforded some protection from surface-derived pollution because dominantly upward-flowing groundwater in this area. However, groundwater from the semi-confined aquifer further south in the Beverley to Hull area, has increased concentrations of NO_3-N (ca. 9 mg l^{-1}) probably as a result of high pumping rates and pollution from urban sources.

Arguably the most significant factor affecting the groundwater chemistry of the region is the redox boundary that is located roughly in correspondence with the position of the buried cliffline, where the aquifer becomes confined by impermeable Drift deposits. This results in a major hydrogeochemical change with large influences on the patterns of the redox-sensitive major and trace elements. Concentrations of Fe up to 5 mg l^{-1} have been found in the confined aquifer. The highest observed As concentration is 63 µg l^{-1}, with 30% of the reducing groundwaters included in the study having concentrations greater than the EC maximum permissible value of 10 µg l^{-1}. Redox processes are also partially responsible for higher HCO_3 concentrations in the confined aquifer.

Nitrate concentrations in the confined aquifer are low, probably as a result of both denitrification and groundwater age (pre-pollution compositions). Concentrations of Cl and SO_4 are determined by the influence of saline intrusion rather than pollution. Phosphorus may be pollution-derived in some sites from the unconfined aquifer, but is mainly derived by reaction of phosphate minerals and iron oxide. Concentrations of NH_4 increase significantly in the confined, saline part of the aquifer because of desorption from clay binding sites due to competition from other cations in saline solutions.

Increasing residence time of groundwater in the aquifer further east is considered important in the generation of increasing concentrations of some inorganic species in the groundwaters (e.g. Li, K, Sr, Mo). However, mixing of fresh groundwater with seawater is also an important cause of the increasing element concentrations down the groundwater-flow gradient. The freshwater and seawater components are of unknown age. Saline samples from the Hull area have chemical and stable-isotopic compositions indistinguishable from those expected for mixing between modern freshwater and seawater but often low tritium concentrations and low dissolved oxygen suggests a period of residence within the aquifer. A Holocene (pre-industrial) age seems likely for the saline end member.

A few of the groundwater samples collected from the confined aquifer in the Holderness–Brandesburton areas have isotopic compositions more depleted than expected for mixing between modern recharge and modern seawater. It is therefore possible that these represent mixtures between seawater and an older fresh end member, recharged under a cooler climatic regime than modern ambient temperatures. This is consistent with other studies which have suggested that the Holderness confined groundwater represents recharge dating back to the Ipswichian Interglacial.

9. REFERENCES

ADAS, 1993. Map of farm type by parish, England and Wales. ADAS, Leeds.

AEA, 2003. Rainfall chemistry data for High Muffles gauging station. AEA website: http://www.aeat.co.uk/netcen/airqual/data/nonauto/raindata.html.

Allen, D.J., Brewerton, L.M., Coleby, L.M., Gibbs, B.R., Lewis, M.A., MacDonald, A.M., Wagstaff, S. and Williams, A.T. 1997. The physical properties of major aquifers in England and Wales. *British Geological Survey Technical Report* WD/97/34. 312pp. Environment Agency R&D Publication 8.

Appelo, C.A.J. and Postma, D. 1993. *Geochemistry, Groundwater and Pollution*, Balkema, Rotterdam.

Aspinwall, 1995. Yorkshire Chalk groundwater model. Report prepared for National Rivers Authority and Yorkshire Water plc. Aspinwall.

Barker, R D, Lloyd, J W, and Peach, D W. 1984. The use of resistivity and gamma logging in lithostratigraphical studies of the Chalk in Lincolnshire and South Humberside. *Quarterly Journal of Engineering Geology,* Vol. 17, 71 -80.

Bath, A.H. and Edmunds, W.M. 1981. Identification of connate water in interstitial solution of Chalk sediment. *Geochimica et Cosmochimica Acta*, 45, 1449-1461.

Berridge, N G and Pattison, J. 1994. Geology of the country around Grimsby and Patrington. Memoir of the British Geological Survey, Sheets 90, 91, 81 and 82 (England and Wales).

British Survey of Fertiliser Practice, 1995.

Buckley, D K and Talbot, J C. 1994. Interpretation of geophysical logs of the Kilham area, Yorkshire Wolds, to support groundwater tracer studies. British Geological Survey Report WD/94/10C.

Catt, J.A. and Digby, P.G.N. 1988. Boreholes in the Wolstonian Basement Till at Easington, Holderness, July 1985. *Proceedings of the Yorkshire Geological Society*, 47, 21-27.

Chadha, D S. 1986. Saline intrusion in the Chalk aquifer of North Humberside, UK. In: Bockelman, R H *et al.* (eds) Proceedings of the 9th Salt Water Intrusion Meeting (SWIM), Delft, The Netherlands.

Chadha, D. S. and Courchee, R. 1978. Groundwater resources in the Chalk aquifer of the North Wolds, with particular reference to Bartindale. Yorkshire Water Authority Report, 20 pp.

Chadha, D.S., Kirk, S. and Watkins, J. 1997. Groundwater pollution threat to public water supplies from urbanisation. In: *Groundwater in the Urban Environment: Problems, Processes and Management*, ed: Chilton, J.C. Balkema, Rotterdam, 297-301.

Chilton, P. J., Gibbs, B. R., Marks, R. J., Coleby, L. M., Buckley, D. K., Williams, A. T. and Bird, M. J. 1997. Trends in nitrate concentration in the Yorkshire Chalk aquifer: Etton water supply. British Geological Survey Technical Report, WD/97/8C.

Chilton, P. J., Lawrence, A. R. and Barker, J. A. 1989. Chlorinated solvents in chalk aquifers: some preliminary observations on behaviour and transport. International Chalk Symposium, Thomas Telford London.

Darling, W. G., Edmunds, W. M. and Smedley, P. L. 1997. Isotopic evidence for palaeowaters in the British Isles. *Applied Geochemistry*, 12, 813-829.

Edmunds, W M, Bath, A H, and Miles, D L. 1982. Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. *Geochimica et Cosmochimica Acta*, 46, 2069-2081.

Edmunds, W.M., Darling, W.G., Kinniburgh, D.G., Dever, L. and Vachier, P. 1992. Chalk groundwater in England and France: hydrogeochemistry and water quality. British Geological Survey Research Report, SD/92/2.

Edmunds, W.M., Shand, P., Hart, P. and Ward, R. 2003. The natural (baseline) quality of groundwater in England and Wales: UK pilot studies. *The Science of the Total Environment*, 310, 25-35.

Elliot, T., Chadha, D.S. and Younger, P.L. 2001. Water quality impacts and palaeohydrology in the Yorkshire Chalk aquifer, UK. *Quarterly Journal of Engineering Geology & Hydrogeology*, 34, 385-398.

Eyles, N., McCabe, A.M. and Bowen, D.Q. 1994. The stratigraphic and sedimentological significance of Late Devensian ice sheet surging in Holderness, Yorkshire, UK. *Quaternary Science Reviews*, 13, 727-759.

Foster, S S D. 1974. Groundwater storage – river flow relations in a chalk catchment. *Journal of Hydrology*, 23, 229-311.

Foster, S. S. D. and Crease, I. 1974. Nitrate pollution of Chalk groundwater in East Yorkshire – a hydrogeological appraisal. *Journal of the Institute of Water Engineers & Scientists*, 28, 178-194.

Foster, S. S. D. and Milton, V. A. 1976. The permeability and storage of an unconfined Chalk aquifer. *Hydrological Sciences Bulletin*, 19, 485-500.

Foster, S. S. D., Parry, E. L. and Chilton, P. J. 1976. Groundwater resource development and saline intrusion in the Chalk aquifer of North Humberside. *British Geological Survey Research Report*, 76/4.

Gaunt, G D, Fletcher, T P and Wood, C. 1992. Geology of the country around Kingston upon Hull and Brigg. *Memoir of the British Geological Survey*, Sheets 80 and 89 (England and Wales).

Hancock, J M. 1975. The petrology of the Chalk. *Proceedings of the Geologists' Association*, 86, 499-535.

Hancock, J. M., 1993. The formation and diagenesis of the Chalk. In: R.A. Downing, M. Price and G.P. Jones (Editors), The hydrogeology of the Chalk of North-West Europe, Clarendon Press, Oxford. pp 14-34.

Hem, J. D. 1992. Study and Interpretation of the Chemical Characteristics of Natural Water. *United States Geological Survey Water-Supply Paper,* 2254.

Lawrence, A. R., Foster, S. S. D. and Izzard, P. W. 1983. Nitrate pollution of Chalk groundwater in East Yorkshire – a decade on. *Journal of the Institute of Water Engineers & Scientists*, 37, 410-419.

Mortimore, R.N., Wood, C.J. and Gallois, R.W. 2001. *British Upper Cretaceous Stratigraphy*. Joint Nature Conservation Committee, Peterborough.

Pacey, N. R. 1989. Organic matter in Cretaceous chalks from eastern England. *Chemical Geology*, 75, 191-208.

Pitman, J.I. 1978. Carbonate chemistry of groundwater from Chalk, Givendale, East Yorkshire. *Geochim. Cosmochim. Acta*, 42, 1885-1897.

Pitman, J. I. 1986. Groundwater geochemistry and mass transfer in the East Yorkshire Chalk. In: Groundwater in Engineering Geology, eds: Cripps, J. C., Bell, F. G. and Culshaw, M. G., Geological Society Special Publication No. 3, pp 177-185.

Robertson, A. S. 1984. BGS contribution to the Yorkshire Water Authority Kilham area river augmentation scheme. British Geological Survey Technical Report, WD/ST/84/9R.

Shand, P. and Frengstad, B. 2001. Baseline groundwater quality: A comparison of selected British and Norwegian aquifers. British Geological Survey Internal Report, IR/01/177.

Smedley, P.L. and Edmunds, W.M. 2002. Redox patterns and trace-element behavior in the East Midlands Triassic Sandstone Aquifer, UK. *Ground Water*, 40, 44-58.

Smedley, P.L., Gibbs, B.R. and Trafford, J.M. 1996. Hydrogeochemistry and water quality of the Chalk aquifer of North Humberside and Yorkshire. British Geological Survey Technical Report, WD/96/80C, 67pp.

Smedley, P.L., Griffiths, K., Tyler-Whittle, R., Hargreaves, R., Lawrence, A.R. and Besien, T. 2003. Baseline Report Series: 5. The Chalk of the North Downs, Kent and East Surrey. British Geological Survey Technical Report, CR/03/033N and Environment Agency Report NC/99/74/5.

Smedley, P L, Shand, P, and Edmunds, W M. 1993. Hydrogeochemistry of the Sherwood Sandstone aquifer of the Doncaster area. British Geological Survey Report WD/93/41R.

University of Birmingham, 1978. South Humberside Salinity Research Project: Final Report to the Anglian Water Authority. Departments of Geol. Science and Civil Engineering, University of Birmingham.

Ward, R. , Williams, A.T., and Chadha, D.S. 1997. The use of groundwater tracers for assessment of protection zones around water supply boreholes – a case study. In: Trace Hydrology 97, ed: Kranjc, A., AA Balkema, Rotterdam.

Wood, C. J. and Smith, E. G. 1978. Lithostratigraphical classification of the Chalk of North Yorkshire, Humberside and Lincolnshire. *Proceedings of the Yorkshire Geological Society*, 42, 263-287.

Younger, P. et al. 1997. Groundwater resources and climate change effects – GRACE. Final report of EC Framework III Environment Programme Contract CEC EV5V – CT94 – 0471.

Zang, B. and Lerner, D.N. 2002. Understanding the complex adit and shaft groundwater source in a Chalk aquifer. *Quarterly Journal of Engineering Geology and Hydrogeology*, 35, 371-380.

ACKNOWLEDGEMENTS

Acknowledgements are due to Mark Morton and Darminda Chadha (Environment Agency) for helpful discussions during the early part of this project. Groundwater sampling was carried out by Ilka Neumann and Dan Lapworth (BGS) and chemical analysis by Debbie Allen, George Darling, Sarah Hannay, Dan Lapworth, Chris Milne (all BGS) and Alan Ward (EA). Yorkshire Water staff are thanked for help with sampling at water-supply pumping stations. ICP-MS analysis was carried out at the Acme Laboratory, Canada. We are also grateful to Mark Antrobus of SPSS for his development work on PIPER diagrams in Sigmaplot.