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13. The Great Ouse Chalk aquifer, East Anglia

Groundwater Systems and Water Quality

Commissioned Report CR/04/236N

Environment Agency Science Group Report NC/99/74/13



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/04/236N

ENVIRONMENT AGENCY
Science Group: Air, Land & Water
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The river Little Ouse, Thetford

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Baseline Report Series: 13. The Great Ouse Chalk aquifer, East Anglia

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Contents

FOREWORD.....	iv
BACKGROUND TO THE BASELINE PROJECT	v
1. EXECUTIVE SUMMARY.....	1
2. PERSPECTIVE.....	2
3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY.....	5
3.1 Introduction.....	5
3.2 Geology.....	5
3.3 Hydrogeology	11
3.4 Aquifer mineralogy.....	12
3.5 Rainfall chemistry.....	14
3.6 Land use in the area	14
4. DATA AND INTERPRETATION	17
4.1 Project sampling programme	17
4.2 Historical data	17
4.3 Processes affecting the composition of pumped borehole groundwaters	18
4.4 Data handling	19
5. HYDROCHEMICAL CHARACTERISTICS	20
5.1 Introduction.....	20
5.2 Water types and physicochemical characteristics	21
5.3 Major elements.....	22
5.4 Minor and trace elements.....	25
5.5 Pollution indicators	26
6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS.....	29
6.1 Introduction.....	29
6.2 Chemical evolution along the regional flow direction.....	29
6.3 Temporal variations	34
6.4 Regional variations	35
7. BASELINE CHEMISTRY OF THE AQUIFER	43
8. SUMMARY AND CONCLUSIONS	44
9. REFERENCES.....	45
ACKNOWLEDGEMENTS	48

List of Figures

Figure 2.1	Comparative uses of Chalk groundwater in the study area of East Anglia.	2
Figure 2.2	Geographical setting of the study areas across the East Anglia chalk outcrop	3
Figure 3.1	Solid geological outcrop in relation to the sampling region and the cross section shown in figures 3.3 and 3.4.	6
Figure 3.2	Relationship of the study area to Quaternary drift deposits and the cross section shown in figures 3.3 and 3.4.	7
Figure 3.3	Geological cross section A, of the area around Bury St Edmunds	8
Figure 3.4	Geological cross section B, of the area north of Saffron Walden	8
Figure 3.5	Groundwater level contours for the central and north part of the study area.	13
Figure 3.6	Land use in relation to the Chalk outcrop	16
Figure 5.1	Piper plot of major ions in groundwaters of the Great Ouse Chalk aquifer	21
Figure 5.2	Box plot summary of (a) major and (b) minor element concentrations in the study area. Solid line shows the seawater dilution curve based on median Cl of the groundwaters and grey line shows typical detection limits.....	23
Figure 5.3	Cumulative probability plots of major and trace elements in groundwaters of the Great Ouse Chalk aquifer.....	24
Figure 6.1	Changes in hydrochemistry along the regional flow direction (regional flow is east to west). Data are shown for the northern section (groundwater contours are shown in figure 3.5).....	30
Figure 6.2	Plots of D.O and Fe against NO ₃ in the Ouse groundwaters. Data are shown for the groundwaters sampled during this study.	33
Figure 6.3	Plots of Cl vs. Na/Cl and Br/Cl ratio in the Great Ouse Chalk groundwaters.	34
Figure 6.4	Time series data from selected public supplies (raw water)	35
Figure 6.5	Spatial variations in HCO ₃ and SEC in the study area (see Figure 3.1 for geological units).....	37
Figure 6.6	Spatial variations in NO ₃ -N and TOC in the study area (see Figure 3.1 for geological units).....	38
Figure 6.7	Spatial variations in Si and F in the study area (see Figure 3.2 for geological units) ..	39
Figure 6.8	Spatial variations in Sr/Ca ratio and Ni in the study area (see Figure 3.2 for geological units).....	40
Figure 6.9	Variations in the (a) stable isotopes δ ² H and δ ¹⁸ O (b) spatial variations in δ ¹⁸ O (see Figure 3.2 for geological units).	41

List of Tables

Table 3.1	Lithostratigraphy of the Chalk Group in the district.....	9
Table 3.2	Rainfall chemistry in the study region, measured at Stoke Ferry, Norfolk, (1998) (NETCEN, 2002).	14
Table 3.3	Land use variation in the three study sections	15
Table 5.1	Major and minor element concentrations in groundwaters of the Great Ouse Chalk study area	20
Table 5.2	Trace element concentrations in groundwaters of the Great Ouse Chalk study area.....	27

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 status of groundwater may represent the starting point of monitoring. This may be defined as background and such an initial condition may include some anthropogenic component in the water quality.

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

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

The BASELINE objectives are:

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

1. EXECUTIVE SUMMARY

The Cretaceous Chalk forms the most important aquifer in England. In the Great Ouse river catchment of East Anglia, the Chalk provides public water supplies as well as extensive irrigation for the predominantly arable rural economy. Chalk groundwater is also important for the maintenance of flows in nationally and internationally important hydrological systems. The chemistry of the groundwaters sampled during this study are overwhelmingly controlled by natural reactions with the aquifer minerals. Dissolution of the calcite matrix controls the major ion chemistry as well as some trace elements (Sr, Mn) which are present as impurities in the calcite. The presence of Till deposits in the upper parts of the catchment and interfluvial regions has had a significant impact on groundwater chemistry. It is likely that modern recharge is focused at the edges of the Till sheets, and is mixing with groundwater derived from an older more mineralised water beneath the Till. It is likely that the Till deposits also provide important contributions of trace metals to the Chalk such as Ni and Co. Nitrate shows the greatest deviation from the expected baseline range within this aquifer, mainly due to recent agricultural practices. Several other elements may also be enhanced over the baseline for the unconfined Chalk. Insufficient historical data for many elements in these groundwaters reinforces the need for adequate temporal data in order to understand the baseline.

2. PERSPECTIVE

The Chalk in the Great Ouse river basin of East Anglia is one of the most important aquifers in England with considerable quantities of groundwater being abstracted to meet demand, in particular for potable and irrigation supplies (Figure 2.1). Groundwater also plays a key role in sustaining river flow in the eastern Great Ouse river catchment, as well as at important wetland sites in west Norfolk and north west Suffolk.

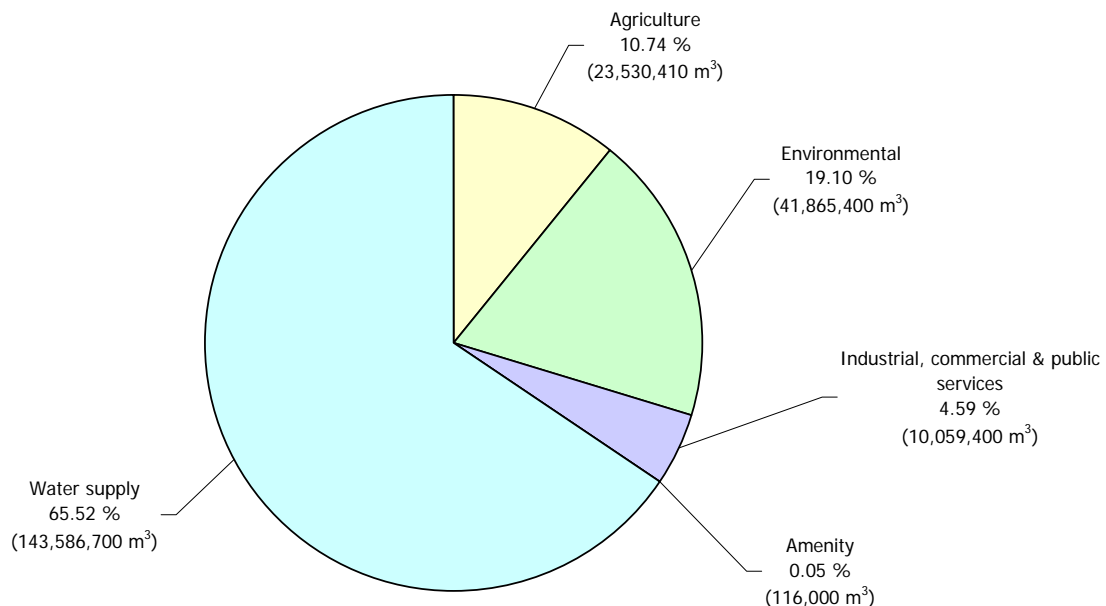


Figure 2.1 Comparative uses of Chalk groundwater in the study area of East Anglia.

The study area of the Great Ouse Chalk encompasses the aquifer lying west of the Chalk escarpment that approximately divides groundwater flowing to the Wash from groundwater flowing to the main part of the East Anglian coastline. It is bounded to the south-west by the groundwater divide of the Chilterns escarpment in Bedfordshire and Hertfordshire. (The baseline chemistry of the groundwater in the Chilterns and Thames region has been reported by Shand et al., 2003). Three study areas were selected, one in each of the catchments of the rivers Cam (or Rhee), Lark, and Little Ouse (Figure 2.2). These discharge to the river Great Ouse and ultimately drain to the Wash. Data from other sources have been incorporated into the study to cover the wider Great Ouse Chalk aquifer system.

The Great Ouse Chalk outcrop has little surface relief, from up to 140 m AOD in the southernmost area to *c.*60 m AOD in the upper Little Ouse catchment. All the rivers fall close to sea level as the main river system runs through the fens via natural and artificial drainage channels (Figure 2.1). The three areas selected for field sampling and close study exhibit geographical and geological variations that have been recognised in the data analysis.

Groundwater resources in this area are vitally important to the environment, society and the economy, evidenced by high demand for potable supplies (private and public), irrigation, industry (e.g. food processing, brewing, medical supplies and mineral extraction) and protected ecological areas. In the future it is likely that the quality and quantity of supply, and the demand balance will be under pressure from the combined effects of increases in demand due to population growth, and the threat of reduced recharge due to climate change.

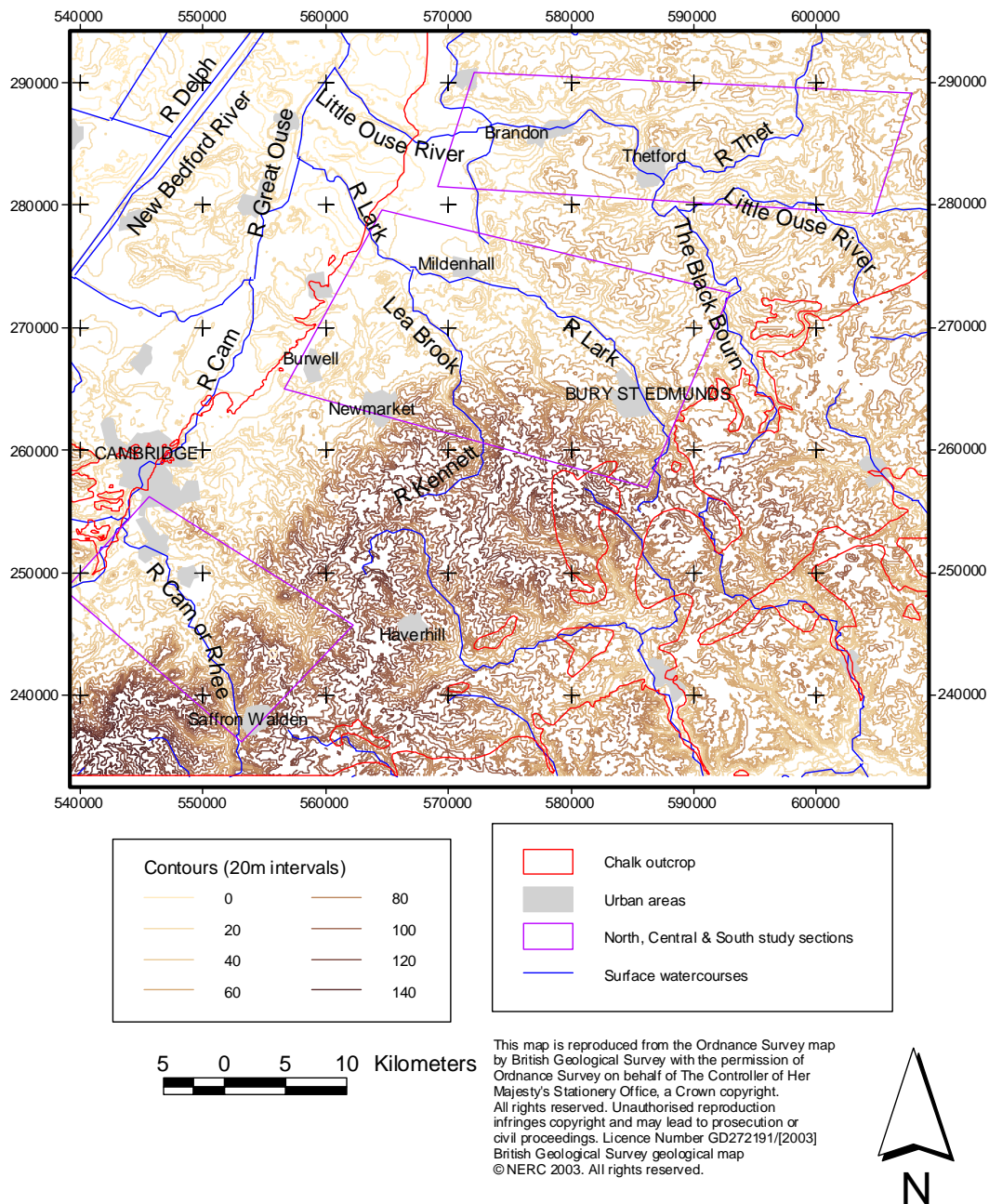


Figure 2.2 Geographical setting of the study areas across the East Anglia chalk outcrop

The Chalk is a major aquifer (Allen et al., 1997) and understanding natural and anthropogenic hydrochemical variations is an essential requirement of the Water Framework Directive (Environment Agency, 2002). For many years prior to this major legislative framework, groundwater in the Chalk has been the subject of monitoring, protection and restoration measures under other EC Directives and national legislation. Under the Nitrates Directive, the majority of the Great Ouse Chalk aquifer is designated Nitrate Vulnerable Zone status, where farmers must comply with good agricultural practices to reduce nitrate leaching from soils. Under the Habitats Directive, there are requirements to protect designated wetlands and the habitats they support from the potential effects of over abstraction and effluent discharges and disposals.

Other stresses on the quality of groundwater arise from urban development particularly around the M11 motorway, construction and redevelopment, particularly on contaminated sites, and diffuse pollution by pesticides, and contaminants associated with transportation systems. The Great Ouse Chalk outcrop has, in general, a much lower population density than over the Chalk north and south of London. The major urban centres are Saffron Walden, Cambridge, Bury St Edmunds, Newmarket and Thetford. In particular, the area around Cambridge is set to grow in population over twenty years under Government plans for development of new communities.

Transport infrastructure has the potential to affect the quality of recharge to the aquifer. Major road networks (M11, A11 and A14) cross the aquifer, and drainage systems vary in their ability to attenuate contaminants from accidental spills and diffuse pollution. Historical and modern aerodromes, civil and military, are a feature of the landscape, covering large areas, particularly at Mildenhall, Lakenheath, Cambridge, and Duxford. Several sites have set aside areas for industrial usage which are important to the rural economy.

Intensive arable farming and free-range pig farming are important components to the region's economy. Many of the cereal and vegetable crops grown on the shallow or sandy soils found over some of the chalk outcrop require extensive irrigation in order to be successful (Hodge et al., 1984). Application of agricultural fertilisers may result in concentrations of nitrate greater than the maximum admissible concentration for drinking water of $11.3 \text{ mg l}^{-1} \text{ NO}_3 \text{ as N}$. The region is also recognised for its forestry in the north of the region at Thetford Forest, and its stud farms associated with the horse racing centre around Newmarket.

Severe pollution of the aquifer by industry has occurred in numerous places. Of note is the pollution of Sawston Mill PWS by chlorinated solvents from a tannery, the court case eventually reaching the House of Lords in 1993. The verdict was a landmark in groundwater pollution litigation because it ruled that the tannery, during normal operations in the past, could not have foreseen the consequences of their actions.

Mineral extraction has occurred across the Chalk outcrop, and continues at several quarries in Cambridgeshire and west Norfolk. The Chalk yields high purity calcium carbonate which is of high value to the food, chemical and pharmaceutical industries at home and abroad.

This report focuses on the variations in groundwater quality related to natural geochemical processes and how these vary spatially across the aquifer. The approach adopted is to include reviews of the area taken mainly from published and unpublished BGS and Environment Agency sources. Existing water quality data are supplemented by comprehensive new analyses. Attempts have been made to ascertain relative groundwater ages and recent temporal variations.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

The hydrochemical evolution of groundwater, from its initial composition as rainfall, is dependant on the complex interplay of the processes taking place in the unsaturated zone (including the soil), any overlying formations, and the composition of the aquifer and existing groundwater. These processes will also be influenced by land and water use and management. Flow systems in the aquifer will be controlled primarily by the geological and hydrogeological properties of the aquifer. A brief summary of the controlling influences is given below in order to provide the context to the hydrochemical results and interpretation.

3.2 Geology

The solid and drift geology of the study area are summarised in Figure 3.1 and Figure 3.2, with cross-sections in Figures 3.3 and 3.4.

The strata of the Cretaceous Chalk aquifer in East Anglia (Figure 3.1) are contiguous with, and form the most easterly onshore extension of the Chalk of the London basin. The Chalk overlies the clays and marls of the Gault (15-20 m thick), which form a lower aquitard. The thickness of individual formations generally increases northwards within the study area from Cambridgeshire to Norfolk, and the strata dip gently to the east (Figure 3.3).

The stratigraphy of the Chalk in the study area is shown in Table 3.1, which summarises the new nomenclature for the sub-groups of the Upper Cretaceous Chalk. However, whilst those classifications have been reported in the most recent publication of the region (Moorlock et al., 2003), these terms are not reflected in the available simplified maps of the area (e.g. Figure 3.1), and the relevant hydrogeological literature (e.g. Allen et al., 1997). Thus, this report will use the previous nomenclature, at the sub-group level. In this report, the term 'Chalk' should be taken to include all of the litho-stratigraphic units comprising the aquifer studied and term 'chalk' is reserved for the lithological description of the aquifer sediments only (Allen et al., 1997). The general geology of the East Anglian Chalk is described in the regional geological guide (Chatwin, 1961) as well as the relevant published memoirs at 1:50,000 scale (incomplete series for the area (Bristow, 1990; Lake and Wilson, 1990; Mathers et al., 1993; Moorlock et al., 2003; Worssam and Taylor, 1969). A recent summary, with particular reference to the East Anglian Chalk as an aquifer, can be found in Allen et al. (1997).

The very low supply of terrigenous material (marl, clay and silt) through much of the Upper Cretaceous resulted in the deposition of very pure, fine grained micritic chalk sediments. These are composed of algal coccoliths (1-20 μm) and coccolithic fragments (laths of 0.5-1 μm), and more rarely, larger skeletal fragments (10-100 μm). The predominance of chalk increases upwards in the Chalk as the supply of terrigenous material decreased, with the Middle and Upper Chalk being much more pure in composition than the Lower Chalk (Chatwin, 1961). The total sequence also thickens from outcrop in the east (c.100 m) to the west (c.400 m) of the study area (Allen et al., 1997), with individual strata also increasing in thickness northwards from Cambridgeshire to Norfolk.

Whilst there are no major unconformities which can be recognised on structural grounds, non-depositional erosive surfaces are thought to be represented by 'hardgrounds'. These are more brittle than the majority of chalk sediments, have a lower porosity and may be glauconized or phosphatised. They are ubiquitous through the East Anglian Chalk and are very important for their effect on groundwater flow through the Chalk aquifer (Section 3.3).

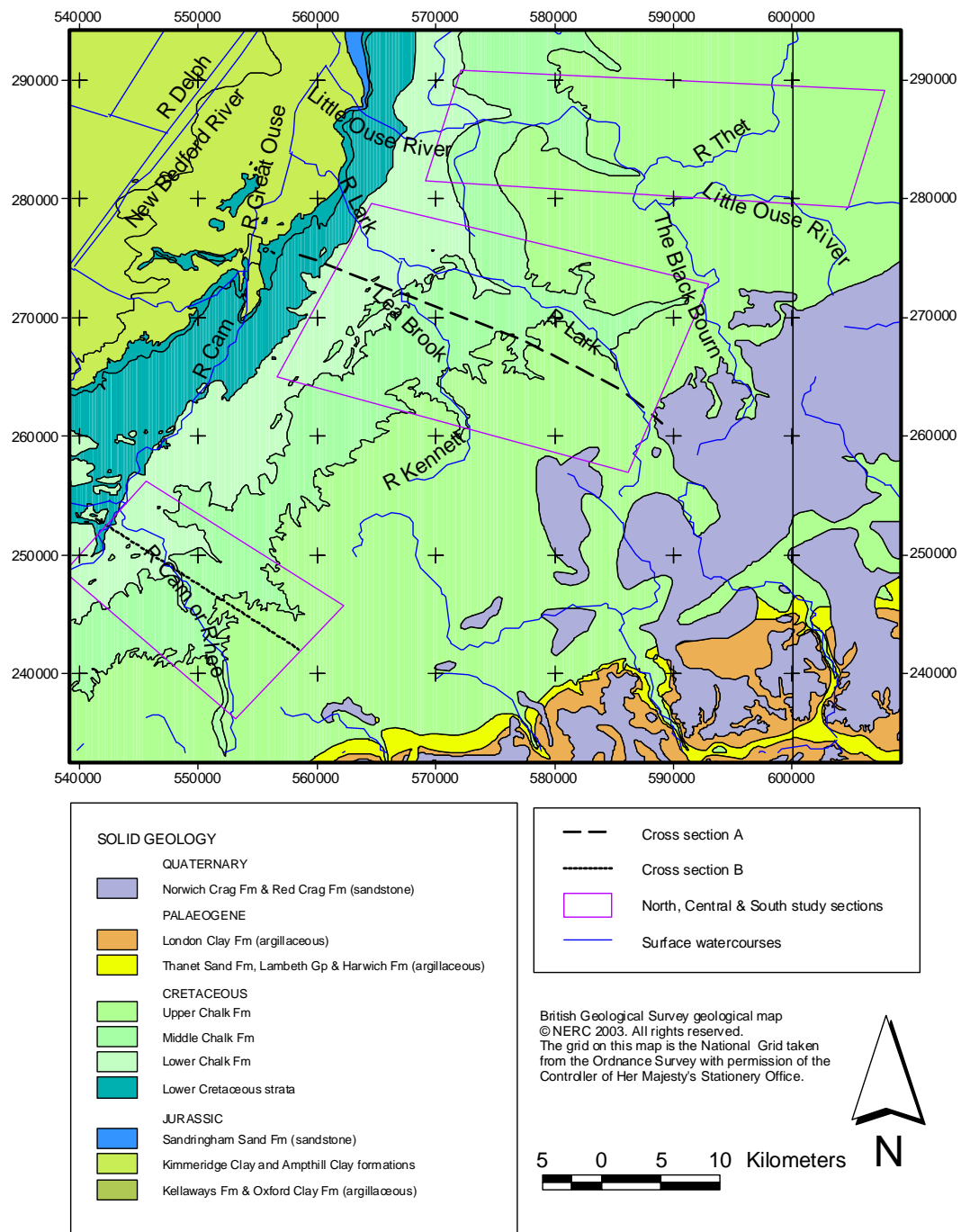


Figure 3.1 Solid geological outcrop in relation to the sampling region and the cross section shown in figures 3.3 and 3.4.

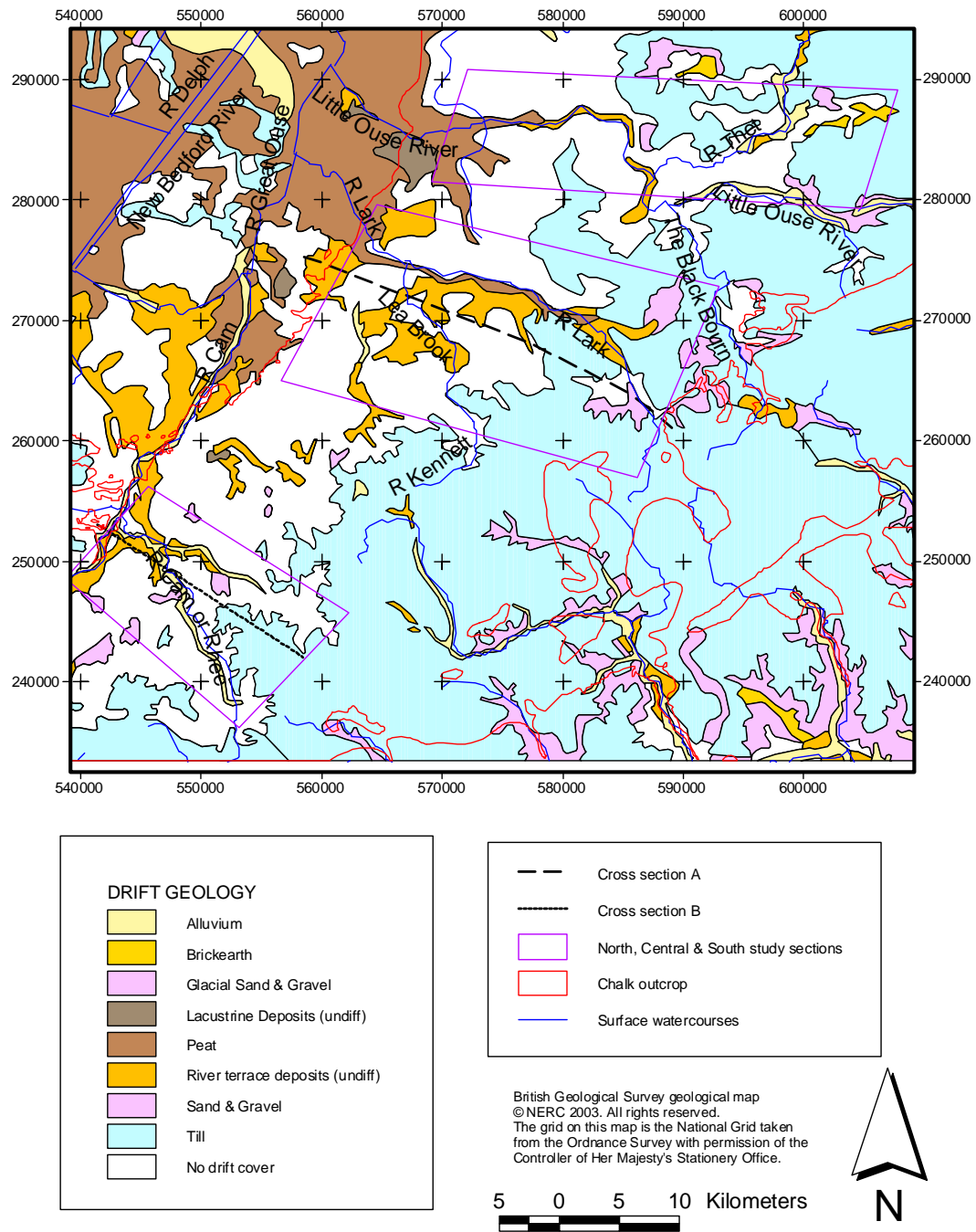


Figure 3.2 Relationship of the study area to Quaternary drift deposits and the cross section shown in figures 3.3 and 3.4.

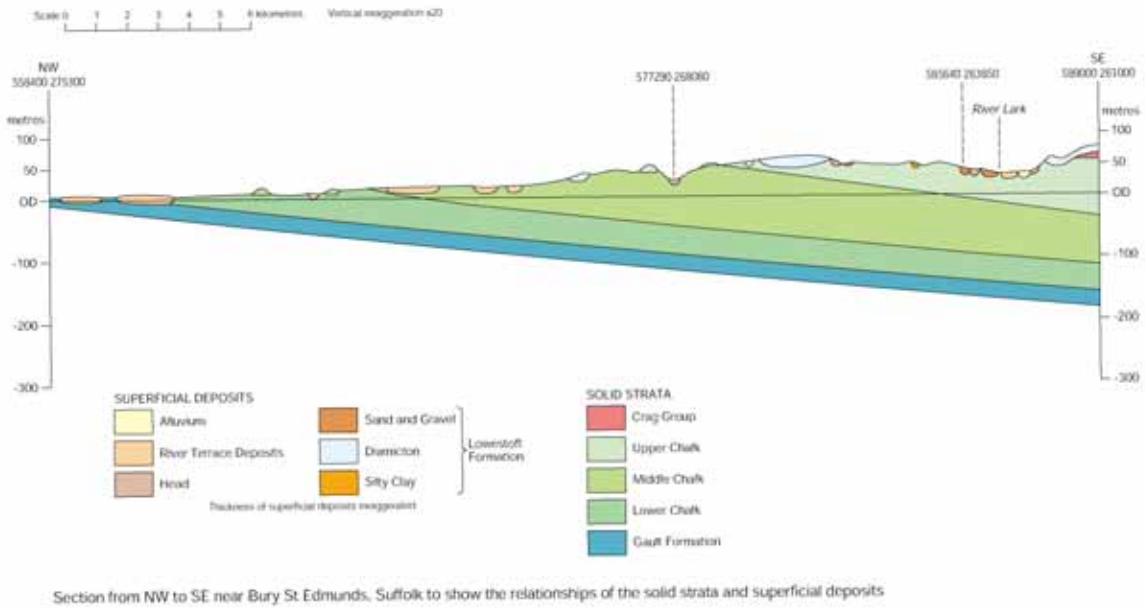


Figure 3.3 Geological cross section A, of the area around Bury St Edmunds

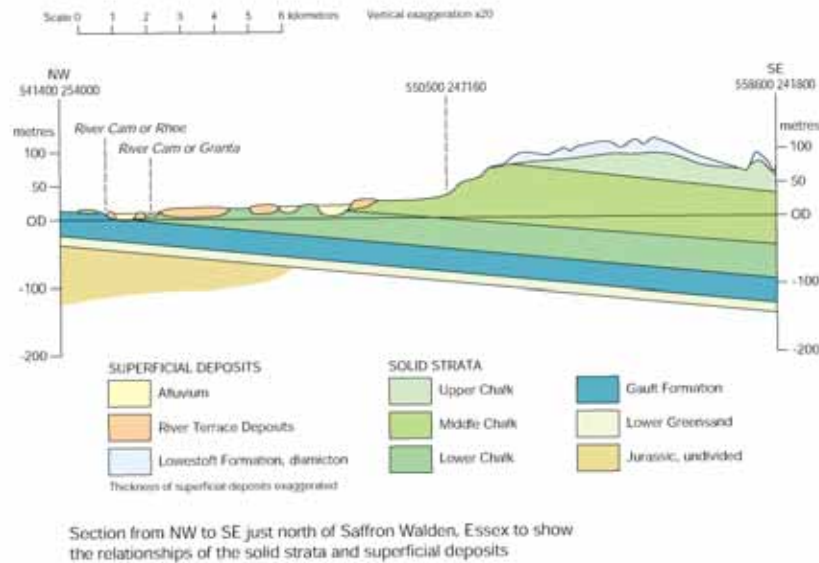


Figure 3.4 Geological cross section B, of the area north of Saffron Walden

Flint bands are also common through the Chalk, with some horizons being formed of massive flints, which can be over 1 m in height. These flints are thought to be the result of diagenetic post-depositional concentration of biogenic silica.

The present day dip of the Cretaceous Chalk is approximately 1° to the east. Faults, bedding plane fractures and joints can all be recognised in the Chalk and it is the lack of lithological contrast that probably prevents all the faults present being discernible (Allen et al., 1997).

Table 3.1 Lithostratigraphy of the Chalk Group in the district

Group	Subgroup	Formation	Member	Former classification
Chalk	White Chalk	Seaford Chalk		Upper Chalk
		Lewes Nodular Chalk	Top Rock Chalk Rock	
		New Pit Chalk		Middle Chalk
		HOLYWELL NODULAR CHALK	Melbourn Rock	
	Grey Chalk	Zig Zag Chalk	Totternhoe Stone	Lower Chalk
		West Melbury Marly Chalk	Cambridge Greensand	

Lower Chalk

The Lower Chalk is the least pure sequence within the aquifer. It is composed of a series of intercalated marl and chalk strata, with decreasing terrigenous material (marl, clay) upwards in the sequence. The base of the Lower Chalk (Chalk Marl) is defined by the Cambridge Greensand Member: a glauconitic sandy marl containing phosphatic nodules, which may be as little as 75% chalk.

The Totternhoe Stone (brown, gritty chalk) is a hard ground, which often forms a prominent topographical feature with a spring line (Whittaker, 1922) in the study area, and separates the Chalk Marl (interbedded chalk and marl) from the Zig Zag Chalk (massive bedded chalk sediment). Very few flints occur in these strata.

Middle Chalk

There are fewer marl horizons in these strata than in the underlying Lower Chalk, giving rise to a much purer chalk sediment. The chalk is generally free of flints, until the top of the New Pit Chalk is reached (top of the Middle Chalk). The base of the sequence is defined by the Melbourn Rock (hardground). The New Pit and Holywell Chalk formations generally comprise very pure chalk sequences.

Upper Chalk

This is the most extensive subgroup in the study area. The total thickness of this Chalk reaches 400 m in west Norfolk. It is very pure, predominantly soft white chalk sediments, with hardgrounds and

flints common (Chatwin, 1961). Two main hardground members occur, the Chalk Rock defining the base of the Upper Chalk and the Top Rock within the Lewes Nodular Chalk member.

3.2.1 Quaternary superficial deposits

Superficial deposits occur extensively over the Chalk aquifer outcrop (Figure 3.2), and can be up to 70 m thick (Chatwin, 1961). These are composed of glacial deposits from the Pleistocene Anglian glaciation and Holocene alluvial sediments. The Anglian and Devensian glaciations also modified and then concealed the sub-Quaternary chalk surface, and periglacial weathering of the chalk affects the physical nature of the chalk close to the modern land surface (Hiscock et al., 1996).

Pleistocene glacial deposits

The glacial deposits over the East Anglian Chalk were largely formed during the Anglian glaciation, the younger Devensian glaciation not being thought to have extended further south than the north Norfolk coast. This period of glaciation generated the modern hydrological setting with the till forming radial drainage patterns, and generated buried tunnel valleys (Allen et al., 1997).

During the Anglian period, erosion by ice streams led to the formation of valley systems in the Chalk. The valleys, up to 100 m deep and often with very steep sides were infilled with sediments after the retreat of the Anglian ice sheet (Allen et al., 1997). The trends of these ‘buried valleys’ are frequently different to modern surface and groundwater flow orientations, representing an earlier hydrological network. The deposits formed during the Anglian glaciation include tills (‘Chalky Boulder Clay’ in the area of study) and glacial sands and gravels. These are complex systems, with gross heterogeneities in clast size and composition, and matrix composition. Within areas of drift, ‘recharge windows’, where the till is missing or highly permeable, can occur over an aquifer, such as those observed at Bury St Edmunds (Bristow, 1990). Isolated lenses of sands and gravel may occur within otherwise clayey till complexes and large rafts of chalk in till have been identified elsewhere in East Anglia within buried valley systems (Chatwin, 1961).

The Devensian glaciation affected the Chalk through the fall in sea level (c.120-150 m below OD), leading to erosive down-cutting by surface waters, and the formation of highly permeable features below the present day water table. In the top 5-6 m of the Chalk, there is increased fracturing due to periglacial weathering, and in some valleys this extends to 20-30 m below OD. Periglacial weathering formed a weathered mantle of up to 1 to 2 m thick due to the freeze-thaw cycle above the permanently frozen chalk. This material is still present as a broken rubbly chalk or a ‘putty-chalk’, (structureless chalk with irregular blocks in a ‘putty’ matrix). Periglacial weathering is also recognised as the most likely cause of modern day dry valley systems (Allen et al., 1997).

Historically, the drift deposits which are predominantly till (clayey) have been considered to provide considerable protection to the underlying Chalk aquifer due to the retardation of contaminants in the clay (high surface area and cation exchange capacity), the reduction of oxidised contaminants (e.g. denitrification in oxygen-poor environment) and the protection of older water beneath (by reduced infiltration rate resulting from low hydraulic conductivities). However, more recent studies have called these assumptions into question and the degree of protection which can be assumed is currently the subject of ongoing investigation by BGS and the EA (Marks et al., 2004).

Holocene alluvial deposits

Alluvial deposits are present along modern floodplains, and comprise a heterogeneous assemblage of gravels, sands, silts and clays. The natural migration of stream channels and changes in sea level through the Holocene has affected the exact juxtaposition of the different lithologies within these sediments, and their relative distribution along stream networks.

3.3 Hydrogeology

The hydrogeology of the Chalk aquifer has been summarised by Allen et al. (1997) and MacDonald & Allen (2001). Whilst the composition of the Chalk (particularly the Middle and Upper Chalk) generally shows a great deal of homogeneity (Section 3.2), the distribution of some physical properties show considerable variation according to geographical location. Much of the data presented by Allen et al., 1997 is derived from boreholes in valleys, and thus may lead to bias in the overall physical properties data-set, because it is largely derived from borehole pumping test that are preferentially located where water is likely to be most easily abstracted. The whole sequence of Chalk is generally considered one aquifer unit, but localised zones of enhanced groundwater flow are encountered. Overlying argillaceous Quaternary deposits are thought to act as partially confining deposits in places, otherwise the aquifer is unconfined in the study area.

The porosity of the Upper Chalk in East Anglia has a mean value of 38.4% and the combined Middle and Lower Chalk a mean of 34.3% based on 127 and 281 measurements respectively (Allen et al., 1997). Such values are generally high in comparison to other areas of the Cretaceous Chalk. Unlike other regions of the Chalk aquifer of England, the porosity of the Lower and Middle Chalk is thought to be very similar in East Anglia (Allen et al., 1997). The average hydraulic conductivity of the matrix of the Chalk is $6.3 \times 10^{-4} \text{ m d}^{-1}$, much less than the value for the whole (bulk) aquifer, suggesting that the fracture system dominates flow in the aquifer (Allen et al., 1997).

Permeability is often conceptualised as depending on the occurrence of minor and major fractures, but is considered by Price (1987) to exist as a continuum between large pores and small fractures up to larger dissolution enhanced fissures. Permeability varies significantly increasing with depth and distance from river valleys: generally with a reduction in the frequency and aperture of fractures (Allen et al., 1997; MacDonald and Allen, 2001). Smaller apertures with increasing depth results from increased overburden pressure and reduced groundwater circulation. As well as increasing permeability in the Chalk towards valley bottoms, the low permeability tills are thin or absent due to erosion by the rivers. This has the effect of both reducing overburden pressure to increase fracture aperture and increasing recharge and thus groundwater circulation (Price, 1987).

Transmissivity in the study area is generally higher in the Great Ouse catchment than to the east of the groundwater divide. This is thought to be due to less coverage by till deposits and the increased number of hardgrounds closer to the surface which contribute to groundwater flow to boreholes (Allen et al., 1997). Median values are $780 \text{ m}^2 \text{ d}^{-1}$ in west Suffolk and $800 \text{ m}^2 \text{ d}^{-1}$ in Cambridgeshire (MacDonald and Allen, 2001). It is noteworthy that transmissivity values have been recorded to change by over two orders of magnitude within distances of 20 m, due to the dependence of transmissivity on secondary porosity features. Some of the valley zone public supply abstraction boreholes used in this study have transmissivity values of $>2000 \text{ m}^2 \text{ d}^{-1}$.

The till is thought to have inhibited solution enhancement of fractures in the East Anglian Chalk (e.g. Hiscock, 1993), and this leads to reduced transmissivity beneath the interfluves, although very little information exists on the physical properties of the Chalk beneath the interfluves compared with valleys (MacDonald and Allen, 2001).

The information on groundwater flow variations can be summarised in the following general observations (Allen et al., 1997):

- small fractures in the Chalk ensure that the overall permeability of Chalk is at least an order of magnitude greater than the matrix for all depths;
- the high transmissivity observed in many Chalk boreholes is usually accounted for by a few larger aperture fractures;

- the most important flow horizons are located near the top of the Chalk, with little flow deeper than 50 m below the water table (or less if confined);
- where hardgrounds occur, the hardened but brittle chalk fractures more cleanly and will generally have more fractures and thus higher permeability up to 100 m below ground level.

The Lower Chalk behaves differently to the Upper and Middle Chalk; perched water tables can be observed where marls (e.g. the Totternhoe Stone and the Melbourn Rock) or hardgrounds occur (Allen et al., 1997). Historically, the Lower and Middle Chalk were the most important aquifer units for the supply of Cambridge (Chatwin, 1961).

Whilst the clay-rich till deposits are thought to significantly reduce recharge, they have also long been known to provide a protective function to the quality of groundwater (National Rivers Authority, 1994; Whittaker, 1906). However, recent research shows that discontinuities (fractures) and lithological heterogeneities in the till may result in more recharge than was previously thought (Klinck et al., 1996; Marks et al., 2004). In addition, dating of these confined Chalk groundwaters using CFC's shows that there is evidence for some modern recharge (Marks et al., 2004). The feather edges of these low permeability sediments (and associated clay rich soils) have been conceptualised as zones of preferential recharge within the East Anglian Chalk.

The effect on local groundwater flow of buried valleys will be determined by the nature and physical properties of the infill materials, which vary greatly in different buried valley systems (Allen et al., 1997).

3.3.1 *Groundwater levels*

Groundwater levels closely mimic topography, and groundwater divides generally coincide with surface water divides in the region. Thus, the groundwater levels are highest in the east of the study region and decrease north-westwards towards the main river valleys (Figure 3.5). Spring lines occur, and these are often associated with hardgrounds. The valleys are groundwater discharge areas and stream flow is often maintained by groundwater base-flow. It can be seen from Figure 3.5 that regional groundwater levels are not greatly affected by lithological variations between Chalk sub-groups.

3.4 **Aquifer mineralogy**

The Chalk was deposited as a very pure low-Mg calcite (<5 mole percent Mg; (Hancock, 1975) generally with <2% non-carbonate fraction. However, accessory minerals can be disproportionately important in terms of their effect on the groundwater chemistry. The occurrence and composition of the non-carbonate fraction in the aquifer matrix varies across the Chalk formations (Section 3.2), but several general observations can be made. Finely disseminated pyrite (cubic FeS₂) may be present in the matrix which, when oxidised, can result in the precipitation of gypsum (CaSO₄.2H₂O) (Morgan-Jones, 1977). Marcasite (orthorhombic FeS₂) nodules are also common (Hancock, 1975). Sulphide minerals are frequently the major hosts for accessory elements such as As, Ni and Cr in the Chalk. The low abundance of glauconite (Hancock, 1975) may also be expected to act as a source of Fe in the aquifer.

The Lower Chalk has a much wider assemblage of non-carbonate minerals as well as a much larger proportion than the younger Chalk strata. Kaolinite is abundant in the Lower Chalk. The clay fraction may account for up to 30% of the matrix. In a study of clays in the Chalk around Burwell (Cambridgeshire) and Lakenheath and Elveden (Suffolk), smectite and illite were recorded in all samples, with vermiculite and kaolinite also being recorded in the Burwell samples (Perrin, 1957).

The Burwell samples were probably from the Lower Chalk, consistent with observations from the Trunch (NE Norfolk) borehole (Bath and Edmunds, 1981).

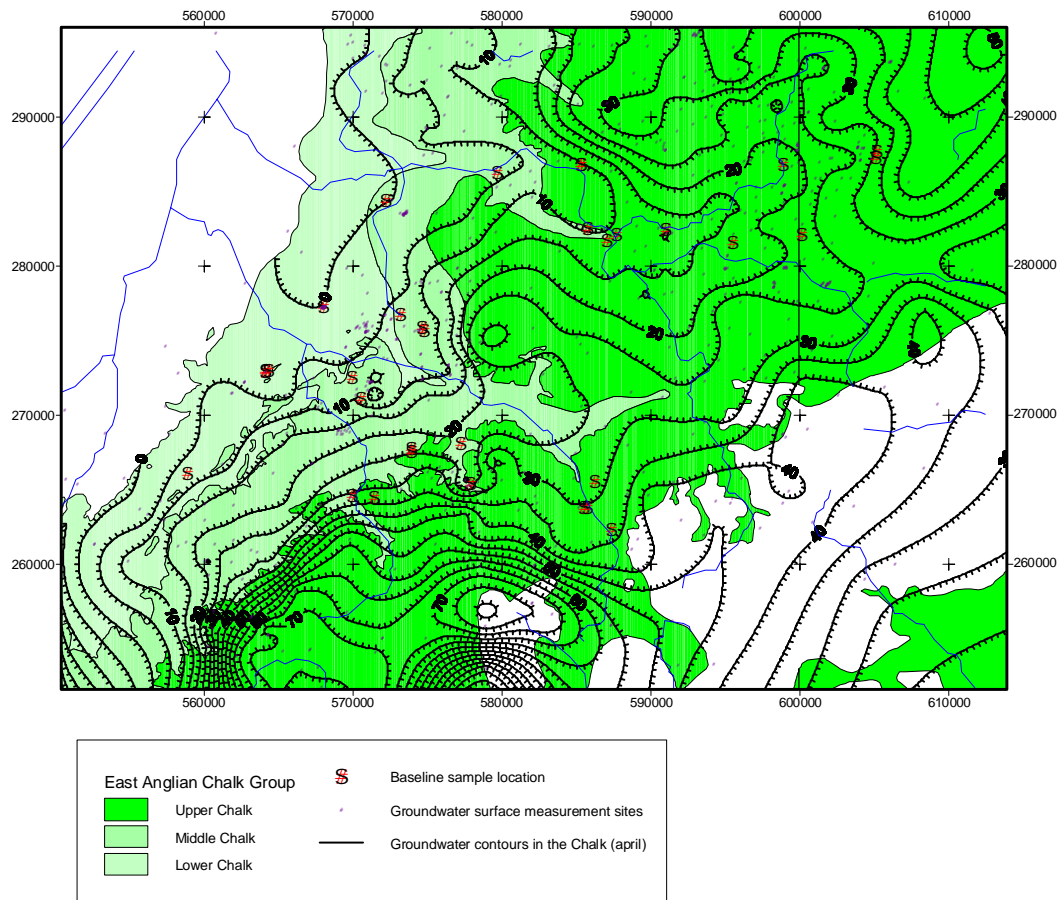


Figure 3.5 Groundwater level contours for the central and north part of the study area.

The non-carbonate fraction of the Upper and Middle Chalk is dominated by quartz, montmorillonite and mica (illite, muscovite and some glauconite) in southern England (Hancock, 1975; Morgan-Jones, 1977). Thus silica occurs in both detrital and authigenic phases throughout the Chalk matrix (Morgan-Jones, 1977). Apatite, feldspar and pyrite although present are less abundant than those minerals. Phosphates occur as nodular or concretionary phases, or dispersed through the Chalk matrix. Hardgrounds may contain over 5% apatite and a greater concentration of mica (Hancock, 1975).

The mineralogy of fracture faces in the Chalk may be as important in determining the hydrochemical composition of groundwaters as the Chalk itself, because the Chalk acts as a dual porosity aquifer. Studies in the unsaturated zone of the Chalk of southern England have demonstrated that fractures can be coated by abundant clay minerals, which can almost entirely isolate the fracture face from the aquifer matrix (Shand and Bloomfield, 1995). Widespread Mn coatings have been observed throughout the aquifer. The source is thought to be from the calcite matrix (100-200 mg kg⁻¹ Mn in the Berkshire Chalk; (Edmunds et al., 1987), being released during mineral dissolution. Iron oxyhydroxide mineralisation has also been observed in more discrete locations especially where marcasite and pyrite nodules occur (Shand and Bloomfield, 1995).

3.5 Rainfall chemistry

Rainfall is the primary source of recharge to the aquifer, and thus the primary source of solutes to groundwater, prior to water-soil reactions. The annual mean rainfall composition for the closest available national monitoring station is shown in Table 3.2 for Stoke Ferry, Norfolk (NETCEN, 2002). In Table 3.2, multiplication of the composition by 3 is to approximate the effects of evapotranspiration. This composition will be further modified by uptake and cycling of plant nutrients, such as K and N, but the data provide an estimate for initial inputs against which to compare groundwater composition. Chloride is assumed to behave conservatively during recharge, which would suggest that concentrations in recharge waters unaffected by other sources of chloride, e.g. leachate or road salts, and prior to mixing with older waters should have a concentration of about 7 mg l⁻¹.

Table 3.2 Rainfall chemistry in the study region, measured at Stoke Ferry, Norfolk, (1998) (NETCEN, 2002).

Parameter (annual mean value)	Rainfall composition	Rainfall composition x 3
pH	5.1	
Na (mg l ⁻¹)	1.26	3.79
K (mg l ⁻¹)	0.12	0.35
Ca (mg l ⁻¹)	0.78	2.34
Mg (mg l ⁻¹)	0.27	0.80
Cl (mg l ⁻¹)	2.20	6.59
SO ₄ (mg l ⁻¹)	2.26	6.77
NO ₃ (mg l ⁻¹)	2.48	7.44
NH ₄ (mg l ⁻¹)	0.90	7.21
Total N (mg l ⁻¹)	1.26	3.78
SEC (µS cm ⁻¹)	27.2	81.80
Rainfall amount (mm)	435	

3.6 Land use in the area

Land use varies over the unconfined Chalk outcrop, but is dominated by arable agriculture. The three selected study regions have varying proportions of land uses, summarised in Table 3.3.

The southern section is almost wholly dominated by arable farming, (Figure 3.6). During sampling, the crops were largely wheat and other cereals. The area has many villages and small towns, and several major roads (the M11, A11 and A14), the only major towns being Saffron Walden in the upper groundwater catchment and Cambridge which is down-gradient of the study area. Industry is generally confined to light industrial units in towns such as Duxford, and civilian and former military airfields.

The central study area includes the major town of Bury St Edmunds in the upper catchment, and Mildenhall, Newmarket and Burwell further down gradient (Figure 3.6), and associated major trunk roads such as the A11 and A14. The proportion of land devoted to arable crops is less than in the

southern section, and managed grassland is a more important land use. This managed grassland, which dominates in the Newmarket area, is generally associated with the racehorse industry (stud farms, training tracks, racing stables and racecourses). Free range pig farming and some intensive poultry units are also present in the area. As with the southern section, military airfields (both operational and former wartime aerodromes) constitute an important industrial land use (with respect to potential groundwater quality impacts) in otherwise rural areas.

Land use in the northern section changes along the line studied. The uppermost catchment is dominated by arable farming with some managed grassland (including cattle and sheep). Down-gradient, coniferous forest and semi-natural heathland of the Breckland district dominates, with local arable farming, particularly potatoes, in the area. The only major settlement in the field area is that of Thetford. Beyond the Breckland region the study area includes a small area of Fenland farming, characterised by arable farming and cattle rearing. The only major industry in the area is found in Thetford, which has some light industrial estates, and former and current military airfields and firing ranges.

Table 3.3 Land use variation in the three study sections

Section Landuse	North		Central		South	
	(km ²)	(%)	(km ²)	(%)	(km ²)	(%)
Arable	151	43	320	64	209	93
Managed Grassland	85	24	127	26	11	5
Forestry / Woodland	95	27	30	6	0	0
Semi-natural vegetation	6	2	0	0	0	0
Urban	12	3	21	4	4	2
<i>Total</i>	<i>349</i>		<i>498</i>		<i>224</i>	

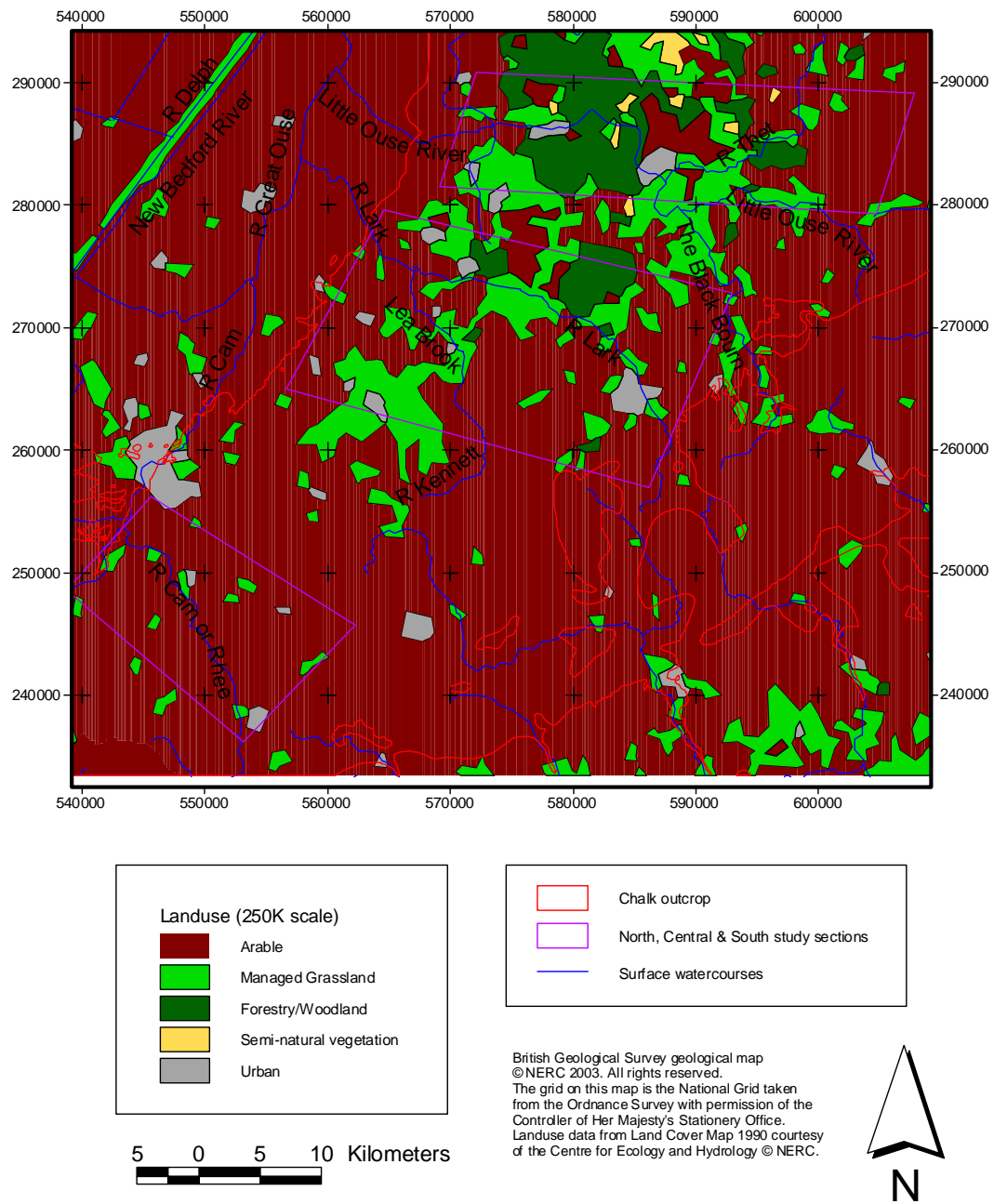


Figure 3.6 Land use in relation to the Chalk outcrop

4. DATA AND INTERPRETATION

4.1 Project sampling programme

Forty four samples were collected in July and September 2002 from 38 different sites. These were taken from a variety of sources, including public and private water supply boreholes, industrial abstraction sites and springs. Three river catchments were selected as the focus of the study to allow sufficient samples to be collected in each area to adequately characterise its hydrochemistry (Figure 3.1). Many of the boreholes sampled (particularly the public water supply and industrial sites) were pumping constantly, or for regular extended periods on a daily basis, and were thus expected to be compositionally stable. Most other boreholes had been pumped for a day prior to sampling, with the exception of one site (Newton Farm, NGR 5431 2489), which was taken in the absence of any other known sites in the area, and with no local flowing springs due to the dry weather (July 2002). Two sites at Park Farm (NGR's 5699 2725 and 5705 2710) were mixtures of water from two boreholes on an agricultural (irrigation) ring main. Again, these samples were taken in order to provide information in an area that would otherwise have been poorly covered. It is also important to note that all samples potentially represent mixing of water from different depths and preferential flow paths in the aquifer.

The parameters pH, redox potential (Eh) and dissolved oxygen (DO) were measured on site using a flow-through cell where possible. Otherwise the measurements were made by inserting the probes as close as possible to spring outlets, or measured as quickly as possible where it was not possible to attach the flow-through cell to the water outlet. Other on-site measurements made were alkalinity (by titration), temperature (T) and specific electrical conductance (SEC). Samples were filtered (<0.45 μm) into NalgeneTM polythene bottles for major and trace cation and SO_4 analyses (acidified with 1% v/v HNO_3). Filtered (<0.45 μm), unacidified, samples were also collected for anion analysis. Samples were also collected in glass bottles for total organic carbon (TOC), dissolved organic carbon (DOC) (filtered to <0.45 μm through a Ag-membrane filter), and stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$).

Analysis of the major cations and sulphate was undertaken by inductively coupled plasma atomic emission spectrometry (ICP-AES). Trace elements were determined using inductively coupled plasma mass spectrometry (ICP-MS). Nitrogen species and Cl, Br, F and I were determined by automated colorimetry (SKALAR). Stable isotope analyses were measured by mass spectrometry and values reported relative to VSMOW for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and relative to VPDB for $\delta^{13}\text{C}$.

In addition to the new data measured as part of this study, data from the Environment Agency (Anglian region) WIMS database and national network monitoring scheme were incorporated where the samples had been filtered. Additionally two sites had been sampled as the baseline to the ongoing investigations of the Thriplow landfill site and the most recent results of that sampling have been incorporated (Williams et al., 2000). This increased the number of samples for which there was major ion analyses in the Great Ouse Chalk to 77, although most of these samples do not have nitrogen species or trace element analyses.

4.2 Historical data

There are limited numbers of historical datasets for this area. A compilation of data from many public supply boreholes in the Cambridge area for the period 1945-1984 was published by Carey & Lloyd (1985) for nitrate. This clearly demonstrated a trend of increasing concentrations of nitrate in these sources through time, although short term variations and pumping regime changes are also evident. Extensive datasets are available for public supply sources, although little other historical data exists.

4.3 Processes affecting the composition of pumped borehole groundwaters

The chemical composition of a groundwater sample will be a function of many factors and the very act of drilling and pumping water from a borehole will cause variations in the chemistry. These variations may arise as a result of differences in:

- borehole design and construction (depth of borehole, depth(s) of casing, drilling mud/lubricant used)
- stratigraphic horizons occurring in the borehole (including fractures intersected)
- pumping histories of a borehole and differences in pumping regimes at different boreholes otherwise very similar in design and geological setting

4.3.1 *Different borehole designs*

Occurrence of different flow regimes within the Chalk (Section 3.3) means that not only will differences between fracture and pore water chemistry be probable, but lateral and vertical stratification may occur. Where a screened borehole intersects these chemically stratified groundwaters, mixing will be expected to occur within the borehole. Thus the borehole depth, orientation and length of casing will all have the potential to affect the borehole water chemistry simply by affecting the nature and quantity of groundwater drawn into the borehole.

4.3.2 *Differences in stratigraphy*

Natural variability of the structure, mineralogy and geochemistry of the Chalk will result in variations in the groundwater chemistry. The Chalk is a dual porosity aquifer, which may result in pore water chemistry (dominated by diffusion processes) being different to fracture network water chemistry (dominated by advection and dispersion). The composition of Chalk pore waters in adjacent areas of aquifer has been studied in Berkshire, Hertfordshire and north Norfolk (Bath and Edmunds, 1981; Edmunds et al., 1973; Shand et al., 2003), although no studies have been found from the area covered by this report. It has been found that the fracture water composition can differ considerably from the matrix water; the matrix water forms the greater volume within the aquifer. The water sampled by boreholes will be overwhelmingly fracture waters. Fracture waters mix by diffusional exchange with pore waters, and the latter may contribute or remove solutes to or from water in the fractures.

A significant issue in the representative sampling of the Chalk groundwaters results from the highly variable transmissivity of the aquifer, particularly over the catchment scale from interfluvial to valley (discharge) regions (Section 3.3). This has had the effect of biasing the location of pumping boreholes to the higher transmissivity zones in the valleys, in order to maximise the probability of intersecting fractures, and thus greatly increasing yields. Where boreholes are sited over till covered interfluvial areas elsewhere in the East Anglian Chalk, the aggressive nature of reducing waters to the pumping equipment increases the costs of running such boreholes, reinforcing the economic desirability of siting boreholes in valley locations. Therefore, valley sampling locations far outweigh interfluvial locations, and hence bias the resulting dataset.

4.3.3 *Differences in pumping history*

The dual porosity nature of the Chalk means that variations in the rate and quantity of water abstracted will affect the lateral and vertical extent from which water is drawn via fracture flow in particular. Vertical and lateral variations in baseline quality are significantly affected by changes in the redox status of the waters. Thus, when water is drawn from depth or from beneath semi-confining Quaternary sediments (i.e. poorly oxidising or reducing groundwaters) this may affect the redox potential if mixing takes place in the borehole. The effect of pumping history has been shown in the

long records of nitrate data for some Cambridgeshire public water supply sources, where sharp steps in the data are artefacts attributable to pumping history, rather than changing fluxes of nitrate into the aquifer (Carey and Lloyd, 1985).

This report presents a broad assessment of the water quality variations observed across the aquifer and the controlling geochemical processes. Groundwater chemical composition is both time and space dependant and the data presented simply represent a snapshot of the water quality, which is in a constant state of change.

4.4 Data handling

Sample site selection was dictated by the occurrence of available, suitable sampling locations within the selected study areas and by avoiding any known areas of point-source pollution.

The data from this study, and pre-existing data are described in Section 5. Where data were less than the detection limit for the method used, a value of half the detection limit has been applied for statistical purposes. Analytical detection limits vary both with time and between laboratories and this makes calculating low level average concentrations difficult. Accordingly, all data have been adjusted to half the detection limit value of data from the present study. Where such data occur, this will particularly affect trace elements, because their natural abundance in Chalk groundwater is frequently lower than the detection limits cited.

Pre-existing data were rejected where charge balance errors were greater than 10%. Analyses of samples collected for the present study had charge imbalances of less than $\pm 6\%$ occurred, with most samples being less than $\pm 5\%$

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

The data used in this study are summarised in Table 5.1. The data range, median and mean are used to provide information on the statistical distribution of the data. The median is the preferred indicator of the average values for the groundwater, as it is less affected by outlier values than the mean. The 97.7 percentile value (defined as the mean + 2σ , where σ represents the standard deviation) is provided to represent the upper limit for the range of data to remove outlying values. This chapter describes the hydrochemical characteristics of the groundwaters studied, highlighting data of interest. Chapter 6 presents interpretation of the data in a regional hydrogeochemical framework to understand the processes controlling the observed baseline geochemistry.

Table 5.1 Major and minor element concentrations in groundwaters of the Great Ouse Chalk study area

Parameter	units	min.	max.	median	mean	97.7th percentile	Upper baseline*	N
T	°C	10.5	13.1	11.5	11.6	13.1		46
pH		6.6	8.1	7.1	7.2	7.7		58
Eh	mV	227	449	423	402	449		40
DO	mg l ⁻¹	0.32	10.0	6.2	5.5	9.8		43
SEC	µS cm ⁻¹	469	1112	688	723	1082		77
δ²H	‰	-54.9	-45.8	-51.0	-50.9	-46.8		38
δ¹⁸O	‰	-8.0	-7.1	-7.6	-7.5	-7.2		38
δ¹³C	‰	-15.4	-12.2	-14.1	-14.0	-12.3		38
Ca	mg l ⁻¹	81	188	128	130	183		77
Mg	mg l ⁻¹	1.1	15	3.3	3.9	11		77
Na	mg l ⁻¹	7.0	65	14	17	43		77
K	mg l ⁻¹	0.41	15	2.7	3.2	8.3		77
Cl	mg l ⁻¹	9.0	126	30	36	88		77
SO₄	mg l ⁻¹	10	120	34	41	108		77
HCO₃	mg l ⁻¹	190	398	277	283	371		77
NO₃ as N	mg l ⁻¹	0.287	38.4	9.5	10.3	25.0	2-3	77
NO₂ as N	mg l ⁻¹	<0.001	0.101	0.006	0.019	0.093		44
NH₄ as N	mg l ⁻¹	<0.003	0.17	<0.003	0.011	0.088		77
P	mg l ⁻¹	<0.1	0.20	<0.1	<0.1	<0.1		46
TOC	mg l ⁻¹	0.4	5.6	1.3	1.6	4.9		76
DOC	mg l ⁻¹	0.2	4.1	1.5	1.7	3.5		44
F	mg l ⁻¹	0.10	0.58	0.17	0.20	0.53		47
Br	mg l ⁻¹	<0.03	0.210	0.080	0.086	0.160		46
I	mg l ⁻¹	0.002	0.034	0.005	0.006	0.012		44
Si	mg l ⁻¹	4.5	13.3	7.4	8.0	13.0		46

* estimated upper baseline for elements modified by anthropogenic influences.



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

Summary presentations of data are given in the Piper plot (Figure 5.1), box-and-whisker (box) plots (Figure 5.2) and cumulative frequency plots (Figure 5.3).

Cumulative frequency plots (Figure 5.3) are useful tools in visualising the distribution of data and for determining different data populations, including outlying data or pollution affected samples. Time and space dependant geochemical processes may be expected to affect data distributions, and thus baseline, throughout an aquifer (Box 5.1).

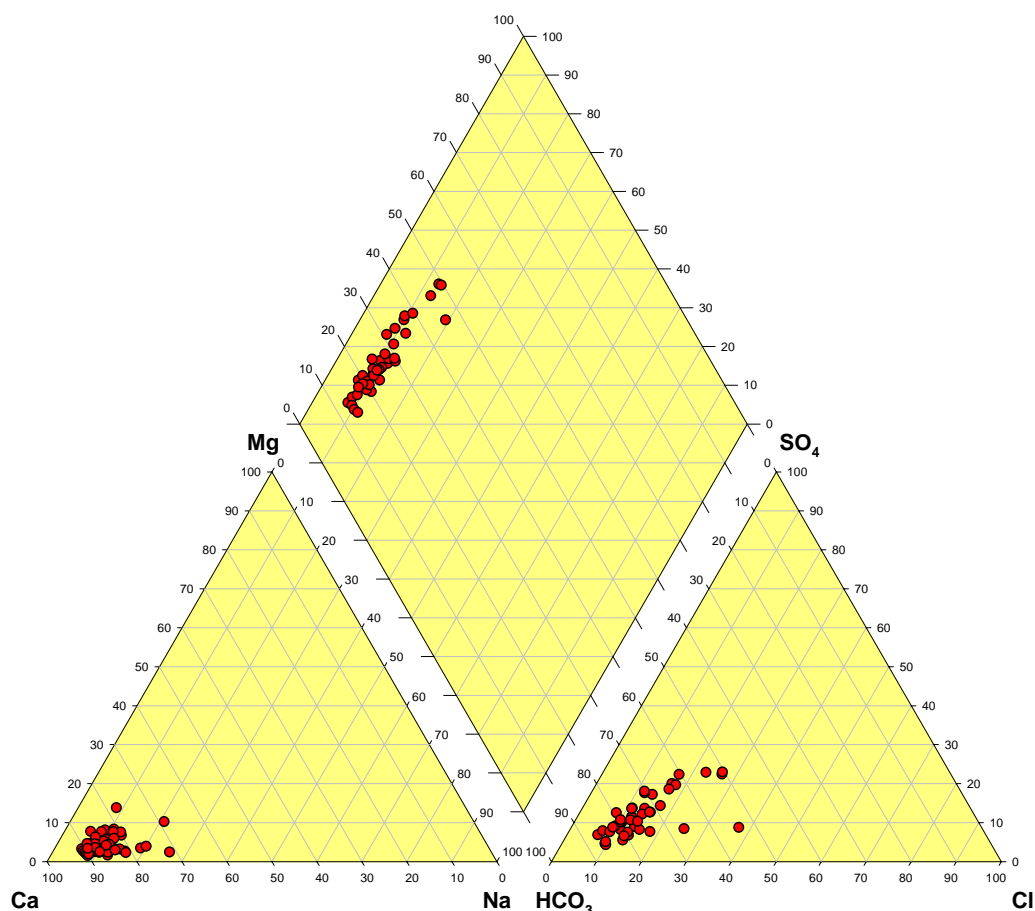


Figure 5.1 Piper plot of major ions in groundwaters of the Great Ouse Chalk aquifer

5.2 Water types and physicochemical characteristics

The summary of the composition of waters in the Great Ouse Chalk are given in Table 5.1 and Table 5.2, which show the low concentrations of most trace elements through the aquifer, and the major ion predominance of Ca and HCO₃.

The physico-chemical parameters were measured on site (Section 4), including dissolved oxygen (DO) and redox potential (Eh) where possible; these parameters are generally only available for the samples collected during this study.

The waters are generally weakly mineralised (median conductivity of 688 $\mu\text{S cm}^{-1}$), although higher values ($>1000 \mu\text{S cm}^{-1}$) are found in the northern area from deep boreholes beneath Boulder Clay (till) deposits. The values are also higher at the easterly extreme of the Chalk in the central study section. The median value of pH (7.14) and small range are all consistent with well buffered groundwater controlled by carbonate equilibrium. The range of Eh values measured is small and consistently

oxidising, with a median value of 423 mV. However, these data show poor agreement with the DO data, with which they would be expected to co-vary: this results from the well established difficulties in obtaining representative Eh measurements. The DO data show a greater range in the redox conditions than implied by the Eh values. The samples generally associated with the upper catchment contain lower DO concentrations ($<4 \text{ mg l}^{-1}$), whilst those lower in the catchment for all three areas have higher concentrations. The overall median value is 6.2 mg l^{-1} , reflecting the larger number of samples from the middle and lower reaches of the study areas. Groundwater temperatures show little variation (range $10.5 - 13 \text{ }^\circ\text{C}$), all the higher temperature samples being associated with irrigator boreholes where the sample outlet is situated some distance from the source, as this is affected by the ambient air temperature.

The Piper Plot (Figure 5.1) shows the major ions (Ca, Mg, Na, K, HCO_3 , SO_4 and Cl) plotted as relative proportions calculated from their concentration in milli-equivalents. This diagram demonstrates the dominance of any cationic or anionic species rather than their absolute concentration. It can be seen that the Great Ouse Chalk aquifer groundwaters are all of Ca- HCO_3 type, which is typical of unconfined Chalk groundwaters from other baseline studies (Edmunds et al., 2002; Shand et al., 2003; Smedley et al., 2003).

The major element composition of the groundwaters is very consistent, with all but one sample having relative proportions of Ca $>70\%$, with Na forming much of the rest of the cation species. The concentrations of Ca and Mg increase simultaneously, maintaining the similar proportions shown in Figure 5.1. The proportion of Mg, compared to Ca, is greater than that observed in the Chalk matrix from the Trunch borehole in Norfolk (Bath and Edmunds, 1981). Whilst the proportions of the anions vary more than the cations, HCO_3 is always the dominant ion. No systematic difference can be seen between the three study areas, with the anion composition showing close to the full range of variation in all three areas.

5.3 Major elements

The major element chemistry of these groundwaters is summarised in Table 5.1 and the box-plots shown in Figure 5.2. The box-plots are arranged in order of abundance in seawater using a logarithmic concentration scale. For comparison the relative composition of seawater normalised to the median Cl concentration of these samples, is shown. This provides an indication of the enrichment due to water-rock interaction within the aquifer i.e. generally above the marine derived input (connate water and rainfall). The range for Na and Cl is small and close to this median value.

The median concentration of Cl is 30 mg l^{-1} , enriched compared to that estimated for rainfall derived recharge (6.59 mg l^{-1} in Table 3.2), suggesting that rainfall is not the only source of Cl in the groundwaters. The Na to Cl ratio closely mimics that observed in seawater (Figure 5.2), whilst K and SO_4 are enriched relative to the ratio in seawater. The concentrations of Ca and HCO_3 are greater than any other ions, and have a very narrow range compared to the other major ions. Nitrate has a high median value ($9.5 \text{ mg l}^{-1} \text{ NO}_3 - \text{N}$), also reflected in the interquartile range of $6-13.4 \text{ mg l}^{-1} \text{ NO}_3 - \text{N}$, and of the samples collected during the present survey only one sample has $<3.5 \text{ mg l}^{-1}$ (associated with low DO, high Fe and Mn).

The cumulative probability plots (Figure 5.3) illustrate the distribution, range and relative abundance of solutes in groundwater. The shape of the curve for each parameter conveys information about the hydrogeochemistry and overall controlling factors (Box 5.1) and therefore provides an insight into both the natural processes and human influences on groundwater. The diagram shows that Ca and HCO_3 display an almost linear shape probably controlled by rapid saturation with respect to calcite. The other major elements and dissolved organic carbon (DOC) also display relatively linear distributions, but there is a slight shift at around the 80th percentile for Na, Cl, K and SO_4 .

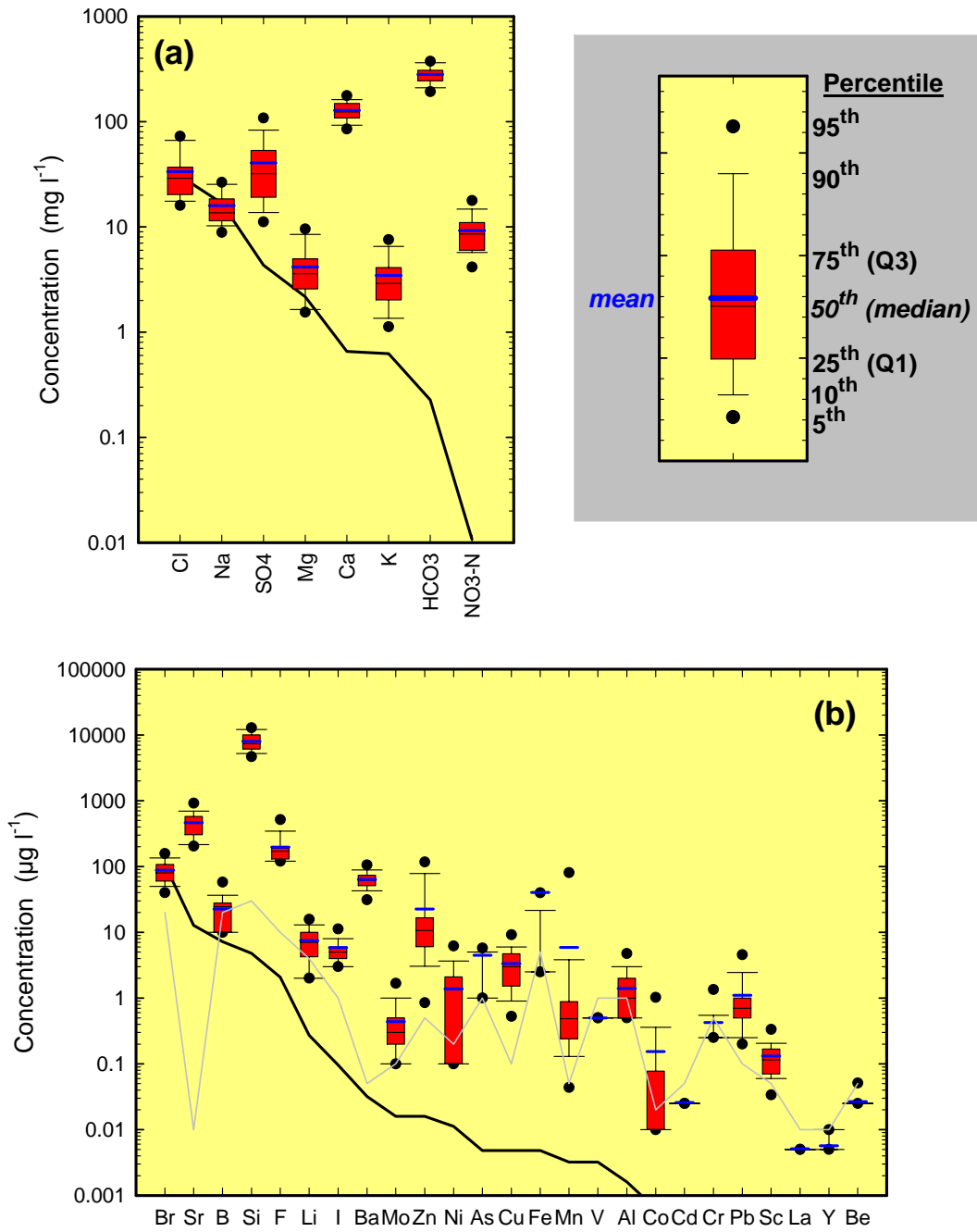


Figure 5.2 Box plot summary of (a) major and (b) minor element concentrations in the study area. Solid line shows the seawater dilution curve based on median Cl of the groundwaters and grey line shows typical detection limits.

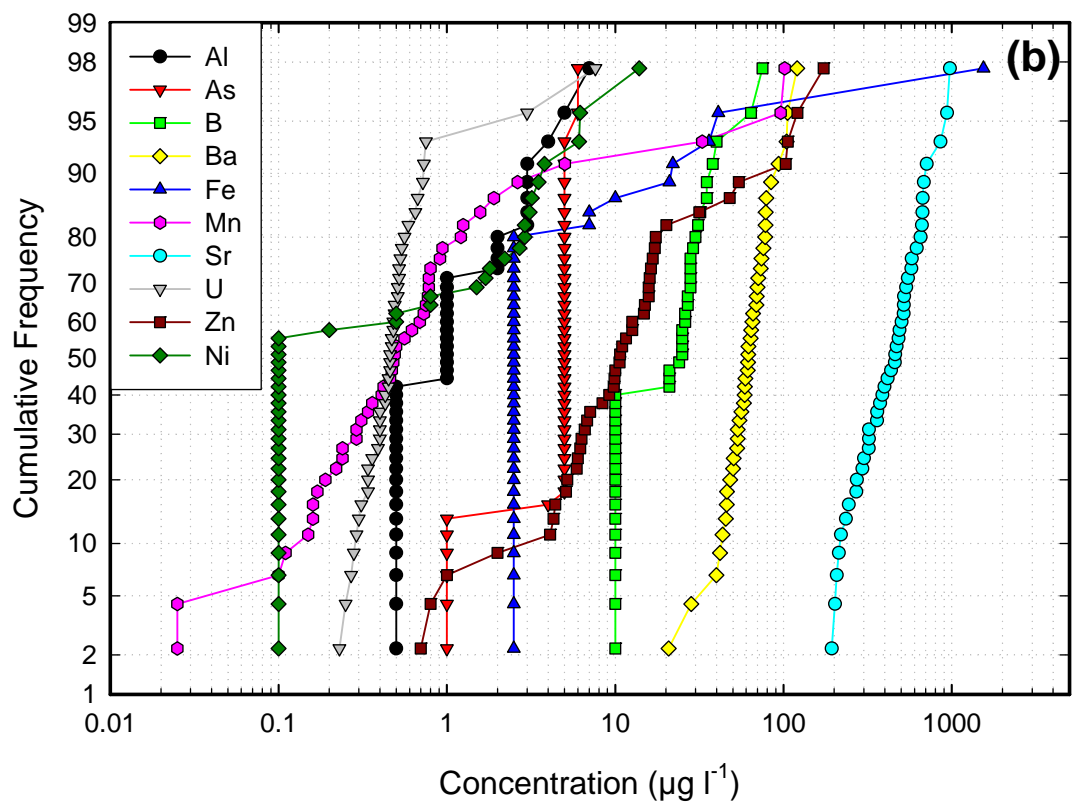
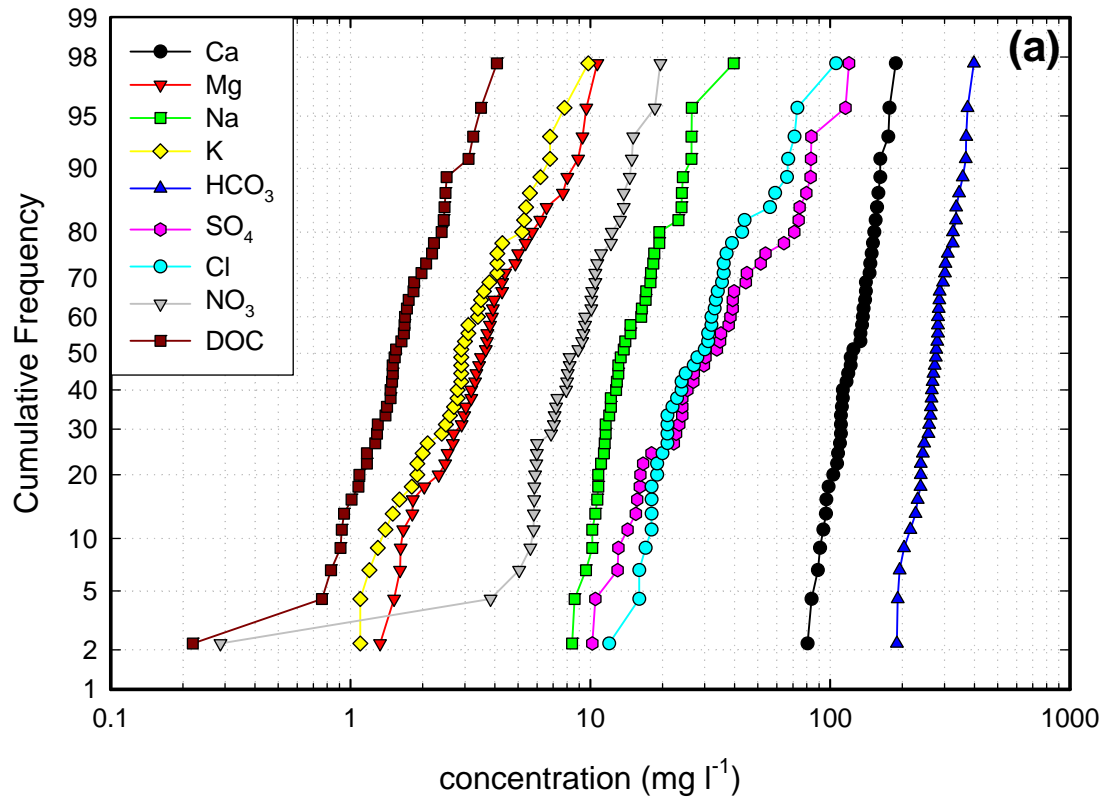
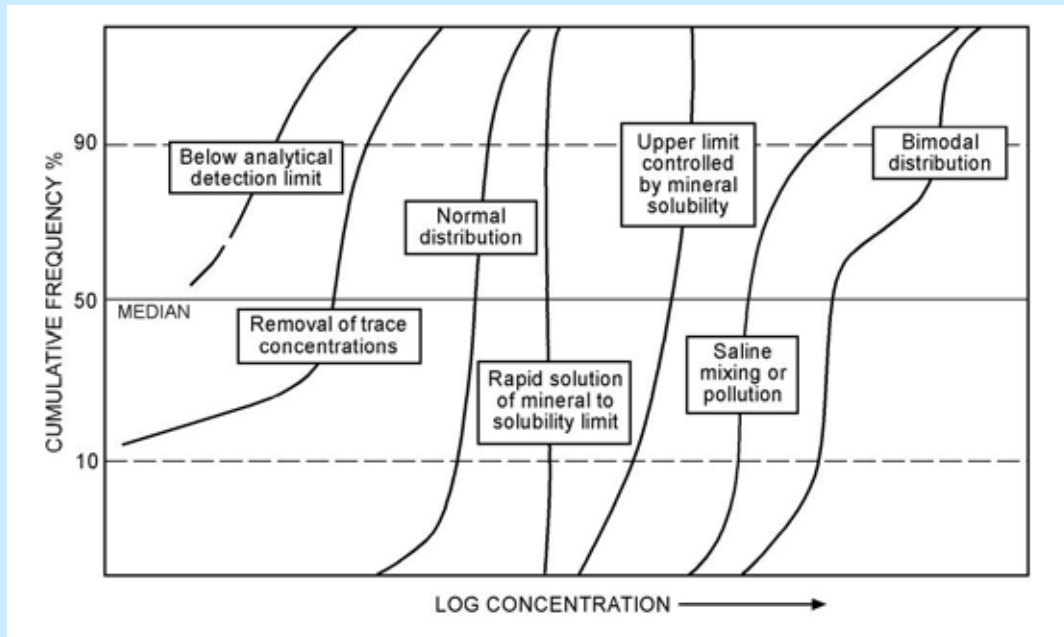


Figure 5.3 Cumulative probability plots of major and trace elements in groundwaters of the Great Ouse Chalk aquifer.

Box 5.1. Use of cumulative frequency diagrams to indicate baseline characteristics in 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).

Box 5.1 Use of cumulative frequency diagrams to indicate baseline characteristics in groundwaters

5.4 Minor and trace elements

The minor and trace element data are summarised in Table 5.2 and displayed on Figures 5.2 and 5.3. It should be noted on Figure 5.3 that where vertical lines occur at low concentrations these represent data below the detection limit. The data shown here are only those which were obtained as a result of the sampling carried out for this study, as these data are rarely collected for routine analyses, and thus all are for samples filtered at 0.45 μm . The sample numbers are shown in Tables 5.1 and 5.2. It can be seen from Figure 5.2 that many of the trace elements are at or below detection limit, which is also reflected in the shape of the cumulative frequency curves (Figure 5.3). This is consistent with the low mobility of many trace metals at circum-neutral pH and oxidising conditions in much of the groundwater.

Manganese concentrations vary by nearly four orders of magnitude, reflecting the ubiquitous occurrence of Mn in the Chalk (Section 3.4). Iron concentrations are generally below the analytical detection limit, with the only one sample significantly above (1.54 mg l^{-1}), being associated with reducing conditions in the upper catchment of the northern section.

Strontium and Ba are typically the highest trace elements in the groundwaters. Strontium is not limited by solubility controls in these groundwaters and is a good indicator of residence time of the groundwater in the Chalk. By contrast Ba is generally limited in solution by the solubility of barite (BaSO_4). Concentrations of SO_4 are low to moderate and saturation indices for barite are all low (-2.5 to -3.6) indicating that all groundwaters are under-saturated with respect this mineral. Uranium would also be expected to be mobile in an oxidising carbonate aquifer and concentrations are generally within the range $0.2 - 0.8 \text{ mg l}^{-1}$, with two samples having higher concentrations (Figure 5.3) (these samples have the highest SEC). Fluoride concentrations are low to moderate and all are under-saturated with respect to fluorite.

Nickel concentrations show a strongly bimodal distribution, with 50% of the samples being below the detection limit ($0.05 \mu\text{g l}^{-1}$) and the remainder varying between $0.2 - 6.2 \mu\text{g l}^{-1}$, with one value of $14 \mu\text{g l}^{-1}$ (Figure 5.3). The high Ni concentrations are closely associated with the till deposits in the east of the study area.

5.5 Pollution indicators

Ideally, samples used to determine the hydrochemical baseline of an aquifer system should contain no traces of human impact. Pollution alters baseline concentrations either directly through the addition of solutes, or indirectly by promoting chemical reactions within the aquifer. However, the extensive nature of diffuse pollution and the high demand for groundwater resources makes the acquisition of such data very difficult (Box 5.2).

Boreholes affected by point source pollution were identified and avoided at the site selection stage. However, diffuse pollution is widespread in urban and rural areas and this is reflected in nitrate concentrations in most groundwaters. Only one of the 46 samples collected during this study had $\text{NO}_3\text{-N}$ concentrations $<3.5 \text{ mg l}^{-1}$, and 10 of the samples had concentrations greater than the maximum admissible level in drinking water ($11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$). The sample with the lowest $\text{NO}_3\text{-N}$ concentration (0.3 mg l^{-1}) also had one of the highest NH_4 concentrations and an association with other species expected in reduced waters (e.g. Fe, Mn), suggesting that denitrification may be responsible for the low concentration. This is a process that will 'remediate' any contaminant NO_3 , thus the baseline for such waters is quite different to that for oxidised waters. Dissolved organic carbon and Cl concentrations may also be increased as a result of diffuse pollution. However, the majority of the samples in this aquifer have a DOC concentration $<2 \text{ mg l}^{-1}$. Chloride concentrations vary, but these may also be affected by natural sources of Cl, in addition to road salting and agricultural sources (e.g. Edmunds et al., 2003). Potassium is a major plant nutrient, and is often a component of fertilisers; its high solubility may result in enhanced concentrations in groundwaters recharging through improved agricultural land. As was also found in a study of the Berkshire Chalk, no correlation exists between NO_3 concentrations and K, which is also expected to have a contribution from diffuse fertiliser sources (Edmunds et al., 1987). In some areas, natural soil deficiencies in essential elements for specific crops may result in enhanced concentrations as a result of application and subsequent leaching to groundwater. For example, sugar beet grown on sandy soils such as the Brecklands may require B supplementation (Hodge et al., 1984).

Table 5.2 Trace element concentrations in groundwaters of the Great Ouse Chalk study area.

Parameter	units	min.	max.	median	mean	97.7th percentile	N
Ag	µg l ⁻¹	<0.05	0.06	<0.05	<0.05	<0.05	44
Al	µg l ⁻¹	<1.0	7.0	1.0	1.4	5.0	46
As	µg l ⁻¹	<0.015	6.0	5.0	4.3	6.0	46
Au	µg l ⁻¹	<0.05	0.23	<0.05	<0.05	0.16	44
B	µg l ⁻¹	<20	75	23	22	63	46
Ba	µg l ⁻¹	21	121	61	63	106	46
Be	µg l ⁻¹	<0.05	0.06	<0.05	<0.05	0.060	44
Bi	µg l ⁻¹	<0.05	0.09	<0.05	<0.05	0.090	44
Cd	µg l ⁻¹	<0.05	0.12	<0.05	<0.05	0.071	76
Ce	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	44
Co	µg l ⁻¹	<0.02	2.85	<0.02	0.15	1.13	46
Cr	µg l ⁻¹	<0.5	5.00	<0.5	<0.5	1.26	76
Cs	µg l ⁻¹	<0.01	0.05	<0.01	0.01	0.03	44
Cu	µg l ⁻¹	<0.1	99	3.2	7.5	52	76
Dy	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Er	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Eu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Fe	mg l ⁻¹	<0.005	2.1	<0.005	0.083	0.77	69
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
Gd	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Ge	µg l ⁻¹	<0.05	0.15	<0.05	<0.05	0.14	44
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	44
Hg	µg l ⁻¹	<0.1	0.10	<0.1	<0.1	0.10	44
Ho	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
In	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	0.01	44
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
La	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	44
Li	µg l ⁻¹	<0.025	17	7.0	7.2	16	46
Lu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Mn	µg l ⁻¹	<0.05	102	0.16	3.4	49	77
Mo	µg l ⁻¹	<0.1	1.8	0.30	0.42	1.7	46
Nb	µg l ⁻¹	<0.01	0.03	<0.01	<0.01	0.01	44
Nd	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	44
Ni	µg l ⁻¹	<0.2	13.9	<0.2	1.47	12.3	75
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
Pb	µg l ⁻¹	<0.1	14.8	0.60	1.31	10.3	75
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	44
Pr	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Pt	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	44
Rb	µg l ⁻¹	0.19	4.72	1.78	2.01	4.20	44
Re	µg l ⁻¹	<0.01	0.030	0.010	0.011	0.030	44
Rh	µg l ⁻¹	<0.01	0.030	0.010	0.015	0.030	44
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
Sb	µg l ⁻¹	<0.05	0.57	0.12	0.13	0.36	44
Sc	µg l ⁻¹	0.99	6.7	3.6	3.8	6.3	44
Se	µg l ⁻¹	<0.015	7.1	1.1	1.3	3.2	46
Sm	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
Sn	µg l ⁻¹	0.20	0.51	0.37	0.36	0.43	44
Sr	µg l ⁻¹	193	974	465	467	933	46
Ta	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
Tb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
Te	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	44
Th	µg l ⁻¹	<0.05	0.13	<0.05	<0.05	0.061	44
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	44
Tl	µg l ⁻¹	<0.01	0.070	<0.01	0.014	0.060	44
Tm	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	44
U	µg l ⁻¹	0.23	7.6	0.46	0.68	3.0	44
V	µg l ⁻¹	<1.0	<1.0	<1.0	<1.0	<1.0	46

Parameter	units	min.	max.	median	mean	97.7th percentile	N
W	$\mu\text{g l}^{-1}$	<0.1	<0.1	<0.1	<0.1	<0.1	44
Y	$\mu\text{g l}^{-1}$	<0.01	0.01	<0.01	<0.01	0.01	44
Yb	$\mu\text{g l}^{-1}$	<0.01	<0.01	<0.01	<0.01	<0.01	44
Zn	$\mu\text{g l}^{-1}$	<0.05	6080	11	105	196	76
Zr	$\mu\text{g l}^{-1}$	<0.5	<0.5	<0.5	<0.5	<0.5	44

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

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

The approach adopted is threefold:

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

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The primary source of recharge to the aquifer is rainfall, a dilute solution with a slightly acidic pH (Table 3.2), which will dissolve carbonate minerals in the soil and unsaturated zone. Thus, the chemistry of water entering the saturated aquifer has generally already acquired its dominant hydrochemical characteristics. The increased partial pressure of carbon dioxide in the soil zone may also increase the dissolution of carbonate minerals. Until the waters reach equilibrium with calcite, the initial dissolution will be congruent. With increasing residence time incongruent dissolution of calcite, dissolution of silicate minerals, redox reactions, ion exchange and mixing all contribute to modify the groundwater composition.

Baseline conditions vary spatially and temporally due to different recharge and flow paths, aquifer composition and groundwater residence time. The geochemical variations observed during this study are evaluated below and placed in their regional context. The limited temporal data available are also evaluated.

Of the three study areas, none conform perfectly to the concept of being able to follow a ‘flowline’ as demonstrated in other reports in this series (e.g. Shand et al., 2003). The concept of a flowline is that any changes in the composition of the groundwater can be followed from the area of recharge to discharge. However, problems exist with such a study, due to the constant recharge being received by the unconfined aquifer (Section 3.3) along the length of any flowline, as well as the discharge of water via pumping boreholes which will modify local flow regimes.

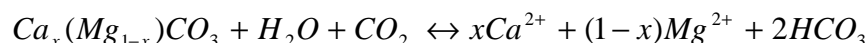
This study has not included any confined Chalk groundwaters, which means that all samples are potentially affected by these processes. Despite these limitations the northern study section (Thetford area) will be examined in some detail to determine spatial variations along the regional flow direction. The spatial comparison of the data will be described in section 6.4.

6.2 Chemical evolution along the regional flow direction

The nature of groundwater flux in the Chalk is such that the upper catchment, particularly beneath less permeable drift deposits, may be expected to have had a greater residence time than those waters in valley environments where active recharge is occurring (Section 3.3).

6.2.1 Mineral dissolution reactions

The most reactive minerals in the aquifer will determine the composition of young groundwaters. Chalk groundwater is thus dominated by the dissolution of calcite:



The dissolution kinetics of calcite is rapid (Appelo and Postma, 1994), meaning that even where the soil zone is depleted in calcite, recharge waters are expected to equilibrate in the unsaturated zone. In general, many of the solutes that typically increase with residence time show a decrease along the regional flow direction (Figure 6.1). Calcium concentrations generally decrease in the direction of regional groundwater flow. The most likely causes are that the mineralogy of the aquifer changes along this line or that the mean residence time decreases. This is thought to be due to increased residence time and decreased flux of water associated with poorly permeable till cover (up to 35 m at

Garboldisham to East Harling (Klinck and Wealthall, 1996)), and more rapid recharge and mixing taking place in the lower valley system (Section 3.3). This concentration trend is largely dictated by the first two samples from beneath the till (Figure 6.1), with subsequent concentrations following a more subtle decrease, with a slight increase in the last sample collected, along this flowline.

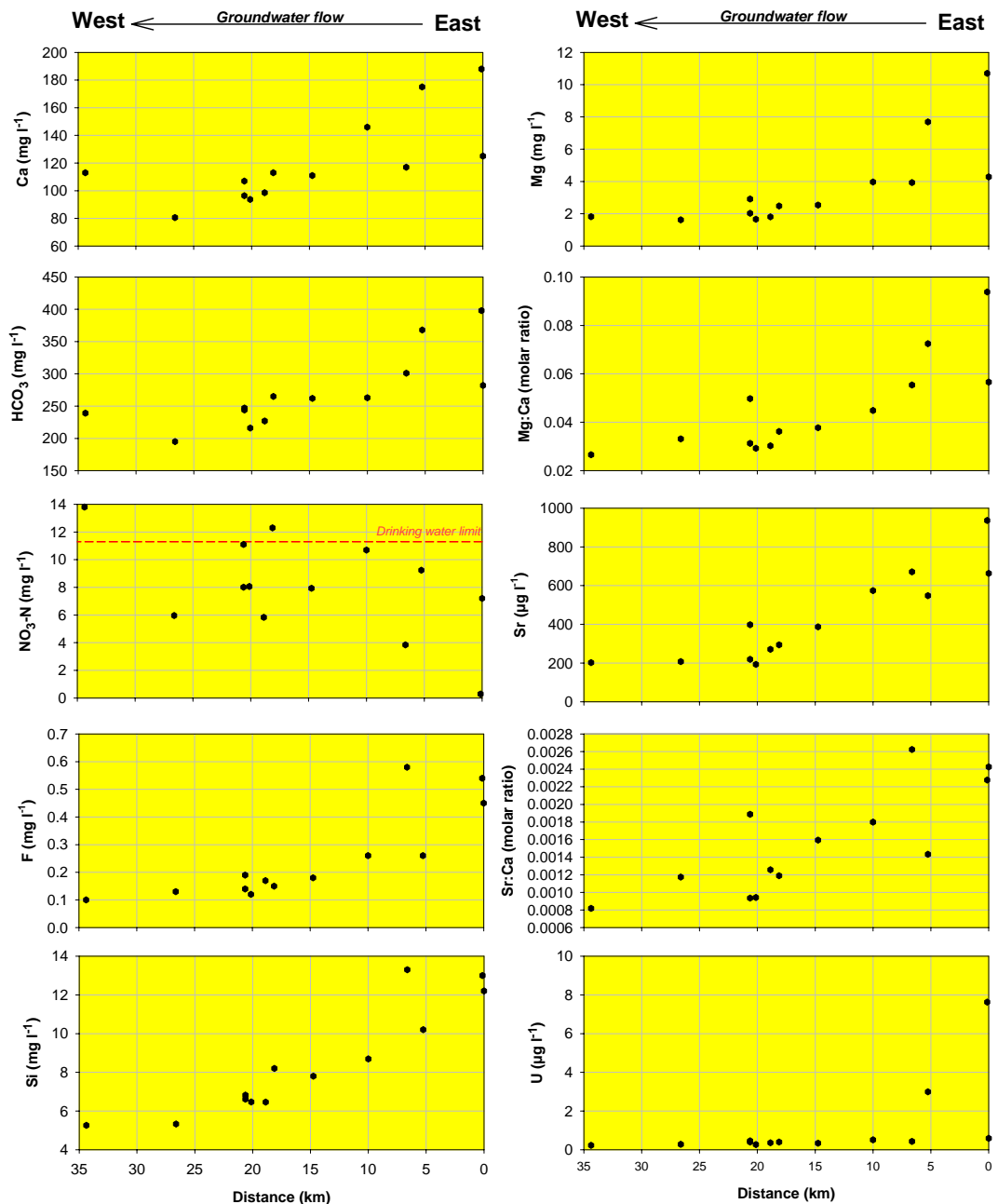
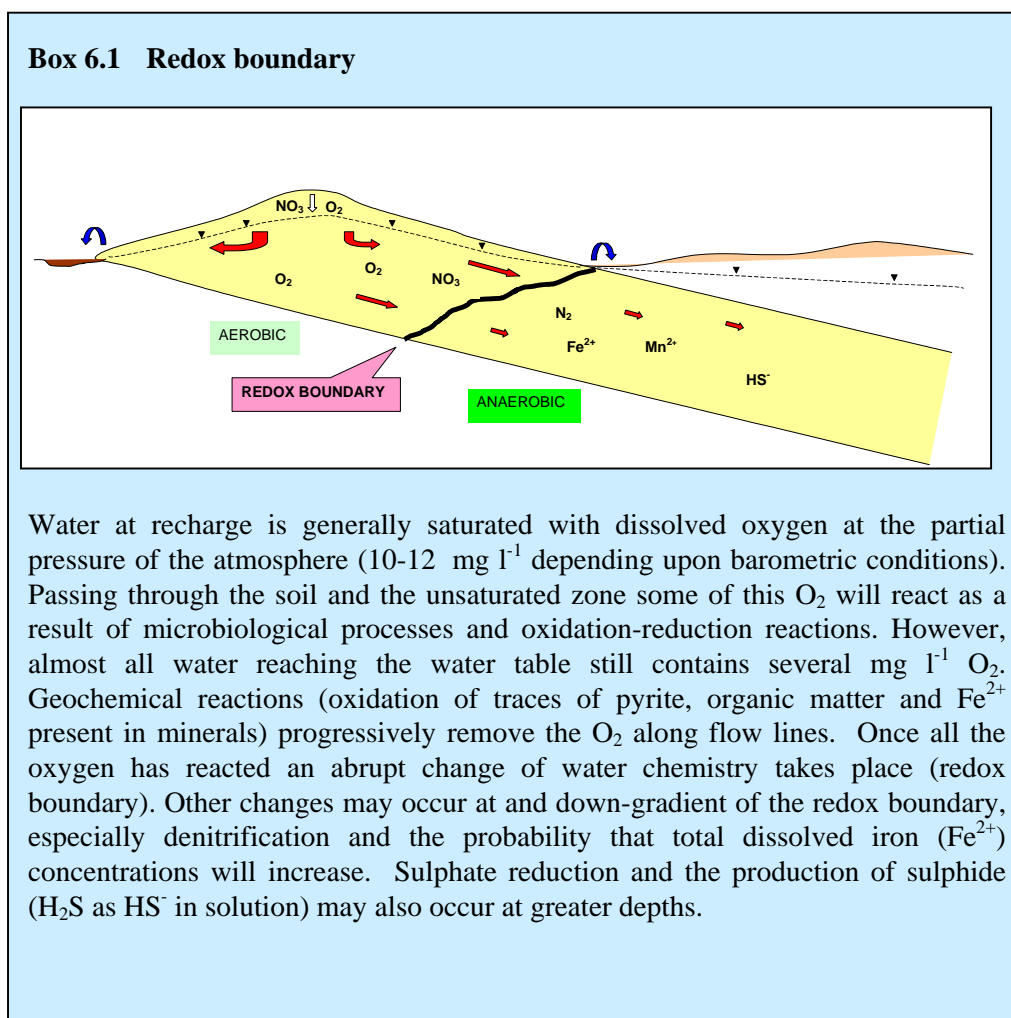


Figure 6.1 Changes in hydrochemistry along the regional flow direction (regional flow is east to west). Data are shown for the northern section (groundwater contours are shown in figure 3.5)

This hypothesis of longer residence time beneath the Tills is supported by the increase in concentrations of elements which substitute into the calcite lattice and increase in time due to the incongruent dissolution of calcite after the initial equilibrium has occurred. Typically Sr and Mg may be released by this process (Edmunds et al., 1992). It can be seen from Figure 6.1 that these elements decrease in absolute concentration and that the molar ratios of Mg/Ca and Sr/Ca also decrease.

Fluoride concentrations increase with residence time in the Chalk aquifer and F shows a similar increase to Sr and Mg (Figure 6.1).

The heterogeneous composition of the Tills means that it may be difficult to recognise where the water composition has been modified by the leakage of waters from the till, compared to the dissolution of matrix and clay minerals in the Chalk aquifer. Sulphate concentrations are higher in the samples from beneath the till, as are Si concentrations (Figure 6.1). In both cases these are significantly higher than in the Berkshire and Thames unconfined Chalk aquifers (Edmunds et al., 1987; Shand et al., 2003), and are similar to those encountered at the onset of reducing conditions in the Thames Chalk. The sulphate may arise from the reaction with gypsum or pyrite, which could be derived from the chalk or the till. Silicon and other elements that may be indicators of increased residence time and reaction with aquifer clay minerals, such as Li and K are marginally elevated in these samples.



6.2.2 Redox reactions

The primary indicators of redox status are Eh and dissolved oxygen (DO), however, elevated concentrations of redox sensitive elements can also be indicative of such conditions (Box 6.1). Dissolved oxygen was determined at most localities in the northern section, and the samples from the upper catchment are characterised by lower DO concentration than most of the rest of the samples (with the exception of Barnhamcross Common see Section 6.4.2 below). However, most samples

contained dissolved oxygen (Figure 6.2) and therefore denitrification is not likely to modify nitrate concentrations in the aquifer.

Key chemical determinands which are indicators of reducing conditions are Fe and Mn, which are more soluble in their reduced form, as well as the absence of NO_3 (Appelo and Postma, 1994). Iron and Mn are generally low in the groundwaters and NO_3 is moderately high (Figure 6.2), in agreement with the redox indicators. The one sample that had very low DO also contained high Fe (1.54 mg l^{-1}) and Mn (0.1 mg l^{-1}). However, several groundwaters contain elevated Fe and Mn concentrations as well as oxygen and nitrate. These occur close to the junction with the Till deposits in the east of the aquifer and it is likely that these represent mixed waters. Marks et al. (2004) noted that run off from impermeable Till caused focussed recharge of high nitrate water at the Till-Chalk boundary, but the groundwater beneath the Till was older and more reducing. The combination of high nitrate, moderate Fe and Mn and higher concentrations of weathering-derived components may therefore be explained by in-borehole mixing of these two types of waters in the upper parts of the catchment.

In oxidising groundwaters, Fe forms insoluble oxyhydroxides which are important sorption sites for many trace metals, especially for elements such as Mn, Co, Ni. The oxidising and neutral pH conditions are thus responsible for limiting many trace elements in solution in the aquifer, but they may be mobilised under reducing conditions.

6.2.3 Ion exchange reactions

Ion exchange is an important chemical process in many aquifer systems. Ion-exchange of dissolved Ca for adsorbed Na is generally only important in older confined parts of the Chalk aquifer which has not been sufficiently flushed of formation water (Edmunds et al., 1987; Shand et al., 2003). There is no evidence in the groundwaters from the study area, of such a trend towards Na-HCO_3 type waters. The implication is that there is insufficient cation exchange taking place to modify the major ion chemistry of the waters (Figure 5.1). This is confirmed by the low Na/Cl ratios in groundwaters with high Na, the opposite of that expected through ion-exchange.

Some of the groundwaters, however, show a slight trend towards Ca-Cl type water. The Piper plot shows that the high relative Cl in some samples is not matched by similar sodium. It is therefore possible that reverse ion-exchange may be occurring as more Na-rich waters from Till deposits mix with Ca-rich waters in the Chalk.

6.2.4 Mixing with older formation water

The best indicator of mixing with formation water in the Chalk is enhanced Cl concentrations, although moderate concentrations can also be due to diffuse anthropogenic inputs. The maximum Cl concentrations are found in the eastern part of the section in boreholes close to the junction with the Till deposits. Nitrate concentrations are variable in these samples ($0.3 - 10.7 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) and it is possible that the Cl may also be of anthropogenic origin. The ratios Na/Cl and Br/Cl are low in the higher Cl groundwaters that may indicate a non-marine source (Figure 6.3). However, there is little correlation between NO_3 and other parameters indicative of diffuse pollution such as K/Na or DOC. The higher Cl groundwaters here also contain higher concentrations of weathering-derived (e.g. Si, Ca, Mg, Sr) or formation-type (SO_4 , Li) elements and it is considered likely that much of the Cl is derived from leakage from the Till or from older groundwaters beneath the Tills (in areas of lower transmissivity). Further work on the hydrochemistry of Till deposits and the underlying Chalk groundwater would be useful to discriminate the origin of Cl.

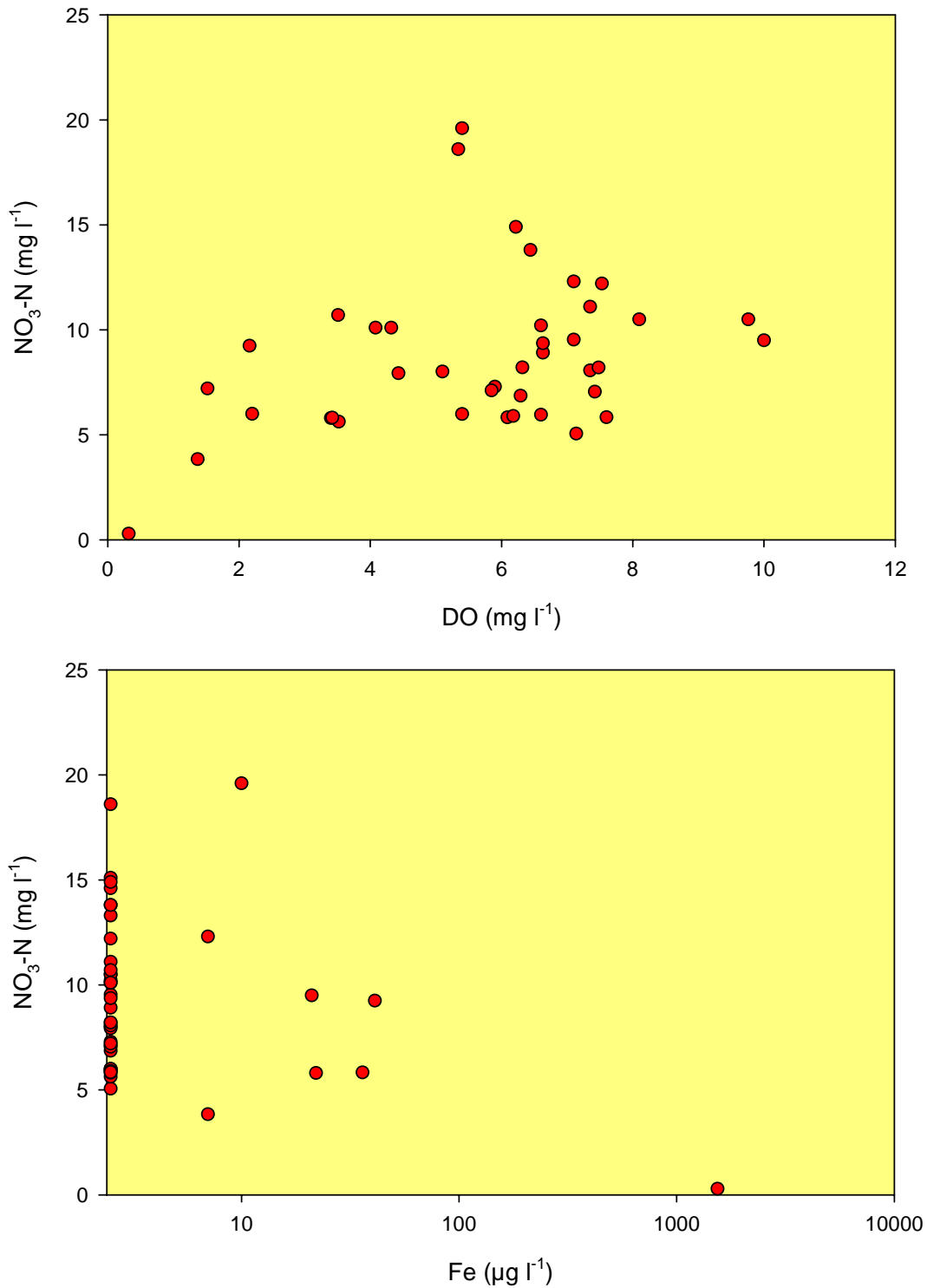


Figure 6.2 Plots of D.O and Fe against NO₃ in the Ouse groundwaters. Data are shown for the groundwaters sampled during this study.

The decrease in concentrations along the flow gradient indicates that mixing with formation water is not important over much of the outcrop area. In fact, it implies that the higher SEC groundwaters become diluted along this section, possibly as a consequence of higher recharge and transmissivity in the valley areas.

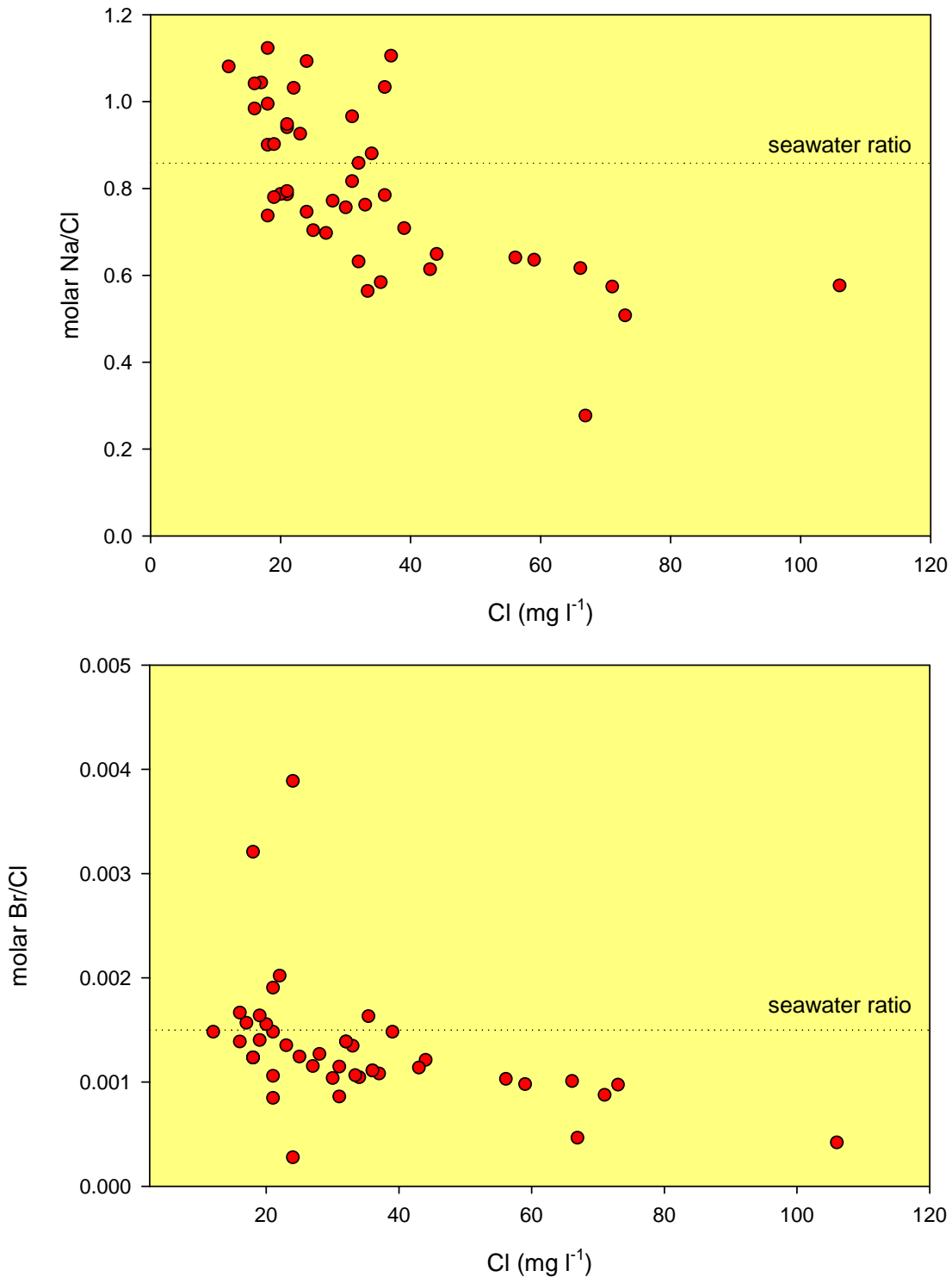


Figure 6.3 Plots of Cl vs. Na/Cl and Br/Cl ratio in the Great Ouse Chalk groundwaters.

6.3 Temporal variations

The most contiguous record of temporal variations of nitrate in the region is found in a study by Carey & Lloyd (1985). This showed a systematic increase in nitrate concentrations with time from the earliest data in the 1940s. Concentrations were *c.* 6 mg l⁻¹ NO₃-N in pre-1950 data from two boreholes (Fleam Dyke and Fulbourn) and are generally below 10 mg l⁻¹ NO₃-N up to the time of publication in 1985. For comparison, two public supplies reported by Carey & Lloyd were sampled as part of this

study. The nitrate concentrations at Babraham were $c.9 \text{ mg l}^{-1}$ in 1984 and were measured at 10 mg l^{-1} in this study (compared with $ca.6 \text{ mg l}^{-1}$ in 1961). The Linton source showed complex trends in nitrate concentrations: due to the two boreholes comprising the source being of different depth, hydraulic continuity with the river Granta, and changes in pumping regime (Carey and Lloyd, 1985). Comparison of the data acquired for this study (9.5 mg l^{-1}) with the concentrations generally of a similar value from 1965-1984 (Carey and Lloyd, 1985) are thus tentative at best.

No other published data have been found during the course of this study. Trends identified by Carey and Lloyd clearly show how the current concentrations of a parameter in groundwater may not represent the baseline of that system, and the need to have such baseline data with which to compare modern values. A dataset made available by Anglian Water Services for two of the public supplies sampled during this exercise is summarised in Figure 6.4. This shows that during the period of time of the data, concentrations in both sources increased. The rate of rise in NO_3 is however very different for these sources. These data are indicative and no attempt has been made to interpret the data with respect to pumping regimes.

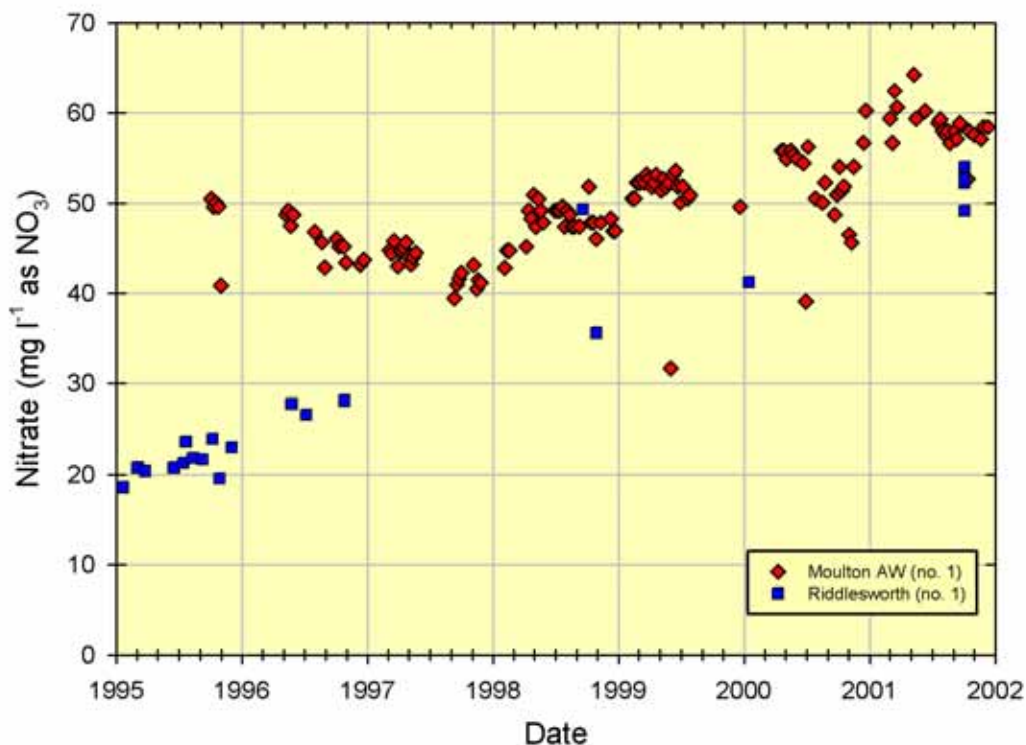


Figure 6.4 Time series data from selected public supplies (raw water)

6.4 Regional variations

6.4.1 Spatial variations

The current sampling was undertaken in three different areas across the Great Ouse catchment, with a view to establishing whether the baseline chemistry varies across the region for this aquifer. This sampling was augmented by a further 31 samples from the EA archive and other sources. It has been suggested that more than one flow system is present in the Great Ouse Chalk aquifer, based on chemical variations along the regional flow direction (Section 6.2).

The most westerly end of the northern section has amongst the lowest concentrations of bicarbonate measured in the study, whilst the highest concentrations are found in the eastern parts of the aquifer. There is less variation in the southern section (Figure 6.5).

The regional variation in SEC is consistent with the general trends noted above for the major ions (Figure 6.5). The additional data from the EA archive generally reinforce the findings of the baseline sampling, for the limited range of parameters available. Thus, the lower SEC values extend north of the Thetford section and similarity between the middle and southern regions is shown. The lack of regional systematic variation in NO_3 can be seen in Figure 6.6; the greater part of the aquifer system has values over $6 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ and many exceed the drinking water MAC of $11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. Concentrations of TOC (Figure 6.6) are highest in the northern section close to the junction with the Till deposits and may be derived from the Till since the highest concentration was found in the sample with the low DO and NO_3 . Overall, there is a poor correlation of TOC with NO_3 .

The Si concentrations are highest in the eastern part of the study area (Figure 6.7) with particularly low concentrations in the Lower Chalk outcrop samples. The generally higher concentration of clays in the Lower Chalk, compared to the Middle and Upper Chalk, (section 3.4) is not reflected in higher Si concentrations. Highest concentrations are in the east and display a similar distribution to F (Figure 6.7), where samples with high Si and F also correlate with Sr, Sr/Ca and Mg/Ca. This suggests a long residence time component in the groundwaters and the preferred interpretation is that the main control on these solutes is from the flow of older groundwaters beneath the Till moving along the regional flow system. However, as indicated above, these waters also contain a younger NO_3 -rich component probably from run off over the tills.

The southern section groundwater is also generally associated with higher Mg/Ca and Sr/Ca ratios (Figure 6.8). Both of these parameters would usually be associated with increased residence time (as suggested for the northern section, above). The smaller area of outcrop west of the Till may have limited dilution by more modern recharge in this area.

Trace element concentrations are more variable across the catchments. The regional concentrations of Sr are similar in relative distribution to Ca, due to their similar geochemical source and behaviour in waters. Nickel concentrations range from 0.1 to $13.9 \mu\text{g l}^{-1}$, less than the new European drinking water limit of $20 \mu\text{g l}^{-1}$. Higher concentrations, up to around $40 \mu\text{g l}^{-1}$, were reported by Smedley (2003) mainly to the east of the study area. It was concluded that Ni was derived from the oxidation of pyrite in Drift deposits. This also seems likely for the present study. Although there is a poor correlation between Ni and SO_4 , this is most likely due to additional sources of SO_4 such as from mixing with remnant formation water, sulphate minerals or fertilizer inputs.

6.4.2 *Depth variations*

There are no data available on depth profiles in any of the boreholes and little is known about stratification in the aquifer.

There are no direct determinations of groundwater age in the study area. Hiscock (1993) showed that there is a range in the ages of Chalk groundwater in north Norfolk from modern to more than 10,000 years old. Feast et al. (1997) also showed that that a mineralised palaeowater is present in the same area at depth, with $\delta^{18}\text{O}$ values as light as -8.25 . However, the groundwaters in the study area have relatively low Cl concentrations. Analyses of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were undertaken on a selection of the samples from the unconfined aquifer of this study in order to determine if Pleistocene recharge was present.

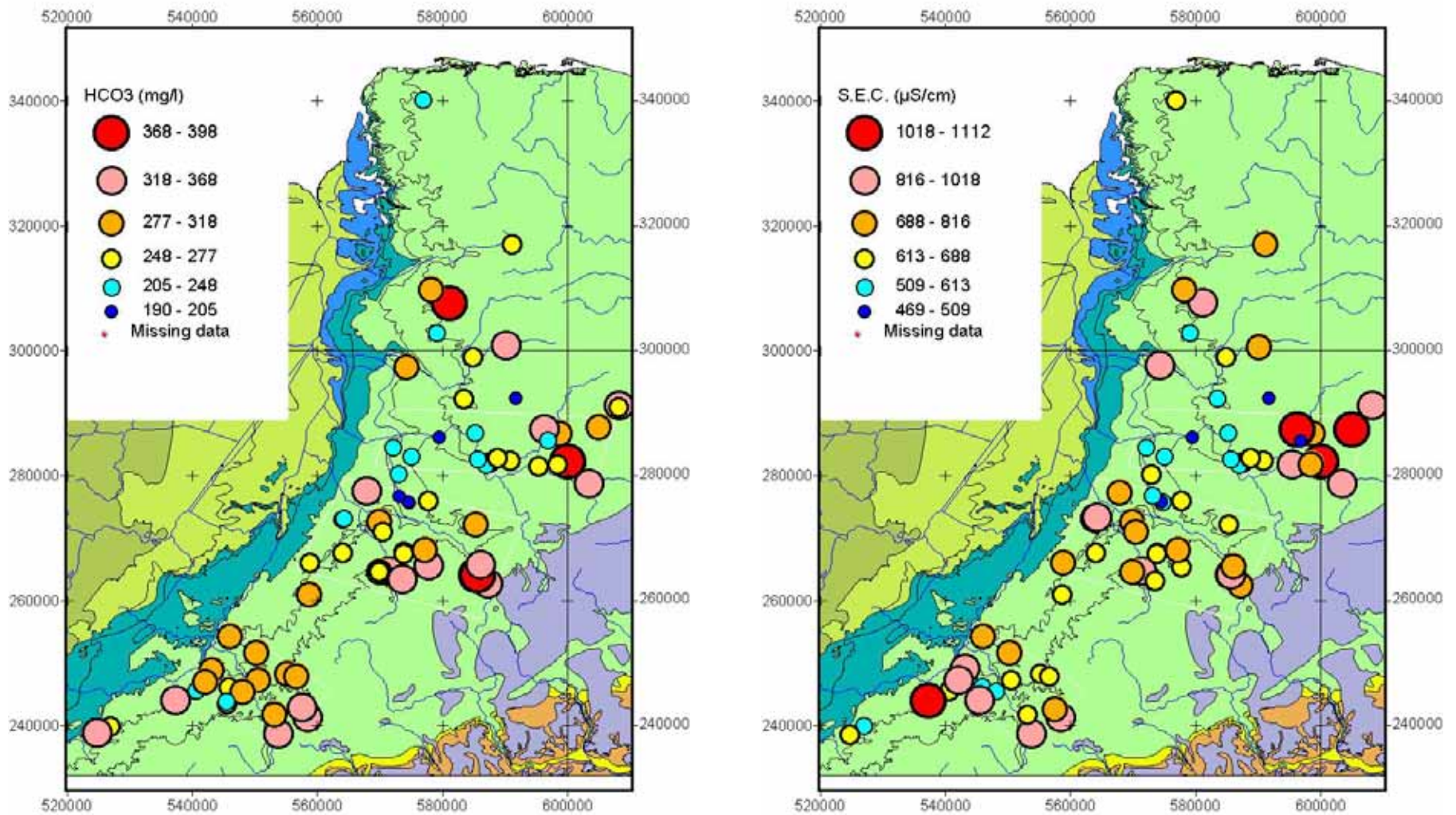


Figure 6.5 Spatial variations in HCO₃ and SEC in the study area (see Figure 3.1 for geological units).

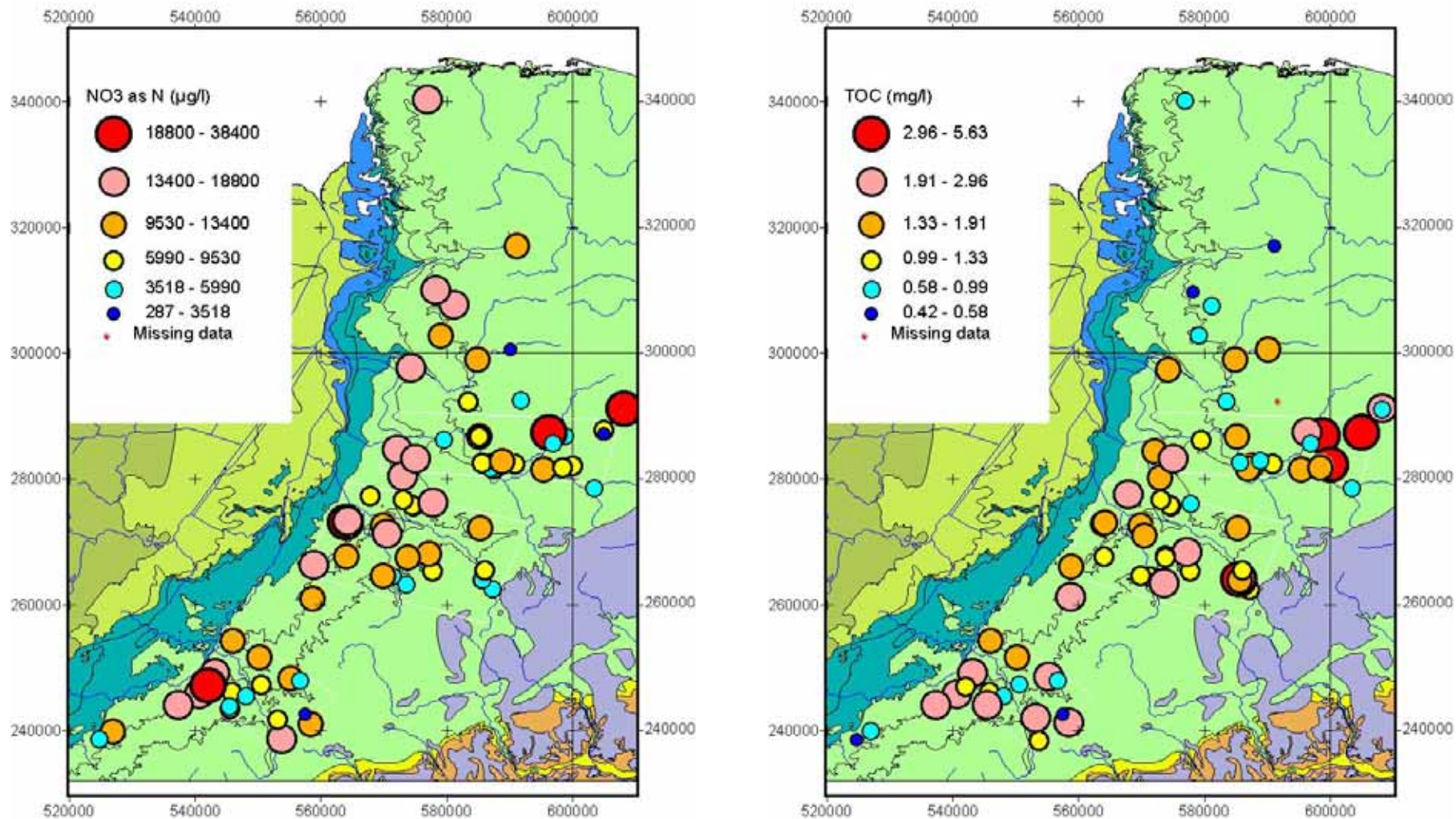


Figure 6.6 Spatial variations in NO₃-N and TOC in the study area (see Figure 3.1 for geological units).

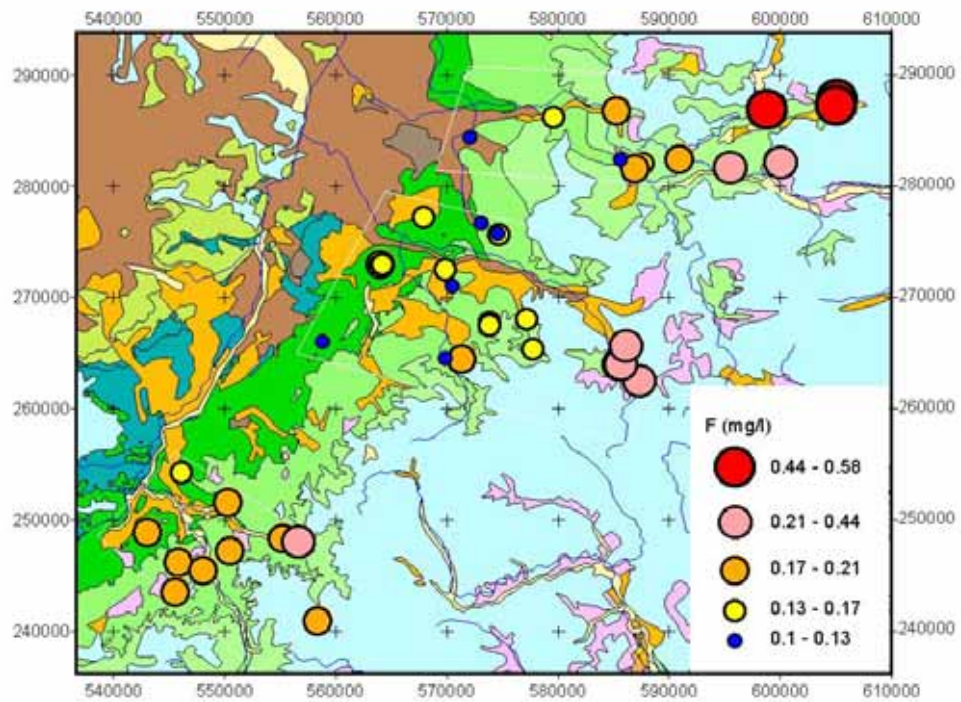
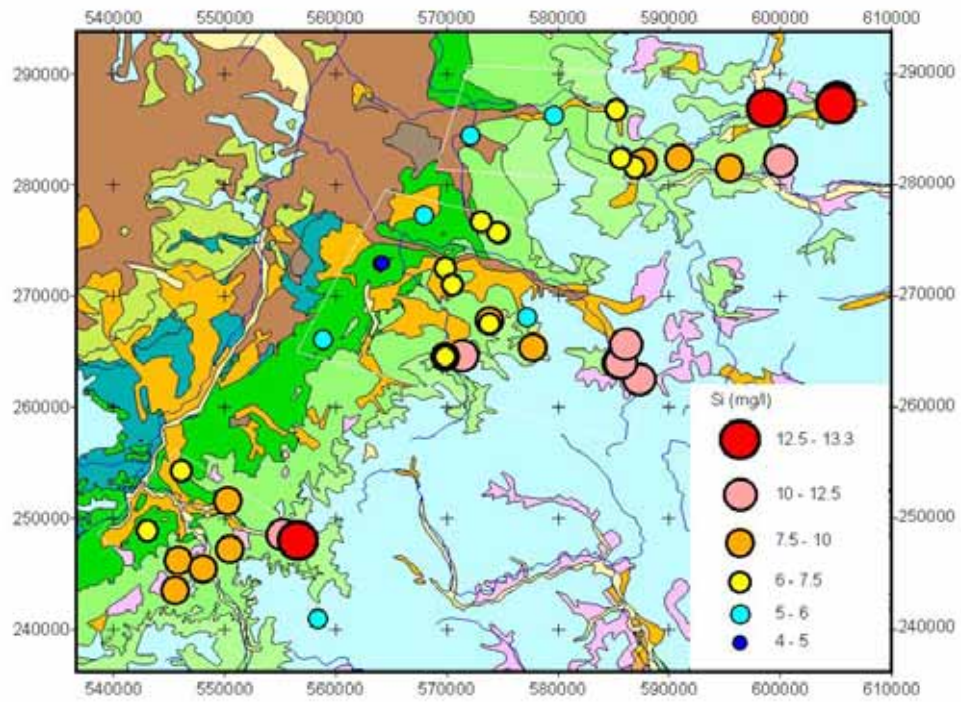


Figure 6.7 Spatial variations in Si and F in the study area (see Figure 3.2 for geological units).

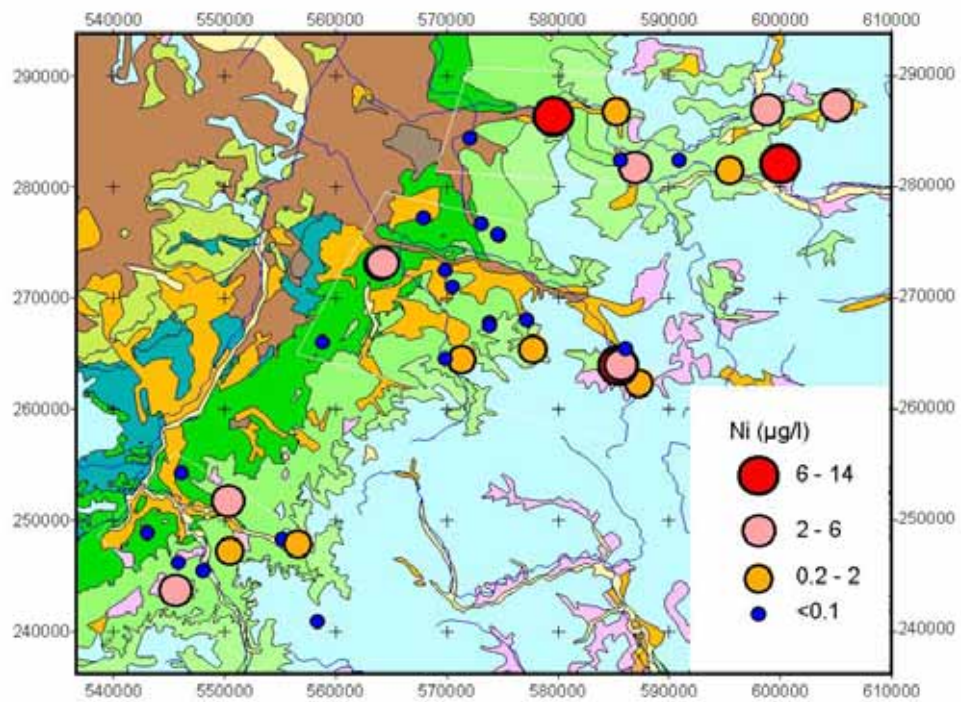
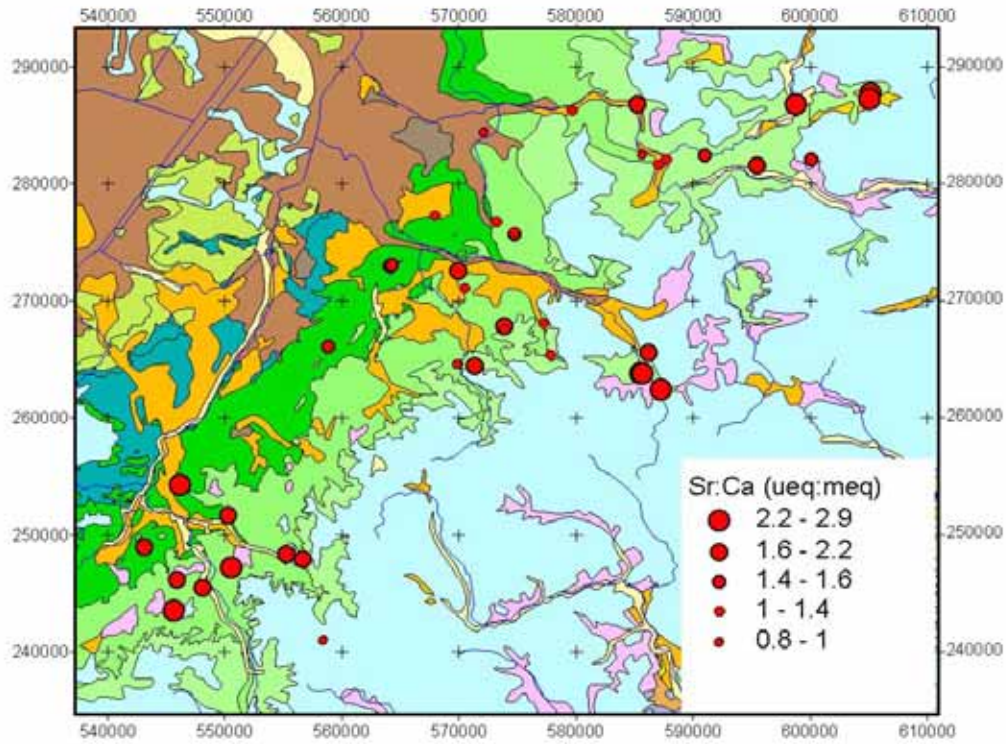


Figure 6.8 Spatial variations in Sr/Ca ratio and Ni in the study area (see Figure 3.2 for geological units).

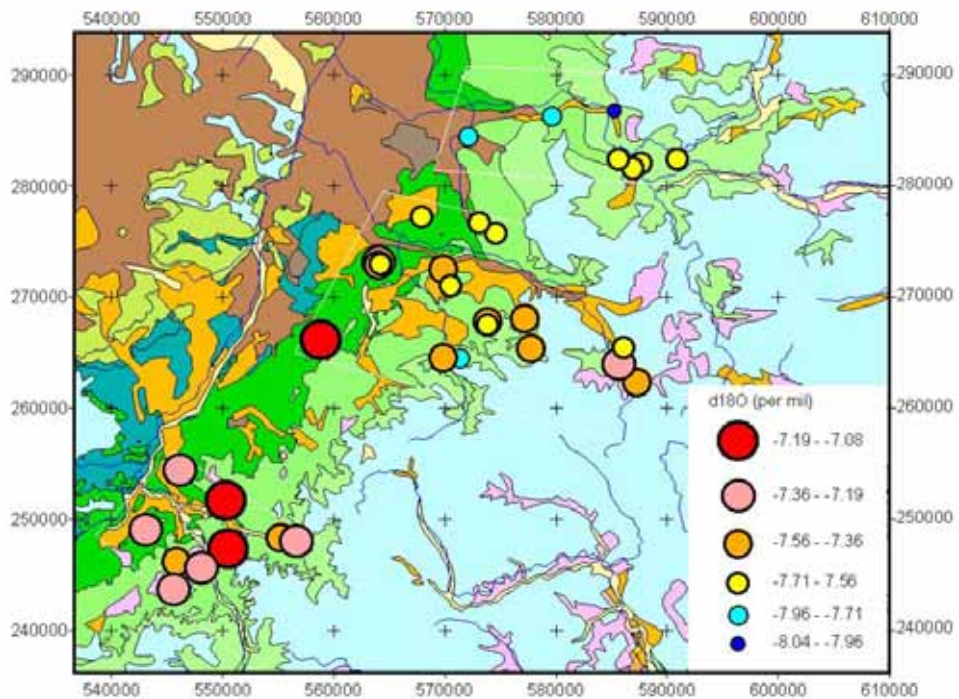
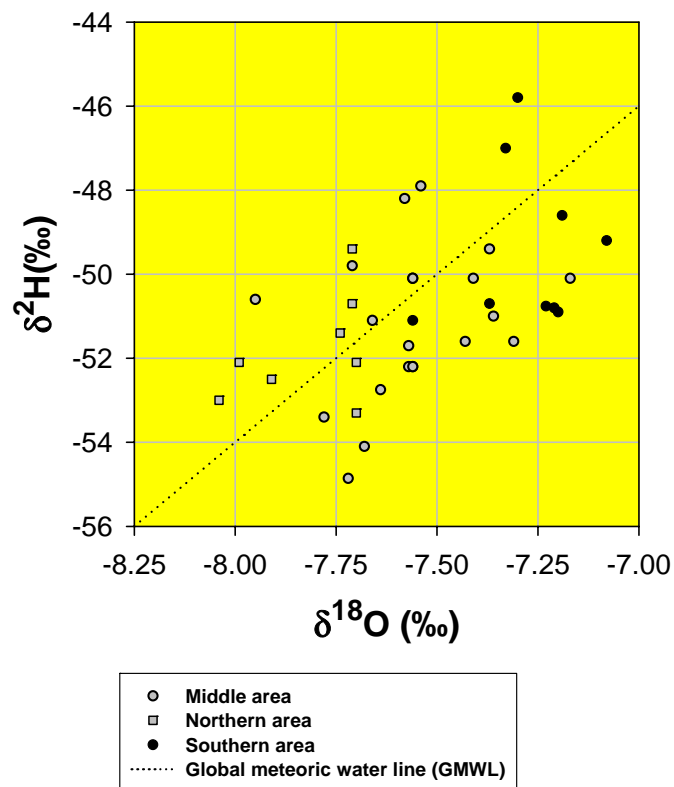


Figure 6.9 Variations in the (a) stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (b) spatial variations in $\delta^{18}\text{O}$ (see Figure 3.2 for geological units).

The results from the study area have sufficient range in isotopic values (Figure 6.9), to enable some geographical variation to be identified. In general, the waters from the northern area have isotopically lighter (more negative) values than those from the southern area; the data from the central area being intermediate in characteristics. The isotopically lightest waters were those with lower concentrations of solutes which typically increase with residence time. In addition $\delta^{13}\text{C}$ ratios are not very heavy (as would be indicated in palaeowaters), thus it is likely that all waters have been recharged during Holocene or modern times. There is little variation in the $\delta^{13}\text{C}$ values of the groundwaters throughout the field area (-15 ‰ to -12 ‰) suggesting $\delta^{13}\text{C}$ is a mixture between organically derived C from the soil and from chalk matrix (which also occurs as abundant soil clasts in much of this field area). No systematic differences can be observed in this narrow range of values.

Further work to date the spatial variations in age would be useful (e.g. CFC's) to assess areas of active recharge and the presence of older groundwaters, particularly beneath and adjacent to the Till deposits (see Marks et al., 2004).

7. BASELINE CHEMISTRY OF THE AQUIFER

The calcium carbonate composition of the chalk matrix dominates the major element characteristics of the groundwaters in the Great Ouse Chalk aquifer. The waters contain significantly enhanced concentrations of major ions when compared to rainfall (Section 3.5), showing that considerable water-rock interaction has taken place. The low-Mg calcite which forms the aquifer matrix gives rise to waters which are predominantly Ca-HCO₃ in their composition. The data indicate that mixing of groundwaters of different ages, especially along the junction of the Chalk with Till deposits. The baseline chemistry has been given in Tables 5.1 and 5.2 for the area but sampling has been biased to the valley systems. This is a common problem in the Chalk, where the highly transmissive valley zones are a focus for groundwater abstraction and the interfluves generally have few abstractions. In this region, very few private supplies depend on the Chalk abstraction from the interfluves. Clearly, more work would need to be done in order to assess the baseline of the interfluve and upper catchment regions of this aquifer.

The range of concentrations for most elements is relatively small compared to other studies where large variations are found between unconfined and confined parts of the aquifer. However, the local scale of variation is significant within this dataset and some elements have higher concentrations than found in the studies of similar unconfined Chalk aquifers immediately to the west of this study area (Edmunds et al., 1987; Shand et al., 2003).

Whilst the dominant factor determining the chemical composition of these waters is natural, high concentrations of NO₃ cannot be considered as baseline. Historical evidence back to the 1940s and more recent data all show a continued upward trend in NO₃ concentrations. This is significant both with respect to the estimated natural background of 2-4 mg l⁻¹ in the Chalk (Shand et al., 2003) and the present MAC for drinking water (11.3 mg l⁻¹ NO₃-N). Of 77 sites included in this study, only 2 samples had less than 2 mg l⁻¹ NO₃-N. In the Great Ouse Chalk area, diffuse agricultural sources are expected to dominate, although both point sources and leakage from sewers and septic tanks are also possible sources of NO₃ to the aquifer. It would seem that none of the waters from the unconfined aquifer system in this area are unaffected by NO₃, making the establishment of a baseline impossible from present day conditions. The diffuse inputs of NO₃ to the aquifer are likely to continue to affect the baseline in the future if concentrations in the unsaturated zone are still high (Jones and Cooper, 1998).

Remedial measures and the reversal of trends of groundwater quality in a particular area requires the determination of local baseline, in order to quantify the desired target composition. It is also important to ascertain the heterogeneity of baseline components, and regional maps provide a synoptic picture of the variations across the aquifer which can aid this spatial understanding.

The baseline data presented in this report refers, in general, to pumped groundwaters and it could be argued that the baseline of the matrix porewater should also be established. It is to be recommended that porewater profiles are collected to provide such a baseline. The aquifer matrix and geochemical environment can be extremely important in terms of natural attenuation processes. Diffusional exchange and mixing between fracture water and porewater may lessen the initial effects of pollution, but equally may retain pollutants for long periods of time or delay arrival of modern high NO₃ groundwater.

8. SUMMARY AND CONCLUSIONS

The chemistry of the groundwaters in the Great Ouse Chalk are dominated by natural reactions between the Chalk aquifer and the groundwater. Most of the parameters measured in the groundwaters represent baseline. Much of the chemical composition is derived from water rock interactions, dependant on both the natural acidity of rainfall (due to dissolved CO₂) and to the enhanced partial pressures of CO₂ frequently found in soil zones due to microbial respiration. The reactivity of this dilute acid towards the calcite matrix is such that rapid congruent dissolution of the carbonate fraction takes place until equilibrium with calcite is reached. Subsequent incongruent dissolution continues to release minor ions from the calcite lattice, such as Mg and Sr, into the groundwater as a more pure calcite phase reprecipitates.

Within the saturated zone of the aquifer mixing of different groundwater bodies, diffusional exchange between matrix pores and fracture water and redox reactions all take place. It is suggested that more than one baseline system may occur within this aquifer: older waters beneath the Till deposits and modern recharge in the Till-free valley areas. There are considerable spatial variations in hydrochemistry with groundwaters becoming more dilute along the regional flow direction from east to west. This is considered to be due to the influence of Till deposits which cover the upper reaches and interfluves of the valley systems. It is probable that modern recharge is located only in the Till-free areas in the valleys and that focussed recharge may occur along the edge of the Till. The high concentrations of solutes at these points may be due to leakage from the Till or from flow beneath the Till of older higher SEC groundwaters. Further work is recommended in such areas to understand the recharge mechanisms and flow beneath the Till. Surface runoff from the Till deposits may also have a high SEC due to increased concentrations of NO₃ and SO₄.

Historical data are available from some public water supplies. These provide excellent time series data for nitrate, but rarely for other elements. A knowledge of the baseline composition of these waters with respect to nitrate is impossible to gauge in the oxidised waters as concentrations approaching the MAC limit of 11.3 mg l⁻¹ NO₃-N are common throughout this study area. The importance of establishing long term historical records for aquifers cannot be overstated, in order to permit the determination of baseline hydrochemical quality.

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