Baseline Report Series:
21. The Chalk and Crag of north Norfolk and the Waveney Catchment

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

Baseline Report Series: 21. The Chalk and Crag of north Norfolk and the Waveney Catchment

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FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

In order to interpret the water quality variations in terms of the baseline, some knowledge of the residence times of groundwater is required. For this purpose both inert and reactive chemical and isotopic tracers are essential. Measurement of the absolute age of groundwater presents many difficulties and radiocarbon dating is the most widely used technique. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water may also provide indirect evidence of residence time. The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium (^{3}H), dissolved greenhouse gases -chlorofluorocarbons (CFCs) - and certain micro-organic pollutants may provide evidence of a recent component in the groundwater. The baseline has been modified by man since earliest times due to settlement and agricultural practices. However, for practical purposes, it is convenient to be able to distinguish water of different 'ages': (i) palaeowater - recharge originating during or before the last glacial era i.e. older than c.10 ka (ii) pre-industrial water (pre 1800s), (iii) water predating modern agricultural practices (pre 1940s) and (iv) modern post-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 (Shand & Frengstad, 2001; Edmunds et al., 2003). The "baseline" refers to a *specified system* (e.g. aquifer, groundwater body or formation) and is represented by a range of concentrations within that system. This range can then be specified by the median and lower and upper limits of concentration.

The BASELINE objectives are:

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

2. to characterise a series of reference aquifers across England and Wales that can be used to illustrate the ranges in natural groundwater quality. The baseline conditions will be investigated as far as possible by cross-sections along the hydraulic gradient, in well characterised aquifers. Sequential changes in water-rock interaction (redox, dissolution-precipitation, surface reactions) as well as mixing, will be investigated. These results will then be extrapolated to the region surrounding each reference area. Lithofacies and mineralogical controls will also be taken into account. A wide range of inorganic constituents as well as organic carbon will be analysed to a common standard within the project. Although the focus will be on pristine groundwaters, the interface zone between unpolluted and polluted groundwaters will be investigated; this is because, even in polluted 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, whilst the Crag is a locally important resource over its outcrop area in East Anglia. The utilisation of these aquifers in this region includes public and private drinking water supplies, irrigation of agriculture and amenity lands as well as minor industrial uses. The surface water – groundwater interaction of both aquifers at outcrop is responsible for the maintenance of flows in locally and nationally important wetland systems, including those of the Norfolk Broads.

The baseline chemistry of the Chalk groundwaters are predominantly controlled by natural reactions with the aquifer minerals. Dissolution of calcite controls the major element chemistry, and increasing residence time leads to the relative increase in concentration of other solutes which occur as impurities within the calcite (e.g. Sr, Mn). The overlying Crag and Till deposits present in the east of the study area result in longer residence times for the underlying Chalk aquifer, and increasing concentrations of total dissolved solids and other indicators of groundwater 'age'. The Crag groundwaters exhibit a locally variable chemical composition, but one dominated by natural inputs through reaction with the aquifer minerals. The concentration of solutes such as Ca and HCO_3 in solution is controlled by reactions with shelly carbonate material in the aquifer, and high concentrations of Fe by redox reactions and the occurrence of glauconite within the aquifer. In both aquifers, solutes may be enhanced over the baseline concentrations by anthropogenic perturbation of the hydrogeochemical cycle, such as nitrate which shows the greatest deviation from the baseline in the unconfined aquifer. Insufficient historical data for many solutes in both aquifers reinforces the need for adequate temporal data in order to understand the historical baseline.

2. PERSPECTIVE

The groundwater resources of East Anglia are under pressure due to the demand for good quality water for public and private supplies, irrigation and industrial use. These requirements must be balanced with the need to protect aquatic ecosystems from possible detrimental effects caused by over-abstraction or chemical deterioration. This report focuses on two different aquifers in two regions of Norfolk and Suffolk (Figure 2.1) where previous information on the quality of groundwater was often restricted to major ion chemistry, and derives from a variety of sources.

The Cretaceous Chalk forms the most important groundwater resource in East Anglia and, despite the low population density, there is a limitation of this resource on further development in some areas. The Chalk is confined in the far east of the region by argillaceous Palaeogene deposits. These are overlapped by the Neogene and early-Quaternary Crag sediments. The Crag comprises heterogeneous sediments and is a locally important private water supply, with areas of the Broadland being outside of the public distribution network. There are over 600 private supplies in Broadland and over 300 in the coastal Suffolk area (usually in drift and Crag). However, there are few public supplies: only Ludham in Broadland and a small number in Suffolk. Both these aquifers form an integral part of the aquatic ecosystems of the river networks and wetland systems in the study area, including those of the Broads National Park. The Waveney catchment passes from the Chalk in its upper reaches, to the Crag just north of Hoxne. Whilst a small number of public supply boreholes are located along the river valley and in the upper catchment, little information exists on the chemical quality of groundwaters from either the Chalk or the Crag aquifer through the wider catchment. Recent piezometer installation by the Environment Agency has provided the scope for further work. Both aquifers are covered across wide areas of their outcrop by glacial and recent sediments, which can influence groundwater recharge, flow and water quality.

These two aquifers have been studied simultaneously due to their geographical coincidence and the urgent need to obtain more information on their baseline characteristics and the interrelationships between the aquifers. The data is presented separately for the two aquifers for much of the report, in Sections 5 and 6, with a brief comparison of the two aquifers, and data collected from some superficial aquifers (Section 4) in the Waveney catchment at the end of Section 6.

2.1   North Norfolk

The 'North Norfolk' region, for the purposes of this report, extends from Fakenham in the north-west to Caister-on-Sea in the south-east, and is otherwise bounded by the Norfolk coastline (Figure 2.1). It encompasses the rivers Stiffkey and Glaven draining north to the North Sea, and the upper Wensum catchment and the Bure catchment in the Broadlands, both ultimately discharging to the sea at Great Yarmouth (Figure 2.1). The Bure and its tributaries drain much of the Broads National Park and large areas are protected sites for nature conservation with particular regard to aquatic flora and fauna. The urban centre of Norwich lies immediately to the south of the area. The population distribution of North Norfolk is otherwise concentrated in smaller towns such as Sheringham, Cromer, Fakenham, East Dereham and North Walsham. The holiday resorts of the coastal and Broads regions undergo significant population expansions in the summer months, with tourism being a major source of revenue to the whole region. More details on the county of Norfolk can be found in the Environmental Overview (Environment Agency, 1999). The seasonally high summer demand placed upon water resources is coincident with the greatest demand requirements from the agricultural sector.

Both the Chalk and the Crag aquifers in this area are largely covered by drift deposits, with only areas such as the river Yare downstream from Norwich, having Chalk outcropping at the surface. The Chalk extends to the west of the study area from a line running approximately north from Taverham (Figure 2.1); to the east of this boundary the outcrop 'solid' lithology is the Crag, although this over-steps the Palaeogene in the region east of the river Ant (Figure 2.1).
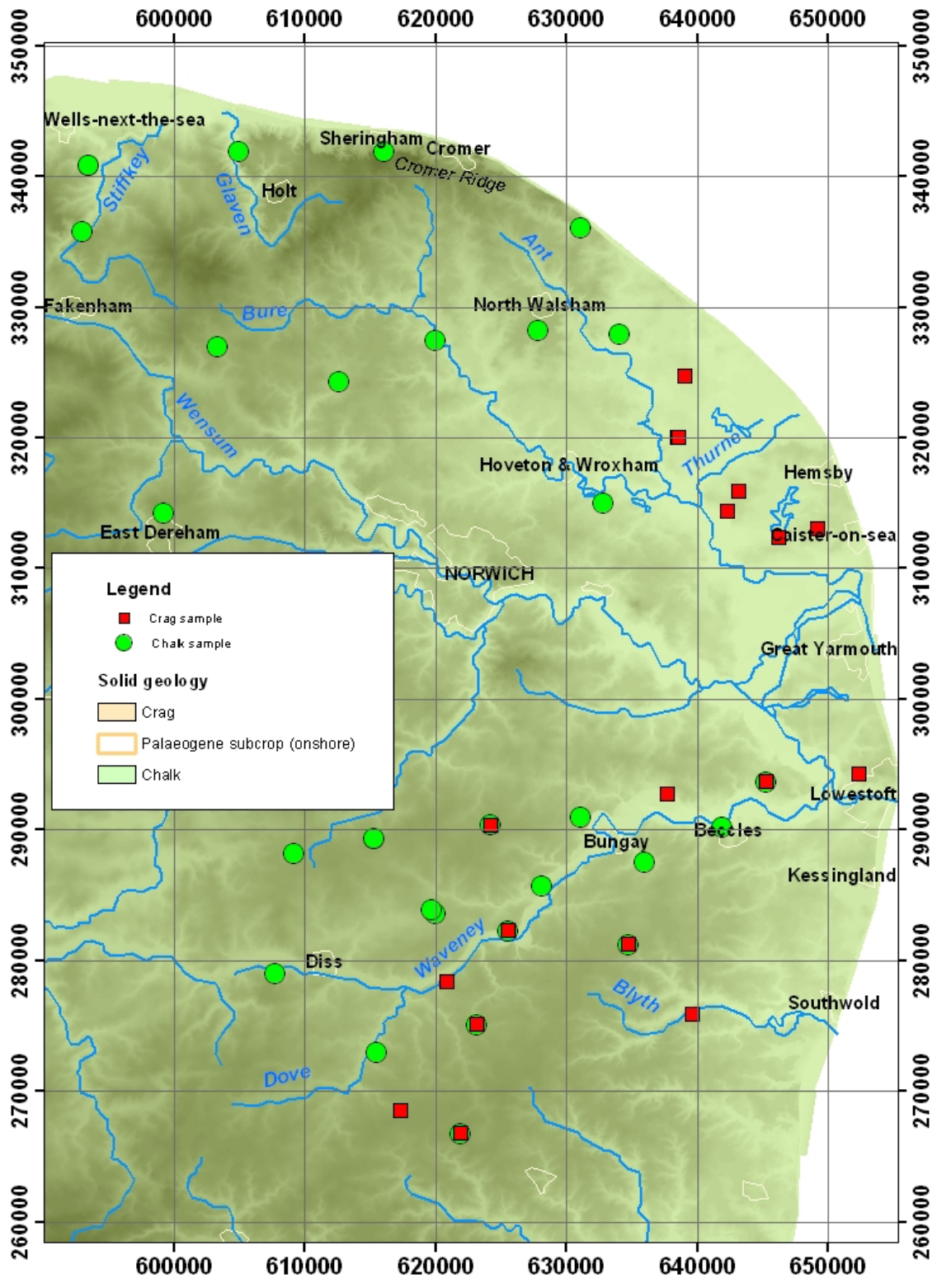
Figure 2.1 **Location of the north Norfolk and Waveney study areas**
The thematic shading represents the surface topography from sea-level (lightest colour) to a maximum altitude of 110 m (darkest colour) above sea-level. Topographical data courtesy of the Centre for Ecology and Hydrology DTM © NERC

The north coastal area is characterised by a Chalk ridge from Cromer to Syderstone (Figure 2.1), rising up to 90 m aOD; this is the highest ground in the study area. The generally subdued relief is a reflection of extensive glacial erosion and subsequent deposition of glacial and post-glacial sediments. In the Cromer and Sheringham areas, there are no northerly draining surface waters; further west the rivers Stiffkey and Glaven flow to the coastal marshes at Stiffkey and Cley-next-the-Sea respectively. Much of the area of north Norfolk is drained by the tributaries of the Wensum and Bure rivers. The headwaters of the Bure rise south of the Cromer Ridge, before becoming dominated by artificial drainage channels and the Broads south-east of Hoveton and Wroxham. The Broads National Park is an area of low lying (sometimes below sea-level) relief with reclaimed marshland and artificial drainage. These artificial drainage networks were originally powered by widespread windmills, some of which can still be seen across the landscape. The broads have been formed from the 12th and 13th Century onwards by cutting of what would have been very extensive, deep peat deposits in the lower catchments when 'natural' drainage conditions existed. They represent a remnant of one of the earliest widespread industrial processes in the area (Jennings and Lambert, 1953, Lambert, 1960). Channel modifications have been made over centuries; the River Ant was diverted from the River Thurne to the River Bure between the 11th and 14th centuries. The Broads area has also been affected by recent transgressions, the largest recorded c.2200 BP, with the largest flood in living memory having occurred in 1953 (Arthurton et al., 1994).

Where surface relief is above sea level, it can generally be assumed that in general groundwater movement is closely related to topography. The interactions between groundwater and surface water in the low-lying broads has to be conceptualised in more complex terms. Artificial drainage means that river bottoms may be above the local water table, and conversely the low relief means that any measurement of discharge of groundwater has been a very difficult undertaking. Density-dependant heads at the coastal freshwater – saline water interface also complicate physical models of groundwater flow. It has been shown that, although the groundwater discharge from the Crag to the broads may be of low total volume, this pathway can be essential in maintaining surface water levels. However, the specific hydrological pathways in any one region can be a complex series of rainwater, surface water and groundwater fed areas, which are temporally variable (Gilvear et al., 1997), and the evapotranspirative demand of the broads vegetation is also significant and temporally variable. Recent developments have improved the understanding of the hydrogeology of this aquifer (ENTEC, 2001, Holman et al., 1999).

The Chalk is exploited for public supply in this area by a wide distribution of boreholes, not all of which could be sampled during this study, although a good geographical spread was aimed for. Licensed abstraction from the Chalk in this area is ~200,000 $m^2\,d^{-1}$ (Allen et al., 1997). A public water supply draws from the Crag at Ludham. The Crag (and overlying superficial deposits) provide the potable source for over 600 homes in this area. From these, care was taken to sample wells which were thought to be screened only in the Crag, as many of the supplies are combined Crag and superficial deposit sources. The Chalk is recognised as a 'major' aquifer (Allen et al., 1997). The Crag is considered a major aquifer in Norfolk under the groundwater vulnerability and Part IIA Contaminated Land classifications, although it is reported in the minor aquifer properties manual (Jones et al., 2000), and considered a minor aquifer in Suffolk due to its limited saturated thickness. The implementation of the Water Framework Directive ensures that the importance of both units as both potable resources and ecosystem components is recognised.

Regionally, agricultural practices have had a major impact on the quality of groundwater through the leaching of fertilisers, although in the Wensum catchment and on the Suffolk Crag, both intensive and outdoor pig rearing have affected water quality. There are a number of landfills which have had a local impact on groundwater quality, largely through the contribution of chlorides and ammonia.

2.2 The Waveney catchment

The river Waveney rises at Redgrave Fen and flows to the North Sea at Lowestoft (Figure 2.1), forming the boundary between Norfolk and Suffolk along its course. The only major tributary of the Waveney is the Dove, which rises to the south-west of Eye, and joins the Waveney close to Hoxne (Figure 2.1). The only settlement with significant industrial and commercial development in the catchment is the coastal town of Lowestoft. The smaller towns of Diss, Bungay and Beccles lie along the river valley, and the catchment contains a large number of small towns and villages in a predominantly rural landscape. The area generally, and the coastal area in particular, experience large seasonal changes in population as a result of the tourist industry which is an important part of the local economy. Historically, industry was more widespread in the area; the basal Red Crag of Suffolk was sufficiently phosphate rich to support the world's first commercial extraction of rock phosphate to be used as fertiliser (Balson, 1999).

The highest land, forming the watershed to the north and south, rarely rises above 60 m and the topography is subdued throughout the area. The low-lying river valley of the Waveney is characterised by wetlands along its length, some of which are protected by statutory designations for their importance to aquatic and marginal aquatic ecosystems. The headwaters rise in Redgrave Fen, which is separated from the headwaters of the westerly draining Little Ouse River by less than 100 m. The hydrological conditions at Redgrave and Lopham Fen have long been the subject of research in relation to the interactions between groundwater discharge from the base-poor superficial deposits and the Chalk (e.g. Bellamy and Rose, 1960) (Figure 2.2). It is now thought that the influence of drift geology is more significant than groundwater in relation to the base-nutrient status of the individual Fens, particularly in the supply of nutrient poor recharge waters at Redgrave Fen. Changes in land drainage practice, as well as groundwater abstraction over the last 50 years, have contributed to the changes in the hydrology in that time, resulting in a flashier response to rainfall (Environment Agency, 2004).
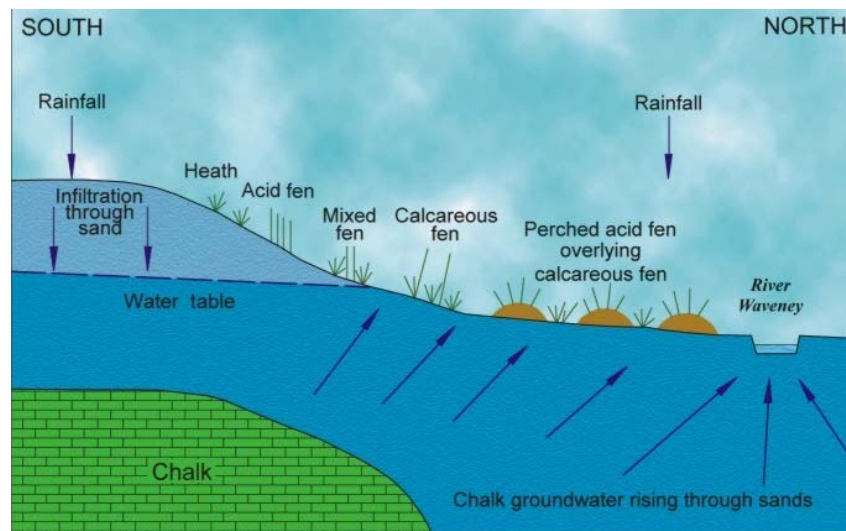
Figure 2.2   Schematic section through Redgrave and Lopham Fen
From: Groundwater Forum (1998)

The geological environment of the Waveney valley is characterised by terrace, peat and alluvial deposits laid down in a valley incised through the till plateau. These superficial deposits lie over the Chalk in the upper catchment, and the Crag downstream from the area between Scole and Hoxne. The groundwater catchment broadly reflects topography, and thus is similar to the surface water catchment. In the area around Lowestoft, the hydrology becomes more complex with artificial drainage channels, such as those linking the rivers Yare and Waveney via the New Cut. The

considerations described for the Broads with respect to the complexity of the intercalated and interdigitating coarse gravels, sands and muds of the Neogene and Quaternary Crag sediments are equally valid for the Crag aquifer in the Waveney area. As is the case further north, the Palaeogene clays ('London Clay') overlying the Chalk are entirely concealed by the Crag, and act an aquitard between the Crag and Chalk aquifers.

The Chalk, Crag and superficial deposits are all exploited for public water supply in the Waveney catchment. A summary of the wider area groundwater usage is shown in Table 2.1. The groundwater sources tend to be concentrated in the upper catchment and the valley bottom. Abstraction for agriculture represents an important use of groundwater resources, and there are also sources using the Crag and Chalk for amenity (e.g. leisure parks, golf courses) and industrial use. The information derived from sampling a selection of those sources is augmented in this study by data sampled as part of the Environment Agency Waveney observation piezometer network. This recently installed network comprises some 28 piezometers in 12 different locations, with multi-level piezometers installed to intersect the different aquifers (or more than one depth in the Chalk) occurring at each location. These piezometers have well-constrained construction details, with casing designed to restrict the interval of the aquifer sampled by pumping. These piezometers are designed to increase the knowledge of the aquifers in areas where they are not otherwise possible to sample. The river terrace and glacial gravels have been exploited for aggregate extraction along the valley. Where agricultural land improvement has taken place on the very stony soils overlying these types of Quaternary sediments, this has resulted in the leaching of nutrients to groundwater.

Table 2.1 **Quantity of water licensed for abstraction in the Lowestoft and Saxmundham area in October 1994, from the National Rivers Authority* (Moorlock et al., 2000)**

	Public & private water supply	Spray irrigation	Industry	Other	Total
	10^6 m^3 a^{-1}				
Drift	2.8	1.6	0.1	1.1	5.6
Crag	2.3	1.7	0.2	0.3	4.5
Chalk	10.2	0.3	0.3	0.7	11.5
Total groundwater	15.3	3.6	0.6	2.2	21.6
Surface water	7.5	2.0	0.0	0.2	9.7
Total	22.8	5.5	0.6	2.4	31.3

* Now the Environment Agency

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

The hydrochemical evolution of groundwater, from its initial source as rainfall, is dependant on complex processes in the soil and unsaturated and saturated zone of the aquifer and overlying deposits. This is largely dependent on the mineralogy and chemistry of the aquifer and mixing with existing groundwater. This evolution can also be affected 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. This section reviews the geological, hydrological, mineralogical and some geographical information in order to provide a context for the presentation and discussion of results in chapters 5 and 6.

3.1 Geology

3.1.1 Cretaceous Chalk

The strata of the Cretaceous Chalk aquifer in East Anglia are contiguous with, and form the most easterly onshore extension of, the Chalk of the London Basin (Figure 3.1). In the present study area, the full depth of the Chalk is considerable, with the youngest onshore strata occurring in the north-east of Norfolk: the Trunch borehole [6293 3345] recorded some 462 m of Chalk. The strata which crop out in the study area are entirely Upper Chalk, and have a gentle dip (<1°) to the east (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 sediment. 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) e.g. foraminifera. Whilst no major unconformities are recognised on structural grounds, there are physical features which may lead to a variation in aquifer properties. The Upper Chalk of east Norfolk may contain more marl strata than are observed further west, which could account for some of the variations in aquifer properties (Allen et al., 1997). Two south-west to north-east trending depressions occur in the vicinity of Eye (including the Stradbroke Trough) (Allen et al., 1997); these structural lows in the surface of the Chalk are due to faulting or erosion (such as sea bed scour) (Bristow, 1983, Mathers and Zalasiewicz, 1988). Buried tunnel valleys are found throughout the North Norfolk Chalk region, and a deep buried channel extends from Redgrave to Stuston [6135 3790] in the upper Waveney valley (Allen et al., 1997).

The upper surface of the Chalk is frequently observed to have been softened and weathered to a 'putty chalk' by cryoturbation during the Pleistocene (Moorlock et al., 2000).

3.1.2 Palaeogene Clays ('London Clay')

The Palaeogene clays are entirely concealed by the Crag deposits (Figure 3.1). These strata are shallow marine and estuarine deposits, which are entirely argillaceous in east Norfolk, with minor arenaceous beds (of the Reading and Woolwich Formations) in east Suffolk (Moorlock et al., 2000). The strata dip 1° E, and increase in thickness from a low escarpment on the Upper Chalk at their western limit to a maximum of 72 m recorded for the onshore strata of this area (Moorlock et al., 2000).

These strata comprise predominantly argillaceous units, and are thus generally considered to act as an effective aquiclude which compartmentalises the groundwater of the underlying Chalk and overlying Crag into separate systems (Jones et al., 2000).
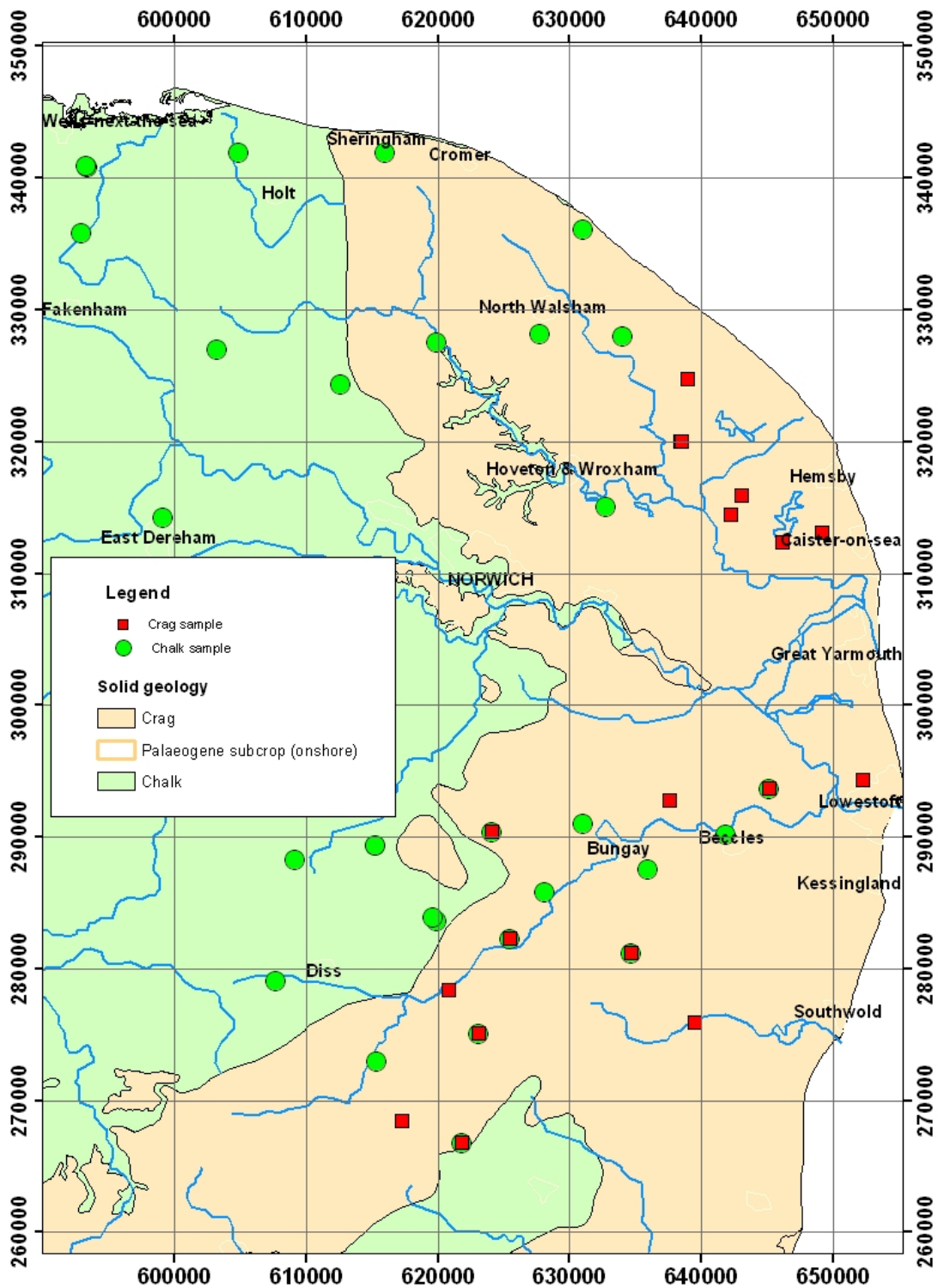
Figure 3.1   Solid geology of the study areas

3.1.3   *Quaternary Crags*

These strata, located in eastern Norfolk and Suffolk, consist of unconsolidated, intercalated clays, silts, sands and gravels unconformably overlying Cretaceous Chalk and Palaeogene Clays in the study area (Figure 3.1). The stratigraphical classification scheme of these strata has evolved over time, and the framework used by (Jones et al., 2000) is shown in Figure 3.2. Whilst the Crag was deposited in

the Neogene and early-Quaternary, it is the Quaternary sequence which is observed in the area of study. Difficulties exist in defining the boundaries for some of these units, and it is particularly poorly represented in the hydrogeological literature. Thus, they are frequently all grouped together as 'the Crag' (Jones et al., 2000).

The stages within the Crag sediments are separated by unconformities (Figure 3.2). Where the Wroxham and Norwich Crags are observed, they overstep the older Crag deposits and have a successively decreasing angle of dip upwards through the sequence (Moorlock et al., 2002a, Moorlock et al., 2000). The original thickness of deposition is not known, but the greatest total thickness in north-east Norfolk is 58 m in Ormesby [651 314] (Moorlock et al., 2000), and over 70 m of entirely Red Crag has been observed in the Stradbroke Borehole [623 274], suggesting that the total depositional thickness would have been considerably greater.

Deposition of these sediments occurred through a period of overall shallowing sedimentation as a result of the infilling of the western North Sea. Under these conditions, the proto-Thames and Ancaster rivers drained to the North Sea across what is now Norfolk and Suffolk (Moorlock et al., 2002a, Moorlock et al., 2000). By the Beestonian Stage (Figure 3.2), the depositional environment had become fluvial (Jones et al., 2000, Moorlock et al., 2000). The oldest strata of 'the Crag' belong to the Coralline Crag which occurs only in areas to the south of the present study, and so are not considered further.

The deposition of the **Red Crag** occurred in a series of basins on the surface of the Chalk. It is not clear whether sedimentation post-dated trough formation or was pene-contemporaneous (Moorlock et al., 2000). Within the study area, such basins have been recorded at Ludham [638 319] and the Stradbroke Trough, with up to 30 m and 70 m of Red Crag respectively. The Red Crag is predominantly composed of shelly sands with interbedded silty-clay and clays i.e. deeper water facies than the succeeding formations (Moorlock et al., 2000). The clays can be up to 10 m thick (Jones et al., 2000). Two vertical orthogonal joint sets have been observed in the Red Crag to the south of the Waveney catchment, but it is not clear that they occur in other areas (especially where the Crag is unconsolidated over much of the area). These are thought to result from stresses induced by subsidence of the southern North Sea Basin, and are generally c.5 cm wide and 2-3 m high. Infilling occurs, with micritic calcite, but some of the fractures appear to have remained open (Balson and Humphreys, 1986).

The **Norwich Crag** is a tabular sheet formation, uniformly around 30 m thick with a low dip to the north-east, and has an unconformable contact with all older sequences of the Crag. It is observed beyond the southern boundary of the present study area, and is found as far north as Ludham, but is not observed in Wroxham. The Norwich Crag is predominantly composed of interbedded fine- to medium-grained sands and clays, with a upwardly decreasing proportion of shelly beds. Decalcification may have altered shelly beds, which become more frequent lower down the sequence. Mica and glauconite are common with shelly sands but the loss of these via decalcification has been questioned (Moorlock et al., 2000). Interbedded gravels of the Westleton Beds and lenticular grey-blue clays (Easton Bavents Clay) are found in the Norwich Crag, which pass laterally and vertically into sandy facies (Hamblin et al., 1997). The clays can be of considerable thickness where they do occur, 5-8 m being recorded between Beccles and Lowestoft (Hamblin et al., 1997).

The **Wroxham Crag** dips gently to the north-east, resting unconformably on the Norwich Crag in the Ludham area and on the Upper Chalk in the Wroxham area. The lateral extent of the deposits is not completely known, but they are known from the Lowestoft area and are thought to occur beneath superficial deposits as far south as Southwold. The maximum total thickness is recorded as 20 m. These sediments represent the outer proto-Thames estuary environment, and are a complex mixture of estuarine and freshwater strata with a much higher proportion of gravels than the older Crag sediments. The gravels, sands and clays tend to exhibit finer interbedding than the Norwich Crag,

limiting the mapping of them as separate units, although clay beds up to 4 m thick have been recorded.

The *Cromer Forest Bed* represents freshwater and estuarine sedimentary environments, and for geological mapping purposes is considered to be 'drift' rather than 'solid' geology. However, from the hydrogeological perspective this distinction is superfluous, as these sediments are synchronous and interdigitate with the marine and estuarine Wroxham Crag strata in the North Norfolk area (Moorlock et al., 2002a). The sediments are freshwater organic muds, clays and sands with estuarine sediments also occurring.

|	East Anglian Stage	East Anglian lithostratigraphic units	
Quaternary	Cromerian	Bacton Member Mundesley Member West Runton Member	Cromer Forest-Bed Formation
	Beestonian	Runton Member	
	Pastonian	Paston Member Sheringham Member	Wroxham Crag Formation
	Pre-Pastonian	Sidestrand Member	
	Baventian	Westleton Beds Easton Bavents Clay	Norwich Crag Formation
	Bramertonian Antian	Chillesford Clay Member Chillesford Sand Member	
	Thurnian Ludhamian	Thorpness Member	Red Crag Formation
Neogene	Pre-Ludhamian	Sizewell Member	
		Aldeburgh Member Sudbourne Member Ramsholt Member	Coralline Crag Formation

〰〰〰〰〰〰〰   Unconformable sedimentary relationships

Figure 3**.2**   **Summary of the East Anglian Crag stratigraphy (Jones et al., 2000).**

3.1.4   Quaternary glacial and post-glacial deposits

These sediments form a complex sequence of glacial and post-glacial strata which occur over much of the study area (Figure 3.3). Hydrogeologically, these may act as aquifers or aquicludes providing storage or protection to the underlying Crag or Chalk aquifers.

The Anglian glaciation gave rise to two till deposits, thought to have come from separate ice-sheets, the Corton Formation and the Lowestoft Till. The *Corton Formation* is dominated by well-sorted, fine- to medium-grained sands, proved in boreholes of the Waveney valley and overlying the Cromer Forest-Bed in the Lowestoft area (Moorlock et al., 2000). It is synonymous with the term 'North Sea Drift', and derived from a proglacial lake associated with the Scandinavian Ice Sheet (Moorlock et al., 2000). The formation is up to 20 m thick, with the sands comprising up to 15 m of the total thickness, with subordinate tills at the base of the succession. The sands are dominated by quartz, but include chalk and mica fragments and calcretes in the upper sequence. Where clay occurs within the Corton Formation, it may restrict leakage and thus recharge to the Crag aquifer (Jones et al., 2000). These sediments are generally overlain by the Lowestoft Till (Moorlock et al., 2000).
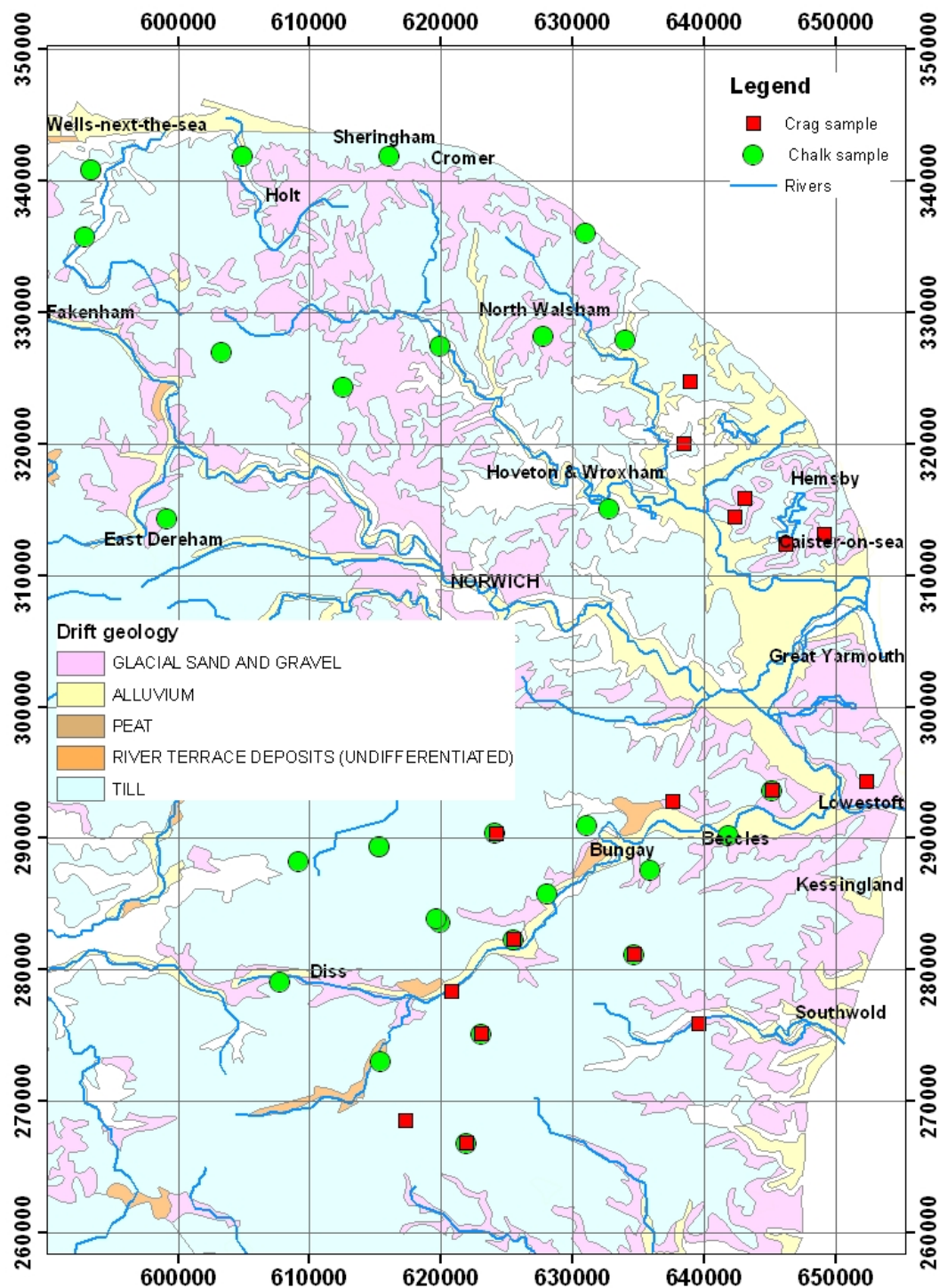
Figure 3.3   Superficial geology of the North Norfolk and Waveney study areas.
Unshaded areas indicate an absence of superficial deposits.

The *Lowestoft Formation (Till)* is the most widespread till in the Waveney valley, occurring from the highest ground to the valley sides. Although largely composed of argillaceous material, it characteristically includes irregular but frequent sands and gravels (Jones et al., 2000, Moorlock et al., 2000). In the Waveney valley, the argillaceous till is recorded as having been completely eroded, with glacial sands and gravels resting on the Chalk in the Roydon area [609 280] (Mathers et al., 1993). In

north-east Norfolk, this till formation becomes more chalky than further south and west in East Anglia (Moorlock et al., 2002a). The term 'Chalky Boulder Clay', widely used in the hydrogeological literature, is synonymous with the term Lowestoft Till.

The fresh boulder clay is an over-consolidated dark-grey clast-rich silty sediment. When weathered it becomes a yellow-brown mottled clay. Upper and lower contacts are typically oxidised, with pyrite occurring in the rest.

The Devensian glaciation only reached the very north coast of Norfolk, and whether deposits arise from this period is disputed (Moorlock et al., 2002a). Gravelly, clast supported eskers and kames are reported in the Glaven valley area, and are associated with till that may be Anglian or Devensian (Moorlock et al., 2002a) These sediments are limited in their lateral extent to the north Norfolk coastal area.

Subsequent interglacial and ***Holocene deposits*** are geographically restricted but river terrace deposits and alluvium are significant in the Waveney valley. During the Devensian glaciation, sea levels were considerably lower than present, with the Bure valley floor c.-7.5 mOD, the Waveney -12 mOD (Beccles – Lowestoft), and similar values for the Glaven (Moorlock et al., 2002a, Moorlock et al., 2000, Moorlock et al., 2002b). Additionally, the coastline during the Devensian glaciation was some 7 km east of its present location. Successive fluctuations in sea level since the Devensian glaciation (18 ka BP) have resulted in a series of estuarine and freshwater peats, clays, silts, sands and gravels in the river valleys and Broads (Moorlock et al., 2002b). The accumulation of the extensive coastal tidal flats and marshes at the coast is caused by the accretion of sediment on an over-deepened river valley. Subsequently, sea-level rise has resulted in a sequence of sands and gravels overlain by peat, which is in turn overlain by estuarine sediments. The marshland deposits have been classified separately, and are described by Moorlock et al. (2000). Details of these, and other, vertically or laterally less significant strata can be found in the memoirs cited above.

3.2   Hydrogeology

The physical hydrogeology of the Chalk is described in the Major Aquifer Properties Manual (Allen et al., 1997) and that of the Crag in the Minor Aquifer Properties Manual (Jones et al., 2000), where more details can be found. Information on the groundwater divides and contours, and regional Cl and total hardness variations, are mapped for both North Norfolk and the Waveney from data obtained in the 1970s (Institute of Geological Sciences, 1976; 1981). Considerable recent advances have been made on conceptualising and modelling the Chalk and Crag aquifer, and their inter-relationships (ENTEC, 2001).

3.2.1   Chalk

The Chalk is a dual-porosity aquifer, with both matrix pores and fracture voids, both of which contribute to the overall permeability of the aquifer. However, the pore throat diameter of average chalk pores is too small to allow significant drainage. Thus the permeability of the aquifer is derived from a continuum from large pores through small fractures up to larger dissolution-enhanced fractures (Price, 1987).

The Upper Chalk of East Anglia has a mean porosity of 38.4% (from 127 measurements) (Allen et al., 1997). The transmissivity is generally lower in east Suffolk and Norfolk than it is in the Great Ouse catchment to the west, which is considered to reflect the greater degree of confinement by low permeability sediments in the eastern area, and the possible occurrence of more marl horizons in the Upper Chalk. In the Norwich area, transmissivity values >2000 m^2 d^{-1} have been recorded in the Bure and Wensum valleys, and high transmissivities have been recorded in other areas of North Norfolk, such as Houghton St Giles (Stiffkey valley) and Glandford (Glaven valley). However, the median transmissivity for the area is much lower, being 277 m^2 d^{-1} (Allen et al., 1997). Whilst

transmissivity values are generally higher in the valleys, in keeping with observations through much of the Chalk, some valleys have low transmissivity, such as those of the lower Burn Valley at South Creake (Allen et al., 1997). However, this valley is semi-karstic and has high transmissivity further upstream.

Storage coefficients in the North Norfolk area have a geometric mean of 2.2×10^{-3} (Allen et al., 1997). Significant storage can be contained within the Crag and drift deposits where these overlie the Chalk, and can result in a ten- to hundred-fold increase in storage when they are taken into account (Allen et al., 1997). However, Price (1987) notes that release from elastic storage in the Norfolk Chalk could result in delayed yield from the Chalk itself, which could be misinterpreted as leakage from adjacent formations. In the east Suffolk area, the geometric mean transmissivity value is $255 \, m^2 \, d^{-1}$, and whilst high values frequently lie along valleys, some low values are reported for the Waveney, and for its tributary the Dove (at Eye). Pumping tests in the upper Waveney have revealed low transmissivity zones along the axis of the buried channel, but narrow high transmissivity zones running parallel on either side, which may be a result of dissolution and subsidence in the chalk (Professor RJ West, pers. comm.). Where the rivers have not eroded through overlying sediments to the Chalk, transmissivity values as low as $20 \, m^2 \, d^{-1}$ have been recorded to the south of the present area in the Gipping catchment, near Ipswich (Allen et al., 1997). Where the permeability of the aquifer is lower, this is thought to be reflected in substantially longer residence times for groundwater in the Chalk in these regions, which in turn has implications for the baseline chemistry of groundwaters.

The water table reflects topographical variations. Seasonal variations in water level below the till are generally less than 1 m (Moorlock et al., 2000). Where the Chalk is confined, the potentiometric surface is generally within the overlying deposits, although artesian conditions of up to 2 m above the land surface have been recorded at Halesworth, which is to the east of the Palaeogene boundary (Moorlock et al., 2000). The potentiometric surface of the Chalk and Crag in the lower Waveney catchment are very similar, and where the isobar is over 0 mOD, they are identical (Moorlock et al., 2000).

Where superficial deposits overlie the Chalk aquifer, groundwater heads are often within the superficial sediments. However, the aquifer is generally conceptualised as semi-confined rather than fully confined due to the possibility of recharge via arenaceous lenses within the tills (Allen et al., 1997). An example of this occurs in the Waveney catchment, where the Chalk, Crag and superficial deposits are considered to be in hydraulic continuity in the Waveney valley but not so in that of its tributary, the Dove (Allen et al., 1997). The occurrence of Putty Chalk is expected to restrict recharge from superficial deposits (Jones et al., 2000), such as observed at Rushall (Parker et al., 1987). In the Stradbroke trough, little hydraulic connectivity occurs between the Crag and Chalk (Jones et al., 2000). Overlying strata can affect the groundwater chemistry, such as the greater quantity of SO_4 expected in waters which have percolated through tills compared to recharge which has entered via the Crag (Price, 1987).

Post-glacially infilled buried valleys are widely recognised in the Chalk of East Anglia. It is difficult to ascertain the influence of buried valleys on physical properties – the buried valley at Rushall is thought to have resulted in the erosion of highly permeable chalk resulting in lower transmissivities, whilst in other areas, high transmissivities associated with sand and gravel-infill may occur (Allen et al., 1997).

The Palaeogene clays (London Clay) are an effective aquiclude where they occur at sufficient continuity and thickness, separating the Chalk and Quaternary aquifers (Allen et al., 1997). The feather edge of the clay is often locally incised and generally semi-confined; a thickness of less than 10 m along this boundary leads to some leakage through the clay. The quality of groundwater in the Chalk beneath the Palaeogene boundary shows a rapid and marked change in quality parameters. East of the Palaeogene boundary there is no natural drainage, and only minor abstractions (Moorlock et al.,

2000). Chloride concentrations were measured as 4000 mg l^{-1} in 1954 in groundwater at Aldeby [645 293] and an increase in Cl from 50 to 500 mg l^{-1} occurred over a distance of 1.5 km near Peasenhall [635 269] in the river Yox catchment, directly south of the Waveney catchment. Over pumping in the adjacent unconfined zone has to be monitored in order to prevent a reversal of gradient, and westward flow of saline water (of which there are records at Holton [639 277] (Moorlock et al., 2000) and Strumpshaw PS [635 307] (Arthurton et al., 1994). It has been suggested that the salinity originates from connate waters in the Chalk that have never been flushed out (Bath and Edmunds, 1981), although Heathcote and Lloyd suggested that the saline end-member in the Chalk in East Anglia may be Crag seawater which they considered to have flushed the Chalk (Heathcote and Lloyd, 1984).

High groundwater Cl zones (>100 mg l^{-1}) are shown on the regional hydrogeological map for the area between the Waveney and Dove, close to Diss (Institute of Geological Sciences, 1981), and Cl is generally elevated at depth in the Stradbroke depression. Saline intrusions (Cl >300 mg l^{-1}) have been observed in the coastal north Norfolk Chalk aquifer at several locations including Salthouse [607 343], and general areas of moderately high Cl (Cl >50 mg l^{-1}) north-east of North Walsham and between Wells-next-the-Sea and Sheringham (Institute of Geological Sciences, 1976). These may be related to intrusion along fractures as a result of pumping, because there are generally steep seaward hydraulic gradients in the Chalk of this region.

3.2.2   Crag

The Crag is important as an aquifer in its own right, and as a source of significant storage for the Chalk when the two formations are in hydraulic continuity. The aquifer properties of the Crag vary greatly depending upon the grain size of the sediments, degree of sedimentation and presence of semi-confining glacial sediments, although it is largely unconfined (Jones et al., 2000). However, the dominance of intergranular flow means that modelling of the flow in the Crag is generally more robust than that of the Chalk, despite the physical variability of the sediments.

Existing information on the physical properties of the Crag deposits is limited, and may also be compromised by the difficulties in unequivocally differentiating these from younger Quaternary deposits (Jones et al., 2000). In the Minor Aquifer Properties Manual, the only core values of permeability (14.8 m d^{-1}) and porosity (54%) given are derived from the Coralline Crag and considered to be unrepresentative of the aquifer as a whole (Jones et al., 2000). However, Gilvear et al. (1997) in the Ormesby area calculated a mean permeability of 14 m d^{-1} from multiple (12) piezometer measurements. Permeability data calculated from falling-head piezometer tests, and water-balance studies fell in the range 5 - 30 m d^{-1}. Porosity measurements using electrical-resistivity sounding indicate that 25% - 40% may be more appropriate than 54% (Jones et al., 2000). Borehole construction also greatly affects the physical properties data obtained. Median transmissivity is 412 m^2 d^{-1}, with an interquartile range of 238-772 m^2 d^{-1} (obtained from 179 records), whilst the median storage coefficient is 4.0×10^{-3} (from 140 records). A test at an Environment Agency borehole in Hickling, of 50 m depth, indicated a transmissivity of 1000 m^2 d^{-1} and an average permeability of 20 m d^{-1}. Specific yield values have an interquartile range of 0.004 to 0.011 (based on 179 tests) (Jones et al., 2000).

Where the Crag directly overlies the Upper Chalk, the potentiometric surface in the Chalk is generally lower than that of the Crag, indicating that the Crag is a source of recharge to the Chalk (Jones et al., 2000). Where the Crag overlies Palaeogene deposits, the Crag is isolated from the Chalk aquifer, and discharge is generally of a diffuse nature as springs or directly into surface water (e.g. the Broads). Generalised groundwater contours for the Crag were produced by Price and Tuson (1961). Spring and seep discharge is hard to identify due to the problems of accurately distinguishing the (decalcified) Crag from overlying later Quaternary deposits. Seasonal water table fluctuations in the Crag are generally less than 1 m due to the high storage coefficient of the aquifer, and groundwater contours reflect topography where the Crag is underlain by Palaeogene clays (Moorlock et al., 2000). Locally,

layered aquifer bodies can occur within the Crag when clay horizons are laterally persistent for some distance (Jones et al., 2000). Where the Crag is overlain by Till, this is thought to increase the residence time of the groundwaters, although not as substantially as those in the Chalk (Moorlock et al., 2000).

The factors other than topography which are expected to control the predominantly intergranular flow of water are (Jones et al., 2000):

- discontinuous layering of sediments with contrasting permeability;

- vertical fractures observed in the Red Crag;

- overlying glacial and inter-glacial sediments affecting recharge rate;

- the low elevation of the ground surface and wide spread land drainage, resulting in saline intrusions at the coast and potential recharge from rivers elevated above the surrounding drained land.

Where argillaceous layers occur within the Crag, there is some evidence that they can be sufficiently laterally and vertically continuous to result in a locally stratified aquifer. Studies of the groundwater at Ludham [638 319] showed that water below a significant clay layer was largely pre-modern (low tritium and nitrate; (Jones et al., 2000), in contrast to water above the clay layer. The importance of recharge 'windows' in the glacial sediments for recharge and discharge of Crag groundwaters was highlighted by the study of Gilvear et al. (1977) who found that an area of the Broads was supported by discharge from such a window. Recharge to the Crag may take place from rain-fed Broads (Gilvear et al., 1997). In some areas, the Crag waters flow up into the peat deposits.

Generally low yields (although improvements are helped by good borehole construction), the construction difficulties (running sands) and high iron concentrations are issues in the use of the groundwater from the Crag aquifer (Jones et al., 2000), although lack of resource is the main limitation on further exploitation. Where construction is carried out to a high standard, yields can be high, as at Ludham PS, where 2600 $m^3 d^{-1}$ was achieved (Jones et al., 2000). There is also hydraulic continuity with deposits offshore. Saline coastal waters occur due to saline ingress arising from land drainage (Holman, 1994) and intermittent but extensive flooding over the last 2000 years (Price and Tuson, 1961).

The main problems restricting the development of the aquifer are (Jones et al., 2000):

- running sands from the poorly-sorted and poorly-cemented sediments;

- variable and unpredictable yields;

- water-quality problems (Fe, Mn, H_2S and NO_3);

The water-quality problems will be discussed further in Section 5.

3.2.3 Quaternary deposits

The hydrogeology of the Quaternary deposits (particularly the tills) are of importance with respect to their impact on recharge and flow in the Chalk and Crag aquifers.

Till is distributed over large areas, with the exception of the valley bottoms where it has often been eroded away. Whilst the argillaceous strata are predominantly stiff grey silty-clays and clays, they may be weathered (oxidised) to a depth of 3 m below the surface, which alters them to a friable rust-

brown, decalcified sediment (Arthurton et al., 1994). Field permeability measurements for oxidised till have been found to have a range of 4.47×10^{-7} m d^{-1} to 6.37×10^{-9} m d^{-1}, whilst studies on the unoxidised till indicate a range from 1.17×10^{-11} m d^{-1} to 8.03×10^{-9} m d^{-1}. However, in addition to primary permeability, it has been observed that fractures occur in the tills, and that these are more common in the oxidised layers. These oxidised fractures may be a dominant control on recharge to the underlying aquifer (Klinck et al., 1996, Klinck and Wealthall, 1996). In addition, it has been observed that the Chalk aquifer beneath the till is not always confined by the till, and Feast (1998) observed that relative heads in the till and chalk in the Bure valley indicate egress of water from the chalk to the till.

Where clean sands and gravels are found, permeability will undoubtedly be substantially higher than for the poorly sorted or argillaceous strata.

3.3 Aquifer mineralogy

3.3.1 Chalk

The principal mineralogy of the Chalk is that of complete (1-20 µm) and fragmented (0.5-1 µm) algal coccoliths, with occasional larger skeletal fragments (10-100 µm), deposited as very pure low-Mg (<5 mole percent) calcite (Hancock, 1975). Whilst the Upper Chalk is expected to be >97% $CaCO_3$, and generally >99% $CaCO_3$ (Bath and Edmunds, 1981, Heathcote and Lloyd, 1984), the co-precipitated trace elements within the calcite structure and the accessory minerals within the strata, assume more importance in controlling chalk groundwater chemistry as the residence time of groundwaters increase. Concentrations of trace elements within the calcite phase reported by Heathcote and Lloyd are shown in Table 3.1 and for the Trunch borehole (Bath and Edmunds, 1981) (Figure 3.4).

Table 3.1   Composition of the Chalk

Chemical component	Data	Geographical area	Reference
$CaCO_3$	>98%	Suffolk / Essex	Heathcote and Lloyd 1984
Sr	500 – 800 mg kg^{-1}	Suffolk / Essex	Heathcote and Lloyd 1984
F	200 mg kg^{-1}	Suffolk / Essex	Heathcote and Lloyd 1984
I	2 mg kg^{-1}	Suffolk / Essex	Heathcote and Lloyd 1984
Mn	100 - 200 mg kg^{-1}	Berkshire	Edmunds et al. 1987

The non-carbonate phases are predominantly quartz, montmorillonite and mica (illite, muscovite and some glauconite) (Hancock, 1975, Morgan-Jones, 1977). The clay phases within the aquifer are of low abundance in relation to calcite, but they have a substantially higher surface area, and ion exchange capacity than calcite. Whilst laboratory-scale measurements may thus suggest that the scope for ion exchange within the aquifer is limited (Gillespie et al., 2001), on a regional scale the ubiquitous presence of clay minerals ensures that ion exchange processes can be important (e.g. Shand et al., 2003).

Other mineral phases occurring include pyrite (cubic FeS_2) and marcasite (orthorhombic FeS_2). These sulphide phases are likely to be the major hosts of As, Ni and Cr in the Chalk (Hancock, 1975). The oxidation of these minerals in a calcium-rich aquifer leads to the deposition of gypsum ($CaSO_4.2H_2O$) (Morgan-Jones, 1977). Glauconite is an additional source of Fe in the aquifer (Hancock, 1975). Song and Atkinson found that aqueous Fe^{2+} concentrations in the Bure valley decreased along the groundwater flow paths from the interfluves, which they calculated to be due to the precipitation of siderite ($FeCO_3$), suggesting that this mineral phase could occur within the aquifer. The reaction:

$$FeCO_{3(s)} + Ca^{2+}_{(aq)} \leftrightarrow CaCO_{3(s)} + Fe^{2+}_{(aq)}$$
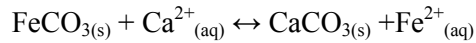
favours calcite unless $[Fe^{2+}]/[Ca^{2+}] \geq 0.05$ (Song and Atkinson, 1985).
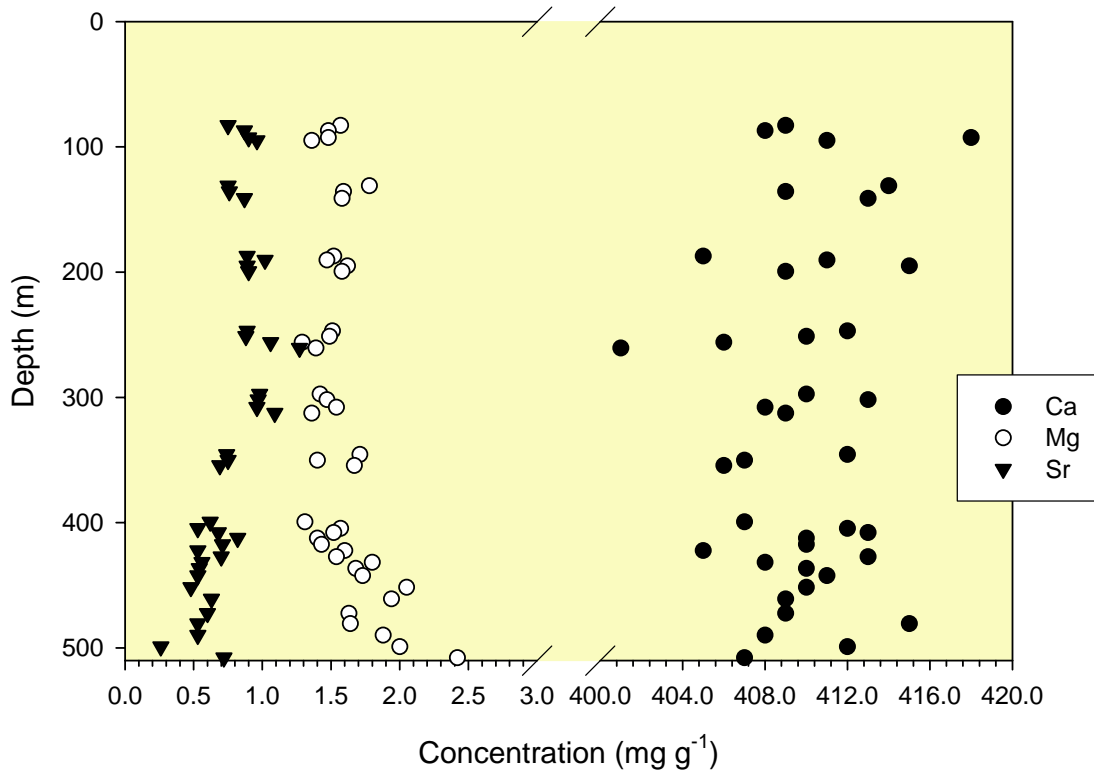
Figure 3.4   **Trace-element concentrations in the Chalk of the Trunch borehole (Bath and Edmunds, 1984)**

The changes in chemistry as pore and fracture fluids mix may account for the observation of frequent precipitation of Fe and Mn mineral phases on fracture faces (Shand and Bloomfield, 1995). Because the chalk acts as a dual-porosity aquifer, it is likely that these phases are important for both the cycling of trace elements in the aquifer, and may act to isolate the matrix from the fracture flow groundwater.

3.3.2   Crag

As is the case with aquifer properties, very little information exists on the mineralogy of the Crag aquifer. The proportions of clay minerals to sand-size fractions varies considerably both vertically and laterally within the aquifer. Little information exists on the composition of the clay-size fraction, particularly of alumino-silicate phases, apart from that of glauconite (see below). Carbonate, mica and glauconite are the minerals generally identified in the literature, with much phosphate deposition at the base of the Red Crag (which formed the basis of the fertiliser industry).

The sand (and coarser) fractions are frequently carbonate-rich (up to 60% whole and comminuted shells) and micaceous (Balson and Humphreys, 1986, Hamblin et al., 1997). Although considerable loss of $CaCO_3$ from the upper horizons of the sediments has been observed, it is not clear whether this is entirely due to chemical erosion or is a depositional feature (Moorlock et al., 2000). This decalcification process can result in high concentrations of Ca and HCO_3 in the groundwaters, and involves the dissolution of metastable aragonite and re-precipitation of the $CaCO_3$ as calcite.

The sediments are always observed to be dark-green at depth, as a result of the high concentrations of glauconite, up to 3% by volume in the Red Crag (Humphreys and Balson, 1985, Moorlock et al., 2002b). Glauconite is a term used to cover material from smectite to mica compositions. Strictly the composition is as follows:

$$(K,Na,Ca)_{1.2-2.0}(Fe^{3+},Al,Fe^{2+},Mg)_{4.0}[Si_{7-7.6}Al_{1-0.4}O_{20}](OH)_4.n(H_2O)$$
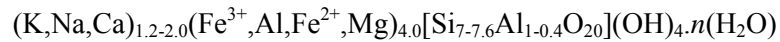
Glauconite contains mixed-valency iron, suggesting precipitation in a moderately reducing environment. It has been disputed whether this is authigenic or allogenic in origin (Humphreys and Balson, 1985, Merriman, 1983). The glauconitic material includes discrete grains (200-500 μm), coatings on flints and infilling of pore spaces (Humphreys and Balson, 1985). Generally the glaucony is as glauconitic smectite (Humphreys and Balson, 1985). Oxidation of the glauconite greatly contributes to the near ubiquitous reddening of the Crag in surface or coastal exposures; on a microscopic scale the oxidation products can occur as a rim on the glauconite or penetrate the whole grain, or can result in the irregular cementation of the sediments away from the original source of the Fe^{2+}. It has been suggested that the onset of oxidation of the Fe in the sediments was during the periods of hiatus within the overall deposition of the sediments. The glauconite also results in the Crag generally having a significant ion-exchange capacity (Heathcote and Lloyd, 1984), in the order of 5-40 meq/100g for glauconite (Appelo and Postma, 1994), although this is substantially higher than the value of 3.5 meq 100 g^{-1} recorded for the clean sands of the Chillesford Sand Member (Norwich Crag) [6383 2523] (Gillespie et al., 2001).

3.3.3   Quaternary superficial deposits

The mineralogy of these deposits is important as they affect the quality of recharge to underlying aquifers. The tills in south Suffolk have pyritic Jurassic and Tertiary clays as their major source rocks, oxidation of which leads to high SO_4 concentrations in porewaters (Heathcote and Lloyd, 1984). The reduced species may also be oxidised by the reduction of NO_3 in recharge waters, which provides an additional protective function to the underlying aquifer (Parker et al., 1987). It is suggested that gypsum in the till is a source of Ca and SO_4. The marine nature of the source rocks may also contribute Na, Mg and Cl (Heathcote and Lloyd, 1984).

The clays of the Lowestoft Till are dominated by mica and kaolinite, with subordinate and variable smectite and chlorite (Moorlock et al., 2000). Chalk and flints are the dominant clasts in the till with a mean of 40% carbonate (up to 70%) and a matrix texture of a sand or silty-clay. The unweathered clay is blue-grey and weathers to a yellow-brown, as a result of the oxidation of Fe^{2+} bearing mineral phases.

3.4   Rainfall chemistry

Rainfall provides the recharge for the Chalk and most of the Crag under study, and its composition is thus the minimum baseline condition. The coastal location of much of the Chalk and Crag aquifers studied here plays a role in the recharge chemistry, with greater concentrations of marine derived Na and Cl than would be observed further inland. The composition of rainfall is also illustrated (Table 3.2) with a threefold multiplication to approximate for the effects of evapotranspiration.

Table 3.2 **Representative rainfall chemistry for the study region, measured at Stoke Ferry, Norfolk [5700 2988] for 1998, to the west of the present study area (retrieved from The UK National Air Quality Information Archive at http://www.aeat.co.uk/netcen/airqual/ on 18 April 2002).**

Parameter (annual mean value)	Rainfall composition	Rainfall composition × 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	

3.5 Landuse

North Norfolk is a predominantly arable farming area, with wheat, barley, potatoes and sugar beet as the most important crops. There are some areas of woodland and heathland particularly along the sand soils of the Cromer ridge and to the north of Taverham (Figure 3.5). The artificially drained areas of the Broads are largely used for livestock farming, with some areas (e.g. around Horning) managed as semi-natural woodlands. Market gardening and horticultural landuses also occur in this area. A decline in industry using the groundwater resources of the area has taken place, which used to include mushroom growing and packaging. Brewing is still a user of the groundwater from the Chalk.

The landuse in the river Waveney catchment is dominated by arable farming, with similar crops as north Norfolk (Figure 3.5) in the valley sides. The drained soils of the floodplain are often used for cattle grazing, particularly in the summer. Tourism is an important source of revenue for the area, particularly centred on the coast and Broads. This has consequences for development in the coastal areas in particular, and seasonal changes in road use intensity. Industrial uses in the Lowestoft area for the Crag aquifer include commercial amenity lands and industrial units.

Figure 3.5   Landuse in the study areas

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 56 samples were collected from two regions of East Anglia during June 2003 in order to characterise the nature of groundwater within the Crag and Chalk aquifer systems. The sampling was undertaken in two aquifers, the Crag and the Chalk, from two distinct geographical areas, the Waveney valley and North Norfolk. Within the Waveney valley, samples were collected predominantly from Environment Agency piezometers installed during 2002, with some public water supply sites also being sampled. The samples in North Norfolk were from public water supply sources in the Chalk aquifer and private water supply sources in the Crag aquifer. A summary of the samples collected from each aquifer and each area is shown in Table 4.1. No springs were sampled in either field area, due to the difficulty in ascertaining whether surface springs are associated with the Crag, or whether they are derived largely from glacial and post-glacial sediments.

For the Environment Agency piezometers, sampling was carried out simultaneously with that for the Environment Agency groundwater network sampling programme. At each site, the piezometers were purged for three borehole volumes prior to sampling. Several samples were also collected from piezometers in the superficial deposits of the area installed at locations where chalk or Crag piezometers were present.

Table 4.1   Summary of the samples collected

Aquifer	Waveney catchment	North Norfolk	Total
Chalk	17	13	30
Crag	11	7	18
Glacial / alluvial sands & gravels	6	0	6
Boulder Clay / till	2	0	2
Total	36	20	56

The physico-chemical parameters of pH, redox potential (Eh), and dissolved oxygen (DO) were measured on-site whenever possible by connecting an air-tight flow-through cell to the rising pipe. At four sites (CC53-CC56), measurements are those taken using the Environment Agency flow-through cell (which had previously shown good agreement with data collected using the BGS flow-through cell). At two sites (CC07 and CC37) it was not possible to connect the pump outlet to the flow-through cell, so measurements were made as quickly as possible within a large container. At another site (CC15), pumping from the Wortwell boulder clay piezometer, pumping had to be undertaken at a slow rate due to the high draw down encountered, so the flow-through cell was not used. The temperature is, therefore, likely to be artificially high due. Measurements of temperature (T), specific electrical conductance (SEC), and alkalinity (by titration) were also made whilst on site. Water samples were filtered (<0.45 μm) into Nalgene polyethylene bottles for major and trace cation and SO_4 analyses (acidified to 1% v/v HNO_3). Filtered (<0.45 μm), unacidified, water samples were also collected into Nalgene bottles for anion analysis. Samples were collected in glass bottles for dissolved organic carbon (DOC) (filtered through a 0.45 μm Ag-membrane filter), and stable isotopes (δ^2H, $\delta^{18}O$ and $\delta^{13}C$).

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, Cl, Br, F and I were determined by automated colorimetry (SKALAR). Stable isotopes were measured by mass spectrometry and values reported relative to VSMOW for δ^2H and $\delta^{18}O$, and VPDB for $\delta^{13}C$.

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 and had good charge balances.

Data has also been incorporated where appropriate from the scientific literature, for which major element data are available for the North Norfolk Chalk, through the publications summarised in Table 4.2.

Table 4.2   **Literature data sources for the Chalk and Crag aquifers.**

Aquifer	Number of sample points used	Region	Source
Crag	5	North Norfolk	Hudson et al. (2003)
Crag	15	North Norfolk	ENTEC (2001)
Crag	17	North Norfolk	Cook
Crag	7	North Norfolk	Hiscock (1987)
Crag	20	North Norfolk	Holman (1994)
Chalk	52	North Norfolk	Feast et al. (1998)
Chalk	2	North Norfolk	Bath and Edmunds (1981)

4.2   Historical data

A few reference sources provided historical comparative information for the aquifers (e.g. Whittaker, 1906, Whittaker, 1921). From such sources it can be recognised that some 'modern' problems with establishing baseline may have comparisons stretching back over 100 years. For instance the high nitrate concentrations which are found in the Crag are not necessarily recent in origin e.g. a concentration of 93 mg l^{-1} as NO_3 was found in Southwold in 1888 (this area has light soils which would readily leach any agricultural NO_3 applications). Few datasets are available over a very long period (>50 years) for a single source, and no information could be found for a complete suite of major elements or trace elements collected over such a period of time although some information provided is summarised in Section 6.

4.3   Processes affecting the composition of pumped groundwater

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 deviations in the chemistry from that characteristic of the undisturbed aquifer. These variations may arise as a result of:

• differences in borehole design and construction (depth, depth of casing);

• different stratigraphic horizons present in the borehole (including fractures intersected);

• different 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

The occurrence of different flow regimes within the Chalk (Section 3.3) means that differences between fracture and pore water chemistry are likely, as well as lateral and vertical stratification. Where a borehole intersects these chemically stratified groundwaters, mixing will be expected to occur in the borehole column. Thus the borehole depth and length of casing will all have the potential to affect water chemistry simply by differences in the nature and quantity of groundwater drawn into the borehole.

Wells and boreholes in the Crag generally require screening because the sediments are prone to problems with running sands. Running sands can locally alter the flow of groundwater to the borehole. It is also likely that vertical stratification of groundwaters within the Crag occurs where contiguous clays act as effective barriers to groundwater flow. If two bodies of water are intersected by a borehole, then mixing may be expected whilst pumping takes place.

4.3.2   Differences in stratigraphy

The natural variability of the structure, mineralogy and geochemistry of the Chalk will result in variations in the groundwater chemistry. The dual-porosity nature of the aquifer may result in porewater chemistry (where diffusion may be important) being different to fracture water chemistry (dominated by advection and dispersion). The aqueous composition sampled by pumped boreholes will be overwhelmingly dominated by fracture water. Whilst the Crag is a heterogeneous aquifer matrix, its overall physical properties have been found to be more consistent and predictable than the Chalk.

The in-situ composition of Chalk porewaters has been studied in this region by Bath and Edmunds (1981), using material from the 472 m Trunch borehole in north-east Norfolk. Data from their study of the Chalk porewater compositions, and comparison with pumped (fracture flow dominated) waters are reproduced in Figure 4.1. The porewater profile is interpreted as a diffusion controlled mixing between older (saline) waters at depth and younger, fresher waters towards the top of the profile (Bath and Edmunds, 1981). The data for the White House PWS (1 km from the Trunch borehole) cited by Bath and Edmunds is also plotted on the figure for comparison (at an arbitrary depth for plotting purposes), and shows that the composition of elements associated with increasing residence time (particularly Sr) are much lower (note the log scale) than those observed in the porewaters. Celestite ($SrSO_4$) was observed in fracture fill material at depth in the borehole, limiting further increases in Sr concentration above c.30 mg l^{-1} (Bath and Edmunds, 1981).

A significant issue in the representative sampling of Chalk groundwaters is due to a biasing in the distribution of 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 in the interfluve areas elsewhere in the East Anglian Chalk, the aggressive nature of the reducing waters to the pumping equipment increases the costs of running such boreholes, reinforcing the economic desirability of siting boreholes and pumping from valley locations. This makes the even distribution of the sampling sites across the groundwater catchment extremely difficult. The distribution vastly increases the proportion of samples from valleys, at the expense of those from the interfluves. The design of the Waveney network has been specifically to avoid these issues, but it is not clear whether these piezometers have been pumped sufficiently to remove any perturbations to the local hydrochemical regime caused by installation. No data on porewater analysis of core from the Crag has been located during this study.

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 may have a significant effect on the lateral extent from which water is drawn. Considerations of sediment heterogeneity suggest that flow paths within the Crag may be locally complex and thus affected by pumping regimes employed. When the Chalk groundwater is abstracted from depth, or from beneath the Crag or confining Quaternary sediments, this may affect the redox status and composition of the waters due to drawdown of overlying water. 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). Horizontal flow components may be replaced over time by vertical flow after the commencement of pumping from a borehole, and that this effect will accentuate the ingress of nitrate into the supply.

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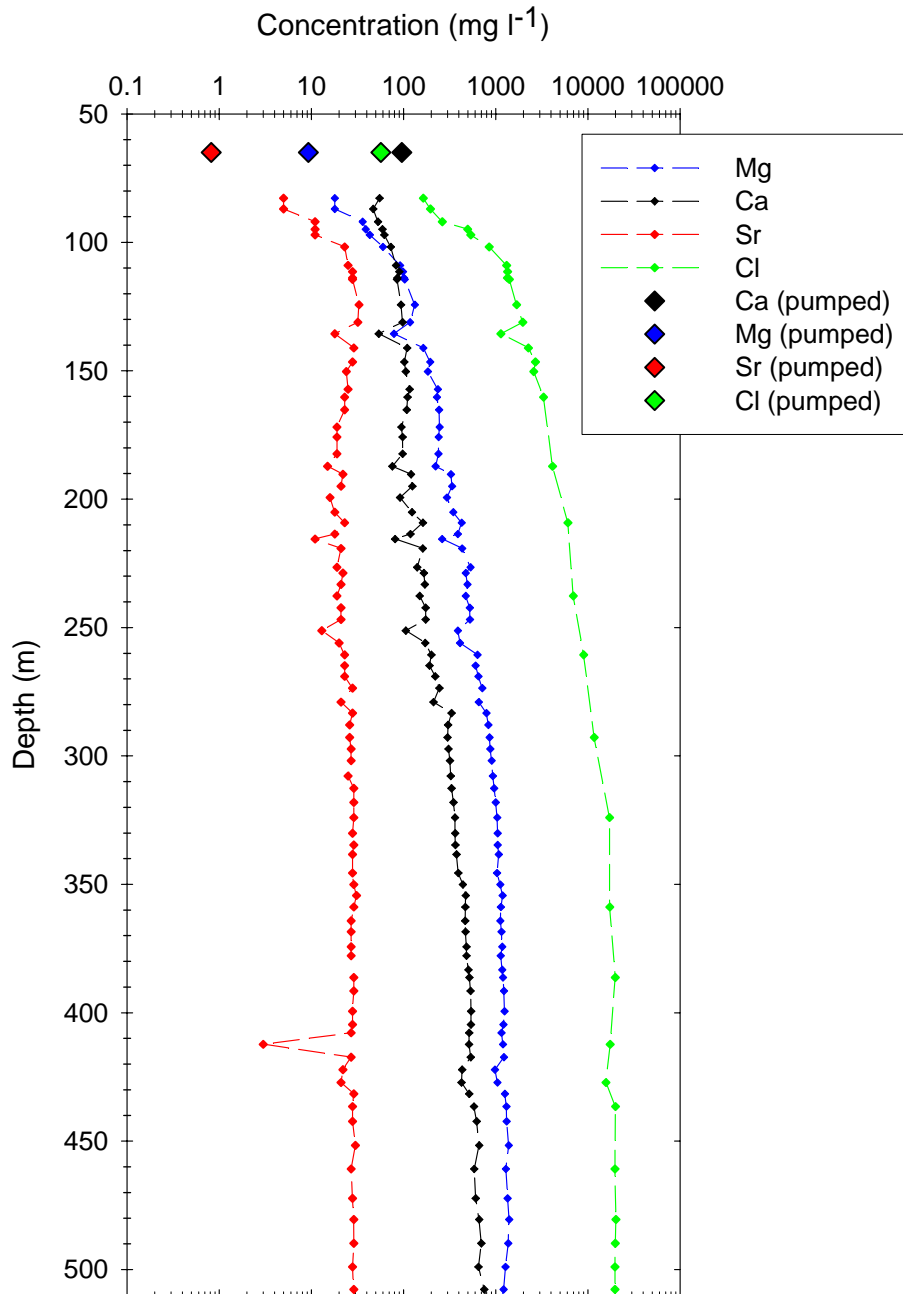
Figure 4.1   Pore-water profile of the Trunch borehole (Bath & Edmunds, 1981). The samples marked 'pumped' are plotted at an arbitrary depth for comparative purposes only.

This report presents a broad assessment of the water-quality variations observed across the aquifers studied and the controlling geochemical processes. Chemical reactions are both time- and space-dependent 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 undertaken in the Waveney valley with a view to augmenting the samples collected from the Environment Agency piezometers. Samples in the North Norfolk area were also selected to give a good coverage of the aquifer through the designated region; for the Chalk this was

achieved by additional sampling of public supply sources. Locating private supplies which are unequivocally from the Crag, rather than a combination of Crag and overlying Superficial deposits, was difficult in the North Norfolk area. Thus the samples were selected by this criterion rather than purely that of geographical distribution. Known areas of point-source pollution were avoided.

The data from this study, and pre-existing data, are described in Section 5. Where analytical results were below the detection limit of the method used, a value of half of that detection limit has been applied to the data for statistical purposes. For consistency, the same value has been applied to historical data, irrespective of the actual detection limit quoted. Such variations in detection limit are an inevitable consequence of variations in, and improvements to, analytical methodologies.

Pre-existing data were rejected when charge balance errors were greater than 10%. Those collected for the present study had charge balance values better than ±5%, with the exception of one sample which was +6%.

5.   HYDROCHEMICAL CHARACTERISTICS

5.1   Introduction

This section describes the hydrochemical characteristics of the aquifers studied in this report. Because the Chalk and Crag are so different in their groundwater characteristics, they are described in separate sections below. Chapter 6 presents interpretation of the data in a regional hydrogeochemical framework to understand the processes controlling the observed baseline geochemistry.

A distinction in the composition within each aquifer is only described when differences in the baseline chemistry make such an approach appropriate.

5.2   The Chalk Aquifer

5.2.1   Introduction

A summary of major and minor element data of the Chalk groundwaters from north Norfolk and the river Waveney catchment areas are presented in Table 5.1 and for trace elements in Table 5.2. The tables show the data range, median, mean and 97.7 percentile values for each parameter. The 97.7 percentile represents the mean + 2σ (where σ is standard deviation), and is used simply to remove outlying data.

Table 5.1   Summary of major and minor ion data for the Chalk groundwaters.

Parameter	units	min.	max.	median	mean	97.7th percentile	N
T	^{o}C	10.4	17.3	11.9	11.6	15.5	30
pH		6.73	8.90	7.18	7.10	7.89	41
Eh	mV	-128	467	67	32	333	28
DO	mg l^{-1}	<0.05	5.02	0.85	<0.05	3.98	30
SEC	μS cm^{-1}	380	12420	1325	809	4772	42
δ^2H	‰	-51.50	-44.00	-47.03	-47.15	-44.00	12
δ^{18}O	‰	-7.98	-7.01	-7.55	-7.55	-7.16	56
δ^{13}C	‰	-17.26	-4.91	-10.15	-10.02	-5.21	10
Ca	mg l^{-1}	48	301	124	126	231	96
Mg	mg l^{-1}	2.00	212	13	8.20	41	96
Na	mg l^{-1}	11	2010	63	27	238	96
K	mg l^{-1}	0.60	91	6.06	3.20	31	92
Cl	mg l^{-1}	18	3650	110	55	385	96
SO$_4$	mg l^{-1}	6.41	1180	93	71	369	96
HCO$_3$	mg l^{-1}	110	561	295	287	464	96
NO$_3$ as N	mg l^{-1}	0.001	21.8	3.6	0.09	17.3	87
NO$_2$ as N	mg l^{-1}	0.0015	4.07	0.34	0.09	1.99	33
NH$_4$ as N	mg l^{-1}	0.0005	0.01	0.00	0.0005	0.01	30
P	μg l^{-1}	10	120	52.6	45	104	30
DOC	mg l^{-1}	0.74	23.2	3.221	1.840	13.09	29
F	mg l^{-1}	0.05	1.94	0.462	0.280	1.85	43
Br	mg l^{-1}	0.015	11	0.694	0.184	4.51	34
I	mg l^{-1}	0.0027	0.114	0.020	0.011	0.082	30
Si	mg l^{-1}	4.4	15.1	8.878	9.130	14.85	37

Table 5.2   Summary of trace element data for the Chalk groundwaters

Parameter	units	min.	max.	median	mean	97.7th percentile	N
Ag	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
Al	µg l^{-1}	0.5	8	1.867	1	5.999	30
As	µg l^{-1}	0.25	18.1	2.375	0.85	12.1637	30
Au	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
B	µg l^{-1}	10	1000	96.5	33	639	30
Ba	µg l^{-1}	11.0	156	50.2	48.9	101	30
Be	µg l^{-1}	0.025	0.16	0.037	0.025	0.133	30
Bi	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
Cd	µg l^{-1}	<0.025	3.93	0.386	0.1	3.54	30
Ce	µg l^{-1}	0.005	0.02	0.0075	0.005	0.02	30
Co	µg l^{-1}	0.01	2.24	0.315	0.08	1.893	30
Cr	µg l^{-1}	0.25	2	0.618	0.425	1.933	30
Cs	µg l^{-1}	0.005	0.25	0.020	0.005	0.150	30
Cu	µg l^{-1}	0.1	20	2.817	0.9	15.66	30
Dy	µg l^{-1}	<0.005	0.01	0.0053	<0.005	0.01	30
Er	µg l^{-1}	0.005	0.01	0.0052	0.005	0.0067	30
Eu	µg l^{-1}	<0.005	<0.005	<0.005	<0.005	<0.005	30
Fe	mg l^{-1}	5	16600	1490	402	7875	94
Ga	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
Gd	µg l^{-1}	0.005	0.06	0.0085	0.005	0.033	30
Ge	µg l^{-1}	<0.025	0.61	0.0928	0.065	0.450	30
Hf	µg l^{-1}	0.01	0.03	0.0107	0.01	0.017	30
Hg	µg l^{-1}	0.05	0.05	0.05	0.05	0.05	30
Ho	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
In	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
Ir	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
La	µg l^{-1}	<0.005	0.02	0.007	<0.005	0.02	30
Li	µg l^{-1}	2.3	466	33.5	10.8	221	32
Lu	µg l^{-1}	<0.005	<0.005	<0.005	<0.005	<0.005	30
Mn	µg l^{-1}	0.005	520	97.4	70.7	365	42
Mo	µg l^{-1}	0.1	2.7	0.6933	0.45	2.633	30
Nb	µg l^{-1}	<0.005	0.01	0.0052	<0.005	0.007	30
Nd	µg l^{-1}	0.005	0.02	0.0073	0.005	0.020	30
Ni	µg l^{-1}	0.1	9.3	0.8467	0.1	5.965	30
Os	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
Pb	µg l^{-1}	0.05	4.1	0.298	0.075	1.899	30
Pd	µg l^{-1}	0.1	0.1	0.1	0.1	0.1	30
Pr	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
Pt	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
Rb	µg l^{-1}	0.46	37.55	5.007	1.62	33.11	30
Re	µg l^{-1}	<0.005	0.02	0.008	<0.005	0.02	30
Rh	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
Ru	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30
Sb	µg l^{-1}	0.025	0.87	0.081	0.025	0.563	30
Sc	µg l^{-1}	1	4	2.7	3	4	30
Se	µg l^{-1}	<0.025	15.5	1.51	0.6	11.23	30
Sm	µg l^{-1}	0.01	0.01	0.01	0.01	0.01	30
Sn	µg l^{-1}	<0.025	0.17	0.04	<0.025	0.117	30
Sr	µg l^{-1}	262	25121	3082	1201	14190	34
Ta	µg l^{-1}	0.01	0.01	0.01	0.01	0.01	30
Tb	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
Te	µg l^{-1}	0.025	0.07	0.027	0.025	0.040	30
Th	µg l^{-1}	0.025	0.025	0.025	0.025	0.025	30

Parameter	units	min.	max.	median	mean	97.7th percentile	N
Ti	µg l^{-1}	5	5	5	5	5	30
Tl	µg l^{-1}	0.005	0.05	0.009	0.005	0.037	30
Tm	µg l^{-1}	0.005	0.005	0.005	0.005	0.005	30
U	µg l^{-1}	0.01	4.21	0.472	0.015	2.863	30
V	µg l^{-1}	0.1	20.3	1.147	0.1	9.495	30
W	µg l^{-1}	<0.01	0.44	0.040	<0.01	0.280	30
Y	µg l^{-1}	0.005	0.07	0.017	0.01	0.063	30
Yb	µg l^{-1}	0.005	<0.01	0.006	0.005	<0.010	30
Zn	µg l^{-1}	0.25	114	19.3	14.6	63	30
Zr	µg l^{-1}	0.01	1.17	0.053	0.01	0.430	30

Summary presentations of the data are shown as a Piper Plot (Figure 5.1), box-and-whisker plots (Figure 5.2) and cumulative frequency plots (Figure 5.3).
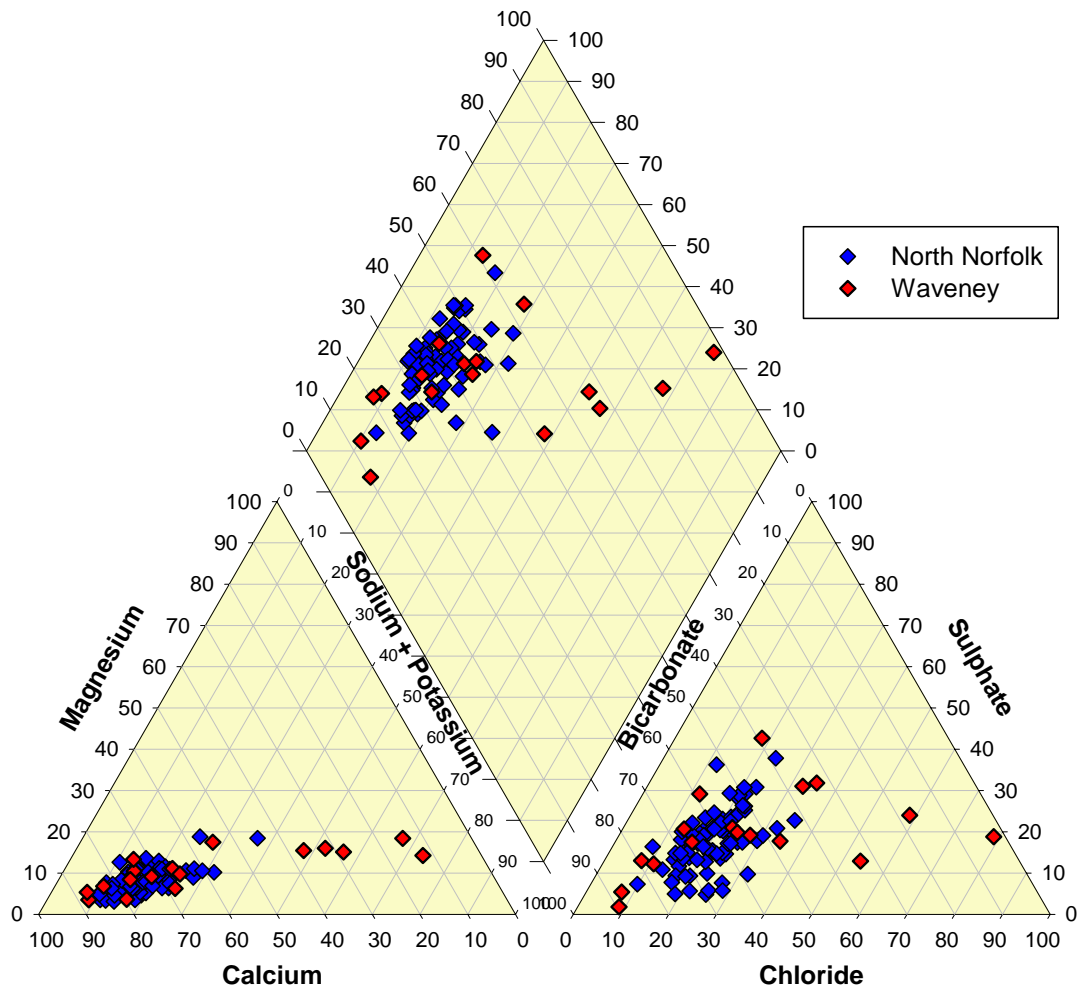

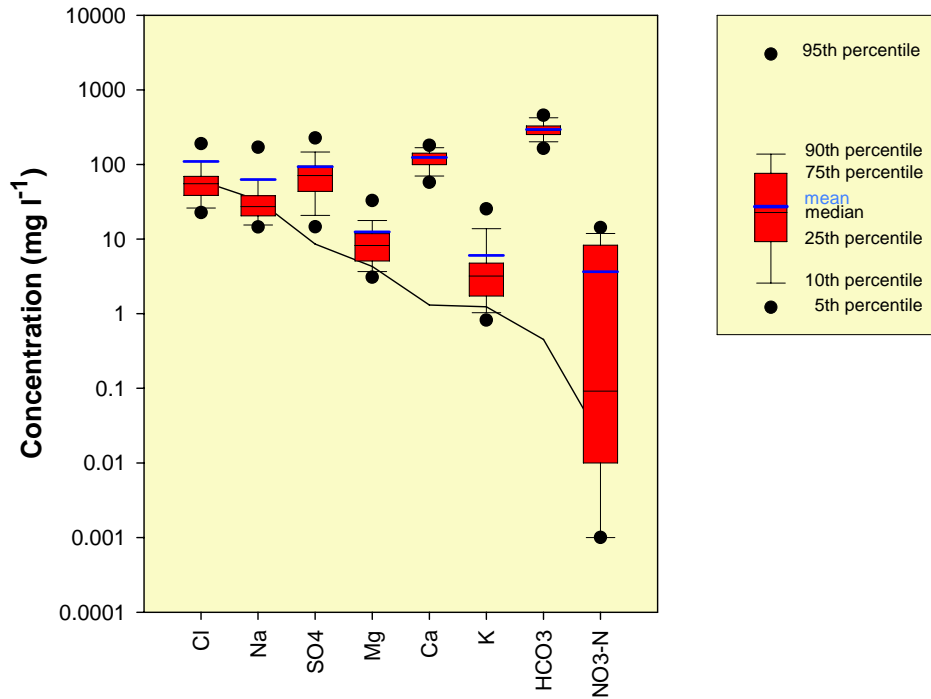**Figure 5.1   Piper diagram for the North Norfolk and Waveney Chalk groundwaters**

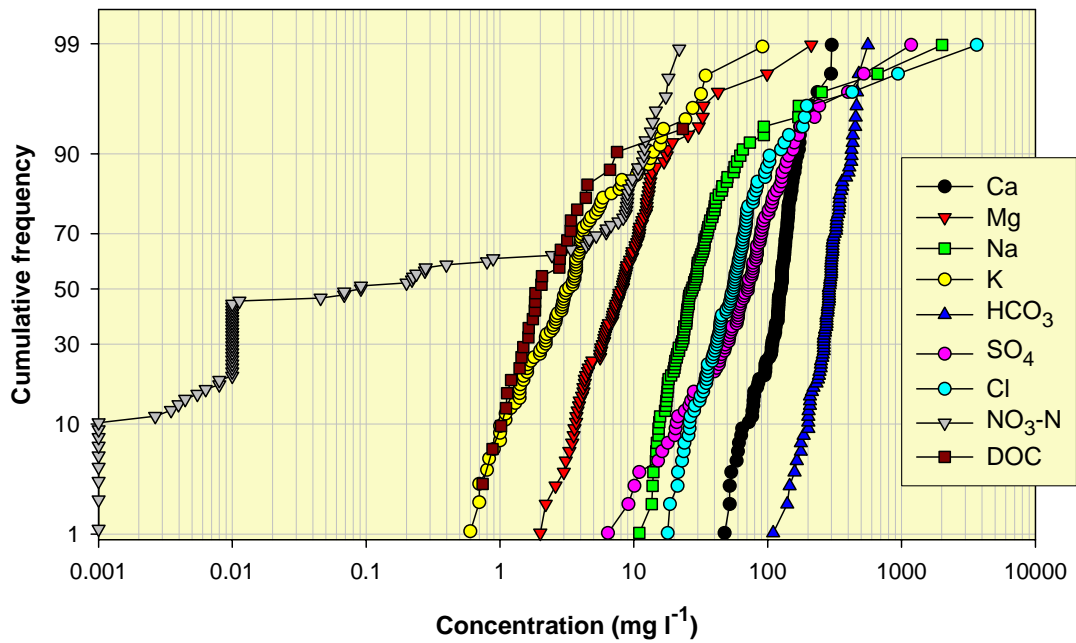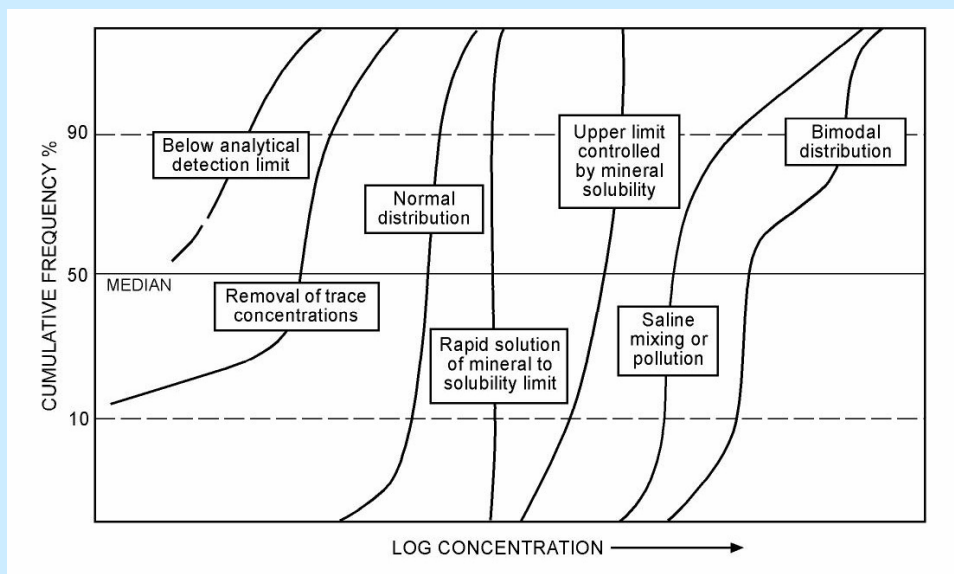**Figure 5.2   Box-plot of major elements in the Chalk groundwaters**

Figure 5.3   Cumulative probability plot of major elements in the Chalk groundwaters

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).

5.2.2   *Water types and physico-chemical characteristics*

The statistical summary of the data for the Chalk in both North Norfolk and the Waveney catchment is shown in Table 5.1, which shows that the range in concentrations of many of the major elements ranges over two orders of magnitude.

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

Specific electrical conductivity measurements show that the waters range from weakly to highly mineralised (maximum SEC >12,000 µS cm^{-1}). There is a general trend of higher values in the Waveney catchment than in the North Norfolk area, with the maximum conductivity in North Norfolk being 873 µS cm^{-1}, whilst only four sites in the Waveney region have a conductivity below 873 µS cm^{-1}. The temperature of the waters sampled ranged from 10.4 to 17.3 °C, but was generally between 10 and 12 °C. Dissolved oxygen (DO) was below the detection limit in some samples, but ranged up to 5 mg l^{-1}. Despite the well established difficulties in measuring Eh, the range of values (-128 to 467 mV) reflect the variable redox status suggested by the DO data.

The major element chemistry of groundwater from the two aquifer areas is presented on a Piper diagram in Figure 5.1. This 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, and demonstrates the major element dominance of a given sample, rather than absolute concentrations. The two study areas have been distinguished as they show differing overall characteristics. In North Norfolk, all the waters sampled are of a Ca-HCO_3 type, with two samples showing a moderate trend towards Na-Cl. Within the Waveney catchment, a range of water types was found, from Ca-HCO_3 to Na-Cl. In a general sense, these follow a relationship from the upper catchment to the confined coastal aquifer, but the varying depth of the boreholes in the chalk at different localities may also be important in determining these variations.

5.2.3 Major elements

The major element chemistry of the Chalk groundwaters is summarised in Table 5.1. The box-plots shown in Figure 5.2 are arranged in order of abundance in seawater, using a logarithmic scale. The seawater concentrations, normalised to the median Cl of the dataset, are shown for comparison. The relationship between the seawater concentration and the measured concentrations provides an indicator of the extent of water-rock interaction over and above the marine- derived input (rainwater, seawater, connate water).

The box-plots show that, apart from the normalised Cl data, the rest of the major elements are enhanced relative to the concentration expected from a dilute seawater (or rainfall) source. The range of Na data is very close to that of Cl, although the median concentration is slightly elevated. There is a large range in NO_3-N concentrations, from below the detection limit to above the present EC drinking water limit of 11.3 mg l^{-1} NO_3-N.

The cumulative frequency plots (Figure 5.3) illustrate the population distribution, range and relative concentrations of selected parameters in the Chalk groundwaters. The population distribution can be discerned from the shape of the curve, which can indicate controlling processes on the hydrochemical environment (Box 5.1). The curves for the major elements and DOC indicate multimodal populations in most cases (e.g. for NO_3). However, Ca and HCO_3 concentrations show a narrow range, suggesting rapid equilibrium with respect to a carbonate mineral phase. The groundwaters are all at saturation with respect to calcite and many are saturated with respect to dolomite and siderite.

5.2.4 Minor and trace elements

The minor and trace element data which are summarised in Table 5.2, are also plotted as box-plots (relative to seawater) and cumulative probability plots on Figures 5.4 and 5.5 respectively. Where the trace elements were below the detection limit of the method used, vertical lines will appear at the low end of the concentration range for the elements in Figure 5.5 (e.g. Ni and U). This is consistent with the low mobility of many elements in neutral pH, moderately oxidising chalk groundwaters. The data shown here are largely those collected for this study, as the trace elements were rarely measured in other studies.

The probability plot for trace elements also shows some multi-modal population distributions. Redox sensitive elements such as As, Fe and Mn show large variations in concentrations. The variation of Fe and Mn, by three orders of magnitude, reflects their ubiquitous occurrence through the aquifer, allowing relatively high concentrations to be reached when sufficiently reducing conditions become prevalent. The box-plots show the relative abundance of the elements in comparison to a dilute seawater line, with all elements showing enrichment. With some this may be as a result of variations in the ratio in rainfall recharging the aquifer (e.g. I/Cl is commonly higher in rainfall than seawater), whilst for other elements (e.g. Fe, Sr) it clearly indicates water-mineral interaction in the soil, unsaturated or saturated zones as water flows into and through the aquifer.
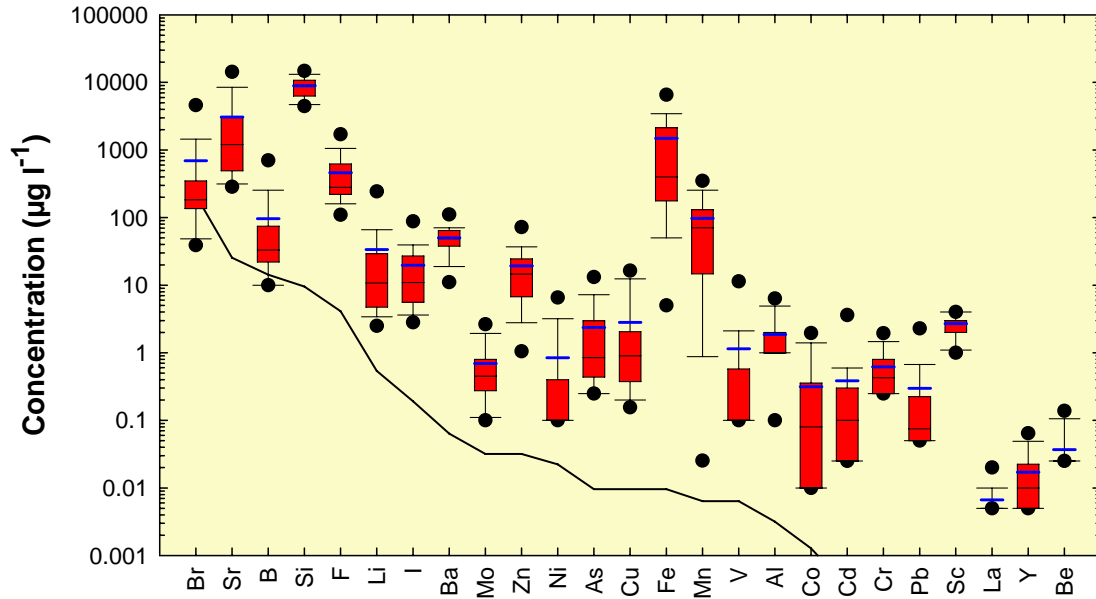
Figure 5.4   Box-plot of minor and trace elements in the Chalk groundwaters
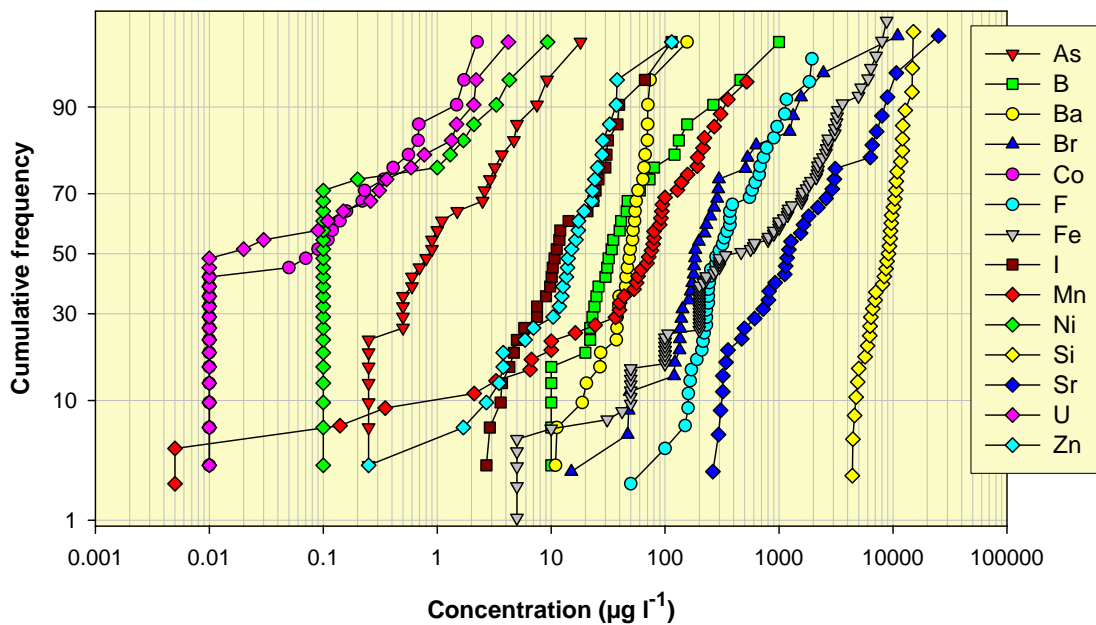
Figure 5.5   Cumulative probability plot of minor and trace elements in the Chalk groundwaters

Other trace elements, which are insensitive to redox conditions, have multi-modal population distributions reflecting residence time within the aquifer. Strontium concentrations in groundwaters are usually not limited by the solubility of a Sr bearing mineral, but saturation is approached in some of the waters where Sr concentrations are high (up to 25 mg l^{-1}).

Uranium displays a bimodal distribution, which may in part be due to increased mobility in oxidising carbonate waters. Silicon concentrations would be expected to be controlled by the solubility of Si bearing minerals within the aquifer, and Figure 5.5 suggests that equilibrium is rapidly attained to a Si phase (probably chalcedony).

Nickel varies up to 10 g l^{-1}, but with 70% of the samples being below the detection limit. The remainder of the samples vary with concentrations up to 10 μg l^{-1} (Figure 5.5).

5.2.5   Pollution indicators

The concept of baseline ideally requires that samples used for its numerical characterisation are free of anthropogenic influence. Pollution can directly alter the baseline either by the addition of solutes, or indirectly by promoting chemical reactions within the aquifer (Box 5.2). The almost ubiquitous nature of diffuse pollution within some aquifers makes diffuse sources very hard to avoid when sampling.

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

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

The approach adopted is threefold:

(i) to have evidence of groundwater age

(ii)to extrapolate data series back to an initial time

(iii)to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced TOC and N species – especially NO$_3$ – the presence of foreign substances such as agro-chemicals or industrial chemicals. The sets of data are examined for these substances as a clue to the presence of "contamination", although it is stressed that it is impossible to quantify this. However, traces of contamination may have little impact on the overall chemistry of the groundwater.

Boreholes known to be affected by point source pollution were avoided in this study at the site selection phase. The high nitrate concentrations observed in some groundwater sources indicates that diffuse pollution has occurred, for instance, through fertilisation application. Other elements, such as K, SO$_4$ or Cl, may be affected by urban or agricultural diffuse pollution, but can be harder to delineate due to the relative natural abundance of these ions, and their occurrence in formation waters within parts of the Chalk aquifer.

5.3   The Crag aquifer

5.3.1   Introduction

A summary of the major and minor ion data is provided in Table 5.3. This shows the range, mean, median and 97.7th percentile. The 97.7th percentile (mean + 2σ) represents an upper concentration used to exclude outliers. As a description of the central tendency of the data population, the median is preferred as being more robust against outlying data.

The data are shown on a Piper plot (Figure 5.6) and the ranges displayed using box-plots (Figure 5.7). The boxplots summarise the data, and a comparison with normalised seawater concentrations is included: where concentrations are normalised to the median Cl concentration of the dataset. Cumulative probability plots (Figure 5.8) are used to study the distribution of the data population, the

shape of the curve when plotted on a probability scale being indicative of different distributions which may, in turn, reflect geochemical processes in the aquifer (Box 5.1).

Table 5.3 **Summary of major and minor trace element data for the Crag groundwaters**

Parameter	units	min.	max.	median	mean	97.7th percentile	N
T	°C	6.7	15.4	11.6	11.6	15.1	25
pH		4.23	8.40	7.29	7.31	8.17	62
Eh	mV	-76	410	107	25	391	19
DO	mg l^{-1}	<0.05	6.64	1.60	0.08	5.95	18
SEC	µS cm^{-1}	291	9200	1234	960	6118	63
δ^2H	‰	-49.70	-43.30	-45.75	-45.80	-43.34	10
δ^{18}O	‰	-7.66	-7.05	-7.30	-7.25	-7.05	10
δ^{13}C	‰	-15.77	-11.82	-14.19	-14.31	-12.04	10
Ca	mg l^{-1}	29	350	125	110	275	81
Mg	mg l^{-1}	2.3	290	21	13	77	81
Na	mg l^{-1}	19	1140	75	41	353	81
K	mg l^{-1}	<0.3	220	16	4.8	92	81
Cl	mg l^{-1}	13	2680	141	77	660	81
SO$_4$	mg l^{-1}	8	1480	155	115	596	80
HCO$_3$	mg l^{-1}	11	610	265	248	466	80
NO$_3$ as N	mg l^{-1}	0.001	49	9.7	6.8	35	78
NO$_2$ as N	mg l^{-1}	0.0015	2.6	0.207	0.008	1.7	21
NH$_4$ as N	mg l^{-1}	0.0005	0.016	0.003	0.0005	0.014	18
P	µg l^{-1}	10	922	163	99	723	18
DOC	mg l^{-1}	0.82	6.66	2.01	1.69	5.39	17
F	mg l^{-1}	0.01	11.2	0.54	0.22	1.44	43
Br	mg l^{-1}	0.015	0.316	0.20	0.20	0.31	18
I	mg l^{-1}	0.004	20.8	1.85	0.01	15.1	23
Si	mg l^{-1}	2.60	11.4	7.46	7.48	11.0	23

5.3.2   Water types and physico-chemical characteristics

The Crag groundwaters are generally moderately mineralised, with only one sample having SEC less than 700 µS cm^{-1}, and 50% of the samples being greater than1000 µS cm^{-1}. Temperatures were generally between 10 and 12 °C, higher values being unrepresentative, as they are associated with non-ideal sampling points (for these unstable parameters). The pH is well buffered to circum-neutral values (Table 5.3), with the interquartile range being between 6.9 and 7.3. Half of the samples collected did not contain detectable dissolved oxygen, largely those from the Waveney Crag groundwaters, with those from North Norfolk private supplies having moderate concentrations (3 – 7 mg l^{-1}). The Eh has a broadly positive correlation with the DO concentrations, but well-established limitations on the measurement of the redox potential limit the interpretation of Eh data.

The water-type varied across the aquifer, from Ca-HCO$_3$ dominated to mixed cation-SO$_4$ and Na-Cl type waters, as shown on the Piper diagram (Figure 5.6). The North Norfolk samples appear to show more of an influence of Na and Cl, which are from published data sources.
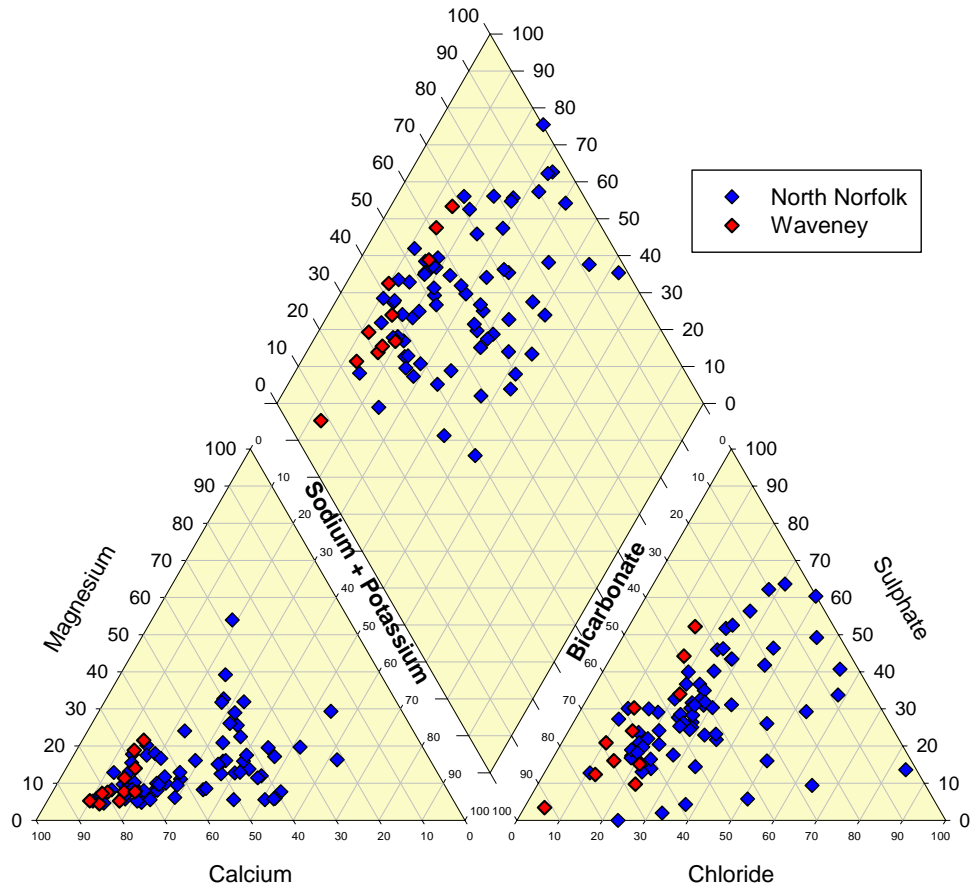
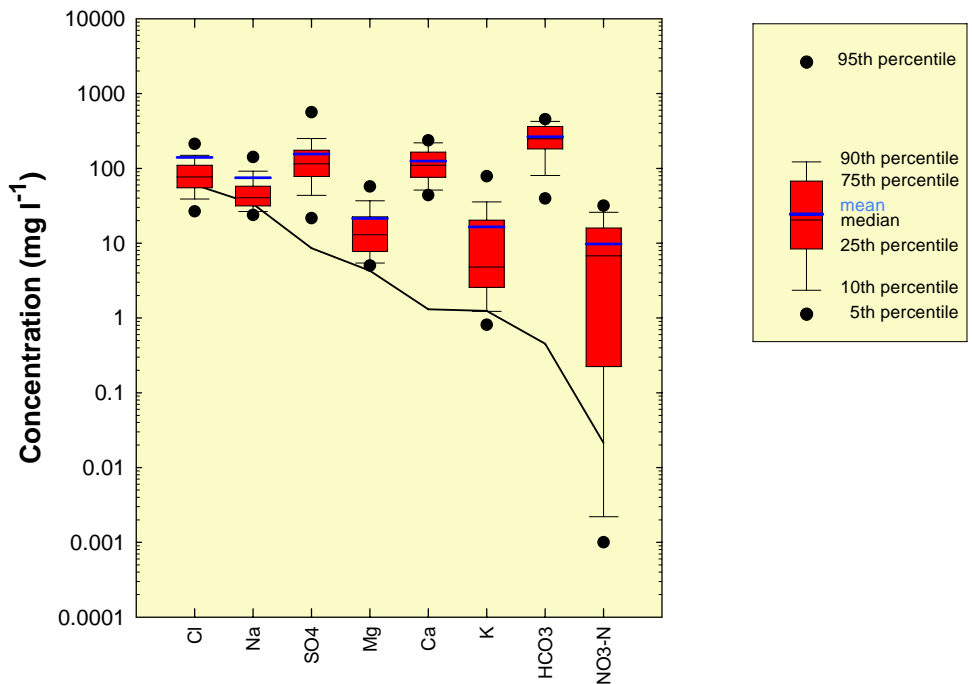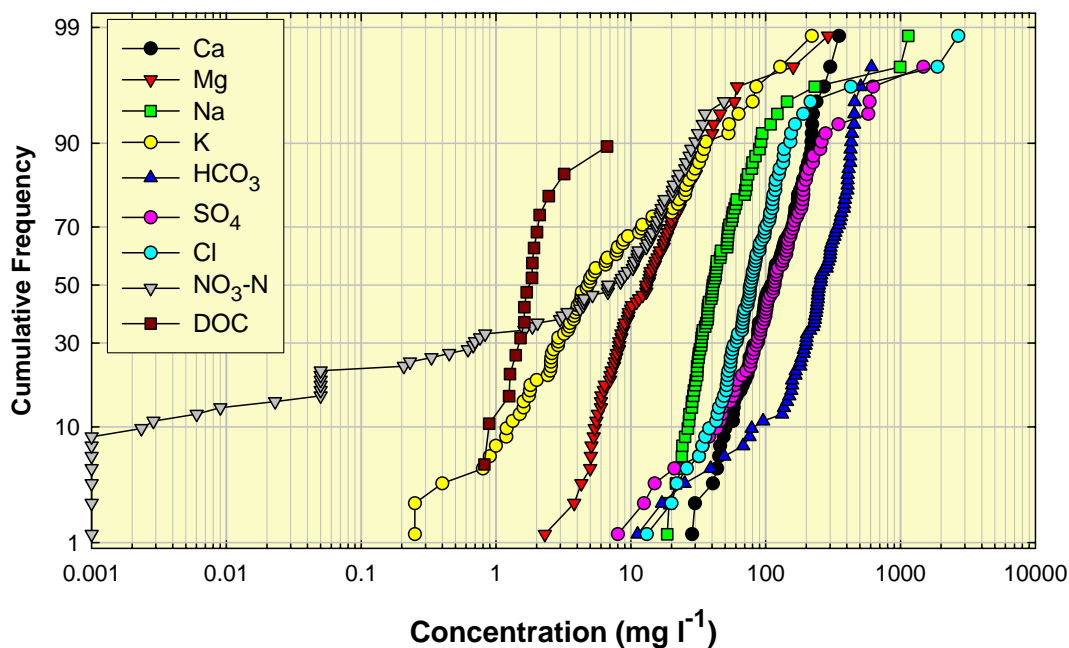**Figure 5.6   Piper diagram for the (a) North Norfolk and (b) Waveney Crag groundwaters**

Figure 5.7   Boxplot of major elements in the Crag groundwaters

Figure 5.8   **Cumulative probability plot of major elements in the Crag groundwater**

5.3.3   Major elements

The composition of the Crag groundwaters with respect to the major ions is summarised in Table 5.3 and Figures 5.7 and 5.8. Average Cl concentrations were significantly higher than in the underlying Chalk groundwaters (c.f. Figure 5.2), and the median Na showed little enhancement over the normalised seawater signature. The enhanced Cl concentrations are largely as a result of the inclusion of literature data, which included studies of seawater ingress into Broadland groundwater, where surface elevations are at or below sea level (Holman et al., 1999). Most of the other major elements are enhanced relative to the seawater curve. Those elements which are enhanced have been introduced via water-rock interaction or extraneous sources (such as diffuse pollution for NO_3). The probability plots (Figure 5.8) show the population distributions of these ions. The dominant major elements are Ca, HCO_3 and SO_4 which show a skew at low concentrations. The highest sulphate concentrations appear to represent a different population, associated with an increase in SEC, Na and Cl. The Mg and NO_3 data also indicate several potential populations.

5.3.4   Minor and trace elements

These data are summarised in Table 5.4 and Figures 5.9 and 5.10. As is the case for major ions, the box-plots compare the data summary to the normalised seawater curve. The Br concentrations can be seen to lie close to this curve, but most other elements show enrichment relative to a marine source. Relatively high concentrations of the redox sensitive elements, Fe and Mn, were present, reaching maxima of 8.7 mg l^{-1} and 0.5 mg l^{-1} respectively.

Silicon concentrations show a near normal distribution, which suggests rapid equilibrium with a solubility limiting phase (Box 5.1). For all samples where Si was measured the groundwaters are close to equilibrium with chalcedony. The waters are undersaturated with respect to F, with concentrations in general being lower than those in the Chalk.

Table 5.4   Summary of trace element data for the Chalk groundwaters

Parameter	units	min.	max.	median	mean	97.7th percentile	N
Ag	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
Al	µg l⁻¹	1.0	23	3.0	1.0	17.5	18
As	µg l⁻¹	0.25	23	3.4	1.2	18.5	18
Au	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
B	µg l⁻¹	20	331	67	34	274	18
Ba	µg l⁻¹	3	79	47	47	77	18
Be	µg l⁻¹	0.025	0.080	0.028	0.025	0.058	18
Bi	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
Cd	µg l⁻¹	<0.03	0.43	0.17	0.10	0.43	18
Ce	µg l⁻¹	0.01	0.12	0.024	0.008	0.11	18
Co	µg l⁻¹	0.01	3.01	0.41	0.06	2.30	18
Cr	µg l⁻¹	0.25	1.50	0.74	0.80	1.46	18
Cs	µg l⁻¹	0.005	0.020	0.006	0.005	0.016	18
Cu	µg l⁻¹	0.2	37.3	4.39	0.8	30.8	18
Dy	µg l⁻¹	<0.005	0.02	0.0069	<0.005	0.016	18
Er	µg l⁻¹	0.005	0.01	0.0061	0.005	0.01	18
Eu	µg l⁻¹	<0.005	<0.005	<0.005	<0.005	<0.005	18
Fe	mg l⁻¹	5	41700	2226	375	19440	60
Ga	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
Gd	µg l⁻¹	0.005	0.010	0.007	0.005	0.010	18
Ge	µg l⁻¹	<0.025	0.130	0.039	<0.025	0.118	18
Hf	µg l⁻¹	0.01	0.01	0.01	0.01	0.01	18
Hg	µg l⁻¹	0.05	0.05	0.05	0.05	0.05	18
Ho	µg l⁻¹	0.005	0.005	0.005	0.005	0.005	18
In	µg l⁻¹	0.005	0.100	0.010	0.005	0.063	18
Ir	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
La	µg l⁻¹	<0.01	0.06	0.02	0.01	0.05	18
Li	µg l⁻¹	1.30	49.20	13.83	10.00	43.61	19
Lu	µg l⁻¹	<0.005	<0.005	<0.005	<0.005	<0.005	18
Mn	µg l⁻¹	2	1970	296	135	1381	43
Mo	µg l⁻¹	0.05	1	0.361	0.25	0.961	18
Nb	µg l⁻¹	<0.005	0.01	0.006	<0.005	0.01	18
Nd	µg l⁻¹	0.005	0.06	0.017	0.01	0.056	18
Ni	µg l⁻¹	0.1	8.1	0.744	0.1	5.52	18
Os	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
Pb	µg l⁻¹	0.05	5.8	0.49	<0.1	3.8	18
Pd	µg l⁻¹	0.1	0.1	0.1	0.1	0.1	18
Pr	µg l⁻¹	0.005	0.01	0.006	0.005	0.01	18
Pt	µg l⁻¹	0.005	0.005	0.005	0.005	0.005	18
Rb	µg l⁻¹	0.05	9.45	2.02	1.725	7.63	18
Re	µg l⁻¹	<0.005	0.03	0.008	<0.005	0.022	18
Rh	µg l⁻¹	0.005	0.005	0.005	0.005	0.005	18
Ru	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
Sb	µg l⁻¹	0.025	0.29	0.048	0.025	0.224	18
Sc	µg l⁻¹	1	4	2.33	2	3.61	18
Se	µg l⁻¹	<0.025	3.9	0.70	<0.025	3.67	18
Sm	µg l⁻¹	0.01	0.01	0.01	0.01	0.01	18
Sn	µg l⁻¹	<0.025	2.29	0.15	<0.025	1.40	18
Sr	µg l⁻¹	280	3835	801	465	3162	23
Ta	µg l⁻¹	0.01	0.01	0.01	0.01	0.01	18
Tb	µg l⁻¹	0.005	0.005	0.005	0.005	0.005	18
Te	µg l⁻¹	0.025	0.06	0.027	0.025	0.046	18
Th	µg l⁻¹	0.025	0.025	0.025	0.025	0.025	18
Ti	µg l⁻¹	5	5	5	5	5	18
Tl	µg l⁻¹	0.005	0.01	0.005	0.005	0.008	18
Tm	µg l⁻¹	0.005	0.005	0.005	0.005	0.005	18
U	µg l⁻¹	0.010	0.370	0.120	0.045	0.354	18

Parameter	units	min.	max.	median	mean	97.7th percentile	N
V	µg l⁻¹	0.1	1.2	0.417	0.3	1.16	18
W	µg l⁻¹	<0.01	0.1	0.034	0.035	0.092	18
Y	µg l⁻¹	0.005	0.12	0.046	0.025	0.112	18
Yb	µg l⁻¹	0.005	<0.01	0.006	0.005	<0.01	18
Zn	µg l⁻¹	3.0	3997	255	18	2519	18
Zr	µg l⁻¹	0.01	0.13	0.031	0.015	0.118	18
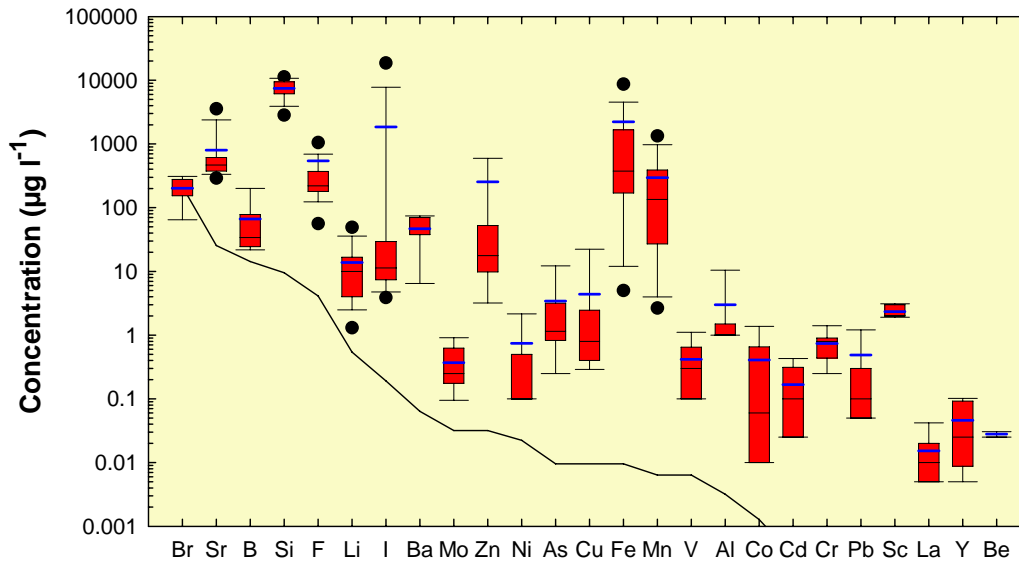
Figure 5.9   Boxplot of minor and trace elements in the Crag groundwaters

5.3.5   Pollution indicators

As discussed previously (Section 5.2.5), a baseline survey should ideally sample from areas of the aquifer which are unaffected by both diffuse and point source pollution. Due to widespread diffuse pollution in the region, it is impossible to achieve this. Whilst NO_3 is widely recognised as being elevated, diffuse pollution may also increase the concentrations of Na, K and Cl. Such increases may be more difficult to unequivocally identify in the context of the natural variability of the aquifer groundwater composition. A determination of the baseline for areas of aquifer which may be so affected requires a good historical record with which to compare the data (Box 5.2). Such data are limited from the Crag aquifer in this area.
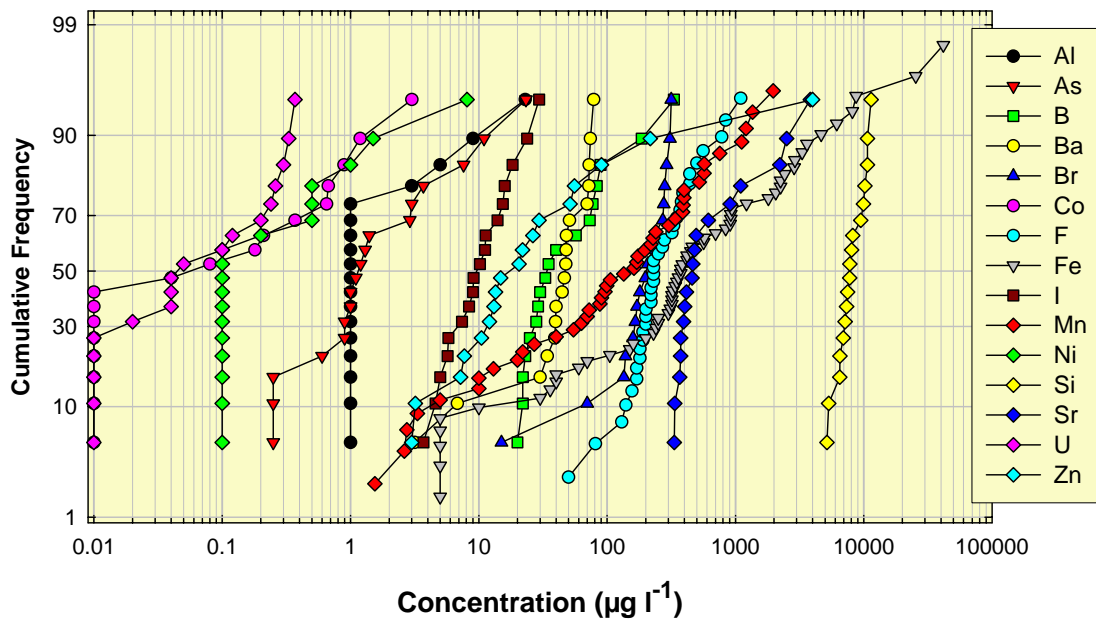
Figure 5.10 **Cumulative probability plot of minor and trace elements in the Crag groundwaters**

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The primary source of recharge to the aquifers is rainfall, a dilute solution with a slightly acidic pH (Table 3.2). This acidic recharge will dissolve carbonate minerals in the soil and unsaturated zone, if they are present, and may result in the chemistry of water entering the saturated aquifer having already acquired its dominant hydrochemical characteristics. The increased partial pressure of carbon dioxide in the soil zone (due to microbial respiration) 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. Where soils are very sandy and have little or sparse carbonate mineral phases, these reactions will take place rapidly upon reaching the Chalk unsaturated zone or calcareous Crag sediments.

Baseline conditions vary spatially and temporally due to different recharge history 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.

The aquifers studied do not conform to the ideal of 'flow-line' as used to present and interpret the geochemical evolution of groundwater in other chalk aquifers (e.g. Shand et al., 2003). Thus the primary interpretation of the data is undertaken in the section on spatial relationships, and incorporates the understanding of the evolution of the hydrochemistry.

6.2 The Chalk aquifer

6.2.1 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. Differences between the Waveney and North Norfolk catchment areas are discussed separately where pertinent. The limited temporal data available are also evaluated. Through much of this discussion, importance is placed on the use of minor and trace ion data in understanding the geochemical processes. Where this is the case, the data used is that collected during the BGS sampling, rather than the full set of major ion data presented in Table 5.1 and Figure 5.1.

6.2.2 Depth variations

A detailed study of the major-ion concentrations in porewaters from a deep borehole in the North Norfolk area was carried out by Bath and Edmunds (1981), which has been summarised in Figure 4.1, and demonstrates the vertical variation in porewaters in the Chalk. The systematic variations observed have been related to the mixing (by diffusion and advection along micro-fractures) of connate

Cretaceous porewater and post-Tertiary meteoric waters, with an increasing influence of connate water with increasing depth, although this origin of the saline water has been disputed by Hiscock (1993). The interpretation of these data also indicated that the pumped samples from two local PWS boreholes are part of the mixing series, which is inferred from a Cl concentration which is greater than that which can be accounted for by local rainfall and the concentration effect of evapo-transpiration. It should be noted, however, that other studies have attributed the additional source of Cl to be of diffuse origin, from agricultural application (Hiscock et al., 1996).

Analysis of data from the Bure catchment of Norfolk, led Hiscock et al. (1996) to conclude that the vertical extent of the effective Chalk aquifer is a maximum of 60 m, and as little as 25 m deep, and mixing with a more saline, Pleistocene recharge end-member takes places below the effective aquifer depth.

The highly detailed information on the installation of the EA piezometers in the Waveney catchment has allowed the plotting of the depth of the piezometers against various measured parameters. These are particularly suitable for this process as only a small part of the length of the piezometer is open to the aquifer, providing more control over the sampling depth than is generally the case with large commercial wells. Figure 6.1 shows selected determinands plotted against depth of these piezometers (12 samples), and suggests that there is little direct relationship between depth and hydrochemical composition, including for redox sensitive elements such as NO_3-N. This is largely controlled by the depth and nature of the overlying drift and/ or Crag deposits determining the degree of confinement of the aquifer, which is described further in Section 6.2.5.

6.2.3   *Temporal variations*

The most marked temporal variations which may be expected to have affected the determination of baseline in this aquifer are those associated with agricultural and waste-water additions of NO_3 to the aquifer. Monitoring data for the period 1990-2000 are shown in Figure 6.2 for 5 PWS boreholes in the North Norfolk area. These show little variation in most cases for Fe and NO_3, with the exception of Wighton No 2 which appears to have a trend of increasing NO_3, and the large variation in Fe concentrations in the two boreholes with reducing compositions (Mundsley and East Ruston No 2). Further interpretation, including whether step-changes and outliers are representative or not, is not appropriate without more information on pumping regimes.

The relatively short timescale of these data, and the lower concentrations of NO_3 reported using much older data (from the 1940s) in the adjacent area of Cambridgeshire (Carey and Lloyd, 1985), suggests that NO_3 concentrations could have been lower than those reported here (in oxidising environment boreholes), if regionally increasing concentration trends have been repeated in this aquifer area. The long-term trends identified by Carey and Lloyd clearly illustrate how the present concentrations of a parameter in groundwater may not truly represent baseline, and the importance of such data with which to compare modern measurements.
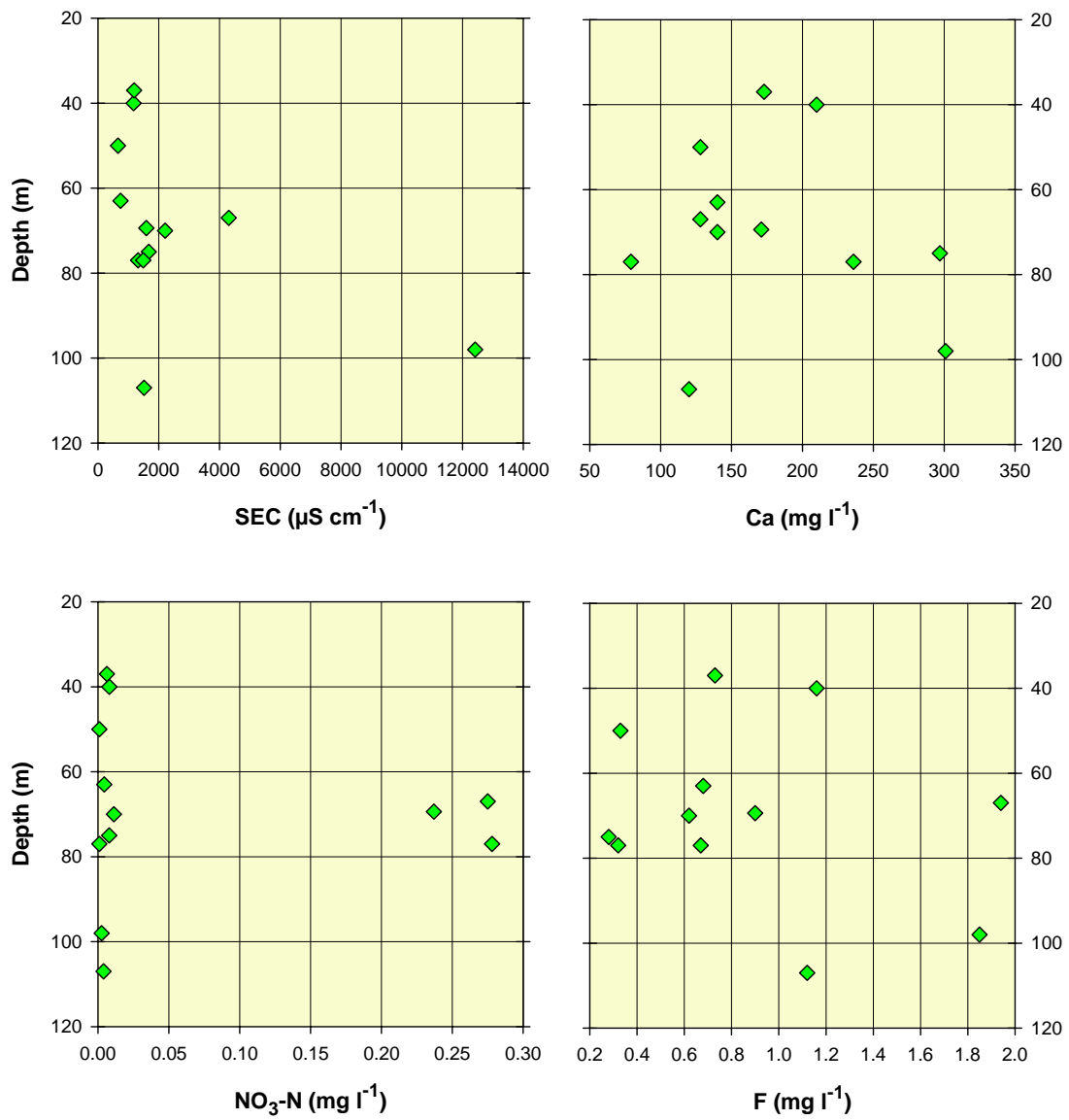
Figure 6.1   Comparison of analytes with depth for the chalk aquifer
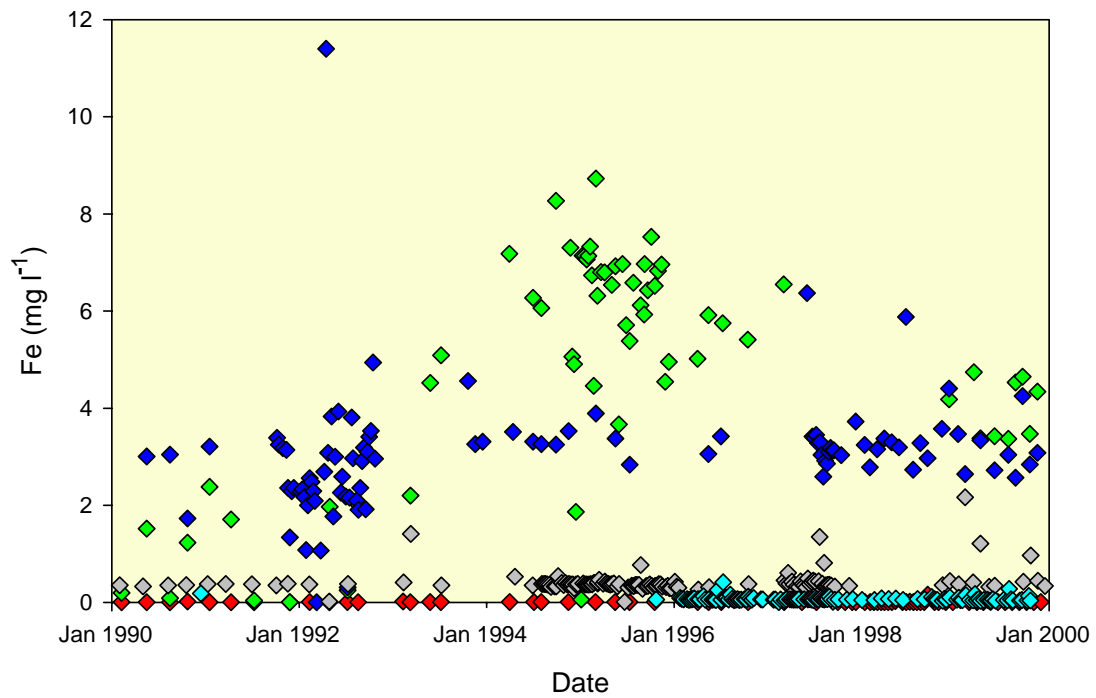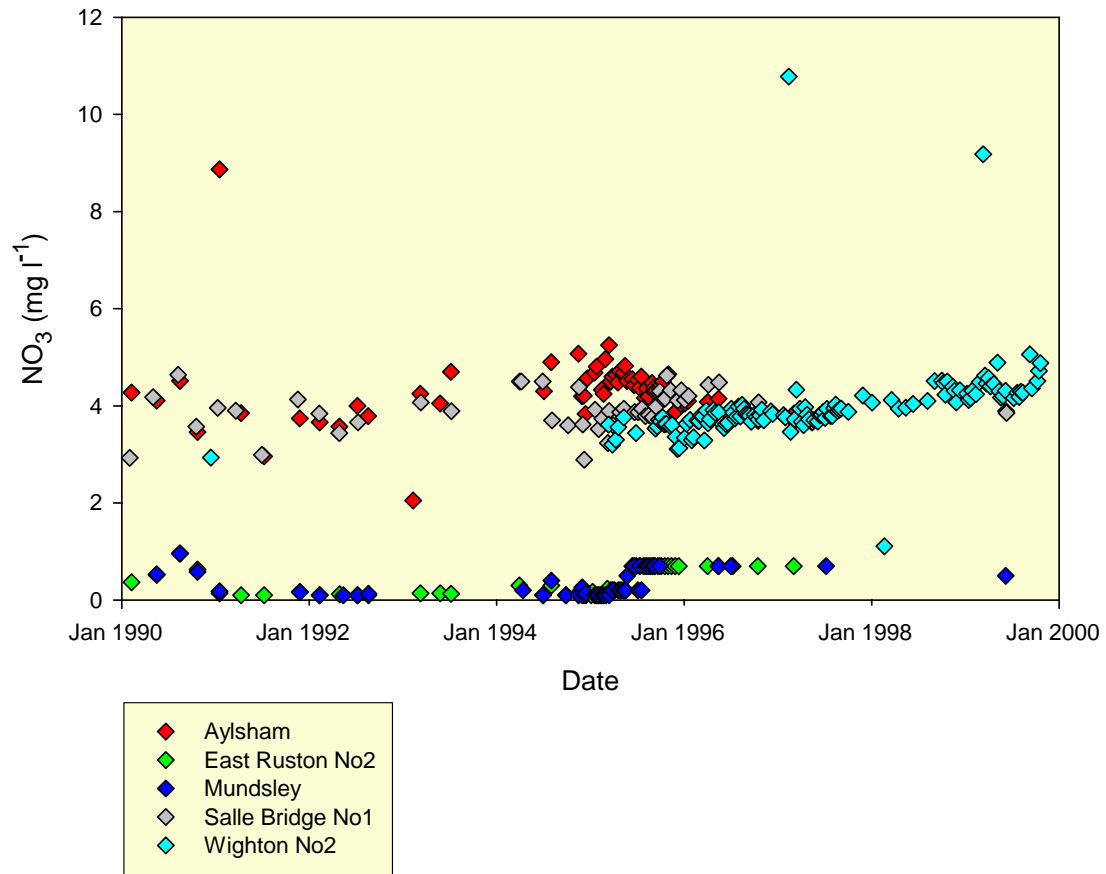
Figure 6.2   Temporal trends in selected AWS bores for Fe and NO3.

6.2.4   *Regional variations*

Changes in the baseline composition of groundwater are expected to occur naturally as it flows from the recharge area through the aquifer. Many reports in the baseline series have studied these processes along flow-lines (e.g. Shand et al., 2003), however, such a concept is difficult to illustrate for the current study areas. The North Norfolk aquifer has been sampled over a wide spatial area, but not along the length of a particular catchment, whilst the Waveney catchment has been sampled extensively, but lateral variations in the nature of the overlying sediments and variations in the depths of the boreholes used preclude presentation of data from a single flow-line. Thus the data is presented here on a spatial basis.

Spatial variations in the data are presented for both catchments in Figure 6.3. Figure 6.3a shows that that the variation in SEC is greatest within the Waveney catchment, but that North Norfolk generally has fresher waters with lower overall dissolved solids. This may reflect a lesser degree of water-rock interaction, resulting in mineral dissolution, and an absence of saline waters in the boreholes sampled, which were biased towards high transmissivity valley zones, discussed further below.

MINERAL DISSOLUTION REACTIONS

The most reactive minerals in the aquifer will determine the composition of the young groundwaters. Chalk groundwater is thus dominated by the dissolution of calcite
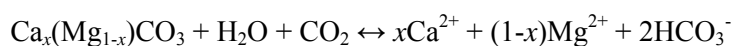
$$Ca_x(Mg_{1-x})CO_3 + H_2O + CO_2 \leftrightarrow xCa^{2+} + (1-x)Mg^{2+} + 2HCO_3^-$$

The dissolution kinetics of calcite are rapid (Appelo and Postma, 1994), such that equilibrium should be attained in the unsaturated zone, even where the soil zone is depleted in carbonate minerals. Figure 6.3b shows that Ca concentrations are generally lower in the North Norfolk area than the Waveney catchment. This is also reflected in the other major ions, as shown for Mg and HCO_3 (Figure 6.3c and d). The difference between the two aquifer regions is likely to reflect the increased residence time of the groundwater in many of the Waveney catchment piezometers due to the thickness of the overlying Crag and/ or till sediments. These concentrations are comparable with those of the Great Ouse catchment (Ander et al., 2004) in North Norfolk, but the higher concentrations measured in the Waveney catchment exceed those in the area of aquifer to the west of the regional groundwater divide.

Carbonate reactions are dominant in this aquifer, but despite the high purity of the calcite phase occurring in this aquifer (Section 3) the congruent and incongruent dissolution and re-precipitation of the calcite will lead to an increase in the concentration of ions originally incorporated into the calcite matrix in trace amounts, such as Sr and F. Increases in other trace elements will arise from the dissolution of accessory phases, such the release of Si, Li and NH_4^+ from silicates (Edmunds et al., 1992). Where the concentrations of ions is not limited by solubility controls, such as for Sr and Li, these may serve as indicators for residence time.

Silicon is released into solution primarily from the weathering of the alumino-silicate phases found in the aquifer. Concentrations of Si are in the range 4–15 mg l^{-1}, which indicates a considerable variation in the degree of clay mineral weathering. These concentrations can be seen to be highest (10-15 mg l^{-1}) in the upper Waveney catchment (Figure 6.4a), reflecting ingress of recharge from the Boulder Clay cover, and concentrations are generally lower on the North Norfolk coast (4-6 mg l^{-1}), where glacial sediments are more sandy, and flow through the aquifer appears to be more shallow and rapid. This regional distribution of concentrations reflects that observed in the Great Ouse region, where similar concentrations were seen in the upper catchments (partially confined by till), and low concentrations of Si in the lower catchment where a greater flux of groundwater occurs.
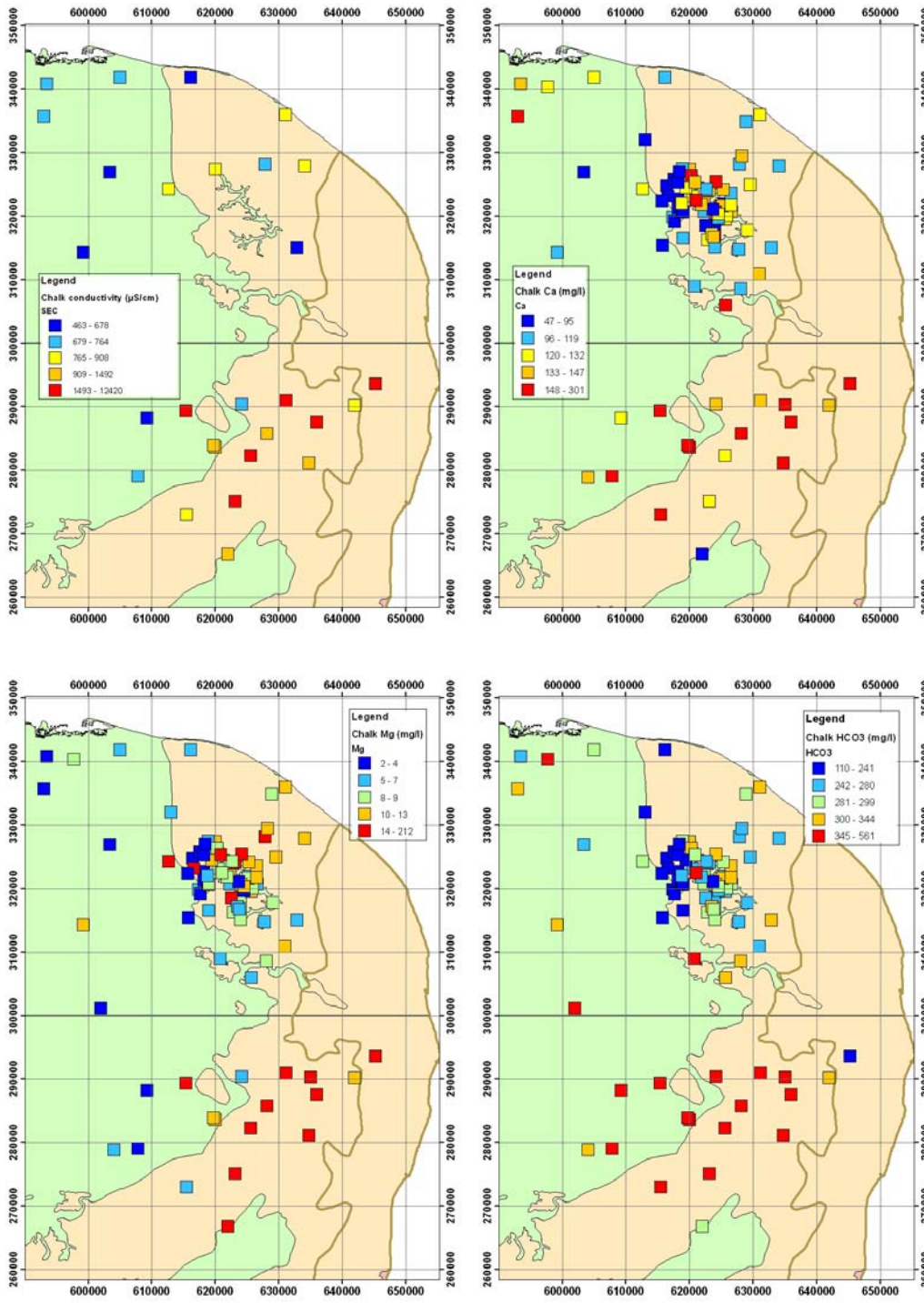
Figure 6.3 **Spatial distribution of analyte concentrations in the Chalk aquifer (a) SEC (b) Ca (c) Mg (d) HCO₃**

Figure 6.4 **Spatial distribution of ion concentrations in the Chalk aquifer (a) Si (b) F (c) Sr (d) SO$_4$**

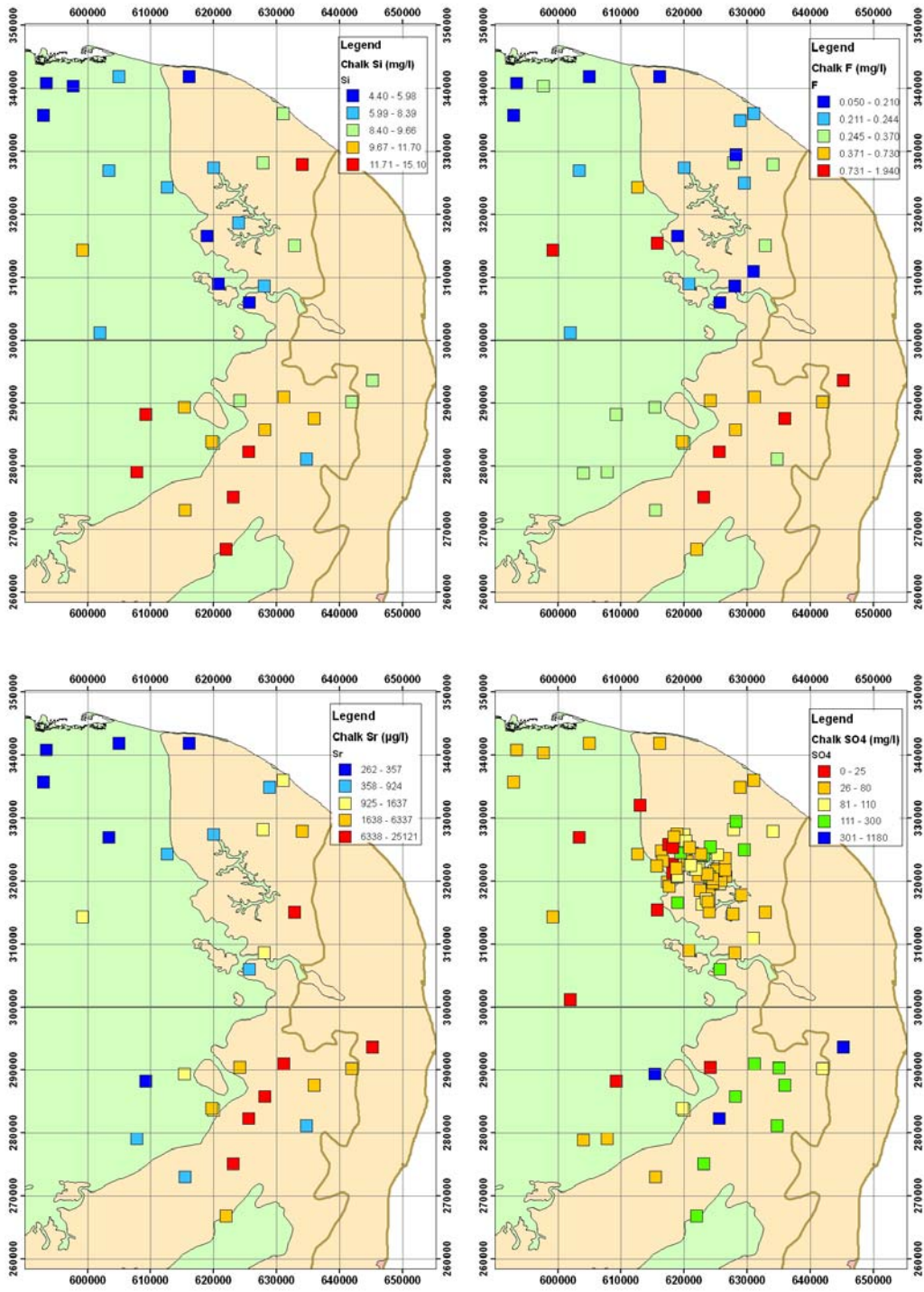Fluoride concentrations are regionally lowest (Figure 6.4b) in the sampling areas of North Norfolk, and the upper Waveney catchment, generally below 0.5 mg l^{-1}, and increase substantially in the central and lower Waveney catchment to a maximum of 1.9 mg l^{-1} at Needham, compatible with regional variations of other indicators of increased groundwater residence time, and likely recharge components from (semi)-confining overlying sediments. Strontium concentrations show a systematic variation (Figure 6.4c) in keeping with observations from other major and minor ions in solution, with low concentrations for the aquifer (*ca*.300 μg l^{-1}) in North Norfolk, rising to >1000 μg l^{-1} in samples where the Chalk is confined by the Palaeogene. The maximum concentration recorded (25 mg l^{-1}) occurs in the Bungay piezometer of the Waveney catchment, which is an extremely high concentration of Sr, in relation to both this aquifer, and other Chalk aquifers in the Baseline report series (e.g. Ander et al., 2004, Shand et al., 2003).

Sulphate concentrations may increase as a result of weathering of overlying tills, or of pyrite within the aquifer. Concentrations are moderate (40-70 mg l^{-1}) in the coastal area of North Norfolk, by with much higher concentrations (90-522 mg l^{-1}) in the area around the river Ant and the majority of the samples beneath Palaeogene cover in the Waveney catchment (Figure 6.4d). The concentrations along the coast are elevated in comparison to those found in unconfined Chalk catchments in the Colne and Lee valleys of Hertfordshire (Shand et al., 2003), which reflects the greater concentration of SO_4 arising from locally derived marine influenced recharge. The highest concentrations observed in the Waveney catchment are comparable with concentrations observed in the confined aquifer of Hertfordshire (Shand et al., 2003) and in the Great Ouse region (Ander et al., 2004). The highest concentration (1180 mg l^{-1}) at Aldeby is likely to be related to mixing with saline water (see below).

REDOX REACTIONS

The primary indicators of the redox status of groundwaters are the redox potential (Eh) and dissolved oxygen (DO) (Figure 6.6a). These parameters are very unstable and can only be measured using a flow-through cell at the time of sampling. The analysis of redox-sensitive elements also provides information on the redox status of the aquifer (Box 6.1), and can be a useful check on Eh measurements, which are well recognised to have limitations (Appelo and Postma, 1994), as noted in Section 5, it is unlikely that the Eh measurement for the sample at Shelton (467 mV) is accurate, as it compares poorly with all other redox sensitive indicators.

Nitrate is stable in the presence of oxygen, but once the oxygen contained in recharge is consumed, nitrate becomes unstable, the resulting denitrification resulting in negligible concentrations (Box 6.1). It should be noted that the dominant product of denitrification is $N_{2(g)}$ rather than ammonia ($NH_4^+{}_{(aq)}$) (Appelo and Postma, 1994). Figure 6.5b shows that NO_3-N concentrations vary across the aquifer, with lowest concentrations in boreholes beneath the Palaeogene cover and highest in the North Norfolk coastal, unconfined, samples, where concentrations approach the present EC MAC of 11.3 mg l^{-1} in several boreholes.

Variation in redox conditions in the aquifer can clearly be seen to take place with Figure 6.5b, with the hydrochemical spatial variation found in the NO_3-N data being broadly the expected inverse relationship with the Fe data (Figure 6.5c), confirming the interpretation of the spatial variation in redox conditions. Comparison of results of various redox sensitive species can be used to illustrate positive and negative relationships between parameters. Iron measurements are available on all samples collected during the BGS sampling, unlike Eh and DO which can only be measured using the flow-through cell, and are thus used to plot against other potentially redox sensitive elements in Figure 6.6. It can be seen that the (corrected) values of Eh have the expected positive and inverse relationships with DO and Fe respectively (Figure 6.6). Both Fe and Mn would be expected to be ubiquitous in the aquifer, with the Mn being released from the calcite phase during re-precipitation, although in oxidising conditions this can be seen to re-precipitate as Mn-oxide coatings on fracture surfaces on the chalk (Shand and Bloomfield, 1995). Whilst both would be expected to be more soluble in reducing conditions, it would seem that there is a lack of correlation between boreholes

where Mn is elevated and those where Fe is elevated (Figure 6.6). Arsenic is known to be redox sensitive and Figure 6.6 shows the relationship with Fe, as a proxy for redox status. Concentrations were found to be highest (18 µg l^{-1}) at Aldeby (Figure 6.5d) and are clearly associated with elevated Fe, and thus low redox potential. Ammonium (NH_4^+) concentrations are elevated in several of the samples (Figure 6.6), associated with reducing conditions, and are probably derived from clays (see ion exchange, below).

BOX 6.1 REDOX BOUNDARY
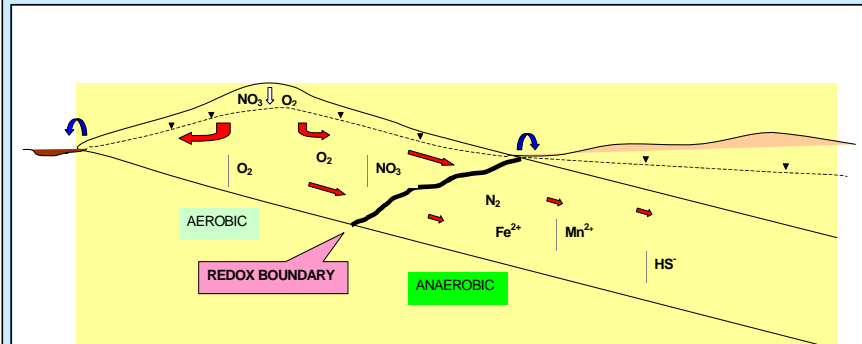
Water at recharge is generally saturated with dissolved oxygen at the partial pressure of the atmosphere (10-12 mg l^{-1} depending upon barometric conditions). Passing through the soil and the unsaturated zone some of this O_2 will react as a result of microbiological processes and oxidation-reduction reactions. However, almost all water reaching the water table still contains several mg l^{-1} O_2. Geochemical reactions (oxidation of traces of pyrite, organic matter and Fe^{2+} present in minerals) progressively remove the O_2 along flow lines. Once all the oxygen has reacted an abrupt change of water chemistry takes place (redox boundary). Other changes may occur at and down-gradient of the redox boundary, especially denitrification and the probability that total dissolved iron (Fe^{2+}) concentrations will increase. Sulphate reduction and the production of sulphide (H_2S as HS^- in solution) may also occur at greater depths.
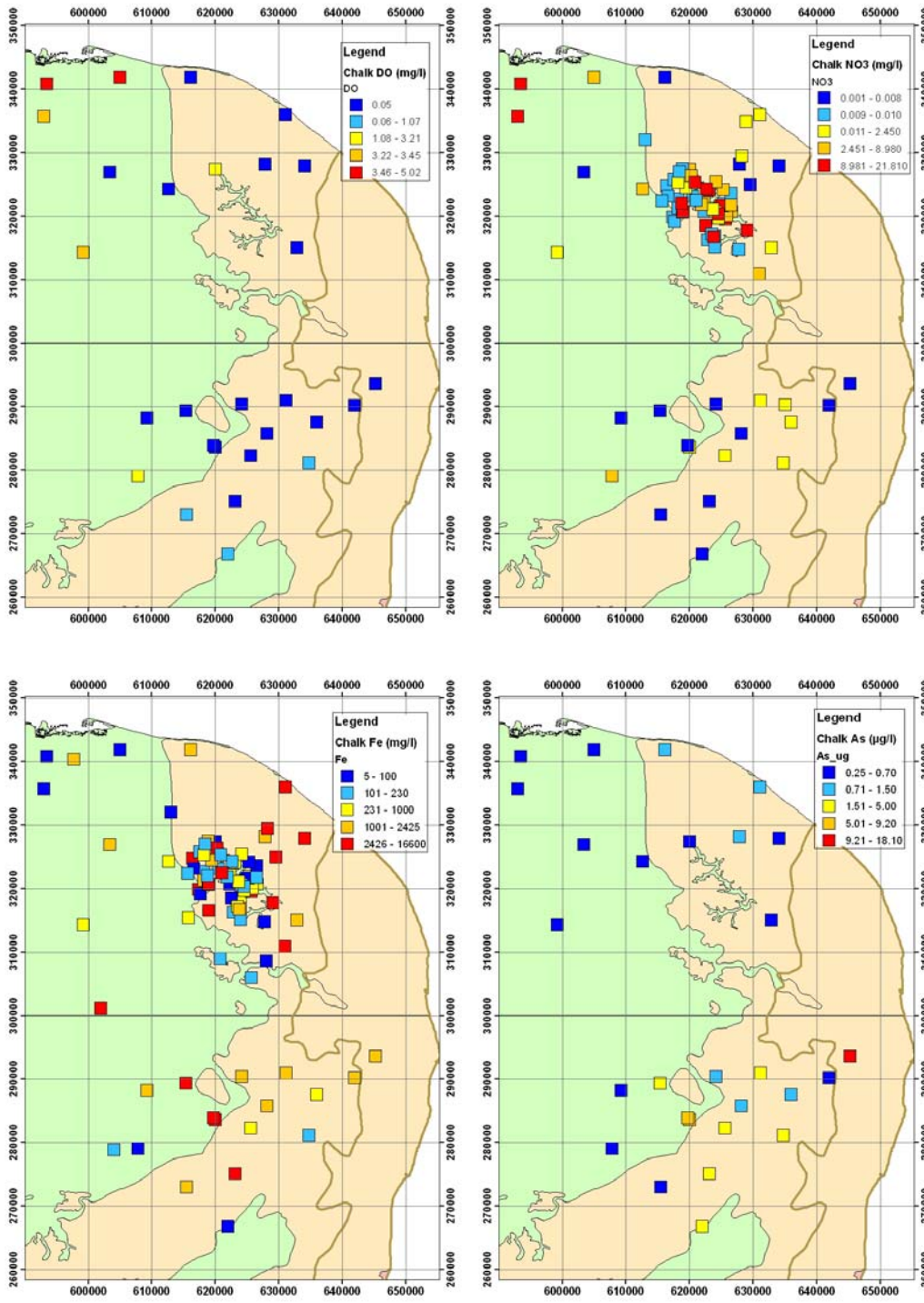
Figure 6.5 **Spatial distribution of selected redox indicators over the Chalk outcrop (a) DO (b) NO$_3$ (c) Fe (d) As**
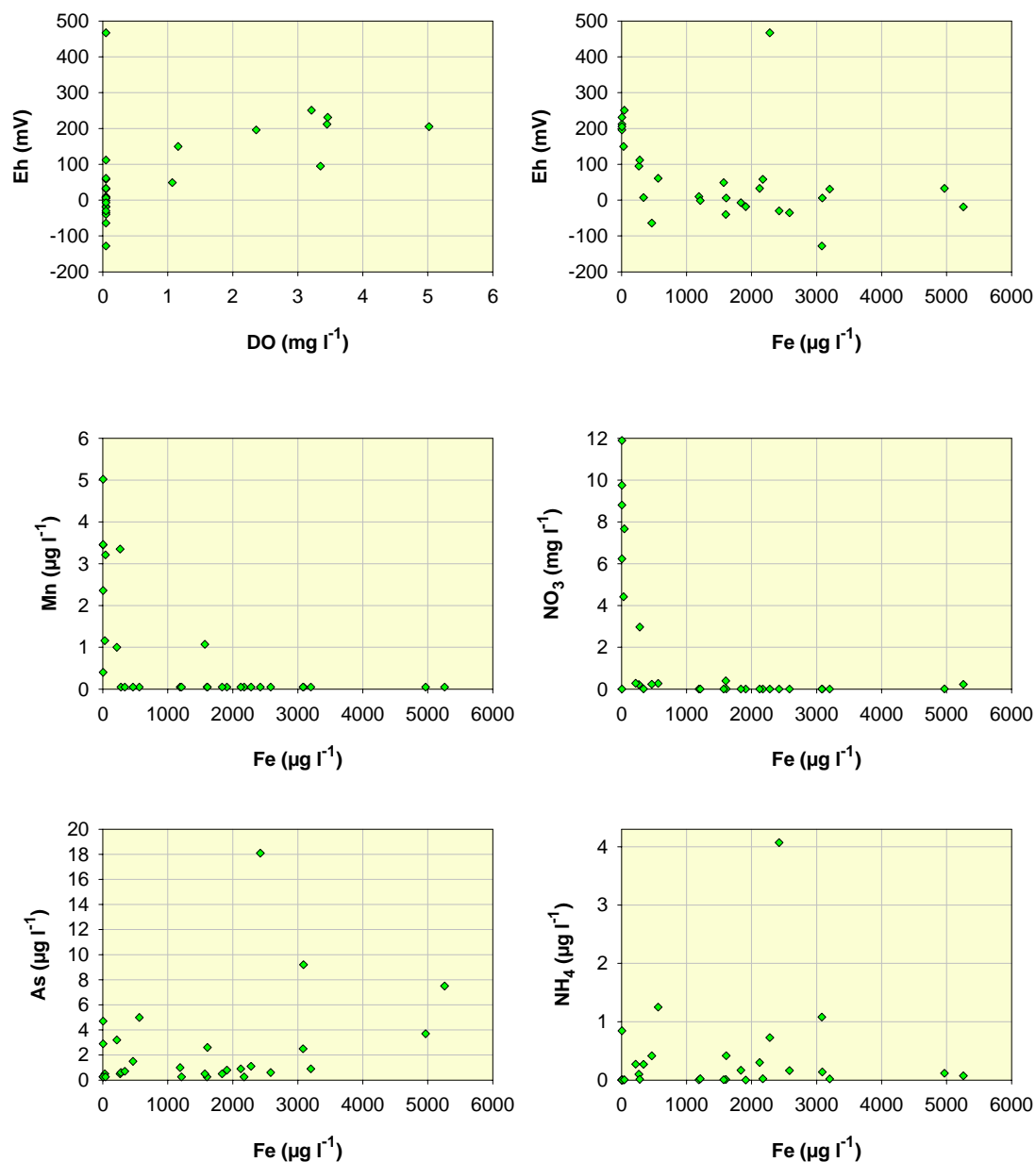
Figure 6.6   Redox indicator species

ION EXCHANGE

Ion exchange is an important chemical process in many aquifer systems, and manifests itself when there is a change in the composition of water flushing the aquifer from that which it had been in equilibrium with (Appelo and Postma, 1994). Studies of Chalk aquifers along flow-lines from recharge areas to confinement have shown that 'freshening', which typically causes the exchange of dissolved Ca for adsorbed Na, is generally only important in older confined parts of Chalk aquifers which have not been sufficiently flushed of formation waters (e.g. Shand et al., 2003). Such a change will be indicated on the Piper Plot by a change in water type from the Ca-HCO$_3$ of recharge areas, to that of Na-HCO$_3$ from ion exchange (Appelo and Postma, 1994):

$$\tfrac{1}{2}Ca^{2+} + Na - X \rightarrow \tfrac{1}{2}Ca^{2+}-X_2 + Na^+$$

50
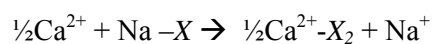
Where Na-rich seawater enters an aquifer ('salinisation'), it is possible that the reverse of this process will take place, and Na will be adsorbed onto clay minerals, releasing Ca to solution and producing a Ca-Cl water type from the Na-Cl seawater (Appelo and Postma, 1994):

$$Na^+ + \frac{1}{2} Ca - X_2 \rightarrow Na\text{-}X + \frac{1}{2}Ca^{2+}$$
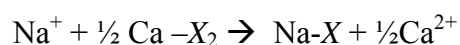
(where *X* represents the exchange site on the mineral phase)

In the Waveney catchment there is a considerable variation in water types (see Figure 5.1), however, there is little indication on the Piper Plot of evolution due to ion exchange, with the possible exception of the samples from Stradbroke, Needham and Bedfield. The use of Cl as a conservative tracer suggests that any perturbation to the Na/Cl ratio from that expected from recharge water mixing with sea water could result from ion exchange. If Na is being released from the aquifer minerals then the Na/Cl ratio would be expected to increase. Figure 6.7 shows the comparison of Na/Cl molar ratio with the measured concentration of Cl. This shows that of the two most saline samples, Needham has a slight excess of Na which may be from ion exchange, whilst Aldeby appears to be represented by simple mixing towards a seawater end-member (see below).

At the lower concentration range samples from both the North Norfolk and Waveney catchments have ratios which vary above and below the expected equilibrium, particularly that of Winfarthing. Some of these may be affected by surficial inputs, such as road salts and fertilisers, as they are not considered to have undergone significant evolution based on other hydrochemical parameters.

MIXING WITH OLDER FORMATION WATERS

An increase in element concentration may be related to groundwater residence time ('groundwater age'), in Chalk aquifers and results from mineral dissolution, ion exchange or mixing with formation waters. Geochemical indicators of mixing with older saline waters are most useful when they have greatly differing concentrations in recharge waters, in comparison with saline waters, and are largely unmodified by reactions within the aquifer. The Na-Cl nature of the most saline waters found in the study area (Aldeby), confined by the Palaeogene clays, demonstrate mixing of a recharge water with saline waters using these major ions, and by examination of minor and trace element data such as Br and B (where neither are affected by contaminant sources). Thus the Figure 6.7 shows the Na/Cl ratio and the Br/Cl ratio, which can be used to study the dilution of a saline solution irrespective of total Cl concentration. These data would appear to indicate that the samples at Aldeby and some of the other deep samples in the Waveney catchment (with high Cl) represent part of a dilution series with a saline solution (in contrast with those possibly modified by ion-exchange). Similar results are obtained for B, which reaches a maximum concentration of 1 mg l^{-1} in the Aldeby piezometer. This would is also supported by the stable isotope data (see below). The age of such saline waters has been postulated as both connate water (Bath and Edmunds, 1981), and remnant Neogene-Quaternary Crag seawater (Hiscock et al., 1996) in the Chalk of North Norfolk.

6.2.5   Age of the groundwater

Groundwater age measurement is difficult without specific age dating measurements (e.g. ^{14}C or CFCs), and assessment using geochemical variations between different bodies of water may only be able to lead to the assessment of relative ages. Stable isotopes can be used to discriminate older Pleistocene (>10,000 years old) and Holocene (<10,000 years old) waters with lighter (more negative) δ^2H and δ^{18}O values being expected from Pleistocene recharge. It has been suggested, from radiocarbon data and hydrogeological considerations, that values of δ^{18}O more negative than –8.0 ‰ are indicative of such recharge (Hiscock et al., 1996). Stable isotopes (δ^2H and δ^{18}O) have been used by Hiscock (1993) and Feast et al. (1997) in the area of North Norfolk. Hiscocks work estimated groundwater ages of ca.10,000 years underneath thick Boulder Clay on interfluves, to 1,000-2,000 years where the Chalk is overlain by more permeable sediments, whilst Feast et al. found δ^{18}O values

as light as −8.25 ‰. No measurements of stable isotopes were made on the samples from North Norfolk in this study, as much data has already been published by Hiscock and colleagues, but stable isotope analysis was undertaken on selected samples from the Waveney catchment, where there was no existing published information.
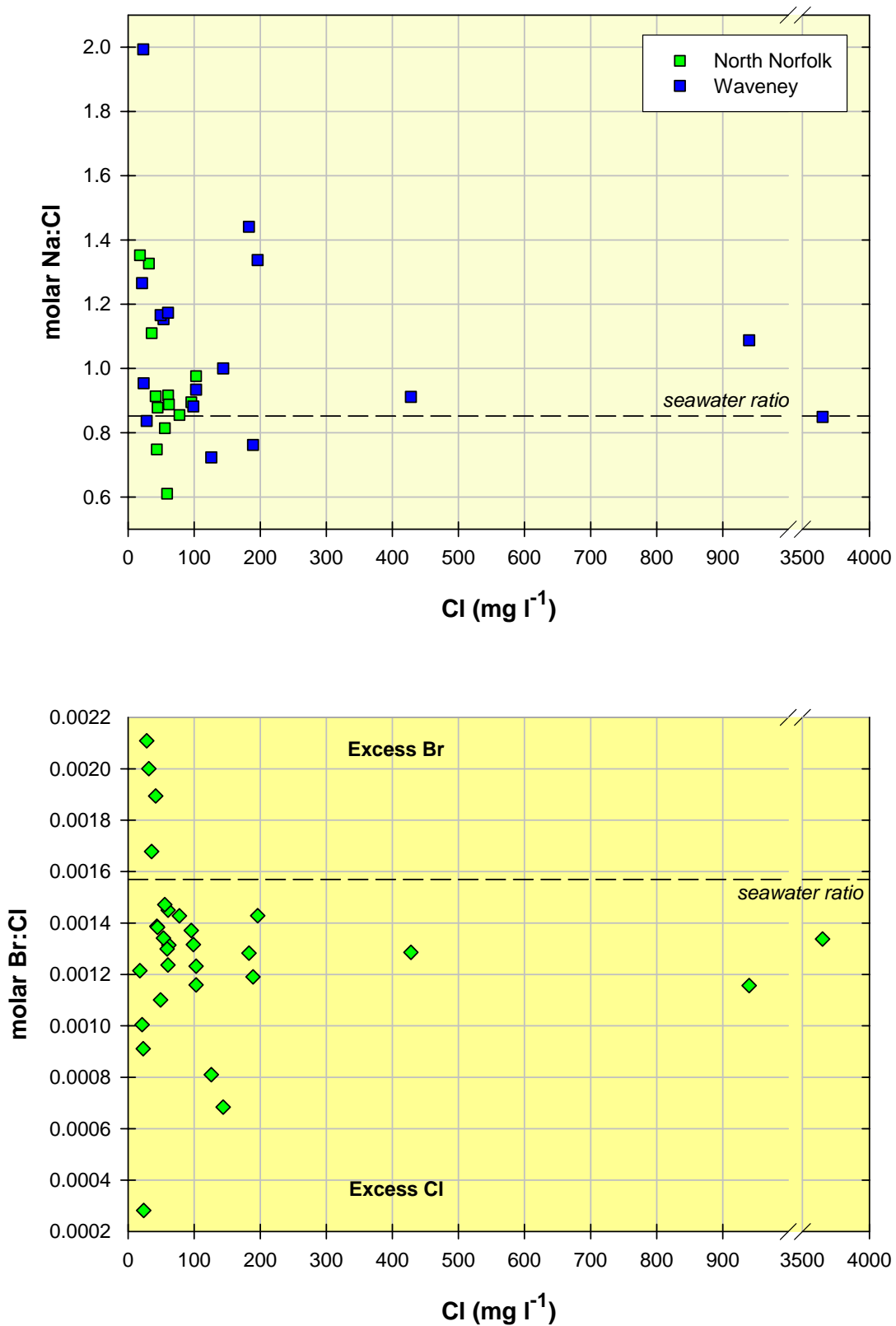
Figure 6.7   Chloride ratios compared to seawater dilution

Figure 6.3 shows that the data for the Waveney chalk plot with a generally less negative $\delta^{18}O$ value than the data from the adjacent Great Ouse Chalk (Ander et al., 2004). These data all fall within the values expected for those dominated by modern day groundwaters of -7.5 ±0.5 (Edmunds et al., 1992), although the sample from Needham in particular appears to show possible mixing with older water as it has a value of -7.98 ‰ and -51.5 ‰ for $\delta^{18}O$ and δ^2H respectively (Figure 6.8). This sample is of Na-Cl type, with high SEC (4310 µS cm^{-1}) and it is possible that it shows a trend towards mixing with an older saline groundwater (Figure 5.1).
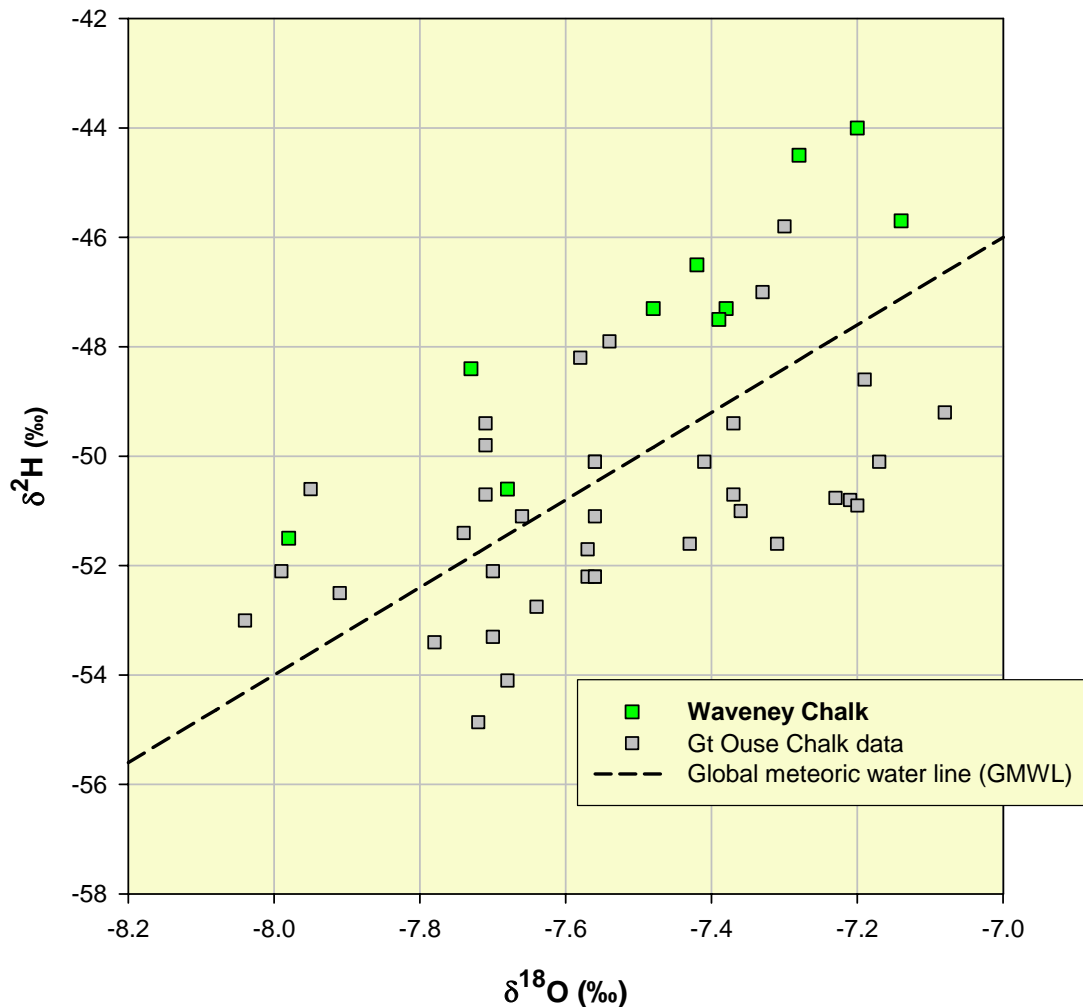
Figure 6.8   **Stable isotope composition of the Waveney chalk groundwaters**

The evolution of the groundwater through increased water-rock interaction can also be studied using the stable isotope $\delta^{13}C$ values, which are shown in Figure 6.9 related to the Sr/Ca ratio. The $\delta^{13}C$ value for the Chalk matrix is approximately +2.4 ‰, whilst that associated with soil and unsaturated zone microbial activity is generally of the order of –25 ‰ (Edmunds et al., 1992), thus recharge waters will be expected to have a $\delta^{13}C$ of the order of –14 ‰ (Shand et al., 2003), thus the $\delta^{13}C$ of groundwater may be expected to evolve towards the Chalk matrix value with increasing water-rock interaction time. The Sr/Ca ratio is a useful measure of residence time because Sr is released during the equilibrium dissolution-recrystallisation of calcite, but is not incorporated into the newly formed calcite. Thus, the ratio should increase with increase residence time, whilst the Ca concentrations are limited by calcite equilibria (Edmunds et al., 1992) or ion-exchange (Edmunds et al., 1992). This often results in an increase in the Sr/Ca value with increasing recrystallisation, and hence loosely

residence time. These parameters very clearly show a positive relationship, most likely indicating variations in residence time of the groundwaters.
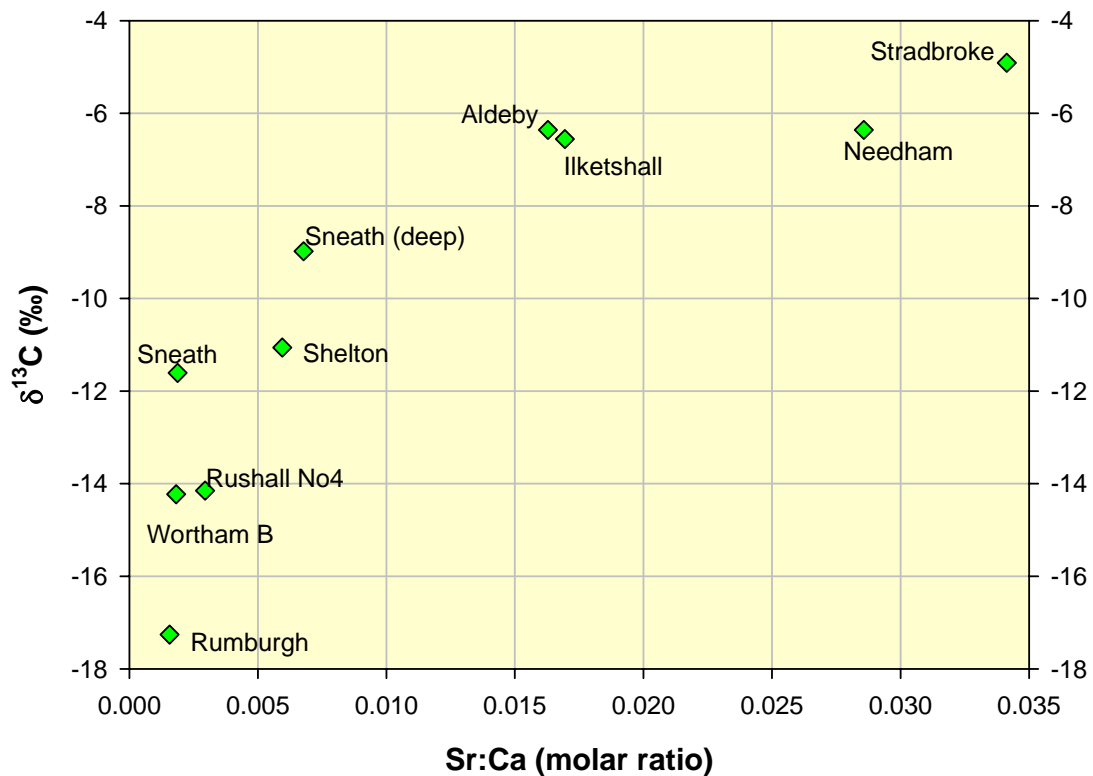
Figure 6.9   Comparison of Sr/Ca with δ^{13}C in the Waveney Chalk aquifer

6.3   The Crag aquifer

6.3.1   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. These reactions are rapid in comparison to those of the alumino-silicates, and the chemistry of water entering the saturated aquifer has generally already reached equilibrium with calcite. The continued reaction with both carbonate and silicate phases will result in the continued evolution of the hydrochemical characteristics of the groundwater, and these changes can be used to understand the flow paths and residence time of the groundwater.

Flow in the Crag aquifer is conceptualised as being inter-granular, with lateral and vertical permeability contrasts likely to be more influential over local flow directions than any minor fractures. Factors which control the variations observed in groundwater chemistry are studied in this section, with importance placed on the use of minor and trace ion data in understanding the geochemical processes. Where this is the case, the data used is that collected during the BGS sampling, rather than the full set of major ion data presented in Table 5.2 and Figures 5.7 and 5.8.

6.3.2   Depth variations

The interpretation of aqueous chemistry in relation to vertical and lateral differences within aquifers is complicated by the mixture of water when boreholes are pumped (see Section 4.3). Techniques such as packer tests, specific depth sampling and comparison of adjacent, but different depth boreholes can

all help to provide additional information on this process. The sampling and analysis of porewater may also provide detail of vertical variations within the matrix. In contrast to the more intensively studied Chalk aquifer, very little information is available for the Crag.

The Ludham PWS boreholes are sited to differing depths within the Ludham Trough. The interval between the uncased termini includes a laterally contiguous clay horizon which has previously been invoked as acting as an effective aquiclude (Holman et al., 1999), and protecting the abstracted groundwaters from (near)-surface sources of NO_3 (Jones et al., 2000), resulting in minimal NO_3-N concentrations in the PWS. In this study Ludham no 1 was found to have 0.21 mg l^{-1} NO_3-N, whilst that of Ludham no 2 was below the detection limit (0.01 mg l^{-1}). Shallow private supplies in the area of the Broads were associated with the highest NO_3-N concentrations found in this study (13-18 mg l^{-1}).

In the Waveney catchment, far greater control exists on understanding of the depth interval from which pumping took place, although the piezometers were sited widely across the aquifer outcrop. Examples of the comparison of the piezometer depth with analytical determinands are shown in Figure 6.10. It can be seen that there is little systematic relationship between solute concentration and depth, with the exception of NO_3, which is higher in the more shallow piezometers. This may be a result of interactions between the overlying tills and underlying Chalk, as well as lateral variations within the Crag. These data appear to indicate that the depth and age relationships are not linearly related within the aquifer (see Section 6.3.3).

6.3.3 Temporal variations

Little time-series data exists with which to study temporal variations in the composition of the groundwater chemistry. The records compiled by Whittaker (1906) suggest that locally high concentrations of NO_3 were found in the Crag aquifer in the 1870s (e.g. *ca.*80 mg l^{-1} in a Crag borehole in Lowestoft), but no very long term records for wells sampled during this study could be found. The importance of having long-term data from areas which represent baseline conditions, with which to set data into context, are emphasised by the limited and relatively short-term nature of the data available during this study.

The data available from the Ludham boreholes in the North Norfolk area show little variation in Fe and Mn concentrations over a 5 year period (Figure 6.11). The data is indicative however, of the water quality problems, for potable supply, routinely associated with the natural composition of the Crag groundwaters (Section 3) with Fe and Mn systematically exceeding the MAC concentrations (0.2 mg l^{-1} and 0.05 mg l^{-1} respectively).

6.3.4 Spatial variations

The baseline chemistry of an aquifer naturally varies as water moves from the recharge area to the discharge zone. Different areas of the aquifer may be characterised by longer residence times, and thus increased time available for reaction with the aquifer minerals. Identification of these zones is complicated by the aquifer heterogeneity, the influence of overlying tills and the low lying topography of the area (especially in North Norfolk). Thus the concept of sampling along a 'flowline' cannot be regarded as appropriate for this area, and the spatial variations in water chemistry have been examined. The major control on the hydrochemistry is the interaction between the waters and the aquifer minerals.
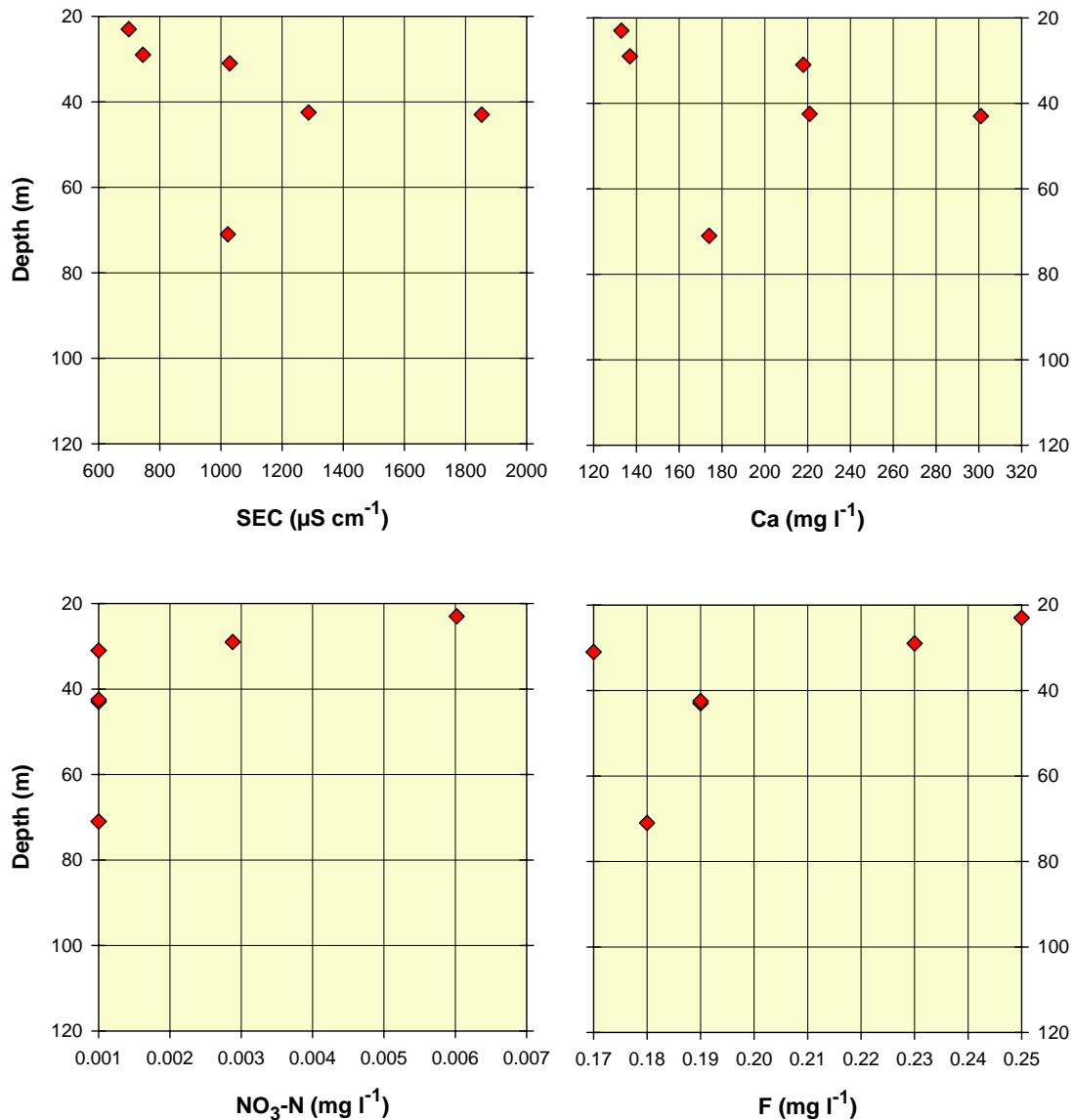
Figure 6.10   Comparison of selected determinands with borehole depth for the Waveney Crag aquifer.

MINERAL DISSOLUTION REACTIONS

The most chemically reactive minerals within the Crag are key for determining the chemical evolution of groundwater in the aquifer. Thus, the generally abundant, and reactive, carbonate and alumino-silicate minerals are likely to be the principal controlling reactions.

The re-crystallisation of the $CaCO_3$ polymorph aragonite (orthorhombic $CaCO_3$) to calcite, or the incongruent dissolution of calcite, results in the release to solution of associated trace elements which do not tend to be accepted into the freshwater calcite structure, particularly Mg and Sr^{2+} (Deer et al., 1966). Thus with increasing residence time, Sr concentrations may be expected to increase in the aquifer.

The dissolution of calcite in the presence of dissolved $CO_{2(g)}$ results in the release of bicarbonate ions and Ca to solution:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^-$$
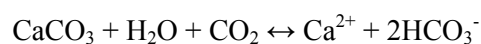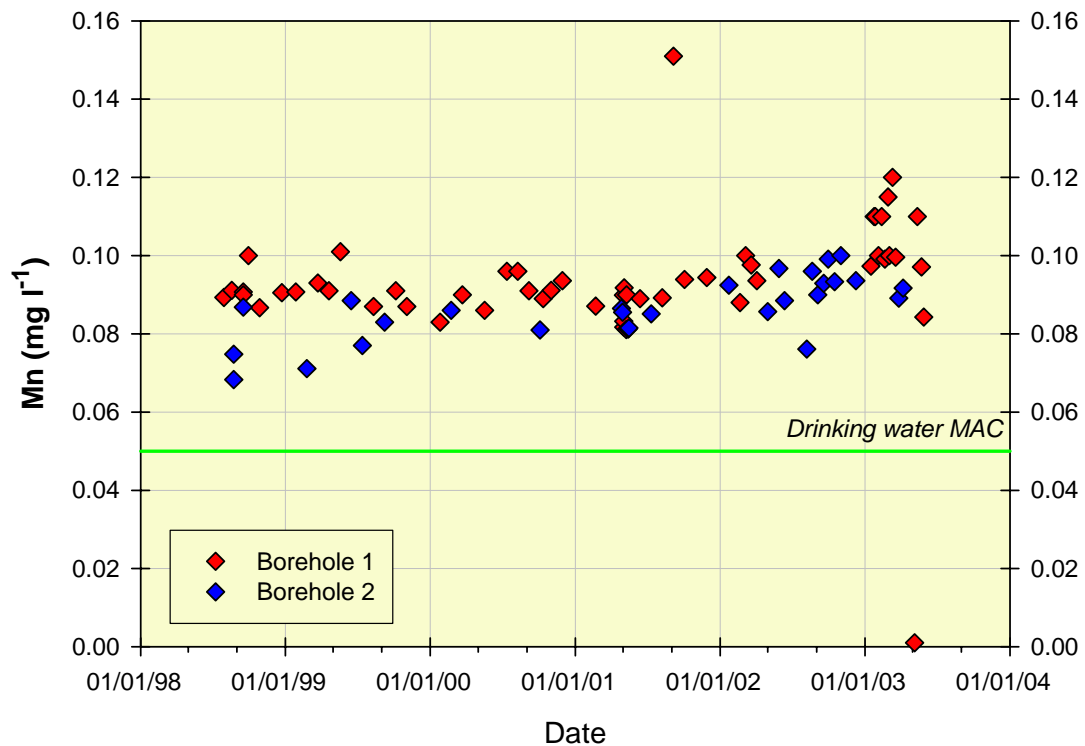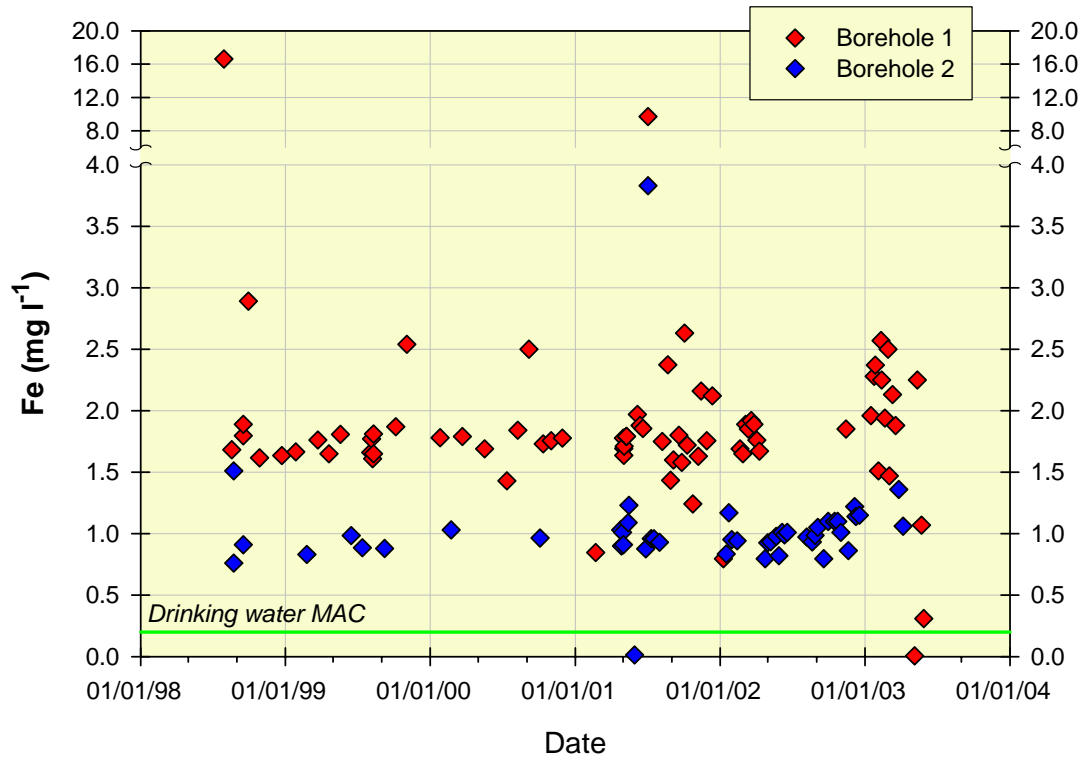
Figure 6.11   Time series data for the Ludham PWS boreholes in the Crag.

The dissolution of calcite is also an important pH buffering reaction (related to multiple dissociation constants), and typically buffers pH to neutral to slightly alkaline pH. pH values in the Crag samples collected during this study range between 6.8 – 7.8, with the exception of one samples (Landseer) with a pH of 5.9, suggesting that the aquifer is carbonate depleted in the capture zone of that private supply. The distribution of Ca across the aquifer outcrop (Figure 6.12a) can be seen to have little systematic variation, in contrast to the HCO_3 concentrations which are generally higher in the Waveney than in North Norfolk (Figure 6.12b), and appear to be solubility controlled (Figure 5.8) at similar concentration to the samples from the Chalk (cf. Figure 5.3). As would be expected, the low pH sample has the lowest HCO_3 concentration (68 mg l^{-1}). It is not clear whether sources of Mg into solution in the Crag aquifer are dominated by release from a carbonate phase, or whether silicate weathering is influential. Concentrations are largely low ($\leq$16 mg l^{-1}), of the order of those observed in the Chalk in modern, less evolved waters. Where Mg concentrations in the Waveney catchment are higher (Figure 6.12c), these are generally associated with deeper waters, which may be inferred to have had a longer residence time.

The reaction of carbonate phases in the aquifer matrix may be expected to release into solution ions originally incorporated into the matrix during the dissolution of aragonite or calcite, and recrystallisation of calcite. Such ions typically include Sr and F in a very pure calcite aquifer such as the Chalk, although other mineral sources of these ions cannot be ruled out in this mineralogically heterogeneous aquifer. Concentrations of F (Figure 6.13a) vary little across the aquifer, and these variations do not appear to show any systematic pattern. Strontium concentrations vary substantially; those associated with the boreholes in the Broads area are generally moderate (<460 μg^{-1}), as are some of the samples in the Waveney area (Figure 6.13b). However, concentrations in deeper piezometers into the Crag in the Waveney catchment are substantially higher (maximum of 3835 $\mu g\ l^{-1}$), and may indicate (with other parameters, see below) an increased residence time and, thus, water-rock interaction in these samples.

Silicon is released into solution primarily from the weathering of alumino-silicate phases, which are expected to be abundant in this aquifer. Concentrations are systematically higher in the Waveney catchment than observed in the North Norfolk field area, but do not exceed 11.4 mg l^{-1} in any sample (6.13c). The exception to this distribution pattern is Ludham where concentrations reach 10.8 mg l^{-1}. In addition to Si, an indication of the other elements which may be released into solution from silicate weathering can be gained from consideration of the typical composition of glauconite $[(K,Na,Ca)_{2.0}(Fe^{3+},Al,Fe^{2+},Mg)_{4.0}[Si_7Al_1O_{20}](OH)_4.n(H_2O)]$ a locally abundant reactive mineral in the aquifer, which is potentially a major source of dissolved Fe (see below). Trace elements frequently associated with alumino-silicate lattices include Li, Rb, NH_4^+ and B; concentrations of these generally follow the relative abundance of Si, as exemplified in Figure 6.14d for Rb. Concentrations of Rb are low (<1 $\mu g\ l^{-1}$) in samples with lower concentrations of Si, and reach a high concentration (9.45 $\mu g\ l^{-1}$) in the sample from Rumburgh.

Dissolved SO_4 may be derived from the weathering of any sulphide minerals in the aquifer (although these are not widely recorded (Section 3)), and in overlying tills (where pyrite is known to occur), or the dissolution of sulphate minerals in the aquifer matrix. Concentrations across the aquifer are largely moderate (<100 mg l^{-1}) (Figure 6.12d) although these are higher concentrations than would be found in an aquifer further inland where the recharge is more distal with respect to seawater.

The highest concentration is found in the sample from Rumburgh (576 mg l^{-1}), which is one of two samples from the Waveney catchment where the water type is $Ca-SO_4$, and a further sample is $Ca-HCO_3-SO_4$. These groundwaters have a considerable excess of SO_4, compared to Cl, than would be expected from seawater mixing. These three samples have SO_4 concentrations from 260-576 mg l^{-1}, which are the highest concentrations measured in the Waveney Crag groundwater samples, the remainder of which are all <150 mg l^{-1}.
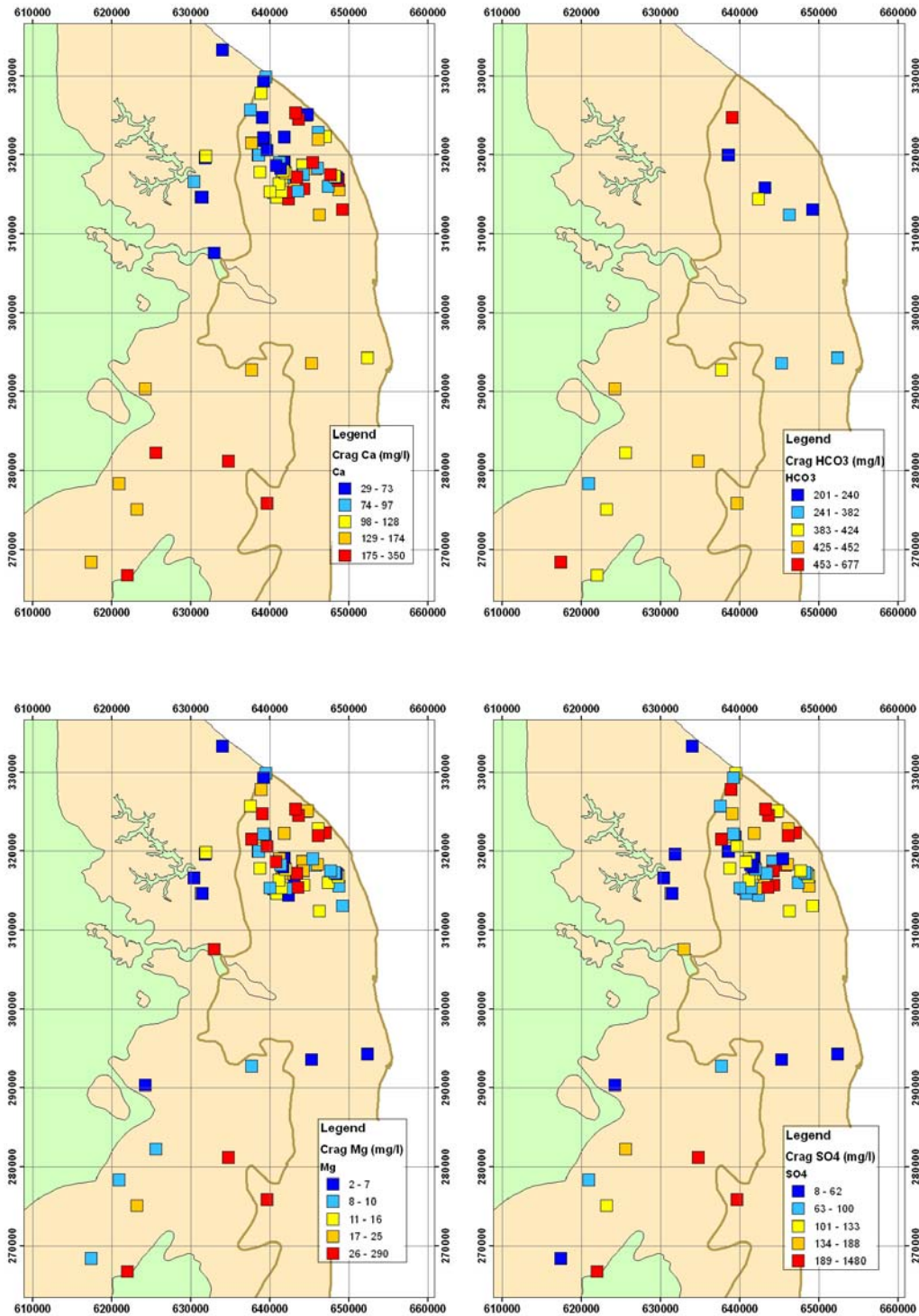
Figure 6.12   Spatial distribution of concentrations in the Crag aquifer (a) Ca (b) HCO3 (c) Mg (d) SO4
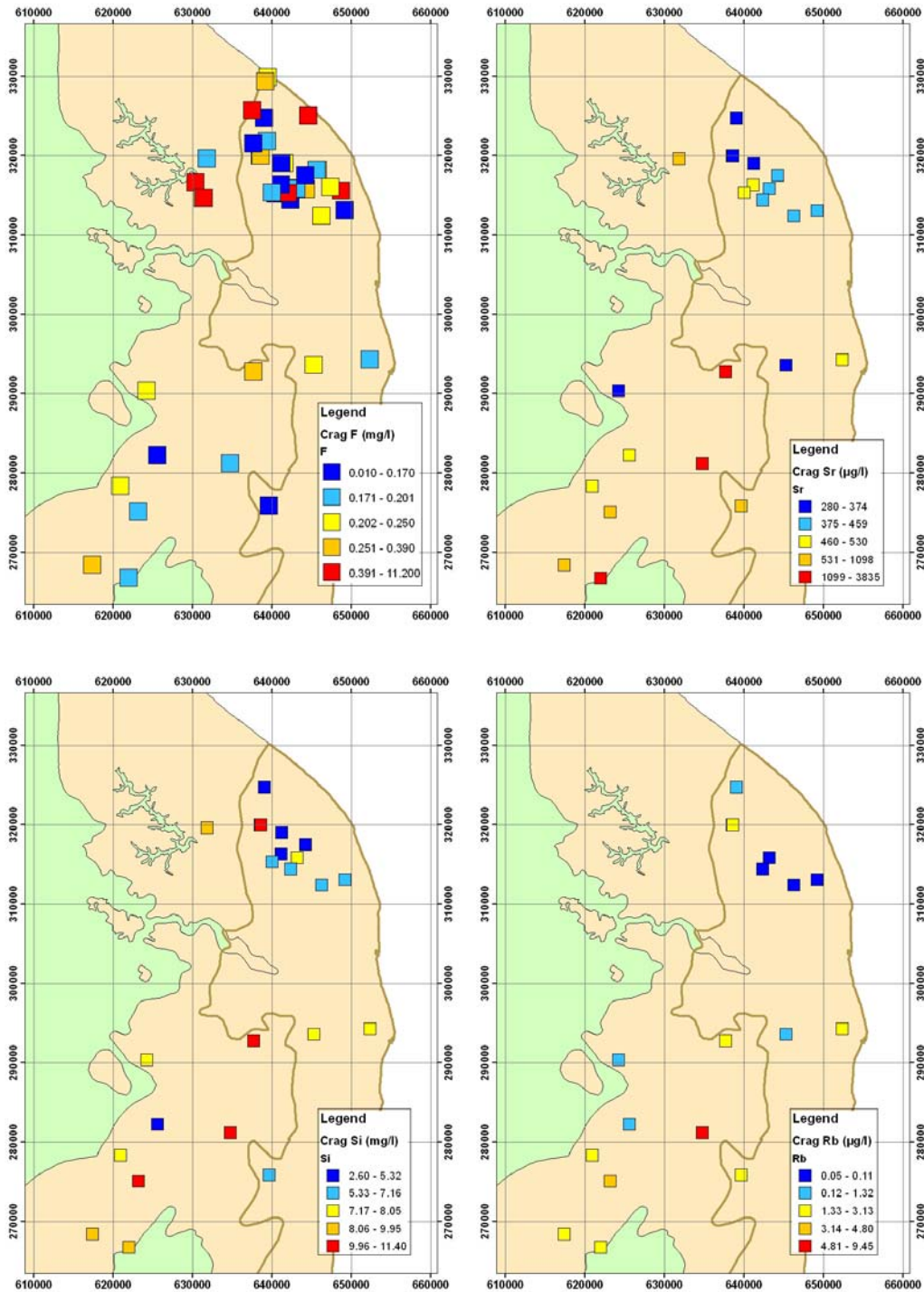
59

Figure 6.13   Spatial distribution of selected trace elements over the outcrop of the Crag aquifer (a) F (b) Sr (c) Si (d) Rb

Possible geological sources are the dissolution of sulphate minerals, such as gypsum salts. These can either be primary mineral phases, or can occur as secondary mineralisation from the oxidation of pyrite, liberating sulphide ions into solution which are then oxidised to sulphate ions. Observations of pyrite in the aquifer sediments have not been reported in the literature cited in this report. It is, however, possible that disseminated pyrite is under-recorded where lithological studies are carried out primarily for stratigraphical correlation purposes rather than hydrogeological investigations. An additional source of SO_4 to the aquifer could be via leakage from overlying till deposits (Section 3.3.3). The Chalky Boulder Clay is derived from the early Cretaceous and Jurassic strata to the west of the Chalk outcrop, and as such tends to contain appreciable concentrations of pyrite. It is also plausible that excess SO_4 could be sourced from anthropogenic contamination. Landuses immediately around these sites varied from a golf course to cereal production at the time of sampling, which may supply SO_4 from fertiliser applications. Alternatively contamination could come from the borehole itself, but these boreholes varied from commercial to EA installations, and similar SO_4 concentrations were not observed at other sites, which would seem to rule out such a problem.

REDOX REACTIONS

The primary indicators of the redox status of groundwaters are the redox potential (Eh) and dissolved oxygen (DO) (Figure 6.14a). These parameters are very unstable and can only be measured using a flow-through cell at the time of sampling. The analysis of redox sensitive elements also provides information on the redox status of the aquifer (Box 6.1), and can be a useful check on Eh measurements, which are well recognised to have limitations (Appelo and Postma, 1994).

The groundwaters of the Crag have varying redox status across the outcrop. The direct measurements of Eh and DO compare well, despite the well documented difficulties in measuring Eh (e.g. Appelo and Postma, 1994). These indicate that the groundwaters sampled in the Waveney catchment are generally poorly oxidising or reducing in nature, with no detectable DO in any of the samples where it was possible to use the flow-through cell. In North Norfolk, with the exception of the Ludham PWS boreholes, the groundwaters can be seen to be generally oxidising, with detectable DO. It is likely that this systematic variation reflects the deeper installation of the EA piezometers in the Wavney catchment than the private wells sampled in North Norfolk. These data and other hydrochemical indicators described in this section suggest a longer residence time for the Waveney Crag groundwater than observed in North Norfolk. The solubility of Fe and Mn is greatly affected by variations in aquifer redox status, with concentrations greatest in reducing environments, as the soluble divalent forms of the elements are prevalent. These data correspond to those of the physico-chemical measurements, with concentrations of Fe generally exceeding 2 mg l^{-1} in the Waveney catchment (Figure 6.14b). Concentrations of Mn and Fe are low in the North Norfolk region, with the exception of Ludham.

Iron(II) is unstable in oxidising waters and rapidly oxidises to Fe(III). The solubility of Fe(III) is very low, and the precipitation of iron oxyhydroxides is greatly favoured.

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$$
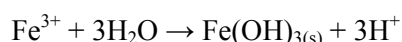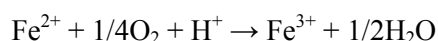
These Fe phases are responsible for the ubiquitous reddening of Crag strata exposed to the atmosphere (and reduced Fe for the grey-green colour of the unoxidised sediments). Whilst this reaction series liberates H^+, the frequent observation of calcite (and aragonitic) shell debris and secondary calcite precipitates suggests that the aquifer should have sufficient pH buffering capacity to minimise any effects on pH. The mineralogical source of Fe to groundwaters is likely to be the glauconitic minerals which are found through the aquifer (Section 4) (Cook, 1979).
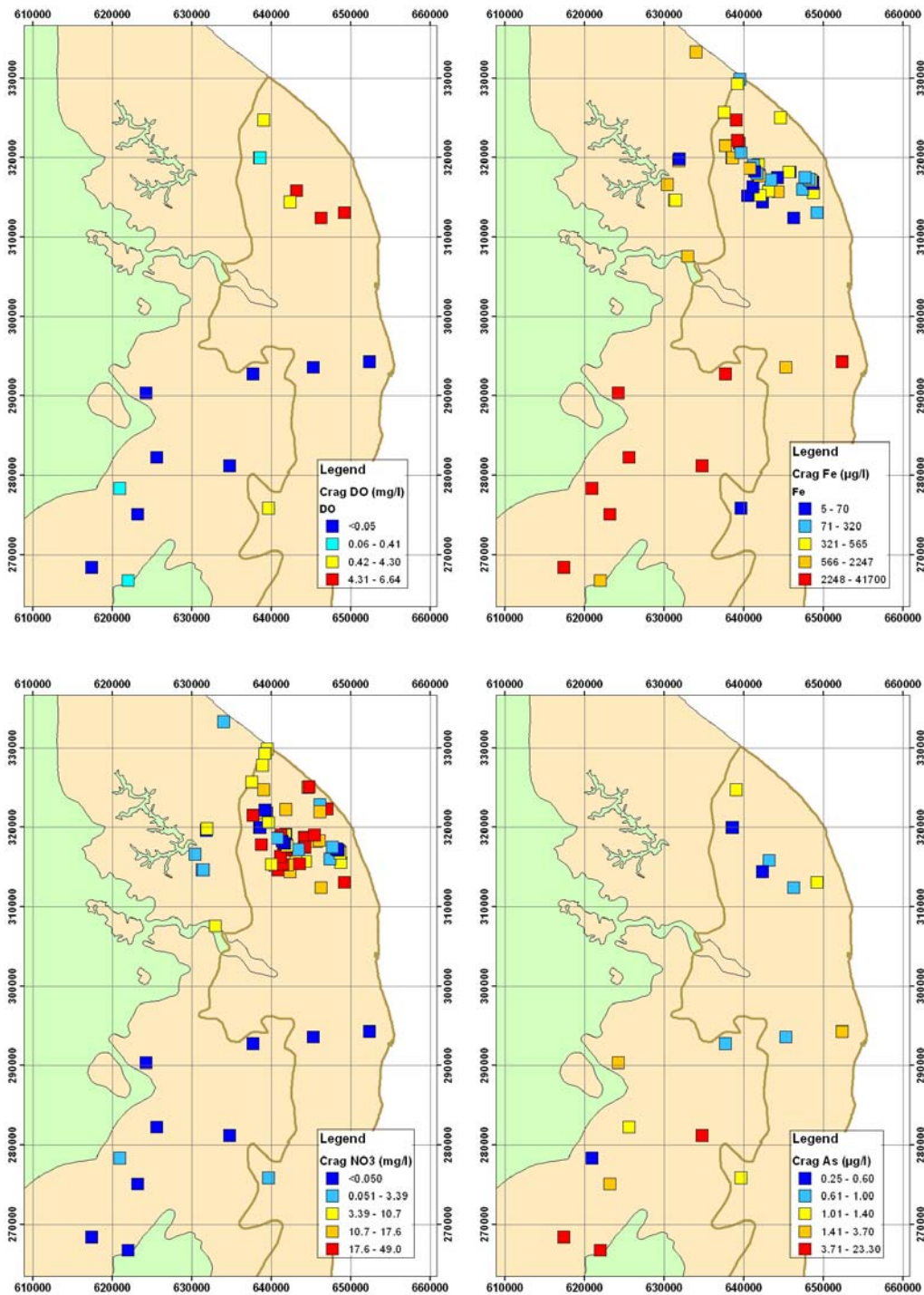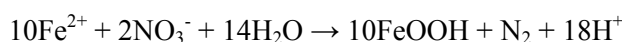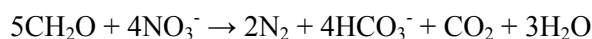
Figure 6.14   Spatial distribution of redox indicators in the Crag aquifer (a) DO (b) Fe (c) NO3 (d) As

Nitrate is largely unaffected by solubility or sorption controls of its mobility within aquifers, and is thus liable to reach high concentrations if leaching takes place from land where fertiliser has been applied, or from inadvertent release of organic waste leachate. However, a natural restriction on the transport of NO_3 occurs in reducing conditions, when NO_3 is reduced (ultimately) to N_2 (Appelo and Postma, 1994). The electron donor sources within the aquifer which can reduce nitrate and are common are organic carbon, pyrite and Fe(II)-silicates. Pyrite is not recorded from this aquifer, and little information can be found on the organic carbon content, the concentration of dissolved organic carbon (DOC) in this study varied between 0.8-6.7 mg l^{-1}). Glauconite is abundant in some parts of the aquifer and may lead to increased NO_3 reduction potential. Indicative overall reactions for these processes are shown below (Appelo and Postma, 1994).

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$$

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow 10FeOOH + N_2 + 18H^+$$

The NO_3 data (Figure 6.14c) correspond well to the other indicators of the redox status of the waters already described (above), with high concentrations in the oxidising waters of North Norfolk (17.6 – 36.7 mg l^{-1} NO_3-N), exceeding the present drinking water MAC (11.3 mg l^{-1} NO_3-N). The low redox potential, and thus NO_3-N concentrations found in the Waveney catchment may reflect the protective function of the more argillaceous nature of the till (Chalk Boulder Clay) that is dominant in this area, compared to North Norfolk (Corton Formation) and the more argillaceous and glauconitic nature of the aquifer materials. The occurrence of reduced Fe in the till and the glauconite minerals both represent a considerable reducing potential within the Crag, although this reaction is considered to be required to be bacterially mediated to proceed at rates sufficiently fast to be significant (Appelo and Postma, 1994).

Trace elements which are redox sensitive may reach high concentrations as a result of variations in the groundwater physico-chemistry. An example of this is As, which is shown in Figure 6.14d and Figure 6.15, where the oxidised waters of North Norfolk can be seen to have low concentrations of As (<1.2 μg l^{-1}), whilst concentrations rise to 23 μg l^{-1} in one sample of the Waveney catchment, in the expected inverse concentration relationship with DO. Uranium chemistry is different to that of many other trace elements of concern, and has its greatest solubility in oxidising, HCO_3 rich waters, which would appear to largely restrict U concentrations in the Crag aquifer (all data <0.27 μg l^{-1}). Whilst many other trace elements are low in these waters, reflecting a low mobility, some probable contamination is observed in the Landseer sample, specifically in the concentrations of Zn (4.0 mg l^{-1}) and Ni (8 μg l^{-1}).

ION EXCHANGE REACTIONS

The process of ion exchange has been described in Section 6.2.4. There is no evidence from the data itself, and in the visualisation of the data (Figure 5.6), that ion exchange is a dominant process in the groundwaters collected during this study. Where saline ingress is occurring in areas of the Broads (Holman and Hiscock, 1998), it is possible that water types of Ca-Cl composition could occur (Appelo and Postma, 1994), which has been invoked to explain complex Na/Cl in the coastal Crag groundwaters (ENTEC, 2001).
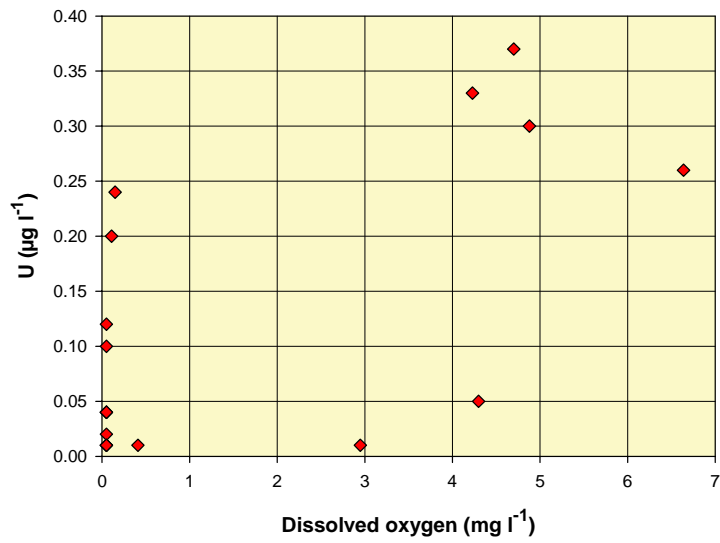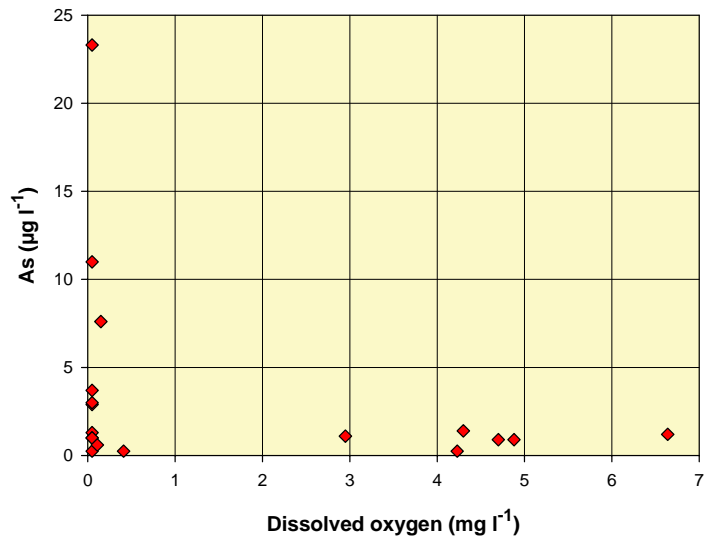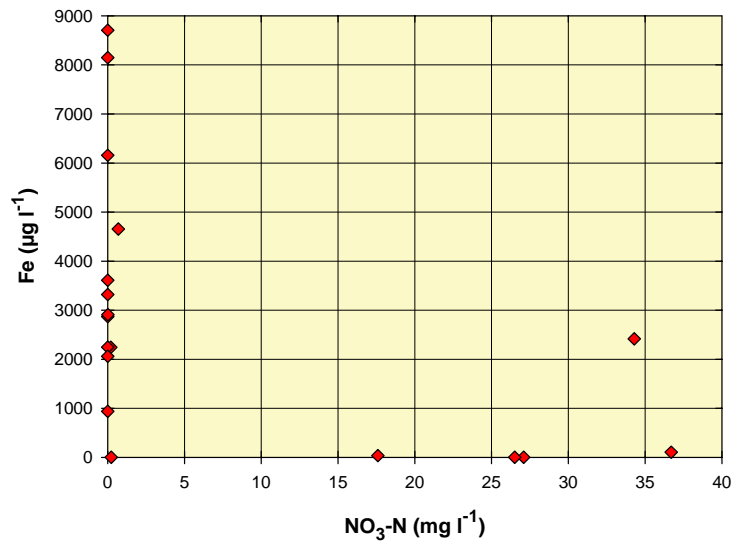
Figure 6.15   **Redox indicator species in the Crag aquifer (a) NO$_3$-N and Fe (b) As and DO (c) U and DO**

The evidence for mixing with saline waters is conflicting in the Waveney catchment, with the sample from Rumburgh having the highest SEC (1853 μS cm^{-1}), and high concentrations of trace element indicators such Li, Rb and B and generally high concentrations of major ions (in the context of this aquifer). The same is also true, to a slightly lesser extent, for Stradbroke. However, these samples show an overall water composition of Ca-SO$_4$ and Ca-HCO$_3$ types respectively, with no evolution towards cation-exchange (towards Na-HCO$_3$) or saline mixing (with a presumed Na-Cl end-member) on the Piper Plot. Additional information suggesting that these groundwaters may not have a significant connate water component comes from stable isotope analysis (see below). These waters are very reducing, with high Fe concentrations (6.2 and 4.7 mg l^{-1} respectively), and it may be that these conditions have accelerated the processes of carbonate and silicate weathering, to give an apparently greater residence time based on trace element indicators alone. An alternative hypothesis is that the Crag has been completely flushed of Tertiary and early-Quaternary seawaters, due to the intergrannular nature of the flow, and thus the oldest waters will not reflect a seawater component. There is, thus, no evidence for mixing with older formation waters in any of these samples.

6.3.5 Age of the groundwater

There are no published data on the residence time (age) of the Crag groundwater in the North Norfolk or Waveney areas. The presence of a Pleistocene palaeowater component (> 10000 yrs BP) can be indicated from the variation in δ^{18}O and δ^2H, which was isotopically lighter (more negative) during colder recharge periods of the last glaciation. Stable isotope analyses were undertaken on a subset of the samples collected, in order to obtain some indication of residence time in the aquifer.

It can be seen from Figure 6.16, that the data plot along the GMWL similar to that expected from modern or Holocene recharge. There is no clear trend of salinity with stable isotope signature. The sample with the heaviest isotope composition (δ^{18}O of –7.66 ‰, δ^2H of –49.7 ‰) located in the north of the North Norfolk Crag sampling area, is only moderately saline (888 μS cm^{-1}), and does not otherwise have a chemical composition different to the other private supplies in the area (e.g. oxygenated with a DO of 3 mg l^{-1} and NO$_3$-N of 16.6 mg l^{-1}), although the pH is unusually low in comparison to other samples (5.91), and elevated trace elements are suggestive of local contamination of the sample. The sample analysed from the Ludham borehole has an isotope signature indicative of modern recharge, δ^{18}O of –7.23 ‰, δ^2H of –45 ‰. All the samples analysed from the Waveney catchment had a stable isotope composition indicating modern recharge (Figure 6.16).

The stable isotope δ^{13}C can be indicative of the interaction with carbonate in the aquifer matrix, particularly under closed system conditions. As the Crag is frequently a very shelly sediment, it is assumed that the reservoir of carbonate C is not limited within the bulk aquifer, and thus interaction will be as for the Chalk. Although no information could be found on the stable isotope composition of the Crag carbonate where it is of marine origin it is likely to be representative of marine carbonate (i.e. similar to that of the Chalk, *ca.*–25 ‰).

The value of δ^{13}C can be seen to vary positively with Sr/Ca (Figure 6.17), both of which may be used as indicators of increasing water-mineral reaction and more loosely as indicator of residence time. The shelly deposits of the Crag may be expected to be originally dominated by aragonite, and thus subject to the same slow recrystallisation to calcite process that the Chalk aquifer undergoes. In this recrystallisation process, the Sr co-precipitated into the aragonite lattice is preferentially retained in solution rather than being incorporated into the calcite mineral. A good correlation exists for these parameters (Figure 6.17) indicating that incongruent dissolution dominates the carbonate evolution of the groundwaters. The sample which is apparently most evolved (δ^{13}C of –11.82 ‰), at Rumburgh, is one of the deepest of the Crag boreholes, at 43 m, lending support to the hydrochemical evidence of an increased residence time at this site. Whilst artefacts arising from any systematic variations in the

mineralogical and isotopic composition of the Crag aquifer cannot be accounted for in this study, the correlations observed broadly support the model of assessing groundwater residence used.

6.4   Comparison of hydrochemical data from the Waveney piezometer samples

A brief comparison of the hydrochemical environments in the Waveney presented here. The major ions are presented as a Piper Plot (Figure 6.18) containing data for the Chalk, Crag and Superficial aquifers of the Waveney catchment (Section 4 for details of sample numbers). These data include all the samples collected during this study in the Waveney catchment. These data illustrate the mixing of recent Chalk groundwaters with a more saline end-member, as described above (Section 6.2); where this occurs to the east of the Palaeogene subcrop then the Chalk groundwater is expected to be isolated from that of the Crag and superficial strata. To the west of the Palaeogene subcrop the Quaternary, Crag and Chalk are considered to be in hydraulic continuity (Allen et al., 1997). The Crag groundwaters have also already been discussed (Section 6.3), and the trend from a Ca-HCO$_3$ type towards a Ca-SO$_4$ type in some samples is clearly shown in Figure 6.18. The superficial groundwater samples appear to follow a very similar trend to that of the Crag. Whilst the small sample size (8) prevents definitive conclusions being drawn, this would seem to support the possibility that the SO$_4$ excess in the Crag samples is derived from a source in the overlying glacial sands and gravels or till deposits.

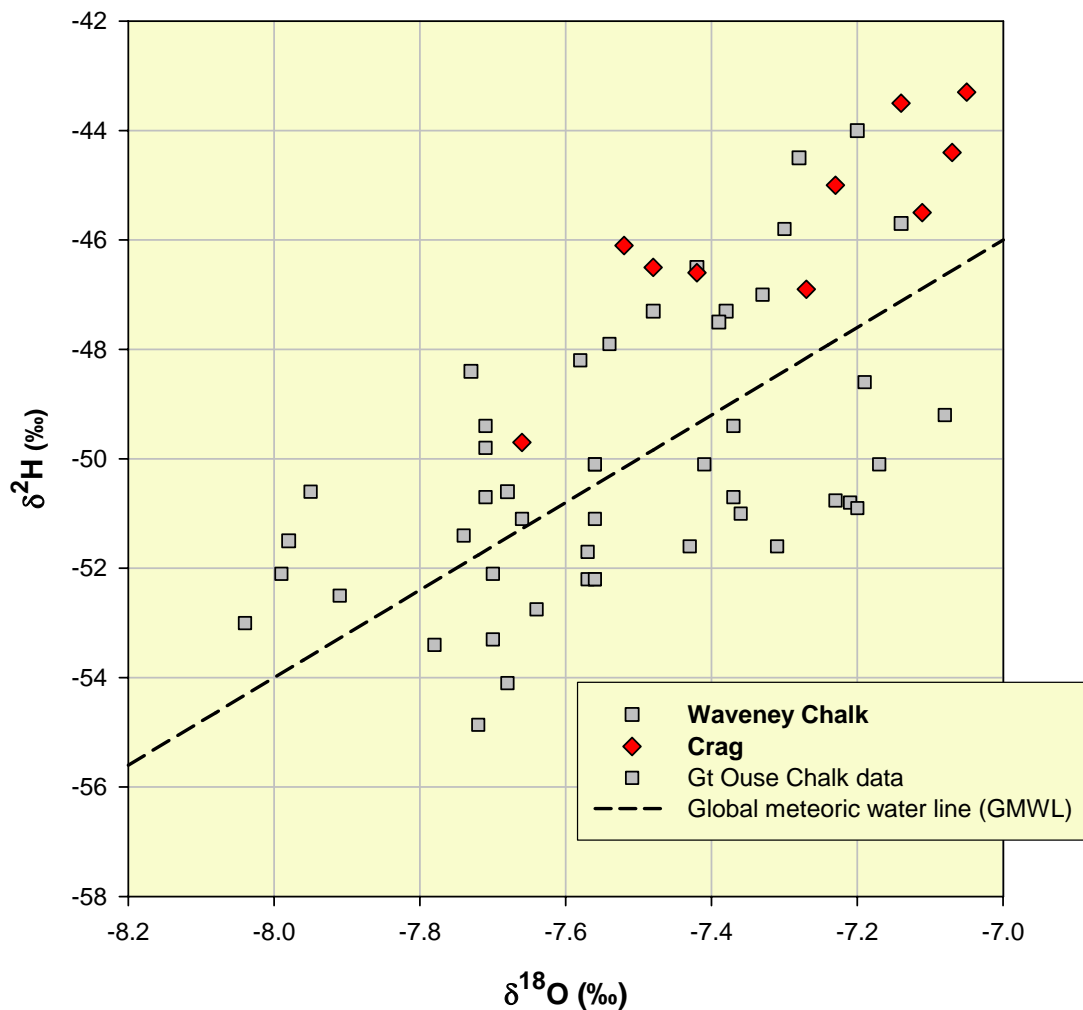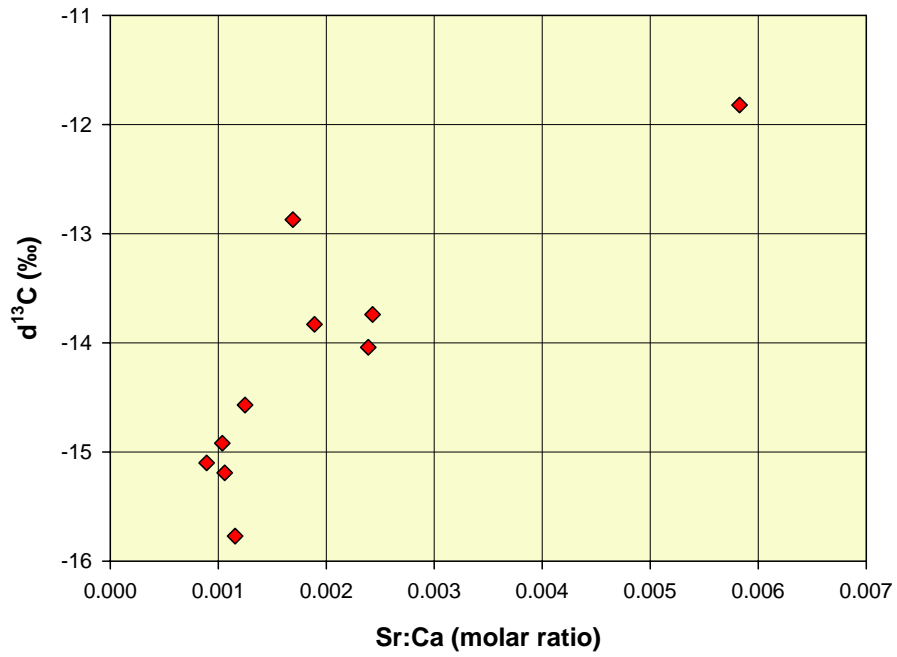**Figure 6.16** δ^2H-δ^{18}O plot for Crag groundwaters

Figure 6.17   Comparison of Sr/Ca with $\delta^{13}C$ in the Crag aquifer
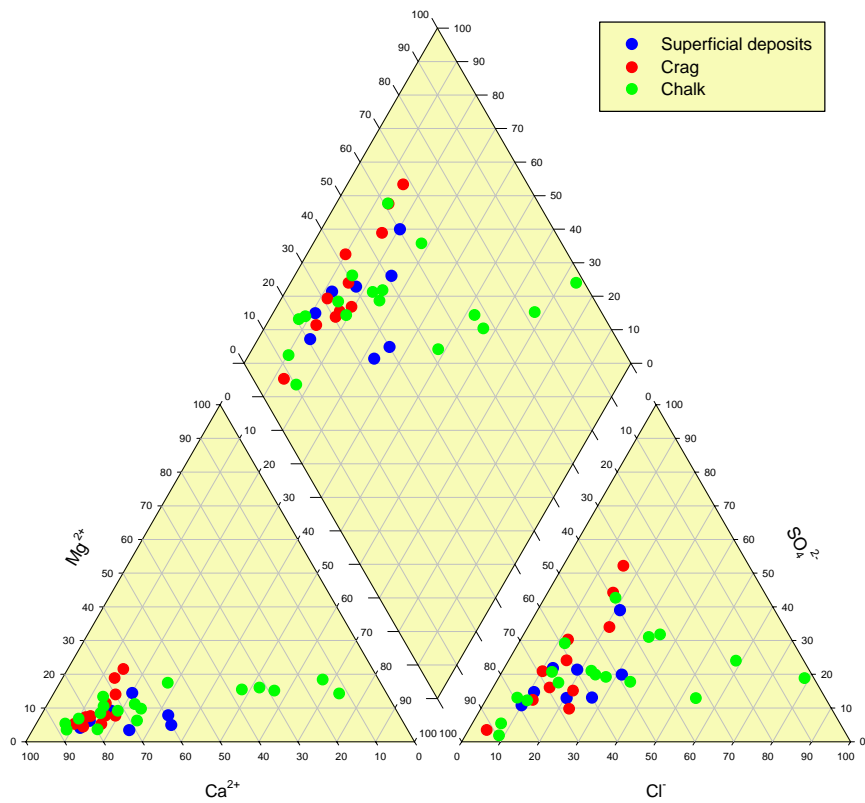
Figure 6.18   Comparative Piper Plot of different aquifers in the Waveney catchment

The close parallels in the hydrochemical trends of selected parameters is shown in the cumulative frequency plot (Figure 6.19). The higher concentration of Cl in most Chalk groundwater samples reflects the mixing with more saline waters, whilst there is no evidence for such a process in the Crag, and it would not be a process anticipated to occur in the superficial sediments (which are well away from the coastline and above sea level). Whilst the SO_4 content of the Crag is more dominant than that of the Chalk, it can be seen that the distribution of concentrations is very similar in these two aquifers. Calcium concentration distributions are almost identical in all the aquifer units sampled, and the shape of the cumulative frequency curve indicates a solubility control on Ca concentrations in all three aquifer units (Box 5.1), suggesting that availability of calcite (or aragonite) is not limited at the regional scale in the argillaceous sediments. Despite the purity of the Chalk it can be seen that Si concentrations are higher in the Chalk than in the arenaceous and argillaceous sediments of the Crag and glacial deposits, and appears to be limited by solubility controls of two different mineral phases. The mobility of the trace element As is seen to be greater in the Crag and Quaternary sediments, which may be due a greater source term (i.e. more As mineralisation in the aquifer), but will also reflect conditions more generally favouring the aqueous transport in the aquifer units. It can be seen that there is very little regional difference between the Crag and Quaternary aquifer units, and that the intra-aquifer variations in major and trace element chemistry are greater than those between the aquifers. Notwithstanding the small sample size, these data also support the occurrence of more than one baseline system for the Quaternary aquifers (cf. Figures 6.18 and 6.19), with a variation in major and trace element chemistry as large as that found in the Crag aquifer.
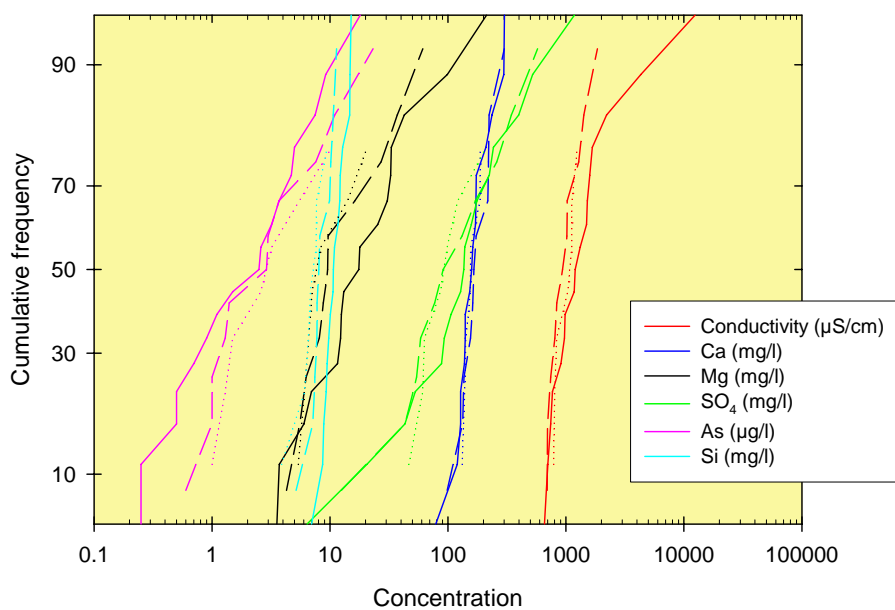
Figure 6.19   Cumulative frequency plot of different aquifers in the Waveney catchment

7. BASELINE CHEMISTRY OF THE AQUIFERS

7.1 Chalk

The calcium carbonate composition of the Chalk matrix dominates the major element chemistry of the groundwaters in all the samples collected in North Norfolk and the Waveney catchment. The waters contain significantly enhanced concentrations in comparison to rainfall (Section 3.5), showing that considerable water rock interaction has taken place. The proximal marine influence on recharge is reflected in the moderate, but higher Cl and SO_4 concentrations in the modern groundwaters of the North Norfolk coastal than those observed in other similar boreholes from other baseline aquifer regions (e.g. Shand et al., 2003). The low-Mg calcite of the matrix gives rise to waters which are predominantly Ca-HCO3 in their composition. The data indicate mixing of waters of an older age and more saline composition beneath the Palaeogene cover of the lower Waveney catchment. This study has been able to take advantage of a series of observation and sampling piezometers installed by the EA in the Waveney catchment, which has avoided a common problem in studying the Chalk aquifer, of most boreholes being situated in highly transmissive zones (e.g. Ander et al., 2004, Shand et al., 2003). These samples have a considerable cover of till and Crag sediments, before becoming confined by the Palaeogene clays in the lower part of the catchment, allowing mixing and increasing age to be observed, by major and trace element analysis and using isotopic indicators. Whilst ion exchange is commonly observed when Chalk aquifers become confined (Edmunds et al., 1987, Shand et al., 2003), there is no evidence for this process occurring the Waveney groundwater samples, from the samples collected. The samples from North Norfolk were from PWS or commercial boreholes, and thus generally reflected a more modern composition, although vertical and lateral variations in composition underneath till cover in this area have been published elsewhere (e.g. Feast et al., 1997, Hiscock et al., 1996).

The range of concentrations of major and trace elements is high across both areas of the aquifer, reflecting the variation in the degree of residence time, and thus water-rock interaction or mixing with older waters, observed. The concentration variations of many of the trace elements are (generally) adequately explained by natural processes, and are not thought to reflect contamination.

Whilst natural processes dominate the hydrochemical characteristics of these waters, the high concentrations observed of NO_3 in the Chalk of North Norfolk cannot be considered natural. In half the samples studied concentrations range between 3.0-11.9 mg l^{-1} NO_3-N, and 7.7 mg l^{-1} NO_3-N in one borehole in the upper Waveney catchment. These data are, with one exception, in excess of the baseline value of 2-4 mg l^{-1} NO_3-N suggested by Shand et al. (2003), and approach the present MAC for drinking water (11.3 mg l^{-1} NO_3-N). All reflect highly transmissive areas, with relatively low total solute concentrations, in comparison with other areas of the aquifer. The other samples all have very low concentrations of NO_3-N, which frequently reflects a reducing environment where NO_3 is removed by natural processes (see box 5.1). However, NO_3-N concentrations in this study are generally lower than those of the adjoining baseline area of the Great Ouse Chalk (Ander et al., 2004).

An understanding of spatial and temporal variations in the aquifer is important in assessing the local baseline. Spatial presentation of the data has facilitated this understanding. A previous pore-water study (Bath and Edmunds, 1981) provides useful information against which to compare the data obtained from pumped groundwaters, for a limited range of trace elements as well as for the major ions and some stable isotopes. The paucity of very long-term data with which to analyse historical variations hinders the understanding of any long-term effects of groundwater use or ingress of diffuse pollutants on the baseline quality currently observed in the aquifer.

7.2 Crag

The Crag aquifer is a heterogeneous (locally and regionally) series of intercalated sediments with locally abundant shelly material. The hydrochemical data indicates that the abundance of shelly material is sufficient to maintain the circum-neutral pH expected from calcite weathering, and thus exerts a strong control on the major element characteristics of the groundwaters of the Crag aquifer in North Norfolk and the Waveney catchment. Systematic variations are seen between the Waveney catchment where more argillaceous till covers the upper part of the catchment, and the EA piezometers, which provided the majority of the samples collected are screened off to a deeper sampling interval than it is thought that the public and private supplies in North Norfolk are. The waters are generally of a $Ca-HCO_3$ composition, with an evolution towards a $Ca-SO_4$ type observed in several of the samples collected in this study. Other regional studies have also observed saline mixing (Na-Cl types) as a result of the low-lying nature of the land surface of the Broadlands, resulting in areas where saline intrusion is occurring. Thus for the samples collected in this study, natural processes in the aquifer govern the major ion composition. The concentrations of Fe can be elevated locally which is likely to be due to the weathering of glauconitic material in the aquifer (the subsequent precipitation of insoluble Fe minerals when the groundwater becomes oxidised is responsible for the almost ubiquitous reddening of the sediments where they are exposed).

The range of concentrations observed is generally small, although where older samples, with very reducing environments occur in the deeper areas of Crag sedimentation in the Waveney catchment, concentrations of trace elements may increase. This is not found to be associated with mixing with a Na-Cl saline end-member, in contrast to the Chalk aquifer in the Waveney catchment.

Where the aquifer is confined by overlying argillaceous till, particularly in the Waveney, or protected by intra-formational clay horizons as is the case for the Ludham public supply in North Norfolk, concentrations of NO_3 are low (<0.7 mg l^{-1}). However, in shallow Crag private supplies of North Norfolk the concentrations is much higher (13.0-17.8 mg l^{-1} NO_3-N), exceeding what may be expected in truly baseline conditions and that of the present drinking water MAC of 11.3 mg l^{-1} NO_3-N (Shand et al., 2003). There is no historical data available to this study to assess whether the concentrations at these sources have remained unaltered for some period of time, or whether there is a systematic trend in their composition. It is suggested that these high concentrations do not reflect natural baseline conditions for this parameter in this aquifer.

The baseline data presented in this aquifer represents that of pumped groundwaters; in the case of those from the Waveney catchment a great deal of confidence exists as to their depth and thus the interpretation of the data with respect to that parameter. The siting of the EA piezometers was based on considerations of representative sampling of the aquifer, rather than water supply considerations. However, no information could be found on porewater compositions in the Crag, and it is recommended that such a study is undertaken, so that the baseline of matrix porewaters can also be established. 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 retard surface applied diffuse pollutants.

8.   SUMMARY AND CONCLUSIONS

The chemistry of groundwaters in the two aquifers studied in the Waveney catchment and North Norfolk are both dominated by natural geochemical processes taking place between the aquifer minerals and the groundwater. Most of the parameters measured in the groundwaters represent baseline. The reaction of carbonate minerals in the soil, unsaturated zone and saturated zone are key in the evolution of recharge and groundwater in both aquifers. In the Crag aquifer the much higher abundance of clay minerals than in the very pure Upper Chalk do not appear to have a substantial influence on the baseline chemistry of many elements in the shallow aquifer, where the groundwaters least affected by water-rock interaction were sampled.

It is suggested that in both aquifers more than one baseline system exists. In the Chalk, a variation between waters with a low concentration of solutes, where the chalk is unconfined and the boreholes are located in highly transmissive valley zones, to those where confinement by till or Crag shows a greater influence on the groundwater evolution, with a general increase in the concentration of many elements, to that of a mixing zone with old saline water in the most easterly samples, confined by the Palaeogene clays. In the Crag there are at least two baseline systems which have been sampled; those of a very shallow nature with the least chemical evolution as a result of water-rock interaction, but with the most vulnerability to surface applied diffuse contaminants (such as nitrate from agriculture and septic tanks). The second baseline system is one of waters with a far greater degree of hydrochemical evolution, as a result of a longer residence time in the aquifer. These waters are very reducing, with higher concentrations of trace elements, but no evidence of mixing with older saline waters.

Historical records are available from some public sources, providing time-series data for iron and manganese over a relatively short time period. Longer term time series data have not been found in this study, and would be extremely useful in establishing baseline concentrations for those solutes (particularly nitrate) which are elevated as a result of diffuse anthropogenic sources. The importance of establishing long term historical records for aquifers cannot be overstated, in order to permit the determination of baseline hydrochemical quality.

ACKNOWLEDGEMENTS

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