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Baseline Report Series: 23. The Lincolnshire Limestone

Groundwater Systems and Water Quality
Commissioned Report CR/06/060N

Science Group: Air, Land & Water
Technical Report NC/99/74/22



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

BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/06/060N

ENVIRONMENT AGENCY
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Cover illustration

Oolitic Lincolnshire Limestone, sample from Metheringham Quarry.

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

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

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

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

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer's physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use of 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 good quality groundwater.

1. EXECUTIVE SUMMARY

The Lincolnshire Limestone forms an important aquifer in the Lincolnshire area. The groundwater abstracted is used mainly for public supply, but also supplies agricultural, industrial and private needs. The area covered in this study includes the southern, central and northern Lincolnshire Limestone, although the project focuses on the Lincoln and Sleaford area. This report describes the regional variations in the baseline hydrochemistry of groundwaters and the dominant geochemical processes taking place in the limestone aquifer.

The Lincolnshire Limestone crops out in the west of the study area, but dips gently eastwards where it is progressively covered by younger deposits where confined conditions prevail. The direction of groundwater flow generally follows the direction of dip to the east. The Lincolnshire Limestone aquifer provides a good case study for examining the geochemical changes in groundwater chemistry which take place in the direction of groundwater flow and as such the hydrogeochemistry of the aquifer has been well-studied in the past. In addition to the effect of increased residence time permitting greater water-rock interaction, the geochemical processes of carbonate dissolution and equilibria, ion-exchange, redox reactions and mixing with old formation water are all significant in determining the groundwater chemistry in the aquifer.

Carbonate dissolution is the most important factor affecting the chemical composition of groundwater in the Lincolnshire Limestone in the unconfined and shallow confined part of the aquifer. Close to the recharge area, the groundwaters are oxidising and strongly pH-buffered with Ca and HCO_3 as the dominant dissolved ions. Distinct hydrochemical changes are observed down the hydraulic gradient as the aquifer becomes progressively more confined. Ion-exchange processes become significant and the groundwater chemistry evolves to a Na- HCO_3 type. Redox-sensitive elements document the onset of reducing conditions. Further along the direction of regional groundwater flow, deep within the confined limestone, mixing with old formation waters influences the water chemistry, resulting in a trend towards Na-Cl type groundwater. Distinct stable-isotopic compositions indicate long residence times in the order of several thousands to tens of thousands of years of age for these waters.

The majority of unconfined groundwaters in the region are affected by agricultural pollution, as indicated by high nitrate concentrations. In the confined groundwaters, where dissolved oxygen is low or absent, nitrate concentrations are lower reflecting either baseline concentrations or denitrification. A significant proportion of the groundwater in the confined part of the aquifer may represent pre-industrial water.

It is concluded that the hydrochemical properties of the groundwaters in the Lincolnshire Limestone are mainly determined by natural reactions between the rainfall-derived recharge and the limestone rock. Natural baseline concentrations for some elements are found to range over several orders of magnitude.

2. PERSPECTIVE

The Lincolnshire Limestone aquifer forms an important aquifer and represents the major carbonate aquifer in the Jurassic succession of eastern England. It forms an easterly dipping escarpment trending broadly north-south. The escarpment is cut through by the former glacial drainage channels of the Lincoln Gap and the Ancaster Gap. To the west of the escarpment the land is drained by the River Witham, which flows northwards before turning eastwards through the Lincoln Gap. The River Witham is channelised through Lincoln. To the south, the River Slea flows north eastwards through Sleaford. To the east of the escarpment, the low lying land is drained by a series of drainage channels (brooks, becks and dykes) which drain towards the east coast (Figure 2.1).

The Lincolnshire Limestone Formation is divided vertically into the Upper and Lower Lincolnshire Limestone. For management purposes, it is also often divided into three geographic areas: southern, central and northern, based on geographical, geological and hydrogeological variations. Most of the large abstractions tend to be located in the central or southern limestone areas.

The Lincolnshire Limestone aquifer is an important aquifer and it is predominantly used for public water supply: nearly 80% of total licensed abstraction is for public water supply. Much of the abstraction for public water supply occurs in the Sleaford area. Anglian Water plc obtain up to $7.6 \text{ Mm}^3 \text{ a}^{-1}$ from the aquifer via wellfields at Kirkby la Thorpe [TF 095 456], Aswarby [TF 067 391] and Drove Lane [TF 055 462]. Nearly 10% of licensed abstractions from the Lincolnshire Limestone in the area are for spray irrigation and about 9% of the total licensed abstractions are for industrial use. Farms form the bulk of the other licensed abstractors of groundwater in the region (Berridge et al., 1999).

The average annual rainfall varies from less than 600 mm at the base of the escarpment (both west and east) to 650 mm along the escarpment itself. Evapotranspiration is estimated to be between 430 and 510 mm per annum with over 80 % of total evapotranspiration occurring during the summer months. The winter rainfall is therefore the primary source of recharge to the Lincolnshire Limestone aquifer and average annual recharge is estimated to be between 167 and 195 mm (Berridge et al., 1999)

In the northern and central areas, there is relatively little cover of superficial deposits except in the river valleys. To the south the aquifer is partly covered by till, which has an important moderating impact on the recharge to the aquifer (this will be discussed further in Section 3.3)

Land use is dominated by farming, although there are some industrial areas present around the larger urban areas of Lincoln, Sleaford and Grantham. The aquifer is fractured and travel times can be very rapid. The nature of the aquifer coupled with the thin soil cover over the outcrop area means that it is vulnerable to pollution from the surface. The greatest current impact is from diffuse sources, predominantly nitrate and pesticides from agricultural activity. The unconfined Lincolnshire Limestone aquifer currently faces problems with high nitrate concentrations. Point source pollution from industrial activities, waste disposal and spills can have a devastating effect on individual abstractions. There are also concerns regarding over-abstraction, notably in the Sleaford area. The implementation of the Water Framework Directive has led to a recent review of the monitoring network for the region which was undertaken by Entec (2004).

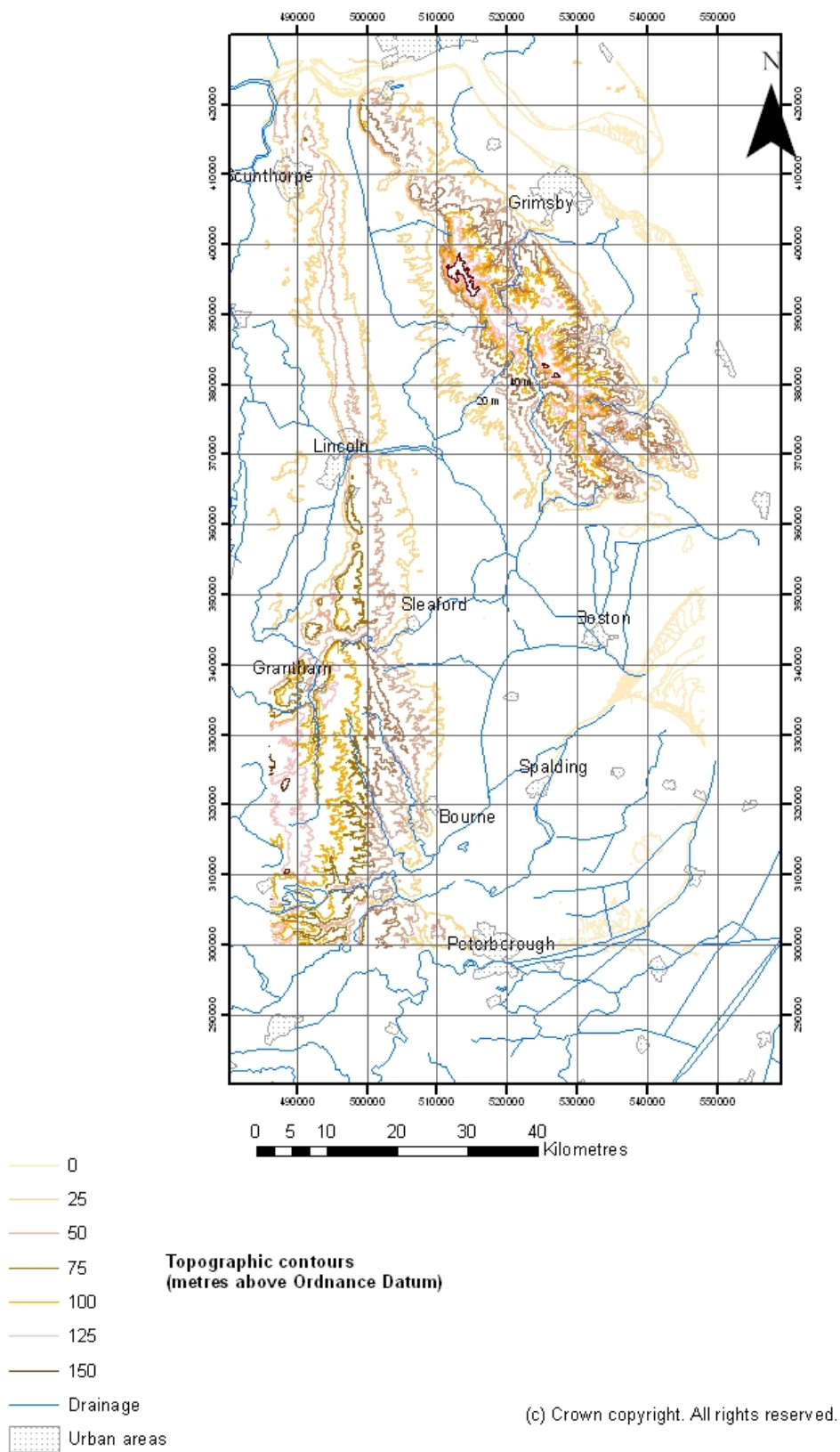


Figure 2.1 Topography and drainage in the Lincolnshire Limestone study area.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

In order to assess the baseline groundwater quality, it is necessary to understand the system within which the groundwater is contained. This requires information on the geological and hydrogeological properties, the mineralogy and geochemistry of the component minerals and the rainfall chemistry, to define the initial source term.

3.2 Geology

The Lincolnshire Limestone Formation is of Middle Jurassic age (Figure 3.1). The Formation is divided into the Upper and Lower Lincolnshire Limestone and the Upper Lincolnshire Limestone succeeds the Lower Lincolnshire Limestone unconformably. The Upper Lincolnshire Limestone has a variable thickness but is dominantly a coarse, shelly cross-bedded oolite. The Lower Lincolnshire Limestone is mainly a fine-grained, micritic and peloidal limestone (Allen et al., 1997). Ashton (1980) outlines the stratigraphy of the Lincolnshire Limestone Formation (Table 3.1). The sequence is transgressive and is believed to have been deposited during the landward migration of an offshore barrier complex across lagoonal and tidal flat deposits (Ashton, 1977; 1980).

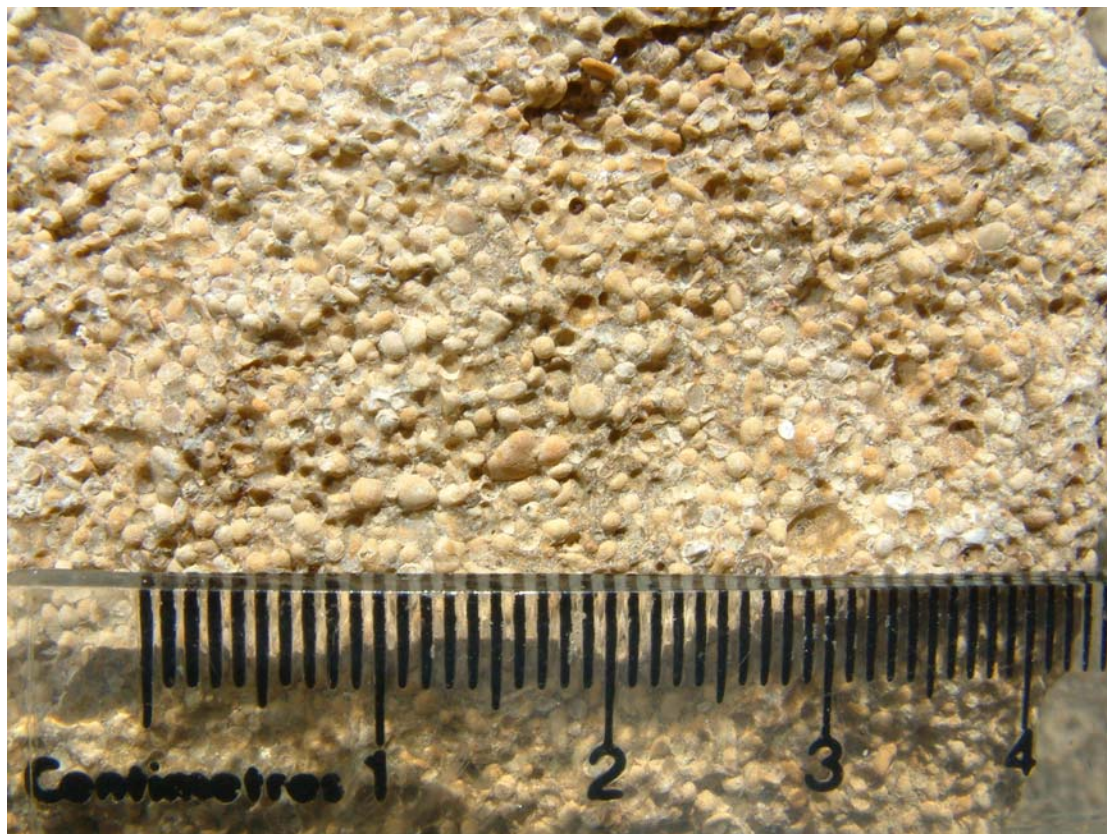
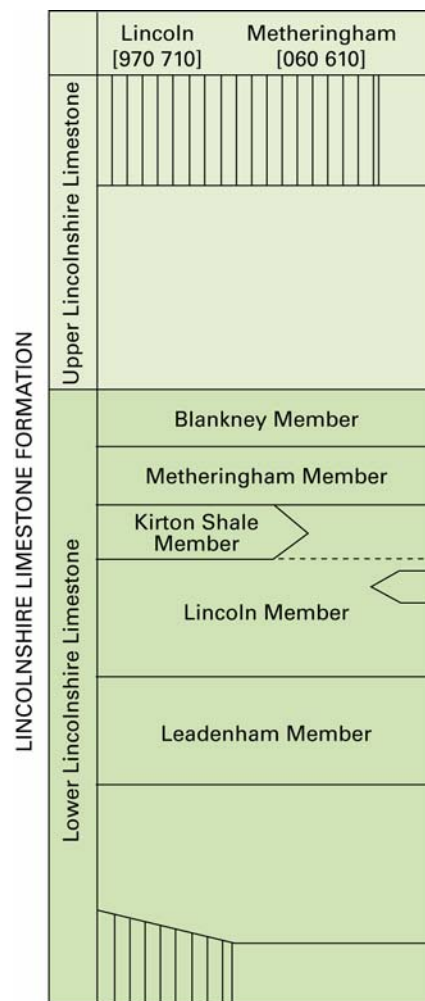


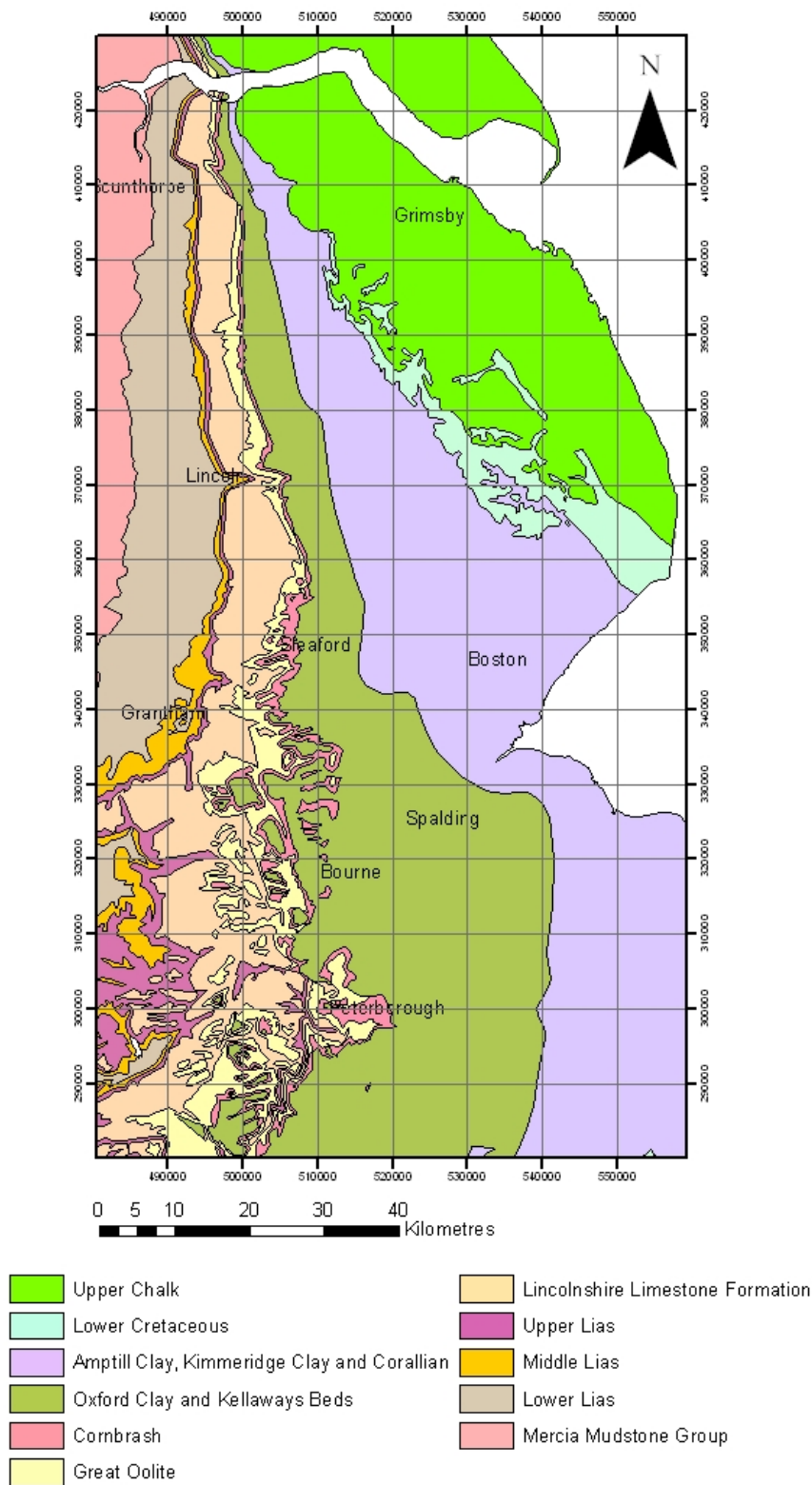
Figure 3.1 Oolitic Limestone

Table 3.1 Stratigraphy of Jurassic sequence in Lincolnshire (after Berridge et al, 1999).



The limestone outcrop extends broadly north-south in the west of the area from the Humber through Lincoln and Sleaford towards Grantham (Figure 3.2). To the east of the outcrop the limestone is overlain by mudstones, clays and limestones of the Upper Estuarine Series. Northwards, it passes into the Cave Oolite between the Humber and Market Weighton. The Formation is absent south of Kettering (Sylvester Bradley, 1968). The width of the outcrop ranges from 0.5 km on the outskirts of Ancaster to approximately 8 km elsewhere. The base of the limestone commonly lies only a few metres below the crest of the west-facing scarp slope of the Lincoln Edge, however the limestone is typically about 30 m thick, and reaches a maximum thickness of over 40 m in south Lincolnshire. There is considerable variation in the thickness of the individual beds and members. The Lower Lincolnshire Limestone varies in thickness between 15 m and 21 m and the Upper Lincolnshire Limestone is typically between 10 m and 16 m thick.

The Lincolnshire Limestone dips to the east at about 1° and is traversed by a series of west-east trending folds and associated faults. A monoclinical structure running through the Lincoln Gap has been detected from geophysical logs (Peach, 1984). A strike fault system running through Washingborough and Ruskington has an important impact on the hydrogeology of the Central Lincolnshire Limestone. North of Scopwick it marks the edge of the outcrop and serves to separate the outcrop from the confined part of the aquifer. In the Sleaford area, Peach (1984) reinterpreted borehole evidence and geophysical data and postulated that there are a series of en echelon faults which run west-east and culminate in the Syston-Dembleby fault. This structure seems to divide the central and southern Limestone areas and reduces the dip of the formation. The postulated fault through Sleaford provides a possible explanation for formation of the Ancaster Gap.



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Figure 3.2 Map showing solid geology for the study area

The unaltered limestone is typically grey in colour due to fine-grained iron sulphide (pyrite), but where it has been oxidised by migrating groundwaters it is buff-coloured or brown (Figure 3.3). The

oxidation of the limestone adjacent to fracture surfaces indicates the importance of fracture groundwater in the redox process and helps to highlight zones of groundwater movement, past and/or present. Fossil remains are abundant in parts of the sequence (Figure 3.4). The lithology of the limestone varies vertically and laterally: the Lower Lincolnshire Limestone is dominated by carbonate mudstones, wackestones and packstones whereas the Upper Lincolnshire Limestone consists of cross-bedded, ooidal grainstones with coarse-grained 'Rag' facies. Clay facies are better developed north of Blankney and a distinctive clay horizon called the Kirton Shale is well developed north of Scopwick but can still be detected as far south as Ruskington (Peach, 1984). The further north towards Hibaldstow, the more likely that the Lincolnshire Limestone will be acting as two separate aquifers, separated by the shale. The Upper Lincolnshire Limestone is an important building stone and there are a number of large quarries in the study area (Figure 3.5).



Figure 3.3 Samples showing differences in colour in the Lincolnshire Limestone. The sample on the left hand side is of the more oxidised buff coloured limestone where as the samples on the right hand side are less oxidised and grey in colour. All samples are from Metheringham Quarry.



Figure 3.4 Gastropod fossils in the Lincolnshire Limestone



Figure 3.5 Lincolnshire Limestone outcrop in Metherringham Quarry

Superficial deposits are poorly developed over much of the outcrop area of the Lincolnshire Limestone, particularly north and south of Lincoln (Figure 3.6). Till and morainic drift cover parts of the aquifer south-east of Grantham and may have a significant impact on recharge in these areas. Alluvium and river terrace deposits occur in the major valleys such as the River Sleaford and the River Witham.

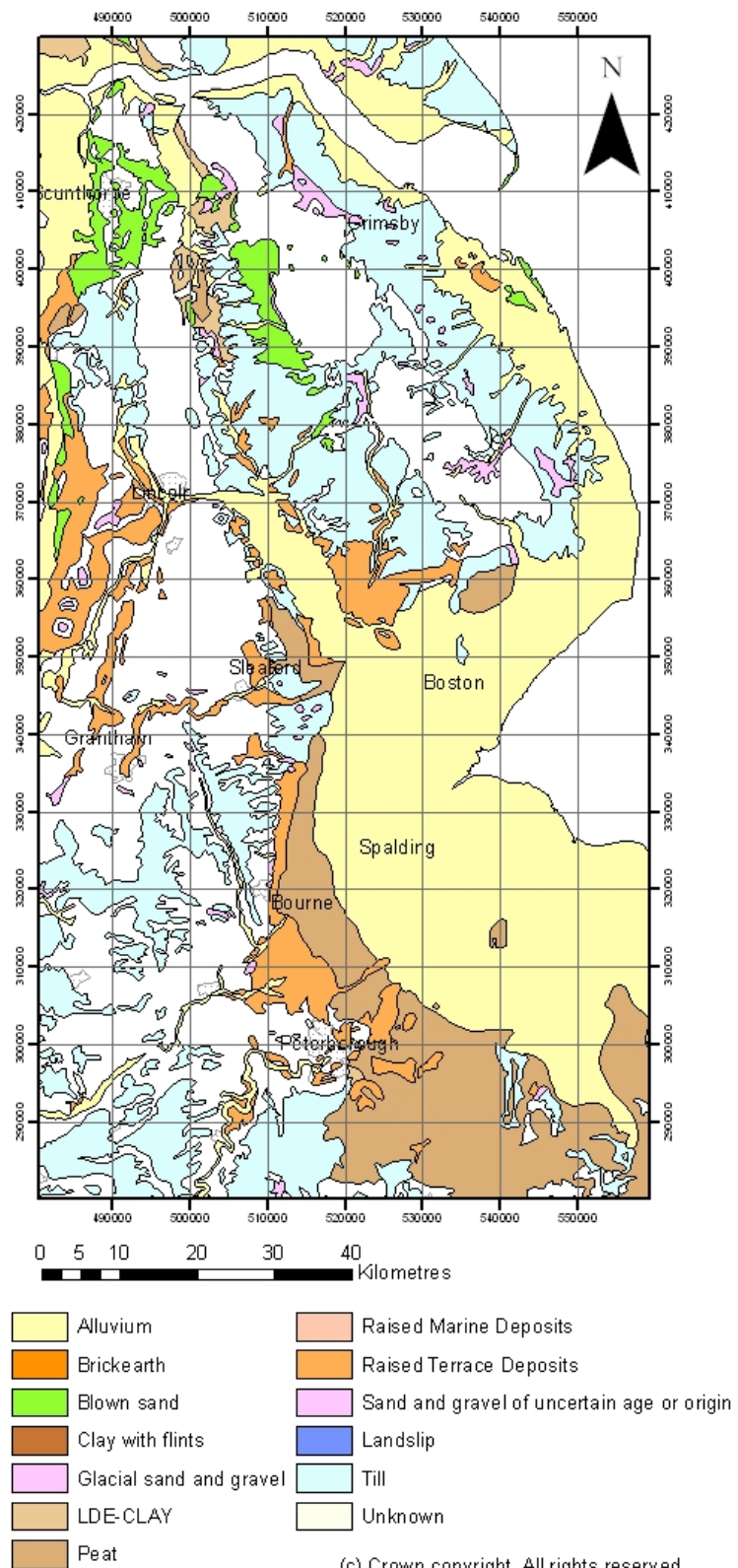


Figure 3.6 Superficial deposits in the study area

3.3 Hydrogeology

The Lincolnshire Limestone is a hard, fractured carbonate aquifer. The aquifer dips to the east and thins from more than 30 m thick at outcrop to less than 20 m in the east where it is confined by the overlying mudstones and clays of the Upper Estuarine Series. Groundwater movement occurs almost exclusively via fracture flow. The Lincolnshire Limestone is often in hydraulic continuity with the underlying Northampton Sand Formation, and boreholes into the Lincolnshire Limestone often extend through both aquifers.

The main recharge to the aquifer is direct rainfall recharge, however, focussed recharge through swallow holes is an important mechanism, particularly in the southern limestone area and influent seepage from rivers and streams also contributes. Spring lines occur along the top and base of the Lincolnshire Limestone. Natural discharge from the aquifer occurs via springs and effluent flow. The general direction of groundwater flow is down-dip. In the unconfined zone of aquifer, the water table declines from over 80 m above Ordnance Datum (m aOD) at the groundwater divide to less than 20 m aOD 10 km to the east. Further east, where the aquifer is confined by the Middle Jurassic clays, it becomes increasingly artesian in nature.

The compact oolitic limestones which form much of the formation have low primary intergranular porosity and permeability ($3 \times 10^{-4} \text{ m d}^{-1}$; Bird, 1974). The formation has a high secondary permeability resulting from fractures and micro-fractures of tectonic origin which have been enhanced by karstic weathering. The development of karstic features reflects long term changes in the base-level during successive Pleistocene glacial stages. Fracturing appears to be best-developed in the top few metres of the aquifer at outcrop (Rushton and Redshaw, 1979). Total porosity is estimated to vary from 13 to 18% (Edmunds and Walton, 1983). Groundwater movement therefore occurs predominantly by fracture flow and also along well-developed bedding plane fractures and joints. Transmissivity often exceeds $1000 \text{ m}^2 \text{ d}^{-1}$ but can be as high as 5000 to 10 000 $\text{m}^2 \text{ d}^{-1}$ (Downing et al., 1977) depending on the density, connectivity and dimensions of the fracturing. Pumping tests undertaken by Anglian Water at Kirkby la Thorpe, east of Sleaford, indicated a transmissivity of 700 to 1280 $\text{m}^2 \text{ d}^{-1}$. Production boreholes in the area typically yield around 2000 $\text{m}^3 \text{ d}^{-1}$.

Table 3.2 Summary of some of the hydrogeological properties of the Lincolnshire Limestone mentioned in the literature.

Author	Porosity (%)	Intergranular permeability (m d^{-1})	Transmissivity ($\text{m}^2 \text{ d}^{-1}$)
Allen et al. (1997)	13 to 18		
Bird (1977)		3×10^{-4}	
Edmunds & Walton (1983)		6×10^{-4}	
Rushton (1975)			100-250 (unconfined) 2000-10 000 (confined)
Downing et al. (1977)			Up to 10 000 (average 1500)

Water levels have been monitored at the Silk Willoughby borehole [0429 4273] since 1972. Seasonal variations in the rest water level in the Lincolnshire Limestone are typically of the order of 10 to 15 metres. These large seasonal head differences and the rapid response time of the aquifer have been successfully modelled by Fox and Rushton (1976) using the concept of “rapid recharge” whereby significant quantities of runoff access the aquifer directly via swallow holes and are then rapidly transported in the well-developed fracture system.

Extensive abstraction in the Bourne area and southwards has reduced the amount of water available to flow to the east. In 1977, water balance estimates suggested that the easterly flow was just 2 % of

average infiltration, however, there were uncertainties in the balance calculations.

Glacio-fluvial sands and gravels are important in the Lincoln and Ancaster Gaps, where they impact upon stream hydrology and aquifer storage (Figure 3.6). In the southern Lincolnshire Limestone, there is relatively extensive till cover, which reduces direct recharge, however, where swallow hole development occurs at the edge of the till, focussed recharge may occur (Downing and Williams, 1969).

3.4 Aquifer mineralogy

In addition to carbonate minerals, the Lincolnshire Limestone contains clays and carbonaceous material as a minor constituent. Pyrite and other ferrous minerals are finely disseminated throughout the grey limestone (Edmunds and Walton, 1983), but these have been oxidised in the brown limestone, the brown colouration being due to iron oxy-hydroxides.

Chemical analyses of limestone core (Lewin, 1988) showed that the rock can be divided into two broad classifications: pure oolitic limestones containing 90 to 96% (by weight) CaCO_3 and argillaceous limestones containing less than 36% CaCO_3 . The remainder is predominantly SiO_2 . MgCO_3 constitutes approximately 1.5% of the bulk rock composition (Emery, 1986). Organic carbon can be relatively high up to 5 % by weight of the limestone.

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharge waters and can be considered as representing minimum background concentrations at the present day. The nearest rainfall chemistry monitoring site in the National Air Quality Information Archive is Bottesford [NGR SK 797 376], which is located approximately 10 km to the west of Grantham. The data have been multiplied by 3 in the last column in order to represent the approximate enrichment due to evapotranspiration and hence chemistry of infiltrating rainwater. Although Cl may be assumed to behave conservatively during most recharge conditions, this is not the case for other elements e.g. K and N-species which may be taken up by vegetation, and concentrations may therefore be less in recharge waters than rainfall. Nevertheless, the table indicates the order of magnitude of concentrations expected in young waters, which have not interacted with vegetation, soils or aquifer minerals. For chloride, concentrations in recharge waters prior to anthropogenic influences or mixing with other waters would be expected to be around 5-6 mg l^{-1} .

Table 3.3 Rainfall chemistry data from Bottesford [NGR SK 797 376]. Data are for 2002 from The UK National Air Quality Information Archive (Hayman et al., 2004).

Parameter	Rainfall	Rainfall (x3) Enrichment by evapotranspiration
pH	4.90	
Na (mg l^{-1})	0.94	2.88
K (mg l^{-1})	0.11	0.33
Ca (mg l^{-1})	0.29	0.87
Mg (mg l^{-1})	0.13	0.39
Cl (mg l^{-1})	1.82	5.46
SO_4 (mg l^{-1})	4.34	13.02
NO_3 (mg l^{-1})	2.34	7.02

NH ₄ (mg l ⁻¹)	0.86	25.8
SEC (μS cm ⁻¹)	25.7	
Rainfall amount	614 mm per annum	

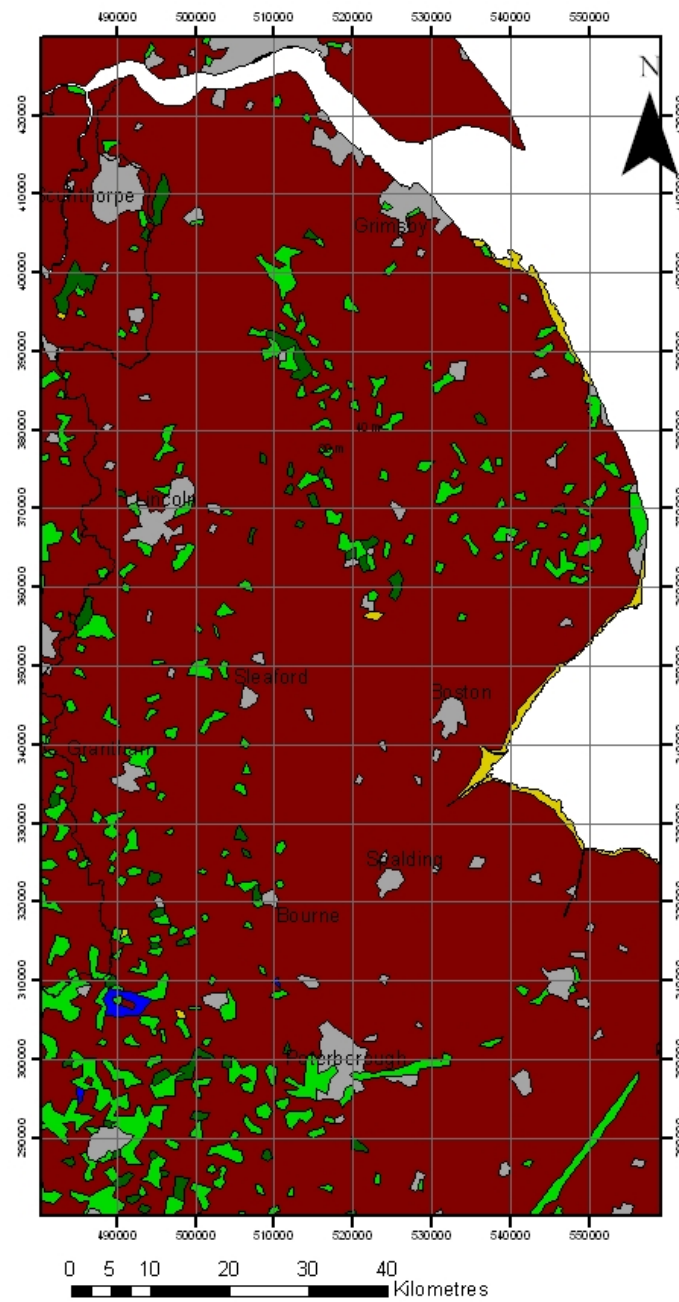
3.6 Landuse in the area

The dominant land use is arable (Figures 3.7 and 3.8). Managed grassland and forestry/woodland from a relatively small proportion of the landuse of the total area. There are several urban areas, notably Lincoln, Sleaford, Grantham and Bourne. An important landuse in the area which is not differentiated on the map but could have a significant impact on groundwater quality through drainage systems, is the large number of military airfields which are found in the area e.g. RAF Waddington, RAF Cranwell, Barkston Heath etc. There are also several industrial estates in the urban centres within the study area e.g. Lincoln, Sleaford etc.

Much of the region, particularly in the south and east of the study area is low lying fenland which is drained by a series of dikes (Figure 3.9).



Figure 3.7 Arable landuse is extensive within the study area



- Arable
- Managed grassland
- Forestry/Woodland
- Semi-nat. veg
- Urban
- Water
- No Data

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Figure 3.8 Generalised land use map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology ©NERC



Figure 3.9 Typical dike encountered in low lying fenland areas

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 23 samples were collected in July 2004 from public and private groundwater supplies from different sites across the study area. The samples were collected along two main transects running broadly from west to east from the outcrop area into the confined part of the aquifer with four further samples collected along a more southerly transect (Figure 4.1). The three transects are referred to as the northern, central and southern sections for the remainder of this report. The northern section includes 6 sites, is less than 5 km long and extends from Washingborough to Heighington Fen just to the south of Lincoln. The central section includes thirteen boreholes and extends 26 km south-eastwards from Cranwell Plantation located to the north east of Sleaford to Caythorpe Donnington in the Fens. The southern-most transect of just 4 sites extends approximately 26 km from Bitchfield (SK 983 285) to Deeping St Nicholas (TF 222 180). Although the northern and southern sections contained relatively few samples it was felt that it would be useful to include these sites so that we had some information on geochemical variations along the strike in the aquifer. The southern section lies largely in the area which has been extensively sampled by previous authors (e.g. Edmunds, 1973) so it seemed sensible to concentrate efforts elsewhere, particularly in the central limestone area where the aquifer is heavily utilised.

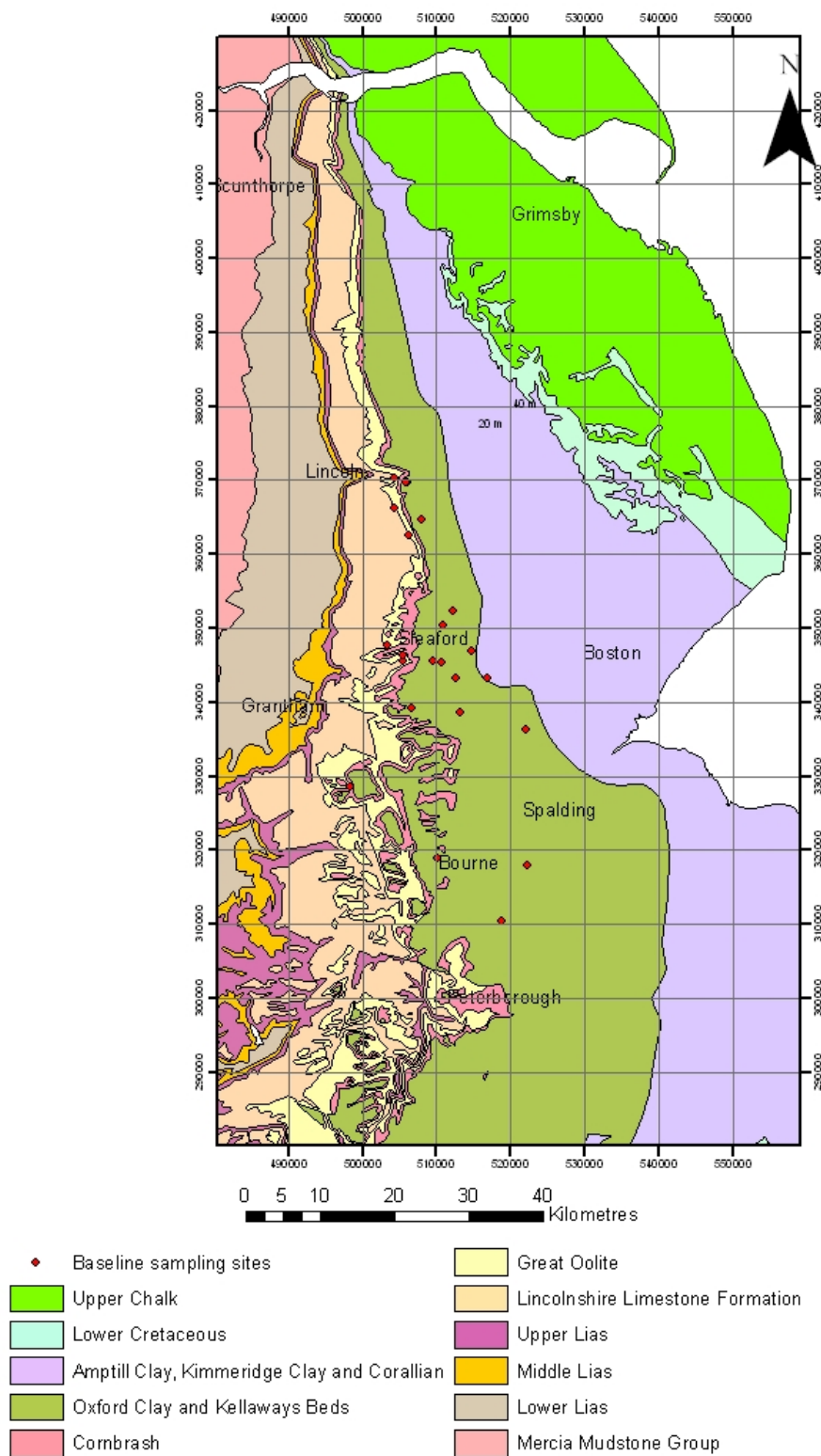
Many of the borehole samples did not lie directly along a transect line but were located on the transect at the distance at which they would intersect it.

Eight of the boreholes sampled were public water supply boreholes owned by Anglian Water. All of the other boreholes are Environment Agency monitoring network boreholes. Of the Environment Agency monitoring network boreholes all except three were artesian (Figure 4.2). These non-artesian boreholes (Bitchfield, Potterhanworth and Cranwell Plantation) were sampled with a portable pump after field measurements had stabilised (Figure 4.3). Washingborough Fen borehole was not sampled as the water level was lower than expected and the borehole was neither overflowing nor accessible without a pump. A couple of other boreholes visited were also inaccessible or had insufficient water in them to take a sample.

The pumped samples represent the sum of water coming into the borehole over the screened interval. Therefore, the sample may represent a mixture of waters with different chemistry, especially if the aquifer is vertically stratified. This may be the case, for example, if the aquifer shows strong vertical anisotropy or if the aquifer acts as a dual porosity medium.

At all sites, the parameters pH, DO and Eh were measured on-site in an anaerobic flow-through cell (Figure 4.4). Other on-site measurements included temperature, specific electrical conductance (SEC) and alkalinity. Samples were collected for major and trace chemical analysis in polyethylene bottles. Those for major and trace elements were filtered through 0.45 μm membrane filters and the aliquot for cation and trace elements was acidified to 1% v/v HNO_3 to preserve composition (i.e. prevent precipitation) and minimise adsorption onto container walls. Additional samples were collected in glass bottles for stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$).

Major cations and sulphate were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry and a wide range of trace elements by Inductively Coupled Plasma Mass Spectrometry. Nitrogen species and the halogen elements (Cl, Br, I, F) were analysed by colorimetry. Stable isotope analyses were completed by mass spectrometry and the results reported relative to the standards VSMOW for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and VPDB for $\delta^{13}\text{C}$.



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Figure 4.1 Location map showing sample sites and transects across the aquifer



Figure 4.2 **Artesian borehole at Asgarby**



Figure 4.3 Sampling at Potterhanworth borehole using pump



Figure 4.4 Unstable parameters are sampled using a flow through cell

4.2 Historical data

Historical water quality data were available for the area. In order to obtain a representative spread of samples over the study area, data were obtained from the Environment Agency's water quality database (WIMS). These data were limited to 1981 onwards and included many of the sites sampled as part of the Baseline project enabling changes in geochemistry with time to be examined.

Previous studies, notably Lawrence et al (1977), Edmunds and Walton (1983), Peach (1984), and Bishop and Lloyd (1990) provide good historical datasets from which hydrogeochemical changes with time can be examined. These changes will be further discussed in the section examining time variant trends in water quality.

4.3 Interpretation of pumped groundwater samples

When interpreting trends in regional water quality data it is important to bear in mind the variations in water quality that may arise between sampling boreholes due to:

- differences in borehole design and construction
- different stratigraphic horizons being tapped
- different pumping histories

4.4 Data handling

All plots and tables showing data are based on the new sampling programme with additional data (39 records) from the Environment Agency WIMS database unless otherwise specified. One WIMS analysis was selected for each site and the selection was made by choosing the most comprehensive) analysis from between 1994-1996 (i.e. most representative and comprehensive set of determinands). The WIMS data for boreholes which were sampled in the new programme were excluded. Only pumped samples were included. Where data are below the detection limit of analysis, a concentration equal to half the detection limit has been substituted for plotting and statistical purposes.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section deals with the fundamental hydrochemical characteristics of the groundwaters and Section 6 with controls and geochemical processes which determine and modify the groundwater chemistry, placing the variations in a regional context.

A summary of the hydrochemical data is shown in Table 5.1 for the study area. This shows the ranges and averages of data as well as an upper concentration (defined as mean plus 2 standard deviations or 97.7th percentile) which is used as a cut off to distinguish outlying data. The median is preferred to the mean as an average because it is more robust and less affected by extreme values. Summary statistics for the whole of the data set are presented and the data are divided between unconfined or confined part of the aquifer and the appropriate summary statistics provided. Samples were allocated to the confined or unconfined part of the aquifer according to location, field chemistry data and concentrations of redox-sensitive species. Comparison of the tables highlights the variations in baseline chemistry within the unconfined and confined parts of the aquifer.

The summary data are shown graphically on a Piper plot (Figure 5.1), box plots (Figure 5.2 and 5.3) and cumulative frequency plots (Figure 5.4 and 5.5). The box and whisker plots display the ranges of data and highlight the distribution of data on a percentile basis (the boxes show the range between the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles and the dots the 5th and 95th percentiles). In addition, the median is shown as a horizontal black line and the mean as a blue line within the box. The solid black line on the graph represents a diluted seawater curve which has been normalised to the median Cl concentration of the samples. This provides a general indication, in most aquifers, of enrichments due to water-rock interaction above the marine-derived rainfall input. The solid grey line on Figure 5.3 shows typical detection limits for each element. Cumulative probability plots are useful in visualising the distribution of data and may be of use in determining outlying data or discriminating pollution. Geochemical processes may alter the distribution of populations in several different ways (Box 5.1).

Piper Plot for Lincolnshire Limestone

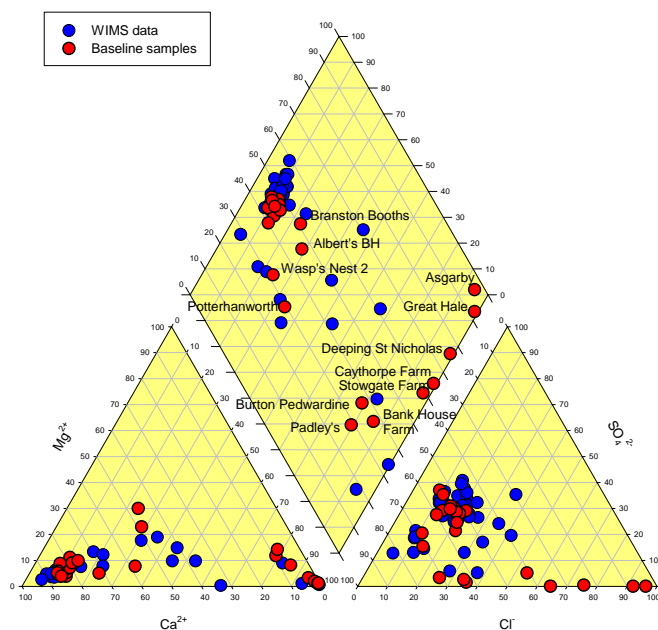


Figure 5.1 Piper diagram showing major ion concentrations and water types

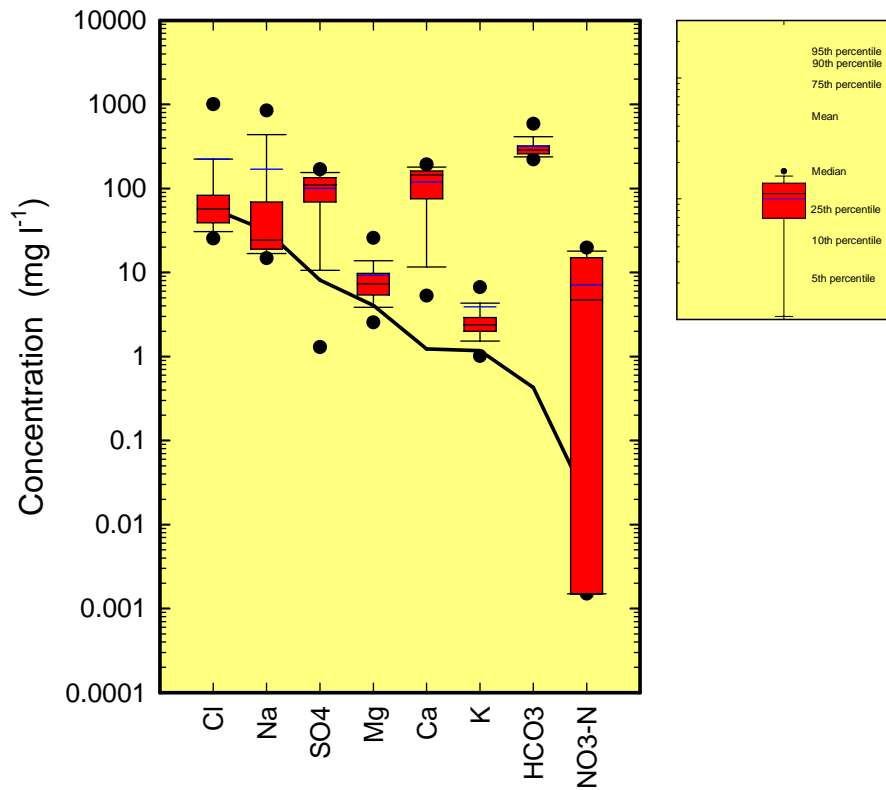


Figure 5.2 Range of major ion concentrations in the Lincolnshire Limestone

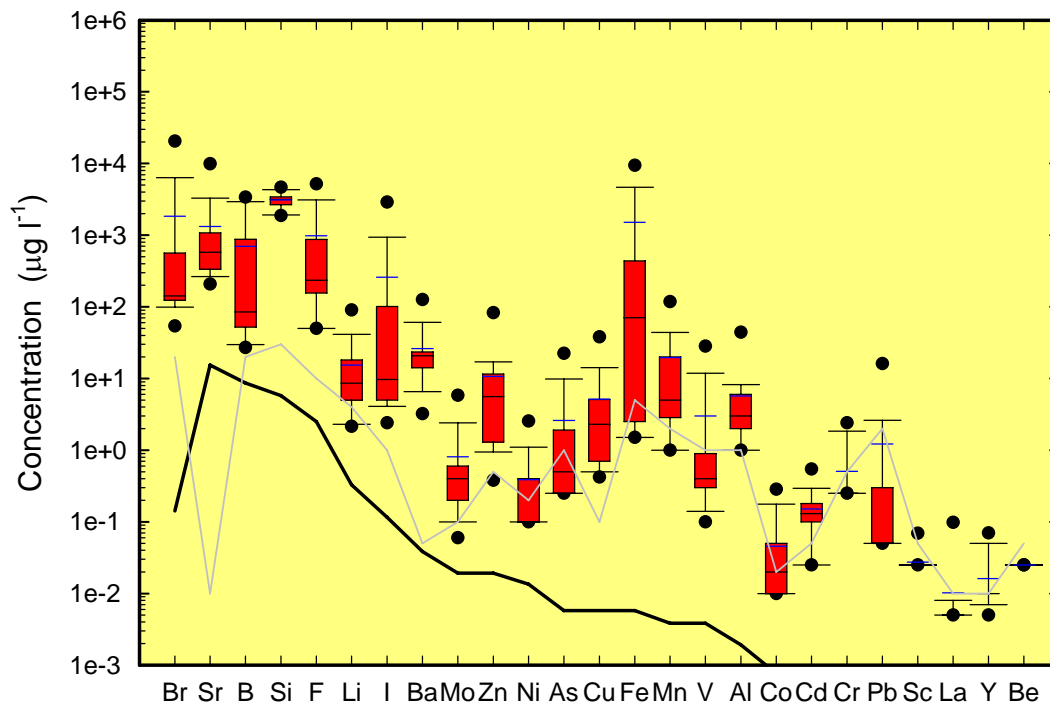


Figure 5.3 Range of minor and trace element concentrations in the Lincolnshire Limestone

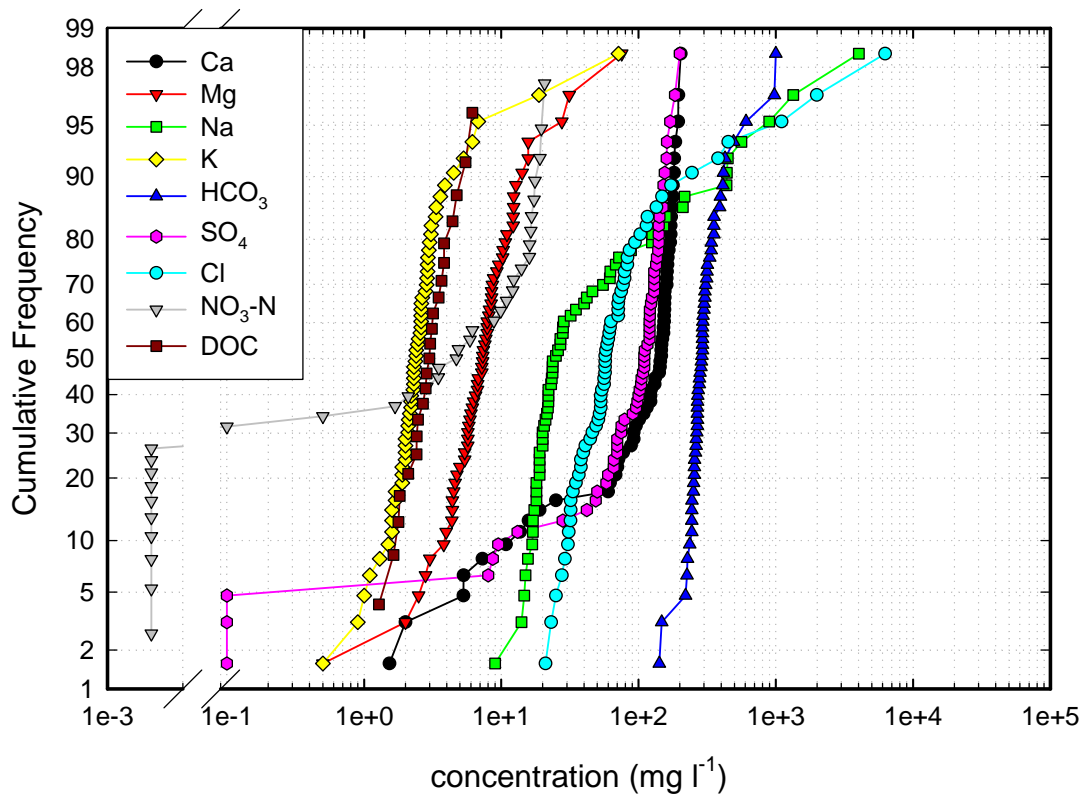


Figure 5.4 Cumulative probability plot for major ions

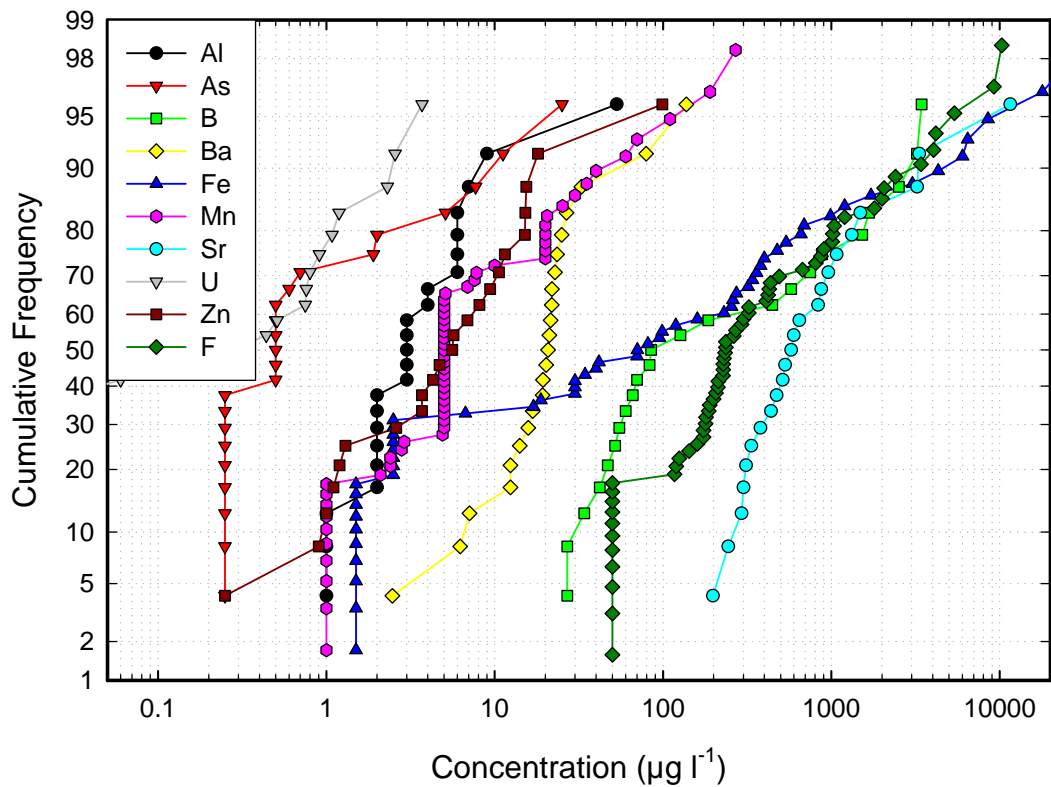
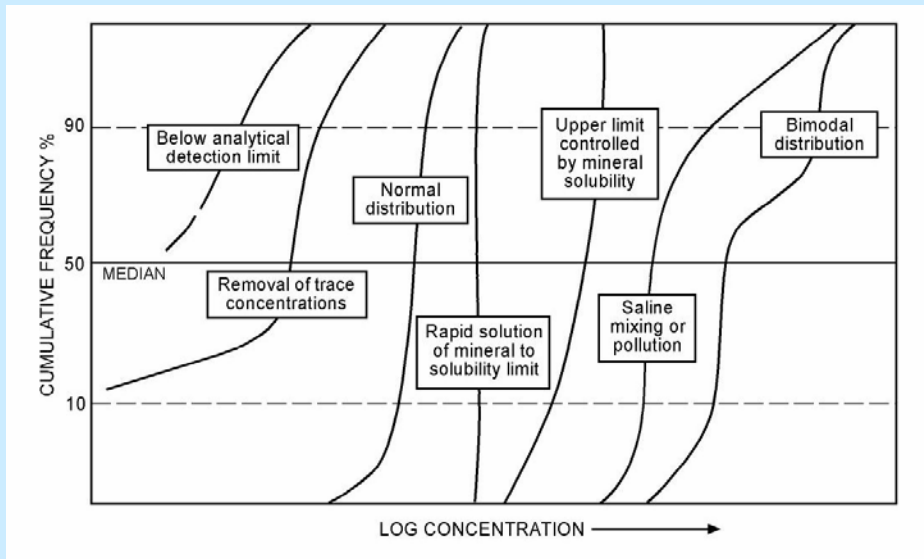


Figure 5.5 Cumulative probability plot for minor and trace elements

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



- i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.
- ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.
- iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).
- iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. N₂ by *in situ* denitrification).
- v) A narrow range in concentration at the upper limit may indicate a mineral solubility control (e.g. F by fluorite)
- vi) A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of natural higher salinity.

5.2 Water types and physicochemical characteristics

Groundwaters in the Lincolnshire Limestone aquifer show a wide range of characteristics in terms of physicochemical parameters and element concentrations (Table 5.1). The median temperature is 10.8°C although temperatures range from 9.6 to 14.7 °C. The pH of the waters ranges from 7.05 to 9.6 with a median value of 7.4. Redox potential (Eh) ranges from reducing to oxidising (–88 to 322 mV). Dissolved oxygen concentrations range from <0.1 to 8.1 mg l⁻¹, with a median value of <0.1 mg l⁻¹, which is indicative of reducing conditions over much of the aquifer (discussed in later sections).

The Piper diagram (Figure 5.1) shows there is a range of water types. The majority of the samples are of Ca-HCO₃ to Ca-HCO₃-SO₄-Cl type which are typical of shallow, fresh groundwaters. Several Na-Cl type waters (e.g. Asgarby and Great Hale) are also present, which are similar in composition to seawater but with lower SO₄/Cl and Mg/Na ratios (Figure 5.1). The third main set of groundwaters is represented by a trend towards Na-HCO₃ type and probably represent groundwater in which ion-exchange has had an important influence on the geochemical evolution. Many of the samples also lie intermediate between these three types.

Table 5.1 Summary statistics for field parameters, isotope data and major ion concentrations in the Lincolnshire Limestone.

Parameter	Units	Min			Max			Median			Mean			97.7th percentile			95th percentile			N		
		All	Confined	Unconfined	All	C	U	All	C	U	All	C	U	All	C	U	All	C	U	All	C	U
T	°C	9.6	10.0	9.6	14.7	13.7	14.7	10.8	11.2	10.4	11.0	11.4	10.6	13.6	13.4	13.0	13.0	13.1	11.7	50	23	27
pH	field	7.1	7.3	7.1	9.6	9.6	8.5	7.4	7.7	7.3	7.6	7.9	7.4	9.1	9.3	8.4	8.9	9.1	8.1	61	29	32
Eh	mV	-188	-188	80	322	194	322	113	-5	135	74	17	148	257	193	291	194	193	256	23	13	10
DO	mg l ⁻¹	<0.1	<0.1	0.2	8.1	2.3	13.1	<0.1	<0.1	5.9	1.8	0.4	6.0	8.0	2.3	12.0	<0.1	2.3	10.7	23	18	30
SEC	µS cm ⁻¹	610	610	738	20500	20500	1090	894	841	917	1446	2000	927	6067	11542	1066	2307	5949	1048	62	30	32
d2H	o/oo	-60.3	-60.3	-53.8	-45.8	-45.8	-50.7	-52.8	-54.1	-52.4	-53.0	-53.6	-52.3	-47.8	-46.9	-50.7	-49.8	-48.2	-50.8	23	13	10
d18O	o/oo	-8.9	-8.9	-8.4	-7.7	-7.9	-7.7	-8.0	-8.2	-7.9	-8.1	-8.3	-8.0	-7.7	-7.9	-7.7	-7.7	-7.9	-7.7	23	13	10
d13C	o/oo	-15.9	-12.4	-15.9	-1.1	-1.1	-8.8	-8.1	-5.3	-10.3	-8.2	-5.7	-11.4	-2.5	-1.9	-8.9	-3.9	-2.8	-9.1	23	13	10
Ca	mg l ⁻¹	1.53	1.5	95.5	203.0	153.0	203.0	145.0	74.2	161.5	119.5	72.8	163.2	194.6	149.0	197.3	184.9	145.7	194.5	62	30	32
Mg	mg l ⁻¹	0.50	0.5	2.5	75.5	75.5	12.8	7.3	8.9	6.1	9.2	12.4	6.3	29.7	46.0	10.5	15.7	29.6	9.2	62	30	32
Na	mg l ⁻¹	9.00	14.7	9.0	4030.0	4030.0	62.1	24.4	70.1	21.7	169.7	325.2	23.8	1161.1	2235.8	61.9	554.3	1140.2	47.1	62	30	32
K	mg l ⁻¹	0.50	1.6	0.5	71.5	71.5	5.3	2.4	2.7	2.3	3.9	5.6	2.3	14.0	36.3	4.7	6.1	13.4	4.2	62	30	32
Cl	mg l ⁻¹	21.00	21.0	25.0	6250.0	6250.0	94.0	57.1	64.3	57.1	223.3	398.5	59.1	1631.3	3408.6	88.3	447.4	1589.5	84.4	62	30	32
SO ₄	mg l ⁻¹	<10	0.1	58.2	200.0	160.0	200.0	110.0	72.3	120.5	100.0	76.9	121.7	178.4	148.0	188.6	161.0	141.1	176.3	62	30	32
HCO ₃	mg l ⁻¹	141	148	141.4	1000	1000	353.5	288	295	268.2	319	368	272.6	826	983	343.1	489	809	338.4	62	30	32
NO ₃ as N	mg l ⁻¹	<0.001	<0.003	0.1000	20.70	3.4700	20.70	4.70	<0.003	11.50	7.12	0.307	10.80	19.79	2.650	20.12	19.20	1.688	19.53	37	13	30
NO ₂ as N	mg l ⁻¹	<0.001	0.0004	0.0004	0.0120	0.0071	0.012	0.0020	0.0008	0.002	0.0029	0.002	0.004	0.0082	0.006	0.010	0.0074	0.005	0.007	38	14	32
NH ₄ as N	mg l ⁻¹	<0.003	<0.003	<0.003	1.81	1.8100	0.210	0.04	0.2200	0.015	0.18	0.354	0.027	1.13	1.379	0.132	0.77	1.132	0.084	61	29	32
P	µg l ⁻¹	10	10	10	1287	250	1287	20	20	20	54	39	66	206	169	441	101	107	100	58	26	32
TOC	mg l ⁻¹	0.25	0.25	0.5	14.5	5.32	14.5	1.735	2.575	1.625	2.72	2.74	2.71	8.95	5.12	10.97	5.97	4.89	7.02	34	12	22
DOC	mg l ⁻¹	1.28	1.28	1.64	6.15	6.15	5.47	2.99	3.03	2.9	3.14	3.26	2.98	5.81	5.76	5.10	5.40	5.30	4.66	23	13	10
F	mg l ⁻¹	0.05	0.05	0.05	10.3	10.3	1.01	0.235	0.837	0.1765	0.98	1.84	0.18	7.68	9.59	0.52	4.16	7.50	0.32	62	30	32
Br	mg l ⁻¹	0.044	0.106	0.044	23.8	23.8	0.227	0.142	0.339	0.1315	1.84	3.16	0.13	15.59	19.32	0.21	7.27	14.07	0.20	23	13	10
I	mg l ⁻¹	0.001	0.001	0.002	0.006	0.006	0.0118	0.003	0.003	0.00515	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	23	13	10
Si	mg l ⁻²	1.87	1.87	2.57	4.7	4.7	4.04	3.16	3.25	2.97	3.10	3.11	3.08	4.60	4.64	3.91	4.45	4.58	3.75	23	13	10

Table 5.2 Summary statistics for minor ion concentrations in the Lincolnshire Limestone.

Parameter	Units	Min			Max			Median			Mean			97.7th percentile			95th percentile			N		
		All	Confined	Unconfined	All	C	U	All	C	U	All	C	U	All	C	U	All	C	U	All	C	U
Ag	µg l ⁻¹	<0.05	<0.05	<0.05	1.1	1.1	<0.05	<0.05	<0.05	<0.05	0.10	0.16	<0.05	0.76	0.92	<0.05	0.415	0.698	<0.05	23	13	10
Al	µg l ⁻¹	2	1	1	53	53	6	3	4	2	5.70	8.08	2.6	30.74	40.86	5.586	8.8	26.6	5.1	23	13	10
As	µg l ⁻¹	<0.5	<0.5	<0.5	25.1	25.1	0.6	0.5	0.7	0.375	2.59	4.28	0.385	18.07	21.26	0.5793	10.85	16.76	0.555	23	13	10
Au	µg l ⁻¹	<0.05	<0.05	<0.05	0.78	0.78	<0.05	<0.05	<0.05	<0.05	0.06	0.09	<0.05	0.42	0.58	<0.05	0.0565	0.348	<0.05	23	13	10
B	µg l ⁻¹	27	66	27	3442	3442	127	85	749	49.5	696	1188	55.6	3332	3382	118	3154.2	3311.8	108.1	23	13	10
Ba	µg l ⁻¹	2.47	2.47	14.09	137.44	137.44	24.95	20.73	21.12	20.47	26.1	30.8	20.1	108.1	121.4	24.5	74.732	102.616	23.987	23	13	10
Be	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	23	13	10
Bi	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	23	13	10
Cd	µg l ⁻¹	<0.05	<0.05	<0.05	0.59	0.59	0.2	0.13	0.13	0.165	0.15	0.16	0.1435	0.469	0.524	0.20	0.336	0.446	0.191	23	13	10
Ce	µg l ⁻¹	<0.01	<0.01	<0.01	0.06	0.06	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.040	0.049	0.01	0.019	0.036	0.01	23	13	10
Co	µg l ⁻¹	<0.02	<0.02	<0.02	0.3	0.22	0.3	0.02	0.01	0.035	0.05	0.03	0.06	0.260	0.190	0.25	0.209	0.154	0.192	23	13	10
Cr	µg l ⁻¹	<0.5	<0.5	<0.5	2.5	2.5	<0.5	<0.5	<0.5	<0.5	0.51	0.70	<0.5	2.247	2.362	<0.5	1.96	2.2	<0.5	23	13	10
Cs	µg l ⁻¹	<0.01	<0.02	<0.01	0.52	0.52	0.03	0.02	0.03	0.01	0.05	0.08	0.015	0.343	0.423	0.03	0.164	0.31	0.0255	23	13	10
Cu	µg l ⁻¹	0.4	0.4	0.6	43.8	43.8	4.5	2.3	2.7	2.2	5.14	7.35	2.27	29.38	35.93	4.23	15.02	26.7	3.915	23	13	10
Dy	µg l ⁻¹	<0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.012	0.016	<0.01	<0.01	0.011	<0.01	23	13	10
Er	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.005	<0.01	23	13	10
Eu	µg l ⁻¹	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	23	13	10
Fe	µg l ⁻¹	<0.03	<0.03	<0.03	30.1	30.1	8.53	0.0704	0.34	0.0025	1.52	2.73	0.57	15.20	23.37	7.05	6.866	15.524	3.8485	57	25	32
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	0.06	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.05	<0.05	0.025	0.039	<0.05	23	13	10
Gd	µg l ⁻¹	<0.01	<0.01	<0.01	0.03	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01	0.018	<0.01	23	13	10
Ge	µg l ⁻¹	<0.05	<0.05	<0.05	0.47	0.47	<0.05	<0.05	0.13	<0.05	0.09	0.15	<0.05	0.38	0.42	<0.05	0.29	0.362	<0.05	23	13	10
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	23	13	10
Hg	µg l ⁻¹	<0.1	<0.1	<0.1	0.8	0.8	<0.1	<0.1	<0.1	<0.1	<0.1	0.11	<0.1	0.4458	0.593	<0.1	<0.1	0.35	<0.1	23	13	10
Ho	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	23	13	10
In	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.04	<0.01	<0.01	0.023	<0.01	23	13	10
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	0.09	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	0.03	<0.05	0.06	0.07	<0.05	<0.05	0.051	<0.05	23	13	10
La	µg l ⁻¹	<0.01	<0.01	<0.01	0.12	0.12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.09	<0.01	<0.01	0.051	<0.01	23	13	10
Li	µg l ⁻¹	2.1	5.4	2.1	102	102	8.6	8.6	13.3	4.55	15.40	23.56	4.79	72.9	86.1	8.5	43.65	67.44	8.33	23	13	10
Lu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	23	13	10
Mn	µg l ⁻¹	<0.05	<0.05	<0.05	0.27	0.27	0.11	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.17	0.23	0.08	0.078	0.16	0.0645	57	25	32
Mo	µg l ⁻¹	<0.1	<0.1	0.3	6.7	6.7	0.6	0.4	0.2	0.4	0.81	1.11	0.41	4.52	5.51	0.60	2.4	4.12	0.6	23	13	10
Nb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	23	13	10
Nd	µg l ⁻¹	<0.01	<0.01	<0.01	0.02	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	<0.01	0.019	0.02	<0.01	23	13	10
Ni	µg l ⁻¹	<0.2	<0.2	<0.2	2.9	0.7	2.9	<0.2	<0.2	<0.2	0.39	0.22	0.61	1.99	0.70	2.53	1.1	0.7	2.09	23	13	10
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	0.025	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	23	13	10
Pb	µg l ⁻¹	<0.1	<0.1	<0.1	19.5	2.8	19.5	<0.1	<0.1	0.2	1.22	0.28	2.44	11.05	2.11	15.94	2.75	1.3	11.76	23	13	10
Pd	µg l ⁻¹	<0.2	<0.2	<0.05	0.5	0.5	<0.05	<0.2	<0.2	0.05	0.14	0.18	0.1	0.45	0.47	0.1	0.39	0.44	0.1	23	13	10
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	23	13	10
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	23	13	10
Rb	µg l ⁻¹	1.02	1.03	1.02	11.25	11.25	2.47	1.48	1.59	1.385	2.24	2.75	1.571	7.63	9.27	2.41	4.047	6.954	2.3485	23	13	10
Re	µg l ⁻¹	<0.01	<0.01	0.02	0.08	0.08	0.08	0.02	0.005	0.045	0.03	0.02	0.046	0.08	0.07	0.08	0.078	0.056	0.071	23	13	10
Rh	µg l ⁻¹	<0.01	<0.01	<0.01	0.03	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	<0.01	<0.01	0.018	<0.01	23	13	10
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	23	13	10
Sb	µg l ⁻¹	<0.05	<0.05	<0.05	0.08	0.08	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.05	0.06	<0.05	<0.05	<0.05	<0.05	23	13	10
Sc	µg l ⁻¹	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	23	13	10
Se	µg l ⁻¹	0.6	0.6	0.7	121.3	2.6	1.8	1.2	0.8	1.05	9.76	1.3	1.07	80.11	2.50	1.70	38.3	2.39	1.575	23	7	10
Sm	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	23	13	10
Sn	µg l ⁻¹	0.09	0.09	0.09	0.64	0.64	0.18	0.15	0.16	0.15	0.18	0.20	0.146	0.52	0.58	0.18	0.388	0.502	0.1755	23	13	10
Sr	µg l ⁻¹	197.9	334.7	197.9	11552.3	11552.3	645.3	577.4	959.6	345.0	1325.78	2048.88	385.8	7387.9	9280.8	631.2	3313.6	6614.3	614.7	23	13	10
Ta	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	23	13	10
Tb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	23	13	10
Te	µg l ⁻¹	<0.05	<0.05	<0.05	0.1	0.1	<0.05	<0.05	0.025	<0.05	<0.05	0.04	<0.05	0.095	0.097	<0.05	0.089	0.094	<0.05	23	13	10
Th	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.025	<0.05	<0.05	0.025	<0.05	<0.05	0.025	<0.05	<0.05	0.025	<0.05	23	13	

5.3 Major elements

The box plot (Figure 5.2) for major elements highlights the dominance of Ca and HCO_3 in most groundwaters. Median K, Mg and particularly SO_4 concentrations are also elevated above the marine-derived input to the system. The high median SO_4 concentrations in excess of the diluted sea water line implies that extensive water-rock interaction has occurred. The high median chloride of 57.1 mg l^{-1} indicates a source additional to the rainfall input. Nitrate ($\text{NO}_3\text{-N}$) concentrations display a particularly wide range from below detection limit to 20.7 mg l^{-1} which reflects the high nitrate concentrations of the unconfined aquifer and low concentrations within the confined aquifer. The cumulative frequency plot for major elements (Figure 5.4) shows that most major elements vary over two to three orders of magnitude, except HCO_3 and DOC which show a narrower distribution over one order of magnitude and $\text{NO}_3\text{-N}$ which varies over four orders of magnitude. DOC displays a broadly log normal distribution. Calcium and SO_4 display very similar shaped curves which appear to indicate a mineral solubility control (gypsum). The curve for $\text{NO}_3\text{-N}$ suggests a loss of NO_3 , possibly due to denitrification. All of the others curves show trends indicative of more than one population possibly due to saline mixing or pollution, and will be discussed in Chapter 6.

5.4 Minor and trace elements

The box plot for minor and trace elements highlights the wide range of concentrations present in the groundwaters (Figure 5.3). Although Br lies close to the seawater line determined using median Cl, most other elements are significantly higher than this.

Boron concentrations in the Lincolnshire Limestone samples taken as part of the Baseline sampling programme vary from 0.027 mg l^{-1} to 3.4 mg l^{-1} . Eight of the 23 samples have B concentrations in excess of 0.5 mg l^{-1} WHO Provisional Guideline Value. The maximum fluoride concentration was 10.3 mg l^{-1} , nearly seven times the EU maximum admissible concentration (MAC) of 1.5 mg l^{-1} , but the median value is 0.235 mg l^{-1} . Ten of the 64 samples exceed the EC drinking water limit for F of 1.5 mg l^{-1} .

Silicon displays a relatively narrow range of concentrations from 1.9 to 4.7 mg l^{-1} . Some of the trace elements have a relatively low median value but may occur locally in very high concentrations. Iodide ranges from 2 to $3340 \text{ } \mu\text{g l}^{-1}$ with a median value of $9.7 \text{ } \mu\text{g l}^{-1}$. Iron displays a large range in concentrations over several orders of magnitude, however the median Fe concentration is low 0.07 mg l^{-1} . Bitchfield has a concentration of $19 \text{ } \mu\text{g l}^{-1}$ and exceeds the EC drinking water level for Pb of $10 \text{ } \mu\text{g l}^{-1}$. The Asgarby borehole exceeds the EC Guide Level Ba concentration of $100 \text{ } \mu\text{g l}^{-1}$ but the median Ba concentration for all of the samples is $20.7 \text{ } \mu\text{g l}^{-1}$. Asgarby and Great Hale also exceed the EC drinking water standard for As of $10 \text{ } \mu\text{g l}^{-1}$ with concentrations of $25 \text{ } \mu\text{g l}^{-1}$ and $11 \text{ } \mu\text{g l}^{-1}$ respectively. However, the median As concentration is low ($0.5 \text{ } \mu\text{g l}^{-1}$). Asgarby also has relatively high concentrations of many other trace elements, notably Cu, Fe, Rb, and Sr. Asgarby, Great Hale and Deeping St Nicholas appear to exceed the EC drinking water level for Se of $10 \text{ } \mu\text{g l}^{-1}$, however high Se is not normal in reducing conditions. The elevated concentrations of Se are the result of interference effects with bromide which occur when analysing using ICP-MS in saline waters (Tirez et al, 2000). Albert's borehole has a relatively high Zn concentration of $99 \text{ } \mu\text{g l}^{-1}$, however the median value for all samples is $5.6 \text{ } \mu\text{g l}^{-1}$. In general the trace elements tend to be elevated in boreholes within the deep confined part of the aquifer e.g. Asgarby, Great Hale, Deeping St Nicholas and Caythorpe Donnington.

The cumulative frequency plot for minor and trace elements (Figure 5.5) shows that for many elements concentrations vary over 2 to 3 orders of magnitude and that Fe varies by up to 4 orders of magnitude. Most elements have a number of different populations within the data. Straight lines on the cumulative frequency plots at low concentrations are an artefact resulting from measurements that were below the detection limit.

It is possible that the high concentrations of Fe and other trace elements are due to the fact that the WIMS database includes results from analysis of unfiltered samples.

5.5 Pollution indicators

In order to determine baseline concentrations, it is desirable to study only pristine waters, avoiding polluted waters since these may alter baseline concentrations either directly by adding solutes or indirectly by promoting chemical reactions in the aquifer (Box 5.2).

It is generally difficult to obtain pristine waters, in part because waters may be sampled over a large screened interval where polluted waters are present at shallow depth or because diffuse pollution (especially agricultural pollution) is present in large parts of the aquifers, especially where unconfined. Boreholes affected by point source pollution have been avoided but most groundwaters in unconfined aquifers show the effects of agricultural pollution due to the application of fertilisers or pesticides over the past decades. Indicators of agricultural pollution are indicated by high nitrate concentrations and the presence of pesticides/herbicides (Box 5.2).

Nitrate concentrations are generally high over the unconfined part of the aquifer and decrease to the east as the aquifer becomes increasingly confined. It has been suggested that denitrification due to reducing conditions is a significant process (Edmunds et al, 1984; Lawrence and Foster, 1986). However, Bishop and Lloyd (1990) used isotope and hydrochemical modelling to suggest that substantial amounts of nitrate reduction had not occurred and that the low nitrate concentrations in the confined part of the aquifer are predominantly the result of lower nitrate inputs in the past.

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

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The aquifer has been the subject of numerous hydrochemical studies since the late 1960s: Downing and Williams (1969), Edmunds (1973; 1976), Lawrence et al (1976), Downing et al (1977), Edmunds and Walton (1983), Peach (1984), Bishop and Lloyd (1990) and most recently, Entec (2004). This Section will outline the geochemical controls and regional characteristics of the aquifer based in part on the samples collected but also taking into account the wealth of knowledge of the Lincolnshire Limestone which exists in the literature. The aquifer is well-studied largely because of its relatively simple structure at a regional scale and the large down-dip variations in hydrochemistry. Within the scope of this report it is only possible to provide an overview but for further information the reader is referred to the literature.

6.2 Chemical evolution along flowlines

In the unconfined part of the aquifer initial concentrations of many elements are largely controlled by atmospheric inputs, modified by evapotranspiration. Nitrate and sulphate concentrations may be influenced by any excess of agricultural fertiliser regularly applied in this intensively cultivated area. Groundwater becomes increasingly mineralised with depth and distance from outcrop as increased residence time allows for greater water rock interaction. The processes of solution, redox reaction, ion-exchange and mixing with saline formation water are occurring within the Lincolnshire Limestone aquifer. At outcrop the groundwater quality is likely to be hard but progressive softening occurs towards the east as the aquifer is increasingly confined by clay.

A number of previous studies of the Lincolnshire Limestone aquifer have looked at the chemical evolution of groundwater as it moves from the outcrop and recharge area of the aquifer eastwards into the confined part of the aquifer. The down-dip sequence within the aquifer may be divided into three parts: oxidising, reducing fresh, and reducing saline conditions.

Edmunds (1973, 1976) studied hydrochemical variations along a 28 km flow line in the southern Lincolnshire Limestone in 1969 and found solution, redox and ion-exchange reactions, sulphate reduction and mixing with saline formation water to all be important processes within the aquifer. Edmunds and Walton (1983) re-sampled the same aquifer profile after 10 years to look at hydrogeochemical evolution with time and found that the overall sequence was remarkably similar in both distance from outcrop and absolute concentration but that, close to the redox boundary, down-gradient increases in Ca, SO₄, Cl and NO₃ had occurred, together with a less abrupt redox boundary. Edmunds and Walton (1983) postulated that these changes were initiated by the migration of agricultural pollutants and that the results indicate that the aquifer has a considerable capacity for in-situ nitrate reduction.

In contrast, Peach (1984) found that in the northern Lincolnshire Limestone, modern recharge appears not to be flowing down dip to a large extent, as there was little evidence for high nitrate, sulphate, chloride or calcium groundwater downgradient. In the north, Peach described three ages of water with different origins:

- (i) relatively modern recharge water with leakage of high-Na water from the overlying Upper Estuarine Series (Thorncroft Sand);
- (ii) old recharge water, probably post-last glaciation to present;
- (iii) very old saline water, probably emplaced during Upper Estuarine Series times.

Figures 6.1 and 6.2 show the chemical evolution down-gradient for the three areas of the Lincolnshire Limestone aquifer: northern, central and southern (each represented by different coloured dots). The corresponding edge of the outcrop area for each section across the aquifer is represented as a dashed line in the same colour as the dots.

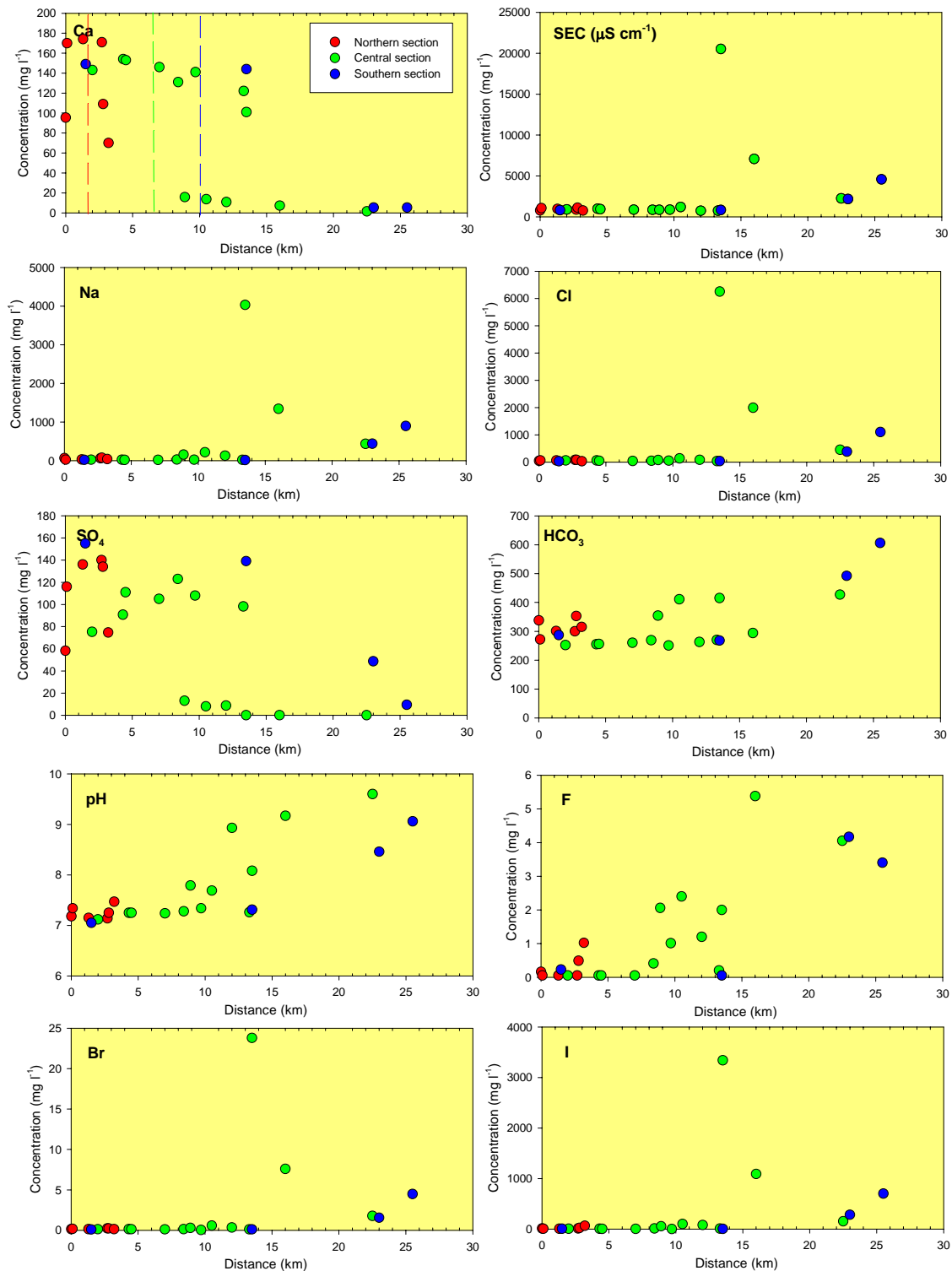


Figure 6.1 Variation in some parameters and major ions across the aquifer. Samples plotted across down-dip sections in the north, centre and south of the study area to illustrate geochemical evolution as groundwater moves downgradient from the outcrop area.

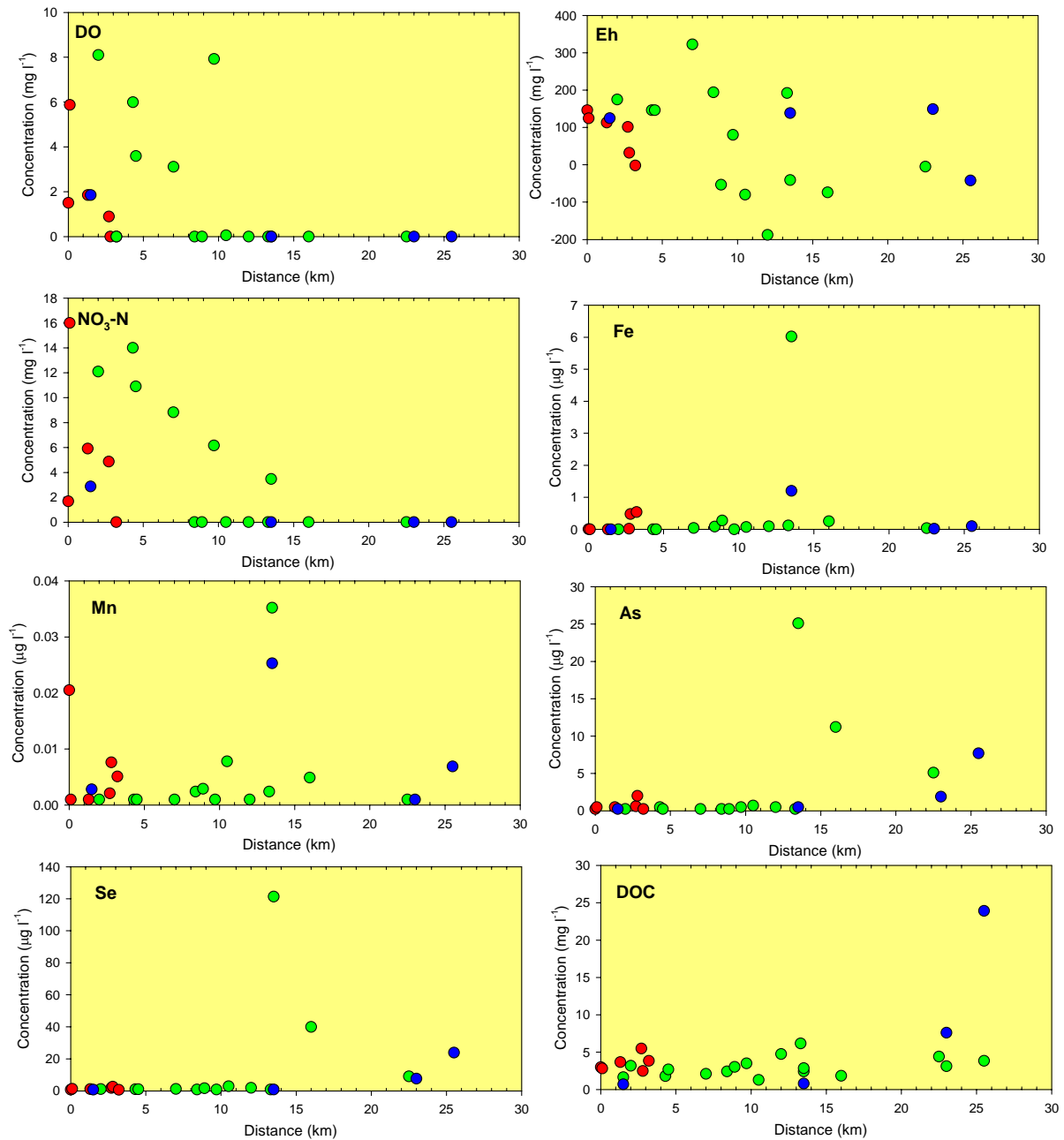
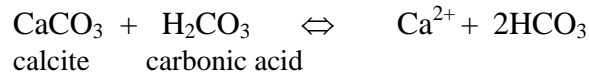


Figure 6.2 Variation in redox sensitive parameters and species across the aquifer. Samples plotted across down-dip sections in the north, centre and south of the study area to illustrate geochemical evolution as groundwater moves downgradient from the outcrop area.

6.2.1 Mineral dissolution reactions

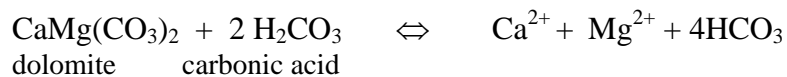
For aquifers containing carbonate or evaporite minerals as a matrix cement, the chemistry of groundwaters is strongly influenced by the rapid dissolution of these minerals. Infiltrating groundwater is often acidic due to the presence of carbonic acid derived from CO₂ production in the soil zone. However, where carbonates are present, this acidity is rapidly neutralised through dissolution of carbonate minerals e.g. calcite:



Carbonate dissolution is an important process in the Lincolnshire Limestone, particularly in the unconfined and shallow confined groundwaters. Carbonate reaction controls the pH as well as Ca and HCO₃ concentrations. In general, calcite saturation is rapidly determined at or near outcrop in carbonate aquifers. This was confirmed for the Lincolnshire Limestone by Bishop and Lloyd (1990) who showed that calcite saturation of outcrop groundwaters occurred at shallow depth in the soil zone. They found the δ¹³C ratios of outcrop groundwaters to be consistent with evolution under open-system conditions, although acknowledged the possibility that partial and simultaneous isotope exchange between soil CO₂ and soil carbonate could be occurring. Stable isotope ratios of soil carbonate also indicated significant re-precipitation of carbonate in the shallow soil zone. Bishop and Lloyd (1990) also studied secondary calcite on fracture surfaces and concluded that this was formed by incongruent dissolution of carbonate: dissolution of primary depositional carbonate followed by deposition of a more pure secondary carbonate.

The groundwaters sampled in this study are all saturated with respect to calcite and some of the deeper confined groundwaters are slightly oversaturated.

Dolomite dissolution is controlled by the following reaction:



Dolomite undersaturation occurs throughout the unconfined zone. In the central and southern areas at distances of more than 5 km into the confined part of the aquifer supersaturation with respect to dolomite occurs. The source of increased Mg in the latter cases is most likely to be due to incongruent dissolution of calcite.

The stable isotope of carbon (δ¹³C) can be used as indicator of the extent and type of carbonate reactions. There is a large range of isotopic compositions from -15.9 to -1.1 ‰. The more negative values are consistent with open system (in equilibrium with soil CO₂ of ca. -27 ‰) dissolution of calcite (bulk mean of +2.35 ‰; Bishop and Lloyd, 1990). Closed system dissolution leads to slightly more positive values of δ¹³C (depending on the initial pCO₂) as CO₂ is not replenished from the unsaturated zone. The trend towards values approaching the rock matrix indicates that incongruent dissolution and/or exchange with the matrix is important. The more positive signatures may be considered to relate to more extensive reaction and longer residence times. Although mixing with a formation water is considered to be important in some parts of the aquifer (section 6.2.3), it cannot explain the large changes in δ¹³C in low Cl groundwaters.

Selected major and trace elements are plotted against δ¹³C on Figure 6.3. Calcium and HCO₃ show different trends: HCO₃ shows a general increase, especially at high δ¹³C, whereas Ca shows the opposite trend. This implies that geochemical processes other than simple calcite equilibrium affect these species in the groundwater (discussed in section 6.2.3 and 6.2.4). The extent of incongruent dissolution can be assessed by the enrichment in Sr and Mg (trace constituents in calcite which are effectively removed from the matrix during reaction). Sr/Ca and Mg/Ca display a positive correlation with δ¹³C (Figure 6.3) indicating that incongruent dissolution with calcite in the matrix is a major control on δ¹³C in the groundwaters. The pH also increases and pCO₂ decreases (from 10^{-1.6} to 10^{-4.2}) as the groundwaters evolve along flow pathways. The pH also correlates extremely well with Sr/Ca and Mg/Ca (r² of 0.9 for both) indicating a strong relationship between carbonate dissolution and pH.

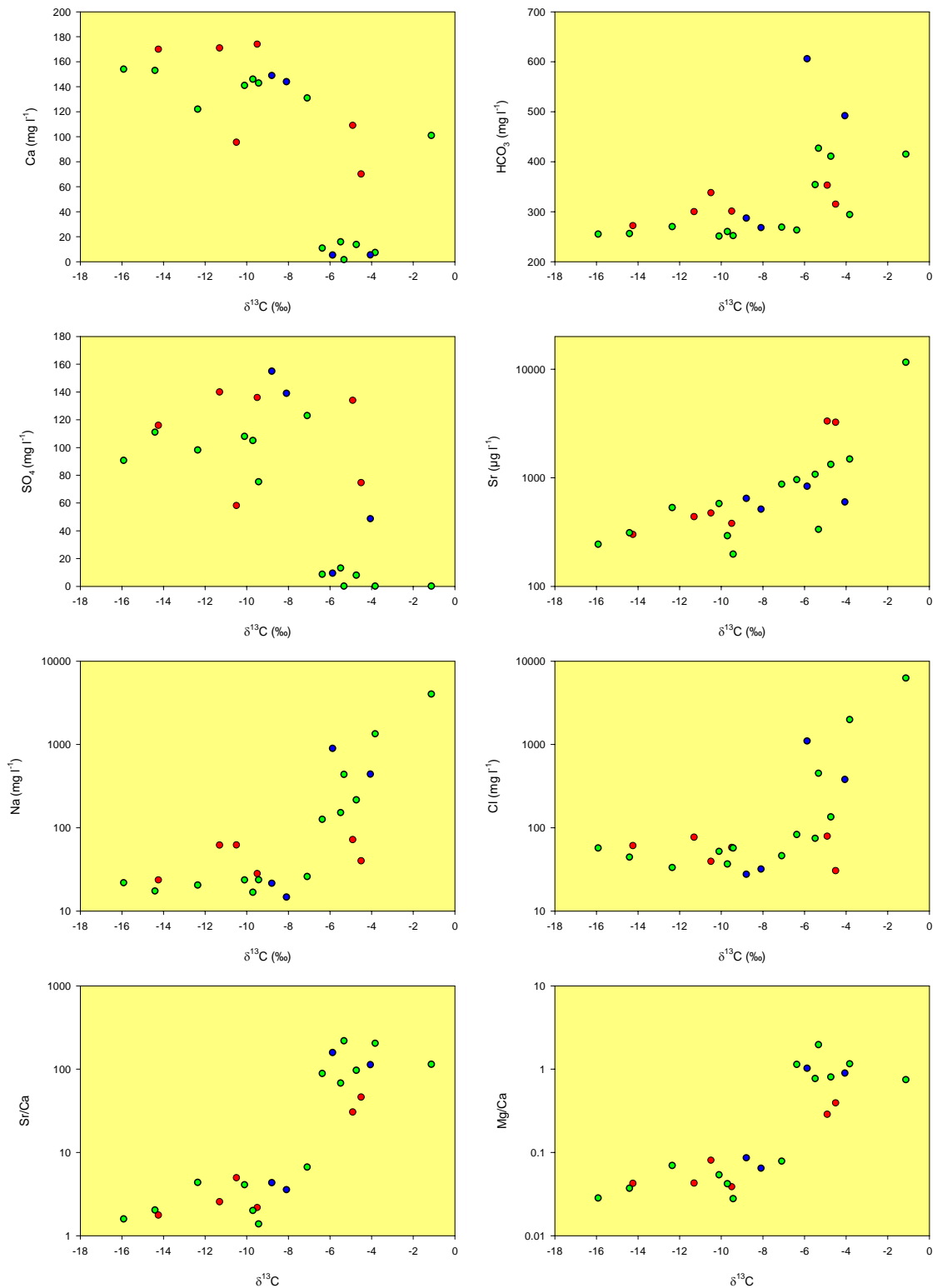


Figure 6.3 Selected major and trace elements plotted against $\delta^{13}\text{C}$

Silicon concentrations were generally low (maximum of 4.7 mg l^{-1}), and were close to saturation with respect to quartz. The Si is most likely derived from clay minerals present in the aquifer. The groundwaters were all undersaturated with respect to fluorite, although concentrations in the Na-

HCO₃ waters were high, several times EU drinking water standards (up to 5.4 mg l⁻¹; EU MAC 1.5 mg l⁻¹).

6.2.2 Redox reactions

The redox potential (Eh) and dissolved oxygen (DO) concentration provide the primary indicators of the redox status of natural groundwaters. These parameters are extremely sensitive to changes caused by contact with the atmosphere and were therefore monitored using a flow-through cell. Readings were monitored until they were considered to be stable.

As the aquifer becomes increasingly confined, dissolved oxygen becomes depleted due to redox reactions which are often microbially mediated. These include oxidation of organic carbon, finely disseminated pyrite and other ferrous minerals. According to Edmunds and Walton (1983), for the southern part of the aquifer Eh remains relatively high (+400 mV) in the shallow confined part of the aquifer, buffered by dissolved oxygen. Once contact with oxygen ceases, Eh falls by ca. 300 mV. This marked redox boundary has considerable implications for the subsequent down-gradient hydrogeochemistry. On the basis of the samples collected as part of this project the initial Eh values appear to be lower (+100 to +300 mV) and the reduction in Eh with distance down gradient less marked. The change in redox conditions is more obviously seen in the dissolved oxygen concentrations which are reduced to less than detection (< 0.1 mg l⁻¹) within a couple of kilometres of the aquifer becoming confined.

The decrease in nitrate concentrations down the hydraulic gradient (Figure 6.2) is consistent with denitrification: nitrate is only stable in the presence of oxygen. Although old (pre-intensive agriculture) groundwaters are expected to have lower concentrations, it is likely that recharge waters contain detectable nitrate. Edmunds and Walton (1983) observed that nitrate levels decrease gradually due to dispersion and in situ microbial reduction and become consistently low (<1 mg l⁻¹ as NO₃-N) once oxygen is below 0.2 mg l⁻¹ as NO₃-N (or even less). The samples collected as part of this study also follow this pattern.

Several of the low nitrate public water supply boreholes in the confined part of the aquifer are blended with high nitrate water from the unconfined part of the aquifer to produce water that is of potable quality. Investigations were undertaken by Lawrence and Foster (1986) to address whether this low nitrate water was under threat due to abstraction which might draw in nitrate and other inorganic pollutants to the confined part of the aquifer in a section of the aquifer from Grantham eastwards. They suggested that the penetration of nitrate and other pollutants is being strongly attenuated by diffusion into the limestone matrix and that where dissolved oxygen is absent, bacteriological denitrification is an important process.

The occurrence of denitrification is also supported by high levels of nitrate reducing bacteria (Downing et al, 1977; Peach 1984) and the geochemistry of nitrogen species (Towler, 1982). However, according to Bishop and Lloyd (1990) nitrate reduction does not appear to have had an observable impact on the overall carbonate or isotope chemistry of the shallow confined zone (their type 2 groundwater). Bishop and Lloyd (1990) suggest that the downgradient decreases in nitrate concentration therefore reflect lower past nitrate inputs rather than denitrification.

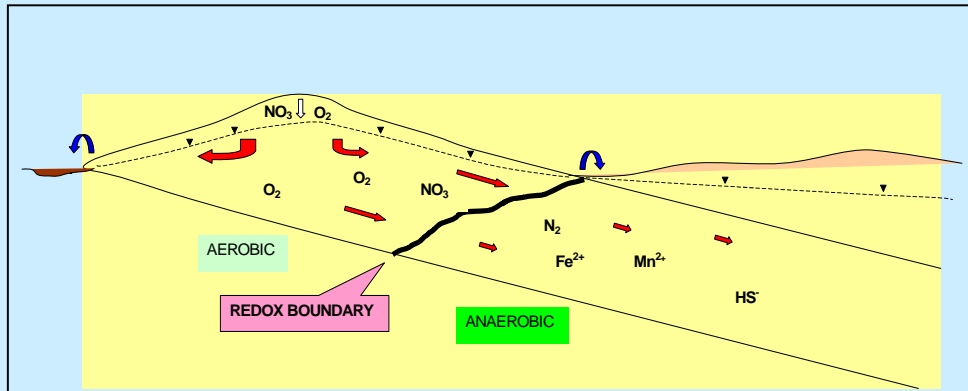
Sulphate concentrations also decrease down gradient (Figure 6.1) and for several samples sulphate was below the limit of detection. Edmunds and Walton (1983) observed a reduction in sulphate approximately 3 km to the east of the redox boundary and suggested that sulphate reduction rates were therefore fairly sluggish. Evidence from past studies for sulphate reduction in the Lincolnshire Limestone aquifer includes the detection of sulphide species in reducing waters (Edmunds, 1973; Lewin, 1988); the detection of hydrogen sulphide (H₂S) at well-heads down gradient of the redox boundary (also noted at several sites sampled as part of this project) and the presence of sulphate

reducing bacteria, albeit at relatively low concentrations (Downing et al, 1977; Peach 1984). However, Bishop and Lloyd (1990) suggest that sulphate reduction alone is unlikely to be responsible for the c. 100 mg l⁻¹ decrease in sulphate observed, as originally suggested by Lawrence et al. (1976). This is suggested because the fate of the sulphide has yet to be determined – there is insufficient dissolved iron to account for all of the sulphide; the rate of sulphate reduction is likely to be slow and the ¹³C ratios do not support significant sulphate reduction in zone 3. The lower SO₄ concentrations in the confined part of the aquifer may also be due to lower S- inputs in pre-industrial rainwater compared with modern S inputs in rain. Sulphate reduction and methanogenesis may however be important in affecting the isotopic and chemical compositions of the saline groundwaters (Bishop and Lloyd, 1990). The low sulphate waters analysed in this study are geochemically-evolved i.e. in waters with enriched δ¹³C (Figure 6.3) and high alkalinity (a consequence of sulphate reduction). Although sulphate reduction by organic matter produces lighter δ¹³C, this may be masked by incongruent dissolution or exchange with calcite. The driving mechanism for incongruent dissolution may well be ion-exchange which occurs in the deeper parts of the aquifer (section 6.2.3).

Iron concentrations are high in the reducing groundwaters, but may be removed from solution in very reducing waters where pyrite (FeS₂) becomes stable. Manganese concentrations are generally relatively low throughout the aquifer, with the exception of a couple of samples in the confined part of the aquifer.

In the central and southern sections, As and Se show an increase in concentration with distance from the outcrop area of the aquifer. However, this is likely to reflect, in part, analytical interferences by Cl and Br in the technique used (ICP MS). In the southern section, even though there are relatively few samples, DOC shows a progressive increase with distance from outcrop and therefore these elevated concentrations are unlikely to be the result of pollution. The Lincolnshire Limestone contains relatively high organic carbon providing the dominant reductant as groundwaters increase in residence time. However, other reducing species such as pyrite and ferrous iron are likely to contribute to redox reactions.

Box 6.1 Redox Boundary



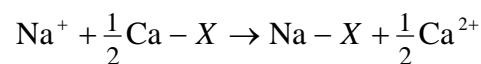
Water at recharge is generally saturated with dissolved oxygen at the partial pressure of the atmosphere ($10\text{--}12\text{ mg l}^{-1}$ depending upon barometric conditions). Passing through the soil and the unsaturated zone some of this O_2 will react as a result of microbiological processes and 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.

6.2.3 Ion exchange reactions

Downing and Williams (1969) attributed major element changes in the Lincolnshire Limestone aquifer to ionic replacement:

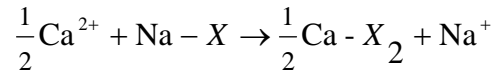
- (i) Unconfined zone. Solution reactions predominate. Ca-HCO_3 type water with significant SO_4 .
- (ii) Predominantly confined zone. Carbonate and non-carbonate hardness increase. Sulphate increases related to sink hole recharge close to edge of outcrop area.
- (iii) Confined zone. Ca , SO_4 and non-carbonate hardness peak, Carbonate hardness and bicarbonate decrease.

The majority of recharge groundwaters are dominated by Ca and HCO_3 ions owing to the dissolution of calcite. Cation exchangers within the freshened aquifer are likely to have a dominance of Ca adsorbed on to their surfaces. In aquifers containing formation water of Na-Cl type, Na and Cl are the dominant ions in solution, and exchange complexes will have largely adsorbed Na . When seawater intrudes a freshwater aquifer the following exchange takes place:



where X indicates the soil exchanger. Sodium is taken up by the exchanger and Ca is released which

alters the water chemistry from a Na-Cl type to a Ca-Cl₂ type. This process will operate in reverse if freshening occurs i.e. freshwater flushing through a salt water aquifer:



Here Ca²⁺ is taken up from the water and exchanged for Na, producing a Na-HCO₃ type water, (Appelo and Postma, 1994).

Edmunds and Walton (1983) observed Ca-Na exchange reactions occurring almost co-incident with the redox boundary, 12 km east of outcrop. This suggests a strong link with the reducing lithology of the aquifer, especially the clay and organic minerals which act as reactive exchange sites. Over the next 12 km down dip, Ca concentrations decrease but incongruent dissolution of the carbonate enhances Sr, and to a lesser extent, Mg. However once Ca/Sr and Ca/Mg ratios fall below critical levels then cation-exchange reactions dominate and Sr and Mg concentrations begin to decrease.

Calcium concentrations decrease (down to 1.5 mg l⁻¹) with increasing δ¹³C (chemical evolution), whereas Na increases (Figure 6.4). The increase in Na relative to Cl in some samples (Figure 6.5) and Ca removal is indicative of Ca-Na exchange as indicated on the Piper plot (Figure 5.1), although the increase in Cl is indicative of mixing in the most saline samples mixing.

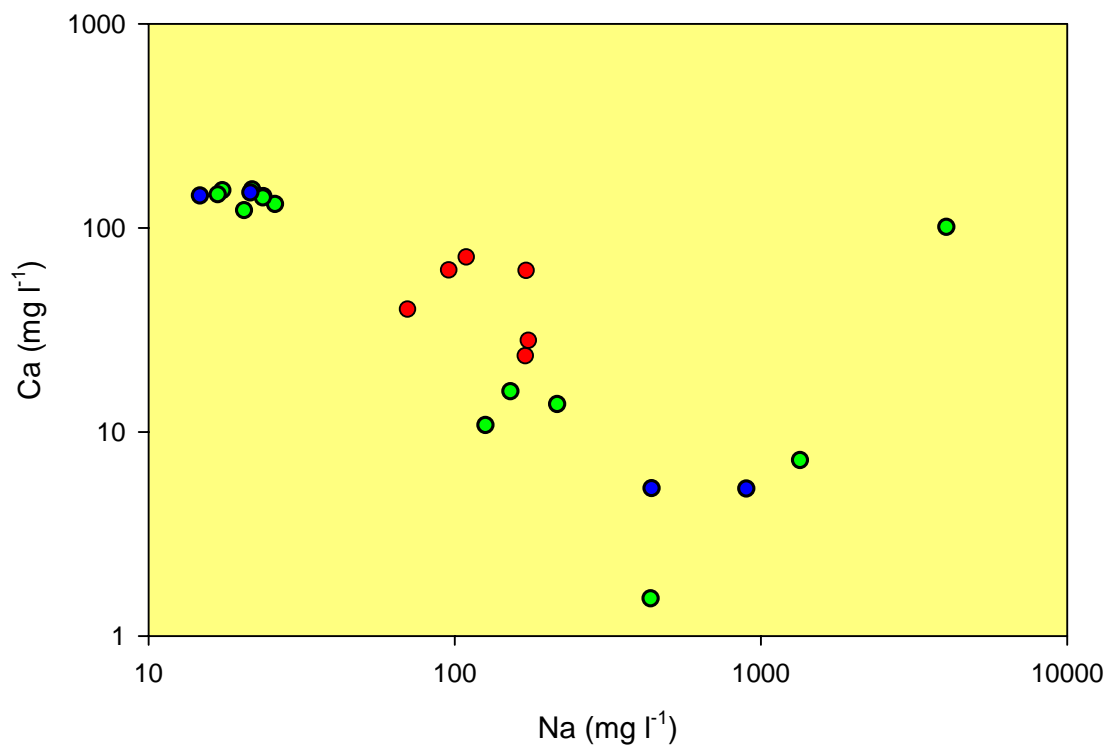


Figure 6.4 Na plotted against Cl

6.2.4 Mixing with older formation water

Mixing with an older, deeper connate or formation water is indicated by an increase in salinity, especially Cl in the deeper confined groundwaters. In all three sections across the aquifer, chloride increases with distance from outcrop. Edmunds (1973, 1976) observed that in the southern Lincolnshire Limestone chloride levels started to increase slowly, and then increased exponentially

about 18 km east of the outcrop area. This increase was attributed to the first appearance of saline formation water and also marked the limit of the 1969 detectable tritium limit. An increase in Na, in excess of that due to mixing with saline water, occurs along the direction of flow, especially at distances of more than 10 km from the recharge area.

The Br/Cl ratio is a useful indicator of the source of salinity (Edmunds, 1996). Figure 6.5 shows the Lincolnshire Limestone samples plotted with dilute seawater. It appears that most of the samples follow the sea water dilution line relatively closely. The samples which trend towards sea water Br/Cl ratio are those which are down gradient in the confined part of the aquifer. The one sample which has a low Br/Cl ratio is from Asgarby West. This borehole is located adjacent to the A17 dual carriageway and it may be that the elevated Cl is due to road salt. Some of the other sites seem to have slightly elevated Br/Cl ratios which can be indicative of evolution within an organic rich sediment or to anthropogenic inputs.

Using a value of 0.06 mg I^{-1} for I in sea water it can be seen that iodine is also relatively enriched in the Lincolnshire Limestone aquifer (8 of the 23 samples have I concentrations in excess of seawater). High I/Cl ratios are another possible indicator of an organic sedimentary influence (Edmunds, 1996).

Lawrence et al. (1976) stated that modern recharge water was mixing with an ancient, possibly connate water in the Lincolnshire Limestone aquifer. They conducted a detailed hydrochemical study of the 'interface zone' between the two water types. In the modern recharge water an increase in bicarbonate concentration was found to be associated with sulphate reduction as the "interface zone" was approached. This relationship was considered to be directly related to the mixing, however increasing HCO_3 may be due to oxidation of organic matter during sulphate reduction. The groundwater in the southern part of the Lincolnshire Limestone aquifer was found to fall into three main zones:

- (1) a zone which extends 10 to 20 km into the confined section, Ca- HCO_3 waters (Type I);
- (2) a narrow zone in which sodium becomes the dominant cation, bicarbonate is the dominant anion and where chloride becomes increasingly important, (Type II);
- (3) a zone in the eastern confined section of the aquifer, Na-Cl type (Type III).

Between zones 1 and 2 (Type I and II) the following changes take place over a relatively short distance:

- (1) decrease in Eh
- (2) increase in Cl and TDS
- (3) cessation of decreasing sulphate concentration
- (4) start of an increase in Na, increased rate of Ca decrease, and an increase in pH
- (5) start of an increase in HCO_3

Between zones 2 and 3 (Type II and III) the most significant change is a marked increase in the chloride and total salinity gradient which occurs where chloride concentrations exceed 250 mg I^{-1} . The Type II water occupies an area with a width of only 3 to 5 km which is indicative of abrupt changes in the groundwater chemistry with the characteristics of an interface zone (Lawrence et al, 1976). The Type II zone is therefore considered to be the product of mixing between Type I and III water.

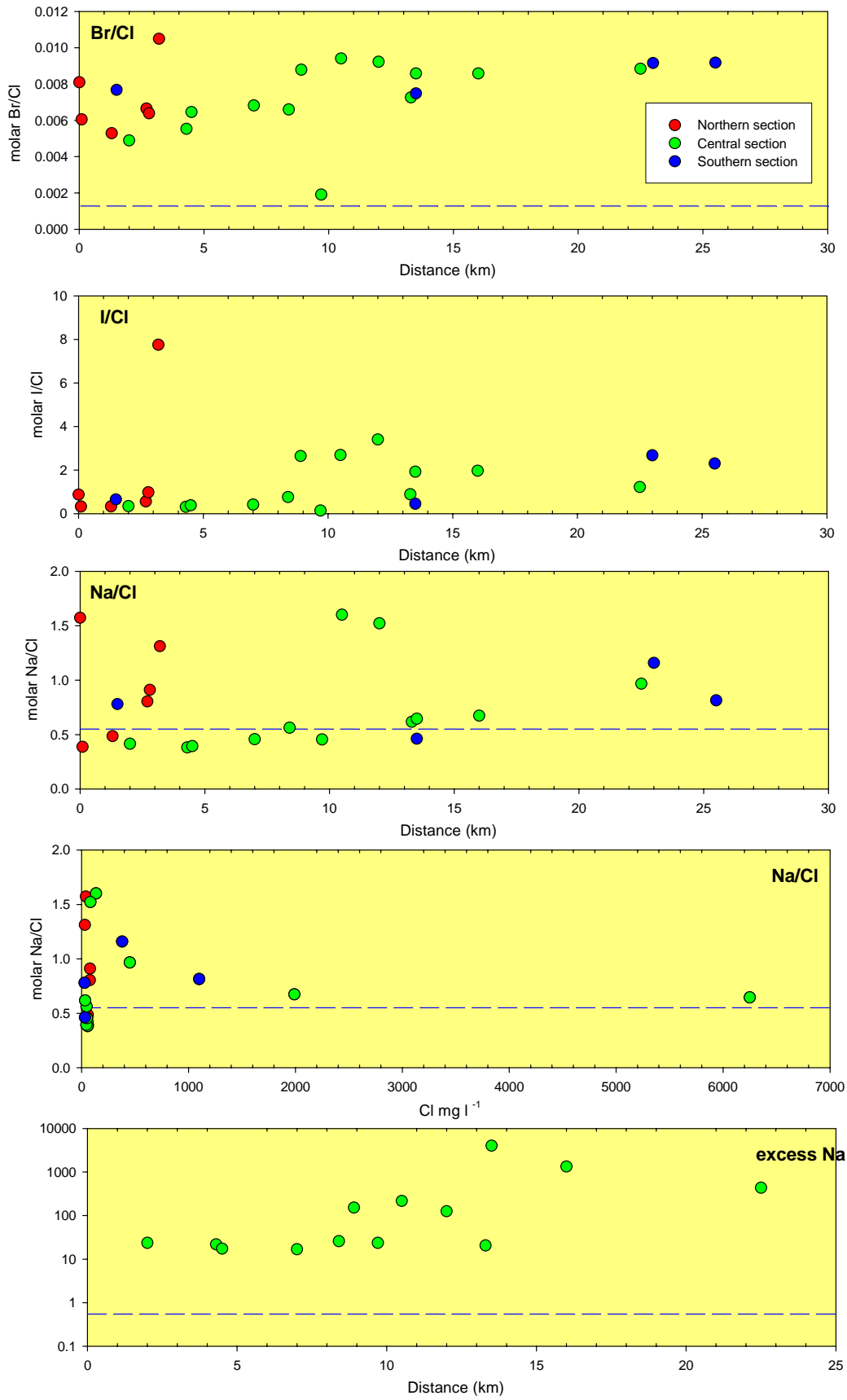


Figure 6.5 Br/Cl, I/Cl and Na/Cl plots. Blue dashed line indicates seawater ratios. Excess sodium is also calculated.

Bishop and Lloyd (1990) noted that mixing between fresh and saline waters is coincident with the onset of ion-exchange conditions within the aquifer. As will be described in Section 6.5 there is some uncertainty regarding the chemical composition and origin of the saline end-member. Bishop and Lloyd (1990) state that overall consideration of the isotopic and hydrochemical data point toward ancient saline groundwaters ($>250 \text{ mg l}^{-1} \text{ Cl}$). Downing and Williams (1969) suggested that the saline water was connate and this hypothesis was supported by evidence from Andrews and Lee (1980). Emery (1986) proposed that the saline end-member was the product of water-rock interaction. Smalley et al (1988) suggested that it was more likely to have evolved as Pliocene or younger seawater, or as a high ionic strength solution evolved by diffusion or by expulsion from the argillaceous confining and down-dip beds. Downing et al. (1997) suggest the further possibility that the saline groundwaters have evolved by cross-formational flow from the confining sequences.

There is a general decrease in $\delta^{18}\text{O}$ when plotted against Cl concentration (Figure 6.6) which indicates that mixing with a modified seawater cannot explain the variation in Cl. Mixing with seawater or a chemically modified seawater ($\delta^{18}\text{O} = 0$) would produce the opposite trend. There appears, therefore, to be a source of salinity within the Lincolnshire Limestone aquifer.

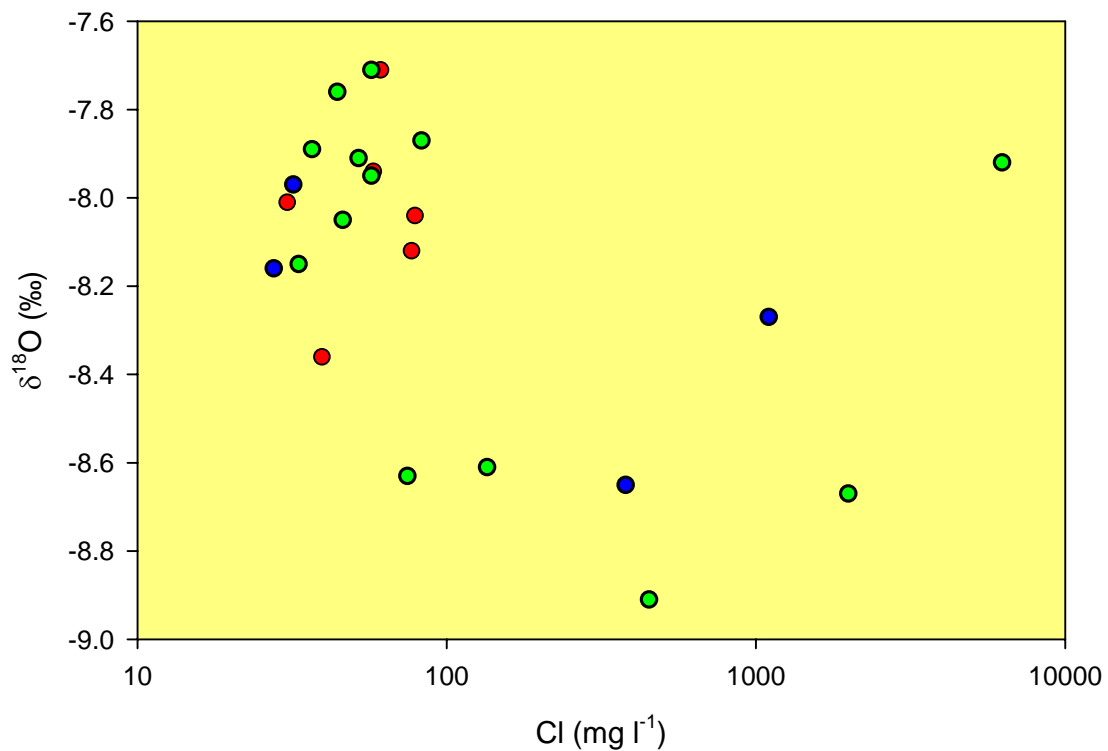


Figure 6.6 The relationship between $\delta^{18}\text{O}$ and Cl concentration

6.2.5 Trace elements

Barium concentrations are limited in groundwater where concentrations of sulphate are high due to saturation with the mineral barite (BaSO_4). In the Lincolnshire Limestone the maximum Ba concentration is $137 \mu\text{g l}^{-1}$. Saturation indices show that most samples are close to saturation with respect to barite, but those having undergone sulphate reduction are undersaturated (including the sample with highest Ba concentration at Asgarby of $137 \mu\text{g l}^{-1}$).

Boron occurs naturally in rocks, soils and groundwater and typically varies with salinity. Boron is also associated with the use of bleaching agents used in washing powders and as a result boron may be indicative of contamination by sewage and industrial wastes. However, in Lincolnshire the samples with the highest B concentrations (in excess of the EU drinking water limits) are those which are

located in the confined part of the aquifer which would suggest that the high concentrations are likely to be naturally derived through water-rock interaction and/or mixing processes. Boron concentration in seawater is about 4.6 mg l⁻¹ (Hem, 1992). Some of the higher concentrations in the deep confined part of the aquifer are up to 3.4 mg l⁻¹ and have much higher B/Cl ratios than seawater, indicating an internal source in the aquifer.

Fluoride concentrations are higher for samples from the deep confined part of the aquifer, i.e. where reducing conditions occur. The concentration of fluoride in seawater is 1.3 mg l⁻¹ (Hem, 1992). Seven of the Lincolnshire samples exceed the seawater concentration (in some instances three-fold) and it is evident the high fluoride concentrations are derived from water-rock interaction. Low calcium concentrations and dominance of Na-HCO₃ type water allows F concentrations to build up because F is controlled by the solubility of fluorite (CaF₂).

Edmunds and Walton (1983) suggested that oxidation of organic material within the aquifer may be responsible for increases in iodide which are observed to coincide with the redox boundary. Lloyd (1982) suggested that contribution of fluid from the clay-rich confining sequence could explain the high iodide concentrations encountered in the Lincolnshire Limestone aquifer. Lithium is derived dominantly from water-rock interaction as Li/Cl ratios are 1-2 orders of magnitude higher than seawater.

6.3 Temporal variations

Comparison of data from Peach (1984), WIMS data (1994 to 1996) and the present Baseline survey (2004) enabled geochemical changes with time to be examined (Table 6.1). Analyses for eight different boreholes from unconfined through to down-dip confined samples were examined. The most significant changes appears to have occurred in the Stow No. 5 borehole, which was not sampled as part of the Baseline survey (Figure 6.7). Between the early 1980s and 1996 Stow No. 5 showed a considerable reduction in Ca and an increase in Na suggested that ion exchange processes are playing a more important role in that borehole than they had been previously. Increases in chloride were also observed in this borehole and it is suggested that this is indicative of a movement of water from the eastern part of the confined aquifer up-gradient, possibly as a result of pumping.

Table 6.1 Groundwater analyses over time for eight different boreholes

Site name	Source and date of sampling	SEC (mS cm ⁻¹)	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	Field HCO ₃ (mg l ⁻¹)	NO ₃ as N (mg l ⁻¹)
Asgarby	Baseline sample (2004)	20.50	101	75.5	4030	18.8	6250	0.1	415	3.47
	WIMS data (1996)	18.90	41	80	3860	17	6530	21		
	Peach (1984)	11.38	114	84	4200	22.4	6600	30	297	0.1
Great Hale	Baseline sample (2004)	7.07	7.27	8.42	1340	6.78	1990	0.1	294	0.0015
	Peach (1984)	3.81	8	14	1340	8.8	2020	43	363	0.9
Stow No 5	WIMS data (1994)	0.65	59.8	7.9	68.2	1.7	103	140		
	Peach (1984)	0.67	152	6	31	2.3	43	162	278	0.1
Clay Hill	Baseline sample (2004)	0.93	153	5.68	17.4	2.61	44.3	111	256	10.9
	Peach (1984)	0.61	144	9	14	2.5	38	140	254	9.6
Foster's Bridge	Baseline sample (2004)	0.97	174	6.73	28.1	2.92	57.9	136	301	5.9
	Peach (1984)	0.74	187	7	21	2.5	50	178	276	13.6
Spanby	WIMS data (1996)	0.63	123	7.4	17	2.2	32	120		
	Peach (1984)	0.57	118	12	16	2.1	25	119	273	1.1
Drove Lane	Baseline sample (2004)	0.98	154	4.36	21.8	2.57	57.1	90.7	255	14
	Peach (1984)	0.62	160	3	16	2.4	49	128	241	18.5
Washingborough Fen Road	WIMS data (1995)	1.02	178	6.8	27	2.1	71	170		9.9
	Peach (1984)	0.72	170	13	24	3.3	54	176	263	10.4

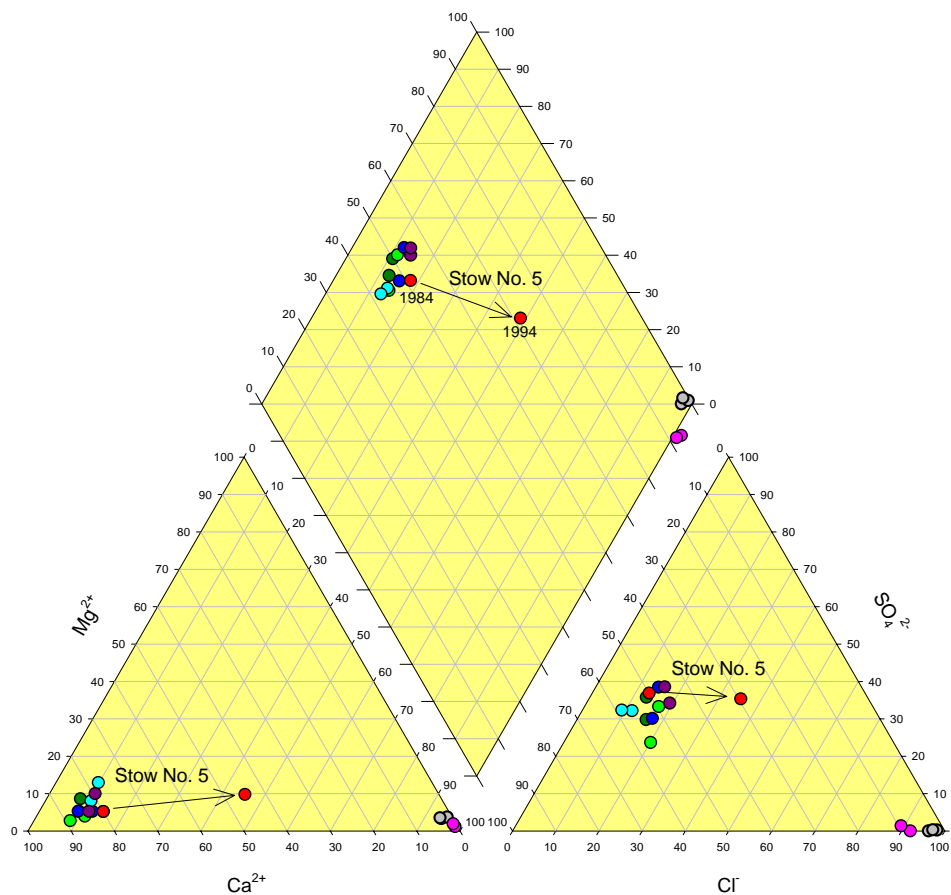


Figure 6.7 Piper plot showing evolution of groundwater over time for eight different borehole abstracting from the Lincolnshire Limestone

Entec (2004) examined trends in groundwater chemistry from 1980 to 2004 for two spring sources in the unconfined part of the aquifer, Springwell and Dunston Beck and also for Scabcroft borehole in the confined section of the aquifer. The two spring sites displayed seasonal variations in nitrate, chloride and sodium concentrations. Scabcroft displayed an increase in sodium and chloride concentrations and a decrease in sulphate concentrations.

6.4 Depth variations

There are many problems involved in the interpretation of pumped groundwater samples, in particular the fact that such samples may represent a mixture of waters from different horizons (see Section 4.3). This can be partly overcome by sampling from specific depths in a borehole from multi-level boreholes or packer tests (although some mixing is inevitable even with packers), porewater extraction (for sampling the matrix) or by comparing the chemistry from adjacent boreholes drilled to different depths. Most of the boreholes sampled were uncased apart from in the upper few metres, and therefore represent an integrated sample. There are few data available on depth variations in the aquifer.

6.5 Age of the groundwater

A number of the previous studies into the hydrogeochemistry of the Lincolnshire Limestone have included investigations into the age of the groundwater within the aquifer. Analyses of CFCs and

stable isotopes for oxygen, deuterium and carbon-13 were sampled in the present study to provide evidence of groundwater age.

Four CFC samples were collected as part of the Baseline study (Table 6.2). The samples were collected from Albert's Borehole, Bitchfield, Cranwell Plantation and Great Hale. The CFC data indicate a component of old water in Albert's Borehole and Great Hale whereas the Bitchfield and Cranwell Plantation samples indicate a high proportion of modern water. There is not a consistent relationship between CFC-12 and CFC-11. Caution should be taken in interpreting the CFC residence time data as it is possible that the anomalies are due to contamination from the large number of landfill sites across the outcrop area of the limestone. The highly fractured nature of the aquifer means that contaminants can be rapidly transported within the aquifer.

Table 6.2 CFC data for four sites

Sample	pmol/L	pmol/L	Frac Modern	Frac Modern	Recharge Yr	
	CFC-12	CFC-11	CFC-12	CFC-11	CFC-12	CFC-11
Albert's Borehole	0.00	3.37	0.00	0.62	<1948	1978
Bitchfield	0.26	6.60	0.09	1.21	1962	>modern
Great Hale	0.00	2.23	0.00	0.41	<1948	1974
Cranwell Plantation	2.08	8.43	0.69	1.54	1984	>modern

Stable isotope data collected as part of the current study agree with previous analyses taken for the Lincolnshire Limestone. The oxygen and deuterium isotope data become increasingly negative down dip implying a component of older Pleistocene water. Carbon-13 becomes less negative down-dip indicating enhanced reaction with the carbonate matrix, consistent with increasing groundwater age (Figure 6.8).

Previous stable isotope studies (Lawrence et al, 1976; Downing et al, 1977; Bath, 1983; Bishop and Lloyd, 1990, 1991; Darling et al, 1997) support the expected increase in age of groundwater with increased distance from outcrop with younger oxidising waters in the west and older saline waters further east than are more depleted in oxygen and deuterium. Downing et al (1977) noted a slight depletion in stable isotopes towards the east. Bath (1983), who examined saline waters, found that they exhibited isotopic enrichment. When the Cl content of these samples was considered it appeared likely that the saline end-member could be seawater.

Stable isotope ratios of carbon indicate increasing water-rock interaction towards the east, however this is only a qualitative indicator of residence time (Darling et al., 1995). Peach (1984) looked at the effects of pumping on carbon isotopes for two boreholes during step test at Hilbaldstow Bridge. The results indicated that in the long term, little water is drawn from down dip once an initial cone of depression forms. The old groundwater, which is essentially "mined", appears to be replaced by modern water from up dip. The exception to this appears to be down dip from Sleaford where some of the older saline water appears to have migrated westwards. Peach (1984) found that the carbon isotope data for the northern Lincolnshire Limestone demonstrated a different flow regime to that of the southern Limestone. The results reflect mixing, with only a minor amount of groundwater circulation, limited to around 4 km down-dip of the outcrop area.

In addition to oxygen and carbon stable isotope analyses a number of other techniques have been conducted during previous studies to determine the age of the groundwater within the aquifer. These techniques include tritium, ⁴He and noble gases. A brief summary of the findings related to each of these techniques is presented below but for a more complete review the reader is referred to Darling et al. (1997) or the individual papers.

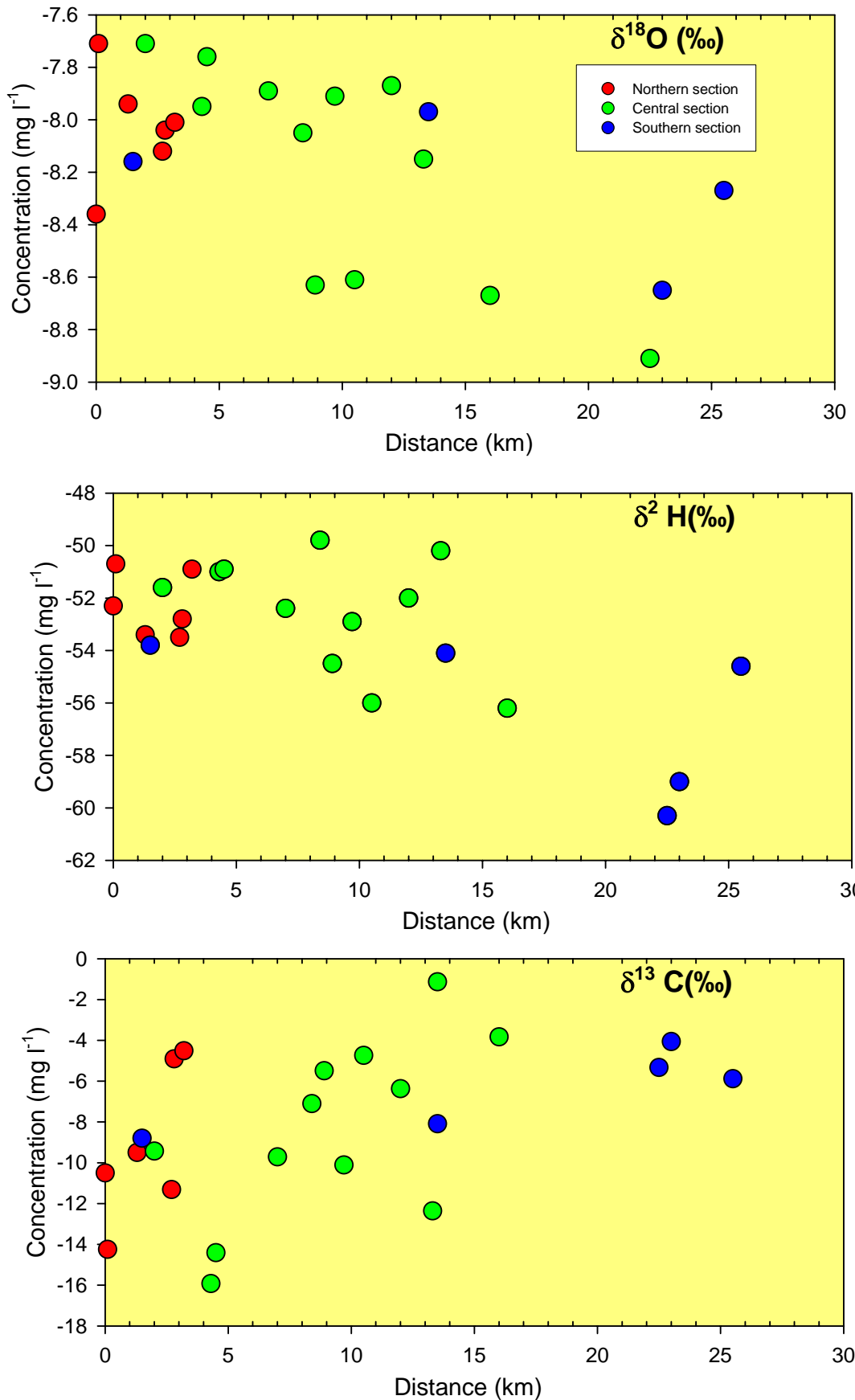


Figure 6.8 Variations in stable isotopes with distance from area of outcrop.

In the unsaturated zone, tritium measurements carried out on pore waters from a cored borehole at Ashby (17 km SSE of Lincoln) indicated that the bulk of water and solutes travel from the surface to the water table (c. 10 m) in approximately a decade (Smith-Carrington et al. 1983). In the saturated zone tritium can be traced into the reducing zone of the aquifer, up to 15 km from outcrop, presumably drawn down-dip via fractures as a result of heavy abstraction (Edmunds, 1973; Downing et al, 1977). This has also caused older water to move up-dip by as much as 5 km.

Lawrence et al. (1976) and Downing et al. (1977) measured radiocarbon ^{14}C (and ^{13}C) in the Spalding-Stamford area, and Bishop and Lloyd (1990) made measurements in the central part of the aquifer as far as 10 km north of Sleaford. Interpretation of radiocarbon measurements is very difficult due to the extensive precipitation-redissolution processes between carbonate and water and therefore initial estimates made by Downing et al. (1977) of groundwater ages of 9000 to 25 000 years BP (away from the saline zone) are almost certainly too high (Darling et al., 1995). Bishop and Lloyd (1990) used corrections for incongruent dissolution of carbonate and soil-zone exchange. They found that waters in the oxidising zone and the western part of the reducing zone gave negative ages when modelled, which indicates that recent water extends well into the reducing part of the aquifer, thus supporting the tritium data. In the zone of significant ion-exchange, they applied a further correction based on the work of Wigley et al. (1978) to allow for carbonate dissolution in relation to the Ca-Na ion exchange. In this zone, they estimated the groundwater age to be 3.1 and 5.7 ka which is significantly less than the suggestions by Downing et al. (1977). There is no way to assess which of these ages is correct, however the O and H stable isotope palaeoshifts are smaller than those identified in the East Midlands Triassic Sandstone aquifer for which age estimates of up to 20 to 30 ka have been made by a variety of methods (Darling et al., 1995).

In the saline zone, high concentrations of ^4He indicate a considerable age for the groundwater, with a saline end-member originally interpreted to be true Jurassic connate water. However, strontium isotope evidence provided by Smalley et al. (1988) does not support a Jurassic age and suggests a minimum age of Pliocene, assuming the water had a marine origin. This influx would have had to have occurred through overlying formations as the last inundation of the Lincolnshire Limestone outcrop is thought to have occurred during the Jurassic (Bennison and Wright, 1969).

Measurements of $\delta^{15}\text{N}$ in dissolved nitrogen were conducted by Wilson et al. (1990), however it was concluded that denitrification processes are not readily interpreted in terms of residence times. $\delta^{34}\text{S}$ samples were analysed for a down-dip sequence by Moncaster et al. (1992). 'Acid rain' signatures of around 0 ‰ were found at outcrop compared with background values of -15 ‰ in the fresher part of the confined zone.

Noble gas measurements by Andrews and Lee (1980) suggest a drop in average recharge temperature of about 1.6 °C between the outcrop area and groundwaters at depth. Darling et al. (1997) concluded that the overall interpretation of groundwater residence time in the aquifer was that the bulk of the less mineralised water has a residence time of up to a maximum of 10 ka, while the saline component may have a residence time of the order of 1 Ma. Most of the data reported are for the southern part of the aquifer. However, Darling et al (1997) suggested a similar situation in the northern part of the aquifer except that the zones are narrower, most probably because of the increased dip of the aquifer. Peach (1984) argued that in the northern part of the Limestone there is a different flow regime and that the highly saline water in the east must be very old to have high concentrations of iodide ($> 5 \text{ mg l}^{-1}$) compared with modern seawater (which contains about 0.06 mg l^{-1}). The results for the northern Limestone reflect mixing, but with only minor groundwater circulation, reaching to about 4 km down dip from the outcrop area. Peach suggested that the mixing was with relatively modern but pre-nitrated water giving an apparent age for the middle zone of only 2000 to 4000 years.

6.6 Regional variations

Figure 6.9 shows the concentrations of different elements plotted spatially over the geology map. The spatial plots corroborate the trends identified in Section 6.2 on the chemical evolution in the direction of groundwater flow, however the spatial plots are able to represent all of the available data, including the Environment Agency WIMS data and the samples collected for the Baseline project. As would be anticipated DO concentrations are highest over the unconfined area of the aquifer (Figure 6.9a). SEC is generally greatest in the east of the aquifer, however there are relatively high SEC values in unconfined groundwaters around Lincoln. SEC values are lowest in the south of the study area east and south east of Grantham (Figure 6.9b) in the outcrop area and shallow confined part of the aquifer. pH also increase towards the east of the aquifer (Figure 6.9c).

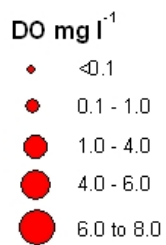
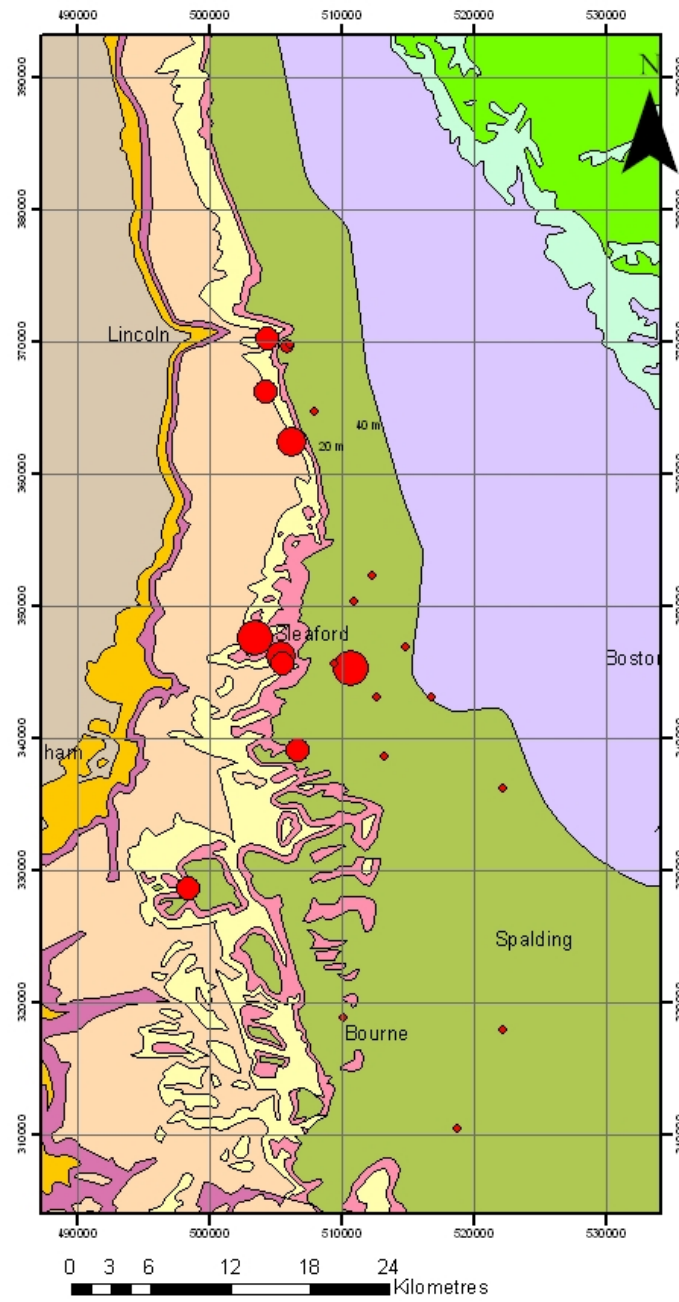
Chloride concentrations are generally higher in the confined part of the aquifer where saline conditions are encountered (Figure 6.9) . However, some relatively high chloride concentrations are found on the outcrop area, notably to the south of Lincoln, these may be the result of contamination e.g. by road salt run-off, agriculture.

Bicarbonate concentrations are high in the eastern confined part of the aquifer (Figure 6.9e). They are also relatively high in the area to the south and east of Lincoln in the unconfined and shallow confined aquifer. The decrease in HCO_3 in the deepest, most confined part of the aquifer proposed by Edmunds is not apparent. Calcium concentrations are high at or near outcrop where Ca- HCO_3 type groundwaters predominate (Figure 6.9f). As ion-exchange processes become increasingly important down-dip, lower Ca concentrations are matched by corresponding increases in Na (Figure 6.9g). Potassium and magnesium concentrations are variable across the aquifer but in general are also highest in the easternmost part of the study area with some locally elevated concentrations in the shallower parts of the aquifer (Figures 6.9h and i).

Iodide, lithium and boron concentrations are also highest in the confined part of the aquifer. Their concentrations are likely be influenced by the presence and oxidation state of organic material within the aquifer, residence times and ion-exchange (Figures 6.9j, k and l).

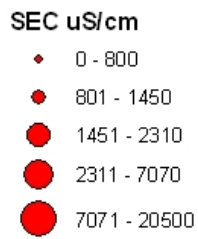
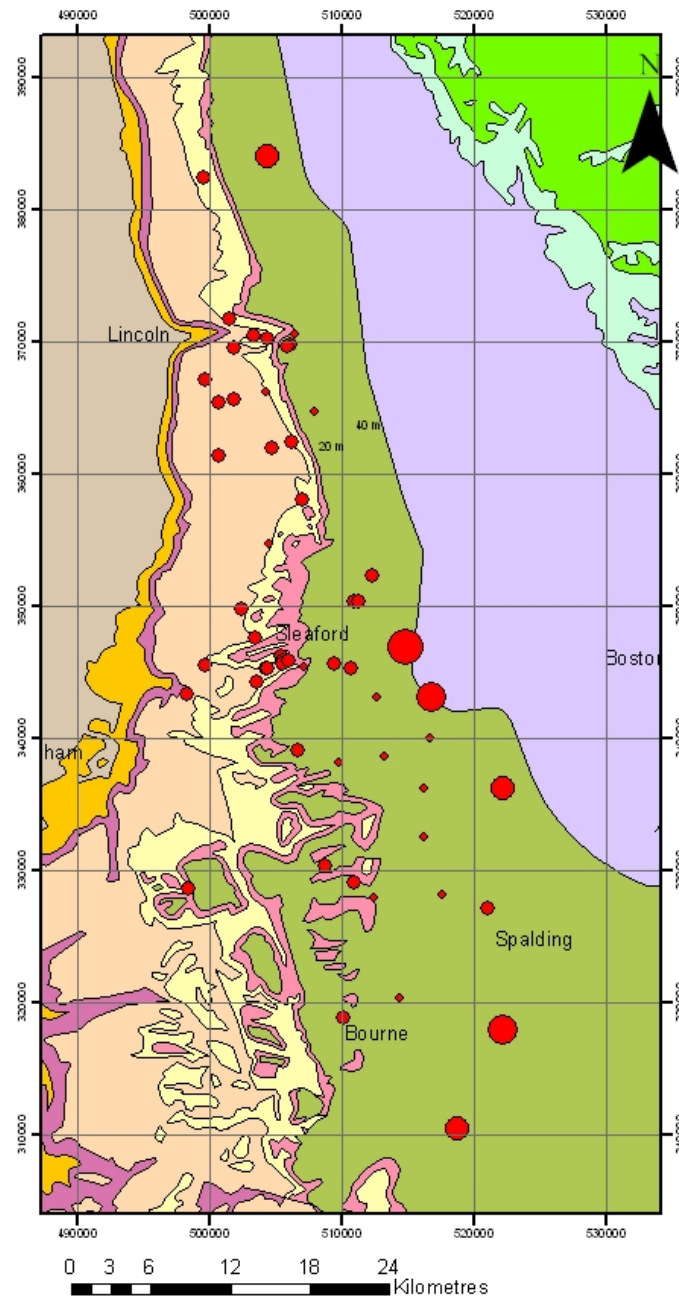
As discussed in Section 6.2.2, nitrate concentrations are high over much of the unconfined part of the aquifer (Figure 6.9m). The low concentration/absence of nitrate in the confined part of the aquifer could reflect denitrification in the confined part of the aquifer. However, older water recharged prior to intensive agriculture and urbanisation are likely to have lower concentrations.

Zinc concentrations vary across the aquifer but generally seem to be highest in the shallow confined and confined part of the aquifer, although relatively low concentrations are also encountered in the confined zone (Figure 6.9n).



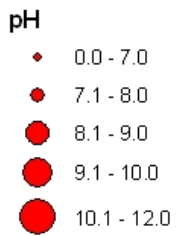
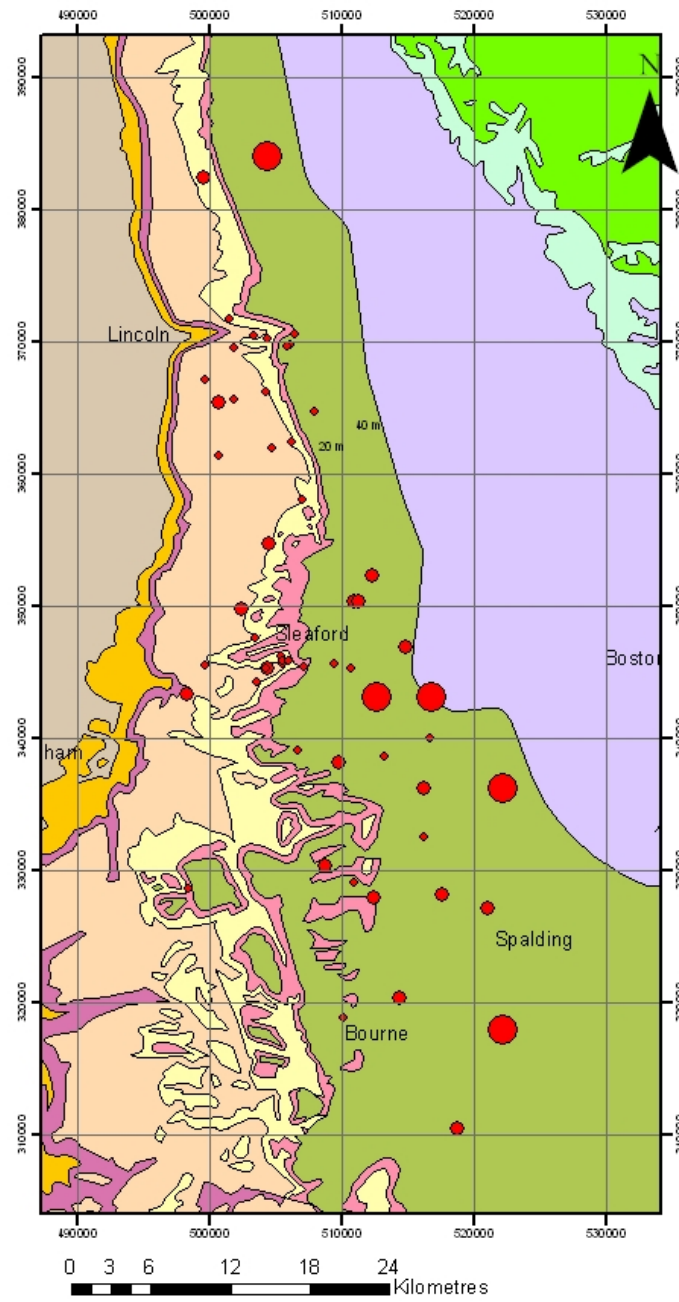
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Figure 6.9a Spatial variation in DO over the study area



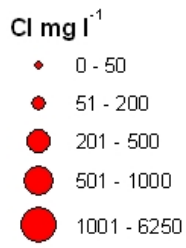
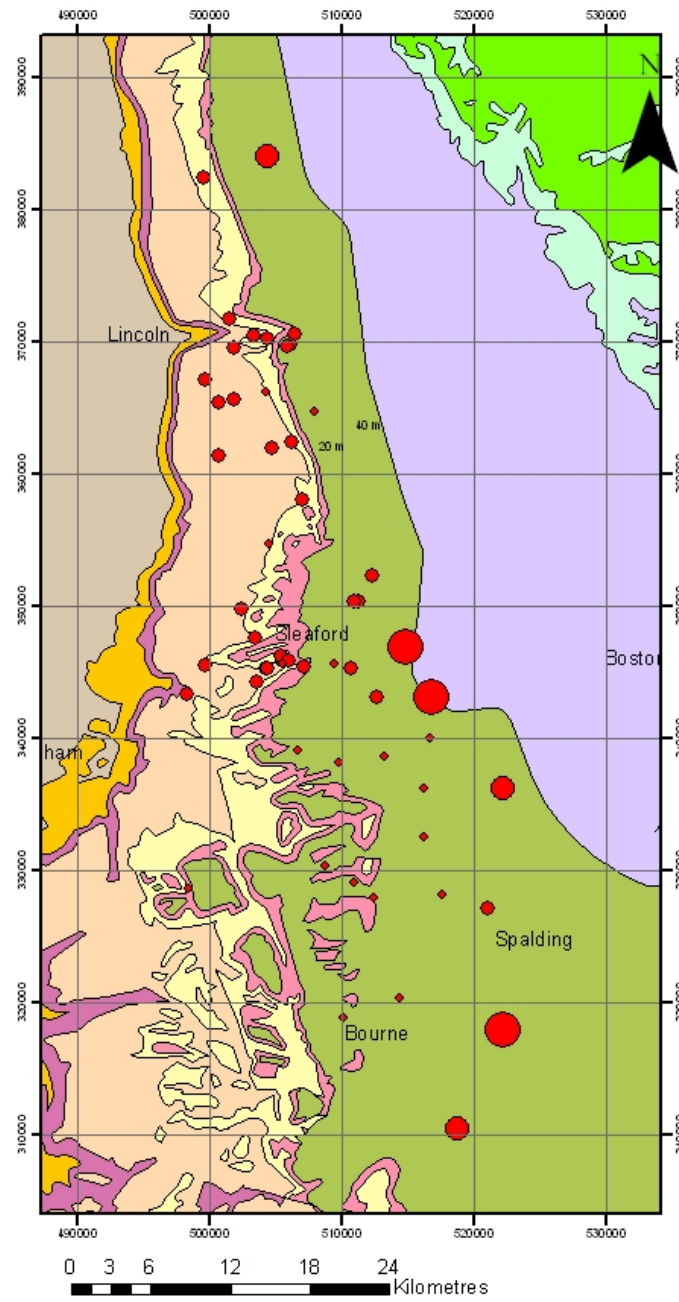
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Figure 6.9b Spatial variation in SEC over the study area



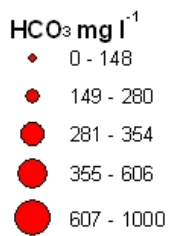
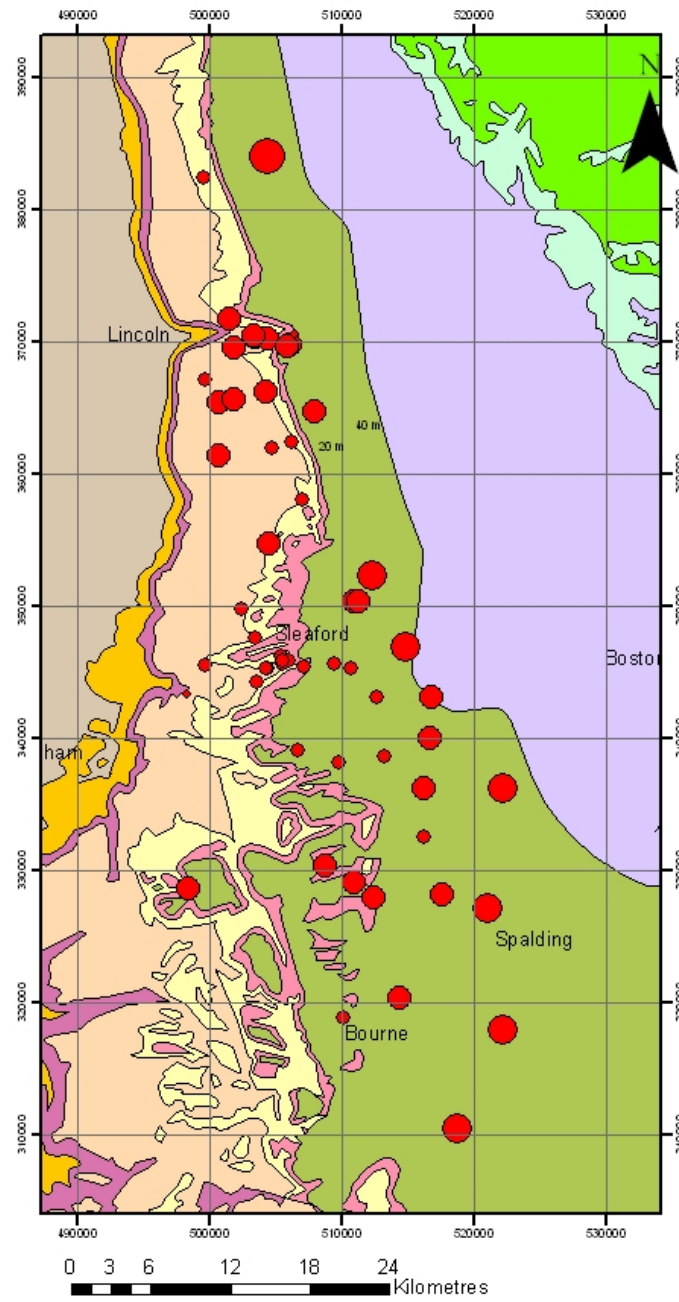
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Figure 6.9c Spatial variation in pH over the study area



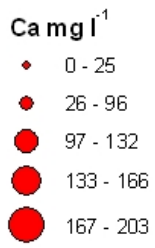
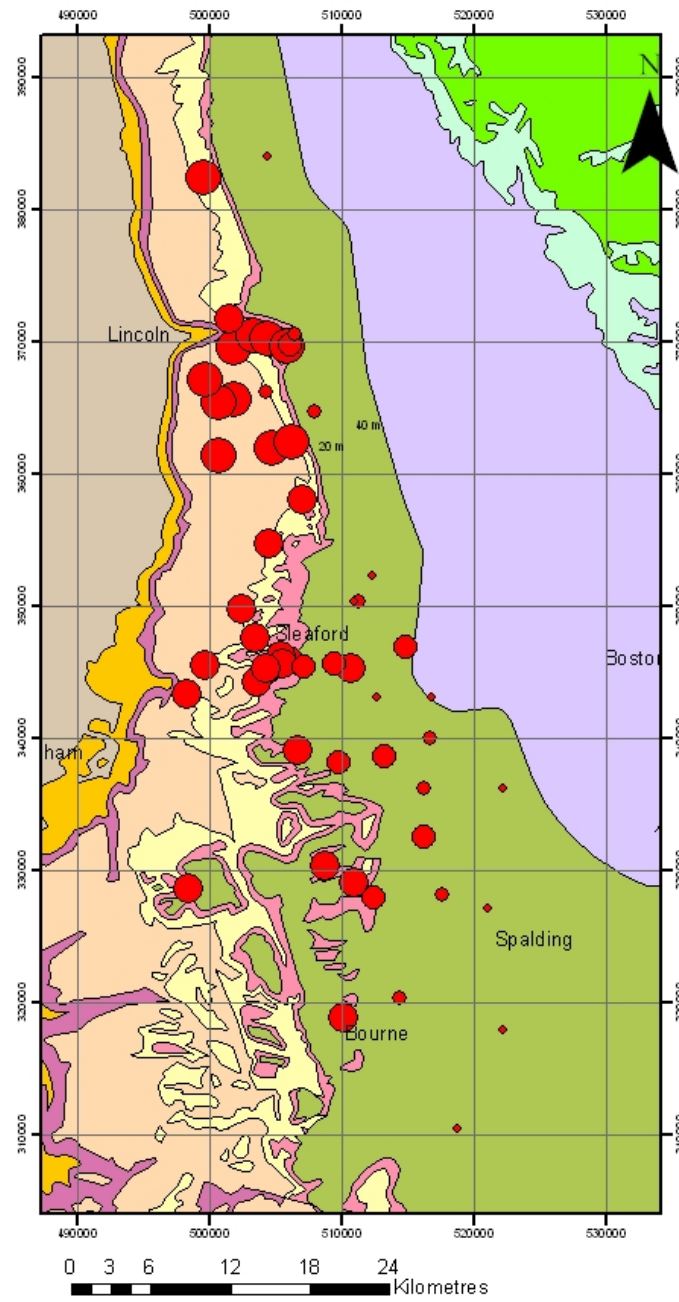
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Figure 6.9d Spatial variation in Cl over the study area



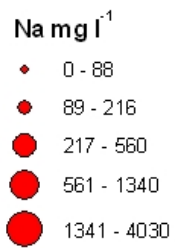
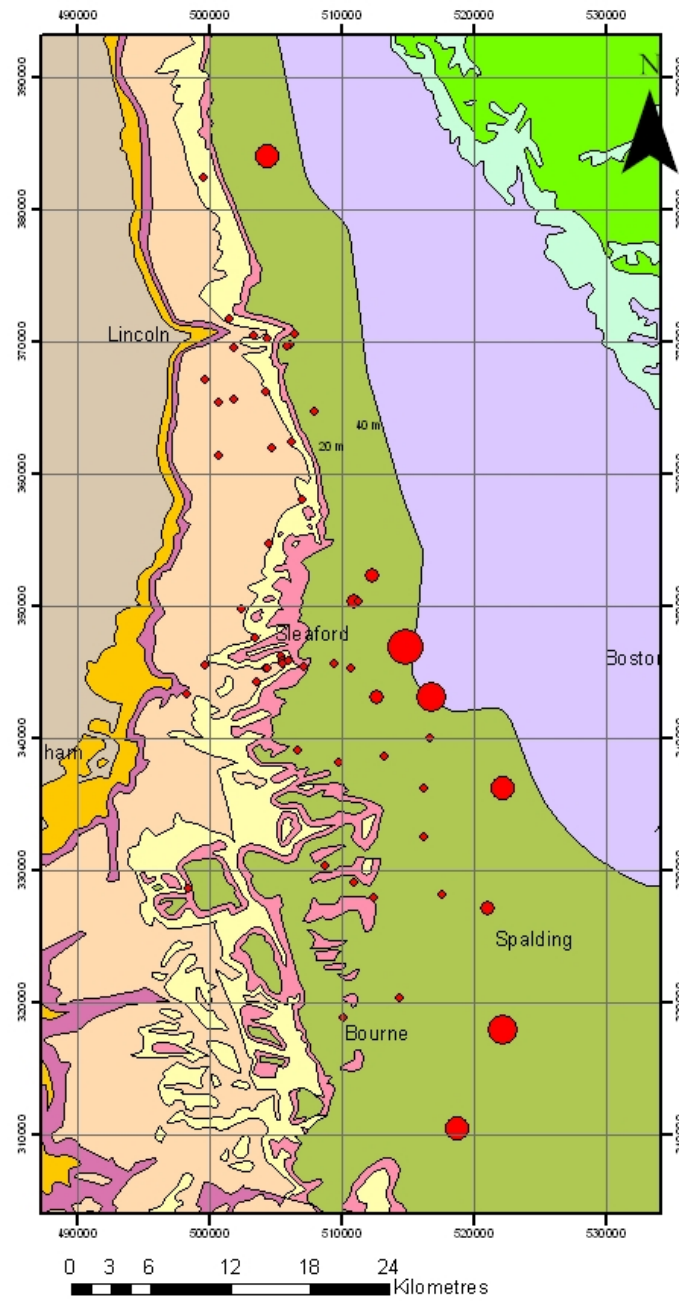
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Figure 6.9e Spatial variation in HCO_3 over the study area



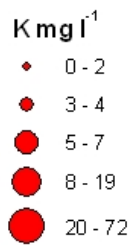
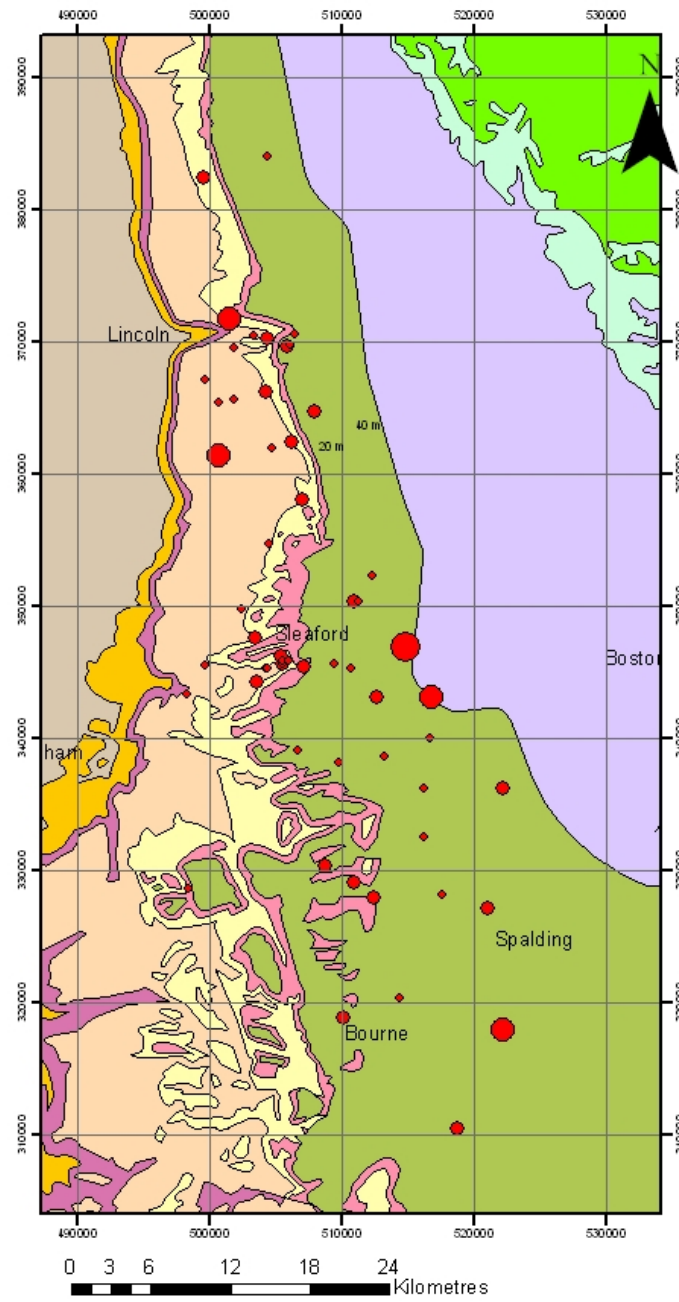
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Figure 6.9f Spatial variation in Ca over the study area



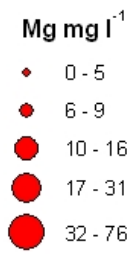
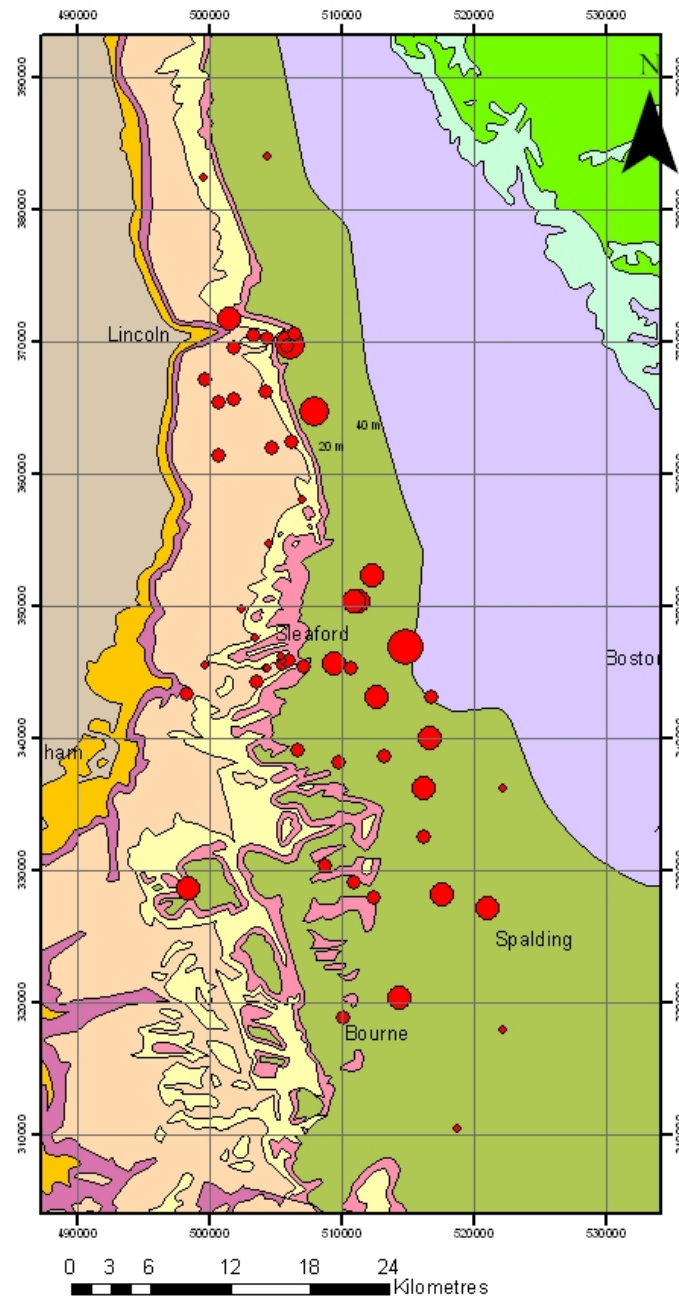
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Figure 6.9g Spatial variation in Na over the study area



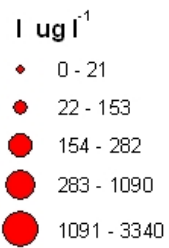
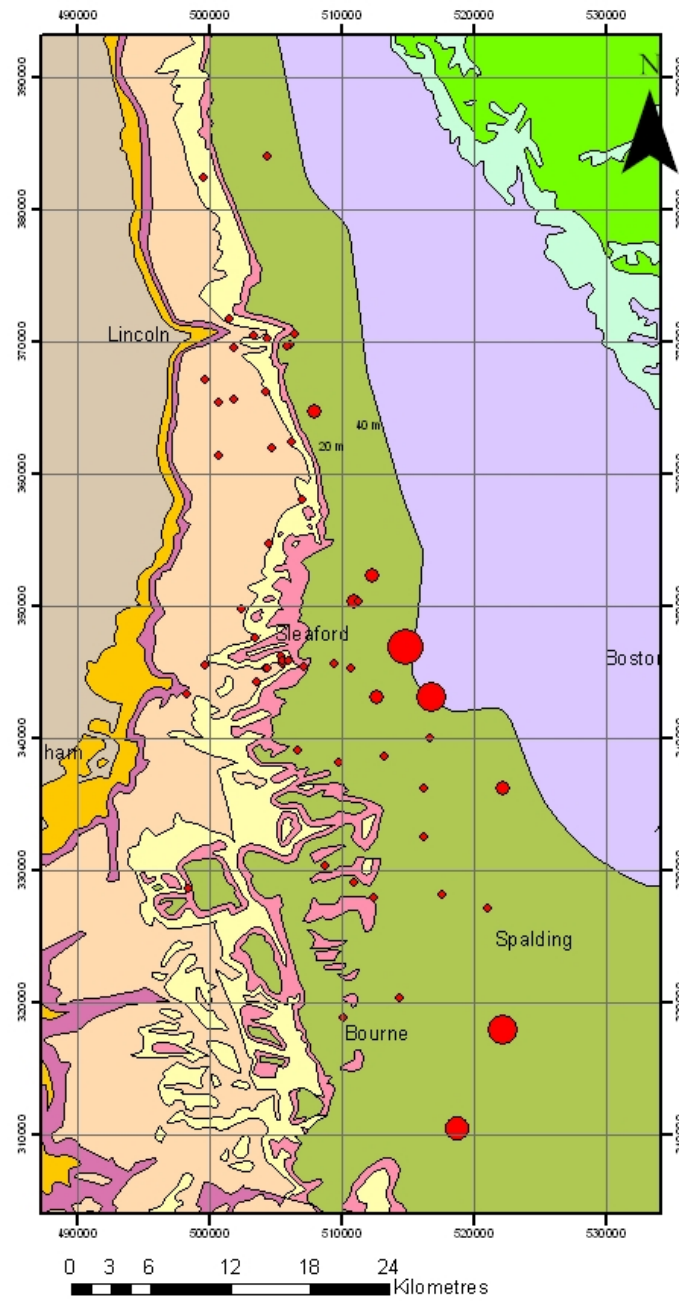
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Figure 6.9h Spatial variation in K over the study area



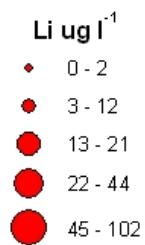
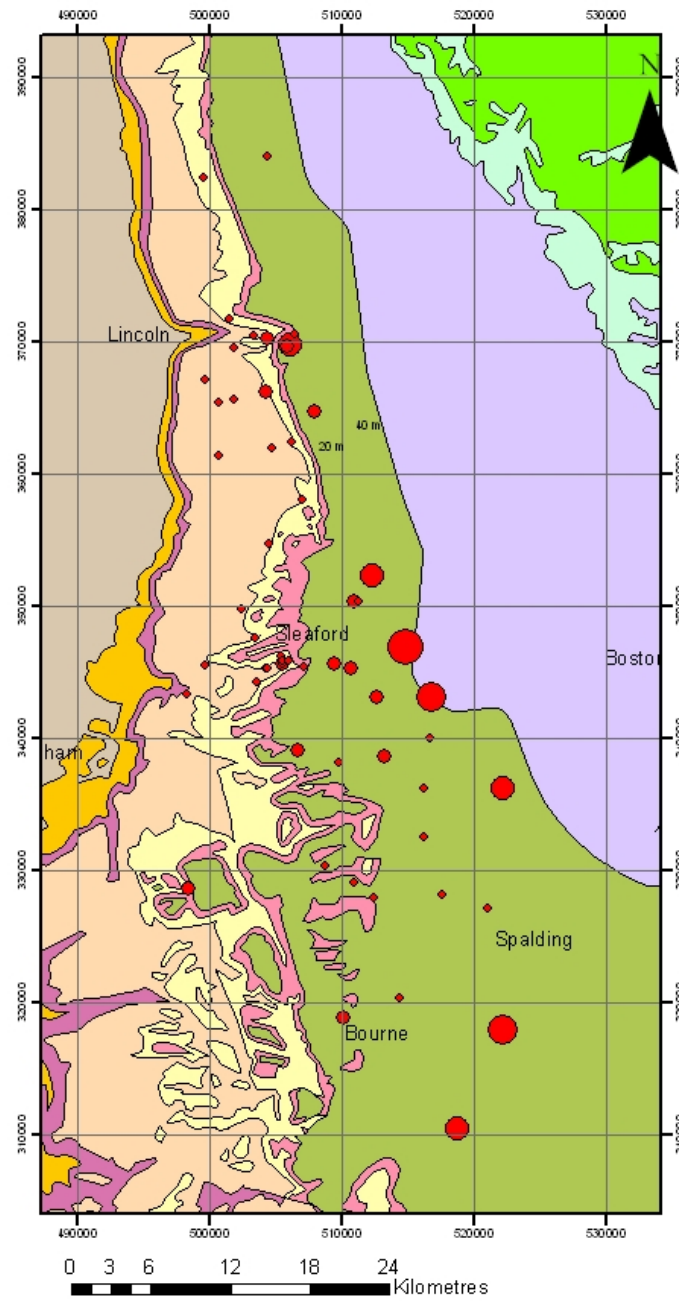
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Figure 6.9i Spatial variation in Mg over the study area



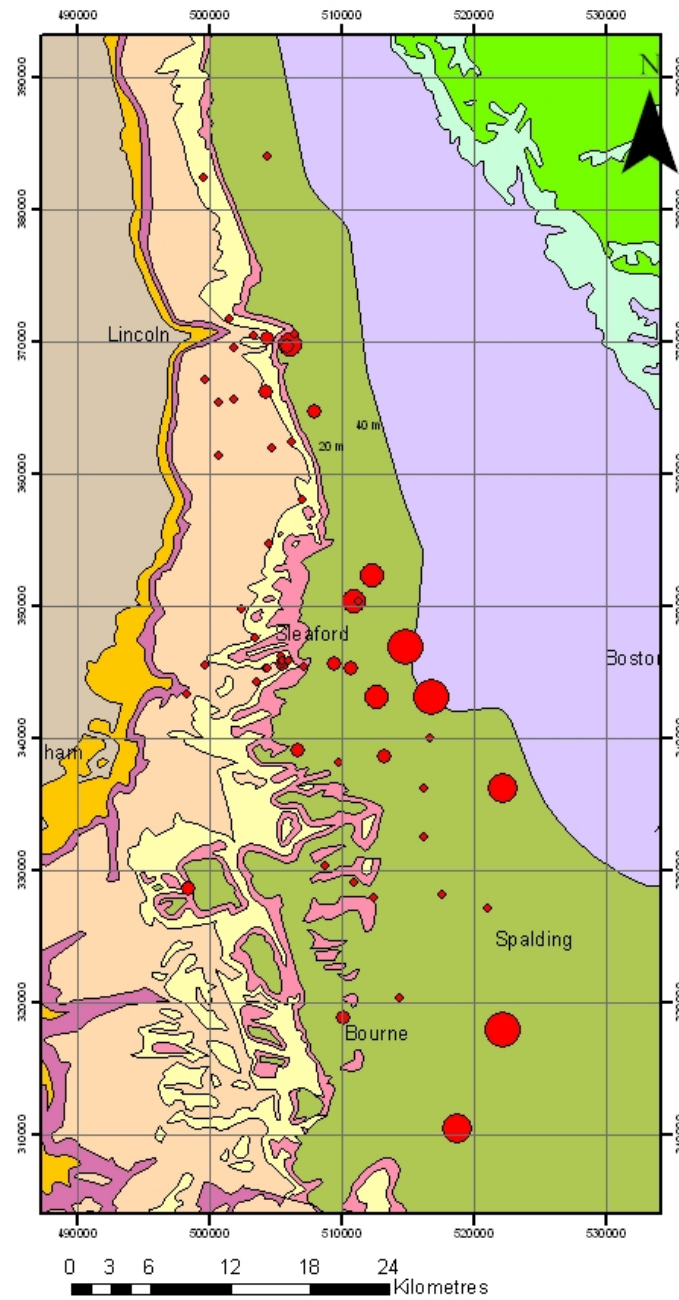
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Figure 6.9j Spatial variation in I over the study area



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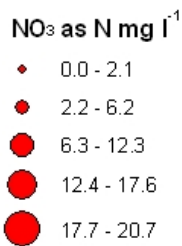
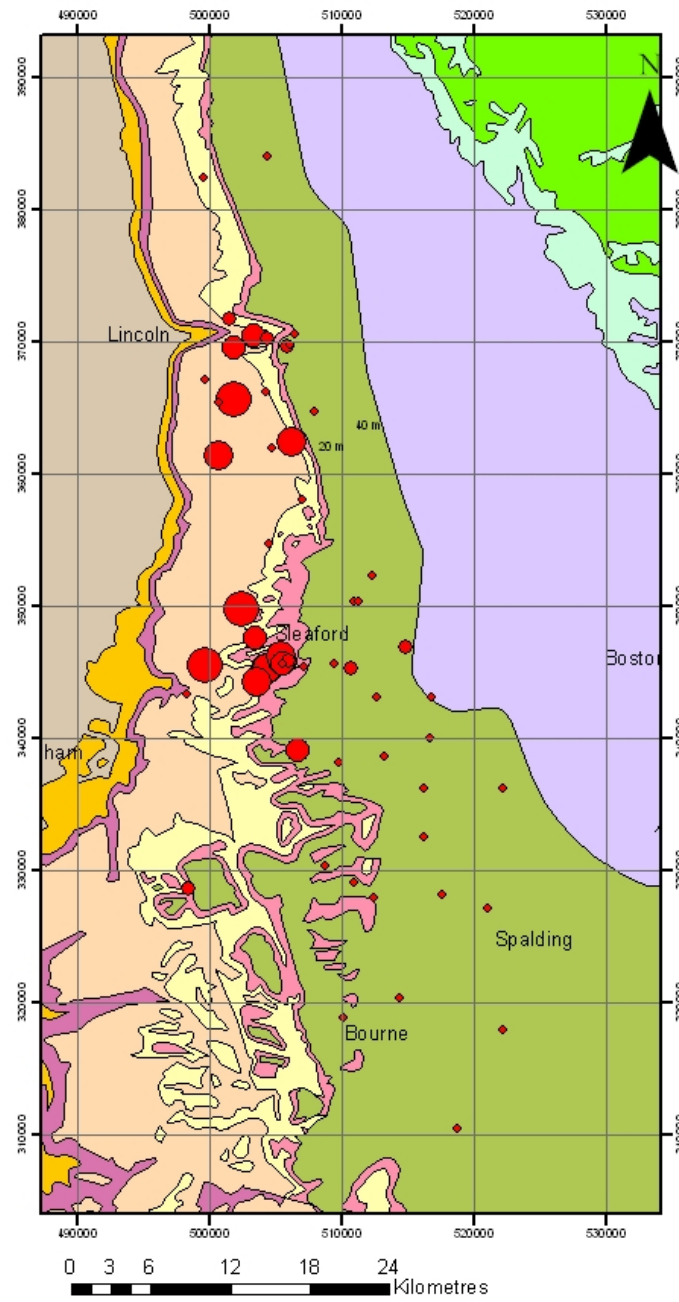
Figure 6.9k Spatial variation in Li over the study area



- B ug l⁻¹**
- 0 - 34
 - 35 - 186
 - 187 - 880
 - 881 - 1676
 - 1677 - 3442

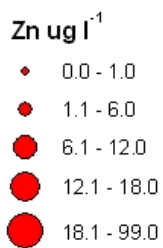
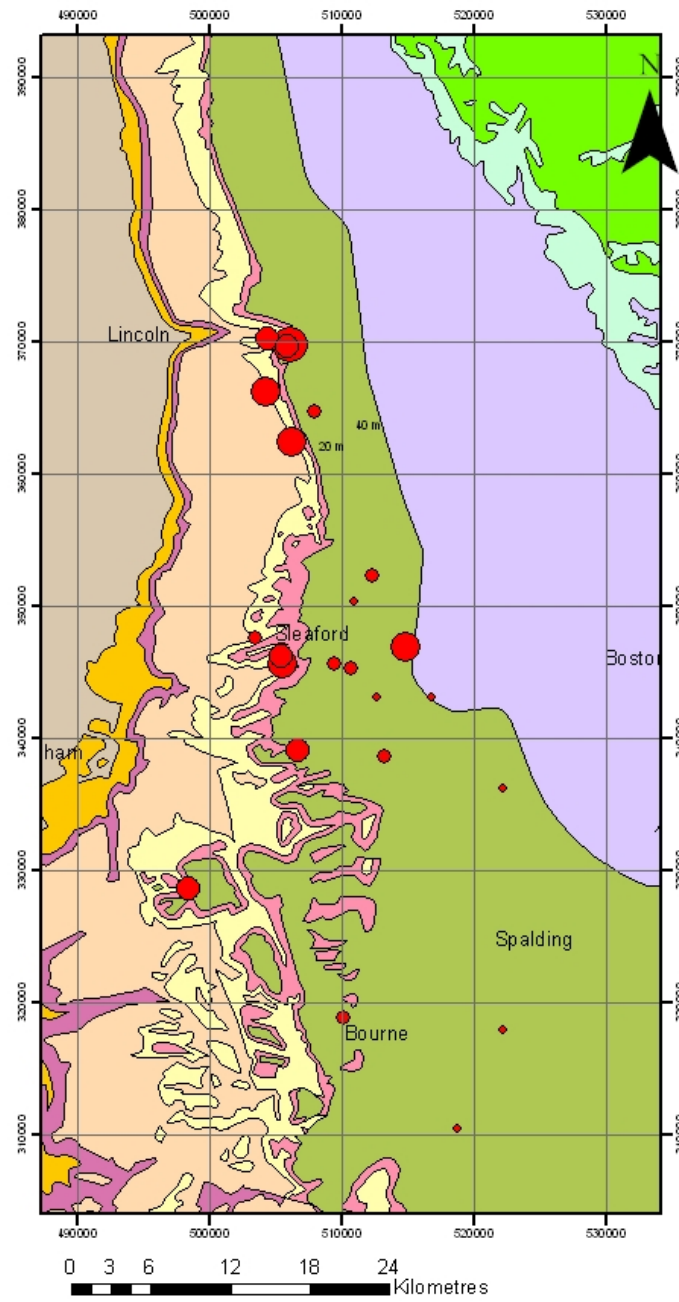
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Figure 6.91 Spatial variation in B over the study area



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Figure 6.9m Spatial variation in NO₃ over the study area



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Figure 6.9n Spatial variation in Zn over the study area

7. BASELINE CHEMISTRY OF THE AQUIFER

The Lincolnshire Limestone aquifer is a complex hydrogeological system. Its fractured nature gives rise to rapid travel times in some parts of the aquifer. This, coupled with thin soil and relatively little cover by superficial deposits over much of the aquifer makes it highly vulnerable to pollutants. The aquifer contains recent groundwater in the unconfined zone, but in the confined part of the aquifer the waters are significantly older. Mixing with remnant formation groundwater (Pliocene or possibly much older) occurs in the deepest parts of the aquifer sampled.

The heterogeneity and geochemical evolution within the aquifer as groundwater moves eastwards, down hydraulic gradient from the recharge area gives rise to large variations in baseline chemistry over short spatial scales. It is apparent that over much of the unconfined part of the aquifer, the extensive arable land use has given rise to high nitrate concentrations (pesticides were not analysed as part of this study). Relatively high nitrate concentrations ($>10 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) are commonly found in boreholes located in or near the unconfined part of the aquifer. However, in some boreholes in the unconfined aquifer, relatively low nitrate concentrations were encountered e.g. Bitchfield (c. $2.9 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) – a value which could be considered to be closer to ‘baseline’. Bitchfield is located in the southern part of the aquifer, it is also some distance away from any significant abstractions so it may well be that high abstraction rates in the Sleaford area are drawing in high nitrate water. Where there is high nitrate, it is also likely that other elements indicative of pollution e.g. SO_4 and Cl may also be elevated. Over much of the unconfined part of the aquifer ‘baseline’ conditions are anticipated to have been modified by anthropogenic influences.

Within the confined part of the aquifer it is more likely that ‘baseline’ conditions exist. However, significant hydrogeochemical evolution and mixing have taken place as the groundwater moves down gradient. The concentrations of many of the elements vary over one to two orders of magnitude, controlled by a combination of geochemical processes taking place in the aquifer. All of these values may represent baseline conditions. The Lincolnshire Limestone aquifer therefore provides a good example of how baseline is represented by a range rather than any single value. This range will vary spatially and also with time.

Redox conditions within the aquifer have an important effect on the concentration of many elements. However because of the gradational nature of many of the changes in the geochemistry it was not felt appropriate to divide the aquifer into oxidising and reducing as obviously there is an interface between the two. The redox zone appears to vary in its abruptness from the north to the south of the aquifer, which is likely to reflect rates of groundwater movement within the aquifer.

8. SUMMARY AND CONCLUSIONS

Although the Lincolnshire Limestone aquifer has been intensively studied over the last 30 to 40 years there are still some uncertainties regarding the geochemical evolution taking place within the system. These uncertainties are largely the product of the heterogeneity of the system and also complex and overlapping nature of the geochemical processes operating within it. This study provides an overview of the current groundwater chemistry and also of the current understanding of the hydrogeochemistry of the aquifer. Although many of the boreholes sampled as part of the project are routinely monitored by the Environment Agency the additional analyses undertaken, particularly the trace element and stable isotope data provide useful information on the groundwater chemistry of the aquifer.

The wealth of previous studies enables the current results to be put in the context of the wider knowledge of the aquifer. It also enables valuable comparison of changes in the geochemistry with time to be examined which is essential for examining the impact of anthropogenic activities on the aquifer. In the Lincolnshire Limestone, the most significant anthropogenic impact appears to be diffuse pollution (most notably nitrate) over the unconfined part of the aquifer and also the effect of abstraction, particularly in the Sleaford area. Edmunds and Walton (1983) proposed that the changes they observed taking place over a 10 year period were largely due to the migration of agricultural pollutants down gradient. In the confined groundwaters, where dissolved oxygen is reduced or absent, nitrate concentrations are lower possibly indicating that denitrification has occurred in addition to reflecting older water with lower initial nitrate inputs.

The Lincolnshire Limestone aquifer provides a good case study for examining the geochemical changes in groundwater chemistry which take place in the direction of groundwater flow. In addition to the effect of increased residence time permitting greater water-rock interaction, the geochemical processes of carbonate reaction, ion-exchange, redox reaction and mixing with old formation water are all significant in determining the groundwater chemistry throughout the aquifer. In general the groundwater becomes increasingly mineralised with depth and distance away from the recharge area.

The most important factor affecting the chemical composition of groundwater of the Lincolnshire Limestone in the unconfined and shallow confined part of the aquifer is carbonate reaction. Close to the recharge area, waters are oxidising and strongly pH-buffered with Ca and HCO_3 as the dominant dissolved ions. Distinct hydrochemical changes are observed down hydraulic gradient as the aquifer becomes progressively more confined. Redox-sensitive elements document the onset of reducing conditions. It seems likely that the oxidation of organic material is an important process within the deep confined part of the aquifer giving rise to elevated concentrations of Br, I and F. Ion-exchange processes become significant and the groundwater chemistry evolves to become of Na- HCO_3 type. Further along the direction of groundwater flow, deep within the confined limestone, mixing with old formation waters influences the water chemistry, resulting in a Na-Cl type groundwater. Palaeowaters exist in the deeper parts of the aquifer as indicated by very light $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures. However, mixing of fresh palaeowater with a remnant saline water has given rise to isotopic signatures in Cl-rich waters more typical of those found in the Holocene. High Cl groundwaters (approximately one third of the salinity of seawater) with relatively light isotopic signatures imply that the salinity cannot be explained simply by mixing with an original seawater, and another source of Cl is required. Trace element concentrations are highest in the deep confined groundwater in the east of the study area.

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