Baseline Report Series:
6. The Chalk of the Colne and Lee River Catchments

Groundwater Systems and Water Quality
Commissioned Report CR/03/69N

Science Group: Air, Land & Water
Technical Report NC/99/74/6

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/03/69N

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6. The Chalk of the Colne and Lee River Catchments

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Environment Agency Dissemination status
Internal: Release to Regions
External: Public Domain
ISBN: 978-1-84432-631-0
Product code: SCHO0207BLYD-E-P
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Statement of use
This document forms one of a series of reports describing the baseline chemistry of selected reference aquifers in England and Wales.

Cover illustration
River Colne at Bushy Mill Lane.

Key words
Baseline, Chalk, York, water quality, hydrogeochemistry, UK aquifer.

Bibliographic Reference
Shand, P, Tyler-Whittle, Besien, T, , Peach, D W, Lawrence, A R & H O Lewis 2003 Baseline Report Series 6: The Chalk of the Colne and Lee River Catchments. British Geological Survey Commissioned Report No. CR/03/69N

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

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

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

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer's physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use historical records and the application of graphical procedures such as probability plots to discriminate different populations (Shand & Frengstad, 2001; Edmunds et al., 2002). The "baseline" refers to a *specified system* (e.g. aquifer, groundwater body or formation) and is represented by a range of concentrations within that system. This range can then be specified by the median and lower and upper limits of concentration.

The BASELINE objectives are:

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

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

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

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

1. EXECUTIVE SUMMARY

The Chalk forms a major aquifer accounting for more than half of all groundwater use in England. This report presents a summary of the hydrochemical characteristics of groundwater in the Chalk aquifer in the catchments of the rivers Colne and Lee which flow south from the Chiltern hills to the centre of the London Basin. It also attempts to understand the dominant geochemical processes which give rise to the natural chemical variations seen in the region and to determine the natural or "baseline" characteristics of the groundwater. This report focuses on the variations in groundwater quality related to natural geochemical processes and how these vary spatially, based on both existing water quality data and new hydrochemical data.

The Chalk is a dual porosity aquifer with high storage in the matrix, where permeability is low due to small pore throat diameters, and high permeability in the fracture or secondary fissure system. The Chalk is, therefore, a complex aquifer and diffusional exchange between fracture and matrix water (which may be of different composition) makes geochemical interpretation difficult. A combination of new chemical analyses from groundwater sampled along a potential flowline and regional data from the Environment Agency database have been used to understand the evolution of groundwater from outcrop areas of the Chalk to the centre of the London Basin where the Chalk is confined beneath Palaeogene cover.

The chemistry of chalk groundwaters in the study area is dominated by natural reactions with the chalk matrix. Groundwaters rapidly reach saturation with calcite during infiltration due to the fine-grained nature of the matrix and, in the unconfined aquifer, are of Ca-HCO_3 type. Continued reaction by incongruent dissolution releases impurities in the chalk (Mg, Sr) which increase in concentration with the age of the groundwater. The groundwater is further modified by mixing with remnants of formation water which have not been flushed from the aquifer, giving rise to higher concentrations of elements such as Cl. Ion-exchange reactions at depth or within the chalk matrix provide additional Na from clays which is exchanged for dissolved Ca as a consequence of aquifer freshening. The most dramatic changes in water quality occur where the Chalk becomes confined beneath Palaeogene sediments coinciding approximately with the redox boundary in the aquifer. This is partly due to the development of a redox boundary, situated close the boundary with overlying Palaeogene rocks. Oxygen decreases to less than detection limit in the confined aquifer and as a consequence nitrate is removed from the system by denitrification and Fe and Mn increase. The concentrations of non redox-sensitive elements (Mg, Sr, F) also increase significantly in the confined aquifer and it is likely that there is a large difference in groundwater age across this boundary. These large differences make it practical to characterise the baseline chemistry of groundwaters separately for the unconfined and confined parts of the aquifer.

Hydrochemical data for pumped Chalk groundwater and for porewater from both the Chalk and the drift deposits at a site adjacent to the River Lee, highlight the natural variations with depth and between the Chalk and overlying drift deposits. Time-series data from selected boreholes across the aquifer have been used to help determine changes in the concentration of selected elements modified by anthropogenic sources. Increases in the concentrations of NO_3 and Cl were noted in some boreholes in the unconfined aquifer, and are likely to result from diffuse pollution from agricultural or domestic sources. The hydrochemistry of pristine waters from the confined aquifer sheds little light on baseline concentrations in the unconfined aquifer due to large differences in geochemical environment (e.g. denitrification has reduced nitrate concentration), age (solute concentrations are higher due to time dependent chemical reactions) and flow regime (less flushing of formation water from the deeper aquifer).

Regional maps showing the concentrations of dissolved components are used to display synoptic variations across the aquifer and provide a useful way of visualising the spatial variability of individual elements.

2. PERSPECTIVE

The Chalk forms one of the most important aquifers in England. It contains large volumes of high quality potable water which is abstracted principally by water companies, for industry, agriculture and private supply. It also provides an essential input to rivers maintaining quality and surface water dependent ecosystems.

This report presents a summary of the natural groundwater quality in the Chalk aquifer within the catchments of the rivers Lee and Colne between Luton and London (Figure 2.1). The northern limit of the study area is defined by the Chalk escarpment of the Chilterns and the southern boundary by the River Thames which flows from the west to the east.

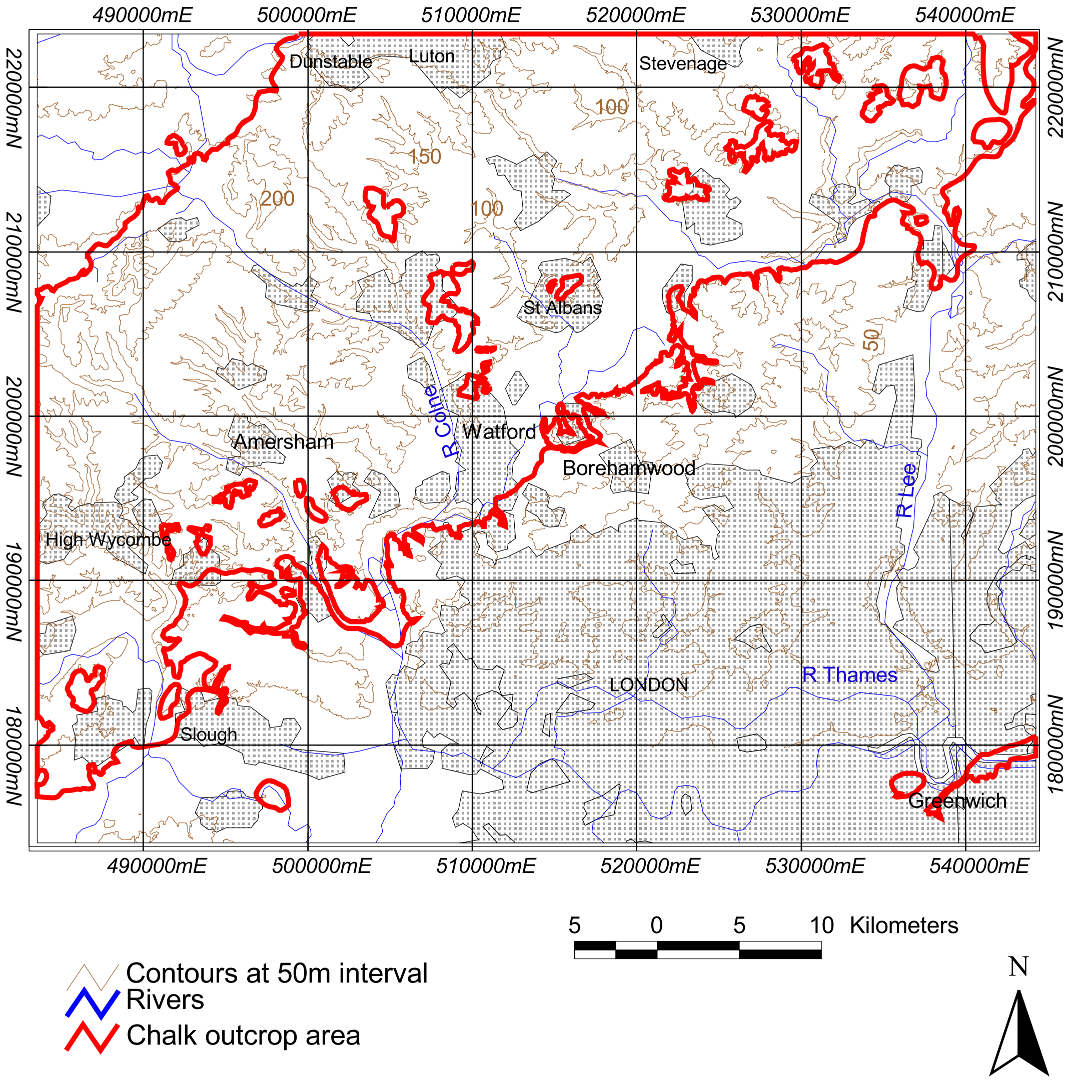

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Figure 2.1 Map of the study area showing topography, main towns and cities (shaded). The outcrop area of the Chalk is shown in red.

The catchments of the Rivers Colne and Lee drain approximately southwards towards London, forming tributaries of the River Thames. The landscape varies from the escarpments of the Chiltern Hills to the relatively flat lying Colne Valley in the south (Figure 2.2). The topography of the region ranges from approximately 250 m AOD in the Chilterns in the North, to less than 20 m AOD close to the River Thames in the south. The mean annual rainfall for the area is 700 mm a^{-1}. The study area is characterised by large population density, relatively low rainfall and high demand for good quality drinking water. It was chosen because it is typical of the other Chalk areas that drain the London Basin.

Figure 2.2 The River Misbourne (Tributary of the Colne) north of Denham, Buckinghamshire.

Groundwater is an important resource in Chalk of the study area that needs to be managed both in terms of its quality and quantity. Approximately 80% of licensed groundwater is utilised for public water supply in the Colne catchment. Of the remaining groundwater abstractions, 7.4% is abstracted for growing water cress, 3.2% for industrial processes and 2.3% for sand and gravel washing. Rural areas are situated mainly in the north of the region where the Chalk is unconfined although a number of urban and industrial centres are present in the area including Luton, Dunstable and St Albans. Many towns are located along or near major river valleys where most of the public supply boreholes are sited. Major railways and roads also traverse the area, including the M25, M1, and M40 motorways. Most of the region towards the south of the study area, includes the urban development of North London with its many past and present heavy industries. However, the aquifer becomes confined beneath Palaeogene sediments south of Watford (Figure 2.1) which affords some protection to the Chalk beneath London. There are many potential threats of contamination to the groundwater. Nitrate in groundwater is often elevated in the unconfined parts of the aquifer, largely due to agricultural activity and may exceed drinking water standards. The cessation of pumping from boreholes beneath London has resulted in rising groundwater levels which has caused some concern e.g. related to the flooding of basements.

Artificial recharge was carried out in the Lower Lee Valley (Boniface, 1959) and the effects on the natural baseline may be significant (Smith et al., 1976). The North London Artificial Recharge Scheme was originally started over 40 years ago in the Lee Valley around Enfield and Haringey and it operated by pumping surplus treated water into the confined Chalk aquifer in the winter and abstracting it in the summer during times of need. There is a component of natural groundwater flow through Chalk inliers in the Thames tideway. Currently this groundwater flow is helping groundwater levels in London to recover from the impacts of substantial abstraction in the first half of the 20th century which resulted in a significant lowering of water levels beneath London.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

An essential first step for assessing the natural (baseline) quality is an understanding of the geological and hydrogeological setting and the groundwater flow regime. To explain the characteristic groundwater chemistry, an understanding of the initial input(s) to the system (principally rainfall chemistry), together with knowledge of the mineralogy and geochemistry of the component minerals in the aquifer is also required.

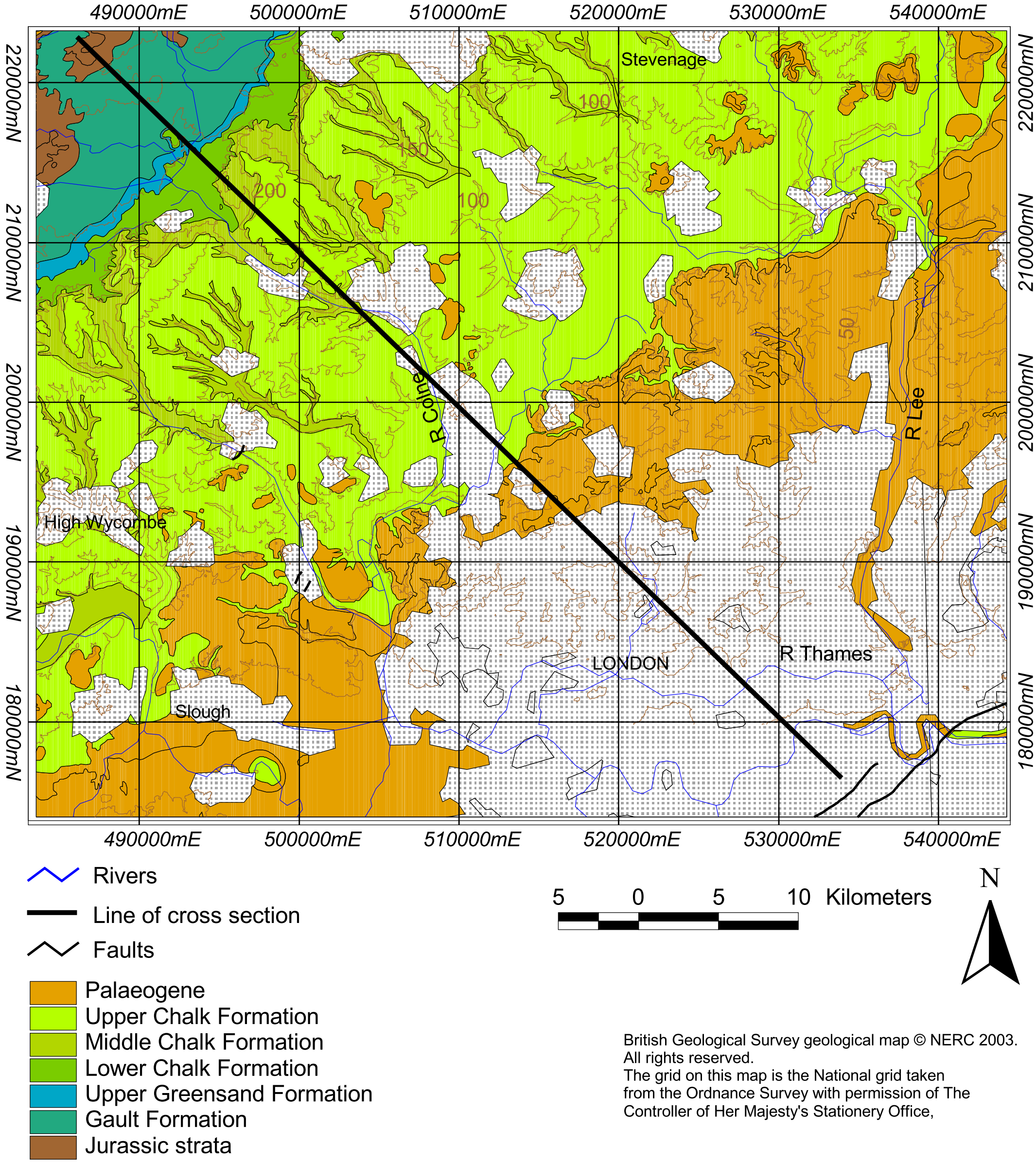

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Figure 3.1 Geological map of the study area. Black line represent line of cross section shown on Figure 3.3.

3.2 Geology

The area of interest in this study is located on the northern limb of the London Basin between the Rivers Colne and Lee (Figure 3.1). The London Basin is an asymmetrical syncline with an axis broadly SW-NE-east and plunging to the east below London. The regional geomorphology is largely controlled by this geological structure.

The northern boundary of the London Basin is formed by the Chiltern Hills and the southern boundary by the North Downs. The Chalk (a dominantly microporous limestone with numerous marl horizons and flint bands) dips gently towards the south-east at an angle of less than 1 degree towards the centre of the London Basin (Downing et al., 1972), where it becomes confined beneath Palaeogene sediments. The entire area is covered with a patchwork of superficial Quaternary glacial deposits and younger alluvial deposits. As a result of tectonic influences, there are a number of minor folds and faults super-imposed on the main syncline and influence groundwater flow in the basin.

The north of the study comprises unconfined Chalk, which is exposed in a southwest to northeast band forming the Chiltern hills (Figure 3.1). The Chalk has traditionally been sub-divided into Lower, Middle and Upper units, but has been reclassified into the Formations shown on Table 3.1. However, the modern classification is not available in digital format for the study area and the old classification is used here (Table 3.1). The Lower Chalk forms the scarp of the Chilterns, the Middle Chalk is exposed in the base of the valleys and the lowest 35 m of the Upper Chalk forms much of the unconfined chalk of the region. The Chalk dips below younger Palaeogene rocks towards central London (Figure 3.1). Quaternary deposits are found overlying the Chalk (Figure 3.2). In the south-east of the unconfined region, Pleistocene glacial gravels are generally found in river valleys and boulder clay on the interfluves. Further north, the upland areas of the Chalk are partially covered by clay-with-flints or pebbly sand and clay. More recent Holocene alluvium is found along the valley floors, where river gravels often cover the Chalk, for example to form the floodplains of the River Thames. A simplified north-south cross-section of the area is shown on Figure 3.3 which illustrates the stratigraphy and generalised structure of the region.

Table 3.1 Modern nomenclature of the southern England Chalk (based on Bristow et al., 1998).

	Formation	*Member*
Chalk	Upper Chalk	Portsdown Chalk
		Spetisbury Chalk
		Tarrant Chalk
		Newhaven Chalk
		Seaford Chalk
		Lewes Nodular Chalk
	Middle Chalk	New Pit Chalk
		Holywell Nodular Chalk
	Lower Chalk	Zig Zag Chalk
		West Melbury Marly Chalk

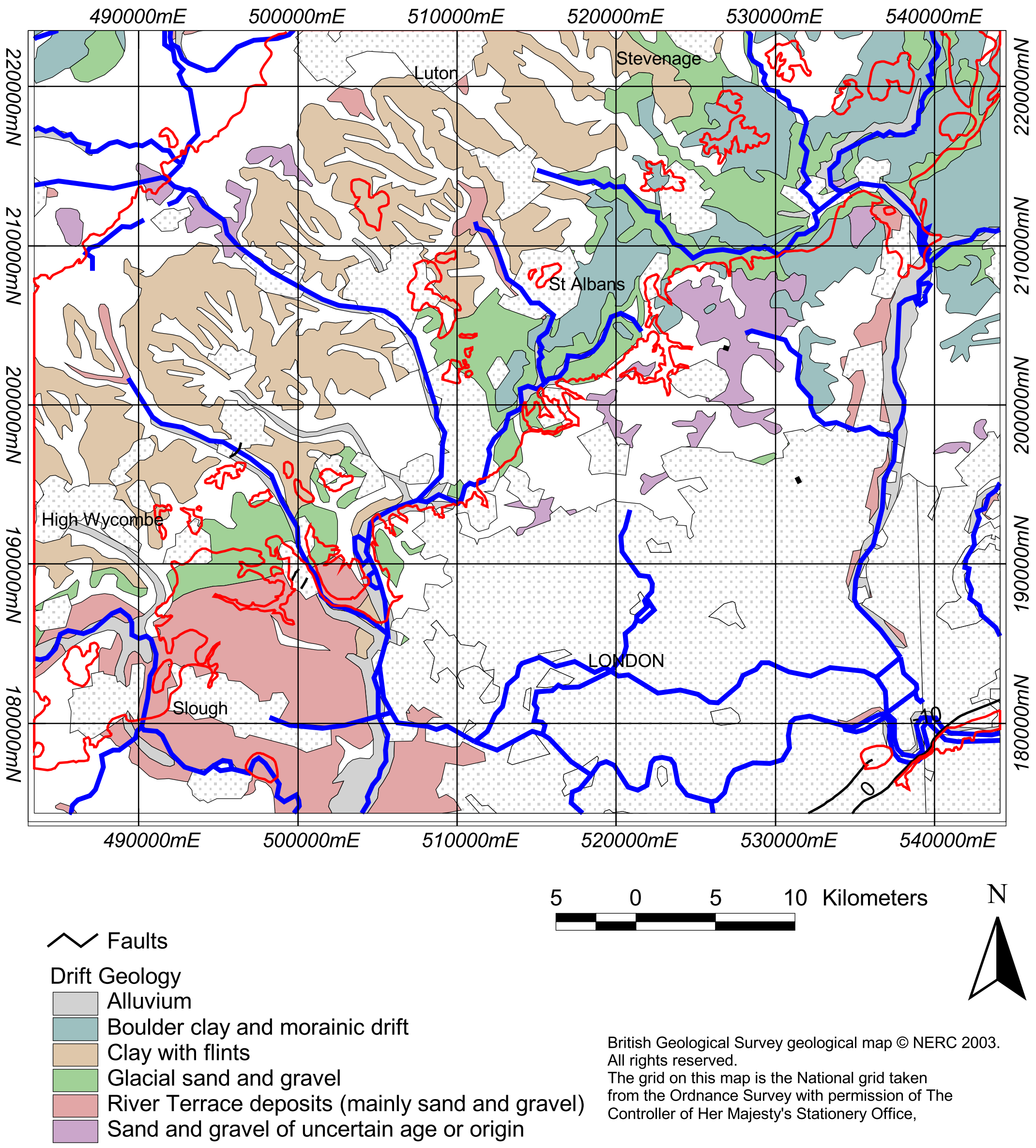

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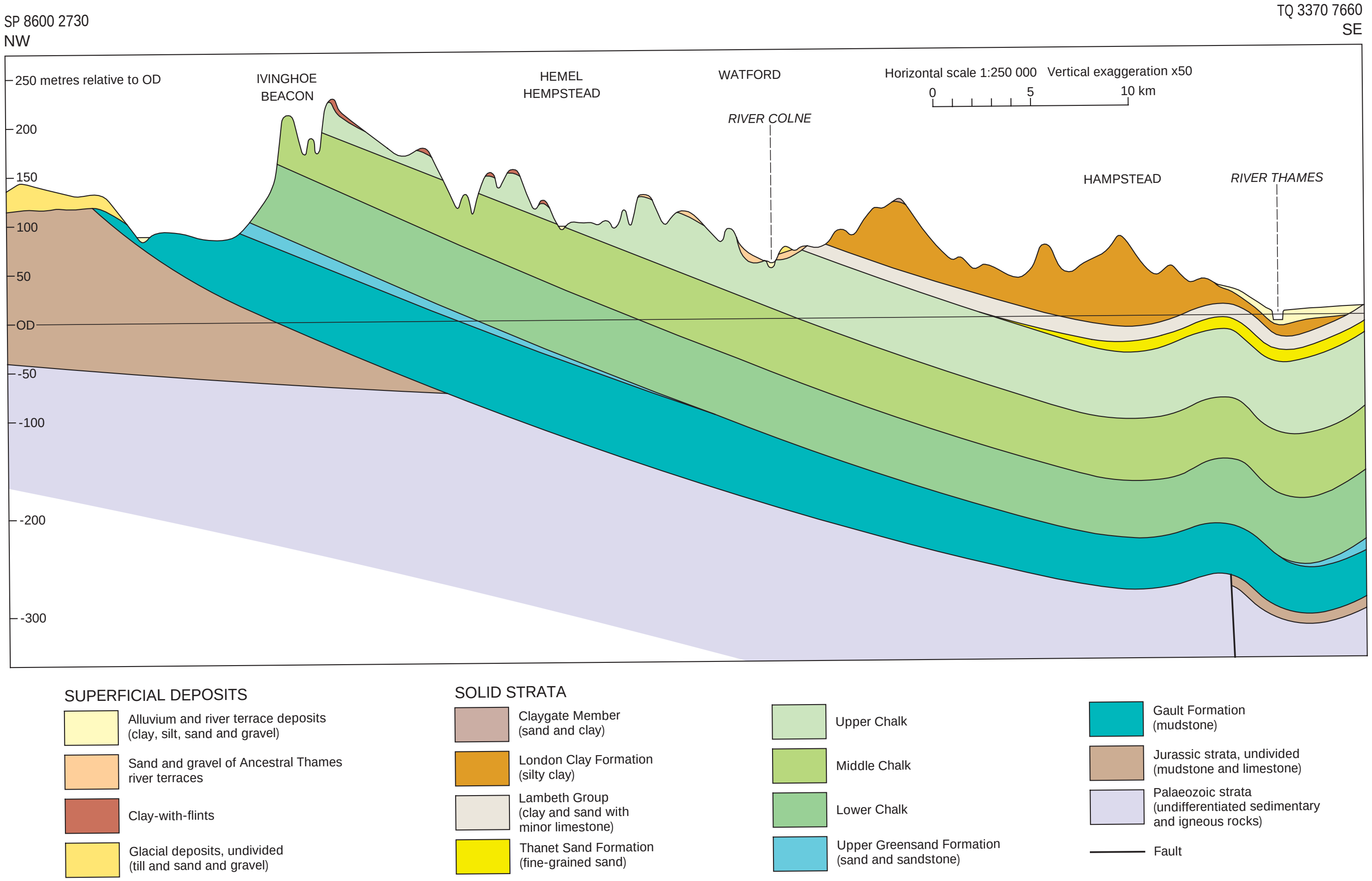
Figure 3.2 Geological map of the study area showing distribution of superficial deposits. Rivers are shown in blue and the outline of chalk outcrop in red.

The Palaeogene sequence above the Chalk comprises a mixed sequence of clays, sands and pebble beds, which vary both laterally and vertically, but generally increase in sand content towards the east. The oldest Palaeogene rocks are sandstones and silts of the Thanet Formation which are overlain by the Reading Formation (formerly the Woolwich and Reading Beds) which together form a minor aquifer and are often in hydraulic continuity with the Chalk. The London Clay Formation of Eocene age (Figure 3.3) forms the primary confining layer (aquitard) above the Thanet and Reading Formations. The succession may be incomplete locally, due to faulting, erosion or incomplete deposition and the reader is referred to Sumbler (1996) for further details.



Section from NW to SE across the Chilterns and London to show the relationships of the solid strata and superficial deposits

Figure 3.3 Simplified geological cross section trending north to south through the study area. Line of section is shown on Figure 3.1.

3.3 Hydrogeology

The Chalk aquifer is unconfined over much of the area but becomes confined beneath Palaeogene sediments towards the south and east (Figure 3.1). The Chalk and the lower Palaeogene sediments (Reading Formation comprising sands and clays) are often in hydraulic continuity and represent the principal aquifer in the London Basin. This aquifer system is overlain by the London Clay Group which forms an overlying aquitard. Where the Upper Greensand is present beneath the Chalk aquifer, it is generally in hydraulic connectivity with it. The Gault Formation, with a thickness up to 70 m forms a lower aquitard. This report concentrates on the Chalk which forms the major aquifer of the groundwater system in the area.

The chalk is a fine-grained, highly porous soft limestone, composed dominantly of coccolithic fragments. The Chalk is described as a dual-porosity aquifer. In a classic dual-porosity aquifer, the matrix pores provide the storage and the fractures provide permeable pathways. However, the Chalk is more complex because the high matrix porosity is not easily drained due to its low permeability (several orders of magnitude lower than the fractures) as a consequence of the small pore-throat diameters of the calcite matrix (Price et al., 1976). The Chalk is also a dual permeability aquifer and most of the flow occurs in a few dilated fractures, typically occurring at or within a few tens of metres of the water table through dissolution enhanced fissures. The dual porosity nature of the aquifer is important to the transport of solutes, and diffusional exchange of solutes between the matrix and fractures is likely to be important.

The average thickness of the Chalk is approximately 200-215 m in the area, although it thins towards the north (Allen et al., 1977). It is known to be most productive for water supply in the Lee Valley. The hydrogeology and aquifer properties of the area have been described by Allen et al. (1997) and the reader is referred to this text for more detailed description. Transmissivity and storage generally mirror topography in the Chalk and aquifer properties tend to be favourable beneath valleys with a reduction in transmissivity and storage beneath interfluves. Transmissivity is high along the valleys of the Rivers Lee and Colne and pumping has little effect on water levels. The ranges in transmissivity and storage for the Chalk aquifer of the London Basin are presented in Table 3.2. Geophysical logs of boreholes indicate that the majority of inflows are from the top 30 m of the aquifer. The higher permeability along the main valleys such as the Lee has allowed the ingress of calcium bicarbonate waters well into the confined part of the aquifer (Smith et al., 1976). The yield-drawdown characteristics of boreholes in the Chalk of the area are highly variable and depend both on well construction and the intersection of the borehole with transmissive fractures and fissures. High transmissivity is present in areas with well developed fracturing and low overburden thickness and is lower where the Chalk is confined (Allen et al., 1997).

Table 3.2 Range of values of Transmissivity and Storage Coefficient for the Chalk of the London Basin (from Allen et al., 1997)

	Minimum	**Maximum**	**Median**	**N**
Transmissivity ($m^2 d^{-1}$)	1	4300	230	88
Storage Coefficient*	$3.5x10^{-5}$	0.05	0.0024	41 (excluding S<0.1)

* Changes in the groundwater levels in central London with time have affected the state of the Chalk aquifer between confined or unconfined states. These changes have affected the measurements of storage coefficient (Allen et al., 1997).

The Chalk acts as a multi-layer aquifer with groundwater flow principally in the upper layers from close to the water table to depths of a few tens of metres. In Central London, boreholes mostly abstract from the Upper Chalk, which is known to be the main contributor to groundwater flow

Box 3.1 Rising groundwater levels in the Chalk-Basal sands aquifer of the central London basin.

Rising groundwater levels beneath London are the result of a significant reduction in abstraction from the Chalk aquifer since the mid-1960s. Prior to this, the aquifer had been increasingly exploited through the development of groundwater sources during the 19th and first half of the 20th centuries. By the time abstraction peaked in the 1960s, groundwater levels below central London had dropped to 88 metres below sea-level, creating a large depression in the water-table. The subsequent reduction in abstraction resulted in groundwater levels recovering by as much as 3 metres per year in places by the early 1990s. This has led to a gradual re-filling of the water-table cone of depression, although the Chalk aquifer is confined over most of London by a layer of London Clay, up to 80 metres thick in places. The rise in Chalk groundwater level could potentially affect the stability of foundations and tunnels in the London Clay. The extent to which the stability of buildings and tunnels could be compromised by continuing re-saturation of the Chalk and London Clay has not been quantified, but the potential disruption and damage is such to merit preventative action.

The GARDIT (General Aquifer Research, Development and Investigation Team) five-phase strategy to control London's rising groundwater was published in March 1999 and is now being implemented. Thames Water Utilities Ltd are project managing a strategy to control the rising groundwater level by developing additional means of abstracting groundwater for public water supply, and the Environment Agency is ensuring that this is done in a sustainable way.

The first phase of the GARDIT scheme is already having a clear impact in reducing and controlling levels in south London and the effect appears to be spreading north of the Thames into the central London Area. Later phases of the GARDIT strategy are now being put in place and this combined with other resource development options indicate that the effective and sustainable control of groundwater levels is achievable.

(Allen et al., 1997). As a result of high permeability zones close to the water table, changes in groundwater level may significantly modify the hydraulic characteristic of the aquifer. Significant changes in groundwater level have been observed beneath London during the last century (Box 3.1).

Solution features (e.g. dolines) are found near the junction of the Chalk and Palaeogene strata, where acidic run-off from the Palaeogene strata has dissolved the underlying Chalk causing collapse. Solution features are also present in the beds of many rivers, for example along the River Colne. The North Mimms swallow holes were shown to discharge into the River Colne during a tracer test in 1920. Buried streams were noted by Downing et al. (1972), and they may still form a major contribution to water flows in the tidal reaches of the River Thames. Interaction between surface water and groundwater is likely to play an important role in this region, and river water or discharges of sewage effluent may enter groundwater rapidly e.g. through swallow holes. The karstic properties of the Chalk result in an aquifer particularly vulnerable to contamination (Box 3.2). The soils provide minimal protection and soil leaching potential is high in the unconfined Chalk. As the groundwater becomes confined beneath the Palaeogene deposits, a greater degree of protection is provided to the Chalk aquifer.

Box 3.2 Groundwater contamination – risk and vulnerability

A wide variety of contaminants including nitrate, ammonia, pesticides, bromate, hydrocarbons and solvents have been detected in the unsaturated Chalk between the River Colne and the River Lee. There are two main reasons for the extent of this contamination. Firstly, there are a large number of potential sources of contamination in this region including landfills, industrial sites, petrol stations, laundries as well as agricultural, domestic and municipal sources. Secondly, the area is believed to be one of the more vulnerable areas to groundwater pollution in the Thames Region. This enhanced vulnerability is a result of a number of factors including: the dual porosity nature of the Chalk aquifer (described in section 3.3), the presence of solution features and a shallow water table in valley bottoms and in the low-lying zone adjacent to the confined Chalk.

The solution features include enlarged joints and fissures, swallow holes, sinkholes, caves and solution pipes and they are formed by the dissolution of the chalk matrix of fissure walls. This is frequently observed at the edge of the clay cover due to focussed recharge of weakly acidic rainfall and runoff. These solution features are important within the unsaturated zone because they provide conduits for the rapid transport of contaminants from the surface to groundwater thus bypassing the attenuation capacity of the soil and unsaturated zones.

Similarly, a shallow water table in valley bottoms and in the zone adjacent to the confined chalk means that the attenuation capacity of the unsaturated zone is reduced thus allowing the rapid transfer of contaminants from the surface to groundwater.

3.3.1 Development of the Groundwater flow system

Following formation and uplift of the London Basin, flow in the confined Chalk would have been limited due to the lack of natural outlets, with only minor leakage through the overlying rocks. However, erosion of the overlying sediments by the River Thames allowed natural outlets to form. Groundwater discharge through more permeable sections of the London Clay, or gravels to the River Thames has helped to enlarge fractures in the Chalk thereby increasing transmissivity (Allen et al., 1997). Although freshening of the aquifer began after the time of Eocene marine transgressions, it is likely that further ingress of saline water occurred during the Pliocene. Changes in climate have also influenced the hydraulic properties of the rocks e.g. periglaciation during the last Ice Age.

Large quantities of groundwater were pumped from the Chalk aquifer in the 19th and early 20th centuries and groundwater levels in the centre of the basin had declined by up to 70 m. This pumping would have induced greater flow from the unconfined aquifer and possibly leakage from the overlying Palaeogene sediments. However, since the 1950s, pumping has decreased (Box 3.1) and, as a consequence, groundwater levels are recovering (Lucas & Robinson, 1995).

The present-day groundwater flow system can be summarised as follows: the main area of recharge is the Chiltern Hills along the northern boundary of the area where the escarpment forms a major groundwater divide (Figure 3.4). The water table attains a maximum of 130 m AOD in the area to the south-west of Dunstable and both surface water and groundwater flow towards the south-southeast in the dip direction of the Chalk as illustrated in Figure 3.4. This regional flow system is likely to be locally modified by abstraction of groundwater from the aquifer. Recharge also occurs across the entire outcrop area of the Chalk and will modify water chemistry along the regional flow direction. Groundwater also forms an important contribution to river flow particularly during baseflow and will have a significant effect on river water quality.

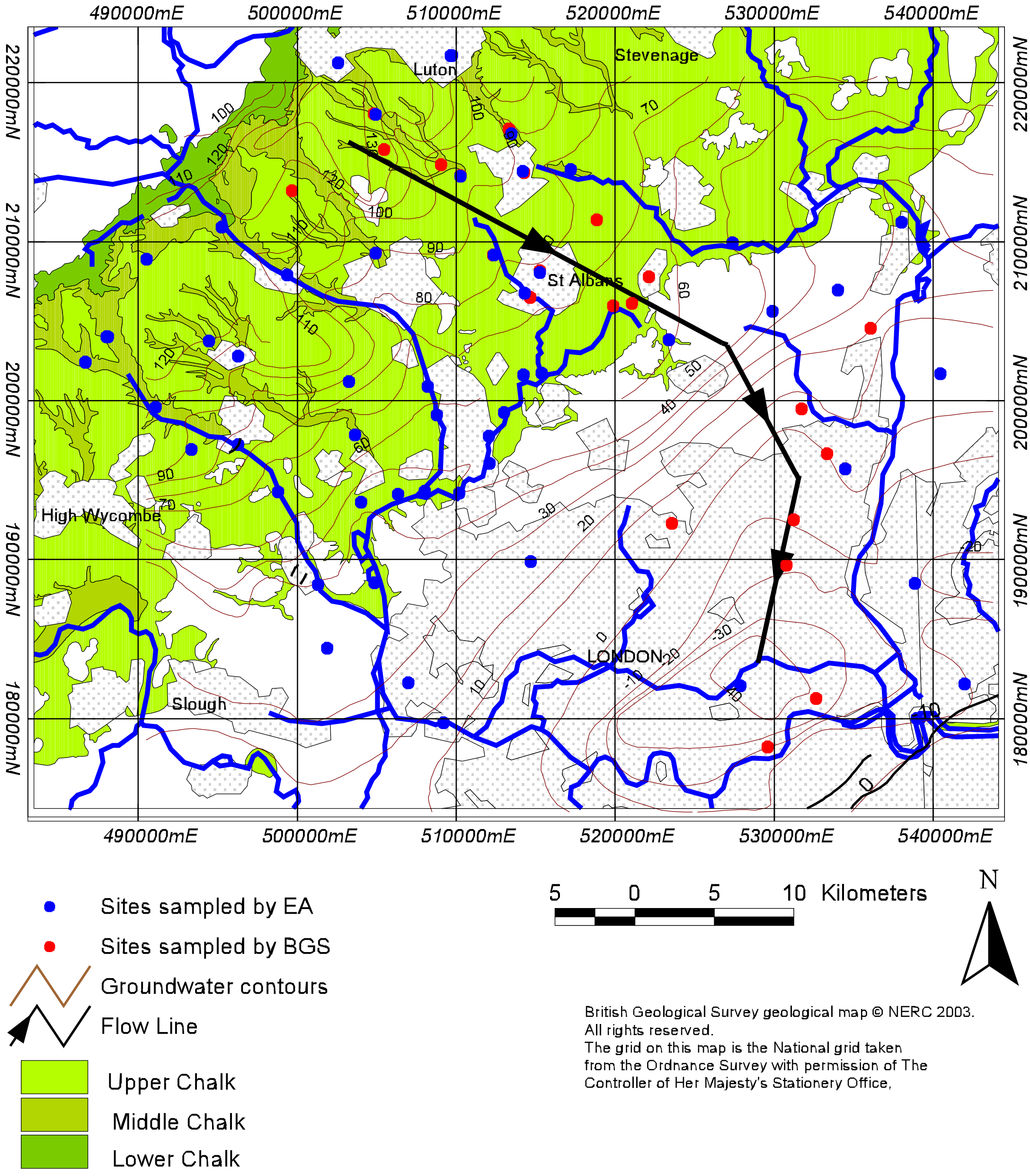


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Figure 3.4 Hydrogeological map showing groundwater level contours, sample sites considered in this report and a potential flowline where new samples were collected for this study. Rivers shown as blue lines.

3.4 Aquifer mineralogy

Chalk is a marine sediment composed dominantly of plankton microfossils (coccoliths) along with the remains of other biogenically-derived carbonates (e.g. Foraminifera) and silica which accumulated slowly on the sea floor. Precipitation of amorphous silica occurred at shallow depth beneath the sediment surface and early diagenetic reactions modified the silica to form flint nodules. Where extensive, the flint forms distinct horizontal and subhorizontal beds of flint. The microscopic texture of chalk, illustrated in Figure 3.5, shows that the microfossil remains are well preserved and the diameter of the pore spaces is approximately one micron. This small grain size and high matrix porosity provides a large reactive surface area for chemical processes to take place allowing rapid interaction between water and rock.

The Upper and Middle Chalk consist of relatively pure calcite (ca.98% calcium carbonate). However, minor amounts of other elements (Mg, Sr, Mn, Fe) are present in the calcite structure, which helped to stabilise the carbonate in the marine environment. These impurities in the carbonate lattice play an important role in the evolution of the groundwater chemistry, since they are slowly released to the groundwater as the chalk recrystallises under freshwater conditions. Numerous horizons of marl, flint and more lithified bands of hard and nodular chalk also occur throughout the sequence. Flint horizons are particularly prevalent in the Middle and Upper Chalk and are thought to form by biogenic redistribution of silica during early diagenesis.

Marl bands occur in chalk, often at erosional surfaces and contain Mg-rich smectite probably of volcanic origin (Pacey, 1984; Hancock, 1993). Iron oxides were found to be always less than 0.13%, although in the near-surface, iron staining is common and manganese oxide coatings are also found commonly on fracture surfaces (Morgan-Jones, 1977; Shand & Bloomfield, 1995).

Hardgrounds are zones of more intense lithification. These are considered to represent periods of non-deposition and active diagenesis (Hancock, 1975). Phosphate mineralisation is particularly prevalent in the marls and hardgrounds and can be identified by yellow staining (collophane: a carbonate-apatite) within the Chalk. Phosphatisation of the chalk is also often accompanied by glauconitisation which may be greater in the marl and hard bands. Glauconitic marl may contain additional accessory mineral phases such as mica, zircon, rutile and tourmaline. Pyrite is commonly found in association with the phosphate concretions and is particularly common in the Chalk Rock. Pyrite occurs both as tiny dispersed authigenic crystals, especially in the more argillaceous horizons, and as cylindrical concretions often infilling burrows.

Other impurities include zeolites at some locations, especially in the Lower Chalk, and trace amounts of chlorite. The Upper and Middle Chalk contains between 1-5% non-carbonate fraction, although this rises to 5-12% in the Lower Chalk. This fraction consists of quartz, clay minerals (montmorillonite, white mica and in the Lower Chalk, kaolinite), as well as phosphate minerals (francolite, fluorapatite).

Figure 3.5 SEM photomicrograph of the Chalk showing round coccolithic fragments and calcite platelets (Field of view approximately 5 µm).

Figure 3.6 illustrates the relationship between fracture and pore waters. Water moving rapidly along the fractures brings in new (reactive) water which dissolves fresh chalk, but may also lead to new minerals precipitating on the Chalk surface. There is slow exchange and diffusion between the water in the matrix and water in the fractures which has a strong influence on the resulting groundwater chemistry with time as water moves through the aquifer.

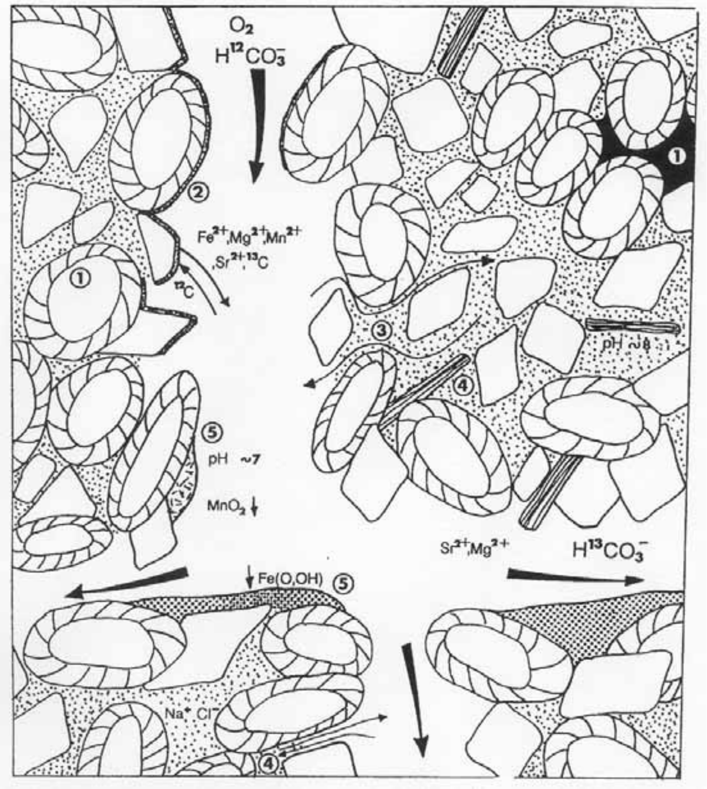

Figure 3.6 Diagrammatic sketch of chalk showing important chemical interactions at the microscopic scale (stippled region indicates matrix and clear area represents a fracture). The solid phase comprises mainly coccolithic fragments (1), foraminifera and other microfossils, and pyrite (black, (1)). Congruent and incongruent reactions occur on fracture surfaces forming mineral coatings or dissolution which may locally enhance porosity (2). Exchange of solutes between the fracture and matrix waters may occur (3). Ion-exchange reactions occur on clay mineral surfaces (4). The precipitation of Fe and Mn oxyhydroxides on fracture surfaces may also modify diffusional interchange (5).

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharge water and could be considered as representing the minimum baseline concentrations. The nearest rainfall chemistry available to the area is from Brooms Barn (TL 753656), located on the Chalk outcrop to the north west of the area. Data from Brooms Barn, averaged for 1988 are summarised in Table 3.1. The concentrations have been multiplied by 3 simply as an estimate of the approximate enrichment that might be expected due to evapotranspiration. 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 that may be taken up by vegetation, and concentrations may therefore be less in recharge waters than rainfall. Despite these influences, Table 3.3 provides the order of magnitude concentrations expected in young waters, which have not reacted with vegetation or aquifer minerals. For chloride, concentrations in groundwaters prior to anthropogenic inputs or mixing with other waters might be expected to be around 9-10 mgl^{-1}. Comparison of solute concentrations with other regions in the UK suggest that K concentrations are relatively low. In contrast SO_4 concentrations are particularly high, possibly due to atmospheric pollution from industrial effluents. NH_4 is the main source of N and background concentrations of N may be as high as 4.5 mg l^{-1} after allowing for evapotranspiration.

Table 3.3 Rainfall chemistry for Brooms Barn for 1998.

Parameter	**Rainfall**	**Rainfall (X3)**
pH	4.67	
Na (mg l^{-1})	1.69	5.06
K (mg l^{-1})	0.02	0.05
Ca (mg l^{-1})	1.06	3.17
Mg (mg l^{-1})	0.21	0.62
Cl (mg l^{-1})	3.09	9.27
SO_4 (mg l^{-1})	5.33	16.00
NO_3 (mg l^{-1})	0.40	1.20
NH_4 (mg l^{-1})	1.49	4.46
SEC (uS cm^{-1})	49.90	
Total rainfall (mm)	384.20	

The data are for 1988 taken from The UK National Air Quality Information Archive (www.airquality.co.uk).

3.6 Landuse in the area

A simplified land cover map of the area is shown on Figure 3.7. Much of the area is classed as urban, especially over the Palaeogene rocks of the south. The dominant land use over the Chalk outcrop comprises managed grassland and to a lesser degree arable land.

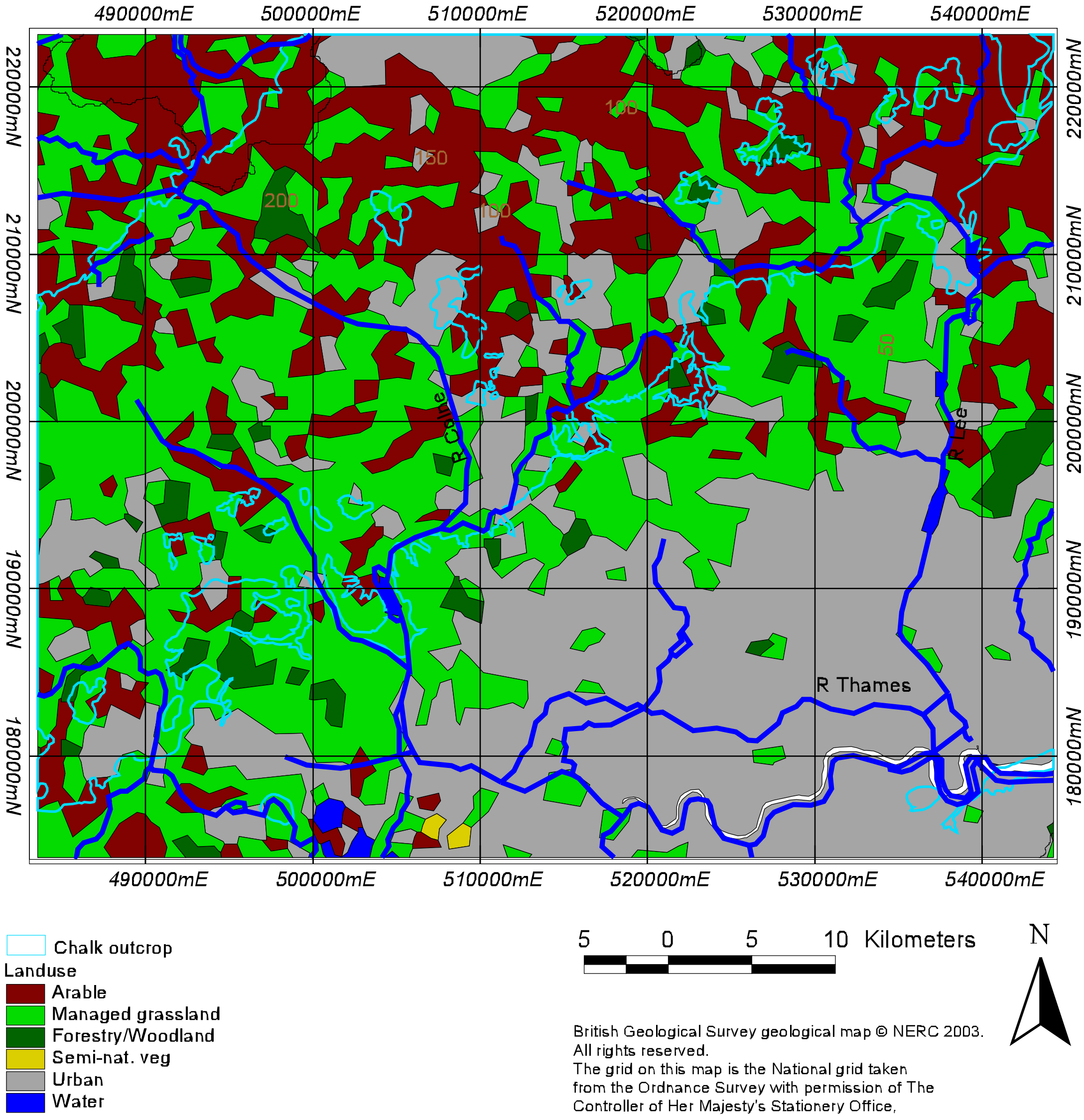

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Figure 3.7 Generalised landuse map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology © NERC.

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 27 public supply and private abstraction boreholes were sampled during September 2000. The boreholes were chosen so that they fell approximately upon a flow line beginning in the outcrop Chalk, running down hydraulic gradient towards the River Thames between Dunstable in the north west and north London. It was hoped that this would provide a representative long-term groundwater chemical evolution path. The flow line (Figure 3.5), which avoids crossing any rivers and includes both the unconfined and confined Chalk was chosen so that changes in the hydrogeochemistry along a groundwater flow path might be examined. There are, however, significant difficulties in delineating flowlines because groundwater flow may be modified locally by (1) geological structure, (2) differences in hydraulic parameters and (3) groundwater abstraction. The interaction between groundwater and surface water is also of particular interest in this region and monitoring boreholes were drilled adjacent to the River Lee in order to investigate this. Pumped groundwater and porewaters (extracted by centrifugation from rock core) were sampled from one of the boreholes and analysed for a range of chemical parameters.

In order to collect groundwater samples representative of the Chalk aquifer, all boreholes were pumped for an average of three well bore volumes prior to sampling. At each site, pH, Eh, temperature, specific electrical conductance (SEC) and alkalinity were measured. Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured in an anaerobic flow-through cell. Samples were collected for chemical analysis in polyethylene bottles. Those for major and trace elements were filtered through 0.45 µm filters, and the sample collected for cation and trace elements was acidified to 1% v/v HNO_3 to minimise adsorption onto container walls. Total and dissolved organic carbon (TOC and DOC) samples were also collected in Cr-acid washed glass bottles and, for the DOC samples, a 0.45µm silver-membrane filter was used. Additional samples were also collected in glass bottles for stable isotopes (δ^2H, δ^{18}O and δ^{13}C) and all samples were kept cool prior to analysis.

Major cations and sulphate were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP AES) and a wide range of trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP MS). Nitrogen species were analysed by colorimetry at the Environment Agency laboratories in Nottingham and the halogen (Cl, Br, I, F) elements analysed by automated colorimetry at and BGS laboratories. TOC and DOC were analysed by a TOCSIN II analyser. Stable isotope analyses were completed in the BGS laboratory by mass spectrometry and the results reported relative to SMOW for δ^2H and δ^{18}O and PDB for δ^{13}C.

4.2 Other data

In order to provide a good regional coverage of the aquifer the samples were augmented by data from a further 60 boreholes monitored as part of the Environment Agency's groundwater quality monitoring network. The most extensive analyses were available from 1997 and 60 analyses from September 1997 were added to the database to assess spatial variations.

4.3 Problems in obtaining representative samples

The chemical composition of a groundwater sample will be a function of many factors. Variations in water quality may arise simply as a result of differences between the boreholes sampled, for example:

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

4.3.1 Different borehole designs

A groundwater sample from a known position within the Chalk may represent a unique chemistry. However, boreholes penetrate different depths and may be open throughout much of their length allowing mixing to occur. Differences in borehole design, in particular depth of borehole and depth of casing may therefore lead to the identification of differences in water quality not related to geochemical reactions along a simple 2-D flow path. In addition, the construction of a borehole is likely to disturb the original stratification of water quality and provide a pathway for water to migrate from zones of higher head to zones of lower head.

4.3.2 Differences in stratigraphy

Stratification of groundwater quality develops as a result of natural variations in the chemical and physical properties of aquifers. Pumped samples inevitably represent a mixture of a stratified system and this is further complicated due to the nature of the Chalk aquifer: The Chalk acts as a dual-porosity aquifer and pumped samples will represent predominantly fracture-derived water, which may be different from the matrix of the Chalk: water in the fractures will generally have much higher flow velocities and therefore a different residence time in the aquifer. The identification of vertical chemical variations in the matrix of the chalk is attempted in this project on the core drilled from close to the River Lee.

4.3.3 Different pumping history

Groundwater abstraction, especially where large volumes of water have historically been pumped, is likely to have modified the groundwater chemistry from its original composition. For example, in areas where the Chalk aquifer is overlain by the Lower London Tertiaries, extensive abstraction has had a significant impact on water quality. The large groundwater abstraction in central London resulted in a lowering of groundwater levels to such an extent that the aquifer changed from a reducing to an oxidising environment with significant repercussions on the groundwater chemistry. Extensive groundwater abstraction may also induce significant leakage from the overlying Palaeogene or permeable drift deposits which may influence the groundwater quality. Variable flow rates and differing hydraulic gradients within the aquifer may also exaggerate differences in groundwater chemistry.

This report presents a broad assessment of the water quality variations observed across the aquifer and the controlling geochemical processes. Chemical reactions are both time and space dependent and the data presented simply represents a snapshot of the water quality, which is in a constant state of change.

4.4 Data handling

For the purposes of this report, any historical data with an ionic charge imbalance greater than 10% were rejected and for samples collected within the project, the maximum ionic balance accepted was 5%. Boreholes which were known to be contaminated or were situated in areas of point-source pollution were avoided. For plotting purposes, data below the detection limit were substituted with half of the detection limit. Changes in the detection limit, both with time and between laboratories often prove problematical in the calculation of average results. The median is least affected by outlying data and is used, together with the minimum, maximum and 97.7 percentile (mean + 2 σ (sigma)) to describe the average and range of baseline data.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section deals with the fundamental hydrochemical characteristics of the groundwater in the Chalk between the Rivers Lee and Colne. A summary of the data are presented in Tables 5.1 and 5.2 and includes analyses from all 87 sites studied within the study area. The table shows the ranges and averages of data as well as an upper concentration (mean + 2σ or 97.7th percentile) representing the upper limit of baseline in pristine waters. Where anthropogenic inputs are evident, an upper baseline has to be estimated (chapter 8). The median is preferred to the mean as an average as it is more robust and less affected by extreme values. The 97.7 percentile is used as a practical cut off to define outlying data.

Table 5.1 Field parameters, isotope data and range of major and minor element concentrations in the Chalk aquifer between the River Lee and River Colne catchments.

		Unconfined						**Confined**					
	Units	**Minimum**	**Maximum**	**Median**	**Mean**	**97.7th %**	**n**	**Minimum**	**Maximum**	**Median**	**Mean**	**97.7th %**	**n**
T	°C	9	13	11.3	11.3	12.2	38	12	14.9	12.8	13.3	14.8	9
pH		6.94	8.00	7.20	7.27	7.90	62	7.00	8.30	7.40	7.48	8.25	21
Eh	mV	378	659	409	447	609	18	-2	660	352	353	627	8
DO	mg l^{-1}	0.3	7.8	5.7	5.2	7.7	18	<0.1	5.1	<0.1	0.7	4.3	9
SEC	µS cm^{-1}	466	880	596	617	819	61	442	4410	741	978	3296	20
δ^2H	‰	-51.1	-48.9	-49.6	-49.8	-48.9	4	-53.3	-44.6	-48.1	-48.1	-44.8	8
δ^{18}O	‰	-7.7	-7.2	-7.4	-7.5	-7.2	4	-7.9	-7.1	-7.2	-7.3	-7.1	8
δ^{13}C	‰	-14.2	-9.5	-12.7	-12.1	-9.6	3	-11.5	-3.3	-6.9	-7.2	-3.3	5
Ca	mg l^{-1}	106	156	125	127	152	38	17	204	93.2	88.0	169	21
Mg	mg l^{-1}	1.7	7.9	2.3	3.0	7.2	38	3.9	113	24	27.8	82.7	21
Na	mg l^{-1}	6	47	12.1	16.0	46.1	38	8	589	83	115	460	21
K	mg l^{-1}	0.8	9	1.9	2.3	6.5	38	2	28.5	9.2	10.2	25.1	21
Cl	mg l^{-1}	11.5	74	23.0	28.7	67.6	53	14	1250	40	119	764	21
SO_4	mg l^{-1}	5	78	22.0	28.1	76.9	53	5	562	102	155	525	21
HCO_3	mg l^{-1}	289	367	329	329	364	12	256	447	323	325	442	21
NO_3-N	mg l^{-1}	3.2	11.2	5.9	6.4	10.1	55	<0.01	2.18	0.1	0.265	1.867	21
NO_2-N	mg l^{-1}	<0.001	0.053	0.002	0.006	0.038	59	<0.001	0.021	0.002	0.004	0.016	21
NH_4-N	mg l^{-1}	<0.003	0.150	0.015	0.017	0.060	60	0.004	1.660	0.240	0.408	1.370	21
P	mg l^{-1}	0.042	0.211	0.078	0.085	0.204	18	<0.02	0.107	0.01	0.027	0.094	9
TOC	mg l^{-1}	0.37	3.45	1.54	1.56	3.28	38	0.05	6.00	1.66	1.64	5.14	14
DOC	mg l^{-1}	1.15	3.09	1.66	1.86	2.95	11	1.29	7.29	2.34	3.17	6.92	6
F	mg l^{-1}	<0.05	0.186	0.098	0.094	0.170	49	0.267	1.875	1.05	1.049	1.859	21
Br	mg l^{-1}	0.030	0.680	0.060	0.133	0.663	38	<0.1	0.430	0.130	0.164	0.426	18
I	mg l^{-1}	0.003	0.168	0.006	0.023	0.150	18	0.001	0.040	0.010	0.015	0.038	9
Si	mg l^{-1}	4.5	10.9	7.3	7.2	10.2	18	5.9	10.7	8.7	8.3	10.6	9

5.2 Water types and physicochemical characteristics

Groundwaters sampled from the outcrop area of the Chalk are of Ca-HCO_3 type, typical of the unconfined Chalk. The Piper Plot (Figure 5.1) illustrates the relative proportions of elements which determine the groundwater composition. The cation trilinear plot shows that most groundwaters in the unconfined aquifer have a very low Mg/Ca ratio, close to or slightly above that of the carbonate matrix of the Chalk. The confined groundwaters initially trend towards a higher Mg/Ca ratio with age, followed by a clear trend towards Na dominance (Figure 5.1). In terms of anions, there is a distinct trend from HCO_3 towards SO_4 for most samples in the confined groundwaters. The groundwaters show a range in water types from fresh Ca-HCO_3 waters in the unconfined aquifer towards a Na-$SO_4(HCO_3)$, or occasionally Na-Cl type in central London.

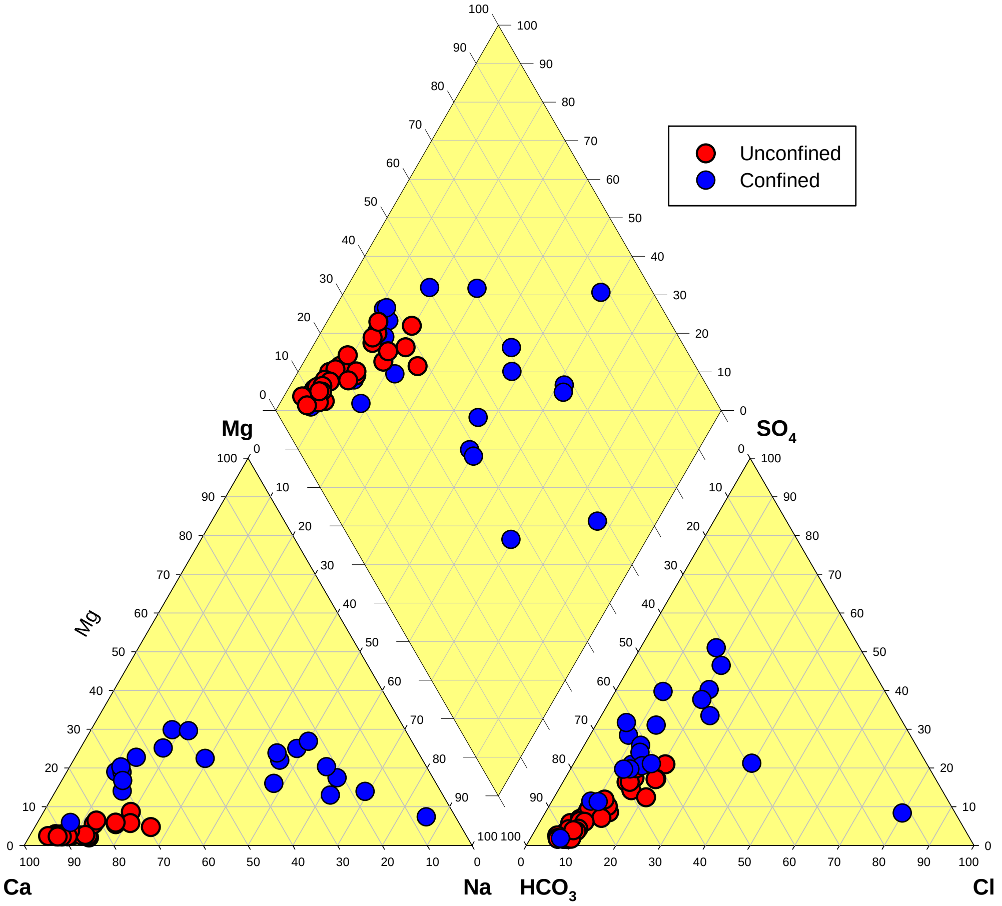


Figure 5.1 PIPER plot showing the relative concentrations of major cations and anions in the unconfined and confined parts of the Chalk aquifer.

Physicochemical parameters were recorded on site for all samples collected within this study. The results demonstrate that the waters are generally fresh: mineralisation varies from weak to moderately mineralised (median SEC of 618 µS cm^{-1}), with a gradual increase towards the south where the aquifer becomes more confined. Temperatures also increase towards the deeper confined parts of the aquifer in Central London with a maximum of 14.9° C and the groundwaters are generally well buffered in terms of acidity with a circumneutral pH (median value of 7.2). Dissolved oxygen (DO) was typically high in groundwater from outcrop areas but below the limit of detection in groundwaters beneath Central London, demonstrating that the aquifer changes from an oxidising environment in the north to a reducing environment towards central London. It was not possible to measure DO or redox potential in a flow-through cell at many sites and the median Eh of 407 mV is probably, therefore, an overestimate: Eh would become more positive on contact with the atmosphere.

The chemistry of groundwaters from the unconfined and confined parts of the aquifer have different hydrochemical characteristics. The baseline chemistry of the two “systems” (see baseline definition on page v) is so different that it is logical to subdivide the samples into unconfined and confined groundwaters. The data presented in Tables 5.1 and 5.2 and on subsequent plots have been subdivided on this basis.

Table 5.2 Trace concentrations in the Chalk aquifer of the River Lee and River Colne catchments.

		Unconfined						Confined					
	Units	Minimum	Maximum	Median	Mean	97.7th %	n	Minimum	Maximum	Median	Mean	97.7th %	n
Ag	ug l^{-1}	<0.05	0.25	<0.05	0.04	0.16	20	<0.05	0.06	<0.05	0.03	0.05	9
Al	ug l^{-1}	<1	46	2	6.63	29.44	31	<1	20	4	5.83	18.53	9
As	ug l^{-1}	<1	5	0.5	1.27	5	30	<1	4	1	1.33	3.82	9
Au	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
B	ug l^{-1}	<100	300	<100	<100	215	38	<100	600	128	209	563	19
Ba	ug l^{-1}	25	69.2	43.6	43.1	62.9	29	31.1	93.6	53.5	55.9	92.8	9
Be	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
Bi	ug l^{-1}	<0.05	0.12	<0.05	<0.05	0.10	18	<0.05	0.19	<0.05	0.05	0.17	9
Cd	ug l^{-1}	<0.05	0.05	0.05	<0.05	0.05	37	<0.05	0.35	0.05	0.06	0.26	18
Ce	ug l^{-1}	<0.01	0.04	<0.01	<0.01	0.03	18	<0.01	0.01	<0.01	<0.01	<0.01	9
Co	ug l^{-1}	<0.02	0.59	<0.02	0.12	0.56	18	<0.02	12.4	0.18	1.70	10.3	9
Cr	ug l^{-1}	<0.5	3	0.5	0.72	2.50	37	<0.5	1.8	0.5	<0.5	1.29	18
Cs	ug l^{-1}	<0.01	0.01	<0.01	<0.01	0.01	18	<0.01	0.02	<0.01	<0.01	0.02	9
Cu	ug l^{-1}	0.6	21.8	4.9	6.77	21.5	38	0.4	37.1	2.05	4.63	27.7	18
Dy	ug l^{-1}	<0.01	0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Er	ug l^{-1}	<0.01	0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Eu	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Fe	ug l^{-1}	<5	23	15	10	19	38	9	1280	140	234	1007	21
Ga	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
Gd	ug l^{-1}	<0.01	0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Ge	ug l^{-1}	<0.05	0.06	<0.05	<0.05	<0.05	18	0.07	2.27	0.14	0.55	2.16	9
Hf	ug l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	18	<0.02	0.02	<0.02	<0.02	<0.02	9
Hg	ug l^{-1}	<0.1	0.2	<0.1	<0.1	0.11	38	<0.1	0.7	<0.1	0.12	0.54	18
Ho	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
In	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Ir	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
La	ug l^{-1}	<0.01	0.05	<0.01	<0.01	0.04	18	<0.01	0.02	<0.01	<0.01	0.02	9
Li	ug l^{-1}	<10	<10	<10	<10	<10	18	20	150	50	52	133	9
Lu	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Mn	ug l^{-1}	<2	40	5	4.53	14.5	38	3	40	6	13.8	37.7	21
Mo	ug l^{-1}	<0.1	1.5	0.05	0.20	1.38	18	0.2	3.5	1.5	1.4	3.30	9
Nb	ug l^{-1}	<0.01	0.02	<0.01	<0.01	0.02	18	<0.01	0.03	<0.01	0.01	0.03	9
Nd	ug l^{-1}	<0.01	0.07	<0.01	0.01	0.05	18	<0.01	0.02	<0.01	<0.01	0.02	9
Ni	ug l^{-1}	<0.2	12	2.5	2.59	7.03	37	<0.2	78.0	2.5	9.58	60.6	18
Os	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
Pb	ug l^{-1}	<0.4	1.7	1	0.72	1.20	38	<0.4	1	0.6	0.6	1	18
Pd	ug l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	18	<0.2	<0.2	<0.2	<0.2	<0.2	9
Pr	ug l^{-1}	<0.01	0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Pt	ug l^{-1}	<0.01	0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Rb	ug l^{-1}	0.89	2.81	1.60	1.68	2.78	18	1.68	6.44	3.35	3.68	6.20	9
Re	ug l^{-1}	<0.01	0.02	<0.01	<0.01	0.02	18	<0.01	0.29	0.04	0.10	0.28	9
Rh	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	0.01	<0.01	<0.01	<0.01	9
Ru	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
Sb	ug l^{-1}	<0.05	1	0.05	<0.05	0.83	30	<0.05	0.58	0.07	0.24	0.57	9
Sc	ug l^{-1}	0.88	3.02	2.04	2.02	2.92	18	2.13	2.93	2.41	2.44	2.87	9
Se	ug l^{-1}	<0.5	1.9	<0.5	<0.5	1.46	25	<0.5	9.8	<0.5	1.66	8.55	9
Sm	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
Sn	ug l^{-1}	0.11	0.28	0.16	0.17	0.27	18	0.11	0.6	0.28	0.27	0.58	9
Sr	ug l^{-1}	210	553	310	325	526	37	1009	5996	2707	2793	5724	18
Ta	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	<0.05	<0.05	<0.05	<0.05	9
Tb	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Te	ug l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	18	<0.05	0.09	<0.05	<0.05	0.08	9
Th	ug l^{-1}	<0.05	0.2	<0.05	<0.05	0.16	18	<0.05	1.47	0.16	0.34	1.29	9
Ti	ug l^{-1}	<10	<10	<10	<10	<10	18	<10	<10	<10	<10	<10	9
Tl	ug l^{-1}	<0.01	0.08	<0.01	0.02	0.07	18	<0.01	0.11	0.01	0.03	0.10	9
Tm	ug l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
U	ug l^{-1}	0.17	0.53	0.31	0.33	0.53	18	<0.05	0.8	0.31	0.33	0.77	9
V	ug l^{-1}	<1	<1	<1	<1	<1	18	<1	1	<1	<1	1	9
W	ug l^{-1}	<0.1	<0.1	<0.1	<0.1	<0.1	18	<0.1	<0.1	<0.1	<0.1	<0.1	9
Y	ug l^{-1}	<0.01	0.1	<0.01	0.01	0.08	18	0.01	0.07	0.03	0.03	0.07	9
Yb	ug l^{-1}	<0.01	0.02	<0.01	<0.01	0.02	18	<0.01	<0.01	<0.01	<0.01	<0.01	9
Zn	ug l^{-1}	1.8	298	9	20	109	37	<2	245	14	33	180	18
Zr	ug l^{-1}	<0.5	<0.5	<0.5	<0.5	<0.5	18	<0.5	<0.5	<0.5	<0.5	<0.5	9

Box plots (Figures 5.2 and 5.4) are plotted on a logarithmic scale with the order of elements on the x-axis plotted in order of abundance in seawater. For reference, the dilute seawater line normalised to the median Cl of the unconfined samples is plotted. This provides a general indication of enrichment, in most aquifers, above the marine-derived input (rainfall input and mixing with connate water) due to water-rock interaction.

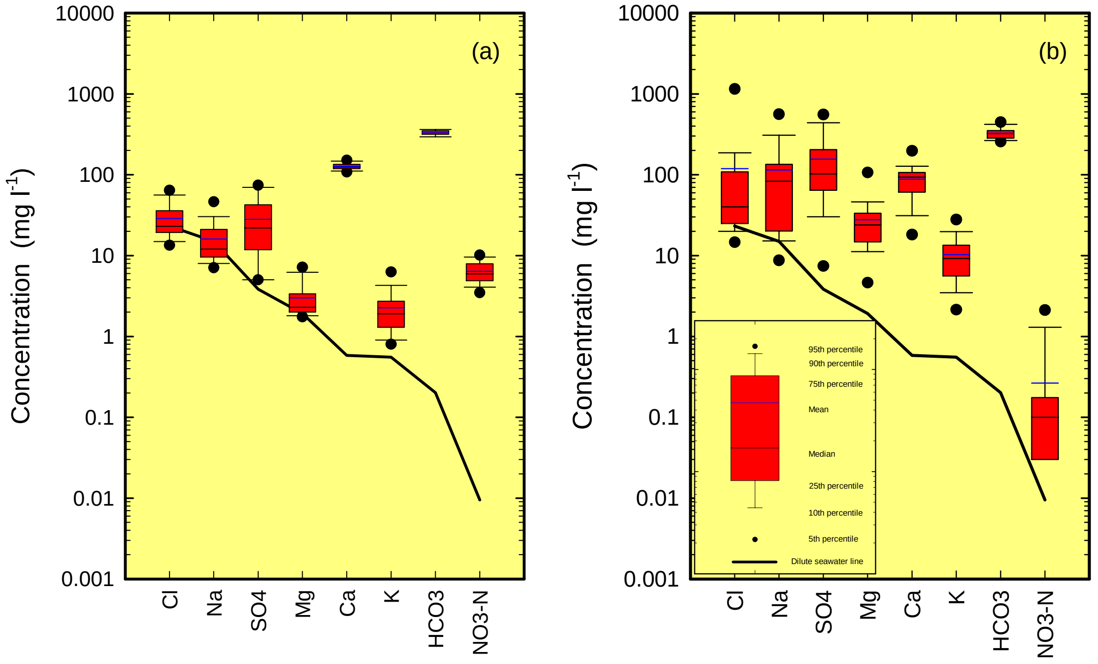


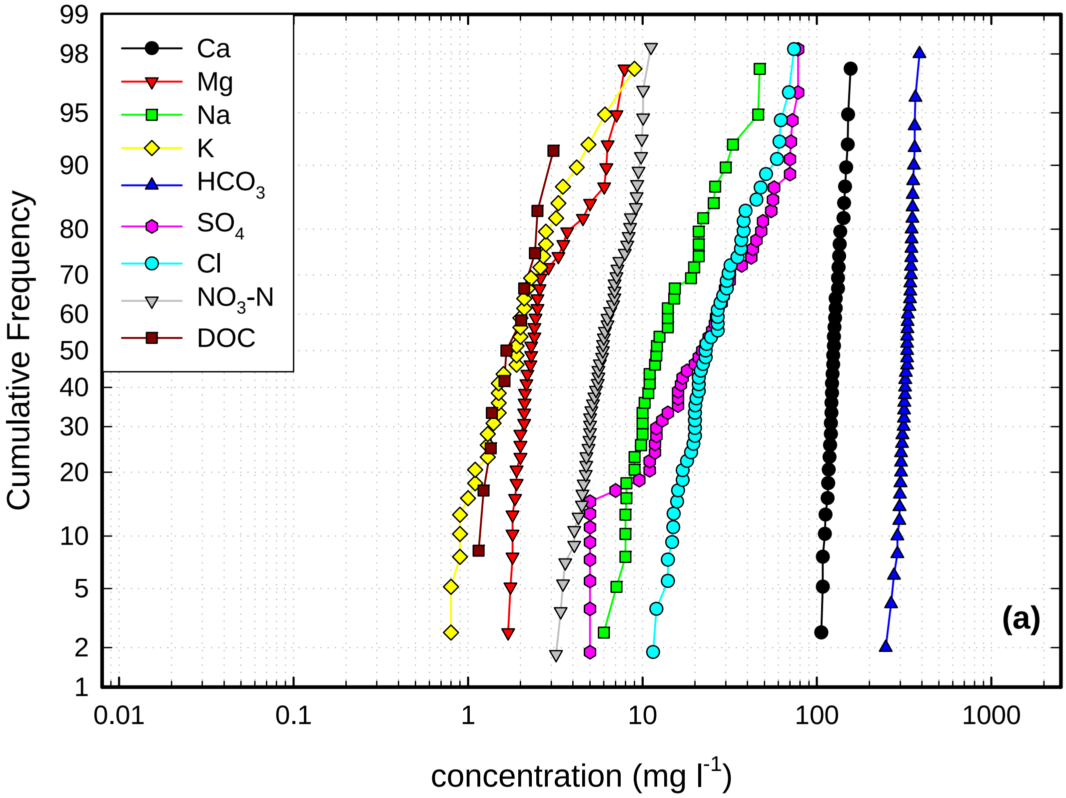
Figure 5.2 Boxplots showing major element concentrations in groundwaters of the (a) unconfined and (b) confined Chalk aquifer of the study area. Solid line shows the seawater dilution curve based on median Cl of the unconfined groundwater.

The cumulative probability plots (Figures 5.3 and 5.5) illustrate the distribution, range and relative abundance of the solutes in the groundwater. The form of the curve conveys information about the hydrogeochemistry and overall controlling factors (Box 5.1) and provides an insight into both the natural processes and human influences on groundwater.

5.3 Major elements

The median concentration of Cl (23 mg l^{-1}) in the unconfined groundwaters suggests an additional source to rainfall for this element as very few samples have concentrations close to that estimated for precipitation after allowing for evapotranspiration (ca. 9 mg l^{-1}; Table 3.2). Calcium and HCO_3 dominate the major ion chemistry, plotting furthest above the dilute seawater line, and have very narrow ranges in concentration (Figure 5.2). Nitrate and to a lesser degree sulphate also plot significantly above this line. The confined groundwaters generally show a wider spread of data and higher concentrations, except for nitrate which is often below the limit of detection.

The major element data are shown on a cumulative probability plot (Figure 5.3). Where vertical lines are plotted at low concentrations, these indicate concentrations below the limit of detection (plotted as half of the limit of detection). Many major elements approach log-normal distributions which plot as straight lines on cumulative probability plots. Calcium and HCO_3 show steep gradients in the unconfined groundwaters suggesting rapid saturation with respect to calcite (Box 5.1). The higher median concentrations and greater ranges of most elements in the confined groundwaters (e.g. K, Mg, SO_4) are also highlighted on Figure 5.3.



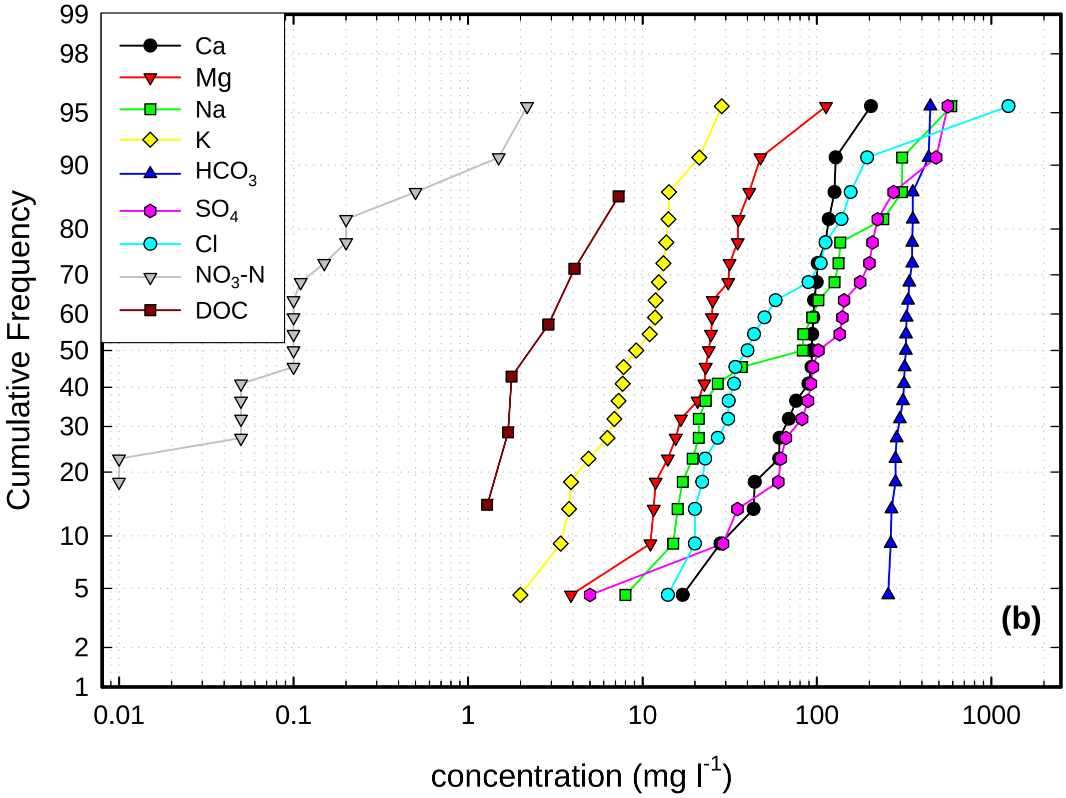


Figure 5.3 **Cumulative frequency diagrams showing the distribution of major element concentrations in (a) the unconfined and (b) the confined chalk aquifer of the study area.**

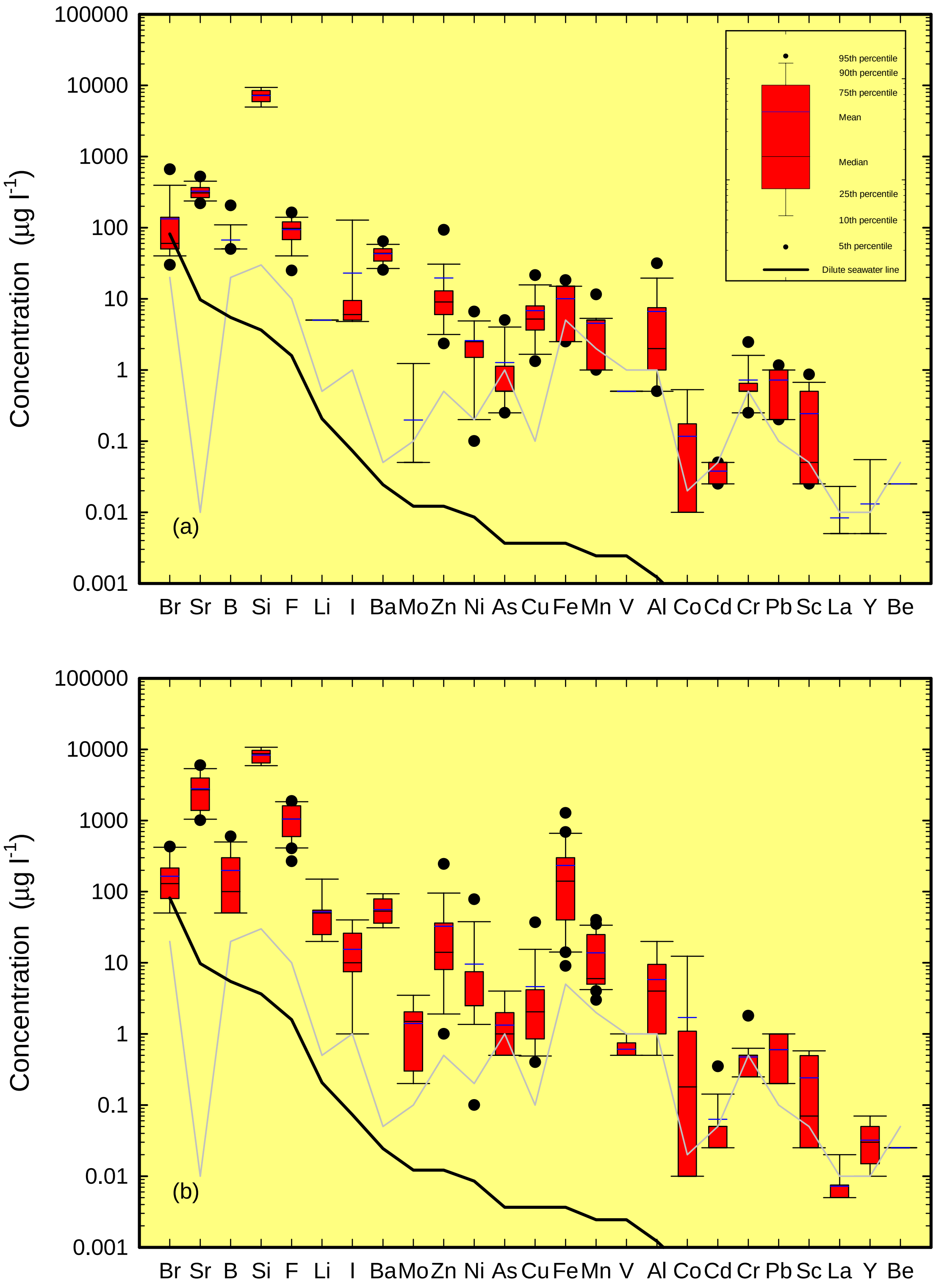


Figure 5.4 Boxplots showing minor and trace element concentrations in groundwaters of the (a) unconfined and (b) confined chalk aquifer of the study area. Solid line shows the seawater dilution curve based on median Cl of the unconfined groundwater and grey line shows typical detection limits.

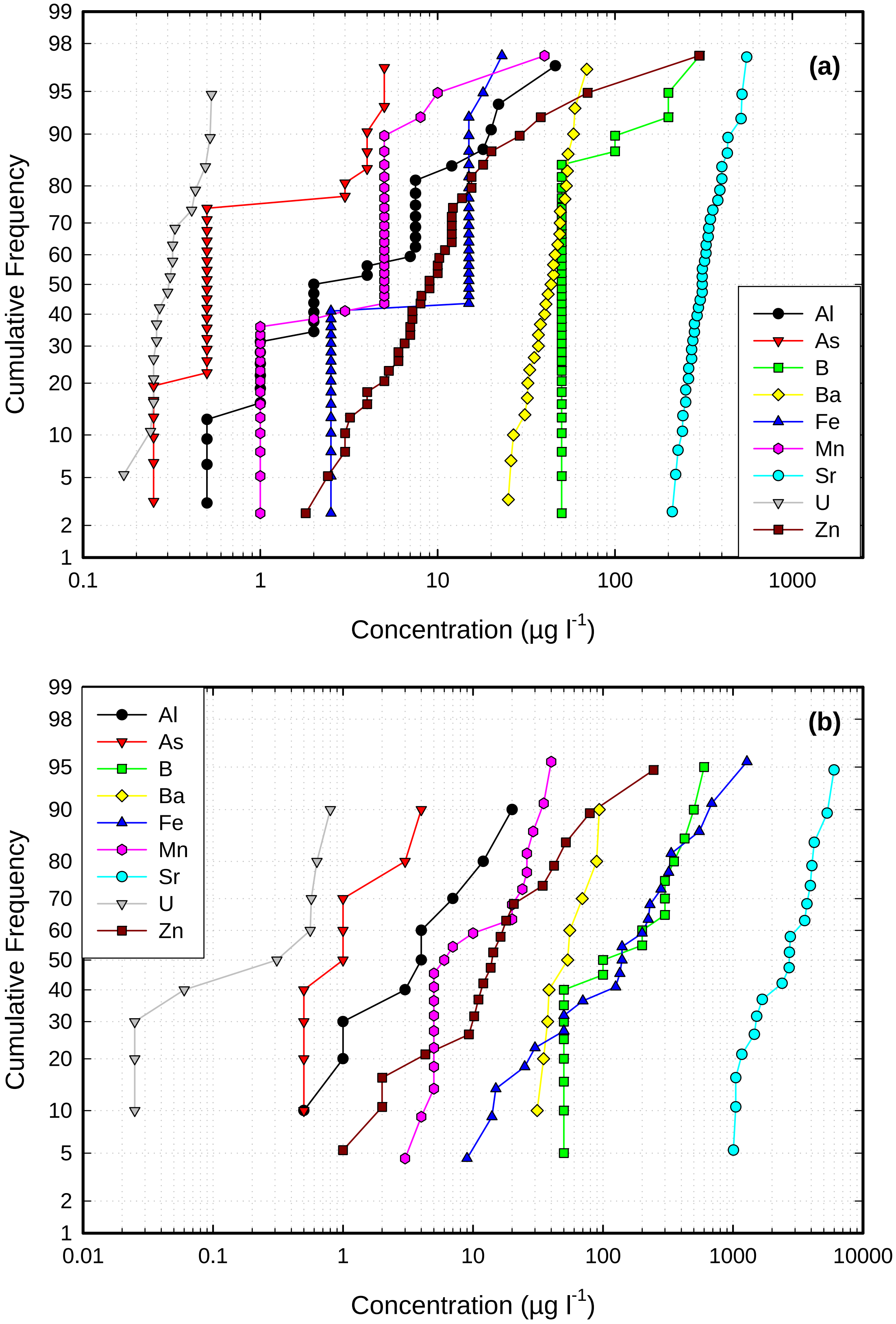
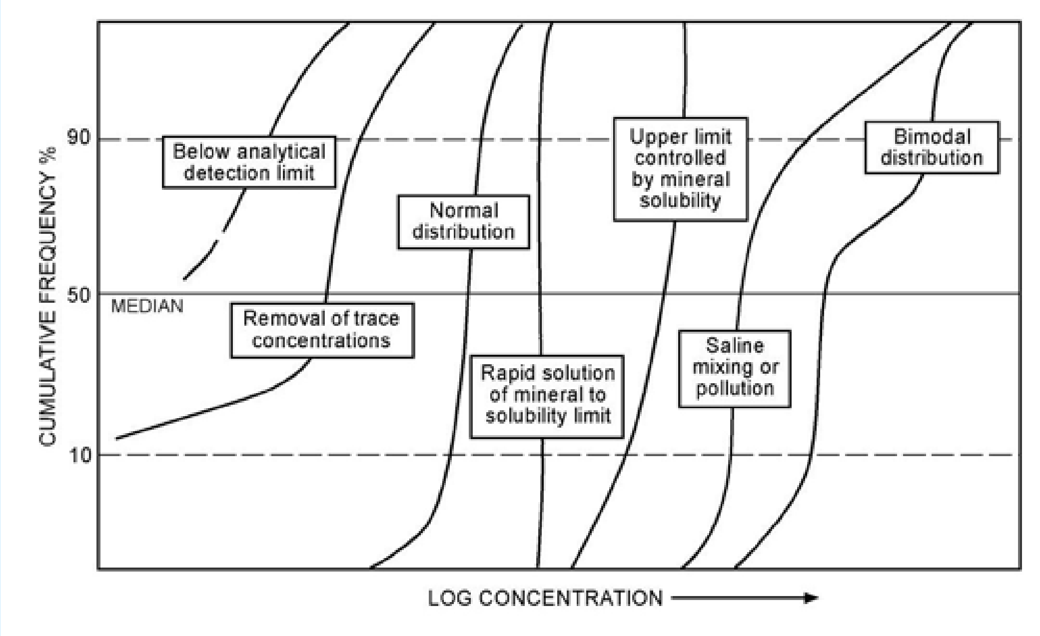


Figure 5.5 Cumulative frequency diagrams showing the distribution of minor and trace element concentrations in (a) the unconfined and (b) the confined chalk aquifer of the study area.

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



i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.
ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.
iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).
iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO_3 by *in situ* denitrification).
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.

5.4 Minor and trace elements

Minor and trace element concentrations are illustrated in Figures 5.4 and 5.5. In Figure 5.4 the seawater line is determined using the median Cl. The concentrations of most metals are relatively low in the unconfined groundwaters reflecting their limited mobility at circumneutral pH and in oxidising conditions. The confined groundwater tend to have a higher median and greater range of concentrations for most minor and trace elements. Iron, and to a lesser degree manganese, are significantly higher in the confined groundwaters as a consequence of more reducing conditions. Fluoride and Sr are also higher in the confined groundwaters by at least an order of magnitude. Bromide is slightly lower than diluted seawater in groundwaters of the outcrop area, possibly reflecting anthropogenic modification.

Silicon is similar in the two parts of the aquifer and likely controlled by saturation with respect to a silica phase. Concentrations approach a normal distribution (Figure 5.5) as indicated by the similarity of the median to mean concentrations (Table 5.1).

Many of the cumulative frequency plots for trace elements illustrate a wide range of concentrations and generally more complex distributions (Figure 5.5) than the major ions, particularly in the confined aquifer. Strontium can provide an indication of residence time and concentrations appear to be significantly higher in the confined region of the aquifer, where they reach almost 6 mg l^{-1}. Figure 5.5 also suggests the presence of more than one population in the confined aquifer. Metals are generally low in concentration due to their low solubility at the circumneutral pH values of the groundwaters. However, concentrations may be relatively high locally and the distributions of some elements in Figure 5.5 suggest the possibility of several sources.

A selection of samples were analysed for $\delta^{2}H$, $\delta^{18}O$ and $\delta^{13}C$ to estimate the approximate age of the groundwater. The results show a significant variation across the aquifer and are discussed in Chapter 6.

5.5 Pollution indicators

Ideally, groundwater samples that are used in the determination of the baseline should contain no traces of human impact. Pollution alters baseline concentrations either directly through the addition of solutes or indirectly by promoting chemical reactions within the aquifer (Box 5.2). However, due to the demands on water resources and the extent of diffuse pollution, it is difficult to obtain pristine groundwaters.

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

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

The approach adopted is threefold:

(i) to have evidence of groundwater age

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

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

Boreholes affected by point source pollution have been avoided within this study, but most groundwaters in the unconfined aquifer show the effects of agricultural pollution due to the application of fertilisers or pesticides over the past decades. The majority of samples included within this study demonstrate significant contributions of NO_3 (above 5 mg l^{-1} NO_3-N) although all the results are below the maximum admissible concentration for drinking water (11.3 mg l^{-1} NO_3-N). Many of the waters in the confined Chalk are reducing and denitrification or nitrate reduction may have naturally helped to lower concentrations within the confined aquifer.

Relatively high levels of Cl (above 20 mg l^{-1}) in the unconfined aquifer also suggest anthropogenic inputs, possibly from diffuse agricultural pollution. Higher concentrations in the deeper confined aquifer are likely to be due to mixing with remnants of formation water**.**

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The primary inputs to the aquifer are derived from rainfall which is a dilute, slightly acidic solution. However, the dominant chemical characteristics of Chalk groundwater are acquired during the percolation of water within the top few metres of the soil and upper unsaturated zone. Congruent dissolution of calcite takes place in the soil and unsaturated zone until calcite saturation is reached. As groundwater moves further down-gradient, the groundwater chemistry evolves more slowly and is modified by several geochemical processes including mineral dissolution and precipitation, redox reactions, ion exchange and mixing with older formation waters. All of these reactions are important in determining the natural baseline groundwater chemistry and need to be understood before any modification to the baseline can be recognised.

Baseline conditions will vary spatially and with depth as a consequence of different flow-pathways and residence time. In order to gain more insight into the spatial geochemical controls, groundwater samples were collected along a potential flow line. The geochemical changes are evaluated and then put into a regional context across the study area. Pore waters were also collected from a 30 m section of core from the unconfined region of the Upper Chalk in order to an assess variations in chemistry with depth. Lastly, where data are available temporal trends have been evaluated.

6.2 Chemical evolution along flowlines

Hydrochemical changes in the study area were studied down-gradient from the outcrop area of the Chalk in the north to the centre of the London Basin where the aquifer is overlain by thick Palaeogene sediments. The Chalk becomes confined where overlain by Palaeogene strata approximately 30 km from the edge of the outcrop. There are many problems inherent in determining the existence of a flowline which has implications for understanding geochemical evolution. These include mixing with recharge in outcrop areas, groundwater abstraction, which is likely to modify pre-existing flowlines and sampling from open boreholes where the sample represents an average of all inflows into the borehole. Abstraction from the confined aquifer may have induced or increased flow velocities from the unconfined part of the aquifer. Extensive abstraction from the confined Chalk beneath London during the 19th and early 20th centuries for example, may have led to modifications in water chemistry. Nevertheless, the spatial changes taking place along regional flow directions (determined by groundwater level contours) can still be interpreted in an evolutionary framework. The changes in chemistry along the regional flow direction are illustrated in Figures 6.1-6.3. Most of the groundwater in the unconfined aquifer is of Ca-HCO_3 type. Changes in Ca and Mg concentrations in the confined aquifer are associated with increases in other elements including e.g. Sr, Mn, K, Li, SO_4, F, Fe and Si. These changes precede the increase in Na, Cl, I, Br and B.

6.2.1 Mineral dissolution reactions

The most reactive minerals in the aquifer initially provide the major control on groundwater chemistry, particularly in young groundwaters. Much of the chemistry of the Chalk groundwaters is established at the start of the flowline due to the rapid dissolution of the calcite matrix. The overall trends in the carbonate system can be followed through variations in the pH, HCO_3, Ca and Mg concentrations in Chalk groundwaters. These variations are all closely related by the fundamental reaction below, which represents how rainwater, assisted by CO_2 produced microbiologically in the soil, reacts with chalk. The production of CO_2 in the soil zone will initially lead to slightly acidic waters due to the production of carbonic acid, but this acidity will be rapidly neutralised through reaction with carbonate minerals e.g. the dissolution of calcite:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO^-_3$$

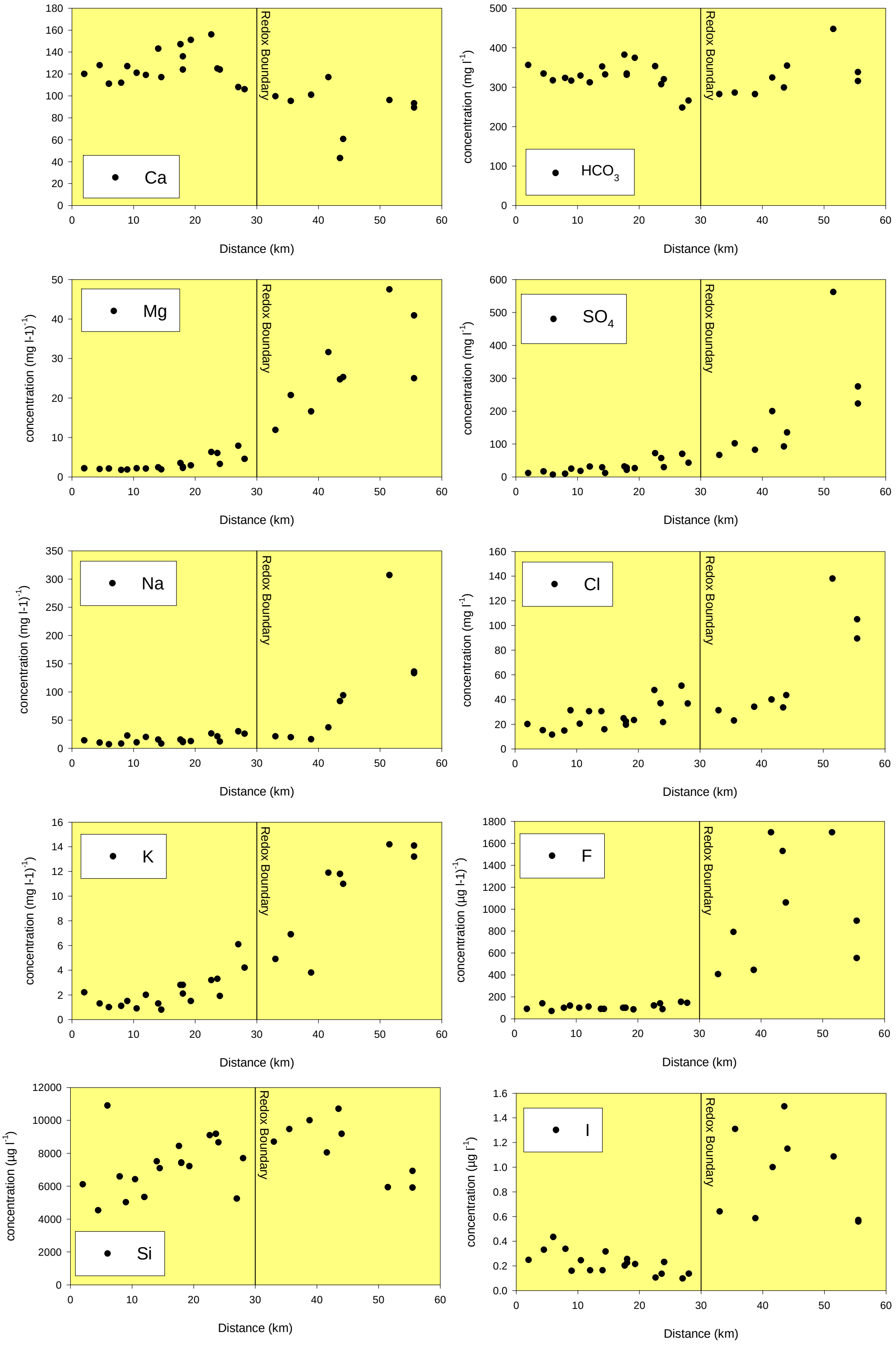


Figure 6.1 **Major and minor element variations along the flowline (see Figure 3.5 for location of flowline).**

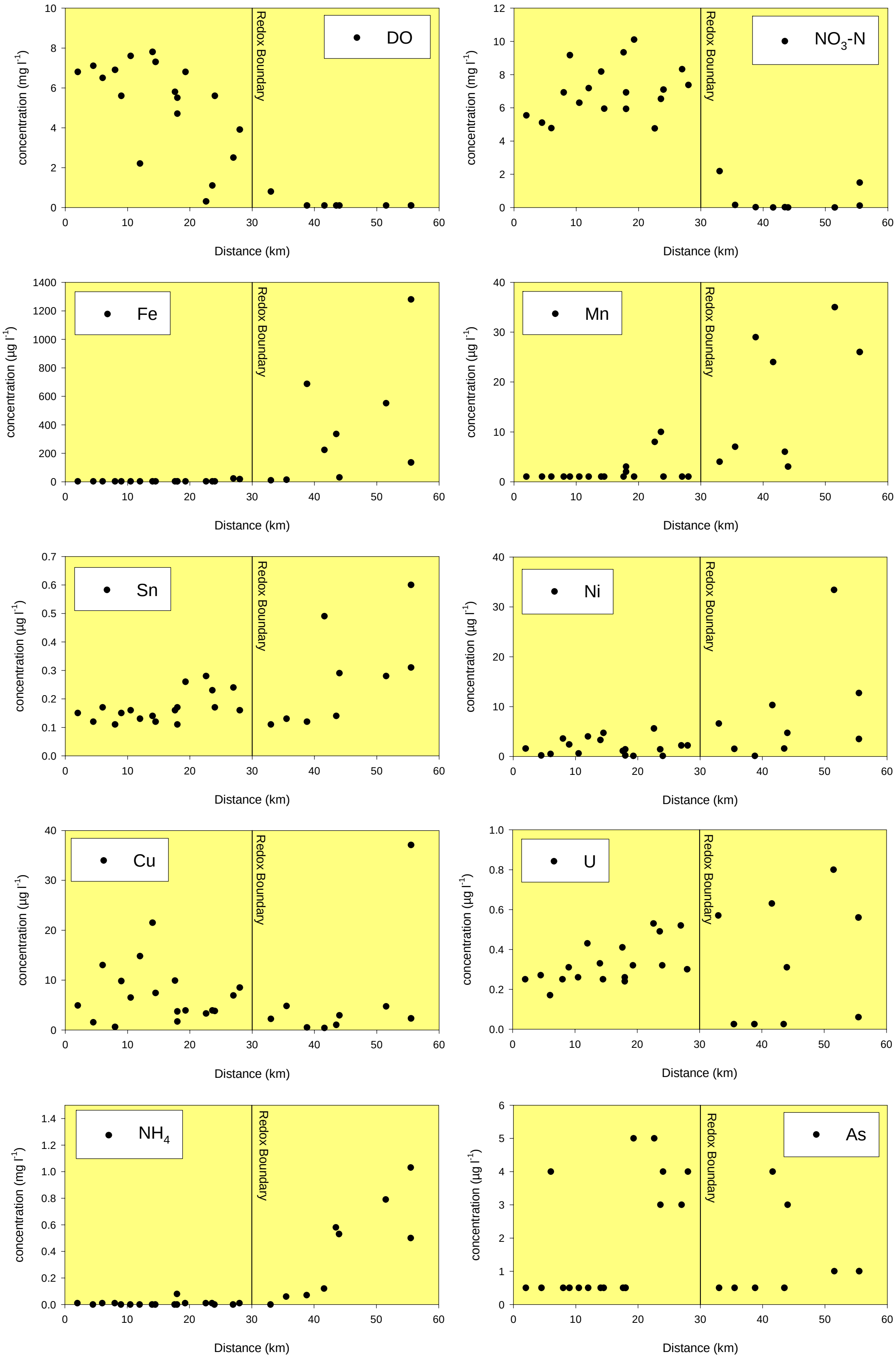


Figure 6.2 Redox sensitive species and trace metal variations along the flowline (see Figure 3.5 for location of flowline).

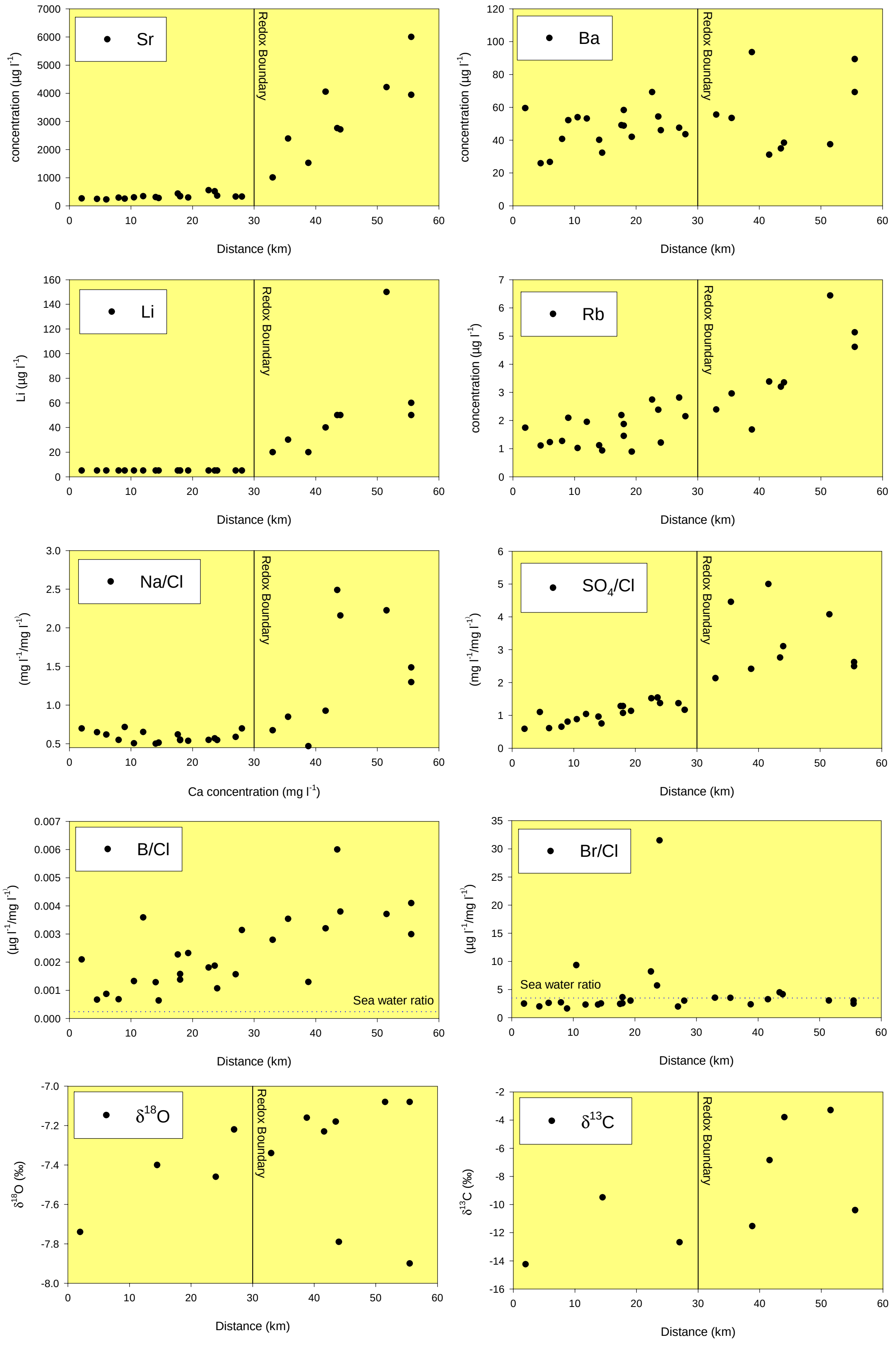


Figure 6.3 **Trace element and ratio variations along the flowline (see Figure 3.5 for location of flowline).**

The above reaction is rapid, and all sampled groundwaters were at saturation with respect to calcite. Although the Chalk is composed dominantly of a relatively pure calcite, the calcite contains minor amounts of “impurities” such as Mg, Sr and Mn. Dissolution initially takes place through incongruent reactions where the dissolved components occur in the same proportions as the parent calcite. This is confirmed by the low Sr/Ca and Mg/Ca ratios in the groundwaters from outcrop areas which are similar to the chalk matrix. Once saturation is reached, calcite may continue to dissolve through incongruent dissolution. However, in order to maintain equilibrium, an equivalent amount of calcite must precipitate. The re-precipitated calcite is purer than the original calcite (due to the freshwater environment), hence the impurities are effectively released to solution and increase with the amount of reaction. This leads to an increase in Sr/Ca and Mg/Ca ratios in the groundwaters with time.

The Mg and Sr concentrations and Mg/Ca and Sr/Ca ratios increase slightly along the general flow direction within the outcrop area of the Chalk (Figures 6.1 and 6.3). There is a more dramatic increase in the confined groundwaters reflecting greater reaction most likely due to an increase in residence time. The increase in the Mg/Ca ratio is initiated before the Chalk dips beneath Palaeogene strata, confirming that Mg is not derived from a source in the overlying sediments.

Dolomite dissolution is not considered to be important and dolomite is rare in the Chalk matrix (Shand, 1999). Only a few groundwater samples from the confined aquifer reached saturation with respect to dolomite.

An increase in SO_4 from ca. 30 mg l^{-1} in the unconfined region to over 200 mg l^{-1} in the confined aquifer far exceeds concentrations identified in the adjacent Berkshire Chalk. The dominant source is possibly from the overlying Eocene clays as a consequence of changes in groundwater potential caused by modern pumping (Smith et al., 1976). High concentrations of SO_4 may also result from extensive water-rock interaction with S-rich minerals such as gypsum or pyrite, or to mixing with saline waters at depth. The SO_4/Cl ratios are much higher than seawater (0.14) indicating that there is an important contribution derived from water-rock interaction. Although minor gypsum is occasionally found in the Chalk associated with marl horizons, it is considered to be secondary and to have formed locally from the oxidation of pyrite. Gypsum contains high concentrations of Sr and the fact that Sr correlates extremely well with Mg (both derived from calcite) rather than with SO_4 also indicates a minor role of gypsum dissolution. It is likely that some of the SO_4 is derived from oxidation of pyrite or marcasite which is found as nodules or disseminated throughout the chalk.

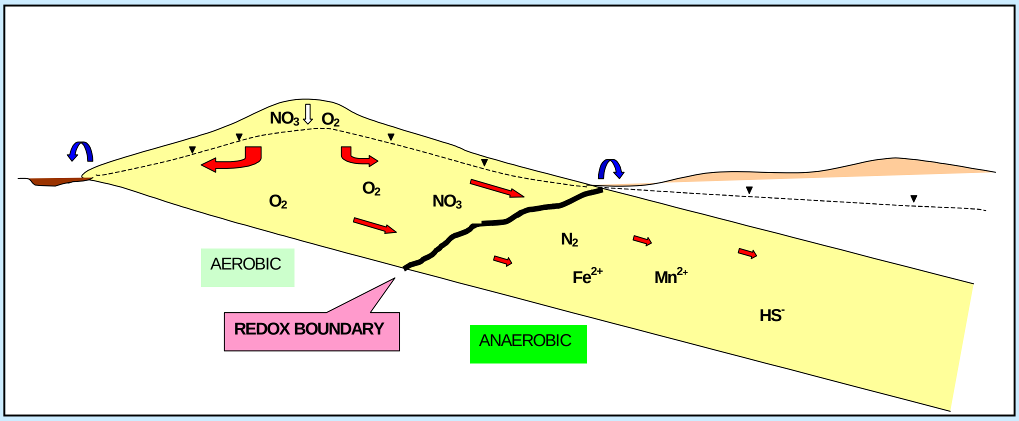
The presence of high SO_4 waters can limit Ba concentrations in groundwater due to the low solubility barite ($BaSO_4$). Barium concentrations in the groundwaters were similar in the confined and unconfined regions of the aquifer, ranging between 25-94 µg l^{-1}. The waters varied from undersaturated with respect to barite in the unconfined to oversaturated in the confined aquifer where SO_4 is high.

Silicon concentrations reach a maximum of 11 mg l^{-1} limited by the solubility of SiO_2 (quartz or chalcedony). There is a gradual increase in concentration along the flowline which is most likely to result from clay mineral diagenesis or K-feldspar dissolution..

6.2.2 *Redox reactions*

The primary indicators of the redox status of natural groundwaters are the redox potential (Eh) and dissolved oxygen (DO). These parameters are unstable and extremely sensitive to changes caused by contact with the atmosphere and should therefore be monitored on-site in a flow-through cell. It was not possible to use a flow cell for all samples, but despite this, DO shows a sharp decrease from ca.6-8 mg l^{-1} in the unconfined aquifer to less than detection limit with the onset of confining conditions. A redox boundary (Box 6.1) occurs approximately 30 km along the flowline as the chalk becomes confined under the Palaeogene. Nitrate is stable in the presence of oxygen, but once DO is consumed, nitrate becomes unstable and concentrations decrease rapidly (Figure 6.2) due to denitrification. Both oxygen consumption and denitrification are considered to occur due to the oxidation of organic matter and Fe^{2+}; tritium studies have shown that such reactions occur over a period of 25 years or more in the adjacent Berkshire Chalk (Edmunds et al., 1987). The ammonium ion (NH_4^+) is present at significant concentrations in the confined groundwaters towards the centre of the basin, probably derived by desorption from clay surfaces.

Box 6.1 Redox Boundary



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

Iron and Mn are not present in solution at appreciable concentrations in the oxidising part of the aquifer due to the limited solubility of Fe and Mn oxyhydroxides. The concentration of Fe increases under reducing conditions, with concentrations increasing from below detection limit in the unconfined groundwater to 1.3 mg l^{-1}. Although Mn is released by congruent and incongruent reactions with the chalk, it is removed from solution by oxidation, often forming “Mn spots” on fracture surfaces (Shand & Bloomfield, 1995). The concentrations of Mn are therefore extremely low in the unconfined region but increase in the confined aquifer, in a similar pattern to that of Fe.

Some of the metal species are associated with sorption sites on Fe and Mn oxyhydroxides and may therefore be related to the mobilisation of Fe and Mn in the reducing groundwaters. Trace elements that are known to be redox-sensitive include As, Cr, Se, Sn and U. Arsenic, Se and Cr show no obvious trend in relation to the redox boundary, but Cu is generally higher in the unconfined and Ni, Sn and U are often higher in the confined parts of the aquifer.

6.2.3 Ion exchange reactions

Ion exchange acts as a temporary buffer in a non-steady state environment and is therefore difficult to identify. Soils and aquifers contain abundant materials that are able to sorb chemicals from water and this adsorption capacity is largely related to the clay content within the aquifer. Most aquifers contain clay minerals, which hold exchangeable cations adsorbed to their surface. Under certain conditions these cations will be exchanged for other ions from the aqueous solution resulting in changes in the concentrations of solutes in the groundwater.

Ion exchange reactions may modify the groundwater type during both aquifer freshening and salinisation. Each of these processes imparts a distinctive change in groundwater chemistry: freshening (displacement of more saline formation water by fresher groundwater) generally causes an evolutionary trend from a typical $Ca\text{-}HCO_3$ type towards $Na\text{-}HCO_3$ type, and salinisation towards $Ca\text{-}Cl_2$ type waters (Appelo & Postma, 1993). The trend of decreasing Ca and increasing Na in some samples from the confined aquifer is most likely caused by continued freshening of the aquifer. This can be seen on the Piper plot (Figure 6.1) as a trend towards the lower part of the central plot. An increase in Na concentration occurs at about 10 km after the unconfined/confined boundary, but there is no apparent increase in Cl concentration, suggesting that there is an additional source of Na than that produced by mixing with formation waters. This is also confirmed by higher Na/Cl ratios (Figure 6.3). The Na/Cl ratio increases up to a factor of 4 in the confined aquifer, indicating that ion exchange is more important here in the Berkshire chalk, where an increase in only 30 mg l^{-1} of Na was attributed to ion exchange (Edmunds et al. 1992). A similar conclusion regarding the importance of ion-exchange was reached by Buckley et al. (1998) in the confined chalk of the Wessex Basin.

The presence of marine clay minerals in chalk provides the source of many elements, which are released or adsorbed from solution. The concentrations of several elements, including K, Rb, NH_4 and Li, increase in the confined region as they are released from the clay minerals, most likely due to ion exchange.

6.2.4 Mixing with older formation water

The deepest waters present in the Chalk aquifer are of Na-Cl composition and are found in the confined aquifer beneath central London. Chloride concentrations in the unconfined groundwaters are generally between 20-40 mg l^{-1} (median of 23 mg l^{-1}) and increase in the confined part (median of 40 mg l^{-1}). This increase is typical of many parts of the Chalk and considered to be due to mixing with remnants of formation water present at depth or within the matrix of the Chalk. Although the maximum Cl concentration along the flowline is only 140 mg l^{-1}, it reaches higher concentrations (up to 1250 mg l^{-1}) in the east of the study area. The increase in salinity could be due to a source of pollution, leakage from overlying strata or from the River Thames, but is more likely to result from groundwater mixing with formation waters at depth. The ratios of Br/Cl in the more saline waters are mostly close to the seawater value (Figure 6.3) indicating that pollution is unlikely to have a major effect on these elements. However, some samples (mainly from the area in and around Hatfield) had a relatively high Br/Cl ratio and these are most likely due to contamination. The very high B/Cl ratios (Figure 6.3) show that the dominant source of B is from mixing with formation waters rather than modern seawater intrusion, as shown elsewhere in the London Basin (Edmunds et al., 1992).

6.2.5 Trace elements

Many trace elements increase with "groundwater age" in aquifers as a consequence of dissolution, exchange or mixing. The slow release of trace elements such as Li and Sr into the groundwater makes them useful for providing relative ages, providing that concentrations are not limited by saturation with a phase containing these elements. The concentrations of Sr and Li show little increase in the unconfined part of the aquifer (Figure 6.3). The rapid increase in the confined part of the aquifer is considered to represent an increase in residence time. Although similar trends can be caused by mixing with formation water, there is a much larger increase in Li compared to Cl, with Li/Cl ratios (1.5×10^{-3}) being much higher than seawater (8.9×10^{-6}). Lithium is preferentially released from clays or chalk surfaces during freshwater diagenesis in a similar process to K, and reaches a maximum of 80 µg l^{-1}, whereas Sr is released from the carbonate matrix as discussed previously.

The dominant source of F in the chalk is in fluorapatite which is present as an accessory mineral. The dissolution kinetics of this mineral is slow and, therefore, F increases slowly in the groundwater, perhaps taking thousands of years to reach the maximum concentration of 1.9 mg l^{-1}. Only the groundwaters with high F are close to saturation with respect to the mineral fluorite (CaF_2). Fluorite and a F-rich phosphate mineral have been found on chalk fractures in Wessex (Shand, 1999), but only in areas where the groundwaters are old and these are likely to be of secondary origin. Fluoride concentrations range from ca.80-200 µg l^{-1} in the unconfined aquifer and increase dramatically to concentrations of 1700 µg l^{-1}, when the aquifer becomes confined.

The concentrations of most metals are low, particularly in the unconfined aquifer where oxidising, neutral pH conditions limit solubility. The redox-sensitive metal species have been discussed in Section 6.2.2. In addition, Ni shows a gradual increase towards the centre of the Basin, the source most likely being from reduction of Mn-oxides which contain high Ni (Shand & Bloomfield, 1995). Zinc is quite variable and shows little consistent spatial behaviour.

6.3 Temporal variations

A selection of boreholes were chosen to study temporal variations in the groundwater chemistry of different parts of the aquifer. The boreholes selected were Periwinkle Lane (Dunstable) and Codicote PS (Luton) from the unconfined aquifer; Rye Common PS and Burnham PS which are partly confined; and Hoe Lane Well (Enfield) and East Ham Well in the confined part of the aquifer. The available data for N-species and Cl are shown in Figure 6.4.

The records of nitrate concentrations over the last century (Figure 6.4) show a marked contrast between those for the unconfined and confined groundwaters. As might be expected, nitrate concentrations in the confined parts of the aquifer were originally low, although they rose slightly to around 1 mg l^{-1} N during the 1970s before decreasing again in the 1980's. In the unconfined portions of the aquifer nitrate concentrations were higher and varied considerably between different abstractions and at individual abstractions over time. At Codicote, Burnham and Rye Common, nitrate concentrations rose over time, while at Dunstable they fell from the 1960s to the 1970s and then returned to around the original high level. Since the early 1980s, nitrate concentrations appear to have remained stable, although this may, in part, reflect the fact that fewer data are available describing nitrate concentrations in recent years. It is clear that present day levels in the unconfined aquifer are significantly higher than the naturally-derived baseline concentrations. The oldest records from before the 1920's imply that concentrations of around 2-4 mg l^{-1} would be typical of baseline.

Concentrations of the ammonium ion (NH_4-N) were measured at Burnham from 1973/74 to 1978, at Rye Common from ca. 1920 to 1985, at Hoe Lane from ca. 1920 to 1983 and at East Ham from before 1920 to 1978 (Figure 6.4). At the two unconfined abstractions (Periwinkle Lane and Codicote), NH_4-N concentrations have historically been very low: NH_4-N was only detected in one sample from Burnham and the mean value at Rye Common was approximately 0.03 mg l^{-1} NH_4-N. Waters from the confined portions of the aquifer have higher NH_4-N concentrations: the mean value at Hoe Lane was 0.125 mg l^{-1} N and at East Ham the figure was 0.46 mg l^{-1} N. There was some variation in NH_4-N concentration with time at Hoe Lane and East Ham, but no clear trend.

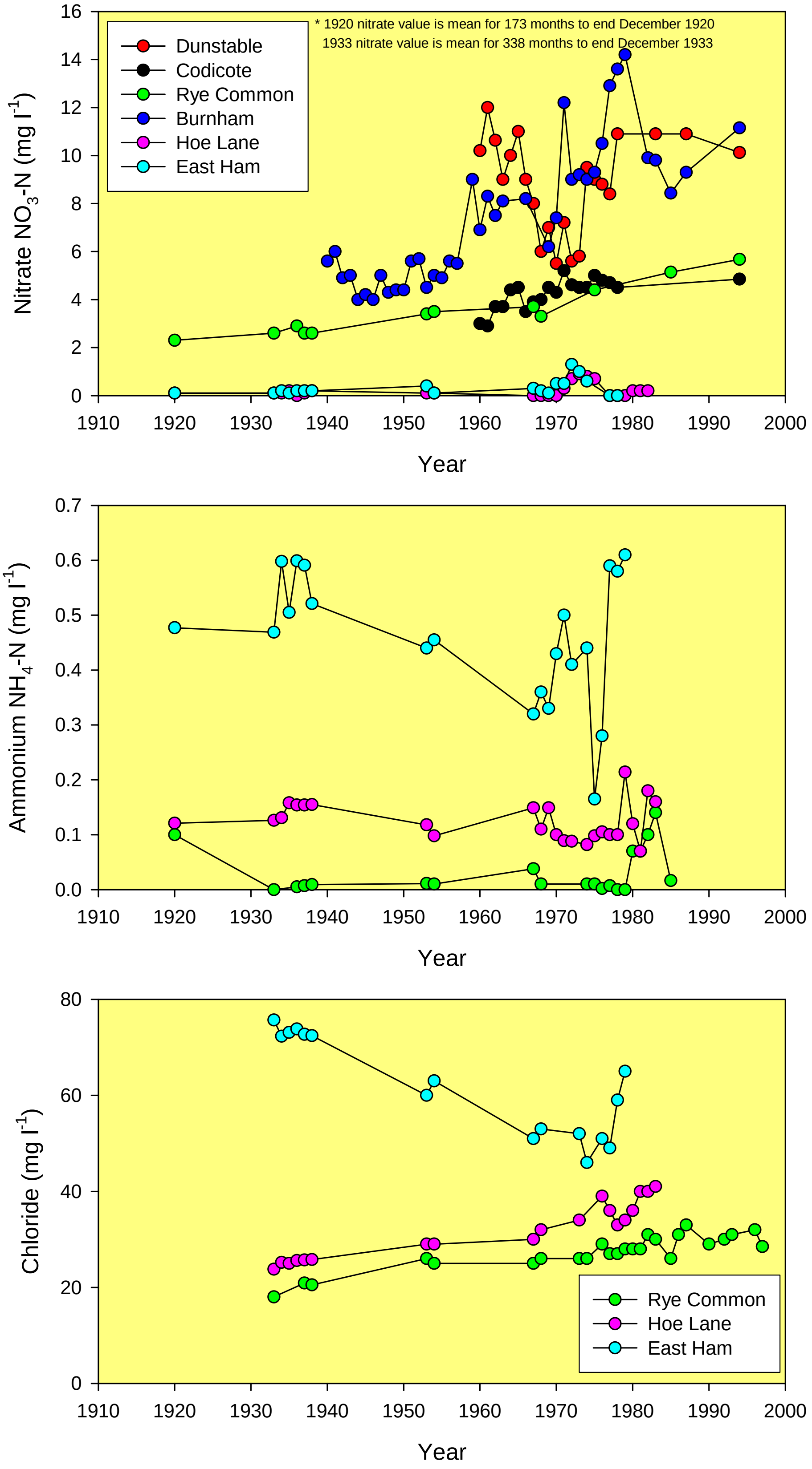


Figure 6.4 Selected time series data for NO_3-N, NH_4-N and Cl from the unconfined and confined parts of the Chalk aquifer. See text for explanation.

Chloride concentrations increase towards the centre of the London Basin. The highest concentrations were measured at East Ham, where the concentration was approximately 75 mg l^{-1} before 1933. The chloride concentration here appears to have fallen slowly from 1933 until around 1974, when a minimum recorded value of 46 mg l^{-1} was reached. The chloride concentration then started to rise again in the late 1970s, reaching 65 mgl^{-1} in 1979, after which time records ceased to be kept. Possible explanations for the high chloride concentrations at East Ham include saline intrusion by water from Thames and the mixing of recent waters with formation water. The other boreholes originally had lower Cl, but showed a steady increase: Hoe Lane rose from 24 mg l^{-1} (average between 1904-1932) to 41 mgl^{-1} in 1983, and at Rye Common rose from 18 mg l^{-1} before 1933 to 28.5 mg l^{-1} in 1997. The mean chloride concentration of Cl at Burnham PS, sampled between 1973-74 and 1982-83 was 28.6 mg l^{-1}. One explanation for the rise in chloride levels at these boreholes is the application of chloride containing fertilisers to land in unconfined sections of the aquifer.

6.4 Depth variations

There are few studies which highlight the variations in chemistry with depth in the Chalk of the region. Individual boreholes often display marked changes in chemistry with depth (e.g. Bath & Edmunds, 1981; Edmunds et al., 1973) related to physical and chemical processes. It is also not uncommon to find that the chemistry of porewaters is different from that in the fractures. The movement of water through the unsaturated zone of the Chalk will in general be downward but in detail the transport is relatively poorly understood. Recent research has highlighted the role of thin film flow along fracture/fissure surfaces as well as through the matrix and in fractures where the water table is close to the surface. Below the water table, the dominant bulk water and solute movement in the shallow saturated Chalk is by advective transport through fractures and fissures. The relatively slow diffusive exchange between fractures and matrix often means that the matrix is not at equilibrium with the water in the fractures (Edmunds et al., 1973; Shand, 1999), although more rapid mixing will occur if the matrix close to fracture surfaces has enhanced porosity e.g. due to dissolution reactions.

6.4.1 Porewater variations with depth

Three boreholes were drilled in the unconfined part of the aquifer in 2002 at Hatfield, adjacent to the River Lee (NGR: 525348 209774) as part of a programme to extend the Environment Agency Thames Region groundwater monitoring network and to investigate groundwater-surface water interaction. The area is believed to represent the basal 40 m of the Upper Chalk. Two vertical boreholes were cored to depths of 32.8 m and 20 m below ground level (bgl). A third inclined borehole was also drilled, terminating beneath the River Lee. Samples of core were collected every metre from the deepest vertical borehole and several groundwater samples were also collected.

Superficial deposits were present beneath a shallow (0.5 m) reddy-brown sandy topsoil. The drift comprised 0.7 m of dense reddy-brown clay-bound flinty gravel at the top, followed by 3.7 m of claybound, stiff reddy brown flinty gravel. The chalk core consisted mainly of putty chalk with many flints and occasional hardgrounds. Some of the putty chalk appeared grey in colour due to the abundance of clay. Hard, brittle Chalk was noted between 7.7-9.2 m, 24.7-27.2 m bgl and ca.28.7-32.8 m bgl. Sub-vertical fractures were noted at depths of ca. 9.5 m, 12.5 m and 15 m bgl and a larger fracture with an orientation of ca. 45° was recorded at ca.19 m bgl, which showed some Fe staining and Mn-oxide spotting. Core recovery was relatively poor at less than 50 %. Groundwater was first struck at 9.7 m bgl and the rest water level was 9.2 m bgl. This depth is close to the depth of a fracture displaying Fe staining and Mn coatings.

Interpretation of the groundwater chemistry in the borehole is difficult due to its location adjacent to the river Lee and beneath superficial deposits. Monitoring changes in groundwater level and chemistry during pump testing or at different river flow conditions would be required to assess the degree of river-groundwater interaction. Nevertheless, the chemistry can be described in terms of quality and changes with depth. The groundwaters have been divided into drift groundwater, porewaters (the porewaters from the nodular hardgrounds have been separated for clarity) and fracture derived waters and are shown on Figures 6.5 – 6.8.

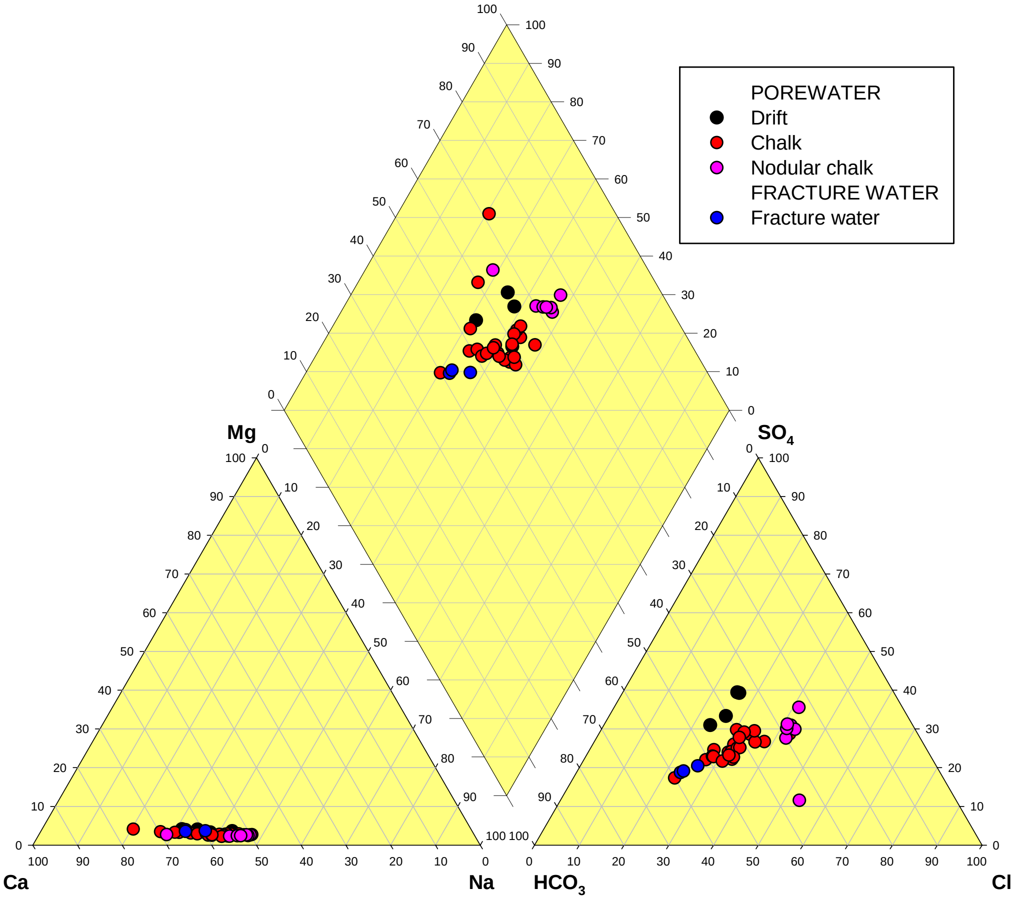


Figure 6.5 PIPER plot showing the relative concentrations of major cations and anions in the new Hatfield borehole.

A Piper plot (Figure 6.5) shows that the groundwaters vary from a Ca-HCO$_3$ to Ca-mixed anion types, and all have low Mg/Ca ratios. There is considerable overlap in the relative proportions of cations but the groups show more separation for anions: the hardground samples have lower HCO$_3$, the drift porewater samples having generally higher SO$_4$ and the chalk porewaters generally having higher HCO$_3$. Selected porewater depth profiles are shown on Figures 6.6-6.8. A comparison can be made between the borehole waters and the range of concentrations present in groundwaters of the area (Tables 5.1 and 5.2). For many major elements, the concentrations are in the upper range of the regional data, with the fracture waters being slightly higher than found in the matrix pores. Both major and trace elements show variations with depth but there is a great variation in the behaviour of different elements. Several interesting features can be summarised from the profiles:

1) The drift porewaters are distinct from the chalk porewaters at depth e.g. they generally have higher concentrations of Mg, SO$_4$, P, Br, I as well as the trace metal species Co, Fe, Mn, Mo, Ni, Sb Se, Sn, U, W and Y. However, many of these solutes (Mg, SO$_4$, P, Br, Mn, U, Y) are enhanced in the chalk immediately beneath the drift, implying transfer of solutes from the drift to at least the upper part of the chalk.

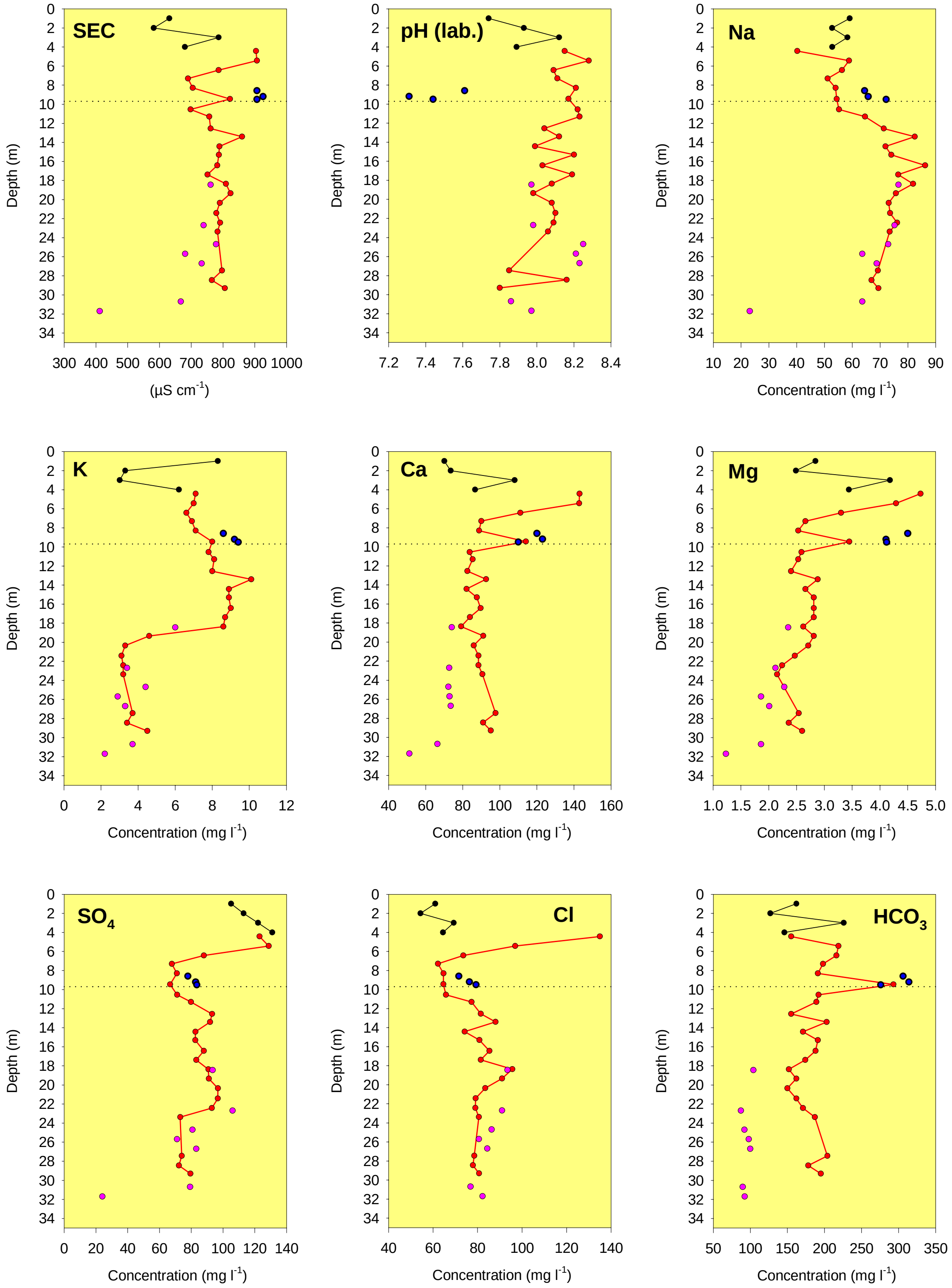


Figure 6.6 **Depth profiles for porewaters (black: drift; red: chalk; pink: hardground) and groundwater from the water table (dark blue). See text for discussion.**

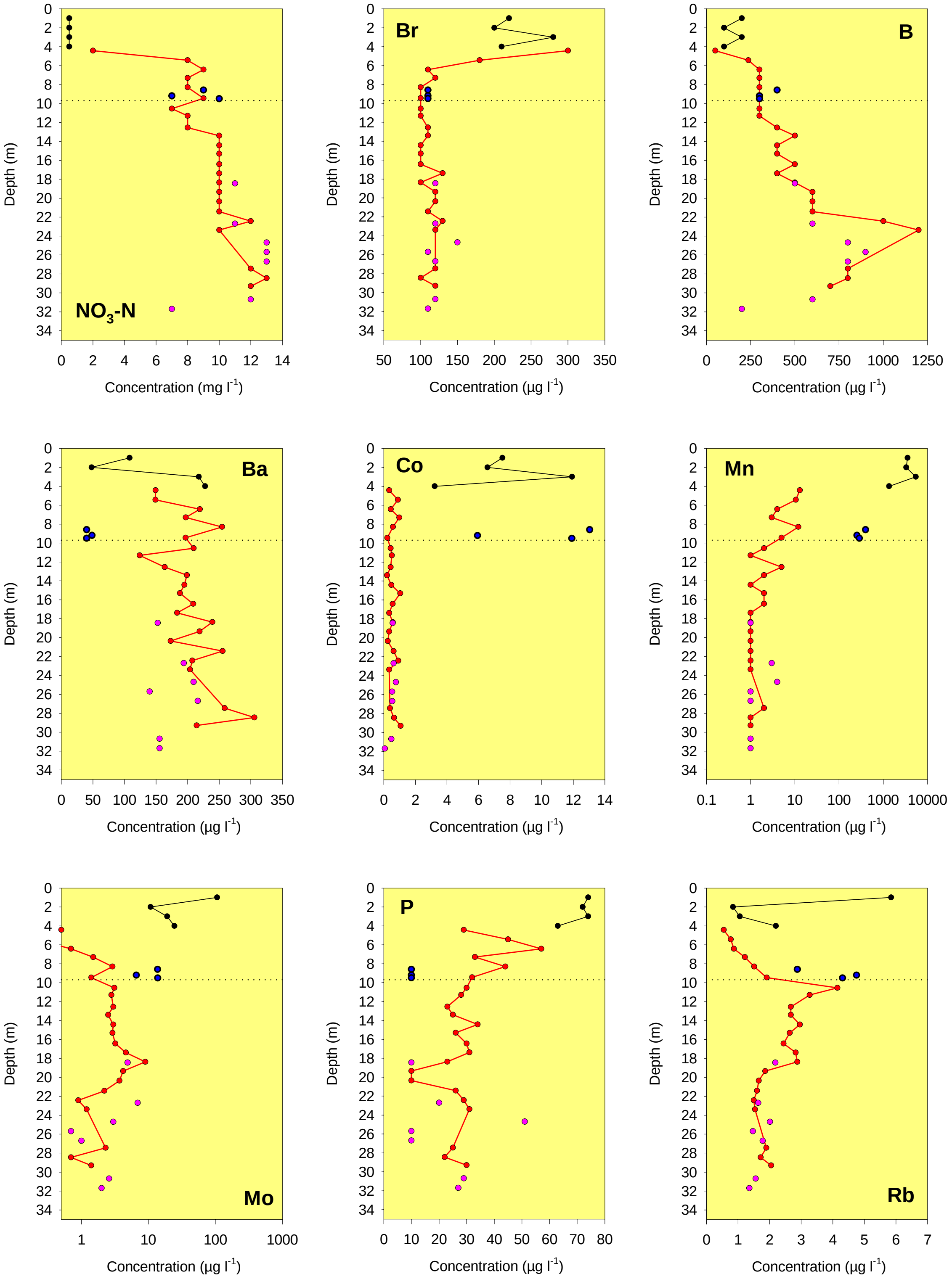


Figure 6.7 **Depth profiles for porewaters (black: drift; red: chalk; pink: hardground) and groundwater from the water table (dark blue). See text for discussion.**

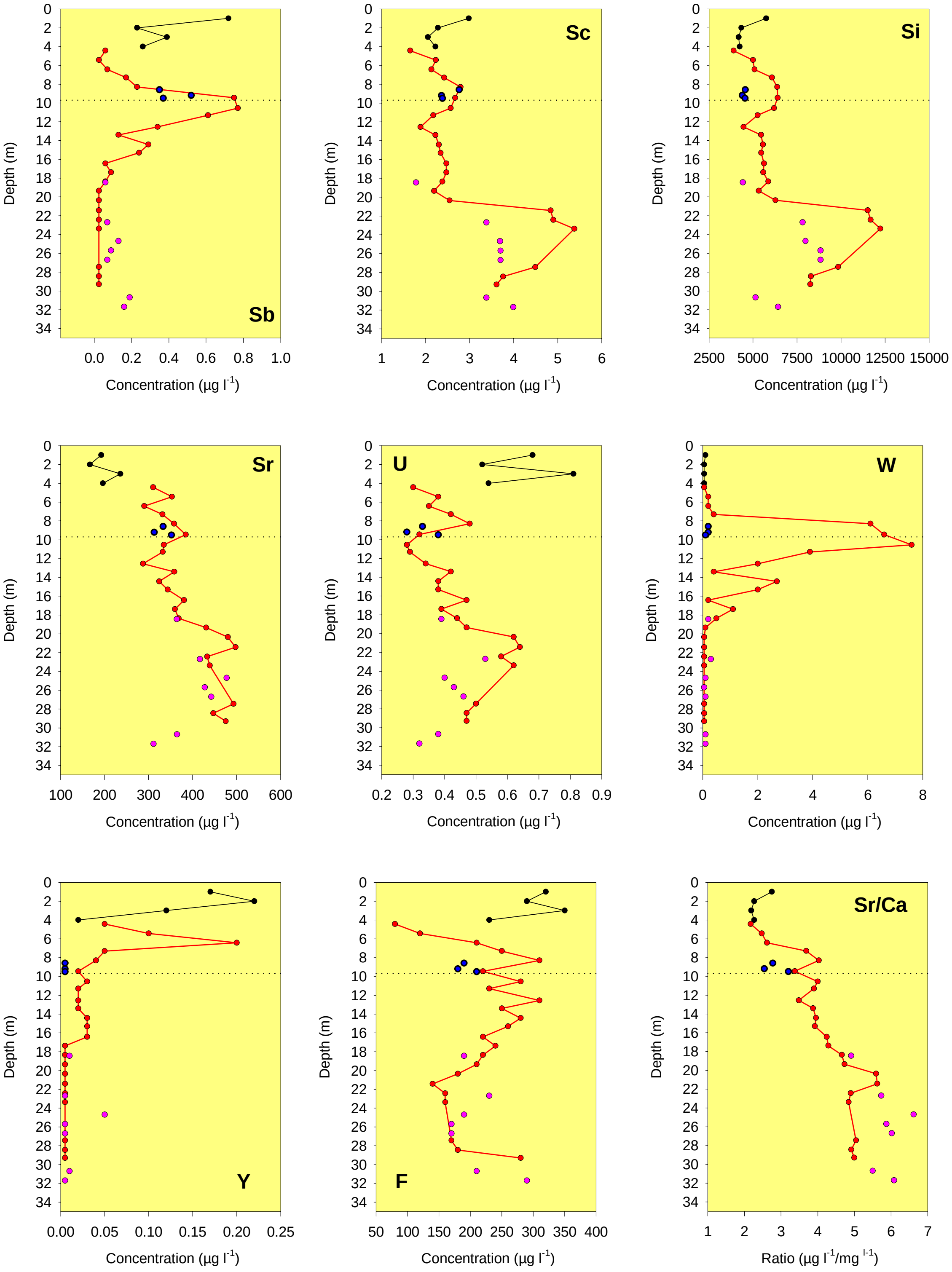


Figure 6.8 Depth profiles for porewaters (black: drift; red: chalk; pink: hardground) and groundwater from the water table (dark blue). See text for discussion.

2) The fracture-derived water has high concentrations of some metal species which are also high in the drift, but low in the surrounding porewaters (Co, Mn, Mo, Ni, Rb, Sb ,Sn). Although this may imply a rapid bypass flow from the drift to the fracture, it is clear that the drift and fracture waters are very different with regard to other elements e.g. the fracture waters have much lower SO_4 and higher Cl and Li.

3) The drift porewaters are relatively reducing; nitrate concentrations are below the detection limit and Fe and Mn are relatively high. The presence of high SO_4 shows that sulphate reduction has not been significant.

4) Some elements show a small peak or trough at the water table which is reflected in the surrounding porewaters (Ca, Mg, HCO_3, SO_4, Cl, Rb Sb, Sr/Ca ratio). This may provide evidence for diffusive exchange between the fracture and matrix.

5) The concentrations of contaminant elements typically associated with anthropogenic influences such as agricultural practices (fertiliser or sludge application) or urban areas are relatively high and enhanced over typical baseline (NO_3, Cl, SO_4, K, P). Interestingly, the highest Cl is found in groundwaters immediately beneath the drift, but drift porewaters have relatively low Cl. Potassium is quite unique in displaying a distinct change in concentration below ca. 20 m, beneath the most prominent fracture at 19 m. This is seen to a lesser degree with some other elements and may imply a different flow system.

6) Several elements and ratios which are generally good indicators of residence time, increase with depth in the chalk porewaters including Li, B and Sr/Ca. The high boron in all samples is likely to be related to pollution. The Mg/Ca ratio in contrast shows an overall decrease but the reasons for this are not clear.

7) The porewaters from the nodular horizons often have lower concentrations of some elements (and SEC).

8) Tungsten (W) concentrations are extremely high for chalk porewaters close to the water table but concentrations are low in the fracture waters.

The overall picture of chemical variations at this site is that of a complex system and one which would benefit from further work. Although the bulk of the chemistry can be explained by water-rock interaction, the presence of high concentrations of some metal species is unusual. The origin of the drift and its physical characterisation are not well established. It is recommended that further work on these as well as monitoring, geophysical logging and assessment of previous pollution be established to aid the interpretation of the borehole. It is possible to speculate that several flow systems exist within this borehole but this needs to be assessed in conjunction with physical constraints. The fracture at around 19 m is considered to be significant considering the changes in several elements which occur at this depth.

6.5 Age of the groundwater

Many of the geochemical changes observed along the flowline can be used to indicate relative ages. The use of trace elements in determining relative ages or extending known dating tools has been applied by Edmunds & Smedley (1998). However, geochemical concentrations can only be used as a guide to relative ages, providing little direct evidence of true age: facies changes and kinetic factors make such estimates fraught with difficulties and without specific dating tools (e.g. ^{14}C, CFCs) precise ages cannot be given. The dating of groundwaters was beyond the scope of the present investigation, but a significant amount of work has already been published on groundwater ages in chalk groundwaters of the London Basin (Smith et al., 1976; Elliot et al., 1999). Carbon-14 was used to date groundwater between the River Lee and Windsor (Smith et al., 1976). Their results showed that the mean age of the groundwaters varied from modern in the outcrop areas to greater than 25,000 years in the centre of the Basin. They also suggested, on the basis of δ^2H and $\delta^{18}O$ results, that there was limited recharge during the period 20,000 – 10,000 years when permafrost conditions would have prevailed. Dennis et al. (1997) also used ^{14}C, $\delta^{13}C$, ^3H, δ^2H and $\delta^{18}O$ and concluded that there is a general increase in the groundwater age in a down-gradient direction, with the oldest water found slightly north of the centre of the London Basin. The residence time of the groundwaters was estimated to be between 10 000 and 25 000 years old. Elliot et al. (1999) suggested, on the basis of noble gas measurements, that the older groundwaters in the centre of the basin were recharged during periods of lower temperature, probably the Pleistocene. These authors concluded that the confined groundwaters represent a mixture of groundwaters recharged during the Holocene and Late Pleistocene epochs.

Stable isotopes (δ^2H and $\delta^{18}O$) have been used to distinguish older Pleistocene (pre 10,000 year old) water from Holocene (post 10 000 year old) groundwaters in sandstone aquifers of the UK (Edmunds et al., 1982). The basis of this interpretation is that the climate during the Pleistocene period was colder resulting in lighter (more negative) signatures of the stable isotopes δ^2H and $\delta^{18}O$. Values of δ^2H and $\delta^{18}O$ analysed within this study, range from -44.6 ‰ to -53.3 ‰ and -7.08 ‰ and -7.90 ‰, respectively, and appear very similar to those analysed in previous studies of the aquifer in the Berkshire Chalk (Edmunds and Brewerton, 1997). Results plotted along the flowline (Figure 6.3) appear to trend towards heavier isotopic values deeper into the basin suggesting recharge occurred during a temperate climate. This is similar to results from the baseline study in the Vale of York (Shand et al., 2002). Most groundwaters, therefore, do not indicate recharge during a colder climate, a conclusion also reached by Smith et al. (1976). However, two sites in central London approach more negative $\delta^{18}O$ values of –7.8 ‰ and –7.9 ‰, which may indicate the presence of some palaeowater in some parts of the London Basin. The isotope data overall are difficult to reconcile with the noble gas studies which implied recharge during colder periods over much of the Basin and this problem remains unresolved.

The isotopic signature of carbon-13 ($\delta^{13}C$) in the solid chalk is approximately +2.35. The $\delta^{13}C$ in the groundwaters changes along the flowline from -14 in the unconfined aquifer to ca. -2 in the deeper parts of the basin. In the unconfined aquifer, the $\delta^{13}C$ results suggest reflect a mixture of organically-derived C from soil and the chalk itself. In the confined aquifer, these values change with time to become more like the chalk due to isotopic exchange and incongruent dissolution. The change in $\delta^{13}C$ is therefore a function of the extent of dissolution and a good indicator of relative residence time.

6.6 Regional variations

The geochemical controls highlighted in the previous sections can be applied to the chemical variations present regionally in the study area. Selected maps showing solute concentrations are shown on Figures 6.9 - 6.11. The major cations Mg, Na and K are generally higher in the confined groundwaters due to enhanced water-rock interaction with longer residence time in the aquifer (Figure 6.9). However, Ca shows contrasting behaviour with a decrease in the confined groundwaters, the exceptions being groundwaters in the south-east of the study area close to the Thames, where mixing with a Na-Cl saline water has occurred. Higher Mg/Ca ratios in the confined aquifer reflect the enhanced degree of incongruent dissolution of calcite, although part of this increase is related to loss of Ca through ion-exchange with Na during aquifer freshening. The increase in Na is dominantly related to mixing with older formation water, either at depth, or in porewaters of the chalk matrix, explaining the good correlation of Na and Cl. However, most groundwaters have an excess of Na, mainly as a consequence of ion-exchange, and calculations show that this excess is around 8-40 mg l^{-1} in the unconfined groundwaters to 8-107 mg l^{-1} in the confined aquifer (although one exceptional borehole in central London had an excess of 690 mg l^{-1}).

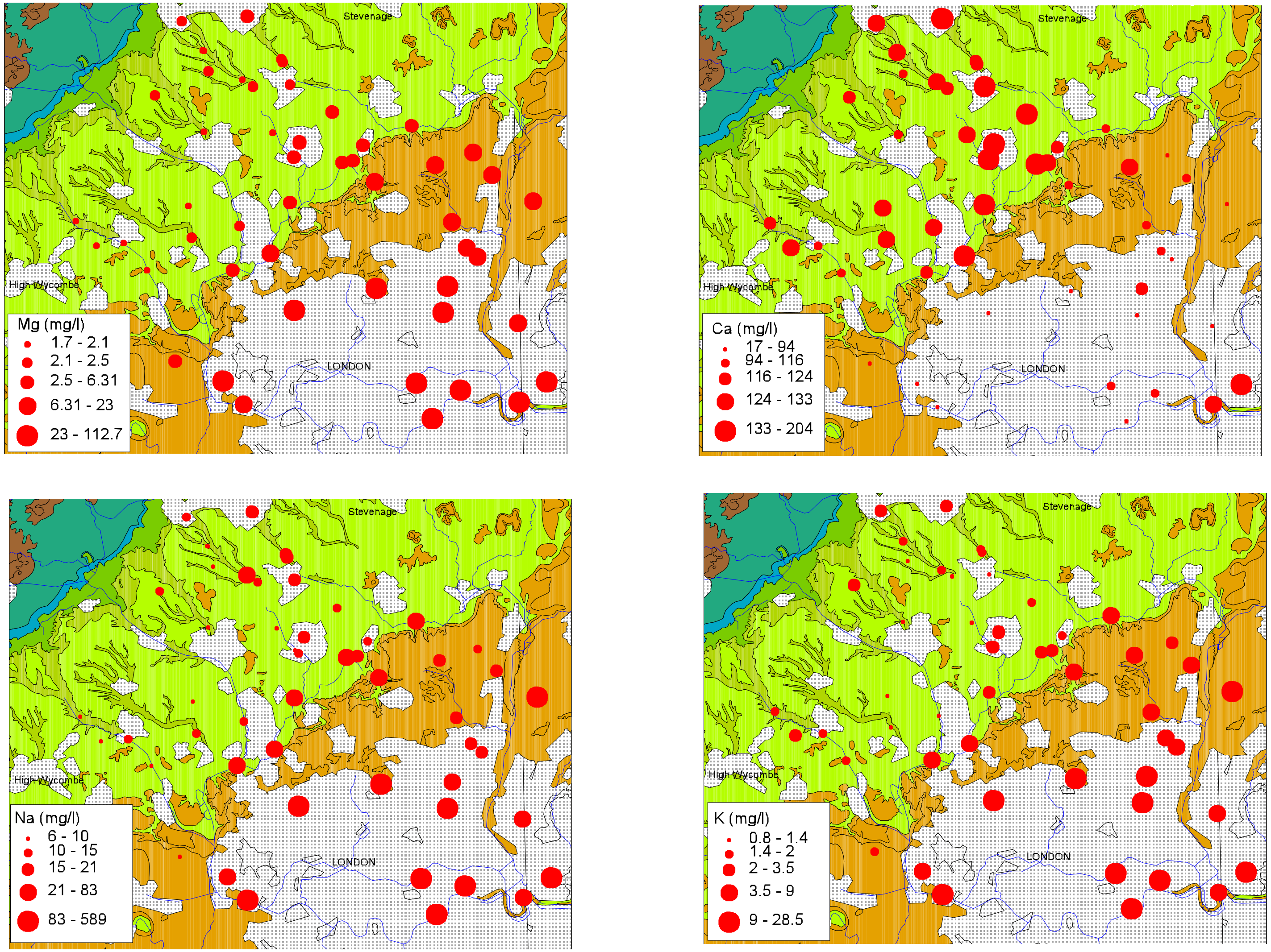


Figure 6.9 **Spatial variation of major cations in groundwaters of the chalk.**

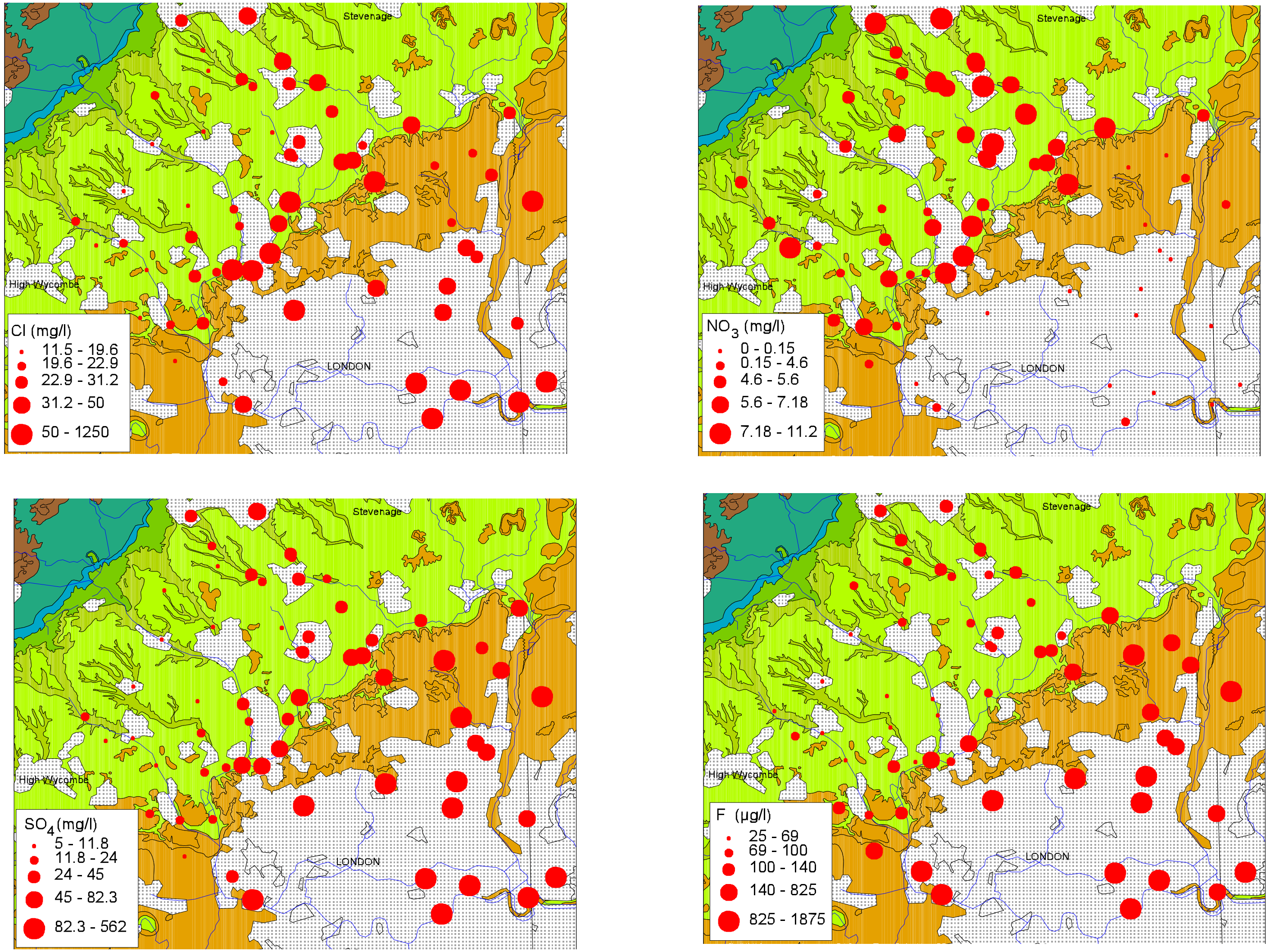


Figure 6.10 Spatial variation of selected major and minor anions in groundwaters of the chalk

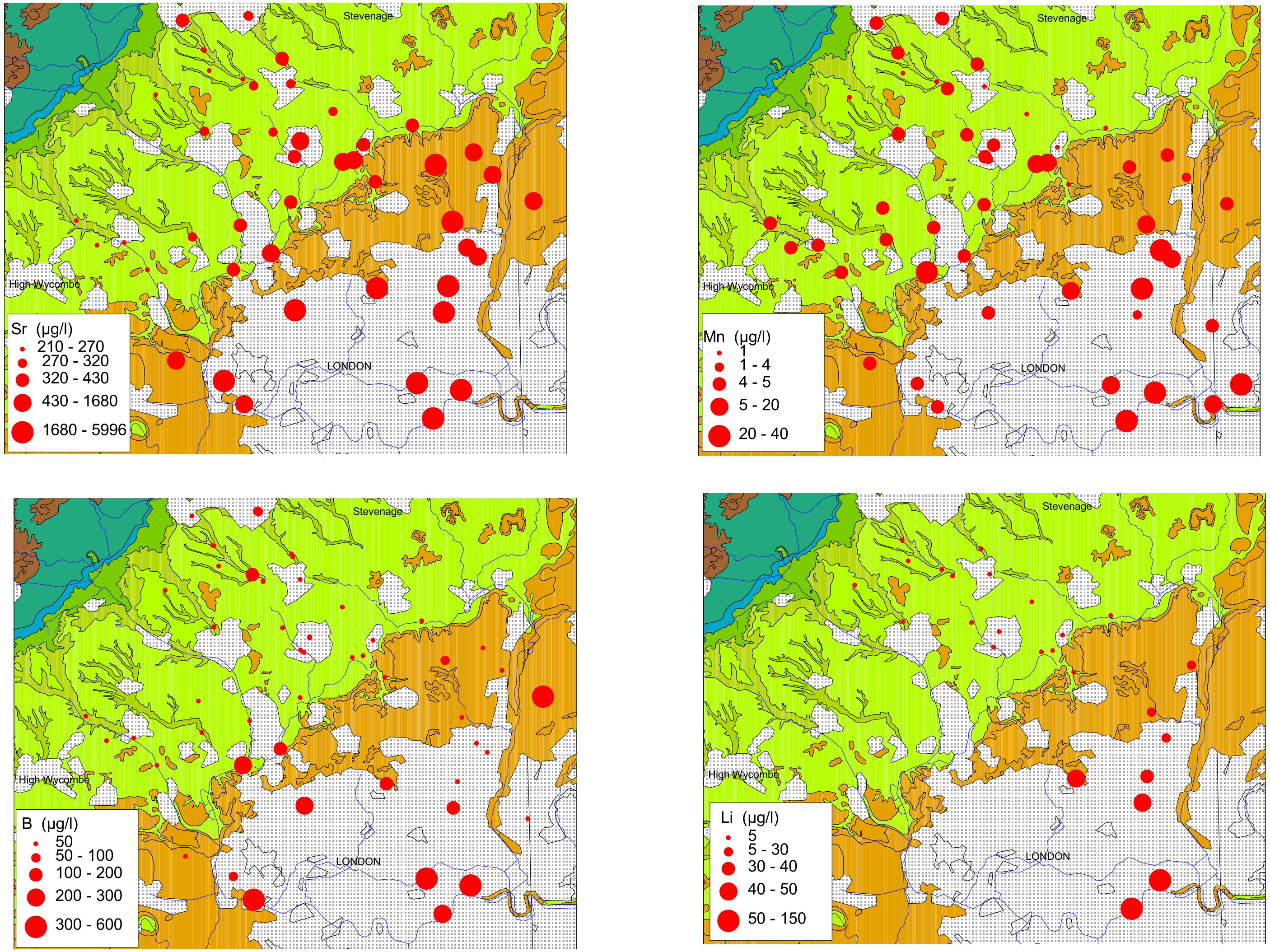


Figure 6.11 **Spatial variation of selected trace elements in groundwaters of the chalk.**

The major anions Cl and SO_4 show similar distributions to the major cations with higher concentrations in the confined groundwaters (Figure 6.10). The SO_4/Cl ratio also increases along flowlines (Figure 6.3) but it is not clear whether this is due to leakage from the overlying Palaeogene or to dissolution of sulphide minerals within the aquifer. The increase occurs also in the unconfined aquifer but this may in part be related to anthropogenic influence. Fluoride shows a clear increase in the confined aquifer, caused by the slow dissolution of fluorapatite in the chalk.

Although the dominant changes take place at the junction between the unconfined and confined aquifer, there is considerable spatial variation in concentrations, particularly in the unconfined groundwaters. This spatial variation is also apparent for NO_3 where concentrations are significantly higher than that expected for baseline. This increase above baseline may be a consequence of both diffuse agricultural and point-source pollution.

Selected trace elements are shown on Figure 6.11. Strontium generally correlates strongly with Ca in groundwaters due to similar chemical behaviour. However, this is not the case in the chalk groundwaters, where incongruent dissolution has allowed Sr to increase with residence time. In the chalk groundwaters in the study area, Sr correlates well with Mg, but not Ca (Figures 6.9 and 6.11). The increase in B is closely related to salinity and the higher concentrations in the confined aquifer is related to mixing with formation water. Many of the unconfined boreholes show elevated B in excess of atmospheric inputs and it is likely that these have been affected by anthropogenic influences: typical sources include sewage effluent and detergents. Lithium generally occurs at low concentrations in the chalk and often shows an increase with groundwater age in aquifers. The higher concentrations in the confined aquifer result from increased residence time with only a small increase due to mixing with formation waters (Li concentrations in seawater are relatively low).

7. BASELINE CHEMISTRY OF THE AQUIFER

The dominant characteristics of groundwater chemistry in the Chalk of the study area are determined by natural reactions with the chalk matrix. Rainfall acidity is rapidly neutralised in the soil and unsaturated zone through reaction with low magnesium calcite which forms the bulk of the chalk. The congruent dissolution of chalk rapidly leads to saturation with respect to calcite. The outcrop areas of the chalk are relatively well flushed and contain groundwater of Ca-HCO_3 type. At depth, mixing with remnants of formation water, either in the matrix or within fractures leads to a change in water chemistry indicated by an increase in Na, Cl, SO_4 and B. Incongruent dissolution of the chalk with time leads to increases in Mg and Sr derived from the carbonate matrix. Ion exchange reactions also occur, dominated by exchange of Na adsorbed on clays for Ca in the groundwater. Clay minerals occur both as marl horizons and in the Chalk matrix. These ion-exchange reactions lead to changes in water type from Ca-HCO_3 type through Na-HCO_3 type and ultimately to Na-Cl type in the deepest parts of the aquifer.

Significant changes take place in the redox status of the groundwaters where the Chalk dips below younger Palaeogene strata. The complete loss of oxygen, due to the oxidation of organic matter or reduced metal species, leads to a decrease in nitrate through denitrification and an increase in Fe and Mn concentrations. Sulphate remains high in the confined groundwaters although some sulphate reduction may be occurring in the deeper parts of the aquifer. The changes in redox species occur over a short distance whereas a zonation would be expected to occur along a flowline.

The most significant changes in the major and trace element hydrochemistry also occur where the Chalk dips beneath Palaeogene cover. The increase in Mg and Sr is due to the incongruent dissolution of the calcite matrix. There is a much more rapid increase across the redox boundary in the concentrations of many elements that are good indicators of residence time e.g. Sr, Li and F which may imply that the confined groundwaters are significantly older than those in the unconfined aquifer.

Redox boundaries often occur close to the confined/unconfined boundary and at depth in aquifers. The formation of such a boundary is likely to occur at the interface between slow moving (older) water and parts of the aquifer where active circulation is occurring. The large changes across the redox boundary and the lack of redox zonation can be explained if there is a significant change in residence time between the Chalk outcrop and down-dip sections of the aquifer. The contrasting chemistry between the unconfined and confined groundwaters has meant that, for practical purposes, two baseline “systems” need to be defined. However, it is probable that some mixing has occurred as a consequence of abstraction from the confined aquifer.

Although the clearest differences occur between the unconfined and confined aquifer, there is also significant spatial variation within these systems. This large spatial variation makes it difficult to predict, in detail, the composition of many elements at a specific site and a local baseline needs to be established.

Although the chemistry of the groundwaters is dominated by natural reactions, the baseline has been modified by several processes. There is clear evidence from historical data showing that there has been an increase in solutes typically associated with potentially polluting activities. Nitrate-N concentrations have increased in many groundwaters during the last century, the dominant source probably being from the application of fertilisers. This source of diffuse pollution is likely to continue to modify the baseline in the future due to high nitrate concentrations still being present in the unsaturated zone. This is particularly the case with the Chalk because the low permeability of the matrix means that transfer times to the water table are of the order of decades. Other sources of NO_3 pollution include leakage from sewers and septic tanks. It is, therefore, likely that most unconfined groundwaters are affected by anthropogenic inputs of nitrate, making it difficult to determine the baseline nitrate concentrations. Historical records are limited, but the data indicate a baseline range of around 2-4 mg l^{-1}. The nitrate concentrations in the older confined groundwaters cannot be used to determine the baseline in the past because natural denitrification has led to the loss of N (in gaseous form) from the system. Diffuse pollution is also believed to have enhanced concentrations of other elements such as K, P, Cl and most likely Na, SO_4, NH_4-N and Br. Although elevated concentrations of these elements may affect the local baseline, these elements also occur naturally and it is likely that in most cases the modified local baseline is less than the upper value of the baseline range for the region (unconfined and confined aquifer). Remedial measures and the reversal of trends in a particular area does need, therefore, to rely on the determination of local baselines. Anthropogenic influences can sometimes be determined using ratios of elements which do not vary significantly in nature or where the baseline is well characterised. This was highlighted for the Br/Cl ratio on Figure 6.2 where samples from the vicinity of Hatfield had high Br/Cl ratios. The Br/Cl ratio has a marine signature controlled by mixing of rainfall-derived Cl with remnant formation water. This is consistent with the good correlations observed for other "marine-derived" minor and trace elements such as B (Figure 7.1), defining a baseline trend. The samples with high Br and Br/Cl ratios plot above this trend (Figure 7.1a). It is important to note that although absolute concentrations in these samples overlap with the regional baseline, they are much higher than the local baseline. The presentation of regional maps (Figures 6.9-6.11) helps to provide a synoptic picture of spatial variations and a good starting point in the determination of local baselines.

The differences between water chemistry in fractures and porewaters have been discussed. The baseline chemistry presented in this study refers to pumped groundwater samples and it could be argued that the baseline of the matrix porewater should also be established, since this will modify fracture water chemistry by diffusional exchange and reaction. It is to be recommended that porewater profiles are collected to provide such a baseline. The geochemical environment of the aquifer (e.g. oxidising/reducing) provides an important control on many solute concentrations species in the groundwater. Such knowledge can be extremely useful in assessing the degree to which natural remediation is possible e.g. precipitation of Fe in oxidising parts and denitrification in reducing parts of the aquifer. The aquifer may also modify and retard pollutants present in fractures by diffusional exchange with the matrix. (but equally the matrix may retain pollutants for long periods of time).

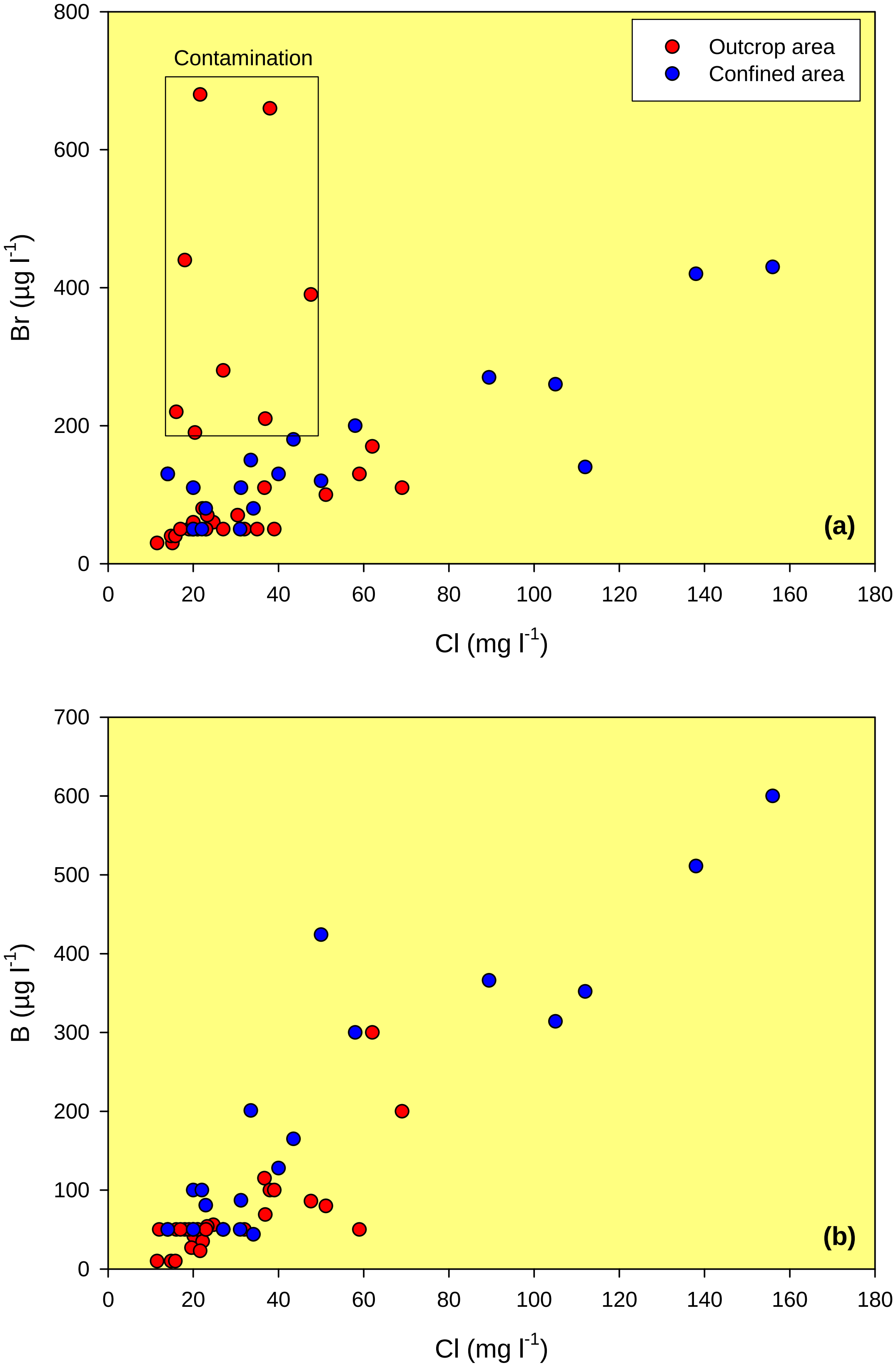


Figure 7.1 Plot of (a) Br and (b) B vs. Cl concentrations in groundwaters.

8. SUMMARY AND CONCLUSIONS

The chemistry of many solutes groundwaters in the study area is overwhelmingly determined by natural reactions between the groundwater and the chalk, and therefore represent baseline concentrations. The initial inputs of solutes to the aquifer from rainfall are minor but the overall chemistry is controlled by the acidity of the rainfall and CO_2 (forming carbonic acid) introduced into the system from the soil. Much of the chemistry is established in the soil and unsaturated zones due to rapid reaction of infiltration water with the fine-grained carbonate (calcite) matrix which forms the bulk of the chalk. Initially, the calcite dissolves congruently with the dissolved components having the same stoichiometry as the calcite. Once saturation is reached, incongruent dissolution occurs with the effect of increasing impurities present in the calcite such as Mg and Sr.

A range of geochemical and physical processes also operate in the saturated part of the aquifer including mixing, diffusional exchange between the matrix and fractures, ion-exchange, mineral dissolution/precipitation and redox reactions. A redox boundary is situated close to the unconfined/confined boundary and this is thought to represent a distinct break in groundwater age. The large increases in concentrations of elements across this boundary which typically show an increase with residence time (e.g. Sr, Mg) also implies that there are large differences in age between the unconfined and confined aquifer. However, groundwater abstraction from within and close to the confined aquifer will have modified flow, and hence chemistry, across this boundary.

There are limited data available on changes in chemistry with depth at individual sites but it is likely that there is significant vertical stratification, based on studies elsewhere in the Chalk. Data from one site close to the River Lee, where the Chalk is overlain by drift deposits, show that there is considerable heterogeneity in chalk porewaters with depth over a scale of metres. Pumped groundwater (fracture dominated) from this site was different from the porewater, as expected in such a dual porosity aquifer. However, matrix water can have a significant effect on fracture water chemistry through diffusional exchange (Gaus et al., 2002) and it is recommended that baseline hydrochemistry be established both for porewater and fracture water in the Chalk.

Historical data from selected sites across the aquifer show that large changes in the concentrations of NO_3 and Cl, most likely as a consequence of anthropogenic influences, have occurred. Unfortunately there are few data available for many dissolved constituents.

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ACKNOWLEDGEMENTS

This work would not have been possible without the support of the farming and industrial community who allowed access to sample their boreholes. Debbie Allen and Sarah Hannay are thanked for completing chemical analyses. George Darling (BGS) and Alan Ward (EA) are also thanked for stable isotope and N-species analyses respectively. John Arbon is acknowledged for the drafting of Figure 3.3. We are also grateful to Mark Antrobus of SPSS for his development work on PIPER diagrams in Sigmaplot.