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Groundwater Systems and Water Quality
Commissioned Report CR/03/273N

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

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River Colne at Bushy Mill Lane.

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Baseline Report Series: 9. The Lower Greensand of southern England

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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 c.10 ka (ii) pre-industrial water (pre 1800s), (iii) water predating modern agricultural practices (pre 1940s) and (iv) modern post-bomb era (post 1963).

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer's physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use historical records and the application of graphical procedures such as probability plots to discriminate different populations (Shand & Frengstad, 2001; Edmunds et al., 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 Lower Greensand forms a major aquifer in the south east of England, providing water to several pumping stations as well as supplying industrial and farm water supplies. The area covered by this study of the Lower Greensand extends from around Horsham in the east to Guildford and Haslemere in the west. Several deep boreholes in the confined aquifer north of the outcrop area in Slough have also been included.

The Lower Greensand aquifer can be divided into two principal sandstone units, the Hythe and the Folkestone Formations, which are bounded by less-permeable layers. Groundwater flow in the aquifer is intergranular where the sands are poorly consolidated, but fissure flow becomes important in harder lithologies. Groundwater in the Lower Greensand is mainly the Ca-HCO₃ type, and mineral dissolution is the primary control on groundwater chemistry. However, as the aquifer has little carbonate cement, it has a limited capacity to buffer acidic infiltration. One consequence is that waters in the unsaturated zone are often acidic and can result in increased mobility of some metals (e.g. Al). The groundwater in the Lower Greensand is fresher than water from most other aquifers in the United Kingdom, due mainly to the relative purity of the sands and often short residence times. Where the aquifer is confined, the groundwaters show a distinct chemistry, having lower redox potential (Eh) and dissolved oxygen (DO), and higher iron concentrations. Ion exchange reactions in the confined aquifer result in enhanced concentrations of sodium and a trend towards waters of Na-HCO₃ type.

Certain groundwater sources in the Lower Greensand contain relatively high nitrate concentrations which are the result of human activity. Long-term time series data for the Lower Greensand were not available. However, recent data from a few sources indicate a range of different trends in nitrate. The deeper groundwaters have isotopic characteristics consistent with recharge during the Pleistocene.

With a few exceptions the chemistry of Lower Greensand waters is considered to be mainly a function of natural water-rock interaction. The presence of relatively high concentrations of certain trace elements, such as Fe and Mn, at some sources is considered to be natural. Local enrichments of trace metals in groundwater, such as As, Pb and Ni, are also considered to be naturally-derived. The aquifer is relatively vulnerable to pollution as it has a large area of outcrop with many major roads and urban centres. In addition agricultural activities continue to pose a risk to the aquifer with increased concentrations of nitrate.

2. PERSPECTIVE

This report presents a summary of the natural groundwater quality in the Lower Greensand south of London, mainly around Haslemere, but extending to Maidstone in the east and including samples from Slough further north (Figures 2.1 and 2.2).

The Lower Greensand comprises alternating sandstones and clays with the sandy horizons forming useful aquifers from which groundwater is abstracted. Where relatively hard sandstones outcrop, they form scarps, which rise above the more easily eroded Weald Clay to the south. The Lower Greensand is of Lower Cretaceous age and the main aquifers are the Folkestone Beds and Hythe Beds which overlie the Atherfield Clay and in turn are overlain by Gault Clay. The Folkestone and Hythe Beds are separated by the Sandgate-Bargate Beds, which form a leaky aquitard (Morgan-Jones, 1985). Groundwater is abstracted from both the unconfined and confined parts of the aquifer.

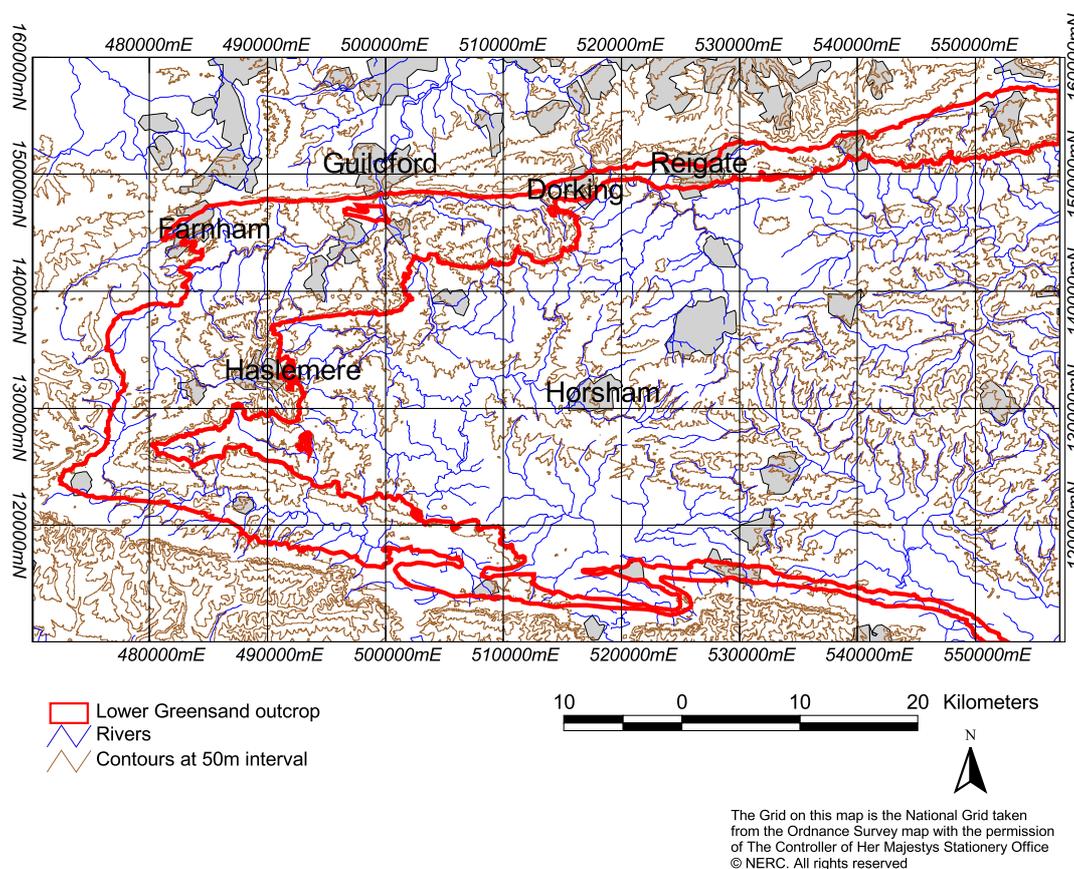


Figure 2.1 Topographic map of the outcrop area of study showing main towns. Outcrop of Lower Greensand shown within red lines.

The sandy beds in the Lower Greensand give rise to well-drained countryside. The soil is sometimes poor, with extensive tracts forming acid heathland (Figure 2.2), however there are fertile areas such as the fruit orchards in Kent (Edmunds et al., 1989). Around Haslemere particularly, wide upland areas are found, with more heathland and pinewood, although the valleys are often fertile (Edmunds et al., 1989). The Folkestone Formation in the Guildford area is characterised by sandy heathland dominated by birch, gorse and pine plantations (Ellison et al., 2002). Springs or boggy ground are frequently found towards the base of the Lower Greensand, notably at the junction of the permeable Hythe Formation with the Atherfield Clay.



Figure 2.2 Sandy heathland at Lower Greensand outcrop.

The Lower Greensand of the Weald falls into the Thames and Southern Hydrometric areas (Marsh and Lees, 1998) with average annual rainfall of 688 mm and 776 mm respectively (based on data recorded between 1961 and 1990). The average rainfall measured for sites on the Lower Greensand of the Environment Agency Southern Region is 830 mm calculated for data between 1961-1990. The Lower Greensand around Haslemere and to the south is drained by the Rivers Rother and Arun and its tributaries (Figure 2.1). The River Wey drains the area of Lower Greensand around Guildford and Godalming, flowing approximately northwards towards the Thames. Most of the area around Reigate and Dorking, to the east of the Wey catchment, is drained by the north-flowing River Mole and its tributaries which also drain the Weald Clay to the south. There is a low watershed near Godstone (about five miles east of Reigate) which separates the basin of the Mole from the headwaters of the tributaries of the River Medway (Dines and Edmunds; 1933). The River Medway drains much of the Lower Greensand to the east of Reigate, and flows northwards through a gap in the North Downs north of Maidstone in Kent.

The aquifer is vulnerable to pollution in the study area where relatively high population densities coincide with the surface outcrop of permeable units in the aquifer. For example, the Folkestone and Sandgate formations are unconfined in the area southeast of Farnham, which has a sizeable population (Ellison et al., 2002). In addition, the limited ability of the aquifer to buffer acidity can lead to increased mobility of metallic elements and aggravate incidents of pollution.

The Lower Greensand is of minor economic importance apart from its use as an aquifer. However, the sands in the Folkestone Formation are used for construction and other purposes and are quarried, particularly between Farnham and Maidstone (Shepard-Thorn et al; 1986). Fuller's Earth has been commercially exploited in the study area near Redhill in Surrey and Maidstone in Kent, and also near Baulking in Oxfordshire.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

In order to assess the baseline groundwater quality of the aquifer, it is necessary to understand the groundwater system. This requires information on the geological and hydrogeological properties in order to provide the physical framework of the system. Knowledge of the mineralogy and geochemistry of the component minerals is also required to explain the characteristic groundwater chemistry. Finally the initial input to the system, rainfall, needs to be known to define the initial composition.

3.2 Geology

The name “Lower Greensand” arose from confusion with the Upper Greensand in the nineteenth century. It is widely used but imprecise, because the sediments are generally not green and not always sandy (Allen et al., 1997). The main outcrop of the Lower Greensand in the study area (Figure 3.1) is found around the margin of the Wealden pericline north and south of Haslemere, but extends eastwards along the northern and southern margins of the Weald to the coast. The Lower Greensand becomes confined immediately to the north of this area, where it thins rapidly. It is not found at all under most of the London Basin where it is overstepped by the Gault Clay (Allen et al., 1997). It is not present in the centre of the Wealden pericline, as it has been removed by erosion. The Lower Greensand tends to dip away from the older rocks exposed in the Weald (Figure 3.2), thus in the eastern part of the study area around Maidstone the strata dip steeply in a northerly direction, where they form part of the southern limb of the London Basin syncline (Morgan-Jones; 1985). In the west, around Guildford and Haslemere, the dip is in a more westerly direction and is shallower. Outcrops of Lower Greensand also occur on the Isle of Wight, in the Cambridge-Bedford area (where it is known as the Woburn Sands), and in parts of Lincolnshire, Norfolk, Berkshire and Wiltshire.

The Lower Greensand attains a maximum thickness of about 220 m just west of the western outcrop in the Weald, and thins along both the northern and southern limbs. It is only a few metres thick near the coast at Eastbourne and Folkestone (Allen et al., 1997). The confined strata are thickest in the area around Slough (around 80 m thick), where a number of large abstractions are sited. The confined strata south of the southern limb were shown to be 52.5 m thick in the Sompting borehole (TQ 1661 0636) at a depth of 439 m below ground level (Young and Monkhouse, 1980).

The Lower Greensand was deposited in a variety of shallow-water near-shore marine environments during the Aptian and Lower Albian stages of the Lower Cretaceous, giving rise to a complex series of sands, silts and clays (Allen et al., 1997). The environment of deposition ensured that local variations in lithology and thickness are common. In the study area, the Lower Greensand can be divided into four formations on the basis of age and lithology (Figure 3.2). The lowest formation is the Atherfield Clay Formation, which comprises stiff brown and dark grey silty fossiliferous clays, with some subordinate sandy clays, and which rests unconformably on the Weald Clay. This junction is usually sharply defined and marked by changes in fossils reflecting the shift from a non-marine to a marine environment. The Atherfield Clay is of early Aptian age (Farrant, 2002) and is generally between 6 and 18 m thick (Edmunds et al., 1989).

The Hythe Formation overlies the Atherfield Clay and consists of fine- to medium-grained sands, calcareous sands, sandstones and limestones with some clays. The formation becomes more calcareous towards the east: in Kent the Hythe beds consist of alternating layers of sandy limestone (“rag”) and calcareous, argillaceous sandstone (“hassock”) which vary in thickness from c. 15-60 cm (Worssam, 1963). Lenticular chert seams occur in both lithologies in the upper parts of the formation (Worssam, 1963). Along the western part of the outcrop the beds are more arenaceous, comprising greenish-grey sandstones with subordinate lenticular beds of chert. The age of the formation is

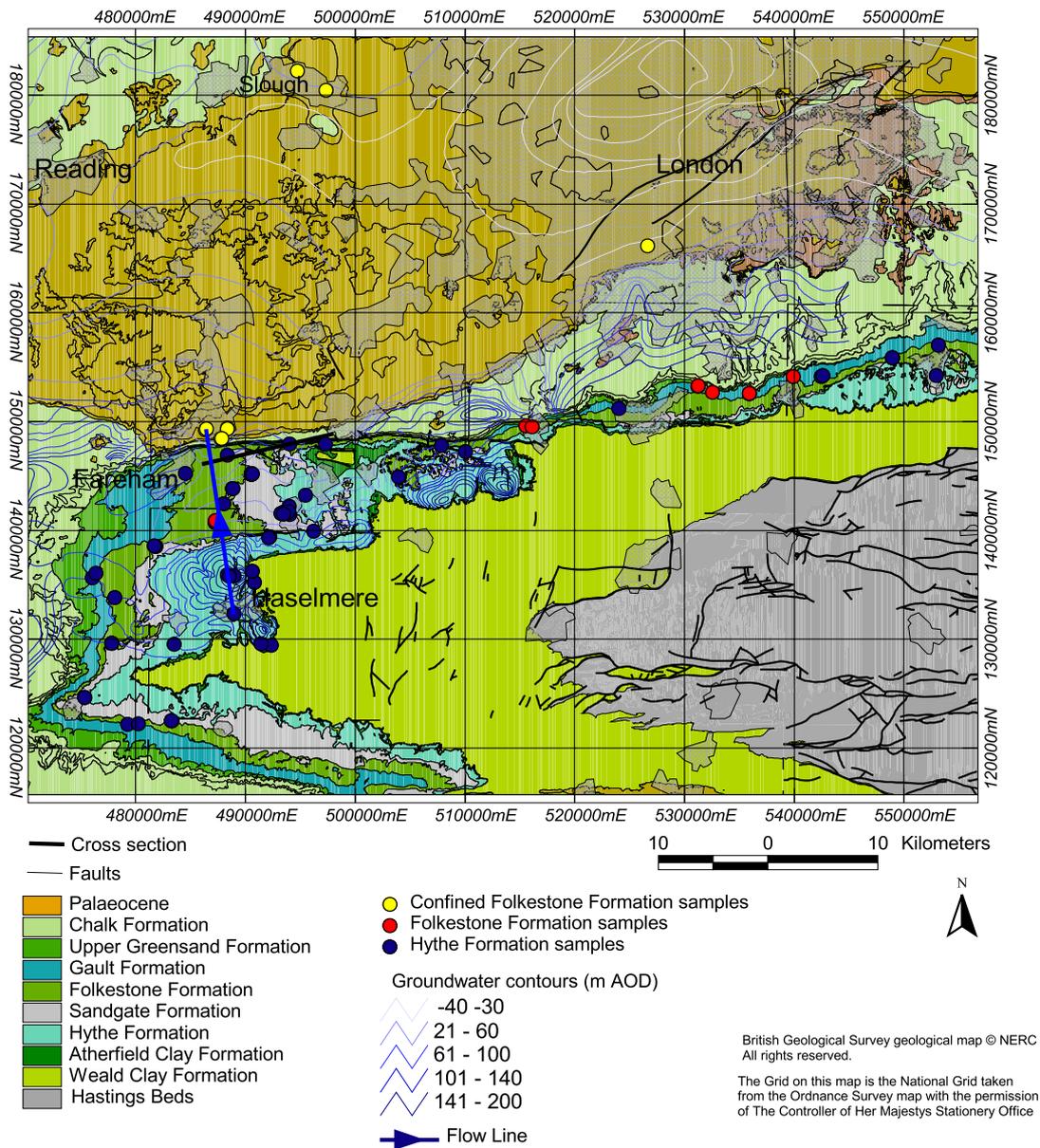


Figure 3.1 Geological map showing the main formations of the Lower Greensand. Samples used in this study and groundwater levels are also shown.

thought to straddle the Lower to Upper Aptian boundary (Farrant, 2002). Chert beds are common (Farrant, 2002). The sediments are frequently bioturbated and lamination is rare. Relatively resistant beds of fine-grained sandstone are found which can form positive topographic features, particularly towards the top of the formation. The top of the Atherfield Clay is commonly sandy and glauconitic (Edmunds et al., 1989) and the junction with the Hythe Formation is frequently difficult to define. A spring line commonly marks the boundary between the Atherfield Clay and the Hythe Formation (Thurrell et al., 1968). The Hythe Formation is thought to reach its maximum thickness of 92 m near Farnham (Farrant, 2002).

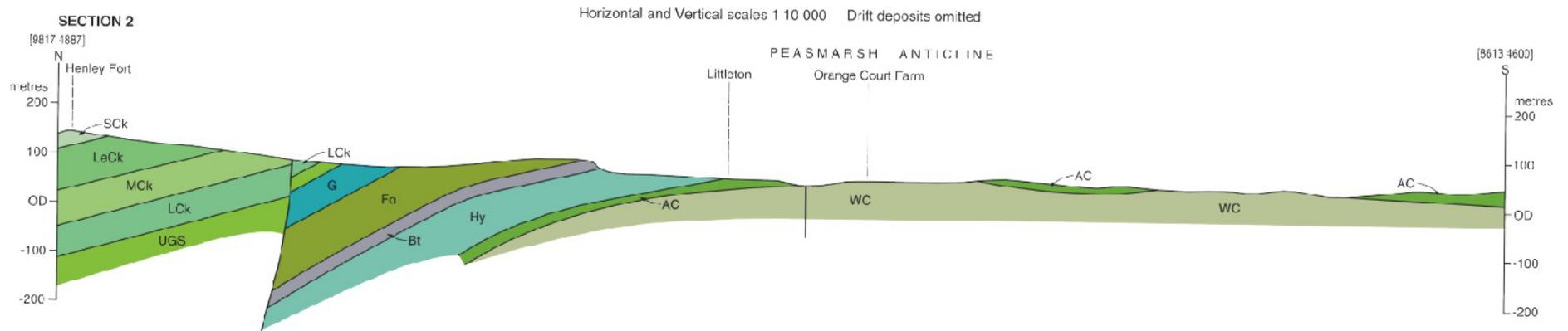


Figure 3.2 Cross section through the Lower Greensand showing individual units: AC: Atherfield Clay; Hy: Hythe Formation; Bt: Sandgate Formation (Bargate Beds); Fo: Folkestone Formation. G: Gault; Ck: Chalk; WC Weald Clay.

Overlying the Hythe Formation are a variable series of sands, silts and clays together known as the Sandgate Formation. Loose, argillaceous, medium grey, glauconitic, ferruginous fine- to coarse-grained sand and sandstone layers are found, which are characteristically poorly-sorted (Ellison et al., 2002). This formation is the most variable of the Lower Greensand Formations in terms of lithology and of thickness (Edmunds et al., 1989). Seams of Fuller's Earth may be present in these strata, and these are up to 2 m thick near Maidstone. Part of the lower Sandgate Formation, present only in the vicinity of Godalming, is known as the Bargate Beds, which consist of a series of grey sands and sandstones characterised by large glauconitic grains and the presence of hard calcareous flattened concretions called doggers (Allen et al., 1997). Pebbles of quartz and chert may be found. Locally, the Bargate Beds may be present where the Sandgate Formation is not (Ellison et al., 2002). The basal contact of the Bargate Beds with the Hythe Formation may be gradational, suggesting an element of recycling. Elsewhere, a basal pebble bed has been recorded that contains reworked clasts of Hythe Formation, glauconite pellets, quartz granules, phosphatic pebbles up to 10 mm in size, and pebbles of fossiliferous limestone of Jurassic age derived from sediments from the London platform to the north (Ellison et al., 2002). The Sandgate Formation is thought to reach its maximum thickness of about 50 m near Petersfield (Allen et al., 1997).

The uppermost formation of the Lower Greensand is known as the Folkestone Formation and consists mainly of poorly consolidated cross-bedded medium-grained quartz sand, thought to have been deposited in a shallow marine environment (Allen et al., 1997). The sand is ferruginous, and glauconitic at depth. Seams of iron-oxide-cemented sandstone typically 5-10 cm wide, known as "carstone" occur throughout. Irregular ironstone veining, bearing little resemblance to the sedimentary structure, also occurs (Allen et al., 1997). The cross-bedding forms foresets up to 2 m thick (Ellison., 2002). There are small amounts of silt and clay present, although less than that found in the Hythe Formation, and the formation is considered to be lithologically relatively uniform. The pale grey-green silt and clay occur in beds generally 1-2 cm thick, particularly in the middle of the succession (Ellison, 2002). However, clay usually makes up less than 2% of the total rock (Allen et al., 1997). At the top of the Folkestone Formation in the Chichester district, a thin brightly coloured sandy ironstone (the "iron grit"), up to 10 cm thick, is well-developed (Farrant, 2002). The thickness of the Folkestone Formation follows a similar pattern to the Hythe Formation: it reaches a maximum thickness of about 85 m at Farnham and thins towards Eastbourne where it is only about 3 m thick (Allen et al., 1997). The base of the Folkestone Formation often forms a topographic feature (Thurrell et al., 1968), and at outcrop the formation is often marked by barren heathland or woodland which reflects the good drainage (Allen et al., 1997).

Soils comprise silty or fine sandy loams. Soils developed over the Folkestone and Hythe formations are classified by the EA as being a mixture of high and intermediate leaching potential, with soils developed over the Sandgate Beds being of intermediate leaching potential.

3.3 Hydrogeology

The Lower Greensand of southeast England is regarded as a major aquifer despite the relatively small outcrop area, and it supports several public water supply boreholes as well as numerous private sources. Yields of up to 76 l s⁻¹ have been recorded from large public water supply boreholes in the undifferentiated Lower Greensand (Farrant, 2002). The hydrogeology and aquifer properties of the Lower Greensand have been summarised by Allen et al. (1997) and the reader is referred to this text for a more detailed description.

The main hydrogeological units in the Lower Greensand are the Hythe Formation and the Folkestone Formation, which are separated by the Sandgate Formation in the study area. The Hythe Formation is confined by the Atherfield and Weald Clays at its base, and the Folkestone Formation is confined by the Gault Clay at the top of the sequence. Springs tend to occur at the junction of the Atherfield Clay

and the Hythe Formation (Edmunds et al., 1989). The fine sediment (material below a grain size of 0.21 mm) of the Hythe Formation is estimated at between 15% and 30% of the total, whilst the figure for the Folkestone Formation is only 5%. This is thought to explain the generally lower intergranular permeabilities of the former (Morgan-Jones, 1985). Although the Lower Greensand is often considered to be an intergranular aquifer, fractures are widespread and contribute significantly to the permeability in many places. A mean porosity value of 28% for undifferentiated Lower Greensand is quoted in Allen et al. (1997), from a dataset with a porosity range from 6% to 41%. The lower values are likely to be derived from the more consolidated and fractured parts of the aquifers.

The Sandgate Formation, which is of variable lithology, usually acts as an aquitard and separates the two aquifer units hydraulically, producing differences in piezometric levels between the two units (Morgan-Jones, 1985). However, some leakage undoubtedly occurs, especially towards the east as the Sandgate Formation thins (Allen et al., 1997). It is exploited for small amounts of water in some locations; a borehole in the Haslemere area drawing water exclusively from the Sandgate Formation was recorded as having a yield of 0.45 l s^{-1} (Thurrell et al., 1968). Where present, the Bargate Beds are often treated as part of the Hythe Formation aquifer, and similarly upper permeable layers in the Sandgate Formation may be in continuity with the Folkestone aquifer (Allen et al., 1997).

The Lower Greensand is, therefore, usually considered to be two separate aquifers, namely the Hythe and Folkestone Formations and this is borne out by the different water chemistries and piezometric levels commonly observed between the two formations. In places, the Sandgate Formation has sufficient hydraulic conductivity to be exploited for water supply. Hydraulic conductivity generally decreases for both aquifers both away from outcrop and towards the eastern ends of the north and south limbs, although aquifer properties data for the Lower Greensand are generally limited and of variable quality (Allen et al., 1997).

Groundwater flow in the Hythe Formation is predominantly intergranular where the sands are poorly cemented, but fracture flow dominates where the aquifer is more consolidated. The geometric mean of transmissivities from all parts of the Hythe Formation is $310 \text{ m}^2 \text{ d}^{-1}$, with higher values (up to $1500 \text{ m}^2 \text{ d}^{-1}$) being recorded where the aquifer is fractured. Transmissivities in the southern province of the study area tend to be quite high (around $1000 \text{ m}^2 \text{ d}^{-1}$), whilst north towards Guildford they are thought to be lower, around $200 \text{ m}^2 \text{ d}^{-1}$, because the sands are less well consolidated and flow is mainly intergranular (Allen et al., 1997). The Bargate Beds contribute to transmissivities where they are present, mainly via fractures. Transmissivities decline where the aquifer is confined. A 300 mm diameter borehole in the Bargate and Hythe Beds in the Haslemere area was recorded as yielding 50 l s^{-1} (Thurrell, 1968). Smaller diameter boreholes in the Hythe Formation typically yield $0.5\text{-}1.25 \text{ l s}^{-1}$.

Groundwater flow in the Folkestone Formation is principally intergranular, and the sands are relatively uniform. Therefore, transmissivity is believed to be mainly a function of aquifer thickness. Measured transmissivities in the Folkestone Formation range from $150 \text{ m}^2 \text{ d}^{-1}$ to $1200 \text{ m}^2 \text{ d}^{-1}$, with a geometric mean of $260 \text{ m}^2 \text{ d}^{-1}$ (Allen et al., 1997). The aquifer is thickest around Farnham and transmissivities are believed to be highest in this area. Ironstone hard-bands may cause locally important stratification of flow in the aquifer: whilst the formation is commonly regarded as exhibiting true homogeneous, intergranular flow, at a local level groundwater flow is more complex (Allen et al., 1997).

Where the Lower Greensand is confined, the transmissivity decreases and its potential as an aquifer is reduced. The confined Lower Greensand aquifer has only been exploited to a significant degree beneath Slough where the Lower Greensand is up to about 80 m thick (a transmissivity of $700 \text{ m}^2 \text{ d}^{-1}$ was recorded; Allen et al., 1997) and further east of the study area in Kent. The Sompting borehole in the confined Lower Greensand south of the southern Wealden outcrop (TQ 1661 0636) was tested by pumping at 12 l s^{-1} and a transmissivity of $77 \text{ m}^2 \text{ d}^{-1}$ was calculated (Young and Monkhouse, 1980). Buckley and Edmunds (1998) reported that the Folkestone Formation at this location is relatively

thick compared with other sites in the vicinity (35 m thick compared with 12-14 m elsewhere), and therefore this transmissivity may be higher than average for the confined Lower Greensand south of the southern outcrop. At depth, away from outcrop, the Lower Greensand is thought to act as a single aquifer (Allen et al., 1997). Under the London Basin the Lower Greensand forms a single sandstone unit of approximately Folkestone Formation age (Morgan-Jones, 1985).

Recharge to the aquifer is primarily via infiltration at areas of outcrop, although steep sided valleys in some areas allow for some surface run-off at the expense of infiltration. A study of recharge through the matrix of the Folkestone Formation by Edmunds et al. (1992) gave a figure of 165 mm yr⁻¹ using chloride profiles in the unsaturated zone, although this figure is probably a minimum value. Morgan-Jones (1985) reported a calculated recharge figure of 285 mm yr⁻¹, leading to approximate recharge figures for the Folkestone and Hythe Formations of 88701 m² d⁻¹ and 143167 m³ d⁻¹ respectively. There is very little superficial cover overlying the Lower Greensand (Figure 3.3), and the recharge areas for the two principal aquifers are therefore essentially the areas of outcrop (Morgan-Jones, 1985).

Groundwater in the Lower Greensand of the study area generally flows away from the Wealden pericline i.e. towards the north around Ashford, Maidstone and Guildford, towards the north west and west around Haslemere, and southwards from the south-eastern part. Groundwater in both the Hythe and Folkestone formations flows predominantly northwards, following the dip of the strata, but is modified locally by regional piezometric high points, such as exist around Sevenoaks and Caterham, and also to the south-east of Maidstone. Groundwater also tends to flow towards the major rivers, the Rivers Mole, Wey and Medway. Confinement of the strata leads to localised areas of artesian head, such as exist near the town of Wye, north-east of Ashford. Pumping further modifies flows locally (Edmunds et al., 1989). The piezometric contours of the two aquifers in the western part of the area rarely coincide (Morgan-Jones, 1985). The flow in the Folkestone Formation in the study area is dominated by continuity with the River Wey (Morgan-Jones, 1985).

Groundwater-level data are shown in Figure 3.4 for several sites in the southern part of the study area. The sites were chosen to indicate trends in groundwater levels in the Sussex part of the study area, and vary in depth from approximately 15 m to 95 m below ground level. Essentially, groundwater levels are constant over time, with distinctive seasonal variations being largely absent, with the exception of Harting Down where low-amplitude cycles occur. This lack of seasonal variation is in line with trends in Kent where groundwater levels are also largely unresponsive to surface rainfall events. An exception to this trend was the observed response to the floods of October 2000, when levels rose gradually until a peak in August 2001, followed by a gradual decrease. The lack of response to surface recharge events is probably a function of the high storativity of the Lower Greensand aquifer lithologies.

3.4 Aquifer mineralogy

The purity of the sands in the different facies of the Lower Greensand varies considerably, but increases where the depositional environment involved sediment transport by moving sand waves, or deposition near the sites of river inputs to the Aptian sea (Shepard-Thorn et al., 1986). The overall carbonate content of both the Hythe Formation and the Folkestone Formation is very low with the exception of the Rag and Hassock Beds, and there is generally a lack of available carbonate to neutralise infiltrating acidic recharge water (Edmunds et al., 1989). A brief summary of each of the major units in the Lower Greensand follows.

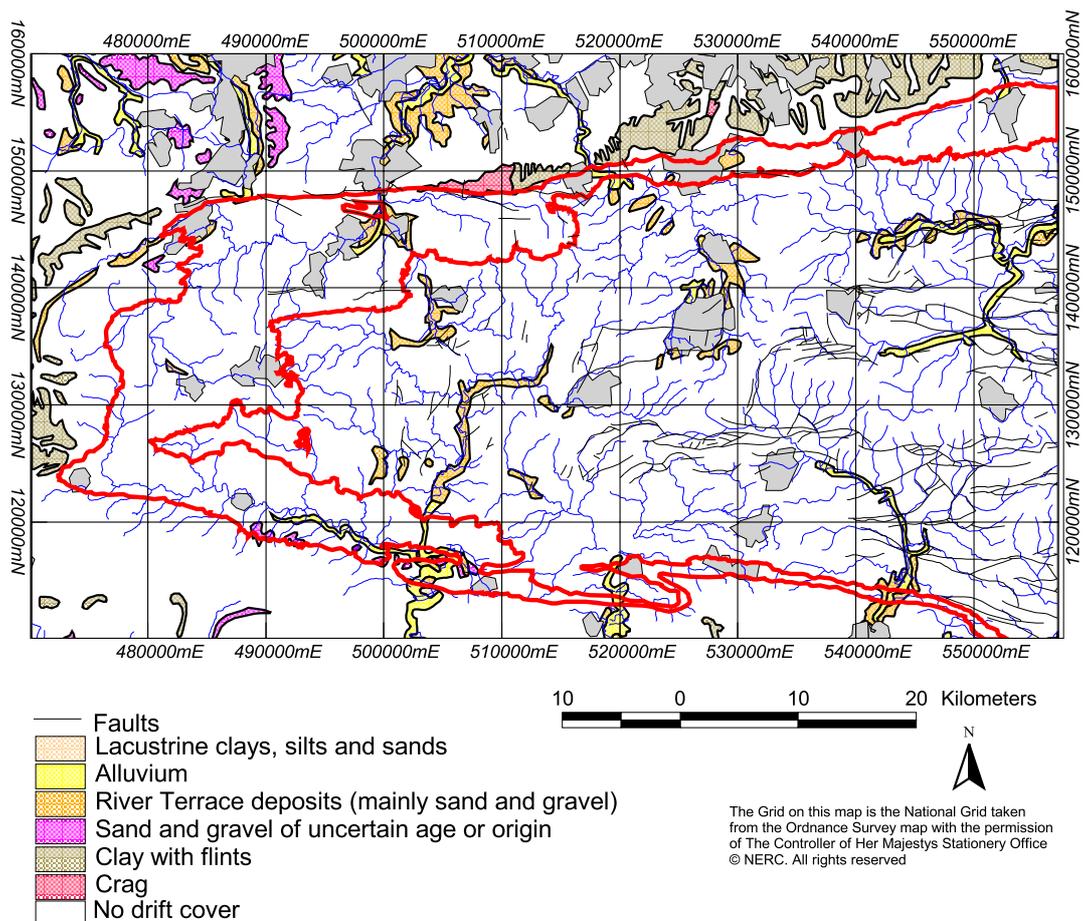


Figure 3.3 Geological map of the study area showing the distribution of drift types. Outcrop area bounded by red line.

The Atherfield Clay consists mainly of shales and mudstones, weathering to clays and silty clays (Edmunds et al., 1989). Clay ironstone concretions up to 300 mm in size, and fine grained sandstones are sometimes found towards the base. A rich molluscan fauna is present. The top of the Atherfield Clay is often sandy and glauconitic, and the junction with the lacustrine Weald Clay at the bottom is usually well defined.

The Hythe Formation comprises mainly quartzose sands with fine to medium glauconite grains at the top, which can give a distinctive “salt and pepper” appearance. Grains of magnetite are also abundant (Morgan-Jones, 1985). The clay content of the Hythe Beds is usually between 5 and 10 % of the total sandstone and consists of mica and smectite, with little or no kaolinite (Morgan-Jones, 1985). Chert nodules and thinly bedded cherts are found in the middle part of the Formation. In Kent (from Hythe westwards to Sevenoaks) layers of hard bluish-grey sandy limestone (“rag”) alternate with grey, loosely-cemented calcareous, argillaceous sandstone, speckled with glauconite (“hassock”). These vary in thickness from c. 15-60 cm and lenticular chert seams occur in both lithologies in the upper area of the formation (Worssam, 1963). The calcareous cementation is probably due to redistribution of calcite from shelly material within the sands (Shepard-Thorn et al., 1986). The Rag beds consist of subangular to angular quartz grains, round green glauconite grains and organic debris (fossil fragments and organic phosphate) in an abundant calcite matrix. The Hassock beds comprise the same constituents for Hassock Beds but with great proportions of quartz and lesser proportions of calcite (Worssam, 1963). Along the western part of the outcrop the beds are more arenaceous (Edmunds et al., 1989). Three “event horizons” marked by smectite-rich clays, phosphatic nodules or

shell beds have been identified, which may be a result of hiatuses in sedimentation during transgression (Ellison et al., 2002). Sands from the Hythe Formation are regarded as inferior to those of the Folkestone Formation for commercial purposes as they are too variable and fine-grained (Shepard-Thorn et al., 1986). Iron oxide surface coatings, chromite and iron-bearing heavy minerals are found within the sands. Some Fuller's Earth is present in the Hythe Formation, but none of commercial importance.

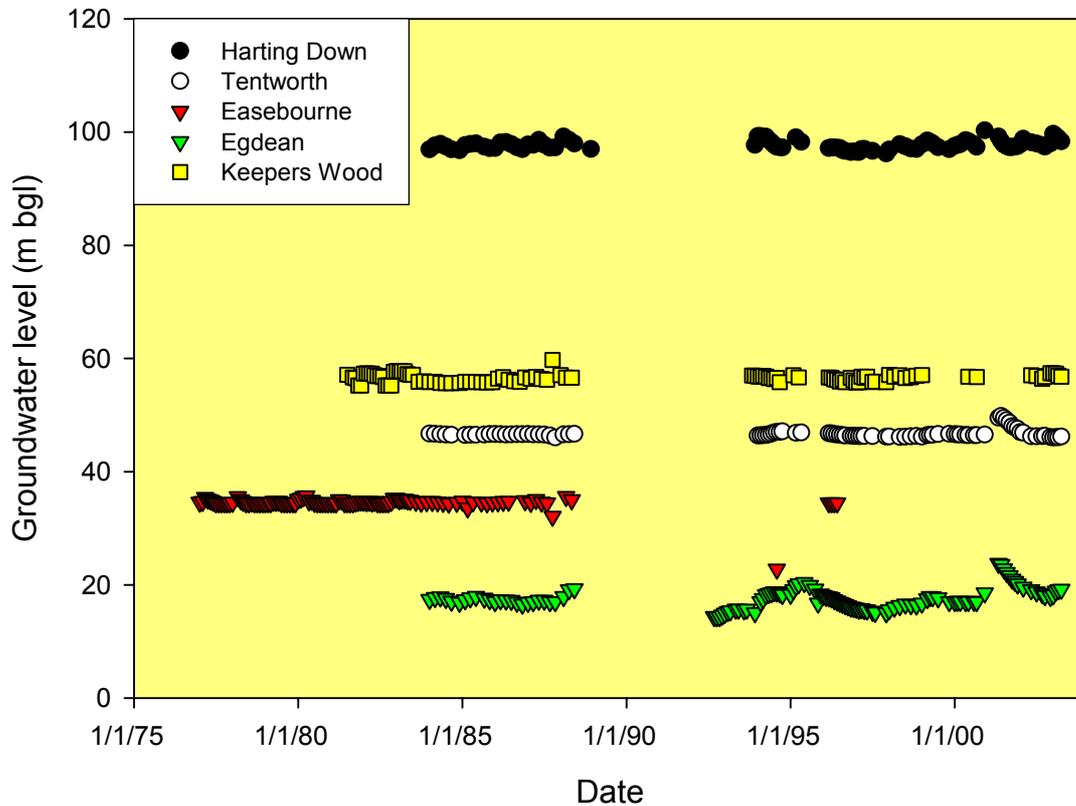


Figure 3.4 Groundwater levels in selected boreholes in the Lower Greensand: Harting Down (SU 80162612), Tentworth (SU85282425), Easebourne (SU89252346), Egdean (SU99821986) and Keepers Wood (SU94322281).

The Bargate Beds are ferruginous and calcareous cemented sandstones. Brown, 10 mm phosphatic pebbles and pebbles of fossiliferous limestone may be present at the base. Chert beds up to 0.3 m thick occurring at 1-2 m intervals have been recorded. In the western Weald, harder beds of cherty and calcareous sandstones up to 0.5 m in thickness are present (Shepard-Thorn et al., 1986).

The Sandgate Formation consists mainly of clays, together with glauconitic, limonitic and ferruginous sands. Seams of Fuller's Earth are present, sometimes in commercial quantities, derived from in-situ alteration of volcanic ash, and have been linked to volcanicity in the southern North Sea area at the time of deposition. Fuller's Earth is a highly plastic clay with a waxy or soap-like texture and consists essentially of clay minerals of the smectite group, chiefly calcium montmorillonite (Shepard-Thorn et al., 1986). The thicker, lenticular seams of commercial interest are thought to be a result of reworking in the shallow marine environment, and their presence in the formation is difficult to predict (Shepard-Thorn et al., 1986). Only traces of Fuller's Earth have been found west of Reigate.

The Folkestone Formation comprises mainly ferruginous and glauconitic quartz sand. Some silt and clay is present, although generally less than 2% clay (Allen et al., 1997). The clays comprise kaolinite and mica together with mixed-layer vermiculite and smectite (Morgan-Jones, 1985). The sand is principally medium grained quartz grains with some secondary micro-quartz. Hard iron-pan deposits are common, together with irregular ironstone veining, thought to be a result of the re-precipitation of indigenous iron. The overall carbonate content of both the Hythe and the Folkestone Formations is very low (averaging 1%) although there is a slight increase in the eastern part of the Hythe Formation where calcareous bands (Rag and Hassock Beds) occur. Young and Monkhouse (1980) reported 5 m of calcareous sands in the Folkestone Formation at depth in the confined strata south of the southern limb in the Sompting borehole. The Folkestone Formation has been described as “entirely carbonate free” (Edmunds et al., 1992: 133). Polished, dark brown grains of limonite are found, and are probably reworked from Jurassic rocks on the London platform source area (Shepard-Thorn et al., 1986). The Folkestone Formation north of the Weald is an important source of industrial “silica sand”, a high purity (free of iron and other material) sand of uniform grain size (Shepard-Thorn et al., 1986). Morgan-Jones (1985) found that the natural concentrations of heavy metals (apart from iron and manganese) in both the Folkestone and Hythe Formations is very low. Morgan-Jones (1985) noted that magnetite and pyrite were only present at depth in the Folkestone Formation.

3.5 Rainfall chemistry

An analysis of rainfall from Barcombe Mills (NGR 5437 1149, to the southeast of the main aquifer outcrop) is shown in the Table 3.1. The site is at an altitude of 10 m above Ordnance Datum. The average annual rainfall at the site (based on a 30 year mean, 1940 – 1971) is 876 mm. The 33 samples used in the summary were collected between January and December 2001. The mean pH value for all the rainfall samples collected is 5.15, and the median value is 4.95. The mean electrical conductivity of all the rainfall samples is 27.7 $\mu\text{S cm}^{-1}$. The solutes derived from rainfall typically increase during evapotranspiration and the data have been multiplied by three in Table 3.1 to estimate the approximate enrichment expected in infiltrating waters. However, nutrient (e.g. N, K) concentrations may be used during biomass uptake and recharge waters may contain lower concentrations than rainfall.

Table 3.1 Rainfall Chemistry from the Barcombe Mills site (NGR 5437 1149). The data are for 2001 and are taken from The UK National Air Quality Information Archive (<http://www.aeat.co.uk/netcen/airqual/>).

solute	mg l⁻¹	x 3
SO₄	1.74	5.22
NO₃	1.34	4.02
NH₄	0.41	1.23
Na	2.09	6.27
Mg	0.52	1.56
Ca	0.32	0.96
Cl	3.92	11.76
K	0.25	0.75

3.6 Land use

Several urban centres are found on or near the outcrop of the Lower Greensand Aquifer of the study area including Farnham, Haslemere, Godalming, Guildford, Dorking, Reigate and Redhill. Land use (Figure 3.5) is dominated by managed grassland followed by urban, arable, forest and minor areas of semi-natural vegetation. Fruit orchards are found where the Ragstones (sandy limestones) break down into fertile soils. Much of the region is highly developed, and there is a consequent risk of pollution to the aquifer.

In order to avoid contamination of groundwater resources, Source Protection Zones (SPZs) are determined by the Environment Agency for every source. The zones are modelled using information on abstraction volumes and rates, the average recharge over the groundwater catchment area, and the effective thickness and effective porosity of the aquifer (Box 3.1).

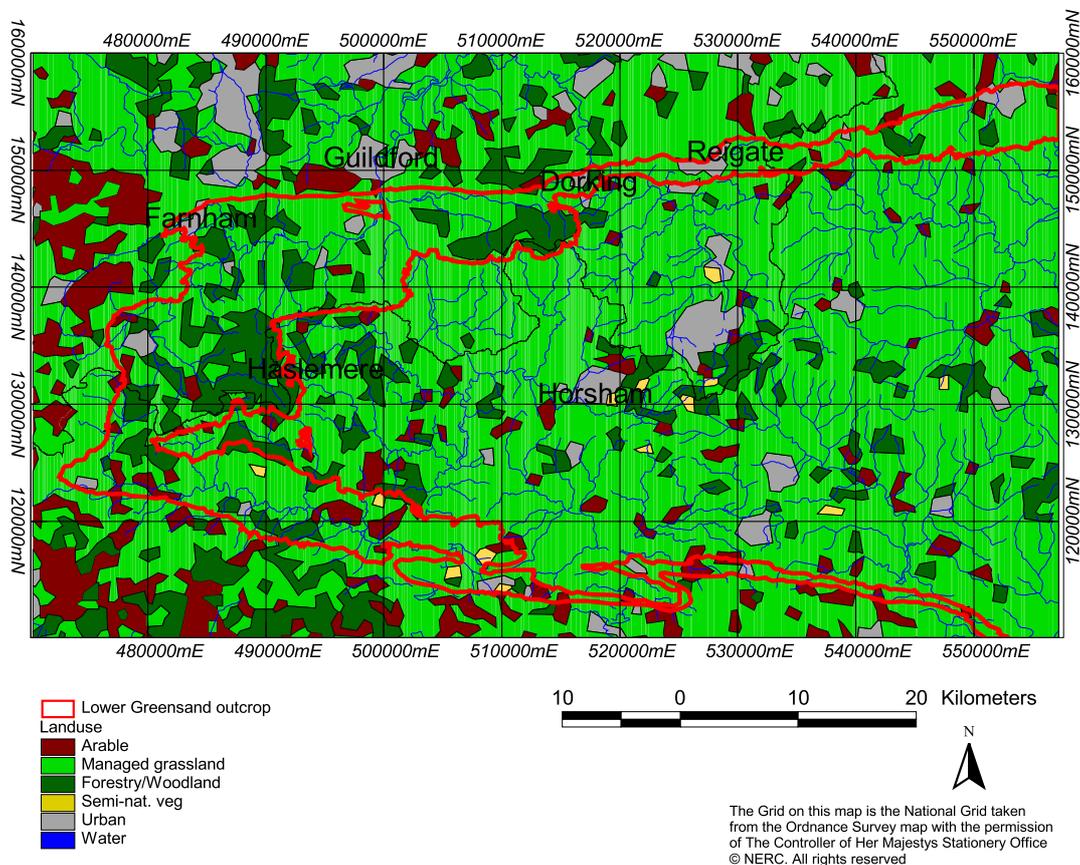
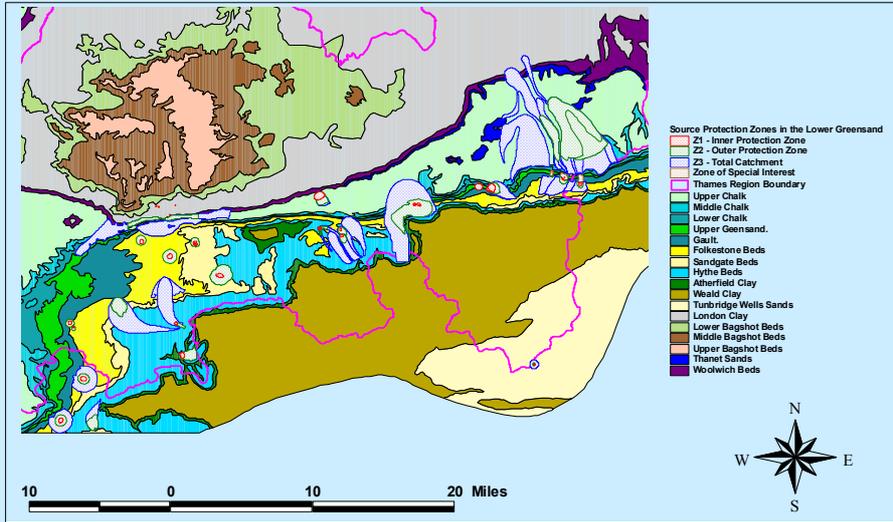


Figure 3.5 Generalised land use map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology © NERC.

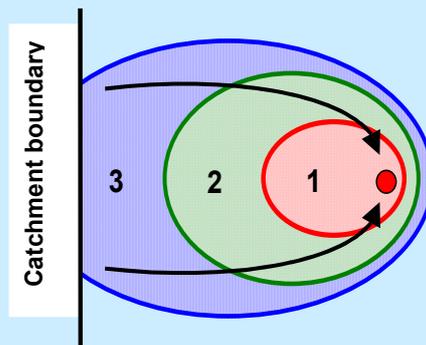
BOX 3.1 SOURCE PROTECTION ZONES

Source Protection Zones (SPZs) are determined for every source. The zones are modelled using information on abstraction volumes and rates, the average recharge over the groundwater catchment area, and the effective thickness and effective porosity of the aquifer.



Each SPZ comprises:

Zone 1, the Inner Source Protection Zone, has an area determined by the distance a particle of water will travel through the saturated zone over a 50 day time period, based on the time necessary for bacterial decay. The boundary is always a minimum distance of 50m away from the source and is designed to protect against toxic chemicals and water-borne disease.



Zone 2, the Outer Source Protection Zone, has an area based on the distance a particle of water will travel through the saturated zone over 400 days *or* 25% of the total catchment area (whichever is larger). This time period is based upon that needed to delay, dilute and attenuate any slowly degrading pollutants.

Zone 3, the Source Catchment, comprises the entire catchment area of the groundwater source.

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 17 samples were collected from a series of springs and boreholes in the Lower Greensand in February 2002 and a further 12 samples in June 2002 (Figure 4.1). Most of the boreholes sampled were pumping at the time of sampling, ensuring that representative groundwater samples were obtained. Where this was not the case, purging of at least two borehole volumes was carried out if possible prior to sampling.



Figure 4.1 Chemical sampling of a source in the Lower Greensand.

Pumped groundwater samples represent the sum of all waters entering the borehole over the screened interval. Therefore, the sample may represent a mixture of waters with different chemistry, especially where the borehole screen extends over more than one permeable unit in the Lower Greensand. There are few data available from most sites to identify where this is the case. However, valid conclusions may still be drawn in interpreting regional variations which exist in the aquifer.

Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured in an anaerobic flow-through cell (Figure 4.2). Other on-site measurements included temperature (T°C), specific electrical conductance (SEC) and bicarbonate alkalinity. Samples were collected for major and trace chemical analysis in polyethylene bottles. Those for major and trace elements were filtered through 0.45 µm filters and the aliquot for cation and trace elements was acidified to 1% v/v HNO₃ to minimise precipitation and adsorption onto container walls. Additional samples were collected in glass bottles for stable isotope analyses ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$).



Figure 4.2 Anaerobic flow cell used for chemical sampling.

4.2 Previous data

The sampling campaign in 2002 was augmented with data from 33 sites taken from the Environment Agency's groundwater monitoring network database. Historical data were available for a number of years providing a useful indication of changes with time as well as spatial variations. Samples were selected which contained the largest number of analysed constituents with preference being given to recent analyses. A further 24 analyses were also used from the study of Edmunds et al. (1989). The locations of samples used in this study are shown on Figure 3.1.

4.3 Interpretation of pumped groundwater samples

The Lower Greensand functions in places as two or more separate aquifers, whilst in other places there is considerable hydraulic connection between the different stratigraphic units making it behave as a single aquifer. Different flow horizons can exist within the permeable formations, separated by iron deposits or clay layers. Boreholes in the Lower Greensand may penetrate more than one permeable unit, and the sources of the water will depend on the position of casing and screen in the borehole. Many boreholes undoubtedly provide a mixture of waters drawn from more than one permeable unit. Geophysical logging of boreholes shows that the screen is not always emplaced as reported on borehole completion diagrams, and in addition cracked, poorly joined, rusty or otherwise damaged casing admits waters from “cased out” horizons. For these reasons it is often difficult to deduce exactly from which stratum a given borehole draws its water in some locations. Boreholes in this study have been classified according to the dominant aquifer unit where known. Many of boreholes sampled extract groundwater from both the Hythe beds and Sandgate beds and therefore these have been grouped together in comparisons of groundwater from different units described in Chapter 6. Thus, it should be borne in mind during interpretation that groundwater sampled from an individual borehole may be derived from more than one aquifer unit.

4.4 Data handling

The groundwater chemistry data from different sources were amalgamated into a single database. The limits of detection for solutes were typically different as a consequence of using different analytical techniques with different sensitivity and differing censoring criteria, and also probably reflect analytical precision improvements over time. Where data were below the detection limit of analysis, a concentration equal to half the detection limit has been substituted for statistical and plotting purposes.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

A summary of the data is shown in Tables 5.1 and 5.2 for the study area. This shows the ranges and averages of data as well as an upper concentration (defined as mean + 2 σ or 97.7th percentile) which is used as a cut off to distinguish outlying data. The median is preferred to the mean as an average as it is more robust and less affected by extreme values. This chapter deals with the fundamental hydrochemical characteristics of the groundwaters in the study area highlighting the main features of the summary table.

Table 5.1 Field parameters, stable isotope data and the range of major and minor element concentrations in the Lower Greensand of the Weald.

		Min	Median	Max	Mean	97.7 th percentile	Upper baseline*	N
T	°C	7.2	11	23	12.2	21.2		78
PH		5.80	7.18	8.10	7.14	8.00		80
Eh	mV	-52	126	641	191	460		51
DO	mg l ⁻¹	<0.1	0.3	13	2.3	9.8		46
SEC	μS cm ⁻¹	109	366	827	374	660		81
δ²H	‰	-55.0	-46.4	-44.5	-47.3	-44.5		19
δ¹⁸O	‰	-8.14	-7.07	-6.73	-7.19	-6.76		19
δ¹³C	‰	-18.1	-14.2	-11.2	-14.1	-11.4		19
Ca	mg l ⁻¹	9.3	51.7	182	58.6	122.4		84
Mg	mg l ⁻¹	1.4	2.8	7.2	3.1	6.0		84
Na	mg l ⁻¹	5	10.2	111	18.8	92.4		84
K	mg l ⁻¹	0.94	2.5	20	3.0	7.0		84
Cl	mg l ⁻¹	9.6	20	82	25.0	76.2		85
SO₄	mg l ⁻¹	6.9	21.8	182	29.4	67.6		84
HCO₃	mg l ⁻¹	6	148	339	145	249		81
NO₃ as N	mg l ⁻¹	< 0.003	0.20	16.3	2.39	15.5	1-3	68
NO₂ as N	mg l ⁻¹	<0.001	0.002	0.10	0.006	0.035		49
NH₄ as N	mg l ⁻¹	< 0.003	0.030	1.36	0.093	0.96		56
P	mg l ⁻¹	<0.02	0.032	0.311	0.070	0.301		30
TOC	mg l ⁻¹	0.2	1	4.5	1.2	4.0		42
DOC	mg l ⁻¹	0.74	2.7	10.1	3.6	9.7		29
F	mg l ⁻¹	0.030	0.138	0.370	0.147	0.298		82
Br	mg l ⁻¹	0.015	0.078	0.370	0.100	0.350		75
I	mg l ⁻¹	0.001	0.004	0.041	0.010	0.030		53
Si	mg l ⁻¹	3.5	6.7	13.2	7.1	11.3		52

* estimated upper baseline for elements modified by anthropogenic influences.



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

Table 5.2 Trace element concentrations in the Lower Greensand of the Weald.

		Minimum	Median	Maximum	Mean	97.7th percentile	N
Ag	µg l ⁻¹	<0.05	<0.05	<0.05	0.05	0.20	35
Al	µg l ⁻¹	<1	<1	246	12.13	116	35
As	µg l ⁻¹	<1	3.0	20.0	4.75	15.7	59
Au	µg l ⁻¹	<0.05	0.03	0.03	0.03	0.03	29
B	µg l ⁻¹	<20	<20	150	34.3	150	53
Ba	µg l ⁻¹	3.53	59.1	380	91.1	225	59
Be	µg l ⁻¹	<0.05	<0.05	1.26	0.07	0.60	29
Bi	µg l ⁻¹	<0.05	<0.05	0.11	0.03	0.06	29
Cd	µg l ⁻¹	<0.05	<0.05	0.50	0.13	0.50	57
Ce	µg l ⁻¹	<0.01	<0.01	1.25	0.08	0.81	29
Co	µg l ⁻¹	<0.02	<0.02	3.79	0.36	2.66	29
Cr	µg l ⁻¹	<0.5	0.60	8.50	1.24	5.57	57
Cs	µg l ⁻¹	<0.01	0.01	0.06	0.01	0.05	29
Cu	µg l ⁻¹	<0.1	1.40	134	5.2	20.0	57
Dy	µg l ⁻¹	<0.01	<0.01	0.39	0.03	0.27	29
Er	µg l ⁻¹	<0.01	<0.01	0.29	0.02	0.16	29
Eu	µg l ⁻¹	<0.01	<0.01	0.10	0.01	0.09	29
Fe	mg l ⁻¹	<0.005	0.115	1.74	0.226	1.201	48
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
Gd	µg l ⁻¹	<0.01	<0.01	0.55	0.04	0.38	29
Ge	µg l ⁻¹	<0.05	<0.05	0.09	<0.05	0.09	29
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	29
Hg	µg l ⁻¹	<0.02	0.05	0.05	0.03	0.05	56
Ho	µg l ⁻¹	<0.01	<0.01	0.10	<0.01	0.05	29
In	µg l ⁻¹	<0.01	<0.01	0.01	<0.01	<0.01	29
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
La	µg l ⁻¹	<0.01	<0.01	0.95	0.06	0.51	29
Li	µg l ⁻¹	2.0	5.4	32.0	8.65	29.6	53
Lu	µg l ⁻¹	<0.01	<0.01	0.05	<0.01	0.02	29
Mn	mg l ⁻¹	<0.002	0.011	0.100	0.020	0.075	48
Mo	µg l ⁻¹	<0.1	<0.1	0.50	<0.1	0.37	29
Nb	µg l ⁻¹	<0.01	<0.01	0.01	<0.01	<0.01	29
Nd	µg l ⁻¹	<0.01	<0.01	2.00	0.15	1.65	29
Ni	µg l ⁻¹	<0.2	2.80	22.0	3.61	10.8	57
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
Pb	µg l ⁻¹	<0.1	0.40	8.60	1.12	7.28	57
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	29
Pr	µg l ⁻¹	<0.01	<0.01	0.42	0.03	0.27	29
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	29
Rb	µg l ⁻¹	0.96	2.22	10.2	2.9	7.0	29
Re	µg l ⁻¹	<0.01	<0.01	0.01	<0.01	<0.01	29
Rh	µg l ⁻¹	<0.01	<0.01	0.03	<0.01	0.02	29
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
Sb	µg l ⁻¹	<0.05	<0.05	0.07	<0.05	0.06	29
Sc	µg l ⁻¹	1.50	3.28	6.0	3.7	5.9	29
Se	µg l ⁻¹	<0.5	0.25	3.9	1.0	3.4	29
Sm	µg l ⁻¹	<0.05	<0.05	0.44	0.06	0.41	29
Sn	µg l ⁻¹	<0.05	0.06	3.4	0.18	1.3	29
Sr	µg l ⁻¹	30.0	162	3110	255	905	75
Ta	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
Tb	µg l ⁻¹	<0.01	<0.01	0.08	<0.01	0.06	29
Te	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
Th	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	29
Ti	µg l ⁻¹	<10	5.00	5.00	5.00	5.00	29
Tl	µg l ⁻¹	<0.01	<0.01	0.02	<0.01	0.02	29
Tm	µg l ⁻¹	<0.01	<0.01	0.04	<0.01	0.02	29
U	µg l ⁻¹	<0.05	<0.05	0.81	0.07	0.48	29
V	µg l ⁻¹	<1	0.50	1.00	0.52	0.68	29
W	µg l ⁻¹	<0.1	<0.1	0.10	<0.1	<0.1	29
Y	µg l ⁻¹	<0.01	0.01	5.7	0.27	2.6	29
Yb	µg l ⁻¹	<0.01	<0.01	0.21	0.02	0.12	29
Zn	µg l ⁻¹	2.00	22.8	215	36.1	118	51
Zr	µg l ⁻¹	<0.5	0.25	0.25	0.25	0.25	29

The summary data are shown graphically on a Piper Plot, boxplots and cumulative probability plots (Figures 5.1-5.5). The boxplots display the ranges of data and are designed to highlight the distribution of data on a percentile basis (Figure 5.2). The boxes show the range between the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles and the dots the 5th and 95th percentiles). In addition the median is shown as a horizontal black line and the mean as a blue line within the box. The solid black line on the graph represents a diluted seawater curve which has been normalised to the median Cl of the samples. This provides a general indication, in most aquifers, of inputs from water-rock interaction above the marine-derived (rainfall or connate) inputs. The solid grey line on Figure 5.4 shows typical detection limits for each element. Cumulative probability plots are useful in visualising the distribution of data and may be of use in determining outlying data or discerning pollution. Geochemical processes may alter the distribution of populations in several different ways giving rise to complex distributions. Box 5.1 illustrates how cumulative probability plots can be used to infer a range of processes occurring in the aquifer.

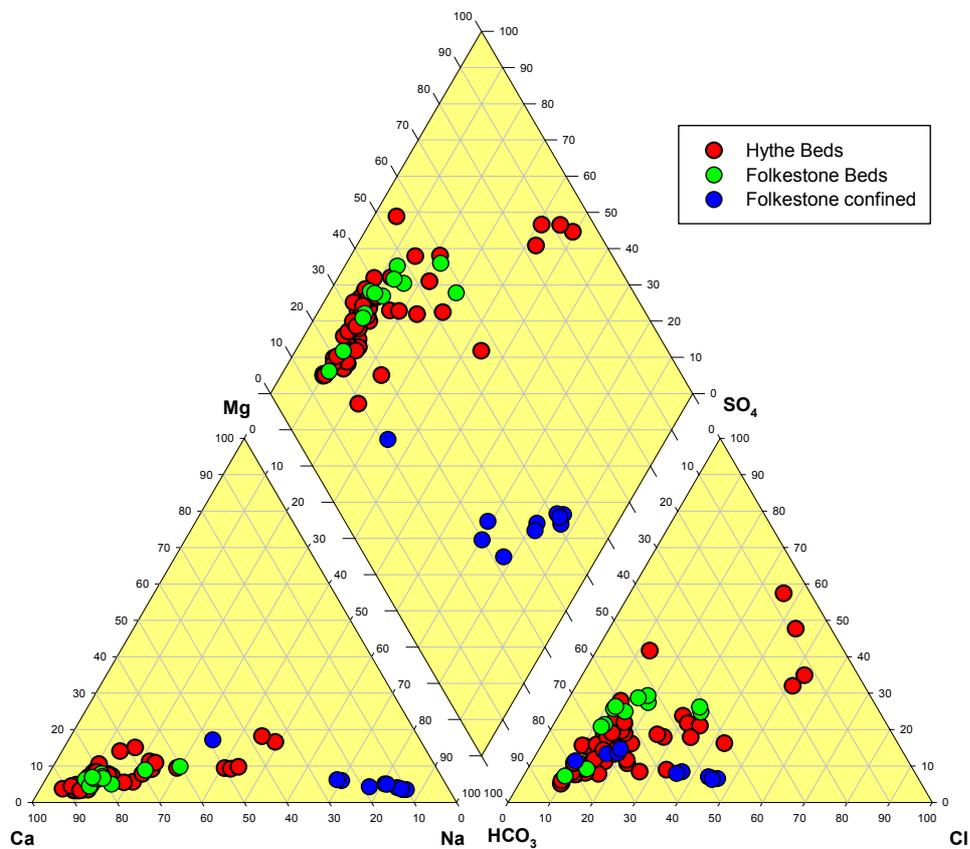


Figure 5.1 Piper Plot of Lower Greensand samples.

5.2 Water types and physicochemical characteristics

The groundwaters of the Lower Greensand are generally very fresh: specific electrical conductance (SEC) varies from 109 $\mu\text{S cm}^{-1}$ to 827 $\mu\text{S cm}^{-1}$, with a median value of 366 $\mu\text{S cm}^{-1}$. Temperatures show a wide range, varying from a minimum of 7.2 °C to a maximum of 23 °C, with the warmer waters being drawn generally from deeper boreholes of the confined part of the aquifer. The median pH value of the data is 7.2. However, there is a relatively large range in pH from 5.8 to 8.1, with the higher values found in groundwaters of the confined Folkestone Beds. There is generally little carbonate to buffer pH values, particularly in the sandier units, and as the recharge to the aquifer tends to have a low pH (the mean pH of rainfall at the Barcombe Mills site is 5.1), this leads to waters with

pH values of 6.5 or lower in places (10 out of 75 samples have pH values less than or equal to 6.5). This has led to concerns over the mobility of metals in groundwaters of the Lower Greensand, even under oxidising conditions (Edmunds et al., 1989). The low pH groundwaters occur particularly at the base of the Lower Greensand, but also in the some parts of the unconfined Hythe Beds.

Groundwater in the Lower Greensand is dominantly of Ca-HCO₃ type, although there is a trend towards Na-HCO₃ and mixed types (Figure 5.1). The majority of unconfined groundwaters from both the Hythe and Folkestone beds are dominated by Ca as the dominant cation, but show a greater spread of anion compositions. Some samples contain Ca and Na in approximately equal abundance and these also form a distinct grouping on the anion plot being dominated by SO₄ and Cl. These samples are mainly from springs or shallow boreholes with low pH (5.8–6.8) and SEC (132–190 μS cm⁻¹). The confined groundwaters are mostly dominated by Na and HCO₃ although there is also a trend towards Cl (Figure 5.1).

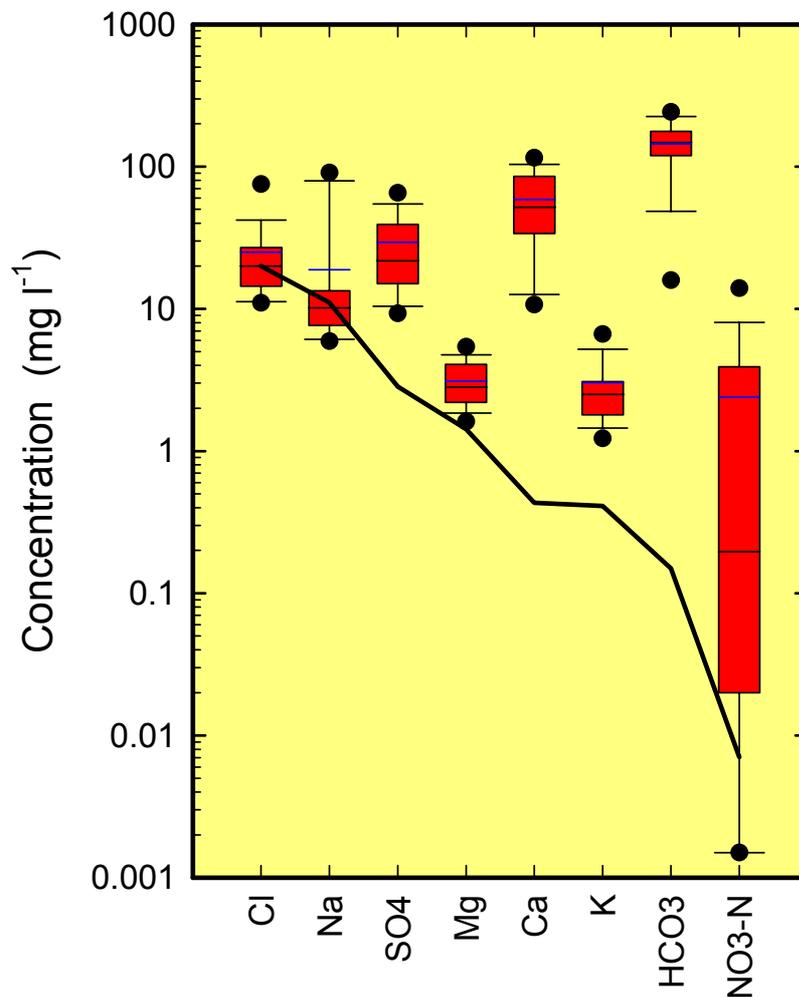


Figure 5.2 Boxplot of major ions in the Lower Greensand. Black line represents diluted sweater line normalised to the median Cl concentration of the samples.

5.3 Major elements

Major element concentrations are shown in box plots in Figure 5.2. The median Cl concentration of 20 mg l⁻¹ is slightly higher than expected for the baseline, compared to rainfall. The median Na lies

close to the diluted seawater curve, but some groundwaters are relatively high in Na. The other major elements all plot above the seawater dilution line indicating sources derived from or introduced to the aquifer. The most abundant solutes are Ca, HCO₃ and SO₄. Bicarbonate shows a relatively narrow range in concentrations compared to Ca and SO₄. The median sulphate concentration is 24 mg l⁻¹, and the range of concentrations is quite variable (minimum of 5.9 mg l⁻¹ and maximum of 182 mg l⁻¹).

Nitrate varies in concentration from below detection limit in the more reducing groundwaters to 16.3 mg l⁻¹ NO₃-N in the more oxidising groundwaters, the higher concentrations implying anthropogenic inputs. The unconfined Folkestone beds all have high NO₃ except for one (Tilford PS 2) which has a concentration of 0.14 mg l⁻¹ NO₃-N. This is a relatively deep borehole (176 m) compared with an adjacent borehole (Tilford PS 1: 76 m; 1.35 mg l⁻¹ NO₃-N) and may imply more reducing conditions at depth (PS 2 has an Eh of +116 mV compared with PS1 which is +465 mV).

The Hythe Beds show a wide range in NO₃ concentrations (<0.03–15.8 mg l⁻¹) the lower concentrations being from parts of the aquifer confined beneath the Folkestone, Bargate and Sandgate beds. There is a distinct change in population at around 3 mg l⁻¹. Many reducing groundwaters also have concentrations below the detection limit.

The data are shown on a cumulative probability plot on Figure 5.3. It is evident that none of the major elements show lognormal distributions, although Mg shows a near-linear distribution. There is a pronounced change in Na at around the 90th percentile, highlighting a separate high Na population. Although there is a slight shift in Cl, it is much less pronounced than for Na. The Ca and HCO₃ distributions show a separate population with low concentrations corresponding to the more acidic groundwaters.

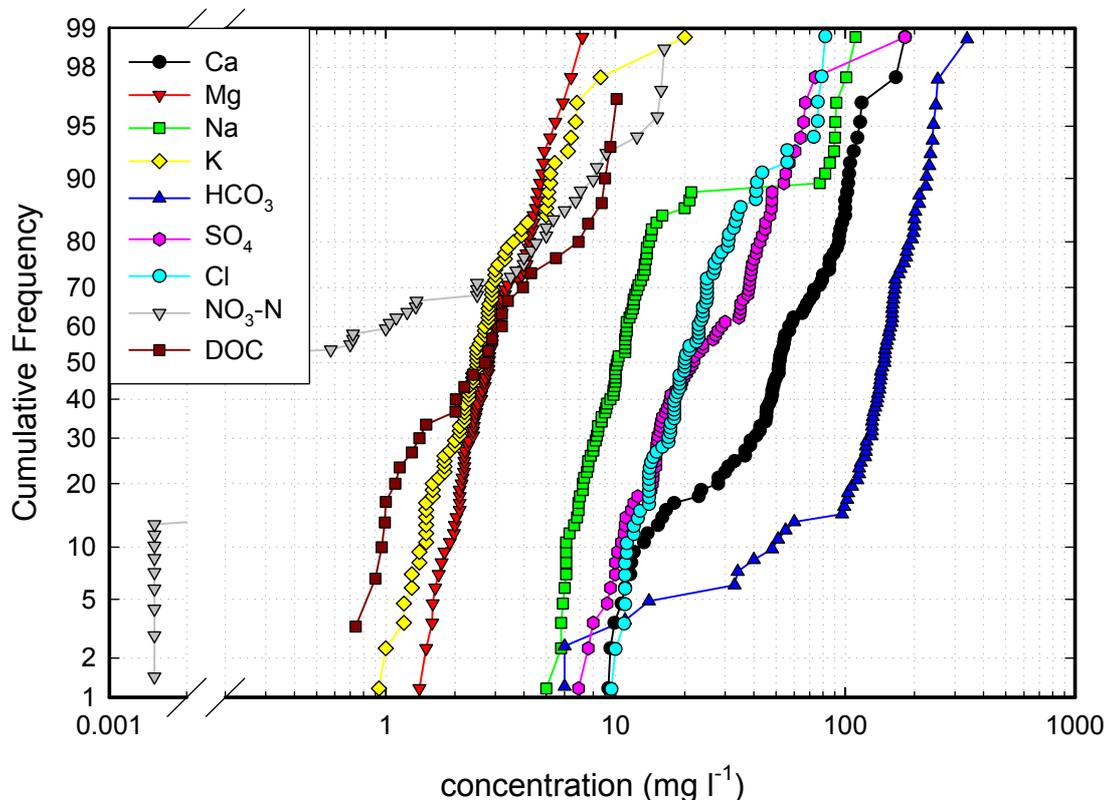


Figure 5.3 Cumulative frequency plot of major ions in the Lower Greensand.

5.4 Minor and trace elements

Minor and trace elements are displayed on boxplots in Figure 5.4 and cumulative probability plots on Figure 5.5. Although bromide, and to a lesser degree boron, lie close to the seawater line determined using the median chloride value, most other elements are significantly higher than this. The halogen elements F and I plot significantly above this line but concentrations are still low (Figure 5.4; Table 5.2). The highest concentrations are for Si which shows a relatively narrow range. Strontium, which behaves similarly to Ca, is present at relatively low concentrations and displays a typical range for sandstone aquifers where calcite is rare or absent. There is a relatively wide range in the concentrations of Ba with approximately 40% of the sites having concentrations above the current EU Guide Level of $100 \mu\text{g l}^{-1}$.

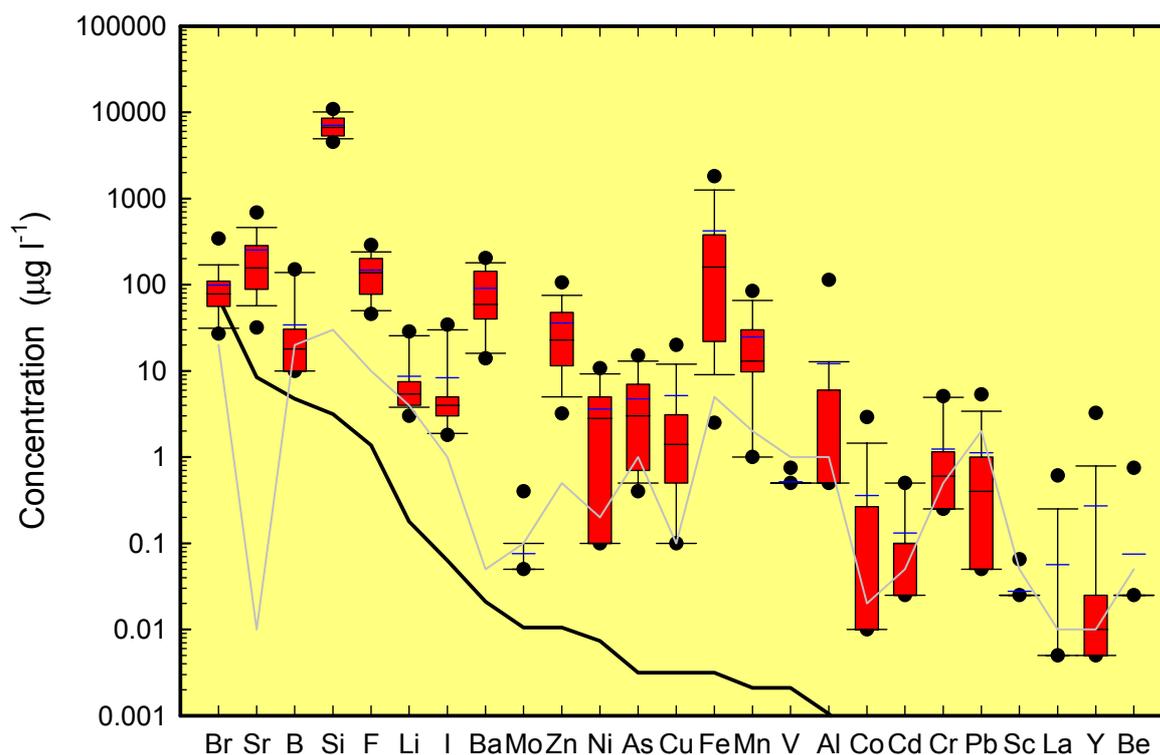


Figure 5.4 Boxplot of minor ions in the Lower Greensand. Black line represents a diluted seawater line normalised to the median Cl of the samples and grey line represents typical detection limits.

Of the trace metals, Fe shows the highest concentrations varying from less than the detection limit up to 6.3 mg l^{-1} with a median of 0.11 mg l^{-1} . High Mn concentrations (up to 0.15 mg l^{-1}) may also occur locally. Zinc varies over two orders of magnitude, but is generally well below current drinking water standards (EU Guide Level concentration is $5000 \mu\text{g l}^{-1}$). Most other metals have low median concentrations but concentrations may be locally high. Aluminium is mobile under low pH conditions and this is reflected in the relatively high concentration in one of the springs ($246 \mu\text{g l}^{-1}$), however the median Al concentration is low ($< 1 \mu\text{g l}^{-1}$) in the groundwaters analysed. Arsenic was detected in most samples (43 out of 59) and although the median is relatively low ($3 \mu\text{g l}^{-1}$), concentrations up to $20 \mu\text{g l}^{-1}$ were measured. In general, the high As is associated with reducing groundwaters. Nickel was found in some groundwaters up to $22 \mu\text{g l}^{-1}$, Be up to $1.3 \mu\text{g l}^{-1}$, Cr up to $8.5 \mu\text{g l}^{-1}$, Pb up to $8.6 \mu\text{g l}^{-1}$ and Cu up to $134 \mu\text{g l}^{-1}$ (Table 5.2).

5.5 Pollution indicators

The carbonate-poor nature of the shallow aquifer, as well as locally dense urban development, make the Lower Greensand susceptible to pollution. Boreholes showing obvious signs of point source pollution were avoided in this study. Nitrate concentrations are relatively high (up to $16.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$) in parts of the aquifer, but there is no correlation with urban areas and the increase probably due to inputs from agricultural activities. Compounds such as atrazine, MTBE, and CCl_4 have been detected in some boreholes, also indicating anthropogenic pollution.

Morgan-Jones (1985) suggested that the Hythe Formation may be more effective at removing or retarding pollutants than the Folkestone Formation, due to a higher proportion of clays which help to retard or modify some pollutants and carbonate which may buffer chemical changes, and to the fact that the Hythe Formation is finer grained and less well sorted.

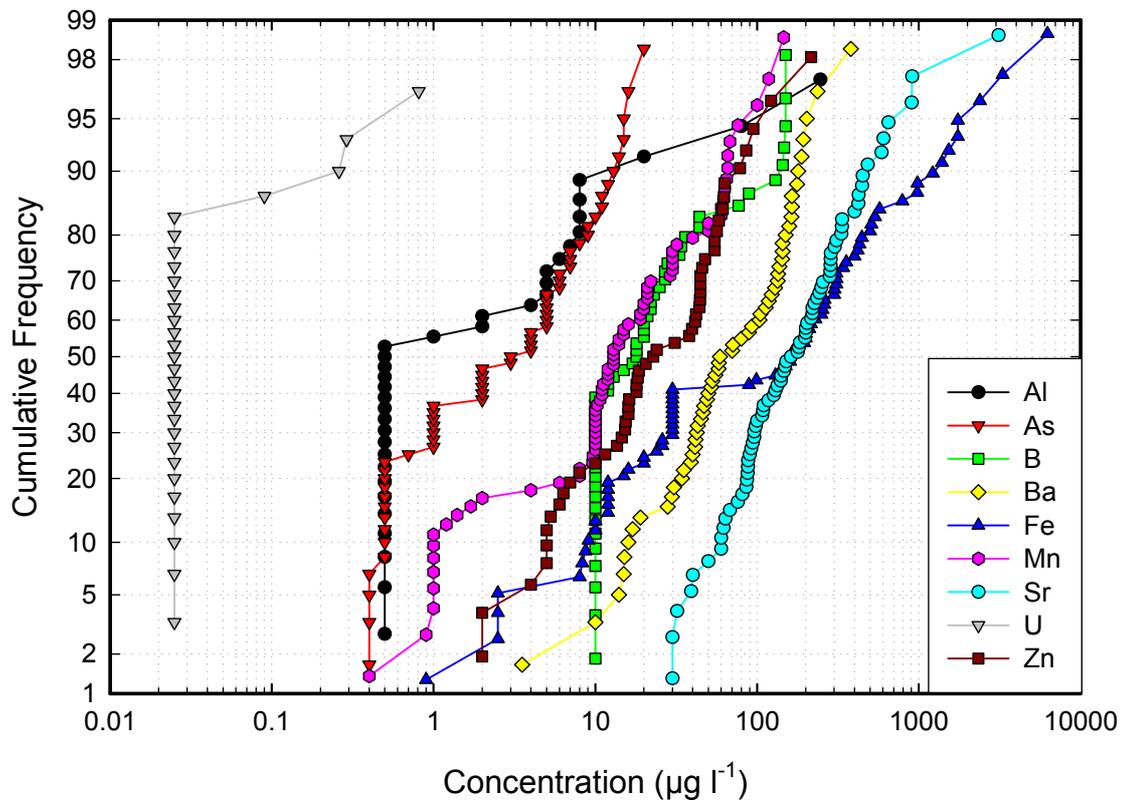
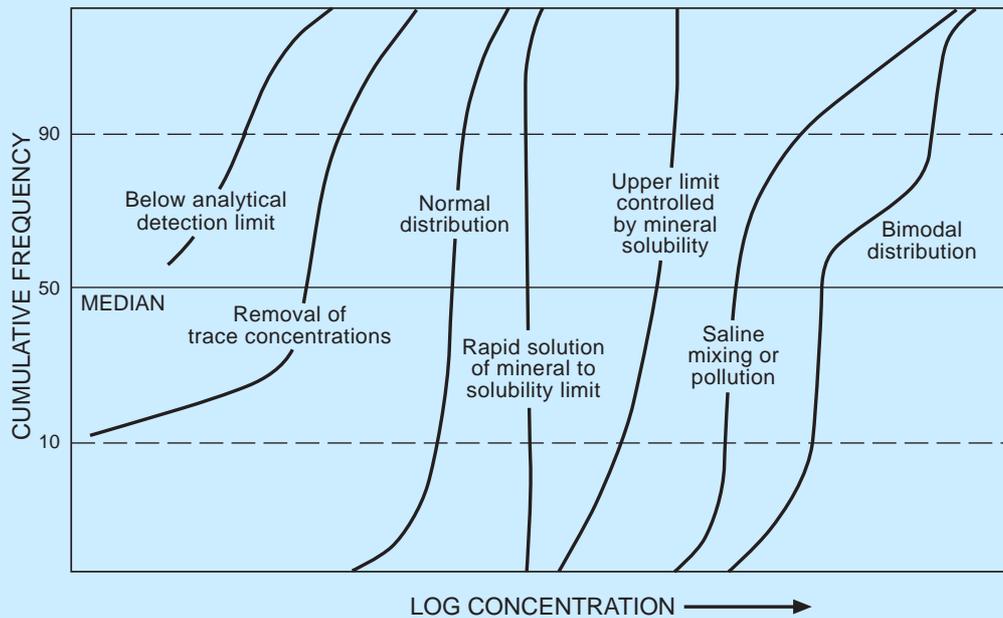


Figure 5.5 Cumulative frequency plot of minor ions in the Lower Greensand.

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.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The hydrochemistry of the Lower Greensand is controlled both by natural inputs (baseline) and inputs derived from anthropogenic sources. The initial input of solutes to aquifers is from rainfall which is generally very dilute and acidic (Table 3.1). Infiltration through soils generally increases rainfall-derived acidity due to an increase in carbonic acid derived from root respiration and organic matter decomposition. The chemistry of recharge water as it passes through the unsaturated zone is generally controlled by the presence of soluble minerals particularly carbonates such as calcite or dolomite. The unsaturated zone of the Lower Greensand is typically devoid of carbonate mineral phases and the consequent lack of buffering of acidity means that trace metal species can be mobilised more readily and enter into the groundwater. Further reaction takes place as the groundwater moves along regional flowpaths and gives rise to a wide range of chemistries depending on the minerals forming the aquifer matrix. This chapter aims to characterise the dominant processes controlling water chemistry in the Lower Greensand and to characterise regional variations.

6.2 Unsaturated zone hydrochemistry

The chemistry of the unsaturated zone is in general poorly documented. However, porewater chemistry has been analysed from a core drilled into Folkestone Beds at Crooksbury Common near Farnham in 1992. Interpretation of the data is complicated by the fact that part of the area was burned and cleared in 1984 and then replanted with pine trees in 1986. Nevertheless, the data provide useful information on the unsaturated zone porewater chemistry in this carbonate-free lithology. The results for selected parameters and solute concentrations are shown on Figure 6.1. The pH was very acidic (<4.5) down to a depth of around 8 m, where it increased to around pH 5 at 10 m depth and subsequently fell again to pH 4.1 just above the water table (14.5 m). The concentrations of most major elements are relatively low (Figure 6.1). Bicarbonate was less than the detection limit due to the low pH, and the anions are dominated by SO_4 and Cl . The compositions are similar to the chemistry of the springs discussed in Chapter 5.

Nitrate is higher at depth in contrast to the findings from an earlier profile investigated by Edmunds et al. (1989). Sulphate concentrations were higher in the shallow part of the profile and it was suggested that this change to lower concentrations represents the timing of the forest fire (Edmunds et al, 1989). Interestingly, many chemical changes occurred where the pH suddenly increased: many elements (e.g. Ca, Mg, Si, K) were high in porewaters above this depth but decreased dramatically where the pH rose. Due to the lack of carbonate minerals, the dominant reactions in the unsaturated zone are dominated by silicate hydrolysis (reaction of acidic waters with feldspar and glauconite) as well as reactions involving Fe-oxide minerals. This rapid decrease was also seen for trace elements (Al, Mn, Ni, Co, Pb, Sr, Ge, Ga, Y, rare earth elements) which showed a distinct peak in the profile immediately above the section where pH increased (Figure 6.1). The subsequent behaviour is different for different elements, although the reasons for this are not clear. It is evident from the Crooksbury Common data that the unsaturated zone contains water with high concentrations of trace metals mobilised by infiltrating acidic water. The lack of chemical buffering of pH highlights the fact that such aquifers are at high risk from some types of pollution.

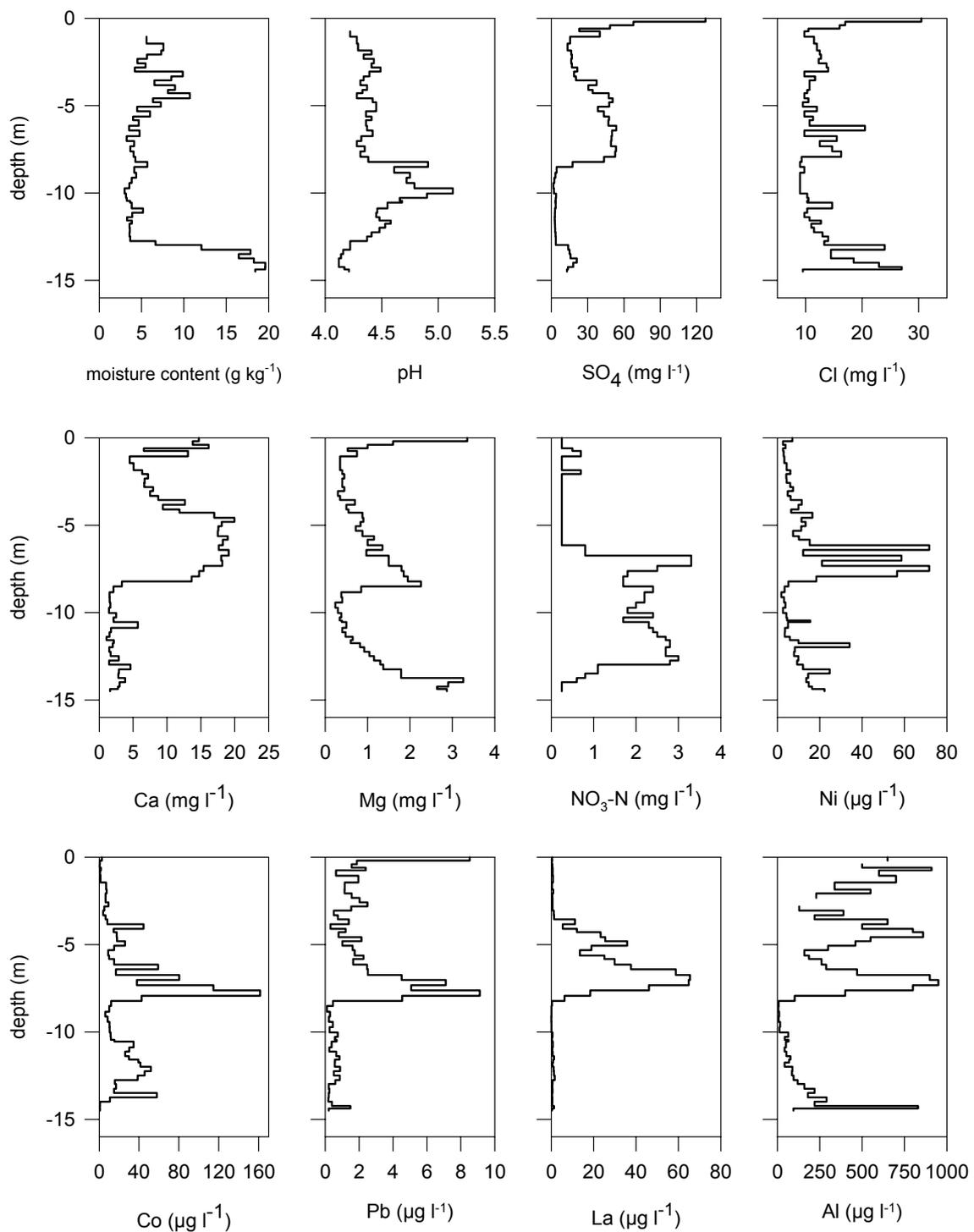


Figure 6.1 Unsaturated zone profiles from the Folkestone Formation near Farnham.

6.3 Chemical evolution along flowlines

The chemistry of groundwaters evolves over time in response to time-dependent chemical reactions, the mineralogy of the aquifer and the geochemical environment in terms of pH and redox potential. A series of boreholes (Table 6.1) have been selected to highlight chemical changes along the direction of

regional groundwater flow as indicated by piezometric levels and these are shown on Figures 6.2 and 6.3. The “distance” column in the table refers to the approximate distance in kilometres along the flow direction from the location of the first sample point. There are many difficulties in determining chemical evolution along specific flowlines over such distances, particularly in the unconfined part of the aquifer where active recharge is occurring. In the Lower Greensand, confining layers and a complex geology also complicate interpretation. Nevertheless, the regional variations do provide indicators of the geochemical processes taking place as groundwaters evolve with time.

Table 6.1 Boreholes along the regional flow direction in the Lower Greensand.

Site Name	Site No.	Distance (km)	Temp (°C)	DO (%)	Eh (mV)	SEC ($\mu\text{S cm}^{-1}$)	Cl (mg l^{-1})	Fe (mg l^{-1})	Depth (m)	Aquifer
Sturt Rd PS Raw	1	0.0					23.0	0.012		Hythe
Hindhead PS	2	3.6	11.1	9.85	641	109	14.3	0.024	82.0	Hythe
Tower PS	3	3.6	10.2			260	32.7	0.030		Hythe
Tower Road PS	4	3.6	10.8	9.10	387	265	31.2	0.016	83.0	Hythe
Tilford PS 3	5	8.7	10.9	4.92	465	157	15.1	0.026	76.2	Folkestone
Rushmoor PS 3	6	8.7	10.3			117	14.1	0.030		Hythe
Tilford PS, 2	7	8.7	11.7	0.42	116	274	9.6	0.215	176.3	Folkestone
Hankley Common	8	10.1	17.1	3.04	126	312	11.0	0.340	83.0	Hythe
Tilford Meads PS 3	9	11.5	11.7	0.05	75	305	11.2	0.445	60.0	Hythe
Tilford Meads PS 2	10	11.5	11.4	0.05	87	309	12.8	0.301	91.0	Hythe
Boxalls Lane 15	11	13.6	21.0	0.50	18	480	76.0	0.160		Folkestone
Bourne PS	14	13.8	12.0	<0.1	144	444	17.4	1.390	134.0	Hythe
Farnham Sands	15	14.5	18.4	3.53	312	290	16.0	0.010		Hythe
Tongham PS 1	16	16.1	20.6	0.05	-52	443	56.0	0.254	441.0	Folkestone confined
Boxalls Lane 16	18	17.1	21.7	0.40	3	440	73.0	0.140		Folkestone confined

The temperature and SEC both increase with distance along the direction of groundwater flow and there is a decrease in both Eh (Figure 6.2) and DO. The Hythe and Folkestone Beds show contrasting behaviour in terms of Ca: the Hythe Beds display a continuous increase whereas Ca is typically low in the Folkestone Beds of this area. The confined Folkestone Beds are distinct in having much higher Na, Cl and K concentrations. The lowest concentrations of Cl and SO_4 in the Hythe Beds are generally where the aquifer becomes confined. The higher concentrations in the unconfined part of the aquifer may, therefore, be due to anthropogenic inputs. A redox boundary is indicated by a decrease in DO and Eh where the aquifers become confined leading to a decrease in NO_3 and increase in Fe. Arsenic concentrations also increase in the more reducing groundwaters whereas Cr decreases reflecting their different mobilities in terms of redox potential. The minor and trace elements Sr, Li and F are often good indicators of residence time and these all show a general increase along the direction of flow (Figure 6.3).

6.4 Hydrochemistry of different lithological units

The samples were sub-divided into the Hythe and Folkestone Beds in order to ascertain if differences exist between these aquifer units. However, many boreholes abstract from more than one unit including the Sandgate and Bargate Beds. These have therefore been assigned to the dominant lithology (where known). This is particularly the case for many of the groundwater samples collected in this study, which represent a mixture of Hythe Beds and Sandgate and Bargate Beds. These have been grouped together as Hythe Beds. As discussed previously, the Hythe and Folkestone Beds have been classed as one aquifer unit where both units are confined beneath the Weald Clays. This group has been classed as a separate group (confined Folkestone Beds) due to the very different chemistry from that in the unconfined aquifers. A summary of selected differences is shown on Table 6.2 (Note that more data were available for the Hythe Beds).

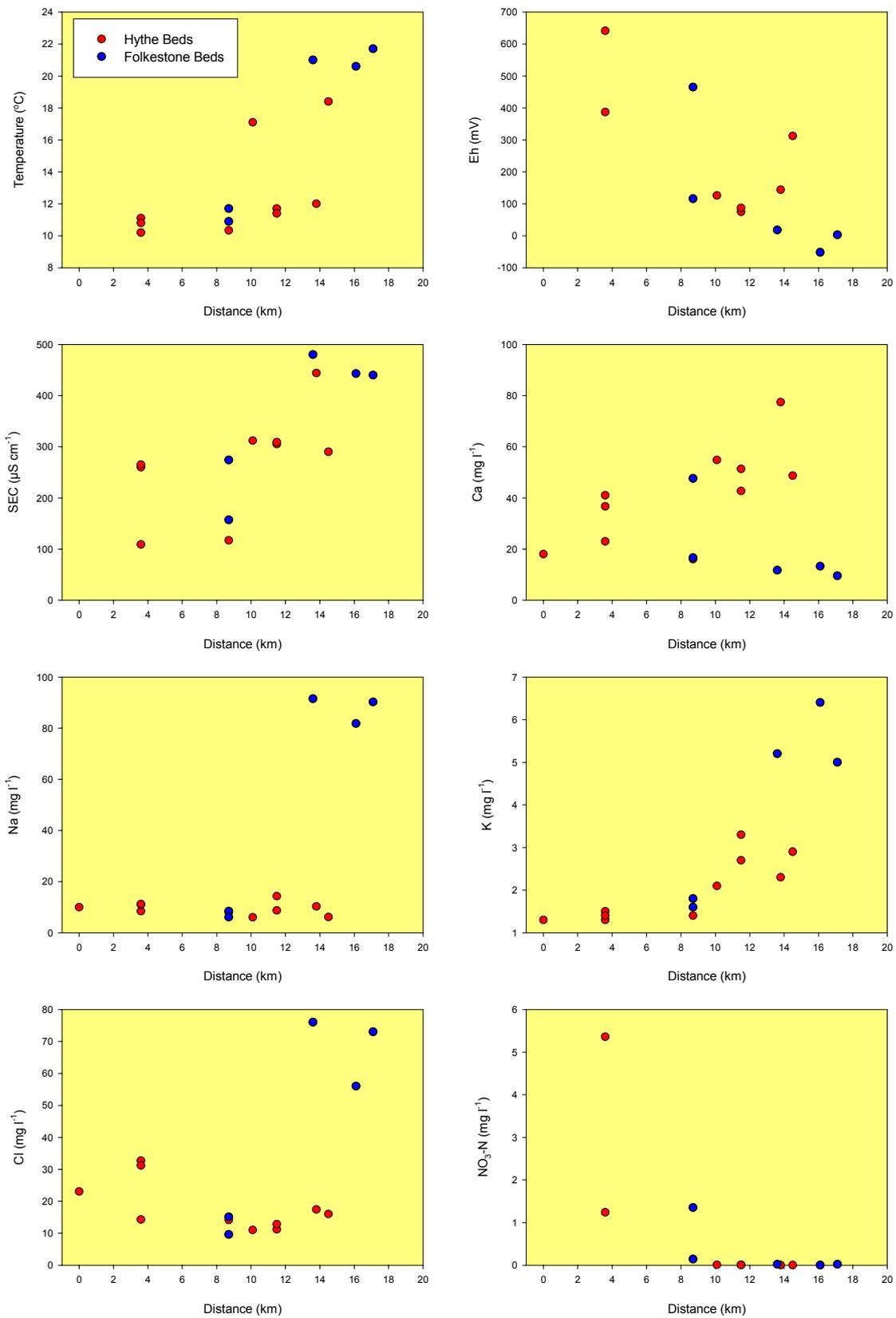


Figure 6.2 Hydrochemical changes in the regional flow direction.

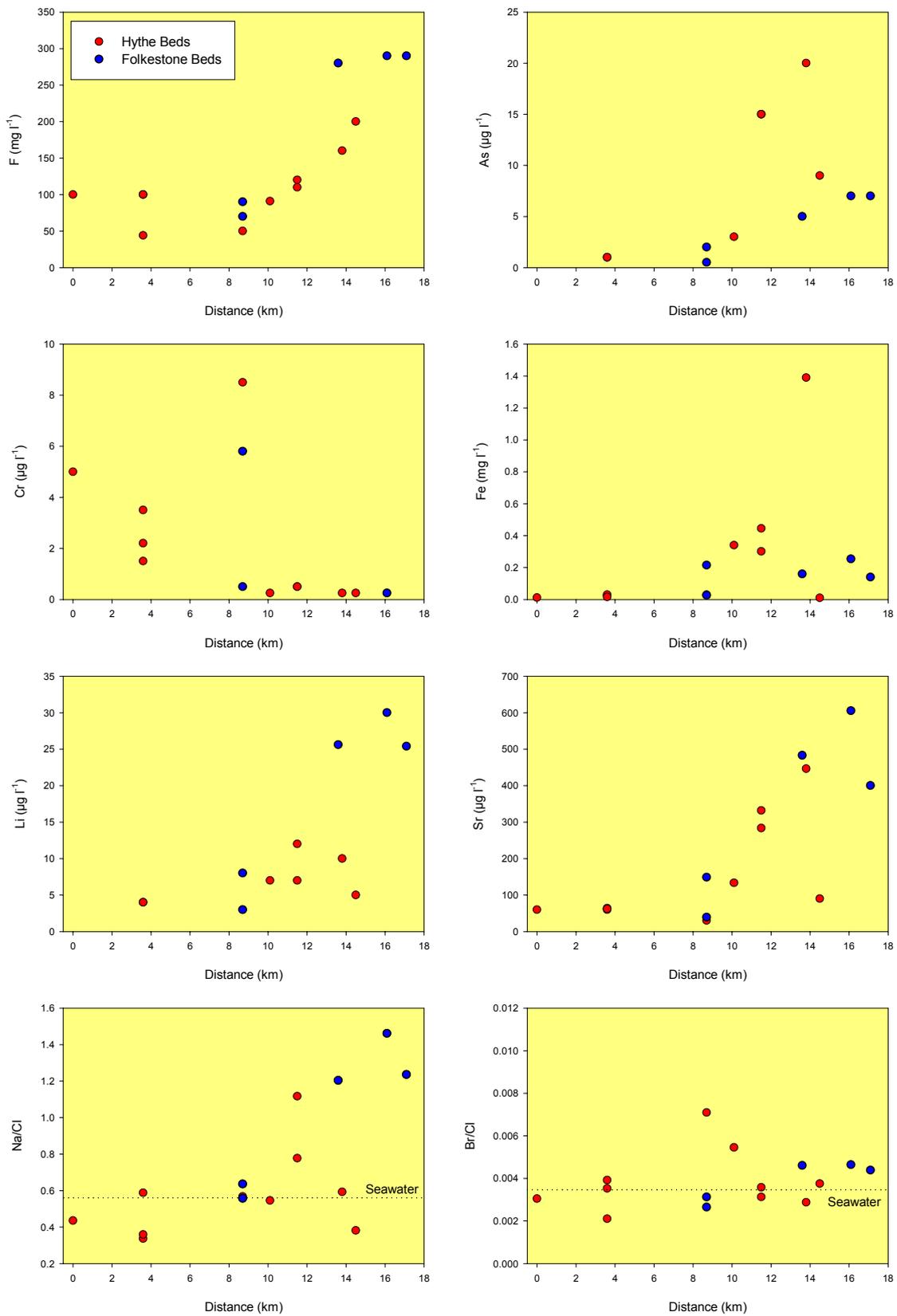


Figure 6.3 Hydrochemical changes in the regional flow direction.

Table 6.2 Median and range of concentrations for groundwaters in the different aquifer units of the Lower Greensand.

	units	Hythe			Folkestone			Confined Folkestone		
		minimum	median	maximum	minimum	median	maximum	minimum	median	maximum
T	°C	7.2	10.8	19.5	10.6	11.1	13.5	12.0	19.9	23.0
pH	field	5.80	7.20	8.10	6.02	6.60	7.90	7.10	7.74	8.00
Eh	mV	60	144	641	116	335	465	-52	10.5	48
DO	mg l ⁻¹	<0.1	0.2	9.85	0.42	1.8	13	<0.1	0.175	0.5
SEC	µS cm ⁻¹	109	315	827	157	463	632	267	459	562
δ ¹⁸ O	‰	-7.4	-7.1	-6.7	-7.1	-7.1	-7.1	-8.1	-7.9	-7.6
δ ¹³ C	‰	-16.0	-14.4	-11.2	-12.4	-12.4	-12.4	-18.1	-12.9	-12.4
Ca	mg l ⁻¹	9.3	52.4	182	16.6	79.7	109	9.5	12.7	30
Mg	mg l ⁻¹	1.4	2.76	7.17	1.6	4.1	5.19	2	2.71	6.4
Na	mg l ⁻¹	5	9.85	21	6.1	11.6	21.4	20	89.8	111
K	mg l ⁻¹	0.94	2.3	8.6	1.2	2.8	20	4.14	5.15	6.8
Cl	mg l ⁻¹	10.9	19	82	9.6	20	43.5	10	56	78.9
SO ₄	mg l ⁻¹	6.9	21.3	182	9.5	48.0	67	14.3	16.3	39.3
HCO ₃	mg l ⁻¹	6	148	339	33	147	202	131	143	248
NO ₃ as N	mg l ⁻¹	<0.003	0.196	15.8	0.141	4.25	16.3	<0.003	0.02	0.035
NO ₂ as N	mg l ⁻¹	<0.001	0.002	0.035	<0.001	0.004	0.1	<0.001	0.5	0.004
NH ₄ as N	mg l ⁻¹	<0.003	0.03	1.36	0.003	0.03	1.2	0.152	0.225	0.298
P	mg l ⁻¹	<0.02	0.04	0.31	<0.02	<0.02	<0.02	<0.02	0.025	0.035
DOC	mg l ⁻¹	0.74	2.4	10.1	1.1	4	6.9	1.5	2.95	7.6
F	mg l ⁻¹	0.03	0.13	0.27	0.05	0.15	0.24	0.07	0.27	0.37
Br	mg l ⁻¹	0.015	0.068	0.17	0.03	0.077	0.11	0.1	0.29	0.37
I	mg l ⁻¹	0.001	0.003	0.03	0.003	0.005	0.023	0.011	0.0305	0.041
Si	mg l ⁻¹	4.8	7.54	13.2	3.49	5.1	5.92	4.7	5.23	6.07
Al	µg l ⁻¹	0.5	1	246	0.5	40.3	80	0.5	0.5	0.5
As	µg l ⁻¹	0.4	2	20	0.5	6.5	14	2	5	7
B	µg l ⁻¹	10	10	36	10	20.5	44	77	146	150
Ba	µg l ⁻¹	3.53	105	380	10	16.5	189	15.11	43.7	55.3
Co	µg l ⁻¹	0.01	0.02	2.03	0.01	1.9	3.79	0.01	0.01	0.01
Cr	µg l ⁻¹	0.25	0.5	8.5	0.5	1.15	5.8	0.25	0.6	1
Fe	µg l ⁻¹	0.9	200	6250	2.5	65	420	140	185	254
Li	µg l ⁻¹	2	5	12	3	5	8	22.6	25.8	32
Mn	µg l ⁻¹	0.4	14	146	1.2	33	100	8	11	30
Ni	µg l ⁻¹	0.1	2.8	22	0.1	5	10.9	0.1	0.1	5
Pb	µg l ⁻¹	0.05	0.6	8.6	0.05	0.4	0.6	0.05	0.05	2
Rb	µg l ⁻¹	0.96	2.12	10.17	1.25	1.66	2.06	2.56	3.575	4.26
Sr	µg l ⁻¹	30	117	588	39.13	202	310	400	544	3110
Y	µg l ⁻¹	0.005	0.005	0.83	0.03	2.86	5.68	0.01	0.01	0.01
Zn	µg l ⁻¹	2	22.8	215	2	12	122	5	42	63.1

The groundwater chemistry of the Hythe and Folkestone Beds are in general terms relatively similar. The samples collected from the Hythe Beds are more reducing but this is due to the fact that many samples were collected from boreholes confined beneath the Folkestone Beds. The pH of groundwater in the Folkestone Beds was more acidic. This is unlikely to simply reflect the degree of reaction with carbonate minerals because HCO₃ concentrations are similar in both aquifers. It is possible that the recharge water to the Folkestone aquifer had higher dissolved CO₂ (related to land use) or that many of the Hythe Beds groundwaters have undergone ion-exchange of Ca for Na causing an increase in pH (this would also explain the lower Ca concentrations). Median concentrations of the trace metals Al, Cr, Co, Ni, Y and the rare earth elements are higher in the Folkestone Bed groundwaters mainly due to the lower pH.

The deeper confined groundwaters of the Folkestone Beds are very distinct in terms of overall chemistry. Although there is little difference in terms of total dissolved solids, these confined groundwaters have higher temperature and are much more reducing. This is reflected in lower Eh and DO and higher concentrations of Fe. Although bicarbonate concentrations are similar to the Hythe and unconfined Folkestone Bed groundwaters, Ca is very low and Na (and to a lesser degree Cl) are relatively high.

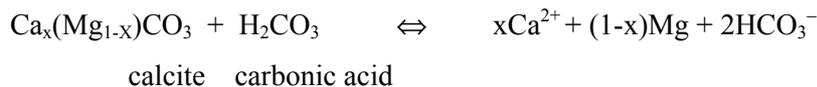
6.5 Controls on the geochemistry of the Lower Greensand aquifer

This section deals with the dominant geochemical processes which influence groundwater chemistry including:

- mineral dissolution/precipitation
- redox reactions
- ion exchange
- mixing with older formation water

6.5.1 Mineral dissolution reactions

Dissolution reactions involving mineral phases present in the aquifer generally form an important control on groundwater chemistry. Due to differing reaction rates (kinetics of reaction) the chemistry is controlled by only a few mineral phases. The kinetics of reaction for carbonate and evaporite minerals is rapid and these minerals may dominate groundwater chemistry even if present in small amounts. In the unsaturated zone, any such minerals, if originally present, have been dissolved away. The solutes Ca, Mg and HCO₃ increase in the groundwaters and show a wide range of saturation with respect to calcite and dolomite (Figure 6.4). The most acidic groundwaters represent areas where carbonate minerals are either not present or where they have been removed by dissolution in the shallow parts of the aquifer during recharge. The increase in these solutes and the trend towards saturation are most likely related to dissolution of small amounts of calcite (which may also contain Mg):



The shallowest groundwaters show a range in $\delta^{13}\text{C}$ values from -16 to -11 ‰ and the deeper ones are around -12 ‰. The precise degree of reaction with carbonates is difficult to determine for individual waters because both marine and freshwater carbonates (with different $\delta^{13}\text{C}$ signatures) are present within the aquifer (Evans et al., 1979).

Incongruent dissolution of the dioctahedral mica, glauconite (a complex hydrous potassium iron alumino-silicate mineral), may form a source in the groundwater for dissolved K, Fe, Mg and, in acidic waters, Al.

Evaporite minerals such as gypsum or halite have not been found in the aquifer and the low concentrations of SO₄ and Cl are consistent with this. Fluoride concentrations are generally low indicating a low abundance in the aquifer, increasing slightly with age of groundwater. This is most likely derived from the slow release of F from apatite which has slow dissolution kinetics.

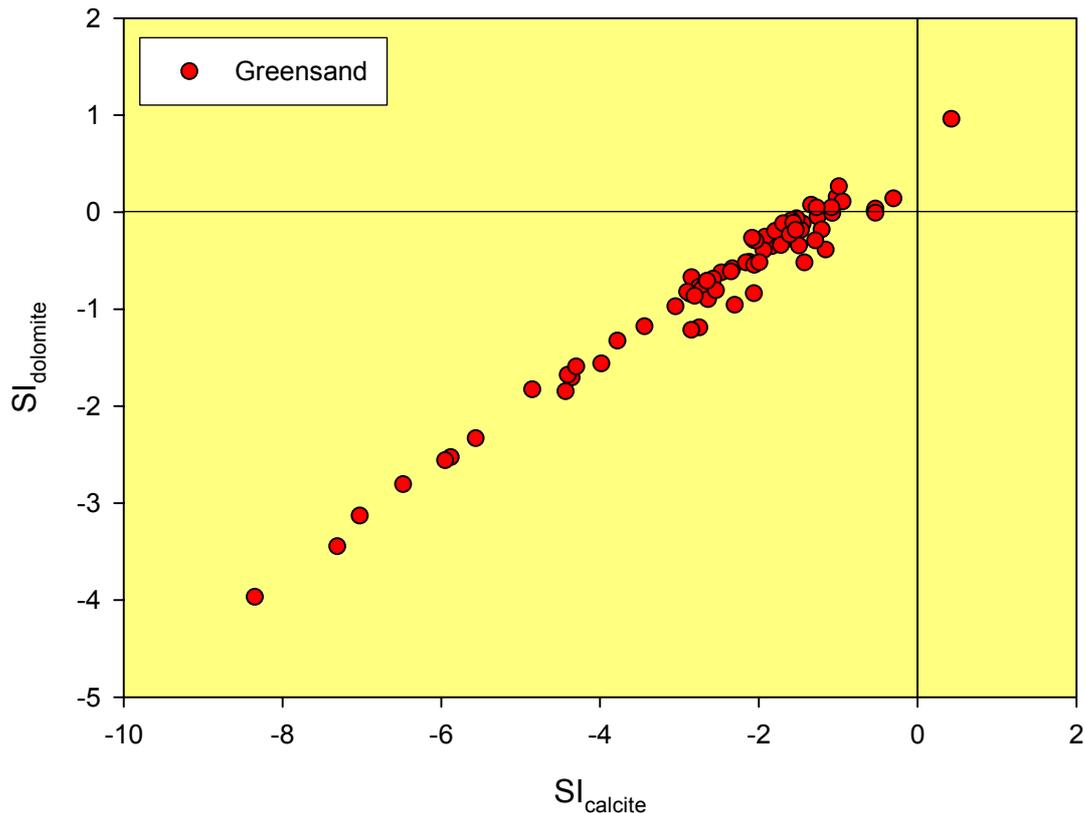


Figure 6.4 Variations in saturation index for calcite and dolomite in groundwaters from the Lower Greensand aquifer.

The Folkestone Beds (unconfined and confined) vary from undersaturated to saturated with respect to chalcedony (SiO_2) but the Hythe Beds vary from saturation to slight oversaturation (Figure 6.5). Although the aquifer sediments are dominated by quartz, the principal source of the Si is likely to be derived from silicate minerals such as feldspar, mica or ferromagnesian silicate minerals due to the high stability of quartz. In the case of the Hythe Beds, it is possible that dissolution of the chert beds present in parts of the aquifer may be enhancing dissolved Si concentrations. Potassium concentrations are highest in the confined groundwaters and most likely derived from clay or mica (including glauconite) minerals. The dramatic increase close to the unconfined/confined boundary is probably a consequence of residence time because the flow in the confined aquifer is much slower.

6.5.2 Redox reactions

Redox boundaries (Box 6.1) are relatively common in aquifers, particularly where they become confined, or at the boundaries of flow systems. The redox potential (Eh) and dissolved oxygen (DO) concentration provide the primary indicators of the redox status of natural groundwaters. These parameters are unstable and extremely sensitive to changes caused by contact with the atmosphere and, therefore, should be monitored in a flow-through cell where the water is pumped directly from the borehole. The Hythe and Folkestone Beds both show a wide range in terms of DO and Eh. The unconfined parts of the aquifer are oxidising and the confined parts are reducing: the loss of oxygen leads to a rapid decrease in Eh. In the Slough boreholes, the presence of H_2S gas was noted whilst sampling. The confined parts of the aquifer, therefore contain elevated concentrations of Fe. In contrast, Mn is often low most likely due to the low Mn concentrations in the aquifer. The oxidation of pyrite which is abundant locally, sometimes as a cement, can lead to increased SO_4 and acidic

conditions. In addition, sulphide minerals often contain high concentrations of other metals such as As, Ni and Cr.

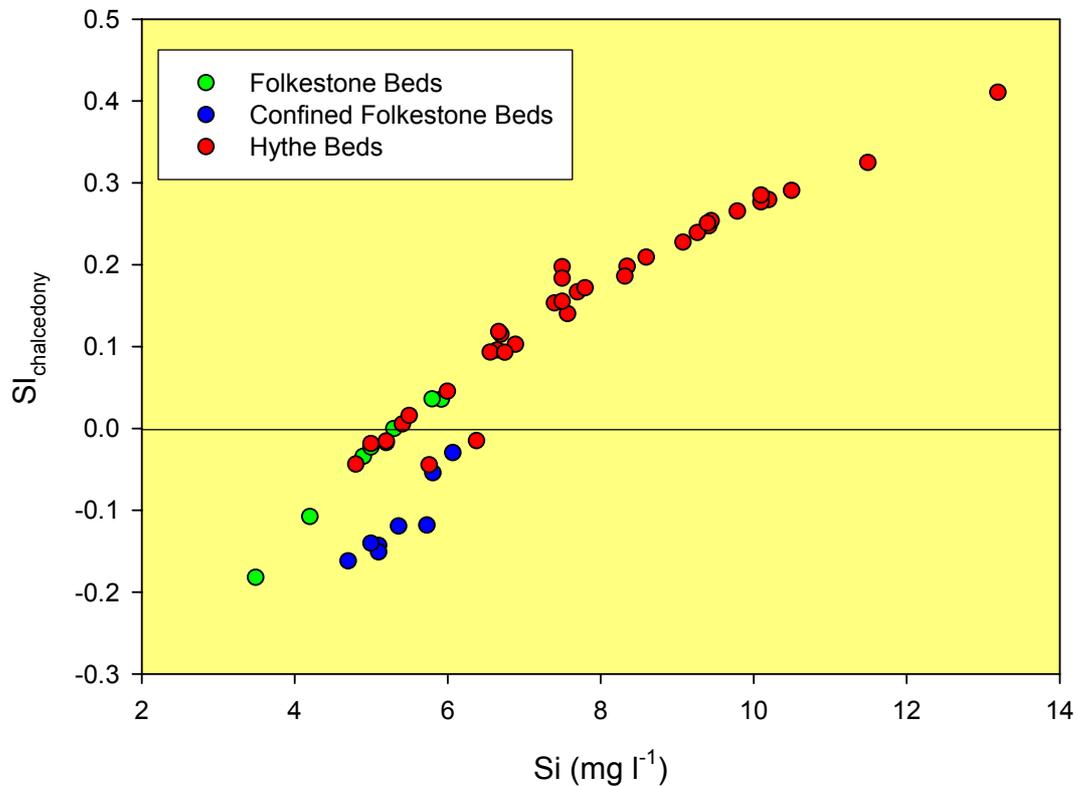
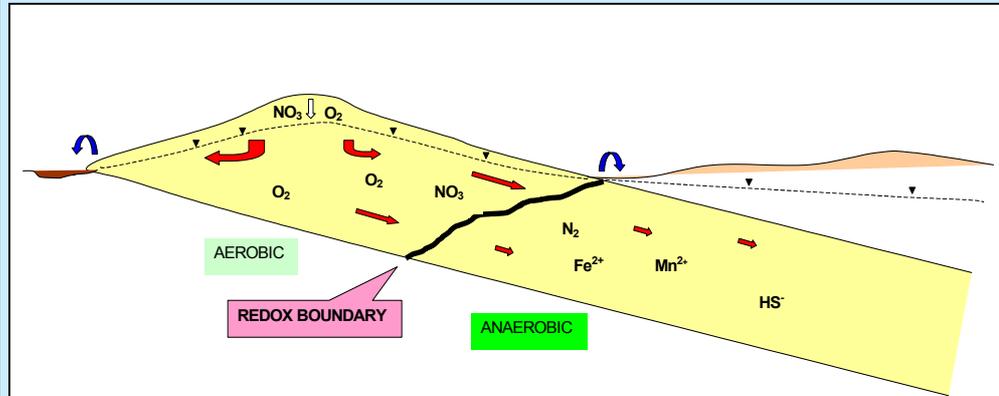


Figure 6.5 Silicon concentrations plotted against the saturation index for chalcedony for the Lower Greensand groundwaters.

Many trace metals are controlled by redox conditions. Chromium (Cr), for example is more mobile under oxidising conditions and this can be seen as a decrease along the direction of flow in Figure 6.3. The mobility of As is often greater under reducing conditions, commonly showing contrasting behaviour to Cr. The highest As concentrations were typically found where oxygen concentrations were low (Figure 6.6), however, concentrations were not particularly high in the deeper confined Folkestone groundwaters. This may relate to availability of As but there is insufficient solid phase data to confirm this.

Nitrate is only stable in the presence of oxygen but undergoes denitrification when oxygen is lost by reaction with reduced species. Nitrogen is either lost from the system as a gaseous phase or may be present as dissolved NO₂ (an intermediate product in the denitrification of nitrate). NH₄ is stable in reducing groundwaters most likely desorbed from clay mineral surfaces in the aquifer.

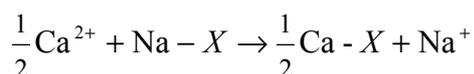
BOX 6.1 REDOX BOUNDARY



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

6.5.3 Ion-exchange reactions

The freshening of aquifers which originally contained seawater can lead to significant chemical changes in groundwater as it flows through and displaces the original 'connate' or a modified formation water. Any clays present will initially have Na as the dominant sorbed cation and freshening by a typical Ca-HCO_3 type recharge groundwater will change the composition of this groundwater to attain equilibrium with the clays. In this case Ca in the groundwater will exchange with Na on the clays leading to groundwaters of Na-HCO_3 type:



The clearest example of this type of ion exchange in the Lower Greensand aquifer is displayed by the deeper confined Folkestone groundwaters (Figures 5.1 and 6.3): there is a large increase in the relative proportions of Na to Ca (Figure 6.2). Such a trend cannot be due simply to mixing with connate or formation water as Cl is affected to a much lesser degree: Na/Cl ratios increase in the confined waters up to 2.7 compared to seawater which has a weight ratio of 0.56 (Figure 6.3). It is possible that minor ion-exchange of dissolved Ca for adsorbed Mg is occurring, but Mg inputs are likely to be dominated by dissolution of glauconite or from calcite or dolomite if present.

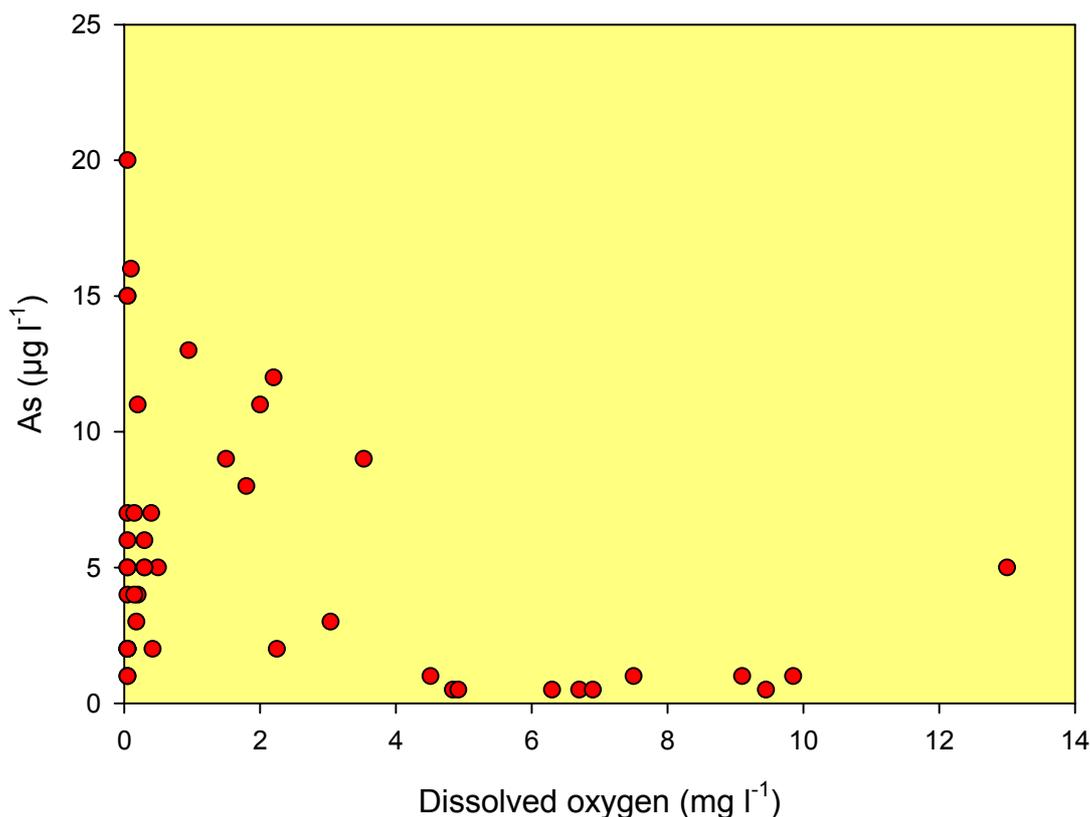


Figure 6.6 Arsenic concentrations plotted against dissolved oxygen for the Lower Greensand groundwaters.

6.5.4 *Mixing with formation water*

The concentrations of Cl are generally low in the Lower Greensand groundwaters (Tables 5.1 and 6.1). The highest concentrations are found in groundwaters within the confined Folkestone Beds, but these are still relatively low (up to 80 mg l⁻¹). The deeper groundwaters have Br/Cl ratios similar to seawater, consistent with the Cl concentrations being mainly derived by mixing with a formation water. The low Cl concentrations show that the aquifer has been well flushed in the past, more so than in many other UK aquifer systems. Chloride concentrations are slightly higher in many of the unconfined groundwaters compared to those a short distance into the confined parts of the aquifer (Figure 6.2), but this is less evident for Na: this increase is, therefore, probably of anthropogenic origin and is also evident for SO₄, P and B.

6.5.5 *Trace elements*

Trace-element concentrations are often low in the Lower Greensand groundwaters reflecting the lack of reactive minerals. Dissolved Sr concentrations are greater in the confined Folkestone Beds, an increase related to residence time and availability of carbonate and to a lesser degree feldspar. Barium concentrations are limited in solution by SO₄, due to barite (BaSO₄) saturation. The low concentration of sulphate in many groundwaters has allowed Ba to reach relatively high concentrations (the median concentration is 105 µg l⁻¹ compared to the EU Guide Level of 100 µg l⁻¹). Boron concentrations are relatively low but increase in the deeper confined groundwaters as a result of increased salinity. The onset of reducing conditions has allowed Fe to be stable in solution and this probably also impacts on trace-metal species adsorbed to Fe oxyhydroxides. However, the low

abundance of most metals in the sandstones (Morgan-Jones, 1985) means that concentrations are generally not high enough to present any water quality problems, apart from high Fe and locally enhanced As and Ni. The highest Ni concentrations are generally present in moderately oxidising groundwater and may be related to release during pyrite oxidation, but more data detailed studies are needed to ascertain this. Slightly elevated Pb was found in a slightly acidic spring ($8.6 \mu\text{g l}^{-1}$) and in one circum-neutral pH borehole sample ($8.2 \mu\text{g l}^{-1}$), but it is unclear if the latter is natural or due to local contamination. The increase in Li along general flow directions (Figure 6.3) is probably caused by ion exchange reactions on clays. In the more acidic groundwaters high Al concentrations can occur, but this would appear to be only a local problem with only one sample greater than $100 \mu\text{g l}^{-1}$.

6.6 Temporal variations

Historical records provide critical data for determining baseline concentrations in the aquifer since they provide a direct determination of concentrations in the past. Ideally these would have chemical analyses for a wide range of parameters of interest and extend back to a time when the aquifer was not impacted by anthropogenic inputs. Unfortunately there are few long-term historical records available for the Lower Greensand, so it has not been possible to describe temporal changes. Environment Agency data from 1989 onwards have been studied in order to determine changes which have taken place over approximately the last decade.

One of the most common impacts on groundwater quality in UK aquifers has been an increase in nitrate, in part due to agricultural practices including fertiliser application since the 1940s. From the limited data available there are variable trends for the sources with respect to nitrate (Figure 6.7). Some groundwaters show a gradual increase in nitrate concentration whilst others show a decreasing trend.

Comparisons can be made with other potential pollutants and naturally-derived species to assess if any trend is likely to be of anthropogenic origin. Nitrate concentrations at Loseley Park and Arunshhead Farm have been rising gradually over time. However, this rise is not matched by similar increases in chloride concentration and conductivity. In contrast nitrate is seen to decrease along with SEC and Cl (Figure 6.7) in the Brewer Street borehole indicating a change in chemistry of the groundwater source. There was a large increase between the first and subsequent points at High Button (Figure 6.7) and a gradual decrease since 2000, during which time chloride ion concentration and conductivity remained relatively stable. Several hydrochemical parameters are shown for one borehole in Figure 6.8. The similarity between NO_3 , K and Cl would indicate an agricultural source for this generally increasing trend.

The available historical data provide information on trends, indications of possible anthropogenic sources and changes in flow regime that may affect water quality. However, the limited availability of historical data makes an assessment of baseline concentrations difficult.

6.7 Depth variations

There are few data available on depth samples from individual boreholes in which to assess depth variations in the aquifer units. Information regarding screen and casing details, and the exact inflow horizons in the boreholes were also not available. However, selected data have been plotted against 'depth of borehole' in an attempt to see if major differences exist between the shallower and deeper groundwaters (Figure 6.9). Borehole depths, where known, vary from 5 m to 468 m. There is a wide scatter in terms of SEC in the Hythe and Folkestone Beds with no obvious change with depth. The deeper groundwaters in the confined Folkestone Beds overlap with the shallower groundwaters indicating that even at these depths, the aquifer has been well flushed. There is a wide scatter in the pH of the shallower boreholes, but a general decrease in acidity is apparent, with most deeper (>100 m) groundwaters having neutral to slightly alkaline pH (Figure 6.9; note that spring samples are

plotted at zero depth). Calcium is very variable in the Hythe Beds and decreases with depth in contrast to Na which increases due to ion exchange in the deeper groundwaters. Potassium is slightly higher in the deeper groundwaters reflecting the small increase in salinity due to mixing with a remnant of formation water (indicated by the higher Cl). Enhanced Cl, K, P and NO₃ are seen in some groundwaters indicating local agriculturally-derived inputs. Sulphate is also very variable but the highest concentrations are present in the shallower groundwaters, even those in which pollution indicators are absent. This could be due to enrichment in the shallower groundwaters caused by oxidation of pyrite (which is known to be present in the Lower Greensand) or loss of sulphate from deeper groundwater due to sulphate reduction. It is likely that both processes contribute to the profiles shown in Figure 6.9. The presence of H₂S gas was noted whilst sampling the deeper boreholes in Slough.

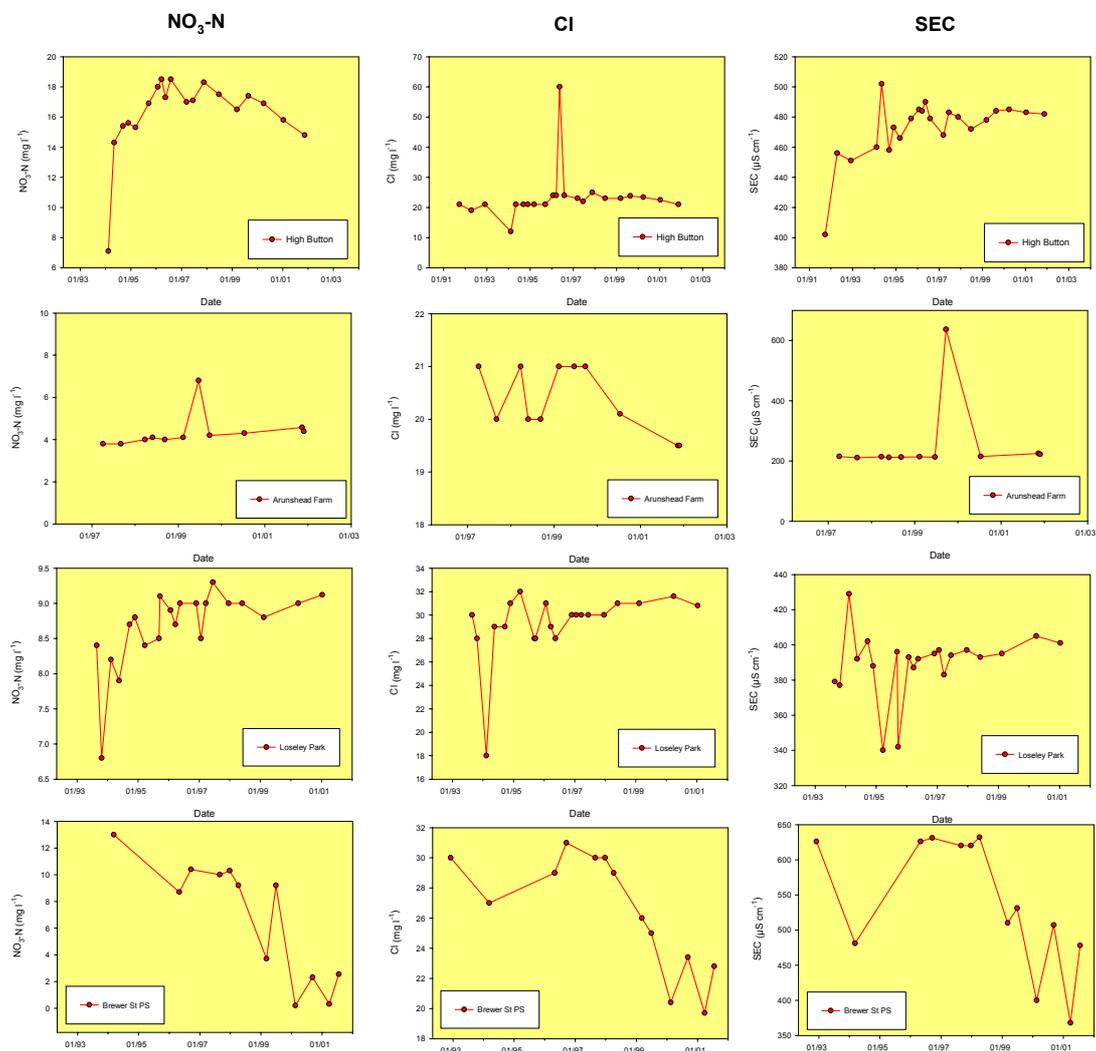


Figure 6.7 Temporal variations in selected groundwaters of the Lower Greensand. The Brewer St borehole abstracts groundwater from the Folkestone Formation and the others from the Hythe Formation.

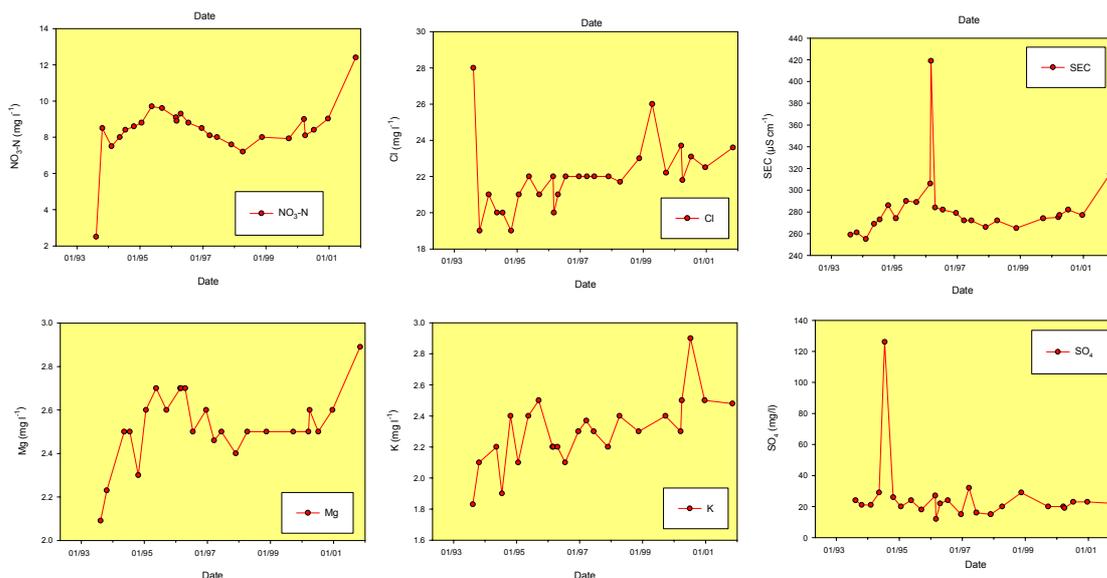


Figure 6.8 Temporal variations in the hydrochemistry of selected solutes from a borehole in the Hythe Formation.

The deeper confined groundwaters are reducing and this is reflected in high concentrations of Fe ($0.14\text{--}0.23\text{ mg l}^{-1}$) at depth. Manganese is not particularly high (0.01 mg l^{-1}) in these groundwaters probably as a result of low concentrations in the aquifer at depth. Both Eh and pH are also variable in the Hythe Beds varying from moderately reducing to oxidising. Very high Fe concentrations (up to 6.2 mg l^{-1}) and higher Mn are found at depths between 80 and 100 m (Figure 6.9). These groundwaters are from the same geographic area and all are moderately reducing (Eh from +77 to +200 mV). Variations in Fe concentrations in groundwater from 8 boreholes located within a 1 km radius had Fe varying from 0.02 to 6.3 mg l^{-1} . The major element hydrochemistry of these boreholes varies within a relatively narrow range (e.g. Cl varies from 14 to 24 mg l^{-1}) as does Eh. It therefore seems likely that there may be significant depth variations in the source and availability of Fe and Mn. It is possible that the high iron may be derived from Fe-rich horizons in the aquifer: abundant ironstone pebbles were common on the ground surface in this area.

6.8 Age of the groundwater

Previous age studies have been completed on the age of groundwaters in the Lower Greensand. Radiocarbon values range from about 85 pmc (per cent modern carbon) to <1 pmc between the outcrop and confined aquifer with the lowest values being found in the axial region of the western London Basin (Darling et al., 1997). Evans et al. (1979) calculated ages, based on ^{14}C and tritium, from an area further east of the study area to the north of Maidstone. Their results indicated that the age increased from modern at outcrop to around 21,300 years at the centre of the basin. A groundwater from Slough (Industrial Estate) gave a calculated age of 29,000 years (Evans et al., 1979). The older groundwaters were also depleted in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ consistent with recharge during a colder climatic period: the climate during the Pleistocene period was colder, resulting in lighter (more negative) isotopic signatures of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (Darling et al., 1997). The stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were measured on selected samples during this study and are shown on Figure 6.10a. There is a considerable range in isotope ratios with the deeper confined groundwaters having a much lighter isotopic signature (Figure 6.10b). The deeper groundwaters with lighter isotope ratios represent palaeowaters which were recharged during the Pleistocene (>10,000 years BP) when the climate was

colder. Most other groundwaters are consistent with modern or Holocene (<10,000 years BP) recharge.

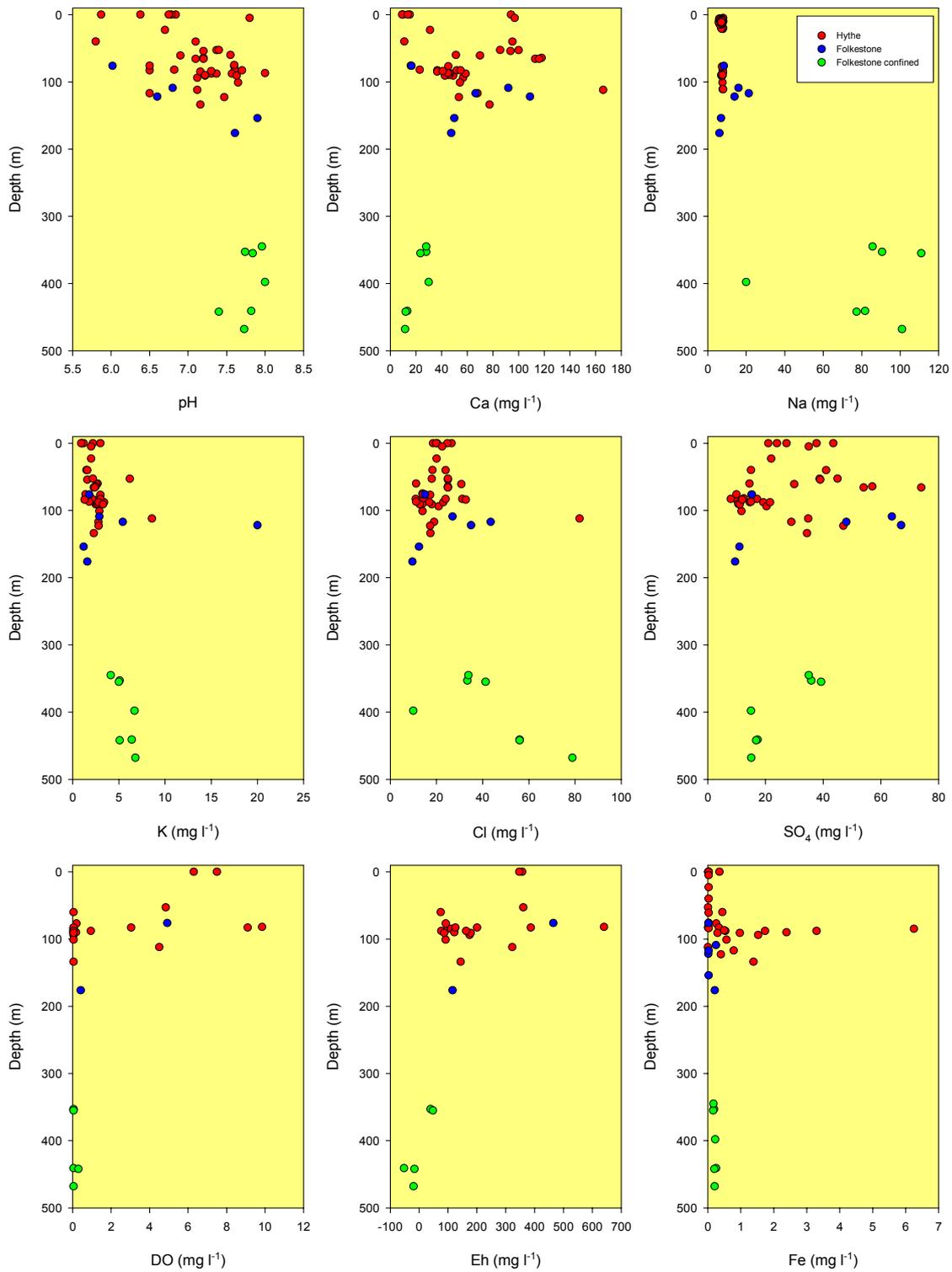


Figure 6.9 Hydrochemical variations of selected parameters plotted against depth of borehole.

6.9 Regional variations

The spatial variations in chemistry across the area are shown on Figures 6.11-6.15 for the study area. These reflect much of what was discussed in previous sections but help to identify the degree of spatial variation at both regional and local scales. In the east of the area there is a contrast in the pH between the Folkestone and Hythe beds with the most acidic groundwaters being found in the unconfined Folkestone Beds (Figure 6.11). In the west the most acidic groundwaters in the Hythe Beds appear to be present in the recharge area; there is limited data from the west of the area for the Folkestone Beds. The confined groundwaters in the Folkestone Beds all have circumneutral pH. Dissolved oxygen is high in most of the unconfined aquifer but this falls rapidly once confining conditions are achieved.

The major elements Ca, Na, Cl and SO₄ have been plotted on Figures 6.12-6.13. The contrasting behaviour of Ca and Na between the unconfined and confined parts of the aquifer is clearly seen where Na increases in the confined aquifer due to ion-exchange of Na for Ca. The spatial variations of both elements are considerable in the Folkestone and Hythe Bed groundwaters related both to depth and residence time in the aquifer. The low Ca in many of the Hythe groundwaters is related to the presence of carbonate minerals and correlates well with low pH. The map of Cl is very different to that of Na with regional Cl being related to atmospheric inputs and mixing with (a small) remnant of formation water especially in the confined part of the aquifer. Part of the spatial variation in younger groundwaters is also related to anthropogenic inputs, but such additions are well within the regional baseline. This highlights the need to assess baseline concentrations at a local scale if the original baseline is to be deduced. Many of the low-pH Folkestone Bed groundwaters in the east of the study area (Figure 6.11) also have relatively high sulphate and further work to assess the origin of this sulphate (pyrite oxidation or anthropogenic) would be useful.

Maps for nitrate-N and selected trace elements are shown on Figure 6.14a. Nitrate concentrations are variable in both the Hythe and Folkestone Beds and show no obvious regional control related to inputs. The main control on the stability of nitrate is the presence of oxygen: nitrate is stable in the presence of dissolved oxygen but undergoes denitrification in the presence of reducing agents once oxygen is consumed. This is clearly seen in the Hythe Beds in the west and north of the region where concentrations decrease once the aquifer becomes confined beneath the Sandgate and Folkestone Formations. The concentrations of Fe (Figure 6.14b) are also redox controlled. Iron rapidly forms insoluble oxyhydroxide minerals where oxygen is present, limiting its concentration in oxygenated waters (unless pH is low). The regional variations are variable and reflect the redox conditions. However this is also controlled by the availability of Fe. Dissolved Fe can vary over short distances, as discussed in section 6.7. The trace element As (Figure 6.15a) is also redox sensitive: mobility is increased under reducing conditions (as As³⁺) while the oxidised species (As⁵⁺) is more easily sorbed onto ferric hydroxide in the oxidised part of the aquifer. The regional distribution is a function of redox conditions (see also Figure 6.6) and also availability as indicated by the relatively low concentrations in the deep confined groundwaters around Slough.

Strontium is often a good indicator of residence time because concentrations are not generally limited by mineral solubility. Where studies have been undertaken using dating tools, the concentrations often show a good correlation with Sr concentration. The regional variations (Figure 6.15b) show that concentrations are lowest in recharge areas and highest in the deep confined groundwaters. This largely reflects the availability of carbonate mineral phases in the aquifer because the dominant source of Sr in the aquifer is derived from calcite and dolomite with a lesser amount provided by feldspars.

These regional plots provide an overview of the spatial variations in hydrochemistry and help to indicate the degree of heterogeneity of chemical parameters at the regional scale and also to a lesser degree at local levels. These can be interpreted with reference to the previous sections which have highlighted the main geochemical controls on the hydrochemistry of the groundwaters on the Lower Greensand aquifers.

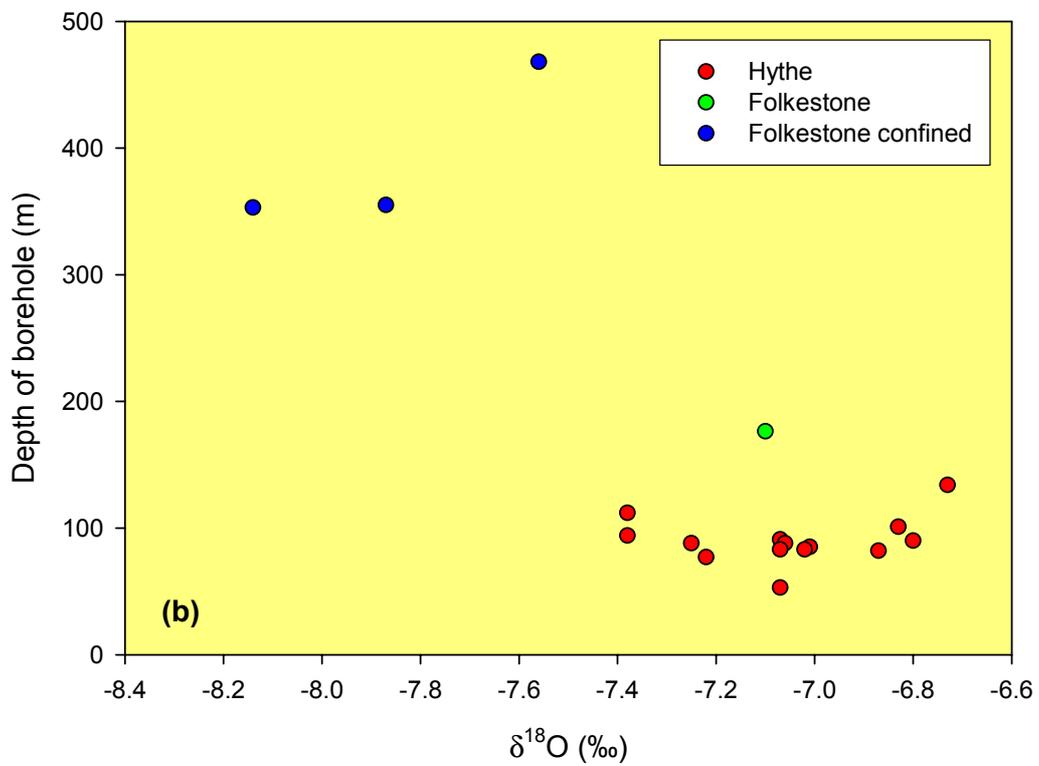
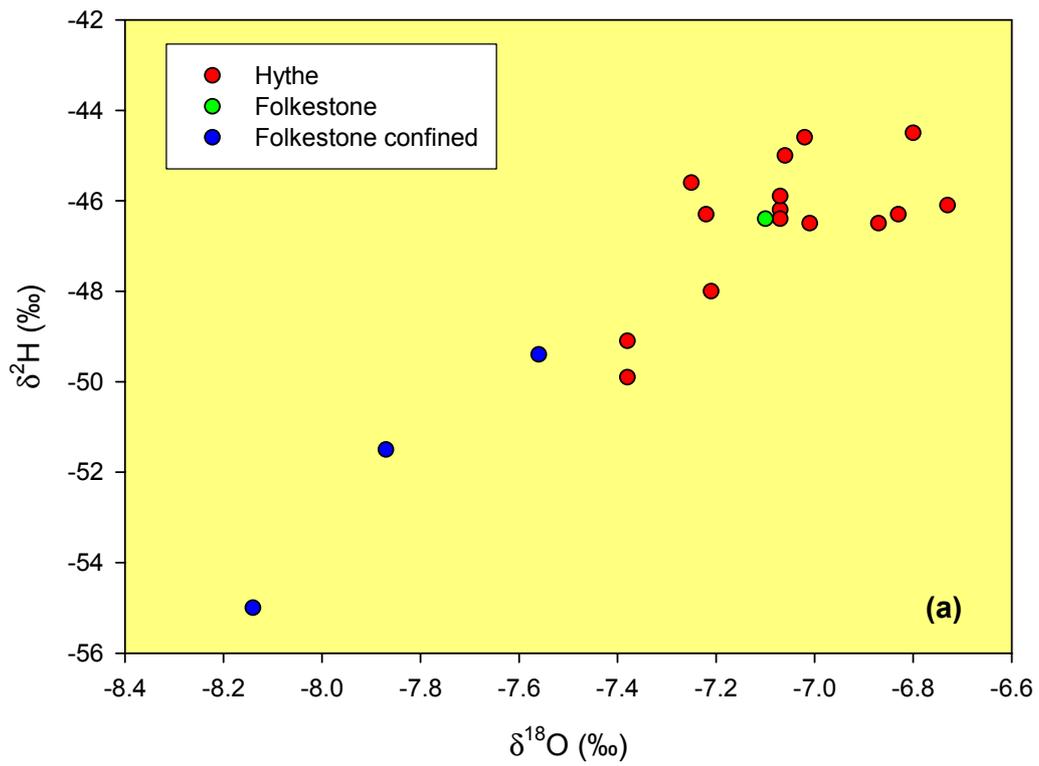


Figure 6.10 Plot of (a) stable isotopes ($\delta^2\text{H}$ vs. $\delta^{18}\text{O}$) for Lower Greensand groundwaters analysed as part of this study and (b) $\delta^{18}\text{O}$ variations with depth.

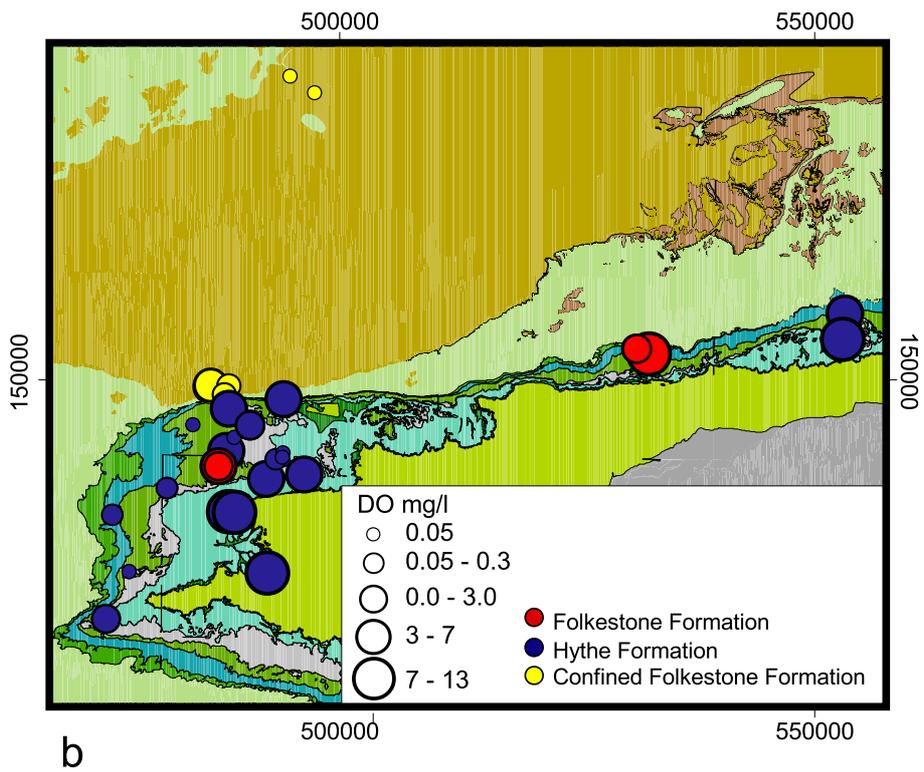
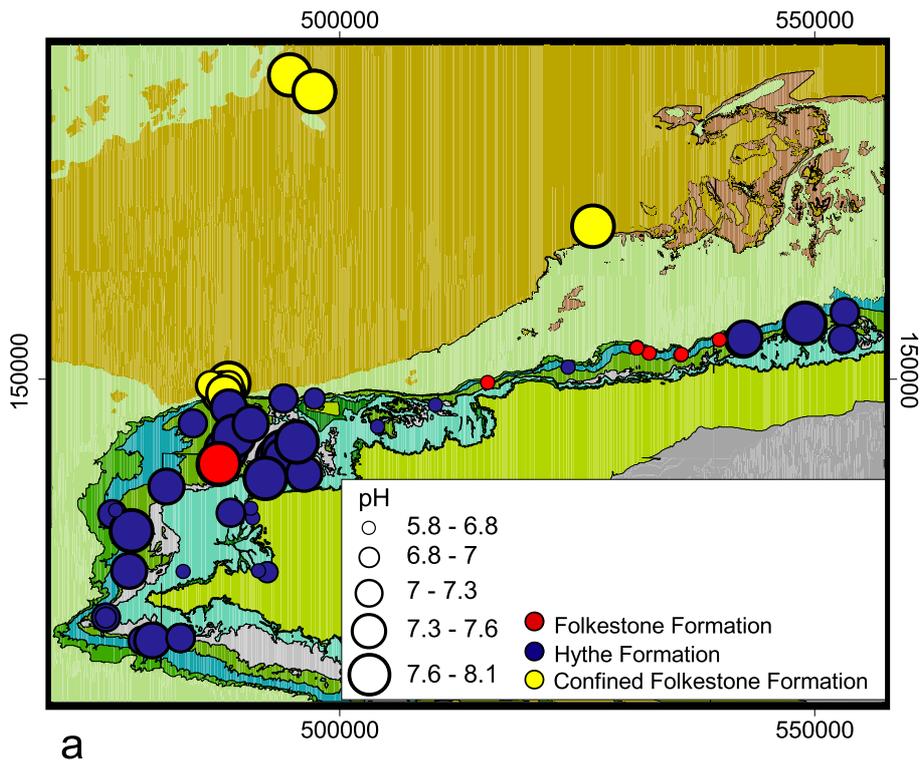


Figure 6.11 Regional variations in pH and dissolved oxygen (DO) in the Lower Greensand groundwaters.

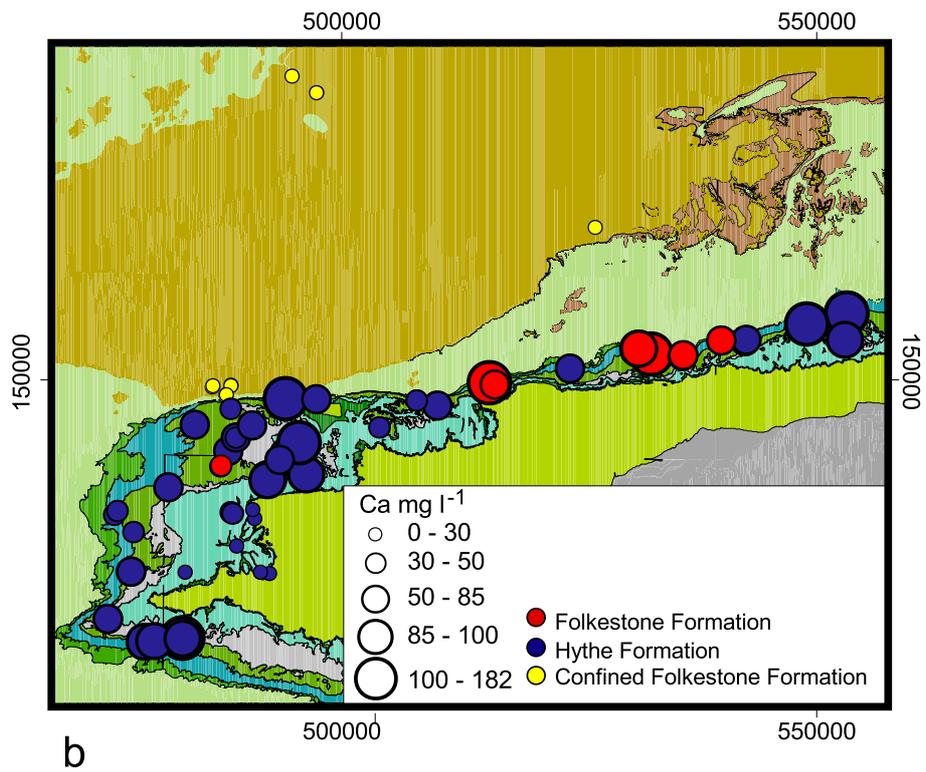
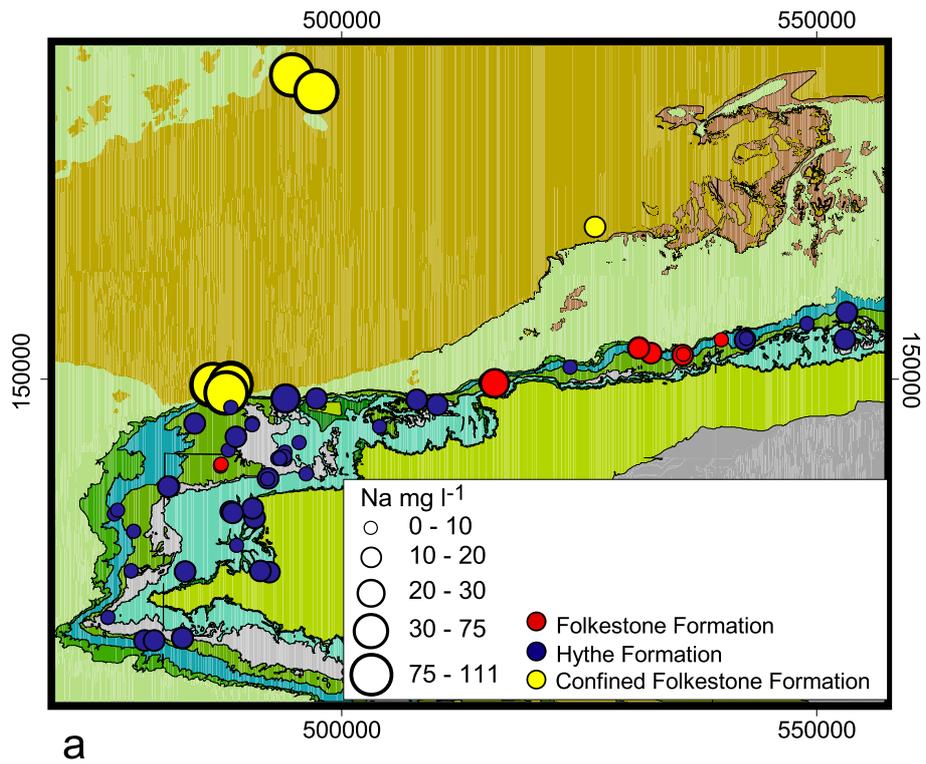


Figure 6.12 Regional variations in Na and Ca concentration in the Lower Greensand groundwaters.

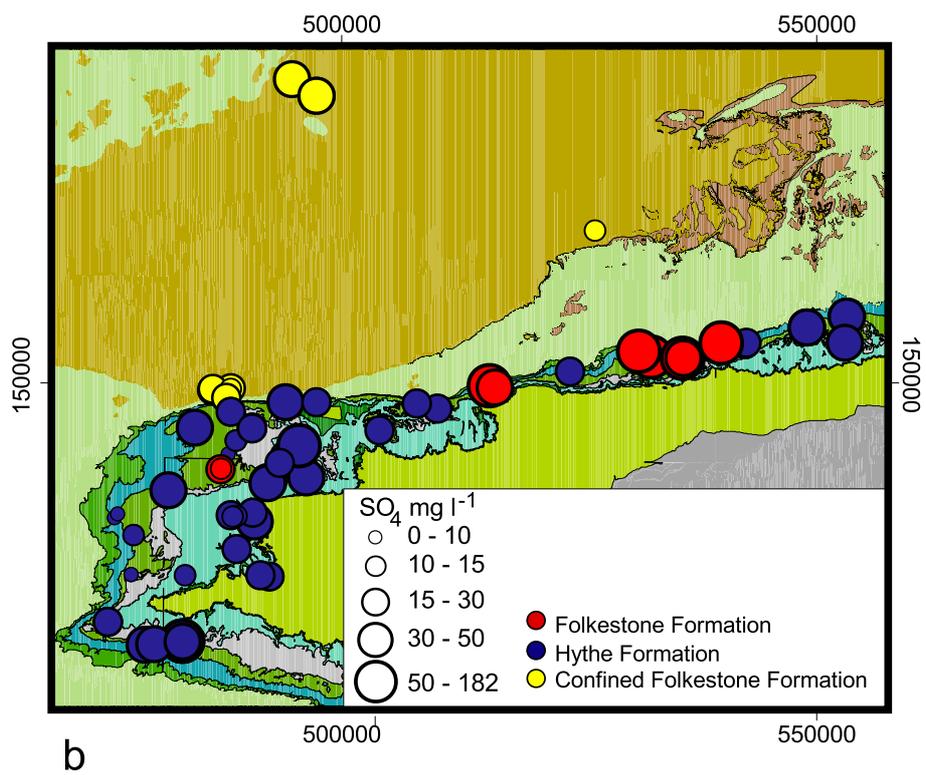
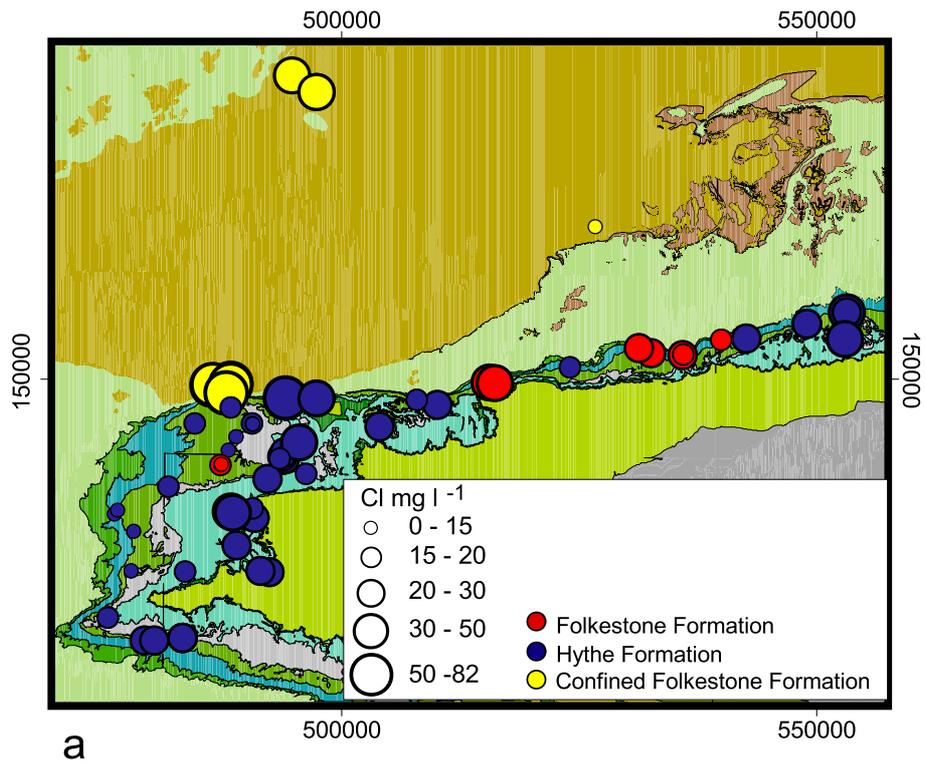


Figure 6.13 Regional variations in Cl and SO₄ concentration in the Lower Greensand groundwaters.

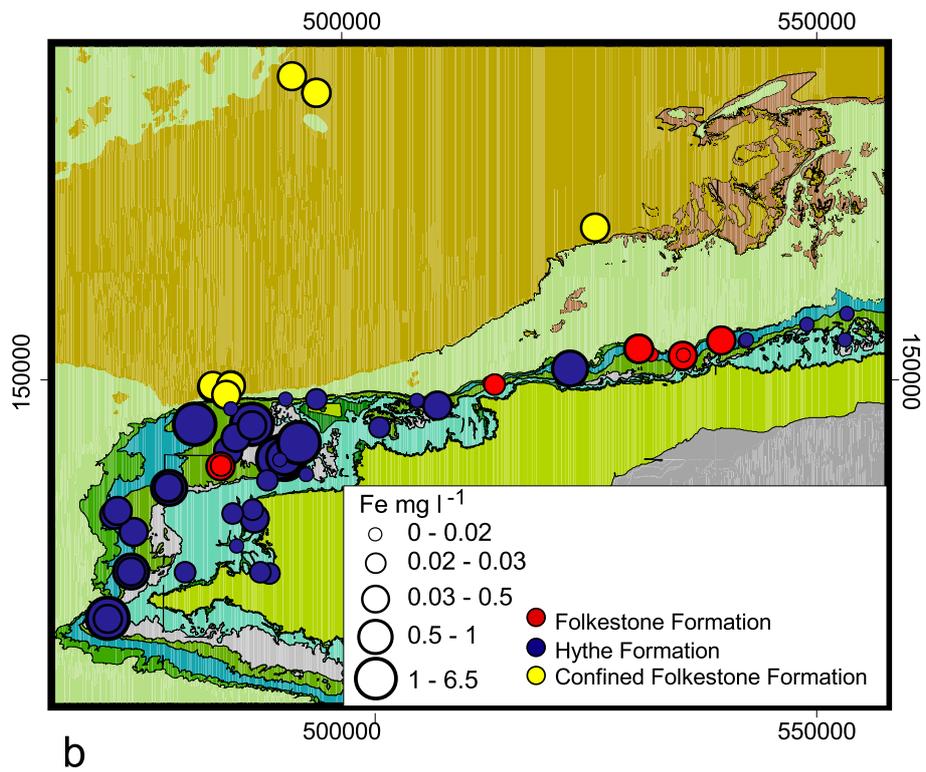
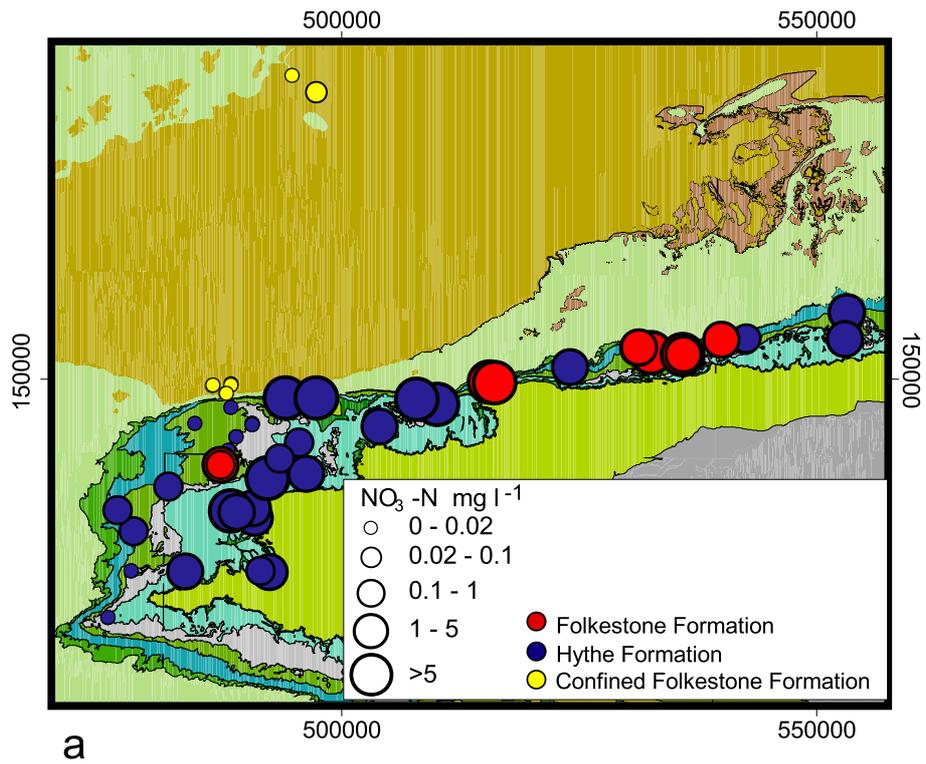


Figure 6.14 Regional variations in NO₃ and Fe concentration in the Lower Greensand groundwaters.

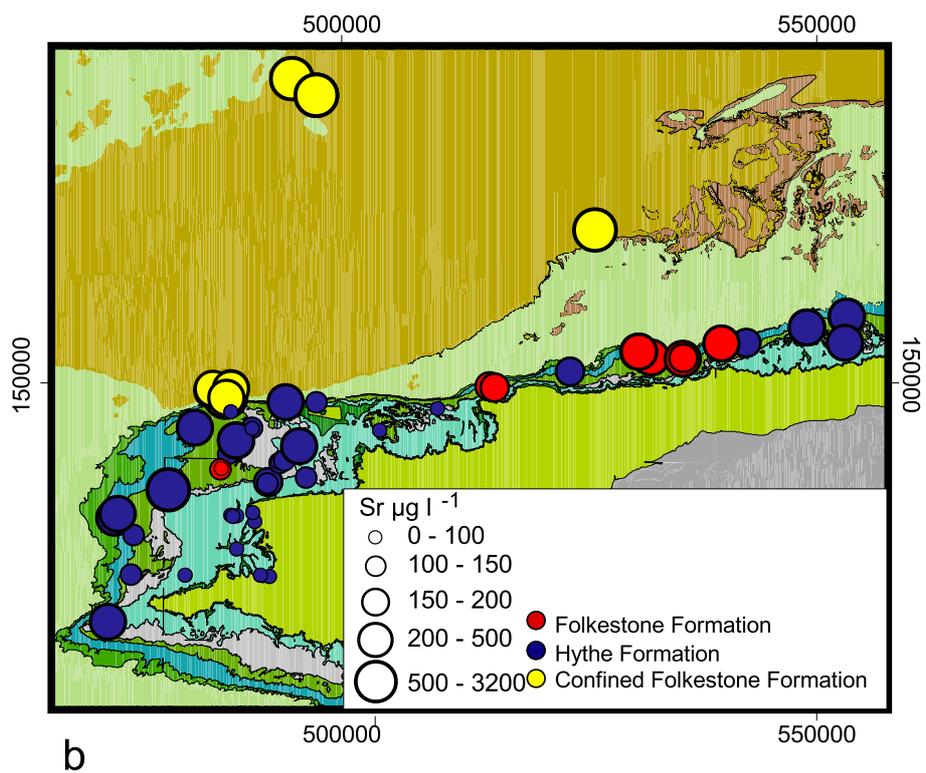
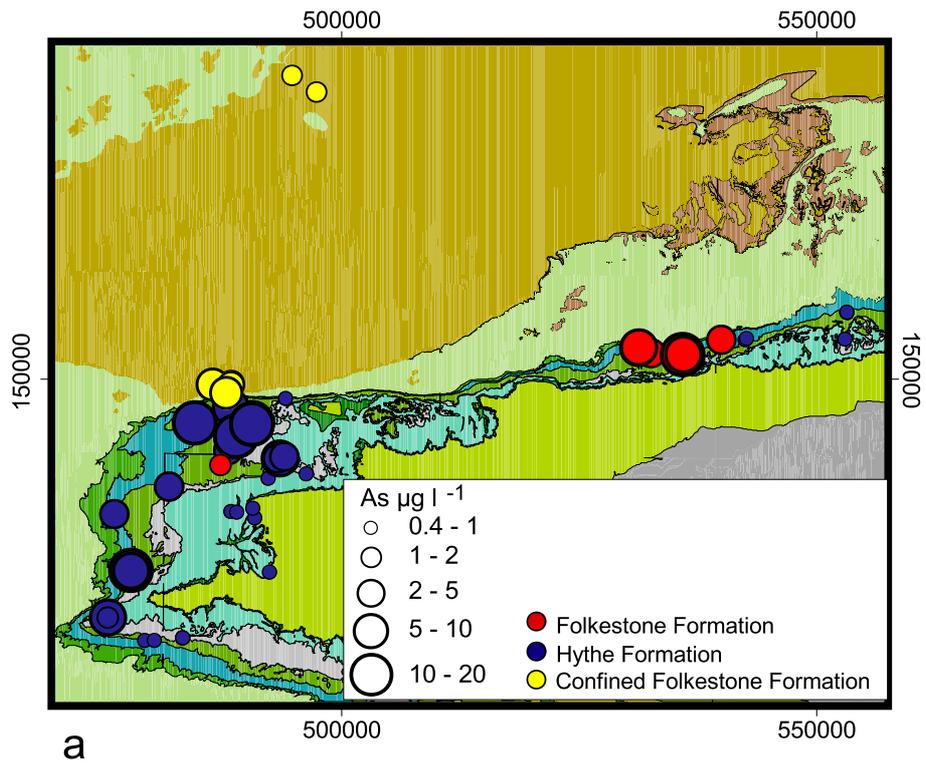


Figure 6.15 Regional variations in As and Sr concentration in the Lower Greensand groundwaters.

7. BASELINE CHEMISTRY OF THE AQUIFER

The baseline groundwater chemistry of any aquifer is determined by a wide range of physical as well as chemical processes. The primary input to most major aquifers is rainfall although connate or formation water may be present in parts of the aquifer where flushing has not been complete. In addition, leakage from underlying or overlying aquifer units may modify the groundwater chemistry either locally or regionally. A series of chemical reactions take place during recharge and groundwater flow, the most important being mineral dissolution and precipitation, mixing, redox reactions, ion exchange and sorption/desorption reactions. Water-rock interaction is complicated by the fact that most aquifers are heterogeneous in terms of mineralogy and geochemical environment (e.g. redox status). Many of the above mentioned reactions are also time-dependent and this gives rise to a range in baseline chemistry as the groundwaters move from areas of recharge to discharge.

Superimposed on this “natural” baseline are anthropogenic influences. These include point-source and diffuse pollution which directly modify the baseline chemistry. However, the baseline can be modified indirectly, for example, by abstraction: this can induce leakage from overlying units or upconing of deeper water of a different chemical composition. Although such changes can occur where the introduced solutes are derived “naturally”, and therefore represent baseline, the aquifer or unit being characterised has been modified, hence the need to define the baseline of a specified system.

In the present study, boreholes which are known to be affected by point-source pollution have been excluded from the database. However, many groundwaters in major aquifers, especially where unconfined, show signs of diffuse pollution, dominantly from urban or agricultural activities and these have been included. The determination of baseline in such cases can be determined from historical records, where these exist, by comparing with pristine areas, applying statistical techniques or modelling. Most of these have limitations and should be used together to provide a reasonable estimate of the baseline composition (Shand & Frengstad, 2001).

The composition of the waters from most of the boreholes sampled in the Lower Greensand can be ascribed primarily to natural processes of water-rock interaction: the majority of sources sampled have solute concentrations that are within baseline values (as indicated in Tables 5.1 a and b). These natural processes include mineral dissolution and ion exchange, redox reactions, particularly where the aquifer becomes confined and to a lesser degree the mixing of infiltrating waters with formation water. Rainwater tends to be acidic, and this, coupled with an increase in the partial pressure of CO₂ in the soil zone and the limited buffering capacity of the aquifer, leads to the mobilisation of certain metal species such as aluminium and chromium. In some localised areas, concentrations of these species are greater than the EU guideline values for drinking water. Lower Greensand waters are fresh and tend to have low conductivities compared with other UK groundwaters due to the relative purity of the aquifer material.

Trace-element concentrations are generally low, with most being within EU guide values for human consumption. Exceptions to this include Ba, whose median concentration is slightly higher than the EU guide value, and Fe, which is present in higher concentrations, particularly at depth where dissolved oxygen concentrations are low.

It is likely that most unconfined groundwaters in the UK have been impacted by anthropogenic influences, either through changes in flow or the direct addition of pollutants. It is tempting to use the chemistry of deep confined groundwaters in order to estimate the baseline concentrations but there are many problems associated with this (apart from mixing with older formation or connate water): firstly the deeper groundwaters are generally reducing and many elements of interest are redox-sensitive and

secondly many reactions are time-dependent and are expected to be different in both regions of the aquifer.

Anthropogenic influences on the chemistry of the aquifer water are evidenced by elevated nitrate and locally by chloride and potassium concentrations that are above local baseline values. In certain sources there is a trend towards an increase in these concentrations with time, which can be seen over the last decade or so. It is likely that agricultural practices have been primarily responsible for the increases. The concentrations of nitrate are higher than local baseline values (baseline nitrate-N concentrations are likely to be of the order of 1-3 mg l⁻¹: this value is similar to the lower concentrations in oxygenated groundwaters, the deeper waters of the unsaturated zone profile and the shift in populations noted on the cumulative probability plots. For other elements introduced anthropogenically (Na, Cl, K, SO₄) they are nonetheless within general baseline values for UK aquifers as a whole.

The spatial variations in solute concentrations over relatively short distances in the Greensand may be large and care should be taken extrapolating baseline concentrations across the aquifer.

8. SUMMARY AND CONCLUSIONS

The Lower Greensand is divided into four formations with two of these forming important aquifers: the Hythe Formation and the Folkestone Formation, separated by the Sandgate Formation which forms a leaky aquitard. The aquifer units are confined beneath by Atherfield Clays and above by the younger Gault Clay.

The chemistry of groundwater in the Lower Greensand aquifer of the study area is dominated by natural processes of water-rock interaction. The dominant processes on groundwater chemistry are mineral dissolution, redox reactions and, in the deeper groundwaters, ion-exchange. The groundwaters are dominantly of Ca-HCO₃ type but Na-HCO₃ types are present in deeper parts of the aquifer. The groundwaters generally have low solute concentrations reflecting the relative purity of the aquifer material and lack of rapidly dissolving mineral phases such as carbonate or evaporite minerals. The paucity of drift deposits and general lack of reactivity of shallow aquifer sediments make the Lower Greensand aquifer vulnerable to pollution. The low salinities of groundwater even in the deep confined parts of the aquifer show that it has been well flushed of any formation or connate water.

The general lack of carbonate minerals in many parts of the aquifer, particularly in the Folkestone Formation, means that significant parts of the aquifer are poorly buffered with respect to acidity. The confined groundwaters are reducing which has led to denitrification and an increase in Fe and Mn concentrations. Trace element concentrations are generally low but Ba may be locally relatively high. Elevated concentrations of some trace metals such as As, Pb and Ni were found in some groundwaters and are considered to be naturally-derived. With the exception of the unsaturated zone where waters are acidic, most trace metals are only present at low concentrations. Arsenic is present in most groundwaters with the highest concentrations being found in the reducing groundwaters. However, concentrations are not particularly high in the deeper Slough boreholes.

Superimposed on the natural baseline chemistry are the effects of man. This is most apparent in the increased nitrate concentrations in the unconfined groundwaters resulting from diffuse pollution. There are few historical data available for the aquifer and determination of the baseline is difficult to establish. It is likely that baseline concentrations of NO₃-N are of the order of 2-4 mg l⁻¹ as indicated by the lowest concentrations in oxygenated waters, waters from the unsaturated zone at depth and population distributions. Other elements influenced by diffuse pollution most probably include K, Cl and SO₄.

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