Baseline Report Series:
5. The Chalk of the North Downs, Kent and East Surrey

Groundwater Systems and Water Quality
Commissioned Report CR/03/033N

National Groundwater & Contaminated Land Centre
Technical Report NC/99/74/5

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

BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/03/033N

ENVIRONMENT AGENCY
National Groundwater & Contaminated Land Centre
Technical Report NC/99/74/5

Baseline Report 5. The Chalk Aquifer of Kent and East Surrey

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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 (^{3}H), dissolved greenhouse gases – chlorofluorocarbons (CFCs) – and certain micro-organic pollutants may provide evidence of a recent component in the groundwater. The baseline has been modified by man since earliest times due to settlement and agricultural practices. However, for practical purposes, it is convenient to be able to distinguish water of different 'ages': (i) palaeowater – recharge originating during or before the last glacial era i.e. older than c.10 ka (ii) pre-industrial water (pre 1800s), (iii) water predating modern agricultural practices (pre 1940s) and (iv) modern post-bomb era (post 1963).

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

The BASELINE objectives are:

1.   to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound

geochemical principles, as a basis for defining water quality status and standards in England and Wales (in the context of UK and Europe); also to assess anomalies due to geological conditions and to formulate a quantitative basis for the definition of groundwater pollution;

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

This report describes the regional variations in chemistry of groundwater from the Chalk aquifer of north Kent and east Surrey, including the North Downs. The aquifer is an important source of water for the region: groundwater supplies some 80% of public water supply. As a result of already heavy abstraction, there exists little scope for extra groundwater development. The aquifer crops out in the Downs in the southern part of the region, but dips gently northward where it is covered by Palaeogene and younger deposits of varying lithology and permeability. These include the Thanet Sand Formation at the base of the sequence, the Lambeth and Thames Groups and the London Clay, as well as sporadic Quaternary deposits. Groundwater resources are abstracted dominantly from the unconfined section of the aquifer.

Groundwater from the Chalk aquifer has evolved through a complex set of geochemical processes. Amongst the most important of these is the reaction of groundwater with the carbonate matrix. This has resulted in strongly pH-buffered compositions, with Ca and HCO_3 as the dominant dissolved ions, particularly in the unconfined aquifer. Distinct hydrochemical changes are observed downgradient as the aquifer is confined by the overlying Palaeocene and younger sediments. A number of redox-sensitive elements (notably iron and manganese) show distinctive baseline concentration ranges in the confined and unconfined sections of the aquifer, as do a number of elements involved in ion-exchange reactions. The northern section of the confined aquifer close to the coast has been strongly influenced by saline intrusion and accompanying ion exchange. This has affected a number of inorganic constituents, especially Na, Mg, Cl, SO_4, HCO_3, Br, I, F, B, Li and Sr. Some of the reducing, near-coastal groundwaters also appear to have had long residence times in the aquifer, as indicated by distinctive stable-isotopic compositions. Chalk groundwater in some coastal areas may be of Pleistocene age.

Some unconfined Chalk groundwaters show the effects of pollution from industrial, domestic and agricultural sources. Numerous sites of contaminated land, including landfills, occur across the region. The clearest effects of pollution are seen with nitrate, pesticides and organic compounds, although concentrations of many inorganic constituents (e.g. SO_4, K, Cl, Zn and possibly Cu) also appear to have increased as a result of pollution. This makes if difficult to define the baseline characteristics of groundwater in the unconfined aquifer for a number of chemical constituents. In the confined aquifer, concentrations of dissolved solids are higher (with resultant increased concentrations of a large number of elements) than in the unconfined aquifer. However, these represent largely naturally-derived concentrations rather than pollution, as the groundwaters have been protected from surface-derived pollutants by the overlying sediments.

Significant variations in groundwater flow and hence chemistry, both laterally and with depth, are also thought to be associated with the structure and weathering patterns of the Chalk. Such structural influences are particularly pronounced in the confined, near-coastal, sections of the aquifer.

2. PERSPECTIVE

2.1 Regional setting

The Chalk of the North Downs forms the northern limb of the Wealden Anticline and the Chalk escarpment forms the northern margin of the Weald Basin. It also forms the southern limb of the London Basin. The Chalk outcrop extends from the Hog's Back west of Guildford to Folkestone and Dover on the east Kent coast (Figure 2.1). The area covered in this investigation is the part of the Chalk aquifer extending from Guildford in the west [SU 99 50], to the east Kent coast and to the Thames Estuary in the north, including that part of the Chalk confined by overlying Palaeogene sediments. The study area covers some 120 km x 30 km (Figure 2.1).
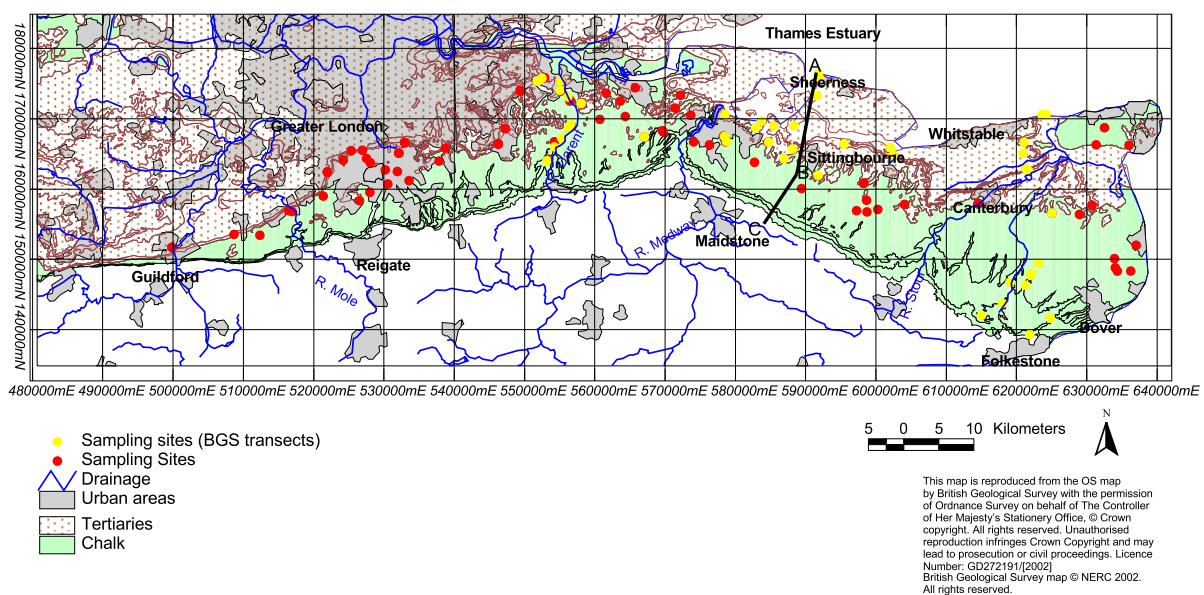
Figure 2.1 Map of the study area, showing the simplified geology, main river valleys and locations of groundwater sources used in this investigation. Sample sites given in red are Environment Agency or water-company data, those in yellow are samples collected and analysed by BGS for this investigation (three transects) or during previous studies in Kent. Line A-B-C is the line of geological cross section given in Figure 3.4

The region of Kent and east Surrey investigated in this study is relatively densely populated, particularly in the west which includes the suburbs of south-west London. The main urban centres besides these suburbs are Gravesend, Chatham and Gillingham on the Thames Estuary, Sittingbourne and Faversham south of the Isle of Sheppey, Canterbury in east Kent and Dover, Ramsgate and Folkestone on the south-east Kent coast.

Most employment is within the service sector and tourism is an important input to the economy of Kent, particularly around the coastal areas. Although heavy industry is today much diminished, a number of industrial developments are still important in the region. Kent is the dominant UK centre for paper manufacture, with five paper mills operating in the Medway area. Cement manufacture has also become established as a result of chalk quarrying (e.g. Halling, Northfleet, Rochester). Mineral extraction also includes alluvial gravels (e.g. Mitcham/Beddington area), clay for brick and tile manufacture (e.g. Funton) and flint gravel (Darent Valley, south of Dartford). Chemical and pharmaceutical industries have also developed in the Thames Gateway. Steel works also operate at Sheerness. A number of ports are of national or regional importance, including the major ferry ports

of Dover, Ramsgate, Folkestone and Dartford and the cargo ports of Gravesend, Thamesport, Sheerness, Chatham and Swale. Although now in decline, a long history of heavy industry has in places left a legacy of derelict land and some areas of contaminated land (e.g. old gas works, disused oil refinery and disused pesticide manufacturing plants). The industrial remains also include the abandoned workings of the deep East Kent coalfield.

Groundwater is heavily utilised as a result of the high population density and a major dependence on the Chalk aquifer for water supply. Housing development places extra strain on the resources available and tourism further enhances this demand during the summer months. The demand is likely to increase further from pressures imposed by climate change. Water companies have been exploring various options to increase their water resources, including reservoir development, measures to reduce mains leakage, storage by artificial recharge, groundwater desalination and use of marginal resources. Despite these shortages in the east, the Chalk aquifer beneath London has experienced recent rises in groundwater level as a response to decreased abstraction since the 1960s. In central London, levels have risen more than 50 m over the last 30 years (Environment Agency, 2000). London Underground currently pumps some 30,000 m^3 day^{-1} from its network of tunnels in order to maintain operations. GARDIT, the General Aquifer Research & Development Team, is a consortium of organisations with interests in groundwater and development in London and has been responsible for investigating means of bringing groundwater levels in London under control (GARDIT, 2001). The GARDIT strategy has involved drilling seven boreholes across London (Merton, Streatham, Honour Oak, Wanstead, Brixton, Battersea and Islington) in order to abstract and utilise the groundwater.

2.2   Role of groundwater

Early records (Whitaker, 1908) show that the Chalk of the North Downs has long been an important source of water supply for the region. Today, around 80% of Kent's water supply (200 Mm^3 a^{-1}, Environment Agency, 1998) is from groundwater. This rises to >90% in the Kentish Stour region. Groundwater abstraction is dominantly from the Chalk and five separate water-supply companies abstract groundwater from the aquifer. The majority of public-supply boreholes are in unconfined sections of the aquifer.

In Kent, the total deployable output of groundwater for public supply is of the order of 630 ML day^{-1}. Outputs from the five water companies are listed in Table 2.1. Additional groundwater resources in Surrey are abstracted by Thames Water and the Sutton & East Surrey Water Co.

There are also a large number of licensed private sources which abstract mainly, though not entirely, from the unconfined Chalk aquifer. Of these, the principal uses are for agriculture (supply to farms, spray irrigation) and industry. Some licensed boreholes are also located in the underlying Lower Greensand, though volumes abstracted from this aquifer are less significant.

Table 2.1   Output of groundwater for public supply in Kent (Environment Agency, 1998).

Water company	Licensed abstraction (ML day^{-1})	Deployable output (ML day^{-1})
Southern Water	265	191
Mid Kent Water Co.	215	168
Thames Water	179	154
Folkestone & Dover Water Co.	88	50
Sutton & East Surrey Water Co.	16	16

The aquifer is heavily committed with respect to abstraction licences and this factor, combined with recent droughts and resultant water shortages, has led the Environment Agency to restrict further abstraction.

Box 2.1. Nitrate Vulnerable Zones

Nitrate is the most significant pollutant of groundwater in England and Wales and the major source of this nitrate pollution is agriculture. During and after the Second World War, as agriculture was modernised, farming practices became more intensive. This led to both the ploughing up of virgin grassland and the increased application of chemical fertilisers, sewage sludge and manure. The over-application of fertilisers resulted in surplus nitrogen leaching from the soil into groundwater and surface water. This has resulted in increased concentrations of nitrate in groundwater in many unconfined aquifers in England and Wales.

In response to this problem, the European Community issued the Nitrate Directive in 1991 (91/676/EC). This requires member states to identify water bodies that are or could be affected by nitrogen pollution from agricultural sources, and to designate these as 'nitrate vulnerable zones' (NVZs). The Directive then requires Member States to initiate measures, targeted at farmers, to reduce nitrate leaching within these NVZs.

Following a consultation, 66 NVZs, covering some 600,000 hectares (8%) of England, were designated in 1996. However, a judgement by the European Court of Justice in December 2000 ruled that the UK had failed to designate sufficient areas to protect all surface waters and groundwaters, not just drinking-water sources, against diffuse nitrate pollution from agriculture. The Government therefore took action to comply with this judgement and in 2002, following consultation, a total of 55% of England was designated within NVZs (including the 8% originally designated in 1996).

The map shows the area of NVZs across the study area, as of December 2002. Although a significant percentage of the Chalk outcrop area of the North Downs is covered by NVZs, not all of it was designated for groundwater purposes. The North Downs Chalk in the east of the outcrop area is a 'groundwater' NVZ. However, the NVZs in the west of the North Downs were designated as a result of high nitrate concentrations in surface water.

Key

- NVZ
- Chalk
- Urban area
- River

10 0 10 20 30 Kilometres

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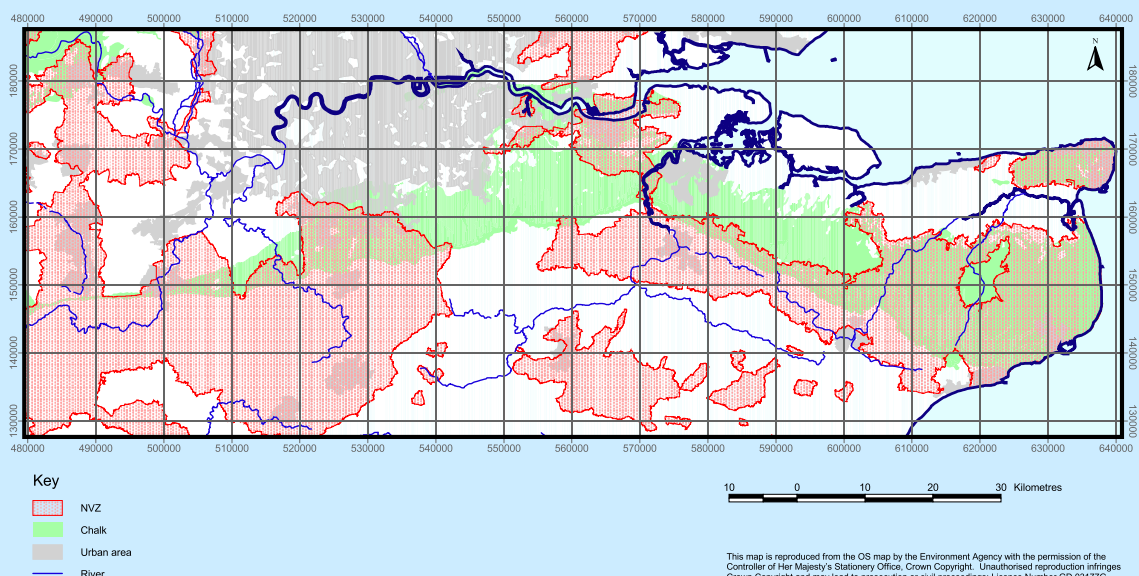
2.3   Current issues in groundwater quality

As the majority of water abstracted from the Chalk of north Kent is from the unconfined sections of the aquifer, significant issues arise from the potential contamination of groundwater by surface-derived contaminants from both diffuse and point sources. These include in particular contaminants from agricultural and industrial activities as well as from historically contaminated land. Mineral extraction sites are often also used for landfill and can pose localised risks to groundwater quality from leachate, especially if the organic waste content is high. Many landfill sites exist across the area of investigation and the area of landfilling has more than doubled since the 1960s (Environment Agency, 1998). A number of these landfills are developed over aquifers. High densities of septic tanks also occur in some parts of the Downs. Seepage from soakaways adjacent to roads provides additional pollution potential from salt, de-icers, hydrocarbons, herbicides and accidental spillages. Salinisation of surface waters and some groundwater has occurred in places as a result of discharges from the abandoned Kent coalfield. Pumping of groundwater from Eastry borehole [TR 3038 5334], installed 30 years ago to assess the degree of mine-related pollution, has confirmed the poor quality of chalk groundwater in that area.

High concentrations of nitrate and organic carbon have been observed in the groundwater from many parts of the unconfined Chalk. Nitrate Vulnerable Zones (NVZs) have been designated over a significant part of the unconfined aquifer (Box 2.1). Detectable concentrations of a number of pesticides and organic solvents have also been observed in some areas. Concerns over regional groundwater quality have resulted in regular monitoring of public-supply sources for a large range of organic constituents as well as nitrate by the water companies and the Environment Agency over a number of years.

In the confined sections of the aquifer, conditions are typically reducing and while nitrate concentrations are low in these conditions (as a result of denitrification reactions and the presence of unpolluted waters), concentrations of other undesirable inorganic constituents such as iron and manganese can be more problematic. As the water companies abstract almost entirely from the unconfined Chalk, high iron and manganese concentrations are generally only a problem for private abstractors. In the northern, coastal sections of the aquifer, saline intrusion is a problem and severely restricts groundwater development potential.

3.   BACKGROUND TO THE UNDERSTANDING OF BASELINE QUALITY

This section provides an overview of the current knowledge relating to the geography, geology and hydrogeology of the Chalk aquifer of the North Downs. Understanding of the geological and hydrogeological system is essential for assessing the natural (baseline) groundwater quality.

3.1   Regional geography

The topography of the North Downs is dominated by the chalk dip slope but with a prominent escarpment which reaches a height of up to 267 m above OD at Titsey [TQ 396 553]. Much of the Downland comprises gently undulating hills (Figure 3.1). The dip slope (gradient about 1:75) is broken into a number of blocks by the rivers Wey, Mole, Darent, Medway, Great Stour and Little Stour which flow northwards towards the Thames Estuary. These are typically associated with high-angle fractures within the chalk. Additionally, as is typical for Chalk Downland, there are a number of ephemeral rivers and streams, such as the Dour and the Cray and a network of dry valleys.

Average annual rainfall ranges from 530 mm to more than 800 mm (Folkestone & District Water Co., 1991) with an average for Kent of around 750 mm (Environment Agency, 1998). Rainfall is generally greatest in the south-east (Dover area) and diminishes to the north-west and west. Annual potential evapotranspiration is estimated to be between 500 mm and 575 mm (mainly during spring and summer), although actual evapotranspiration is thought to be about 10% less than the potential values (Holmes, 1981). Effective rainfall (recharge) is therefore of the order of 200–250 mm year^{-1}.

The geomorphology, hydrology and hydrogeology of the region have been modified extensively by periglacial processes during the Quaternary period. Deposits of Quaternary age are represented by extensive Clay-with-Flints in interfluve areas and head deposits and alluvium within valleys.

Figure 3.1   **Undulating hills of the North Downs, from [TQ 102 465] (photograph: Tim Besien)**

3.2   Land use

Much of the area under investigation is densely populated. Surrey is the most densely populated shire county in England, with a population of around 6.5 people hectare^{-1} compared to a national average of 3.8 people hectare^{-1} (ONS, 2000). Approximately 10% of Kent and 15% of Surrey is designated as urban development. This includes housing developments and industrial workings. Urban developments are particularly dense in the north-west which forms part of the Greater London conurbation (Figure 3.2). A major network of roads cross-cuts the area and motorways include the M25 which runs across the western part of the region, the M20 Swanley–Folkestone and M2 Rochester–Faversham. Following a long history of manufacturing industry in the region, there also exists a significant proportion of derelict contaminated land.

Despite urban pressures, farmland is extensive, especially in the eastern areas and the uplands of the North Downs. Agricultural land use is dominated by pasture for cattle and sheep, although much also comprises arable and horticultural land. Arable land is more prevalent in Kent than in Surrey (Figure 3.2). Orchards are developed on the narrow strip of the Thanet Sands where soils are fertile and sandy. Orchards and hops constitute around 6% of the land use of Kent (Environment Agency, 1998). Broadleaf woodland is well-developed on parts of the Downs. Parts of the area of investigation are designated as Green Belt land.

Much of the lower-lying land of the Medway–Stour area comprises salt marsh and wetland. These areas are protected in places by sea defences and have in parts been drained for agricultural, urban or industrial development. Such development pressures have been greatest in the west (Medway Marshes). Parts of the marshland have been preserved for wildlife and recreation.

Landuse
- Arable
- Managed Grassland
- Forestry/Woodland
- Semi-natural vegetation
- Urban
- Water

■ Waste disposal site

5 0 5 10 Kilometers
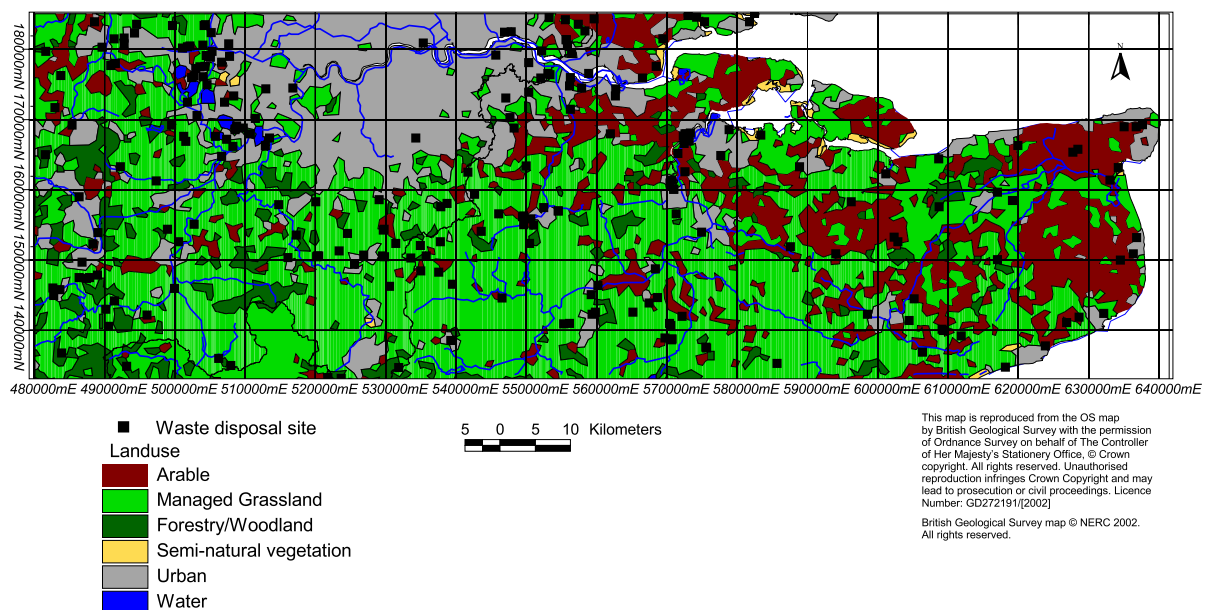
Figure 3.2   Map of land use for the area (data from Land Cover Map, 1990, supplied courtesy of the Centre for Ecology and Hydrology, ©NERC, 2002).

3.3   Geology

The Chalk reaches a thickness of around 200 m towards the axis of the London Basin syncline. Chalk deposition represents a large-scale marine transgression during the Upper Cretaceous (Cenomanian to Campanian), with development of widespread marine conditions over much of Europe. Traditionally, the Chalk has been divided into three divisions: Lower, Middle and Upper Chalk. Recent

reclassification has divided these into nine formations from the basal West Melbury Marly Chalk (Cenomanian) to the topmost Portsdown Chalk (upper Campanian) (Mortimore et al., 2001).
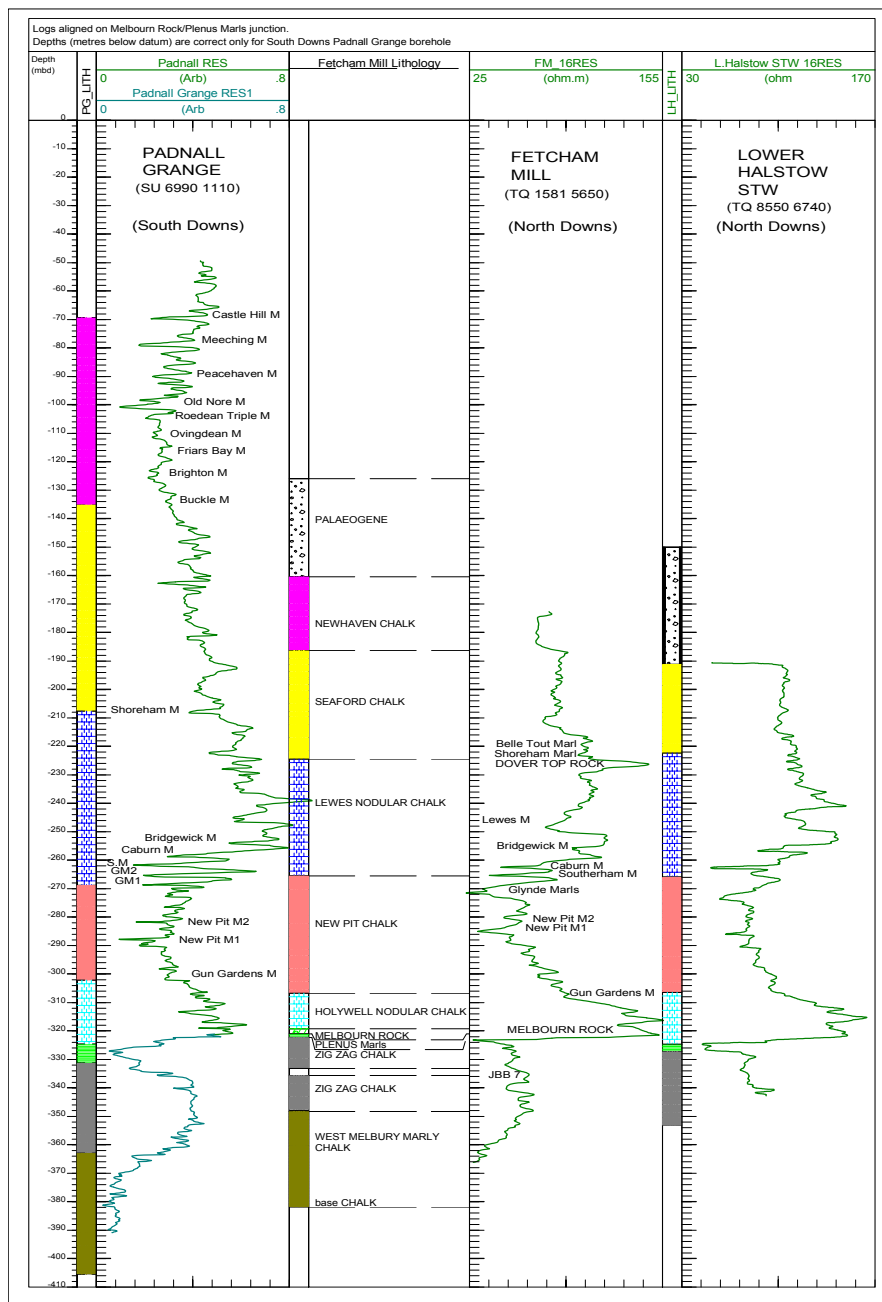
Figure 3.3   Stratigraphy of the south-east England Chalk and comparison of electrical resistivity logs from selected boreholes in the North and South Downs (from Buckley, in press). Formations overlying the Newhaven Chalk (i.e. Culver and Portsdown Chalk Formations) are missing from the local stratigraphic sequence.
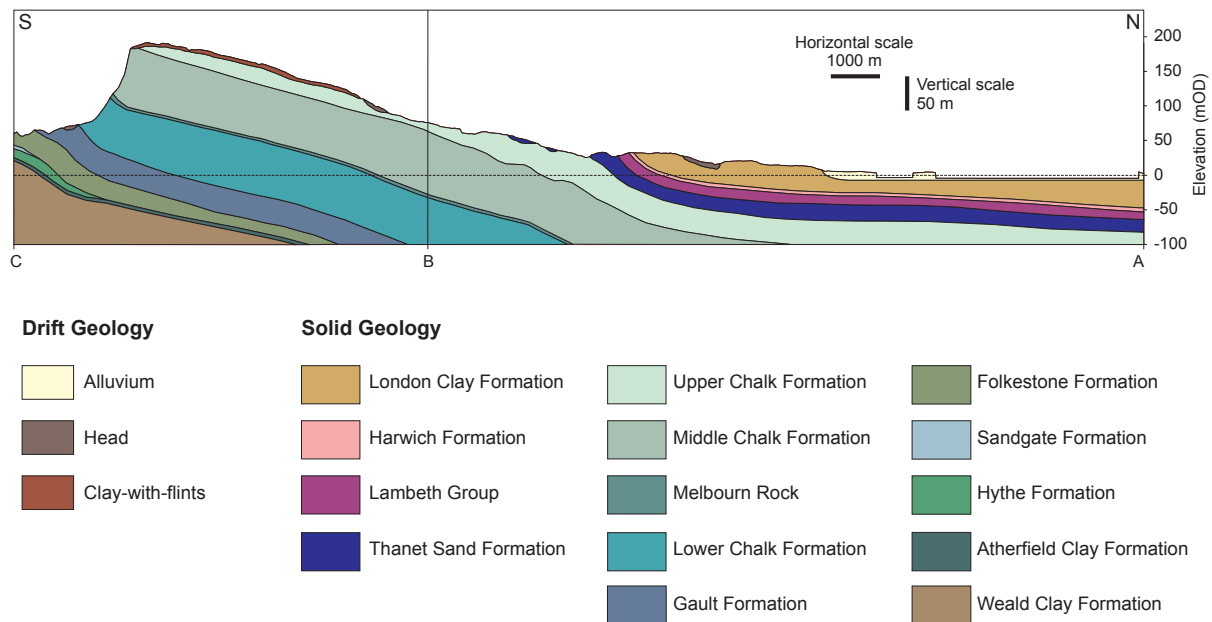
Figure 3.4   Geological cross section of the study area. Line of section is given in Figure 2.1.

Numerous marl layers occur within the sequence, particularly in the lower horizons (West Melbury and Zig Zag Chalk Formations; Figure 3.3). These are usually distinctive and correlatable across the region. The most notable of the marl bands in the lower part of the Chalk is the Plenus Marls (upper Cenomanian). This is overlain directly by the Melbourn Rock, a band of hard nodular chalk with thin marl partings and little shell material, being around 1.8–4.6 m thick in the Chatham area. The Dover Top Rock is a further distinct marl horizon (Mortimore et al., 2001; Hopson, in press). The marl bands largely reflect the amounts of terrigenous inputs to the Chalk seas during the depositional history.

The Chalk dips gently northwards at an angle of around 2º (Figures 3.4, 3.5). Structural features are common in the strata and despite the overall northwards dip, gentle folds exist with their axes parallel to strike and discontinuities occur perpendicular to strike. The network of dry valleys which dissects the North Downs is thought to be structurally controlled (Allen et al, 1997). In the region of the Hog's Back in the west, the angle of dip of the strata can be up to 55º northwards as a result of the reactivation of deep faults (Allen et al., 1997; Hopson, in press). Gentle folding with fold axes parallel to the coast has also been identified from borehole logs in the vicinity of Reculver on the north Kent coast (Buckley, in press; Figure 3.6). The dominant structural features trend NNW–SSE or NNE–SSW. A local synclinal structure in the Isle of Thanet gives rise to a localised outcrop of chalk surrounded by younger Palaeogene sediments. Fractures are dominantly located within the Upper and Middle Chalk.

The Chalk is immediately underlain by deposits of Lower Cretaceous age. West of Sevenoaks, the Chalk rests on deposits of the Upper Greensand which reach a thickness of 35 m near Guildford. To the east of Sevenoaks the Upper Greensand is absent and the Chalk is underlain directly by Gault Clay. This formation reaches up to 45 m thick at the coast in Folkestone and beneath the Chalk in north-east Kent but thickens westward to 68 m north of Maidstone and up to 85 m in Surrey (Hopson, in press).

Figure 3.5 **Outcrop of the Chalk in a quarry at Swanscombe, Kent (photograph: Richeldis Tyler-Whittle).**
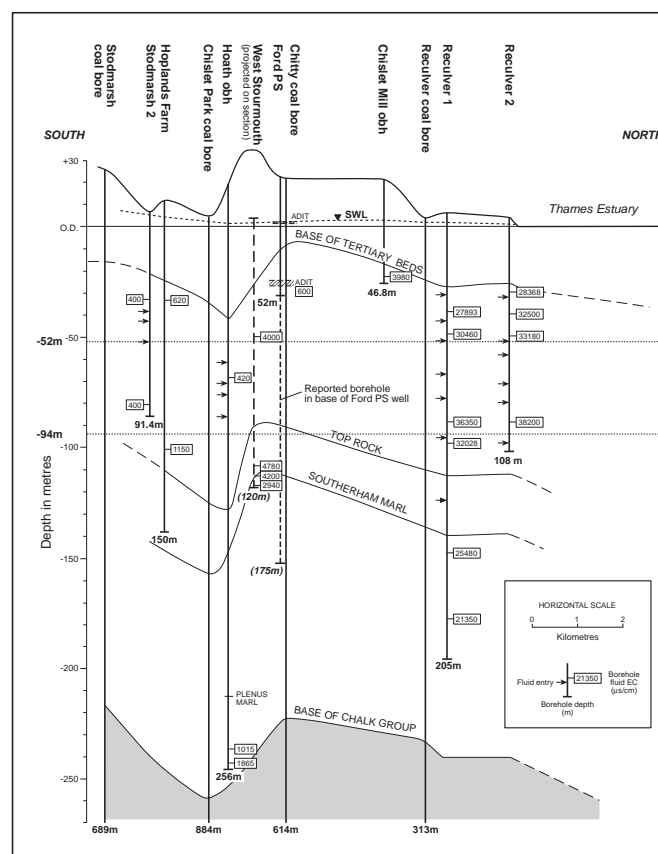
Figure 3.6 **North-south cross section through east Kent showing the relative positions of the Reculver boreholes and the local structural variations in the Chalk (from PALAEAUX, 1999).**

The Chalk is overlain by sediments of the Lower London Palaeogene Group which comprise the Thanet Sand Formation, Lambeth Group and Thames Group. The lowermost (Palaeocene) part of the sequence comprises mixed sandy and silty sediments with variable glauconite content. They are thought to have been deposited in a shallow marine to brackish lagoonal environment and show evidence of progressive shallowing and development of more terrigenous conditions through the Palaeocene (Hopson, in press). The oldest formation, the Thanet Sand Formation is at its thickest in the Thames Estuary and around Herne Bay, reaching up to 35 m (Hopson, in press). The base is composed of a thin (<0.5 m) flinty conglomeratic horizon, known as the Bullhead Bed. The Lambeth Formation (formerly known as the Woolwich & Reading Beds) consists of sandy and silty glauconitic deposits around 10–20 m thick, with a basal pebble bed (the 'Bottom Bed' of older literature). Overlying these are sediments of the Thames Group. These comprise the Harwich Formation (formerly collectively the Blackheath and Oldhaven Beds and the London Clay Basement Bed) and the London Clay. Deposits of the Harwich Formation are estuarine or freshwater sands, often cross-bedded, with occasional pebble beds. The London Clay (Eocene) is a thick deposit of marine clay reaching 150 m in north Kent but thinning westwards, to around 90 m near Reading.

Superficial deposits of Quaternary age are abundant in parts of north Kent and east Surrey. During the Pleistocene, large climatic fluctuations led to major changes in relative sea level and numerous cycles of erosion and deposition. Three glacial maxima occurred during the Pleistocene, the most significant of which was the Anglian interval. During these periods, periglacial conditions prevailed in the region and erosion was effected by solifluction processes and river incision. During intervening warm stages, marine transgressions caused inundation of lower river catchments, principally the Thames and Medway Rivers and their tributaries, and breaching of the Straits of Dover. Quaternary deposits of north Kent include the Clay-with-Flints, a sequence a red-brown clay with abundant flints and pebbles, deposited as the products of mass movements during glacial intervals. Where present, the deposit is typically around 5 m thick, although thicknesses up to 10 m have been recorded (Hopson, in press). Clay-with-Flints deposits are typically found in modern interfluves. Quaternary deposits also include Head deposits, formed by solifluction under periglacial conditions. These, together with alluvium, occur in river valleys. The alluvial deposits are commonly recognised in river terraces and range from coarse terrace gravels to fine silts. Mud flat deposits, estuarine alluvium and beach shingle also occur in coastal and low-lying areas.

Soils of the region vary as a function of the underlying geology and have variable thickness. The soils on the Chalk escarpment are generally thin grey rendzinas but thicken further north on the Downs where they are mainly brown rendzinas and calcareous brown earths. Where capping the Thanet Sands, they are typically light and fertile and have given rise to the development of the 'fruit belt'. Some soils developed on the Thanet Sands and Harwich Formation (Blackheath Beds) are sandy and acidic. In the north, soils developed on the London Clay are dominantly shallow, heavy gley soils with poor permeability. These have given rise to prominent coastal marshes (e.g. lower catchments of the Medway and Stour and Swale Marshes) which are fed by springs from the chalk (Environment Agency, 1998). Soils above the Drift deposits are typically fine loamy and clayey soils.

3.4   Hydrogeology

Regional groundwater flow in the North Downs Chalk is generally to the north or north-east, reflecting the geological and topographical controls (IGS, 1968). The Chalk is considered a dual-porosity aquifer with high matrix porosity and low primary permeability. Chalk porosity depends strongly on lithology and diagenetic history (Price, 1987). The lower parts of the sequence (West Melbury Marly Chalk and Zig Zag Chalk; Cenomanian) typically have a porosity of 20–40%, the Holywell and New Pit Formations (middle part; Turonian) around 30–40% and the upper parts (e.g. Lewes Nodular Chalk; Coniacian) around 30–50%. Porosity values are significantly lower in the hardgrounds with high clay and marl content. The Melbourn Rock (Turonian) has typical values of 16–18% for example (Adams, in press). Significant flow occurs in fractures which are best developed

in the shallow horizons, dominantly in the zones of modern and past water-table fluctuation (Bibby, 1981). Marl bands also have an important impact on groundwater flow in the Chalk, indicated by a frequent concentration of fractures above the indurated marl horizons. Additional evidence for this is provided by observed vertical restrictions in flow of the saline plume discharging from Tilmanstone colliery (Cross et al., 1995; Hazell, 1998).

Transmissivity values are variable in the Chalk, but tend to be higher in the valleys (typically around 2500 m^2 day^{-1}) than in the interfluves (10–20 m^2 day^{-1}; Price et al., 1993). Such variations are likely to result from a combination of increased prevalence of fractures and a shallower water table in the valleys (Cross et al., 1995). Hence, pumping stations for public water supply are often concentrated in valleys (e.g. Denton Valley in east Kent). The variations in transmissivity are particularly marked in the unconfined aquifer, but are also apparent in the confined sections.

Groundwater hydrographs for a selection of sites across the region are given in Figure 3.7. These show Environment Agency water-level monitoring data in some cases dating from the 1970s and demonstrate the range in responses observed. The amplitude of water-level fluctuations differs considerably but temporal variations in levels are roughly coincident at all sites. Large fluctuations are seen in some hydrographs particularly at some sites on the North Downs (up to 30 m at Little Bucket Farm). Hydrographs show relatively little variation in the few sites from the confined Chalk. Large amplitudes may be a result of a high degree of interconnectivity of fractures at a site, whilst lower amplitudes may result from increased dominance of the intergranular flow component.

The Lower London Palaeogene deposits overlying the Chalk are variably permeable and act as a semi-confining layer to the aquifer. The London Clay is a thick and poorly permeable deposit which fully confines the underlying strata.

Recharge is mostly via the Chalk outcrop where fractures are best developed and where soils are light and permeable. Some recharge is also likely via the semi-permeable Palaeocene deposits (Thanet Sands, Woolwich & Reading Beds, Blackheath Beds, Oldhaven Beds) but is likely to be reduced in the northern part of the region where London Clay and overlying impermeable clay soils occur, and in urban areas, although additional recharge from leaking sewers and water mains will offset this to some extent. As the dominant recharge occurs in the unconfined sections of the Chalk, these are the areas most vulnerable to surface-derived pollutant inputs. Source Protection Zones (SPZs) have been defined around groundwater-supply pumping stations in the unconfined Chalk in order to protect groundwater from contamination (Box 3.1).

The Chalk also provides discharge to the rivers, with a substantial proportion of the river volume comprising baseflow during dry periods. Recent increases in abstraction from the Chalk have significantly diminished baseflow to the Rivers Darent, Little Stour, Great Stour and Dour in particular. As a result, the Darent Low Flow Alleviation Scheme was developed by the Environment Agency to supplement flows in the River Darent (Figure 2.1) from chalk boreholes at Lullingstone, Eynsford and Farningham (Figure 3.8) at times of drought. These boreholes each have a capacity to abstract 4–5 ML day^{-1} (Environment Agency, 1999b). Flow augmentation of the River Medway in dry periods is also achieved by storage in Bewl reservoir of water abstracted during the winter from the river at Yalding and from the River Teise at Smallbridge. Considerable seasonal fluctuations occur in the water table in the unconfined aquifer.
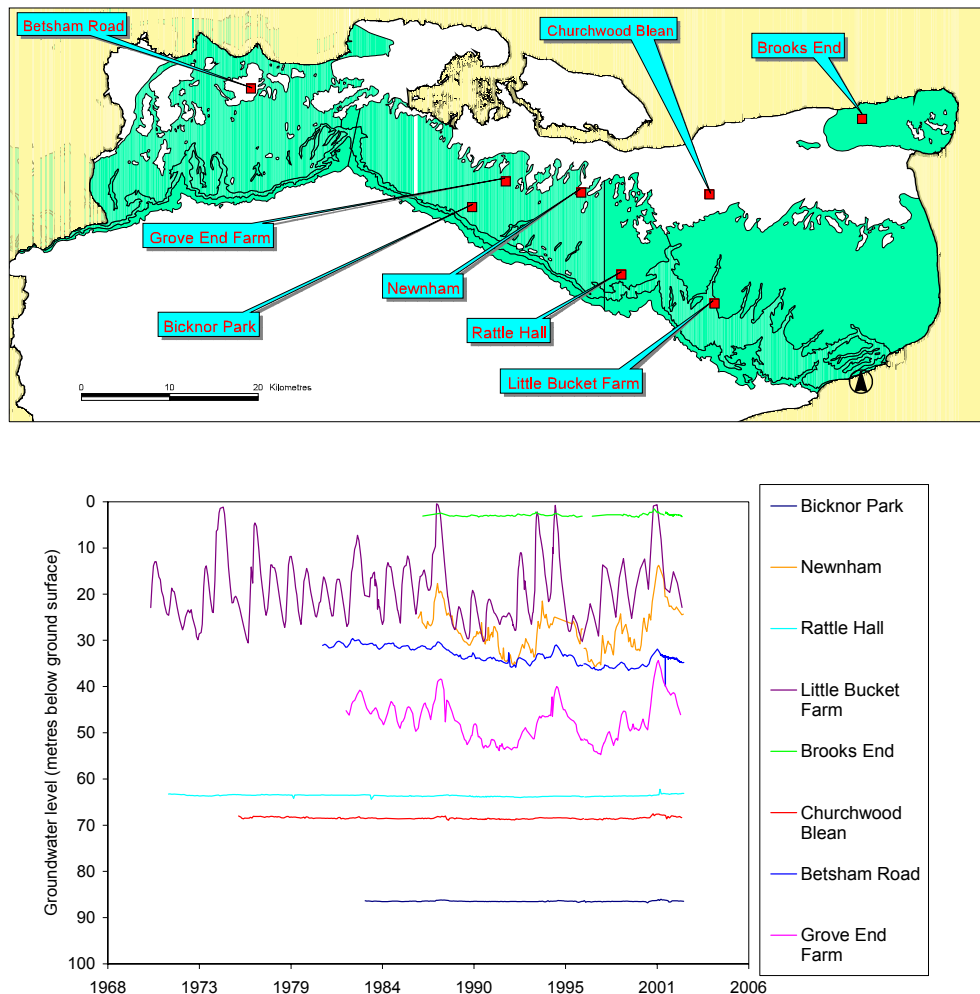
Figure 3.7 **Location of sites (above) and groundwater hydrographs (below) for boreholes in the Chalk of Kent (data source: Environment Agency).**

Major chalk springs issue at the sources of many of the dip-slope rivers (including the sources of the Hogsmill, Wandle, Medway Rivers). Smaller dip-slope springs also discharge in some places, but these have experienced diminished flow in recent years as a result of increased groundwater abstraction. Many once active springs have dried up recently (Environment Agency, 2000), although heavy rains since 2000 have led to renewed flow in some. Springs also issue from the Chalk and overlying Palaeocene deposits in the lower catchments of the Medway area and feed the marsh and wetland areas. A number of springs also discharge from the Chalk escarpment, notably the Lydden Spout, which emerges from the cliffs west of Dover. Folkestone & Dover Water Co. also utilise water issuing from springs at the base of the Chalk escarpment in Folkestone by supplying it to a local drinks factory (Figure 3.9).

Karstic features are developed in some parts of the aquifer. In the Mole Valley, 25 active swallow holes have been identified and during dry periods, water flows below ground through the Mole Gap, an incised section of the Chalk escarpment (Environment Agency, 1999a). Swallow holes, including those covered by Recent deposits may provide a mechanism for rapid recharge to the Chalk.

Figure 3.8   **Flow augmentation of the River Darent from pumping of a Chalk borehole at Eynsford (photograph: Pauline Smedley).**

Figure 3.9   **Terlingham Tunnel spring source, Folkestone is Chalk springwater discharging from the base of the formation at a rate of 65 m^3 hour^{-1}. The source is used by Folkestone & Dover Water Co. to supply a local drinks factory (photograph: Pauline Smedley).**

A degree of hydraulic connection exists between the Chalk and the overlying Palaeocene deposits where they are relatively permeable (e.g. the Thanet Sands). The Upper Greensand also comprises deposits of silt and fine sand and where present below the Chalk, this is also likely to be in hydraulic continuity. In areas where the Gault Clay directly underlies the Chalk however, this forms the effective base of the aquifer.

Sea-level changes during the Quaternary have had an important influence on the physical development of the aquifer. During the last maximum glacial period (ca. 12,000 BP), relative sea level

was some 130 m below the present level (PALAEAUX, 1999). This led to a major lowering of the base level of erosion and more active groundwater movement during this time resulted in the development of a number of fissures in the top few tens of metres of the chalk. These have provided significant channels for modern groundwater flow in the aquifer. Sea-level variations during the

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Box 3.1: Source Protection Zones (SPZs)

In order to protect groundwater resources, Source Protection Zones (SPZs) are defined for every public-supply water source. The zones are modelled using information on groundwater abstraction volumes and rates from the supply boreholes, the average recharge over the groundwater catchment area and the effective thickness and effective porosity of the aquifer. The effective thickness of the Chalk is estimated to be around 50–60 m despite the total thickness of 150–200 m in the North Downs. The effective porosity of the Chalk is determined by fractures that permit rapid flow over large distances. Hence, Chalk groundwater sources have larger SPZs than those in lithologies dominated by intergranular flow, such as sandstones. Each SPZ comprises three zones.
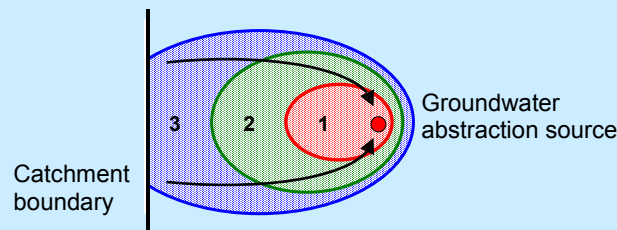
Zone 1, the Inner Source Protection Zone, has an area determined by the distance a particle of water will travel through the saturated zone over a 50 day period, based on the time necessary for bacterial decay. The boundary is always a minimum distance of 50 m from the source and is designed to protect against toxic chemicals and waterborne 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). The period is based on the time needed to delay, dilute and attenuate any slowly degrading pollutants.

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

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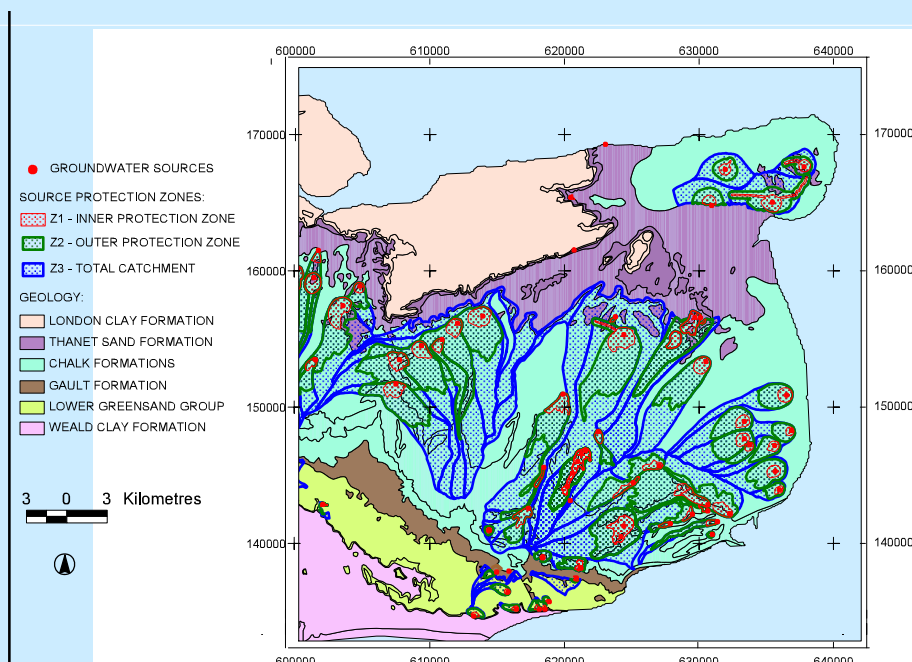
Pleistocene and subsequent Holocene have also had a major influence on the regional groundwater chemistry.

3.5   Aquifer mineralogy and petrology

The Chalk comprises predominantly soft, white fine-grained limestone with subordinate hardgrounds and beds of marl, calcarenite and flint (Hancock, 1975). Chalk is composed largely of the microscopic calcareous remains of coccoliths with additional foraminifera, ostracods and other skeletal remains (Black, 1953; Hancock, 1975; Hancock and Kennedy, 1967; Scholle, 1974). Analyses indicate that $CaCO_3$ normally exceeds 98% (Table 3.1) in the white-chalk facies of Kent. The chalk is composed of low-magnesium carbonate with an MgO content typically less than 0.4%. Besides the soft white chalk, numerous horizons of marl, flint and more lithified bands of hard and nodular chalk occur throughout the sediment sequence. Marl bands are taken to represent periods of deposition with a diminished supply of carbonate coupled with increases in the supply of terrigenous material (clay). Mechanisms of flint formation are still debated, but are generally taken to involve biogenic redistribution of silica during post-depositional diagenesis. Flint horizons are particularly prevalent in the Middle and Upper Chalk. Hardgrounds are zones of more intense lithification, believed to indicate periods of non-deposition and active diagenesis (Hancock, 1975).

Table 3.1   Chemical analysis of representative white chalk samples from Kent (data from Hancock, 1975).

Determinand	Units	1	2	3	4
SiO_2	wt %	0.90	1.15	0.37	0.50
Al_2O_3	wt %	0.23	0.21	0.69	0.14
Fe_2O_3	wt %	0.08	0.06	0.11	0.05
MnO	wt %	0.03	0.03	–	0.03
MgO	wt %	0.33	0.25	0.26	0.33
CaO	wt %	54.65	54.75	54.76	54.96
Na_2O	wt %	0.06	0.04	–	0.16
K_2O	wt %	0.05	0.04	–	0.03
P_2O_5	wt %	0.09	0.09	0.05	0.08
CO_2	wt %	43.61	43.67	43.26	43.85
$CaCO_3$	wt %	98.00	98.22	97.74	98.55
Total	wt %	100.03	100.29	99.50	100.13
Ba	mg kg^{-1}	215	135	–	125
Sr	mg kg^{-1}	387	637	–	737

1: St Margaret's Bay, Kent; 2: Langdon Steps, Dover; 3: Cliftonville, Kent; 4: Foreness Point, east of Margate

Within the pure white chalk, there are small quantities (generally less than 1%) of clay minerals and clay-grade detritus, principally quartz. The clay fraction increases markedly (to around 30–40%) in marl bands such as the Chalk Marl in the Lower Chalk and thin bands (typically less than 1 cm thick) in the Middle and Upper Chalk (Hopson, in press). In the Upper Chalk, clay mineralogy is dominated by illite and smectite (Hancock, 1975). Kaolinite is important in the Lower Chalk in some areas (Jeans, 1968). Material of silt and fine-sand grade is also generally minor, around 1% of the chalk. In studies of the non-carbonate sections of the Chalk formation of Oxfordshire and Berkshire, Fe_2O_3 concentrations were found to be always less than 0.13%, although in the near-surface, iron staining is common (Morgan-Jones, 1977). Manganese-oxide coatings are also found commonly on fracture surfaces.

Yellow staining within the Chalk is frequently associated with phosphatic material (collophane, typically concentrated around foraminifera, coprolites, fish scales and bones). The collophane is

predominantly a mixed carbonate-apatite assemblage and occurs in both nodular and granular form. Phosphate mineralisation is particularly prevalent in the marls and hardgrounds. Phosphatisation of the chalk is often accompanied by glauconitisation. Diagenetic glauconite has been found at a maximum concentration of 0.077% in white chalk from Sussex (Weir and Catt, 1965), but can occur at greater concentrations locally in hard bands, notably the Glauconitic Marl (Hancock, 1975). It is disseminated throughout the chalk but is also more prevalent in the marl and hard bands. Pyrite is particularly common in the Chalk Rock. Pyrite occurs both as tiny dispersed authigenic crystals, especially in the more argillaceous horizons, and as cylindrical concretions often infilling burrows. It is also commonly found in association with the phosphate concretions.

Other impurities include diagenetic zeolite at some locations, especially in the Lower Chalk. Trace amounts of chlorite are also commonly observed. Some horizons, notably the Glauconitic Marl, contain additional accessory mineral phases such as mica, zircon, rutile and tourmaline (Hopson, in press).

3.6   Rainfall chemistry

Rainfall is the dominant source of recharge to most aquifers and the chemistry of local rainfall, corrected for evapotranspiration effects, can be largely considered as the primary input composition. Rainfall may be the dominant source of a number of solutes in groundwater. For others, significant additions to groundwater can be imposed by chemical reactions with the host rocks or by inputs from other sources such as pollutants. Data for major-element compositions of rainfall from Plaxtol rain gauging site, near Maidstone, are given in Table 3.2. Average data are given for 1988, the most recent data available for the site (AEA, 2001). Evapotranspiration of rain in the UK can be expected to concentrate solutes in recharge roughly threefold. This is supported by the fact that the estimated average annual potential recharge for the region is around 250 mm compared with the average annual rainfall of 750 mm (Section 3.1). This simple calculation ignores additional factors such as runoff and utilisation of rain by plants or soil processes but gives a guideline to the scale of concentration. Threefold concentrated values for the Plaxtol rainfall are also given in Table 3.2. These values provide a useful guide against which the chemistry of Chalk groundwaters from the region can be assessed.

Table 3.2   Average rainfall chemistry for Plaxtol rain gauging station [TQ 618 521] for 1988 (34 samples); from AEA, 2001).

Determinand	Concentration (mg l^{-1*})	Concentrated rainfall (mg l^{-1})
pH	4.77	
Ca	0.90	2.71
Mg	0.26	0.79
Na	2.51	7.53
K	0.32	0.97
Cl	5.11	15.33
SO_4	5.20	15.59
NO_3-N	0.82	2.46
NH_4-N	0.83	2.49

*except pH

High Na, Cl and SO_4 concentrations in the Plaxtol rainfall probably reflect mainly the influence of maritime rainfall, although a component from atmospheric emissions of anthropogenic origin is also likely. Baseline concentrations of these constituents in the local groundwater are therefore difficult to estimate, although concentrations expected directly from modern rainfall should be of the order of 8 mg l^{-1}, 15 mg l^{-1} and 16 mg l^{-1} for Na, Cl and SO_4 respectively. Likewise, modern baseline concentrations of total nitrogen (NO_3-N plus NH_4-N) can be expected to be around 5 mg l^{-1}, although again, the atmospheric inputs of modern nitrogen to aquifers can be expected to be influenced to some

extent by anthropogenic sources. 'Concentrated' rainfall of pre-industrial age recharged to aquifers would likely have been less than 5 mg l^{-1}, although still detectable.

The primary pH of the rainfall is 4.77, i.e. acidic. This reflects both equilibration with atmospheric CO_2 and likely additional effects from atmospheric pollutants (SO_2). Rapid equilibration of acidic water with the Chalk will occur on infiltration, with carbonate reactions buffering the groundwater compositions at near-neutral compositions and with resulting increases in Ca concentrations and alkalinity.

3.7   Previous and ongoing investigations in the region

There have been a number of investigations of the hydrogeology and hydrogeochemistry of the Chalk aquifer of Kent over the last few years. The North Downs Chalk aquifer is currently being investigated by the British Geological Survey as part of its wider 'National Groundwater Survey'. This aims to provide a comprehensive description of the major British aquifers and the groundwater resources they contain. Much of the information presented in this report has been taken from results obtained during that investigation (e.g. Allen et al., 1997; Smedley et al., in press; Hopson, in press).

Box 3.2: Tilmanstone and Snowdown colliery drainage

Discharge of minewater from Tilmanstone and Snowdown collieries in the Kent coalfield via lagoon seepage to the unconfined Chalk has resulted in more than 30 km^2 of the aquifer becoming contaminated with saline water (Bibby, 1981; Headworth et al., 1980; Carneiro, 1996). The discharge to the Chalk began in 1907 and has been most serious from the Tilmanstone colliery where discharge to lagoons continued until 1974, at which point a pipeline was constructed to transport the mine effluent directly to sea. An estimated 358,000 tonnes of chloride (Cl) had infiltrated the aquifer from Tilmanstone and Snowdown (Carneiro, 1996), with only a limited amount (around 15%; Headworth et al., 1980) having been subsequently discharged from the aquifer. During the 1970s, test pumping of a borehole at Eastry and two other borehole sites close to the points of mine discharge revealed concentrations of Cl at shallow levels in the aquifer up to 3000 mg l^{-1}. Concentrations diminished slightly with greater distance from the plume source and with depth. The quality of groundwater at Wingham pumping station was also impacted by contamination from Snowdown, with observed Cl concentrations reaching in excess of 300 mg l^{-1} during the 1930s (Bibby, 1981). By 1996, the maximum concentration of Cl in the groundwater plume was around 1000 mg l^{-1} (SO_4 up to 200 mg l^{-1}) and the plume was estimated to be 100 m thick (Carneiro, 1996).

Surface-water quality has also been severely impaired in both the North and South streams, some 6 km north-east of Tilmanstone. These each receive a significant proportion of baseflow from the contaminated part of the aquifer. Water from the North and South streams has been monitored regularly since 1973 (Carneiro, 1996). A range of parameters were also measured in the three observation boreholes at Thornton Farm, Venson Farm and Eastry by the NRA in 1995. Complete analyses for major cations and anions have been made by Buchan (1962), Oteri (1980), Peedell (1994) and Hazell (1998). The impaired quality of groundwater in the Chalk of east Kent has persisted, particularly in the area impacted by discharge from Tilmanstone colliery. However, conditions have been gradually improving since the 1970s. At Wingham pumping station, Cl concentrations were around 44–45 mg l^{-1} in 1998. Today, the concentration is close to an estimated baseline (pre-contamination) value.

A number of other more local investigations have been carried out in the aquifer over the last few years. The incidence of mining contamination arising from operations in the east Kent coalfield is one of the most investigated topics (Headworth et al., 1980; Bibby, 1981; Carneiro, 1996). Although mining operations ceased in the region in 1988, minewater discharge from the Tilmanstone and Snowdown collieries has left a residue of contaminated saline water in the Chalk aquifer locally which has still not fully dissipated in some areas (Box 3.2). Chloride concentrations have been used most often as a diagnostic indicator of contamination and boreholes and rivers in the area of the plume have been monitored regularly over the last few decades (Table 3.3). Baseline concentrations of Cl in this area of the Chalk are likely to be of the order of 15–30 mg l^{-1}.

Table 3.3 **Average Cl concentrations (mg l^{-1}) in groundwater pumped from boreholes at three sites close to the Tilmanstone colliery discharge (from Southern Water, 1976).**

Borehole depth range	Thornton Farm	Venson Farm	Eastry
Shallow (ca. 36 m)	3010	1190	1630
Intermediate (73–97 m)	2230	1490	811
Deep (ca. 150 m)	358	544	–

Several investigations of parts of the Chalk of north Kent have also been carried out by BGS during the 1990s. These include studies of the saline groundwaters in the coastal part of the aquifer at Reculver and the potential for groundwater desalination (e.g. Buckley et al., 1996; Box 3.2) and investigations of the palaeohistory of groundwater evolution in the confined coastal aquifer of north Kent (PALAEAUX, 1999). Results from a number of these investigations are incorporated into the following sections of the report to provide a description of the main geochemical processes active in the Chalk aquifer of the region and the regional variations encountered.

Box 3.2: Desalination of coastal groundwater, Reculver

Urban pressures to provide water for the increasing population of Kent, together with increasing frequency of droughts have led water companies to consider other potential resources of water in the region. One option under investigation by Mid Kent Water Company during the 1990s, was the potential for desalination of brackish groundwater in the coastal Chalk aquifer of north Kent. The area chosen for further study was Reculver, east of Herne Bay (Mid Kent Water, 1992). Two boreholes were drilled close to the shoreline at Reculver during the early 1990s. Test pumping was carried out in Reculver borehole 1 over several months to investigate groundwater salinity and salinity variation, and a pilot-scale reverse osmosis plant was installed with a capacity of 4.8 m^3 day^{-1}. Combined chemical and isotopic evidence from the Reculver groundwaters suggests that they represent mixtures between fresh groundwater and seawater, with groundwater pumped from around 37 metres depth having each end member present in the proportion 1:1. Continuous pumping of the borehole over a 204 day period revealed no major changes in groundwater salinity with time. The pumped groundwater had moderate turbidity and high Fe and F concentrations, which promoted potential problems for treatment by desalination. The plan was deferred following the trial pumping on the basis of the high treatment and development costs in favour of more cost-effective solutions in the short to medium term.

4. DATA AND INTERPRETATION

4.1 Data sources

The chemical data used in this study incorporate datasets from a number of different sources. Most are analyses selected from the databases of Thames Water, Southern Water and Mid-Kent Water Company. Additional data were also from Sutton & East Surrey Water Co. Data from Thames Water and Sutton & East Surrey Water Co. were supplied by Thames Region Environment Agency and data for Southern Water and Mid-Kent Water Company were supplied by Southern Region Environment Agency. For the Southern Water and Thames Water sites, the first available analyses in the database for the period 1997–1998 were selected. For the Mid Kent Water Co. analyses, few data were available for this time interval and so the last available analysis in 1995 was selected. Of these data, 49 sample sources were from Thames Water, 33 from Southern Water and 7 from Mid Kent Water Co.

In addition, chemical data were collated from BGS databases, which included samples from the Sittingbourne–Isle of Sheppey area collected during 1997 and from Reculver–Hoplands Farm area, collected over the interval 1993–1996. These were included as many had a relatively comprehensive suite of trace-element data and incorporated sites not covered by public supply sources.

Sampling specifically for the current investigation involved the collection of 26 extra groundwater samples from 25 sites. As the aquifer block being investigated is large, sampling was restricted to three south–north transects running approximately along the groundwater flow line. These transects were along the Darent Valley (Crayford–Lullingstone) in the west, the Sheppey–Highstead area in the central part of the North Downs and the Folkestone–Denton Valley–Reculver area to the east (Figure 2.1). Most samples from the Denton Valley were from Folkestone and Dover Water Company sites. Where feasible, these flow lines incorporate groundwaters from both the unconfined and confined parts of the aquifer.

Where sites were duplicated in the different datasets, BGS analyses were used in preference because of the larger number of analysed determinands and the lower detection limits for trace elements. In total, data from 135 borehole and well sites across the Chalk aquifer of North Kent have been used in this investigation. Of these, the substantial majority were from the Chalk outcrop. Only 10 sample sources were from the confined aquifer along the north Kent coast. All these latter samples were BGS analyses.

4.2 Data quality and handling

Chemical analyses of samples analysed specifically for this project underwent routine quality-control checks with calibration against known standards and regular cross checks against standard reference materials. Charge imbalances for these determinations were in all cases less than 5% and usually less than 3%. Imbalances for all other BGS analyses discussed in this report are also less than 5% and of good quality. As many of the water-quality analyses carried out by the water companies often do not include a comprehensive suite of major-element measurements for a given sample, the quality of data produced by them is difficult to assess. The water company analyses used in this report are assumed to have undergone reasonable quality-control checks and hence to be representative of true compositions. However, the quality cannot be guaranteed in all cases for third-party chemical analyses and this should be borne in mind when considering the interpretation of analytical results.

5. RESULTS AND DATA PRESENTATION

5.1 Introduction

Summary statistics for a large range of chemical determinands considered in this report are given in Table 5.1. The data sets in the table and throughout this report have been divided into oxidising and reducing categories as the compositional ranges for a large number of solutes are highly distinctive in these different sections of the aquifer. For each of the oxidising and reducing data sets, minima, maxima and median values are given, together with values for the 97.7th percentile, equivalent to the mean + 2σ value on a log-normalised data set. Where analysed concentrations were below the detection limit, a value equivalent to half the detection limit was substituted for statistical purposes. Median values are useful indicators of average baseline concentrations in each section of the aquifer, but the 2σ values are taken to represent approximate upper baseline concentrations for most solutes.

Statistical summaries of the data are presented in Table 5.1. Where median values are less than the detection limit, the detection limit values have been substituted. Summaries are also given as a Piper diagram in Figure 5.1 and as summary box-and-whisker plots in Figures 5.2 and 5.3. Box-and-whisker plots give an indication of the 10th, 25th, 75th and 90th percentile values for the data range for each element. Curves in Figures 5.2 and 5.3 are the values for diluted seawater at the median Cl concentration of the groundwater data set plotted, and are given for comparison. Cumulative-frequency diagrams are also given for selected major and trace constituents in Figures 5.4–5.7 and an explanation of the value of the cumulative-frequency diagram is given in Box 5.1.
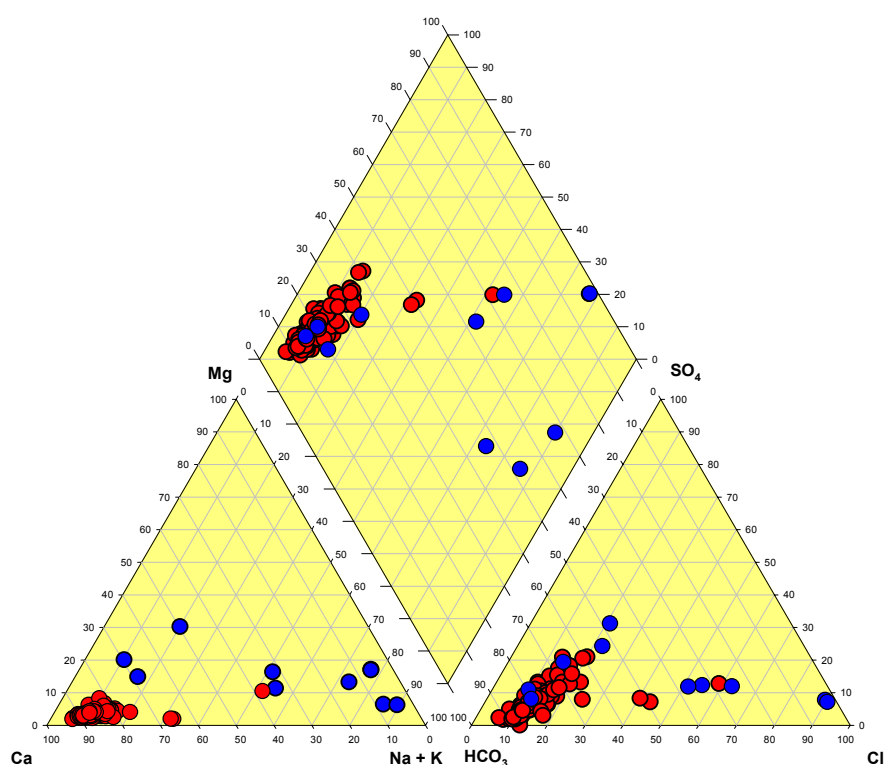

Figure 5.1   Piper diagram for the groundwater samples investigated from the Chalk aquifer. Red symbols: oxidising groundwaters, blue symbols: reducing groundwaters. Groundwaters show a prominent mixing line from freshwater compositions (Ca-HCO₃) to saline (NaCl) compositions, the latter being represented by saline water from Reculver.

5.2   Chemical compositions

The distribution of data shown in Figure 5.1 indicates that oxidising groundwaters from the region are dominantly of Ca-HCO$_3$ type. The range of Ca in the outcrop groundwaters is 62–220 mg l^{-1}, (2σ 150 mg l^{-1}) with a more variable range in the groundwaters affected by saline intrusion. Alkalinity values (HCO$_3$) are variable but are also relatively high with a range around 260–340 mg l^{-1} at outcrop, increasing to around 500 mg l^{-1} in the confined groundwaters. Magnesium values typically range between 1–27 mg l^{-1} (2σ 6.6 mg l^{-1}) in the outcrop zone.

Most of the Chalk groundwaters are fresh with low Na and Cl concentrations but these increase appreciably in the estuarine/coastal areas where saline intrusion has occurred. Median Na and Cl concentrations in the unconfined aquifer are found to be 15 mg l^{-1} and 25 mg l^{-1} respectively. However, in the near-coastal confined groundwaters of Reculver, near Herne Bay [TR 235 694], they each reach in excess of 5000 mg l^{-1} and are of Na-Cl type (Figure 5.1; Table 5.1). In the saline groundwaters, increased concentrations of K, Mg and SO$_4$ are also observed (Section 6.1.1). A few of the confined groundwaters have Na-HCO$_3$ dominant compositions (Figure 5.1). These are located in parts of the aquifer on the Isle of Sheppey and close to Reculver.

Groundwaters from the unconfined aquifer are generally aerobic with observed concentrations of dissolved oxygen up to saturated values (around 10 mg l^{-1}) and redox potentials (Eh values) often in excess of 220 mV. Under the aerobic conditions, concentrations of nitrate reach up to 28 mg l^{-1} (as NO$_3$-N). Nitrite (NO$_2$-N) and ammonium (NH$_4$-N) concentrations are low and most frequently below analytical detection limits. These are typically <5 μg l^{-1} and <9 μg l^{-1} respectively.

In the confined aquifer, available data indicate that the groundwater becomes progressively more reducing with low or no detectable dissolved oxygen and redox potentials of typically less than 200 mV. Under these conditions, nitrate concentrations diminish significantly. Nitrite concentrations are also low, but those of ammonium are higher, in some cases considerably. A value of 4.4 mg l^{-1} NH$_4$-N was detected at Reculver. Under the reducing conditions, concentrations of Fe and Mn also increase, to maxima of 2500 μg l^{-1} and 74 μg l^{-1} respectively (Table 5.1).

A range of other trace elements also show some notable variations across the aquifer from the unconfined to the confined sections. The range in Sr found in chalk groundwaters at outcrop is around 160–710 μg l^{-1} but reaches up to 16 mg l^{-1} in the confined near-coastal aquifer (Table 5.1). Similar increases in the confined groundwaters downgradient are also observed for Br (up to 37 mg l^{-1} in analysed brackish groundwaters), B (up to 2400 μg l^{-1}), Li (up to 130 μg l^{-1}), I (up to 280 μg l^{-1}), F (up to 2200 μg l^{-1}) and P (up to 300 μg l^{-1}).

Concentrations of dissolved Zn are also variable across the aquifer, although median values are comparable in the unconfined and confined groundwaters, being 6.7 μg l^{-1} and 8.1 μg l^{-1} respectively (Table 5.1).

Measured concentrations of many other trace elements, particularly metals, are low in the Chalk groundwaters under the near-neutral conditions. Concentrations of Be are <0.05 μg l^{-1}, Cd typically <0.5 μg l^{-1}, Cs <0.09 μg l^{-1} Pb mostly <5 μg l^{-1} (up to 7 μg l^{-1}), Mo <0.7 μg l^{-1}, Ag usually <0.1 μg l^{-1} but up to 8 μg l^{-1}, Ni mostly <5 μg l^{-1} but with values up to around 15 μg l^{-1}, and Al with mostly <20 μg l^{-1} but reaching up to 83 μg l^{-1}.

Concentrations of Cu are typically <20 μg l^{-1} but with a maximum observed value of 60 μg l^{-1}. The median value for Cu is higher in the unconfined groundwaters than in those from the confined aquifer (Table 5.1).

Concentrations of Cr are typically <5 μg l^{-1} but with some high values in the saline groundwaters from the confined aquifer (up to 390 μg l^{-1}). Little can be said about the distribution of B

concentrations in the unconfined groundwaters as most are below analytical detection limits which for water-company data are rather high (up to 100 µg l^{-1}). However concentrations are notably higher in the groundwaters from the confined aquifer (median 150 µg l^{-1}, up to 2500 µg l^{-1}).

Dissolved As is present at low concentrations (<2 µg l^{-1}) throughout the aquifer, even in the confined zone. Selenium concentrations are <3 µg l^{-1} in most analysed samples, although no data are available for the reducing groundwaters. Under reducing conditions, Se concentrations are expected to be lower than this owing to the relative immobility of the Se(IV) redox species. Rare earth elements are almost entirely below detection limits throughout, as expected for near-neutral groundwaters from a carbonate aquifer.

Cumulative-frequency plots in Figures 5.4–5.7 give an indication of the distributions of concentrations of a number of solutes in the groundwaters. In the groundwaters from the unconfined aquifer, many of the major elements and a number of trace elements (Ba, Sr) have normal distributions. Nitrate (N) is an exception to this, with the frequency curve indicating a cluster of samples having concentrations <3 mg l^{-1} (Figure 5.4).

BOX 5.1: Use of cumulative-frequency diagrams to indicate baseline characteristics in groundwaters
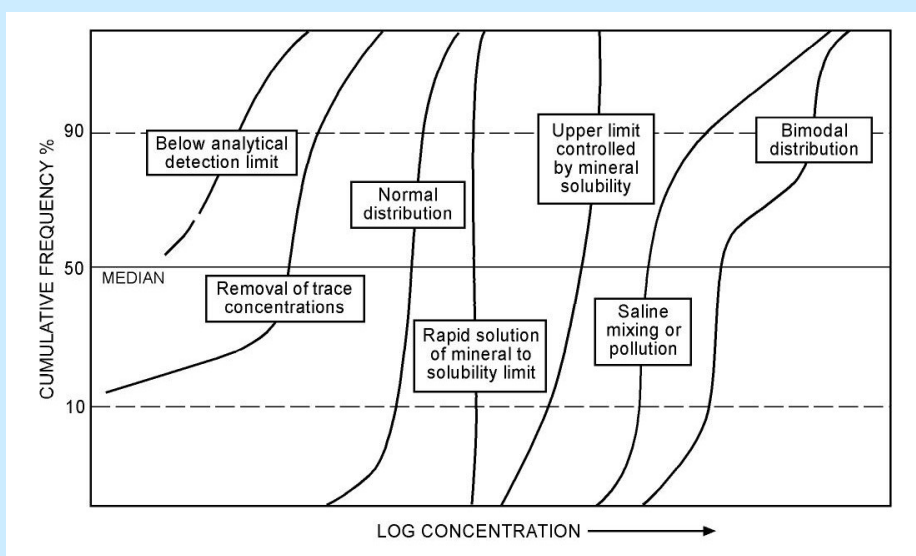
i)   The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.

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.

Table 5.1 Statistical summary of groundwater chemistry in the Chalk aquifer of the study area, divided on the basis of reducing and oxidising conditions (defined by the concentrations of dissolved oxygen and nitrate).

Determinand	Units	Reducing					Oxidising				
		Minimum	Median	97.7 centile	Maximum	N	Minimum	Median	97.7 centile	Maximum	n
Temperature	ºC	12.1	13.5	16.8	16.9	9	7.9	11.5	15.1	17.6	114
pH		6.8	7.14	8.04	8.05	10	6.4	7.2	7.8	7.9	118
Eh	mV	73	226	387	396	7	135	219	379	431	35
DO	mg l^{-1}	<0.1	<0.1	0.1	0.1	9	0.3	7.4	10.6	10.9	39
SEC	µS cm^{-1}	623	1310	26700	26800	10	400	580	810	2030	123
δ^2H	‰	-56	-50	-38	-34	8	-50	-47	-44	-43	22
δ^{18}O	‰	-8.4	-7.8	-5.4	-4.8	7	-7.8	-7.3	-6.9	-6.9	22
δ^{13}C	‰	-14.8	-14.3	-8.2	-6.7	5	-16.5	-15	-12.7	-11.3	21
Ca	mg l^{-1}	15.7	98.2	386	399	10	61.9	117	150	218	125
Mg	mg l^{-1}	7.72	21.7	670	689	10	1.1	2.69	6.61	27.1	125
Na	mg l^{-1}	14.6	182	5650	5820	10	6.2	14.6	52.5	245	125
K	mg l^{-1}	3.79	11.0	173	175	10	<0.4	1.9	4.72	14.2	125
Cl	mg l^{-1}	23.8	179	10400	10700	10	10.0	25.0	78.0	392	127
SO$_4$	mg l^{-1}	24.2	107	1123	1140	10	<10	18.1	69.2	115	127
HCO$_3$ (field)	mg l^{-1}	271	345	488	493	10	256	303	338	343	36
HCO$_3$ (lab)	mg l^{-1}					0	162	254	316	329	62
NO$_3$-N	mg l^{-1}	<0.01	<0.3	0.38	0.42	9	0.2	6.4	22.5	28.2	127
NO$_2$-N	mg l^{-1}	<0.002	<0.005	0.004	0.005	9	<0.003	<0.005	0.007	0.008	72
NH$_4$-N	mg l^{-1}	<0.01	0.56	4.18	4.40	10	<0.009	<0.05	0.016	12	122
P	mg l^{-1}	<0.5	0.10	0.27	0.30	10	<0.01	<0.1	0.078	0.129	85
TOC	mg l^{-1}					0	<0.5	1.1	3.6	37	82
DOC	mg l^{-1}					0	0.6	1.4	4.1	4.6	26
F	µg l^{-1}	160	540	2060	2200	7	<50	116	279	400	124
Br	µg l^{-1}	78	260	30100	36500	9	<20	70	1119	2220	75
I	µg l^{-1}	5.7	16.5	265	280	9	1.4	5.0	30	60	36
Si	µg l^{-1}	4.48	6.31	9.62	9.73	9	3.55	6.05	11.0	12.7	36
Ag	µg l^{-1}	<0.05	<0.05	0.06	0.07	9	<0.05	<0.1	0.008	7.9	70
Al	µg l^{-1}	<1	<1	24	29	9	<1	1.0	48	83	78
As	µg l^{-1}	<1	<1	1.6	1.8	9	<1	<1	1..3	1.7	71
Au	µg l^{-1}						<0.05	<0.05	<0.05	<0.05	26
B	µg l^{-1}	35.4	149	2430	2480	10	<20	<100	140	230	118
Ba	µg l^{-1}	24.6	40.0	71.3	72.1	10	18	34	105	129	71
Be	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	5	<0.05	<0.05	0.014	0.015	35
Bi	µg l^{-1}	<0.05	<0.05	<0.050	<0.050	5	<0.05	<0.05	0.016	0.018	35
Cd	µg l^{-1}	<0.05	<0.05	0.048	0.049	9	<0.05	<0.5	0.19	0.60	109
Ce	µg l^{-1}	<0.01	0.019	0.033	0.034	5	<0.01	<0.01	0.05	0.08	35
Co	µg l^{-1}	<0.02	0.083	0.21	0.21	5	<0.02	<0.02	0.75	1.6	35
Cr	µg l^{-1}	<0.5	<0.50	308	386	10	<0.5	<5	1.1	47	109
Cs	µg l^{-1}	0.021	0.057	0.070	0.070	5	<0.01	0.01	0.04	0.09	35
Cu	µg l^{-1}	0.004	0.71	3.9	4.2	9	<4	1.2	27	60	116
Dy	µg l^{-1}					0	<0.01	<0.01	<0.01	0.01	26
Er	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
Eu	µg l^{-1}	<0.01	<0.02	<0.02	<0.02	5	<0.01	<0.01	0.002	0.002	35
Fe	µg l^{-1}	<4	191	2250	2470	10	<5	<30	69	159	125
Ga	µg l^{-1}	<0.05	<0.05	<0.050	<0.05	5	<0.05	<0.05	0.005	0.006	35
Gd	µg l^{-1}					0	<0.01	<0.01	0.010	0.010	26
Ge	µg l^{-1}	<0.05	<0.05	0.15	0.16	5	<0.05	<0.05	0.092	0.13	35
Hf	µg l^{-1}					0	<0.02	<0.02	<0.02	<0.02	26
Hg	µg l^{-1}					0	<0.01	<0.1	0.18	2.3	99

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| Determinand | Units | Reducing | | | | | Oxidising | | | | |
		Minimum	Median	97.7 centile	Maximum	N	Minimum	Median	97.7 centile	Maximum	n
Ho	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
In	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
Ir	µg l^{-1}					0	<0.05	<0.05	<0.05	<0.05	26
La	µg l^{-1}	<0.01	<0.01	0.010	0.011	5	<0.01	<0.01	0.02	0.02	35
Li	µg l^{-1}	10	45	116	129	9	<4	2.12	10.3	11.8	36
Lu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	4	<0.01	<0.01	<0.01	<0.01	35
Mn	µg l^{-1}	<0.2	19.6	66.3	73.7	10	<0.05	<10	4.58	13.3	114
Mo	µg l^{-1}	<0.1	0.21	0.41	0.43	5	<0.1	0.1	0.34	0.61	35
Nb	µg l^{-1}					0	<0.01	<0.01	<0.01	0.01	26
Nd	µg l^{-1}	<0.01	0.016	0.020	0.020	5	<0.01	<0.01	0.02	0.02	35
Ni	µg l^{-1}	<0.2	1.7	16.6	17.5	9	<0.2	<5	9.3	15	109
Os	µg l^{-1}					0	<0.05	<0.05	<0.05	<0.05	26
Pb	µg l^{-1}	<0.05	0.06	0.36	0.38	9	<0.05	<5	4.0	7.0	117
Pd	µg l^{-1}					0	<0.2	<0.2	<0.2	<0.2	26
Pr	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	5	<0.01	<0.01	0.006	0.010	35
Pt	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
Rb	µg l^{-1}	1.5	2.5	4.5	4.6	5	0.88	1.4	3.1	3.3	35
Re	µg l^{-1}					0	<0.01	<0.01	0.02	0.02	26
Rh	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
Ru	µg l^{-1}					0	<0.05	<0.05	<0.05	<0.05	26
Sb	µg l^{-1}	<0.01	<0.01	0.034	0.035	5	<0.05	<0.4	0.70	0.70	69
Sc	µg l^{-1}					0	0.5	0.8	1.0	1.0	26
Se	µg l^{-1}					0	<0.5	<1	3.0	3.5	61
Sm	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	5	<0.05	<0.05	0.005	0.008	35
Sn	µg l^{-1}					0	<0.05	0.11	0.24	0.33	26
Sr	µg l^{-1}	834	2791	15659	15700	10	160	310	712	1860	75
Ta	µg l^{-1}					0	<0.05	<0.05	<0.05	<0.05	26
Tb	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
Te	µg l^{-1}					0	<0.05	<0.05	0.08	0.09	26
Th	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	5	<0.05	<0.05	0.020	0.025	35
Ti	µg l^{-1}					0	<10	<10	<10	<10	26
Tl	µg l^{-1}	<0.01	<0.01	0.05	0.06	5	<0.01	0.01	0.059	0.090	35
Tm	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
U	µg l^{-1}	<0.01	0.04	0.61	0.66	5	0.23	0.35	1.3	1.3	35
V	µg l^{-1}					0	<1	<1	1.4	2.0	26
W	µg l^{-1}					0	<0.1	<0.1	<0.1	<0.1	26
Y	µg l^{-1}	<0.01	0.02	0.057	0.060	5	<0.01	<0.01	0.020	0.037	35
Yb	µg l^{-1}					0	<0.01	<0.01	<0.01	<0.01	26
Zn	µg l^{-1}	<0.1	8.1	38	39	9	<2	6.7	320	520	116
Zr	µg l^{-1}					0	<0.5	<0.5	<0.5	<0.5	26
Atrazine	µg l^{-1}					0	<0.01	0.012	0.14	0.19	80
Simazine	µg l^{-1}					0	<0.01	<0.034	0.06	0.12	80
Isoproturon	µg l^{-1}					0	<0.01	<0.04	<0.04	0.018	80
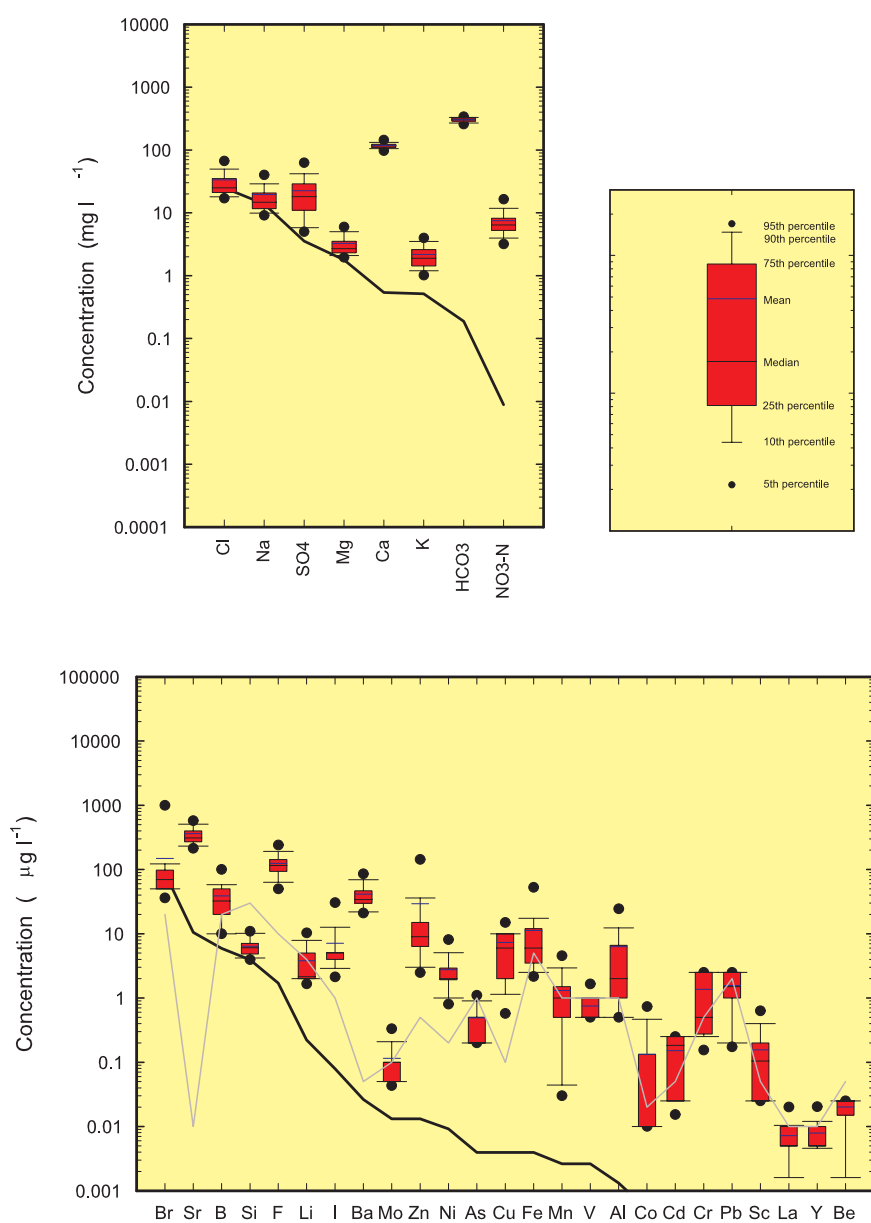
Figure 5.2 **Box plots showing the distribution of major and trace elements in oxidising groundwaters from the Chalk aquifer. Black lines represent the element concentrations in diluted seawater at the median chloride concentration of the groundwater datasets (see text). Blue lines represent the typical detection limit values for the trace elements.**

Figure 5.3 **Box plots showing the distribution of major and trace elements in reducing groundwaters from the Chalk aquifer. Black lines represent the element concentrations in diluted seawater at the median Cl concentration of the groundwater datasets (see text). Blue lines represent the typical detection limit values for the trace elements.**
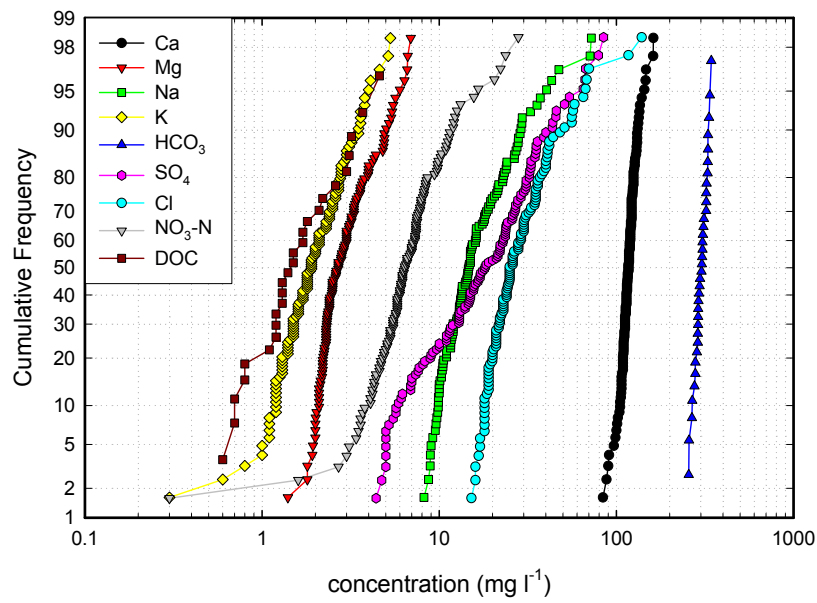
Figure 5.4   Cumulative-frequency diagram for major constituents from oxidising groundwaters in the Chalk aquifer.
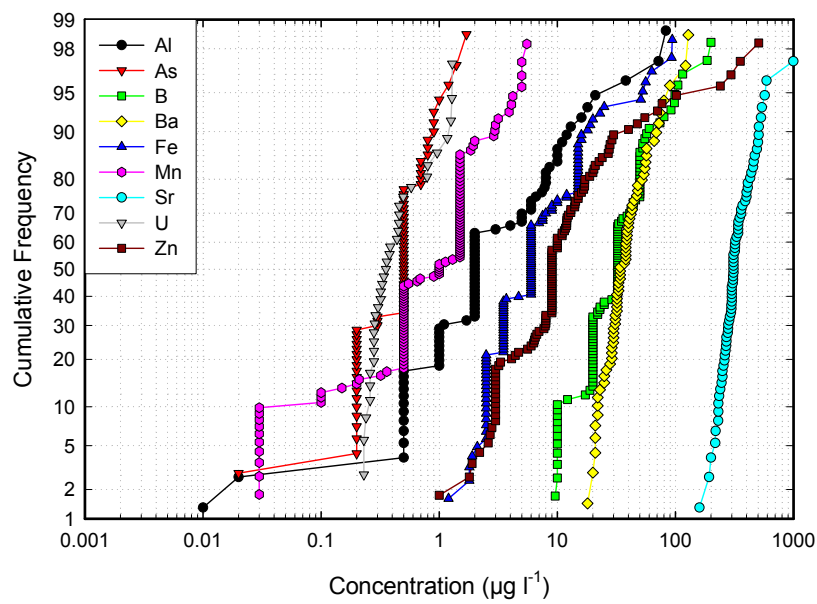
Figure 5.5   Cumulative-frequency diagram for minor elements from oxidising groundwaters in the Chalk aquifer.
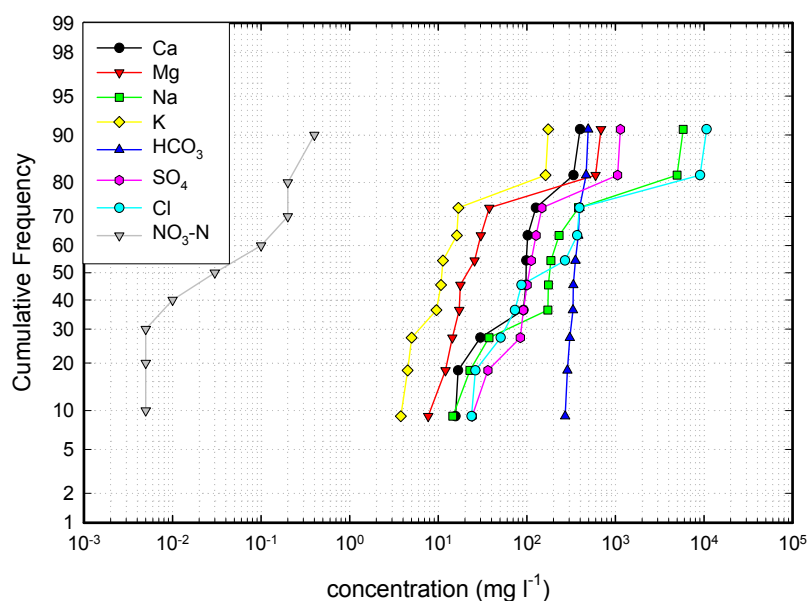
Figure 5.6 **Cumulative-frequency diagram for major constituents from reducing groundwaters in the Chalk aquifer.**
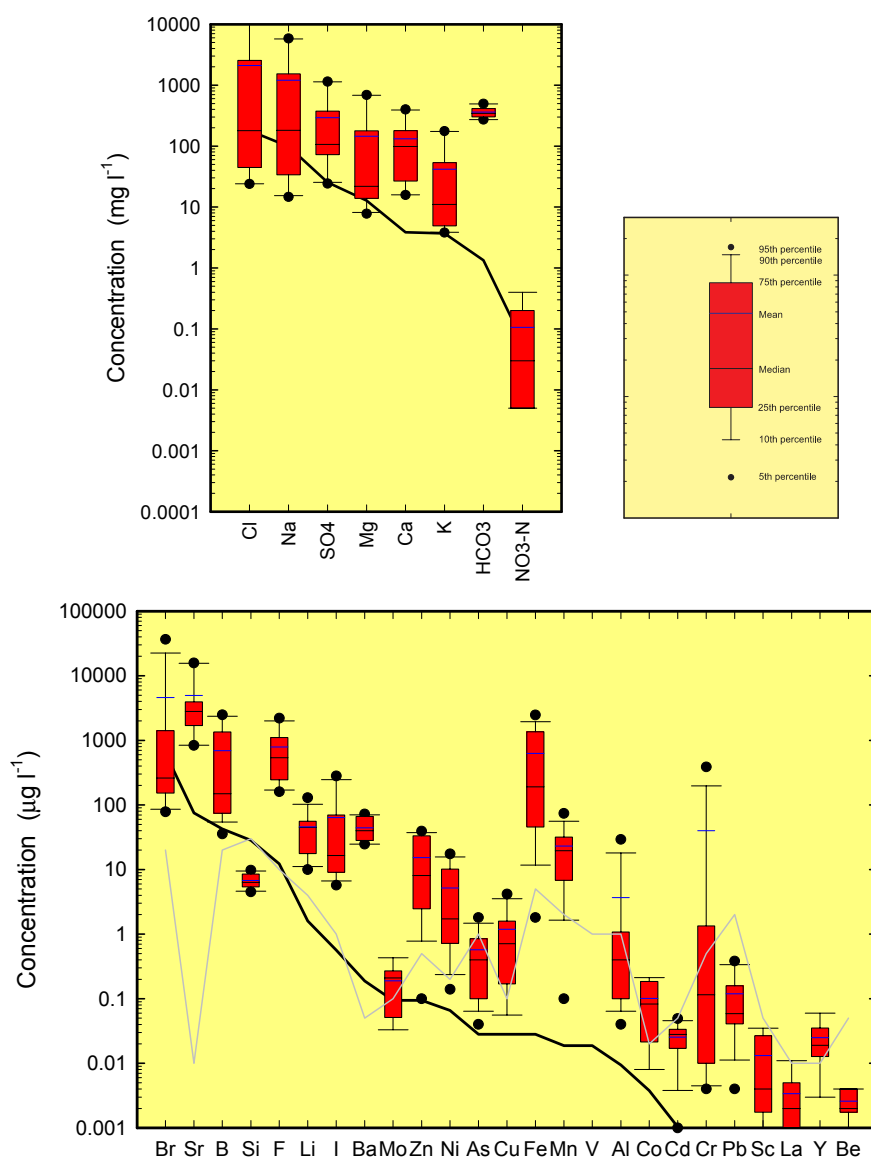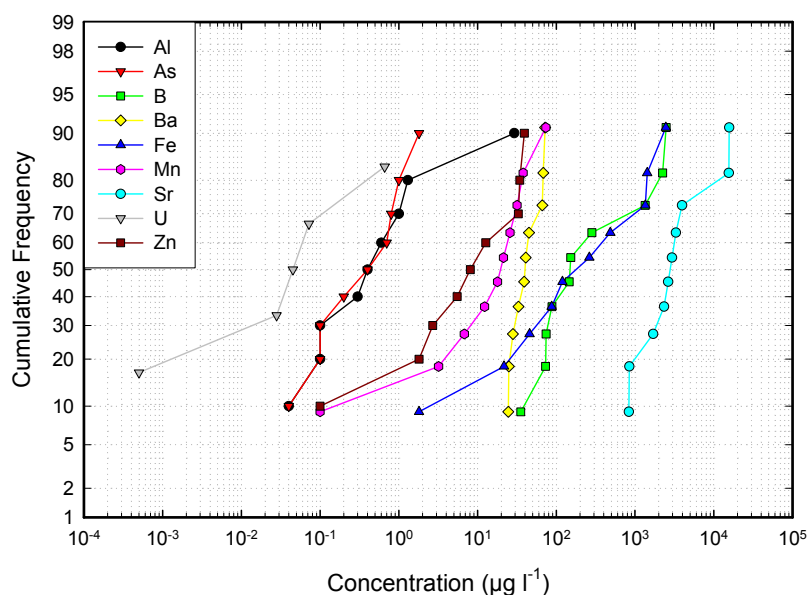

Figure 5.7 **Cumulative-frequency diagram for minor constituents from reducing groundwaters in the Chalk aquifer.**

Chemical constituents in the groundwaters from the confined aquifer, most of which are reducing, generally show a much broader range of concentrations and many have a bi-modal distribution (e.g. K, Mg, Na, SO_4, Cl, B, Sr; Figure 5.6, 5.7). Many of the trace-element cumulative frequency distributions, particularly for the oxidising groundwaters, are affected by analytical uncertainties. Vertical sections of the curves for many trace elements in Figure 5.5 indicate limitations on data presentation and interpretation imposed by detection limits (which may vary in concentration for a given element because of the use of a diverse set of analytical data from different laboratories and equipment).

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Dominant geochemical processes

Some of the key factors involved in generating the regional variations in groundwater chemistry across the Chalk aquifer of north Kent and east Surrey are outlined below. The main features of the major-, trace-element and isotopic compositions are assessed in relation to geochemical processes and groundwater residence times. Chemical variations along three groundwater flowlines (Crayford–Lullingstone, Sheppey–Highstead and Reculver–Folkestone transects) are also discussed. When interpreting variations in regional water-quality data it is important to bear in mind the variations that may arise as a result of factors such as differences in borehole design and construction, tapping of different stratigraphic horizons in a given aquifer, and differing borehole pumping histories. Differences in borehole design, including variations in casing and well depth may lead to localised water-quality variations. Differences in aquifer lithology may include facies changes and variations in type and degree of cementation. Variations in pumping history may also have imposed differences in water quality as differing pumping rates may affect the degree of flushing of solutes from parts of the aquifer. Pumping may also have induced vertical or lateral flow from overlying Palaeogene and Quaternary sediments where present, or of more saline pockets of groundwater in coastal areas. Such chemical variations are quite apart from the variations observed along groundwater flow lines that result from progressive water-rock interaction processes with increased residence time in aquifers. It is beyond the scope and resources of this project to assess in detail the factors influencing water quality for each of the boreholes in the sample set. The report presents a broad assessment of the groundwater-quality variations observed across the aquifer and the main geochemical processes that are likely to control them. It is accepted that some water-quality variation may be due to the factors described above.

One of the most important factors affecting the chemical compositions of the Chalk groundwaters of the region is carbonate reaction. This is rapid and leads to strongly buffered groundwater compositions. As the northern section of the North Downs aquifer along the estuarine and coastal margin is confined respectively by Tertiary sediments of the Thanet Beds and the London Clay, groundwaters in this section become confined and redox processes become an important control on the water chemistry, with the redox boundary (Box 6.1) marking a zone of significant change in groundwater compositions. Saline intrusion is observed in groundwater from some estuarine and coastal sites and this has a marked effect on chemical composition locally. While most groundwater samples affected by saline intrusion are reducing groundwaters from the confined aquifer, one sample in the dataset is an oxidising groundwater from the coastal Medway area (Akzo Nobel borehole, [TQ 7776 6040]). This sample has a relatively high salinity (Cl 392 mg l^{-1}) and hence skews the distribution of the oxidising groundwater set to some extent. The effect of such outliers is minimised by use of the median and 2σ values rather than the maxima.

As most abstraction for public supply and industrial use is from the unconfined Chalk aquifer, groundwater pollution from agricultural, industrial and domestic sources is also an important issue in some areas. Concentrations of nitrate are high in some groundwaters from the unconfined aquifer, and pesticides and organic solvents have also been detected in some abstraction sources. These are monitored closely by the Environment Agency and the water companies. Many of these processes act together and it is therefore difficult to separate out the effects of individual processes on the major- and trace-element compositions of the Chalk groundwaters from the region (Box 6.2).

BOX 6.1 REDOX BOUNDARY
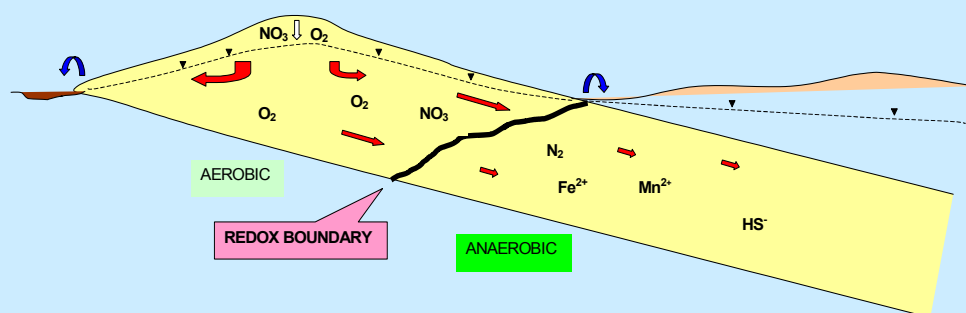
Water at recharge is generally saturated with dissolved oxygen at the partial pressure of the atmosphere (10–12 mg l^{-1} depending upon barometric conditions). Passing through the soil and the unsaturated zone, some of this O_2 will react as a result of microbiological processes and oxidation-reduction reactions. However, almost all water reaching the water table still contains several mg l^{-1} O_2. Geochemical reactions (oxidation of traces of pyrite, organic matter and Fe^{2+} present in minerals) progressively remove the O_2 along flow lines. Once all the oxygen has reacted, an abrupt change of water chemistry takes place (at the redox boundary). Other changes may occur downgradient of the redox boundary, especially denitrification and likely increases in concentrations of dissolved iron (Fe^{2+}). Sulphate reduction and the production of sulphide (H_2S as HS^- in solution) may also occur at greater depths.

6.1.1   Major-element variations

Recharge to the Chalk aquifer of Kent occurs over the North Downs outcrop area and infiltrating groundwaters reach equilibrium rapidly with the Chalk matrix. They therefore show the typical features of carbonate-dominated groundwaters. Most are saturated or near-saturated with respect to calcite and the pH values are buffered at near-neutral compositions. The groundwaters have typically high total hardness and high Ca concentrations.

The groundwater compositions evolve downgradient from the unconfined to the confined aquifer. In the unconfined section, most of the groundwaters are fresh with Ca and HCO_3 as the dominant ions. These give way downgradient to waters which become progressively more Na-Cl dominant as a result of saline water intrusion. Ion exchange (Na with Ca) is also a likely factor in the near-coastal groundwaters. A few confined groundwater samples observed with Na-HCO_3-dominant compositions (Figure 5.1) are most likely the result of 'freshening' of salinised sections of the Chalk, where relatively young fresh recharge water has partially flushed saline groundwater from the aquifer. These are found in parts of the confined aquifer from the Isle of Sheppey and near Reculver.

Sodium and Cl also increase as a result of pollution in some outcrop areas, and concentrations of each element in excess of 50 mg l^{-1} are not uncommon. The regional variations in Na concentration are shown in Figure 6.1.
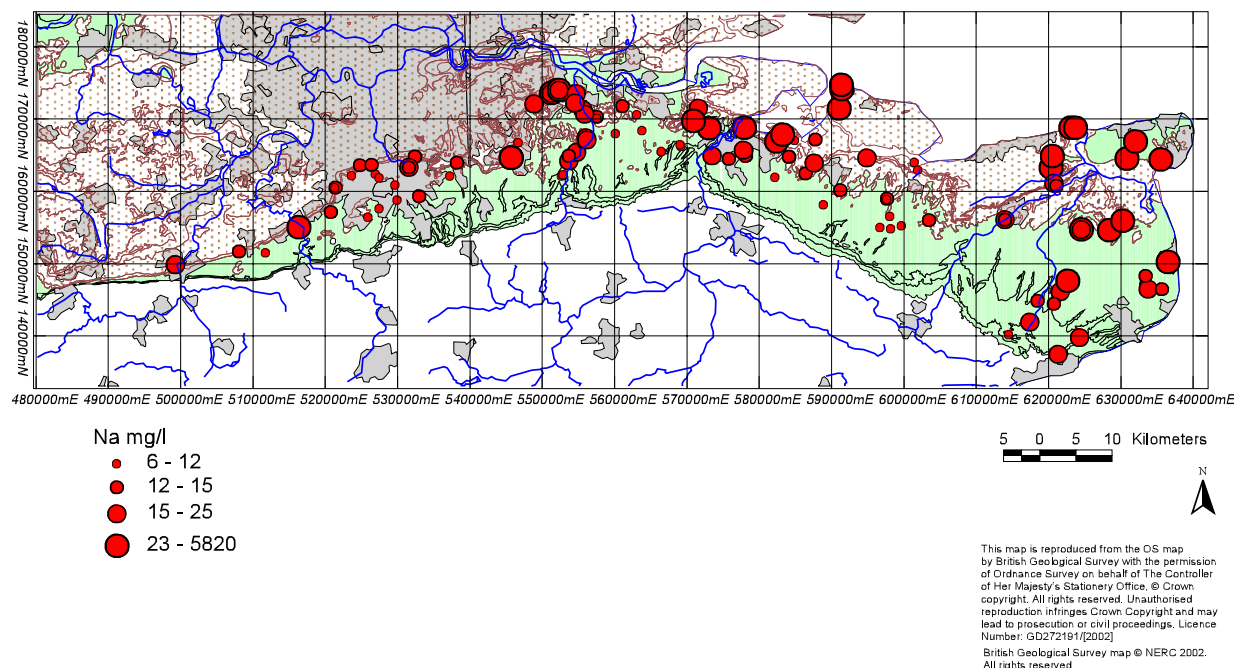
Figure 6.1   Regional variation in Na concentration (mg l⁻¹) in groundwater from the Chalk of North Kent and east Surrey.
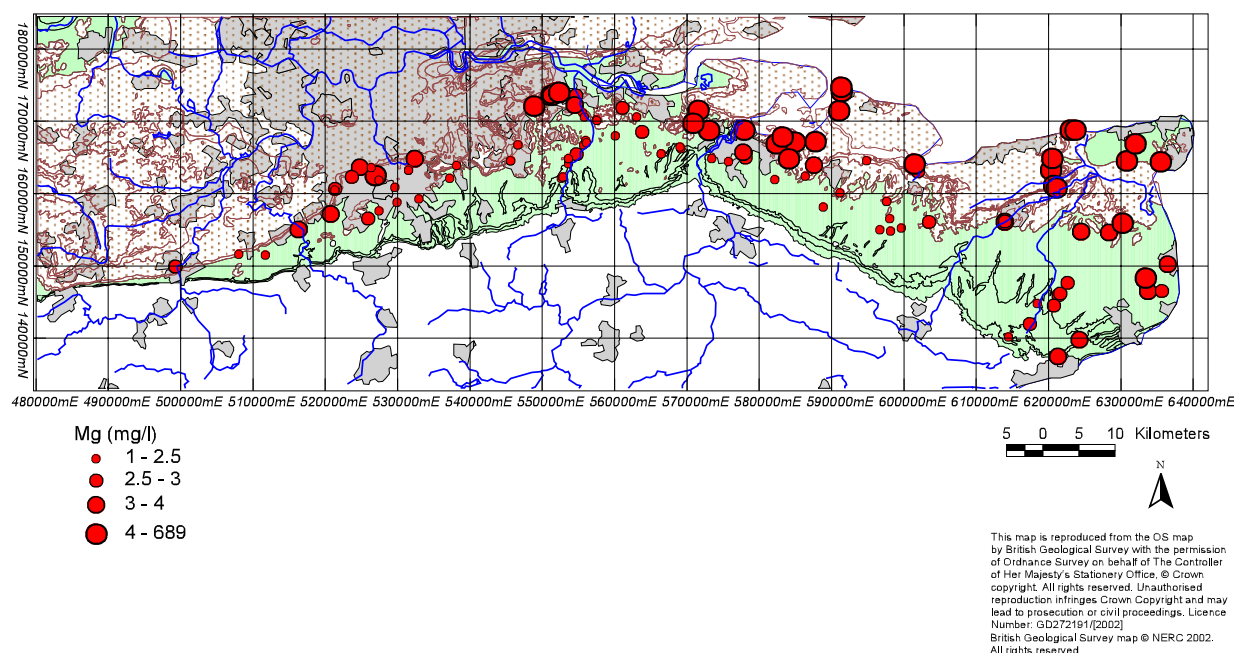
Figure 6.2   Regional variation in Mg concentration (mg l⁻¹) in groundwater from the Chalk of north Kent and east Surrey.

Saline intrusion (and ion exchange) also has an impact on several other major elements, with increased concentrations of Mg, K, HCO_3 and SO_4 in the more saline groundwaters. Regional variations in Mg concentrations are shown in Figure 6.2. The distribution generally shows low concentrations (1–27 mg l⁻¹, typically <3 mg l⁻¹) in the Chalk outcrop areas, consistent with reaction of low-Mg calcite, but increasing concentrations below the confining cover of Thanet Sands and other Palaeocene formations (7.7–689 mg l⁻¹), likely as a result of ion exchange and possibly some influence of solute leakage from the overlying sediments. High Mg in the groundwaters from the

coastal sections of the aquifer are likely a result of saline intrusion. Variations of Mg concentrations with Cl (Figure 6.3) indicate that many of the Chalk groundwaters have Mg concentrations greater than diluted seawater and demonstrate that Mg has increased in the groundwaters relative to compositions representing simple mixtures between seawater and fresh recharge water, as a result of additional inputs from the Chalk sediment.
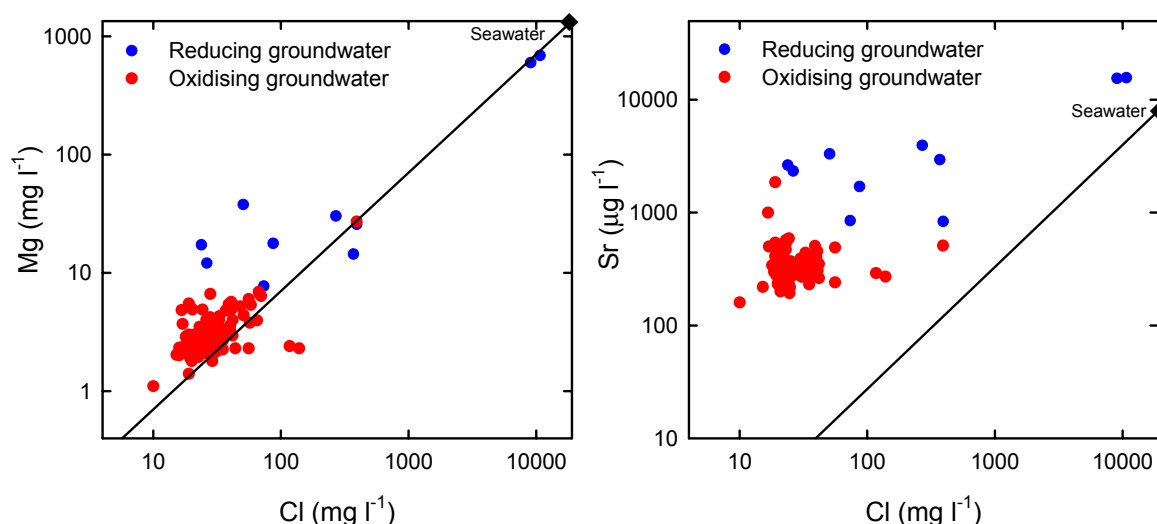
Figure 6.3   Variations in Mg and Sr with Cl in groundwaters from the Chalk of North Kent. The seawater dilution curve is also given for comparison.

Some increases in K and SO_4 in groundwaters from the confined aquifer may also derive from leakage from the overlying Tertiary sediments. However, increases in these elements above expected baseline concentrations in fresh groundwaters from the outcrop (concentrations up to 14 mg l^{-1} and 115 mg l^{-1} respectively), particularly observed in the Darent catchment, may be related to pollution. Leachate from landfills in particular may have contributed towards the increased concentrations of these elements. Diffuse pollution from agricultural sources is also likely.

Under the oxidising conditions in the unconfined aquifer, nitrate is a stable species in solution. Concentrations of NO_3-N in groundwater from rainfall inputs (Table 3.2) would be expected to amount to around 5 mg l^{-1} or slightly higher, allowing for additional inputs of naturally derived nitrogen from the soil zone. This is already a figure influenced to some extent by anthropogenic factors, including atmospheric increases caused by combustion of fossil fuels and agricultural activities. Hence, a value of 5 mg l^{-1} is likely an upper estimate of baseline concentrations of NO_3-N in the aquifer. In practice, many of the oxidising groundwaters from the unconfined aquifer have concentrations much higher than 5 mg l^{-1} as a result of pollution from agricultural, urban and industrial sources. Hence, NO_3-N concentrations in groundwaters from the unconfined aquifer often reach close to or in excess of the EC maximum permissible value for drinking water of 11.3 mg l^{-1} (up to 28 mg l^{-1} observed). The regional distribution of groundwater NO_3-N concentrations is shown in Figure 6.4. In the outcrop area, values of NO_3-N in excess of 6 mg l^{-1} (median value) are common, but are lowest (often <4 mg l^{-1}) in the central North Downs (Throwley to Nashenden), perhaps reflecting smaller applications of agricultural nitrate, smaller nitrate leaching losses and/or lower inputs of urban pollutants in that area. Land-use mapping (Figure 3.2) does not provide conclusive evidence for these possibilities however.

Figure 6.4 **Regional variation NO₃-N concentration (mg l⁻¹) in groundwater from the Chalk of North Kent and east Surrey.**

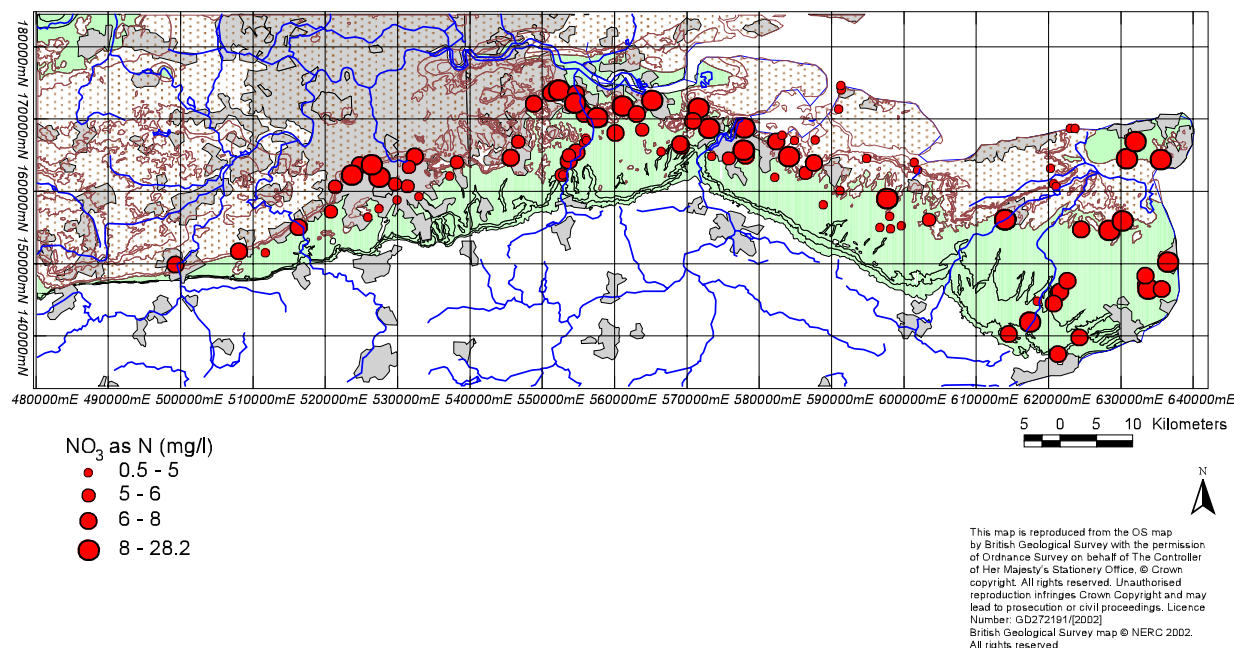In the confined aquifer, the reducing conditions observed produce groundwaters with low nitrate concentrations, either due to denitrification or to the presence of pre-modern (unpolluted) recharge. The relatively high concentrations of NH_4-N observed in the confined aquifer (up to 4.4 mg l⁻¹; Table 5.1) are a relatively common feature of groundwaters from reducing aquifers and are considered to be naturally-derived, rather than as a result of local pollution. Potential release processes include decomposition of organic matter and desorption of NH_4^+ from clay-mineral surfaces, especially under more saline (high Na) conditions.

Box 6.2 **How can we distinguish pristine waters from polluted groundwater?**

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

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

6.1.2   Trace-element variations

A number of analysed trace elements also demonstrate the prominent effects of carbonate reaction, redox processes and saline intrusion. Pollution is also likely to have impacted the concentrations of some trace elements in the unconfined section of the aquifer.

One of the main trace elements controlled by carbonate reaction is Sr. This is commonly found as a substitute for Ca in the calcite structure and is therefore often found in high concentrations in chalk. Concentrations in the pure white-chalk of Kent are around 390–740 mg kg^{-1} (Table 3.1). As described in Section 5.2, concentrations of Sr are generally low in the unconfined aquifer but reach up to 16 mg l^{-1} in the confined near-coast section of the aquifer. Increases in Sr concentration can also be related to saline intrusion, but since Sr in seawater has a concentration of around 8 mg l^{-1} (Hem, 1992), not all the observed dissolved Sr in the coastal groundwaters can be seawater-derived. This effect is seen particularly clearly in Figure 6.3, where Sr concentrations in the groundwaters are much higher than diluted seawater concentrations. The relative increases are also much greater than are observed for Mg. The extreme Sr concentrations in the brackish groundwaters indicate significant mineral reaction (calcite and possibly aragonite and celestite) as a result of chalk diagenesis and imply a prolonged groundwater residence time. Similar enrichments in Sr have been recorded in porewaters from deep chalk boreholes elsewhere in Britain (Edmunds et al., 1992) and have been attributed to water-rock reaction given long residence times in the Chalk aquifer. Barium is also likely to derive in part from dissolution of the chalk: concentrations of Ba in typical white-chalk facies samples are in the range 130–220 mg kg^{-1} (Table 3.1). Concentrations of Ba vary between the unconfined and confined sections as described in Section 5.2, being generally lower in the groundwaters from the confined aquifer. The lower values reflect barite (BaSO$_4$) solubility control in groundwaters with higher SO$_4$ concentrations.

Some of the key trace-element indicators of saline intrusion are B, Li and Br, and to some extent I and F. Variations in Br concentration in the groundwaters suggest that increases are specifically related to saline intrusion in the coastal areas. Observed concentrations in groundwaters from the Isle of Sheppey and Reculver have Br compositions which lie on a simple mixing line between rainfall and seawater (Smedley et al., in press) and indicate that little additional Br has been derived from mineral reactions in the aquifer.

Dissolved I also shows a distinct range of compositions in the groundwaters, with much higher values observed in the confined sections. The increases are likely to be related to the effects of saline intrusion. However, concentrations in the brackish groundwaters increase significantly above those in typical seawater (around 60 µg l^{-1}; Hem, 1992). As with Sr, this suggests that values are further enhanced by water-rock reaction. Potential sources of I include organic matter in the chalk and the carbonate matrix itself. Development of high I concentrations also implies that the brackish groundwaters have had a prolonged residence time, though more precise dating is not possible with the trace elements alone.

The regional variations in dissolved fluoride also show a relationship with salinity and groundwater residence time. Generally low values in the outcrop groundwaters (typically <100 µg l^{-1}; Figure 6.5) result from short residence times of groundwater in the aquifer. Reaction of groundwater with F-bearing minerals under these conditions will have been relatively minor. Dissolved F concentrations increase in the reducing, more saline groundwaters as a result of ion-exchange reactions and mixing. These processes produce groundwaters with high Na and relatively low Ca concentrations which can build up higher concentrations of dissolved F before saturation with respect to the mineral fluorite (CaF$_2$) is achieved. The dominant sources of fluoride are likely to be fluorapatite in the chalk. Concentrations of dissolved F reach up to 2.2 mg l^{-1} in the confined groundwaters. Concentrations of P also reach higher extremes in these confined samples, as a result of natural mineral reaction, principally of apatite and fluorapatite.
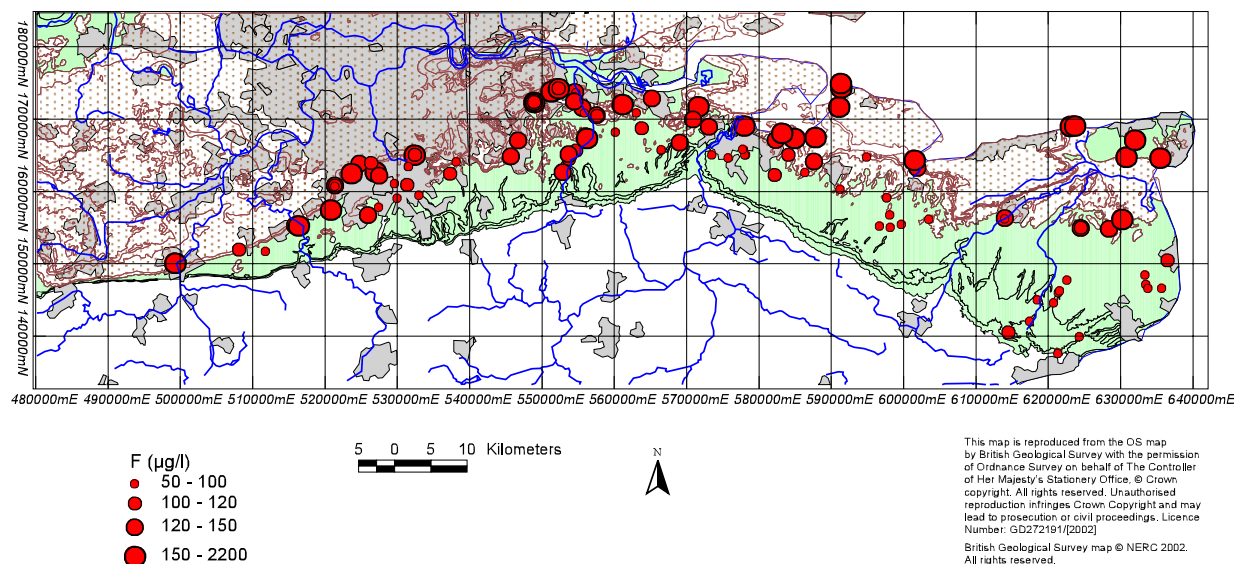
Figure 6.5 **Regional variation in F concentrations (µg l⁻¹) in groundwaters from the Chalk aquifer of north Kent and east Surrey. The variations reflect groundwater residence time and the influence of ion exchange in more saline waters.**

Diagnostic trace elements indicative of changing redox conditions across the aquifer include Fe and Mn in particular. In the unconfined aquifer, concentrations of dissolved Fe and Mn are low as a result of the oxidising conditions. However, concentrations increase where groundwaters become anaerobic under confined conditions. Greatest increases are seen with Fe, which is found occasionally in excess of 2 mg l⁻¹. Increases in Mn are less extreme, but nonetheless reach up to 74 µg l⁻¹ in the confined groundwaters. Both are principally derived by natural dissolution (principally of iron and manganese oxides) under the reducing conditions.

Regional variations in dissolved Zn are shown in Figure 6.6. Concentrations are high in a number of the groundwater sources from the unconfined aquifer (up to 520 µg l⁻¹ compared to a maximum of 39 µg l⁻¹ in the confined aquifer). The high values are indicated by a flexure in the cumulative-frequency plot (Figure 5.5). The source of the high Zn values is unclear. They may be derived from sulphide minerals in the chalk (notably pyrite) by oxidation of the minerals in the aerobic aquifer conditions. They may alternatively be associated with pollutant inputs, such as from landfill sites. Zinc is often a significant trace metal in landfill material. Christensen et al. (1994) gave Zn concentrations in the range 0.03–1000 mg l⁻¹ for landfill leachate from mixed domestic, commercial and industrial waste, representative of typical landfill sites (excluding concentrated chemical waste). Landfills therefore represent possible sources of Zn for some of the groundwater samples investigated. However, the distribution of Zn in the groundwaters does not show any clear relationship with the locations of waste-disposal sites in the area (Figure 3.2) and so this association remains speculative. Concentrations of Zn appear to be relatively low south of Sittingbourne and in east Kent (Figure 6.6) but are high (>50 µg l⁻¹) in borehole sources at Capstone, Lullingstone, Effingham, Belmont and Thanington.

Lower concentrations of Zn in groundwater from Chalk below Palaeogene sediments (Figure 6.6) may be a result of retardation of Zn (and possibly other trace metals) from pollution sources by the overlying Palaeogene silts and clays. Lack of oxidation of Zn-bearing sulphide minerals (pyrite) in the Chalk under the reducing conditions is also a possible cause.

The sources of other trace metals such as Cd, Cr, Cu, Pb, and Ni in the groundwaters are also unclear. As with Zn, these elements may be present at significant concentrations in domestic landfill leachate (Christensen et al., 1994). Higher median Cu concentrations are observed in the unconfined

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groundwaters compared to those in the confined aquifer and it is possible that landfills have had an impact on Cu concentrations in the unconfined groundwaters. Sporadic high values are observed in groundwaters from boreholes at Gore, Strood and Southfleet in the unconfined aquifer. If landfills are responsible for increased concentrations of some trace metals in unconfined groundwaters, the effect is likely to be localised because of the strong adsorption capacity of metal oxides and clays for trace cations (Christensen et al., 1994). Like Zn, contamination with Cu from borehole metalwork or oxidation of sulphide minerals are also possible sources, although there is no apparent correlation between dissolved Cu and Zn concentrations.

As noted in Section 5.2, the concentrations of most other analysed trace elements are low in the near-neutral conditions found in the Chalk groundwaters. The regionally low concentrations of As even in the confined aquifer are worthy of note given the reducing nature of the confined groundwaters. Concentrations in other aquifers are sometimes observed to increase under such conditions, although concentrations in reducing Chalk groundwaters elsewhere in the UK are also often low or very low ($<5 \mu g \, l^{-1}$).

Observed increases in dissolved P in the confined groundwaters (up to 0.3 mg l^{-1}) are taken to be a function of natural reaction with P-bearing minerals, notably fluorapatite in the aquifer, rather than a result of pollution from agricultural or industrial sources.
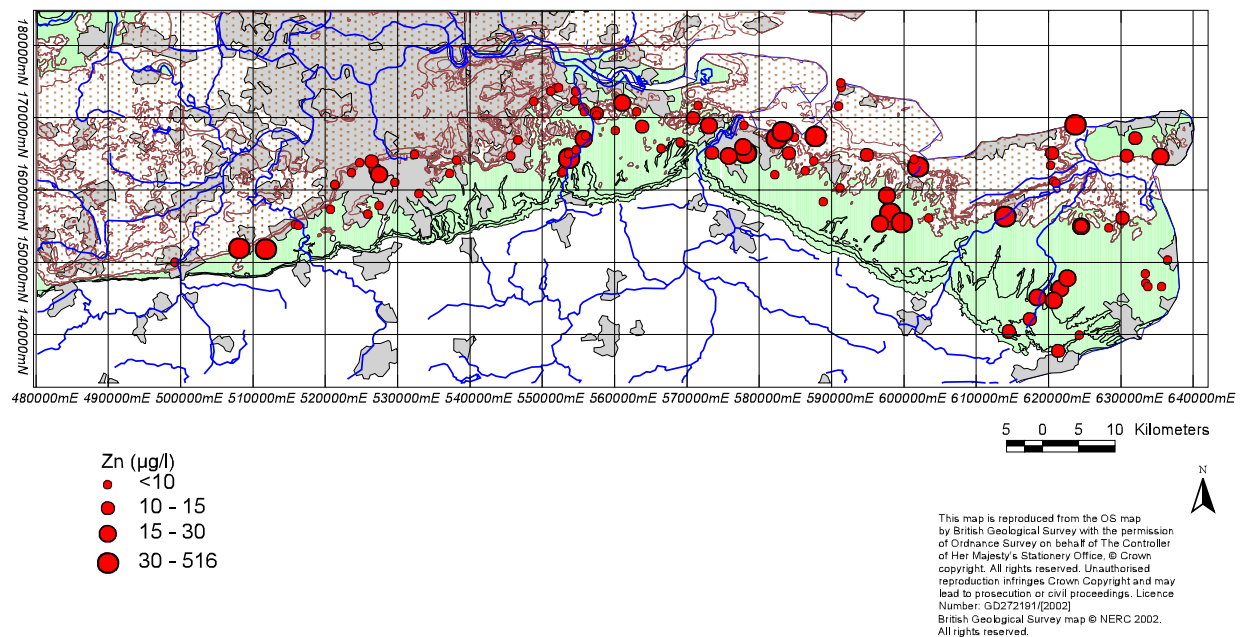

Figure 6.6   Regional variation in Zn concentration ($\mu g \, l^{-1}$) in groundwaters from the Chalk aquifer of north Kent and east Surrey.
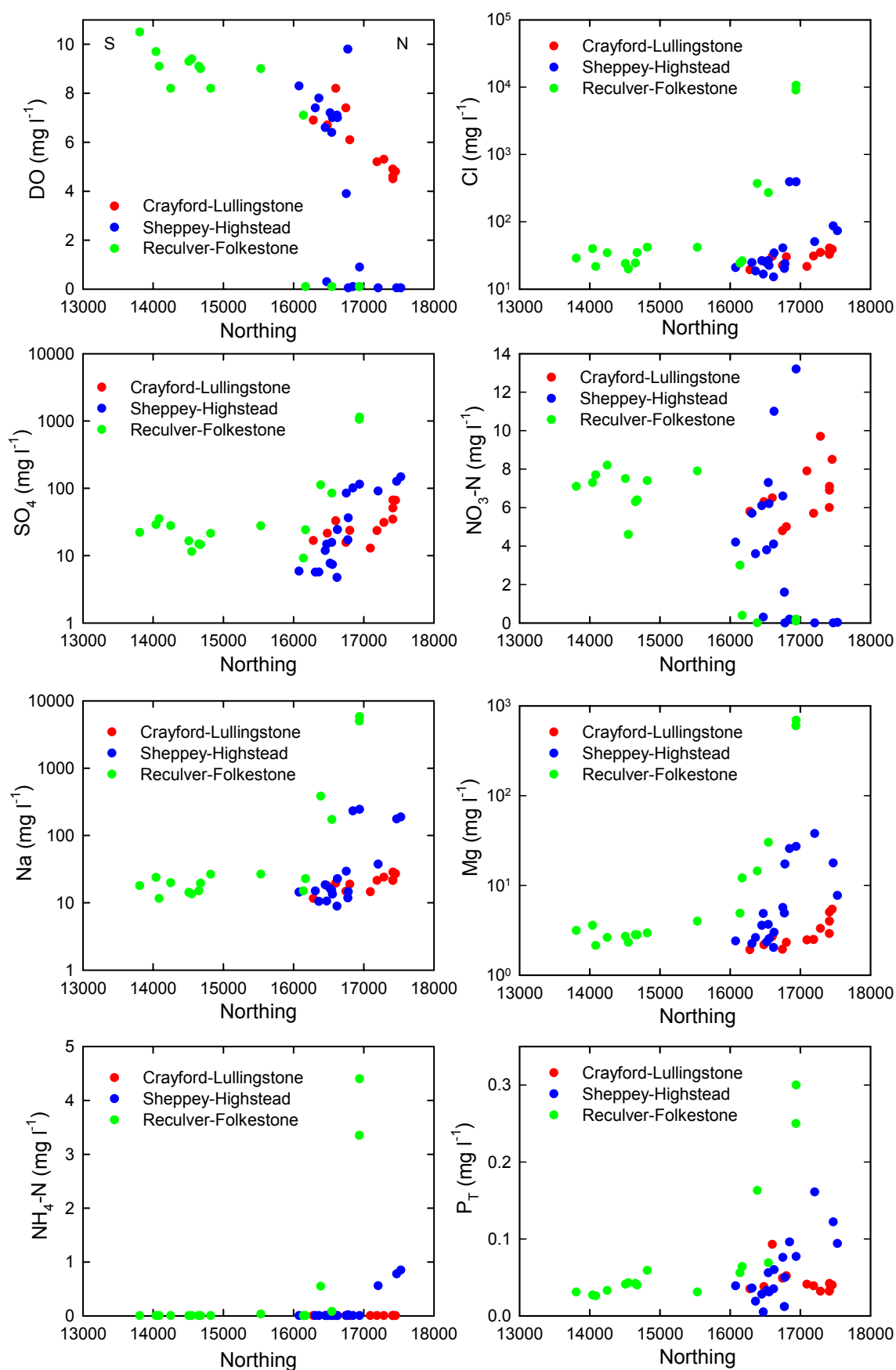
Figure 6.7 Variation of a selection of chemical parameters in groundwaters along three north-south transects in the Chalk aquifer. Location of transects is on Figure 2.1.

6.2 Regional variations along flow lines

Three transects of the Chalk aquifer have been investigated in more detail in this project. These are the Crayford–Lullingstone transect in the west of the region, the Isle-of-Sheppey–Highstead transect in the central region and the Reculver–Folkestone transect in the eastern part of the region. Samples collected from these transects are highlighted in yellow in Figure 2.1. A description of the chemical variations along each of them, together with information obtained from previous BGS projects in the region, are given below. Plots of the distribution of a number of major and trace elements are given for the three transects in Figures 6.7–6.9. As the transects are each aligned roughly north-south, the x-axes in each of these plots are the Northings values.

6.2.1   Crayford–Lullingstone (Darent) transect

All samples collected from this transect across the aquifer were from the oxidising, unconfined section, most being from public-supply sources. Dissolved oxygen concentrations were in the range 4–8 mg l^{-1} and all are fresh groundwaters with low Na, Cl, SO$_4$ concentrations. Figures 6.7–6.9 demonstrate that concentrations of many of the major and trace elements are low (e.g. Mg, NH$_4$-N, Ba, Cr, Cu, F, Fe, Li, Mo, Ni, Sr) or very low (Co) in these groundwaters compared to those from the other transects. These are probably low mainly as a result of the groundwaters having not undergone changes imposed by redox reactions or increases in concentrations resulting from saline intrusion. Figure 6.9 shows that U concentrations are relatively high however in these groundwaters. Uranium is known to be relatively mobile in hexavalent form under oxidising conditions. Uranium sources are most likely to be iron oxides in the carbonate matrix and along fractures. Concentrations typically diminish in reducing groundwater as reduction to tetravalent U initiates precipitation, or in the case of the Chalk aquifer, more likely adsorption onto metal oxides in the sediment. Concentrations of U in the Crayford–Lullingstone waters reach up to 1.3 µg l^{-1}, the highest observed in this study.

Slight trends are observed in a number of constituents along the transect. Increases are noted for example in concentrations of SO$_4$, Mg, B, F, Sr and U and slight decreases in dissolved oxygen. The reasons for this are not clear, but increasing residence time of groundwater along the flow gradient may be a factor.

6.2.2   Sheppey–Highstead transect

Samples in this transect include those collected specifically for this project as well as previous samples collected as part of an investigation of palaeowaters in the coastal Kent aquifer (PALAEAUX, 1999; Edmunds et al., 2001). The samples (18 in total) span the range from fully oxidising (DO 10 mg l^{-1}) to reducing groundwaters (DO <0.1 mg l^{-1}; Figure 6.7). Nitrate concentrations similarly span a large range from almost 14 mg l^{-1} at outcrop to below-detection-limit values in the reducing aquifer. Ammonium shows the converse relationship, with NH$_4$-N concentrations up to 1 mg l^{-1} under reducing conditions.

Most of the groundwaters from the transect are fresh, although those from the Isle of Sheppey at the northern end of the transect have Na concentrations of around 180 mg l^{-1} and Cl 100 mg l^{-1} or less. These indicate that some saline intrusion is likely to have taken place (age of seawater influx unknown) although given the fact that boreholes from the Sheerness area are directly on the present-day coast, the effect is relatively small.

Figure 6.8 **Variations in a number of trace elements in groundwaters from three north-south transects across the North Kent Chalk aquifer.**

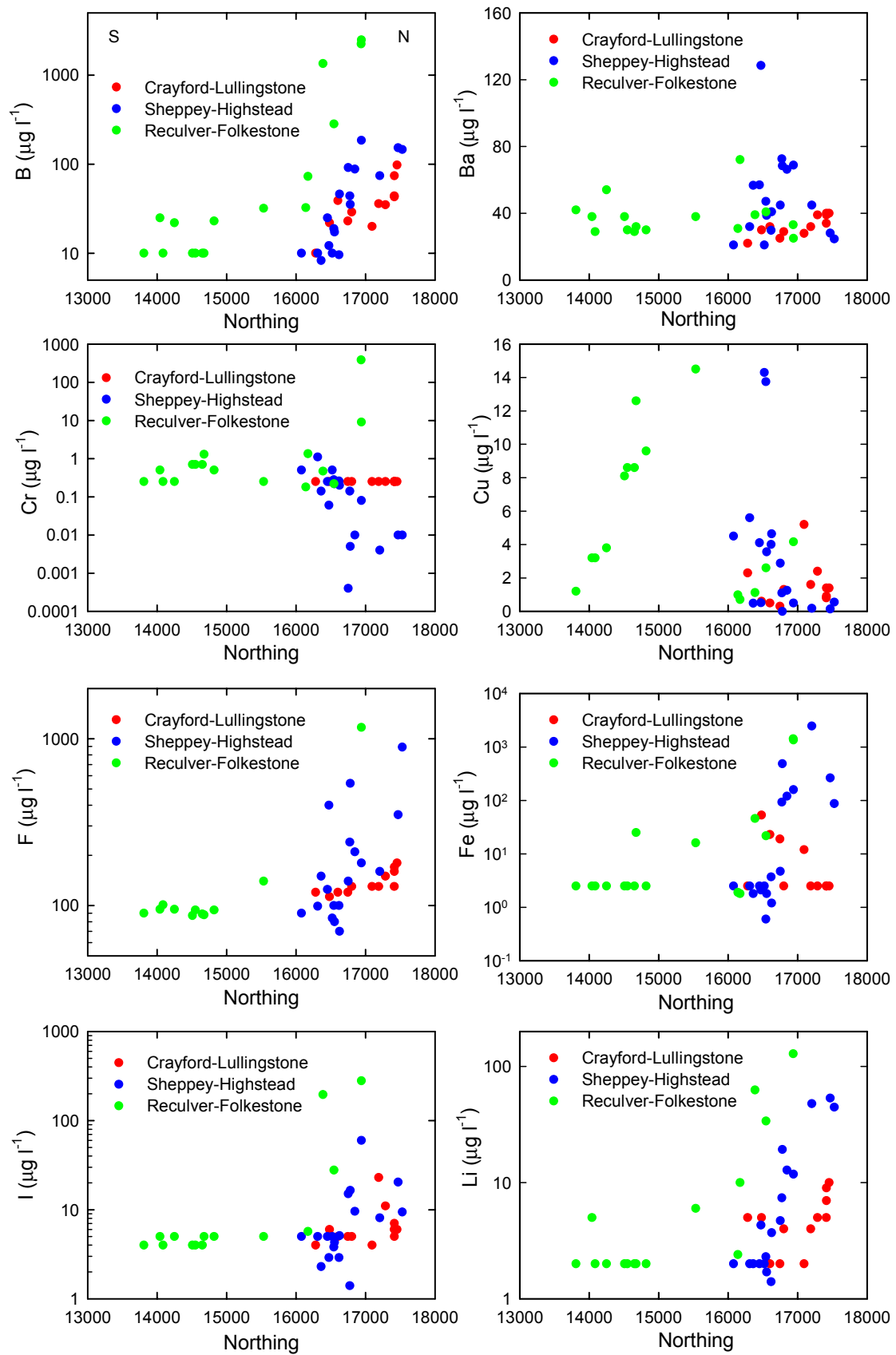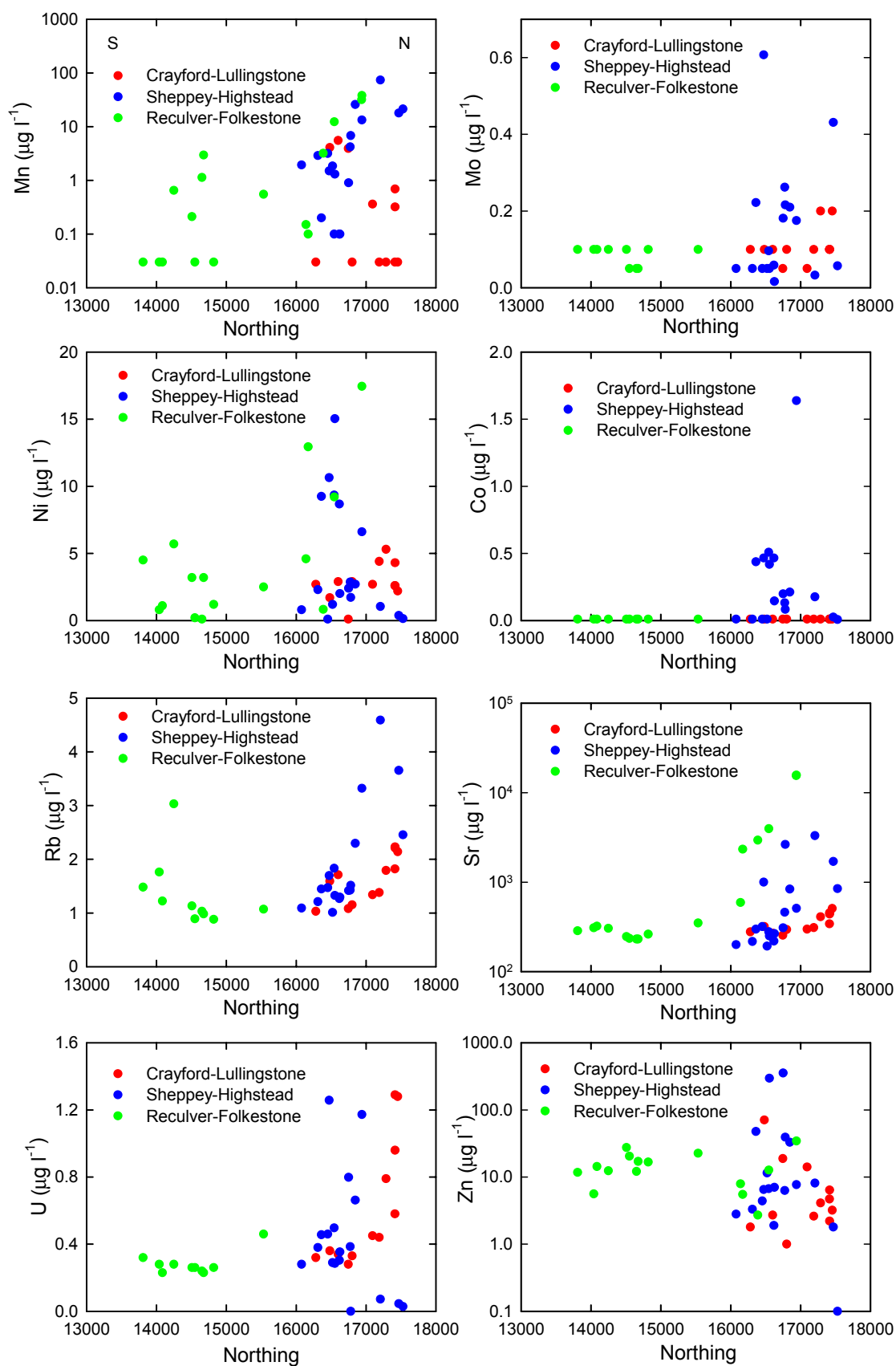**Figure 6.9** **Variations in a number of trace elements in groundwaters from three north-south transects across the North Kent Chalk aquifer.**

The samples have relatively high concentrations of Fe and Mn under reducing conditions (up to 2500 μg l⁻¹ and 100 μg l⁻¹ respectively). Concentrations of Mo, Ni, Co, Rb, and Zn are also relatively high compared to those in groundwaters from other transects (Figures 6.8, 6.9), although they are not unusually high relative to compositions in other aquifers and the values are not generally of concern for drinking-water purposes. Fluoride concentrations are high (up to 1 mg l⁻¹) in the confined aquifer, but this value is still below the EC maximum permissible value for F in drinking water (1.5 mg l⁻¹). As mentioned above, the build-up of F in the groundwater reflects in part extended residence time of the groundwater in the aquifer and in part, the high-Na, low-Ca compositions of the near-coastal groundwaters.

Combined trace-element and isotopic investigations of confined groundwater samples from the Isle of Sheppey and Medway areas (Edmunds et al., 2001) have highlighted the presence of old groundwater in this part of the aquifer. Groundwater from a deep (>150 m) borehole at Sheerness had an observed ¹⁴C activity of less then 5 percent modern carbon (pmc) and depleted δ¹⁸O values (-8.4‰) compared to groundwaters from the unconfined aquifer upgradient. This suggests that groundwater was emplaced during a colder period earlier in the Quaternary (possibly late Pleistocene). Although as noted above, salinity is slightly elevated in groundwater from this part of the aquifer, the fact that these groundwaters are not highly saline (electrical conductance of around 1000 μS cm⁻¹) indicates that subsequent saline intrusion has not occurred or has been minimal. The thick cover of London Clay in the Isle of Sheppey and relatively large distance from the North Downs recharge area are likely to have protected the aquifer from recent saline intrusion and preserved the existence of old 'fresh' groundwater. The existence of such palaeowaters is however of rather localised extent in north Kent.

6.2.3   Reculver–Folkestone transect

Groundwaters from the Reculver–Folkestone transect (Figure 2.1) also span the range from oxidising to reducing compositions. Dissolved-oxygen concentrations range from >10 mg l⁻¹ to below detection limits. Nitrate concentrations were only observed in this transect up to 8 mg l⁻¹ (Figure 6.7). Groundwaters from this region show the largest ranges in major- and trace-element concentrations and those near the coast (Reculver) are the most saline samples observed in the study. Extremes in concentrations of Cl, Na, Mg, SO₄, P and Sr are all related to saline intrusion. The Reculver groundwaters also have the highest observed concentrations of NH₄-N (up to 4.4 mg l⁻¹). Unfortunately, many trace elements were not analysed in the samples investigated by Buckley et al. (1996), PALAEAUX (1999) and Edmunds et al. (2001). Data for many elements given in Figures 6.8 and 6.9 are therefore missing from the confined section of the transect.

Detailed investigations of groundwater chemical and isotopic evolution along a flowline from Stodmarsh [TR 2090 6139] to Reculver [TR 22 69] in north-east Kent have been reported previously by Buckley et al. (1996) and summarised by PALAEAUX (1999) and Edmunds et al. (2001). Data for groundwater samples from Stodmarsh, Hoplands Farm, Hoath and Ford indicate a complex regional picture of groundwater flow and chemistry. Groundwater from Stodmarsh is fresh, oxygenated and potentially young, having been recharged from outcrop Chalk some four km to the south-west, and/or having experienced some vertical leakage via the overlying Tertiary sediments. A low tritium concentration (1 tritium unit, TU) suggests that the Chalk groundwater from this site may represent a mixture of recent and older water. The groundwater sampled from Stodmarsh is the most oxygenated, the least mineralised and the least evolved along the flow line studied by Buckley et al. (1996).

Hoplands Farm is just 500 m north-west of Stodmarsh but despite its proximity, has a distinctive chemistry, being reducing and with a low tritium value (0.3 TU) and slightly more depleted stable-isotopic composition (δ¹⁸O –7 ‰; δ²H –51 ‰), suggesting an older generation of groundwater. Groundwater from Ford has a small component of young groundwater evidenced by detectable tritium (possibly derived by inflow from the Isle of Thanet to the east as a consequence of pumping). However, ¹⁴C data for the groundwater from this borehole gave a model age of around 1000–2000

years and hence suggests that the groundwater is of mixed origin and age. Enhanced summer pumping of Ford groundwater encourages saline influx, probably of old trapped saline groundwater to the north of the site (Buckley et al., 1996).

Groundwater from Hoath, intermediate in the flow line between Hoplands Farm and Ford, is of distinct chemical and isotopic composition, being more saline (although apparently changeable with time) and much more depleted in ^{18}O and ^2H composition ($\delta^{18}O$ -8.1 ‰, δ^2H −58 ‰). The groundwater at this site is believed to be old, likely of pre-Holocene age. Hoath borehole lies within the axis of a local anticlinal structure (Figure 3.6). This has probably been a key factor in retaining old groundwater in this part of the aquifer by generating low-flow conditions locally (Buckley et al., 1996). Similar sluggish groundwater flow conditions were also postulated for two boreholes at Pluck's Gutter (West Stourmouth) [TR 272 638] and [TR 276 618], around 6 km to the south-east of Hoath (Shaw, 1981). This site is also located north of the east-west trending anticlinal structure (Figure 3.6) and has similar salinity characteristics to those observed at Hoath.

Groundwater from the two boreholes in the confined aquifer at the coast in Reculver has a reducing character, with a composition indicative of saline intrusion. Salinity of the groundwater pumped from the two boreholes at this site is around half that of modern seawater (Buckley et al., 1996). As noted above, the groundwater also has high concentrations of F (up to 2200 µg l^{-1}) and Sr (up to 16 mg l^{-1}), suggesting prolonged residence time of the groundwaters in the aquifer. The Reculver boreholes are at the end of the confined chalk groundwater flow system on land, but the system is assumed to continue offshore below the Thames Estuary, under an increasing thickness of Tertiary sediments. Isotopic data have provided more information on the age relationships of groundwater at Reculver and of their variations with depth (Section 6.3).

The local geological structure is also likely to have influenced the flow and salinity distribution in the confined aquifer around Reculver. The anticlinal and synclinal folds in the Chalk locally have axes running approximately parallel to the coast and also plunge, thus influencing the distribution of the Palaeogene confining beds. This not only impacts regional flow patterns but is also likely to have influenced the areas of past and present marine water inundation of the aquifer (Buckley, in press). The presence of the anticlinal structure in the area (Figure 3.6) may also explain why increased salinity occurs in groundwater from boreholes north of the structure compared with that in boreholes located to the south of it. The geological structure would have limited groundwater movement and hence the degree of refreshening of the aquifer with 'modern' fresh groundwater following earlier Holocene seawater invasion. The folding also provides a partial barrier to the inland advance of seawater, except where drainage has cut through the structures and allows short-circuiting (Buckley, in press). Such structural influences on groundwater stratification and regional flow have also been observed in the Chalk from the South Downs (PALAEAUX, 1999).

6.3   Variations in groundwater chemistry with depth

Relatively few investigations have been carried out of vertical variations in groundwater quality in the Kent Chalk aquifer, although some results are available from borehole logging and from specific studies of sections of the aquifer. Chemical variations with depth in the unconfined aquifer appear to be relatively small compared to those from the confined aquifer, although variations related to pollution may occur in some boreholes, particularly at shallow depths.

Several borehole depth profiles are available from studies carried out at Reculver (Buckley et al., 1996; PALAEAUX, 1999). Borehole logging and depth sampling of Reculver boreholes 1 and 2 and Hoath borehole, together with limited porewater profiling at Reculver, reveal variations in groundwater age and salinity that allow an interpretation of the regional groundwater flow patterns and history of development to be assessed.

Reculver 1 was drilled as an exploration borehole to a depth of 205 m depth in 1991 (Figure 3.6). The borehole penetrated 32 m of Palaeocene sands and clays (Thanet Sands) and 170 m of Chalk, including the Plenus Marls and Melbourne Rock. The site is just a few metres above high water and the static water level was found to be around 1.5 m above mean sea level. Reculver 2 was drilled in 1995 to a depth of 104 m.

Combined geophysical and flow logging, depth sampling and porewater profiling in the Reculver boreholes has revealed a distinct stratification of groundwater salinity with depth. A zone of high salinity (Cl up to 15,000 mg l^{-1}) was observed in the depth range 70–100 m (Figure 6.10), while groundwater in the chalk from <50 m and >140 m had lower salinity values, with Cl typically around 4000 mg l^{-1}. The chemical compositions reveal distinct similarities between fracture water (from pumped and bailed depth samples) and matrix water (extracted porewater). The similarities indicate equilibration between the fracture-hosted and matrix-hosted water bodies and imply limited recent groundwater movement (Figure 6.10). The two Reculver boreholes also showed close correlations in chemical profiles between each other, although comparison of the two profiles is not possible below 104 m depth due to the shallower total depth of the Reculver 2 borehole.

Flowmeter logging of the Reculver boreholes indicated that most of the pumping-induced groundwater movement in the aquifer was from the shallower parts of the Chalk. In Reculver 1, some 40% of the flow in the borehole was induced from a fracture at 56 m depth below surface, while in Reculver 2, 65% of the flow was from a number of fractures, all at less than 58 m below surface (Buckley et al., 1996). Little or no flow was induced from horizons below this depth. Fluid logging of the Reculver boreholes after a period without pumping showed invasion of the lower sections of the borehole with more saline groundwater as a result of gravitational settling of the higher-density saline water. Re-establishment of the tripartite division of groundwater salinity could be achieved by renewed pumping (Buckley, in press).

Isotopic evidence has confirmed that groundwater from Reculver boreholes is not of modern origin. Groundwater pumped from the boreholes was derived from the shallowest zone of brackish water (30–50 m depth) where the major flowing horizons occur. Measured tritium values in the pumped waters were low (<0.7±0.2 TU). Radiocarbon dating of pumped groundwater gave ^{14}C activities of 11.0–11.5 pmc, with model ages of several hundred to 2000 years. This indicates that the shallow Chalk aquifer from Reculver has a component of relatively young, but nonetheless still pre-modern, groundwater (Buckley et al., 1996). Groundwater in the middle saline zone has the closest composition to seawater observed in the profiles. This is thought to predate the groundwater from the shallow zone and is likely to have been emplaced in the aquifer following the major sea-level rise that was experienced across Europe (and beyond) in the early part of the Holocene, around 7500 years ago (Shackleton and Opdyke, 1973; Jelgersma, 1979; Edmunds et al., 2001).

Despite the similar salinity values of the pumped groundwaters and porewaters from the shallowest and deeper zone (35–70 m and >140 m below surface respectively; Figure 6.10), the stable isotopic composition of the deep groundwater is distinctive. The δ^{18}O compositions of deep porewaters for example are depleted (around -6 ‰ at 160 m depth) compared to porewater compositions at <100 m (ca. -4 to -5 ‰ at 50 m depth). This suggests that age differences exist between the two zones. The deep (>140 m) groundwaters are believed to be an older generation of groundwater, emplaced probably during the late Pleistocene (>10,000 years BP) at a time of low relative sea level and maintained in the aquifer as a result of poor aquifer permeability and hence lack of flushing. The groundwater from this lower zone has correspondingly high Sr, Ba and F concentrations, supporting evidence of prolonged residence time in the Chalk aquifer. Groundwater from the middle saline zone is interpreted as having undergone major influx of seawater at the time of the Holocene sea-level rise (ca. 7500 years BP). Brackish water in the shallowest horizons (<70 m) is interpreted as a more modern influx of relatively fresh water, emplaced in the last few hundreds to thousands of years by

aquifer refreshening subsequent to the influx of Holocene saline water in the middle section of the aquifer. Such refreshening will likely have been greatest in the shallowest sections of the Chalk because of the greater prevalence of fractures within the top 30 m or so of the formation. This more active flow appears to be above a prominent hard band, the Dover Top Rock (Buckley, in press). Development of these fractures may well have been promoted during the last glacial period, when a fall in relative sea level up to 130 m below that of the present day would have lowered base levels of erosion and generated more active groundwater flow (PALAEAUX, 1999; Buckley, in press). The morphology and depth of buried channels immediately offshore strongly suggest a link between the development of permeability and former hydraulic base level at around 50–60 m below ground level at the coast.
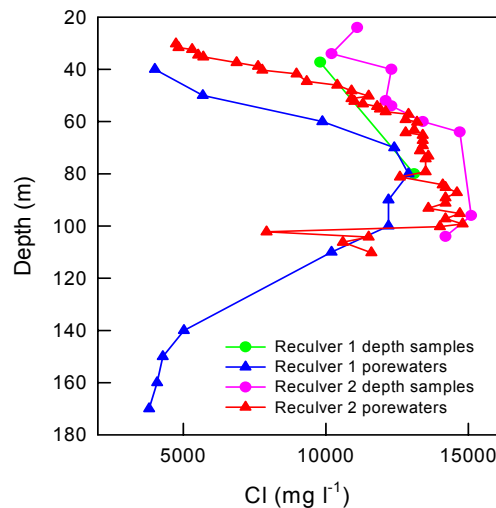

Figure 6.10   Variation in Cl concentration with depth in depth samples and porewaters from the chalk in two boreholes at Reculver (from PALAEAUX, 1999). The base of the Thanet Beds in these boreholes occurs at approximately 30 m below ground surface with the static water level some 2–3 m below surface.

6.3.2   *Hoath borehole*

Hoath observation borehole is 256 m deep and located around 5 km inland from the north Kent coast. The lithology comprises 63 m of Palaeogene strata overlying Upper Chalk and the borehole penetrates almost to the base of the Chalk sequence. The Plenus Marls horizon occurs at around 232 m below surface. Although the borehole is deep, the groundwater yield is rather poor and a large degree of drawdown has been observed during pumping (Buckley and Cripps, 1992). Salinity is very variable with depth. Depth samples collected in 1996 (Buckley et al., 1996) indicate a progressive increase in groundwater salinity with depth, electrical conductance increasing from 0.81 mS cm^{-1} at 80 m below surface to 2.32 mS cm^{-1} at 240 m depth. This increasing salinity profile may reflect density stratification in the borehole: earlier conductivity logs (e.g. Shaw, 1981) carried out after purging of the borehole, have demonstrated a freshening of groundwater below about 220 m depth in the borehole. Flowmeter logging of the borehole has revealed few fractures and no flowing groundwater in the borehole below about 120 m depth. The chemical profiles confirm that the Chalk aquifer around Hoath is a zone of low-flow conditions with potential for retention of old groundwater in the deeper section of the aquifer at this location.

6.4   Variations with time

Water-quality monitoring data collected by the water companies and the Environment Agency over the last 10–15 years for the chalk groundwaters suggest that major-element compositions have been broadly stable, although variations occur in some elements. Constituents of possible pollutant origin appear to show some of the greatest variations. Concentrations of SO_4 for example show some temporal variations, particularly in the groundwaters with higher SO_4 concentrations. Variations up to 30% are seen in some groundwaters with average concentrations of around 60 mg l^{-1} (Figure 6.11). It is possible that these higher values reflect a component of pollution, with the fluctuations reflecting variations in pollutant inputs with time. Where SO_4 concentrations are lower in the groundwaters (20 mg l^{-1} or less), these are likely to be closer to baseline compositions that reflect rainfall inputs (concentrated by evapotranspiration) and derivation from the reaction of minerals, including pyrite, in the aquifer. Variations in the concentrations of naturally-derived SO_4 appear to be less extreme.
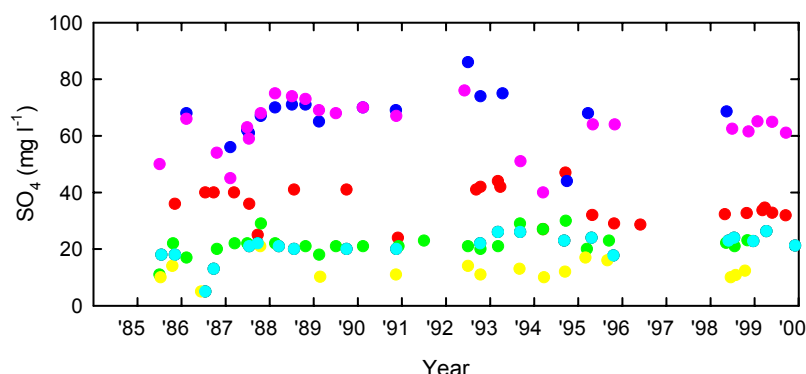

Figure 6.11   Temporal variation in SO$_4$ concentrations in groundwaters from the North Kent chalk over the interval 1985–2000 (data from Thames Water).

Nitrate has been one of the most frequently measured of the inorganic compounds because, of the inorganic constituents present in the unconfined groundwaters, it is the most likely to exceed existing drinking-water regulations. Some variations in nitrate concentrations have been apparent in individual boreholes over the last decade, with both increases and decreases observed over timescales of a few years. However, there appear to have been no distinctive longer-term changes over the period of monitoring (i.e. 10 years; Figure 6.12).

Among the most prevalent pesticides in the unconfined chalk groundwaters are atrazine and simazine. Some of this may have been derived from agricultural activities, but is most likely to have been derived from more localised roadside and railside applications, as well as from applications to gardens. Although now banned for agricultural use, they are persistent pesticides and where past applications have been made, these are often detected in shallow groundwater.

Where atrazine and simazine are detectable in the Chalk groundwater, concentrations appear to have in most cases decreased over the last decade, as observed for some sites from the unconfined Chalk aquifer in Figure 6.13. The trend for simazine is complicated somewhat by the poorer detection limits obtained in earlier samples. However, values of both compounds appear to have been relatively high during the early 1990s with lower, though often still detectable, values since around 1996. The decreases with time are likely a direct reflection of the restrictions imposed on atrazine and simazine use in the UK since the early 1990s. If so, the reductions in concentrations over time imply relatively rapid flow of groundwater in the unconfined Chalk.

No time-series data for saline water sources were available to assess temporal variations in saline intrusion in the near-coastal parts of the aquifer. However, abstraction of groundwater from the saline zone of the aquifer is minimal and so little effect is expected from current pumping regimes.
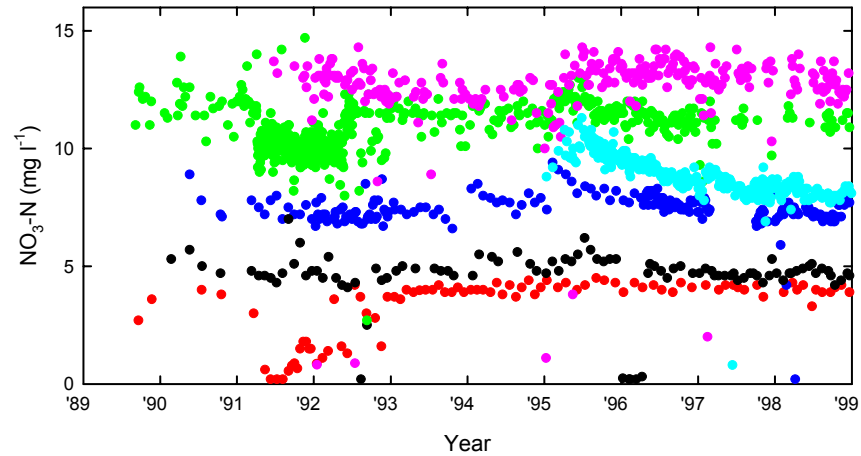
Figure 6.12 **Temporal variation in NO_3-N concentrations in groundwater from selected boreholes in the Chalk aquifer over the interval 1989–1999. Sites are Lord of the Manor (purple), Luton (green), Gore (light blue), Capstone (dark blue), Luddesdown (black), Belmont (red) (data from Southern Water).**
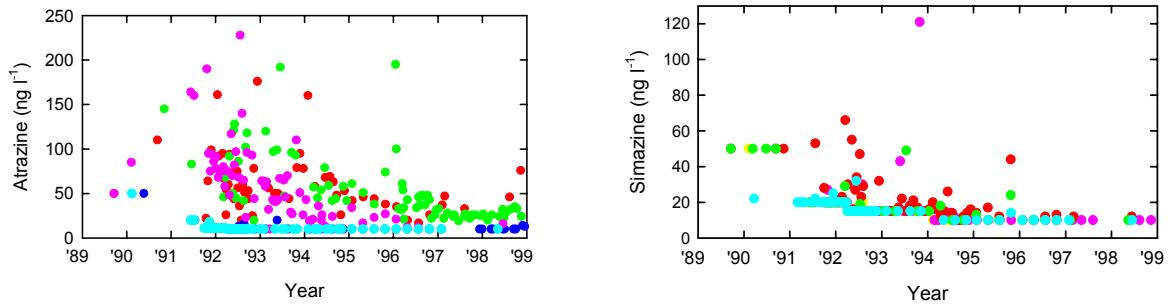

Figure 6.13 **Temporal variations in atrazine and simazine concentrations in groundwater from selected sites in the unconfined Chalk aquifer over the interval 1989–1999. Sites plotted are: Lord of the Manor, Capstone, Higham, Sparrow Castle, Minster B, Hazells, Highstead, Strood, Throwley and Wingham (data from Southern Water).**

7. BASELINE CHEMISTRY OF THE AQUIFER

It is clear from the previous sections that the concept of 'baseline' for a given constituent in the groundwaters represents a range of concentrations rather than a single value. The concentrations vary according to the mineralogy of the aquifer, groundwater flow conditions and residence time, mixing between freshwater and saline water bodies, and, not least, redox processes. Hence, the baseline concentrations of inorganic constituents vary in different parts of the aquifer and can be very different in the unconfined compared to the confined parts, and in the freshwater parts compared to the coastal saline parts.

These variations are quite apart from those imposed by inputs from pollution sources. However, such sources are most likely to impact on compositions of groundwater in the unconfined aquifer since those from the confined portion have a large degree of protection from the overlying Palaeogene deposits of relatively poor permeability.

The cumulative-frequency diagrams and statistical tables given in Section 5 give an indication of the likely baseline ranges of concentrations for the investigated inorganic constituents and for many elements, the 97.7% percentile value can give an estimate of the upper end of the range of expected baseline concentrations. Possible exceptions to this include (in the unconfined aquifer) the concentrations of NO_3-N which are clearly raised in parts of the aquifer as a result of pollution. This is likely to be mainly from agricultural sources but may also include domestic and industrial sources, at least locally. A value around 5 mg l^{-1} has been adopted here as an estimate of the local upper baseline concentration for NO_3-N under unconfined (aerobic) conditions, although this itself represents recharge inputs that have been modified to some extent by anthropogenic inputs to rainfall. As NO_3-N is recognised as a compound occurring significantly above baseline concentrations in groundwaters from the unconfined aquifer, the concentrations of other constituents likely to accompany NO_3-N from agricultural sources, particularly Cl and SO_4 are also suspected to be present at above-baseline concentrations in this part of the aquifer. The 97.7 percentile values for the distribution of Cl and SO_4 in the unconfined groundwaters are respectively 78 mg l^{-1} and 69 mg l^{-1}. Values less than around 40 mg l^{-1} for each are considered more likely to represent baseline concentrations.

Relatively high concentrations of Zn (up to 520 μg l^{-1}) in the unconfined aquifer have also been suggested to be of potential pollutant origin. Looking at the cumulative-frequency plot for Zn in the unconfined groundwaters (Figure 5.5), a flexure occurs at around 30 μg l^{-1}. An approximate upper baseline concentration for Zn in the unconfined groundwaters may therefore be of that order of magnitude. Relatively high values for Cu (up to 60 μg l^{-1} in unconfined conditions) may also be due to pollution inputs from landfill and other sources and baseline concentrations may be expected to be lower than this. An upper baseline concentration for Cu should therefore probably be of the order of 20 μg l^{-1} (97.7[th] percentile Cu 27 μg l^{-1}; Table 5.1). Pollution from landfill and other sources might also have affected other trace metals such as Cd, Cr, Pb and Ni to some extent, though the effects are not readily quantifiable. None of these elements was observed to be present in sources studied at concentrations above EC maximum permissible values for drinking water.

For many of the trace elements, delineating baseline concentrations is a difficult task either because available data are sporadic or have high limits of detection, or both. For most trace elements however, concentrations in groundwater from the unconfined Chalk aquifer are low or very low. This is to a large extent a function of the near-neutral and oxic conditions in this part of the aquifer and the consequent immobilisation of many trace elements by adsorption or precipitation, irrespective of whether they arise from pollution or from natural (geological) sources.

In the confined aquifer, a much larger range of concentrations of inorganic constituents is observed. However, these are not related to pollutant inputs but are considered to be entirely natural. In some sources, these result from prolonged residence time of groundwater in the aquifer, resulting in

advance water-rock reactions. In other near-coastal sources, the high values reflect influxes of various generations of saline water over long timescales (thousands of years). Many of the near-coastal waters of Kent are of poor quality and hence represent marginal water resources of limited practical use. However, although to some extent affected by modern groundwater abstraction, the compositions reflect baseline concentrations.

8.   SUMMARY AND CONCLUSIONS

Groundwater from the Chalk aquifer of north Kent and east Surrey has evolved through a complex set of geochemical processes. Amongst the most dominant processes is reaction of the groundwater with the chalk matrix, which produces strongly pH-buffered compositions, with Ca and HCO_3 as the dominant ions in solution. Such groundwaters are particularly evident in the unconfined oxidising aquifer. Further downgradient, redox changes imposed by progressive confinement of the aquifer in turn by Palaeocene sands, silts and clays (e.g. the Thanet Sands), and by the London Clay initiate additional reactions which serve to modify the concentrations of many redox-sensitive and ion-exchangeable elements and produce strongly distinctive baseline concentration ranges in the confined and unconfined sections of the aquifer. Elements particularly affected by redox changes include Fe and Mn. In the northern parts of the aquifer, the incidence of reducing conditions often coincides with the occurrence of the present-day coastline. Hence, additional influences from saline intrusion (and salinity-driven ion exchange) are also active in near-coastal parts of the confined aquifer. Saline intrusion has a strong effect on the concentrations of many elements, in particular, Na, Mg, Cl, SO_4, HCO_3, Br, I, F, B, Li and Sr. In some downgradient sections of the aquifer (reducing and near-coastal), isotopic evidence points to the occurrence of long-residence-time groundwaters, in some localised areas likely to be of Pleistocene age. However, the relatively thin section of confined aquifer in north Kent means that these are of localised extent.

As many of the abstracted groundwaters are from the unconfined aquifer and the region is heavily populated with a strong agricultural tradition, influences of pollution are also potentially severe. The most clear effects are seen with nitrate and pesticides as these are typically more regularly monitored than other parameters. However, concentrations of many major elements (especially Cl, SO_4 and possibly K) have been increased by pollution inputs. Some trace elements (e.g. Zn and possibly Cu, Cd, Cr, Ni, Pb) may also have been increased from pollution sources, such as landfills. In the unconfined aquifer, baseline concentrations of a number of elements in the groundwaters are difficult to define because many are believed to have been modified by such pollution inputs. In the confined aquifer, although concentrations of many elements are higher, these represent naturally-derived (baseline) concentrations. Pumping is unlikely to have initiated significant amounts of saline intrusion as the amount of abstraction from the confined near-coastal aquifer is minimal.

In addition, as with other parts of the Chalk of southern Britain, geological structure and weathering patterns have been influential in controlling groundwater flow and flow rates. These have resulted in significant variations in groundwater chemistry, both laterally and with depth, particularly in the confined near-coastal parts of the aquifer.

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ACKNOWLEDGEMENTS

APPENDIX 1. LIST OF GROUNDWATER SOURCES USED IN THIS STUDY

Locality	Easting	Northing
Reducing groundwater sources:		
Sheppey Ltd, Rushenden	59085	17204
Ibstock, Funton Brick Works	58760	16780
Co-Steel, Sheerness	59118	17469
Sheerness Port, Grand well	59113	17528
Motney Hill Water Treatment Works	58299	16845
Hoath (depth sample)	62015	16387
Hoplands Farm, No. 1	62055	16170
Ford PS	62033	16545
Reculver No. 1	62287	16936
Reculver No. 2	62350	16940
Street Farm	58472	16772
Oxidising groundwater sources:		
Akzo Nobel	57776	16940
MC Air Filtration	58216	16750
Capstone PS	57798	16554
Gore PS	58397	16543
Luddesdown PS (Chalk)	56630	16618
Luton PS	57768	16625
Shipwrights Arms	60173	16360
Harty Ferry	60129	16471
Stodmarsh	62090	16139
Danaway PS	58620	16310
Keycol PS	58740	16450
Highstead PS	59104	16076
Blacketts Farm	59471	16521
Tappington North PS	62120	14650
Denton South PS	62142	14675
Broome PS	62241	14819
Rakeshole North PS	62054	14508
Ottinge PS	61723	14249
Worlds Wonder PS	61830	14550
Skeete PS	61430	14085
Standen PS	62410	14040
Lullingstone Augmentation BH	55350	16480
Eynsford Augmentation BH	55453	16600
Farningham PS	55555	16744
Terlingham Tunnel	62115	13808
Wilmington No. 3 PS	55432	17286
Darent PS	55542	17189
Horton Kirby No. 2 PS	55584	16800
Lullingstone No. 2 PS	55248	16280
Green St Green No. 2 PS	55734	17092
Wingham PS	62432	15532
Crayford No. 3 PS	55174	17453
Wansunt Well	55108	17415
Wansunt BH	55108	17415
Overy Street/Dartford PS	55442	17412
Bexley Borehole No.1	54870	17270
Bexley Borehole No.2	54870	17270
Bexley Well	54870	17270

Locality	Easting	Northing
Carshalton Beeches, Langley PS	52676	16311
Carshalton Beeches, Oaks PS No. 1	52730	16255
Cheam, Cheam PS No. 5	52459	16423
Chipstead, Parrots Farm PS	52575	15712
Coulsdon, Smitham PS., No. 3	52980	15950
Crayford No. 1	55210	17460
Crayford No. 2	55210	17460
Croydon, Addington PS, Well	53708	16278
Croydon, Surrey Street PS, No. 1	53218	16541
Croydon, Surrey Street PS, No. 5	53223	16538
Croydon, Surrey Street PS, Well 3	53222	16538
Darenth Well	55570	17130
Dartford Borehole	55450	17410
Effingham, Effingham Golf Club Bh	51160	15218
Epsom PS. (Rail), No. 2	52120	16120
Epsom PS, No. 1	52122	16115
Epsom PS, Well, Pump 1	52120	16120
Epsom, Nonsuch PS	52348	16287
Eynsford Borehole	55350	16550
Eynsford Well	55350	16550
Green Street Green No.1	55740	17080
Guildford, Dapdune Road PS, No. 1	49907	15046
Guildford, Dapdune Road PS, No. 2	49910	15047
Horton Kirby No.1	55600	16770
Kenley, Kenley PS, No. 1	53280	15995
Langley, Langley Vale PS	52060	15778
Leatherhead, Fetcham PS (Mixed Spring Raw), at Elmer	51570	15570
Leatherhead, Young Street PS,, No. 2	51614	15560
Lullingstone No, 1	55270	16300
Lullingstone No, 2	55270	16300
New Addington, West Wickham PS, Well 2	53800	16457
North Orpington No. 1	54650	16740
North Orpington No. 2	54650	16740
Orpington No.2	54550	16520
Orpington No. 3	54550	16520
Orpington Well No. 1	54550	16520
Purley, Purley PS, No. 6	53119	16126
Southfleet Well	56090	17240
Sutton, Sutton PS, No. 1	52620	16429
Waddon, Waddon PS, Well 1	53136	16391
Waddon, Waddon PS., Well 2	53138	16391
West Horsley, West Horsley PS	50792	15232
Wilmington Well No.1	55430	17280
Wilmington Well No. 2	55430	17280
Woodcote, Woodcote PS	52947	16153
Woodmansterne, Holly Lane PS	52727	15831
Belmont	59790	15720
Capstone Chalk borehole	57790	16550
Cuxton borehole	56900	16690
Cuxton well	56890	16710
Deal	63630	15080
Fawkham	55996	16867
Flemings	62820	15520

Locality	Easting	Northing
Gore	58390	16540
Hazells	56290	17130
Higham	57140	17210
Hockley Hole	59800	15550
Kettle Hill	59650	15570
Lord Of The Manor	63530	16500
Luddesdown PS No. 1 Chalk	56630	16620
Luton PS	57760	16630
Martin Gorse	63330	14760
Martin Mill	63360	14710
Matts Hill	58200	16260
Minster B	63060	16510
Nashenden	57330	16550
Northfleet Chalk Borehole	56360	16910
Ringwould Borehole	63550	14710
Selling	60330	15660
Snodhurst	57560	16510
Sparrow Castle	63180	16750
Strood	57290	16930
Sutton	63320	14890
Three Crutches	57070	17030
Throwley Borehole	59950	15590
Trundle Wood	58870	15882
Windmill Hill	56500	17320
Wingham	62432	15532
Woodnesborough	63000	15650
Newnham No. 1	59750	15960
Newnham No. 3	59750	15960
Newnham No. 5	59750	15960
Thanington No. 1	61380	15670
Thanington No. 2	61380	15670
Thanington No. 3	61380	15670
Thanington No. 4	61380	15670

PS: pumping station, borehole identification numbers are given where multiple boreholes exist