Baseline Report Series:
15. The Palaeogene of the Wessex Basin

Groundwater Systems and Water Quality
Commissioned Report CR/04/254N

Science Group: Air, Land & Water
Technical Report NC/99/74/15

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/04/254N

ENVIRONMENT AGENCY
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15. The Palaeogene of the Wessex Basin

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Iron stains around borehole outlet at Paultons Park (SU 314 167)

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

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

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

The BASELINE objectives are:

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

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

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

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

1. EXECUTIVE SUMMARY

The Palaeogene strata in the study area range from the oldest, the Reading and Woolwich Formation, to the youngest, the Headon Hill Formation. The strata dip gently in a southerly direction towards the centre of a syncline. The older Palaeogene formations therefore crop out along the northern margin of the basin, and younger strata towards the south.

The sedimentary sequence is characterised by relatively rapid vertical and lateral changes within the succession from clays and silts to sands. The more sandy, and consequently more permeable strata form minor aquifers, while the clay-dominated strata form aquitards and aquicludes. The various aquifer bodies are often discontinuous and hydraulically isolated due to the presence of confining clay-rich layers. Confined and semi-confined conditions are common, and sub-artesian and artesian boreholes are a consequence.

Regional groundwater flow in the basin is predominantly towards the south, following the dip of the strata towards the centre of the basin. However, the heterogeneous nature of the aquifer makes both the delineation of the flow direction and hydrochemical interpretation difficult. Local drainage patterns and lithological sequences govern flow direction, groundwater travel times and the geochemical evolution of the groundwaters.

The most important factor affecting the chemical composition of the Paleogene groundwaters in the region is carbonate dissolution. As a consequence, most of the groundwaters are of Ca-HCO_3 type. However, the overall carbonate content of the Palaeogene aquifer is low. The limited availability of carbonate to neutralise acidic infiltrating recharge water leads to the slightly acidic conditions of most sampled groundwater sources. Oxidation of pyrite generates additional acidity and leads, in the absence of carbonate, to $NaSO_4$ type waters, which are rich in Fe^{2+} and SO_4^{2-}. The acidity of the groundwaters has had a considerable effect on the mobilisation of trace elements such as Al, Be, Ni and Co. Some Ca-HCO_3 waters in the study area have been modified towards a Na-HCO_3 composition as a result of ion exchange. Stable-isotope data suggest that these waters contain a component of groundwater of Pleistocene age and that they are derived through recharge from the underlying Chalk.

The majority of unconfined groundwaters in the Palaeogene sediments are affected by agricultural pollution, showing elevated nitrate concentrations. However, 70% of sampled groundwaters were strongly reducing, with some waters having a strong hydrogen sulphide (H_2S) smell. In these waters, iron and manganese concentrations are elevated while nitrate concentrations are low indicating that denitrification is likely to have occurred. Some groundwaters might be of sufficient age to have been recharged with pre-modern water, unaffected by pollution.

There is evidence that the geochemistry of waters in the Palaeogene sediments is not only influenced by water-rock interaction due to prolonged residence time, but by the geological nature of the aquifers themselves. Elevated Na and SO_4 concentrations occur mainly in groundwaters obtained from boreholes penetrating into the London Clay Formation while Ca-HCO_3 and Ca-Na-HCO_3 waters were mainly from the Bracklesham Group, Barton Group or Headon Formation.

2. PERSPECTIVE

The study area is situated within the counties of Dorset and Hampshire in the south of England. It extends from Wareham in the West to Southampton in the East with the coastline as its southern boundary and reaches to about 115 000 northing (Figure 2.1). The principal drainage is by the rivers Poole and Frome in the south-west, flowing to the sea via the Wareham Channel. The centre of the study area is drained by the River Stour and the River Avon, which flow into Christchurch Bay. To the east, the Lymington and Beaulieu Rivers flow from north to south and drain to the sea via the The Solent.

Several large urban areas are present along the coastline, namely Poole, Bournemouth, Christchurch and Southampton. Smaller towns and villages are found throughout the region. Outside these areas, the district is rural with large parts being occupied by woodland and heathland of the New Forest.

The study area occupies the majority of the Wessex Basin, a broad downwarp filled with Tertiary (Palaeogene) clays and sands. The strata dip gently towards the centre of the basin in a roughly southerly direction. The oldest Palaeogene formation, the Reading Formation crops out along the outer margin of the basin and the youngest, the Headon Formation towards the south. The Palaeogene is overlain by Quaternary deposits in a strip along the coast and along river courses.

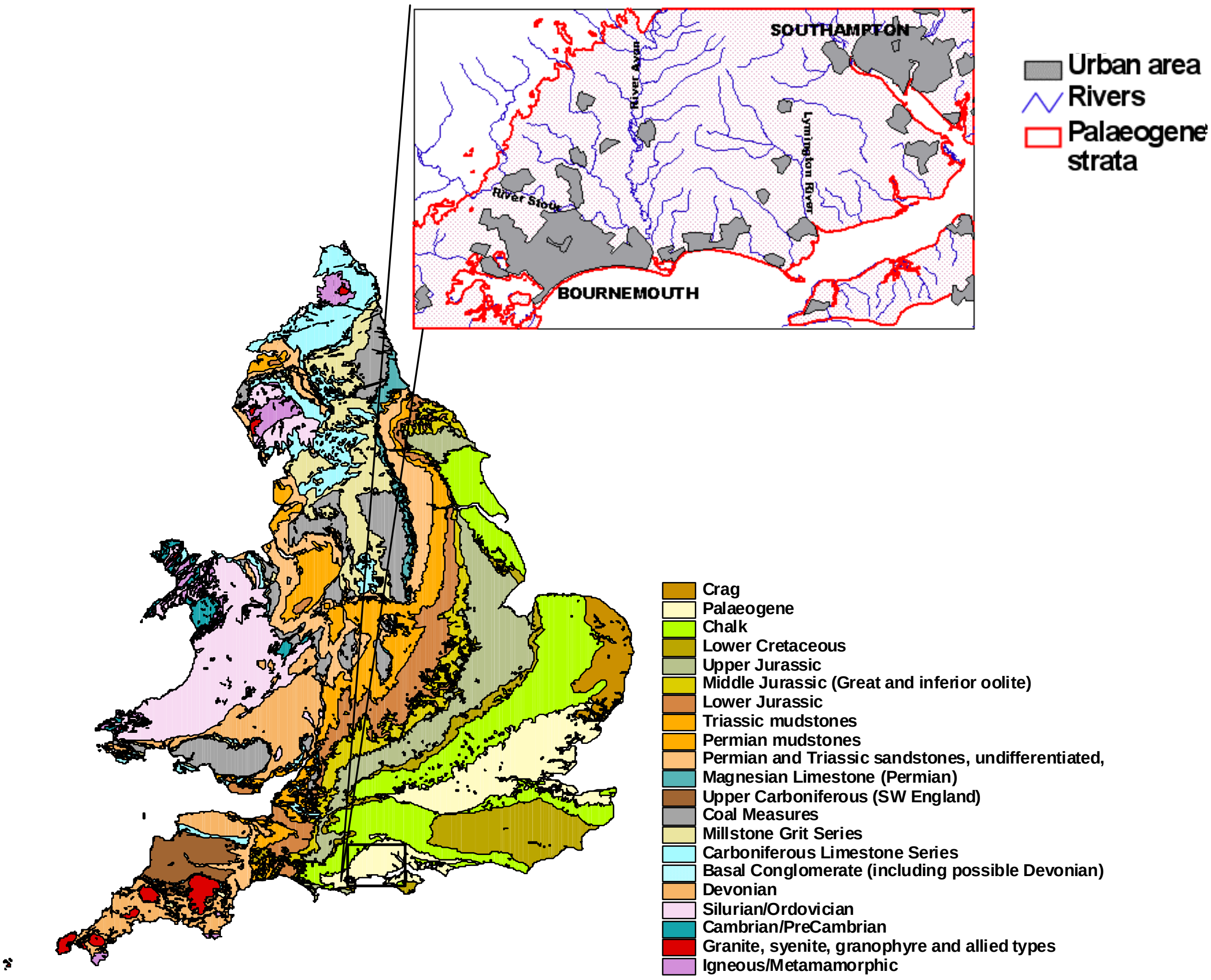

Figure 2.1 Location map of the Palaeogene study area

The area is of low relief with the majority of land remaining below 25 metres above Ordnance Datum (aOD) but rising towards the north to about 120 metres aOD (Figure 2.2).

The Palaeogene sediments form a minor aquifer with licensed abstractions generally being small to medium local supplies for spray irrigation, farming and domestic usage including hospitals, with the exception of the Ampress public-supply source in Lymington (Bournemouth and West Hampshire Water). Other uses of groundwater in the area are for sand and gravel quarries, water bottling and stream augmentation. Yields are very variable throughout the strata and generally lie between 40 and 1300 m^3/day.

The area receives annual precipitation of about 900 mm. Permeable sand strata within the Palaeogene tend to constitute aquifers which respond quickly to rain events if they are at outcrop, resulting in rapid changes in groundwater levels and river flows. As a result, rivers can show marked decreases in flow in dry summer periods. Groundwater abstracted from the Palaeogene strata plays an important role in the alleviation of these river low-flows e.g. for the Lymington River. Other roles are maintenance of the Pennington Marshes, including wet heath, bog woodland and seepage step mires.

Current groundwater quality issues in the area include herbicide and pesticide related contamination, especially where the aquifer is at outcrop beneath arable land, and high metal concentrations associated with low pH in the confined Poole Formation. Contamination with oils and solvents in areas underlying industrialised zones e.g. Poole Harbour and Southampton is of concern. Other potential pollution sources in the area include landfills and other waste management facilities and urban soakaways. The threat of pollution to groundwater is heightened by the often freely-draining sandy soils and shallow water table over much of the Palaeogene outcrop. To the west of Southampton where factories and an oil refinery and a power station are sited, there is the potential problem of hydrocarbon contamination. Saline intrusion has not been identified along the coastal portion of the area so far.

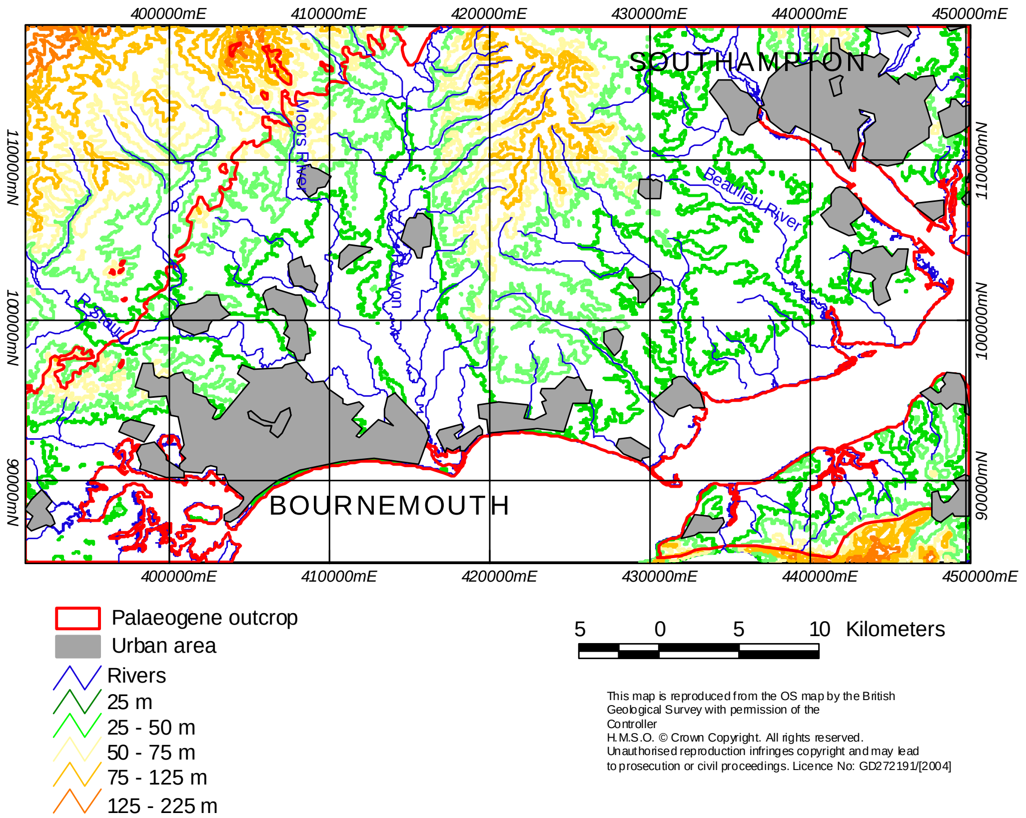

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Figure 2.2 Topographical map of the Palaeogene study area

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

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

3.2 Geology

The Palaeogene rocks of the Wessex Basin vary in lithology from coarse sands to dense clays (Figure 3.1). An overview of the outcrop area of the various formations is given in Figure 3.2. Deposition of the Palaeogene strata took place predominantly in shallow marine environments, including tidal estuaries, brackish lagoons and embayments, in a series of transgressive/regressive marine and estuarine sedimentary cycles (Jones et al., 2000). Sedimentary cycles are likely to have commenced with marine transgressions, often marked by beds of flint pebbles, which were then succeeded by more terrigenous deposits as the coastline advanced (Edwards and Freshney, 1987), with each cycle probably lasting 1-2 million years. The process of sedimentation was sensitive to small changes in sea level as well as to minor tectonic movements, and explains the common and relatively rapid vertical and lateral changes within the succession from clays and silts to sands. Discrete shelly concentrations may have been formed during storms. The resulting complex succession of siliciclastic clays, silts, sands and pebble beds is estimated to be up to 700 m thick in total, although the complete sequence is not present at any one locality and local thicknesses are therefore less.

Figure 3.1 Part of the Palaeogene sedimentary sequence exposed along the coastline [SZ 195 927]

The strata in the Wessex Basin dip gently in a southerly direction towards the centre of a syncline that extends offshore southeastwards. Smaller-scale structures such as gentle folds affect the strata locally. The older Palaeogene formations therefore crop out in the north, and the younger strata towards the south. Isopachytes for many of the Palaeogene strata in the Wessex Basin show that the formations tend to thicken from the southwest to the northeast, and this is thought to indicate that pre-existing tectonic structures influenced sedimentation (Edwards and Freshney, 1987). An overview of the sedimentary succession from the Reading Formation to the Barton Clay is shown on the geological cross section in Figure 3.3, which is based on geophysical borehole logs. The various Palaeogene units have a distinct gamma-ray log pattern that allows their recognition throughout the Wessex Basin (Newell, 2001). The section is drawn from the westernmost extent of the Palaeogene in the study area near Warmwell to Christchurch further east and demonstrates the dip of the strata and thickening of the Palaeogene sequence towards the east.

The nomenclature of the strata is relatively complex, as it needs to take into account the common lateral facies changes. The stratigraphy and relationships between beds across the basin are shown in Table 3.1. The horizons recognised are, however, not always coincident with mappable lithological units (Edwards and Freshney, 1987). Fossils, including planktonic foraminifera, molluscs, dinoflagellates and pollen assemblages have been used by various authors for stratigraphical correlation.

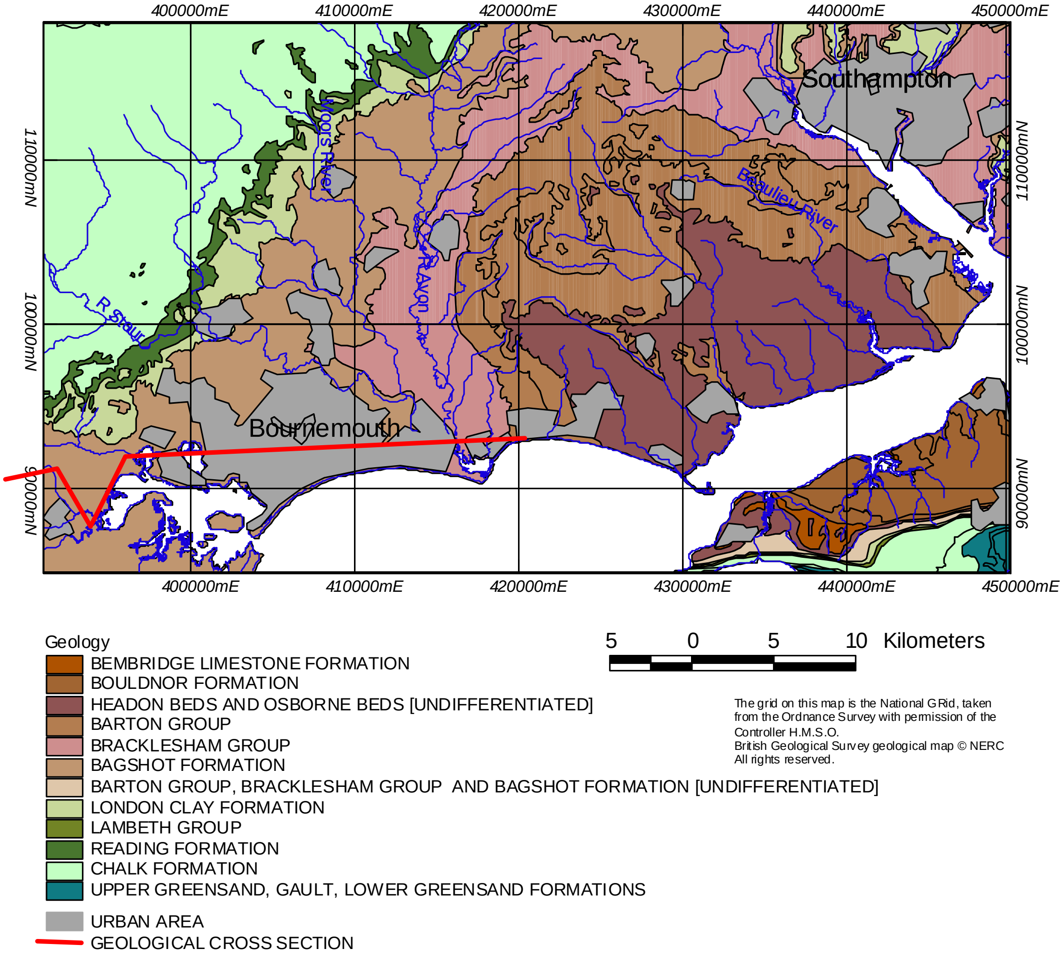

Figure 3.2 **Solid geology map of the Palaeogene study area (geological cross-section is given in Figure 3.3).**

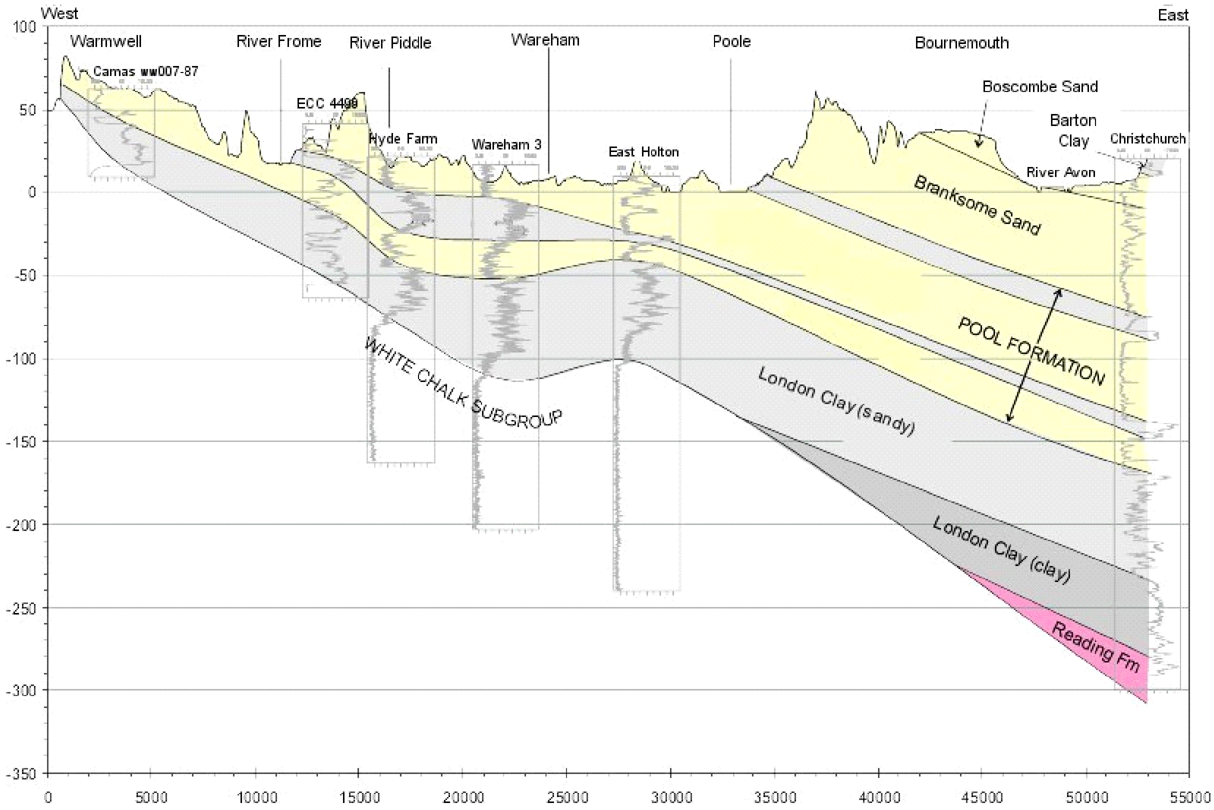

Figure 3.3 **Cross section through the geological sequence from W (375000 easting) to E (420000 easting), yellow: sandy strata, grey: clayey strata. Geophysical gamma-ray logs in light grey.**

The Palaeogene sequence begins with the lithologically-variable sands, silts and mottled clays of the Reading & Woolwich Formations, which thicken towards the south and the east, attaining a maximum thickness of about 50 m. These strata rest unconformably on the Upper Chalk. They were deposited under marine and marine-lagoonal conditions, and were later exposed to subaerial weathering.

The Reading & Woolwich Formations are succeeded by the London Clay Formation, a stiff, silty and sandy clay with occasional thin beds of flint pebbles, which can be divided into upwards-coarsening sedimentary cycles. The formation is generally more sandy in the Wessex Basin compared to its equivalent in the London Basin. The thickness of the London Clay of the Wessex Basin varies from as little as 30 m in the west to over 140 m in the east (Jones et al., 2000). The upper part of the London Clay is sandy, and was formerly known as the Bagshot Sands. These sands are nowadays subdivided into the Whitecliff Sand, Durley Sand, Nursling Sand and Portsmouth Sand. The Whitecliff Sand has a thickness of 10 to 25 m, thins from west to east, and represents the bulk of strata formerly known as the Bagshot Sands. The Durley Sand is only found around the village of Durley, just to the northeast of Southampton near Botley. The Nursling Sand outcrops in the north and northwest of the basin between Hamptworth and East Bellow, and is up to 30 m thick (Jones et al., 2000). It forms a minor topographic feature on the underlying clays in this area (Edwards and Freshney, 1987). The Portsmouth Sands are present in the eastern part of the basin.

Table 3.1 An outline of the Palaeogene Strata of the Wessex Basin (after Jones et al., 2000).

			Hampshire Basin and Isle of Wight (west)	**Hampshire Basin and Isle of Wight (east)**	
EOCENE	**LATE**	Solent Group	Headon Hill Formation	Osborne Member	
				Headon Member	
		Barton Group	Becton Sand Formation		
			Chama Sand Formation		
			Barton Clay Formation		
	MIDDLE	Bournemouth Group	Boscombe Sand/Huntingbridge Beds		
			Branksome Sand Formation	Bracklesham Group	Selsey Sand
					Marsh Farm
			Poole Formation		Earnley Sand
	EARLY				Wittering Formation
			London Clay Formation including the following members: Whitecliff Sand, Durley Sand, Portsmouth and Nursling Sand		
PALAEOCENE	**LATE**		Reading and Woolwich Formation		

The Bracklesham Group or Bournemouth Group succeeds the London Clay Formation. This comprises a series of clayey sands and corresponds with the strata formerly known as the Middle and Upper Bagshot Sands and the Bracklesham Beds. In the east of the Wessex Basin, where the sediments are known as the Bracklesham Group, deposition took place under marine and intertidal conditions as a series of four major sedimentary cycles, giving rise to four formations. These are, in ascending order, the Wittering Formation (laminated and glauconitic sandy clays), the Earnley Sand Formation (bioturbated marine sandy silts and silty sands), the Marsh Farm Formation (carbonaceous laminated clays and fine sands and silt) and the Selsey Sand Formation (fine-grained sand with a variable clay content). The Group thins from east to west and from south to north, and reaches a maximum thickness of about 180 m (Jones et al., 2000). In the west of the Wessex Basin, the group is divided into two units rather than four, namely the Poole Formation (corresponding to the Wittering, Earnley Sand and part of the Marsh Farm Formations), and the overlying Branksome Sand Formation, which are thought to have been deposited under mainly continental conditions (Jones et al., 2000). Together with the overlying Boscombe Sand Formation or Huntingbridge Beds (silt and silty sand with abundant molluscan fauna) these form the complete Bournemouth or Bracklesham Group.

The Barton Group can be divided into a lower clay-rich unit known as the Barton Clay Formation, and upper more sandy layers called the Chama Sand Formation and the Becton Sand Formation. The group is only present to the west of Southampton Water and on the Isle of Wight, and can reach more than 100 m thick in places. It thins from south to north and in the New Forest varies from 50 m to 80 m thick (Jones et al., 2000). A section of the Barton Group sedimentary sequence is shown in Figure 3.5. The photograph was taken to the west of Christchurch, where the Palaeogene sediments form the coastal cliff.

The Barton Clay Formation was deposited on a marine shelf, and consists of fossiliferous clay and fine-grained sand. An abundant fauna is present, although at outcrop the formation is often decalcified. The Barton Clay varies in the study area from 50 m to 90 m thick. The Chama Sand Formation consists of very fine-grained sand and sandy clay. It is up to about 15 m thick in the Wessex Basin (Edwards and Freshney, 1987). The Becton Sand consists of fine sands, with relatively little clay. It ranges from a maximum of about 70 m thick to less than 20 m thick.

The Solent Group overlies the Barton Group at the top of the Palaeogene sequence and is represented in the study area by the Headon Hill Formation. The Headon Hill Formation consists mainly of clay with beds of limestone, and comprises the units formerly known as the Osborne and Headon Beds. The formation is thought to have been deposited in freshwater lagoons.

About half of the study area is overlain by superficial deposits (Figure 3.4). These consist predominantly of river terrace deposits, alluvium and sand and gravel deposits of uncertain age and/or origin. Floodplains of river courses and estuarine creeks are floored by alluvium, with river terrace deposits occurring above their respective alluvial plains, comprising mainly flint gravel.

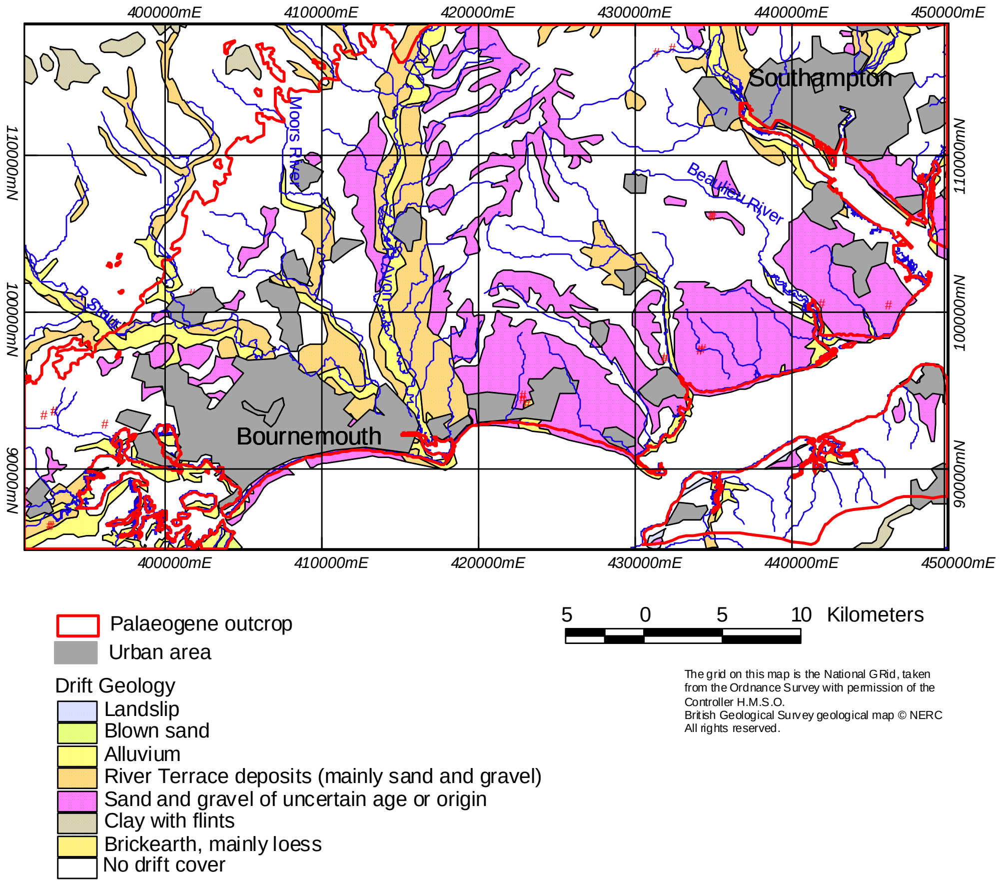

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Figure 3.4 **Drift map of the Palaeogene study area.**

3.3 Hydrogeology

The Palaeogene strata are characterised by alternating minor aquifers, aquitards and aquicludes. The more sandy, and consequently more permeable strata form the minor aquifers (Table 3.2), while the clay-dominated strata comprise the aquitards and aquicludes. Weathering frequently increases the permeability of the strata to depths of several tens of metres below ground surface (Jones et al., 2000). The aquifer bodies are often discontinuous as the permeable units such as sand lenses pinch out, and they may be isolated hydraulically due to confining clay-rich layers. In other locations, hydraulic continuity between permeable strata may be only sporadic. Confined and semi-confined conditions are common, and sub-artesian and artesian boreholes are a consequence. Perched water tables are frequently found. Where the basal Palaeogene strata are permeable, it is thought to be in hydraulic continuity with the underlying Chalk, acting effectively as one aquifer.

Regional groundwater flow in the basin is predominantly towards the south, following the dip of the strata towards the centre of the basin. However, local groundwater flow is not easy to predict due to discontinuities in the geology. Structural changes such as faults may have some local control on groundwater flow, but lithological controls are much more important.

Table 3.2 The principal Palaeogene formations that act as aquifers in the Wessex Basin. After Jones et al. (2000).

Palaeogene aquifer unit	Distribution	Lithology	Comments
Headon Hill Formation	New Forest, Isle of Wight	Variable: sands, silts, clays, thin lignites, limestones.	Includes strata formerly known as the Osborne and Headon beds.
Becton Sand Formation	New Forest, Isle of Wight	Well-sorted, fine-grained sand; locally thick clays in middle part.	Formerly mapped as Barton Sand.
Chama Sand Formation	New Forest, Isle of Wight	Clayey, glauconitic fine-grained sand.	Formerly mapped as Barton Sand.
Boscombe Sand Formation	Bournemouth – Ringwood area	Well-sorted fine-grained sand.	Passes into Barton Clay east of Christchurch.
Selsey Sand Formation	Eastern part of the basin.	Silty sand and sandy clayey silt.	Part of the Bracklesham Group.
Earnley Sand Formation	Eastern part of the basin.	Mainly glauconitic silty sand.	Part of the Bracklesham Group.
Branksome Sand	Bournemouth – Ringwood area.	Fine to very coarse-grained sand, alternating with brown, red-brown and pale grey clays.	Formerly known as Lower Bagshot Beds.
Poole Formation	Between Poole and Wareham.	Medium to coarse-grained sand, alternating with brown, red-brown and pale grey clays.	Formerly known as Lower Bagshot Beds.
London Clay Formation: Nursling Sand Portsmouth Sand Durley Sand Whitecliff Sand	 West of Southampton Most of basin Around Durley Most of basin	Lenticular, variably silty fine- to coarse-grained sands.	London Clay thins to 20 m in Dorset.
Reading Formation	Entire basin	Highly variable. Mostly brightly mottled clays in Isle of Wight. In north of basin, almost entirely sand with lenticular gravel and ironstone bands.	

Borehole yields from the Palaeogene strata are generally moderate to poor. The assessment of yield is complicated by the discontinuous nature of the strata, and the fact that many boreholes penetrate more than one of the aquifer units.

The Reading Formation is thought to be able to yield up to about 200 m^3 d^{-1}, although some of this water may come from the underlying Upper Chalk (Edwards and Freshney, 1987). In the western, southern and eastern parts of the basin the formation is predominantly clay and unproductive for water supply (Allen et al., 1997).

The majority of the London Clay Formation is of little significance as an aquifer, due to its predominantly clayey nature. However, the more sandy upper part of the formation, especially the Whitecliff Sand, provides permeable horizons and the increased chance of a successful abstraction borehole, with reported yields of around 500 m^3 d^{-1}. Sandy units elsewhere in the London Clay can yield about 100 m^3d^{-1}, although the sustainability of these sources is dependent on a suitable mode of recharge. Commonly, springs occur at the junction with the underlying clay-rich sediments.

The Bracklesham Group has a variable lithology and thickness, and borehole yields are consequently variable. In the Bournemouth area, the Poole Formation, Branksome Sand and Boscombe Sand formations are the principal water-bearing formations of the district. Water is frequently discharged in the form of springs at intersections with localised clayey beds at various levels. However, most of the groundwater in the Bracklesham Group discharges along river courses or at the coast.

Within the Barton Group the Becton Sand forms the most permeable horizon and most reliable aquifer. Yields of up to 600 m^3d^{-1} are reported. Where the Becton Sand is absent, the Barton Group is poorly productive (Allen at al., 1997). Where the group is overlain by the Headon Hill Formation, it is confined.

Small groundwater supplies have been obtained from the Solent Group (Headon Hill Formation) suitable for domestic or limited agricultural use. In the New Forest, however, the strata are predominantly clayey and act as an aquiclude over the underlying Barton Group.

An estimation of aquifer properties such as storage and transmissivity is complicated due to the stratigraphic and lithological complexity of the Palaeogene strata. Transmissivities of between 50 and 100 m^2 d^{-1} were obtained for the Bracklesham Group, where they were in hydraulic continuity with the Whitecliff Sands (Jones et al., 2000). For other formations in the Palaeogene, assumed regional values are often used, due to insufficient numbers of discharge tests (Allen et al., 1997). For the Poole Formation, the Environment Agency employ an estimated regional transmissivity of around 20 m^2 d^{-1}. For the Barton Group (Becton Sand) transmissivities are estimated to be in the order of 50 to 100 m^2 d^{-1}. The storage coefficient is approximated to be 0.02% where the Becton Sand is confined and 5% where unconfined.

Eight values for transmissivity (Table 3.3) have been obtained from pumping tests for boreholes in the Palaeogene strata as a whole, and these vary from 1.1 to 1600 m^2 d^{-1}. Forty two values for specific capacity have been recorded, ranging from 3.6 to 4000 m^3 d^{-1} m^{-1}, with a geometric mean of 44.5 m^3 d^{-1} m^{-1} (Jones et al., 2000). Porosities in the range of 29% to 40% have been recorded.

Table 3.3 **Summary of the aquifer properties data held by the British Geological Survey for Palaeogene minor aquifers of the Wessex Basin (after Jones et al., 2000).**

Total Number of Records: Palaeogene of the Wessex Basin	46	
Number of transmissivity records	8	
Min/Max transmissivity value (m^2/d)	1.05	1600
Arithmetic/Geometric mean of transmissivity (m^2/day)	429	72.2
Median/Interquartile range of transmissivity (m^2/day)	72.5	756
25/75 percentile of transmissivity (m^2/d)	17.8	774
Number of storage coefficient records	6	
Min/Max storage coefficient value	0.00002	0.05
Number of specific capacity records	43	
Min/Max specific capacity (m^3/d/m)	3.61	400

Recharge to the aquifers of the Palaeogene is complicated by the numerous clay horizons in the sequence. The drift cover in the area is frequently permeable, for example the river gravels and river terrace deposits, since the glacial till sheets found further to the north did not reach the Wessex Basin (Edwards and Freshney, 1987). Exceptions to this are the Clay-with-Flints and river alluvium, which have low permeabilities and impede recharge to underlying strata.

3.4 Aquifer mineralogy

Information on the mineralogy of the different formations in the Wessex Basin has been presented under the main formation headings below:

3.4.1 Reading and Woolwich Formation:

This formation consists mainly of clays, thought to be of volcanic origin, and cross-bedded sands and pebble beds. Clays are dominated by illite (roughly 50%), with lesser amounts of smectite and kaolinite (Edwards and Freshney, 1987). Chlorite and vermiculite are present in small amounts. Fossils are confined to the basal part of the formation.

3.4.2 London Clay Formation:

This formation consists of silts, sands and clays. Of the clays, illite and smectite are the most abundant, followed by kaolinite. The sand consists of quartz, together with heavy minerals consisting mainly of garnet and epidote, with tourmaline, zircon, staurolite, kyanite, chloritoid minerals, glaucophane, hornblende, sphene and tremolite all occurring in lesser amounts (Edwards and Freshney, 1987). Mica is common, and small amounts of glauconite are widely distributed throughout the formation. Molluscan shell banks occur in more sandy layers, and a diverse fossil macro- and micro-fauna is present throughout. Flint pebbles are found, particularly at the base of each depositional cycle. The Whitecliffe and Durley Sands at the top of the formation are commonly decalcified, and contain few or no fauna.

3.4.3 Bracklesham/Bournemouth Group:

Wittering Formation: This consists of clays, sands and silts. Glauconitic sands (1-5% glauconite) and carbonaceous material are found in places and pyritic sands have been recorded (Edwards and Freshney, 1987). The clay mineralogy (<2 µm fraction) is commonly about 50% illite, 25% kaolinite, and 25% smectite and vermiculite, although the proportions change across the formation. Carbonaceous clays and lignites are present in the upper part. Vertebrate fossils have been found at the top of the formation, and abundant microfaunal fossils are found throughout (Edwards and Freshney, 1987).

Earnley Sand: This is a fairly uniform glauconitic clayey, silty fine-grained sand and sandy silt. Glauconite grains are abundant, and calcareous nodules occur in places. Up to 30% of the clay fraction is kaolinite, although the clay mineral assemblage of illite> kaolinite> smectite is most common.

Marsh Farm Formation: This consists of variably carbonaceous laminated clays with thin beds of sand and silt (Edwards and Freshney, 1987). The coarser fractions of the clays are mainly of quartz. Kaolinite contents of up to 35% occur in the clays. The sands are more sparsely glauconitic than those found in the Earnley Sand. Marcasite is common and mica is also present.

Selsey Sand: This is glauconitic, shelly sandy silt to silty sand, with a variable clay content (Edwards and Freshney, 1987). Carbonate concretions are common at certain levels. The sands consist mainly of quartz. The kaolinite content of the clay is generally less than 20%. Marcasite is fairly common, and mica occurs occasionally. Shell debris and other marine macrofaunal fossils are common. Calcareous cements are found in the sands.

3.4.4 Barton Group

The lower part (Barton Clay) is mainly clay, with variable amounts of glauconite and very fine sand. The sands consist mainly of quartz. Heavy minerals include tourmaline, zircon, garnet and epidote. The upper part (Chama Sand and Becton Sand) consists of slightly glauconitic very fine sand, with silts and clays. The sand is again mainly quartz. Clays consist largely of illite, smectite and kaolinite, with small amounts of vermiculite. Heavy minerals include garnet and epidote. Grains of well-rounded glauconite and flakes of mica are common. Fine-grained lignitic debris and a moderately diverse fossil fauna are present.

Figure 3.5 Palaeogene outcrop west of Christchurch showing sediments of the Barton Group [SZ 195 927]

3.4.5 Solent Group

This consists mainly of shelly clay with silt and very fine-grained sand. Carbonaceous silt with lignite is present. Fossils are common. The sands are mainly quartz, and marcasite is occasionally present. Limestones are found in the upper parts.

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharge waters and can be considered as representing minimum baseline concentrations. The nearest rainfall station monitoring hydrochemical results is from a site at Yarner Wood, to the west of the Palaeogene outcrop [SX 786 789]. Results from January 2003 are shown in Table 3.4. The data have been multiplied by 3 in a second column in order to estimate the approximate enrichment due to evapotranspiration. Although Cl may be assumed to behave conservatively during most recharge conditions, this is not the case for other elements e.g. K and N-species which may be taken up by vegetation, and concentrations may therefore be less in recharge waters than rainfall. Nevertheless, the table indicates the order of magnitude of concentrations expected in young waters, which have not reacted with vegetation, soils or aquifer minerals.

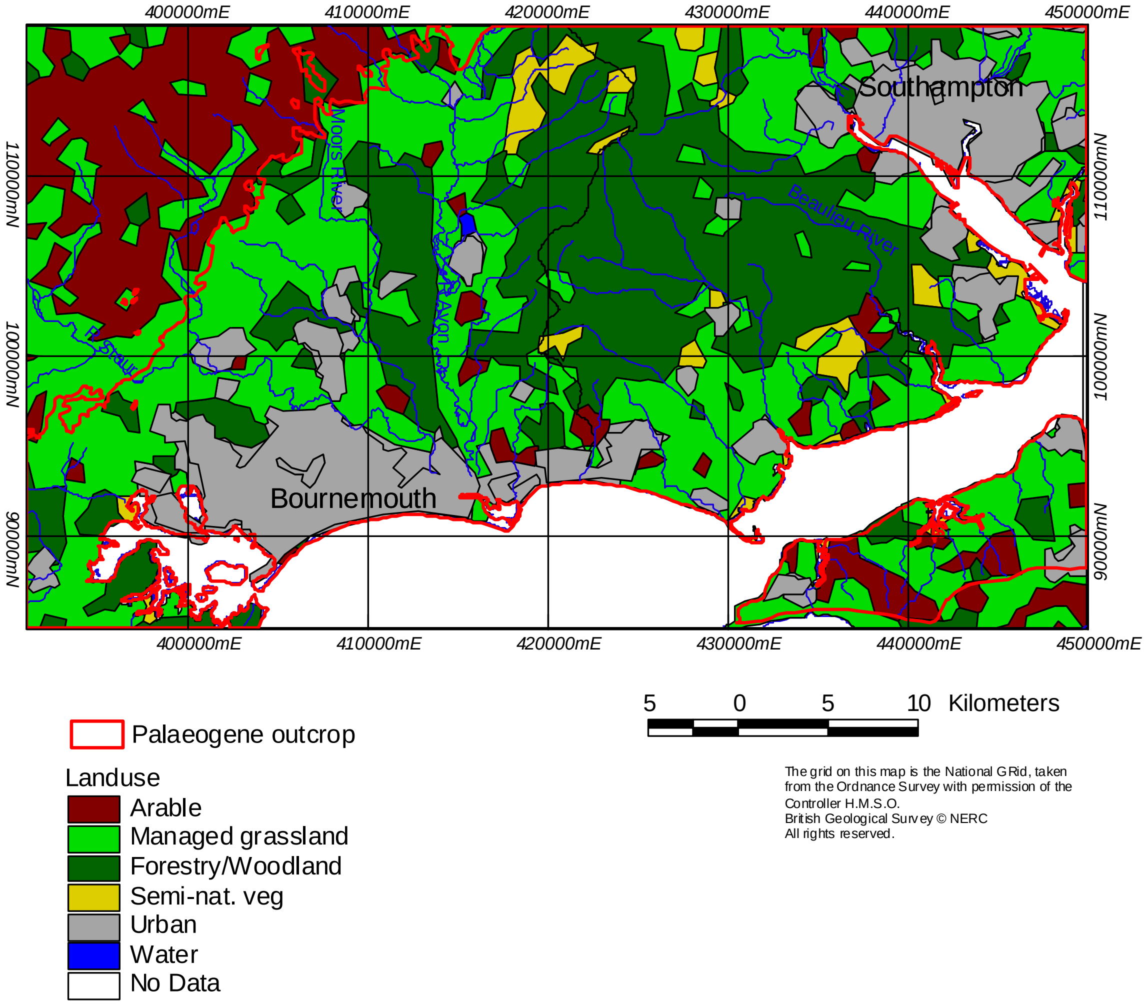
Table 3.4 Rainfall Chemistry from Yarner Wood, to the west of the Palaeogene outcrop (SX 786 789). All determinands are in mg l^{-1}. The data are for January 2003, obtained from the UK National Air Quality Information Archive website at: http://www.airquality.co.uk/archive/index.php

Element/parameter	Rainfall	Rainfall x 3
Ca (mg l^{-1})	0.075	0.225
Cl (mg l^{-1})	2.984	8.95
K (mg l^{-1})	0.069	0.207
Mg (mg l^{-1})	0.195	0.585
NH_4-N (mg l^{-1})	0.113	0.339
NO_3-N (mg l^{-1})	0.134	0.402
Na (mg l^{-1})	1.7	5.1
P (mg l^{-1})	<0.01	<0.03
SO_4 (mg l^{-1})	0.279	0.837
SEC (µS cm^{-1})	28	84
pH	4.62	
Rainfall (mm)	148	

3.6 Landuse in the area

Several large urban areas with motorways and railway lines are situated along the coastline in the south of the study area. Outside these areas, the district is mainly rural, with some smaller villages and towns scattered throughout the region. Large areas are occupied by heathland of the New Forest, formed on infertile soils developed on the sandy Palaeogene formations of the district (Figure 3.6). The more clayey formations give rise to more fertile soils that are mainly covered by woodland (Edwards and Freshney, 1987). Outside the New Forest, the area is characterised by a mixture of managed grassland and forestry/woodland. Arable land area is generally small and only becomes a significant landuse outside the Palaeogene outcrop area (Figure 3.7).

Figure 3.6 Heathland in the New Forest formed on infertile soils on sandy formations of the Palaeogene.



The grid on this map is the National GRid, taken from the Ordnance Survey with permission of the Controller H.M.S.O.
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Figure 3.7 Landuse map of the Palaeogene study area.

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 23 samples were collected during September and October 2003 from private supplies, Wessex Water observation boreholes and Ampress Water Works sources (Bournemouth and West Hampshire Water plc), spanning an area from Wareham in the west to Southampton in the east. Due to the limited number of boreholes tapping only the Palaeogene aquifer without penetrating further into the Chalk, the sampling locations were chosen where possible to provide a good regional coverage, but are mainly determined by borehole availability. Table 4.1 provides information on depth and tapped aquifer for all sampled boreholes. However, no details of screened intervals are known. Five samples were collected from the Bracklesham Group, while four sources penetrated the Bracklesham Group and the London Clay Formation. Three sources drew water from the London Clay Formation only, another eight samples from the Barton Group, while two sources tap the Headon Formation and Barton Group.

Table 4.1 Summary of sample sites in the study area

Borehole	Aquifer tapped	Depth of borehole [m]
Exbury Gardens	Plateau Gravels/ Headon F.	84.7
Exbury Gardens	Headon F. into Becton Sand/Chama Sand	53
Lee’s Nursery	Barton Group	40
Lee’s Nursery	Barton Group	60.5
HH Nursery	Barton Group	20-30
HH Nursery	Barton Group	45-50
Milton Sports Ground	Barton Group	35
Station House	Barton Sand into Barton Clay	49
Beaulieu Hotel	Barton Group into Barton Clay	27
Stanwood Farm	Barton Group	23
Poole Hospital	Bracklesham Group (Poole F.)	102
Ampress WW No 1 (B3)	Bracklesham Group	116
Ampress WW No 5 (B2)	Bracklesham Group	149
Wareham, Briantspuddle PZ 2	Bracklesham Group and London Clay	59
Wareham, Briantspuddle PZ 1	Bracklesham Group and London Clay	9.6
Paultons Park	Bracklesham Group and London Clay	76
Wisteria House	Bracklesham Group and London Clay	76
Hamworthy Engineering	London Clay F. (possibly Whitecliff Sand)	41
Lychett Minster PZ 2	Bracklesham Group and London Clay	47.6
Walford Farm	London Clay	4.6
Bulbury PZ 2	London Clay	38.7
Bulbury PZ 1	London Clay	17.6
Bulbury Golf	Bracklesham Group and London Clay	15

Whenever possible, boreholes were pumped prior to sampling in order to purge at least three borehole volumes. Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured on-site in a flow-through cell (Figure 4.1). Additionally, temperature, specific electrical conductance (SEC) and alkalinity were measured on-site. Samples were filtered through 0.45 µm membrane filters and collected for major- and minor-element chemistry in polyethylene bottles.

Samples for major cations and SO_4 and trace elements were acidified to 1% v/v HNO_3. In addition, eight unfiltered samples were collected in glass bottles for the analysis of the isotopic composition of $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$.

Major and minor cations and SO_4 were analysed by ICP AES and trace cations by ICP-MS. Anion concentrations were measured by automated colorimetry (Skalar continuous-flow colorimeter) and stable isotopes by mass spectrometry.

4.2 Historical data

There are very few historical water-chemistry data available for the Palaeogene aquifers. Ampress Water Works boreholes, a public water-supply source (Bournemouth and West Hampshire Water plc), have been monitored regularly and the Environment Agency holds records from 1991 to 1995. The Environment Agency, Southern Region, added another 8 sites to the Palaeogene section of its groundwater quality monitoring network in 2003/2004 and is going to add further sites so that water-quality data will be available in the future. The Environment Agency, South-West Region, introduced three monitoring sites in the study area. However, monitoring only started in 2003 and no long-term records are available.

4.3 Data handling

The data used in this study included those collected from the sampling programme carried out, plus three groundwaters sampled during a study in 1998 (Buckley et al., 1998). Bournemouth and West Hampshire Water plc holds additional data for Ampress Water Works boreholes, which were used to address historical changes in water chemistry in the area. These data were not merged with the data collected for the present project sampling, as it would duplicate data collected during the BGS sampling program. Where data were below detection limit of analysis, a concentration equal to half the detection limit has been substituted for statistical purposes.

Figure 4.1 On-site measurements of pH, dissolved oxygen (DO) and redox potential (Eh) in groundwater, determined in a flow-through cell.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

Summary statistics for major, minor and trace element concentrations are given in Table 5.1 and Table 5.2. These show the ranges and averages of data as well as an upper concentration (defined as mean plus 2 standard deviations or 97.7th percentile), which is used as a cut off to distinguish outlying data. The major element data are presented graphically on a Piper plot (Figure 5.1), box-plots (Figure 5.2) and cumulative-frequency plots (Figure 5.3). The box-plots display the ranges of data and are designed to highlight the distribution of data on a percentile basis (the boxes show the range between the 25th and 75th percentiles and the whiskers the 5th and 95th percentiles). In addition, the median is shown as a horizontal black line within the box and the mean as a blue line. Median values are useful indicators of average baseline concentrations in the aquifer. The solid black line on the graph represents a diluted seawater curve, which has been normalised to the median Cl concentration of the samples. This provides a general indication of enrichments due to water-rock interaction above the marine-derived rainfall input. Cumulative-frequency plots are useful in visualizing the distribution of data and may be of use in determining different populations of data such as pollution inputs (Box 5.1).

Table 5.1 Field parameters, isotope data and range of major and minor element concentrations in groundwaters of the Palaeogene in the Wessex Basin

	Units	Min	Max	Median	Mean	97.7th	N
Temperature	°C	11.6	21.1	13.4	13.9	18.2	26
pH		4.69	7.33	6.73	6.50	7.33	26
Redox potential	mV	-182	168	28.0	-17.1	135	23
Dissolved oxygen	mg l^{-1}	<0.1	7.6	0.73	1.62	6.56	26
SEC	µS cm^{-1}	165	823	396	442	818	26
δ^{2}H	$^{0}/_{00}$	-47.6	-35.6	-39.1	-40.0	-35.6	8
δ^{18}O	$^{0}/_{00}$	-7.66	-5.82	-6.47	-6.62	-5.90	8
δ^{13}C	$^{0}/_{00}$	-18.4	-8.84	-15.1	-14.6	-9.48	8
Ca	mg l^{-1}	5.20	128	47.0	48.8	102	26
Mg	mg l^{-1}	1.72	15.7	5.46	7.37	15.1	26
Na	mg l^{-1}	11.4	111	19.2	25.5	105.3	26
K	mg l^{-1}	0.9	15.5	2.4	3.61	11.02	26
Cl	mg l^{-1}	17.4	108	33.7	37.5	104	26
SO_4	mg l^{-1}	2.7	91.8	29.6	33.7	87.8	26
HCO_3	mg l^{-1}	5.2	315	153	146	306	25
NO_3 as N	mg l^{-1}	<0.2	34.8	<0.2	4.32	33.7	26
NO_2 as N	mg l^{-1}	<0.004	0.05	<0.004	0.006	0.0348	23
NH_4 as N	mg l^{-1}	<0.03	0.323	0.0375	0.0646	0.232	26
P	µg l^{-1}	<20	329	48	86.70	310	23
DOC	mg l^{-1}	0.4	8	1.1	1.82	7.75	23
F	µg l^{-1}	<100	3400	<100	454	3147	23
Br	µg l^{-1}	<30	230	120	121	225	23
I	µg l^{-1}	<4	46	6	9.9	45.5	23
Si	mg l^{-1}	2.47	10.4	4.5	4.95	9.54	26

Table 5.2 **Trace element concentrations in groundwaters of the Palaeogene of the Wessex Basin**

	Units	Min	Max	Median	Mean	97.7th	N
Ag	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	23
Al	µg l^{-1}	<1.0	1152	5	99.0	728	25
As	µg l^{-1}	<0.5	3.1	<0.5	0.61	3.1	23
Au	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	23
B	µg l^{-1}	5	310	26.5	51.2	302	26
Ba	µg l^{-1}	13.9	404	65.4	90.6	324	24
Be	µg l^{-1}	<0.05	2.2	<0.05	0.20	1.59	23
Bi	µg l^{-1}	<0.05	0.11	<0.05	0.03	0.07	23
Cd	µg l^{-1}	<0.05	0.33	<0.05	0.05	0.31	23
Ce	µg l^{-1}	<0.01	6.88	0.02	0.78	6.24	23
Co	µg l^{-1}	<0.02	10.9	0.12	2.49	10.2	23
Cr	µg l^{-1}	<0.5	0.9	<0.5	0.35	0.9	23
Cs	µg l^{-1}	<0.01	0.21	0.01	0.03	0.18	23
Cu	µg l^{-1}	0.4	7.8	1.2	1.85	6.79	23
Dy	µg l^{-1}	<0.01	1.02	0.01	0.12	0.79	23
Er	µg l^{-1}	<0.01	0.66	<0.01	0.07	0.46	23
Eu	µg l^{-1}	<0.01	0.35	<0.01	0.04	0.26	23
Fe	mg l^{-1}	0.007	11.3	0.68	1.97	11.1	26
Ga	µg l^{-1}	<0.05	0.08	<0.05	0.03	0.05	23
Gd	µg l^{-1}	<0.01	1.32	0.01	0.15	1.08	23
Ge	µg l^{-1}	<0.05	0.12	<0.05	0.04	0.12	23
Hf	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	23
Hg	µg l^{-1}	<0.1	0.1	<0.1	0.07	<0.1	23
Ho	µg l^{-1}	<0.01	0.18	<0.01	0.02	0.14	23
In	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	23
Ir	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	23
La	µg l^{-1}	<0.01	6.04	0.01	0.52	4.27	23
Li	mg l^{-1}	<0.004	0.11	0.01	0.02	0.07	25
Lu	µg l^{-1}	<0.01	0.2	<0.01	0.02	0.12	23
Mn	mg l^{-1}	<0.002	0.31	0.05	0.09	0.31	26
Mo	µg l^{-1}	<0.1	8.1	0.1	0.56	4.91	23
Nb	µg l^{-1}	<0.01	0.03	<0.01	0.007	0.02	23
Nd	µg l^{-1}	<0.01	8.49	0.02	0.73	5.79	23
Ni	µg l^{-1}	<0.2	26.1	0.6	5.12	23.3	23
Os	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	23
Pb	µg l^{-1}	<0.1	2.9	0.1	0.36	2.09	23
Pd	µg l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	23
Pr	µg l^{-1}	<0.01	2.01	<0.01	0.17	1.36	23
Pt	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	23
Rb	µg l^{-1}	0.87	53.8	3.42	5.81	30.3	23
Re	µg l^{-1}	<0.01	0.02	<0.01	0.007	0.02	23
Rh	µg l^{-1}	<0.01	0.01	<0.01	0.005	0.01	23
Ru	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	23
Sb	µg l^{-1}	<0.05	0.22	<0.05	0.05	0.20	23
Sc	µg l^{-1}	<1.0	1.0	<1.0	0.57	1.0	23
Se	µg l^{-1}	<0.5	3.4	<0.5	0.51	2.29	23
Sm	µg l^{-1}	<0.02	1.54	<0.02	0.15	1.13	23
Sn	µg l^{-1}	<0.05	0.17	0.07	0.07	0.14	23
Sr	µg l^{-1}	49.2	3545	287	634	3421	26
Ta	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	23
Tb	µg l^{-1}	<0.01	0.18	<0.01	0.02	0.15	23
Te	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	23
Th	µg l^{-1}	<0.05	0.07	<0.05	0.03	0.06	23
Ti	µg l^{-1}	<10	<10	<10	<10	<10	23
Tl	µg l^{-1}	<0.01	0.1	<0.01	0.01	0.06	23
Tm	µg l^{-1}	<0.01	0.12	<0.01	0.01	0.07	23
U	µg l^{-1}	<0.02	0.77	0.02	0.07	0.48	23
V	µg l^{-1}	<0.2	1.9	0.2	0.41	1.80	23
W	µg l^{-1}	<0.02	0.05	<0.02	0.01	0.05	23
Y	µg l^{-1}	<0.02	5.5	0.04	0.67	4.57	23
Yb	µg l^{-1}	<0.01	0.89	<0.01	0.08	0.57	23
Zn	µg l^{-1}	2.1	373	18.8	58.9	332	26
Zr	µg l^{-1}	<0.02	0.34	<0.02	0.05	0.28	23

5.2 Water types and physicochemical characteristics

The groundwaters in the Palaeogene strata have a median temperature of 13.4 ^{o}C. The measured range of temperatures however varies widely (11.6 and 21.1 ^{o}C), with the higher temperatures relating to samples obtained from storage tanks, rather than from the borehole directly. The pH varies from moderately acidic to neutral (pH 4.7 – 7.33) with a median of 6.73. The waters are generally fresh: mineralisation varies from weakly to moderately mineralised (median SEC of 396 µS cm^{-1}). Redox potential is very variable in the groundwaters, ranging from reducing (minimum Eh of 68 mV) to oxidising (maximum Eh of 422 mV).

The most common water type encountered in the Palaeogene aquifer is Ca-HCO_3 type (Figure 5.1). These waters are generally fresh with low Na and Cl concentrations and pH between 6.17 and 7.33 and are present under oxidising as well as reducing conditions. A relative decrease in HCO_3 and relative increase in Cl and Na was observed in some groundwaters, which were of a mixed Ca-Na-HCO_3 type. Two of the samples contained high Na and Cl concentrations, but Na was much more enriched giving rise to a trend towards Na-HCO_3 type. These samples have the highest mineralisation (SEC > 800 µS cm^{-1}) and are well buffered with a median pH of 7.11. The majority of waters enriched in Na were obtained from boreholes extending into the London Clay Formation (Figure 5.1). The last water type recognised in the study area is a Na-SO_4 type water. Waters of this type are acidic (median pH = 5.19) with a low degree of mineralisation (median SEC 235 µS cm^{-1}).

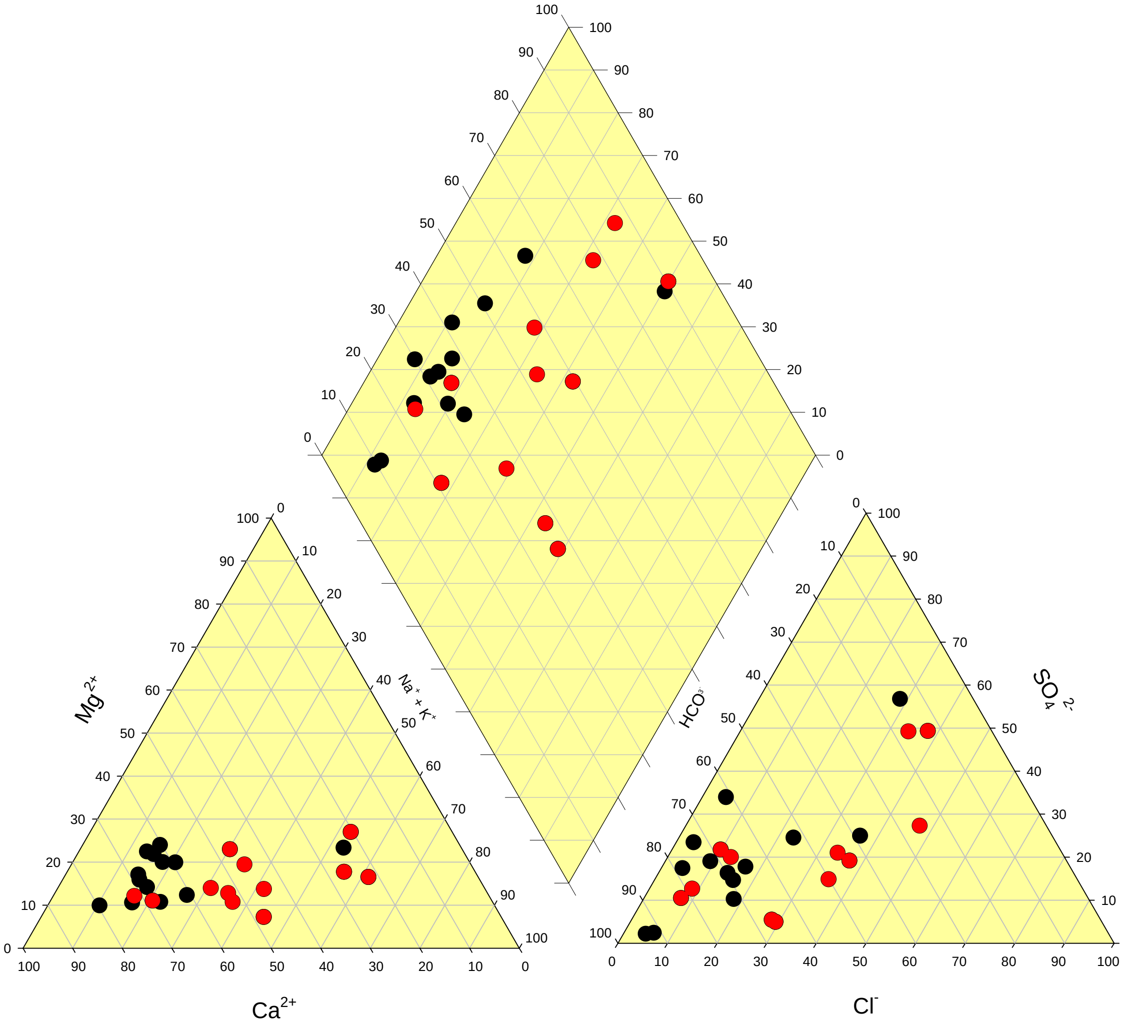
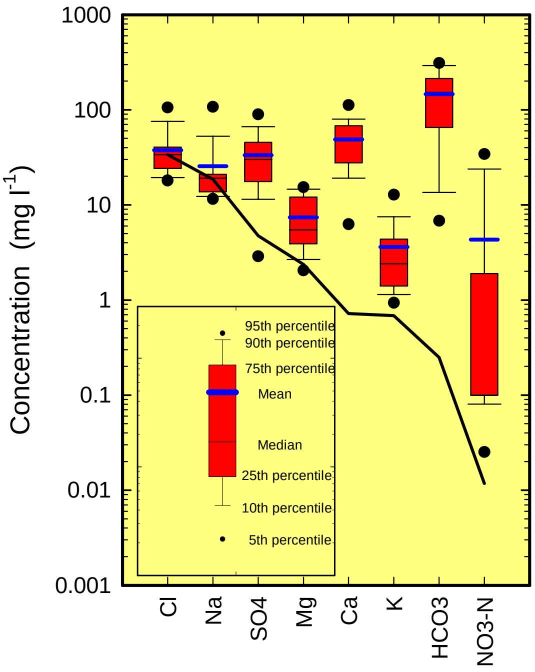
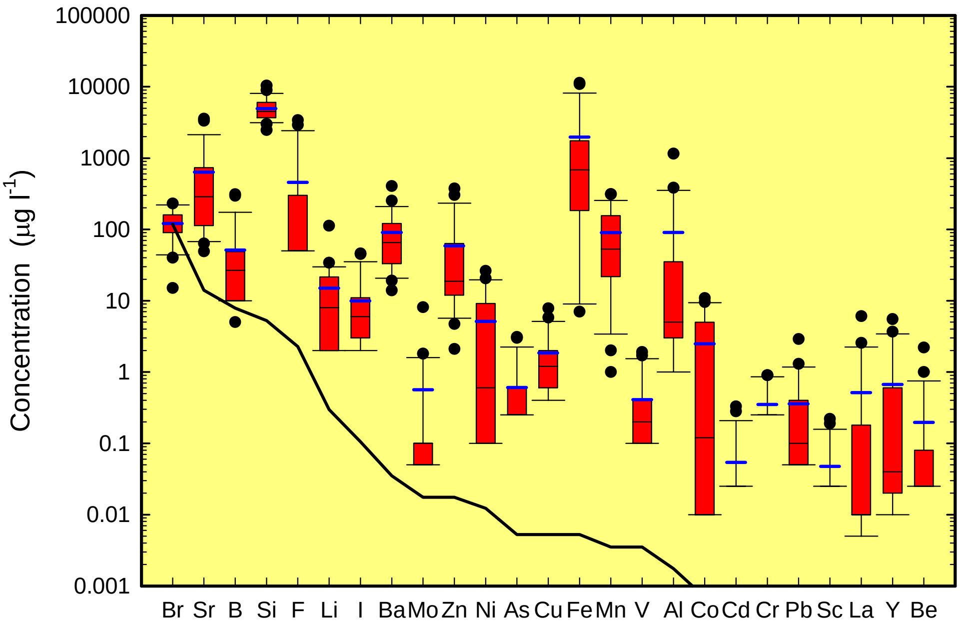


Figure 5.1 **Piper plot showing relative concentrations of major cations and anions in the Palaeogene aquifers of the Wessex Basin (red symbols show groundwaters from boreholes which extend to the London Clay Formation).**



Range of major ion concentrations in the Palaeogene groundwaters.



Range of minor and trace element concentrations in the Palaeogene groundwaters.

Figure 5.2 **Range of major and minor ion and trace element concentrations in the Palaeogene aquifers in the Wessex Basin. The black line represents the element concentrations in diluted seawater at the median Cl concentration of the groundwater dataset.**

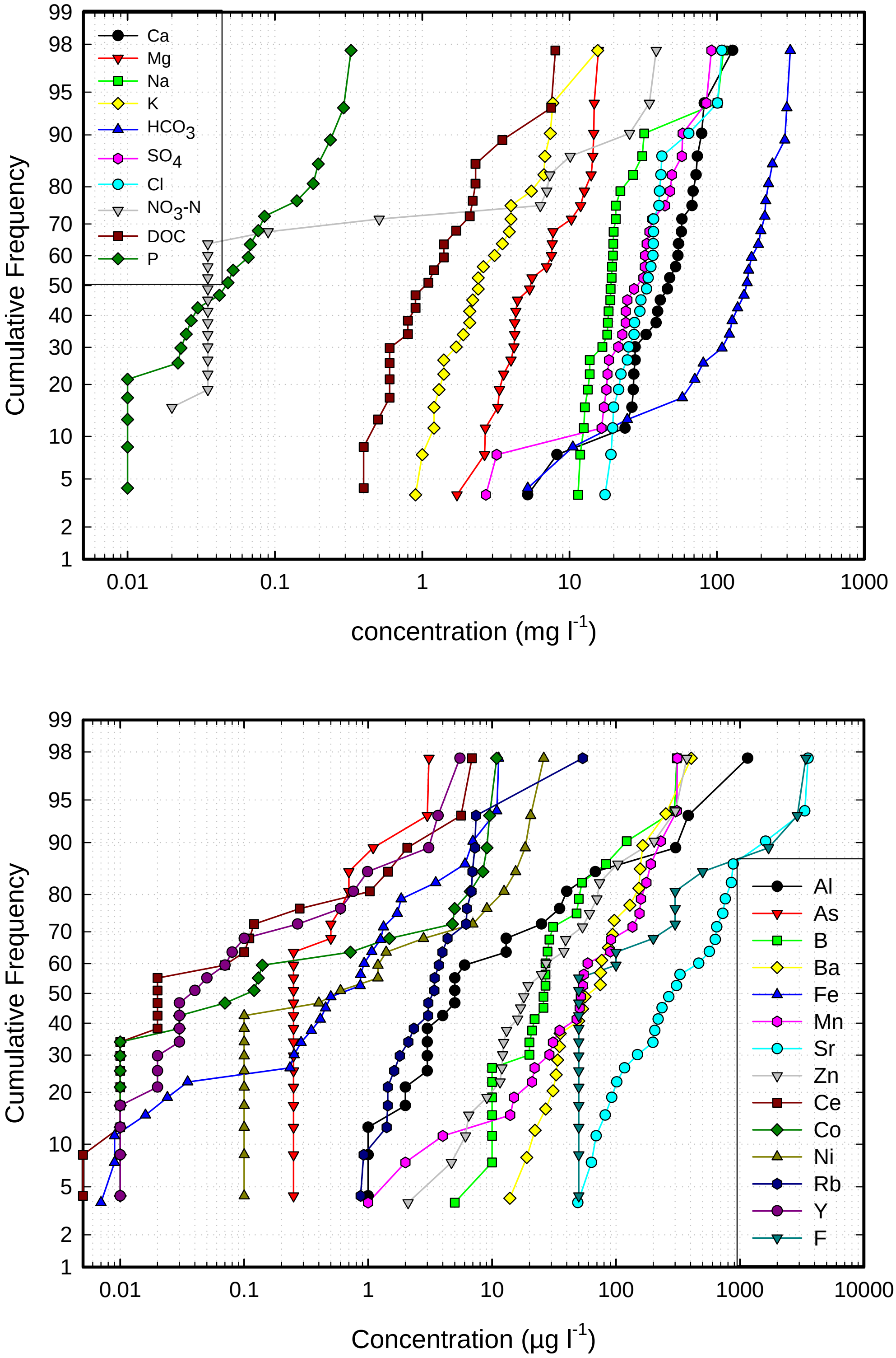


Figure 5.3 **Cumulative probability plots for groundwaters from the Palaeogene aquifers in the Wessex Basin**

5.3 Major elements

Major-element concentrations are shown in boxplots in Figure 5.2. The median chloride concentration of 33.7 mg l^{-1} is about 3 to 4 times higher than the concentration of the estimated bulk precipitation (Table 3.4, “Rainfall x 3”), indicating that the groundwaters contain a source of Cl in addition to rainfall. The median concentrations of the other major elements, except Na, plot above the diluted seawater curve, indicating that solutes have been accumulated in the groundwaters as a result of water-rock interaction or anthropogenic inputs and are not simply the remnants of a marine depositional origin. Nitrate has a wide range of concentrations, with the maximum concentration being much higher than that expected from rainfall inputs. The other major elements show less variation and reflect the diverse water types in the study area.

The cumulative-frequency plots of the major ions show bicarbonate to have a very wide range of concentrations, ranging over two orders of magnitude. A similar distribution is observed for SO_4 and Ca with a negative skew in the lower 15% of the data. Sodium and Cl concentrations exhibit a positive skew in the upper 10% of the data, indicating waters of naturally higher salinity.

There is a strong negative skew in the the cumulative frequency plot for NO_3 coincident with the more reducing groundwaters. Additonally, old formation waters will exhibit low nitrate concentrations, being recharged before agricultural pollution occurred, while some groundwaters might generally be unaffected by agricultural pollution e.g. within the New Forest National Park. The most notable break of slope occurs at approximately 6 mg l^{-1}. Some waters contain NO_3-N concentrations above the EC limit for drinking water of 11.3 mg $l^{-1.}$

Concentrations of P are moderately high in many of the groundwaters (up to 330 µg l^{-1}). A positive skew is observed in the upper 25% of the data, indicating waters of relatively high P concentrations. The lower 20% of the data are below detection limit (<20 µg l^{-1}), reflected in a straight line in the cumulative frequency plots.

5.4 Minor and trace elements

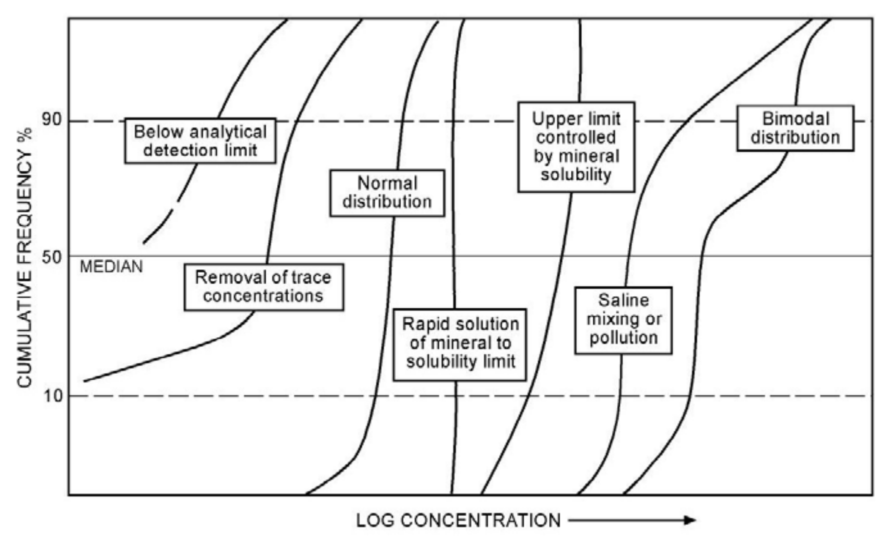
Most minor and trace elements are present at low concentrations, but lie above the dilute seawater line (Figure 5.3). Silicon shows a narrow range of concentrations suggesting saturation with respect to a silica mineral phase, probably Chalcedony. However, most trace elements show a wide range of concentrations often varying over three orders of magnitude. The highest concentrations of several trace metals are found in the lower pH groundwaters, reflecting the mobility of these elements under acidic conditions. Al concentrations exceed the EC guide level for drinking water of 200 µg l^{-1} in three sources. Ni also varies in concentration over three orders of magnitude, with two samples exceeding the EC drinking water standard of 20 µg l^{-1}.

A positive skew in the upper 15 % of the data is observed on the frequency distribution plots for a number of minor and trace elements e.g. B, As and F, with the latter reaching up to a maximum of 3400 µg l^{-1} with three samples exceeding the EC drinking water limit for F of 1500 µg l^{-1}. However, As concentrations (maximum of 3.1 µg l^{-1}) and B concentrations (maximum of 310 µg l^{-1}) remain below the EC drinking water limits for all samples.

Iron and Mn show a broad range of concentrations (Figure 5.3) with median concentrations of 683 and 53 µg l^{-1} respectively. Iron concentrations are generally high, reaching up to 11300 µg l^{-1}, well above the EC drinking water limit of 200 µg l^{-1}. In total, 18 samples out of 23 exceeded the EC drinking water limit for Fe, equating to nearly 80% of the sampled sources. The EC drinking water limit for manganese is exceeded in 60 % of the groundwaters sampled.

Many trace elements were present at concentrations below the detection limit of the analytical techniques used, and these are indicated by a vertical line at low concentrations in the cumulative probability plots.

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



i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.

ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.

iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).

iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO_3 by *in situ* denitrification).

v) A narrow range in concentration at the upper limit may indicate a mineral solubility control (e.g. F by fluorite)

vi) A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of natural higher salinity.

5.5 Pollution indicators

In order to determine baseline concentrations, it is preferable to study only pristine waters. Polluted waters may alter baseline concentrations either directly by adding solutes or indirectly by promoting chemical reactions within the aquifer (Box 5.2). It is generally difficult to find and sample pristine waters, in part because waters may be sampled over a large screened interval where polluted waters are present at shallow depth, or because diffuse pollution (especially agricultural pollution) is present in parts of the unconfined aquifer. The presence of detectable concentrations of anthropogenic origin help to highlight the occurrence of modern waters and hence the likelihood of potential contamination by other substances.

Nitrate concentrations in the study area are very variable, ranging from <0.07 mg l^{-1} to 38.8 mg l^{-1} as NO_3-N. The majority of the groundwater sources show concentrations below detection limit. Only 25% of the groundwaters sampled contained nitrate above 1 mg l^{-1} NO_3-N with three sources having concentrations above EC drinking water limit of 11.3 mg l^{-1} NO_3-N. The occurrence of nitrate in the study area appears to be a function of borehole depth and redox state of the groundwater. Sources containing nitrate are restricted to shallow boreholes. The deepest borehole in which nitrate concentrations are detectable is Milton Sports Ground, a borehole of 35 m depth. Waters containing nitrate are found to be oxidising.

The importance of the depth of a borehole with regard to nitrate concentrations can be demonstrated in the study area for Wessex Water observation boreholes at Stoborough and Briantspuddle, where boreholes have been drilled in close proximity but to different depths. The shallow boreholes (below 10 m depth) contained groundwater with nitrate concentrations of up to 34.8 mg l^{-1} NO_3-N, while in deep boreholes (down to 59 metres) nitrate concentrations were below detection limit.

No clear correlation can be found for boreholes with nitrate concentrations above detection limit and other common indicators of pollution such as Cl, SO_4, K or DOC. Sites with detectable quantities of nitrate are located in both rural and urban locations. The former are likely to be related to agricultural pollution. Sites in urban settings are in nurseries and open green spaces, where the application of fertilizers could be the cause of elevated NO_3-N concentrations. Concentrations of P, commonly related to agricultural pollution, are moderately high in many groundwaters (up to 330 µg l^{-1}). However, phosphorus does not correlate with many solutes including N-species, DOC, Cl or K, elements which are commonly associated with anthropogenic influence. The highest concentrations of P (> 100 µg l^{-1}) were present in moderately reducing groundwaters. There are insufficient data to ascertain whether P inputs are natural or anthropogenic but the lack of high concentrations in the most aerobic groundwaters points to a natural source.

Locally high concentrations of trace metals occur in the slightly acidic groundwaters in the study area and reflect the higher mobility of these elements under low pH conditions.

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

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

(i) to have evidence of groundwater age

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

(iii) to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced TOC and N species – especially NO_3 – the presence of 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.

To minimise risk of any surface pollution occurring close to public groundwater abstraction sources, source protection zones have been created around water abstraction points such as Ampress public water abstraction boreholes near Lymington (see Text Box 5.3).

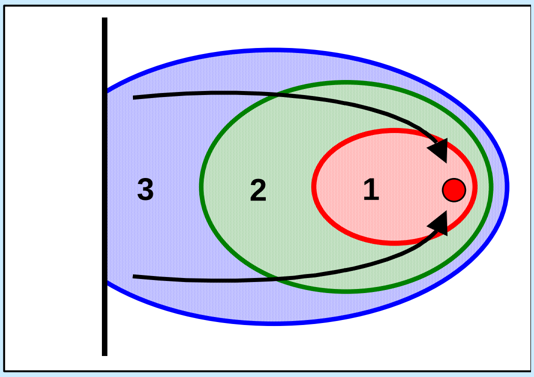
Box 5.3 Source protection zones in the study area

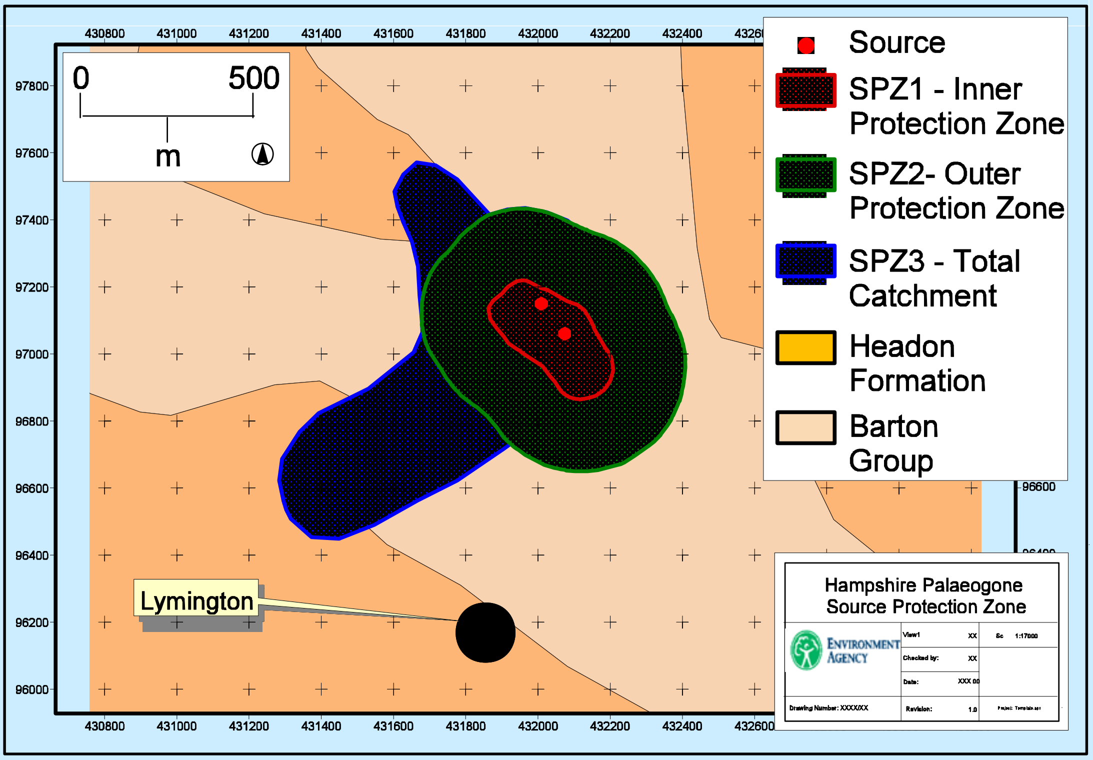
In order to avoid contamination of groundwater resources, Source Protection Zones (SPZs) are determined for every public water supply source. The zones are modelled using information on abstraction volumes and rates, the average recharge over the groundwater catchment area, and the effective thickness and effective porosity of the aquifer. The Palaeogene aquifers are characterised by intergranular flow with groundwater movement occurring slowly. Therefore, Palaeogene aquifer sources have smaller SPZs than those in other lithologies, such as Chalk and limestones, which are characterised by fracture flow that can rapidly traverse greater distances. Each SPZ comprises:

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

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

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





Source protection zone around Ampress Water Works boreholes near Lymington

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

The following sections outline some of the key factors involved in generating the regional variations in groundwater chemistry across the Palaeogene aquifers of the Wessex Basin.

It is important to bear in mind that some variations in chemical composition may be due to differences in borehole construction and different pumping histories. Differences in borehole design, including variations in casing and well depth may affect sampling caused by stratification in the aquifer or mixing. Variations in pumping history may also result in differences in water quality as differing pumping rates can affect the degree of flushing of solutes from parts of the aquifer. Pumping may also induce vertical or lateral flow from overlying formations where present. Such chemical variations are quite different from the variations observed along groundwater flow lines that result from progressive water-rock interaction with increased residence time and from variations in chemistry related to differences in aquifer lithology. 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 data set. The report presents a broad assessment of the groundwater-quality variations observed across the aquifers and the main geochemical processes that are likely to control them. It is accepted that some water-quality variation may be due to the artificial influences described above.

6.2 Chemical evolution of groundwaters

There are significant differences in the lithology within and between the formations which make up the Palaeogene aquifer in this region. The heterogeneous nature of the aquifer makes both the delineation of the flow direction as well as hydrochemical interpretation difficult. Changes in the water chemistry along the general north-south flow direction are not necessarily attributable to the geochemical evolution of the groundwater. Local drainage patterns and lithological sequences govern flow direction, groundwater travel times and the geochemical evolution of the groundwaters.

Therefore, the distance along the regional north-south flow path cannot be used as a measure of the degree of evolution of groundwaters in the Palaeogene aquifer. The extent to which waters have undergone water-rock interaction has to be evaluated with the help of residence-time indicators and the broad range of hydrochemical parameters measured in this study.

There is evidence that the geochemistry of waters in the Palaeogene sediments is not only influenced by water-rock interaction due to prolonged residence time, but by the geological nature of the aquifers themselves. The variations in water type can be broadly related to lithological units e.g. Ca-HCO_3 and Ca-Na-HCO_3 waters are mainly related to sources drawing water from the Bracklesham Group, Barton Group or Headon Formation. Elevated Na and SO_4 concentrations are observed for boreholes penetrating into the London Clay Formation resulting in waters of Na-Ca-HCO_3, Na-HCO_3 or Na-SO_4 type, indicated as red symbols on the Piper diagram (Figure 5.1).

The variability in concentrations of solutes in groundwaters of the Palaeogene aquifer can be explained by a series of processes including:

- Mineral dissolution reactions (section 6.2.1)
- Redox reactions (section 6.2.2)
- Ion exchange reactions (section 6.2.3)
- Mixing with older formation water (section 6.2.4)

- Groundwater acidification` (section 6.2.5)
- Groundwater residence time (section 6.2.6)

6.2.1 Mineral dissolution reactions

The most reactive minerals in the aquifer provide the major control on groundwater chemistry, particularly in young groundwaters. The most reactive minerals often found in aquifers include carbonate minerals (e.g. calcite, dolomite). Calcite is the most reactive mineral in the Palaeogene strata and provides the dominant control on the chemistry of the Ca-HCO_3 type waters through calcite dissolution:

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

Most of the groundwaters are of Ca-HCO_3 type as a consequence of the above reaction. However, the overall carbonate content of the Palaeogene aquifer is low which is reflected in the median bicarbonate concentration of 153 mg l^{-1}. This is similar to carbonate-poor aquifers such as the Lower Greensand (Shand et al., 2003). The limited availability of carbonate to neutralise acidic recharge water leads to the slightly acidic conditions of most sampled sources. Only a few groundwaters show slightly elevated bicarbonate concentrations (> 200 mg l^{-1}), all of which approach saturation with respect to calcite. In general, groundwaters from the Palaeogene remain undersaturated with respect to calcite and dolomite and therefore have potential to dissolve further carbonate (Figure 6.1). This suggest, that carbonate cements are not widely distributed in the Palaeogene or that decalcification might have occurred within the flow system. There is no clear trend between HCO_3 concentration and depth of borehole, most likely due to the heterogeneity of carbonate mineral distribution. Sulphate concentrations in most groundwaters are above the dilute seawater line (Figure 5.2), indicating an additional source of S in the aquifer. The low Ca concentrations in these waters exclude gypsum dissolution as source of SO_4. The most likely source is from the oxidation of pyrite:

$$FeS_2 + 15/4\ O_2 + 7/2H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

This process generates acid, and if oxidation occurs, Fe^{3+}. However, under natural conditions, incomplete oxidation of pyrite is common, and SO_4 is produced, but Fe^{2+} is not oxidized to Fe^{3+}. This leads to waters rich in Fe^{2+} and SO_4^{2-}, as observed in the study area for the Poole Hospital and the Hamworthy Engineering sources.

The Palaeogene aquifers are largely composed of quartz. However, the reaction of silica minerals is relatively minor compared to carbonate dissolution and pyrite oxidation outlined above. Quartz is extremely unreactive and the main source of Si is from silicate minerals such as K-feldspar or clay minerals (e.g. illite). Silicon concentrations vary in the study area between 2.5 and 10.4 mg l^{-1} with a median concentration of 4.5 mg l^{-1}. The widest range in concentrations is observed for Ca-HCO_3 type waters, with the lowest concentrations typically being in the Na-SO_4 and Na-HCO_3 waters. No increase in Si is identified with depth or age. The upper concentration limit of Si is controlled by saturation with respect to a silica phase, most likely chalcedony, as shown by the saturation indices data (Figure 6.1).

While the dissolution of calcite provides the dominant control for the majority of major-element concentrations in Palaeogene groundwaters, some waters are modified by other processes including redox reactions (section 6.2.2), ion-exchange (section 6.2.3) and mixing (section 6.2.4).

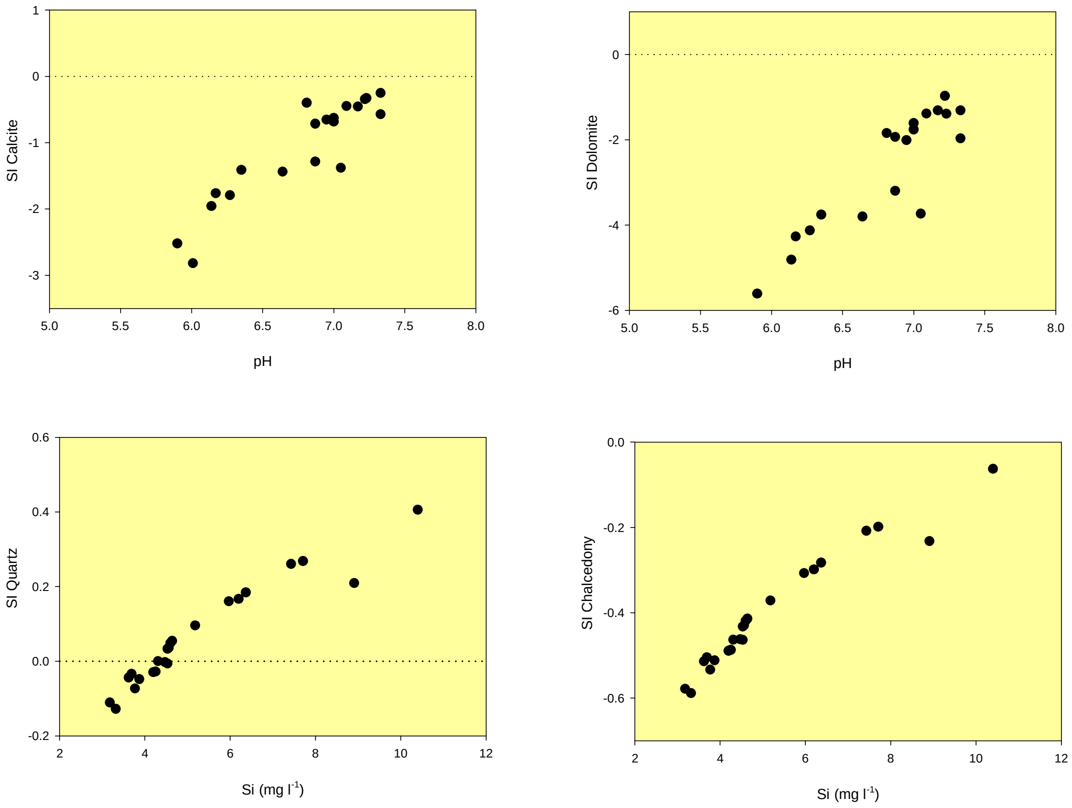


Figure 6.1 Saturation indices of groundwaters of the Palaeogene aquifers.

6.2.2 *Redox reactions*

Dissolved oxygen (DO) and Eh measurements give an indication of the redox status of the groundwaters. The absence of oxygen and NO_3-N, the presence of Fe^{2+}, and low Eh values indicate that reducing conditions are present throughout large parts of the aquifers (see Box 6.1). Approximately 30% of the sampled groundwaters are oxidising to slightly reducing, while 70% are more reducing, with some waters having a strong H_2S smell.

There is a tendency for shallower boreholes to yield oxidising groundwaters. This is the case in several of the shallow observation boreholes belonging to Wessex Water as well as for shallow private supplies such as Walford Farm in the west and Stanswood Farm in the east of the study area. However, not all shallow boreholes tap oxidising waters nor do all deep boreholes solely yield reducing waters. This reflects the layered nature of the Palaeogene aquifer with interbedding of low-permeability and high-permeability strata. This could explain strongly reducing waters in boreholes of 15 metres depth at Bulbery Golf course and 17.6 m depth at Bulbery. These shallow aquifers are possibly overlain by a low-permeability confining layer.

Selected redox sensitive species have been plotted against Eh on Figure 6.2. The redox potential should be used only as a guide because it was not possible to measure directly from the borehole outlet for some samples. However, it can be seen that the concentrations of Fe and Mn are generally higher in the low-Eh groundwaters, reflecting the increased solubility of Fe and Mn oxides under reducing conditions. In oxidising groundwaters NO_3 is stable in the presence of dissolved oxygen but undergoes denitrification when all of the oxygen is consumed during redox reactions. Nitrate has been plotted against Fe on Figure 6.3 since the presence of redox indicator species may indicate better the redox conditions in the aquifer where Eh and DO are not determined accurately. Here it can be seen that the groundwaters with high NO_3-N have low Fe^{2+} concentrations and vice-versa, consistent with the stability of these species under different redox conditions. Baseline concentrations of NO_3-N in the aerobic groundwaters would be expected to be around 1-2 mg l^{-1}, allowing for addition or removal from the soil zone. However, oxidising waters in the area show a wide distribution of nitrate concentrations with 6 out of 26 samples exhibiting concentrations above likely baseline concentrations, reflecting the influence of agricultural pollution sources. Under anaerobic conditions, nitrate concentrations generally decrease and reducing waters in the area exhibit values close to, or less than, the detection limit. However, it is not always clear whether anaerobic groundwaters have ever contained appreciable nitrate concentrations because of their possible pre-modern age (see section 6.4). Where nitrate concentrations decrease due to nitrate reduction, concentrations of the reduced nitrogen metastable species NO_2 would be expected to increase and ammonium can be stable (Environment Agency, 2003). There is potentially evidence for this in several sources drawing anaerobic groundwater, with the highest concentrations of 0.27 mg l^{-1} NH_4-N being recorded for Paultons Park, a borehole of 76 m depth in the north of the study area. However, elevated NH_4-H concentrations could also occur naturally in older formation waters.

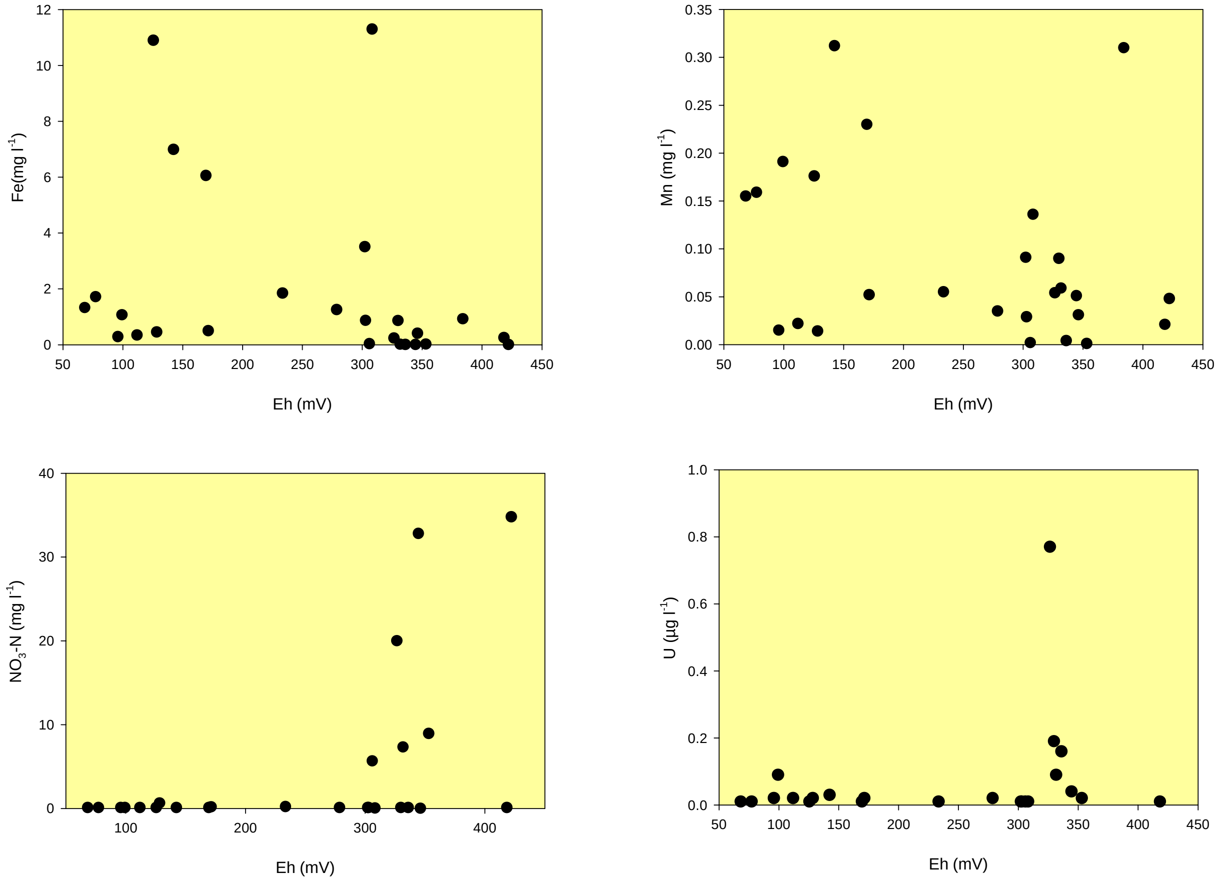


Figure 6.2 Redox parameters and redox sensitive species in the Palaeogene aquifers.

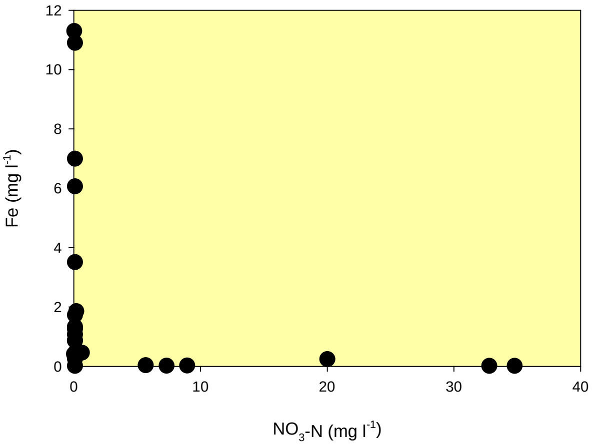


Figure 6.3 Fe^{2+} and NO_3 as indicators of the redox state of the aquifer.

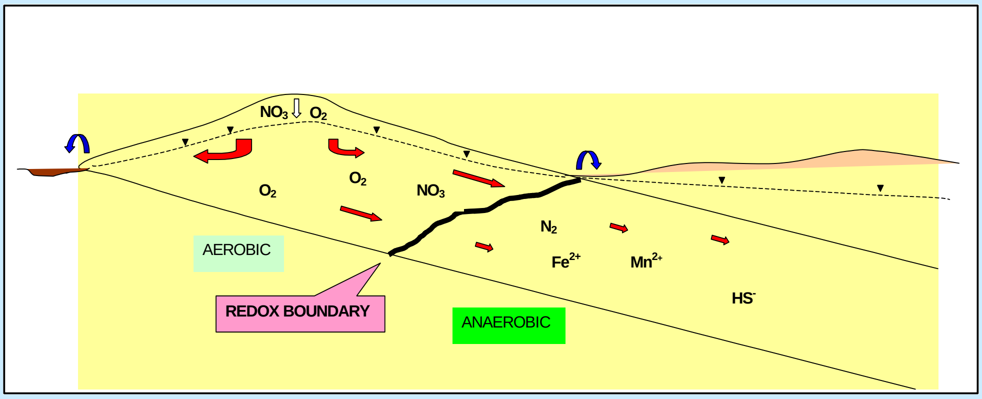
Iron concentrations (as Fe^{2+}) increase in reducing groundwaters to concentrations of up to 11.3 mg l^{-1}, thereby exceeding the EC drinking water limit by several mg l^{-1}. Figure 6.4 is an example of an iron-rich groundwater source in the study area. At the outlet of the Bulbery Golf course borehole Fe^{3+} forms insoluble hydroxides under now oxidising conditions forming brownish-red stains.

Manganese concentrations are also high in reducing waters, with the highest concentrations being recorded for Lytchett Minster with 0.19 mg l^{-1}, from a borehole of 47.6 m depth, penetrating the Bagshot Formation/London Clay Formation.

Figure 6.4 Iron stains at the outlet of a pipe conveying water from a borehole into a small pond at Bulbery Golf course [SY 923 934].

Sulphate reduction is believed to have occurred in at least two boreholes, Poole Hospital and Hamworthy Engineering. Both sources exhibit low DO, elevated NH_4-N and high Fe concentrations and a strong smell of H_2S (a product of sulphate reduction), although this was not measured directly. However, sulphate is still moderately high in these groundwaters (32-58 mg l^{-1}), although as the ICP-AES technique used measures total S (as SO_4), a proportion of this could be dissolved sulphide. Other boreholes showing strongly reducing conditions and relatively low concentrations of SO_4 include the Na-HCO_3 type waters (Paultons Park and Wisteria House) and Beaulieu Hotel and Station House boreholes in the New Forest. However, the presence of H_2S was not noted at these sites.

Box 6.1 Redox Boundary



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

6.2.3 *Ion-exchange reactions*

The fresh waters in the study area are dominated by Ca^{2+} and HCO_3^- ions as a result of the dissolution of calcite. As this groundwater flows through the Palaeogene aquifer, freshening (i.e. more recently recharged fresh water comes in contact with parts of the aquifer containing remnants of older formation water) may cause cation exchange of Ca for Na according to:

$$\tfrac{1}{2}\, Ca^{2+} + \text{Na (adsorbed)} = Na^+ + \tfrac{1}{2}\, \text{Ca (adsorbed)}$$

where adsorbed denotes cations adsorbed on clays. Ca^{2+} is taken up from water, in return for Na^+, with a Na-HCO_3 type water being produced. There are two Na-HCO_3 type waters in the study area, Wisteria House and Paultons Park, from boreholes penetrating both the Bracklesham Group and

London Clay Formation. The groundwater from a 47.6 m borehole at Lychett Minster, which penetrates the same lithologies, also has elevated Na/Ca ratios. The effect of ion exchange in the aquifer is illustrated in Figure 6.5, where groundwaters have relatively high Na concentrations for their respective Ca and HCO_3 concentrations. Within the study area, the generally low abundance of Ca might limit the exchange reaction. Clay minerals with exchangeable Na within the Palaeogene aquifers are considered to be the source of Na for the exchange process.

The process described above will work in reverse if seawater intrudes the freshwater aquifer:

$$Na^+ + \tfrac{1}{2}\,Ca\ (adsorbed) = Na(adsorbed) + \tfrac{1}{2}\,Ca^{2+}$$

Na is taken up by the clay minerals and Ca^{2+} is released, resulting in a shift towards a $CaCl_2$ type water.

There is a trend towards a $CaCl_2$ type water in one borehole sampled (Figure 5.1), which indicates that saline intrusion may be taking place. It is a shallow borehole (9.6m), situated ca. 700 metres south of the tidal part of the River Frome and ca. 2 km south-west of the Wareham Channel. However, generally chloride concentrations remain low even close to the coast (median Cl 33.7 mg l^{-1}) and current groundwater abstractions do not seem to result in significant seawater ingress in the near coastal regions.

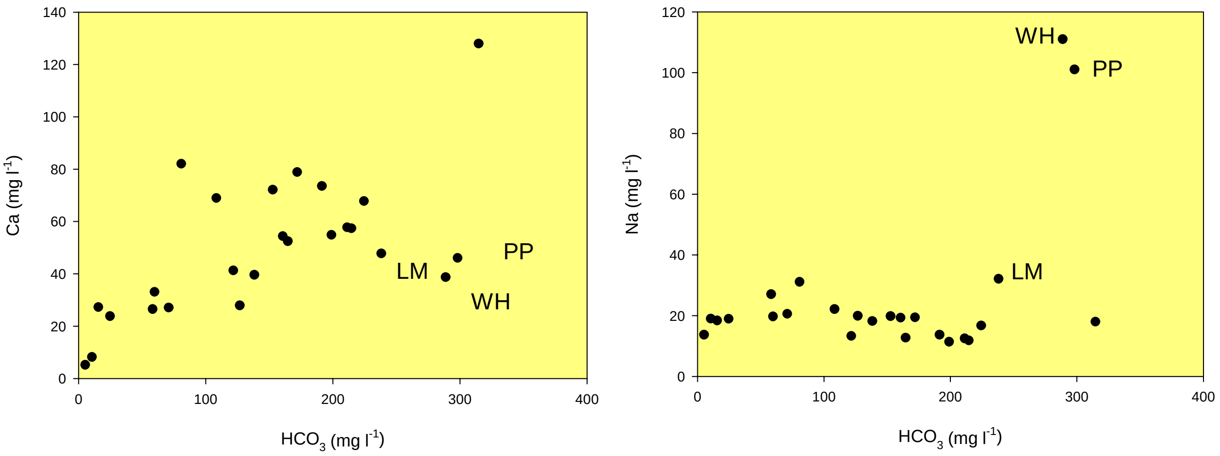


Figure 6.5 **Plot of (a) HCO_3 vs. Ca and (b) HCO_3 vs. Na showing the low Ca/HCO_3 and high Na/HCO_3 ratios in the groundwaters sampled from Wisteria House (WH), Paultons Park (PP) and Lychett Minster (LM).**

6.2.4 Mixing with older formation water

It is generally considered that chloride behaves conservatively (i.e. non-reactively) in groundwater systems and therefore may provide a good indicator that mixing processes are taking place between recharge and formation waters. The chloride concentrations are generally low within the Palaeogene aquifers (median concentration: 33.7 mg l^{-1}). However, the $Na\text{-}HCO_3$ waters, Paultons Park and Wisteria House and the Lytchett Minster groundwater source contain significantly elevated chloride concentrations (up to 108 mg l^{-1}). A similar increase is observed in Na concentrations. These sources also contain elevated concentrations of various trace elements, including Br, I and B, indicating that mixing with older formation water may take place as well as the ion-exchange described in the previous section. These groundwaters also contain very high concentrations of F and Sr (Figure 6.6), which is typical of old confined Chalk groundwaters in the Wessex Basin (Buckley et al., 1998). It is thought that the sands at the base of the Palaeogene, from which the Lytchett Minster sample was abstracted, are in hydraulic continuity with the Chalk beneath, which provides the source of the unusually high concentrations of F and Sr. It is not known if this is the case for groundwater in boreholes at Paultons Park and Wisteria House, but the hydrochemical similarities make it likely that the high F and Sr (and also Cl) are also derived from the underlying Chalk. This is also indicated by the limited $\delta^{13}C$ data and Sr/Ca ratios which are higher than other Palaeogene samples and closer to Chalk groundwater e.g. at Lytchett Minster the Chalk had a $\delta^{13}C$ value of around –5 $^{0}/_{00}$ and a Sr/Ca ratio of 0.06 (Buckley et al., 1998).

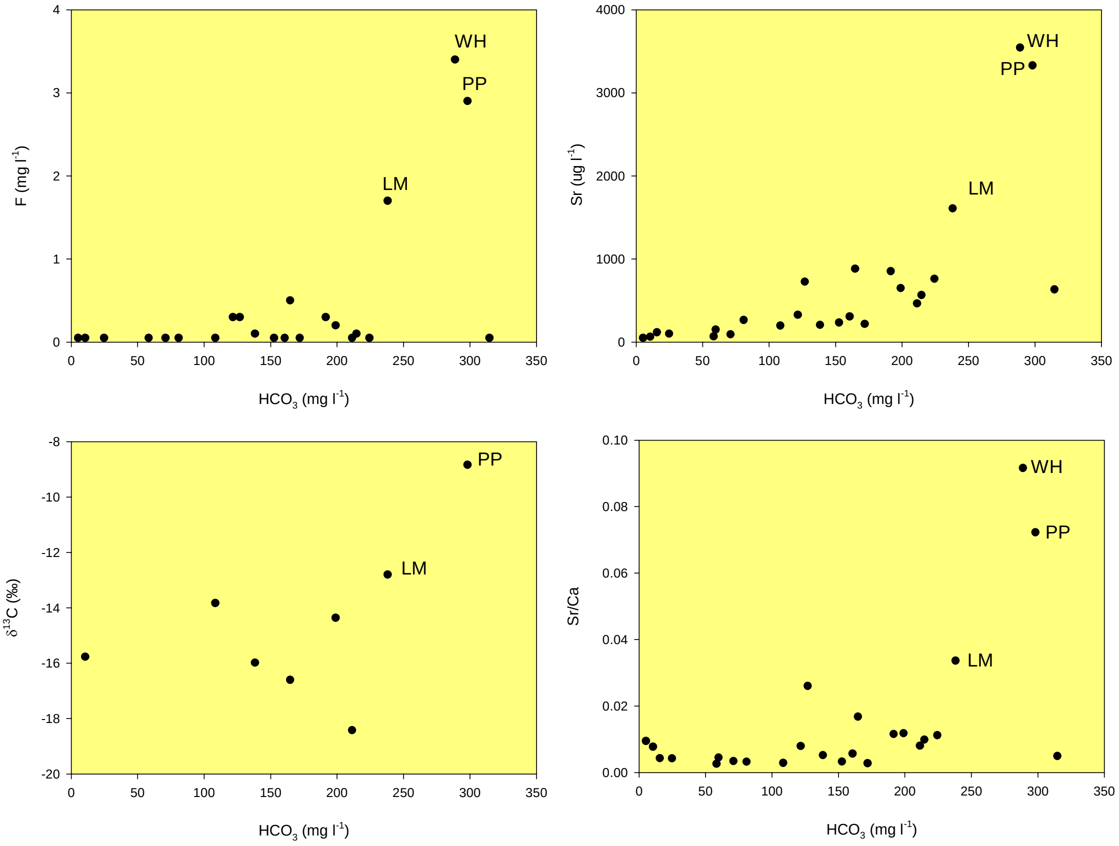


Figure 6.6 **Indicators of groundwater mixing in the Palaeogene aquifers (Wisteria House (WH), Paultons Park (PP) and Lychett Minster (LM)).**

6.2.5 Groundwater acidification

Acidic groundwaters were recognised in a number of sources in the study area. The median pH of all sampled sources is 6.7. However, some sources had pH as low as 4.7. A range of different processes may cause acidification, including natural occurrence through CO_2 production in the soil:

$$CH_2O + O_2 = H_2O + CO_2$$

Additionally, anthropogenic acidification occurs through acid rain and/or the excessive use of ammonium-based fertilisers and manure. With the latter process, the oxidation of ammonium by oxygen is the main acidifying process according to the reaction:

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O$$

Sources not influenced by agriculture in the study area might, besides acid rain deposition, acquire their low pH through oxidation of pyrite (FeS_2). Traces of pyrite are found in various Palaeogene lithologies under reducing conditions, particularly in the London Clay. Lowering of the water table by pumping may result in the oxidation of pyrite (see section 6.2.1 for equation). This process is likely to be the cause for the very low pH measured in the Poole Hospital and Hamworthy Engineering sources, both of which have high SO_4 and Fe concentrations. Sulphate concentrations are relatively high in the lower pH groundwaters (Figure 6.8) indicating that pyrite oxidation might be of importance for several sources. Figure 6.7 is an example for the ferruginous sediments present in the Palaeogene.

Figure 6.7 Ferruginous deposits within the Palaeogene sedimentary sequence [SZ 195 927].

The groundwater in the Palaeogene aquifers is susceptible to acidification due to the low buffering capacity of the rocks in which carbonate is low or absent. A decrease in alkalinity over time would be a good indicator for progressing acidification, however, such time series data are not available in the study area. A study by Edmunds and Kinniburgh (1989) on the hydrochemistry of poorly-buffered lithologies in the UK, investigated unsaturated zone profiles of Eocene Sands near Camberley, Surrey. The pH profile showed values as low as 3.5 close to the surface, rising to 5.3 below 3 m depth. The study pointed out, that acidic conditions in the unsaturated zone might lead to increased mobility of heavy metals and their transfer to shallow groundwaters. A more detailed discussion of the abundance of heavy metals in the study area is given in section 6.2.6.

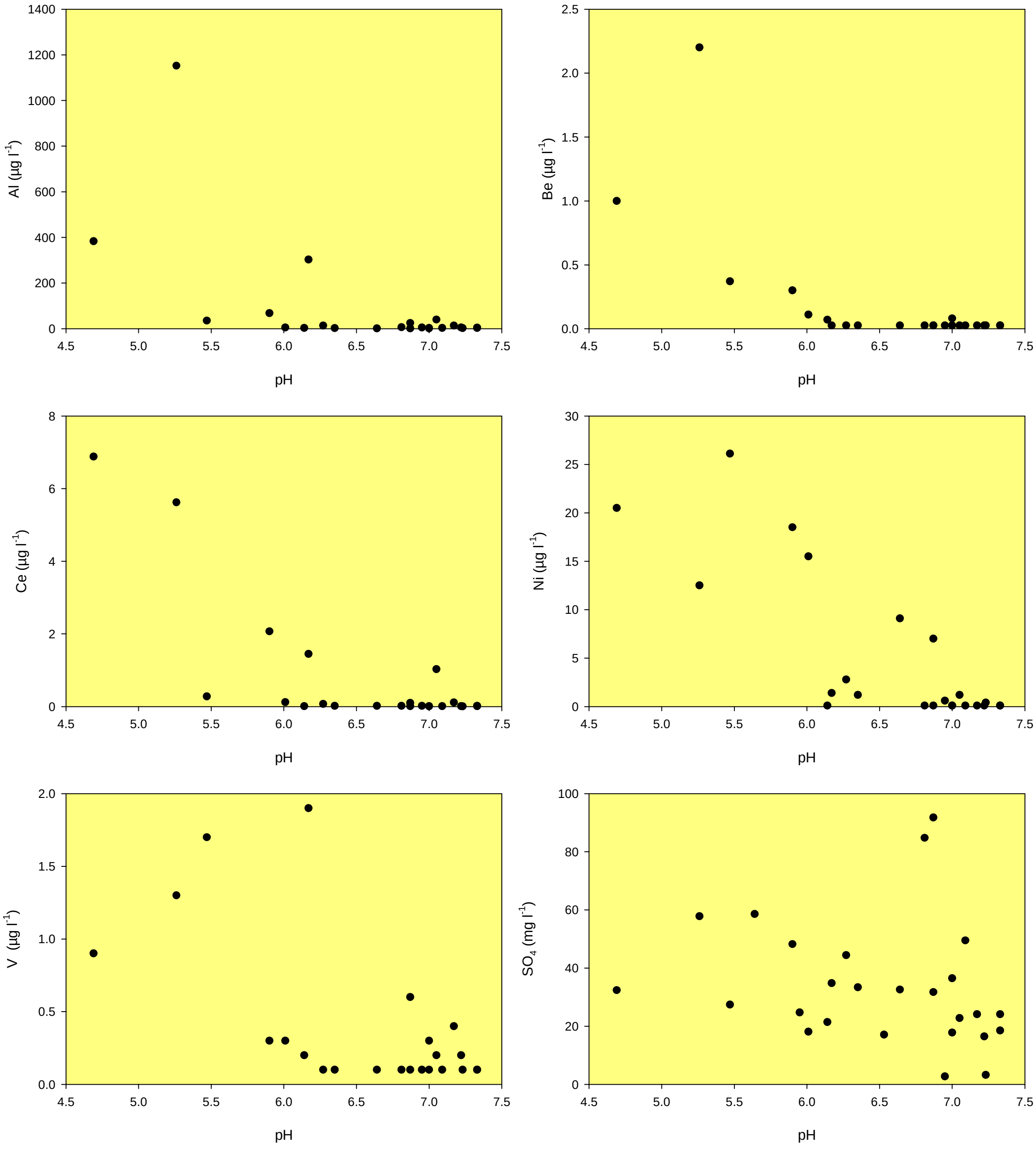


Figure 6.8 **Selection of determinands influenced by pH in the Palaeogene aquifers.**

6.2.6 Trace elements

Trace-element concentrations in groundwater are controlled by a wide range of processes and their behaviour is often much less well-understood than for the major elements. The distribution of many trace elements, such as Sr, Ba and Rb are controlled by mineral dissolution reactions of their host minerals such as feldspar. Their upper limits are often controlled by saturation or adsorption processes. For redox sensitive species, the redox conditions in the aquifer exert an important control and many metals are also controlled by the pH, being mobile at low pH, but undergoing adsorption at higher pH.

Strontium generally behaves similarly to Ca geochemically, often correlating with Ca in minerals and rocks. The main source of Sr in groundwater within carbonate aquifers is typically from calcite, whereas in carbonate-free silicate aquifers, plagioclase may be the dominant source. Strontium, unlike Ca, is generally not limited by saturation with respect to a mineral phase in most groundwaters in the

UK. Hence it is often used as a relative indicator of the residence time of groundwaters (Edmunds & Smedley, 1998). Strontium correlates rather poorly with Ca (Figure 6.9), which reflects the various sources in the aquifer (calcite plus feldspar) and the limits on Ca imposed by saturation with respect to calcite and ion-exchange. A better correlation was observed with SEC and HCO_3 (Figure 6.9).

K-feldspar can have high concentrations of Barium and this provides the most likely source in the aquifer. Where SO_4 concentrations are high in groundwater, Ba concentrations are limited due to saturation with respect to the mineral barite ($BaSO_4$). However, the Palaeogene groundwaters generally contain low SO_4 concentrations, which has allowed relatively high Ba concentrations to occur (maximum 404 µg l^{-1}, median 65 µg l^{-1}) (Figure 6.9). Most of the high-Ba groundwaters are oversaturated with respect to barite, a situation found in other UK sandstone aquifers (Griffiths et al., 2002; Shand et al., 2002) probably due to very slow precipitation kinetics.

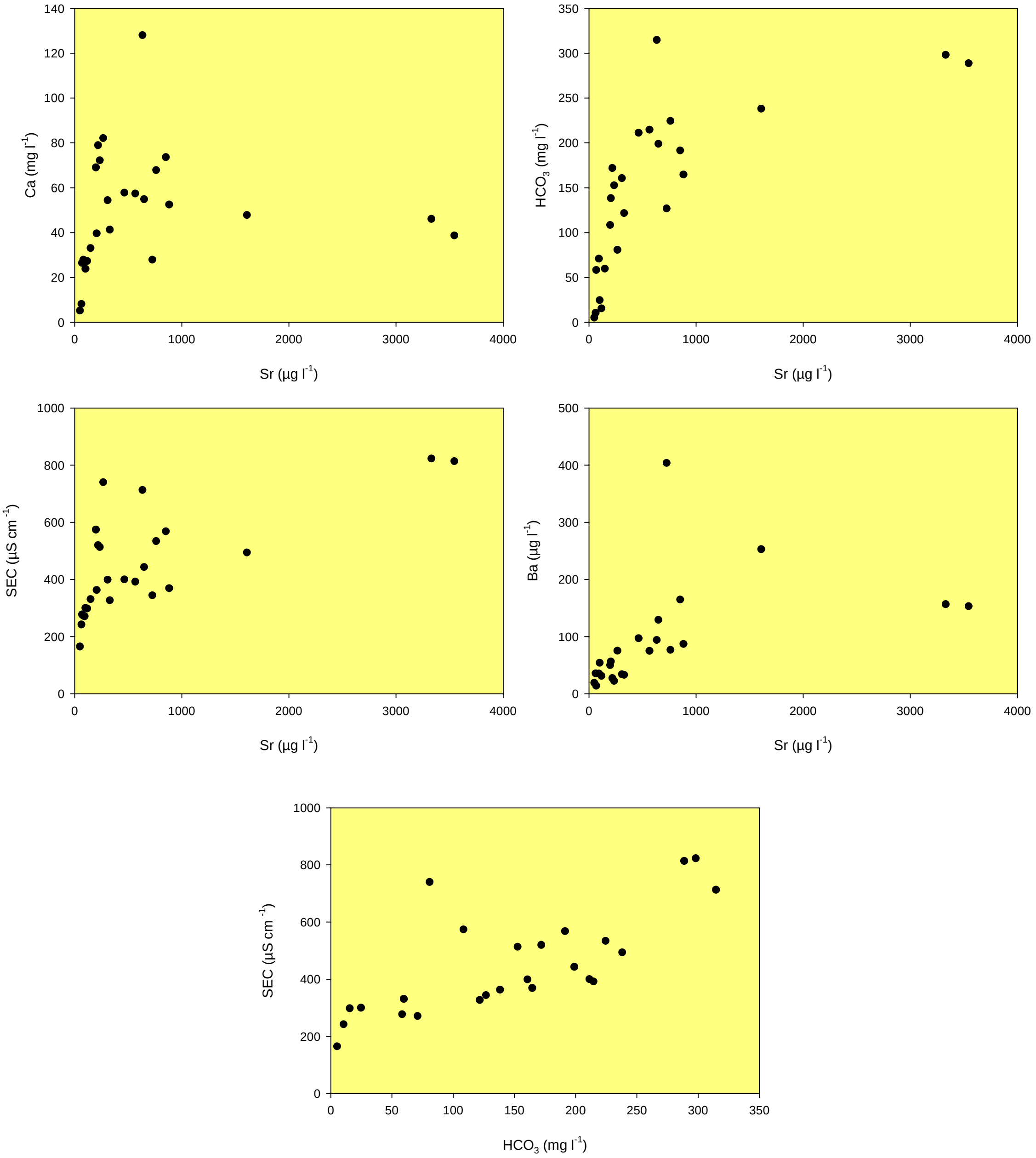


Figure 6.9 **Trace element concentrations and HCO_3 and conductivity values in Palaeogene groundwaters.**

The acidity of the groundwaters has had a considerable effect on the mobilisation of trace elements (see section 6.2.5). Under conditions of lower pH a number of metals are mobile even under oxidising conditions. These include Al, Be, Ni and Co. The highest Ni concentrations are found in the most acidic waters in the study area, with values reaching up to 26 µg l^{-1}, while Ni in groundwaters at neutral pH is often below the detection limit. The abundance and behaviour of Co closely follows that of nickel with concentrations ranging from <0.02 µg l^{-1} (detection limit) to 10.9 µg l^{-1}. The abundance of aluminium is also controlled by pH, with higher concentrations being apparent in the more acidic waters (Figure 6.8). In one sample, with a pH of 5.26, the concentration reached 1152 µg l^{-1}, exceeding the EC drinking water limit. Above pH 6.3 aluminium concentrations often remain below 10 µg l^{-1}.

6.3 Temporal variations

The only long-term records of water chemistry available in the study area are for the Ampress Waterworks borehole AMP5 from 1991 to 1995.

Figure 6.10 shows concentrations over time for major ions, nitrate and pH. Within this period conductivity was the most frequently measured determinand.

No significant trend can be observed for any major ion. However, conductivity measurements appear to exhibit a steady decrease between December 1991 and October 1995, with the average conductivity falling from 552 µS cm^{-1} during 1991 to 468 µS cm^{-1} during 1995. This is not mirrored in the major elements, possibly a result of their infrequent measurement.

Nitrate concentrations vary over a wide range between 1991 and 1993. Minimum concentrations remain below the detection limit of 0.1 mg l^{-1} , while the maximum recorded concentration is 10.3 mg l^{-1} as NO_3. After 1993, nitrate concentrations appear to be generally lower, with the majority of samples exhibiting concentrations below the detection limit. The variability in concentrations could be a result of the pumping regime at this public water supply source, or it might reflect the amount of recently recharged oxidising and high NO_3 water contributing to the aquifer depending on rainfall intensities. A general decrease in concentrations, if present, could possibly be the result of changed land-use practices within the catchment of the abstraction boreholes.

Figure 6.10 shows variations in pH between 1991 and 1993. The pH range is 7.6 to 8.5 but no obvious trend is observed. The pH cannot be correlated with any pH-dependent trace elements such as aluminium due to their infrequent measurements.

6.4 Age of the groundwater

There are no direct age determinations for the Palaeogene groundwaters. However, stable isotopes and solute concentrations may be used to estimate relative ages assuming that their geochemical controls are well established.

The stable isotopes $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$ have been analysed in six groundwater samples during this study, and two boreholes (Bulbery PZ2 and Lychett Minster PZ2) were measured in 1998 (Buckley et al., 1998). Unlike most chemical species in water, stable isotopes of O and H behave conservatively in groundwater systems as they are an integral part of the water molecule, while carbon stable isotope ratios in waters are a function of interactions between water, rock and gases. The stable isotopes $\delta^{2}H$ and $\delta^{18}O$ lie close to the World Meteoric Line of Craig (1961) (Figure 6.11) indicating an atmospheric origin. However, two of the samples (Paultons Park: PP and Ampress: AM) have lighter isotopic signatures. The isotopic signatures in these samples are lighter than expected for modern recharge and are interpreted as having at least a component of recharge from Pleistocene times when the climate was colder. As discussed in section 6.2.4, it is considered that these waters are recharged from the underlying confined Chalk which is supported by the isotopic data.

During infiltration, soil carbon dioxide reacts with rock carbonate to form dissolved inorganic carbon with a $\delta^{13}C$ value intermediate between the two reactants. Subsequent to this, the $\delta^{13}C$ values may become more depleted (more negative) by further exchange with soil CO_2, or more enriched by carbonate dissolution-precipitation reactions. Hence, the $\delta^{13}C$ values may provide some idea of a relative age, whereby increasing $\delta^{13}C$ values suggest increased residence time of the water in a carbonate-bearing aquifer.

The $\delta^{13}C$ values in the groundwaters of the study area cover a range of approximately 10 ‰. Groundwater obtained from Paultons Park (PP) shows the strongest enrichment with a value of –8.84 ‰. The least mature water is Beaulieu Hotel with a value of –18.42 ‰. A plot of $\delta^{13}C$ versus $\delta^{18}O$ (Figure 6.11) confirms that the strongest enrichment in $\delta^{13}C$ coincides with the most depleted waters with regard to $\delta^{18}O$ and $\delta^{2}H$ and support the view that Paultons Park and probably Ampress Water Works borehole (AM) is an older (longer-residence-time) groundwater.

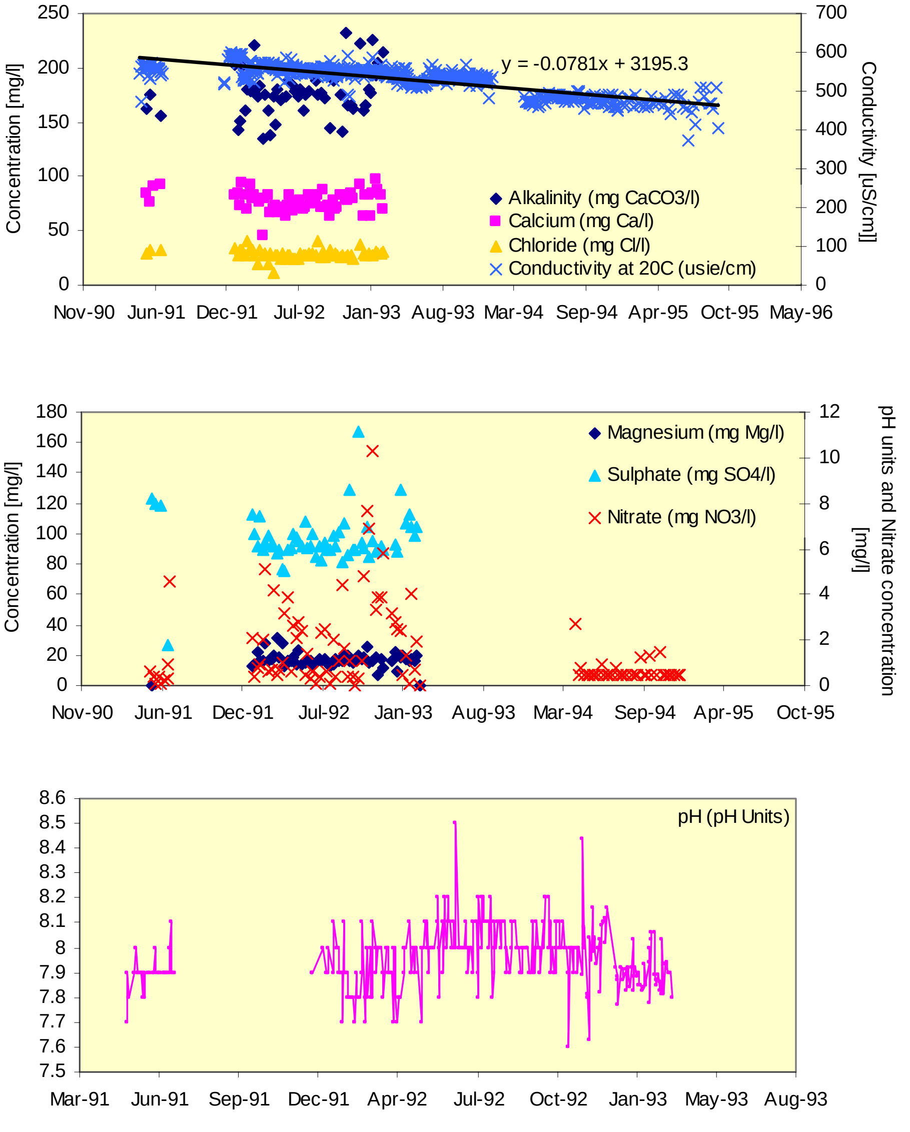


Figure 6.10 **Variations in selected major ions, conductivity and iron over time in the Ampress Water Works borehole AMP5.**

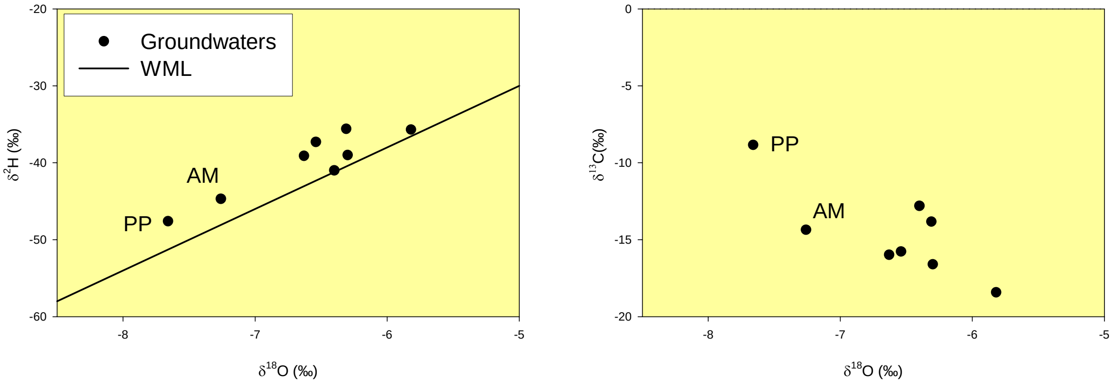


Figure 6.11 Isotopic composition of groundwaters in the Palaeogene aquifers. World Meteoric Line from Craig (1961). (PP:Paultons Park, AM: Ampress Water Works borehole)

6.5 Regional variations

The regional chemical variations across the study area are shown for selected elements in Figure 6.12, with concentration classifications based on quartiles, except for elements Ni and NO_3-N, where classifications have been altered to include cut-offs according to the respective EC guideline limits. The geochemical controls discussed in the preceding sections can be applied to the chemical changes across the study area. However, the very sparse regional coverage of sources across the Palaeogene severely restricts regional interpretation.

Whilst the general flow direction is from the north toward the coast, the heterogeneity of the Palaeogene strata makes the delineation of the flow direction difficult. Local drainage pattern and lithological sequences probably govern flow direction, groundwater travel times and the geochemical evolution of the groundwaters. Therefore, regional variations in terms of the evolution of groundwaters do not correspond with a general north-south flow path.

Besides geochemical evolution of groundwater through progressive water rock interaction with residence time, waters in the Palaeogene are influenced by the geological nature of the aquifer rocks themselves. Ca-HCO_3 and Ca-Na-HCO_3 waters are mainly present in groundwaters abstracted from the Bracklesham Group, Barton Group or Headon Formation. Elevated Na and SO_4 concentrations are observed for boreholes penetrating into the London Clay Formation resulting in waters of Na-Ca-HCO_3, Na-HCO_3 or Na-SO_4 type. This is indicated in Figure 5.1, with sources penetrating into the London Clay being represented as red points.

The regional distribution of pH indicates near-neutral conditions for the centre of the study area, with acidic waters occurring mainly in the west and in one source in the east, which is possibly affected by manure application. This distribution is mirrored in Figure 6.12, where the regional distribution of HCO_3 is presented. Highest bicarbonate concentrations thereby correspond with the highest pH. The distribution of various trace elements, such as Co and Ni are closely related to the pH of water sources and are high in the west of the study area, low in the centre and high in the source furthest east.

The distribution of chloride in the study area shows that concentrations are moderate in the majority of sources and that no significant increase is apparent for sources close to the coast line. The highest salinity is associated with groundwaters which contain a small component of formation water (in the two sources furthest north in the study area) with concentrations of chloride exceeding 100 mg l^{-1}. The influence of old formation waters is also apparent in the distribution of some trace elements e.g. Sr, with highest concentrations being present in the north of the study area and in the source close to

Lychett Minster in the west. However, this older component is likely to be derived from palaeowaters from the Chalk aquifer beneath.

The distribution of NO_3 highlights two areas of higher concentrations, which are related to rural agricultural activity and plant nurseries respectively. Groundwater beneath areas unaffected by agriculture, such the heathland in the centre of the study area have nitrate concentrations below the detection limit, even though oxidising conditions prevail. Reducing conditions e.g. in the west of the study area, lead to low nitrate concentrations in the groundwaters, despite agricultural activities above.

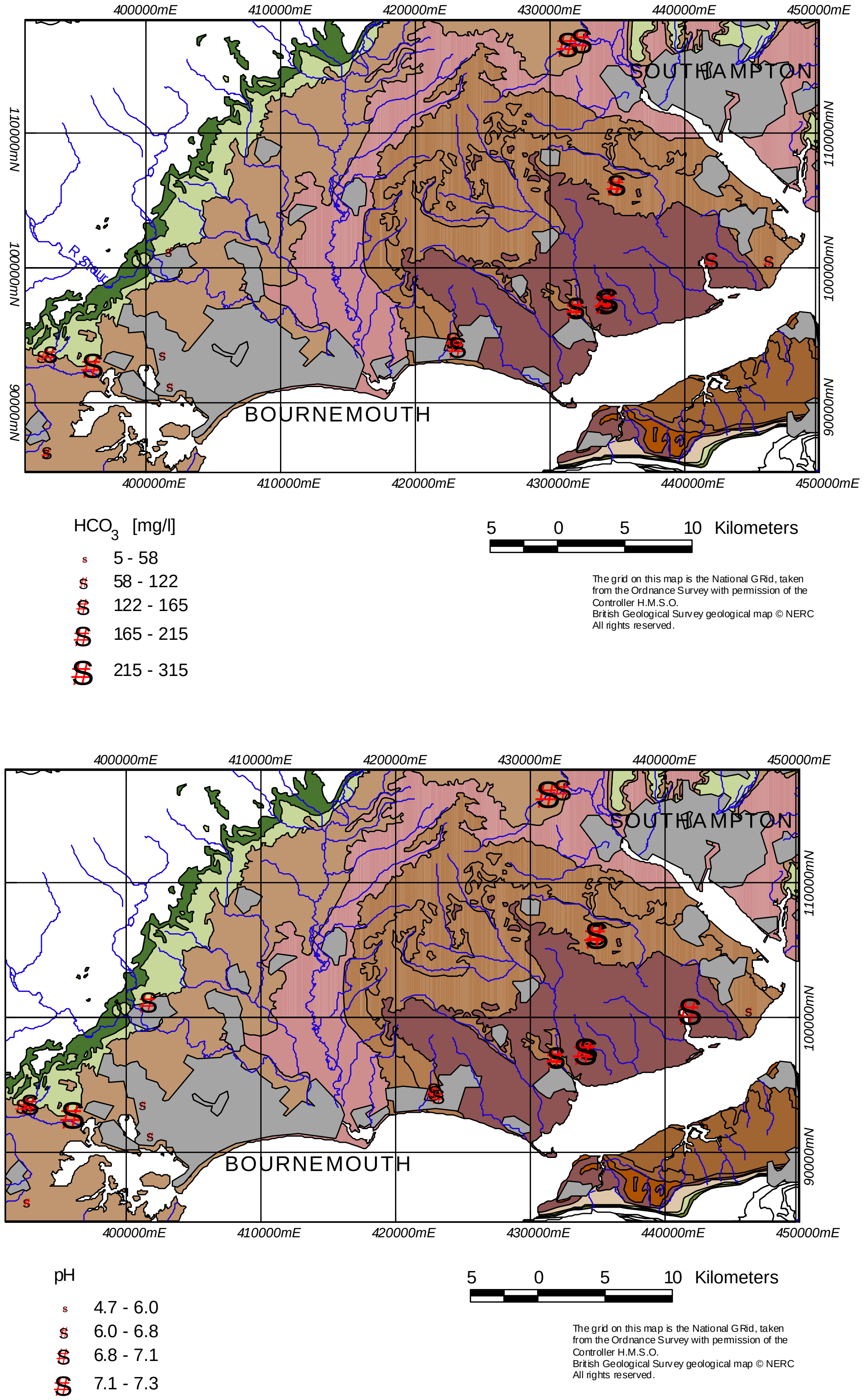


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Figure 6.12 **Regional variations in selected major and minor determinands in the Palaeogene aquifers.**

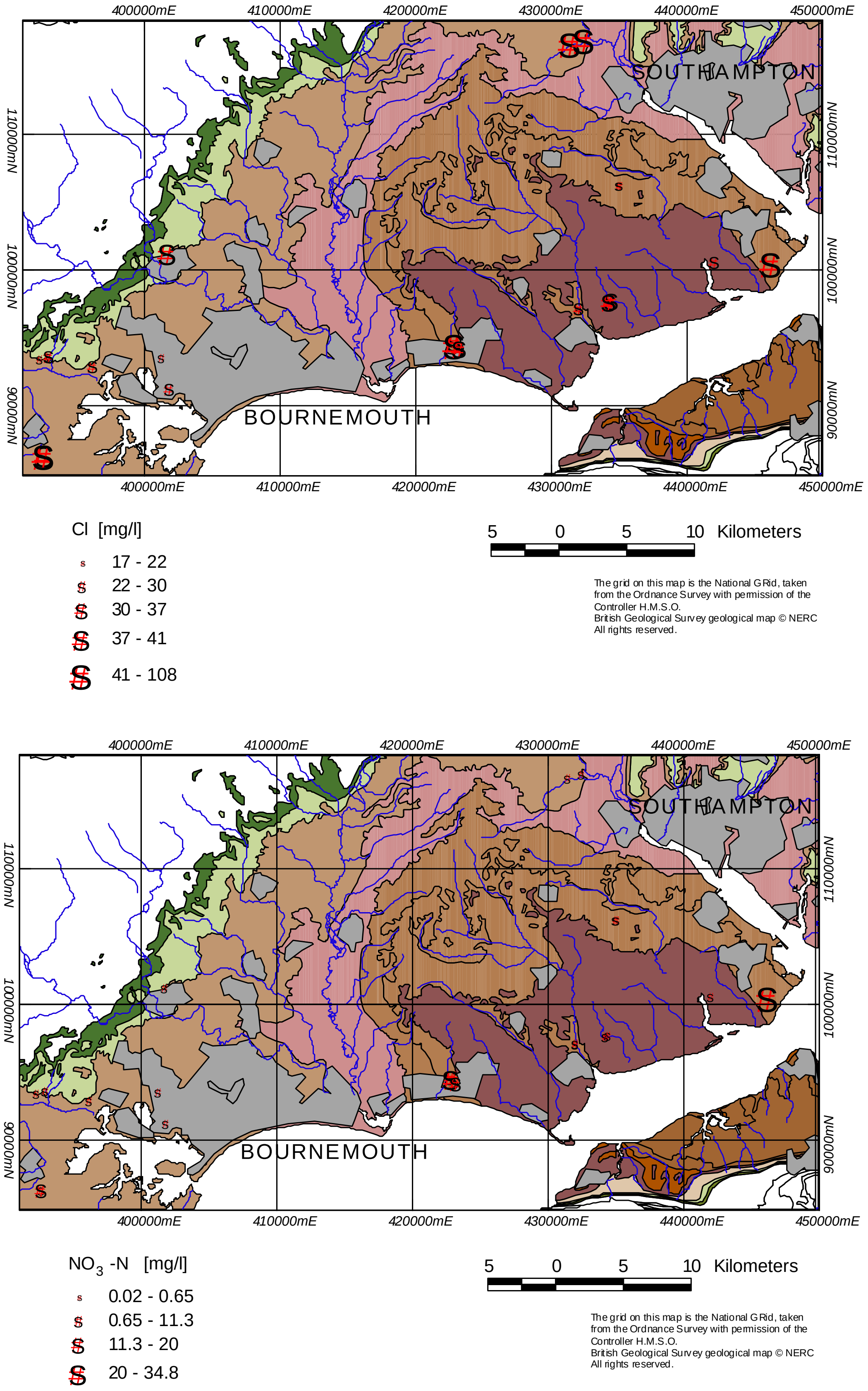

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Figure 6.13 (cont'd) .

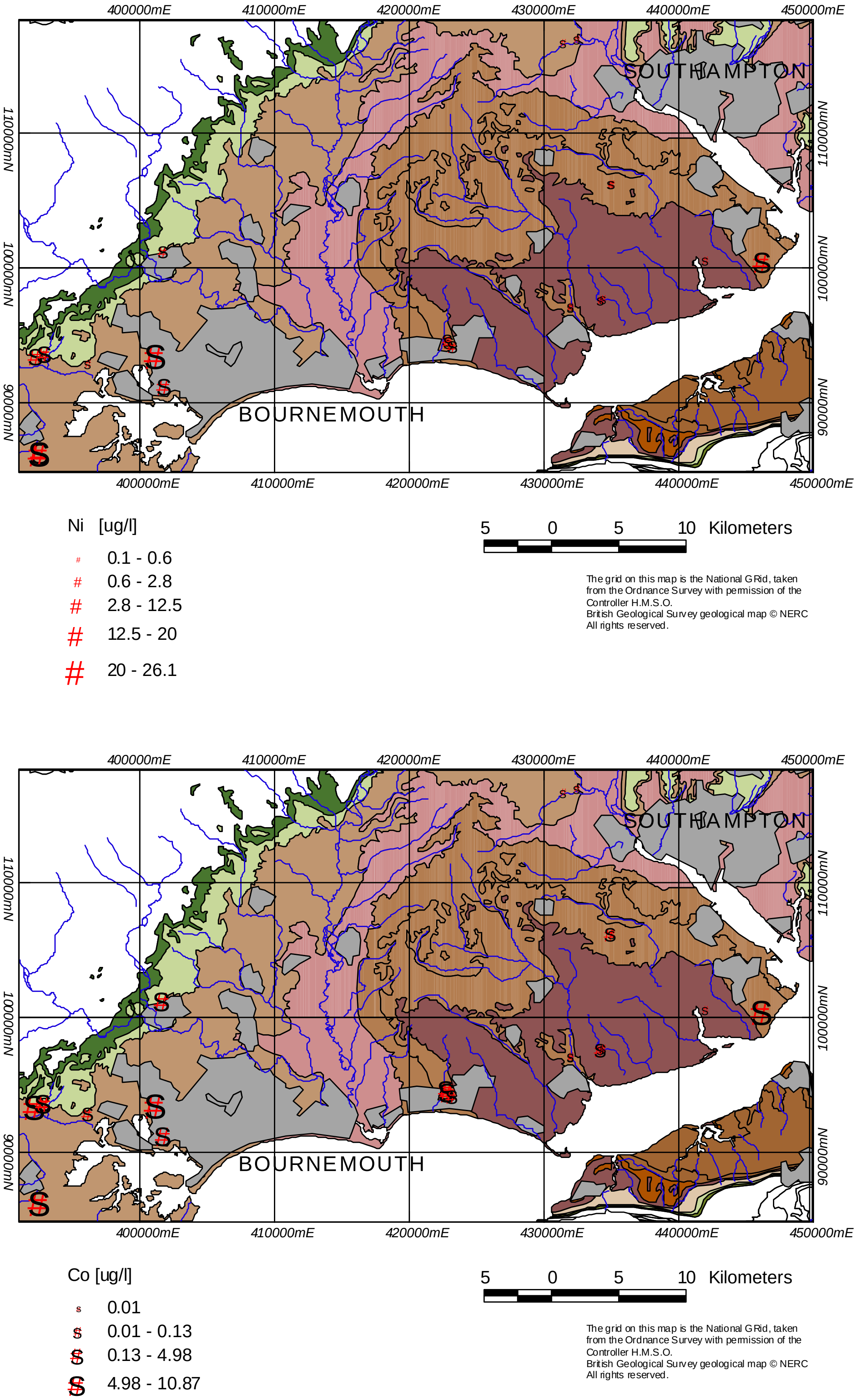

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Figure 6.13 **(cont’d)**

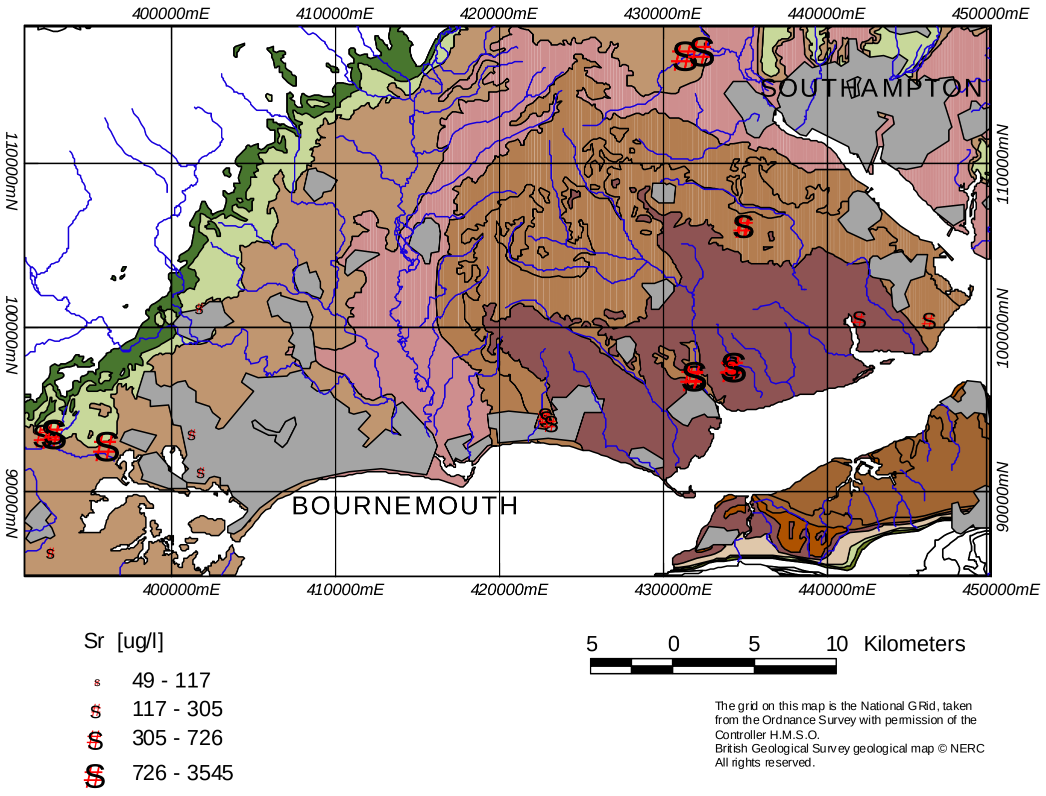

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Figure 6.13 (cont'd)

7. BASELINE CHEMISTRY OF THE AQUIFER

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

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

The sequence of Palaeogene rocks in the Wessex Basin is very complex and aquifer units are often discontinuous as the permeable units such as sand lenses pinch out, and they may be isolated hydraulically due to confining clay-rich layers. In other locations, hydraulic continuity between permeable strata may be only sporadic. This makes interpretation of the chemical processes affecting groundwater and spatial relationships difficult to assess. The more sandy, and consequently more permeable, strata in the Palaeogene Wessex Basin form aquifers of local importance.

The composition of the waters from most of the boreholes sampled in the Palaeogene aquifer can be ascribed primarily to natural processes of water-rock interaction: the majority of sources sampled have solute concentrations that are within baseline values (as indicated in Tables 5.1 and 5.2). The groundwaters are generally fresh with low SEC and of $Ca\text{-}HCO_3$ type but also include mixed water types e.g. $Ca\text{-}Na\text{-}HCO_3$ and $Na\text{-}HCO_3$ type. The aquifer is carbonate-poor in places which gives rise to acidic groundwater, particularly in the shallow system where residence times are likely to be low. Redox processes play an important part in modifying the concentrations of some elements. Many of the groundwaters are reducing and contain low NO_3 and DO along with high Fe and Mn concentrations. Ion-exchange has produced an increase in Na at the expense of Ca in a few of the deeper groundwaters in the London Clay Formation. Some boreholes also contained very high F and Sr concentrations, characteristics of the confined Chalk in the Wessex Basin. It is concluded that these waters were recharged from the Chalk beneath the Palaeogene and this is supported by stable isotope data which additionally indicate that there is a component of palaeowater present i.e. water recharged during the colder Pleistocene Period greater than 10 ka ago.

The clearest indicator of anthropogenic influence is the high nitrate in some groundwaters, up to 35 mg l^{-1} NO_3-N. However, only six groundwaters (23 %) contained nitrate greater than 5 mg l^{-1} and many were below detection limit. The groundwaters with low concentrations were relatively reducing and it is likely that denitrification has lowered initial concentrations. Some groundwaters might be of sufficient age to have been recharged with pre-modern water and others will be entirely unaffected by agricultural pollution. However, it is unlikely that baseline concentrations were below detection limit for most recharge waters. Unfortunately the lack of good historical records make it difficult to assess the baseline for nitrate. The cumulative frequency plots are difficult to interpret for nitrate due to the changes imposed during denitrification which will have modified original distributions. Shallow boreholes are more vulnerable to surface pollution, as polluted waters present at shallow depths are not being diluted with pristine waters from deeper parts of the aquifer. Additionally, reducing conditions are more likely to occur at greater depths enabling concentrations to be lowered due to denitrification. The baseline nitrate concentration for the reducing groundwaters is therefore below the limit of detection, but the oxidising groundwaters are difficult to assess, most likely an upper baseline is of the order of 2-3 mg l^{-1} NO_3-N.

Concentrations of P are moderately high in many groundwaters (up to 330 µg l^{-1}). Phosphorus does not correlate with many solutes including N-species, DOC, Cl or K, elements which are commonly associated with anthropogenic influence. The highest concentrations (> 100 µg l^{-1}) were present in moderately reducing groundwaters. There are insufficient data to ascertain whether P inputs are natural or anthropogenic, but the lack of high concentrations in the most aerobic groundwaters points to a natural source.

Other elements which may have been modified by anthropogenic inputs include K, Br, Cl, Na and DOC. The highest DOC was present in the groundwater sampled from Paultons Park which is thought to contain a significant amount of palaeowater. It is unlikely that this source contains a large modern component and the high DOC is considered natural. Although local baseline concentrations may have been modified by anthropogenic inputs, it is likely that they fall within the overall baseline range for the aquifer. Hence the upper baselines established in Tables 5.1 and 5.2 are considered to be realistic, the exception clearly being nitrate.

The regional plots highlight the spatial variations in baseline chemistry, but the lack of spatial coverage of groundwater sources and the complexity of the aquifer mean that care needs to be taken extrapolating baseline across the aquifer. For local problems, a local baseline needs to be established and a comprehensive search for historical data would be invaluable in this context.

8. SUMMARY AND CONCLUSIONS

The Palaeogene strata form a minor aquifer in the Wessex Basin of southern England. Groundwater abstraction from this aquifer is used mainly for private supplies and agricultural needs, especially nurseries, with a small fraction serving public supply sources.

The sediments of the Wessex Basin consist of a series of cyclic marine deposits that fine upwards, ranging from coarse sands and flint pebbles to muds and clays. The hydrogeology of the basin is best described in terms of a series of aquifer units, which may be hydraulically separated by low-permeability units. The thickness and areal extent of the individual aquifers are variable and depend on the conditions of deposition. Whilst groundwater flow in the basin generally follows the dip of the strata, from north to south, hydraulic heads are likely to vary vertically as the various layers are frequently hydraulically separate. The lowest unit (Reading Formation) is generally in hydraulic continuity with the underlying Chalk. Whilst borehole yields from the Wessex Basin can be reasonably good, at up to about 20 l s^{-1}, the aquifer is generally regarded as being a minor aquifer of local importance.

The most important controlling factor affecting the chemical composition of the majority of the Palaeogene groundwaters in the region is the presence or absence of carbonate minerals in the host rock. The dissolution of calcite has resulted in elevated Ca and HCO_3 concentrations waters of Ca-HCO_3 type. However, the overall carbonate content of the Palaeogene sediments is low. This limited availability of carbonate to neutralise acidic infiltrating recharge waters in some parts of the aquifer has led to acidic conditions in numerous sampled sources.

Some waters are affected by oxidation of pyrite, leading to high SO_4 and Fe concentrations and low pH. Where carbonate is absent, this has resulted in Na-SO_4 type waters. Some Ca-HCO_3 waters have been modified towards a Na-HCO_3 composition due to ion exchange. Stable isotope data suggest that some of these waters contain probably a component of Pleistocene age and that they are derived through recharge from the underlying Chalk. These waters also contain high Sr and F, the latter exceeding the EC drinking water guidelines in three cases.

The natural baseline concentrations for some elements range over several orders of magnitude in groundwaters from the Palaeogene aquifer. In shallow boreholes, these might be partly influenced by anthropogenic input, which is difficult to quantify. In confined aquifers, concentrations of many elements appear elevated, but these represent naturally derived baseline concentrations. For instance, the high iron and manganese concentrations are characteristic of many Palaeogene waters and naturally derived. In 80% of all samples analysed in this study, iron exceeded the EC drinking water limit, while 60% of analysed waters exceeded the guidelines for manganese. In the more acidic groundwaters, mobilisation of some trace metals has occurred, with Al and Ni exceeding the EC drinking water limits in some cases.

Some unconfined waters in the Palaeogene are influenced by agricultural activities, showing elevated nitrate concentrations. In one case manure application is thought to be contributing to low pH and elevated heavy metals. In the confined groundwaters, where the aquifer is reducing, nitrate concentrations are low, possibly due to denitrification.

It is concluded, that high iron and manganese as well as slightly acidic conditions are characteristics of the Palaeogene groundwaters. From the chemical data available, it appears that the water quality of oxidising groundwaters of near-neutral pH is, in most part, good. In the more acidic groundwaters, mobilisation of some trace metals can occur, and EC drinking water limits can be exceeded, as described above. In more reducing waters iron and manganese concentrations have been shown to exceed the EC limits in many cases. The hydrochemical properties of the groundwaters in the Palaeogene aquifers are overwhelmingly determined by natural reactions between recharge water and the Palaeogene host rocks.

9. REFERENCES

Allen, D.J., Brewerton, L.M., Coleby, L.M., Gibbs, B.R., Lewis, M.A., MacDonald, A.M., Wagstaff, S. & Williams, A.T. 1997 The physical properties of major aquifers in England and Wales. British Geological Survey Technical Report **WD/97/34**. 312pp. Environment Agency R&D Publication 8.

Bristow, C.R., Freshney, E.C., and Penn, I.E, 1991. Geology of the country around Bournemouth. Memoir of the Geological Survey of Great Britain, Sheet 329 (England and Wales). London: Her Majesty's Stationery Office.

Buckley, D.K., Shand, P. & Gale, I.N. 1998 Geophysical and geochemical investigations related to the ASR trial at Lytchett Minster, Dorset. British Geological Survey Technical Report **WD/98/27C**.

Craig, H 1961 Isotopic variations in meteoric waters. Science **133**, 1702-1703.

Griffiths, K.J., Shand, P. & Ingram, J. 2002 Baseline Report Series: 2. The Permo-Triassic Sandstones of west Cheshire and the Wirral. British Geological Survey Commissioned Report, **CR/02/109N**, 54pp.

Edmunds, W.M., Shand, P., Hart, P. & Ward, R. 2003 The natural (baseline) quality of groundwater in England and Wales: a UK pilot study. The Science of the Total Environment. **310**, 25-35.

Edmunds, W.M. & Smedley, P.L. 1998 Trace elements as residence time indicators in groundwaters: The East Midlands Triassic sandstone aquifer, England. In, G.B. Arehart & J.R. Hulston (eds.), Water-Rock Interaction 9, Balkema, 215-218.

Edmunds, W.M., Cook, J.M., Kinniburgh, D.G., Miles, D. L. & Trafford, J.M. 1989 Trace element occurrence in British groundwaters. British Geological Survey, Research Report **SD/89/31**.

Edwards, R A and Freshney, E C, 1987. Geology of the country around Southampton. Memoir of the Geological Survey of Great Britain, Sheet 315 (England and Wales). London: Her Majesty's Stationery Office.

Environment Agency 2003 Review of ammonium attenuation in soil and groundwater. National Groundwater and Contaminated Land Centre Report NC/02/49. Environment Agency, Bristol.

Jones, H.K., Morris, B.L., Cheney, C.S., Brewerton, L.S., Merrin, P.D., Coleby, L.M., Lewis, M.A., MacDonald, A.M., Talbot, J.C., McKenzie, A.A., Bird, M.J., Cunningham, J. & Robinson, V.K. 2000 The physical properties of minor aquifers in England and Wales: British Geological Survey, Hydrogeology Series, Technical Report **WD/00/04** /

Newell, A.J. 2001 Construction of a Palaeogene tide-dominated shelf: influence of Top Chalk topography and sediment supply (Wessex Basin, UK). J. Geol. Soc. Vol. **158**, pp. 379-390.

Shand, P., Cobbing, J., Tyler-Whittle, R., Tooth, A., Lancaster, A. & Lewis, O.H. 2003 Baseline Reports Series: 9. The Lower Greensand of southern England. British Geological Survey Commissioned Report, **CR/03/273N**, 54 pp.

Shand, P. & Frengstad 2001 Baseline groundwater quality: A comparison of selected British and Norwegian aquifers. British Geological Survey Internal Report, **IR/01/177**.

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