Baseline Report Series:

19. The Permo-Triassic Sandstones of Liverpool and Rufford

Groundwater Systems and Water Quality
Commissioned Report CR/05/131N

Science Group: Air, Land & Water
Technical Report NC/99/74/19

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/05/131N

ENVIRONMENT AGENCY
Science Group: Air, Land & Water
Technical Report NC/99/74/19

Environment Agency Dissemination status
Internal: Release to Regions
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Project No. SC990024

Statement of use
This document forms one of a series of reports describing the baseline chemistry of selected reference aquifers in England and Wales.

Cover illustration
View from the parade at Albert Dock, Liverpool.

Key words
Baseline, Sherwood Sandstone, Liverpool, Rufford, water quality, hydrogeochemistry, UK aquifer.

Bibliographic reference
Griffiths, KJ, Shand, P and Ingram J, 2005. Baseline Report Series: 19. The Permo-Triassic Sandstones of Liverpool and Rufford
British Geological Survey Commissioned Report No. CR/05/131N

Baseline Report Series:
19. The Permo-Triassic Sandstones of Liverpool and Rufford

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Environment Agency Science Group, Solihull 2005
British Geological Survey, Keyworth, Nottingham 2005

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FOREWORD

Groundwater issuing from springs has been regarded since the earliest recorded history as something pure, even sacred. In its natural state, it is generally of excellent quality and an essential natural resource. However, the natural quality of groundwater in our aquifers is continually being modified by the influence of man. This occurs due to groundwater abstraction and the consequent change in groundwater flow, artificial recharge and direct inputs of anthropogenic substances. A thorough knowledge of the quantity and quality of groundwaters in our aquifers, including a good understanding of the physical and chemical processes that control these, is therefore essential for effective management of this valuable resource.

About 35 per cent of public water supply in England and Wales is provided by groundwater resources, this figure being higher in the south and east of England where the figure exceeds 70 per cent. Groundwater is also extremely important for private water supplies and in some areas, often those with the highest concentration of private abstractions, alternative supplies are generally not available. Groundwater flows and seepages are also vital for maintaining summer flows in rivers, streams and wetland habitats, some of which rely solely on groundwater, especially in eastern and southern England. The quantity and quality of groundwater is therefore extremely important to sustain both water supply and sensitive ecosystems.

Until now there has not been a common approach, either in the UK or across Europe, to define the natural "baseline" quality of groundwater. Such a standard is needed as the scientific basis for defining natural variations in groundwater quality and whether or not anthropogenic pollution is taking place. It is not uncommon for existing limits for drinking water quality to be breached by entirely natural processes. This means that it is essential to understand the natural quality of groundwater to enable the necessary protection, management and restoration measures for groundwater to be adopted.

One of the main problems pertinent to groundwater remediation issues concerns the background or baseline to which remedial measures must, or can, be taken. Naturally high concentrations of some elements in particular areas may make it impossible or uneconomic to remediate to levels below the natural background which may already breach certain environmental standards. The Baseline Reports Series assesses the controls on water quality which are responsible for causing the natural variations seen in groundwater and provides a background for assessing the likely outcomes and timescales for restoration.

This report builds on a scoping study of England and Wales, carried out in 1996 by the British Geological Survey for the Environment Agency, which reviewed the approach to be adopted in producing a series of reports on the principal aquifers in England and Wales. The initial phase of this work was completed in 1998 and comprised reports on seven aquifers. This report forms part of the second phase of the work that will extend coverage to all the important aquifers in England and Wales. The Baseline reports will be of use not only to regulatory agencies but also to all users of groundwater, including water companies, industry and agriculture, and all those involved in the protection and remediation of groundwater.

BACKGROUND TO THE BASELINE PROJECT

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

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

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

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

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

The BASELINE objectives are:

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

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

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

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

1. EXECUTIVE SUMMARY

The Permo-Triassic Sandstone forms the second most important aquifer in the UK. In the Liverpool and Rufford area, it provides groundwater sources for public supply as well as for a large number of industrial users, agriculture and leisure activities. The geology and distribution of drift deposits in the region are complex and this has had a pronounced effect on the baseline chemistry of the underlying aquifer. The chemistry of the groundwaters is overwhelmingly controlled by natural reactions between the groundwater and bedrock. Solute concentrations typically vary over several orders of magnitude. Dissolution of cements, mainly calcite and dolomite strongly influence the major-element composition of most groundwater. In addition, redox processes, ion exchange, seawater intrusion and mixing with remnant formation water all contribute to the chemical composition of groundwater in this area. Natural geochemical processes have been modified by the anthropogenic effects of pollution and groundwater abstraction. In an urban area such as Liverpool, which has a long industrial history in which groundwater has played an integral part, it is perhaps not surprising that these activities have significantly impacted the groundwater chemistry, particularly with respect to nitrate (both agriculture-derived and sewage-derived) and chloride.

This report provides an overview of the baseline chemistry and the dominant geochemical processes occurring in the Permo-Triassic aquifer of Liverpool and Rufford. It provides information to aid the management of groundwater and provides a basis from which to identify future impacts on the quality of groundwater.

The natural baseline within the aquifer is expressed by a range of concentrations which can vary over several orders of magnitude for some elements. The concentrations of some elements are enhanced over the natural baseline due to pollution. For example, elevated nitrate and chloride concentrations may indicate modification by agricultural and industrial practices. In parts of the aquifer, arsenic and barium occur at concentrations which exceed European drinking-water standards. However, these concentrations are not considered to be the impact of pollution; they result from water-rock interaction and reflect aquifer mineralogy. In cases where natural water quality exceeds guide levels it is important that baseline conditions are understood so that water resource managers can take them into account in regional-scale resource planning.

2. PERSPECTIVE

This study focuses on the Permo-Triassic Sandstone aquifer of the Liverpool area (Figure 2.1). The area examined in this study encompasses what is referred to by the Environment Agency as the Liverpool and Rufford aquifers and includes the urban area of Liverpool. The southern boundary of the study area is delineated by the River Mersey and the western boundary by the Irish Sea. To the north the sandstone aquifer is overlain by marls and mudstones of the Mercia Mudstone Group and the eastern boundary of the study area is formed by the boundary fault along which the Carboniferous Coal Measures have been upthrown. This region forms the core area for evaluating the regional baseline groundwater quality and selected groundwater data have been used to provide an areal coverage. The Rufford aquifer is a relatively isolated block of Permo-Triassic Sandstone located to the north of Burscough (Seymour, 1993).

The Permo-Triassic Sandstone aquifer of the Liverpool area has been the subject of numerous studies during the past two centuries. Houlston's (1773) monograph on Liverpool Spa Water is believed to be the first publication but comments on water quality exist from the 17th century onwards (Allen, 1969). In more recent years, hydrogeological and hydrogeochemical investigations have been undertaken by the North West Water Authority, the Environment Agency and the University of Birmingham. For a review of previous publications on the area the reader is referred to Tellam (1996).

The Permo-Triassic Sandstone forms the second most important aquifer in the UK, supplying approximately 25% of licensed groundwater abstractions in England and Wales (Monkhouse and Richards, 1982). Total licensed abstractions from the Permo-Triassic Sandstone within the study area are of the order of 200 Ml d^{-1}. In the Liverpool area, the Permo-Triassic Sandstone aquifer provides groundwater sources for a large number of industrial users as well as public water supply, agriculture and leisure activity e.g. golf courses (Figure 2.2). In the north of the study area, spray irrigation is one of the main groundwater uses. The aquifer also provides an essential source of baseflow to maintain river flow and sustain wetlands such as Martin Mere. The Liverpool area has supported a range of heavy industries, particularly from the 19th Century, which resulted in an increase in groundwater abstraction, peaking in the 1970's (Howard, 1987). Decreased abstraction in more recent years, associated with the decline of heavy industry, has resulted in a rise of several metres in the groundwater levels beneath Liverpool (Brassington and Ruston, 1987). However, groundwater abstraction by Network Rail designed to control groundwater levels along the Liverpool Loop underground railway line has now halted the rise in groundwater levels in the area adjacent to the railway line.

The drainage network of the study area is shown in Figure 2.1. The south east of the study area is drained by the Ditton Brook into the River Mersey. The River Alt drains from Maghull to the coast just south of Formby. The River Douglas and its tributaries drain the area north of Burscough. Between Ormskirk/Burscough and the coast there are a series of brooks and drainage channels that drain this relatively low lying area of land (Figure 2.3). Two kilometres north west of Burscough lies Martin Mere, a wetland with SSSI status managed by the Wildfowl and Wetlands Trust. The Leeds and Liverpool Canal runs broadly from the south west to the north east of the study area passing through Liverpool and Maghull to Burscough where it divides and runs northwards and south eastwards towards Wigan.

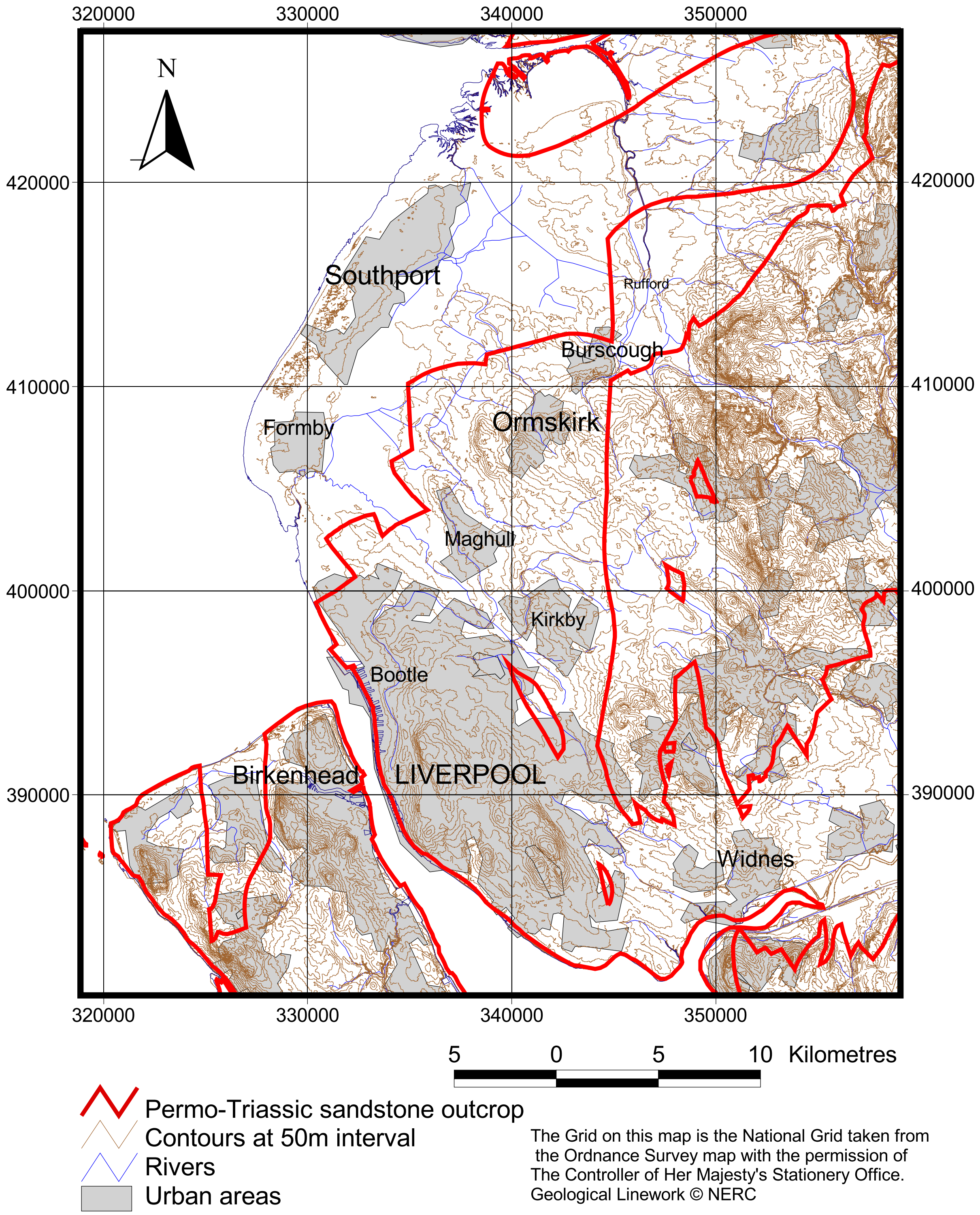

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Figure 2.1 **Topographic map of study area**

Figure 2.2 Golf courses often use groundwater sources for irrigation. West Derby Golf Course, Liverpool (SJ 412 929).

Figure 2.3 Drainage channel near Rufford (SD 435 154)

Mean annual rainfall varies across the region from c. 880 mm in the west of the area to c. 1060 mm in the north east of the study area (Institute of Hydrology and British Geological Survey, 1993).

The study area includes Liverpool, which is predominantly urban with a legacy of industrial activity. Historical industrial land use has resulted in diffuse and point-source pollution, and land contamination is an important issue. North of Liverpool, the area is more rural with dairy farming, arable farming and market gardening being significant land uses (Figure 2.4). A large proportion of the study area falls within groundwater source protection zones (SPZs) which have been defined for public water supply abstraction boreholes (Figure 2.5).

Figure 2.4 View across the valley of the River Douglas from Parbold viewpoint showing agricultural landuse in the north of the study area (SD 507 106).

Saline groundwaters are found at depth in the aquifer and may be two to three times the salinity of seawater (Tellam, 1995). These brines are present mainly in parts of the Sherwood Sandstone that are consequently not used as an aquifer for potable supply. The highly mineralised groundwaters are not described in detail in this report. Their impact on the overlying fresh groundwater, however, needs to be borne in mind for the management of the aquifer. Brackish and saline groundwaters are also present adjacent to and beneath the Mersey estuary resulting from seawater intrusion.

The Rufford aquifer faces pressure in terms of local water demand. Water resources in the aquifer are fully committed (Seymour, 1993).

The focus of this report is on the variations in water quality related to natural geochemical processes and how these vary spatially across the aquifer. Where possible, data are used to ascertain relative groundwater ages and temporal variations are described.

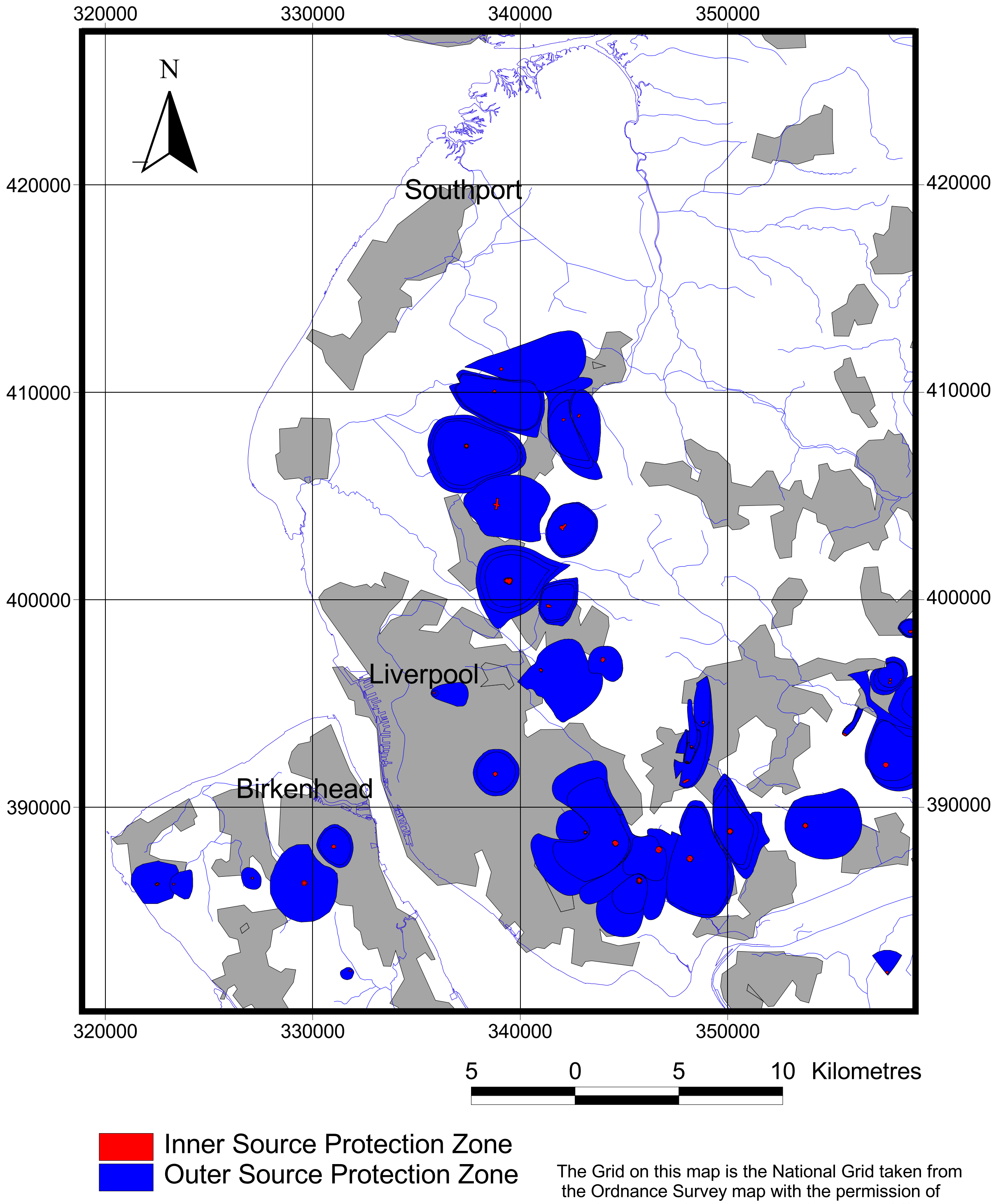

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Figure 2.5 **Map of Source Protection Zones (source Environment Agency)**

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

In order to assess the baseline groundwater quality, it is necessary to understand the system within which the groundwater is contained. This requires information on the geological and hydrogeological properties to provide the physical framework of the system. Knowledge of the mineralogy and geochemistry of the component minerals is required to explain the characteristic groundwater chemistry and rainfall chemistry is required to define the initial recharge.

3.2 Geology

3.2.1 Solid Geology

As elsewhere in Britain, the Permian and Triassic sequences are usually treated as one system in the Liverpool region (as elsewhere in Britain) due to the absence of palaeontological evidence to differentiate between the two systems (Warrington, 1980). The stratigraphy and estimated thickness of the different lithologies is given in Table 3.1.

Table 3.1 Permo-Triassic stratigraphy of Cheshire and south Lancashire (after University of Birmingham 1984).

System and Lithostratigraphical Division		**Previous Division**	**Hydrogeological Unit**	**Thickness**
TRIASSIC Mercia Mudstone Group	Bollin Mudstone Formation	Lower Keuper Marl	Aquitard	405
	Tarporley Siltstone Formation	Keuper Waterstones	Mainly aquitard	30-60
TRIASSIC Sherwood Sandstone Group	Ormskirk / Helsby Sandstone Formation	Lower Keuper Sandstones	Aquifer	>181-295
	Wilmslow Sandstone Formation	Upper Mottled Sandstone		>205-480
	Chester Pebble Beds Formation	Bunter Pebble Beds		>316-375
	Kinnerton Sandstone Formation	Lower Mottled Sandstone (upper unit)	Aquifer	0->80
PERMIAN	Manchester Marl Formation/ *Bold Formation*	Manchester Marls	Mainly aquitard/*aquifer*	10-225
	Collyhurst Sandstone Formation	Lower Mottled Sandstone (lower unit)	Aquifer	283-720

The Permo-Triassic sediments of West Lancashire (Figure 3.1) were deposited in the Permo-Triassic north-eastern Irish Sea Basin. The sedimentary infill of the basin was contiguous with the sequences deposited in the Cheshire Basin to the south (Warrington, 1980).

The Collyhurst Sandstone rests unconformably on Carboniferous strata and attains its maximum thickness in the north of the study area close to Formby. It consists of red to grey fine- to medium-grained sandstones. The Manchester Marl Formation is the lateral equivalent of the Bold Formation. It has been found in an exploratory borehole drilled by BP in the Formby area. However, due to a lack of deep boreholes in the study area its distribution is not well known. The Manchester Marl becomes increasingly sandy in its upper section. The Bold Formation is also sandy which makes the division between these Formations and the overlying Sherwood Sandstone Group often difficult to define precisely (University of Birmingham, 1984).

The Sherwood Sandstone Group consists of the Kinnerton Sandstone Formation, the Chester Pebble Beds Formation, the Wilmslow Sandstone Formation and the Helsby/Ormskirk Sandstone Formation. The nomenclature used for the region is based on the Cheshire basin nomenclature. However, the area of study borders both the northern edges of the Cheshire basin and the south-eastern edge of the Irish Sea basin. In the vicinity of Ormskirk, the Helsby Sandstone Formation becomes the Ormskirk Sandstone Formation. However, the boundary between the two Formations is gradational (Ed Hough, pers. comm. 2004).

The boundary between the Sherwood Sandstone Group and the Mercia Mudstone Group in the Rufford area has recently been revised using investigation boreholes and geophysics (Ingram, 2001). To the east of the Woodsfold Fault, the Sherwood Sandstone Group is more extensive than previously thought. In the Tarleton area there is a narrow, two kilometre wide, downfaulted area of Mercia Mudstone which separates the Rufford aquifer from the Fylde aquifer to the north (Ingram, 2001).

3.2.2 Drift Geology

The area is in general extensively covered by drift deposits which range in lithology and thickness (Figures 3.2, 3.3 and 3.4). Locally, thicknesses in excess of 50 m have been recorded at Aintree (SJ 3799), Burscough Bridge (SD 4412) and Simonswood (SJ 4599), but more commonly the drift ranges from 5 to 10 metres thick and in some areas is absent e.g. Liverpool, Kirkby and Ormskirk (University of Birmingham, 1984).

The Stockport Formation is composed of glacial tills and sands, with fluvioglacial sands and some gravels, and represents a substantial component of the Quaternary sequence in the area of study. It varies in thickness up to 50 metres although is typically less than 10 metres thick. The variation in thickness is typically related to variations in the bedrock topography. The lithology of the Stockport Formation has been studied extensively as it was believed to have a significant impact on recharge to the aquifer. It is typically sandier where it overlies the Sherwood Sandstone Group as opposed to the Mercia Mudstone Group (University of Birmingham, 1984).

Holocene deposits in the area include the Shirdley Hill Sand Formation which is thought to be derived from reworking of fluvioglacial outwash deposits by the wind and contains some peat development. Other peat deposits occur in the east and northwest of the study area, notably where drainage is poor e.g. in the low lying area east of Formby (SD 3007) and overlying the Shirdley Hill Sand Formation. Saturated conditions in the shallow subsurface give rise to strongly acidic (pH 4 to 5), fibrous, yellow-brown peats. This initial peat development is called ‘low moor stage’. Low moor stage peats occur west of Maghull (SD 3702) and Haskayne (SD 3608). In areas of better drainage, these peats go on to form fen-carr peats, such as at Lydiate (SD 3604) (University of Birmingham, 1984).

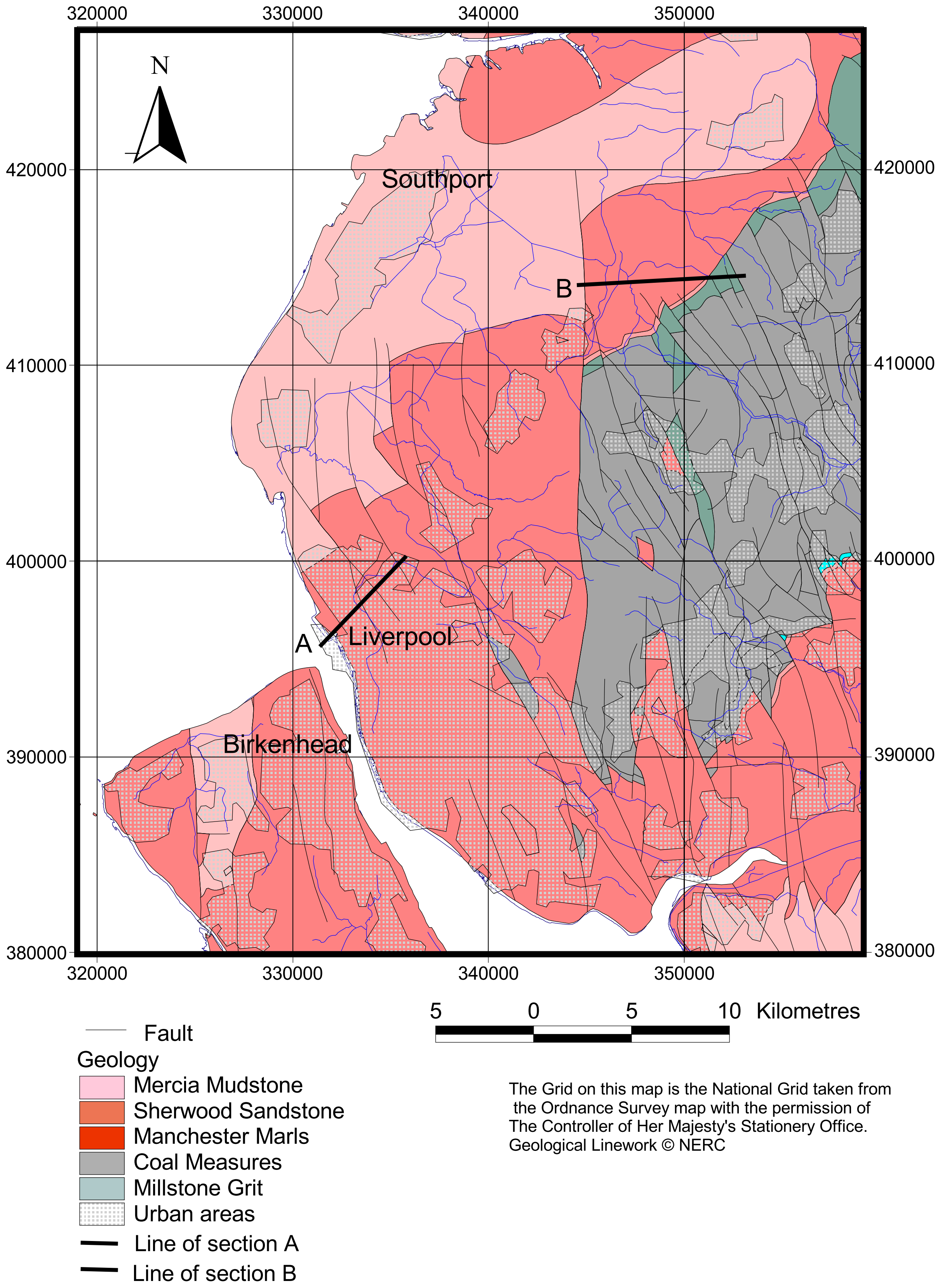

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Figure 3.1 **Geological map of the study area**

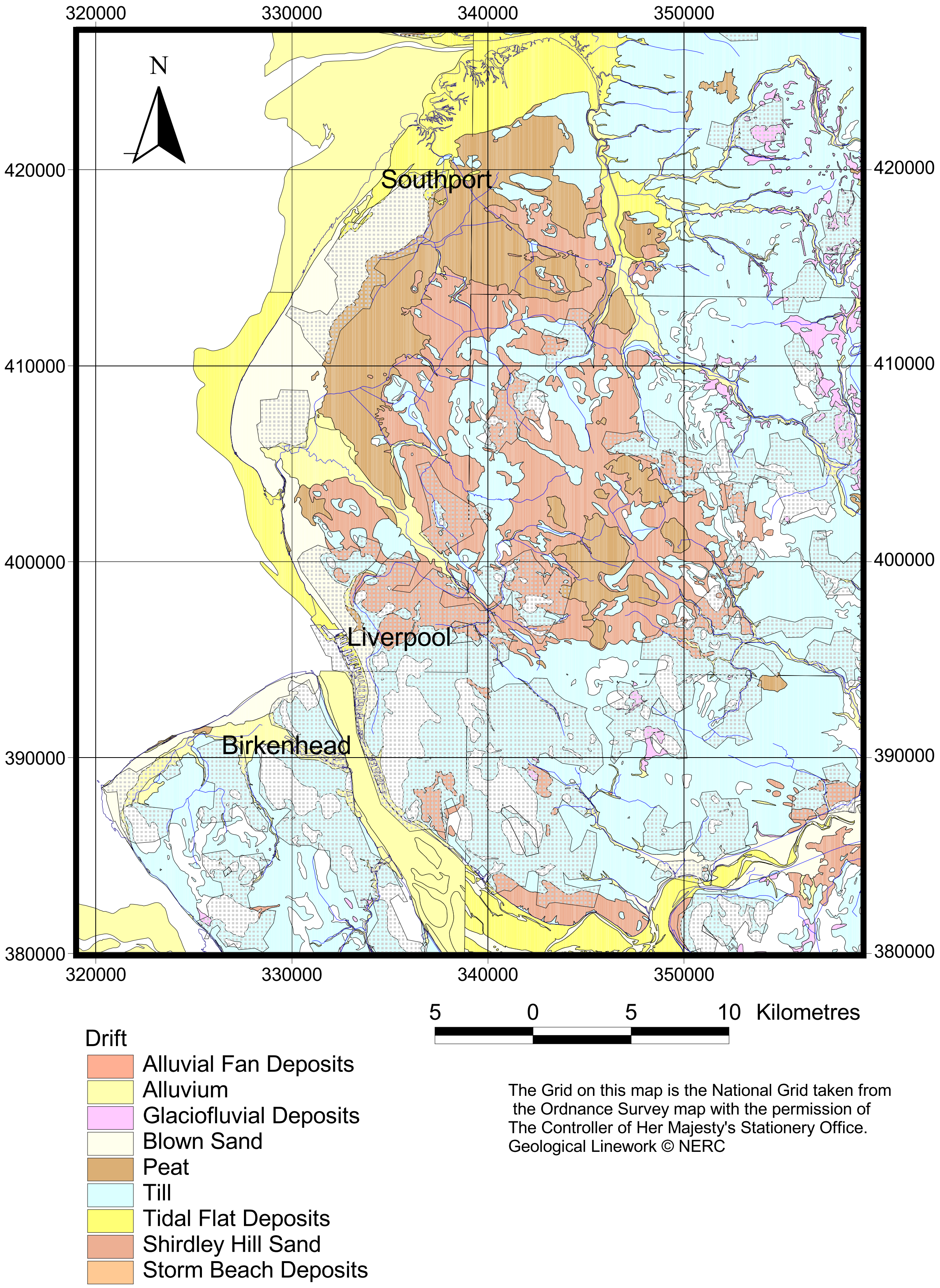

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Figure 3.2 **Drift map of the study area.**

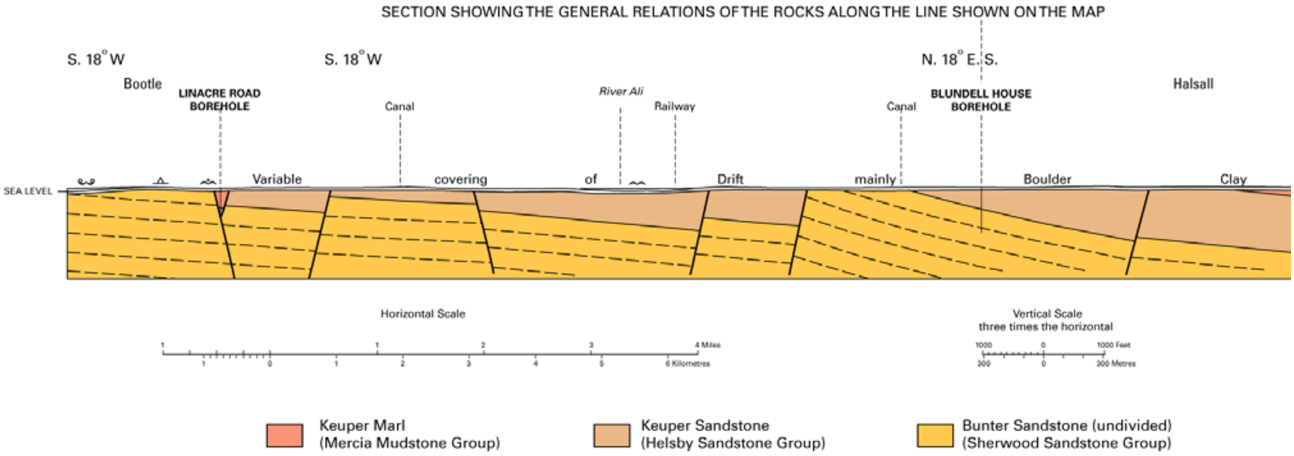

Figure 3.3 **Formby map cross-section (section 'A' on Figure 3.1.).**

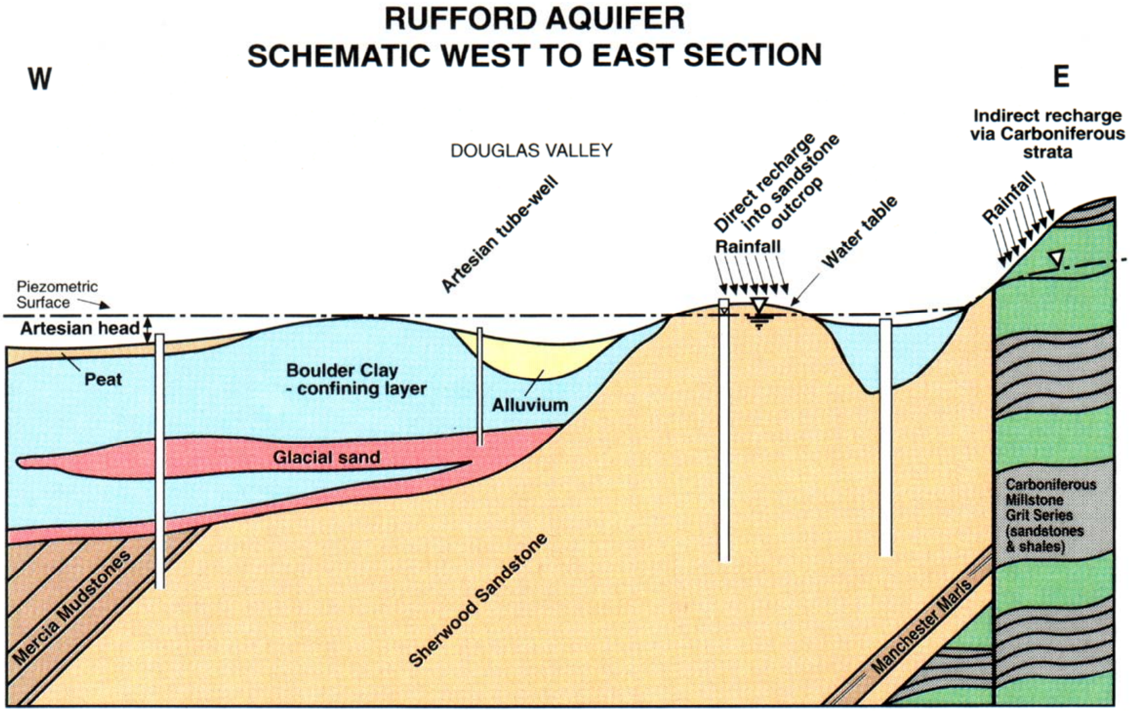

Figure 3.4 **Schematic cross-section of the Rufford aquifer (after Seymour, 1993). Section 'B' on Figure 3.1.**

River alluvium deposits occur along the valleys of the River Alt and the River Douglas in the vicinity of some of the brooks e.g. Ditton Brook (SJ 45 88). Estuarine alluvium occurs along the Mersey estuary and also in the vicinity of Hightown on the coast (SD 30 03). Recent blown sand deposits occur between Southport (SD 33 17) and Bootle (SJ 33 96) with extensive sand dune development, up to 25 metres in height, between Formby and Southport (see Figure 3.5) (University of Birmingham, 1984).

Figure 3.5 Sand dunes at Formby

The study area lies on the south eastern margin of the Irish Sea Basin. There is a south westerly trending anticline at Knowsley which gives rise to a northwesterly dip over much of the study area and a south easterly dip over the Halewood and Speke areas. There is a small syncline which has its axis just south of Ormskirk resulting in a southeasterly dip around Ormskirk, but this is obliterated by an anticline north of Ormskirk. Dips have been modified by the tilting of fault blocks. The simple regional fold pattern has been disrupted by faulting since the Permo-Triassic. There are a number of predominantly NNW-SSE trending faults which dissect the area. The throws on some of these faults are in excess of 200 m (University of Birmingham, 1984).

3.3 Hydrogeology

The Liverpool aquifer comprises sandstones of the Sherwood Sandstone Group (i.e. the Kinnerton Sandstone, Helsby, Wilmslow and Chester Pebble Bed formations), which are all in hydraulic continuity. The Collyhurst Sandstone also forms an aquifer in the study area but is separated from the Sherwood Sandstone Group by the Manchester Marl Formation/ Bold Formation which can act as an aquiclude. Table 3.2 outlines the hydrogeological significance of each of the units.

The Sherwood Sandstone Group stores and transmits water by both intergranular and fracture flow. Figure 3.6 shows water discharging from fractures within the sandstones at a quarry wall near Widnes.

Mudstones occur throughout the Sherwood Sandstone Group but most notably within the Chester Pebble Beds. Mudstone bands tend to be less than 1 m thick and are usually laterally discontinuous. Thick mudstones may form barriers to vertical flow locally. However, because of their limited lateral extent they are unlikely to form regional barriers. The frequency of mudstone bands increases towards the top of the sequence as the Mercia Mudstone Group is approached, causing an increase in anisotropy towards the top of the Ormskirk Formation. Perched water levels often occur above the mudstone bands.

Faulting in the area has in some instances caused impermeable strata to be faulted up against permeable strata thereby causing a local reduction in hydraulic conductivity e.g. along the Croxteth Fault where Carboniferous strata have been faulted up against the Permo-Triassic sequence.

Transmissivities ranging from 140 to 780 m^3/day have been reported in the Sherwood Sandstone aquifer from analysis of pumping tests conducted by the University of Birmingham (1984) who used a regional transmissivity of 250 m^3/day in a regional flow model which reportedly produced a satisfactory simulation. Specific yield for the model was set at 0.14. However, the storage coefficient where the water level lies within the drift deposits was set at 0.0035 and where the Mercia Mudstone Group confines the aquifer a storage coefficient of 0.0005 was applied.

Recharge to the Liverpool and Rufford aquifers is limited to areas where the sandstone crops out, and areas where the aquifers are overlain by thin or permeable drift deposits. In 1982, recharge was estimated to be an average of 150 Ml d^{-1}, with a total abstraction of 100 Ml d^{-1}. Recharge to the underlying aquifer will be influenced by the piezometric surface which, when lowered will induce more leakage through the overlying Quaternary deposits into the aquifer (Tellam, 1994, 1996). Vines (1984a) suggested a figure of 53 mm a^{-1} for recharge through the boulder clay. Leakage from pipelines, sewers and soakways may also contribute to recharge of the aquifer because the area of study is extensively urbanised. This additional urban recharge has not been quantified. Groundwater levels in the Liverpool area are currently rising as a response to the decrease in industrial abstractions (Brassington and Rushton, 1987), although in the vicinity of the Liverpool Loop underground railway line, this rise has now been halted due to groundwater pumping by Network Rail for the purpose of dewatering. Recent groundwater contours are shown in Figure 3.7. The direction of groundwater flow is generally westwards towards the coast and the River Mersey.

The area surrounding Rufford is relatively low lying and much of the aquifer is confined by thick, low permeability boulder clay which gives rise to artesian heads within the sandstone and the overlying drift deposits.

Table 3.2 Stratigraphy and hydrogeological characteristics of the different units (after University of Birmingham, 1984).

Period	**Geological Unit**	**Hydrogeological characteristics**	**Hydrogeological significance**
Quaternary	Blown sand River alluvium Estuarine alluvium Shirdley Hill Sand Formation	Permeable	Deposits contain small quantities of groundwater
	Peat deposits	Semi-permeable	Deposits may provide additional storage for main sandstone aquifer where in hydraulic continuity
	Stockport Formation	Impermeable with permeable horizons	Acts as confining layer in places, may contain local perched water tables. Permeable horizons may provide additional storage
Triassic	Mercia Mudstone Group	Generally impermeable but with permeable horizons	Confines the Permo-Triassic aquifer. Permeable horizons may yield small quantities of groundwater
	Sherwood Sandstone Group	Generally highly permeable with some semi-permeable and impermeable horizons. Fractured near surface.	Main aquifer. Unconfined over most of the area of study
--?--?--?--?--?--?--?--?-	Manchester Marl Formation	Generally impermeable with some semi-permeable horizons	Occurs in the north of the area of study. May act to confine the Collyhurst Sandstone
Permian	Bold Formation	Semi-permeable with some impermeable horizons	Occurs in the centre and south of the area of study and may locally inhibit flow.
	Collyhurst Sandstone Formation	Highly permeable	Unconfined in the south east of the study area. Increases in thickness in the north where it becomes confined.
Carboniferous	Westphalian Stage	Mainly impermeable but with permeable horizons	Series of small fault bounded aquifers. Fracture related permeability to c. 250 m depth.

Groundwater discharges to the surface by slow seepage and is vital for maintaining flows in streams and rivers and supporting wetlands. Sands and gravels within the drift deposits are often in hydraulic continuity with the underlying sandstone aquifer.

Figure 3.6 Groundwater discharging from fractures in a quarry wall

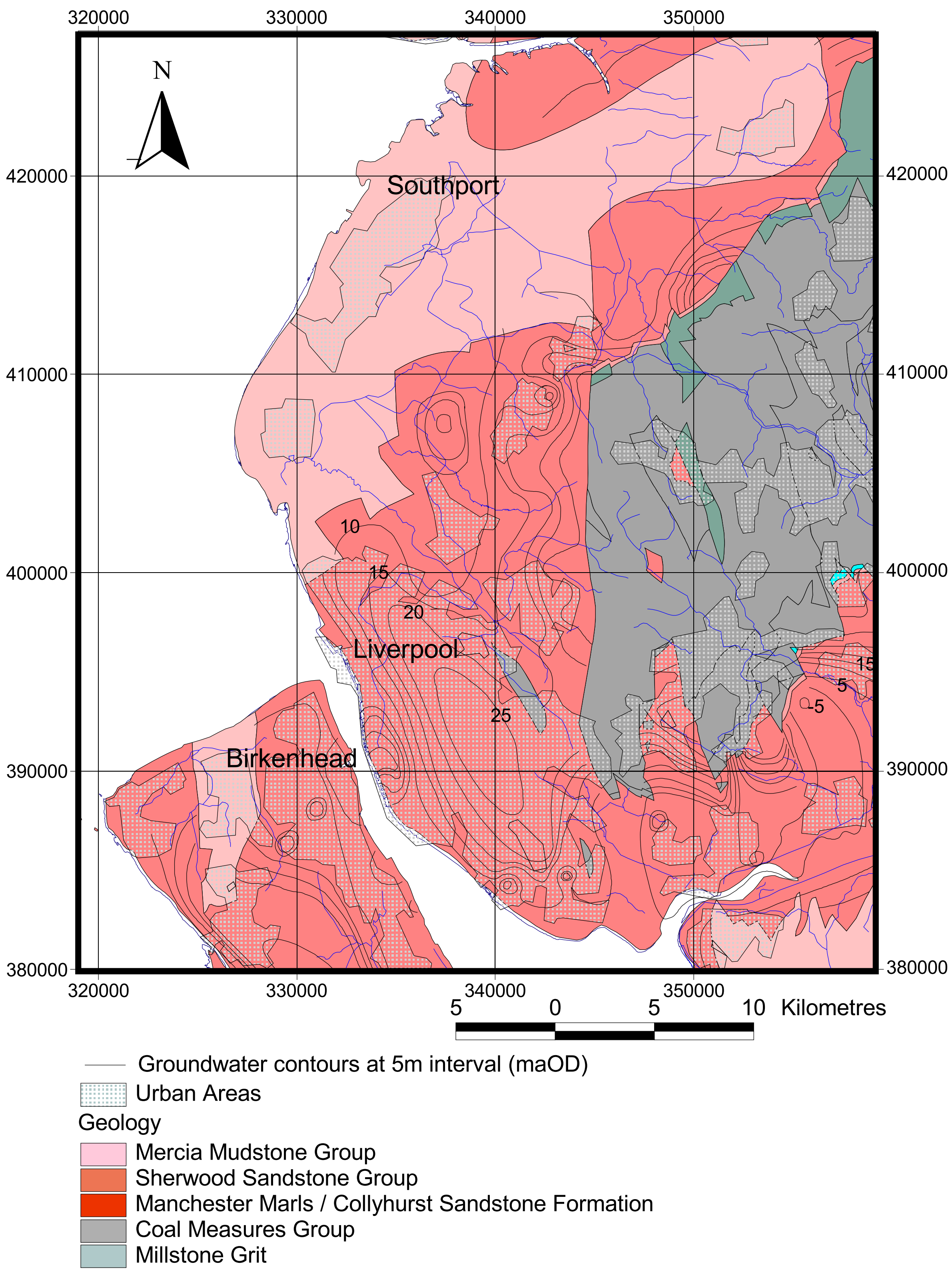

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Figure 3.7 **Groundwater level contours (data provided by the Environment Agency).**

3.4 Aquifer mineralogy

Haines (1984) reported that the sandstones comprise 55 to 85% quartz, 1 to 16% feldspar, 5 to 30% clays and 0 to 2% mica clasts. The sandstone cements include a wide range of minerals including calcite, dolomite, gypsum, anhydrite, halite, iron oxide and clays. The carbonate and evaporite minerals may exert the dominant control on groundwater chemistry because they dissolve much more rapidly than the quartz and silicate mineral phases and (for the evaporite minerals) may be highly soluble. Much of the original evaporite minerals, where present, have been dissolved away in the upper parts of the aquifer. Carbonate still forms an important cement but in the upper parts of the aquifer it has been removed by dissolution by recharge waters (Greenwood and Travis, 1915). The clay mineralogy is generally dominated by kaolinite, and in deeper parts of the aquifer, by illite (Plant et al., 1999).

Grain coatings within the Sherwood Sandstone Group include iron oxides and authigenic smectite. Pressure solution and compaction during early burial of the sediments resulted in quartz and K-feldspar overgrowths and cements and non-ferroan dolomite cements. Anhydrite and other evaporite mineral cements are now only present at depth within the basin, having been removed by groundwater circulation in the upper parts of the sequence. During burial, anhydrite and halite were remobilised from the overlying Mercia Mudstone Group and were introduced to the Sherwood Sandstone Group via fractures to form cement. Adjacent to faults, complex calcite-barite-Cu-Ag-Pb-As-Co-Hg-Ni-Se-V-Zn-Mn-sulphide mineralisation occurred and replaced earlier anhydrite or halite cement (Plant et al., 1999).

The overlying Mercia Mudstone Group comprises reddish brown and less commonly greenish grey, dolomitic mudstone with evaporite minerals, especially gypsum and anhydrite but including halite and locally celestite. The Bollin Mudstone Formation contains thin halite beds (<2 m) in the top 20 m.

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharge waters and, for some elements, can be considered as representing minimum background concentrations at the present day. There are no rainfall chemistry data sites in the National Air Quality Information Archive located within the study area. The nearest site is Preston Montfort (NGR SJ 432 143), which is located approximately 70 km to the south. As Preston Montford is located further inland than Liverpool it is anticipated that the rainfall chemistry for Liverpool may have higher concentrations of marine-derived elements, notably sodium and chloride. The data have been multiplied by 3 in the last column in order to estimate the approximate enrichment due to evapotranspiration and hence chemistry of infiltrating rainwater. Although Cl may be assumed to behave conservatively during most recharge conditions, this is not the case for other elements e.g. K and N-species, which may be taken up by vegetation, and concentrations may therefore be lower in recharge waters than rainfall. Nevertheless, the Table indicates the order of magnitude of concentrations expected in recent waters, which have not reacted with vegetation, soils or aquifer minerals. For chloride, concentrations in recharge waters prior to anthropogenic influences or mixing with other groundwaters would therefore be expected to be around 4 to 5 mg l^{-1}.

3.6 Land use in the area

The study area includes the urban and industrial areas of Liverpool, Widnes, Maghull and Ormskirk. The southern part of the study area, adjacent to the Mersey estuary and including the docks, is particularly industrial (Figure 3.8). To the north of the study area the much of the land is used for arable farming and market gardening.

Table 3.3 Rainfall chemistry data from Preston Montford [NGR SJ 432 143]. The data are from the year 2000 taken from The UK National Air Quality Information Archive. Rainfall was 788 mm per annum.

Parameter	**Rainfall**	**Rainfall (x3) enrichment by evapotranspiration**
pH	5.73	
Na (mg l^{-1})	0.76	2.27
K (mg l^{-1})	0.11	0.33
Ca (mg l^{-1})	0.17	0.51
Mg (mg l^{-1})	0.11	0.33
Cl (mg l^{-1})	1.49	4.47
SO_4 (mg l^{-1})	2.75	8.25
NO_3 (mg l^{-1})	1.34	4.02
NH_4 (mg l^{-1})	0.55	1.65
SEC (µS cm^{-1})	18.8	

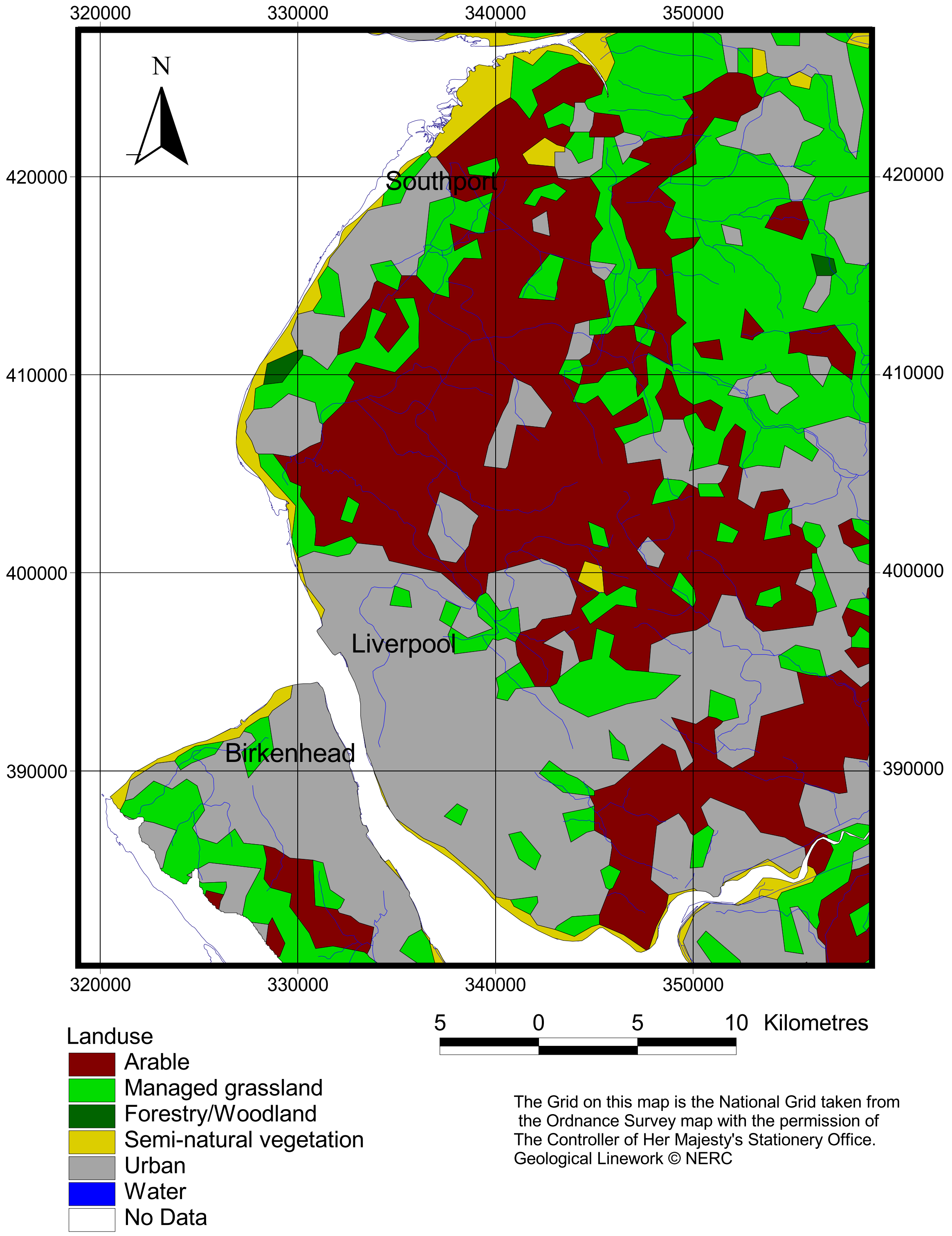

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Figure 3. Generalised landuse map of the study area. Data from land Cover Map 1990 (supplied courtesy of the Centre for Ecology and Hydrology © NERC)

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 29 samples were collected during May 2002 from public and private groundwater supplies at 29 different sites across the area providing good regional coverage of the aquifer (Figure 4.1). The samples were collected from boreholes used by the Environment Agency's groundwater monitoring programme. All boreholes were pumped for an estimated three borehole volumes prior to sampling. The pumped samples represent the average composition of water coming into the borehole over the screened interval. Therefore, the sample may represent a mixture of waters with different chemistry, especially if the aquifer is vertically stratified in terms of water quality. This may be the case, for example, if the aquifers show strong vertical anisotropy or if the aquifer acts as a dual porosity medium. At present there are few data available from most sites to establish if this is the case. Regardless, valid conclusions can still be drawn on the regional variations which exist in the aquifer.

Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured on-site in a flow-through cell (Figure 4.2). Other on-site measurements included temperature, specific electrical conductance (SEC) and alkalinity (by titration). Samples were collected for major and trace chemical analysis in polyethylene bottles. Those for major and trace elements were filtered through 0.45 µm membrane filters and the aliquot for cation and trace elements was acidified with 1% v/v HNO_3 to minimise adsorption onto container walls. Additional samples were collected in glass bottles for stable isotopes (δ^2H, $\delta^{18}O$ and $\delta^{13}C$).

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

4.2 Historical data

Excellent historical water quality data records are available for the area. In order to obtain a representative spatial sample of water quality data over the Liverpool area, data were obtained from the Environment Agency's water quality database (WIMS). The earliest record is from 1900 and the most recent data presented are from the year 2002. Some good time series data are available and will be further discussed in the section examining time variant trends in water quality. Pore water and depth samples are also available for some boreholes.

4.3 Interpretation of pumped groundwater samples

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

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

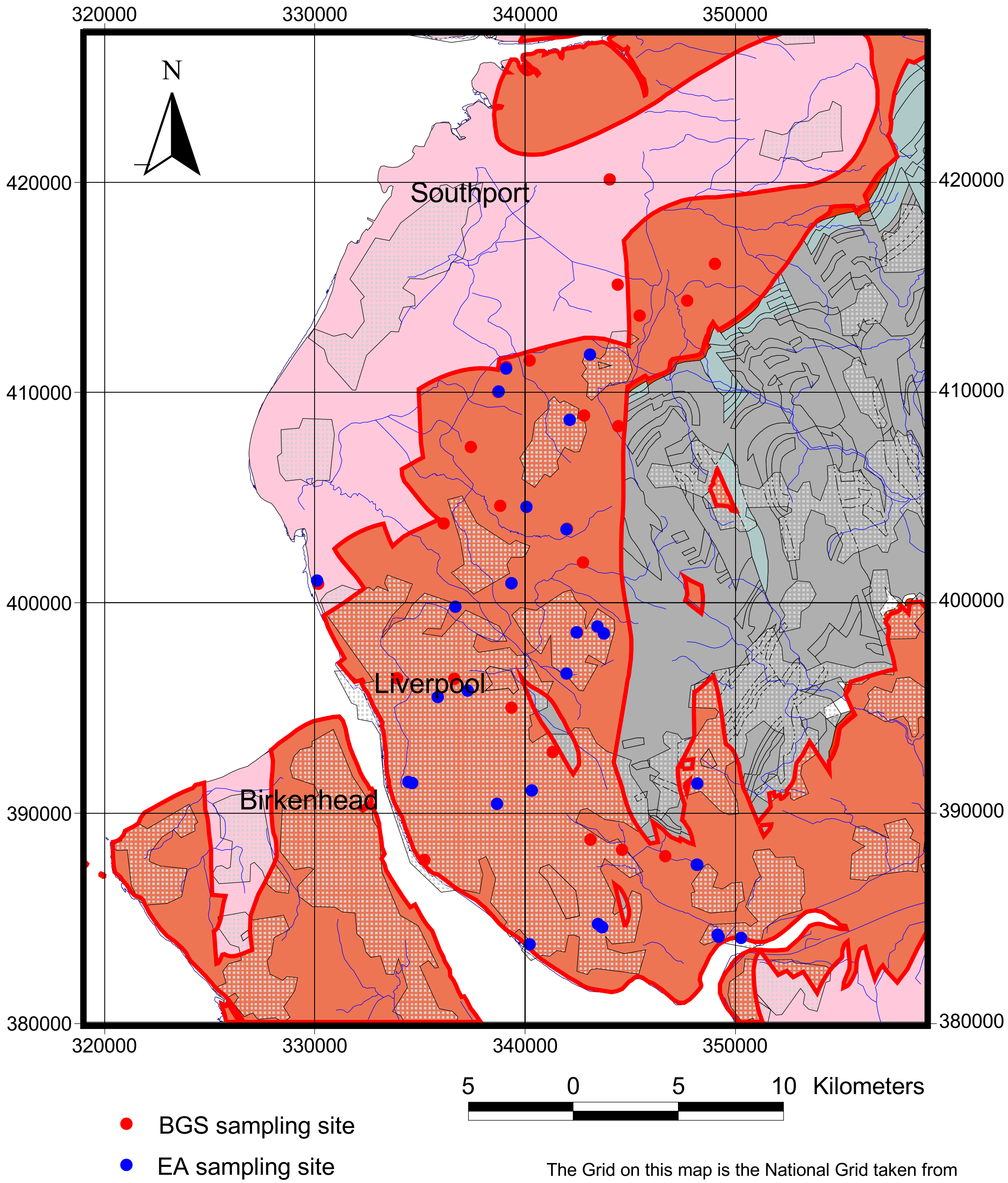

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Figure 4.1 **Map showing location of sampling points.**

Figure 4.2 **Measurement of Eh, DO and pH using a flow through cell.**

4.3.1 Different borehole designs

As mentioned previously, water quality stratification may exist in the Sherwood Sandstone aquifer. As a consequence, differences in borehole design, in particular depth of casing, length of screen and depth of borehole may produce differences in water chemistry unrelated to geochemical reactions along a flow path or a result of mixing.

4.3.2 Differences in stratigraphy

The presence of evaporite deposits or differences in cement type within the sandstones may produce significant variation in the baseline water quality for the different stratigraphic horizons. Boreholes are likely to intercept different stratigraphic horizons especially where these boreholes are distant from each other, even where geological dip is low.

4.3.3 Different pumping history

In areas where the Permo-Triassic sandstone aquifer is overlain by permeable drift deposits, the pumping history of an individual borehole may have a significant impact on water quality. For instance, abstraction boreholes where large volumes of water have been pumped historically are likely to have induced significant recharge through the permeable drift deposits. Thus the proportion of modern, high nitrate water in the pumped sample may be relatively high, compared with a borehole where only small volumes have been pumped.

It was not possible, within the resources available to this project, to evaluate which factors may be influencing water quality for each of the water sampling boreholes. Instead, this report presents a broad assessment of the water quality variations observed across the aquifer and the controlling geochemical processes. It is accepted that some water quality variation may be due to the factors described above.

4.4 Data handling

All plots and tables showing summary data and synoptic maps are based on the new sampling programme data with additional data from 34 records from the Environment Agency's water quality database (WIMS) unless otherwise specified. One WIMS analysis for each site was selected and the selection was made by choosing the most comprehensive (i.e. most relevant and numerous determinands) and most recent analysis. Only sites with analyses dating from after 1990 were used. The WIMS data for boreholes which were sampled in the new programme were excluded to avoid double counting. Only pumped samples were included. Where data are below the detection limit of analysis, a concentration equal to half the detection limit has been substituted for plotting and statistical purposes.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

A summary of the hydrochemical data is shown in Table 5.1a and 5.1b for the study area. This shows the ranges and averages of data as well as an upper concentration (defined as mean plus 2 standard deviations or 97.7th percentile) which is used as a cut off to distinguish outlying data at the upper end of the range. The median is preferred to the mean as an average because it is more robust and less affected by extreme values. This section deals with the fundamental hydrochemical characteristics of the groundwaters. The following section (Section 6) deals with the controls and geochemical processes that determine and modify the groundwater chemistry, placing the variations in a regional context.

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

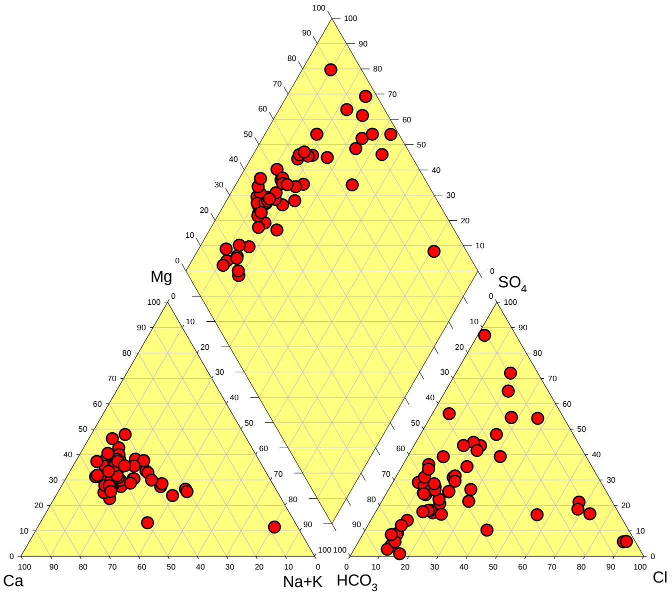


Figure 5.1 **Piper plot showing the relative concentrations of major cations and anions for groundwater in the Liverpool and Rufford Sherwood Sandstone aquifer.**

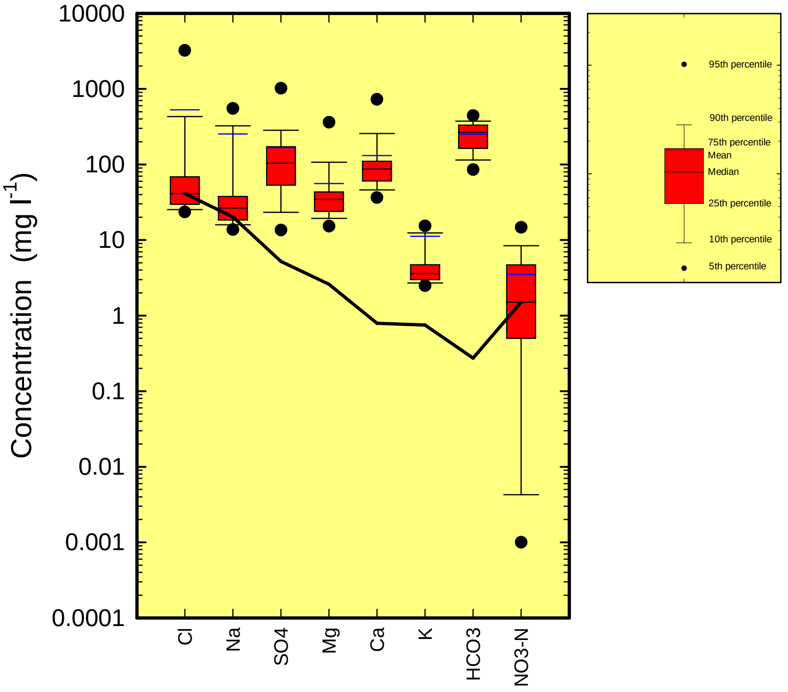


Figure 5.2 Box plot showing range of major ion concentrations in the Liverpool and Rufford groundwaters.

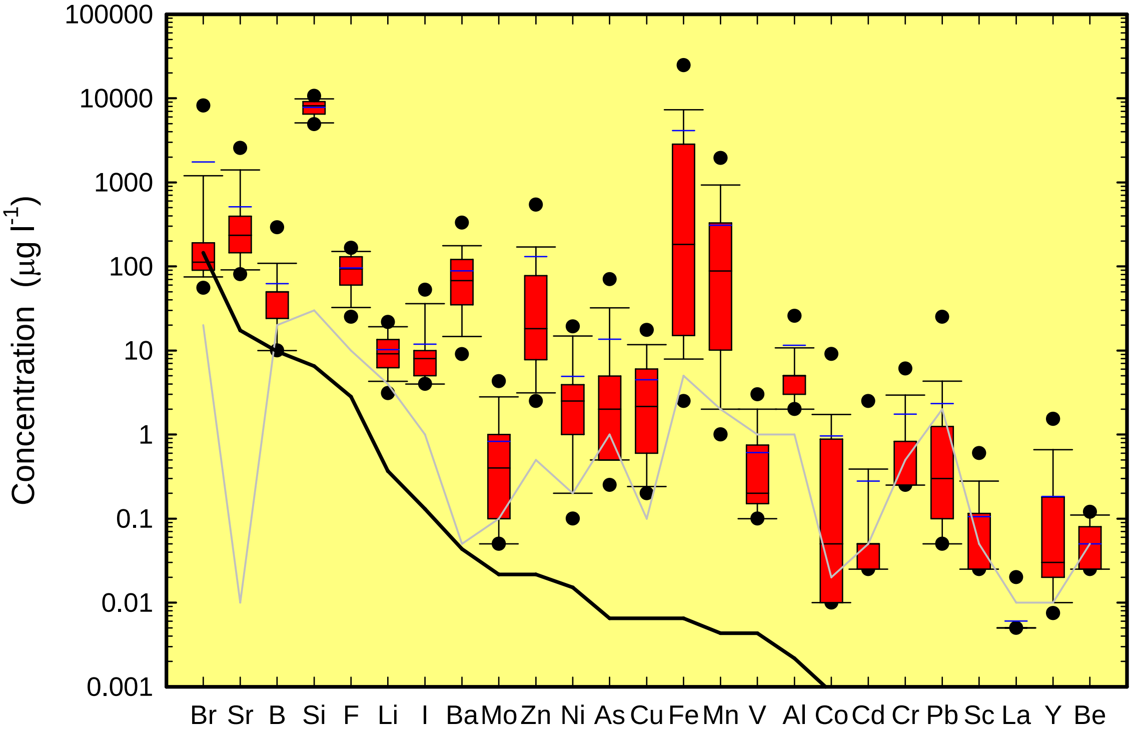


Figure 5.3 Box plot showing range of minor and trace element concentrations in the Liverpool and Rufford groundwaters.

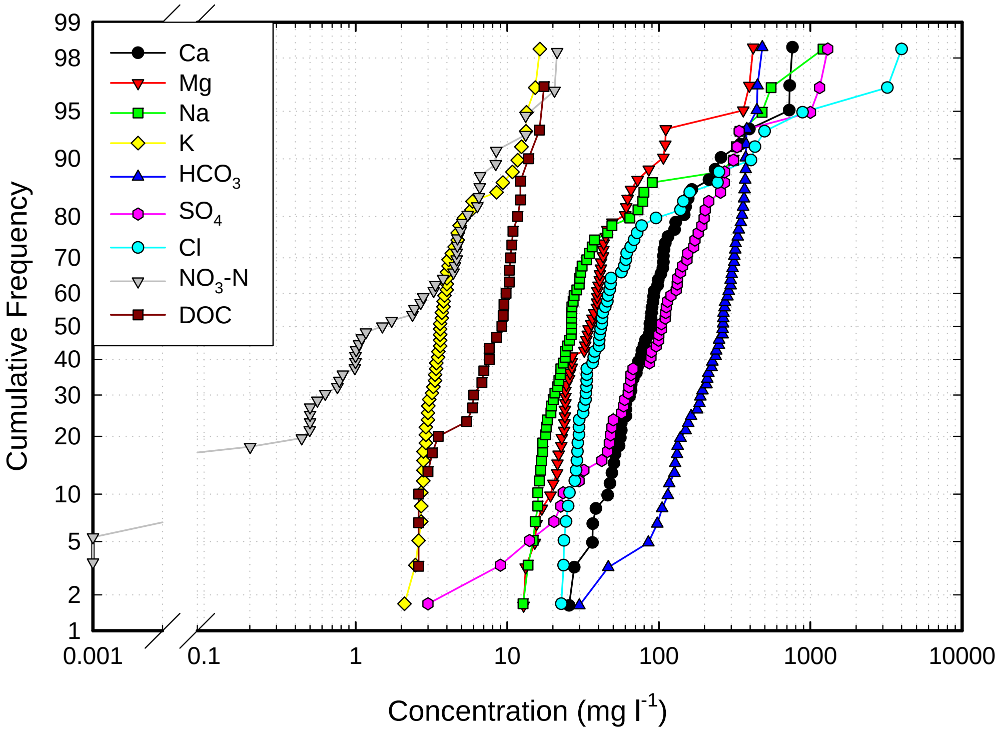


Figure 5.4 **Cumulative probability plots for major ion concentrations in the Liverpool and Rufford groundwaters.**

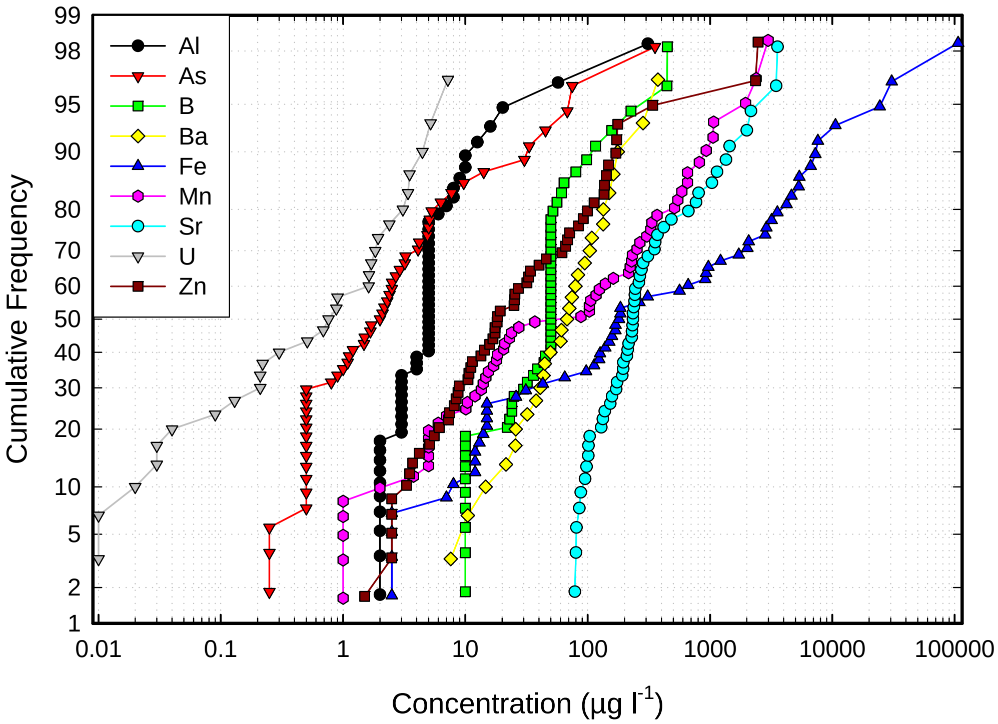
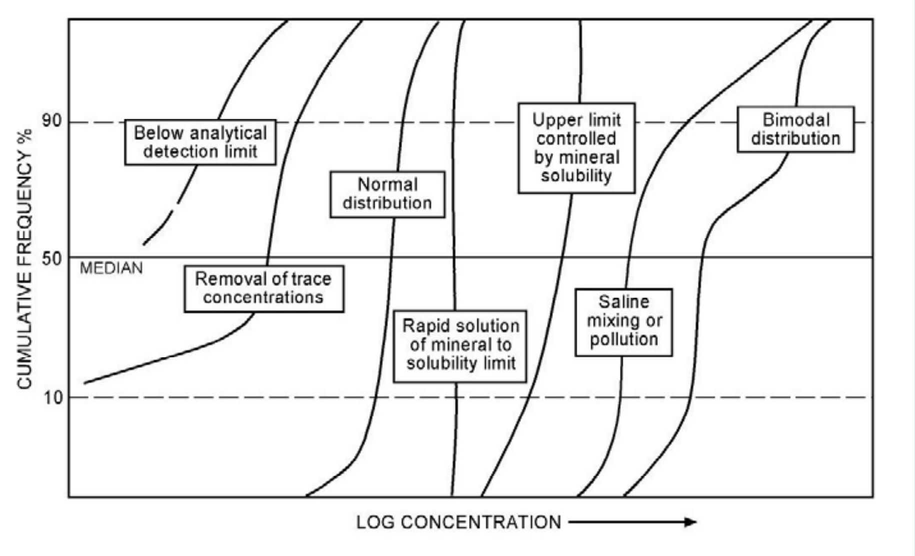


Figure 5.5 **Cumulative probability plots for minor and trace element concentrations in the Liverpool and Rufford groundwaters.**

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.

5.2 Water types and physicochemical characteristics

Groundwaters in the Liverpool and Rufford sandstone aquifer show a wide range of characteristics in terms of physicochemical parameters and element concentrations (Table 5.1a and 5.1b). The median temperature is 11.6 ^{o}C. The pH of the waters ranges from 5.9 to 7.7 with a median value of 7.2. Where Eh has been measured, the waters are shown to be mainly oxidising. However, some of the dissolved oxygen concentrations are low and indicative of reducing conditions (median values for DO and Eh are 2.7 mg l^{-1} and 361 mV respectively). The relatively high dissolved iron and manganese concentrations are also indicative of reducing conditions.

Table 5.1a **Field parameters, isotope data and range of major and minor element concentrations in groundwaters of the Sherwood Sandstone of the Liverpool and Rufford area.**

Parameter	Units	Min	Max	Median	Mean	97.7th percentile	95th percentile	Upper Baseline*	N
T	^{o}C	7.4	19.1	11.55	11.8	14.4	14.2		50
pH	field	5.88	7.72	7.19	7.07	7.64	7.58		57
Eh	mV	91	452	361	309	448	444		13
DO	mg l^{-1}	<0.1	11.1	2.7	3.7	10.6	10.0		49
SEC	µS cm^{-1}	321	10090	789	1314	8521	3275		48
δ^{2}H	‰	-46.5	-40.2	-43.10	-43.24	-40.43	-40.69		8
δ^{18}O	‰	-7.27	-6.41	-6.78	-6.79	-6.45	-6.49		8
δ^{13}C	‰	-18.69	-14.67	-15.55	-16.00	-14.70	-14.73		8
Ca	mg l^{-1}	25.6	761	87.2	131	728	428		59
Mg	mg l^{-1}	12.8	419	34.4	56	383	136		59
Na	mg l^{-1}	12.7	1210	26.5	86.4	530	370	▨	57
K	mg l^{-1}	2.1	16.4	3.6	5.0	14.8	13.3	▨	57
Cl	mg l^{-1}	22.7	3990	41	213	2548	575	▨	57
SO_4	mg l^{-1}	3.0	1300	104	167	1107	470	▨	57
HCO_3	mg l^{-1}	29.9	480	265	252	446	387		59
NO_3 as N	mg l^{-1}	0.001	21.3	1.50	3.48	18.73	13.20	▨ 0 - 6 mg l^{-1} ?	55
NO_2 as N	mg l^{-1}	0.001	0.112	0.002	0.008	0.043	0.036	▨	58
NH_4 as N	mg l^{-1}	0.002	2.31	0.02	0.14	0.62	0.31	▨	58
P	µg l^{-1}	25	800	100	158	695	534		51
DOC	mg l^{-1}	2.60	17.5	9.20	8.50	16.73	15.30	▨	29
F	mg l^{-1}	0.025	0.2	0.0935	0.097	0.169	0.162		52
Br	mg l^{-1}	0.015	11.3	0.086	0.54	6.44	1.76		53
I	mg l^{-1}	0.004	0.055	0.008	0.012	0.05	0.044		29
Si	mg l^{-1}	3	13	8	8	11	10		56

* estimated upper baseline for elements modified by anthropogenic influences.

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

Table 5.1b Trace element concentrations in groundwaters of the Sherwood Sandstone of the Liverpool and Rufford area.

Parameter	Units	Min	Max	Median	Mean	97.7th percentile	95th percentile	N
Ag	µg l^{-1}	<0.05	0.06	<0.05	<0.05	<0.05	<0.05	29
Al	µg l^{-1}	2	310	5	11.5	47.3	17.1	56
As	µg l^{-1}	<0.05	355	2	13.6	73.4	54.4	53
Au	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
B	µg l^{-1}	10	448	50	62.2	401	185	53
Ba	µg l^{-1}	7.58	376	67.7	88.703	316	240	29
Be	µg l^{-1}	<0.05	0.12	<0.05	0.05	0.12	0.116	29
Bi	µg l^{-1}	<0.05	0.18	<0.05	<0.05	0.10	<0.05	29
Cd	µg l^{-1}	<0.05	6.25	<0.05	0.2796	2.5	1.788	57
Ce	µg l^{-1}	<0.05	0.03	<0.05	<0.05	<0.05	<0.05	29
Co	µg l^{-1}	<0.02	15.3	0.025	0.9662	7.3	2.4	29
Cr	µg l^{-1}	<0.5	42.8	<0.5	1.7	12.7	5	57
Cs	µg l^{-1}	<0.01	0.07	0.01	0.0141	0.05	0.04	29
Cu	µg l^{-1}	<0.5	39.9	2.16	4.48	19.3	13.4	57
Dy	µg l^{-1}	<0.01	0.19	0.005	0.0171	0.12	0.072	29
Er	µg l^{-1}	<0.01	0.11	0.005	0.0133	0.09	0.064	29
Eu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
Fe	µg l^{-1}	2.5	107000	180	4070.9	28529	11980	59
Ga	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
Gd	µg l^{-1}	<0.01	0.17	<0.01	0.0164	0.12	0.084	29
Ge	µg l^{-1}	<0.05	0.15	<0.05	0.0469	0.14	0.126	29
Hf	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	29
Hg	µg l^{-1}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	29
Ho	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
In	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
Ir	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
La	µg l^{-1}	<0.01	0.03	<0.01	<0.01	0.02	<0.01	29
Li	µg l^{-1}	2.3	22.2	9.1	10.2	21.6	20.4	29
Lu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
Mn	µg l^{-1}	1	2990	88.1	308	2236	1158	59
Mo	µg l^{-1}	0.05	5	0.4	0.8293	4.1	3.28	29
Nb	µg l^{-1}	<0.01	0.01	<0.01	0.0129	0.06	0.046	29
Nd	µg l^{-1}	<0.01	0.07	<0.01	0.009	0.05	0.03	29
Ni	µg l^{-1}	<0.2	54.7	2.5	4.93	24.8	15.7	57
Os	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
Pb	µg l^{-1}	<1	27.8	0.3	2.34	25	18.3	57
Pd	µg l^{-1}	<0.2	0.2	<0.2	<0.2	<0.2	<0.2	29
Pr	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
Pt	µg l^{-1}	<0.01	0.04	<0.01	<0.01	0.02	<0.01	29
Rb	µg l^{-1}	0.25	15.0	2.53	3.68	10.5	7.97	29
Re	µg l^{-1}	<0.01	0.02	<0.01	<0.01	0.01	0.01	29
Rh	µg l^{-1}	<0.01	0.005	<0.01	<0.01	<0.01	<0.01	29
Ru	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
Sb	µg l^{-1}	<0.05	0.79	<0.05	0.1057	0.55	0.358	29
Sc	µg l^{-1}	1	3	2	2.1034	3	3	29
Se	µg l^{-1}	<0.5	2.5	<0.5	0.5414	1.92	1.32	29
Sm	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
Sn	µg l^{-1}	<0.05	0.27	0.14	0.1317	0.22	0.19	29
Sr	µg l^{-1}	78.4	3570	234	511	3211	2064	53
Ta	µg l^{-1}	<0.05	0.03	<0.05	<0.05	<0.05	<0.05	29
Tb	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
Te	µg l^{-1}	<0.05	0.07	<0.05	<0.05	<0.05	<0.05	29
Th	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	29
Ti	µg l^{-1}	< 10	< 10	< 10	< 10	< 10	< 10	29
Tl	µg l^{-1}	<0.01	0.25	<0.01	0.0169	0.11	0.03	29
Tm	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	29
U	µg l^{-1}	<0.5	7.2	0.76	1.48	5.91	4.89	29
V	µg l^{-1}	0.1	3.1	0.2	0.6103	2.97	2.54	29
W	µg l^{-1}	<0.01	0.57	<0.01	0.180	0.24	0.05	29
Y	µg l^{-1}	<0.01	2	0.03	0.1836	1.40	0.91	29
Yb	µg l^{-1}	<0.01	0.09	<0.01	0.0114	0.06	<0.01	29
Zn	µg l^{-1}	1.5	2469	18.2	130	1771	209	57
Zr	µg l^{-1}	<0.5	0.98	<0.5	<0.5	0.72	<0.5	29

The Piper diagram (Figure 5.1) illustrates the range of major element compositions found within the Liverpool and Rufford aquifer. The groundwaters are predominantly of Ca-HCO_3 to mixed Ca-Mg-HCO_3-SO_4-Cl types. The anions show a greater scatter than the cation data with the majority of the samples being of HCO_3 and SO_4 type. Several samples show a trend towards Cl. However, this is not reflected by a corresponding trend in the cations towards Na. There is one Na-Cl type water but most of the higher Cl type waters are Ca-Cl types which is indicative of ion exchange during salinisation. Almost all of the high Cl samples are located close to the coast/Mersey estuary with the exception of one which was taken from a relatively shallow borehole and which may be affected by pollution.

5.3 Major elements

The box plot (Figure 5.2) for major elements highlights the dominance of calcium and bicarbonate ions within the groundwater. Sulphate and Mg (and to a lesser degree K) concentrations are also elevated above the marine-derived input to the system. There is a high mean chloride value which exceeds the median and reflects the fact that there are a few samples which have high chloride concentrations. The median Na concentration exceeds the diluted sea water line which indicates that there is an excess of Na over Cl. Most of the other major elements have median concentrations in excess of the diluted sea water line which implies that water-rock interaction is important. Sulphate displays a wide range of concentrations from 3 mg l^{-1} to 1300 mg l^{-1}. NO_3-N concentrations also display a wide range from below detection limit to 21.3 mg l^{-1}. The cumulative frequency plot for major elements (Figure 5.4) shows that most major elements vary over two orders of magnitude. The chloride and sodium curves show a shift at around 80% (similar to the Manchester groundwaters; Griffiths et al., 2003), indicating that a population of higher salinity groundwaters are present. Several elements (K-Ca-HCO_3-SO_4-Mg) show a population shift at about the 95th percentile (similar to groundwaters in the Manchester study; Griffiths et al., 2003). The curves for these elements are indicative of mixing between at least two populations. The nitrate plot shows a complex distribution indicating mixing between two or more different populations and a tail at low concentrations indicating a potential role for denitrification controls. Sulphate concentrations display a shift at around 15% with concentrations less than approximately 40 mg l^{-1}. DOC showed a slight shift at 20%. Samples which have lower DOC concentrations tend to be covered by till deposits, although one of the low DOC samples is overlain by sand.

5.4 Minor and trace elements

The box plot for minor and trace elements indicates a wide range of concentrations present in the groundwater (Figure 5.3). Bromide has a median value of less than the diluted seawater line. Fluoride is generally at low concentrations and ranges from below detection limit to 200 μg l^{-1}. Silicon displays a relatively narrow range of concentrations. Iron and Mn display a large range in concentrations over several orders of magnitude. Some of the highest concentrations are for samples collected by BGS which are known to have been filtered. Barium and Sr are present in relatively high concentrations, with a number of the samples exceeding the EC Guide Level Ba concentration of 100 μg l^{-1}. Most other trace elements are present in relatively low concentrations reflecting the circum-neutral pH of most of the groundwaters. Some of the trace elements have a relatively low median value but may occur locally in very high concentrations. For example, As has a median value of 2 μg l^{-1}, but concentrations in excess of the EC maximum permissible value in drinking water of 10 μg l^{-1} have been recorded in approximately 15% of samples. The highest observed As concentration in the area was in excess of 300 μg l^{-1}. This sample was from a borehole located in the confined part of the aquifer, where it is overlain by the Mercia Mudstone Group. Nickel has a median value of 2.5 μg l^{-1} but concentrations of up to 54.7 μg l^{-1} have been recorded, above the EC limit (20 μg l^{-1}). Several of the sites with high Ni are likely to be contaminated (one is a tannery and another is a refinery). However, some of the high Ni concentrations may represent baseline and these correlate with low pH which will promote mobilisation of trace elements sorbed to aquifer materials. One of the samples with high Ni concentration also has high Pb. Zinc concentrations are also locally elevated. The cumulative frequency plot for minor and trace elements (Figure 5.5) shows that for many elements concentrations vary over 3 or 4 orders of magnitude and some elements e.g. Mn and Fe vary by up to 5 orders of magnitude. Most solutes display have a number of different populations within the data set. Uranium concentrations were locally enhanced and concentrations up to 7.2 $\mu g\ l^{-1}$ were measured.

Straight vertical lines on the cumulative frequency plots at low concentrations are an artefact resulting from measurements that were below the detection limit. It is possible that the high concentrations of some trace elements are due to the fact that the database includes results from analysis of unfiltered samples. This will be discussed in more detail in Chapter 6.

5.5 Pollution indicators

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

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

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

The approach adopted is threefold:

(i) to have evidence of groundwater age

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

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

The most obvious indicator of diffuse pollution is the presence of high nitrate concentrations. Nitrate levels are high over much of the urban part of Liverpool and have been attributed to sewer leakage (Tellam, 1996; Brennan, 1997; Whitehead, 1998). Tellam (1996) and Brennan (1997) noted elevated concentrations of potassium and nitrate in the groundwater beneath Liverpool compared with groundwater from surrounding rural areas. However, as there are several potential sources of nitrate, further evidence was required to confirm a sewage source. Whitehead (1998) used nitrogen isotopes and other markers to determine whether the source of the nitrate was sewage-derived. High nitrate concentrations relating to wastewater contamination were found to be associated with elevated concentrations of boron (present in washing powder), potassium and microbiological indicators.

High nitrate concentrations also occur in rural areas as a result of agricultural pollution. Vines (1984) conducted an investigation into nitrate in groundwater in the Permo-Triassic Sandstones of the North West. As part of the investigation, porewater samples were obtained from a borehole called the Rock at Ormskirk which was an arable site located on the outcrop of the Permo-Triassic Sandstone aquifer.
The major ion chemistry was found to be in agreement with previous studies indicating saline

intrusion and widespread contamination. Elevated concentrations of sulphate, usually in association with high nitrate concentration, at industrial sites may be attributed to pollution (Tellam 1996). However, as naturally elevated concentrations of sulphate may occur, it is often difficult to separate these effects and identify the natural component.

DOC concentrations are often taken as an indicator of pollution but other parts of the Sherwood Sandstone contain high concentrations of DOC which are considered to be natural (Shand et al., 2002). The groundwaters in the study area all have a moderately high DOC but this is unlikely to simply relate to anthropogenic inputs and will be discussed later. The database of historical water chemistry analyses that was used for this study does not contain any information on pesticide concentrations, and organic contaminants were not considered in this study.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

This section deals with the dominant geochemical processes that influence groundwater chemistry and provides an overview of the regional variations. The dominant geochemical processes include mineral dissolution/precipitation, redox reactions, ion exchange and mixing. Groundwater chemistry will evolve as water moves from recharge to discharge areas. The baseline chemistry within an aquifer varies with depth, geographical location and also with time.

6.2 Depth variations

There are many problems involved in the interpretation of pumped groundwater samples, in particular the fact that such samples may represent a mixture of waters from different horizons (see Section 4.3). This can be partly overcome by sampling from specific depths in a borehole, from multi-level boreholes or using packers (although some mixing is inevitable even with packers), porewater extraction (for sampling water in the matrix) or by comparing the chemistry from adjacent boreholes drilled to different depths. Most of the boreholes sampled were uncased, and samples from them therefore represent compositions integrated over a range of inflow depths.

There are few data available on depth variations in the aquifer. Barker (1996) found high SO_4 concentrations in the shallow parts of the aquifer near Haskayne in the north of the study area, concluding that this was derived from the overlying till deposits which contain gypsum. Tellam (1996) considered that the leakage was increased by excavation of a railway tunnel. Saline waters are also present at the base of the aquifer, due to the dissolution of evaporite minerals.

Figure 6.1 illustrates selected major element concentrations (plus I and ^{18}O) plotted against borehole depth for the samples collected as part of this project. As mentioned previously, the samples will be integrated and not necessarily from the base of each borehole. The high SEC groundwaters include Na-Cl, Ca-SO_4 and mixed water types indicating different sources for the increased salinity. Sample No. 17 (Figure 6.1), taken from a borehole located adjacent to the Mersey estuary, is of Na-Cl type, indicating modern saline intrusion. Sample No. 20 is a Ca-SO_4 type water with low Cl and high Cl and SO_4 are most likely derived from gypsum dissolution. The sample No. 25 contains high SO_4 as well as high Na and Cl, indicating mixing with formation water as well as gypsum dissolution (Figure 6.1). These samples will be discussed in more detail in Section 6.5.4.

With the exception of one sample, stable isotopes (Figure 6.1) showed a depletion in $\delta^{18}O$ with depth of borehole and may indicate a component of palaeowater in parts of the aquifer. However, the data are limited and changes may also occur due to mixing with seawater.

The depth variations noted above are likely to relate to geological factors such as the presence of drift deposits and proximity to the coast, and will be discussed in later sections.

Porewater profiles taken as part of the nitrate in groundwater investigations undertaken by Vines (1984) illustrate variations in nitrate concentrations with depth in two boreholes (Figure 6.2). High concentrations of NO_3 were present in the shallower Rock borehole, but were slightly lower at the shallowest depths (< c. 10 m) which coincides with the depth of the rest water level. The deeper samples from Breeze Hill indicate low concentrations of NO_3 in the deeper parts of the aquifer.

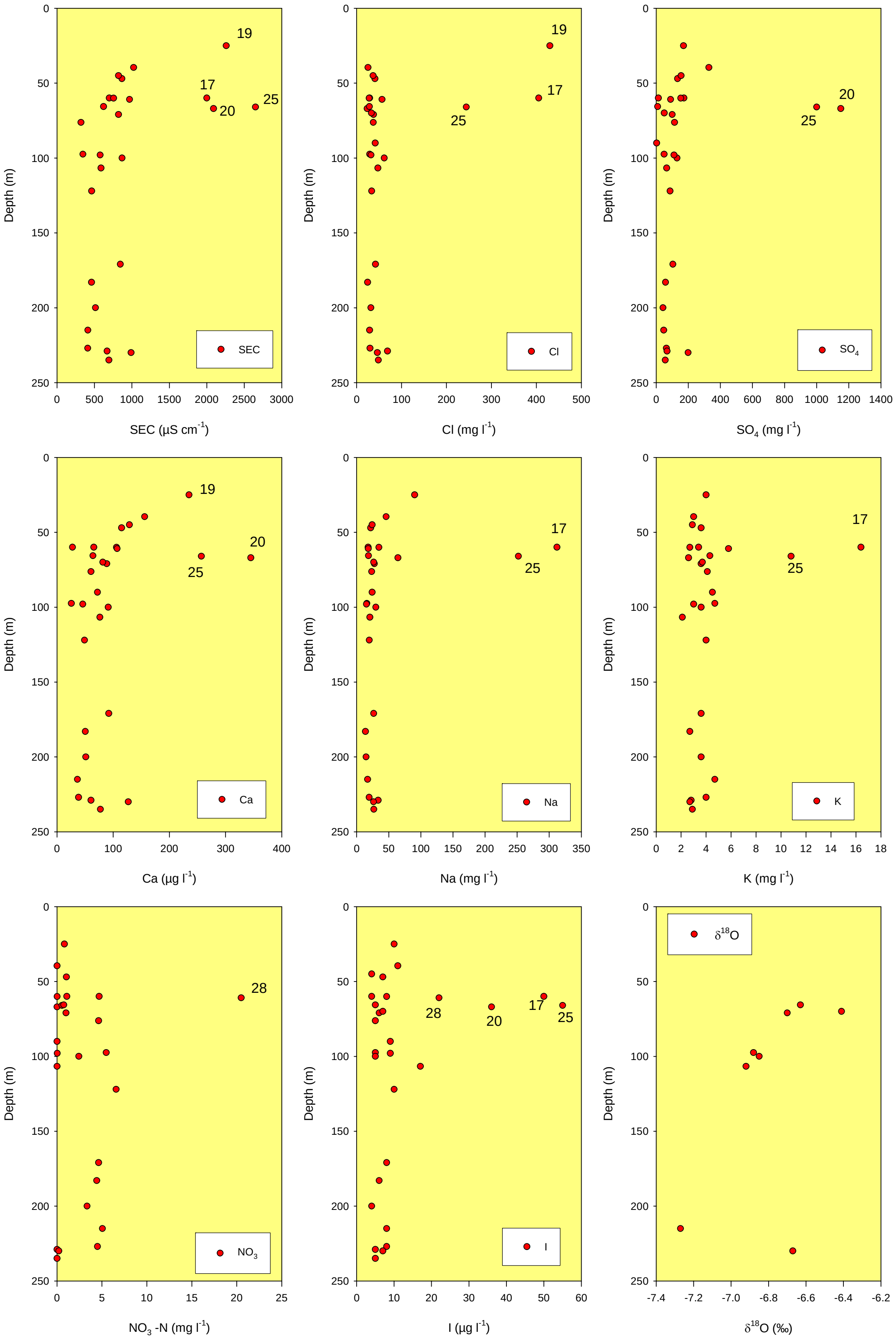


Figure 6.1 Variations in SEC, $\delta^{18}O$, Cl, SO_4, Ca, Na, K, NO_3 and I concentrations with depth of borehole (samples are integrated over the whole of the length of the open section of borehole). Numbers indicate site number and discussed in the text.

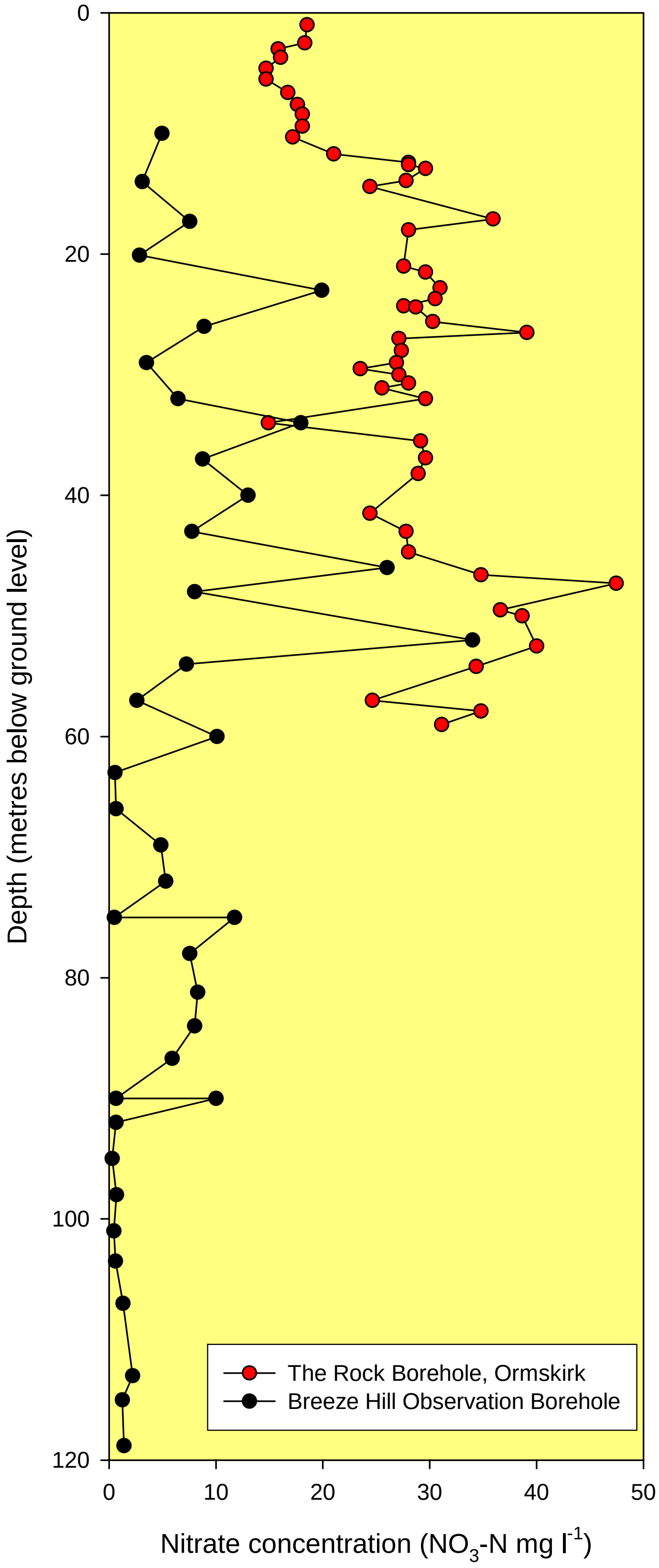


Figure 6.2 **Porewater nitrate profiles with depth.**

6.3 Temporal variations

Tellam (1996) examined water quality variations through time for a number of boreholes in the study area. He classified groundwater samples into water types and looked at the evolution of these types with time. The main factors considered to influence the type of groundwater chemistry were proximity to the Collyhurst Sandstone Formation, nature and thickness of drift, water level and changes in water level and proximity to the Mersey estuary. Tellam (1996) concluded that the main features of chemical distributions were consistent over time, with the exception of areas where pumping has induced leakage through the Quaternary deposits e.g. in the Bootle area and in the Ormskirk-Formby area.

Figure 6.3 illustrates trends in nitrate concentrations for three selected pumping stations. Knowsley showed a complex trend alternating between low and high NO_3. Belle Vale and Melling displayed a slight increase in concentrations from 1980 to present. This is consistent with the observations made by Vines (1984b) for boreholes in the Liverpool and Ormskirk area. With the exception of Melling, Knowsley and Kirkby, nitrate variations were extremely irregular, possibly due to variations in pumping rate. Despite this irregularity, Vines (1984b) stated there was a clear upward trend for all sites, with the exception of Knowsley, which showed a temporary rise in the early 1950's which was followed by stabilization, more or less, at pre 1950 values. Vines (1984b) observed that for this group of boreholes there was not a great problem with nitrate concentrations. Even concentrations at Whiston, which were relatively high, had not changed greatly from concentrations measured in the 1940's and 50's.

Interestingly, NO_3 concentrations from the early part of the twentieth century are of the order of 5-6 mg l^{-1} NO_3-N. In 1900, Dudlow Lane Pumping Station Borehole No. 1 had a concentration of 5.74 mg l^{-1} NO_3-N while Green Lane Pumping Station Borehole No.1 had a similar concentration of 5.83 mg l^{-1} NO_3-N, which corresponds with the present concentrations that occur in deeper boreholes. Such concentrations are often considered to be above the natural baseline levels.

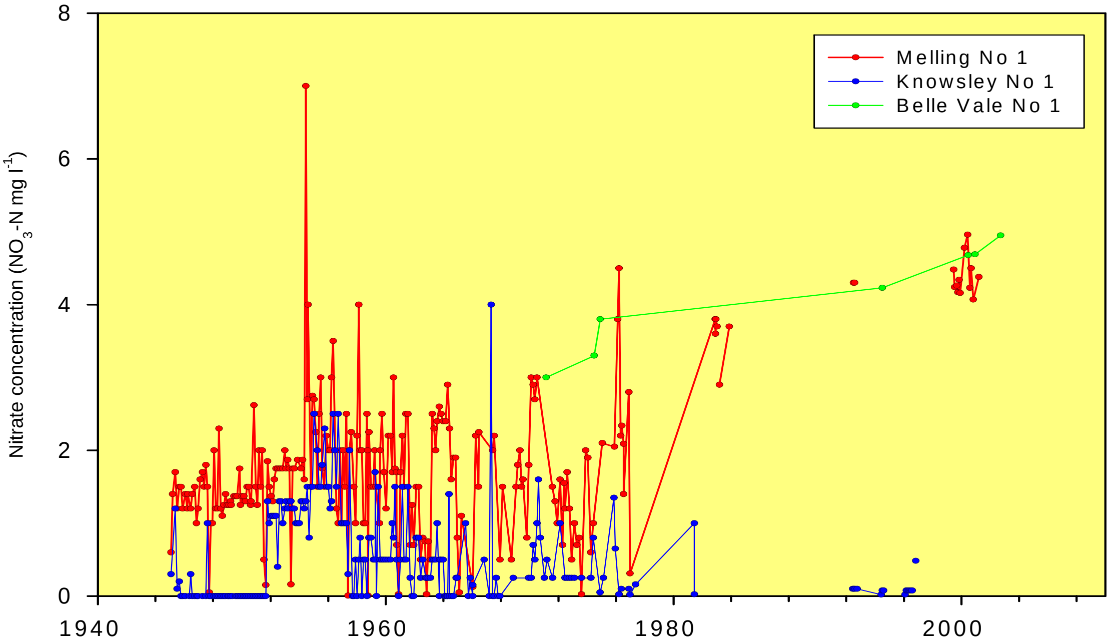


Figure 6.3 **Nitrate concentrations with time for three public water supply boreholes in the study area**

6.4 Age of the groundwater

There are no direct measurements of groundwater age in the study area. Stable isotope analyses of δ^{2}H and δ^{18}O (Figure 6.4) were measured on selected samples in order to assess if palaeowaters were present. These stable isotopes have been used successfully to discriminate older Pleistocene (pre 10,000 year old) water from Holocene (post 10 000 year old) groundwaters in the Sherwood Sandstone of the East Midlands (Edmunds et al., 1982). The climate during the Pleistocene period was colder than at present, resulting in lighter (more negative) signatures of the stable isotopes δ^{2}H and δ^{18}O. The range of δ^{2}H and δ^{18}O values observed are similar to modern rainfall inputs and indicate that the groundwaters are is likely to be of Holocene or recent age. However, the presence of lighter signatures in some samples may imply that there is a component of palaeowater.

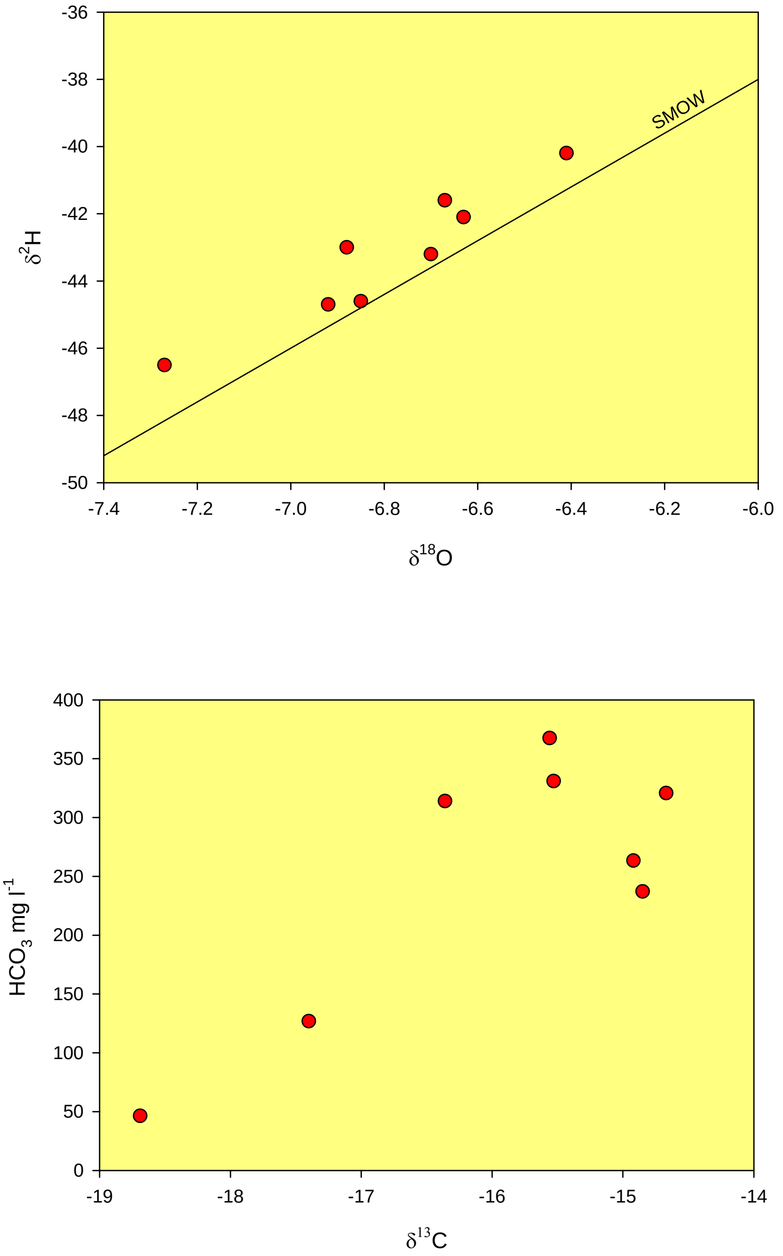


Figure 6.4. **Stable isotope correlations (a) δ^{2}H and δ^{18}O (b) δ^{13}C and HCO_3.**

6.5 Geochemical evolution

6.5.1 Mineral dissolution reactions

For aquifers containing carbonate or evaporite minerals as a matrix cement, the chemistry of groundwaters will be strongly influenced by the rapid dissolution of these minerals. Infiltrating groundwater will initially be acidic due to the presence of carbonic acid derived from CO_2 production in the soil zone and from equilibration with CO_2 in the atmosphere. This acidity will be rapidly neutralised through reaction with carbonate minerals:

$$CaCO_3 + H_2CO_3 \Leftrightarrow Ca^{2+} + 2HCO_3$$

calcite carbonic acid

Dolomite dissolution is controlled by the following reaction:

$$CaMg(CO_3)_2 + 2\,H_2CO_3 \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3$$

dolomite carbonic acid

The saturation indices for calcite and dolomite are variable from strongly undersaturated to slightly oversaturated, with the more acidic waters being the most strongly undersaturated (Figure 6.5). It is likely that the lower pH samples are from parts of the aquifer that are carbonate poor or have been decalcified, the former being more likely since the lower pH is present at intermediate depths in the aquifer rather than close to the surface. The high Mg/Ca molar ratio in most groundwater samples (Figure 5.1) indicates that dolomite dissolution is an important control on the groundwater chemistry.

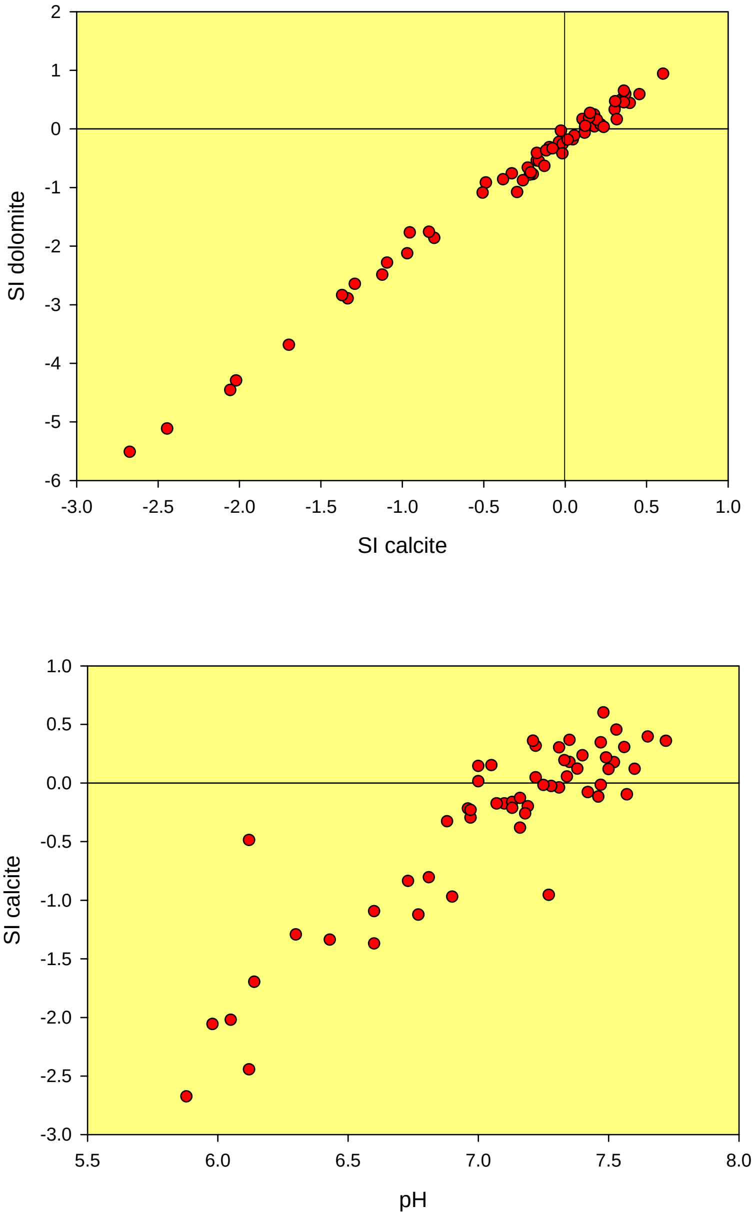


Figure 6.5 Saturation indices (a) dolomite-calcite (b) calcite-pH

Another reaction likely to be influencing the water chemistry is that of gypsum (or anhydrite: $CaSO_4$) dissolution:

$$\underset{\text{gypsum}}{CaSO_4.2H_2O(s)} \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

The Piper plot shows that there is a trend towards SO_4 in the groundwater compositions. Calcium and Mg typically remain the dominant cations, giving rise to waters of Ca-Mg-SO_4 composition. A plot of SO_4 vs. Cl (Figure 6.6) shows two distinct trends in the data. The first is a trend for some samples (mainly coastal) displaying an increase in both SO_4 and Cl, which is indicative of mixing with a saline source is indicated. Most other samples have a much higher SO_4/Cl ratio indicating an additional source of sulphate (Figure 6.6) and the correlation of Ca with SO_4 implies that gypsum or anhydrite dissolution is the major control on dissolved SO_4. The samples with very high SO_4 concentrations approach saturation with respect to gypsum (SI of c. -0.2; Figure 6.6). The source of the gypsum will be discussed in the section on spatial variations (Section 6.7).

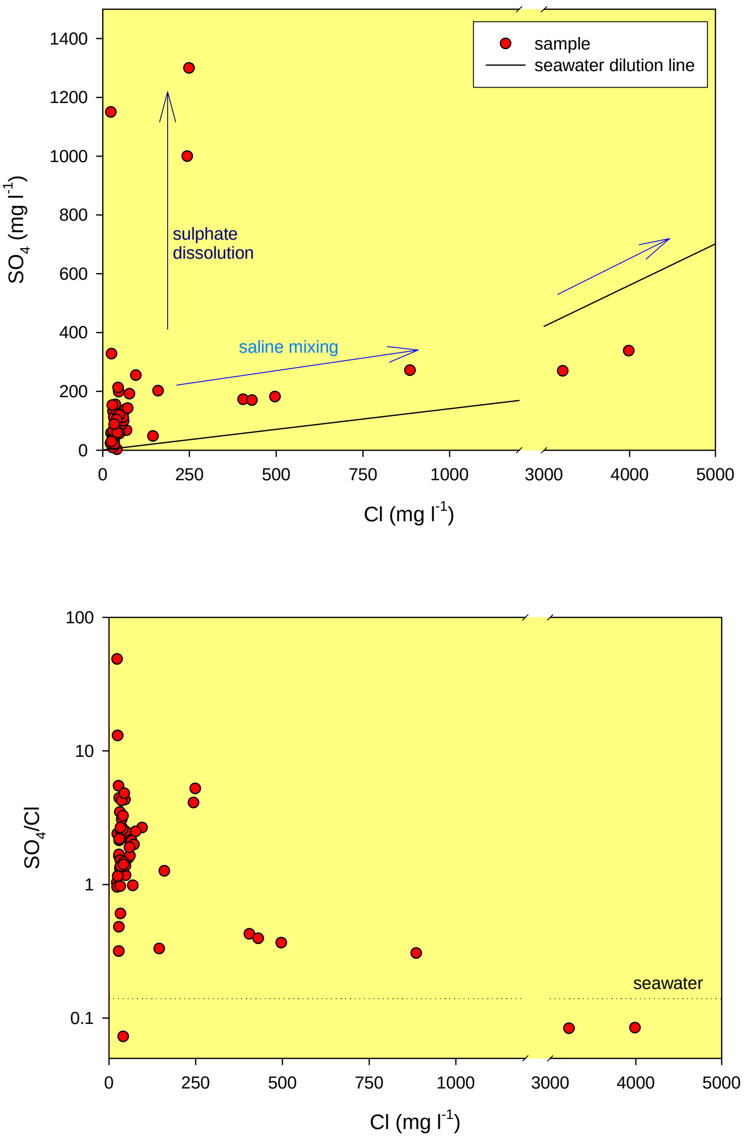
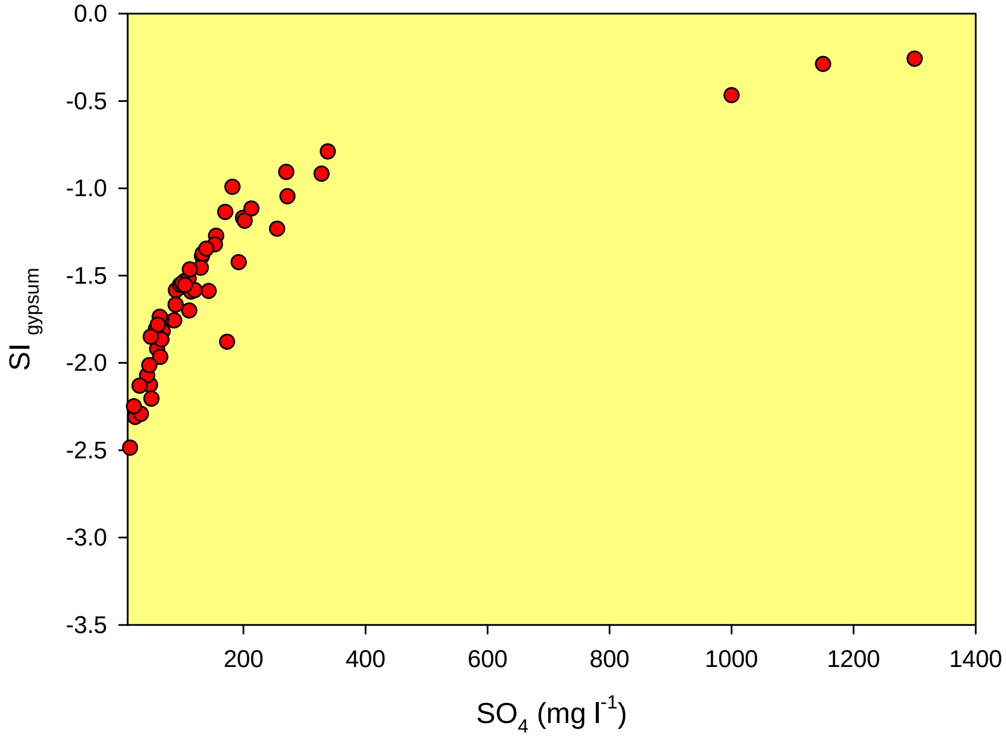


Figure 6.6 **Plots of SO_4 vs. Cl (top) and SO_4/Cl vs. Cl (bottom) for Liverpool and Rufford area groundwaters.**



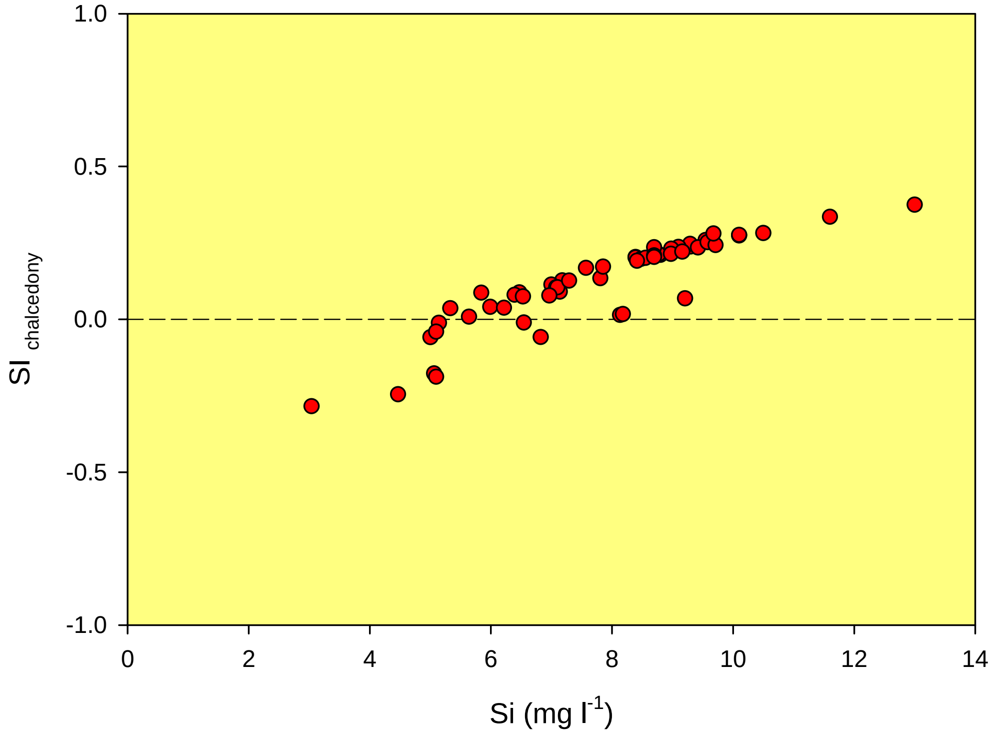


Figure 6.7 **Saturation indices for gypsum(top) and chalcedony(bottom).**

Less rapid silicate dissolution reactions may also be occurring. Silica concentrations within the groundwaters range from 3 to 13 mg l^{-1}. Although the aquifer is composed dominantly of quartz, this mineral is extremely unreactive and the source of Si is most likely to be from silicate minerals such as K- or plagioclase-feldspar. The amount and rate of dissolution will be controlled by saturation with respect to a silicate mineral or phase. Most groundwaters in the study area are close to saturation or slightly oversaturated with respect to chalcedony (Figure 6.7).

Concentrations of fluoride are generally low (<0.2 mg l^{-1}) in the groundwaters which are undersaturated with respect to fluorite implying that fluorite is not present in significant quantities in the aquifer.

6.5.2 Redox reactions

The redox potential (Eh) and dissolved oxygen (DO) concentration are important indicators of the redox status of natural groundwaters. These parameters are unstable and extremely sensitive to changes caused by contact with the atmosphere and, therefore, should be monitored in a flow-through cell where the water is pumped directly from the borehole and contact with the air is prevented. Eh measurements were only completed at a few sites. The redox status of groundwaters in the study area is complex, mainly due to the variations in drift thickness and type and possibly to locally confining layers within the sandstone. This is reflected in the large spatial variations and range of redox parameters (DO and Eh) and redox sensitive species. Redox conditions are likely to be significantly affected by the nature and thickness of drift cover across the aquifer. Unfortunately, detailed construction details are not known for many of the boreholes sampled and it is difficult to assess vertical changes in redox potential.

Selected redox sensitive elements have been plotted against Eh on Figure 6.8. Dissolved organic carbon (DOC) is variable and shows no clear relationship with Eh. Barker (1996) found high DOC concentrations in a borehole near Haskayne in the north of the study area and considered that this was due to contamination from a polymer added to the drilling fluid. It is unlikely that this can explain the high concentrations in all samples in the study area since high concentrations are found in deep boreholes and the boreholes are well-pumped. Shand et al. (2002) concluded that high DOC (up to 19 mg l^{-1}) in the Vale of York aquifer was derived from drift deposits which were up to 40 m thick in the areas of high DOC. In this area, it is likely that both natural and anthropogenic inputs are present.

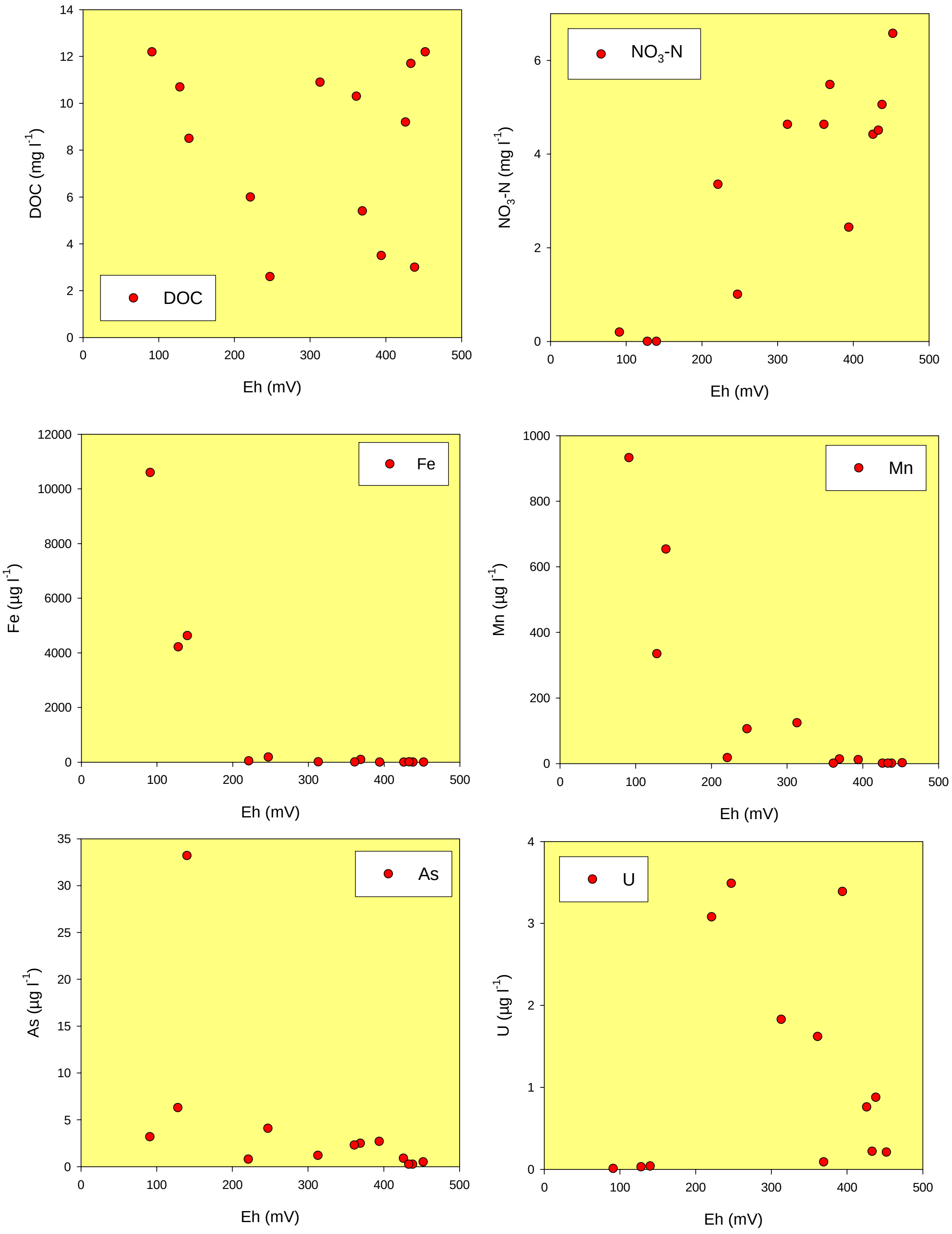


Figure 6.8 **Correlation of Eh and solute concentrations of redox-sensitive elements.**

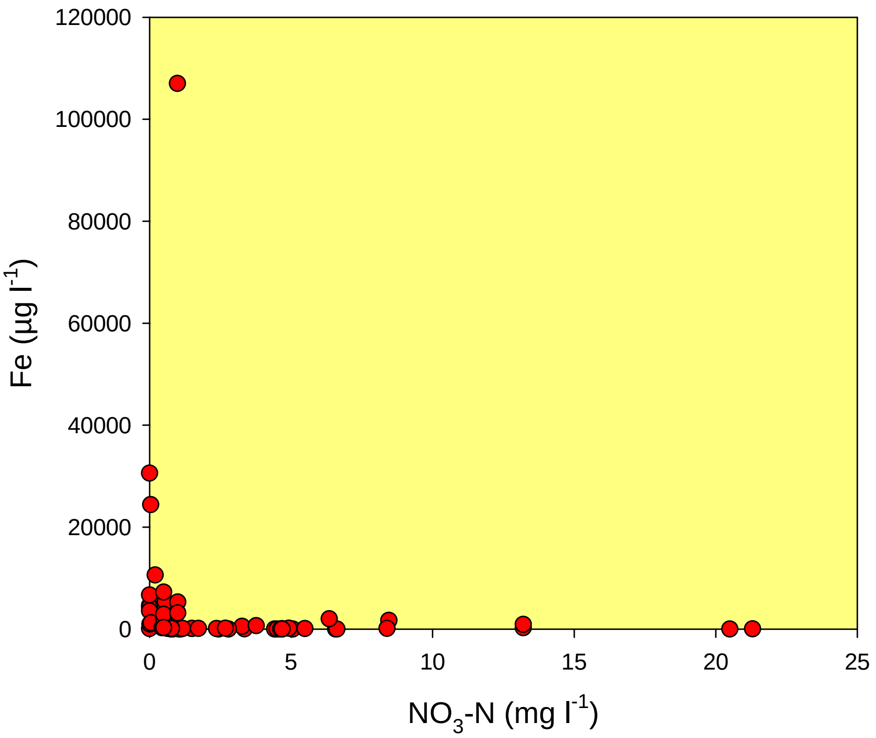


Figure 6.9 Correlation between nitrate and iron

Nitrate concentrations are higher, as expected, in the oxidising waters with denitrification probably creating low concentrations where the groundwaters are reducing. Low concentrations may also be the result of older, pre-pollution groundwater particularly at depth. Iron and Mn concentrations are low in the oxidising groundwaters, due to the low solubility of Fe and Mn oxyhdroxide under oxidising conditions. Most groundwaters with high Fe also have low NO_3-N and it is therefore likely that the process of denitrification contributes to low NO_3-N concentrations found in many groundwaters (Figure 6.9). Sewer leakage and the effects of agricultural pollution are likely provide important inputs of nitrate to the groundwater locally. The spatial distributions are determined by the local geology and hydrogeology, in particular the type and thickness of drift which may afford valuable protection to the underlying aquifer.

The redox environment also controls the distribution of many trace elements which are redox sensitive. Uranium concentrations are higher as expected in the oxidising groundwaters and As concentrations are generally higher in reducing groundwaters (Figure 6.8).

6.5.3 Ion exchange reactions and aquifer freshening

The majority of recharge groundwaters are dominated by Ca and HCO_3 ions owing to the dissolution of calcite. Cation exchangers within the aquifer will therefore have a dominance of Ca adsorbed onto their surfaces. In aquifers containing dominantly seawater, Na and Cl are the dominant ions in solution, thus sediments in contact with seawater will have largely adsorbed Na. When seawater intrudes a freshwater aquifer the following exchange takes place:

$$\mathrm{Na}^{+} + \tfrac{1}{2}\mathrm{Ca}-X_2 \rightarrow \mathrm{Na}-X + \tfrac{1}{2}\mathrm{Ca}^{2+}$$

where X indicates the soil or sediment exchanger. Sodium is taken up by the exchanger and Ca is released which alters the water chemistry from a Na-Cl type to a $Ca\text{-}Cl_2$ type. This process will operate in reverse if freshening occurs i.e. freshwater flushing through a salt water aquifer:

$$\frac{1}{2}\mathrm{Ca}^{2+} + \mathrm{Na} - X \rightarrow \frac{1}{2}\mathrm{Ca}\text{ - }X + \mathrm{Na}^{+}$$

Here Ca^{2+} is taken up from the water and exchanged for Na, producing a $Na\text{-}HCO_3$ type water, (Appelo and Postma, 1994).

There is no trend towards $Na\text{-}HCO_3$ type waters showing that ion exchange induced by freshening is not a dominant process. There are a range of Na/Cl ratios in the groundwaters but in general there is a good correlation of Na with Cl indicating that Na addition through exchange or dissolution is not a dominant process. The Piper plot indicates a reduction in Na/Cl ratio for samples near the coast which suggest that the groundwater chemistry has not simply evolved due to mixing. Salinisation may produce waters of $Ca\text{-}Cl_2$ type due to reverse ion-exchange. The molar Na/Cl ratios in the most saline samples (Cl concentrations > 3000 mg l^{-1}) are very low (0.2) implying that if these are derived from seawater or formation water, then considerable ion-exchange of sorbed Ca for Na has occurred.

6.5.4 Seawater intrusion and mixing with formation water

An increase in chloride concentration occurs in groundwater close to the coast and has been interpreted as seawater intrusion. Work in the Mersey tunnel (Newton, 1993) has confirmed that seawater intrusion, from the Mersey estuary above, is leaking into the tunnel. Newton (1993) considered that the interface was moving towards the estuary as a consequence of decreased abstraction from the aquifer. This was also observed by Tellam (1995) in the Lower Mersey Basin. Evidence now suggests that the saline interface is moving inland again due to National Rail’s abstractions along the Loop Line underground railway tunnel which commenced in 1998 (John Ingram, pers. comm. 2004)

Relatively high Cl concentrations have also been found in the present study in groundwaters close to the Mersey Estuary (Figures 5.1 and 6.6). As suggested in the previous section, the more saline groundwaters along the coast have undergone significant ion exchange. The high SO_4/Cl ratios and Ca/Cl in most other coastal groundwaters indicate that other geochemical processes such as gypsum dissolution have occurred. The highest Cl samples also have very low SO_4/Cl, less than seawater, and indicate that sulphate reduction is likely to have occurred, a conclusion reached by Newton (1993) for waters from inside the Mersey Tunnel where active modern seawater intrusion is occurring. Mixing with a more saline component is necessary to explain the increase in Cl concentration. The age of this saline (formation water) component is not known and neither is the extent to which seawater intrusion is currently occurring.

In the Rufford area, the influence of the River Douglas on drift water quality is uncertain. The river is tidal and elevated above the flood plain. It may therefore be responsible for saline groundwater observed in the Douglas Valley (Seymour, 1993).

Mixing with an older, deeper connate or formation water is generally indicated by an increase in salinity, especially Cl. However, as discussed previously, the dissolution of evaporite minerals may also lead to increases in salinity because of the high solubility and rapid reaction kinetics of such mineral phases. The clearest indication of mixing with deeper formation waters is an increase in Cl concentration. Several boreholes sampled inland also show higher concentrations of Cl (up to 250 mg l^{1}). This indicates that a remnant formation water exists away from the coast. The highest Cl concentrations were found at moderately shallow depths, but close to the edge of the Mercia

Mudstone or drift deposits and it is therefore likely that they are derived from parts of the aquifer where groundwater flow is low. This will be discussed in the section on regional variations.

6.5.5 Trace elements

Iron and manganese are present in the groundwater, often at relatively high concentrations, although in some instances this may be due to the fact that some older data include from unfiltered samples which contained particulate Fe and Mn. However, these elements can reach very high concentrations even in filtered samples (up to 30.6 and 3 mg l^{-1} respectively). This reflects the reducing conditions in much of the aquifer (Figure 6.8). The source of the iron and manganese is most likely to be from reductive dissolution of Fe and Mn oxyhydroxides, which form cements within the sandstones and grain coatings, although pyrite within the Boulder Clay (drift) and Coal Measures might also be additional sources of Fe.

Iron and manganese oxyhydroxides also represent important adsorption sites, and dissolution under reducing conditions may lead to high concentrations of trace elements such as Co, Ni and As. Most of the high concentrations of Co and As are in high-Fe and high-Mn groundwaters (Figure 6.10) and desorption or reductive dissolution are likely causes of elevated concentration. There was, however, a poor correlation between Ni and Fe or Mn.

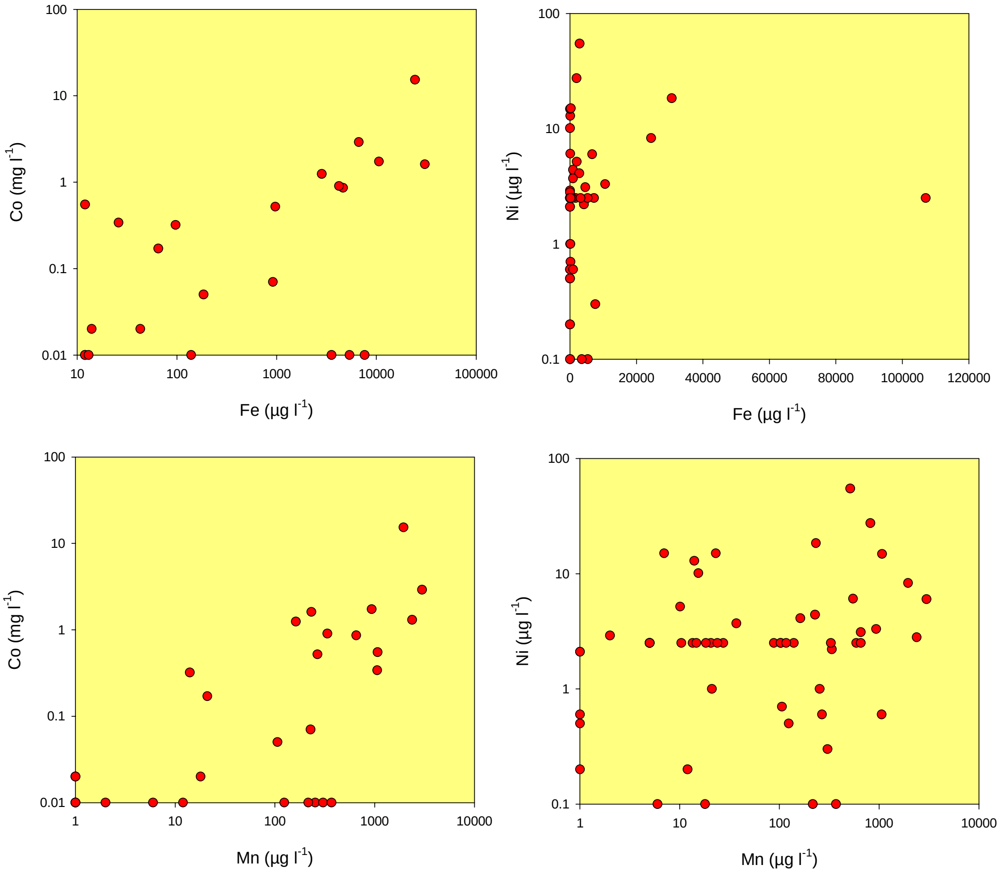


Figure 6.10 Concentrations of Co and Ni against Mn and Fe.

The source of Sr in most groundwaters is dominantly from calcite or gypsum, concentrations in the latter typically being much higher. In silicate aquifers, Sr may also be derived from Ca-bearing minerals such as Ca-rich plagioclase feldspar. Groundwaters with high Sr concentrations are found both in the high SO_4-low Cl and high Cl-low SO_4 groundwaters (Figure 6.11). In the high SO_4 groundwaters, the origin of Sr is dominantly from gypsum dissolution whereas in the Cl-rich waters the Sr is derived from mixing with a formation water having Sr/Cl ratios higher than seawater.

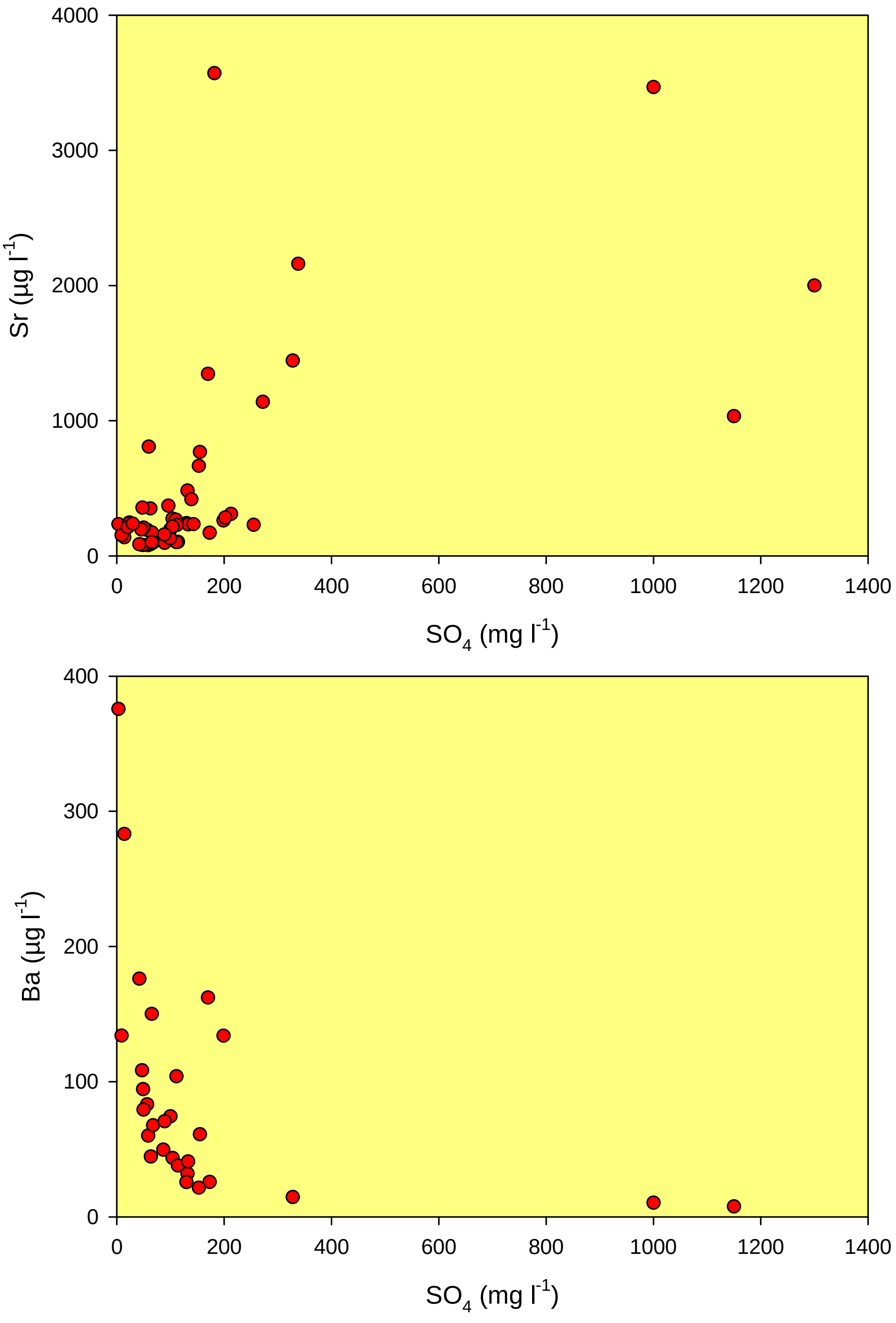


Figure 6.11 Correlations between Sr and Ba with SO_4.

Barium concentrations are limited in groundwater where concentrations of sulphate are high due to saturation with the mineral barite ($BaSO_4$). The median Ba concentration of 68 µg l^{-1} in the Liverpool groundwaters is similar to that found for the Manchester area, but considerably lower than the median Ba value of 271 µg l^{-1} for the Cheshire Basin (Griffiths et al., 2002; Griffiths et al. 2003). However, many individual Ba concentrations exceed the EC Guide Level for drinking water of 100 µg l^{-1}. Figure 6.11 shows that there is a negative relationship between Ba and SO_4, as would be anticipated due to the concentration of barium being controlled by the solubility of barite.

Boron concentrations typically vary with salinity. In the study area, the high Cl waters have B/Cl ratios similar to seawater (concentration of B up to 157 µg l^{-1}). Two samples with moderate Cl concentrations had high B concentrations (444 and 448 µg l^{-1}) and high B/Cl ratios which may indicate an anthropogenic source. Lithium is derived both from water-rock interaction and mixing with formation waters. Concentrations of Li are high in the high-SO_4 groundwaters but low in the Cl-rich groundwaters, although in the latter they are still enhanced over modern seawater.

Most groundwaters contain low concentrations of most metal species due to the low mobility at circum-neutral pH. Those metals which are redox-sensitive have been discussed in Section 6.5.2. Other trace elements which are present above detection limit include Zn (up to 2.5 mg l^{-1}), Ni (up to 55 µg l^{-1}) and Al (up to 310 µg l^{-1}), although median concentrations for these are relatively low.

6.5.6 Spatial variations

As observed by Tellam (1996), the older waters, which often occur where the sandstone is covered by Quaternary drift deposits, tend to be saturated with respect to calcite, with low NO_3, SO_4 and Cl concentrations. In areas where the sandstones are not overlain by drift, the groundwaters tend to be characterised by low alkalinity and pH, with high concentrations of NO_3, SO_4 and Cl. Close to outcrop of the sandstone or where the drift deposits are thin, water samples have higher alkalinity and pH and lower anion concentrations. Groundwaters from the Collyhurst Sandstone, which contains a limited amount of calcite, have a tendency to be depleted in HCO_3. Tellam (1996) noted that some sites had high SO_4 and NO_3 concentrations, which he attributed to industrial pollution where close to industrial areas. In rural areas, high SO_4 may be attributable to leakage from the sulphur-bearing tills where water levels have been lowered. Tellam (1996) also noted that saline waters adjacent to the Mersey estuary have a composition equivalent to diluted estuary water. Slightly saline, reduced waters were also found beneath the Mercia Mudstone Group in the north of the area which is consistent with our findings.

Barker (1996) showed, using S isotopes, that the high salinity of groundwaters at the base of the aquifer is derived from dissolution of Triassic evaporites. His study also included S-isotope data from the Liverpool railway tunnels beneath the Mersey estuary, which showed that infiltrating water originated from the estuary above, modified by sulphate reduction. The flow of saline water inland was found to be limited due to the presence of a fault which acted as an impermeable barrier to flow inland (Barker, 1996). Many of the recharge waters studied contained moderate SO_4 concentrations (around 150 mg l^{-1}). The SO_4 was found to be dominated by a fertilizer S-isotope signature and, to a limited degree, by atmospheric inputs.

The ranges in sulphate concentrations and SO_4/Cl ratios show that there are several origins for the sulphate. Spatial variations of sulphate are shown in Figure 6.12a. A number of the samples with high sulphate concentrations are associated with the boundary of the aquifer and the Mercia Mudstone. In general, these waters also have high chloride concentrations (Figure 6.12b), implying both mixing with formation waters and gypsum and/or halite dissolution. High sulphate concentrations were also found close to the coast. These waters contain high chloride, up to 4000 mg l^{-1}, indicating saline intrusion. However, SO_4/Cl ratios are much higher than seawater indicating that these have been modified and therefore may not represent present-day saline intrusion. A number of groundwater samples which are inland, but not associated with the contact with the Mercia Mudstone, also contain high sulphate concentrations. The Cl concentration of these samples is typically lower than those mentioned above. These samples are commonly associated with impermeable drift deposits, which are known to contain gypsum (Magraw and Ramsbottom, 1956; Nicholls, 1880). This implies leakage through the drift which may have been enhanced due to heavy abstraction or possibly to previous climate regimes.

Nitrate concentrations are very variable across the aquifer (Figure 6.12c). High concentrations are often associated with permeable drift, especially in some of the shallower boreholes, or unconfined conditions. High concentrations were also found in areas covered by impermeable drift deposits but these tend to be located along river valleys where drift thicknesses may be less due to erosion and local drift windows.

Iron and manganese concentrations tend to be highest in the deepest parts of the aquifer, particularly where it is confined beneath the Mercia Mudstone (Figure 6.12d and 6.12e). Several trace elements including As, showed a similar regional distribution to Fe and Mn (Figure 6.12f). The distribution of Sr (not shown) closely follows that of Ca reflecting both gypsum dissolution and mixing with formation or seawater (Figure 6.12g). Uranium concentrations may be locally elevated in the more oxidising groundwaters. (Figure 6.12h)

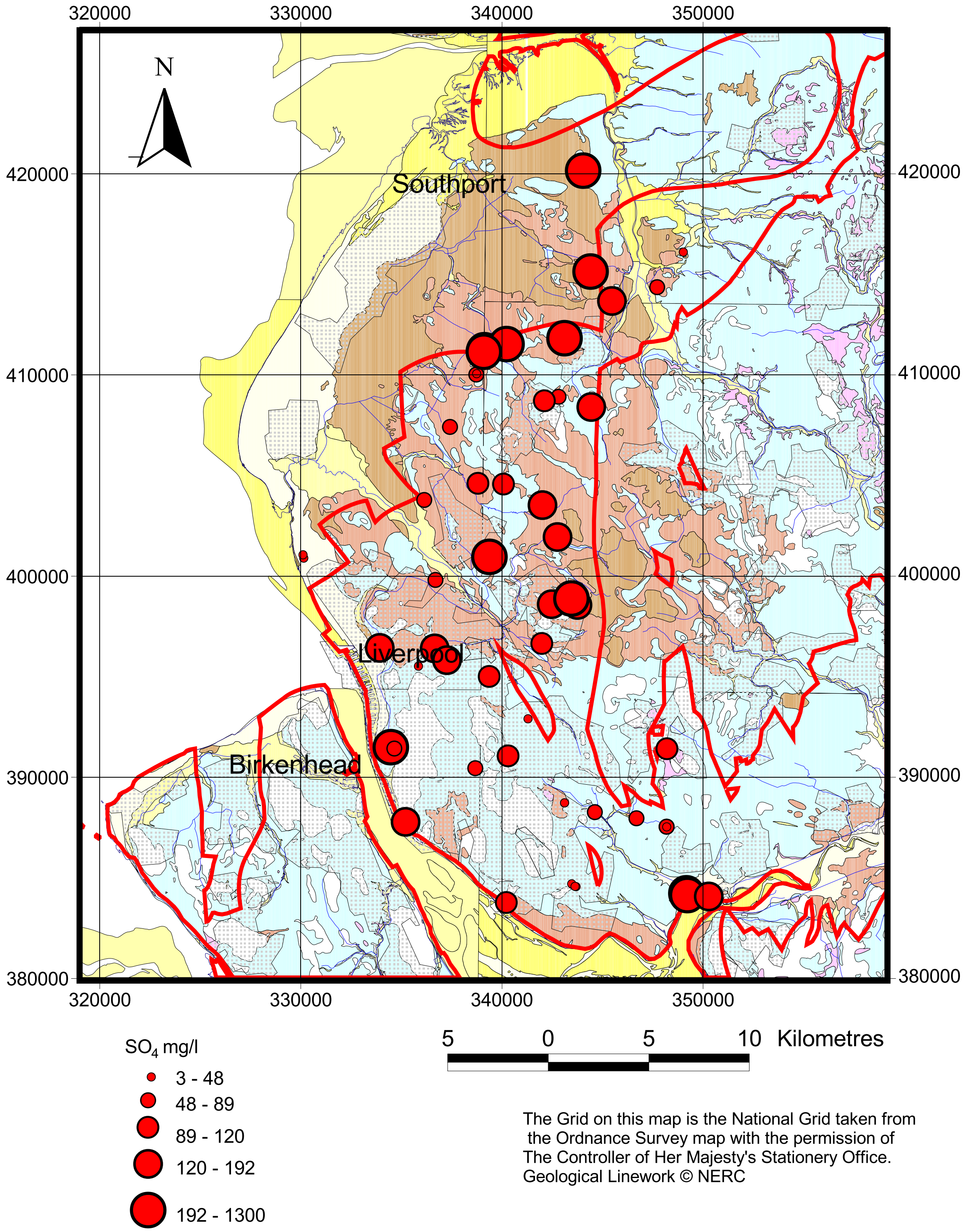


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Figure 6.12a **Spatial variation of SO$_4$ in groundwaters of the study area. The red line indicates the outline of the Sherwood Sandstone outcrop.**

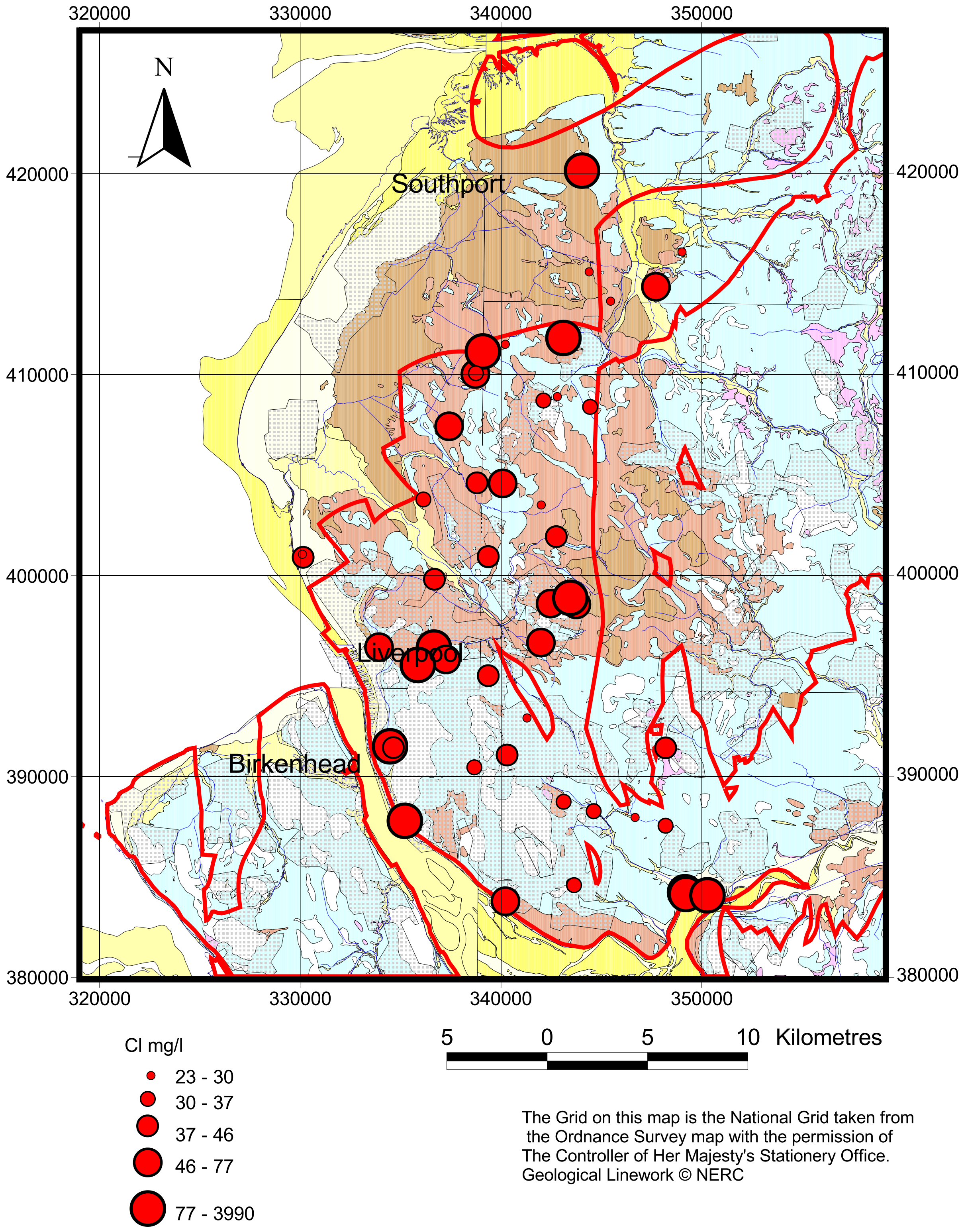

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Figure 6.12b Spatial variation of Cl in groundwaters of the study area.

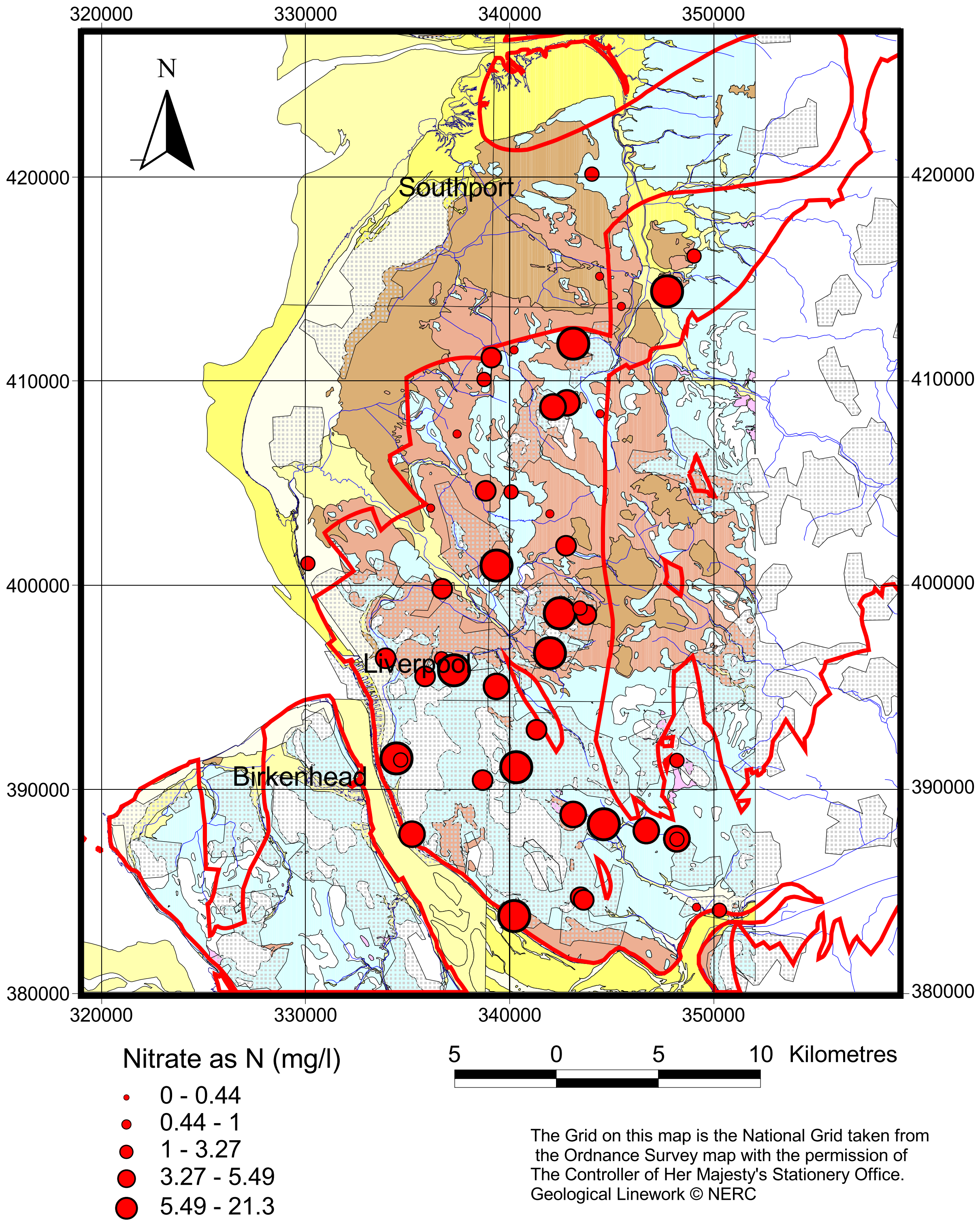

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Figure 6.12c **Spatial variation of NO_3-N in groundwaters of the study area.**

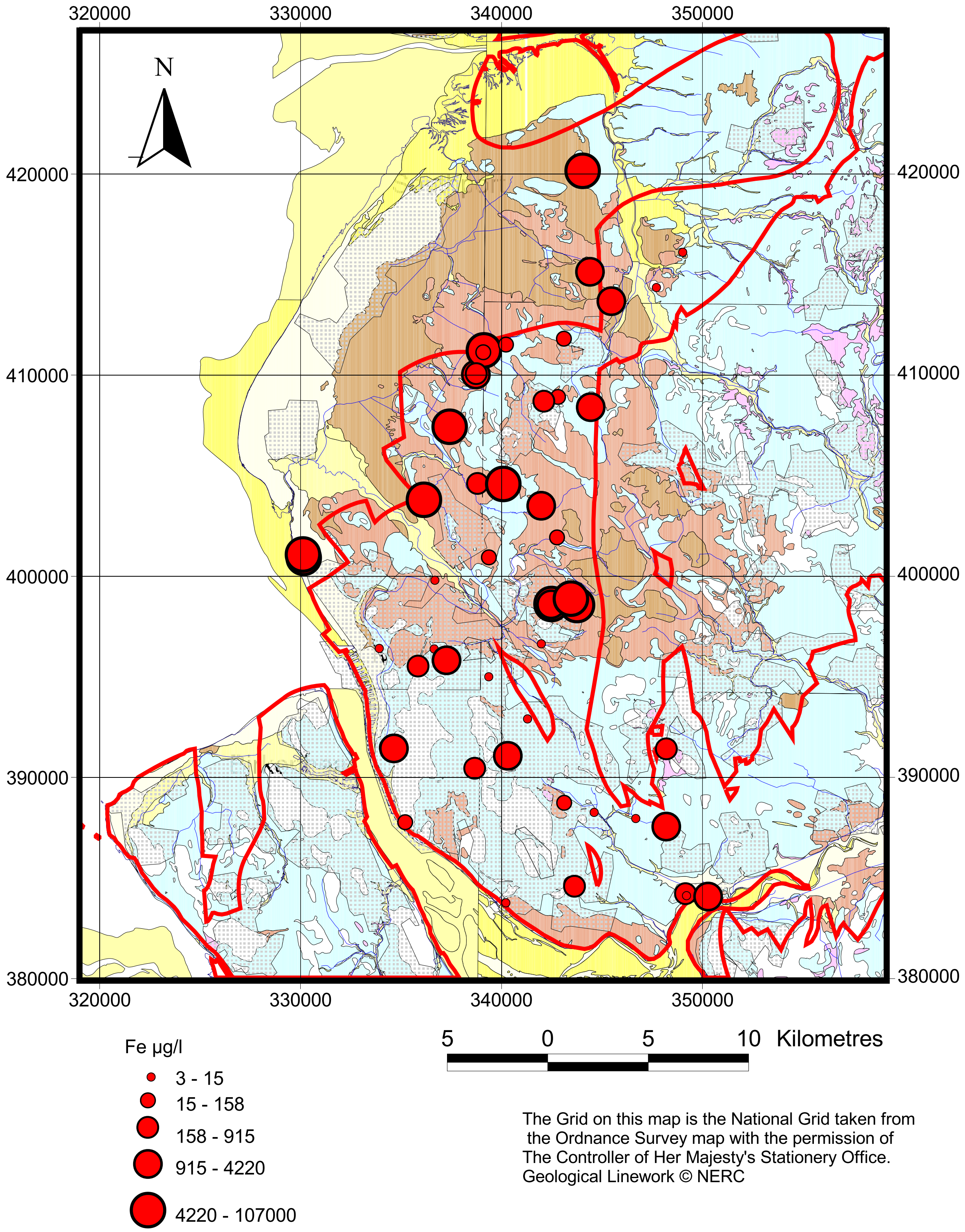

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Figure 6.12d Spatial variation of Fe in groundwaters of the study area.

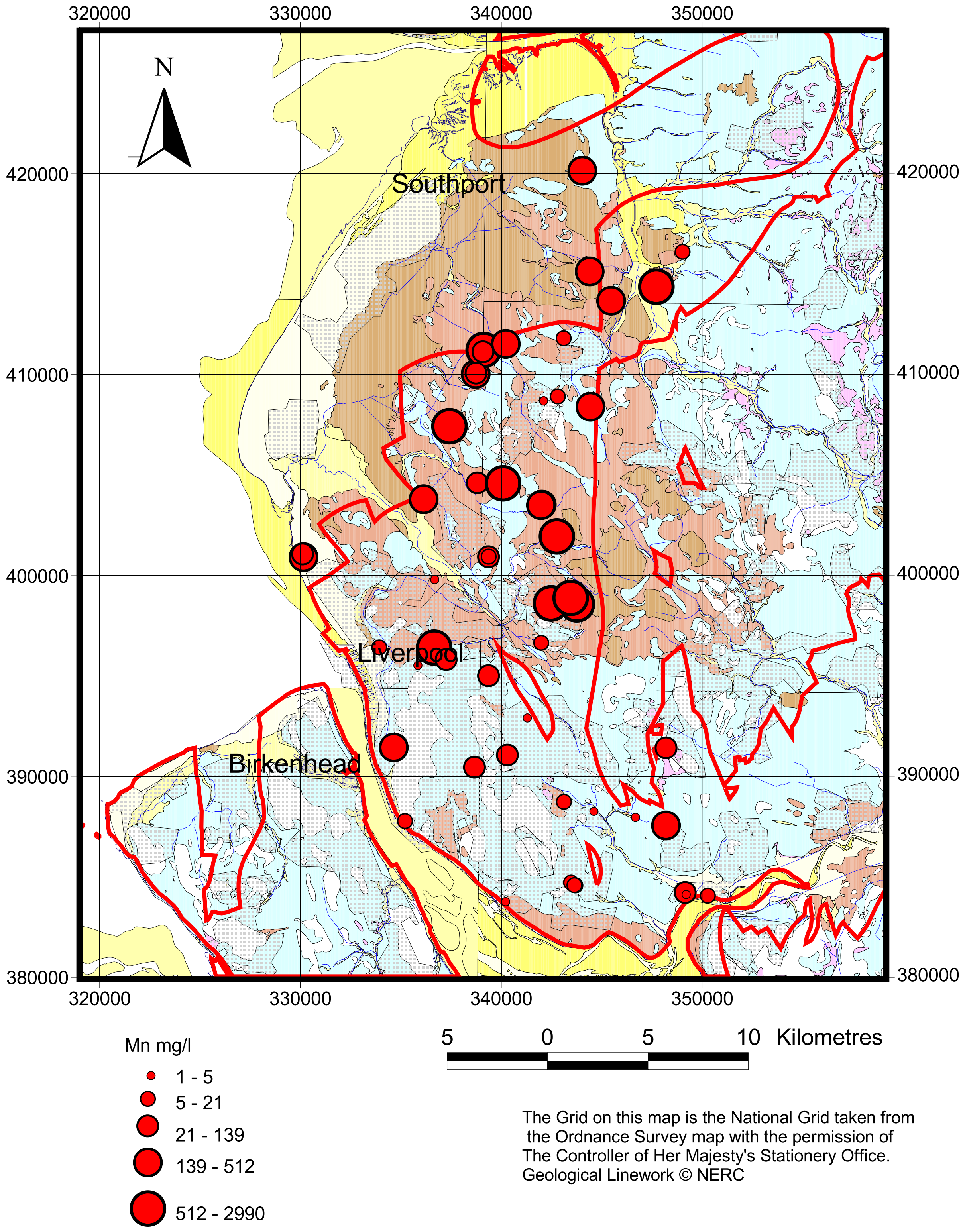

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Figure 6.12e **Spatial variation of Mn in groundwaters of the study area.**

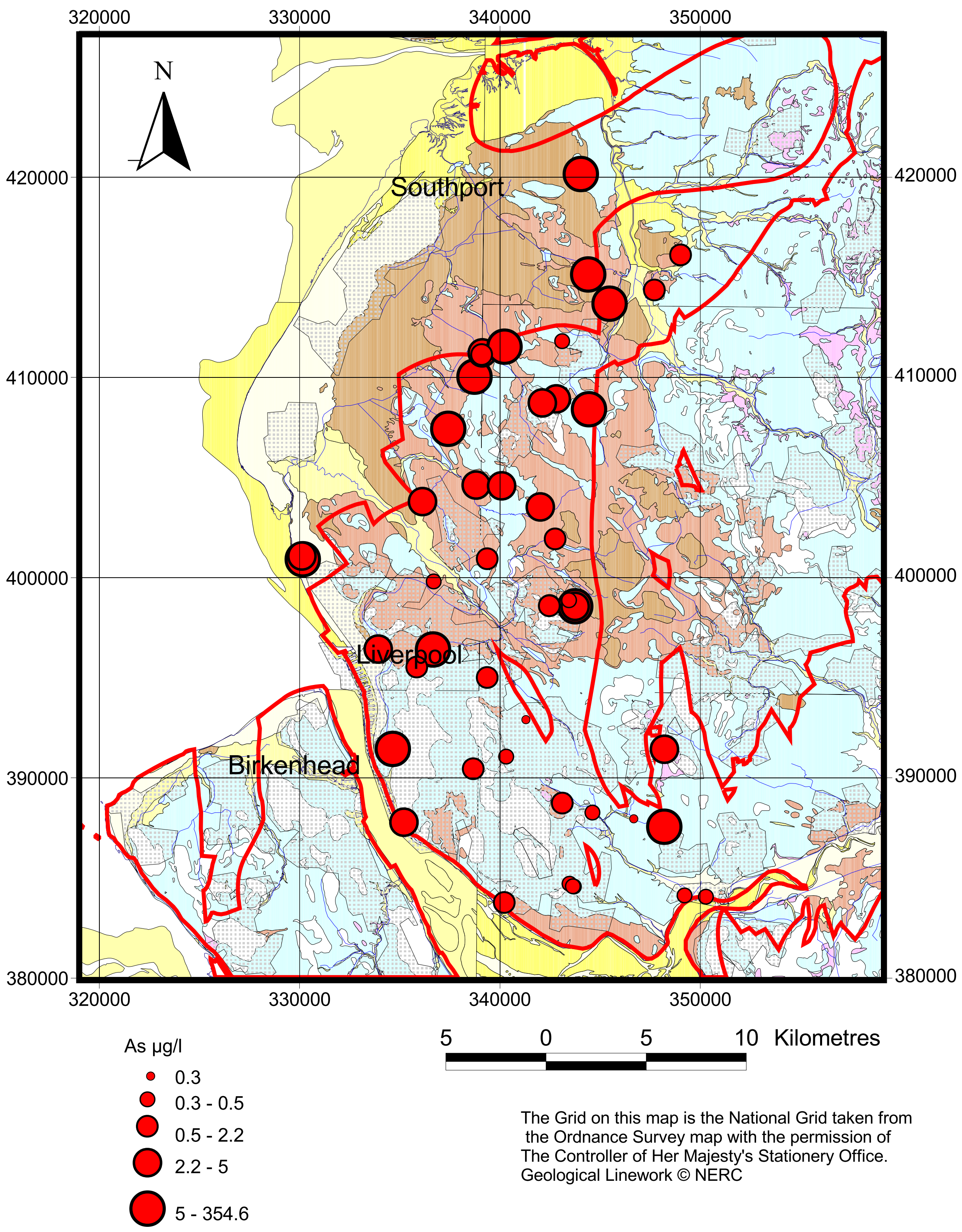

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Figure 6.12f Spatial variation of As in groundwaters of the study area.

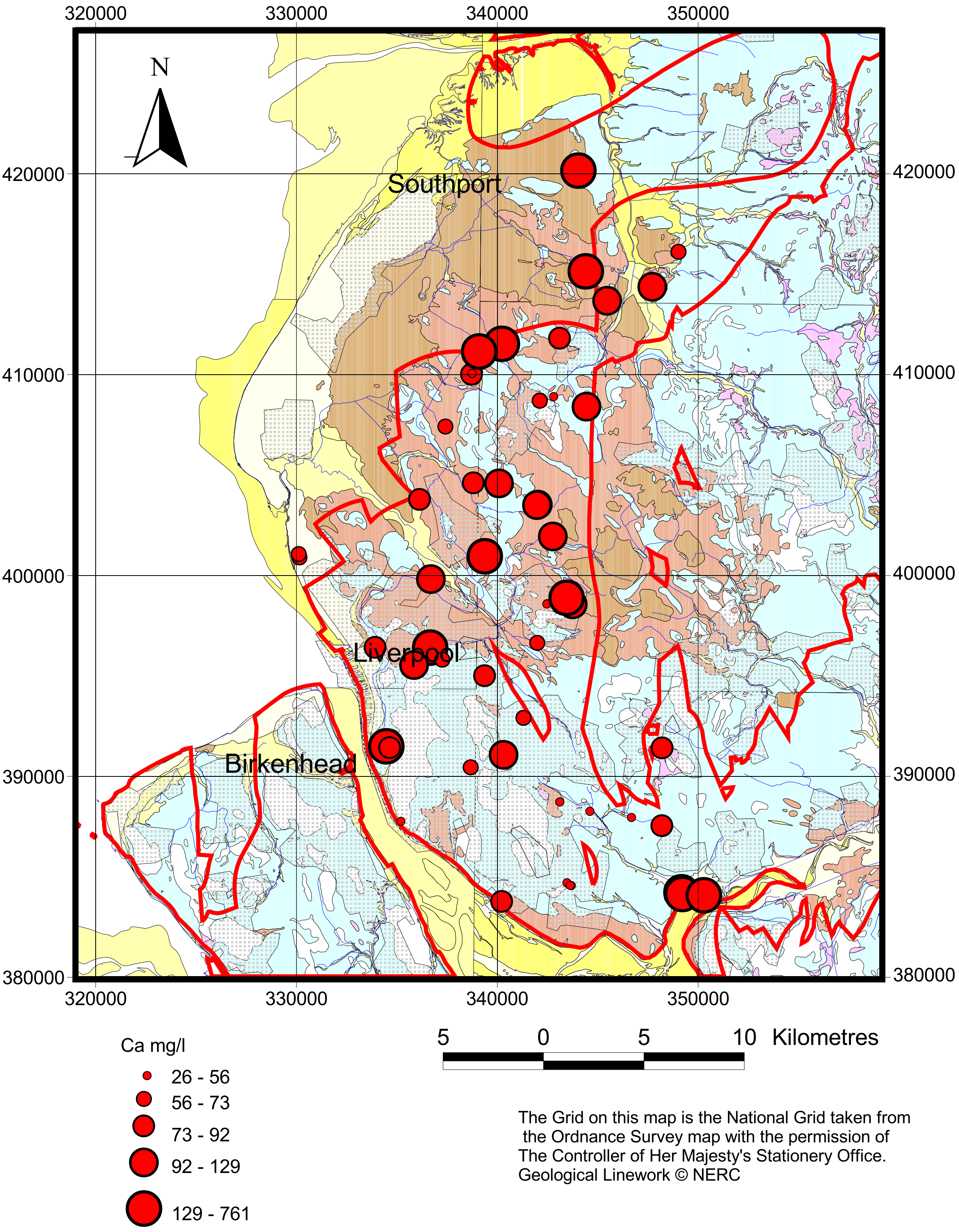

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Figure 6.12g **Spatial variation of Ca in groundwaters of the study area.**

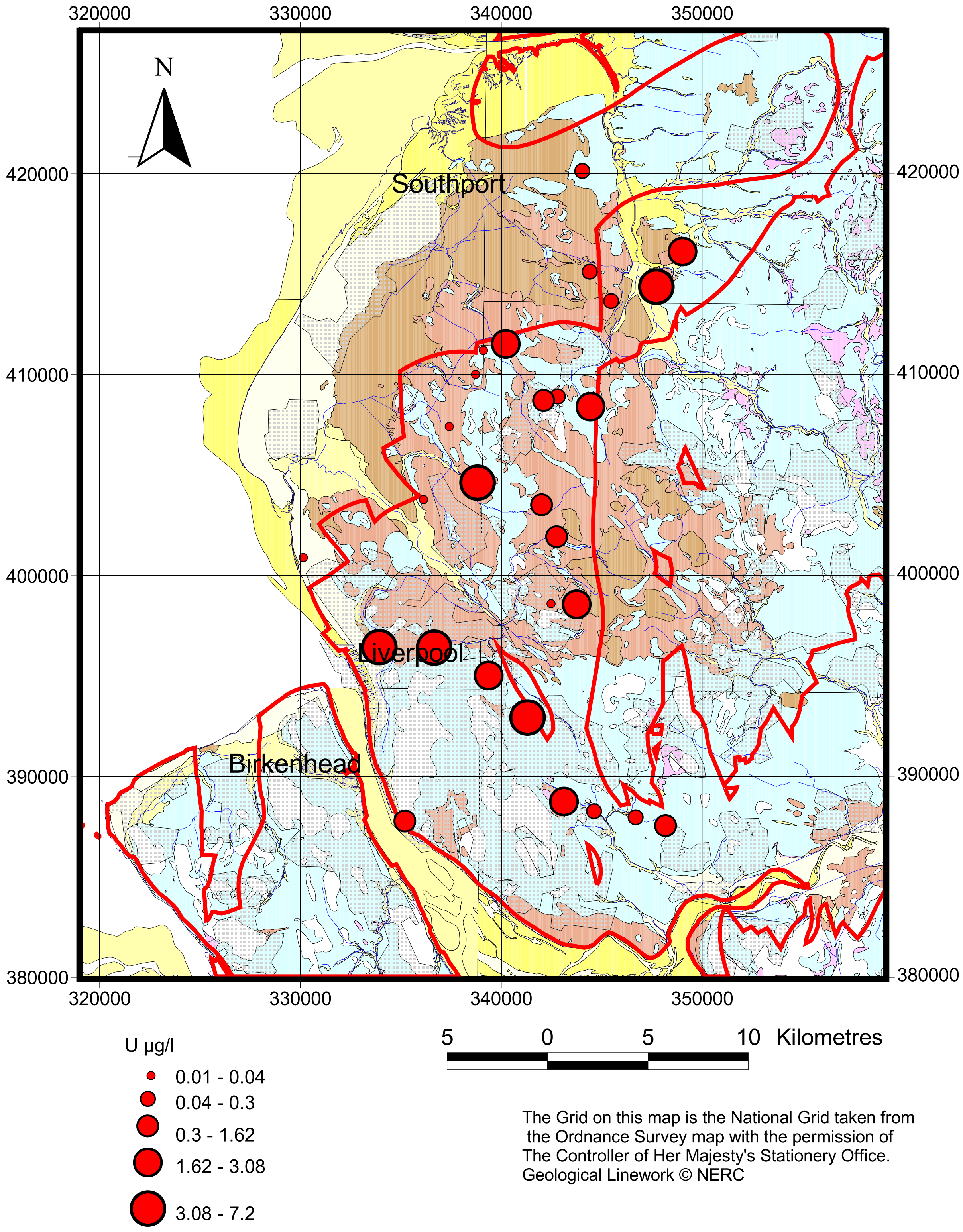

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Figure 6.12h Spatial variation of U in groundwaters of the study area.

7. BASELINE CHEMISTRY OF THE AQUIFER

The baseline groundwater chemistry of any aquifer is determined by a wide range of physical, chemical and biological processes. The primary input to most major aquifers is rainfall, although connate or formation water may be present in parts of an aquifer where groundwater circulation is poor. In addition, leakage from underlying or overlying aquifer units may modify the groundwater chemistry, either locally or regionally. A series of chemical reactions takes 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 aforementioned 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, and are subject to differing residence time in contact with the variable mineral/geochemical assemblages.

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

The baseline chemistry of groundwaters in the Permo-Triassic aquifer of the Liverpool area is extremely variable. The data have been presented in Tables 5.1 and 5.2, which show the ranges, median and an upper limit (97.7 percentile) of baseline compositions. The chemistry of the groundwaters presented in this study is overwhelmingly determined by natural reactions taking place between the groundwater and constituent minerals of the aquifer. A range of geochemical processes has been shown to operate in the aquifer.

The chemistry of the groundwater in the Liverpool area varies according to geology, pollution and pumping regime. Spatial variations are enhanced due to a complex system of recharge and discharge zones and spatially variable chemical inputs. Aquifer mineralogy, and in particular the processes of dolomite and gypsum dissolution, are the dominant controls on groundwater chemistry. Superimposed on this are the effects of drift cover, particularly where water level decline has induced leakage through the Quaternary deposits (Tellam,1996), and pollution arising from a legacy of industrial land use, agriculture and urbanisation. Nitrate and chloride are perhaps the two elements which have been most greatly influenced by these anthropogenic impacts e.g. through agricultural pollution and sewage leakages, and seawater intrusion respectively.

Redox processes and the concentration of redox sensitive elements appear to be influenced by the nature and thickness of drift cover, as would be anticipated. However the absence of detailed information on vertical variations in redox status and the complexity of the drift cover, coupled with water level changes make these variations difficult to interpret. Denitrification occurs where conditions are reducing.

It is very difficult to distinguish the precise contribution of the different processes determining the baseline geochemistry for the study area. Firstly the area is very heterogeneous in terms of its solid and drift geology which obviously influences the mineralogical and geochemical properties of the drift/aquifer and the hydrogeology of the aquifer. Superimposed upon this complex system are the complicating anthropogenic effects of pollution and groundwater abstraction, which in an urban and industrial area such as Liverpool have been occurring over the past two centuries. It is therefore difficult to find groundwater in which the baseline chemistry has not been modified.

8. SUMMARY AND CONCLUSIONS

The Permo-Triassic Sandstone forms the second most important aquifer in the UK. In the Liverpool and Rufford area, it provides groundwater sources for public supply as well as for a large number of industrial users, agriculture and leisure activities. The geology and distribution of drift deposits in the region are complex and this has had a pronounced effect on the baseline chemistry of the aquifer. Solute concentrations in the aquifer typically vary over several orders of magnitude. The chemistry of the groundwaters is overwhelmingly controlled by natural reactions between the groundwater and bedrock. Dissolution of cements, mainly calcite and dolomite, strongly influences the major element composition of most groundwater.

This report presented an overview of the baseline chemistry and the dominant geochemical processes occurring in the Permo-Triassic aquifer of the Liverpool and Rufford areas. This provides information to aid the management of groundwater and provide a basis from which to identify future impacts on the quality of groundwater.

The natural baseline within the aquifer is expressed by a range of concentrations, which can vary over several orders of magnitude for some elements. The concentrations of some elements are enhanced over the natural baseline due to pollution. For example, elevated nitrate and chloride concentrations may indicate modification by agricultural and industrial practices. In parts of the aquifer, arsenic and barium occur at concentrations in excess of European drinking water standards. However, these concentrations are not considered to be due to pollution; they result from water-rock interaction and reflect the mineralogy of the aquifer. In cases where natural water quality exceeds guideline values or standards, it is important that baseline conditions are understood so that water resource managers can take account of these in regional-scale resource planning.

In the Liverpool and Rufford area, water-rock interactions are the dominant influence on groundwater chemistry. The nature and thickness of the drift in the area also has an important influence on the chemistry, particularly with respect to redox-sensitive parameters. Ion-exchange reactions, redox processes, seawater intrusion and mixing with older formation water also have an impact on the chemistry of the groundwater in the study area. Superimposed upon these processes are the anthropogenic effects of pollution and groundwater abstraction which give rise to a complex hydrogeology and hydrogeochemistry of this area.

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ACKNOWLEDGEMENTS

This work would not have been possible without the support of the farming and industrial community who allowed access to sample their boreholes. In particular we would like to thank Phil Merrin and the operations team at United Utilities plc for allowing us access to their sites. We would like to thank Louise Ander for her invaluable assistance with field sampling. The chemical analyses were completed by Debbie Allen, Sarah Trickett and Daniel Lapworth under the supervision of Marianne Stuart and Chris Milne. George Darling (BGS) and Jane Sanderson (EA) are also thanked for stable isotope and N-species analyses respectively. We would like to thank Paul Lappage from the BGS Drawing Office for his efforts digitising Figure 3.3 from the geological map and Ed Hough for the geological cross sections. We are also grateful to Mark Antrobus of SPSS for his development work on PIPER diagrams in Sigmaplot. Finally we are very grateful to Adrian Lawrence (BGS) and the EA project board for reviewing this report.