Baseline Report Series:

8. The Permo-Triassic Sandstones of Manchester and East Cheshire

Groundwater Systems and Water Quality
Commissioned Report CR/03/265N

Science Group: Air, Land & Water
Technical Report NC/99/74/8

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

BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/03/265N

ENVIRONMENT AGENCY
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8. The Permo-Triassic Sandstones of Manchester and East Cheshire

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

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Sherwood Sandstone (Wilmslow Formation) outcrop, Alderley Edge.

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Contents

List of Figures

List of Tables

FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

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

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

The BASELINE objectives are:

1. to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound geochemical principles, as a basis for defining water quality status and standards in England

and Wales (in the context of UK and Europe); also to assess anomalies due to geological conditions and to formulate a quantitative basis for the definition of groundwater pollution.

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

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

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

1. EXECUTIVE SUMMARY

The Permo-Triassic Sandstone forms the second most important aquifer in the UK. In the Manchester and East Cheshire 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. The chemistry of the groundwaters is overwhelmingly controlled by natural reactions between the groundwater and bedrock. Dissolution of cements, mainly carbonate and dolomite strongly influence the major element composition of most groundwater, and solute concentrations vary over several orders of magnitude. It is likely that parts of the shallow system have been decalcified as indicated by low alkalinity and pH in some groundwaters. The redox status is also variable and the presence of thick impermeable drift over much of the aquifer has allowed reducing conditions to exist even at shallow depth. Although this has given rise to high dissolved Fe, nitrate concentrations are very low due to denitrification. Upconing of deeper saline groundwater is a problem in parts of the aquifer and this is considered to be due to over-abstraction. The origin of the high salinity, giving rise to Na-Cl type waters, is thought to be from dissolution of halite (NaCl), probably derived from the overlying Triassic Mercia Mudstone Group which contains thick halite deposits. The baseline has been modified by anthropogenic influences. Nitrate concentrations are locally high, where the aquifer is oxidising, but a significant degree of protection is afforded by thick impermeable drift over much of the area. Although the aquifer is likely to have been impacted by other anthropogenically derived solutes (K, Na, Cl, SO_4), these are within the natural range of concentrations found within the aquifer. The large spatial variations in hydrochemistry caused by the complex geology (especially the drift type and thickness) makes prediction of local baselines difficult.

2. PERSPECTIVE

This study focuses on the Permo-Triassic Sandstone aquifer of Manchester and East Cheshire, situated on the north eastern edge of the Cheshire Basin. The main aquifer outcrop extends from Macclesfield in the south to Prestwich in the north and incorporates Stockport and most of Greater Manchester (Figure 2.1). The eastern and northern boundaries of the study area are formed by the Carboniferous Coal Measures Group. The southern and western boundaries of the study area are flanked by the Mercia Mudstone Group. 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 Permo-Triassic Sandstones form the second most important aquifer in the UK, supplying approximately 25% of licensed groundwater abstractions in England and Wales (Monkhouse and Richards, 1982). In the Manchester and East Cheshire 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. Total licensed abstractions from the Permo-Triassic Sandstone within the study area are of the order of 26 000 Ml a^{-1}. The aquifer also provides an essential source of baseflow to maintain river flow.

In this area the Permo-Triassic aquifer system includes the Lower Permian Collyhurst Sandstone Formation and the Triassic Sherwood Sandstone Group. The sandstones are separated by the Manchester Marl Formation. Drift deposits cover much of the area of interest, and where the deposits are clayey in nature they limit recharge to the aquifer and hydraulic contact between the rivers and the aquifer, helping to protect the groundwater from surface pollution.

The drainage network of the study area is shown in Figure 2.1. Most of the rivers rise on the high ground to the north and east of the study area and have gained significant flows by the time they reach the study area. All rivers in the area are tributaries of the River Mersey, however the River Bollin and its tributaries (River Dean and Mobberley Brook) do not enter the Mersey until downstream of the study area. The Manchester Ship Canal traverses the region and receives flows from the Rivers Irwell, Medlock, Irk and Mersey. There are also a number of other small canals within the study area. River flows are artificially influenced by reservoirs and sewage work discharges. Much of Manchester's drinking water comes from the Lake District and therefore sewage discharges represent an additional input to the catchment. (ESI, 2001).

Mean annual rainfall varies across the region from c. 750 mm to 1200 mm with the highest values occurring towards the east of the study area on the fringes of the Pennines and north of the Cheshire Plain.

The study area includes Greater Manchester, which is predominantly urban with a legacy of industrial activity (Figure 2.2). Historical industrial land use has resulted in diffuse and point source pollution and contaminated land is an important issue. Increasing demand for land in the city of Manchester has resulted in extensive redevelopment of brownfield sites particularly along the Manchester Ship Canal with Trafford Park [NGR SJ 78 96], Salford [NGR SJ 80 98] and Castlefields [NGR SJ 833 978] having undergone considerable regeneration. Excluding the urban centres of Stockport, Wilmslow, Alderley Edge and Macclesfield the southern part of the study area is more rural with dairy farming dominating the land use. In the south of the study area a number of source protection zones (SPZs) have been defined for the public water supply sources. SPZs have also been defined for some of the larger abstractions in Manchester used by breweries. In the north, along the Irwell Valley there are a number of old landfill sites close to the fault which forms the boundary between the Permo-Triassic and Carboniferous strata.

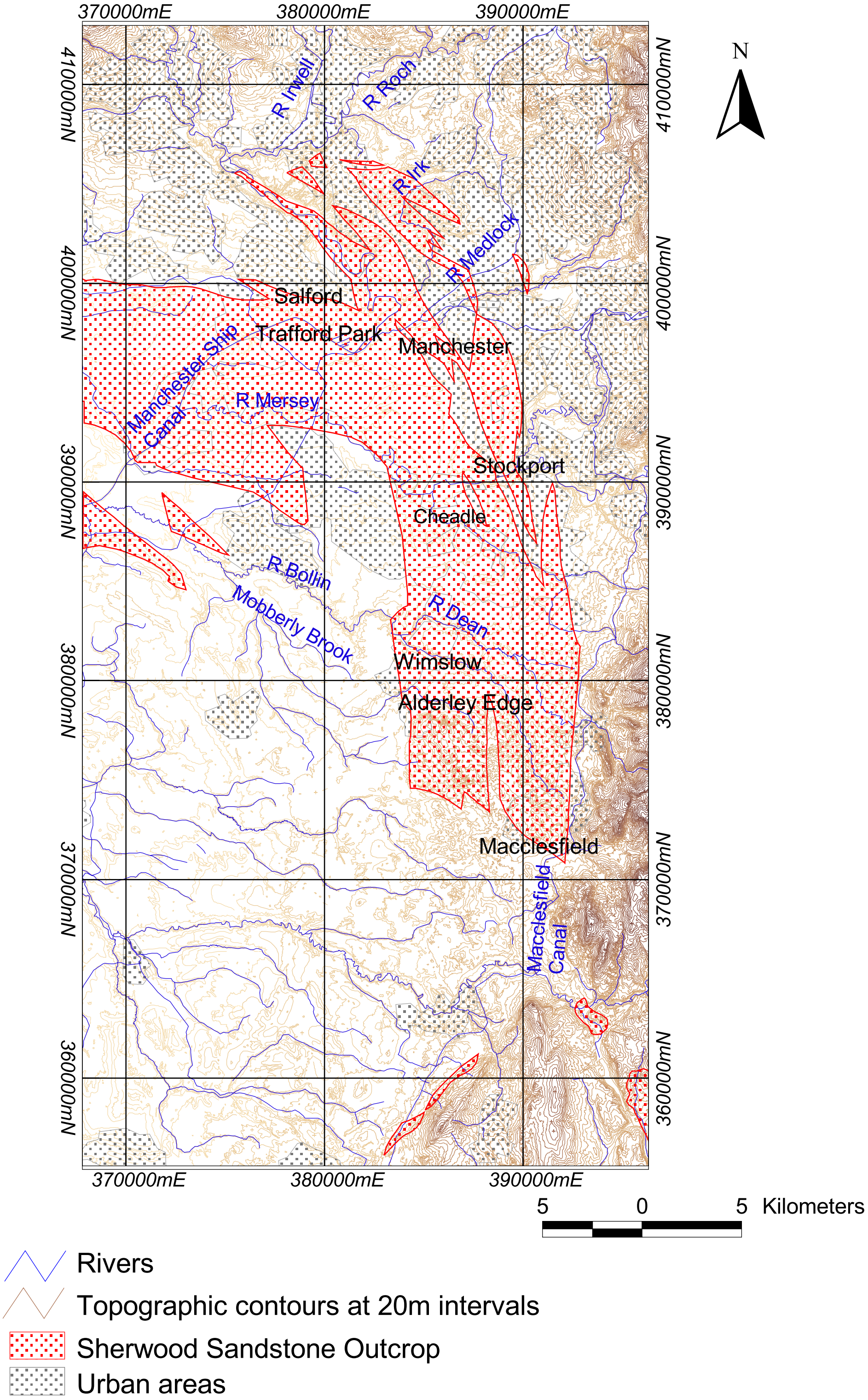

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Figure 2.1 Topographic and drainage map of the Manchester and East Cheshire Study area. Red lines indicate the outline of the Permo-Triassic Sandstone outcrop.

Figure 2.2. **Industrial land use is widespread throughout the study area. The photograph was taken in the north of the study area [NGR SD 849 029] at a site where groundwater is abstracted for cooling in the manufacturing process.**

Historic over-abstraction in some parts of the aquifer, notably in Trafford Park, resulted in falling groundwater levels and the localised upflow of saline water. However, recent changes in patterns of abstraction have resulted in the recovery of water levels in some parts of the aquifer, including Trafford Park. Despite this there remains a level of uncertainty as to the sustainable level of abstraction in the aquifer and as a result a water resources study of the aquifer is currently being carried out for the Environment Agency (ESI, 2003).

Other issues in the area include elevated arsenic concentrations in the groundwater in parts of the aquifer and the problems caused by the abandonment of coal mines to the north of the area, which potentially may affect the groundwater quality within adjacent parts of the aquifer.

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. Data are used to estimate relative groundwater ages and temporal variations are described.

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 to explain the characteristic groundwater chemistry; and finally the initial input to the system, principally rainfall chemistry, to define the source term.

3.2 Geology

The development of the Cheshire Basin was initiated at the end of the Variscan (late Carboniferous) period as a result of faulting and uplift. Faulting during the Permo-Triassic, while sediments were being deposited, allowed the rapid accumulation of a thick sedimentary sequence. The lower part of the basin is filled by an arenaceous (sandy) red-bed sequence which includes the Permian Manchester Marl and Collyhurst Sandstone Formation and the Triassic Sherwood Sandstone Group (SSG). These sediments were deposited under fluvial and aeolian environments. The Sherwood Sandstone Group is overlain by the Merica Mudstone Group which comprises an argillaceous red-bed sequence. The Permo-Triassic sediments rest unconformably on Carboniferous rocks (Plant et al, 1999). Figure 3.1 illustrates the solid geology of the study area and Figures 3.2 and 3.3 are geological cross-sections running N-S and E-W to illustrate the complexity of the geological sequence in the area.

The Permo-Triassic stratigraphy for the area is given in Table 3.1. The Collyhurst Sandstone Formation outcrops along the north and east margins of the aquifer. In the vicinity of Stockport it is of the order of 280 m thick. However, in the west of the area, around Eccles, it is locally absent.

The Manchester Marl Formation overlies the Collyhurst Formation and varies from 40 to 75 m thick in the Manchester area up to 100 m near Stockport. The overlying Chester Pebble Beds are estimated to be in excess of 240 m thick in the Manchester area (Taylor et al., 1963).

The most extensive subcrop component of the Manchester and East Cheshire aquifer is the Wilmslow Sandstone Formation (Figure 3.4), which is estimated to be c. 280 metres thick in the Manchester area.

The overlying Helsby Sandstone Formation was observed to have a thickness of 205 m in the Knutsford borehole [NGR SJ 703 778] but in the area of study it is more likely to be of the order of 100 to 120 metres thick. It forms the outcrop area of the aquifer along the western boundary of the study area where it is faulted against the Mercia Mudstone Group. The Helsby Sandstone Formation is more competent than the Wilmslow Sandstones and Tarporley Siltstones and consequently forms areas of higher relief including Alderley Edge where it may be seen at outcrop (Figure 3.5 and 3.6).

The Tarporley Siltstone Formation ranges from 280 m thick beneath Altrincham to approximately 100 m thick towards the edges of the basin. The Bollin Mudstone Member exceeds 500 m thickness in the centre of the Cheshire Basin but is likely to be of the order of 200 metres thick in the vicinity of Manchester airport. The Bollin Mudstone is overlain by the Northwich Halite.

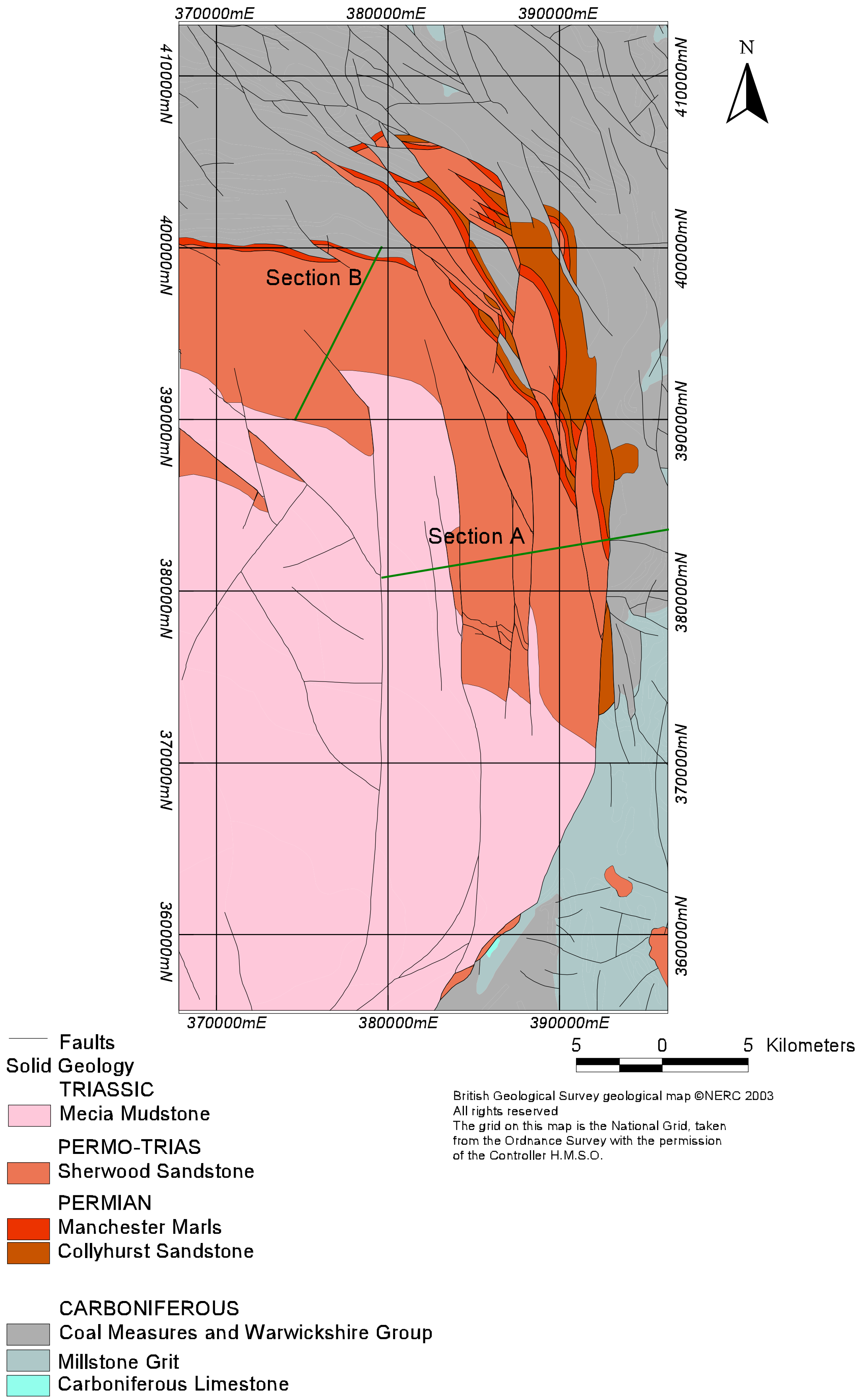

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Figure 3.1 **Geological map of the Manchester and East Cheshire study area. The position of lines of section A and B (Figures 3.2 and 3.3) are marked.**

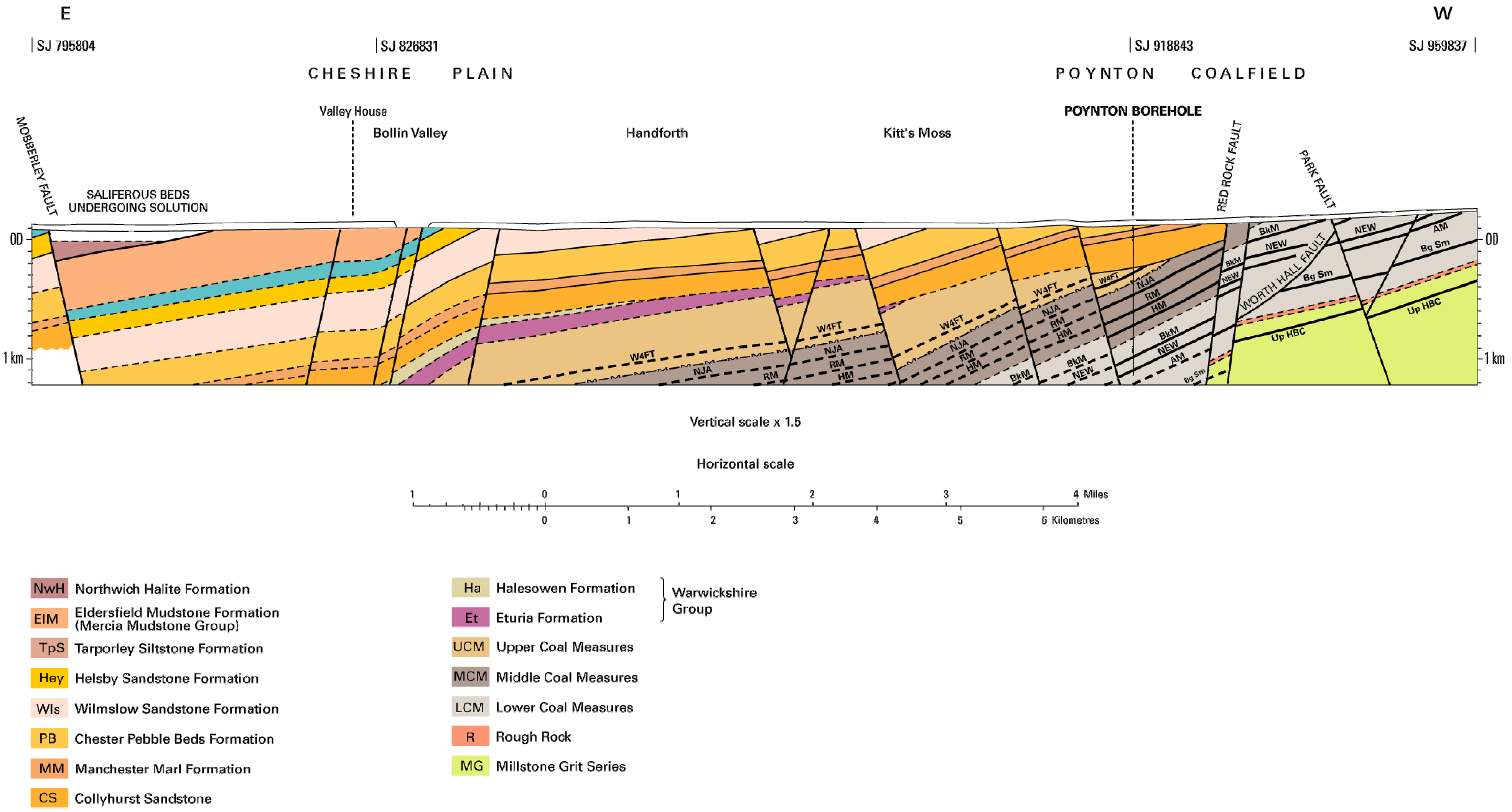
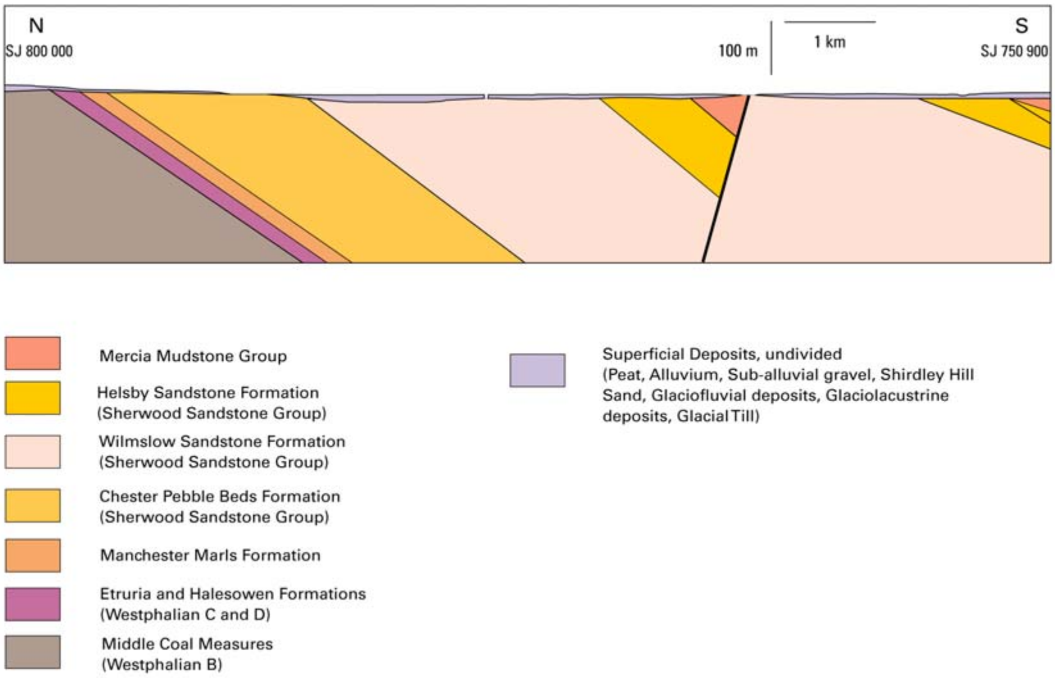
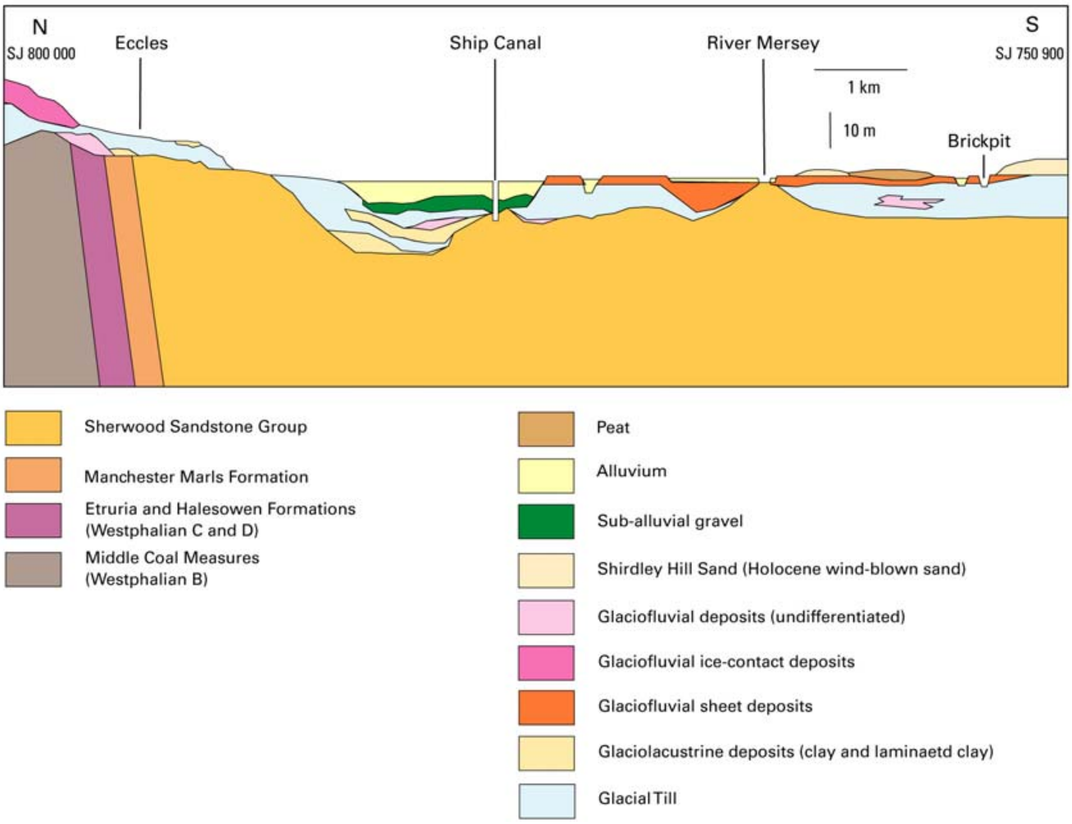


Figure 3.2 Section A: west-east geological cross-section from NGR SJ 795 804 to NGR SJ 959 837 illustrating structural complexity of the sandstone aquifer (after British Geological Survey 1:50 000 Geological Map 98 (Solid) Stockport).



(a)



(b)

Figure 3.3 **Section B: geological cross sections (north-south) through the study area for (a) solid geology and (b) drift (vertical scale is exaggerated to show the complexity of the drift sequence). Line of section shown on Figure 3.1**

Table 3.1 Permo-Triassic stratigraphy of Cheshire and south Lancashire (after University of Birmingham 1981 and 1984)

System and Lithostratigraphical Division		Previous Division	Aquifer Unit	Thickness Lower Mersey Basin (m)	Thickness North Mersey-side (m)
TRIASSIC Mercia Mudstone Group	Bollin Mudstone Formation	Lower Keuper Marl	Aquitard	405	200
	Tarporley Siltstone Formation	Keuper Waterstones	Mainly Aquitard	30-60	45-75
TRIASSIC Sherwood Sandstone Group	Ormskirk / Helsby Sandstone Formation	Lower Keuper sandstones	Aquifer	>181-295	100-120
	Wilmslow Sandstone Formation	Upper Mottled Sandstone		>205-480	280
	Chester Pebble Beds Formation	Bunter Pebble Beds		>316-375	145-420
	Kinnerton Sandstone Formation	Lower Mottled Sandstone (upper unit)	Aquifer	0->80	10-80
PERMIAN	Manchester Marl Formation/ *Bold Formation*	Manchester Marls	mainly aquitard/ *aquifer*	10-225	0-40/ *10-50*
	Collyhurst Sandstone Formation	Lower Mottled Sandstone (lower unit)	Aquifer	283-720	0-300

Figure 3.4 Fractured Wilmslow Sandstone outcrop at Alderley Edge [NGR SJ 8640 7808].

Figure 3.5 View to the north east from Alderley Edge [NGR SJ 8608 7766] where the Sherwood Sandstone crops out.

Figure 3.6 Conglomerate within the Helsby Sandstone at Alderley Edge.

The area of study is extensively covered by drift deposits which attain thicknesses of more than 70 m in places. The drift deposits comprise glacial deposits of varied nature overlain by river terrace deposits, alluvium and peat. It is thought that the drift deposits may represent as many as five glaciations (Pitman, 1981). Boulder Clay crops out over most of the area to the east of Salford and the area south of Cheadle and Stockport. Glacial sands and gravels crop out along the edges of the Mersey Valley, east of Cheadle and to the north of Macclesfield. River terrace gravels and alluvium occur along the river valleys (Figure 3.3b and 3.7). Around Chat Moss [NGR SJ 700 960] there is an area of lowland peat. There is a zone of thick drift deposits in the Trafford Park area infilling a feature named the Didsbury Depression which is thought to relate to the Worsley fault extension. It is believed that the Worsley Fault was preferentially eroded during glaciation and subsequently infilled with glacial deposits (Grayson, 1972).

The eastern boundary of the aquifer is formed by the Red Rock Fault (Figure 3.2) which is actually a fault zone rather than a single discontinuity. The dominant directional trend for faults across the area of study is north-south, veering towards north west-south east in the Manchester area. Faulting in the area is thought to have a considerable impact on the hydrogeology. Pitman (1981) found that faulting had altered the dip of the Sherwood Sandstone and had brought the Sherwood Sandstone into hydraulic contact with the Collyhurst Sandstone.

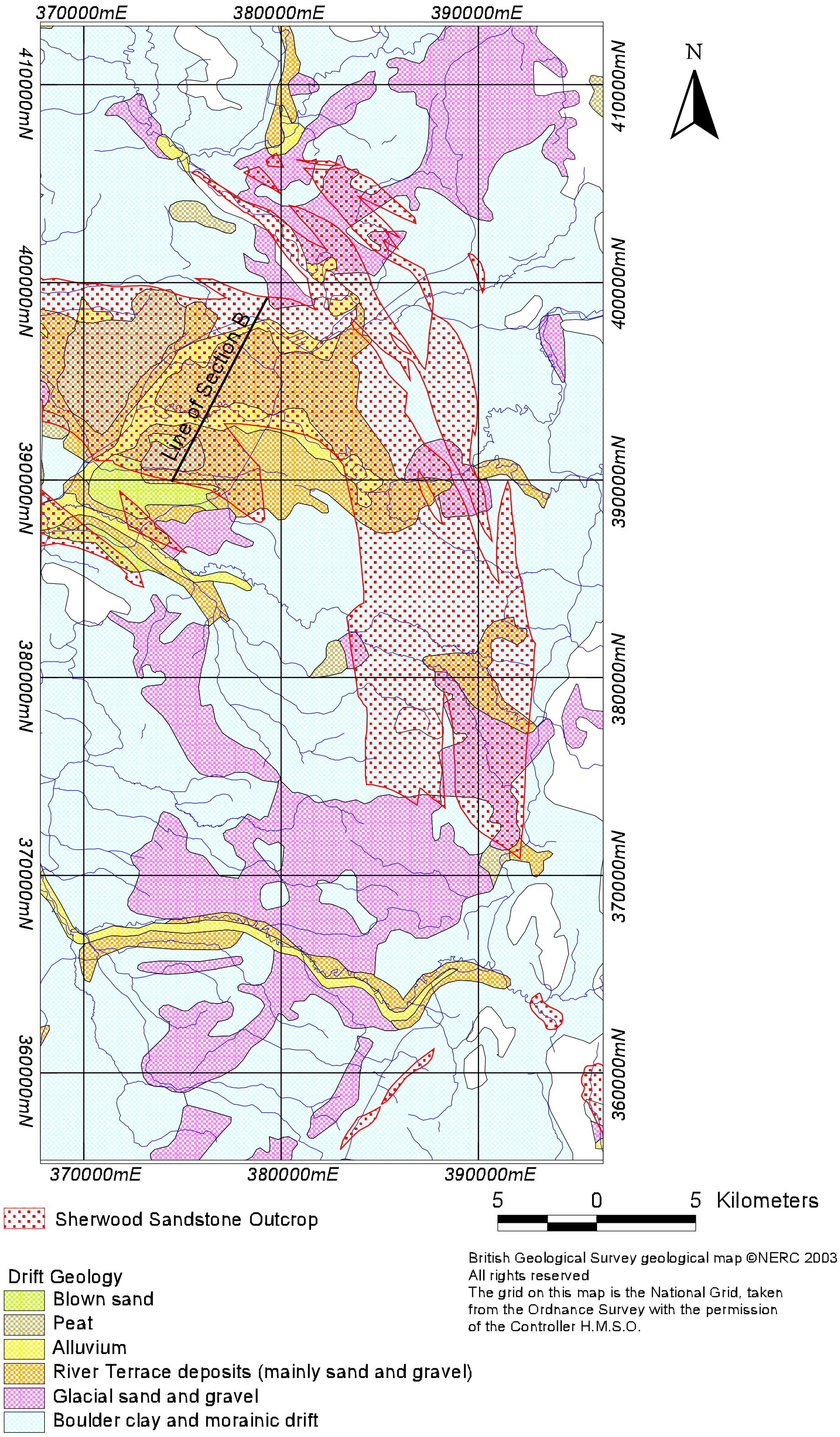


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Figure 3.7 **Drift geology of the Manchester and East Cheshire Study area. Red line and shading indicate the Permo-Triassic Sandstone aquifer outcrop area.**

3.3 Hydrogeology

The Manchester and East Cheshire aquifer comprises sandstones of the Sherwood Sandstone Group (i.e. the Helsby, Wilmslow and Chester Pebble Bed Formations), which are all in hydraulic continuity. The Collyhurst Sandstone also forms a significant aquifer in the study area, where it is present. It is separated from the Sherwood Sandstone Group by the Manchester Marl Formation which is considered to act as an aquiclude. Together the Sherwood Sandstone Group and Collyhurst Sandstone comprise the sandstone aquifer in this study.

Pitman (1981) divided the aquifer into units, separated by less permeable rocks i.e. the Manchester Marl and Carboniferous. These units have been used by later studies (Stansbury, 1994) and Gunnemyr, 1998) as the basis for modelling studies and chemical characterisation.

Coarse-grained horizons within the Chester Pebble Beds are often strongly cemented with carbonate cements. Their relatively high strength often gives rise to widespread jointing with open fractures. In contrast, the Wilmslow Formation is poorly cemented and soft which often causes fractures within it to be closed or in-filled with sediment.

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 Helsby Formation. Perched water levels often occur above the mudstone bands.

Water bearing units may also occur within the Tarporley Siltstones and grit layers within the Carboniferous Coal Measures. These may have some impact on the water resources of the main Sherwood Sandstone aquifer.

Sands and gravels within the drift deposits also form locally important aquifers and in places may be in hydraulic continuity with the underlying sandstone aquifer.

At outcrop the Collyhurst Sandstone Formation is considered to be a good aquifer - yields from large-diameter boreholes are of the order of 20 – 30 litres per second ($l\ s^{-1}$). Values of hydraulic conductivity and porosity for the different formations of the Permo-Triassic Sandstone aquifer of the Manchester area are given in Table 3.2. The Kinnerton Sandstone Formation does not crop out within the area of study but where it does, its properties are similar to those of the Collyhurst Sandstone. Values of hydraulic conductivity within the Tarporley Siltstone Formation are generally low, however faulting can create hydraulic continuity with the Helsby Sandstone.

Pitman (1981) analysed 35 pumping tests which yielded only 3 values for storage co-efficient which were 0.02, 0.004 and 0.0009. Pumping tests indicate that the sandstone aquifer is confined or leaky for the most part because of the thick Boulder Clay cover over much of its outcrop area.

Table 3.2 **Hydraulic conductivity and porosity values for the different formations of the Permo-Triassic Sandstone aquifer of the Manchester area (after Allen et al. 1997).**

Formation	Hydraulic conductivity (m d^{-1})	Porosity at outcrop (%)
Collyhurst Sandstone	> 1	20 – 24
Chester Pebble Beds	0.5 - 5	20 - 30
Wilmslow Sandstone	0.006 - 6	13 - 30
Helsby Sandstone	> 10	25 – 30

'Potential recharge' in the Manchester area was estimated by Pitman (1981) to be between 366 and 513 millimetres per annum (mm a^{-1}). However, these figures do not take into account the effect that the drift sequence overlying the sandstone aquifers in the area of study will have on recharge. The drift cover is predominantly Boulder Clay or sand and gravel underlain by Boulder Clay, which is likely to significantly reduce the amount of recharge to the sandstone aquifer. Recharge through the drift occurs predominantly via interconnected sand lenses and fractures. A number of values of recharge through the drift have been proposed. The Mersey and Weaver River Authority (1969) suggest average recharge rates of 100 mm a^{-1} in the Manchester area and 127 mm a^{-1} in the Wilmslow area. Vines (1984) suggested a figure of 53 mm a^{-1} for recharge through the boulder clay. In the SPZ model for Woodford [NGR SJ 884 823] the best calibration was provided using values of 350 mm a^{-1} for outcrop, 200 mm a^{-1} for permeable drift and 70 mm a^{-1} for Boulder Clay. Leakage from pipelines, sewers and soakaways may also contribute to recharge to the aquifer because the area of study is extensively urbanised. This additional urban recharge has not been quantified.

The reduction in recharge caused by the Boulder Clay is reflected in the hydrochemistry, which is indicative of low levels of flushing throughout most of the aquifer, and groundwater level fluctuations, which show limited response to precipitation.

The groundwater contours (Figure 3.8) show a fairly steep gradient from south to north in the eastern part of the study area which flattens out considerably to the north of the River Mersey. Groundwater flows from topographically high areas in the north, south and east towards the north west of the study area towards the River Mersey. There is a notable cone of depression created by abstraction in the Trafford Park area. There is likely to be a significant degree of surface water –groundwater interaction taking place on the basis of groundwater level/ river elevation information.

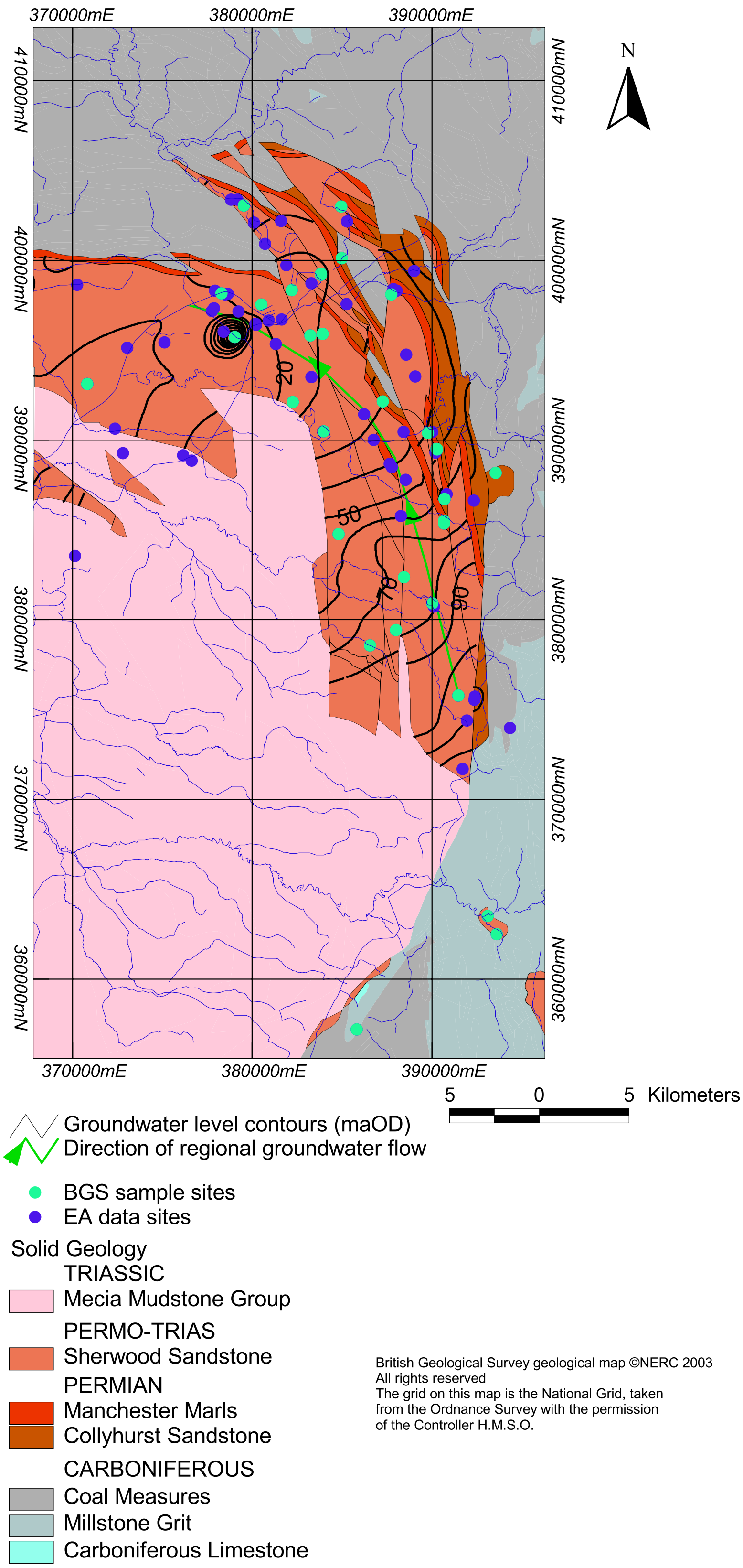

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Figure 3.8 **Groundwater flow contours and direction of regional groundwater flow (based on groundwater contours produced by ESI, 2001)**

3.4 Aquifer mineralogy

Although the Sherwood Sandstone is dominated by quartz and feldspar, it contains a wide variety of cements including calcite, dolomite, gypsum, anhydrite, halite, iron oxide and clay minerals (Figure 3.9). In particular, the carbonate and evaporite minerals may exert the dominant control on groundwater quality because these dissolve much more rapidly than the quartz and silicate mineral phases and (for the evaporite minerals) may be highly soluble. The clay mineralogy is generally dominated by kaolinite, and in deeper parts of the aquifer, illite (Plant et al., 1999).

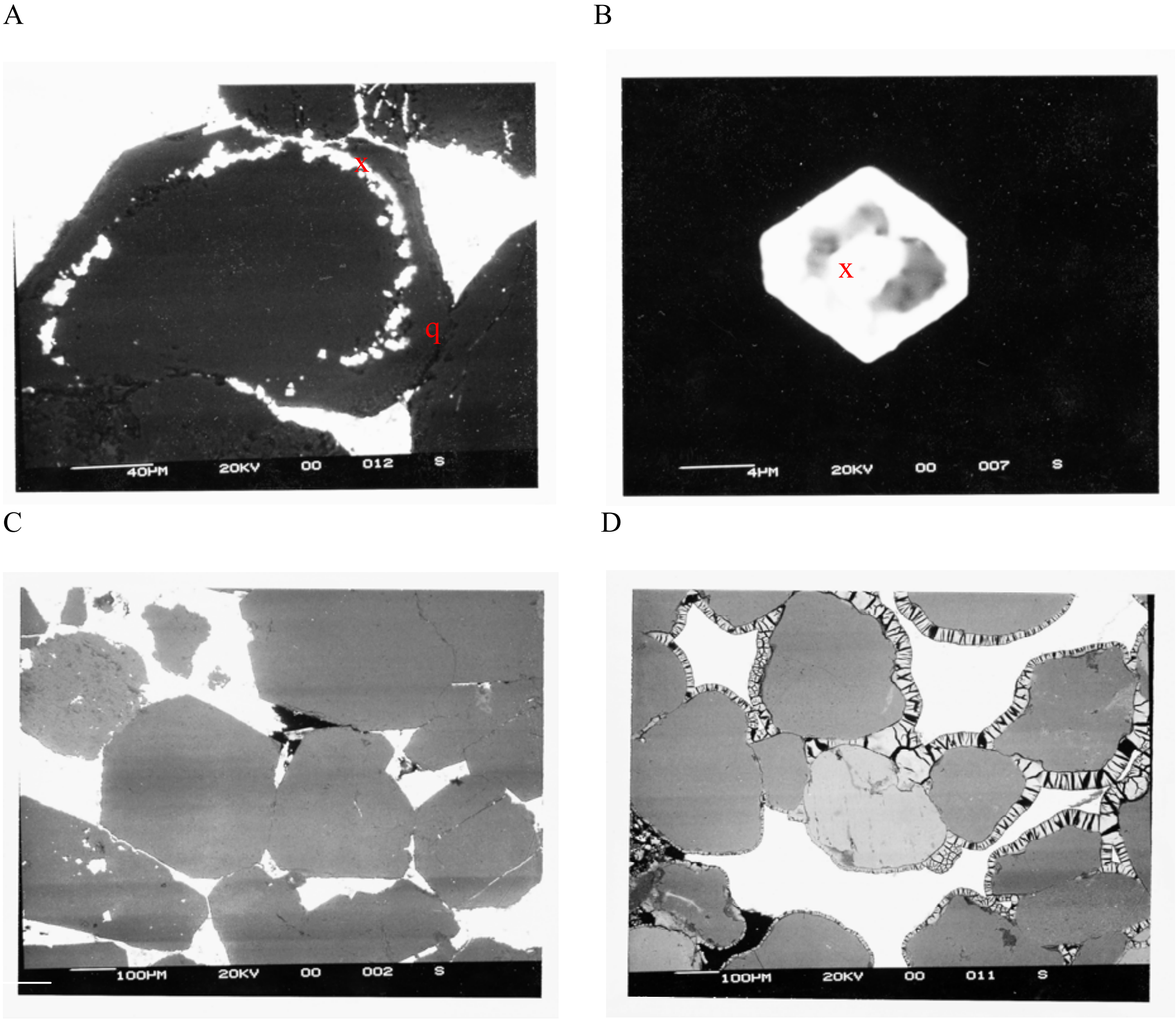


Figure 3.9 **BSEM photomicrographs (A) tiny inclusions (x) of cobaltite, galena and Co-Ni-As sulphide trapped beneath quartz overgrowths (q), Helsby Sandstone Formation, West Mine Alderley Edge. (B) octahedral crystal with complex intergrowth of galena and Co-(Ni)-As sulphide. Occurs as an inclusion as seen in plate (A). (C) clean aeolian sandstone with well-developed quartz overgrowths, cemented by secondary mimetite. (D) clean aeolian sandstone with well-rounded quartz (dark grey) and minor K-feldspar (mid-grey, Helsby Sandstone Formation, West Mine Alderley Edge. (From Plant et al., 1999).**

Grain coatings within the SSG 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 SSG 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). At Alderley Edge [NGR SJ 858 775] faulting has given rise to sulphide mineralisation at the top of the Wilmslow and the base of the Helsby Formations. There are a number of ore bodies related to the sulphide mineralisation at Alderley Edge, consisting predominantly of copper with associated silver, lead and cobalt. The ore deposits have worked, possibly since the Neolithic or Bronze Age. Roman mining has also been suggested but certainly after c. 1660 AD mining became an important industry at Alderley Edge (Figure 3.10). The mines were last worked by Alderley Copper Ltd in 1919 (Carlon, 1981).

Figure 3.10 Alderley Edge Mine Entrance [NGR SJ 860 775].

The Manchester Marl Formation, at the base of the SSG, consists of dolomitic and gypsiferous mudstones. The overlying Mercia Mudstone Group comprises reddish brown and to a lesser degree, greenish grey, dolomitic mudstone also with evaporite minerals, especially gypsum and anhydrite but also including halite and locally celestite. The Bollin Mudstone Member contains thin halite beds (<2 m) in the top 20 m.

3.5 Rainfall chemistry

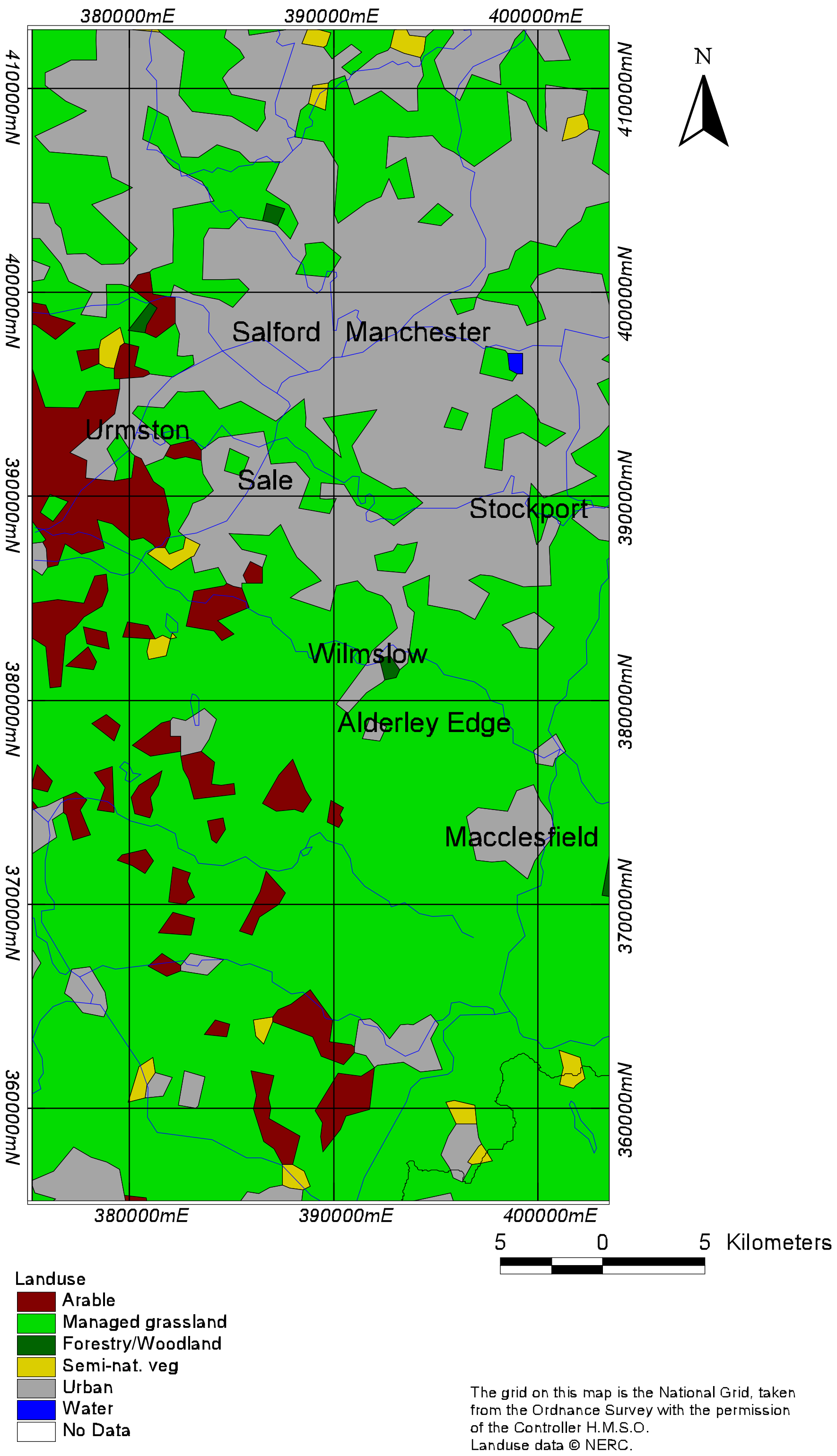
Rainfall provides the primary input of solutes to recharge waters and can be considered as representing minimum background concentrations at the present day. Tellam (1994) estimated present rainfall recharge to be 15-30 milligrams per litre (mg l^{-1}) SO_4, 10 - 40 mg l^{-1} Cl and 3-24 mg l^{-1} nitrate NO_3. The precipitation weighted annual mean rainfall chemistry for the year 2000 is shown in Table 3.2 for Wardlow Hay Cop [NGR SK 177 739], the nearest site for which data are available. The site is located approximately 30 km to the east of the study area. 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 less in recharge waters than rainfall. Nevertheless, the table indicates the order of magnitude of concentrations expected in young waters, which have not reacted with vegetation, soils or aquifer minerals. For chloride, concentrations in recharge waters prior to anthropogenic influences or mixing with other waters would be expected to be around 5-6 mg l^{-1}.

Table 3.3 Rainfall chemistry data from Wardlow Hay Cop [SK 177 739] from The UK National Air Quality Information Archive (http://www.aeat.co.uk/netcen/airqual/data/nonauto/rain.html)

Parameter	Rainfall	Rainfall (x3) - enrichment by evapotranspiration
pH	5.37	
Na (mg l^{-1})	0.91	2.73
K (mg l^{-1})	0.09	0.27
Ca (mg l^{-1})	0.56	1.68
Mg (mg l^{-1})	0.11	0.33
Cl (mg l^{-1})	1.78	5.34
SO_4 (mg l^{-1})	4.35	13.05
NO_3 (mg l^{-1})	1.56	4.68
NH_4 (mg l^{-1})	0.53	1.59
SEC (µS cm^{-1})	23.6	
Rainfall amount	1068 mm per annum	

3.6 Landuse in the area

The study area incorporates a number of urban and industrial areas (Figure 3.11) including most of Greater Manchester and Stockport. Manchester has been an important industrial centre since the Industrial Revolution and there are a number of industrial estates in the area, one of the largest being Trafford Park where historical over abstraction has resulted in high salinity. In addition to United Utilities Plc. (formerly North West Water), significant groundwater users in the study area include breweries, golf courses and plant nurseries. To the west and south of the study area the main landuse is rural including dairy farming and agriculture.



The grid on this map is the National Grid, taken from the Ordnance Survey with the permission of the Controller H.M.S.O.
Landuse data © NERC.

Figure 3.11 **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 32 samples were collected during May 2002 from public and private groundwater supplies at 28 different sites across the area providing good regional coverage of the aquifer (Figure 3.8). The samples were collected from boreholes used by the Environment Agency's groundwater monitoring programme. All boreholes were pumped for an estimated three well bore volumes prior to sampling. It needs to be borne in mind that the pumped samples represent the sum of water coming into the borehole over the screened or open 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 little data available from most sites to establish if this is the case, however valid conclusions may still be drawn in interpreting regional variations which exist in the aquifer.

Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured on-site in an anaerobic flow-through cell at the time of sample collection (Figure 4.1). Other on-site measurements included temperature, specific electrical conductance (SEC) and alkalinity. Samples were collected for major and trace chemical analysis in polyethylene bottles. Those for major and trace elements were filtered through 0.45 µm membrane filters and an aliquot for cation and trace elements was acidified to 1% HNO_3 to minimise adsorption onto container walls. Additional samples were collected in glass bottles for the analysis of stable isotopes (δ^2H, $\delta^{18}O$ and $\delta^{13}C$).

Figure 4.1 Collecting samples from a borehole at an industrial site [NGR SJ 782 981].

Major cations and sulphate were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry and a wide range of trace elements by Inductively Coupled Plasma Mass Spectrometry at BGS Wallingford and by ACME laboratories, Canada. Nitrogen species were analysed by colorimetry at the Environment Agency laboratories in Nottingham and other anion species (chloride, bromide, iodide and fluoride) by automated colorimetry at the BGS laboratory in Wallingford. Stable isotope analyses were completed in the BGS laboratory by mass spectrometry and the results reported relative to the standards Standard Mean Ocean Water (SMOW) for δ^2H and δ^{18}O and PeeDee Formation Belemnites (PDB) for δ^{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 Manchester and east Cheshire area, data were obtained from the Environment Agency's water quality database (WIMS). The earliest record is from 1947 and the most recent from the year 2001. Some good time series data are available and will be further discussed in the section examining time variant trends in water quality.

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

4.3.1 Different borehole designs

As mentioned earlier, water quality stratification may exist in the Sherwood Sandstone aquifer. As a consequence, differences in borehole design, in particular depth of plain casing, length of screen and depth of borehole, may produce differences in water quality not related 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 Differences in 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 is 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 used data obtained from the new sampling programme carried out as part of the Baseline project together with additional data from 59 records from the Environment Agency's water quality database (WIMS) unless otherwise specified. One Environment Agency analysis for each site was selected by choosing the most comprehensive (i.e. most relevant and numerous determinands) and most recent analysis. The Environment Agency data are likely to be based on unfiltered samples therefore in some instances only BGS data have been used. 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 Tables 5.1 and 5.2 for the study area. This shows the ranges and averages of data as well as an upper concentration (defined as mean plus 2 standard deviations or 97.7th percentile) which is used as a cut off to distinguish outlying data. The median is preferred to the mean as an average 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) will deal with controls and geochemical processes which 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 (Figures 5.2 and 5.4) and cumulative frequency plots (Figures 5.3 and 5.5). The box plots (or box and whisker 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 (where the mean and median are the same value then only one line is visible). 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 5.4 shows typical detection limits for each element. Cumulative probability plots are useful in visualising the distribution of data and may be of use in determining outlying data or discriminating pollution. Geochemical processes may alter the distribution of populations in several different ways (Box 5.1).

Table 5.1 Summary of hydrochemical parameters in groundwaters of the Manchester and East Cheshire area.

Parameter	Units	Min	Max	Median	Mean	97.7th percentile	95th percentile	Upper Baseline*	N
T	°C	6.5	21.2	11.5	11.9	15.4	14.1		55
pH	field	6.0	9.1	7.2	7.2	8.3	8.0		91
Eh	mV	55.0	437.0	298.0	255.5	414.9	403.0		31
DO	mg l^{-1}	0.0	11.1	2.9	3.7	9.7	8.3		51
SEC	µS cm^{-1}	320.0	17100.0	679.0	1173.2	5805.5	2605.0		91
δ^{2}H	‰	-50.3	-39.9	-47.0	-46.4	-40.8	-41.8		12
δ^{18}O	‰	-7.6	-6.3	-7.2	-7.2	-6.4	-6.6		12
δ^{13}C	‰	-15.7	-8.3	-14.7	-13.9	-9.0	-9.9		12
Ca	mg l^{-1}	12.0	350.0	77.5	86.2	281.5	162.2		90
Mg	mg l^{-1}	2.5	122.0	25.1	26.8	60.6	50.9		90
Na	mg l^{-1}	8.4	3360.0	24.8	132.6	1042.4	505.5	▨	90
K	mg l^{-1}	1.0	30.0	3.6	4.9	17.6	9.7	▨	90
Cl	mg l^{-1}	8.9	5400.0	28.7	185.2	819.9	683.0	▨	88
SO_4	mg l^{-1}	2.5	666.0	53.5	82.9	278.9	246.7	▨	90
HCO_3	mg l^{-1}	40.0	1310.0	298.0	316.2	903.6	526.0		89
NO_3 as N	mg l^{-1}	<0.0025	33.4	0.3	1.6	8.9	6.7	2-4 mg l^{-1}	90
NO_2 as N	mg l^{-1}	<0.001	0.1	0.0	0.0	0.1	0.1		88
NH_4 as N	mg l^{-1}	<0.003	5.4	0.0	0.2	1.7	0.4	▨	88
P	mg l^{-1}	0.0	0.7	0.1	0.1	0.5	0.5	▨	79
TOC	mg l^{-1}	0.2	7.7	1.4	1.8	6.9	5.4	▨	32
DOC	mg l^{-1}	0.1	6.7	1.1	1.5	6.4	5.1	▨	32
F	µg l^{-1}	25.0	750.0	100.0	119.8	348.2	248.4		60
Br	µg l^{-1}	25.0	2600.0	100.0	221.3	1538.8	690.0	▨	62
I	µg l^{-1}	3.0	40.0	6.0	11.5	40.0	38.0		41
Si	µg l^{-1}	840.0	11000.0	6113.0	6357.0	9548.0	9294.0		89

*estimated upper baseline for elements modified by anthropogenic influences.

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

Table 5.2 Summary of trace element chemistry of groundwaters from the Manchester and East Cheshire area.

Parameter	Units	Min	Max	Median	Mean	97.7th percentile	95th percentile	N
Ag	µg l^{-1}	<0.05	1.0	<0.05	0.1	<0.05	<0.05	32
Al	µg l^{-1}	0.1	3980	5	85	357	142	61
As	µg l^{-1}	<0.05	215.5	1.2	11.5	120.4	59.0	54
Au	µg l^{-1}	<0.05	10.0	<0.05	0.3	2.9	<0.05	32
B	µg l^{-1}	10	600	50	65	339	198	62
Ba	µg l^{-1}	<0.05	312	69	82	271	230	32
Be	µg l^{-1}	<0.05	0.1	0.0	<0.05	0.1	0.1	32
Bi	µg l^{-1}	<0.05	99.0	0.0	3.1	28.4	<0.05	32
Cd	µg l^{-1}	<0.05	42.0	0.6	1.9	5.2	5.0	80
Ce	µg l^{-1}	<0.05	0.1	<0.05	<0.05	<0.05	0.0	32
Co	µg l^{-1}	<0.02	1.4	0.0	0.1	0.8	0.6	32
Cr	µg l^{-1}	<0.5	25.0	5.0	3.4	10.3	5.7	80
Cs	µg l^{-1}	<0.01	0.1	0.0	0.0	0.1	0.1	32
Cu	µg l^{-1}	<0.5	420.0	7.5	16.2	113.0	28.0	81
Dy	µg l^{-1}	<0.01	0.0	0.0	0.0	0.0	0.0	32
Er	µg l^{-1}	<0.01	0.0	0.0	0.0	0.0	0.0	32
Eu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
Fe	µg l^{-1}	3	13100	274	1203	6524	5472	85
Fe (new)*	*µg l^{-1}*	*3*	*2980*	*51*	*638*	*2766*	*2488*	*32*
Ga	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
Gd	µg l^{-1}	<0.01	0.0	<0.01	<0.01	0.0	0.0	32
Ge	µg l^{-1}	<0.05	0.2	<0.05	0.1	0.2	0.2	32
Hf	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	32
Hg	µg l^{-1}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	32
Ho	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
In	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
Ir	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
La	µg l^{-1}	<0.01	0.1	<0.01	0.0	0.0	0.0	32
Li	µg l^{-1}	3.0	298	17	41	245	180	41
Lu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
Mn	µg l^{-1}	0.3	6000	196	499	3193	2410	91
Mn (new)*	*µg l^{-1}*	*1.0*	*1790*	*136*	*292*	*1483*	*1097*	*32*
Mo	µg l^{-1}	0.1	5.8	0.2	0.7	3.9	2.7	32
Nb	µg l^{-1}	<0.01	0.0	<0.01	0.0	0.0	<0.01	32
Nd	µg l^{-1}	<0.01	0.1	<0.01	0.0	0.1	0.0	32
Ni	µg l^{-1}	<0.2	59.0	15.0	9.1	26.3	15.3	80
Os	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
Pb	µg l^{-1}	<1	6.8	<1	<1	4.4	2.4	32
Pd	µg l^{-1}	<0.2	0.3	<0.2	<0.2	<0.2	<0.2	32
Pr	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
Pt	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
Rb	µg l^{-1}	0.2	4.4	1.5	1.6	4.0	3.7	32
Re	µg l^{-1}	<0.01	0.1	<0.01	0.0	0.0	0.0	32
Rh	µg l^{-1}	<0.01	0.1	<0.01	0.0	0.0	0.0	32
Ru	µg l^{-1}	<0.05	0.1	<0.05	<0.05	<0.05	<0.05	32
Sb	µg l^{-1}	<0.05	3.0	<0.05	0.2	1.4	0.4	32
Sc	µg l^{-1}	0.4	4.3	2.7	2.8	4.2	3.9	32
Se	µg l^{-1}	<0.5	4.7	<0.5	0.4	1.8	0.5	32
Sm	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
Sn	µg l^{-1}	<0.05	3.4	0.1	0.2	1.2	0.3	32
Sr	µg l^{-1}	30	3500	208	398	2536	1898	62
Ta	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
Tb	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
Te	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
Th	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	32
Ti	µg l^{-1}	< 10	< 10	< 10	< 10	< 10	< 10	32
Tl	µg l^{-1}	<0.01	3.5	<0.01	0.1	1.0	0.0	32
Tm	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	32
U	µg l^{-1}	<0.5	12.5	1.3	1.9	7.4	4.8	32
V	µg l^{-1}	<1	13.0	<1	1.1	8.0	3.8	32
W	µg l^{-1}	<0.01	2.5	<0.01	0.2	1.4	0.6	32
Y	µg l^{-1}	0.01	0.50	0.01	0.04	0.21	0.08	32
Yb	µg l^{-1}	0.005	0.020	0.005	0.006	0.013	0.010	32
Zn	µg l^{-1}	3.4	177.4	8.6	26.5	130.4	111.5	32
Zr	µg l^{-1}	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	32

*Mn and Fe data for all samples (WIMS data plus new samples), as well as for the new samples, are shown

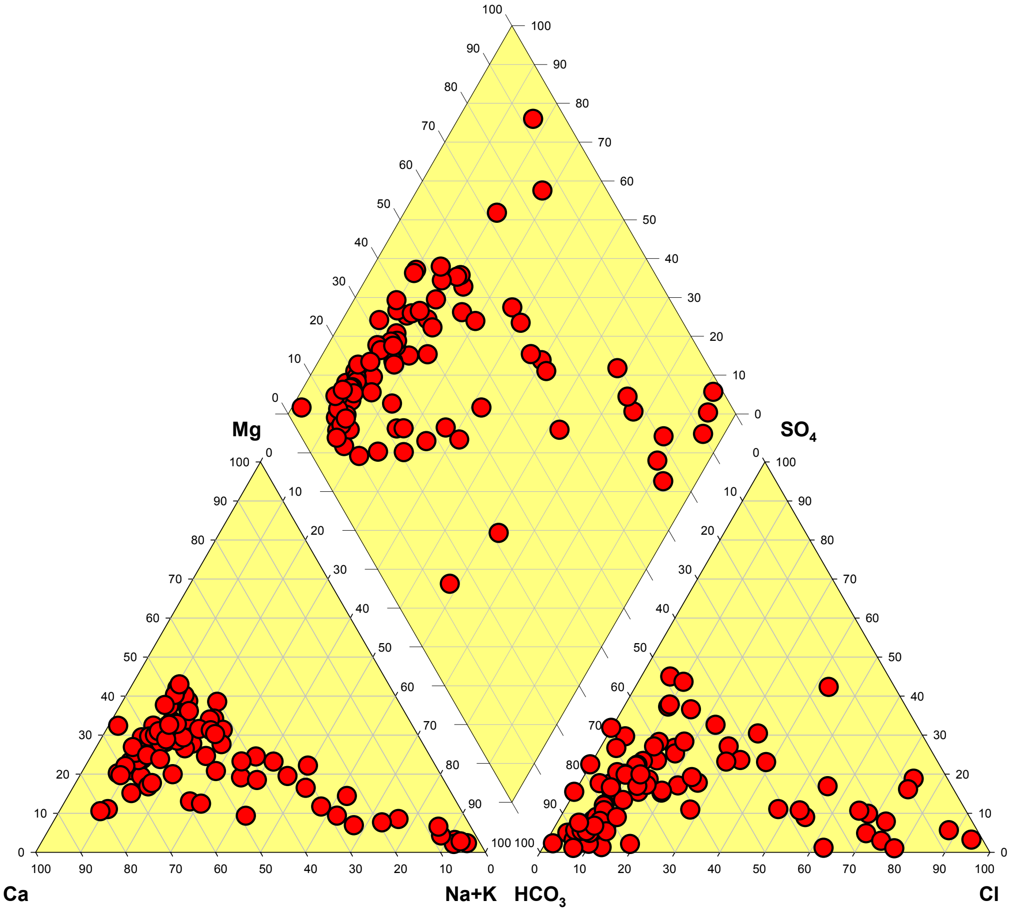
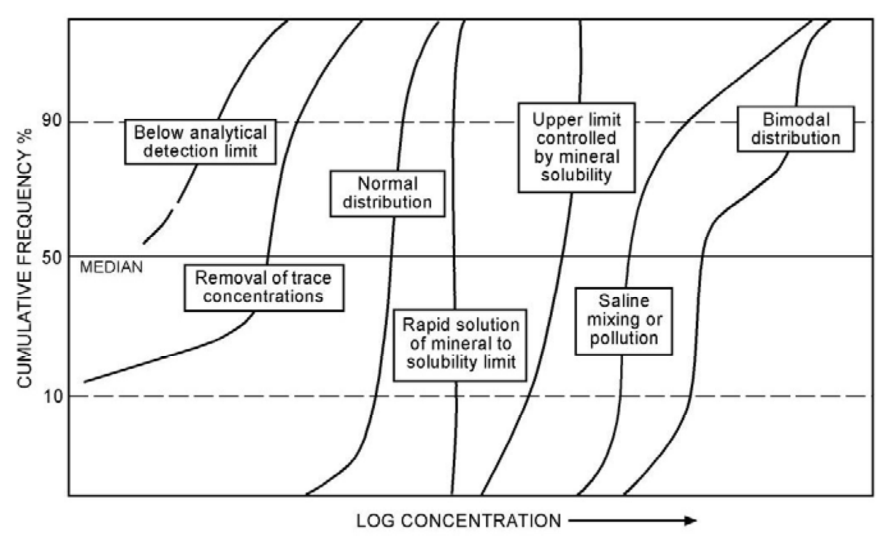


Figure 5.1 **Piper plot showing the relative concentrations of major cations and anions in groundwaters of Manchester and East Cheshire.**

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 Manchester and East Cheshire sandstone aquifer show a wide range of characteristics in terms of physicochemical parameters and solute concentrations (Table 5.1 and 5.2). The median temperature is 11.5 ^{o}C. The pH of the waters ranges from 6.0 to 9.1 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 or indicative of reducing conditions (median values for DO and Eh are 2.92 mg l^{-1} and 298 mV respectively). High iron and manganese concentrations also indicate that reducing conditions are present.

The Piper diagram (Figure 5.1) illustrates the range of major element compositions found within the Manchester and East Cheshire aquifer. The groundwaters are predominantly of Ca-HCO_3 or Ca-Mg-HCO_3 type but show a trend towards Ca-Mg-HCO_3-SO_4 type. There are a significant number of Na-Cl type groundwaters and a few of the samples trend towards Na-HCO_3 type.

5.3 Major elements

The box plot (Figure 5.2) for major elements highlights the dominance of calcium and bicarbonate ions within the groundwater. Potassium, Mg and SO_4 concentrations are elevated above the marine-derived input to the system. The median Na values are also elevated above the rainfall derived input. The median NO_3-N concentration is relatively low at 0.25 mg l^{-1}. The cumulative frequency plot for major elements (Figure 5.3) shows that most major elements vary over two orders of magnitude with the exception of chloride and sodium which vary over nearly three orders of magnitude. The chloride and sodium curves show a shift at around 80%. Several elements (K-Ca-HCO_3-SO_4-Mg) show a population shift at or above the 95th percentile. The curves for these elements are indicative of mixing between at least two populations. The top 5% concentrations of Cl, Mg and K are from boreholes located in the vicinity of Trafford Park where saline waters are encountered. The nitrate plot indicates a number of different populations and many of the samples are below the detection limit. Sulphate concentrations display a shift at around 10% and below this some of the concentrations are very low (<10 mg l^{-1}). A couple of the samples collected during the field programme were noted as smelling of H_2S (one in the Heaton Moor area which had a low SO_4 of 8 mg l^{-1} and another from Trafford Park had 200 mgl^{-1} SO_4).

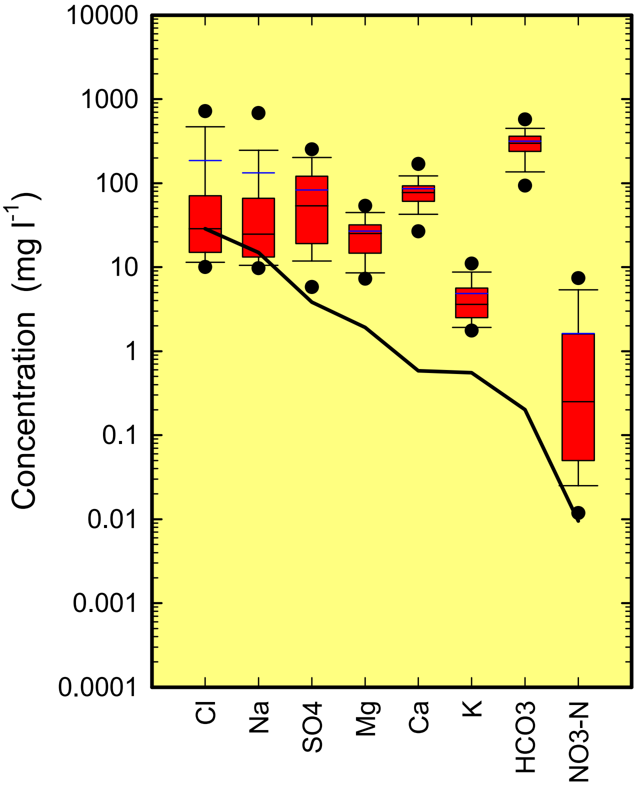


Figure 5.2 **Range of major ion concentrations in Permo-Triassic Sandstone groundwaters in the Manchester and East Cheshire area. The black line represents a diluted seawater curve which has been normalised to the median Cl of the samples.**

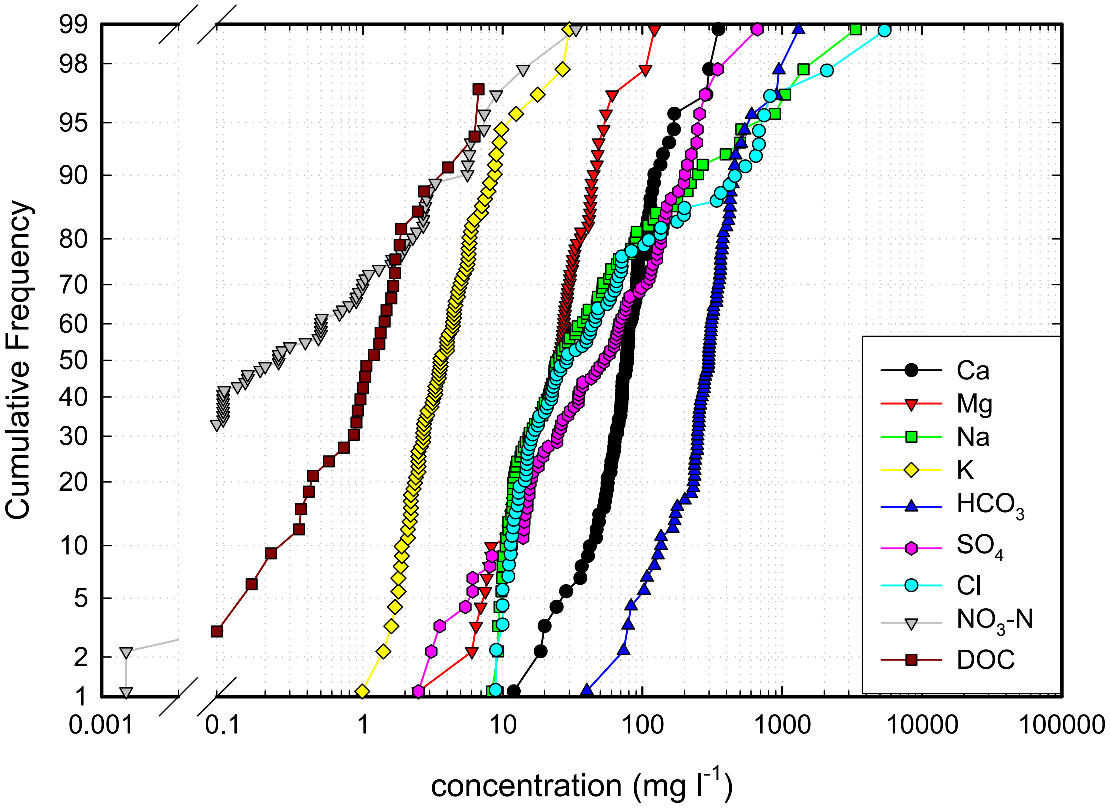


Figure 5.3 **Cumulative probability plot for major elements**

5.4 Minor and trace elements

The box plot for minor and trace elements indicates the wide range of concentrations present in the groundwater (Figure 5.4). Silicon, Ba, Zn, Fe and Mn are present at relatively high concentrations. Some of the trace elements have a relatively low median value but individual concentrations may be very high. For example, As has a median value of 1.18 µg l^{-1}, but concentrations in excess of the EU Maximum Admissible Concentration (MAC) drinking water standard of 50 µg l^{-1} have been recorded. Cadmium has a median value of 0.55 µg l^{-1} but some values also exceed the MAC of 5 µg l^{-1}. 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, Fe and As, vary by up to 5 orders of magnitude. Most elements seem to show a population shift at around 90%. Straight lines at low concentrations are an artefact resulting from measurements that were below the detection limit. Older data with high detection limits were excluded.

It is likely 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.

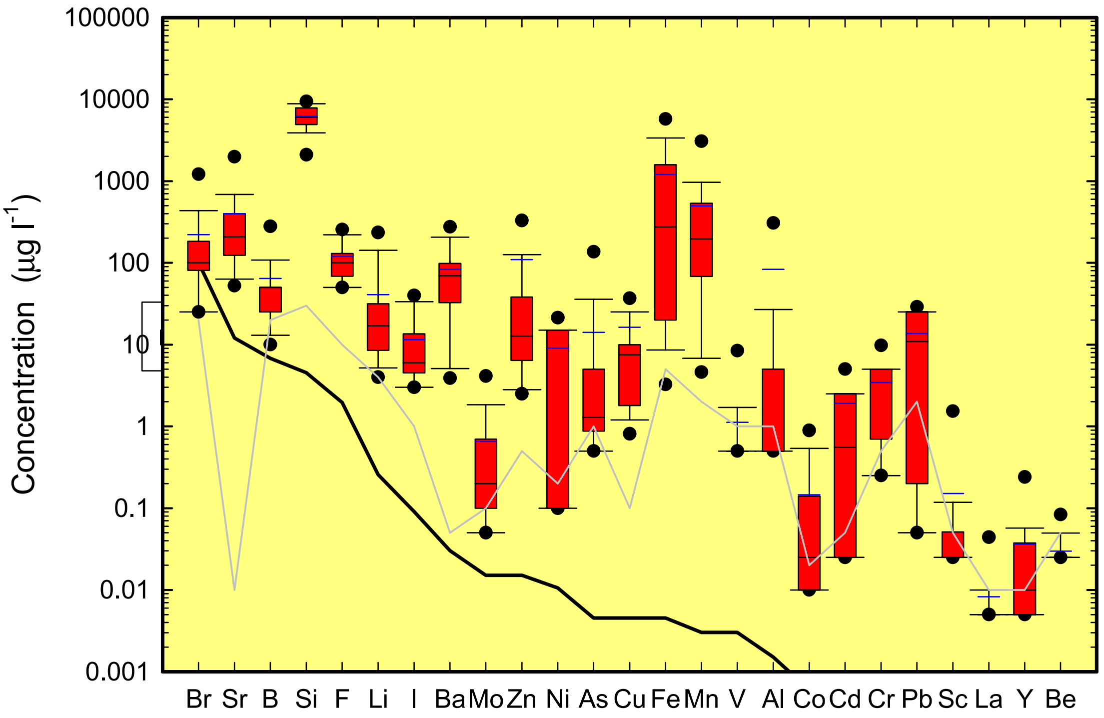


Figure 5.4 Range of minor and trace element concentrations in Permo-Triassic Sandstone groundwaters in the Manchester and East Cheshire area. The black line represents a diluted seawater curve which has been normalised to the median Cl of the samples. The grey line indicates detection limit of the recent analyses.

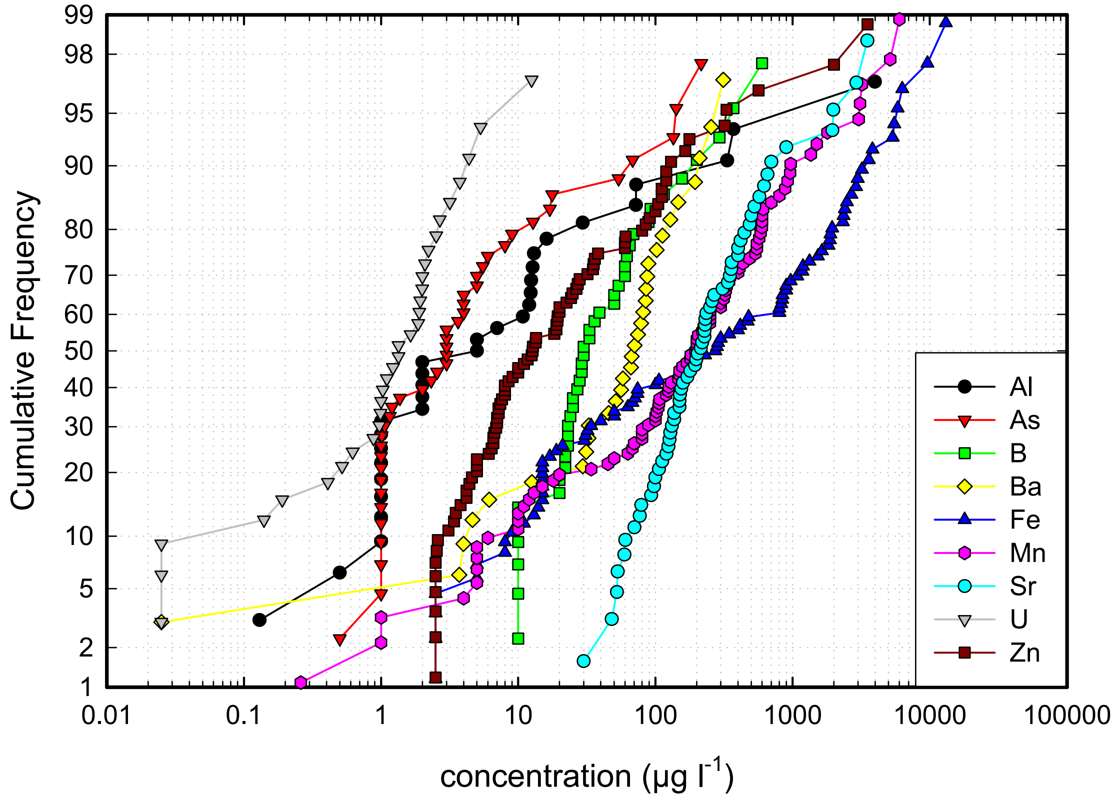


Figure 5.5 Cumulative probability plot for minor and trace elements

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).

The most obvious indicator of diffuse pollution is the presence of high nitrate. Nitrate concentrations are naturally generally low throughout much of the aquifer. The relatively reducing conditions, which occur in some parts of the aquifer, mean that any anthropogenic inputs of nitrate will have been reduced by denitrification. This is an example of how the geochemical environment can induce natural attenuation and therefore remediate pollution within the aquifer. The highest nitrate value of the BGS samples (33.4 mg l^{-1} at NGR SJ 822 921) is associated with relatively elevated K and Cl values (12.5 and 136 mg l^{-1} respectively) compared with boreholes in a similar setting, which suggests that this site may have been affected by pollution (probably from fertilisers).

The database of historical water chemistry analyses that was used for this study does not contain any information on pesticide concentrations. Organic contaminants were not considered in this study, however, Stansbury (1994) noted that in the Trafford Park area the surface and shallow sub-surface at a number of sites have been contaminated by hydrocarbons and metals. Stansbury (1994) suggested that surface hydrocarbon pollution had not yet reached the aquifer. The apparent failure of hydrocarbons to reach the water table may be due to degradation, dilution, sorption, insufficient travel time, run-off to surface water courses, site remediation works and/or the effect of the Manchester Ship Canal acting as a drain (Stansbury, 1994).

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 human activities over and above the natural groundwater chemistry in the data sets used.

The approach adopted is threefold:

(i) to have evidence of groundwater age

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

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

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

This section deals with the dominant geochemical processes which influence groundwater chemistry and provides an overview of the regional variations in groundwater chemistry. The dominant geochemical processes controlling groundwater chemistry are mineral dissolution/precipitation, redox reactions, ion exchange and mixing. Groundwater chemistry evolves as water moves from recharge to discharge areas. The baseline chemistry within an aquifer is likely to vary with depth, areally and also with time. The variations with depth and time are assessed and the spatial variations interpreted within a geochemical framework.

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 packer tests (although some mixing is inevitable even with packers), porewater extraction (for sampling the matrix) or by comparing the chemistry from adjacent boreholes drilled to different depths.

There are few data available on depth variations, however there are porewater data available for the Chat Moss observation borehole [NGR SJ 704 956]. The porewater profile (Figure 6.1) shows a freshwater/saline interface at about 190 m depth. Selected parameters for pumped samples across the study area have been plotted against borehole depth (Figure 6.2). Perhaps unsurprisingly there is no consistent behaviour between elemental concentration with depth and the same is true of redox status for these mixed, pumped samples. Further work, including porewater profiles and multiple piezometer arrays would be useful to ascertain in detail the effects of drift on baseline chemistry and drift -aquifer groundwater interactions.

In the Trafford Park area, there are problems with high Fe concentrations and salinity. Groundwater with high iron concentrations has been identified at shallow depth (<20 m) in parts of Trafford Park e.g. at NGR SJ 783 981. Below this depth at c. 40 m, the iron concentrations are much lower. Abstraction in the Trafford Park area has also led to an increase in salinity from upwelling of saline groundwater from depth. There is therefore, in this area, a marked stratification in baseline quality that contributes to water quality problems; it is possible to get reasonably good quality water, providing that the borehole is not sufficiently deep to intersect the upconed saline water and providing that the shallow high iron water is cased out. However, it is not known whether the abstraction of this good quality water will be sustainable in the long term and management of the aquifer is an important issue.

6.3 Temporal variations

As discussed above, there have been significant temporal changes in the groundwater chemistry in the Trafford Park area as a result of heavy abstraction. The area provides a good example of how anthropogenic influences (in this instance, the pumping regime) can cause water with a different baseline chemistry to migrate beneath this site. The salinity at Trafford Park is entirely from natural sources but the upwelling has been induced by anthropogenic stresses on the groundwater system. For some boreholes within Trafford Park [NGR SJ 790 957], there has been a large increase (3-4 fold) in the concentrations of all major elements except HCO_3 over the past few decades but the groundwaters have not changed from a Na-Cl type (Figure 6.3). The oldest records for these boreholes only go as far back as 1968 so it is not possible to determine the chemistry of the original water. Chloride data from two adjacent boreholes in Trafford Park are shown on Figure 6.4. The plot shows the difference in chloride concentration in the two boreholes resulting from the different sampling depth. Borehole No. 1 is 183 m deep while Borehole No. 2 is 165 m deep. The changes in chloride levels over time are due to the relative rates at which the boreholes have been pumped but the graph also highlights the variation in salinity over a relatively small depth range in the Trafford Park area. Throughout much of the aquifer there is relatively little change with time for many elements (Figure 6.5). Some sites with higher nitrate concentrations e.g. at NGR SJ 779 982 and NGR SD 791 033, seem to show a reduction in the concentration of NO_3 over the last 30 to 35 years. Unfortunately there is no time series data for these boreholes which pre-dates 1968, making determination of the natural baseline difficult. Figure 6.6 shows changes in major element concentrations with time for a borehole located to the north of the study area [NGR SD 795 030]. Sulphate, Cl, Mg, Ca, Na and HCO_3 all display significant increases with time, sometimes orders of magnitude, which may relate to mixing with water from deeper in the aquifer or from the Coal Measures aquifer located to the north of the site.

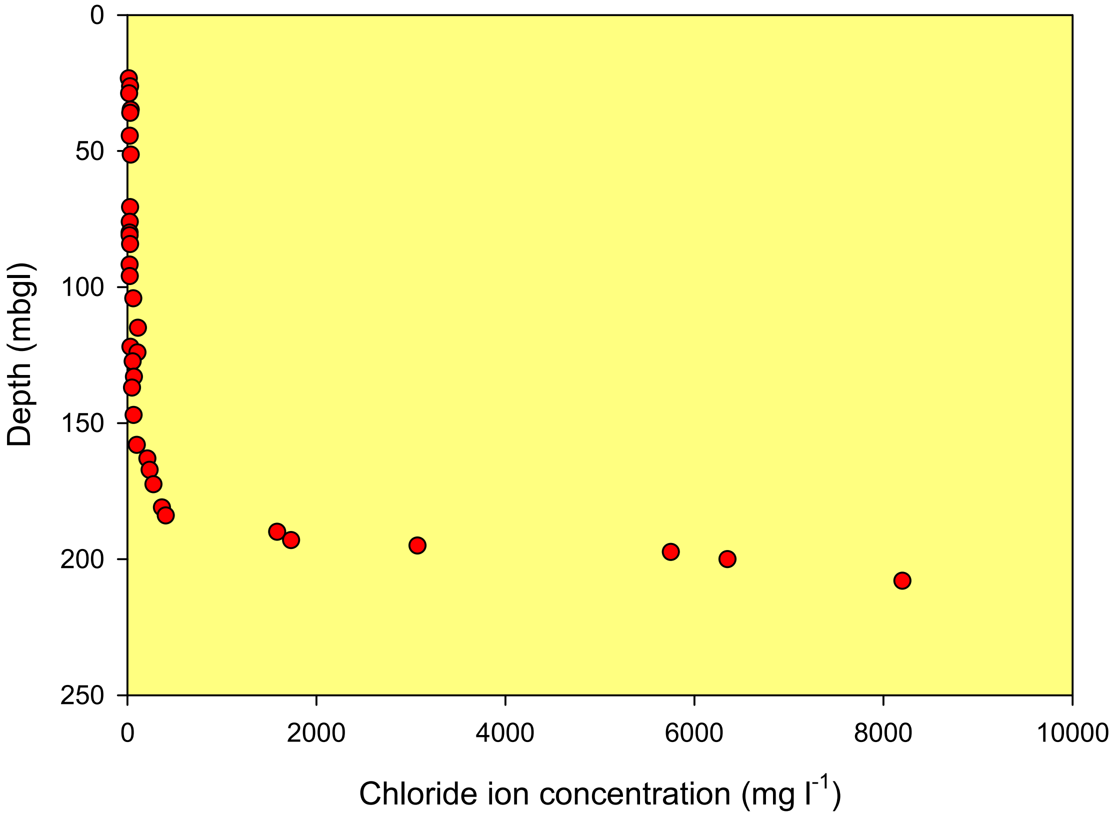


Figure 6.1 **Chat Moss observation borehole [NGR SJ 704 956] porewater profile showing saline interface at depth.**

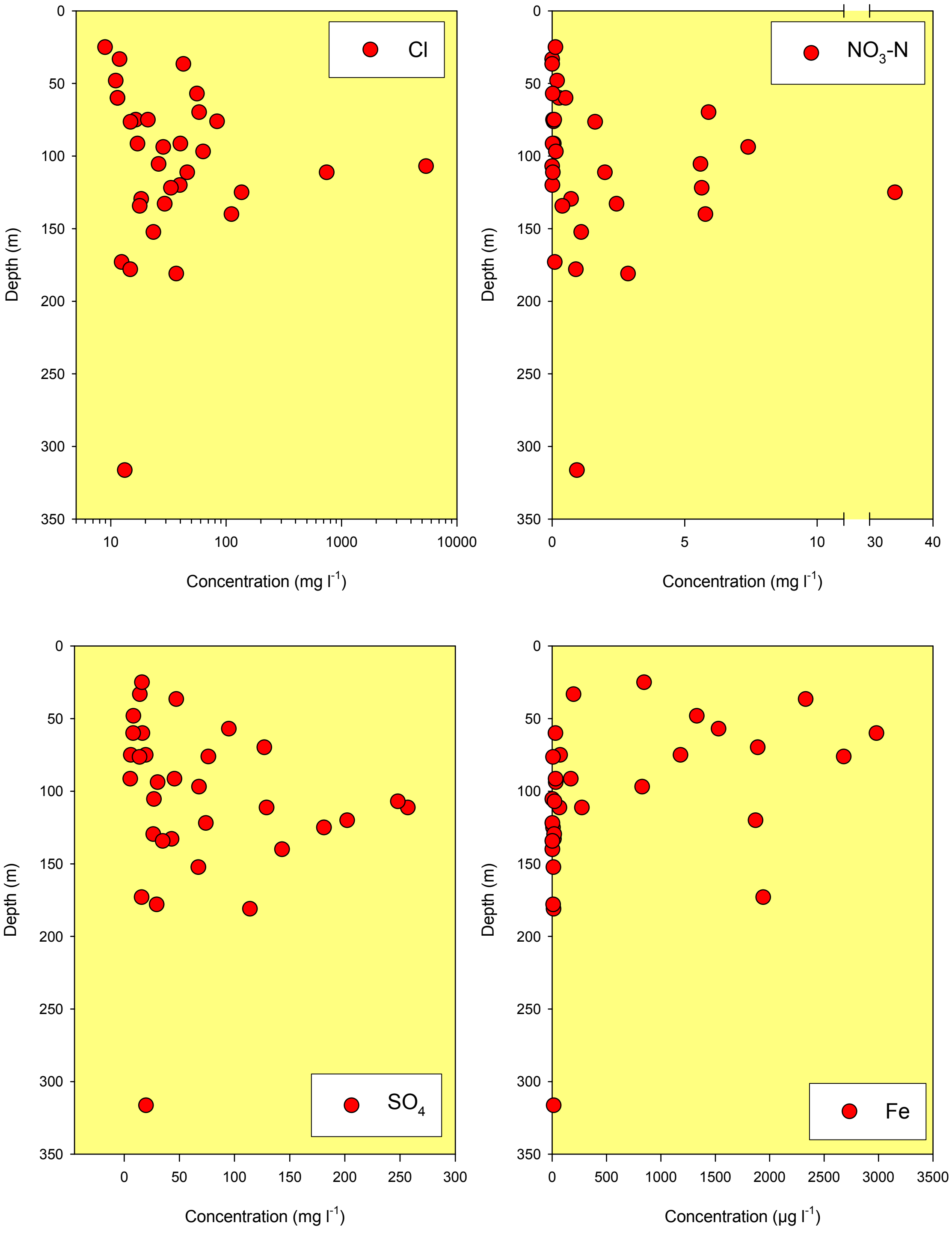


Figure 6.2 **Plots of Cl, NO$_3$-N, SO$_4$ and Fe against depth of borehole.**

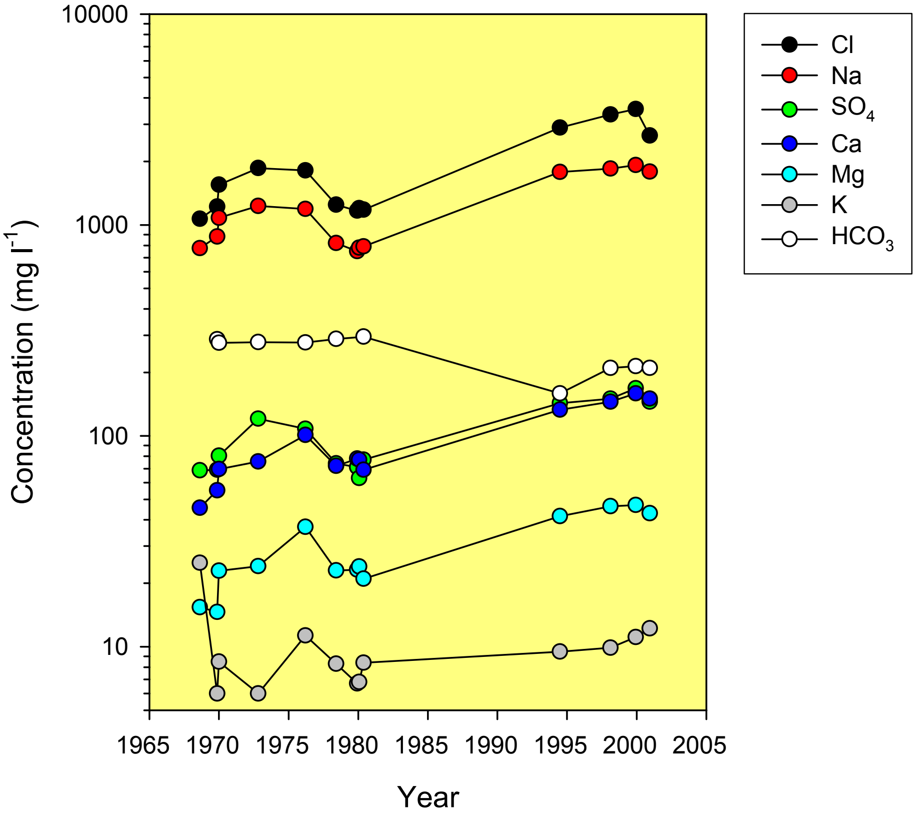


Figure 6.3 Time series data for a borehole in the Trafford Park area [NGR SJ 790 957] showing the increase in salinity over the past few decades.

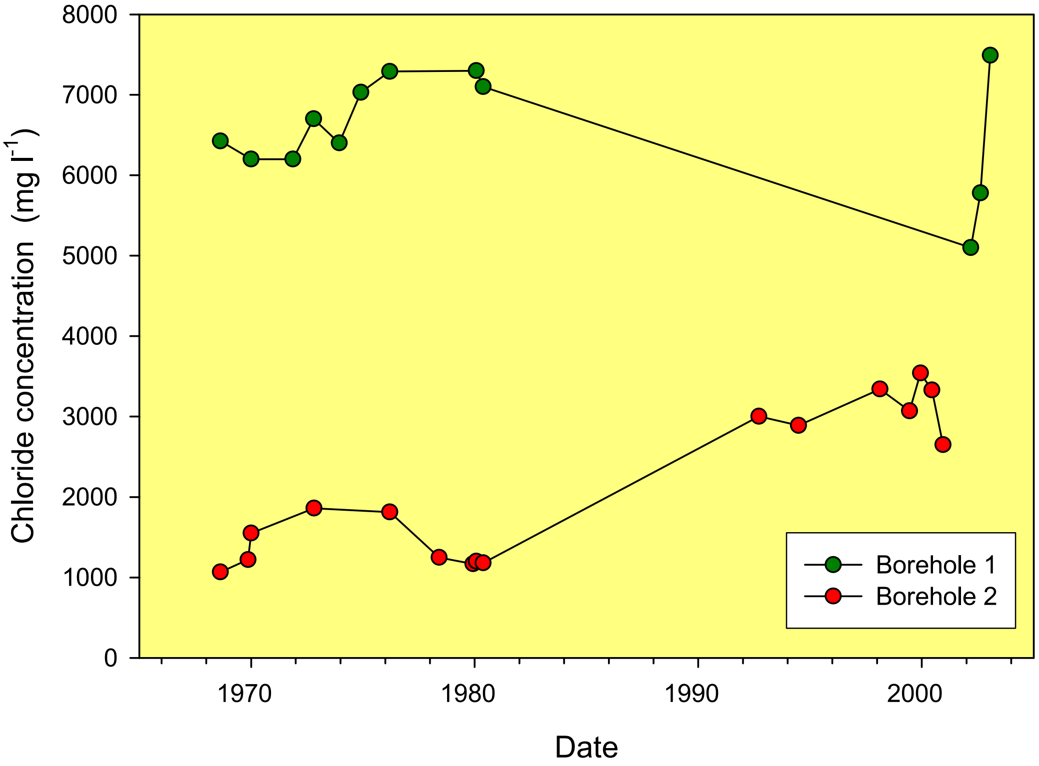
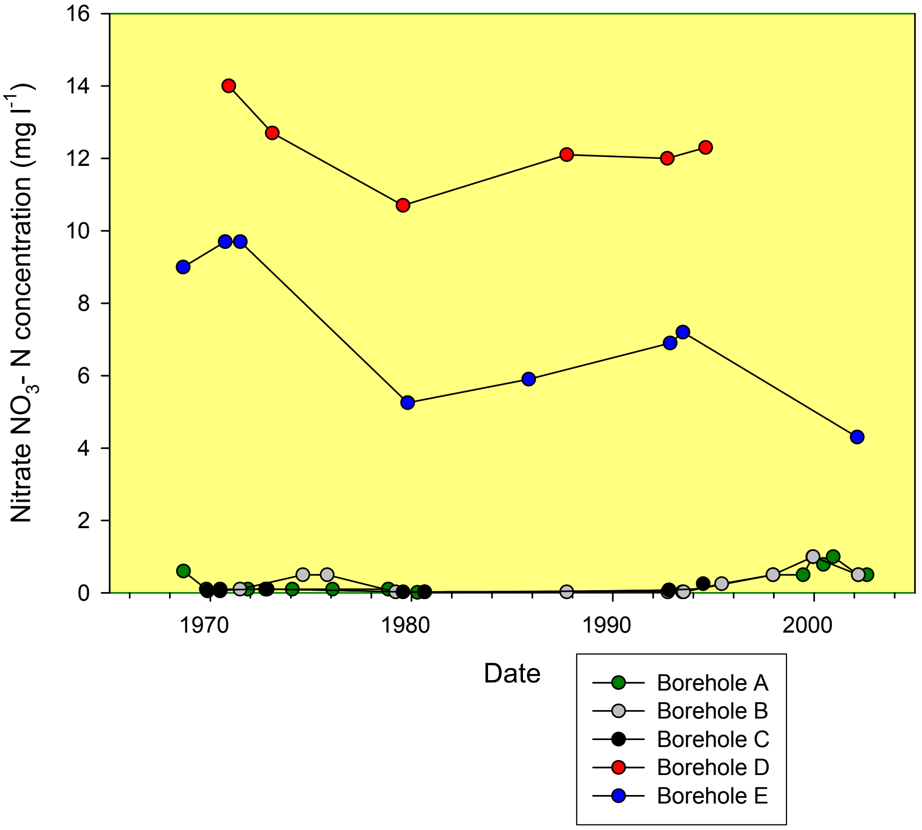


Figure 6.4 Changes in chloride concentration with time for two Trafford Park [NGR SJ 790 957] boreholes.



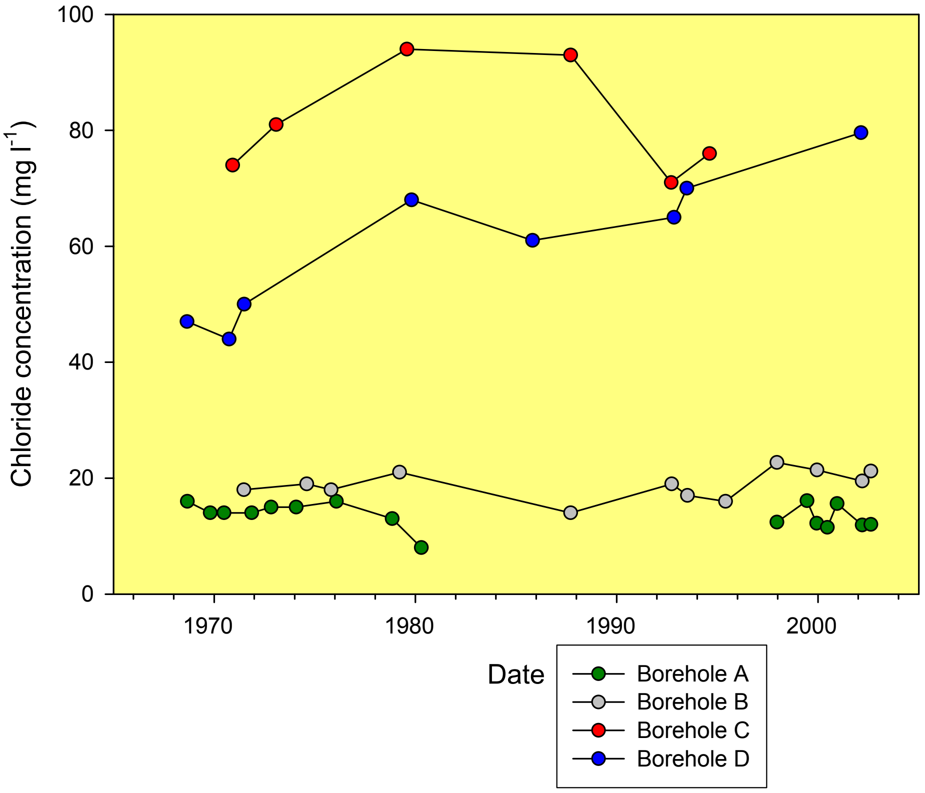
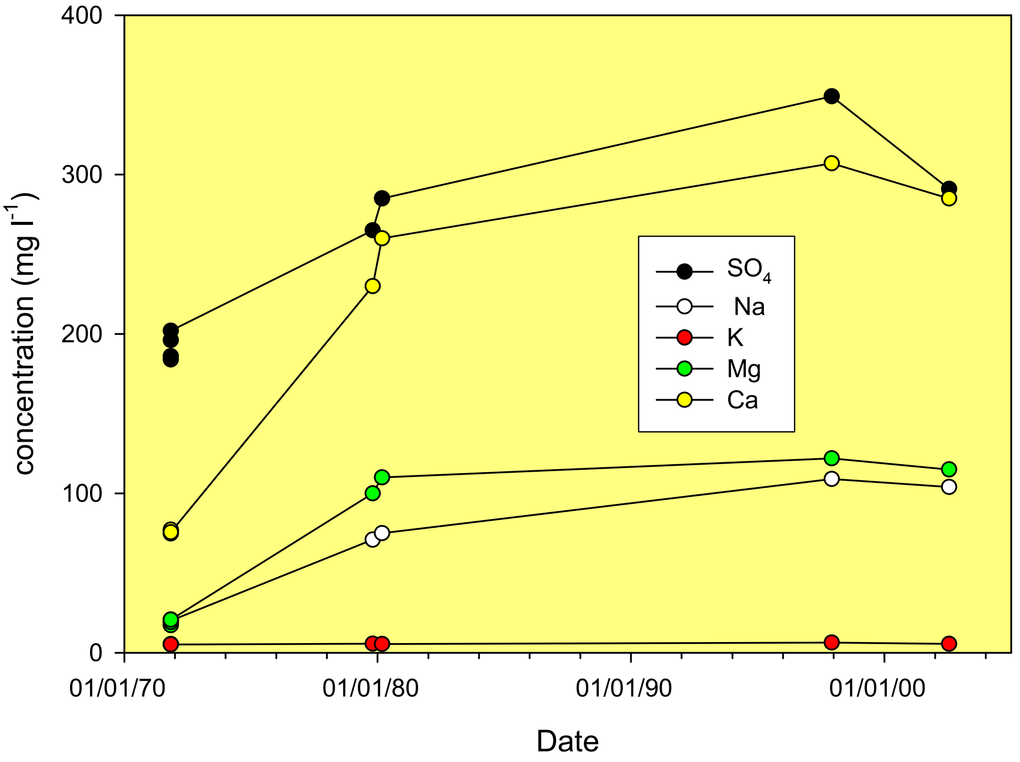


Figure 6.5 **Changes in nitrate and chloride concentrations with time for a number of boreholes from 1968 to present. Borehole A [NGR SJ 890 994], Borehole B [NGR SJ 839 959], Borehole C [NGR SJ 784 960], Borehole D [NGR SJ 779 982] and Borehole E [NGR SD 791 033].**



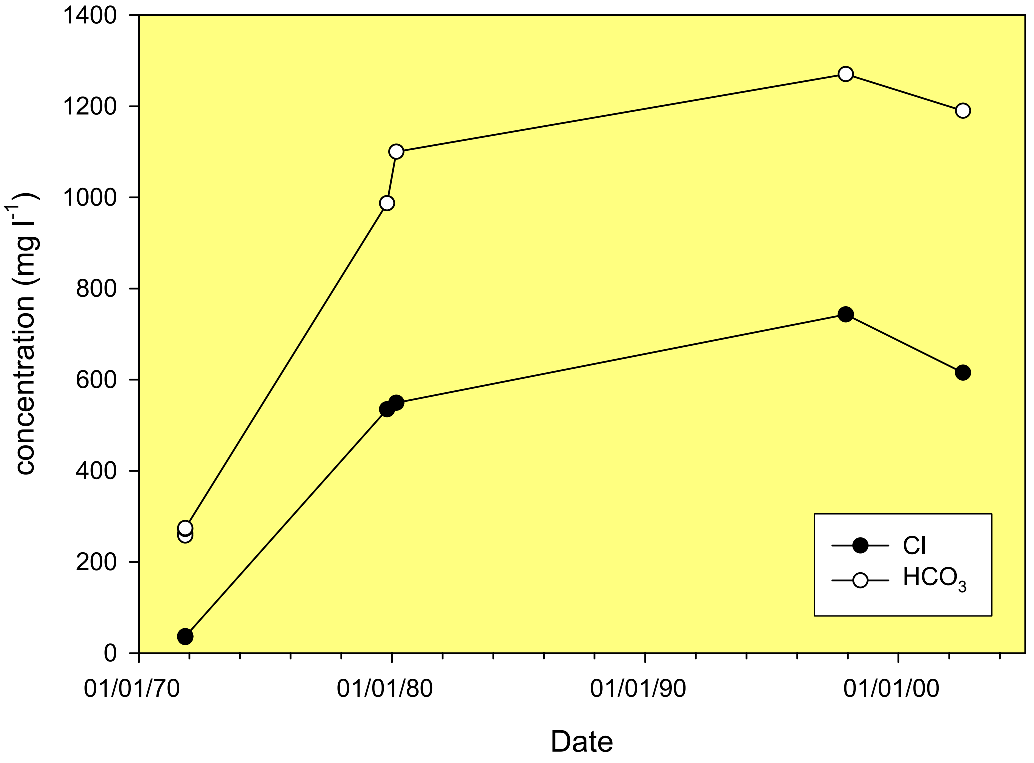


Figure 6.6 **Time series data for a borehole in the north of the study area [NGR SD 795 030].**

6.4 Age of the groundwater

There are no published data on the age of groundwater in the study area. Stable isotope analyses (Figure 6.7) were completed on selected samples in order to ascertain if palaeowaters were present in the aquifer. 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 present, resulting in lighter (more negative) signatures of the stable isotopes δ^2H and δ^{18}O. The range of δ^2H and δ^{18}O values obtained are what would be expected from rainfall input and indicate that the recharge is likely to be of Holocene or recent age i.e. there is no evidence of palaeowaters. In general, lighter signatures are found toward the south of the study area but are still considered to be modern or Holocene age. There is one slightly anomalous sample, in the west of the study area [at NGR SJ 708 931], which has heavier δ^2H, δ^{18}O and δ^{13}C signatures than the other samples. This anomaly is not thought to result from mixing with seawater because the sample has relatively low Cl and Na concentrations.

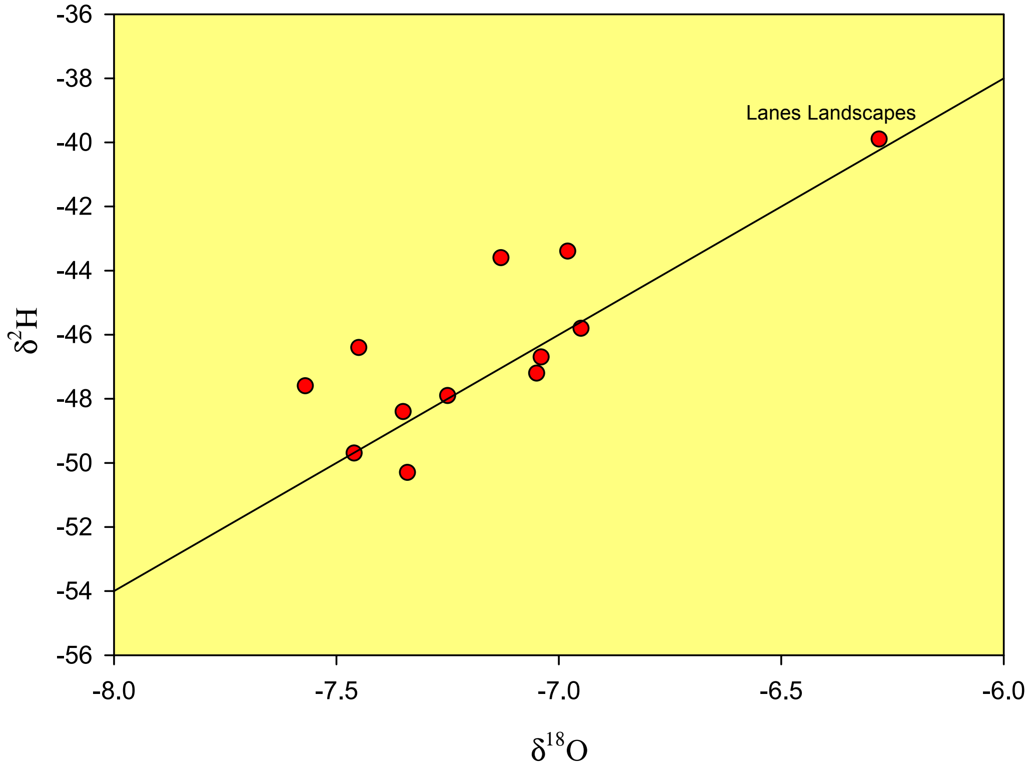


Figure 6.7 **δ^2H - δ^2H plot for selected groundwaters.**

6.5 Spatial variations

Changes in the baseline chemistry are expected to occur as water moves from the recharge to the discharge areas of the aquifer. It is very difficult to evaluate hydrochemical changes along a flowline in the present study because the aquifer is compartmentalised by a series of faults and low permeability horizons (principally the Manchester Marl), and flow patterns are affected by abstractions in the area. In addition, zones of recharge and discharge are strongly influenced and complicated by drift cover. Although the direction of flow at a regional scale can be identified, the concept of sampling along a "flowline" is not deemed to be appropriate or meaningful for this area. Therefore, overall spatial variations in water chemistry have been examined. These are largely determined by water-rock interaction and mixing, but it is likely that the thickness and nature of the overlying drift material will influence the rate of recharge and residence time. Chemical evolution in the direction of groundwater flow has also been overprinted by other effects e.g. in the Trafford Park area, where over abstraction in the past has resulted in upconing of saline water.

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. This acidity will be rapidly neutralised through reaction with carbonate minerals:

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{carbonic acid}}{H_2CO_3} \Leftrightarrow Ca^{2+} + 2HCO_3$$

Dolomite dissolution is controlled by the following reaction:

$$\underset{\text{dolomite}}{CaMg(CO_3)_2} + \underset{\text{carbonic acid}}{2\,H_2CO_3} \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3$$

Many of the samples within the aquifer are undersaturated with respect to calcite and dolomite and it seems likely that these groundwaters occur in parts of the aquifer which have become decalcified i.e. the original calcite has been dissolved. There is no clear relationship between the degree of saturation with respect to calcite or dolomite and depth of borehole, and more detailed work would be required to establish if this is the case. Mixing of groundwaters, even where both are saturated with respect to calcite, can lead to slight undersaturation but not to the degree noted here. The most saline groundwater (with a SEC of 17,100 µS cm^{-1}) is supersaturated with respect to both calcite and dolomite but the reason for this not clear, possibly pH was unstable during measurement. Calcium and Mg also show a large degree of spatial heterogeneity and their distributions are thus complex (Figure 6.8).

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

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

Sulphate concentrations are relatively low in the Manchester and East Cheshire aquifer and all samples are undersaturated with respect to gypsum. This may also be due to loss of original cement in the uppermost part of the aquifer. Other potential sources of sulphate include the oxidation of pyrite, acid rain or fertilizers (Appelo and Postma, 1991). Anthropogenic inputs are likely to be within the aquifer regional baseline range and will therefore be difficult to identify.

Nevertheless, carbonate and sulphate reactions are the dominant reactions determining groundwater chemistry within the aquifer. Less rapid silicate dissolution reactions may also be occurring. Silicon concentrations within the aquifer range from 0.84 to 11 mg l^{-1}. The amount and rate of dissolution will be controlled by saturation with respect to a silicate mineral or phase. 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. Most groundwaters in the study area are close to saturation with respect to chalcedony (SiO_2).

Concentrations of fluoride are generally low (median of 0.15 mg l^{-1}) in the groundwaters and the waters are undersaturated with respect to fluorite implying that F-bearing minerals are not significant in the aquifer. Distributions are also spatially variable (Figure 6.8). Potassium shows little variation with depth and there is little evidence for anthropogenic input. The dominant input of K is considered to be from K-feldspar.

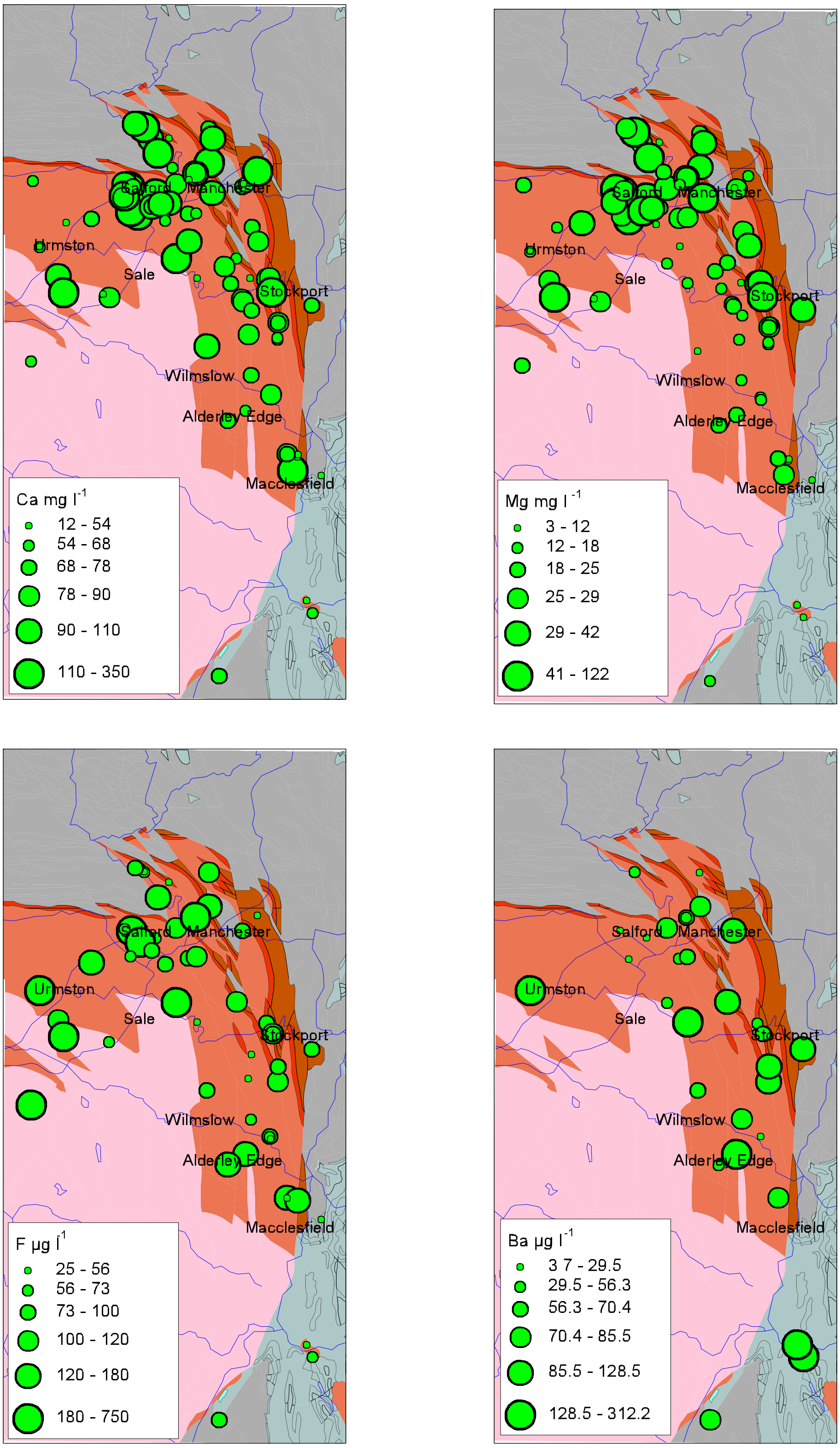


Figure 6.8 Spatial variations in the concentrations of Ca, Mg, F and Ba superimposed on solid geology (refer to Figure 3.1 for geological legend).

6.5.2 Redox reactions

The redox status of groundwaters in the study area is complex, mainly due to the variations in drift thickness and type and possibly due to locally confining layers within the sandstone. This is reflected in the large spatial variations of redox sensitive species and range of redox parameters (DO and Eh). Most samples are from areas where the aquifer is not confined beneath Mercia Mudstone and there is no obvious regional redox boundary. Redox conditions are likely to be significantly affected by the nature and thickness of drift cover across the aquifer. The median nitrate concentration is 0.25 mg l^{-1} (NO_3-N) which is relatively low (under pristine conditions in an oxidising aquifer nitrate is typically of the order of 1 to 3 mg l^{-1}). When compared with median nitrate concentrations for other Permo-Triassic aquifers, the Manchester area median concentration is lower than in the South Staffordshire and North Worcestershire area (9.4 mg l^{-1} NO_3-N; Tyler-Whittle et al., 2002) and Cheshire (3.3 mg l^{-1} NO_3-N; Griffiths et al., 2002) but higher than in the Vale of York (0.05 mg l^{-1} NO_3-N; Shand et al., 2002). Most groundwaters with high Fe (taken as a proxy for redox status) 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. Unfortunately, detailed construction details are not known for many of the boreholes sampled and it is difficult to assess vertical changes in redox potential. Nitrate concentrations are generally higher in river valleys and where drift deposits are more permeable (Figure 6.9) indicating that recharge is occurring through windows in the drift. Nitrate concentrations appear to be relatively evenly distributed across the different land uses with the most extreme values being associated with sandy drift deposits. Although sewer leakage and the effects of agricultural pollution may provide locally important inputs to the groundwater, 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.

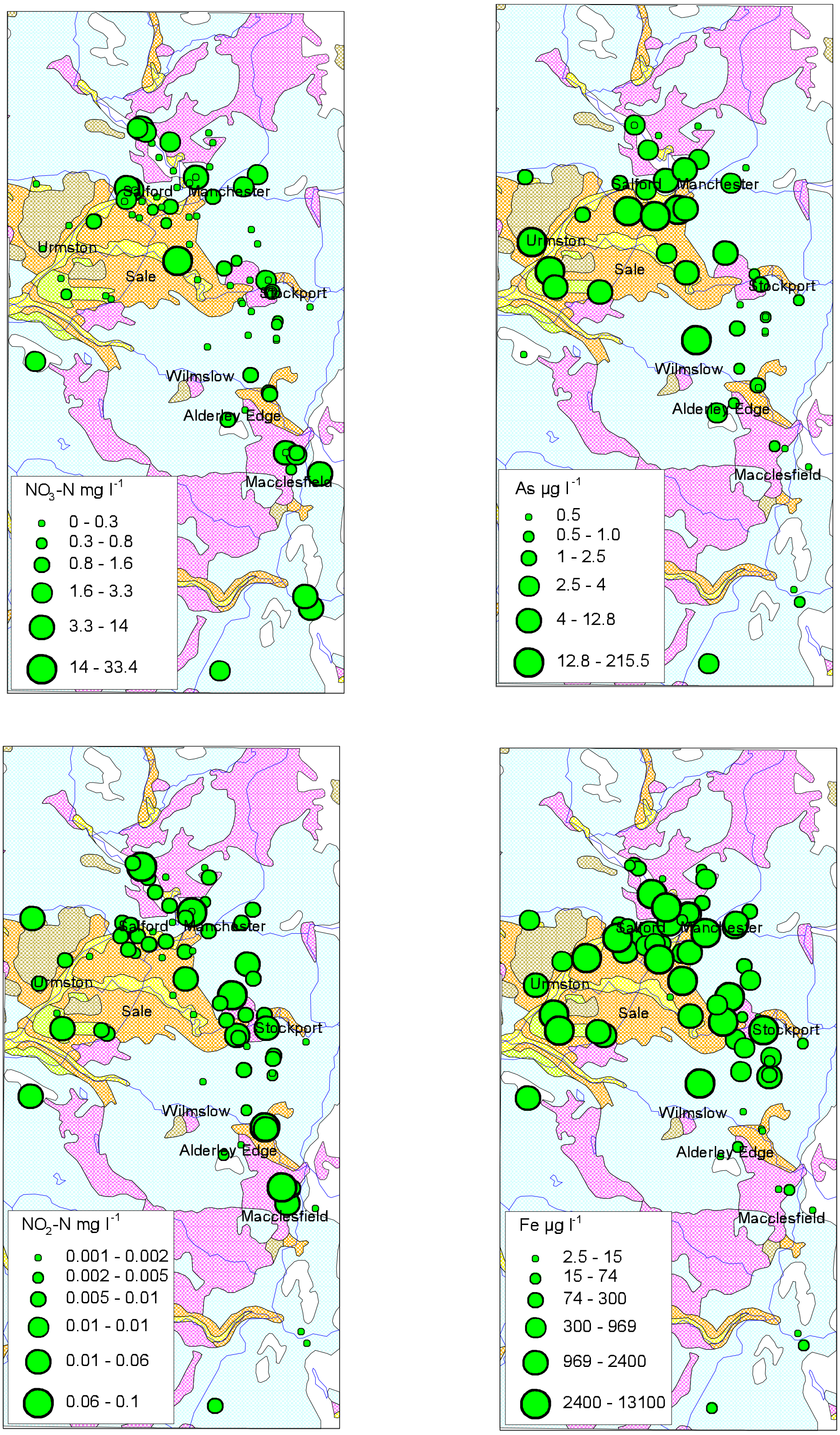


Figure 6.9 **Spatial variations in the concentrations of NO_3-N, NO_2-N, As and Fe superimposed on drift geology (refer to Figure 3.7 for drift legend).**

Several trace elements which are redox-sensitive, such as As, reach very high concentrations. The data from filtered samples indicate that the higher concentrations are present only in moderately reducing conditions (Figure 6.10). Although the median value for arsenic is 1.18 µg l^{-1} locally very high concentrations have been observed. Of 54 samples analysed for As, 8 exceed the Drinking Water Standard of 10 µg l^{-1}. The high arsenic samples include new data for samples that had been filtered. One site had an As concentration of 215 µg l^{-1} and four others exceeded 50 µg l^{-1}. Two of the high As concentrations are located in the west of the study area whilst the lower concentrations generally seem to be in the area south of Manchester. It has been noted that As concentrations seem to increase in the younger formations within the Triassic sequence and may relate to mineralising fluids spreading out beneath the Mercia Mudstone Group (ESI, 2001).

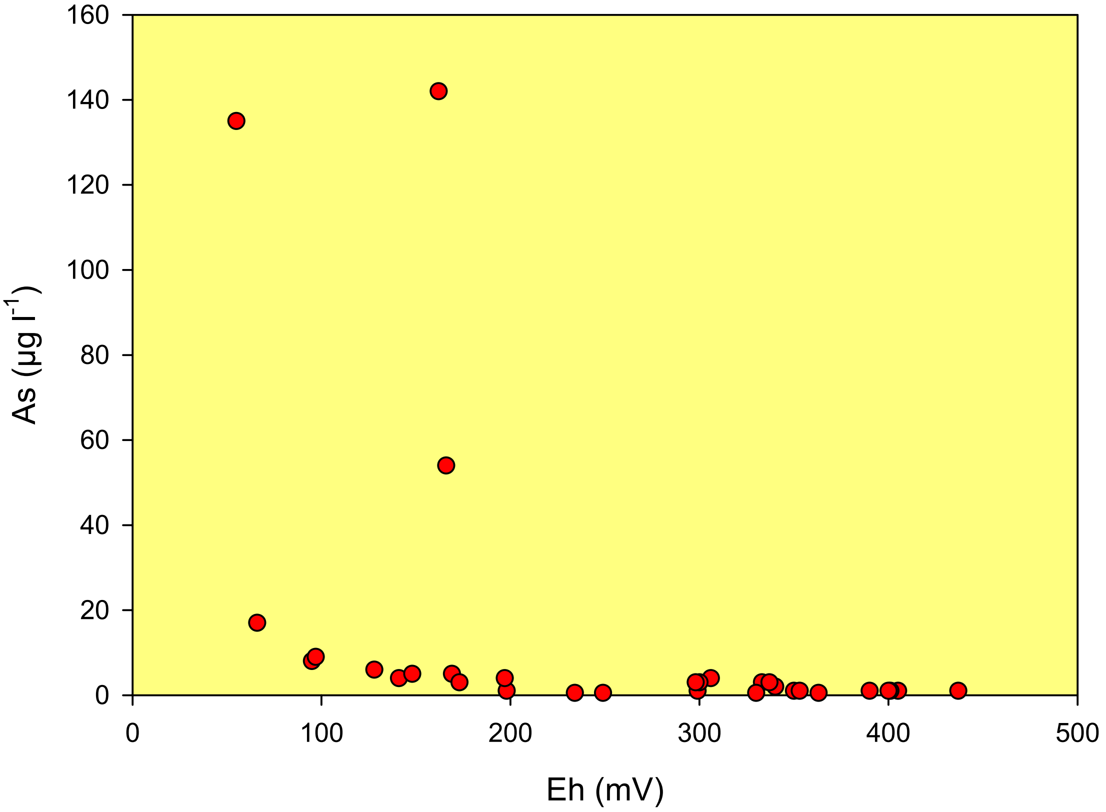


Figure 6.10 **Plot of As concentration in filtered samples against Eh. There is a general increase in concentration in more reducing groundwaters and three samples have particularly high concentrations.**

6.5.3 Ion exchange reactions

The majority of recharge groundwaters are dominated by Ca and HCO_3 ions owing to the dissolution of calcite cement. Cation exchangers within the recharge zone of the aquifer will therefore have a dominance of Ca adsorbed on to 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:

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

where X indicates the soil 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-Cl_2 type. This process will operate in reverse if groundwater 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-HCO_3 type water, (Appelo and Postma, 1991).

The range of chemical compositions encountered in the Manchester and East Cheshire aquifer indicate that a diverse range of exchange processes are taking place. Two of the samples (Threfals, Cook Street and Lanes Landscapes) trend towards Na-HCO_3 type which indicates that freshening is occurring within the aquifer but conversely other samples (e.g. Magnesium Elektron) trend towards Ca-Cl type, which is characteristic of an aquifer undergoing salinisation.

The Na/Cl ratio is a useful indicator of whether any increase in Na is due to mineral weathering and ion exchange or mixing with an older connate water. An excess of Na above the molar Na/Cl seawater ratio of 0.85 implies that there is an additional source of Na in the system i.e. Na derived from water-rock interaction. Many of the samples for the Manchester and East Cheshire area have elevated Na/Cl ratios some of which are greater than 4, indicating that water-rock interaction is important in contributing Na to the groundwater. ESI (2003) interpreted the elevated Na/Ca and depressed Ca/Cl ratios as indicating that sodium was being actively displaced from ion exchange sites by calcium in the recharge waters. This was also observed by Tellam (1995) in the Lower Mersey Basin. Furlong (2001) calculated that only twenty to thirty pore volumes of fresh groundwater had passed through the aquifer since it last contained saline groundwater.

6.5.4 Mixing with older formation water

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. The high chloride to sulphate ratios observed in the Manchester and East Cheshire aquifer suggest that much of the increase in salinity in the area is due to mixing between saline and fresh groundwater as well as water-rock interaction.

The Trafford Park area has been the subject of a number of investigations into its groundwater chemistry, notably its high salinity. The salinity problems were first documented in the wartime pamphlet for the area (Robertson, 1941). Saline groundwater also occurs in the vicinity of Chat Moss [NGR SJ 704 956]. The values of SEC in the Trafford Park area have been found to exceed 10 000 $\mu s\ cm^{-1}$. Elevated concentrations of Na and Cl are predominantly responsible for the high SEC, however, other major cations i.e. Ca, Mg and K are also present at high concentration in this area. Investigations by Tellam (1995) concluded that the salinity was most likely to be derived from evaporite dissolution. Pitman (1981) suggested that the salinity resulted from intense groundwater abstraction in the area. A mound of saline groundwater at ca. -100 m aOD was observed (with a depression of the water table to -12 m aOD. Stansbury (1994) re-evaluated the distribution of saline groundwaters and noted a correlation with the area of thicker drift in the Didsbury Depression, thought to be an extension of the Worsley Fault. It was suggested that the raised mound of more saline water might be the result of incomplete flushing of older saline waters or preferential flow of saline waters from depth moving along the Worsley fault.

A ridge of saline water has been noted beneath the Lower Irwell and Mersey (Tellam et al., 1986) and is thought to be the result of incomplete flushing in an area where groundwater is discharging to rivers. Variations in the spatial distribution of saline groundwater in the Lower Mersey Basin have been ascribed to incomplete flushing through impermeable fault blocks. ESI (2001) suggest that a similar mechanism along the Worsley Fault could be responsible for the high salinity at Trafford Park.

In the central and southern part of the aquifer, the spatial distribution of chloride has no clear pattern: differences in Cl concentration are found between boreholes which are close to each other and of similar depth. It is possible that this relates to the complex geology of the area and variations in transmissivity. In parts of the aquifer, notably the northern part, chloride and sulphate are both found in high concentrations. Conversely, to the south, particularly adjacent to faults, chloride and sulphate are relatively low. Fluoride concentrations are also low adjacent to the fault and in the north of the study area in the Irwell Valley.

Br/Cl ratios have been used to help determine sources of salinity (Edmunds, 1996). Bromide concentrations may reflect marine-derived inputs (i.e. between the rainfall ratio: 4.2 to 6.3 x 10^{-3} (Edmunds, 1996) and seawater ratio 3.47 x 10^{-3}). The Manchester groundwaters show a large range of Br/Cl ratios from 5.1 x 10^{-4} to 4.16 x 10^{-3}. Low ratios of Br/Cl are typical of the evaporite mineral halite (NaCl) which generally has a value of around 1 x 10^{-3}. The Br/Cl ratio shows a negative correlation with Cl (Figure 6.11) implying that much of the increase in salinity especially in the high Cl groundwaters is related to halite dissolution, probably from evaporite sequences. Both Pitman (1981) and Tellam (1995) suggest that the saline water originated by dissolution of halite deposits in the overlying Triassic Mercia Mudstone Group. Tellam (1995) suggested that the saline waters entered the aquifer following basin inversion, probably in the Tertiary, which would have permitted contact along fault boundaries between the Mercia Mudstone Group evaporites and the sandstones. Fresh groundwater flushing would have occurred during the intervals of low sea-level in the Quaternary and mixing with meteoric recharge water would have diluted the saline waters.

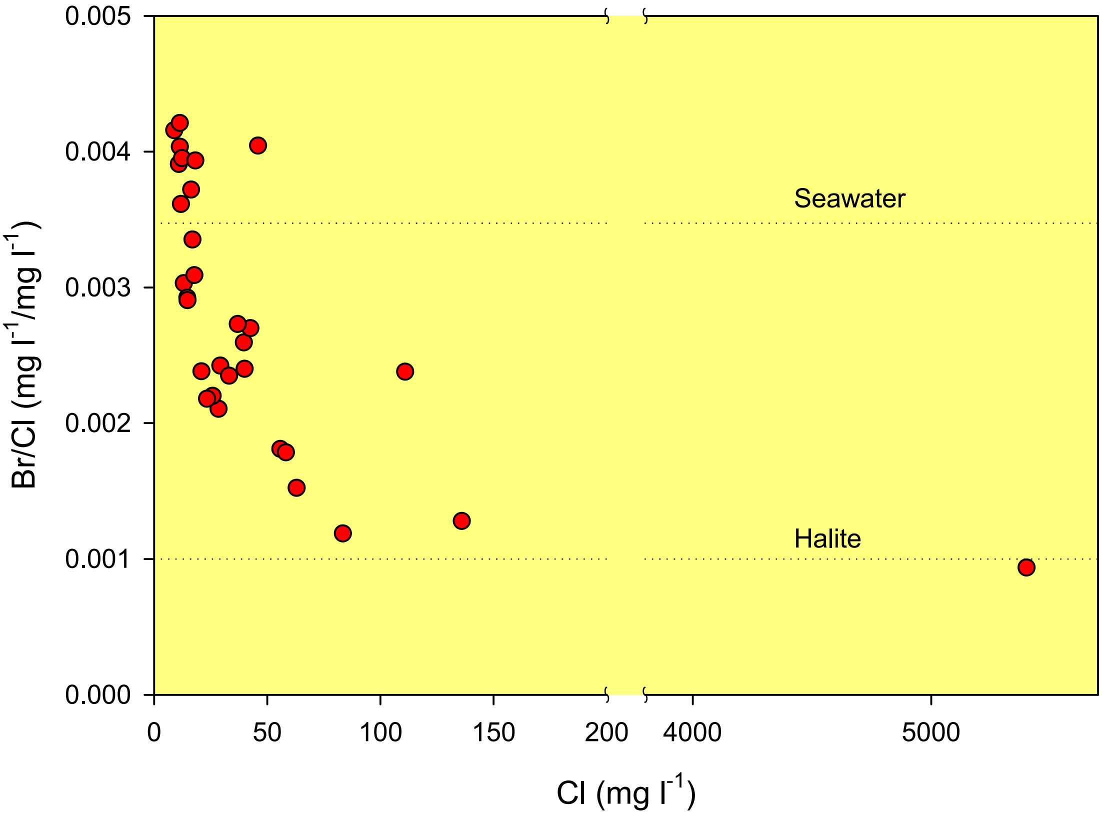


Figure 6.11 Plot of Br/Cl ratio against Cl.

6.5.5 Trace elements

Iron and manganese are present within the groundwater, often at relatively high concentrations, although in some instances this may in part be due to the fact that some samples may not have been filtered and contain particulate Fe and Mn. Since many trace elements are easily sorbed onto Fe and Mn hydroxides, the fact that the waters have not been filtered makes the interpretation of trace elements and redox sensitive species difficult.

The current Drinking Water Standards (DETR, 2000) are 200 $\mu g\ l^{-1}$ for Fe and 50 $\mu g\ l^{-1}$ for Mn. The median values for the Manchester and East Cheshire aquifer are 274 $\mu g\ l^{-1}$ and 196 $\mu g\ l^{-1}$ respectively. Of the new samples (which were filtered) 12 out of 32 samples exceeded the Drinking Water Standard for Fe, and 22 out of 32 exceeded the standard for Mn by more than an order of magnitude. High Fe and Mn concentrations are found in the Trafford Park area and along the Irwell Valley in particular. High Fe concentrations in the Trafford Park area are found at shallow depths. Gunnemyr (1998) noted that high iron concentrations were found in the vicinity of surface water courses and suggested that this may related to organic material from the river being drawn into the aquifer where its breakdown gives rise to reducing conditions. Lower Fe concentrations occur to the south of Manchester and may be related to oxidising conditions as a consequence of thin or more permeable cover (Figure 6.9). The distribution of Mn in groundwater is more variable but lower concentrations generally seem to occur in valleys and may therefore also relate to drift cover or perhaps recharge from the rivers.

The source of the Fe and Mn is most likely to come from reductive dissolution of Fe and Mn oxyhydroxides, which form cements within the sandstones, although pyrite within the Boulder Clay (Drift) and Coal Measures might also be important sources. It has been suggested that sewer leakage in urban areas may be an important process in causing reducing conditions, as in the aquifer beneath Liverpool (Tellam et al., 1986; Tellam, 1995), giving rise to high iron concentrations. Organic matter within the drift may also create locally reducing conditions.

The source of Sr in most groundwaters is dominantly from calcite or gypsum, Sr 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. Strontium concentrations are generally much lower than those encountered in the Vale of York (Shand et al., 2002) where Sr is mostly derived from gypsum dissolution. There is no clear correlation between Sr and SO_4 or HCO_3 and it is likely that there are several sources of Sr including both carbonate (calcite, dolomite) and evaporite (gypsum, anhydrite) minerals.

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 $\mu g\ l^{-1}$ in the Manchester area is considerably lower than the median Ba concentration of 271 $\mu g\ l^{-1}$ for the Cheshire area (Griffiths et al., 2002), however many of the Ba values exceed the EC Guide Level for drinking water of 100 $\mu g\ l^{-1}$. The highest recorded Cd value is for a site in the north of the study area and may be the result of pollution. The median U concentration is also quite high at 1.34 $\mu g\ l^{-1}$ and a number of the samples exceed (up to 10 $\mu g\ l^{-1}$) the WHO guide value of 2 $\mu g\ l^{-1}$. The trace elements Li and B generally increase with residence time in aquifers. They are both found at lower concentrations towards the south of the study area where groundwater levels are highest. Uranium concentrations were found to be relatively high in groundwaters in the Vale of York, where drift deposits are thick (Shand et al, 2002). In the Manchester and East Cheshire area, higher U concentrations also seem to be found in areas where thick Boulder Clay is present and lower concentrations occur where the drift deposits are thinner and/or sandier in nature.

7. BASELINE CHEMISTRY OF THE AQUIFER

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

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

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

The baseline chemistry of groundwaters in the Permo-Triasssic aquifer of Manchester and East Cheshire area is extremely variable. The data have been presented in Tables 5.1 and 5.2, which shows the ranges, median and an upper limit (97.7 percentile). The chemistry of the groundwaters presented in this study is overwhelming 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 recharge waters is modified rapidly through the dissolution of carbonate cements. Many of the groundwaters are unsaturated with respect to calcite and dolomite and this may indicate that parts of the aquifer have been decalcified; this is consistent with the presence of slightly acidic waters with low HCO_3 in some parts of the aquifer. There is a significant change in the slope of HCO_3 on a cumulative probability plot (Figure 5.4). Such a change, highlighting different populations of HCO_3, is in contrast to many aquifers. Silicate dissolution is much slower, limited by both reaction kinetics as well as silica saturation. However, this has introduced elements such as K into the groundwaters as well as minor amounts of Na, Ca and the trace elements Sr and Ba.

Mixing with more saline groundwaters has also occurred and there has been an evolution in some parts of the aquifer to waters of Na-Cl type. The area of Trafford Park in the north of the region is well known for the presence of such waters and increased salinity with time is thought to be due to over-abstraction which has induced upconing of saline water from depth. The high Cl salinity groundwaters are thought to have been modified by dissolution of halite (NaCl), possibly from the Triassic Mercia Mudstone Group and may date from Pleistocene times. The distribution of these saline waters will have been influenced by the regional flow patterns which will have determined the extent to which flushing of saline water has taken place. Flow towards the River Mersey may have produced regional upconing beneath groundwater discharge points. It has also been postulated that the regional distribution of salinity results from the contact between the Northwich Halite Formation and the Sherwood Sandstone Group (University of Birmingham, 1981). A few groundwaters also show a change towards Na-HCO_3 type, most likely as a consequence of ion-exchange during continued freshening of the aquifer.

The distribution of oxidising and reducing parts of the aquifer is extremely complex and appears unrelated to depth of borehole or bedrock geology. In fact, many shallow groundwaters are known to contain high Fe due to a relatively reducing environment. These reducing groundwaters are generally present in areas covered with poorly permeable drift. Drift deposits in the study area are often thick but very heterogeneous. This not only affects the geochemical environment of the groundwater, but also strongly modifies recharge and flow. A further complication in this area is the compartmentalisation of the aquifer due to faulting and the presence of impermeable layers within the aquifer. Overall, this has led to a complex spatial distribution which is difficult to interpret in terms of a simple flowline. This large spatial variability also makes it difficult to predict the chemistry of parts of the aquifer and requires more detailed study at the local level.

There is little information available on depth variations. Overall, there does not appear to be a consistent variation in chemistry with depth across the aquifer, probably due to the complexities mentioned above. The data from Trafford Park indicate that more saline groundwater is present at depth but it is not known how extensive this is over the aquifer as a whole.

Although most of the hydrochemical characteristics of the groundwaters represent baseline, the baseline has been significantly modified for some solutes; in particular, concentrations of elements derived e.g. from septic systems, animal wastes or the application of fertilisers. An increase in nitrate has been noted in many aquifers, particularly unconfined aquifers with little or no drift cover. A large number (ca. 30 %) of the groundwaters in the study area have very low concentrations of nitrate (Figure 5.4), as a consequence of reducing conditions. Any nitrate entering these reducing environments is likely to undergo denitrification. There are few long term historical records in the study area with which to establish the natural baseline in oxidising parts of the aquifer. There would appear to be a change in population for NO_3-N on the probability plot at around 3 mg l^{-1} which is a reasonable estimate of naturally derived NO_3-N. Other elements which are likely to have been modified by diffuse anthropogenic inputs include Na, Cl, K and SO_4. These elements are also naturally derived and are present at high concentrations in more saline groundwaters. It is, therefore, unlikely that they have extended the upper baseline of the aquifer overall. However, at a local scale they may impact significantly on the baseline. Due to the heterogeneity of groundwater chemistry across the aquifer it is difficult to assess spatially the impact of such inputs and a local baseline would need to be established for individual sites or areas of interest. The elements which are likely to have been affected by anthropogenic influences have been highlighted on Table 5.1.

8. SUMMARY AND CONCLUSIONS

The groundwaters of the Permo-Triassic aquifer of Manchester and East Cheshire display a wide range of chemical characteristics with concentrations for most elements varying over several orders of magnitude. These characteristics are determined largely by natural reactions between the groundwater and the rocks through which it passes. This baseline has been modified by diffuse pollutants including agricultural fertilisers leading locally to high nitrate and increases in other major elements such as K, Na and SO_4. Groundwaters which have been affected by point source pollution have been avoided in order to better estimate the range of the natural baseline.

A range of geochemical processes is responsible for modifying the groundwater chemistry during recharge and groundwater flow. These include:

Carbonate dissolution

The presence of carbonate cements allows rapid changes to occur during and following recharge. However, some groundwaters with relatively low pH and alkalinity may indicate areas where the aquifer has been decalcified and, therefore, buffering capacities have been reduced.

Redox reactions

Many of the groundwaters are relatively reducing, particularly in areas where thick poorly permeable drift is present. Although this has allowed reductive dissolution of Fe to occur (leading to high Fe concentrations), the reducing nature of the groundwaters has also allowed denitrification to take place. Locally high concentrations of trace elements, including As are found in moderately reducing groundwater.

Mixing with formation water

Upconing of saline groundwaters is known to occur in some parts of the aquifer e.g. Trafford Park. In this area, there has been an increase in salinity over the past few decades which is considered to be caused by over-abstraction. The increased salinity is due to elevated Na and Cl concentrations, and Br/Cl ratios indicate that the most likely source of these solutes is from the dissolution of halite present in the Triassic Mercia Mudstone Group which is consistent with previous work (University of Brimingham, 1981; Tellam et al, 1986; Tellam, 1995). There is little data on the chemistry of deep groundwater over most of the aquifer but this upconing is a potential problem if the aquifer is not managed carefully.

Other important processes include silicate dissolution of feldspar which provides most of the Si and K, and ion exchange of Ca for Na which leads to Na-HCO_3 type groundwaters or Na for Ca giving rise to Ca-Cl_2 type waters.

There is considerable spatial heterogeneity of most chemical parameters and solute concentrations. This largely reflects the complex and heterogeneous geology which is compartmentalised due to faulting and the presence of clay-rich horizons which may impede groundwater flow. This is further complicated by the presence of drift deposits which are also of variable thickness and type. These drift deposits have a significant effect on recharge of the aquifer but afford a degree of protection from diffuse or point source pollution.

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