



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL



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Baseline Report Series **1: THE TRIASSIC SANDSTONES OF THE VALE OF YORK**

Groundwater Systems and Water Quality Programme
Commissioned Report CR/02/102N



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Environment Agency Dissemination status

Internal: Release to Regions

External: Public Domain

ISBN: 978-1-84432-626-6

Product code: SCHO0207BLXX-E-P

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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.

Cover illustration

Vale of York from Sutton Bank (NGR 451 582).

Key words

Baseline, Sherwood Sandstone, York, water quality, hydrogeochemistry, UK aquifer.

Bibliographic Reference

Shand, P, Tyler-Whittle, Morton, M, Simpson, E, Lawrence, A R, Pacey, J & Hargreaves, R. 2002 Baseline Report Series 1: The Permo-Triassic Sandstones of the Vale of York
British Geological Survey Commissioned Report No. CR/02/102N

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Baseline Report Series: 1. The Triassic Sandstones of the Vale of York

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FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

In order to interpret the water quality variations in terms of the baseline, some knowledge of the residence times of groundwater is required. For this purpose both inert and reactive chemical and isotopic tracers are essential. Measurement of the absolute age of groundwater presents many difficulties and radiocarbon dating is the most widely used technique. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water may also provide indirect evidence of residence time. The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium (^3H), dissolved greenhouse gases -chlorofluorocarbons (CFCs) - and certain micro-organic pollutants may provide evidence of a recent component in the groundwater. The baseline has been modified by man since earliest times due to settlement and agricultural practices. However, for practical purposes, it is convenient to be able to distinguish water of different 'ages': (i) Palaeowater - recharge originating during or before the last glacial era i.e. older than c.10 ka (ii) Pre-Industrial Water (pre 1800s), (iii) Pre-War (1940's) and (iv) modern 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 Triassic Sherwood Sandstone forms an important aquifer in the north east of England. The area covered in this study extends from Cleveland to Selby including the Vale of York. The report provides a guide to assess the variations in baseline chemistry and the dominant geochemical processes operative in this part of the Sherwood Sandstone aquifer. It is hoped that it will be of use in water quality management and also a basis on which to manage future incidents of contamination of the aquifer.

Much of the area is dominated by farmland although local light industries are present around some of the larger towns. The aquifer provides public and private water supplies to towns, farms and industry. The hydrochemistry of the groundwater is variable but, in general, salinity is higher than further south around Nottinghamshire. This is in part related to the fact that the aquifer sediments change northwards to become finer grained sandstones, hence transmissivities are low and groundwater circulation is slower. However, the dominant control on groundwater chemistry is related to the dissolution of carbonate (calcite, dolomite) and sulphate (gypsum, anhydrite) cements which are present in the aquifer. Increases in salinity close to the confined margin of the Mercia Mudstone are most likely caused by dissolution of evaporites at the base of the Mercia Mudstone Group. Sulphate concentrations are also high at the western margin of the aquifer and may be related to dissolution of evaporite minerals from the underlying Permian strata.

Drift deposits also become more important than further south, reaching thicknesses of more than 40 m in the north of the study area. These drift deposits are variable, ranging from permeable sands and gravels to impermeable lacustrine clays (especially between Thirsk and Selby). Drift “windows” exist in the more permeable deposits allowing oxygenated, nitrate-rich recharge to occur. The flow of this water beneath the impermeable drift, where a redox boundary is formed, has allowed nitrate reduction to occur. The redox control is also manifested by increases of Fe, Mn and NO₂ along flowlines beneath the clays.

It is concluded that the properties of groundwater in the Vale of York area are overwhelmingly determined by natural reactions between rainwater reacting with the bedrock and drift deposits. This natural baseline is expressed as a range of concentrations which, for some elements, can vary over several orders of magnitude. The concentrations of some elements are enhanced over the natural baseline. Nitrate and chloride, for example, have been modified by agricultural and industrial practices. The presence of relatively high concentrations of several trace elements is considered to be due to entirely natural processes. These include locally enhanced levels of arsenic, barium and uranium which may exceed drinking water standards.

2. PERSPECTIVE

The area of this study comprises the Permo-Triassic sandstone aquifer stretching from Cleveland in the north to Selby in the south and includes the Vale of York (Figure 2.1). It is flanked to the west by the scarp of the Permian Magnesian Limestone and the older mainly Carboniferous rocks of the Pennines. The area to the east is dominated by low lying land of upper Triassic mudstones and by younger Jurassic rocks. The Rivers Ouse and Swale drain from the Pennines to the west before flowing south through the Vale of York to meet the Humber. The River Tees drains eastwards over the northern part of the Sherwood Sandstone through Middlesbrough.

The Permo-Triassic sandstones form the second most important aquifer in the UK, supplying around 25% of licensed groundwater abstractions in England and Wales (Monkhouse & Richards, 1982). The aquifer provides water supplies to a number of large towns particularly in northern and central England where it is the most important aquifer. The groundwater of the Sherwood Sandstone aquifer is used both as a potable resource and for a wide variety of farming (including spray irrigation) and industrial uses. Licensed abstraction rates are of the order of 44,000 MI a⁻¹.

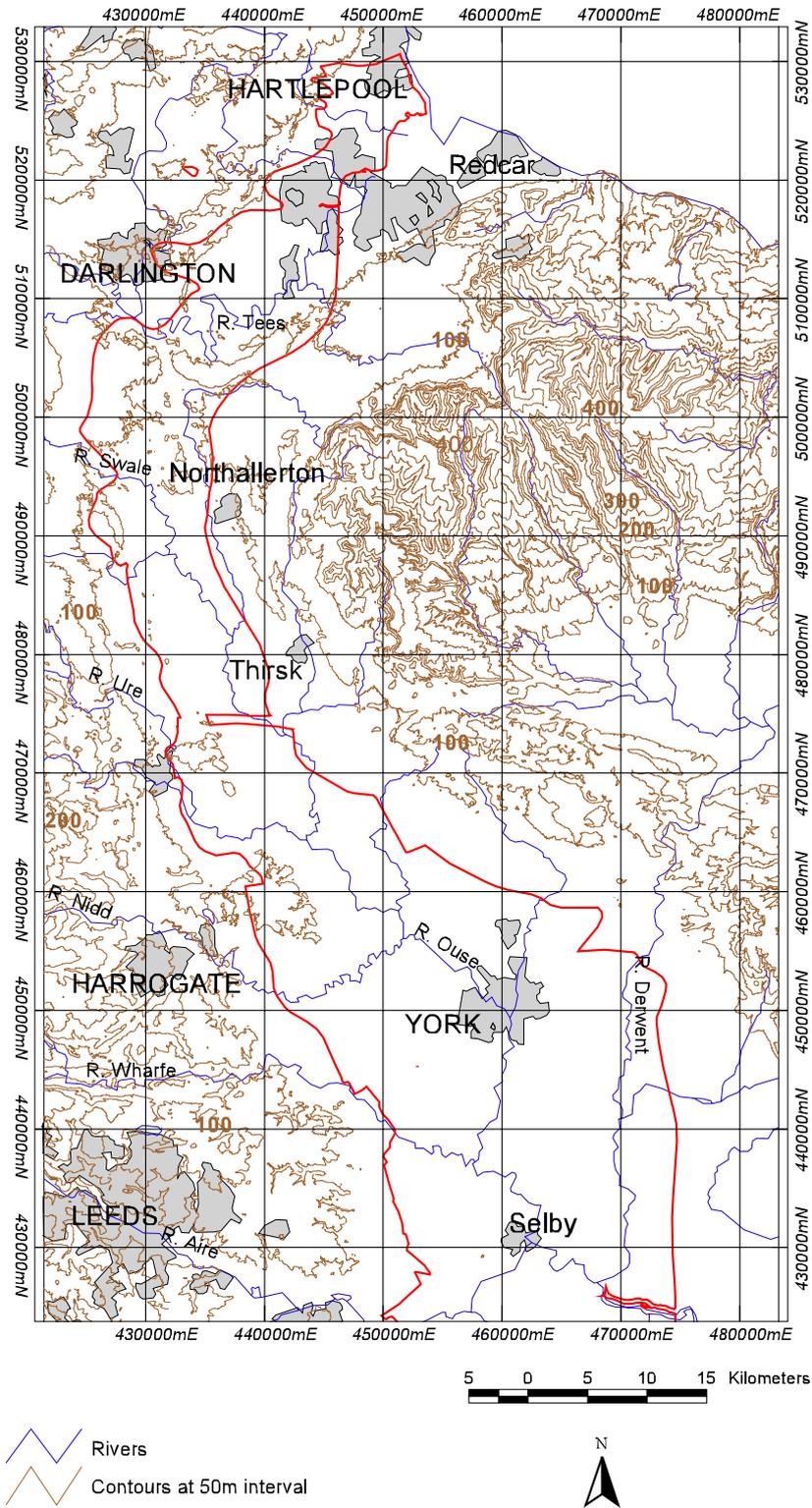
The total is split by use as shown below.

Abstraction use	% of total licensed abstraction
Agriculture	33
Industrial	32
Public Water Supply	25
Amenity	5
Power generation	5

Shallow wells into the superficial deposits were used for the supply of farms and cottages (Gray, 1961). These were often unreliable, of varying quality and prone to pollution and have generally long been abandoned.

Land use is dominated by farming (arable and livestock; Figure 2.2) although industrial areas are present around some of the larger towns (e.g. York, Selby; Figure 2.3) and particularly in the north around Middlesbrough and Darlington where development of extensive steel making and chemical industries occurred. However, this northern portion of the aquifer suffers from naturally derived poor water quality and there is less abstraction than in the more southerly areas.

Most of the area is covered with thick drift deposits limiting both recharge to the aquifer and hydraulic contact between the rivers and the aquifer. However, the drift provides the groundwater with protection from pollution at the surface, although “windows” of thin permeable drift can provide pathways for pollution. There are lots of potential pollution sources and these can, and do, result in anthropogenic impacts on groundwater chemistry. The greatest current impact is from diffuse or wide-spread pollution sources, dominantly agriculture. The impact is seen as high nitrate concentrations from the use of fertilisers and increasing levels of pesticides in some sources of groundwater. Point source pollution from industrial activities, waste disposal and spills can have a devastating effect on individual abstractions.



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Figure 2.1 Topographic map of the study area. Red outline shows outcrop area of the Sherwood Sandstone.



Figure 2.2 Arable farming in the Vale of York near Ellerton (NGR 425 525).

Current issues in the area relate to:

- restricted areas of heavily utilised groundwater resources particularly in the south around Selby
- water quality issues related to salinity or high Fe and Mn in reducing parts of the aquifer
- nitrates from the dominant rural land use in recharge areas.
- the need to understand the surface-water groundwater interaction and the links to environmental requirements
- use of the aquifer for storage through Aquifer Storage and Recovery (ASR) schemes
- impact of climate change

The relationship between groundwater, drift and rivers is poorly understood, but a knowledge surface-groundwater interaction is essential for the effective management of both the aquifer and rivers, and for implementation of the Water Framework Directive.

The focus of this report is on the variations in water quality related to natural geochemical processes and how these vary spatially and with depth across the aquifer. Attempts will be made to ascertain relative groundwater ages and to describe temporal variations, but relevant data are limited.



Figure 2.3 Light industry in the Vale of York from York Minster.

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 Permian and Triassic rocks of Britain were formed under arid conditions when Britain was much closer to the equator than today. The sedimentary sequence comprises fluvial and desert sands with marine and evaporite sequences forming an important component of the stratigraphy. Due to a lack of fossil evidence the boundary between the Permian and Triassic is often not well established. In north-east England these strata form the onshore extension of a major sedimentary basin dipping towards the east and into the North Sea where they are covered with younger Jurassic and Cretaceous rocks.

The Permian rocks comprise a lower and upper sequence divided on the basis of the onset of a marine succession. The lower Permian generally comprises a sequence of basal breccias and yellow sands. The upper sequence (including the Magnesian Limestone) comprises a complex series of evaporites, limestone and dolomites formed during incursions of the “Zechstein Sea” and subsequent evaporation cycles. Detailed studies show that these result from at least five periods of marine transgression and regression (Smith, 1992). The Triassic rocks of England and Wales comprise:

- a lower sandy sequence the Sherwood Sandstone Group;
- an upper mudstone series called the Mercia Mudstone Group and;
- a limestone series (the Penarth Group) at the top.

The Sherwood Sandstone formed dominantly in continental fluvial and aeolian environments. In the study area (Figure 3.1), it is underlain by marls and saliferous marls of Permian age and the aquifer becomes confined eastwards beneath the Mercia Mudstone (Figure 3.2). The Sherwood Sandstone Group comprises sandstone formations which are locally pebbly (Bunter Pebble Beds). They are largely of fluvial origin but wind-blown deposits, marls and breccias also occur suggesting local depositional environments typical of modern desert basins. Within the Mercia Mudstone Group, beds and nodules of gypsum and anhydrite are present.

In Yorkshire and Cleveland, the Sherwood Sandstone Group comprises a thick sequence (thickening northward from 250 to 450 m) of fine- to medium-grained sandstones with common argillaceous beds and lenses. It is of early Triassic (Scythian) age and is underlain by mudstones and siltstones of the Roxby Formation (formerly Upper Permian Marl). Although largely impermeable, the marls beneath the sandstone have been affected by faulting which may allow groundwater movement between the Magnesian Limestone and Sherwood Sandstone (Aldrick, 1974). The aquifer generally dips gently (ca. $1 - 2^\circ$) towards the east, forming an outcrop 8 to 20 km wide, before dipping below the mid to late Triassic Mercia Mudstone Group. Faulting is present in several areas: around Teesside and Thirsk these faults have an E-W trend whereas further south around Selby they have a NW-SE trend. One major fault (Topcliffe Fault, NGR 440 476) traverses the sequence in a 0.5 km wide zone, acting as a barrier to groundwater flow (Koukis, 1974). Geophysical techniques (surface resistivity) have shown that east-west or northeast trending faults are common close to the junction of the Sherwood Sandstone and Mercia Mudstone east of York, with throws of up to 80 m (Hawkins & Chadha, 1990).

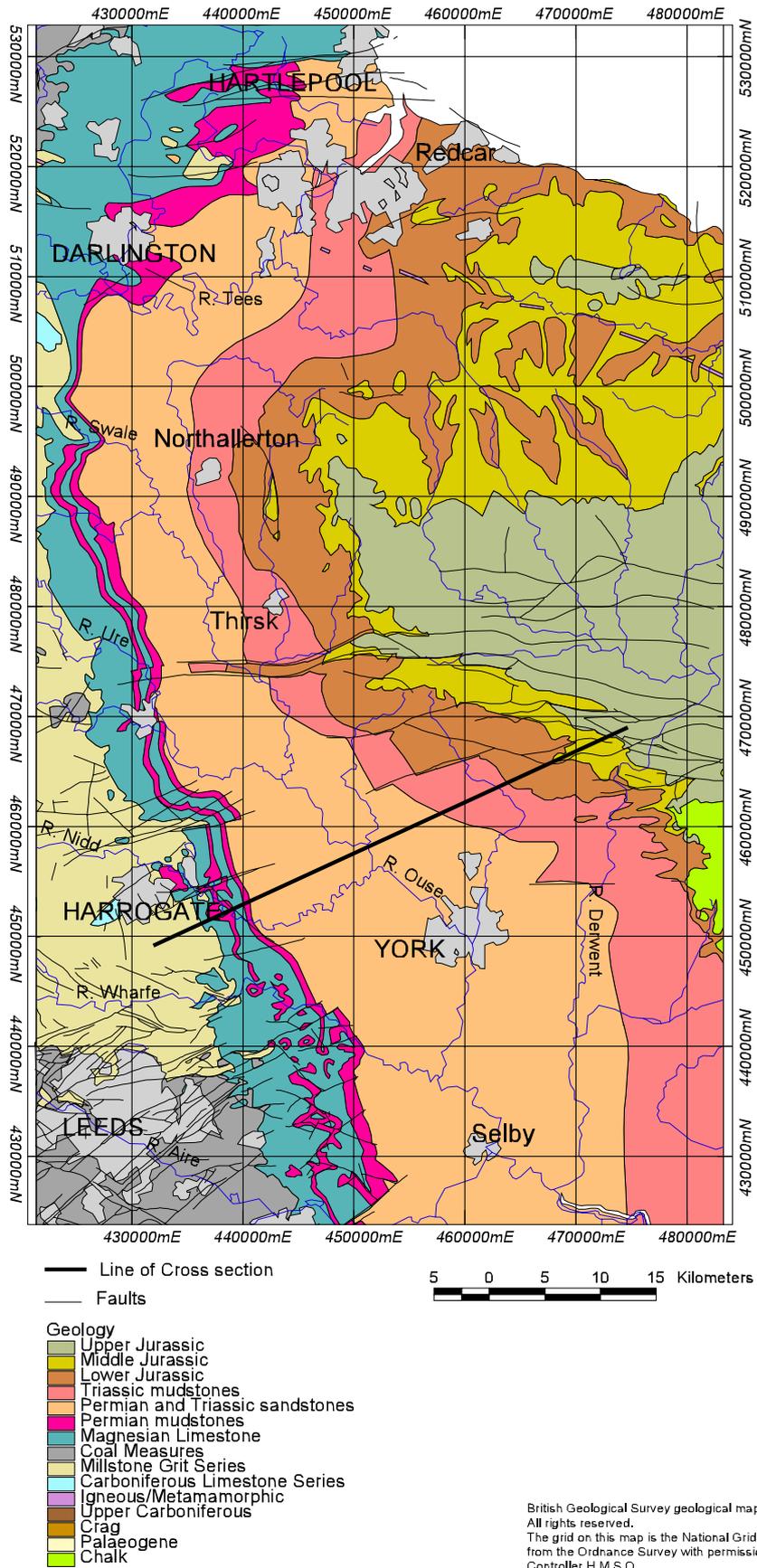


Figure 3.1 Geological map of the study area showing main towns and rivers. (Line of section shown on Figure 3.2).

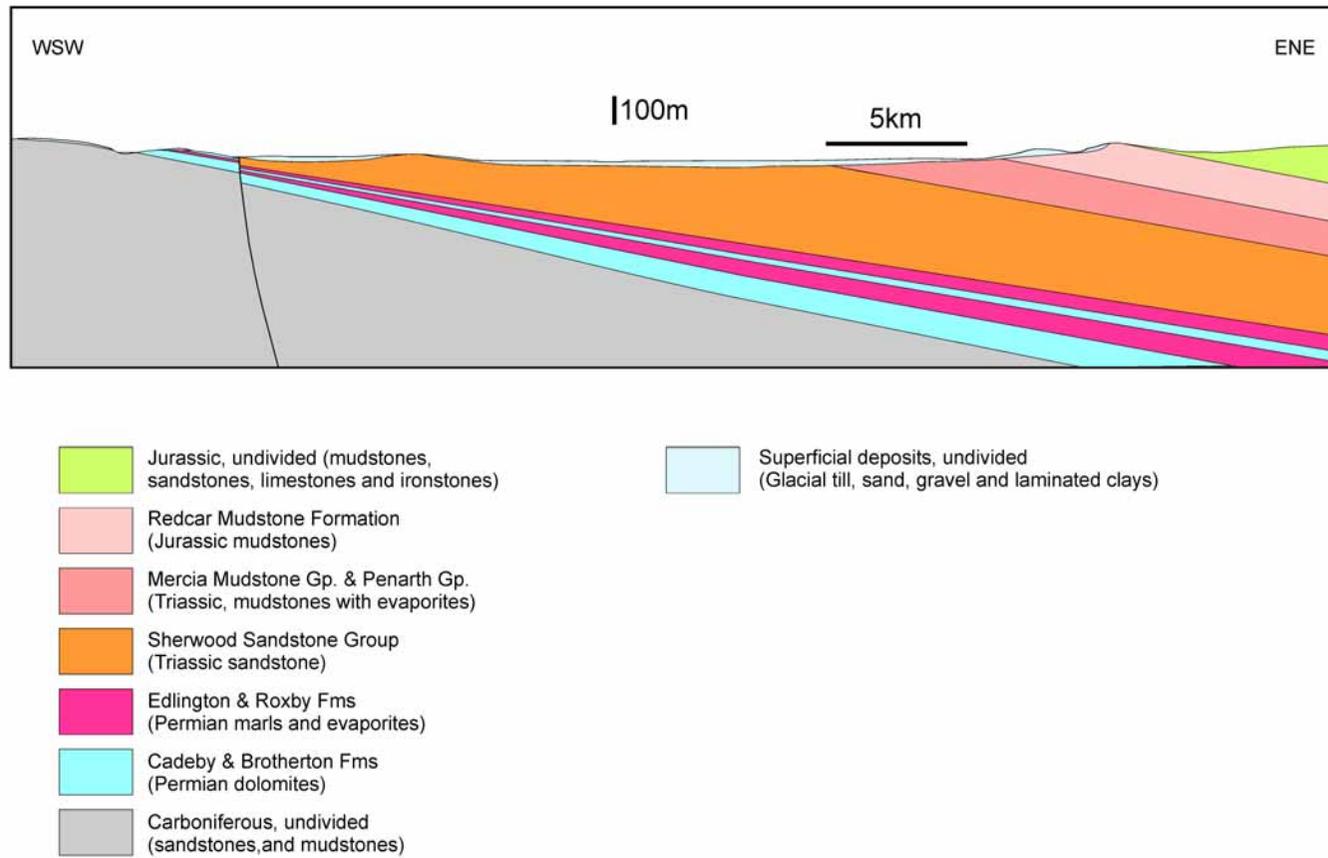


Figure 3.2 Simplified geological section trending WSW to ENE from around Harrogate (see Figure 3.1 for location).

There are no formally defined formations in the Sherwood Sandstone in the Yorkshire to Cleveland area but three informal units can be recognised. The lowest unit (18 - 44 m thick) comprises variably coloured red, brown, orange, grey, buff and white sandstones which are micaceous, clayey, silty, well-sorted and fine-grained. Much of the sequence is cemented by a white calcareous and locally gypsiferous clay matrix. Thin beds of red, gypsiferous mudstone occur throughout, becoming thicker and more common towards the east (Allen et al., 1997). The middle unit thickens northwards from about 230 m to nearly 400 m. It comprises red, less argillaceous sandstones which vary from fine to coarse grained with grains varying from sub-angular to rounded. A white, slightly calcareous clay-matrix is locally present but much of the sequence is uncemented, unconsolidated, friable, porous and permeable. Some of the beds are dolomitic or gypsiferous. The upper unit thickens northwards from 5 to 45 m and consists dominantly of white, grey or buff, fine- to medium-grained, micaceous, argillaceous silty sandstone, typically loosely cemented and friable. The aquifer sediments are generally finer in the north and coarsen towards the centre and east of the study area. In the Vale of York, the sandstone varies from friable to well cemented, the cement typically being secondary quartz with carbonate.

The Quaternary Ice Age had a significant effect in Britain and has exerted an important control on the geomorphology. The ice sheets left behind a complex set of deposits referred to as drift which includes boulder clay, sands and gravels. Significant drift deposits are present in the study area and thicken northwards from Doncaster through North Yorkshire (Figure 3.3). Lacustrine clays stretch from Doncaster to Thirsk and were deposited in pro-glacial lakes towards the end of the last (Devensian) ice age. However, just north of the River Aire in the Selby area there are areas of drift free outcrop of the Sherwood Sandstone. North of York the deposits are more variable but comprise mainly boulder clay. In some areas, sandy drift deposits occur (particularly on higher ground) allowing limited connection between the drift and the aquifer which allows for some recharge potential (Figure 3.4). These Quaternary deposits provide sand and gravel resources in the area (Figure 3.5). Drift thicknesses of around 15 m extend to Northallerton but this increases to over 40 m further north.

3.3 Hydrogeology

The hydrogeology and aquifer properties of the area have been summarised by Allen et al. (1997) and the reader is referred to this text for a more detailed description. The Triassic Sherwood Sandstone Group forms the main aquifer. Permian marls form a lower aquitard separating the Permian sandstones from the overlying Triassic sandstones; the Mercia Mudstone Group, which overlies and confines the Sherwood Sandstone Group forms an upper aquitard. Fine grained layers within the Sherwood Sandstone may also act as confining layers. There is a significant facies change in the aquifer with the grain size decreasing northwards from Nottinghamshire through Yorkshire.

The aquifer properties of the sandstones are significantly affected by their sedimentary structure and by post-depositional diagenesis. The high porosity of the Sherwood Sandstone suggests that much of the primary cements have been dissolved (Allen et al., 1997). The aquifer is anisotropic on a scale of metres with considerable interlayering of sands and less permeable silts present in a series of fluvial cycles; vertical permeability is generally around one tenth of the horizontal permeability.

Fractures occur widely in the Sherwood Sandstone and include bedding plane fractures, subvertical joints and faults. Fractures are known to make a significant contribution to inflow into individual boreholes (Lovell 1972, Price et al 1982). However when modelling the aquifer on a regional scale, the matrix permeability dominates suggesting only a limited lateral continuity of fractures and that fracture flow is only important probably on a scale of 10's or 100's of metres.

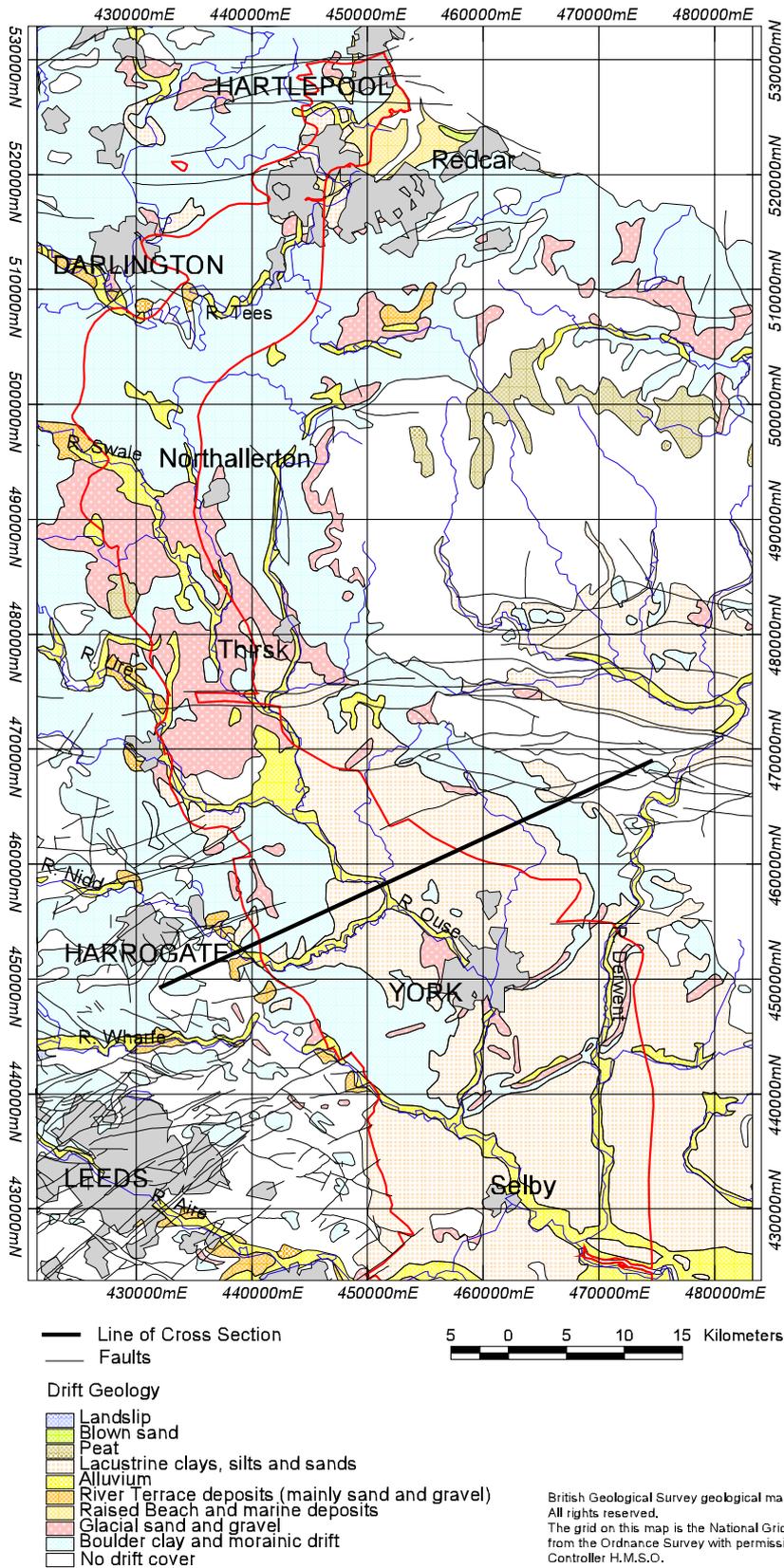


Figure 3.3 Geological map of the study area showing the distribution of drift types (Line of section shown on Figure 3.4).

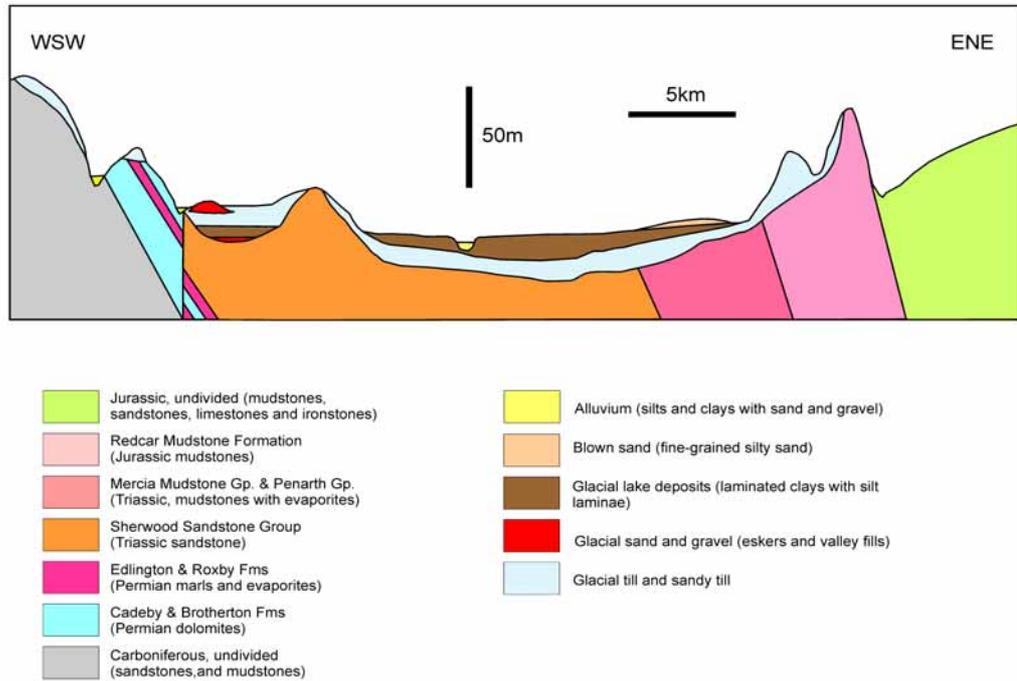


Figure 3.4 Section from WSW to ENE across the aquifer north of York to show the relationships of the superficial deposits; large vertical exaggeration to highlight the detail of the drift deposits (see Figure 3.2 for location).



Figure 3.5 Quaternary Sand and gravel deposits provide a useful resource in the Vale of York at Kiplin Hall.

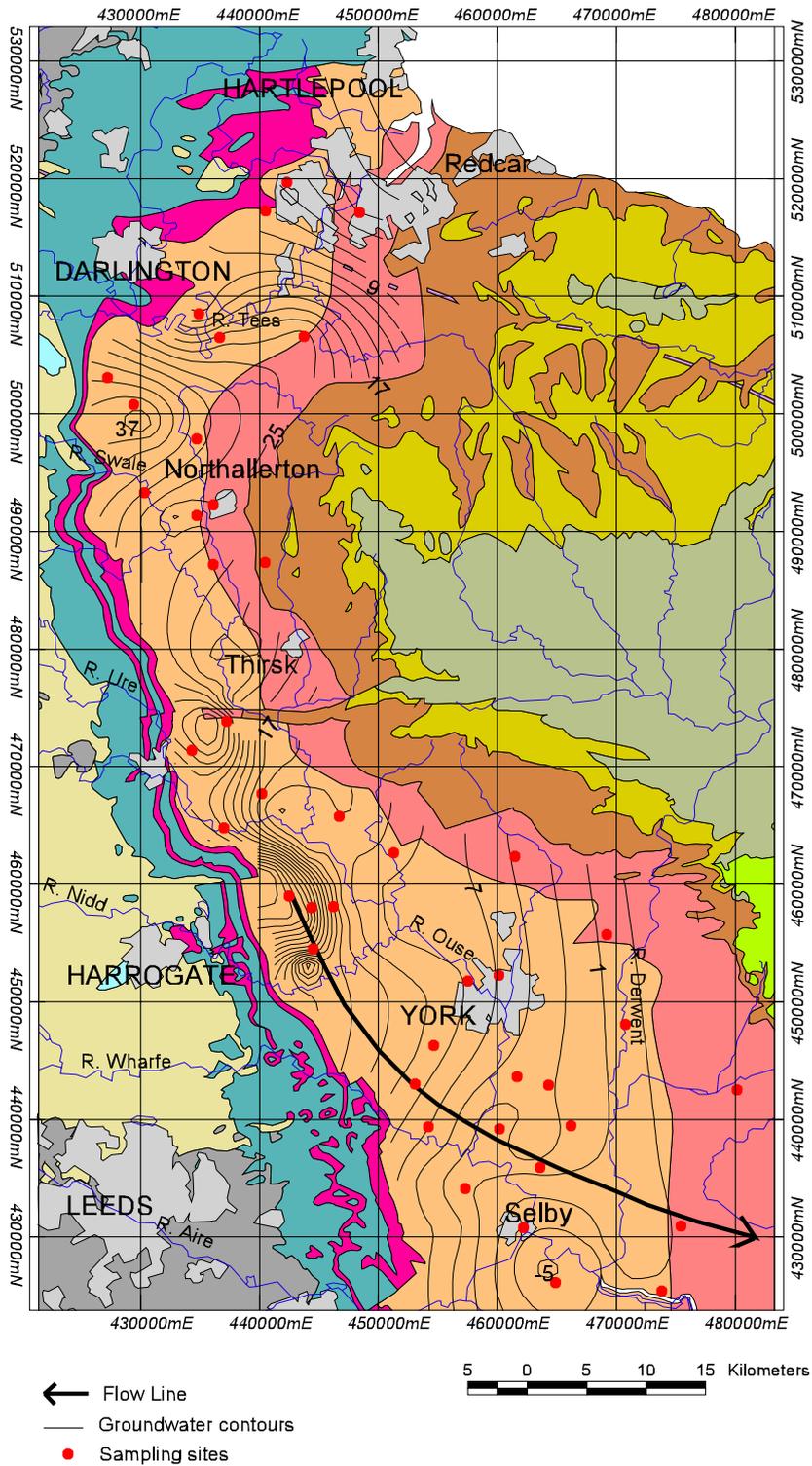
Fault planes may act to enhance flow forming recharge boundaries or form impermeable barriers to flow. Dissolution of gypsum in the top most Permian sediments can cause fractures close the Western feather edge of the outcrop and recharge to the Sherwood Sandstone appears to run down the top of the Roxby Formation.

Recharge to the Sherwood Sandstone Group at its western feather edge appears to flow along the top of the Roxby Formation (formerly Upper Permian Marl). However, recharge is significantly reduced by the thick drift deposits although sandy deposits do allow localised recharge to the Sherwood Sandstone aquifer, particularly in the west of the outcrop where the overlying drift consists of permeable sands rather than the clay found in the centre of the Vale (Allen et al., 1997). The maximum rate of infiltration is likely to be around 300-350 mm a⁻¹ in drift-free areas reducing to less than 50 mm a⁻¹ where the drift is thick (Aldrick, 1974). Interpretation of pump test data from boreholes in the drift indicate that there is little hydraulic connection between the drift and the sandstone over much of the Vale of York. The groundwater is generally effluent to the major rivers flowing over the aquifer (Aldrick, 1974).

Much of the outcrop area is low lying, especially in the valley of the River Ouse resulting in low hydraulic gradients (Figure 3.6) with only small seasonal fluctuations in water levels (typically 2-3 m). The groundwater contours are similar to those drawn by Aldrick (1974). Groundwater levels are often highest in February or March and decline until November when a more rapid rise occurs during winter (Aldrick, 1974). Local artesian heads may develop in areas where drift is present and a complex relationship exists between the drift and the underlying aquifer. In the southern part of the area the aquifer is extensively used for public and private water supplies and borehole yields are good (may be in excess of 10 000 m³/d). Aldrick (1974) noted in early pump tests that transmissivity and storage coefficients vary widely across the aquifer. In the north of the area, the finer grained nature of the sediments and lower porosity results in substantially lower permeability's with transmissivity generally less than 80 m²/d (Allen et al., 1997). This increases southwards to around 250 m²/d around York. Nevertheless, licensed abstractions amount to approximately 12 500 m³/d (Allen et al., 1997). The confined part of the aquifer generally has low transmissivities which can be attributed to intergranular flow, most of the fractures being closed due to the overburden of the Mercia Mudstone Group. Porosities are variable (ca. 8 - 38 %) with a median value of around 28% and with no significant trend with depth.

Locally, for example in the Vale of York, some boreholes may pump sand due to variably cemented, unconsolidated to friable sandstone and require screening, but in general only the Mercia Mudstone Group is cased out leaving the Sherwood Sandstone parts unscreened. Fractures are considered to be important flowpaths in the aquifer and provide higher transmissivities than expected for the fine-grained sediments in the study area. Most fracture flow occurs in the top 100 m with most fractures below this depth being closed (Allen et al., 1997). In Yorkshire and Cleveland, there is less water circulation with depth than further south giving rise to poorer water deeper in the aquifer. In the Vale of York the rivers are only locally in contact with the aquifer, and where this does occur the aquifer is naturally effluent (Gray et al. 1965). In most areas the river flows over alluvium and till.

The groundwater flow direction (as indicated by water level contours) shows a general trend eastwards from the western outcrop to below the Mercia Mudstone Group. Local groundwater highs are present east of Ripon and Catterick (Figure 3.6). The flow trend to the south of York is south-eastwards below the Mercia Mudstone but a local groundwater low is present around Selby as a result of heavily utilised resources. In the northern part of the study area there is a groundwater divide between the River Swale and Tees where the flow direction is northwards towards Darlington (Figure 3.6). There is good continuity with the River Tees in places where Sherwood Sandstone outcrops can be seen in river cuttings.



British Geological Survey geological map © NERC 2001.
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 from the Ordnance Survey with permission of the
 Controller H.M.S.O.

Figure 3.6 Geological map displaying groundwater level contours for the Sherwood Sandstone from April, 2000. Sampling sites for the present study are shown as red dots and the arrow indicates likely flow direction (see text for details).

A potential groundwater flow path is shown on Figure 3.6 based on current groundwater levels. The flow path starts on the western edge of the Permo-Triassic Sandstone aquifer outcrop east of Harrogate, and trends in a broadly SE direction before passing under the Mercia Mudstone outcrop after some 50 km.

Hydrogeologically, the flow path can be subdivided into four zones:

Zone 1: In this zone the sandstone is overlain by permeable drift (see Figure 3.3) and is characterised by steep water table gradients (c. $1/100$) indicating active recharge is occurring.

Zone 2: The Sandstone aquifer is also overlain here by low permeability drift but the water table here has only a shallow gradient ($<1/1000$).

Zone 3: Here the Sandstone aquifer passes under low permeability drift (lacustrine deposits of clay and silt; Figure 3.3). The aquifer is effectively confined and recharge through the drift is likely to be minimal.

Zone 4: In this zone, the Sandstone is confined by the Mercia Mudstone.

Within Zones 2-4, the groundwater gradient is low, typically less than $1/1000$ and, assuming an average permeability of 1-2 m/d and a porosity of about 0.25, groundwater velocities are likely to be less than 3 m per year.

It is pertinent, in the context of baseline water quality, to consider how the groundwater flow system may have changed over time. Prior to the development of the aquifer by boreholes, the groundwater flow system would be controlled by natural discharge. It is postulated here that active groundwater circulation would be largely restricted to Zone 1 with discharge from the aquifer being controlled by springs. Later as deep abstraction boreholes were drilled in Zones 1-4, pumping would induce greater recharge through the permeable drift cover (Zones 1 and 2) and through permeable “windows” within the low permeability drift in Zone 3 (e.g. where alluvium cuts through the drift to the underlying sandstone).

Given the slow rates of groundwater flow, the front of modern (<30 years) high nitrate groundwater is unlikely to penetrate more than a few hundred metres at most. Thus the boundary between where the sandstone aquifer is overlain by permeable and relatively impermeable drift is likely to represent a boundary between groundwater having a significant component of recent (<30 years) water and groundwater where the water is mainly older than 30 years. Groundwater beneath the Mercia Mudstone could be several thousand years old.

Gray (1961) noted three zones in terms of water quality in the Vale of York: (i) a zone of relatively high sulphate and hardness on the western margin of the aquifer; (ii) a zone in the centre of the outcrop along the rivers Swale and Ouse; (iii) a zone of high sulphate and hardness along the eastern margin towards the Mercia Mudstone. The higher sulphate in some boreholes in Zone 1 was considered to be due to dissolution from Permian evaporites (Aldrick, 1964). In the Ripon area, Thompson et al. (1996) have shown that groundwater under artesian pressure within the Permian Cadeby Formation (limestone) moves upwards through massive gypsum deposits and into the valley deposits of the River Ure. It is therefore possible that leakage from such formations takes place into the Sherwood Sandstone aquifer, particularly where extensive faulting occurs. Groundwater levels indicate that the low salinity groundwater in the central zone cannot be due to recharge from rivers since the rivers are effluent. There are few data available on groundwater quality in the superficial and drift deposits, but early work (Gray, 1961) indicated that water quality is extremely variable, both in terms of chemistry and bacterial quality.

3.4 Aquifer mineralogy

The Roxby Formation below the Sherwood Sandstone consists predominantly of reddish brown mudstone and siltstone with beds of gypsum and anhydrite. Potash salts, which imply extensive evaporation are present in the Permian of north-east Yorkshire

Rhythmic units are commonly present within the Sherwood Sandstone, and generally change from clay-flake breccias at the base fining upwards through cross-bedded sandstone, fine-grained sandstone and silt to marl. However, not all units contain the complete sequence and the upper marls are frequently absent (Aldrick, 1974). The sandstones varies from friable to well-cemented. Although the mineralogy is dominated by quartz and feldspar, the sandstones contain a wide variety of cements including quartz, calcite, dolomite, gypsum, anhydrite, halite, iron oxide and clay minerals. Other accessory minerals include muscovite, biotite, chlorite, iron oxide, tourmaline, apatite and zircon. The cementation of quartz and carbonates is generally more uniform in the north of the study area (Koukis, 1974). In particular, the carbonate and evaporite minerals exert a dominant control on groundwater quality because these dissolve much more rapidly than the silica and silicate mineral phases and (for the evaporite minerals) may be highly soluble. The diagenetic influences following sedimentation have had a dramatic effect on the porosity and permeability of the sandstones (Milodowski et al., 1987). The sandstones still contain remnants of calcite and dolomite at outcrop (Figure 3.7) but much of the cement has been dissolved or where present shows signs of dissolution (Figure 3.7b). In places calcite is often fresh in contrast to dolomite (Figure 3.7c) which shows extensive dissolution indicating that dedolomitisation is occurring in the aquifer. Deeper in the aquifer calcite and dolomite cements are more abundant. The clay minerals are dominated by kaolinite, montmorillonite and illite (often in association with grain rims). Montmorillonite-illite is dominant in the northern part of the area (north of northing 470), increasing northwards and with depth. These clays are less abundant further south where kaolinite plays a more predominant role (Koukis, 1974). Lithic clasts are also common and the sandstones are therefore strictly classed as feldspar arenites or litharenites.

The Mercia Mudstone Group comprises reddish brown and to a lesser degree, greenish grey, dolomitic mudstones with evaporite minerals especially gypsum and anhydrite but also including halite and locally celestite.

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharge waters and should be considered as representing minimum baseline concentrations. The rainfall chemistry averaged for 1988 is shown in Table 3.1 for Thorganby (SE 676 428) north of Selby. The data have been multiplied by 3 in the last column in order to estimate the approximate enrichment due to evapotranspiration. Although Cl may be assumed to behave conservatively during most recharge conditions, this is not the case for other elements e.g. K and N species which may be taken up by vegetation, and concentrations may therefore be less in recharge waters than rainfall. Nevertheless, the table indicates the order of magnitude of concentrations expected in young waters which have not reacted with vegetation, soils or aquifer minerals. For chloride, concentrations in groundwaters prior to agricultural pollution or mixing with other waters would be expected to be around 11-12 mg l⁻¹.

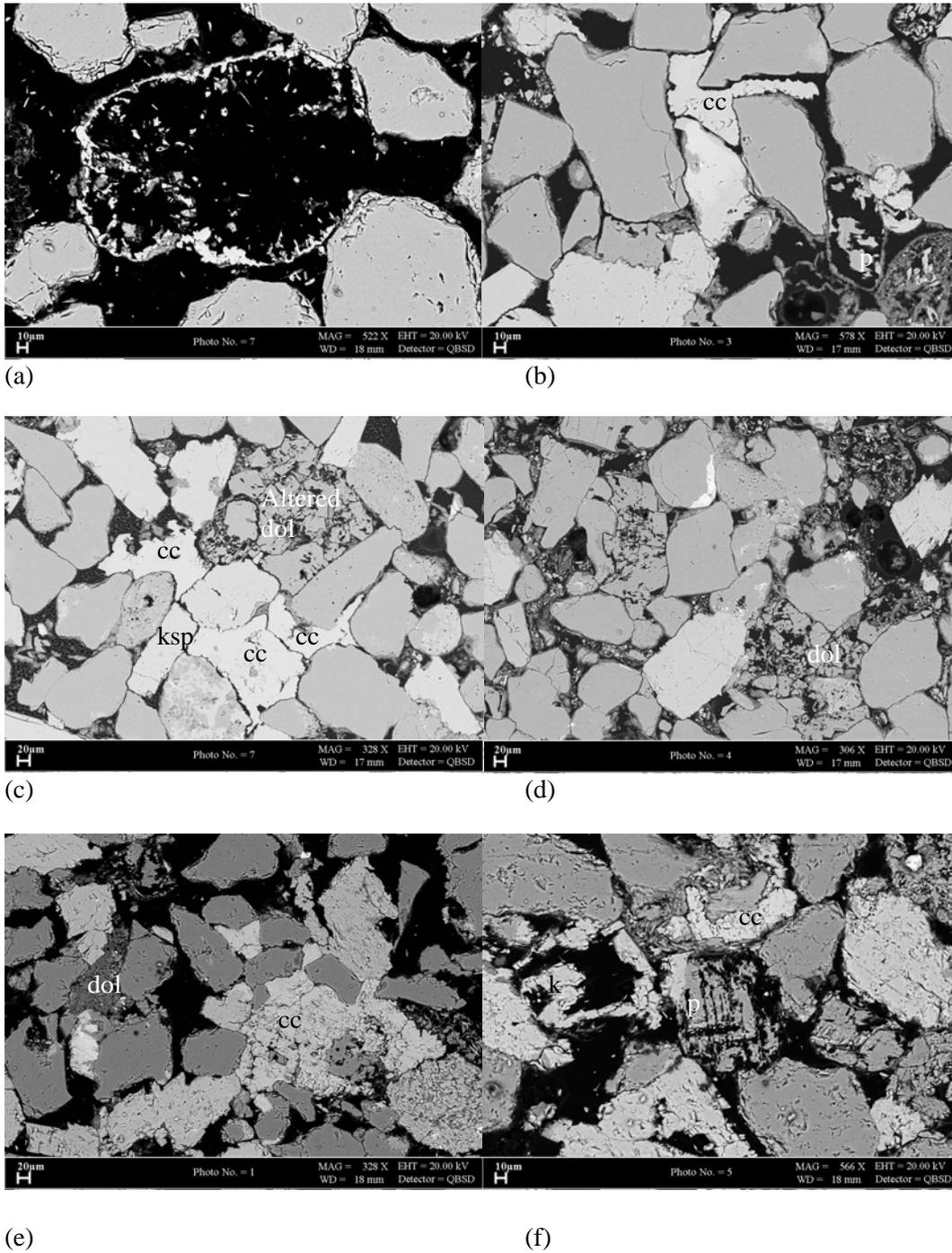


Figure 3.7 SEM photographs of the Sherwood sandstone from outcrop (a-d) and the Wistow borehole. (a) Rim of secondary potassium feldspar preserved as remnant following dissolution of primary potassium feldspar; (b) Quartz grains (grey), partially dissolved plagioclase feldspar (p) and calcite (cc); (c) remnant dolomite (dol) with fresher calcite (cc) and potassium feldspar (light); (d) sandstone showing region of partially dissolved dolomite (dol); (e) Wistow borehole (57.7m depth) showing altered K-feldspar (lower right) and more abundant calcite (cc), and dolomitic cement (dol); (f) Alteration of plagioclase (p) and K-feldspar (k).

Table 3.1 Rainfall chemistry from Thorganby

The data are for 1988 taken from The UK National Air Quality Information Archive (<http://www.aeat.co.uk/netcen/airqual/>).

<i>Thorganby</i> Parameter	Rainfall	Rainfall (x3)
pH	4.40	
Na (mg l ⁻¹)	1.54	4.62
K (mg l ⁻¹)	0.19	0.56
Ca (mg l ⁻¹)	1.06	3.19
Mg (mg l ⁻¹)	0.27	0.82
Cl (mg l ⁻¹)	3.80	11.4
SO ₄ (mg l ⁻¹)	3.29	9.87
NO ₃ (mg l ⁻¹)	2.10	6.30
NH ₄ (mg l ⁻¹)	0.95	2.85
Total N (mg l ⁻¹)	1.21	3.64
SEC (µS cm ⁻¹)	42.9	
Rainfall amount (mm)	448.3	

3.6 Landuse in the area

The dominant land use over the aquifer is arable with minor areas of managed grassland (Figure 3.8). The main Urban areas are present mainly in the north around Middlesbrough and in the south around York, although many smaller towns and villages are found throughout the region.

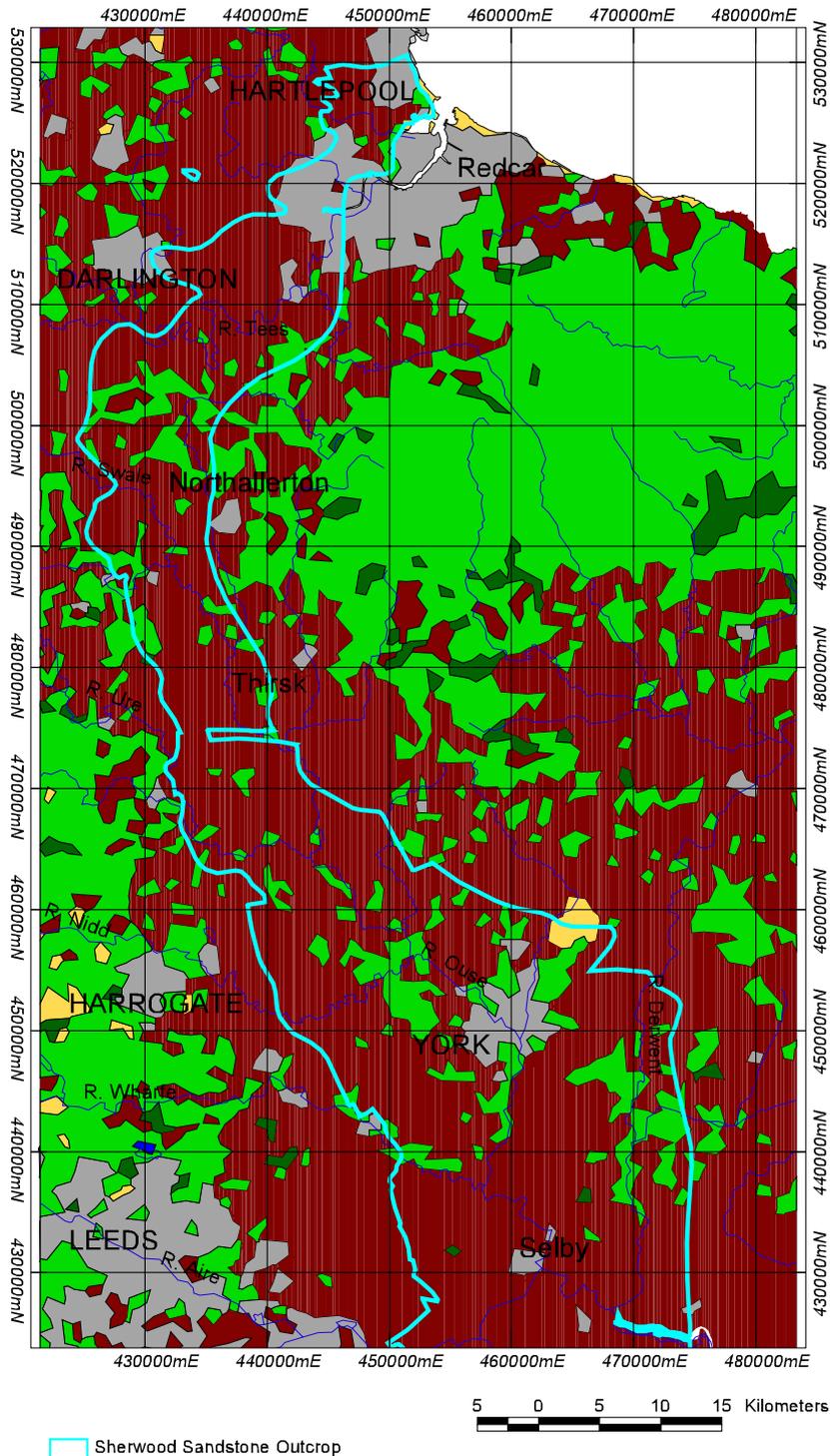


Figure 3.8 Generalised landuse map of the study area. Data from Land Cover Map 1990, supplied courtesy of the Centre for Ecology and Hydrology © NERC.

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 44 samples were collected during October 2000 from private supplies between Selby in the south and Darlington in the north. These provide a good regional coverage of the aquifer (Figure 3.6). The samples were collected from boreholes used for the Environment Agency's groundwater monitoring programme. All boreholes were pumped for an estimated 2 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 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 is 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 (Figure 4.1). Other on-site measurements included temperature ($T^{\circ}\text{C}$), 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 $0.45\ \mu\text{m}$ filters and the aliquot for cation and trace elements was acidified to 1% v/v HNO_3 to minimise adsorption onto container walls. Additional samples were collected in glass bottles for stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$).



Figure 4.1 Unstable parameters are measured in an anaerobic throughflow cell.

A statistical summary of the chemical data is shown on Tables 5.1a and 5.1b. 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. Nitrogen species were analysed at the Environment Agency laboratories in Nottingham and other anion species (Cl, Br, I, F) by automated colorimetry at the BGS laboratory in Wallingford. Stable isotope analysis was also completed in the BGS laboratory by mass spectrometry and the results reported relative to the standards SMOW for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and PDB for $\delta^{13}\text{C}$.

4.2 Historical data

There is limited historical data available for the study area which still survives and a search during the present programme did not locate significant numbers of old data with which to determine long-term trends. Information on trends comes from monitored data provided by Yorkshire Water which exists for a number of boreholes in the area covering the period 1982-present. A comparable number of samples to the new sampling programme collected during 1992 as part of the EA groundwater monitoring network also provides a regional comparison of changes over the last two decades. A survey of major elements was completed in the Vale of York by Aldrick (1974) who produced contour maps showing regional chemical variations.

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 casing and depth of borehole, may produce differences in water quality not related to geochemical reactions along a flow path .

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 different stratigraphic horizons. Water quality boreholes are likely to intercept different stratigraphic horizons especially where these boreholes are distant from each other, even where stratigraphic dip is low.

4.3.3 Different pumping history

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

It 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 showing data are based on the new sampling programme with additional data from seven Yorkshire Water abstraction boreholes. A comparison is also made with previous EA data from 1995. Where data are below the detection limit of analysis, a concentration equal to half the detection limit has been substituted for statistical purposes.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

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

Table 5.1a Field parameters, isotope data and range of major and minor element concentrations in the Triassic Sherwood Sandstone of the Vale of York and surrounding area.

Parameter	units	min.	max.	Median	mean	97.7th percentile	Upper baseline*	N
T	°C	10	14.8	11.35	11.5	14.3		42
pH		6.49	7.88	7.26	7.25	7.80		43
Eh	mV	9	820	216	244	628		42
DO	mg l ⁻¹	0	9.1	0.75	2.3	8.5		42
SEC	μS cm ⁻¹	270	3170	1025	1373	2991		41
δ²H	‰	-58.3	-48.6	-53.8	-53.5	-49.3		43
δ¹⁸O	‰	-8.6	-7.3	-7.9	-7.9	-7.4		43
δ¹³C	‰	-16.87	-7.99	-14.64	-14.20	-9.45		15
Ca	mg l ⁻¹	55.3	556	140	194	480		43
Mg	mg l ⁻¹	20.6	133	34.7	51.75	121		43
Na	mg l ⁻¹	7.0	402	36.2	75.18	284		43
K	mg l ⁻¹	0.25	13.50	4.0	4.61	10.95		43
Cl	mg l ⁻¹	12.5	307	36.6	52.45	154		43
SO₄	mg l ⁻¹	6.1	1760	170	471	1722		43
HCO₃	mg l ⁻¹	234	498	333	351	493		43
NO₃-N	mg l ⁻¹	<0.002	41.1	0.053	4.11	31.48	2-4	43
NO₂-N	mg l ⁻¹	<0.001	0.514	0.003	0.024	0.319		43
NH₄-N	mg l ⁻¹	<0.003	3.01	0.011	0.192	2.71		43
P	mg l ⁻¹	<0.02	0.299	0.027	0.05	0.28		43
TOC	mg l ⁻¹	0.8	19.1	3.1	4.3	13.4		42
DOC	mg l ⁻¹	0.9	19.2	3.0	4.9	18.7		42
F	mg l ⁻¹	0.04	0.82	0.17	0.23	0.80		43
Br	mg l ⁻¹	0.047	1.002	0.113	0.171	0.669		43
I	μg l ⁻¹	<1	126	14	25	106		43
Si	mg l ⁻¹	4.4	10.0	6.7	6.7	9.1		43

* estimated upper baseline for elements modified by anthropogenic influences.



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

Table 5.1b Trace concentrations in the Triassic Sherwood Sandstone of the Vale of York and surrounding area.

Trace elements		min.	max.	median	mean	97.7th percentile	N
Ag	µg l ⁻¹	<0.05	0.06	<0.05	<0.05	0.06	43
Al	µg l ⁻¹	<1	6.00	1.00	1.58	4.11	43
As	µg l ⁻¹	<1	39.00	<1	2.34	18.25	43
Au	µg l ⁻¹	<0.05	0.05	<0.05	<0.05	<0.05	43
B	µg l ⁻¹	<20	644	61	115	435	43
Ba	µg l ⁻¹	7.38	347	47.6	91.5	342	43
Be	µg l ⁻¹	<0.05	0.13	<0.05	<0.05	0.11	43
Bi	µg l ⁻¹	<0.05	0.11	<0.05	<0.05	0.09	43
Cd	µg l ⁻¹	<0.05	0.15	<0.05	<0.05	0.07	43
Ce	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
Co	µg l ⁻¹	<0.02	1.00	0.15	0.23	0.96	43
Cr	µg l ⁻¹	<0.5	0.50	0.25	0.26	0.26	43
Cs	µg l ⁻¹	0.02	1.36	0.09	0.21	1.24	43
Cu	µg l ⁻¹	0.30	12.10	1.90	2.72	8.80	43
Dy	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
Er	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	0.01	43
Eu	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
Fe	µg l ⁻¹	<5	6570	361	1134	5985	43
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	0.03	43
Gd	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
Ge	µg l ⁻¹	<0.05	5.12	<0.05	0.22	1.07	43
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	0.01	43
Hg	µg l ⁻¹	<0.1	0.30	<0.1	<0.1	0.21	43
Ho	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
In	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	43
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	43
La	µg l ⁻¹	<0.01	0.03	<0.01	<0.01	0.02	43
Li	µg l ⁻¹	2.00	648	34.0	73.7	299	43
Lu	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	43
Mn	µg l ⁻¹	<2	1400	214	297	1155	43
Mo	µg l ⁻¹	<0.1	5.70	0.80	1.31	4.66	43
Nb	µg l ⁻¹	<0.01	0.02	0.01	0.01	0.02	43
Nd	µg l ⁻¹	<0.01	0.09	<0.01	<0.01	0.03	43
Ni	µg l ⁻¹	<0.2	25.30	1.20	4.68	17.76	43
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	43
Pb	µg l ⁻¹	<2.0	4.00	<2.0	<2.0	<2.0	43
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	43
Pr	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	43
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	43
Rb	µg l ⁻¹	0.90	10.36	2.54	3.29	8.11	43
Re	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
Rh	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	<0.01	43
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	43
Sb	µg l ⁻¹	<0.05	0.94	<0.05	0.06	0.20	43
Sc	µg l ⁻¹	1.40	3.47	2.06	2.16	3.08	43
Se	µg l ⁻¹	<0.5	4.40	0.90	1.21	3.83	43
Sm	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	43
Sn	µg l ⁻¹	0.09	1.20	0.18	0.22	0.48	43
Sr	µg l ⁻¹	48.7	14536	853	2804	11920	43
Ta	µg l ⁻¹	< .05	< .05	< .05	< .05	< .05	43
Tb	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	<0.01	43
Te	µg l ⁻¹	<0.05	0.18	<0.05	<0.05	0.16	43
Th	µg l ⁻¹	<0.05	1.85	<0.05	0.13	0.79	43
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	43
Tl	µg l ⁻¹	<0.01	0.16	<0.01	0.01	0.04	43
Tm	µg l ⁻¹	<0.01	0.01	<0.01	<0.01	<0.01	43
U	µg l ⁻¹	0.07	20.7	1.37	3.28	17.8	43
V	µg l ⁻¹	<1.0	3.00	<1.0	<1.0	<1.0	43
W	µg l ⁻¹	<0.1	0.20	<0.1	<0.1	0.11	43
Y	µg l ⁻¹	<0.01	0.16	0.02	0.03	0.11	43
Yb	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	0.01	43
Zn	µg l ⁻¹	1.70	548	9.20	56.1	350	43
Zr	µg l ⁻¹	<0.5	0.70	<0.5	<0.5	0.51	43

The summary data are shown graphically on a Piper plot (Figure 5.1), boxplots (Figure 5.2) and cumulative frequency plots (Figure 5.3). The boxplots (or box and whisker plots) display the ranges of data and are designed to highlight the distribution of data on a percentile basis (the boxes show the range between the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentiles and the dots the 5th and 95th percentiles). In addition the median is shown as a horizontal black line and the mean as a blue line within the box. The solid black line on the graph represents a diluted seawater curve which has been normalised to the median Cl of the samples. This provides a general indication in most aquifers of enrichments due to water-rock interaction above the marine-derived rainfall input. The solid grey line on Figure 5.2b shows the 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).

5.2 Water types and physicochemical characteristics

Groundwaters in the Selby to Cleveland section of the Sherwood Sandstone aquifer show a wide range of characteristics in terms of physicochemical parameters and element concentrations (Table 5.1a and b). Although the waters are fresh, mineralisation varies from weakly to moderately mineralised (SEC from 270 to 3170 $\mu\text{S cm}^{-1}$). Temperatures are as high as 14.8 °C in the deeper parts of the aquifer confined beneath the Mercia Mudstone but are more generally between 10 and 11 °C in the outcrop area regardless of drift cover. The waters appear to be well buffered at circumneutral pH with a median value of 7.25. Many groundwaters contain relatively low concentrations of dissolved oxygen and have low Eh values indicating that the aquifer varies from moderately reducing to oxidising. However, it was not possible to measure these parameters at all sites in a flow-through cell and the median Eh of 216 mV is likely to be an overestimate.

The groundwaters in the Sherwood Sandstone aquifer vary from Ca-HCO₃ and Ca-Mg-HCO₃ to Ca-Mg-SO₄ and Ca-SO₄ types as shown on the Piper diagram in Figure 5.1. Although Na and Cl concentrations are generally low in most groundwaters, concentrations can be relatively high locally and the waters may be of Na-Ca-SO₄ or Ca-Mg-HCO₃-Cl type. There is no trend towards Na-Cl type waters in the samples collected.

5.3 Major elements

Major element concentrations are shown on boxplots on Figure 5.2a. The median value of Cl of 36.5 mg l⁻¹ indicates a source additional to rainfall, although some samples have concentrations of 12.5 mg l⁻¹ close to that estimated for bulk precipitation. Most other elements, including Na, plot above the curve even for the normalised Cl indicating extensive water-rock interaction. The elements Ca, Mg and HCO₃ show a relatively narrow range of concentrations. Sulphate, on the other hand shows a much wider range over 2 orders of magnitude. The large range of NO₃ concentrations is partly due to the fact that it displays a bimodal distribution as shown on the cumulative probability plot (Figure 5.3a). The distribution of SO₄ likewise shows a complex distribution and may be described as polymodal. Most major elements display trends on a cumulative frequency plot that tend to approach linearity (or approach what appears to be a log-normal distribution).

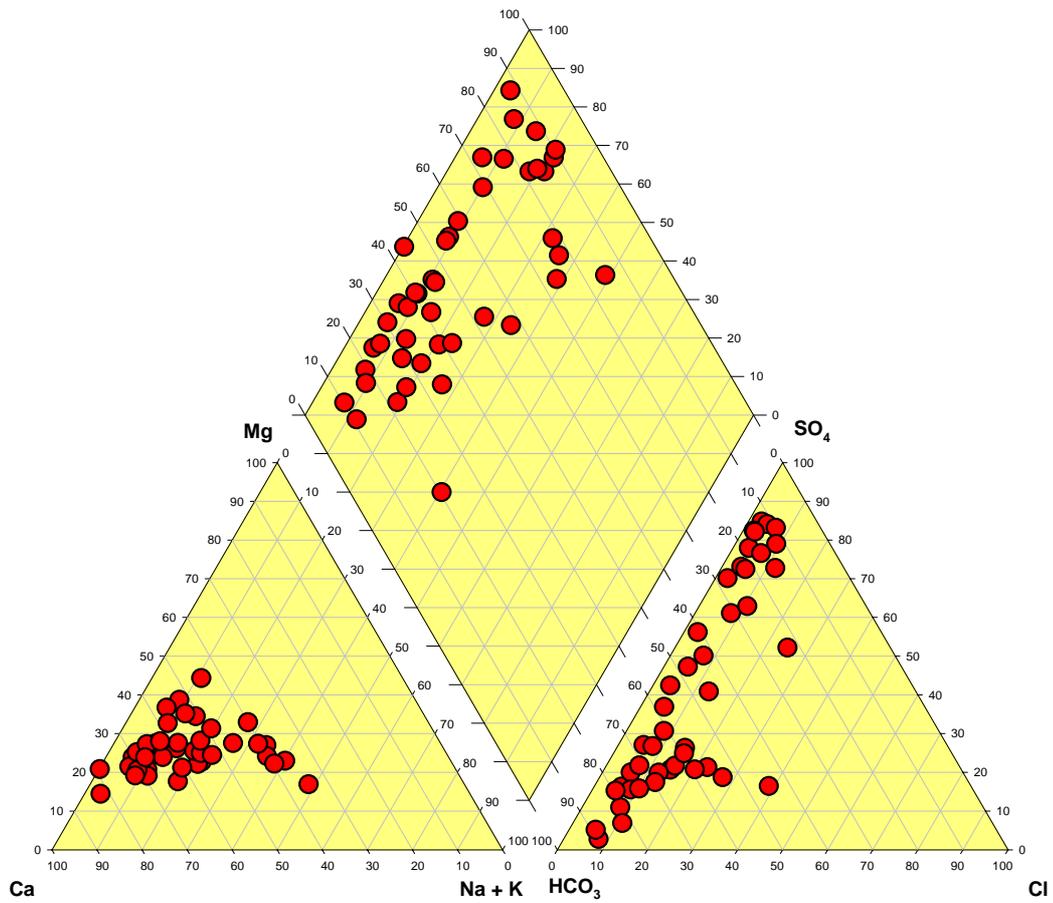


Figure 5.1 PIPER plot showing the relative concentrations of major cations and anions in the Vale of York study area.

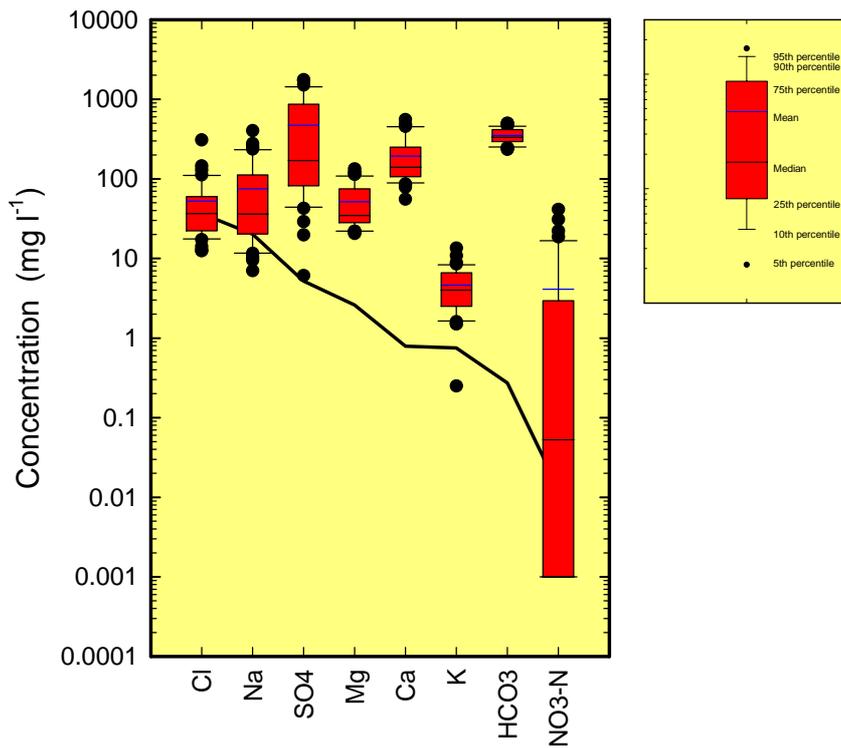


Figure 5.2a. Range of major ion concentrations in the Vale of York groundwaters.

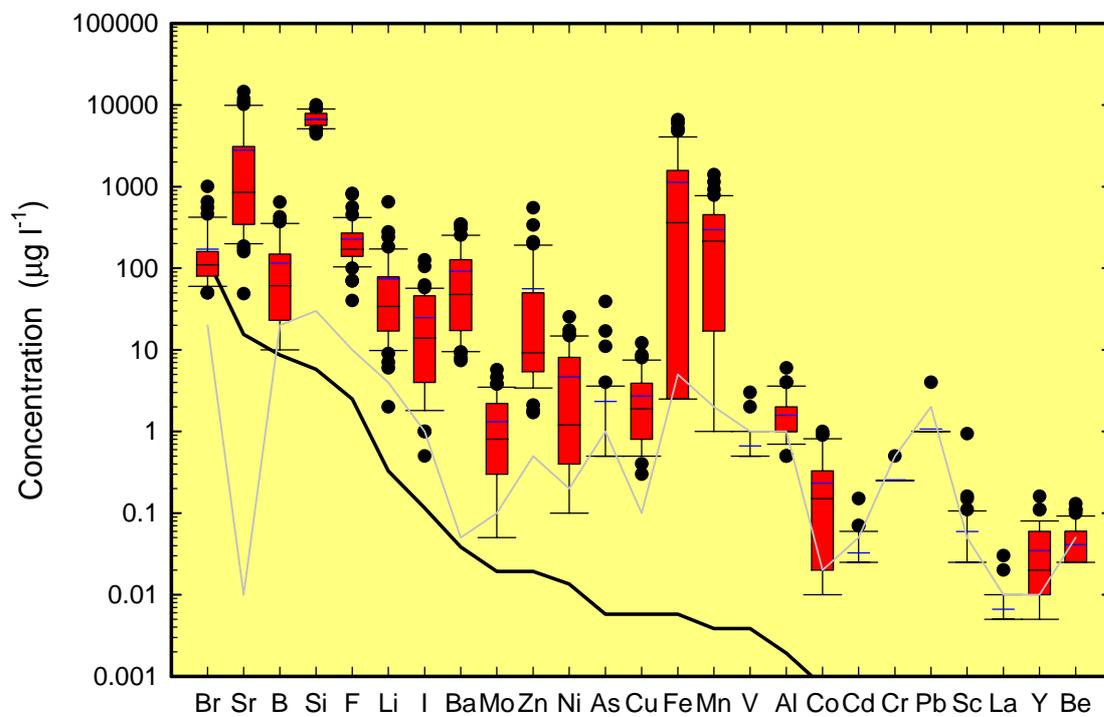


Figure 5.2b. Range of minor and trace element concentrations in the Vale of York groundwaters.

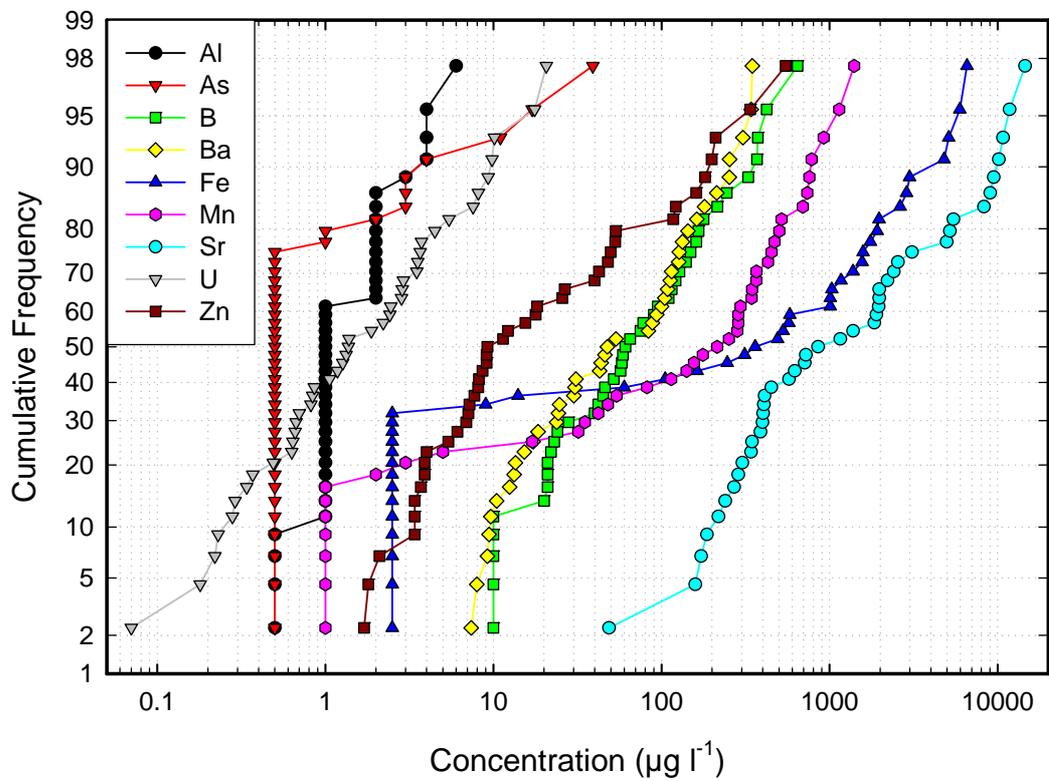
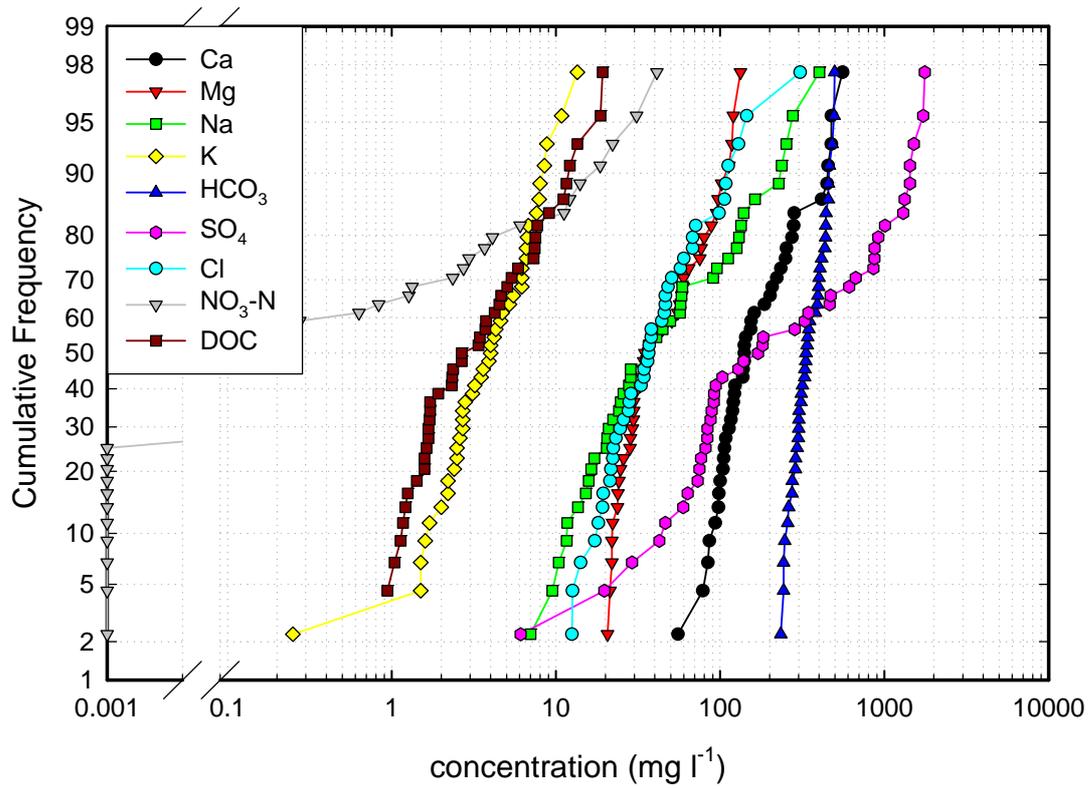
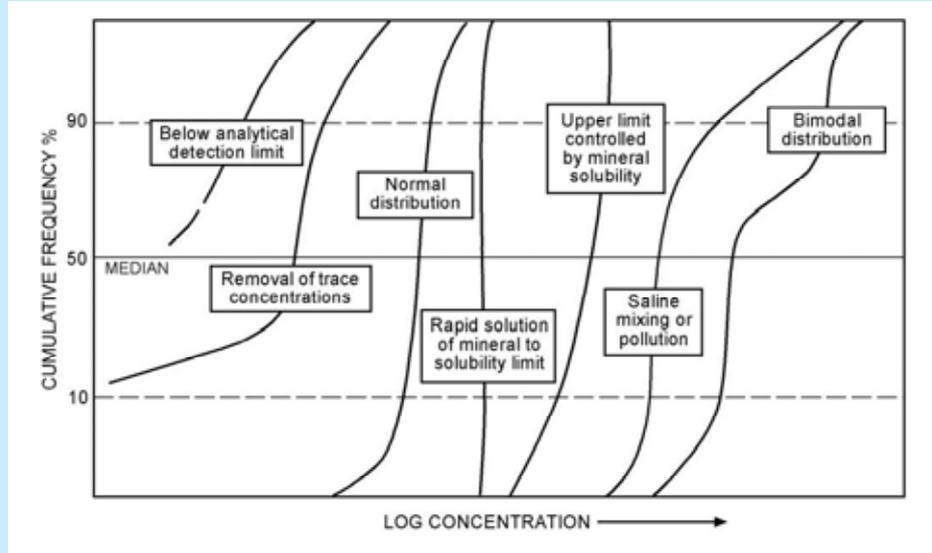


Figure 5.3 Cumulative probability plots for Vale of York.

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 fluoride)
- 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.

5.4 Minor and trace elements

Minor and trace elements are displayed on boxplots in Figure 5.2b. Although Br lies close to the seawater line, determined using median Cl, most other elements are significantly higher than this. The other halide elements, I and F, are higher than expected in comparison with Br and Cl and would appear to have a different geochemical controls on their distribution.

Silicon shows a limited range of concentrations and approaches a normal distribution as indicated by the similarity of the median (6.63 mg l^{-1}) to mean (6.67 mg l^{-1}) concentrations (Table 5.1a and b). The cations Sr and Ba in contrast have widely varying concentrations; Sr reaches more than 14.5 mg l^{-1} and Ba although limited in many waters by high SO_4 (due to barite: BaSO_4 saturation) can be higher (up to $347 \text{ } \mu\text{g l}^{-1}$) than the EU MAC (maximum admissible concentration) of $150 \text{ } \mu\text{g l}^{-1}$.

Iron and Mn likewise show an extremely large variations. On a cumulative probability plot it can be seen that although many samples are below the limit of detection (shown by vertical lines at low concentration), Mn may reach more than 1 mg l^{-1} , and iron in excess of 5.9 mg l^{-1} in the more reducing groundwaters. In general, the trace elements show a wide range of concentrations and generally more complex distributions (Figure 5.3b). The heavy metals Cd and Pb, as well as Al are generally low due to their low solubility at the circumneutral pH values of the groundwaters. Zinc and Cu may be locally relatively high and Ni is slightly elevated but Cr is generally very low (Table

5.1a and b). Of some concern is the presence of As which may reach concentrations of $39 \mu\text{g l}^{-1}$ (compared to the MAC $50 \mu\text{g l}^{-1}$) in some of the waters analysed, however, the median concentration is below the detection limit of $1 \mu\text{g/l}$. Uranium is present at unusually high concentrations (up to $21 \mu\text{g l}^{-1}$) and the median concentration ($1.35 \mu\text{g l}^{-1}$) is considered to be moderately high for UK aquifers, although there are limited data available at present

Stable isotope data will be discussed in detail in the following section but these show a significant variation (Table 5.1a and b) similar to those found further south in the East Midlands and South Yorkshire (Smedley & Trafford, 1999). A selection of samples were also analysed for $\delta^{13}\text{C}$ and these show a significant variation across the aquifer (Table 5.1a and b).

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 (see Box 5.2).

It is generally difficult to obtain pristine waters, in part because waters may be sampled over a large screened interval where polluted waters are present at shallow depth or because diffuse pollution (especially agricultural pollution) is present in large parts of the unconfined aquifer. Boreholes affected by point source pollution have been avoided but most groundwaters in unconfined aquifers do show the effects of agricultural pollution due to the application of fertilisers or pesticides over the past decades, indicated by high nitrate concentrations and the presence of pesticides (Box 5.2).

Concentrations of nitrate are generally low although some boreholes clearly show enhanced levels. However, many of the waters are relatively reducing and denitrification or nitrate reduction may have lowered concentrations. Data from the EA for 1995 provide information on the extent of modern contamination. A wide range of organic components have been studied to indicate the extent of aquifer contamination. In general, the groundwaters are free from organic contaminants, however a range of petroleum hydrocarbon products (BTEX) and THM's were detected in one borehole and a range of phenyl-urea herbicides (chlorotoluron, isoproturon, linuron) as well as high nitrate were noted at another.

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 baseline is to recognise the impact of any of human activities over and above the natural baseline in the data sets used.

The approach adopted is threefold:

- (i) to have evidence of groundwater age
- (ii) to extrapolate data series back to an initial time
- (iii) to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced TOC and N species – especially NO_3 – the presence of 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 including:

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

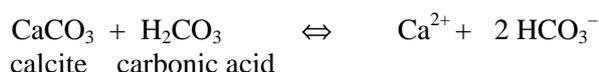
Samples have been studied in detail along a potential flow line in order to understand the geochemical changes that take place with distance and time in the aquifer. These geochemical changes are evaluated and put into a regional context. Temporal trends are also established for areas where data is available.

6.2 Chemical evolution along flowlines

The main flowline studied stretches from south of Boroughbridge near the western limit of the aquifer to north of Goole in the south-east (Figure 3.6) and was estimated using water-level data collected in April 2000. Although the main lithological change in geology along the flowline occurs between the Sherwood Sandstone and the overlying Mercia Mudstone, there are significant chemical changes which coincide with changes in drift type. The samples closest to the feather edge of the outcrop are covered by drift classified as “boulder clay and morainic drift”. South of York, these drift deposits are overlain by thick “lacustrine clays, silts and sands” which extend over the Sherwood Sandstone-Mercia Mudstone contact (Figure 3.3). The hydrochemical data are plotted against distance in Figures 6.1-6.3. The SEC varies little along the flowline but increases dramatically once the aquifer becomes confined below the Mercia Mudstone Group. The groundwaters are mostly of Ca-Mg-HCO₃ types changing to SO₄-types along the flowline. One of the boreholes (Bolton Grange NGR 4544 4405) trends towards a Ca-Na-HCO₃-type but this is a relatively shallow borehole.

6.2.1 Mineral dissolution reactions

Much of the chemistry is already established in the samples collected at the start of the flowline due to dissolution reactions involving the calcite and dolomite cements which form the matrix of the sandstone. The production of CO₂ in the soil zone will initially lead to slightly acidic waters due to production of carbonic acid, but this acidity will be rapidly neutralised through reaction with carbonate minerals. All groundwaters along the flowline are at saturation with respect to calcite, controlled by the reaction:



The first samples at the feather edge are undersaturated with respect to dolomite but reach saturation approximately 10 km along the flowline by dolomite dissolution:



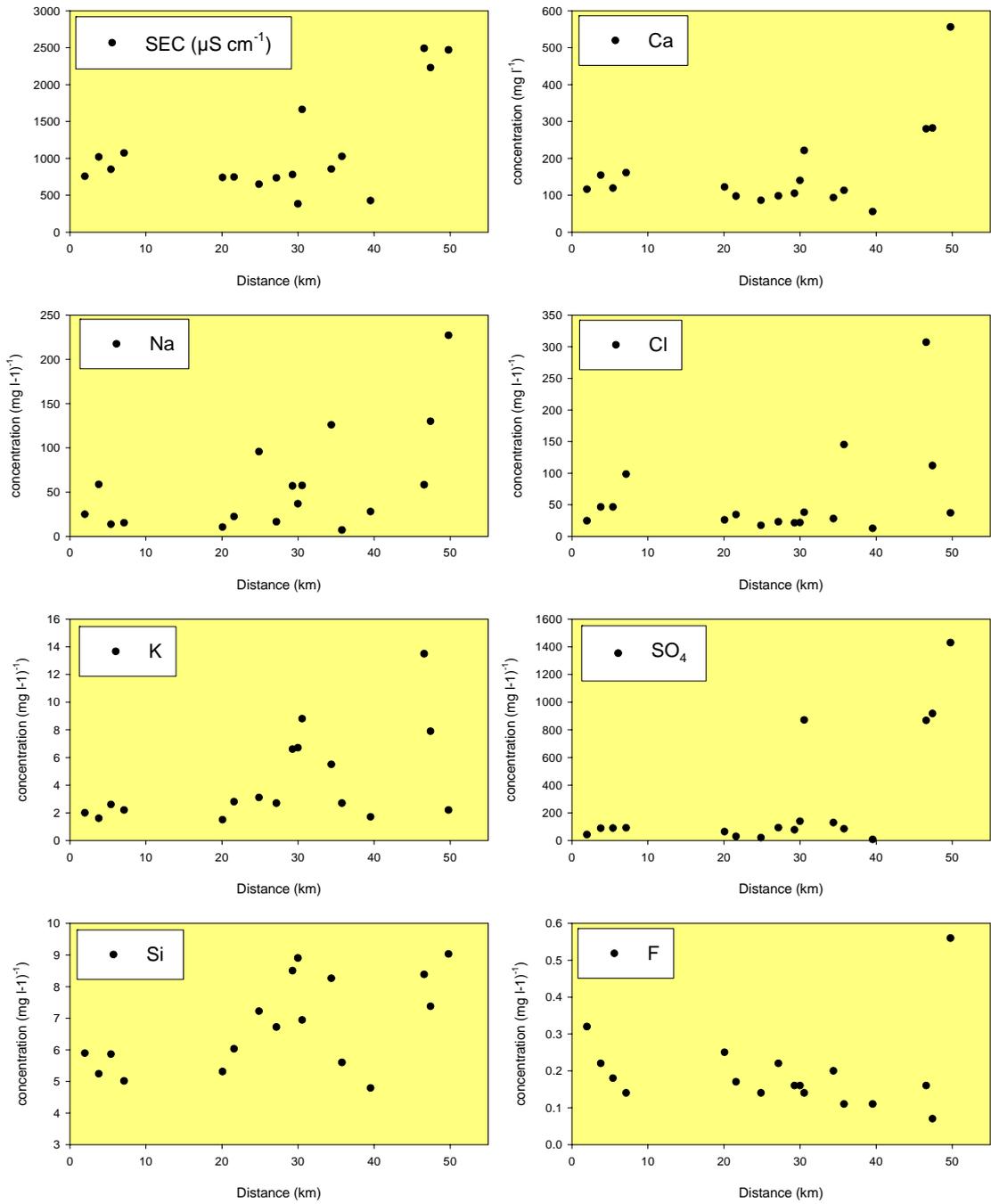


Figure 6.1 Major and minor element characteristics of the groundwaters along the flowline.

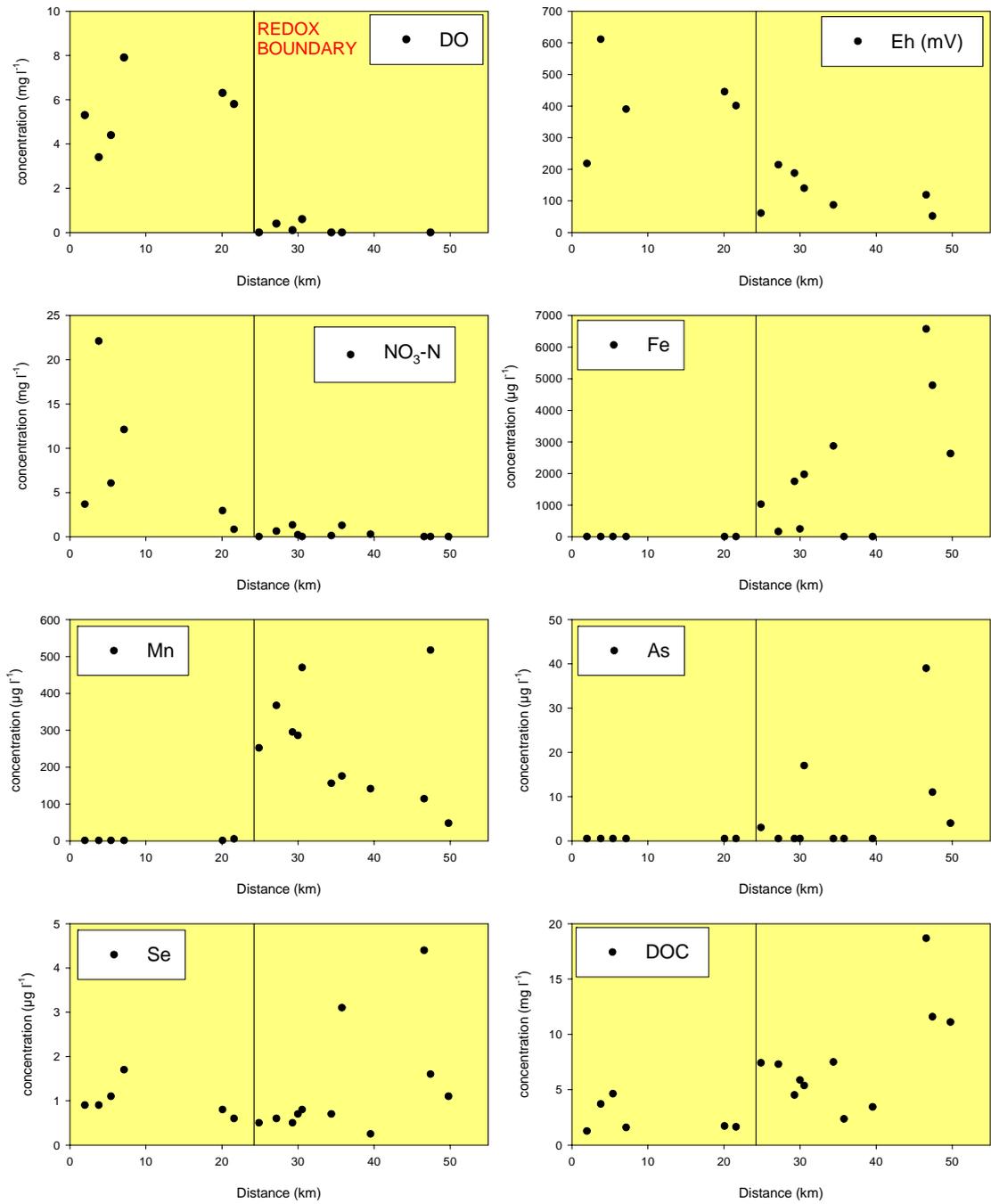


Figure 6.2 Redox parameters and redox sensitive species along the flowline.

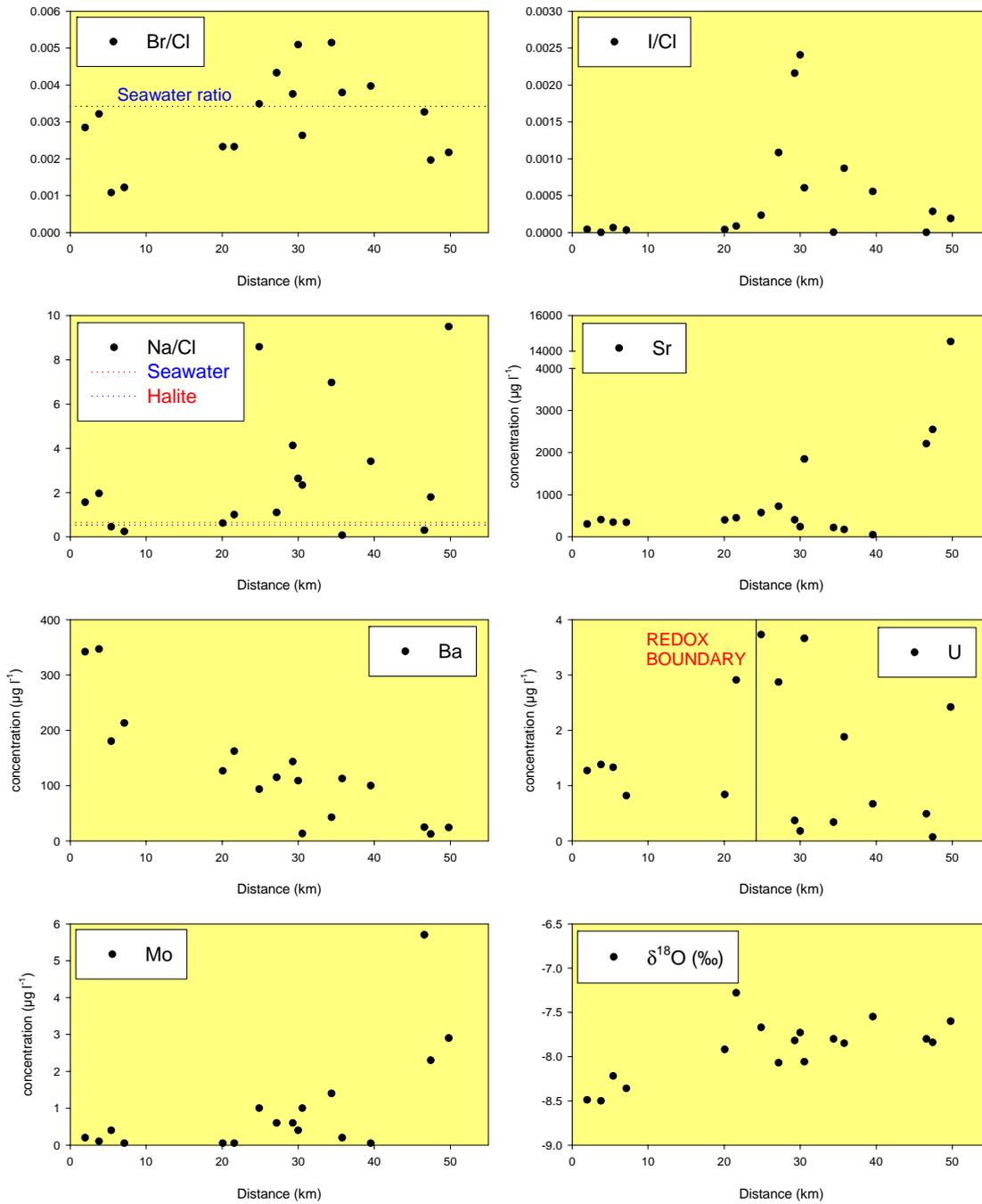
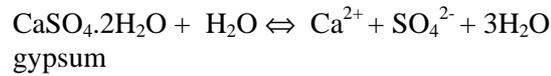


Figure 6.3 Elemental ratios and trace element characteristics along the flowline.

The dissolution of calcite and dolomite provide the initial dominant controls on water chemistry but the increase in both Ca and SO₄ show that gypsum dissolution becomes of major significance. Although undersaturation exists for gypsum in the outcrop area of the aquifer, the dissolution of gypsum has led to saturation in groundwaters where the aquifer is confined beneath the Mercia Mudstone:



The increase in SO₄ along this flowline (Figure 6.1) is probably due to dissolution of gypsum or anhydrite at the base of the Mercia Mudstone Group. The above reactions are considered to be the main reactions determining groundwater chemistry along the flowline. However, slower silicate dissolution reactions also occur. An increase in Si occurs at around 40 km along the flowline where the lacustrine clays are encountered. Although the aquifer is composed dominantly of quartz, this mineral is extremely unreactive and the source of Si is from silicate minerals such as K-feldspar or plagioclase feldspar. The similarities between K and Si indicates that the source of K is likely to be from the dissolution of K-feldspar which often displays the effects of dissolution (Figure 3.7a).

Concentrations of F are generally low in the groundwaters implying that F-bearing minerals are not significant in the aquifer. The dissolution of halite is not considered to be important along the feather edge of the aquifer or in general in waters confined beneath the Mercia Mudstone, locally high chloride probably being due to mixing with deeper more saline groundwater. Chloride concentrations may be enhanced above baseline in the outcrop area due to anthropogenic inputs and will be discussed later. Iodide concentrations are highest close to the central part of the flowline with I/Cl ratios being similar to the seawater at the beginning of the flowline and where the Sherwood Sandstone is confined beneath the Mercia Mudstone. Iodide has previously been found to be highest in the confined parts of the Chalk aquifer (Edmunds et al., 1987) but in the Vale of York the highest ratios appear to be associated with areas where the aquifer is confined beneath drift deposits and conditions are reducing.

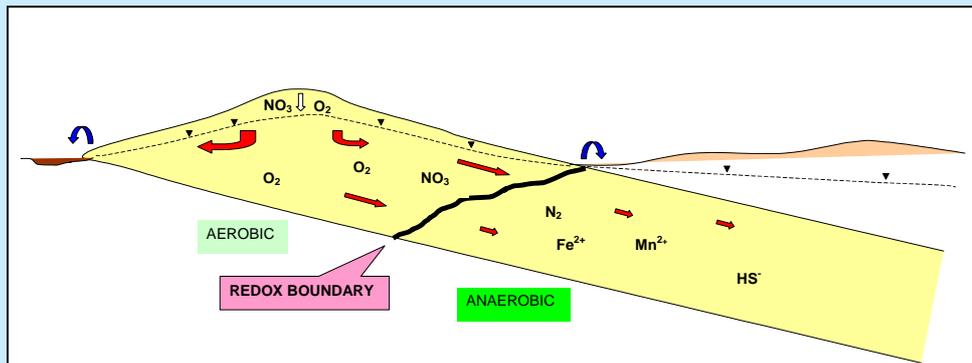
6.2.2 Redox reactions

The redox potential (Eh) and dissolved oxygen (DO) concentration provide the primary indicators of the redox status of natural groundwaters. These parameters are unstable and extremely sensitive to changes caused by contact with the atmosphere and, therefore, should be monitored in a flow-through cell where the water is pumped directly from the borehole. Unfortunately this was not possible for many samples due to sampling from an intermediate storage tank or because the diameter of the outflow was too large to connect to the flow-through cell. The redox potential and dissolved oxygen concentrations are plotted in Figure 6.2 which displays the samples collected in a flow-through cell. A redox boundary (Box 6.1) can be recognised based on this data which occurs at the junction between two major drift types.

This boundary is also apparent when considering redox sensitive species such as NO₃, Fe and Mn. Nitrate concentrations are relatively high north-west of the redox boundary but concentrations rapidly decrease to the south-east. The reduced nitrogen species NO₂ and NH₄ are present in some samples beyond this boundary indicating that denitrification and nitrate reduction have occurred. Iron and Mn concentrations increase beyond the boundary consistent with the change in redox conditions. The redox-sensitive trace elements As, Se and Sn are found to be higher in the more reducing waters but their chemistry is relatively poorly understood in terms of mobility and speciation in the aquifer. Uranium in contrast is highest around the redox boundary and moderate concentrations are found beyond this where U mobility is expected to be low. Concentrations of dissolved organic carbon (DOC) are surprisingly high in groundwaters beneath the Mercia Mudstone and more typical of polluted groundwaters. Concentrations increase in the reduced groundwaters and it is surprising to find such high concentrations in confined parts of the aquifer where the groundwaters are likely to be

relatively old. In the northern part of the study area, high DOC is also found in groundwaters beneath thick drift deposits. The reasons for such high DOC are not clear. The source may possibly be related to drift deposits and their preservation in the aquifer related to the reducing conditions, although an anthropogenic source is impossible to rule out. It is therefore difficult to assess baseline DOC concentrations until more data are available regionally over the aquifer and more generally in UK aquifers.

BOX 6.1 REDOX BOUNDARY



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

Redox reactions are, therefore, a very important control on a range of elements in the Vale of York area. Although drift deposits are important, the presence of oxygenated, high nitrate groundwater indicates that drift windows are present in the western part of the area allowing recharge to the aquifer. This will be discussed in more detail in the section on regional variations.

6.2.3 Ion exchange reactions

The role of ion-exchange in the aquifer is difficult to assess because of the lack of solid phase data (e.g. exchangeable Na contents on clays) and the complex nature of the aquifer mineralogy. The Na/Cl ratio is useful to determine whether any increase in Na is due to mineral weathering and ion-exchange or mixing with an older formation water. This ratio varies significantly and reaches relatively high values (up to 9) implying that the water-rock interaction is an important process. Chloride concentrations are generally low indicating that the aquifer has been well flushed of original formation waters. The additional Na may be derived either from silicate weathering of phases such as plagioclase feldspars (e.g. albite) or through ion-exchange of Na on clay minerals for Ca or Mg. The

high Ca and Mg concentrations in comparison with that likely to be produced by ion-exchange makes this difficult to establish but the lack of correlation between Ca and Na shows that ion-exchange is unlikely to be a dominant process in the aquifer.

6.2.4 *Mixing with older formation water*

The oldest groundwaters present deep in the Triassic aquifer further south around Nottinghamshire are of Na-Cl composition and mixing with this water would produce groundwaters with high Na and Cl as well as relatively high SO₄ and Mg. Although Na, Mg and SO₄ are not conservative and may therefore be changed by processes apart from mixing, Cl behaves conservatively and provides a good indicator of mixing. Chloride concentrations are in general low, except where the aquifer becomes confined beneath the Mercia Mudstone. The concentration of Cl is variable at the beginning of the flowline, possibly indicating some anthropogenic inputs and this is consistent with the higher NO₃ concentrations found. Chloride then decreases along the flowline but increases substantially close to the boundary with the Mercia Mudstone. Bromide/chloride ratios can be used as an indicator of the source of salinity (Edmunds, 1996) and are shown on Figure 6.3 along with the seawater ratio. Initially, the Br/Cl is similar to the seawater ratio (and rainfall) but this decreases rapidly in the next two samples. Low Na/Cl ratios (0.1-0.4) in these samples also implies that the low Br/Cl is not due to halite dissolution (Na/Cl of 1) or mixing with a deeper Na-Cl type water, but is likely to be a consequence of anthropogenic inputs. Some of the samples situated towards the end of the flowline likewise have high Cl but low Na/Cl indicating that much of the Cl in these samples may be anthropogenically derived. The role of mixing with a deeper connate or formation water is, therefore, considered to be an important process only locally along this flowline.

6.2.5 *Trace elements*

The trace elements Sr and Ba behave very differently in the aquifer (Figure 6.3). The source of Sr is from both calcite and gypsum, concentrations in the latter typically being higher. There is a good correlation of Sr, both with Ca (with which it shows similar behaviour) and sulphate implying that the dominant source is through gypsum dissolution. Strontium concentrations can be very high (up to 14.5 mg l⁻¹) and the groundwaters with the highest Sr concentrations are at saturation with respect to celestite (SrSO₄). The source of the high Sr, therefore, is from the dissolution gypsum as confirmed by the good correlation of Sr with SO₄.

Ba concentrations are higher closer to the feather edge of the aquifer and decrease with distance along the flowline. This is in contrast to the distribution found in the northwest Cheshire Basin where concentrations are closely associated with the junction of the Sherwood Sandstone and the Mercia Mudstone (Griffiths et al., 2002). The dominant control on Ba in the groundwaters is the concentration of SO₄ which at high concentrations limits Ba due to precipitation of the mineral barite (BaSO₄).

The trace elements Li and B may be good indicators of residence time in aquifers and both increase along the flowpath. Rubidium and Cs show similar behaviour to K geochemically, and are most likely related to ion-exchange involving clay minerals. Several other trace elements are found at higher concentrations where the Sherwood Sandstone becomes confined beneath the lacustrine drift deposits including Al, Be, Co, I, Mo, Ni, Sb and Y. Some of the metal species are associated with sorption sites on Fe and Mn oxyhydroxides and are most likely related to the mobilisation of these oxy-hydroxides in the reducing groundwaters.

6.3 Temporal variations

There is very little historical data available for the region. A knowledge of the baseline conditions is therefore difficult to assess directly. Temporal variations were studied using data supplied by Yorkshire Water plc for the period 1980 to present. Most boreholes had limited data for many solutes

but it was clear that in most cases no significant trends were apparent (Figure 6.4). This was also the case for nitrogen species and contrasts with many UK aquifers where nitrate shows an increase with time.

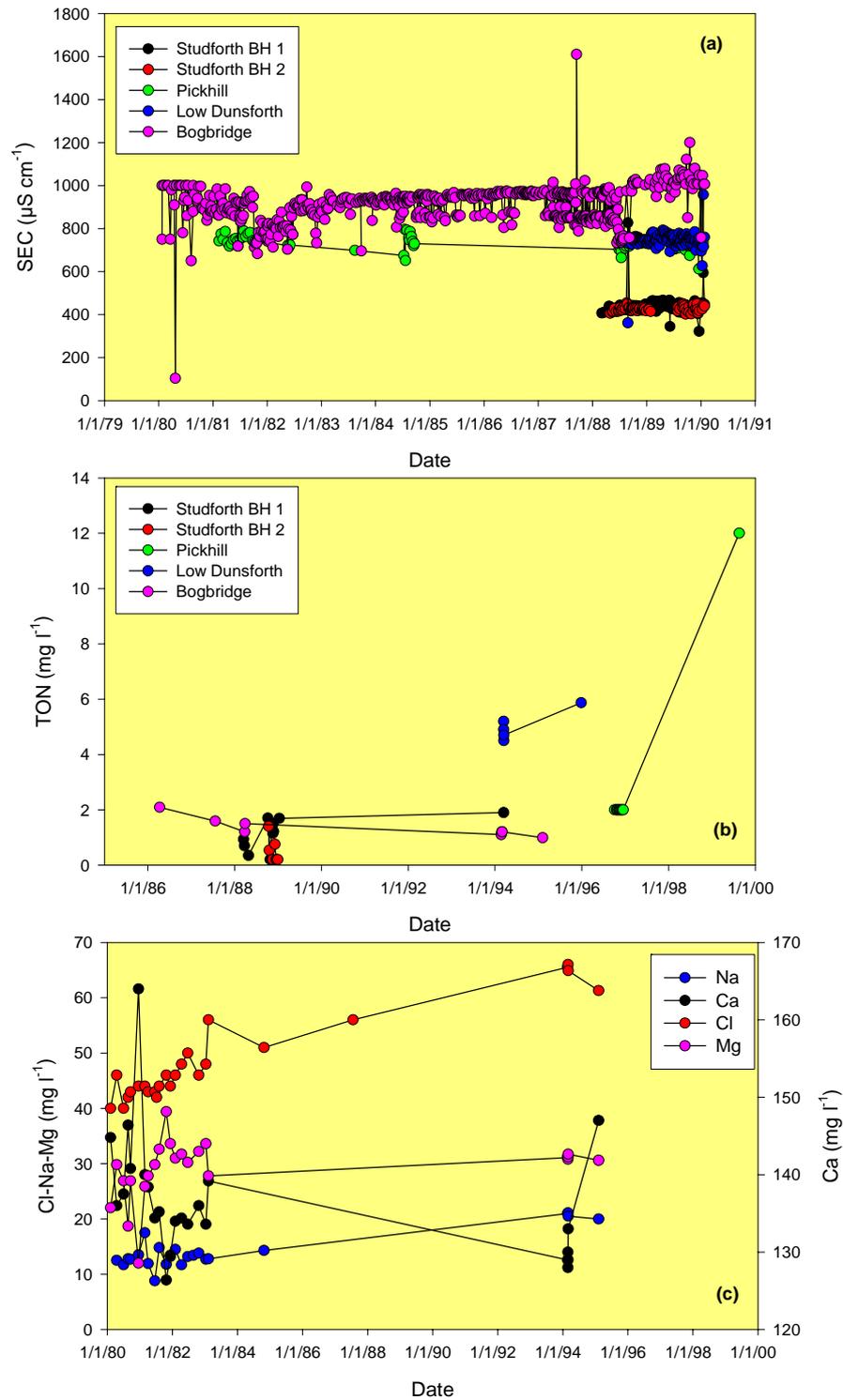


Figure 6.4 Time series data for selected boreholes showing (a) specific electrical conductance, (b) total oxidisable nitrogen and (c) parameters from Bogbridge borehole which shows a slight trend of increasing salinity.

Data for one borehole (Bogbridge) which had a wide range of parameters analysed is shown on Figure 6.4c. There is a clear increasing trend in Cl (and possibly reflected in Na, Mg and SEC) between 1980 and 1995. This is most likely related to the movement of groundwater from depth and not pollution as it affects most solutes derived from water-rock interaction in a similar way.

6.4 Depth variations

There is little data available on depth variations within the aquifer. Aldrick (1974) reported some data collected during pump testing and depth sampling of boreholes at Scruton (NGR 432 492) and Ainderby Steeple (NGR 4332 4925) during 1970. The results are shown on Figure 6.5 for Scruton. There is little difference in most parameters with depth although Ca, Mg and Na show a small increase and SO_4 shows a more significant increase in concentration. Similar profiles were also evident in the Ainderby Steeple borehole. There are few deep boreholes drilled into the outcrop of Sherwood Sandstone in this area, however, the presence of gypsum/anhydrite in deeper parts of the aquifer where groundwater is not exploited, implies that salinity will increase significantly with depth.

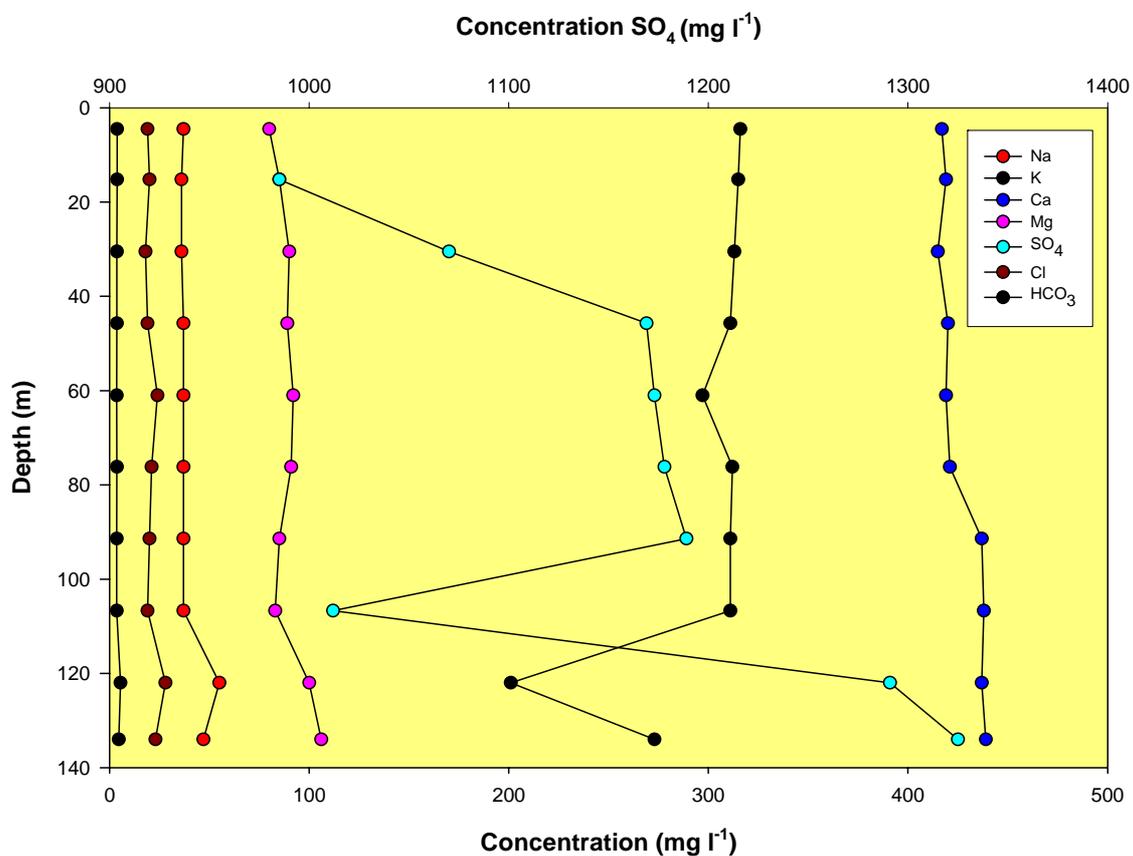


Figure 6.5. Depth samples from the Scruton (NGR 432 492) borehole. Data from Aldrick (1974).

A recent study of salinity increase with time in the Selby area (Buckley et al., 2001) has shown that the groundwater in this area is chemically stratified (Figure 6.6a) showing significant increases in salinity with depth. Figure 6(b) shows the reverse, where fresher waters are present at depth. This is due to the movement of a deeper more saline groundwater moving up the borehole and into shallow fractures which this borehole also intersects. This clearly shows the effect that abstraction may have in modifying the baseline chemistry of individual boreholes.

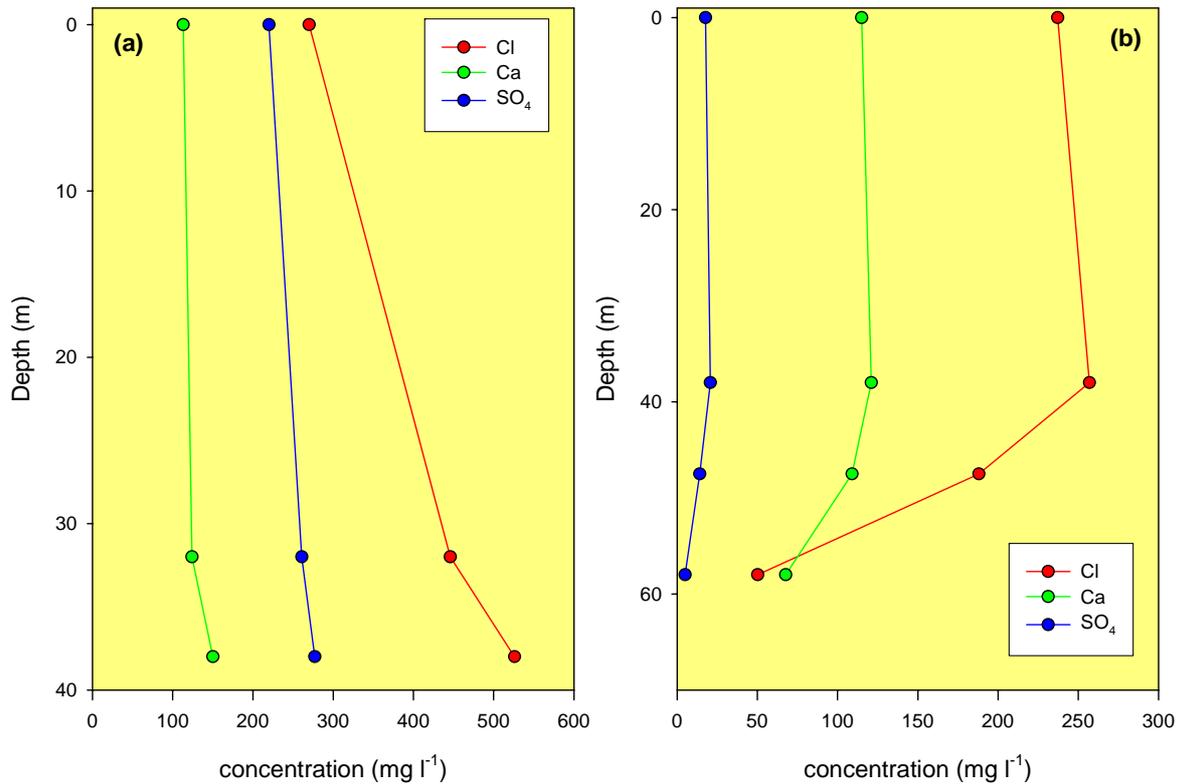


Figure 6.6 Groundwater quality profiles from boreholes in the Selby area. (a) a typical increase in concentration with depth; (b) a decrease in concentration with depth due to cross contamination from a nearby borehole where deep, more saline Ca-Cl₂ type waters are moving upwards before intersecting a shallow fracture and contaminating the shallow aquifer system.

6.5 Age of the groundwater

There are no data available providing a direct estimate of groundwater age in the study area. Although geochemical concentrations can be used as guide to relative ages, they provide little direct evidence of age. Furthermore facies changes and kinetic factors make such estimates fraught with difficulties. The fact that the waters do show a trend of increasing concentrations along the flowline for some elements implies a longer residence time but without specific dating tools (e.g. ¹⁴C, CFC's) precise ages cannot be given.

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 more southerly, East Midlands section of the aquifer. The climate during the Pleistocene period was colder resulting in lighter (more negative) signatures of the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$. A plot of $\delta^{18}\text{O}$ along the flowpath is shown in Figure 6.3, and shows that lighter signatures occur at the beginning of the flowpath, in contrast to the distribution shown in the East Midlands, where the signatures become more negative at depth in the confined aquifer. A similar situation was found in the area immediately south around Goole and Selby (Smedley & Trafford, 1999) but the reason for this behaviour could not be established.

It is unlikely that the waters at the feather edge are old waters (e.g. from the Permian rocks) for several reasons:

1. Permian waters are likely to be more saline and characteristically have high concentrations of Sr and Mg.
2. These groundwaters are oxidising and contain high nitrate implying recent recharge.

Carbon isotopes can also be useful since they provide evidence of the degree of reaction with carbonate minerals which may be loosely related to residence time. Limited samples were analysed but these also agree with the conclusions drawn above i.e. that the western waters appear to be older. It is possible that the relatively heavier $\delta^{18}\text{O}$ signatures may be related to water coming from drift deposits as previous studies have noted a correlation between drift and isotope ratio (Parker et al; 1985), but further work is required on such drift deposits to confirm this.

6.6 Regional variations

The geochemical controls highlighted in the preceding discussion can be applied to the chemical variations present regionally in the study area. The regional variations across the study area between Cleveland and Selby are shown for selected elements in Figure 6.7. There is a clear contrast in chemistry between the areas north and south of Thirsk. Lower SEC waters are found in the southern sector where the Sherwood Sandstone is not confined beneath the Mercia Mudstone, but the groundwaters in the north generally have higher SEC. The data from the flowline west and south of York showed that most of the TDS increase occurred only in the vicinity of the Mercia Mudstone. The higher SEC present over much of the northern area is related to higher Ca, Na, Mg, SO_4 and Cl, although the largest increases occur for Ca and SO_4 . As mentioned previously, there are significant facies changes in the aquifer with the sandstones becoming much finer grained to the north which can explain the increases in elements such as Cl in terms of less flushing of formation water. High Ca and SO_4 concentrations in the southern area are generally related spatially to the junction with the Mercia Mudstone group where evaporite minerals are present. However, in the northern area, the dominance of Ca and SO_4 and high SO_4/Cl ratios imply that a source of gypsum or anhydrite is present in the sandstone aquifer here which has not been removed by previous flushing. This is also supported by the very high Sr concentrations (up to $11,764 \mu\text{g l}^{-1}$) which are typically enriched in gypsum. The northern sector, therefore, shows many of the characteristics that would be expected only in confined waters further south from Thirsk to Nottingham.

Gray (1961) and Aldrick (1974) noted that the groundwater showed distinct zones across the aquifer, particularly in terms of Ca, SO_4 and hardness: (i) a zone of relatively high sulphate and hardness on the western margin of the aquifer; (ii) a zone in the centre of the outcrop along the rivers Swale and Ouse; (iii) a zone of high sulphate and hardness along the eastern margin towards the Mercia Mudstone. As these authors pointed out, this is unlikely to be a consequence of dilution by river recharge because the rivers here are effluent. Much of the lower conductivity central zone is also protected by impermeable drift deposits. Although sampling was limited along the western edge of the aquifer in this study, higher SO_4 groundwaters were found close to the feather edge e.g. Roecliff Nurseries borehole (NGR 437 466; SO_4 of 670 mg l^{-1}). There is insufficient data at present to determine whether this increase in Ca and SO_4 are derived from gypsum/anhydrite within the aquifer, the Permian marls or the Magnesian limestone. The distribution of lower TDS groundwaters in the central-southern area is relatively complex. This may result from vertical stratification in the aquifer minerals or groundwater chemistry, distribution of recharge areas or leakage from the drift. The increase in Ca and SO_4 along the eastern edge is related to the presence of gypsum at the top of the Sherwood Sandstone or from the overlying Mercia Mudstone. The older studies did not include the northern part of the area, where it can be seen that the groundwaters have generally higher TDS, consistent with lower permeability, porosity and transmissivities. It is, therefore, likely that the aquifer

has been flushed to a lesser degree (as indicated by higher Cl concentrations) and preservation of cements such as gypsum/anhydrite.

Although many of the major and trace element characteristics can be explained in terms of the changing nature of the aquifer host rocks, this is not the case for redox indicators and redox-sensitive species. A redox boundary has been noted by several workers in the Sherwood Sandstone of Nottinghamshire (Edmunds et al., 1982; Smedley & Brewerton, 1997) coinciding with confining conditions beneath the Mercia Mudstone. In the Vale of York, the onset of reducing conditions occurs within the Sherwood Sandstone itself. The position of this redox boundary coincides with a change in drift deposits from “boulder clay and morainic drift” to “lacustrine clays, silts and sands”. The cross section chemistry has highlighted the fact that oxidising, nitrate-rich groundwaters occur in groundwater beneath the boulder clay and morainic drift implying that active recharge is occurring up gradient of the lacustrine clay boundary. The drift in this area is known to be sandy becoming more clay rich in the north. Aldrick (1974) produced contour maps of drift thickness and thickness of clay in drift. The presence of oxidising nitrate-rich groundwaters coincides extremely well with areas where the thickness of clay in the drift is low or absent.

Several redox parameters and redox-sensitive species have been plotted on the existing BGS drift map (Figure 6.8). High concentrations of Fe and Mn are clearly associated with the lacustrine deposits. It would appear, therefore, that the drift in the area north and north-west of York is permeable and allows recharge to take place, whereas the lacustrine clays, sands and silts appear, in general from barriers to recharge. Oxidising, nitrate-rich waters are also found beneath sand and gravel in the area north and south of Thirsk. In the northern area, the boulder clay and moraine are relatively impermeable as indicated by the relatively reducing groundwaters containing high Fe and Mn. Therefore, the redox chemistry of the groundwaters implies that recharge windows through the drift are present in parts of the study area, particularly in area north and north-west of York. Other isolated samples, including those associated with rivers and alluvium, contain high nitrate and are oxidising implying that recharge may occur locally through superficial deposits, such as alluvial sands and gravels along valley bottoms. This suggests that there is some connection locally between the rivers and underlying aquifer probably where erosion of impermeable drift has occurred.

Many of the minor and trace elements show similar trends to the major elements with higher concentrations where the aquifer is confined beneath the Mercia Mudstone or beneath thick drift in the north. This includes many of the alkali (Li, Rb, Cs), Sr, B elements and metals such as Al, As, Co, Mo, Ni and Y. Other metals (Cu, Pb, Zn) may show higher concentrations in the recharge areas and thus be related to anthropogenic inputs. The geochemistry of uranium is not clear; it is typically mobile under oxidising conditions but the highest concentrations are found in the northern area and may, therefore be source controlled. Barium concentrations appear to be unrelated to geology or drift type. There is an antithetic relationship between Ba and SO_4 due to the low solubility of barite, therefore Ba is only high where gypsum dissolution has not been significant, mainly in the recharge areas. Although the aquifer along the western feather edge lies directly on Permian dolomites (Figure 3.4), there is no clear evidence that groundwater derived from these units are recharging the aquifer.

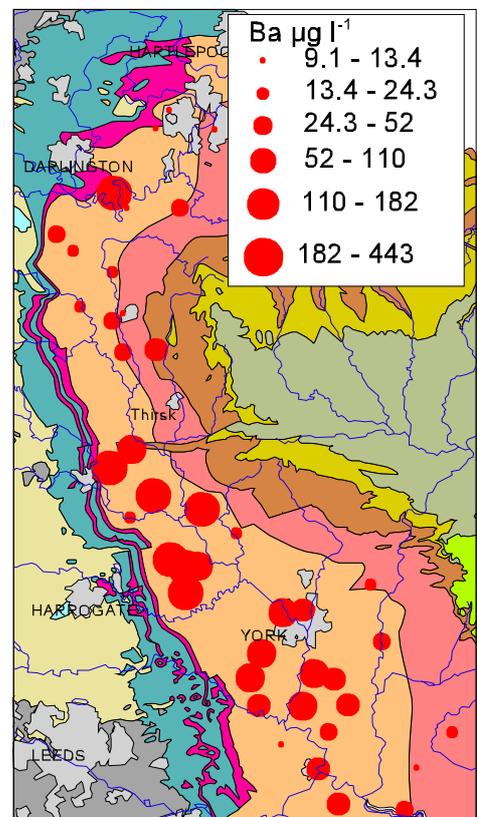
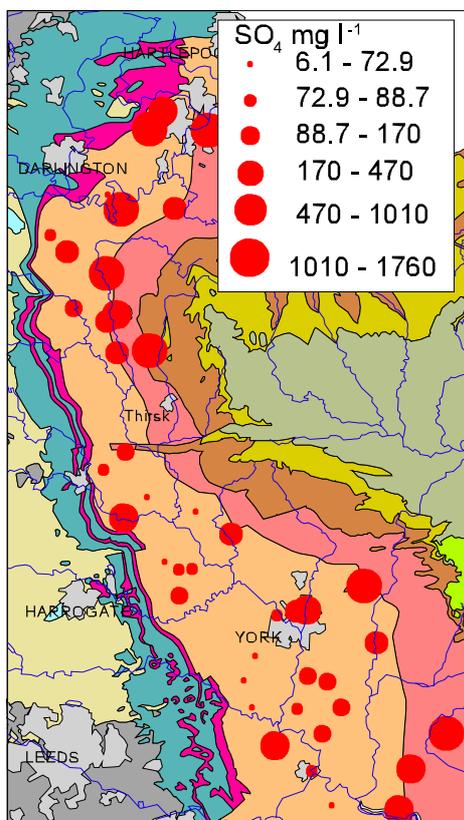
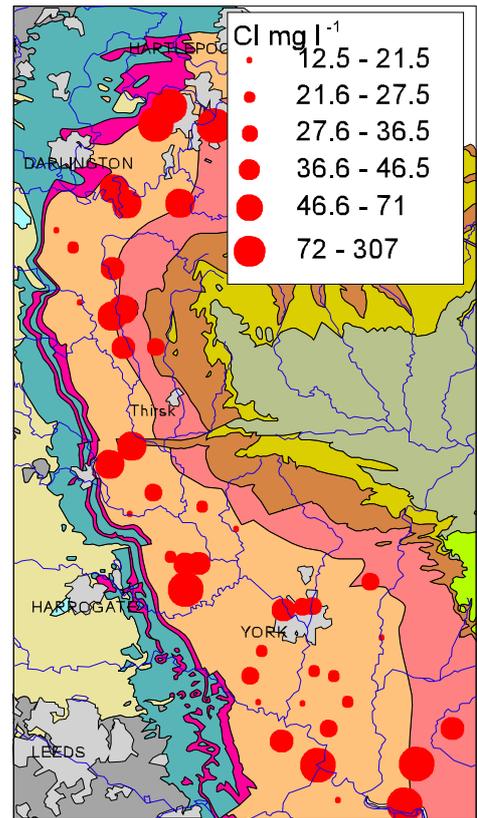
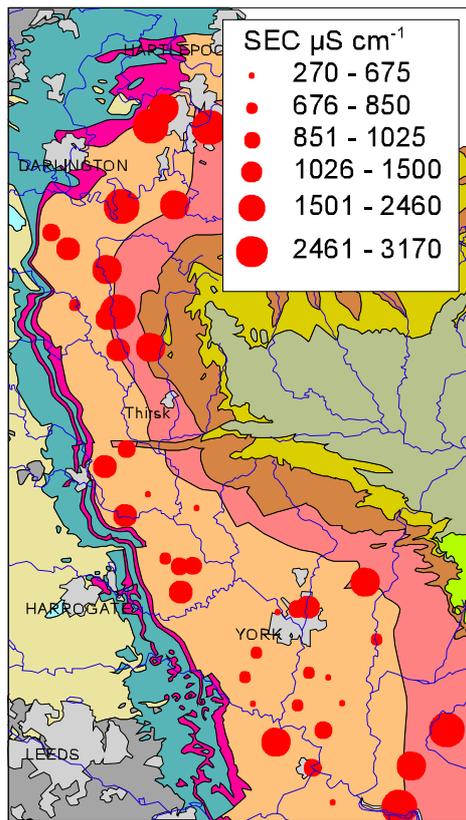


Figure 6.7 Regional variations in selected hydrochemical parameters in the study area.

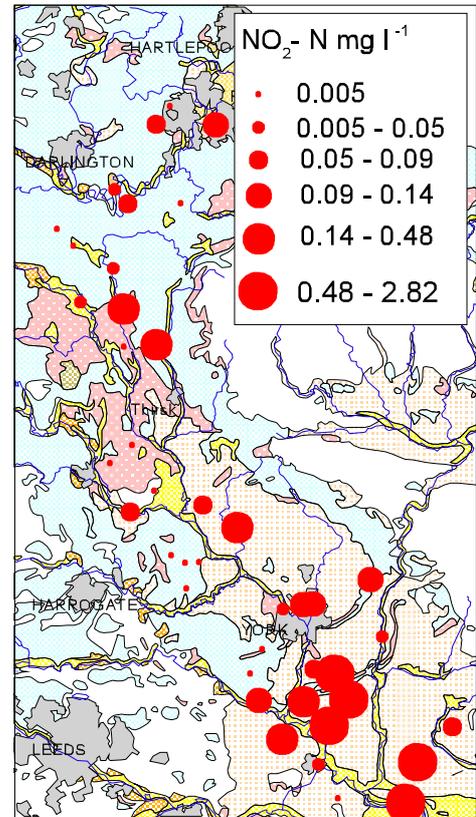
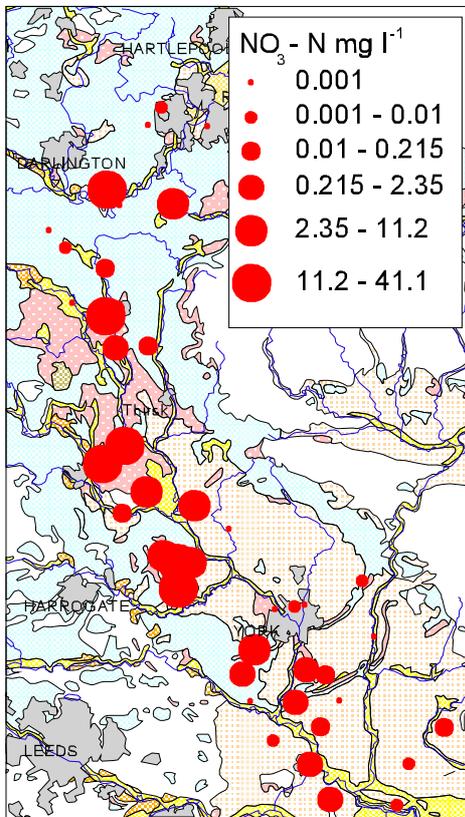
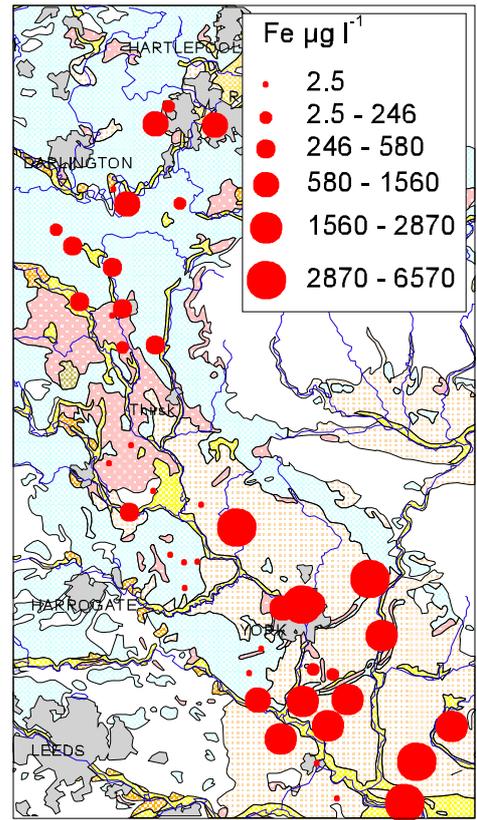
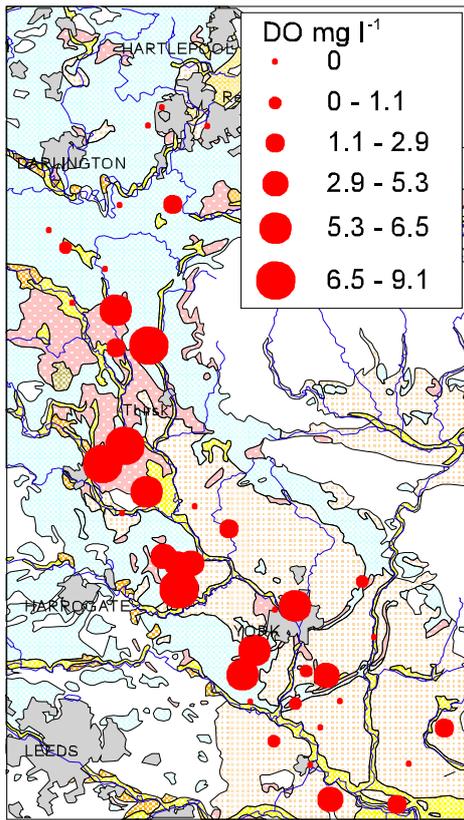


Figure 6.8 Regional variations in selected redox-sensitive parameters in the study area showing the relationship with drift deposits.

7. BASELINE CHEMISTRY OF THE AQUIFER

The chemical data show that the most important influences on water chemistry are mineral dissolution reactions, involving in particular calcite, dolomite and gypsum/anhydrite. This has resulted in relatively high natural concentrations of Ca, SO₄ and Mg. Silicate reactions, although slower, have provided significant amounts of silica and cations including Na, K and to a lesser degree Ca. The concentrations of Si are limited by saturation with a silica phase, most likely chalcedony. In addition, redox reactions are important for many species due to the confined nature of the aquifer as a consequence of the extensive distribution of impermeable drift. Anthropogenic inputs over much of the aquifer are minimised by the protection afforded by the thick drift deposits, particularly in the northern part of the study area. Therefore, for most elements, the concentrations measured and the ranges found can be taken as representative of the natural baseline.

The data have been presented in Table 5.1a and b and the median value and 97.7 percentile provide a good estimate of the average and upper baseline concentrations in the aquifer. However, this should be used in conjunction with maps which show that regional variations do exist in the aquifer. The baseline chemistry changes spatially across the aquifer in relation to the extent of water-rock interaction (hence residence time) and to geochemical controls imposed by the local geochemical environment (e.g. oxidation-reduction controls). The baseline concentrations beneath the Mercia Mudstone, for example, in the southern area are clearly distinct from those in central part of the unconfined aquifer. In addition, the effect of both facies changes in the aquifer and drift thickness means that baseline concentrations increase northwards for many parameters. These regional variations must be taken into account when defining the local baseline for the aquifer. It is clear that the baseline concentrations and ranges are different between unconfined and confined areas and in this region the drift and sedimentary facies control the water quality locally and regionally.

Although most groundwaters are dominated by baseline concentrations of solutes, this is not the case for all solutes. The effect of anthropogenic inputs is indicated by enhanced concentrations of N-species, pesticides and potentially a range of other solutes from urban and industrial usage. The most obvious inputs over the last few decades have been derived from agricultural activities. Baseline nitrate concentrations are most likely to be around a few mg l⁻¹ as indicated by the limited historical data. The use of cumulative probability plots in the study area is difficult because much the original nitrate has been reduced in the confining parts of the aquifer. A cumulative probability plot has been drawn for nitrate on Figure 7.1. The main curvature occurs at around 4 mg l⁻¹ and this is around the concentration expected for nitrate-N baseline concentrations. Unfortunately, there is little historical data available in the oxidising parts of the aquifer to be able to estimate such a baseline from historical records. Other elements which may have been modified by agriculturally-derived anthropogenic inputs include K, Cl and P (Shand et al., 1999). Some boreholes show little evidence of increasing Cl e.g. data from the Nestle borehole in York has a present day Cl concentration of 38 mg l⁻¹, and concentrations in 1941 and 1959 were reported as between 40 and 47 mg l⁻¹. Chloride displays a relatively linear profile on a cumulative probability plot (Figure 5.3), with a slight shift at high concentrations probably related to inputs from evaporite deposits. The complex sources of Cl in this area makes it difficult to determine the regional effects of pollution on baseline Cl, since the addition is likely to be within the natural range of concentrations. Phosphate concentrations are generally low due limited mobility in the aqueous environment and the timescales involved for recharge to occur. Enhanced K and Cl have been discussed and there may be a significant input locally. The dominant source of K is most likely to be from dissolution reactions of K-feldspar, biotite and possibly evaporite minerals. Potassium is not very mobile in the surface environment and most anthropogenic inputs will be consumed by biomass or through sorption processes. Chloride, on the other hand, is very mobile and likely to modify the baseline significantly where evaporites are not present. A comparison of Br/Cl and Na/Cl ratios indicate that Cl may be enhanced locally, in general around urban areas such as Selby, York and Middlesbrough. Although individual water samples may

have been affected by such inputs, these are generally within the range of baseline concentrations produced through natural processes.

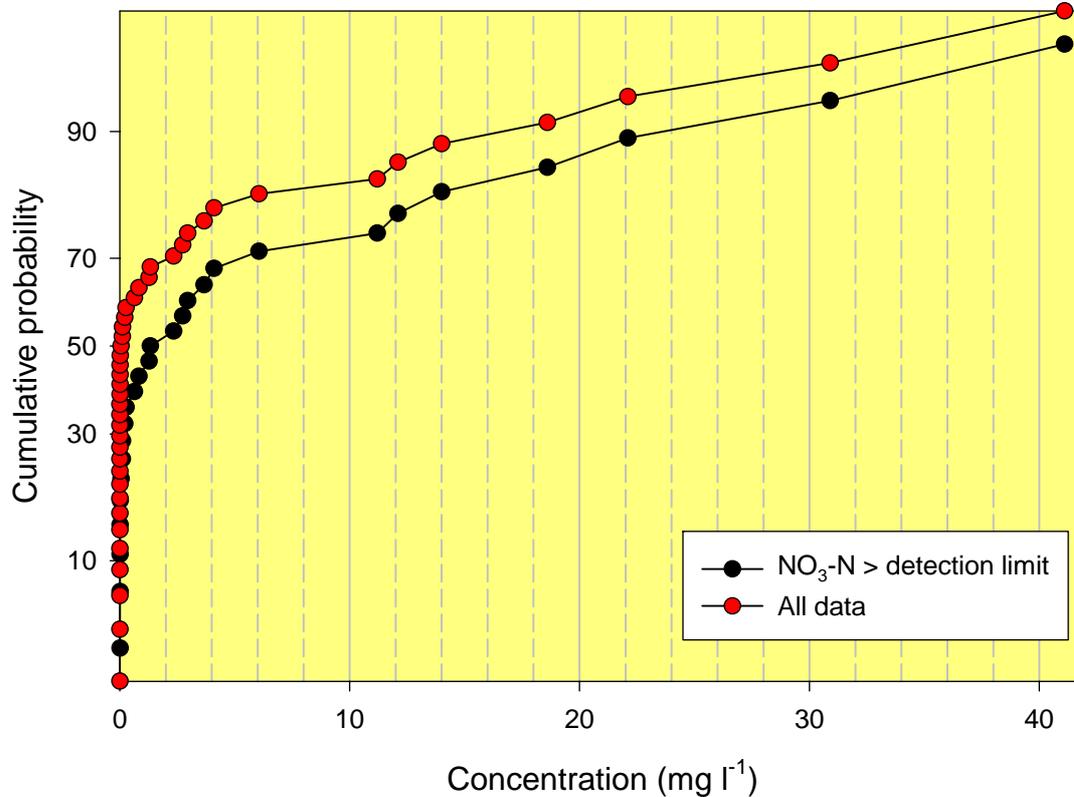


Figure 7.1 Cumulative probability plot showing NO₃-N. A main change in concentration in samples at around 4 mg l⁻¹ may be related the separation of two populations: one baseline and the other pollution.

Some trace elements including As, Ba and U are relatively high in parts of the aquifer but they are considered to represent natural baseline. High concentrations of dissolved As are known from other Triassic sandstone groundwaters in the UK (Griffiths et al., 2002) and other parts of Europe (Heinrichs & Udluft, 1999). The range in concentration of elements such as As, Se and U are related both to variations in source as well as geochemical environment, particularly the redox status. There is little data available on many UK aquifers for U, but again other studies in the present series (Tyler-Whittle et al., 2002; Griffiths et al., 2002) show that moderate concentrations may be present in groundwaters in Triassic sandstone aquifers.

8. SUMMARY AND CONCLUSIONS

The Triassic Sherwood Sandstone in the Vale of York and surrounding areas forms an important aquifer and is used for public supply as well as for industrial and agricultural use. The aquifer becomes progressively finer grained in a northerly direction in comparison with the sandstone further south around Nottingham. The finer grained nature of the aquifer has had a significant effect on its baseline chemistry producing groundwaters with a higher salinity. This is most likely due to reduced natural circulation and transmissivity related to the finer grain size of the aquifer sediments and the preservation of grain cements which would have been lost in coarser grained sediments. The salinities of the groundwaters are higher than found further south largely a consequence of greater calcium and sulphate derived from gypsum/anhydrite dissolution. The highest salinities (again related to higher Ca and SO₄ concentrations) are present in the eastern confined part of the aquifer due to dissolution of gypsum or anhydrite in the sandstone matrix or from the overlying Mercia Mudstone Group. High sulphate along the western margin of the aquifer may be due to leakage from the underlying Permian aquifers which have reacted with bedded gypsum deposits en route.

The presence of thick drift deposits are shown to have a significant effect on groundwater chemistry and recharge to the aquifer. Relatively oxidising, young groundwaters are found in areas covered with permeable drift. These waters are oxidising and contain relatively high nitrate but low concentrations of Fe and Mn. Such areas represent “drift windows” allowing recharge to the underlying aquifer. Groundwaters beneath areas covered with “lacustrine clays, silts and sands” are generally more reducing with low nitrate but high Fe and Mn. In the north of the study area the waters are moderately reducing, indicating that the thick drift deposits are generally impermeable. Sulphate concentrations also tend to be higher and may reflect either a different type of drift or more likely higher abundances of gypsum/anhydrite in the Sherwood Sandstone. There is generally little connection between rivers and the groundwater, especially over the areas overlain by lacustrine clay drift. However, relatively oxygenated, nitrate-rich groundwaters are often associated with river valleys and indicate that active recharge is occurring locally, probably through alluvial deposits in valley bottoms.

It is concluded that the properties of groundwater in the Vale of York area are overwhelmingly determined by natural reactions between groundwater and the bedrock and drift deposits. The natural baseline is expressed as a range of concentrations which, for some elements, can vary over several orders of magnitude. Some elements are enhanced over the natural baseline due to anthropogenic influences. The baseline concentrations of nitrate and chloride, for example, have been significantly modified by agricultural and industrial practices. The presence of relatively high concentrations of several trace elements is considered to be due to entirely natural processes. These include locally enhanced levels of arsenic, barium and uranium which may breach drinking water standards. The complex nature of the geology and drift deposits in this area has given rise to significant local and regional variations in baseline quality which need to be taken into account in characterising the aquifer, in defining drilling targets and in dealing with remedial issues.

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ACKNOWLEDGEMENTS

We are extremely grateful to Stuart Furness, Phil Myers and Richard Kramer of the Environment Agency for their invaluable help and support during fieldwork. This work would not have been possible without the support of the farming and industrial community who allowed access to sample their boreholes. Yorkshire Water plc is thanked for supplying time series data for boreholes in the region. The chemical analyses were completed by Debbie Allen and Sarah Trickett under the supervision of Janice Trafford. George Darling (BGS) and Alan Ward (EA) are also thanked for stable isotope and N-species analyses respectively. Ian Gale, Denis Peach and the Environment Agency Steering Committee kindly reviewed the report. We are also grateful to Mark Antrobus of SPSS for his development work on PIPER diagrams in Sigmaplot.