Baseline Report Series:
3. The Permo-Triassic Sandstones of South Staffordshire and North Worcestershire

Groundwater Systems and Water Quality
Commissioned Report CR/02/119N

National Groundwater & Contaminated Land Centre
Technical Report NC/99/74/3

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

BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/02/119N

ENVIRONMENT AGENCY
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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
Kinver Edge, west of Stourbridge. The well used to provide groundwater to the adjacent house built into Triassic Sandstone.

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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 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) 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

This report investigates the variations in natural water quality and the dominant geochemical processes operative in the Permo-Triassic aquifer in the South Staffordshire and North Worcestershire region. The area of study lies west of Birmingham and principally includes the unconfined sandstone catchment of the River Stour, stretching between Wolverhampton and Kidderminster. The Permo-Triassic Sandstone is an important aquifer providing public and private water supplies to towns, farms and industries in the region. Land use is dominated by agriculture although industries are present in and around some of the larger towns. Low permeability drift is largely absent in the area and the aquifer is classified as vulnerable to pollution. However, less permeable horizons are present within the aquifer, which can constrain flow and therefore provide some protection to groundwater from pollution.

The aquifer comprises several geological formations and, although they are often considered together as a unit, each formation clearly imparts strong controls on the hydrogeology and hydrochemistry of the region. Hydrochemical data show that there are differences in water quality both within and between the formations, resulting in strong lateral and vertical variations within the aquifer. Faulting in the aquifer is extensive and has a strong influence on the hydrogeological and hydrochemical characteristics.

An understanding of the geochemical processes involved can significantly aid groundwater management when dealing with such complicated systems. The dominant control on the groundwater chemistry of the in the region is dissolution of carbonate (calcite, dolomite) and sulphate (gypsum) cements which are present in the aquifer. Ion exchange also provides an important control on the groundwater chemistry due to the presence of clays and clay horizons. Mixing with original connate or a modified connate (formation) water does not appear to be significant and chloride concentrations are relatively low compared to other regions of the Permo-Triassic aquifer (Edmunds et al., 1982; Shand et al., 2002). Stable isotope results suggest that the majority of groundwater is relatively young in age (post Holocene). Oxidising conditions extend up to depths of 380 m below ground level (bgl) and concentrations of nitrate are high throughout most of the region. Reducing conditions are present beneath the Mercia Mudstone, to the south east of the study area and at isolated sites within the Permo-Triassic outcrop due to the presence of less permeable horizons within the aquifer. Therefore, the hydrochemistry appears to be primarily influenced by water-rock interaction modified by residence time and redox status of the aquifer.

Regional variations in groundwater chemistry have been used within the Baseline project in an attempt to assess the evolution of the groundwater chemistry. The geological and hydrogeological complexity of this area complicates the identification of flowlines. Most of the study area is also unconfined and groundwater abstraction is likely to have strongly modified natural groundwater flow patterns. Despite these problems, regional trends can be identified e.g. an increase in some elements is seen near the Worcestershire Canal and the River Stour, suggesting groundwater-surface water interaction.

The quality of groundwater in the South Staffordshire and North Worcestershire region is generally good and dominated by natural sources of solutes. The natural baseline quality is expressed as a range of concentrations, which can vary over several orders of magnitude. Some elements are enhanced above the natural baseline due to anthropogenic inputs including nitrate from agricultural practices or leakage from industrial effluent along the River Stour. Water of poor quality also occurs due to entirely natural processes and trace elements, including barium and arsenic, were found to exceed drinking water standards in some samples. It is hoped that the results will provide useful information to aid groundwater management and provide a basis from which to identify future impacts on the quality of groundwater.

2. PERSPECTIVE

The Permo-Triassic sandstone is classified as a major aquifer in Britain and is the second most important aquifer in the UK, supplying approximately 25% of all licensed abstractions in England and Wales (Monkhouse & Richards, 1982). This report presents the results of a hydrochemical study of the Permo-Triassic aquifer in the South Staffordshire and North Worcestershire region between Wolverhampton and Kidderminster (Figure 2.1).

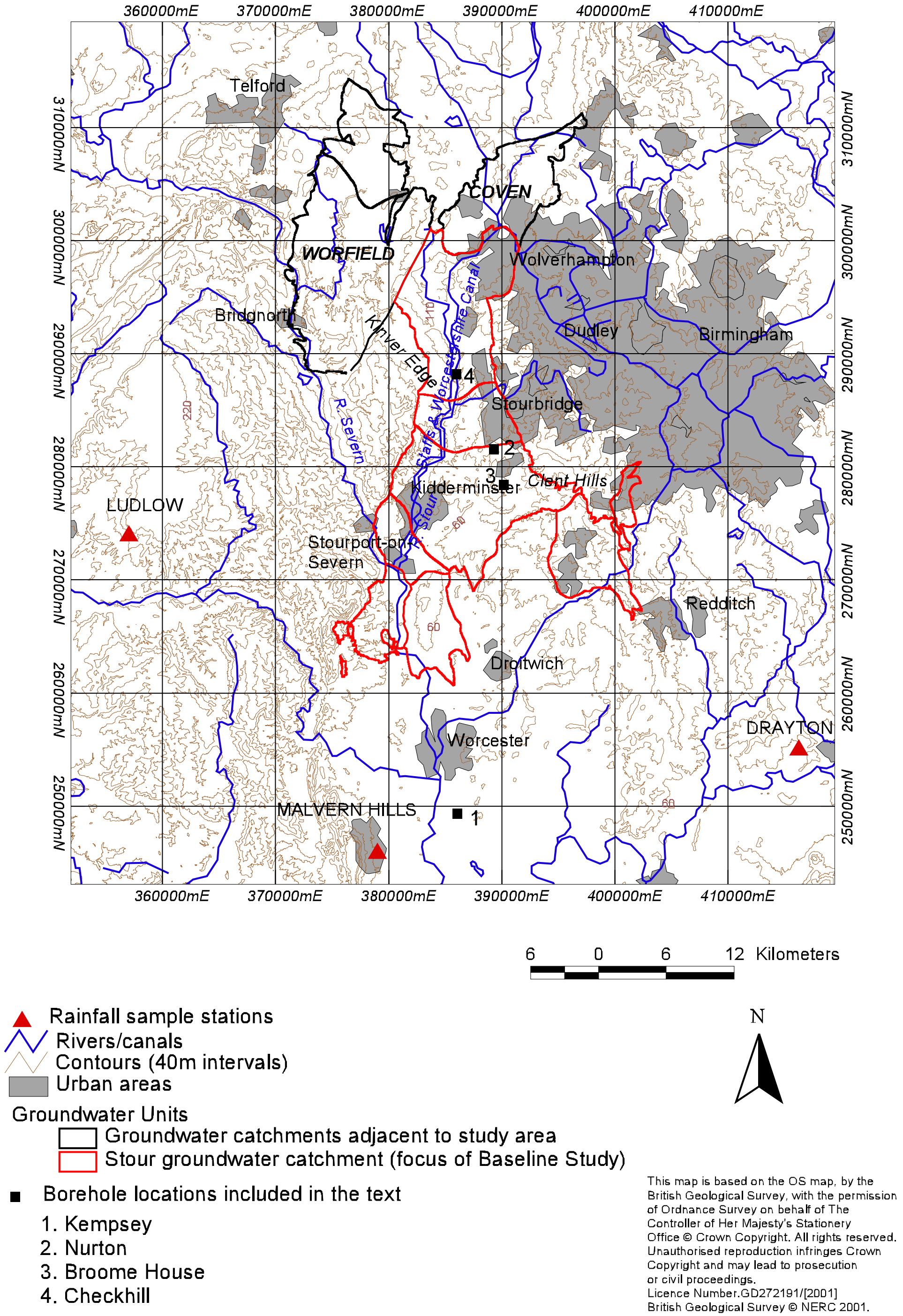


Figure 2.1 Location of the South Staffordshire and North Worcestershire study area.

The Permo-Triassic sandstones in this area form relatively low-lying ground and are bounded to the east and west by older Carboniferous rocks. Variation in the hardness of rocks within the Permo-Triassic sandstones has, however, resulted in a varied landscape of steep scarps (Kidderminster and Bromsgrove Sandstones) and gentle slopes (Bridgnorth and Wildmoor Sandstones). Sandstone ridges exist near the eastern and western boundaries of the sandstone outcrop (Figure 2.2), with the highest point in the area situated on the Kidderminster conglomerate of the Clent Hills, at approximately 220 m AOD. The River Stour forms the lowest point of the catchment at approximately 80 m AOD.

Figure 2.2 **View of Birmingham looking east across the Permo-Triassic outcrop from Kinver Edge (NGR: 383500 283000)**

The River Stour and its tributaries provide the main drainage of the catchment and flow southwards to join the River Severn at Stourport-on-Severn. The Staffordshire and Worcestershire Canal also lies adjacent to most of the River Stour's path (Figure 2.3). Groundwater flow to the River Stour has largely ceased and the river is now believed to be predominantly sustained by sewage effluent discharges (Johnstone, 1997). The relationship between river water and groundwater in the aquifer or drift is poorly understood yet it is an area of particular interest with regard to the definition of groundwater bodies and for quantifying surface water-groundwater interaction (Box 2.1). Baseline groundwater sampling has helped to understand the interaction between the aquifer and the River Stour, a river historically influenced by pollution.

Figure 2.3 **The Staffordshire and Worcestershire canal bounded by Permo-Triassic sandstone rocks.**

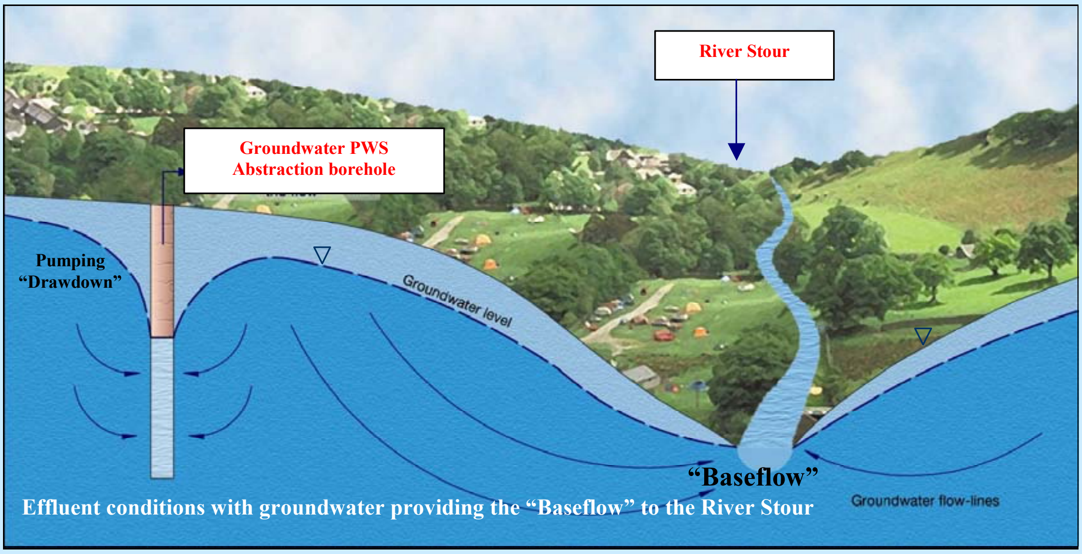
There are many pressures on groundwater in the area including over-abstraction and pollution. These issues are addressed in the Local Environment Agency Plan (LEAP) reports for the area. Rapid population growth has resulted in an increase in the demand for water resources, and supplies of good quality water during peak summer demands can be problematical (Entec, 1998). Since 1990, there has been a gradual shift from groundwater to surface water sources in the area, mainly due to the relatively high nitrate concentrations present in the groundwater. Over 90% of the public water supply in the Stour catchment is still supplied from groundwater (West Midlands Stour, LEAP, Environment Agency 1998). Public Water Supply accounts for over 92% of the licensed abstraction with sources operated by Severn Trent Water Plc and South Staffordshire Water Plc. The aquifer provides potable supplies to the Black Country (Stourbridge, Dudley and Wolverhampton), Kidderminster and the smaller towns of Bridgnorth, Bromsgrove, Bewdley and Stourport.

Urban areas cover over 32% of the study area and significant pressures exist for further development in the region (LEAP, Environment Agency 1998). The urban areas are located mainly to the north and east of the sandstone outcrop and include Stourbridge, Wolverhampton and Birmingham (Figure 2.1). The densely-populated areas around Kidderminster and Stourport-on-Severn developed due to their proximity to the River Stour and the presence of the Staffordshire and Worcestershire Canal (Mitchell, et. al, 1962). Both Kidderminster and Stourport supported the carpet industry, together with other industries such as iron-works and the manufacture of porcelain goods (Box 2.2).

Box 2.1: Groundwater-Surface water interaction in the Kidderminster/Stourbridge area

Groundwater in the Kidderminster area is abstracted from boreholes in the Sherwood Sandstones aquifer, mainly for drinking water and for industrial and agricultural purposes. These sandstones form high yielding aquifers and represent the major aquifer type in the Midlands Region. The aquifers around Wombourne, Stourbridge and Kidderminster supply around 140 Mega-litres per day (Ml d^{-1}) of groundwater which is utilised in the surrounding 'Black Country' towns.

Several watercourses cross the Sherwood Sandstone aquifer outcrop from east to west and north to south forming an integral component of the hydrological system. The River Stour is one of the main rivers which flows from its source on the Clent Hills, past its confluence with the Smestow Brook, it's major tributary, and eventually into the River Severn. Interactions between rivers and the underlying aquifer occur where "effluent" and "influent" conditions exist over different stretches of the same river. Effluent conditions occur where groundwater head is significantly *above* the river level and groundwater discharges into the river providing a "baseflow" component to the river. Groundwater flows and seepages are critical in providing summer flows into rivers and streams, otherwise they could periodically dry up. Regional groundwater flow is generally towards the River Stour and is controlled by topography. Under "influent" conditions, the groundwater head is *below* the surface water level of the river and seepage takes place back into the aquifer by "leakage" providing a recharge component. The location of public water supply (PWS) boreholes within close proximity to watercourses results in a number of such localised inflows, reducing flows in the River Stour.



Effluent conditions with groundwater providing the "Baseflow" to the River Stour

The upper reaches of the Stour flow through the rural Stourton area as well as through the highly industrialised area of Stourbridge where a large number of abstractions and discharges are made along its length. In the middle reach, the river flows over the Stourbridge Sherwood Sandstone aquifer where abstractions heavily outweigh replenishment by recharge, severely limiting baseflow support to the river. Discharged sewage effluent has masked the unsustainable levels of groundwater abstractions as they have helped to maintain flows along the upper reaches of the river. The Environment Agency is working to achieve reductions in groundwater abstraction in this area to a more sustainable level which would provide an increase in baseflow to the river.

Pollution from both industrial and agricultural activities can pose a threat to groundwater quality. Successful management of groundwater resources requires knowledge of the natural baseline quality in order to identify whether or not pollution is occurring from agricultural or industrial sources. Historical changes of land use through time have been summarised by Entec (1998) for this area and Figure 2.4 illustrates the most recent land use map available. Agricultural land covers approximately 60% of the area, particularly in the south and west of the area. Present day agricultural landuse is influenced in part by the near-surface geology and soil distribution. For example, the area where Mercia Mudstone crops out to the south east of the study area is mainly used for grazing, unless the land can be well drained to aid crop growth.

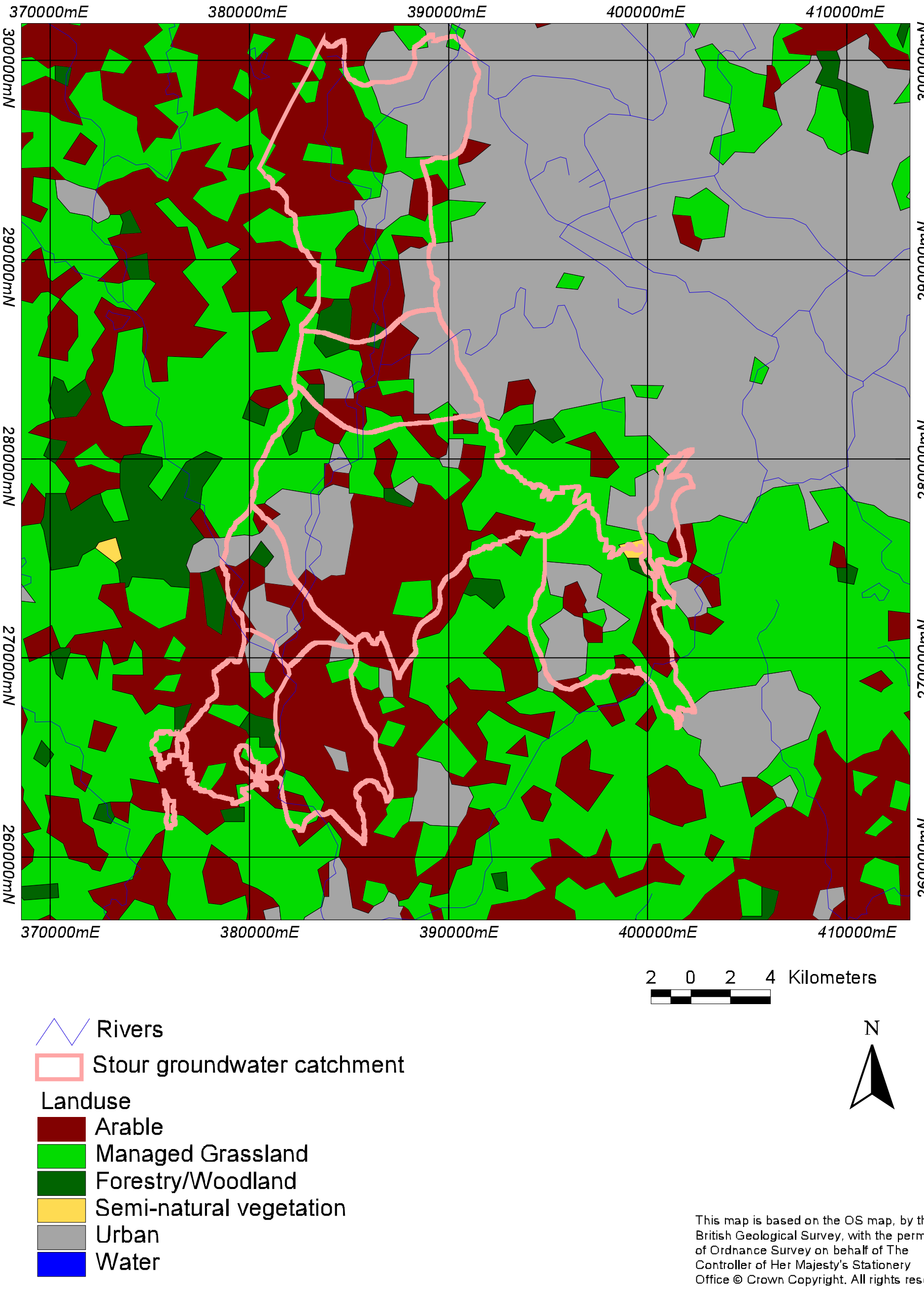


Figure 2.4 Land Use in the South Staffordshire and North Worcestershire region

Box 2.2: The carpet industry in Kidderminster

River Stour at Kidderminster

The River Stour in the Kidderminster area has a history of industrial usage and for more than a century has been affected by waste effluents from the town's carpet manufacturing trade which had formed the back bone to the local economy for many years. Whilst providing the area with an industrial heritage, it also left behind a less desirable legacy in the form of water pollution and contaminated land. During the 1800's and up to the 1930's, many of the streams in the area were exploited as a source for water power and industry located itself in close proximity to rivers. Water played an essential part in the manufacture of carpets and both surface waters from the River Stour and groundwater from local sandstone aquifers were utilised in the industrial process.

There was no controlled method for disposing of liquid waste effluent from industry and local rivers and streams provided the means of carrying away waste waters. This impacted badly on local rivers killing most aquatic life. Discolouration of the river by wool dye and discharges of organic matter, solids and grease were commonplace, but these issues have long since been resolved, as these effluents now drain to sewage treatment works. However, the river has continued to suffer from local toxicity problems caused by the use of pesticides, particularly *permethrin*, which is used as a mothproofing agent in carpets. Ground contamination may also have resulted from the accidental spillage of chemicals in storage areas or during the various stages of manufacture, in making dye and textile dyeing. The persistence of the contaminants and their impacts on groundwater, particularly with solvents, acids, alkalis and bleaching agents will depend on their solubility and volatility as well as their physical, chemical and biological properties.

Several watercourses flow across the Sherwood Sandstone aquifer outcrop. The River Stour interacts with the underlying aquifer where influent and effluent conditions exist over different stretches of the river. Pollutants from the Stour can enter groundwater when the conditions are influent by seepage, affecting groundwater quality. This would be particularly relevant in the past when groundwater levels would have been higher. Groundwater flow is slow and it can take decades or even millennia to move through the aquifer. Therefore, such contamination can continue to pose serious problems to quality for many years.

Today, we are facing the legacy for what has happened in the past. Although the quality of the water in the River Stour has started to improve, its urban location means that intermittent discharges of storm sewage can still affect the quality. In the last 10 years, *permethrin* has fallen by 92.5% and biological status of the River Severn downstream of the Stour confluence has improved in quality from "fair" to "good". Such resources continue to need protection and the Environment Agency is working in partnership with water companies and the carpet industry trade association to protect and restore water quality in the Stour catchment.

Groundwater vulnerability maps highlight the areas of an aquifer which are susceptible to groundwater pollution. These maps account for the effectiveness of soil and superficial deposits to retard the movement of pollutants into the aquifer. With the exception of some areas to the west of Wolverhampton and adjacent to the River Stour, which are protected by areas of less permeable drift, the entire area is classified as highly vulnerable.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Geology

The Permo-Triassic sandstone in the South Staffordshire and North Worcestershire region lies within the Worcester Basin, which formed during the Permian and early Triassic. During this time, several phases of rifting resulted in the formation of a complex system of interconnected basins. This resulted in thick sequences of Permian and early Triassic sandy deposits, which form the Permo-Triassic sandstone aquifer (Allen et. al., 1997). The geology of the area is illustrated in Figure 3.1.

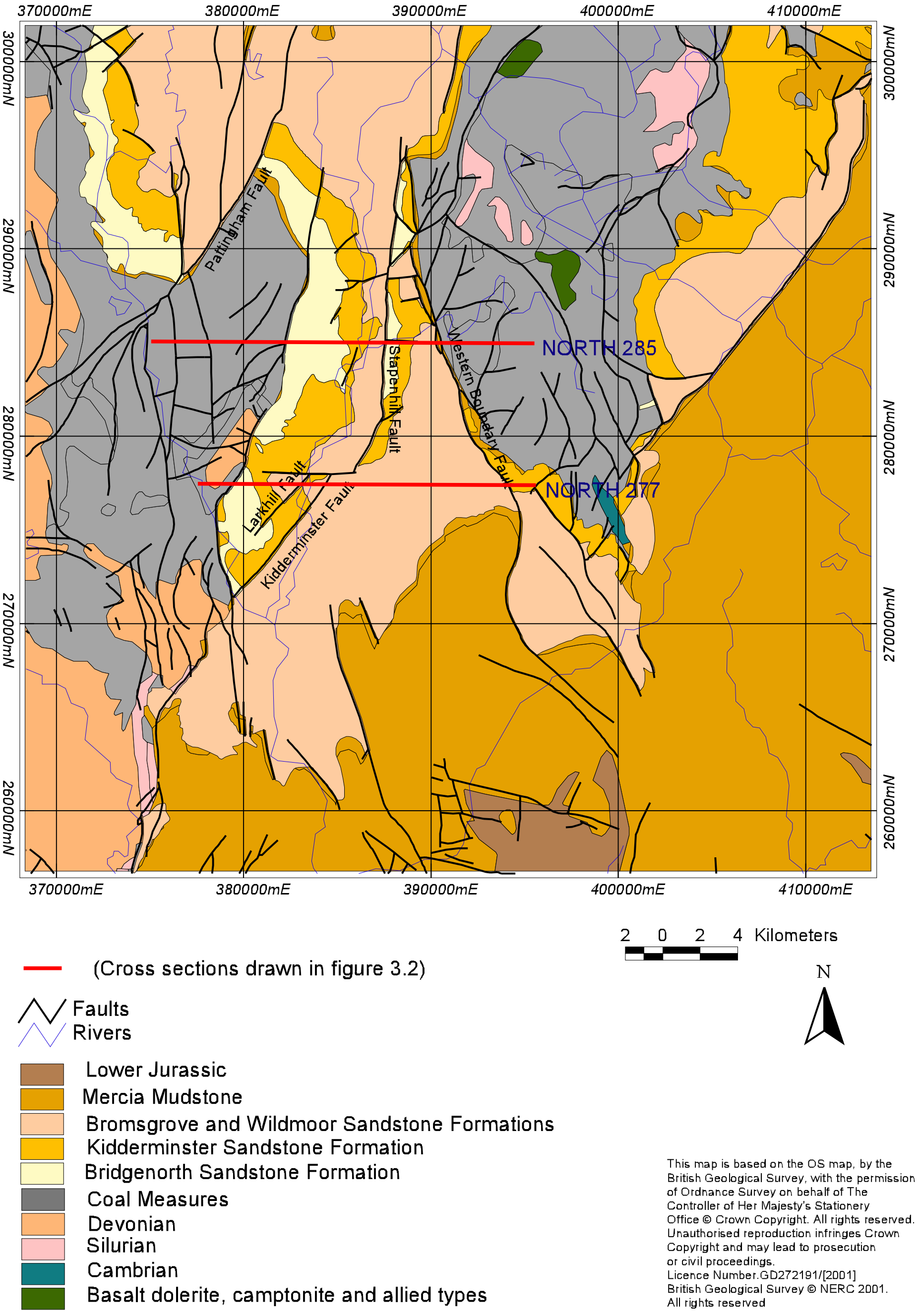


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Figure 3.1 Geological map of the South Staffordshire and North Worcestershire study area

An understanding of the structure and stratigraphy of the Permo-Triassic sandstones in the region is vital for the interpretation of the hydrogeochemistry. The lithologies of the Permo-Triassic sandstones are varied and different properties are identified both between and within the formations. The rocks of the Worcester Basin are folded along north-south axes forming a syncline, which is faulted in the north of the basin along north-east to south-west trending faults (Figure 3.2). Within the basin there are also several smaller normal faults with the same orientation and minor faults with an approximate east-west trend (Figure 3.1). The sandstone formations dip approximately 5-10° eastwards towards the centre of the basin and the syncline plunges at an angle of 5° towards the south.

The Permo-Triassic rocks lie unconformably on a Precambrian to Palaeozoic basement of varied relief and geology. The thickness of the Permo-Triassic sandstones range from approximately 650 m at Wildmoor in the south-east of the outcrop to 100 m west of Kidderminster. This variation is due to erosion, faulting and deposition of sediment onto an irregular topographical surface, causing the oldest formation (Bridgnorth Sandstone) to have the largest variation in thickness (Figure 3.2). Seismic reflection data have identified the subsurface structure in the Worcester Basin (Barclay et al., 1997).

The Permo-Triassic outcrop lies between two areas of Coal Measures, which provide the eastern and western boundaries to the area of study. The overlying outcrop of Triassic Mercia Mudstone marks the southern boundary to the study area (Figure 3.1). All formations of the Permo-Triassic crop out in the area of study and are present in sequence with the youngest exposed towards the south-east (Figure 3.1). Within the South Staffordshire and North Worcestershire region the Permo-Triassic sandstone succession is subdivided into four formations (oldest first): the Bridgnorth Sandstone, the Kidderminster Sandstone, the Wildmoor Sandstone and the Bromsgrove Formation. The formations are varied but generally fine upwards from the Bridgnorth to the Bromsgrove Formations. Lithological and hydrogeological descriptions of the formations are given in Table 3.1, illustrated in Figure 3.3 and are analogous to other Permo-Triassic formations in the UK.

Figure 3.3 Typical Permo-Triassic outcrop of the Kidderminster Sandstone showing cross-bedding.

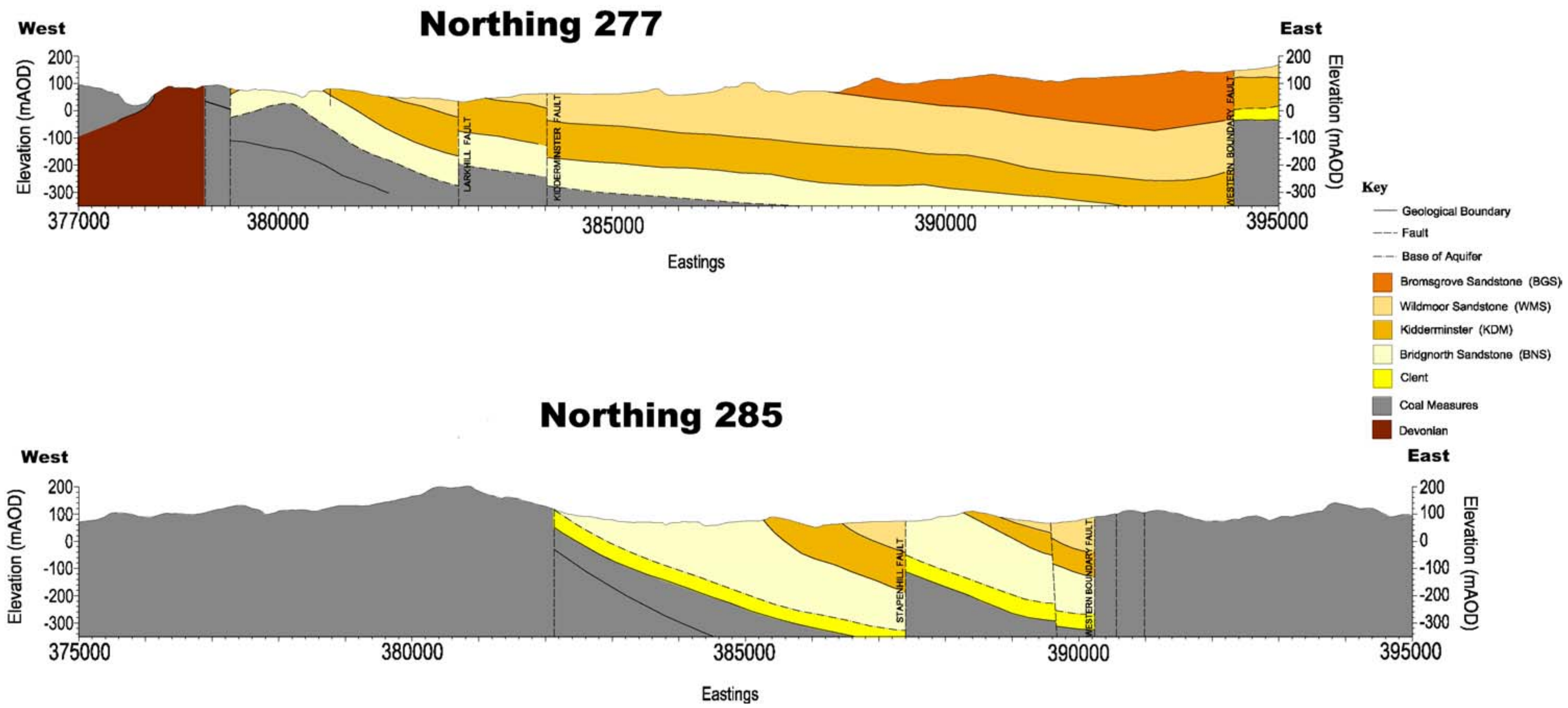


Figure 3.2 East-west cross-sections across the South Staffordshire and North Worcestershire study area (after Entec, 1998). Lines of section are shown on Figure 3.1.

Table 3.1 **Permo-Triassic Stratigraphy in the South Staffordshire and North Worcestershire region (after Allen et al., 1998 and Mitchell, 1962).**

System	Lithostratigraphic Division	Previous name for division	Aquifer Unit	Thickness (m)	Lithology	Depositional environment
TRIASSIC Mercia Mudstone Group	Mudstone Unit	Keuper Marl	Aquitard	140-550	Argillaceous. Mudstones interbedded with thin impersistent siltstones and sandstones. Some lenses of evaportites and gypsum.	Marine environment with arid periods.
TRIASSIC Sherwood Sandstone Group	Bromsgrove Sandstone Formation	Keuper Sandstone	Aquifer	0-350	Fine micaceous sandstones, interbedded with red-green marls. Varied calcareous and dolomite sandstones. Cyclic deposition	Freshwater environment with arid periods, prior to marine transgression.
	Wildmoor Sandstone Formation	Upper Mottled Sandstone	Aquifer	0-150	Fine, well-sorted, poorly-cemented sandstone with mudstone horizons. Sandstone ferruginous, with calcareous and dolomite cement.	Low energy, fluvial/ lacustrine environment.
	Kidderminster Formation	Bunter Pebble Beds	Aquifer	0-200	Conglomerates, sands and marls. Medium-coarse grained with strong calcite/ dolomite cement. Well developed breccias at edge of basin.	Gravel fans deposited in a high energy environment, ie: Wadi's.

Drift deposits are generally absent in the south of the area, and where present, mostly follow the River Stour. These superficial deposits are largely permeable, consisting of fluvioglacial sands and gravels, together with some silt and clay. Towards the north of the area, the topography is smoother and overlain by some Boulder Clay and gravel and sands.

3.2 Aquifer Mineralogy and Petrology

The coarse-grained fraction of the Permo-Triassic sandstones is relatively unreactive consisting largely of rounded to sub-angular quartz grains and feldspar (Figure 3.4). The grains are held together by a wide variety of matrix cements including calcite, dolomite, gypsum, anhydrite, halite, iron oxide and clay minerals. However, post-depositional diagenesis has significantly affected both the aquifer properties and hydrogeochemistry of the Permo-Triassic Sandstones. It is important to understand the potential contribution of the mineralogy to groundwater chemistry and Backscattered Scanning Electron Microscope (BSEM) pictures from the Kidderminster Formation (Figure 3.4) have been included to illustrate the textures and mineralogy of the Permo-Triassic aquifer. These indicate a relatively high porosity suggesting that much of the primary cements have been dissolved. For example, most anhydrite and other evaporite mineral cements have been removed by groundwater circulation and are only present at depth within the basin. Dissolution of the carbonate and evaporite cements are very important in modifying the groundwater composition, because they dissolve much more rapidly than the quartz and silicate mineral phases.

The sandstones have undergone diagenetic alteration with time and burial. These changes can be seen in altered and secondary (authigenic) phases, including quartz, iron mineralisation and clays. Quartz provides the skeletal fabric of the sandstone and tends to resist alteration. However, the presence of large pores (black) indicate dissolution of the framework grains, and this is probably a result of corrosion of plagioclase and K-feldspar (Figure 3.4B). Calcite occurs both as individual grains and as patchy interstitial cement. Much of the calcite is primary, but euhedral crystal faces into open pores (black) and indicate relatively modern precipitation. The calcite cement may also demonstrate concentric growth patterns (light grey) with alternating illitic clay (dark grey) within the calcite fabric (Figure 3.4D).

The clay minerals are dominated by kaolinite within the shallow aquifer, and illite in deeper parts of the aquifer. Further diagenetic alteration can be seen by the presence of authigenic kaolinite and areas of fine siltstone lamina (Figure 3.4E). The dissolution of feldspars, as well as matrix cements, leads to enhanced porosity and original grain outlines are preserved by thin illite clays which originally coated the grains (Figure 3.4F).

3.3 Hydrogeology

The Permo-Triassic sandstones form the major aquifer in the South Staffordshire and North Worcestershire region and are generally considered to act as a single hydrogeological unit. Fine-grained Permian marls form the base of the aquifer and the Mercia Mudstone forms the overlying aquitard in the south-east of the region, although few boreholes are drilled where the sandstones are confined. Groundwater generally flows towards the River Stour, which bisects the aquifer and flows from north to south (Figure 3.5). The hydraulic gradient of the groundwater is influenced by the topography, with steep contours identified at the edge of the Sandstone outcrop where topography is higher, and shallower gradients in the valleys.

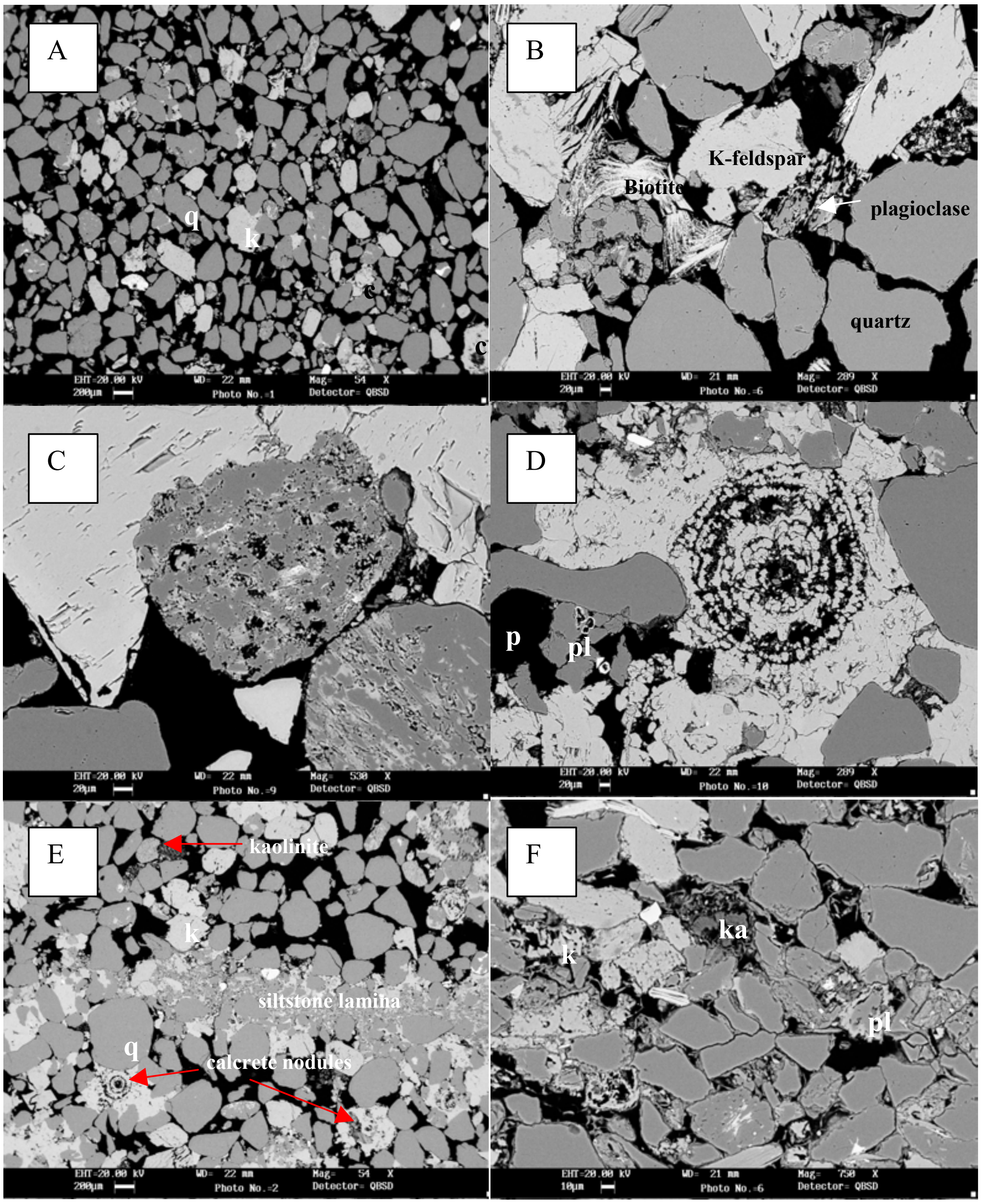


Figure 3.4 **Backscattered Scanning Electron Microscope pictures of the Kidderminster Formation, north Birmingham.** A. Well-sorted, porous sandstone, with an uncompacted open grain framework of detrital quartz (q) and K-feldspar grains (k). B. Biotite may showing deformation by compaction and alteration along cleavage to illite. C. A corroded, microporous plagioclase feldspar grain (dull grey, centre), partially enclosed in an intergranular calcite cement (light grey). D. Concentric growth fabric of calcite (light grey) with alternating illitic clay (dark grey) within a calcite cement. Corroded relicts of plagioclase feldspar (pl). E. Fine ‘siltstone lamina’ includes patches of reworked calcrete grains (‘cornstones’) and quartz silt grains (grey). Authigenic kaolinite probably formed as a result of alteration of a detrital feldspar grain. F. Authigenic kaolinite (ka) replacing unstable detrital grains and the original grain outline is delineated by a thin illite clay pellicle which coated the grain. Both Plagioclase (pl) and K-feldspar (k) show corrosion effects

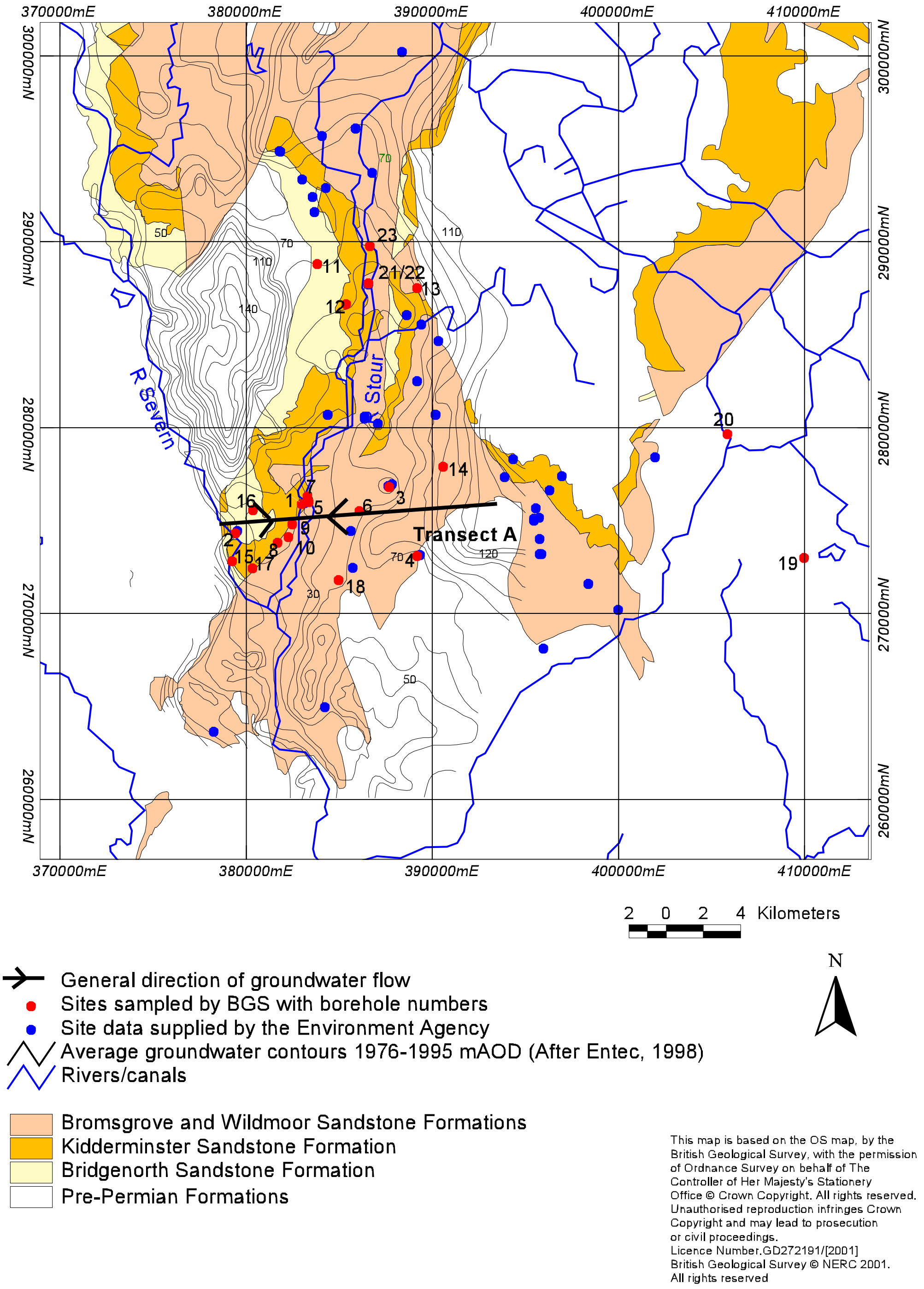


Figure 3.5 **Groundwater contours in the Permo-Triassic aquifer of the South Staffordshire and North Worcestershire study area.**

Although the Permo-Triassic sandstones are considered to act as a single hydrogeological unit, water levels are strongly influenced by the heterogeneous nature of the stratigraphy and faulting in the area. In reality, this produces hydraulic stratification and results in multi-layered aquifer systems. The Bromsgrove Sandstone formation, in particular, forms a multiple aquifer system, due to the strongly cemented marl breccias, shale, marl and mudstone layers, interbedded with the sandstone. Permeable units within the formation have different hydrostatic pressures and respond differently to pumping. Boreholes will have different yields depending on which units are screened and will therefore yield groundwater from more than one geological formation. Although low permeability layers exist within and between the Bridgnorth, Kidderminster and Wildmoor Sandstone formations, they are generally found to be more permeable aquifers than the Bromsgrove Sandstone formation.

Marl bands can give rise to locally confined conditions and artesian flow has been identified at Stourport and Kidderminster. Springs were sampled within this project (Sites 6, 7, 18; Figures 3.5 and 3.6) which issue from within the Bromsgrove Sandstone. In the north of the area, springs historically issued from near the top of a hill due to the presence of localised clay bands within the Kidderminster Formation (Figure 3.7).

Figure 3.6 Perry Farm pond fed by natural springs (Site 18).

The horizontal permeability is often greater than vertical permeability due to the layering of fine-grained (less permeable) and coarse-grained (more permeable) sediments. Horizontal permeability can be up to four times greater than vertical permeability in the Bridgnorth Sandstone (Allen et al., 1997). However, no significant differences in hydraulic conductivity or porosity of the sandstones with depth have been found (Allen et al., 1997). A summary of the hydrogeological parameters are shown in Table 3.2.

Figure 3.7 **An artesian borehole abstracting from the Kidderminster Formation at site 12.**

Bulk hydraulic conductivity values derived from pumping tests are several orders of magnitude larger than intergranular (core) hydraulic conductivity, reflecting a considerable contribution from fracture flow. Although matrix flow dominates groundwater movement on a regional basis, fractures are important locally in the saturated zone of the aquifer in providing preferential flow paths on a scale of 0-10's metres. The range of transmissivity values derived from aquifer testing indicates a complex hydraulic system.

Table 3.2 **Physical properties of the Sherwood Sandstone Group of the West Midlands (data from Allen et al., 1997 and Bridge and Hough, 2001).**

Parameter	Minimum	Maximum	No.of measurements
Matrix porosity (%)	2	36	
Core Hydraulic Conductivity (Average) m/d	1×10^{-6}	18	88
Bulk Hydraulic conductivity (m/d)	0.014	486	88
Storativity (confined)	2×10^{-4}	0.15	11
Specific Capacity (m3/d/m)	0.34	81000	71
Specific Yield (%)	10	15	
Transmissivity (m2/d)	2	5200	88

The presence of faults can increase or decrease permeability within the aquifer by either forming zones of enhanced permeability or impermeable barriers to flow. Direct recharge occurs through the sandstone outcrop but additional recharge may occur where there is intensive faulting, for example in the Coven groundwater catchment or where the sandstones are adjacent to abandoned coal mine workings (e.g. beneath Stourbridge). In contrast, the Pattingham Fault (Figure 3.1) forms an impermeable boundary with a significant head difference (21-27 m) across it, and is associated with a spring line.

In 1998 a water resources study was completed in the area (Entec, 1998). Preliminary water balance calculations concluded that the River Stour Catchment retains a small surplus of ca. 9 mm a^{-1}, despite the wider area (including the Worfield catchment) having a deficit of 46 mm a^{-1}. Entec (1998) also noted that long-term abstraction has reversed vertical gradients that were originally artesian and there has been a gradual lowering of the water table over a wide area. (Figure 3.8).

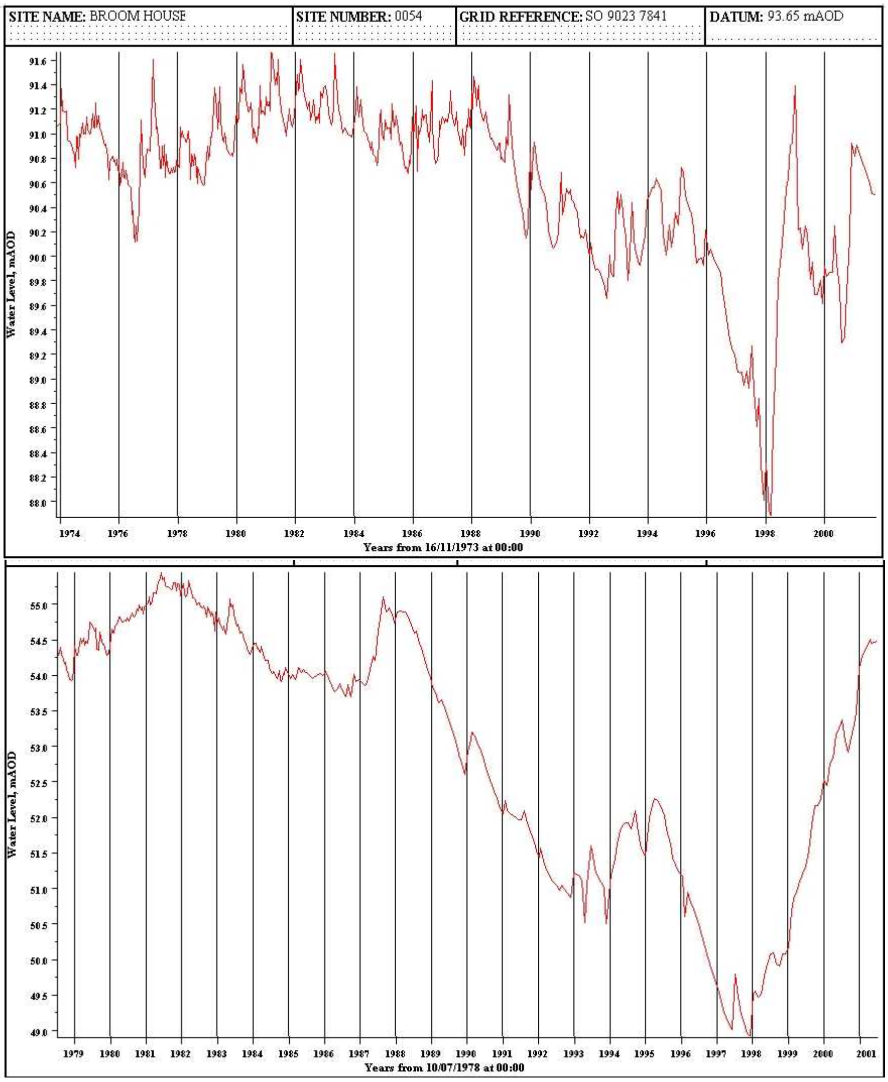


Figure 3.8 **Groundwater hydrographs for boreholes Broome House (94 m aOD) and Check Hill (67 m aOD) from the Permo-Triassic aquifers of South Staffordshire and North Worcestershire.**

Groundwater abstraction for public supply forms by far the largest use of groundwater in the region. Public water supply sources accounted for 94.5% of the total actual groundwater abstraction between March 1995 and March 1996. Industry accounted for another 5.7 % and the remainder was used for agricultural, private domestic and amenity uses.

Rainfall is greatest on higher ground (approximately 700 mm a^{-1}) in the north and east of the area which comprises largely Carboniferous strata with poor groundwater storage potential. In contrast, effective rainfall is lowest on the low-lying agricultural land of the sandstone basin (c. 600 mm/a near Kidderminster). Recharge processes can be affected by urbanisation and leakage from mains supplies or canals. In particular, since the 1980s the spreading of effluent from sewage treatment works onto land has ceased, resulting in a reduction in recharge to the aquifer from this artificial source. Extensive coal mining to the east of the Western Boundary fault is also likely to have affected groundwater flow in the past. Pumping ceased with mine closure approximately 30 years ago and it is believed that groundwater discharge from the Carboniferous rocks towards the sandstone has subsequently increased.

3.4 Rainfall Chemistry

Rainfall provides the initial input of solutes to recharge waters and can generally be considered to represent minimum baseline concentrations. The nearest rainfall monitoring sites to the study area, with appropriate data are Ludlow, Drayton and the Malverns (Figure 2.1). Rainwater chemistry samples have been collected from these locations at different times and the average rainwater chemistry is given in Table 3.3. The data have been multiplied by 3 in the last column of the table, in order to estimate the approximate enrichment due to evapotranspiration.

Chloride may be assumed to behave conservatively and concentrations in groundwaters prior to agricultural pollution or mixing with other waters would be expected to be around 6-7 mg l^{-1}. However, this assumption is not appropriate for other elements, for example K and N may be taken up by vegetation, thereby reducing concentrations in recharge waters compared to rainfall. Despite these influences, the table provides an indication of the order of magnitude of element concentrations in rainfall. The data are for 1988 taken from The UK National Air Quality Information Archive (http://www.aeat.co.uk/netcen/airqual/).

Table 3.3 Average rainfall chemistry data from Ludlow, Drayton and the Malverns.

	Median Rainfall Values			Median Rainfall (X3)			
Parameter	Ludlow	Drayton	Malverns	Ludlow	Drayton	Malverns	Av. Median
pH	5.20	5.80	6.40				5.80
SEC (µS/cm)	26.00	30.50	26.00				
Na (mg/l)	0.89	1.14	1.30	2.68	3.42	3.90	3.42
K (mg/l)	0.10	0.21	0.20	0.30	0.63	0.60	0.60
Ca (mg/l)	0.23	0.66	1.00	0.70	1.97	3.00	1.97
Mg (mg/l)	0.13	0.17	0.40	0.39	0.51	1.20	0.51
Cl (mg/l)	1.84	2.15	2.00	5.53	6.45	6.00	6.00
SO_4 (mg/l)	3.10	0.91	14.00	9.30	2.73	42.00	9.30
NO_3 (mg/l)	1.77	0.43		5.32	1.29		3.30
NH_4 (mg/l)	1.54	0.84	0.78	4.61	2.52	2.34	2.52
Total N (mg/l)		1.06	0.60		3.17	1.80	2.48
Fe (mg/l)		0.005	0.06		0.015	0.18	0.10
Al (mg/l)		0.008			0.024		0.02
PO_4-P (mg/l)		0.012			0.036		0.04
DOC (mg/l)		2.30	2.60		6.9	7.8	7.35
Mn (mg/l)			0.005			0.015	0.02
F (mg/l)			0.05			0.15	0.15
Cd (mg/l)			0.005			0.015	0.02
Cr (mg/l)			0.015			0.045	0.05
Cu (mg/l)			5.85			17.55	17.55
Pb (mg/l)			0.02			0.06	0.06
Ni (mg/l)			0.015			0.045	0.05
Zn (mg/l)			1.05			3.15	3.15
Total rainfall (mm)	2985	56892					
No. of samples	286	244	5				
Dates of samples	1984-1989	1993-1998	1978-1982				
Source of data	AEA	ECN	Severn Trent				
NGR	35702741	41625 25515					

4. DATA AND INTERPRETATION

4.1 New sampling programme

A total of 23 samples were collected from Permo-Triassic sandstone boreholes during November 2000, including Water Company and private-supply boreholes. Most were sampled from a section along an approximate E-W line in the south of the study area (Figure 3.5). Additional samples were collected from NW of Stourbridge (Figures 2.1 and 3.5). These areas were chosen to investigate the hydrochemical evolution of groundwater quality in the aquifer and to help identify the primary geochemical controls. The main section (section A, Figure 3.5) represents an east-west traverse near Kidderminster, the choice being restricted by available boreholes, rivers, and the presence of faults. Most boreholes abstract from the unconfined aquifer and are therefore likely to receive direct recharge. In addition, two boreholes (most likely from a different flow system) were sampled from the confined Permo-Triassic Sandstone to the south east of Birmingham, in order to provide a comparison of groundwater chemistry to that in the unconfined aquifer.

Prior to sampling, boreholes were pumped for approximately 15-30 minutes in order to avoid collecting stagnant water. Where possible, an anaerobic flow-through cell was used to monitor the parameters pH, dissolved oxygen (DO) and redox potential (Eh) using electrodes (Figure 4.1). Other on-site measurements included temperature, specific electrical conductance (SEC) and alkalinity. Samples were collected for chemical analysis in polyethylene bottles. The samples for major and trace element analysis were filtered through 0.45 µm membrane filters and those collected for cation and trace elements were acidified to 1% v/v with HNO_3 to minimise adsorption onto container walls. Organic carbon samples required Cr-acid washed glass bottles and, for the dissolved organic carbon (DOC) samples, a 0.45 µm silver membrane filter was used. Additional samples were also collected in glass bottles for stable isotopes (δ^2H, $\delta^{18}O$ and $\delta^{13}C$).

Figure 4.1 On-site sampling using a flow through cell .

Major cations and sulphate were analysed by ICP AES, and a wide range of trace elements by ICP MS. 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. For comparison, nitrogen species were also analysed by BGS and the results showed a good correlation between laboratories (Nitrate data from the Agency was used in the final interpretation). Stable isotope analysis was also completed in the BGS laboratory by mass spectrometry and the results reported relative to SMOW for δ^2H and δ^{18}O and PDB for δ^{13}C.

4.2 Historical Data

In order to account for the spatial variation in baseline quality, Environment Agency historical water quality data for 61 additional sites within the River Stour catchment (Figure 3.5). In the absence of a regular groundwater quality monitoring network and with limited historical data available for the area, it was decided that analyses would be accepted from 1985 to 2000. For each site, the most recent analysis with the maximum number of determinands was extracted for use within the project. If data existed for sites that had been sampled within the project, the historical results were removed to avoid duplication. Any data with an ionic charge imbalance greater than 10% was also rejected.

4.3 Interpretation of pumped groundwater samples

The geochemical evolution of groundwater can best be explained by studying variations along flowlines. This has proved difficult in the present case due to the lack of a good hydrogeological framework in which to interpret the data. Boreholes often penetrate different depths and are open throughout much of their length. In particular, the depth of casing and the depth of a borehole may produce differences in water quality which are not related to geochemical reactions along a flow path. The pumping history of an individual borehole may also have a significant impact on water quality, particularly in areas where the aquifer is overlain by permeable drift deposits. 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.

Under natural conditions, aquifers are likely to be vertically stratified in terms of water quality and pumped samples often represent a mixture of waters with different chemistries. The presence of evaporite deposits or differences in cement type within the sandstones, for example, may produce significant variation in the baseline water quality with depth. Head differences may also exist which, in turn, could result in downward or upward flow, short-circuiting groundwater flow between units. Therefore, 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

It is beyond the scope of this study to evaluate in detail which factors may be influencing water quality for each of the individual boreholes. Instead, this report presents a broad assessment of the water quality variations observed across the aquifer and the controlling geochemical processes. The data will be presented both as summary statistics of the hydrochemistry and in a more regional context highlighting variations across a transect of the aquifer and spatially. It is accepted that some water quality variations may be due to the factors described above.

4.4 Data Handling

A total of 84 analyses were used in the study. For statistical purposes, concentrations below detection limits were dealt with by substituting half of the detection limit. However, changes in the detection limits with time and between laboratories affect calculations of the mean results. The median value is used to represent average concentrations because it is more robust and least affected by outlying data.

The 97.7 percentile (mean plus 2 standard deviations) is used as an upper baseline for each determinand to remove outlying data. Where the groundwaters have been affected by anthropogenic influences, an estimate is given of the most likely upper baseline concentration. All statistical plots and tables used illustrate the data in the following sections are based on both the new sites sampled within this study and the historical data.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section deals with the fundamental hydrochemical characteristics of the groundwaters in the South Staffordshire and North Worcestershire study area. The range of concentrations for each element is summarised in Tables 5.1a and 5.1b and the data are shown on a Piper plot, boxplots and cumulative frequency plots on Figures 5.1-5.5. The box plots provide a summary of the ranges in concentration of elements in the order of their abundance in seawater (Figure 5.2). Cumulative probability plots are effective in showing the nature of distributions, particularly with regard to highlighting different populations of data.

Table 5.1a Summary of field parameters, isotope data and major and minor element concentrations in groundwater from the Permo-Triassic sandstones in the South Staffordshire and North Worcestershire region.

Parameter	Units	Minimum	Maximum	Median	Mean	97.7th percentile	Upper Baseline*	N
T	^{o}C	3.0	16.0	11.6	11.2	15.4		39
pH (Field)	pH UNITS	5.70	8.10	7.21	7.19	8.00		87
Eh	mV	280	719	387	400	615		22
DO	mg l^{-1}	< 0.1	8.1	5.1	5.0	7.6		22
SEC	µS cm^{-1}	261	2510	547	665	1501		35
δ^{2}H	‰	-52.8	-45.5	-50.5	-50.3	-46.5		23
δ^{18}O	‰	-8.25	-7.21	-7.81	-7.79	-7.30		23
δ^{13}C	‰	-20.9	-12.09	-16.44	-16.25	-12.28		23
Ca	mg l^{-1}	25.6	545	68.2	83.8	186		80
Mg	mg l^{-1}	2.4	84.1	9.3	13.3	32.5		80
Na	mg l^{-1}	6.8	98.8	14.2	21.5	76.4	▨	81
K	mg l^{-1}	1.5	68.1	4.0	6.0	28.0	▨	81
Cl	mg l^{-1}	5.4	102.0	31.1	35.3	79.6	▨	84
SO_4	mg l^{-1}	2.4	1790	50.4	79.0	151	▨	82
HCO_3	mg l^{-1}	8.5	360	177	173	349		72
NO_3-N	mg l^{-1}	0.4	26.9	9.4	9.6	22.7	5.0	60
NO_2-N	mg l^{-1}	< 0.001	0.173	0.003	0.013	0.134		77
NH_4-N	mg l^{-1}	< 0.003	0.435	0.015	0.033	0.200	▨	59
P	mg l^{-1}	< 0.02	1.13	0.05	0.11	0.53	▨	31
TOC	mg l^{-1}	0.1	9.3	0.9	1.4	6.2	▨	60
DOC	mg l^{-1}	0.3	8.9	1.7	2.4	7.9	▨	47
F	mg l^{-1}	0.025	0.309	0.086	0.096	0.188		60
Br	mg l^{-1}	0.030	0.360	0.090	0.126	0.340	▨	23
I	mg l^{-1}	0.001	0.019	0.004	0.005	0.013		23
Si	mg l^{-1}	0.6	13.0	6.0	6.3	10.6		43

*estimated upper baseline for elements modified by anthropogenic influences

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

Table 5.1b Summary of concentrations of trace elements in groundwater from the Permo-Triassic sandstones in the South Staffordshire and North Worcestershire region.

Parameter	Units	Minimum	Maximum	Median	Mean	97.7th percentile	N
Ag	µg l^{-1}	< 0.05	5.00	< 0.05	0.34	0.86	41
Al	µg l^{-1}	< 1	1550	5	42.0	159	52
As	µg l^{-1}	< 1	26	< 1	3.63	24.2	42
Au	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
B	µg l^{-1}	10	1000	50	173	1000	37
Ba	µg l^{-1}	< 5	745	96.5	162	491	61
Be	µg l^{-1}	< 0.05	0.5	< 0.05	0.22	0.50	37
Bi	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Cd	µg l^{-1}	< 0.05	1.49	0.14	0.22	1.00	23
Ce	µg l^{-1}	< 0.05	0.08	< 0.05	< 0.05	0.065	23
Co	µg l^{-1}	< 0.02	53.4	0.37	3.17	47.3	37
Cr	µg l^{-1}	< 0.5	7.9	< 0.5	0.857	5.370	23
Cs	µg l^{-1}	< 0.01	0.06	0.01	0.02	0.05	23
Cu	µg l^{-1}	0.9	1261	10	44.6	314	64
Dy	µg l^{-1}	< 0.01	0.15	< 0.01	0.02	0.12	23
Er	µg l^{-1}	< 0.01	0.1	< 0.01	0.02	0.09	23
Eu	µg l^{-1}	< 0.01	0.02	< 0.01	< 0.01	0.020	23
Fe	µg l^{-1}	< 5	151	10	24.9	124	52
Ga	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Gd	µg l^{-1}	< 0.01	0.17	0.01	0.023	0.145	23
Ge	µg l^{-1}	< 0.05	0.14	< 0.05	< 0.05	0.100	23
Hf	µg l^{-1}	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	23
Hg	µg l^{-1}	0.01	0.42	0.05	0.06	0.21	39
Ho	µg l^{-1}	< 0.01	0.03	< 0.01	< 0.01	0.020	23
In	µg l^{-1}	< 0.01	0.01	< 0.01	< 0.01	< 0.01	23
Ir	µg l^{-1}	< 0.05	0.14	< 0.05	< 0.05	0.08	23
La	µg l^{-1}	< 0.01	0.05	< 0.01	< 0.01	0.03	23
Li	µg l^{-1}	< 4	293	13	27.7	163	23
Lu	µg l^{-1}	< 0.01	0.09	< 0.01	0.01	0.06	23
Mn	µg l^{-1}	< 2	224	5	15.7	103	41
Mo	µg l^{-1}	< 0.1	10.1	0.2	0.90	6.76	23
Nb	µg l^{-1}	< 0.01	0.01	< 0.01	< 0.01	< 0.01	23
Nd	µg l^{-1}	< 0.01	0.44	< 0.01	0.04	0.30	23
Ni	µg l^{-1}	< 0.2	36.9	2.4	4.90	28.0	23
Os	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Pb	µg l^{-1}	< 2	< 2	< 2	< 2	< 2	23
Pd	µg l^{-1}	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	23
Pr	µg l^{-1}	< 0.01	0.05	< 0.01	< 0.01	0.030	23
Pt	µg l^{-1}	< 0.01	0.01	< 0.01	< 0.01	< 0.01	23
Rb	µg l^{-1}	0.41	13.31	1.28	2.48	11.1	23
Re	µg l^{-1}	< 0.01	0.15	< 0.01	0.01	0.08	23
Rh	µg l^{-1}	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	23
Ru	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Sc	µg l^{-1}	1.71	3.43	2.54	2.61	3.40	23
Sb	µg l^{-1}	< 0.05	1.06	< 0.05	0.07	0.57	23
Se	µg l^{-1}	< 0.5	8.4	0.5	1.06	5.52	23
Sm	µg l^{-1}	< 0.05	0.12	< 0.05	< 0.05	0.09	23
Sn	µg l^{-1}	< 0.05	0.22	< 0.05	0.05	0.19	23
Sr	µg l^{-1}	28.5	5145	76.2	312	2676	23
Ta	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Tb	µg l^{-1}	< 0.01	0.02	< 0.01	< 0.01	0.015	23
Te	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Th	µg l^{-1}	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23
Ti	µg l^{-1}	< 10	36	< 10	< 10	20.3	23
Tl	µg l^{-1}	< 0.01	0.26	< 0.01	0.018	0.14	23
Tm	µg l^{-1}	< 0.01	0.02	< 0.01	< 0.01	0.01	23
U	µg l^{-1}	< 0.05	10.9	0.67	1.47	8.88	23
V	µg l^{-1}	< 1	33.9	1	3.271	31.4	37
W	µg l^{-1}	< 0.1	0.4	< 0.1	< 0.1	0.22	23
Y	µg l^{-1}	< 0.01	1.63	0.02	0.17	1.17	23
Yb	µg l^{-1}	< 0.01	0.35	< 0.01	0.03	0.26	23
Zn	µg l^{-1}	< 0.5	5170	19	135	703	64
Zr	µg l^{-1}	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	23

5.2 Physicochemical characteristics and water types

The physicochemical parameters and element concentrations in Table 5.1a and 5.1b indicate a wide range of characteristics. Dissolved oxygen (DO) varies from < 0.1 mg l^{-1} in the confined part of the aquifer, up to 8 mg/l in the oxidising unconfined areas. The majority of boreholes are situated in the unconfined part of the aquifer and most of the groundwater sampled is therefore oxidising with a median DO value of 5.1 mg l^{-1} and relatively high redox potential (Eh). Groundwater wellhead temperatures show a slight increase downgradient reaching 14 ^{0}C near the River Stour, although the median value of 11.6 ^{0}C is more typical of groundwater temperatures.

The groundwater is well buffered in terms of acidity, with a median pH value of 7.2. The most acidic pH samples were collected in the west of the unconfined aquifer (sites 11, 12 and 16) and pH generally increases towards the east reaching 7.8 in the confined samples. Although most of the groundwater is fresh (median SEC of 550 µS cm^{-1}), mineralisation varies from weak to moderately mineralised (SEC ranging from 260 to 2510 µS cm^{-1}).

The major ion chemistry is summarised on the piper diagram, which displays the relative concentrations of major elements (Figure 5.1). The cation trilinear field (bottom left) illustrates that groundwater trends from a Ca dominant water towards a Ca-Mg type with a Mg/Ca ratio of 1. The Mg/Ca ratio of these samples is then limited to a ratio of 1:1 by dolomite saturation. In contrast, the anion trilinear field shows a larger spread of data. The main groundwater types include Ca-HCO_3 and Ca-Mg-HCO_3 type waters, with some extremes of Ca-SO_4 and Ca-Mg-SO_4 types. A few samples also show a trend towards Na or Cl type waters, where groundwaters may be of Na-Ca-SO_4 or Ca-Mg-HCO_3-Cl type.

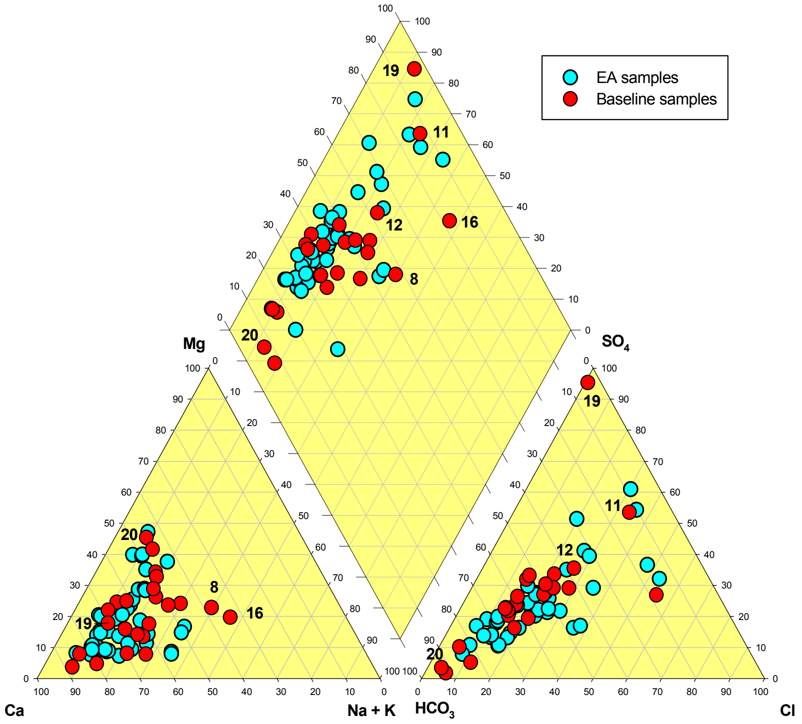


Figure 5.1 **PIPER plot showing the relative concentrations of major elements (numbers refer to selected baseline sites referred to in text).**

5.3 Major elements

The median value of Cl (31 mg l^{-1}) indicates a that the groundwaters contain a source in addition to rainfall, although a few samples (boreholes 5 and 20) have concentrations similar to average rainfall (around 6 mg l^{-1}). Most other elements plot above the seawater line suggesting enrichments due to water-rock interaction or anthropogenic inputs. Sodium is closely related to Cl as indicated by the proximity of Na to the dilute seawater line. However, the median Na plots slightly below the seawater line, indicating either an anthropogenic source of Cl, for example from fertiliser, or a process of removal of Na. Calcium, HCO_3 and SO_4 dominate the major ion chemistry, with concentrations plotting well above the dilute seawater line.

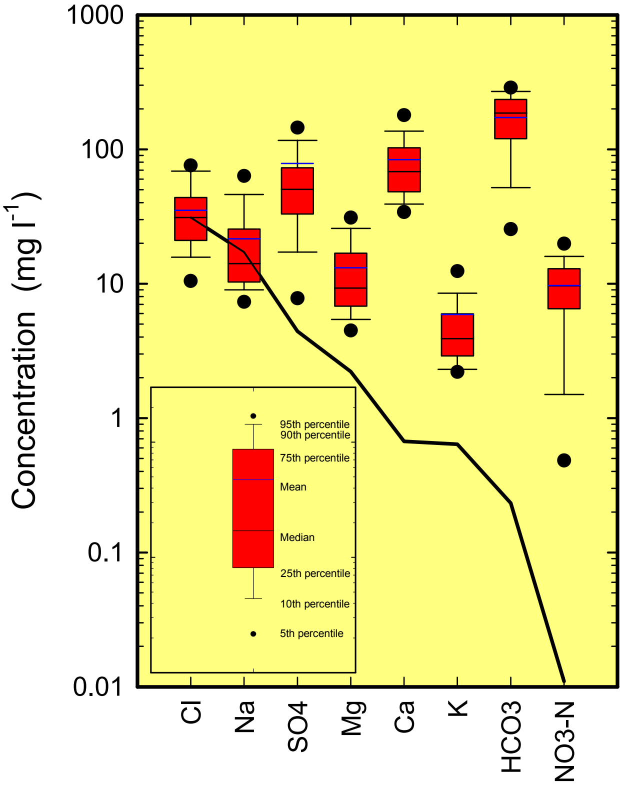
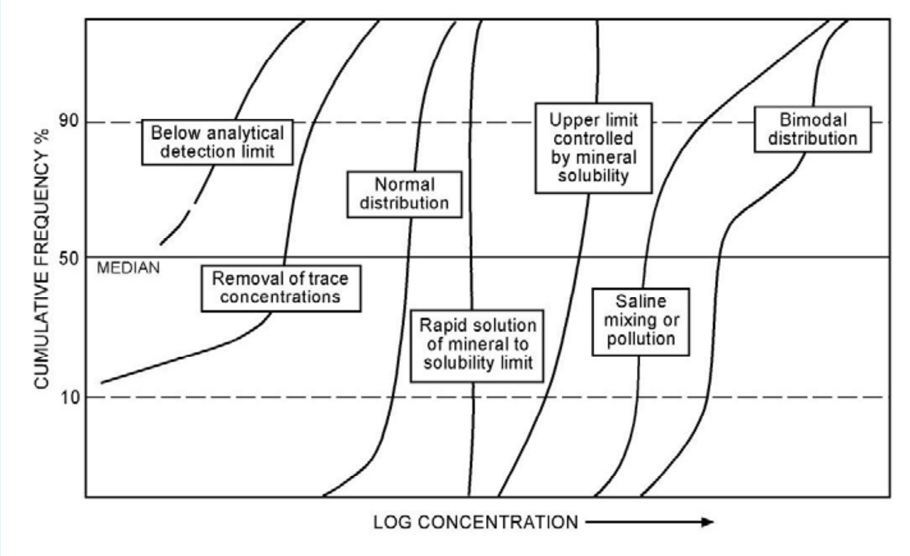


Figure 5.2 Boxplot showing the range of major element concentrations in the South Staffordshire and North Worcestershire region.

Cumulative frequency diagrams illustrate the distribution of data for each element and the form of the curve can suggest important influences on the hydrogeochemistry (Box 5.1). Most of the major ions trend towards log-normal distributions with relatively steep gradients and parallel trends (Figure 5.3).

The cumulative frequency plot of HCO_3 indicates gradual saturation of bicarbonate in groundwater and the upper HCO_3 limit is controlled by carbonate mineral solubility. The shape of the plot suggests the presence of at least 2 different sources, with the main divide in population occurring at 300-350 mg l^{-1}, which coincides with the median. Sulphate concentrations demonstrate the widest range of major element concentrations ranging over 3 orders of magnitude. A large range in NO_3 concentrations is also illustrated in Figure 5.3 and the most notable break of slope occurs at approximately 5 mg l^{-1}. The strong negative indicates at least two different populations with lowest concentrations probably being due to removal by denitrification.

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



i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.
ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural aquifer conditions.
iii) Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).
iv) A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO_3 by *in situ* denitrification).
v) A narrow range in concentration at the upper limit may indicate a mineral solubility control (e.g. F by fluorite)
vi) A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of natural higher salinity.

5.4 Minor and trace elements

Minor and trace elements are also shown graphically on boxplots and cumulative frequency plots (Figures 5.4 and 5.5). The dilute seawater line is determined from the median Cl concentration using the same method as for the major element boxplot. The median bromide plots slightly lower than Cl on the boxplot suggesting either a low Br/Cl source (e.g. halite) or anthropogenic influence. The other halide elements, I and F, plot higher than the seawater line on the box plots, suggesting different geochemical controls on their distribution compared to Br and Cl. Most other minor and trace elements are present at low concentrations, but lie above the dilute seawater line (Figure 5.4).

Silicon shows a narrow range of concentrations suggesting saturation with respect to a silica mineral phase. In general, trace elements show a wide range of concentrations. Barium has a median concentration of 96.5 $\mu g\ l^{-1}$ with a maximum concentration of 745 $\mu g\ l^{-1}$. Strontium lies above the seawater line on Figure 5.4, and reaches a maximum concentration of 5 mg l^{-1} deep in the confined aquifer. Iron and Mn concentrations are relatively low, with narrow ranges of concentrations compared to the Sherwood Sandstone groundwaters of Yorkshire (Shand et. al., 2001). Figure 5.5 illustrates that trace element distributions display more shallow gradients than the major ions and many are below the limit of detection (shown by vertical lines at low concentration).

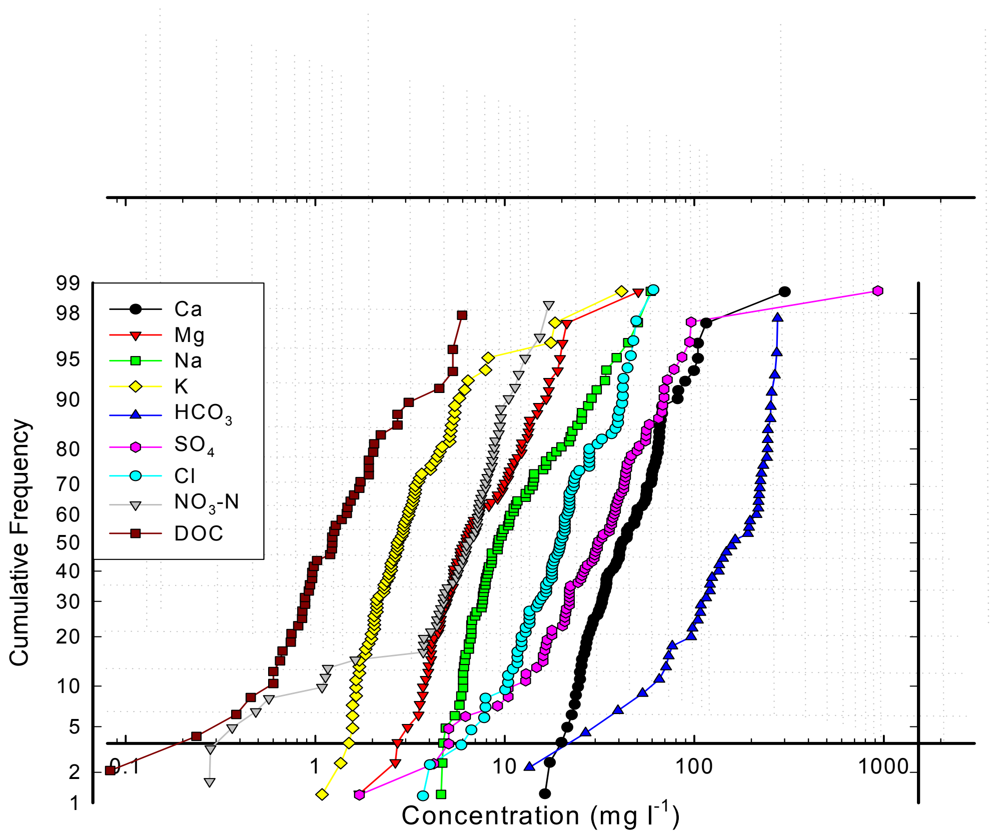


Figure 5.3 Cumulative probability plot of major elements in the South Staffordshire and North Worcestershire region.

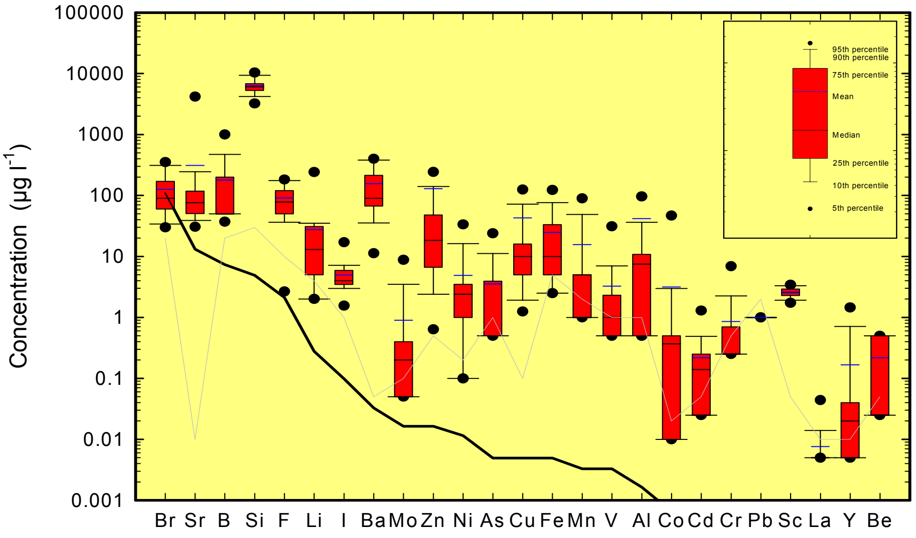


Figure 5.4 Boxplot showing the range of minor and trace element concentrations in the South Staffordshire and North Worcestershire region. Grey line represents typical detection limits for analyses.

Low concentrations of Al and the heavy metals Cd and Pb, are generally expected due to their low solubility in groundwaters of circumneutral pH. However, Zn concentrations range over 5 orders of magnitude (Figure 5.5) and Ni, Cu and Cr are locally high (Figure 5.4). Although the median concentration of As is below the detection limit of 1 μg l^{-1}, some of the confined groundwaters are relatively high (up to 26 μg l^{-1}).

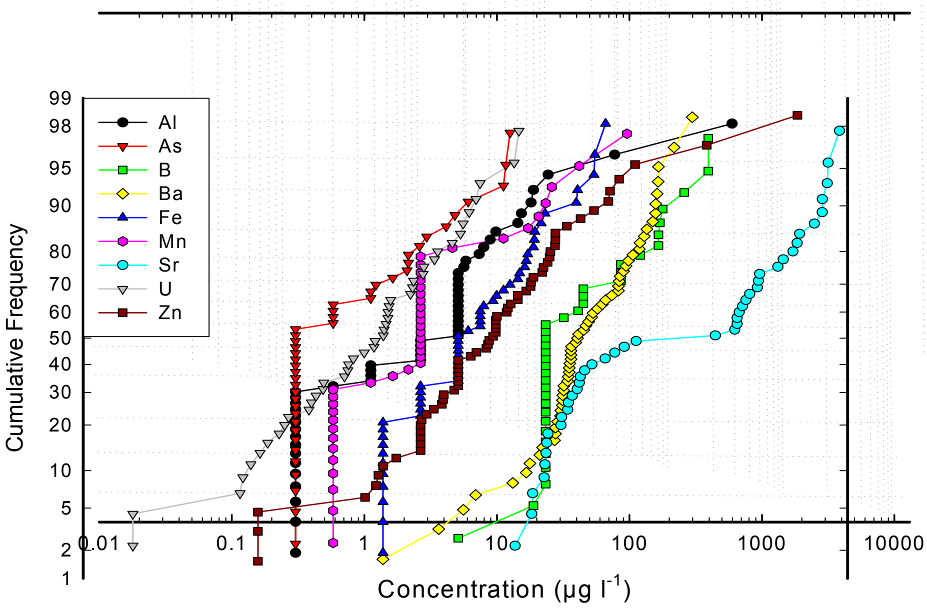


Figure 5.5 Cumulative probability plot of minor and trace elements in the South Staffordshire and North Worcestershire region.

5.5 Pollution indicators

In order to determine baseline concentrations, it is preferable to study only pristine waters. Polluted waters may alter baseline concentrations either directly by adding solutes or indirectly by promoting chemical reactions within the aquifer (Box 5.2). The South Staffordshire and North Worcestershire region has supported agriculture (Box 5.3) and a variety of industries over a long period of time (Box 2.2). These activities pose potentially serious threats to the shallow groundwater and it is generally difficult to identify pristine waters, which have been protected from both point and diffuse pollution. Previous studies of groundwater quality in the Sherwood Sandstone around Birmingham suggest that near surface groundwater is becoming more acidic with time and some groundwaters are grossly polluted with heavy metals (Buss, 1997). Chlorinated solvents have also increased with time in groundwater and highlight the potential vulnerability of the aquifer. Table 5.2 provides a summary of available data for this area. Although analyses are limited, the results demonstrate that maximum concentrations were well below MAC's. Any boreholes known to be significantly affected by point source pollution were not included in this study.

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

Groundwater prior to the industrial era (before c. 1800) emerged as springs or was taken from shallow wells, whilst the deeper reserves were in a pristine condition. The water first encountered using modern drilling practices would have had compositions reflecting true baseline determined only by geological and geochemical processes. Only rarely is it possible to find such waters because the majority of groundwaters sampled in the present study are derived from aquifers which have been developed for decades. The challenge in baseline is to recognise the impact of any 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 substances such as agro-chemicals or industrial chemicals. The sets of data are examined for these substances as a clue to the presence of "contamination", although it is difficult to quantify this. Even iwhere traces of contamination are present, this may have little impact on the overall chemistry of the groundwater.

Table 5.2 Summary of concentrations of some organics sampled from the Permo-Triassic aquifer of the South Staffordshire and North Worcestershire region

Parameter ($\mu g\ l^{-1}$)	Minimum	Maximum	Median	Mean	95th percentile	97.7th percentile	MAC	N
ATRAZINE	0.034	0.155	0.149	0.122	0.154	0.155	2	5
SIMAZINE	< 0.02	0.01	0.01	0.01	0.01	0.01	2	2
TETRACHLOROMETHANE	<0.05	0.5	0.025	0.078	0.310	0.413	3	10
TRICHLOROMETHANE	<0.2	0.5	0.1	0.135	0.320	0.417	12	11
TETRACHLOROETHENE	<0.05	4	0.025	0.487	2.425	3.276	10	11
TRICHLOROETHENE	<0.1	2.5	0.05	0.347	1.6	2.086	10	11

Pesticide concentrations (Atrazine and Simazine) appear to be low, despite most groundwater in the unconfined aquifer demonstrating the effects of agriculturally derived nitrate pollution (NO_3-N median: 9.4 mg l^{-1}). Median nitrate concentrations are higher than in other Permo-Triassic aquifers in Yorkshire (NO_3-N median: 0.05 mg l^{-1}, Shand et al., 2002) and Cheshire (NO_3-N median: 3.3 mg l^{-1} Griffiths et al., 2002). The shallow groundwater table (Figure 5.6) and extensive use of fertilisers (Box 5.4) and the makes groundwater highly vulnerable to pollution. The highest DOC concentrations were found in groundwater from two unconfined sites and contained concentrations (6-9 mg l^{-1}) more typical of polluted groundwaters. The cumulative frequency plot (Figure 5.3) also indicates the presence of several populations of DOC, suggesting several sources of organic carbon.

Box 5.3: Sewage Farms


Sewage farm spreading

The Stour basin relies almost entirely on local groundwater resources for public water supply. The threat of contamination to these boreholes, which are unconfined and classified as highly vulnerable, has caused concern for a number of years. The main threats to groundwater quality within the catchment are excessive application of fertilisers, urbanisation and sewage spreading operations. Although sewage farms were once widespread, only two areas remained active after 1970; at Whittington Hall (SO 860820), east of the Stour near Stourbridge and to the west of the Smestow Brook at Swindon near Wombourne (SO 848 910).

Sewage works provide an essential service to society processing human waste by-products. After treatment, two by-products are produced, namely a solid component (sludge) and a liquid effluent. These products were disposed of by spreading the sludge on land and allowing it to dry before being ploughed into the soil and by field irrigation of the liquid wastes. From the 1800's up to the 1980s, this was the standard method of effluent treatment and disposal. However, by enhancing recharge to the local aquifer groundwater quality was impacted and the baseline nitrate concentrations significantly modified.

Within the Stour basin, liquid effluent irrigation from sewage farm sites has raised groundwater levels in the local area, and as a consequence, increased the potential to contaminate local public water supply boreholes. Contamination in groundwater can be detected by increases in indicator chemical species including nitrates, sulphates, chlorides and phosphates. In soils, heavy metals can build up from the disposal of sewage sludge over many years which can then leach into groundwater and surface waters. Natural attenuation processes help to breakdown these contaminants, but overloading can increase the risks of groundwater contamination.

The implementation of the EC Groundwater Directive (80/68/EEC) heavily restricted the discharge of contaminants to groundwater. A progressive change in practice with sewage treatment works has led to increased discharge of treated effluent to surface watercourses and incineration of sludge.

Chloride concentrations can also increase due to anthropogenic inputs e.g. from fertilisers or road salt. In this study, chloride concentrations are higher in areas which have been designated as Nitrate Sensitive Areas by DEFRA (formerly MAFF), suggesting that the some Cl is agriculturally derived (Wildmoor and Tom Hill, in Box 10.6). High SO_4 concentrations (42 mg l^{-1}) were noted in the rainfall chemistry from the Malvern Hills, suggesting the possibility of acid rain, which may contribute to decalcification of the shallow aquifer. Sulphate levels are relatively high in the groundwater of the unconfined aquifer and baseline concentrations may be contributed to by anthropogenic sources both from the atmosphere and perhaps agricultural practices (Figure 5.7).

Figure 5.6 Kidderminster golf course is fed by springs and requires careful groundwater management.

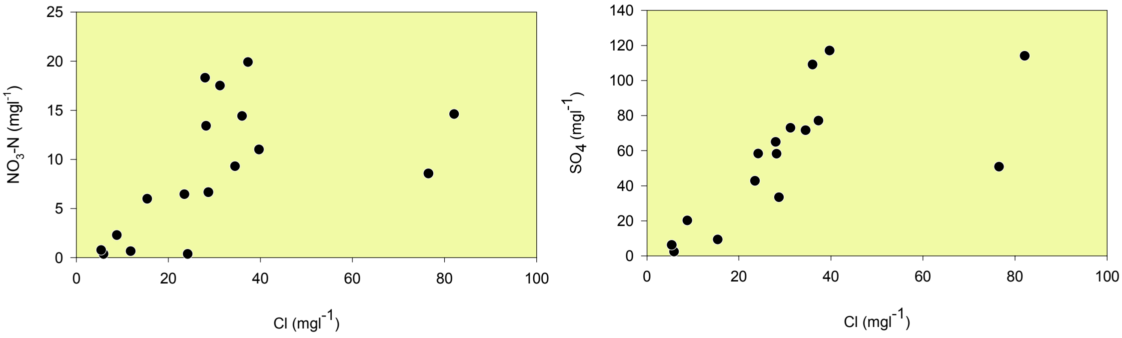
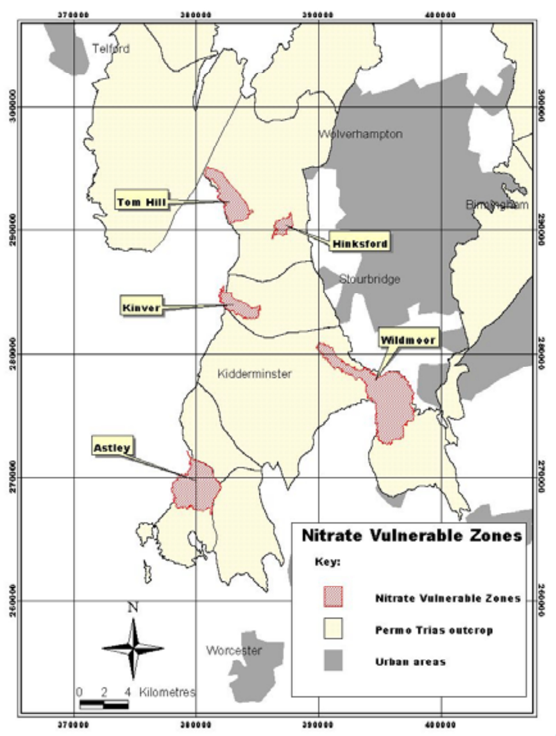


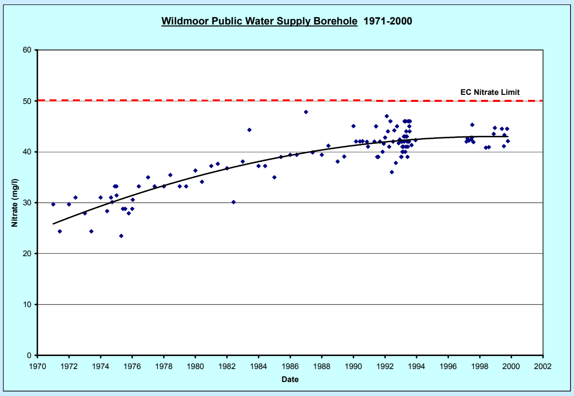
Figure 5.7 Hydrochemical data illustrating nitrate and sulphate concentrations plotted against chloride.

Box 5.4: Nitrate Vulnerable Zone's



The majority of the Stour catchment is underlain by the Sherwood Sandstone which is a major aquifer of significant importance. Historically, the aquifer has been used to support a high level of groundwater abstraction for both public and private supplies. Pollution to groundwater by nitrate from agricultural sources can pose a risk to human health as well as to the environment. Agricultural fertilisers used for crop production and organic wastes from sewage farm spreading are diffuse sources of nitrate that leach into groundwater and pollute natural groundwater resources. The loss of nitrate from agricultural land can effect the quality of drinking water supplies and can last for decades, even centuries in groundwaters. This can be overcome by the blending of high nitrate supplies with low nitrate supplies, but the Environment Agency and water companies also play an active role in monitoring the nitrate concentration in areas of the aquifer which are potentially at risk from nitrate leaching.

In response to the EC Nitrate Directive (91/676/EEC), the Ministry of Agriculture, Fisheries and Food (MAFF - now part of DEFRA), has defined Nitrate Vulnerable Zones (NVZ's) around public water supply abstractions. NVZ's are designated to protect groundwater resources where nitrate concentrations have been found to exceed or approach the maximum admissible concentration (MAC) of 50 mg l^{-1} NO_3. Within the Permo-Triassic Sandstone of Wolverhampton and Kidderminster, five NVZ's have been defined around the public water supply abstractions at Tom Hill, Hinksford, Kinver, Wildmoor and Astley. At these boreholes, the monitoring programme has shown that groundwater nitrate concentrations either exceed 50 mg l^{-1}, or are expected to do so by 2010.



Within NVZ's, it is compulsory for farmers to abide by a number of rules called "Action Programme Measures" where the careful management of fertilisers/manures and associated agricultural activities will help to reduce any future nitrate leaching through the soil, into groundwater. These measures are long term and compliance will insure the future protection of groundwater quality for drinking water supplies. The Agency will continue to monitor nitrate levels in groundwater.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

Changes in the chemical environment and the residence time of groundwater provide the dominant controls on the groundwater chemistry. This section deals with the main geochemical processes which influence groundwater chemistry including:

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

The geochemical changes taking place along potential flowlines are evaluated and placed into a regional context, with the aim of understanding the geochemical processes which control water chemistry in the aquifer.

6.2 Chemical evolution along transect

Groundwater often displays changes in chemistry along flowlines in response to chemical reactions. In the South Staffordshire and North Worcestershire region, groundwater generally flows towards the River Stour in the centre of the Sherwood Sandstone outcrop and samples were collected along a transect of the aquifer for this project (Figure 3.3). Most of the study area is unconfined and, therefore, likely to be strongly influenced by recharge and anthropogenic inputs. The groundwaters sampled in this area are, therefore, likely to be a mixture of older water and younger recharge water due to extensive abstraction, making identification of processes difficult.

There are significant differences in the lithology within and between the formations which make up the aquifer in this region. Such heterogeneity makes both flow modelling as well as hydrochemical interpretation difficult. Changes in chemistry identified along flowlines may, therefore, not be fully attributable to the geochemical evolution of the groundwater, and flowlines are likely to oversimplify the processes involved. Despite these limitations, the data are plotted against distance in Figures 6.1 to 6.3 so that trends and regional differences in chemistry can be identified. Groundwater flows from the east and the west towards the River Stour along Transect A (Figure 3.3), and from the north to the south along the River Stour. There are few boreholes situated in the confined region, and the two boreholes sampled within this study are outside the influence of the flow patterns of the Stour catchment. However, they provide an example of confined groundwater quality and are included in Figure 6.1 to 6.3 as part of the plots.

The main changes in groundwater chemistry are also reflected in the trilinear diagram (Figure 5.1), which illustrates that most of the groundwater is of Ca-Mg-HCO_3 type with a relative increase in SO_4 and Cl at some sites. The majority of the samples collected within this study are similar in range and concentration, with the exception of one sample from the confined region(site 19, Figure 3.3), where the anions are dominated by SO_4. The other groundwater from the confined part of the aquifer (site 20, Figure 3.3) contains high HCO_3 and low SO_4.

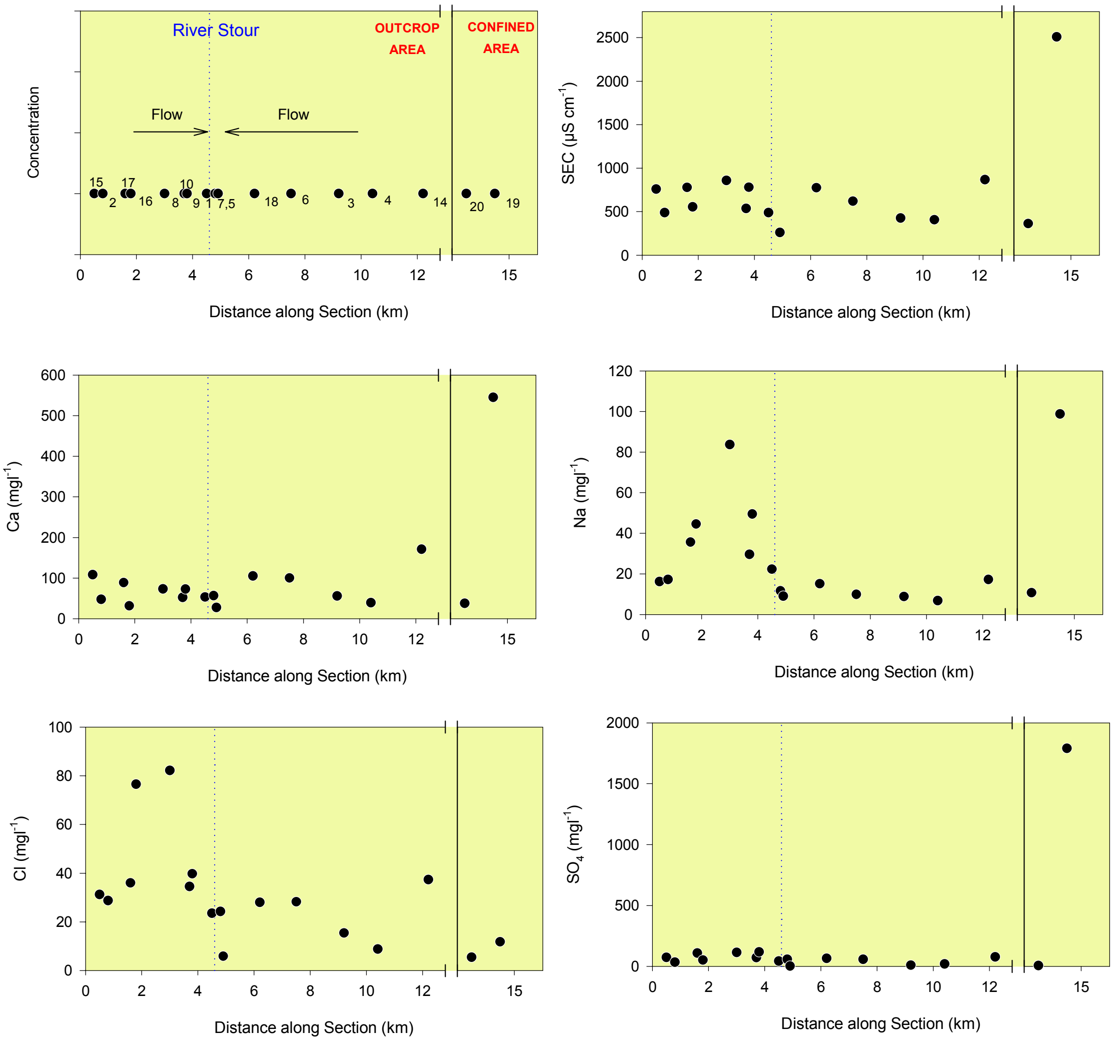


Figure 6.1 **Field parameters and major element concentrations in the South Staffordshire and North Worcestershire region.**

6.2.1 Mineral dissolution reactions

The most reactive minerals in the aquifer, and those which provide a dominant control on water quality, are the carbonate and evaporite minerals which form the matrix of the sandstone. In the shallow parts of the aquifer, matrix calcite and dolomite provide the initial control on groundwater chemistry due to their relatively fast dissolution. Recharge waters are therefore of Ca-HCO_3 type, saturated with respect to calcite and controlled by the congruent dissolution of the calcite. The influence of dolomite is indicated by an increase in Mg/Ca ratio up to 1, at which stage dolomite saturation is reached. Most groundwater in the study area is either at saturation, or approaching saturation, with respect to both calcite and dolomite and this is controlled by the following reactions:

$$\underset{\text{Calcite}}{CaCO_3} + \underset{\text{Carbonic acid}}{H_2CO_3} \Leftrightarrow Ca^{2+} + 2\,HCO_3$$

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

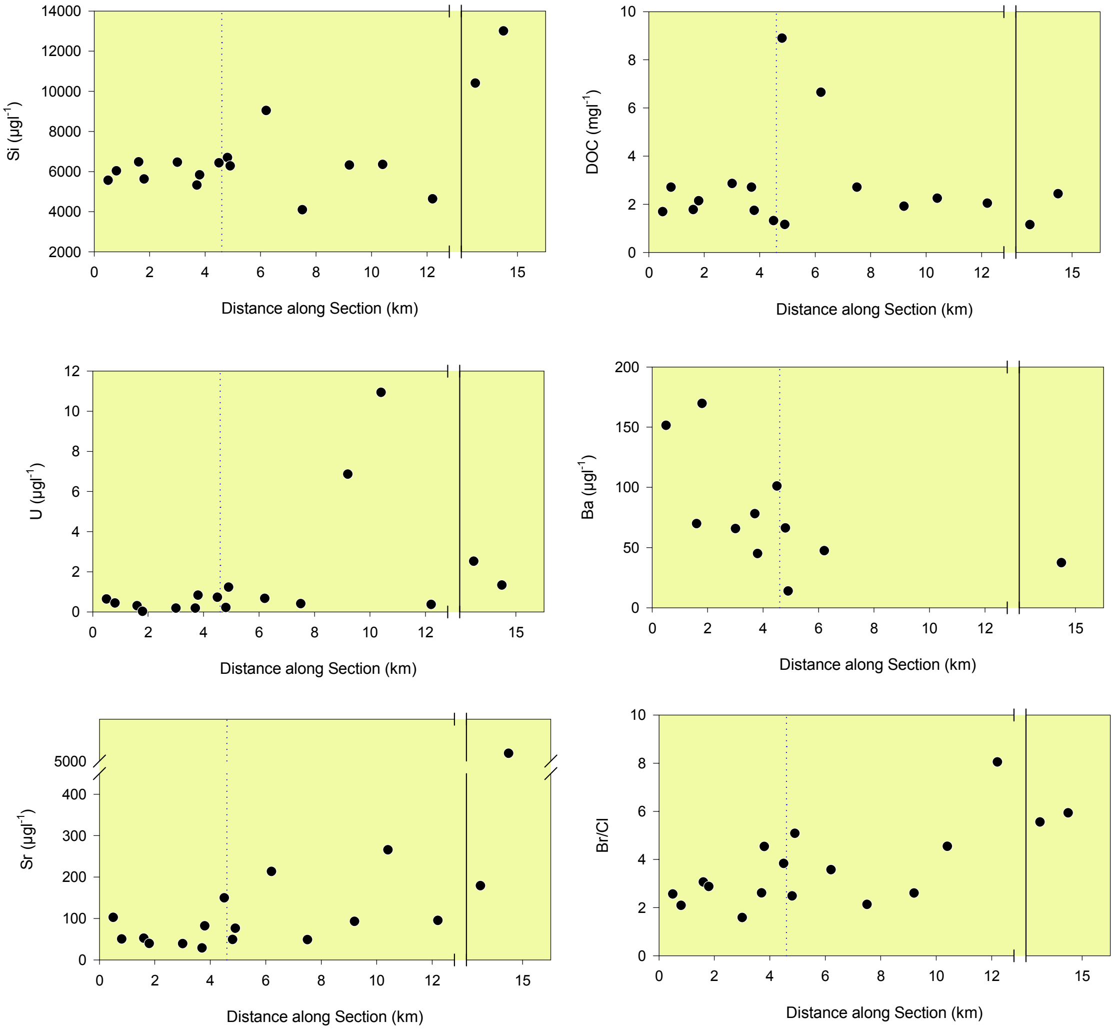


Figure 6.2 **Trace elements, Si and DOC concentrations in the South Staffordshire and North Worcestershire region.**

The dissolution of gypsum is also of major significance in the Sherwood Sandstone as illustrated by a linear relationship between Ca and SO_4 in the groundwater. Undersaturation of gypsum exists in the unconfined aquifer, but with time, increased dissolution has led to saturation in the confined groundwaters, where SO_4 is often very high (Figure 6.1). The most likely source of gypsum is from the base of the Mercia Mudstone or from cements deeper in the aquifer, and dissolution occurs by the following reaction:

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

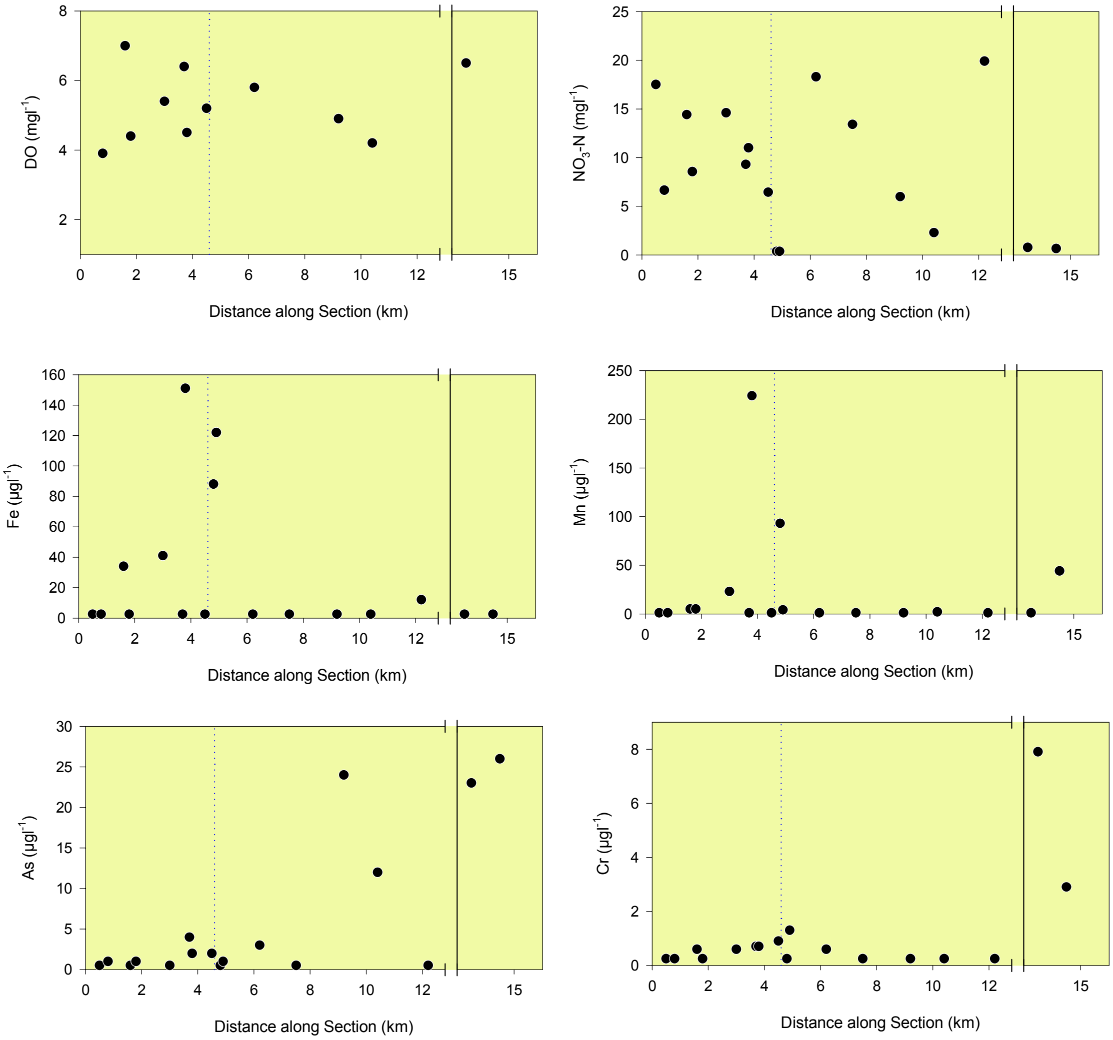


Figure 6.3 **Redox sensitive elements in the South Staffordshire and North Worcestershire region.**

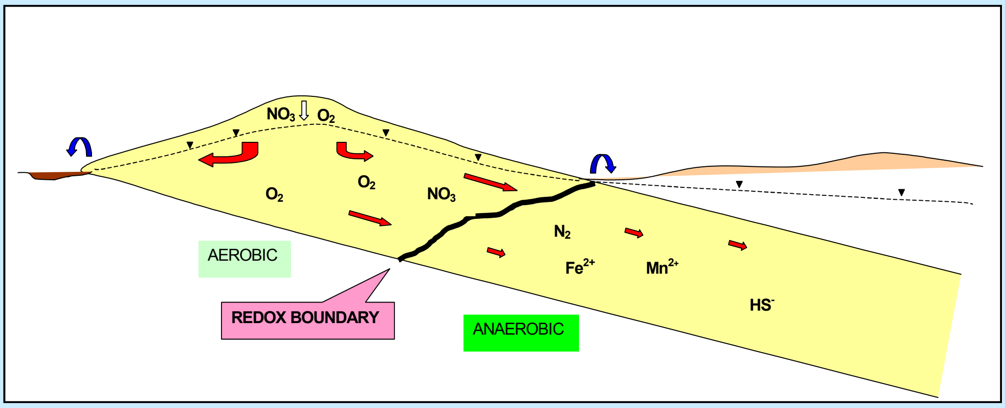
Although the aquifer is composed mainly of quartz, this mineral is extremely unreactive and the main source of Si is from silicate minerals such as K-feldspar or plagioclase feldspar. Silicon concentrations are fairly constant along the transect (approximately 6 mg l^{-1}), with an increase to 12 mg l^{-1} in the confined aquifer (Figure 6.2). The concentration of Si is controlled by saturation with respect to a silica phase and most samples are approaching saturation with respect to chalcedony.

The above reactions are the main influences determining groundwater chemistry in the South Staffordshire and North Worcestershire region, however, other water-rock reactions are important in terms of determining trace element concentrations. The concentrations of Ba are variable across the transect (Figure 6.2), being generally higher east of the River Stour. The solubility of Ba is limited in groundwaters where SO_4 concentrations are high due to saturation with the mineral barite (BaSO4), and the lower Ba west of the River Stour is related to the higher SO_4 concentrations (Figure 6.1). Strontium concentrations are high in gypsum/anhydrite and dissolution of these phases is reflected in the high Sr in groundwaters (up to 5 mg l^{-1}).

6.2.2 Redox reactions

Dissolved oxygen (DO) and redox potential (Eh) provide the primary indicators of the redox status of groundwater (Figure 6.1). However, both Eh and DO are unstable and are extremely sensitive to changes caused by contact with the atmosphere. The parameters are therefore measured on site with electrodes using in a flow-through cell and water is pumped directly from the borehole (Figure 4.1). Unfortunately, it was not possible to use a flow-through cell for seven of the samples, and hence these sites are not included in the plots of DO and Eh in Figure 6.1. The majority of the groundwaters are oxidising, the main exception being the sample from the deep confined aquifer, where DO is less than detection limit.

BOX 6.1 REDOX BOUNDARY



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

A redox boundary is likely to be present close to the unconfined-confined boundary and this is also indicated by other redox sensitive species such as NO_3, Fe and Mn (Figure 6.1). Nitrate concentrations are relatively high in the unconfined area and generally reflect relatively modern recharge to the aquifer (Edmunds et al., 1976). Approximately 40% of the samples exceed the EU MAC (11.3 mg l^{-1}). These concentrations are higher than the expected baseline and are present as a consequence of anthropogenic influences and the minimal protection of the aquifer by thin or absent drift deposits. Nitrate is stable when oxygen is present but reduces rapidly once oxygen is consumed. The reduced nitrogen species NO_2 and NH_4 are only present in the confined reduced groundwater, indicating that denitrification and/or nitrate reduction has occurred.

Iron and Mn solubility increases in reducing waters, but this is not seen in the two samples collected from the confined aquifer within this study, perhaps due to limited presence of Fe and Mn mineral phases in the aquifer. However, some sites in the unconfined area do demonstrate high Fe, Mn, NO_2 or NH_4 and/or low NO_3, suggesting locally reducing conditions and an available source of Fe and Mn. The waters are not reducing enough to promote sulphate reduction which remains high in the confined aquifer.

Changes in the redox conditions may also lead to removal/addition of metals to the aqueous environment. For example, oxidation of Fe^{2+} present in solution may lead to precipitation of $Fe(OH)_3$ which can also result in adsorption of trace elements or vice versa. Other redox-sensitive elements include As, Se, Sn and Cr, which would be expected to be present at higher concentrations in the more reducing waters and are important due to their toxicity. The concentration of arsenic is high in the confined aquifer, but also at some individual unconfined sites, where it reaches 24 $\mu g\ l^{-1}$. Tin and Se are also present at elevated concentrations in the same unconfined sites as As, although not in the deeper confined boreholes. Chromium, however, increases at both confined sites (Figure 6.3). Uranium is generally mobile under oxidising conditions. The highest U concentrations are found in some of the deepest boreholes, at sites 3 and 4 (Figure 6.3).

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 and the complex nature of the aquifer mineralogy. However, most aquifers contain clay minerals which hold exchangeable cations adsorbed on to their surface. Under certain conditions these cations can be exchanged for other ions from the aqueous solution and there is a general ordering of cation exchangeability: $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. However, in real systems the order also depends on an equilibrium established between the dissolved and exchangeable concentrations.

Ion exchange can be an important process, which occurs during salt-water intrusion or aquifer freshening. This often leads to a change in water type depending on the dominant cations in solution and on exchange sites (e.g. clays). During aquifer freshening, for example, high concentrations of Na on clays will exchange for Ca in solution leading to waters of Na-HCO_3 type. During salinisation, Ca on exchange sites may exchange with Na in solution leading to waters of Ca-Cl type

The Na/Cl ratio is also useful to determine whether an increase in Na is due to mineral weathering and ion-exchange or mixing with an older formation water (Figure 6.3). In the study area the ratio varies significantly with the highest ratios (up to 8.4) being found in the confined region and close to the River Stour. However, the role of ion exchange is difficult to quantify because mineral dissolution, mixing and anthropogenic influences are more dominant. Increases in the trace elements Li, Rb and Cs are most likely related to ion-exchange involving clay minerals.

6.2.4 Mixing with older Formation water

Limited data exist from the confined aquifer, but from the two samples collected within this study it is shown that the oldest deeper waters are of Ca-Mg-SO_4 composition. Chloride generally behaves conservatively and provides a good indicator of mixing. Concentrations of Cl are generally low, even where the aquifer becomes confined beneath the Mercia Mudstone. This is in contrast to the saline waters identified to the north east of the area in the Worfield catchment (Edmunds et. al., 1976), where Cl concentrations are seen to increase with depth with the underlying Upper Carboniferous Enville formation being suggested as the source (Entec, 1998).

The low Na and low Br, plotted relative to the seawater line in the Box plots (Figures 5.2 and 5.4) suggest an additional input of Cl from anthropogenic sources. However, some sites have a higher Br/Cl ratio than seawater, an enrichment that could result from drainage from the Coal Measures. The

Br/Cl plotted for all the sites (Figure 6.3) indicate that samples towards the east of the transect have a similar Br/Cl ratio to seawater, but this is higher in the confined part of the aquifer and close to the River Stour. The higher Br/Cl and Na/Cl ratios close to the River Stour may indicate a deeper source for these groundwaters but there is insufficient data to prove this. However, mixing with deeper connate or formation waters is generally not considered to be a dominant control in the majority of boreholes in the unconfined region, which appear to be well flushed.

6.2.5 Trace Elements

Once groundwater reaches saturation with respect to calcite, the calcite may still dissolve incongruently to release Mg^{2+} and Sr^{2+}. Strontium concentrations and the Sr/Ca ratio therefore provide a good indicator of continued reaction in the aquifer and can be used as a reasonable indicator of relative age. However, another possible source of Sr is gypsum ($CaSO_4.H_2O$) and correlations of Sr with Ca and SO_4 indicate that both sources have a significant influence on the groundwater chemistry. The groundwater with the highest Sr concentration (5.1 mg l^{-1}) is from the confined area and saturated with respect to celestite ($SrSO_4$), suggesting that the source of Sr is principally from gypsum at this site.

High concentrations of SO_4 limit Ba concentrations due to saturation with respect to the mineral barite ($BaSO_4$) (Figure 6.3). Therefore, both the presence of high SO_4 concentrations and Ba availability are important in determining the Ba concentrations in solution. Barium concentrations were found to be high in some deep public water supplies in the South Staffordshire and North Worcestershire region which have low SO_4 concentrations.

The trace elements Li and B are often good indicators of residence time in aquifers. Once dissolved, Li remains in solution and the results suggest that a widely distributed, readily available and significant source of Li exists in the Stour catchment. Li is likely to be controlled by the nature and amount of clay or detrital minerals in the sediments. Isolated highs of Li exist generally in deeper boreholes (Figure 6.4) and a high of 293 µg l^{-1} is found at the deep confined site (number 19) suggesting a much longer residence time than the unconfined samples. Although B may also provide a good indication of residence time, the increase in B concentrations identified near the River Stour in Figure 6.3 suggest that detergents are more likely to be the main source of B in the groundwater as a result of groundwater: surface water interaction.

Fluoride concentrations are generally low and increase slightly in the confined aquifer probably as result of longer residence time. Copper was mined from the Permo-Triassic sandstones in North Shropshire, and Smart (1978) suggested that Cu was concentrated along fault planes. In the Worfield groundwater catchment to the north-east of the region, it was also suggested that the main controls on the mobility of trace elements were the same factors controlling the solubility of Fe minerals. This is likely to be similar in the Stour catchment where higher metal values reflect locally reducing conditions.

6.3 Variations with depth

Chloride, NO_3 and SO_4 concentrations are observed to decrease in concentration with depth (Figure 6.4), suggesting an anthropogenic contribution at surface. The low Cl concentrations at depth could indicate waters of pre-industrial age that may include post-glacial melt waters (Kinniburgh et al., 1984). The decrease in NO_3 and SO_4 concentration may be due to more reducing conditions at depth, such that nitrate or sulphate reduction has occurred. However, the decrease in all three parameters and the fact that sulphate reduction is not common in this part of the aquifer, makes it more likely that these reflect baseline concentrations. The low permeability layers within the Permo-Triassic sandstones may also affect the groundwater quality at depth, perhaps restricting recharge by modern waters and resulting in a groundwater with higher concentrations of some ions due to increased water-rock interaction, for example Li concentrations are seen to increase with depth (Figure 6.4).

The depth to which modern water will be pulled down is dependent on both the permeability of the aquifer and on the depth and construction details of the major abstraction boreholes. The low permeable layers may also affect groundwater quality due to the relatively high sorption capacity for toxic metals (Buss, 1997). The vertical stratification of water quality highlights the importance of understanding the geology and hydrogeology of the system and is illustrated further in Box 6.2.

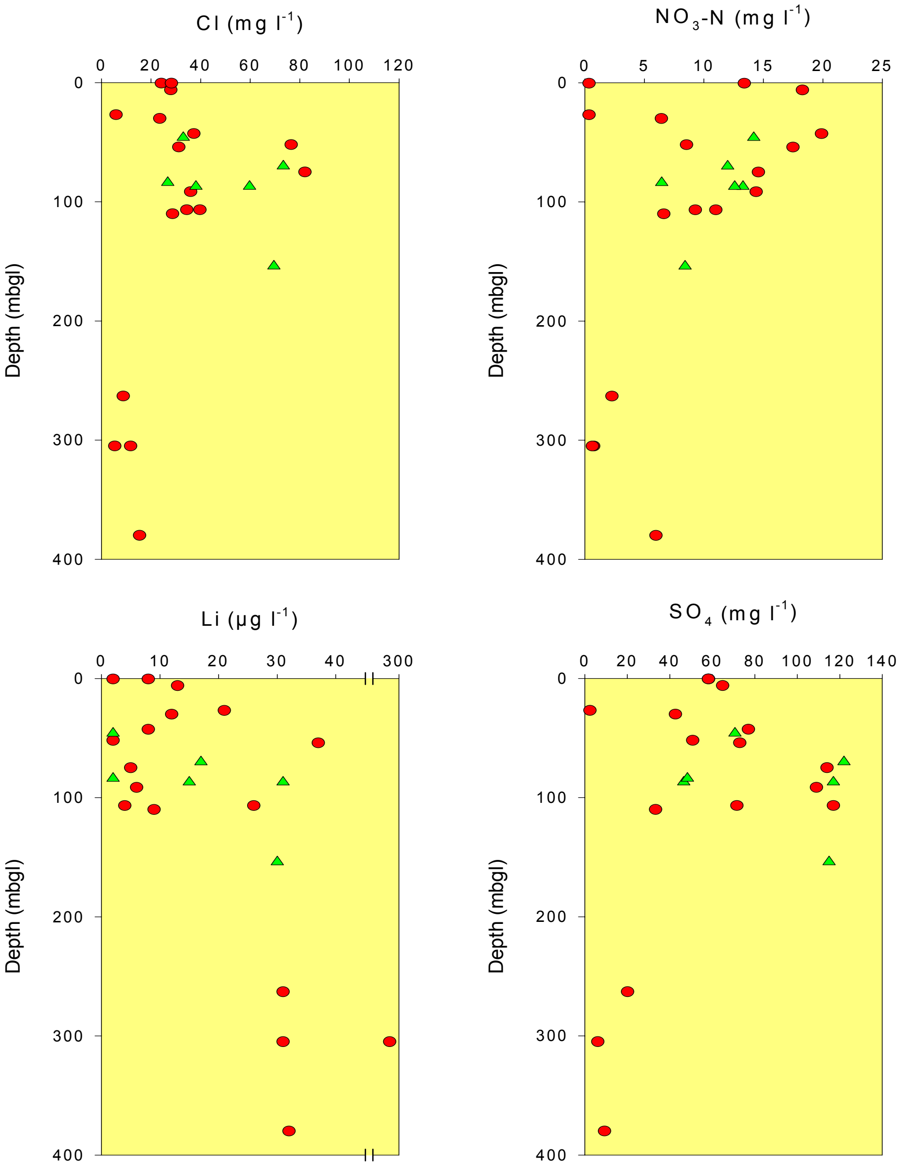
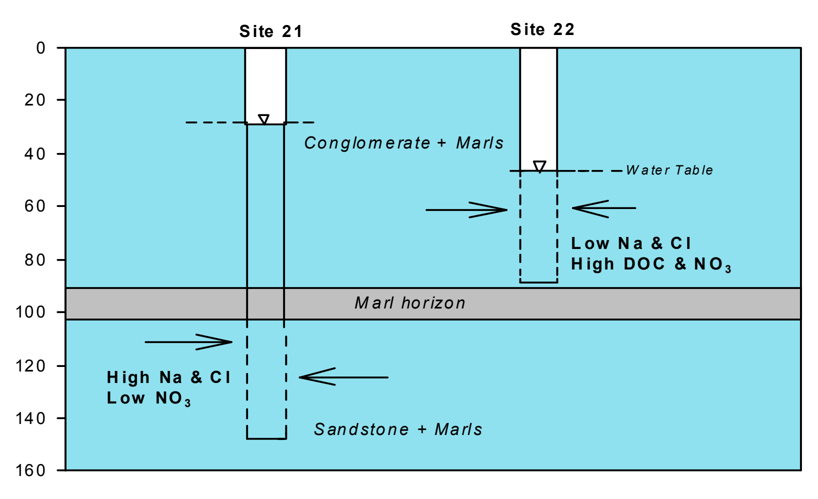


Figure 6.4 **Changes in concentration of elements with depth of borehole. Circles represent boreholes from the flowline and triangles from along the River Stour.**

Box 6.2: Hydrogeochemical variations between and within the Permo-Triassic sandstones

The results from this project show that geochemical changes occur both between and within the sandstone formations. Previous studies have also demonstrated variable hydrochemistry between formations e.g. the Bromsgrove and Wildmoor sandstones at Nurton (Hunter-Williams, 1995). The Smestow Valley Nitrate Study (Harris, 1985) concluded that maximum nitrate concentrations were associated with the Kidderminster formation. The same sites were sampled within this study and changes in chemistry are identified both between the Permo-Triassic formations and with depth. Two adjacent boreholes abstracting from different depths within the Kidderminster formation separated by a thick marl band (see figure). The groundwater chemistry in each borehole is notably different as shown below.



		Site 21	Site 22
TEMP	?C	12	11.4
pH	pH units	6.96	7.21
DO	mg l^{-1}	3.9	2.9
SEC	uS/cm^{-1}	458	867
Na	mg l^{-1}	63.9	46.4
K	mg l^{-1}	8.6	8
CL	mg l^{-1}	69.6	59.8
NO3-N	mg l^{-1}	8.44	12.6
DOC	mg l^{-1}	1.28	3.16
NO2-N	mg l^{-1}	0.003	0.001
NH4-N	mg l^{-1}	0.011	0.002
Co	µg l^{-1}	2.05	0.56
Cu	µg l^{-1}	11.6	20.9
F	µg l^{-1}	84	77
Fe	µg l^{-1}	26	16
Mo	µg l^{-1}	0.2	0.05
Ni	µg l^{-1}	2.4	3.4
P	µg l^{-1}	50	37
Sn	µg l^{-1}	0.08	0.025
Sr	µg l^{-1}	75.2	89.33
Zn	µg l^{-1}	14	7.4

1. The deeper borehole at site 21 (145 m bgl) suggests slightly more reducing conditions with higher NO$_2$, NH$_4$ and Fe concentrations. It also contains higher Na, Cl, As, Zn, V, F, and P concentrations, and a slightly lower pH.
2. The shallower borehole at site 22 (87 m bgl) appears more oxidising with higher levels of NO$_3$, probably derived from agricultural inputs. Site 22 also contains higher concentrations of Sr, Br and Cu.

6.4 Temporal Variations

A search for historical records revealed that very little long-term data exists in the South Staffordshire and North Worcestershire region with which to investigate temporal trends. However, samples collected in 1987 from the same region provide an insight into changes that may have occurred in groundwater quality (Edmunds et al., 1989). The results are provided in Table 6.1 and indicate some changes in water chemistry between 1987 and the present day. The most notable changes include a slight increase in concentration of Cu, Mn, Ni and Zn and a decrease in F, Ba, Sr, and U since 1987. However, the changes are relatively small and may in part simply reflect errors in chemical analysis or sampling.

Table 6.1 Comparison of Median Concentrations of groundwater quality in the South Staffordshire and North Worcestershire area, between 1987 and 2000.

Parameter	Units	(Edmunds et.al.,1987) 1987	Baseline data 2000
Ca	mg/l	58	68
Mg	mg/l	8.8	9
Na	mg/l	13.7	14
K	mg/l	2.9	4
Cl	mg/l	28	31
SO_4	mg/l	41	50
HCO_3	mg/l	161	177
NO_3-N	mg/l	7.2	9
F	ug/l	140	86
Br	ug/l	80	90
I	ug/l	4	4
Si	ug/l	5100	6030
Al	ug/l	<3	5
B	ug/l	40	50
Ba	ug/l	137	97
Cd	ug/l	<0.1	0.14
Co	ug/l	<0.1	0.37
Cu	ug/l	4	10
Fe	ug/l	<15	10
Li	ug/l	13	13
Mn	ug/l	1	5
Mo	ug/l	<0.2	0.2
Ni	ug/l	1	2.4
Pb	ug/l	<0.2	1
Rb	ug/l	1.2	1.3
Sr	ug/l	89	76
U	ug/l	1.5	0.7
V	ug/l	<15	1
Zn	ug/l	10	19

6.5 Spatial variations

Spatial variation across the study area are displayed, for selected elements, in Figures 6.5a and 6.5b. Due to the complexity of the geology and stratigraphy of the area it becomes more difficult to identify trends than other regions of the Permo-Triass studied within Baseline. However, despite the complexities, some differences are identified in the hydrochemistry across the area. More acidic waters are found towards the west of the unconfined aquifer, particularly in the north west and this is likely to affect the concentrations of trace elements (Figure 6.5). Previous work in this area attributed the more acidic groundwaters to the absence of carbonate minerals in the unsaturated zone (Moss and Edmunds, 1992). Most of these boreholes abstract from the Bridgnorth sandstone, which contains fewer clay horizons that the other Permo-Triassic formations. The presence of carbonate minerals in the clay horizons help to neutralise the acidity of recharge.

Plots for Na and Cl illustrate that concentrations are generally low throughout the aquifer, even in the deeper boreholes (sites 3 and 4). Low Cl concentrations were also noted near the boundary with the Mercia Mudstone and in the confined region to the south east. Concentrations of SO_4 do not show any systematic variation across the aquifer (Figure 6.5) suggesting a source of gypsum in the matrix of the Permo-Triassic sandstones, rather than any dominant influence from the Coal Measures. Higher concentrations of Ba are generally found towards the south-south east of the unconfined region relatively close to the Mercia Mudstone. This is similar to the Cheshire Basin, where Ba concentrations were high at the junction between the Sherwood Sandstone and the Mercia Mudstone (Griffiths et al., 2001). However, the main control is the low SO_4 concentrations rather than the Ba being derived from any specific horizon.

Nitrate concentrations are relatively high throughout the unconfined aquifer, but spatially variable. The lowest concentrations are present in the confined part of the aquifer and in deeper boreholes where denitrification has likely occurred. The transition metals Fe, Mn and Cr form local highs suggesting reducing conditions due to confining layers within the formations. Samples to the south west of the Permo-Triassic outcrop appear to be affected by the presence of the Kidderminster Fault (Figure 3.1). The area to the east of the fault is aerobic, for samples collected both from springs (at sites 6 and 18) and boreholes reaching depths up to 380 m. In contrast, samples west of the fault tend to suggest more reducing conditions with increased concentrations of redox-sensitive species e.g. Fe and Mn. A higher Mg/Ca ratio is also identified towards the south, particularly to the west of the Kidderminster fault. This distribution suggests dolomite rich cements in the older formations (i.e. the Bridgnorth and Kidderminster Formations). These results contrast with the findings of Edmunds et al. (1976) and Entec, (1998) who noted higher concentrations of Mg in groundwaters of the younger Bromsgrove sandstone and Wildmoor formations in the area.

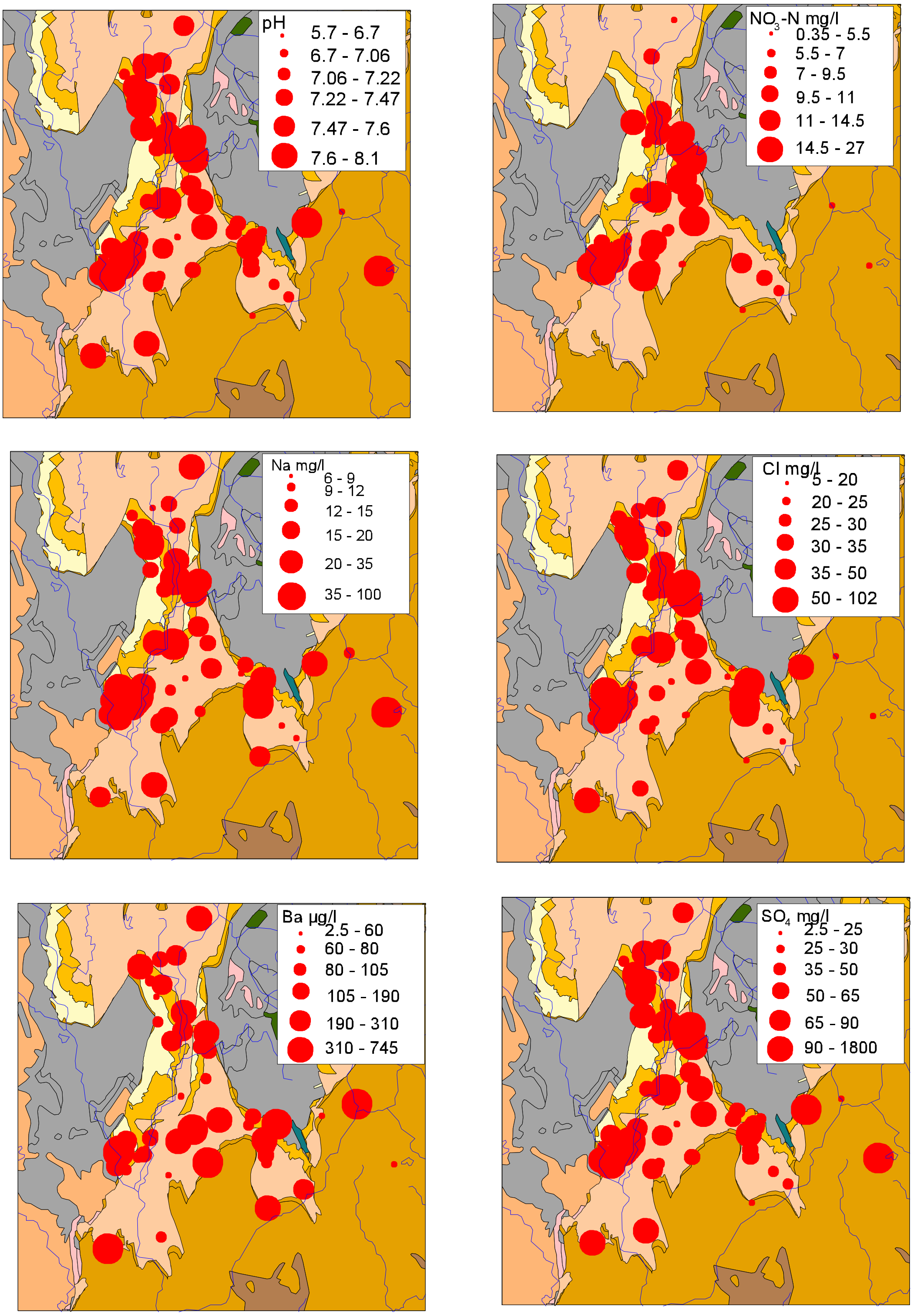


Figure 6.5 Spatial variations of selected elements in the South Staffordshire and North Worcestershire region.

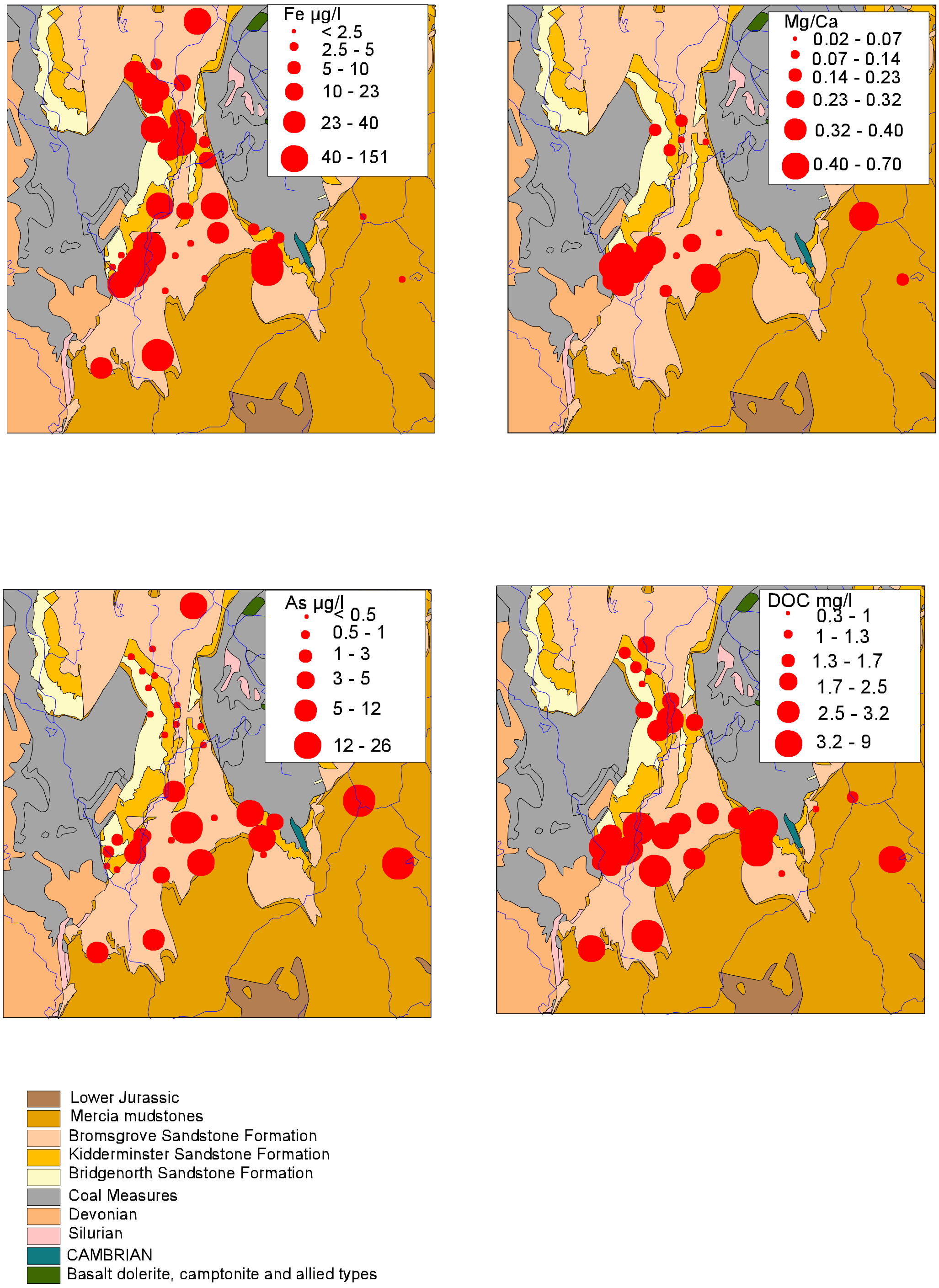


Figure 6.5 (cont'd) **Spatial variations of selected elements in the South Staffordshire and North Worcestershire region.**

In the deep confined groundwater sample (site 19) the SEC and Na, B, Cs, F, I, SO_4, and Sr concentrations are all significantly higher compared to the unconfined samples. Little historic data exists from the confined aquifer and further sampling is required in the confined areas in order to improve the understanding of the controls on baseline groundwater chemistry.

Silicon is slightly higher in the north of the study area and concentrations of dissolved organic carbon (DOC) were generally found to be higher in the south of the unconfined area (Figure 6.5b). However, the median concentration of DOC of 1.7 mg l^{-1} is much lower than those found in the Sherwood Sandstone in the Vale of York (median of 3 mg l^{-1}, Shand et al., 2001).

6.6 Age of the groundwater

Although geochemical concentrations can be used as a guide to relative age, facies changes and kinetic factors make such estimates fraught with difficulties. Previous samples from the deep Kempsey borehole in the Worcester Basin suggest a source from Quaternary recharge and conclude that if any older groundwater existed in any of the Permo-Triassic aquifers, the evidence no longer exists (Darling et al., 1997).

Measurements of the stable isotope ratios of δ^2H and $\delta^{18}O$ in groundwater can be used to distinguish groundwaters of different ages, and in particular those of Pleistocene (pre 10,000 years old) and Holocene (post 10,000 years old) age. The climate during the Pleistocene period was colder, resulting in characteristically lighter (more negative) signatures of the stable isotopes δ^2H and $\delta^{18}O$. The results given in Table 5.1a indicate isotope signatures consistent with waters of Holocene or more recent age. Therefore, no palaeowaters were identified in the South Staffordshire and North Worcestershire region.

7. BASELINE CHEMISTRY OF THE AQUIFER

The Baseline data show that the most important influences on the groundwater chemistry are mineral dissolution reactions, in particular involving calcite, dolomite and gypsum. Although silicate reactions are slower, cations and silica are introduced to the groundwater through reaction of the groundwater with plagioclase and potassium feldspar. Redox reactions are also important for many species in the unconfined region, where locally reducing conditions exist due to the layered nature of the aquifer. The presence of clay horizons throughout the aquifer also suggests the potential for ion exchange. The groundwaters studied are relatively fresh and indicate that mixing with older formation waters is not a dominant process.

Although vertical heterogeneity may provide some protection to the groundwater quality from pollution, the majority of boreholes abstract from the unconfined regions of the Permo-Triassic sandstones and the minimal presence of drift in this area results in an aquifer vulnerable to anthropogenic pollution. The most obvious anthropogenic inputs over the last few decades have been from agricultural activities and concentrations of NO_3 are found to be relatively high. Cumulative probability plots suggest that Baseline nitrate concentrations are most likely to be below 5 mg l^{-1}. Such diagrams should be treated with caution where redox processes have been important e.g. in the study area the removal of baseline under reducing conditions will alter any primary distributions.

Other elements which may have been modified by agriculturally-derived inputs include K, Cl and P (Shand et. al., 1999). Enhanced K is derived from the dissolution reactions of K-feldspar and biotite, although K is not very mobile in the surface environment and most anthropogenic inputs will be consumed by biomass or through incorporation into clay minerals. Phosphate concentrations are low due to limited mobility in the aqueous environment and the timescales involved for recharge to occur. Chloride, on the other hand, is very mobile and likely to modify the baseline significantly even where evaporites are not present. A comparison of Br/Cl and Na/Cl ratios indicates that Cl may be enhanced over baseline in the unconfined parts of the aquifer (Figures 5.2 and 5.4). Mixing with formation waters is not considered to be to be an important process in the study area (even in the part of the confined aquifer studied), unlike the adjacent Worfield catchment, where Cl is naturally elevated due to water-rock interaction with the underlying Enville formation (Entec, 1998).

Anthropogenic influences on groundwater quality are also suggested as a result of groundwater-surface water interaction. The water flow in the canal networks and the River Stour are artificially maintained with treated industrial and sewage effluent. An increase in concentrations of SO_4, Cl, Na and K are noted in the vicinity of the canals and the River Stour. In particular, B is elevated near to the River Stour and this may originate from detergents in the surface waters.

Although some elements are enhanced due to anthropogenic influences, most element concentrations are similar to natural baseline values and can be explained by natural geochemical processes. The natural baseline is expressed as a range of concentrations which, for some elements, varies over several orders of magnitude. The data provides a starting point in identifying natural concentrations of elements in the Permo-Triassic aquifer of the South Staffordshire and North Worcestershire region, and the groundwater quality appears generally to be good. However, the Baseline concentrations should be used in conjunction with regional hydrochemical maps because large spatial variations, as well as variations with depth, exist within the groundwaters of the region.

Enhanced concentrations of some elements e.g. As and Ba, occur due to entirely natural processes and these may exceed the drinking water standards due to simply to water-rock interaction. Arsenic concentrations are slightly elevated, although not as high as in other Permo-Triassic aquifers in the UK (Griffiths et al., 2001) and other parts of Europe (Heinrichs & Udluft, 1999). There are few data available on many UK aquifers for U, and although concentrations appear low in this area, moderate concentrations are present in other Triassic sandstone aquifers (Shand et al., 2001 and Griffiths et al., 2001). For many elements, the concentrations measured, and the ranges found, can be taken to be representative of the baseline. The baseline quality of the confined groundwaters beneath the Mercia Mudstone is significantly different to the unconfined groundwaters and further research is required to provide a clearer picture of the quality of these groundwaters.

8. SUMMARY AND CONCLUSIONS

The Permo-Triassic sandstones provide the principal source of groundwater in the South Staffordshire and North Worcestershire region. Groundwater is exploited mainly for public supply as well as for industrial and agricultural purposes. Whilst acknowledging the complexity of the stratigraphy and structure of the study area, this report aims to summarise the natural element distributions and the dominant controls on the groundwater chemistry.

A wide range of geochemical reactions can impart specific characteristics to the groundwater quality. The main influences on the groundwater chemistry in the South Staffordshire and North Worcestershire region include water-rock reactions, in particular with the dissolution of the carbonate and sulphate cements. The main groundwater types which are present include Ca-HCO_3 and Ca-Mg-HCO_3 type waters, with some extremes of Ca-SO_4 and Ca-Mg-SO_4 types. Ion exchange reactions also occur, but are swamped by mineral dissolution, anthropogenic inputs and mixing. Mixing with formation water is not considered a major process in this area and relatively low Cl concentrations indicate that recharge has flushed away any pre-existing connate waters within the aquifer. Isotope results suggest that the groundwater is post Holocene in age. Neither saline intrusion nor dissolution of halite appears to be a major influence on the groundwater chemistry in this area.

The majority of boreholes in the South Staffordshire and North Worcestershire region abstract from the unconfined sandstone, where aerobic conditions extend up to depths of 380 m below ground level. However, clay and silt layers within the sandstone formations can result in locally confining conditions. This produces many apparently isolated changes in the groundwater chemistry as low permeability layers may restrict groundwater flow, resulting in naturally high concentrations of some ions. In particular, some minor and trace elements e.g. Fe and F are higher at isolated sites in the south of the unconfined area and in the confined aquifer. High trace element concentrations (e.g. As, Fe, Cu and Cr) have been noted in the groundwaters of other Permo-Triassic aquifers but occur at lower concentrations in the present study area. Although the presence of trace metals in groundwater is controlled by the composition and reactivity of the iron oxide cement, oxidising conditions will ensure that the concentration of many trace elements remains low.

The influence of redox reactions on the hydrochemistry is extremely complex due to the heterogeneity of the aquifer. However, such reactions provide a strong control on nitrate concentrations, which undergo nitrate reduction where oxygen has been removed from the groundwater. The presence of the Kidderminster fault within the unconfined region also appears to have an effect on the redox conditions of the aquifer. Groundwaters at depth beneath the Mercia Mudstone are reducing and relatively more saline but data was limited in the present study.

Anthropogenic inputs to the aquifer are important resulting from agricultural practices and surface water-groundwater interaction between the aquifer and the River Stour and canal networks. Surface water flow is largely maintained artificially with treated industrial and sewage effluent and an increase in concentrations of Na, Cl, SO_4, K and B in the groundwater is identified in the vicinity of the River Stour and Staffordshire and Worcestershire canal. At present, the aquifer is classified as highly vulnerable to pollution, although the deeper groundwater quality may be protected to some extent by low permeability layers and the relatively high sorption capacity of the Permo-Triassic sandstones for toxic metals (Buss, 1999). Although the groundwater is generally of good quality, pollution from agricultural sources may be responsible for elevated NO_3, Cl and K concentrations throughout the unconfined aquifer.

Successful groundwater management relies on a clear understanding of the geochemical processes involved. There is a need to understand hydrochemical variations spatially and with depth in the aquifer and this study has attempted to identify such variations and the dominant geochemical processes controlling water quality. The use of flowlines to delineate processes has proved difficult in this area:

- The majority of the study area is unconfined and therefore subject to influences such as recharge, groundwater abstraction and surface water courses, all of which may influence the groundwater quality and therefore interfere with the interpretation of the hydrogeochemical evolution.

- Complex structure (dipping beds and faulting) and stratigraphy (heterogeneous lithology) complicates identification of the direction of groundwater flow.

- No confined samples were available to sample within the catchments of the identified flowlines. Samples were therefore collected, for comparison, from a different groundwater catchment unit.

The geological heterogeneity of the aquifer in this area is perhaps the biggest problem in understanding the hydrogeology and hydrochemistry and further detailed investigations on the variations between and within geological units is recommended in order to better estimate the baseline chemistry.

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Environmental Change Network website: http://www.ecn.ac.uk

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