Baseline Report Series:
20. The Permo-Triassic Sandstone Aquifer of Shropshire

Groundwater Systems and Water Quality
Commissioned Report CR/05/061N

Environment Agency Science Group
Technical Report NC/99/74/20

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

BRITISH GEOLOGICAL SURVEY
Commissioned Report CR/05/061N

ENVIRONMENT AGENCY
Science Group: Air, Land & Water
Technical Report NC/99/74/20

Baseline Report Series: 20. The Permo-Triassic Sandstone Aquifer of Shropshire

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Outcrop of the Kidderminster Sandstone at Grindleforge [SJ 753 034] (©NERC 2005).

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FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

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

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

The BASELINE objectives are:

1. to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound

geochemical principles, as a basis for defining water quality status and standards in England and Wales (in the context of UK and Europe); also to assess anomalies due to geological conditions and to formulate a quantitative basis for the definition of groundwater pollution;

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

Groundwater from the Permo-Triassic Sandstone aquifer of Shropshire has a range of chemical compositions that have evolved by several interacting hydrochemical processes, including mineral reactions, influx of groundwaters of distinct chemistry from other rock formations and diffuse pollution. The variability in concentrations of many chemical constituents is large and the spatial distribution often sporadic with few regionally consistent trends.

In a few places where the aquifer outcrops at surface, rainfall recharges the aquifer directly. Calcite is a common mineral in the Sandstones as detrital grains and secondary cements. Recharging groundwaters equilibrate rapidly with calcite where it is present, and produce calcite-saturated groundwaters with near-neutral pH values (7–8) and a major-ion chemistry dominated by Ca and HCO_3. Such waters are typical of the region. Dolomite is also present as an accessory mineral in the Sandstone aquifer, although most groundwaters observed are undersaturated with dolomite, suggesting that most of the waters have had insufficient time to reach equilibrium with this mineral. In a number of boreholes that only penetrate shallow levels of the aquifer (<50 m depth), groundwaters are undersaturated with calcite, have high pCO_2 values and low pH (down to 5.2), suggesting that they have not reacted with calcite. These tend to be of mixed-ion composition but with low HCO_3 concentrations. The most likely reason for lack of reaction is historic dissolution and removal of carbonate cements from the Sandstone by more rapidly flowing groundwater in the shallowest parts of the aquifer. Silicate reactions, especially feldspar dissolution, have also influenced groundwater chemistry.

Drift deposits have had a major impact on the quantity and quality of groundwater recharging the aquifer. Areas of the Sandstone covered by thick clayey Drift deposits experience very limited recharge via the superficial deposits. These therefore do not receive significant inputs of solutes via the Drift and the groundwaters within them are likely to be relatively old compared to groundwaters in outcrop or partly confined areas of the aquifer. By contrast, recharge can occur via thin, patchy, or more sandy Drift and solutes from the Drift can reach the underlying aquifer. There is evidence that Sandstone groundwaters in areas covered by partly-permeable Drift have higher concentrations of Na, Cl and SO_4 in particular, probably derived from the Drift deposits. As the Drift distribution is heterogeneous, so too is the distribution of these Drift-impacted groundwaters.

From the data included in this study, the majority of groundwaters in the area appear to be oxic with dissolved oxygen typically greater than 1 mg l^{-1} and up to 10 mg l^{-1} and redox potentials around 400 mV or more. As a result, concentrations of dissolved Fe and Mn are usually low although values up to 1.3 mg l^{-1} and 1.5 mg l^{-1} respectively have been found in some groundwaters. Even under Drift-confined artesian conditions, groundwaters can remain oxic, presumably because of the discontinuous nature of Drift deposits and a paucity in the aquifer of reducing agents capable of removing the dissolved oxygen and generating anoxic conditions. In the area of investigation, anoxic conditions appear to be relatively localised. Where such conditions exist, groundwaters can have higher concentrations of dissolved Fe and Mn. Mildly reducing groundwaters occur for example in boreholes at Kinsall [SJ 349 330], Hollies [SJ 224 382], Standford Bridge [SJ 705 240] and in part of the northern Tern catchment.

A few analysed groundwaters from areas of Permo-Triassic Sandstone confined by sediments of the Mercia Mudstone Group were also included in the study and these also appear to be oxic. The boreholes sampled were only just into the confined aquifer on the margins of the Mercia Mudstone outcrop but suggest that oxic conditions can exist for a few (at least one or two) kilometres downgradient into the Mudstone-confined aquifer. The main part of the Mudstone-confined Sandstone (e.g. Wem to Whitchurch area) appears to be under-utilised for groundwater abstraction and few data exist to assess the chemistry of its groundwater.

As large parts of the aquifer are unconfined or only semi-confined, the groundwater is potentially vulnerable to pollution. The area is dominantly rural, so diffuse pollutants of agricultural origin are a particular concern. The largely oxic nature of the groundwaters means that infiltrating NO_3-N can also remain stable. As a result, concentrations of NO_3-N are often high, reaching an observed maximum in this study of 51 mg l^{-1}. Temporal variations in NO_3-N concentration are also notable in some boreholes, and a few show evidence of increases with time, presumably as a result of increasing inputs of pollutants since the 1970s when the earliest groundwater-monitoring data were collected. The spatial distribution of NO_3-N in the groundwater is highly variable, reflecting the variation in Drift distribution and permeability and likely spatial variations in inputs of both diffuse and point-source pollutants. Inputs of nitrate are likely to originate mainly from agricultural sources and septic tanks. Variable depth to water table may also have an influence. Inputs of pollutants also have an impact on the concentration ranges of chemical parameters such as DOC, NH_4-N, P and K.

Besides these varying influences, inputs of highly saline groundwaters are observed in a few groundwaters (e.g. Frank Brook [SJ 431 198], Woodfield [SJ 631 164]) that are likely to derive from saliniferous sediments such as evaporitic horizons in the Mercia Mudstone or horizons in the Carboniferous Coal Measures. The high degree of faulting in the study area means that such formations can be juxtaposed with the Permo-Triassic Sandstone and the faults themselves can be conduits for cross-formational groundwater flow. The Wem and Hodnet Faults in particular have been highlighted as loci of preferential cross-formational flow.

Trace elements show a correspondingly large range of concentrations, consistent with the numerous interacting processes outlined above. Ranges of some elements are worthy of note, including concentrations of As up to 26 µg l^{-1}, U up to 67 µg l^{-1} and Ni up to 43 µg l^{-1}. The origins of these trace elements are uncertain, but iron oxides are believed to be the most likely mineral sources, the As and U being mobilised under the conditions of near-neutral pH, while the Ni appears to be associated with acidic, low-alkalinity shallow groundwaters that have not reacted with carbonate cements.

2. PERSPECTIVE

2.1 Study area

The Permo-Triassic Sandstone aquifer of Shropshire has an irregular, distorted W-shaped outcrop which extends from Whittington in the north-west to Shrewsbury, Telford and Bridgnorth in the south and to Market Drayton in the north-east. The eastern margin of the aquifer for the purposes of this report is at the longitude of Stoke-on-Trent. The Sandstone outcrop, including areas covered by Drift, has an areal extent of around 800 km^2 (Figure 2.1).

The area comprises mainly flat-lying agricultural land with elevations of around 200 m above OD near Market Drayton, to around 100 m above OD in the north-west around Whittington, and 45 m above OD at the confluence of the Tern and Severn in the south-east (Figure 2.1). A series of sandstone escarpments, typically 20–50 m above the surrounding land, define the eastern and northern boundaries of the Permo-Triassic Sandstone outcrop. The main river courses drain south towards the River Severn. These include the Rivers Morda, Roden, Perry, Tern and Meese.

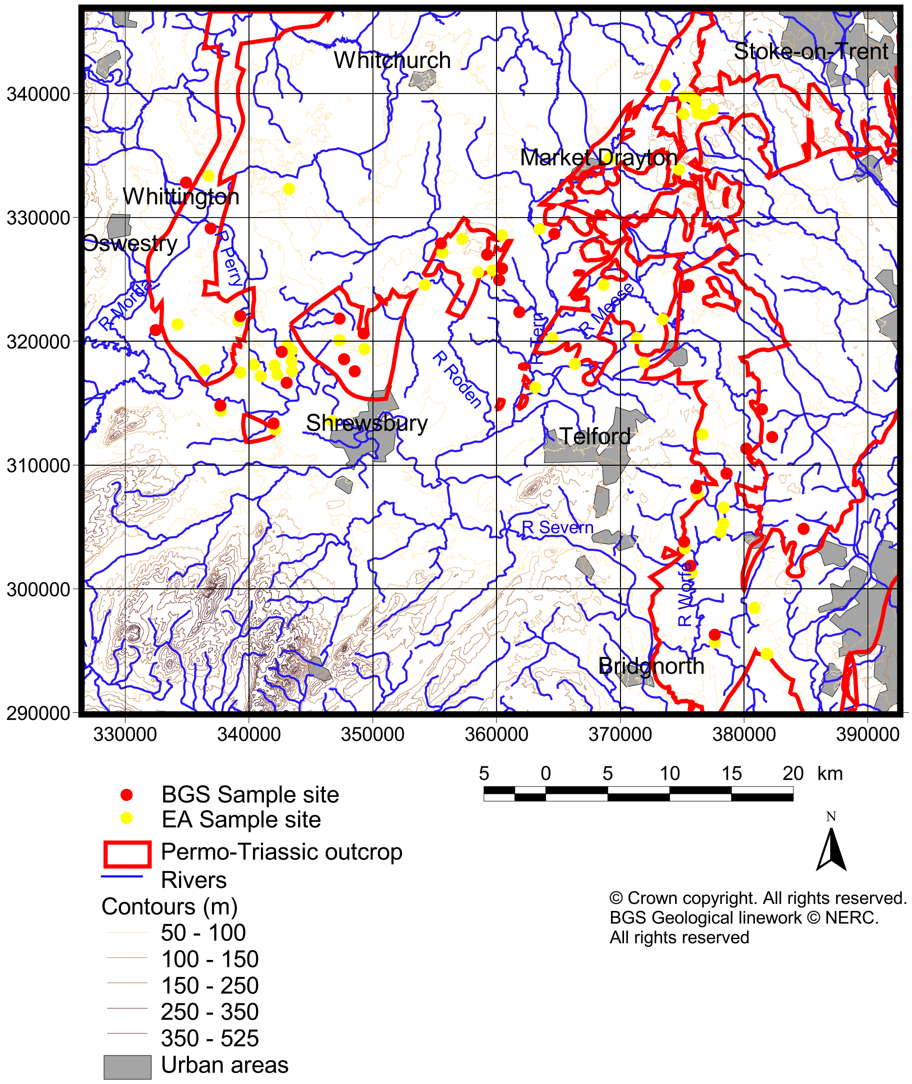

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Figure 2.1. Map of the study area in Shropshire showing the location of the Permo-Triassic Sandstone aquifer outcrop.

Figure 2.2. **Rolling hills of the Shropshire Permo-Triassic Sandstone looking east towards the Ironbridge power station [SJ 655 038] (photograph: I. Neumann).**

The landscape is mainly rural but a number of small towns are included within the area of Sandstone outcrop and Shrewsbury is a regional commercial centre. The soils are generally fertile and agriculture is mainly of mixed arable type with wheat, sugar beet, barley and potatoes dominating. Cattle and sheep grazing is common on higher grassland areas.

Average annual rainfall is mainly less than 700 mm, with lowest rainfall figures in the Shropshire floodplains and highest (>750 mm) in the hilly areas around Oswestry, Telford and Market Drayton.

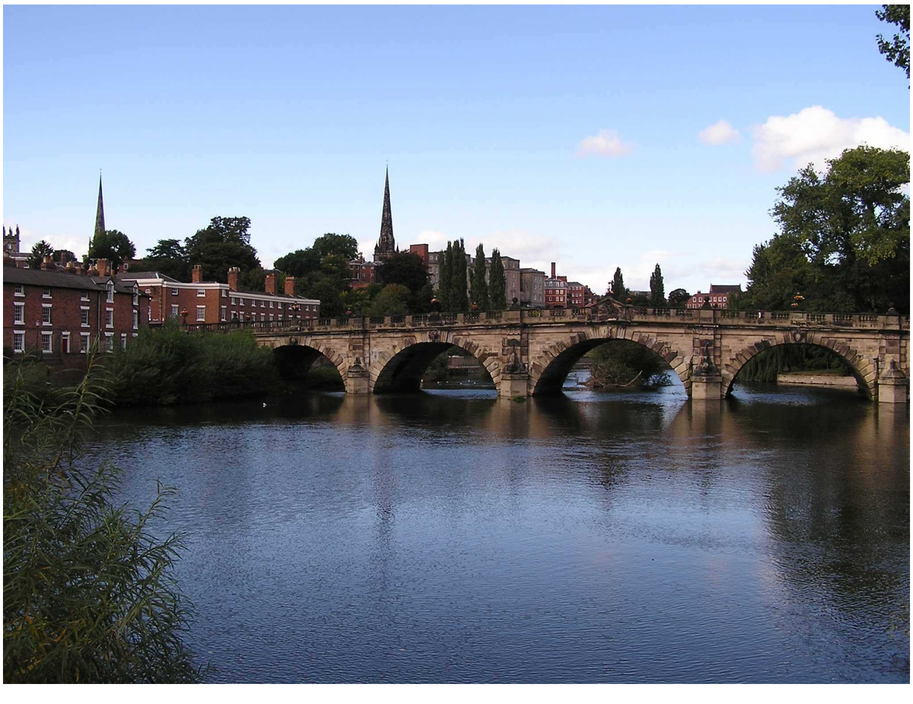


Figure 2.3. **The River Severn at Shrewsbury [SJ 496 122] (photograph: S. Brown).**

Figure 2.4. **View of a large meander in the River Severn near Leighton with rolling hills formed by the Permo-Triassic Sandstone [SJ 620 045] (photograph: I. Neumann).**

Potential evaporation is estimated at around 500 mm year^{-1} (Environment Agency, 2000a).

Groundwater from the Permo-Triassic Sandstone of Shropshire is heavily used for public water supply, irrigation and other agricultural purposes. The aquifer also supports the Shropshire Groundwater Scheme, one of the largest groundwater augmentation schemes currently operating in the UK. Some industrial abstractions also operate, mainly around Shrewsbury. As the area is largely rural (Figure 2.2), groundwater is also abstracted from numerous private boreholes. Groundwater levels (as well as river flows) in some areas have declined as a result of overabstraction following increased licensing of abstractions during the 1960s (Environment Agency, 2000b) and as a result of licences of right for both private and public boreholes.

Shrewsbury was originally built on high ground on the inside of a meander in the River Severn (Figure 2.3). More recent urban development has encroached onto the river floodplain, resulting in periodic flooding and high flood risk. Further downstream, the towns of Ironbridge, Bridgnorth, Bewdley and Stourport are also flood-risk areas (Environment Agency, 2000b).

2.2 Current issues in groundwater quality

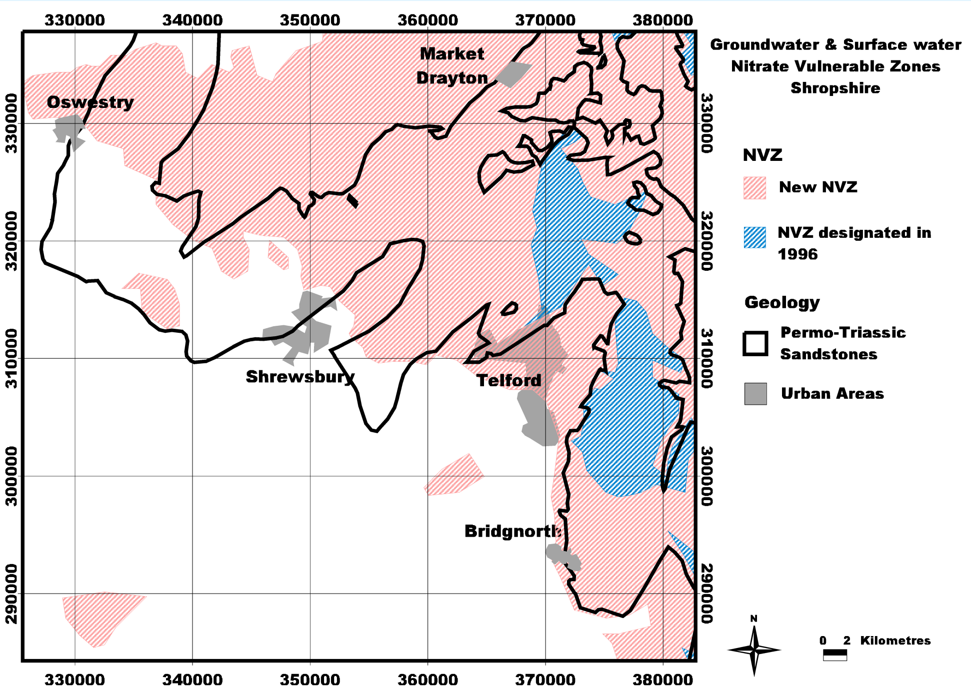
The Permo-Triassic Sandstone of Shropshire generally has groundwater of good inorganic chemical quality although high and increasing concentrations of nitrate are a major problem for drinking-water supply. The nitrate probably derives mainly from agricultural sources, following the increased use of nitrogenous fertiliser over the last few decades, but may also be partly derived from domestic pollutant sources such as septic tanks. Groundwater from some boreholes in the region has concentrations approaching or exceeding the current EC and UK drinking-water limit for nitrate of 11.3 mg l^{-1} as N. As a result, large areas of the unconfined Permo-Triassic Sandstone aquifer have been defined as nitrate vulnerable zones (NVZs) (Box 2.1). Public water supply in affected areas is generally blended in order to reduce concentrations sufficiently to meet the water-quality regulations.

Box 2.1 Nitrate Vulnerable Zones (NVZs)

Historically, the Shropshire Permo-Triassic Sandstone aquifers have been used to support a number of important local groundwater abstractions for both public and private supplies. However, pollution of these supplies by nitrate from agricultural sources is becoming an increasing problem. During and after the Second World War, farming practices became much more intensive and modern farming methods use large quantities manures, sewage sludge and chemical fertilizers. Overuse with resultant surplus nitrogen can lead to problems in the groundwater environment which can last for decades or even centuries.

Agricultural fertilisers and organic wastes from sewage spreading are ‘diffuse sources’ of nitrate. Excess nitrate can leach into aquifers with infiltrating rainwater and can pollute groundwater sources such as springs and boreholes. Recharging rainwater can pass quickly through fractures and through the pore matrix in the Permo-Triassic Sandstone aquifers, making them highly vulnerable to pollution. In recent years, high concentrations of nitrate in groundwater have been dealt with by blending with low-nitrate water in order to reduce concentrations and achieve compliance with drinking-water standards for public supply.

The Ministry of Agriculture, Fisheries and Food (MAFF, now part of the Department for Food & Rural Affairs, DEFRA) established Nitrate Sensitive Areas (NSAs) in the late 1980s to address the nitrate problem, as laid down under the 1989 Water Act. NSAs were selected catchments where nitrate concentrations in sources of public drinking water exceeded, or were at risk of exceeding, the EC drinking-water limit for NO_3-N of 11.3 mg l^{-1}. Initially, farmers who worked land within these designated areas joined voluntary schemes where compensation was available for those introducing action measures to reduce fertiliser applications. NSAs were replaced in 1996 by Nitrate Vulnerable Zones (NVZs) which were introduced under the EC Nitrate Directive. NVZs still covered small discrete catchments similar to NSAs. However, in December 2002 these were superseded when zones of surface water and groundwater were combined to form larger NVZs, now covering large parts of Shropshire across the Permo-Triassic Sandstone aquifer and surface-water catchments (see map below). It will be many years before any beneficial effects from changes in farming practices are detected in the quality of groundwater. The Environment Agency will continue to monitor concentrations of nitrate in groundwater.



Unconfined groundwaters in the Sandstone also face pressures from other pollutants. Industrial operations are minor and not believed to be a major problem, but concerns exist over the vulnerability of large parts of the aquifer to contamination from pesticides and hydrocarbon-based compounds derived from sources such as fuel-filling stations, heating units and tanks.

High salinity also constitutes a problem in some areas, particularly along the margins of the aquifer. This is mainly due to infiltration of groundwater from adjacent strata, notably the Upper Carboniferous Salop Formation (formerly the Keele Beds, part of the Upper Coal Measures) or the Triassic Mercia Mudstone. Tate and Robertson (1971) reported Cl concentrations up to 520 mg l^{-1} in groundwater from the Permo-Triassic Sandstone at Woodfield pumping station near Wellington [SJ 630 164]. This compares with typical concentrations of Cl in the aquifer of <50 mg l^{-1}. An increase of some 250 mg l^{-1} was observed in borehole No. 1 between the periods 1948 and 1964, linked to increasing abstraction at the site. The saline source was taken to be water infiltrating the aquifer at depth from the Salop Formation. A secondary source, also thought to be derived from the Salop Formation, entered the aquifer via surface infiltration from the Beanhill Brook.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

This section provides an overview of the geography, geology, hydrogeology and environmental conditions in the study area. Understanding of these factors is a prerequisite for the characterisation and definition of the natural (baseline) quality of the groundwater in the Permo-Triassic Sandstone aquifer of Shropshire.

3.2 Geology

3.2.1 Permo-Triassic sediments

The Permo-Triassic strata of Shropshire lie on the southern margin of the Cheshire Basin and the eastern margin of the Stafford Basin. The stratigraphic nomenclature differs for the two basins, but that of the Stafford Basin has mainly been used in this study. The strata include the lowermost Bridgnorth Sandstone of Permian age which is overlain by the Triassic Sherwood Sandstone Group and in turn in the northern part of the study area by the Triassic Mercia Mudstone Group (Table 3.1). The regional geology is shown in Figure 3.1 and a cross section of the sediments along the course of the River Tern is shown in Figure 3.2.

The Bridgnorth Sandstone and overlying Sherwood Sandstone formations form the main aquifer of the region and consist of red-bed aeolian sandstone (Figure 3.3; Figure 3.4) with some conglomerates and marls. The Sherwood Sandstone varies in thickness from a few tens of metres to around 1800 m. Geophysical surveys suggest that it may approach 450 m thickness in parts of the Perry catchment (Severn Trent Water Authority, 1977). In boreholes at Knutsford and Prees in the Cheshire Basin, total thicknesses of the Sherwood Sandstone Group are around 1400 m and 1000 m respectively (Warrington et al., 1999).

The Sherwood Sandstone is subdivided (oldest first) into the Kidderminster Formation, Wildmoor Sandstone and Bromsgrove Sandstone Formation. The sequence forms a series of fault-bounded blocks which in the south overlap onto Palaeozoic rocks, principally of Carboniferous age (Figure 3.1). Dips vary as a result of faulting but are typically northwards or eastwards at angles of 5–10°.

Table 3.1. Generalised lithostratigraphy of east Shropshire following the nomenclature of the Stafford Basin classification (after Whitehead et al., 1928; Warrington et al., 1980 and Papatolios and Lerner, 1993; Bridge et al., 2002).

Age	Group	Formation	Lithology	Approximate thickness (m)	Aquifer type
Quaternary		Drift	Clay, sand, gravel	0–40	Minor/non
Triassic	Mercia Mudstone	Mercia Mudstone	Marl with sandy/ silty layers	up to 2000	Minor/non-aquifer
	Sherwood Sandstone	Bromsgrove Sandstone	Sandstone	30–230	Major
		Wildmoor Sandstone	Sandstone	up to 900	Major
		Kidderminster Sandstone	Sandstone	<100–160	Major
Permian		Bridgnorth Sandstone	Sandstone	50–180	Major
Carboniferous	Coal Measures	Salop Formation	Shale, marl, sandstone, limestone	>250	Minor/non-aquifer

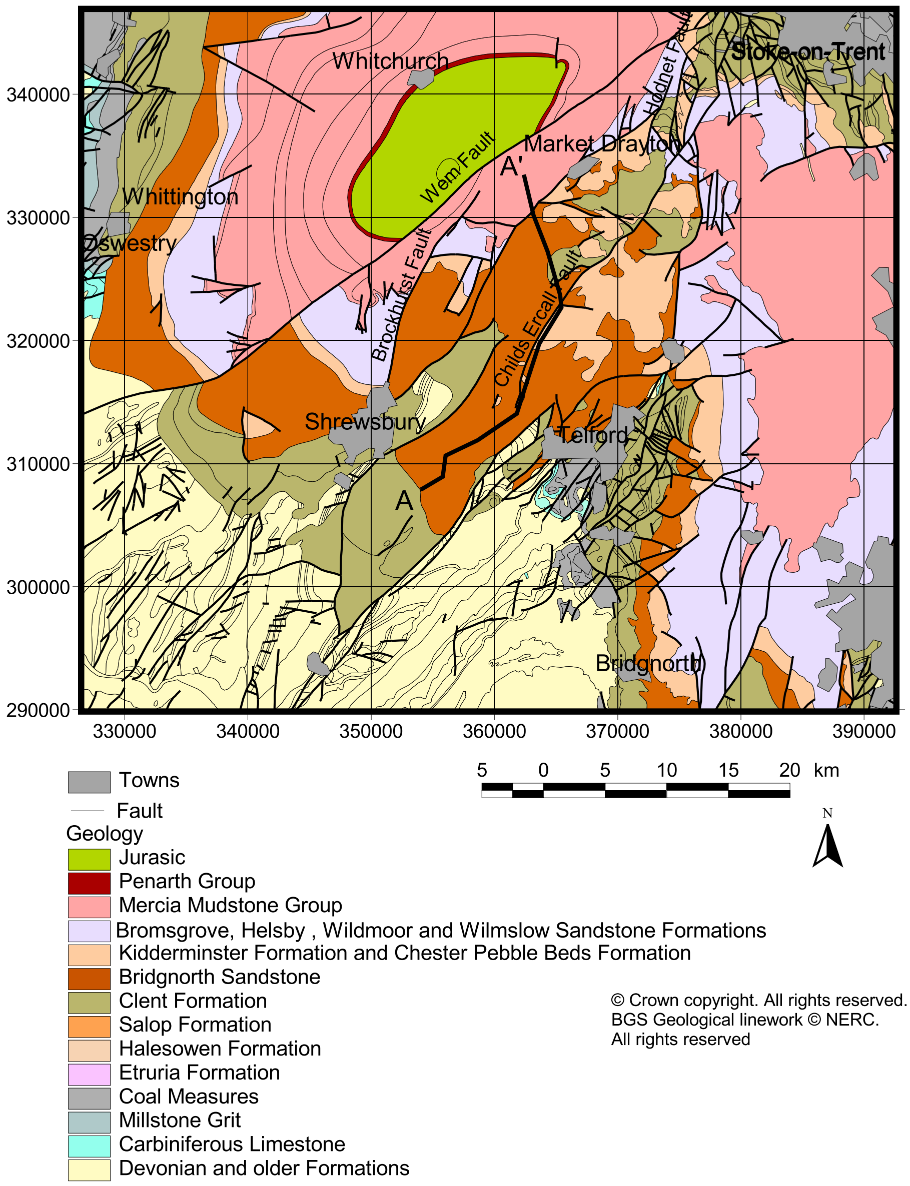


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Figure 3.1 **Geological map of Shropshire showing the area of outcrop of the Permo-Triassic Sandstone.**

The Permian Bridgnorth Sandstone Formation was formerly known as the Lower Mottled Sandstone and is also known as the Kinnerton Sandstone in stratigraphic terminology used to describe the Cheshire Basin (Bridge et al., 2002). This deposit is typically a laminated, cross-bedded or dune-bedded red aeolian sandstone (Figure 3.6, Figure 3.7) with some yellow mottling and intraformational conglomerate horizons (Pocock and Wray, 1925). The formation is free of mudstones (Streetly and Shepley, 2002). In most places it is over 100 m thick. The sequence was proved as 209 m thick in the Childs Ercall borehole [SJ 668 367] and comprised red sandstone with yellow mottling, possibly owing to periglacial alteration processes, in the upper 52 m (Klinck and Trick, 2001). Borehole logs commonly record a weathered upper portion to this formation.

The overlying Kidderminster Formation, formerly the Bunter Pebble Beds (equivalent to the Chester Pebble Beds of the Cheshire Basin) comprises coarse red pebbly sandstone with conglomeratic and mudstone bands of fluvial/deltaic origin and a basal breccia. The unit is typically well-cemented. These sediments are exposed throughout much of the central Tern catchment. The formation is

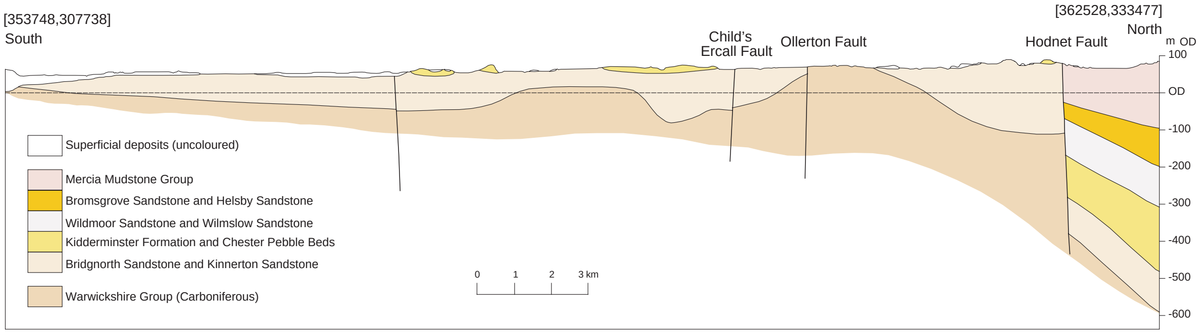

Figure 3.2 **Geological cross-section of the Permo-Triassic Sandstone extending along the course of the River Tern (see Figure 2.1) (from Bridge et al., 2002).**

usually around 10–100 m thick, though borehole logs have proved the sequence to be 111 m thick at Prees, and 125 m thick at Childs Ercall.

The Wildmoor Sandstone, formerly the Upper Mottled Sandstone (Wilmslow Sandstone in the Cheshire Basin), is a finer-grained soft and poorly-cemented pebble-free red sandstone with subordinate siltstone. This is mainly of aeolian origin but with local fluviatile beds. In the Prees borehole [SJ 560 330], this is 595 m thick. Between the Wem and Brockhurst Faults, the sequence may be 300 m thick (Bridge et al., 2002).

The Wildmoor Sandstone is overlain in turn by the Bromsgrove Sandstone Formation (Helsby Sandstone in the Cheshire Basin). This is a hard, calcite-cemented thinly-bedded micaceous red-brown sandstone, locally pebbly, with fining-upward sequences. The sediment is of fluvial and subordinate aeolian origin. The deposits are generally thin, around 20–50 m at outcrop but thicken to around 50 m on the edge of the Stafford Basin and 75 m below the Mercia Mudstone sediments (Bridge et al., 2002).

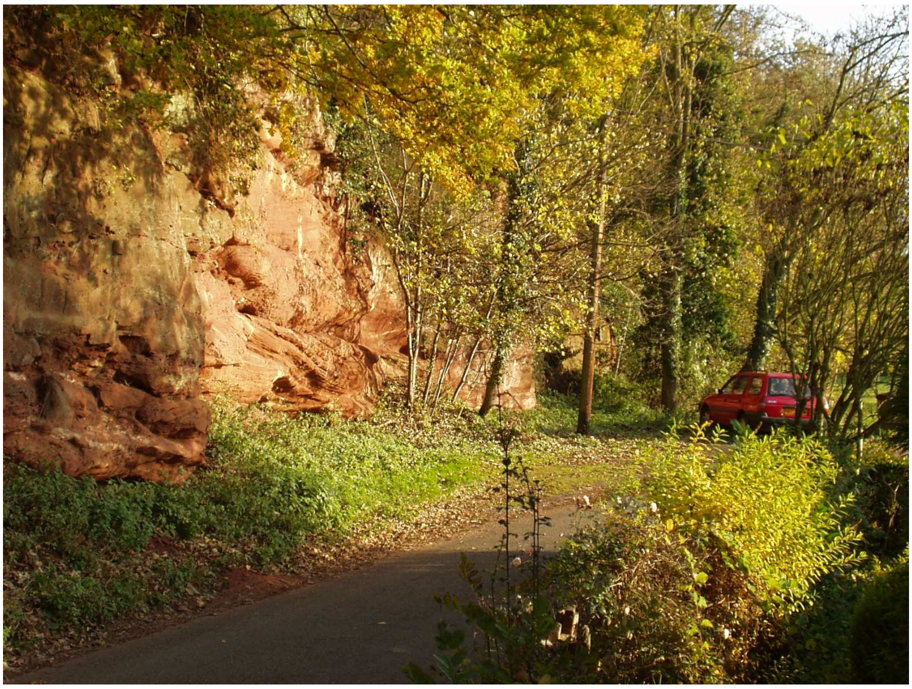

Figure 3.3. **View of quarry face in the Permo-Triassic Sandstone near Grindleforge [SJ 753 035] (photograph: I. Neumann).**

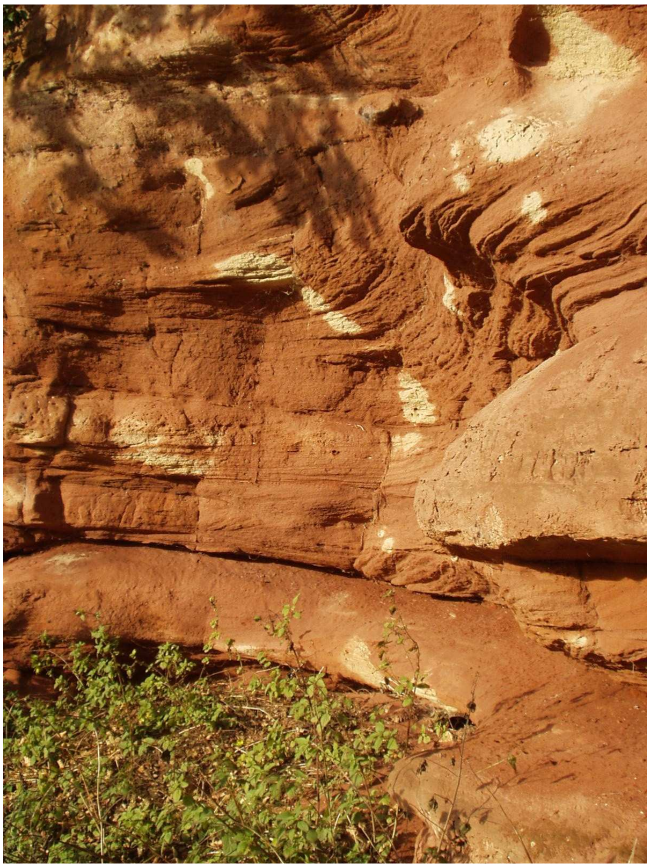

Figure 3.4. **Outcrop of the Sherwood Sandstone showing the typical red-bed lithology with cross-bedding and local yellow mottling [SJ 753 035] (photograph: I. Neumann).**

In the northern parts of the study area, the Triassic Mercia Mudstone Group sediments, formerly known as the Keuper Marl, conformably overlie the Bromsgrove Sandstone. These comprise mainly fine-grained lacustrine red marls with abundant evaporite deposits (gypsum, halite), which reach up to 2000 m thick in the Cheshire Basin (Warrington et al., 1999). Evaporitic horizons include the Saliferous Beds. The Mercia Mudstone sediments were deposited in a flat-lying inland playa lake environment in desert climatic conditions. Towards the late Triassic, marine incursions are evident in the sediment sequence.

The Sandstone is heavily dissected by a series of north-east–south-west-trending extensional faults, notably the Wem and Church Stretton Faults which produce a series of half grabens (Bridge et al., 2002). The faults often have large downthrows and have a great impact on sandstone thickness (Smart, 1977). The lower part of the Sherwood Sandstone Group is faulted against the younger Mercia Mudstone by the north-north-east-trending Hodnet Fault (Klinck and Trick, 2001) which extends between Shrewsbury and Market Drayton and by the Brockhurst Fault between Grinshall and Lee Brockhurst. The Hodnet Fault has been assigned arbitrarily as the demarcating structure separating the Cheshire Basin in the north-west from the Stafford Basin in the east (Bridge et al., 2001).

3.2.2 Superficial deposits

The Permo-Triassic rocks are overlain by variable thicknesses of Drift deposits. These include glacial outwash gravels, till deposits (boulder clay) and lacustrine clays as well as river alluvium. The Drift is notably thicker in the west of the study area than further east (Figure 3.5), being commonly over 50 m thick in the north Perry catchment and to the north and west of Shrewsbury. East of the River Roden, deposits are usually thin and relatively permeable. Till is the most widespread deposit, being over

30 m thick in parts of the west and north-west of the study area (Worsley, 1991). Thick clays are a particular feature of the north Perry catchment along the watershed with the Dee catchment in the north. At Lower Frankton [SJ 366 312], the Triassic sequence is overlain by 53 m of dominantly clay (Severn Trent Water Authority, 1978). The till is typically poorly-sorted material with a large component of stiff red-brown or grey-brown clay (Bridge et al., 2002).

Glacial outwash deposits range from coarse gravels to pebbly sands and clayey sands. Where present, the glacial outwash deposits are often in excess of 20 m thick although on average are closer to 2–3 m thick (Streetly and Shepley, 2001). They are well-developed around Prees, Shawbury, Wem and north of Wellington. Glaciolacustrine deposits are typically soft brown, pebble-free laminated clays.

Three large glacial channels have been identified in the area to the north and west of Shrewsbury, each infilled with thick Drift deposits of till, glacial outwash gravels and lacustrine clays. The largest is the Severn Trench (Box 3.1) which runs westwards from Shrewsbury and contains Drift deposits in places up to 120 m thick. Clayey deposits of lacustrine origin, reach up to 115 m thick in the channel at Cae Howel [SJ 341 173] (Smart, 1977; 1978). A borehole at Wilcott Marsh [SJ 376 176] also proved 71 m of dominantly blue-grey clay, only the basal 4 m comprising sand and gravel.

A second glacial channel runs north–south through Ellesmere, then subdivides north of Baschurch, one branch passing through Baschurch [SJ 425 220] and Broomfields and joining the Severn Trench near Felton Butler [SJ 394 174]. This channel contains mainly sandy deposits. The other branch passes through Myddlewood and Alkmund Park [SJ 482 156], then joins the main trench at Hencott, [SJ 495 153] just to the north of Shrewsbury (Severn Trent Water Authority, 1978; Smart, 1978). This

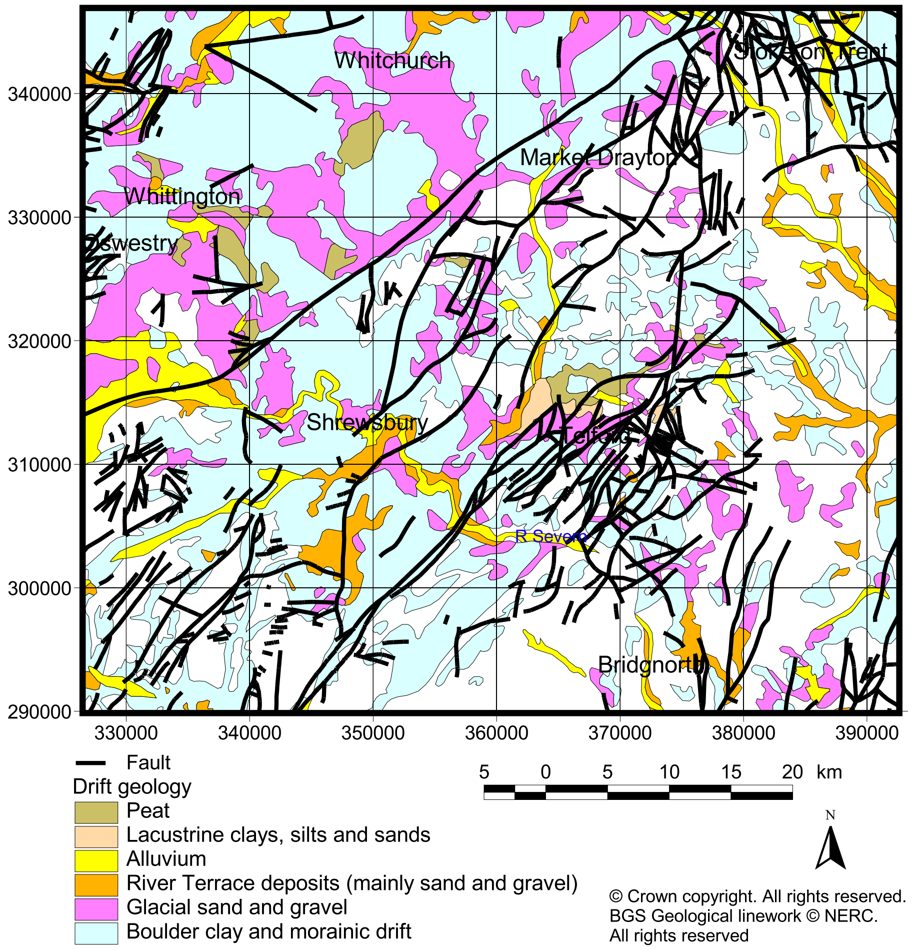

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Figure 3.5. Map of the distribution of Drift deposits in the study area.

Figure 3.6. Outcrop showing detail of dune-bedded Bridgnorth Sandstone cross-bedded with fluvial Kidderminster Conglomerate [SO 733 959] (photograph: S. Brown).

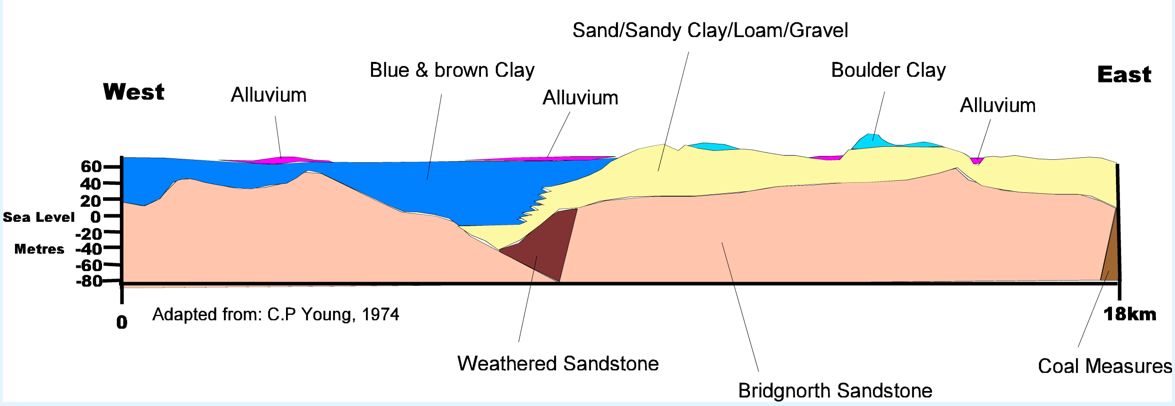
channel is infilled by mainly clay deposits. In the Ellesmere area, the Drift infill has been described as blue-grey laminated clay of likely lacustrine origin (Severn Trent Water Authority, 1978). Geophysical investigations suggest that Drift deposits in the two channels reach up to 60 m thick (Smart, 1978).

Post-glacial deposits include river terraces and alluvium which occupy the main valleys. Terracing is well-developed in the Tern and Severn valleys. Alluvium consists of clay, sand and gravel, with occasional lenses of humic-rich deposits (Bridge et al., 2002). The alluvium is mainly derived from

Figure 3.7. Detail of cross-bedding in the Sherwood Sandstone showing variation in iron-oxide concentration and possibly redox condition (red/yellow coloration) from a stone wall, Beckbury Church [SJ 764 016] (photograph: I. Neumann).

Box 3.1 Glacial channels: the Severn Trench

Deep glacier-cut channels are a notable feature of the superficial geology of the Shropshire area and have a major impact on hydrogeology. The channels are steep-sided and infilled with thick deposits of sand, gravel and clay that constitute till deposits, glacial outwash material and lake clays. The deepest and most prominent of the glacial channels is the Severn Trench (figure below) which extends west of Shrewsbury via Shrawardine [SJ 400 152] and Melverley [SJ 335 165] and is deepest, extending down to –53 m AOD, at Cae Howel [SJ 341 173]. The channel has thick clay deposits along its centre but more sandy material along its northern margins (Streetly and Shepley, 2001). Extension of the channel east of Shrewsbury has been postulated but is not well-defined. The depth of these channels can locally influence groundwater flows and produce productive aquifers from the superficial deposits. Locally confined piezometric surfaces produce artesian conditions in several boreholes, the Wilcott Marsh borehole [SJ 376 176] being a good example.



Adapted from: C.P Young, 1974

erosion of glacial Drift. In the Tern and Severn valleys, alluvial deposits are typically <5–8 m thick.

3.3 Hydrogeology

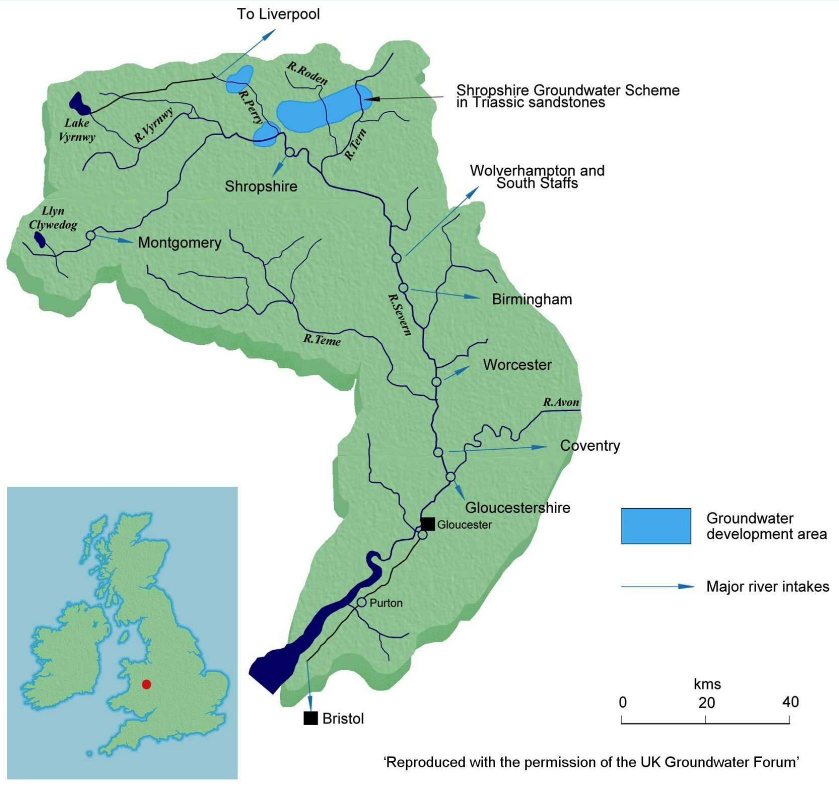
Numerous reports have been produced describing the hydrogeology of the Shropshire Permo-Triassic Sandstone and a recent conceptual model of groundwater flow has been developed for the region (Streetly et al., 2003). The Environment Agency plans to produce a numerical flow model of the aquifer in order to facilitate future licensing decisions and catchment abstraction management systems (CAMS).

The Permo-Triassic Sandstone is a high-yielding aquifer and is regionally important for groundwater supply. Both the Bridgnorth Sandstone and Sherwood Sandstone formations provide high yields and they are believed to be in hydraulic connection, hence largely behaving as a single aquifer (Papatolios and Lerner, 1993). The total available groundwater resource of the region has been estimated as 230 Ml day^{-1} (Severn Trent Water Authority, 1977; 1979). The aquifer currently has 38 licensed public-supply sites, with numerous private abstractions and a large network of boreholes in the Shropshire Groundwater Scheme (SGS), developed to augment and protect flows in the River Severn during periods of drought (Box 3.2). Public-supply boreholes are typically 70–300 m deep. Those in the SGS network are typically 100–200 m deep.

The adjoining Coal Measures and Mercia Mudstone sediments are both considered to be aquitards and thus act as barriers to groundwater flow. The superficial Drift deposits constitute either aquitards, leaky aquitards or aquifers in hydraulic connection with the Sandstones, depending on lithology and Drift thickness.

Box 3.2 The Shropshire Groundwater Scheme (SGS)

The River Severn is a major source of water for communities in the West Midlands between Shrewsbury and Bristol, including the cities of Worcester and Gloucester. The river provides supplies for public drinking water, industry and agriculture. During the summer months the volume of water in the river may be insufficient to meet these abstraction needs and the need to protect the river ecosystems. The flow is therefore regulated by release of surface water stored in the Llyn Clywedog [SN 9021 8808] and Lake Vyrnwy [SH 9927 2125] reservoirs, located at the headwaters of the Severn. During drought periods, the surface-water resources are insufficient to maintain an adequate flow in the river and so a new source has been sought: groundwater. The Shropshire Groundwater Scheme provides a continuous supply of water to the River Severn during dry years from deep boreholes in the Sherwood Sandstone. This aquifer provides a large underground storage capacity, which no surface reservoir can match in terms of quantity and quality.



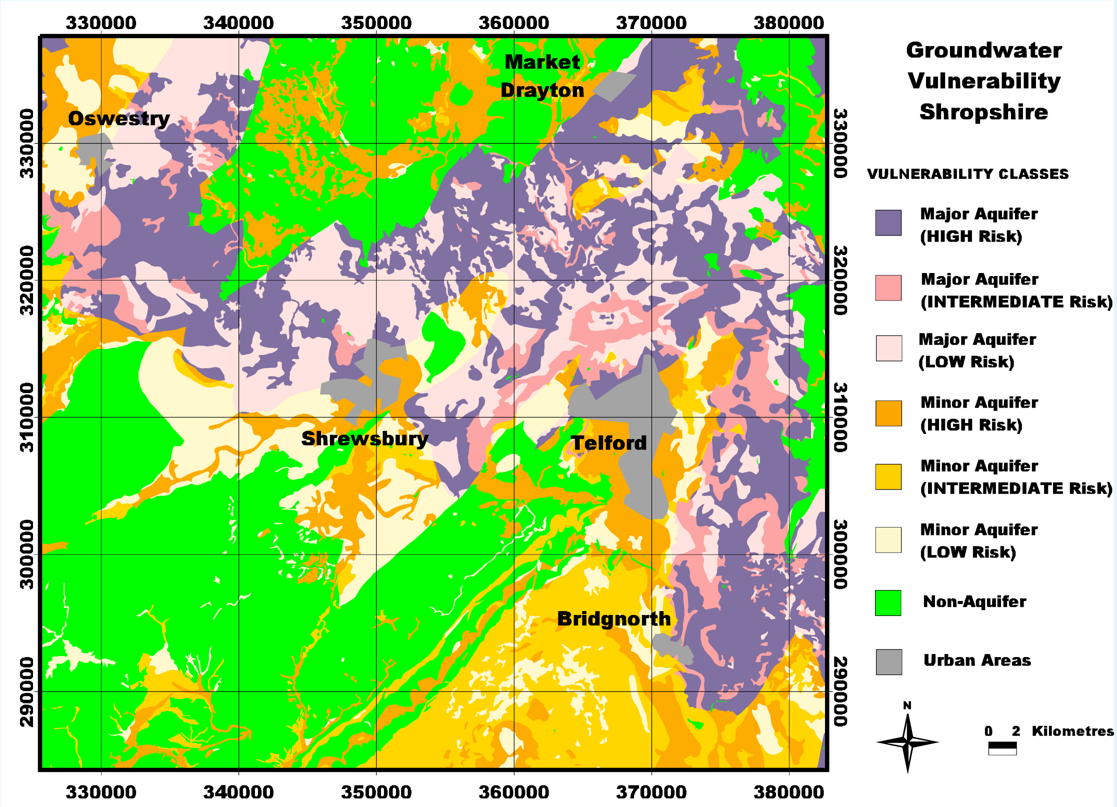
'Reproduced with the permission of the UK Groundwater Forum'

The SGS is one of the largest groundwater-sourced river augmentation schemes in the UK. The scheme began in 1981 and is still being developed today. Five phases have so far been completed, with flexibility to construct to up eight in total. Each phase consists of a series of abstraction boreholes linked by underground pipelines to discharge points (outfalls) either directly into the River Severn or into its tributaries, the Perry, Roden, Tern and Meese rivers. On completion of the scheme, 64 groundwater pumping stations will be available for abstraction and these will be monitored by 91 observation boreholes. Typical abstraction yields from the completed scheme will be of the order of 4000–7000 m^3 day^{-1} and water will be piped through 73 km of pipeline where 9 major outfalls can discharge in excess of 10,000 m^3 day^{-1} if necessary.

Each new phase has been designed to cater for future increases in water demand and so proposed further extension and expenditure on the next phase(s) will be demand-driven. Phases 1, 2 and 3 have already been commissioned and collectively can provide 150 Ml day^{-1}. Phases 4 and 5 are currently undergoing commissioning trials and should contribute an additional 100 Ml day^{-1}. The total abstraction permitted from the Permo-Triassic Sandstone aquifer will be 330 Ml day^{-1} which will ensure continuing water supplies and protection of the river ecosystem during future droughts.

Box 3.3 Groundwater vulnerability mapping

The Shropshire Permo-Triassic Sandstone aquifer is classified as a Major Aquifer (purple on map) which is at high risk of contamination from human activities associated with agricultural practices, urbanisation, industrial processes, disposal of wastes and spillages of solvents and fuel oils. As Shropshire is characteristically a rural landscape with arable and grassland the dominant land-use, the aquifer is most at risk from agricultural chemicals such as pesticides and fertilisers (natural and man-made), from agricultural runoff and from domestic oil storage tanks and septic tanks. The overlying soils have little ability to attenuate pollutants and the fractured nature of the geological strata can provide pollutants with fast pathways into the deeper saturated zone which can make the aquifer highly susceptible to contamination.



The vulnerability of an aquifer can be assessed from the nature and thickness of the unsaturated zone and overlying deposits (soil and Drift) and the rate of water flow through this zone. The Environment Agency has prepared groundwater vulnerability maps covering the UK (Environment Agency, 1998). These use information on soil properties to predict their leaching characteristics. The soil leaching information is combined with the aquifer classification to provide an overall assessment of vulnerability. Planning authorities, consultants, water companies, waste management companies and industry use these maps to help them assess groundwater vulnerability. They are also useful for emergency planning, especially where chemical spillages have occurred.

Groundwater flow in the Sandstone formations occurs by a combination of intergranular and fissure flow (Tate and Robertson, 1971; Streetly, 2003; Streetly et al., 2003). Flow is largely directed southwards towards the river valleys. An exception is in the north-western limb of the Sandstone outcrop where groundwater flows towards the Dee catchment in the north. Many of the rivers (e.g. the Tern, Roden, Meese and Strine) are in good hydraulic connection with the Sandstone aquifer, particularly where Drift is absent, as evidenced in several places by similar river and groundwater hydrograph trends.

Box 3.4 Source protection zones

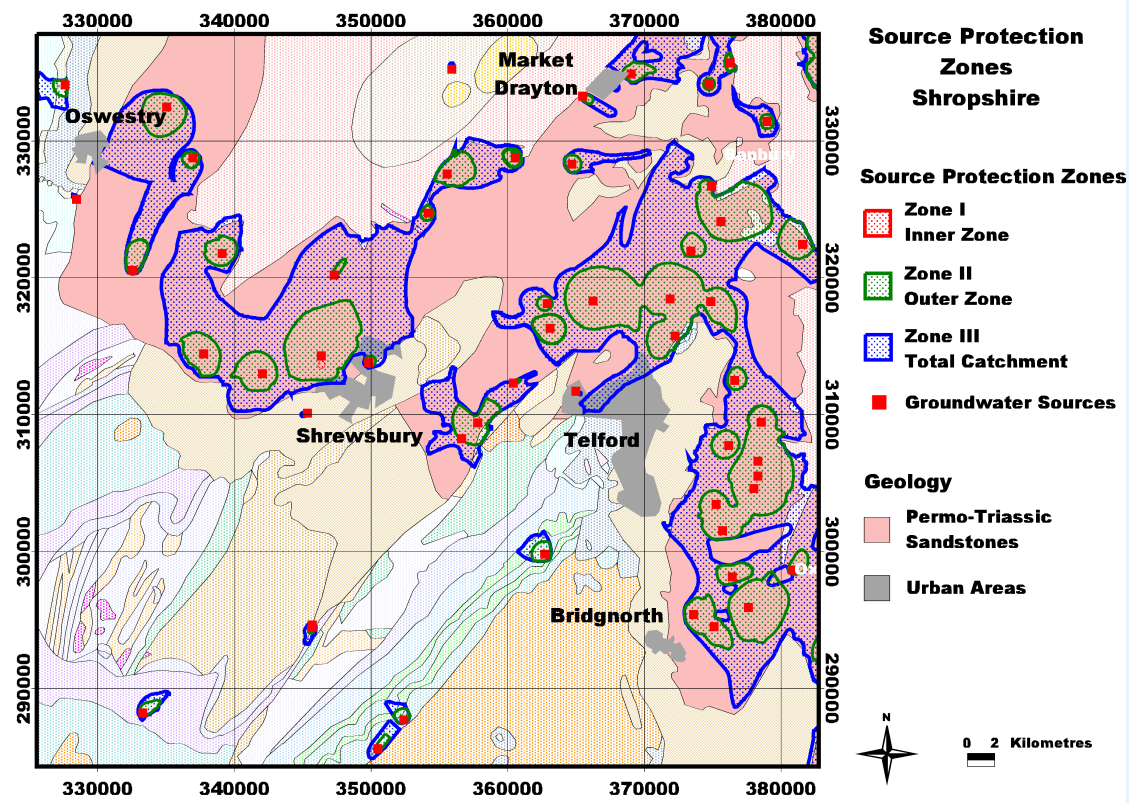
As most groundwater sources have the potential to become contaminated by pollutants, the Environment Agency has defined Source Protection Zones (SPZs) around groundwater sources (Environment Agency, 1998). These zones vary in size and shape as they are determined by local hydrogeological conditions, including geology, groundwater flow direction, effective rainfall, permeability and quantity of groundwater abstracted. All the major public-supply boreholes and the majority of the food-industry boreholes abstracting groundwater from the Shropshire Permo-Triassic Sandstone aquifers have a defined SPZ. Three groundwater Source Protection Zones are recognised:

Zone I (Inner Source Protection Zone): this zone is designed to protect against the effects of human activity, which might have an immediate effect upon the source. The area is defined by the distance a particle of water travels through the saturated zone in 50 days (minimum of 50 m) and is based on the principle that bacteria in the saturated zone will be eliminated within 50 days.

Zone II (Outer Source Protection Zone): this zone is larger than Zone I and is defined by a 400 day travel time or 25% of the catchment area (which ever is larger) through the saturated zone. The travel time is based on the minimum time required for the dilution and attenuation of pollutants that degrade slowly.

Zone III (Total Catchment Source Protection Zone): this zone is equivalent to the complete groundwater catchment area of the source and all groundwater will eventually discharge to the borehole or spring.

Although non-statutory, SPZs provide a useful tool for the Environment Agency, Planning Authorities, Water Companies, Industry, Consultants and Waste Management companies to help protect groundwater from pollution.



Most of the river flows in the study area are effluent, i.e. groundwater discharges to the river. This has been well-investigated for the River Tern in particular and is supported by often artesian conditions close to the river (Streetly et al., 2003). The Tern catchment is the subject of ongoing research into the interactions between surface water and groundwater as part of the Natural Environment Research Council's LOCAR programme.

Recharge is largely by infiltrating rainfall to the unconfined sections of the aquifer, though cross-boundary flow from neighbouring strata is apparent in some areas. Papatolios and Lerner (1993) concluded for the Telford area that river infiltration, urban losses and agricultural irrigation were insignificant sources of recharge. Average annual recharge was taken to approximate 112 mm. Annual recharge for the Lee Brockhurst area has also been estimated as 118 mm (Entec, 1999). Average annual recharge for the region from a synthesis of available data is 188 mm (Streetly and Shepley, 2002). Annual effective rainfall is of the order of 260 mm.

Groundwater flow rates tend to be lower in the areas covered by thick clayey Drift deposits than in exposed areas or areas covered by thin sandy Drift. Groundwater levels in boreholes in the Telford area have shown decreases over the last few decades of only a few metres, except close to major abstractions, where drawdown has been greater (Papatolios and Lerner, 1993).

The Sandstone has variable but often high hydraulic conductivity, the high values reflecting the importance of fissure flow. Considerable variations are apparent in both vertical and horizontal hydraulic conductivity values. Allen et al. (1997) quoted the interquartile range for bulk hydraulic conductivity in the Sherwood Sandstone as 1.8–8.4 m day^{-1}. Klinck and Trick (2001) reported hydraulic conductivities of between 2 x 10^{-5} and 15 m day^{-1} for the Bridgnorth Sandstone, the lowest values corresponding with fine sands and siltstones and the higher values with millet-seed sandstone in the lower part of the formation. Streetly and Shepley (2002) suggested from data produced by the Shropshire Groundwater Scheme test pumping, that the Bridgnorth Sandstone is relatively homogeneous compared to the overlying formations and that vertical hydraulic gradients in this unit are insignificant. However, more recent test pumping has indicated that some lithological variation and hence layering effects do occur in the Bridgnorth Sandstone.

Hydraulic conductivity values for the Kidderminster Formation have been reported to range between $3x10^{-4}$ and 15 m day^{-1}, the variation largely reflecting degree of cementation. Streetly (2003) noted differences in the hydraulic conductivity measurements between the borehole scale and the pore scale, with ranges respectively given as 5.9–15 m day^{-1} and 0.02–2.6 m day^{-1} from tests in the Bridgnorth Sandstone. The differences largely reflect the varying abundance of fractures. As a result of high aquifer permeability and abundant fracturing, large parts of the unconfined aquifer are considered vulnerable to the effects of groundwater pollution (Box 3.3). Source protection zones have been defined for all groundwater sources used for public supply in the region (Box 3.4).

Allen et al. (1997) gave a geometric mean transmissivity for the Sherwood Sandstone of 200 m^2 day^{-1}. Streetly (2003) gave a typical range for transmissivity of 150–510 m^2 day^{-1}, mostly from data for the Bridgnorth Sandstone. Papatolios and Lerner (1993) reported values in the range 10–500 m^2 day^{-1}. Low values (around 10–50 m^2 day^{-1}) largely reflect greater sandstone cementation, folding and mudstone horizons. Higher values (1000–2000 m^2 day^{-1}) reflect the effects of fractures (Streetly, 2003). Pumping tests at Lodge Bank [SJ 596 259] and Hopton [SJ 593 266] for example suggest enhanced transmissivity along the line of the Hodnet Fault (Streetly, 2003). Hydraulic conductivity and transmissivity are generally higher in the upper parts of the Sandstone and hence, although the sediment sequence is of the order of 900 m thick in places, effective aquifer thickness (i.e. interval over which groundwater flows) is of the order of 500 m (Alloisio and Shepley, 2002). Porosity measurements on core samples give values around 6–34% in the Bridgnorth Sandstone and 12–33% in the Kidderminster Formation (Allen et al., 1997).

Drift deposits have a considerable influence on regional recharge. The main groundwater recharge zones are in the east where Drift deposits are thin or absent. Limited sandstone exposures occur in the Grinshall and Knockin Heath areas. Where Drift deposits are permeable sands and gravels, they are in hydraulic continuity with the underlying sandstones. Thin and sandy deposits in the Tern and Roden catchments allow recharge to the Sandstone. Even the clayey Drift deposits can experience leakage to the underlying Sandstone aquifer: pumping tests carried out at Edgmond Bridge revealed a vertical hydraulic conductivity through the clayey Drift there of 0.038 m day^{-1} (Streetly, 2003).

Groundwater is mainly confined by Drift deposits to the west of Shrewsbury. Artesian boreholes linked to local confinement occur in the Melverley/Shrawardine area within the Severn Trench where Drift can reach over 120 m thick. A piezometric head of 3 m above ground level was described by Severn Trent Water Authority (1978) for Wilcott Marsh borehole [SJ 376 176] in the Severn Trench. Local confinement elsewhere also leads to artesian flows. Childs Ercall borehole in the Tern catchment has artesian conditions imposed by 7 m of clayey till. A borehole at Harcourt Mill [SJ 560 248] in the Roden catchment is also artesian (Smart, 1977; 1978), generated by vertical head gradients around a zone of groundwater convergence and discharge to surface water.

3.4 Mineralogy and mineral chemistry

The Sherwood Sandstone is mainly composed of sub-angular to rounded quartz grains with additional sodic plagioclase, orthoclase and microcline, both as detrital minerals and late overgrowths. Clay and marl horizons are common and some units are micaceous.

The sandstones have a characteristic red-brown coloration (Figure 3.7) due to the presence of iron oxide, principally haematite (Fe_2O_3), which occurs as grain coatings 1–2 µm in thickness, as a cement and as part of the argillaceous fraction. The sandstones typically contain about 1 weight % total Fe as Fe_2O_3 (Table 3.2). The red-brown coloration indicates the generally oxic character of the sediments. Localised reduction spots or mottling are characterised by greenish or yellow-white zones where iron-oxide coatings have been leached (Figure 3.7). A marked difference exists between the Fe content of oxidised red-brown lithologies and reduced greenish lithologies, with higher concentrations in the former (Milodowski et al., 1999).

The formations contain variable amounts of calcite and dolomite, both as detrital grains and cement overgrowths. This is reflected by CaO concentrations typically around 1–8 weight % (Table 3.2). Diagenetic dolomite and calcite are both found to be manganoan (Mn-rich; Jones et al., 1999). Some shallow outcrop sandstones display evidence of former dolomitic cements, but which have subsequently dissolved by circulating groundwater. The dolomite typically has a $\delta^{13}C$ composition of 0 to -1 ‰ (Milodowski et al., 1999). The Sherwood Sandstone typically contains around 1–4 weight % carbonate (e.g. Edmunds et al., 1982).

The sediments of the Cheshire Basin have been described in detail by Milodowski et al. (1999) and Jones et al. (1999). The Kinnerton Sandstone Formation (equivalent to the Bridgnorth Sandstone Formation) is noted to be dominated by quartz with a detrital mineralogy comprising 1–10% alkali feldspar, mudclasts, chert and volcanic fragments, with albite composing <1% (Jones et al., 1999). The overlying formations have a similar mineralogy although the Chester Pebble Beds (equivalent to the Kidderminster Formation) have a greater proportion of lithic clasts, chert and alkali feldspar and the formation has a more well-developed calcite and dolomite cement (Milodowski et al., 1999). This is reflected by often much higher observed CaO concentrations (Table 3.2) than the other formations. The Wilmslow Sandstone (equivalent to the Wildmoor Sandstone Formation) is generally more argillaceous than the underlying formations. Clay minerals include smectite, illite and minor chlorite. The Helsby Sandstone Formation (equivalent to the Bromsgrove Sandstone) is relatively feldspathic (Jones et al., 1999). This may explain the higher average Na_2O concentration of samples from this formation (Table 3.2).

Table 3.2. Average chemical compositions of selected formations from the Permo-Triassic Sandstone of Shropshire.

Borehole	Units	Hodnet Station	Sanshaw Heath	Childs Ercall	Perry Farm	Broad Oak	Bearstone Mill pumping stn	Coton Fields
Easting		362110	351540	366570	334670	349790	372380	392760
Northing		328150	321980	323320	330300	317410	338950	324440
Stratigraphy		Bridgnorth Sst	Wildmoor Sst	Bridgnorth Sst	Bridgnorth Sst	Wildmoor Sst	Kidderm'er Fm	Bromsgrove Sst
Bh depth	m	174	61	207	142	50	174	314
n^o samples		16	11	6	11	8	3	2
SiO_2	wt %	85.14	88.83	85.08	81.18	85.68	71.42	78.79
TiO_2	wt %	0.17	0.17	0.17	0.29	0.26	0.33	0.49
Al_2O_3	wt %	4.21	4.70	3.99	6.48	5.91	6.22	8.95
Fe_2O_{3T}	wt %	1.38	0.75	1.37	1.46	1.28	1.90	1.89
MnO	wt %	0.02	0.01	0.01	0.03	0.01	0.07	0.03
MgO	wt %	0.29	0.21	0.30	1.30	0.41	0.35	1.35
CaO	wt %	1.92	0.06	2.10	1.71	0.47	8.65	0.92
Na_2O	wt %	0.15	0.20	0.16	0.19	0.21	0.24	0.82
K_2O	wt %	2.20	2.80	1.99	3.11	3.27	2.29	3.57
P_2O_5	wt %	0.06	0.06	0.07	0.11	0.14	0.08	0.09
LOI	wt %	2.23	0.68	2.32	3.37	1.14	7.83	2.42
Total	wt %	97.76	98.47	97.57	99.24	98.77	99.37	99.30
As	mg kg^{-1}	8	6	6	8	10	5	3
Ba	mg kg^{-1}	221	320	216	333	335	275	945
Ce	mg kg^{-1}	32	33	31	43	39	35	43
Co	mg kg^{-1}	3	5	3	5	3	7	12
Cr	mg kg^{-1}	17	18	16	23	19	33	41
Cu	mg kg^{-1}	1	1	1	1	1	13	9
La	mg kg^{-1}	9	10	9	14	12	16	21
Mo	mg kg^{-1}	1	<1	1	1	1	1	1
Nb	mg kg^{-1}	3	2	3	5	4	5	8
Ni	mg kg^{-1}	7	5	7	8	5	8	19
Pb	mg kg^{-1}	12	10	7	9	11	7	25
Rb	mg kg^{-1}	46	76	44	82	81	60	93
Sr	mg kg^{-1}	39	56	39	60	56	50	82
Th	mg kg^{-1}	3	3	2	5	4	5	6
U	mg kg^{-1}	<1	1	1	1	1	2	2
V	mg kg^{-1}	15	10	14	19	16	30	45
Y	mg kg^{-1}	7	9	8	12	11	18	18
Zn	mg kg^{-1}	36	5	7	7	8	14	37
Zr	mg kg^{-1}	120	134	104	224	209	178	208

Source: BGS unpublished data (courtesy D. Jones); summarised in Jones et al. (1999). Fe_2O_{3T}: total iron.

Trace-element concentrations of the sediment samples summarised in Table 3.2 also reflect the mineralogy, with high Ba and Rb concentrations being associated with alkali feldspar and plagioclase respectively. Strontium concentrations are largely linked to carbonate distribution.

Many of the trace elements have compositions comparable to other English Permo-Triassic Sandstones (e.g. Haslam and Sandon, 1991). Average As concentrations from the boreholes given in Table 3.2 are in the range 3–10 mg kg^{-1}. This range is typical of sandstones elsewhere (Smedley and Kinniburgh, 2002). Higher As concentrations have been found in mineralised sediments (e.g. samples from West Mine [SJ 850 750] (Jones et al., 1999) had concentrations in the range 4–511 mg kg^{-1} with a mean of 85 mg kg^{-1}; BGS unpublished data) but these are atypical of the region as a whole.

Average Ni concentrations are in the range 5–19 mg kg^{-1}. Concentrations of U are also typical of those found elsewhere in the Permo-Triassic Sandstone, being <1–2 mg kg^{-1}.

3.5 Rainfall chemistry

Rainfall provides the primary input of solutes to recharging water and may be considered as approximating minimum baseline concentrations of solutes, except where severely impacted by atmospheric pollution, particularly in urban areas affected by smelting and combustion of fossil fuels. Chemical compositions of rainfall in the region have been assessed from weighted-mean annual concentrations for the latest available year, 2000, for Preston Montford gauging station [SJ 432 143] (from IAEA/WMO, 2004). The rainfall total for 2000 at the site was 789 mm. Concentrations in the rainfall are given in Table 3.3, along with values for 'concentrated rainfall' calculated as three times the weighted-mean values, and approximating the enrichment expected due to evapotranspiration (cf. effective rainfall of 260 mm; Section 3.3). Such enriched concentrations are those likely to be infiltrating the aquifers of the region.

For elements such as Cl, little interaction with soils and vegetation is expected on recharge and baseline concentrations of modern recharge could therefore be as low as 4 mg l^{-1}, although in practice such low values are rarely observed in modern groundwaters. For other elements, especially Ca, Mg and K, some changes are likely on infiltration, with increases resulting from mineral dissolution and decreases potentially caused by uptake by clay minerals and, in the case of K, by plants.

Concentrations of SO_4 in recharge are likely to be of the order of 4 mg l^{-1} as a result of both natural inputs and airborne sulphur but can also increase in soils and aquifers as a result of mineral reactions. The average non sea-salt SO_4 in Preston Montford rainfall as a proportion of the total for 2000 was 82%. This reflects the inland setting of the rainfall gauging station and indicates that most of the SO_4 in the rainfall derives from non-marine atmospheric sources, including pollutants.

Assuming that all the NH_4 in rainfall oxidises to NO_3 on infiltration to groundwater, modern baseline concentrations of dissolved NO_3-N derived from rainfall (NH_4-N and NO_3-N combined) are likely to be of the order of 2.2 mg l^{-1} (Table 3.3). The presence of dissolved NH_4^+ ions in local rainfall suggests that the pH of recharge may be even lower than that indicated from the rain compositions as a result of oxidation to NO_3, which results in the release of protons (H^+ ions). Recharge is therefore likely to have pH values close to or less than 4.

Table 3.3. Weighted mean annual solute concentrations in rainfall for 2000 at Preston Montford [SJ 432 143] rainfall gauging station (data from AEA, 2004) and compositions of estimated recharge (3 times concentration).

Determinand		Concentration	Concentrated rainfall
Annual rainfall	mm	789	
SEC	µS cm^{-1}	18.8	56.4
pH		4.69	3.61*
Ca	mg l^{-1}	0.17	0.52
Mg	mg l^{-1}	0.11	0.34
Na	mg l^{-1}	0.76	2.29
K	mg l^{-1}	0.11	0.34
Cl	mg l^{-1}	1.49	4.47
SO_4	mg l^{-1}	1.38	4.14
NO_3-N	mg l^{-1}	0.30	2.18*
NH_4-N	mg l^{-1}	0.42	–

*Assuming all NH_4-N is oxidised to NO_3-N on infiltration

3.6 Land use

Land use is dominantly grassland and arable agriculture. Grassland predominates in the clay-rich areas west of Shrewsbury while arable land is more prevalent further east. Urban areas are mainly concentrated around Shrewsbury, Shawbury and Market Drayton. Industrial development is minor and mainly concentrated around Shrewsbury.

As the map (Figure 3.8) shows, there are few landfill sites located in the study area.

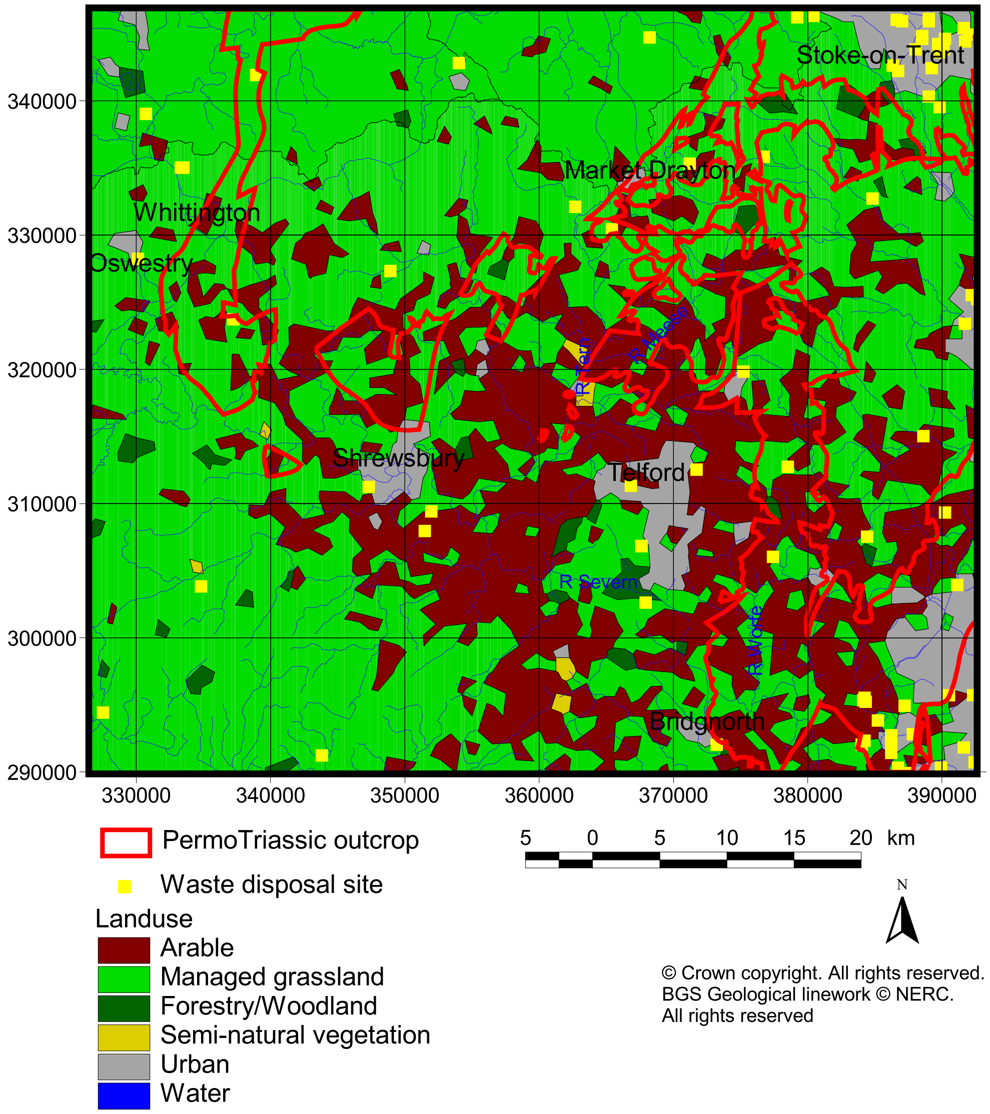


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Figure 3.8. **Simplified map of land use in the study area showing location of landfill sites. Land-use data are from Land Cover Map 1990, supplied courtesy of the Centre for Ecology & Hydrology, ©NERC.**

4. DATA AND INTERPRETATION

4.1 Data sources

Chemical data for this study have mainly been collated from the Environment Agency (WIMS water-quality archive) database and from a new groundwater sampling campaign carried out by BGS in November 2003. From the Environment Agency database, data were chosen on the basis of dates with the greatest number of inorganic determinands over the interval 1996–2001. From this batch, sites were excluded if they were sampled subsequently in the BGS sampling campaign. The Environment Agency dataset therefore incorporates a total of 64 groundwater samples. The BGS sampling campaign incorporated 31 samples. Groundwater chemistry data were also given by Klinck and Trick (2001) but these were from a mixture of Sandstone and Drift boreholes which were often difficult to distinguish from the data given. Many also appeared to show evidence of surface contamination and the units of some of the trace-element data were also dubious. They have therefore not been incorporated into the dataset used here. In an attempt to capture the regional water quality of the Sandstone aquifer over a limited time span, pre-1996 data (e.g. from Severn Trent Water Authority, 1978) were also excluded from the statistical analysis and regional maps in this study. The total number of sample points included in the statistical summary and interpretation is therefore 95.

The new BGS sampling campaign involved collection of groundwater from 14 public-supply boreholes from Severn Trent Water plc, 13 Environment Agency SGS network boreholes and 4 private-supply (farm) boreholes. Sampling involved on-site analysis of water temperature, alkalinity, specific electrical conductance (SEC), pH, Eh and dissolved oxygen. Where possible, the latter three determinands were measured in an in-line flow cell to exclude air which can alter the chemical composition of the samples. Alkalinity was measured by titrating against H_2SO_4 and is quoted as HCO_3. Filtered (0.45 µm) samples were also collected in polyethylene bottles for subsequent laboratory analysis of major and trace elements. At each site, four aliquots were collected. Two were acidified with 1% HNO_3 for the analysis of cations, SO_4 and trace elements by inductively-coupled plasma optical-emission spectrometry (ICP-OES) and inductively-coupled plasma mass spectrometry (ICP-MS). The other two were left unacidified for the analysis of anions by automated colorimetry (Cl, I, NO_2-N and NH_4-N) and ion chromatography (NO_3-N, F). At selected sites, further unfiltered samples were collected in glass bottles for the analysis of $\delta^{18}O$, δ^2H and $\delta^{13}C$ by mass spectrometry. All analyses were carried out at the BGS laboratory in Wallingford, except NO_2-N and NH_4-N (Environment Agency laboratory, Nottingham) and ICP-MS (Acme laboratory, Canada). Results of $\delta^{18}O$ and δ^2H have been calculated as ‰ deviations relative to SMOW and $\delta^{13}C$ relative to PDB.

4.2 Data quality and handling

From the Environment Agency archive data, samples for which complete major-element analyses were available gave analytical charge imbalances of 5% or less in all but 7 cases. Some of the poorer charge balances were due to low precision of analytical results and/or low major-element concentrations. Charge imbalances for the 31 newly-collected BGS groundwater samples were all 2.5% or less. Duplicate analysis of some elements by ICP-OES and ICP-MS also showed excellent overall agreement: Ba correlations were all within 12% and mostly within 5%. Concentrations of K, Cl, and Mn were mostly within 10%. In the case of most trace elements, analytical sensitivity was much better in the ICP-MS data and so (with the exception of Fe and Sr) the ICP-MS data were used in preference for interpretation and statistical handling. ICP-MS data were also used for Br.

Some of the trace-element data from the Environment Agency database had detection limits significantly higher than the BGS analyses which produced problems with the statistical handling of the data. Where this occurred, the data from the Environment Agency database were excluded. This applied to Ag (Environment Agency detection limit typically 1 $\mu g\ l^{-1}$), Al (detection limit typically

100 µg l^{-1}), B (detection limit typically 100 µg l^{-1}), Co (detection limit typically 1 µg l^{-1}), Cr (typically 5 µg l^{-1}) and Zn (typically 10 µg l^{-1}).

The Environment Agency dataset included data for As from unfiltered samples since fewer determinations of filtered samples were available in the database extracted from WIMS. Where data for both were available at a given site, comparisons showed good agreement. Therefore, an assumption was made that the As analyses of unfiltered water samples represented predominantly dissolved As. This is probably a safe assumption for the high-volume groundwater sources that are pumped regularly as these should contain negligible amounts of particulate matter. For the sources in the dataset that are pumped only intermittently, particulate matter may be present in larger amounts. However, no samples with high concentrations of Fe had corresponding As analyses available. The impact of particulate matter on the distribution of As concentrations from the Environment Agency dataset is therefore believed to be insignificant.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section describes the main characteristics and regional variations in groundwater chemistry observed in the Shropshire Permo-Triassic Sandstone and presents data in the form of statistical summaries and in graphical form as a Piper diagram (Figure 5.1), box plots (Figures 5.2 and 5.3) and cumulative-frequency diagrams (Figures 5.4 and 5.5). Summary statistical data for a large range of chemical determinands are given in Table 5.1. These include minima, maxima, median and mean values, together with the 97.7th percentile, equivalent to the mean + 2σ value on a log-normalised data set. Median values are useful indicators of approximate average baseline concentrations, but the mean + 2σ values are given as representative of approximate upper baseline concentrations for most solutes.

The groundwaters included in this study are almost all from the unconfined (including Drift-covered) sections of the Permo-Triassic Sandstone aquifer as this reflects the distribution of available boreholes and the better groundwater yields obtained from unconfined sources. Comparatively few water-supply boreholes exist in the Permo-Triassic Sandstone confined by the Mercia Mudstone Group. The BGS sampling campaign included two groundwater samples from the Permo-Triassic Sandstone below Mercia Mudstone Group sediments but these were quite close to (within a few kilometres of) the margin of the outcropping aquifer. The groundwater samples are all treated as a single group in the statistical summary and diagrams.

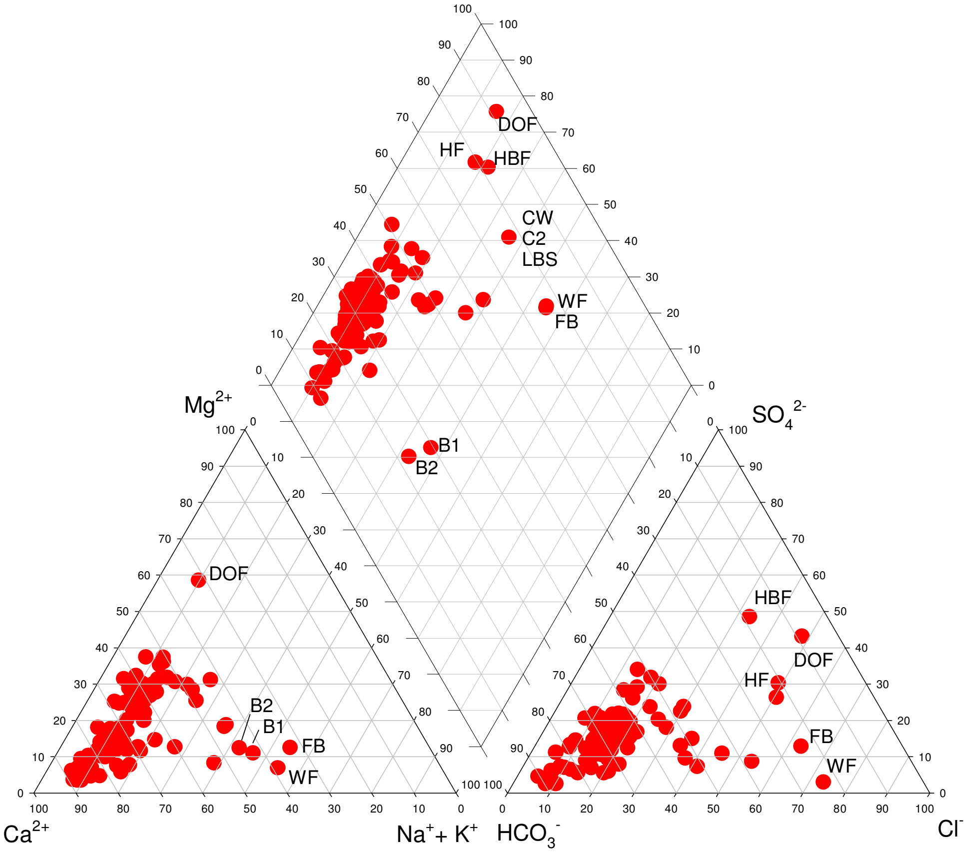


Figure 5.1. Piper diagram for groundwater samples from the Shropshire Permo-Triassic Sandstone. Sample locality annotations are referred to in the text.

Table 5.1. **Statistical summary of major and trace constituents and stable isotopic compositions of groundwaters from the Shropshire Permo-Triassic Sandstone.**

Parameter	Units	Min	5th centile	Median	Mean	97.7th centile	Max	n
Temp	°C	8.0	9.0	10.8	11.3	16.1	24.0	87
pH	field	5.20	6.52	7.32	7.28	7.90	8.00	93
Eh	mV	356	364	392	395	433	435	31
DO	mg l^{-1}	<0.1	0.11	5.3	5.1	10.3	10.5	55
SEC	µS cm^{-1}	280	343	545	583	937	2023	90
δ^{2}H	‰	-53.5	-53.4	-53.5	-51.0	-46.1	-53.5	10
δ^{18}O	‰	-6.7	-7.8	-7.9	-7.5	-6.7	-7.9	10
δ^{13}C	‰	-14.0	-18.0	-18.0	-16.5	-14.3	-18.0	10
Ca	mg l^{-1}	25.4	40.2	76.0	77.7	128	148	95
Mg	mg l^{-1}	2.0	3.0	11.0	13.1	33.4	76.3	95
Na	mg l^{-1}	5.0	7.68	12.5	20.1	72.8	234.0	95
K	mg l^{-1}	<1	1.4	2.6	3.2	9.8	12.3	93
Cl	mg l^{-1}	<10	14.8	29.0	41.7	140	500	95
SO$_4$	mg l^{-1}	4.5	11.9	36.6	39.1	100	136	95
HCO$_3$	mg l^{-1}	12.9	93.0	207	204	304	539	95
NO$_3$-N	mg l^{-1}	<0.2	0.70	6.3	8.2	28.9	50.8	90
NO$_2$-N	mg l^{-1}	<0.001	<0.005	<0.005	0.004	0.031	0.096	76
NH$_4$-N	mg l^{-1}	<0.003	<0.04	<0.04	<0.04	0.18	0.31	92
P	mg l^{-1}	<0.02	<0.05	0.055	0.08	0.25	0.32	57
TOC	mg l^{-1}	<0.3	<0.3	0.55	0.65	1.52	1.60	6
DOC	mg l^{-1}	<0.5	<0.5	0.8	1.1	3.7	4.8	63
F	µg l^{-1}	<100	<100	100	107	227	331	59
Br	µg l^{-1}	29	35	58	61	110	118	31
I	µg l^{-1}	2.0	2.0	4.0	4.3	8.2	11	31
Si	µg l^{-1}	2640	3979	5190	5304	8050	8559	53
Ag	µg l^{-1}	<0.05	<0.2	<0.2	<0.2	<0.2	<0.2	42
Al	µg l^{-1}	<1	1.0	7.0	9.4	42	67	31
As	µg l^{-1}	<0.5	<1	2.3	4.1	18.3	25.6	60
Au	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
B	µg l^{-1}	<20	<50	<50	<50	78	165	59
Ba	µg l^{-1}	6.7	38.8	190	227	672	710	60
Be	µg l^{-1}	<0.05	<1	<1	<1	<1	0.1	47
Bi	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
Cd	µg l^{-1}	<0.05	<0.5	<0.5	<0.5	0.8	1.1	67
Ce	µg l^{-1}	<0.01	<0.01	<0.01	0.012	0.064	0.14	31
Co	µg l^{-1}	<0.02	<0.02	<0.02	0.11	1.0	1.8	32
Cr	µg l^{-1}	<0.5	<1	<1	1.0	3.6	4.1	56
Cs	µg l^{-1}	<0.01	<0.01	0.01	0.02	0.08	0.09	31
Cu	µg l^{-1}	1.2	1.3	4.9	21	195	275	60
Dy	µg l^{-1}	<0.01	<0.01	<0.01	0.01	<0.01	0.01	31
Er	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.02	0.02	31
Eu	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.02	0.02	31
Fe	µg l^{-1}	<5	<30	<30	59	688	1320	62
Ga	µg l^{-1}	<0.05	<0.05	<0.05	0.03	<0.05	<0.05	31
Gd	µg l^{-1}	<0.01	<0.01	<0.01	0.01	<0.01	0.01	31
Ge	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
Hf	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	31
Hg	µg l^{-1}	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	58
Ho	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	31
In	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
Ir	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
La	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.02	0.04	31

Parameter	Units	Min	5th centile	Median	Mean	97.7th centile	Max	n
Li	µg l^{-1}	3.7	4.7	7.2	11	34	49	31
Lu	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
Mn	µg l^{-1}	<5	<10	6	90	870	1480	82
Mo	µg l^{-1}	<0.1	<0.1	0.2	0.3	1.1	1.5	31
Nb	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.01	0.01	31
Nd	µg l^{-1}	<0.01	<0.01	0.01	0.01	0.04	0.05	31
Ni	µg l^{-1}	<0.2	<5	<5	2.6	15	43	67
Os	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
Pb	µg l^{-1}	<0.4	<1	0.7	2.2	8.9	10.4	66
Pd	µg l^{-1}	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	31
Pr	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
Pt	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
Rb	µg l^{-1}	0.7	0.7	1.5	1.6	3.3	3.8	31
Re	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.02	0.03	31
Rh	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
Ru	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
Sb	µg l^{-1}	<0.05	<3	<3	0.4	0.2	1.1	58
Sc	µg l^{-1}	<0.4	<0.4	<0.4	0.3	0.5	0.5	31
Se	µg l^{-1}	<0.5	<1	<1	0.5	0.9	2.3	58
Sm	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	31
Sn	µg l^{-1}	<0.05	<0.05	0.07	0.14	0.70	1.84	31
Sr	µg l^{-1}	28	37	100	119	319	330	31
Ta	µg l^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	31
Tb	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
Te	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	0.11	0.12	31
Th	µg l^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	31
Ti	µg l^{-1}	<10	<10	<10	<10	<10	<10	31
Tl	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	0.01	0.05	31
Tm	µg l^{-1}	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31
U	µg l^{-1}	0.13	0.23	1.04	3.75	26	67	31
V	µg l^{-1}	<0.2	<1	<1	<1	1.1	10.2	47
W	µg l^{-1}	<0.02	<0.02	0.02	0.02	0.06	0.07	31
Y	µg l^{-1}	<0.01	<0.01	0.01	0.02	0.09	0.12	31
Yb	µg l^{-1}	<0.01	<0.01	<0.01	0.01	0.01	0.01	31
Zn	µg l^{-1}	<5	4	19	63	607	954	60
Zr	µg l^{-1}	<0.02	<0.02	<0.02	0.07	0.73	1.41	31

SEC at 25°C; HCO_3 is alkalinity as HCO_3, almost all as field measurements; TOC/DOC: total and dissolved organic carbon respectively

5.2 Major constituents

Most of the groundwaters included in the study are of Ca-HCO_3 type, as reflected by the Piper diagram in Figure 5.1. Two samples are of Ca-Na-HCO_3 composition (Beckbury samples [SJ 756 020] B1 and B2 in Figure 5.1). One sample (Dovaston Old Farm, DOF [SJ 342 215]) is of Mg-SO_4-Cl type, several others (Frank Brook, FB [SJ 431 198]; Woodfield, WF [SJ 631 164]; Hinheath Farm, HF [SJ 585 257]; Clowes Wood, CW [SJ 775 388]; Copley, C2 [SJ 808 986]; Lee Brockhurst Sherwood, LBS [SJ 556 273]) are of Na-Ca-Cl type and one (Harebutts Farm, HBF [SJ 645 204]) is of Na-Ca-SO_4-Cl type. Most groundwaters are fresh with TDS (total dissolved solids) concentrations of around 400 mg l^{-1} and SEC around 500–600 µS cm^{-1}, although a large range of compositions is observed. The highest values of TDS and SEC (1200 mg l^{-1} and 2000 µg l^{-1} respectively) are found in groundwater from Woodfield (WF).

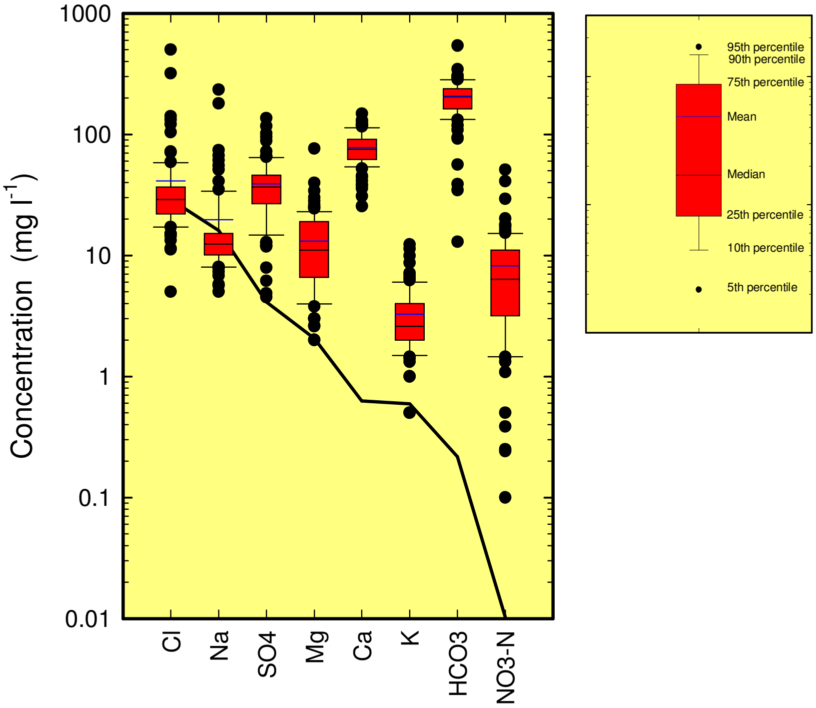


Figure 5.2. **Box-and-whiskers plots showing the ranges of major constituents in groundwaters from the outcropping (including Drift-covered) Shropshire Permo-Triassic Sandstone. Black line: concentrations of 'diluted' seawater (normalised to median groundwater Cl concentration).**

Calcium concentrations lie in the range 25–148 mg l^{-1} (median 76 mg l^{-1}) and HCO$_3$ in the range 13–539 mg l^{-1} (median 207 mg l^{-1}) (Table 5.1, Figure 5.2). Several of the samples investigated are undersaturated with respect to calcite and most are undersaturated with respect to dolomite.

Concentrations of Cl and SO$_4$ are usually each less than 50 mg l^{-1}, though the maximum observed Cl concentration is 500 mg l^{-1} and the maximum SO$_4$ 136 mg l^{-1}. Smart (1978) noted an average Cl concentration for groundwaters from the Sherwood Sandstone of the region of 20–30 mg l^{-1}. The median given here is at the high end of that range (29 mg l^{-1}).

Sodium has a median of 12.5 mg l^{-1} though reaches up to 234 mg l^{-1}. Groundwater pH is mostly near-neutral with a median of 7.3, although the range is 5.2–8.0. The most acidic sample in the dataset is from Dovaston Old Farm (DOF). The DOF sample clearly has a very distinct composition from most of the Permo-Triassic Sandstone samples.

Most of the groundwaters are oxidising as reflected by detectable and usually high concentrations of dissolved oxygen (DO in the range <0.1–10.5 mg l^{-1} with a median of 5.3 mg l^{-1}) and high redox potentials (Eh in the range 356–435 mV where measured). This oxidising condition is also reflected in the often high concentrations of nitrate (NO$_3$-N ranges between <1–51 mg l^{-1} with a median of 6.3 mg l^{-1}). Most groundwaters contain concentrations of DOC (dissolved organic carbon) of around 1 mg l^{-1} or less though the maximum is 4.8 mg l^{-1} (Table 5.1).

Cumulative-frequency trends of the major constituents (Figure 5.4) reveal a relatively narrow range of Ca concentrations in the groundwaters but most other parameters included have a larger range, with pronounced breaks of slope in the trends for K, DOC, Na, Cl and SO$_4$ in particular. The flexures occur at around 5 mg l^{-1} for K, 2 mg l^{-1} for DOC, 15 mg l^{-1} for Na, 40 mg l^{-1} for Cl and 60 mg l^{-1} for SO$_4$,

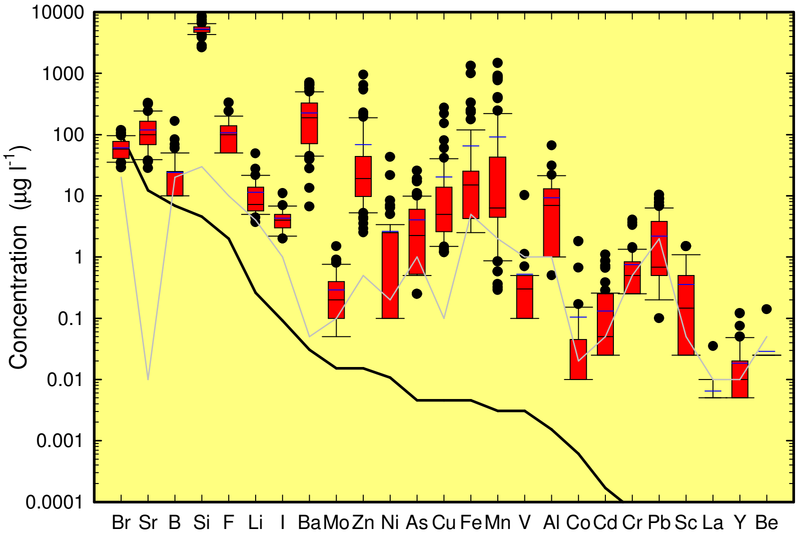


Figure 5.3. **Box-and-whiskers plots showing the ranges of minor constituents in groundwaters from the Shropshire Permo-Triassic Sandstone. Black line: concentrations of 'diluted' seawater (normalised to median Cl concentration); grey line: typical detection limits. Legend as in Figure 5.2.**

and probably reflect mixing of different water bodies within the aquifer. The likely processes involved are discussed in more detail in Section 6.

5.3 Trace elements

Ranges of trace-element concentrations in the groundwaters are shown in Table 5.1, Figure 5.3 and Figure 5.5. The concentrations of most trace elements are within the range typical of unconfined Sherwood Sandstone groundwaters found elsewhere in Britain (e.g. Edmunds et al., 1982; Smedley and Edmunds, 2002). Concentrations of NO_2-N and NH_4-N are mostly low (<0.005 mg l^{-1} and <0.04 mg l^{-1} respectively) although the maxima were 0.096 mg l^{-1} and 0.31 mg l^{-1} respectively. Concentrations of P reach up to 0.32 mg l^{-1} though are mostly <0.08 mg l^{-1}. In addition, generally low concentrations are observed for REE (rare-earth elements), several transition metals (V concentrations up to 10 µg l^{-1}, Cr up to 4 µg l^{-1}, Co up to 1.8 µg l^{-1}) and halogen elements (F, Br, I), as expected from their near-neutral pH values and usually unconfined condition.

In the groundwaters investigated, concentrations of Fe and Mn are usually low but with maxima up to 1.3 mg l^{-1} and 1.5 mg l^{-1} respectively. These high concentrations indicate that some of the samples are mildly reducing with respect to these elements. Several groundwater sources from the SGS network have high concentrations of dissolved Fe and Mn indicating reducing conditions. Smart (1978) also noted some high concentrations of Fe (up to around 10 mg l^{-1}) in groundwaters from an abstraction borehole at Adcote [SJ 421 187], although it is not known whether the water samples were filtered hence represent truly dissolved iron. Severn Trent Water Authority (1974) also noted a concentration of iron of 20 mg l^{-1} in groundwater from a borehole at Avenue Farm [SJ 627 259] although the same uncertainty about sample filtering also applies. An adjacent borehole at shallower depth in the Sandstone did not have such a high concentration. The results suggest that groundwaters from the Permo-Triassic Sandstone are usually oxidising, but with some areas where reducing conditions occur.

Concentrations of Ba reach up to 710 µg l^{-1} and Sr up to 330 µg l^{-1}. The cumulative-frequency diagram for Ba shows a steep cut-off at the upper end of the concentration range consistent with barite

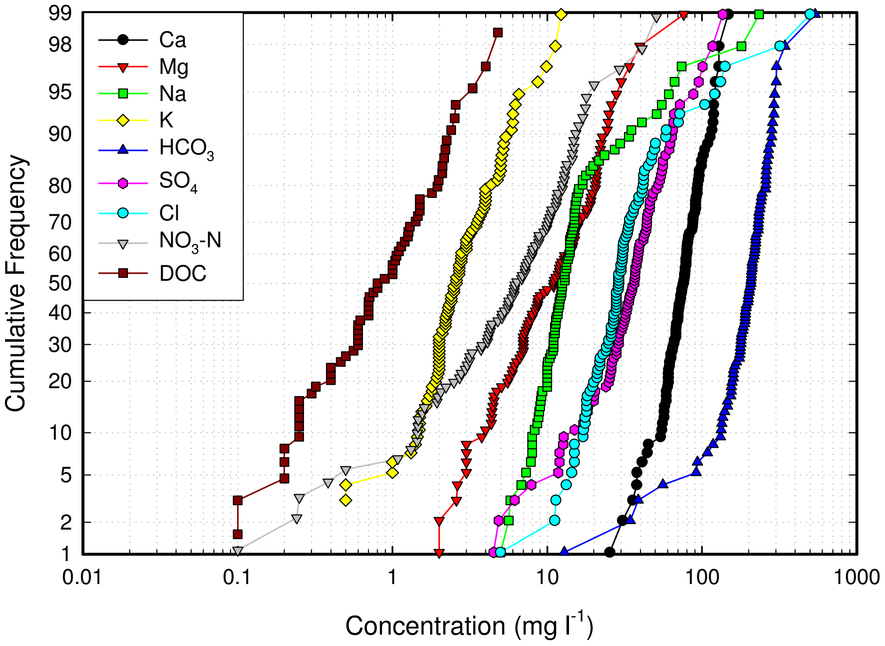


Figure 5.4. **Cumulative-frequency plots for the major constituents in groundwaters from the Shropshire Permo-Triassic Sandstone.**

saturation. The groundwaters are undersaturated with respect to celestite ($SrSO_4$) and strontianite ($SrCO_3$).

A number of other trace-element maximum concentrations are worthy of note. Arsenic concentrations reach up to 26 µg l^{-1}. From the dataset, 4 samples (6.7%) were above the EC drinking-water limit for As of 10 µg l^{-1}. Nickel concentrations reach up to 43 µg l^{-1}, 2 samples (3%) exceeding the EC limit of 20 µg l^{-1} and Pb concentrations reach up to 10.4 µg l^{-1}, with just 1 sample (1.5%) above the EC drinking-water limit of 10 µg l^{-1}.

Uranium concentrations also have a large range, with a maximum of 67 µg l^{-1}. This is the highest recorded value for U in groundwater from all the 'Baseline' groundwater surveys for England and Wales produced so far. Although the EC does not have a drinking-water limit for U in water, the maximum observed is well above the WHO (2004) provisional guideline value of 15 µg l^{-1}. One sample (3.2%) exceeded 15 µg l^{-1}. The maximum As and U concentrations were found in the samples collected from the BGS sampling campaign and so a reasonably high confidence is placed on the sampling and analytical quality. The maximum Ni concentration in the BGS batch was 2.6 µg l^{-1}, much lower than the total population maximum, but the maximum Pb concentration was comparable at 9.1 µg l^{-1}. Some high concentrations of Ni and Pb (up to 96 µg l^{-1} and 15 µg l^{-1} respectively) were also reported by Klinck and Trick (2001) for unconfined Sherwood Sandstone groundwaters from the Tern catchment, although the representativeness of these samples of the unconfined aquifer in the region is less certain. These authors also reported Cd concentrations up to 18 µg l^{-1}, a value much higher than the maximum observed in this study.

5.4 Organic compounds

Organic compounds are not a major component of this study but can yield information about baseline conditions in aquifers and their vulnerability to pollution. No data for organic compounds were collected in the BGS sampling campaign. Few also included pesticides in the Environment Agency dataset, although those that did had concentrations of total pesticides below detection limits (<0.05 µg l^{-1}). In other data from the Environment Agency WIMS database, pesticides are occasionally detected, principally atrazine and its daughter products as well as linuron. Low or

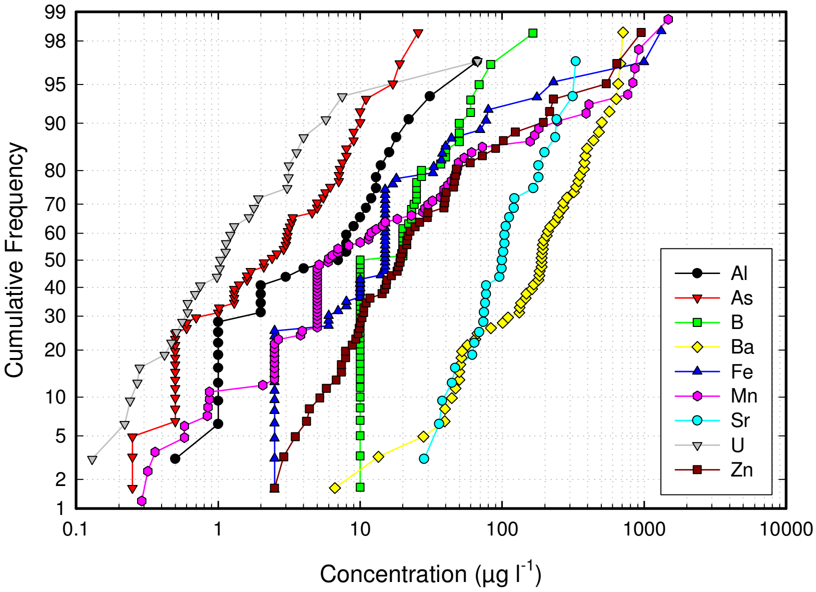


Figure 5.5. Cumulative-frequency plots for the minor constituents in groundwaters from the Shropshire Permo-Triassic Sandstone.

undetectable concentrations of pesticide compounds were also generally found in groundwaters from the Tern catchment by Klinck and Trick (2001). One sample from that study contained detectable chlortoluron, at a concentration of 0.88 µg l^{-1}.

Rather higher concentrations of BTEX products were detected by Klinck and Trick (2001). The study incorporated groundwater data from Drift boreholes as well as the Sherwood Sandstone. Of the groundwaters sampled from the Sherwood Sandstone, one at Heath House ([SJ 603 246], an SGS site) had detectable concentrations of ethylbenzene and toluene (0.12 µg l^{-1} and 0.27 µg l^{-1} respectively). BTEX compounds were found to be relatively widespread in the shallow Drift boreholes sampled. Carbon tetrachloride, 3clethene and chloroform were also occasionally detected. The data indicate the vulnerability of the shallower superficial Drift deposits, especially the more permeable lithologies. They also suggest that while most Sandstone groundwaters had few or no detectable organic compounds where tested, the aquifer is potentially vulnerable to pollution where Drift deposits are permeable or absent, a feature supported by the high concentrations of nitrate in the groundwaters, largely believed to be of agricultural origin.

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

This section describes the main geochemical processes that are likely to be controlling the compositions of groundwater in the Shropshire Permo-Triassic Sandstone aquifer and the spatial and temporal variations that are observed. Identifying the main controlling processes is an important prerequisite for attempting to define baseline compositions of groundwaters in a given aquifer (Box 6.1). The varying influences of recharge, mineral dissolution/precipitation reactions, redox processes, groundwater mixing and pollution are outlined below and the spatial variations are highlighted by a number of regional groundwater-chemistry maps. In each of these, the chemical constituents have been classified on the basis of rounded quartiles.

6.2 Geochemical controls

6.2.1 Carbonate reactions

As noted in Section 5, most groundwaters from the Permo-Triassic Sandstone are of Ca-HCO_3 type. This reflects the important influence of calcite dissolution. Many, though not all, groundwaters are saturated with respect to calcite and although calcite constitutes a minor component of the Sherwood Sandstone mineralogy, it exerts a disproportionate influence on groundwater chemistry as carbonate dissolution rates are relatively rapid. Calcite reaction also largely buffers the pH at near-neutral values. However, the observed groundwater pH range extends down to 5.2, indicating that acidic groundwaters are present in some areas. This most extreme groundwater sample (Dovaston Old Farm) has a high pCO_2 ($10^{-1.09}$) and is from a shallow depth in the Sandstone aquifer (borehole depth 24 m). It is concluded that the acidic conditions are caused by a paucity of carbonate minerals in the upper part of the Sandstone resulting from past leaching losses of carbonate cements by flowing groundwater. The sample has low measured alkalinity (HCO_3 13 mg l^{-1}) and is therefore of mixed-ion

Box 6.1 How can we distinguish pristine waters from polluted groundwater?

Groundwater prior to the industrial era (before ca. 1800) emerged as springs or was taken from shallow wells. The water would have had compositions largely reflecting true baseline, determined by natural geological and geochemical processes. Today, the influences of modern anthropogenic activities mean that only rarely is it possible to find such waters, particularly in shallow aquifers which are most vulnerable to contamination. The problem in defining baseline conditions for a given aquifer or region is to recognise the impact of any human activities over and above the natural baseline in the data sets used.

The logical approach adopted is threefold:

(i) to have evidence of groundwater age;
(ii) where available, to extrapolate data back to a pre-industrial time;
(iii) to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced organic carbon and N species, especially NO_3. These indicate the presence of foreign substances such as agricultural or industrial chemicals. The sets of data are examined for these substances to identify the presence of “contamination”, although it is stressed that it is impossible to quantify this. Although contaminants may be identifiable, traces of such contaminants may have little impact on the overall chemistry of the groundwater.

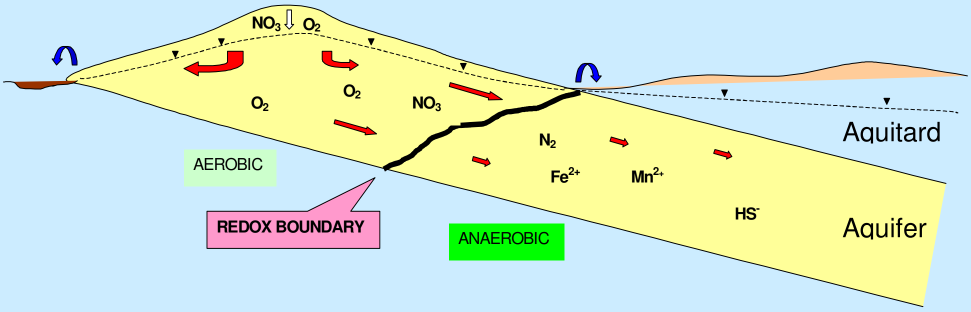
composition (Ca-Mg-SO_4-Cl) rather than the typical Ca-HCO_3 type (Section 5.2). A study by Smart (1978) also found four groundwater samples from the north Shropshire Permo-Triassic Sandstone with acidic pH values (range 4.9–5.9). These were also attributed to areas of sandstone with lack of carbonate cements.

Dolomite (along with clays) is likely to be an important source of Mg in the groundwaters, although most samples are undersaturated with respect to dolomite. Molar Mg/Ca ratios of the groundwaters are in the range 0.04–0.7, much lower than the ratio of around 1 which would be expected for simple congruent dissolution of dolomite ($Ca,Mg(CO_3)_2$). They are also lower than the molar ratios of around 1–2 observed for long-residence-time groundwaters from the Sherwood Sandstone of the English East Midlands (Edmunds et al., 1982; Edmunds and Smedley, 2000; Smedley and Edmunds, 2002). The ratios for the Shropshire groundwaters suggest that they are relatively young, having had insufficiently long residence times in the Sandstone to equilibrate with dolomite. A young groundwater age is also indicated by the depleted $\delta^{13}C$ isotopic compositions of the few groundwaters analysed in this study. Compositions for 10 groundwater samples were in the range -18 to -14 ‰, consistent with the total inorganic carbon in the groundwaters representing a mixture between soil-derived CO_2 ($\delta^{13}C$ around -25 ‰) and dolomite (-1–0 ‰, Section 3.4) or calcite (around +7 ‰; Edmunds and Smedley, 2000). Groundwaters of long residence time tend to have more enriched (more positive) $\delta^{13}C$ isotopic compositions reflecting increased reaction of the $\delta^{13}C$-enriched carbonate minerals.

Carbonate minerals also contain abundant Sr which substitutes for Ca in the crystal lattice. Carbonate mineral reactions also therefore have a dominant influence on the Sr concentrations in the groundwaters, which reach up to 330 $\mu g\ l^{-1}$.

As the calcite and dolomite cements in the Sherwood Sandstone are also Mn-rich (Jones et al., 1999), carbonate reaction is likely to release Mn into solution on reaction of carbonate minerals in the aquifer. However, Mn is redox-controlled and will be quickly removed by precipitation of Mn oxides or adsorption onto Fe oxides under oxidising conditions.

Box 6.2 Redox boundary (schematic)



Recharging water 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} dissolved 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. This zone is known as the redox boundary. Other changes may occur at and further down-gradient of the redox boundary, especially denitrification and increased concentrations of dissolved iron (Fe^{2+}). Sulphate reduction and the production of sulphide (H_2S as HS^- in solution) may also occur at greater depths.

6.2.2 Redox processes

Most groundwaters from the Permo-Triassic Sandstone included in this study are oxic. Where dissolved oxygen has been measured, it is usually detectable and redox potentials tend to be greater than about 400 mV. As a result, most groundwaters have low concentrations of dissolved Fe and Mn, reflecting the extremely low solubility of Fe and Mn oxides under such conditions. The oxidising conditions are also reflected by often high concentrations of NO_3-N (up to 51 mg l^{-1}) and low NH_4-N concentrations, typically <0.04 mg l^{-1}. Concentrations of nitrite, NO_2-N, are also usually low, although they reach up to 0.096 mg l^{-1}. Even the artesian groundwater from the Childs Ercall borehole, which occurs where the Sandstone is locally confined by Drift deposits, appears to be oxic in character. The groundwater from this site has a DO concentration of 2.3 mg l^{-1} and an NO_3-N concentration of 2.5 mg l^{-1}. These concentrations are at the low end of their respective ranges but nonetheless reflect an oxic groundwater environment (Box 6.2).

A small proportion of the groundwater samples show evidence for the occurrence of mildly reducing conditions, with low concentrations of NO_3-N (<1 mg l^{-1}), relatively high concentrations of NH_4-N

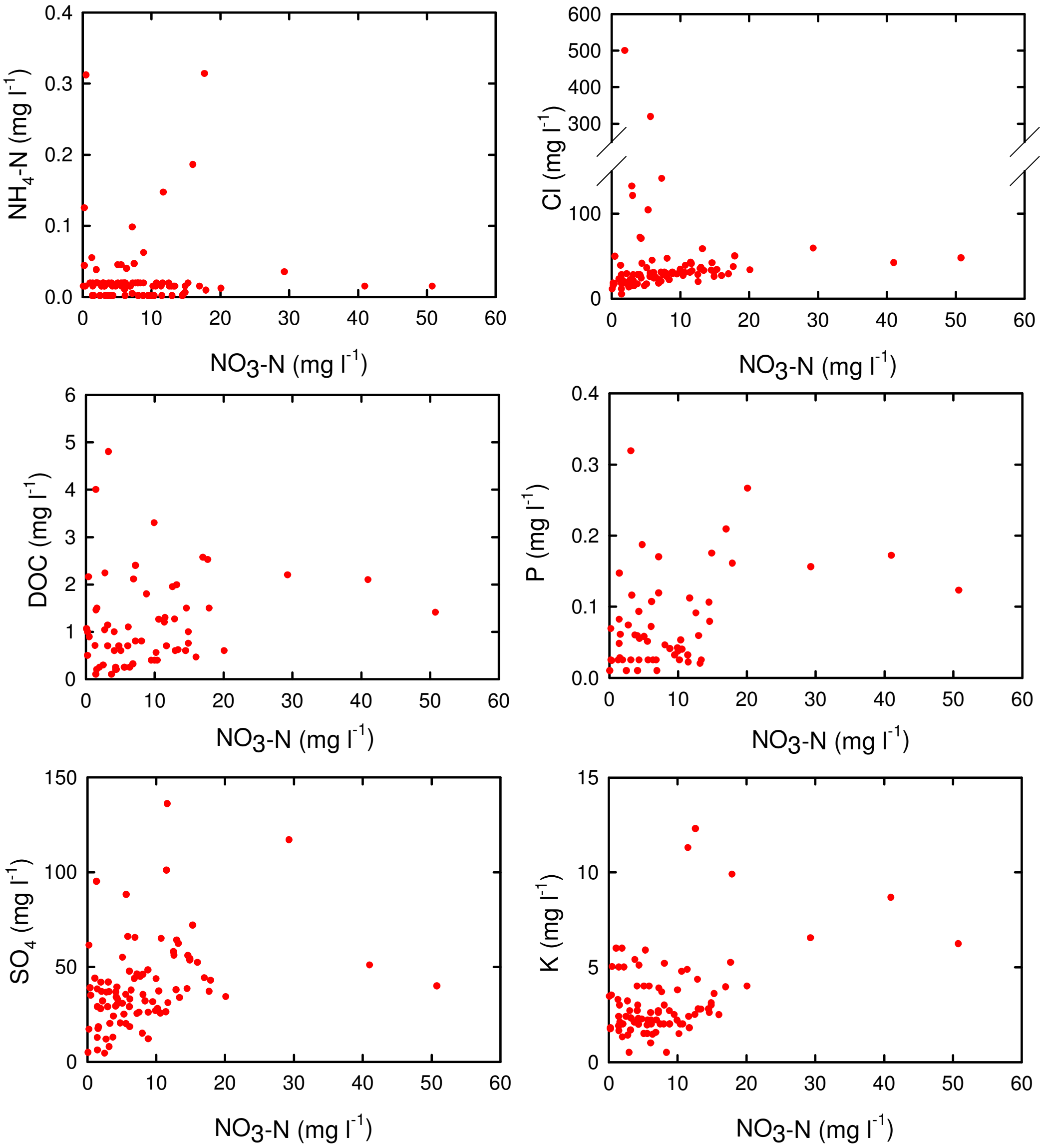


Figure 6.1. Variation of several parameters with NO_3-N in groundwaters from the Shropshire Permo-Triassic Sandstone.

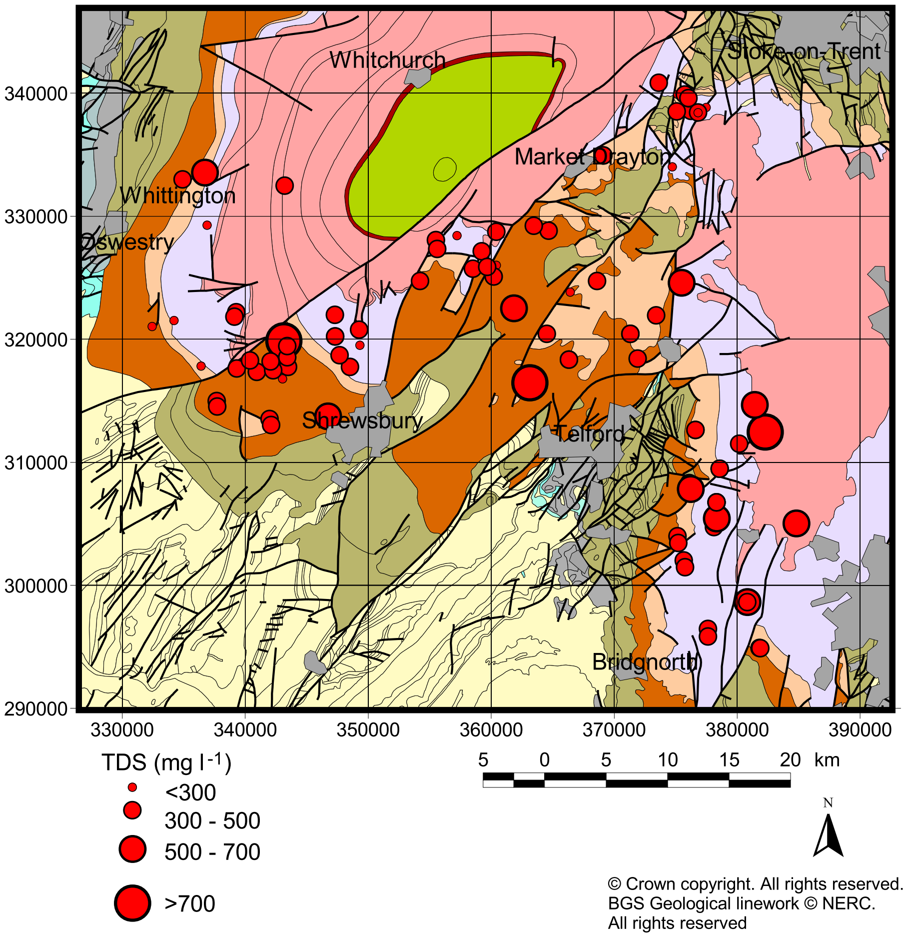


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Figure 6.2. **Regional variations of TDS (total dissolved solids) concentrations in groundwaters from the Shropshire Permo-Triassic Sandstone.**

and moderate to high concentrations of Fe and Mn. These include the Kinsall borehole, which has groundwater with undetectable DO concentrations, a NO_3-N concentration of 0.24 mg l^{-1}, NH_4-N of 0.13 mg l^{-1} and Mn of 0.18 mg l^{-1}. The groundwater from this site appears not to be sufficiently reducing to have led to reduction of Fe however, as the dissolved Fe concentration is <0.005 mg l^{-1}. A second borehole at Clowes Wood (northern Tern catchment) [SJ 775 388] also has undetectable NO_3-N with an NH_4-N concentration of 0.31 mg l^{-1} and Mn of 0.83 mg l^{-1}. The groundwater also has the highest observed concentration of Fe in the dataset (1.3 mg l^{-1}). The reducing conditions in the vicinity of these two boreholes are most likely the result of confinement by poorly-permeable Drift deposits. Streetly and Shepley (2002) also reported high concentrations of Fe and Mn and low nitrate concentrations in locally Drift-confined groundwater from the Standford Bridge borehole [SJ 705 240] (now disused) and a borehole at the Hollies pumping station [SJ 224 382]. However, the limited occurrence of observed reducing groundwaters suggests that either such conditions are of localised extent or that they have not been developed significantly for groundwater use. The reducing groundwaters are apparently distributed sporadically across the aquifer, related to the distribution of Drift deposits.

High concentrations of NH_4-N could be present in either oxidising conditions as a result of direct input from surface agricultural or domestic pollutants that have not yet had time to react (oxidise) in the aquifer, or as a result of decomposition of natural organic matter, particularly that derived from the Drift, under reducing conditions. There is evidence that both processes have been taking place in the Shropshire groundwaters, though not in the same locations. High concentrations of NH_4-N derived from surface pollutants are in some cases accompanied by relatively high concentrations of NO_3-N

(Figure 6.1), presumably from the same source. Under reducing conditions, high concentrations of NH_4-N are accompanied by low NO_3-N concentrations (Figure 6.1).

Of the three groundwater samples collected from the Sandstone below the Mercia Mudstone cover, all were also oxic with DO in the range 3.4–7.8 mg l^{-1}. Nitrate-N concentrations were also in the range 4.1–14.6 mg l^{-1}, indicating that denitrification has not taken place. Such conditions accord with evidence from the English East Midlands where oxidising conditions persist in the Sherwood Sandstone along the groundwater flow gradient for some 3–5 km beyond the point where it becomes confined by the Mercia Mudstone (Smedley and Edmunds, 2002). The persistence of oxidising conditions can be linked with the generally paucity of reducing agents (e.g. solid or dissolved organic carbon, sulphide, ferrous iron) in the Mercia Mudstone and Permo-Triassic Sandstone as well as in the recharging groundwaters in these areas. There is no information on the groundwater quality in the main part of the Mercia-Mudstone-confined Sandstone in the Wem to Whitchurch area because of the lower density of boreholes there.

6.2.3 *Influence of Drift deposits*

The groundwater compositions have been greatly influenced by the thickness, distribution and texture of overlying Drift deposits. These determine both the extent and chemistry of incoming recharge to the aquifer. Drift groundwaters in the region are typically characterised by relatively high TDS concentrations compared with Sandstone groundwaters, with values being greater than around 600 mg l^{-1}, (Smart, 1978). Drift deposits contain young and reactive minerals and dissolution and

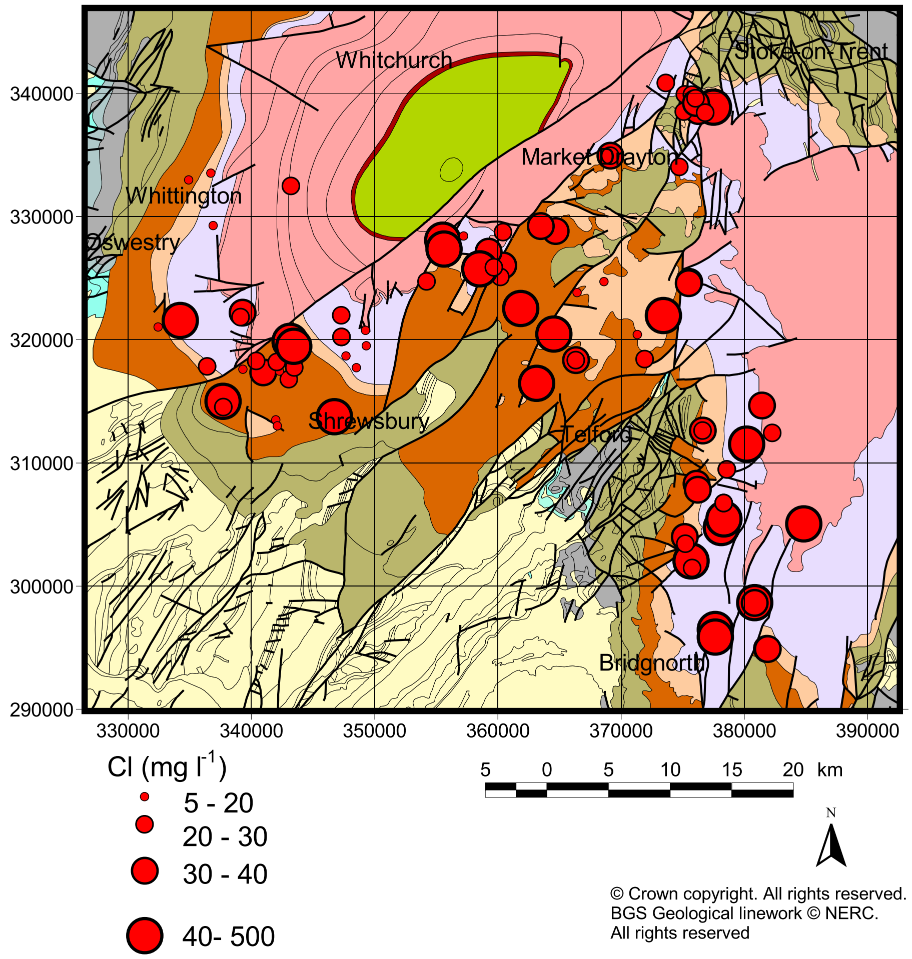

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Figure 6.3. Regional variation of Cl in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.

desorption reactions are therefore likely to be of greater significance than in the older, less reactive Sandstone. They also often contain detrital evaporite minerals (e.g. gypsum, anhydrite) derived by erosion of the Mercia Mudstone sediments. Smart (1978) noted that the Drift groundwaters were still mainly of Ca-HCO_3 type but with often relatively high concentrations of SO_4, Cl and NO_3, suggesting an important influence of surface pollution. Additional SO_4 may also be derived from gypsum or anhydrite dissolution. Klinck and Trick (2001) reported generally higher concentrations of NH_4-N in groundwaters from Drift compared to groundwaters from Sandstone in the Tern catchment. This they attributed to agricultural pollution, notably from slurry.

Various previous studies have intimated that the chemistry of groundwater in the Sandstone differs greatly depending on the nature of the overlying deposits. Smart (1978) noted relatively low concentrations of SO_4 in groundwaters where thick clay Drift deposits overlie the Sandstone. This presumably reflects lack of recharge through the poorly-permeable clay Drift and protection of the aquifer from both SO_4 derived from modern pollutant sources and from the Drift itself. Variations in alkalinity have also been reported, with HCO_3 concentrations of around 150 mg l^{-1} or less in the groundwaters from outcropping Sandstone but closer to 200 mg l^{-1} in groundwaters below argillaceous Drift.

Smart (1977) reported that Na and Cl become of increasing importance in groundwater from the Sandstone below the Severn Trench. The Drift deposits of the Severn Trench are of variable composition (Box 3.1), and the increased concentrations in the Sandstone groundwaters presumably reflect leakage of high-Na, high-Cl groundwater from the overlying deposits. Smart suggested that

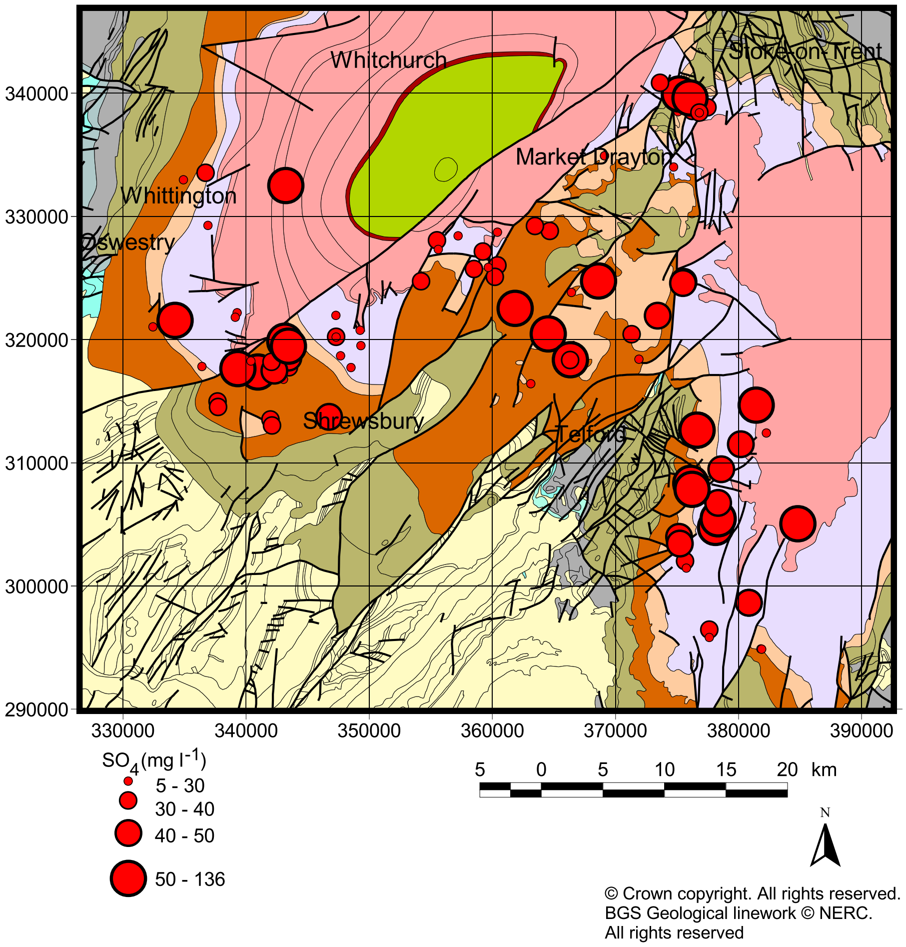

Figure 6.4. Regional variations of SO_4 in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.

some groundwater sources in that area were of Na-HCO_3 or Na-Cl type in contrast with the more usual Ca-HCO_3 composition.

Smart (1977) also reported relatively low TDS concentrations (<250 mg l^{-1}) in areas where the groundwater is locally confined by clayey Drift deposits and is artesian. In the dataset from this study, the Childs Ercall artesian borehole has groundwater with a TDS concentration of 290 mg l^{-1}. This relatively low concentration is believed to reflect the dominance of upward-flowing groundwater and the protection of the groundwater in the Sandstone from the leakage of poorer-quality Drift water from above.

6.2.4 Structural influences and groundwater mixing

The Shropshire Permo-Triassic Sandstone is heavily faulted and the influence of faults has often been cited in areas where groundwater with anomalous chemical compositions occurs. Smart (1977, 1978) for instance noted average Cl concentrations for groundwaters from the Sherwood Sandstone of around 20–30 mg l^{-1} but with locally higher concentrations in the vicinity of the Hodnet Fault and the Wem Faults. Faults can bring the Permo-Triassic Sandstone aquifer into contact with other strata such as the Mercia Mudstone or Carboniferous rocks and can act as conduits for groundwater flow from these strata.

Groundwater from the Mercia Mudstone is known to have relatively high TDS concentrations and high concentrations of dissolved SO_4 as a result of the importance of evaporite minerals in the

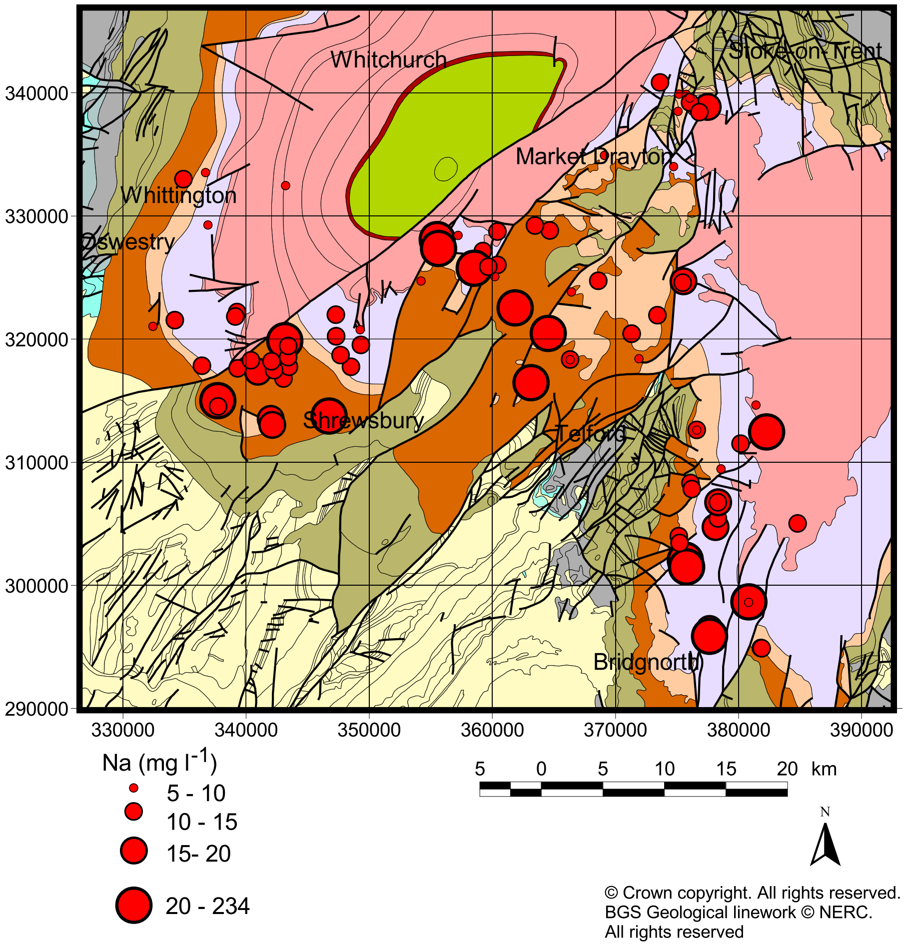

Figure 6.5. Regional variation of Na in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.

sequence. Smart (1977) reported a TDS concentration of 1322 mg l^{-1} for a groundwater of Ca-SO$_4$ composition from a borehole in the Mercia Mudstone at Top Farm [SJ 378 265]. This composition presumably results from dissolution of gypsum or anhydrite within the sediments.

Some poor-quality groundwaters in the Shropshire Permo-Triassic Sandstone have also been attributed to intrusion of saline water from the neighbouring Salop Formation (Carboniferous). Woodfield pumping station has well-known groundwater salinity problems, that have been associated with both upflow of groundwater from the underlying Salop Formation and with surface infiltration from the Beanhill Brook which also had saline water of likely Salop Formation origin (Tate and Robinson, 1971). Groundwater salinity is greatest at depths greater than 50 m below surface. Resistivity surveys highlighted a low-resistivity layer at 40 m below surface, consistent with flow across the Brockton Fault (Streetly and Shepley, 2002). The Cl concentrations of the Beanhill Brook were also observed to increase significantly downstream of the Brockton Fault. Today, the brook has largely dried up as a result of inceptor drain installations and so is no longer considered a source of Cl in the Woodfield borehole (Streetly and Shepley, 2002). A potential replacement borehole at Longdon [SJ 615 155] also has high salinity with Cl concentrations of around 250 mg l^{-1}. Smart (1978) also reported a Cl concentration of 650 mg l^{-1} at Poynton Green [SJ 570 168], probably linked to mixing with saline groundwater from the Salop Formation.

Bromine has often been used as an indicator of the origins of end members in mixed groundwaters (e.g. Metcalfe et al., 1999) and high Br/Cl ratios have been observed in Coal Measures groundwaters, probably as a result of reactions involving organic matter. Edmunds (1975) found molar Br/Cl ratios

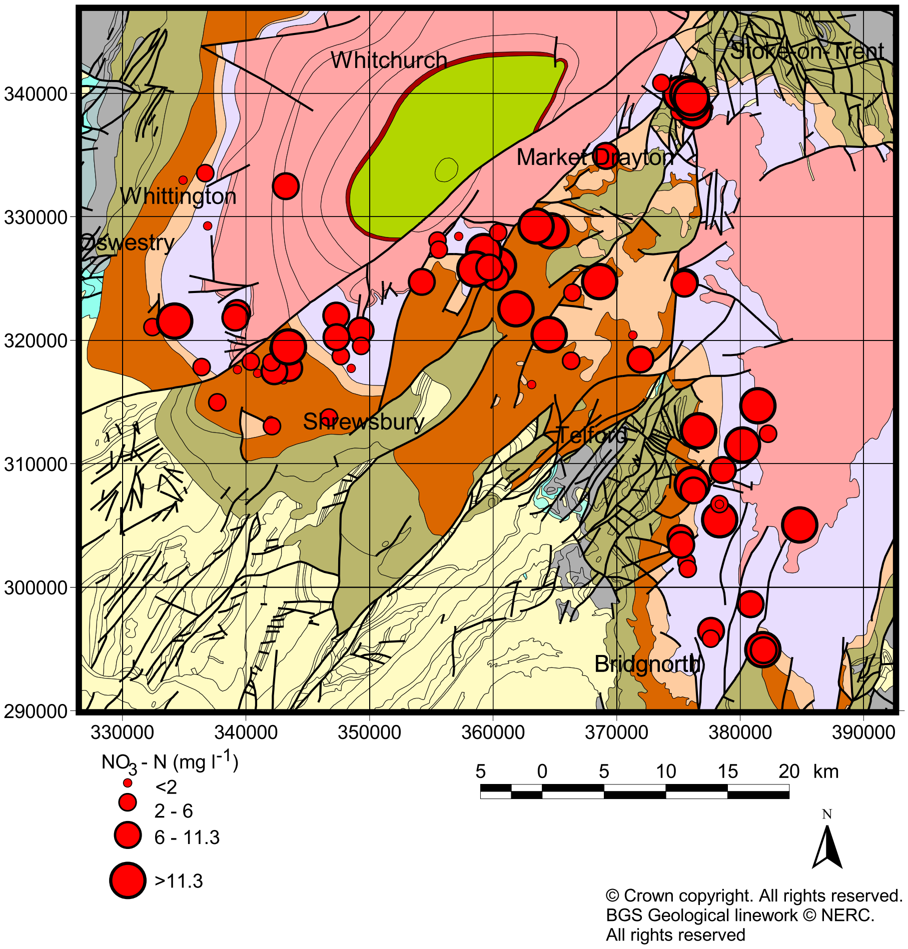

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Figure 6.6. **Regional variations in NO$_3$-N in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.**

in Coal Measures water from north-east England up to 4.08 x 10^{-3}. Metcalfe et al. (1999) quoted a molar Br/Cl ratio of 2.02 x 10^{-3} for Coal Measures groundwater from Cheshire. These compare with a ratio for modern rainfall of around 1.83 x 10^{-3} (Edmunds and Smedley, 2000). The dataset for Br in the groundwaters in this study is limited (BGS 2003 samples only), but the observed range in molar Br/Cl ratio is 0.52 x 10^{-3}–1.3 x 10^{-3}, suggesting that there has been little or no influence from Coal Measures-derived water in the analysed samples. The ratio is slightly lower than that for modern rainfall which may reflect relative increases in Cl from other sources (evaporites, pollutants). Unfortunately, the most saline samples incorporated in the present study were not analysed for Br and so the concentrations and the Br/Cl ratios are unknown. Analysis of Br/Cl ratios in groundwater from the Woodfield site may help to constrain the origins of the groundwater salinity.

6.2.5 Influence of pollution

As the aquifer is in large part unconfined, being covered by variable thicknesses of relatively permeable Drift deposits or in places having no Drift cover, it is potentially vulnerable to the effects of surface pollution. The effects are seen from the high concentrations of NO_3-N (up to 51 mg l^{-1}) in many samples (Figure 6.1). The source of the nitrate in the groundwater is uncertain but as the area is predominantly rural with comparatively few landfill sites (Figure 3.8), especially close to abstraction boreholes, it is probable that much of the NO_3-N derives from septic tanks or from the use of agricultural fertilisers. Atmospheric deposition is another potential minor source.

Klinck and Trick (2001) determined the δ^{15}N compositions of a selection of groundwaters from the

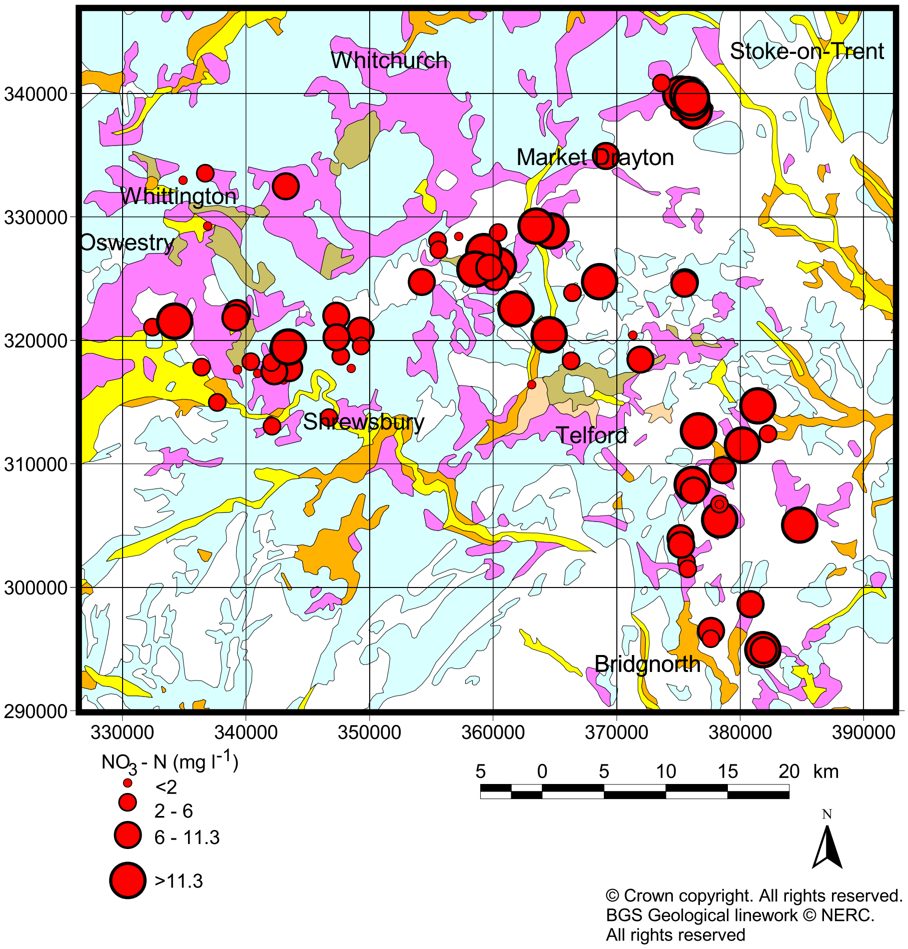

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Figure 6.7. Regional variations in NO_3-N in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer and the distribution of superficial Drift deposits.

Tern catchment and found a large range of 4.1–13.3 ‰. This range made it difficult to identify unequivocally the source of N in the groundwaters but suggested that it had mixed origins, potentially including fertiliser and farm slurry as well as natural soil N.

Elevated concentrations of NO_3-N in the groundwaters also lead to the possibility that other inorganic contaminants of similar origin, notably Cl, SO_4 and DOC will also have impacted the groundwater compositions in the area. The relationships between NO_3-N and a number of potential pollutants are also shown in Figure 6.1. Few of the parameters correlate well but this reflects the complexities arising from additional sources such as evaporate dissolution (SO_4 from gypsum and anhydrite, Cl from halite; K from clays; P from iron oxides or rare apatite; DOC from solid organic matter) and mixing of groundwaters from different strata (Drift, Mercia Mudstone, Carboniferous sediments). The relative influences on the concentrations and distributions of Cl, SO_4, P, DOC and K are difficult to identify.

The Childs Ercall borehole sampled in this study has comparatively low concentrations of NO_3-N (2.5 mg l^{-1}), Cl (13 mg l^{-1}), SO_4 (4.5 mg l^{-1}), P (0.01 mg l^{-1}) and DOC (0.3 mg l^{-1}) and it is likely that these represent the concentrations of oxic Sherwood Sandstone groundwater that has not been influenced significantly by inputs from pollution sources, has not undergone denitrification and has not impacted by leakage of overlying Drift deposits.

The NO_3-N versus Cl plot in Figure 6.1 shows clearly a bi-modal distribution of samples, a set with high NO_3 and moderately high Cl probably linked to pollution and a high-Cl, low-NO_3-N set probably

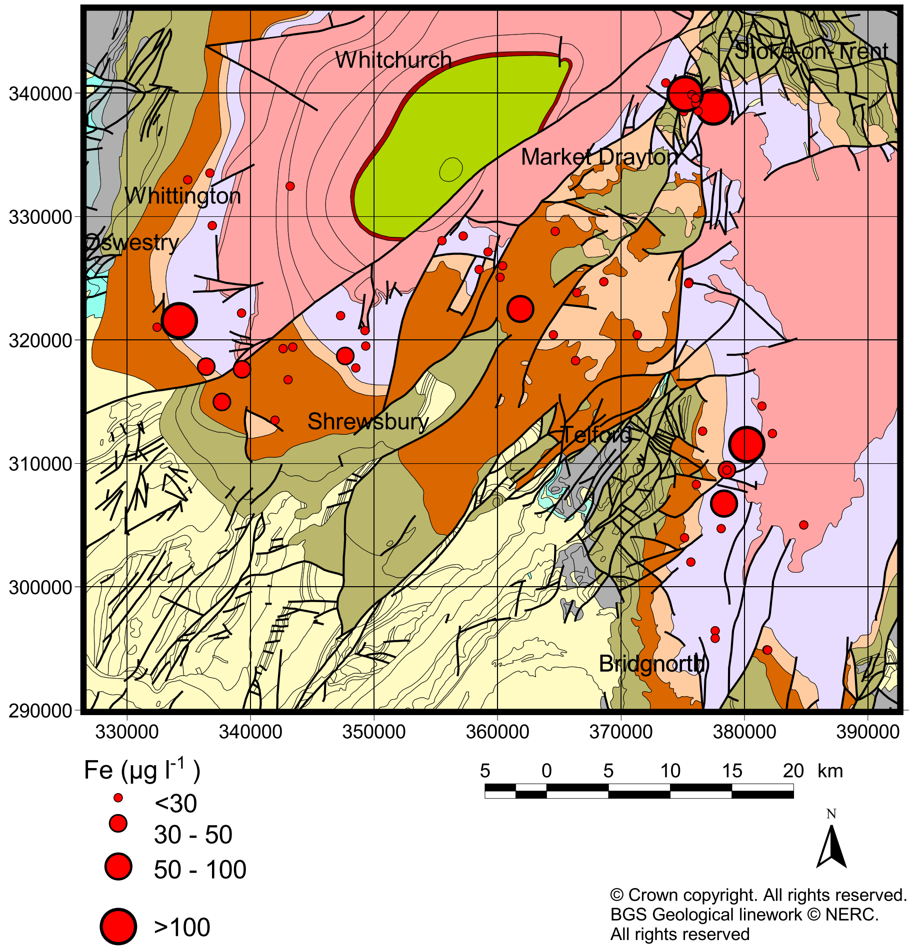

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Figure 6.8. **Regional variations in Fe in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.**

derived by mixing following cross-formational flow.

6.2.6 Trace-element controls

Although carbonate mineral reactions have an important influence on groundwater chemistry in the Sandstone aquifer, silicate mineral reactions also exert an influence. These control the concentrations of some of the major elements (notably Na from feldspar and K from albite dissolution and clay-mineral interactions), but also have an effect on a large number of the trace elements. Silicon concentrations (range 2.6–8.6 mg l^{-1}) are variably influenced by rapid dissolution of silicate minerals or silica from soil complexes. The groundwaters are mostly undersaturated with chalcedony and amorphous silica but most are saturated with respect to quartz. The silica mineral controlling the upper concentrations is therefore unclear.

Reaction of silicate minerals is also likely to be the dominant control on distributions of trace alkali metals such as Li, Rb and Cs. Concentrations of these tend to be very low, reaching up to 49 µg l^{-1}, 3.8 µg l^{-1} and 0.09 µg l^{-1} respectively. Feldspars are also a likely source of Ba, concentrations of which are limited in the aquifer by the precipitation of barite.

As described in Section 5.3, many of the trace metals in the Permo-Triassic Sandstone groundwaters are present in low concentrations, particularly those that typically form cations in solution. Examples include Al (up to 67 µg l^{-1}), Cd (up to 1.1 µg l^{-1}) and Co (up to 1.8 µg l^{-1}). These tend to have low concentrations because of the normally near-neutral pH values of the groundwaters. Concentrations of

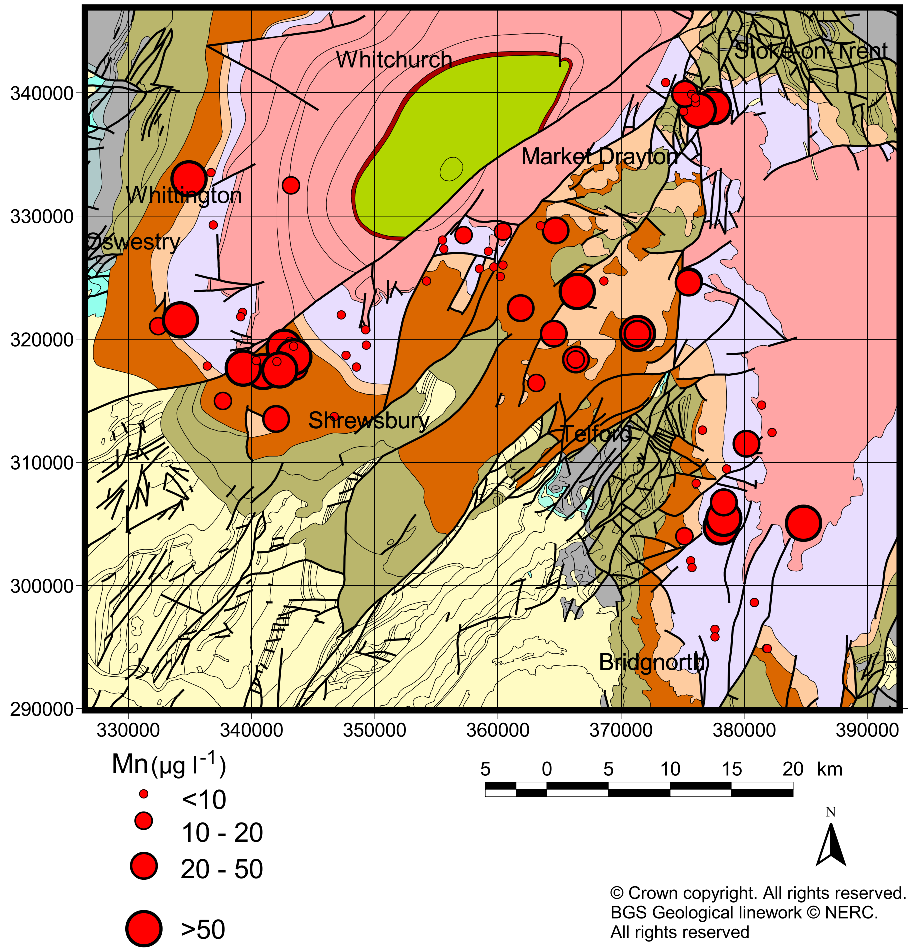

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Figure 6.9. Regional variations in Mn in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.

Cu and Zn are also usually low but with extremes up to 275 µg l^{-1} and 954 µg l^{-1} respectively, possibly resulting from corrosion of metallic pipework in the boreholes. Concentrations of Pb up to 10.8 µg l^{-1} are of unknown origin, but the groundwaters with highest concentrations may contain Pb from corrosion of lead pipes. It is probably significant that the sample with the highest concentration of Pb also had the highest Cu and among the highest Zn concentration.

Concentrations of some other trace elements are worthy of note. Concentrations of As reach up to 26 µg l^{-1}. While not high in geochemical terms, this is above the EC limit for drinking water as observed in Section 5.3. The cause of the elevated concentration is not easily established: the groundwater sample has a near-neutral pH (7.32), is oxic and the does not contain high concentrations of other key parameters (e.g dissolved Fe, Mn, P). Desorption from iron oxides in the sandstone is the most likely source of the As but the mobilisation mechanism is unclear.

The highest concentration of Ni (43 µg l^{-1}) is found in the Dovaston Old Farm groundwater sample. The most likely explanation is that Ni^{2+} has been desorbed from iron oxides in the Sandstone under the acidic conditions (pH 5.2) which are maintained by lack of available calcite. The normally neutral pH values of the groundwaters tends to maintain low concentrations of Ni, usually <5 µg l^{-1} and often <1 µg l^{-1}.

Concentrations of U up to 67 µg l^{-1} are also observed, although the U dataset is limited (data are only available for the BGS 2003 samples). This concentration is also unusually high, most being less than 4 µg l^{-1}. The high U concentration is from Ellerdine Heath borehole. This borehole penetrates the

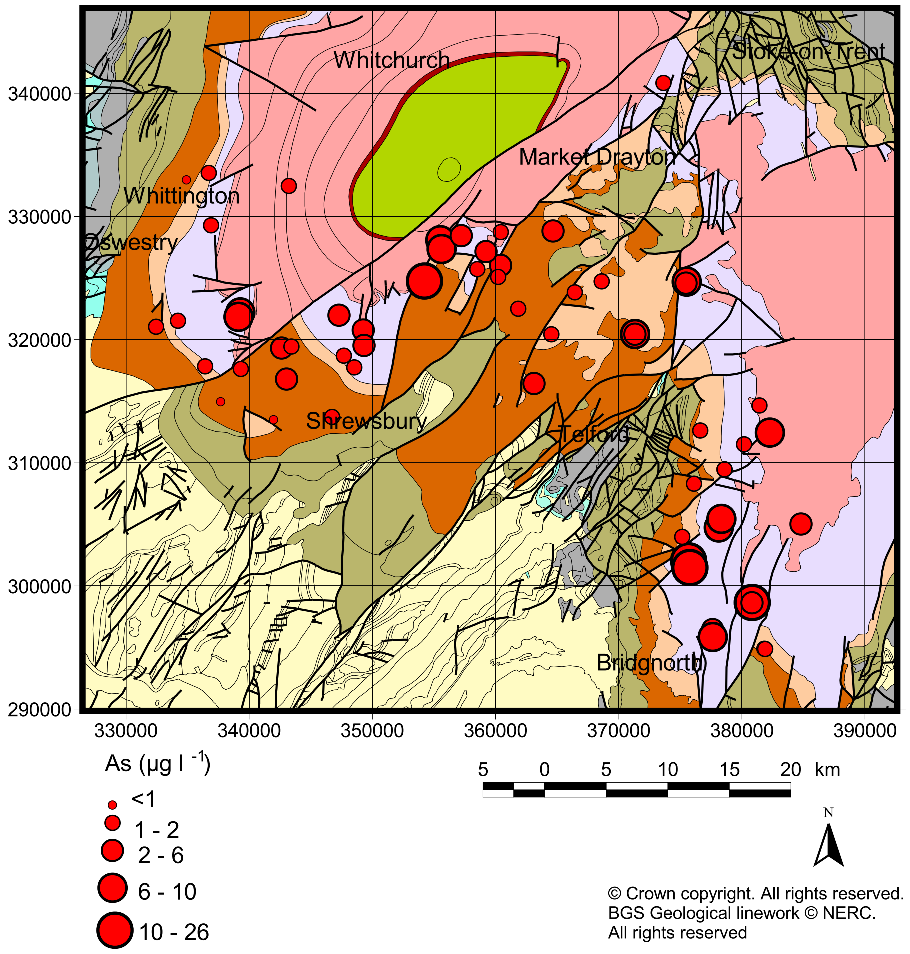

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Figure 6.10. **Regional variations in As in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.**

Permo-Triassic Sandstone with no overlying Drift deposits. The U is therefore most likely to be derived from iron oxides in the sandstone by desorption under the oxic conditions present in the groundwater from the borehole.

6.3 Regional trends

As a result of these diverse influences, regional variations in major-element compositions of the Permo-Triassic Sandstone groundwaters are highly complex and few clear spatial trends are recognisable from the dataset incorporated in this study. The regional variations in TDS are given in Figure 6.2, Na in Figure 6.5 and Cl in Figure 6.3. Occurrences of high concentrations of both Na and Cl are distributed sporadically around the area with highest concentrations occurring at Frank Brook (FB), Woodfield (WF), Beckbury (B1, B2) and Copley (C2), as also indicated by the Piper diagram in Figure 5.1. Confirmation of Smart's (1977) report of higher Na and Cl concentrations in groundwater from the area of the Severn Trench, with occasional groundwaters of Na-Cl or Na-HCO_3 type, is not possible here because of the paucity of data from the area of the Severn Trench in this study. The lowest overall concentrations of Na and Cl (and TDS values) are from the area to the north and north-west of Shrewsbury. This may be because of a greater thickness and proportion of clayey Drift in this area and resultant restriction in recharge via the Drift deposits.

The regional variations in SO_4 (Figure 6.4) and NO_3-N (Figure 6.6) also show relatively low concentrations in this area to the north and north-west of Shrewsbury, probably also as a result of restricted recharge and protection of the aquifer from the effects of pollution. Elsewhere, the

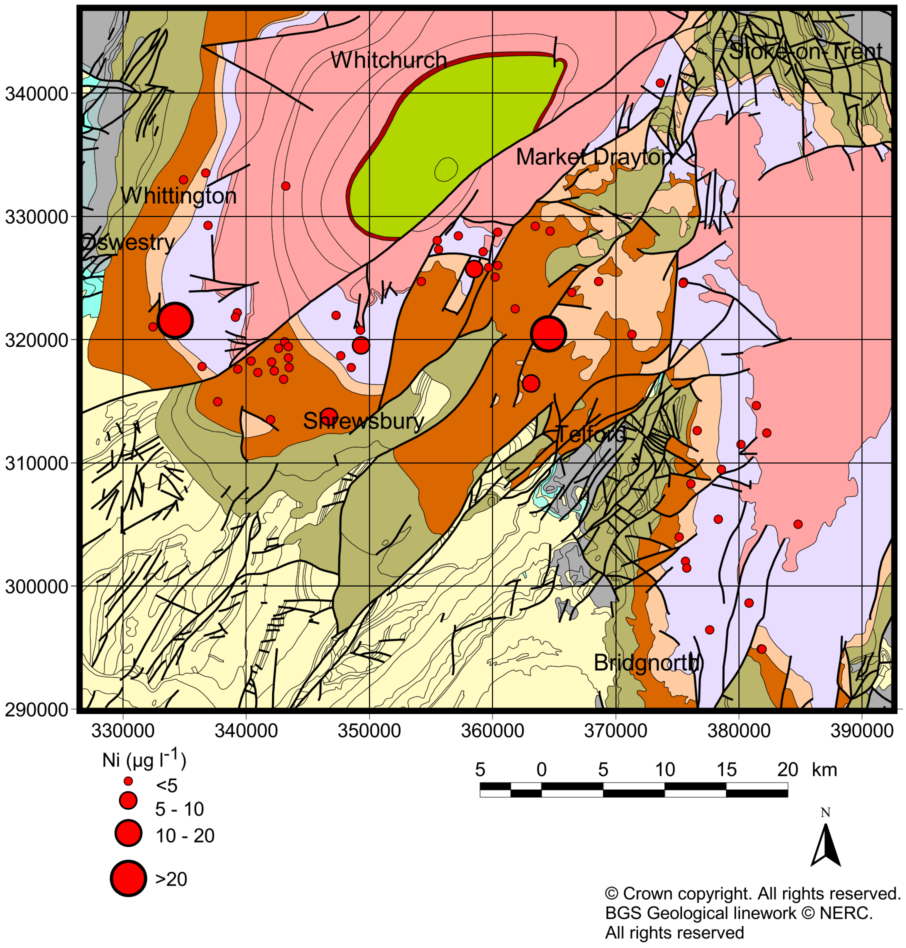

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Figure 6.11. **Regional variations in Ni in groundwaters from the Shropshire Permo-Triassic Sandstone aquifer.**

distribution of these parameters are very variable, and concentrations of NO_3-N greater than the EC limit for drinking water of 11.3 mg l^{-1} occur sporadically throughout the aquifer. The distribution of NO3-N concentrations in relation to the Drift deposits is shown in .

Regional variations in Fe and Mn are given in Figure 6.8 and Figure 6.9. These maps also show little spatial trend in element concentrations. There is also not much consistency between the two elements.

Spatial variations in As concentration are given in Figure 6.10. The map shows that there is no discernible pattern in the distribution of high As concentrations (>10 µg l^{-1}). Some low concentrations are observed in groundwaters north and north-west of Shrewsbury where the TDS values were correspondingly low. Some low concentrations north of Bridgnorth are also apparent.

Spatial patterns in Ni concentrations (Figure 6.11) show some of the highest concentrations in the Shrewsbury to Hodnet area and in the Tern catchment. Lowest concentrations are typically found in the east of the study area along the River Worfe. The reasons for the distribution of these low concentrations are unclear.

6.4 Groundwater dating

No specific radiometric data are known to exist for groundwater samples from the Permo-Triassic Sandstone aquifer from which the ages of groundwater can be assessed directly. However, various ancillary lines of evidence suggest that most of the groundwaters in the aquifer represent relatively young recharge water. High concentrations of NO_3-N and DOC, together with P and K are an indication of inputs of recent pollutants to the aquifer. Although most of the groundwaters are saturated with respect to calcite, most appear not to be saturated with dolomite despite the fact that it is known to be present within the aquifer. As noted in Section 6.2.1, this points to the groundwaters having had insufficient residence times in the aquifer for equilibration to take place and is supported by the relatively depleted $\delta^{13}C$ isotopic compositions.

Available $\delta^{18}O$ and $\delta^{2}H$ data, although comparatively limited, also suggest that most of the groundwaters are of young age. The $\delta^{18}O$ compositions (range -7.9 to -6.7 ‰) are within the range of other 'young' groundwaters in the British Isles (Darling et al., 1997) and are relatively enriched compared to older, deeper groundwaters from the Sherwood Sandstone in the English East Midlands (Figure 6.12). These were noted to have compositions as depleted as -9.5 ‰ resulting from recharge

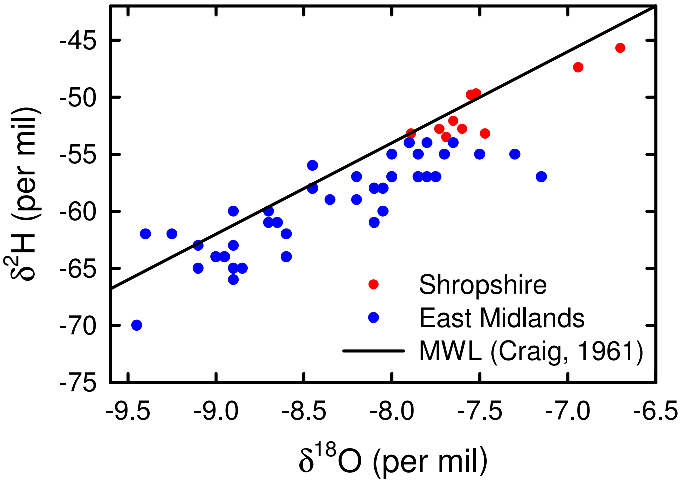

Figure 6.12. Variation in δ^{180} with $\delta^{2}H$ in groundwaters from the Permo-Triassic Sandstone aquifer of Shropshire, compared with groundwaters from the East Midlands Sherwood Sandstone (Edmunds and Smedley, 2000). The Meteoric Water Line (MWL) from Craig (1961) is given for comparison.

during colder climatic conditions during the Pleistocene than occur today. The groundwater samples lie close to the Meteoric Water Line (MWL), defined by Craig (1961) and are a further indication that the groundwaters result from recharge of modern rainfall.

It has been suggested (Section 6.2.3) that groundwater from confined sections of the aquifer below clayey Drift can be relatively old as local recharge is restricted and the groundwater is therefore protected from direct inputs of modern pollutants. However, no isotopic data are available for the groundwaters to ascertain their ages. Further studies would be needed to constrain the residence times of these confined groundwaters.

6.5 Temporal variations

Groundwater monitoring data are limited for most chemical constituents. Nitrate is one of the more frequently monitored of the inorganic constituents. Data for several boreholes show very variable concentrations of nitrate with time. Groundwater data from boreholes at Hilton [SO 776 958] and Copley [SO 808 986] monitored during the 1970s and 1980s (Environment Agency WIMS data) are shown in Figure 6.13. A very small increase in NO_3-N concentrations with time is noted in the groundwater from the Hilton boreholes, but a more pronounced increase is visible in groundwater from the Copley boreholes, notably borehole No. 1. During 1977, the earliest date for which data are available, concentrations in Copley No. 2 borehole were between around 4 mg l^{-1} and 6 mg l^{-1} and for Copley No. 1 were around 5–6 mg l^{-1}. By 1988, both boreholes had groundwater with NO_3-N concentrations around 7 mg l^{-1} (albeit with more limited data). The data for Copley No. 2 appear to fall into two distinct populations, one higher than the concentrations observed in Copley No. 1 and the other lower. The differences between these two are hard to explain without detailed knowledge of the site. However, it is possible that the variations relate to variable pumping regimes on the site and cross-borehole flow of groundwater with distinctive NO_3-N concentrations.

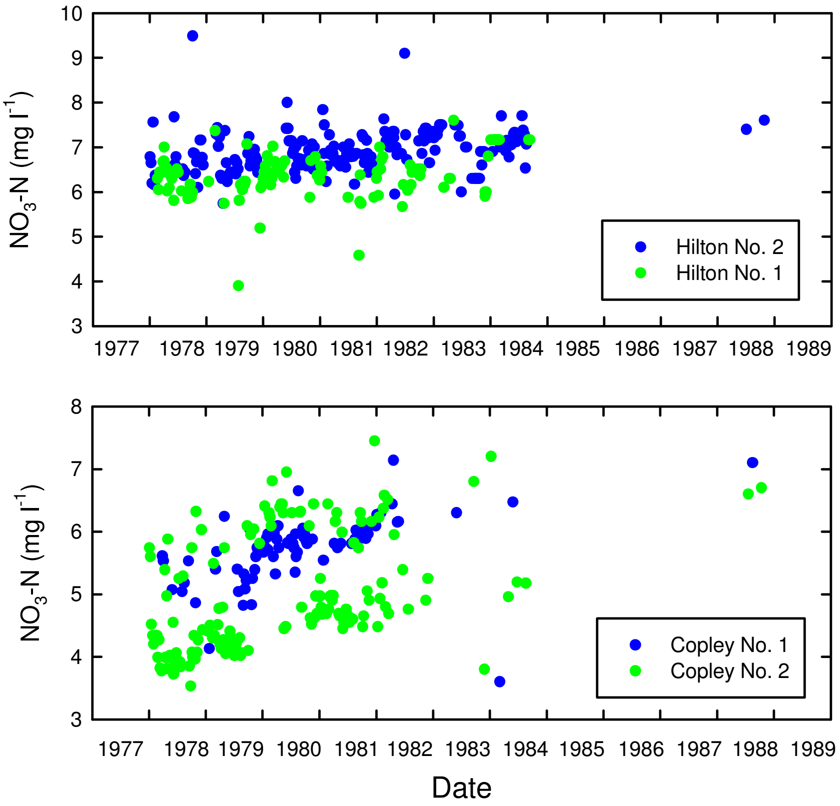

Figure 6.13. Temporal variation in NO_3-N concentration in boreholes at Hilton [SO 776 958] and Copley [SO 808 986].

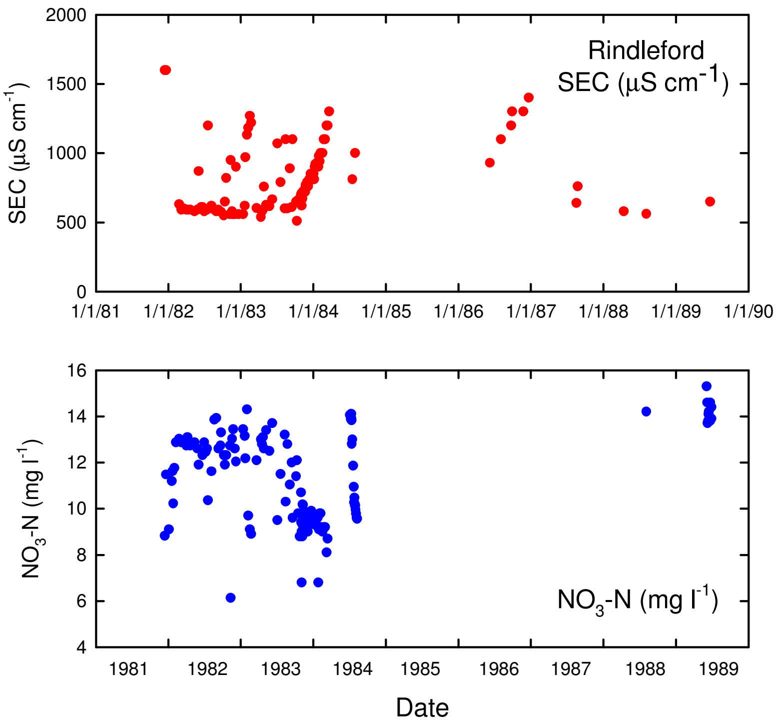

Figure 6.14. **Temporal variation in SEC and NO_3-N concentration in a borehole at Rindleford [SO 738 956].**

It is noteworthy that in the Hilton boreholes, the NO_3-N concentrations were also around 6–8 mg l^{-1}, rather higher than the projected 'baseline' concentration for NO_3-N in the area. It is likely that even by the late 1970s, the unconfined groundwater from the Permo-Triassic Sandstone aquifer had been changed by influxes of modern nitrate-bearing water.

Monitoring of groundwater quality in several other boreholes has also revealed increases in the concentrations of NO_3-N in groundwater, widely thought to be derived from the use of agricultural fertiliser. Entec (1999) showed increases in NO_3-N concentration in groundwater from boreholes at Childs Ercall, Manor House and Hine Heath over an interval of up to 10 years from the late 1960s. Concentrations apparently rose in these boreholes from 9–15 mg l^{-1}, 19–30 mg l^{-1} and 22–40 mg l^{-1} respectively. Such increases have also been found elsewhere in the aquifer. However, the data range quoted for the Childs Ercall borehole is very different from that used in this study (2.5 mg l^{-1} as N) and the discrepancy is not easy to resolve. It is probable that the borehole monitored in the 1960s is different from that included in this study (which is part of the SGS, first developed in the 1980s), although they should be abstracting groundwater from the same area of the aquifer. The discrepancy suggests large lateral variation in groundwater NO_3-N concentrations on a local scale.

Although the Sandstone groundwaters in the dataset used in this study typically have concentrations of Ca around 60–95 mg l^{-1}, Na of 8–14 mg l^{-1}, K of 1–4 mg l^{-1}, Cl of 10–30 mg l^{-1} and SO_4 of 5–45 mg l^{-1}, some departures from this are observed. A sample from Ellerdine Heath borehole [SJ 618 225] for example has relatively high concentrations of Ca (116 mg l^{-1}), Na (27 mg l^{-1}), K (11.3 mg l^{-1}), Cl (43 mg l^{-1}) and SO_4 (101 mg l^{-1}). Its B concentration (165 µg l^{-1}) is also unusually high (<50 µg l^{-1} is typical). Environment Agency records suggest that the composition of groundwater pumped from this borehole has been variable over time. Concentrations of the above elements are more typically respectively 88 mg l^{-1}, 14 mg l^{-1}, 5 mg l^{-1}, 29 mg l^{-1} and 70 mg l^{-1} (B not determined), although an Environment Agency sample collected on 10/08/95 showed very similar major-element compositions to those determined for this study and outlined above. The implication is that groundwater of mixed origins is present in the borehole. The end member giving rise to the anomalous chemical compositions is uncertain, but may be linked to domestic or agricultural pollution. The variation with time may also be linked to pumping regimes since the SGS boreholes are pumped infrequently. Similarly high concentrations of many of the major elements outlined above are also present in groundwaters from the Shifnal [SJ 761 083] and Sheriffhales [SJ 766 126] boreholes.

Temporal variations in chemical composition are apparent in groundwater from Rindleford borehole [SO 738 956] in the southern part of the study area (Figure 6.14). Here, groundwater monitoring during the 1980s (Environment Agency WIMS data) showed variation in SEC values between 500–1500 µS cm^{-1}. The higher SEC values in this dataset represent relatively high salinity and are presumably a result of influxes of saline water from cross-formational flow.

Monitoring of groundwater at Adcote and Frank Brook boreholes (south Perry catchment) has also revealed temporal variations in water quality caused by influx of varying amounts of saline water from the Wem Fault. Smart (1977) reported that SEC values in groundwater from the Frank Brook borehole increased from 980 µS cm^{-1} to 1250 µS cm^{-1} and Cl from 160 mg l^{-1} to 260 mg l^{-1} during pump testing in the 1970s as a result of saline influxes.

6.6 Depth variations

Little information has been published on variations in groundwater quality with depth in the Permo-Triassic sequence of Shropshire. Papatolios and Lerner (1993) noted decreases in the concentrations of NO_3-N and SO_4 in a borehole at Edgmond Bridge [SJ 7188 1845], but the variations and depth ranges were not described in detail and the concentration variations were in any case less than 20% and therefore not significant.

Studies by Severn Trent Water Authority (1974) found little vertical variation in groundwater quality at Childs Ercall borehole, confirming a lack of surface infiltration of pollutants at the site, and being in line with the artesian condition of the borehole. A report by the Environment Agency (2000a) also found little vertical variation in conductivity or temperature values from logging of SGS boreholes in the Tern catchment. Logs of electrical conductance were a constant 500 µS cm^{-1} down to 88 m below ground level at Green Fields [SJ 616 262]; at Green Lane [SJ 605 255], conductivity was around 800 µS cm^{-1} down to the base of the borehole at 112 m below ground level; and at Heath House, groundwater from two boreholes down to 120 m had constant values around 350 µS cm^{-1} and 600 µS cm^{-1}. The profiles show no marked vertical stratification in groundwater quality in these areas.

The anomalously high salinity of groundwater from the borehole at Woodfield pumping station has been described earlier (Section 5). Increasing salinity values have been found at depth in the borehole (Tate and Robertson, 1971). Increased abstraction at the site during the 1970s resulted in a notable deterioration in groundwater quality at >50 m depth due to infiltration of saline groundwater from the Salop Formation (Coal Measures).

The variation in concentrations of a number of parameters with borehole depth in the samples incorporated in this study is shown in Figure 6.15. These include samples from all over the study area and are necessarily difficult to interpret because of spatial variations in parameters such as elevation, groundwater level, Drift thickness and geological structure. However, some general conclusions can be made from the observations. Firstly, although pH values are typically near 7, the most acidic samples tend to be from the boreholes with shallowest depths. This is consistent with a paucity of calcite in the unconfined Sandstone aquifer at the shallowest depths related to more active groundwater flow and leaching of carbonate cements and detrital grains. Such paucity of calcite at shallow depths is consistent with observations for the Sherwood Sandstone of Nottinghamshire (BGS, unpublished data).

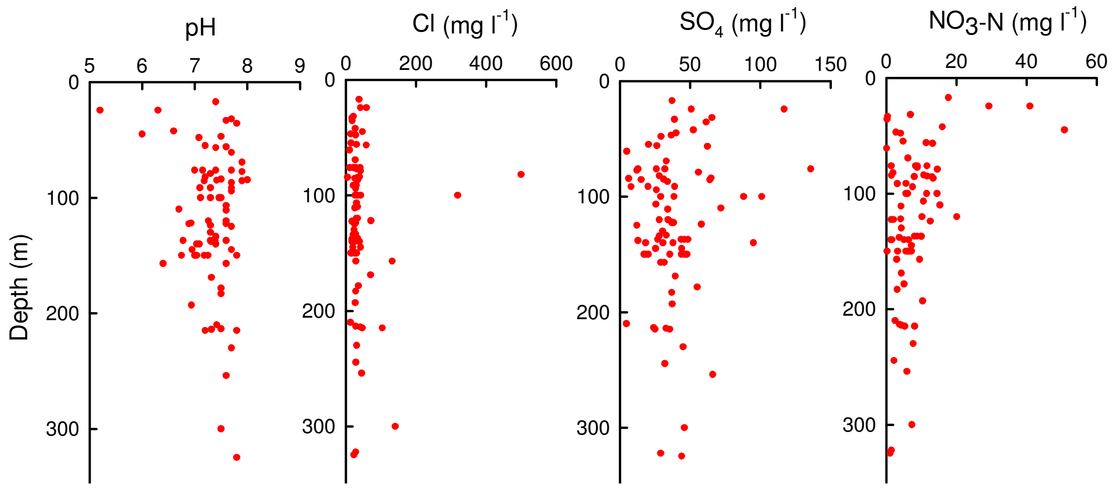

Figure 6.15. Variation in pH, Cl, SO_4 and NO_3-N with borehole depth in groundwaters from the Permo-Triassic Sandstone of Shropshire.

Chloride concentrations show little trend with depth across the aquifer, most groundwaters tending to have Cl concentrations less than around 50 mg l^{-1}. The largest range and highest concentrations occur in boreholes with depths around 100 m (Figure 6.15). The two samples with the highest concentrations are from the Frank Brook and Woodfield boreholes. As noted earlier, the salinity in the groundwater from these boreholes is believed to be due to inflows from Carboniferous or Mercia Mudstone strata rather than surface pollutants (confirmed by increasing salinity with increasing depth at Woodfield).

Variations in SO_4 (Figure 6.15) are generally greater in the shallower boreholes, <100 m total depth. In boreholes greater than 100 m deep, concentrations are mostly less than 50 mg l^{-1}. A similar observation applies with NO_3-N, with the highest concentrations and greatest range occurring in groundwaters with depths <50 m (Figure 6.15). The higher concentrations are believed to reflect inputs from Drift-derived groundwaters and from direct pollutant inputs. Quantifying the relative contributions of these would need further investigation.

7. BASELINE CHEMISTRY OF THE AQUIFER

The complex interactions of a number of processes in the Permo-Triassic Sandstone aquifer make attempting to define the 'baseline' chemistry of the aquifer difficult. The definition of baseline is in any case open to interpretation. Inputs of point-source and diffuse pollutants from the ground surface represent obvious departures from baseline conditions, but whether or not variations due to inputs from overlying Drift deposits or from groundwaters derived from extra-formational deposits such as the Salop Formation can still be interpreted as baseline is questionable. The chemistry of these groundwaters is likely to be defined largely by natural processes and cross-formational flow can be a natural occurrence even without the influence of recent groundwater pumping. Groundwaters that have not been chemically influenced by Drift deposits are likely to have been more directly impacted by surface pollutants because of direct recharge. This will have a particular effect on NO_3-N concentrations as well as other elements such as SO_4 and Cl. The chemistry of groundwaters below the Mercia Mudstone Group sediments also has some distinctions from the unconfined Permo-Triassic Sandstone groundwaters, adding further variation to the observed ranges of chemical compositions.

Given all these complexities, the statistical summary data (Table 5.1) provide a first step towards attempting to estimate the likely baseline ranges of various chemical parameters in the groundwaters and serve to reiterate that 'baseline' concentrations must necessarily encompass a range of compositions rather than a single value. The median, 5th and 97.7th percentiles give an idea respectively of the central tendency and typical ranges of element concentrations, while excluding much of the effect of the outliers caused by inputs from extra-formational groundwaters or spurious data. Obvious exceptions include Cl, Na and SO_4 where the 97.7th percentile values are respectively 140 mg l^{-1}, 73 and 100 mg l^{-1}. If the inputs from cross-formational flow are discounted, the upper baseline concentrations should probably be around 40 mg l^{-1} for Cl, 15 mg l^{-1} for Na and 60 mg l^{-1} for SO_4, in line with the flexures (breaks in slope) observed in their respective cumulative-frequency diagrams.

The cumulative-frequency diagrams for K and DOC show flexures at around 6 mg l^{-1} and 2 mg l^{-1} respectively. These values also lower than the 97.7th percentile value for each parameter. The concentrations at the higher end of the compositional range are likely to represent inputs from pollution and hence the values given above for these parameters probably represent better upper baseline concentrations than those indicated by the 97.7th percentiles. For other parameters likely to be affected by pollution, such as NH_4-N and P, the 97.7th percentile values (0.18 mg l^{-1} and 0.25 mg l^{-1} respectively) probably represent useful indicators of upper baseline compositions. Cumulative-frequency diagrams show slight flexures at around 0.15 mg l^{-1} for NH_4-N and 0.2 mg l^{-1} for P (not shown), suggesting a change in sample populations at these concentrations.

It is probably helpful to think of the confined artesian boreholes as representing groundwater in the Permo-Triassic Sandstone that has not been influenced in any substantial way by surface pollutants or by Drift deposits, since the groundwater flow should be upwards towards the Drift rather than downwards from the surface. Groundwater in the Childs Ercall borehole is a good indicator of this. The groundwater from this borehole is also oxic and so has not undergone redox modifications. As noted above (Section 6.2.5), many of the major-element concentrations in this groundwater are at the low end of the compositional range and the NO_3-N has a concentration of 2.5 mg l^{-1}. This compares well with the estimated value for concentrated rainfall (Section 3.5) and is believed to be the likely upper value for the baseline concentrations of NO_3-N in the aquifer.

8. SUMMARY AND CONCLUSIONS

The chemical compositions of groundwaters in the Permo-Triassic Sandstone are highly spatially variable as a result of the varying lithological, hydrogeological and structural influences. Temporal variations in groundwater chemistry are also notable in several boreholes. The groundwaters have chemical compositions which have evolved from local rainfall (recharge) by mineral dissolution and precipitation reactions in the soils, superficial deposits and bedrocks. This interaction varies particularly in relation to the thickness and lithology of Drift deposits. Where Drift is mainly permeable sands and gravel, these are in hydraulic connection with the underlying aquifer. Where boulder clay occurs, this acts to impede the infiltration of groundwater, thus confining the underlying aquifer and protecting it from contaminants. The region is also heavily faulted and groundwater in some boreholes appears to have been impacted by influxes of water of different chemistry from neighbouring lithologies, facilitated by movement and interaction along fault zones. The distribution of observed influxes from different lithologies is however very sporadic.

Redox processes appear not to have been of regional significance in the unconfined and partially confined groundwaters investigated in the study, although a number of groundwater samples with low dissolved-oxygen concentrations and higher concentrations of Fe and/or Mn show evidence of locally reducing conditions. These reflect the local influence of confinement by clay Drift deposits. Some groundwaters also show evidence of inputs of surface pollutants, most notably in the distribution and concentrations of dissolved nitrate, DOC, P and K.

As a result of the numerous interacting physical and chemical processes, the concentration ranges of various hydrochemical constituents that can be considered as baseline in the Shropshire groundwaters are difficult to quantify and interpret. However the summary statistics, box-and-whiskers plots and cumulative-frequency diagrams presented in this report should provide a guide to the typical concentration ranges expected in the Permo-Triassic Sandstone groundwaters in Shropshire. An understanding of the dominant controlling processes outlined above should also give an appreciation of the causes of the outlying element concentrations and the mechanisms involved.

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