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Baseline Report Series: 12. The Devonian aquifer of South Wales and Herefordshire

Groundwater Systems and Water Quality
Commissioned Report CR/04/185N

Science Group: Air, Land & Water
Technical Report NC/99/74/12



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/04/185N

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Baseline Report Series: 12. The Devonian aquifer of South Wales and Herefordshire

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FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

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

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

The BASELINE objectives are:

1. to establish criteria for defining the baseline concentrations of a wide range of substances that occur naturally in groundwater, as well as their chemical controls, based on sound geochemical principles, as a basis for defining water quality status and standards in England and Wales (in the context of UK and Europe); also to assess anomalies due to geological conditions and to formulate a quantitative basis for the definition of groundwater pollution.
2. to characterise a series of reference aquifers across England and Wales that can be used to illustrate the ranges in natural groundwater quality. The baseline conditions will be investigated as far as possible by cross-sections along the hydraulic gradient, in well characterised aquifers. Sequential changes in water-rock interaction (redox, dissolution-precipitation, surface reactions) as well as mixing, will be investigated. These results will then be extrapolated to the region surrounding each reference area. Lithofacies and mineralogical controls will also be taken into account. A wide range of inorganic constituents as well as organic carbon will be analysed to a common standard within the project. Although the focus will be on pristine groundwaters, the interface zone between uncontaminated and contaminated groundwaters will be investigated; this is because, even in contaminated systems, the main constituents of the water are also controlled by geological factors, amount of recharge and natural climate variation.
3. to establish long term trends in water quality at representative localities in the selected reference aquifers and to interpret these in relation to past changes due to natural geochemical as well as hydrogeological responses or anthropogenic effects.
4. to provide a scientific foundation to underpin UK and EU water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

1. EXECUTIVE SUMMARY

This report describes the variations in baseline chemistry and the dominant geochemical processes occurring in the Devonian Sandstone aquifer of south Wales and Herefordshire. It is hoped that it will be of use in water quality management and also form a basis from which to manage future aquifer contamination.

The Devonian Sandstone area selected for study has a triangular shape and is bounded to the south and east by rocks of Carboniferous and younger age, and to the north and west by older rocks of Ordovician and Silurian age. The study area is restricted to the Wye Valley around Leominster, Brecon and Hereford; here the River Wye flows through a U-shaped valley surrounded by steep-sloped hills. In the valleys elevations range from 50 to 100 m above Ordnance Datum (aOD) with the tops of the hills and mountains reaching more than 700 m aOD. Topography and geology combine to give rise to numerous surface water streams and springs that contribute to the River Wye. Within the study area managed grassland and arable farming are the main land uses.

The Devonian Sandstone comprises a series of interbedded sandstones, siltstones and mudstones of Silurian to Devonian age, most of the formations being Lower Devonian. Any Middle Devonian deposits originally present in the study were eroded away during the Caledonian uplift (c. 395-410 Ma). Upper Devonian formations are present on very limited areas, mostly on top of hills, and are generally limited to a few metres in thickness. Forming the capping layer on higher ground the role on the hydrogeological system is limited to recharge areas. Groundwater residence time within the Upper Devonian is expected to be minimal, therefore, these formations were not considered in the study. The Lower Devonian Sandstone is divided into the Raglan Mudstone Formation (thick succession of red-brown mudstone and siltstone, with subordinate cross-bedded sandstone), St Maughans Formation (thick sequence of mudstones and siltstones, sandstones and subordinate conglomerates) and the Senni Beds and Brownstones formations (predominantly sandstones). Dolomite and calcite cements are common amongst the Raglan Mudstone and the St Maughans formations. Superficial deposits, mainly present within the large river valley, originated from glaciation during the Devensian (70-10 Ka) (mainly till and glacial sand and gravel). Where groundwater is present in the Superficial Deposits it is commonly in hydraulic continuity with the surface waters or, less frequently, the underlying Devonian strata.

The Devonian Sandstone Group typically exhibits low primary porosity with predominant groundwater flow occurring through fractures. The majority of groundwater flow occurs within the upper 50 metres, as fractures tend to close up at depth. It is expected that one of the major controls on groundwater flow is topography rather than geology.

The groundwaters sampled from the Wye valley were generally oxidising with contained low to moderate solute concentrations implying relatively short residence times. The dominant process controlling groundwater chemistry is carbonate mineral dissolution and, in the deeper groundwaters, ion-exchange. The groundwaters are mostly of Ca-HCO₃ type but Na-HCO₃ types are present in deeper parts of the aquifer. Trace elements such as strontium and uranium are locally elevated and originate from carbonate (calcite or dolomite) dissolution. Barium concentrations also show elevated concentrations, up to 659 µg l⁻¹. There is no evidence of groundwater mixing with older formation waters, however, it is possible that this occurs at depth in the aquifer. Interaction with surface waters is likely to be important and some signs of anthropogenic inputs, such as high nitrate, were observed locally. In general, the Devonian Sandstone groundwaters are moderately pristine and close to their natural baseline chemistry, although locally human activity may have modified these.

2. PERSPECTIVE

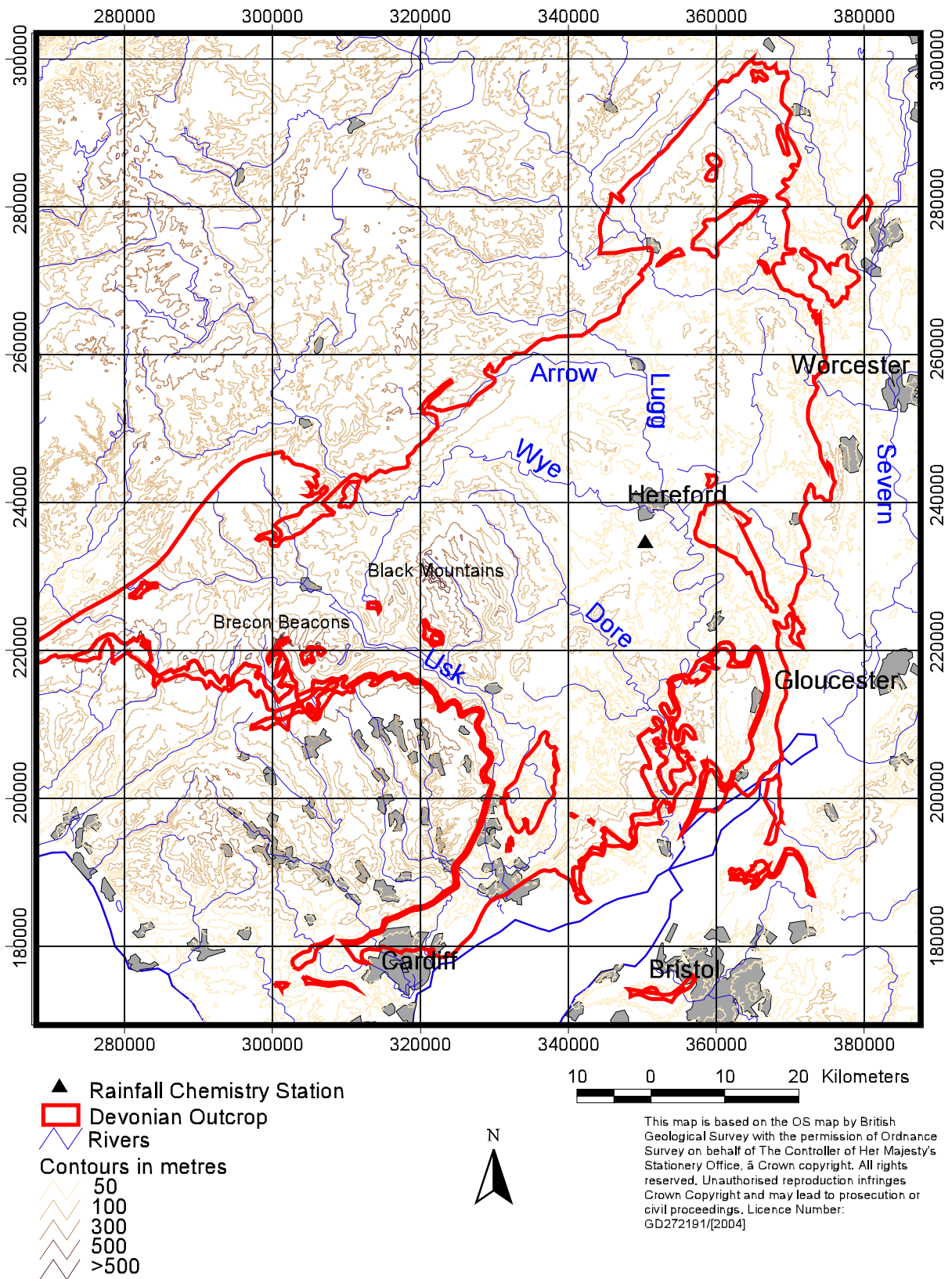


Figure 2.1 Topographic map and outcrop area of the Devonian Sandstone.

Rocks of Old Red Sandstone facies crop out over a large area of southeast Wales and Herefordshire forming an important local aquifer. The Old Red Sandstone, now called the Devonian Sandstone, comprises rocks from Upper Silurian to lower Carboniferous, most of it being of Devonian age. The outcrop of the Devonian Sandstone aquifer in Wales extends to south Pembrokeshire in the west, where it is highly faulted and behaves differently from the rest of the formation (Jones et al., 2000). The aquifer outcrop in Wales and the Welsh borderland is bounded to the south and east by rocks of Carboniferous and younger age and to the north and west by older rocks of Ordovician and Silurian age.

The surface topography of the area is variable from low lying hills to steep sided valleys (Figure 2.1, Figure 2.2). The Black Mountains and the Brecon Beacons, in the south and west of the area, constitute the highest elevations and provide a strong topographic divide for the area, forming rugged, sloping escarpments. These upland areas vary between 700 to 810 m above Ordnance Datum (aOD), the land slopes steeply away towards the broad river valleys (Figure 2.3) where elevations are typically between 50 and 100 m aOD. In the Wye Valley, the topographical divide lies typically around 700 m aOD. The main rivers are the Usk (south of the area draining eastwards and then southwards), the Wye (centre of the area again draining eastwards and then southwards) and the Lugg and Arrow (east of the area, draining mainly southwards). The Usk, Lugg and Arrow rivers are tributaries of the River Wye. The headwaters of these rivers lie outside the study area on Silurian or older aged rocks. Due to the steep slopes and the high ground there are many springs and abundant streams across the area.



Figure 2.2 Typical Devonian landscape: valley view from the slopes of the Black Mountains [SO 2327 3528].



Figure 2.3 View of Ross-on-Wye and the River Wye [SO 5930 2476].

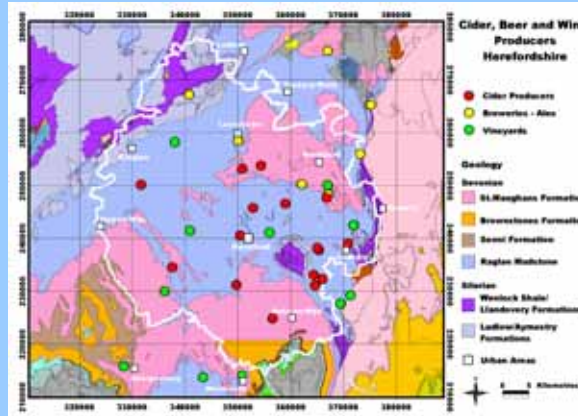
The Devonian sandstone crops out over some 4500 km² and reaches a thickness of up to 2000 m (Dineley, 1992). Although classified as a minor aquifer, the Devonian sandstone is one of the most important aquifers in the Environment Agency Wales Region. The main outcrop of the aquifer contains at least 2650 licensed abstractions. Over 80% of these are licensed for groundwater abstractions (boreholes, wells or springs). The majority of abstractions are for domestic, agricultural and industrial supply. Of the licences granted for agricultural purposes a significant proportion are for spray irrigation. The dominant land-use comprises agriculture mainly arable and grazing land. Orchards are also widespread for the production of cider and perry (Box 2.1), as well as fruit production.



Figure 2.4 Goodrich Castle [NGR SO 5770 1998] near Ross-on-Wye built of Devonian Sandstone

Box 2.1 The Geology and Hydrogeology of beer, cider and wine in Herefordshire

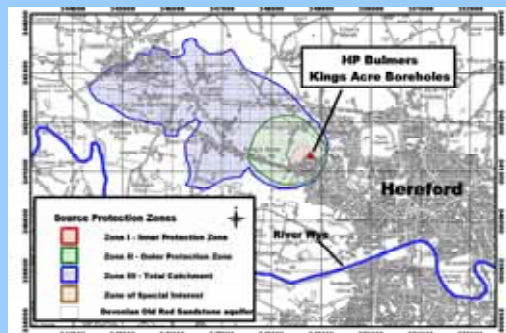
The county of Herefordshire and in particular the valleys of the Rivers Wye, Teme and Frome are important for the production of cider and to a lesser extent, beer (ale) and wine. The ciders and beers produced here are internationally famed with names such as Bulmer's Cider in Hereford (Strongbow and Woodpecker cider), Weston's Cider in Much Marcle (Stowford Press) and Wye Valley Ale near Bromyard just a few of the products synonymous with the county of Herefordshire.



The county is mainly underlain by Devonian Sandstone, which influences the success of apple orchards, hop fields and vineyards. The microclimate in valleys, physiography (south facing slopes and windflow) and particularly the well-drained fertile red sandy soils with underlying clays in the rain shadow of the Welsh Hills promotes ideal conditions necessary for the growing of good yields of apples, hops and vines.

Water is a major ingredient of beer but is also important in wine and cider production where it is used mainly for cooling purposes during fermentation. Historically, the presence of a good reliable source of potable drinking water from groundwater boreholes and springs has played a vital role in the siting and growth of breweries (and cider/wine producers) in Herefordshire. Groundwater sources are preferred because the water tends to be consistent and of 'the right quality' for use in the brewing process. For century's, cider, beer and some wines, including perry, have been produced on farms, commercially utilising groundwater for crop irrigation and in the manufacturing process, abstracted from the local Devonian Sandstone aquifers and overlying shallow sand/gravel superficial deposits. Mains supplies are also now used in some instances.

Natural groundwater chemistry is related to the geology through which it percolates and this affects the chemistry of the brewing water which can influence the produced beer. The hydrochemistry can have a direct effect on the type of beer produced, which combined with the hops, produce a uniquely distinctive flavour, colour and smell with each brewery producing their own trademark beer. The major natural inorganic constituents calcium (Ca^{2+}), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}) are important in the brewing process and varying degrees of these ions can alter the beer characteristics. Sulphate is the main controlling ion used to enhance the 'bitter' taste of beer. Calcium can decrease pH and alter the fermentability and clarification of the beer. Bicarbonate on the other hand leads to higher pH and increases the 'sweetness' of beer.



Groundwater sources require protection from potentially polluting activities, which could affect the water quality of the source. The Environment Agency have defined Source Protection Zones (SPZs) which have been afforded to some of the bigger abstractions particularly in Hereford where Bulmers Cider has six boreholes protected at Kings Acre.

The number of abstraction licences for the Devonian aquifer constitutes around 45% of all the recorded licensed abstractions within Environment Agency Wales. In addition, there are over 2300 private water supplies registered with the Local Authorities. This is most likely a very conservative estimate of the true figure with many private water sources, especially for single dwellings, being unregistered. At least 50% of the known private supplies are for domestic use only.

The Devonian Sandstone has been extensively used as building stone in the past (Figure 2.4). Silty mudstones were formerly used for brick and tile clay whereas sandstones were used locally for building stone. The fissile St Maughans Formation sandstone was used for paving and roofing. Limestone from the Bishop's Frome Limestone (Lower Devonian Sandstone) was quarried for building stone as well as lime burning (Barclay and Smith, 2002; Brandon, 1989). Along the valleys of the Lugg, Arrow and Wye glacial sand and gravel deposits overlie the Devonian bedrock. These deposits have been heavily exploited as sources of aggregate.

The main urban areas within the study area are Hereford, Leominster and Brecon. The dominant land uses in the study area are dairy and sheep farming as well as arable and grazing land.

Groundwater quality issues include the widespread use of nitrogen and phosphate rich fertilisers and the application of herbicides and pesticides. During 2001 Herefordshire and the south-east borderlands of Wales were heavily affected by Foot and Mouth disease with several hundred carcass disposal pyres on the Devonian Sandstone outcrop area. Ash from these pyres was buried at some sites. Due to the nature of the aquifer effects from these activities are likely to be very localised and there have not been any recorded impacts on groundwater quality. Within Hereford and its environs groundwater is utilised extensively being abstracted from the shallow sand and gravel aquifer as well as the Devonian Sandstone bedrock. The groundwater quality of drift deposits in particular is likely to have been affected by a wide range of industrial pollutants reflecting the range of overlying urban and agricultural land-uses.

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

In order to assess the baseline groundwater quality, it is necessary to understand the system in which the groundwater is present i.e. the aquifer, its history and the surrounding geology. This requires information on the geology/stratigraphy, hydrogeological controls and mineralogy of the aquifer. These are described in this chapter prior to an assessment of the hydrochemical characteristics and geochemical interpretation.

3.2 Geology

The Devonian Sandstone outcrops in Wales and the Welsh borders covering a large triangular area of around 4500 km² from south Shropshire down to the Severn Estuary and westwards into South Wales (Figures 3.1-3.3). An isolated faulted block also crops out in Pembrokeshire. It consists of interbedded marls, mudstones, siltstones, calcretes and sandstone among which typical “red bed” hard sandstone is predominant. It includes the upper part of the Silurian (Downtonian age) in south Wales and the Welsh borderland (a transition from marine to fresh water deposition). Most of the formation outcropping in Wales is of continental facies (coastal plain, alluvial plain and fluvial deposits) which was deposited on the flanks of an eroding mountain chain, lying towards the north of Britain (Caledonian Highlands). The Upper and Lower parts of the succession nevertheless show some marine influence.

The Devonian Sandstone in Wales rests uncomfortably on Silurian rocks, deposited towards the end of the Caledonian orogeny. The orogeny caused a major uplift (rising of St George’s Land), resulting in a lack of Middle Devonian deposits across south and east Wales. In the Welsh Borders, there is a varied succession of Lower Devonian Sandstone Formation with thin representatives of the uppermost stage whereas in South Wales, the Lower Devonian sequences are thick and extensive, occasionally including Middle Devonian age rocks. Due to its complex stratigraphy, the strata are often defined by regions (south Wales, Hereford, Worcester and south Shropshire) and the relationship between Formations is complicated. The Devonian Sandstone becomes increasingly deformed towards the south, where it dips beneath the Carboniferous Coal Measures (Figure 3.3). The eastern border marks an erosional front to the formation. The Upper Devonian Sandstones, where present, rest uncomfortably upon Lower Devonian Sandstones.

The stratigraphy of the Devonian Sandstone aquifer in the area is shown in Table 3.1. The oldest formation is the Raglan Mudstone Formation of upper Silurian age (Downtonian). This is overlain by the Devonian St Maughans Formation (Dittonian), the Senni Beds and the Brownstones Formation (Breconian). The Upper Devonian rests unconformably upon the Lower Devonian whose strata thicken towards the south. There are few deposits of Middle Devonian in the study area. The Lower Devonian consists of fine-grained siltstones and mudstones, sandstone sheets and lenses overlain by cross-bedded sandstones and intraclast beds with intra-formational erosion surfaces. The uppermost Senni and Brownstones Formations comprise coarser lithologies with less siltstone and mudstone. The Upper Devonian Sandstone comprises grits, quartzite conglomerates, plateau beds and thick sandstones. Its limited outcrop is recorded mainly around the coalfields and on the peaks of the Brecon Beacon mountains.

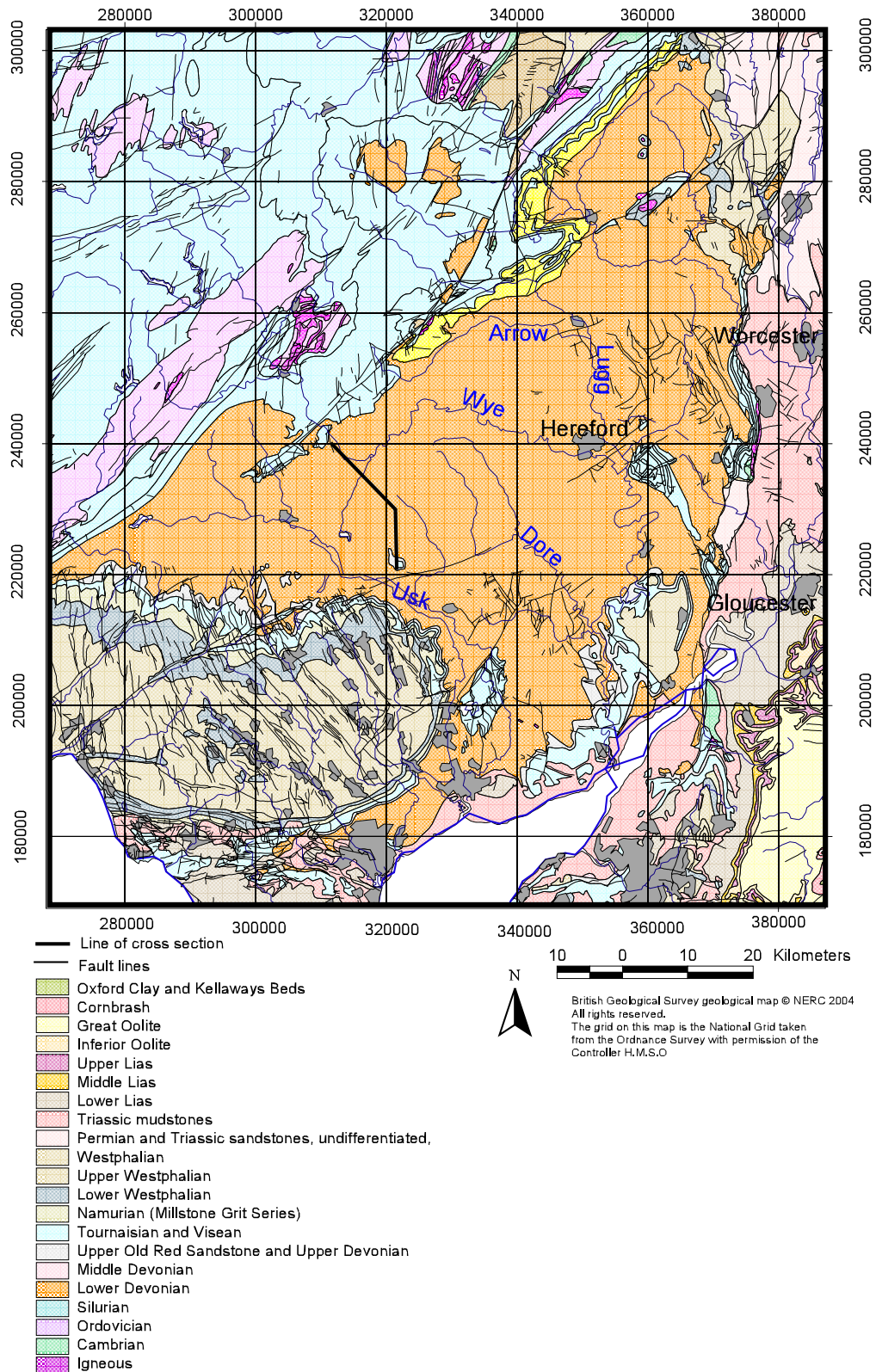


Figure 3.1 Geological map of the study area showing outcrop of Devonian Sandstone. Line of cross section shown on Figure 3.3.

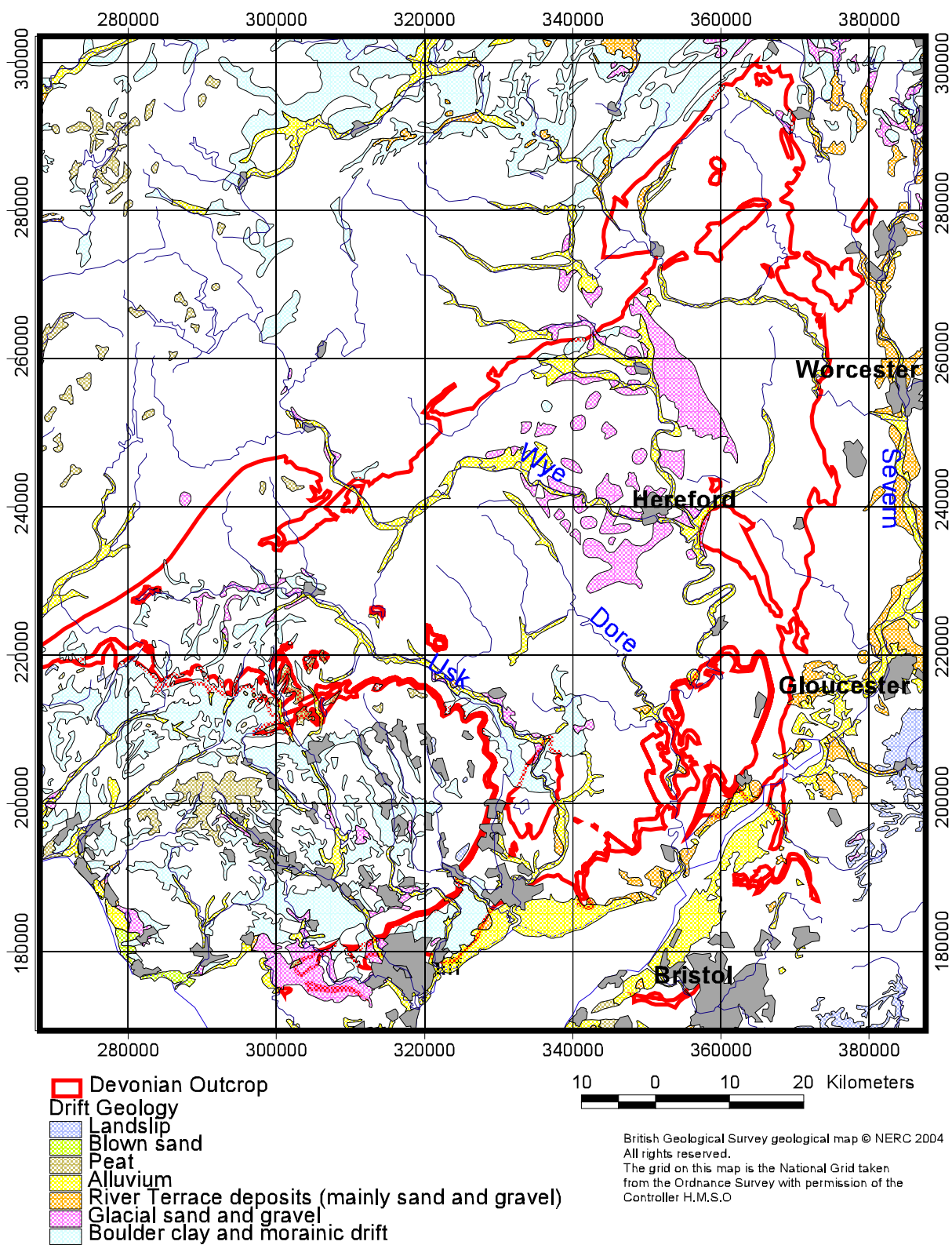


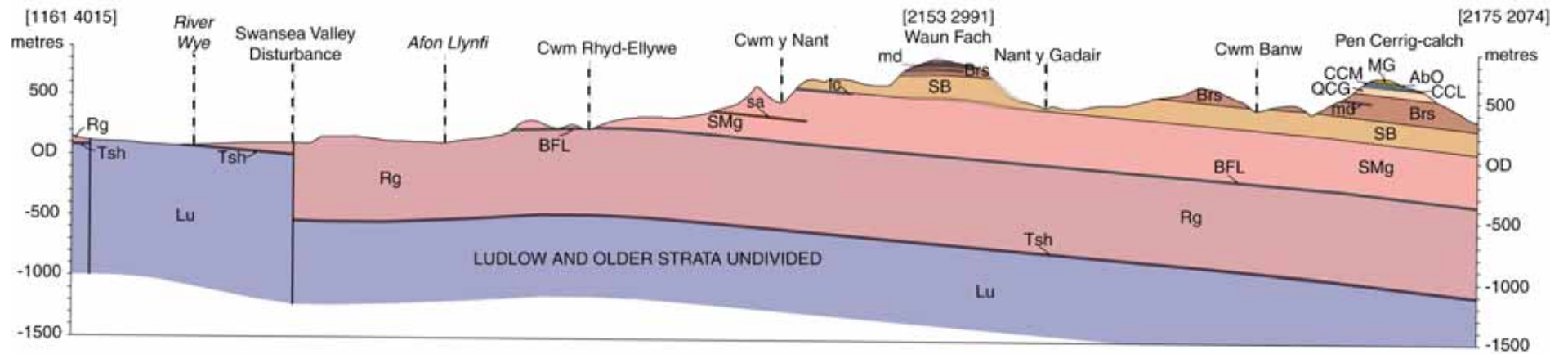
Figure 3.2 Map of superficial deposits in the study area. Solid black lines represent hydrochemical sections discussed in section 6.10.



Figure 3.3 Geological cross-section across the Black Mountains from (SO 1161 4015) to (SO 2175 2074) via Waun Fach (SO 2153 2991).

Table 3.1 Stratigraphy of the Devonian Sandstone in South Wales and Hertfordshire.

Age	Stage	Formation	Lithological Description
Quaternary		Superficial Deposits	Alluvium
			Glacial sand and gravel
Upper Devonian		Tintern Sandstone	Sandstone with subordinate mudstone and calcrete
		Quartz Conglomerate	Sandstone and quartz pebble conglomerate
Lower Devonian	Breconian	Brownstones	Fluvial channel sandstones with some mudstones
		Senni Beds	Fine to coarse-grained sandstones with calcrete and siltstone horizons
	Dittonian	St Maughans	Mudstones, siltstones, sandstones with infraformational conglomerates
	Downtonian	Raglan Mudstone	Mudstones and siltstones with subordinate sandstone, some calcrete horizons



KEY:

MG = Millstone Grit

QCG = Quartz Conglomerate Group

BFL = Bishop's Frome Limestone

sa = Sandstone

AbO = Abercriban Oolite

Brs = Brownstones Formation

Rg = Raglan Mudstone Formation

lc = Calcrete

CCM = Cwmyniscoy Mudstone Formation

SB = Senni Formation

Tsh = Temeside Mudstone Formation

md = mudstone

CCL = Castle Coch Limestone Formation

SMg = St. Maughans Formation

Lu = Ludlow and strata undifferentiated

Figure 3.4 Geological cross-section across the Black Mountains from [SO 1161 4015] to [SO 2175 2074] via Waun Fach [SO 2153 2991]

The Raglan Mudstone Formation comprises a thick succession of red-brown mudstone and siltstone, with subordinate cross-bedded sandstone (Figure 3.4). Generally, sandstone forms about 10% of the succession. The thickness of the formation varies from 385 m near Ross-on-Wye in the east to 800 m in the west. The succession was deposited in coastal alluvial floodplains, with sporadic marine influences. The climate was tropical (palaeogeographical reconstructions indicate that the area lay in the southern hemisphere within 30° of the Equator), with seasonal rainfall forming carbonate soils. The most mature and best developed of these calcretes lie at the top of the formation forming the Bishop's Frome Member, generally 2 to 5 m thick (regionally called Psammosteus Limestone).

The St Maughans Formation consists of around 630 m of mudstones and siltstones, sandstones and subordinate intraformational conglomerates. Most sandstones are red-brown to purple-brown but can also be yellow-brown to green-grey. A few calcretes also occur, but these have been mostly reworked. This formation is differentiated from the Raglan Mudstone Formation by thicker and coarser sandstone and conglomerate bands formed as the Anglo-Welsh basin became smaller, and therefore increasingly continental, as a result of uplift. However, mudstone and siltstone make up at least 60% of the St Maughans Formation.

The Senni Beds Formation consists dominantly of green sandstones. These sandstones range from fine to coarse-grained and are characterised by parallel lamination and cross-bedding with mica prominent on the bedding planes. Intraformation debris in the form of clasts of calcrete, siltstone and siderite litter the bases of individual sandstone bands. The Senni Beds are interpreted as representing relatively high discharge, mixed load, sand-dominated braided stream complexes. The conglomerates and sandstones represent in-channel deposits and the finer-grained lithologies overbank deposits.

The Brownstones Formation comprises pebbly cross-bedded, red-brown sandstones which formed an alluvial braided river system. Thickness of up to 1200 m have been recorded. Overall the formation shows an upward transition from sandstone with subordinate mudstones to a succession largely of sandstones. The deposits were carried by southerly flowing streams, the composition of detrital garnets suggesting that the dispersal system differed from those of the underlying St Maughans Formation.

The Upper Devonian deposits have a very limited outcrop, usually the uppermost metres on top of mountains. They have been subdivided into the Quartz Conglomerate Formation (red-brown sandstone and quartz pebble conglomerate) overlain by the Tintern Sandstone Formation (red-brown sandstone, pebbly in the upper part with subordinate red-brown mudstone and calcrete).

Superficial deposits cover less than 10% of the outcrop area. (Figure 3.2) Where present, they vary from a few metres to up to approximately 15 m in thickness and comprise mainly alluvium, river terrace deposits and glacial sand and gravel. The Wye Valley was affected by glaciation during the Devensian and the late Wye Glacier deposited gravel on outwash plains. Much of the areas around the River Lugg and Usk are covered by Till and fluvio-glacial gravels. Hence, the Superficial Deposits systematically occur in valleys and low altitude areas. Head is not mapped in the area, however it is likely that it occurs toward the base of the Brecon Beacons and Black Mountains.

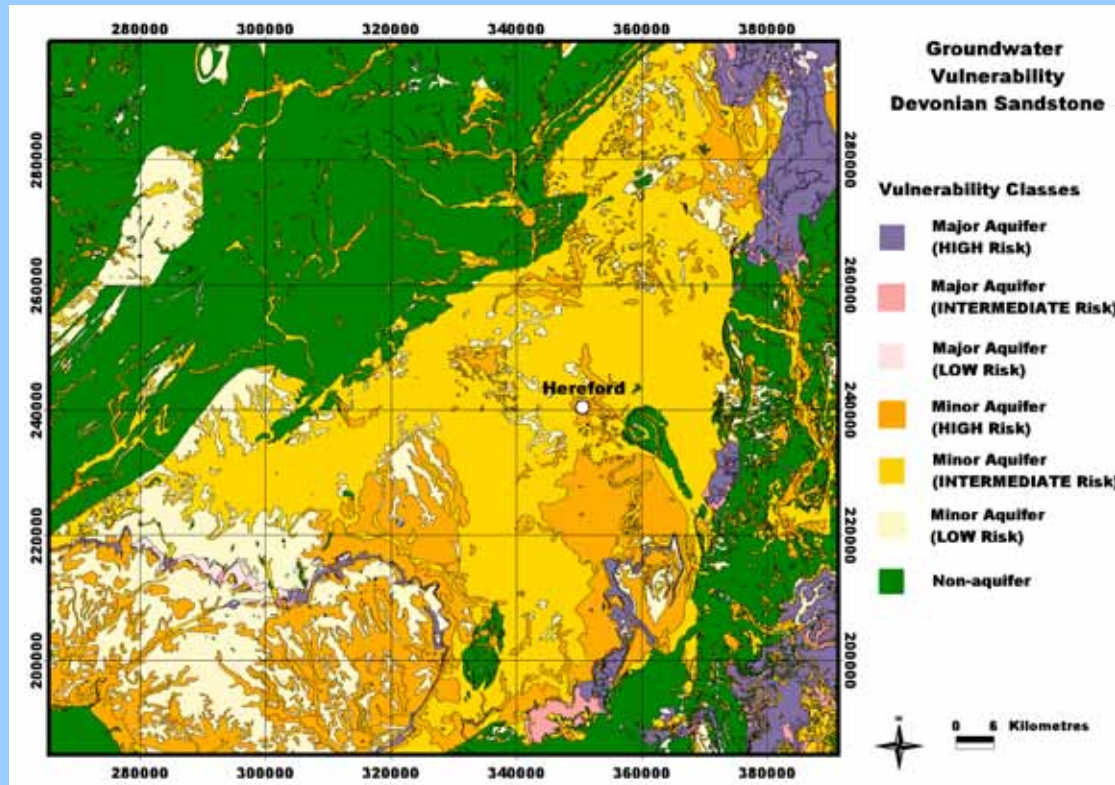
3.3 Hydrogeology

Superficial deposits are used as a groundwater source locally, mostly where they are in hydraulic continuity with the overlying rivers and, therefore, possess a greater yield potential for water use. However, such aquifers are vulnerable to surface contamination (Box 3.1). It is also possible that isolated sand and gravel lenses form small aquifers.

Box 3.1 The vulnerability of groundwater in the Devonian Sandstone aquifer

The Devonian Sandstone is classified as a Minor Aquifer (orange on map) that is sub-divided according to the risk of becoming contaminated from human activities (associated mainly with agricultural practices, urbanisation, industrial processes, disposal of wastes and spillage's of chemicals) on the basis of the leaching potential of overlying soil and drift. The Wye Valley is typically a rural landscape with arable and grassland being the dominant land-use. The aquifers are at most risk from agricultural chemicals such as pesticides and fertilisers (natural and man-made), from diffuse agricultural runoff and from domestic oil storage tanks and septic tanks in particular.

Figure 1. The designation of Nitrate vulnerable Zones across much of Herefordshire in an attempt to control the diffuse pollution risk posed to surface and groundwater.



The vulnerability of an aquifer can be assessed from the nature and thickness of the unsaturated zone and overlying deposits (soil and drift), the depth of the water table and the speed with which water flows through this zone. The Environment Agency has therefore prepared groundwater vulnerability maps covering the UK (Refer to Policy and Practice for the Protection of Groundwater, 1998 for more detailed information). These maps utilise soil property information to predict leaching characteristics of the soil. 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.

The Devonian Sandstone aquifers are multi-layered aquifers with interbedded mudstone (marls), siltstone, limestone and sandstone strata. The marls (where present at outcrop), which help to confine the underlying, sandstone aquifers afford some degree of protection. However, locally exposed siltstones, limestones (cornstones) and sandstones are more susceptible to pollution. The Devonian Sandstone is highly fractured and fissured, which may allow faster pathways into the aquifer. The overlying soils have little ability to attenuate diffuse source pollutants, particularly in the 'higher risk' zones on the map

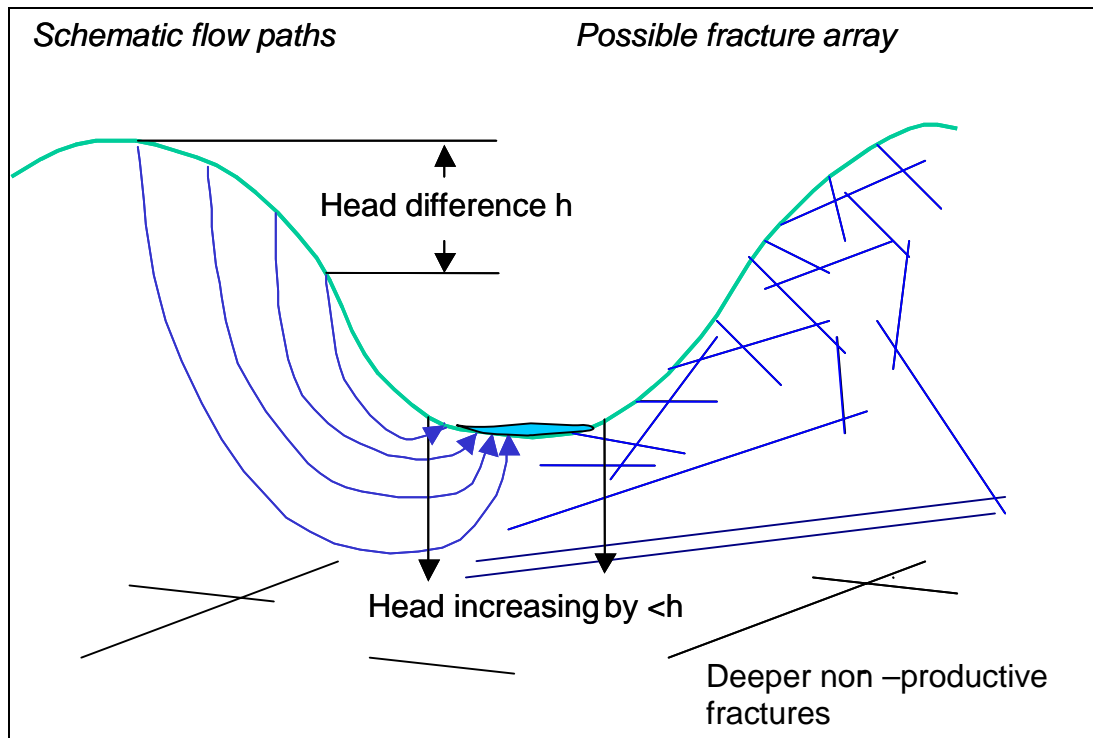


Figure 3.5 Simplified schematic diagram showing groundwater flow in an upland fractured aquifer.

The Devonian Sandstone Group exhibits a low primary porosity with predominant groundwater flow occurring through fractures (Jones et al., 2000). The fractured nature of the aquifer implies a decrease of permeability with depth as fractures tend to tighten. The figure of 40 to 50 metres is often regarded as a maximum depth for fracture development (Jones et al., 2000; Lewis et al., 1983). It is highly likely that the groundwater flow is topographically controlled in the upper weathered horizons of the sandstone regardless of lithology. In addition, the large differences in altitude provide a strong potential hydraulic gradient forcing groundwater movement through the aquifer (measured rest water levels range from 46 to 160 m aOD). A simplified schematic showing the dominant groundwater flow in an upland fractured aquifer is shown on Figure 3.5. It is likely that a similar flow system can be applied to the Devonian aquifer. A rough estimate of hydraulic gradient from the Black Mountain to the Wye Valley is 9.7×10^{-4} , the topographic gradient in the Black Mountains being of the order of 9.0×10^{-2} .

The Brownstones Formation and the Senni Beds are the best yielding formations in the Devonian. The Raglan Mudstone and St Maughans formations comprising largely mudstones and finer-grained sandstones are less productive, although they do sustain local supplies and springs. The Upper Devonian Sandstone, due to its limited outcrop in the area, does not play a significant role in the local hydrogeology. The base of the St Maughans sandstone units are commonly marked by large springs, for example the Cross Well near Bodenham (NGR 3513 2513). Most of the waters from the Devonian Sandstone are hard (Jones et al., 2000; Lewis et al., 1983). The hard water favours tufa formation and fractures are commonly lined with travertine in cuttings or excavations (e.g. NGR 3508 2508). Tufa was also observed along a spring line during the field sampling near Lower Blakemere (Figure 3.6; NGR 3357 2404). Richardson (1946) describes spring lines linked to the Bishop's Frome Limestone occurrence within the Devonian. Reports of saliferous and saline (connate) waters (Box 3.2) are made by Richardson (1947). More recent investigations have also recorded the occurrence of localised groundwater sources with elevated chloride. Both the Upper and the Lower Devonian Sandstone are significantly anisotropic and, in general, they behave as a multi-layered aquifer (alternation of low to high permeability strata) containing perched water within

isolated sandstone blocks. The aquifer properties of the Devonian are summarised in Table 3.2 from Wilton (2003). The typical range for hydraulic transmissivity is 10 to 100 m² d⁻¹. Pumping test analyses give transmissivity ranges between 10⁻⁶ to 350 m² d⁻¹ with a mean value of 51 m² d⁻¹ and a median of 14.3 m² d⁻¹. There are no permeability or porosity measurements available for the Devonian outcrop. The only existing data are for Devonian rocks at depth, highlighting low values (porosity from less than 3% to 20% countrywide). Permeability measurements of up to 0.11 m d⁻¹ have been obtained at depths greater than 800 m (Jones et al., 2000).



Figure 3.6 Sample of tufa found near Blakemere showing small shell fragments and root channels (SO 3570 4041)

3.4 Aquifer mineralogy

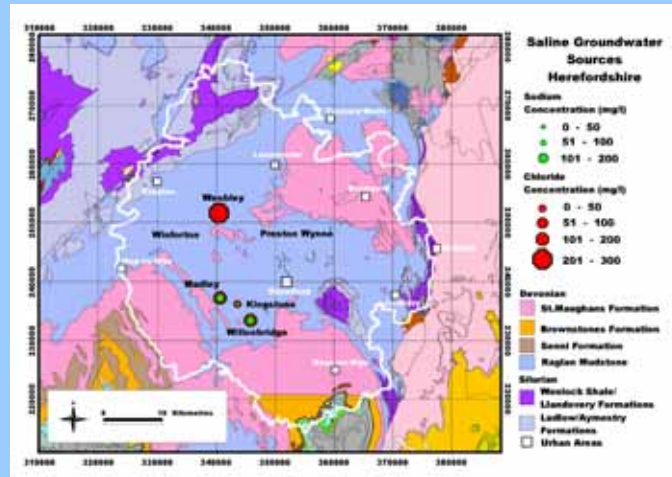
The sandstones from the Raglan Mudstone Formation are generally medium- to coarse-grained with large-scale cross-bedding. They are conspicuously micaceous with large muscovite¹ flakes, particularly in the upper parts weakening the overall rock competence. Carbonaceous plant fragment are not uncommon. The sandstones are generally highly calcareous, usually greywackes and sub-greywackes with variable amounts of biotite, muscovite, potassium feldspar, albite-oligoclase and some fine-grained igneous rock-fragments. Mudstone pellets and abundant calcrete clasts also occur. Detrital garnet is common and traces of tourmaline, zircon, sphene, epidote and pyroxene as well as glauconite and phosphatic fish fragments are found. Secondary quartz occurs as a cement forming syntaxial overgrowths. Authigenic clays (kaolinite, chlorite and white-mica) are common. Chlorite² commonly replaces biotite. Most of the rocks are iron stained giving rise to the characteristic red-brown colour of outcrops and soils. The overall mineral suite, especially the large abundance of garnet and muscovite flakes is consistent with derivation from the Caledonian metamorphic complexes further north. Dolomite is known to be present in some of the Devonian calcretes (Allen, 1961; Jenkins, 1998). Jenkins (1998) showed extensive dolomitisation at Lydney and a patchy distribution of dolomite at Llansteffan. In the Clee Hills, to the north of the study area there is sufficient dolomite in the lower part of the Abdon calcretes for Allen (1961) to name it the Hillside Dolomite Formation. Stream sediment data (BGS, 2000) show that the Devonian outcrop area has high Mg which may reflect the presence of high-Mg calcite cement as well as dolomite in the calcretes.

¹ Muscovite: $KAl_2[Si_3AlO_{10}(OH,F)_2]$

² Chlorite: "ideal formula" $(Mg)_3(OH)_6Mg_3[Si_4O_{10}(OH)_2]$

Box 3.2 The occurrence of brackish groundwaters

Occurrences of 'slightly brackish' or 'salty' springs and boreholes have been recorded across Herefordshire and the borderlands of Wales since the 1920's. Springs sources are noted in the Wye valley at Winforton and north at Weobley. More recently, elevated chloride concentrations have been recorded in boreholes to the south and west of Hereford and also to the north-west of Ledbury:



Conductivity (SEC) values at these sites have been recorded up to $>1300 \mu\text{S cm}^{-1}$ with concentrations of chloride exceeding 100 mg l^{-1} . The highest conductivity values appear to correlate with abstraction of groundwater from below 50m depth from the Raglan Mudstone Formation.

What is the source of chloride?

Chloride is a conservative ion and whilst ion exchange may account for the elevated sodium concentrations also found at these sites it cannot account for the elevated Cl^- concentrations recorded. The source of this 'brackish or salty' groundwater is unknown but potential sources for Cl^- ions include:

- Dissolution of evaporite deposits at depth
- Mixing with saline waters from underlying strata
- Anthropogenic inputs from substances such as road salts and/or fertilisers.

There are no known occurrences of evaporite minerals within the Devonian Sandstone making it unlikely that dissolution of such minerals is important.

Marine sediments may retain chloride for long periods of time, either as Na-Cl crystals or as a Na-Cl-rich solution. Such conditions were present during the transition from the later Silurian into the more deltaic/fluvial Devonian period and these impregnated sediments may now be acting as a slow-release source of chloride rich water. The correlation of Cl with Na, I and B also supports the mixing of recent and (saline) formation waters.

A number of major faults run through the Devonian sediments and these along with deep groundwater circulation are proposed as a mechanism for groundwater mixing with the shallower flow pathways.

Locally, human activities such as road salting and the use of fertilisers will add to Na and Cl levels in shallow groundwaters.

Table 3.2 Devonian Sandstone aquifer properties (from Wilton 2003).

Aquifer Property	Description
Aquifer classification	Minor aquifer, intermediate to high vulnerability
Lithology	Extremely stratified, interbedded mudstone, siltstone and sandstones
Porosity (intergranular)	<20%
Flow mechanisms	predominantly fracture flow. Within the Brownstones Formation intergranular flow may become important. Localised calcareous bands and/or areas where calcareous cement has been leached may provide zones of increased permeability. The Bishop's Frome limestone is a known spring horizon. Within drift deposits sand and gravel lenses may also provide areas of localised higher permeability.
Transmissivity	Typically $10^{-6} \text{ m}^2 \text{ d}^{-1}$ to $350 \text{ m}^2 \text{ d}^{-1}$. Regional values likely to be 5 to $30 \text{ m}^2 \text{ d}^{-1}$ for the Raglan Mudstone and St Maughans Formation and up to $250 \text{ m}^2 \text{ d}^{-1}$ for the Brownstones Formation.
Permeability	Low primary permeability, estimated $0.1\text{-}5 \text{ m.d}^{-1}$. Fractures, faulting and mineral dissolution give rise to higher secondary permeability.
Effective aquifer thickness	50-100 m
Hydraulic gradient	Estimated as $10^{-2}\text{-}10^{-1}$ regionally, down to 10^{-3} locally Steep regional values reflect heterogeneity of aquifer and the influence of topography.
Storativity	$1.9 \times 10^{-4} - 5.0 \times 10^{-2}$ Values indicate semi-confined to confined conditions.
Specific capacity	$8\text{-}40 \text{ m}^3 \text{ d}^{-1} \text{ m}$
Recharge	Total rainfall (MORECS) 820 mm a^{-1} Effective precipitation $150\text{-}200 \text{ mm a}^{-1}$

Mudstones from the Raglan Mudstone Formation are mainly red-brown to brick-red and in places display green-grey beds or “reduction” spots. The mudstones lying directly beneath sandstone are generally green in colour due to the presence of reduced Fe (Fe^{2+}). The mudstones are technically siltstones as the clay fraction forms only 12% of the detrital grains. Most of the grains are quartz and brown mica flakes. The clay component comprises 40 to 45% illite, 20 to 40% smectite and 15 to 25% chlorite. Ferric oxides form most of the cement and impart the characteristic red colour. The mudstones are only weakly calcareous in their fresh state (less than 0.5% CaCO_3). The calcrete contains a cement of up to 10% CaCO_3 .

The sandstones from the St Maughans Formation are less micaceous than the Raglan Mudstone Formation although they are similar in composition. Garnets are less abundant, however, there is an increase in igneous and sedimentary rock fragments. Heavy metal analyses show that the decrease in garnet content is compensated by apatite, rutile, tourmaline and zircon. Epidote, staurolite and chromite are very minor constituents.

Mudstones from the St Maughans Formation are also similar to those of the Raglan Mudstone Formation, although generally thinner. Calcretes present at the top of the Raglan Mudstone Formation and within the St Maughans Formation form calcium-rich deposits.

3.5 Rainfall chemistry

Rainfall provides the initial input of solutes to groundwater. The rainfall derived fraction of some solutes such as Na, Cl and N-species in groundwater can be significant. An average precipitation composition for the Welsh uplands was taken from the Plynlimon Station (NGR SN 823 854; Neal et al., 1992). A second analysis from Ridgehill Station (SO 508 353) for 1988 data, closer to the site area, is given in Table 3.3 for comparison. The data from Plynlimon has been multiplied by 3 in the right-hand column in order to estimate the approximate enrichment due to evapotranspiration and hence the chemistry of infiltrating rainwater. Although Cl may be assumed to behave conservatively during most recharge conditions, this is not the case for other elements e.g. K and N-species which may be taken up by vegetation, and concentrations may, therefore, be less in recharge waters than rainfall. Atmospheric inputs of chloride are typically around 6 to 7 mg l⁻¹ (although this may still be above 'baseline' concentration because of atmospheric pollution inputs). Chloride concentrations may be subject to alteration by agricultural pollution or mixing with other water. Nevertheless, Table 3.3 indicates the order of magnitude of concentrations expected prior to reaction with vegetation or aquifer minerals.

3.6 Land use in the area

Most of the area of study is utilised for either arable crops, mostly fruit and hops (17.9%) or managed grassland including sheep and dairy farming or park recreation (74.7%). Urban areas occupy only about 2% of the sandstone outcrop. The remainder is mainly forested. Arable land occurs across the east, north and south. Forestry occurs mainly in the western areas (Figure 3.7).

Table 3.3 Summary of rainfall data for the Plynlimon and Ridgehill weather stations.

	Mean rainfall concentration, Plynlimon, (Neal et al., 1992)	Rainfall (x3) Enrichment by evapotranspiration	Annual mean Ridgehill Station, 1988
Ca (mg l ⁻¹)	0.18	0.54	0.40
Mg (mg l ⁻¹)	0.3	0.9	0.24
Na (mg l ⁻¹)	2.6	7.8	1.79
K (mg l ⁻¹)	0.13	0.39	
Cl (mg l ⁻¹)	5.1	15.3	3.48
SO ₄ (mg l ⁻¹)	1.6	4.8	3.31
NO ₃ - N (mg l ⁻¹)	0.8	2.4	1.92
PO ₄ (mg l ⁻¹)	0.04	0.12	
F (µg l ⁻¹)	30	90	
Si (µg l ⁻¹)	340	1020	
Al (µg l ⁻¹)	8.0	24	
B (µg l ⁻¹)	3.4	10.2	
Ba (µg l ⁻¹)	1.6	4.8	
Cr (µg l ⁻¹)	2.3	6.9	
Cu (µg l ⁻¹)	1.6	4.8	
Fe (µg l ⁻¹)	6.6	19.8	
Li (µg l ⁻¹)	0.1	0.3	
Mn (µg l ⁻¹)	1.2	3.6	
Ni (µg l ⁻¹)	0.4	1.2	
Pb (µg l ⁻¹)	6.0	18	
Sr (µg l ⁻¹)	2.1	6.3	
Zn (µg l ⁻¹)	9.2	27.6	

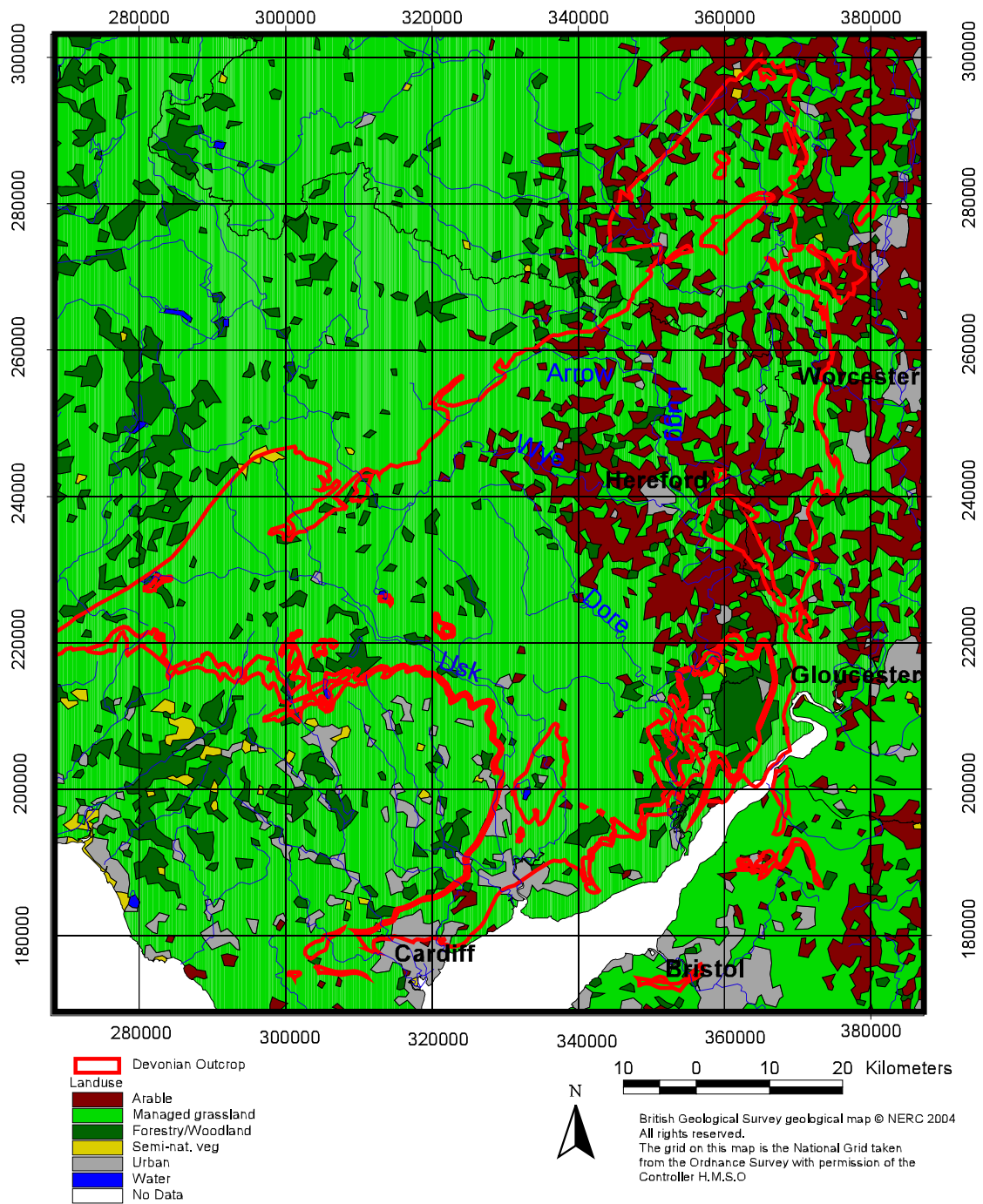


Figure 3.7 Land use map of the study area.

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 29 water samples were collected during June 2003. Twenty-three of these samples were taken from private farm boreholes (11) and springs (12) mainly from the catchment of the River Wye. The remaining six samples were collected from surface water (4 from the River Wye and two upstream, one from a tributary located on the western edge of the Black Mountains and the other from the River Wye at BUILT Wells (where the River Wye flows over Silurian rocks). The sample sites were selected to provide a good areal coverage over the Wye catchment. River samples were also included to enable a comparison between surface and groundwater geochemistry. The sampling was focussed along two main traverses (Figure 4.1) in order to study the chemical evolution of groundwater along the expected direction of groundwater flow.

Pumped groundwater samples represent water entering the borehole over the entire length of any screened interval. The sample may, therefore, represent a mixture of waters with different chemistries especially if the aquifer is vertically stratified in terms of water quality. Despite this, the results can be used to interpret regional variations which exist within the aquifer and to assist in predicting groundwater chemistry across the aquifer. It was also requested that the borehole owners allow the pump to run for about 15 min prior to sampling, in order to purge the borehole of any stagnant water.

Where possible, the parameters pH, dissolved oxygen (DO) and redox potential (Eh) were measured in an anaerobic flow-through cell (Figure 4.2 and Figure 4.3). For the springs, the parameters were measured close to the point of discharge. Other on-site measurements included temperature, specific electrical conductance (SEC) and alkalinity by titration. Samples were collected for chemical analysis in polyethylene bottles. Water to be analysed for major and trace elements was filtered through 0.45 µm filters. Water for cation and trace element analysis was acidified within an aliquot to 1% v/v HNO₃ to minimise adsorption onto container walls. Additional samples were collected in glass bottles for stable isotope ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) analysis. Samples for dissolved organic carbon (DOC) were filtered using a 0.45µm Ag-membrane filter and collected in Cr-acid washed glass bottles.

Major cations and sulphate were analysed by ICP AES and a wide range of trace elements by ICP MS. Nitrogen species were analysed using automated colorimetry (SKALAR) at the Environment Agency laboratories in Nottingham. Iodide was measured by automated colorimetry using a Technicon AAI, and Br, F and Cl were analysed by ion chromatography using Dionex in the BGS laboratory in Wallingford. Stable isotope analysis was also completed in the BGS laboratories by mass spectrometry and the results reported relative to SMOW for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and PDB for $\delta^{13}\text{C}$.

4.2 Historical data

Very limited historical water quality data records were available for this area. The Environment Agency monitoring network for most of this region is fairly recent (data from 2000). A further 31 groundwater analyses were used, mainly relating to samples from the eastern edge of the Devonian outcrop, from 1988 to present. Some old analyses were also found in the National Well Archive in BGS Wallingford, however they were not included as the analyses were incomplete. Such sites, however, are useful guides while assessing spatial and temporal variations.

4.3 Data handling

The plots and tables of geochemical data are based on both the new sampling programme and historical data (one analysis per site for analyses from 2001 to 2002). Historical data with an ionic charge balance greater than 10% were rejected. For samples collected within the project, all samples presented an ionic balance below 10% (15 samples within 5%). A few spring samples did not have HCO₃⁻ concentrations so an assessment of ionic balance for these sites could not be completed.

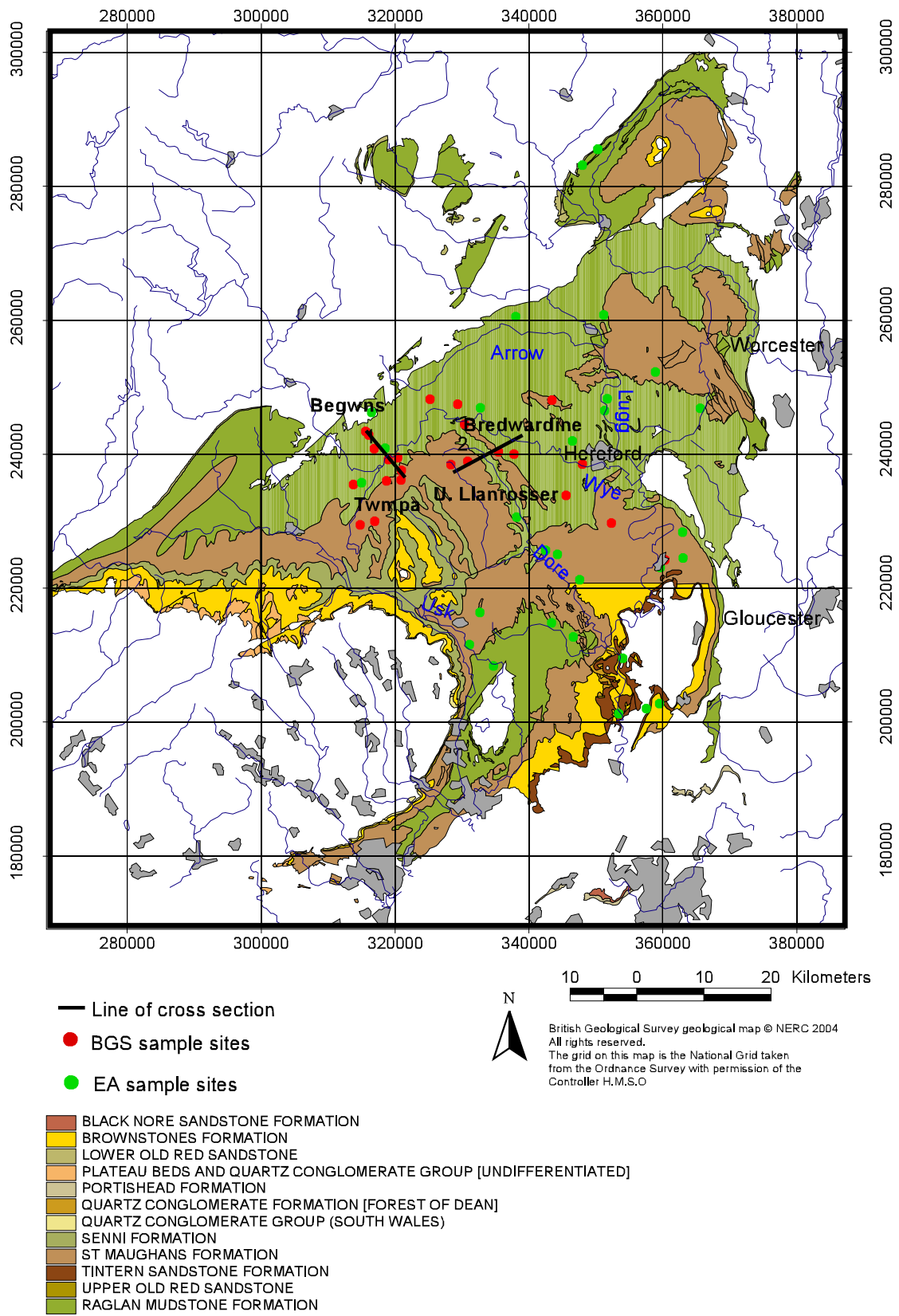


Figure 4.1 Map of the Devonian Sandstone showing sampling points, chemical traverses (section 6.10) and Environment Agency data locations.

Results which fell below detection limits were dealt with by substitution with half of the detection limit. However, changes in the detection limits both with time and between laboratories proved problematic in calculation of average result values. The median is more robust than the mean as an average, being less affected by outlying data and is, therefore, used together with the minimum, maximum and 97.7 percentile (mean plus two standard deviations). The 97.7 percentile for each determinant has been taken as an estimate of the upper limit of the concentration range being used to exclude outliers.

(a)



(b)



Figure 4.2 Sampling of the Devonian Sandstone: (a) from well at Little Maestroglywd (SO 2115 3765) and (b) from a spring at Pen-y-Cwm (SO 2107 3602).



Figure 4.3 Measuring pH, DO and Eh in a flow-through cell.

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

A summary of the data is shown in Table 5.1 and Table 5.2 for the study area. This section presents the fundamental hydrochemical characteristics of the groundwaters in the study area highlighting the features of the summary table. The geochemical processes responsible for controlling groundwater chemistry are reviewed and discussed in Chapter 6.

Table 5.1 Summary of major and minor elements in the Devonian Sandstone.

Parameter	units	Field data, Major & minor elements					Upper baseline*	N
		min.	max.	median	mean	97.7th percentile		
T	°C	9.5	16.9	11.5	12.1	16.6		46
pH		6.29	9.85	7.32	7.48	8.66		53
Eh	mV	293	459	378	385	448		20
DO	mg l ⁻¹	0.70	10.0	5.61	5.53	9.86		41
SEC	µS cm ⁻¹	140	1338	523	577	926		53
δ²H	‰	-50.1	-43.1	-47.9	-47.4	-43.6		10
δ¹⁸O	‰	-7.5	-5.9	-7.2	-7.1	-6.2		10
δ¹³C	‰	-22.0	-15.7	-18.4	-18.6	-16.2		10
Ca	mg l ⁻¹	4.11	157	77.3	76.3	141		54
Mg	mg l ⁻¹	0.55	33.6	8.27	11.1	29.4		54
Na	mg l ⁻¹	5.12	273	13	28.7	139		54
K	mg l ⁻¹	0.05	18.0	1.9	3.08	12.7		54
Cl	mg l ⁻¹	5.68	226	21.2	32.6	108		54
SO₄	mg l ⁻¹	7.73	43.5	19.5	21.5	41.7		54
HCO₃	mg l ⁻¹	91.4	398	241	252	385		50
NO₃-N	mg l ⁻¹	<0.002	15.6	2.15	4.05	13.3	1-3	49
NO₂-N	mg l ⁻¹	<0.001	0.033	0.001	0.002	0.009		50
NH₄-N	mg l ⁻¹	<0.003	0.150	0.009	0.018	0.093		50
P	mg l ⁻¹	<0.02	0.075	<0.02	<0.02	0.07		48
DOC	mg l ⁻¹	0.49	3.99	1.06	1.45	3.88		23
F	mg l ⁻¹	<0.1	1.45	0.13	0.15	0.22		23
Br	mg l ⁻¹	0.015	0.960	0.050	0.102	0.544		23
I	mg l ⁻¹	0.002	0.064	0.003	0.007	0.038		23
Si	mg l ⁻¹	1.43	13.33	4.01	4.20	6.04		48

* estimated upper baseline for elements modified by anthropogenic influences

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

Table 5.2 Summary of trace elements in the Devonian Sandstone.

Trace elements	units	min.	max.	median	mean	97.7th percentile	N
Ag	µg l ⁻¹	<0.05	0.13	0.03	0.04	0.12	23
Al	µg l ⁻¹	<1	69	7	11	60	24
As	µg l ⁻¹	<0.5	12.6	<0.5	0.922	2.98	43
Au	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
B	µg l ⁻¹	<20	161	<20	29.3	137	27
Ba	µg l ⁻¹	91.7	659	337	349	624	23
Be	µg l ⁻¹	<0.05	0.09	<0.05	<0.05	<0.05	23
Bi	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
Cd	µg l ⁻¹	<0.05	0.10	<0.05	0.04	0.05	44
Ce	µg l ⁻¹	<0.01	0.22	<0.01	0.03	0.19	23
Co	µg l ⁻¹	<0.02	0.08	<0.02	<0.02	0.07	23
Cr	µg l ⁻¹	<0.5	4.14	1.95	1.75	3.76	44
Cs	µg l ⁻¹	<0.01	0.020	<0.01	<0.01	0.013	23
Cu	µg l ⁻¹	0.40	18.10	1.22	2.49	9.37	46
Dy	µg l ⁻¹	<0.01	0.080	<0.01	0.019	0.080	23
Er	µg l ⁻¹	<0.01	0.080	<0.01	0.014	0.060	23
Eu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Fe	µg l ⁻¹	1.5	3170	20.0	225	2115	44
Ga	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
Gd	µg l ⁻¹	<0.01	0.120	0.020	0.028	0.107	23
Ge	µg l ⁻¹	<0.05	0.060	<0.05	0.027	0.037	23
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	23
Hg	µg l ⁻¹	<0.1	0.200	<0.1	<0.1	0.134	23
Ho	µg l ⁻¹	<0.01	0.020	<0.01	<0.01	0.013	23
In	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
La	µg l ⁻¹	<0.01	0.150	<0.01	0.031	0.137	23
Li	µg l ⁻¹	2.00	27.0	5.00	7.48	26.3	23
Lu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Mn	µg l ⁻¹	<2	950	3.0	37.4	174	45
Mo	µg l ⁻¹	<0.1	4.50	<0.1	0.491	2.26	23
Nb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Nd	µg l ⁻¹	<0.01	0.350	0.040	0.073	0.343	23
Ni	µg l ⁻¹	<0.2	0.500	<0.2	0.126	0.302	23
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
Pb	µg l ⁻¹	<0.1	5.760	<0.1	0.691	1.00	42
Pd	µg l ⁻¹	<0.2	1.00	<0.2	0.237	1.00	27
Pr	µg l ⁻¹	<0.01	0.060	<0.01	0.012	0.053	23
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Rb	µg l ⁻¹	0.470	6.81	1.72	1.88	4.95	23
Re	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Rh	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
Sb	µg l ⁻¹	<0.05	0.100	<0.05	<0.05	0.080	23
Sc	µg l ⁻¹	1.00	1.00	1.00	1.00	1.00	23
Se	µg l ⁻¹	<0.5	2.50	0.500	0.639	2.30	23
Sm	µg l ⁻¹	<0.05	0.100	0.010	0.022	0.087	23
Sn	µg l ⁻¹	<0.05	0.450	<0.05	0.060	0.212	23
Sr	µg l ⁻¹	65.0	1962	275	390	1356	23
Ta	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	23
Tb	µg l ⁻¹	<0.01	0.010	<0.01	<0.01	0.010	23
Te	µg l ⁻¹	<0.05	0.080	<0.05	<0.05	<0.05	23
Th	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	23
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	23
Tl	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	23
Tm	µg l ⁻¹	<0.01	0.010	<0.01	<0.01	<0.01	23
U	µg l ⁻¹	0.25	39.2	1.38	4.89	28.4	23
V	µg l ⁻¹	<0.2	11.5	1.10	2.15	8.99	23
W	µg l ⁻¹	<0.02	0.24	<0.02	0.02	0.13	23
Y	µg l ⁻¹	0.01	0.96	0.11	0.19	0.66	23
Yb	µg l ⁻¹	<0.01	0.10	0.01	0.01	0.05	23
Zn	µg l ⁻¹	0.25	105.8	6.30	17.4	61.1	46
Zr	µg l ⁻¹	<0.02	0.090	0.020	0.034	0.083	23

5.2 Water types and physicochemical characteristics

The pH of the groundwaters showed a relatively wide range (6.29–9.85) but were generally circumneutral to slightly alkaline (median pH 7.32). Most of the waters are fresh (SEC mean and median values are respectively 523 and 576 $\mu\text{S cm}^{-1}$), however some samples had a higher SEC between 800 and 1340 $\mu\text{S cm}^{-1}$. Where DO and Eh have been measured, the waters are mainly moderately reducing to oxidising (minimum and median values for DO and Eh were 0.7 and 5.61 mg l^{-1} and 293 and 378 mV respectively).

The data are plotted on a Piper diagram in **Error! Reference source not found.** Most of the groundwaters were of Ca-HCO₃ to Ca-Mg-HCO₃ type. Several groundwaters from the Raglan Mudstone (and one from the St Maughans Formation) trend towards higher Na. However, this increase in Na is not reflected to the same degree in Cl, giving rise to waters of Na-HCO₃ type (Figure 5.1).

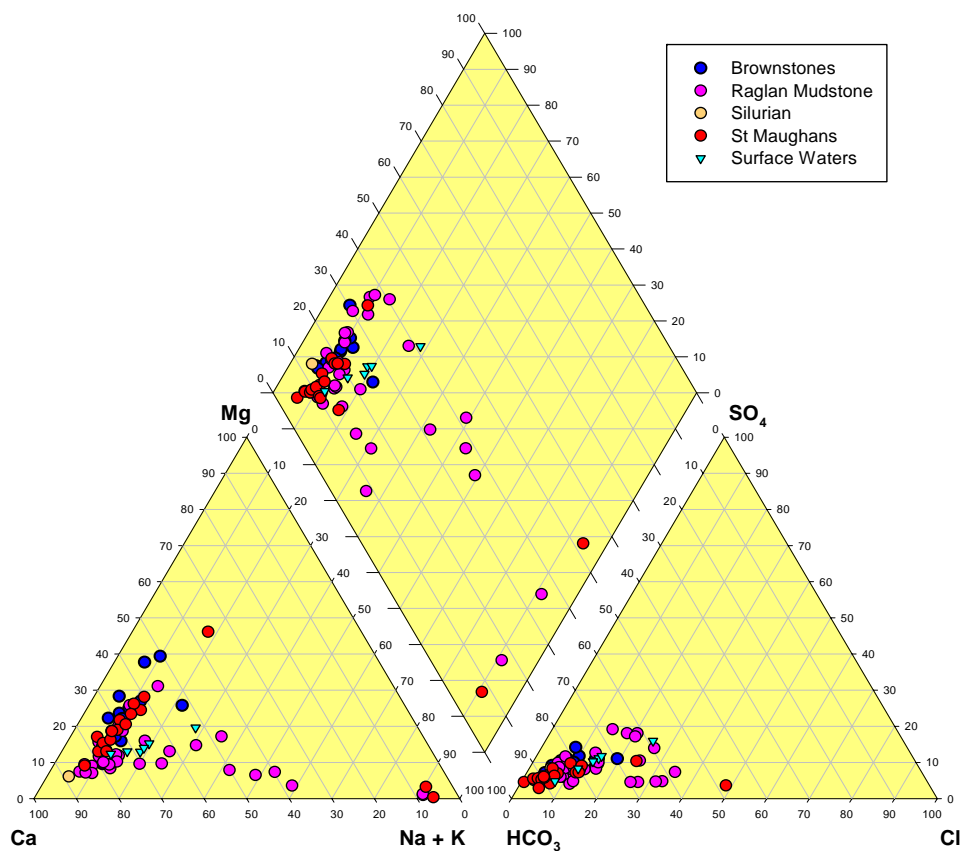


Figure 5.1 Piper plot Devonian Sandstone waters.

The samples collected from the River Wye samples overlap with those of the groundwaters regarding the relative proportion of anions and cations (Figure 5.1). The river sample containing the greater Mg and Na was taken on Silurian rocks before the river flows onto Devonian sandstone.

Summary data are shown graphically on boxplots (Figure 5.2 and Figure 5.4) and cumulative frequency plots (Figure 5.3 and Figure 5.5). The boxplots (or box and whisker plots) display the ranges of data and are designed to highlight the distribution of data on a percentile basis. The black line represents a diluted seawater curve which has been normalised to the median Cl of the samples. This provides a general indication in most aquifers of enrichments due to water-rock interaction above the marine-derived rainfall or connate water input. Cumulative probability plots are useful in

visualising the distribution of data and may be of use in determining outlying data or discriminating pollution. Geochemical processes may alter the distribution of populations in several ways (Box 5.1).

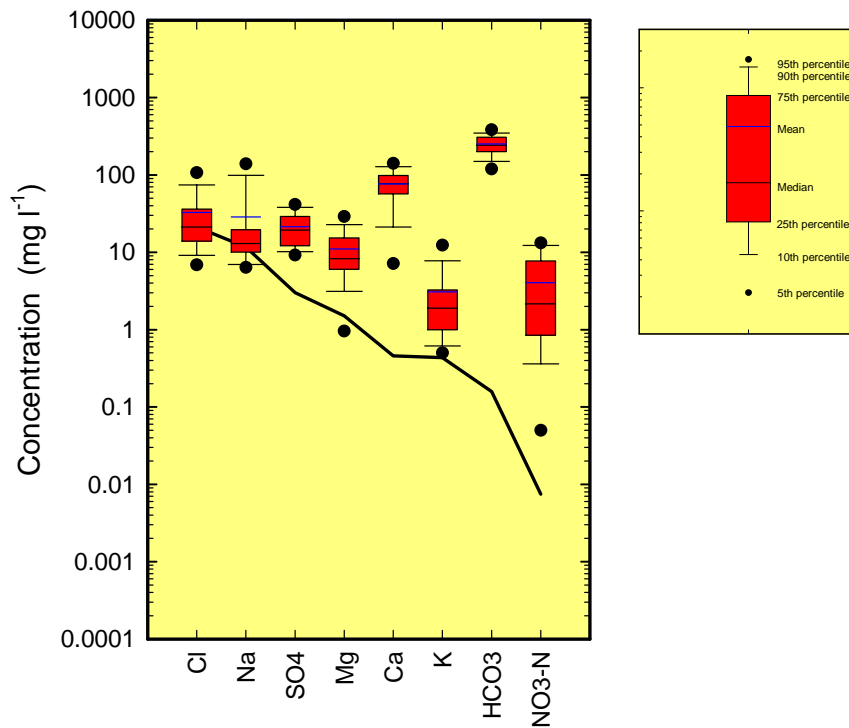


Figure 5.2 Range of major ion concentrations in the Devonian Sandstone.

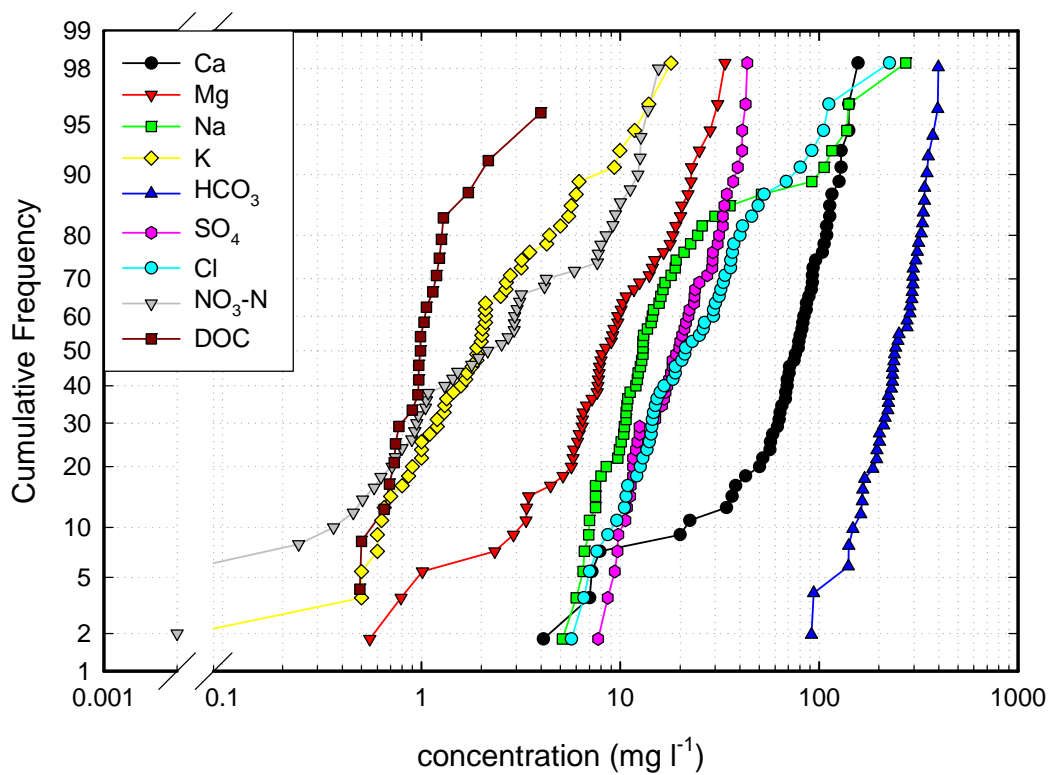


Figure 5.3 Cumulative plots of major elements for the Devonian Sandstone.

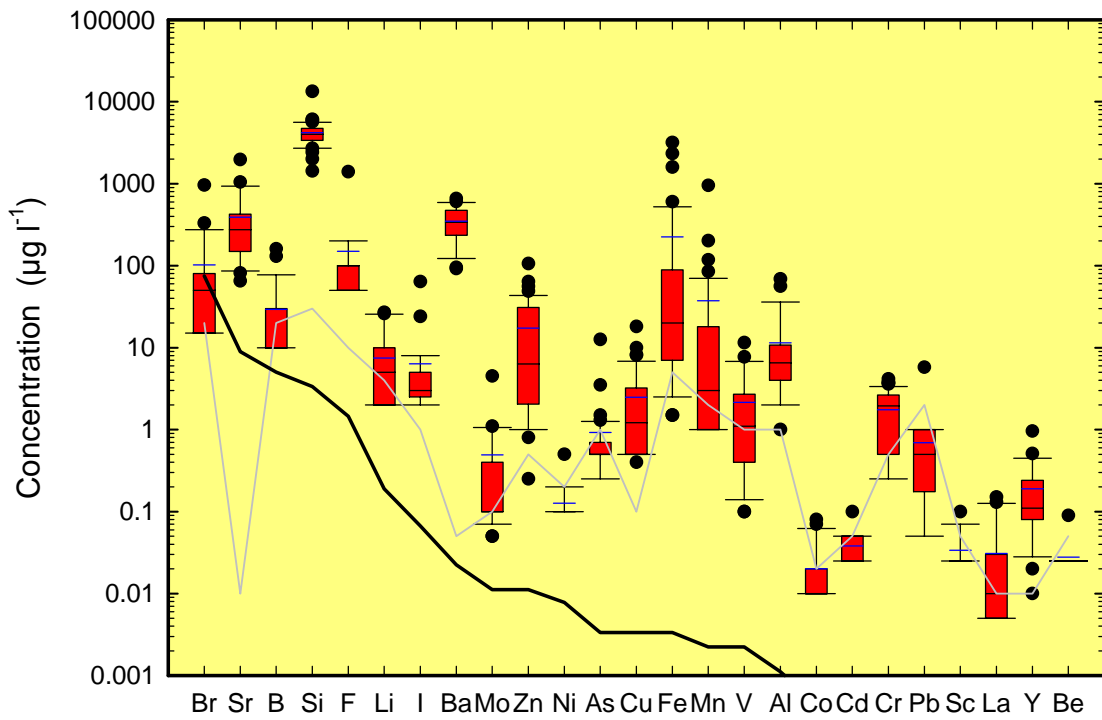


Figure 5.4 Range of minor ion concentrations in the Devonian Sandstone.

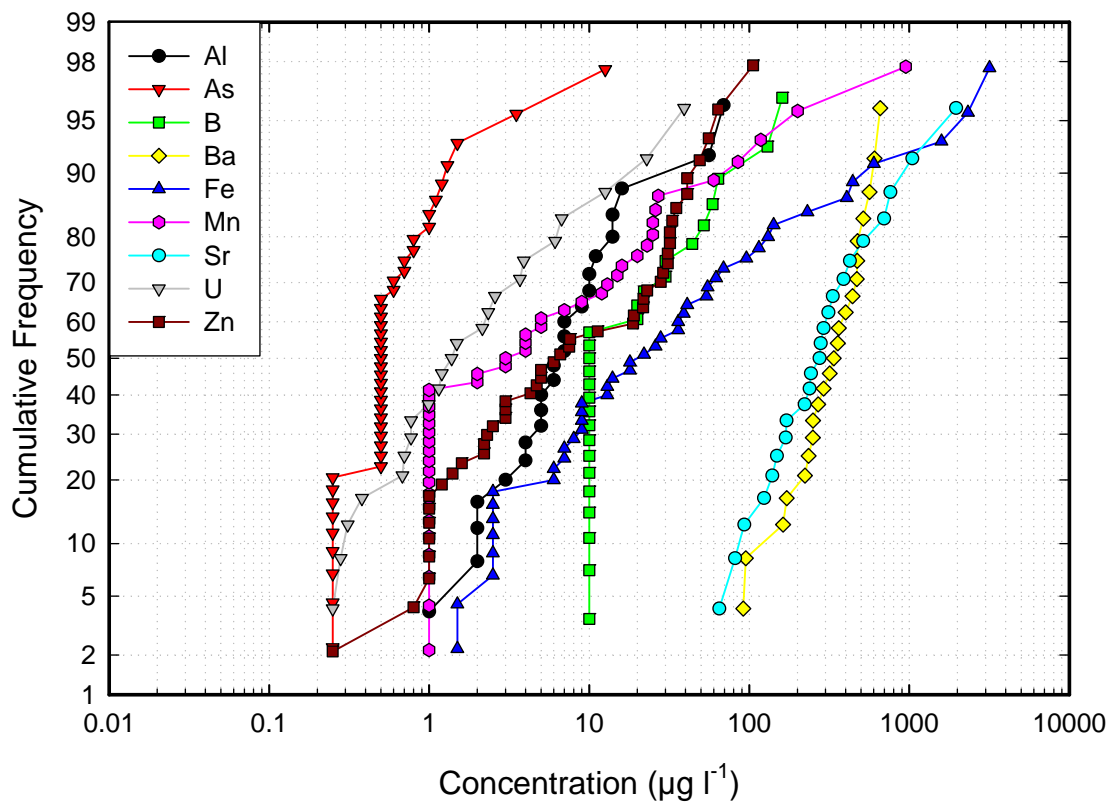
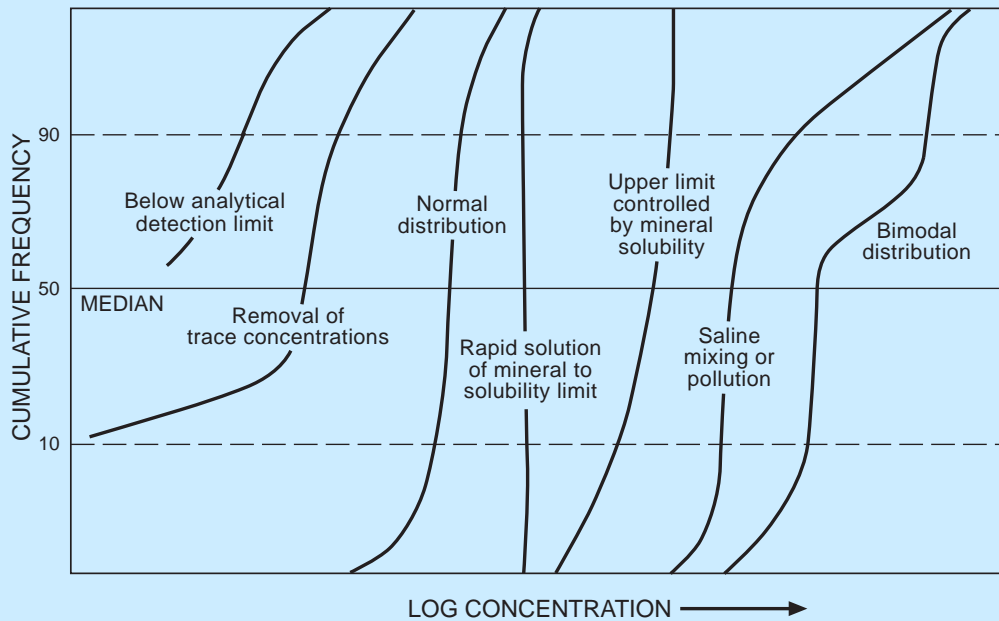


Figure 5.5 Cumulative plots of Minor elements for the Devonian Sandstone.

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



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

5.3 Major elements

The box plot for major elements (Figure 5.2) illustrates the dominance of calcium and bicarbonate in most of the Devonian groundwaters, shown by high median concentrations. Most of the data for these solutes fall within a relatively narrow range. The median Na concentration is slightly above the diluted sea water composition, whereas K, SO_4 , Mg and NO_3 median concentrations are all significantly above the diluted seawater line. Most elements show a significant range (about 2 orders of magnitude) especially NO_3 with a range of about 4 order of magnitude.

Bicarbonate shows a relatively linear (log-normal) trend on the probability plot (Figure 5.3), typical of carbonate-bearing aquifers. In contrast, Ca and Mg show a distinct population shift at low concentrations, these samples corresponding to the Na-HCO_3 type waters shown on Figure 5.1. Sodium and Cl show similar shapes at lower concentrations, but there is a shift in Na at the 90th percentile, again corresponding to Na-HCO_3 type waters. Sulphate concentrations are generally low in

the Devonian Sandstone groundwaters. The trend of NO₃-N is quite complex showing a multi-modal distribution.

5.4 Minor and trace elements

Figure 5.4 presents the box plots for minor and trace elements. Most trace elements lie above the seawater dilution curve, however, the median for bromide is lower, indicative of a low Br/Cl source. Ba and Sr concentrations are present at relatively high concentrations. Most heavy metals concentrations are low as they are typically least soluble in waters with circumneutral pH. Median concentrations of Fe and Mn are relatively low, but display a wide range of concentrations, up to 3.2 and 0.95 mg l⁻¹ respectively.

Figure 5.5 shows the cumulative frequency plots of the Devonian groundwaters. Barium concentrations are high with a median concentration of 337 µg l⁻¹, significantly higher than the EU Guide Level value of 100 µg l⁻¹ and displays a near log-normal distribution. Strontium is also relatively high reaching concentrations up to 1962 µg l⁻¹. Many trace elements show concentrations spread over several order of magnitude. Arsenic was detected in more than 30% of the samples with concentrations up to 12.6 µg l⁻¹, although most were below 2 µg l⁻¹. It is noticeable that uranium is present at concentrations as high as 39.2 µg l⁻¹, with a median value of 1.4 µg l⁻¹ (US new Maximum Admissible Concentration is 30 µg l⁻¹ and the Canadian MAC is 100 µg l⁻¹).

5.5 Pollution indicators

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

The most obvious indicator of diffuse pollution is the presence of high nitrate (Box 5.3). Nitrate concentrations are naturally low throughout much of the aquifer. The highest nitrate concentration of the new data (15.6 mg l⁻¹ as N) is associated with relatively elevated K (18 mg l⁻¹) compared with boreholes in a similar setting, which suggests that this site may have been affected by pollution (probably from fertilisers).

The database of historical water chemistry analyses that was used for this study contains very limited information on organic contaminants. Pesticide concentrations were not considered in this study, however, some Environment Agency samples contained high simazine and MTBE (Methyl Tertiary Butyl Ether). The maximum concentration of simazine was 0.18 µg l⁻¹ and the maximum concentration of MTBE was 6.1 µg l⁻¹. These indicate recent contaminated groundwaters in the Devonian Sandstone aquifer, however, this should not affect baseline concentrations of other elements.

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

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

The approach adopted is threefold:

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

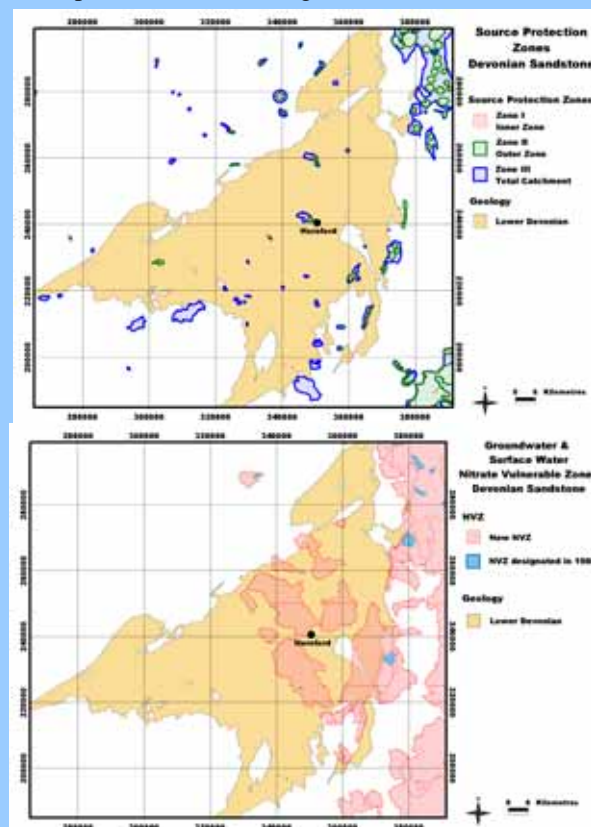
Box 5.3 Is nitrate a problem in the Devonian sandstone aquifer?

Across the counties of the Welsh Borderlands and Herefordshire, agriculture is the dominant land-use. The use of nitrogen-rich fertilisers is widespread and contributes significantly the occurrence of nitrate within groundwaters of the Devonian Sandstones, but how significant are the inputs and are they a cause for concern?

Results from sampling in conjunction with this report show nitrate concentrations to be generally low across much of the aquifer. The highest concentration recorded was $15.6 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$, whereas the median concentration value was much lower at $2.15 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. The high nitrate concentrations are very localised and closely associated with local farming practice. Despite this, 70-80% of the UK's nitrate input countrywide to the water environment comes from the diffuse input of multiple sources of which agriculture is the main contributor, which can lead to contamination of drinking water with exceedences of WHO and EC DWS, both of which require drinking water to contain $< 11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. High nitrate loads to rivers from runoff or groundwater can also result in eutrophication with devastating effects on surface water ecosystems.

In 1996, in accordance with the EC Nitrate Directive, the Government designated Nitrate Vulnerable Zones in order to try to reduce the loss of nitrate from agricultural land and to reduce nitrate levels in water. Within each of these zones nitrate reducing farming practices are encouraged and action plans put in place for the use of nitrogen fertilisers, manure, slurry and silage. 2002 saw the designation of considerably more widespread NVZ's. (Figure 1)

Figure 1. The designation of Nitrate vulnerable Zones across much of Herefordshire in an attempt to control the diffuse pollution risk posed to surface and groundwater.



6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

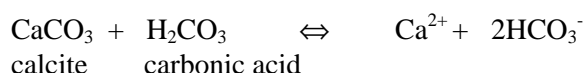
6.1 Introduction

Samples were collected from various sources (springs, boreholes) to represent the Devonian aquifer groundwater. The large variations in aquifer properties (Jones et al., 2000) implies that the aquifer is multi-layered, and hence that different geochemical processes will be occurring dependent on the geological units encountered along each flow path. This makes the identification of flow paths very difficult, although it likely that the steep nature of the catchments means that shallow flow paths may exist. These may well be superimposed on deeper, longer residence time flow pathways.

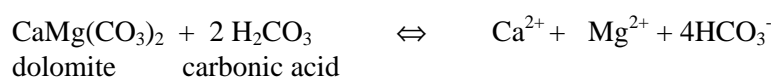
The hydrochemistry of groundwaters in the Devonian aquifer is controlled both by natural inputs (baseline) and inputs derived from anthropogenic sources. Recharge waters are initially controlled by rainfall inputs which subsequently become modified through soil and unsaturated-zone processes. Infiltration through soils often increases acidity due to an increase in dissolved CO₂ derived from organic matter breakdown and plant respiration. However, this is rapidly neutralised if carbonate is present. Further chemical changes occur along flow paths as the groundwater slowly equilibrates with the minerals present in the aquifer. The dominant processes taking place include mineral dissolution/precipitation, ion-exchange, sorption/desorption and mixing. The importance of these processes is discussed in this chapter.

6.2 Mineral dissolution reactions

For aquifers containing carbonate or evaporite, either as a discrete mineral phase or cement, the chemistry of groundwaters will be strongly influenced by the rapid dissolution of these minerals. Infiltrating groundwater will initially be acidic due to the presence of carbonic acid derived from CO₂ production in the soil zone. The presence of carbonate cements and calcrete horizons in the aquifer will lead to rapid neutralisation of incoming acidity. Dissolution of calcite will lead to an increase in Ca and HCO₃⁻ in the groundwaters until saturation is reached:



Dolomite dissolution is controlled by the following reaction:



A number of the samples within the aquifer are undersaturated with respect to calcite and dolomite and it seems likely that these groundwaters occur in parts of the aquifer which have either become decalcified i.e. the original calcite has been removed by dissolution or where residence time is short. There is no clear relationship between the degree of saturation with respect to calcite or dolomite and depth of borehole. However, most groundwaters are saturated (or close to saturation) with respect to calcite and dolomite (Figure 6.1). The positive relationship between Ca and TDS also suggests that calcite dissolution is one of the major driving processes within the aquifer. The most undersaturated groundwaters are those with lowest pH and HCO₃⁻ concentrations, however it is not clear if this is due to short residence times or lack of carbonate minerals in the matrix.

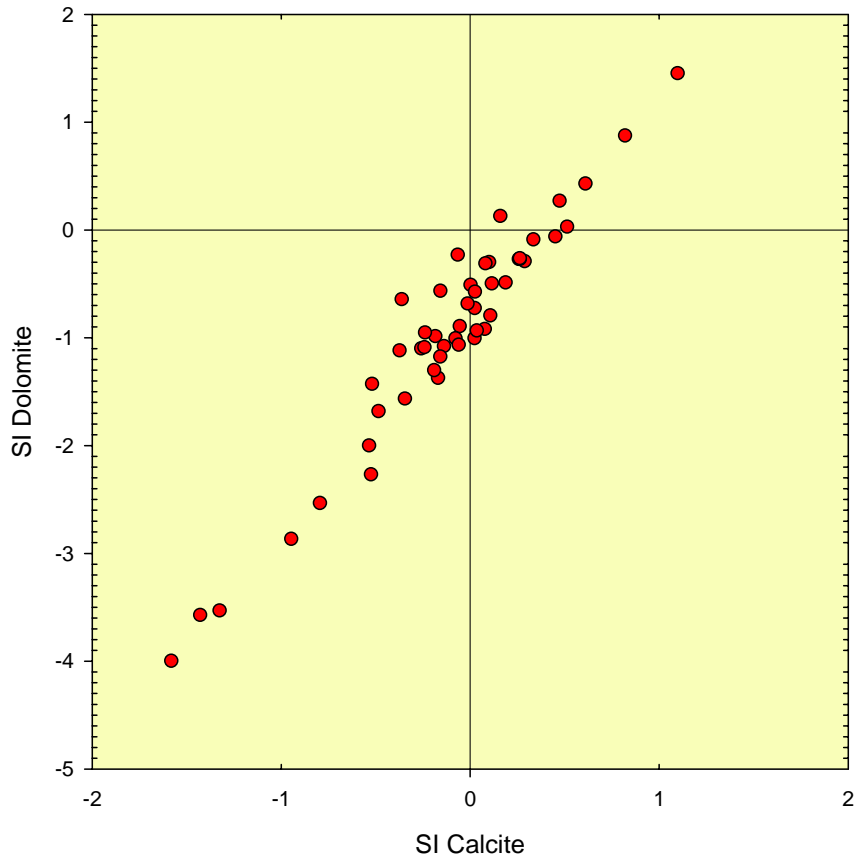


Figure 6.1 Saturation indices for calcite and dolomite in waters of the Devonian aquifer.

There are no known occurrences of evaporite minerals in the aquifer or surrounding rocks and this is consistent with the low SEC, SO_4 and Cl contents of the groundwaters. Sulphate concentrations are relatively low and all samples are undersaturated with respect to gypsum.

Carbonate reactions are the dominant reactions determining groundwater chemistry within the aquifer. However, less rapid silicate dissolution reactions are also occurring. Silicon concentrations within the aquifer range from 1.4 to 13 mg l^{-1} . The amount and rate of dissolution is controlled by saturation with respect to a silicate mineral or phase. Although the aquifer is composed dominantly of quartz, this mineral is extremely unreactive and the source of Si is most likely to be from silicate minerals such as K- or plagioclase-feldspar. Most groundwaters in the study area are undersaturated with respect to chalcedony (SiO_2) and this mineral places upper limits on Si concentration. Silicate minerals also provide inputs of the major elements Ca, Na and K, with K-feldspars providing important contributions of K to the groundwater along with rainfall and local anthropogenic (e.g., fertilizer) inputs.

6.3 Minor and trace elements

The fluoride concentrations in Devonian groundwaters are generally low, less than 0.1 mg l^{-1} . There is little variation, although older and deeper groundwaters have concentrations up to 1.4 mg l^{-1} . The low concentrations and degree of undersaturation with respect to fluorite imply that F-bearing minerals are not significant in the aquifer or that the kinetics of dissolution for F-bearing minerals is slow. Bromide and iodide concentrations are low, mainly controlled by rainfall composition or mixing with formation water (Section 6.6).

The predominant source of Sr in most groundwaters is calcite. In silicate aquifers, Sr may also be derived from Ca-bearing minerals such as Ca-rich plagioclase feldspar. Strontium concentrations are generally much lower than those encountered in other sandstone aquifers such as the Triassic sandstones in the Vale of York where Sr is mainly derived from gypsum dissolution (Shand et al., 2002). There is a good correlation between Sr and HCO_3^- but no clear correlation of Sr with SO_4 , implying a carbonate source.

The median Ba concentration of $337 \mu\text{g l}^{-1}$ is relatively high, and 90% of the groundwater samples are above the EU Guide Value of $100 \mu\text{g l}^{-1}$. The solubility of Ba in groundwaters is often controlled by the mineral barite (BaSO_4): where SO_4 concentrations are high, Ba concentrations are low. The low SO_4 concentrations in the groundwaters has allowed Ba to reach high concentrations. The groundwaters are oversaturated with respect to barite, a common occurrence in groundwaters due to slow kinetics of precipitation of barite. The Ba concentrations correlate reasonably well with Si but not SO_4 indicating that the source of the high Ba is most likely to be from K-feldspars which are typically enriched in this trace element. There is no evidence to suggest that the mineral barite is present in the aquifer.

Concentrations of most trace elements are low due to short residence time, and for many trace metals, limited mobility in waters with circumneutral pH. Aluminium concentrations are generally low ($< 20 \mu\text{g l}^{-1}$) but increase slightly (up to $69 \mu\text{g l}^{-1}$) at higher pH. Zinc concentrations range up to $106 \mu\text{g l}^{-1}$, but it is not clear if this is the baseline range or due to local contamination (e.g. galvanized metal around pipe-work). Ni, Cr and the other heavy metals are generally low or below detection limit (Table 5.2).

The trace elements Li and B may be good indicators of residence time in aquifers. They are both found in lower concentrations towards the south of the study area. Boron is also generally low, the highest concentration being in the groundwaters sampled at St Michael's Abbey where Cl is also high. Many of the samples have higher B/Cl ratios than seawater and this may indicate pollution.

6.4 Redox

Many trace metal species (those with different valencies e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$) display different behaviour under different redox conditions. Recharge waters, which are typically oxidising, often undergo sequential changes in redox potential as groundwaters evolve in response to changing aquifer conditions and reduced species. There is insufficient data to ascertain if a redox boundary exists along flow paths or with depth in the aquifer.

Most of the groundwaters studied contained oxygen and had moderately high Eh (redox potential). Nitrate concentrations are stable in the presence of dissolved oxygen and $\text{NO}_3\text{-N}$ concentrations in the groundwaters varied from below the detection limit (0.002 mg l^{-1}) up to 15.6 mg l^{-1} (The median value was 2.2 mg l^{-1}). The samples where nitrate was below the limit of detection were moderately reducing and have most likely undergone denitrification. Ammonium concentrations are generally highest in the reducing groundwaters (up to 0.07 mg l^{-1}), but the sample with the highest nitrate (15.6 mg l^{-1} $\text{NO}_3\text{-N}$) also contained NH_4 with a concentration of 0.11 mg l^{-1} , probably as a result of pollution.

The abundance of oxidising groundwaters is reflected in low median concentrations of Fe and Mn (0.02 and 0.003 mg l^{-1} respectively), even though iron oxides are abundant as cements in the aquifer. However, under reducing conditions Fe and Mn are mobile and the more reducing groundwaters contain relatively high concentrations, up to 3.2 and 0.95 mg l^{-1} respectively. It is possible that some of the higher concentrations are due to unfiltered samples being analysed, but the new data (filtered) also contain moderately high concentrations (Fe up to 0.13 and Mn up to 0.10 mg l^{-1}).

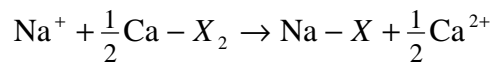
Many trace elements are also sensitive to redox reactions. Arsenic is more mobile under reducing conditions (as As^{3+}) and As^{5+} is also more strongly sorbed, hence it is common to find higher

concentrations in reduced groundwaters. The majority of samples contain As at concentrations less than $1.5 \mu\text{g l}^{-1}$, but one sample contained $12.6 \mu\text{g l}^{-1}$.

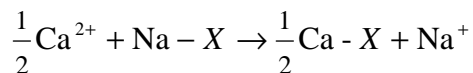
Uranium is typically mobile only under oxidising conditions. All of the new samples contained concentrations above the detection limit ($0.02 \mu\text{g l}^{-1}$). The concentration data approach a log-normal distribution (Figure 5.5) with a median of $1.4 \mu\text{g l}^{-1}$ and a maximum of $39 \mu\text{g l}^{-1}$. Eight groundwater samples out of 23 exceeded the WHO Guide Value of $2 \mu\text{g l}^{-1}$. Apart from one sample (St Michaels's Abbey), U displayed a good correlation with Sr ($r^2 = 0.97$) and the source is therefore most likely to be from dissolution of carbonates.

6.5 Ion exchange reactions

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



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



Here Ca^{2+} is taken up from the water and exchanged for Na, producing a Na- HCO_3 type water, (Appelo and Postma, 1991).

There is no evidence for salinisation in any of the groundwaters as Cl concentrations are generally very low. However, there is a trend towards Na- HCO_3 type waters (Figure 5.1) which may indicate that aquifer freshening is occurring. The higher Na groundwaters are associated with a decrease in Ca and Mg consistent with exchange of adsorbed Na for Ca and Mg (Figure 6.2). The Na- HCO_3 type waters are also enriched in other elements which increase with residence time such as Li, U and Sr and hence may imply extended residence time compared with the Ca- HCO_3 type waters.

6.6 Mixing with older formation water

Mixing with an older, deeper connate or formation water is generally indicated by an increase in salinity, especially Cl. The median Cl of 25mg l^{-1} is probably slightly higher than rainwater modified by evapotranspiration. The groundwaters with the highest Cl concentrations (e.g. St Michael's Abbey 226mg l^{-1} Cl) have Br/Cl ratios similar to the sea water ratio. The Cl also correlates with Na, I and B indicating mixing with an older formation water. There is no clear relationship between chloride ion concentration and depth of the sample, except that the highest chloride was recorded in a deep borehole. Many of the low Cl samples had low Br/Cl ratios and it is possible that this is due to anthropogenic modification such as road salting, agricultural practices or from septic tanks. However, such inputs are not large enough to increase Cl significantly in these groundwaters. Richardson (1947) reported that salt water had been encountered at Bromyard Pumping Station and at Tenbury Wells, which was known as a Spa town. This saline water has led to the abandonment of some sources, suggesting the occurrence of older formation water at depth.

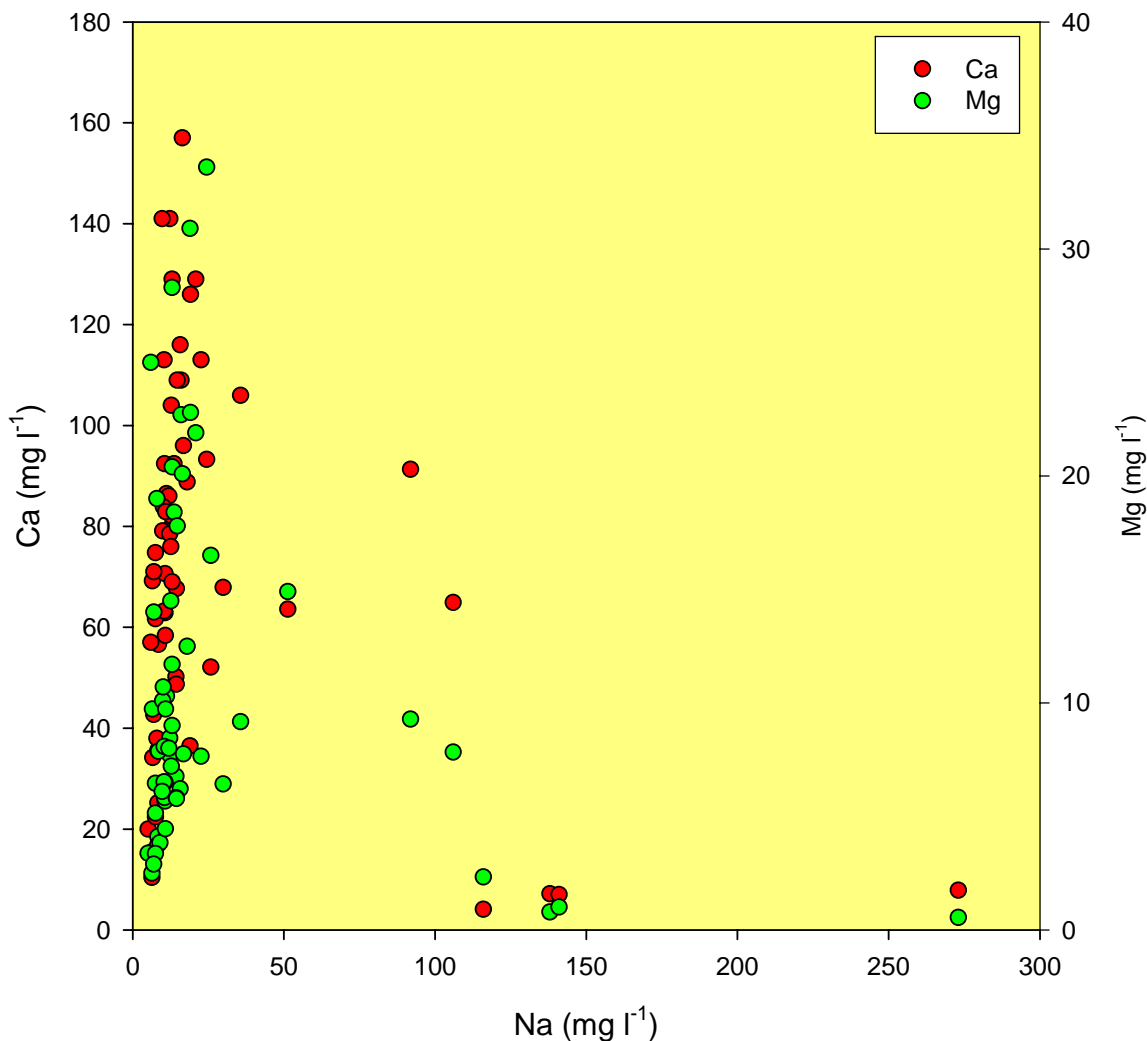


Figure 6.2 Relative Ca, Mg and Na concentrations for Devonian Sandstone groundwaters.

6.7 Age of the groundwater

There are no data available on the direct age of the groundwater. However, the stable isotope measurements of O and H ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in selected samples (with one exception) fall within a narrow range (Figure 6.3). These plot on the World Meteoric Line (WML) and are slightly lighter than expected for modern recharge waters (Darling et al., 2003). This may simply be an altitudinal effect. It is evident, however, that the waters are of Holocene (< 10 000 yr BP) or modern age and no Pleistocene waters have been sampled from the aquifer. There is a slight trend for $\delta^2\text{H}$, $\delta^{18}\text{O}$ to decrease with increasing depth, regardless of the geology.

One of the samples shows a heavy isotope signature and sits to the right of the WML. This sample is from a 93 m borehole pumping everyday from the Raglan Mudstone Formation, this sample would appear to have been affected by evaporation or possibly much of its recharge is derived from a surface water body such as a lake.

Carbon isotopes can also be useful since they provide evidence of the degree of reaction with carbonate minerals which may be loosely related to residence time. The $\delta^{13}\text{C}$ signatures do not vary significantly and do not show any clear relationship with other parameters or concentrations such as

SEC, HCO₃, Cl and Sr. The light signatures may imply that open system conditions have prevailed over much of the geochemical evolution of the waters.

Although there may be a general relationship between the amount of dissolved solutes and age, care needs to be taken in ascribing relative ages on this basis e.g. due to the heterogeneity of the aquifer minerals and hydrochemical conditions across the aquifer. The Na-HCO₃ groundwaters showed evolved characteristics such as heavy $\delta^{13}\text{C}$ and high concentrations of Sr indicating that these represent the oldest groundwaters but a true age determination requires further data.

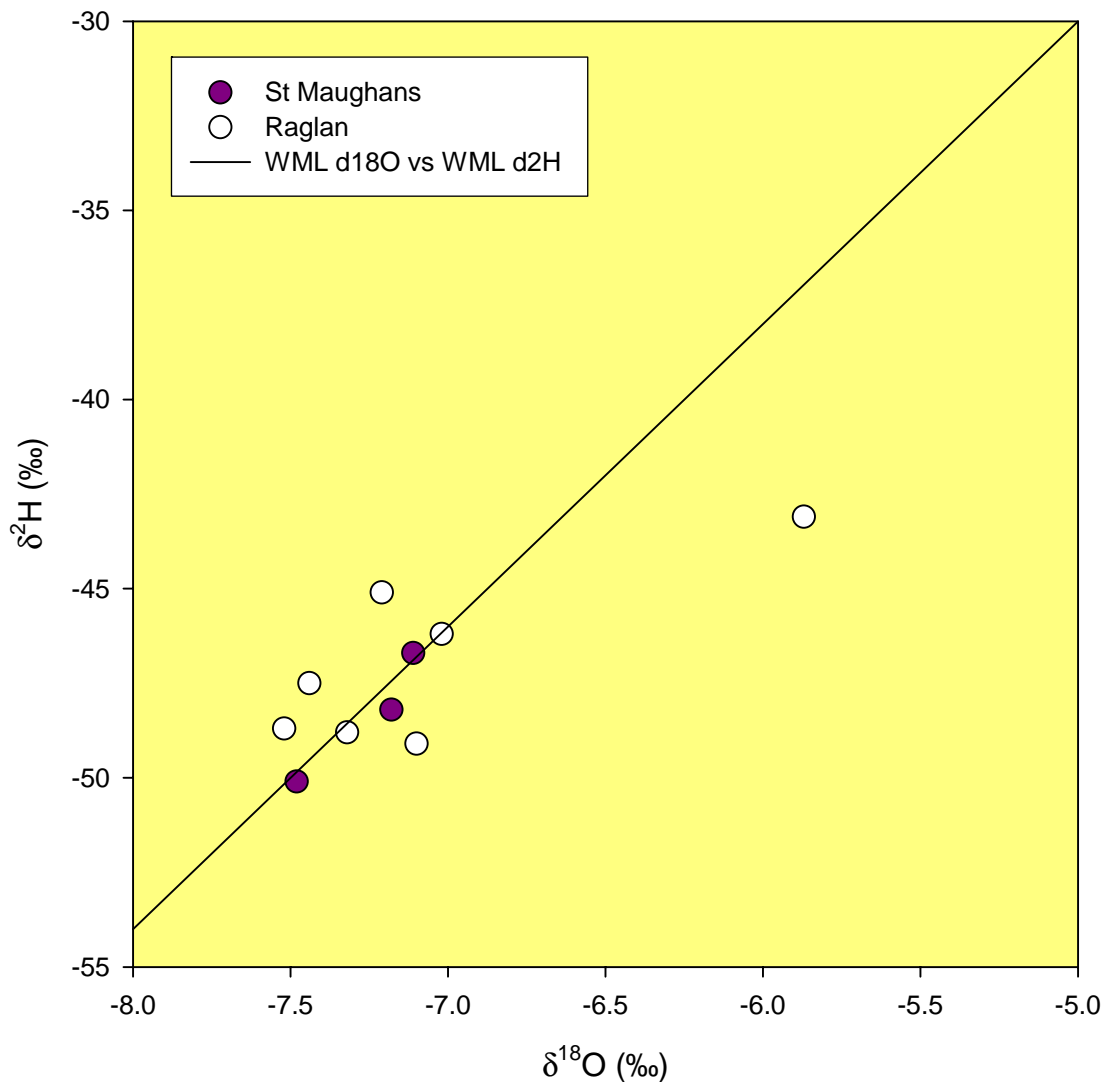


Figure 6.3 Isotope plot for Devonian Sandstone groundwaters.

6.8 Surface waters

The river waters over the Devonian outcrop are oxidising and of Ca-HCO₃ type, similar to most of the groundwaters (Figure 5.1). Although average solute concentrations and SEC in the river samples are often lower than groundwaters, there is typically some overlap (Figure 6.4). One of the tributaries (Afon Llynfi) has much higher Ca and HCO₃ than the main river (Figure 6.4). The River Wye waters show an increase in the concentrations of many elements as it flows downstream.

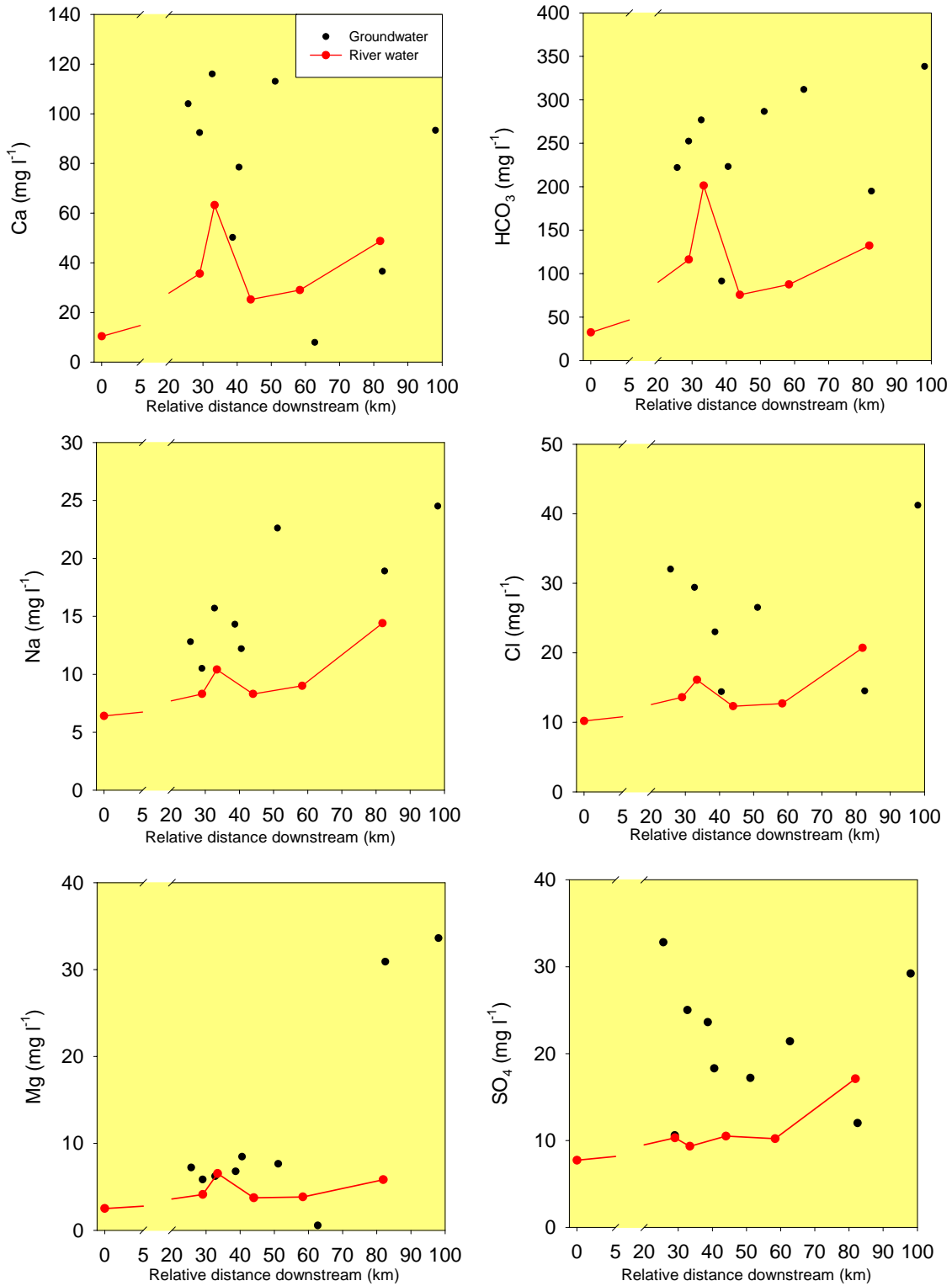


Figure 6.4 Variations in groundwater and surface waters along the Wye Valley.

The river sample collected from upstream of the Devonian outcrop, flowing over Ordovician/Silurian bedrock, has a lower SEC and lower concentrations of most solutes. It also contains a more mixed cation and anion composition (Figure 5.1). The River Wye changes in composition as it flows from the Ordovician/Silurian rocks over the Devonian rocks, towards the composition of the Devonian

aquifer groundwaters. Similar changes were seen at a regional scale in streams across Wales (British Geological Survey, 1999). The changes in river water chemistry highlight the role of geology in controlling surface water chemistry and the changes downstream across the Devonian outcrop imply an important contribution of groundwater. The interaction between groundwater and surface water in the Devonian aquifer is likely to be significant and an area worthy of further research.

6.9 Depth variations

There are no hydrochemical data available for depth profiles in any of the boreholes. However, several physicochemical parameters and solute concentrations have been plotted against borehole depth, where available, to ascertain if there are differences between shallow and deeper parts of the aquifer (Figure 6.5). Springs have been plotted on the depth axis at 0 m. The spring samples show a wide range in measurements of SEC, Eh, DO and pH, but overlap with the groundwaters. This probably indicates a wide range of flowpaths and residence times with both shallow (younger) and deeper (older) groundwater components.

The groundwater does not show significant variation in trends in most solute concentrations derived from water-rock interaction, although the deepest sample plotted (St Michael's Abbey) is distinct in terms of its low Ca and high Na and Cl (due to mixing and ion-exchange). The shallower parts of the aquifer contain low Cl and are well flushed of any formation waters. The plots do highlight that NO₃ and DOC are higher where boreholes are shallow, probably indicating the depth to which agricultural pollution has reached. The springs again show a large range in these solutes reflecting a range in flowpaths and residence times. Several have moderately high nitrate, but some have very low nitrate concentrations (down to the detection limit). There is no evidence for denitrification in these samples and they may represent relatively pristine conditions along flow paths.

6.10 Regional variations

Changes in the baseline chemistry are expected to occur as water moves from the recharge (dominantly upper slopes) to the discharge areas (lower slopes and rivers) of the aquifer. It is difficult to evaluate hydrochemical changes along a flow path in the present study as there was no piezometric surface map of the area. In addition, flowpaths are likely to be complex and may be locally controlled by topography. However, two small sections were studied to assess variations across valley bottoms and interfluvial areas of the Wye Valley. The first section represents a NW-SW section across the Wye valley between Begwns and Twmpa (Figure 6.6), approximately crossing Hay-on-Wye, and the second between Upper Llanrosser in the Golden Valley to Bredwardine on the south bank of the River Wye (Figure 6.7). The SEC in the River Wye is similar in section 1 (Begwns to Twmpa) to the local groundwaters and slightly lower in section 2 (Upper Llanrosser to Bredwardine). The river samples do, however, have slightly higher NO₂ and P probably derived from shallow diffuse pollution.

Although data are limited and there is some scatter, there does appear to be an increase in Ca, HCO₃, Cl and N-species from the interfluvial areas to the valley bottom. This is consistent with an increase in residence time along these sections. Some of the boreholes close to the river show slightly elevated concentrations of DOC, which may indicate some recharge from the river. Similarly, Mn is elevated in the groundwater sampled from some near-river boreholes.

Devonian groundwaters show a wide range of SEC as illustrated by the regional plot. Many high SEC values are associated with valley bottom, suggesting a higher residence time (Figure 6.8). The SO₄ and Cl regional plots (Figure 6.9 and Figure 6.10) present a similar distribution, higher values are generally found in valley bottom, highlighting the degree of mixing and water-rock interaction. However, the Cl and HCO₃ regional plots are not similar. This difference could be explained as Cl is usually associated with mixing with older formation water, whereas the bicarbonate component is derived from rock-water interaction.

Nitrate concentrations are spatially variable and do not show any clear regional trend (Figure 6.11). However, many of the highest concentrations are present in the Wye Valley. Nitrite (Figure 6.12) is also variable and is present at low concentrations. Several groundwaters contain both NO_3 and NO_2 , probably a result of recent pollution or incomplete equilibrium of controlling redox reactions. Anthropogenic influences in the Wye valley are likely – agriculture, use of pesticides and fertilisers. The locally high iron and manganese concentrations indicate the presence of reducing groundwaters (Figure 6.13 and Figure 6.14).

The calcium and sodium regional plots (Figures 6.15 – 6.16) also illustrate the heterogeneity of solute concentrations in the groundwaters of the Devonian Sandstone. In some of the boreholes in the Wye valley, and to the south along the Dore and Usk valleys, low Ca concentrations are associated with high Na suggesting ion exchange processes.

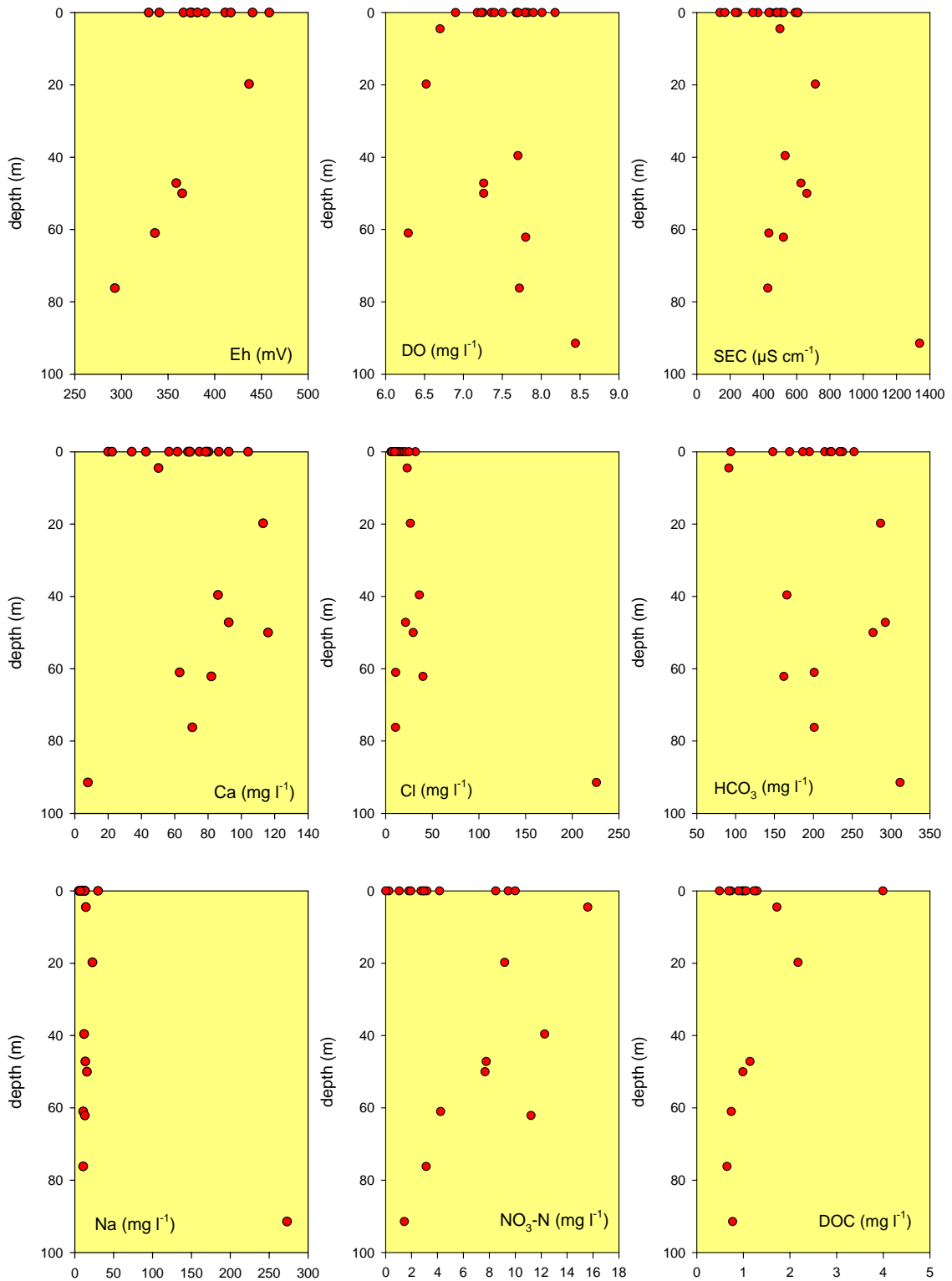


Figure 6.5 Groundwater chemistry changes plotted against depth of borehole.

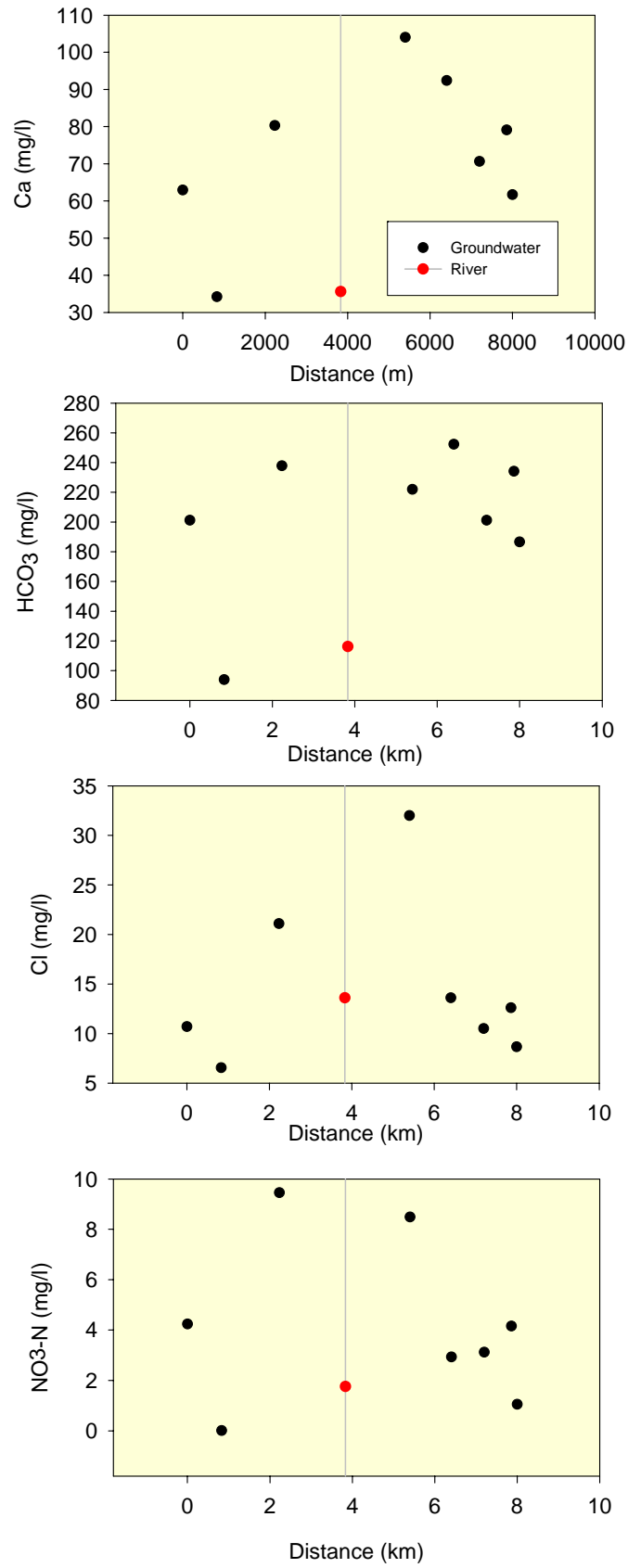


Figure 6.6 Hydrochemical variations across transect from Begwns (SO 1627 4291) to Twmpa (SO 2107 3620).

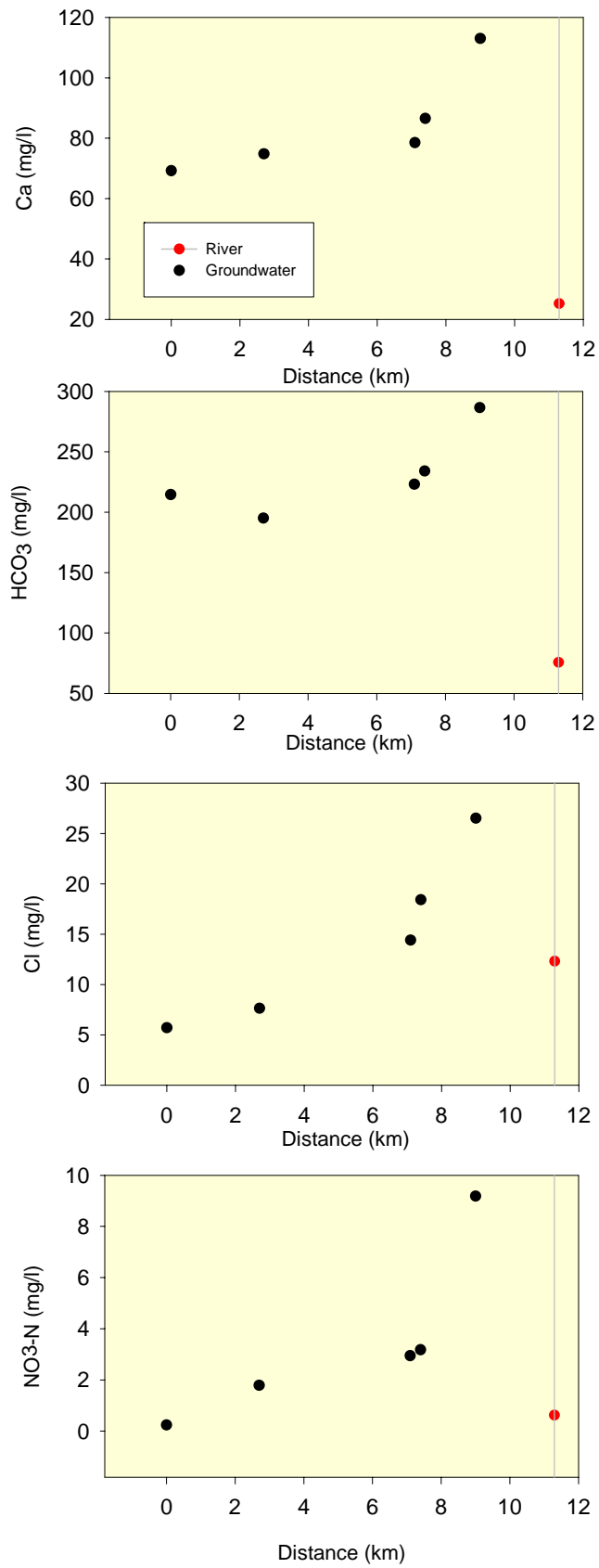


Figure 6.7 Hydrochemical variations across transect from Upper Llandrosser (SO 2855 3852) to Bredwardine (SO 3359 4515).

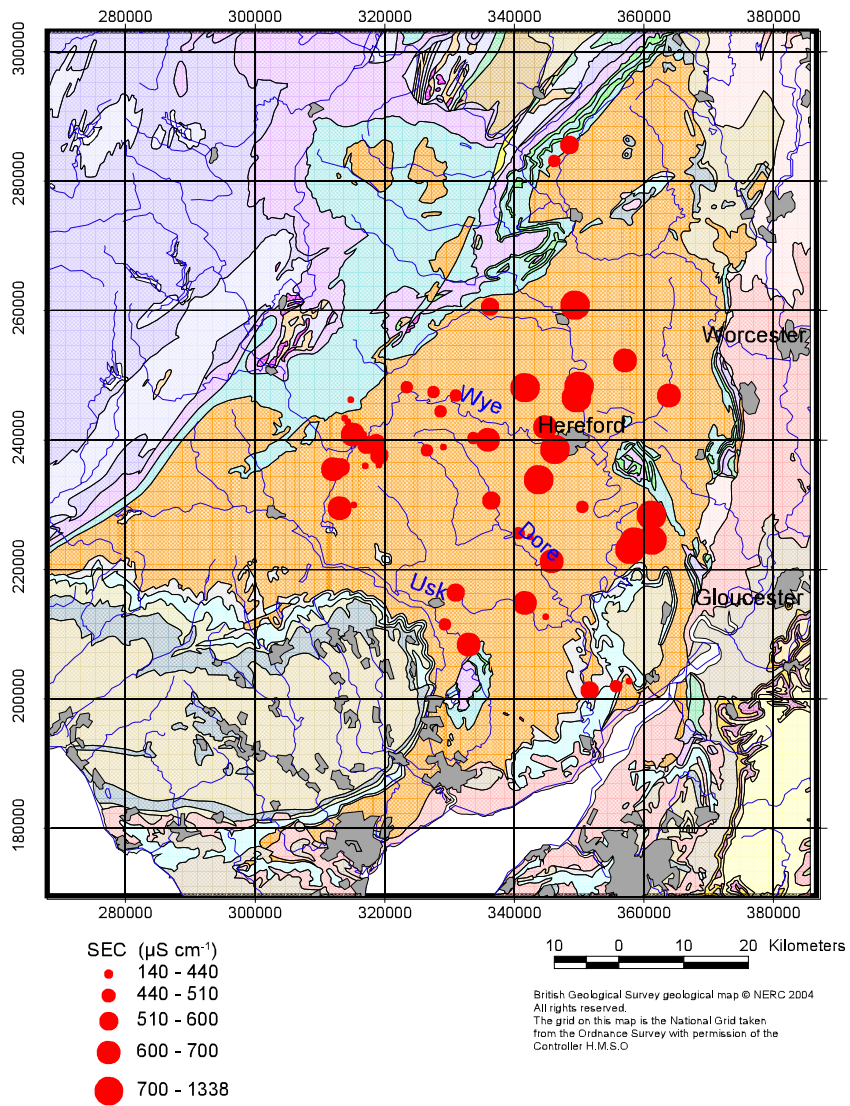


Figure 6.8 Regional variations of SEC in the Devonian Aquifer groundwaters.

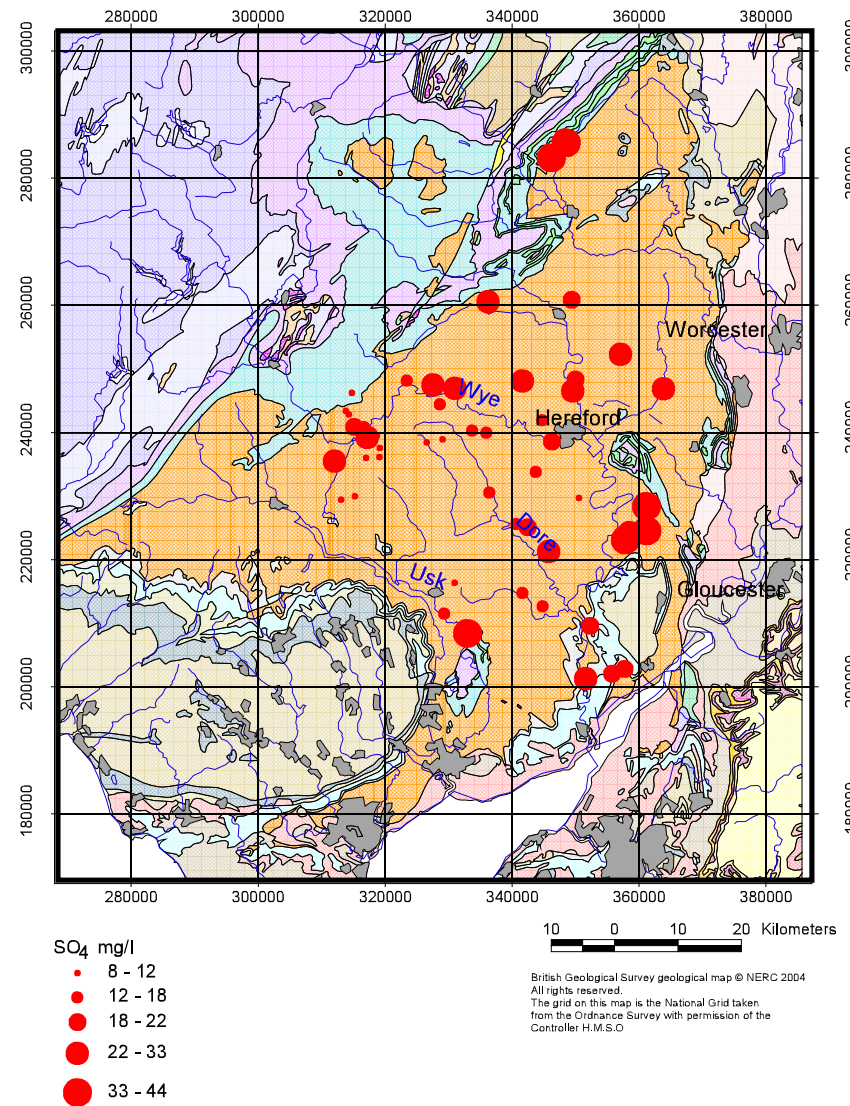


Figure 6.9 Regional variations of SO₄ in the Devonian Aquifer groundwaters.

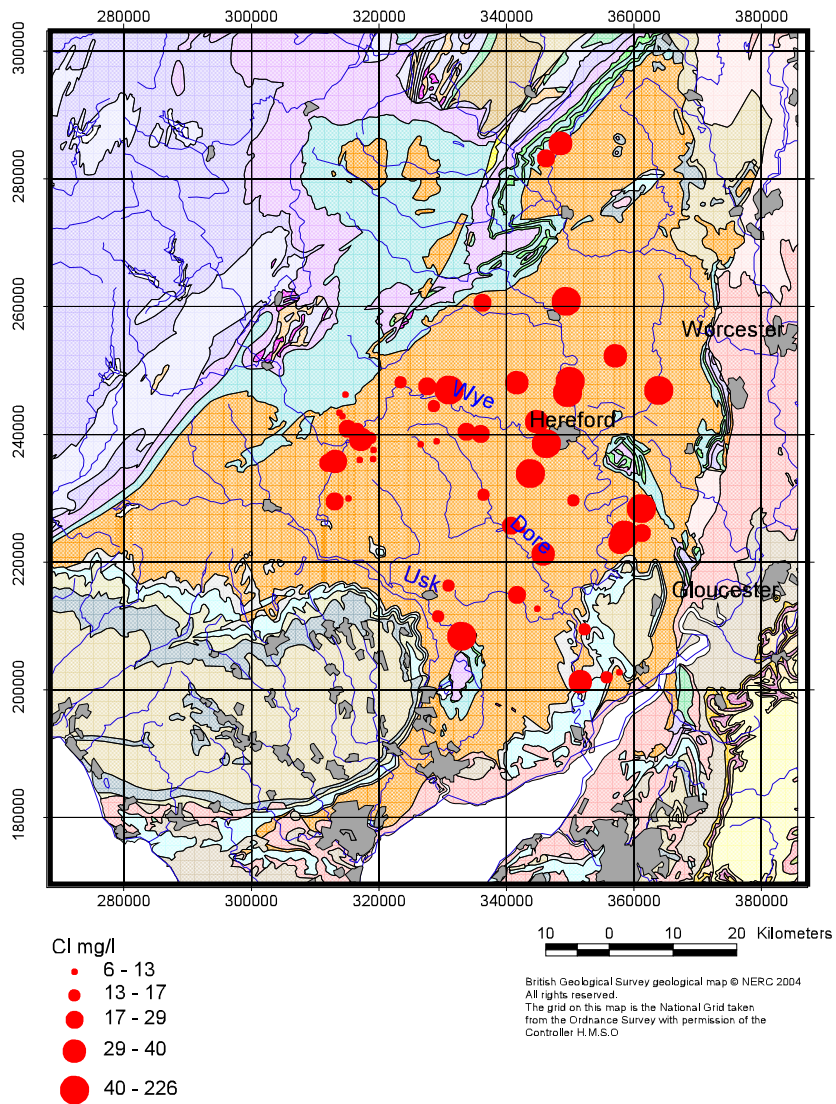


Figure 6.10 Regional variations of Cl in the Devonian Aquifer groundwaters.

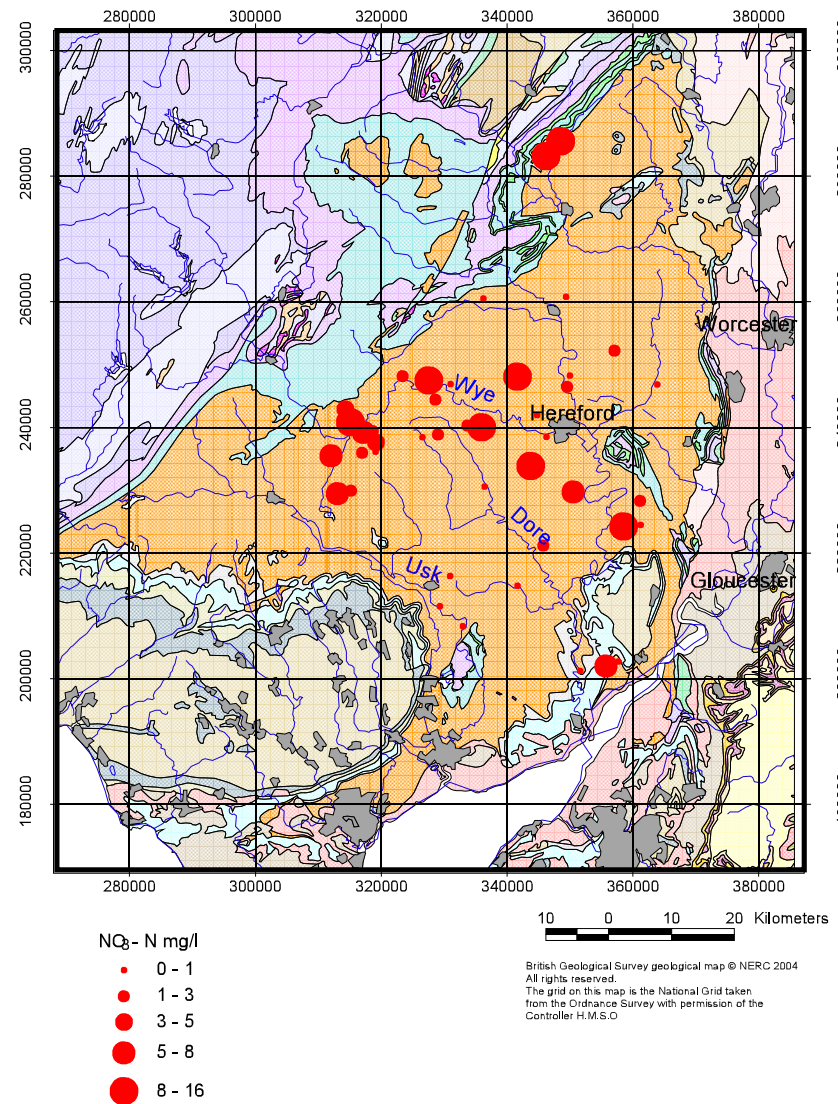


Figure 6.11 Regional variations of NO₃ in the Devonian Aquifer groundwaters.

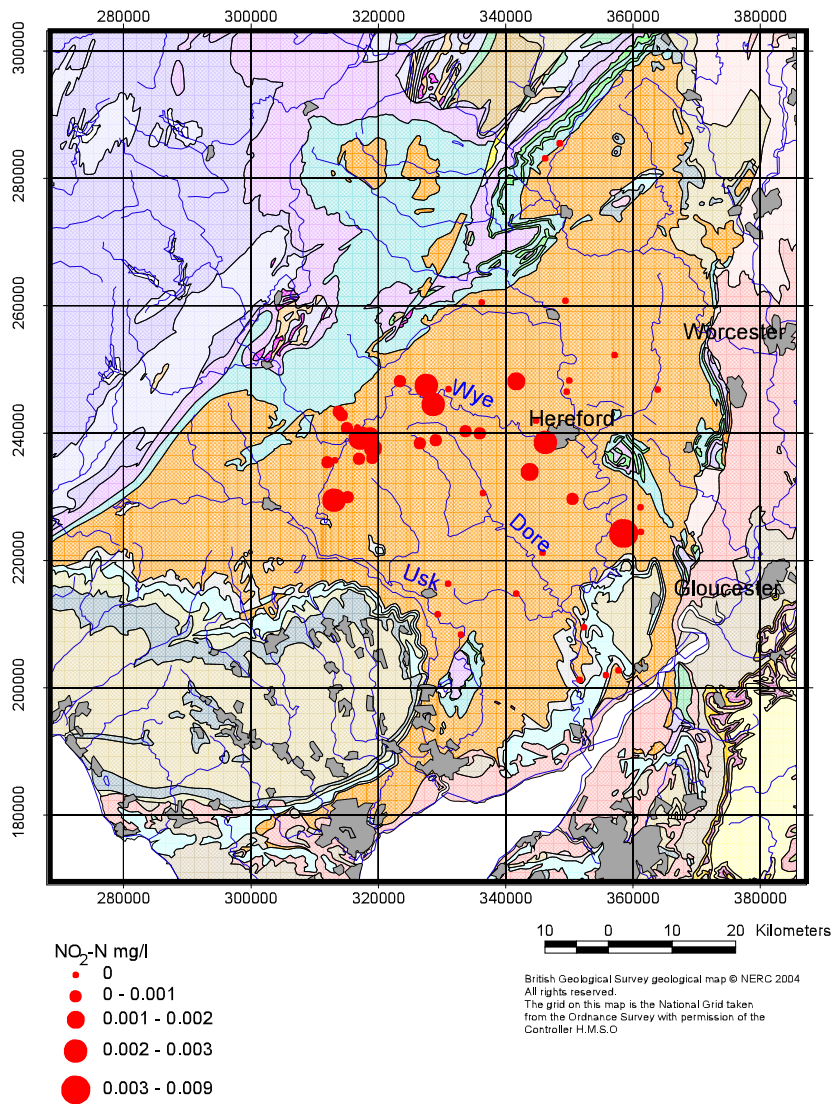


Figure 6.12 Regional variations of NO₂ in the Devonian Aquifer groundwaters.

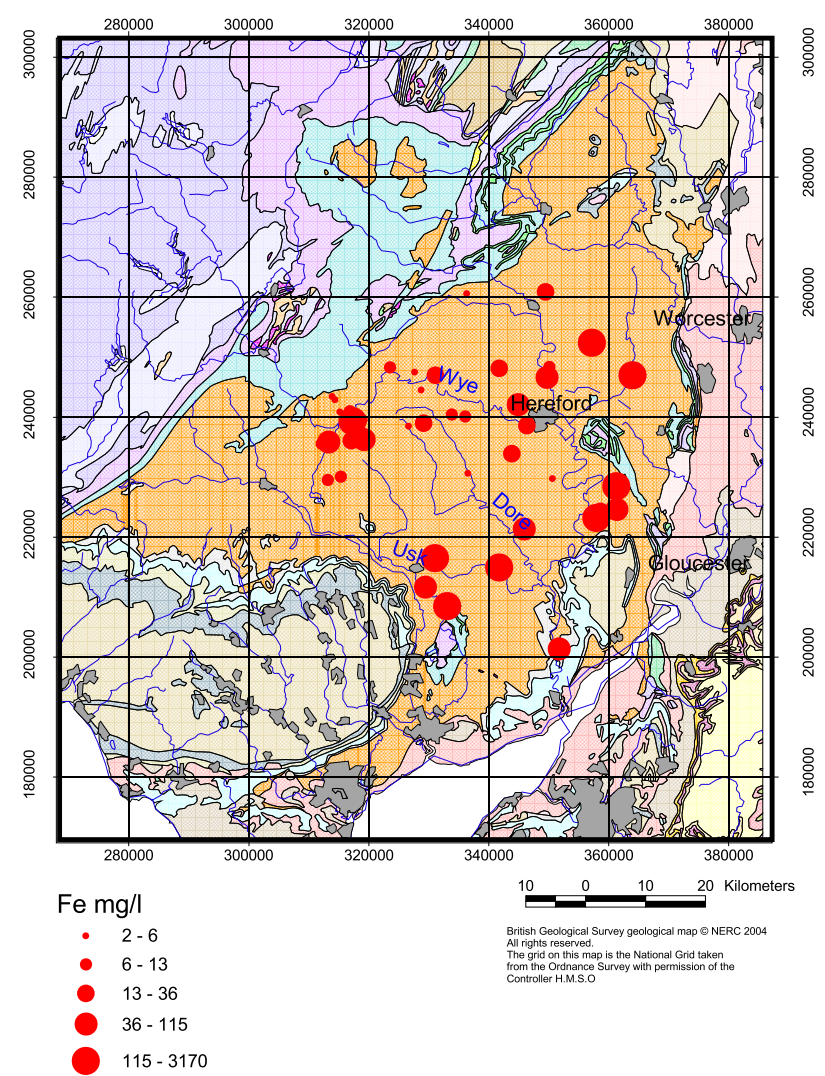


Figure 6.13 Regional variations of Fe in the Devonian Aquifer groundwaters.

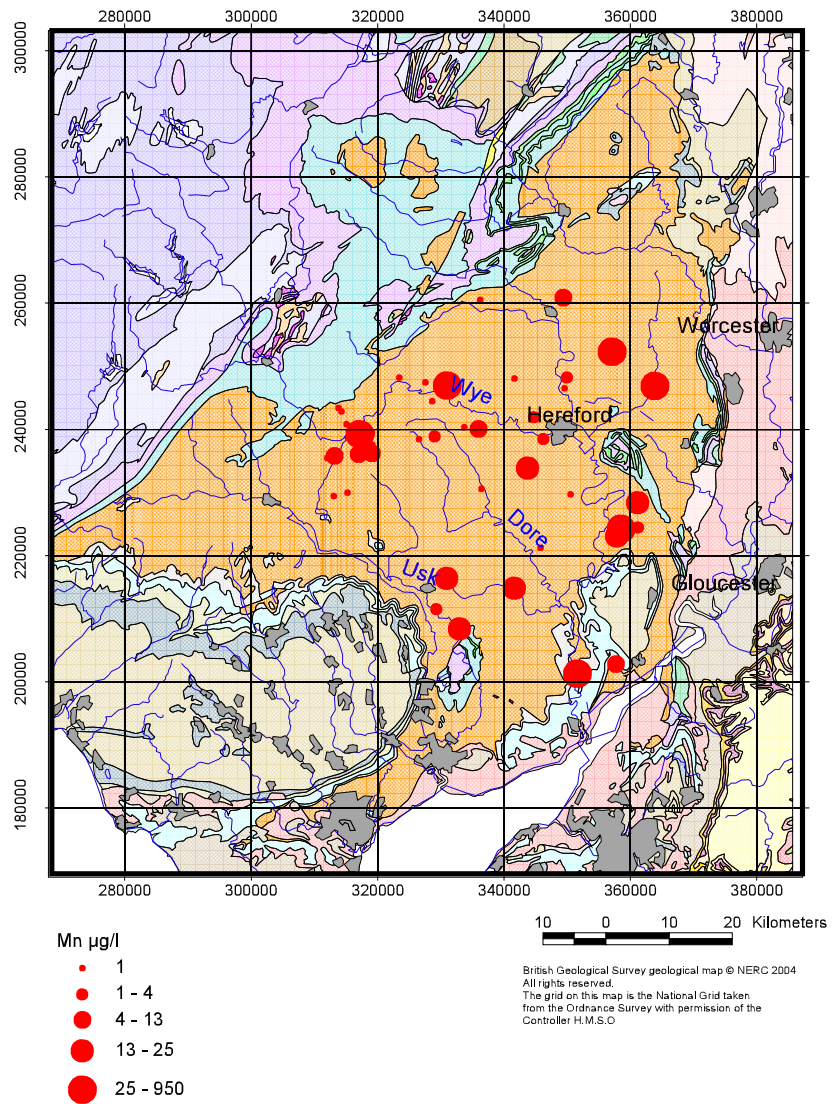


Figure 6.14 Regional variations of Mn in the Devonian Aquifer groundwaters.

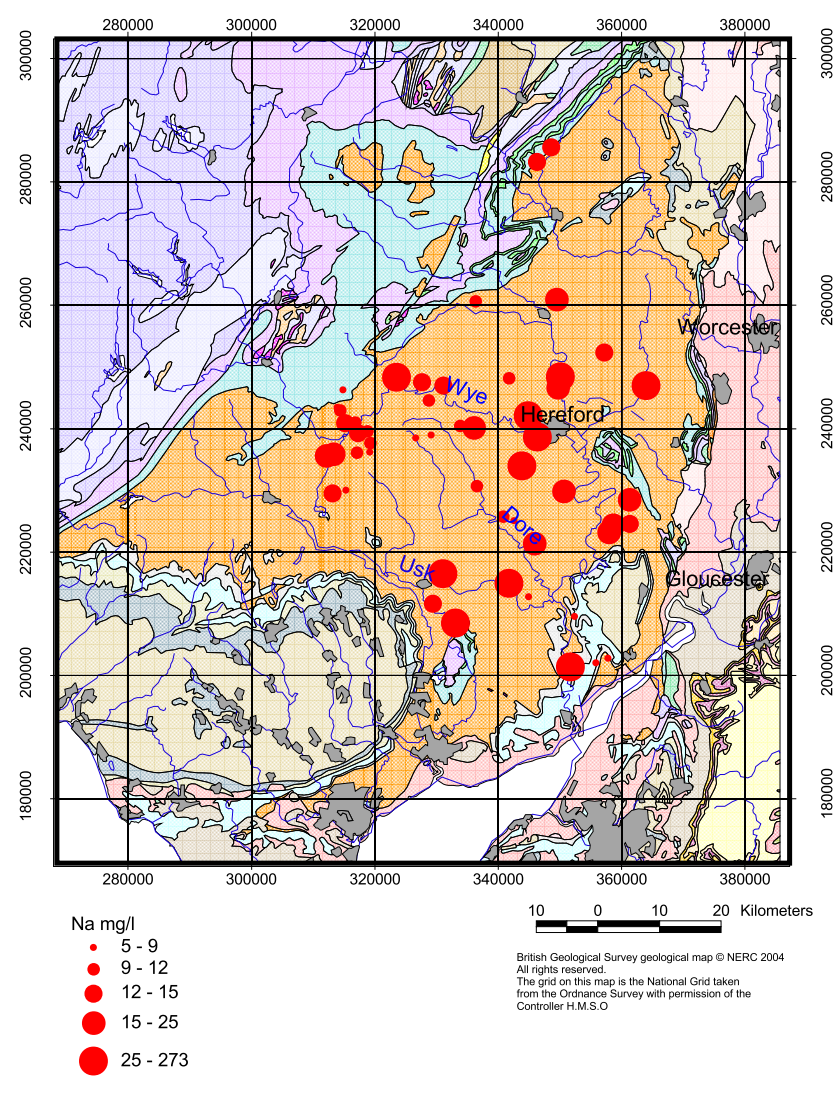


Figure 6.15 Regional variations of Na in the Devonian Aquifer groundwaters.

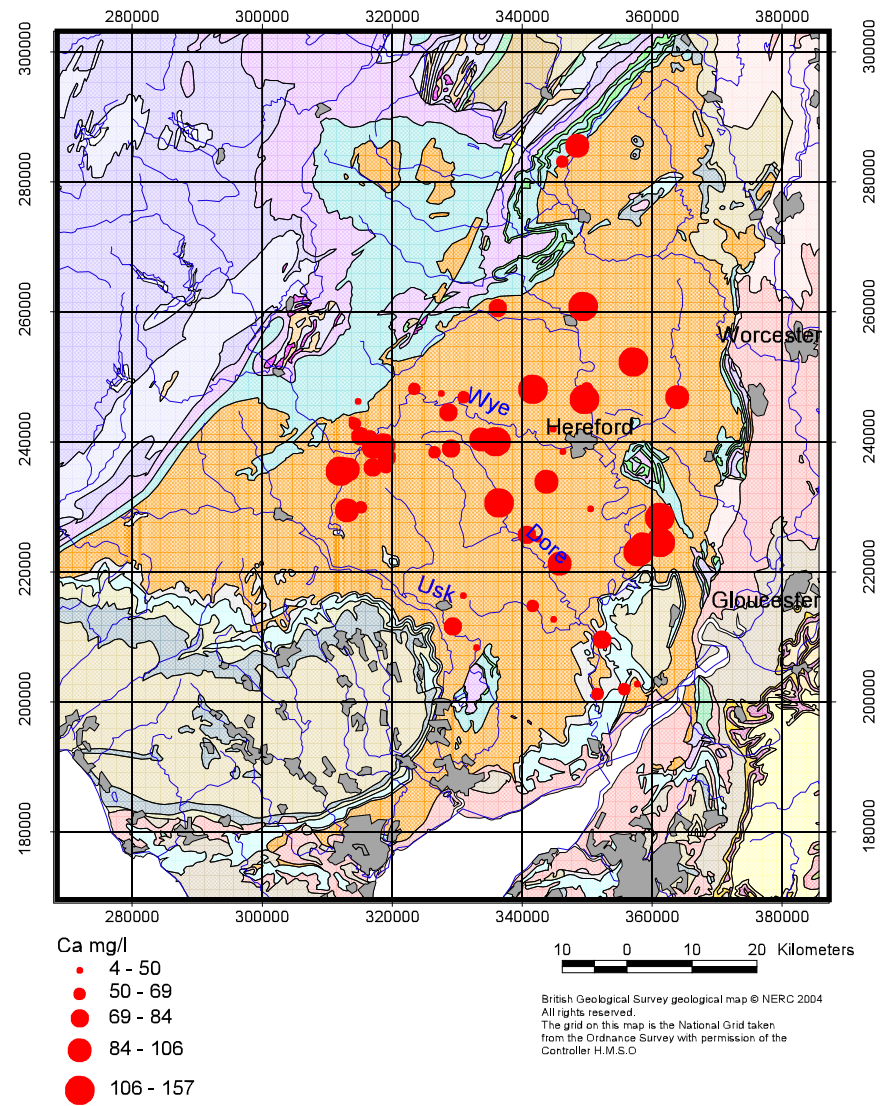


Figure 6.16 Regional variations of Ca in the Devonian Aquifer groundwaters.

7. BASELINE CHEMISTRY OF THE AQUIFER

The baseline groundwater chemistry of any aquifer is determined by a wide range of physical as well as chemical processes. The primary input to most major aquifers is rainfall, especially for the Devonian Sandstone where the groundwater flow is expected to be concentrated in shallow fractured/weathered horizons. However, saline formation water may be present in parts of the aquifer where confinement occurs. A series of chemical reactions take place during recharge and groundwater flow, the most important being mineral dissolution and precipitation, mixing, redox reactions, ion exchange and sorption/desorption reactions. Water-rock interaction is complicated by the fact that most aquifers are heterogeneous in terms of mineralogy and geochemical environment (e.g. redox status). Many of the above-mentioned reactions are also time-dependent and this gives rise to a range in baseline chemistry as the groundwaters move from areas of recharge to discharge. These processes give rise to spatial variations and trends along flowpaths, which in some instances was observed along the two sections.

Superimposed on this “natural” baseline are anthropogenic influences. These include point-source and diffuse pollution which directly modify the baseline chemistry. However, the baseline can be modified indirectly, for example, by abstraction: this can induce leakage from overlying units or up-coning of deeper water of a different chemical composition or induce chemical changes such as oxidation reactions. In such cases, the origin of solutes may well be natural and represent baseline. However, the baseline chemistry of the aquifer itself has changed highlighting the need to characterise the baseline of a specific system.

In the present study boreholes which are believed to be affected by point-source pollution have been excluded from the database. However, many groundwaters in major aquifers, especially where unconfined, show signs of diffuse pollution, dominantly from urban or agricultural activities and these have been included. The determination of baseline in such cases can be ascertained from historical records, where these exist, by comparing with pristine areas, applying statistical techniques or modelling. Most of these have limitations and should be used together to provide a reasonable estimate of the baseline composition (Shand & Frengstad, 2001). However there are no historical records for the Devonian Sandstone, which complicates the establishment of the baseline of groundwaters.

The Devonian Sandstone waters are moderately fresh and tend to have low conductivities compared with other UK groundwaters, which is probably due to shallow and rapid groundwater circulation in the aquifer and relatively pristine conditions. At the local scale, concentrations might be greater than the true baseline but fall within the overall range of natural baseline within the aquifer. This emphasizes the need to determine the system in which baseline concentrations are reported. The large range in baseline for some parameters is due to the large area of sampling including the uplands (recharge areas) as well as valleys. Locally, the presence of thick superficial deposits in valleys (glacial sand, gravel and till) will have an impact on groundwaters. This could explain some of the high uranium concentrations, found at low elevations where till deposits are present. Glacial sand and gravel lenses are also likely to hold some groundwater and are expected to have a hydrochemistry somewhat different to the Devonian groundwaters.

Most waters are either at or approaching saturation with respect to both calcite and dolomite. Locally, nitrate, phosphate and ammonium highlight the anthropogenic impact on groundwaters. Enhanced sodium, potassium and sulphate concentrations are also signs of agricultural pollution. The composition of the waters from most of the boreholes sampled in the Devonian Sandstone can be ascribed primarily to natural processes of water-rock interaction: the majority of sources sampled have solute concentrations that are within baseline values (97.7 % as indicated in Table 5.1 and Table 5.2). These natural processes include mineral dissolution and ion exchange, redox reactions, particularly where the aquifer becomes confined and to a lesser degree the mixing of infiltrating

waters with formation water. According to the cumulative plots (Figure 5.3 and Figure 5.5) nitrate shows a distinct shift in concentration with high measured concentrations (particularly in valleys) unlikely to be derived from a natural background, highlighting an anthropogenic component. The baseline for NO_3 is likely to be about 1 to 2 mg l^{-1} as $\text{NO}_3\text{-N}$. Time series for six abstractions points (data from 1974 to 1991) located on the edges of the Devonian outcrop show nitrate concentrations ranging from 2 to 12 mg l^{-1} of $\text{NO}_3\text{-N}$, most analyses being below the EC guideline value of 11.3 mg l^{-1} . Some of these show clearly an increase of nitrate concentrations with time. It is very likely that by 1974 nitrate application and contamination of groundwaters had already taken place, hence even the lowest recorded concentrations in 1974 may be significantly above the actual natural baseline.

Trace element concentrations are generally low, with most being below EU guidelines for human consumption. Many heavy metals concentrations reflect low baseline conditions. Although barium, strontium and uranium concentrations can attain high levels, they are considered to represent baseline. Arsenic is present in low concentration except for two samples with significantly higher concentrations, showing a shift in the cumulative plots. These two samples are from groundwaters of Na-HCO_3 type with high total dissolved solid content and are likely to be relatively old waters unaffected by pollution.

8. SUMMARY AND CONCLUSIONS

The Devonian Sandstone is divided into six formations with four of these forming important aquifers: the Brownstones and Senni Beds Formations, the St Maughans Formation, and the Raglan Mudstone Formation which forms a less productive aquifer. The Devonian Sandstone comprises many rock-types such as mudstones, calcretes, sandstone and siltstone and consists of a complex multi-layered aquifer, with predominant fracture-flow, although some intergranular flow occur in the sandstones. The aquifer units are generally unconfined, however, the age and nature of the aquifer induces confining mudstone bands at depth. In spite of the great thickness of the Devonian Sandstone, the permeability is limited to the fracture network found within the upper 50 metres, the number of fractures decreasing rapidly with depth.

The chemistry of groundwater in the Devonian Sandstone aquifer of the study area is dominated by natural processes of water-rock interaction. The dominant process controlling groundwater chemistry is carbonate mineral dissolution and, in the deeper groundwaters, ion-exchange. Slower silicate dissolution reactions are also important in providing Si, K and Na to the groundwaters. The groundwaters are mostly of Ca-HCO₃ type but Na-HCO₃ types are present in deeper parts of the aquifer. In many places, tufa deposits around springs are observed, hence calcite precipitation also helps to modify groundwater chemistry in these discharge zones. The flow mechanism, dominantly via fractures, and the heterogeneous nature of the aquifer has given rise to widespread regional variations in baseline solute concentrations. Upland groundwaters show significant rock interaction even where residence times are short. In valleys this is complicated by mixing with older, probably confined groundwaters bodies as well as anthropogenic inputs.

The groundwaters generally have low solute concentrations reflecting the relative purity of the aquifer material. The localised drift deposits and the hydraulic connectivity of the surface and groundwaters make the Devonian Sandstone aquifer vulnerable to pollution. The low salinities of groundwater indicate shallow groundwater flow in uplands areas, where the aquifer is well flushed of any older formation waters. In the valleys, remnants of older formation groundwaters identified by high Na, Cl, Br and I content as well as salinity occur at depth beneath protective mudstones horizons. In these areas ion-exchange of Na adsorbed on clays for solute Ca occurs leading to Na-HCO₃ type groundwaters.

Some reducing waters exist but it is difficult to relate these to a redox boundary along flow pathways. Iron and Mn are generally low reflecting the dominance of oxidising conditions in most of the aquifer but may be locally high (up to 3.2 and 0.95 mg l⁻¹ respectively). Trace metal concentrations are generally low, reflecting the circumneutral pH and oxidising conditions over much of the aquifer. However, barium, uranium and strontium may be locally relatively high. These are thought to be naturally derived, most of the Ba from feldspars and Sr from either calcite or dolomite dissolution. Uranium concentrations are generally higher in the valley bottoms, and it is possible that the superficial deposits may act as a source. Trace metals such as As, Pb and Ni were typically found at very low concentrations or below detection limit.

Superimposed on the natural baseline chemistry are the effects of human activity. This is most apparent from the increased nitrate concentrations in the unconfined groundwaters resulting from diffuse pollution. However, the little historical data available for the aquifer does not allow determination of the baseline to be refined to account for these influences. It is likely that baseline concentrations of NO₃-N are of the order of 1-2 mg l⁻¹ as indicated by the lowest concentrations in oxygenated waters. Other elements most likely to be influenced by diffuse pollution include K, Cl and SO₄.

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