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Baseline Report Series: 22. The Carboniferous Limestone of Northern England

Groundwater Systems and Water Quality
Commissioned Report CR/05/076N

Science Group: Air, Land & Water
Technical Report NC/99/74/22



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
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Baseline Report Series: 22. The Carboniferous Limestone of Northern England

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FOREWORD

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

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

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

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

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

BACKGROUND TO THE BASELINE PROJECT

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

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

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

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

Thus an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era, although this is not always easy for several reasons. Groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth as a result of the stratification that invariably develops. This stratification is a result of different flow paths and flow rates being established as a consequence of prevailing hydraulic gradients and the natural variation in the aquifer's physical and geochemical properties. The drilling and installation of boreholes may penetrate this stratified groundwater and pumped samples will therefore often represent mixtures of the stratified system. In dual porosity aquifers, such as the Chalk, the water contained in the fractures may be considerably different chemically from the water contained in the matrix because of differences in residence time. The determination of the natural baseline can be achieved by several means including the study of pristine (unaffected by anthropogenic influence) environments, the use historical records and the application of graphical procedures such as probability plots to discriminate different populations (Shand & Frengstad, 2001; Edmunds et al., 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 unpolluted and polluted groundwaters will be investigated; this is because, even in polluted systems, the main constituents of the water are also controlled by geological factors, amount of recharge and natural climate variation.
3. to establish long term trends in water quality at representative localities in the selected reference aquifers and to interpret these in relation to past changes due to natural geochemical as well as hydrogeological responses or anthropogenic effects.
4. to provide a scientific foundation to underpin UK and EU water quality guideline policy, notably the Water Framework Directive, with an emphasis on the protection and sustainable development of high quality groundwater.

1. EXECUTIVE SUMMARY

The Carboniferous Limestone of the Central Pennines of Yorkshire and Lancashire is an important local aquifer providing water for potable and industrial use. It forms the oldest of a multi-layered series of (minor) aquifers, which lithologically varies considerably across the region. The geology and distribution of drift deposits in the region are complex and this also has an effect on the baseline chemistry of the aquifer resulting in considerable spatial heterogeneity. Karstification has occurred in parts of the aquifer and the rapid flow rates and transport associated with the presence of large interconnected conduit systems make the aquifer highly vulnerable to pollution, especially in areas where drift deposits are absent. Landuse in the area is predominantly managed grassland and only a few urban and industrial areas are present in the study area.

The chemistry of the groundwaters is overwhelmingly controlled by natural reactions between the groundwater and the bedrock, predominantly carbonate dissolution reactions. Dolomitisation and chertification have occurred in parts of the aquifer and the presence or absence of these processes is reflected in the chemical signatures of the groundwaters. The redox conditions of the groundwater are variable. Where reducing environments are encountered, the natural baseline is influenced by the reductive dissolution of secondary Fe and Mn oxyhydroxides. Such groundwaters often contain high levels of naturally derived Fe and/or Mn, but are low in $\text{NO}_3\text{-N}$ due to denitrification. There is evidence for some bedrock mineralisation in the study area, probably of hydrothermal origin, reflected in high levels of F, Ba and trace elements (e.g. Cu, Pb, U, Zn) in the groundwaters, and EC Guide levels for Ba and F are exceeded locally. Ion exchange and mixing influence the baseline chemistry and have given rise to the formation of Na-HCO_3 -type waters. The source of the high salinity in some groundwaters is mostly due to mixing with older formation waters, but leakage from younger deposits of Namurian/Westphalian, Permian and/or Triassic age seem also likely. Nitrate concentrations are generally low throughout the aquifer due to denitrification, protection of the aquifer by impermeable strata within the aquifer as well as by the overlying drift. Although the aquifer is likely to have been impacted by other anthropogenically-derived solutes (Na, Cl, SO_4), these are generally within the overall natural range of concentrations found within the aquifer. The large spatial variability in the hydrogeochemistry of the aquifer, caused by its complex geology (including bedrock mineralisation and karstification) and by the distribution of drift deposits, make prediction of the baseline conditions difficult to assess on a local scale.

2. PERSPECTIVE

The Carboniferous Limestone of Dinantian age is not considered to constitute a major aquifer, except in Derbyshire, the Mendips and South Wales, but can be nevertheless an important local aquifer providing water for potable and industrial use. It outcrops in northern England, the Central Pennines of Yorkshire and Lancashire, extending as far south as Cornwall and Devon.

The Dinantian outcrop considered in this report stretches between Kendal in the north, Barrow in Furness in the east and Burnley in the south-east (Figure 2.1). In the north-east, the Carboniferous Limestone group is flanked by Millstone Grit, which is also present in form of an outlier in the central part of the study area. The north-western boundary of the outcrop is formed by Silurian shales and greywackes while Namurian and Westphalian deposits mark the boundaries in the south. This region forms the core area for evaluating the regional baseline groundwater quality and selected groundwater data have been used to provide an areal coverage.

The Carboniferous Limestone aquifer of the study area is the oldest in a multi-layered series of minor aquifers. Its nature varies considerably across the region from a predominance of massive limestones with interbedded mudstones in the north to predominantly mudstones and shales in the south. It is commonly the limestones that provide the water-bearing strata whereas the interbedded mudstones act as aquicludes or aquitards. Glacial and postglacial deposits cover much of the study area, and where the deposits are clayey (till), they limit recharge to the aquifer.

Surface drainage in the area is shown in Figure 2.1. The drainage pattern is dominated by the River Lune, the River Ribble and the River Wyre and their tributaries, which were essentially established as a result of meltwater erosion during the last deglaciation. The drainage system as such is relatively immature, hence most upland rivers and streams are juvenile and are still down-cutting to a lower base level through drift and bedrock (Brandon et al., 1998).

The dominant land use is managed grassland (Figure 2.2). The study area incorporates only a few urban and industrial areas. Where thick sequences of Carboniferous Limestone are present in the study area, these are often exploited by limestone quarrying (Figure 2.3), mainly for the production of agricultural lime, road aggregates or locally used building stones.

Groundwater from springs and boreholes in the Carboniferous Limestone aquifer is used principally for agricultural, industrial and domestic water supply. There are also a number of sources which are used for public water supply. Groundwater from the Carboniferous Limestone aquifers also contributes significantly to the baseflow of surface waters.

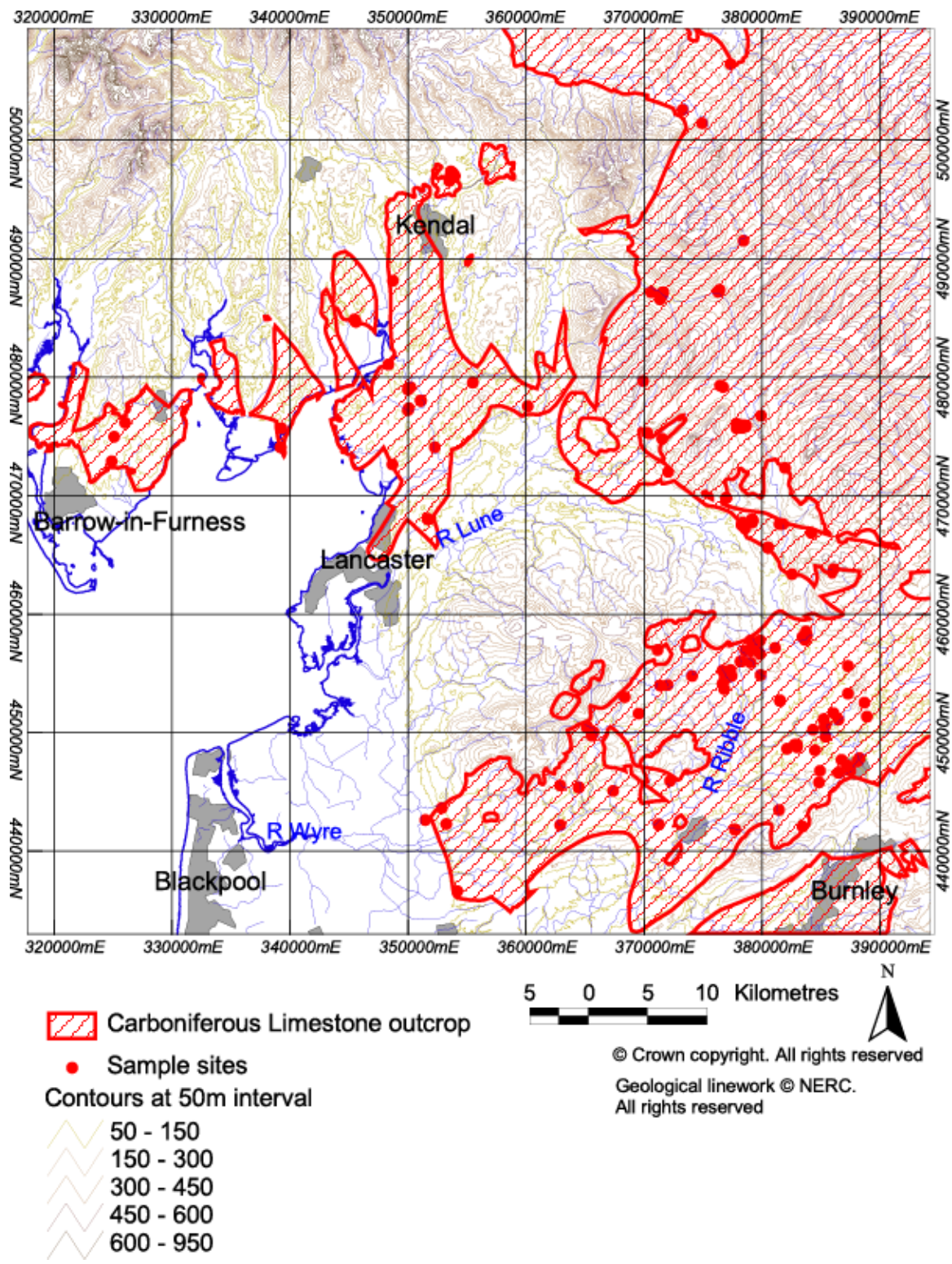


Figure 2.1 Topography and Surface drainage of the study area

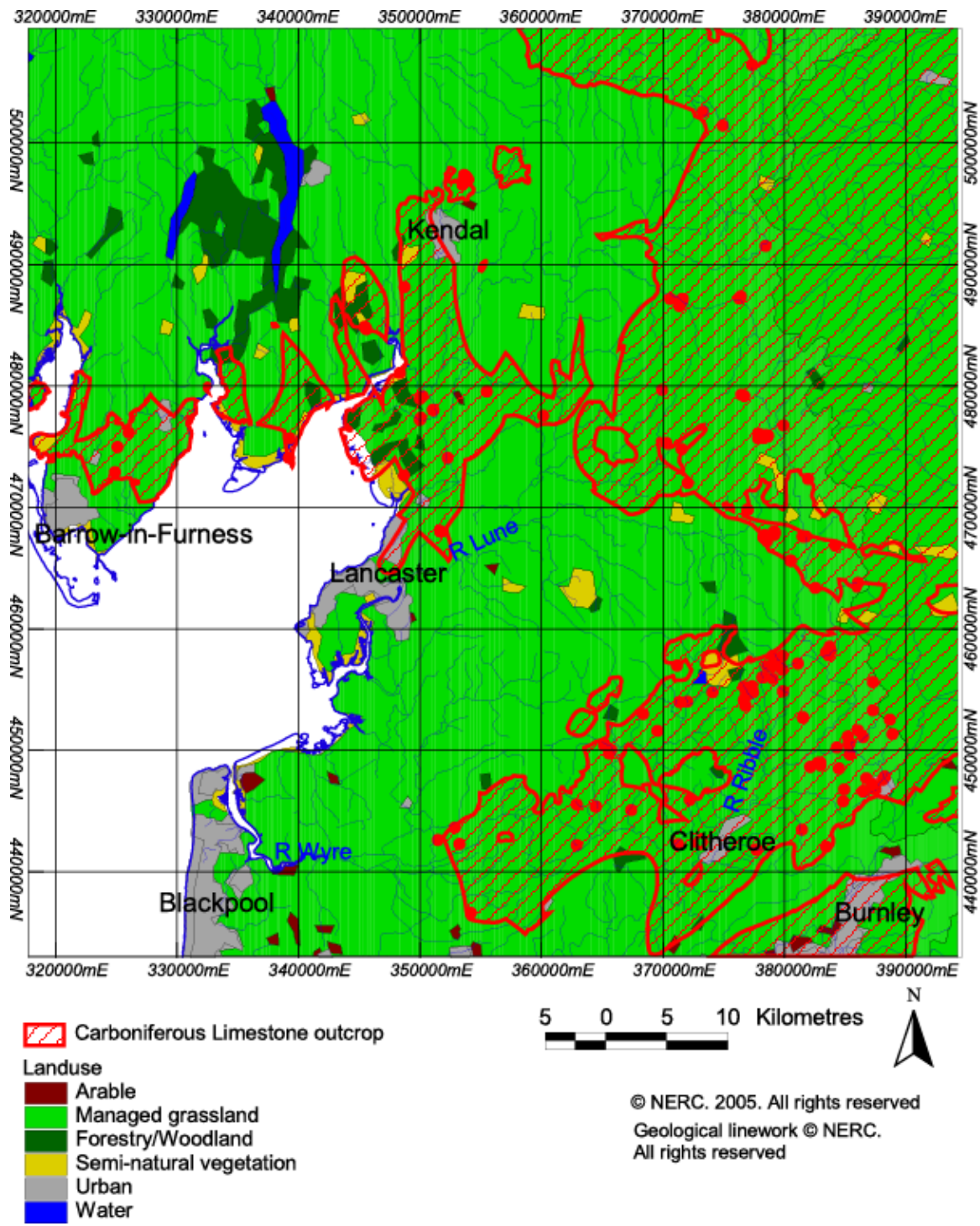


Figure 2.2 Landuse in the study area



Figure 2.3 Limestone quarrying in the study area, Stainton Quarry [BNG 32470 47271]

3. BACKGROUND TO UNDERSTANDING BASELINE QUALITY

3.1 Introduction

In order to assess the baseline groundwater quality, it is necessary to have some knowledge of the geological, hydrogeological and chemical characteristics of the aquifer. The initial characteristics of recharge water are determined by the interaction of rainfall (which also provides solutes) with vegetation, soils and the unsaturated zone. Further changes occur in relation to residence time and differences in mineralogy along flow paths in the aquifer.

3.2 Geology

The Carboniferous rocks include Carboniferous Limestone, Millstone Grit and Coal Measures and can be broadly equated with the chronostratigraphical divisions Dinantian, Namurian and Westphalian. During the Dinantian, carbonate deposition was dominant, represented by the Carboniferous Limestone, which formed during a period of active tectonic movements and rift subsidence. The variety of rock types, including mudstones, siltstones and sandstones, in addition to limestones, reflects the diversity of depositional environments present at that time ranging from shallow shelf seas.

The area of the present study is located in the Central Pennines of Yorkshire and Lancashire (Figures 2.1 and 3.1). Dinantian rocks underlie the entire study area and crop out in two main areas, the Askrigg Block and the Craven Basin, which are located to the north and the south-west of the Craven Fault System, respectively. In the central area, beneath the Lancaster Fells, the Dinantian rocks are confined by the Namurian (Silesian) outcrop, while faulted against and overstepped by a sequence of Permo-Triassic rocks in the west.

During the Quaternary, the study area was glaciated on several occasions. As a result, much of the area is covered with extensive drift material of glacial and postglacial origin (Figure 3.2). During glacial advance, extensive glacial till deposits were laid down over large parts of the area, predominantly on the lower ground in the west and north. The composition of the till deposits mostly reflects the local bedrock geology and comprises rock fragments and boulders in a matrix of sandy-clay, silty clay or clayey sands. The thickness of the till varies greatly across the study area: while generally less than 4 m, thicknesses of up to 34.5 m have been recorded locally. During glacial retreat, large volumes of water were released, cutting networks of channels into the landscape and depositing gravelly sediments throughout the area. The upland regions remained for the most part till free, but are commonly covered by postglacial head deposits, derived through processes of gelifluctation and solifluctation. The head deposits are heterogeneous and vary in thickness between < 1 m on steep slopes to > 5 m on more gently sloping grounds. They are most commonly found in the central and southern upland parts of the study area and comprise poorly consolidated, sandy silts to silty sands with sandstone fragments up to boulder size. The till deposits of the lower ground are commonly covered by postglacial, glaciofluvial sands and gravels (Brandon et al., 1998).

3.2.1 Structural settings

From Late Devonian times onwards, the southern continent of Gondwana was in collision with the northern continent of Laurentia, leading to the Variscan Orogeny and creating the supercontinent Pangaea. The strong Variscan deformation in the south (which extended across southern Britain between the Thames and Severn Estuaries) was accompanied by back-arc extension in the north, which controlled structure, sedimentation and igneous activity in the British Isles throughout the Late Devonian and Carboniferous times (JNCC, 2005).

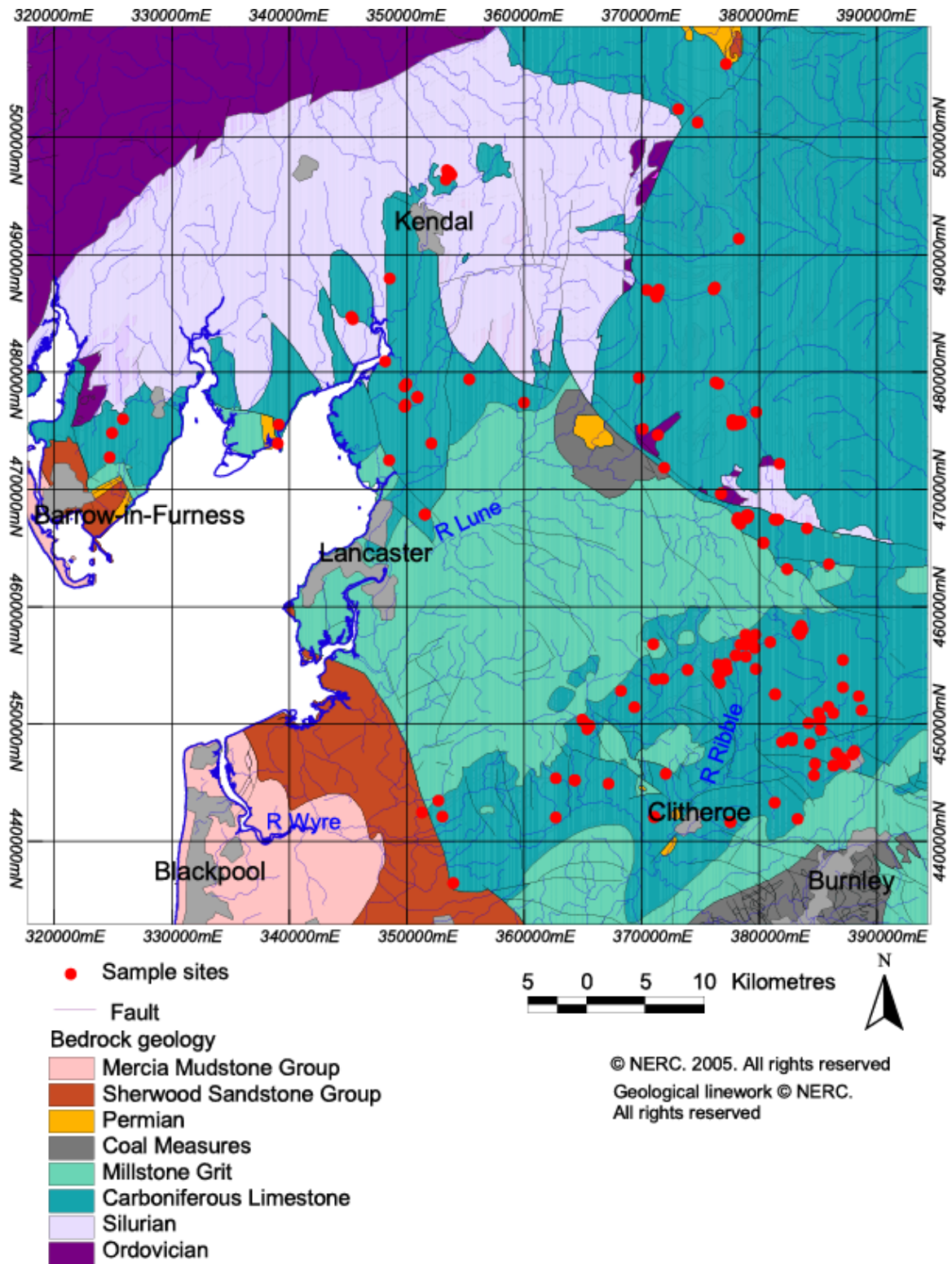


Figure 3.1 Geology of the study area

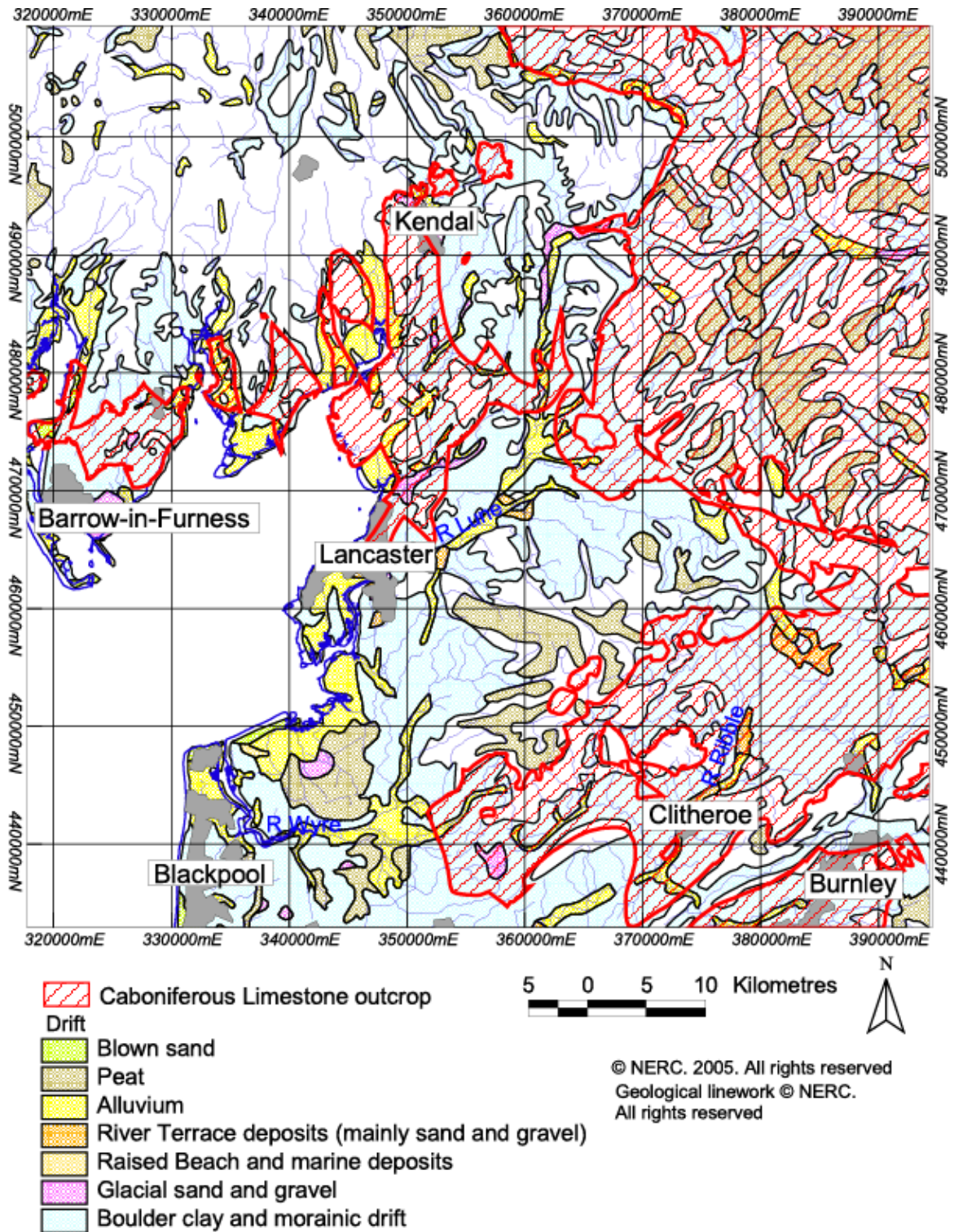


Figure 3.2 Drift deposits in the study area

In northern and central England, structural setting and sedimentation during the Dinantian were strongly controlled by the rifted topography of fault-bounded blocks (highs), such as the Askrigg Block and the Lake District High, and intervening, rapidly subsiding grabens and half-grabens (basins) such as the Craven Basin and the Stainmore Basin (Figure 3.3). Basin formation was a direct result of lithospheric stretching (back-arc extension) associated with the Variscan Orogeny, and was dominated by the development of half-grabens and tilted blocks. The intervening areas of basement

highs (or blocks) of Lower Palaeozoic strata are commonly cored by granitic plutons and were separated from the basins by hinge-lines and normal faults, which remained active during sedimentation (Leeder, 1992).

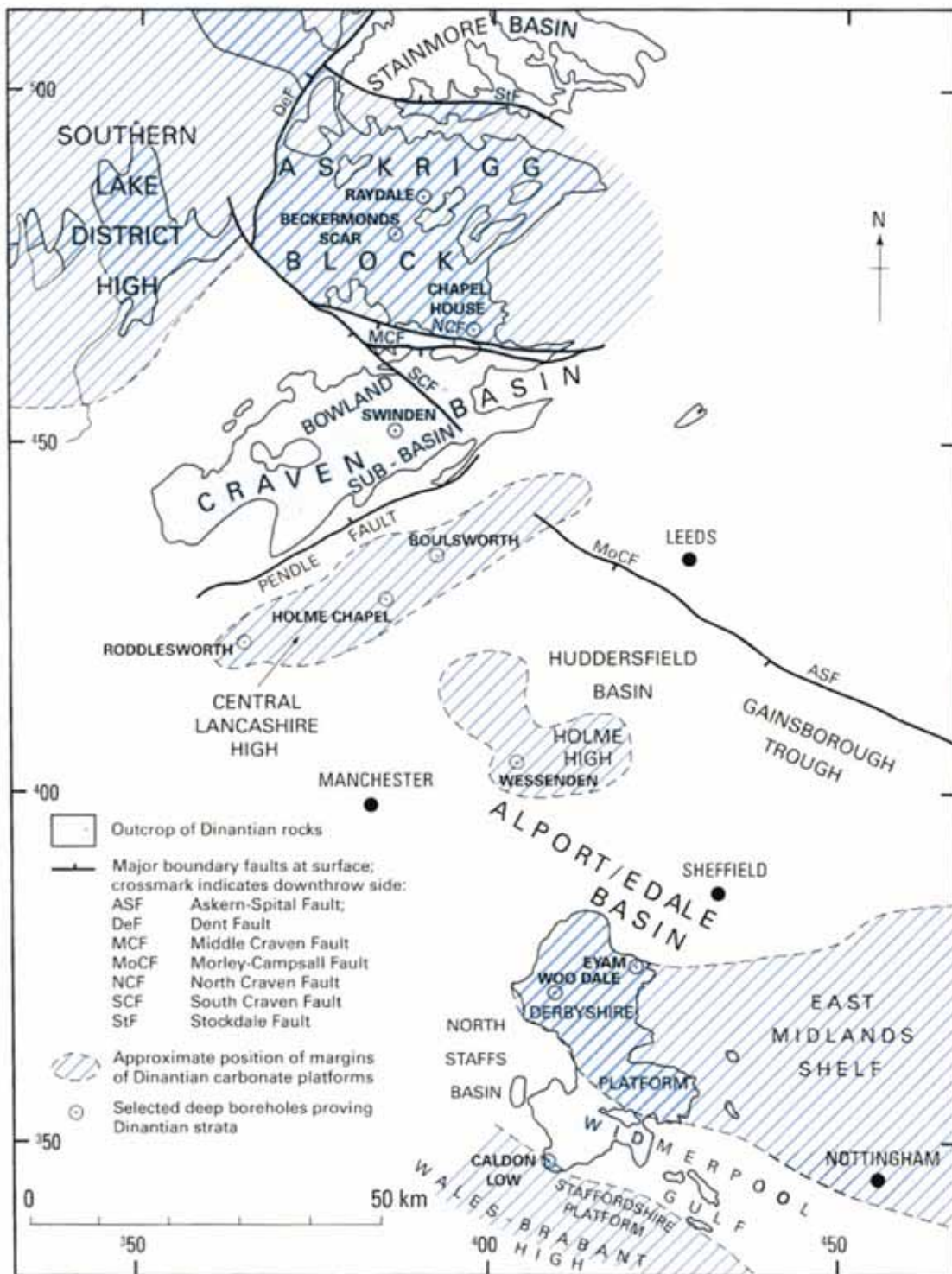


Figure 3.3 Outcrops of Dinantian rocks and principal structural features of the Dinantian Palaeogeography of the study region and surrounding areas (Aitkenhead et al., 2002)

Crustal extension continued throughout most of the Dinantian and rifting related structures were constantly growing beneath the area of Dinantian deposition. As a result, the sea was persistently deeper in some places relative to others and a diverse range of sediments was deposited in the area. The tilting movements continued during sedimentation and sequences thicken markedly in the direction of tilt. In the generally northerly tilting Askrigg Block, for example, sequences thicken markedly towards the north (Figure 3.4). Throughout the Dinantian, syndimentary tectonic movements and faulting occurred, evidence of which is preserved in many sedimentary features such as slumped horizons, local development of debris flow, turbidites and foundered slabs present in the study area.

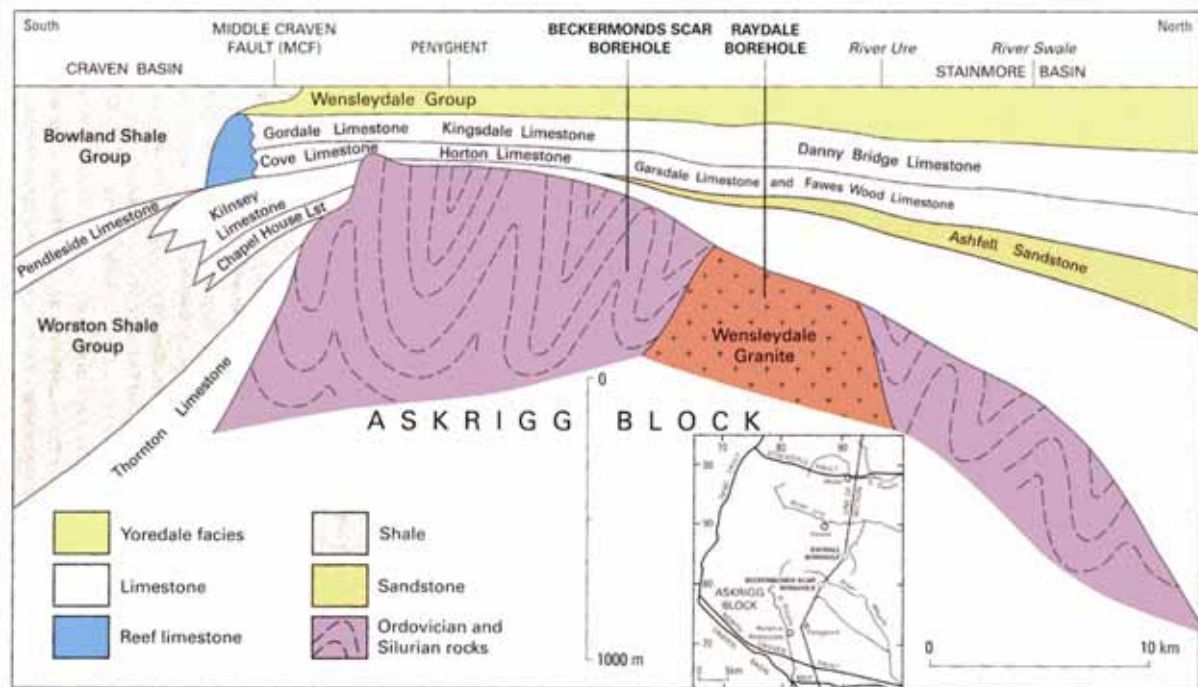


Figure 3.4 Schematic cross-section of the Askrigg Block (after Wilson, 1992, in Aitkenhead et al., 2002)

In the mid-Carboniferous, rifting and crustal extension ceased, and by late Carboniferous times, basin subsidence in the region gave way to regional uplift. As part of that movement, inversion of pre-existing Dinantian extensional faults as well as folding and erosion of the Carboniferous strata occurred, which, in the study area, is most evident as the NE-SW trending anticlines and synclines of the Ribblesdale Fold Belt.

In the study area, the most important tectonic structures are the Askrigg Block and the Craven Basin. The Craven Basin (Figure 3.3) is an asymmetrical graben, tilted to the south. During Dinantian times, it was bounded by the Southern Lake District High to the north-west, the Craven Fault to the north-east and the Central Lancashire High to the south. The basin contained a number of intra-basinal tectonic features, such as subordinate half-grabens, which locally affected the sedimentation. Thus, in the Craven Basin, Dinantian strata are highly variable depending on the position relative to tilted blocks and basins.

The Askrigg Block (Figure 3.3) lies north-east of the Craven Basin and of the Middle Craven Fault. During Dinantian times, the block intermittently tilted to the north (Aitkenhead et al., 1992) as is reflected in some northward thickening of the early Dinantian strata in the Stainmore Basin, which merges the block at the northern margin.

3.2.2 *Sedimentary environment*

A tropical sea transgressed the area during the Dinantian. Thick deep-water, sedimentary sequences, such as the deeper water mudstone-limestone successions of the Craven Basin (Figure 3.4), accumulated in the basins. On platform areas and tilt-block highs, which commonly formed low-lying land and shelf areas, shallow-water repetitive sequences of marine limestones and terrigenous clastic rocks accumulated, such as the Yoredale facies of the Askrigg Block (Figure 3.4).

Commonly, sedimentation started earliest in the downfaulted basinal areas, such as the Craven Basin, where fairly complete successions of Dinantian strata reach total thicknesses of 2500 m or more (Aitkenhead et al., 2002). The Dinantian conformably overlies Devonian strata, although in most areas, the base of the sequence remains largely unproven. On the structural highs, by way of contrast, Dinantian strata are comparatively thin and lie unconformably on the Lower Palaeozoic basement. This indicates that much of the platform areas must have been emergent land surface during most of the early Dinantian sedimentation.

3.2.3 *Lithology*

Dinantian rocks in the study area crop out in two main areas, the Askrigg Block and the Craven Basin, each of which have their own succession of strata (Figure 3.5). The rocks have formed from a variety of carbonate sediments ranging in grain size from mud to limestone pebbles and boulder beds, and were deposited in a range of marine environments. The different depositional environments (Table 3.1) have been summarised by Aitkenhead et al. (2002) whereby the boundaries between the depositional environments are commonly gradational and some thicker formations can extend laterally and vertically across the boundaries. Some land-derived, clastic rocks are also present in the Dinantian sequence of the study area.

In the Askrigg Block area (spanning between NGR 370 470 and NGR 420 500), the Carboniferous succession is mainly composed of massive bioclastic limestones and reef limestones, with some clastic sandstone layers in the upper parts of the sequence (Figure 3.5). The limestones often show paleokarstic features in the form of pot-holed and scalloped bedding surfaces, which have been subject to karstification and early diagenetic cementation.

In the Craven Basin (spanning between NGR 350 440 and NGR 410 460), the Carboniferous sequence is dominated by deeper marine, dark, thinly bedded, cherty, fine-grained limestones and dark grey to black, fissile and blocky mudstones. Interbedded limestones with silty mud occur in deeper sections of the profile, while dark, organic-rich mudstones, with varying proportions of fine calcareous sediments and reworked sandstones and siltstones form the upper part of the sequence.

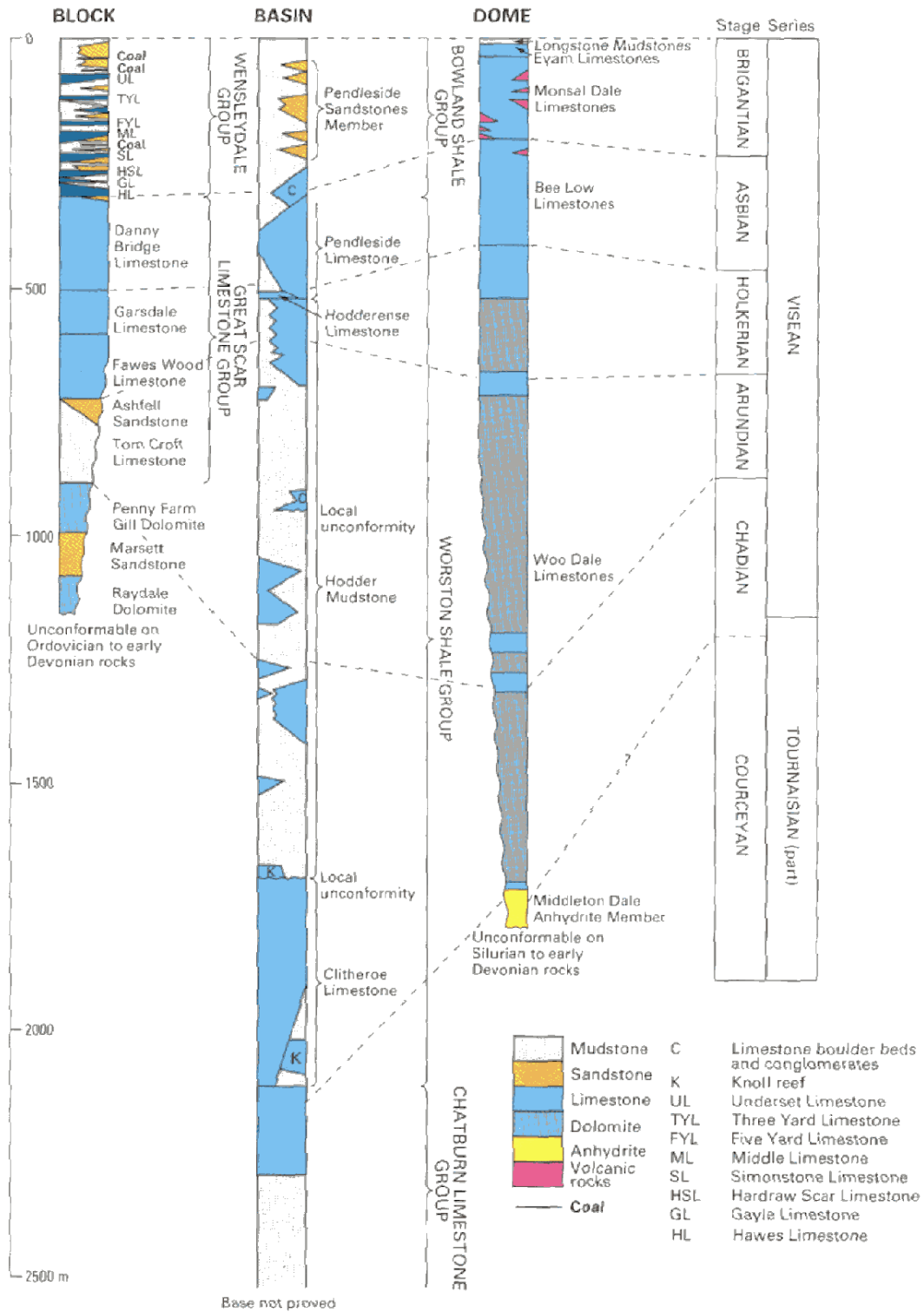


Figure 3.5 Generalised vertical sections of the Dinantian strata of the Askrigg Block, Craven Basin and Derbyshire Dome (Aitkenhead et al., 2002)

Table 3.1 Summary of main depositional environments and lithologies of some of the principal Dinantian formations and groups (Aitkenhead et al., 2002)

Paleo-environment	Typical lithologies	Examples of outcrop in the region
Platform	Thickly bedded, pale grey to grey, massive bioclastic limestones (packstones and grainstones), dolomitised limestones and dolomites	Great Scar Limestone Group (A), Woo Dale Limestones, Bee Low Limestones and Monsal Dale Limestone (D), Kevin Limestones and Milldale Limestones (S)
Ramp	Grey to dark grey, thinly bedded, bioclastic limestones (packstones) commonly with chert nodules and pale grey micritic limestones forming knoll reefs (mud mounds)	Clitheroe Limestone (C), Eyam Limestones (D), Hopedale Limestones and Milldale Limestones (W)
Slope	Limestone conglomerates and boulder beds, limestone turbidites commonly showing soft-sediment deformation structures and chert nodules	Pendleside Limestone, and limestone in the Hodder Mudstone (C), Ecton Limestones and limestones in the Widmerpool Formation (W)
Basin	Dark, thinly bedded, cherty, fine-grained limestones (wackestones) and dark grey to black, fissile and blocky mudstones	Hodderense Limestone and Hodder Mudstone (C), Widmerpool Formation (W), Bowland Shale Group (C), with Pendleside Sandstones Member (C)

A	Askrigg Block	S	Staffordshire Platform
C	Craven Basin	W	Widmerpool Gulf/ North Staffordshire Basin
D	Derbyshire Platform		

3.3 Hydrogeology

In the study area, the Carboniferous Limestone forms predominantly minor aquifers, although major Carboniferous Limestone aquifers are well developed in the Peak District of Derbyshire, the Mendip Hills, north and south Wales, and north-west Yorkshire (Allen et al., 1997).

The Carboniferous Limestone aquifer is the oldest in a multi-layered series of minor aquifers. Its nature varies considerably across the region mainly due to variations in lithology and the amount of limestone present. In northern Yorkshire, massive limestones with relatively minor interbedded mudstones occur, while in the Craven district and in the northwest of the region, shales predominate (Figure 3.6). It is commonly the limestones that provide the water-bearing strata whereas the interbedded mudstones act as aquicludes or aquitards.

The limestones are water bearing where dissolution processes have produced flow pathways, and groundwater occurrence in the Carboniferous Limestone aquifer is generally associated with a secondary network of fractures and joints (conduits). Enlarged by solution, these structures commonly form a complex branching system of different scales, ranging from micro-fractures to extensive cave systems. In contrast, the limestone matrix has a very low porosity (average 1–1.3 %) (Jones et al., 2000) and permeability (average 0.14 m d^{-1}) (Holliday, 1986) and makes only a negligible contribution to the water-bearing properties of the aquifer. Extensive dolomitisation may have increased the porosity locally, but this seems to have little effect on the permeability (Aitkenhead et al., 2002).

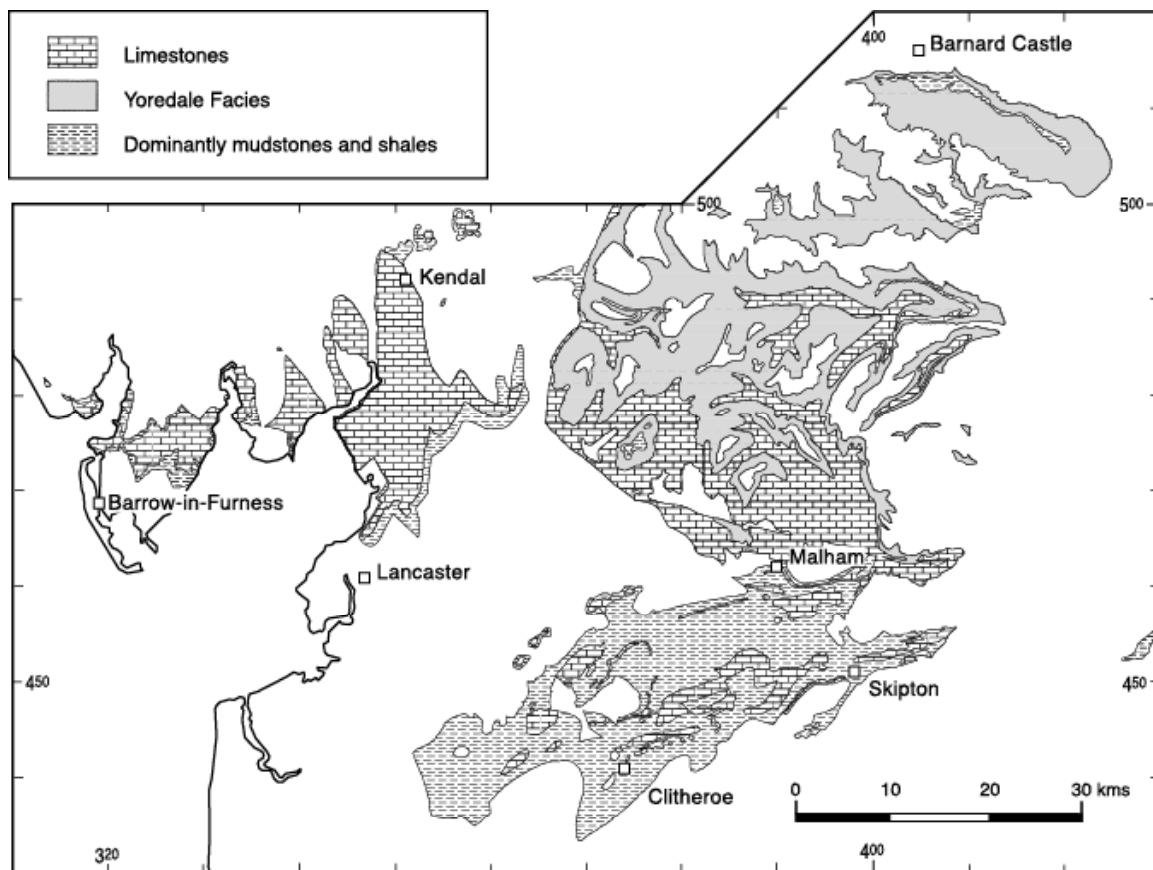


Figure 3.6 Distribution of outcrops of various Carboniferous Limestone lithologies in Northern England (Jones et al., 2000)

In general, the groundwater flow in the well-developed karstic terrain is largely concentrated in the larger conduits and directed towards discrete discharge points at a spring or a group of springs. The velocity of groundwater flow is highly variable and often difficult to predict as it depends on the prevailing hydraulic gradient, the size of the fractures as well as on rainfall effects. In the presence of large interconnected conduit systems, flow can be very rapid and flow velocities between 240 m d^{-1} to over 9600 m d^{-1} have been measured in the Malham area, east of Settle (Jones et al., 2000). Such fast rates of transport make the aquifer highly vulnerable to pollution, especially in areas where it is not overlain by low permeability strata. In regions without such conduit systems, flow velocities will be much smaller.

Groundwater flow directions are also difficult to predict. While the regional drainage is to the south, joints and faults exert a strong local influence on the groundwater flow direction (Gunn, 1992), so that flow may not be perpendicular to lines of equipotential, which themselves are difficult or impossible to ascribe, especially in the more karstic areas (Allen et al., 1997). Besides, flow direction may change markedly with variations in water table levels as discrete channel networks are dewatered. Such changes may also be brought about by extensive pumping and groundwater abstraction. The complex interconnections between sinks and points of discharge as well as the temporal (natural) variability in flow response have been demonstrated by Smith and Atkinson (1977) and underline the uncertainties associated with inferring flow pathways and assessing pollutant transport in the aquifer. It is pertinent, within the context of baseline chemistry, to note that temporal water table variations not only change flow pathways but can also affect the groundwater chemistry in the area, as variations in the saturated aquifer thickness may promote mineral dissolution in sediments not usually in contact with water.

Borehole yields in the Carboniferous Limestone are variable, and even boreholes in close proximity of each other can produce very different yields if water-bearing structures are intersected in some boreholes but not in others. In the northern Pennines, the majority of borehole yields lie in the range of 240 to 1920 m³ d⁻¹, although very low yielding and dry boreholes are by no means uncommon (Jones et al., 2000).

The density and size of fractures commonly decreases rapidly with depth, providing an effective aquifer thickness of only 50-80 m, although the actual thickness of the limestone formation may be considerably greater. However, the unpredictability of the aquifer has resulted in few wells being drilled and much of the groundwater abstraction is derived from springs.

Previous investigations have shown that groundwaters in the area are generally of calcium bicarbonate type and has a high alkalinity (Brandon et al., 1998), although where deeply buried by younger strata, the groundwater is commonly saline, in some cases excessively so.

3.4 Aquifer mineralogy

Studies on the mineralogical composition of the Carboniferous Limestone in the Craven Basin have found that regional variations in the limestone composition are mostly related to the amounts of bioclasts (e.g. crinoids, spicules, calcispheres, foraminifera, bryozoa) and intraclasts in the bedrock and to the presence of different iron minerals (hematite, magnetite, pyrite) (Figure 3.7) (Addison et al., 1985). The purity of the limestone is primarily controlled by the amount of silica present (Harrison, 1982).

Calcite is the most common cement in the Carboniferous Limestone and occurs in ferroan and non-ferroan form. Replacement of the limestone and cement by dolomite and silica is common and has been observed in both, the Askrigg Block (Brandon et al., 1998) and in the Craven Basin (Addison et al., 1985; Jones et al., 2000). The silification (chertification) is stratigraphically transgressive and cherts occur as discrete bodies of lensoid sheets and nodules, parallel or sub-parallel to bedding (Addison et al., 1985), or in disseminated form.

In the Craven Basin, dolomitisation appears to be strata bound and is mainly confined to the Pendleside Formation, which extensively outcrops in the south of the study area. It often only affects certain beds or groups of beds within the formation so that vertical changes in lithology are commonly associated with the extent of dolomitisation and chertification in the limestone beds (Addison et al., 1985). The composition of un-altered Pendleside Limestone is illustrated in Figure 3.7, displaying variations in the amount of bioclasts and lithoclasts and in the presence of iron in the limestone. From the graphs, it is also apparent that replacement of both, grains and cement with euhedral (idiomorphic) rhombs of dolomite occurs in the Pendleside Limestone, the degree of which corresponds to the different stages of dolomitisation and chertification. Addison et al. (1985) suggest that dolomitisation and chertification are genetically and spatially related, and they propose 'mudrock-dewatering' as a mechanism for generating dolomitising fluids rather than meteoric waters. Thus, lithological alteration of this kind may be particularly common in areas where limestone is overlain by thick mudstone sequences, which impede the upward flow of silica- and magnesium rich waters and/or where structural controls localise such chertification/dolomitisation solutions.

Besides changes in the carbonate mineralogy, dolomitisation may also affect the mineralogy of iron-bearing phases. Addison et al. (1985) found that iron oxides in the form of magnetite were mostly present in unaltered limestones, while dolomitised and chertified limestones hematite and goethite were the common iron minerals.

There is evidence for mineralisation in the study area, comprising primary sulphides of lead, zinc, copper and iron and their alteration products as well as barite and fluorite. The minerals are probably

of hydrothermal origin and are thought to have formed from hot brines that were expelled from Carboniferous basinal argillaceous rocks during deep burial and under tectonic stress (Dunham and Wilson, 1985). Subsequently, alteration of the primary minerals, mainly pyrite (FeS_2), galena (PbS), sphalerite (ZnS) and chalcopyrite (CuFeS_2) by oxygen-bearing groundwaters has occurred which favoured re-mobilisation processes and the formation of secondary mineral deposits.

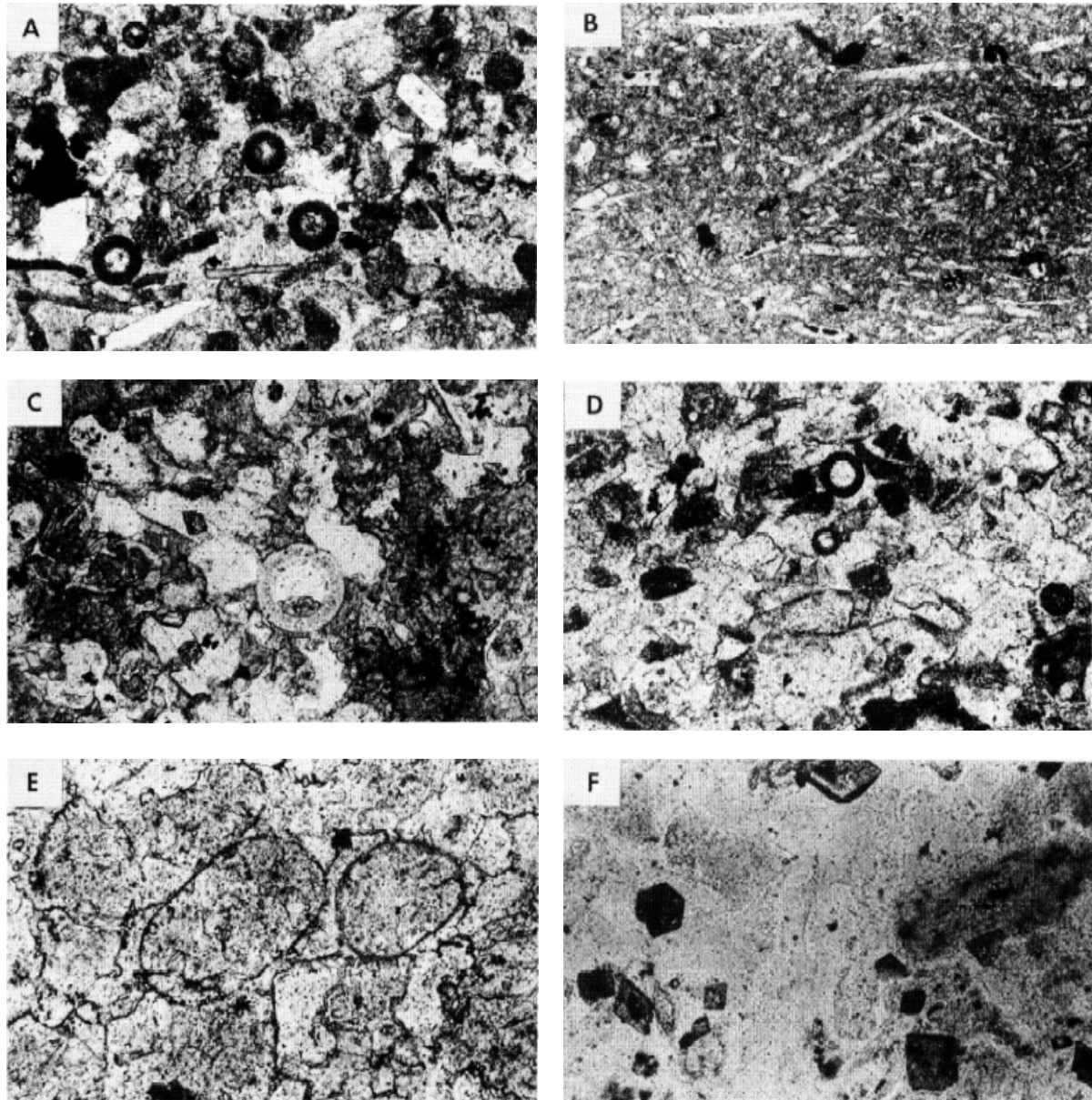


Figure 3.7 Photomicrographs illustrating the progressive dolomitization and chertification of the Pendleside Formation. The width of each photomicrograph = 0.571 mm. Undolomitized calcisphere packstone. Cement is ferroan calcite. The white euhedral crystals are authigenic albite and the irregular opaque patches are authigenic pyrite. B. Undolomitized micritic packstone. C. Similar to A but partially dolomitized. D. Similar to A but partially chertified. E. Completely dolomitized grainstone. The original grain boundaries are 'ghosted' by hematite dustlines. F. Completely chertified limestone with euhedral ferroan dolomite rhombs. (Addison et al., 1985)

There is evidence for mineralisation in the study area, comprising primary sulphides of lead, zinc, copper and iron and their alteration products as well as barite and fluorite. The minerals are probably of hydrothermal origin and are thought to have formed from hot brines that were expelled from Carboniferous basinal argillaceous rocks during deep burial and under tectonic stress (Dunham and Wilson, 1985). Subsequently, alteration of the primary minerals, mainly pyrite (FeS₂), galena (PbS), sphalerite (ZnS) and chalcopyrite (CuFeS₂) by oxygen-bearing groundwaters has occurred which favoured re-mobilisation processes and the formation of secondary mineral deposits.

Mineralisation mostly occurs in the north-east of the study area, associated with the Northern Pennine Orefields, and in the southern part of the study area, in the Carboniferous Limestone outcrop of the Craven Basin. Here, mineralisation is strata bound, mainly in disseminated and veinlet form (Carlson, 1983 in Brandon et al., 1998) or related to local faults (Aitkenhead et al. 1992). Although of minor economic significance, several small veins have been worked for lead and zinc minerals at a number of sites within the study area; e.g. at Sykes [NGR 36290 45150], Moor End [NGR 36751 45091], Dinkling Green [NGR 36442 44753] Brennard [NGR 36450 45410] and Whitendale [NGR 36610 45500]. Besides the general sulphide assemblage, veins of barite and/or fluorite commonly occur within these mineralisation areas.

3.5 Rainfall chemistry

Rainfall is the principal source of recharge to most aquifers, and the local rainfall chemistry, corrected for evapotranspiration effects, can be considered as the primary input contributing to the baseline composition. For some elements, rainfall may be the dominant source of solutes in the groundwater. For others, significant additions to the groundwater may occur resulting from chemical reactions with the bedrock or due to inputs from other sources, such as pollutants.

The precipitation-weighted annual means (averaged for 1996-2000) of the major-element composition of rainfall in the study area is given in Table 3.2. The data were collected at the Cow Green Reservoir monitoring site [NGR 3817 5298], which is located approximately 50 km to the north of the study area. To account for the effect of evapotranspiration, which under the prevailing climatic conditions can be expected to concentrate solutes in recharge about threefold, the data were multiplied by a factor of 3. This simple conversion gives an indication of the order of magnitude of concentrations prior to reaction with vegetation or aquifer minerals. Hence, the resulting values provide a useful background against which the chemistry of the Limestone groundwaters in the region can be assessed.

Table 3.2 Rainfall chemistry for Cow Green Reservoir rainfall monitoring site (BNG 3817 5298). The precipitation-weighted annual averages were calculated from 1996-2000 weekly data taken from The UK National Air Quality Information Archive (<http://www.aeat.co.uk/netcen/airqual/>)

Cow Green Reservoir	Rainfall	Concentrated Rainfall
Parameter		(x3)-Enrichment by evapotranspiration
pH	4.82	
Na (mg l ⁻¹)	2.00	6.00
K (mg l ⁻¹)	0.09	0.26
Mg (mg l ⁻¹)	0.32	0.96
Ca (mg l ⁻¹)	0.29	0.88
Cl (mg l ⁻¹)	3.55	10.65
SO ₄ (mg l ⁻¹)	1.67	5.01
NO ₃ -N (mg l ⁻¹)	0.41	1.23
NH ₄ -N (mg l ⁻¹)	0.09	0.28
SEC (μS cm ⁻¹)	25.6	76.8
Rainfall amount (mm y ⁻¹)	1172	

The relatively high concentrations of Na, Cl and SO₄ in the rainfall suggest inputs from maritime sources, although contributions from an atmospheric emission component of anthropogenic origin are also likely. Chloride is generally regarded as a conservative ion and groundwater concentrations may be largely rainfall derived. Hence, background concentrations expected at the present day should be in the order of 11 mg l⁻¹ Cl. Likewise, 6 mg l⁻¹ Na and 6 mg l⁻¹ SO₄ can be expected in present day recharge to the aquifer.

Nitrate presents the main N source in the rainfall and is mainly derived from anthropogenic emissions. Modern baseline concentrations of total nitrogen (NO₃-N plus NH₄-N) can be expected to be less than ca. 1.5 mg l⁻¹ due to N-uptake by vegetation, and 'concentrated' rainfall of pre-industrial age recharged to the aquifer would probably have been even less.

The pH of the rainfall is acidic (4.82), reflecting equilibrium with atmospheric CO₂ and the effects of other atmospheric pollutants (SO₂, NO₃). In contact with the limestone aquifer, rapid equilibration of the acidic waters will occur, with carbonate reactions buffering the groundwater composition at near-neutral composition with resulting increases in Ca concentration and alkalinity.

3.6 Landuse in the area

The dominant land use in the study area is managed grassland with minor areas of forestry/woodland and semi-natural vegetation (Figure 2.2). The area incorporates only a few urban and industrial areas including Lancaster in the west, Settle in the east, Clitheroe in the south and Kendal in the north.

4. DATA AND INTERPRETATION

4.1 Project sampling programme

A total of 24 samples were collected in December 2003 from springs and industrial and farm boreholes in the area between Brough in the north to Burnley in the south. The sites form part of the Environment Agency's groundwater monitoring network and could therefore be compared with historical analyses. The sampling sites were selected to provide good areal coverage.

Sampling included on-site measurements of temperature, specific electrical conductance (SEC) and alkalinity (by titration) as well as pH, dissolved oxygen (DO) and redox potential (Eh) (Figure 4.1). Where possible, the latter parameters were measured in an anaerobic flow cell. At each site, samples for the analysis of major and trace elements were collected in Nalgene bottles. All samples were filtered through a 0.45µm filter and aliquots for cation and trace element analysis were acidified to 1% v/v HNO₃ to prevent precipitation and to minimise adsorption onto container walls. Samples for dissolved organic carbon (DOC) were filtered through a 0.45 µm silver filter and collected in Cr-acid washed glass vials. At selected sites, additional samples were collected for the analyses of stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$).

Ideally, samples were collected from permanently pumped boreholes and/or after a minimum of 2 borehole volumes had been removed prior to sampling. However, where this was not possible due to the large borehole volume (e.g. Rolls Royce factory, Banksfield [NGR 38808 44763]), samples were collected after on-site readings of temperature, conductivity, pH, DO and Eh had stabilised. Efforts were made to sample groundwater as close to the discharge point as possible. Sampling from storage tanks was generally avoided unless a representative sample of groundwater was considered to be obtainable.

Analyses of major cations and sulphate by ICP OES and analysis of anion species (Cl, Br, I, F) by automated colorimetry were carried out. A wide range of trace elements was analysed by ICP MS. Nitrogen species were determined colorimetrically for NO₂-N and TON, and NO₃-N was calculated as the difference between these two values. Stable isotopes analyses were also completed using mass spectrometry and the results are reported as ‰ deviation relative to VSMOW for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and VPDB for $\delta^{13}\text{C}$.

4.2 Historical data

Historical water quality data from the Environment Agency groundwater-monitoring database were selected and appended to the project sampling campaign. This included information from boreholes, wells and springs, a number of which form part of the EA's regular sampling network. In order to examine the spatial variations in baseline water quality of the area, analyses from 136 different locations collected between 1949 and 2003 were selected to provide a synoptic overview. However, trace metal data from these analyses could not be included in the dataset as metal analyses in the Environment Agency laboratories were carried out on unfiltered samples, determining the concentrations of total (particulate and dissolved) metals rather than the dissolved metal concentrations. The dissolved loads, however, are more meaningful when within-aquifer processes, which determine the groundwater chemical composition, are of interest.

For each site, the analysis with the most determinands analysed were used. Sites that were re-sampled during the recent field survey in December 2003 were excluded from the dataset to avoid data redundancy and to prevent over-representation of individual sites.

4.3 Interpretation of groundwater samples

When interpreting borehole data, it is important to bear in mind that pumped samples represent the sum of water coming into the borehole from different horizons over the screened interval. Therefore, the samples may represent a mixture of waters with different chemistries, especially if the aquifer is vertically stratified in terms of water quality. Differences in borehole design, in particular the depth of casing or borehole depths, may produce differences in water quality not related to geochemical reactions along a flow path.

In the case of spring sampling, contact with the atmosphere prior to sampling could not often be avoided, as many springs discharge into standing pools or collector systems and the exact location of the spring pit/exit was difficult to ascertain. On exposure to the atmosphere, unstable parameters such as pH, Eh, and dissolved oxygen may change and the chemical composition of the water may also be altered. This needs being borne in mind when interpreting the data from springs.

4.4 Data handling

The plots and tables of geochemical data are based on data from the new sampling programme (December 2003) and historical data (one analysis per site for analysis from 1949 to 2003) unless otherwise specified. For samples collected within this project, the analytical ionic balance had values <5%. The data quality of EA data was more difficult to assess because of incomplete analysis. Of those with complete major-element analysis, most had ionic balances below 10% (often less). Data with ionic charge balances greater than 10% were rejected.

Results that fell below the limit of detection were substituted with half of the detection limit value. However, changes in the detection limits occurred both with time and between laboratories. The median is least affected by outlying data and is therefore used to represent the average of the results. Minimum and maximum values are used to show the full spread (range) of the data, while the 97.7 percentile (mean plus two standard deviations) is taken as an estimate of the upper limit of the concentration range, excluding any outliers.



Figure 4.1: Spring sampling site (Carboniferous Limestone Aquifer)

5. HYDROCHEMICAL CHARACTERISTICS

5.1 Introduction

This section presents a description of the fundamental characteristics of the groundwaters in the Carboniferous Limestone aquifer. A summary of the data is given in Tables 5.1 and 5.2 for the major and trace elements, respectively. The tables show ranges and average values of data as well as an upper concentration (defined as mean + 2 σ or 97.7th percentile). The median is preferred to the mean as an average as it is more robust and less affected by extreme values. The 97.7 percentile is used as a practical cut off to define outlying data, and where the chemistry has not been modified by anthropogenic inputs, can be defined as the upper baseline.

Table 5.1 Field parameters, isotope data and range of major and minor element concentrations in the Carboniferous Limestone Aquifer

		min	max	median	mean	97.70%	N
T	°C	5.3	12.8	8.6	8.8	11.8	40
pH	field	6.44	9.25	7.40	7.44	8.39	156
Eh	mV	186	519	366	373	512	24
DO	mg l ⁻¹	0.0	11.3	5.5	5.6	11.0	32
SEC	µS cm ⁻¹	207	1055	479	537	940	28
δ²H	‰	-7.6	-6.4	-6.7	-6.8	-6.4	10
δ¹⁸O	‰	-47.2	-39.4	-43.7	-43.2	-39.5	10
δ¹³C	‰	-17.8	-7.7	-15.4	-14.6	-9.1	10
Ca	mg l ⁻¹	<1	428.0	69.4	71.9	123.4	145
Mg	mg l ⁻¹	0.3	138.0	11.0	13.2	38.3	145
Na	mg l ⁻¹	2.1	1980.0	11.5	43.6	141.6	144
K	mg l ⁻¹	<0.6	65.3	1.8	3.2	11.8	144
Cl	mg l ⁻¹	<10	3260.0	13.0	55.4	94.9	156
SO₄	mg l ⁻¹	<4	1160.0	19.7	38.8	135.7	146
HCO₃	mg l ⁻¹	7	1195	280	278	475	158
NO₃-N	mg l ⁻¹	<1	46.101	<1	1.642	5.464	157
NO₂-N	mg l ⁻¹	<0.02	0.220	<0.02	<0.02	0.098	141
NH₄-N	mg l ⁻¹	<0.05	11.30	<0.05	0.25	1.28	155
P	mg l ⁻¹	<0.02	0.15	<0.02	0.02	0.07	24
DOC	mg l ⁻¹	<0.1	5.510	0.980	1.655	4.562	28
F	µg l ⁻¹	<100	3470	184	530	1964	70
Br	µg l ⁻¹	<50	250.0	<50	61.0	200.7	70
I	µg l ⁻¹	2	85	5	16	81	24
Si	µg l ⁻¹	234	8831	2688	3361	8453	146

Table 5.2 Trace element concentrations in the Carboniferous Limestone Aquifer

		min	max	median	mean	97.70%	N
Ag	µg l ⁻¹	<0.05	0.09	<0.05	<0.05	<0.05	24
Al	µg l ⁻¹	<1	103	<1	12	97	24
As	µg l ⁻¹	<0.5	5.0	<0.5	0.6	2.3	24
Au	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	24
B	µg l ⁻¹	<20	287	<20	52	215	24
Ba	µg l ⁻¹	2.57	466.72	59.64	87.40	355.69	24
Be	µg l ⁻¹	<0.05	0.07	<0.05	<0.05	<0.05	24
Bi	µg l ⁻¹	<0.05	0.12	<0.05	<0.05	<0.05	24
Cd	µg l ⁻¹	<0.05	0.09	<0.05	<0.05	0.09	24
Ce	µg l ⁻¹	<0.01	0.07	<0.01	<0.01	0.05	24
Co	µg l ⁻¹	<0.02	0.34	<0.02	0.05	0.28	24
Cr	µg l ⁻¹	<0.5	1.1	<0.5	<0.5	1.0	24
Cs	µg l ⁻¹	<0.01	0.44	0.025	0.06	0.27	24
Cu	µg l ⁻¹	<0.1	44.20	0.75	3.05	17.36	24
Dy	µg l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	24
Er	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Eu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Fe	µg l ⁻¹	<5	2030	12	136	850	24
Ga	µg l ⁻¹	<0.05	0.08	<0.05	<0.05	<0.05	24
Gd	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Ge	µg l ⁻¹	<0.05	0.16	<0.05	<0.05	0.15	24
Hf	µg l ⁻¹	<0.02	<0.02	<0.02	<0.02	<0.02	24
Hg	µg l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	24
Ho	µg l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	24
In	µg l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	24
Ir	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	24
La	µg l ⁻¹	<0.01	0.03	<0.01	<0.01	0.02	24
Li	µg l ⁻¹	0.1	46.8	2.6	11.1	44.7	24
Lu	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Mn	µg l ⁻¹	<2	255	5	37	242	24
Mo	µg l ⁻¹	0.1	67.7	0.3	3.2	23.3	24
Nb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Nd	µg l ⁻¹	<0.01	0.06	<0.01	<0.01	0.05	24
Ni	µg l ⁻¹	<0.2	2.8	<0.2	0.5	2.2	24
Os	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	24
Pb	µg l ⁻¹	<0.1	1.4	0.1	0.2	0.7	24
Pd	µg l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	24
Pr	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Pt	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Rb	µg l ⁻¹	0.13	8.25	1.23	2.31	7.28	24
Re	µg l ⁻¹	<0.01	0.07	<0.01	<0.01	0.05	24
Rh	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Ru	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	24
Sb	µg l ⁻¹	<0.05	0.19	<0.05	0.07	0.17	24
Sc	µg l ⁻¹	<1	1	<1	<1	1	24
Se	µg l ⁻¹	<0.5	2.7	0.6	0.7	2.1	24
Sm	µg l ⁻¹	<0.02	0.02	<0.02	<0.02	<0.02	24
Sn	µg l ⁻¹	<0.05	0.37	0.06	0.07	0.18	24
Sr	µg l ⁻¹	38	5482	188	898	4339	24
Ta	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Tb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Te	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	24
Th	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	24
Ti	µg l ⁻¹	<10	<10	<10	<10	<10	24
Tl	µg l ⁻¹	<0.01	0.02	<0.01	<0.01	<0.01	24
Tm	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
U	µg l ⁻¹	<0.02	7.84	0.31	0.73	3.21	24
V	µg l ⁻¹	<0.2	0.6	<0.2	<0.2	0.4	24
W	µg l ⁻¹	<0.02	0.02	<0.02	<0.02	<0.02	24
Y	µg l ⁻¹	<0.01	0.08	0.03	0.04	0.08	24
Yb	µg l ⁻¹	<0.01	<0.01	<0.01	<0.01	<0.01	24
Zn	µg l ⁻¹	1	4991.6	5.65	238.59	1680.22	24
Zr	µg l ⁻¹	<0.02	0.45	<0.02	0.03	0.19	24

5.2 Water types and physicochemical characteristics

Groundwaters from the Carboniferous Limestone Aquifer of the study area display a wide range of physicochemical characteristics and element concentrations (Tables 5.1 and 5.2).

The waters are fresh and only weakly mineralised ($207\text{-}1450\ \mu\text{S cm}^{-1}$) and appear to be well buffered at circumneutral pH with a median value of 7.4. Temperatures average around $8.6\ ^\circ\text{C}$, the low values of $5.3\ ^\circ\text{C}$ being due to the influence of air temperature at sites where samples were collected from outside storage tanks and vessels or from open catch pits. Dissolved oxygen concentrations in the groundwaters are low to intermediate and Eh values indicate that moderately reducing to oxidising conditions prevail in the aquifer. However, as it was not always possible to measure these parameters in a flow cell, the median Eh of 366 mV is likely to overestimate the conditions in the aquifer.

From the Piper diagram (Figure 5.1), it is evident that the groundwaters of the Carboniferous Limestone Aquifer are mostly Ca-HCO₃ type waters with some Na-HCO₃, Ca-SO₄ and Na-Cl type waters. The samples collected during the present sampling campaign, represented as green dots in the Piper plot, show much less variation than those compiled for the whole area, in general waters with SO₄ or Cl as the dominant anion are not represented.

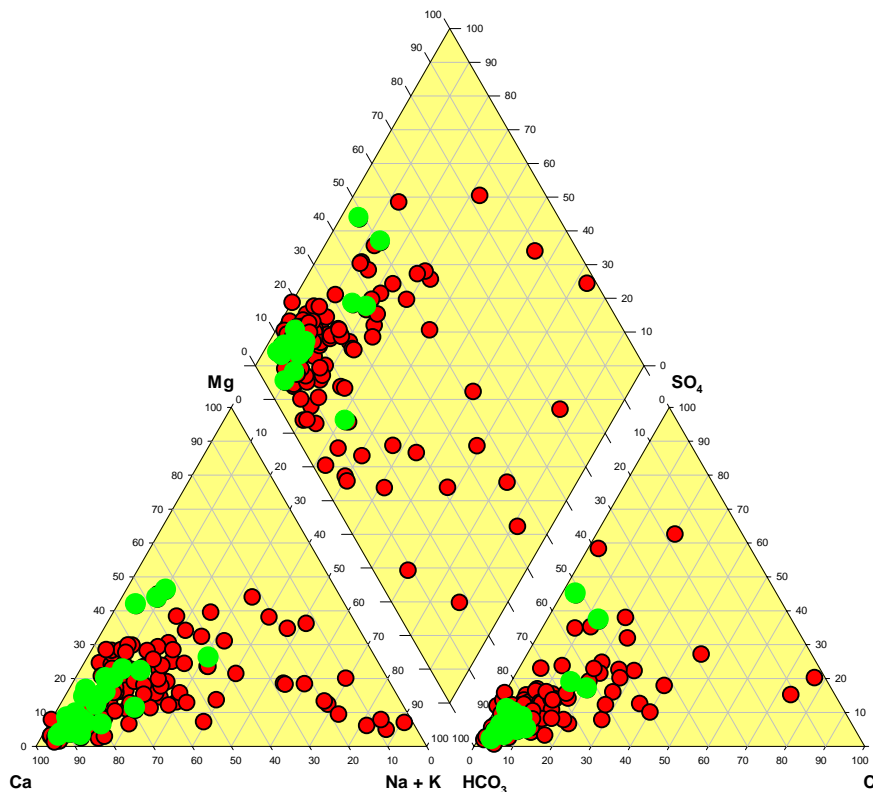


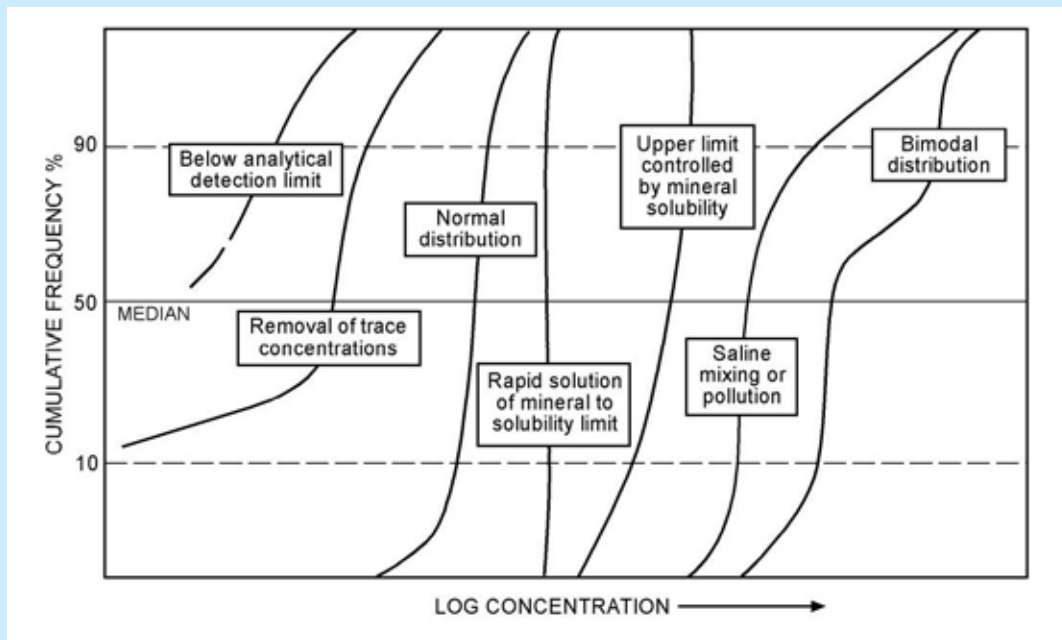
Figure 5.1 PIPER Plot showing the relative concentrations of major cations and anions in the carboniferous limestone groundwaters (Green circles = Data from 2003 survey, Red circles = Historical data)

5.3 Major elements

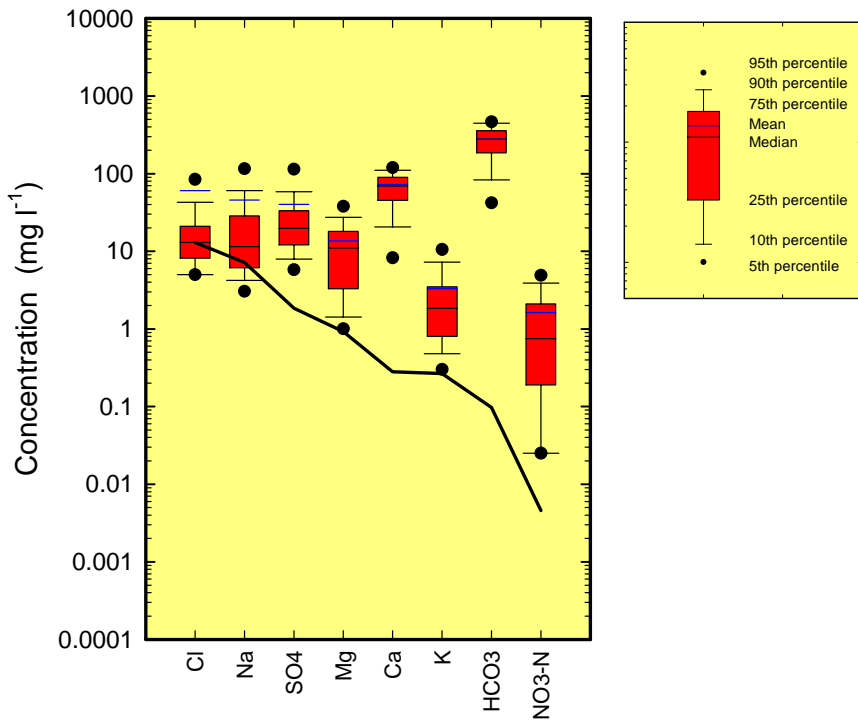
The summary data are shown graphically on boxplots and cumulative frequency plots (Figures 5.2 and 5.3). The boxplots (or box and whisker plots) display the ranges of data and are designed to highlight the distribution of data on a percentile basis (the boxes show the range between the 25th and 75th

percentiles, the whiskers represent the 10th and 90th percentiles and the dots the 5th and 95th percentiles). In addition, the median is shown as a horizontal black line and the mean as a blue line within the box. The 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 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 different ways (Box 5.1).

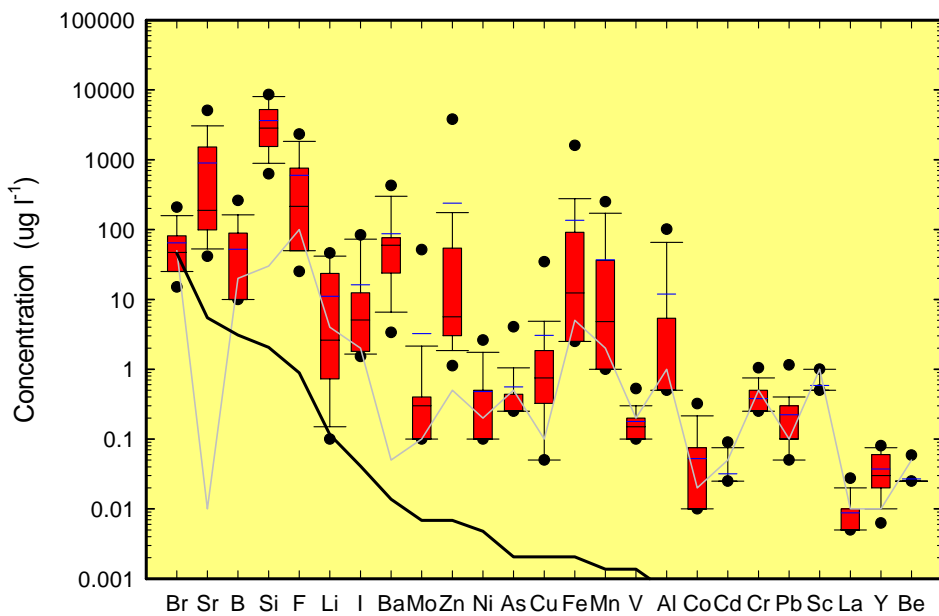
BOX 5.1. Use of cumulative frequency diagrams to indicate baseline characteristics in groundwaters



- 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.



(a)



(b)

Figure 5.2 Range of (a) major ion concentrations and (b) minor and trace element concentrations in the Carboniferous Limestone groundwaters. Black line = seawater line (normalised for median Cl). Grey line = detection limit for individual elements

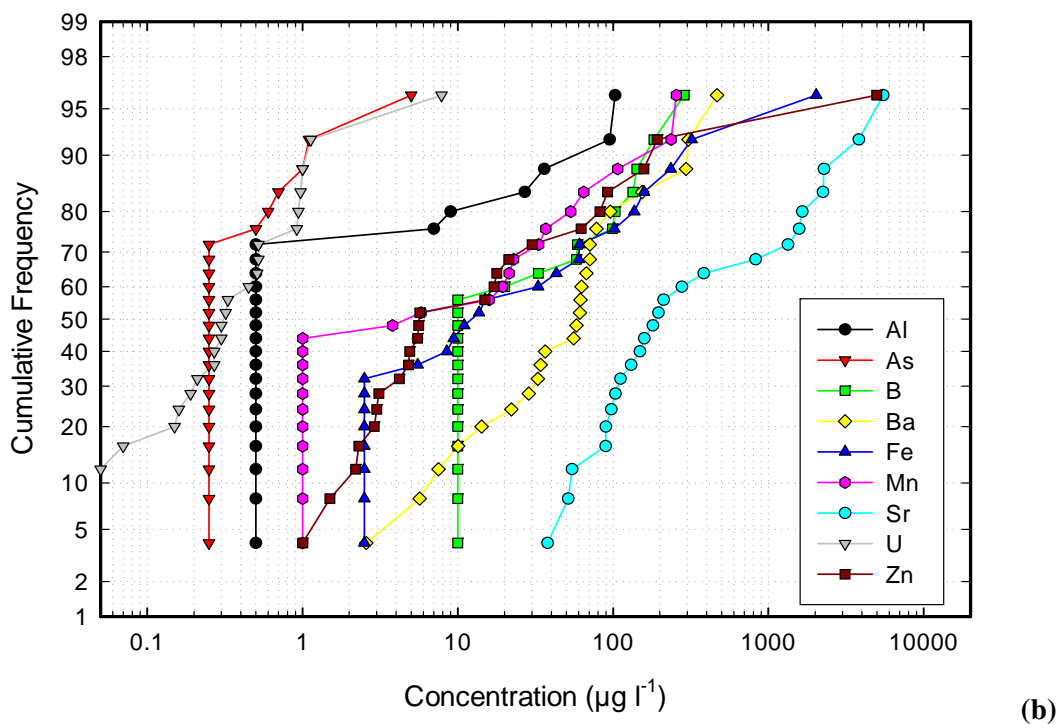
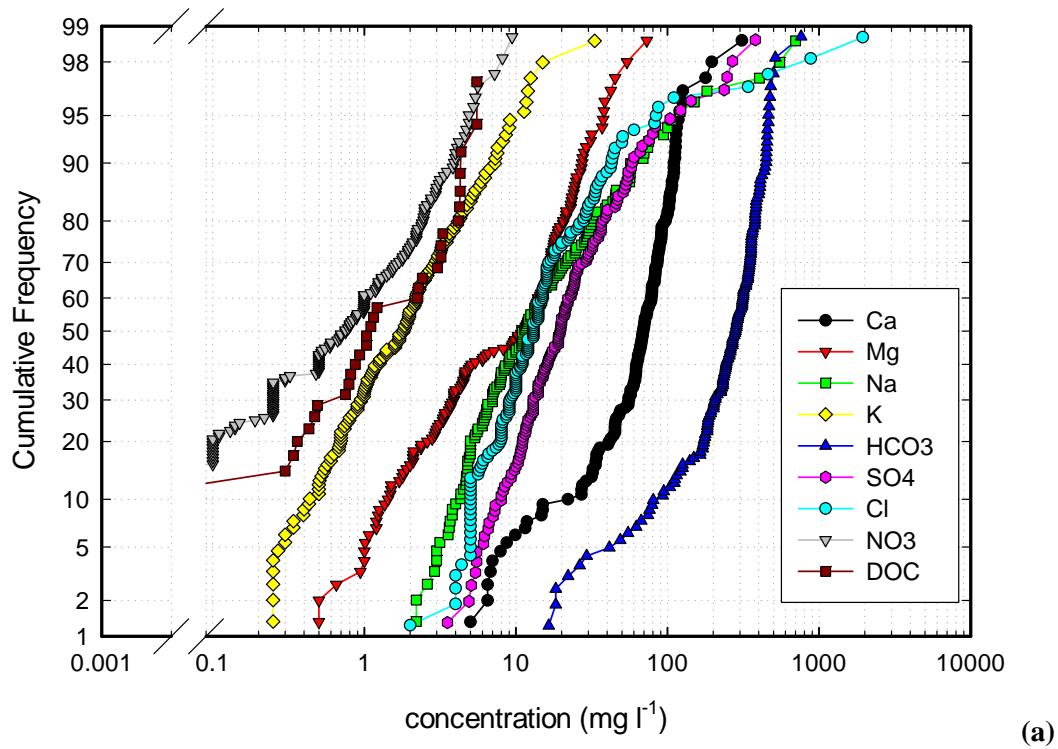


Figure 5.3 Cumulative Probability plot of (a) major ion concentrations and (b) minor and trace element concentrations in the Carboniferous Limestone groundwaters

Concentrations of major elements are given in Table 5.1, Figure 5.2a and Figure 5.3a. The median Cl concentration of 13.0 mg l^{-1} is close to that estimated for bulk precipitation (incl. effects of evapotranspiration) in the region (Table 3.2). High Cl concentrations with maximum values of up to 3260 mg l^{-1} occur at a number of sites, indicating that Cl sources additional to that of rainfall are present within the aquifer. Sodium and SO_4 show a similar trend. Median concentrations in the range of 11.5 mg l^{-1} Na and 19.5 mg l^{-1} SO_4 are locally exceeded by up to two orders of magnitudes with maximum values of 1980 mg l^{-1} Na and 1160 mg l^{-1} SO_4 . The positive skew in the cumulative probability curves of these elements and the population shift at or above the 95th percentile suggests that mixing between at least two populations occurs in the aquifer.

Most elements plot above the seawater line (normalised for median Cl) indicating extensive water-rock interactions. Bicarbonate encompasses a wide range of concentrations throughout the aquifer and displays a bimodal distribution on the cumulative frequency plot. The steep slope at the upper limit of the curve indicates that HCO_3 concentrations are controlled by mineral solubility, probably calcite, at least in parts of the aquifer, where groundwaters are supersaturated with respect to calcite and, to a lesser degree, dolomite. A similar trend is seen for Ca as well as for Mg, suggesting a dolomite solubility control. Nitrate and DOC also show relatively wide concentration ranges, which on the cumulative frequency plot display trends that tend to approach log-normal distributions.

5.4 Minor and trace elements

The boxplots for minor and trace elements, displayed in Figure 5.2, show that most elements lie above the normalised seawater line. The halide elements Br and I have low median values of $<50 \text{ } \mu\text{g l}^{-1}$ and $5 \text{ } \mu\text{g l}^{-1}$, respectively, but a number of groundwaters are enriched in these elements. Fluoride also shows a wide range of concentrations throughout the aquifer, with maximum values of up to $3470 \text{ } \mu\text{g l}^{-1}$. Such high concentrations are far above the natural baseline values encountered in most British aquifers (Edmunds et al., 1989).

Concentrations of Ba and Sr vary greatly throughout the aquifer, with values as high as $466 \text{ } \mu\text{g l}^{-1}$ and $5482 \text{ } \mu\text{g l}^{-1}$, respectively. Silicon, likewise, shows a wide range of concentrations and while the majority of sampled groundwaters are equilibrated with respect to quartz, a significant number are still undersaturated, in particular with respect to chalcedony.

Iron and Mn concentrations show large variations throughout the aquifer. Although many samples have concentrations below the detection limit, concentrations in excess of the EU maximum admissible concentrations (MAC) of $200 \text{ } \mu\text{g l}^{-1}$ and $50 \text{ } \mu\text{g l}^{-1}$, respectively, occur in the more reducing groundwaters.

Concentrations of other trace elements in the aquifer are generally low, in many cases below the ICP-OES/ICP-MS detection limits, although local enrichment occurs in areas of mineralisation. Zinc, for example, shows exceptionally high values (maximum: $4992 \text{ } \mu\text{g l}^{-1}$) in some groundwaters although the median of $5.65 \text{ } \mu\text{g l}^{-1}$ is comparatively low. In the Carboniferous Limestone aquifer of Derbyshire, for example, median Zn values of $69 \text{ } \mu\text{g l}^{-1}$ were observed (Edmunds et al., 1989). In contrast, the median Cu concentrations of $0.75 \text{ } \mu\text{g l}^{-1}$ are somewhat higher than those found in the Derbyshire Carboniferous groundwaters (median $0.4 \text{ } \mu\text{g l}^{-1}$) (Edmunds et al., 1989). There is relatively little Li and B in the groundwater, but high concentrations are observed in a number of groundwaters. Aluminium concentrations in the groundwater are generally low due to its limited solubility at circumneutral pH and Al values in excess of the detection limit only occur at a number of sites, probably as a result of colloidal suspension. Uranium is present at relatively low concentrations with a median value of $0.31 \text{ } \mu\text{g l}^{-1}$.

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 (see Box 5.2).

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

Concentrations of nitrate are generally low. Some groundwaters clearly show enhanced levels, even in the deeper parts of the aquifer (see section 6.2), but only at one site exceed the MAC of $11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ ($50 \text{ mg NO}_3 \text{ l}^{-1}$). The $\text{NO}_3\text{-N}$ levels ($46 \text{ mg NO}_3\text{-N l}^{-1}$) in the groundwater at Greenlands Farm [NGR 35210 47390] are too high to represent baseline concentrations and are likely to originate from inputs from the adjacent dairy farm. An anthropogenic source is also indicated by the high levels of K (65 mg l^{-1}) in the groundwater- an element commonly enriched in dairy farm effluent (Longhurst et al., 2000). Because many of the waters are relatively reducing, denitrification or nitrate reduction may have lowered the concentrations. Nitrite and in particular $\text{NH}_4\text{-N}$ concentrations above the EU MAC of 0.03 mg l^{-1} and 0.38 mg l^{-1} occur more commonly, although median values for the aquifer are low.

Analyses of organic contaminants have not been included in this study, but dissolved organic carbon (DOC) data are available for a small number of sites. The DOC concentrations in the groundwater range between $1\text{-}6 \text{ mg l}^{-1}$, suggesting that these groundwaters are not affected by gross pollution with organic components. However, considering the extensive agricultural land use in the area, the presence of other contaminants such as herbicides and/or petroleum hydrocarbon products at trace concentrations in the groundwater cannot be excluded.

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

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

The approach adopted is threefold:

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

6. GEOCHEMICAL CONTROLS AND REGIONAL CHARACTERISTICS

6.1 Introduction

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

6.2 Depth variations

There are a number of problems associated with the interpretation of pumped groundwater samples, in particular the fact that such samples often represent a mixture of waters from different horizons. Without additional data from specific depths, sampling at multi-level boreholes or from packer tests, it is difficult to identify the aquifer horizons that predominantly control the groundwater chemistry at the sampled location.

Groundwater solute concentrations in relation to borehole depth can be used as a general guide to assess if depth variations are likely to exist in solute chemistry. In Figures 6.1 and 6.2, selected parameters for pumped samples across the study have been plotted against borehole depth. There is no consistent behaviour between concentration and depth for most elements, although a few trends can be inferred from the data.

Elemental concentrations for a number of determinants increase with borehole depth, for example high concentrations in Mg, K and Si occur at depths between 40 m and 60 m. The trend is less pronounced for Ca but the increase in Sr (and Li), which accumulate in the groundwater as a result of incongruent mineral dissolution, in the deeper boreholes (> 40 m) may be indicative for the longer residence times of these deeper groundwaters.

With the exception of Holy Well Spring [NGR 33901 47392] and Garnet Folds Farm Spring [NGR 35381 49682], Na and Cl concentrations are highest in the deeper groundwaters (> 40 m) and may be the result of mixing with saline formation waters. However, some high Na groundwaters are depleted in Ca (<40 mg l⁻¹) and SO₄ (<20 mg l⁻¹) compared to the other samples. Their high molar Na/Cl ratios suggest that water-rock interactions, such as ion exchange are an important control on the chemical composition of these groundwaters.

There is no clear distinction in pH values between spring groundwater and borehole groundwaters, but a shift towards higher pH values is observed with increasing borehole depth. This trend is consistent with the gradual change in groundwater chemistry due to progressive water-rock interactions, such as dissolution of carbonate and/or silicate minerals which tend to deplete the CO₂ content (hence rise the pH) in these groundwaters as it moves from the recharge zone to the deeper parts of the aquifer. The carbonate system is a major control on the pH in the study area (Figure 6.3) but mixing with well-buffered saline formation waters rather than carbonate solution may also be important.

Nitrate concentrations are variable, but concentrations in excess of 3 mg l⁻¹ NO₃-N are mainly limited to the shallow groundwaters (< 40 m) and springs (Figure 6.2), reflecting agricultural inputs from diffuse and/or point sources. However, high NO₃ levels are also found in deep groundwaters, eg. at Woodhouse Gate Farm [NGR 37118 45380], Rawlinshaw Farm [37841 46739] and at Whin Yeat [35532 47936], indicating the presence of a young polluted component. The relatively low salinity of

these groundwaters suggests anthropogenic inputs as a possible source, implying that fast groundwater pathways in the karstic limestone exist, which could quickly transfer agricultural surface inputs to such great depths. However, without any detailed knowledge of the borehole construction, this can only be hypothesised as in an open borehole structure these high NO₃ levels could also be associated with inputs from shallower fractures. Transport via fast groundwater pathways and/or in-borehole mixing between shallow and deep groundwaters need also be invoked to explain the high NO₃ levels in the deep groundwater at Greenlands Farm [NGR 352100 473900], which appears to be impacted by inputs from the adjacent dairy farm.

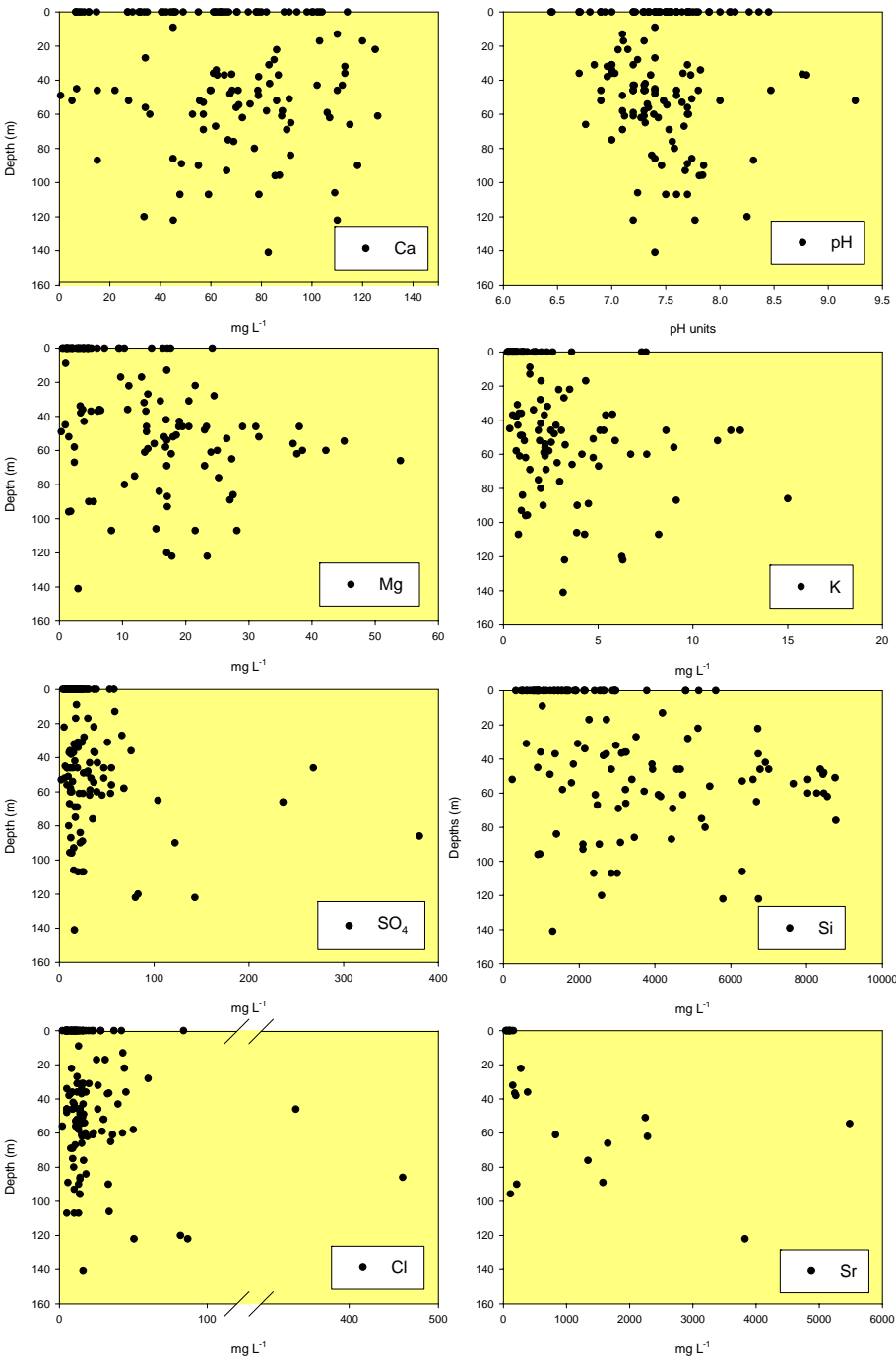


Figure 6.1 Depth variations of pH and concentrations of Ca, Mg, K, SO₄, Si Cl and Sr in the groundwaters

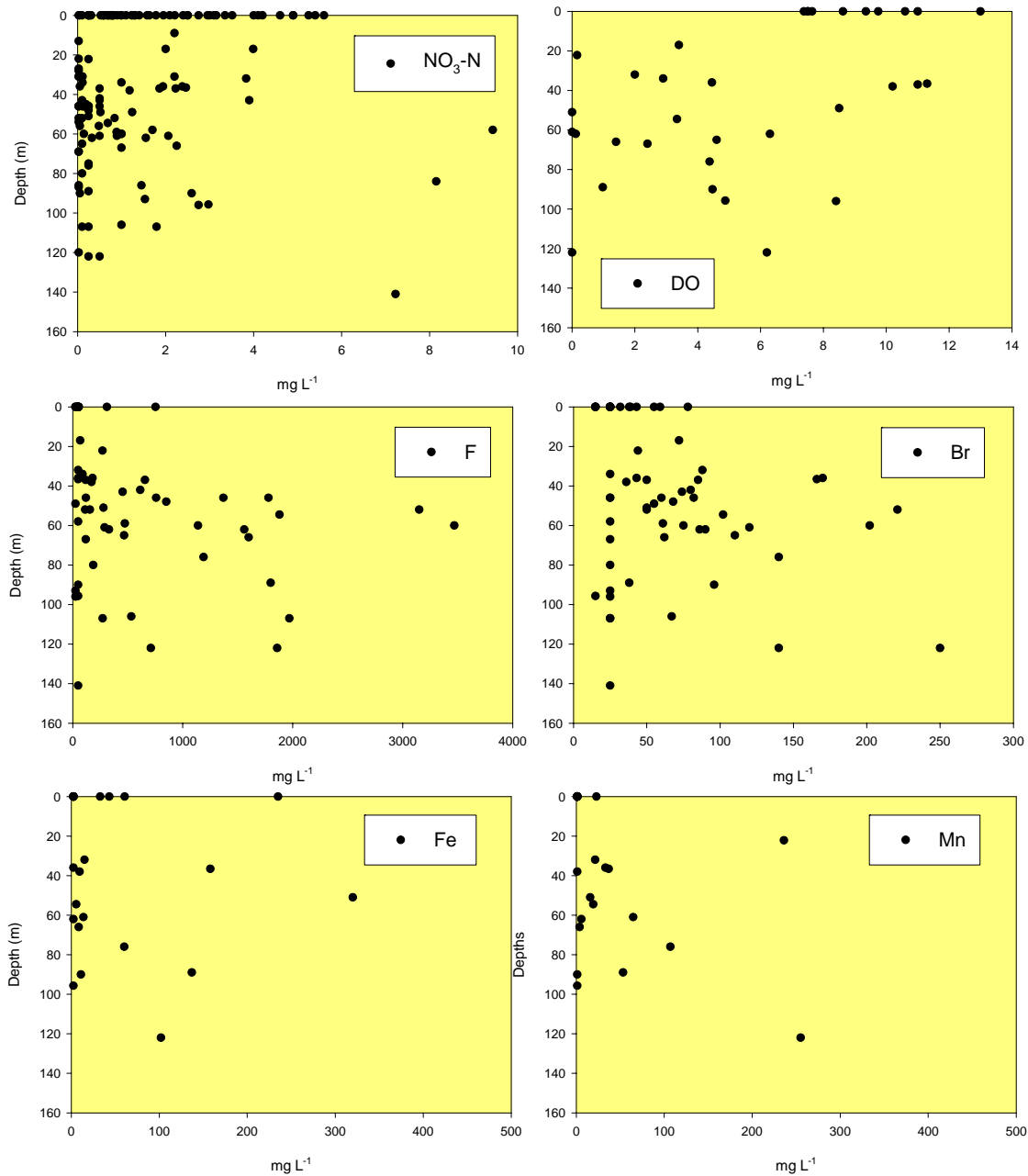


Figure 6.2 Variations in NO₃-N, Dissolved Oxygen, F, Br, Mn and Fe concentrations with borehole depth

Oxygen depletion and low redox conditions are typically associated with deeper groundwaters (Figure 6.2) which frequently show increased Fe and Mn levels (Figure 6.2). However, concentrations in excess of the drinking water limits of 250 µg l⁻¹ for Fe and 50 µg l⁻¹ for Mn only occur where DO levels < 2 mg l⁻¹ and Eh < 350 mV provide favourable conditions for reductive oxide dissolution. Similarly, NH₄-N concentrations in excess of 0.5 mg l⁻¹ are found in deeper, mostly reducing (Eh < 350 mV) groundwaters. The NO₃-N levels of these high NH₄-N groundwaters are generally low (Figure 6.4), signifying that dissimilatory nitrate reduction (NO₃⁻ → NO₂⁻ → NH₄⁺) may take place.

Fluoride and Br concentrations also increase with depth and are highest in the deeper groundwaters (> 40m) (Figure 6.2). Dissolution of hydrothermal vein fluorite (CaF₂) is the main source of F in the aquifer (e.g., Station Inn, Ribblesdale NGR 37634 47907; Station House, NGR 37653 47898; Nether Lodge, NGR 38136 45253). High Br levels are generally associated with more saline formation waters

and highest Br concentrations occur in areas of bedrock mineralisation (e.g. Fernbank Shed, NGR 38702 44707; Higher Gills Barn, Tosside, NGR 37648 455074; Low Pyethorns NGR 37888 45674).

6.3 Temporal variations

Very few long-term records are available for groundwater chemistry from the study area. Baseline conditions are therefore difficult to assess. Limited hydrochemical data exist for a number of boreholes, which are part of the Environment Agency monitoring network. Temporal variations in groundwater chemistry are displayed in Figure 6.5 for a number of components. From the graphs it is clear that in most cases no significant trend in solute concentrations is apparent. The data show a significant drop in pH in all groundwaters during spring 2004. However, the decrease is not reflected in the Ca or alkalinity values available for this period and considering the well-buffered nature of the Carboniferous Limestone aquifer, it is believed to be related to laboratory practices (measurement errors) rather than to the groundwater chemistry.

Since the time series data only cover a period of up to 15 years or less and often vary with respect to sampling intervals, monitored parameters and/or detection limits, long-term changes in groundwater chemistry cannot be inferred from the available data.

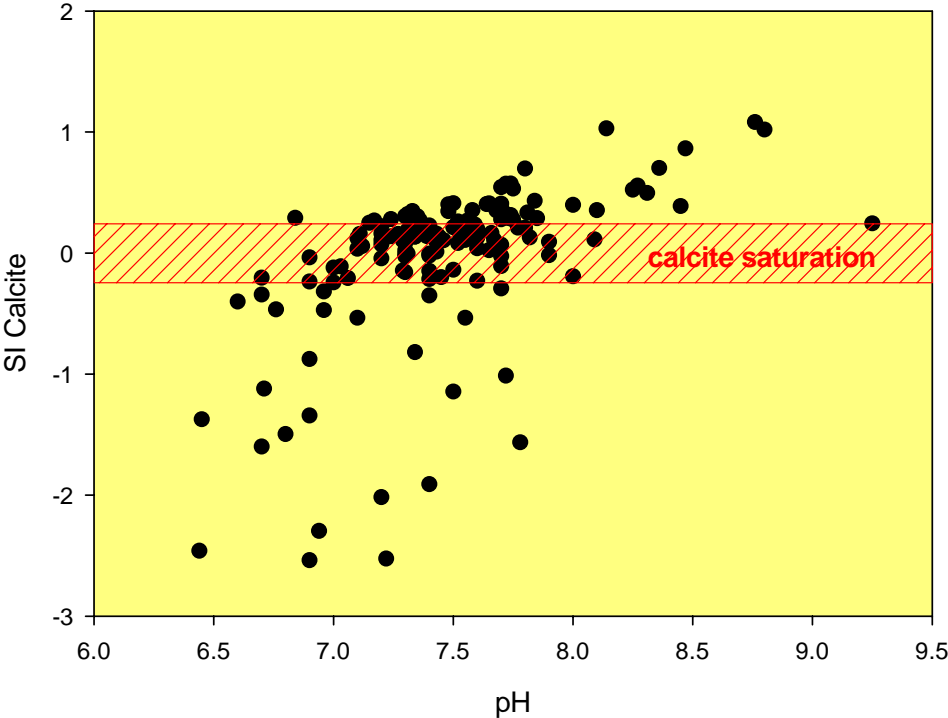


Figure 6.3 Relationship between pH and calcite saturation in the Carboniferous Limestone groundwaters

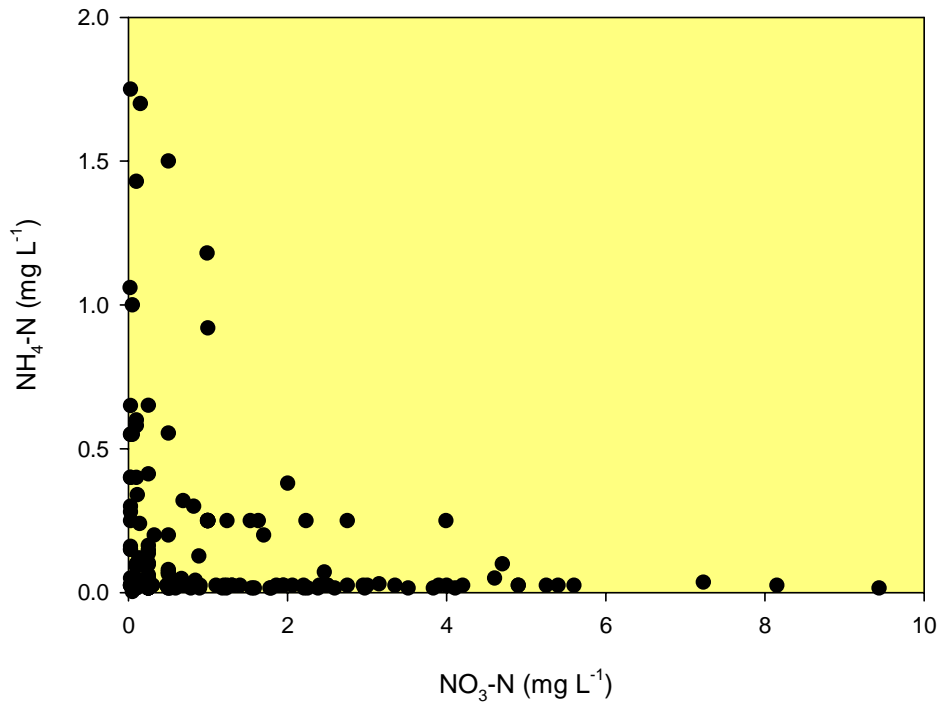


Figure 6.4 Inverse relationship between $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the groundwaters of the Carboniferous Limestone aquifer

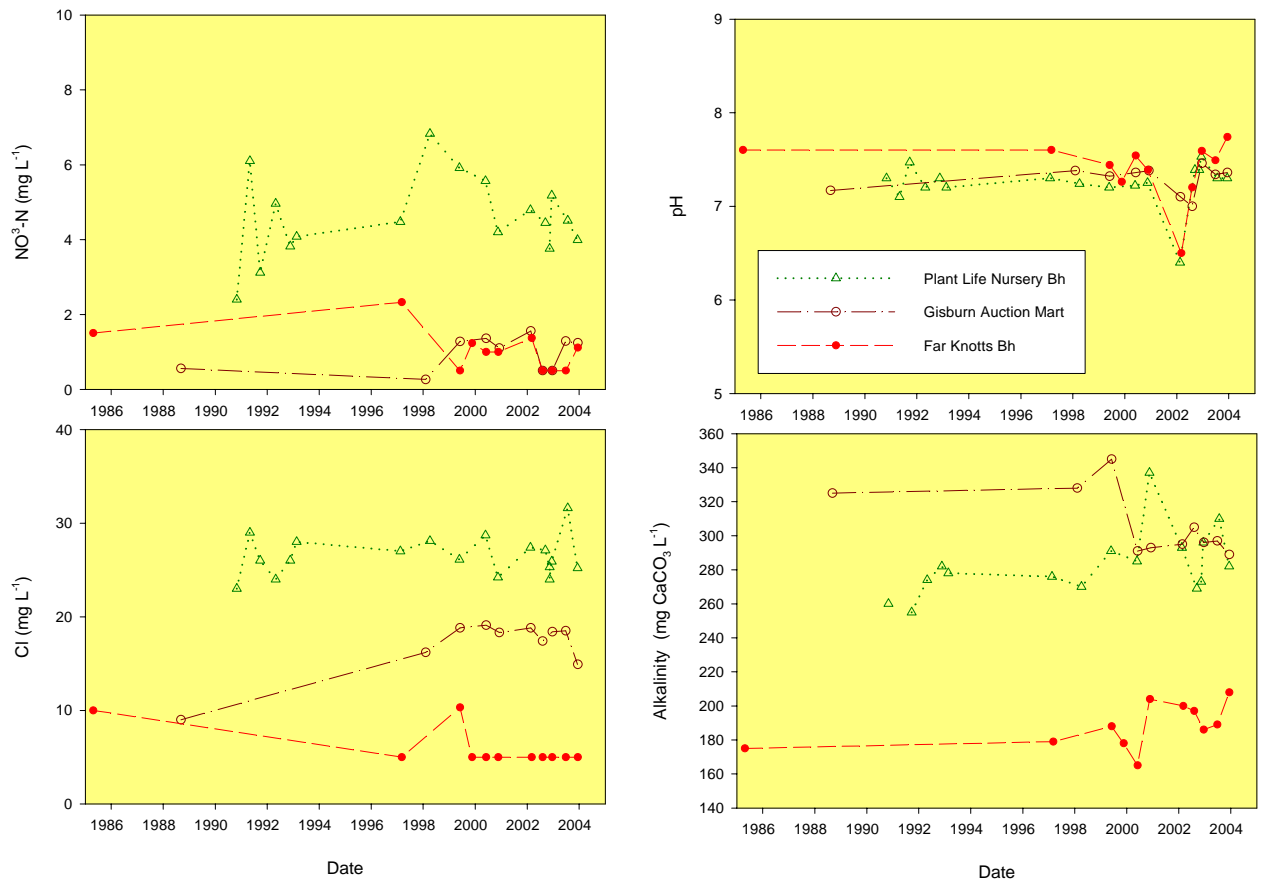


Figure 6.5 Temporal variations in groundwater chemistry of the Carboniferous Limestone aquifer

6.4 Age of groundwater

Stable isotope analyses were carried out on selected samples in order to investigate the presence of paleowaters (> 10,000 years old) in the aquifer. Stable isotopes have been used successfully to discriminate older Pleistocene waters (> 10,000 years old) from younger Holocene groundwaters (< 10,000 years old) in the Sherwood Sandstone of the East Midlands (Edmunds et al., 1982). The discrimination is based on the signature of the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$, which are lighter (more negative) in Pleistocene groundwaters due to the colder climate during that period. The range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values observed in the Carboniferous Limestone groundwaters agrees well with recently published contour maps of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in post-Pleistocene groundwaters (Darling et al., 2003). For the study area, these maps predict values around -45‰ and -7‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively, and some variation can be expected with increasing distance from the coast. Seasonal variations in the isotope signature of the Carboniferous Limestones aquifer were found to be small, despite the rapidly-responding fracture permeability. At Malham, for example, groundwater $\delta^{18}\text{O}$ values only varied by 0.5‰ (range -7.5‰ and -8.0‰) over the two-year sampling period (12/1981 – 10/1983) (Lawler, 1987 in Darling et al., 2003). The range of observed $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values would be expected from rainfall inputs and indicates that the recharge is of Holocene or Recent age.

The carbon isotope $\delta^{13}\text{C}$ is directly linked to the carbonate system and to carbon cycling in groundwaters. In conjunction with chemical data, $\delta^{13}\text{C}$ can provide some insight in the groundwater evolution and can help interpreting groundwater age. Fresh groundwaters invariably originate as meteoric water, which then infiltrates through the soils and into the aquifer. Along the way, the $\delta^{13}\text{C}$ signature of the water shifts towards heavier (more positive) values under closed system conditions as the water evolves through mineral weathering. The degree of change in $\delta^{13}\text{C}$ signature depends on the availability of CO_2 in the aquifer and the $\delta^{13}\text{C}$ of carbonate minerals. In the Carboniferous Limestone aquifer, where carbonate minerals are abundant, groundwaters are generally enriched in $\delta^{13}\text{C}$ due to calcite dissolution. The shallower groundwaters are generally more depleted in $\delta^{13}\text{C}$ (-15.5‰ to -16‰) (Figure 6.6) owing to the shorter groundwater residence times. While the high $\delta^{13}\text{C}$ value (-7.7‰) at Tewitt Hall [NGR 38136 45253] indicates a prolonged water-rock contact, the depleted $\delta^{13}\text{C}$ signature (-17.8‰) in the deeper groundwater at Home Barn [NGR 37836 47567] suggests a lithological control (e.g., dolomite content), which is also reflected in the low Mg and Sr concentrations of the groundwater.

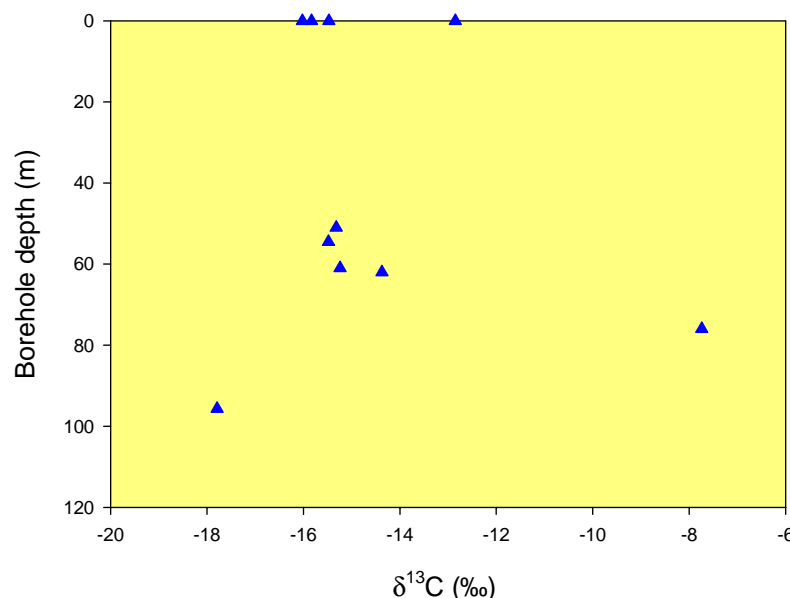


Figure 6.6 Relationship between $\delta^{13}\text{C}$ and depths

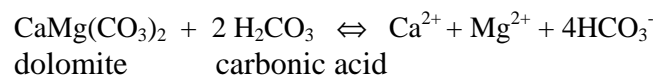
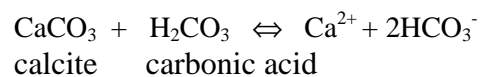
6.5 Spatial variations

6.5.1 Introduction

Changes in groundwater baseline chemistry are expected to occur as water moves from the recharge to the discharge areas of the aquifer. In the Carboniferous Limestone, groundwater flow paths are difficult to assess due to the karstic nature of parts of the aquifer and due to the local occurrence of permeability barriers and horizontal discontinuities formed by shales and micritic horizons which influence the direction and pattern of underground drainage. The concept of sampling along a “flow path” could therefore not be applied for this area; instead the overall spatial variations in water chemistry have been examined. Water-rock interactions and mixing processes will largely be responsible for these spatial variations, but the nature of the overlying drift deposits may also have an influence, in particular on the recharge rates and residence times of the groundwaters.

6.5.2 Mineral dissolution reactions

The chemistry of the groundwater is largely determined by water-rock interactions within the aquifer. One of the most important processes in aquifers containing carbonate minerals, is the dissolution of these minerals through the reaction with the infiltrating, acidic rainwater:



The importance of these reactions within the aquifer is indicated by the dominance of Ca and Mg and the degree of saturation with respect to calcite and dolomite of most samples. This is also apparent from Figure 6.7, which illustrates the asymptotic relationship between calcite saturation and Ca and Mg in the aquifer.

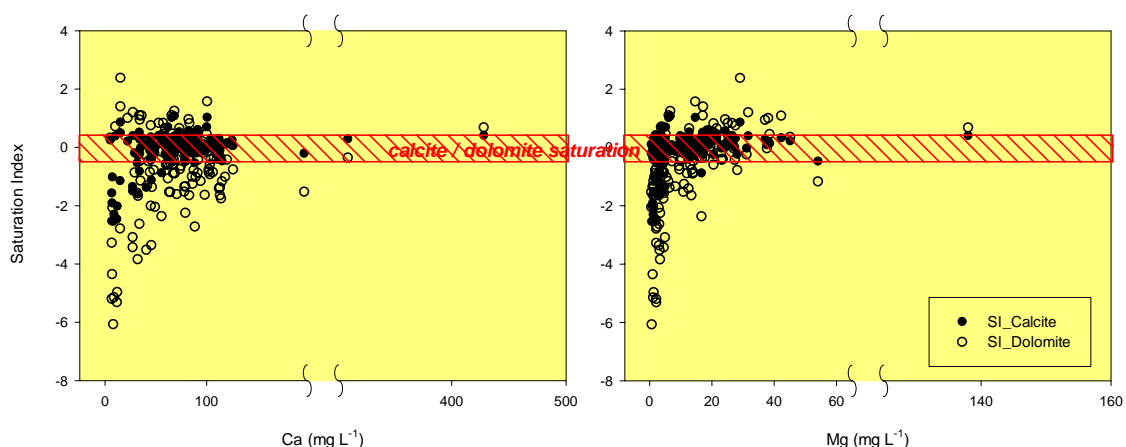


Figure 6.7 Relationship between Ca and Mg concentrations and calcite/dolomite saturation in the groundwater

The spatial distribution of Ca and Mg is complex (Figure 6.9) but most groundwaters in the study area are saturated with respect to calcite and often also with respect to dolomite. This is illustrated in Figure 6.7, where SI values around 0 (± 0.3) indicate saturation of the groundwater with respect to the

considered mineral phase. Figure 6.8 shows that most samples from the deeper boreholes are close to calcite and/or dolomite saturation due to the longer residence times of these waters. In shallower groundwaters and in particular in groundwaters from springs, undersaturation is more common, suggesting a higher proportion of younger waters with shorter residence times. Mixing of groundwaters can also result in undersaturation, even where both groundwaters are saturated with respect to calcite and dolomite. Mixing-related undersaturation may have occurred in some of the groundwaters, e.g. at Wharton Hall Farm [NGR 377150 506230] where the groundwater is undersaturated with respect to both mineral phases even though its Ca (115 mg l^{-1}) and Mg (54 mg l^{-1}) content is high. Dolomite saturation predominates in groundwaters in the south of the study area and at depths $> 40 \text{ m}$ (e.g., Fernbank Shed, NGR 38702 44707; Low Pyethorns, NGR 37888 45674; Melling Dub, Tosside, NGR 37787 45585). This spatial trend is probably associated with bedrock dolomitisation which, in the study area, is mainly confined to the Pendleside Formation (Addison et al., 1985) and often only affects certain beds or groups of beds within the formation (see also section 3.4).

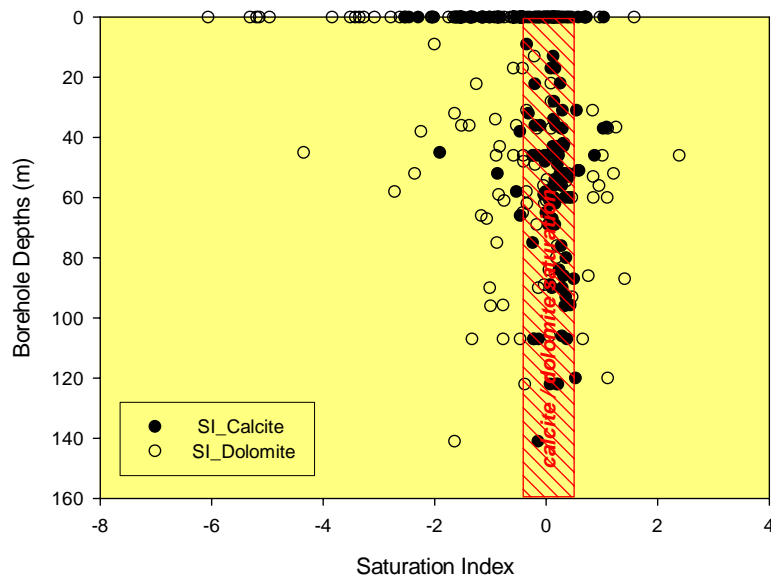


Figure 6.8 Relationship between borehole depths and calcite/dolomite saturation in the groundwaters

The dissolution of calcite and dolomite provide the dominant controls on water chemistry in the aquifer, but silicate dissolution also influences the groundwater composition. Silicon concentrations within the aquifer are relatively low, ranging from 0.2 to 8.8 mg l^{-1} and are controlled by the presence of silicate minerals, groundwater residence times as well as by the saturation of the groundwater with respect to a silicate mineral or phase. While a large number of groundwaters in the study area remain undersaturated with respect to chalcedony (SiO_2) and/or quartz, indicating little contact or time, many deeper groundwaters show saturation with respect to these mineral phases (e.g. Merrybent Farm, NGR 37100 45680; Stock Green Farm, NGR 38682 44904; Three Rivers Caravan Park, NGR 37755 44162; Fernbank Shed, NGR 38702 44707). This reflects the prolonged water-rock contact and the long residence times of these deeper groundwaters, but also indicates areas where the bedrock is relatively enriched in Si as a result of post-depositional chertification processes and/or due to bedrock mineralisation (see section 3.4).

Dissolution of carbonates and silicate minerals may be restricted where the aquifer is confined and the CO_2 supply is limited. Since CO_2 is rapidly consumed by calcite (and/or silicate) dissolution, the CO_2 pressure in such confined systems will drop and if CO_2 is not replenished, less calcite (and/or silicate) will be dissolved. Such closed environments, hence, lead to low Ca, Mg and alkalinity concentrations as well as to low CO_2 pressure in the groundwater, and to a high pH. High pH (9.25) in conjunction

with low Ca, Mg and alkalinity (5 mg l^{-1} , 1.5 mg l^{-1} and 79 mg l^{-1}) levels have been observed in the deeper groundwater at Lodge Lane T58 [NGR 35129 44242] suggesting that confined conditions and limited CO_2 availability may control the groundwater chemistry in this part of the aquifer.

The distribution of SO_4 varies throughout the aquifer (Figure 6.9). Concentrations are relatively low (median 19.4 mg l^{-1}) but a number of groundwaters have very high SO_4 ($104\text{--}1160 \text{ mg l}^{-1}$) concentrations occur. A common source of sulphate in many groundwaters is the dissolution of gypsum (or anhydrite). While anhydrite is known to occur in the Carboniferous Limestone (Falcon and Kent, 1960), its regional distribution is unknown. The low saturation of the groundwaters with respect to anhydrite (SI -0.7 to -3.5) suggests that inputs from anhydrite dissolution are of minor importance for the groundwater quality in the study area. Other potential sources of sulphate include the oxidation of pyrite, acid rain or fertilizer application as well as mixing with seawater (Appelo and Postma, 1993) and/or older formation waters. The latter is probably responsible for the extremely high SO_4 levels of 1160 mg l^{-1} in the groundwater at Holy Well Spring Humphrey Head [NGR 33901 47392] and evidence for mixing with formation water is also seen in the groundwaters at the Royal Observer Corps [NGR 35397 43644], the Dent Utilities Compound borehole [NGR 37040 48700] and the borehole at A.Hartley Ltd. Crownest Mill [NGR 38794 44739].

Dissolution of calcium sulphate (gypsum), formed as a result of the oxidation of pyrite and/or other sulphides, has also been suggested as a source of sulphate in the Carboniferous Limestone aquifer (Downing, 1967) and may have contributed to the high Ca and SO_4 levels in the groundwaters at Wharton Hall Farm [NGR 37715 50623] and Stainton Quarry [NGR 32470 47271]. Oxidation of sulphides appears to be particularly important in areas of bedrock mineralisation as will be discussed in section 6.5.3.

Sulphate removal from the groundwater may also occur e.g. through the formation of barite (BaSO_4) or through bacterially mediated sulphate reduction under low Eh conditions. However, the molar SO_4/Cl ratios show that most groundwaters are enriched in SO_4 relative to seawater and it appears that sulphate reduction is less important and/or balanced by inputs from sulphate sources.

Fluoride concentrations in the study area vary greatly (range $< 100\text{--}3470 \text{ } \mu\text{g l}^{-1}$, median $184 \text{ } \mu\text{g l}^{-1}$), but are generally higher in the groundwaters of the Craven Basin, in the southern part of the study area (Figure 6.11). Previous studies have linked the occurrence of F in the Carboniferous Limestone groundwaters to areas of bedrock mineralisation (Edmunds, 1971) and suggested that it is strongly controlled by the presence of hydrothermal vein fluorites. The positive correlation between F and elements such as I, Br and some trace metals (Figure 6.12) supports this assumption since these elements are generally enriched in hot, saline brines from which the hydrothermal mineral deposits are thought to have formed (see section 3.4). In most groundwaters, F concentrations are limited by the solubility of fluorite (CaF_2) as well as by the Ca concentrations (Figure 6.13) and high F levels (in excess of 1 mg l^{-1}) mostly occur in groundwaters with low Ca contents ($< 80 \text{ mg l}^{-1}$). While most shallow groundwaters are undersaturated with respect to CaF_2 , there is an increase in CaF_2 saturation with depth (Figure 6.14). A number of deeper groundwaters are (near-)saturated with respect to CaF_2 reflecting longer groundwater residence times as well as interactions with mineralised bedrock formations (e.g. Station Inn, Ribblesdale, NGR 37634 47907; Higher Gills Barn, Tosside, NGR 37648 45507; Station House, NGR 37653 47898 and Low Pyethorns, NGR 37888 45674).

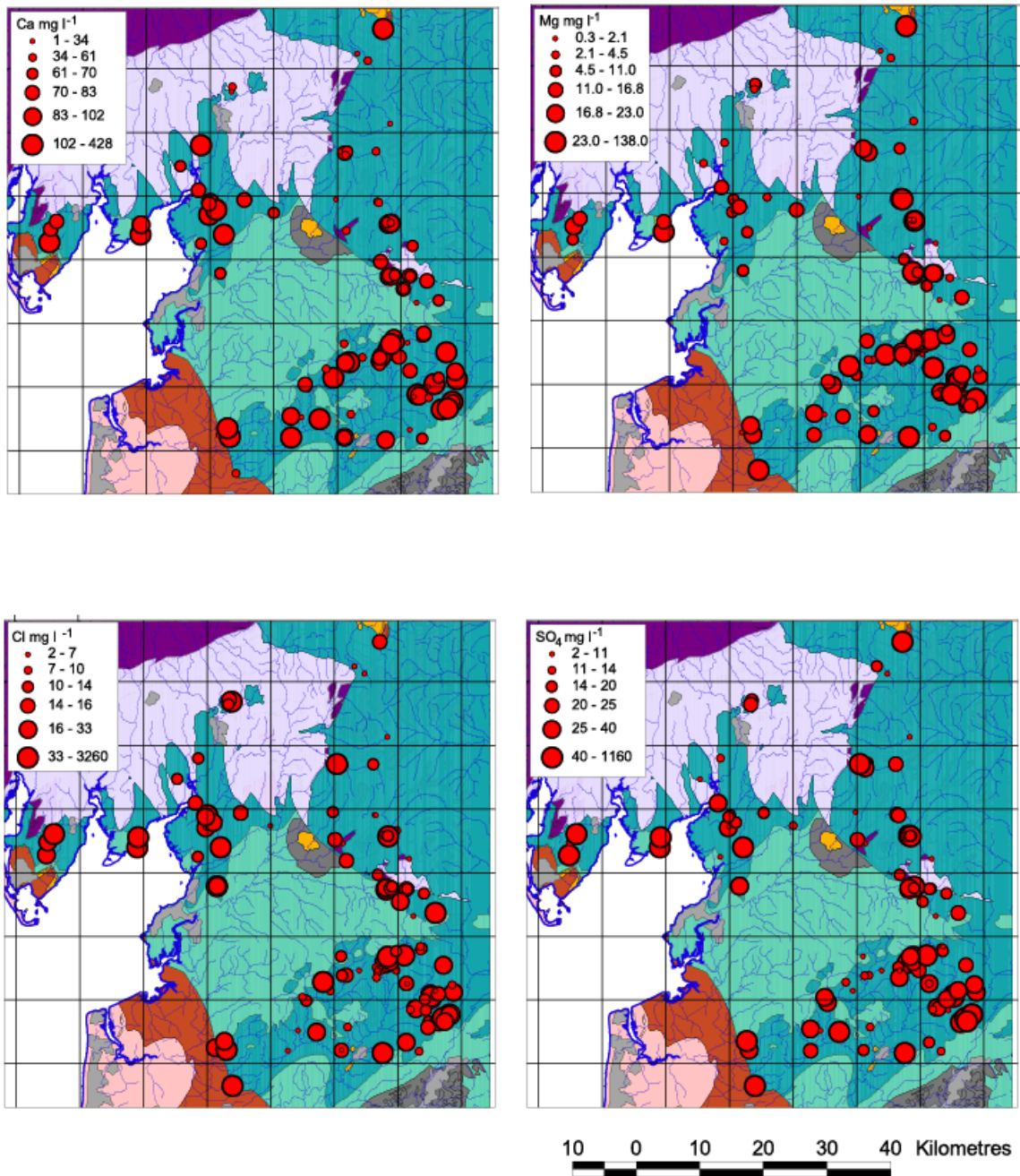
Barium concentrations in the Carboniferous Limestone groundwaters are relatively high (median $60 \text{ } \mu\text{g l}^{-1}$) compared with other carbonate aquifers in the UK (Edmunds et al. 1989). While impoverished in the limestone, high Ba concentrations are probably related to secondary bedrock mineralisation and increased Ba levels, similar to increased F levels, are often associated with elevated trace element contents. In addition to bedrock abundance, the solubility of barite (BaSO_4) exercises a strong control on the Ba concentrations in the groundwaters (Figure 6.15a) and Ba in excess of $100 \text{ } \mu\text{g l}^{-1}$ only occurs in groundwaters where SO_4 levels are low ($< 12 \text{ mg l}^{-1}$). Most waters analysed

for Ba are in equilibrium/near saturation with respect to barite (Figure 6.15b).

6.5.3 Redox reactions

The distribution of redox status in the groundwaters of the study area is complex, due to the variations in the occurrence of impermeable drift deposits as well as due to the layered nature of the aquifer where limestones provide the water-bearing strata whereas the interbedded mudstones act as aquicludes or aquitards. This is reflected in the large spatial variations of redox sensitive species and redox parameters (Eh and DO) illustrated in Figure 6.10 for Fe and DO. The graphs illustrate that nitrate ($\text{NO}_3\text{-N}$) concentrations in the groundwaters have a median value of $<1 \text{ mg l}^{-1}$, which is comparatively low, as under pristine conditions and in an oxidising aquifer nitrate is typically of the order of 1 to 3 mg l^{-1} . However, the inverse relationships between $\text{NO}_3\text{-N}$ and the more reduced N-species $\text{NO}_2\text{-N}$ and $\text{NH}_4\text{-N}$ suggest that processes of denitrification and/or dissimilative nitrate reduction contribute to the low $\text{NO}_3\text{-N}$ concentrations found in most groundwaters. The relationship between N-species and redox is illustrated in Figure 6.16. It appears that nitrate reduction becomes important in waters with Eh $< 300 \text{ mV}$, although the relationship to Eh is less defined for the metastable $\text{NO}_2\text{-N}$. Groundwaters with Eh values below 300 mV and low concentrations of DO also contain high concentration of dissolved Fe, which is easily mobilised under such reducing conditions and is another indicator for the low redox status of these waters. Unfortunately, detailed construction details are not known for many of the sampled boreholes and it is difficult to assess vertical changes in redox potential. Nitrate concentrations are often higher in shallow boreholes and springs, suggesting an agricultural source. Highest $\text{NO}_3\text{-N}$ levels occur in areas where impermeable drift deposits, such as boulder clay and tills, are absent (Figure 6.10), and where surface runoff can rapidly be discharged into the limestone aquifer. Recharge in these drift-free areas, hence, provides a fast pathway for $\text{NO}_3\text{-N}$ from surface applications into the groundwater, especially in the well-developed karstic terrain where dissolution processes have produced a secondary network of fractures and joints. Such fast groundwater pathways may have contributed to the high nitrate concentrations $> 4 \text{ mg l}^{-1}$ observed in some deeper groundwaters ($>60 \text{ m}$). However, high $\text{NO}_3\text{-N}$ levels in deep groundwaters can also be an artefact of the open-hole construction of the borehole, which allows mixing between deeper, low $\text{NO}_3\text{-N}$ groundwaters with shallow, high $\text{NO}_3\text{-N}$ groundwaters in the borehole.

Other important redox processes include the oxidation of sulphides, such as pyrite (FeS_2), galena (PbS), sphalerite (ZnS) and chalcopyrite (CuFeS_2). These processes are particularly important in areas of bedrock mineralisation where these primary sulphides and their alteration products are common. Oxidation of sulphides by oxygen-bearing groundwaters causes sulphate formation but also favours the release of associated metals such as Fe, Pb, Zn and Cu. This leads to enrichment of trace metal and/or SO_4 in the groundwater as has been observed at a number of sites in the study area, e.g. at the Station Inn, Ribblesdale [NGR 37634 47907], the Stainton Quarry [NGR 32470 47271], the Lakeland Wildlife Oasis Park [NGR 35091 47783], Rolls Royce Banksfield [NGR 38808 44763] and at Wharton Hall Farm [NGR 37715 50623].



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Figure 6.9 Spatial distribution of Ca, Mg, Cl and SO₄ in the groundwaters of the study area

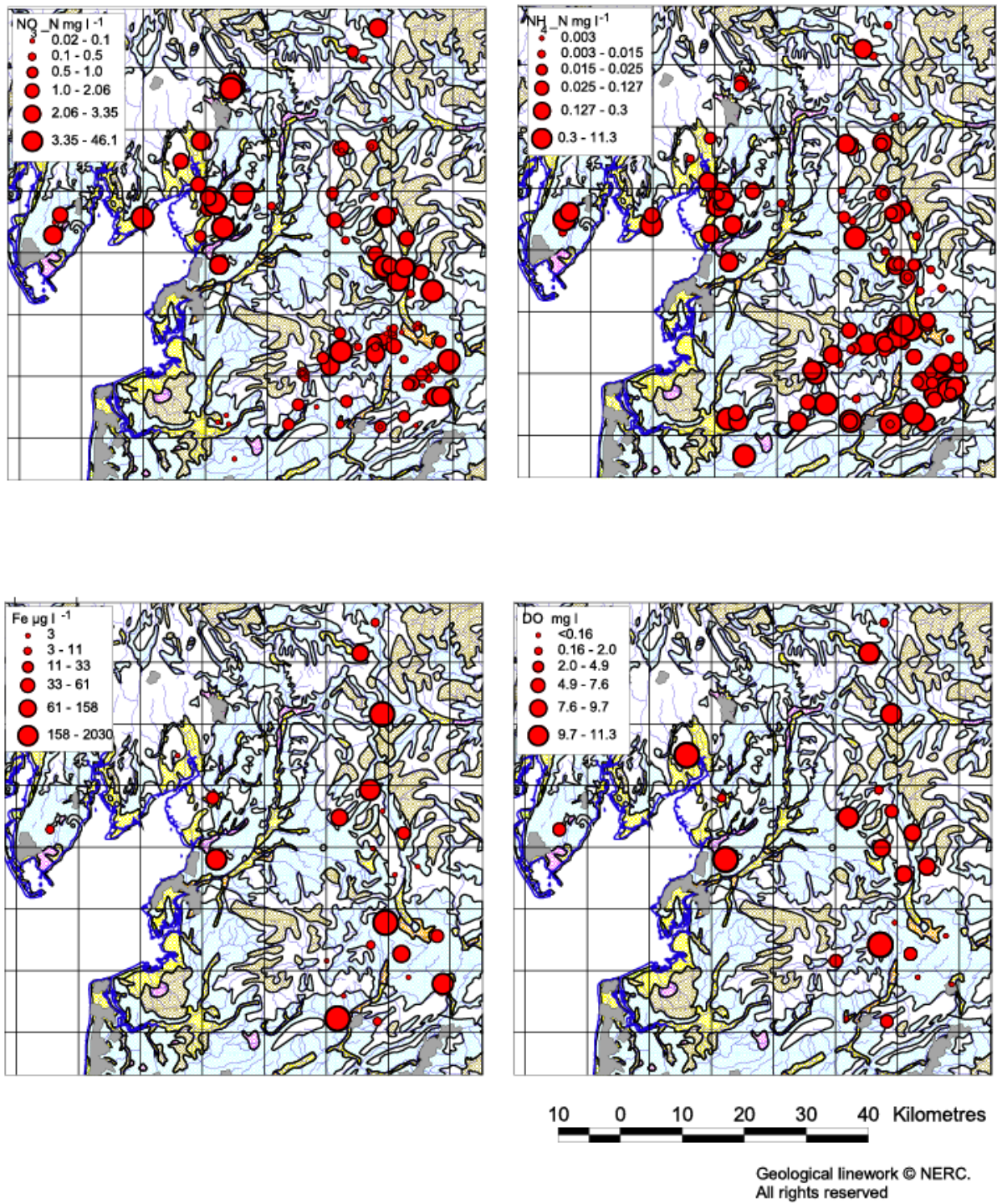


Figure 6.10 Spatial distribution of NO₃-N, NH₄-N, Fe and DO in the groundwaters of the study area

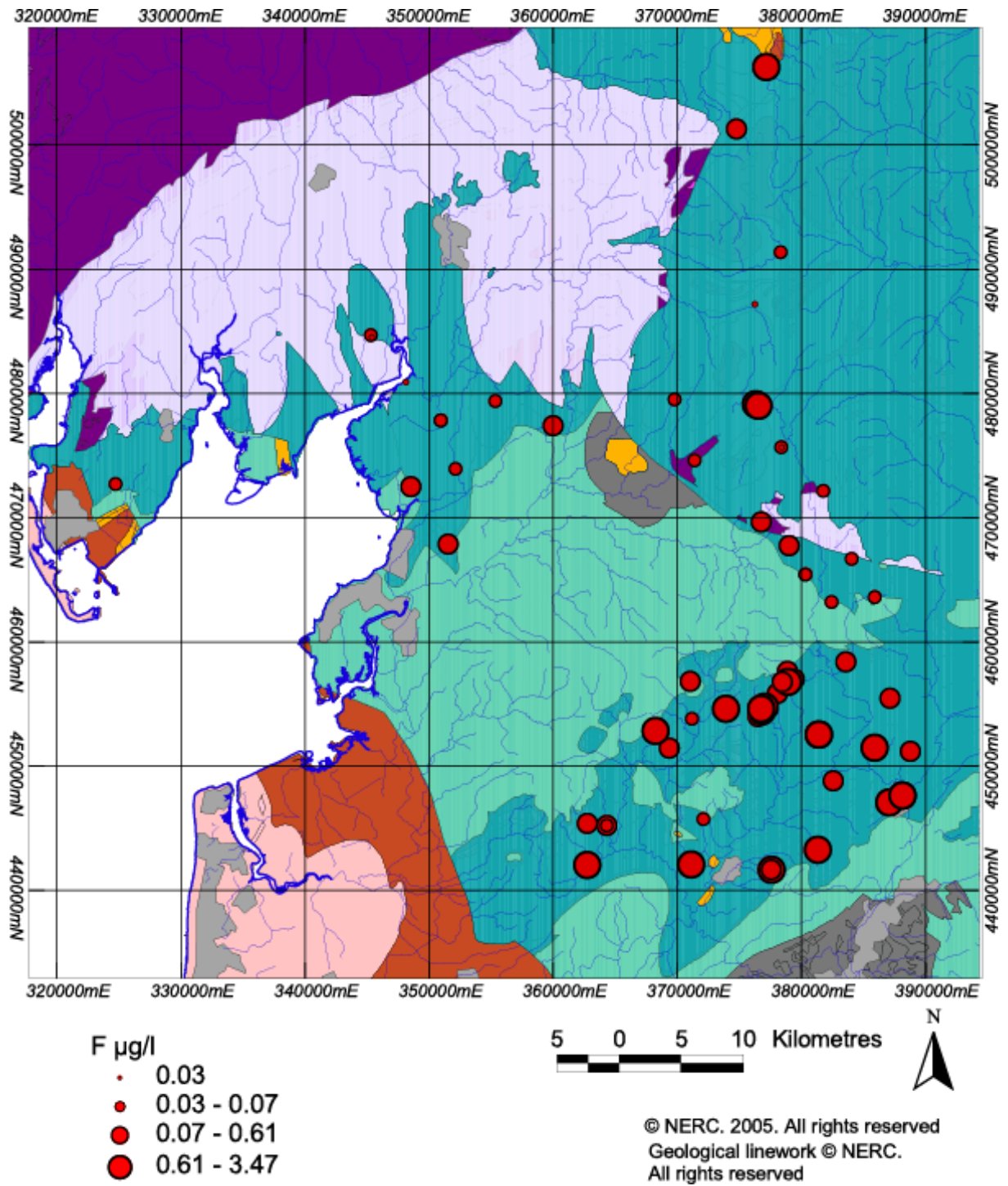


Figure 6.11 Spatial distribution of F in the Carboniferous Limestone aquifer of the study area

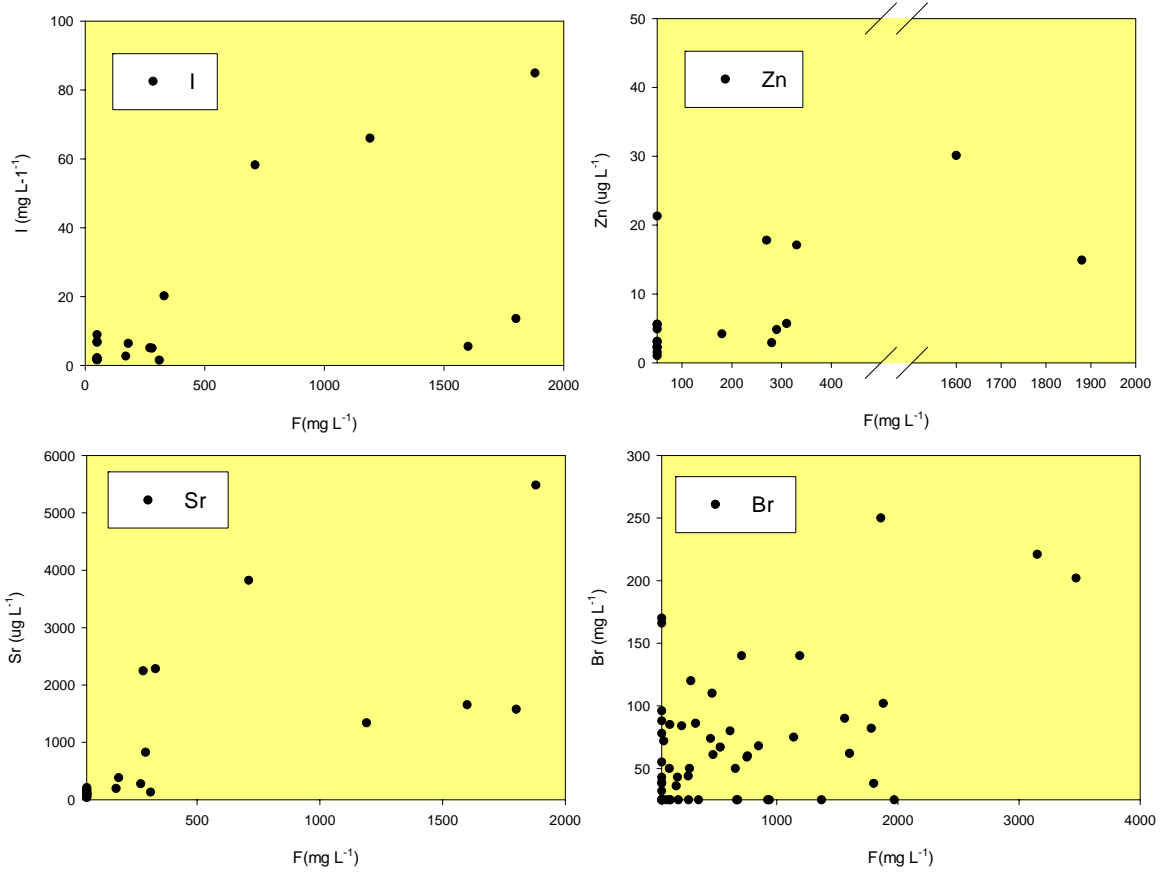


Figure 6.12 Relationship between F and other elements associated with bedrock mineralisation (I, Zn, Sr, Br)

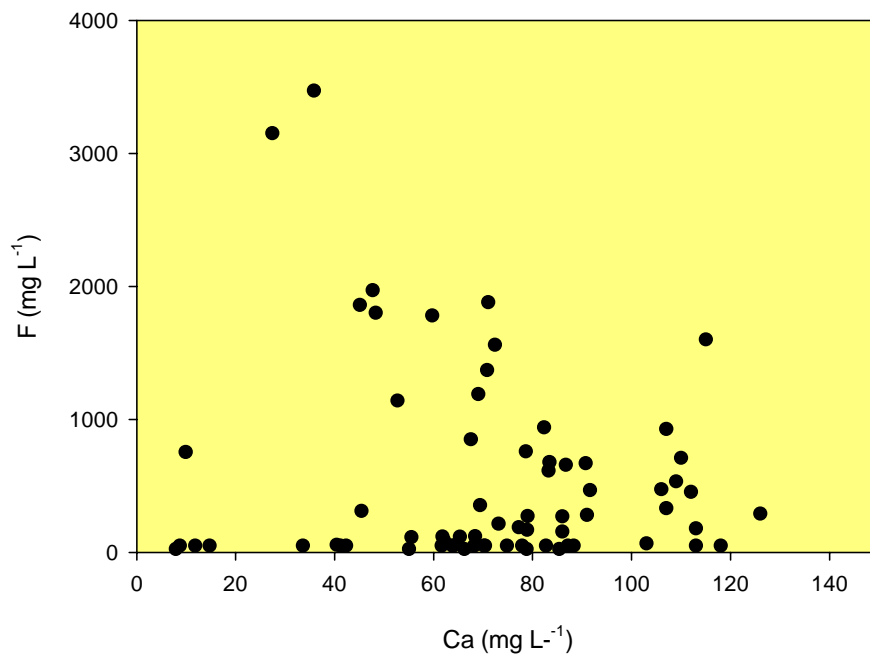


Figure 6.13 Inverse relationship between F and Ca due to CaF₂ solubility control

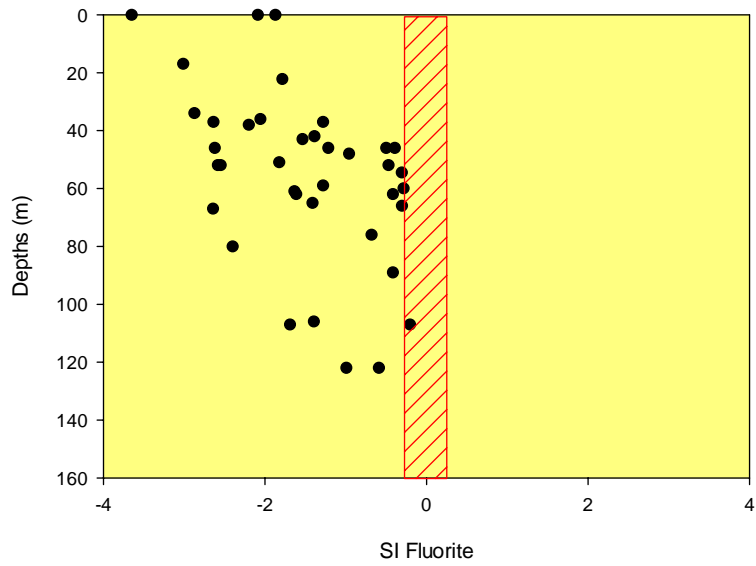


Figure 6.14 Relationship between fluorite saturation and depth

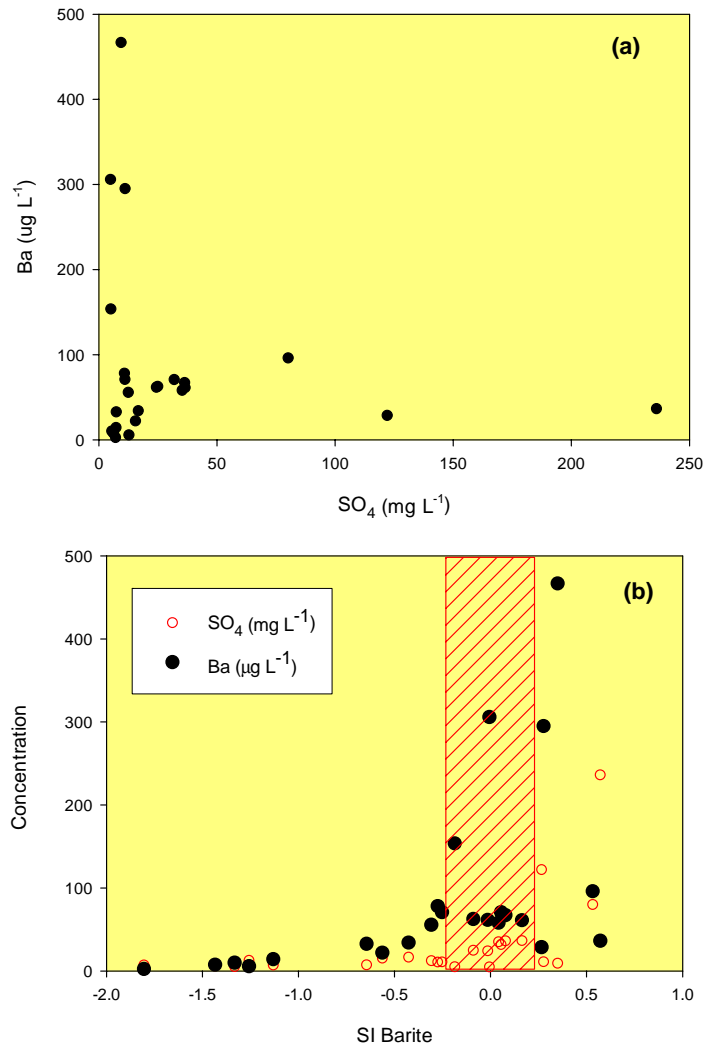


Figure 6.15 Relationship between Ba and SO_4 (a) concentrations in the groundwater and barite saturation (b)

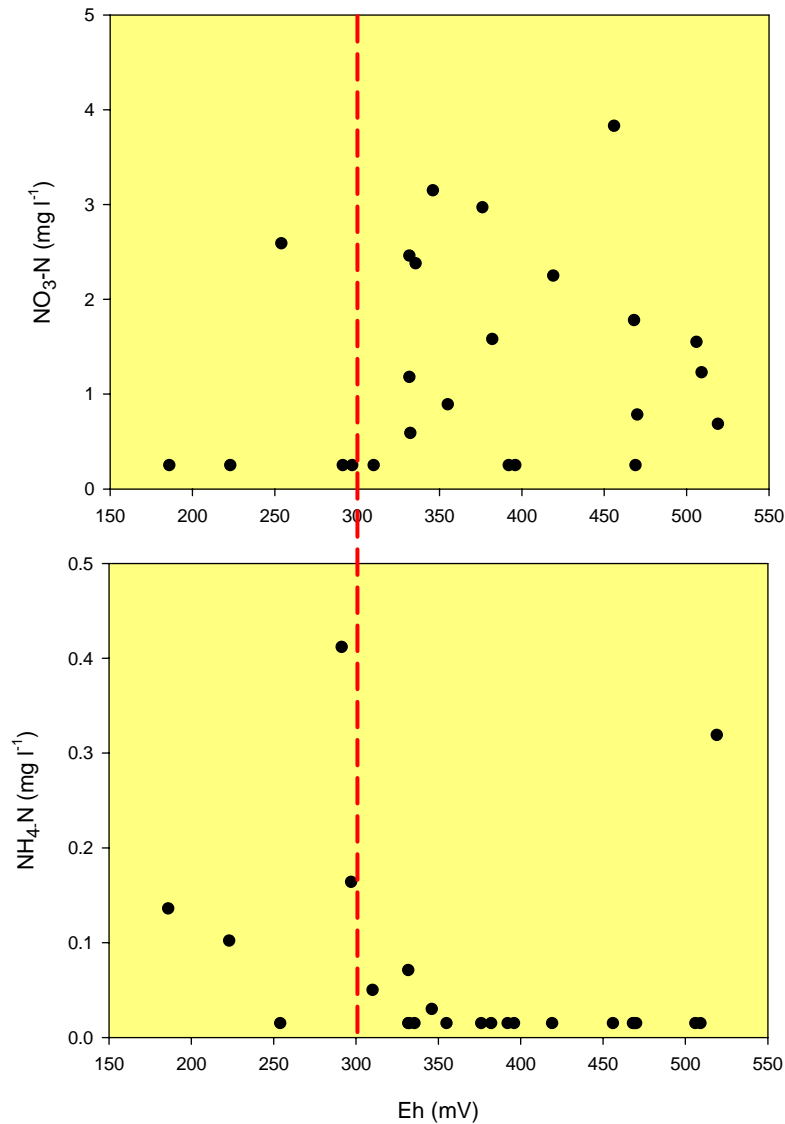
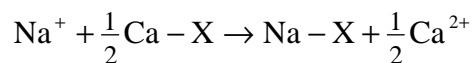


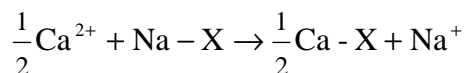
Figure 6.16 Relationship between Eh and N-speciation in the Carboniferous Limestone groundwater

6.5.4 Ion exchange reactions

The majority of recharge groundwaters are of Ca-HCO₃-type controlled by carbonate dissolution. The cation exchangers (X) within the recharge zone of the aquifer will therefore be dominated by Ca adsorbed on to their surfaces. In aquifers containing seawater, Na and Cl are the dominant ions in solution, thus sediments in contact with seawater will have predominantly adsorbed Na on their exchange sites. 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 into the water which alters the water chemistry from a Na-Cl type to a Ca-Cl₂ type. The reverse process will operate if groundwater freshening occurs i.e. freshwater flushing through a saline 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, 1993).

The complex nature of the aquifer mineralogy and the lack of solid phase data make it difficult to assess the role of ion exchange in the aquifer, though Na/Cl ratios can be used as an indicator of whether any increase in Na is due to mineral weathering and ion exchange or mixing with older formation water. The molar Na/Cl ratios in the Carboniferous Limestone groundwaters vary significantly, mostly exceeding that of seawater (0.85), and high values of up to 53 indicate that water-rock interactions are important in the aquifer. The aquifer has generally been well flushed of original formation waters, as indicated by the low Cl levels (median 13 mg l^{-1}) but high Na concentrations in some of the groundwaters (Dunsop Bridge Trout Farm, NGR 36556 44985; Middle Crag Bay Horse, NGR 35132 45492) suggest that ion exchange of Na on clay minerals for Ca or Mg is locally important. These exchange processes are also reflected in the inverse correlation between Na and Ca (and Mg) as exemplified in Figure 6.17. This inverse ion exchange, where Na is released in exchange for Ca, occurs where freshwater intrudes in areas dominated by older formation waters and evidence of such groundwater freshening is also found at a number of other sites (e.g., at Crowtrees Farm, NGR 37800 45580; Black Moss Cottage, NGR 38325 44187; Tewitt Hall Farm, NGR 38136 45253 and Brook House Green, NGR 37390 45460), where groundwaters show a tendency towards Na-HCO_3 type compositions (Figure 5.1).

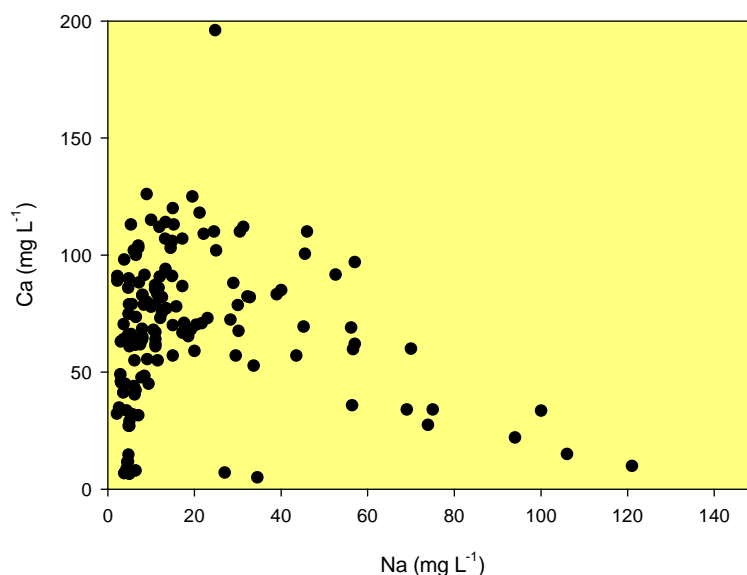


Figure 6.17 Relationship between Na and Ca

6.5.5 Mixing with older formation water

Mixing with older, deeper connate or formation water is generally indicated by increased salinity. High salinity can also be caused by dissolution of evaporite minerals, and in the first instance, Cl provides a better indicator for mixing with deeper formation waters. There is no clear spatial trend in the distribution of Cl within the aquifer (Figure 6.9), although higher Cl levels are often associated with deeper groundwaters (Figure 6.1). While Cl concentrations are mostly low (median: 13 mg l^{-1}), exceptionally high concentrations occur at a number of sites (A. Hartley Ltd. Crownest Mill, NGR 38794 44739; Crownest Field Spring, NGR 37811 46732; Royal Observer Corps, NGR 35397 43644; Kents Bank Allithwaite, NGR 33910 47550; Dent Utilities Compound, NGR 37040 48700). Most of these groundwaters also contain high levels of Na, SO_4 , Mg and Ca and in the Na-Cl diagram plot along the seawater-rainwater mixing line (Figure 6.18a), indicating that mixing between these sources may be important. Comparing the composition of these groundwaters with that of average seawater by

means of molar ratios further shows that the groundwaters are enriched in Mg, Ca (see Figure 6.18b) and/or SO_4 relative to seawater. The deviation from seawater composition suggests that the water is of marine origin but has been residing in the aquifer for some time, during which ion exchange processes and other water-rock interactions (carbonate dissolution) and redox processes (pyrite oxidation) have modified the original seawater composition.

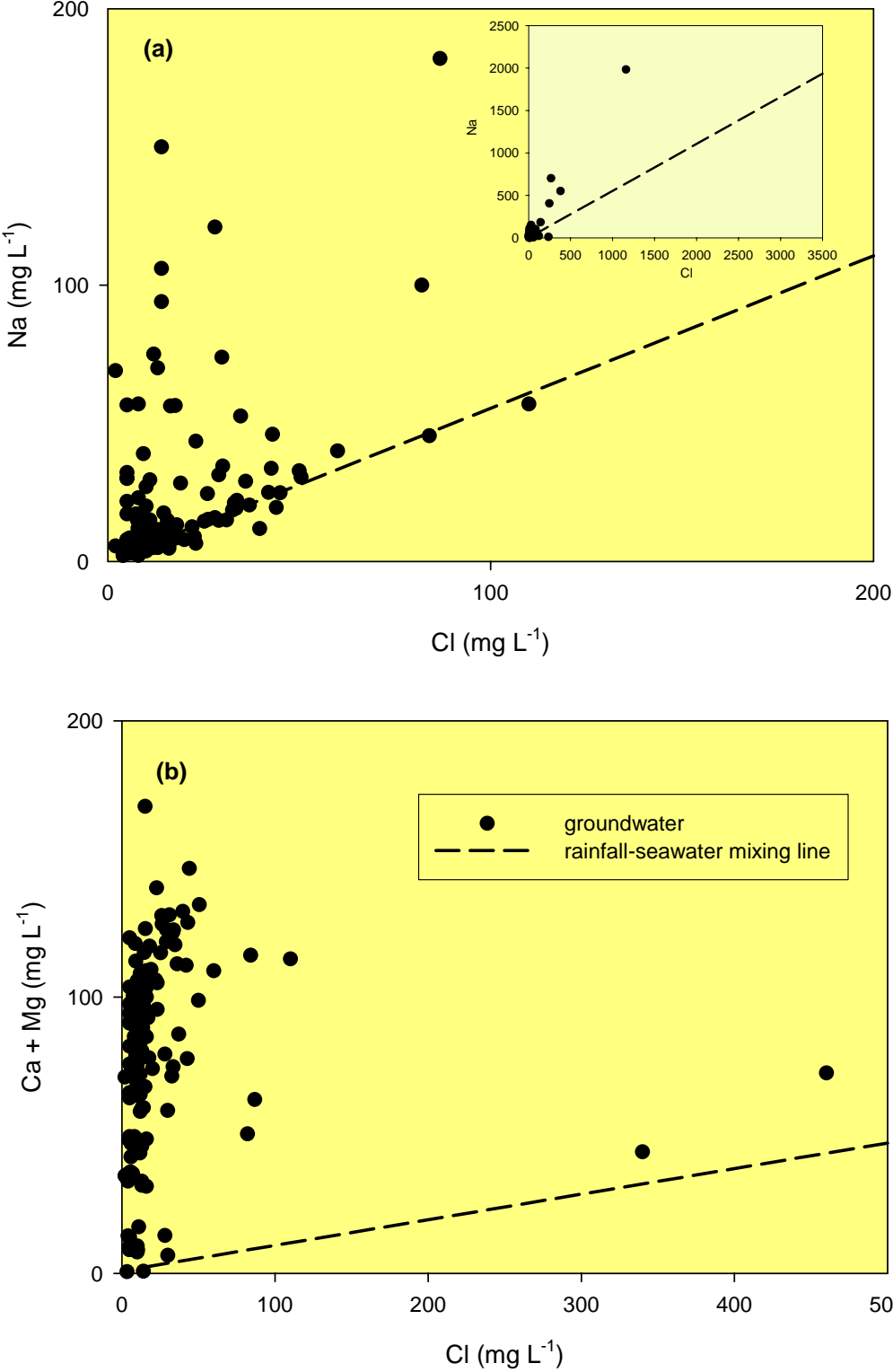


Figure 6.18 Comparison of (a) Na and Cl concentrations and (b) Ca+Mg and Cl concentrations in the Carboniferous Limestone groundwaters (black circles) with (average) seawater (broken line) composition

Highest Cl, Na, SO₄, Mg and Ca concentrations in the groundwater of the study area occur at the Holy Well Spring at Humphrey Head [NGR 33901 47392], which is one of the many wells in the area. It is known for its medicinal qualities and was historically ‘celebrated as a remedy for stone, gout, and cutaneous complaints’ (Hope, 1893). Based on the available information, the source of this ‘brackish’ spring can only be hypothesised. The Mg+Ca/Cl ratio of the spring groundwater (0.17) is relatively low compared to that of other groundwaters in the aquifer (median 6.21), implying that mixing with more recent seawater ingressed at the nearby coast may be important. However, the ratio is still higher than that of seawater (0.09) and given the high Cl concentrations, it is clear that considerable enrichment in Ca and Mg must have taken place. Inputs from a formation water sources (e.g. associated with the adjoining Permian deposits) may also have contributed to these high salinity groundwaters.

There are a number of other locations in the study area, where high salinity groundwaters occur in the vicinity of tectonic fault zones and/or near unconformities (e.g. at A. Hartley Ltd. Crownest Mill, NGR 38794 44739; Royal Observer Corps, NGR 35397 43644; Kents Bank Allithwaite, NGR 33910 47550, Fernbank Shed, NGR 38702 44707) indicating that connections/preferential pathways may exist between the Carboniferous Limestone aquifer and the adjacent deposits of Permian, Triassic and younger Carboniferous (Namurian/Westphalian) age.

6.5.6 Trace elements

Concentrations of several trace elements in the study area are predominantly controlled by the distribution of bedrock mineralisation, which include the primary sulphides of lead, zinc, copper and iron and their alteration products as well as barite and fluorite.

The main source of Sr in the Carboniferous Limestone groundwaters is from congruent or incongruent carbonate dissolution, but the existence of an additional Sr source is suggested by the bi-modal distribution of Sr on the probability plot (Figure 5.3b), which shows a clear change in gradient at 400 µg l⁻¹. In Figures 6.19 and 6.20 it can be seen that groundwaters with Sr levels in excess of 400 µg l⁻¹ are saturated with respect to barite and also contain high levels of F. In the Carboniferous Limestone aquifer of the study area, these elements, Ba and F, are generally derived from hydrothermal vein deposits rather than from bedrock sources. It, hence, appears that the occurrence of secondary mineral deposits controls the high Sr levels in these groundwaters rather than carbonate dissolution in the bedrock. This also explains why the good positive correlation between Sr and Ca seen in the low Sr groundwaters (< 400 µg l⁻¹) is not reflected in groundwaters with high (> 400 µg l⁻¹) Sr contents (Figure 6.21).

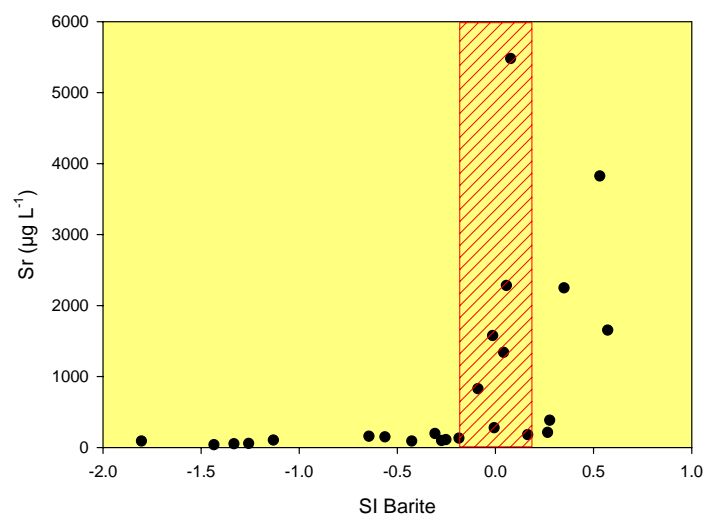


Figure 6.19 High Sr levels in groundwaters saturated with respect to barite

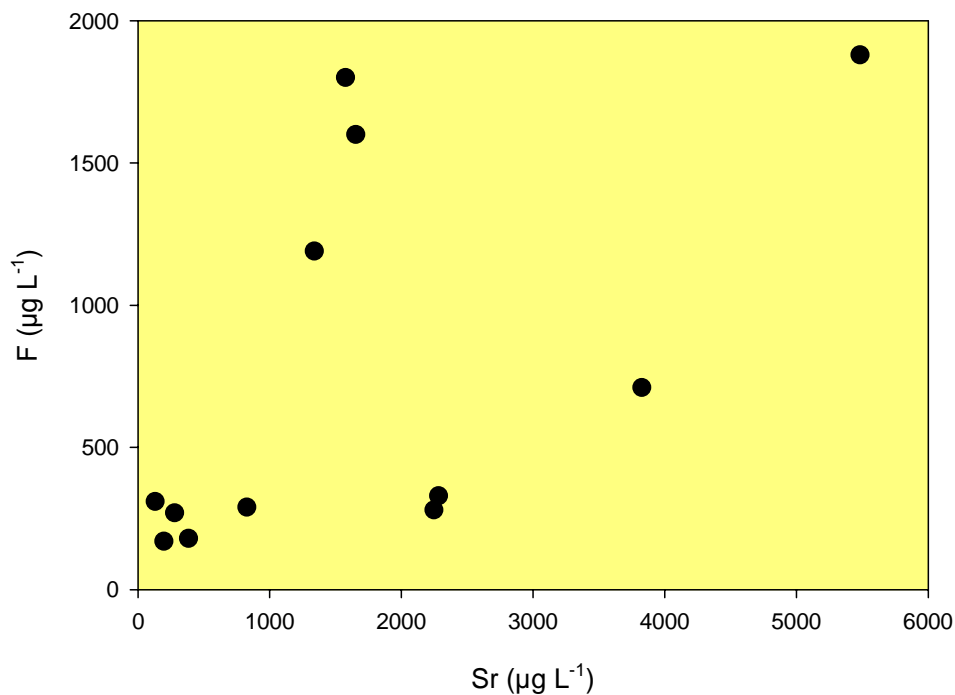


Figure 6.20 Relationship between Sr and F in the groundwaters of the Carboniferous Limestone aquifer

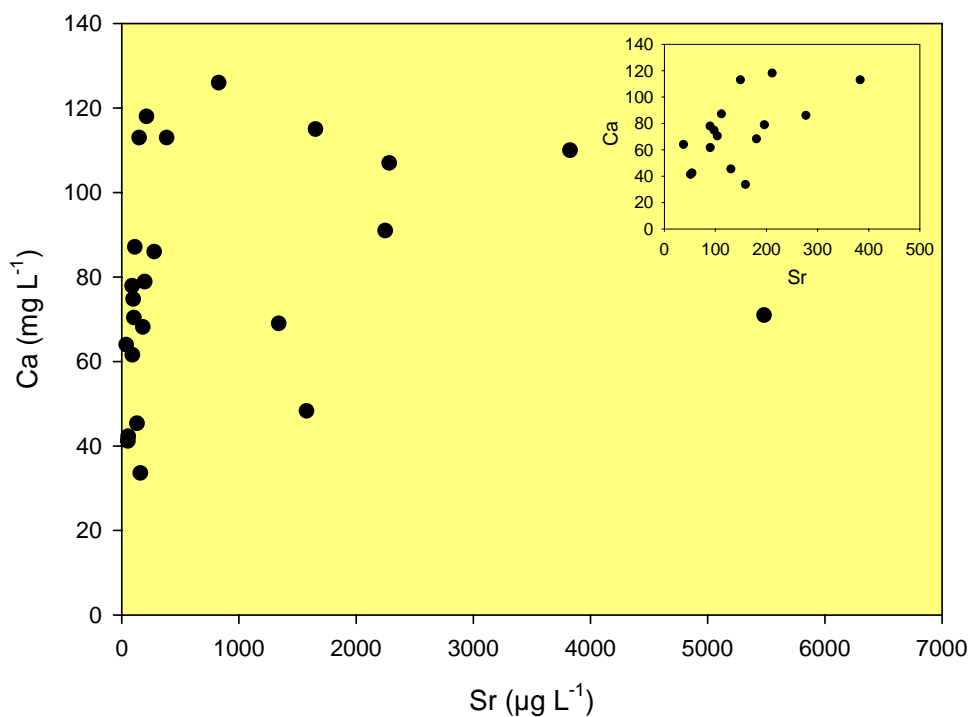


Figure 6.21 Relationship between Sr and Ca in the groundwaters of the Carboniferous Limestone Aquifer

Barium levels in the aquifer are controlled by the barite solubility product, and exceed the EC Guide level for drinking water of $100 \mu\text{g l}^{-1}$ only where SO_4 concentrations are low (e.g., Bashall Town Farm, NGR 37107 44206; Hile Farm, NGR 37884 45761; Crawshaw Farm, NGR 36936 45142 and High Stennerskeugh, NGR 37475 50125).

Fluoride concentrations in the limestone are relatively high (median $184 \mu\text{g l}^{-1}$) compared with other UK aquifers (Edmunds et al., 1989), in many cases exceeding the EC MAC level for drinking water of 1.5 mg l^{-1} . High F levels are associated with the occurrence of secondary hydrothermal mineralisation, which is also reflected in the elevated levels of trace elements such as Li, Ba, Cu and others in many of these groundwaters. Uranium concentrations in the study area are generally low (median $0.31 \mu\text{g l}^{-1}$), but high levels occur in the groundwater at NGR 37629 47909 as well as at NGR 37715 50623. The elevated F, Li, Sr, Zn and Pb levels in these groundwaters imply a hydrothermal mineralisation source.

Iron and Mn are present in the Carboniferous Limestone aquifer of the study area and the EC Guide values of $200 \mu\text{g l}^{-1}$ and $50 \mu\text{g l}^{-1}$ for Fe and Mn, respectively, are exceeded in a number of groundwaters (e.g., Bashall Town Farm, NGR 37107 44206; Far End Farm, NGR 37828 49134; Rolls Royce Banksfield, NGR 38808 44763; High Ground Farm, NGR 38714 45542). Anomalously high Fe and Mn concentrations of $2030 \mu\text{g l}^{-1}$ and $235 \mu\text{g l}^{-1}$ are observed in the groundwater at Hile Farm [NGR 37884 45761], which is also enriched in Ba, Li and other trace elements. Low Eh levels suggest that Fe and Mn may be derived from reductive dissolution of secondary Fe and Mn oxyhydroxides in the mineralised bedrock and low SO_4 suggests that SO_4 reduction may also be important. Another source of Fe in the aquifer is the oxidation of pyrite, which may have contributed to the elevated Fe and SO_4 levels in the groundwater at the Nether Kellet Quarry [NGR 35152 46783]. However, given the various mineral phases present in such areas of mineralisation, it is very likely that Fe and Mn in the groundwater are derived from more than one source depending on the prevailing pH and Eh conditions in the groundwaters. Arsenic levels in the groundwaters are generally low. Concentrations in excess of the detection limit of $0.5 \mu\text{g l}^{-1}$ are associated with high Fe levels implying a sulphide mineral (pyrites) and/or ferric hydroxide source.

Aluminium levels in the Carboniferous Limestone groundwaters are generally low, mostly below detection limit (median $<1 \mu\text{g l}^{-1}$), but concentrations of $103 \mu\text{g l}^{-1}$ and $95 \mu\text{g l}^{-1}$ were observed at the Nether Kellet Quarry [NGR 35152 46783] and at the Lakeland Wildlife Oasis Park [NGR 35091 47783]. Although these groundwaters are also enriched with respect to other trace elements, such as As, Ba, Fe, Mn, Mo as well as As, Cu, U and Zn, they still comply with the UK drinking water requirements as none of the EC Guide values are exceeded.

Zinc levels in the Carboniferous Limestone are high (median $5.65 \mu\text{g l}^{-1}$) compared to other UK groundwaters (Edmunds et al., 1989), reflecting the importance of bedrock mineralisation. Highest concentrations occur in the groundwater at Rolls Royce Banksfield [NGR 38808 44763] which contains Zn levels of 5 mg l^{-1} . Zinc is often derived from oxidation of Zn sulphide (sphalerite, ZnS) and/or released during the oxidation of iron sulphides or secondary zinc minerals, and the contribution from such mineral dissolution processes to the groundwater chemical signature at this site is also reflected in the high Pb, Fe and Mn concentrations.

Nickel, in most groundwaters, is below the limit of the detection ($<2 \mu\text{g l}^{-1}$). Where detected, Ni correlates well with Mn but concentrations remain far below the EC Guide value of $20 \mu\text{g l}^{-1}$. Lead is enriched in groundwaters in mineralised areas, but the maximum concentrations of $1.4 \mu\text{g l}^{-1}$ at Rolls Royce Banksfield [NGR 38808 44763] do not exceed the EC Guide levels.

7. BASELINE CHEMISTRY OF THE AQUIFER

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

The baseline chemistry of the Carboniferous Limestone aquifer of the Central Pennines area of Yorkshire and Lancashire is extremely variable. Changes occur spatially as well as with depths and groundwaters (especially in springs) can show chemically distinct signatures even when occurring in close proximity to each other (Crow Nest Field Spring, NGR 37811 46732, Crow Nest Roadside Spring, NGR 37840 46706), reflecting the extent of water-rock interaction, the bedrock lithology, mineralisation and karstification as well as the different geochemical controls imposed by the local geochemical environment (e.g. oxidation-reduction controls). The widespread drift deposits, covering most of the study area, as well as the layered nature of the aquifer (with its intervening aquicludes and aquitards) have minimised anthropogenic inputs over much of the aquifer. Therefore, for most elements, the concentrations measured and the ranges found can be taken as representative of the natural baseline which, in the case of some trace elements, can be very high. However, in areas of intense karstification and where windows in the drift occur, groundwaters remain vulnerable to pollution.

The data have been presented in Tables 5.1 and 5.2 and the median value and 97.7 percentile provide a good estimate of the average and upper baseline concentrations in the aquifer. The chemical data indicate that water-rock interactions are the most important influences on water chemistry and a range of geochemical processes have been shown to operate in the study area. As recharge water infiltrates into the aquifer, its chemistry is rapidly modified through dissolution of carbonate. While most waters are saturated with respect to calcite, a large number remain undersaturated with respect to dolomite (Figure 6.7). Beside the slower dissolution kinetics of dolomite, this is due to the fact that dolomitisation has only occurred in parts of the aquifer and this is also reflected the spatial distribution of Mg in the groundwaters (Figure 6.8), which is generally higher in the southern part of the aquifer. In areas where bedrock chertification has occurred, silicate dissolution is also contributing to the groundwater signatures.

Concentrations of F and Ba in the aquifer are naturally high (Edmunds et al., 1989) and locally occurring hydrothermal fluorite and barite veins bring the upper limit of the natural baseline concentrations, assessed as the 97.7 percentile, to 2.0 mg l^{-1} and $355 \text{ } \mu\text{g l}^{-1}$, respectively, (although, on average, levels in the groundwater are much less; around 0.2 mg l^{-1} and $60 \text{ } \mu\text{g l}^{-1}$).

Concentrations of several trace elements in the aquifer are controlled by the distribution of bedrock mineralisation, which include the sulphides of lead, zinc, copper and iron and their alteration products. Mineral dissolution and associated mobilisation of trace elements is common in the Carboniferous Limestone aquifer and has led to local enrichments in elements such as Pb, Zn, Cu, Fe, U, or As in the groundwater and to their relatively high baseline levels of $0.7 \text{ } \mu\text{g l}^{-1}$ (Pb), $1680 \text{ } \mu\text{g l}^{-1}$ (Zn), $17 \text{ } \mu\text{g l}^{-1}$ (Cu), $850 \text{ } \mu\text{g l}^{-1}$ (Fe), $3.2 \text{ } \mu\text{g l}^{-1}$ (U) and $2.3 \text{ } \mu\text{g l}^{-1}$ (As).

Variations in the distribution of impermeable drift deposits as well as local reductions in transmissivity related to the occurrence of confining layers of mudstone and/or shales in the bedrock have led to a

complex distribution of redox conditions in the groundwater. Where reducing environments are encountered, the natural baseline is influenced by the reductive dissolution of secondary Fe and Mn oxyhydroxides and groundwaters often maintain high levels of naturally derived Fe, Mn and associated trace metals. These processes are of particular importance in areas of bedrock mineralisation where alteration of the primary ore minerals and re-mobilisation processes have favoured the formation of secondary mineral phases.

Mixing with more saline groundwaters has occurred in the aquifer and there has been an evolution in the deeper parts of the aquifer towards waters of Na-HCO₃ type, implying aquifer freshening. The presence of more saline waters in the aquifer is also indicated by the positive skew in the distribution of Cl and Na on the probability plots (Figure 5.3, see also Box 5.1). Intrusion of recent seawater and salinisation has not been detected in the aquifer, instead mixing with older formation waters in the deeper parts of the aquifer and/or along fault zones appears to be the main source of high salinity in the aquifer. There is some indication that a hydraulic connection exists between the Carboniferous Limestone and the overlying younger deposits of Permian, Triassic and/or Namurian/Westphalian age, in particular in zones of extensive faulting and along unconformities. Some of these high salinity waters are also enriched in trace elements (e.g., at Rolls Royce Banksfield) and are probably associated with hydrothermal mineral deposits or veins. However, without further data (e.g., from isotope studies), the particular origin of the high salinity groundwaters, e.g., at the Holy Well Spring, the Royal Observer borehole or at Rolls Royce Banksfield, remains uncertain.

Most groundwaters in the study area appear not to be largely impacted by direct anthropogenic inputs and thus represent baseline. However, the lack of good historical data makes it difficult to assess the baseline of the region. Locally increased levels in N-species and DOC suggest that diffuse pollutants including agricultural fertilisers have modified this baseline. While NO₃-N concentrations in the study area remain relatively low, this is a consequence of reducing conditions in the groundwater, which promote the reduction of NO₃-N to N_{2(gas)} and evidence for ongoing denitrification and/or dissimilatory nitrate reduction in the groundwater is given by the increased NO₂-N and NH₄-N levels. On the probability plot, there is a shift in NO₃-N population at around 0.3 mg l⁻¹ and in DOC population at around 1 mg l⁻¹, which may discriminate baseline from anthropogenic pollution, but for NO₃-N the trend is obscured by the non-conservative behaviour of N-species as well as by the detection limits.

Other elements which may have been modified by agriculturally-derived anthropogenic inputs include Na, K, Cl and SO₄. The effect of anthropogenic inputs on the baseline concentration of these elements is difficult to assess as concentrations are naturally high in parts of the aquifer. While it is unlikely that anthropogenic inputs have extended the upper baseline for these elements in the aquifer overall, it is possible that they have impact on the baseline at a local scale. However, due to the heterogeneity of groundwater chemistry across the aquifer it is difficult to assess spatially the impact of such inputs and a local baseline would need to be established for individual sites or areas of interest.

Taken as whole, the hydrochemical data show that for some elements the upper limits of the natural baseline concentrations are relatively high due to local bedrock mineralisation and/or due to the presence of formation waters in the aquifer. For other elements, the baseline has clearly been impacted by anthropogenic inputs. The impermeable drift deposits afford a degree of protection from diffuse or point source pollution, but shallow groundwaters are vulnerable to pollution where these drift deposits are absent. Deeper groundwaters are at risk of surface-derived pollution in areas where fast groundwater pathways exist in the karstic limestone and fast transport through the secondary network of fractures and joints (conduits) may have contributed to high NO₃ levels observed in some deeper groundwaters.

8. SUMMARY AND CONCLUSIONS

The Carboniferous Limestone aquifer of the Central Pennines of Yorkshire and Lancashire is an important local aquifer providing water for potable and industrial use. It forms the oldest in a multi-layered series of (minor) aquifers, which lithologically varies considerably across the region. The water-bearing strata are commonly provided by the limestone while the interbedded mudstones act as aquicludes or aquitards. The complex geology and the multilayered nature of the aquifer have had a significant effect on the baseline chemistry of the area resulting in considerable spatial heterogeneity of most chemical parameters and solute concentrations.

Rapid changes occur during recharge and groundwater flow and baseline chemistry is mostly controlled by carbonate, mainly calcite, dissolution reactions. Dolomite and silicate dissolution can also affect the groundwater signature but are generally only important in areas where dolomitisation and/or chertification of the bedrock has occurred.

There is evidence for bedrock mineralisation in the study area and these control the occurrence and the distribution of F, Ba and other trace elements (e.g. Cu, Pb, U, Zn) in the aquifer. Although naturally derived, locally high levels of F and Ba could cause problems where groundwater is to be used as a drinking water source for human consumption as Ba and F levels exceed EC Guide values at a number of sites.

Variations in the spatial distribution of impermeable drift and variations in aquifer transmissivity related to the occurrence of argillaceous units in the bedrock have led to a complex distribution of redox conditions in the groundwater. Where reducing environments are encountered, the natural baseline is influenced by the reductive dissolution of secondary Fe and Mn oxyhydroxides and groundwaters often maintain high levels of naturally derived Fe, Mn and associated trace metals.

Processes of ion exchange and mixing are important for the baseline chemistry and have given rise to the formation of Na-HCO₃-type waters. The occurrence of groundwaters with higher salinity indicates mixing with formation waters in the deeper parts of the aquifer where flushing (freshening) has not been complete. In zones of extensive faulting and along unconformities, the groundwater chemistry may be modified by leakage from the younger Permian, Triassic and/or Namurian/Westphalian units leading to increased groundwater salinity.

It is concluded that the properties of Carboniferous Limestone groundwaters in the Central Pennines area of Yorkshire and Lancashire are overwhelmingly determined by natural reactions between the groundwater and the bedrock. The complex nature of the geology in this area has given rise to significant local and regional variations in the natural baseline, which is expressed as a range of concentrations and can vary over several orders of magnitude for some elements. Diffuse pollutants including agricultural fertilisers have modified this baseline leading locally to increases in N-species. The presence of locally high concentrations of F, Ba and other trace elements is considered to be mostly due to natural processes of fluorite/barite dissolution and sulphide oxidation/ metal oxide reduction, respectively. The impermeable drift deposits (boulder clay and till) afford a degree of protection from diffuse or point source pollution. However, the fast groundwater flow rates associated with the presence of large interconnected conduit systems in areas of karstification make the aquifer highly vulnerable to pollution, especially where windows in the drift occur.

9. REFERENCES

- Addison, F.T., Turner, P. and Tarling, D.H., 1985. Magnetic studies of the Pendleside Limestone: evidence for remagnetization and late-diagenetic dolomitization during a post-Asbian normal event. *Journal of the Geological Society*, **142**(6), 983-994.
- Aitkenhead, N., Barclay, W.J., Brandon, A., Chadwick, R.A., Chisholm, J.I., Cooper, A.H. and Johnson, E.W., 2002. *British Regional Geology: The Pennines and adjacent areas*. British Geological Survey, Nottingham.
- Aitkenhead, N., Bridge, D.M., Riley, N.J. and Kimbell, S.F., 1992. Geology of the country around Garstang. *Memoirs of the British Geological Survey*. Her Majesty's Stationary Office, London.
- Allen, D.J., Brewerton, L.M., Coleby, L.M., Gibbs, B.R., Lewis, M.A., MacDonald, A.M., Wagstaff, S. and Williams, A.T., 1997. The physical properties of major aquifers in England and Wales. *British Geological Survey Technical Report, WD/97/34. Environment Agency R&D Publication 8*.
- Appelo, C.A.J. and Postma, D., 1993. *Geochemistry, Groundwater and Pollution*. Balkema, Rotterdam.
- Brandon, A., Aitkenhead, N., Crofts, R.G., Ellison, R.A., Evans, D.J. and Riley, N.J., 1998. *Geology of the country around Lancaster*. Memoirs of the British Geological Survey. Her Majesty's Stationary Office, London.
- Darling, W.G., Bath, A.H. and Talbot, J.C., 2003. The O & H stable isotope composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrology and Earth System Sciences*, **7**(2), 183-195.
- Dunham, R.J. and Wilson, A.A., 1985. Geology of the Northern Pennine Orefield: Volume 2, Stainmore to Craven. *Economic Memoir of the Geological Survey of Great Britain*.
- Edmunds, W.M., 1971. Hydrogeochemistry of the Derbyshire Dome with special reference to trace constituents. *Report Series of the Institute of Geological Sciences*, 71/7, HSMO, London.
- Edmunds, W.M., Bath, A.H. and Miles, D.L. 1982 Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. *Geochimica et Cosmochimica Acta*, **46**, 2069-2081.
- Edmunds, W.M., Cook, J.M., Kinniburgh, D.G., Miles, D.L. and Trafford, J.M., 1989. Trace-element occurrence in British groundwaters. *Hydrogeological Research Series of the British Geological Survey*, SD/89/3.
- Edmunds, W.M., Shand, P., Hart, P. and Ward, R., 2003. The natural (baseline) quality of groundwater in England and Wales: UK pilot studies. *Science of the Total Environment*, **310** (1-3), 25-35.
- Falcon, N.L. and Kent, P.E., 1960. Geological results of petroleum exploration in Britain 1945-1957. *Memoirs of the Geological Society London*, **2**, 1-56.
- Gunn, J., 1992. Hydrogeological contrasts between British Carboniferous Limestone Aquifers. *International Contributions to Hydrogeology*, **13**, 25-41.

- Harrison, D.J., 1982. The limestone resources of The Craven Lowlands. *Description of parts of 1:50,000 geological sheets 59, 60, 61, 67, 68 and 69* / Enclosures: map: The limestone resources of the Craven Lowlands; Scale: 1:50 000. 116. British Geological Survey.
- Holliday, D.W., 1986. Devonian and Carboniferous Basins. In: R.A. Downing and D.A. Gray (Editors), *Geothermal Energy- The Potential in the United Kingdom*. British Geological Survey, 84-109
- Hope, R.C., 1893. *The Legendary Lore of the Holy Wells of England*, London. Retrieved January 12, 2005 from <http://www.antipope.org/feorag/wells/hope/lancashire.html>.
- JNCC, Joint Nature Conservation Committee, 2005. GCR database (n.d.). Retrieved January 8, 2005 from <http://www.jncc.gov.uk/earthheritage/gcrdb/GCRblock.asp>
- Jones, H.K., Morris, B.L., Cheney, C.S., Brewerton, L.J., Merrin, P.D., Lewis, M.A., MacDonald, A.M., Coleby, L.M., Talbot, J.C., McKenzie, A.A., Bird, M.J., Cunningham, J. and Robinson, V.K., 2000. *The physical properties of minor aquifers in England and Wales*. WD/00/4, British Geological Survey, Keyworth, Nottingham.
- Leeder, M.R., 1992. Dinantian. In: P.M.D. Duff and A.J. Smith (Editors). *Geology of England and Wales*. The Geological Society, London, 207-238.
- Longhurst, R.D., Roberts, A.H.C. and O'Connor, M.B., 2000. Farm dairy effluent: A review of published data on chemical and physical characteristics in New Zealand. *New Zealand Journal of Agricultural Research*, **43**, 7-14.
- Shand, P. and Frengstad 2001 Baseline groundwater quality: A comparison of selected British and Norwegian aquifers. *British Geological Survey Internal Report*, IR/01/177.
- Smith, D.I. and Atkinson, T.C., 1977. Underground flow in cavernous limestones with special reference to the Malham area. *Field Studies*, **4**, 597-616.

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