



**British  
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL



# Baseline Report Series: 18. The Millstone Grit of Northern England

Groundwater Systems and Water Quality  
Commissioned Report CR/05/015N

Science Group: Air, Land & Water  
Technical Report NC/99/74/18



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



BRITISH GEOLOGICAL SURVEY  
Commissioned Report CR/05/015N

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Sandstone of the Pendle Grit Formation in a 20 m face in a disused quarry [SD 6143 3796]

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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 ( $^3\text{H}$ ), 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 (Edmunds et al., 2003; Shand and Frengstad 2001). 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.



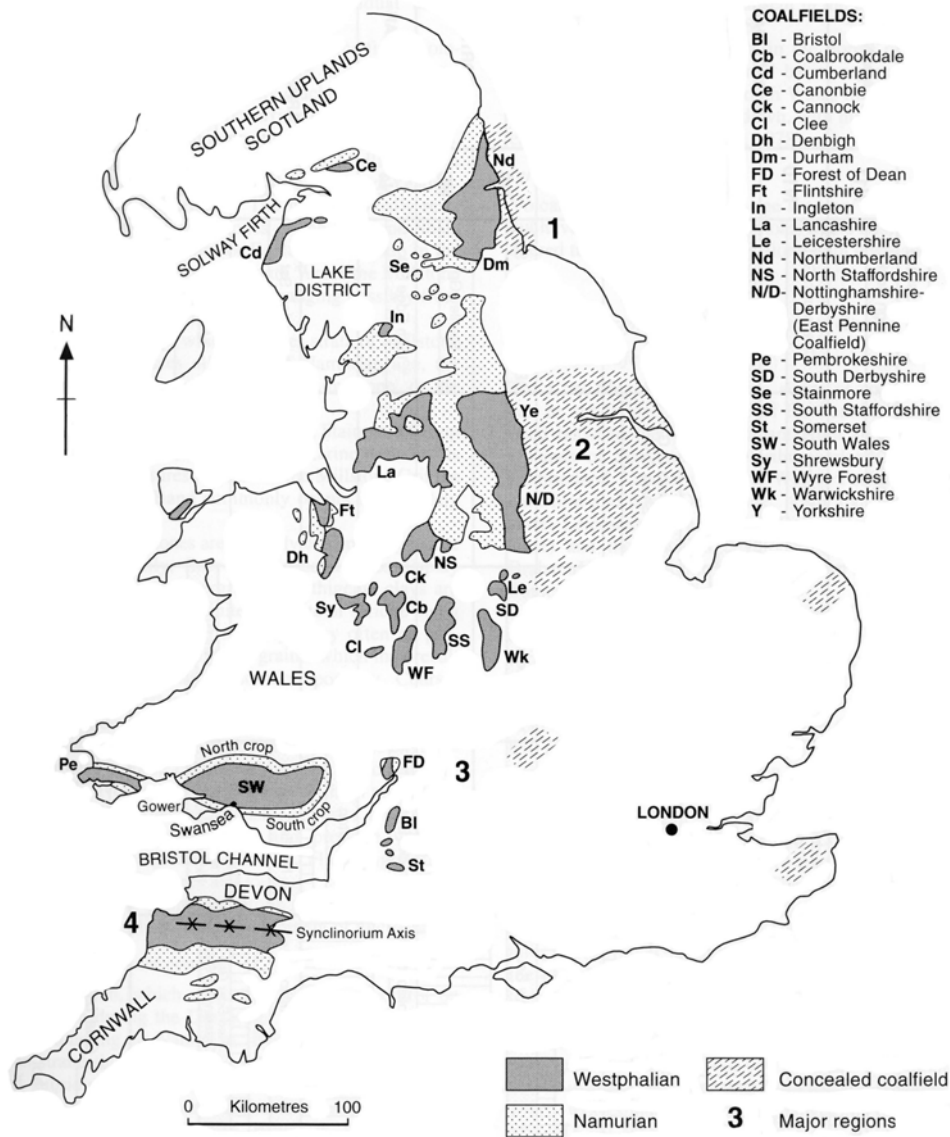
## 1. EXECUTIVE SUMMARY

The Millstone Grit of the Central Pennines of Yorkshire and Lancashire is an important local aquifer providing water for potable and industrial use. It forms a multilayered aquifer in which thick, massive sandstone horizons form discrete aquifers separated by intervening mudstones and shales. The geology and distribution of the drift deposits in the region are complex and this has had a pronounced effect on the baseline chemistry of the aquifer resulting in considerable spatial heterogeneity. Landuse in the area is predominantly managed grassland and there are subordinate urban and industrial areas in the study area.

The chemistry of the groundwaters is overwhelmingly controlled by natural reactions between the groundwater and the bedrock and reflects the presence or absence of carbonate cements in the aquifer. Some groundwaters have relatively low pH and alkalinity indicating a dominant control by silicate dissolution reactions. The redox conditions in the groundwater are variable. Where reducing environments are encountered, the natural baseline is influenced by the reductive solution of secondary Fe and Mn oxyhydroxides. Such groundwaters often maintain high levels of naturally derived Fe, Mn and associated trace metals, but are low in  $\text{NO}_3\text{-N}$  due to denitrification. The bedrock is naturally high in Ba and concentrations in excess of the EC Guide levels occur locally. Processes of ion exchange and mixing influence the baseline chemistry and have given rise to the formation of Na- $\text{HCO}_3$  and Ca-Cl-type waters. In some groundwaters, the source of high salinity and/or high sulphate remains unresolved, but mixing with formation waters and/or leakage from the younger Carboniferous Coal Measures deposits seem likely. The widespread occurrence of Ca- $\text{SO}_4$ -type waters, however, is probably due to the combined occurrence of pyrite oxidation and calcite dissolution in parts of the aquifer. Nitrate concentrations are generally low throughout the aquifer; partly due to denitrification, partly due to the protection of the aquifer provided by its multilayered nature as well as by the overlying drift. Although the aquifer is likely to have been impacted by anthropogenically-derived solutes (K, Na, Cl,  $\text{SO}_4$ ), these are generally within the natural range of concentrations found within the aquifer. The large spatial variability in the hydrogeochemistry of the aquifer, caused by its complex geology and by the distribution of drift deposits, make prediction of the baseline conditions difficult to assess on a local scale.

## 2. PERSPECTIVE

The Millstone Grit of Carboniferous age is not normally considered to represent a major aquifer, but is nevertheless an important local aquifer providing water for potable and industrial use. It outcrops mainly in the Central Pennines of Yorkshire and Lancashire, but extends as far south as the East Midlands, north Staffordshire and south and north-east Wales (Figure 2.1).



**Figure 2.1 Distribution of Millstone Grit (Namurian) deposits in the UK**

The study area for this report stretches between Grange-over-Sands in the NW and Burnley in the SE (Figure 2.2). In the north and west, the Millstone Grit is flanked by the Carboniferous Limestone Group which also appears as an inlier in the central part of the study area. The southern and western boundaries of the study area are formed by an outlier of Carboniferous Coal Measures Group and by Permian and Triassic Sandstones, respectively. This region forms the core area for evaluating the

regional baseline groundwater quality and selected groundwater data have been used to provide areal coverage.

The Millstone Grit forms a multilayered aquifer in which thick, massive sandstone horizons form discrete aquifers with the intervening mudstones and shales acting as aquicludes or aquitards. Glacial and postglacial deposits cover much of the study area, and where the deposits are clayey (till), they inhibit recharge to the aquifer.

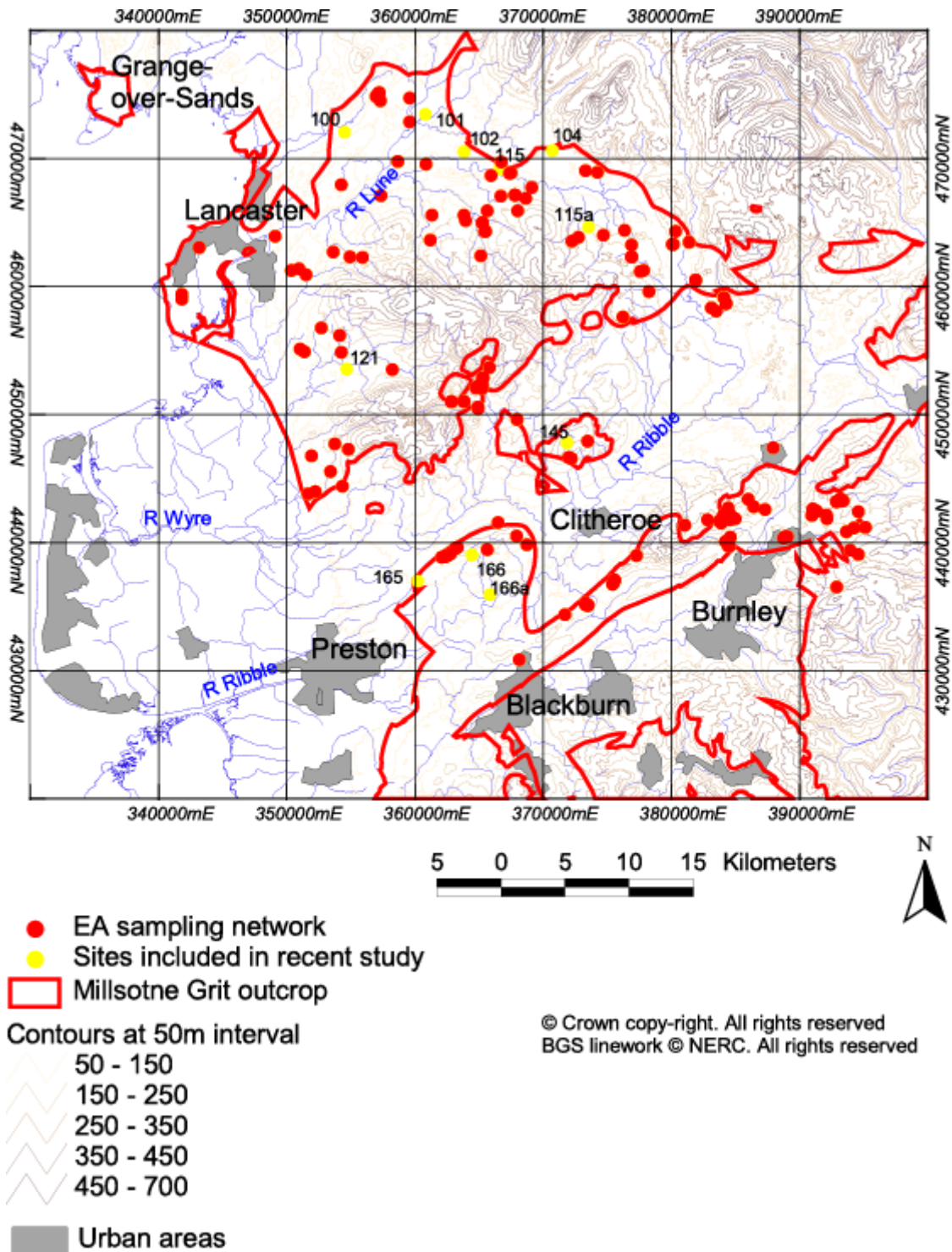


Figure 2.2 Topography and surface drainage of the study area

Surface drainage in the area is shown in Figure 2.2. 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 is immature and most upland rivers and streams are juvenile and are still cutting down to a lower base level through the drift and bedrock. (Brandon et al., 1998).

The dominant land use is managed grassland. The study area incorporates only a few urban and industrial areas.

Groundwater from the Millstone Grit sandstone aquifers is used for agricultural, industrial and domestic water supply. There are also a number of sources, both springs and boreholes, which are used for public water supply. Groundwater from the Millstone Grit aquifers also contributes significantly to the baseflow of surface waters.



### 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 (time) divisions Dinantian and Silesian (Table 3.1). The Carboniferous strata comprise a wide variety of rock types. Dinantian rocks range from deep basinal non-calcareous mudstones to thick massive shelf limestones, reef limestones and massive sandstones. In contrast, the Silesian rocks, which include the Millstone Grit Group, are generally clastic-rich, reflecting depositional environments including alluvial fans, deltas and deep marine basins (Jones et al., 2000).

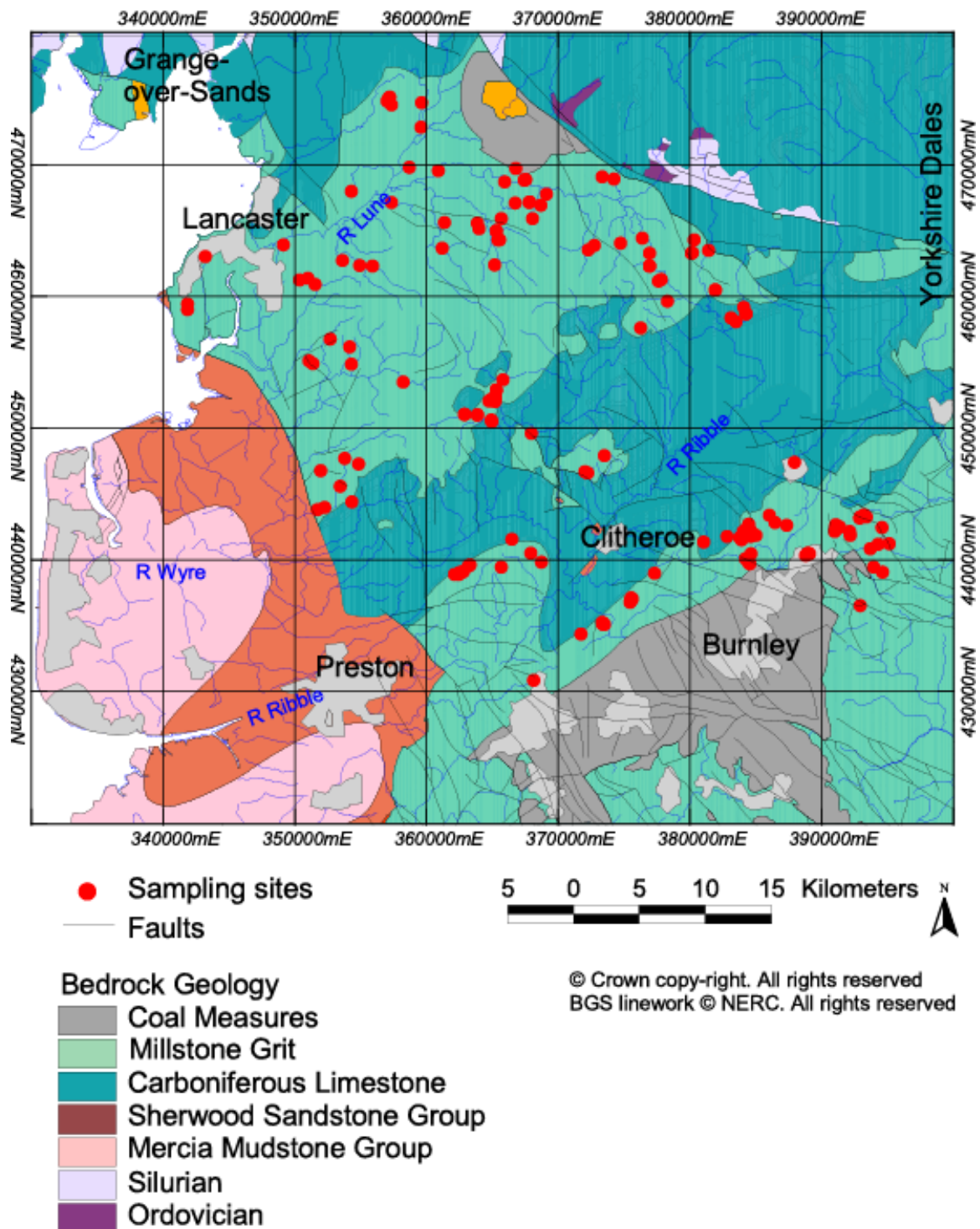
**Table 3.1 Subdivisions of the Carboniferous System (modified from Aitkenhead et al., 2002).**

Chronostratigraphy			Lithostratigraphy
Sub-System	Series	Stage	
Silesian	Westphalian	Westphalian D	WARWICKSHIRE GROUP COAL MEASURES MILLSTONE GRIT GROUP EDALE SHALE GROUP BOWLAND SHALE GROUP WENSLEYDALE GROUP CARBONIFEROUS LIMESTONE WORSTON SHALE GROUP
		Bolsovian (Westphalian C)	
Duckmantian (Westphalian B)			
Langsettian (Westphalian A)			
Dinantian	Namurian	Yeadonian	
		Marsdenian	
Dinantian	Visean	Brigantian	
		Asbian	
Dinantian	Tournasian	Holkerian	
		Arundian	
		Chadian	
		Courseyan	

In this study, the term ‘Millstone Grit’ is used to refer to the Namurian strata of the Millstone Grit facies (including the base of the Pendle Grit of the Pendelian stage); older Namurian strata of predominantly argillaceous strata (e.g., Namurian mudstone) being assigned to the Edale Group (Aitkenhead et al., 2002). The Millstone Grit crops out mainly in the Central Pennines of Yorkshire and Lancashire, but extends as far south as the East Midlands, north Staffordshire and south and north-east Wales.

The area of the present study is located in the Central Pennines of Yorkshire and Lancashire (Figures 2.2 and 3.1). The Millstone Grit is estimated to be up to 2100 m thick in Lancashire and 1800 m thick in West Yorkshire, but thins southwards to less than 200 m in the East Midlands and

north Wales. The base is taken as the first incoming of dominantly feldspathic sandstones and is markedly diachronous. The group typically rests conformably on thick mudstones of the Bowland Shale Group in the central Pennines or the Edale Shale Group in the south Pennines.



**Figure 3.1** Geology of the study area

The Millstone Grit Group comprises a sequence of sandstone units interbedded with argillaceous units. Individual sandstone members are variable in thickness and rarely exceed 30 m. Many of the sandstones have been given local names but may be regionally extensive and part of the same unit. The sandstone units of the Millstone Grit have been used for classification (Figure 3.2.). The Pendle

Grit Formation at the base of the Millstone Grit forms an important unit which varies from about 200 m to 475 m in the study area. Further classification is based on the cyclical nature of the sedimentary sequence, marked by the regular occurrence of marine bands (typically 0.5 to 3 m thick) that define the base of each cycle (Aitkenhead et al., 2002).

Namurian rocks conformably overlie Dinantian strata. The larger, northern outcrop of the Bowland Fells in the Lancaster-Settle area is surrounded by Dinantian outcrops of the Lake District High to the north, the Askrigg Block to the north-east and the Craven Basin to the south (Figure 3.1). In addition, there are a number of smaller outliers in the study area, which often form isolated hills within the Askrigg Block in the north-east and the Craven Basin in the south.

The source of sediment for the Millstone Grit, including coarse-grained and feldspathic pebbly sandstones, is from a granitic/gneiss terrain in the north, probably Scotland and Scandinavia as indicated by provenance studies and radiometric age determinations of zircons (Leeder, 1988; Drewery et al., 1987). There is no mineralogical evidence to suggest that there was a change in the source of the sediment during the Namurian (Brandon et al., 1998).

The study area was glaciated on several occasions during the Quaternary. As a result, much of the area is covered with extensive spreads of drift material of glacial and postglacial origin (Figure 3.3). During glacial advance, extensive glacial till deposits were laid down over large parts of the area, predominantly on the lower grounds 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 gravely 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 of up to boulder size. The till deposits of the lower grounds are commonly covered by postglacial, glaciofluvial sands and gravels (Brandon et al., 1998).

### *3.2.1 Structural settings and depositional controls*

The early Namurian platforms of northern England inherited their basic structural settings of blocks (structural highs e.g., the Askrigg Block and the Lake District Massif), and intervening grabens and half-grabens (basins e.g. the Craven Basin) during the Dinantian period. During the Namurian, the dominating 'rift' subsidence of the Dinantian time gradually gave way to the regional and essentially thermally driven ('sag') subsidence (Kelling and Collinson, 1992) and the definition of the Craven Basin became increasingly weak, both in terms of its bounding structures and its sedimentary infill (Arthurson et al., 1988) (Figure 3.4). The development of a broad subsiding 'sag' basin, the Pennine Basin, became the primary tectonic control on sedimentation and strata thickness during that period. Greatest subsidence rates and hence thicknesses occurred in the areas around Lancaster and North Staffordshire (Aitkenhead et al., 2002; Jones et al., 2000), although more localised thickness variations are often found. These can largely be attributed to infilling of residual topography and differential compaction (Aitkenhead et al., 2002) as well as to continued structural activity (Jones et al., 2000) and differential subsidence of the underlying blocks and basins (Arthurson et al., 1988).

During the latest Carboniferous times, and associated with the final closure of the Rheic Ocean and continent-continent collision in the far south, northern England was subjected to a major uplift as Variscian crustal compression initiated the process of basin inversion. As part of that movement, inversion of pre-existing Dinantian extensional faults occurred, accompanied by folding and erosion

of the Carboniferous strata. Evidence for the late-Namurian tectonics can be seen in the structure of the Ribblesdale Fold Belt, situated in the north-east of the study area.

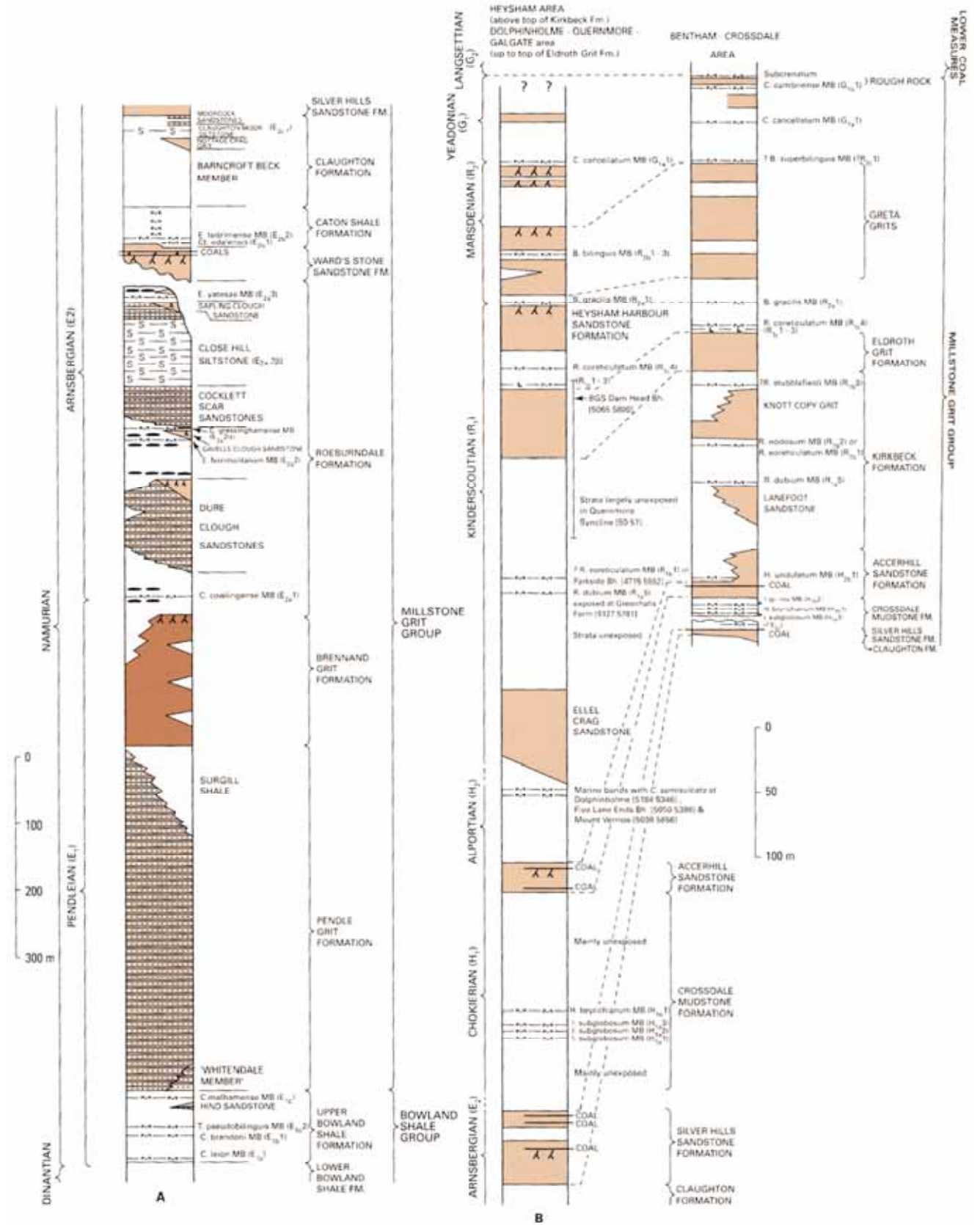


Figure 3.2 Generalised stratigraphy of the Millstone Grit in the study region



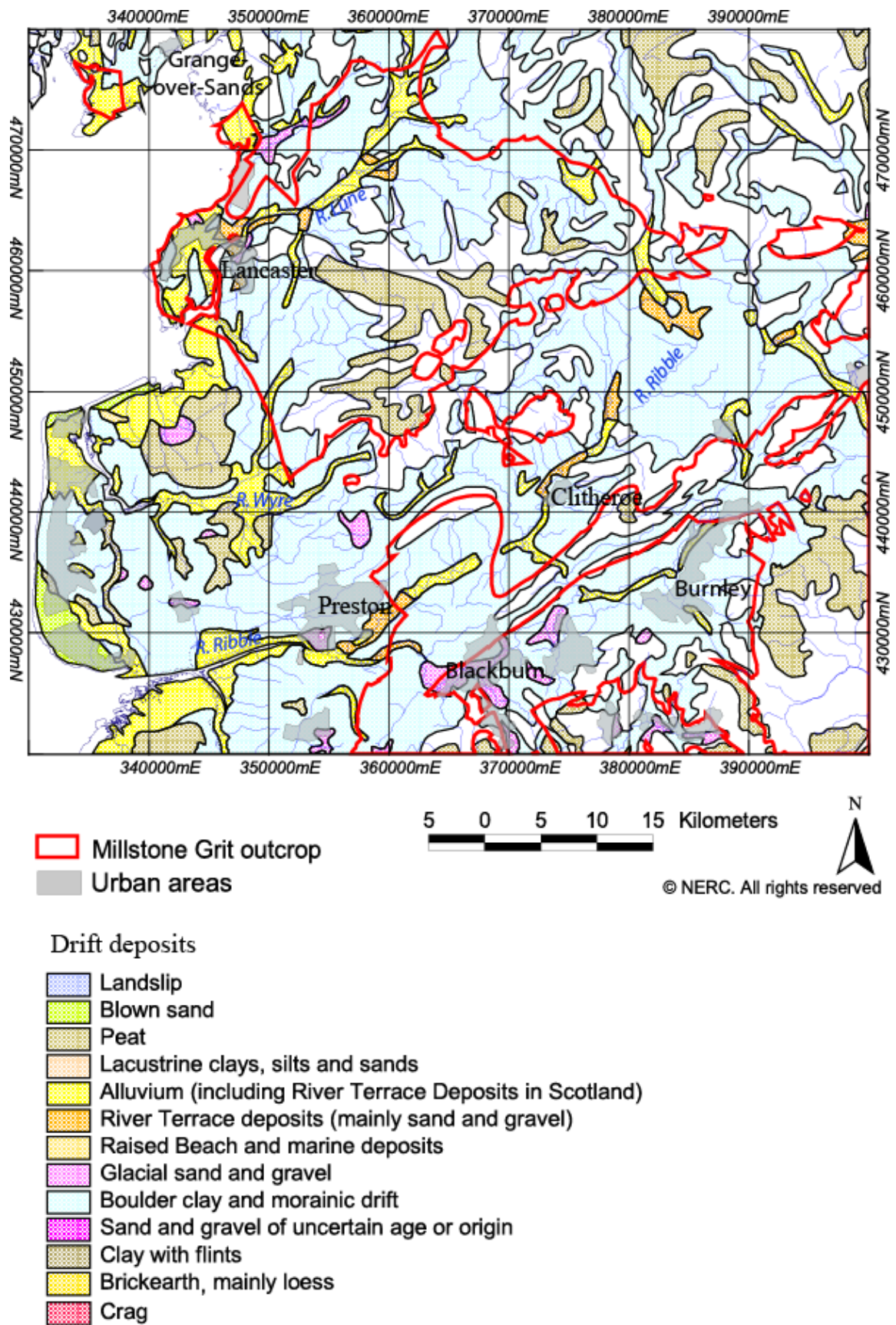
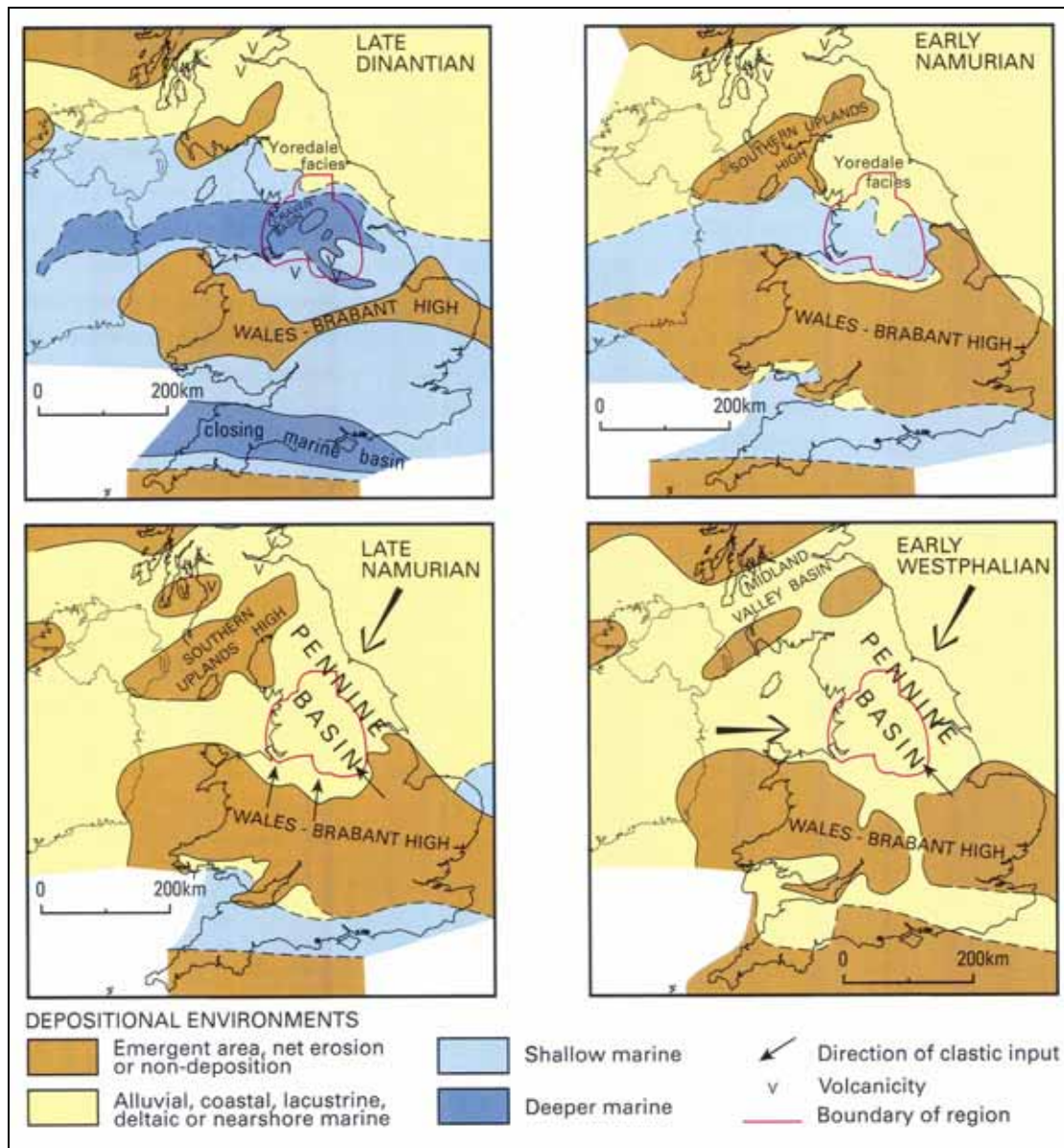


Figure 3.3 Distribution of drift deposits in the study area

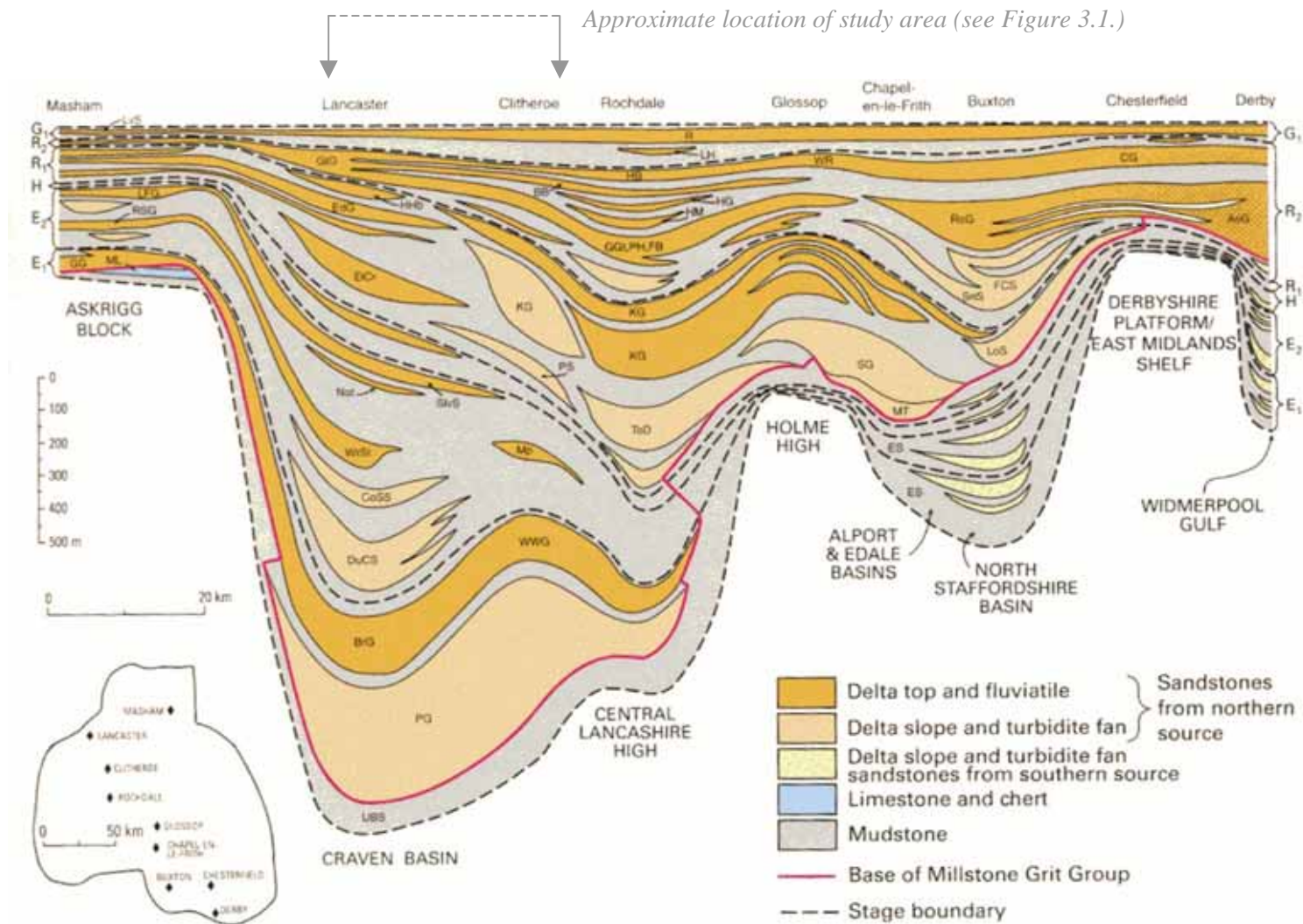


**Figure 3.4 Palaeogeography and depositional environments of the study region (and surrounding areas) from the late Dinantian to early Westphalian (from Aitkenhead et al., 2002)**

### 3.2.2 Sedimentary environment

Throughout the Namurian, sedimentation in Northern England was dominated by intermittently southwards-prograding delta systems, fed by large river systems that drained tectonically active, rapidly eroded mountains in the north (Scandinavia, Greenland) (Aitkenhead et al., 2002). Initially, deltaic conditions were restricted to the Askrigg Block, but during late Pendeleian/Marsdian time, reached the Craven Basin, filling it with deltaic sediments. Periods of deltaic propagation, recorded by sequences of sandstones, were intermittent with periods of delta abandonment and transgression, recorded by thin bands of marine mudstone that abruptly overlie the coarsening upwards sandstone sequences. The intermittent character of delta propagation was primarily due to sea level fluctuations, and the regular occurrence of these marine bands is used to classify the Namurian succession.





**Figure 3.5** Schematic cross section of the region showing the main Namurian Sandstone units and stage boundaries (Aitkenhead et al., 2002). The inset map shows the centre points and names of BGS 1:50,000 sheets, the generalised vertical sections of which were used to construct this cross section.

There are dramatic local and regional variations in the thickness of the Millstone Grit (Figure 3.5). It is estimated to be up to 2100m thick in the Lancashire area, thinning southwards to less than 200m in the East Midlands and north-east Wales. Likewise, individual sandstone members and units of the Millstone Grit are also variable. The important Pendle Grit formation, for example, varies in thickness from 200m to 475m, and is completely absent in the south (Jones et al., 2000).

### 3.3 Hydrogeology

The Millstone Grit forms a multilayered aquifer system in which the persistent, thick sandstone horizons effectively act as separate aquifers with the intervening mudstones and shales acting as aquicludes or aquitards. The more important aquifer units include the Pendle, Wosley Wise, Todmorton, Kinderscout, Chatsworth, Ashover, and Middle Grits, the Rough Rocks and their lateral equivalents.

The sandstones are generally well cemented and groundwater storage and transport is restricted largely to joints and fractures. Flow in the aquifer tends to decrease rapidly with depth as soft and decalcified sandstones of the weathering zone pass into well-cemented, hard and compact bedrock. The relatively low porosity (6-23%, median: 14%) and permeability ( $3 \times 10^{-4} - 0.7 \text{ m d}^{-1}$ , median:  $4 \times 10^{-2} \text{ m d}^{-1}$ ) (BGS Aquifer Properties database) of the sandstone matrix suggest only minor contributions from intergranular flow.

A number of perched water tables occur in the multi-layered aquifer system. Some boreholes are artesian. Abundant springs are located at the base of the sandstone layers and at junctions between shale and sandstone horizons, some of which are used for public supply (Jones et al., 2000). The groundwater potential of the water-bearing horizons, however, is very variable. Borehole yields vary but tend to be greatest in the north and central part of the area, reducing southwards due to thinning of a number of the water-bearing horizons. Borehole yields are also dependent on the number and size of fractures encountered in a productive horizon, and many boreholes penetrate more than one aquifer unit. Commonly, borehole yields between  $432 - 864 \text{ m}^3 \text{ day}^{-1}$  (5 to 10 l sec<sup>-1</sup>) can be expected within the Millstone Grit (Aitkenhead et al., 2002; Jones et al., 2000). At several locations, significantly higher yields have been obtained, mainly from larger diameter boreholes, producing up to  $4320 \text{ m}^3 \text{ day}^{-1}$  in the Pendle Grit at Foot Holme. Significant yields of  $1380 \text{ m}^3 \text{ day}^{-1}$  and  $1296 \text{ m}^3 \text{ day}^{-1}$  were also obtained at Lancaster and along the Whitendale River (Brandon et al., 1998). However, initial yields are not always sustainable, and reductions in transmissivity and yield with time have been reported in a number of boreholes where unconfined storage was depleted by pumping (Jones et al., 2000).

It is pertinent, within the context of baseline chemistry, to note that aquifer development by boreholes could affect the groundwater chemistry in the area, as variations in the saturated aquifer thickness may promote mineral oxidation in usually saturated sediments and intensive abstraction may also change recharge and flow pathways.

Groundwater from the Millstone Grit is generally potable. Soft water of calcium-bicarbonate type is common in confined horizons, but at considerable depths (below the Coal Measures), groundwater is often saline. Elevated concentrations of iron ( $2 \text{ mg l}^{-1}$ ) and more rarely manganese ( $1.8 \text{ mg l}^{-1}$ ) are locally present (Brandon et al., 1998), indicating reducing conditions in some areas of the aquifer.

Little is known in detail about the properties of the mudstones and shales which form a significant proportion of the Millstone Grit. The intergranular hydraulic conductivity is considered to be less than  $0.1 \text{ m d}^{-1}$  (Wagstaff, 1991). These units are also fractured which may allow for groundwater movement between sandstone units.



Since groundwater movement in the aquifer is primarily by fracture flow, directions of groundwater flow are difficult to establish and, as tracer tests have illustrated (Townsend and Aldridge, 1996), cannot be inferred from water level data.

### **3.4 Aquifer mineralogy**

Coarse-grained to granular, feldspathic sandstones are the dominant and characteristic component of the Millstone Grit Group (Figure 3.6). Most of the sandstones have broadly similar detrital compositions and diagenetic mineralogy (Brandon et al., 1998). The dominant minerals throughout the sequence include unstrained quartz and K-feldspar with less abundant albite and mica, suggesting derivation from the same acid igneous or gneissic terrain throughout the Namurian. The sandstones are, therefore, classed as quartz arenites and subarkoses. Opaque minerals comprise secondary iron oxides and carbonaceous material.

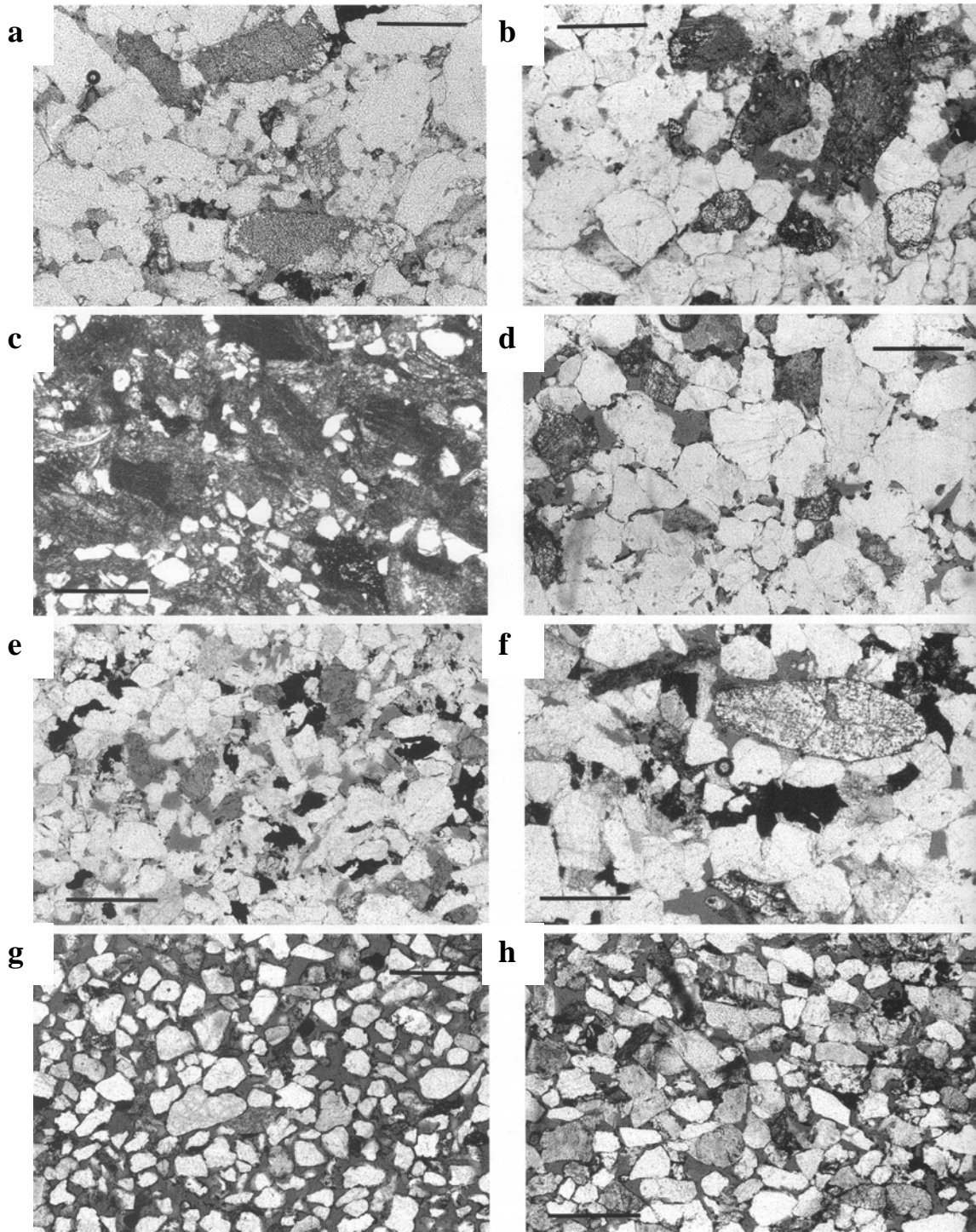
The sandstones in the Millstone Grit vary in feldspar content and grain size distribution. They are typically quartz arenites and subarkoses composed of detrital quartz and potassium feldspar, with minor plagioclase and mica contents. Secondary iron oxides occur as pore linings and pore fillings and may replace ferro-magnesian grains such as biotite. The intervening marine bands are typically 0.5-3.0 m thick and comprise dark grey to black calcareous shaly mudstone, which contains crushed fossilised shells (Aitkenhead et al., 2002) and have been used as marker bands to determine their position in the stratigraphy of the region.

The sandstones have been classified into two groups (Strong, 1991) based on their diagenetic mineral assemblage: a quartz-kaolinite and a carbonate assemblage. Most sandstones in the study area belong to the quartz kaolinite group with the carbonate group being characteristic of sandstones in the Roeburndale (Arnsbergian) and Kirkbeck (Kinderscoutian) Formations (Brandon et al., 1998). The quartz kaolinite group is characterised by quartz overgrowths and cements often associated with later pore-filling kaolinite. The clays, mostly kaolinite and illite or sericite, may often be derived from feldspar weathering, which may result in the development of secondary (grain dissolution) porosity. The carbonate group contains carbonate cements including calcite, ferroan calcite and to a lesser degree, siderite. It has been suggested that the calcite cements represent the influence of marine pore fluids associated with ephemeral marine transgressions (Brandon et al., 1998).

A quantitative study of 38 Millstone Grit sandstones in the Lancaster Area (Brandon et al., 1998) has shown that detrital heavy mineral suites in the Millstone Grit contain variable amounts of eight stable translucent mineral species. The most abundant minerals are zircon, tourmaline and rutile, while monazite is a minor component. There is considerable variation in the abundance of apatite and garnet, the former being depleted or absent in the lower parts of the formation, probably due to percolation of acidic groundwaters. Anatase is present as an accessory mineral in most samples, and rare chrome spinels were occasionally recorded. The low diversity of the heavy metal suite indicates that there has been extensive dissolution of unstable minerals.

### **3.5 Rainfall chemistry**

The local rainfall chemistry, corrected for evapotranspiration effects is the primary input to the baseline groundwater 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.



**Figure 3.6** Photomicrographs of Millstone Grit (a-f) and Permo-Triassic Sandstones (g-h). (a) Pendle Grit Formation, (b) Brennand Grit Formation, (c) Cocklett Scar Sandstone, (d) Ward's Stone Sandstone Formation, (e) Eldroth Grit Formation, (f) Heysham Harbour Sandstone Formation, (g) Collyhurst Sandstone Formation and (h) Sherwood Sandstone Group (Brandon et al., 1998).

Table 3.2 shows the precipitation-weighted annual means (averaged for 1996-2000) of the major-element composition of rainfall from the Cow Green Reservoir monitoring site [BNG 38170 52980], 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 does not account for additional factors such as direct runoff or utilization of rainwater by vegetation and soil processes, but it 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 groundwaters in the region can be assessed.

**Table 3.2 Rainfall chemistry for Cow Green Reservoir rainfall monitoring site (NY 817298). 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		Concentrated Rainfall (x3)- Enrichment by evapotranspiration
Parameter	Rainfall	
pH	4.82	
Na (mg l <sup>-1</sup> )	2.00	6.00
K (mg l <sup>-1</sup> )	0.09	0.26
Mg (mg l <sup>-1</sup> )	0.32	0.96
Ca (mg l <sup>-1</sup> )	0.29	0.88
Cl (mg l <sup>-1</sup> )	3.55	10.65
SO <sub>4</sub> (mg l <sup>-1</sup> )	1.67	5.01
NO <sub>3</sub> -N (mg l <sup>-1</sup> )	0.41	1.23
NH <sub>4</sub> -N (mg l <sup>-1</sup> )	0.09	0.28
SEC (µS cm <sup>-1</sup> )	25.6	76.8
Rainfall amount (mm/y)	1172	

The relatively high concentrations of Na, Cl and SO<sub>4</sub> 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 in recharge waters may be largely rainfall derived. Hence, background concentrations expected at present day should be in the order of 11 mg l<sup>-1</sup> Cl. Likewise, 6 mg l<sup>-1</sup> Na and 6 mg l<sup>-1</sup> SO<sub>4</sub> 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 of NO<sub>x</sub>. Modern baseline concentrations of total nitrogen (NO<sub>3</sub>-N plus NH<sub>4</sub>-N) can be expected to be around 1.5 mg l<sup>-1</sup>, although ‘concentrated’ rainfall of pre-industrial age recharged to the aquifer would have been less.

The pH of the rainfall is acidic (4.82), although weakly buffered, reflecting the effects of other atmospheric pollutants (SO<sub>2</sub>, NO<sub>3</sub>) in addition to that produced in equilibrium with atmospheric CO<sub>2</sub>. Equilibration of the acidic waters with the bedrock will be established in contact with the sandstone aquifer, primarily through mineral dissolution reactions, with resulting increases in pH and solute concentrations. However, the degree of pH buffering of the groundwater may vary greatly throughout the aquifer, depending on the development of carbonate cements in the bedrock material and the presence of marine mudstone layers.

### 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 (Figures 3.7 and 3.8). The area incorporates only a few urban and industrial areas including Lancaster in the west, Settle in the east and Clitheroe and Colne in the south. Adjoining the study area in the south lays the industrial area of Preston, Blackburn and Burnley.

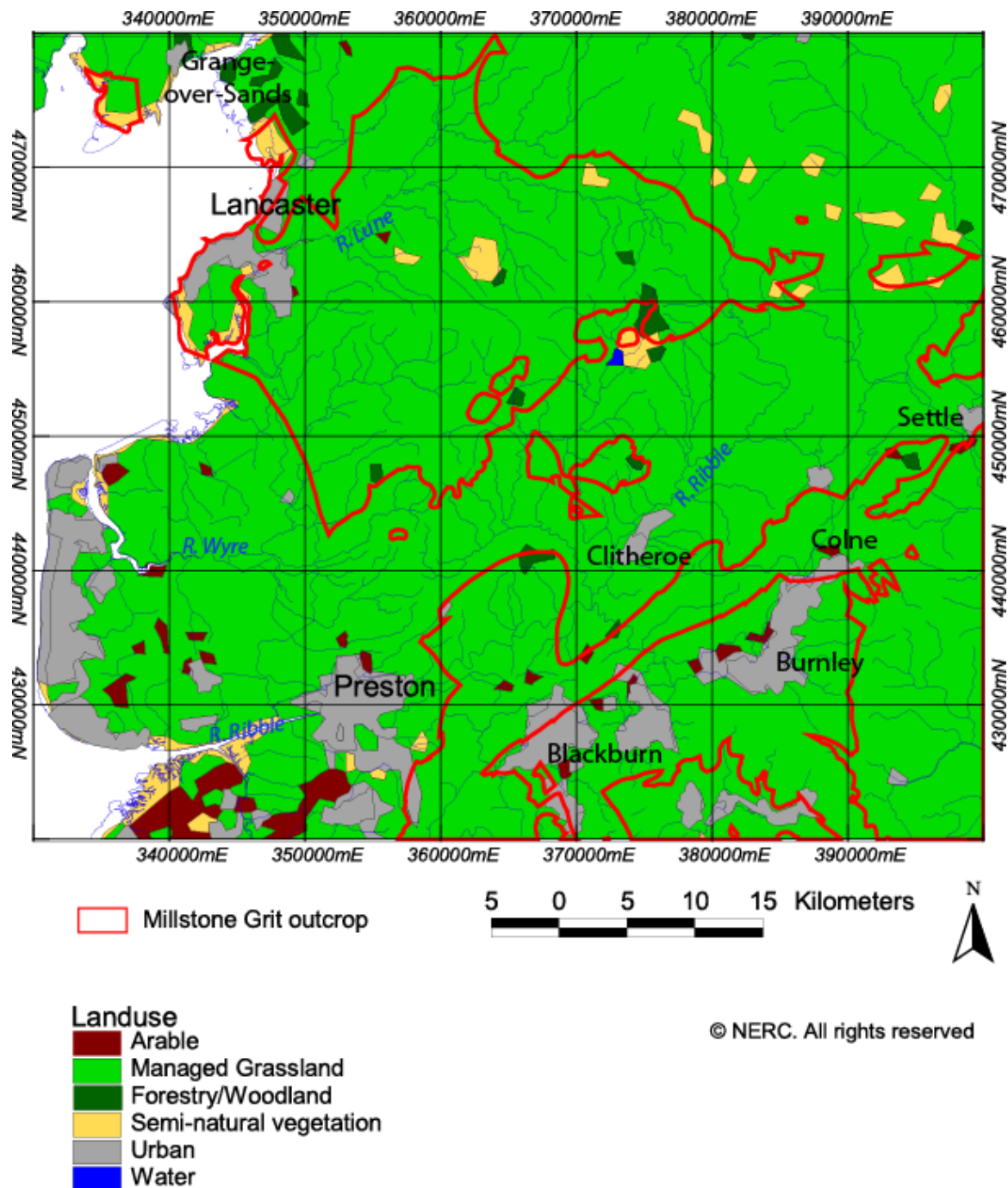


Figure 3.7 Distribution of different landuse types throughout the study area



**Figure 3.8** Managed grassland and sheep grazing are widespread throughout the study area.



## 4. DATA AND INTERPRETATION

### 4.1 Project sampling programme

A total of 23 samples were collected by BGS in December 2003 from natural springs, industrial and farm boreholes in the study area. The sites form part of the Environment Agency's groundwater monitoring network and could, therefore, be compared with previous analysis. 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 HNO<sub>3</sub> to prevent metal precipitation and to minimise adsorption onto container walls. Samples for dissolved organic carbon (DOC) were filtered through a 0.45µm 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  $\delta^{13}\text{C}$ ).



**Figure 4.1** Collecting samples from spring site [SD 384050 459140]

Ideally, samples were collected from permanently pumped boreholes and/or after a minimum pumping of an estimated two well bore volumes, prior to sampling. However, where this was not possible due to the great borehole volume (e.g., at the Growing with Grace Nursery [NGR 37420 46890], samples were collected after on-site readings of temperature, SEC, pH, DO and Eh had stabilised. Efforts were made to sample groundwater as close to the discharge as possible. Sampling

from storage tanks was generally avoided unless a representative sample of groundwater was considered to be obtainable.

Analysis of major cations and sulphate by ICP AES and analysis of anion species (Cl, Br, I, F) by automated colorimetry was carried out by the BGS laboratory in Wallingford. A wide range of trace elements was analysed by ICP MS in the Acme laboratory, Canada. Nitrogen species analysis was carried out by the EA laboratories in Nottingham. Stable isotopes analyses were also completed in the BGS laboratories using mass spectrometry and the results are reported as ‰ deviation relative to SMOW for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  and PDB for  $\delta^{13}\text{C}$ .

## **4.2 Historical data**

Historical water quality data from the EA 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 in the area, analyses from 160 different locations collected between 1962 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 EA laboratories are 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. Here 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 flow path.

In the case of spring sampling, contact with the atmosphere prior to sampling could often not 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.

## **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 1962 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 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.



## 5. HYDROCHEMICAL CHARACTERISTICS

### 5.1 Introduction

This section presents a description of the fundamental characteristics of the groundwaters in the Millstone Grit aquifer. A summary of the data are given in Tables 5.1 and 5.2 for the major and trace elements respectively. The tables show the ranges and averages of data as well as an upper concentration (defined as mean +  $2\sigma$  or 97.7<sup>th</sup> 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.

### 5.2 Water types and physicochemical characteristics

The groundwaters in the Millstone Grit Aquifer of the study area display a wide range of physicochemical characteristics and element concentrations (Table 5.1). The waters are generally weakly mineralised (median of  $402 \mu\text{S cm}^{-1}$ ), although SEC values up to  $3870 \mu\text{S cm}^{-1}$  were measured.

**Table 5.1 Field parameters, isotope data and range of major and minor element concentrations in the Millstone Grit Aquifer**

		min	max	median	mean	97.70%	N
<b>T</b>	°C	6.2	20.0	9.4	9.9	16.0	66
<b>pH</b>	field	4.70	8.50	7.03	6.94	8.07	178
<b>Eh</b>	mV	160	491	345	343	484	23
<b>DO</b>	mg l <sup>-1</sup>	0.0	13.9	5.9	5.8	11.7	42
<b>SEC</b>	$\mu\text{S cm}^{-1}$	47	3870	407	496	754	38
<b><math>\delta^2\text{H}</math></b>	‰	-7.7	-6.6	-7.1	-7.2	-6.7	10
<b><math>\delta^{18}\text{O}</math></b>	‰	-48.2	-39.2	-43.8	-44.1	-40.1	10
<b><math>\delta^{13}\text{C}</math></b>	‰	-23.1	-13.7	-17.9	-18.1	-13.7	10
<b>Ca</b>	mg l <sup>-1</sup>	0.7	322.0	33.5	39.0	90.8	174
<b>Mg</b>	mg l <sup>-1</sup>	<0.5	143.0	7.4	10.0	24.6	173
<b>Na</b>	mg l <sup>-1</sup>	4.4	745.0	11.0	28.2	136.6	171
<b>K</b>	mg l <sup>-1</sup>	<1	14.8	1.9	2.8	8.8	171
<b>Cl</b>	mg l <sup>-1</sup>	<10	1290.0	13.0	28.4	70.5	176
<b>SO<sub>4</sub></b>	mg l <sup>-1</sup>	<5	259.0	15.3	19.2	50.4	172
<b>HCO<sub>3</sub></b>	mg l <sup>-1</sup>	<10	670	163	175	455	183
<b>NO<sub>3</sub> as N</b>	mg l <sup>-1</sup>	<1	12.5	<1	1.2	5.6	179
<b>NO<sub>2</sub> as N</b>	mg l <sup>-1</sup>	<0.02	0.08	<0.02	<0.02	0.04	176
<b>NH<sub>4</sub> as N</b>	mg l <sup>-1</sup>	<0.05	2.23	<0.05	0.15	0.73	180
<b>P</b>	mg l <sup>-1</sup>	<0.02	0.05	<0.02	<0.02	0.05	23
<b>DOC</b>	mg l <sup>-1</sup>	<0.1	4.9	0.8	1.0	3.3	38
<b>F</b>	mg l <sup>-1</sup>	<100	928.0	120.0	176.3	628.3	71
<b>Br</b>	mg l <sup>-1</sup>	<50	4590.00	50.50	121.32	285.26	72
<b>I</b>	$\mu\text{g l}^{-1}$	0.5	20.6	2.3	4.1	16.1	23
<b>Si</b>	mg l <sup>-1</sup>	1.1	17.7	5.4	6.0	11.7	166

**Table 5.2 Trace element concentrations in the Millstone Grit Aquifer**

		<b>min</b>	<b>max</b>	<b>median</b>	<b>mean</b>	<b>97.70%</b>	<b>N</b>
<b>Ag</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Al</b>	µg l <sup>-1</sup>	<1	3	1	<1	2	23
<b>As</b>	µg l <sup>-1</sup>	<0.5	0.9	<0.5	<0.5	0.8	23
<b>Au</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>B</b>	µg l <sup>-1</sup>	<20	258	29	83	257	23
<b>Ba</b>	µg l <sup>-1</sup>	10.36	2967.57	119.14	395.60	2920.49	23
<b>Be</b>	µg l <sup>-1</sup>	<0.05	0.06	<0.05	<0.05	<0.05	23
<b>Bi</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Cd</b>	µg l <sup>-1</sup>	<0.05	0.20	<0.05	<0.05	0.14	23
<b>Ce</b>	µg l <sup>-1</sup>	<0.01	0.02	<0.01	<0.01	<0.01	23
<b>Co</b>	µg l <sup>-1</sup>	<0.02	1.07	<0.02	<0.02	0.56	23
<b>Cr</b>	µg l <sup>-1</sup>	<0.5	0.5	<0.5	<0.5	<0.5	23
<b>Cs</b>	µg l <sup>-1</sup>	<0.01	0.33	<0.01	<0.01	0.30	23
<b>Cu</b>	µg l <sup>-1</sup>	<0.1	176.10	1.60	16.35	117.23	23
<b>Dy</b>	µg l <sup>-1</sup>	<0.1	0.03	<0.1	<0.1	0.02	23
<b>Er</b>	µg l <sup>-1</sup>	<0.1	0.05	<0.1	<0.1	0.04	23
<b>Eu</b>	µg l <sup>-1</sup>	<0.1	0.06	<0.1	<0.1	0.03	23
<b>Fe</b>	µg l <sup>-1</sup>	<5	2460	25	229	1353	23
<b>Ga</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Gd</b>	µg l <sup>-1</sup>	<0.01	0.05	<0.01	<0.01	0.02	23
<b>Ge</b>	µg l <sup>-1</sup>	<0.05	0.68	<0.05	0.12	0.63	23
<b>Hf</b>	µg l <sup>-1</sup>	<0.02	<0.02	<0.02	<0.02	<0.02	23
<b>Hg</b>	µg l <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	<0.1	23
<b>Ho</b>	µg l <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	<0.1	23
<b>In</b>	µg l <sup>-1</sup>	<0.1	<0.1	<0.1	<0.1	<0.1	23
<b>Ir</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>La</b>	µg l <sup>-1</sup>	<0.01	0.08	<0.01	<0.01	0.05	23
<b>Li</b>	µg l <sup>-1</sup>	0.1	63.6	9.3	18.1	60.8	23
<b>Lu</b>	µg l <sup>-1</sup>	<0.01	0.01	<0.01	<0.01	<0.01	23
<b>Mn</b>	µg l <sup>-1</sup>	<2	524	12	92	483	23
<b>Mo</b>	µg l <sup>-1</sup>	<0.1	13.0	<0.1	0.7	5.3	23
<b>Nb</b>	µg l <sup>-1</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	23
<b>Nd</b>	µg l <sup>-1</sup>	<0.01	0.20	<0.01	0.02	0.09	23
<b>Ni</b>	µg l <sup>-1</sup>	<0.2	2.2	<0.2	0.3	1.2	23
<b>Os</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Pb</b>	µg l <sup>-1</sup>	<0.1	0.4	0.1	0.1	0.4	23
<b>Pd</b>	µg l <sup>-1</sup>	<0.2	<0.2	<0.2	<0.2	<0.2	23
<b>Pr</b>	µg l <sup>-1</sup>	<0.01	0.03	<0.01	<0.01	0.02	23
<b>Pt</b>	µg l <sup>-1</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	23
<b>Rb</b>	µg l <sup>-1</sup>	0.20	13.81	2.15	3.97	13.32	23
<b>Re</b>	µg l <sup>-1</sup>	<0.01	0.02	<0.01	<0.01	<0.01	23
<b>Rh</b>	µg l <sup>-1</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	23
<b>Ru</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Sb</b>	µg l <sup>-1</sup>	<0.05	0.23	<0.05	<0.05	0.17	23
<b>Sc</b>	µg l <sup>-1</sup>	<1	1	<1	<1	<1	23
<b>Se</b>	µg l <sup>-1</sup>	<0.5	1.9	<0.5	0.5	1.7	23

		<b>min</b>	<b>max</b>	<b>median</b>	<b>mean</b>	<b>97.70%</b>	<b>N</b>
<b>Sm</b>	µg l <sup>-1</sup>	<0.02	0.04	<0.02	<0.02	<0.02	23
<b>Sn</b>	µg l <sup>-1</sup>	<0.05	0.10	0.07	0.07	0.09	23
<b>Sr</b>	µg l <sup>-1</sup>	22	1061	148	249	760	23
<b>Ta</b>	µg l <sup>-1</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	23
<b>Tb</b>	µg l <sup>-1</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	23
<b>Te</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Th</b>	µg l <sup>-1</sup>	<0.05	<0.05	<0.05	<0.05	<0.05	23
<b>Ti</b>	µg l <sup>-1</sup>	<10	<10	<10	<10	<10	23
<b>Tl</b>	µg l <sup>-1</sup>	<0.01	0.10	<0.01	<0.01	<0.01	23
<b>Tm</b>	µg l <sup>-1</sup>	<0.01	<0.01	<0.01	<0.01	<0.01	23
<b>U</b>	µg l <sup>-1</sup>	<0.02	1.87	0.03	0.21	1.09	23
<b>V</b>	µg l <sup>-1</sup>	<0.2	0.3	<0.2	<0.2	0.2	23
<b>W</b>	µg l <sup>-1</sup>	<0.2	0.03	<0.2	<0.2	<0.2	23
<b>Y</b>	µg l <sup>-1</sup>	0.01	0.35	0.03	0.05	0.29	23
<b>Yb</b>	µg l <sup>-1</sup>	0.01	0.08	0.01	0.01	0.05	23
<b>Zn</b>	µg l <sup>-1</sup>	1.6	103.7	16.1	25.38	97.63	23
<b>Zr</b>	µg l <sup>-1</sup>	<0.02	<0.02	<0.02	<0.02	<0.02	23

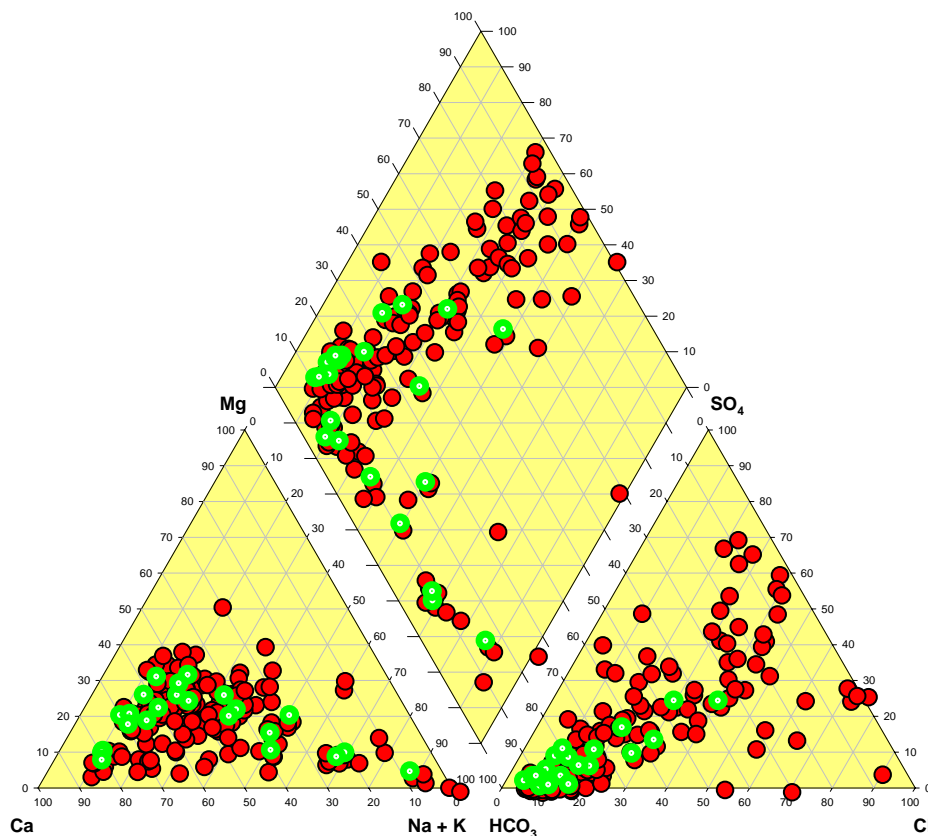
The waters are generally well buffered at circumneutral pH (median 7.0) but more acidic waters (pH<5) occur locally. Groundwater temperatures average around 10°C (median 9.4 °C), the low and high values of 6.2°C and 20°C being due to the influence of air temperature at sites where samples were collected 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 345 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 Millstone Grit aquifer are mainly of Ca-HCO<sub>3</sub> and mixed Ca-Na- HCO<sub>3</sub>-Cl-SO<sub>4</sub> type waters. There is also a trend for some samples towards Na-HCO<sub>3</sub> type.

The samples collected during the present sampling campaign, represented as green dots in the Piper plot (Figure 5.1), show much less variation than those compiled for the whole area, in general waters with SO<sub>4</sub> or Cl as the dominant anion are not represented.

### 5.3 Major elements

The summary data are given in Table 5.1 and 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 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 grey 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 identifying pollution. Geochemical processes may alter the distribution of populations in several different ways (Box 5.1).



**Figure 5.1** PIPER Plot showing the relative concentrations of major cations and anions in the Millstone Grit aquifer. Green dots represent the samples collected during recent (December 2003) sampling campaign.

The median Cl concentration of  $12.5 \text{ mg l}^{-1}$  is close to that estimated for bulk precipitation (including the effects of evapotranspiration) in the region (Table 3.2). High Cl concentrations occur locally within the study area, indicating that Cl sources additional to that of rainfall are present within the aquifer. The high Cl concentrations coincide with high Na concentrations. The positive skew of cumulative frequency curves of Cl and Na suggest that mixing with saline and/or pollution sources may be important. Most other major elements occupy an intermediate range of concentrations and enrichment relative to Cl indicates that extensive water-rock interactions occur.

Bicarbonate shows relatively large variations 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  $\text{HCO}_3$  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, but is less apparent for Mg, although a dolomite solubility control would be expected. Nitrate and DOC show relatively wide concentration ranges, which on the cumulative frequency plot display trends that tend to approach linearity. Several elements (Ca-Na- $\text{SO}_4$ -Mg-Cl) show a population shift at or above the 95<sup>th</sup> percentile, indicating mixing between at least two populations.

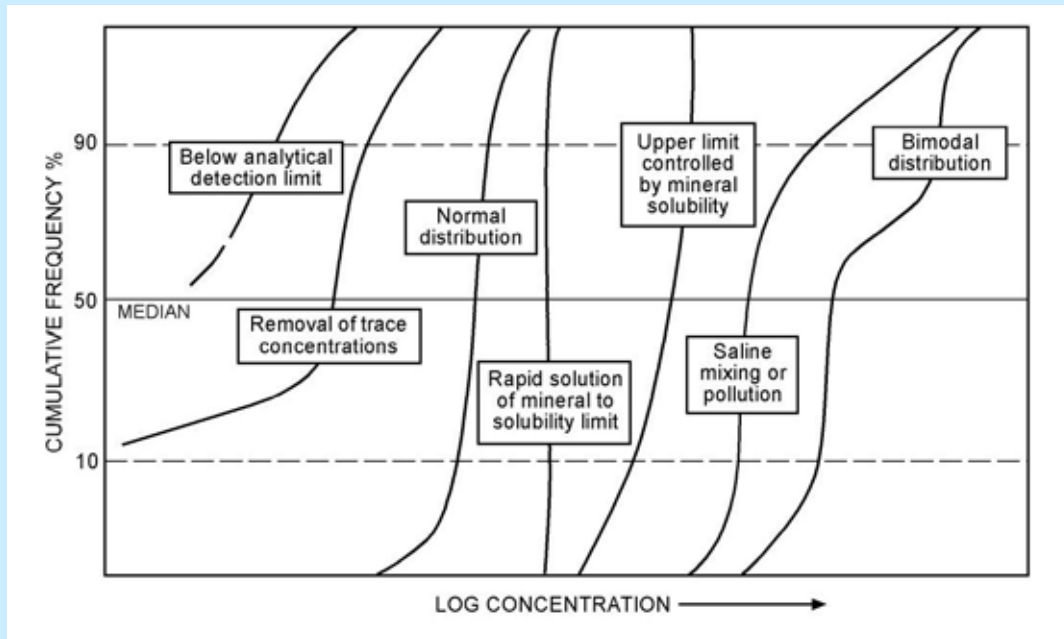
#### 5.4 Minor and trace elements

Minor and trace elements are summarised in Table 5.2 and are also displayed on boxplots in Figure 5.2. The data derive from BGS data only to avoid inconsistencies caused by different sample filtration practices carried out by the EA laboratories. While Br lies close to the normalised seawater line determined using median Cl, most other elements show concentrations higher than this. There is

an enrichment in F relative to Cl suggesting an internal source in the aquifer. Silicon shows a limited range of concentrations and the high concentrations can be related to the quartz-rich bedrock chemistry.

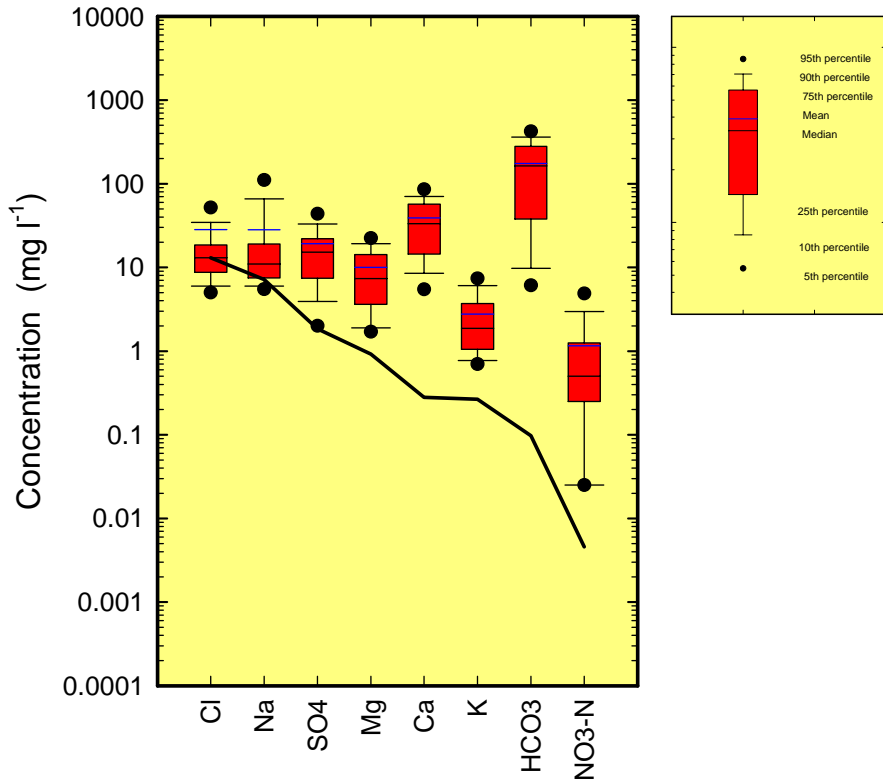
Concentrations of Sr and Ba vary widely throughout the aquifer. While Sr remains  $\leq 1 \text{ mg l}^{-1}$ , Ba reaches concentrations of up to  $2968 \text{ } \mu\text{g l}^{-1}$ , thus exceeding the EC maximum permissible value of  $150 \text{ } \mu\text{g l}^{-1}$  by more than one magnitude. As Ba is strongly controlled by barite ( $\text{BaSO}_4$ ) saturation, such high Ba concentrations only occur where  $\text{SO}_4$  in the groundwater is low.

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

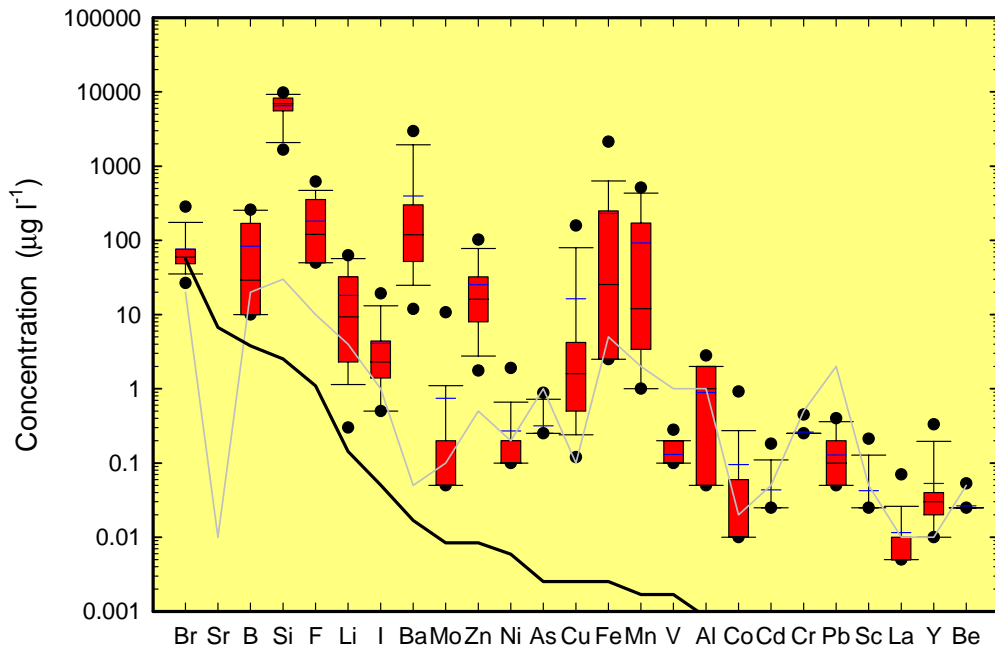


- i) The median and upper and lower percentile concentrations are used as a reference for the element baseline which can be compared regionally or in relation to other elements.
- ii) Normal to multi-modal distributions are to be expected for many elements reflecting the range in recharge conditions, 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.  $\text{NO}_3$  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 major ion concentrations (a) and (b) minor and trace element concentrations in the Millstone Grit groundwaters.

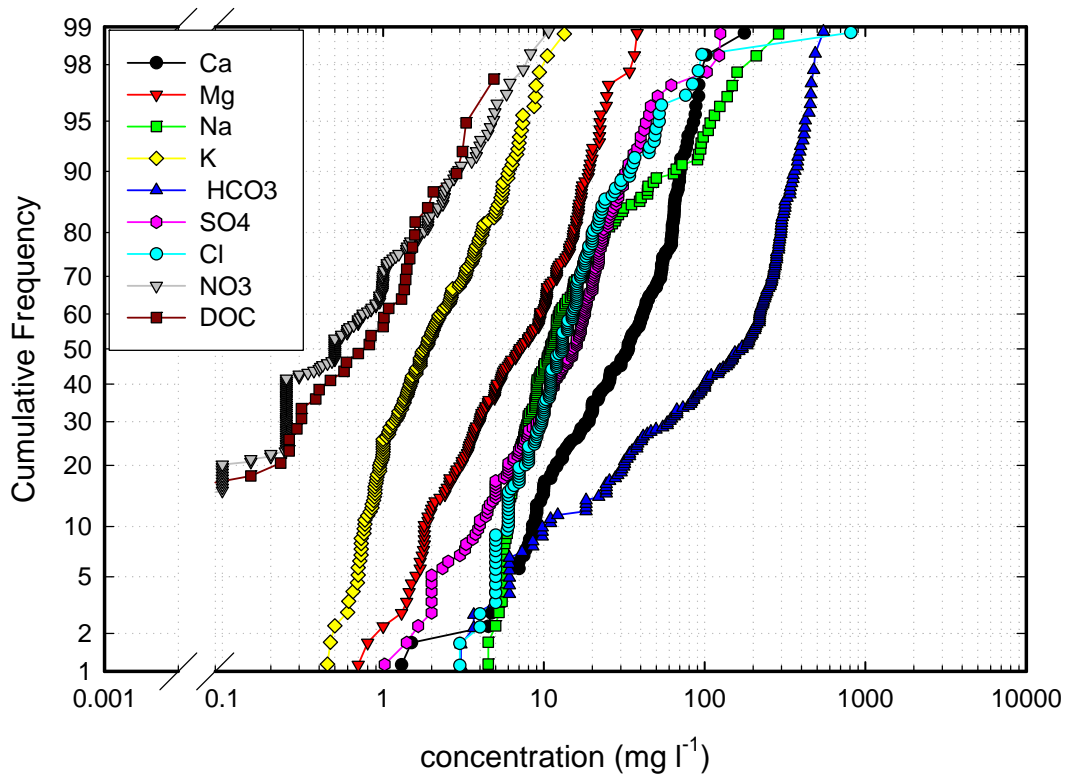
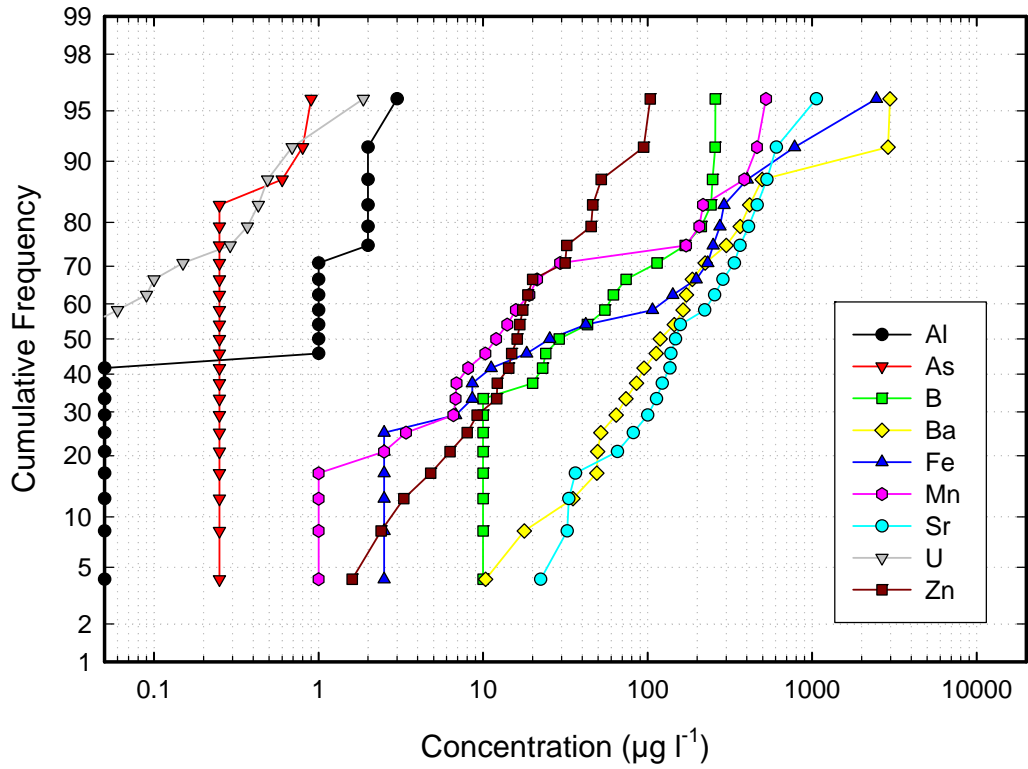


Figure 5.3 Cumulative Probability Plots for the Millstone Grit

Iron and Mn, likewise, show large variations in the aquifer. Although a number of samples have concentrations below the limit of detection (shown by vertical lines on the cumulative frequency plots), Mn in excess of  $0.5 \text{ mg l}^{-1}$ , and Fe as high as  $2.5 \text{ mg l}^{-1}$  occur in the more reducing groundwaters. In general, the trace elements show a wide range of concentrations and generally more complex distributions (Figure 5.3) due to the different controlling factors. Boron, although generally believed to be predominantly of atmospheric origin in the Millstone Grit Aquifer (Edmunds et al., 1989), is locally strongly enriched above rainfall concentrations and the high B/Cl ratio indicates that acquisition of B from bedrock sources may be important. The heavy metals Cd and Pb, as well as Al are generally low due to their low solubility at the circumneutral pH values of the groundwaters. Zinc and Cu may be locally quite high (maximum  $104 \text{ } \mu\text{g l}^{-1}$  and  $176 \text{ } \mu\text{g l}^{-1}$ , respectively) but Ni and Cr are generally low (Table 5.1). Arsenic and U, likewise, are only present at very low concentrations.

## 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).

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

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

The approach adopted is threefold:

(i) to have evidence of groundwater age

(ii) to extrapolate data series back to an initial time

(iii) to use indicator elements in the groundwater, known to result from human activities. The most probable indicators of human activities are enhanced TOC and N species – especially  $\text{NO}_3^-$  – the presence of foreign substances such as agro-chemicals or industrial chemicals. The sets of data are examined for these substances as a clue to the presence of “contamination”, although it is stressed that it is impossible to quantify this. However, traces of contamination may have little impact on the overall chemistry of the groundwater.

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 an 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. Indicators of agricultural pollution are elevated nitrate concentrations and the presence of pesticides/herbicides (Box 5.2).

Concentrations of nitrate are generally low, mostly below detection limit and only at one location exceed the EC maximum permissible value of  $11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ . Because many of the waters are relatively reducing, denitrification or nitrate reduction may have lowered the concentrations. Hence, in low redox waters,  $\text{NO}_3\text{-N}$  levels alone may not be a reliable identifier of pollution and other



indicators such as DOC and other N-species should also be considered. Nitrite and  $\text{NH}_4$  levels are also low throughout the aquifer, although some boreholes clearly show levels above the maximum permissible value of  $0.03 \text{ mg l}^{-1}$   $\text{NO}_2\text{-N}$  and  $0.38 \text{ mg l}^{-1}$   $\text{NH}_4\text{-N}$ . From the limited data it appears that boreholes with high  $\text{NH}_4$  levels are also enriched in DOC ( $> 1 \text{ mg l}^{-1}$ ). At the Settle Creamery borehole [BNG 381380 463460], for example, high  $\text{NH}_4\text{-N}$  concentrations of  $2.23 \text{ mg l}^{-1}$  coincide with DOC values of  $4.9 \text{ mg l}^{-1}$ .

Analysis of organic contaminants has not been included in this study. However, considering the extensive agricultural land use in the area, the presence of other contaminants such as herbicides and/or petroleum hydrocarbon products in the groundwater cannot be excluded.

## **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, areally 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 depth sampling at multi-level boreholes or from packer tests, it is difficult to identify the aquifer horizons, which 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. Selected parameters for pumped samples across the study have been plotted against borehole depths (Figure 6.1). There is no consistent behaviour between concentration and depths for most elements, although a few trends can be inferred from the data.

High Na concentrations ( $>50 \text{ mg l}^{-1}$ ) predominantly occur at depths between 40 m and 80 m. A similar trend is not easily observed in the other profiles, but closer observation of the data shows that most of these high Na groundwaters are depleted in Ca ( $<30 \text{ mg l}^{-1}$ ) and  $\text{SO}_4$  ( $<10 \text{ mg l}^{-1}$ ) compared to the other samples and have a relatively high pH. The 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.

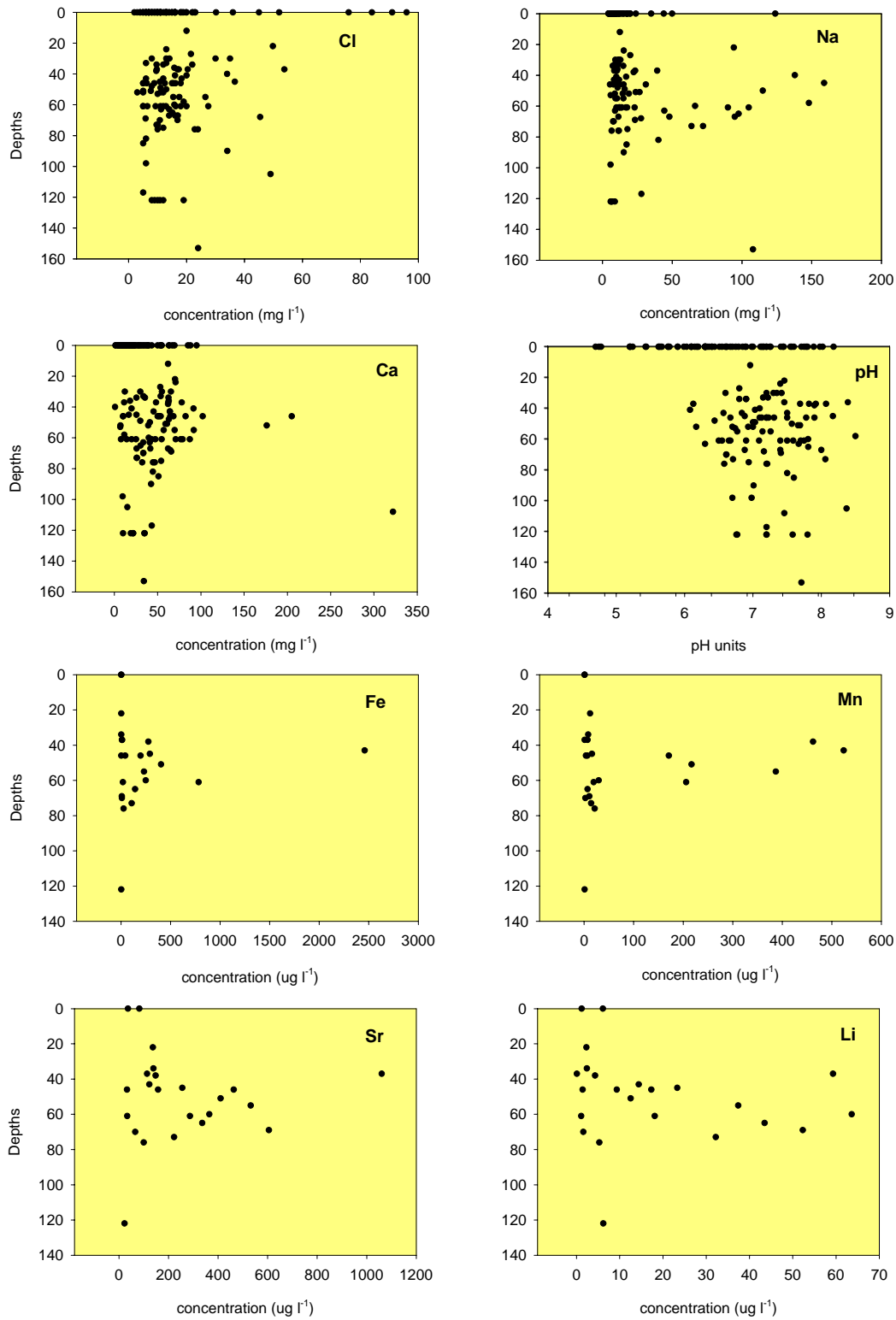
There is no clear trend between pH and borehole depth, but low pH values ( $\text{pH} < 6.5$ ) are typically associated with springs. The carbonate system is a major control on pH in the study area (Figure 6.2) and the low pH values of these spring waters along with low alkalinity, Si and Ca levels suggest relatively shallow flow pathways and short residence times. The elements Li and Sr, which accumulate in the groundwater as a result of incongruent mineral dissolution, are indicative of long residence times and the increase in Li and Sr in the deeper boreholes ( $>40 \text{ m}$ ) suggest longer residence times of these groundwaters.

Oxygen depletion and low redox conditions are typically associated with deeper groundwaters ( $>30 \text{ m}$ ), which frequently show increased Fe and Mn levels. However, concentrations in excess of the drinking water limits of  $250 \mu\text{g l}^{-1}$  for Fe and  $50 \mu\text{g l}^{-1}$  for Mn only occur where DO levels  $< 2 \text{ mg l}^{-1}$  and Eh  $< 350 \text{ mV}$  provide favourable conditions for reductive oxide dissolution.

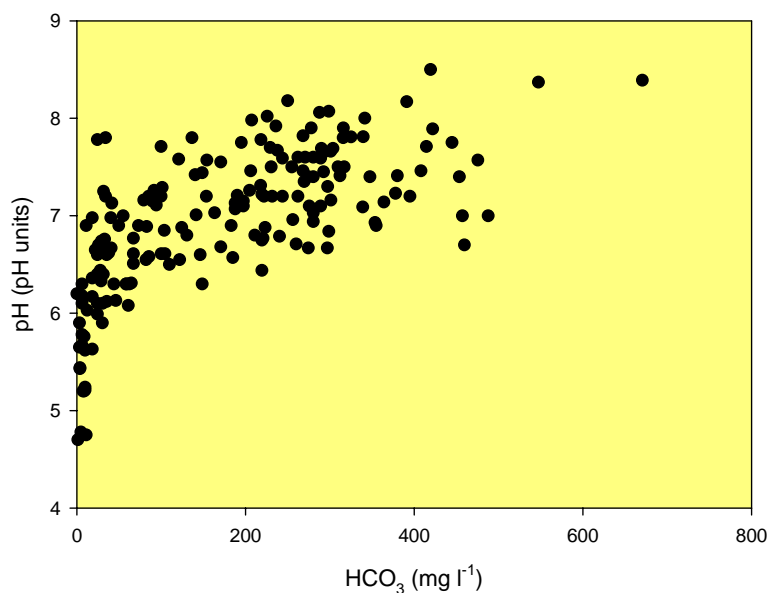
### **6.3 Temporal variations**

Few long-term data are available for groundwaters from the study area. Baseline conditions are, therefore, difficult to assess. Limited data from chemical analysis exist for a number of boreholes, which are part of the EA monitoring network. Temporal variations in groundwater chemistry are displayed in Figure 6.3 for a number of components. From the graphs it is clear that in most cases no

significant trend in solute concentrations is apparent. The sudden increase in conductivity by a factor of 5 in the Lanshaw Bh-1 [BNG 39369 44084] in 1994 is not reflected in the alkalinity or in the hardness values available for these dates and, therefore, is believed to be unrelated to the groundwater chemistry.



**Figure 6.1 Major and minor element characteristics of the groundwaters at different borehole depths**

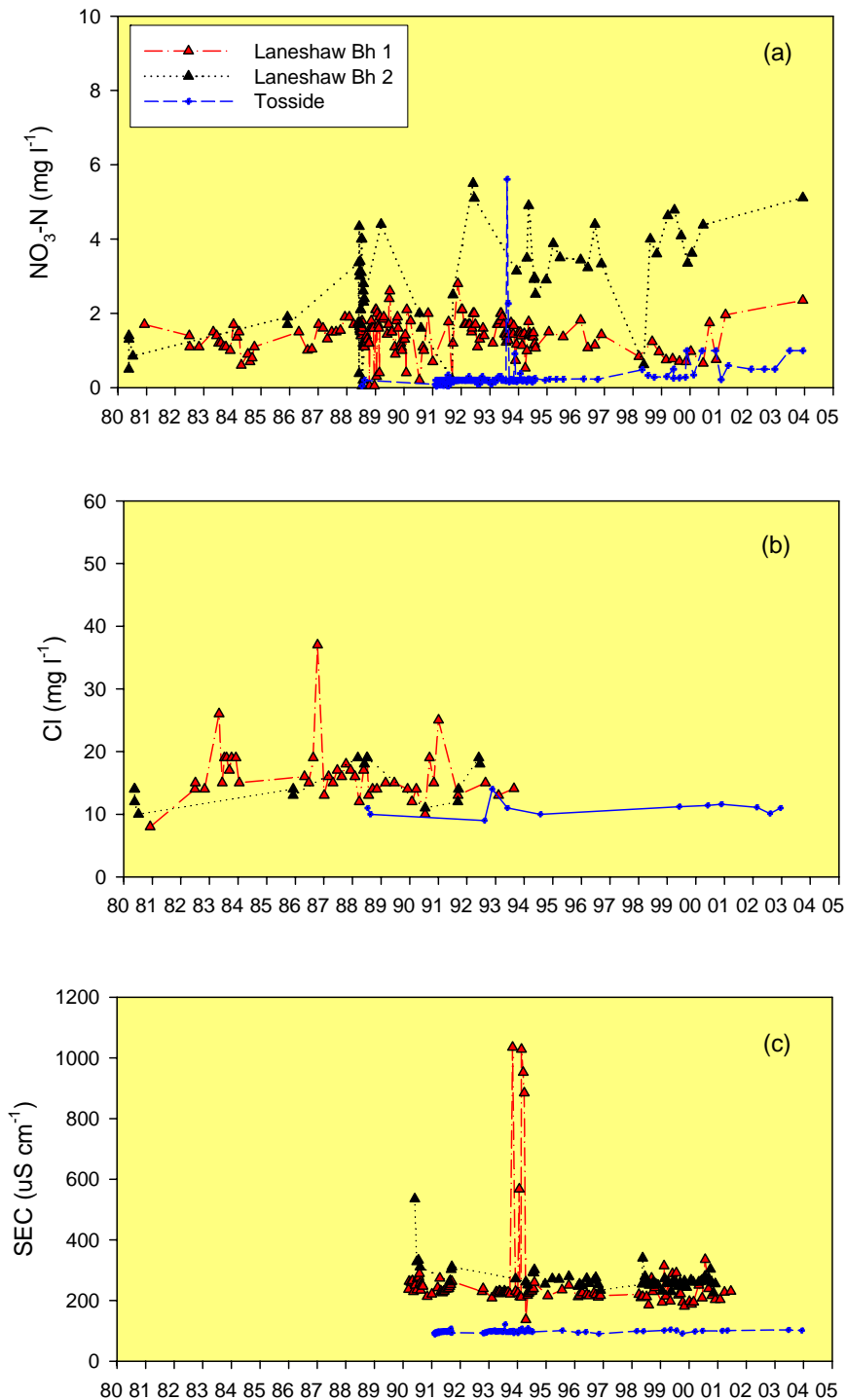


**Figure 6.2 Relationship between pH and bicarbonate in the Millstone Grit groundwaters**

The time series data only cover a period of up to 15 years and are often inconsistent with respect to the monitored parameters and/or detection limits, so that long-term changes in groundwater chemistry cannot be identified. Nitrate concentrations in the groundwaters vary greatly throughout the monitoring period, but show no clear trend with time. A gradual increase in  $\text{NO}_3\text{-N}$  concentration during the last decade can be seen only at the Tosside borehole [BNG 37622 45760] and may be related to changes in land-use and/or in land management practices. This observation concurs with findings from many other UK aquifers that also show an increase in nitrate with time. It is interesting to note the differences in  $\text{NO}_3\text{-N}$  concentrations in the groundwater at Lanshaw Bh-1 and Lanshaw Bh-2 [BNG 39428 44115]. The boreholes are situated within a distance of 500 m from each other and have similar borehole depths of 70 m and 76 m, respectively. From Figure 6.3a it is apparent that  $\text{NO}_3\text{-N}$  concentrations in the Lanshaw Bh-2 are increased by a factor of 2 compared to those in Lanshaw Bh-1. The boreholes are near the Lanshaw water treatment works, but more detailed information on bedrock geology, groundwater pathways as well as on the Water Treatment Works management practices are required before conclusions about possible  $\text{NO}_3$  sources at Lanshaw Bh-2 can be drawn.

#### 6.4 Age of groundwater

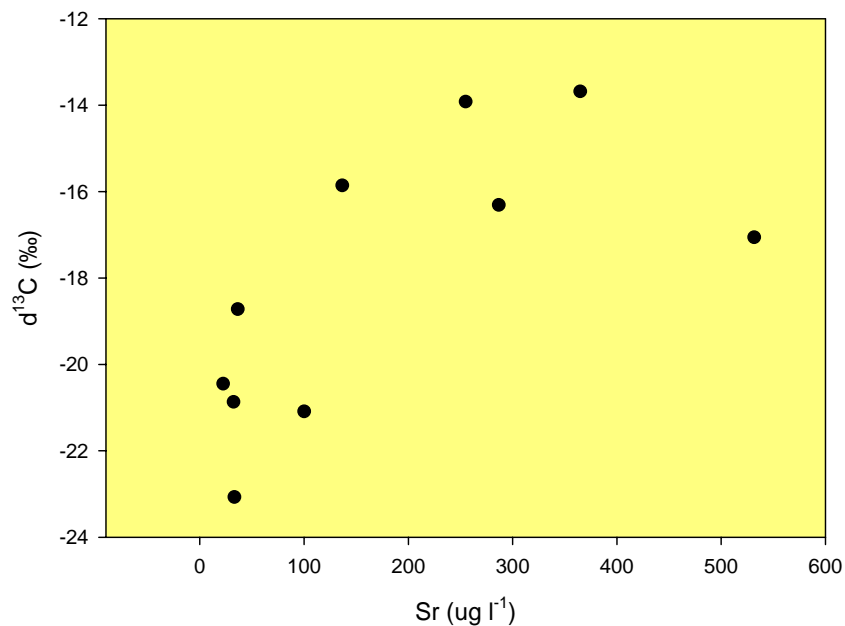
Stable isotope analysis was carried out on selected samples in order to investigate the presence of paleowaters (>10,000 years old) in the aquifer. Stable isotopes have been used successfully to discriminate older Pleistocene waters (>10,000 years old) from younger Holocene groundwaters (<10,000 years 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 is lighter (more negative) in Pleistocene groundwaters due to the colder climate during that period. The range of observed  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values 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), which, for the study area, predict values around -45 ‰ and -7 ‰ for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , respectively. Such values would be expected from rainfall inputs and indicate that the recharge is likely to be of Holocene or Recent age.



**Figure 6.3** Time series data for selected boreholes showing (a) nitrate (as N), (b) chloride and (c) specific electrical conductance for the boreholes at Laneshaw and Tosside.

Another indicator of residence times is the carbon isotope  $\delta^{13}\text{C}$ , which 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 into the groundwater evolution and can help interpret groundwater age. Non-saline (fresh) groundwaters invariably originate as meteoric water, which then infiltrates through the soils and into the aquifer. Along its 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  $\text{CO}_2$  in the aquifer and the bedrock composition, in particular its carbonate content. In the study area, two main types of groundwaters can be distinguished (1) groundwaters enriched in  $\delta^{13}\text{C}$  and (2) groundwaters depleted in  $\delta^{13}\text{C}$ . Shallow travel path and short groundwater residence time (thus limited calcite dissolution) are responsible for the low  $\delta^{13}\text{C}$  value ( $-18\%$ ) at the Knowlmore Manor Spring [BNG 36796 44959]. However, the depleted  $\delta^{13}\text{C}$  signature of the deep boreholes at the New Drop Inn [BNG 36442 43901], the Waddington Fell Quarry [BNG 37187 44780], Lanshaw Bh-1 [BNG 39369 44084] and Tosside [BNG 37622 45760] cannot be explained by calcite dissolution and the  $\delta^{13}\text{C}$  signature appears to be controlled by bedrock lithology (the availability of calcite in the bedrock) rather than by groundwater age. In Figure 6.4,  $\delta^{13}\text{C}$  values are plotted against Sr concentrations. The plot shows that  $\delta^{13}\text{C}$  depleted groundwaters also have low Sr concentrations. Strontium typically accumulates in the groundwater as a result of carbonate and silicate weathering, but accumulation rates are much slower in carbonate poor aquifers, owing to the slow reaction rates of silicates. Because carbonate minerals are deficient in these aquifers, such groundwaters are also depleted in  $\delta^{13}\text{C}$ , as the  $\delta^{13}\text{C}$  signature usually does not evolve much beyond the point established in soils (Clark and Fritz, 1997). There is no clear spatial trend in  $\delta^{13}\text{C}$  distribution, but depleted signatures are mostly found in boreholes with depths  $>60$  m. It, therefore, appears that calcite-depleted bedrock occurs in the deeper parts of the aquifer (e.g., quartz-kaolinite assemblage).



**Figure 6.4 Relationship between  $\delta^{13}\text{C}$  and Strontium for selected groundwaters of the Millstone Grit**

## 6.5 Spatial variations

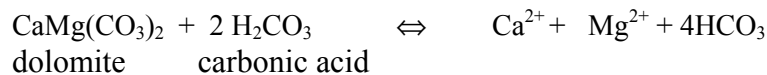
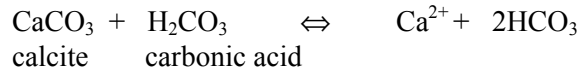
### 6.5.1 Introduction

Changes in groundwater baseline chemistry are expected to occur as water moves from the recharge to discharge areas of the aquifer. In the Millstone Grit, it is very difficult to assess this hydrochemical evolution of the groundwater along flow paths as the aquifer is compartmentalised by a number of low permeability horizons in the sub-horizontal plane as well as by faults in the sub-vertical plane. 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

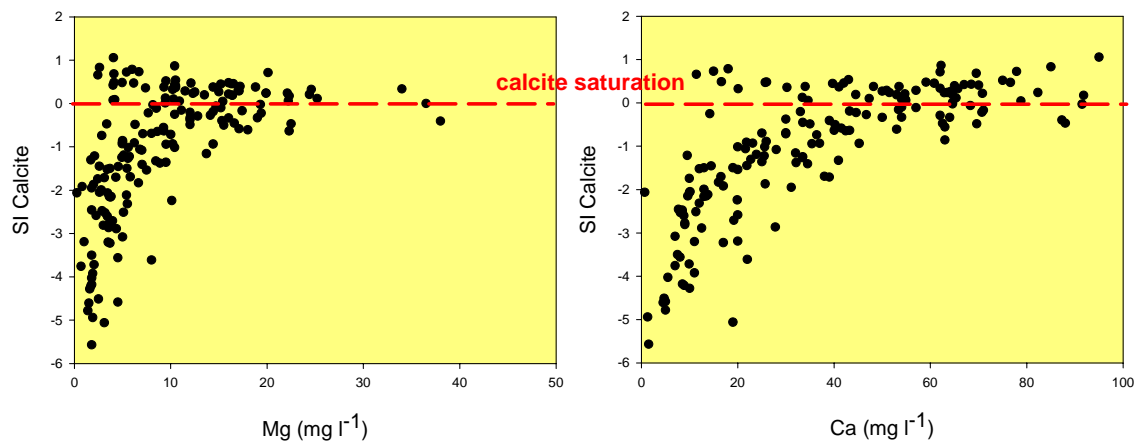
deposits may also have an influence, in particular by varying the recharge rates and residence times of the groundwaters.

### 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 high Ca+Mg/Cl ratio of most samples and is also apparent from Figure 6.5, which illustrates the asymptotic relationship between calcite saturation and Ca and Mg in the aquifer. The spatial distribution of Ca and Mg is complex (Figure 6.11) but many groundwaters in the study area are saturated with respect to dolomite and calcite. This is illustrated in Figure 6.6, where SI values around 0 ( $\pm 0.2$ ) indicate saturation of the groundwater with respect to the considered mineral phase. From Figure 6.6 it is apparent that a relationship exists between the degree of saturation and the borehole depths. Most samples from the deeper boreholes are close to calcite and dolomite saturation and this can be related to the longer residence times of these waters. The saturation-depths relationship is less clear for samples from shallower boreholes and springs, but undersaturation is more common in these groundwaters, 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.

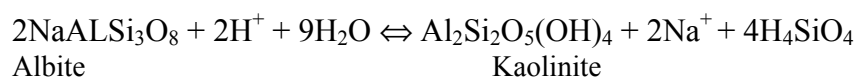
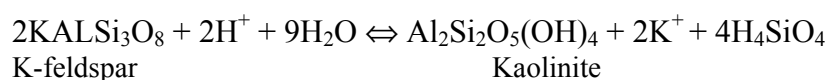


**Figure 6.5** Asymptotic relationship between calcite saturation (Saturation Index-SI) and Ca and Mg in the Millstone Grit groundwaters. The dashed red line indicates calcite saturation (SI=0).

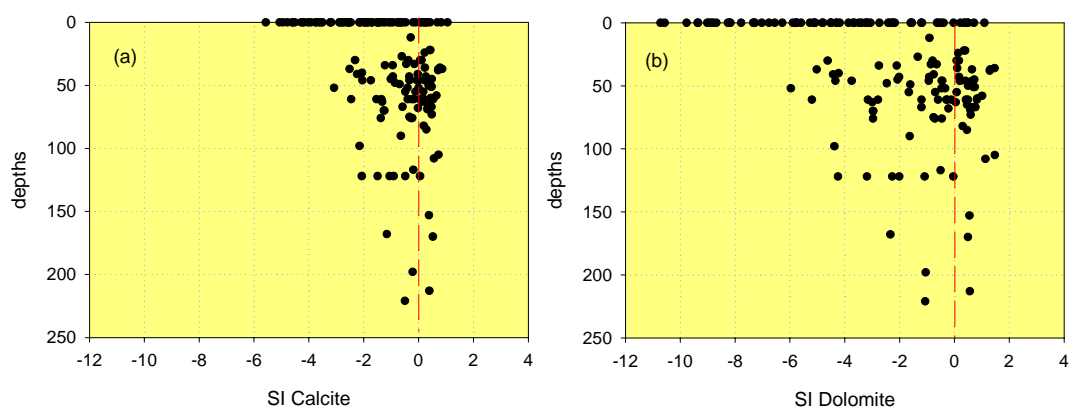
(The wide range saturation pattern in the shallower borehole data may be related to the fact that borehole samples represent a mixture of waters from different horizons, whereby the proportion of younger waters increase in shallower boreholes, and may become the dominant source depending on the distribution of the productive horizons. Similarly, water chemistry and the residence times of

spring waters vary depending on the local geology and may be a mixture of waters from different horizons and of varying age.)

Although the dissolution of calcite and dolomite provide the dominant controls on water chemistry, silicate dissolution is also important. Silicon concentrations within the aquifer range between 1.1 to 17.7 mg l<sup>-1</sup>. The amount and rate of dissolution will mainly be controlled by saturation with respect to a silicate mineral or phase. While all groundwaters in the study area are close to saturation with respect to quartz and chalcedony (SiO<sub>2</sub>), and although the aquifer is composed dominantly of quartz, this mineral is extremely unreactive and the main source of Si is probably from silicate minerals such as K-feldspar or plagioclase feldspar:



The dissolution of feldspar has clearly influenced the general groundwater chemistry in the study area. It is probably of minor importance for the formation of the Na(K)-HCO<sub>3</sub> type waters (e.g. at Holmes Farm [BNG 36584 43595], Brades Farm [BNG 35730 46710], ICI Trimpell Ltd [BNG 34180 45900], Harterbeck [BNG 36118 46364], Tunstall Hall [BNG 36080 47344] and others) as indicated by the indistinct relationship between Sr and Na at these sites, which suggests that ion exchange processes are important for the formation of these high Na-waters rather than lithogenic sources.



**Figure 6.6 Relationship between borehole depths and saturation state of the Millstone Grit groundwaters with respect to (a) calcite and (b) dolomite**

The distribution of SO<sub>4</sub> varies throughout the aquifer (Figure 6.11). Concentrations are relatively low (median 15 mg l<sup>-1</sup>) except for a number of sites where high SO<sub>4</sub> (103- 259 mg l<sup>-1</sup>) concentrations occur. A common source of sulphate in many groundwaters is the dissolution of gypsum (or anhydrite). Secondary gypsum has been found in the eastern part of the study area (Brandon et al., 1998) but, in general, inputs from gypsum dissolution appear to be of minor importance for the groundwater quality in the study area. This is also apparent from the saturation indices, which indicate undersaturation in all samples with respect to gypsum (and anhydrite). Other potential sources of sulphate include the oxidation of pyrite, acid rain or fertilizer application as well as mixing of



freshwater with seawater (Appelo and Postma, 1993). The latter may be responsible for the elevated  $\text{SO}_4$  levels in the groundwater at the South Lakeland Caravan Site [BNG 34317 46303].

Pyrite oxidation may be important locally and combined with calcite dissolution may have contributed to the high  $\text{SO}_4$  levels in the groundwater at Higher Trushgill [BNG 365110 462390], which is also high in Fe and trace elements. Throughout the study area, pyrite most frequently occurs within the organic rich shale and mudstone strata and to a lesser extent in the sandstone strata (Wagstaff, 1991). However, it is mainly found in Carboniferous limestone outcrops rather than in the Millstone Grit strata and is thought to have crystallised from hydrothermal fluids (Brandon et al., 1998).

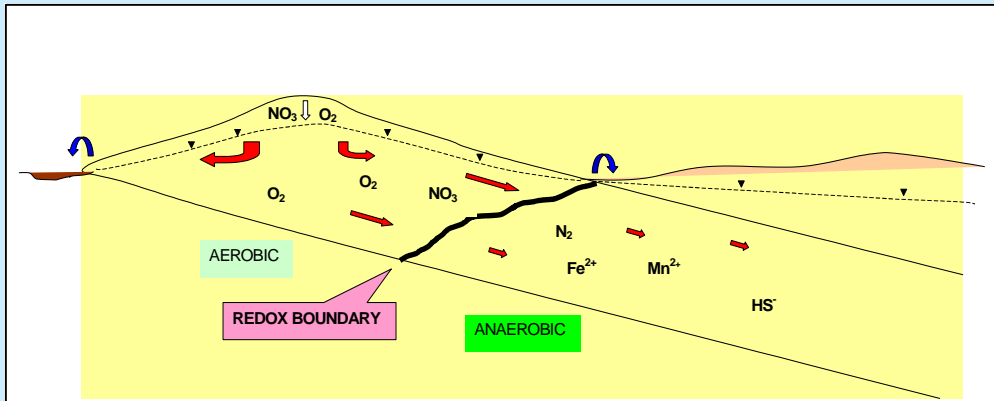
Considering the small availability of sulphate from atmospheric and/or bedrock sources, it is apparent that anthropogenic inputs must also provide an important sulphate source for the aquifer and inputs from agricultural fertiliser applications have previously been considered as the main contributor of sulphates to the groundwater system in the area (Wagstaff, 1991). The high  $\text{SO}_4$  concentration at the Low Bottom Spring [BNG 365900 468670], for example, is unlikely to result from gypsum dissolution, hence pollution from anthropogenic sources and/or pyrite oxidation are more likely to be the controlling factors. There is also the possibility that the groundwater chemistry at Higher Trushgill and at Low Bottom Spring is influenced by mixing with waters from the Carboniferous Coal Measures, which are enriched in  $\text{SO}_4$  and crop out just north of these borehole sites. However, to distinguish between these different processes S isotope studies would be beneficial. Given the limited data, some uncertainty remains as to what the dominant processes are.

Sulphate removal from the groundwater may also occur, e.g. through the formation of Barite ( $\text{BaSO}_4$ ) or through bacterially mediated sulphate reduction under low Eh conditions. The high molar  $\text{Cl}/\text{SO}_4$  ratios of the groundwaters at Ramsgraeve Laundry [BNG 36810 43085], Lower Wheathead Farm Spring [38458 441780] and South Lakeland Caravan site [BNG 34317 46303], which are much higher (617, 124 and 33) than that of seawater (19) indicate that sulphate removal must take place in the groundwater.

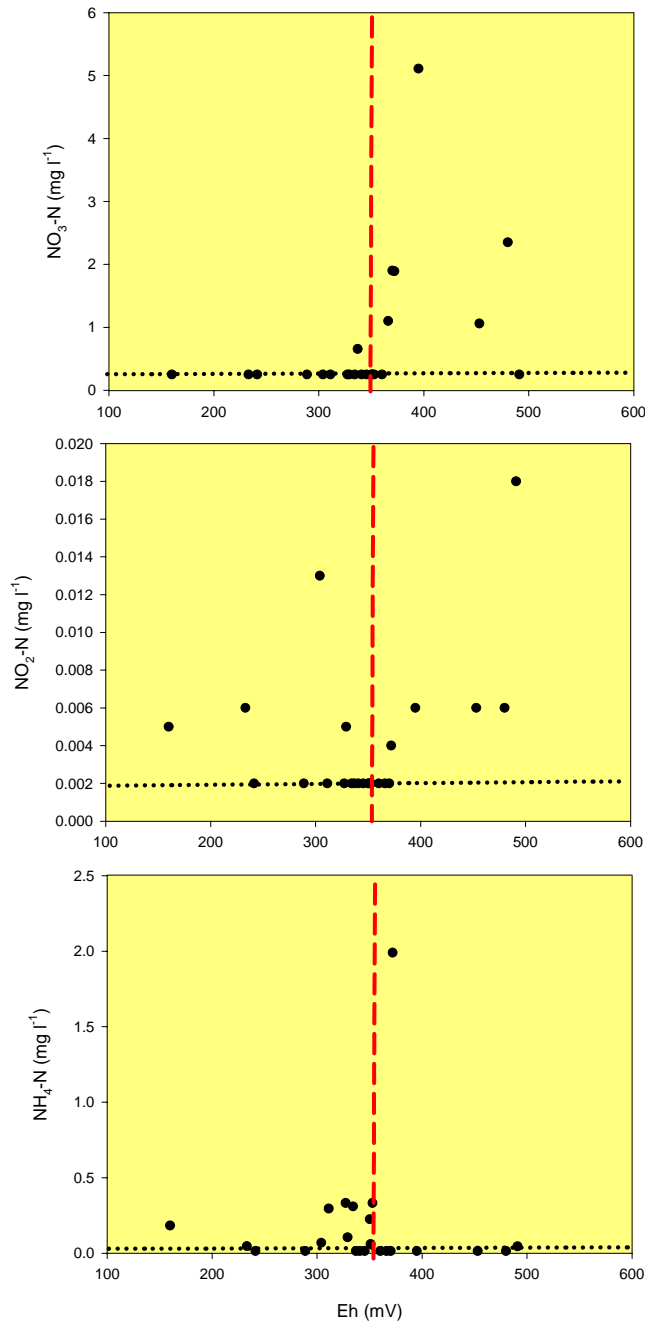
### 6.5.3 Redox reactions

The distribution of redox status in the groundwaters of the study area is complex, mainly due to the layered nature of the aquifer and locally confining units in the sandstone. This is reflected in the large spatial variations of redox sensitive species and redox parameters (Eh and DO) illustrated in Figure 6.12 for Fe and DO. 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  $\text{mg l}^{-1}$ . 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 6.7. It appears that nitrate reduction becomes important in waters with  $\text{Eh} < 350 \text{ mV}$ , although the relationship to Eh is less defined for the meta-stable  $\text{NO}_2\text{-N}$  (Figure 6.7b). Groundwaters with Eh values below 350 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 generally higher in shallow boreholes and springs, suggesting an agricultural rather than a geological source, and mainly occur in areas where impermeable drift deposits are absent. Recharge through these windows in the drift provides a fast pathway for  $\text{NO}_3\text{-N}$  from surface applications into the groundwater, a fact that has been acknowledged by including part of the study area, most vulnerable to  $\text{NO}_3\text{-N}$  pollution, into the recently designated NVZ. Other important redox processes include the oxidation of pyrite as well as the reduction of sulphate (*see also Chapter 6.5.2*). From Figure 6.8 it is apparent that  $\text{SO}_4$  concentrations in excess of  $15 \text{ mg l}^{-1}$  only occur in well-oxygenated waters with Eh level above 300 mV.

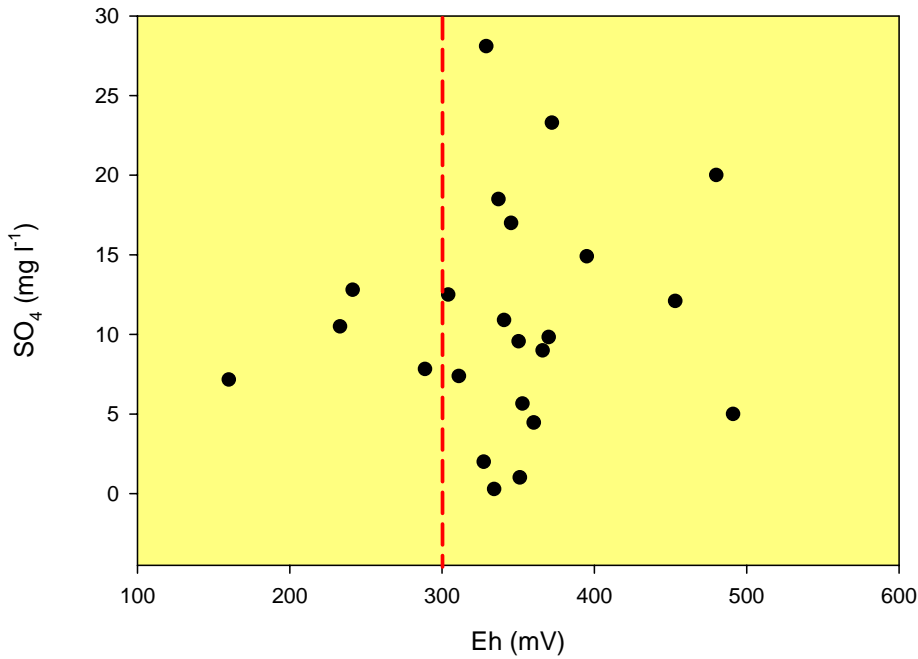
### Box 6.1 Redox Boundary



Water at recharge is generally saturated with dissolved oxygen at the partial pressure of the atmosphere ( $10\text{-}12\text{ mg l}^{-1}$  depending upon barometric conditions). Passing through the soil and the unsaturated zone some of this  $\text{O}_2$  will react as a result of microbiological processes and oxidation-reduction reactions. However, almost all water reaching the water table still contains several  $\text{mg l}^{-1}$   $\text{O}_2$ . Geochemical reactions (oxidation of traces of pyrite, organic matter and  $\text{Fe}^{2+}$  present in minerals) progressively remove the  $\text{O}_2$  along flow lines. Once all the oxygen has reacted an abrupt change of water chemistry takes place (redox boundary). Other changes may occur at and down-gradient of the redox boundary, especially denitrification and the probability that total dissolved iron ( $\text{Fe}^{2+}$ ) concentrations will increase. Sulphate reduction and the production of sulphide ( $\text{H}_2\text{S}$  as  $\text{HS}^-$  in solution) may also occur at greater depths.



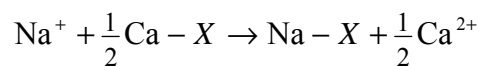
**Figure 6.7** Relationship between N-species and redox potential in the Millstone Grit groundwaters. The dotted black line denotes the detection limits, the red dashed line highlights the redox potential of Eh = 350 mV below which  $\text{NO}_3\text{-N}$  appears to become reduced.



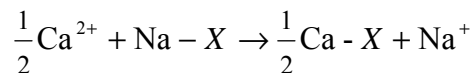
**Figure 6.8** Relationship between sulfate concentrations and redox potential in the Millstone Grit groundwaters. The red dashed line highlights the redox potential of Eh = 300 mV below which SO<sub>4</sub> levels remain relatively low, probably due to reduction processes at low Eh.

#### 6.5.4 Ion exchange reactions

The majority of recharge groundwaters are of Ca-HCO<sub>3</sub>-type due to the dissolution of calcite cement. 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-Cl<sub>2</sub> type. The reverse process will operate if groundwater freshening occurs i.e. freshwater flushing through a saline water aquifer:

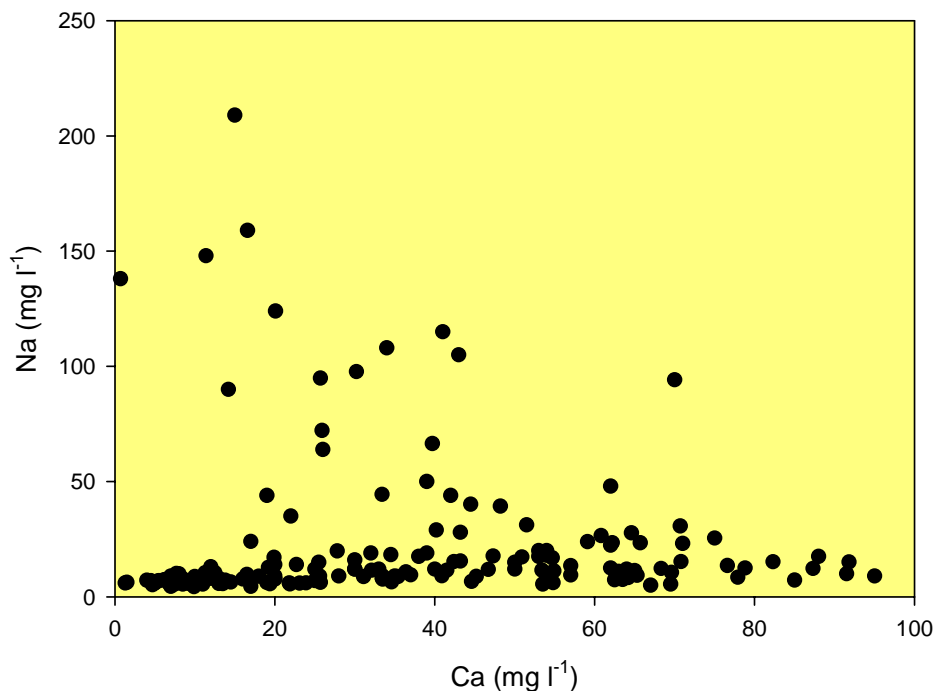


Here Ca<sup>2+</sup> is taken up from the water and exchanged for Na, producing a Na-HCO<sub>3</sub> type water, (Appelo and Postma, 1993).

The range of chemical compositions encountered in the groundwaters of the Millstone Grit aquifer indicates that a diverse range of ion exchange processes takes place. Evidence of groundwater freshening is found at a number of sites (e.g., at Holmes Farm [BNG 36584 43595], Brades Farm [BNG 35730 46710], ICI Trimpell Ltd [BNG 34180 45900], Harterbeck [BNG 36118 46364], Tunstall Hall [BNG 36080 47344]), where groundwaters trend towards Na-HCO<sub>3</sub> type compositions.

Conversely, other samples trend towards Ca-Cl type (e.g., South Lakeland Caravan site [BNG 34317 46303]), which is characteristic for an aquifer undergoing salinisation.

The role of ion exchange in the aquifer is difficult to assess because of the lack of solid phase data and the complex nature of the aquifer mineralogy. The Na/Cl ratio is a useful indicator of whether any increase in Na is due to mineral weathering and ion exchange or mixing with older formation water. In the Millstone Grit aquifer, the molar Na/Cl ratio varies significantly, and the high values of up to 13.67 (compared to 0.85 for seawater) indicate that water-rock interactions are important in the aquifer. The low Cl concentrations in most groundwaters indicate that the aquifer has generally been well flushed of original formation waters and the additional Na is probably derived from silicate weathering of phases such as plagioclase feldspar. However, the high Na concentrations in some of the groundwaters (e.g., Holmes Farm [BNG 36584 43595], Brades Farm [BNG 35730 46710], Tunstall Hall [BNG 36080 47344]) cannot be explained by silicate weathering alone and ion exchange of Na on clay minerals for Ca or Mg is probably important and also explains the inverse correlation between Na and Ca seen in Figure 6.9. Inverse ion exchange, where Na is released in exchange for Ca, occur where freshwater intrudes in areas dominated by older formation waters, but is probably also important in carbonate-poor lithologies, where the exchanger is dominated by Na due to the low availability of Ca.



**Figure 6.9** Correlation between Na and Ca in the Millstone Grit groundwaters. The graphs shows two different trends: (1) the constant increase in Na with Ca probably indicates increasing residence times and (slow) mineral weathering processes in the groundwaters; (2) the inverse relation between Na and Ca is due to processes of ion exchange in the aquifer.

#### 6.5.5 Mixing with older formation water

Mixing with older, deeper connate or formation water is generally indicated by increased salinity and high Cl. High salinity could also be caused by dissolution of evaporite minerals, thus Cl generally 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 6.11). While Cl concentrations are mostly low

(median: 12.5 mg l<sup>-1</sup>), exceptionally high concentrations occur at a number of sites. The high chloride to sulphate ratio of these groundwaters suggests that mixing between saline and fresh groundwaters may be important.

The high salinity (3870 µg cm<sup>-1</sup>) at the South Lakeland Caravan site [BNG 34317 46303] is mainly due to high amounts of Cl and Na in the groundwater, but concentrations in Ca, Mg, K and SO<sub>4</sub> are also high. Comparing the groundwater composition with that of average seawater by means of molar ratios shows that the groundwater is depleted in Na and SO<sub>4</sub> relative to seawater while enriched in Mg and Ca. 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 (Na from intruding seawater is exchanged for Ca in the freshwater aquifer), water-rock interactions (carbonate and silicate dissolution) and redox processes (reduction of SO<sub>4</sub> to H<sub>2</sub>S) have modified the original seawater composition. This interpretation is supported by the high Sr concentration (2990 µg l<sup>-1</sup>) in the groundwater which is an indicator for long residence times.

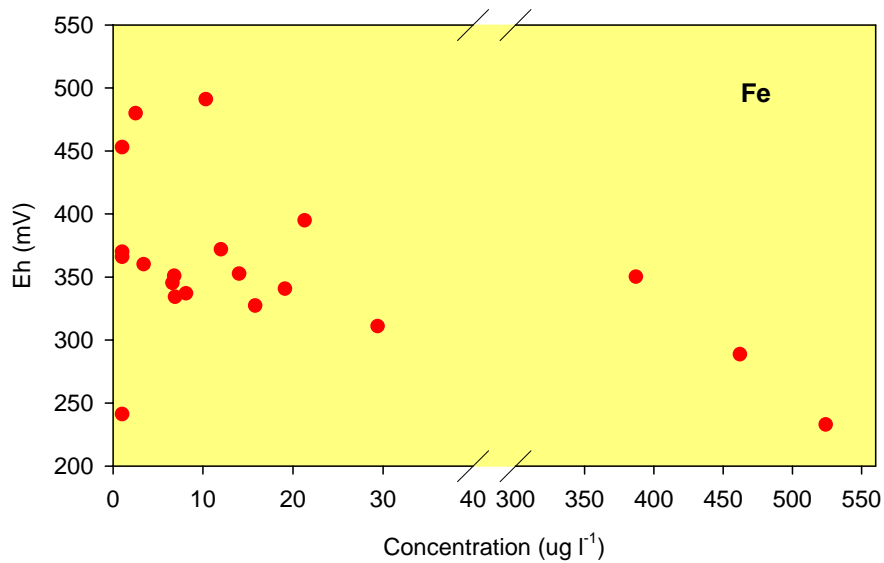
Exceptionally high Cl and Na values are found in the groundwater at Ramsgreave Laundry [BNG 36810 43085], but these high values are not reflected in SO<sub>4</sub>, Mg or Ca. The origin of these saline waters is not known, but the artesian nature of the borehole as well as its high methane content imply that a connection may exist to deeper Namurian strata and/or to overlying Carboniferous Coal Measures deposits. The presence of methane may also promote processes of SO<sub>4</sub> reduction and sulphide formation, leading to the elevated pH and alkalinity and to the low SO<sub>4</sub> concentrations seen in the groundwater. Alternatively, it is possible that the groundwater chemistry at Ramsgreave laundry is related to younger deposits of Permian age, which once must have covered the area and have subsequently been removed. This would explain the molar Na/Cl ratio of 1.4 in the groundwater, which is comparable to that of halite (~1).

#### 6.5.6 Trace elements

The source of Sr in most groundwaters is dominantly from calcite or gypsum, concentrations in the latter being generally higher. In silicate aquifers, Sr is also derived from Ca-bearing minerals such as Ca-rich plagioclase feldspar, but Sr concentrations in such groundwaters are generally low due to the slow reaction rates of silicates. Strontium concentrations in the Millstone Grit groundwaters are much lower than those observed in other aquifers in the UK, probably due to the limited reaction of the highly cemented, low porosity aquifer lithology (Edmunds et al., 1989). The good correlation between Sr and Mg indicates that most Sr comes from a carbonate source although silicate weathering may provide minor inputs. Gypsum dissolution appears not to be important as there is no relationship between Sr and SO<sub>4</sub> and since the overall Sr concentrations are very low.

Barium concentrations in the aquifer are relatively high compared with other UK aquifers (Edmunds et al., 1989), in many cases exceeding the EC Guide level for drinking water of 100 µg l<sup>-1</sup>. Barium concentrations in the groundwater are controlled by the solubility of baryte (BaSO<sub>4</sub>) and concentrations >200 µg l<sup>-1</sup> only occur where SO<sub>4</sub> concentrations are low (<10 mg l<sup>-1</sup>). The high Ba concentrations at Holme Farm and Chenick Lea probably result from localised baryte dissolution in the aquifer. The existence of thin baryte veins associated with joints and faults in the Namurian Sandstone have been reported in the study region (Brandon et al., 1998).

Iron and manganese are present in the aquifer. They are most likely derived from reductive solution of secondary Fe and Mn oxyhydroxides, which occur as pore linings and pore fillings within the bedrock. Concentrations are mostly controlled by the redox conditions in the groundwater and to some degree by its pH. The inverse relationship between Fe and Eh is indicated in Figure 6.10 and the presence of reducing and oxidising waters in the aquifer is also indicated by the bi-modal distribution (Figure 5.3) of Fe and Mn on the probability curve. Locally, Fe may also be derived from pyrite oxidation as has been discussed previously.



**Figure 6.10 Inverse relationship between Fe and redox potential**

Concentrations of Li and B in groundwaters generally increase with residence time and this is seen in the good correlation between Li and B with  $\delta^{13}\text{C}$ . High concentrations of these elements are mostly found towards the north, but also at Holme Farm [BNG 36584 43595] in the south of the study area. Uranium concentrations in the study area are very low. Most samples fall below the detection limit of  $<0.02 \mu\text{g L}^{-1}$  and maximum concentrations of  $1.87 \mu\text{g l}^{-1}$  at Settle Creamery [BNG 381380 463460] are still below the EC Guide value of  $2 \mu\text{g l}^{-1}$ . The median Cu levels are also very low and are probably controlled by the dissolution of iron hydroxides and/or release from adsorption sites. However, high Cu levels in excess of the EC Guide value of  $10 \mu\text{g l}^{-1}$  (up to  $176 \mu\text{g l}^{-1}$ ) cannot be easily explained by natural processes and are unlikely to represent natural baseline concentrations in the aquifer.

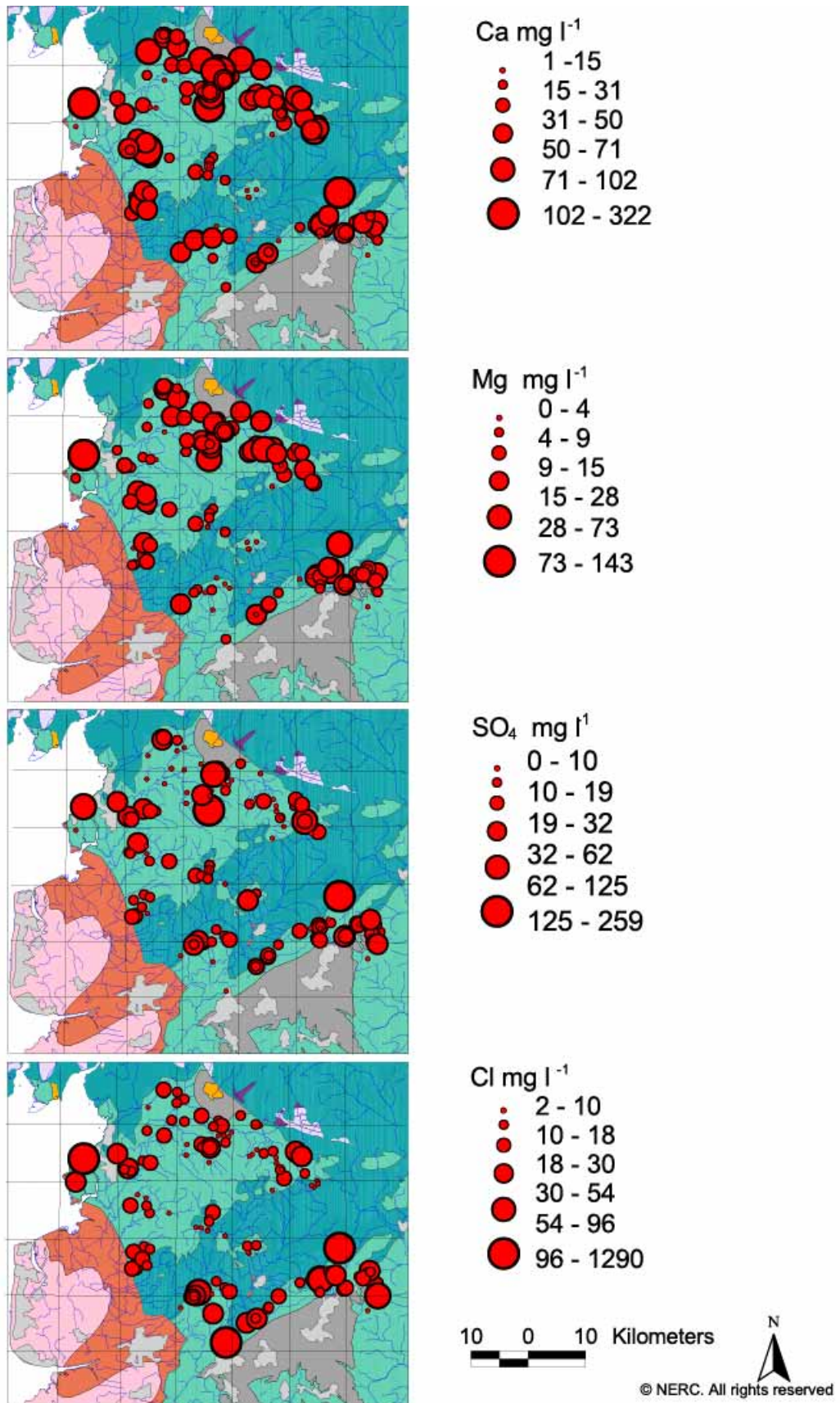


Figure 6.11 Spatial distribution of Ca, Mg, SO<sub>4</sub> and Cl in the groundwaters of the study area



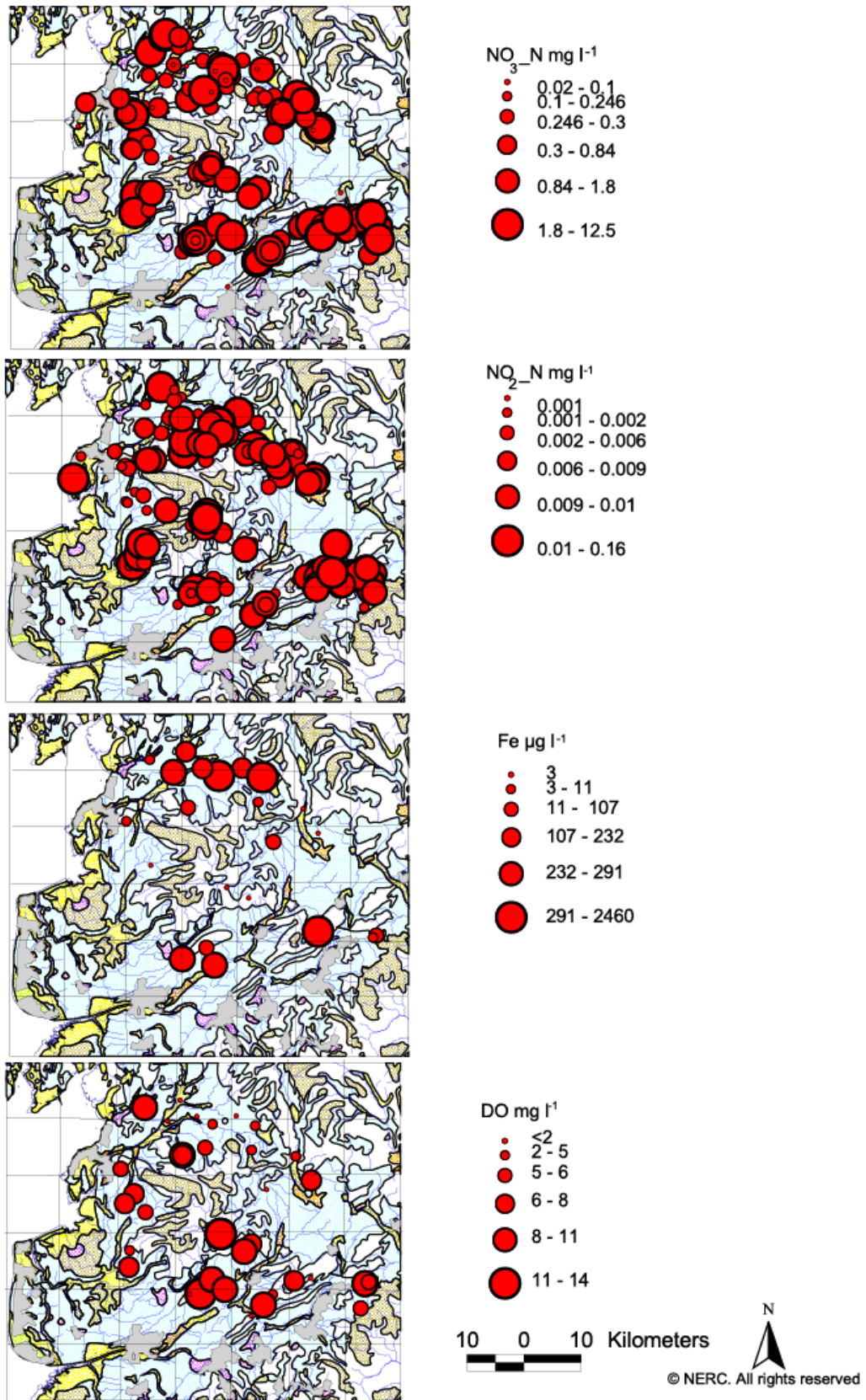


Figure 6.12 Spatial distribution of NO<sub>3</sub>-N, NO<sub>2</sub>-N, Fe and DO in the groundwaters of the study area

## 7. BASELINE CHEMISTRY OF THE AQUIFER

The baseline groundwater chemistry of any aquifer is determined by a wide range of physical as well as chemical processes. The primary input to most major aquifers is rainfall 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 these 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 Millstone Grit aquifer of the Central Pennines area of Yorkshire and Lancashire is extremely variable. Changes occur spatially as well as with depths reflecting the extent of water-rock interaction (hence residence time), the bedrock lithology as well as the different geochemical controls imposed by the local geochemical environment (e.g. oxidation-reduction controls). Widespread drift deposits, which cover 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. However, groundwaters remain vulnerable to pollution where 'windows' in the drift coverage occur.

The data have been presented in Table 5.1a and b and the median value and 97.7 percentile provide a good estimate of the average and upper baseline concentrations in the aquifer. 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 cements. Many groundwaters are undersaturated with respect to calcite and dolomite and it appears that these parts of the aquifer are dominated by sandstones of the quartz-kaolinite assemblage and that in these areas silicate dissolution is controlling the water chemistry. This is consistent with the change in slope of  $\text{HCO}_3$  on the cumulative probability plot, which highlights the different populations of  $\text{HCO}_3$  in the aquifer. Silicate dissolution is much slower due to the low reaction rates (kinetics) and silica saturation and accumulation of elements like K, Sr, Na and Ca in these groundwaters is generally less.

Barium concentrations in the aquifer are naturally high in the study area (Edmunds et al., 1989) and locally occurring baryte veins bring the upper limit of the natural baseline concentrations, assessed as the 97.7 percentile, to  $2.9 \text{ mg l}^{-1}$  (although average baseline levels are more likely to be around  $0.1 \text{ mg l}^{-1}$ ).

The distribution of oxidising and reducing parts of the aquifer is very complex and has been complicated by the compartmentalisation of the aquifer due to the presence of impermeable layers within the aquifer. Redox conditions in the groundwater appear to be unrelated to the distribution of the overlying drift deposits; instead, occurrence of reducing groundwaters is often related to depth of borehole. Low Eh levels are observed in many of the deeper boreholes (>40 m), which often maintain high Fe levels due to the relatively reducing environment. The multilayered nature of the aquifer has led to a complex spatial distribution in redox conditions and makes it difficult to predict the chemistry of parts of the aquifer, which requires assessment at a more local level.

Mixing with more saline groundwaters has occurred in the aquifer and there has been an evolution in some parts of the aquifer towards waters of Na- $\text{HCO}_3$  type, implying aquifer freshening. Salinisation also occurs, most clearly indicated by the  $\text{CaCl}_2$ -type waters in the deep borehole at the South Lakeland Caravan site [BNG 34317 46303], but is thought to be unrelated to over-abstraction. There

is some indication that a hydraulic connection exists between the Millstone Grit and the overlying Coal Measures; however, without further data (e.g., from isotope studies), the origin of the high sulphate and/or high salinity groundwater, e.g., at Ramsgreave Laundry [BNG 36810 43085], remains unresolved.

Although most groundwaters in the study area appear not to be largely impacted by direct anthropogenic inputs and thus represent baseline, the baseline has been modified for some solutes. Enhanced concentrations of N-species and DOC, for example, indicate some agricultural pollution. While  $\text{NO}_3\text{-N}$  concentrations in the study area remain relatively low, this is a consequence of reducing conditions in the groundwater, which promote denitrification of  $\text{NO}_3\text{-N}$  at the expense of increasing  $\text{NO}_2\text{-N}$  and  $\text{NH}_4\text{-N}$  levels. On the probability plot, there is possibly a shift in  $\text{NO}_3\text{-N}$  population around  $0.3 \text{ mg l}^{-1}$ , which could be related to pollution, but the trend is obscured by the detection limits. Also, long-term historical records in the study area are very few, so that natural baseline of  $\text{NO}_3\text{-N}$  levels in the aquifer cannot be reliably established, although baseline nitrate concentrations above a few  $\text{mg l}^{-1}$  would not be expected.

Other elements which may have been modified by agriculturally-derived anthropogenic inputs include Na, K, Cl and  $\text{SO}_4$ . There is little evidence of increasing Cl in the historic data, but the data are too short-term and inconsistent with respect to Cl analysis for inferring long-term trends. On the cumulative probability plot (Figure 5.3), Cl displays a relatively linear profile, with a definite shift at high concentrations probably related to mixing with older formation waters. The complex sources of Cl in the study area make it difficult to determine the regional effects of pollution on baseline Cl, since the addition is likely to be within the natural range of concentrations. Na and  $\text{SO}_4$  are also naturally derived. Both elements are enriched in more saline groundwaters, but the initial concentrations have often been modified by ion exchange and reduction/mineral formation processes, respectively. The importance of ion exchange for Na concentrations in the aquifer has been discussed and is consistent with the change in slope of Na on the cumulative probability plot (Figure 5.3), which highlights the different populations of Na in the aquifer. Sulphate, in contrast, displays a relatively linear distribution on the cumulative probability plot (Figure 5.3) and the shift at high concentrations is probably related to inputs from pyrite oxidation. Potassium is most likely to be derived from dissolution reactions of K-feldspar. It is relatively immobile in the surface environment and most anthropogenic inputs will be taken up by biomass or through sorption processes. While it is unlikely that anthropogenic inputs have extended the upper baseline for these elements in the aquifer overall, at a local scale they may impact significantly on the baseline. 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.

## 8. SUMMARY AND CONCLUSIONS

The Millstone Grit aquifer of the Central Pennines of Yorkshire and Lancashire is an important local aquifer providing water for potable and industrial use. The aquifer system is formed by persistent, thick sandstone horizons, which effectively act as separate aquifers with the intervening mudstones and shales acting 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.

In areas where carbonate cements are present, rapid changes occur during recharge and groundwater flow and baseline chemistry is controlled by carbonate dissolution reactions. However, some groundwaters have relatively low pH and alkalinity and probably originate from areas dominated by sandstones of the quartz-kaolinite assemblage, where silicate dissolution controls the groundwater signature.

Locally reduced natural circulation and variations in transmissivity related to the occurrence of argillaceous units 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 solution 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-HCO<sub>3</sub> and CaCl<sub>2</sub>-type waters. The occurrence of groundwaters with a higher salinity indicates mixing with formation waters in parts of the aquifer where flushing (freshening) has not been complete. There is some indication that leakage from the younger Coal Measure units may modify the groundwater chemistry locally leading to increased salinity (salinisation) and/or sulphate levels. The widespread occurrence of Ca-SO<sub>4</sub>-type waters, however, is probably also due to the combined occurrence of pyrite oxidation and calcite dissolution processes in parts of the aquifer.

It is concluded that the properties of Millstone Grit 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 and other major elements such as SO<sub>4</sub>. The presence of locally high concentrations of some trace elements such as Ba and Fe is considered to be mostly due to natural processes of baryte dissolution and pyrite oxidation/iron oxide dissolution, respectively. The drift deposits have a significant effect on the recharge to the aquifer. They afford a degree of protection from diffuse or point source pollution, although shallow groundwaters remain vulnerable to pollution where windows in the drift occur.

## 9. REFERENCES

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