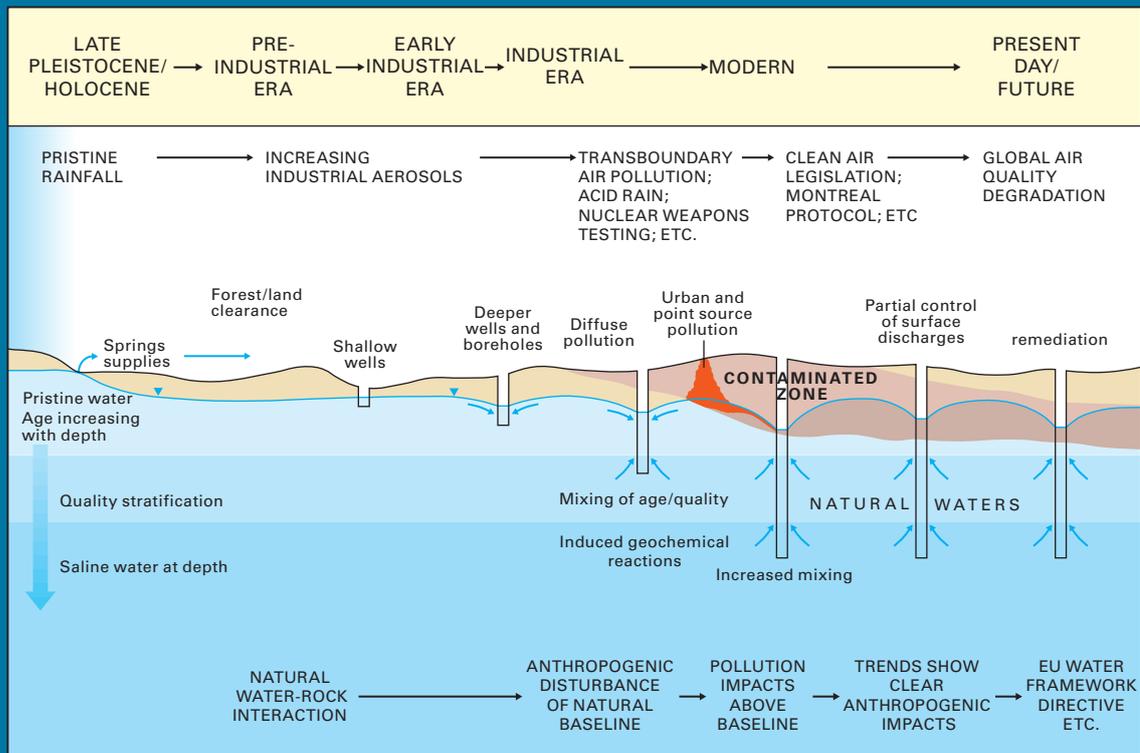




The natural (baseline) quality of groundwater in England and Wales

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Groundwater Programme
RESEARCH REPORT RR/07/06

ENVIRONMENT AGENCY
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The natural (baseline) quality of groundwater in England and Wales

P Shand, W M Edmunds, A R Lawrence, P L Smedley and S Burke

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This document forms a synthesis of a series of reports describing the baseline chemistry of groundwater in selected reference aquifers in England and Wales.

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Conceptual figure highlighting temporal changes from pristine conditions to the modern day.

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Environment Agency Project Manager:

Dr Sean Burke
Science Group: Air, Land and Water

British Geological Survey Project Manager:

Dr Paul Shand
Groundwater Programme

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British Geological Survey offices

BGS Central Enquires Desk

Tel 0115 936 3143 Fax 0115 936 3276

e-mail: enquires@bgs.ac.uk

Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488

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Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

Tel 029 2052 1962 Fax 029 2052 1963

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU

Tel 01392 445271 Fax 01392 445371

Maclea Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

Tel 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

Tel 028 9038 8462 Fax 028 9038 8461

www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

Tel 01793 411500 Fax 01793 411501

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☎ 0121 708 5885 Fax 0121 708 4637

email science@environment-agency.gov.uk

Environment Agency General Enquiry Line

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Environment Agency Regional Offices

Anglian

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Environment Agency Wales

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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 them, 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 it 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. A methodology is required as a scientific basis for defining natural variations in groundwater quality and to ascertain 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 environmental standards. This report presents a synthesis of groundwater chemistry in selected aquifers of England and Wales carried out by the British Geological Survey and the Environment Agency.



Fulking spring [TQ247 113] issues from the scarp slope of the Chalk Downs, West Sussex.

It is based on a series of reports of selected aquifers which aimed to assess the controls on water quality responsible for the natural variations seen in groundwater. It also provides a background for assessing the likely outcomes and timescales for restoration.

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Executive summary

This report provides a summary of data for the chemistry of groundwater from 26 aquifers in 23 areas across England and Wales, studied as part of the British Geological Survey/Environment Agency collaborative project *The natural (baseline) quality of groundwaters in England and Wales*. This was carried out over the period 1999 to 2005. The studies involved collation of available information on regional hydrogeology, aquifer lithology, mineralogy and geochemistry, rainfall chemistry and land use, as well as groundwater chemistry. These lines of evidence have been used to determine the spatial and temporal variations in the concentrations of a large number of inorganic constituents in groundwater, to ascertain the main processes controlling their distributions and in so doing, to characterise the likely natural baseline concentrations. Understanding the baseline chemistry of groundwater in a given aquifer provides an important basis for defining the nature and scale of current pollutant impacts, the scale of past inputs and of any remediation required. Hence, better understanding of the baseline chemistry of groundwater provides the underpinning framework for implementation of European Union legislation aimed at groundwater protection and mitigation.

One important conclusion from the study is that natural variability in groundwater chemistry is large. Groundwater chemistry varies as a function of a number of factors such as rainfall chemistry, aquifer lithology, geochemical environment, groundwater flow paths and residence time. Hence, the baseline for a given element or compound will vary significantly both between and within aquifers. It is, therefore, scale-dependent and should be considered as a range rather than a single value. The upper limits of baseline concentrations can exceed environmental-quality or drinking-water standards as the latter are usually imposed on ecotoxicological or human health grounds and are divorced from observed groundwater concentration distributions. Examples include As, Mn and Ni. For many other trace elements, there is currently no EC drinking-

water limit. This is, for example, the case for U, where a number of groundwaters sampled in the present study had small concentrations exceeding the WHO provisional guideline value for U of $15 \mu\text{g l}^{-1}$.

For many solutes, the baseline concentration range often overlaps with that controlled by pollution. Hence it is often difficult to discriminate between baseline and pollution by a purely statistical approach. It is useful and necessary to study data at relevant scales in order to determine realistic estimates of baseline.

Of the inorganic constituents considered in groundwaters from England and Wales, that which exceeds European drinking-water limits most often is nitrate. The range of baseline concentrations for NO_3 in groundwater is probably significantly lower than the EU drinking-water limit of 11.3 mg l^{-1} as N, the upper limit (threshold) being probably around 4 mg l^{-1} as N. Hence, a substantial number of groundwater samples investigated have NO_3 concentrations resulting from pollution. Phosphorus is also of significant interest since it is a major component in agricultural fertilisers and hence an important diffuse pollutant. Although usually considered to be immobile in the groundwater environment, it has been found at relatively high concentrations in a number of samples in the regional studies. Although some of the P in groundwater is of pollutant origin, some is also derived by natural geochemical processes.

The baseline reports (listed in Appendix 1) give a summary of groundwater data from some 3000 sample sites. As such, they provide a current view of the state of inorganic groundwater chemistry from a range of aquifers across England and Wales. The data and conclusions provided by the regional reports and this summary report are designed to be of use to regulatory authorities, water utilities, groundwater users, and all those involved in the protection and remediation of groundwater. It also provides a useful summary for researchers and other end-users involved in water chemistry and quality.



Artesian flow from Catcraig borehole [NT 717 773], seven kilometres from Dunbar, Scotland, c.1908.

1 Introduction

Groundwater is a valuable natural resource, being both an important source of water supply and a major component of the water cycle. In England and Wales, groundwater supplies around 35 per cent of the total water abstracted for public water supply. In south-eastern England, this figure increases to around 70 per cent, similar to that in Europe as a whole. Groundwater is also critical to maintaining summer baseflow to rivers and wetlands and hence plays a role in sustaining sensitive ecosystems (Plate 1). Monitoring, management and protection of groundwater quantity and quality are therefore important economic and environmental objectives.

The characterisation and monitoring of the chemical quality of groundwater in an aquifer is a critical component of groundwater management and protection. Such assessments provide the basis for defining the suitability of groundwater for its intended purpose (e.g. drinking water), identifying pollution inputs and establishing whether or not groundwater quality is deteriorating with time. The main European driver for the characterisation and monitoring of groundwater quality is European Union legislation in the form of the Water Framework Directive, Groundwater Directive, EC drinking-water regulations



Plate 1 A stream in the Bourne River catchment in Hampshire, illustrating the important role played by groundwater in sustaining baseflow to rivers.

and environmental quality standards. The Water Framework Directive aims to provide for the protection and enhancement of water bodies in Europe by preventing inputs of chemical pollutants or reversing chemical trends to achieve good status. For these objectives to be achieved, a knowledge of the natural or 'baseline' chemistry of the water body is an important starting point in order that anthropogenic impacts can be measured with an acceptable degree of confidence. Knowledge of the baseline thus provides a datum against which changes in chemical composition imposed by pollution can be assessed.

Attempting to define the natural baseline chemistry of groundwater from a number of defined aquifers or aquifer regions in England and Wales has been the objective of the project 'Baseline' (*The natural (baseline) quality of groundwaters in England and Wales*), a collaboration between the British Geological Survey (BGS) and the Environment Agency (EA). The project has involved the characterisation of spatial and temporal variations in groundwater chemistry and interpretation of the dominant controlling processes within a given study area. For each study area, this has been achieved through collation of existing reliable groundwater, rainfall and host-aquifer mineralogical and geochemical data, as well as new strategic sampling of around 25 to 30 groundwater sources for a comprehensive suite of inorganic determinands. For some areas, these newly analysed samples represent the only sources of reliable groundwater chemical data available.

The areas chosen for investigation are intended to provide a chemical dataset for groundwater in aquifers across England and Wales covering a range of lithological types. Study areas were also chosen in accordance with the operational priorities of the Environment Agency regional offices. The studied areas include examples of major aquifers as well as a number of minor aquifers that although less significant in terms of abstraction volume may be important locally, particularly for small-scale private supplies. The areas investigated were not necessarily those defined as groundwater bodies by the Environment Agency as part of the national implementation of the Water Framework Directive, as the project started before these were defined.

Over the period 1999 to 2005, the project investigated the baseline quality of groundwater in aquifers or aquifer blocks in 23 study areas. The areas covered in this phase are:

1. Triassic Sandstones of the Vale of York
2. Permo-Triassic Sandstones of West Cheshire and the Wirral
3. Permo-Triassic Sandstones of South Staffordshire and North Worcestershire
4. Chalk of Dorset
5. Chalk of the North Downs, Kent and East Surrey

6. Chalk of the Colne and Lee River Catchments
7. Great and Inferior Oolite of the Cotswolds District
8. Permo-Triassic Sandstones of Manchester and East Cheshire
9. Lower Greensand of southern England
10. Chalk of Yorkshire and North Humberside
11. Bridport Sands of Dorset and Somerset
12. Devonian aquifer of South Wales and Herefordshire
13. Great Ouse Chalk aquifer, East Anglia
14. Corallian of Oxfordshire and Wiltshire
15. Palaeogene of the Wessex Basin
16. Granites of South-West England
17. Ordovician and Silurian meta-sedimentary aquifers of central and south-west Wales
18. Millstone Grit of Northern England
19. Permo-Triassic Sandstones of Liverpool and Rufford
20. Permo-Triassic Sandstone aquifer of Shropshire
21. Chalk and Crag of North Norfolk and the Waveney Catchment
22. Carboniferous Limestone of northern England
23. Lincolnshire Limestone

A complete bibliography of the reports produced during this phase of the Baseline project is provided in Appendix 1.

This report provides a summary and overview of the results produced from the series of 23 regional reports. The report compares and contrasts the aquifers investigated and aims to provide an overall assessment of the current state of groundwater quality in aquifers in England and Wales.

2 Baseline and groundwater quality

2.1 INTRODUCTION

The chemistry of groundwater varies widely as a function of the many complex geological, geochemical, hydrogeological and climatic factors which control chemical evolution. This gives rise to large spatial and depth variations at a range of scales (Figure 2.1). Temporal variations in groundwater chemistry are also to be expected in response to varying atmospheric inputs, changes in aquifer mineralogy and solubility and kinetic controls related to varying residence times. The pollution of groundwater from agricultural, industrial and urban sources poses a significant threat to sustainable groundwater use in catchments (Figure 2.2), particularly in shallow unconfined aquifers or fractured aquifers that allow rapid flow and transport of pollutants through the unsaturated zone. Understanding the nature and scale of pollution in a given aquifer and any changes in water quality with time is a fundamental requirement for aquifer

Figure 2.1 Graphic to illustrate that baseline quality is likely to vary both in space and time as a result of variations in the landscape, climate, chemical inputs and residence time.

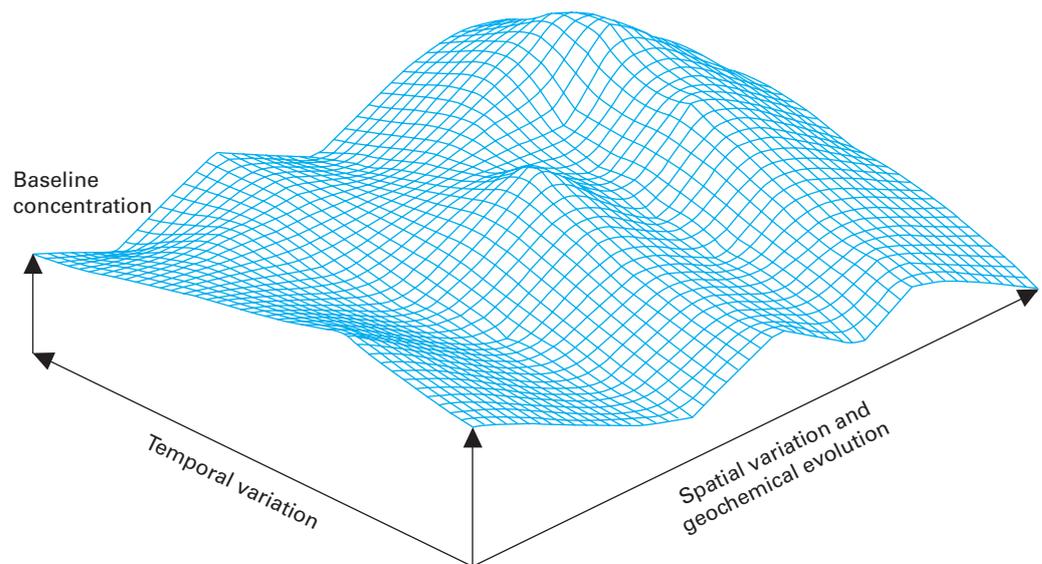
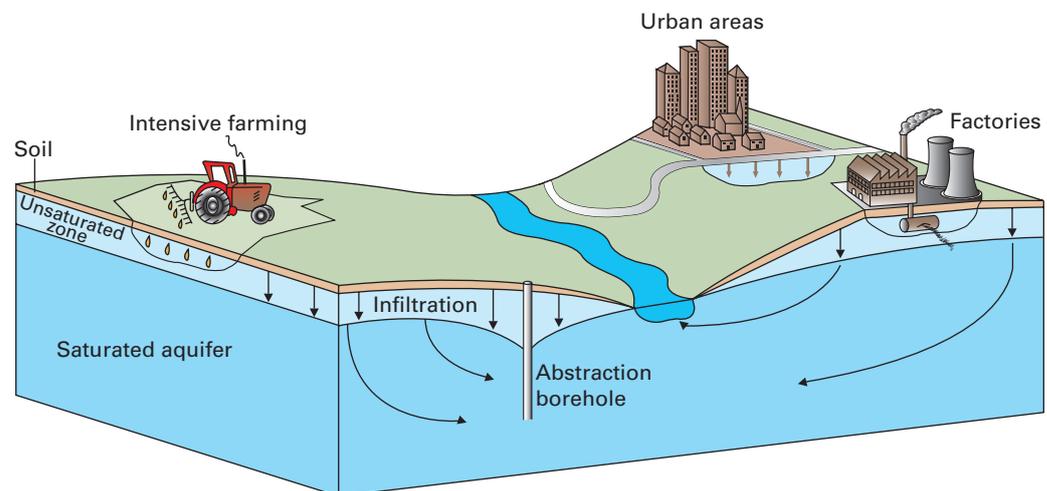


Figure 2.2 Illustration of the variety of natural and anthropogenic inputs and a range of flow pathways that give rise to large variations in water chemistry.



management and protection. The EU Water Framework Directive imposes rigorous controls on the quality of water used for drinking and impacts on specific receptors such as surface water ecosystems. However, the limits for many solutes may be breached due to entirely natural processes as well as pollution inputs (Banks et al., 1998; Shand and Frengstad, 2001). Understanding the nature and scale of pollution requires first a knowledge of the natural or 'baseline' chemistry of groundwater in the aquifer.

2.2 THE CONCEPT OF HYDROCHEMICAL BASELINE

The concept of hydrochemical baseline is difficult to define in detail and opinions differ on the meaning and application of the term. The presence of purely anthropogenic substances (e.g. pesticides, BTEX or

CFCs) indicates a departure from the natural or 'baseline' condition, but for many solutes, which can be derived either from pollution or natural sources (e.g. NO₃, P, As), the distinction is less clear-cut. In addition, although groundwater may be polluted, individual components may be naturally-derived. For the purposes of this study, baseline is defined (Shand et al., 2002) as:

'the range in concentration (within a specified system) of an element, species or chemical substance present in solution which is derived by natural processes from natural geological, biological, or atmospheric sources'.

Terms such as 'background' and 'threshold' have been used synonymously (Matschullat et al., 2000; Reimann and Garrett, 2005), but there exist several definitions of these terms. These were originally coined in exploration geochemistry to distinguish between 'normal' element concentrations in barren areas and geochemical anomalies that might indicate ore occurrence (Hawkes and Webb, 1962) but have been used subsequently in environmental investigations. The term threshold was originally applied as the upper limit of the background range. This was later refined to the 'outer' limit of the background range in recognition that anomalies from the norm may be low as well as high (Reimann and Garrett, 2005). However, for water quality, it is assumed here that pollution effects are generally additive and are therefore manifested by increases in solute concentrations rather than decreases. It has been suggested that the terms background and threshold should be used in preference to baseline in both exploration and environmental contexts (Reimann and Garrett, 2005).

It could be argued that baseline concentrations of solutes in groundwater should be those that pertained in an aquifer in pre-industrial times. However, this promotes some difficulties since data for these are rarely if ever available because monitoring is a relatively recent development. Surrogates for pre-industrial conditions have been taken from palaeowaters deemed to be of pre-industrial origin through radiometric dating evidence (Bath et al., 1979; Darling et al., 1997). However, in such cases care needs to be taken to ensure that the pre-industrial groundwater is representative as an unpolluted form of the groundwater under investigation. This may not be the case if residence

time in the aquifer has led to significant time-dependent modifications to the groundwater chemistry or it has been modified by mixing with old formation waters. As old pre-industrial groundwaters are also typically found in confined aquifers (Plate 2) where reducing conditions prevail, their baseline compositions can differ significantly from those in the unconfined aerobic sections of the same aquifer because of redox-controlled changes.

A further problem with the above definition of baseline regards deciding what constitutes a natural process. Man has had a long-term impact on the environment (Figure 2.3) and many anthropogenic activities, while not directly introducing pollutants to groundwater and the wider environment will have altered the natural system significantly. Mining activity can lead to release of many toxic trace elements into the environment. Oxidation of sulphide minerals is a natural geochemical process though its driver in this case is man. Metal mining has also been carried out in the UK since pre-Roman times and so determining what proportion of solutes in groundwater in the affected area is natural and what proportion influenced by the mining legacy is fraught with difficulty. The same applies to impacts on groundwater chemistry of forest clearances spanning several thousand years as well as impacts from modern groundwater abstraction. Groundwater pumping can lead to large changes in flow patterns and can induce leakage or upwelling from adjacent formations or saline intrusion in coastal areas. All these processes are natural yet catalysed by man.

Such modifications to the natural situation have been described variously as 'ambient background' (Reimann and Garrett, 2005), 'environmental baseline' (Lee and Helsel, 2005) or 'modified baseline'. Lee and Helsel (2005) use the term environmental baseline to represent a summary of existing conditions in an aquifer over a given time frame, a definition which inevitably includes some anthropogenic influences. Most productive aquifers contain groundwater with residence times on the order of tens to hundreds of years and many contain some evidence of recent anthropogenic impacts, either directly or indirectly. Providing criteria for defining baseline status for a given groundwater body is a non-trivial task.

Whatever the semantics of the term baseline, there is a consensus that the baseline concentration of a given solute

Plate 2 Deep artesian borehole in the Chalk aquifer at Lytchett Minister, Dorset. Such groundwaters often represent pristine waters unaffected by the influence of man.



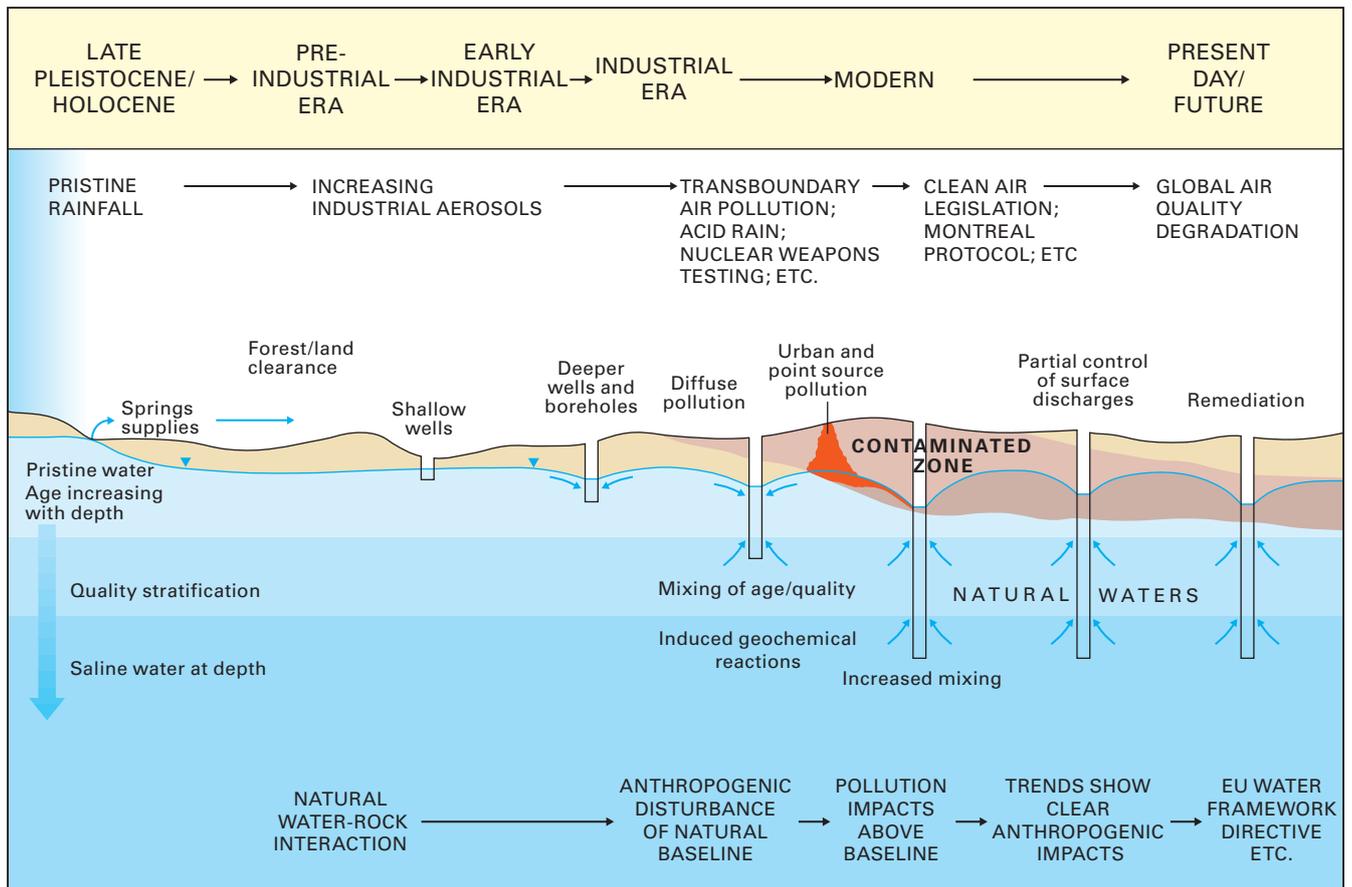


Figure 2.3 Conceptual figure highlighting temporal changes from pristine conditions to the modern day.

can be very variable spatially, both between and within aquifers, as it is controlled by numerous interacting factors including bedrock geology, climate, type and thickness of overlying soils and superficial sediments and groundwater residence time. The large variations in solute concentrations in groundwater at different scales mean therefore that baseline can only be derived for a defined spatial setting, hence the term “system” in the baseline definition. The baseline is therefore inevitably represented by a range rather than a single value. It is important also to stress that although a groundwater body may have been impacted by pollution, the scale of the impact may be significant for some solutes but negligible for others. It is therefore logical to consider baseline status on a solute-by-solute basis rather than attempting to designate the status of a water body overall.

For most inorganic solutes, natural biogeochemical processes have a dominant control on groundwater quality. As these processes are entirely independent of health or ecotoxicological considerations, baseline concentrations of several solutes can exceed regulatory limits such as drinking-water or environmental-quality standards, particularly for some relatively abundant trace elements that are highly toxic (e.g. As). High concentrations of naturally-derived solutes should not be confused with pollution. It is important that this fact is understood by regulators because it has a potentially large impact on groundwater-management and mitigation policy and a major cost implication.

Knowledge of the baseline quality of groundwaters and criteria for defining baseline are needed, both as a reference to establish whether pollution is occurring, and to provide data on the degree to which remediation of polluted environments is possible. This determines

whether or not mitigation measures are deemed necessary. Any attempt at remediation measures to attain values less than the local baseline may be either impractical or prohibitively expensive. Thus it is important to establish the extent to which individual solute concentrations have increased by pollution above the baseline. For this, standard statistical methods are often used. As many of the outlier compositions may be produced by natural biogeochemical processes, it is important that the statistical handling is underpinned by an understanding of the various processes controlling groundwater chemistry. For this, a detailed assessment of available hydrogeological, geochemical, hydrogeochemical and land-use data for the area of investigation is required.

2.3 CHANGES IN GROUNDWATER QUALITY WITH TIME

An ideal starting point for assessing baseline is to locate waters where there are no traces of human impact. As noted above, the modification of groundwater chemistry was probably initiated several thousand years ago when forests began to be cleared to make way for subsistence agriculture (Figure 2.3). It is unlikely that such changes in the water-chemistry record can be distinguished from natural modifications induced by climate change or indeed from modern anthropogenic inputs. This has continued since that time with progressive urbanisation, mining and other industrialisation and agricultural development (Figure 2.3).

One of the most significant historic influences on groundwater chemistry is likely to have occurred during the time of the Industrial Revolution, especially around

the large industrial cities of the Midlands. This not only affected direct inputs of pollutants to the groundwater, but began to modify the composition of the atmosphere which provides an important source of some solutes to groundwaters. Urbanisation and industrialisation will have provided localised contamination, including NO₃ and Cl from domestic wastewater, and a number of trace elements.

Agriculture has had a more widespread impact on groundwater quality by diffuse pollution. As agriculture became more intensive, inputs of agricultural chemicals had a significant effect on groundwater and diffuse pollution. Nitrate, in particular, is now one of the most widespread threats to groundwater. This threat has been most pronounced since the 1940s, with the advent of more intensive agricultural practices. The changes in nitrate concentration in four borehole sources since the early 1900s are shown on Figure 2.4. The increasing gradient in nitrate concentrations over time reflects the historical changes in fertiliser application. However, the timescales of groundwater movement in aquifers mean that there may be a lag of several decades before such applications of nitrate reach the groundwater table, and the problem may persist for hundreds or even thousands of years in some circumstances if no natural degradation of nitrate occurs.

2.4 QUANTIFYING BASELINE

There are no firmly established criteria for defining the baseline or background chemistry of groundwaters. Several approaches have been advocated (Runnells et al., 1998; Shand and Frengstad, 2001; Edmunds et al., 2003 and EC, 2005), including:

- i sampling up-gradient and cross-gradient of contaminated areas

- ii extrapolation using historical water-quality data
- iii extrapolation from similar geochemical environments
- iv dating of groundwaters
- v assessing down gradient changes in hydro-chemistry
- vi geochemical modelling
- vii statistical methods.

All of these methods have potentially useful application (Table 2.1) and can be used together. Indeed, it is unlikely that there will be sufficient data available for any one of these approaches to be wholly successful, and some combination of them is therefore appropriate.

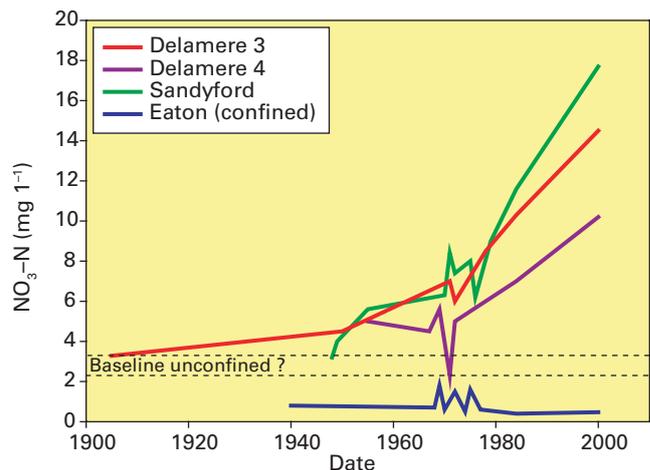


Figure 2.4 Time series data for NO₃-N in groundwaters from three unconfined and one confined site in the Sherwood Sandstone aquifer. Changes with time reflect the intensity of inputs.

Table 2.1 Methods for assessing the baseline chemistry of groundwaters.

Method	Use	Limitations
Assessment of historical groundwater quality data	Reveals any temporal trends that may reflect anthropogenic inputs	Long-term monitoring data are rare Range of solutes monitored is limited (more often for nitrate and organic compounds than other determinands) Data may be of variable quality Detection limits may have changed over time and may be too high to be of relevance
Comparison of up-gradient and cross-gradient groundwater quality	Allows spatial distributions in groundwater chemistry to be assessed relative to point sources of pollution	Not appropriate for areas affected by diffuse pollution or areas where pollution sources are not obvious (e.g. septic tanks) Care needed to ensure like-with-like comparison because of heterogeneity in aquifer lithology, geochemistry and groundwater flow regime
Comparison with similar geochemical environments	Comparison with same/similar aquifer in a different region or with confined section of the same aquifer	Regional heterogeneity in aquifer lithology, geochemistry and groundwater flow Comparison of unconfined groundwater chemistry with confined groundwater chemistry has problems because of differences imposed by groundwater residence time, mixing with old groundwater, differences in groundwater flow and redox changes
Geochemical modelling	Can provide thermodynamic support to hypotheses on groundwater chemical evolution and pollution, and quantitative models of the effects of mixing a baseline groundwater with a pollutant	Requires some geochemical skill Requires sufficient thermodynamic data, understanding of aquifer flow regime and knowledge of end-member compositions to put into the models Biogeochemical reactions not necessarily at thermodynamic equilibrium
Statistics	Can distinguish 'typical' from 'anomalous' compositions and provides a useful summary of groundwater chemistry data for a given area	Needs to be carried out concurrently with a study of hydrogeochemical processes Needs an awareness that anomalous compositions can result from natural processes as well as pollution

2.4.1 Baseline approaches

The simplest way to determine the baseline of a specific substance within a system (as defined above) is to analyse the range in concentration of the baseline substance in pristine waters. There are two main problems with this simple, but ideal, approach. First of all, most pristine groundwaters in aquifers only exist in areas where the resource is low, where it is protected (e.g. confined), the resource is very deep, or where the quality is poor and the aquifer has not been actively developed. In such areas, the groundwaters may also be very old (palaeowaters) and because many chemical reactions are kinetically controlled (i.e. time dependent), these may not be representative of the parts of the aquifer which are actively developed (Figure 2.5). In addition, the geochemical environment may be different e.g. in confined aquifers, groundwater may be reducing and the chemical processes very different from unconfined aquifers which are typically oxidising. Most of the important aquifers in England and Wales show the effects of diffuse pollution such as enhancement of nitrate concentrations, and a methodology needs to be developed to determine the baseline in the groundwater bodies in these aquifers.

The use of historical water-quality data is one of the best and most direct methods to determine the baseline for a solute. Unfortunately, there are very few datasets that extend back more than a few decades, and in many cases, chemical analysis has typically been carried out for only a limited number of determinands. Even where data are available, temporal changes in gradient (e.g. Figure 2.4) can result from changes in pollutant inputs or changes in pumping rates and these can complicate the interpretation of the available data. Problems can also arise if analytical techniques and detection limits have varied over the course of the period of monitoring.

Extrapolation from analogous aquifers or areas can also be useful if applied carefully. However, natural variability in flow pathways, aquifer mineralogy and geochemistry is such that large heterogeneity in groundwater chemistry is expected. Our understanding of the complex interacting processes involved in deriving groundwater chemical compositions is usually sufficiently limited that making such extrapolations is likely to be prone to error, particularly for many of the trace elements where usually far fewer data exist. Extrapolation of likely baseline chemistry from

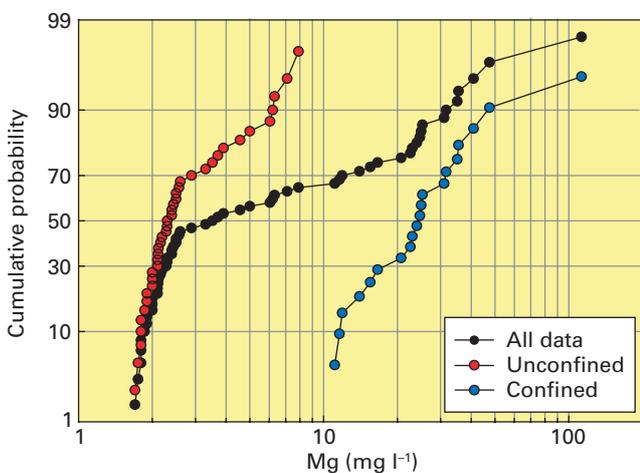


Figure 2.5 Cumulative frequency plot for Mg in groundwaters of the Chalk aquifer (data from Shand et al., 2003). The data for the unconfined and confined parts of the aquifer show distinct populations.

old (pristine) waters in the same aquifer is also prone to difficulties because of differences generated by residence time, mixing and redox processes (Table 2.1). This is well-illustrated for nitrate in Figure 2.4; groundwater from a borehole in the confined Sherwood Sandstone has much lower and less variable concentrations of nitrate than that from a borehole in the unconfined aquifer. It is difficult to know from the graph whether the differences are due to the protection of the confined source from recent pollutant inputs, in which case comparison with an unconfined source would be legitimate, or due to partial denitrification of the confined source, in which case it would not.

Groundwater dating tools are invaluable for assessing changes in chemistry with time. Several techniques are available for dating groundwaters of different age (Chapter 3) and used in combination with chemical variations along hydraulic gradient may help to distinguish polluted sites or highlight changes in baseline with time. Multiple dating tools are recommended due to problems of mixing of water of different residence time during sampling. Geochemical modelling techniques may offer some useful indications of the degree to which some parameters have been modified by pollution. Modelling can be used to substantiate hypotheses on geochemical evolution of groundwaters and may identify changes that are not obvious from a study of the data themselves.

Statistical methods are among the most valuable tools in baseline-quality assessments and have been applied widely. Statistical-summary data (medians, means, standard deviations, quantiles, ranges) can provide useful information but several inherent pitfalls apply with geochemical, and especially hydrochemical data. Firstly, datasets frequently contain a high proportion of non-detects for many trace elements which precludes the calculation of reliable mean values. As a result, medians are often preferred as indicators of central tendency. Secondly, many data populations do not have normal or log-normal distributions and it is recognised that outliers in these populations can produce spuriously large ranges. In most natural systems geochemical distributions are generally polymodal and are usually skewed (Reimann and Filzmoser, 2000). The traditional assumption that geochemical datasets are either normal, or more generally, lognormal (Ahrens, 1954) limits the application of many traditional statistical tests. Ideally, non-parametric statistical tools should be engaged to account for the non-normal distributions of geochemical data since they are not based on model assumptions. Hence, simple maxima, minima and means are often not the best ways of assessing groundwater compositions. As a result, various cut-off points which exclude outliers as well as extremes have been used to try to define an upper limit, or threshold, of baseline concentrations (Edmunds et al., 1997; Kunkel et al., 2004; Reimann et al., 2005).

Hawkes and Webb (1962) used the 'mean + 2 standard deviations' as a threshold to define anomalously high concentrations for use in mineral exploration. Similarly, the median + 2 median absolute deviations (median of the absolute deviations from the median of all data) has been used to exclude extremes (Tukey, 1977; Reimann et al., 2005). Various percentiles have also been used, although the choice of percentile is somewhat arbitrary. Lee and Helsel (2005) used the 90 to 95th percentiles in assessments of baseline groundwater chemistry in the USA. In the first phase of the baseline project, 95th percentile values were calculated and for many determinands taken as indicators of the upper limit of baseline concentrations

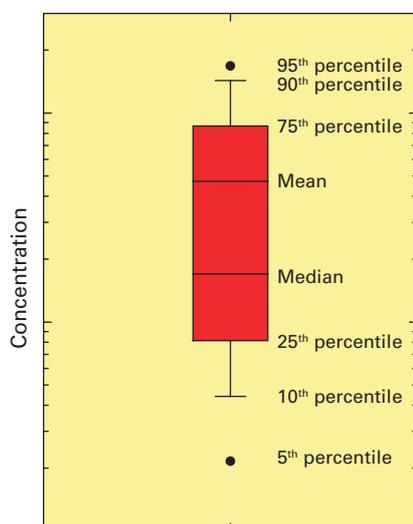
(Edmunds et al., 1997). Similarly, the 97.7th (or 98th) percentile value has been used in groundwater-chemistry investigations (Langmuir, 1997) as a measure of the mean + 2 standard deviations for data fitting a normal (or log-normal) distribution. This does not apply for data which display bi-modal, multi-modal or skewed distributions (Miller and Goldberg, 1955; Reimann and Filzmoser, 2000). In such cases, it would be logical to separate the distributions and define separate medians and quantiles for each.

There is no *a priori* reason why non-baseline data should fit neatly within the upper 2 to 10% of a data population. For example, most groundwaters in unconfined aquifers in England and Wales have enhanced concentrations of nitrate as a result of inputs from agricultural practices. A simple upper threshold concentration defined on a percentile basis is not helpful here as values below the threshold would not necessarily represent baseline. Likewise, data above the selected cut-off percentile may themselves in some cases represent baseline; such techniques do not take into account the fact that anomalous and background concentrations often show significant overlap (Sinclair, 1974). Nevertheless, the 90 to 98th percentiles by definition represent the concentrations that are exceeded by only 2 to 10% of samples and they therefore define the concentrations that are unlikely to be exceeded in subsequently analysed samples unless conditions have changed. Even for multi-modal data populations, an overall cut-off in the 90 to 98th percentile range represents a useful first approximation as it excludes the most significant outliers. The 97.7 percentile has been used in the present study simply as a means to remove outlying data from a population.

2.4.2 Presentation of data

Box plots, histograms and cumulative-frequency (or cumulative-probability) diagrams have also proved useful in characterising chemical data distributions. They are also readily available in many statistical plotting packages. Box plots (Tukey, 1977) can be useful indicators of baseline ranges as they show graphically the data ranges of a population and highlight outliers (Figure 2.6). Here, the upper and lower hinges (margins) of the box are defined as the 25th and 75th percentiles displaying the inter-quartile range (i.e. 50% of the data) and the whiskers usually denote the 10th and 90th percentiles (lowest and highest data points that lie within the range defined as 1.5 times

Figure 2.6 Box plot (or box and whisker plot) showing how the data are plotted on a percentile basis.



the inter-quartile range). Outliers beyond this range can be denoted by separate symbols. The box plot represents a relatively robust approach to data assessment as it makes no prior assumptions about the data distribution. Reimann et al., (2005) concluded that box plots were the most useful statistical tools for assessing baseline (or background) concentrations provided that outliers comprised less than 15% of the dataset.

The use of cumulative-probability diagrams has been promoted as a succinct means of identifying distinct populations in groundwater datasets (Runnells et al., 1998). Probability plots have also been used extensively in the mineral exploration industry to define anomalous concentrations. Cumulative-frequency diagrams and cumulative-probability diagrams are similar except that the y-axis is defined differently. The cumulative frequency represents the cumulative number of observations for each value in the observed range. Each point on the frequency curve represents the total number of samples for all values less than or equal to the current value. The cumulative-probability distribution merely normalises the frequency values by the number of samples in the dataset so that they sum to 1 (or 100%). The cumulative probability plot is preferable as it spreads out the data at the extremes, which are the areas of greatest interest in this context (Reimann et al., 2005).

If the concentration (x-axis) scale in a probability plot is logarithmic, a log-normal distribution will plot as a straight line while a bimodal or multimodal distribution will be curved (Sinclair, 1974). This relationship can be used to identify pollutants because these are subject to different processes or sources and hence may form data populations which are distinct from those derived by natural processes. Hence in cumulative-probability plots, maximum flexure may be used to discriminate baseline chemistry from pollution-impacted compositions. Care must be taken with their interpretation however, as data ranges for baseline populations can overlap with polluted populations and there are several types of natural biogeochemical reaction that can alter data distributions by removing or limiting concentrations in solution (Figure 2.7). These include redox reactions, adsorption reactions and mineral-solubility controls. For example, dissolved nitrate may be lost under reducing conditions through denitrification, adsorption of metals onto mineral surfaces can reduce solute concentrations, and equilibration with aquifer minerals can define upper limits for solute concentrations. For trace elements where many values may be below the detection limit, cumulative-probability plots tend to represent the distributions at the low end as straight lines. These are seen frequently in the plots of the groundwater data from this study.

Maps are also a valuable way of representing spatial geochemical data and can be used to characterise regional variability on various scales (Darnley, 1997; Reimann and Garrett, 2005). Maps allow spatial relationships between groundwater chemistry and factors such as geology, soil type and land use to be assessed. They can also be used in conjunction with cumulative-probability plots to pinpoint the locations of outlier data and potentially help with the interpretation of causal processes. Multi-variation outlier plots have also been used recently to take into account non-normal data distributions and highlight anomalous chemical compositions spatially (Filzmoser et al., 2005). The great advances in GIS software in recent years have been of considerable value in mapping and visual representation of spatial data.

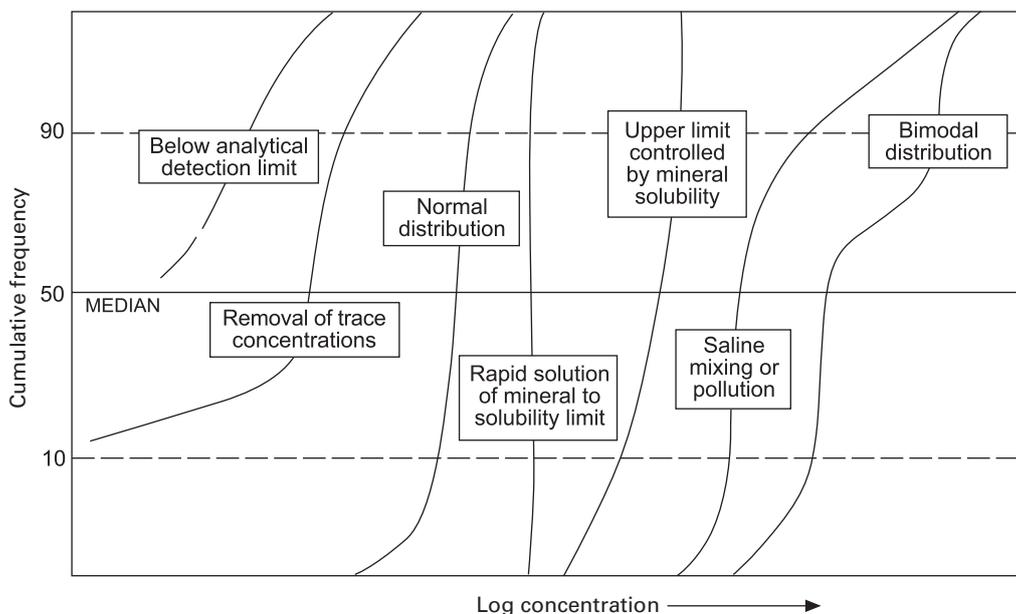


Figure 2.7 The baseline characteristics of groundwaters illustrated by cumulative frequency curves. Curve types include normal and bimodal distributions, and variants due to control by various additional analytical and geochemical factors. The median and upper and lower percentile limits can be used as a reference for the baseline on cumulative probability plots.

For practical purposes, it is necessary to specify the scale of the system of interest. This may vary from the groundwater within an entire aquifer, to a groundwater body within an aquifer section, to a single groundwater source. The observed ranges of solute concentrations will obviously vary at these different scales as a function of the differing controls within the defined area. In order to define baseline, datasets should also ideally exclude samples that are obviously polluted, although as stated above pollution will inevitably affect different solutes to different extents.

The above discussion has covered the main techniques that are considered useful in determining baseline. Individually, these may only provide limited insights into the baseline quality of aquifers, but together they can help to disentangle the often complex natural and anthropogenic processes leading to chemical change in groundwaters. As noted in Section 2.2, although statistical methods are widely used to assess baseline concentrations of solutes in aquifers, they should not be used in isolation and a basic understanding and investigation of the underlying processes controlling groundwater chemistry and chemical variation is also required (Edmunds et al., 1987). In making assessments of the baseline, inevitably some subjective judgement is also required.

In order to use statistical methods, it is important to have representative samples of the system as well as a large number of samples. The characterisation of groundwater chemistry in aquifers is difficult to establish for a number of reasons: sampling is often biased towards parts of the aquifer which are most productive (e.g. valley bottoms in Chalk aquifers), samples may be limited to specific (shallow) horizons in the aquifer, the sample may represent a mixture of waters where long screen intervals are used to maximise groundwater abstraction, and the sample may not, in extreme cases, be representative of any groundwater in the aquifer.

2.5 RELEVANCE OF BASELINE TO GROUNDWATER POLICY AND MANAGEMENT

The most significant legislation in Europe that affects the characterisation and management of groundwater resources are the EU Water Framework Directive (WFD, 2000/60/EC) and the daughter Groundwater Directive which are to supersede the 1980 EC directive (80/68/EEC). A key purpose of these directives is to prevent further deterioration of water quality (both surface water and groundwater) from pollution and to protect, enhance or restore its 'good' status by 2015. This involves prevention or reduction of inputs of pollutants and reversal of any significant and sustained upward trend in the concentration of a pollutant within a decadal time frame. Arrangements for implementing these directives is the responsibility of the individual member states. In the case of England and Wales, this task lies with the Environment Agency.

The procedures for implementation of the WFD and Groundwater Directive in Europe have not yet been fully established and are the subject of much current debate. An important step in the implementation process in respect of groundwater has been the delineation and characterisation of 'groundwater bodies', including their current chemical status and an analysis of the key pollution pressures on the defined body. Some 356 groundwater bodies have been defined by the Environment Agency for England and Wales. These were defined after the studies carried out under this project and so they do not necessarily correspond with the areas covered by the 23 studies summarised in this report.

One of the key steps in the assessment of groundwater chemical status has been the attempt to establish threshold values for chemical parameters against which observations can be compared. Key parameters listed in the Groundwater Directive include, as a minimum, NH_4 , As, Cd, Cl, Pb, Hg and SO_4 , as well as the organic

substances trichloroethene and tetrachloroethene. With the exception of NO_3 , which is covered by the separate EC Nitrate Directive (91/676/EEC), threshold values have not been defined for these parameters, although research on threshold values is continuing under the EU 6th Framework Programme. The definition of an EU-wide set of thresholds is not likely to be achievable and parameters, and their respective threshold values, are likely to be set at national or regional level. This throws some uncertainty on the future of national requirements for monitoring and mitigation. The NO_3 threshold for groundwater is preserved in the Groundwater Directive as 50 mg l^{-1} (11.3 mg l^{-1} as $\text{NO}_3\text{-N}$) as defined in the Nitrate Directive, and is an attempt to restrict pollution from diffuse agricultural sources. However, the value is based on health considerations in respect of drinking water and bears little relationship with baseline concentrations or current chemical status of groundwaters, or indeed with ecotoxicological considerations.

For the Environment Agency to be able to define 'good chemical status' and to implement the WFD and evolving Groundwater Directive, basic information is required on both current groundwater chemistry and the baseline conditions against which pollution impacts can

be measured. This has been one of the drivers for carrying out the regional assessments in the 23 aquifers or areas studied. However, it is likely that the definition of status will be different for different receptors. Understanding the baseline compositions and natural variability in aquifers are also necessary for the optimisation of groundwater monitoring networks and monitoring protocols. These are essential to the implementation of the EC directives and to groundwater management more generally.

Understanding baseline compositions in groundwaters is also of considerable relevance to the water industry. There is a need to assess the natural ranges of solutes in a given environment relative to drinking-water standards and so define the scale, and hence cost, of any mitigation measures required. This is particularly important since the European and national drinking-water limits for a number of trace elements (As, Ni, Pb) have recently become much more stringent and so present new challenges to the water industry. For many trace elements (e.g. As, U), the availability of new data is revealing hitherto unsuspected groundwater-quality problems in some areas and is improving significantly the understanding of their distributions and causes.

3 Controls on baseline

3.1 INTRODUCTION

The chemistry of groundwater is affected by numerous interacting processes which are often difficult to distinguish and quantify. Initial inputs from rainfall are important for some solutes. Once in the subsurface, groundwater chemical compositions evolve through biogeochemical reactions in the soil zone, unsaturated zone and ultimately the saturated zone. Groundwaters evolve by a complex sequence of mineral reactions, many aided by microbial activity, as well as gaseous exchange, sorption reactions, mixing and dilution. Some solutes are also introduced as a result of human activity at the surface. Groundwater flow has an important impact on the spatial diversity of groundwater chemical compositions as rates and patterns of flow affect the transport of solutes (including pollutants), rates of mixing and dilution and groundwater residence time. This chapter describes some of the most significant processes involved in controlling the chemistry of groundwater in aquifers and attempts to explain the reasons behind the large natural variability in chemical composition typically observed in groundwaters. Table 3.1 lists the dominant sources of some of the most important solutes found in groundwater.

3.2 ATMOSPHERIC INPUTS

Rainfall, entering an aquifer as recharge, constitutes an obvious starting point for the evolution of groundwater chemistry. Solute can also enter from atmospheric dry deposition. Although many solutes in groundwater are derived predominantly from mineral reactions in the subsurface, some do not form major constituents of rocks and minerals and so initial atmospheric inputs can provide a significant component of the total input. This is particularly the case for some of the halogen elements (I, Cl, Br). In the UK, rainfall chemistry varies significantly in response to distance from the coast because of the varying contribution from airborne marine salts. This is well-illustrated by mean annual Cl concentrations in rainfall from different gauging stations across England (Table 3.2). The effect is also seen in other solutes (Na, Mg, SO₄) although these usually have additional, and more significant, geological sources in the aquifer. Natural rainwater is slightly acidic as a result of the dissolution of atmospheric CO₂, which forms a weak solution of carbonic acid with an equilibrium pH of around 5.7.

It should also be borne in mind that pollution also has an impact on atmospheric inputs. Pollutants include airborne gases and aerosols such as oxide species of nitrogen (NO_x) and sulphur (SO_x) from fossil-fuel and biomass burning and other industrial emissions. These gases react with other substances to produce acid rain. Ammonia (NH₃) can also be introduced to the atmosphere from industry and agriculture. This can be readily converted to NH₄ ions in rainwater. Oxidation of NH₄ leads to further acidification. Industrial emissions can also account for the addition of a number of other solutes including halogen

compounds and various trace elements to the dissolved load of rainfall.

Evapotranspiration of rainwater leads to a concentration of dissolved salts as water recharges an aquifer. Chloride is regarded as a conservative element that is not involved in geochemical reactions and so has often been used to provide estimates of evapotranspiration rates. Simplified models of the concentration factors involved in the evapotranspiration process have been based on the differences observed in the concentration of Cl in rainwater compared to shallow groundwater (Appelo and Postma, 1993). This simple calculation does not take into account the amount of Cl potentially derived from dry deposition which is itself difficult to quantify, but does give a first approximation. Typical concentration factors for recharge in western Europe on this basis are around three mg l⁻¹ (Appelo and Postma, 1993). This factor has been used as an estimate of likely recharge chemistry in the regional reports. Evapotranspiration of rainwater leads to further acidification as the concentration of H⁺ ions increases along with that of the other solutes. The pH of modern rainwater entering the soil zone is therefore relatively acidic (typically 3 to 5) and hence potentially highly reactive.

Table 3.1 Dominant baseline sources of some solutes in groundwater.

Element	Dominant source of solutes in groundwater
Na	Rainfall, dissolution of halite (NaCl) or feldspar, ion exchange (clays), mixing with connate/formation water
K	Rainfall, dissolution of K-feldspar, biotite
Mg	Rainfall, dissolution of dolomite (CaMg(CO ₃) ₂), ferromagnesian minerals (olivine, amphibole, pyroxene, biotite), mixing with connate/formation water, ion exchange
Ca	Dissolution of calcite (CaCO ₃), dolomite, plagioclase, gypsum (CaSO ₄ .2H ₂ O)
HCO ₃	Dissolution of calcite, dolomite, siderite, silicate hydrolysis, oxidation of organic matter
SO ₄	Rainfall, dissolution of gypsum, oxidation of pyrite (FeS ₂)
Cl	Rainfall, dissolution of halite, mixing with connate/formation water
Si	Dissolution of silicates
I	Rainfall, organic matter
Br	Rainfall, organic matter
F	Rainfall, dissolution of fluorite, apatite and silicate minerals (biotite, amphibole)

Table 3.2 Weighted-mean annual concentrations of major ions in rainfall from gauging stations across England. The rainfall data are described in more detail in Ander et al., (2005); Shand et al., (2002); Cobbing et al., (2004); Smedley et al., (2005) and Smedley and Allen (2004).

Parameter	Units	Stoke Ferry, Norfolk	Thorganby, Yorkshire	Compton, Oxfordshire	Preston Montford, Shropshire	Goonhilly, Cornwall
Mean annual rainfall	mm	435	448	604	789	934
pH		5.1	4.40	4.62	4.69	4.70
SEC	$\mu\text{S cm}^{-1}$	27	43	13	19	60
Ca	mg l^{-1}	0.78	1.06	0.07	0.17	0.40
Mg	mg l^{-1}	0.27	0.27	0.06	0.11	0.88
Na	mg l^{-1}	1.26	1.54	0.47	0.76	6.88
K	mg l^{-1}	0.12	0.19	0.04	0.11	0.30
Cl	mg l^{-1}	2.20	3.80	0.90	1.49	12.5
SO ₄	mg l^{-1}	2.26	3.29	0.85	1.38	2.67
NO ₃ -N	mg l^{-1}	0.56	0.47	0.17	0.30	0.24
NH ₄ -N	mg l^{-1}	0.70	0.74	0.20	0.42	0.18

3.3 LAND USE

Understanding the impacts of pollutants on groundwater chemistry demands an knowledge of the nature, extent and history of pollutant inputs. This is often linked to land use, for example pollutant impacts are likely to vary between urban and rural settings. Changes in land use are likely to have had a significant impact on the baseline chemistry of aquifers, knowledge of which will help define the main pollution pressures for a given area. Modern agriculture introduces diffuse pollutants including nutrients (N, P and K), other major ions (SO₄, Cl) and pesticides to groundwaters. Agricultural and domestic wastes introduce point-source pollutants (e.g. N, Cl, P, pathogens, organic carbon) from slurry pits, septic tanks and soakaways. Industries, including mining, potentially introduce a wide range of pollutants such as trace elements. Fuel filling stations can constitute point sources of various organic compounds. Also, transport infrastructure (roads, railways, airports) can be the sources of inorganic pollutants such as Na and Cl from road salt, as well as pesticides and other fuel-related organic compounds.

3.4 BIOGEOCHEMICAL REACTIONS IN AQUIFERS

3.4.1 Reactions along flow paths

Rainfall entering the soil zone undergoes significant changes in chemical composition and pH. The amount of CO₂ gas dissolved (pCO₂) increases typically by 10 to 100 times that in the atmosphere as a result of root respiration and decomposition of organic matter. Numerous weathering, sorption and redox reactions also take place which change the concentrations of soil solutes. Reactions involve principally silicate weathering, carbonate reactions and reactions with organic matter. Soil compositions usually reflect those of the underlying bedrock e.g. soils developed on carbonate-rich rocks are typically alkaline and those developed on carbonate-free rocks are often acidic. The chemistry and structure of soils

is very variable (Plate 3) depending largely on climate, geology and geomorphology.

Chemical reactions between groundwater and solids continue in the unsaturated and saturated zones of the aquifer. Rates of chemical reactions (kinetics) vary (Table 3.3) and so equilibration may be rapid between water and some minerals, but not achieved at all for others.



Plate 3 Soil profile (podzol) indicating the heterogeneity due to weathering and biochemical reactions.

Table 3.3 Approximate time calculated for a hypothetical sphere of 1 mm diameter to dissolve in a dilute solution at pH 5 (modified from Lasaga, 1984).

Mineral	Time (years)
Quartz	34 000 000
Kaolinite	6 000 000
Muscovite	2 600 000
Epidote	923 000
Microcline	921 000
Albite	575 000
Sanidine	291 000
Gibbsite	276 000
Enstatite	10 100
Diopside	6 800
Forsterite	2 300
Anorthite	112
Dolomite	1.6
Calcite	0.1
Gypsum	short
Halite	very short

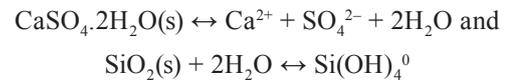
This means that chemical compositions of groundwaters are usually dominated by reactions involving a few relatively reactive minerals, notably carbonate minerals and, where present, evaporite minerals. Rocks containing just a few percent of calcite (e.g. a large proportion of the Permo-Triassic Sandstone) can contain groundwater whose major-ion concentration is dominantly controlled by calcite dissolution. Table 3.3 indicates that relatively long residence times are required to dissolve many silicate minerals and for such reactions to produce high concentrations of solutes. Groundwater in carbonate-free silicate aquifers (notably sandy sediments) is therefore likely to be sensitive to acidification or other changes imposed by changing environmental conditions. The relative proportions of minerals may also vary spatially as a result of past dissolution of more soluble minerals. This can be seen in the shallow parts of some silicate aquifers which originally contained calcite but which over time has been removed by percolating recharge waters, creating a decalcification front and hence spatial variation in pH and major ion compositions. The distribution of minerals in many aquifers is insufficiently well known to predict the concentrations of many solutes, especially for the trace elements.

3.4.2 Mineral dissolution and precipitation

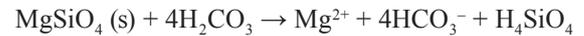
Mineral dissolution and precipitation reactions are generally the most important chemical reactions controlling the major-element chemistry of groundwater. Many reactions can have significant impacts on the porosity and permeability of the aquifer. Dissolution of carbonate cements, for example, can increase porosity and permeability, and in carbonate aquifers the development of karstic conditions leads to rapid groundwater flow. Precipitation of iron oxides can lead to decreased porosity and restricted groundwater flow.

Many dissolution reactions are reversible and the tendency to dissolve or precipitate is controlled by chemical equilibrium. Others, including many silicate dissolution reactions are non-reversible under ambient conditions of the near-surface environment. Minerals

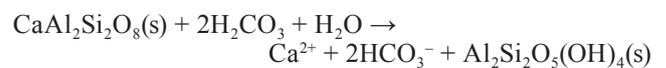
may also dissolve congruently or incongruently. During congruent dissolution, the solutes produced are present in the same proportions as they occur in the mineral. For example, congruent dissolution of gypsum and quartz respectively can be described by the reactions, both of which are reversible.



Silicate minerals may also dissolve congruently, for example, olivine.



During incongruent dissolution, the proportions of solutes produced are not the same as in the solid because of precipitation of other mineral phases. For example, anorthite (Ca-feldspar) may dissolve incongruently to produce dissolved Ca and HCO_3^- and the clay mineral kaolinite.



Most silicate-dissolution reactions are strongly pH-dependent (Appelo and Postma, 1993) with minimum dissolution rates in the pH range 6 to 8, that is, those typical of most groundwaters.

Equilibria involving the carbonate system are among the most important controls on groundwater chemistry. The overall reaction between calcite and CO_2 (the latter produced from respiration or oxidation of organic matter) can be described by the following equation.



In natural systems, the presence of dissolved HCO_3^- is an important pH-buffering control and the dissolution of carbonate minerals in an aquifer (providing HCO_3^-) provides a good mechanism for neutralising acidic inputs and in so doing, immobilising many trace metals.

3.4.3 Redox reactions

Redox reactions can also have a significant impact on groundwater chemistry as they affect the concentrations and speciation of a number of important constituents including dissolved oxygen, organic carbon, S, N, Fe and Mn, as well as a number of other trace elements. The oxidation of organic matter is often a significant driver of chemical changes by redox reactions. This may be present in aquifers naturally as solid or dissolved organic carbon. It may also be introduced as a surface pollutant from landfills, slurry or septic tanks. Other reductants include ferrous iron, Fe^{2+} , either in mineral or dissolved forms, and sulphide. Oxidation of pyrite (FeS_2) for example can have an impact on groundwater chemistry, leading to potentially large increases in concentrations of dissolved Fe, SO_4 and some trace elements, as well as release of protons. Under sufficiently oxic conditions, the Fe(II) released will oxidise to Fe(III) and precipitate as Fe oxide.



Many redox reactions are microbially mediated and microbial catalysis can speed up many reactions which would otherwise be immeasurably slow.

Some of the most significant redox changes in aquifers are observed in groundwaters as they flow from unconfined to confined conditions. Redox reactions tend to follow a well-established sequence as conditions, including those in aquifers, become anoxic (Berner, 1981). This sequence begins with loss of O₂, followed by loss of NO₃⁻ by reduction to metastable NO₂⁻ and then to the gases N₂O and N₂. Thereafter, Mn(IV) in Mn oxides reduces to soluble Mn²⁺ followed by reduction of Fe(III) in Fe oxides to soluble Fe²⁺. Under increasingly reducing conditions, SO₄²⁻ is reduced to S²⁻, then CH₄ production occurs by fermentation and methanogenesis. Finally, N₂ reduces to NH₄⁺. The dominant redox reactions are the loss of O₂ and NO₃⁻, and reduction of Mn(IV) and Fe(III); relatively few aquifers are sufficiently reducing to achieve SO₄ reduction (Griffiths et al., 2006), methanogenesis (Darling and Goody, 2006) or NH₄ production. Some exceptions occur in the deepest aquifers where saline connate or formation waters occur (e.g. Smedley and Edmunds, 2002).

Some of the most important of these redox reactions in groundwater (Figure 3.1) are listed below:

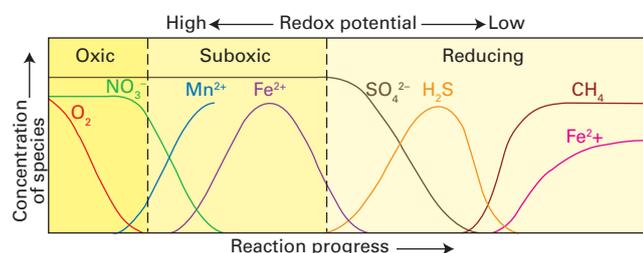
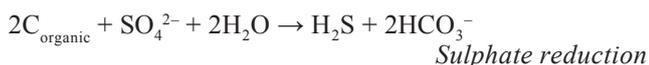
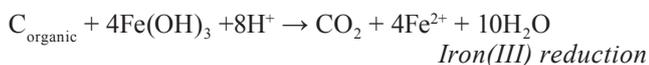
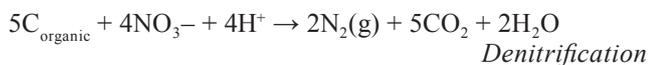


Figure 3.1 The sequence of redox reaction zones developing as groundwaters move along flow pathways from recharge (high redox potential) to confined conditions (low redox potential). The extent to which each zone develops depends on the original water composition and the amount of reducing agents in the aquifer matrix (after Berner, 1981).

These reactions also control the environmental speciation and hence mobility of a number of trace elements, some of which are toxic: As(III)/As(V), Cr(III)/Cr(VI), Se(IV)/Se(VI) and U(IV)/U(VI).

The stability fields of solid and/or aqueous redox species can be displayed effectively on Eh–pH diagrams. The range in pH and Eh in aqueous systems is limited by the stability field of water. Typical conditions of different waters are shown on Figure 3.2 and an example of the stability fields for Fe species is shown on Figure 3.3. It should be noted that these fields are dependent on the activities of species and components considered and can vary for different elements. Under reducing and/or acidic conditions, reduced Fe²⁺ forms an aqueous species. The oxidised aqueous species Fe³⁺ is only stable under strongly acidic, oxic conditions. Under oxic conditions at near-

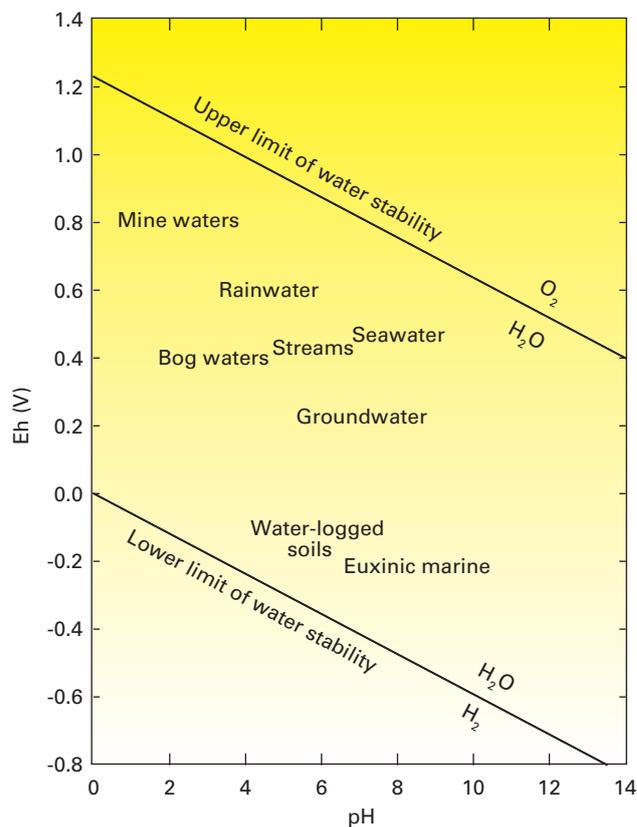


Figure 3.2 Eh-pH diagram showing the stability field of water and typical regions for different environments.

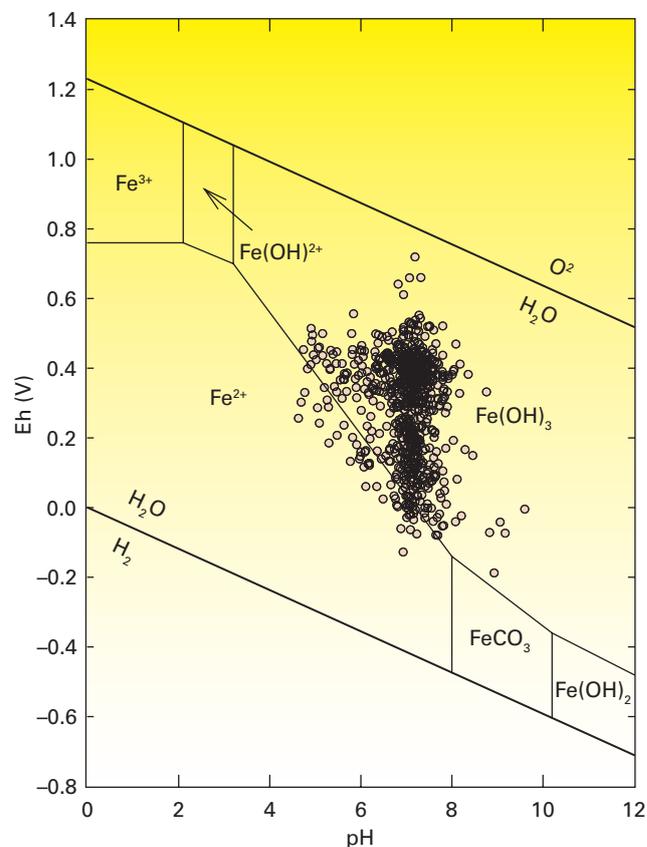


Figure 3.3 Eh-pH diagram showing the stability fields for Fe species (activity of Fe = 10⁻⁶) and water samples from the baseline study (761 samples).

neutral and alkaline pH, the insoluble phase Fe(III)(OH)_3 dominates and gives rise to low concentrations of dissolved Fe. The diagram indicates that oxidation of a reduced Fe^{2+} -bearing groundwater should lead to oxidation to Fe(III) and precipitation. As many trace metals adsorb to Fe(III) oxide, changes in redox conditions in aquifers may lead to significant changes in the concentrations of trace elements in groundwater.

3.4.4 Ion exchange and sorption

Sorption and exchange reactions in soils and aquifers involve the transfer of ions between the solid and the aqueous phases. Adsorption involves the binding of an ion to a solid surface while desorption involves its release. Ion exchange involves the substitution of one ion for another on a chemical surface. Aquifers and soils contain abundant minerals that are capable of controlling major- and trace-element speciation by sorption and ion-exchange processes. The most important minerals are those with large specific surface areas, namely clay minerals, iron oxides and organic matter.

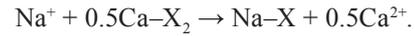
The mica-type clay minerals (e.g. smectite) are particularly capable of binding exchangeable cations. The substitution of Si^{4+} by Al^{3+} in clay structures causes an excess negative charge of -1 , which promotes cation infilling of sites. These can be exchanged for other ions from the aqueous solution. A general ordering of cation exchangeability for common ions in groundwater is:



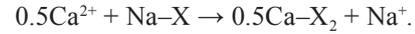
i.e. all things being equal, divalent cations are more strongly adsorbed than monovalent ions and tend to replace them on surface sites. Equilibrium between the solid and dissolved species depends on both solute and adsorbed species and therefore the general ordering above may not be observed in real systems. Clay-mineral surfaces can also have a variable charge because of protonation of surface oxygens and deprotonation of hydroxyls. Specific adsorption of ions can also impart a surface charge (Appelo and Postma, 1993).

Ion-exchange processes are important during salt-water intrusion and aquifer freshening (displacement of more saline water by fresh water). The dominant groundwater in a fresh aquifer is usually of Ca-HCO_3 type as a result of equilibration with calcite. The clay-mineral surfaces

are therefore dominated by Ca^{2+} . When salt water of Na-Cl composition intrudes this aquifer the surface Ca^{2+} is replaced by Na^+ :



The water will then change from a Na-Cl to a Ca-Cl composition. The reverse process takes place in a freshening aquifer where saline water is replaced by fresh groundwater:



The water in this case changes from Ca-HCO_3 type to Na-HCO_3 type. The direction of groundwater movement can thus be determined in such cases from the water types observed. Since most aquifers are of marine sedimentary origin, the latter process is likely to be important for a long time after the aquifer becomes part of the terrestrial environment.

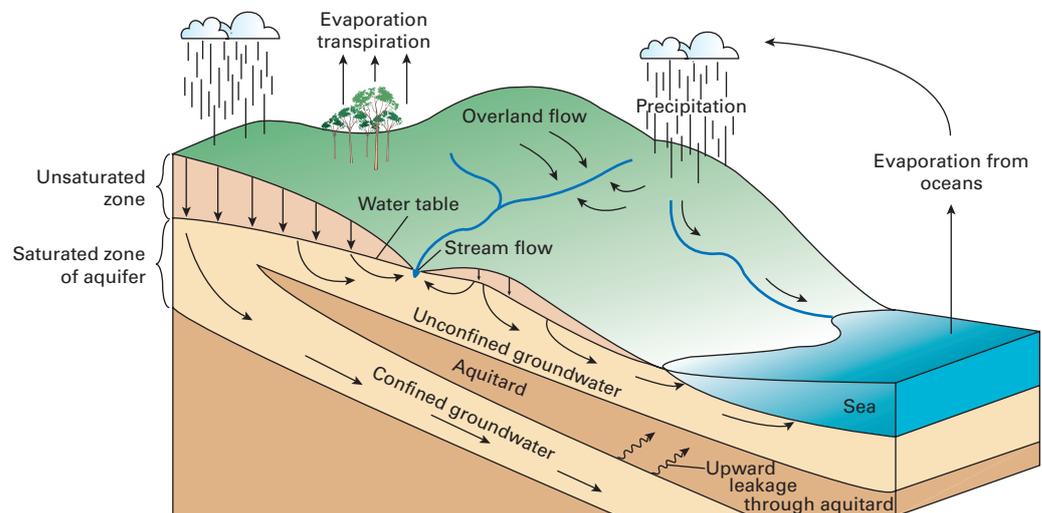
Iron, manganese and aluminium oxides are ubiquitous in oxidising soils and sediments, occurring as discrete grains and as coatings on mineral surfaces. Amorphous and poorly structured forms have large specific surface areas and a particularly large capacity to adsorb trace elements. As such, they are commonly used to remove trace metals in wastewater treatment (e.g. Edwards, 1994). The adsorption capacity of these minerals is pH-dependent. Fe and Al oxides are particularly effective anion adsorbants and can have a marked impact on the speciation and mobility of elements such as As, Mo, P, Se and U.

3.5 GROUNDWATER FLOW AND RESIDENCE TIME

3.5.1 Controls on flow patterns

Groundwater represents an important part of the water cycle (Figure 3.4). Groundwater flow rates and patterns vary greatly between and within aquifers as a result of variations in porosity and permeability, aquifer dimensions, recharge and discharge areas, degree of confinement and abstraction. Rates of groundwater flow are typically 5 to 500 m a^{-1} for granular aquifers, and because of these relatively low rates of flow, the residence time for groundwater is decades, centuries or millennia, hence much slower than for surface waters. As a result,

Figure 3.4 Illustration of the important role played by groundwater in the water cycle.



changes in groundwater chemistry tend to be slower and the effects of chemical changes remain for much longer periods.

The residence times of groundwater in unconfined aquifers are usually much shorter than for confined aquifers. In the former, the annual cycle of recharge during winter months and outflow (mainly to surface water) during summer months promotes active circulation, especially at shallow depths. Thus, groundwaters in unconfined aquifers are relatively young, with typical residence times of years to decades for shallower circulation. They are therefore more vulnerable to pollution. Groundwater in confined aquifers has more typical residence times in the range of centuries to millennia, at least under natural flow conditions, because water outflow from the aquifer is small and consequently flow from the unconfined area into the confined aquifer is also small.

In England, many of the major unconfined aquifers have relatively deep unsaturated zones, typically 10 to 30 m thick, and the time taken for recharge (and solutes) to migrate from the base of the soil to the water table can be years to decades, although the hydraulic response of the water table to an individual recharge event can be within days or weeks as a result of piston displacement. The unsaturated zone can be a significant store of pollutants travelling at rates determined by the rate of recharge and retardation properties down to the water table. In the saturated zone, flow rates vary considerably between granular and fractured aquifers. In consolidated aquifers such as the Carboniferous Limestone, intergranular porosity and permeability are usually low but fractures and joints can enhance the permeability significantly and flow rates are typically of the order of 1 to 100 m day⁻¹. Rates tend to be much slower, of the order of 0.01 to 1 m day⁻¹, in granular aquifers such as the Lower Greensand and the Crag of East Anglia. These slower flow rates mean that groundwater residence times can be on a scale of decades, centuries or even millennia in granular aquifers.

Several dating techniques exist to determine the 'age' of groundwater, but the large range in residence times (days to millennia) in most aquifers means that several different techniques are required to assess the age distribution within an aquifer (Figure 3.5). These methods may require detailed knowledge of inputs as well as assumptions about the geochemical evolution of the groundwater. The mixing of different groundwaters often complicates interpretation, hence the terms 'mean age' or 'bulk age' are often used. In addition, some techniques are expensive or not easily available and very few precise age distributions are available for the majority of aquifers in England and Wales.

Many aquifers combine a fracture-flow regime with a porous matrix and the latter may contribute to groundwater flow or storage in the aquifer. For example, in the Permo-Triassic Sandstone, groundwater flow is largely dominated by fractures at the local scale in individual boreholes, but by the matrix permeability at a regional scale (Worthington, 1977). The matrix of the sandstones provides the bulk of the groundwater storage. In several other aquifers, such as the Chalk and Jurassic Limestone, the pores within the matrix are so small that they do not drain easily under gravity. Under these circumstances, the matrix does not contribute significantly to either the bulk permeability or the usable storage of the aquifer. Even when the porous matrix does not contribute to groundwater flow or drainable storage, it can have a significant impact on water quality because water can diffuse from the fractures to the porewater and

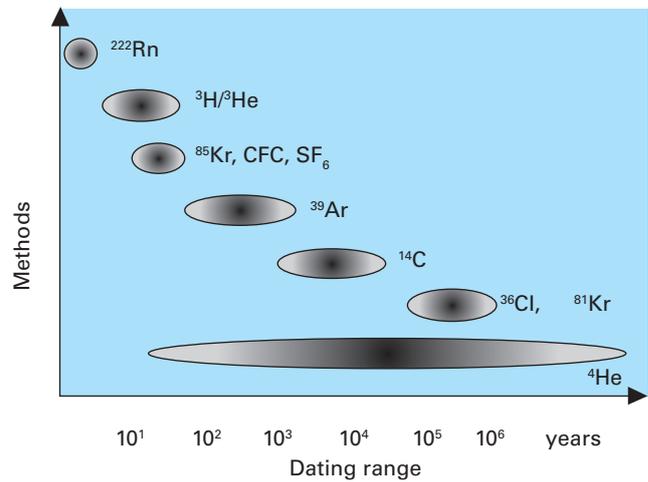


Figure 3.5 The age ranges of different residence-time measurement techniques.

vice versa. Diffusion is a slow process and so it may take many years for equilibrium to be achieved between the porewater and fracture water.

For many aquifers, the hydraulic conductivity varies spatially as a result of variations in lithology (e.g. grain size differences related to facies changes) or post-depositional permeability changes related to cementation and weathering. There is often a distinct pattern to such heterogeneity; two of the most common are; (a) layered heterogeneity e.g. where the aquifer comprises layers with different hydraulic conductivity; and (b) trending heterogeneity where the heterogeneity increases (or decreases) with depth or lateral distance. Most aquifers also show some degree of anisotropy. For example, the hydraulic conductivity of many geological formations is lower in the vertical direction (k_z) than in the horizontal directions (k_x, k_y), a feature often attributed to the orientation of clay minerals in sediments. Both heterogeneity and anisotropy modify groundwater flow pattern, flux and the residence times and so can impact on groundwater quality. Decreasing hydraulic conductivity with depth, for example, is likely to enhance stratification of water quality and groundwater residence time.

3.5.2 Past effects of groundwater flow

In the Chalk aquifer, where the development of permeability is mainly due to dissolution and enlargement of joints and fractures, the spatial variation in hydraulic conductivity is controlled by current and historical groundwater-flow patterns. In vertical profile, the permeability development is often greatest within the zone of present-day water-level fluctuation. Since sea levels have varied by more than 100 m in recent geological time due to glaciation and deglaciation, the development of fracture permeability at elevations above and below the present water table may be associated with past water levels. Regionally, Chalk transmissivity is often greatest beneath valleys where fissure development is greater, having possibly formed largely during Quaternary glacial and inter-glacial periods. Karstic features are also common around the margins of overlying Palaeogene deposits as a consequence of acidic run-off from such deposits. This heterogeneity in the Chalk aquifer can produce complex patterns of water quality related to both current and historical flow patterns.

As a result of slow groundwater flow and often long residence times of groundwaters in the deeper parts of

confined aquifers, some carry signatures of past climatic and flow events. Isotopically-distinct compositions (e.g. depleted $\delta^{18}\text{O}$, $\delta^2\text{H}$ compositions relative to modern groundwaters) have been observed in some groundwaters (e.g. Shand et al., 2003; Griffiths et al., 2006) indicating recharge under colder climatic conditions in the Quaternary past. In some coastal confined aquifers, a lack of active groundwater circulation has preserved bodies of old saline groundwaters infiltrated during post-glacial marine incursions. These have been observed in the confined near-coastal Chalk aquifers of Kent and Yorkshire (Smedley et al., 2003; Smedley et al., 2004).

3.5.3 Effects of recent pumping

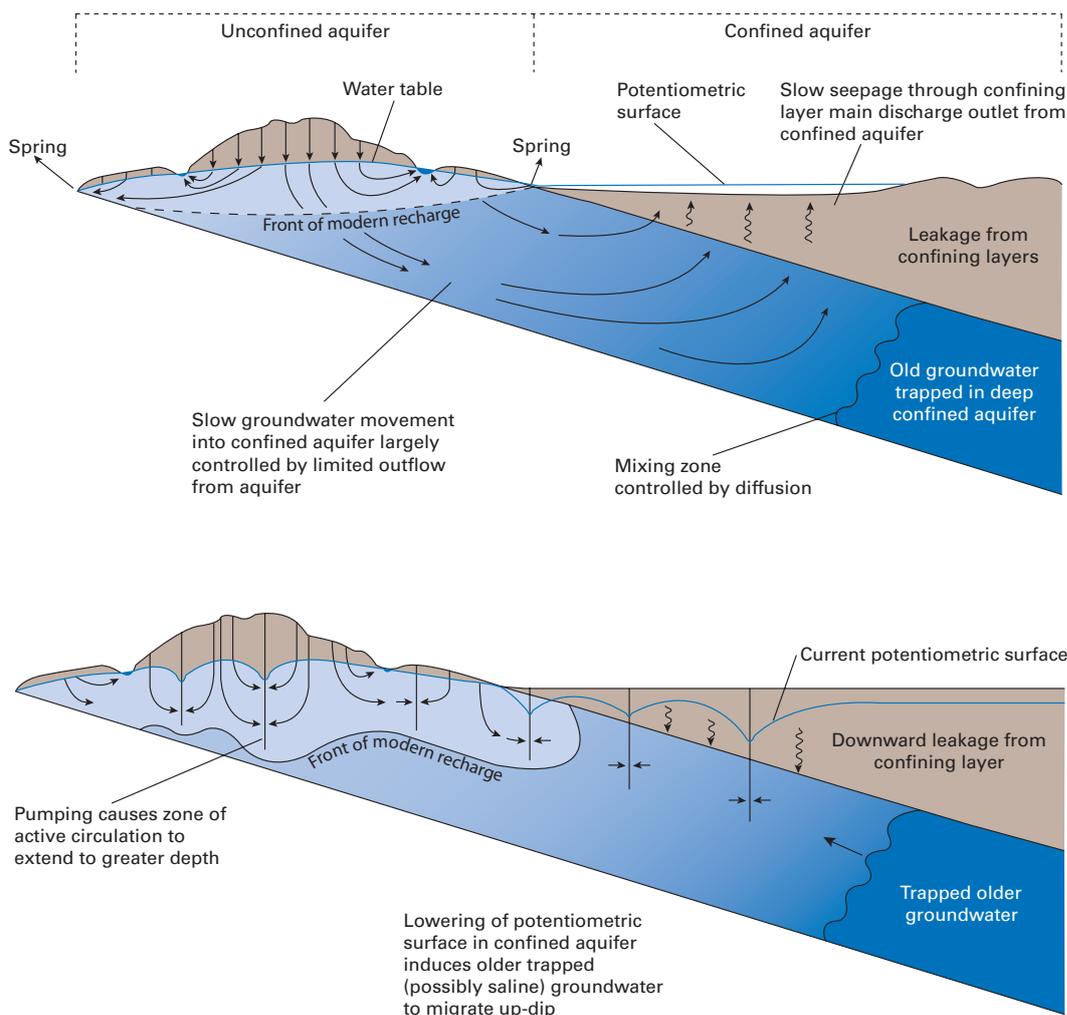
Recent groundwater abstraction has had a significant impact on flow, and in some areas has disturbed the natural flow patterns significantly. Under natural conditions, outflow of groundwater is normally to surface water or the sea (Figure 3.4). However, over the past few decades, increasing numbers of boreholes with motorised pumps have been installed and have significantly modified the modern flow pattern. Groundwater abstraction in unconfined aquifers has resulted in an increase in the depth of penetration of modern groundwaters. It can also induce cross-formational flow, and seawater intrusion

in some coastal aquifers. Abstraction from the confined parts of aquifers can result in steeper hydraulic gradients, which can allow more rapid flow from the unconfined to the confined aquifer. Furthermore, pumping from shallow parts of the confined aquifer may induce upward flow of relatively old and/or saline water. It can also lead to a reduction or reversal of the vertical hydraulic gradient within the confining layer, the latter case inducing downward leakage from the confining layer.

Prior to significant groundwater abstraction, it is likely that there was much more discharge to springs and rivers close to unconfined-confined boundaries (Figure 3.6). The interpretation of groundwater chemistry is best done within a geological framework, since a conceptual understanding of changes in flow rate and direction over time is required to understand the impact of such change on baseline quality.

Mixing of distinct groundwater masses can generate changes in chemical composition simply by conservative mixing. In addition, chemical reactions can be promoted by mixing as infiltrating waters are unlikely to be in equilibrium with the resident groundwaters or the aquifer matrix. Conservative tracers such as Cl and stable isotopes may therefore show the effects of simple mixing, whilst other solutes may have undergone additional solution/precipitation, redox or exchange reactions.

Figure 3.6 The effect of groundwater abstraction on groundwater flow. The upper figure shows a hypothetical example of flow under pristine conditions and the lower figure the potential impact of groundwater abstraction.



4 Methodology

4.1 STUDY AREAS

The methodology employed for the investigation of the 23 study areas has involved a combination of the techniques outlined in Chapter 2. The study areas are of variable shapes and sizes depending on aquifer lithology, use and data availability. They include examples of all the major aquifer types present in England and Wales (Chalk, Triassic Sandstone, Lower Greensand, Lincolnshire Limestone) and a significant number of the minor or local aquifers

(Devonian sandstone, Palaeozoic sediments, Palaeogene sediments, Jurassic limestones and sandstones, Crag, Millstone Grit, Carboniferous Limestone, Cornubian granite). The study areas in central Wales (Shand et al., 2005) and eastern Norfolk (Ander et al., 2006) included sampling of superficial deposits (fluvial gravels) and these are discriminated from the underlying bedrock waters on plots in Chapter 5. The study areas completed are shown on Figure 4.1, superimposed on the geology.

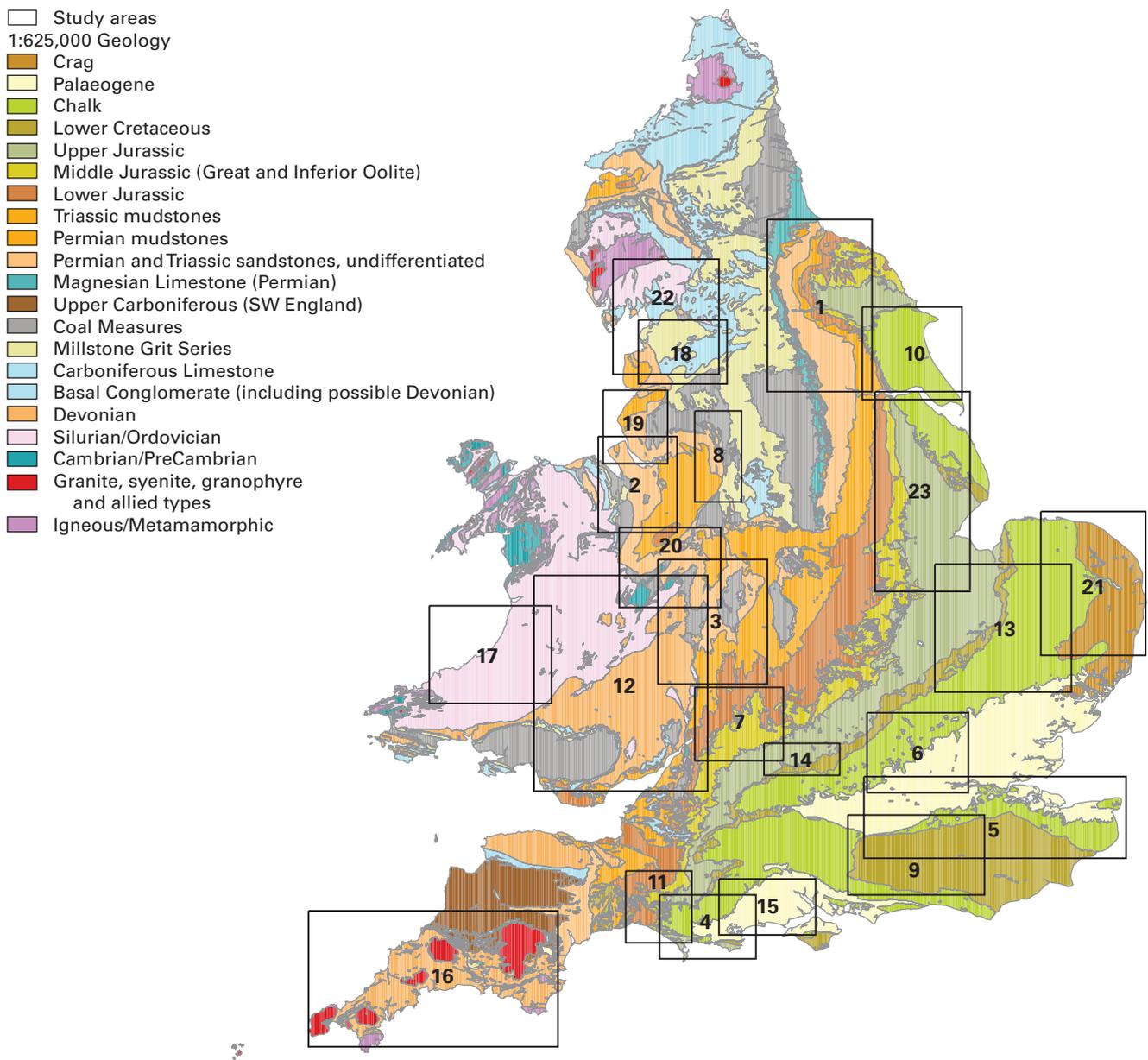


Figure 4.1 Geological map of England and Wales showing the aquifers and regions studied. A list of regional reports is presented in Appendix 1.

Geological linework is © NERC



Plate 4 Sampling of groundwater from different aquifers. Locations are (clockwise from top left) irrigation borehole in the Chalk of Norfolk; artesian borehole in Lincolnshire Limestone; spring in Devonian sandstone, Wales; artesian borehole in Lower Palaeozoic sediments of the Wye Valley.

4.3 DATA HANDLING

The regional reports characterise the collated groundwater datasets in terms of summary statistics, box plots and cumulative-probability diagrams. The summary statistics used included the minimum, median, maximum, and the 97.7th percentile, the latter as a first approximation to the upper limit of baseline concentrations. Where datasets obviously differ in a given study area, for example due to regional lithological or stratigraphical differences or due to differences between confined and unconfined aquifers, these have usually been separated and statistical summaries reported for each (e.g. Neumann et al., 2003; Smedley et al., 2004).

The regional studies handle non-detect data by substituting them with half-detection-limit values, as has been common practice with environmental datasets (Reimann et al., 2005). This is a simple way of treating non-detects but is a rather arbitrary approach as the resulting values bear little relationship to the data distribution, being merely a function of the analytical method and laboratory practice.

Cumulative probability plots have been used as the preferred method to facilitate comparisons of data in the following chapters since they are useful for assessing different populations of data. Spatial distributions are highlighted in individual reports with GIS plots and depth variations using simple X to Y plots.

4.4 REPRESENTATIVE SAMPLING

Representative sampling of groundwater does not have many of the problems inherent in other media such as soils and sediments where concentrations may vary according to grain size, sample size or extraction method. However, it has a number of problems of its own that should be borne in mind during hydrogeochemical investigations. Firstly, many chemical parameters in groundwater are unstable and care needs to be taken to ensure that sample integrity is maintained during sampling and storage. Secondly, purging of boreholes is necessary to ensure that unrepresentative standing water in the borehole conduit is removed before sampling.

Sampling was carried out by the BGS according to standard protocols with care taken to ensure that unstable parameters (e.g. pH, temperature) were measured as close to the well head as possible and as quickly as possible after abstraction. Where possible, parameters subject to aeration or degassing (pH, dissolved oxygen, Eh) were also measured in an in-line flow cell (Plate 5). The chemical constituents present in groundwater can be present in a variety of forms including particulate matter, colloids and dissolved forms. Solutes in groundwater are typically defined as those which pass through a 0.45 µm filter. Although this removes most living matter such as bacteria and plankton, colloidal forms may still be present (Figure 4.3).

Protocols for sampling and analysis of non-BGS datasets are less clear as the WIMS database includes data from various organisations and where published data have been used, the sampling and analytical protocols are not always clearly documented. Nonetheless, care has been taken to ensure as much as possible that poor data are removed and that the remaining dataset is analytically sound.

Spatial variations in borehole availability as a result of variations in aquifer transmissivity or water quality can also lead to uneven coverage of groundwater chemical data which can be a problem in interpreting spatial data. Examples include the greater density of potential sampling points close to rivers where transmissivity can be greater than on interflaves, and the smaller numbers of boreholes in confined aquifers because of problems with Fe, Mn, salinity or poor yields.

A further complication with groundwater sampling is the uncertainty in interpretation of data for pumped groundwater samples. In many cases, groundwater is chemically and age stratified with depth and so a simple pumped sample represents a mixture of water derived from different depths and/or fracture systems with different age and quality (Figure 4.4). In extreme cases (e.g. Figure 4.5), the water sampled by pumping may

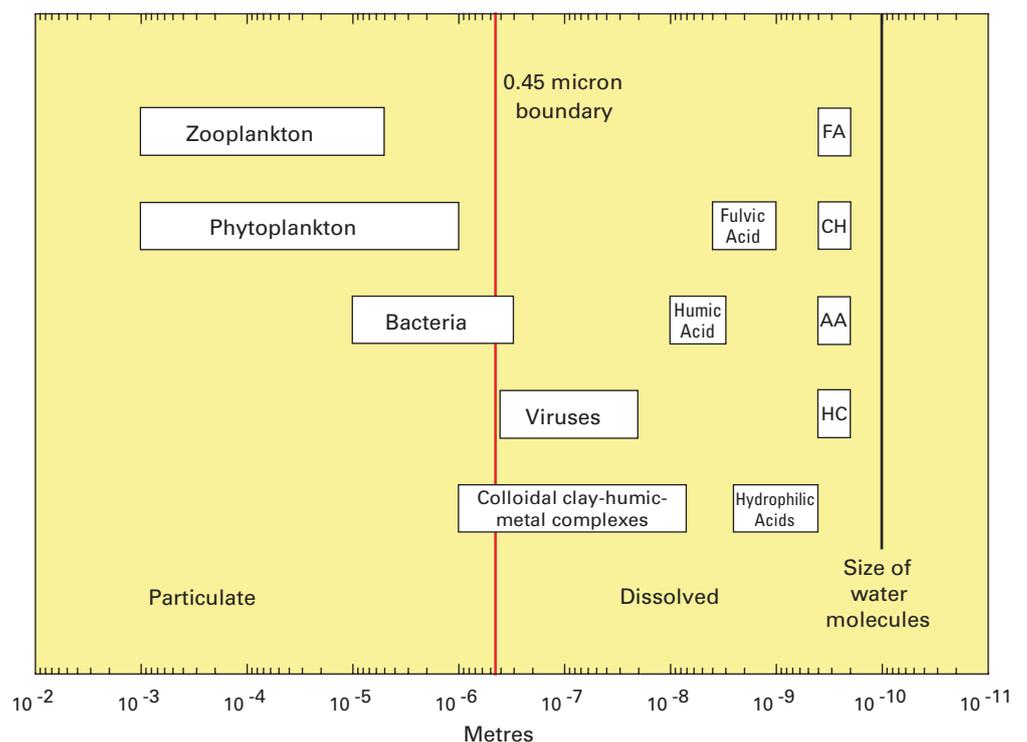
not be representative of any in situ water in the aquifer. The use of packer systems, which sample only discrete depths, is both time-consuming and expensive. The variations present are due to different flow rates related to hydraulic gradients, differences in the physical properties of the aquifer (e.g. fractured, dual porosity) and natural variations in the geochemical and geological properties. In sedimentary aquifers which show strong dual-porosity behaviour (e.g. the Chalk), the water contained in fractures may be chemically different from older water contained in the matrix. Most available data are collected from pumped boreholes and if the screened intervals are large, the above considerations apply. For these reasons, significant differences can exist in the chemistry of groundwater from pumped sources compared with that from discrete depth samples or extracted pore waters.



Plate 5 Measuring the unstable parameters pH, dissolved oxygen (DO) and redox potential (Eh) in a flow-through cell.

Figure 4.3 Size ranges of particulate and dissolved solutes found in water. Dissolved solutes are normally taken to be those which pass through a 0.45 µm membrane-filter. However, this is an arbitrary measure and filtered samples may include small colloidal particles.

FA: Fatty acids
 CH: Carbohydrates
 AA: Amino acids
 HC: Hydrocarbons



4.5 DATA COMPARISONS

A range of problems emerges when different datasets are integrated or compared. The purpose of the groundwater sampling may vary and may affect the choice of sampling technique and procedure as well as the selection of analysed parameters and sample population density. Available equipment for the analysis of solutes varies from one institution to another (e.g. ICP-AES, AAS, or ICP-MS can be used for the analysis of cations) and can result in the production of different suites of determinands. Different laboratories may also report determinands in different ways and care needs to be taken when these are compared. Nitrate can be reported as NO_3 or $\text{NO}_3\text{-N}$ for example and may be given as the single anion or as TON (total oxidised nitrogen) depending on the analytical method used. Different analytical techniques may measure a constituent in different ways, e.g. ion chromatography may determine the anion SO_4^{2-} while the ICP-AES technique determines total sulphur (albeit typically quoted as SO_4). Data may also be reported with different units (e.g. $\mu\text{g L}^{-1}$ or mg l^{-1}) and since concentration ranges for some parameters can span several orders of magnitude, the units are not always obvious. Clearly, care needs to be taken to ensure that data within a given set are directly comparable in these respects.

There is also a tendency for continual improvement in analytical methodology with time, thereby increasing the uncertainty of comparing new datasets with older ones. The analytical results are likely to be less precise when approaching the detection limit or beyond the upper calibration point. Comparison of datasets with different detection limits for the elements thus involves inevitable uncertainty.

Ideally, a comparison of the hydrochemistry of different aquifers should be based on a common sampling protocol

and the elements should be analysed in the same batch at one laboratory. Such a hypothetical idealism is not possible and, as suggested above, the limits of interpretation should be borne in mind at all times.

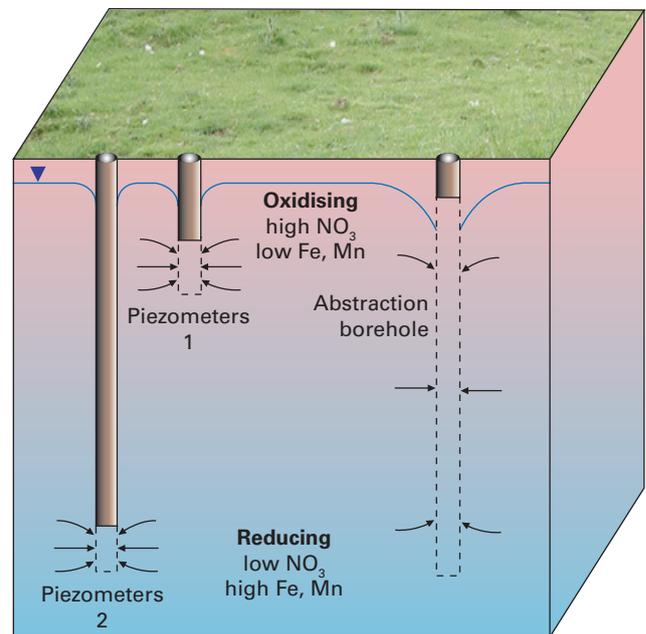
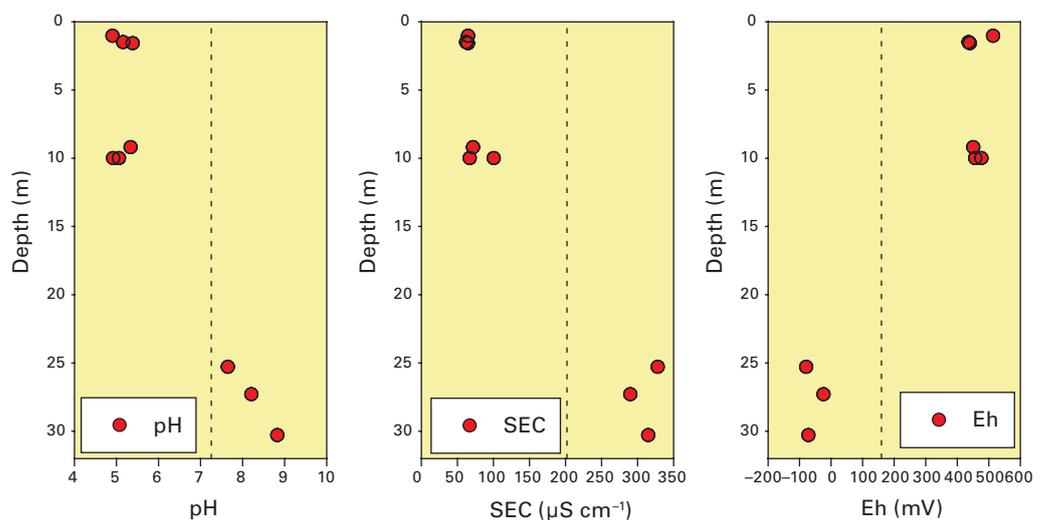


Figure 4.4 Diagram showing that different results will be obtained from an aquifer depending on how the groundwater sample is collected. Sampling from piezometers is preferred to that from abstraction boreholes which may represent a mixed water, if stratification exists in the aquifer.

Figure 4.5 Groundwater data from piezometers (red dots) and a pumped sample from an unscreened borehole (dotted line) in a fractured aquifer. The pumped sample is not representative of any in situ groundwater in the aquifer (from Shand et al., 2004).



5 Review of baseline concentrations

5.1 INTRODUCTION

The aquifers of England and Wales comprise a diverse range of rock types varying from sedimentary carbonates, sandstones and argillaceous rocks to igneous and metamorphic rocks. They are also represented by a wide range of ages and hydrogeological characteristics from porous arenaceous sediments to fractured hard rock aquifers. This chapter presents a summary of the distributions of the most significant chemical parameters measured in the groundwaters from the study areas (Figure 4.1). These are presented as cumulative probability plots for each of the study areas. A total of 26 datasets have been produced from the 23 areas: the Norfolk study (area 21) incorporated data from the Chalk, Crag and fluvial deposits; and the Lower Palaeozoic study (area 17) included fluvial gravels. The reader is referred to the regional reports (listed in Appendix 1) for more detailed descriptions and interpretation of the individual areas. Although in some of the regional reports, the data were subdivided (e.g. into unconfined and confined groundwater), for clarity and to facilitate comparison they have here been combined in this summary.

The data have been subdivided into four groups for plotting purposes (numbers in brackets refer to report number, see Appendix 1):

- *The Chalk aquifers*: Dorset (4); Kent and East Surrey (5); Colne and Lee (6); Yorkshire and North Humberside (10); Great Ouse (13) and East Norfolk (21).
- *Permo-Triassic sandstone aquifers*: Vale of York (1), West Cheshire and the Wirral (2), South Staffordshire and North Worcestershire (3), Manchester and East Cheshire (8), Liverpool (19) and Shropshire (20).
- *Other sandstone aquifers*: Lower Greensand of Southern England (9); Bridport Sands (11); Devonian of south Wales and Herefordshire (12); Palaeogene of Wessex Basin (15); Millstone Grit (18) and Crag (21).
- *Other areas*: Cotswold Oolite (7); Corallian of the Thames Valley (14); granites of south-west England (16); Ordovician/Silurian of south and central Wales (17); Superficial deposits in south and central Wales (17); superficial gravels of Norfolk (21); Carboniferous Limestone (22) and Lincolnshire Limestone (23).

This will help to facilitate comparisons of groundwater chemistry in the Chalk and Permo-Triassic aquifer units in different parts of the country.

Summaries for pH and specific electrical conductance (SEC) are reviewed in Section 5.2; major and minor elements in Section 5.3; nutrients in Section 5.4 and selected trace elements in Section 5.5, including those trace elements (e.g. As, Ni, Cr, U) that are of concern to human health.

A number of trace elements were generally present at concentrations below the limit of detection using ICP MS. Where this is the case, the data have not been plotted, but are summarised in individual reports (Appendix 1) and in Chapter 6. These include (detection limits in parenthesis):

Ag (0.05), Au (0.05), Bi (0.05), Ga (0.05), Hf (0.02), Hg (0.1), In (0.01), Ir (0.05), Nb (0.01), Os (0.05), Pd (0.2), Pt (0.01), Re (0.01), Rh (0.01), Ru (0.05), Sc (0.05), Se (0.5), Ta (0.05), Te (0.05), Th (0.05), Ti (10), Zr (0.5) and most REE's (0.01-0.05).

5.2 PHYSICO-CHEMICAL PARAMETERS

As discussed in Chapter 4, the parameters temperature (T), pH, redox potential (Eh) and dissolved oxygen (DO) may undergo rapid change when groundwater is brought into contact with the atmosphere. They are therefore measured, where possible, in a flow-through cell (Plate 5). For much of the data compiled, Eh and DO were not available, and during project sampling it was often not possible to get reliable values, e.g. in water samples collected from a feeder or storage tank. Nevertheless, DO and Eh varied widely in the different aquifers indicating large variations in the oxidising capacity of the groundwater and aquifer mineralogy. These redox parameters act as important controls on the solubility and speciation, particularly of redox-sensitive species such as N and some trace elements. This will be discussed in more detail in the element descriptions. Temperature, which can be a good indicator of depth, and therefore to some extent of residence time (Edmunds and Smedley, 2000), also varied significantly within aquifers, although median values were similar between aquifers, ranging from 8.6 to 13.4 °C.

5.2.1 pH

The dominant control on the pH (effective hydrogen ion concentration) of groundwaters is the acid-neutralising capacity of the bedrock (and overlying deposits), in particular the presence or absence of reactive carbonate minerals. As noted in Section 3.2, rainfall is generally weakly acidic, and this may be further enhanced in the soil zone. The pH of recharge water will generally increase with residence time with the rate of change being largely dependent on the reactivity of the constituent minerals. Aquifers containing carbonate minerals typically have circumneutral to alkaline pH (depending on initial pCO₂ and open- or closed-system evolution), due to the rapid dissolution kinetics of carbonates. Silicate minerals have slower dissolution rates and most basement aquifers worldwide typically yield more acidic, lower pH waters (Bucher and Stober, 2000). Rocks that have a poor acid-buffering capacity, such as granites, are expected to have lower pH than carbonate-rich aquifers. However, even small amounts of carbonate minerals (ca. 1%) can buffer the pH to near-neutral values as a result of the rapid kinetics of calcite dissolution (Table 3.3). Groundwater pH may also be reduced by oxidation of pyrite (FeS₂; Section 3.4).

The pH of groundwater in the Chalk (Figure 5.1) is well buffered by calcite dissolution, typically displaying a narrow range with median values between 7.1 and 7.3. In unconfined Chalk groundwater, the pH is generally around 7.0 to 7.4, which is expected for equilibrium with calcite at the partial pressures of CO₂ found in temperate

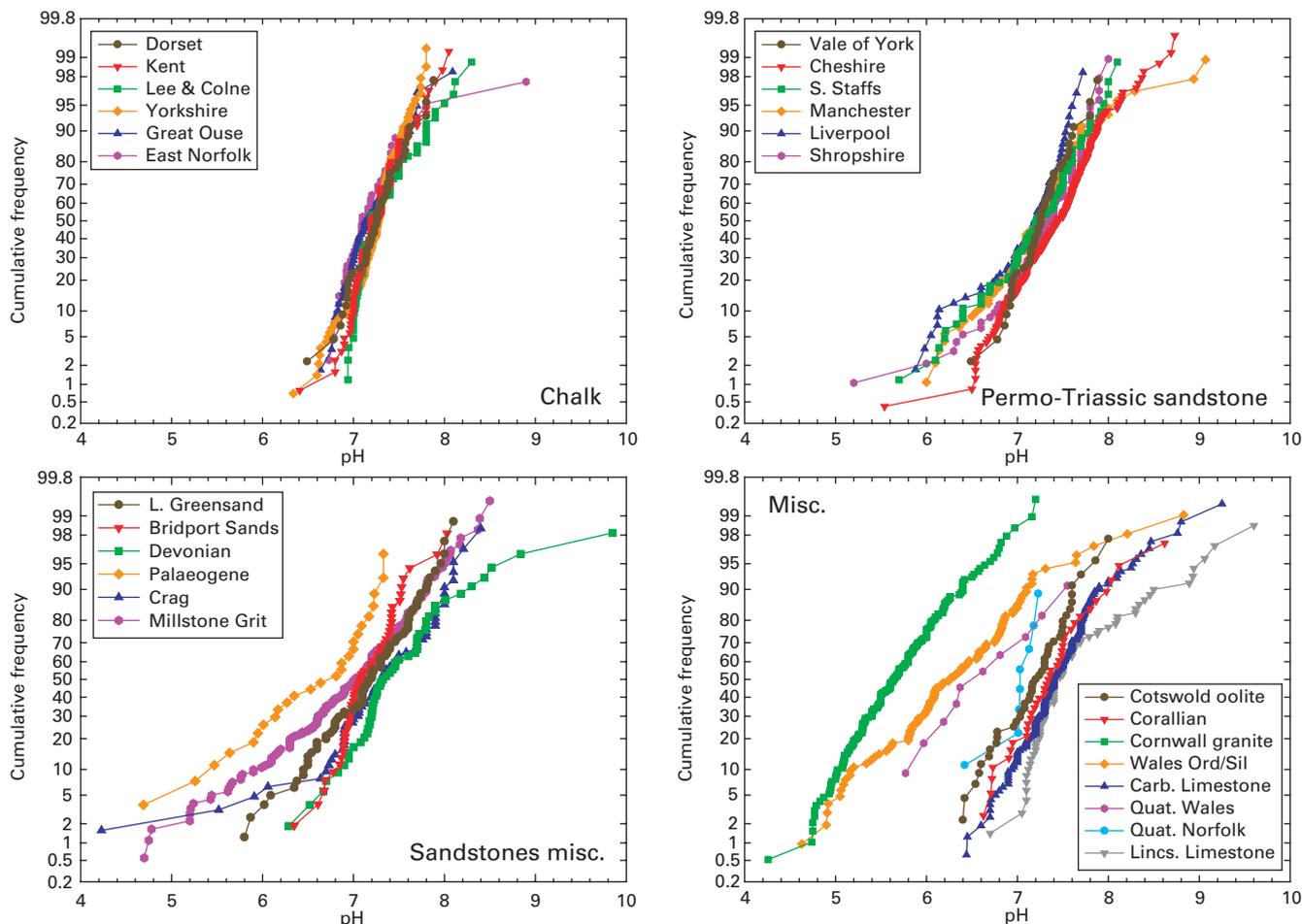


Figure 5.1 Cumulative frequency plots for pH in groundwaters.

soils. Higher pH (>7.8) values are generally present in deeper groundwaters, especially Na-HCO₃ type waters, where the aquifer is confined.

The pH of groundwaters in the Permo-Triassic sandstone aquifers displays a wider range than those in the Chalk (Figure 5.1). However, the median values are also near-neutral because of the buffering produced by carbonate mineral dissolution. Moderately acidic groundwaters were noted in shallow parts of the Permo-Triassic sandstone aquifer where past groundwater flow has removed carbonate cements. The higher pH in samples from the Manchester and Cheshire areas is associated with deeper groundwaters which have undergone ion-exchange. Hydrolysis reactions involving silicates in a system with low CO₂ can also be responsible for higher pH values in some of the Permo-Triassic sandstones. The Cotswolds oolite, Corallian and Carboniferous carbonate aquifers contained groundwaters with pH similar to those present in the Chalk and Permo-Triassic sandstone.

The aquifers with median pH significantly below 7.0 included the granites of south-west England, the Welsh Palaeozoic mudstones and the Palaeogene deposits of the Wessex Basin (Figure 5.1). These aquifers typically have little or no calcite and the pH of the groundwaters is therefore poorly-buffered. Carbonate-poor parts of the Millstone Grit, Crag and Lower Greensand are indicated by a tailing to low pH.

5.2.2 Specific electrical conductance (SEC)

Specific electrical conductance (SEC) is a proxy measure of the total dissolved ions. Median values in the Chalk

were very similar (Figure 5.2), being slightly higher where the Chalk underlies the Crag in East Anglia. Much of the data showed a narrow range in SEC, especially where the Chalk is unconfined. These samples represent the zone of active circulation, where the aquifer has been well flushed of more saline groundwater. The higher values of SEC were generally present in confined parts of the aquifer, although some areas of confined Chalk had relatively low SEC (e.g. Dorset, Edmunds et al., 2002). High SEC has also been noted at depth beneath the active zone of circulation where the Chalk is unconfined, and beneath the Crag deposits of east Norfolk (Ander et al., 2006).

A much wider range in SEC was found in the Permo-Triassic sandstone aquifers. The lowest medians were found in the Cheshire and South Staffordshire studies, although there was significant overlap with the other regions. The highest median, in the Vale of York, reflects more dissolution of gypsum (Ca-SO₄ type waters), particularly in areas covered with thick till deposits (Shand et al., 2002). The highest SEC groundwaters in most areas were of Na-Cl type, often in coastal areas (e.g. Liverpool, Manchester), where seawater intrusion is known to occur or has occurred in the past, or deep groundwaters (e.g. Cheshire Basin) containing remnant connate or formation water.

The other aquifers display a large range in median SEC, typically over three orders of magnitude. The highest medians are typical of carbonate aquifers, and the lowest typical of carbonate-poor silicate aquifers. The highest SEC values were present in groundwaters sampled from the Lincolnshire Limestone, where salinities were up to a third that of seawater (Griffiths et al., 2006).

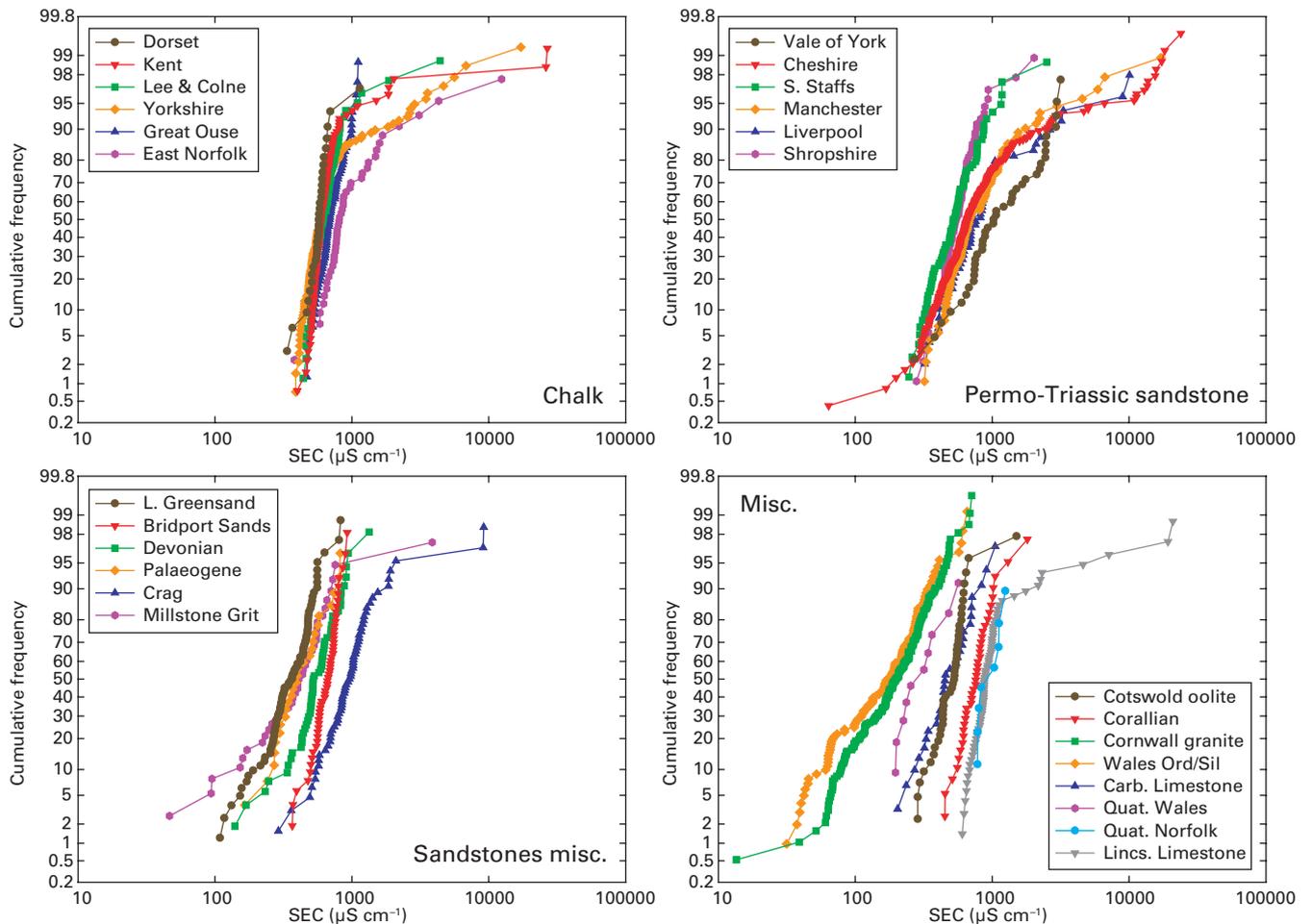


Figure 5.2 Cumulative frequency plots for SEC in groundwaters.

5.3 MAJOR IONS

5.3.1 Calcium (Ca)

Calcium is an abundant element in the Earth's crust and a major component of many rock-forming minerals. It is also an essential element for plants and animals. In sediments, the most important Ca minerals are calcite and dolomite (Section 3.4.1), although plagioclase feldspar may be common in clastic sediments, and gypsum and anhydrite in evaporite deposits. In igneous and metamorphic rocks, Ca is most abundant in feldspar, pyroxene and amphibole. Rainfall inputs of Ca are typically negligible for most groundwaters. Equilibria with respect to the carbonate system forms the dominant control on Ca in natural waters, although ion-exchange may be important.

Most Chalk groundwater distributions show a narrow range in Ca, typically from 100 to 200 mg l⁻¹ (Figure 5.3), reflecting equilibration with calcite at the CO₂ partial pressures typical of temperate latitudes. The highest Ca concentrations are generally in groundwaters with high salinity (Kent, East Norfolk), where Ca is high due to mixing with seawater or remnant formation water. The low Ca concentrations were present in groundwaters in confined parts of the aquifer which showed a trend toward Na-HCO₃ type (Lee and Colne, Kent) as a result of Na-Ca ion exchange. The majority of Chalk groundwaters were at saturation with respect to calcite, an indication of the rapid kinetics of the fine grained calcite matrix.

Calcium concentrations in the Permo-Triassic sandstones show a wide range of concentrations (Figure 5.3), often

over two orders of magnitude for individual study areas. Median concentrations for the study areas were similar (generally <85 mg l⁻¹), except for the Vale of York which had a median concentration of 105 mg l⁻¹. The high Ca in the Vale of York groundwaters is due to gypsum/anhydrite dissolution from within, beneath and above the aquifer (Shand et al., 2002). The high Ca in other areas is partly due to gypsum dissolution particularly for deeper groundwaters, but mixing with formation waters or seawater is also important in some regions (Cheshire, Liverpool). Low concentrations are thought to be a reflection of decalcification of the shallow aquifer over time by recharge waters.

The other sandstone aquifers display variable distributions, dependent largely on whether they are cemented by calcite. The abundance of calcite in the Bridport Sands, for example, has given rise to a solute distribution very similar to the Chalk, whereas, the variability in calcite in the Millstone Grit has given rise to variation over three orders of magnitude. The Carboniferous Limestone, Lincolnshire Limestone, Corallian and oolite carbonate aquifer groundwaters display a strong negative skew (Figure 5.3), representing deeper groundwaters, as a result of Na-Ca ion exchange. The lowest median concentrations are found in the igneous and metamorphic granites and metasediments of Cornwall and Wales.

The dominant source of Ca in groundwaters is considered to be of natural origin. Any local anthropogenic inputs of Ca are likely to be small in comparison with geogenic sources. However, it is possible that pollution, in the form

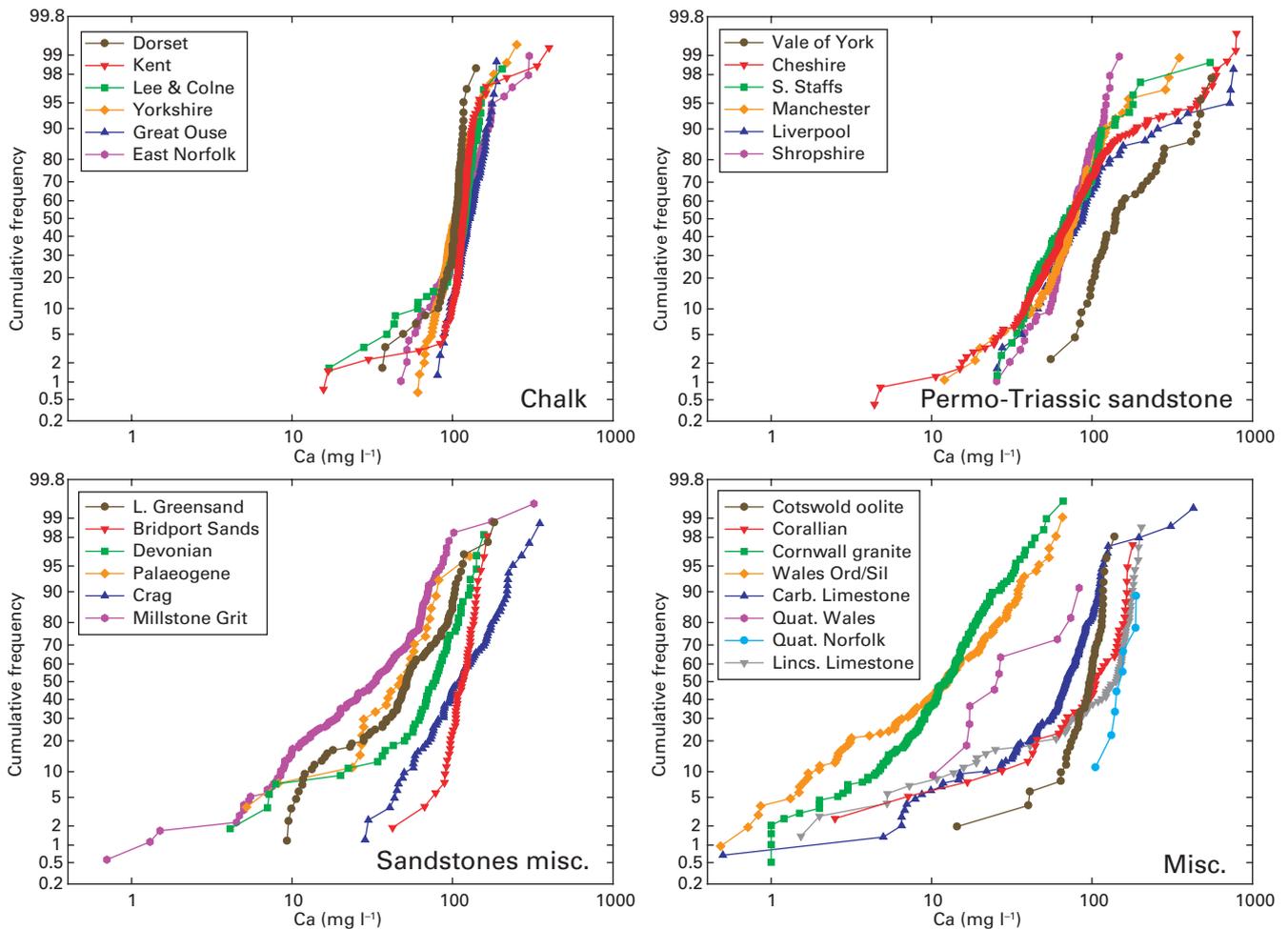


Figure 5.3 Cumulative frequency plots for Ca in groundwaters.

of acid rain, has had an indirect effect e.g. by increasing the rate of decalcification of shallow parts of the aquifer, especially where carbonate minerals are present in only small amounts.

5.3.2 Sodium (Na)

Sodium is most abundant member of the alkali metal group. Unlike Ca, where concentrations are limited in solution by carbonate solubility, there are few precipitation reactions that limit Na in most groundwaters, hence the dominant cation in seawater is Na. Ion-exchange reactions are important controls on Na, particularly during aquifer freshening where Na is released from adsorption sites, and seawater intrusion where Na becomes sorbed. The dominant mineral phases containing Na in aquifers are typically clays and plagioclase (Na-Ca) feldspars, but locally halite (NaCl) may be present in evaporite sediments. Although mineral-water reactions involving Na-bearing minerals are important, the dominant control on Na in most groundwaters is mixing with more saline water.

The Chalk groundwaters display a wide range of Na concentrations, often over two orders of magnitude, and a positive skew (Figure 5.4). The high Na concentrations are typically present at depth, more generally in the confined parts of the aquifer. The distribution of data on the cumulative probability plots is similar to that of Cl (Section 5.3.6), indicating that the most likely control for high Na is from mixing with formation water or seawater. However, a change in population occurs at a

lower percentile than for Cl, indicating a source of Na additional to that from more saline water. The enrichment of these groundwaters in Na has been interpreted as due to ion-exchange of dissolved Ca for adsorbed Na during aquifer freshening i.e. the displacement of formation/connate water by fresh water of meteoric origin. This is consistent with these waters trending towards Na-HCO₃ composition and a concomitant decrease in Ca is solution. Median concentrations are similar in the different study areas (which contain a mixture of unconfined and confined Chalk), but higher in the Chalk beneath Crag deposits in East Anglia where groundwater circulation is likely to be low.

The Permo-Triassic sandstones also display a wide range in concentrations, but with more scatter. The lowest medians are present in the Shropshire and South Staffordshire studies, which may reflect a lower contribution from weathering since Cl concentrations are not so clearly discriminated. The dominant input of Na is considered to be from mixing with older more saline formation water still present in the aquifer, or in some cases locally from underlying aquifers. Plagioclase weathering is likely to make a small contribution of Na (e.g. in the Vale of York where weathered feldspars were noted) but is difficult to distinguish from ion-exchange in more saline waters.

Groundwater in the Lower Greensand has a higher median Na than the other sandstones sampled (Figure 5.4), and most distributions are similar to Cl (Section 5.3.6). The other study areas show a similar picture, indicating the dominance of a marine signature for Na. Some

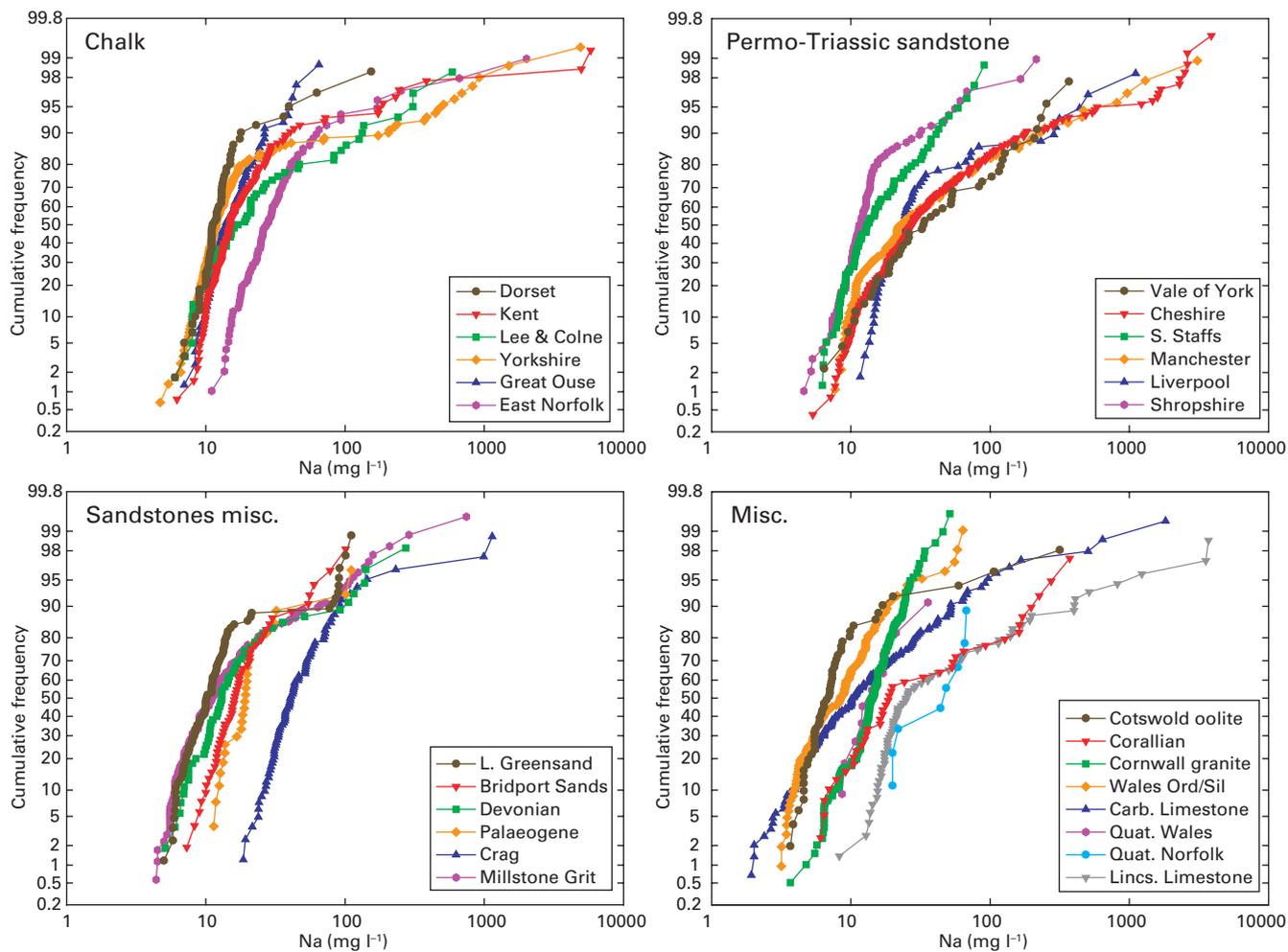


Figure 5.4 Cumulative frequency plots for Na in groundwaters.

distributions display an increase in Na over that expected from mixing with formation water (cf. Cl in the Corallian and Ordovician/Silurian meta-sedimentary aquifers) and are interpreted as an increase due to ion-exchange.

Although Na may be enhanced in groundwaters by pollution (e.g. leakage from septic tanks, road salt application), the distribution range shown is likely to be close to the baseline: contaminated sites were avoided during sampling, the high Na is generally present in deeper parts of the aquifers studied and any local inputs are likely to be swamped by natural sources. Nevertheless, it is possible that the median concentrations may have increased slightly over that of baseline.

5.3.3 Magnesium (Mg)

Magnesium is an alkaline earth metal and the eighth most abundant element in the Earth's crust. It is an essential element for all living matter and forms a component of chlorophyll in plants. Mineral phases in igneous and metamorphic rocks incorporating Mg include the ferromagnesian minerals olivine, pyroxene, mica (biotite and phlogopite), chlorite and amphiboles. It is also present in sedimentary rocks, e.g. in dolomite, and forms a solid solution in other carbonate minerals such as calcite. Dolomite is less reactive than calcite and it is not uncommon to find groundwaters supersaturated with respect to dolomite due to sluggish reaction rates. Magnesium often increases in concentration along flow paths due to the incongruent dissolution of calcite.

The concentration distribution for Mg in Chalk groundwaters (Figure 5.5) is significantly different from that of Ca (Figure 5.3) even though they are both initially sourced from calcite. The highest median is for Chalk groundwater beneath the Crag of east Norfolk, implying a contribution from the overlying Crag which contains groundwaters with moderately high Mg (Figure 5.5). The high concentrations in most study areas are due to a combination of incongruent dissolution of calcite or mixing with more saline waters, generally in confined parts of the aquifer where groundwaters are older and groundwater flow is less than in unconfined Chalk. Magnesium is also likely to be affected by ion-exchange reactions during aquifer freshening which can lead to release of Mg from exchange sites.

The Permo-Triassic sandstone groundwaters display larger differences between study areas, in comparison with Ca. This reflects, in part, the presence of dolomite in the sandstone aquifers compared with low-Mg calcite in the Chalk. The low median concentrations in South Staffordshire and Shropshire may, for example, be due to lower modal abundances of dolomite, whereas dedolomitisation textures were found in core material in the Vale of York area.

The other sandstone aquifers show a range in Mg concentrations, within the range of Permo-Triassic sandstones, with the Lower Greensand having the lowest median and the Crag the highest median concentration. Median concentrations in the miscellaneous aquifer group were typically lower than in the sandstone aquifers, but

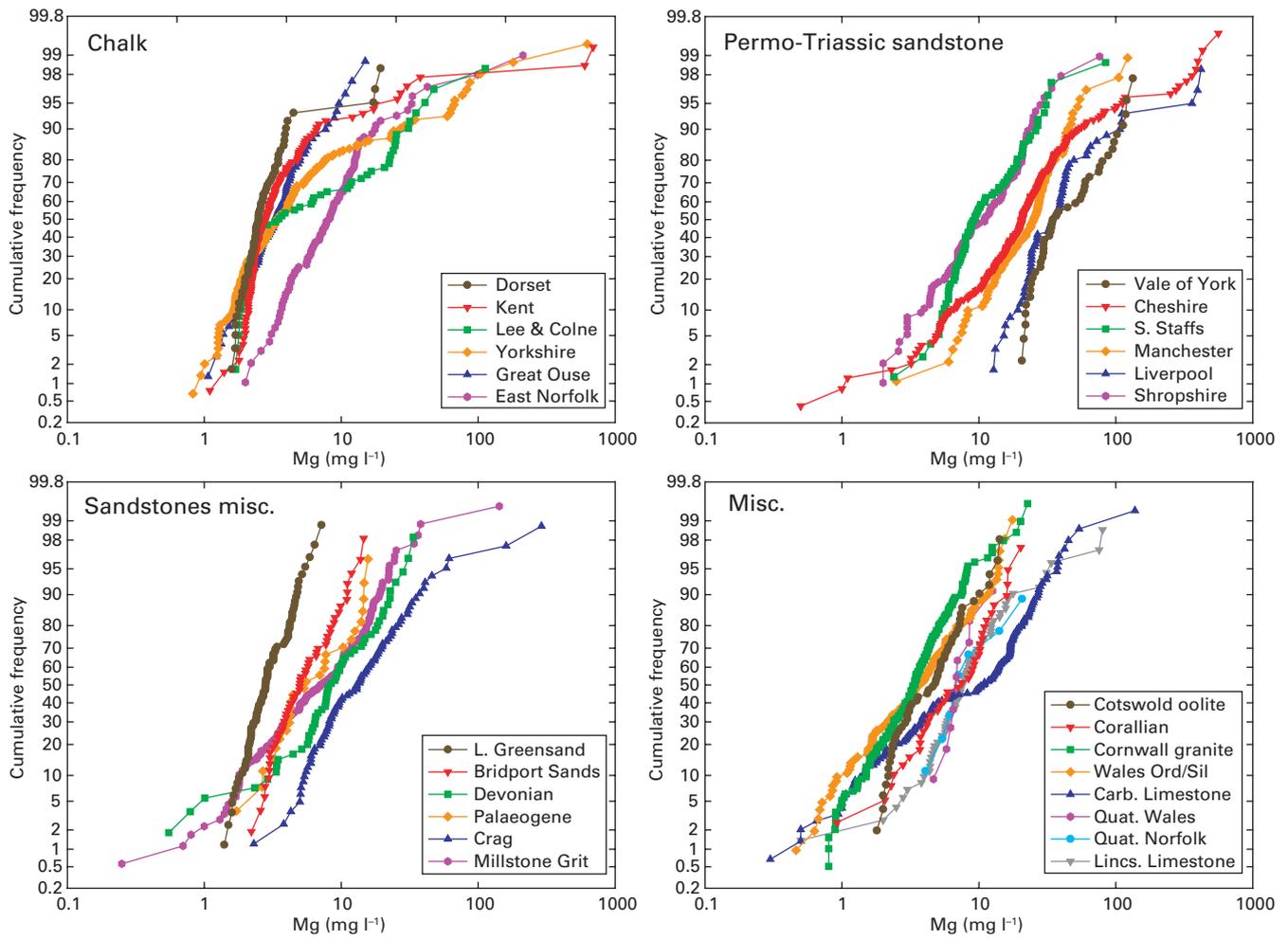


Figure 5.5 Cumulative frequency plots for Mg in groundwaters.

still display a wide range in concentrations. A variety of processes and controls have been described for controlling Mg in the individual study areas, including carbonate dissolution and equilibria, dissolution of ferro-magnesian silicate minerals and ion-exchange. It is likely that the ranges shown on Figure 5.5 are close to baseline, although locally Mg may be enhanced e.g. from agricultural pollution or septic tanks.

5.3.4 Potassium (K)

Potassium is an essential element for plants and animals. Although an alkali metal like Na, it is generally present at much lower concentrations in groundwaters. The source of K in natural waters is dominantly from silicate minerals such as clays, K-feldspars and micas. It is therefore present in minerals which are relatively stable in the weathering environment. As well as uptake by vegetation, K mobility is limited by incorporation into clay minerals such as illite.

All of the Chalk groundwaters show a significant range in K concentrations (up to three orders of magnitude) but with a small range in median values from 1.5 to 3.5 mg l⁻¹ (Figure 5.6). Most of the high K concentrations are associated with the most saline groundwaters indicating a dominant control by mixing with remnant formation waters.

The range of K concentrations in the Permo-Triassic aquifers is similar to those in the Chalk, but median concentrations are slightly higher (Figure 5.6). The higher medians are thought to reflect the dissolution of K-

feldspar, a common constituent mineral in the sandstones. The other sandstone aquifers display a range in median concentrations, being highest in the Crag. Potassium concentrations correlate poorly with salinity in the Crag groundwaters, but show a general correlation with nitrate, thus pointing towards significant contributions from pollutant sources. The groundwaters with the lowest median concentration are those from Ordovician/Silurian metasediments in Wales, related to the inert nature of the rocks (mainly illite and chlorite) and short residence times (weeks to decades) in the waters sampled.

The enhancement of K in groundwaters by pollution (e.g. from fertilisers) is well established. It is likely that a number of samples contain elevated K from pollutant sources, however, the range is dominated by dilute waters of short residence time (low concentrations) and mixing with formation waters (high concentrations). Thus, the median concentrations in some areas may be slightly higher than baseline.

5.3.5 Alkalinity (HCO₃)

High alkalinity in groundwaters, usually as HCO₃, acts as a buffer to changes in pH e.g. it limits the impact of acid rain on groundwater chemistry. Solute concentrations depend on the initial pCO₂ of recharge waters and interactions with the aquifer matrix. Bicarbonate concentrations in the Chalk groundwaters (Figure 5.7) display a narrow range reflecting rapid saturation with respect to calcite, largely due to the fine-grained nature (hence large surface area) of the chalk matrix. The high concentrations indicate a

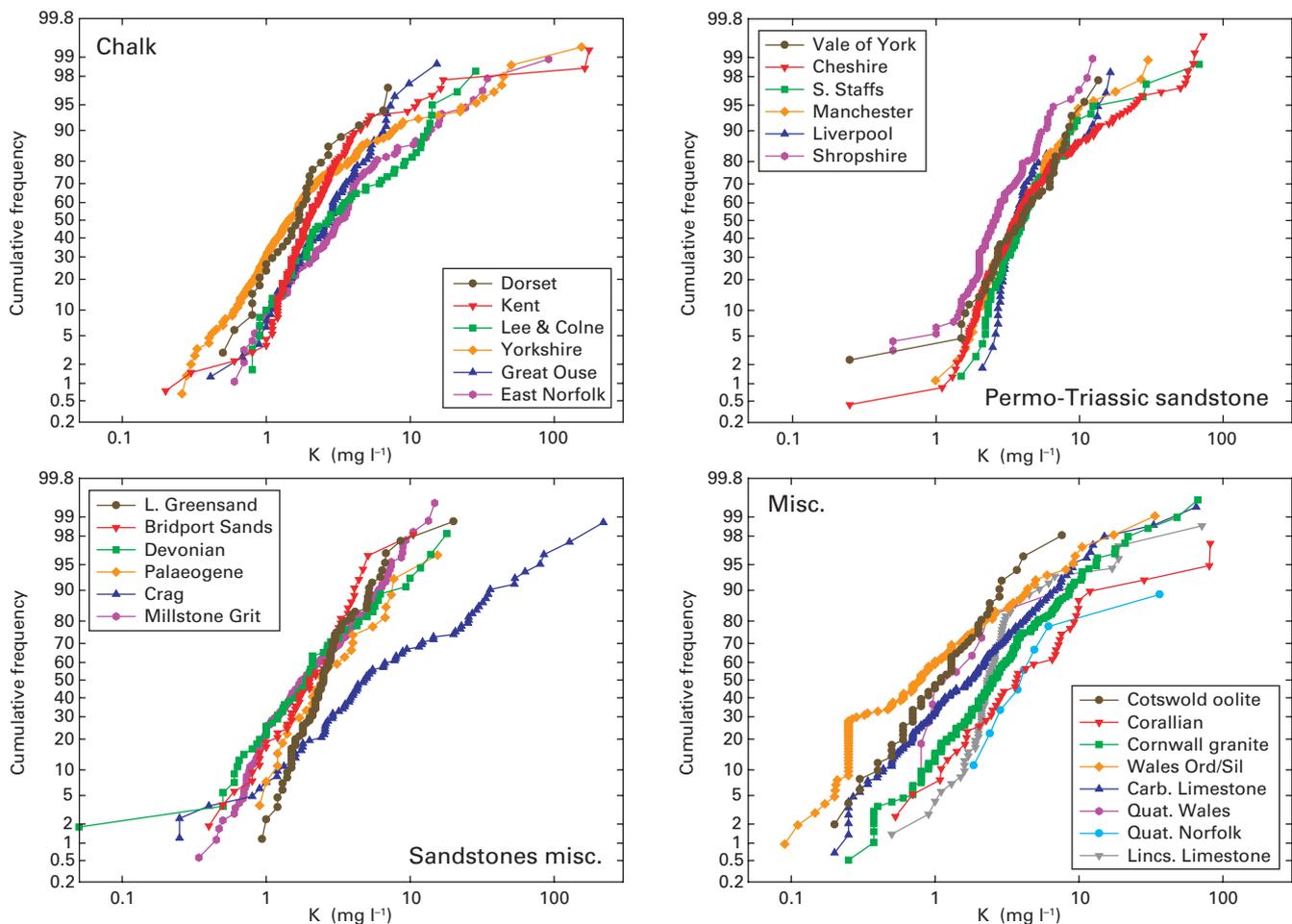


Figure 5.6 Cumulative frequency plots for K in groundwaters.

strong buffering capacity of the groundwater and aquifer, consistent with the narrow range in pH (Figure 5.1).

Groundwaters in the Permo-Triassic sandstones display a wider range in alkalinity. Low HCO_3^- concentrations are associated with shallow parts of the aquifer where decalcification is thought to have occurred. A number of groundwater samples from the Manchester study contained high HCO_3^- (up to 1310 mg l^{-1}). These were Ca-HCO_3^- type waters and it is likely that an additional source of CO_2 , e.g. from sulphate reduction, has contributed to such characteristics.

The carbonate cemented Devonian and Bridport Sands groundwaters have HCO_3^- concentrations similar to those in the Chalk (Figure 5.7). The other sandstone aquifers display a strong negative skew, reflecting either low carbonate contents or short residence times in these samples. Low median concentrations are present in the south-west England granites and Ordovician/Silurian metasediments of Wales where calcite is often rare, and where slow silicate hydrolysis reactions form the dominant control on dissolved HCO_3^- . The other carbonate aquifers are similar to the Chalk, except for the Carboniferous Limestone where short residence times are likely to be the main control responsible for the low concentrations in some of the samples. The distributions shown for all aquifers are dominated by natural inputs and thus considered to reflect baseline.

5.3.6 Chloride (Cl^-)

Chlorine is the most abundant of the halogen elements and exists in solution as the chloride ion (Cl^-). Of all the

major elements present in water, it is the least abundant in the earth's crust, being confined largely to areas where evaporite minerals occur. It is considered to behave conservatively in most aquifers (where sources such as halite are not present) due to its unreactive nature and high solubility. The source of natural Cl in groundwaters is generally from rainfall or due to mixing with formation waters, although concentrations may be high where evaporite minerals (e.g. halite, sylvite) are present and in geothermal areas.

Median concentrations for Chalk groundwaters are generally similar and relatively low (Figure 5.8). Concentrations range from close to that expected from rainfall up to more than $10\,000 \text{ mg l}^{-1}$. The highest Cl concentrations, giving rise to positive skewness, are due largely to mixing with formation water; these were generally groundwaters at depth mainly in the confined Chalk, where the aquifer has not been sufficiently flushed of formation water. The higher median Cl in the east Norfolk groundwater may at least partly reflect recharge through the Crag deposits, which have the highest median Cl of all the aquifers studied (Figure 5.8).

Groundwaters in the Permo-Triassic sandstones show a range of distributions from moderately linear (South Staffordshire, Vale of York) to positively skewed (Cheshire, Manchester, Liverpool). This may in part be a function of sampling, indicating a greater contribution of formation water in the latter regions. Median concentrations, however, were similar for the different study areas.

The other study areas display a wide range in Cl concentrations (Figure 5.8). Although the median may be affected by regional rainfall inputs or anthropogenic

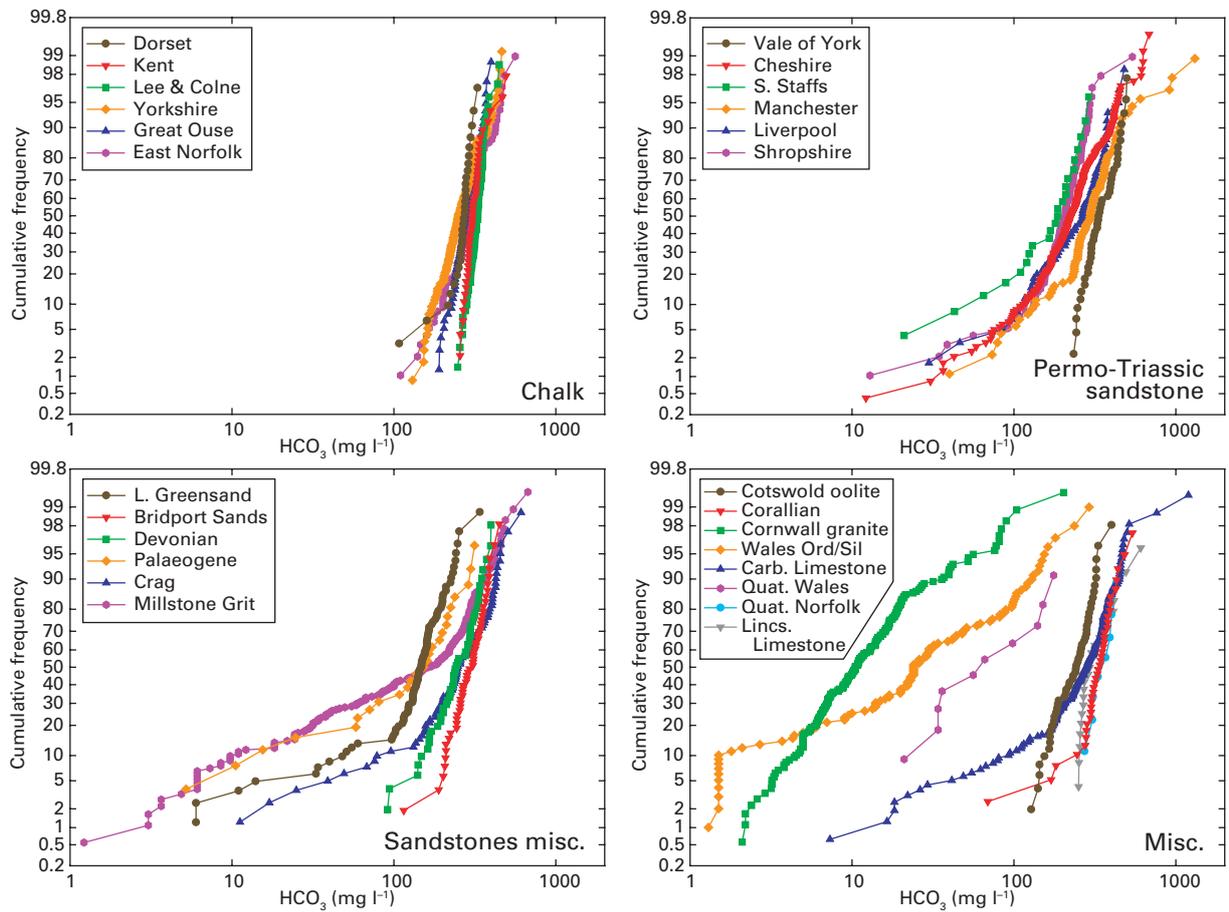


Figure 5.7 Cumulative frequency plots for HCO_3^- in groundwaters.

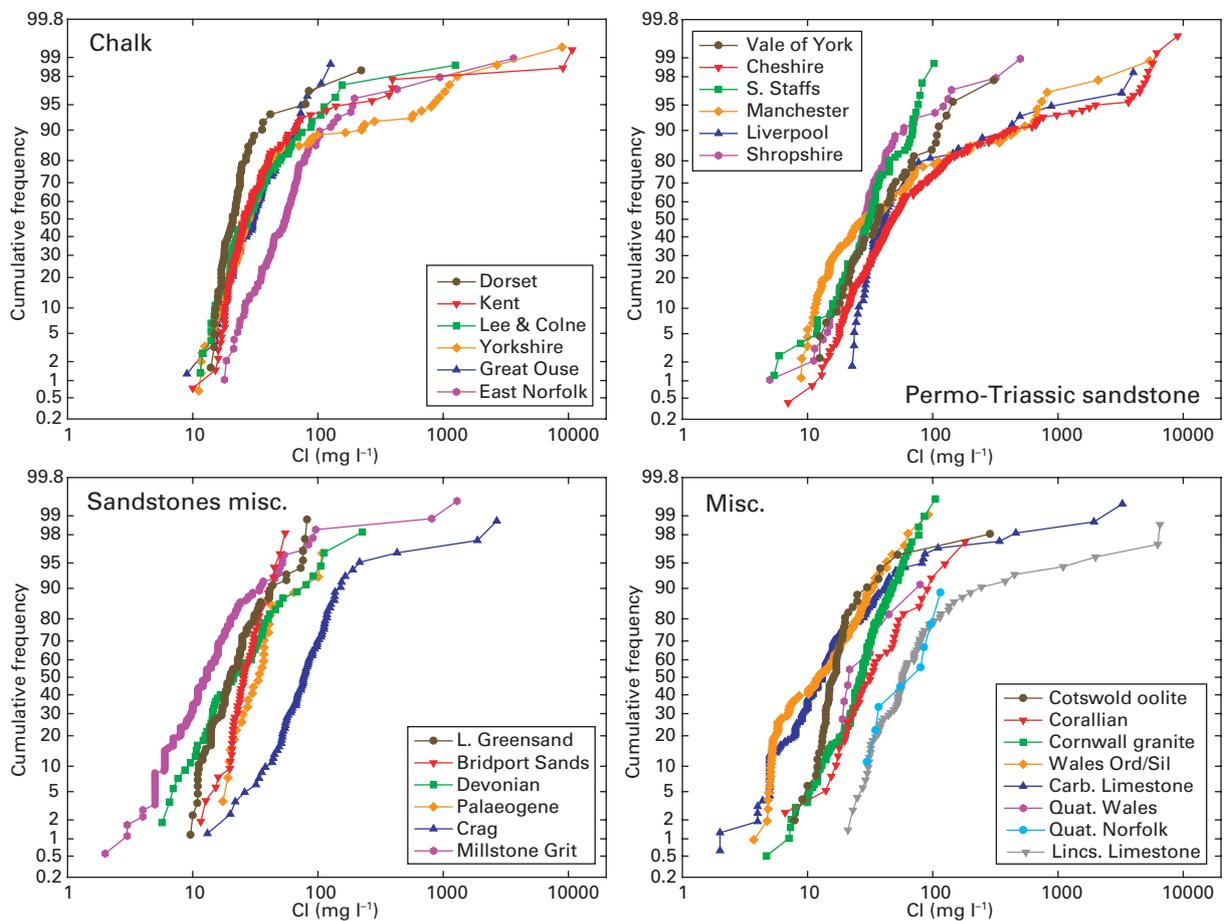


Figure 5.8 Cumulative frequency plots for Cl^- in groundwaters.

activities, the overall range is determined by the degree to which mixing with formation waters has occurred. The lack of positive skewness in some studies may, therefore, simply be due to sampling bias (i.e. only the shallow parts of the aquifer with active circulation have been sampled). Most of the baseline series reports concluded that anthropogenic inputs were locally important. Such inputs include agricultural, industrial, septic tank leakage and road salt applications. It is therefore likely that the median concentrations in some study areas are slightly higher than the baseline.

5.3.7 Sulphate (SO₄)

The most extensive geological occurrences of sulphate minerals occur in evaporite deposits, where sulphate is present in gypsum or anhydrite. Sulphur is also widely distributed in the natural environment in the form of disseminated sulphide minerals or ore deposits, most commonly sulphides of Fe (pyrite), Zn (sphalerite) or Pb (galena). It is the only major element in natural waters that undergoes redox reactions, hence its behaviour is complex. Examples include the oxidation of sulphide minerals which increases SO₄ concentrations and generates acidity (e.g. acid mine drainage) and sulphate reduction where sulphate is incorporated into sulphide minerals and lost from groundwater. The major sources in groundwater include the above mineral phases, rainfall (including anthropogenic inputs) and mixing with seawater or formation water.

Sulphate concentrations in Chalk groundwaters vary up to three orders of magnitude (Figure 5.9). There is a range

in median concentrations with the lowest in the Dorset Chalk and highest in East Norfolk where the Chalk is overlain by Crag and Palaeogene deposits. Correlations of SO₄ with Cl indicate that the highest concentrations are dominated by mixing with formation water within the Chalk or leakage from adjacent formations. The lowest concentrations are most likely controlled by atmospheric inputs or minor sulphur sources such as marcasite/pyrite present in the Chalk.

Groundwaters in the Permo-Triassic sandstones display a similar range to those in the Chalk, although medians are generally higher, especially for the Vale of York and Liverpool areas (Figure 5.9). In the Vale of York groundwaters, high SO₄ concentrations are present in waters with low Cl, being derived largely from the dissolution of gypsum or anhydrite. The high upper quantiles compared with other areas is thought to be due to preservation of evaporite cements in the sandstone because of low transmissivity and thick overlying drift deposits. In Liverpool, high SO₄ is partly derived from dissolution of evaporite minerals or mixing with formation water (or seawater in coastal areas). Apart from the Vale of York, most high SO₄ concentrations are either from areas overlain by the Mercia Mudstone or in deep parts of the aquifer.

For the other sandstone aquifers, the Crag contained the highest concentrations of groundwater SO₄. High concentrations relative to Cl indicate that simple mixing with a marine source cannot explain the data and additional sources are required. The lowest median concentrations were found in the siliclastic aquifers: Ordovician/Silurian metasediments of Wales, south-west England granites

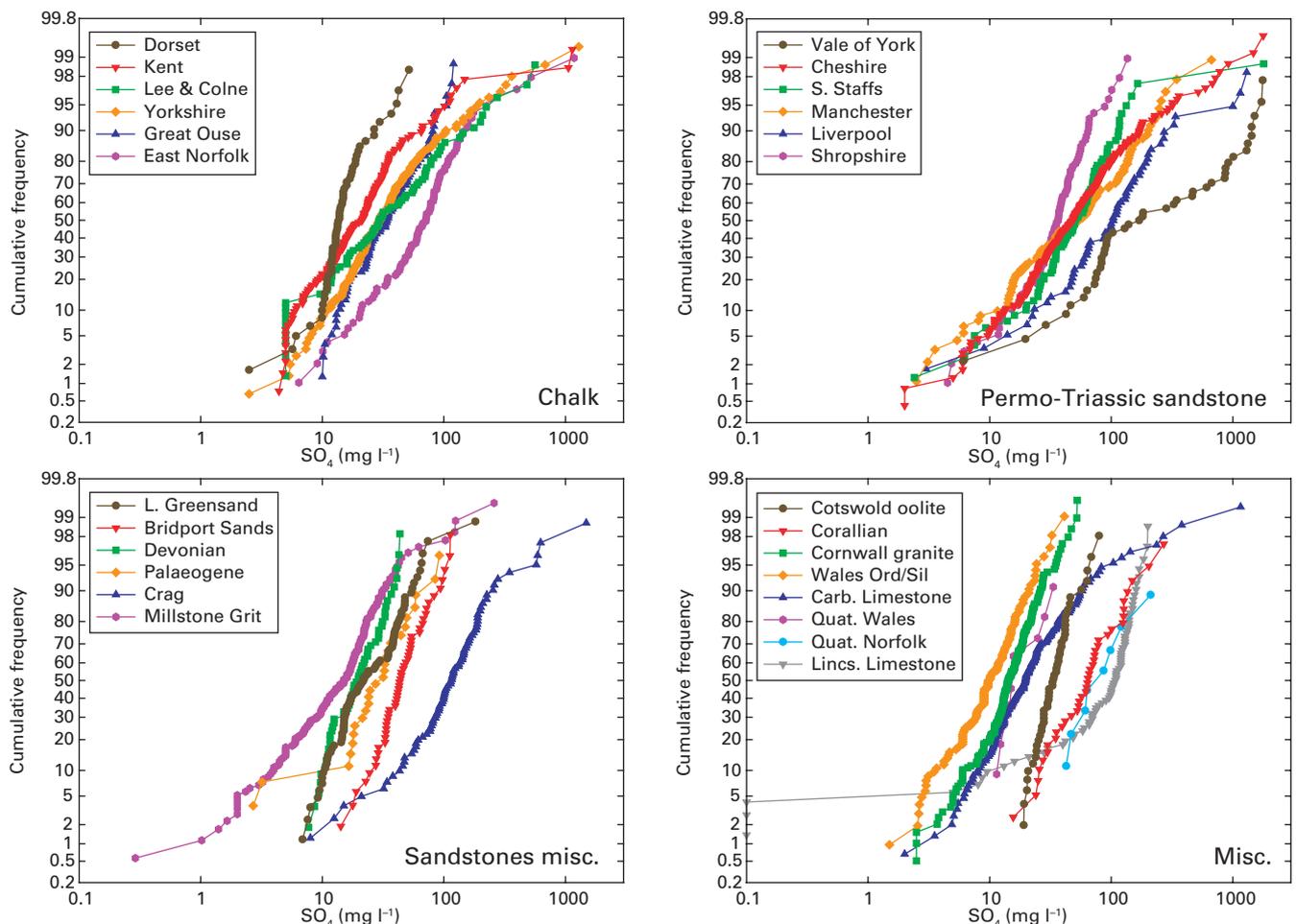


Figure 5.9 Cumulative frequency plots for SO₄ in groundwaters.

and Millstone Grit. The Lincolnshire Limestone had the highest median SO_4 of the carbonate aquifers as a consequence of relatively abundant fine-grained pyrite in the limestone matrix (Griffiths et al., 2006).

Sulphate incorporated in fertilisers and pesticides is likely to have had a significant impact on the baseline of groundwaters over large areas. Although this is unlikely to have modified the range of natural concentrations, it may have slightly increased the median concentrations of most groundwater bodies. In addition to local pollution (e.g. petrol refining, detergents and other industrial uses), the regional baseline of modern recharge waters has also been impacted by anthropogenic atmospheric inputs due to SO_2 emissions.

5.4 NUTRIENT SPECIES (N AND P) AND DOC

Nitrogen is present in water in the form of a number of dissolved species: nitrate (NO_3), ammonium (NH_4), nitrite (NO_2) and organic nitrogen. The inorganic species are largely dependent on the redox condition of the water with NO_3 being stable under oxidising conditions and NH_4 and NO_2 (a metastable species) being more stable under reducing conditions. Organic nitrogen was not analysed as part of this study, but may form a significant component of total nitrogen present in groundwaters (Peach et al., 2006). The main controls on nitrate in groundwater are land use and human impacts. Total dissolved P was included in the suite of determinands for the project sampling. Over the past century, there have been large changes to natural N and P cycles, mainly due to the application of fertilisers

in agriculture. Although point sources of pollution have been avoided, diffuse pollution by fertiliser addition has led to significant increases in nutrient inputs with time (Figure 2.5) over large areas. As well as the extensive but variable applications of fertiliser, geochemical reactions such as denitrification make the determination of baseline very difficult. Atmospheric inputs have also significantly increased in the past due to emissions from the burning of fossil fuels, hence human impacts are present at the regional scale from recharge inputs.

5.4.1 Nitrate ($\text{NO}_3\text{-N}$)

Nitrate data for the majority of aquifer study areas vary over several orders of magnitude (Figure 5.10) and display a strong negative skew (vertical lines on the figure relate to different detection limits). The majority of aquifers have been affected by human impact, especially diffuse agricultural pollution and the higher concentrations of nitrate do not reflect baseline (see individual reports for more details). The use of cumulative probability plots to discriminate different populations (e.g. baseline vs. anthropogenic) is difficult for nitrate because the low concentrations are partly due to denitrification which removes nitrate naturally from the system. Concentrations below the limit of detection are likely to indicate denitrification since they were generally measured in confined groundwaters or deep parts of the aquifer where circulation is slow and where reducing conditions exist.

Median concentrations for nitrate in Chalk groundwaters have a range from 5.9 to 9.5 $\text{NO}_3\text{-N}$ mg l^{-1} , although the east Norfolk area had a low median concentration of 3.7 mg l^{-1} , probably reflecting protection by overlying

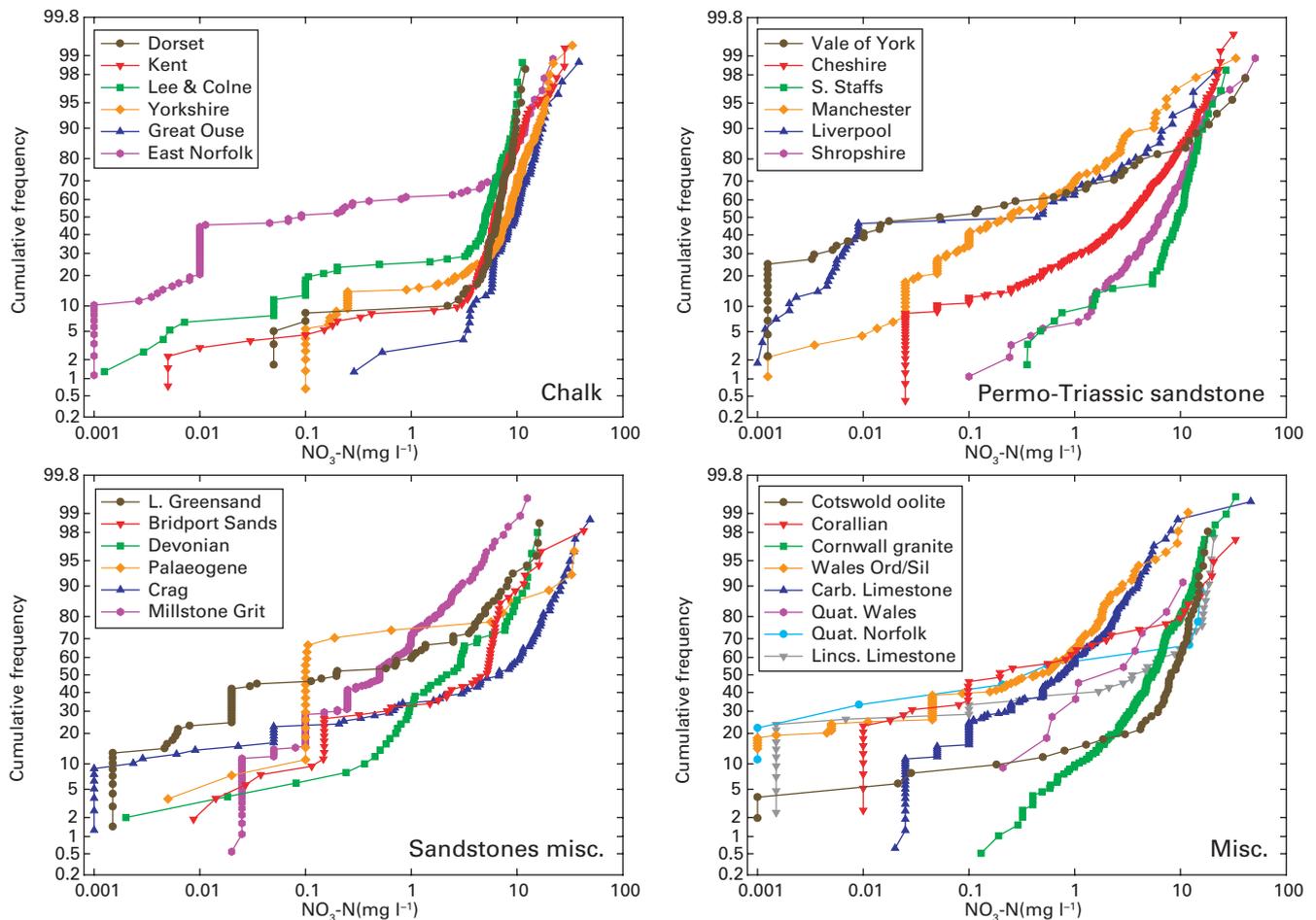


Figure 5.10 Cumulative frequency plots for $\text{NO}_3\text{-N}$ in groundwaters.

deposits as well as more reducing conditions on average than the other areas. The shape of the curves, with a strong negative skew is biased by sampling from across redox boundaries. Such boundaries coincide roughly with unconfined/confined conditions or flow systems (e.g. shallow active circulations and deep stagnant systems).

The Permo-Triassic aquifers also display a large range in concentrations (Figure 5.10). The large variation in median concentrations is in part likely to be controlled by the amount and extent of impermeable drift deposits over the different regions where samples were collected. The range in concentrations found for the Chalk and Permo-Triassic sandstones are typical of most other aquifers studied, the range indicating the degree of anthropogenic inputs and variations in redox status. The upper concentrations in many aquifers exceed the EC drinking water standard of $11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. Although changes in slope occur on many of the probability plots at low concentrations, it is problematic to correlate this to an upper baseline because of competing geochemical controls such as denitrification. An historical assessment is therefore preferred for each individual source. The baseline range of $\text{NO}_3\text{-N}$ in aquifers, as indicated by historical data, is likely to vary from less than 1 mg l^{-1} (e.g. in upland areas which are N-limiting) to possibly around 3 to $4 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$.

5.4.2 Nitrite ($\text{NO}_2\text{-N}$)

Nitrite is produced as an intermediary metastable species during denitrification, and is a good indicator of ongoing denitrification. Concentrations in groundwaters are typically low in comparison with other N-species. The concentrations of $\text{NO}_2\text{-N}$ in most of the groundwaters

studied (Figure 5.11) are rarely above 1 mg l^{-1} , and more typically less than 0.1 mg l^{-1} (the current EC maximum limit for drinking water). As with nitrate, it is difficult to assess the baseline for each study area because of the extent of diffuse anthropogenic inputs of N, both from the atmosphere and agricultural/urban pollution.

5.4.3 Ammonium ($\text{NH}_4\text{-N}$)

The ammonium ion, NH_4^+ , is strongly sorbed on mineral surfaces and stable under reducing conditions. Although high ammonium is often associated with pollution, many of the high concentrations in the present study were found in old reducing groundwaters with the high concentrations derived from ion-exchange reactions on clays. It is not unusual to find concentrations greater than $1 \text{ mg l}^{-1} \text{ NH}_4\text{-N}$ in old reducing groundwaters and some confined groundwaters occasionally exceeded 10 mg l^{-1} (Figure 5.12). The baseline range $\text{NH}_4\text{-N}$ is more easily defined where the maximum concentration is defined by old reducing groundwaters, but the baseline distribution and maximum are more difficult to define in aquifers with young groundwaters due to the human impact on the N-cycle described in the previous sections.

5.4.4 Total dissolved phosphorus (TDP)

Dissolved phosphorus concentrations in groundwater are derived from a variety of natural and anthropogenic sources, occurring as inorganic orthophosphate, inorganic polyphosphates and organic P. The dominant natural source of P is apatite, especially fluorapatite, and exchangeable P on iron oxides (either desorbed or

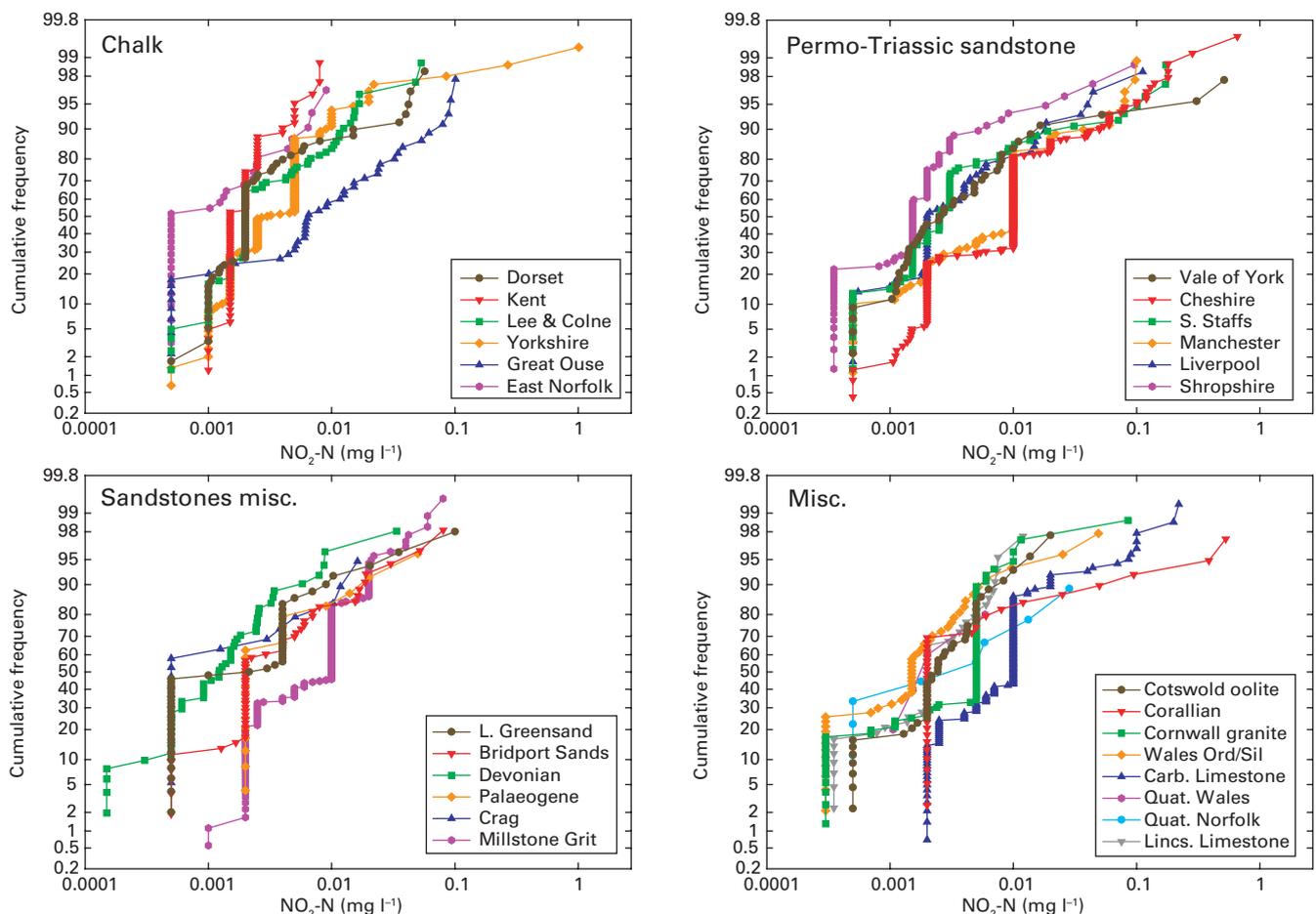


Figure 5.11 Cumulative frequency plots for $\text{NO}_2\text{-N}$ in groundwaters.

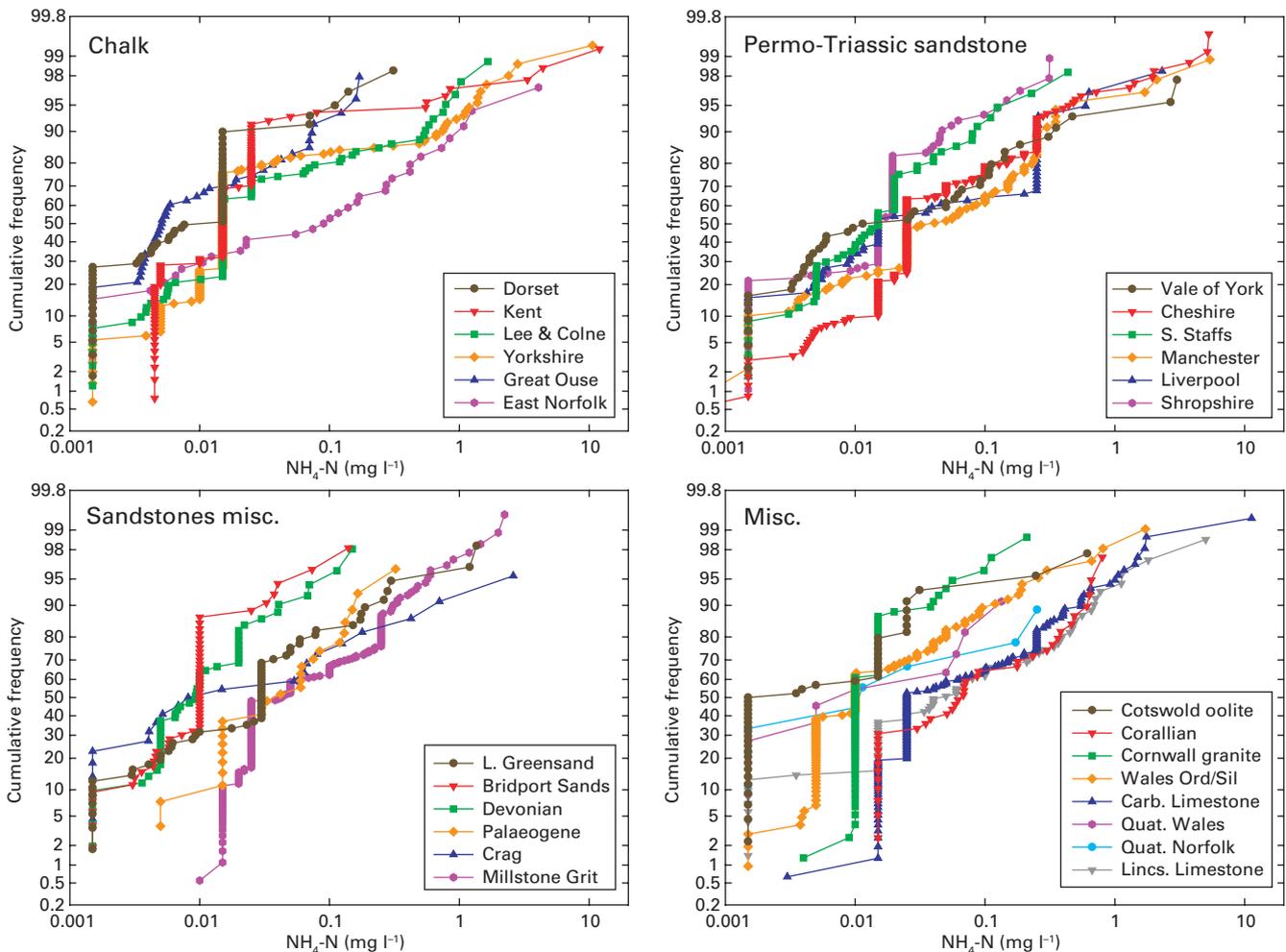


Figure 5.12 Cumulative frequency plots for $\text{NH}_4\text{-N}$ in groundwaters.

dissolved during reductive dissolution). Anthropogenic sources include inorganic and organic fertilisers, water treatment works and farmyard slurry. Under alkaline conditions P is easily sorbed to calcite, hence its mobility is likely to be low. A large proportion of total phosphorus in waters occurs in particulate form and it is likely that the total dissolved phosphorus (TDP) analysed in this study contains a component present as colloidal particles.

Total dissolved phosphorus concentrations in Chalk groundwaters vary over 1 to 2 orders of magnitude (Figure 5.13), with the biggest range being present in the Yorkshire Chalk. High concentrations of P in the confined part of the aquifer are likely to be from natural sources e.g. fluorapatite present in hardgrounds. Although P mobility is often considered to be limited in carbonate aquifers, the data indicate that high concentrations can exist. The sources and transport of TDP in the Chalk are as yet poorly understood, but it is probable that both anthropogenic and natural sources exist, although their relative importance is not yet known.

Permo-Triassic sandstone waters typically show a range of about two orders of magnitude. High concentrations of TDP are sometimes found in groundwaters considered to be relatively old and covered with thick drift deposits, hence it is likely that some of the high TDP is of natural origin. The other aquifers studied show variable distributions, but all display significant ranges in concentrations.

Determining the baseline for P in groundwaters is complicated because of limitations in our knowledge of P behaviour and the multiple natural and pollutant sources. However, the presence of high concentrations in

old groundwaters under confined conditions means that natural ranges are likely to be high under such conditions. Median concentrations, however, are likely to be enhanced in most aquifer systems.

5.4.5 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) mainly comprises mixtures of macro molecules classified as humic and fulvic substances. Dissolved organic carbon in this study represents the sum of organic material after filtering through a $0.45\ \mu\text{m}$ Ag-membrane filter. Most DOC is derived from soils and can play an important part in redox processes and in solute transport, especially of trace metals. The nature of most DOC in groundwater is poorly documented and its ability to modify redox status and solute transport is determined by the reactivity of the organic matter. Aquifers may contain high organic carbon and contribute significantly to the DOC of groundwater. In addition, pollution may also enhance groundwater concentrations e.g. beneath slurry pits and around landfill sites.

Median concentrations in Chalk groundwaters are around 1 to 2 mg l^{-1} (Figure 5.14), although the Dorset Chalk is lower ($0.75\ \text{mg l}^{-1}$) and the Yorkshire Chalk higher ($5.4\ \text{mg l}^{-1}$). The presence of high DOC in the confined parts of the Chalk aquifer (e.g. Lee and Colne, and Yorkshire) indicates that these are likely to be of natural origin.

The groundwaters of the Permo-Triassic sandstone aquifer display a wide range in median concentrations.

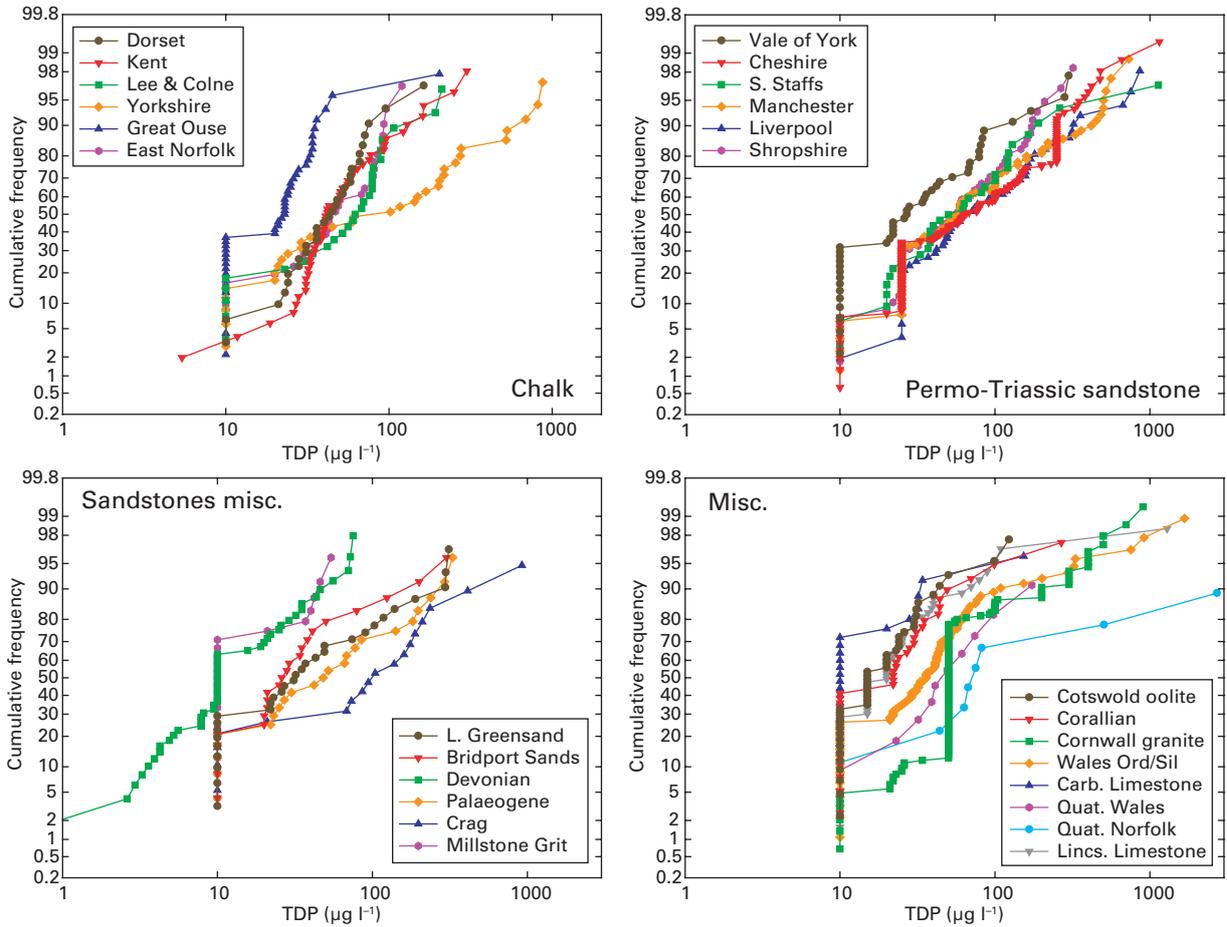


Figure 5.13 Cumulative frequency plots for total dissolved phosphorus (TDP) in groundwaters.

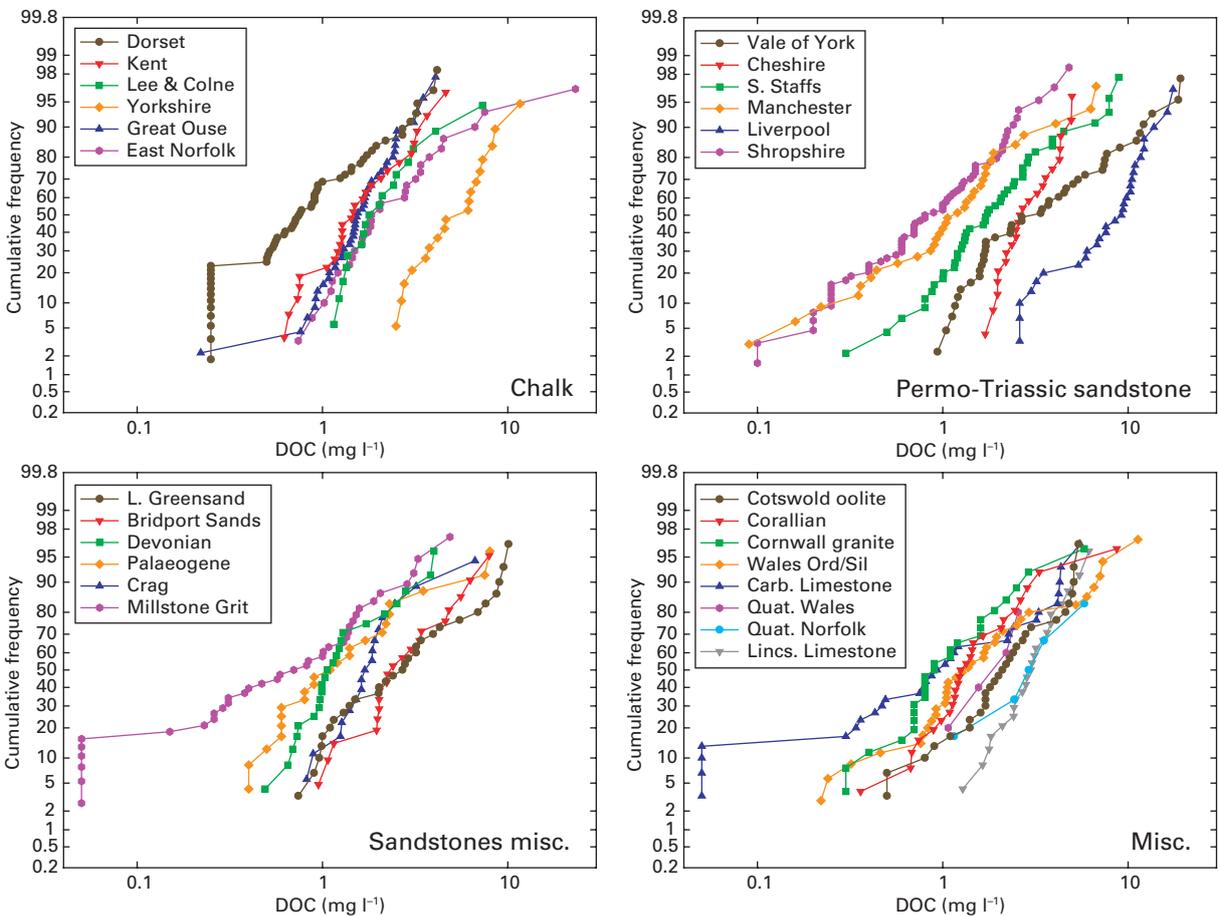


Figure 5.14 Cumulative frequency plots for dissolved organic carbon (DOC) in groundwaters.

Those in the Vale of York and Liverpool are considered to be natural, despite very high concentrations (up to 19 mg l^{-1}): the high concentrations were often found in areas covered with thick drift deposits indicating a potential source of organic carbon. Most other aquifers contain groundwaters with a range of about one order of magnitude. In some areas, such as the Lincolnshire Limestone, where natural organic carbon is high in the aquifer matrix, the ranges are considered to be largely natural. As with TDP, concentrations in many aquifers are likely to be enhanced locally, and a definitive baseline for each system difficult to characterise precisely.

5.5 MINOR ELEMENTS (Si, F, Br, I)

5.5.1 Silicon (Si)

Silicon is the second most abundant element in the Earth's crust. It forms a strong tetrahedral bond with oxygen, which forms the fundamental building block of silica and silicate minerals, the dominant phases in most igneous and metamorphic rocks. Dissolved silicon in waters is hydrated and most accurately represented as the electrically-neutral species H_4SiO_4 or $\text{Si}(\text{OH})_4$ at the pH's typical of natural waters (Hem, 1992). The solubility of Si is generally low, except in geothermal waters, hence it is classed as a minor element. The solubility of Si is limited by saturation with respect to silica (SiO_2) for which a series of Si polymorphs exists; quartz is the least soluble (ca. 6 mg l^{-1}) and amorphous Si (ca. 115 mg l^{-1}) the

most soluble. Solubility controls may also be imposed by clay minerals. Many of the groundwaters are saturated with respect to the silica polymorph chalcedony, and this is likely, along with clays, to control the upper limits of solubility at the ambient temperatures of the aquifers. The dissolution of silica is generally very slow, especially for quartz, and the Si present in most waters is derived from aluminosilicate minerals such as feldspars and ferromagnesian silicates.

The aquifers of England and Wales contain groundwaters with a range of Si concentrations (Figure 5.15) from ca. 0.2 to 20 mg l^{-1} . Chalk groundwaters approach a log-normal distribution, but there are significant differences across the country. For example, the Yorkshire Chalk has a much lower median Si than the other areas. The source of Si is not known but most likely to be from clay minerals or flint (microcrystalline silica with sub microscopic pores). The variations in the Chalk groundwaters may reflect regional variations in the distribution of these phases.

Groundwaters in the Permo-Triassic sandstones display a wider range, due to a few very low concentrations, but their medians are quite similar (Figure 5.15). The negative skew of low concentrations represent shallow groundwaters of short residence time. The source of Si is most likely to be from silicate minerals such as feldspar, which displays dissolution features visible under scanning electron microscopy (e.g. Shand et al., 2002). The Si concentrations in the other sandstones studied vary in range; in general the purer sandstones (such as the Devonian) have lower median concentrations. Some of the other aquifers, such as the Carboniferous Limestone and

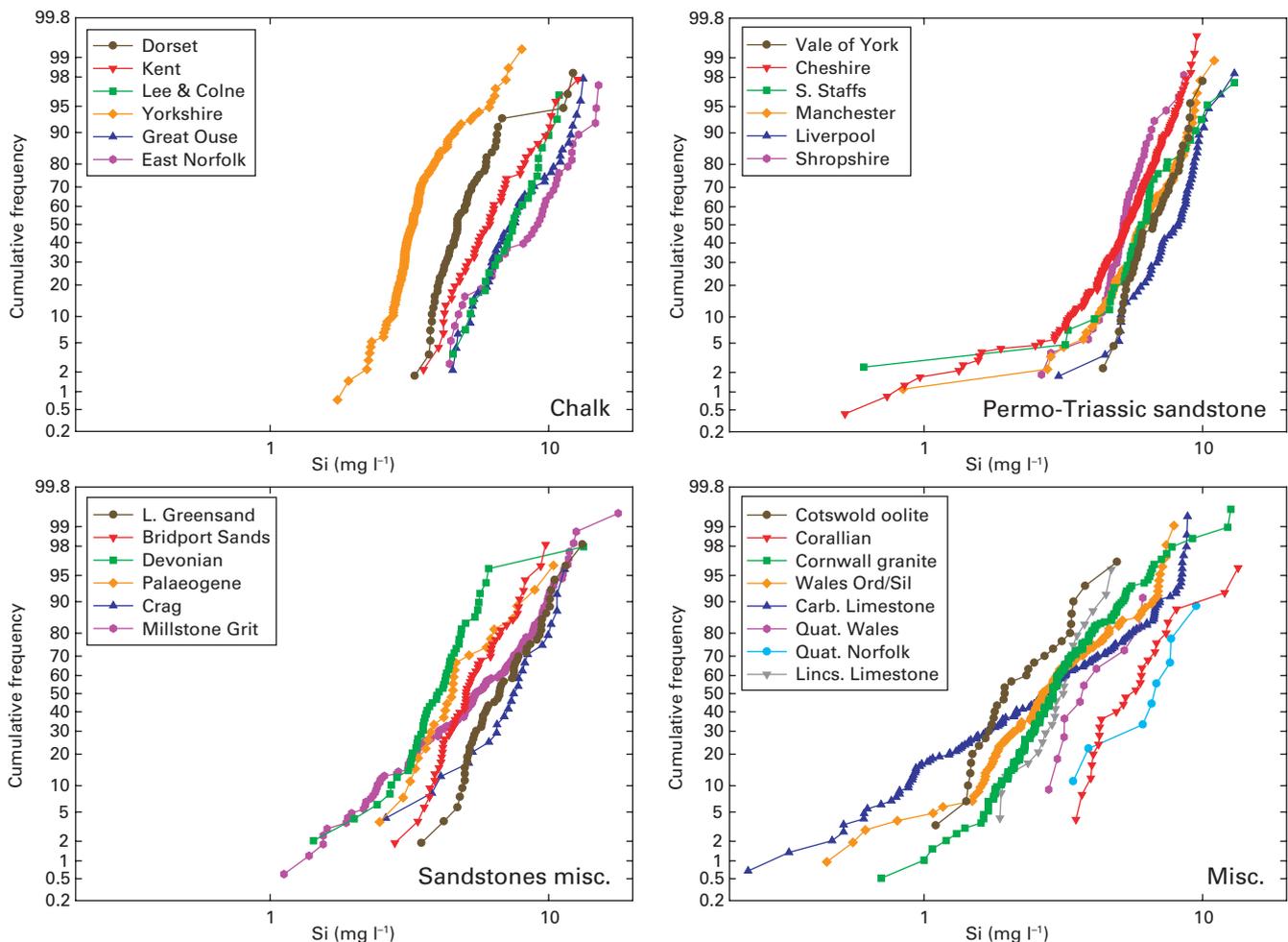


Figure 5.15 Cumulative frequency plots for Si in groundwaters.

Cornish granites, display a wide range in concentrations reflecting the interplay between low contents of silicate minerals and variable residence times respectively (Figure 5.15).

5.5.2 Fluoride (F)

Fluoride concentrations in rainfall are generally low, hence the dominant inputs are from mineral phases present in the aquifer matrix. It occurs in natural waters as the F^- ion, and may form strong complexes with a number of cations. Fluorine is an essential element, being used in the formation of bones and teeth, but is toxic at high concentrations causing dental and skeletal fluorosis if ingested. Fluorite (CaF_2) is the most common mineral containing F as a major component, but other minerals such as apatite, amphiboles and micas contain appreciable concentrations, replacing OH in mineral lattices. Concentrations in most waters are limited by saturation with respect to fluorite, which is relatively insoluble. In waters containing low Ca (e.g. $Na-HCO_3$ type), however, concentrations may reach 10 to 20 $mg\ l^{-1}$ or higher in regions where naturally high F occurs (e.g. in volcanic areas).

Median concentrations in the Chalk groundwaters are generally low ($<0.3\ mg\ l^{-1}$), but variable, and a number of samples are above the present EC drinking water standard of $1.5\ mg\ l^{-1}$ (Figure 5.16). The highest concentrations are normally present in old groundwaters from the confined aquifer. From the ages of these groundwaters (several thousand years), it would appear that F builds up very

slowly in the groundwater. The most likely source of F is fluorapatite, which occurs as fossil material (fish bones, scales) especially in hardbands or marl horizons. The ready availability of Ca, typical of Chalk groundwaters, limits F in the unconfined aquifer. However, ion-exchange of Ca for Na in the confined parts of the aquifer potentially allows F concentrations to increase. For example, Shand (1999) noted concentrations up to $17\ mg\ l^{-1}$ in some Chalk porewaters where Ca was only $3\ mg\ l^{-1}$ due to ion-exchange. The highest median F was present in waters from the east Norfolk Chalk aquifer, which is largely covered with thick till deposits.

Median concentrations in Permo-Triassic sandstone aquifers were mostly very similar at around $0.1\ mg\ l^{-1}$, the exception being groundwaters in the Vale of York where median F was nearly $0.2\ mg\ l^{-1}$ in the largely till covered aquifer. Comparisons with the Chalk point towards either a source in the till or to longer residence times in such areas. Maximum concentrations, however, were less than $1\ mg\ l^{-1}$. The other sandstones displayed a range of distributions, with F often being present at low concentrations in Devonian and Palaeogene groundwaters. The few high concentrations in the latter are probably due to abstraction from sands in contact with the underlying Chalk aquifer (Neumann et al., 2004). In the other aquifer systems studied, F tends to be highest in the carbonate aquifer groundwaters (Figure 5.16). The highest concentrations (up to $10.3\ mg\ l^{-1}$) and highest median were found in groundwaters of the Lincolnshire Limestone aquifer, the source being the recrystallised remains of marine fossils (Edmunds et al., 1999).

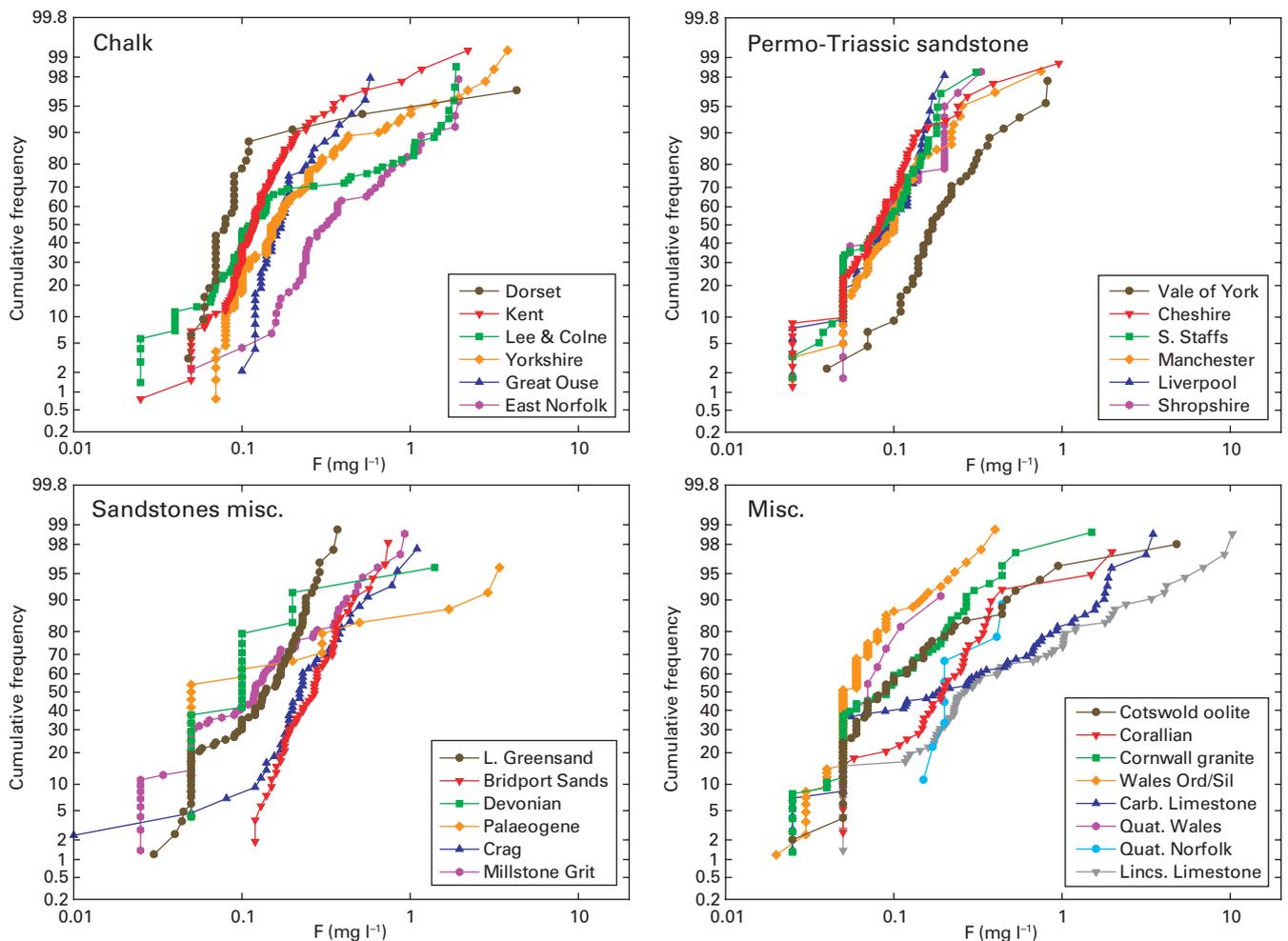


Figure 5.16 Cumulative frequency plots for F in groundwaters.

5.5.3 Bromide (Br)

The geochemistry of Br is similar to that of Cl (Edmunds et al., 1989), and the two are generally highly correlated. The ratio Br/Cl is a useful indicator of the source of salinity, any deviations from the seawater ratio being indicative of non-marine sources or geochemical processes. For example, high ratios may indicate derivation from organic sources and low ratios dissolution of halite. Some slight enrichment in Br/Cl also occurs naturally during infiltration as a result of biogeochemical processes (Edmunds, 1996). Recent shallow groundwaters in the studied aquifers have very variable Br/Cl ratios, in contrast to older deeper groundwaters which often have marine signatures. This is likely to be due to variable anthropogenic inputs such as industrial aerosols, road salt and industrial and agricultural chemicals. This indicates a potential use for this ratio, but further work needs to be carried out to characterise the various anthropogenic inputs.

The data for Br are shown on Figure 5.17, where it can be seen that the distributions are similar to those of Cl (Figure 5.8). The lowest concentrations are similar to those of rainfall, and some increase is due to the effects of evapotranspiration. The positive skew for some of the Chalk and Permo-Triassic groundwaters is due to mixing with formation, connate or old seawater. This is also the case for the high-Cl groundwaters of the Lincolnshire Limestone, although high Br/Cl ratios indicate a contribution from the relatively high organic matter content of the aquifer matrix. Several confined groundwater samples from the Permo-Triassic aquifer had low Br/Cl ratios and this indicates at least some input from the evaporite mineral halite (NaCl).

5.5.4 Iodide (I)

In most aqueous environments, iodine occurs as iodide, I^- , and like its halogen neighbours Br and Cl, it generally displays conservative behaviour. The ratio I/Cl , however, is much higher in rainfall than in seawater indicating a strong fractionation during entrapment of sea salt, possibly by vapour transfer due to the volatility of iodide compounds. Iodine is also strongly associated with organic matter and the breakdown of organic matter may release I to groundwaters.

Most groundwaters in the study areas show variations ranging over approximately two orders of magnitude (Figure 5.18). There are significant variations between different areas of the same aquifer which cannot be simply related to distance from the coast. Correlations with Cl vary from aquifer to aquifer, possibly due to different biogeochemical processes including biological uptake and mixing with formation water.

5.6 TRACE ELEMENTS

5.6.1 Aluminium (Al)

Aluminium (Al) is one of the most abundant elements on Earth, with average crustal and soil concentrations of 6 to 7 wt%. However, Al is classed as a trace element in natural waters due to its generally low solubility at the pHs (pH 6 to 8) typical of surface waters and groundwater. The dominant minerals with Al as a major component are the aluminosilicates including feldspars, micas and clays. The weathering of these minerals represents the

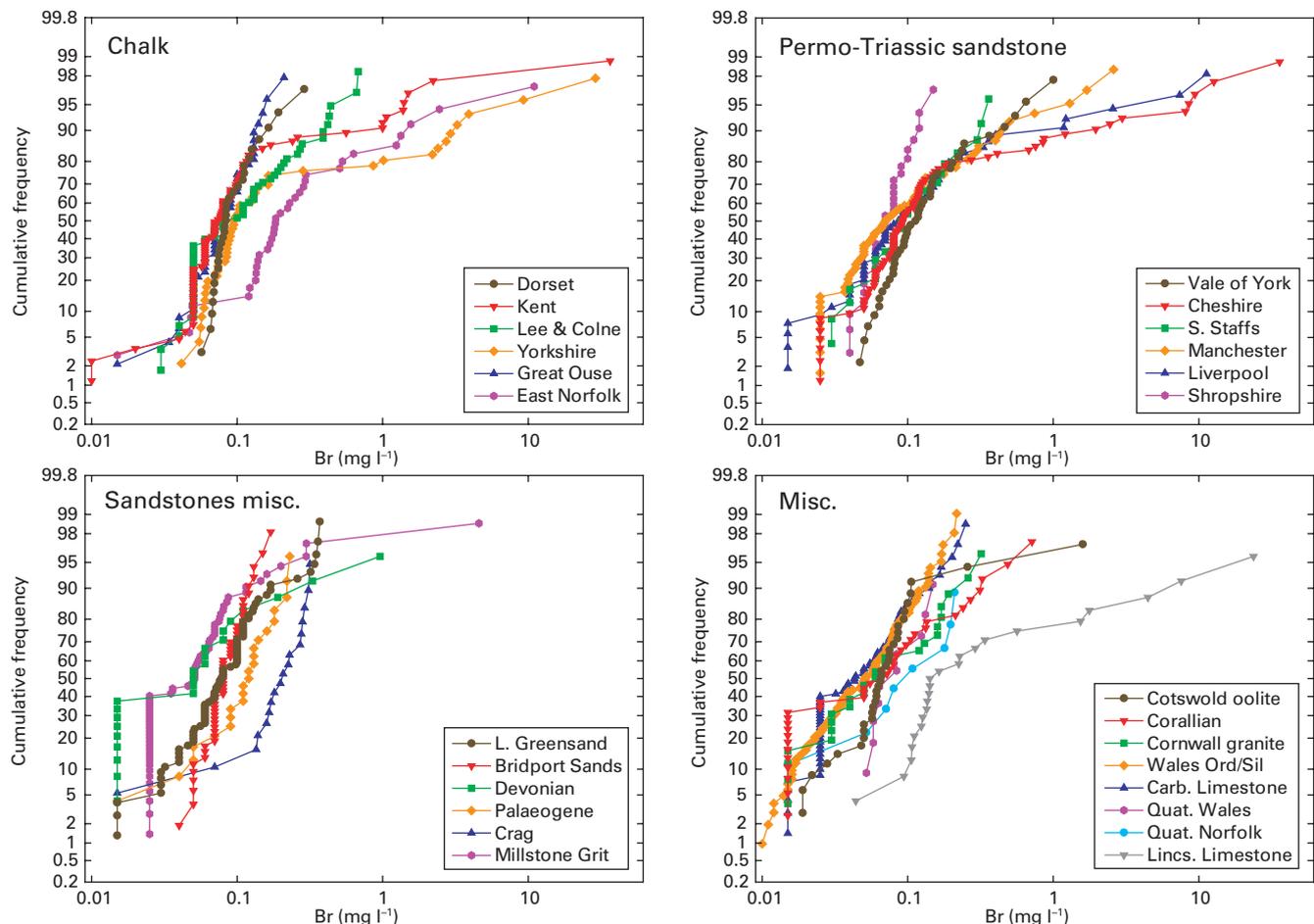


Figure 5.17 Cumulative frequency plots for Br in groundwaters.

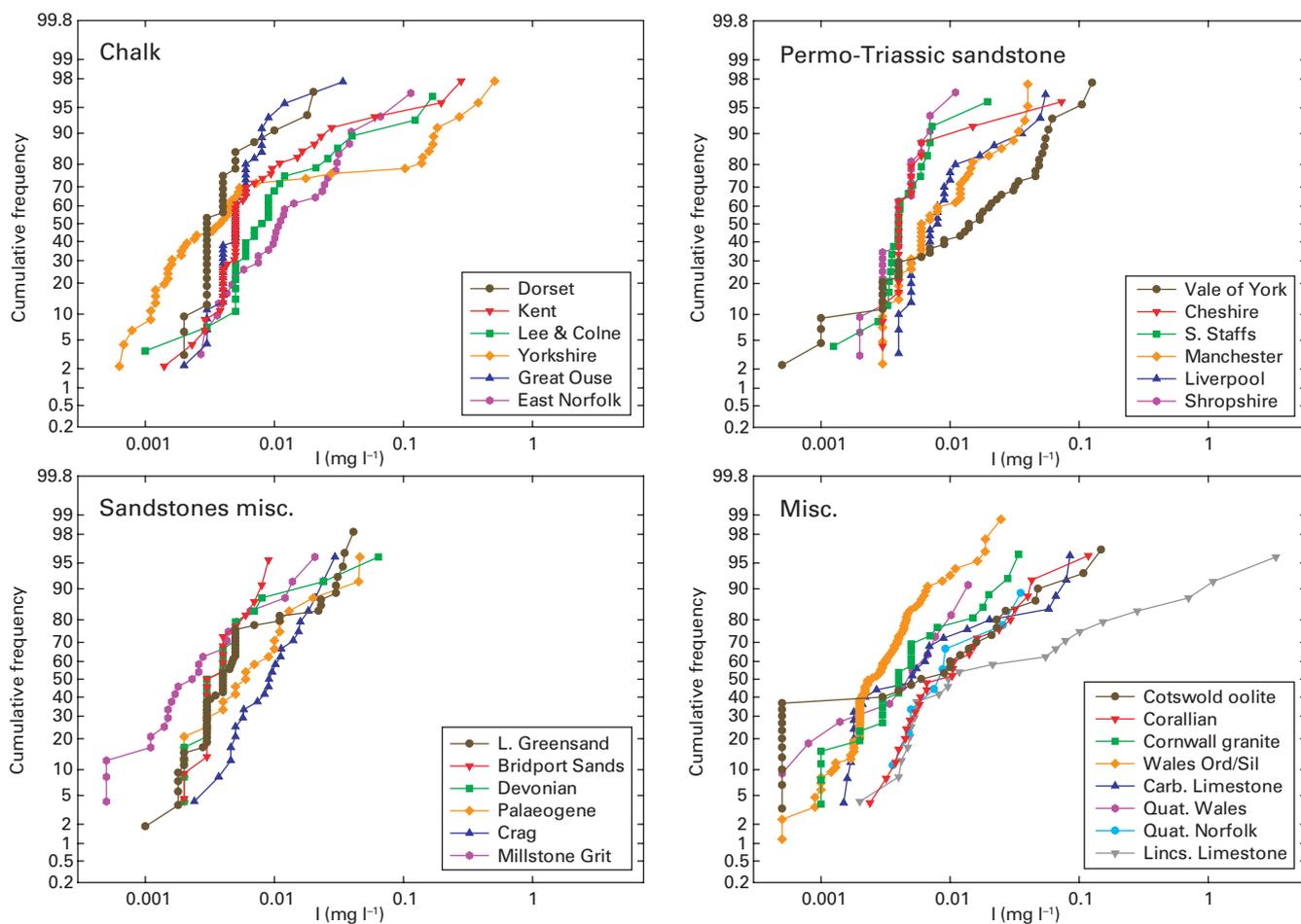


Figure 5.18 Cumulative frequency plots for I in groundwaters.

dominant source of Al in natural waters. Despite its relative abundance, Al occurs at low concentrations, in the $\mu\text{g l}^{-1}$ range in most waters, because the reaction rates (kinetics) of silicate dissolution are typically very slow at circumneutral pH's. However, since aluminium is amphoteric (soluble at both low and high pH), high dissolved concentrations of Al typically occur where the pH of the water is acidic ($\text{pH} < 4$) or alkaline ($\text{pH} > 8$) (Hem, 1992). Under acidic conditions, concentrations can reach 10^2 to $10^3 \mu\text{g l}^{-1}$. The dominant dissolved form of Al in acidic water is likely to be free Al^{3+} (the most toxic form), although aqueous complexation with ligands such as F, P and SO_4 can occur where these are present. Complexation of Al with humic acid is also possible.

The common tendency to filter water samples using a filter mesh size of $0.45 \mu\text{m}$, as in this study, means that some colloidal Al can potentially form a component part of the measured Al concentration. This means that measured concentrations can potentially be higher than equilibrium conditions would predict. The presence of colloidal Al is usually more significant for surface-water samples which can appear cloudy, although it cannot be fully discounted for clear groundwater samples.

Median concentrations of Al in the analysed datasets (Figure 5.19) range from around $1 \mu\text{g l}^{-1}$ to $150 \mu\text{g l}^{-1}$ for individual areas, with an overall median of $3 \mu\text{g l}^{-1}$. High outliers occur in datasets from several areas, but especially the Permo-Triassic sandstones. The dataset with the consistently highest Al concentrations is that of the granites of south-west England. This arises because these are the most acidic groundwaters observed in the study (median pH 5.6). Relatively high concentrations

are also observed for groundwaters from the Lower Palaeozoic aquifer of Wales. These are also of relatively acidic composition (median pH 6.1).

5.6.2 Antimony (Sb)

Antimony is typically present at low concentrations, usually less than $1 \mu\text{g l}^{-1}$ in unpolluted waters (Filella et al., 2002). This is consistent with its low abundance in crustal rocks (around 1 ppm). It is toxic element and has geochemical behaviour similar to As. Dissolved Sb can occur in a variety of oxidation states ($-3, 0, +3, +5$), but is mainly found in the $+3$ and $+5$ states in environmental samples depending on redox conditions. It is commonly associated with ferric hydroxides due to chemisorption of the anionic species. High concentrations of Sb are associated with pollution sources (Filella et al., 2002) but may also reach several hundred $\mu\text{g l}^{-1}$ concentrations in natural geothermal waters (BGS, unpublished data). It is a strongly chalcophile element, occurring mainly as stibnite, Sb_2S_3 , or incorporated into other sulphide minerals such as pyrite.

The concentration of Sb in the majority of groundwaters is very low (Figure 5.20), generally below detection, and only rarely reaching concentrations of around $1 \mu\text{g l}^{-1}$. Median concentrations are typically about $0.1 \mu\text{g l}^{-1}$, with higher concentrations likely to occur around sulphide deposits.

5.6.3 Arsenic (As)

Arsenic occurs naturally as a major constituent of more than 200 minerals, most of which are found in ore

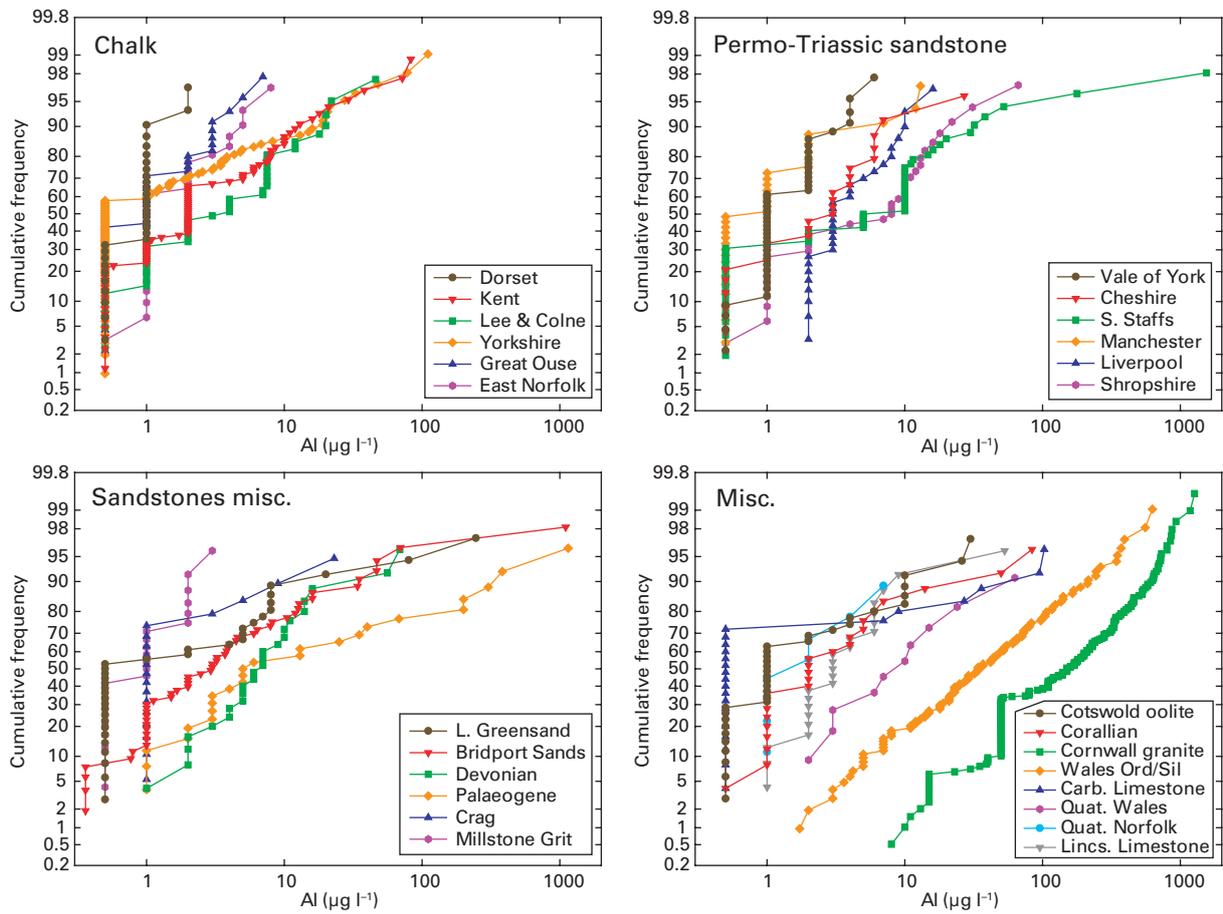


Figure 5.19 Cumulative frequency plots for Al in groundwaters.

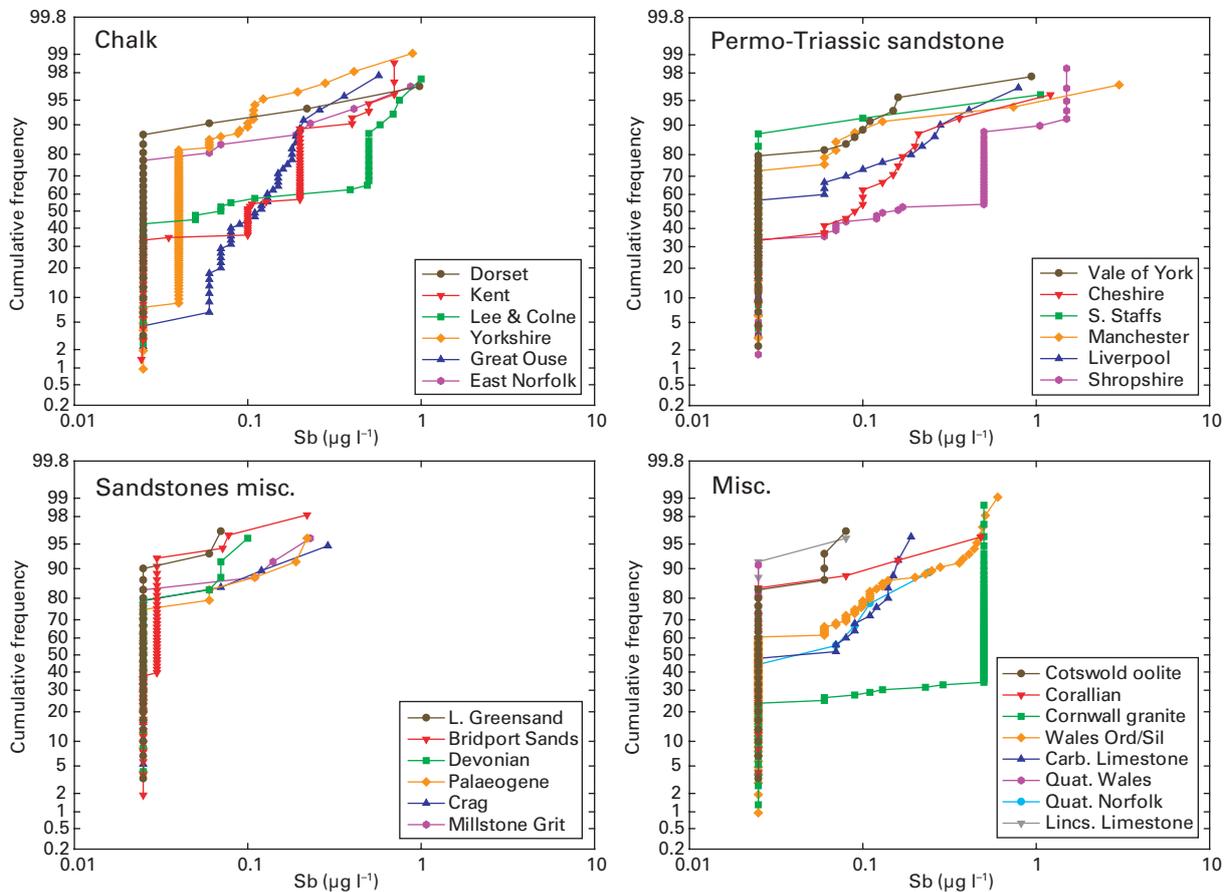


Figure 5.20 Cumulative frequency plots for Sb in groundwaters.

deposits. The most common As-bearing minerals include arsenopyrite (FeAsS) and arsenian pyrite ($\text{Fe}(\text{S},\text{As})_2$). Arsenic can also be present in significant concentrations (up to several weight percent) in low-temperature (sedimentary) pyrite and iron oxides, either as part of the mineral structures or as adsorbed forms. It can also be abundant in aluminium and manganese oxides and in some phosphate minerals. Its presence in silicate minerals and carbonates is usually much lower (Smedley and Kinniburgh, 2002). Sulphide minerals and iron oxides are therefore most often implicated as sources (and sinks) of As in groundwaters. Release from sulphide minerals can occur through oxidation reactions while release from iron oxides can be via reductive dissolution and/or desorption reactions.

Arsenic has two main oxidation states in groundwater, As(III) and As(V). Their distribution in solution is broadly consistent with the redox conditions in an aquifer, with As(III) being the dominant form in reducing conditions and As(V) dominating in oxidising conditions. However, disequilibrium is commonly observed because of slow kinetics of As redox reactions and microbiological effects. The current EC and national limit for As in drinking water is $10 \mu\text{g l}^{-1}$. Concentrations in groundwater are usually less than this, although they can reach several hundreds or even thousands of $\mu\text{g l}^{-1}$ in some circumstances (Smedley and Kinniburgh, 2002).

Adsorption of As to metal oxides is an important process that restricts the mobility of the element in most waters. The capacity of iron oxides to adsorb As(V) is particularly well-documented, although the adsorption is strongly pH-dependent, being much less at high pH

(greater than around 8.5). Under such alkaline conditions, the adsorption of As(III) has been noted to exceed that of As(V) (Hering and Kneebone, 2002). Several other factors are known or suspected to be contributory in the mobilisation of As. High concentrations of phosphate for example can compete with arsenate (As(V)) and restrict As sorption to iron oxides, leading to higher concentrations. The structure of the iron oxides themselves is an important control on adsorption affinity. Microbiology also has a potentially significant though as yet not fully-understood role.

Arsenic has been observed in high concentrations in groundwaters under widely differing geochemical conditions. Oxidation of sulphide minerals can lead to release of As into groundwater, and therefore mineralised and especially mined areas are potentially vulnerable to As mobilisation. The fate of As once released to groundwater depends on the local environmental conditions; much can be immobilised rapidly by adsorption. Arsenic can also be present in groundwater in sedimentary aquifers as a result of release under reducing conditions where adsorbed As is mobilised by reductive dissolution from iron oxides.

In the studied aquifers of England and Wales, median As concentrations are in all cases less than $10 \mu\text{g l}^{-1}$ with an overall median of $0.6 \mu\text{g l}^{-1}$ (Figure 5.21). The highest concentrations are generally observed in groundwaters from the Permo-Triassic sandstones, both under reducing and oxidising conditions. The causes of the high As concentrations in these aquifers are not fully understood (Kinniburgh et al., 2005) but the presence of abundant iron oxide (haematite, goethite) in the red-bed sandstones is likely to be a significant factor.

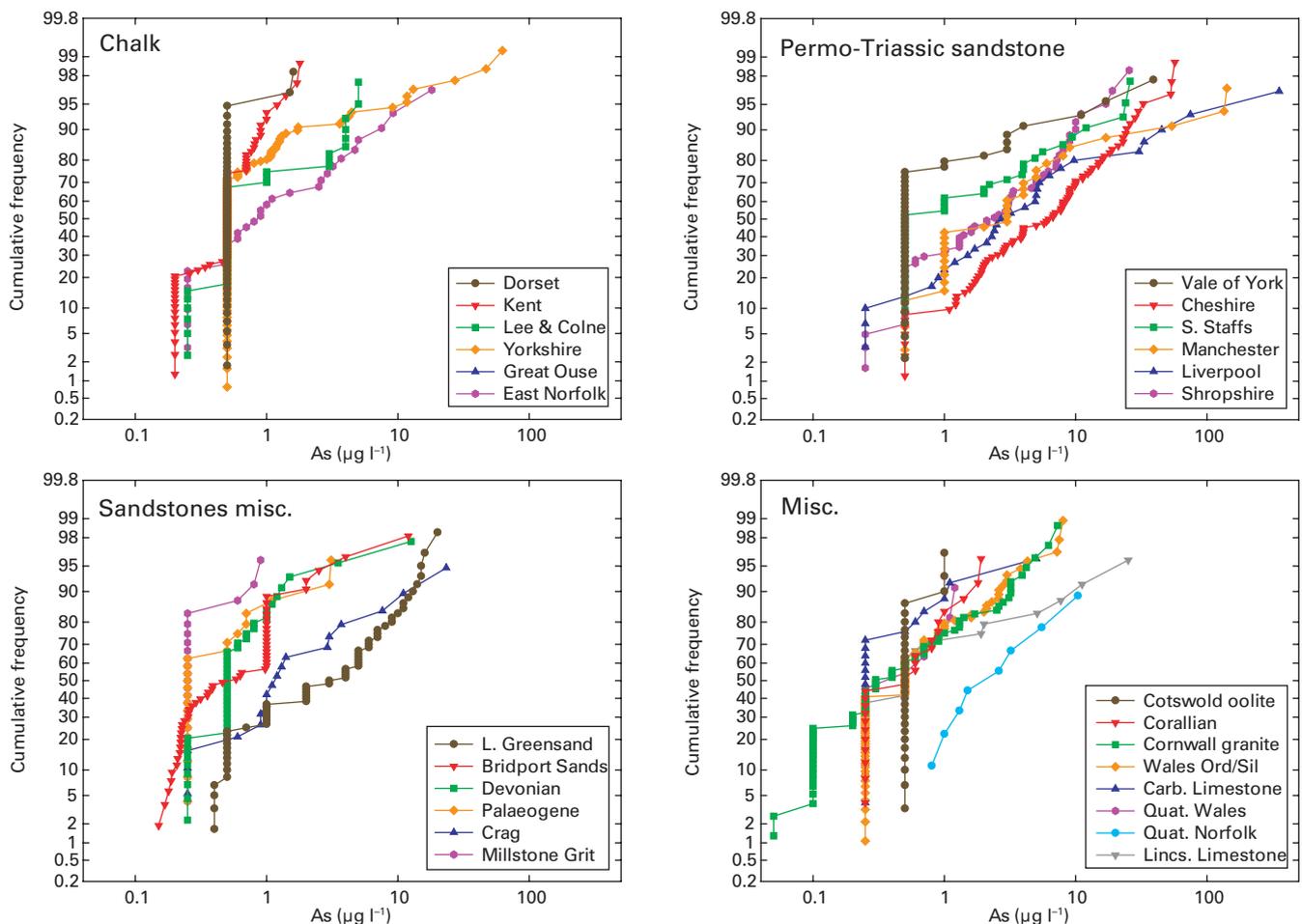


Figure 5.21 Cumulative frequency plots for As in groundwaters.

Groundwater in carbonate aquifers has low concentrations of As (Figure 5.21) although a large number of outliers are observed in groundwaters from the Yorkshire Chalk. These are invariably in the reducing confined aquifer, probably derived from iron oxides or phosphate minerals in hardgrounds, and therefore almost certainly represent baseline contributions. Although groundwaters in mineralised areas often have high concentrations of As, Figure 5.21 indicates that concentrations are in all cases less than $10 \mu\text{g l}^{-1}$ in groundwaters from both the granites of south-west England and the Palaeozoic metasediments of Wales. The implication is that high As concentrations in such aquifers are not expected on a regional scale, although locally high concentrations could exist in some unsampled areas.

5.6.4 Barium (Ba)

Barium concentration tends to be higher in igneous rocks than sedimentary rocks, particularly carbonates. It is often high in K-feldspars or magnesian micas such as phlogopite, due to Ba^{2+} having a similar ionic radius to K^+ . Barium is also a major component of the mineral barite (BaSO_4). Its mobility is often limited in soils because clays and organic matter show a strong cation exchange selectivity for Ba, more than strongly hydrating cations such as Ca and Mg (McBride, 1994). The dominant limiting control on Ba in most groundwaters, however, is saturation with respect to barite since the solubility product is of the order of 10^{-10} . Sulphate concentrations in groundwater of 10 or 100 mg l^{-1} , would limit Ba in solution to around 140 and $14 \mu\text{g l}^{-1}$ respectively (Hem, 1992). Many of the water

samples studied were oversaturated with respect to barite, indicating slow reaction kinetics or mixing of waters during sampling.

Barium concentrations in the Chalk groundwaters display similar distributions, varying from ca. 10 to $100 \mu\text{g l}^{-1}$ with medians of a few tens of $\mu\text{g l}^{-1}$ (Figure 5.22). The most likely source is from clay minerals or possibly from detrital barite (Shand and Bloomfield, 1995). The lowest concentrations are typical of deeper groundwaters with elevated SO_4 , indicating a control by barite saturation. Median concentrations in the Permo-Triassic aquifers tend to be higher than in the Chalk, probably as a result of K-feldspar dissolution. The breakdown of K-feldspar, a common constituent of the sandstones, was observed using SEM in a number of rock samples. The lower concentrations are typical of higher SO_4 groundwaters as in the Chalk. A significant number of groundwaters contain Ba in excess of the EU MAC concentration of $150 \mu\text{g l}^{-1}$.

The other sandstone aquifers studied have a range of median concentrations and ranges (Figure 5.22). The low concentrations in the Bridport Sands reflect low aquifer abundance, since SO_4 concentrations were low and the waters were largely undersaturated with respect to barite. In contrast, the median for the Devonian aquifer groundwaters is significantly higher than the EU MAC. Barite mineralisation, of Carboniferous age, is common in many areas of Devonian sandstone and this may well be the source of high Ba in this aquifer. The Cotswold oolite and Corallian aquifers contain groundwaters with low Ba, typical of most carbonate aquifers, but the Carboniferous groundwaters are high in Ba, as found previously by Edmunds et al., (1989).

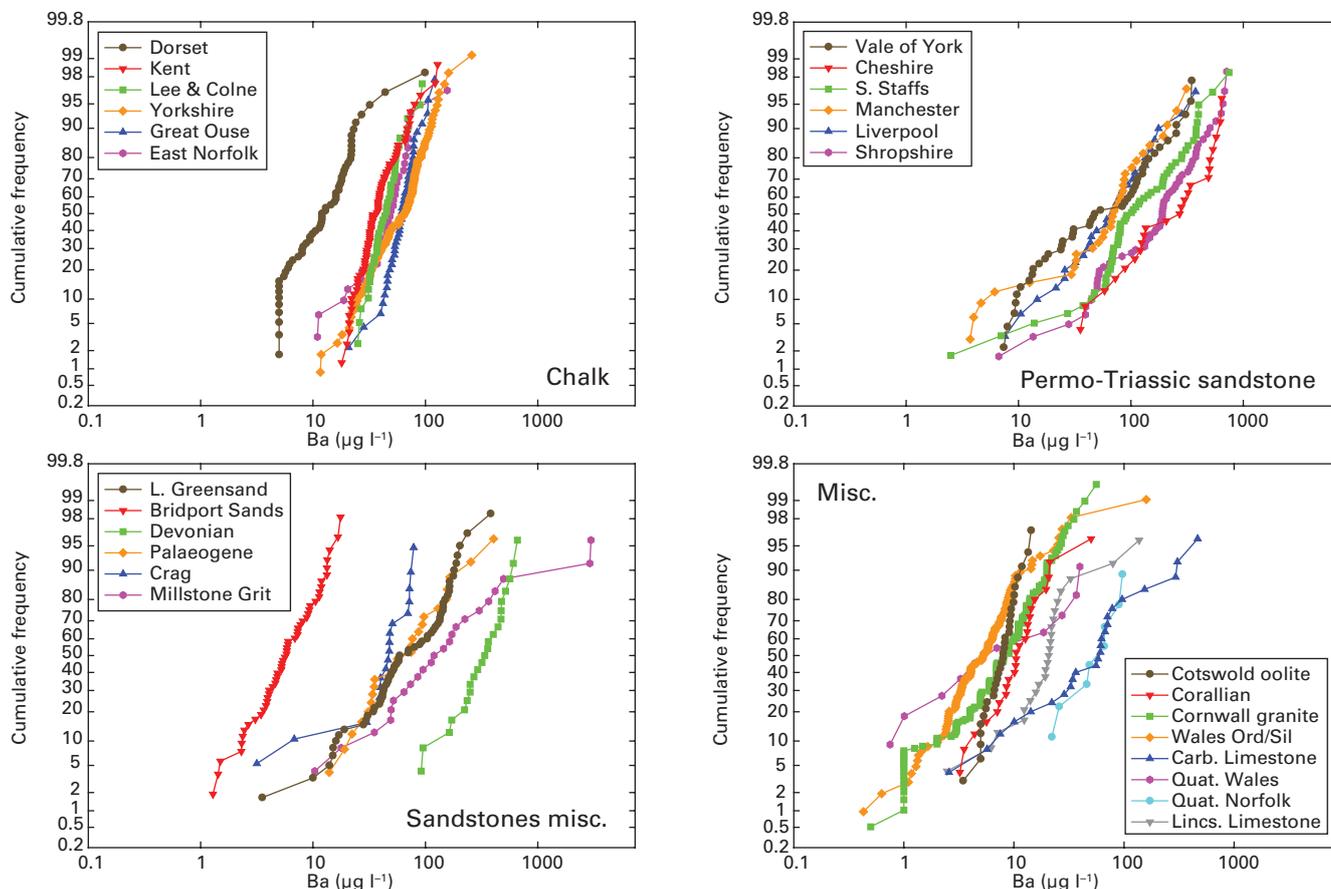


Figure 5.22 Cumulative frequency plots for Ba in groundwaters.

Since there are few diffuse anthropogenic sources for Ba, the ranges and medians shown are considered to represent baseline. Taking into account the regional variations in Ba, it would appear that groundwaters in the south-west of England, regardless of type (sandstone, granite, limestone) are all depleted in Ba. These waters are mainly undersaturated with respect to barite indicating a low-Ba source. It is postulated that this is a reflection of sediment source from different terrains i.e. those in the south-west are of Hercynian origin and those further north are of Caledonian origin, the Caledonian rocks being well established as being rich in Ba.

5.6.5 Beryllium (Be)

All beryllium compounds are toxic or harmful. Beryllium exists in the +2 valence in aqueous solution and has the smallest size of all the metal cations (Baes and Mesmer, 1976). It displays similar chemical characteristics to Al due to its similar ratio of charge to ionic radius. The only ligands that complex Be strongly are OH and F. Beryllium occurs mainly in silicate minerals, substituting for Al or Si and is commonly associated with pegmatites where it may form the mineral beryl ($\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$). Typical concentrations in natural waters are very low, but enhanced concentrations have been found in low pH waters associated with granites (Edmunds and Trafford, 1992; Navretil, 2000).

Median concentrations of Be in the Chalk groundwaters are all below detection limit and maximum concentrations rarely exceed $0.1 \mu\text{g l}^{-1}$ (Figure 5.23). Similar distributions also occur in the Permo-Triassic groundwaters, although several have detectable concentrations e.g. in samples from

the Vale of York and Liverpool aquifers (Figure 5.23). Groundwaters in the Lower Palaeozoic sediments also have slightly higher concentrations (but less than $1 \mu\text{g l}^{-1}$), as did the most acidic groundwaters in the Palaeogene and Lower Greensand, where maximum concentrations are greater than $1 \mu\text{g l}^{-1}$ (Figure 5.23). Groundwaters in the south-west England granites are distinguished from the other aquifers by generally much higher concentrations, up to $4 \mu\text{g l}^{-1}$.

The source of Be in the studied groundwaters is considered to be natural. The baseline for Be is generally therefore expected to be in the ng l^{-1} range, except for acid groundwaters, in particular those associated with granites.

5.6.6 Boron (B)

Boron is an essential element, being important in low concentrations for plant growth. At higher concentrations, however, it may be harmful. It is present in the borate mineral tourmaline, but this is a highly resistant mineral and unlikely to be a source in most groundwaters. Boron is also present in micaceous minerals and is associated with clays and iron oxides as well as being enriched in many evaporite deposits. The seawater concentration is relatively high (4.5 mg l^{-1}), hence mixing with marine-derived formation water is likely to increase groundwater concentrations. Anthropogenic B may also be present in aquifers e.g. in discharge from water treatment plants, since B is a component of detergents and it is also used as a fertiliser.

Concentrations in the study aquifers typically vary over two orders of magnitude (Figure 5.24). Low concentrations

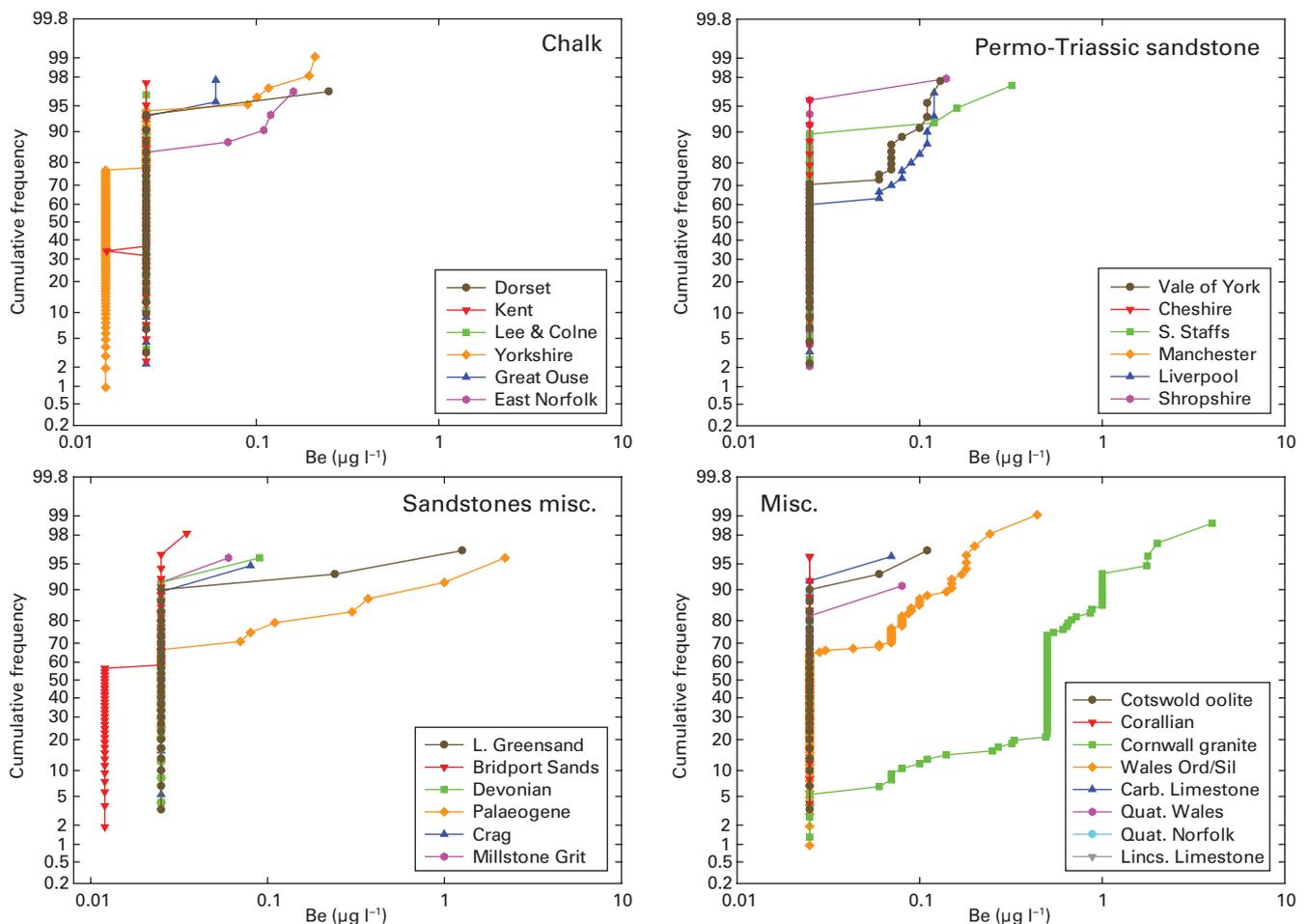


Figure 5.23 Cumulative frequency plots for Be in groundwaters.

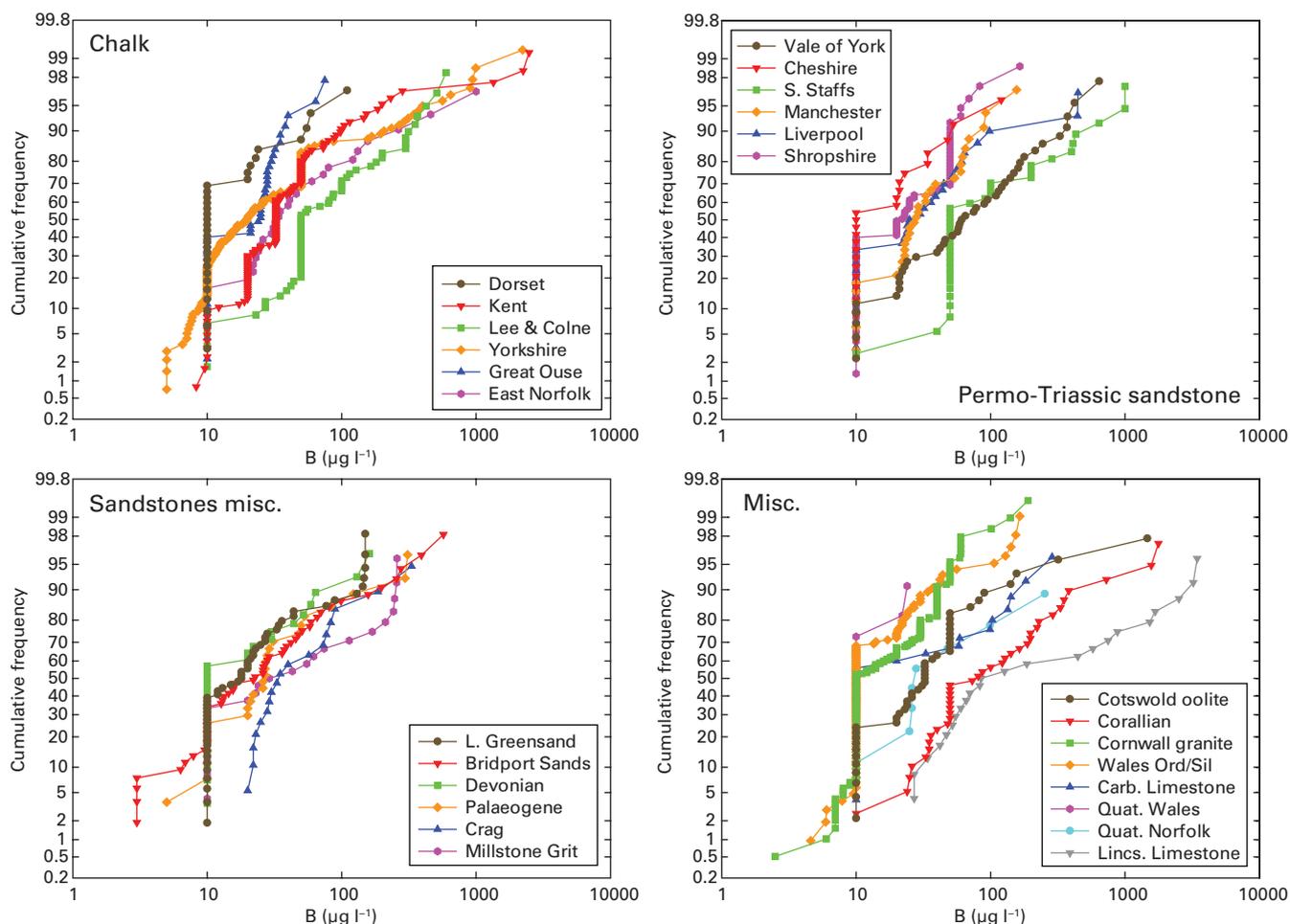


Figure 5.24 Cumulative frequency plots for B in groundwaters.

are indicative of a mainly rainwater-derived source, and typical of aquifers with a short residence time e.g. granites of south-west England and the Lower Palaeozoic aquifers of Wales. The highest concentrations are often present in saline groundwaters, although correlations with Cl are sometimes poor, indicating additional sources of B. High B/Cl ratios also point towards an important input, either from the aquifer matrix (e.g. in old confined waters) or from anthropogenic (e.g. agricultural) inputs (in younger waters). Although the median concentrations may be slightly enhanced, the ranges are dominated by rainfall and old saline water, which therefore represent the baseline end-members for each water body.

5.6.7 Cadmium (Cd)

Cadmium displays chalcophile geochemical behaviour similar to that of Zn, but it is much less abundant. It occurs in ore deposits in the mineral sphalerite (ZnS), but is typically enriched in sulphide deposits generally. It forms a divalent cation in solution under acidic oxidising conditions and may form an anionic species at higher pH. However, concentrations in most groundwaters are limited, most likely by adsorption onto Mn or Fe oxide surfaces, although binding by organic substances may also be significant at high pH. Cadmium may also be adsorbed by calcite surfaces (Davis et al., 1987) or become incorporated into calcite via chemisorption. High concentrations, above 0.5 ppm, in soils are considered to be due to pollution including industrial, high-Cd phosphate fertiliser or sewage sludge applications (McBride, 1994). It forms strong complexes with CN, OH and halide ions.

Median concentrations for Cd in Chalk groundwaters are typically below the limit of detection and maximum concentrations rarely exceed $1 \mu\text{g l}^{-1}$, the highest concentrations being from Chalk beneath the Norfolk Crag (Figure 5.25). The Permo-Triassic sandstone waters are similar, the exception being those in the Cheshire Basin where concentrations occasionally exceeded $10 \mu\text{g l}^{-1}$. However, some the data from the Cheshire Basin have very high detection limits and it is not clear whether the samples were filtered or not (Griffiths et al., 2002). The other sandstone aquifers studied all contain groundwaters below $0.7 \mu\text{g l}^{-1}$ (Figure 5.25). Slightly higher concentrations are found in a few groundwaters in the Lower Palaeozoic metasediments of Wales, but these may be associated with sulphide-rich sediments (Shand et al., 2006). The data indicate that baseline concentrations for Cd are typically low in the aquifers of England and Wales, rarely exceeding $1 \mu\text{g l}^{-1}$.

5.6.8 Cerium (Ce)

The lanthanide series (La to Lu), or rare earth elements (REE), form a coherent group of elements which differ only very slightly in their chemical properties. In igneous and metamorphic rocks, most of the REEs are present in minor accessory minerals such as allanite, apatite, monazite, sphene and zircon. The REEs also display strong sorption characteristics, particularly at high pH, onto mineral surfaces (Bau, 1999; Shand et al., 2005). The pH of natural waters exerts a significant control on REE solubility with concentrations commonly displaying an inverse relationship to pH (Smedley, 1991). Only selected

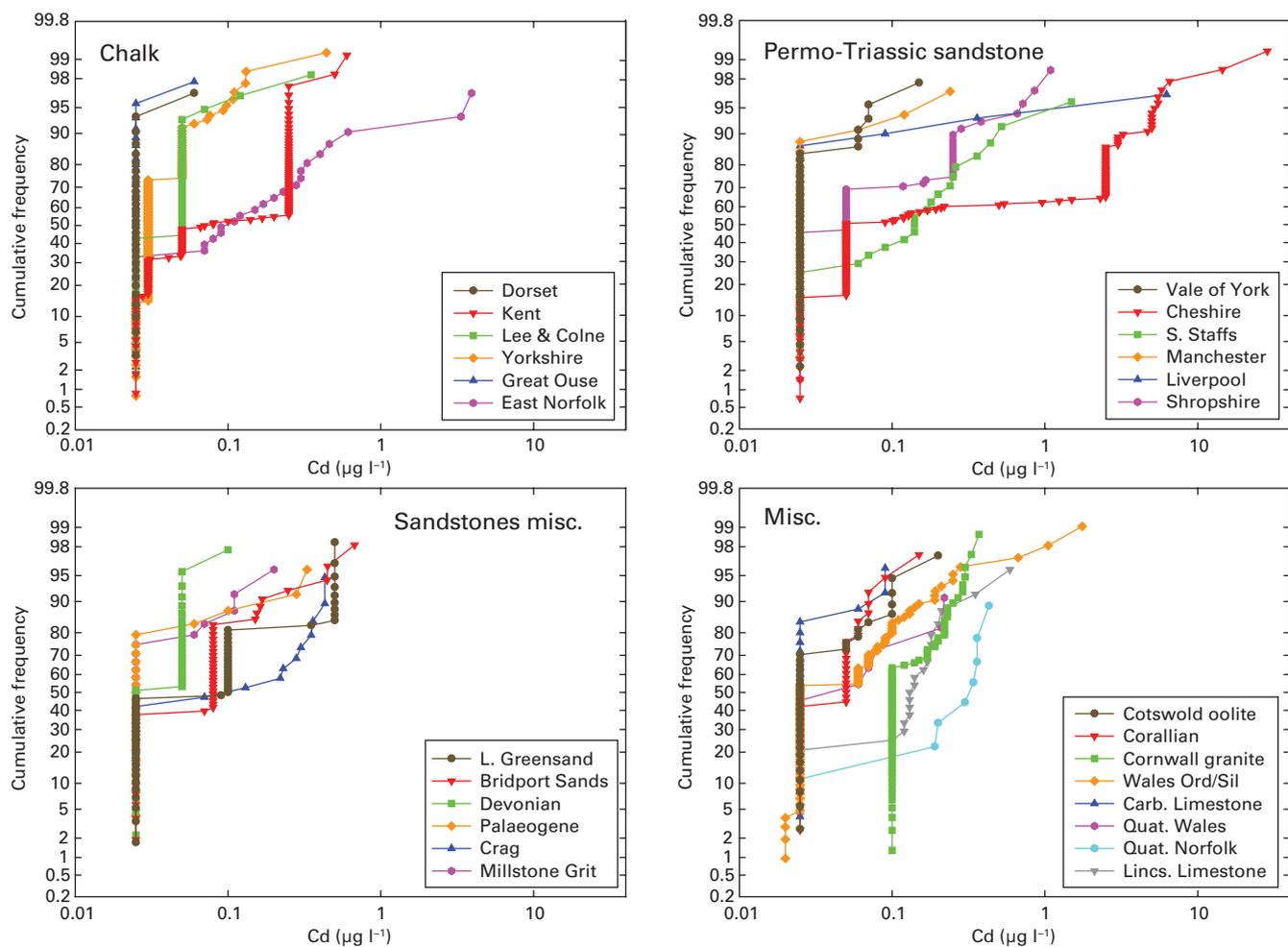


Figure 5.25 Cumulative frequency plots for Cd in groundwaters.

REEs (Ce and La) have been selected for discussion in section 5.6 due to their similar geochemical behaviour and because these are generally the most abundant in natural waters.

The concentrations of Ce in the groundwaters of most carbonate and sandstone aquifers are very low and median concentrations are generally below the limit of detection (Figure 5.26). Of the sandstone aquifers, only a few groundwaters in the Palaeogene have concentrations in the range of a few $\mu\text{g l}^{-1}$, in the more acidic waters (Neumann et al., 2004). The highest median concentration is found in the granite aquifers of south-west England where the groundwaters have generally low pH (median pH 5.6; Smedley et al., 2004). Concentrations above these levels are unlikely to occur in most groundwaters in England and Wales unless the waters are more acidic.

5.6.9 Cesium (Cs)

Cesium is an alkali metal and although its solution chemistry is simple (no hydrolysis, no complex formation), its behaviour is complex (Stumm and Morgan, 1996). It is strongly sorbed on clays, hence its mobility in most aquifers is very low. There are very few published data on Cs in natural waters, probably due to the limited mobility in solution. It displays relatively similar geochemical behaviour to K and Rb, and is most enriched in K-feldspars and K-micas.

Concentrations of Cs in the Chalk groundwaters are all less than $0.5 \mu\text{g l}^{-1}$ (Figure 5.27), with medians less than the limit of detection. Cesium is also present at low

concentrations in the Permo-Triassic sandstone waters, although higher concentrations occur in the Vale of York, possibly being derived from the breakdown of feldspar and clay minerals or the extensive drift deposits covering much of the aquifer. The highest absolute and median concentrations are found for groundwaters in the Lower Palaeozoic and granite aquifers (Figure 5.27), where adsorption is expected to be less at the lower pH of the groundwaters in these aquifers. The concentrations of Cs are of natural origin, and it is likely that any anthropogenic inputs would be largely adsorbed in the soil zone.

5.6.10 Chromium (Cr)

Chromium is an essential nutrient for animal and plant metabolism but is also toxic at high concentrations. High Cr concentrations are found in ferromagnesian minerals such as olivine, pyroxene and amphibole, and is also present at higher than average concentrations in shales and other argillaceous rocks. Chromium can exist in a number of oxidation states (0 to 6+), but only the trivalent and hexavalent states are important in the range of Eh-pH values found in natural waters (Richard and Bourg, 1991). Like other metal cations, Cr^{3+} is easily sorbed onto clay and Fe, Mn hydroxide surfaces, and adsorption increases with pH. It is generally more mobile under acidic oxidising conditions and can also form a number of inorganic and organic complexes. Under highly oxidising conditions, chromate (CrO_4^{2-}), a toxic form of Cr, is stable.

Concentrations of dissolved Cr in the Chalk aquifer are generally low (Figure 5.28), with medians typically being

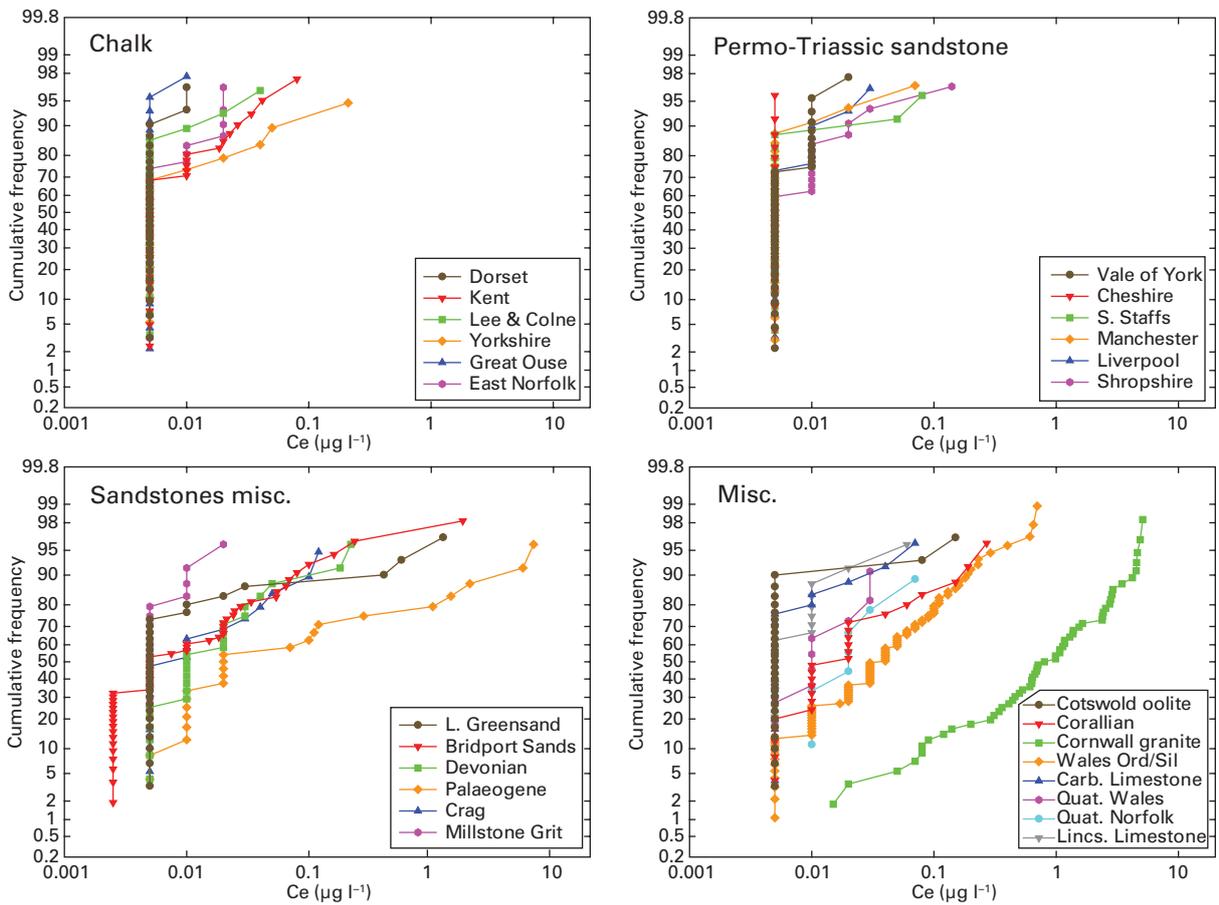


Figure 5.26 Cumulative frequency plots for Ce in groundwaters.

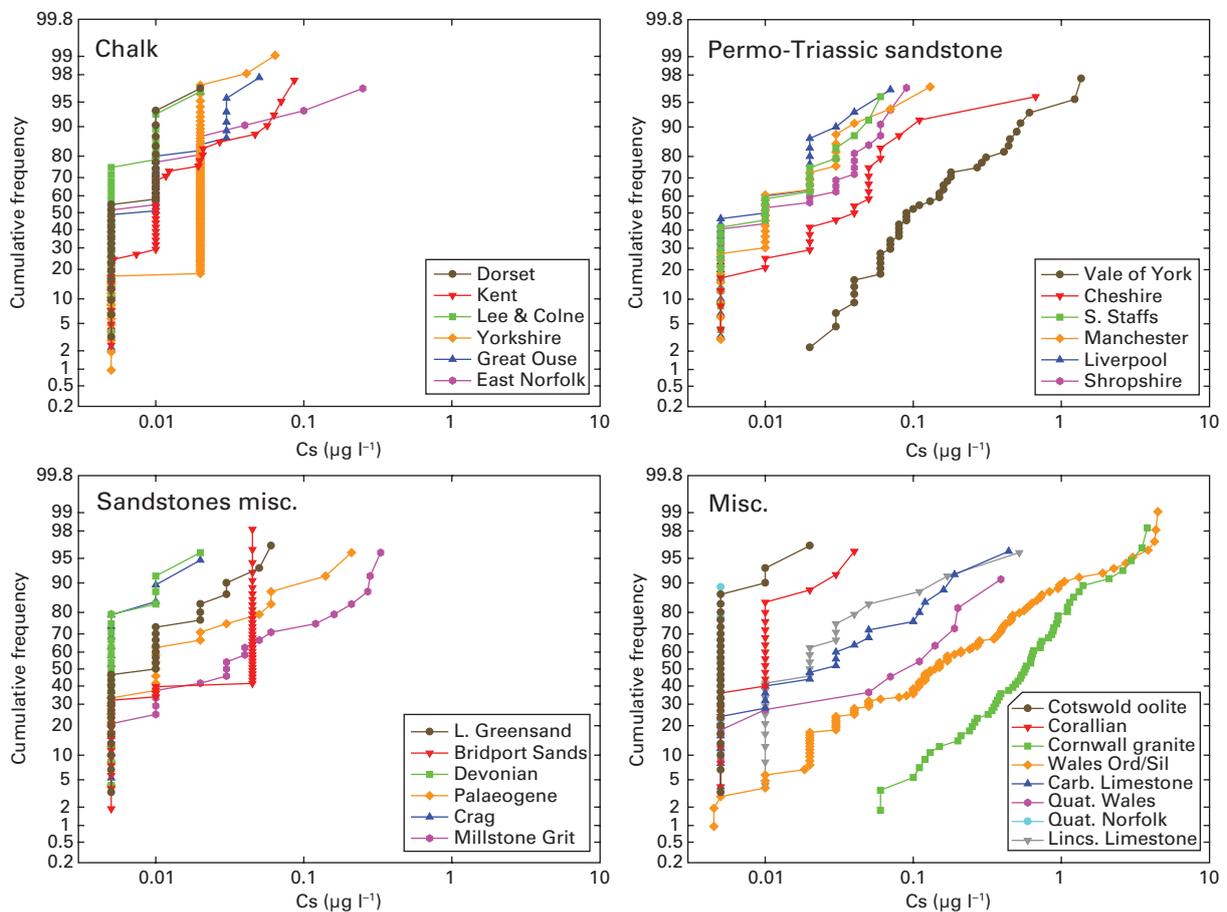


Figure 5.27 Cumulative frequency plots for Cs in groundwaters.

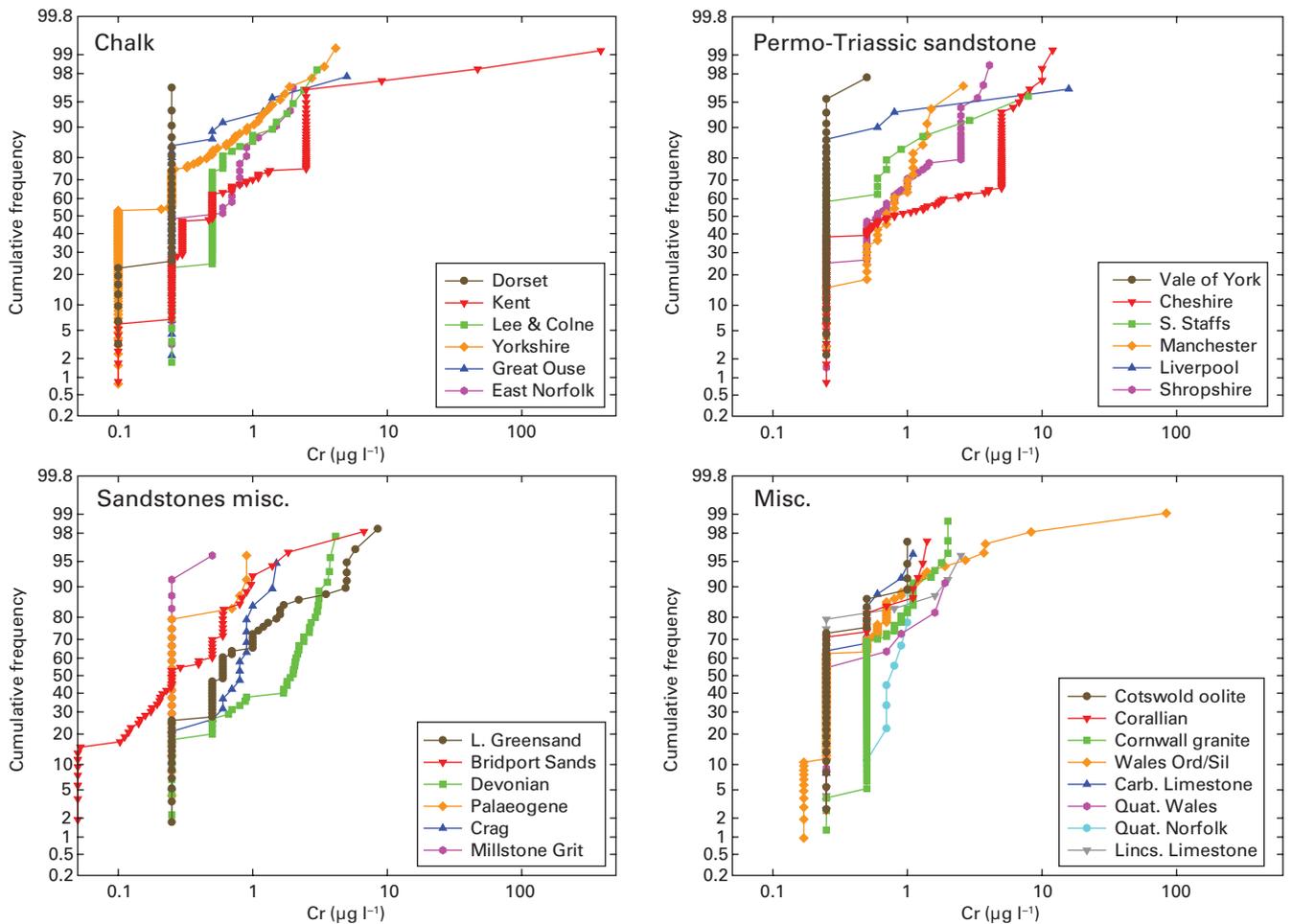


Figure 5.28 Cumulative frequency plots for Cr in groundwaters.

less than the limit of detection. High concentrations in some of the Chalk groundwaters of Kent are from deep confined groundwaters, considered to be pre-modern (Smedley et al., 2003). In the Permo-Triassic waters, concentrations were variable, but only rarely greater than $10 \mu\text{g l}^{-1}$, with median concentrations less than $1 \mu\text{g l}^{-1}$. The highest median concentration ($2.9 \mu\text{g l}^{-1}$) is found in the Devonian aquifer (Figure 5.28). Concentrations are moderately high in some groundwaters in the Lower Palaeozoic sediments known to be affected by sulphide oxidation. Hence it is likely that the source is from pyrite, locally abundant in the sediments. Although the average varies from aquifer to aquifer, median concentrations of less than $1 \mu\text{g l}^{-1}$ are typical of the baseline in these groundwaters.

5.6.11 Cobalt (Co)

Co is derived primarily from weathering of ferromagnesian minerals (e.g. olivine, pyroxene, biotite) but the often close association between high Fe and/or Mn and such trace metals indicates a control largely by desorption/dissolution reactions involving oxide/oxy-hydroxide phases. Such reactions strongly limit Co mobility especially at neutral to high pH. The stable valency of Co in water is Co^{2+} . It is an essential element for mammals being a cofactor in numerous enzymes and has a role in symbiotic N_2 fixation but also toxic at high concentrations (McBride, 1994). Contaminant sources are often limited by natural attenuation in the soil and unsaturated zone.

Cobalt concentrations in Chalk groundwaters are generally low, rarely exceeding $10 \mu\text{g l}^{-1}$, and with median

concentrations often being below the limits of detection (Figure 5.29). The highest concentrations are often present in waters containing high Fe or Mn implying that reductive dissolution is likely to play a part in mobilising Co. Similar ranges are found in the Permo-Triassic groundwaters, although medians are slightly higher. Groundwaters in the other aquifers display a range of median concentrations, being highest in some of the silicate aquifers: Palaeogene of southern England, granites and Lower Palaeozoic groundwaters (Figure 5.29). The higher concentrations are often in acidic or reducing waters. The maximum baseline concentrations of Co in the groundwaters of England and Wales are thus considered to be around $10 \mu\text{g l}^{-1}$.

5.6.12 Copper (Cu)

Copper is an essential trace element in plant and animal metabolism. In nature it occurs as native Cu and in sulphide minerals of ore deposits. Copper has a wide range of uses in industrialised countries, including copper pipes, hence anthropogenic inputs are likely to be significant in young waters. It forms a range of inorganic and especially organic complexes in water. Copper is usually immobile in organic soils due to strong adsorption onto organic matter. Under oxidising conditions, it is soluble under acidic conditions, but solubility is limited at high pH by relatively insoluble carbonate or hydroxide phases (Drever, 1997). However, adsorption by organic matter or Fe and Mn oxyhydroxides are likely to be a dominant control on Cu mobility, especially at high pH.

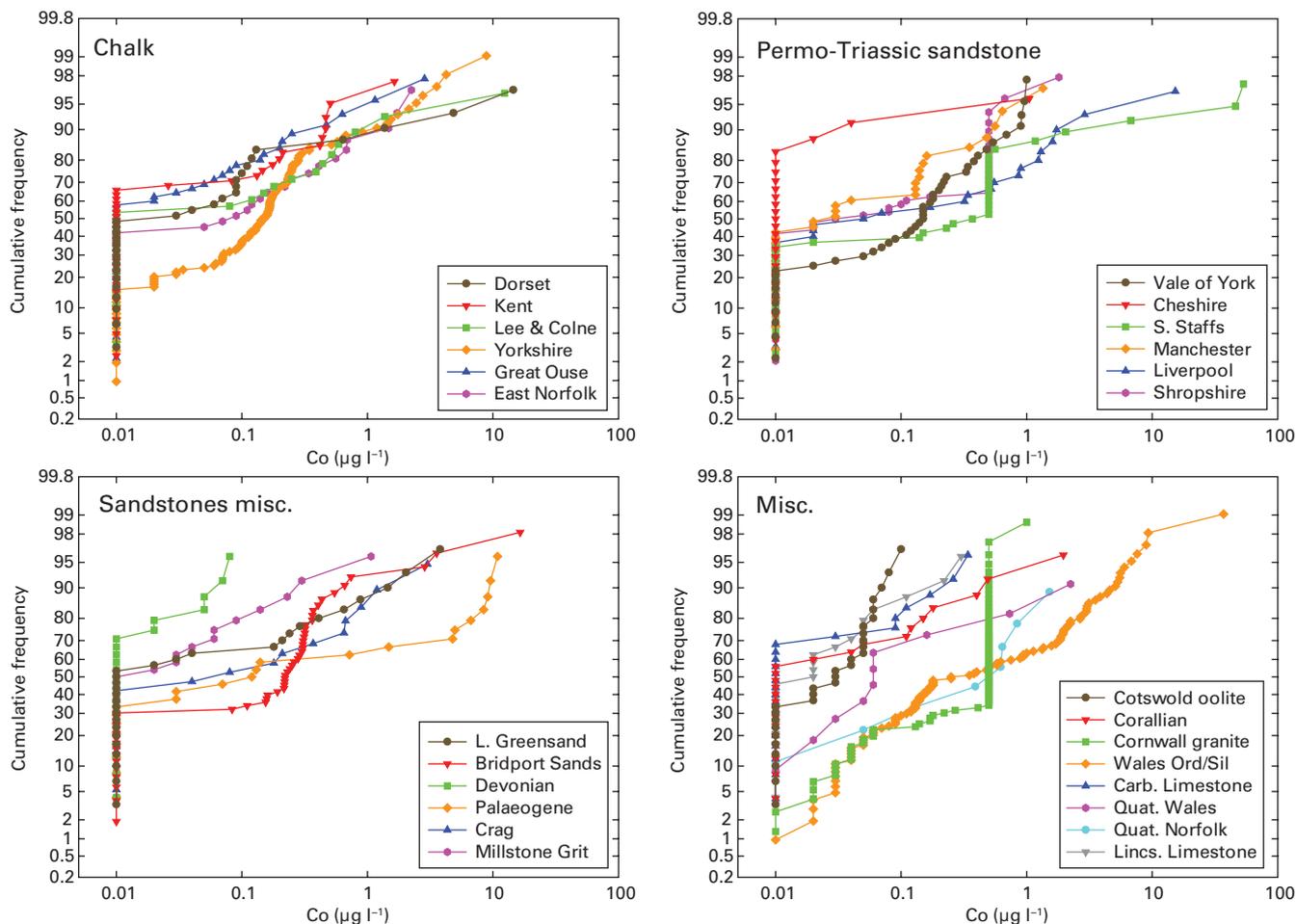


Figure 5.29 Cumulative frequency plots for Co in groundwaters.

Copper concentrations in the groundwaters display a wide range, mainly from about 0.1 to several hundred $\mu\text{g l}^{-1}$ (Figure 5.30). The distributions in Chalk groundwaters are relatively similar, but with median concentrations varying from 0.9 to 6 $\mu\text{g l}^{-1}$. Groundwaters in the Permo-Triassic aquifers display relatively linear distributions with a slightly greater range in median concentrations from 1.3 to 35 $\mu\text{g l}^{-1}$. The areas in the Cheshire Basin (Cheshire, Shropshire, Staffordshire), where sulphide mineralisation is present have the highest medians and maximum concentrations. The other sandstone groundwaters form a relatively tight cluster with median concentrations from <1 to 1.6 $\mu\text{g l}^{-1}$ (Figure 5.30). The groundwaters in the granites of south-west England have the highest median concentrations, most likely from higher bedrock Cu in this area associated with mineralising fluids related to the granites. Although it is possible that the ranges described may be affected by samples with some anthropogenic input of Cu, the correspondence between areas of bedrock geology containing sulphide mineralisation and higher dissolved Cu suggest that the dominant control is geology. It is therefore, considered that the ranges described are broadly representative of baseline.

5.6.13 Germanium (Ge)

Germanium is a relatively low-abundance element in the Earth's crust. It has been found in low temperature ore deposits, in some rare sulphosalts, meteorites and in coal deposits (Goldschmidt, 1970). It is known to substitute for Si in silicate minerals. Concentrations in groundwaters at ambient temperature are typically low, although data are

scarce. However, elevated concentrations are commonly present in geothermal waters (Wood and Samson, 2006). Chudaev et al., (2000), for example, reported concentrations up to a few tens $\mu\text{g l}^{-1}$ in geothermal waters in Kamchatka, Russia.

Median concentrations in most groundwaters in England and Wales are below the detection limit (Figure 5.31) and rarely exceed 1 $\mu\text{g l}^{-1}$. There is no clear correlation with rock type and Ge correlates poorly with other elements.

5.6.14 Iron (Fe)

Iron is a relatively abundant element in the Earth's crust. Primary sources include the aluminosilicate minerals olivine, pyroxene, amphibole and biotite. Secondary iron oxides and oxyhydroxides are ubiquitous in most rock types in oxidising environments. Under reducing conditions, Fe occurs mainly in sulphide minerals such as pyrite (FeS_2) or carbonate minerals such as siderite (FeCO_3). The solubility of Fe is largely controlled by the Eh-pH conditions in groundwaters. Iron commonly exists in solution in two oxidation states: Fe^{2+} and Fe^{3+} . It is soluble under moderately reducing conditions and mobile below a pH of about 7 to 8, usually as uncomplexed Fe^{2+} . However, under sufficiently anaerobic conditions in the presence of sulphur species, sulphate reduction occurs and Fe is removed from solution (Figure 3.2). Under oxidising conditions Fe^{3+} is insoluble, forming oxides and oxyhydroxides at pH's typical of most groundwaters. At pH's below 3 to 4, however, Fe^{3+} is soluble under very oxidising conditions e.g. those occurring in acid mine drainage (Figure 3.3). The oxidised form is also mobile

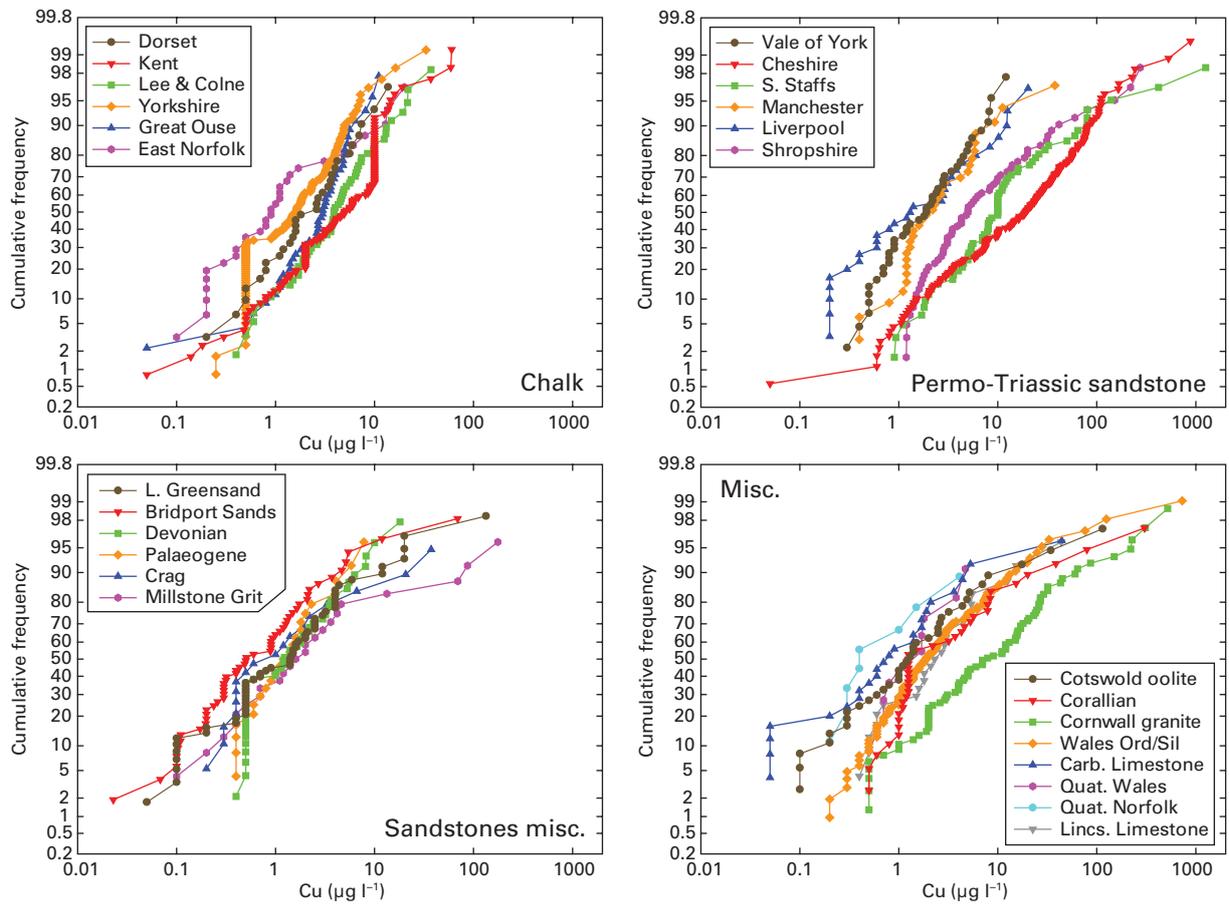


Figure 5.30 Cumulative frequency plots for Cu in groundwaters.

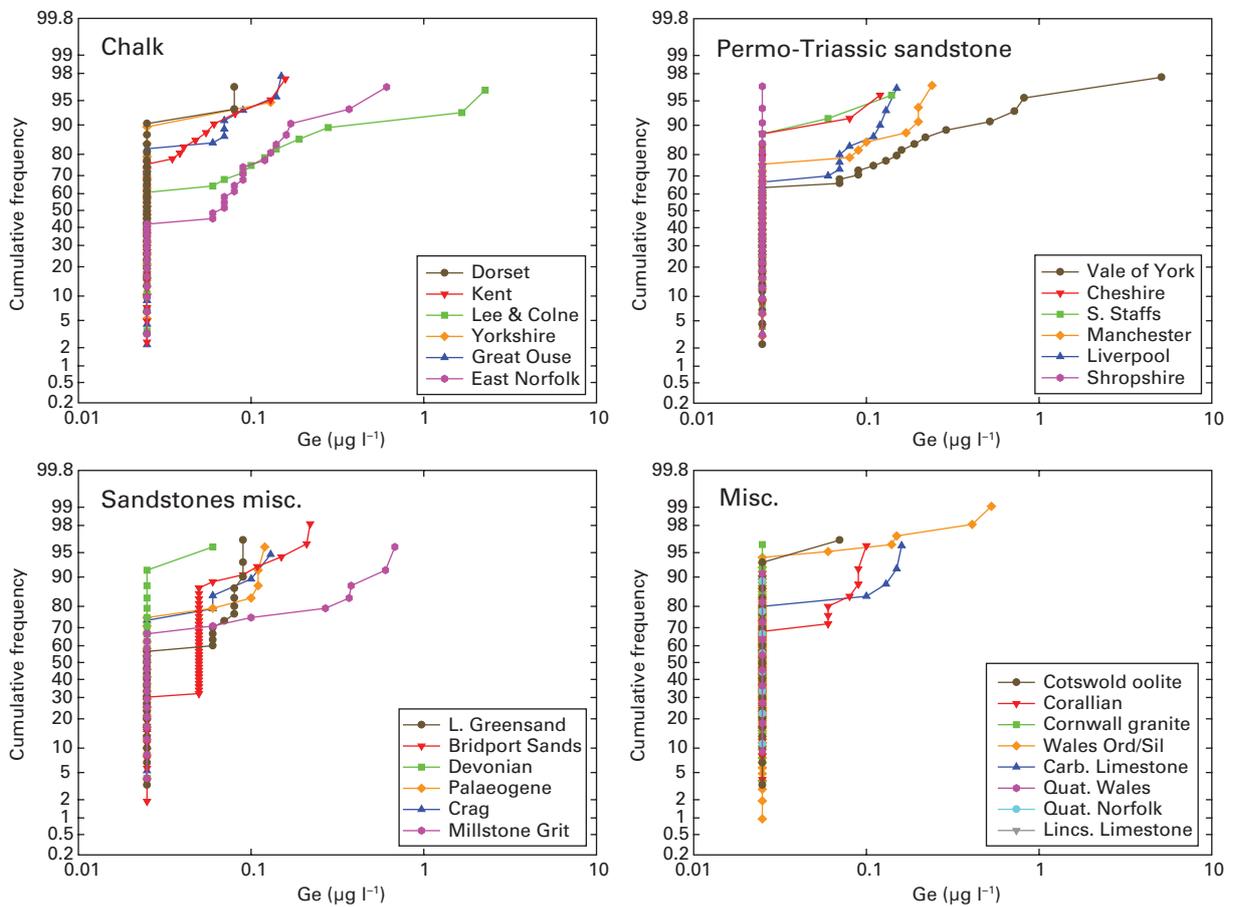


Figure 5.31 Cumulative frequency plots for Ge in groundwaters.

as an organic complex up to about pH 5 to 6 (Langmuir, 1997). The abundances of complexing agents such as organic species, Cl, F, PO₄ and SO₄ also influence dissolved Fe to varying degrees.

The presence of Fe in typical groundwaters can therefore be a useful indicator of redox status in the absence of redox measurements (DO and Eh) since equilibrium concentrations are extremely low at circumneutral pH in oxidising environments. Iron oxyhydroxides may form colloidal species, however, and these may pass through the standard 0.45 µm filter (Figure 4.3).

Iron varies in most groundwater systems studied by three to four orders of magnitude (Figure 5.32). This is largely due to the varying redox conditions in these aquifers, with high Fe being found in reducing groundwaters. The Chalk groundwaters are mostly similar with median concentrations of a few µg l⁻¹. The confined east Norfolk Chalk, however, has a much higher median of 402 µg l⁻¹, reflecting the greater spatial extent of reducing groundwater. The source of the Fe is likely to be from iron oxyhydroxides, pyrite (marcasite), clays and possibly from the Chalk matrix itself.

The groundwaters in the Permo-Triassic sandstones form two groups. Those in the Shropshire and South Staffordshire aquifers display a moderate range of concentrations and a low median (Figure 5.32). The other regions show a much larger range (up to four orders of magnitude) and have median concentrations around 100 µg l⁻¹ (Figure 5.32). These differences relate to the existence of reducing groundwaters, mainly controlled by the extent, type and thickness of drift deposits (as well

as depth). In recharge areas or where drift is permeable or thin, oxygenated waters keep Fe solubility to a minimum.

The other sandstone aquifers studied also display a range of Fe concentrations in the groundwater. The lowest median concentrations are found in the better-sorted sandy aquifers of the Millstone Grit and the Devonian and Bridport Sands aquifers. The heterogeneous Palaeogene and Crag reflect the large number of confined units in these sequences. The Quaternary valley gravels of Wales all have low Fe with a median concentrations close to the detection limit of Fe (Figure 5.32). A wide range was found in all the other aquifer units studied.

5.6.15 Lanthanum (La)

The geochemistry of the Lanthanide series (La-Lu) was introduced in section 5.6.7. Due to the similar behaviour of the REE, the distributions of La are almost identical to those for Ce discussed previously. Baseline median concentrations are thus typically less than 0.1 µg l⁻¹ unless the waters are acidic as in the granites of south-west England. (Figure 5.33).

5.6.16 Lead (Pb)

Lead is a toxic element and may affect aquatic organisms at relatively low concentrations. It forms a major component of ore minerals such as galena (PbS) and secondary sulphate, carbonate and chloride minerals of low solubility. Lead is often present as a trace constituent

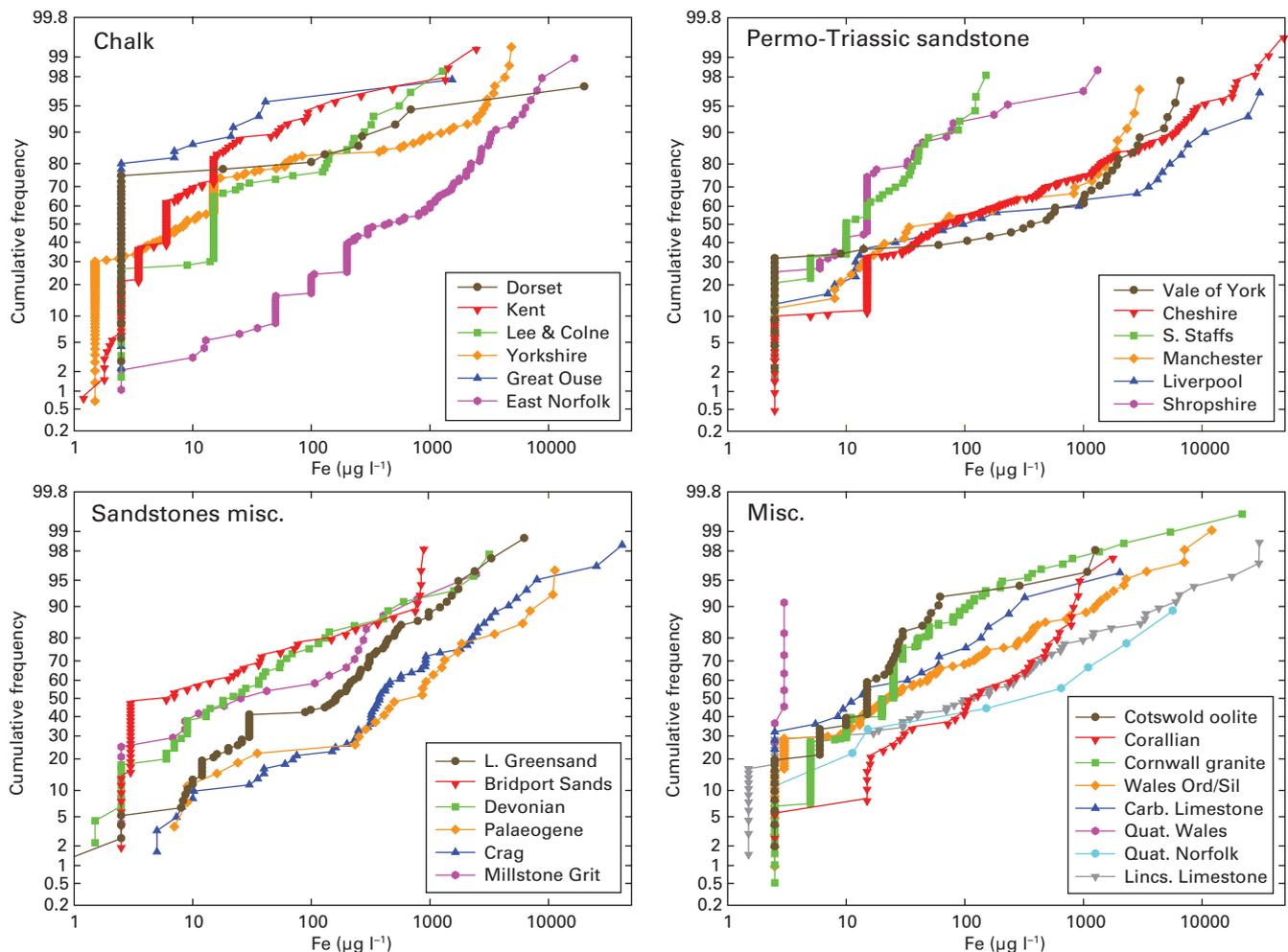


Figure 5.32 Cumulative frequency plots for Fe in groundwaters.

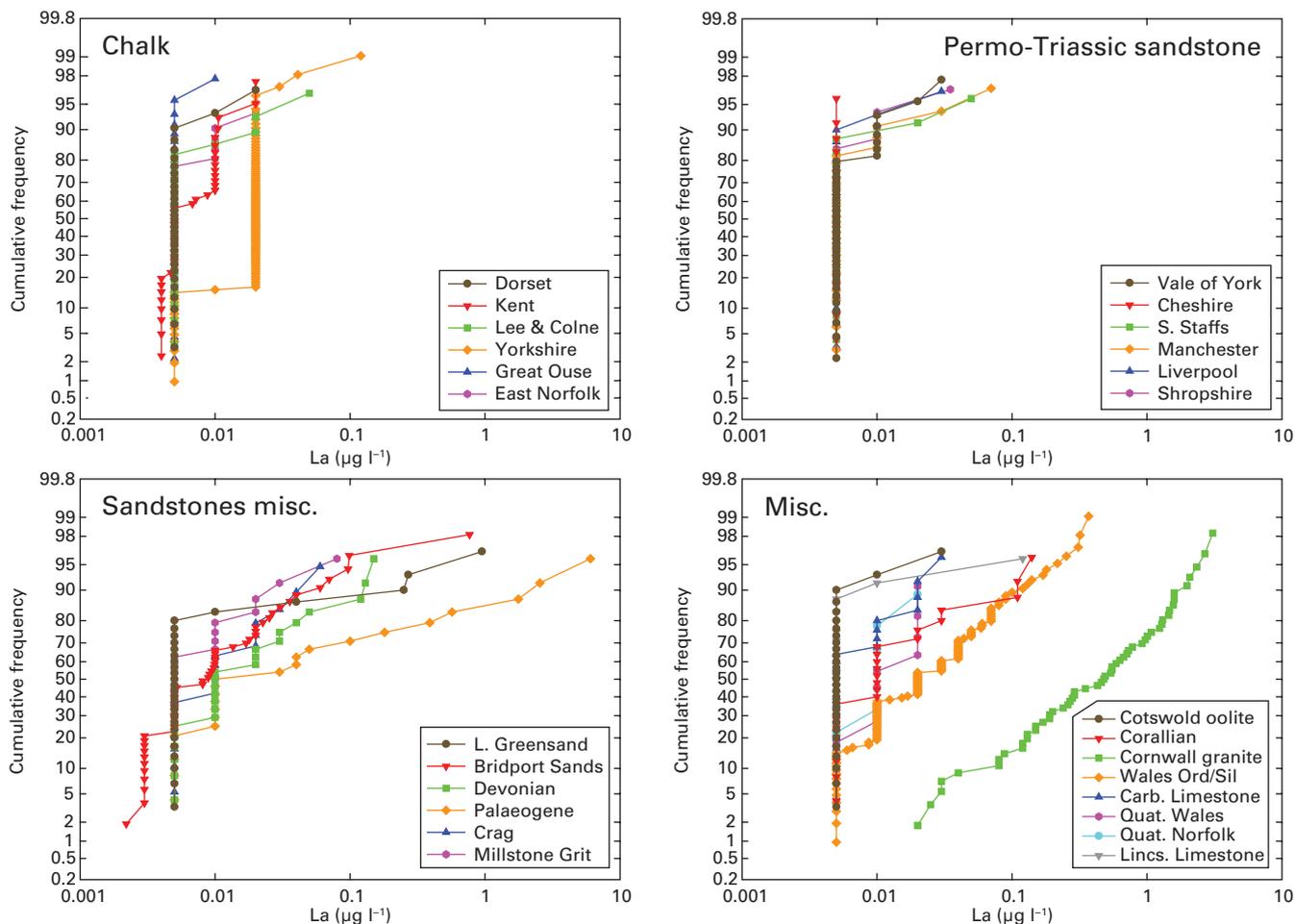


Figure 5.33 Cumulative frequency plots for La in groundwaters.

in K-feldspars and micas replacing K in structural sites. The mobility of Pb is often limited in groundwaters owing to sorption onto clays, organic matter and Fe oxyhydroxide minerals.

The natural baseline of Pb in waters is likely to have been affected around urban and industrial areas as well as in the vicinity of mining activities. In addition, enhanced concentrations have occurred due to the release of tetraethyl lead from vehicle exhausts, although this has been reduced more recently owing to the use of unleaded fuels.

Median lead concentrations in Chalk groundwaters are generally around or below the typical detection limit of analysis (about $1 \mu\text{g l}^{-1}$), although some concentrations up to a few $\mu\text{g l}^{-1}$ are found in most study areas (Figure 5.34). Similar distributions are also found for Permo-Triassic aquifer waters, although a high median was present in the Cheshire study. All groundwaters in the recent sampling are below the limit of detection and it is possible that the other data compiled contains unfiltered samples and these represent enhancements due to the inclusion of particulate matter. It is also noted that the higher concentrations were present in groundwaters analysed prior to the mid-1980s and it is therefore possible that these are due to analytical methodologies with poor sensitivity compared to ICP MS.

The groundwaters in the other sandstone aquifers all have median concentrations less than $1 \mu\text{g l}^{-1}$ and concentrations rarely exceed $10 \mu\text{g l}^{-1}$ (Figure 5.34). Median concentrations in the miscellaneous group vary over an order of magnitude but are also low. The higher concentrations in some groundwaters such as the Lower

Palaeozoic sediments and granites of south-west England may be partly due to Pb-mineralisation but is difficult to rule out local contamination e.g. from pumps or nearby houses.

The median baseline range would thus appear to be variable but for all aquifers is likely to be close to or less than $1 \mu\text{g l}^{-1}$. Baseline ranges are also interpreted to be up to a few $\mu\text{g l}^{-1}$, with a maximum of up to $10 \mu\text{g l}^{-1}$.

5.6.17 Lithium (Li)

The distribution of lithium minerals is generally confined to pegmatitic rocks where it may occur as a major constituent in minerals such as spodumene, amblygonite and the Li-mica lepidolite (Hem, 1992). Lithium is also found as a trace constituent in silicate minerals where it substitutes for Mg and in clays such as illite where it is most likely to be present as an adsorbed cation. In solution Li exists as a univalent cation (Li^+). It is much less easily sorbed than other cations and tends to stay in solution once released from minerals and increases in concentration with residence time. Although seawater concentrations are low (0.17 mg l^{-1}) in comparison with Cl, Li is often enriched in formation waters owing to water-rock interaction, hence mixing with such a source can increase concentrations as well as direct interactions with minerals. Edmunds et al., (1989) noted that the Li/Na ratio increased dramatically during initial infiltration and appeared to reach a steady state and further suggested that the ratio may be used as an indicator of residence time. Li can be toxic to plants, e.g. Bradford (1963) concluded that concentrations above 60 to $100 \mu\text{g l}^{-1}$ can cause damage to citrus trees.

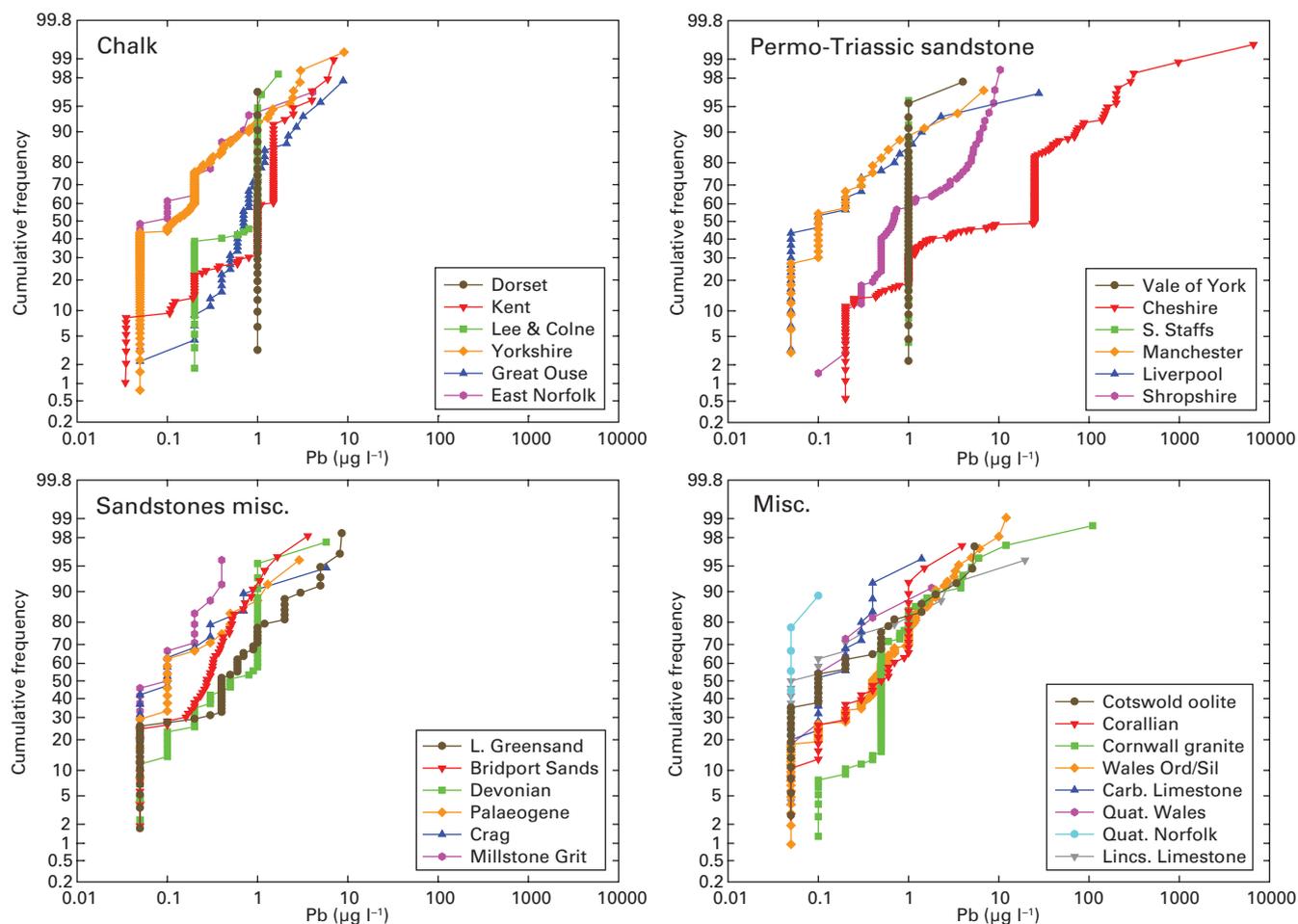


Figure 5.34 Cumulative frequency plots for Pb in groundwaters.

There are significant differences between the median concentrations of Li in Chalk groundwaters, from $0.8 \mu\text{g l}^{-1}$ in the aquifer of Dorset to $34 \mu\text{g l}^{-1}$ in the east Norfolk Chalk underlying the Crag (Figure 5.35). The groundwaters in the Permo-Triassic aquifers mainly form a much tighter group with median concentrations between 6 and $10 \mu\text{g l}^{-1}$. They also display a lower range in concentrations, typically less than two orders of magnitude. The exception to this tight grouping is the Vale of York area which has the highest median Li concentration of $34 \mu\text{g l}^{-1}$. The Vale of York aquifer is largely covered by thick Quaternary clay deposits and it is likely that the clays have enhanced Li in these groundwaters. Lithium often shows an increase in concentration with longer residence time and in most study areas Li increases significantly along flow pathways into the confined parts of aquifers.

The other sandstone groundwaters display a moderate range of median and overall concentrations with the Bridport Sands and Lower Greensand having the lowest medians (Figure 5.35). The other aquifers studied display a range of groundwater concentrations and medians and it is not possible to discriminate based on aquifer lithology e.g. for the carbonate aquifers, Li was low in the Cotswold oolite and Carboniferous Limestone and relatively high in the Corallian and Lincolnshire Limestone. The abundances are a combination of availability and residence time, hence the baseline will vary widely from system to system. The data shown on Figure 5.35 are likely to be a good representation of the baseline, being derived from natural sources and not modified significantly by anthropogenic influences.

5.6.18 Manganese (Mn)

Manganese is an essential element in plant and animal nutrition (Hurley and Keen, 1987). Manganese is less abundant than Fe but the two elements show similar geochemical behaviour, both being redox sensitive and largely controlled by pH-Eh conditions. It can exist in several oxidation states: Mn^{2+} , Mn^{3+} and Mn^{4+} . Under more reducing conditions dissolved Mn will occur as Mn^{2+} . Manganese substitutes for Fe, Mg and Ca in silicate minerals. In contrast to Fe, dissolved Mn remains stable under mildly oxidising conditions, but in more strongly oxidising conditions it precipitates on joint and mineral surfaces. Manganese oxides are effective scavengers of trace metals, particularly of Co, Fe and Ni, although As, Ba, Cu, Pb and Zn are often enriched in Mn oxides. Shand and Bloomfield, (1995) noted very high concentrations of Co and Ni in Mn-dendrites on Chalk fracture surfaces, hence they are important in the retardation and mobility of these elements where present.

In the unconfined Chalk aquifer, Mn 'spots' or dendrites are common on fracture surfaces and dissolved Mn concentrations are generally very low. Median concentrations for the study areas are typically low, often less than $1 \mu\text{g l}^{-1}$ (Figure 5.36). The highest median concentration is found in the largely confined Chalk groundwaters of east Norfolk. The highest concentrations in all areas are generally present in confined groundwaters where conditions are reducing. The source is likely to be from trace concentrations in the calcite matrix. Concentrations in the Permo-Triassic

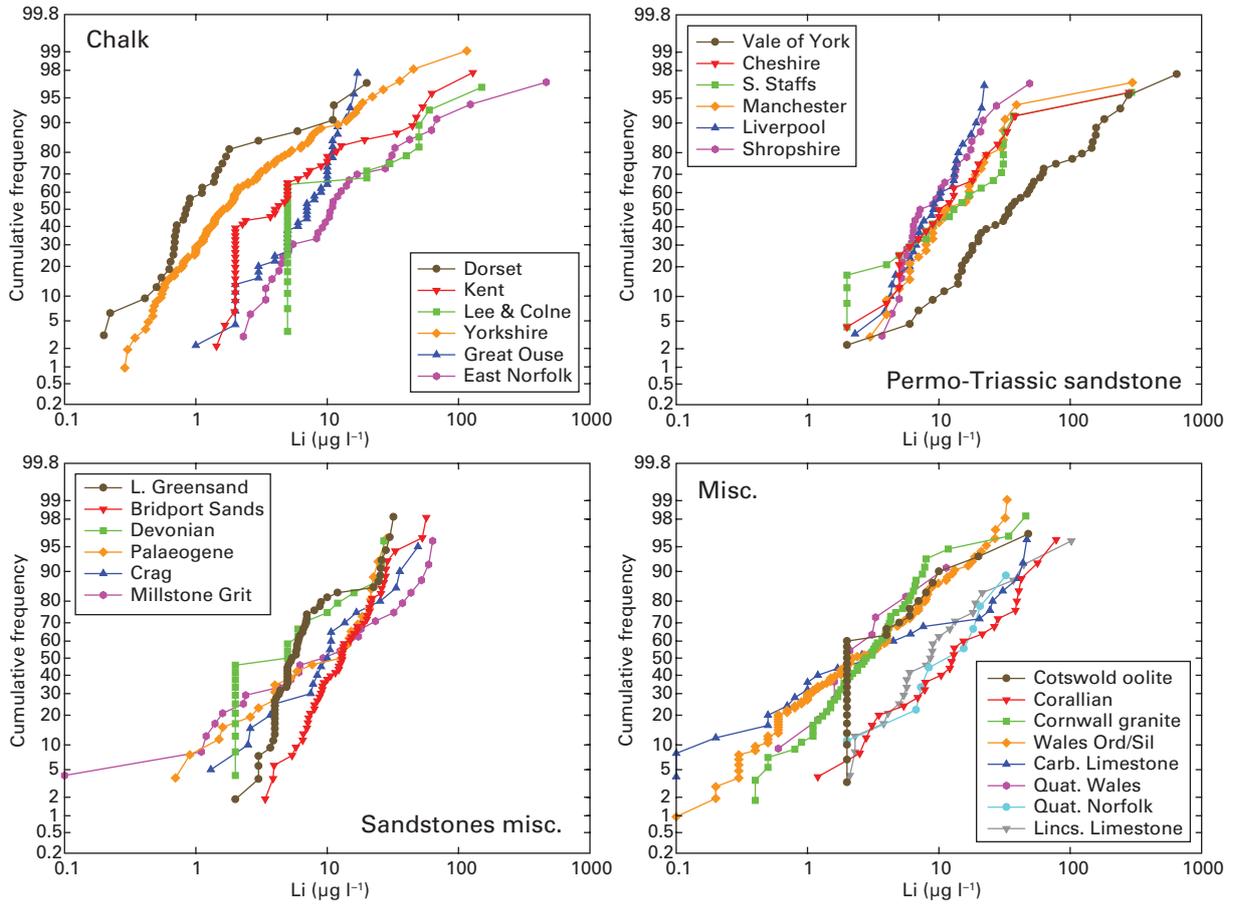


Figure 5.35 Cumulative frequency plots for Li in groundwaters.

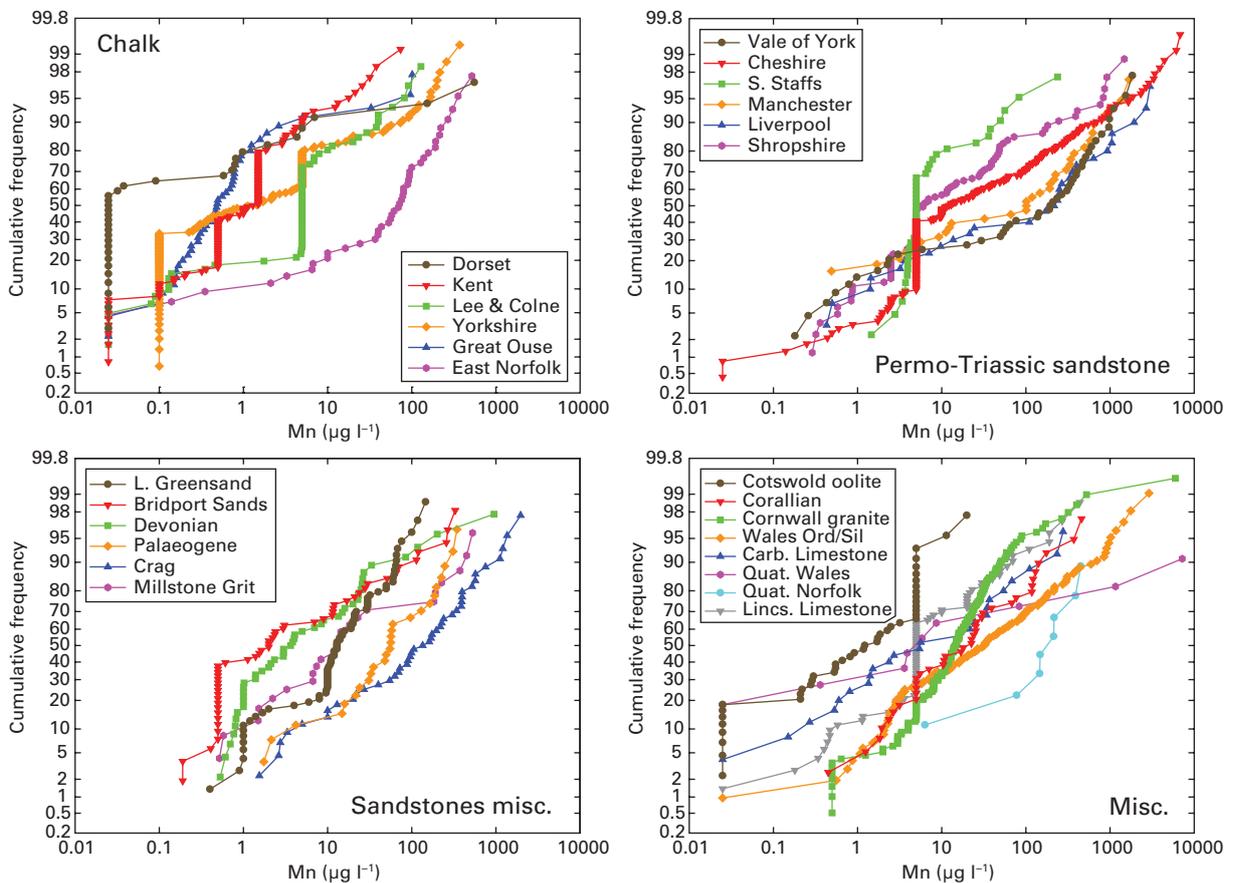


Figure 5.36 Cumulative frequency plots for Mn in groundwaters.

aquifer waters display a wide range, typically around four orders of magnitude (Figure 5.36). Median concentrations are variable, reflecting the variable redox conditions, and maximum concentrations are up to several mg l⁻¹.

The redox control on Mn is also suggested by the distributions in the other sandstone aquifers (Figure 5.36) with the Palaeogene and Crag groundwaters having higher average concentrations. Moderately high concentrations are found in the Ordovician-Silurian metasedimentary aquifers of Wales, although this is in part due to mobilisation under moderately acidic conditions. The Quaternary gravels in Wales also contain relatively high Mn, in contrast to low Fe, reflecting the greater stability field of dissolved Mn as well as a more abundant source.

The baseline ranges for Mn, therefore, vary both within aquifers and between different aquifers over several orders of magnitude, controlled largely by prevailing Eh-pH conditions.

5.6.19 Molybdenum (Mo)

Molybdenum is a relatively rare element that can occur in a number of oxidation states. It occurs as a sulphide mineral molybdenite (MoS₂) in some ore deposits. Under oxidising conditions, the dominant oxidation state is Mo(VI), which forms molybdate anions in water. The dominant species is pH-dependent: at pH less than about 2, the dominant molybdate species is undissociated H₂MoO₄; the HMoO₄⁻ is dominant between pH 2 and 5; and the molybdate ion (MoO₄²⁻) is dominant above pH 5 (Hem, 1992). Molybdenum is an essential element in animal and plant nutrition, in particular for legumes. However, it tends to accumulate in plants and may cause

problems for grazing animals. It is a cofactor in numerous enzymes and involved in photosynthesis (McBride, 1994). Molybdenum has a moderately high mobility in neutral and alkaline soils. However it is sorbed by oxides, non-crystalline aluminosilicates and to a lesser extent clays, sorption increasing with decreasing pH.

The data gathered in the present study provide the most comprehensive dataset for groundwaters in England and Wales. Median concentrations in the Chalk groundwaters are less than 1 µg l⁻¹, with maximum concentrations being less than 5 µg l⁻¹ (Figure 5.37). However, the distributions vary from region to region, with groundwaters in Kent, the Lee and Colne and Yorkshire having the lowest median. The highest concentrations are found in the Yorkshire Chalk and the Lee and Colne, generally being present in oxidising groundwaters.

Median concentrations in Permo-Triassic groundwaters show less variation and rarely exceed 10 µg l⁻¹ (Figure 5.37). These tend to be higher than in most other sandstone groundwaters, although concentrations of a few µg l⁻¹ are present in most study areas. Overall, ranges in most aquifers are at least two orders of magnitude. In summary, the maximum baseline is typically less than 10 µg l⁻¹ and ranges vary from aquifer to aquifer with no clear relationship to lithology (Figure 5.37).

5.6.20 Nickel (Ni)

Nickel has a crustal abundance of around 19 to 25 mg kg⁻¹ (Taylor and McLennan, 1985). It is often closely associated with Cr and Co in minerals and rocks. These elements substitute for Fe in ferromagnesian minerals, and hence Ni concentrations tend to be high in mafic igneous rocks and

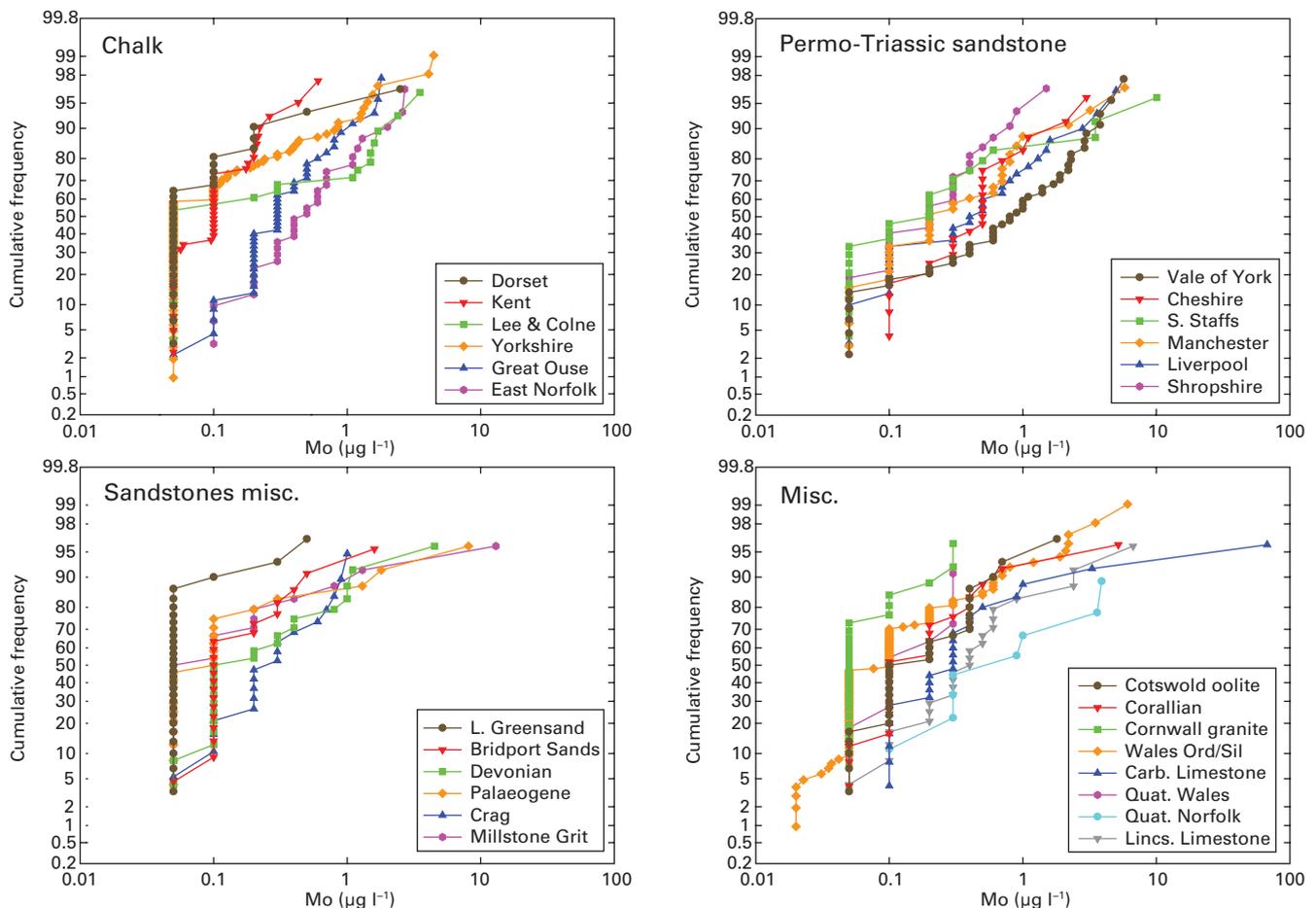


Figure 5.37 Cumulative frequency plots for Mo in groundwaters.

in sediments derived from them. Concentrations are lower in rocks with a predominance of minerals such as quartz and feldspar and in carbonate-dominated rock types.

Among the most important mineral sources of Ni are the sulphide minerals, the most abundant being pyrite. Other potentially important Ni-bearing sulphides (e.g. pyrrhotite, pentlandite, chalcopyrite) are much less common. Nickel may therefore be more concentrated in mineralised ore zones and in fine-grained pyrite-bearing sediments such as shales.

Nickel is also often partitioned strongly with manganese (Postma, 1996), either adsorbed onto the mineral surfaces or incorporated into the crystal structure. High Ni concentrations have been found in marine manganese nodules and in ferromanganese nodules in soils and sediments (Manceau et al., 2003). Nickel was found to be closely associated with Mn oxides in sandy aquifer sediments of the Ejby area of Denmark (Postma, 1996) and present at high concentrations in Mn-oxides on Chalk fracture surfaces (Shand and Bloomfield, 1995).

Nickel is also readily adsorbed to iron oxides, though to a lesser degree than manganese oxides (McKenzie, 1980). Ticknor (1994) reported strong Ni adsorption to haematite. Nickel may also be strongly adsorbed to the edges of clay minerals (Dahn et al., 2003) and to calcite (Hoffmann and Stipp, 2001).

Besides natural mineral sources, Ni may also be introduced to the environment from industrial and urban pollution. Nickel is an important industrial metal, being used in metal alloys and stainless steel. Landfill leachates have often been found to contain high concentrations of Ni, although these vary significantly according to the waste composition, age and landfill construction (Christensen et al., 1994). While such concentrations

are high and can have serious effects on groundwater quality, leachate plumes tend to be localised to the area of the landfill and dispersion of trace metals such as Ni is restricted as a result of the strong adsorption capacity of metal oxides. Dissolved organic carbon present in landfill leachate can complex the Ni and restrict its adsorption although Christensen et al., (1996) found that the organic complexation had minimal practical implication for the dispersion of Ni away from the landfill site studied at the concentrations of organic carbon investigated (up to 250 mg l⁻¹). Widespread pollution of groundwater in aquifers with Ni from landfill and other point-source pollution sources is therefore not usually expected.

Nickel occurs in water principally as the divalent cation, Ni²⁺. In near-neutral groundwaters, Ni can also form carbonate complexes. Although Ni is not itself redox-sensitive in aquifers, it can be strongly affected by redox processes as the redox-sensitive elements Mn and Fe are often linked with its mobilisation in water. These elements are mobilised in either reducing or acidic conditions by the dissolution of Fe and Mn oxides. Hence, Ni concentrations can be high in some reducing and acidic groundwaters. Nickel is also often present in acid mine drainage produced from the oxidation of Ni-rich sulphide minerals in zones of ore mineralisation.

By contrast, oxidising and near-neutral-pH conditions favour stabilisation of Mn and Fe oxides. It is the presence of such minerals in aquifers that keeps the concentration of Ni in most groundwaters low, and usually significantly less than the European limit for Ni in drinking water of 20 µg l⁻¹.

Groundwaters in the study areas display a large range of Ni concentrations (Figure 5.38). Median concentrations in the Chalk groundwaters are low for east Norfolk, the

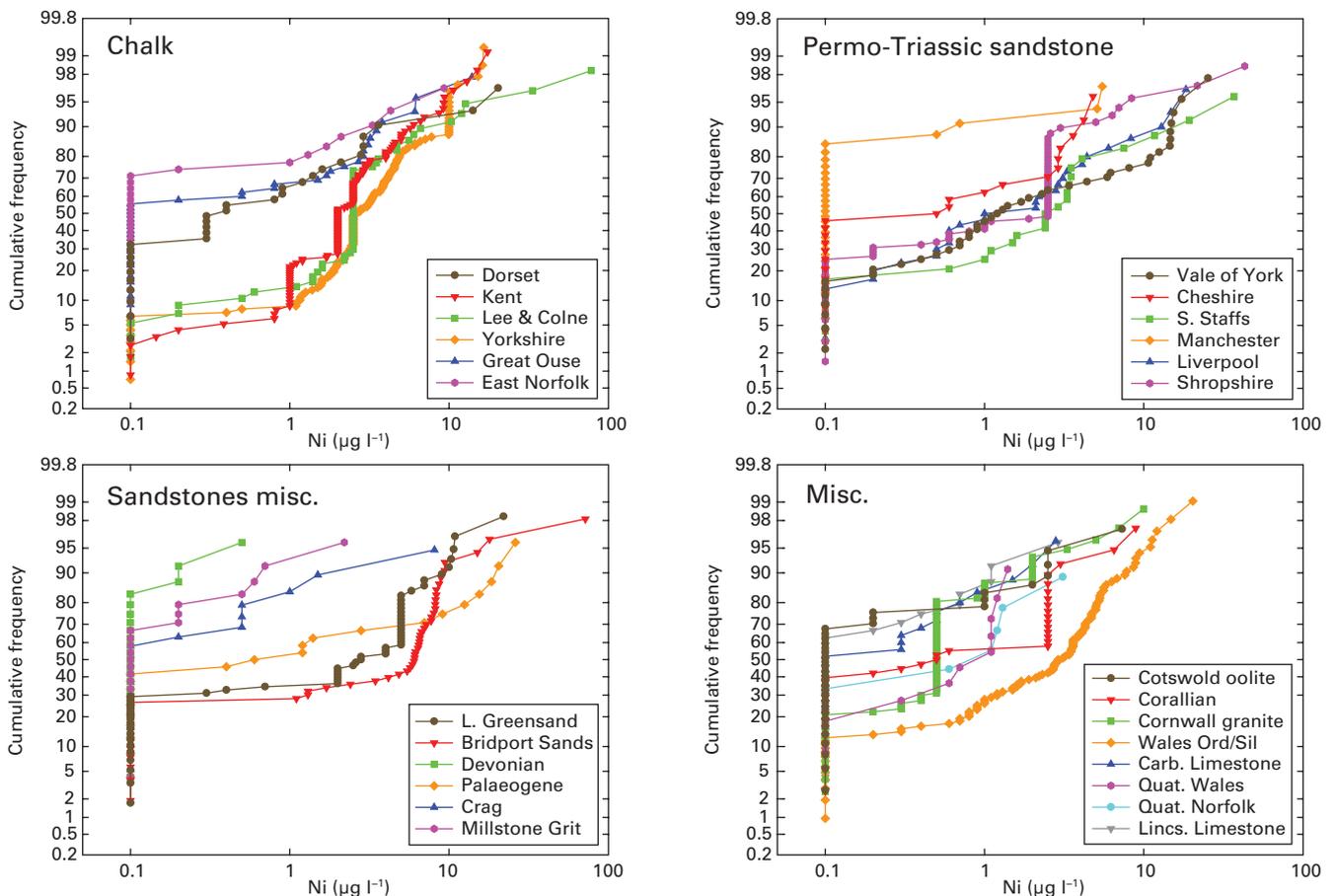


Figure 5.38 Cumulative frequency plots for Ni in groundwaters.

Great Ouse and Dorset, although maximum concentrations approached $20 \mu\text{g l}^{-1}$. Medians for the other areas are higher and the maximum concentration of $78 \mu\text{g l}^{-1}$ was measured in confined groundwater in the Lee and Colne area. The high concentrations are generally in the confined groundwaters, where Mn concentrations are also high, indicating a source from Mn oxy hydroxides.

Nickel concentrations in groundwaters of the Permo-Triassic aquifers also display a wide range from less than detection limit to a few tens of $\mu\text{g l}^{-1}$ (Figure 5.38). The lowest range and maximum concentrations are noted for the Devonian sandstone and Millstone Grit aquifers, most likely due to a combination of availability and more oxidising conditions. Medians are also low in the other carbonate aquifers and moderately high in groundwaters from the Ordovician-Silurian aquifer, possibly due to the breakdown of the Mg-rich mineral chlorite.

5.6.21 Rubidium (Rb)

The trace element rubidium displays similar geochemical behaviour to K, owing to its similar ionic radius. It forms a trace constituent in K-bearing minerals such as K-feldspar, K-micas and sheet silicates (muscovite and biotite). Rubidium is more strongly sorbed than K on exchange sites and its mobility is probably controlled by incorporation into clay minerals and by adsorption onto clays. In most of the aquifers studied, Rb correlates well with K, hence the processes controlling K distribution are likely to apply to Rb. It is therefore possible that anthropogenic impacts have slightly modified the baseline locally.

Median concentrations in Chalk groundwaters form a relatively tight cluster (Figure 5.39), although the median in the Yorkshire Chalk is lower and several samples from the east Norfolk Chalk are relatively high. These differences are not seen for K (Figure 5.6) and it is therefore likely that this is a source control. Groundwaters in the Permo-Triassic sandstone aquifers formed a relatively tight group and distributions approach log-normal. The source in these groundwaters is likely to be from the dissolution of K-feldspar, as was the case for K. The other sandstone aquifers studied display similar distributions, but are slightly lower in the Bridport Sands groundwaters. The groundwaters from the granites of south-west England have the highest median of $9.5 \mu\text{g l}^{-1}$, probably as a result of dissolution of K-feldspar, clays or biotite under more acidic conditions.

5.6.22 Strontium (Sr)

Strontium displays similar geochemical behaviour to Ca owing to its similar ionic radius. It is often present at high concentrations in Ca-bearing minerals such as Ca-plagioclase, calcite and especially aragonite and gypsum/anhydrite. Strontium can be derived from these minerals during congruent dissolution. It is also well established that Sr (and Mg) is released from marine carbonates (e.g. chalk) at calcite saturation due to incongruent dissolution, as the carbonate attains equilibrium in a fresh water environment. Thus increases in Sr/Ca occur along with increasing Sr concentration with residence time. The seawater concentration is 8 mg l^{-1} , hence mixing with seawater can enhance groundwater concentrations.

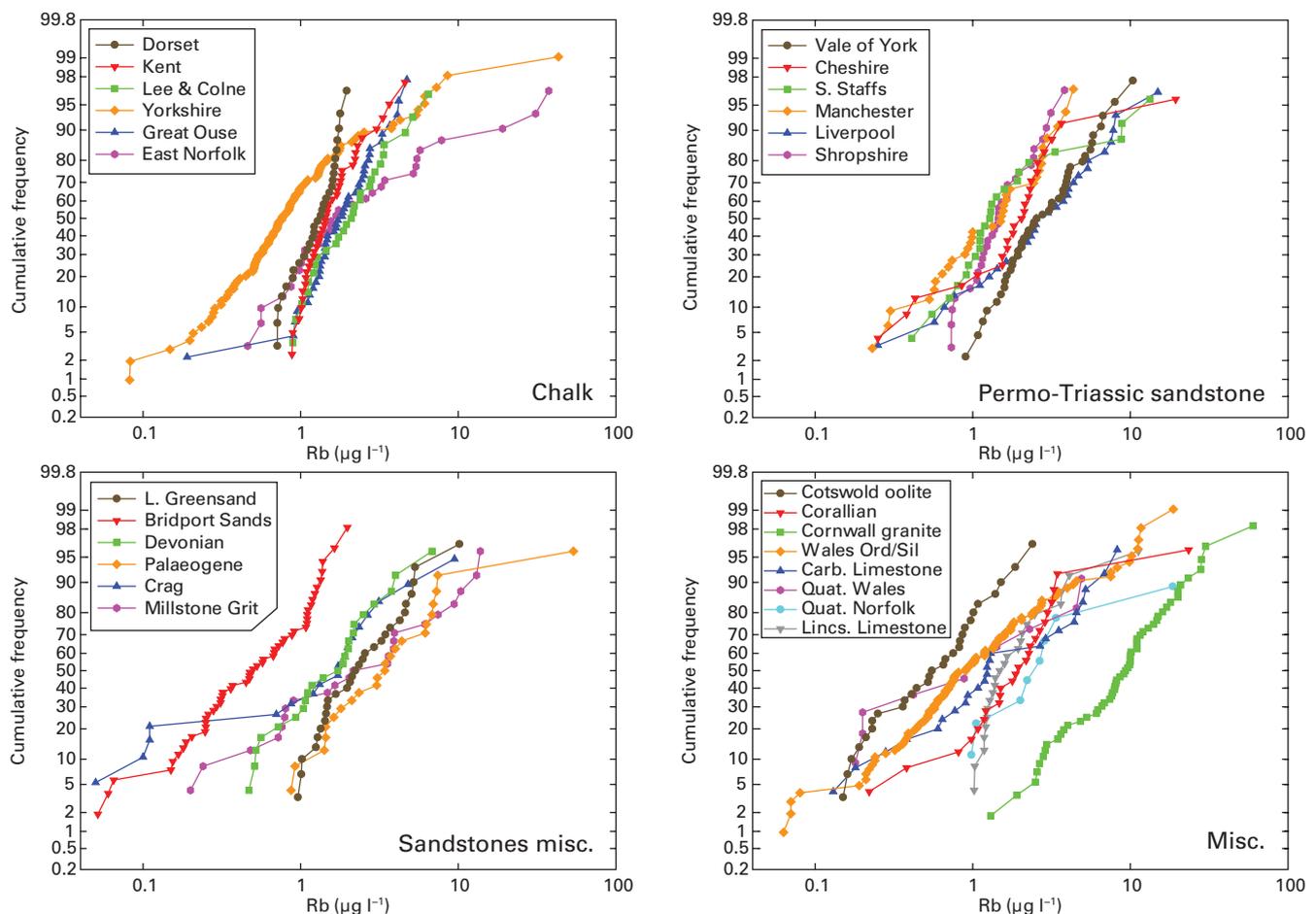


Figure 5.39 Cumulative frequency plots for Rb in groundwaters.

Concentrations in rainwater are typically low (a few $\mu\text{g l}^{-1}$) and the high Sr/Cl ratios in most groundwaters show that the dominant source is from water-rock interaction.

In fresh groundwaters there are generally no solubility controls on Sr and it typically increases with residence time. The upper limit to Sr concentrations is likely to be controlled by saturation with respect to celestite (SrSO_4), however, Sr concentrations typically have to reach several mg l^{-1} at the sulphate concentrations typical of groundwaters in England and Wales.

Median concentrations in the Chalk groundwaters form a relatively tight cluster between 200 and 500 $\mu\text{g l}^{-1}$, with the East Norfolk Chalk median being much higher at 1200 $\mu\text{g l}^{-1}$ (Figure 5.40). Concentrations in the unconfined groundwaters typically have lower concentrations and approach log-normal distributions, with the high concentrations being present in older groundwaters in the confined aquifer. The enrichment in Sr/Ca ratio with higher Sr concentration along flowpaths and good correlations of Sr with $\delta^{13}\text{C}$ (an indicator of the degree of reaction) show a dominant control by incongruent dissolution in the confined aquifer (Ander et al., 2006; Shand et al., 2003). The minimum and maximum Sr concentrations measured in Chalk groundwaters are 142 $\mu\text{g l}^{-1}$ and 27200 $\mu\text{g l}^{-1}$ respectively.

There is a large range in median concentrations in groundwaters from the different Permo-Triassic studies (Figure 5.40), from 76 $\mu\text{g l}^{-1}$ in South Staffordshire to 853 $\mu\text{g l}^{-1}$ in the Vale of York. Relatively low dissolved Sr concentrations were found in most areas, generally in low residence time shallow groundwaters, indicating limited reaction or decalcification of the aquifer and removal of

easily dissolved Sr-bearing minerals such as calcite. The high Sr in the Vale of York groundwaters is derived from dissolution of gypsum or anhydrite, either preserved in the aquifer where groundwater flow is slow (confined beneath Quaternary clays) or from overlying (Triassic Mercia Mudstone Group) or underlying (Permian) evaporites (Shand et al., 2002). Saturation with respect to celestite is achieved in many of these groundwaters at Sr concentrations above about 8000 $\mu\text{g l}^{-1}$ and SO_4 concentrations above about 1400 mg l^{-1} .

Most of the other sandstone aquifers have a relatively linear distribution (Figure 5.40) with medians between about 150 and 500 $\mu\text{g l}^{-1}$. The lowest medians are in the carbonate-poor Lower Greensand and Millstone Grit aquifers. Maximum concentrations of 3 to 4 mg l^{-1} are found in some aquifers e.g. the Palaeogene and the Crag in areas that are likely to be in hydraulic contact with the underlying Chalk aquifer.

In the other aquifers studied, low median concentrations are found in the granites of south-west England and Lower Palaeozoic and Quaternary aquifers of Wales, reflecting the lack of calcite and dominance of slow silicate weathering reactions. The other carbonate aquifers studied tend to have median Sr concentrations above ca. 200 $\mu\text{g l}^{-1}$, with the highest in the Lincolnshire Limestone (Figure 5.40).

The data presented for Sr are considered to represent baseline, being derived from natural sources. The ranges vary both between different rock types and within similar rock types (e.g. for the Chalk and Permo-Triassic sandstone) hence the baseline needs to be established for each system under study. The lack of a clear distinction between sandstone and carbonate aquifers is due to the

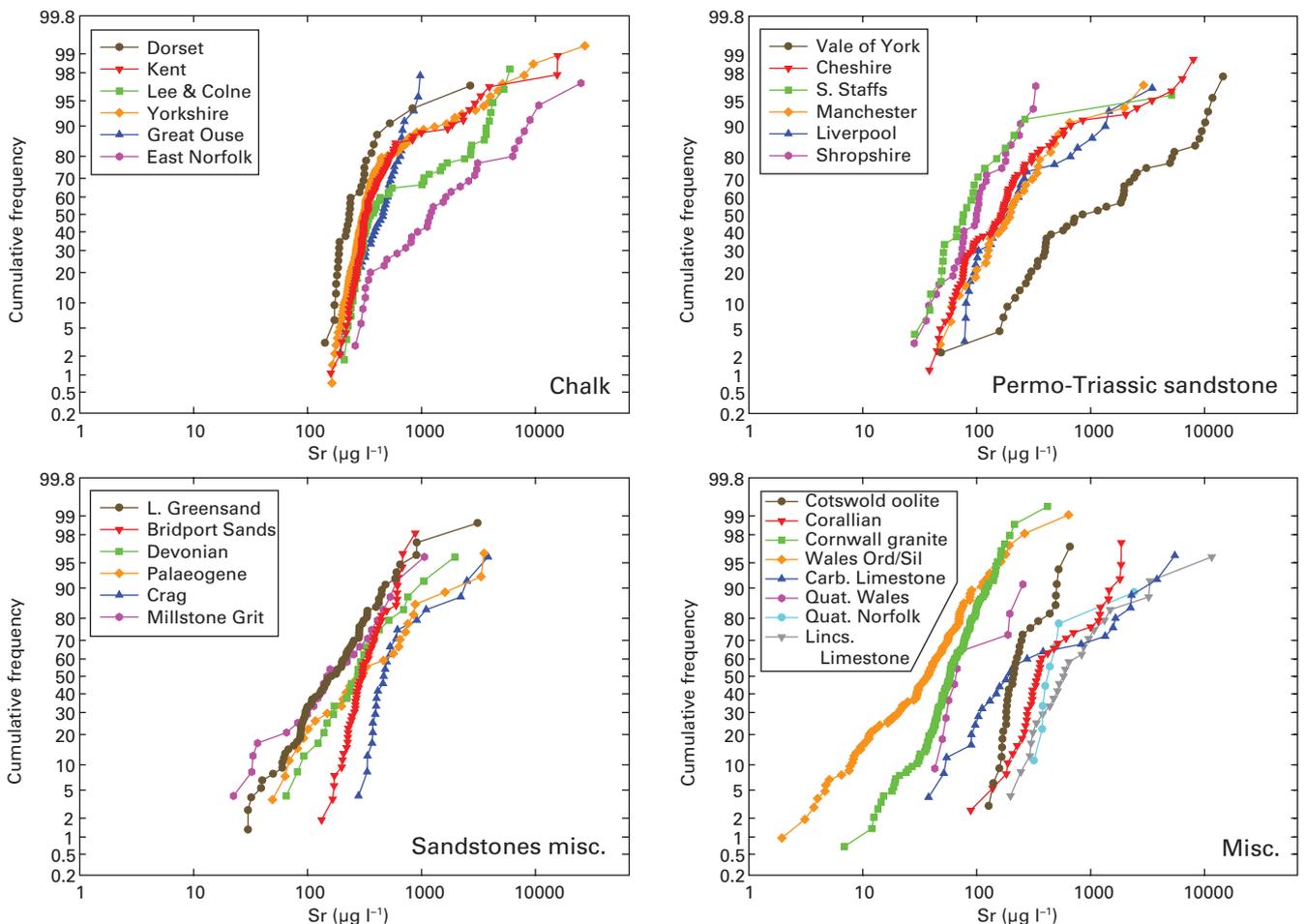


Figure 5.40 Cumulative frequency plots for Sr in groundwaters.

presence of Sr- and Ca-bearing mineral cements in many of the sandstones, which dominates the hydrochemistry of Sr and Ca owing to their rapid dissolution kinetics. The differences between unconfined and confined units also highlights the need to separate or to ensure representative sampling.

5.6.23 Thallium (Tl)

Thallium is one of the most highly toxic elements, being still used in some rodenticides, and also has a wide range of industrial uses. Large amounts are also released in emissions from power plants, smelters, cement plants and in runoff from mines. Thallium substitutes for potassium in many biological processes and is released slowly from the body. The similar behaviour of thallium to potassium and rubidium, due to similar ionic radii, is reflected in similar enrichments in acid igneous rocks, pegmatites and sheet silicates. It is also found as a trace constituent in metal ores, coal and the potassium salts sylvite and carnallite, showing both chalcophile and lithophile behaviour. Marine manganese nodules also have high concentrations of thallium as do rocks with free carbon. Thallium shows little tendency to form inorganic or organic complexes, but biomass uptake may be important. The primary control on aqueous concentrations of thallium is the host rock lithology and mineralogy. Important secondary controls such as adsorption and incorporation into clay minerals strongly limit thallium mobility in most environments. Concentrations in most waters are typically low (10^{-1} to 10^1 ng l⁻¹), requiring pre-concentration techniques, but may be high in geothermal waters (Shand et al., 1998).

Concentrations of Tl were generally below the limit of detection (which varied over the study period) by ICP MS (Figure 5.41). Maximum concentrations in Chalk groundwaters rarely exceed 0.1 µg l⁻¹. A few groundwaters in the Permo-Triassic groundwaters exceeded 0.1 µg l⁻¹, with only one being greater than 1 µg l⁻¹ in the Manchester area. It is not clear if this is natural or due to contamination, but the groundwater was reducing and present beneath thick drift deposits. It also contained high concentrations of other trace elements such as Fe, Mn, U, Sn, Sb, Ni and As and it is possible that it reflects mineralisation at depth, which is known in the Cheshire Basin (Plant et al., 1999). The other aquifers studied were similar to the Chalk. Baseline concentrations for Tl are thus low (< 0.1 µg l⁻¹) and unlikely to exceed 0.5 µg l⁻¹, except possibly around ore deposits or areas of mineralisation.

5.6.24 Tin (Sn)

The geochemistry of Sn in the natural environment is not well documented in the literature. It occurs as the ore mineral cassiterite (SnO₂) in high temperature hydrothermal veins and pegmatites located close to granite intrusions e.g. in Cornwall. Cassiterite is very resistant to weathering and is often found in heavy mineral sands or in residual soils (bauxites) associated with Sn mineralisation (Goldschmidt, 1958). It is only soluble under strongly acid or alkaline conditions.

Tin has been used for coating lead or zinc and steel to prevent corrosion and Sn-plated steel containers are widely used for food preservation. It is also used in alloys such

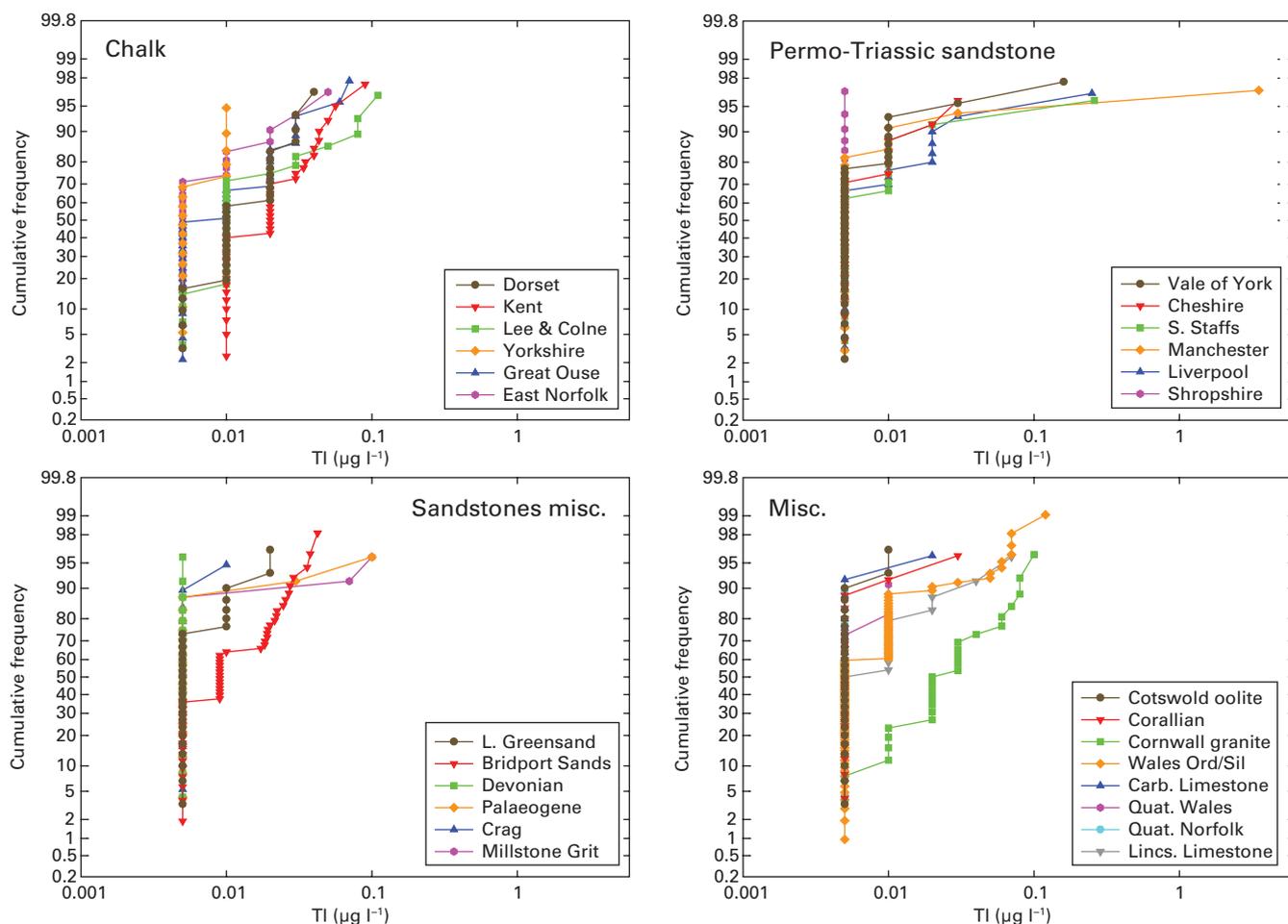


Figure 5.41 Cumulative frequency plots for Tl in groundwaters.

as bronze, die casting alloy, pewter, phosphor bronze, soft solder, and white metal. It may therefore be expected to be higher in urban areas and close to landfills, however, it is rarely analysed in surface waters and groundwaters. Trialkyltin compounds (R_3Sn^+) are used as antifouling agents and are highly toxic towards aquatic organisms (Stumm and Morgan, 1996), however little is known of its distribution and behaviour in groundwaters.

Median concentrations in groundwater vary significantly in the different Chalk aquifers, reaching a maximum of $0.37 \mu\text{g l}^{-1}$ in the Great Ouse area (Figure 5.42). Median concentrations were less than $<0.6 \mu\text{g l}^{-1}$. Concentrations in the Permo-Triassic sandstone aquifers show a similar distribution, with concentrations rarely exceeding $1 \mu\text{g l}^{-1}$. Most other groundwaters are less than $0.7 \mu\text{g l}^{-1}$, with only occasional concentrations exceeding $1 \mu\text{g l}^{-1}$ e.g. in the Lower Palaeozoic sediments, the Crag and Lower Greensand. The data indicate low concentrations and very limited mobility in groundwaters, although much research remains to be done in understanding the transport of Sn in hydrochemical environments. The baseline is thus very low in most aquifers with only occasional samples having concentrations higher than $1 \mu\text{g l}^{-1}$.

5.6.25 Tungsten (W)

Tungsten, like Sn, is commonly associated with granitic rocks and the two elements are often associated in ore deposits of hydrothermal type. The commonest ore minerals of W, wolframite ($(\text{Fe,Mn})\text{WO}_4$) and scheelite (CaWO_4) commonly occur in late stage pegmatite and hydrothermal veins around granites and occasionally

in residual sediments. Tungsten is noted for forming polyoxoanions under neutral and acidic conditions. Only W^{6+} is stable in water in noncomplexing media, and at pH greater than 8 to 9 only the tetrahedral WO_4^{2-} occurs (Baes and Mesmer, 1976).

Tungsten has a wide range of uses, including tungsten carbide in cemented carbides and is used in metalworking, mining, petroleum and construction industries. It is also widely used in light bulb and vacuum tube filaments and in electrical, heating, and welding applications.

Dissolved concentrations of W are generally low in most groundwaters with only one sample in the Manchester Permo-Triassic containing W greater than $1 \mu\text{g l}^{-1}$. Baseline W concentrations are therefore typically much less than $1 \mu\text{g l}^{-1}$ and often below the limit of detection (Figure 5.43).

5.6.26 Uranium (U)

Uranium occurs in nature in two main oxidation states, U(VI) and U(IV). It is present as a major constituent in the mineral uraninite (UO_2) and its oxidised or partly oxidised massive form, pitchblende (U_3O_8), as well as a number of other U-ore minerals. However, U ores are comparatively rare. Uranium(VI) partitions strongly with phosphate and so can occur in a number of phosphate minerals, including hydroxyapatite. High concentrations of U have also been found in zircons, sphenes and monazites. These minerals occur in granitic rocks but as they are poorly soluble, they are unlikely to be a significant influence on the U concentrations in water. The strong affinity of iron oxides for U is also well-established. Concentrations in secondary

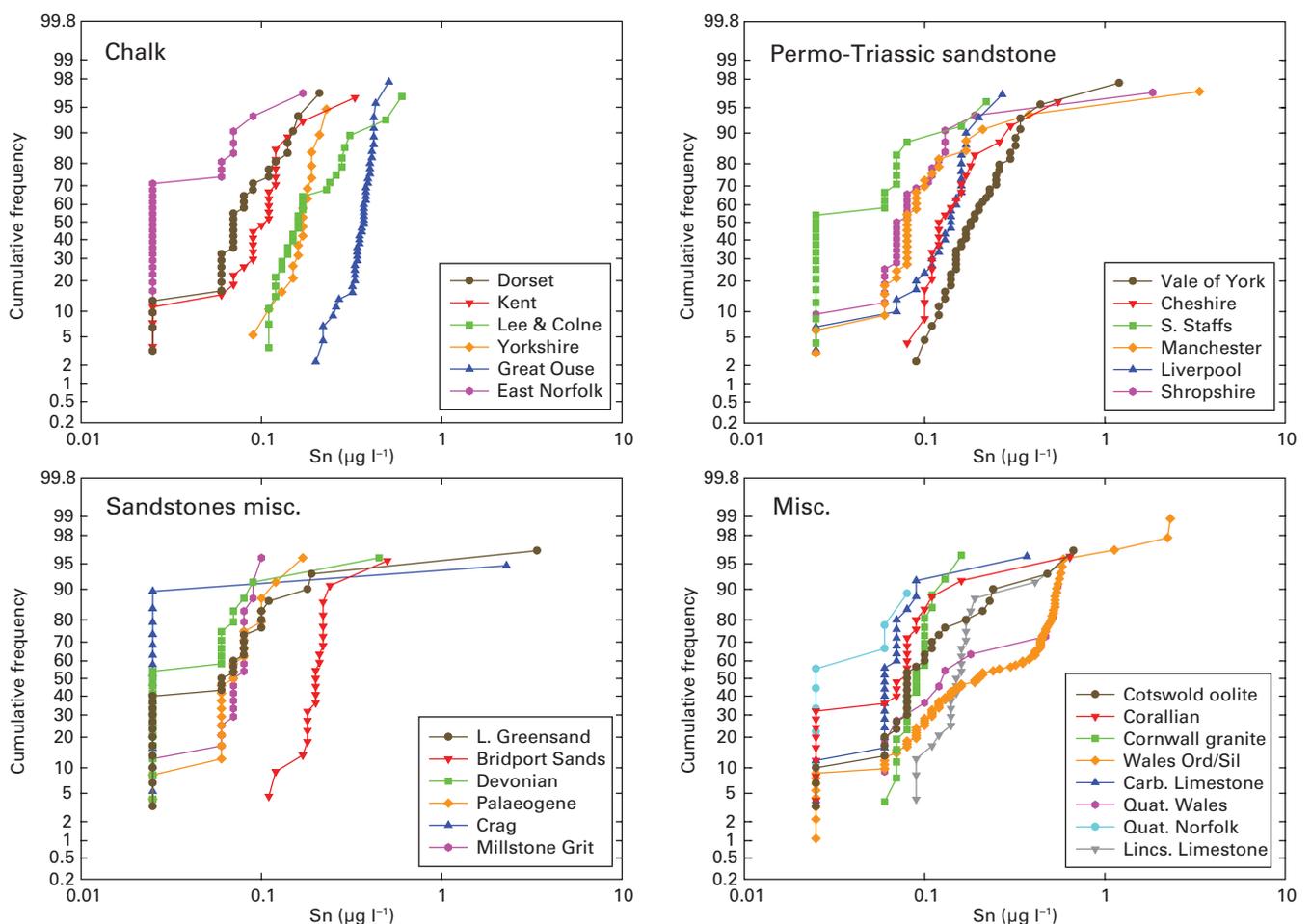


Figure 5.42 Cumulative frequency plots for Sn in groundwaters.

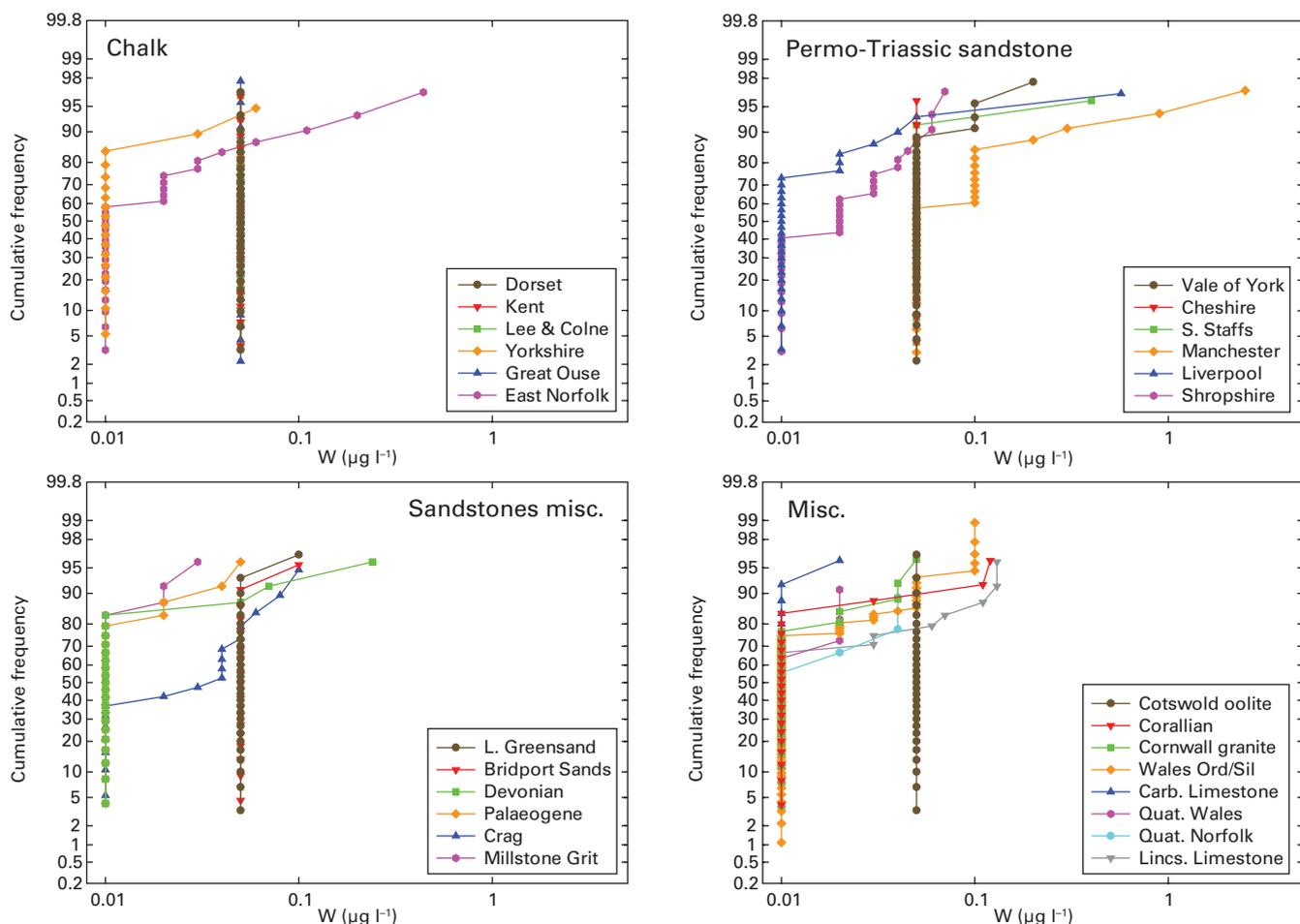


Figure 5.43 Cumulative frequency plots for W in groundwaters.

iron oxides close to uranium deposits have been found to contain total concentrations of up to 8 weight % UO_3 (Sato et al., 1997).

Uranium concentrations in rocks are typically around 1 to 4 mg kg^{-1} (Drever, 1997), being relatively high in granitic rocks, argillaceous sediments (clays, shales) and metamorphic rocks derived from them.

In water, U occurs dominantly as the hexavalent, U(VI), species. U(IV) concentrations are usually low ($<0.06 \mu\text{g l}^{-1}$) because of the low solubility of the mineral uraninite. In oxidising conditions at pH less than around 5, uranyl, UO_2^{2+} , is the dominant dissolved form of U(VI) although uranyl fluoride complexes can occur where F concentrations are sufficiently high. At higher pH, uranyl carbonate species (UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$) become more important. Complexes with phosphate can also occur at near-neutral pH. Drever (1997) concluded that the aqueous species $\text{UO}_2(\text{HPO}_4)_2^{2-}$ could be important in neutral-pH waters. Complexation with sulphide and fluoride can occur under acidic conditions and with Cl and SO_4 in saline conditions.

As a result of this speciation behaviour, U is broadly expected to be more mobile under oxidising conditions and to have low concentrations in reducing groundwaters. There is currently no EC or national limit for U in drinking water although WHO (2004) have recently promulgated a new provisional guideline value of $15 \mu\text{g l}^{-1}$. However, the US EPA maximum contaminant level (MCL) guideline for drinking water is $30 \mu\text{g l}^{-1}$.

Uranium concentrations vary over four orders of magnitude in the groundwaters from the study areas (Figure 5.44). Median concentrations for individual

areas vary between around $0.02 \mu\text{g l}^{-1}$ and $2 \mu\text{g l}^{-1}$ with an overall median for all areas of $0.27 \mu\text{g l}^{-1}$. The highest concentrations are found in groundwaters from the Permo-Triassic sandstones, many areas yielding median values in excess of $1 \mu\text{g l}^{-1}$. The highest observed concentration was $67 \mu\text{g l}^{-1}$ in a sample from the Shropshire Permo-Triassic sandstone. Relatively high concentrations in some areas (e.g. the Vale of York) are associated with impermeable Quaternary drift deposits (Shand et al., 2002). Groundwaters in the Devonian aquifer of Wales were found to have a median of $1.4 \mu\text{g l}^{-1}$. The most likely source of the U in these samples is iron oxides which are abundant in these sandstones. Desorption of U(VI) species from oxide surfaces in the unconfined sections of aquifers is considered the most likely release mechanism. Millstone Grit and Lower Greensand samples in the dataset generally had much lower groundwater U concentrations. Relatively high U concentrations were also observed for groundwaters from the granites of south-west England. These had a median of $0.55 \mu\text{g l}^{-1}$ with a maximum observed value up to $3.6 \mu\text{g l}^{-1}$.

A narrower range of concentrations is observed in groundwaters from most areas of the Chalk, which in all cases had median concentrations $<1 \mu\text{g l}^{-1}$, albeit with a few outliers up to $8 \mu\text{g l}^{-1}$. Other limestone aquifers such as the Carboniferous Limestone, Corallian of the Thames area and the Cotswolds oolite also have mostly low concentrations.

The U concentrations in the groundwaters are likely to be overwhelmingly geogenic in origin and the large observed range is believed to reflect baseline conditions. Observed maximum concentrations rarely exceed

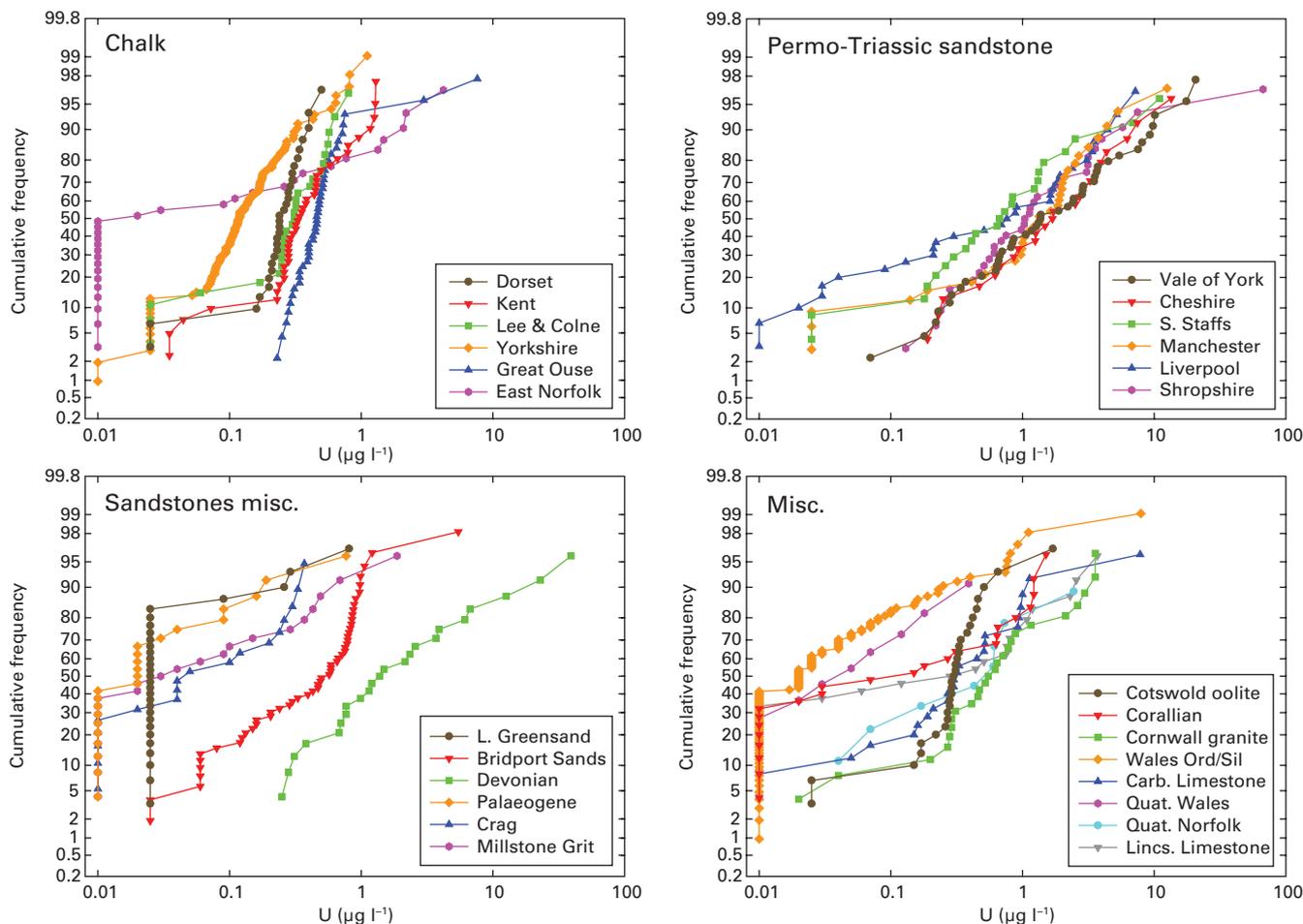


Figure 5.44 Cumulative frequency plots for U in groundwaters.

15 $\mu\text{g l}^{-1}$ (Figure 5.44).

5.6.27 Vanadium (V)

Vanadium exists in three oxidation states in nature, V^{3+} , V^{4+} and V^{5+} . In solution, it has a strong tendency to form complex vanadate anions: $\text{VO}_3(\text{OH})_2^-$, $\text{VO}_2(\text{OH})_2^-$, $\text{VO}(\text{OH})_3^0$, the vanadyl cation VO_2^+ and complex polymeric species (McBride, 1994). The more reduced V^{3+} ion is not stable under oxidising conditions and substitutes for Fe^{3+} in Fe oxide minerals. The mobility of V is thus dependent on redox conditions and pH. Vanadium has a high mobility and bioavailability under oxidising and neutral to alkaline pH. As with other oxyanions it is likely to be sorbed at lower pH especially onto organic matter. It occurs mostly as a minor constituent of Fe-bearing minerals and may also be incorporated into octahedral sites in clays. Vanadium is also involved in biochemical processes and may therefore be relatively high in organic matter and coal, combustion of the latter forming an important pathway into the environment (Hem, 1992).

Median groundwater concentrations in the Chalk aquifer are typically low, with maxima often being at most a few $\mu\text{g l}^{-1}$, and rarely greater than 10 $\mu\text{g l}^{-1}$ (Figure 5.45). Groundwaters in the Permo-Triassic aquifers are only slightly higher and medians are typically less than $\mu\text{g l}^{-1}$. The other aquifers studied showed similar distributions, but varying between individual aquifers. In general, the highest V concentrations exist in oxidising groundwaters, but in the Lincolnshire Limestone, the groundwaters with highest dissolved V are the more reducing high-Fe waters. It is possible that the V is derived from the reductive

dissolution of Fe-oxyhydroxides or that it is present adsorbed onto fine colloidal particles.

Median baseline concentrations are thus considered to be less than 1 $\mu\text{g l}^{-1}$, with maximum concentrations occasionally reaching up to about 10 to 30 $\mu\text{g l}^{-1}$.

5.6.28 Yttrium (Y)

Yttrium displays very similar geochemical behaviour to the rare earth elements (REE), in particular the middle-to-heavy REEs, and it is often treated as a REE in studies of these elements. As with the other REE, Y is often present in minor mineral phases such as monazite, allanite and zircon and commonly associated with phosphate minerals in sediments. Yttrium is similarly mobile under more acidic conditions and displays strong sorption characteristics, particularly at high pH, onto mineral surfaces. However, it tends to occur in solution at higher concentrations than the REEs.

Concentrations of Y in Chalk groundwaters are very low with median concentrations often being below the detection limit, and maximum concentrations rarely exceeding 0.1 $\mu\text{g l}^{-1}$ (Figure 5.46). In the Permo-Triassic sandstone aquifers, groundwaters have slightly higher median concentrations, in a few samples exceeding 1 $\mu\text{g l}^{-1}$. The highest concentrations are found in the more acidic shallow groundwaters where buffering by carbonates is low owing to decalcification.

The other sandstone groundwaters show a large range in median concentrations, and again high concentrations are related to lower pH (<pH 6) e.g. in the Palaeogene and Lower Greensand aquifers. The other carbonate aquifers

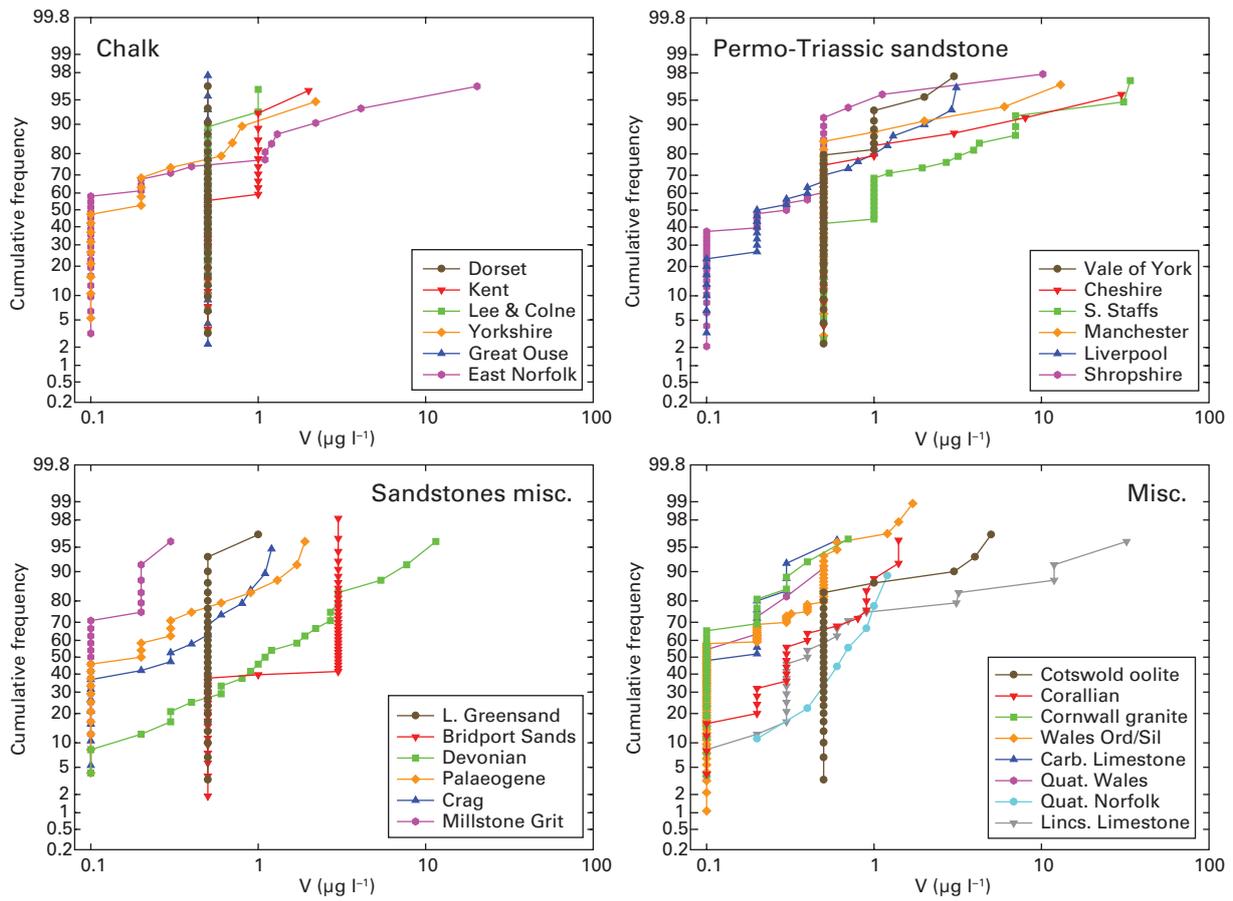


Figure 5.45 Cumulative frequency plots for V in groundwaters.

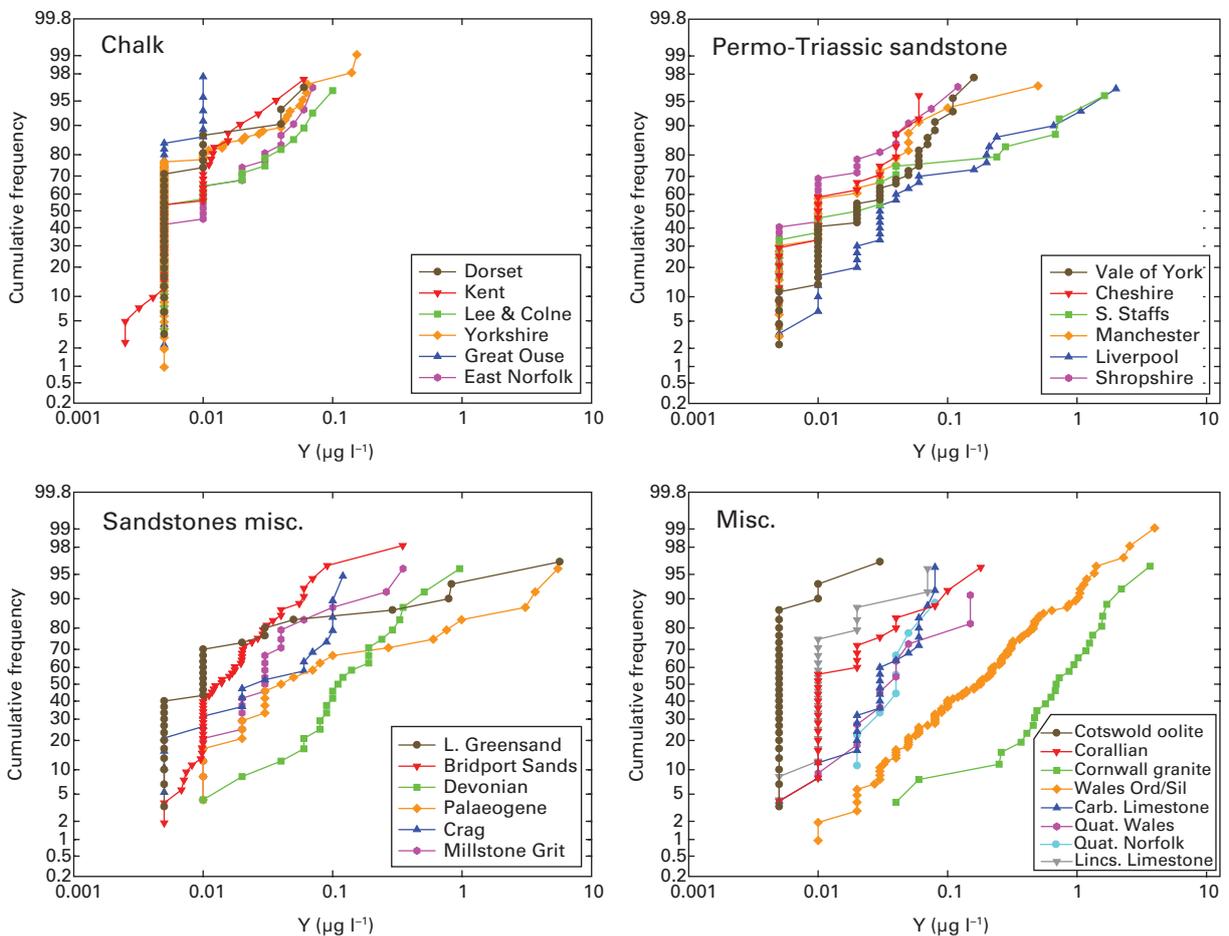


Figure 5.46 Cumulative frequency plots for Y in groundwaters.

are similar to the Chalk, whilst the more acidic granites of south-west England and Lower Palaeozoic sediment groundwaters have concentrations up to about $4 \mu\text{g l}^{-1}$.

Baseline concentrations of Y are therefore strongly pH dependent, increasing in more acidic groundwaters where buffering capacity is low.

5.6.29 Zinc (Zn)

Zinc is an essential element for plant and animal metabolism. It is most commonly associated with ore deposits occurring in the primary zinc sulphide sphalerite (ZnS) and a range of secondary Zn carbonates (e.g. smithsonite, ZnCO_3) and oxides. It also occurs as a trace constituent in a number of common minerals including calcite where it is present at a few tens of ppm, and higher in clays and shales where it may be present in secondary iron oxide and silicate minerals (Edmunds et al., 1989).

The solubilities of Zn carbonate and zinc hydroxides are moderately high and in comparison with other transition metals, Zn is expected to be present more widely and at higher concentrations in groundwaters. It is likely that one of the limiting factors to zinc mobility is the presence of oxide and oxyhydroxide minerals which may adsorb zinc and keep concentrations less than that predicted by mineral solubility controls (Edmunds et al., 1989). Zinc has only one oxidation state (Zn^{2+}), hence it is insensitive to redox conditions, however its ability to be adsorbed to metal oxyhydroxides, albeit at much higher pHs than many other metals, may have an indirect control on concentrations. It is most mobile under acidic oxidising conditions where it may be toxic to plants at high concentrations.

Zinc is a common industrial metal, e.g. it is used extensively in coating metals. Owing to its relatively high mobility, it is likely that anthropogenic inputs will be important close to urban areas or landfill sites. A potential source of Zn is the metal fittings on pumps and pipe work, making it difficult to discount an anthropogenic origin for elevated Zn in pumped groundwaters.

Median concentrations of Zn in Chalk groundwaters form a relatively narrow range from 6 to $15 \mu\text{g l}^{-1}$ (Figure 5.47), in comparison with ranges which are typically three to four orders of magnitude (Figure 5.47). The highest concentrations, of several mg l^{-1} , were found in the Yorkshire Chalk groundwaters. Groundwaters in the Permo-Triassic sandstone aquifers also show a relatively narrow range in median concentrations, but were slightly higher, from 9 to $25 \mu\text{g l}^{-1}$. Often Zn is present along with other metals which are thought to indicate sulphide mineralisation, hence a natural source is considered likely for at least some of the high concentrations (e.g. Griffiths et al., 2002). Several regions also contained groundwater with concentrations greater than 1 mg l^{-1} . For the other sandstone aquifers, medians are more scattered, with the Bridport Sands and Devonian aquifers having the lowest median. Nevertheless, all sandstone aquifers display a large range in concentration. There was no clear demarcation between the other carbonate and silicate groundwaters.

Due to the potential anthropogenic influences it is difficult to discount these inputs. However, the similarity and range of distributions in all study areas, moderately high Zn in spring samples and expected high mobility of Zn suggest that, for the most part, the distributions represent baseline.

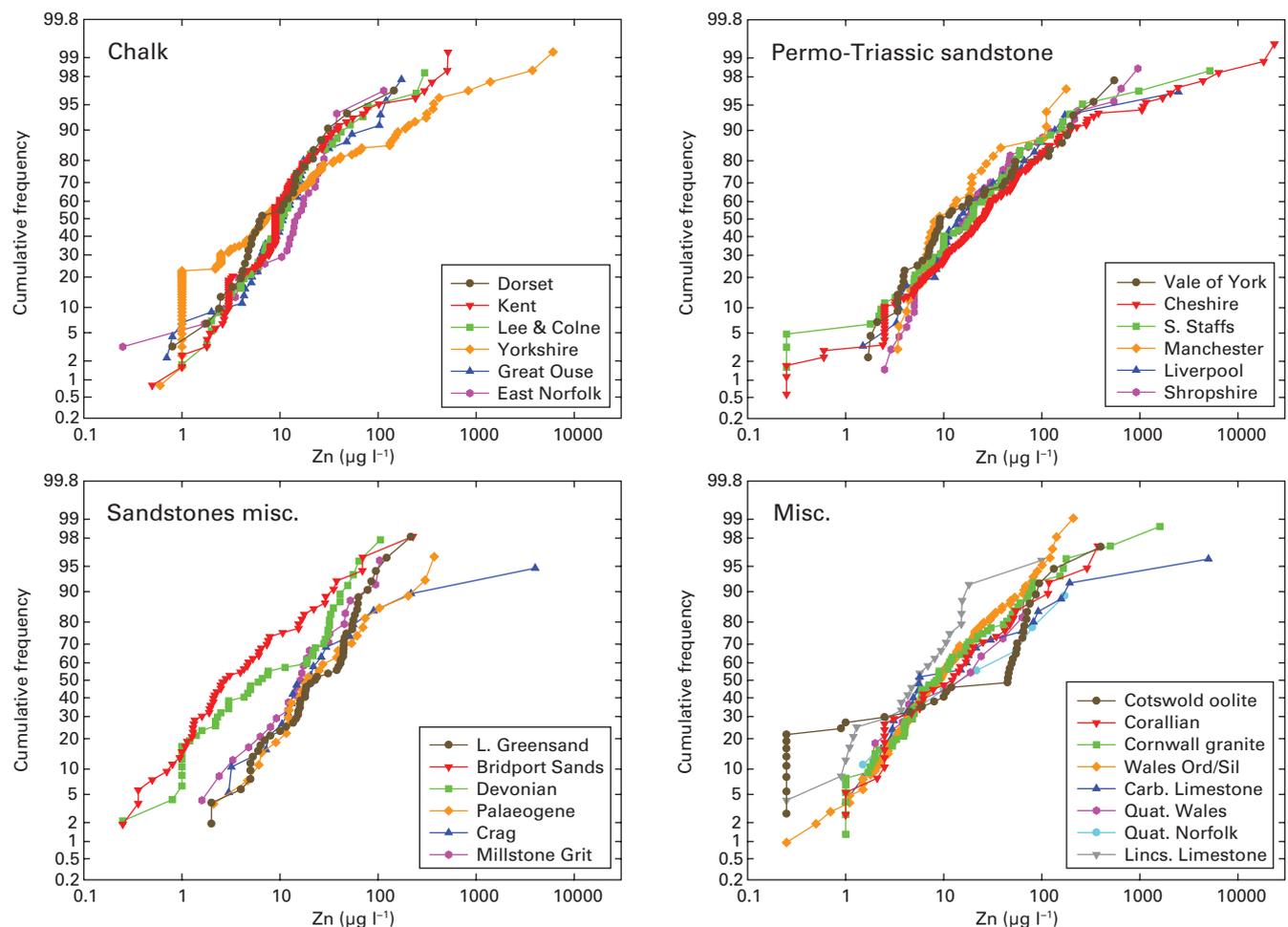


Figure 5.47 Cumulative frequency plots for Zn in groundwaters.

6 Summary and Recommendations

6.1 SUMMARY

6.1.1 Baseline and groundwater quality

The Baseline Project has shown that there are likely to be few areas in England and Wales where groundwaters are 'pristine' and where all elements are present within the range of baseline concentrations. This is because the release into the atmosphere of gases and particles from power stations, car exhausts, etc. has modified the chemistry of the rainfall. It is the rainfall chemistry that provides the primary input of solutes to recharge water. The consequence has been an increase in concentration of oxides of both nitrogen and sulphur and a reduction in the pH. More significantly, most of the recharge areas for aquifers in England and Wales are intensively farmed and chemicals associated with agriculture (NO_3 , SO_4 , Cl, K, PO_4) have been leached in increasing quantities during the past 40 years. Nitrate concentrations approaching, or even exceeding, the Drinking Water Guideline values are now widely observed in many unconfined aquifers in England and Wales.

Because unconfined groundwaters are usually aerobic, denitrification and the mobilisation of iron and manganese tend to be of minor or local importance only. Ion exchange in unconfined groundwaters is not generally a dominant process. It is probably reasonable to assume that the nitrate concentrations in the older (pre-1950) aerobic groundwaters within the unconfined aquifer represent baseline concentrations (typically less than 2 to 4 mg l⁻¹ as NO_3). For solutes derived from both natural and anthropogenic sources (e.g. SO_4 , Cl, K) it is often difficult to establish baseline concentrations. However, given the wide range in concentrations that can be derived from 'natural' sources, it is likely that most groundwater concentrations, although modified, still lie within the upper baseline range.

Confined groundwaters probably correspond more closely to 'natural' water quality and to baseline concentrations for most elements than is the case with unconfined groundwaters. This is because (i) the low-permeability confining beds make them less vulnerable to pollution by activities at the land surface; (ii) solute travel times from outcrop to the confined aquifer are usually long and this ensures that confined groundwaters frequently originated as recharge prior to the 20th century, when industry was less developed and agriculture less intensive. However, groundwater quality in some confined aquifers has been modified by abstraction which can result in modern, aerobic groundwaters being pulled into the confined aquifer more rapidly than under natural flow conditions. Induced leakage, from semi-permeable confining layers, of groundwater with different water chemistry to the main aquifer or movement up-dip of older (possibly saline) groundwater has occurred because of reversal of the hydraulic gradient within the confined aquifer. Groundwater from the confined part of the aquifer cannot be used to indicate baseline concentrations for

specific elements/solutes within the unconfined aquifer because of the potentially much longer residence times that are usually associated with confined groundwaters. Further, confined groundwaters are modified by various processes (e.g. ion exchange, redox and mixing with formation waters) which are less important in the shallower parts of the unconfined aquifer.

Notwithstanding the above, the Baseline Project has shown that while differences in solute/element concentrations do occur between aquifers, there are also many similarities in groundwater chemistry, particularly in the pattern of evolution along groundwater flowpaths. For example, most shallow unconfined groundwaters in England and Wales are of the Ca- HCO_3 type, are aerobic and have pH in the range 6 to 7.5, whereas many confined groundwaters display trends towards Na- HCO_3 or Na-Cl type. Greater differences in water chemistry are, therefore, often observed between unconfined and confined groundwaters within the same aquifer rather than between different unconfined (or confined) aquifers.

The natural flow pattern has been modified in many of the aquifers of England and Wales by groundwater abstraction as well as by the consequences of climate change. This has been most evident in the unconfined parts of aquifers, but this also affects the confined aquifer where decreases in potentiometric level have led to loss of artesian conditions. Such abstraction may disturb the layering typically found in aquifers, by pulling down younger, often polluted groundwater in the cone of depression around a borehole or by causing the upwelling of older, deeper groundwater. In these cases, it is likely that the baseline condition no longer exists. In some cases, this can lead to marked deterioration of the resource, for example due to upconing of saline water or changes in redox status by the introduction of oxygen causing acidification or mobilisation of heavy metals. Similar changes may occur naturally, but the rates of change are generally increased through such influences.

Changes in flow systems since pre-industrial times often make it difficult to interpret hydrochemical data within the context of the modern abstraction regime. However, the natural flow in most aquifers is typically slow (of the order of metres per year, except in karst conditions) and the kinetic dependence of many chemical reactions means that groundwaters often retain a 'memory' of previous flow regimes. In order to assess the dynamic changes caused by abstraction, it is necessary to have a good understanding of both physical and chemical conditions within the aquifer, and processes controlling flow and reaction. This is aided significantly through knowledge of the relative ages of groundwater in the aquifer, and by modelling.

Of the solutes which are found naturally in groundwater at concentrations which may exceed existing regulatory standards, some are a potential health concern (e.g. As, Ba, F, Ni, U), whilst others merely represent a nuisance requiring treatment (e.g. Fe, Mn). Of the anthropogenic substances most commonly found in British groundwaters, most are derived from agricultural practices, although

impacts are also likely to be locally significant in urban, industrial and mining areas.

More than 80 components have been measured in the aquifer studies. A summary of all the data is provided in Tables 6.1 and 6.2. This represents a comprehensive and strategic database of the present day and baseline concentrations for most inorganic substances, and therefore acts as a reference datum to quantify pollution.

The statistical data and plots are useful for comparison between areas, and may be useful in the future to assess changes from the present-day baseline. In addition, they are of strategic value since they include data for elements for which there are no existing guidelines, but which may still be harmful (e.g. Be, Se, Sb, Tl). The present definition of these baseline ranges for a system can be used to recognise contamination incidents by such rare elements as may happen in the future.

The importance of historical data as an aid to determining baseline cannot be overemphasised: it is frequently difficult to establish the natural baseline concentrations for all elements/solutes, especially as long-term records of water quality monitoring are often either not available or not necessarily reliable. Historical records provide the most powerful technique for determining the baseline but are often difficult to find or buried in the archives of organisations. Often, the data are confidential and not available for public use. However, when found, these data have not only provided direct indicators of baseline, but have helped to highlight the temporal changes imposed by abstraction.

6.1.2 Baseline and regulatory issues

An essential requirement for implementation of the European Water Framework Directive is the provision of information on the natural quality of groundwater. This is needed to ensure that reference conditions can be established, and provide a basis for determining whether groundwater is of good or poor status, is deteriorating, or is improving. This synthesis and the Baseline Report Series will thus help the Environment Agency to deliver requirements of the Water Framework Directive. The baseline dataset can also be used to assist in groundwater screening and in the establishment of threshold values (quality standards).

The baseline reports and data should also form a vital component of Water Framework Directive compliance. The availability of the baseline data means that sensible assessments can be made, given the significant natural variability in groundwater quality. Without this there would be a significant risk of misclassifying groundwater which in turn could result in considering and/or initiating costly programmes of measures when they are not needed, or alternatively failing to spot a problem that needs addressing.

It is difficult at present to quantify the cost benefits of the baseline reports and data, but over time these will most likely amount to many times the cost of the project. It is reasonable to speculate that the benefits could be in the millions-of-pounds range, since it is not just Water Framework Directive compliance that will benefit. The

Table 6.1 Statistical summary of field measurements, stable isotopes, and concentrations of major and minor chemical species in groundwaters from the baseline study.

	Units	Minimum	Maximum	Median	Mean	97.7 percentile	N
T	°C	3.0	24	11.3	11.4	16.4	1565
pH		4.23	11.09	7.2	7.07	8.17	2161
Eh	mV	-188	820	339	297	519	770
DO	mg l ⁻¹	<0.1	14.2	4.9	4.6	10.7	1051
SEC	µS cm ⁻¹	14	26800	580	850	3055	1888
δ²H	‰	-59	-30	-49	-48	-32	413
δ¹⁸O	‰	-10.5	-4.8	-7.5	-7.36	-5.48	467
δ¹³C	‰	-24.1	-2.4	-14.7	-14.4	-6.4	362
Ca	mg l ⁻¹	0.48	795	80.6	86.6	235	2270
Mg	mg l ⁻¹	0.25	689	6.43	15.4	76.5	2270
Na	mg l ⁻¹	2.1	5820	15.9	65.9	406	2266
K	mg l ⁻¹	<0.2	220	2.52	4.78	27.0	2227
Cl	mg l ⁻¹	2	10700	28	110	667	2301
SO₄	mg l ⁻¹	0.1	1790	28.1	64.3	326	2284
HCO₃	mg l ⁻¹	<0.1	1310	236	219	461	1936
NO₃-N	mg l ⁻¹	<0.002	50.8	3.1	5.04	20.4	2212
NO₂-N	mg l ⁻¹	<0.001	1.01	0.003	0.01	0.08	1788
NH₄-N	mg l ⁻¹	<0.003	12.0	0.019	0.14	1.12	1961
P	µg l ⁻¹	<10	2706	40	81.74	480	1213
TOC	mg l ⁻¹	<0.1	36.71	1.3	1.80	6.88	707
DOC	mg l ⁻¹	<0.1	23.2	1.65	2.47	10.5	746
F	mg l ⁻¹	<0.1	11.2	0.12	0.27	1.79	1501
Br	mg l ⁻¹	0.007	36.5	0.078	0.34	2.03	1163
I	mg l ⁻¹	<0.001	3.34	0.005	0.02	0.12	805
Si	mg l ⁻¹	0.23	13330	5.67	622	5635	1771

Table 6.2 Statistical summary of trace element concentrations from the baseline study.

	Units	Minimum	Maximum	Median	Mean	97.7 percentile	N
Ag	µg l ⁻¹	<0.05	7.9	<0.05	0.07	0.50	862
Al	µg l ⁻¹	<1	1550	3	56.0	559	1140
As	µg l ⁻¹	<1	355	<1	3.20	23.0	1163
Au	µg l ⁻¹	<0.05	0.78	<0.05	0.03	0.05	727
B	µg l ⁻¹	<20	3442	24	74.5	448	1307
Ba	µg l ⁻¹	0.43	2968	32	72.7	438	1223
Be	µg l ⁻¹	<0.05	4	<0.05	0.10	0.51	949
Bi	µg l ⁻¹	<0.05	0.4	<0.05	0.03	0.09	784
Cd	µg l ⁻¹	<0.05	28.5	0.05	0.25	2.50	1267
Ce	µg l ⁻¹	<0.01	6.88	<0.01	0.14	1.74	803
Co	µg l ⁻¹	<0.02	53.4	0.07	0.64	5.14	949
Cr	µg l ⁻¹	<0.5	386	<0.5	1.25	5.00	1250
Cs	µg l ⁻¹	<0.01	4.48	0.02	0.13	1.10	899
Cu	µg l ⁻¹	<0.1	1261	2.7	14.0	93.1	1339
Dy	µg l ⁻¹	<0.01	1.02	<0.01	0.03	0.27	789
Er	µg l ⁻¹	<0.01	0.66	<0.01	0.02	0.17	789
Eu	µg l ⁻¹	<0.01	0.35	<0.01	0.01	0.08	803
Fe	µg l ⁻¹	<5	41700	15	546	5073	1711
Ga	µg l ⁻¹	<0.05	0.27	<0.05	0.03	0.05	755
Gd	µg l ⁻¹	<0.01	1.32	<0.01	0.04	0.43	789
Ge	µg l ⁻¹	<0.05	5.12	<0.05	0.06	0.28	784
Hf	µg l ⁻¹	<0.02	0.04	<0.02	<0.02	<0.02	727
Hg	µg l ⁻¹	<0.1	2.3	<0.1	<0.1	0.20	988
Ho	µg l ⁻¹	<0.01	0.18	<0.01	<0.01	0.06	789
In	µg l ⁻¹	<0.01	0.1	<0.01	<0.01	<0.01	727
Ir	µg l ⁻¹	<0.05	0.14	<0.05	<0.05	<0.05	727
La	µg l ⁻¹	<0.01	6.04	<0.01	0.07	0.83	899
Li	µg l ⁻¹	<0.03	648	5.336	14.2	66.1	934
Lu	µg l ⁻¹	<0.01	0.2	0.005	<0.01	0.01	773
Mn	µg l ⁻¹	<2	6810	5.8	98.06	910	1603
Mo	µg l ⁻¹	<0.1	67.7	0.1	0.54	3.50	838
Nb	µg l ⁻¹	<0.01	0.08	<0.01	<0.01	0.02	727
Nd	µg l ⁻¹	<0.01	8.49	<0.01	0.12	1.46	803
Ni	µg l ⁻¹	<0.2	78	1.3	2.73	14.8	1143
Os	µg l ⁻¹	<0.05	0.08	<0.05	<0.05	<0.05	727
Pb	µg l ⁻¹	<0.1	6650	0.5	10.3	27.7	1313
Pd	µg l ⁻¹	<0.2	2.6	<0.2	<0.2	<0.2	731
Pr	µg l ⁻¹	<0.01	2.01	<0.01	0.03	0.34	803
Pt	µg l ⁻¹	<0.01	0.05	<0.01	<0.01	<0.01	727
Rb	µg l ⁻¹	0.05	60	1.45	2.82	15.0	899
Re	µg l ⁻¹	<0.01	0.29	<0.01	<0.01	0.04	727
Rh	µg l ⁻¹	<0.01	0.07	<0.01	<0.01	0.02	727
Ru	µg l ⁻¹	<0.05	0.08	<0.05	<0.05	<0.05	727
Sb	µg l ⁻¹	<0.05	3.43	<0.05	0.18	1.75	989
Sc	µg l ⁻¹	<1	6.69	1	1.52	5.15	758
Sm	µg l ⁻¹	<0.05	1.54	<0.05	<0.05	0.34	803
Sn	µg l ⁻¹	<0.05	3.38	0.1	0.17	0.55	727
Sr	µg l ⁻¹	1.95	27200	241	641	5144	1228
Ta	µg l ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	727
Tb	µg l ⁻¹	<0.01	0.18	<0.01	<0.01	0.03	759
Te	µg l ⁻¹	<0.05	1.1	<0.05	<0.05	0.09	727
Th	µg l ⁻¹	<0.05	1.85	<0.05	<0.05	0.12	773
Ti	µg l ⁻¹	<10	36	<10	<10	<10	727
Tl	µg l ⁻¹	<0.01	3.51	<0.01	0.02	0.07	784
Tm	µg l ⁻¹	<0.01	0.12	<0.01	<0.01	0.02	759
U	µg l ⁻¹	<0.02	67.2	0.27	0.93	6.87	869
V	µg l ⁻¹	<0.2	33.9	0.5	0.92	4.24	789
W	µg l ⁻¹	<0.02	2.5	0.05	0.06	0.50	727
Y	µg l ⁻¹	<0.01	5.68	0.01	0.13	1.13	869
Yb	µg l ⁻¹	<0.01	0.89	<0.01	0.02	0.14	789
Zn	µg l ⁻¹	0.06	23500	11.5	102	373	1341
Zr	µg l ⁻¹	<0.02	1.41	0.08	0.14	0.33	737

data will be useful for many other purposes, for example to the water industry, contaminated land remediation and academic research. It should also be noted that the approach adopted here is increasingly being followed across the EU as other countries address the needs of the Water Framework Directive.

6.2 RECOMMENDATIONS

6.2.1 Baseline quality assessment

Establishing baseline water quality for different aquifers (and different regimes within an aquifer) is important because it can help to:

- identify where contamination occurs
- set realistic standards for remediation
- identify/delineate groundwater bodies.

Natural water quality for most aquifers in England and Wales is good and the baseline concentrations for many elements, but not all (and not all aquifers) usually meet drinking water guideline values. However, there is a considerable range in hydrochemistry within all the aquifers studied, with concentrations typically varying over several orders of magnitude. The ranges can be described statistically using the median (more robust than the mean) and an upper limit (97.7 percentile) to remove outlying data. However, the ranges in concentration are of limited use in themselves except to highlight the order-of-magnitude variations in the aquifer or groundwater body. These must be placed in the context of spatial variability to be of assistance to end-users and policy makers. Knowledge of the areal and depth variations is thus essential for the protection as well as management of water resources. *Emphasis should especially be placed on depth variations within aquifers, particularly where groundwater chemistry is vertically zoned or in hydraulic contact with other groundwater bodies of different chemical quality.*

The hydrochemical summary data presented in Chapter 5 show that geochemical distributions vary between aquifers of the same type and age, because external factors such as the presence of superficial deposits may give rise to complex spatial patterns of groundwater chemistry. Characterisation of such heterogeneity is a prerequisite for establishing an effective and efficient monitoring network. It is also commonly the case that pollution inputs are within the overall large range of baseline; *therefore, quantification of pollution must be carried out on a local scale, i.e. within a smaller system.*

Owing to subtle differences in geology, structure, mineralogy etc., care must be taken when extrapolating the results between and within aquifers. Comparisons of different parts of the Permo-Triassic aquifer, for example, show that large differences occur at the national scale related to mineralogical and hydrogeological differences along, and between, different aquifer units. This is particularly the case for trace elements where sources tend to be very heterogeneous. *Data must therefore be sought from each groundwater body, rather than extrapolated from remote or even adjacent areas.*

It is important to establish knowledge of the residence times of groundwater, because time plays a major role in determining the baseline quality, and furthermore provides information on the potential timing and impacts of pollution. This is true for both the saturated

and unsaturated zone. The timescales of groundwater movement are typically of the order of metres per year and it is therefore likely that the influence of pollution from the past few decades will continue to be present in the aquifers for a considerable period of time in the future. Even in presently pristine groundwaters, the risk from pollution still exists up-gradient or travelling through the unsaturated zone. *It is therefore important to monitor in all parts of the aquifer.*

Diffusional exchange between groundwaters in an aquifer and adjacent poorly permeable formations is likely to occur in many of the confined aquifers of England and Wales. The slow movement of groundwater in these formations also means that, if they contain pollutants, they will retain these for much longer than the aquifer itself. *Therefore, these formations should also be characterised and monitored.*

Some solutes, for which regulatory standards are in operation, may have above-limit concentrations in certain parts of an aquifer, but derived from natural sources, i.e. they represent baseline conditions. Trend reversal or remediation may be either impossible or prohibitively expensive in areas where this occurs and special regulations may be required. Many of these solutes can also be derived from pollutants (i.e. of anthropogenic origin); *a careful assessment of the baseline (natural component) needs to be undertaken to quantify the contaminant input.*

It is commonly the case that pollution inputs are within the overall large range of baseline and thus difficult to estimate. Therefore, quantification of pollution needs to be undertaken on a local scale, i.e. within a smaller system. The baseline concept should therefore be applied to specific systems, e.g. aquifer, groundwater body, local system (borehole). This allows consistent regional variations to be characterised and therefore will be of benefit in managing the water resource in terms of quality. Groundwaters provide important inputs to rivers and streams, particularly during low flows. However, the interactions between surface waters and groundwaters are an area where little is known in detail (Peach et al., 2006). Global or regional data are severely limited in their scope for answering local problems: *therefore the data used for answering specific problems must be relevant to scale of interest.*

Statistical methodologies for determining baseline should be treated with caution since they need to be assessed using data acquired by representative sampling and the methodologies used relevant for datasets which typically form non-normal data distributions. *Application of the 'toolbox' approach (Table 2.1), so that several techniques can be compared and contrasted, provides a more realistic determination of the baseline.*

The Baseline Project has provided data for more than 80 components in groundwater, including trace elements which are not commonly measured in groundwater. This has highlighted the presence of a number of uncommon trace elements and has established baseline for these. *This approach should be applied to other aquifers or groundwater bodies to establish a baseline because extrapolation is generally not possible owing to these elements' heterogeneous abundance in nature.*

6.2.2 Future requirements

The Baseline Project has highlighted a number of gaps in our knowledge of water chemistry in the aquifers of England and Wales. Although several parts of the major

aquifers have been well studied, there is still a need to characterise in more detail the three-dimensional variations in age, chemistry and water quality. Such characterisation of groundwater bodies is required by the Water Framework Directive, but there is a lack of good data in most British aquifers, especially for trace elements.

There is a continued requirement for historical data: although a time-consuming task both in terms of data collection and validation, these provide the best evidence for the baseline conditions in aquifers. There is a need to convince relevant holders that such data would benefit the community at large, including themselves.

Further work is required to establish the timescales over which pollution fronts (e.g. NO_3 and acidification in the unsaturated zone) move through an aquifer. The slow

movement of water in natural systems means that such pollutants may still be en route to the water table and may make reversal of trends within short timescales impossible in practical terms.

In a similar manner, research should be directed towards understanding the position and stability of reaction fronts (e.g. shallow decalcified parts of aquifers with low buffering capacity, redox boundaries, ion-exchange fronts) and their role in controlling water chemistry and retarding pollutants.

Groundwaters provide important inputs to rivers and streams, particularly during low flows, while fluxes and transformations of nutrients such as N and P are of critical importance to surface water biotas. So far, this is an area where little is known in detail and should therefore be the subject of future research.

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Appendix 1: Baseline Report Series

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