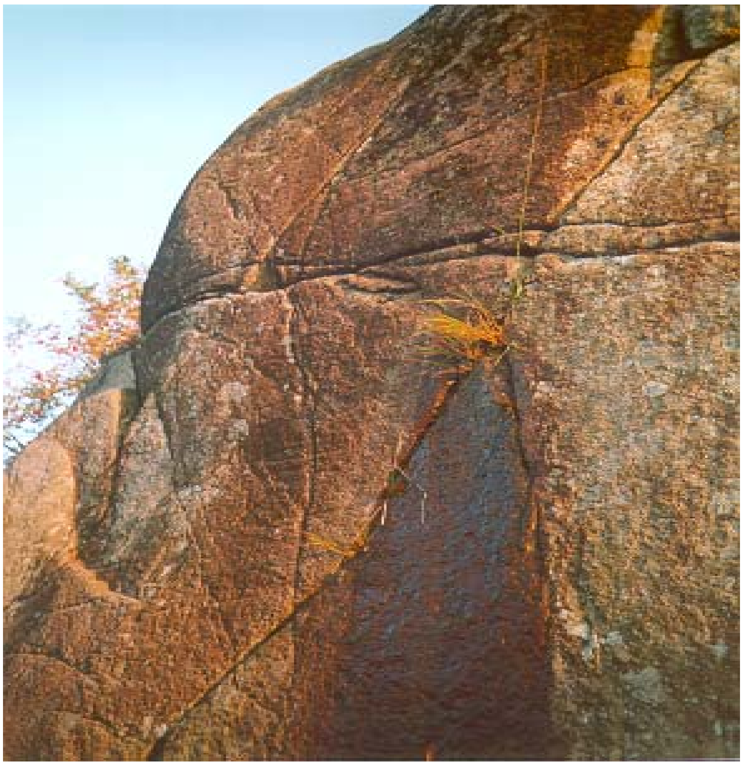
British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

BASELINE GROUNDWATER QUALITY

A Comparison of Selected British and Norwegian Aquifers

Groundwater Systems and Water Quality Programme

Internal Report IR/01/177



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/01/177

BASELINE GROUNDWATER QUALITY

A Comparison of Selected British and Norwegian Aquifers

P Shand and B Frengstad*

*Norwegian University of Science and Technology/Geological Survey of Norway

Key words: groundwater, baseline, aquifer, UK, Norway, hydrochemistry.

Front cover

Anorthosite outcrop at Egersund, Norway.

Bibliographical reference

SHAND P & FRENGSTAD B. 2001. BASELINE GROUNDWATER QUALITY: A Comparison of Selected British and Norwegian Aquifers. *British Geological Survey Internal Report*, IR/01/177

Keyworth, Nottingham British Geological Survey 2001

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham and Edinburgh; see contact details below or shop online at www.thebgs.co.uk

The London Information Office maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG
☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.thebgs.co.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA
☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE
☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgslondon@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU
☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS
☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB
☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU
☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Contents

FIGURES

TABLES

Preface

Both Norway and the United Kingdom are blessed with abundant rainfall. Nevertheless, the water resources have to be carefully managed and monitored to sustain an adequate quality of good quality drinking water. Human activity may have a detrimental impact on groundwater quality, but also "Mother Earth" (i.e. the geology) provides chemical constituents to the water which may be of concern. We have compared chemical data on groundwater from England, Wales, Scotland and Norway, and though the countries have much in common, the local geology imposes characteristic fingerprints on the natural groundwater composition. Thus, the natural baseline in this context has to be a range rather than a single value. Collaboration is an excellent way to exchange knowledge and this project has definitely broadened our view of the range of constituents in natural unpolluted water.

We would like to thank:

- The British Council and The Research Council of Norway for providing travel and subsistence costs for 3 exchange visits between United Kingdom and Norway.
- The British Geological Survey for providing staff time for Paul Shand and working facilities for Bjørn Frengstad in UK. The datasets on British groundwater quality were provided by Pauline Smedley (Carnmenellis granite), Mike Edmunds (the Chalk of Southern England) and Paul Shand (Lower Palaeozoic mudstones and shales of Wales and Devonian sandstone aquifer of Central Scotland).
- The Faculty of Applied Earth Sciences, Norwegian University of Science and Technology where Bjørn Frengstad has a dr.ing. scholarship.
- The Geological Survey of Norway for providing working facilities for Paul Shand in Norway. The chemical data on Norwegian hard rock groundwaters are mainly derived from the SPAGBIFF project (Systematisk prøvetaking av grunnvannsbrønner i fast fjell [Systematic sampling of groundwater wells in hard rock] initiated and led by Terje Strand at the Norwegian Radiation Protection Authority (NRPA) and David Banks at NGU (currently at Holymoor Concultancy). Aase Kjersti Skrede, Jan Reidar Krog and Bjørn Frengstad were co-workers on the project

We would also like to thank:

- Clemens Reimann (NGU) for qualified input and discussions on the natural distribution of elements and the limitations of the baseline concept.
- Janice Trafford (BGS) for a very pleasant dinner party.
- Vicky Edmunds and Darren Gooddy (BGS) for another very pleasant dinner party.
- Atle Dagestad (NGU) for taking a calculated risk by lending Paul cross country and down-hill skis.
- Jan Cramer (NGU) for great hospitality and for preparing excellent (but definitely not Norwegian) food.
- Hanne Charlotte and Carole for letting us go overseas.

A special thanks to David Banks for the pioneering work he has done on groundwater quality in hard rock aquifers in Norway and to Mike Edmunds for similar work on English aquifers and for establishing a framework within which this study could take place.

Executive summary

The aim of this work is to present a discussion on the concept of baseline and to compare the natural variations in inorganic water quality present in a selection of British and Norwegian groundwaters. The use of boxplots and cumulative frequency plots facilitates comparison between individual rock aquifers, different regions with divergent geological and climatic records, and between various elements and parameters. The range of baseline concentrations is often large; e.g. uranium concentrations in Precambrian granitic groundwaters in Norway spans almost 4 orders of magnitude.

Baseline values are useful as a means to assess pollution or to set a realistic base for remediation. Drinking water limits exist for a wide range of parameters based on toxicological or other criteria, but natural unpolluted groundwater may contain elements in concentrations higher than such limits and, therefore, deemed to be harmful.

Most of the groundwaters in hard rock in Norway have relatively high pH compared with those of the UK. Na-HCO_3 type waters seem to be much more common in Norway than in the UK where Ca-HCO_3 type water dominate. High F, U and Rn concentrations are found in many groundwaters in granitic and sedimentary aquifers in Norway, while Ba concentrations tend to be higher in the UK sedimentary aquifers.

Universal baseline values do not exist for any element and statistical representative sampling from all aquifers is necessary to establish reliable knowledge about the natural groundwater quality in each area. A suggested series of methodologies is suggested which can be applied to aquifers where the effects of anthropogenic pollution are present. There is a strong need for time-series data on a wide range of parameters to ascertain the long-term effects of human activity on groundwater quality. The trends of groundwater quality with depth should also be studied more thoroughly.

In order for a European wide policy to be implemented it is necessary to establish protocols for criteria related to data quality, sampling and analytical work.

1 Introduction

The pollution of groundwaters from agricultural, industrial and urban sources is a real threat to many aquifers worldwide, particularly where fracture systems allow rapid transport of pollutants to the groundwater system. In order to understand pollution trends and impacts on an aquifer, it is essential to have knowledge of the natural baseline quality so that imposed environmental change can be measured with an acceptable degree of confidence. EC standards for drinking water quality impose rigorous controls on water quality management issues but the limits may be breached due to entirely natural processes as well as pollution (Edmunds et al. 1997; Banks et al. 1998a). Under certain geochemical conditions several potentially harmful elements (e.g. Al, Be, Cr, F, Ni, Rn, Se, Tl) may be mobile and understanding how and where these occur is necessary for effective aquifer management. There are no firmly established criteria for defining baseline quality in natural waters but the problem is beginning to receive some attention from hydrochemists wishing to establish the variability in natural water quality. This is necessary for the better management of groundwater, its protection from pollution, conservation and cost effective use.

Knowledge of the baseline quality of groundwaters and criteria for defining baseline are needed both as a reference to establish if anthropogenic pollution is taking place and to provide data on the degree to which remediation of polluted environments is realistic. In the latter case, any attempt at remediation measures to attain values less than the local background may be both impossible and uneconomic. It is, therefore, a prerequisite for policy decisions regarding legislation with regard to pollution prevention and remediation. In addition, it also provides guidance in all aspects of policy relating the natural environment. The importance of surface-groundwater interactions, particularly the flux of elements from groundwater to surface waters (Shand et al., 1999), is critical to effective catchment management. Regional baseline variations are necessary to quantify such inputs.

The vulnerability of aquifers to natural or anthropogenic pollution is strongly dependent on many factors including bedrock geology, soil type and thickness, residence time of the groundwater, and the presence of drift deposits. This gives rise to a range in the natural baseline (or background) quality in aquifers with similar properties. Therefore, it is necessary to establish criteria for defining precisely the baseline concept: a simple average concentration is of little use in establishing a meaningful tool for use by policy makers and end users. Nevertheless it is possible to define baseline using simple mathematical tools or the use of simple statistical methods.

The only waters which are likely to have escaped the effects of anthropogenic pollution are those which have been isolated from the atmosphere for some time and these generally occur as palaoewaters or those which are present under confined conditions. Such resources are limited and abstraction may be considered as groundwater "mining" and thus unsustainable. However, younger waters may be present for which many individual components are naturally-derived and represent baseline concentrations. Conversely, many waters contain concentrations of elements which, although naturally derived, exceed drinking water standards. Such "natural" contamination of groundwater should not be confused with anthropogenic pollution, and should also be considered as representing baseline. However, if such data simply represent outliers, their inclusion can be misleading and of less relevance in the practical application to policy decisions related to groundwater issues. The fact that such outliers may significantly affect the output of statistical techniques has led several authors to suggest the use of cut-off points and to determine baseline concentrations which exclude such extreme values.

The fact that global environmental baseline datasets are necessary, and that large gaps still exist, was stipulated by the UN Committee on Natural Resources who provided as their main reason for advocating a global monitoring program: “there is still a huge gap in current environmental monitoring programs in that current programs do not deal with the natural chemical variability of the land surface or with changes brought about by both natural and orthogenic processes” (quoted in Darnley 1997). This study is an attempt to make a small contribution to this large-scale problem.

2 AIMS OF REPORT

This report aims to describe and compare the baseline concentrations of selected aquifers in the UK and Norway based on reliable groundwater quality data. These countries generally possess contrasting aquifer types: Aquifers in the UK are mainly of sedimentary origin with storage dominantly in the rock matrix whilst those in Norway are composed of crystalline rocks where storage is present in fracture systems. However, comparisons will also be made in rocks of similar type in both countries. The techniques used to describe and define baseline are covered in Chapter 3 and the major processes which determine water quality are described in Chapter 4. The rock units and their groundwaters are described in Chapters 5 and 6 for the UK and Norway, respectively, and a comparison of selected elements discussed in Chapter 7. Finally the main conclusions are presented in Chapter 8.

The aquifers chosen for study are:

UK:

1. Chalk (Southern England)
2. Lower Palaeozoic mudstones (Wales)
3. Devonian Sandstone (Scotland)
4. Permian granite (South-western England)

Norway:

1. Precambrian anorthosite (South-western Norway)
2. Precambrian granite (South-eastern Norway)
3. Lower Palaeozoic metasediments (South Norway)

A further aim of this report is to draw attention to areas where further research and to assess potential problems in comparing data from different countries. These may include different approaches to sampling and analysis as well as the integration of datasets with emphasis on different elements and/or with different limits of detection.

3 THE BASELINE CONCEPT

3.1 INTRODUCTION

Baseline concentrations of a substance may be defined in several different ways and a clear definition is required. The definition used here for groundwater baseline is “the range in concentration of an element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources”. Terms such as background or threshold can have a similar meaning. They have often been used to identify “anomalous” concentrations relative to typical values e.g. in mineral exploration, but these terms are not generally used to infer no anthropogenic influence. Baseline is considered to be a more appropriate term to define the natural concentration as it implies the lowest or “base” value of a system. Background can then be used in a less generic sense to specify any defined system, not necessarily the base value. For practical purposes baseline needs to relate to a particular system e.g. “baseline groundwater chemistry” or at a lower generic level “baseline chemistry of a specific aquifer ***type*** or ***area***”. In this study, we will categorise and define groundwater chemistry for different aquifer types. The emerging definition of groundwater bodies in the EU Water Framework Directive could be used as a demarcation of areas but such definitions are yet to be established.

Runnels et al. (1998) listed five approaches to determining background water chemistry relative to pollution from a mining and smelter site which are of use in baseline studies:

1) up-gradient and cross-gradient sampling
2) extrapolation using historical water quality data
3) extrapolation from similar geochemical environments
4) geochemical modelling
5) statistical methods

All of these methods have application in the interpretation and determination of baseline geochemistry and can be used together to deduce the baseline chemistry of groundwaters. It is unlikely that there will be sufficient data available for all of these approaches to be successful, and it is, therefore, highly recommended that these be used together to determine the natural baseline.

An ideal starting point of this study is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era. It is therefore necessary to have knowledge of the age and residence times of groundwater. Measurement of the absolute age of groundwater presents many difficulties and the most widely used technique is the use of radiocarbon (Clark and Fritz 1997). Isotopic measurements of elements such as noble gases or chlorine (^{36}Cl) have also been used and the presence of tritium (^{3}H) or organic substances may be used to indicate if recent waters are present. However, there is little information available on the age of groundwater in most aquifers due to the relative expense and difficulty of the various techniques. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods.

The sampling of representative groundwater provides significantly fewer problems than other media e.g. soils and sediments where concentrations may vary according to grain size, size of sample or extraction method. However, there are several problems inherent in the sampling of groundwater from a borehole. In most cases, chemical and age stratification occurs in groundwater and a simple pumped sample represents a mixture of water derived from different depths and/or fracture systems with different age and quality. 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 and fissures may be considerably different chemically 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 need to be taken into account. Particular care needs to be exercised where polluted waters are being introduced into a borehole and mixed with non-polluted water.

In order for baseline to be used effectively, the data should be collected and analysed according to well-defined protocols and not limited to certain chemical environments. The concentration of existing boreholes in outcrop areas and close to rivers in some aquifers (e.g. due to lower water tables and generally higher transmissivity) means that a spatial bias is often unavoidable. In addition, it is desirable that these protocols are globally compatible so that the application goes beyond political boundaries (Darnley, 1997).

3.2 DETERMINATION OF BASELINE QUALITY

One aspect of baseline geochemistry that has proved difficult to get across to policy makers and stakeholders in the environmental field is the variation that exists in nature; therefore, it is necessary to provide ranges in baseline values and not simply a single concentration. This range can be described in many ways e.g. by giving a mean and standard deviation; the total range in values; or by describing a maximum baseline concentration. The value of traditional statistical parameters such as median or mode are of use when comparing the baseline chemistry of different aquifers. Edmunds et al. (1997) preferred the use of the median value instead of the mean for comparing different datasets because it is much less affected by outlying values.

Many authors have used a limit to define an upper baseline e.g. Edmunds et al., (1997) and Langmuir (1997) chose values of the 95th percentile and 97.7 % (mean + 3-sigma), respectively. This is similar to the way of defining anomalous concentrations in mineral exploration e.g. Hawkes & Webb (1962) recommended mean + 2 sigma as a threshold to define anomalous concentrations. However, there is no a priori reason why anomalous or non-baseline data should fit such an arbitrary choice and the problems of representative sampling are paramount. Most of the outcrop areas of UK aquifers, for example, show the effects of enhanced concentrations of nitrate from agricultural practices. A simple cut-off value or threshold concentration would be meaningless as values below the threshold would not represent baseline. In addition, such techniques do not take into account the fact that anomalous and background concentrations often show significant overlap (Sinclair 1974) or have natural multimodal distributions.

Traditionally, the use of statistical techniques has assumed that geochemical distributions are either normal, or more generally, lognormal (Ahrens 1954). Such an assumption was heavily criticised because the datasets studied did not generally display normal or lognormal distributions (Miller & Goldberg, 1955); therefore statistical techniques which assume such distributions are invalid for their treatment. In most natural systems geochemical distributions are generally polymodal and are usually skewed (Reimann & Filzmoser, 2000). Many of the criticisms of normality are perhaps due to the choice of datasets for testing normality e.g. if a large dataset of unrelated groups e.g. different types of granites with different histories and end-member compositions or a suite of waters from different aquifers is used, then it is perhaps not surprising that the total group is not lognormally distributed. The group may be a mixture of a large number of individual lognormal sets with different numbers of samples from each group. It is not yet clear if the common processes determining the evolution of chemicals in nature would give rise to log-normality but this needs to be tested with well constrained datasets and models. Nevertheless, this does mean that large geochemical datasets, e.g. regional surveys, cannot be manipulated without the use of techniques compatible with non log-normality. As stated by Miller & Goldberg (1955): “We thus doubt the value of a statistical examination of empirical data in the absence of a meaningful hypothesis, and with no attempt to define the universe or universes which are being sampled”.

Probability plots have been extensively used in the mining industry and have particular use in highlighting different populations of data. If the concentration scale is logarithmic, a single lognormal distribution will plot as a straight line. A bimodal distribution comprising two lognormal distributions plots as a curve (Sinclair 1974). Such plots can be used to define “thresholds” defined by points of maximum curvature (Woodsworth 1972; Sinclair 1974). In this context they could be of use in baseline studies to discriminate natural baseline chemistry from that due to pollution. In addition, they display very effectively the range and distribution of data and allow clear comparisons of water quality from different aquifers. However, it needs to be assessed to what degree natural variations produce multi-modal populations. There are several types of geochemical reaction which will alter distributions by removing or limiting concentrations in solution. These include redox processes e.g. in reducing environments nitrate may be completely removed from solution even from polluted waters (as is the case for iron in oxidising waters); adsorption onto solid mineral phases may remove many trace metals or contaminants; and saturation with respect to mineral phases will limit the solubility of one of more elements e.g. Ca and F through precipitation of fluorite.

Runnels et al. (1998) used such diagrams to identify background and anthropogenic populations of elements in surface and groundwater samples adjacent to a mining and smelting area in Utah, USA. The different populations of data (natural and anthropogenic) were identified on probability plots by inflections in the data lines produced. The question still remains how to define baseline for all element distributions using such probability plots as a global protocol: if a separate population exists at high concentrations, can this be used to simply define an upper level of baseline; or in the case of a lognormal population, is it justified to choose an upper level based on a selected arbitrary percentile basis. A combination of this technique along with study of historical data and data from similar environments probably offers the most useful approach.

Other techniques which have been used to illustrate hydrogeochemical datasets include boxplots which display the median and/or the mean, specified percentiles and outliers; histograms (but these can show different distributions depending on buckets used for concentration); Piper diagrams, X-Y plots and maps of data showing the areal variation in concentration. In this report boxplots and probability plots will be used since these show unbiased statistical data (although it must be remembered that analytical and sampling errors still exist).

As mentioned previously, it may be necessary for practical purposes to remove outliers, but it appears that this is to some degree subjective and arbitrary. The range of “natural pollution” may be greater than that shown by anthropogenic inputs in some cases. Nevertheless, it is essential to define the baseline as a practical means of determining whether anthropogenic pollution is occurring or has occurred and whether remedial action can or will be taken – this is the real justification and benefit of defining baseline to the end-user, the public and policy makers.

In order to define “baseline”, datasets should ideally be chosen which are free of any anthropogenic input. This may not always be possible as most waters are likely to have been affected to some degree by pollution. Even in modern polluted waters, some solutes will represent baseline concentrations, but as far as possible it is necessary to avoid obviously polluted waters; where this is impossible, decisions and interpretations have to be made regarding the upper limit of baseline using the techniques and philosophy discussed above.

The discussion above has stressed many of the problems with regard to baseline, a concept which initially appears to be very simple. For the purposes of this report we have chosen samples which may not necessarily be pristine. Where this is the case, it is discussed in the text. Cumulative probability plots will then be used to attempt to classify determinands into uncontaminated and contaminated. These data need to be assessed with regard to statutory limits set by the different countries; these are shown for the EU and Norway in Appendix 1. Tables will be presented showing the median, minimum and maximum concentrations and an upper baseline at the 95th percentile. This upper limit is chosen arbitrarily and much further discussion needs to be undertaken at a global level and with scientists, policy makers and end-users to establish a universal protocol. This is urgently needed in Europe where the EU is currently establishing criteria for the new Water Framework Directive.

3.3 PROBLEMS WITH DATA

A range of inherent problems emerges when different datasets are to be integrated or compared. The purpose of the groundwater sampling varies and may affect the choice of sampling technique and field procedure (e.g. filtration and acidification in the field) as well as the selection of measured and analysed parameters. Available analytical equipment for the determination of chemical elements in groundwater varies from one institution to another and different methods may be employed for the determination of the same elements (e.g. ICP-AES, AAS, or ICP-MS for cations). Even two instruments of the same manufacture may yield results systematically distinct from each other, as may two batches analysed at different times on the same instrument. Therefore, care must be taken in order not to over-interpret the data. However, QA controls should keep such problems to a minimum.

There is also a continuous 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 implicates inherent uncertainties. In addition, values below detection limit may be handled in different ways, which may also confuse the graphical presentation. In the present report values less than the detection limits are presented as half the value of detection limit.

One should be also very careful not to compare elements with different speciation (e.g. sulphate, SO_4 or sulphide, S) or different notation (e.g. NO_3^- given as N or as NO_3^-). As the variation of single element concentrations in natural groundwaters may span up to 7 orders of magnitude (Frengstad et al., 2000), care should also be taken not to confuse the denominators or reported units.

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.

4 PROCESSES CONTROLLING BASELINE QUALITY

Natural baseline chemistry is initially determined by atmospheric inputs, although at the present day these will be affected to some degree by atmospheric pollution unlike the pre-industrial era. The predominant groundwater chemistry develops quite rapidly during infiltration, being strongly influenced by reactions in the top few metres of the soil and in the unsaturated zone. During deeper circulation the water chemistry evolves more slowly by a series of geochemical reactions including mineral dissolution and precipitation, redox reactions, cation exchange and mixing as shown in Table 4.1. Therefore, the resulting groundwater chemistry is strongly controlled by geochemistry and mineralogy such that the baseline conditions will vary characteristically from one aquifer to another. In fact the ‘baseline chemistry’ may dominate even polluted groundwaters. It is necessary to understand these controls on groundwater chemistry as well as the capacity of aquifer materials to attenuate and reduce pollutant transport.

(BIO)GEOCHEMICAL CONTROLS

Soil Processes The biogeochemical reactions in the soil have a marked influence on groundwater chemistry. Acid-base reactions, nitrogen transformations and microbiological activity producing CO_2 are the most important.

Aquifer Lithology and mineralogy Fundamental control by the host rock geochemistry e.g. carbonate versus non-carbonate rock and the degree of heterogeneity. The mineral assemblage of the host rock and secondary minerals along fractures, the relative abundance of minerals, solubilities, crystallinity and purity are primary controls.

Physico-chemical Controls Mineral solubility is dependent on temperature. The pH and Eh are also fundamental controls on mineral solubility. Ion-exchange processes may be important. Reaction rates (kinetics) must also be considered.

Residence Time At outcrop and near-surface in most aquifers, water-rock interaction rapidly leads to characteristic groundwater chemistry and saturation with common minerals such as calcite. At depth, slower reactions (e.g. by incongruent solution) become important. Mixing with deeper groundwater may also increase salinity.

SPATIAL VARIABILITY

Between Aquifer Baseline conditions vary markedly from aquifer to aquifer due to stratigraphic, lithological and mineralogical variations.

Within Aquifer In sedimentary aquifers, facies changes along strike or downgradient within the same stratigraphical unit, either of a geochemical or physical nature must be considered. In fractured hardrock aquifers, joint sets of different age and direction may host different mineral suites. Most importantly, the baseline chemistry will vary along the hydraulic gradient in line with various hydrogeochemical processes (e.g. redox conditions).

RESIDENCE TIME

It is useful to be able to distinguish water of different ‘ages’ using a variety of geochemical indicators:

1. Palaeowater: recharge originating during/before the last glacial era (> 10000 years)
2. Pre-Industrial Water
3. Pre-War (1940s)
4. Modern Era

Table 4.1. Dominant biogeochemical processes controlling baseline chemistry in an aquifer (modified from Edmunds et al. 1987).

Some of the geochemical concepts and terminology used in the report are included here as a reference.

4.1 REDOX BOUNDARY

Water during recharge will generally be saturated with dissolved oxygen at the partial pressure of the atmosphere (10–12 mg l^{-1} depending upon barometric and temperature conditions). Passing through the soil and the unsaturated zone, some of this O_2 will react as a result of microbiological processes and oxidation-reduction reactions. In the Chalk for example, almost all water reaching the water table contains several mg l^{-1} dissolved O_2. Geochemical reactions (oxidation of traces of pyrite and release of ferrous iron (Fe^{2+}) impurities from the Chalk) progressively remove the O_2 within several km along flow lines from the point of recharge. This results in a relatively abrupt change of water chemistry (redox boundary) and downgradient of this zone other transformations may occur, e.g. rapid denitrification and the probability that total dissolved iron (Fe^{2+}) and manganese concentrations will increase. The rate of consumption of oxidising species in the groundwater will depend on the availability of reducing agents in the aquifer. Organic carbon is the most important reducing agent present in groundwater and aquifer matrices but other species capable of driving the redox reactions include ferrous iron and sulphide. Sulphate reduction and the production of sulphide (H_2S) or even methane may also occur under extremely reducing conditions.

4.2 CARBONATE REACTIONS

The concentrations of H^+ (pH), CO_2, Ca and Mg are closely related by the following reaction which represents the attack of rainwater on (impure) carbonate, assisted by CO_2 which builds up in the soil by microbiological activity; the partial pressure in the atmosphere is quite low but may well increase by 1–2 orders of magnitude on passing through the soil:

$Ca(Mg)CO_3 + H_2O + CO_2 = Ca^{2+} + (Mg^{2+}) + 2HCO_3$

The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone of the Chalk or carbonate-bearing aquifers. This process (**congruent dissolution**) yields Ca and Mg concentrations which are identical to those in the dissolving carbonate aquifer. However with passage of time, in waters which are in dynamic equilibrium with the carbonate aquifer (in particular the Chalk), a second process (**incongruent dissolution**) may occur where the impurities (e.g. Mg as well as Fe^{2+}, Sr^{2+}) are slowly released, thereby raising the Mg/Ca and other trace element (e.g. Sr/Ca) ratios. Since carbonates are easily dissolved, even small amounts present in the aquifer will exert a major control on water chemistry, regardless of the aquifer lithology.

4.3 CONGRUENT/INCONGRUENT REACTION

Reactions involving carbonate are described as congruent or incongruent. In a congruent reaction, the components of the dissolving mineral are present in solution in stoichiometric proportion to the original mineral i.e. they are the same as the mineral. Incongruent reaction involves precipitation of a secondary, less soluble, mineral following dissolution of an original mineral. In this case, the aqueous solution does not contain solutes in stoichiometric proportion to the source mineral.

Examples of congruent reactions are:

$CaCO_3 + H_2CO_3^- \rightarrow Ca^{2+} + 2HCO_3^-$

$CaMg(CO_3)_2 + 2H_2CO_3^- \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$.

An incongruent reaction involving dissolution of primary dolomite and precipitation of secondary calcite, thought to be important in some aquifers follows the form:

$CaMg(CO_3)_2 + H_2CO_3 \rightarrow CaCO_3 + Mg^{2+} + 2HCO_3^-$.

Most silicate minerals undergo incongruent dissolution. An example is the reaction of water with albite (a sodium feldspar typically found in granites) which produces cations and silica and leaves behind a residual clay:

$2NaA1Si_3O_8 + 2H^+ + 9H_2O = 2Na^+ + A1_2Si_2O_5(OH)_4 + 4H_4SiO_4$

4.4 ION EXCHANGE REACTIONS

Clays, oxyhydroxides and organic matter all have the capacity to sorb cations and the amount of cations sorbed per unit weight is known as the cation exchange capacity (CEC). The sorbed species on the solid phases will tend towards an equilibrium with solution concentrations. If a change occurs in the solution chemistry, ion exchange reactions will occur between solutes and sorbed species to achieve a new equilibrium e.g. the exchange of Mg ions present on an exchanger by a $CaCl_2$ solution will be expressed by:

$CaCl_2\,(aq) + MgX\,(s) = MgCl_2\,(aq) + CaX_2(s)$

where the exchanger phase is represented by X. Ion exchange is important during the freshening of aquifers where Ca in the groundwater is replaced by high Na on exchange sites. In this case a Ca-HCO_3 groundwater may evolve to a Na-HCO_3 groundwater. In contrast, during seawater intrusion into a fresh aquifer (where the sorbed cations are generally dominated by Ca) the exchange of Na in groundwater for Ca leads to a Ca-Cl type groundwater. A careful consideration of such factors may, therefore, allow the direction of movement of a saline interface to be resolved.

In a similar way exchange of anions may also occur e.g. OH^- exchange for F^- from sorption sites on apatite, sheet silicates or amphiboles.

5 UK BASELINE CHEMISTRY

5.1 INTRODUCTION

The aquifers chosen from the UK are (Fig 5.1.1):

1) The Chalk aquifer of southern England (Berkshire and the Chilterns)
2) Lower Palaeozoic mudstones and shales of Wales (Plynlimon and Teifi Valley)
3) Devonian sandstone aquifer of Central Scotland (Fife) and
4) Permian Carnmenellis granite of Cornwall, southwest England.

On-site measurements included pH, SEC, Eh, dissolved oxygen (DO) and HCO_3. Field parameters were measured where possible in an anaerobic through-flow cell and water samples were analysed for a wide range of parameters by ICP-OES, ICP-MS and automated colorimetry. A summary of the chemical data is presented in Appendix 2, which includes minimum and maximum values, median and "upper baseline" values based on the 95th percentile.

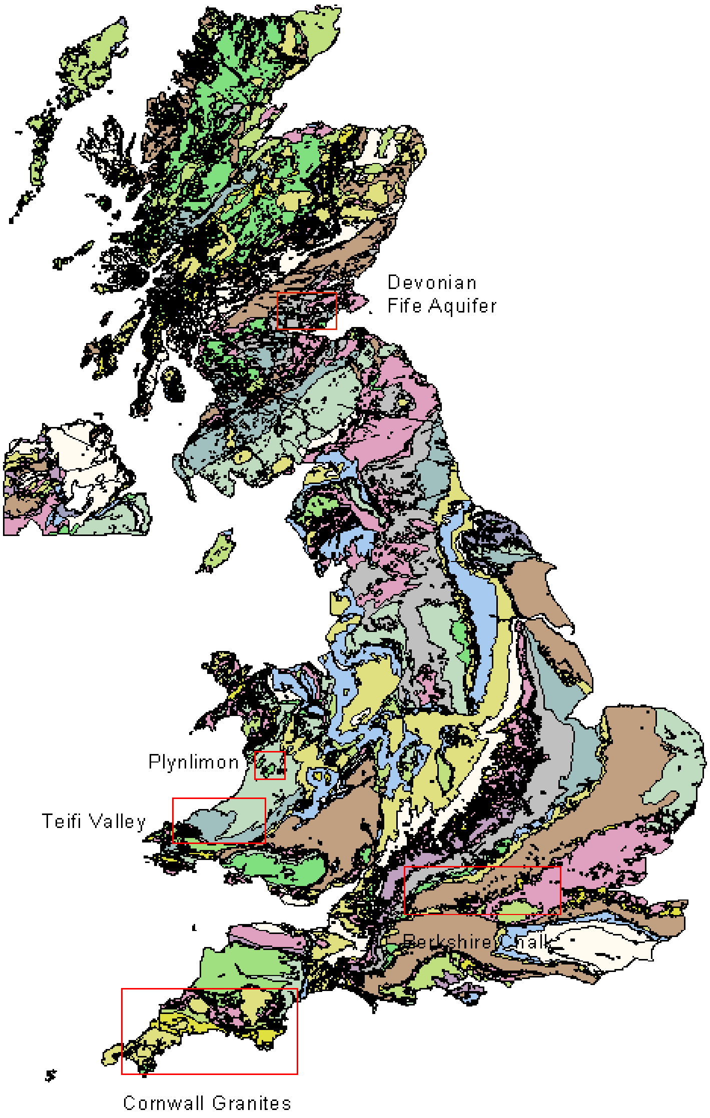


Figure 5.1.1 Map of the UK showing the localities for the selected aquifers.

5.2 CHALK AQUIFER

5.2.1 Introduction

The Chalk forms the most important aquifer in the UK accounting for 53 % of the total abstraction. It is a soft microporous limestone composed dominantly of coccolithic fragments. Porosity can be extremely high (c. 45 %) but the matrix is very fine grained and specific yields are low, of the order of 1%. However, the chalk contains an important secondary fracture network with individual boreholes known to have yields in excess of 10 Ml/day. The Chalk forms a dual porosity aquifer.

5.2.2 Study area

The area of chalk selected for study comprises the Chalk of Berkshire and the Chilterns in Southern England (Edmunds & Brewerton, 1997). Data on the unconfined chalk of the Berkshire and Chiltern Downs and the confined aquifer (which forms the western part of the London Basin) are presented. The population is locally relatively dense but much of the Downs comprise agricultural land. Industry is mainly light and generally situated on the confined part of the aquifer, therefore, its influence on groundwater quality is likely to be local. Many of the unconfined waters are expected to show the effects of anthropogenic influence, particularly agricultural, but the confined waters mainly pre-date the post-war and industrial eras.

5.2.3 Hydrogeology

The Chalk is a microporous limestone composed predominantly of coccolith fragments. It forms a dual porosity aquifer where transmissivity is largely controlled by fracture flow, but where the dominant storage is in the matrix (due to high porosity). Recharge takes place in the outcrop areas and moves down-dip below younger Tertiary sediments where the aquifer becomes confined. In the unconfined aquifer, the main fracturing is developed in the top 60 m, with fissure development being particularly well developed beneath valley bottoms. Transmissivities vary laterally between 50 – 2500 m^2 d^{-1} with the valley bottoms showing the higher values, decreasing rapidly away from these areas. The density of fractures in the confined zone is less and transmissivity values range from 270 – 450 m^2 day^{-1}. The permeability of the matrix is several orders of magnitude lower than the fractures, which may allow older (often more saline) waters to be present within blocks. However, the presence of such waters may affect water quality through slow exchange with the fracture/fissure waters.

5.2.4 Aquifer minerals

The Chalk is composed dominantly of microfossil (coccolith) fragments of low-Mg calcite, a few microns in diameter. The packing of the coccolith fragments permits a high intergranular porosity (mean of 34%). This, combined with a small grain size (several microns) gives rise to a very high specific surface area making the chalk highly reactive. Other microfossils present include foraminifera and siliceous sponges as well as macrofossil fragments such as sharks teeth and echinoderms. Flint horizons are typically present but are much more abundant in the Lower parts of the Chalk. Minor mineral phases present in the Chalk include clays, phosphate (mainly fluorapatite and collophane) and more rarely barite, dolomite and fluorite (Shand, 1999; Shand & Bloomfield, 1995).

5.2.5 Hydrochemical characteristics

Significant chemical variations exist between the unconfined and confined groundwater samples due to differences in geochemical environment (particularly redox conditions) and residence time. These will be shown on separate plots as it is clear that the hydrochemical baseline concentrations are significantly different between the two areas.

The Chalk groundwaters attain relatively high concentrations of Ca and HCO_3 as they pass through the soil and unsaturated zone due to rapid reactions with the calcite of the rock matrix. Saturation with respect to calcite is thus achieved quickly, and below this depth dissolution is greatly reduced. The unconfined groundwaters are of Ca-HCO_3 type and are typified by low Mg/Ca ratios, close to or only slightly higher than that of the Chalk matrix. The confined waters show a trend towards much higher Mg concentrations (Figure 5.2.1) as well as Sr (Figure 5.2.2) through incongruent dissolution of calcite which releases these elements. The ratio of Mg (or Sr) to Ca is therefore, indicative of the degree of reaction and therefore a potential surrogate for residence time or age of the groundwaters.

The confined groundwaters also show elevated concentrations of Na, K, SO_4 and Cl which are likely to be largely controlled by contributions of residual formation water. Nitrate is significantly higher in the unconfined aquifer and the highest values (above c 4 mg l^{-1}) are thought to be due to inputs from agricultural pollution. The cumulative frequency plot (Figure 5.2.3) shows a distinct change at 4 mg l^{-1} and this may indicate the natural baseline of the Chalk in this area: in this case c. 15% of the data show indications of pollution for NO_3.

The unconfined groundwaters are also rich in dissolved oxygen (median of 9 mg l^{-1}) indicating the scarcity of minerals such as pyrite or other reductants. The aquifer becomes reducing a short distance into the confined zone and DO is consumed rapidly. This has allowed Fe^{2+} to increase and denitrification or nitrate reduction to occur (Figures 5.2.1, 5.2.2 & 5.2.4). Cation exchange reactions have also allowed elements such as K, Li, NH_4 and Na to increase with residence time and the higher concentrations of these in the confined aquifer is clear (Figures 5.2.1 & 5.2.2).

Other minor and trace elements which show a general increase in the confined part of the aquifer include B and I (remnant formation water), Ba and F (mineral dissolution), and Zn (possibly from desorption or pyrite oxidation). Uranium is present at low concentrations in the unconfined waters but quickly disappears due to the onset of reducing conditions. Iron is present at concentrations of around 10 µg l^{-1} in the unconfined area, consistent with theoretical predictions of waters at equilibrium with ferric hydroxide. However, in the confined aquifer it increases by up to three orders of magnitude with the onset of reducing conditions. Copper is present in the unconfined groundwaters but appears to be taken out of solution in the more reducing parts of the aquifer.

5.2.6 Depth variations

Two boreholes have been studied for depth variations in the Chalk of Berkshire: Winterbourne and Faircross (Edmunds et al., 1987). The results show that the deeper waters are older, with higher SEC and concentrations of Ca, Mg, K, Na, Cl and Sr. In addition the concentrations of porewaters are often higher than those found in depth samples (derived largely from fractures) of the Winterbourne borehole.

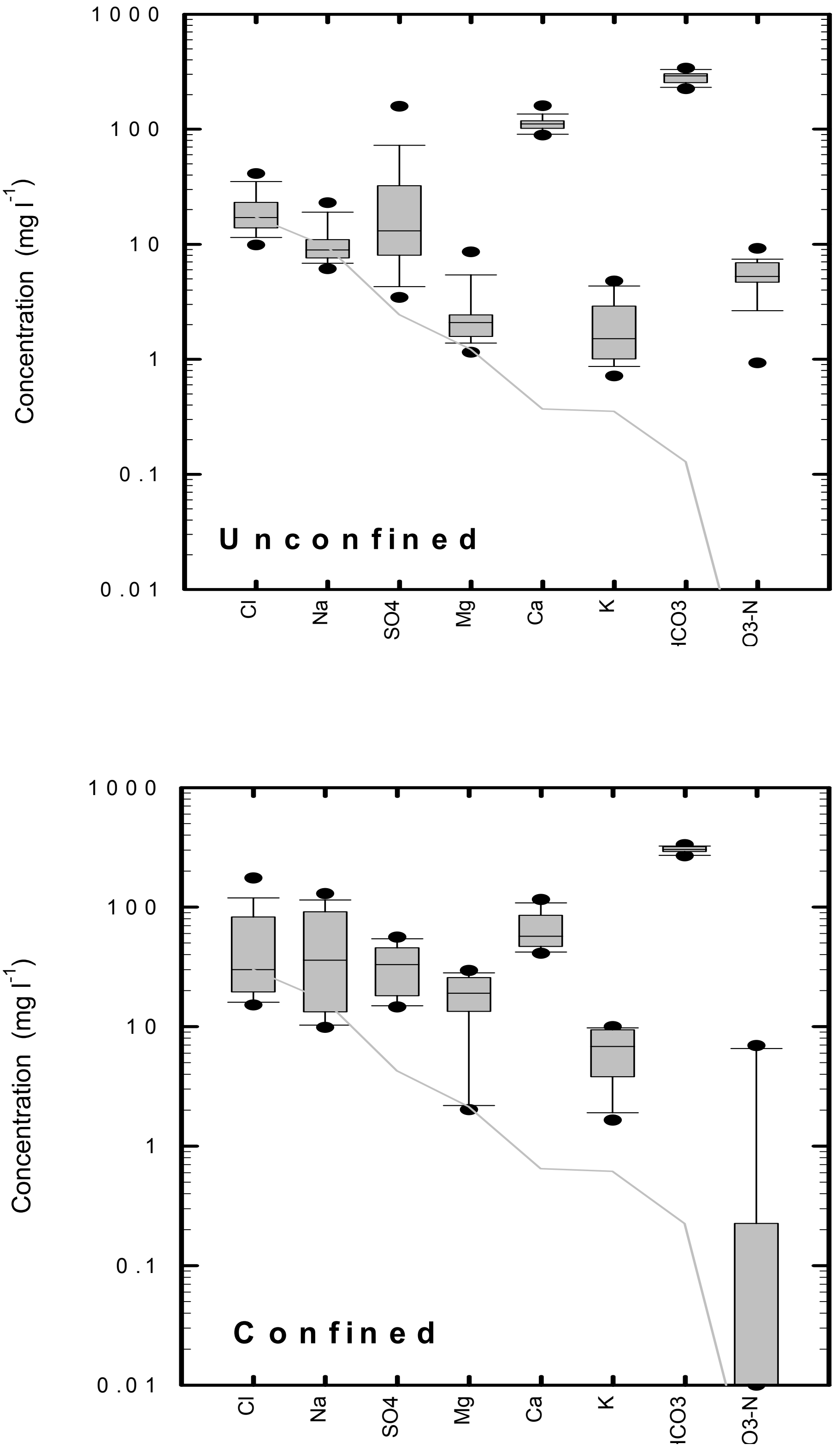
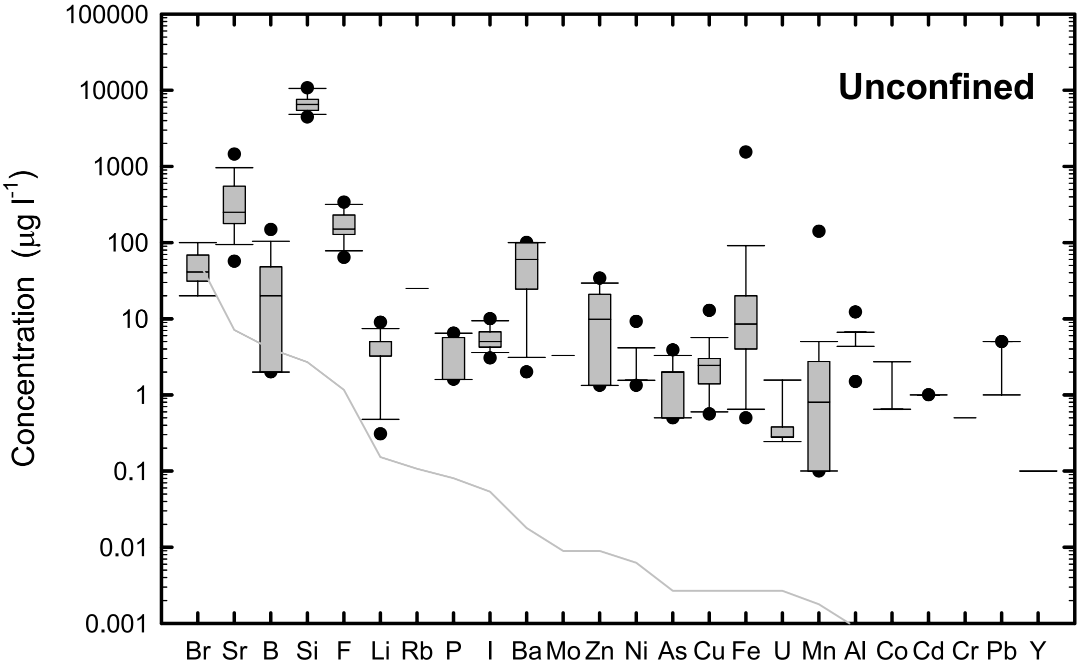


Figure 5.2.1 Boxplots showing major elements in groundwater samples from the Cretaceous Chalk aquifer of southern England. Upper diagram shows data from the unconfined part of the aquifer and the lower diagram shows data from the confined part. The drawn line denotes mean ocean water composition normalised to the median chloride value.



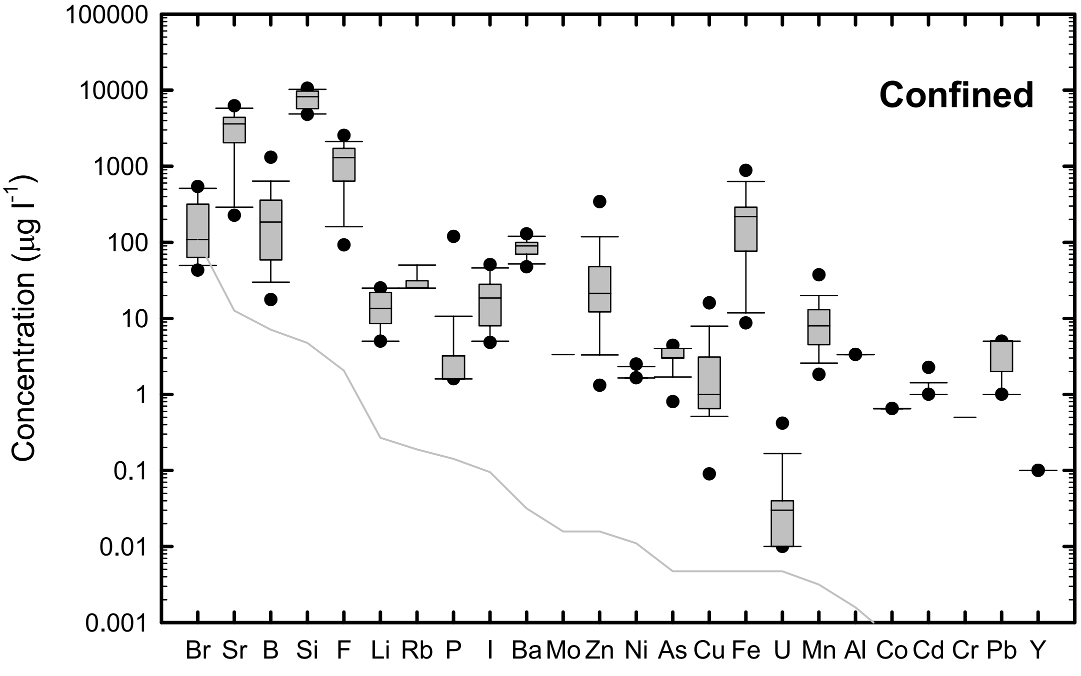
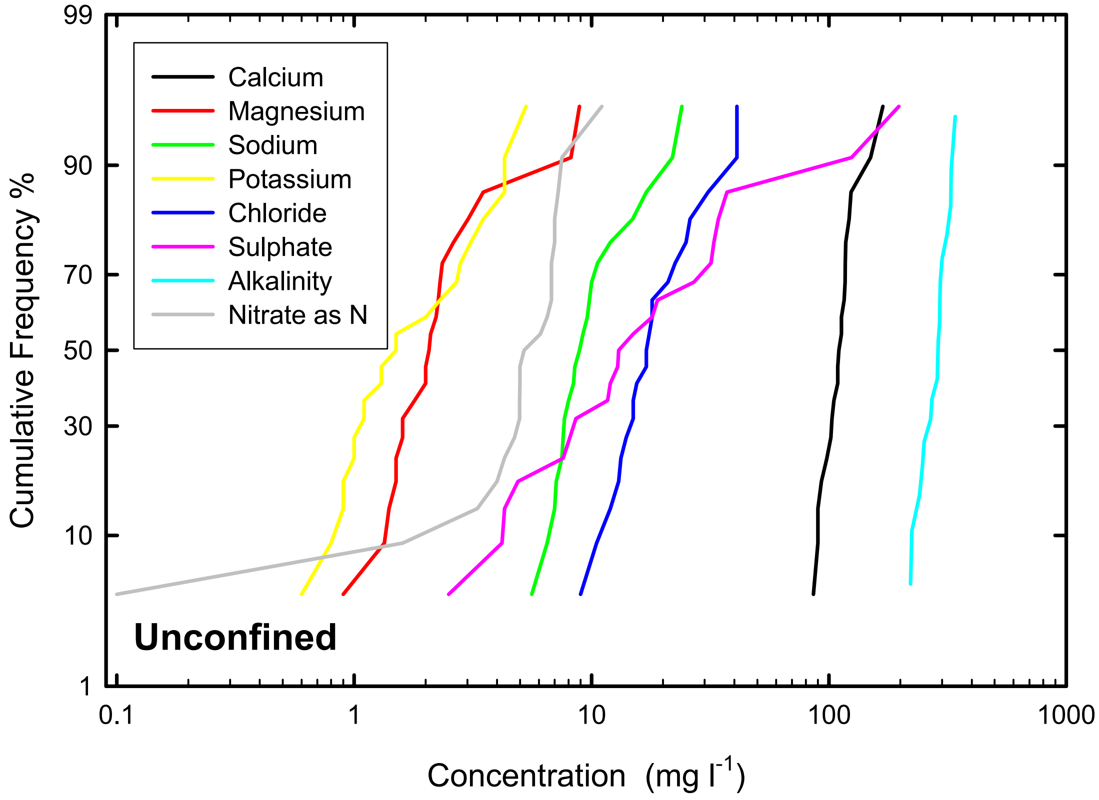


Figure 5.2.2 **Boxplots showing minor and trace elements in groundwater samples from the Cretaceous Chalk aquifer of southern England. Upper diagram shows data from the unconfined part of the aquifer and the lower diagram shows data from the confined part. The drawn line denotes mean ocean water composition normalised to the median chloride value.**



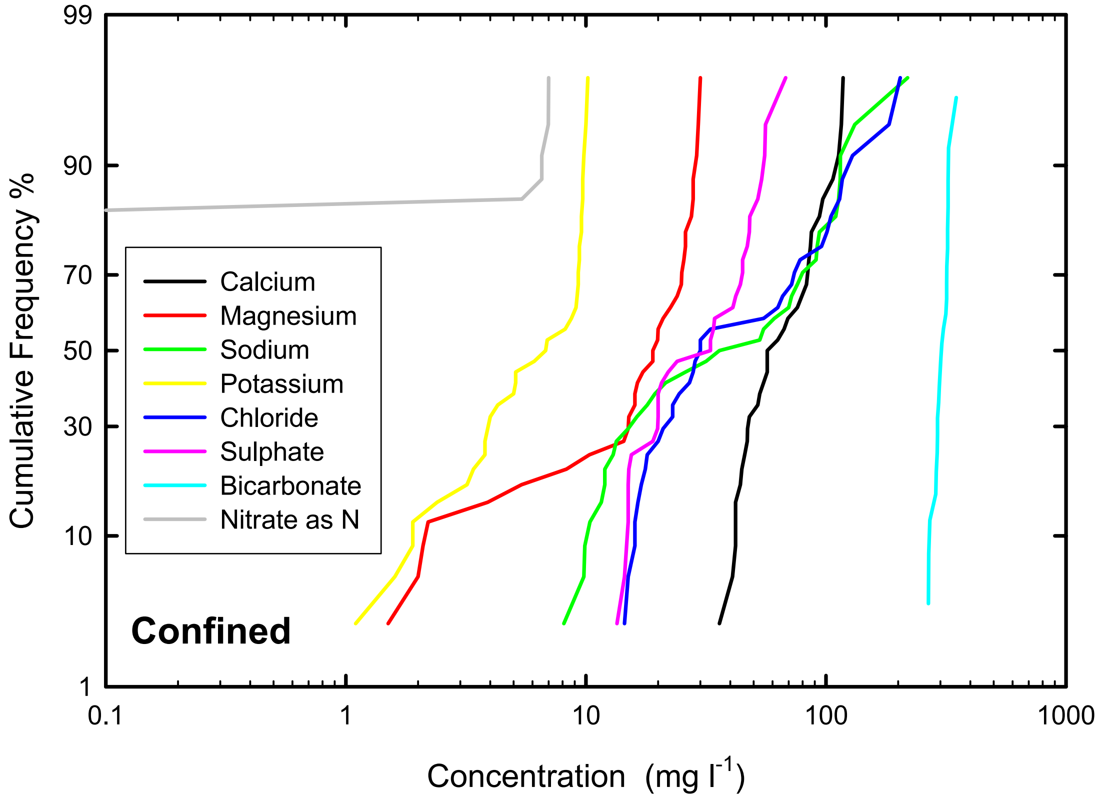
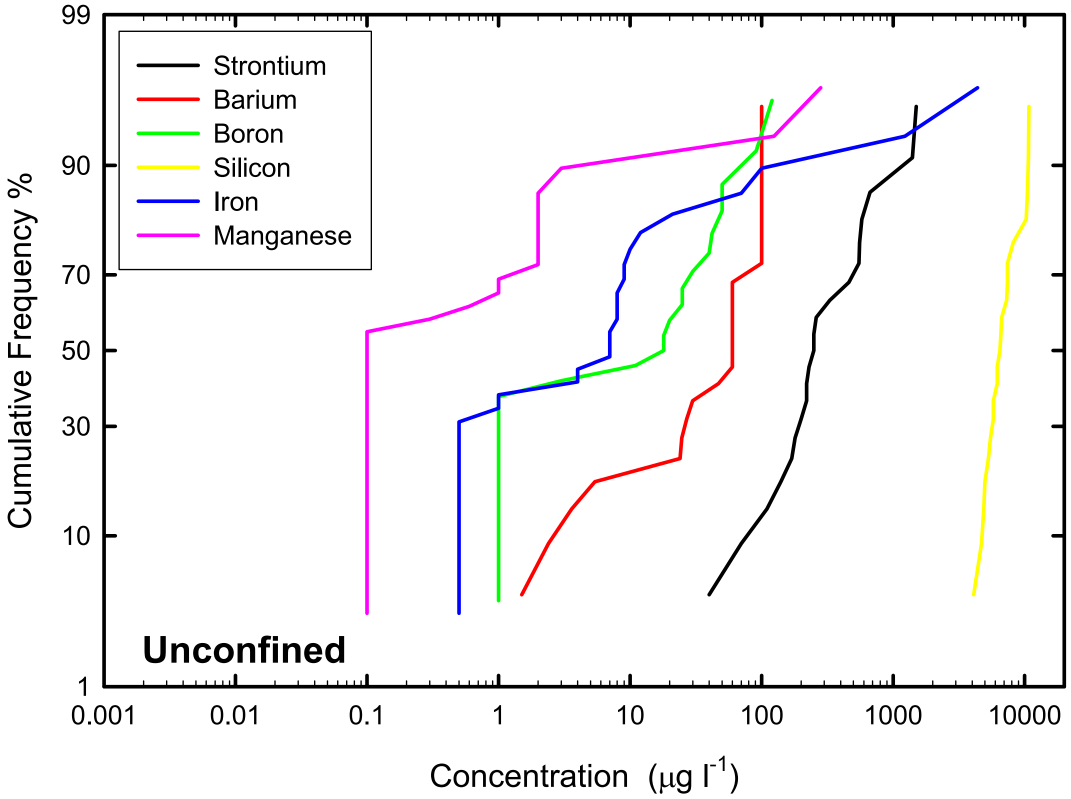


Figure 5.2.3 **Probability plot of major elements in groundwater samples from the Cretaceous Chalk aquifer of southern England. Upper diagram shows data from the unconfined part of the aquifer and the lower diagram shows data from the confined part**



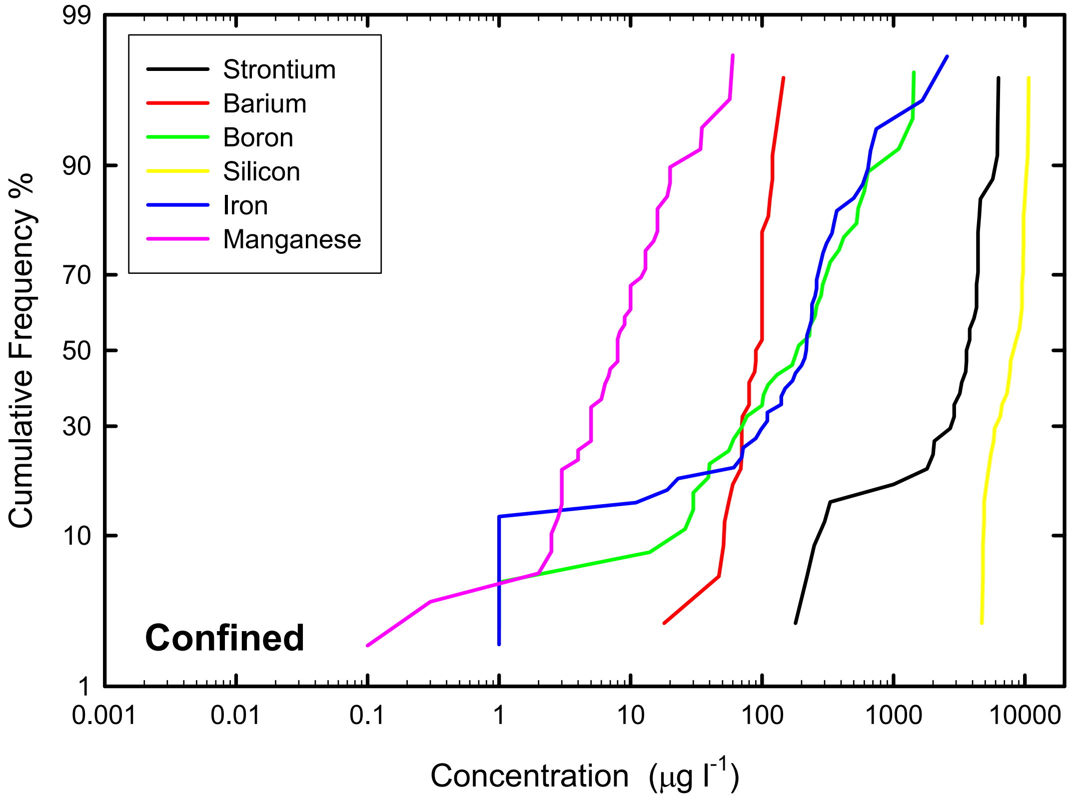


Figure 5.2.4 **Probability plot of selected minor and trace elements in groundwater samples from the Cretaceous Chalk aquifer of southern England. Upper diagram shows data from the unconfined part of the aquifer and the lower diagram shows data from the confined part**

5.2.7 Regional variations

Regional variations across the aquifer are marked and controlled dominantly by the residence time and the geochemical environment. These work together to produce consistent patterns between the recharge area of the unconfined chalk downdip and across the redox boundary. This pattern of increasing mineralisation with age and distance from the recharge zone is locally influenced by pollution inputs, particularly from agricultural pollution and to a lesser degree by local geological features.

5.2.8 Temporal variations

There were no data available at the time of writing for time series data in this area although data are likely to exist within the Environment Agency and local water companies.

5.2.9 Summary

The chalk groundwaters of Berkshire and the Chilterns show a distinct chemical evolution from young Ca-HCO_3 groundwaters towards Ca-Mg-HCO_3-Cl types. This is overprinted by redox reactions which reduce DO, NO_3 and increase Fe and Mn downdip in the confined aquifer. A difference needs to be made between the baseline chemistry of each of these distinct areas although a considerable overlap exists for many measured constituents. The influence of agricultural pollution in the unconfined aquifer is obvious with relatively high NO_3 and a likely input of Cl, K and SO_4. Most other parameters are likely to be representative of baseline concentrations. The natural baseline varies both with depth and areally and the local baseline must be established with regard to this. There are few temporal data available for most of this area but they do likely exist.

5.3 LOWER PALAEOZOIC MUDSTONES

5.3.1 Introduction

The Lower Palaeozoic mudstones, shales and slates of central and southern Wales form a large belt of weakly metamorphosed sediments of Ordovician and Silurian age. Historically, the use of groundwater has been minimal due to the assumption that the bedrock is impermeable. However, recent studies have shown that these rocks contain good quality groundwater which may be of significant benefit to rural communities (Neal et al., 1998; Robins et al., 2000). A good source of potable water is particularly relevant to these areas since surface waters may be slightly acidic and a large number of streams show the effects of previous mining (mainly Pb-Zn ores) including acid waters and high concentrations of metals including Pb, Zn, Cd and Al. In the past few years many farmers have been abstracting groundwater in the Teifi Valley of South Wales and this important source of good quality water is being recognised.

5.3.2 Study area

The two study areas (Figure 5.1.1) where good quality data exist are the Plynlimon experimental catchment of central Wales (Neal et al. 1998, Shand et al. 1999) and the Teifi catchment of southern Wales (Robins et al. 2000). Both areas have relatively high rainfall (2500 and 1400 mm yr^{-1} respectively) but have contrasting physiography: the Plynlimon groundwaters are from an upland area of coniferous forest and the Teifi groundwaters are sampled from a rural lower river valley area dominated by upland farming with small towns and villages. The Plynlimon catchment is covered with thin (0.5 - 1.0m), acidic soils (mainly podsol) in the free draining areas and peat on the flat upper parts of the catchment and wider interfluves. The valley bottoms where drainage has been impeded contain a complex of peat and gleyed mineral soils. In the Teifi Valley, drift deposits are common over much of the area including gravels, sands and lacustrine clays. The western part of the catchment is covered by drift derived from the Irish Sea which locally contains shelly fragments in contrast to the eastern area which only contains local drift derived from Ordovician/Silurian material with little carbonate material present.

5.3.3 Hydrogeology

The Ordovician/Silurian sediments have low primary porosity on account of their fine grain size. The rocks do, however, contain extensive secondary porosity due to the effects of cleavage and fracture development. This is more so at shallow depth due to periglacial activity at the end of the last ice-age and subsequent shallow weathering. There are few data available on borehole yields but values of up to 395m^3 d^{-1} (16,500 l h^{-1}) have been found in the Teifi Valley where gravel deposits are found. Boreholes in the bedrock generally have yields of around 17m^3 d^{-1} (710 l h^{-1}).

5.3.4 Aquifer minerals

The mudstones are composed of an iron magnesium chlorite, a dioctahedral mica (illite) and quartz with lesser amounts of feldspar and iron oxides (Hornung et al. 1986; Shand et al. 1999). Soil mineralogy is closely related to the bedrock but with alteration of the chlorite and transformation of illite to vermiculite. Chlorite is relatively rare in the upper soils but increases with depth in contrast to vermiculite which is high in the upper parts of the soils. Calcite is present in veins in some areas and may have a significant effect on the buffering of water chemistry even where mines are present. However, some catchments contain abundant surface mine waste which may cause acidification of streams during stormflow which causes the release of large amounts of metals to the surface waters.

5.3.5 Hydrochemical characteristics

The groundwaters show a significant variation in pH from 5.16 to 7.55 although most plot between 6 and 7 (median value of 6.47). Dissolved oxygen is present in most waters and Eh is high, but this may in part be due to the fact that it was not always possible to sample in a through-flow cell (many waters in the Teifi study were collected from storage tanks). In the Plynlimon area, all samples were collected from through-flow cells and DO varied from less than detection (0.1 mg l^{-1}) to 10 mg l^{-1} (close to saturation). In boreholes where DO was less than the limit of detection, a faint smell of H_2S was observed indicating strongly reducing conditions. Specific electrical conductance (a measure of the mineralisation of the water) is low to moderate, most likely as a consequence of the rocks being relatively unreactive and also the residence times may be relatively short.

Boxplots are shown for the major and minor elements in Figures 5.3.1 and 5.3.2. Sodium shows a similar median and range to Cl indicating that the element is dominantly derived from atmospheric marine sources, reflecting the proximity of the areas to the sea. Relative increases in the other major elements indicate reaction of rainfall with rocks and soils as the groundwaters have percolated through the soils and aquifer: Ca being derived dominantly from calcite or Ca-bearing feldspars, Mg and K from chlorite and sheet silicates and sulphate from pyrite oxidation (and a component from dry deposition). The median value for NO_3 is relatively low (4.0 mg l^{-1}) and although there is a large range (<0.4 – 41 mg l^{-1}), all values are below the current EU MAC (maximum admissible concentration) of 50 mg l^{-1}. It is interesting that all groundwaters in the Plynlimon area are below detection limit but only 6% of those from Teifi are below detection. The high values of nitrate are thought to be from agricultural pollution and do not reflect the natural baseline.

Selected minor elements are shown on Figure 5.3.2. Fluoride concentrations are low indicating that there is not a major source in the bedrock. Iron and Mn are generally low in the Teifi groundwaters consistent with the presence of DO or the low contents in the bedrock. One sample from Teifi has very high Mn (2.4 mg l^{-1}) but low Fe. The reasons for this are not clear. The absence of DO in some groundwaters in Plynlimon has allowed Fe to be soluble (as Fe^{2+}) and the most likely source is from the oxidation of pyrite present in the rocks. Aluminium is present in all waters but is generally below the EU MAC concentration; samples which exceed this value are generally from very shallow boreholes where the groundwater table is high below acidic soils. Most other metals (e.g. Ni, Cr, Pb) are found at low concentrations but local enrichment of Zn and Cu may be related to sub-surface mineral veins with which the groundwaters have been in contact.

Probability plots are shown in Figures 5.3.3 and 5.3.4 for major and minor elements. The distribution of the different elements and their different sources and behaviour are highlighted as differences in shape of the individual curves. Several of the major elements (Figure 5.3.3) show almost linear trends e.g. Na, Cl, SO_4 but others show a tailing at the low or high end e.g. Ca, Mg, K. This implies more than one population and is due to the sampling of shallow boreholes (at Plynlimon) with a very short residence time. Saturation with respect to most mineral phases, e.g. calcite and dolomite, has not been achieved in these waters and therefore there is no steepening of the curves at high concentration. A slight shift in the Ca trend at c. 40 mg l^{-1} is due to enhanced calcite dissolution in the Teifi groundwaters derived from the Irish Sea Drift as described in section 5.2.2.

Nitrate is strongly controlled by redox processes and will therefore not show a single distribution on probability plots, if for example, nitrate reduction is occurring in part of the aquifer. This is clearly seen on Figure 5.3.3 where a straight line is found representing the samples where NO_3 is below the detection limit. Therefore, the presence of groundwaters with low NO_3 may not mean that they are uncontaminated, because highly polluted sites may be associated with reducing environments e.g. due to high contents of organic matter or other reducing agents. There is a distinct change in slope on the plot at around 2-3 mg l^{-1} NO_3 and this may possibly represent a change from a baseline value to waters which show the effects of agricultural pollution.

Silicon shows a steepening of the curve at high concentrations as saturation with respect to a SiO_2 phase (chalcedony) is approached; this will limit the maximum concentration found in these waters. Most trace elements, however, are far from saturation with respect to mineral phases, and will be expected to increase with residence time. Iron and Mn show a similar behaviour with a cut off at low concentrations: this is due to the presence of oxygen in these waters since in oxidising environments these elements form insoluble oxides or hydroxides. Note that although the shapes for Fe and Mn are similar to NO_3 which is also redox controlled, the high Fe and Mn are present in the more reducing waters, opposite to that for NO_3.

5.3.6 Depth variations

The limited amount of data available (mainly from Plynlimon) indicate extreme vertical heterogeneity in the top 50 m of the groundwater. The shallowest boreholes in the catchment are of low (but variable) alkalinity becoming more acidic during rainfall events. The deeper boreholes show relatively high alkalinity and are moderately reducing with low DO and high Fe concentrations.

5.3.7 Regional variations

There are not enough data available yet to make a sensible conclusion regarding regional variations. However, as mentioned previously the waters from the Teifi Valley do show differences in Ca and HCO_3, which are related to the different Drift types along the catchment. The waters from Plynlimon and Teifi are generally very similar in most respects, the main differences being the lack of high Ca and NO_3 waters in Plynlimon. Although surface waters in the Plynlimon catchment do contain NO_3, the low values in the groundwater are not simply a case of the NO_3 undergoing denitrification in the aquifer: some of the Plynlimon waters are oxidising. It is also likely that nitrate reduction is occurring in the soils and that much of the available nitrate in soils is taken up in forest growth.

5.3.8 Temporal variations

Most of the boreholes studied have been drilled recently and, therefore, there are no long term data available from monitoring. Short term monitoring of selected boreholes from the Plynlimon site demonstrated that the deeper boreholes show little variation over a monthly timescale but that the shallow ones show large variations in response to rainfall events.

5.3.9 Summary

The data presented from the Teifi and Plynlimon areas show that groundwater in Ordovician/Silurian aquifers is generally of good quality. The chemical summary (Appendix 2) indicates that the baseline is variable, although most parameters are below EU MAC and guideline values. The main elements where baseline concentrations are likely to exceed this value include Fe, Mn and potentially NO_3 where agriculture has had an impact on local groundwaters in the Teifi Valley. High Fe and Mn are present where the groundwaters have become relatively reducing and this poses the biggest threat to groundwater usage: these problems are mainly due to the clogging of boreholes caused by mineral precipitation, as well as taste.

It is difficult to assess in detail the effect of agriculture in introducing NO_3 to the Teifi groundwaters due to the general scarcity of data from areas with similar geology and geomorphology. It is clear that more NO_3 data are required from other areas of Ordovician/Silurian rocks where farming has been minimal, in order to determine baseline concentrations. Although a larger database is required for this minor aquifer, a comparison of available groundwater data with that of surface waters in these areas highlights the generally higher quality of groundwaters and the much lower baseline concentrations of metals as well as decreased acidity.

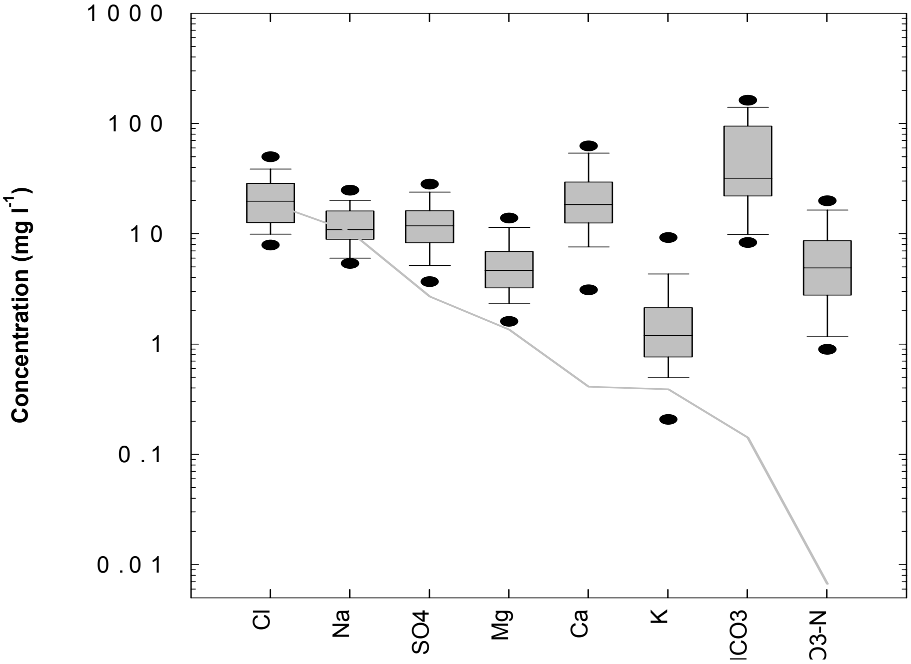


Figure 5.3.1 Boxplots showing major elements in groundwater samples from the Lower Palaeozoic mudstones, shales and slates of central and southern Wales. The drawn line denotes mean ocean water composition normalised to the median chloride value.

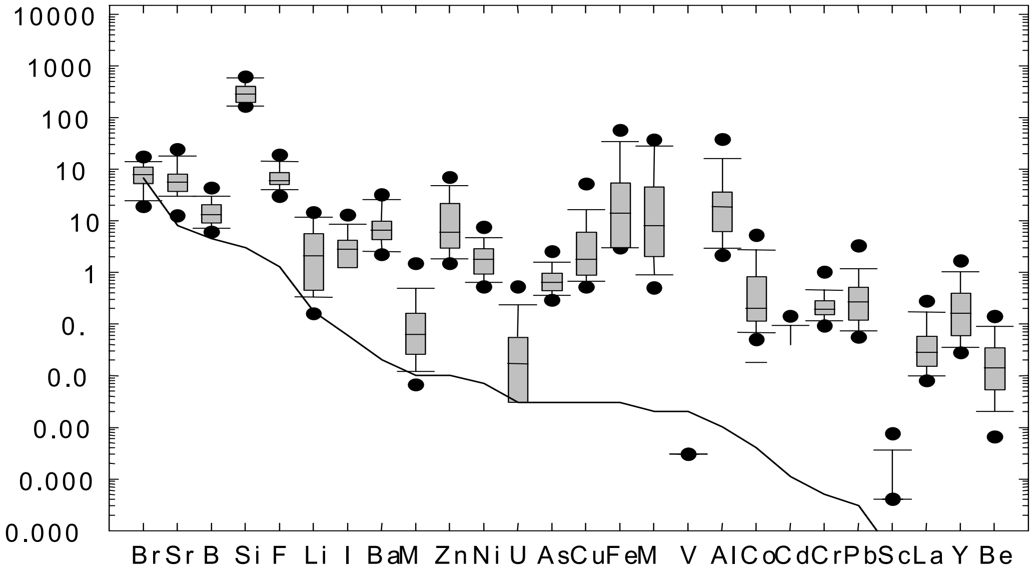


Figure 5.3.2 Boxplots showing minor and trace elements in groundwater samples from the Lower Palaeozoic mudstones, shales and slates of central and southern Wales. The drawn line denotes mean ocean water composition normalised to the median chloride value.

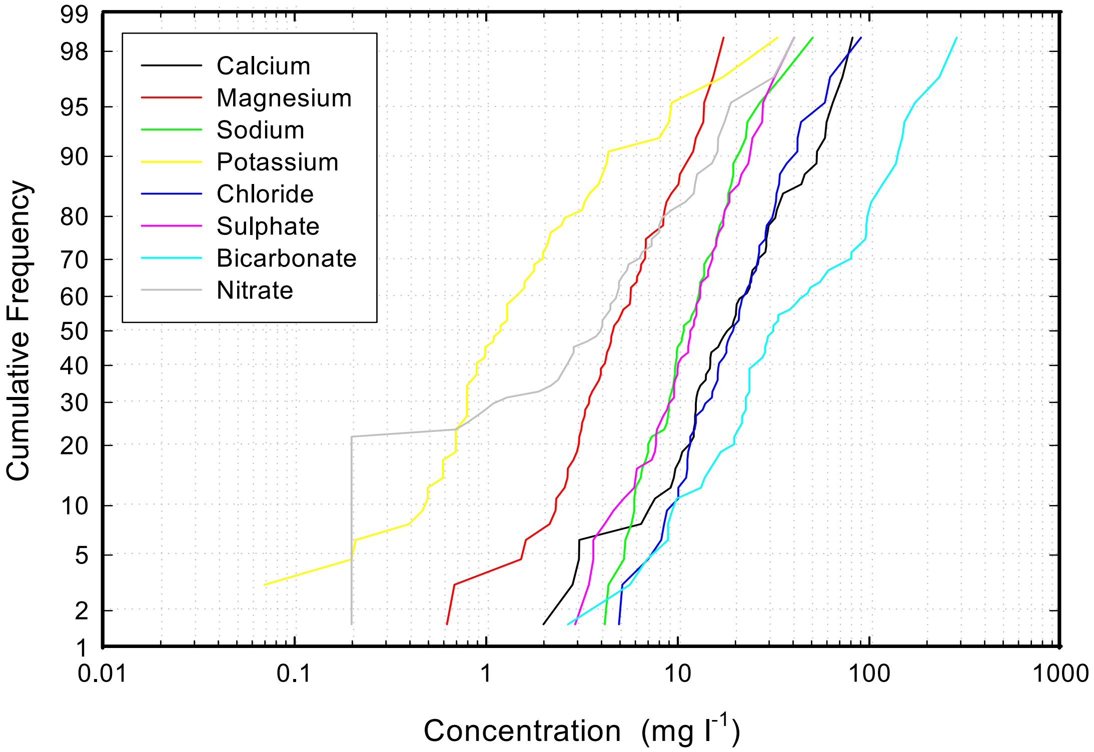


Figure 5.3.3 Probability plot of major elements in groundwater samples from the Lower Palaeozoic mudstones, shales and slates of central and southern Wales.

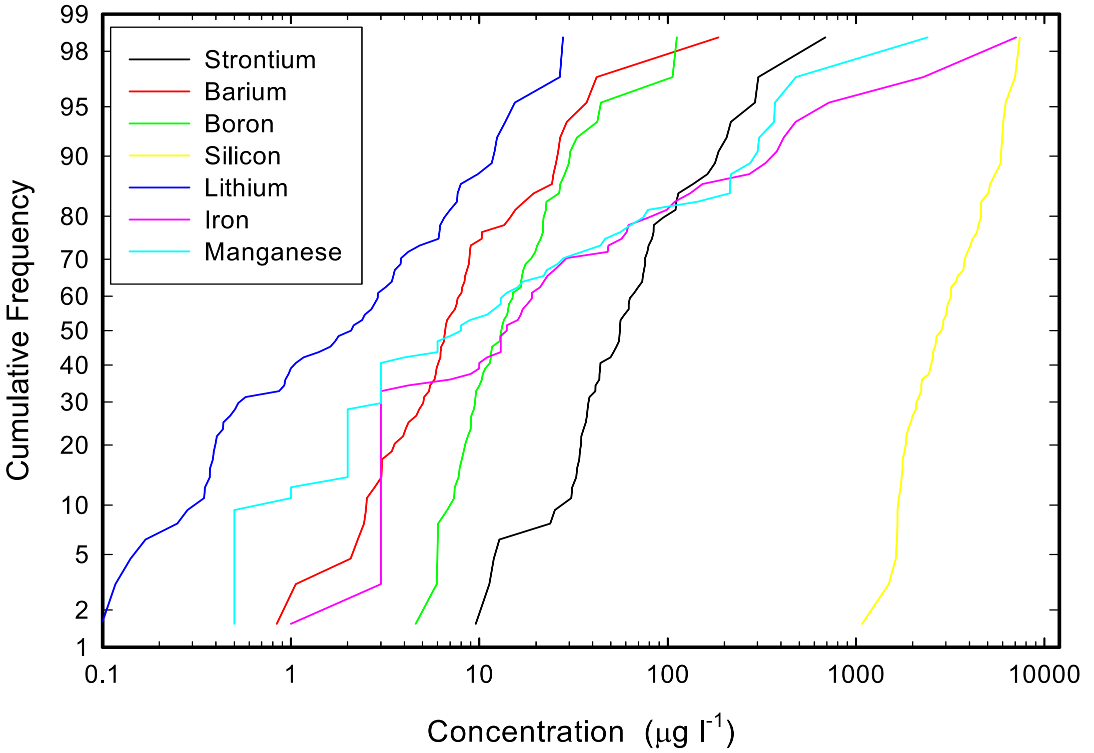


Figure 5.3.4 Probability plot of selected minor and trace elements in groundwater samples from the Lower Palaeozoic mudstones, shales and slates of central and southern Wales.

5.4 THE DEVONIAN AQUIFER OF CENTRAL SCOTLAND

5.4.1 Introduction

The Devonian aquifer of Fife is one of the most important aquifers in Scotland. The aquifer supplies 20 Ml d^{-1} during the winter periods increasing to 40 Ml d^{-1} in the summer due to abstraction for irrigation (O'Dochartaigh et al., 1999). Groundwater is used to supplement public water supplies especially in drier years when river abstraction is restricted and is also used by a small number of industries including vegetable washing and poultry breeding.

5.4.2 Study area

The study area is located in Central part of Scotland in a graben structure called the Midland Valley. This area is located between Lower Palaeozoic (Ordovician-Silurian) metasediments to the south and metamorphic basement rocks to the north. Although the Midland Valley is densely populated, the area of study comprises mainly agricultural land with small towns and villages. The aquifer is present in the low-lying Eden Valley, which is bounded to the north and south by volcanic rocks of Devonian and Carboniferous age.

5.4.3 Hydrogeology

The aquifer comprises rocks of Upper Devonian (the Stratheden Group) and possibly Lower Carboniferous age (Kinnesswood Formation). The Devonian rocks are mainly reddish-brown, yellow and white sandstones (often feldspathic) with subordinate siltstones, mudstones and conglomerates. The sandstones are generally well cemented at the base with a clay-mica matrix and calcite. The upper parts of the succession are more weakly cemented and highly porous, particularly in shallow parts which have undergone weathering. Ochreous decomposed dolomites (cornstone) are present near the top of the succession. The Kinnesswood formation comprises yellow, white to purple sandstones often weakly cemented with a clay-mica matrix containing calcite and dolomite.

Permeability is very variable, related to the degree of cementation and varies overall from as low as 10^{-5} up to 0.5 m d^{-1}. Porosity is also variable, but as a whole varies between 10 and 20 %. Transmissivities measured in the upper unit of the Devonian were as high as 200 m^2 d^{-1} probably related to faulting, but may be as low as 12 m^2 d^{-1} (O'Dochartaigh et al., 1999).

5.4.4 Aquifer minerals

There is little information available on the detailed mineralogy of the sandstone units. At the base of the lowest formation, pebbles of quartz and lava are common and elsewhere in the succession mudstones occur. The sandstones are feldspathic, containing both potassium and plagioclase feldspar. As mentioned above, the degree of cementation is variable, in general being less dominant in the more shallow parts of each sequence where weathering has occurred. The matrix mineralogy comprises variable proportions of clay, mica, calcite and dolomite. Cornstones are more prevalent near the top of the aquifer succession.

5.4.5 Hydrochemical characteristics

The pH of the groundwaters varies from circumneutral to slightly alkaline (range 6.7 – 8.2) and there is a significant range in SEC from 209 to 682 µS cm^{-1}. It was not possible to measure the redox status in most boreholes, but most contained DO. The presence of NO_3, Fe and Mn confirm that the aquifer is generally oxidising. Water quality is in general good but most groundwaters have relatively high hardness.

Water type varies from Ca-HCO_3 to Mg-HCO_3 types, the high Mg/Ca in many groundwaters reflecting the dissolution of dolomite. Most samples are at saturation with respect to dolomite and calcite, but some are significantly undersaturated, which implies either a short residence time or that parts of the aquifer have become decalcified. Sodium, Cl and Br are relatively low and dominated by rainfall inputs (Figures 5.4.1 & 5.4.2). The concentrations of NO_3 are very variable (0.04 – 50 mg l^{-1}). The cumulative frequency plot indicates at least two populations with a threshold value of around 5 mg l^{-1} at the 50th percentile. It is likely that values above this value are caused by anthropogenic inputs.

Fluoride concentrations are low, indicating that fluorite is not present to a significant degree in the aquifer. Iron and Mn are both low, consistent with the oxidising nature of the aquifer. Although the samples were not analysed using analytical techniques providing low detection limits, the concentrations of most trace metals are also well below EU drinking water limits. This may reflect the alkaline nature of the waters or the limited availability of undesirable trace elements in the aquifer minerals. The exception of the trace elements is Ba, which is generally high (median of 170 µg l^{-1}) with some 70% of waters being above the EU MAC of 100 µg l^{-1} (Figure 5.4.4).

5.4.6 Depth variations

There are few data showing direct evidence of depth variations in the aquifer. However, changes in temperature and SEC are known, showing that variations in water quality also exist in relation to depth. The sampling of boreholes with different depths at one pumping station has shown that the deeper waters have lower NO_3, Cl and SEC than the shallower ones, indicating the greater degree of pollution in the latter. In addition, the initial pumped waters from several boreholes are known to contain extremely high NO_3, which decreases with time. This indicates a contribution of polluted water at shallow depth.

5.4.7 Regional variations

The groundwaters show chemical trends in the direction of groundwater flow. Several parameters including pH, SEC, HCO_3 and SO_4 increase in the direction of river flow along the valley. Magnesium and Mg/Ca show an increase followed by a decrease and this ties in with the occurrence of more dolomitic horizons in the aquifer. Barium shows a general decrease and it is probably controlled by barite ($BaSO_4$) solubility: the waters are at or close to saturation with respect to barite and the higher SO_4 in the along the valley limits how much Ba can exist in solution.

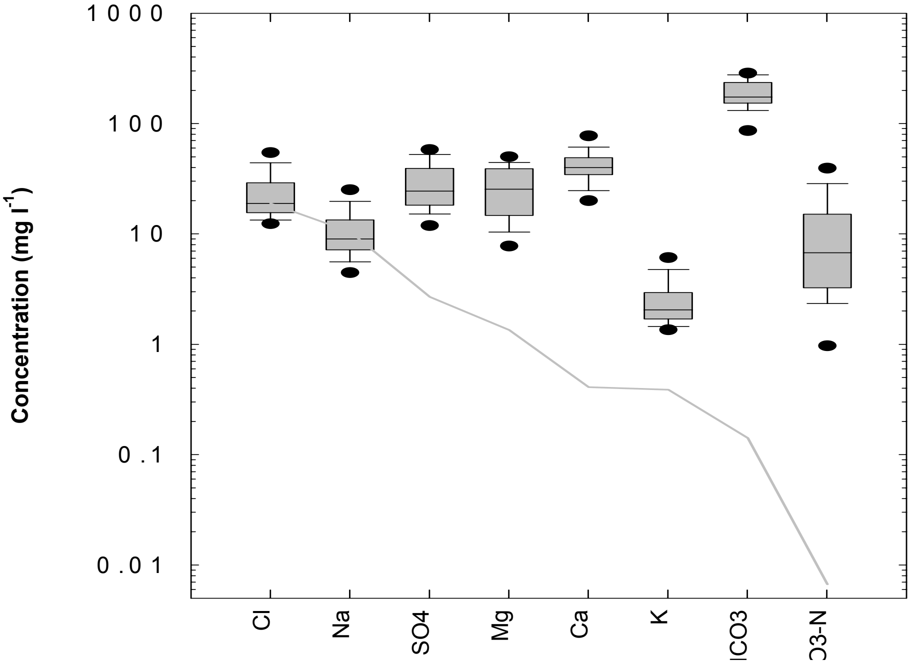


Figure 5.4.1 Boxplots showing major elements in groundwater samples from the Devonian sandstone aquifer of Central Scotland. The drawn line denotes mean ocean water composition normalised to the median chloride value.

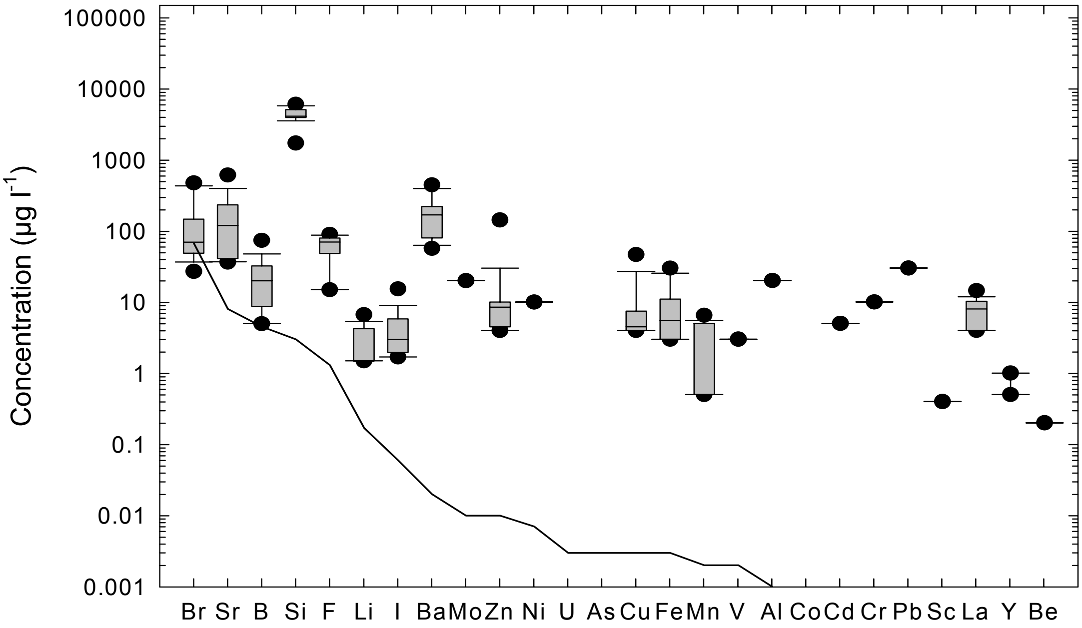


Figure 5.4.2 Boxplots showing minor and trace elements in groundwater samples from the Devonian sandstone aquifer of Central Scotland. The drawn line denotes mean ocean water composition normalised to the median chloride value.

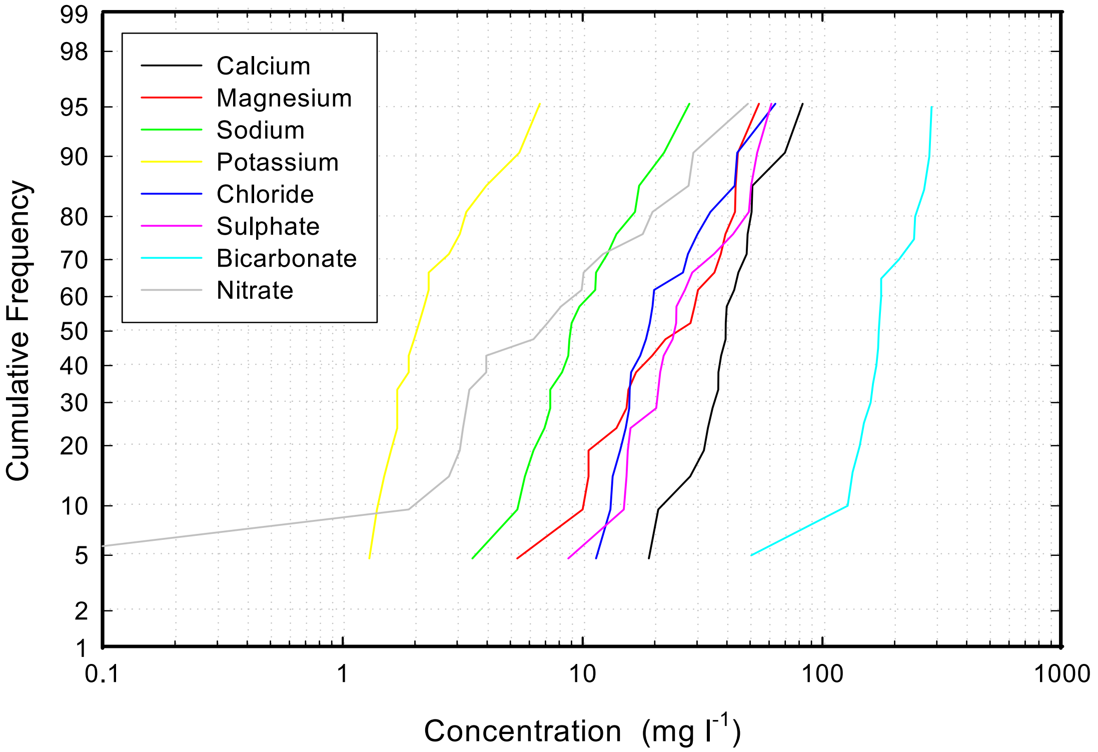


Figure 5.4.3 Probability plot of major elements in groundwater samples from the Devonian sandstone aquifer of Central Scotland.

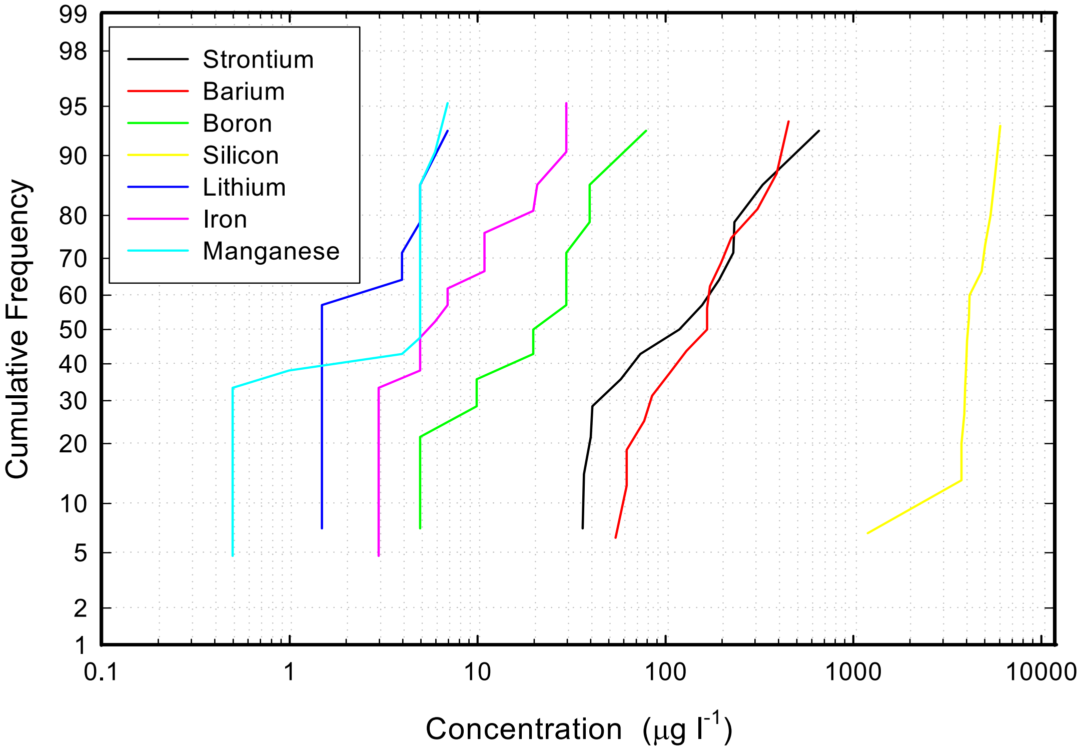


Figure 5.4.4 Probability plot of selected minor and trace elements in groundwater samples from the Devonian sandstone aquifer of Central Scotland.

5.4.8 Temporal variations

As with the other aquifers studied, temporal data are quite limited. Seasonal variations in temperature exist in most boreholes with higher (10 – 12 °C) temperatures in the summer months and lower (7 – 9 °C) temperatures in the winter months. The only species for which long-term data do exist is NO_3. Most boreholes show a clear trend of increasing NO_3 from the period 1972 to 1998 although the rate of increase is different in different boreholes. In some cases the rate of change has decreasing since around 1985. Further data are required in order to assess if the natural baseline for this and other elements is changing.

5.4.9 Summary

The baseline groundwater quality of the Fife aquifer is generally good, but the waters are often hard due to the presence of calcite and dolomite cements throughout much of the aquifer. The main exception is high Ba, which is exceeded in c. 70 % of samples collected. Groundwaters in the eastern part of the aquifer have higher SO_4, which helps to limit the amount of Ba to around 60 $\mu g\ l^{-1}$. The elements which commonly pose a problem in other UK aquifers e.g. Fe, Mn and F are very low as a consequence of oxidising conditions or availability. Superimposed on the natural baseline are the effects of agricultural pollution such as NO_3, with some areas having higher concentrations than the EU MAC value. It is obvious that this aquifer needs careful monitoring, indeed at least one borehole has ceased abstraction and will only be used only as an emergency contingency.

5.5 THE CARNMENELLIS GRANITE OF SW ENGLAND

5.5.1 Introduction

Groundwaters from granites do not represent a major source of groundwater in the UK and existing wells and boreholes are used only for private domestic purposes. The data presented here are taken from a previous study (Smedley at al., 1989) collected as part of a programme studying the geothermal potential of the UK. The data presented here are from shallow wells, boreholes and springs; deep geothermal waters, present in the granite, have been excluded because these are not suitable for potable purposes. Although the number of parameters measured is less than the other areas, it was considered important to include this dataset as a comparison with the data available on Norwegian granite groundwaters.

5.5.2 Study area

The Carnmenellis granite is found in SW England and forms part of the larger, partially concealed, Cornubian Batholith. The dataset is confined to the area of the pluton itself, which has a surface expression covering c. 100 km^2. The granite is a high heat production granite and contains sufficient radioelement concentrations to raise the geothermal gradient to 35 $^{o}C\ km^{-1}$.

5.5.3 Hydrogeology

Water yields are generally small and sufficient only for local small-scale water supply. The primary permeability of the granite is extremely low but secondary permeability is developed along fractures and lodes and this has been artificially enhanced by mining operations in many areas. Hydraulic gradients are steep with radial flow away from the granite towards coastal areas. Natural local discharge occurs as springs or as baseflow to streams. The piezometric surface is generally quite shallow, of the order of 10 m with typical borehole yields around 15 $m^3\ d^{-1}$.

5.5.4 Aquifer minerals

The Carnmenellis granite (dated between 285 and 280 Ma) comprises several distinct plutons and is essentially a peraluminous muscovite-biotite granite containing megacrysts of alkali feldspar. The matrix is composed of varying proportions of plagioclase and quartz with accessory apatite, tourmaline, epidote and chlorite (Smedley et al., 1989). Slightly younger dykes, of similar composition to the granite, were intruded regionally and hydrothermal mineralisation (mainly Sn-W-Cu-Zn) and alteration (forming greissen and tourmaline breccias) occurred during the late stages of magmatism. The granite has suffered many stages of alteration since emplacement including kaolinisation, haematisation and chloritisation (Smedley et al., 1989).

5.5.5 Hydrochemical characteristics

The pH of the groundwaters is very variable but generally acidic with a range from 4.26 to 6.70 and a median of 5.66. Conductivity also shows a large range (14 – 580 µS cm^{-1}) but shows no correlation with pH. This variation probably reflects differences in residence time of the groundwaters. Water types are generally of Na-Ca-Cl type. The low pH and Ca and HCO_3 concentrations (Figure 5.5.1) indicate that there has been little reaction with carbonate minerals. The dominance of Na and Cl and Na/Cl ratios generally close to seawater imply that marine inputs (rainfall or dry deposition) are important inputs to the groundwater. The source of Mg is likely to be dominantly from chlorite dissolution whilst Ca is most likely derived from the weathering of plagioclase. Potassium reached concentrations of over 30 mg l^{-1} which is relatively high for shallow groundwaters (EC MAC is 12 mg l^{-1}) and correlates well with Rb ($r = 0.8$) and these elements, along with Ba are, therefore, most likely to be dominantly derived from K-feldspar or biotite dissolution. Although some K may be derived from agricultural pollution the lack of correlation makes this unlikely to be the dominant control on K. Nitrate shows at least two distinct populations with a threshold of 8 mg l^{-1} at around the 75th percentile (Figure 5.5.3), which may show the distinction between natural and anthropogenic inputs. This threshold is slightly higher than the other aquifer units studied (c. 5 mg l^{-1}) but may be a consequence of the freely draining soil types: coarse sandy acid podsols, which are unlikely to promote natural soil denitrification.

There are few data available on trace elements (Figure 5.5.2). Iron and Mn are low (medians of 0.02 and 0.016 respectively) reflecting the oxidising conditions in the aquifer but the low concentrations even in more acidic waters reflect a general low abundance in the host rocks. However, locally, values may exceed the EU MAC concentrations. Aluminium concentrations are often high (Figure 5.5.4) due to the low pH: all waters which exceed the EU MAC concentration of 500 µg l^{-1} have pH less than 6.0 (around 20% of the data). Fluoride is often a problem in groundwaters hosted by granitic rocks; unfortunately this element was not analysed during the study.

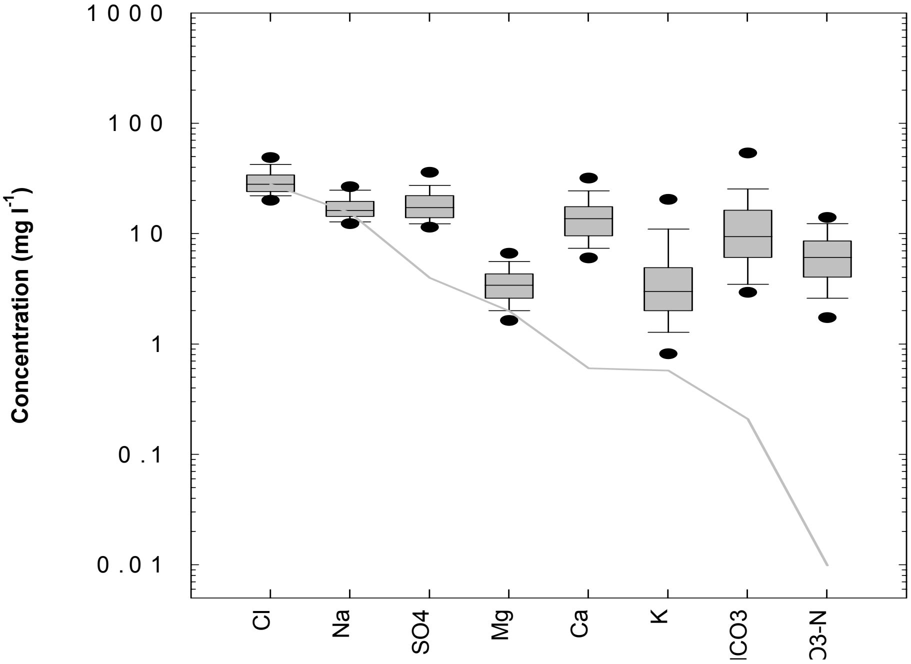


Figure 5.5.1 Boxplots showing major elements in groundwater samples from the Hercynian Carnmenellis granite aquifer of southwest England. The drawn line denotes mean ocean water composition normalised to the median chloride value.

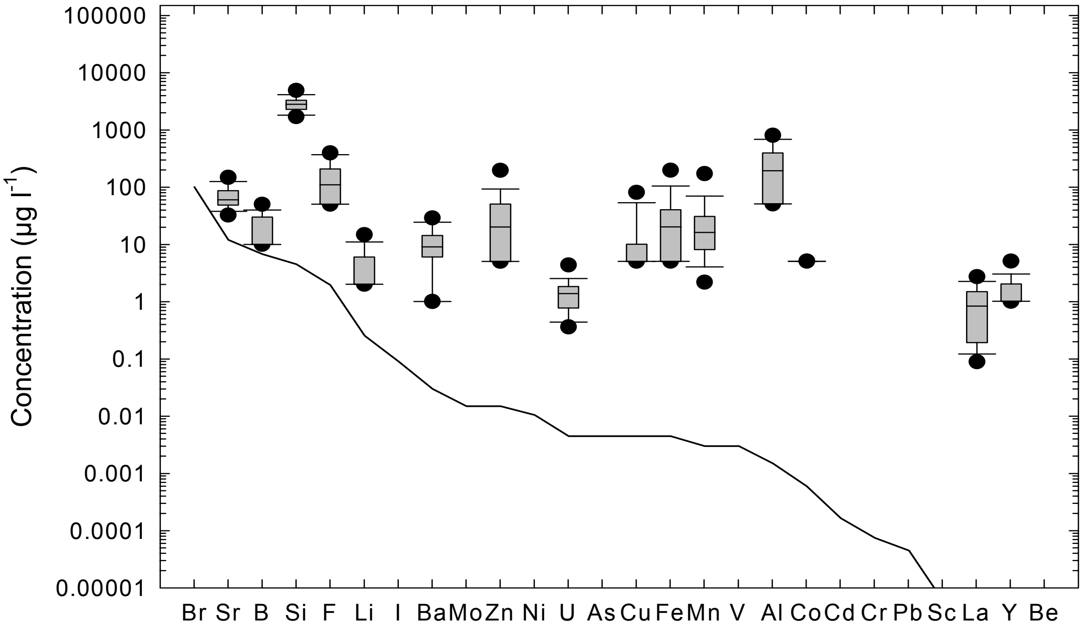


Figure 5.5.2 Boxplots showing minor and trace elements in groundwater samples from the Hercynian Carnmenellis granite aquifer of southwest England. The drawn line denotes mean ocean water composition normalised to the median chloride value.

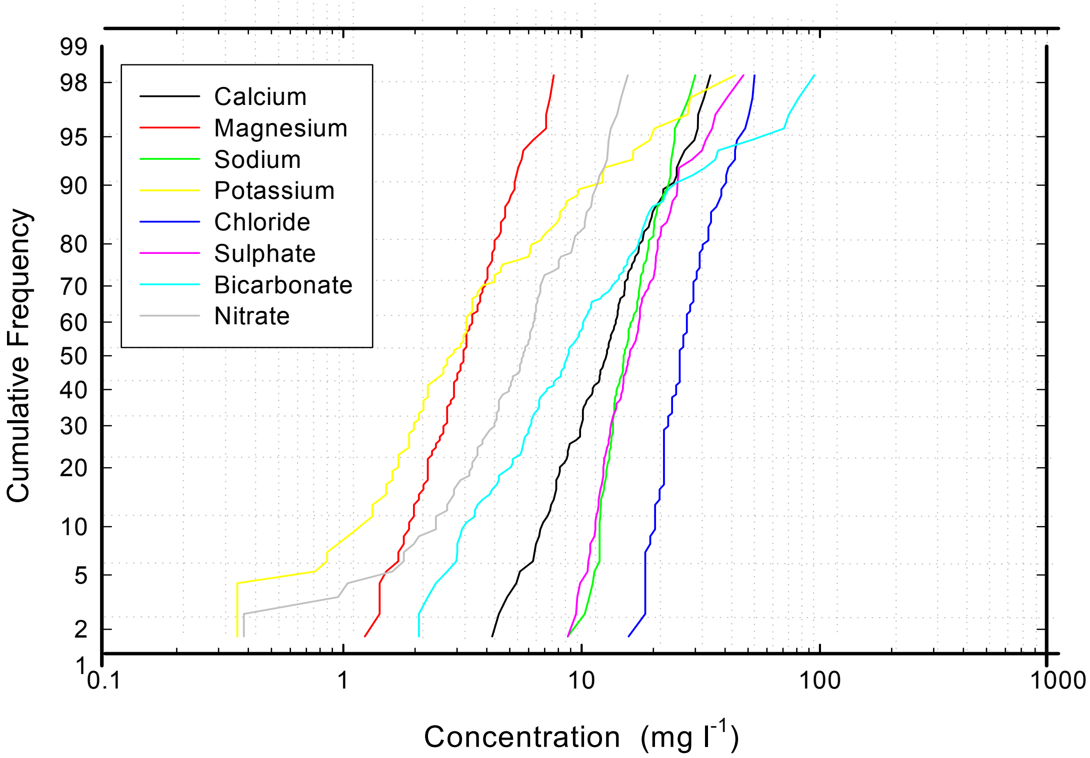


Figure 5.5.3 Probability plot of major elements in groundwater samples from the Hercynian Carnmenellis granite aquifer of southwest England.

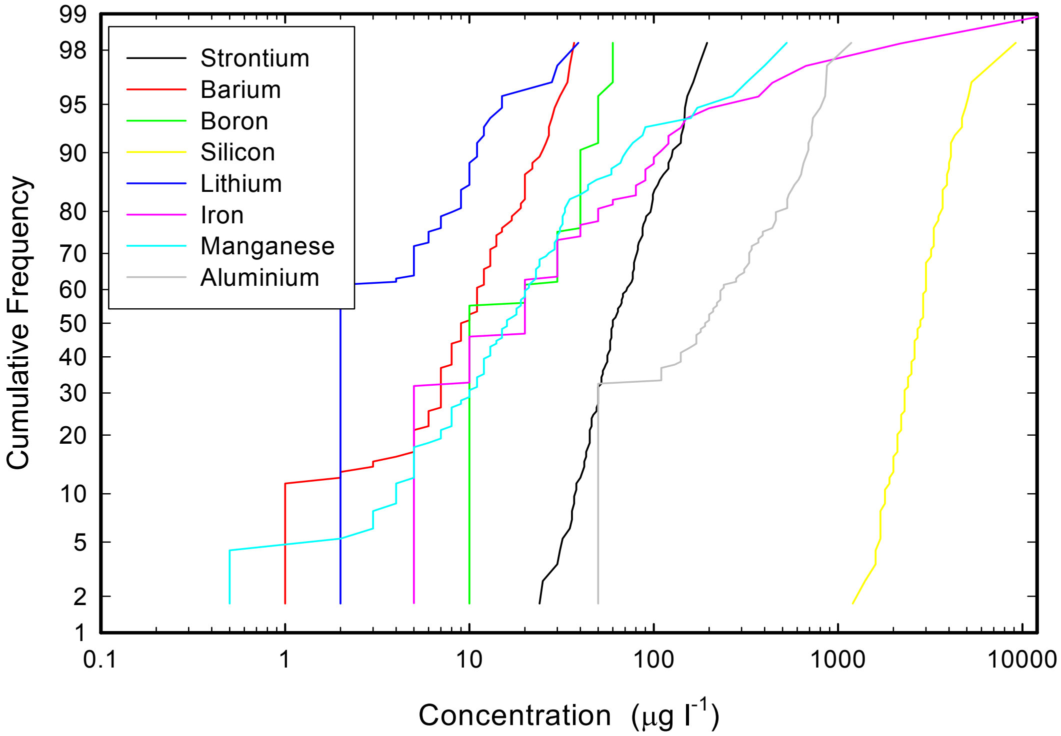


Figure 5.5.4 Probability plot of selected minor and trace elements in groundwater samples from the Hercynian Carnmenellis granite aquifer of southwest England.

5.5.6 Depth variations

There are no data available on depth variations in the shallow groundwater of the granite. Geothermal waters exist at depth reaching temperatures of $55^{o}C$ with TDS contents up to 32 g l^{-1}. The low conductivities and concentrations of minor and trace elements make it unlikely that mixing between the two occurs in the shallow system. The pumping of the mines has also locally increased the depth of the water table; however, with the cessation of pumping, mixing and contamination of the shallow system may occur. Therefore, these data represent an important background dataset with which to assess any local or regional effects in the future.

5.5.7 Regional variations

Regional comparisons of the granite groundwaters with the surrounding altered metasediments (killas) have been completed previously by Smedley et al. (1989) and it was shown that the killas waters tend to have higher concentrations of Cl, HCO_3, SO_4, Na, Ca, Mg, Sr and B whereas the granite waters have higher Al, Ba and Rb and lower pH. Variations within the granite groundwaters show little consistent regional variation of many elements, although Al tends to be higher in the western part of the pluton. The base metals Zn and Cu are particularly sporadic being related to the presence of mineral lodes in the granite and surrounding areas.

5.5.8 Temporal variations

There are no temporal data available for this area.

5.5.9 Summary

The groundwaters of the Carnmenellis granite are relatively acidic and contain high baseline concentrations of elements such as Al. Iron and Mn are generally low due to the oxidising groundwater environment, although locally, high concentrations are present. Local high concentrations of Zn and Cu are related to mineral deposits but in general these are well below the EU MAC concentrations. Agricultural pollution has affected some groundwaters as evidenced by moderately high concentrations of NO_3. Several elements may be enhanced in these groundwaters due to the nature of the granite and alteration style e.g. U, Th, F but these have not been analysed in the study, and further work is required to assess if these pose a serious problem. Likewise, radon, which is known to be high in parts of the Cornish batholith needs to be assessed in relation to groundwater quality. However, a study of the groundwater chemistry in a genetically related granite body at the Isles of Scilly show low concentrations of U and F and only moderate levels of Rn (Banks et al., 1998c).

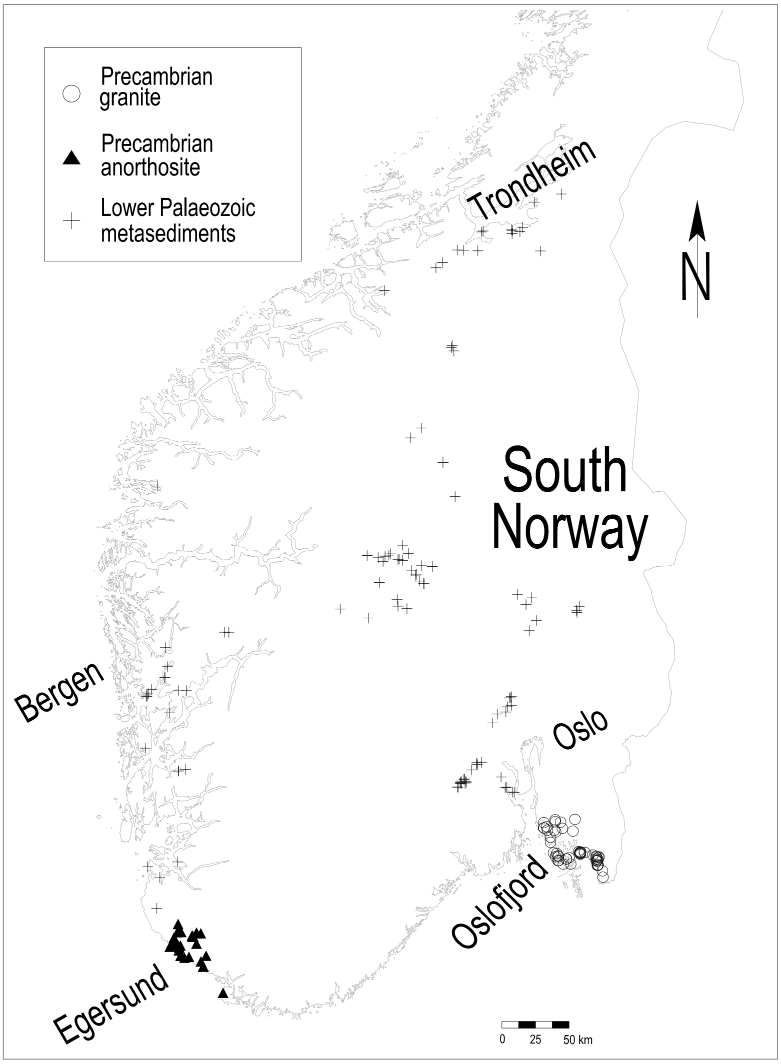
6 NORWAY BASELINE CHEMISTRY

6.1 INTRODUCTION

The aquifers chosen from Norway are:

1) Precambrian granite in the Iddefjord area, south-eastern Norway
2) Precambrian anorthosite in the Egersund area, south-western Norway
3) Lower Palaeozoic (Cambro-Silurian) metasediments mainly from south Norway.

Samples were collected from boreholes by representatives of local public health authorities. The collection, treatment and analysis of aliquots for radon analysis by scintillation counting, cation determination by ICP-AES, anion determination by IC, pH determination by pH meter and alkalinity determination by titration are detailed by Banks et al. (1998b). Trace element analysis by ICP-MS is detailed by Frengstad et al. (2000). Some of the boreholes were re-sampled for quality control and pH and alkalinity were determined in field. The reproducibility was found to be good (Frengstad, *in prep*).



.Figure 6.1.1 Map of South Norway showing the localities of the boreholes in the selected aquifers.

6.2 PRECAMBRIAN IDDEFJORDEN GRANITE

6.2.1 Introduction

The Precambrian Iddefjorden granite is classified under lithological group 92 (Precambrian granites to tonalites) in NGU's digital 1:3 million bedrock map (Sigmond 1992). These magmatic rocks date back to the Sveco-Norwegian orogeny in Middle Proterozoikum (900 million years BP) intruding older metamorphic rocks. Some good quality hydrogeology and hydrochemistry data exist from the Iddefjord granite aquifer at the Hvaler archipelago in south-eastern Norway (Banks et al., 1992, 1995b) and from the islands and the mainland (Frengstad *in prep*). The boreholes have generally low yield and mainly supply single households and farms. At Hvaler they also supply a lot of holiday homes. The lithological group 92 also includes hornblende granite in the Farsund area in the county of Vest-Agder, and fine- to medium-grained granites in Sør-Aurdal in Oppland County.

6.2.2 Study area

The Iddefjorden granite is situated in southern part of Østfold County on the east side of outer Oslofjord, close to Norway's border with Sweden. In fact, the same lithology continues along the Swedish west coast under the name "Bohus granite". Most of the terrain has emerged from the sea during the last 10 000 years due to about 200 m of net isostatic uplift after the last glaciation. The bedrock is glacially scoured and no surficial layer of deep weathered granite is regionally developed. The bedrock outcrops over large areas, intersected by linear valleys partially filled by Quaternary deposits, mainly shallow marine or littoral silts and sands. On the mainland the bedrock is to a large extent covered with a blanket of glaciomarine clay in the vicinity of the Ra terminal moraine deposited under the Younger Dryas standstill/re-advance of the inland ice at the end of the last glaciation.

6.2.3 Hydrogeology

The primary porosity of the granite is negligible and practically all water flow takes place in fractures. Some of the most prominent fracture zones are filled with low-permeability clay minerals and thus yield little water. Test pumping at Hvaler revealed a "two-layered" fractured aquifer where the upper 12 metres contains relatively transmissive fractures (10^{-6} – 10^{-5} m/s) and the deeper part is of very low permeability ($\sim 10^{-9}$ m/s) (Banks et al., 1992). The median yield for the entire lithological group is 600 l h^{-1} and the median normalised yield is 11.4 l h^{-1} per drilled metre (Morland 1997). This is very close to the median normalised yield for all bedrock types in Norway.

6.2.4 Aquifer minerals

The main minerals of the Iddefjord granite are quartz, microcline and plagioclase (oligoclase) with accessory biotite, hornblende, muscovite, iron-oxides, chlorite, apatite, titanite and zircon (Pedersen & Maaløe, 1990). Basic clots, pegmatites and xenoliths of the older gneissic host-rock are common in the Hvaler area (Banks et al., 1992). Fluorite, calcite and epidote mineralisation is widely observed on the fractures, and uranium and thorium mineralisation has been reported from the Hvaler area by Banks et al. (1995). Xenoliths of the host-rocks and dykes of younger basic rocks are less common on the mainland, but pegmatites are widespread. Small grains of pyrite are observed locally (Gautneb et al., 1999).

6.2.5 Hydrochemical characteristics

A summary of the chemical data is presented in Appendix 2, which includes minimum and maximum values, median and “upper baseline” values based on the 95th percentile.

The range of pH in the Precambrian granite groundwater is from 6.18 to 8.57. Most of the samples have pH between 7.5 and 8.2 with a median value of 7.9. Dissolved oxygen and Eh have not been measured. In a smaller survey of 10 boreholes, Frengstad (*in prep.*) observed a faint smell of H_2S in one of the boreholes.

Boxplots are shown for the major elements in Figure 6.2.1. Na concentrations show a relative increase compared to Cl indicating that a significant component of Na is derived from weathering of the soils and rocks. The other major elements show the same evolution, but the Mg content is more closely related to the relative seawater composition. The excess of Na is dominantly derived from plagioclase while K is partly derived from sheet silicates and from feldspars. The excess Na may also be partly derived from Na-loaded marine clay through ion exchange with Ca, as the aquifers were below sea level during and after the ice age and are now freshening as a consequence of isostatic uplift. Calcium is derived from calcite and in part from plagioclase, and SO_4 from pyrite oxidation (with a component from dry deposition). Excess Mg is derived from sheet silicates and hornblende. The median value for NO_3 is very low (0.23 mg l^{-1}) and although there is a large range (<0.05 – 48.2 mgl^{-1}), only one value exceed the current Norwegian MAC value of 44 mg l^{-1}. (For comparison the EU MAC value is 50 mg l^{-1}). This is representative of nitrate in bedrock groundwater in Norway where the median value is 0.46 mg l^{-1} and less than 1 % (13 out of 1604) of the boreholes exceed the Norwegian MAC value (Banks et al. 1998b).

Selected minor elements are shown on Figure 6.2.2. Fluoride concentrations are high, indicating a major source in the bedrock or from the fracture mineralisation. Fluoride in groundwater is also positively correlated with pH. The median value is 2.02 mg l^{-1}, which is significantly higher than the MAC value of 1.5 mg l^{-1} for both Norway and the EC. The highest concentration is 7.18 mg l^{-1}. Iron and Mn are generally high in the Iddefjorden granite groundwaters indicating relatively low dissolved oxygen and slightly reducing conditions. Aluminium concentrations have a median of 0.039 mg l^{-1}, with some high values (up to 1.37 mg l^{-1}) and 23.6 % of the waters are above the Norwegian MAC concentration of 0.2 mg l^{-1}. These samples are not consistently from the low or very high pH waters as one should expect. The Iddefjorden granite is known to have a high concentration of U (Killeen and Heier 1975), which is also reflected in the groundwater samples which have a median value of 0.032 mg l^{-1} of U and a highest recorded value of 0.684 mg l^{-1}. There is currently no limit set in Norway or the EU for uranium in drinking water but 46 % of the samples exceed the new United States MAC of 0.030 mg l^{-1} (Environmental Protection Agency, 2000) while 8 % exceeds the Canadian MAC of 0.1 mg l^{-1} (Health Canada, 1996).

The Precambrian groundwater in the granitic aquifers are enriched in many trace elements, such as Be, Cd, Th, Tl and rare earth elements compared to bulk Norwegian bedrock groundwaters while they are depleted in As (Frengstad et al., 2000). Most other metals (e.g. Ni, Cr, Pb) are present at low concentrations, but a few samples exceed the Norwegian drinking water limits for Zn and Cu. Zinc and Cu may be derived from the host-rock but are more likely derived from plumbing material as the groundwaters were normally sampled at the kitchen tap.

Probability plots are shown in Figures 6.2.3 and 6.2.4 for major and minor elements. The distribution of the different elements and their different sources and behaviour are highlighted as differences in shape of the individual curves. Sodium and K show almost linear trends (Figure 6.2.3) but most of the major elements show a tailing at the low end (Ca, Mg, SO_4, NO_3, HCO_3) and/or at the high end (Cl, NO_3). The samples at the low end may represent groundwater with short residence time and thus low concentrations of elements derived from weathering. A shift in the chloride trend at c. 40 mg l^{-1} is thought to be due to marine salts derived from older seawater, leaching from minerals in the aquifer or from seawater intrusion.

Nitrate is strongly controlled by redox processes. Therefore, it not show a single distribution on probability plots if nitrate reduction is occurring in part of the aquifer. On Figure 6.2.3 there are two distinct changes in slope on the plot at 0.1-0.2 mg l^{-1} and around 2 mg l^{-1}. (The vertical straight line is representing the samples where NO_3 is below the detection limit). The kink at 2 mg l^{-1} may possibly represent a change from a baseline value to groundwaters showing the effects of agricultural pollution. The kink at 0.1-0.2 mg l^{-1} could, therefore, represent samples from reducing environments e.g. due to high contents of organic matter or other reducing agents.

The Si curve shows a steepening at high concentrations as saturation with respect to a SiO_2 phase (chalcedony) is approached; this will limit the maximum concentration found in these waters. Most trace elements, however, are far from saturation with respect to most mineral phases, and will be expected to increase with residence time. Li and Ba show a tailing at the low end probably representing immature groundwaters.

6.2.6 Depth variations

At the depths currently under consideration, there is no correlation between the depth of the boreholes and the concentration of any element in the groundwater, not even the redox-sensitive ones. This is probably due to the fact that the groundwater flow along fractures with different orientation and variable permeability. A given borehole may intercept a water-bearing fracture system with a characteristic hydrogeochemistry at any depth dependent only on the combined geometry of the fracture and the borehole. Groundwater of Na-Ca-Cl type with high total dissolved solids (TDS) and high pH has been found at depths below 700 m in a granitic aquifer at the Stripa research site west of Stockholm (Nordstrom et al.,1989). The authors also noted that when typical Ca-HCO_3 recharge (<300 m depth) mixed with this deep groundwater in the intermediate zone, the resulting groundwater chemistry was highly fracture-dependent rather than depth-dependent.

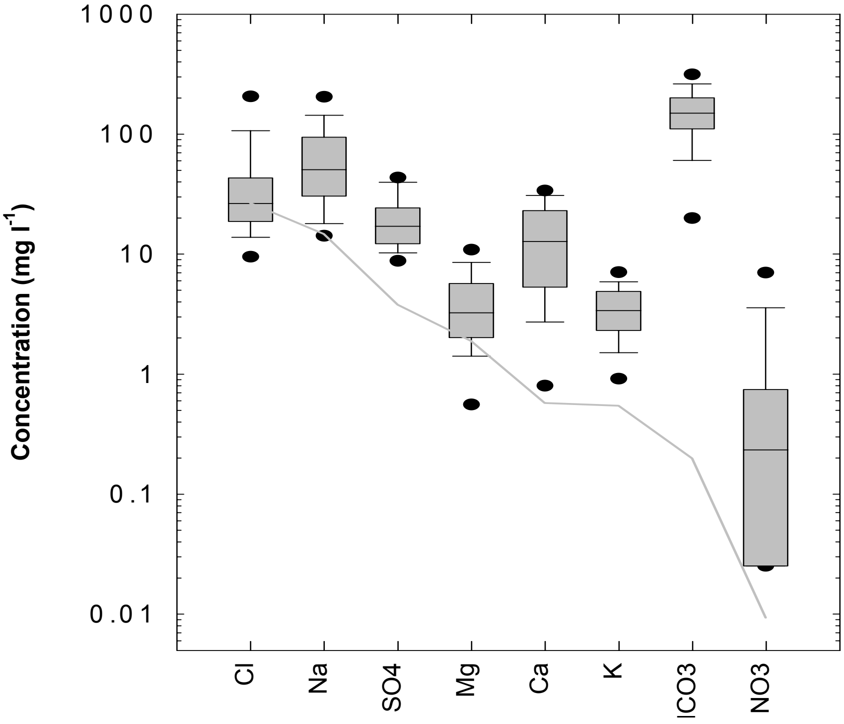


Figure 6.2.1 Boxplots showing major elements in groundwater samples from the Precambrian Iddefjord granite aquifer, Southeast Norway. The drawn line denotes mean ocean water composition normalised to the median chloride value.

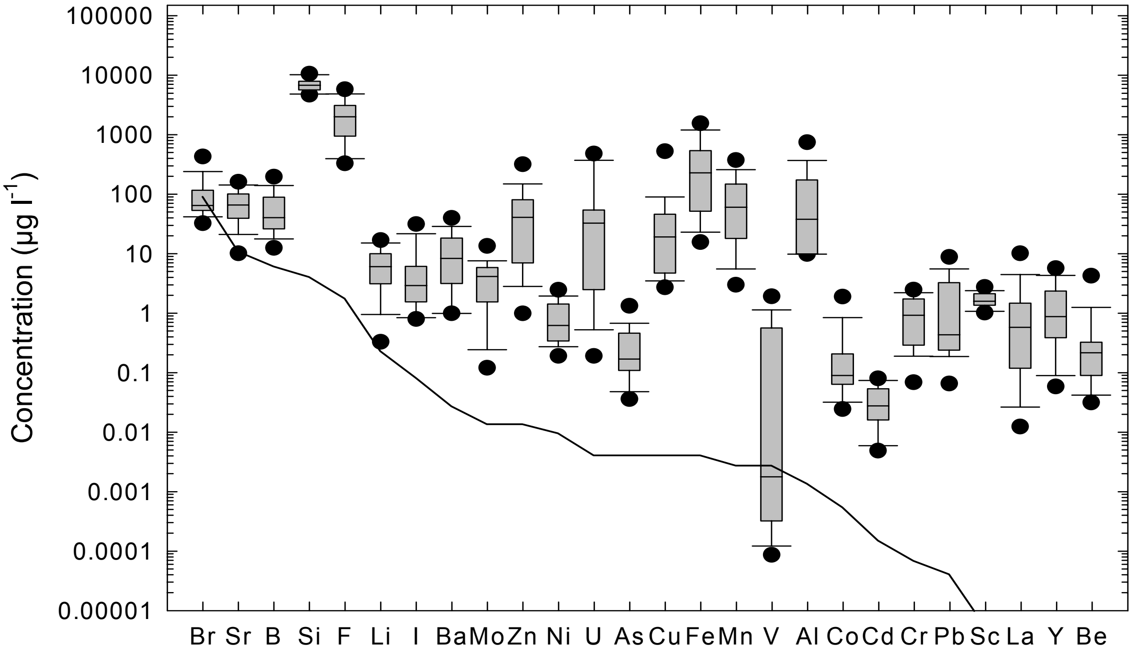


Figure 6.2.2 Boxplots showing minor elements in groundwater samples from the Precambrian Iddefjord granite aquifer, Southeast Norway The drawn line denotes mean ocean water composition normalised to the median chloride value.

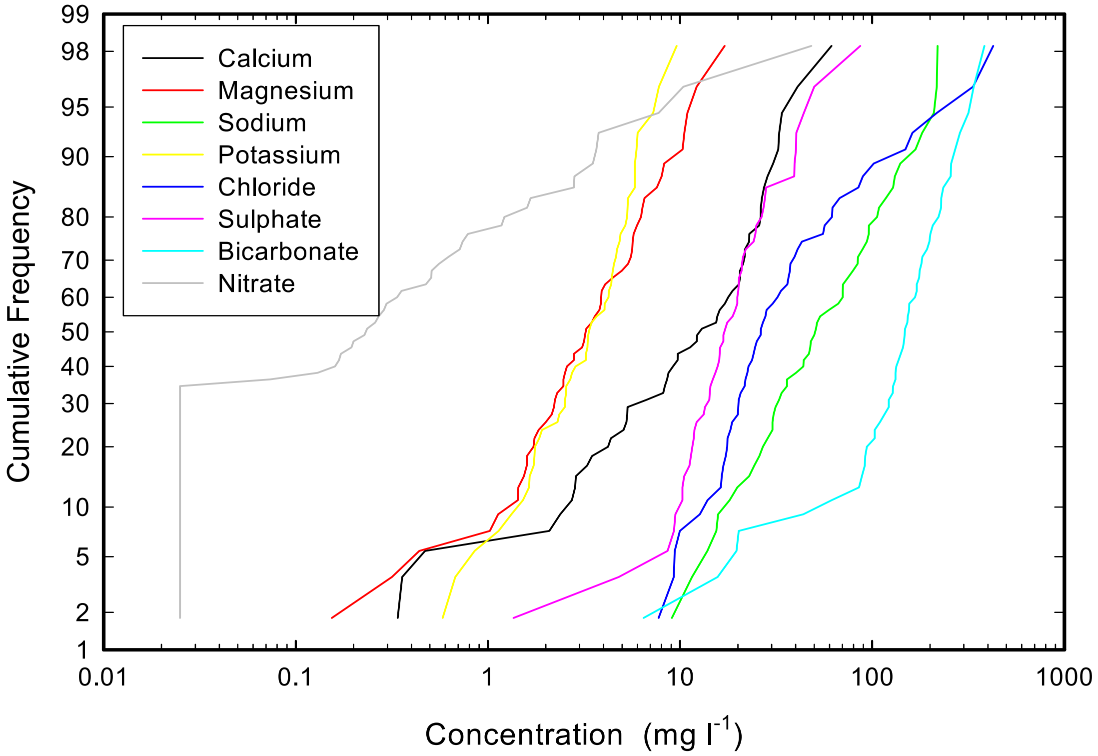


Figure 6.2.3 **Probability plot of major elements in groundwater samples from the Precambrian Iddefjord granite aquifer, Southeast Norway.**

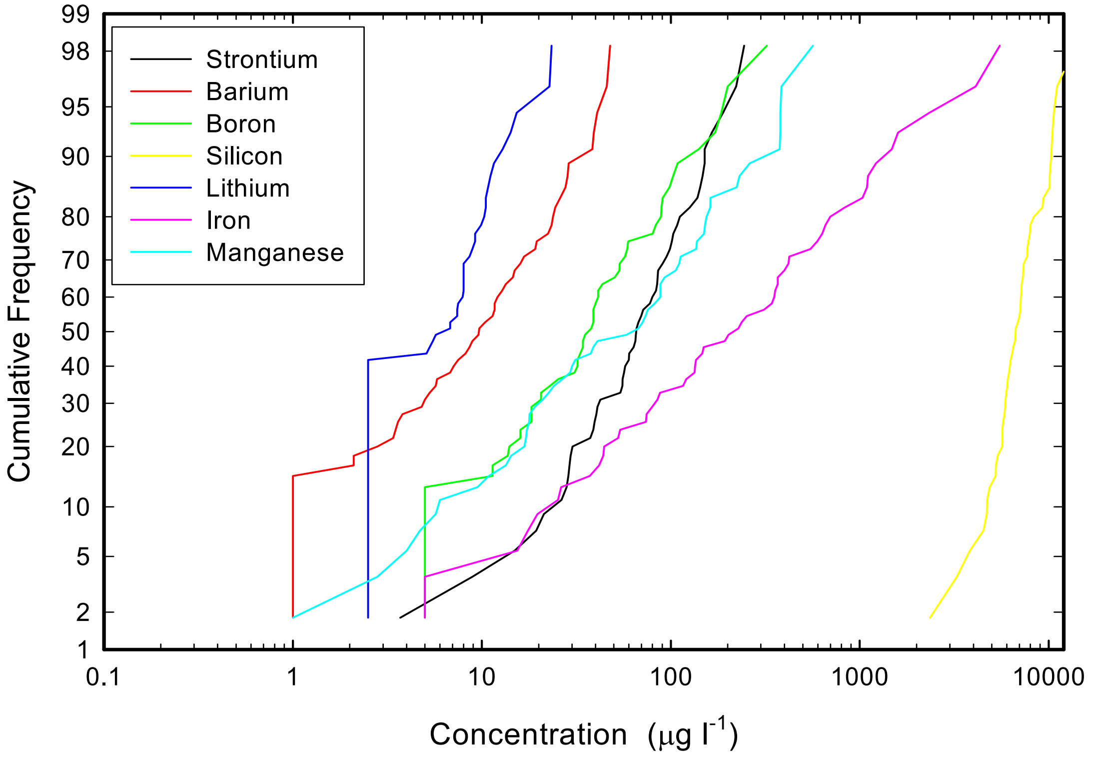


Figure 6.2.4 **Probability plot of selected minor and trace elements in groundwater samples from the Precambrian Iddefjord granite aquifer, Southeast Norway.**

6.2.7 Regional variations

Major elements, Fe and Mn concentrations and pH in wells on the Hvaler islands (n=12) and in wells on the mainland (n=45; data from Banks et al., 1998b) have been compared. The samples from the Hvaler islands seem to have somewhat higher median values of Na, Cl and SO_4 reflecting a stronger marine influence, but the differences are not significant on a 95% confidence interval. A higher median value of Fe concentrations (not significant) for the island samples may indicate more reducing conditions. The median values are similar for the remaining major elements, Mn and pH.

6.2.8 Temporal variations

No consistent data on temporal variations exist from the area.

6.2.9 Summary

The data presented from the Precambrian Iddefjorden granite aquifers show that the natural baseline quality is generally problematic from a drinking water perspective. The chemical summary (Appendix 2) indicates that the baseline for several parameters is above Norwegian and EU MAC and guideline values. The main elements where baseline concentrations are likely to exceed this value include Rn, F, Al, B, (Cu), F, Fe, Mn, (Zn) and potentially NO_3 where agriculture has had a local impact on groundwaters. Beryllium and U may be of concern, but no limits for these elements have been set at either national or European level. High Fe and Mn are present where the groundwaters have become relatively reducing. These problems are of aesthetic and practical concern related to colour and bad taste of the water, staining of laundry and sanitary goods and to the effect of mineral precipitation which may cause clogging of boreholes.

6.3 PRECAMBRIAN ANORTHOSITES

6.3.1 Introduction

The Egersund anorthosites are classified under lithological group 93 (Autochthonous Precambrian charnockite to anorthosites) in NGU's digital 1:3 million bedrock map (Sigmond, 1992). This aquifer is chosen because the mineralogy and geochemistry of the bedrock is relatively simple and homogeneous, and because, in contrast to the granites, it contains only small amounts of most trace elements. Like most boreholes in hard rock aquifers, the boreholes supply water for single households and farms only. The Egersund anorthosite province is part of the Rogaland igneous complex of Middle Proterozoikum age. Dating of the anorthosites using Rb-Sr and U-Pb zircon showed a clustering of ages in the range 900-950 million years old (Ashwal, 1993).

6.3.2 Study area

Egersund is situated on the southwestern coast of Norway, south-east of Stavanger in Rogaland County. The bedrock exhibits very little Quaternary cover and is relatively fresh at outcrop due to glacial scouring up until ~10 000 years ago. The relative uplift during Holocene is less than 20 m (Selmer-Olsen, 1980).

6.3.3 Hydrogeology

There are few existing data on borehole yields, but similar lithologies in the Caledonian mountain range have a median yield of 310 L h^{-1} and a median normalised yield of 5.1 L h^{-1} per drilled metre (Morland 1997). The median borehole depth is 71 m. This is one of the lowest normalised yields among the different lithological groups. In the current data-set the median borehole depth is 80 m, but the range spread from 28 m to 165 m.

6.3.4 Aquifer minerals

The Egersund province comprises three large massif-type anorthositic bodies. The Egersund-Ogna body is chemically monotonous and has a rock composition of coarse-grained, homogeneous, 1-3 cm plagioclase crystals, with sub-ophitic aggregates and megacrysts of plagioclase and high-Al orthopyroxene (Duchesne & Maquil, 1987). The Håland-Helleren body consist of folded and foliated anorthosite and leuconorite in various proportions in the Håland unit, while the Helleren unit is dominated by coarse-grained anorthosite with leuco-noritic parts and giant Al-rich orthopyroxenes. The Åna-Sira body further south is similar to the Helleren massif but also contains two large ilmenite-norite lenses. The whole province is intruded by diabase dykes in a WNW-ESE system (Duchesne & Michot, 1987). Leuconorite also consist of plagioclase and orthopyroxene, but with a somewhat higher proportion of orthopyroxene than the anorthosites. The plagioclase has an anorthite content between 40 and 45 wt% and contains less than 1% K_2O. The orthopyroxene has a Fe/Mg ratio of 0.23-0.33 and an Al_2O_3 content of 7-9% (Duchesne & Maquil, 1987).

6.3.5 Hydrochemical characteristics

A summary of the chemical data is presented in Appendix 2, which includes minimum and maximum values, median and “upper baseline” values based on the 95th percentile.

The range of pH in the Precambrian Egersund anorthosite groundwaters is from 6.66 to 9.58. Most of the samples plot between 7.75 and 8.25 with a median value of 8.05. Dissolved oxygen has not been measured. During a resampling of 9 of the boreholes Frengstad (*in prep.*) reported Eh values between 170 and 270 mV except for the high pH boreholes were the measured Eh values were 70-100 mV. No smell of H_2S was found.

Boxplots are shown for the major elements in Figures 6.3.1. Sodium concentrations show a relative increase over the marine value, compared to Cl, indicating a significant component of Na derived from weathering of the soils and rocks or from ion exchange. The rock and soil weathering contribution to water chemistry is not as pronounced as for the Iddefjorden granite which is also reflected in a somewhat lower alkalinity (HCO_3 concentration). The other major elements show a similar behaviour. The excess Na is dominantly derived from plagioclase feldspar. Calcium is also derived from plagioclase or from calcite. Excess Mg comes from the weathering of pyroxene and SO_4 from pyrite oxidation (with a component from dry deposition). There is a relatively small increase in K compared to seawater composition, probably originated from the accessory amounts in the plagioclase or from agricultural contamination together with NO_3. The median value for NO_3 of 5.54 mg l^{-1} is substantially higher than in the nation-wide bedrock groundwater data set where the median value of NO_3 was 0.46 mg l^{-1}. Despite a large range (<0.17 – 46.2 mg l^{-1}), only one value exceeded the current Norwegian MAC value of 44 mg l^{-1} (for comparison the EU MAC is 50 mg l^{-1}). The generally higher NO_3 concentrations in the Egersund area might be due to more intensive agricultural activity and/or to oxidising groundwater inhibiting the reduction of the NO_3 compound to N_2. (Relatively low Fe and Mn concentrations support the latter explanation). An alternative explanation might be the mild winter climate in this area compared to most of Norway. Banks et al. (1998b) have proposed that the generally low concentrations of nitrate in groundwater compared to continental Europe are due to cold winters with low microbial activity. Thus, little nitrification and leaching of nitrogen from bare agricultural soils occurs. In addition, winter recharge is low due to frozen soils.

Selected minor elements are shown on Figure 6.3.2. Fluoride concentrations are very low, indicating only minor sources in the bedrock or the fracture minerals. The high pH, low Ca groundwaters form geochemical environments ideal for high F concentrations, but only one sample had a F concentration slightly above the detection limit of 0.05 mg l^{-1}. The median values of Fe and Mn respectively are among the lowest of the lithological groups. This indicates relatively high dissolved oxygen and oxidising conditions. Iron and Mn are well correlated (r=0.87), but there is practically no correlation of these element concentrations with well depth. Aluminium concentrations are also generally low, with a median value of 0.014 mg l^{-1}, and no samples exceed the Norwegian MAC concentration of 0.2 mg l^{-1}. The Precambrian anorthositic groundwaters are depleted in many trace elements, such as Be, Cd, Hg, Pb, U, Th, (and thereby Rn), Tl and rare earth elements compared to bulk Norwegian bedrock groundwaters (Frengstad et al., 2000). Other metals (e.g. Cu, Cr, Ni and Pb) are found at low concentrations.

Probability plots for major elements are shown in Figure 6.3.3. The distribution of the different elements and their different sources and behaviour are highlighted as differences in shape of the individual curves. Chloride and SO_4 show roughly linear trends (Figure 6.3.3). Calcium, Mg, HCO_3 and probably K show a tailing at the low end which indicate groundwater samples with short residence time and thus low concentrations of elements derived from weathering. The vertical section of the K curve represents samples below detection limit. Potassium is not an important element in the common minerals in the area. The lowest Ca concentrations may also represent high pH samples were Ca has been removed by calcite precipitation or cation exchange with Na (Frengstad & Banks, 2000). The Na trend exhibits a tailing at the high end representing mature groundwater with long residence time or conceivably indicating cation exchange with Ca. A tailing at the low end is also seen for NO_3. The distinct change in slope on the plot at around 1-2 mg l^{-1} NO_3 may possibly represent a change from a baseline value to groundwaters which show the effects of agricultural pollution.

Probability plots for selected minor and trace elements are shown in Figure 6.3.4. The Fe and Mn curves show a tailing at the high end indicating relatively reducing conditions in a few boreholes. A total of 40% of the samples exhibit Fe concentrations below the detection limit as shown with the vertical section of the curve. The distribution of the lower values would probably show a similar pattern as the Mn distribution.

6.3.6 Depth variations

No consistent data on depth variations exists from the area. Spot tests of the major elements reveal very weak or no correlation between well depth and element concentrations of Na (r=0.27), Ca (r=0.02), Mg (r=0.19), K (r=0.11), Cl (r=0.05), SO_4 (r=0.37), NO_3 (r=0.15), HCO_3 (r=0.36) respectively.

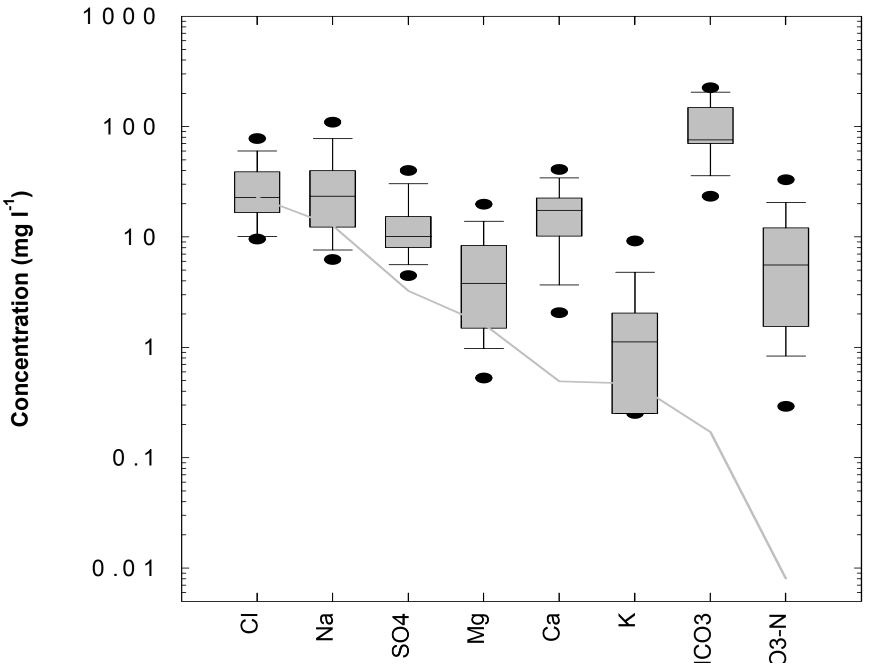


Figure 6.3.1 Boxplots showing major elements in groundwater samples from the Precambrian Egersund anorthosite aquifer, Southwest Norway. The drawn line denotes mean ocean water composition normalised to the median chloride value.

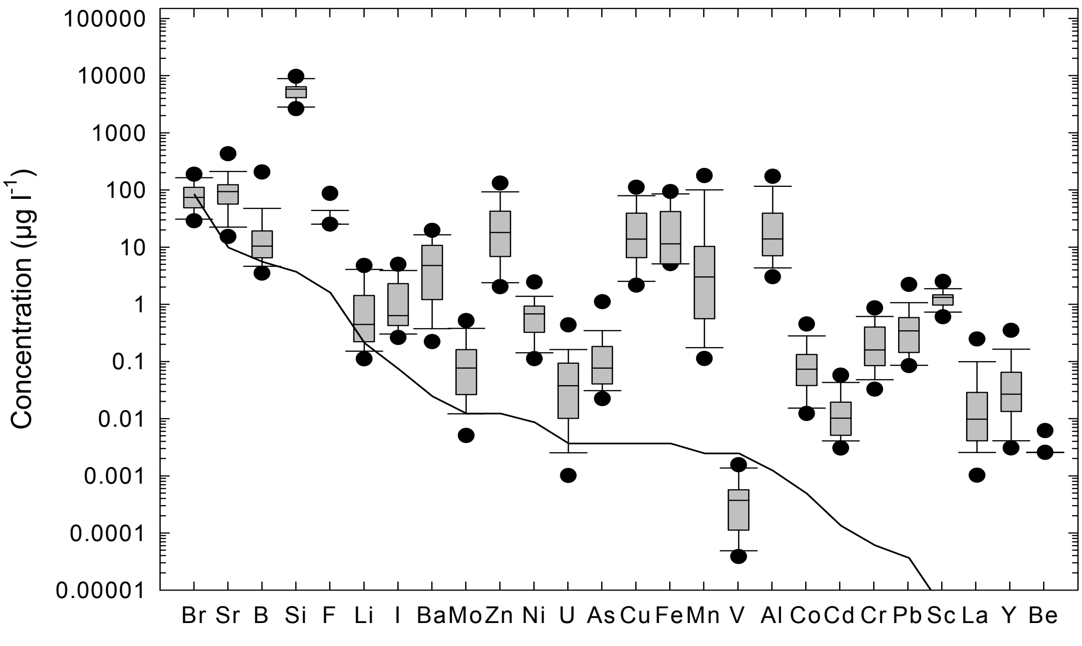


Figure 6.3.2 Boxplots showing major elements in groundwater samples from the Precambrian Egersund anorthosite aquifer, Southwest Norway. The drawn line denotes mean ocean water composition normalised to the median chloride value

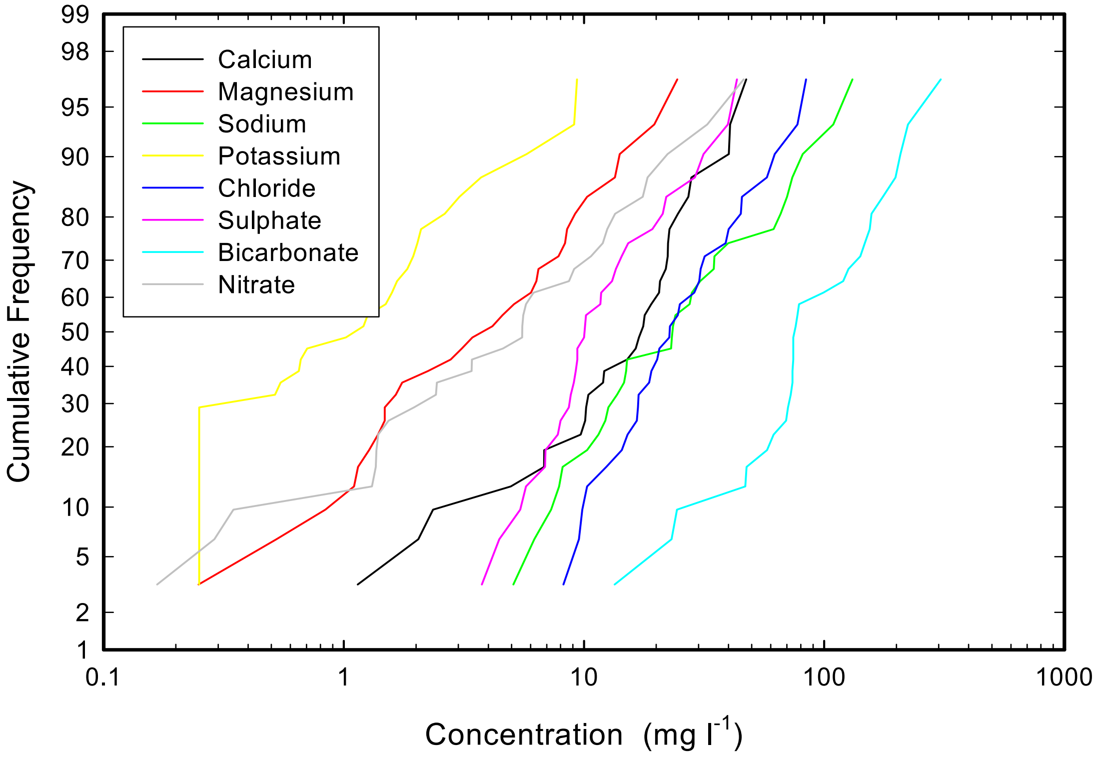


Figure 6.3.3 Probability plot of major elements in groundwater samples from the Precambrian Egersund anorthosite aquifer, Southwest Norway

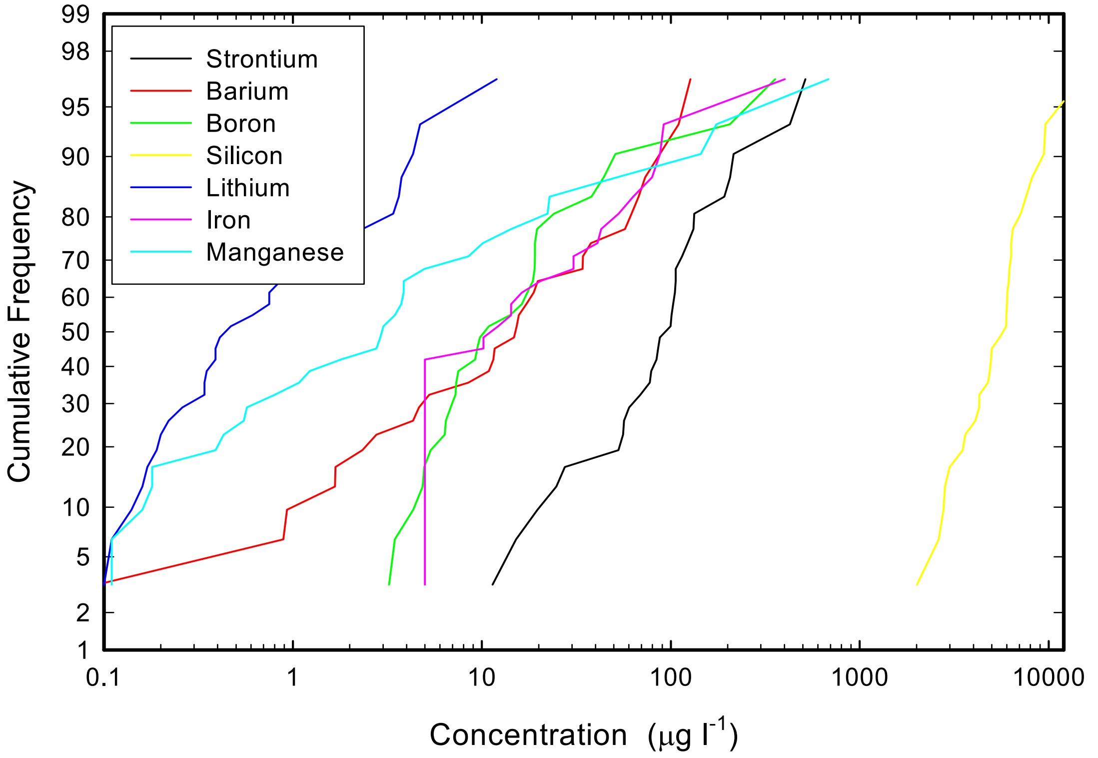


Figure 6.3.4 Probability plot of selected minor and trace elements in groundwater samples from the Precambrian Egersund anorthosite aquifer, Southwest Norway

6.3.7 Regional variations

The geographical distribution shows a decreasing trend in Cl and Na with distance from the coast. The highest pH values are found in boreholes near the coast. The K concentrations also seem to be higher at the coast.

6.3.8 Temporal variations

No consistent data on temporal variations exists from the area.

6.3.9 Summary

The data presented from the Precambrian Egersund anorthosite aquifer show that the natural chemical quality is generally good. The chemical summary (Appendix 2) indicates that the baseline for most parameters is below the Norwegian and EU MAC and guideline values. The Precambrian anorthosites of Norway represent, in many aspects, a counterpart to the Precambrian granites. The melting point of anorthosite is relatively high and as the magma cools, the mineral assemblage will be continuously differentiated. Most incompatible elements are thus enriched in the later products of this chemical differentiation, which are often of granitic composition. The elements where baseline concentrations may exceed the drinking water limits are, Fe and Mn under reducing conditions in the groundwater, and NO_3 where agriculture has had an impact on local groundwaters.

6.4 LOWER PALAEOZOIC METASEDIMENTS

6.4.1 Introduction

The Lower Palaeozoic (Cambro-Silurian) metasediments of the Caledonian mountain chain and the Oslo region (lithological group 74 in NGU's digital 1:1 million bedrock map (Sigmond 1992)) comprise 22 bedrock entities of different lithologies. This group of aquifers are chosen as they represent a petrological and geochemical contrast to the igneous rock aquifers in Norway. They are also time-equivalent and to some degree petrologically related to the Ordovician/Silurian sedimentary rock aquifers in Wales. Unfortunately, the resolution of the digital bedrock map is too coarse and the hydrogeochemical data set does not provide enough data to select only (meta-)mudstones from a restricted geographical area. To what extent it is relevant to apply the baseline concept upon such a spatially and petrologically widespread group of aquifers may thus be a question for further discussion.

6.4.2 Study area

Rocks of this lithological group are present in many localities of southern Norway. They cover large parts of the two counties of Trøndelag, are widespread in the county of Oppland and are found around Oslo, Stavanger and north and east of the Hardanger Fjord. Approximately a quarter of the samples in this data set are derived from inland valleys, with low precipitation (~300 mm/year) due to rain shadow effect from the adjacent mountains. The other samples are from the precipitation-rich western coast (~3000 mm/year) to areas with more moderate precipitation around Oslo and Trondheim (~700 mm/year and ~1100 mm/year, respectively).

6.4.3 Hydrogeology

These rocks as a group yield similar amounts of water to the Precambrian granites with a median yield of 600 l h^{-1} and a median normalised yield of 11.4 l h^{-1} per drilled metre. However, within the group there are significant differences between the bedrock entities. The massive limestones of the Oslo area have 7 times higher median normalised yield (35 l h^{-1} pr drilled metre) than the phyllites of the Bergen area (4.7 l h^{-1} pr drilled metre; Morland 1997).

6.4.4 Aquifer minerals

As this is a very heterogeneous group of rocks, any attempt at an adequate mineralogical description will be incomprehensive. The group comprises limestone (calcite), sandstone (quartz, feldspar, rock fragments), greywacke (quartz, feldspar, rock fragments, clay minerals), phyllite (chlorite, muscovite), mica schist (biotite), slate (various minerals) and alum shales (various minerals, iron sulphide, organic carbon).

6.4.5 Hydrochemical characteristics

A summary of the chemical data is presented in Appendix 2, which includes minimum and maximum values, median and “upper baseline” values based on the 95th percentile.

The lowest and highest pH values measured in the groundwaters from Cambro-Silurian metasediments of the Caledonian mountain chain and the Oslo region are 6.74 and 9.43 respectively. Most of the samples plot between 7.75 and 8.30 with a median value of 8.13. Dissolved oxygen and redox potential (Eh) have not been measured.

Boxplots are shown for the major elements in Figures 6.4.1. Sodium concentrations show a relative increase compared to Cl indicating a significant component of Na derived from weathering of the soils and rocks. The other major elements show a similar behaviour. The excess Na and K are probably derived from feldspars from epiclastic sedimentary rocks, while K is probably also from micas in the same rocks. Calcium is probably derived from dispersed calcite in the sediments, from calcite veins and from the limestones. Excess Mg is derived from chlorite and other mica minerals in the phyllites and shales and SO_4 from pyrite oxidation (with a minor component from dry deposition). The median values of Ca, Mg, SO_4 and HCO_3 are higher than the corresponding median values in the nation-wide bedrock groundwater data set (Banks et al., 1998b). Both the median and the maximum concentrations of NO_3 in rock group 74 are close to the same values in the national data set.

Selected minor elements are shown on Figure 6.4.2. Fluoride concentrations are generally low with a median of 0.1 mg l^{-1}, but there are many outliers. However, 10 % of the samples exceed the Norwegian MAC value of 1.5 mg l^{-1}. Iron and Mn concentrations have similar distributions to bulk Norwegian bedrock groundwaters (Banks et al., 1988). There is no correlation between Fe and Mn. Aluminium concentrations are generally low with a median value of 0.0037 mg l^{-1}, and there is no violation of the Norwegian MAC concentration for Al of 0.2 mg l^{-1}. The median values of many trace element concentrations in rock group 74 groundwaters are close to the median values of the nation-wide data set of selected Norwegian bedrock groundwaters (Frengstad et al., 2000) but they are depleted in Al, Be, Ce, Gd, La, Mo, Y, W, REE, U, Th, (and thereby Rn), and enriched in As, Cs, Ni, and Ta.

Probability plots for major elements are shown in Figure 6.4.3. The plots of Mg and K show a tailing at the low end probably due to different lithological populations. Nitrate also shows a tendency to tailing at the low end, but the curve shows several changes in slope and it is difficult to pinpoint the change from a baseline value to waters which show the effects of agricultural pollution. Calcium, Mg, K and HCO_3 show a steepening of the curve at high concentrations which indicates saturation with respect to calcite ($CaCO_3$) and some immobilisation of K and Mg (secondary clay minerals?). The relatively large spans in Na, Cl and SO_4 concentrations reflect the geographic spread of the samples and varied input of marine ions from precipitation.

Probability plots for selected minor and trace elements are shown in Figure 6.4.4. Most trace elements are far from saturation with respect to mineral phases, and will be expected to increase with residence time. Iron and Mn show a tailing at the high end indicating relatively reducing conditions in a few boreholes. Approximately 25 % of the samples have Fe concentrations below the detection limit as shown with the vertical section of the curve. The distribution of the lower values would probably show a similar pattern as the Mn distribution.

6.4.6 Depth variations

No consistent data on depth variations exist from the area.

6.4.7 Regional variations

A thorough examination of regional variations has not been completed. Map studies of some major and minor elements indicate that F concentrations are higher in groundwater in the Oslo area than in the Caledonian mountain range, probably related to the volcanic activity in the Oslo Rift during Permian time. Chloride, Na, and SO_4 concentrations are higher along the coast than inland due to marine input. There are no low Ca or Fe concentrations in the Stavanger-Hardanger area at the western coast, which is dominated by phyllites and mica schists.

6.4.8 Temporal variations

No consistent data on temporal variations exist from the area.

6.4.9 Summary

The data presented on groundwater from the Cambro-Silurian metasediments show that the natural hydrogeochemical quality is variable and difficult to interpret. This highlights the demand for more detailed studies of the water quality from more specific lithologies and limited areas. The chemical summary (Appendix 2) indicates that the baseline concentrations for most parameters are below Norwegian and EU MAC and guideline values. The elements where baseline concentrations are likely to exceed the drinking water norms are Fe and Mn under reducing conditions in the groundwater and NO_3 where agriculture has had an impact on local groundwaters. Also, F may be of concern.

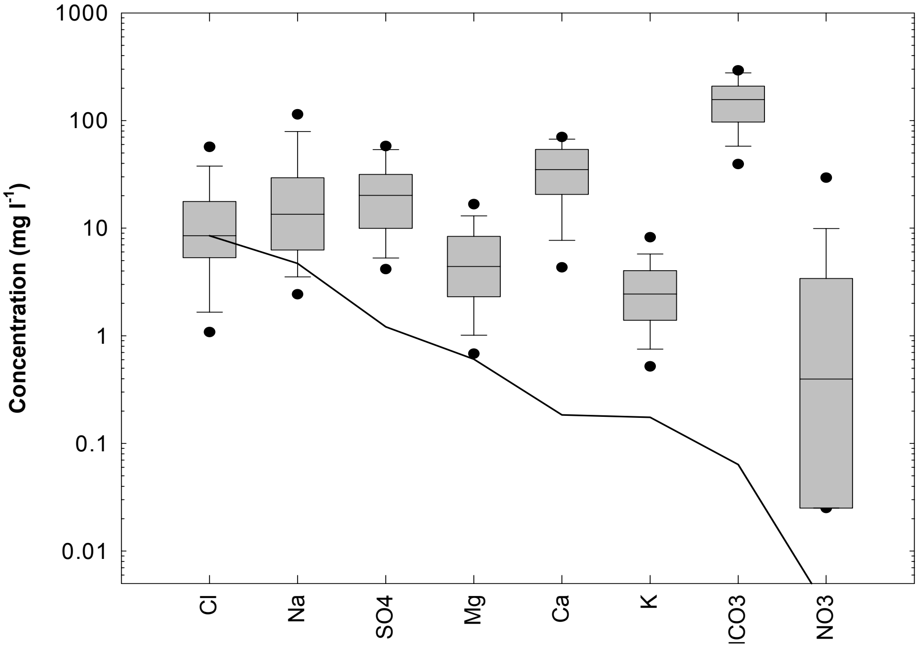


Figure 6.4.1 Boxplots showing major elements in groundwater samples from the Lower Palaeozoic (Cambro-Silurian) metasedimentary aquifers, South Norway. The drawn line denotes mean ocean water composition normalised to the median chloride value.

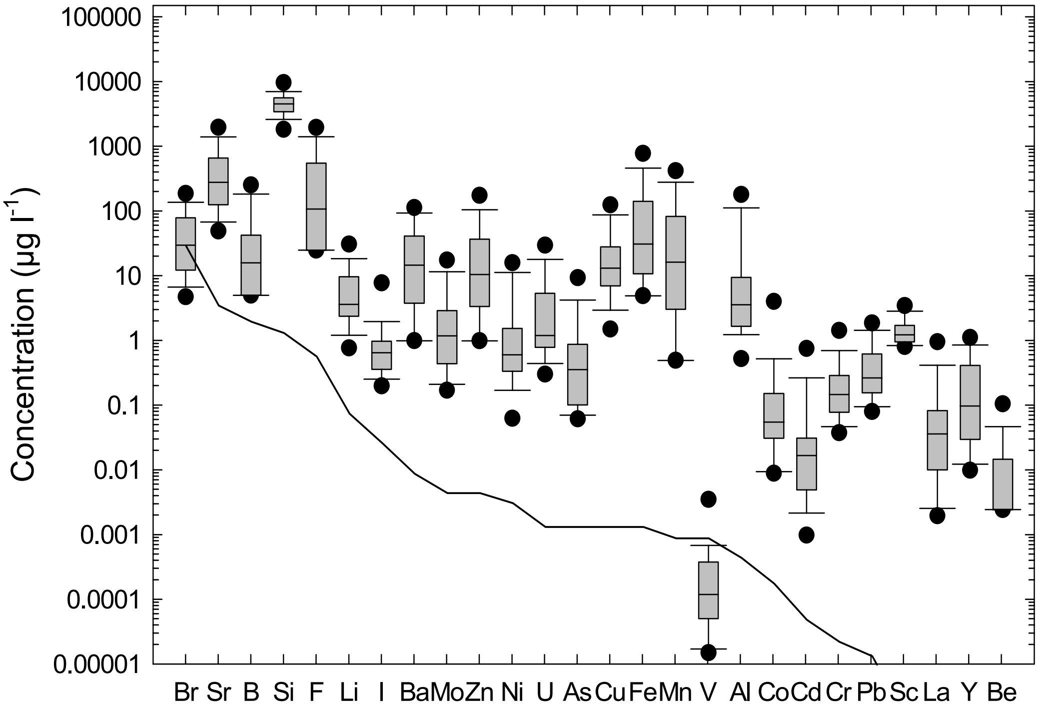


Figure 6.4.2 Boxplots showing major elements in groundwater samples from the Lower Palaeozoic (Cambro-Silurian) metasedimentary aquifers, South Norway. The drawn line denotes mean ocean water composition normalised to the median chloride value

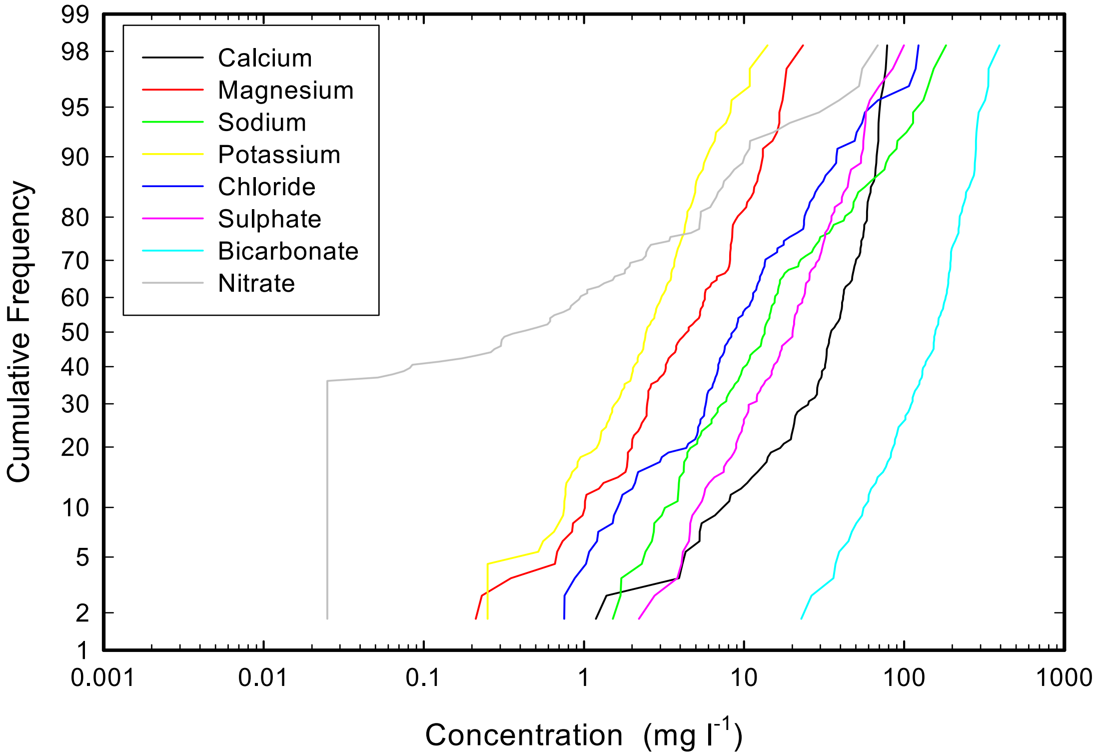


Figure 6.4.3 Probability plot of major elements in groundwaters samples from the Lower Palaeozoic (Cambro-Silurian) metasedimentary aquifers, South Norway

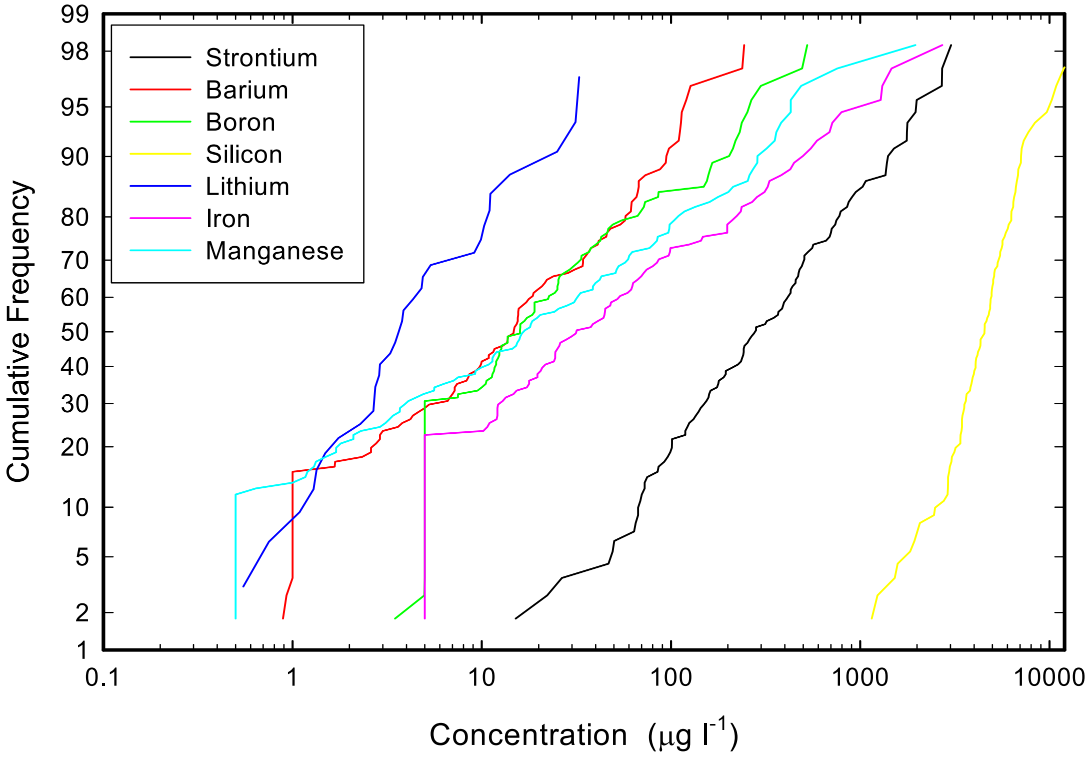


Figure 6.4.4 Probability plot of selected minor and trace elements in groundwater samples from the Lower Palaeozoic (Cambro-Silurian) metasedimentary aquifers, South Norway.

7 COMPARISON OF UK AND NORWEGIAN BASELINE

The main aquifer systems differ significantly between the UK and Norway. The most important aquifers in the UK comprise sedimentary sequences with the majority of abstraction from rocks of Permian to Palaeogene age. In contrast to this, there are few rocks of similar age in Norway, and groundwater abstraction is mainly from hard rock aquifers of Precambrian and Palaeozoic age or locally from Quaternary Drift deposits. The baseline characteristics of the selected aquifers from each country have been described in sections 5 (UK) and 6 (Norway). As mentioned previously, minor aquifers have been chosen from the UK in order to compare similar aquifer lithologies to those found in Norway. This section aims to compare and contrast the baseline chemistry between the aquifer units, selected with particular emphasis on the differences between the two countries.

A range of parameters have been selected as being representative of the major elements in groundwater and also minor or trace elements of concern to health or which commonly exceed guideline or admissible concentrations. Concentrations of these parameters have been presented as boxplots (Figures 7.1.9 and 7.2.9) and probability plots (Figures 7.1.1-8 and 7.2.1-8) and are described below.

7.1 MAJOR ELEMENTS AND PH

7.1.1 pH

There is a considerable range in the median values of pH for the different aquifers (Fig 7.1.1, Fig.7.1.9). The dominant control on pH is the acid neutralising capacity of the bedrock, in particular the presence or absence of carbonate minerals. Rocks which have a poor buffering capacity, such as granites, would be expected to have lower pH than carbonate aquifers. However, even small amounts of calcite present in the aquifer will be able to buffer the pH due to the rapid kinetics of carbonate dissolution compared to most other minerals. Aquifers with carbonate minerals present will generally have circumneutral to alkaline pH (depending on initial pCO_2 and closed or open system conditions). Silicate minerals have slower dissolution rates and most basement aquifers world-wide yield typically low- to moderate- pH waters (Bucher & Stober, 2000. Acidity may also be generated through reactions such as sulphide mineral oxidation or denitrification.

The median slightly alkaline pH for the UK Cretaceous chalk and Devonian sandstone aquifers is typical of well-buffered carbonate-bearing aquifers. In contrast, groundwaters from the Permian (Carnmenellis) granite is relatively acidic (median pH of 5.66) indicating a poor buffering capacity, typical of those granites containing unreactive mineral phases. The high pH values typically found in Norwegian aquifers, including those in granite, is very unusual. The pH in the Norwegian groundwaters is significantly higher than that expected and contrasts with the range of values found in the UK aquifers. Approximately half of the Norwegian samples from the nation-wide SPAGBIFF dataset (Banks et al., 1998b) display pH values around 8.1, thought to be due to buffering by the calcium carbonate system at atmospheric CO_2 pressure. Approximately 6 % of the samples even had pH values in the 8.5-9.8 range. One possible explanation for these unusual characteristics may be based on the fact that many (but not all) of the aquifers contained seawater until relatively recently (on a geological timescale) and were not freshened until following the last glaciation c. 10,000 years BP. This freshening of a saline aquifer has led to the loss of Ca due to ion exchange for Na (forming waters of $Na\text{-}HCO_3$ type) and as a consequence the calcite buffering system is inhibited.

The extensive glacial erosion has also removed deep-weathered rocks, leaving fresh unweathered minerals available for circulating groundwater at depths normally used for drinking water wells (60-120 m). These conditions open offer an alternative or additional explanation, namely that pH of the groundwater increase due to hydrolysis of silicates (Toran & Saunders, 1999, Frengstad & Banks, 2000). As groundwater moves deeper along the flowpath, the system becomes closed with respect to atmospheric CO_2.When pH and alkalinity are high enough, Ca is removed from the water phase by precipitation of calcite while Na continues to accumulate. At the stage where the calcium carbonate buffer is exhausted, pH is allowed to increase further above 8.2.

7.1.2 Sodium

Most of the UK aquifers show a small range in Na concentrations (Fig 7.1.2, Fig 7.1.9). The main exception is the Chalk: high concentrations are found in the older groundwaters of confined aquifer due to exchange with porewaters which have not been sufficiently flushed of original connate water. The Chalk aquifer is known to contain more saline water at depth, particularly in lower transmissivity areas of the aquifer. The origin of sodium, whether from water-rock interaction or mixing with connate water, can be assessed by consideration of ratios such as Na/Cl. Although most of the increase in Na in the chalk is of marine origin (either from rainfall or mixing with remnant connate water), high Na/Cl ratios in the confined aquifer points to a significant component from ion-exchange or mineral dissolution reactions. There is a significant range in the Norwegian aquifers and the higher concentrations might be explained as a result of the incursion of seawater prior to the end of the last glaciation and to exchange reactions with Na-enriched clay as a result of this. The Lower Palaeozoic sediments contain the lowest concentrations and these are generally situated away from the coast and, therefore, have been less affected by seawater intrusion. However, there is a considerable range in the concentration of Na (as well as other elements) in this aquifer reflecting the wide range of rock types, areal coverage of sampling and residence time of the groundwaters. Many groundwaters also evolve high Na due to reaction with aquifer minerals such as albite (sodium-rich feldspar), which are commonly major constituents of igneous and metamorphic rocks.

7.1.3 Chloride

The chloride data for UK aquifers show similar trends to that of Na and can be interpreted in a similar manner i.e. mixing with an old marine component (Fig 7.1.3). The high Na concentrations in the Norwegian aquifers are not, in general, matched by high Cl. However, this is consistent with both the alternative suggestion given in 7.1.1 and 7.1.2 above. According to the cation-exchange suggestion, the Norwegian aquifers have generally undergone almost complete freshening. However, previous marine incursions can leave a “chemical” memory in the aquifer, which will continue to influence the evolution of baseline chemistry long after the seawater has been flushed out. This process will continue until a new chemical equilibrium is achieved between fresh recharge water and the Na-enriched clay minerals. In contrast, most UK aquifers only attain $Na\text{-}HCO_3$ compositions after long residence times or in parts of the aquifer close to the coast. However, some aquifers in the UK (Permo-Triassic Sandstones) contain dilute Pleistocene palaeowaters of $Ca\text{-}(Mg)\text{-}HCO_3$ type at depths up to 350 m. In general old, deep groundwaters in the UK often evolve towards Na-Cl compositions due to mixing with more saline water at depth.

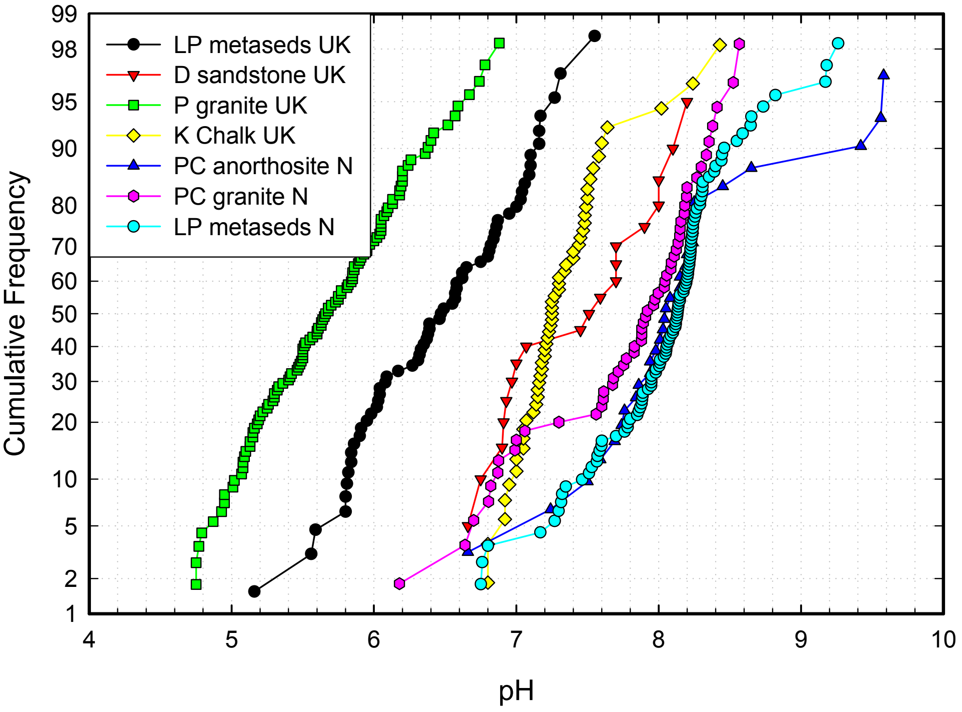


Figure 7.1.1 **Probability plot of pH in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

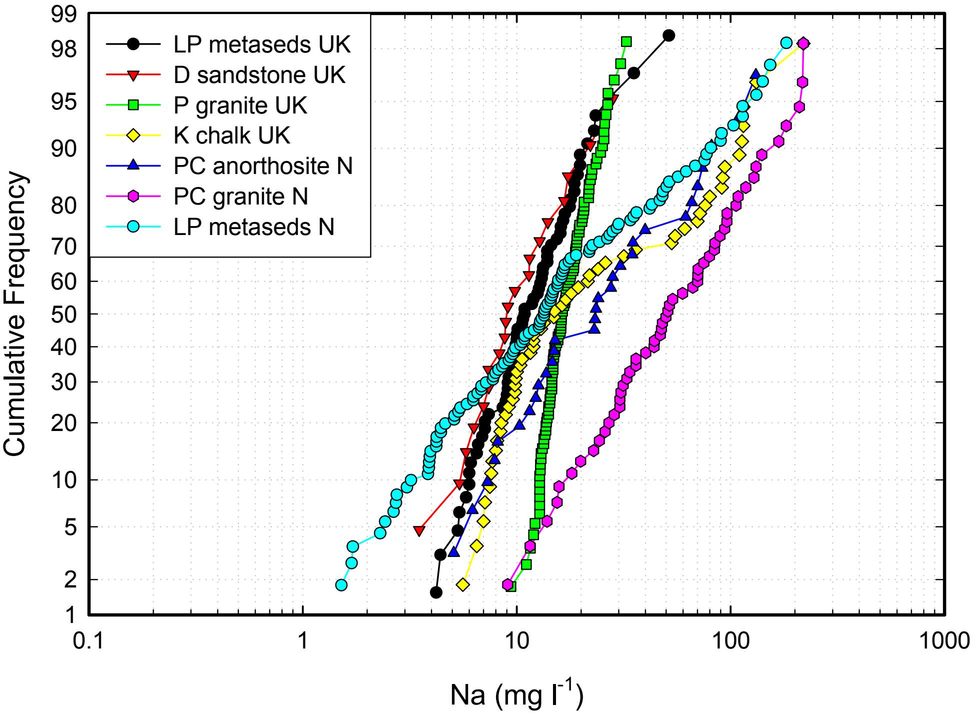


Figure 7.1.2 **Probability plot of sodium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

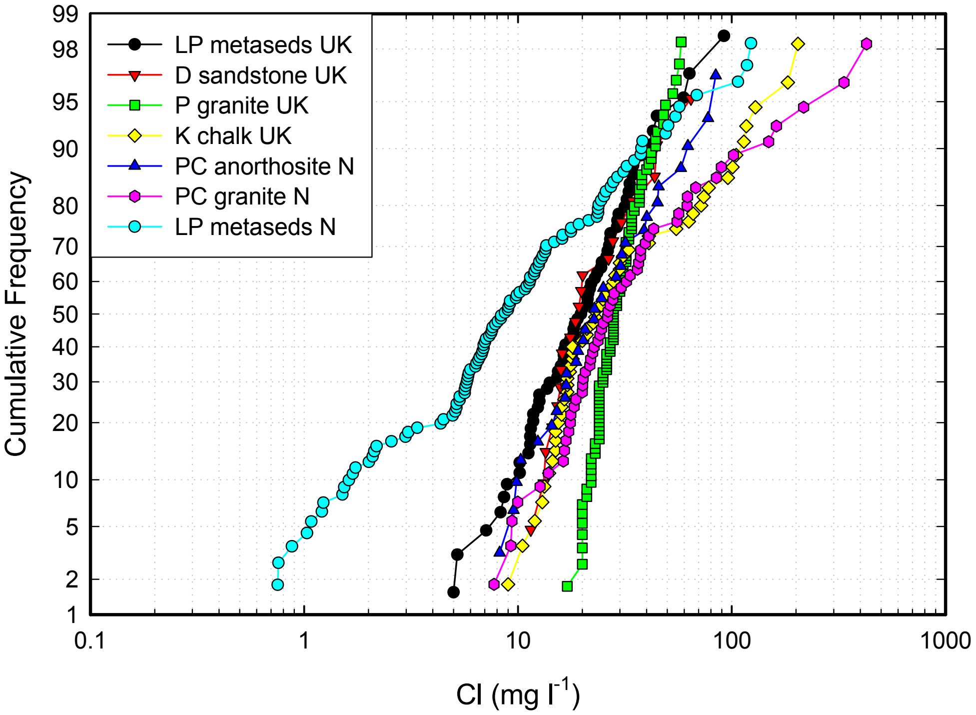


Figure 7.1.3 **Probability plot of chloride concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

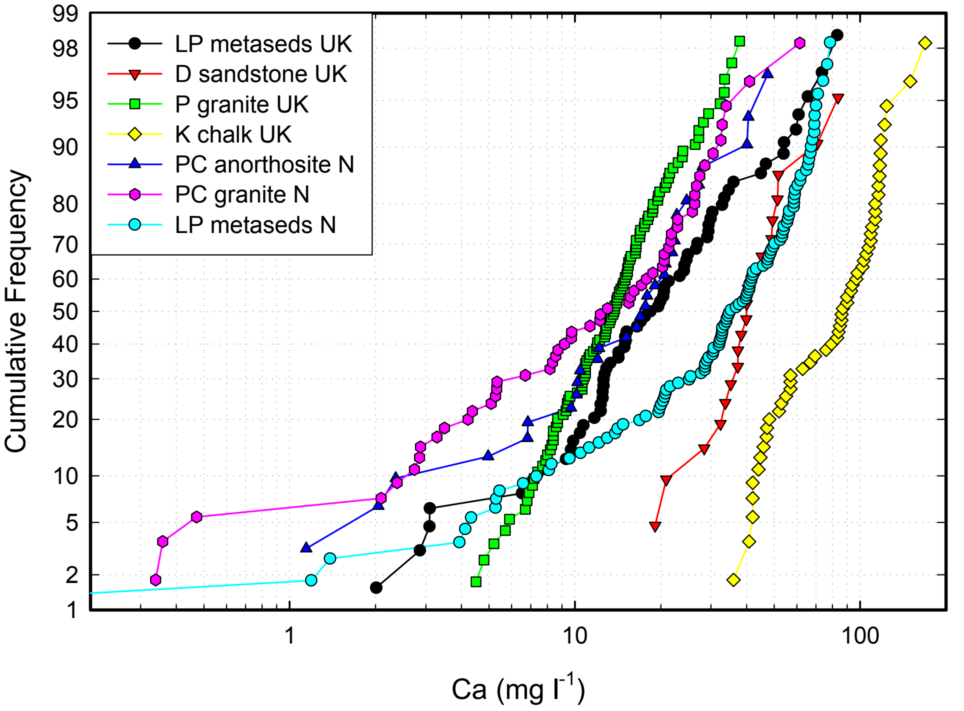


Figure 7.1.4 **Probability plot of calcium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

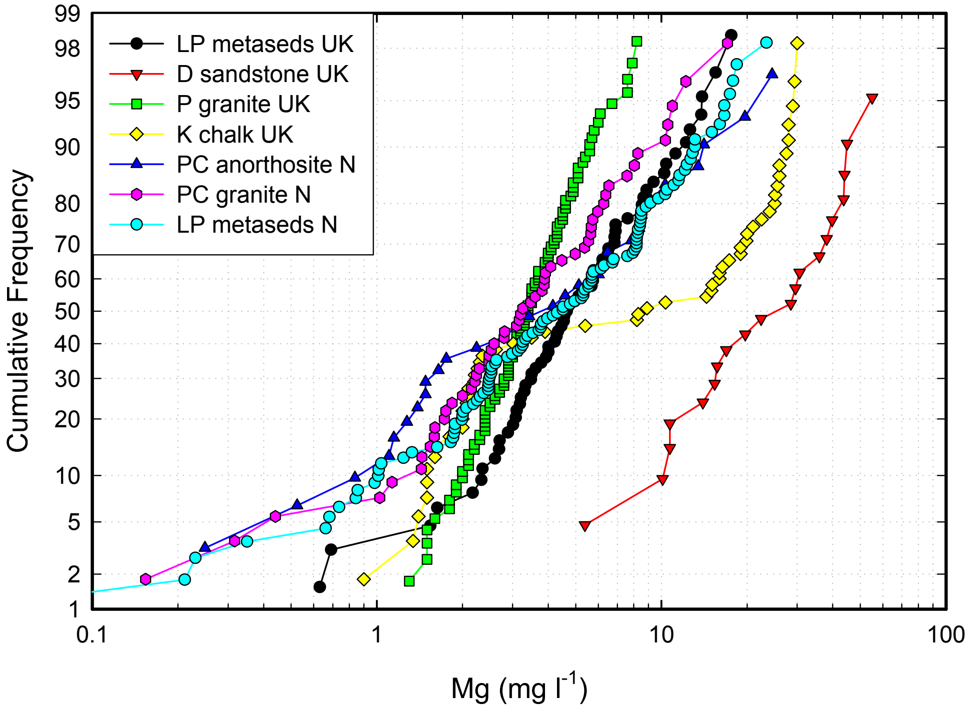


Figure 7.1.5 **Probability plot of magnesium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

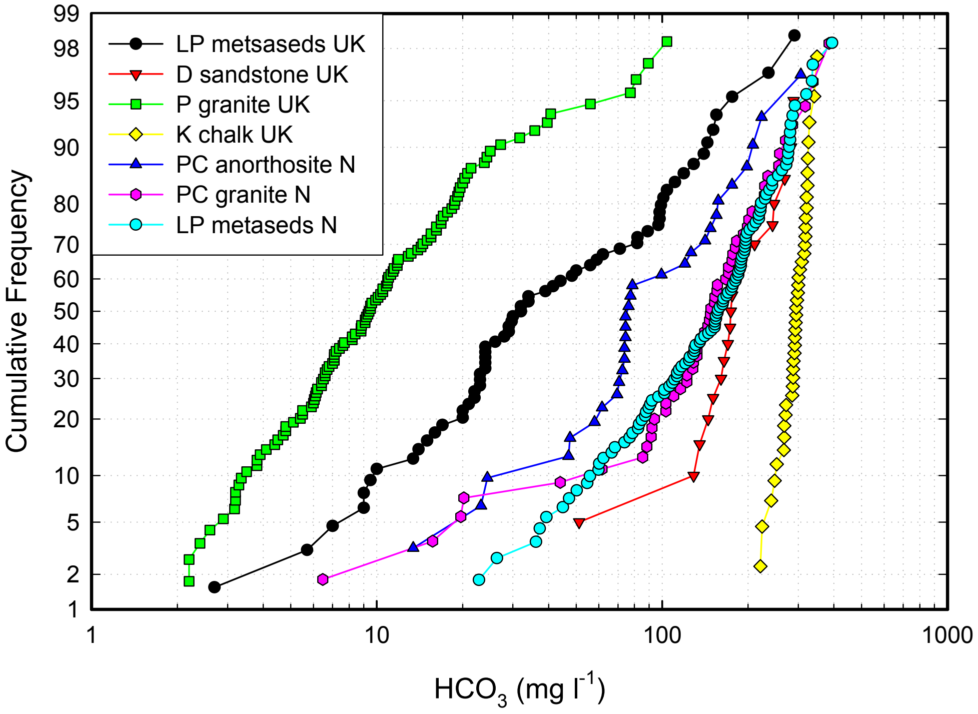


Figure 7.1.6 **Probability plot of bicarbonate concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

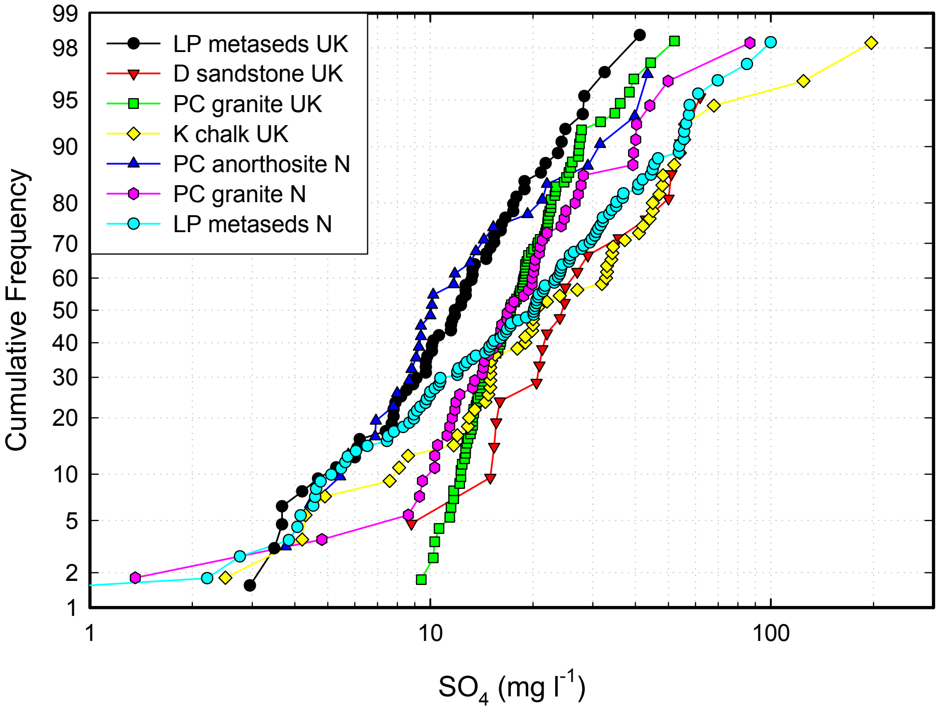


Figure 7.1.7 **Probability plot of sulphate concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

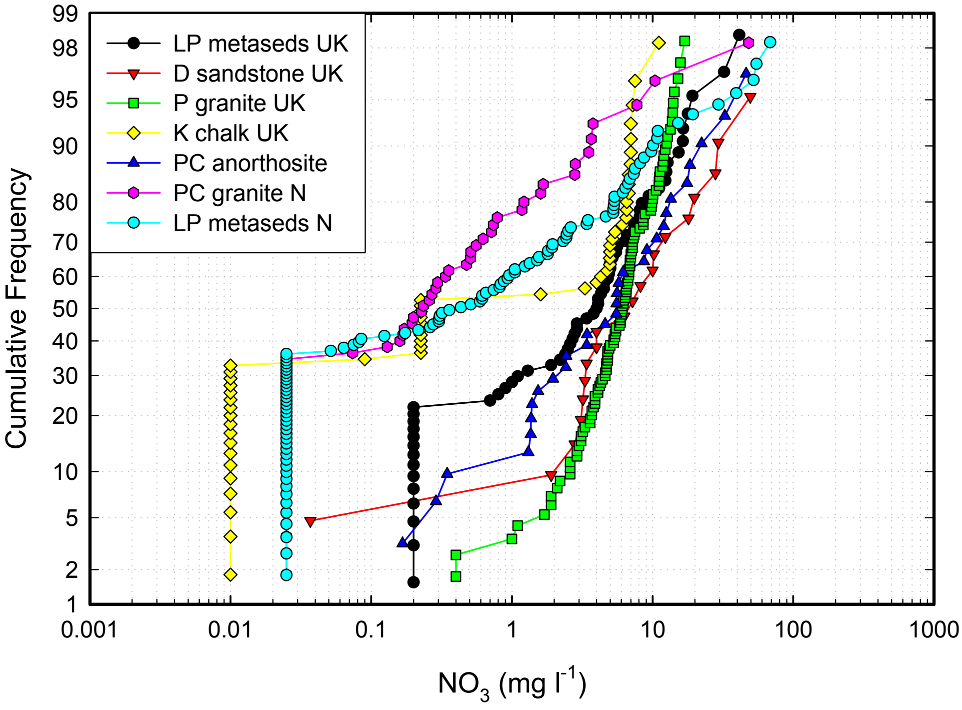


Figure 7.1.8 **Probability plot of nitrate concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

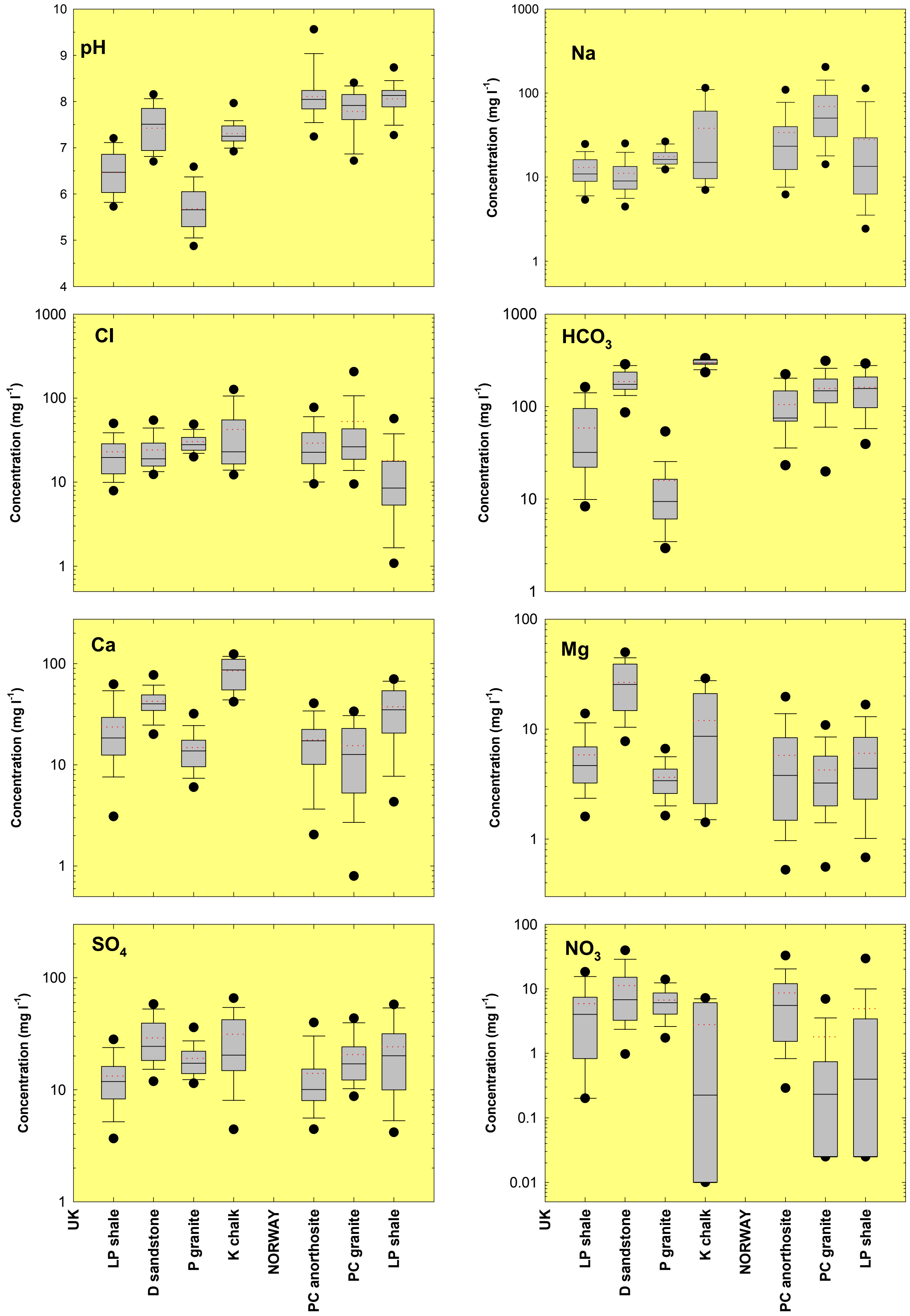


Figure 7.1.9 Boxplots comparing pH and major elements (SO_4, NO_3, Na, Ca, Cl, Mg and HCO_3) in groundwater samples from selected British and Norwegian aquifers.

7.1.4 Calcium

Calcium data for the selected aquifers show considerable variation. However, the lowest median concentrations are found in granite aquifers, which generally contain Ca-poor mineral phases (Fig 7.1.4). The Chalk aquifer of the UK is significantly higher than the others, although the carbonate cemented Devonian aquifer and some groundwaters from the Lower Palaeozoic aquifers reach relatively high concentrations. These higher concentrations are most likely derived from vein calcite present in fractures. An interesting feature of the Norwegian aquifers is the strong skewness at lower concentrations, which is not seen in any of the UK aquifers. Many of these groundwaters are of Na-HCO_3 composition and reflect the loss of Ca due to ion exchange or calcite precipitation as discussed in the previous sections. Although this skewness may in part be related to short residence time, in most waters this cannot be the case because bicarbonate does not show the same pattern.

7.1.5 Magnesium

There is less contrast between the Norwegian and UK aquifers in terms of Mg than many of the other major elements (Fig 7.1.5). The Chalk and Devonian sandstone aquifers of the UK show a slightly different pattern to the other aquifers. The Devonian aquifer contains dolomite and this is clearly reflected in the much higher Mg concentrations in these groundwaters. The Chalk aquifer shows a bimodal distribution in the Chalk aquifer with the low and high concentrations being found in the unconfined and confined aquifers respectively. The high concentrations present in the confined groundwaters are a consequence of incongruent dissolution of the chalk matrix once saturation with respect to calcite has been reached. The skewness noted for Ca in the Norwegian groundwaters is also reflected in Mg, which favours the likelihood that cation exchange is the dominant process.

7.1.6 Bicarbonate

The high HCO_3 of the Chalk and Devonian sandstone groundwaters is similar to that noted for Ca and reflects the carbonate nature or carbonate cement in the aquifer (Fig 7.1.6, Fig 7.1.9). The Carnmenellis granite, and to a lesser degree, the Lower Palaeozoic groundwaters of the UK, contain low HCO_3. These aquifers are poorly buffered in terms of alkalinity and must, therefore, be seen as susceptible to pollution, particularly acidification. Bicarbonate in the Norwegian groundwaters is generally moderately high. This is even the case in the granite aquifer whose groundwaters have, surprisingly, significantly higher bicarbonate than in the anorthosite aquifer. This implies that either the granites contain significant amounts of a reactive mineral phase (e.g. carbonates) or have had a much longer residence time. Although HCO_3 in the granite groundwaters is similar to that in the Lower Palaeozoic Norwegian groundwaters, Ca in contrast is much less. A combination of calcite dissolution followed by ion exchange is the most likely explanation, but silicate weathering followed by calcite precipitation cannot be excluded. These groundwaters are not susceptible to acidification in the short term, but more work is required to understand their geochemical evolution in order to assess the effects of long-term acidic inputs.

7.1.7 Sulphate

The distribution of SO_4 is similar for all aquifer groundwaters, showing an approximately linear pattern on cumulative probability plots (Fig 7.1.7). The bias at lower concentrations for the Chalk and Precambrian granite is most likely related to sulphate reduction in the deeper older groundwaters. The anorthosite of Norway and Lower Palaeozoic groundwaters of Wales have slightly lower median than the others, otherwise SO_4 shows little variation between the different aquifers. The dominant source of SO_4 in these aquifers is likely to be from the oxidation of sulphide minerals with a small input from atmospheric sources. High concentrations in the Chalk (> 95 percentile) are likely to be related to agricultural pollution.

7.1.8 Nitrate

The median concentrations of NO_3 are all relatively low, but show different distributions (Fig. 7.1.8). In the Norwegian aquifers, the median for the anorthosite groundwaters is significantly higher than for the granite and the metasediments. The higher concentrations in these groundwaters probably represent pollution from agriculture. The low median concentrations in Norway in general are thought to be a reflection of the cold winter climate with low microbial activity in the soils, thus limiting nitrification and leaching from bare agricultural soils. Because of snow and ice cover, groundwater recharge is also normally limited during this critical period (Banks et al., 1998). The median concentrations in the UK aquifers are similar (c. 4-7 mg l^{-1}), except for the Chalk which is low. Nitrate concentrations of around 4-5 mg l^{-1} are most likely to represent baseline with higher concentrations being due to agricultural or other forms of pollution. The low median concentration in the Chalk is due to nitrate reduction in the confined parts of the aquifer. The low nitrate in the hard rock aquifers may partly be due to nitrate reduction in the soil, particularly in waterlogged soils or wetlands which promote reducing conditions.

7.2 MINOR AND TRACE ELEMENTS

7.2.1 Iron

The solubility of Fe is strongly controlled by the Eh and pH of groundwater, being more soluble in reducing and/or acidic conditions. The median concentrations are below the EU MAC except for the Norwegian granite aquifer (median of 233 µg l^{-1}), but the groundwaters generally show a large range (Fig 7.2.1, Fig 7.2.9). Higher concentrations in the Carnmenellis granite reflect the relatively acidic nature of the groundwaters, whilst the high concentrations in most other aquifers are due to moderately reducing conditions (the pH is too high for the waters to contain significant Fe). Although Fe is relatively high in the solid phase (as an oxide cement) of the red sandstones of the Devonian aquifer, DO is present which limits concentrations to a few µg l^{-1} dissolved Fe.

7.2.2 Manganese

The distribution of Mn is similar to that of Fe (Fig 7.2.2). Groundwater from the Precambrian granite again contains the highest median concentration and the Devonian sandstone aquifer likewise very low concentrations. However, the Chalk groundwaters contain relatively low concentrations, reflecting low rock concentrations and limited mobility. The large range in baseline concentration in most aquifers reflects the large natural range in redox conditions.

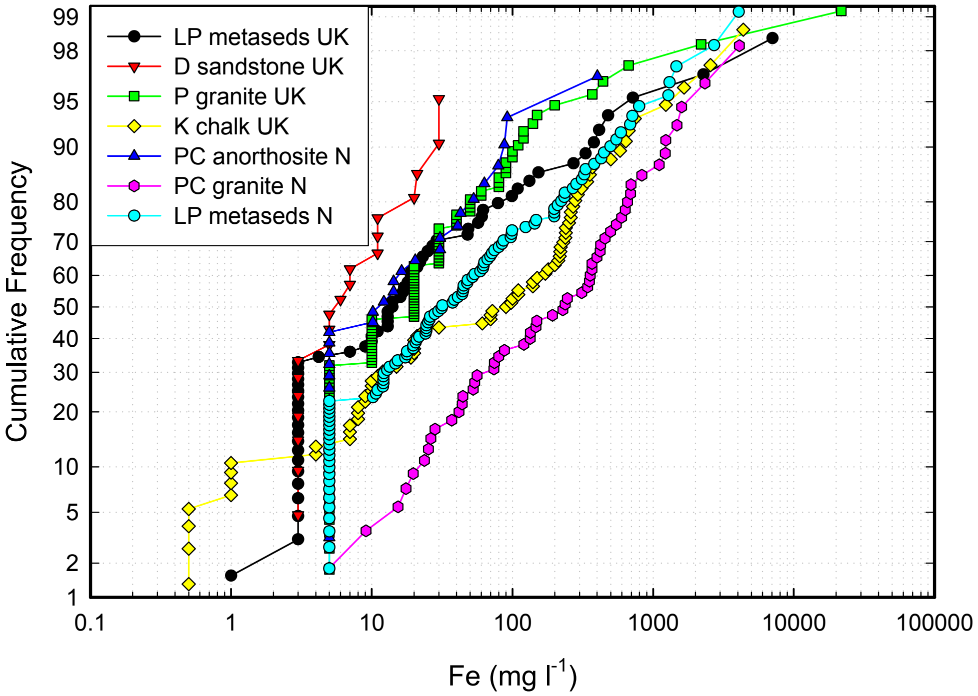


Figure 7.2.1 Probability plot of iron concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.

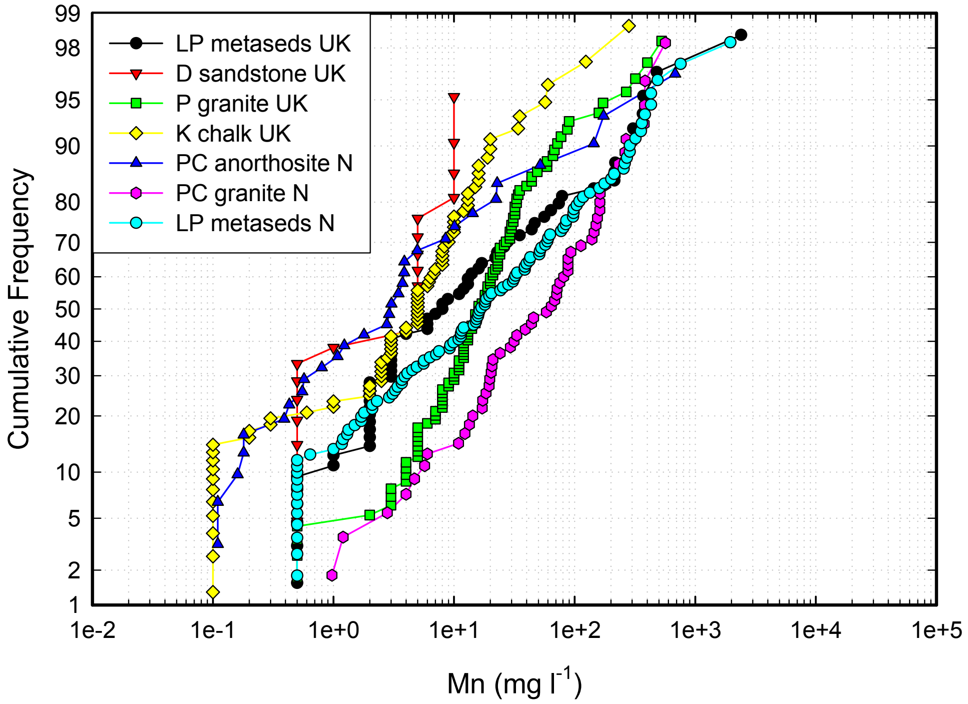


Figure 7.2.2 Probability plot of manganese concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.

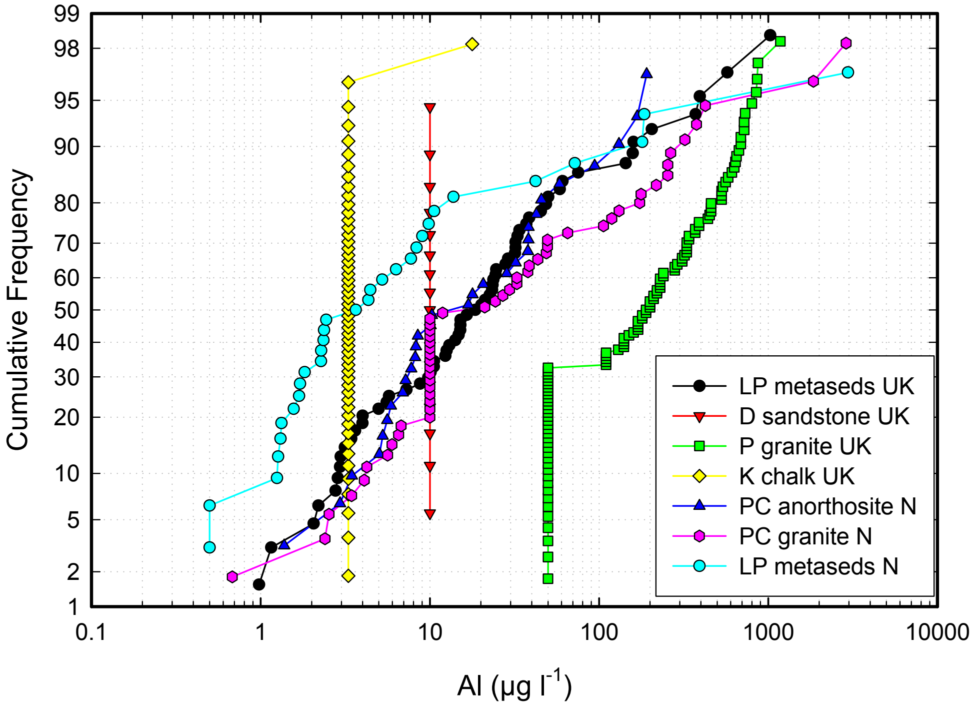


Figure 7.2.3 **Probability plot of aluminium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

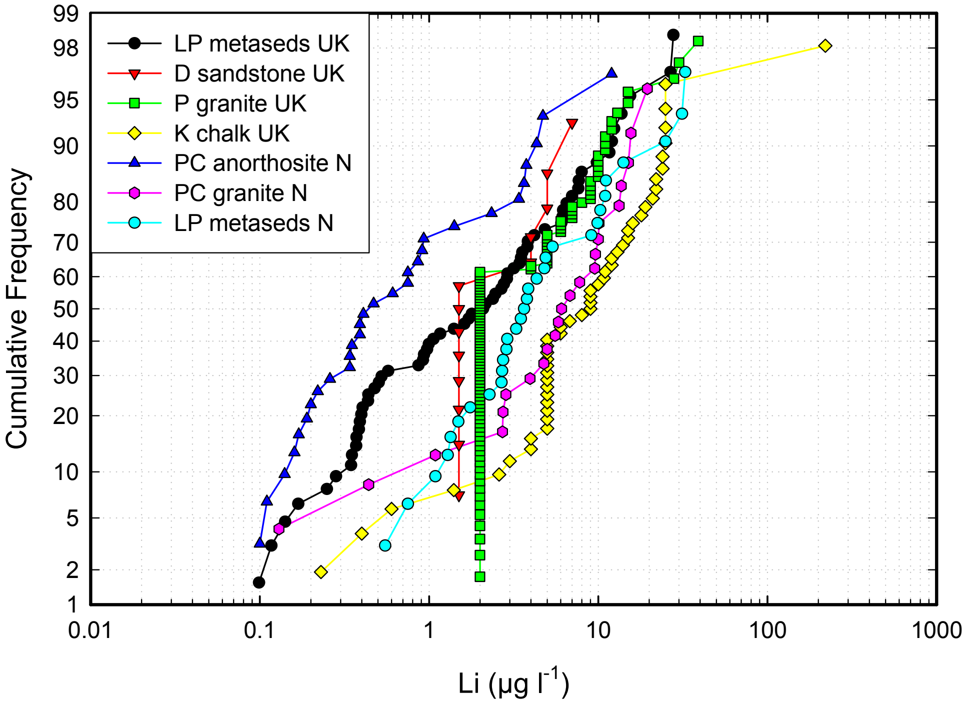


Figure 7.2.4 **Probability plot of lithium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

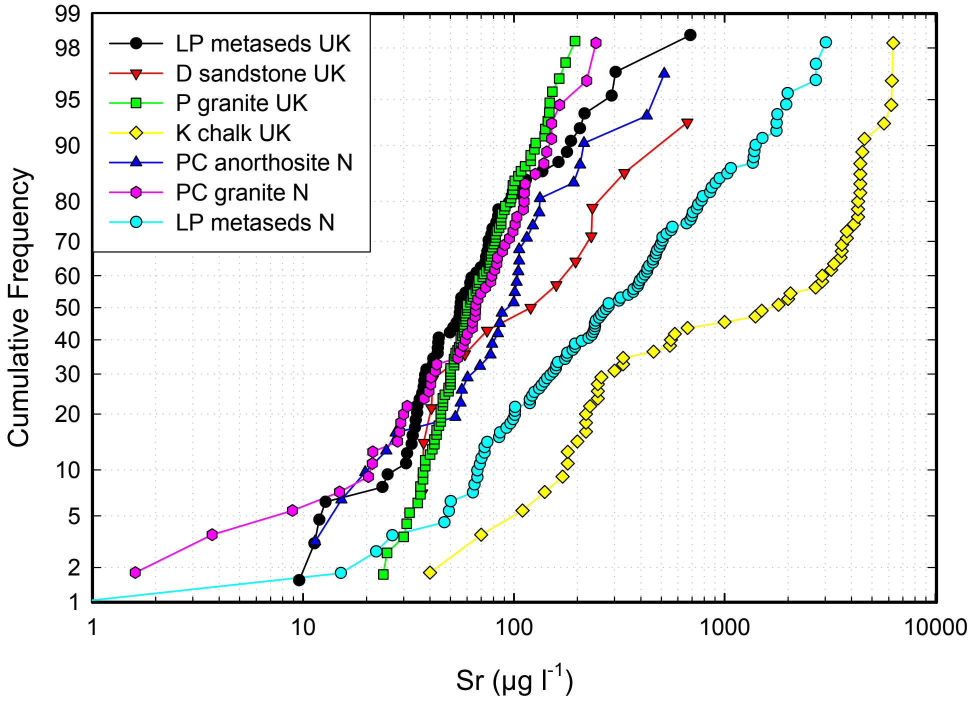


Figure 7.2.5 **Probability plot of Strontium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

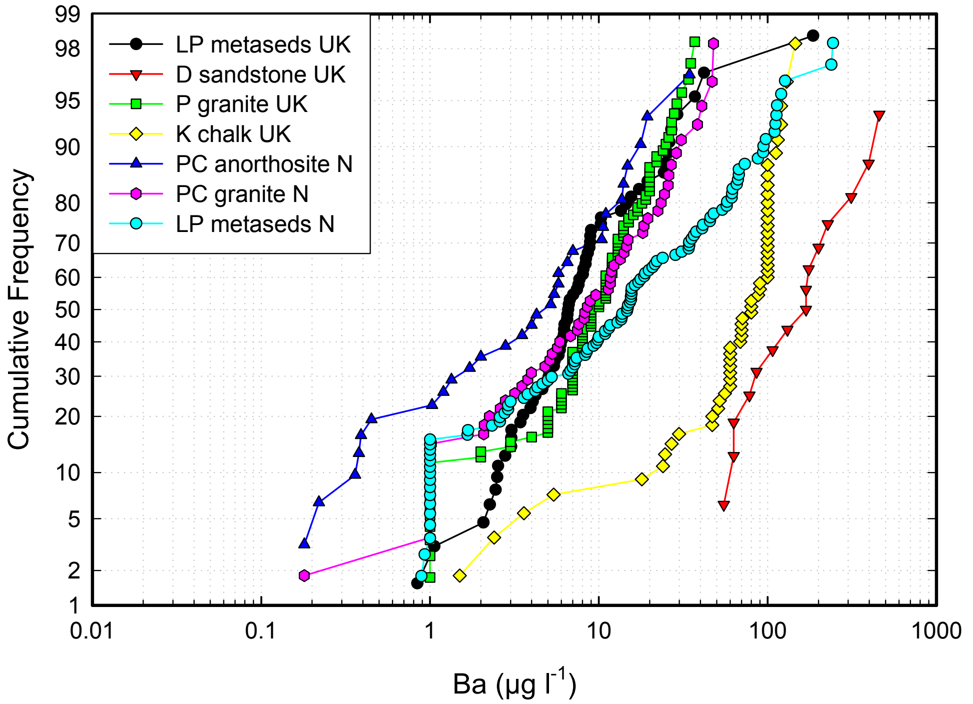


Figure 7.2.6 **Probability plot of barium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

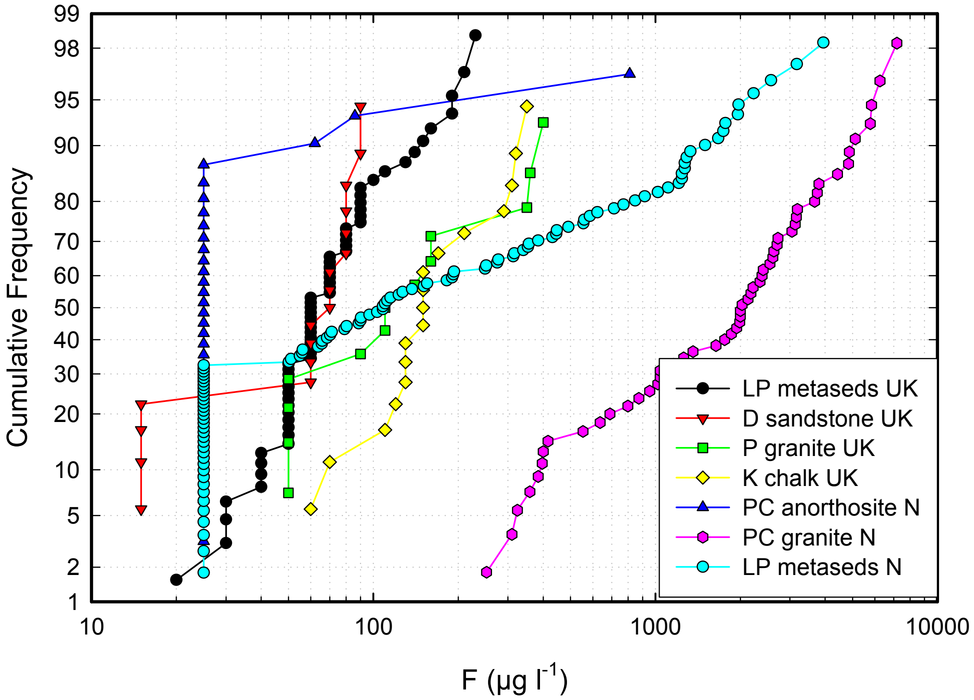


Figure 7.2.7 **Probability plot of fluoride concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

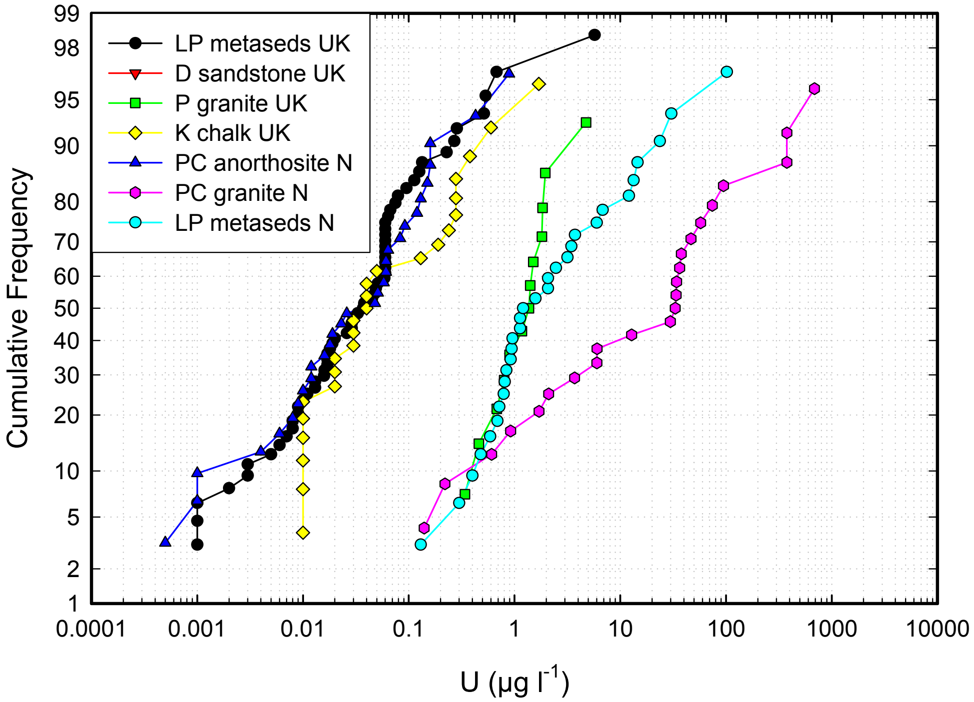


Figure 7.2.8 **Probability plot of uranium concentrations in groundwater from selected British and Norwegian aquifers. LP=Lower Palaeozoic, D=Devonian, P=Permian, K=Cretaceous, PC=Precambrian, UK=United Kingdom, N=Norway.**

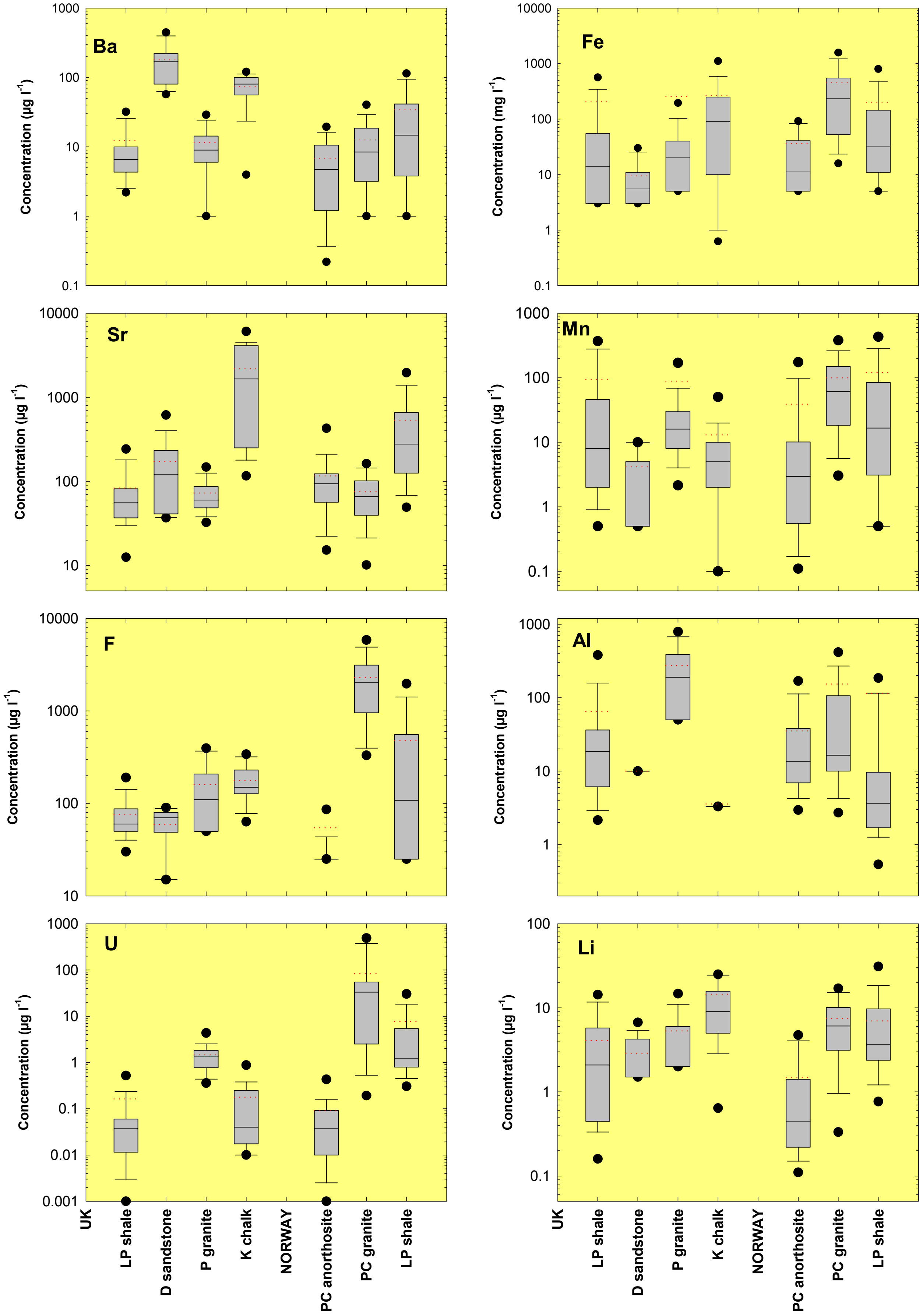


Figure 7.2.9 Boxplots comparing selected minor and trace elements (Ba, Fe, Sr, Mn, F, Al, U, and Li) in groundwater samples from selected British and Norwegian aquifers.

7.2.3 Aluminium

The highest median concentration (190 µg l^{-1}) was found in the Carnmenellis granite of the UK and is more than twice the EU MAC. The highest concentrations are found in the more acid groundwaters (Fig 7.2.3, Fig 7.2.9). Aluminium solubility is lowest in the pH range 6 to 7 and this is reflected in most groundwaters, particularly the carbonate bearing aquifers where pH is circumneutral and bedrock Al is low. In the high pH Norwegian groundwaters complexing with species such as F is likely to be important, as well as anion species ($Al(OH_4)$).

7.2.4 Lithium

Concentrations of the trace element Li are a good indicator of rock type: its concentration is generally higher in granitic rocks and dissolution/desorption from sheet mica/clay minerals in sediments is also important. In addition, Li tends to show an increase with residence time, because concentrations rarely become high enough to reach saturation of any Li forming mineral phase. The lowest concentrations in Norwegian groundwaters are found in the anorthosite aquifer and this undoubtedly reflects the very low concentrations present in basic and intermediate igneous rocks (Fig 7.2.4, Fig 7.2.9). The higher concentrations in the confined groundwaters of the Chalk are due to relatively long residence times, hence significant water-rock interaction and release of Li from marine-derived clays. The low median (2 µg l^{-1}) of the Carnmenellis granite is primarily due to the short residence time and limited degree of water-rock interaction.

7.2.5 Barium

The major sources of Ba include the mineral barite ($BaSO_4$) and K-feldspar and some micaceous minerals (e.g. phlogopite) where Ba is a trace constituent. The solubility of barite forms a major control on the upper limit of Ba in groundwaters and concentrations are typically limited to concentrations below 100 µg l^{-1}. Where sulphate reduction has occurred much higher concentrations may exist. The Devonian sandstone aquifer groundwaters contain the highest concentrations with a median (169 µg l^{-1}) well above the EU MAC concentration of 100 µg l^{-1} (Fig 7.2.5). The actual concentrations correlate negatively with sulphate and most are at saturation with respect to barite. It is likely that barite occurs as an interstitial cement in these sandstones. Concentrations are also high in the confined groundwaters of the Chalk where long residence times and low SO_4 have allowed Ba to increase. The other aquifers are quite similar in terms of dissolved Ba although some of the groundwaters in the Norwegian Lower Palaeozoic sedimentary aquifer contain concentrations above the EU MAC.

7.2.6 Strontium

The behaviour of Sr is strongly akin to that of Ca with which it forms a strong geochemical association. The carbonate minerals, particularly calcite and Ca-rich silicate minerals (e.g. anorthite) are the main sources. Strontium is released to solution relatively rapidly and its concentration is generally not limited by saturation of mineral phases in dilute groundwaters. The highest concentrations are found in the UK chalk and Norwegian Lower Palaeozoic sediments and the Sr in these aquifers is dominantly derived from carbonate minerals (Fig 7.2.6, Fig 7.2.9). The lowest concentrations are found in the granites of both countries and the Lower Palaeozoic groundwaters reflecting low Ca-rich mineral phases. Strontium continues to increase with water-rock interaction in many aquifers and is considered a better estimate of residence time than Ca whose concentration is limited by saturation with respect to calcite.

7.2.7 Fluoride

The median concentrations of F are all below the EU MAC except for the Norwegian Iddefjord granite groundwaters, which are high (median of 1.76 mg l^{-1}) (Fig 7.2.7, Fig 7.2.9). The

Norwegian Lower Palaeozoic rocks also contain groundwaters with high F. The highest concentrations in the UK aquifers are found in the confined Chalk and the Carnmenellis granite, but these are significantly lower than in the Norwegian groundwaters. The source of the F is generally from fluorite in fractures (in granites) or from phosphate minerals (fluorapatite in the Chalk). An upper limit to F in groundwaters is determined by saturation with respect to fluorite (CaF_2), hence Ca will exert the main control on maximum concentrations in solution. Groundwaters low in Ca such, as the Norwegian Iddefjorden granite, can reach higher concentrations of F before saturation is reached. Thus, Na-HCO_3 –type waters often have high concentrations of fluoride if F-bearing minerals are present in the aquifer. Several authors have also noted a positive correlation between pH and F concentration in Norwegian crystalline bedrock groundwaters (Reimann et al., 1996, Banks et al., 1998, Bårdsen et al., 1999) indicative of anion exchange of fluoride for hydroxide ions at high pH on exchangeable sites on micas, amphiboles or pyroxene minerals.

7.2.8 Uranium

Median concentrations of U in the selected aquifers vary by more than three orders of magnitude, reaching very high values in the Norwegian granite (Fig 7.2.8). Groundwaters from the Carnmenellis granite and Lower Palaeozoic aquifer also contain relatively high concentrations in comparison with most groundwaters world-wide. The bimodal pattern in the Chalk is probably related to redox conditions as U is immobile under reducing conditions. Although there is not an EU or Norwegian limit to U in drinking water, several of these groundwaters exceed the new US (30 $\mu g\ l^{-1}$) and Canadian (100 $\mu g\ l^{-1}$) MAC.

8 CONCLUDING REMARKS AND SUGGESTIONS FOR FURTHER WORK

The concept of baseline has been discussed and the problems in defining such a term emphasized. A working definition has been produced: “the range in concentration of an element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources”. It is evident from the datasets presented and a knowledge of hydrogeochemistry, that waters contain a wide range of concentrations produced from natural processes. Therefore, it is concluded that baseline cannot be represented by a single concentration, but typically forms a range of concentrations over several orders of magnitude. This range may include natural concentrations which are significantly above national and international guidelines for drinking water. The relevance of this conclusion was highlighted by Banks et al. (1998a): “Naturally occurring parameters are, by definition, not contamination. Nevertheless, nature is not necessarily nice, and naturally occurring trace toxins can be every bit as undesirable as their counterparts derived from human pollution”. On the other hand, many elements are deemed as essential to both plant and human life and deficiencies in the diet may also cause problems. This is true for elements such as I and F, which may cause goitre and dental caries, respectively, if they are depleted in drinking water and the diet and the intake is too low. The case of F underlines the fact that some elements are both toxic at high concentrations (e.g. too much F causes skeletal and dental fluorosis) and essential.

The geochemical evolution of groundwaters and reactions which limit solute concentrations give rise to a range in the natural baseline chemistry of groundwaters. Large differences in the hydrochemistry are also seen between groundwaters in aquifers of different rock types. Much of the variation in trace elements of concern which are present in rocks is related to the occurrence of accessory or secondary mineral phases and their associated trace constituents e.g. F, Rn, Be, U, and Ba. Even single rock types, such as sandstone or granite, show considerable ranges of elemental concentrations, particularly trace elements, related to their tectonic setting and provenance. Therefore, each individual aquifer needs to be assessed individually and the application of the baseline concept to problems in groundwater quality such as pollution or remediation needs to take into account the natural variation in both lithology and groundwater chemistry. Indeed, the variation of some parameters in natural waters may be as great or greater than that produced by pollution. Thus, baseline standards need to be set against each aquifer and the chemical evolution and regional controls must be well understood.

The types of mathematical distribution found in nature have also been discussed and it is evident that the concentrations of different elements may follow different distribution laws e.g. some elements (in some aquifers) show normal or lognormal distributions whereas others do not show any such distribution. This is important for the application of particular statistical treatments since many assume a specific distribution. However, the aim of this work was to describe the actual data and to produce an output which is both simple and relevant to end-users and policy makers. Several tools have been used to describe the data, which are not critically dependent on the type of distribution. This includes the use of boxplots and cumulative frequency plots, which use percentiles as a basis to compare and discriminate different datasets. Plotting cumulative frequency plots with a probability axis allows different populations (including pollution if present) to be assessed. The median value has been chosen in preference to the mean for inter-comparison, because this parameter is not so greatly affected by very large or small populations and outliers. The range of baseline concentrations is a critical parameter to determine, but this can be misleading if occasional outliers or extreme values are included. For practical purposes an upper limit to baseline has been used, calculated at the 95th percentile. Although this choice is arbitrary (and will exclude a small number of extreme or outlying, but natural data), it does make comparison of different datasets more instructive and sets a realistic and workable estimate of the natural baseline with which to assess pollution or set a realistic base for remediation.

The concentrations of elements in selected aquifers from the UK and Norway have been described and compared. This has highlighted the wide range of parameters present in groundwaters of different rock types and tectonic terranes. There is a large variation in geochemical parameters within each aquifer and considerable overlap between the aquifers of each country. Nevertheless, this study has noted some fundamental differences between the groundwaters of both countries. Most of the groundwaters in Norway have relatively high pH in comparison with those of the UK (including carbonate aquifers), which is surprising considering that they are mainly hard rock aquifers. In addition, Na-HCO_3 type waters are much more prevalent in Norway compared to a dominance of Ca-HCO_3 type waters in the UK. Two possible explanations of these conditions may be put forward. The first interpretation is based on the fact that many of the Norwegian coastal aquifers were below sea level until relatively recently. Although these aquifers have later been well flushed by fresh water, the dominance of Na left behind on the exchange sites of aquifer minerals has allowed the waters to evolve to Na-HCO_3 compositions much more rapidly through ion exchange. This process is still continuing and has led to the loss of calcite buffering, allowing alkaline compositions to evolve through hydrolysis reactions. The second interpretation is based on the fact that recurrent glaciations in Scandinavia during the Quaternary have removed most deep-weathered rock, leaving fresh, scoured rock at outcrop. This implies that even if most of the crystalline bedrock groundwaters utilised by Norwegian well-owners are drawn from the upper 100 m of the crust, there are still abundant reactive minerals along the fractures. Silicate weathering can thus release base cations and alkalinity, and pH is elevated. When the ion concentrations and pH are sufficiently high, calcite saturation is reached and calcite is precipitated. The implication is that, in waters of pH>8.2, the calcite precipitation buffer is exhausted, Ca having largely been removed from the water phase, thus permitting the pH to rise to considerably higher values. Both processes yield similar net results, namely a Na-HCO_3 water type with high pH and low Ca^{2+} concentrations. In contrast to Scandinavia, the erosion of the glaciated areas of the UK has been less profound and periglacial areas like Cornwall have been exposed to subaerial weathering over a much longer period.

It should be noted that the dominance of hard rock aquifers in Norway and sedimentary aquifers in the UK also has led to different minor and trace element assemblages in the main abstractions of groundwater. This is seen, for example, in the high F, U and Rn concentrations in many of the granite and sedimentary groundwaters in Norway. Barium, in contrast to these elements, tends to be higher in the UK sedimentary aquifers. This is particularly the case for the Devonian aquifer of Scotland, a country comprising dominantly Caledonian rocks enriched in Ba (which also hosts a large barite mine). Nevertheless, the granitic groundwaters from Carnmenellis are depleted in most trace elements compared to the groundwaters from the Iddefjord granite. This is probably due to the prolonged suabaerial weathering at Carnmenellis, removing reactive minerals from the unsaturated zone and the zone of active groundwater flow. A similar explanation was given by Banks et al. (1998c) who compared the hydrochemistry of two granitic aquifers (the Isles of Scilly, UK and the Hvaler Islands, Norway), finding many of the same differences between the groundwaters as found in the present study.

Although it is beyond the scope of this report to distinguish large scale “groundwater provinces”, it does appear that regional variations may exist beyond the aquifer rock type, and that regional geochemical variations are reflected and even enhanced in groundwater quality. Also, it seems that the geological history during Quaternary time has had a major impact on the geochemical processes controlling groundwater quality in these countries.

The main area where data are lacking, or potentially exist but are unavailable, is time-series data. Even where long records do exist, the number of analysed parameters is usually small. Such data are invaluable in ascertaining long-term trends and the effects of anthropogenic inputs on water quality. Another area where only limited data exist is the trends of water quality with depth.

Where this has been studied, it is generally the case that groundwater shows significant variation with depth. Pumped borehole samples normally represent a mixture of waters from the main flowing horizons or fracture systems in a borehole and it is difficult to deduce how and where changes are occurring in such a case. Pollution is likely to enter an aquifer through specific pathways and it is important for the protection and management of an aquifer to have knowledge of how and where this occurs. It is clear also that the quality of groundwater data is variable, not only between organisations like research centres, water companies and agencies but also within individual organisations. In order for a European wide policy to be implemented it is necessary that a protocol be established for criteria related to data quality as well as sampling and analytical protocols.

The determination of the natural baseline quality requires a careful analysis of data, because many groundwaters show the effects of pollution over the past. Several potential methodologies may be used. These include:

1) historical data

2) extrapolation using time-series data

3) up-gradient and cross-gradient sampling

4) statistical methods

5) extrapolation from similar geochemical environments

6) geochemical modelling

However, the lack of some types of data from different aquifers means that it is typically the case that a single method cannot be used as a universal tool. It is, therefore, recommended that the combined methodologies be used as a general "toolbox" and the most appropriate tools be selected to apply to the data available. Obviously, where more than one tool gives similar results this gives stronger credence to the interpretation. The baseline concept is relatively simple but imposed changes in the environment may indirectly affect the natural baseline e.g. where groundwater abstraction has caused a lowering of the water table and potential acidification if oxygen is introduced to an aquifer containing abundant pyrite. Although the increased Fe and SO_4 are naturally-derived, the change is anthropogenically induced. Additionally, increased flow-rates in the aquifer may change the natural baseline, because most reactions are kinetically controlled with rates varying over several orders of magnitude. Thus, what appears as a relatively simple concept, turns out to be fraught with difficulties when looked at in detail. Further work will progress in developing this concept, the controls and natural chemical distributions present in groundwater and the tools employed to determine baseline at both the national and international level.

9 REFERENCES

Ahrens, L.H. 1954 The lognormal distribution of the elements (a fundamental law of geochemistry and its subsidiary). *Geochimica et Cosmochimica Acta* **5/2**, 49-74.

Ashwal, L.D. 1993 *Anorthosites*, Springer-Verlag, Berlin.

Banks, D., Rohr-Torp, E. & Skarphagen, H. 1992 An integrated study of a Precambrian granite aquifer, Hvaler, Southeastern Norway. *Norges Geologiske Undersøkelse Bulletin* **422**, 47-66.

Banks, D., Reimann, C., Røyset, O., Skarphagen, H. & Sæther, O.M. 1995a Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters. *Applied Geochemistry* **10**, 1-16.

Banks, D., Røyset, O., Strand, T. & Skarphagen, H. 1995b Radioelement (U, Th, Rn) concentrations in Norwegian bedrock groundwaters. *Environmental Geology* **25**, 165-180.

Banks, D., Midtgard, A.K., Morland, G., Reimann, C., Strand, T., Bjorvatn, K. & Siewers, U. 1998a Is pure groundwater safe to drink ? Natural contamination of groundwater in Norway. *Geology Today*, **14**(3), 105-113.

Banks, D., Frengstad, B., Midtgård, Aa.K., Krog, J.R., & Strand, T. 1998b The chemistry of Norwegian groundwaters. I. The distribution of radon, major and minor elements in 1604 crystalline bedrock groundwaters. *The Science of the Total Environment* **222**, 71-91.

Banks, D., Reimann, C. & Skarphagen, H. 1998c The comparative hydrochemistry of two granitic island aquifers: The Isles of Scilly, UK and the Hvaler Islands, Norway. *The Science of the Total Environment* **209**, 169-183.

Bucher, K & Stober, I.2000 Composition of groundwater in crystalline basement. In: Stober, I & Bucher K. (eds.) *Hydrogeology of crystalline rocks*. Water Science and Technology Library 34. Kluwer Academic Publishers. Dordrecht, 275 pp.

Bårdsen, A., Bjorvatn, K. Sand, K. & Banks, D. 1999 Seasonal variation of fluoride content in groundwater from wells drilled in bedrock. *Norges geologiske undersøkelse Bulletin* **435**, 53-58.

Clark, I.D. & Fritz, P. 1997 Environmental Isotopes in Hydrogeology. CRC Press.

Darnley, A.G. 1997 A global geochemical reference network: the foundation for geochemical baselines. *Journal of Geochemical Exploration*, **60**, 1-5.

Duchesne & Maquil 1987 The Rogaland intrusive masses: Introduction. In: Maijer, C. & Padget, P. (Eds) The geology of southernmost Norway: an excursion guide. *Norges Geologiske Undersøkelse Special Publication* **1**, 48-50

Duchesne & Michot 1987 The Egersund-Ogna massif. In: Maijer, C. & Padget, P. (Eds) The geology of southernmost Norway: an excursion guide. *Norges Geologiske Undersøkelse Special Publication* **1**, 50-56.

Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.L., Bath, A.H., Morgan-Jones, M. & Andrews, J.N. 1987 Baseline geochemical conditions in the Chalk aquifer, Berkshire, UK: A basis for groundwater quality management. *Applied Geochemistry*, **2**, 251-274.

Edmunds, W.M., Brewerton, L.J., Shand, P. & Smedley, P.L. 1997 The natural (baseline) quality of groundwater in England and Wales. Part 1: A guide to the natural (baseline) quality study. *British Geological Survey Technical Report*, **WD/97/51**.

Edmunds, W.M. & Brewerton, L.J. 1997 The Chalk of Berkshire and the Chilterns. British Geological Survey, *Technical Report* **WD/97/57**.

Environmental Protection Agency 2000 National Primary Drinking Water Regulations; Radionuclides; Final Rule. 40 CFR Parts 9, 141 and 142. *Federal Register* **65/236**, 76708-76753.

Frengstad, B. & Banks, D. 2000 Evolution of high-pH Na-HCO_3 groundwaters in anorthosites: silicate weathering or cation exchange? In: Sililo et al. (Eds): *Groundwater: Past achievements and future challenges.* Proceedings of XXX IAH Congress, Cape Town. Balkema, Rotterdam, 493-498.

Frengstad, B. Skrede, A.K.M., Banks, D., Krog, J.R. & Siewers, U. 2000 The chemistry of Norwegian groundwaters. III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP-MS techniques. *The Science of the Total Environment* **222**, 71-91.

Frengstad, B. (in prep) Groundwater geochemistry in crystalline bedrock aquifers of Norway. Doktor Ingeniør Thesis, Department of Geology and Mineral Resources Engineering, NTNU.

Gautneb, H., Øvereng, O. & Heldal, T. 1999 Granittforekomster i Halden kommune *[Granites in the municipality of Halden - in Norwegian]*. *Norges Geologiske Undersøkelse Report* **99.061**, 15 pp + appendices.

Health Canada 1996 *Guidelines for Canadian Drinking Water Quality, 6th edition*. Authority of the Minister of Health. **96-EHD-196**, 90 pp.

Hawkes, H.E. & Webb, J.S. 1962 *Geochemistry in mineral exploration*. Harper & Row, New York, N.Y., 415pp.

Hornung, M., Adamson, J.K., Reynolds & B. Stevens, P.A. 1986 Influence of mineral weathering and catchment hydrology on drainage water chemistry in three upland sites in England and Wales. *Journal of the Geological Society of London*, **143**, 627-634.

Killeen, P.G. & Heier, K.S. 1975 A uranium and thorium enriched province of the Fennoscandian shield in southern Norway. *Geochemica et Cosmochemica Acta* **39**: 1515-1524.

Langmuir, D. 1997 *Aqueous environmental chemistry*. Prentice Hall, New Jersey. 600pp.

Miller, R.L. & Goldberg, E.D. 1955 The normal distribution in geochemistry. *Geochimica et Cosmochimica Acta*, **8**, 53-62.

Morland, G. 1997 Petrology, lithology, Bedrock structures, glaciation and sea level. Important factors for groundwater yield and composition of Norwegian bedrock boreholes? *Norges Geologiske Undersøkelse Report* **97.122 I**, 274 pp.

Pedersen, S. & Maaløe, S. 1990 The Iddefjord granite; geology and age. *Norges geologiske undersøkelse Bulletin* **417**, 55-64.

Miller, R.L. & Goldberg, E.D. 1955 The normal distribution in geochemistry. *Geochimica et Cosmochimica Acta* **8**, 53-62.

Neal, C., Robson, A.J., Shand, P., Edmunds, W.M., Dixon, A.J., Buckley, D.K., Hill, S., Harrow, M., Neal, M. & Reynolds, B. 1997 The occurrence of groundwater in the Lower Palaeozoic rocks of upland Central Wales. *Hydrology and Earth System Sciences*, **1**, 3-18.

Nordstrom, D.K., Ball, J.W., Donahoe, R.J. & Whittemore, D. 1989 Groundwater chemistry and water rock interaction at Stripa. *Geochimica et Cosmochimica Acta* **53**, 1727-1740.

Ó Dochartaigh, B É., Ball, D F., Shand, P., Browne, M A., McNeill, G., MacDonald, A. & Robins, N.S. 1999. The Upper Devonian sandstone aquifer of Fife. British Geological Survey, *Technical Report* **WD/99/21**.

Reimann, C., Hall, G.E.M., Siewers, U., Bjorvatn, K., Morland, G., Skarphagen, H. & Strand, T. (1996) Radon, fluoride and 62 elements as determined by ICP-MS in 145 Norwegian hard rock groundwater samples. *Science of the Total Environment* **192**, 1-19.

Reimann, C. & Filzmoser, P. 2000 Normal and lognormal data distribution in geochemistry: Death of a myth. Consequences for the statistical treatment of geochemical and environmental data. *Environmental Geology* **39/9**, 1001-1014.

Robins, N.S., Shand, P. & Merrin, P.D. 2000 Shallow groundwater in Drift and Lower Palaeozoic bedrock: The Afon Teifi Valley in West Wales. *Geological Society Special Publication* **182**, 123-131.

Runnels, D.D., Dupon, D.P., Jones, R.L. & Cline, D.J. 1998 Determination of background chemistry of water at mining and milling sites, Salt Lake Valley, Utah, USA. In, Arehart & Hulston (eds.), *Water-Rock Interaction #*, Balkema, Rotterdam, 997-1000.

Selmer-Olsen, R 1980 *Ingeniørgeologi. Del 1 Generell geologi [Engineering geology Part 1 General geology – in Norwegian]*. 3rd ed. Tapir, Trondheim, 281 pp.

Shand, P. 1999 A geochemical investigation of chalk porewater samples from pilot ASR boreholes in the southern Wessex Basin. British Geological Survey, *Technical Report* **WD/99/55C**.

Shand, P. & Bloomfield, J. 1995. Mineralisation of shallow fracture surfaces in the chalk and implications for contaminant attenuation. British Geological Survey, *Technical Report* **WD/95/15**.

Shand, P., Darbyshire, D.P.F. & Gooddy, D.C. 1999 The application of strontium isotopes to catchment studies: The Plynlimon upland catchment of Central Wales. British Geological Survey, *Technical Report* **WD/99/56**.

Shand, P., Edmunds, W.M., Wagstaff, S., Flavin, R. & Jones, H.K. 1999 Hydrogeochemical processes determining water quality in upland Britain. *Hydrogeology Report Series of the British Geological Survey*, 38p, ISBN 0-852-72314-8.

Sigmond E.M.O. 1992 *Berggrunnskart, Norge med havområder - Målestokk 1:3 millioner [Bedrock map, Norway with marine areas - Scale 1:3 million]*. Norges geologiske undersøkelse.

Sinclair, A.J. 1974 Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Exploration*, **3**, 129-149.

Smedley, P.L., Bromley, A.V., Shepherd, D.J., Edmunds, W.M. & Kay, R.L.F. 1989 Geochemistry in relation to Hot Dry Rock development in Cornwall, Volume 4 Fluid circulation in the Carnmenellis granite: hydrogeological, hydrogeochemical and palaeofluid evidence. *British Geological Survey Research Report* **SD/89/2**.

Sosial- og helsedepartementet 1995 Forskrifter om vannforsyning og drikkevann m.m. *[Directive on water supply and drinking water etc. - in Norwegian]*. **68. I-9/95**. Oslo, Norway.

Toran, L.E. & Saunders, J.A. Modelling alternative paths of chemical evolution of $Na-HCO_3$–type groundwater near Oak Ridge Tennessee, USA. *Hydrogeology Journal* **7/4**, 355-364.

Woodsworth, G.J 1971 A Geochemical Drainage Survey and its Implications for Metallogenesis, Central Coast Mountains, British Columbia. *Economic Geology and the Bulletin of the Society of Economic Geologists* **66/8**, 1104-1120

Appendix 1 Summary of standards of water quality for human consumption

Parameter		**CEC**[1]	**SHD**[2]		**WHO**[6]
		PV[3] (mg l^{-1})	GL[4] (mg l^{-1})	MAC[5] (mg l^{-1})	GV[7] (mg l^{-1})
Calcium	(Ca^{2+})	-	15-25	-	-
Magnesium	(Mg^{2+})	-	-	20	-
Sodium	(Na^{+})†	200	20	150	200
Potassium	(K^{+})	-	10	12	-
Chloride	(Cl)	250	25	-	250
Sulphate	(SO_4^{2-})	250	25	100	250
Aluminium	(Al^{3+})	0.2	0.05	0.2	0.2
Nitrate	(NO_3^{-})†	50	-	44	50
	(as N)	11.3	-	10	10
Nitrite	(NO_2^{-})†	0.1	-	0.05	0.2 P
Ammonium	(NH_4^{+})	0.5	0.05	0.5	1.5
Iron	(Fe_{Total})	0.2	0.05	0.2	0.3
Manganese	(Mn^{2+})	0.05	0.02	0.05	0.5 P
		(μg/l)	**(μg/l)**	**(μg/l)**	**(μg/l)**
Copper	(Cu^{2+})	2000	100	300	2000 P
Zinc	(Zn^{2+})	-	100	300	-
Phosphate	(HPO_4^{2-})	-	400	5000	-
Fluoride	(F^{-})†	1500	-	1500	1500
Barium	(Ba^{2+})	-	100	-	700
Silver	(Ag)	-	-	10	-
Arsenic	(As)	10	-	10	10 P
Boron	(B)	1000	-	-	500 P
Cadmium	(Cd)	5	-	5	3
Cyanide	(CN)	50	-	10	70
Chromium	(Cr)	50	-	50	50 P
Mercury	(Hg)	1	-	0.5	1
Molybdenum	(Mo)	-	-	-	70
Nickel	(Ni)	20	-	50	20
Lead	(Pb)	10	-	20	10
Antimony	(Sb)	5	-	10	5 P
Selenium	(Se)†	10	-	10	10
Uranium	(U)	-	-	-	2 P
Pesticides	(separately)	0.1	-	0.1	different for
	(total)	0.5	-	0.5	each compound
Temperature	(°C)	-	12	25	70 P
pH		6.5-9.5	7.5-8.5	6.5-8.5	6.5-8.5
Conductivity	(μScm^{-1} at 20°C)	2500	400	-	-

[1]CEU : Council of the European Union Directive 98/83/EC (The Council of the European Union 1998)

[2]SHD Sosial- og helsedepartementet Nr. 68, I-9/95. Forskrift om vannforsyning og drikkevann m.m. [Directive on water supply and drinking water etc. – in Norwegian] (Sosial og helsedepartementet 1995)

[3]PV Parametric value. Member States are free to add other parameters if they see fit

[4]GL : Guide level

[5]MAC : Maximum admissible concentration.

[6]WHO : World Health Organisation. Guidelines for drinking water quality. (WHO 1996, 1998)

[7]GV : Guide value

P : Provisional value

Appendix 2 Hydrochemistry of study aquifers

Determinand		Units	Unconfined Aquifer					Confined Aquifer				
			Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n
T	temperature	°C	10.0	13.0	10.9	11.6	20	10.9	18.0	12.6	15.1	32
pH	(field measured)		6.80	8.43	7.16	7.36	20	7.00	8.24	7.40	7.79	33
Eh	redox potential	mV	130	417	371	416	16	<50	445	80	381	30
DO	dissolved oxygen	mg l^{-1}	0.1	10.5	9	10.5	17	<0.1	10	0.2	9.18	32
SEC	conductivity	µS cm^{-1}	555	1100	683	887	12	636	1500	785	1410	21
Ca	calcium	mg l^{-1}	86	169	110	150	21	36	118	57	114	33
Mg	magnesium	mg l^{-1}	0.9	8.9	2.07	8.2	21	1.5	30	19	29.2	33
Na	sodium	mg l^{-1}	5.6	24	8.9	21.9	21	8.1	219	36	122	33
K	potassium	mg l^{-1}	0.6	5.3	1.5	4.3	21	1.1	10.2	6.8	9.88	33
Cl	chloride	mg l^{-1}	9	41	17	41	21	14.5	204	30	151	33
HCO_3	bicarbonate	mg l^{-1}	221	341	289	330	18	267	349	303	324	24
SO_4	sulphate	mg l^{-1}	2.5	197	13	125	21	13.5	68	33	55.8	33
NO_3	nitrate (N)	mg l^{-1}	0.09	11.1	5.2	7.5	21	<0.02	7	<0.02	6.7	33
NH_4	ammonium (N)	µg l^{-1}	<8	70	<8	69	13	<8	893	198	750	32
Al	aluminium	µg l^{-1}	<7	18	<7	2.8	20	<7	<7	<7	<7	33
As	arsenic	µg l^{-1}	<1	4	2	3.5	12	<1	5	3	4	22
B	boron	µg l^{-1}	<2	120	18	86.9	23	<2	1430	185	1180	36
Ba	barium	µg l^{-1}	1.5	100	60	100	21	18	146	90	124	33
Co	cobalt	µg l^{-1}	<1.33	3.6	<1.33	1.87	8	<1.33	<1.33	<1.33	<1.33	11
Cd	cadmium	µg l^{-1}	<2	<2	<2	<2	8	<2	2.4	<2	<2	12
Cr	chromium	µg l^{-1}	<1	<1	<1	<1	2	<1	<2	<1	<1	4
Cu	copper	µg l^{-1}	<1.33	23	2.45	5.98	22	<1.33	29	1	13.1	35
F	fluoride	µg l^{-1}	60	350	150	326	17	<100	4800	1300	2360	33
Fe_{total}	total iron	µg l^{-1}	<1	4380	7	834	28	<1	2560	217	719	47
Fe(II)	ferrous iron	µg l^{-1}	<10	1900	<10	849	12	<10	1380	130	635	22
I	iodine	µg l^{-1}	3	10	5	9.5	11	4	54	18.5	49.3	26
Li	lithium	µg l^{-1}	<0.5	9	5	9	19	1.4	220	13.5	25	32
Mn	manganese	µg l^{-1}	<0.2	282	<10	81.6	28	<0.2	60	8	34.7	48
Mo	molybdenum	µg l^{-1}	<7	<7	<7	<7	4	<7	<7	<7	<7	2
Ni	nickel	µg l^{-1}	<2	11	<3	7.5	22	<3	7	<3	<3	37
P	orthophosphorus	µg l^{-1}	<3	6.5	<3	6.5	11	<3	278	3.2	12.7	22
Pb	lead	µg l^{-1}	<10	2	<10	<2.8	9	<2	<10	<10	<6.4	12
Rb	rubidium	µg l^{-1}	<50	<50	<50	<50	3	<50	<50	<50	<50	9
Si	silicon	µg l^{-1}	4100	10800	6500	10700	21	4700	10700	8200	10500	33
Sr	strontium	µg l^{-1}	40	1500	250	1400	21	180	6300	3600	6190	33
U	uranium	µg l^{-1}	0.24	1.7	0.28	1.37	6	0.01	0.6	0.03	0.23	19
Y	yttrium	µg l^{-1}	<0.2	<0.2	<0.2	<0.2	7	<0.2	<0.2	<0.2	<0.2	11
Zn	zinc	µg l^{-1}	<1.3	34	9.9	30	10	<1.3	414	21.3	207	15

Hydrochemical summary for Berkshire Chalk groundwaters, South England.

Determinand		Units	Minimum	Maximum	Median	Upper baseline	n
T	temperature	^{o}C	4.4	11.5	9.7	11.4	65
pH	field measured		5.16	7.55	6.49	7.3	65
Eh	redox potential	mV	291	556	445	546	36
DO	dissolved oxygen	mg l^{-1}	<0.1	10.9	5.75	10.7	56
SEC	conductivity	µS cm^{-1}	53.5	662	225	575	65
Ca	calcium	mg l^{-1}	2.01	83.1	17.6	60.6	65
Mg	magnesium	mg l^{-1}	0.63	17.6	4.56	13.6	65
Na	sodium	mg l^{-1}	4.2	51.5	10.7	23.3	65
K	potassium	mg l^{-1}	<0.2	33.7	1.2	8.9	65
Cl	chloride	mg l^{-1}	5	92	19	44.3	65
HCO_3	bicarbonate	mg l^{-1}	2.7	291	30	154	65
SO_4	sulphate	mg l^{-1}	2.95	41.2	11.8	27.4	65
NO_3	nitrate (N)	mg l^{-1}	<0.2	41.3	4.8	18.5	51
NH_4	ammonium (N)	mg l^{-1}	0.01	1.72	0.04	0.7	25
Al	aluminium	µg l^{-1}	0.98	1027	20.2	338	65
As	arsenic	µg l^{-1}	<0.26	6.5	0.70	2.2	54
B	boron	µg l^{-1}	4.60	112	12.9	40.4	65
Ba	barium	µg l^{-1}	0.84	186	6.5	28.7	65
Br	bromide	mg l^{-1}	0.016	0.217	0.077	0.17	65
Cd	cadmium	µg l^{-1}	<0.04	1.76	0.02	0.12	65
Cr	chromium	µg l^{-1}	<0.85	1.92	0.20	0.88	65
Cu	copper	µg l^{-1}	<0.33	818	1.75	37.0	65
F	fluoride	mg l^{-1}	0.02	0.23	0.06	0.18	65
Fe_{total}	iron	mg l^{-1}	0.001	7.061	0.023	0.670	45
I	iodide	mg l^{-1}	0.008	0.025	0.003	0.011	56
La	lanthanum	µg l^{-1}	<0.008	0.50	0.03	0.25	65
Li	lithium	µg l^{-1}	0.10	27.8	1.79	13.5	65
Mn	manganese	mg l^{-1}	<0.001	2.4	0.012	0.37	58
Mo	molybdenum	µg l^{-1}	<0.27	6.5	0.063	1.2	65
Ni	nickel	µg l^{-1}	<0.84	11.1	1.77	6.4	65
P_{total}	phosphorus	mg l^{-1}	<0.2	1.6	<0.2	<0.2	64
Pb	lead	µg l^{-1}	<0.35	5.0	<0.35	2.9	65
Rb	rubidium	µg l^{-1}	<0.1	17.0	0.9	6.0	65
Sb	antimony	µg l^{-1}	<0.11	0.47	0.035	0.26	65
Se	selenium	µg l^{-1}	<0.53	1.3	<0.53	1.2	54
Si	silicon	mg l^{-1}	1.08	7.4	2.68	6.0	65
Sr	strontium	µg l^{-1}	9.58	687	55.5	214	65
U	uranium	µg l^{-1}	<0.06	5.75	<0.06	0.47	65
Y	yttrium	µg l^{-1}	0.01	3.723	0.15	1.4	65
Zn	zinc	µg l^{-1}	<1	129	6.3	61.5	65

Hydrochemical summary for Lower Palaeozoic mudstone groundwaters, Wales.

Determinand		Units	Minimum	Maximum	Median	Upper baseline	n
T	temperature	°C	10.5	18.5	12.6	15.5	113
pH	field measured		4.26	6.97	5.66	6.58	111
Eh	redox potential	mV					
DO	dissolved oxygen	mg l^{-1}					
SEC	conductivity	µS cm^{-1}	14	580	217	468	110
Ca	calcium	mg l^{-1}	2.8	38.4	13.7	30.5	113
Mg	magnesium	mg l^{-1}	0.9	9.3	3.4	6.34	113
Na	sodium	mg l^{-1}	8.5	36.4	16.2	26.4	113
K	potassium	mg l^{-1}	<0.75	66.8	3	19.0	113
CL	chloride	mg l^{-1}	13	61	28	48.4	113
HCO_3	bicarbonate	mg l^{-1}	2.1	203	9.4	46.9	113
SO_4	sulphate	mg l^{-1}	7.8	52.6	17.2	35.3	113
NO_3	nitrate (N)	mg l^{-1}	<0.8	20	6.1	13.9	113
NH_4	ammonium (N)	mg l^{-1}					
Al	aluminium	µg l^{-1}	<0.1	1.27	0.19	0.76	113
As	arsenic	µg l^{-1}					
B	boron	µg l^{-1}	<20	140	<20	50	113
Ba	barium	µg l^{-1}	<2	44	9	28	113
Br	bromide	mg l^{-1}					
Cd	cadmium	µg l^{-1}					
Cr	chromium	µg l^{-1}					
Cu	copper	µg l^{-1}	<10	890	<10	80	112
F	fluoride	mg l^{-1}					
Fe_{total}	iron	mg l^{-1}	<0.01	21.8	0.02	0.173	112
I	iodide	mg l^{-1}					
La	lanthanum	µg l^{-1}	<0.05	3.07	0.82	2.53	30
Li	lithium	µg l^{-1}	<4	49	<4	13.8	113
Mn	manganese	mg l^{-1}	<0.001	5.96	0.016	0.164	113
Mo	molybdenum	µg l^{-1}					
Ni	nickel	µg l^{-1}					
P_{total}	phosphorus	mg l^{-1}	<0.1	0.9	<0.1	0.4	113
Pb	lead	µg l^{-1}					
Rb	rubidium	µg l^{-1}	1.3	60	11	35.5	30
Sb	antimony	µg l^{-1}					
Se	selenium	µg l^{-1}					
Si	silicon	mg l^{-1}	1	12.3	2.8	4.78	113
Sr	strontium	µg l^{-1}	21	215	60	147	113
U	uranium	µg l^{-1}					
Y	yttrium	µg l^{-1}	<2	6	<2	5	113
Zn	zinc	µg l^{-1}					

Hydrochemical summary for Devonian Sandstone groundwaters of Fife, Scotland.

Determinand		Units	Minimum	Maximum	Median	Upper baseline	n
T	temperature	^{o}C	7.5	16.4	9.6	14.72	13
pH	field measured		6.66	8.2	7.595	8.095	22
Eh	redox potential	mV					
DO	dissolved oxygen	mg l^{-1}	0.8	8.3	6.7	8.1	11
SEC	conductivity	µS cm^{-1}	209	682	426	673	22
Ca	calcium	mg l^{-1}	19.1	83.7	40	68.8	23
Mg	magnesium	mg l^{-1}	5.39	55	19.7	44.81	23
Na	sodium	mg l^{-1}	2.4	28.2	8.8	21.63	23
K	potassium	mg l^{-1}	1.3	6.7	2	5.35	23
CL	chloride	mg l^{-1}	11.5	64.5	18.2	44.59	23
HCO$_3$	bicarbonate	mg l^{-1}	51.2	289	171.55	282.3	22
SO$_4$	sulphate	mg l^{-1}	8.8	62	24.9	53.79	23
NO$_3$	nitrate (N)	mg l^{-1}	<0.2	49.5	8.2	42.4	23
NH$_4$	ammonium (N)	mg l^{-1}	<0.01	0.09	-0.01	0.0195	22
Al	aluminium	µg l^{-1}	<50	<50	<50	<50	7
As	arsenic	µg l^{-1}					
B	boron	µg l^{-1}	<5	80	20.0	54.0	14
Ba	barium	µg l^{-1}	55.00	459	169.0	416.0	15
Br	bromide	mg l^{-1}	0.025	0.49	0.07	0.448	13
Cd	cadmium	µg l^{-1}	<5	<6	<7	<8	14
Cr	chromium	µg l^{-1}	<20	<20	<20	<20	15
Cu	copper	µg l^{-1}	<8	818	<8	37.0	23
F	fluoride	mg l^{-1}	0.015	0.09	0.06	0.09	20
Fe$_{total}$	iron	mg l^{-1}	0.003	0.03	0.005	0.0291	23
I	iodine	mg l^{-1}	0.0017	0.0169	0.003	0.01096	13
La	lanthanum	µg l^{-1}	4	15.00	8.00	12.60	13
Li	lithium	µg l^{-1}	<3	7.0	<3	5.8	13
Mn	manganese	mg l^{-1}	<0.001	0.007	<0.001	0.0064	13
Mo	molybdenum	µg l^{-1}	<40	<40	<40	<40	9
Ni	nickel	µg l^{-1}	<20	<20	<20	<20	14
P$_{total}$	phosphorus	mg l^{-1}	<0.2	0.2	<0.2	<0.2	13
Pb	lead	µg l^{-1}	<60	<60	<60	<60	13
Rb	rubidium	µg l^{-1}					
Sb	antimony	µg l^{-1}					
Se	selenium	µg l^{-1}					
Si	silicon	mg l^{-1}	1.21	6.16	4.145	5.8935	14
Sr	strontium	µg l^{-1}	36.7	665	120	466	13
U	uranium	µg l^{-1}					
Y	yttrium	µg l^{-1}	<1	1.00	<1	<1	13
Zn	zinc	µg l^{-1}	<8	253	<8	31.6	23

Hydrochemical summary for Carnmenellis groundwaters of Cornwall, SW England.

Determinand		Units	Detection limit	Min	Max	Median	Upper baseline	n
T	temperature	^{o}C						
pH	lab measured			6.74	9.43	8.13	8.70	110
DO	dissolved oxygen	mg l^{-1}						
SEC	conductivity	µS cm^{-1}						
Ca	calcium	mg l^{-1}	0.02	<0.02	91.9	34.7	69.8	110
Mg	magnesium	mg l^{-1}	0.05	<0.05	25.8	4.51	16.6	110
Na	sodium	mg l^{-1}	0.05	0.932	186	13.4	114	110
K	potassium	mg l^{-1}	0.5	<0.5	19.8	2.46	8.02	110
Cl	chloride	mg l^{-1}	0.1	0.685	251	8.34	55.9	110
SO_4	sulphate	mg l^{-1}	0.1	<0.1	103	20.1	57.6	110
HCO_3	bicarbonate	mg l^{-1}		10.4	415	156	290	110
NO_3-N	nitrate (as N)	mg l^{-1}	0.05	<0.05	86.8	0.435	25.4	110
NO_2-N	nitrite (as N)	mg l^{-1}	0.05	<0.05	0.911	<0.05	<0.05	110
NH_4-N	ammonium	mg l^{-1}						
Al	aluminium	µg l^{-1}	1.0	<1.0	2960	3.65	182.5	31
As	arsenic	µg l^{-1}	0.01	0.048	15.5	0.36	7.805	31
B	boron	µg l^{-1}	0.01	2.84	623.1	17.3	182	31
Ba	barium	µg l^{-1}	0.005	0.092	409.5	15.3	118.5	31
Be	beryllium	µg l^{-1}	0.005	<0.005	0.2	0.005	0.091	31
Br	bromide	µg l^{-1}		3.88	451	29.6	156.5	31
Cd	cadmium	µg l^{-1}	0.002	<0.002	8.09	0.017	0.685	31
Co	cobalt	µg l^{-1}	0.005	<0.005	4.94	0.056	2.505	31
Cr	chromium	µg l^{-1}	0.01	0.036	8.94	0.15	1.23	31
Cu	copper	µg l^{-1}		0.31	149	13.4	121	31
F	fluoride	µg l^{-1}	50	<50	4280	108	1966	110
Fe$_{total}$	iron	µg l^{-1}	10	<10	4065	31.4	763	110
Hg	mercury	µg l^{-1}	0.005	<0.005	0.069	0.021	0.064	31
I	iodide	µg l^{-1}	0.1	0.17	30.9	0.65	5.12	31
La	lanthanum	µg l^{-1}	0.002	0.01	16.1	0.037	0.77	31
Li	lithium	µg l^{-1}	0.002	0.55	32.7	3.64	28.15	31
Mn	manganese	µg l^{-1}	1	<1	1957	15.2	411	110
Mo	molybdenum	µg l^{-1}	0.002	0.14	30.1	1.19	14.85	31
Ni	nickel	µg l^{-1}	0.005	0.59	62.0	0.61	14.6	31
Pb	lead	µg l^{-1}	0.005	0.013	2.91	0.27	1.835	31
Sb	antimony	µg l^{-1}	0.003	0.01	0.41	0.043	0.235	31
Se	selenium	µg l^{-1}	0.01	0.018	1.61	0.19	0.975	31
Si	silicon	µg l^{-1}	20	1063	17146	4541	9168	110
Sr	strontium	µg l^{-1}	1	<1	3622	281	1977	110
U	uranium	µg l^{-1}	0.001	0.13	102	1.21	27.1	31
Y	yttrium	µg l^{-1}	0.002	<0.002	6.69	0.1	1.07	31
Zn	zinc	µg l^{-1}	2	<2	8.63	12	214.5	110

Hydrochemical summary for Iddefjord granite groundwaters, Southeast Norway

Determinand		Units	Detection limit	Min	Max	Median	Upper baseline	n
T	temperature	^{o}C		7.4	9.7	8.6	9.7	9
pH	lab measured			6.66	9.58	8.05	9.49	30
DO	dissolved oxygen	mg l^{-1}						
SEC	conductivity	µS cm^{-1}		164	530	367	524	9
Ca	calcium	mg l^{-1}	0.02	1.14	47.4	17.3	40.4	30
Mg	magnesium	mg l^{-1}	0.05	0.249	24.5	3.79	17.1	30
Na	sodium	mg l^{-1}	0.05	5.08	131	23.3	96.6	30
K	potassium	mg l^{-1}	0.5	<0.5	9.37	1.12	7.61	30
Cl	chloride	mg l^{-1}	0.1	8.22	84.2	22.7	70.7	30
SO_4	sulphate	mg l^{-1}	0.1	3.76	43.4	10.1	36.1	30
HCO_3	bicarbonate	mg l^{-1}		13.4	306	75.4	216	30
NO_3-N	nitrate (as N)	mg l^{-1}	0.05	0.167	46.2	5.53	27.7	30
NO_2-N	nitrite (as N)	mg l^{-1}	0.05	<0.05	<0.05	<0.05	<0.05	30
NH_4-N	ammonium	mg l^{-1}						
Al	aluminium	µg l^{-1}	1	1.38	191	13.6	151	30
As	arsenic	µg l^{-1}	0.01	0.016	3.56	0.0755	0.766	30
B	boron	µg l^{-1}	0.01	3.23	357	10.3	135	30
Ba	barium	µg l^{-1}	0.005	0.18	34.5	4.73	18.6	30
Be	beryllium	µg l^{-1}	0.005	0.005	0.01	0.005	0.0044	30
Br	bromide	µg l^{-1}		27.9	332	74.2	181	30
Cd	cadmium	µg l^{-1}	0.002	<0.002	0.065	0.01	0.0528	30
Co	cobalt	µg l^{-1}	0.005	<0.005	0.76	0.072	0.368	30
Cr	chromium	µg l^{-1}	0.01	0.019	1.41	0.155	0.759	30
Cu	copper	µg l^{-1}		1.01	196	13.6	98.4	30
F	fluoride	µg l^{-1}	50	<50	811	<50	75.2	30
Fe_{total}	iron	µg l^{-1}	10	<10	401	11,2	90,0	30
Hg	mercury	µg l^{-1}	0.005	<0.005	0.04	0.0065	0.029	30
I	iodide	µg l^{-1}	0.1	0.19	10.7	0.63	4.93	30
La	lanthanum	µg l^{-1}	0.002	<0.002	1.35	0.0095	0.186	30
Li	lithium	µg l^{-1}	0.002	0.1	12	0.44	4.54	30
Mn	manganese	µg l^{-1}	1	<1	637	21	151	30
Mo	molybdenum	µg l^{-1}	0.002	<0.002	0.53	0.076	0.51	30
Ni	nickel	µg l^{-1}	0.005	0.092	11.9	0.67	1.96	30
Pb	lead	µg l^{-1}	0.005	0.035	2.75	0.335	1.73	30
Sb	antimony	µg l^{-1}	0.002	0.007	0.21	0.0185	0.10	30
Se	selenium	µg l^{-1}	0.01	<0.01	0.89	0.305	0.73	30
Si	silicon	µg l^{-1}	20	2009	14852	5733	9528	30
Sr	strontium	µg l^{-1}	0.1	11.5	515	95	337	30
U	uranium	µg l^{-1}	0.001	<0.001	0.89	0.037	0.309	30
Y	yttrium	µg l^{-1}	0.002	<0.002	1.25	0.026	0.268	30
Zn	zinc			1.42	134	17.75	120.1	30

Hydrochemical summary for Egersund anorthosite groundwaters.

Determinand		Units	Detection limit	Min	Max	Median	Upper baseline	n
T	temperature	^{o}C						
pH	lab measured			6.74	9.43	8.13	8.70	110
DO	dissolved oxygen	mg l^{-1}						
SEC	conductivity	µS cm^{-1}						
Ca	calcium	mg l^{-1}	0.02	<0.02	91.9	34.7	69.8	110
Mg	magnesium	mg l^{-1}	0.05	<0.05	25.8	4.51	16.6	110
Na	sodium	mg l^{-1}	0.05	0.932	186	13.4	114	110
K	potassium	mg l^{-1}	0.5	<0.5	19.8	2.46	8.02	110
Cl	chloride	mg l^{-1}	0.1	0.685	251	8.34	55.9	110
SO_4	sulphate	mg l^{-1}	0.1	<0.1	103	20.1	57.6	110
HCO_3	bicarbonate	mg l^{-1}		10.4	415	156	290	110
NO_3-N	nitrate (as N)	mg l^{-1}	0.05	<0.05	86.8	0.435	25.4	110
NO_2-N	nitrite (as N)	mg l^{-1}	0.05	<0.05	0.911	<0.05	<0.05	110
NH_4-N	ammonium	mg l^{-1}						
Al	aluminium	µg l^{-1}	1.0	<1.0	2960	3.65	182.5	31
As	arsenic	µg l^{-1}	0.01	0.048	15.5	0.36	7.805	31
B	boron	µg l^{-1}	0.01	2.84	623.1	17.3	182	31
Ba	barium	µg l^{-1}	0.005	0.092	409.5	15.3	118.5	31
Be	beryllium	µg l^{-1}	0.005	<0.005	0.2	0.005	0.091	31
Br	bromide	µg l^{-1}		3.88	451	29.6	156.5	31
Cd	cadmium	µg l^{-1}	0.002	<0.002	8.09	0.017	0.685	31
Co	cobalt	µg l^{-1}	0.005	<0.005	4.94	0.056	2.505	31
Cr	chromium	µg l^{-1}	0.01	0.036	8.94	0.15	1.23	31
Cu	copper	µg l^{-1}		0.31	149	13.4	121	31
F	fluoride	µg l^{-1}	50	<50	4280	108	1966	110
Fe_{total}	iron	µg l^{-1}	10	<10	4065	31.4	763	110
Hg	mercury	µg l^{-1}	0.005	<0.005	0.069	0.021	0.064	31
I	iodide	µg l^{-1}	0.1	0.17	30.9	0.65	5.12	31
La	lanthanum	µg l^{-1}	0.002	0.01	16.1	0.037	0.77	31
Li	lithium	µg l^{-1}	0.002	0.55	32.7	3.64	28.15	31
Mn	manganese	µg l^{-1}	1	<1	1957	15.2	411	110
Mo	molybdenum	µg l^{-1}	0.002	0.14	30.1	1.19	14.85	31
Ni	nickel	µg l^{-1}	0.005	0.59	62.0	0.61	14.6	31
Pb	lead	µg l^{-1}	0.005	0.013	2.91	0.27	1.835	31
Sb	antimony	µg l^{-1}	0.003	0.01	0.41	0.043	0.235	31
Se	selenium	µg l^{-1}	0.01	0.018	1.61	0.19	0.975	31
Si	silicon	µg l^{-1}	20	1063	17146	4541	9168	110
Sr	strontium	µg l^{-1}	1	<1	3622	281	1977	110
U	uranium	µg l^{-1}	0.001	0.13	102	1.21	27.1	31
Y	yttrium	µg l^{-1}	0.002	<0.002	6.69	0.1	1.07	31

Hydrochemical summary for Lower Palaeozoic metasediment groundwaters, Norway