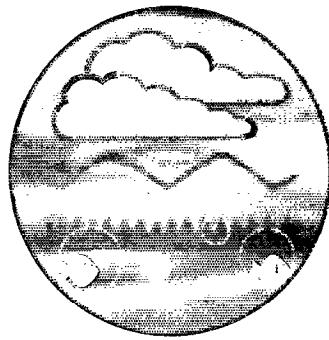
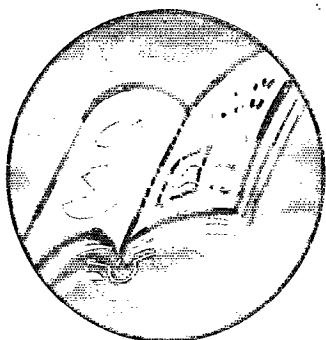
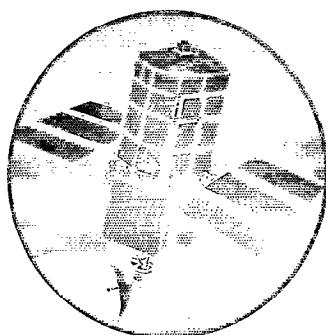


The Natural (Baseline) Quality of Groundwaters in England and Wales

The Culm Aquifers, SW England



Research and Development

Project Record
W6/i722/2



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The Natural (Baseline) Quality of Groundwaters in England and Wales

The Culm Aquifers, South-West England

R&D Project Record W6/1722/2

P Shand and L J Brewerton

Research Contractor:
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Publishing Organisations:

Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD

Tel: 01454 624400
Fax: 01454 624409

ISBN: 1 85705 100 9

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This report provides a summary of groundwater quality in a specific aquifer block, which serves the needs of the British Geological Survey in response to its remit as a national survey within NERC, and serves the needs of the Environment Agency in meeting its regulatory role and in informing its internal and external customers.

Research contractor

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SECTION I. EXECUTIVE SUMMARY

This document forms one of the regional studies being carried out on representative aquifers or parts of aquifers in England and Wales to provide an improved understanding of the natural baseline quality of groundwaters. It serves as a reference document against which current quality and future trends in quality (improvements and deteriorations) may be assessed. The background to the project, the detailed objectives and the methodology are described in Appendix 1.

Section I provides a brief summary of the water-quality situation and in Section II, further information is given to the controls on the hydrogeochemistry necessary for an informed interpretation of the water quality.

Groundwater is important in much of south-west England as a source of potable water for rural communities. The focus of this document is to summarise the baseline chemistry of the groundwaters to be found in the Carboniferous strata, often referred to as the Culm, and especially to demonstrate any variations on the baseline imposed by the geology.

The chemical data used are taken equally from unpublished BGS surveys (1988) of shallow water quality and from the results of a survey of private sources commissioned by the National Rivers Authority (Geotechnics, 1994) in 1993. Although most of the data are taken from private well or borehole sources, some springs are included. Pollution from agricultural sources in particular is a significant problem and any waters considered to have been polluted have been omitted so that the emphasis remains on the natural baseline.

Groundwater in the Culm is slightly acidic but is buffered by traces of carbonate minerals; very few acid (<pH 5.5) waters (with consequent high Al) are to be found, although enrichment of some metals may occur in relation to reducing conditions. The groundwaters show an extremely wide range of major-element compositions (Table I.1, Figure I.1) reflecting differences in depth, residence time and bedrock lithology.

The baseline chemistry of many elements, notably Cl, is influenced by atmospheric inputs, especially in coastal areas, but the influence of reactions with the bedrock may be recognised by the increasing alkalinity and in the concentrations of several major ions relative to chloride. There is little contrast between groundwaters in the three geological sub-units of the Culm (Lower Carboniferous, Crackington and Bude Formations). Reactions with pyrite in the shale members of the Culm give rise to increases in sulphate.

The median concentrations for minor and trace elements provide a good summary of their natural abundance and these mainly reflect the extent of reactions with the bedrock, although in some cases (e.g. F) the atmospheric contribution remains important. The most significant feature of groundwaters in the Culm is the tendency for high concentrations of dissolved Fe and Mn which are produced mainly as a result of sulphide-mineral oxidation and the resultant reducing conditions in the shallow aquifer. The slightly acidic overall conditions probably help to maintain the high dissolved concentrations which may then give rise to metal precipitates on re-aeration.

KEYWORDS

Baseline quality, hydrochemistry, groundwater, Culm, SW England.

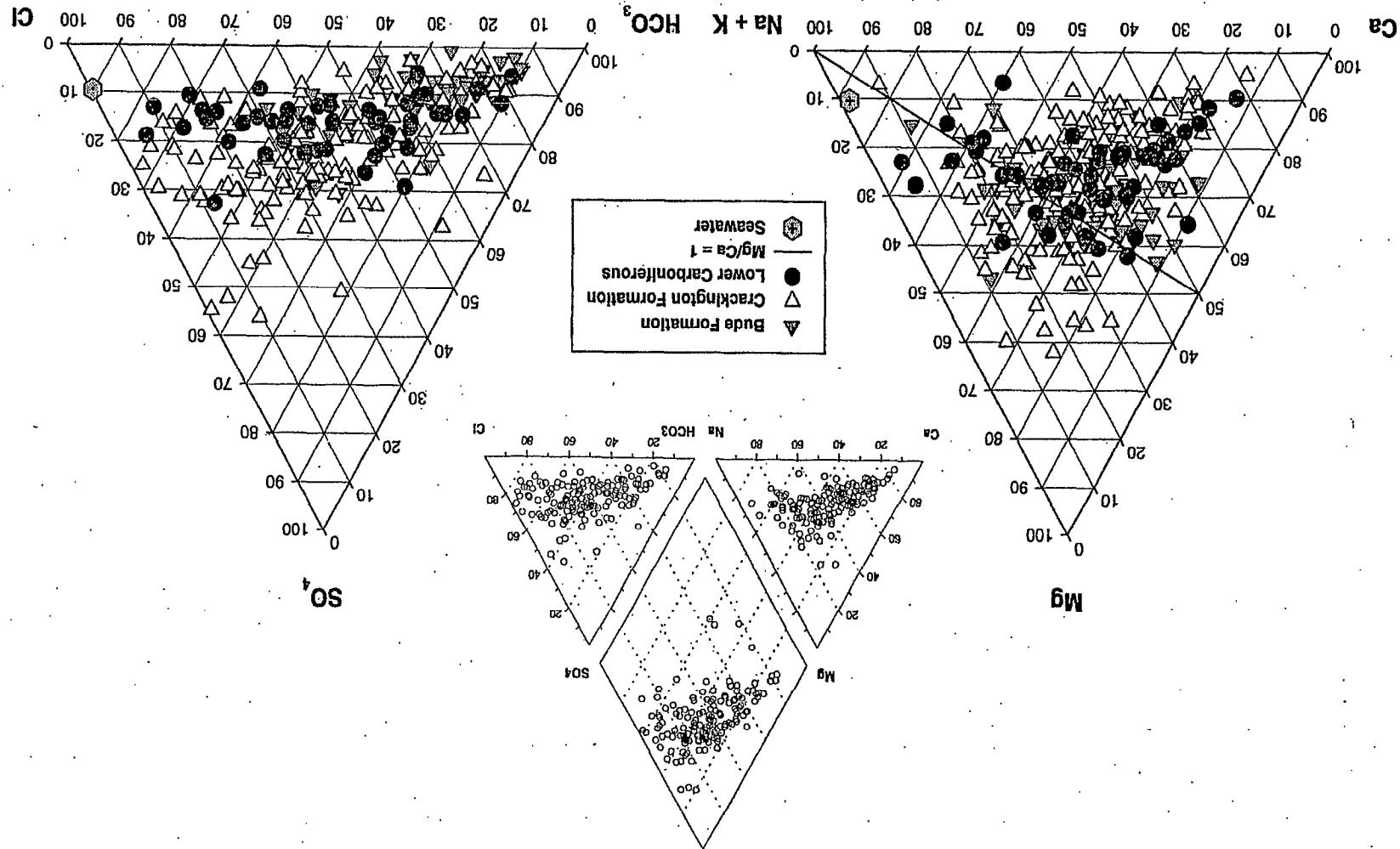


Figure I.1 Piper diagram and trilinear plots for groundwater from the Culm aquifer. Seawater and Mg/Ca ratio=1 are shown for comparison.

Table I.1 Statistical summary of groundwater quality for the Culm aquifer

Determinand	Units	Min	Max	Median	Upper baseline	n
Temp	Temperature	°C	8.1	18	12	15
pH (field)		4.85	8.89	6.25	7.31	265
DO	dissolved oxygen	mg l ⁻¹	0.1	21	4.7	14.7
SEC	electrical conductivity	µS cm ⁻¹	45	904	208	520
Ca	calcium	mg l ⁻¹	0.47	87.7	15	45
Mg	magnesium	mg l ⁻¹	<0.5	55	5.95	25
Na	sodium	mg l ⁻¹	4.9	118	12.2	31
K	potassium	mg l ⁻¹	0.05	24	1.47	9
Cl	chloride	mg l ⁻¹	5.2	93	19	53
SO ₄	sulphate	mg l ⁻¹	2.3	105	14	36
HCO ₃	bicarbonate	mg l ⁻¹	1.2	336	45	199
NO ₃ -N	nitrate (as N)	mg l ⁻¹	0.02	4.9	1.1	8
NO ₂ -N	nitrite (as N)	mg l ⁻¹	<0.001	0.04	<0.003	0.009
NH ₄ -N	ammonium	mg l ⁻¹	<10	403	<15.5	<10
TOC	total organic carbon	mg l ⁻¹	<0.2	5.8	<0.5	1.9
Al	aluminium	µg l ⁻¹	<20	300	<30	61
As	arsenic	µg l ⁻¹	<0.2	17	0.3	6
Ba	barium	µg l ⁻¹	0.2	520	11.8	140
Be	beryllium	µg l ⁻¹	<1	1.48	<1	<1
B	boron	µg l ⁻¹	<6	255	15.7	85
Cd	cadmium	µg l ⁻¹	<0.2	8.42	<6	2.5
Cr	chromium	µg l ⁻¹	<1	10	<8	2.9
Co	cobalt	µg l ⁻¹	<1	170	<4	6
Cu	copper	µg l ⁻¹	<1	14068	<4	206
F	fluoride	µg l ⁻¹	20	890	170	400
Fe _t	iron (total)	µg l ⁻¹	<3	25000	50	4040
Hg	mercury	µg l ⁻¹	<0.02	0.05	<0.02	<0.02
La	lanthanum	µg l ⁻¹	<20	26.5	<20	<20
Li	lithium	µg l ⁻¹	<1.4	38	<1.4	11
Mn	manganese	µg l ⁻¹	<0.6	13000	43	1200
Mo	molybdenum	µg l ⁻¹	<20	22.5	<20	<20
Ni	nickel	µg l ⁻¹	<1	89	<10	36
P _t	phosphorus (total)	µg l ⁻¹	<33	300	<33	83
Pb	lead	µg l ⁻¹	<1	413	<30	44
Sb	antimony	µg l ⁻¹	<1	2	<1	<1
Se	selenium	µg l ⁻¹	<0.2	0.4	<0.2	<0.2
Si	silicon	µg l ⁻¹	<500	15200	3745	9800
Sr	strontium	µg l ⁻¹	6.5	349	49.3	170
Y	yttrium	µg l ⁻¹	<0.6	3.86	<0.6	1
Zn	zinc	µg l ⁻¹	<2	2300	12.9	148
	atrazine	µg l ⁻¹	<0.009	0.027	<0.01	<0.009
TCE	trichloroethene	µg l ⁻¹	<0.3	0.3	<0.3	124

SECTION II.

UNDERSTANDING THE NATURAL QUALITY - CONTROLS AND PROCESSES

1. PERSPECTIVE.

Groundwater is important in much of south-west England as a source of potable water for rural communities especially away from major roads where mains supplies derived from surface water have sometimes been installed. Especially important is the summer demand when shallow groundwater supplies may be used to augment resources. It is estimated that some 500 private water supplies exist within the region.

The shallow groundwater of the Culm is also important in maintaining the baseflow of rivers and streams and may well account for 30–40% of the total flow. Baseflow is typically regarded as a source of pure water, important in buffering the quality of streams and rivers.

Data from around 270 boreholes, wells and springs (Figure II.1.1) provide a representative summary of the natural (baseline) quality of shallow groundwater in the Culm. Contamination (diffuse or point-source) mainly from agricultural sources may present a problem but after removal of data with $\text{NO}_3\text{-N} > 5 \text{ mg l}^{-1}$, the remaining data are found to be little influenced by human activity, as demonstrated by low TOC, NH_4 and total P.

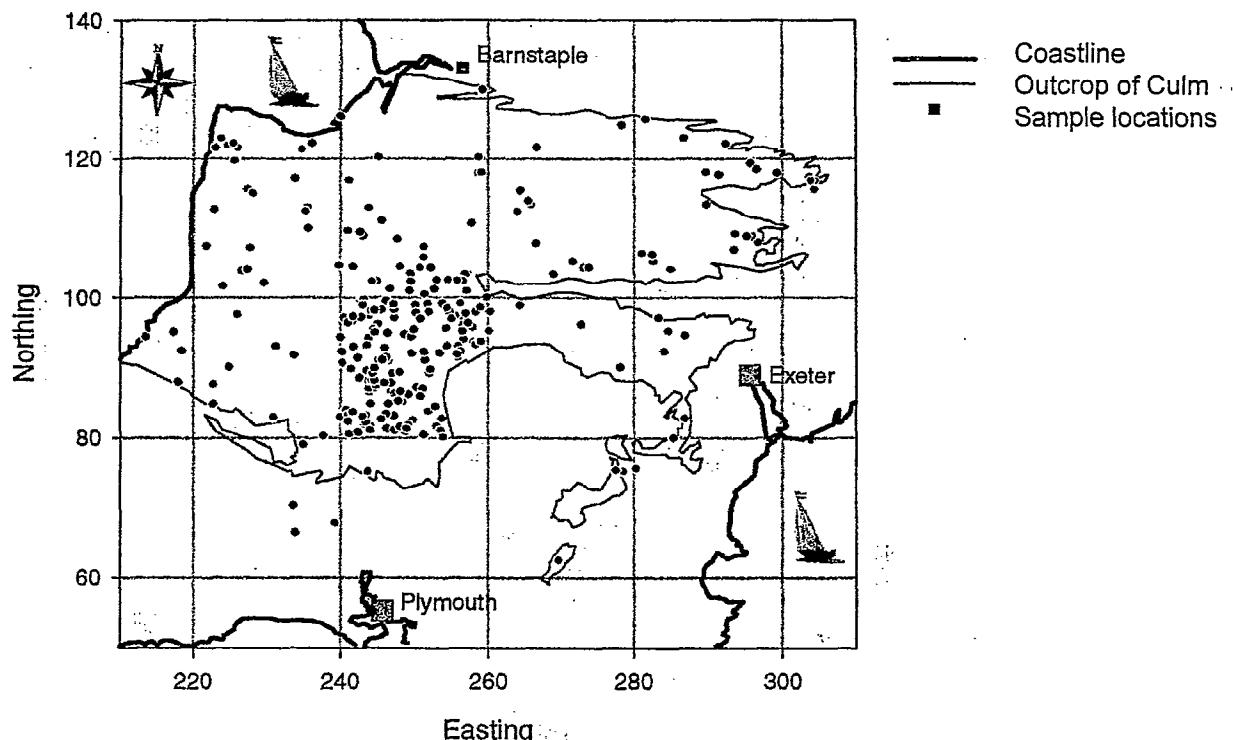


Figure II.1.1 The outcrop of the Lower Carboniferous (Culm) in north Devon with shallow groundwater sites used in this study.

2. BACKGROUND

2.1 Geology

The area described covers the outcrop of the Carboniferous rocks often referred to as the Culm (Figure II.1.1). The sequence forms part of a geosynclinal complex comprising highly folded rocks (Figure II.2.1) aligned along a regional east-west axis. The Culm is sub-divided into an Upper and Lower division.

The Lower Culm is rather heterogeneous but is considered here as a single unit. There are two main subdivisions: i) the Meldon Shale and Quartzite Formation and ii) the Meldon Chert. The Meldon Shale and Quartzite Formation comprises a series of grey shales with thin quartzites and also locally thick volcanic tuff beds. The Meldon Chert Formation is mainly a series of shales and cherts but containing important lenses of massive black limestone (Edmonds et al., 1968).

The Upper Culm may be further subdivided. The lowest member, the Crackington Formation, was deposited near the edge of a former continental shelf and shows evidence of having been deposited by turbidity currents. The rock sequences comprise typically thin fine-grained sandstones, with characteristic turbidite sedimentary structures, interbedded with dark shales and mudstones (Edmonds et al., 1968; Freshney et al., 1979).

The overlying Bude Formation is similar to the Crackington Formation. It was probably formed under shallow water deltaic conditions and typically contains massive sandstones up to 20 m thick with individual units of around 1 m. These sandstones are laterally discontinuous. Grey and black mudstones form partings between the sandstone units.

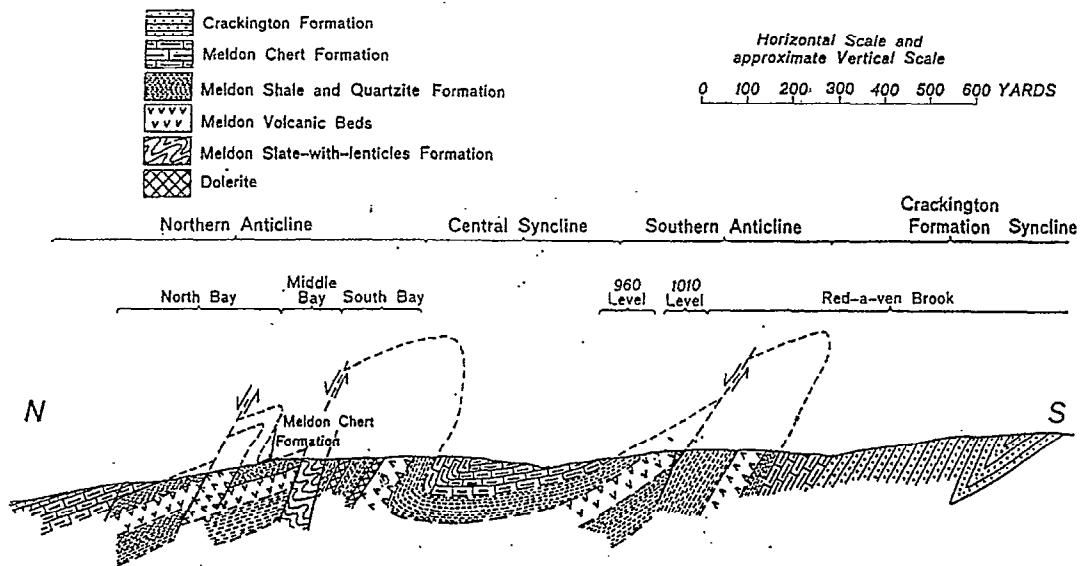


Figure II.2.1 The outcrop of the Lower Carboniferous (Culm) in north Devon with shallow groundwater sites used in this study.

2.2 Hydrogeology

The Carboniferous sediments in general have low primary porosity on account of their fine grain size and indurated nature, an exception possibly being some of the coarser sandstone units of the Bude Formation. However, the heterogeneous nature of the sediments, combined with folding, faulting and jointing have resulted in the production of extensive secondary porosity which allows for the transmission and storage of groundwater. Lateral continuity of fracture porosity may not occur. Yields of groundwater are typically in the range 0.4–0.7 l s⁻¹ from wells up to 30 m depth.

2.2 Aquifer Minerals

The black organic rich shales of the Crackington Formation contain abundant pyrite although in the north of their outcrop, siderite is the predominant iron mineral. Oxidation of the pyrite may give rise locally to an increase in sulphate, lowering of the pH and an increase in the concentration of iron and some trace metals. The Bude Formation is also relatively organic-rich and contains minor coal seams; occasional red beds indicate that some penecontemporaneous oxidation has occurred. The carbonates and volcanic sediments of the Lower Culm where present are likely to lead to relatively alkaline groundwater.

2.3 Rainfall Chemistry

Rainfall chemistry is available for two sites, Lifton [SX 239 084] and Halwill [SX 243 099], within the project area. The average of bulked monthly rainfall for an 18-month period (1987-1989) is shown in Table II.2.12.

Table II.2.1 Chemistry of rainfall at Lifton and Halwill (1987-1989)

Site	Element (mg l ⁻¹)	Na	K	Ca	Mg	SO ₄	Si	Sr
Lifton		5.12	<0.8	1.38	0.81	7.02	0.51	0.007
Halwill		4.29	<0.8	0.98	0.62	4.01	0.36	0.005

3. DATA QUALITY AND HANDLING

3.1 Source of Data and Quality of Data.

There are two main sources of unpublished data for the Culm aquifer which have been combined for the purpose of this study: the results of a survey for the National Rivers Authority (Geotechnics, 1994) and data from surveys carried out by the British Geological Survey (Edmunds and Kinniburgh, 1987; 1988). The former set is a regional survey covering the whole of the outcrop area of the Culm. The BGS surveys provide more detailed information on a smaller area of the Culm based mainly on the Tamar and Torridge catchment areas.

The overall quality of the data is shown by a histogram of the ionic balance (Figure II.3.1) where 89% of the data are within $\pm 10\%$ and 78% are within $\pm 5\%$ error. A statistical summary of all the data is given in Table I.1 and details of the procedures used for its construction are given in Appendix 1.

3.2 The Influence of Pollution.

In order to examine the baseline quality, all data with $\text{NO}_3\text{-N} > 5 \text{ mg l}^{-1}$ (15% of the total data available) have been removed, this being the only parameter considered to be indicative of pollution, common to all data. Other indices of pollution likely to be absent or to occur below threshold values in the natural system are TOC, P and NH_4 . The TOC median concentration of $<0.5 \text{ mg l}^{-1}$ (Table I.1; Figure II.4.1) implies that agricultural pollution is not important and only 14% of the data exceed 1 mg l^{-1} which might be considered as the threshold for contamination. Likewise, there are low concentrations of $\text{NH}_4\text{-N}$ and total P in the set of data used here (Figure II.4.1).

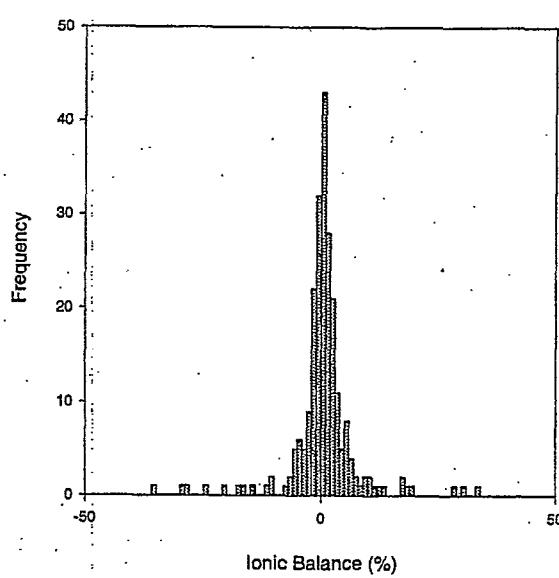


Figure II.3.1 Histogram of ionic balance for combined groundwater analyses.

In a review of contamination of shallow groundwaters (Shand et al., 1994) relating to SW England, the following criteria were used to provide a pollution score:

- K/Na molar ratio > 0.3. By normalising to Na, the enhancement due to increased salinity was reduced and the excess potassium was generally too great to be attributable to mineral weathering.
- TOC > 15 mg l⁻¹. This value is too high for most groundwaters which have natural concentrations of 1-2 mg l⁻¹ TOC.
- NO₃-N > 5 mg l⁻¹; NH₄-N > 0.3 mg l⁻¹. At some sites NH₄-N was high whilst NO₃-N concentrations were low, indicating a source from slurry or silage liquid in which little or no oxidation had occurred during groundwater seepage.
- Ortho-P > 0.2 mg l⁻¹. It is unlikely that P will be present naturally in excess of 0.1 mg l⁻¹, as generally any excess entering the system will coprecipitate with iron.
- Cl > 35 mg l⁻¹. Higher Cl values than expected from rainfall subjected to evaporation are attributable to fertilizer application.

In addition, indicators of groundwater pollution have been proposed by Edmunds (1996) and an extract from this is given in Appendix 1 (Table A1.2.2). It can be concluded that relatively few parameters are needed to be able to monitor or detect pollution from agricultural and/or urban sources (notably the anions Cl, SO₄, NO₃, HCO₃ and DOC). Nitrate above a threshold limit of 5 mg l⁻¹ as N is likely to be derived from contaminant sources together with DOC above 2 mg l⁻¹.

4. HYDROCHEMICAL CHARACTERISTICS

The average pH of groundwaters in the Culm is slightly acidic (field pH median 6.25, range 4.85 to 8.89). The range demonstrates the heterogeneity of waters in the shallow groundwater environment and there is similarly a wide range in major element compositions (Figure I.1).

The relatively high modal value for Cl (Figure II.4.1) reflects the proximity of the area to the coast and the influence of marine aerosol as dry deposition or bulk rainfall. Sodium is also derived largely from marine-derived aerosols (molar Na/Cl = 0.85), as is some Mg. The low alkalinites (median value 45 mg l⁻¹) indicate that on average, the groundwaters are undersaturated with carbonate minerals due mainly to their short residence times. The median NO₃-N value of 1.09 mg l⁻¹ is indicative of the overall quality of the shallow waters (after removal of those suspected of pollution).

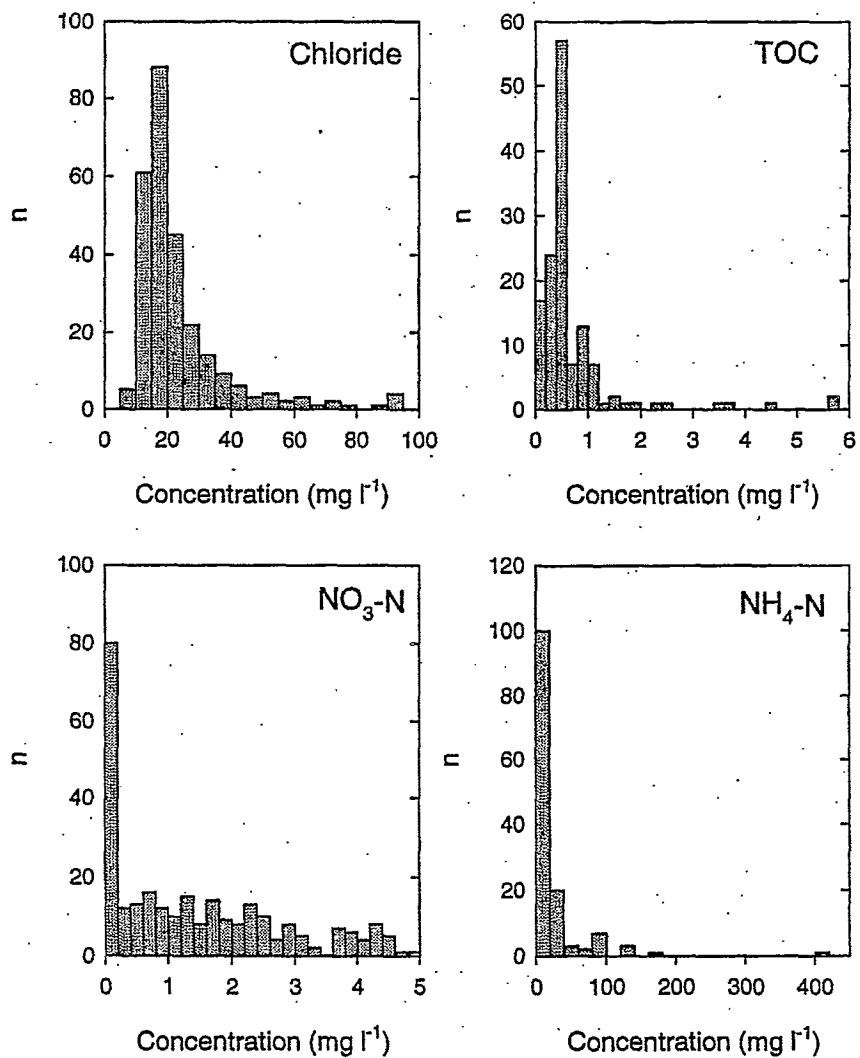


Figure II.4.1 Histograms of Cl, TOC, NO₃-N and NH₄-N concentrations in the Culm groundwaters.

The data are summarised as box plots in which the determinants are ordered for convenience in the order of concentration found in seawater. The major ions all show an enrichment relative to Cl compared with that present in dilute seawater (Figure II.4.2), related to the degree of reaction with soils and aquifer materials. This is particularly marked for Ca, HCO₃ and NO₃-N which are dominantly derived through such interactions.

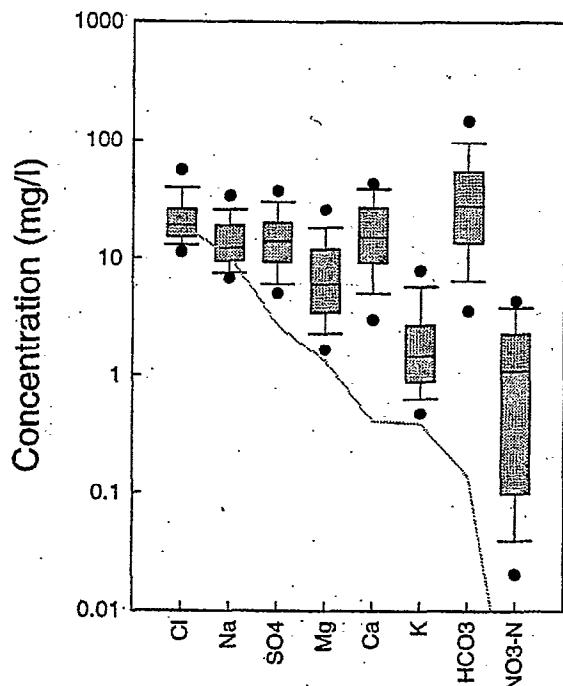


Figure II.4.2 Range of major-ion concentrations in the Culm. The median and 5, 25, 75 and 95 percentiles are shown.

Selected minor and trace element concentrations are shown in Figure II.4.3. Aluminium concentrations are relatively low in the shallow groundwaters and any outliers correspond with the few acid waters. Median concentrations of most of the metals are at or below 1 µg l⁻¹, with the exception of Co (1.12), Cu (3.59), Fe (50), Mn (44), Mo (5.26), Ni (3.23), Pb (2.62), Zn (12.9). Of these, only the concentrations of Fe and Mn (discussed below) present any problems.

The major, minor and selected trace element distributions are further illustrated using cumulative frequency diagrams (Figures II.5.1-3). The narrow range in concentration of several minor ions (F, B) is an expression of the range in input (bulk precipitation) and the lack of any positive skewness implies negligible contribution from geological sources.

The narrow range of Si concentrations and shape of the curve indicates an upper solubility limit (Figure II.5.2). Barium on the other hand, shows a positive skewness indicating that increasing concentrations are the probable result of reactions with the bedrock. The selected trace metals all show a wide compositional range relating to geological factors controlling baseline. Attention is drawn to the large percentage of raw waters which exceed the CEC maximum admissible concentrations for Fe (50%) and Mn (72%) in drinking water (Figure II.5.3).

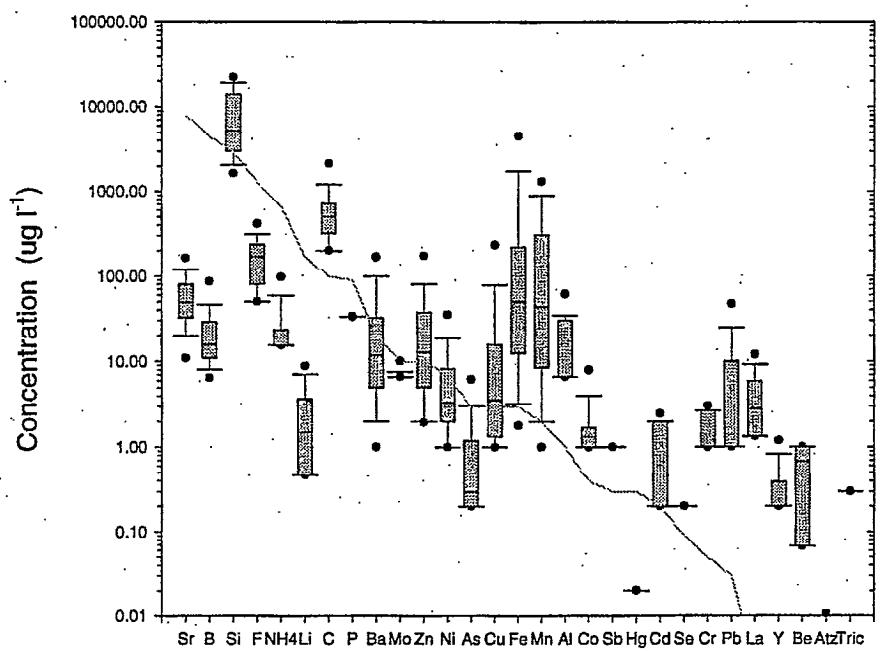


Figure II.4.3 Minor and trace elements in the Culm groundwaters. Elements are ordered according to their concentration in seawater.

5. REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS

5.1 Major ions and pH

The regional plot for Cl (Figure II.5.4) shows that distance from the coast is an important factor and that marine sources are the primary source of Cl. The median value of 19 mg l^{-1} Cl in the groundwaters may be compared with the mean value of 7 mg l^{-1} measured for rainfall in the centre of the area. Assuming that Cl was only atmospherically derived, Cl can be used to estimate evapotranspiration and recharge; a recharge with a minimum of 37% rainfall is indicated.

The distribution of pH and alkalinity over the area bears little relationship to the geological subdivisions of the Culm. The isolated high alkalinity values are scattered across the formation, although the Bude Formation has a slightly higher median concentration. An alkalinity above 75 mg l^{-1} probably indicates buffering by carbonate minerals which are recorded within the shallow parts of the Culm. Vein mineralisation is also a potential source of alkalinity.

Sulphate concentrations above about 3 mg l^{-1} (by analogy with Cl) must be derived from natural sources. The median value is 14 mg l^{-1} and the map (Figure II.5.4) shows that the distribution of higher than average SO_4 is not localised. The most likely geological source for the higher SO_4 is the oxidation of pyrite or other sulphide minerals present in black shales of the Culm formations.

5.2 Minor Elements and Trace Metals

The median concentration of F ($170 \mu\text{g l}^{-1}$) implies that rainfall is the predominant source. Concentrations in excess of $400 \mu\text{g l}^{-1}$ are rare and there is no suggestion of any anomaly which might indicate secondary mineralisation. Higher-than-average F concentrations are most likely related to areas with carbonate or possible apatite. **Barium** concentrations are relatively low in groundwaters from the Lower Carboniferous but locally high in the Crackington Formation (Figure II.5.4). Groundwaters from the lower part of the Bude Formation generally have high concentrations of Ba (up to $520 \mu\text{g l}^{-1}$) but a decrease to the north is probably related to facies changes in the sediments. **Iron** and **Mn** concentrations are related to redox conditions and do not show any correlation with rock type. Aqueous concentrations are highly variable throughout the area (Figure II.5.4) with, locally, extremely high concentrations (up to $25000 \mu\text{g l}^{-1}$ Fe and $13000 \mu\text{g l}^{-1}$ Mn) in the more reducing waters. **Arsenic** concentrations are low, but enrichments around the margins of the Dartmoor granite may be related to sulphide mineralisation; groundwaters from the eastern area of the Bude Formation show a slight enrichment probably related to the predominance of shales. **Nickel** is also variable but, apart from the Bude Formation where concentrations are generally low, average concentrations are quite high in comparison with most UK aquifers. **Aluminium** is also generally low (median $< 30 \mu\text{g l}^{-1}$) but some high concentrations ($> 100 \mu\text{g l}^{-1}$) are present in waters with low pH. Similarly, lead is low with the exception of some of the acid waters. The other base metals **Cu** and **Zn** have baseline concentrations (3.6 and $13 \mu\text{g l}^{-1}$ respectively) which are not exceptional for UK groundwaters, although a few sites have high concentrations (maximum 14068 and $2300 \mu\text{g l}^{-1}$ respectively). **Beryllium** is enriched (up to $1.2 \mu\text{g l}^{-1}$) in one or two sites with acid waters in the granite aureole.

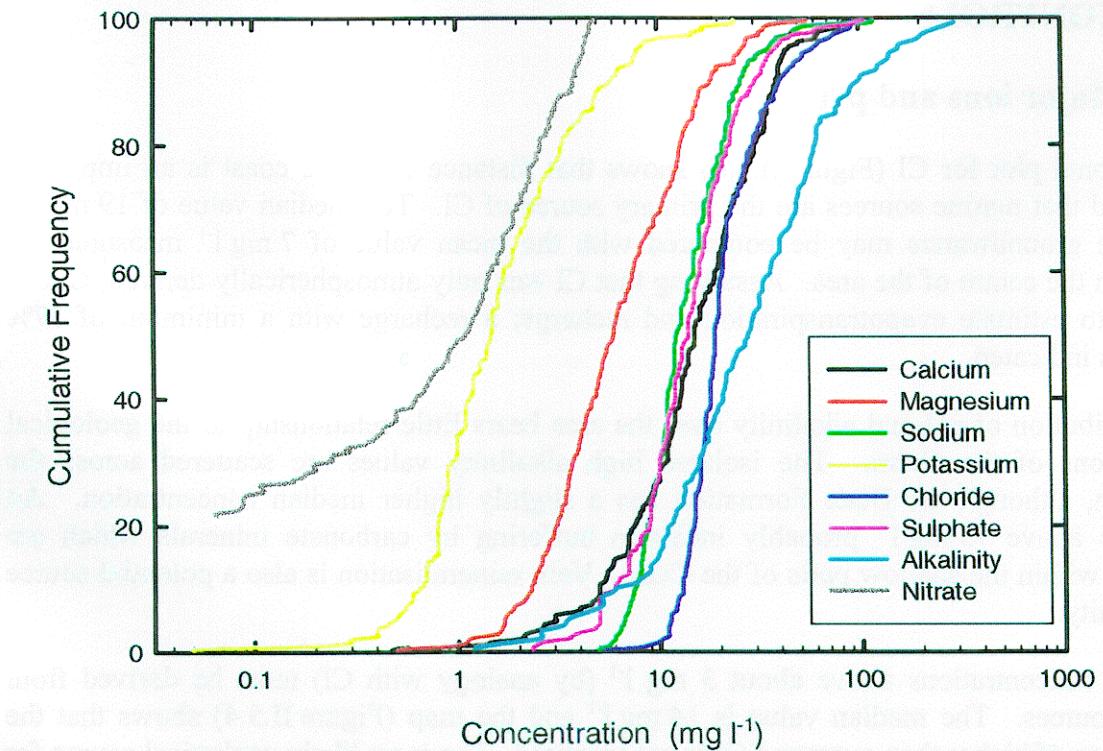


Figure II.5.1 Cumulative-frequency diagram for major ions in Culm groundwaters.

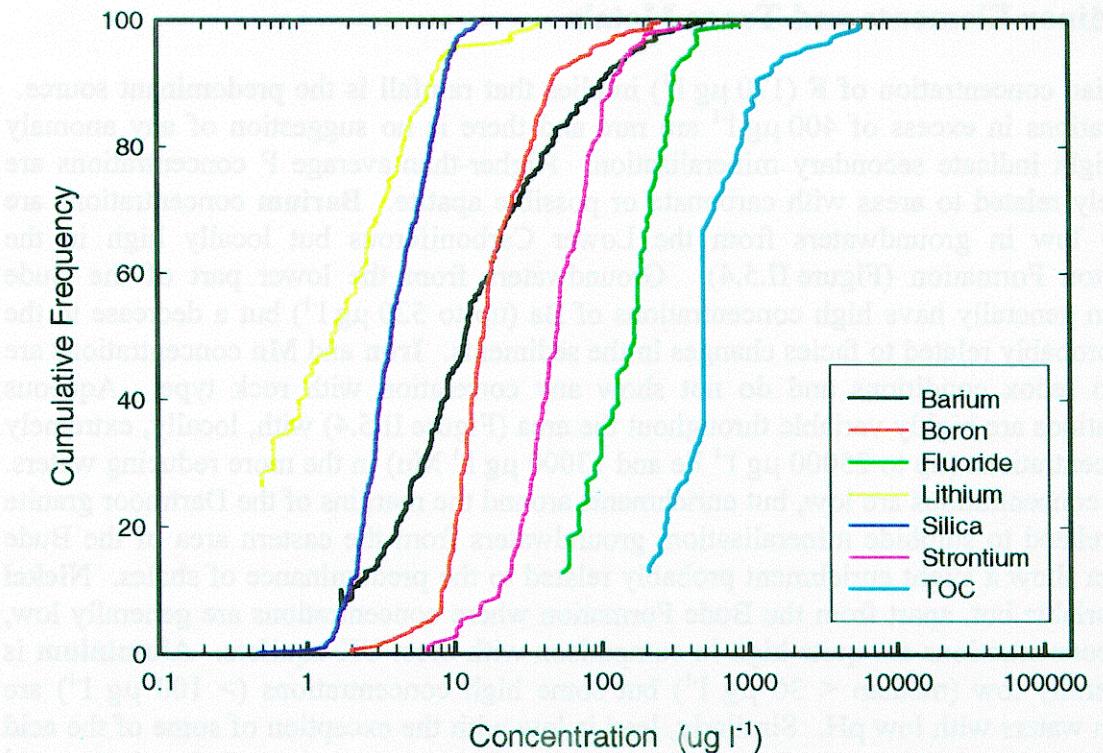


Figure II.5.2 Cumulative-frequency diagram for minor and trace elements (non-metals) in the Culm groundwaters.

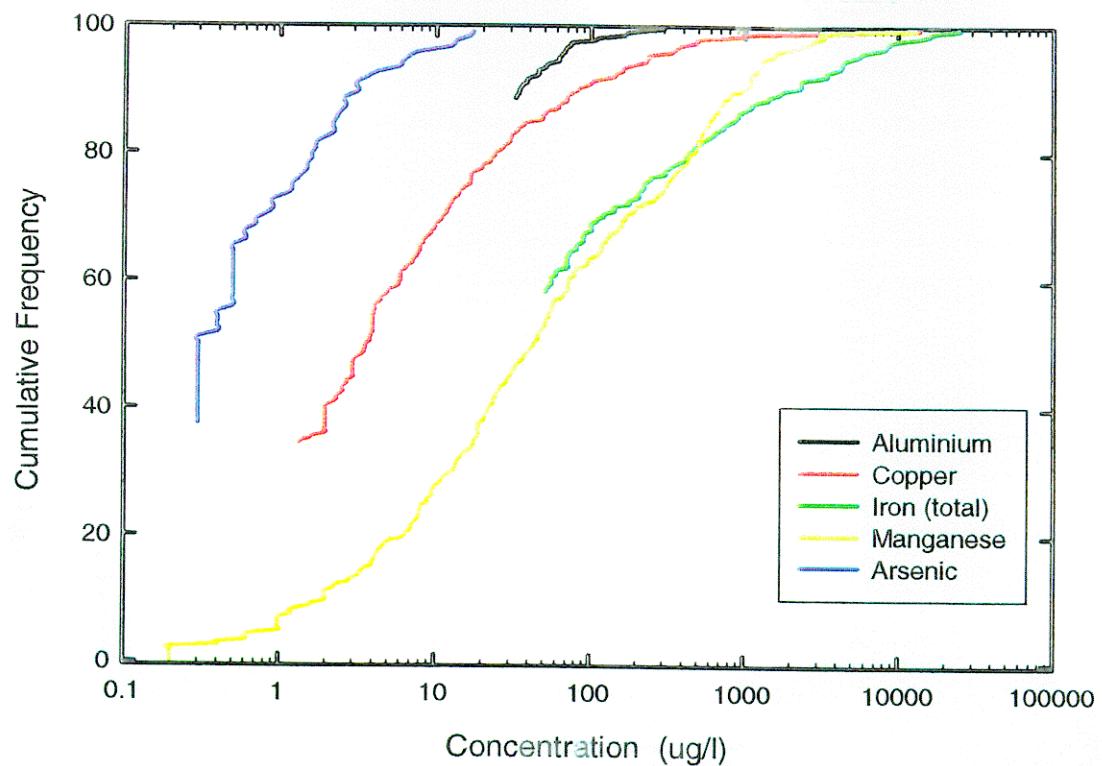


Figure II.5.3 Cumulative-frequency diagram for selected trace elements (Al, Cu, Fe, Mn, As) in the Culm groundwaters.

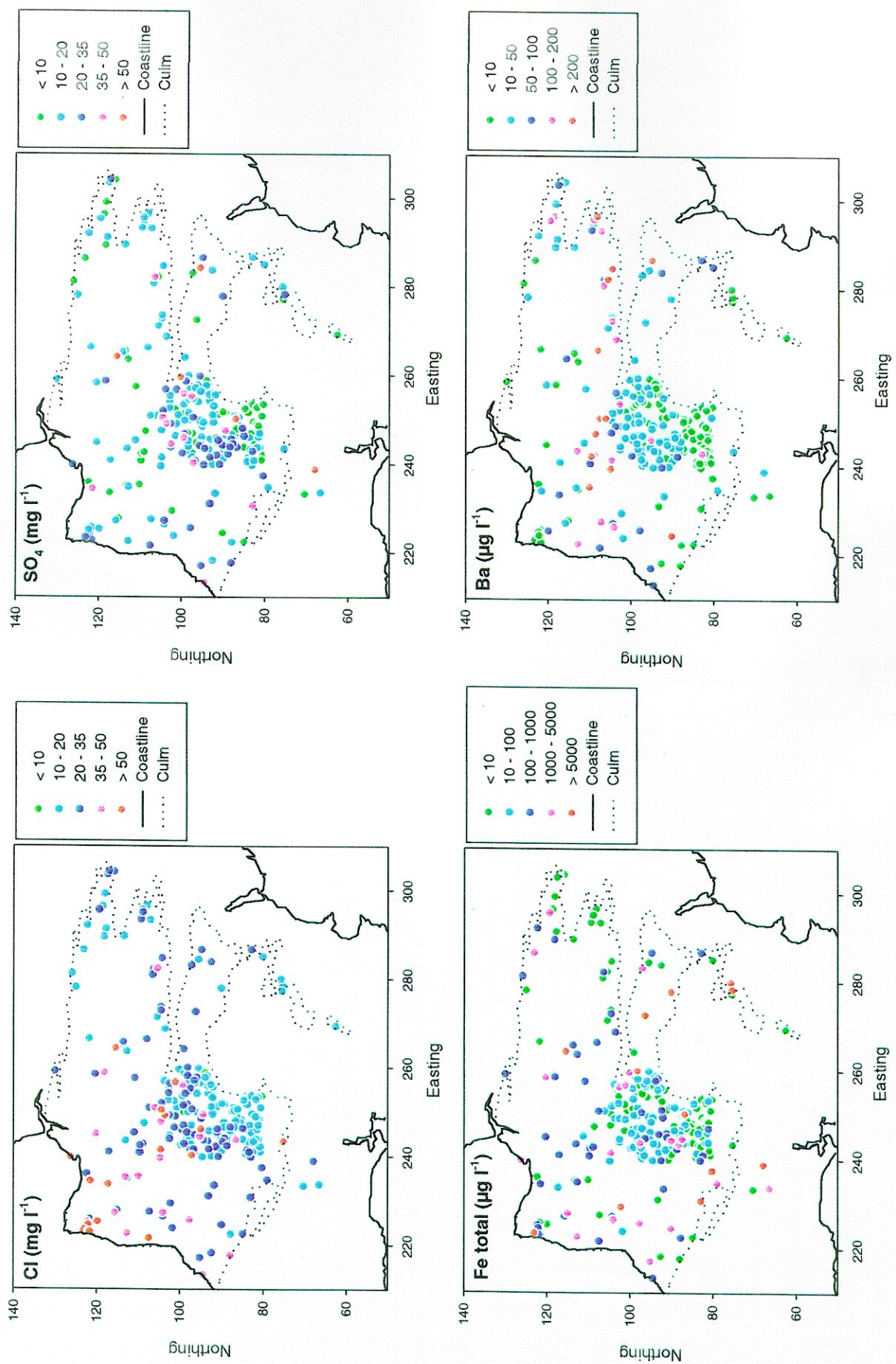


Figure II.5.4 Regional distribution of groundwater quality for Cl , SO_4 , Fe and Ba in the Culm of south-west England.

5.3 Trends with Time

The seasonal variation in chemistry of the shallow groundwater is shown on Figure II.5.5. Fluctuations in water chemistry are present in the winter months most likely in response to periods of high rainfall, implying relatively short residence times for the water in these springs.

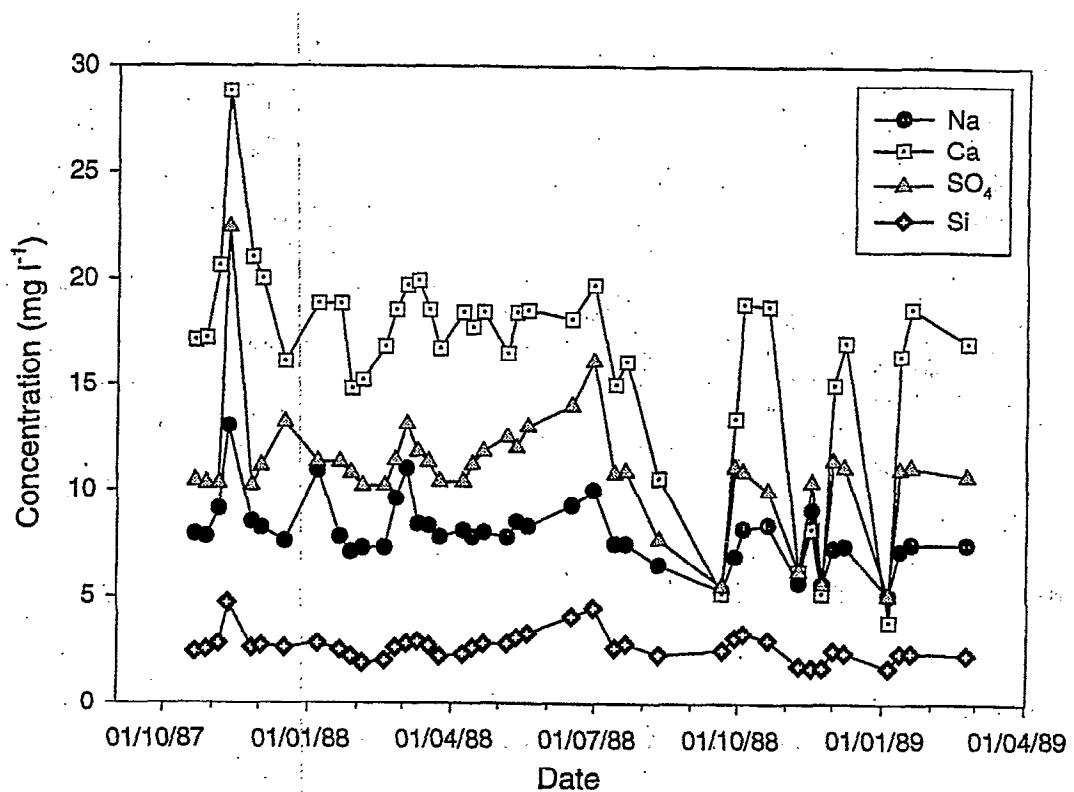


Figure II.5.5 Seasonal chemical variation in waters from the Meldon spring [SX 256 923] on the Culm Formation.

6. SUMMARY

The chemistry of groundwater in the Culm is very variable, reflecting differences in depth, residence time and bedrock lithology. However, there is little contrast between the three geological units of the Culm. The waters are generally slightly acidic, but where carbonate minerals are present locally, the pH values of the waters are well buffered. The baseline water chemistry is controlled by both atmospheric (e.g. Cl, F) and bedrock (e.g. Ca, Si) sources. Baseline concentrations of most elements are relatively low, the exceptions being locally high Fe and Mn. The high Fe is produced mainly from the oxidation of sulphide minerals and mobilised as a consequence of reducing conditions in the aquifer. Iron and Mn are subsequently precipitated on re-aeration and may be an important control on trace-metal concentrations.

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APPENDIX 1. A GUIDE TO THE NATURAL (BASELINE) QUALITY OF GROUNDWATER IN ENGLAND AND WALES.

A1.1 Introduction

The baseline quality of groundwater is overwhelmingly determined by naturally occurring reactions between rain or surface water and rocks. There is, therefore, a need to know the way in which these natural characteristics are acquired and how they affect water quality. It is not possible to assess whether or not contamination is taking place until the baseline quality is known. Up to now, no single document has been available for use by regulators or developers of groundwater to ascertain the baseline quality of groundwater in England and Wales. In particular, such a document or series of documents is needed to be able to assess the extent to which natural inputs affect water quality and UK Drinking Water Standards. These reports therefore provide summary information on the baseline quality of UK groundwaters on a regional basis, using representative areas of the Major and Minor Aquifers in a standard and readily usable format. This Appendix describes the objectives of the study and there is discussion of the baseline concept, geochemical concepts, the methodology used and problems of data collection and collation. In due course as and when the aquifer areas have been reported, an overview report will be produced to provide a summary of groundwater quality from a national perspective using the combined data set.

A1.1.1 Natural Groundwater Quality and the Baseline Concept

Baseline concentrations of a substance in groundwater may be defined in several different ways. For the purpose of this study the definition is given as 'the concentration of a given element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources'. Thus, an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era. To do this some attempt must be made to measure the 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). The interpretation of radiocarbon presents various problems, including the fact that it is a reactive tracer, intimately involved in reactions of the carbonate system; there is also the problem of mixed waters occurring due to pumping from boreholes which are open over large vertical intervals. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water or palaeoclimatic indicators such as noble gases or chloride (Cl) may provide indirect evidence of residence time (Bath and Edmunds, 1978; Andrews et al., 1995). The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium (^3H), dissolved greenhouse gases such as chlorofluorocarbons (CFCs) and certain organic pollutants may also provide evidence of a recent component in the groundwater.

A1.1.2 Controls on the Baseline Chemistry

Natural baseline chemistry is initially determined by atmospheric inputs, although at the present day these will be affected by atmospheric pollution unlike the pre-industrial era. The predominant groundwater mineral composition develops quite rapidly during the infiltration process, being strongly influenced by reactions in the top few metres in the soil and 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 A1.1.1. The resulting groundwater chemistry is thus strongly controlled by geochemistry and mineralogy such that the baseline conditions will vary characteristically from one lithology to another. In fact the 'baseline chemistry' may dominate even polluted groundwaters and therefore one of the objectives of this study is to separate where possible the baseline from any contaminant inputs.

A1.1.3 Limitations of Groundwater Sampling

Any attempt to define true baseline conditions in the aquifer is severely hampered by the problems of sampling. Groundwater quality and age stratification invariably occurs under undisturbed natural conditions. This is the result of different flow rates being a consequence of hydraulic gradients, the natural variation in aquifer physical properties, as well as natural variations in the geochemical and geological properties of aquifers. Borehole construction penetrates this layering and pumped samples will inevitably represent mixtures of the stratified system. In aquifers showing strong dual porosity, such as the Chalk, the water contained in the fissures may be considerably different chemically from the older water contained in the matrix. In this series of reports it is probable that water quality data generally relate to mixed samples. Wherever possible and relevant, examples are included of chemical stratification or discontinuities of the water with depth or within the porosity of the rock.

A1.1.4 Project Aims and Objectives

The overall objective of this project is to collate and review reliable groundwater quality information and to characterise and classify the baseline quality of groundwaters in selected major and minor aquifers. This will establish references against which current and targeted groundwater quality can be compared. From the viewpoint of the water industry, the information allows regulators and their customers to establish a natural standard against which statutory Drinking Water Standards may be compared, assess the variations in water quality with time, assess the need for groundwater remediation, the options for remedial action and the performance of remedial works in reaching any approved target quality. From the viewpoint of BGS, the Baseline Study also provides a series of regional reference documents to assist its role in providing information on aspects of groundwater resources and quality to the professional and lay public.

Table A.1.1.1 Controls on the baseline chemistry of groundwaters.

(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	Fundamental control by the host rock geochemistry e.g. carbonate versus non-carbonate rock and the degree of homogeneity.
Mineralogy	The mineral assemblage of the host rock, the relative abundance of individual 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 and lithological variations.
Within Aquifer	Facies changes along the strike or downgradient within the same stratigraphical unit, either of a geochemical or physical nature must be considered. 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 convenient to be able to distinguish water of different 'ages' using a variety of geochemical indicators:	
<ol style="list-style-type: none"> 1. Palaeowater: recharge originating during/before the last glacial era. 2. Pre-Industrial Water. 3. Pre-War (1940s). 4. Modern Era. 	

A1.2. METHODOLOGY

A1.2.1 Data Collection

An initial scoping study (Edmunds et al., 1996) showed that the majority of suitable data were held in the Environment Agency (EA) and in the British Geological Survey (BGS) archives. Small datasets might be available for some areas in the published literature or from PhD or MSc theses. For each study area data were collected from these sources. Data from the EA were generally available from the current monitoring network, boreholes which had been monitored in the past, and areas of special study. The amount of data available varied from region to region. Most of the data only covered the last decade and few digital data were available before this. The majority of recent data were available in a digital format.

BGS data were obtained from the BGS geochemical database. Many of these were from studies over the past two decades designed specifically to investigate the natural water quality baseline. For some areas, data were entered from paper records although it has not been possible within the terms of reference of this investigation to search the water industry archives systematically for historical data.

The scoping study identified determinands which would be the focus for the natural baseline quality investigation (Table A1.2.1). However, not all the determinands included in this list were available in all the datasets. In particular, as some of the minor elements are not on the EA's standard monitoring list, they are rarely available in the EA datasets. From some data sources, only a restricted set of determinands were therefore available.

In addition, several other elements or species are included which are not on this core list, especially some trace elements. These are included where high-quality data exist since it is common experience that enquiries often request information outside the main database. It is likely that in future years, such data will be sought as the basis of more sophisticated enquiries into environmental trends. Isotopic data from published and unpublished sources are used as a basis for establishing residence times.

Table A.1.2.1 Determinands selected for baseline quality investigation. Determinands of health significance are given in bold.

Physical/Chemical Parameters:	pH, Eh, DO, temperature
Major determinands:	Ca, Mg, Na, K, SO ₄ , Cl, NO ₃ , HCO ₃
Minor determinands:	Organic carbon (TOC), Fe, Mn , F, As, P, Al, NH ₄ , B, Cu, Zn, Cd, Ni, Cr, Co, Pb, Ba, Sr, Sb, Be, Hg, Mo, U
Residence-time indicators:	³ H, ¹⁴ C, δ ¹⁸ O, δ ² H, ¹³ C

A1.2.2 Data Collation

The data from all sources were brought together in a database designed for the project. The database is a Microsoft Access relational database which contains all the water-chemistry data collected for the project. The database is composed of several linked tables containing information on site location, sampling dates and chemical parameters. This set of tables is linked to a second database which contains queries for processing the data into a standard set of units. Finally, the data have been manipulated to calculate the ionic balance, produce summary statistics and allow output of the data in a suitable format for input into other computer software.

A1.2.3 Treatment of Groundwater Pollution in the Baseline Study

As pointed out above, all sources of pumped groundwater are likely to be mixtures of water of different depths and residence times since boreholes penetrate the water quality/age stratification developed naturally over decades or centuries or millennia. A component of most exploited groundwaters is likely to be less than 100 years old and it might be expected that the majority of groundwaters (except in the deeper confined aquifers) would contain traces of solutes derived from the industrial era. However, these concentrations would be below or near detectable limits and are unlikely to present a health hazard. For the purposes of this study, such groundwaters will have a chemical composition similar to baseline. Where possible, for each area described, any reference groundwaters which pre-date the industrial era are identified for example by their isotopic composition. A series of indicators of groundwater pollution from different origins has been proposed (Edmunds, 1996) and summarised in Table A1.2.2.

Therefore, data used in this baseline study have been incorporated without preselection (with the exception of the Culm of south-west England) and the cumulative frequency diagram is used to examine the possibility of pollution as discussed below. Nitrate concentrations in excess of 5 mg l^{-1} can be used safely to divide natural waters from those with an anthropogenic contribution, although in aerobic environments, a natural baseline component may be much lower than this (below 2 mg l^{-1}). However, nitrate is likely to be the principal contaminant in many groundwaters and may not be accompanied by significant concentrations of other ions (since nitrate is derived often from the oxidation of NH_4); increases in SO_4^{2-} are well known from areas with significant fertiliser use.

Table A1.2.2 Indicators of groundwater pollution.

Brief description: the chemistry (quality) of groundwater reflects inputs from the atmosphere, from soil and water-rock reactions (weathering), as well as from pollutant sources such as mining, land clearance, agriculture, acid precipitation, domestic and industrial wastes. The relatively slow movement of water through the ground means that residence times in groundwaters are generally orders of magnitude longer than in surface waters. As in the case of surface-water quality, it is difficult to simplify to a few parameters. However, in the context of geoindicators, a selection has been made of a few important first-order and second-order parameters that can be used in most circumstances to assess significant processes or trends at a time-scale of 50-100 years.

The following first-order indicators of change (in **bold**) are proposed, in association with a number of processes and problems, and supported by a number of second-order parameters:

1. Salinity: **Cl**, SEC (specific electrical conductance), **SO₄**, Br, TDS (total dissolved solids), Mg/Ca, δ¹⁸O, δ²H, F;
2. Acidity and redox status: **pH**, **HCO₃**, Eh, DO, Fe, As;
3. Radioactivity: **³H**, **³⁶Cl**, **²²²Rn**;
4. Agricultural pollution: **NO₃**, **SO₄**, **DOC** (dissolved organic carbon), K/Na, P, pesticides and herbicides;
5. Mining pollution: **SO₄**, **pH**, Fe, As, other metals, F, Sr;
6. Urban pollution: **Cl**, **HCO₃**, **DOC**, B, hydrocarbons, organic solvents.

A1.2.4 UK Water-Industry Standards

Standards of water quality for human consumption are summarised in Table A1.2.3.

A1.2.5 Statistical Treatment of Data

Statistical summaries of data of each of the study areas aid presentation and comparison of the natural baseline chemistry. Whilst it would have been ideal to present maximum and minimum values, medians, means and standard deviations for each determinand, because the datasets comprised data with different detection limits, only the minimum, maximum, median, upper baseline (95 percentile) as well as number of samples used are reported.

When all the data lie above the detection limit the calculation of the mean, standard deviation and median values is straightforward. The mean, X, is calculated as the sum of the data values X_i, divided by the number of values, n:

$$X = \Sigma X_i / n$$

The standard deviation gives a measure of the spread of the data:

$$s^2 = \Sigma (X_i - X)^2 / (n-1) \quad \text{variance}$$

$$s = \sqrt{s^2} \quad \text{standard deviation}$$

Table A1.2.3. Summary of standards of water quality for human consumption (adapted from poster: Groundwater Usage and the Water Industry in the United Kingdom, BGS).

		CEC*	WHO*	CONV.FACTOR
		GL* (mg l ⁻¹)	MAC* (mg l ⁻¹)	GV* (mg l ⁻¹)
Calcium	(Ca ²⁺)	100	-	-
Magnesium	(Mg ²⁺)	30	50	-
Sodium	(Na ⁺)†	20	150	200
Potassium	(K ⁺)	10	12	-
Chloride	(Cl)	25	-	250
Sulphate	(SO ₄ ²⁻)	25	250	250
Aluminium	(Al ³⁺)	0.05	0.5	0.2
Nitrate	(NO ₃)† (as N)	25 5.65	50 11.3	50 10
Nitrate	(NO ₂)†	-	0.1	3 P
Ammonium	(NH ₄ ⁺)	0.05	0.5	1.5
Iron	(Fe ³⁺) (Fe ²⁺)	0.05(Fe _T)	0.2(Fe _T)	0.3(Fe _T)
Manganese	(Mn ²⁺)	0.02	0.05	0.1
		(µg/l)	(µg/l)	(µg/l)
Copper	(Cu ²⁺)	3000	-	1000
Zinc	(Zn ²⁺)	5000	-	3000
Phosphate	(HPO ₄ ²⁻)	400	5000	-
Fluoride	(F)†	8-12°C 25-30°C	1500 700	1500 -
Barium	(Ba ²⁺)	100	-	700
Silver	(Ag ⁺)	-	10	-
Arsenic	(As)†	-	50	10 P
Cadmium	(Cd ²⁺)†	-	5	3
Cyanide	(CN)†	-	50	100
Chromium	(Cr)†	-	50	50 P
Mercury	(Hg)†	-	1	1
Molybdenum	(Mo)†	-	-	70
Nickel	(Ni)	-	50	20
Lead	(Pb ²⁺)†	-	50	10
Antimony	(Sb)	-	10	5 P
Selenium	(Se)†	-	10	10
Pesticides	(separately) (total)	-	0.1 0.5	different for each compound
Polycyclic Aromatic Hydrocarbons	(PAH) (CTC)	-	0.2	-
Carbon tetrachloride	(TCE) (°C)	- 12	- 25	2 -
Trichloroethene		6.5-8.5	-	6.5-8.5
Temperature	(µScm ⁻¹ at 20°C)	400	-	-
pH				
Conductivity				

*CEC : Council of the European Communities Directive 80/778

*GL : Guide level

*MAC : Maximum admissible concentration

*WHO : World Health Organisation. Guidelines for drinking water quality. 1993

*GV : Guide value

† : Inorganic constituents of health significance (WHO, 1993)

[additionally: asbestos, barium, beryllium, nickel, silver, - no guide value set]

P : Provisional value

The median, or 50th percentile, is the central value of the distribution when the data are ranked in order of magnitude:

$$\begin{aligned}\text{median } (P_{50}) &= X_{n+1}/2 && \text{when } n \text{ is odd, and} \\ \text{median } (P_{50}) &= 0.5(X_{n/2} + X_{n/2+1}) && \text{when } n \text{ is even,}\end{aligned}$$

where X is the observation and n is the number of observations. The median value is less affected by outliers in the dataset unlike the mean which can be skewed significantly by one or two very high (or low) values in the dataset. When the dataset contains data below one detection limit for each determinand, there are various statistical techniques to cope with the data below the detection limit. The simplest is a substitution method. This method substitutes a value for each less-than value. The value substituted can be the detection limit (the worst-case scenario resulting in overestimation of the mean), zero (the best-case scenario resulting in underestimation of the mean) or half the reporting limit (a half-way house). The method is illustrated in Figure A1.2.1 (after Helsel and Hirsch, 1992). The results give a range in which the mean and standard deviation will fall. For many determinands, there is little difference between the means or standard deviations calculated using these methods. In this case no other technique is likely to produce a better estimate. However, when the means and standard deviation differ significantly, other more sophisticated techniques could be considered to estimate these statistics. When the dataset contains data below more than one detection limit as well as actual values, it is only possible to quote a mean using the probability plot method (Helsel and Hirsch, 1992). This is outside the scope of the project at present.

If more than 50% of the data are below the detection limit then the median is below the detection limit. Otherwise the median is the 50th percentile:

$$\begin{aligned}<1 <1 <1 <1 &2 3 4 && \text{median is } <1 \\ <1 <1 &1 2 3 3 4 && \text{median is } 2\end{aligned}$$

When the dataset contains more than one detection limit, as in the present study with data from EA and BGS sources, the statistics become more complex. If all the values are below a detection limit then the median can be calculated by removing the $<$ signs, calculating the median and restoring the $<$ sign:

$$<1 <1 <1 <10 <10 <20 <20$$

Here the median is <10 . If the number of values is even, the median is the higher of the two centre observations:

$$<1 <1 <1 <10 <20 <20$$

The median is still <10 .

A mixture of data from EA and BGS sources has resulted in datasets with more than one detection limit. The complex nature of the datasets has led to the decision to quote only the median values as well as the minimum, maximum, upper baseline and n . In these datasets, the mean value is likely to be more influenced by large amounts of data below the detection limit or by outlying high values than the median. It is felt that the mean calculated with a simple substitution method is likely to be misleading in many cases and that more sophisticated techniques may not be appropriate without studying the dataset in more detail than is possible within the project.

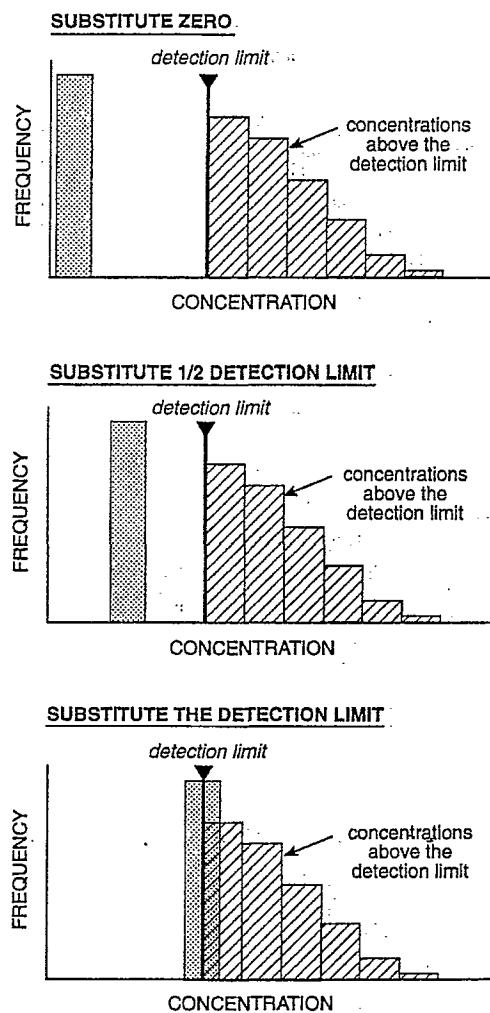


Figure A1.2.1. Illustration of the substitution method for estimating the mean (after Helsel and Hirsch, 1992).

In conclusion, the median value is likely to be more representative of the natural baseline chemistry than the mean. It is preferable as an averaging parameter because it is much less affected by outlying data and is a more robust estimate of the baseline average.

A1.2.6 Data Presentation

A number of graphical presentation techniques and tables have been chosen to aid the interpretation of the chemical and geochemical data. An explanation of the styles used in the project is given below.

Tables

In the report, statistical summaries are presented in table form. In some areas the dataset has been divided, for example, to show regional variations, variations down-dip (unconfined to confined conditions) or variations due to lithological changes. In this case, the table gives the range and median values for each subdivision of the dataset.

A second table gives details of sites used in the analysis, with locations, data source (EA or BGS), numbers of samples and a summary of the determinands available. Other tables are introduced to summarise related information such as host-rock chemistry or rainfall.

Trilinear diagrams

The trilinear diagram and its projection onto a diamond-shaped diagram is used to summarise the major ion chemistry in each aquifer. Major ion data from each analysis, expressed as milliequivalents (meq l^{-1}) are then calculated as a percentage for plotting in the left hand (cations) and right hand (anions) triangular fields. A single point is then produced by projecting the two points in the trilinear fields into the diamond projections. A special form of this plot, the Piper diagram, is produced when the data are ordered according to their total mineralisation (Piper, 1944; Hem 1980).

The trilinear diagram and its derivative, the Piper diagram, are widely used by hydrogeologists and they are a familiar way of presenting major-ion data. The composition of seawater may be included as a reference (note the very high molar Mg/Ca ratio). The molar Mg/Ca ratio of 1 may also be drawn as a reference line. This is useful since many groundwaters especially in carbonate aquifers trend towards this composition as water approaches equilibrium with calcite and dolomite (see Section A3). Waters with $\text{Mg/Ca} > 1$ will usually indicate seawater mixing, a source within dolomitic or basic igneous rocks or weathering of Mg-rich minerals.

Some limitations of the plots should be pointed out:

1. The diamond field is of limited value since the SO_4/Cl ratio and the Mg/Ca ratios are lost in the projection. However, the diamond plot probably indicates quite well the cation-exchange process where increasing HCO_3^- can occur with decreasing $(\text{Ca}+\text{Mg})/\text{Na}$ ratios (but with carbonate mineral saturation being maintained).
2. In carbonate aquifers, the anion trilinear field is of limited value since waters quickly reach saturation with carbonate minerals and thereafter no increase can occur in HCO_3^- (except where cation exchange occurs). The main changes of importance are in the SO_4 and Cl which can be equally well-represented on X-Y plots.

For further discussion on the use of trilinear diagrams to investigate cation exchange the reader is referred to Appelo and Postma (1994) pp 144-148. In addition, the text by Hem (1980) or Langmuir (1997) may be used as reliable general sources of information on hydrogeochemical interpretation.

Cumulative-frequency diagrams

Cumulative-frequency diagrams provide a way of presenting information on the distribution of the population of data for a given element in much the same way as a histogram. However, there is the possibility of presenting data for more than one element on the same diagram. In addition, it is easier to extract information from these diagrams than from histograms.

The form of the curve conveys information about the hydrogeochemistry and some of the information to be obtained is shown in Figure A1.2.2.

The most important concepts are:

1. The median concentration is used as a single reference point for the element baseline which can be compared regionally or in relation to other elements.
2. Log-normal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence times under natural, homogeneous aquifer conditions.
3. Narrow ranges of concentration may indicate rapid attainment of saturation with minerals (e.g. Si with silica, Ca with calcite).
4. A strong negative skew may indicate selective removal of an element by some geochemical process (e.g. NO_3^- by in-situ denitrification).
5. A narrow range in concentration at the upper limit is likely to indicate a mineral-solubility control (e.g. F control by fluorite).
6. A bimodal distribution indicates a heterogeneous system where several controls or sources are operating.
7. A positive skew most probably indicates a contaminant source for a small number of the groundwaters and this gives one simple way of separating those waters above the baseline. Alternatively the highest concentrations may indicate waters of natural higher salinity.

Box plots

Trilinear diagrams only give an overview of the behaviour of the major ions whereas box plots provide one way to represent the statistical distribution of major, minor and trace elements graphically which may be relevant in terms of baseline on a single plot. The data are plotted on a logarithmic scale in the order of the abundance of the elements present in seawater (the dilute seawater line is shown as a reference). For each element, maximum, minimum, median and percentile values are shown as illustrated in Figure A1.2.3. Two diagrams have been used: one for major ions and the other for minor and trace elements.

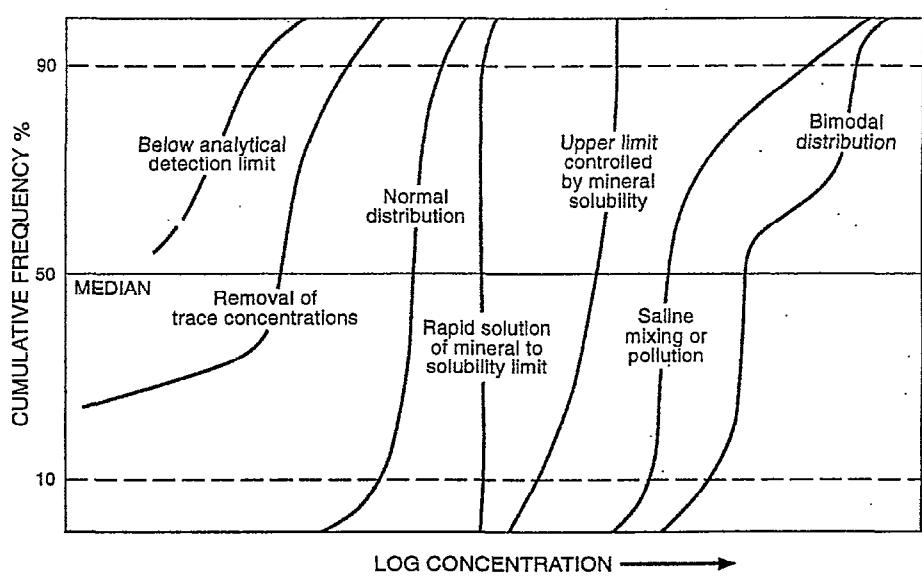


Figure A1.2.2. Illustration of the use of cumulative-frequency diagrams.

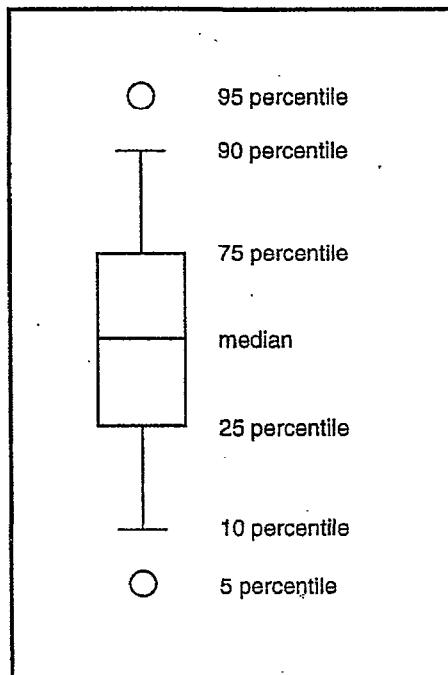


Figure A1.2.3. Key to the structure of the boxes in box plots.

Maps and plates

These are used to illustrate features as outlined below.

1. Maps and plates show the location and amount of data used in a given geographical area especially in relation to geology and major settlements. Of special significance may be the positions of the sample points relative to the coastline (influence of seawater on the baseline chemistry) and the distance from outcrop (chemical evolution downgradient). These have been drawn using a standard software package with symbol sizes proportional to chemical concentration or concentration ranges plotted with different colours (Culm). They are of special value for shallow groundwaters where there is little depth variation and where the baseline is closely linked to geology. However, it must be stressed that important chemical changes can take place in the vertical plane (depth stratification of water of different age or quality) which cannot be represented in map form. Where possible, cross sections or vertical profiles of chemistry are used to illustrate changes within the aquifer. Nevertheless, it should be stressed that almost all groundwater samples from wells or boreholes of the type used in this study are mixtures of water of different quality and/or ages from different depths.
2. For some areas, X-Y plots are used to illustrate overall water-quality variations for a given element. These have been compiled with concentration ranges represented by symbol size.
2. Photographs and photomicrographs are used where relevant as an illustration of the features of the aquifer materials which affect, and are affected by, the hydrogeological and geochemical processes of 2 colours or more which may operate.

A1.2.7 Report format

The report for each study area is in two parts. Section I summarises the natural baseline chemistry and gives a table of statistical data for the determinands available. A trilinear diagram is also presented in this section. Section II gives summary information on the geology and hydrogeology and discusses in more detail the hydrogeochemical data and the geochemical evolution of the aquifer. As far as practicable, the format of each report in the series is the same.

A1.3 GEOCHEMICAL CONCEPTS

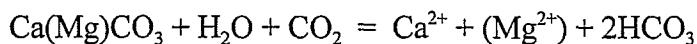
Some of the geochemical concepts and terminology used in the reports are included here as a reference. These terms will be added to in the nationwide report.

Redox boundary

A redox boundary marks a zone in an aquifer characterised by onset of reducing conditions as a result of complete consumption of oxidising species (notably NO_3^- and O_2) present in the water. The boundary is marked as a zone rather than a distinct point because the reduction reactions are sequential. Water at recharge will generally be saturated with dissolved oxygen at the partial pressure of the atmosphere ($10\text{--}12 \text{ mg l}^{-1}$ 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 still 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 and downgradient of this zone (redox boundary) 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 water 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) may also occur in extremely reducing conditions.

Carbonate reactions

The concentrations of H^+ (pH), pCO_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 between 1–2 orders of magnitude on passing through the soil:

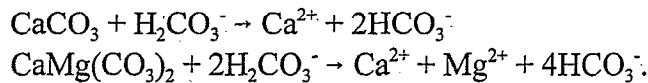


The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone. This process (**congruent dissolution**) yields Ca and Mg concentrations which are identical to those in the dissolving carbonate 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 ratios.

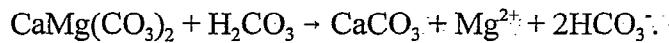
Congruent/incongruent reaction

In the context of groundwater chemical processes in the Sherwood Sandstone for example, 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. 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.

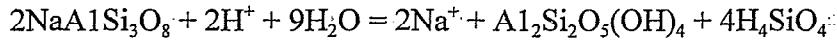
Examples of congruent reactions relevant to the Sherwood Sandstone aquifer are:



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



Most silicate minerals undergo in congruent dissolution. An example is the reaction of water with feldspar which produces cations and silica and leaves behind a residual clay:



A1.4. REFERENCES

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