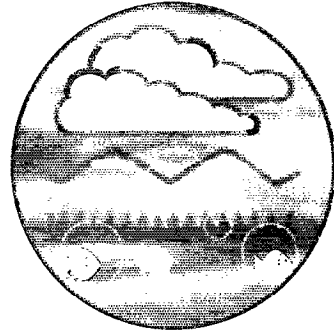
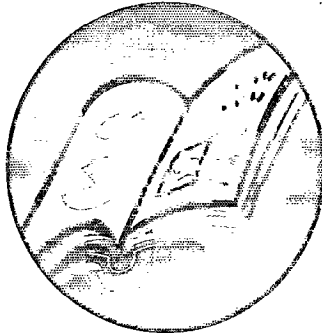
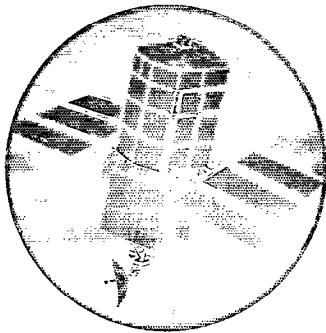


The Natural (Baseline) Quality of Groundwaters in England and Wales

Magnesian Limestone of Yorkshire and Northumbria



Research and Development

**Project Record
W6/i722/7**



**British
Geological
Survey**



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

Magnesian Limestone of Yorkshire and Northumbria

R&D Project Record W6/i722/7

L J Brewerton and W M Edmunds

Research Contractor:
British Geological Survey

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

Tel: 01454 624400

Fax: 01454 624409

Tel: 01793 411500

Fax: 01793 411691

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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

This document was produced under R&D Project i722 by:

British Geological Survey
Crowmarsh Gifford
Wallingford
Oxon
OX10 8BB

Tel: 01491 838800 Fax: 01491 692296

Environment Agency Project Manager

The Environment Agency's Project Manager for R&D Project i722 was:
Dr Paul Hart, Anglian Region

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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. This 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 water quality necessary for an informed interpretation of the water quality.

The natural baseline quality of groundwaters from the Magnesian Limestone (Figure I.1) is discussed in Section II of this report. The approach adopted is described in Appendix 1. The median concentrations given in Table I.1 of this section may be regarded as the best single value for baseline compositions. Two sets of values are given: one for the Yorkshire area and the other for Northumbria. The upper baseline value is defined by the 95 percentile. Values in excess of this are likely to be due to pollution. In the Yorkshire Magnesian limestone sources, some 60% of the groundwaters analysed have significant contributions from agricultural nitrate. In Northumbria the number is probably around 20%.

The major ion characteristics of the Magnesian Limestone aquifer are summarised in two Piper diagrams (Figures I.2 and I.3). The cations are dominated by Ca and Mg derived from the dolomitic limestone. The anions are dominated by HCO_3 from carbonate minerals and SO_4 derived from gypsum. Sulphate concentrations tend to be higher in Yorkshire groundwaters than in Northumbria, probably due to more extensive dissolution of gypsum. Chloride concentrations are generally low but occasional high values occur, probably due to the dissolution of halite.

The concentrations of most minor and trace elements are low with the exception of Fe, Mn and F. The median concentration of F in the Northumbria section is 0.7 mg l^{-1} and indicates that a source of F must exist within the formation probably as traces of fluorapatite in the carbonates. Selenium is detectable in the Yorkshire groundwaters (median $5.2 \text{ } \mu\text{g l}^{-1} \text{ Se}$).

KEYWORDS

Baseline quality, hydrochemistry, groundwater, Magnesian Limestone, Yorkshire, Northumbria

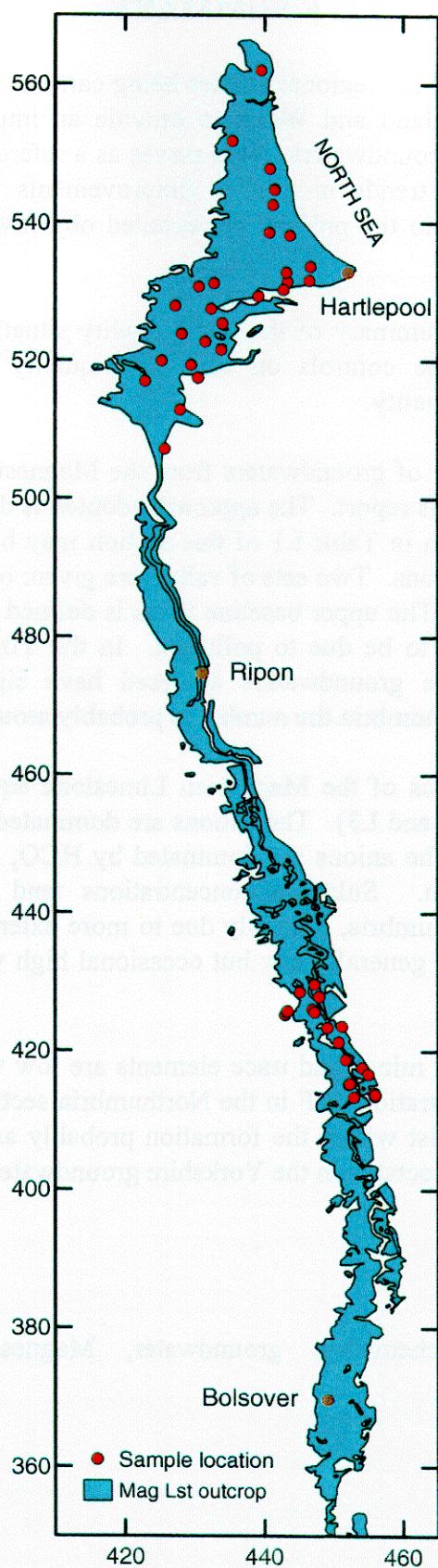


Figure I.1 Map showing outcrop of the Magnesian Limestone aquifer and locations of sites used in this study.

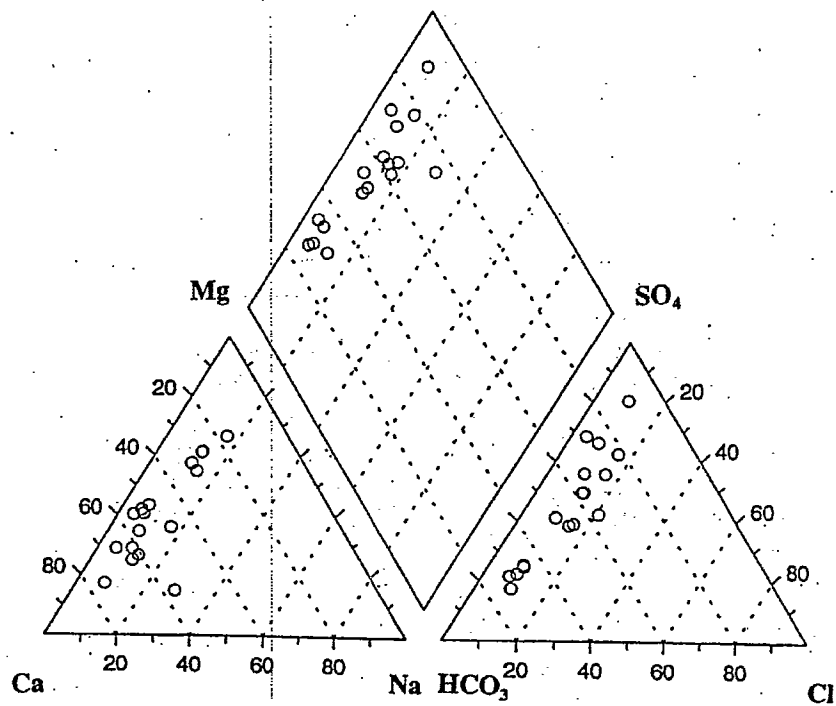


Figure I.2 Trilinear (Piper) diagram of groundwater samples from Yorkshire.

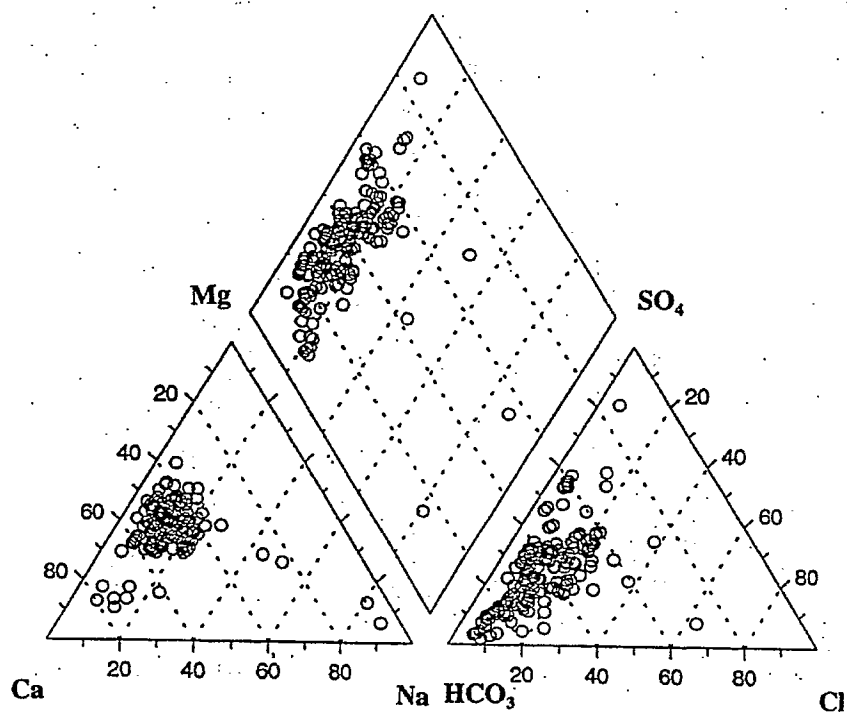


Figure I.3 Trilinear (Piper) diagram of groundwater samples from Northumbria.

Table I.1 Statistical summary of groundwater quality in the Magnesian Limestone of Yorkshire and Northumbria. Estimates of the upper limit of baseline concentrations are calculated on the basis of the 95 percentile and correspond roughly with the change in slope (representing outlying chemical compositions) in the cumulative-frequency diagrams (Figures II.4.5- II.4.7).

Determinand	Units	Northumbria					Yorkshire					
		Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n	
Filtered samples												
Temp	temperature	° C	5.1	13.6	10.2	12.9	95	6.0	15.4	10.0	13.9	10
pH	field values		4.9	8.6	7.3	8.1	84	6.4	7.6	7.4	7.6	7
Eh	redox potential	mV		63	-71	45	54					
Ca	calcium	mg l ⁻¹	5.4	298	91.75	178	270	40	784	114	573	35
Mg	magnesium	mg l ⁻¹	<0.3	195	42.5	83.6	267	25.8	119	71	103	35
Na	sodium	mg l ⁻¹	<0.3	204	27.25	61.0	268	10	566	34	329	33
K	potassium	mg l ⁻¹	<0.2	30	2.33	6.69	261	0.8	12.7	3.7	8.66	28
Cl	chloride	mg l ⁻¹	10.9	394	33.5	93.5	271	19.1	800	44.5	245	36
SO ₄	sulphate	mg l ⁻¹	<10	587	105	375	269	58	2200	215	1430	36
HCO ₃	bicarbonate	mg l ⁻¹	273	482	355	451	43	219	817	302	435	36
NO ₃ -N	nitrate as N	mg l ⁻¹	<0.01	18	0.86	15.0	168	0.74	13.5	7.98	13.0	12
NO ₂ -N	nitrite as N	µg l ⁻¹	<4	90	<20	30	259	<0.01	0.08	<0.01	0.02	21
NH ₄ -N	ammonium as N	µg l ⁻¹	<30	730	<50	213	259					
TOC	total org carbon	µg l ⁻¹	<0.2	23.5	0.56	7.4	189					
DOC	dissolved org C	µg l ⁻¹						27	35	28.5	34.3	4
Al	aluminium	µg l ⁻¹	<10	114	<10	11.0	93					
As	arsenic	µg l ⁻¹	<1	1.77	<1	1.16	93	<1	2.0	<1	1.7	7
B	boron	µg l ⁻¹	<80	550	<80	249	123	30.3	303	51	300	7
Ba	barium	µg l ⁻¹	14.8	273	51.7	186	93					
Cd	cadmium	µg l ⁻¹	<0.1	0.157	<0.1	<0.1	96	<0.1	0.25	<0.1	0.14	7
Cr	chromium	µg l ⁻¹	<1	25.1	<1	4.65	89	<1	1.21	<1	0.55	7
Cu	copper	µg l ⁻¹	<1	6.96	1.89	5.21	88	<1	475	3.72	381	5
Fe	total iron	µg l ⁻¹	<1	1140	<30	525	100	<40	189	53	170	7
Hg	mercury	µg l ⁻¹	<0.02	0.23	<0.02	0.04	100					
Mn	manganese	µg l ⁻¹	<10	309	<10	186	92	<10	175	<10	103	7
Ni	nickel	µg l ⁻¹	<1	8.2	<1	3.38	88	<1	3.11	<1	2.65	6
P	total phosphorus	µg l ⁻¹	<10	5300	<50	535	251					
P	orthophosphorus	µg l ⁻¹						<10	<10	<10	<10	1
Pb	lead	µg l ⁻¹	<1	46.3	<1	12.7	89	<1	4.9	<1	3.10	7
Sb	antimony	µg l ⁻¹	<2.5	<2.5	<2.5	<2.5	93					
Se	selenium	µg l ⁻¹						<1	6.19	5.17	5.97	7
Si	silicon	µg l ⁻¹	2400	4100	3900	4100	7					
Sr	strontium	µg l ⁻¹						262	5620	712	5140	6
Zn	zinc	µg l ⁻¹	<5	339	5	141	93	<20	881	<25	723	7
Unfiltered samples												
Al	aluminium	µg l ⁻¹	<1	1850	9.6	82	157					
As	arsenic	µg l ⁻¹	<0.2	6.3	<0.2	0.9	162	<1	<1	<1	<1	7
B	boron	µg l ⁻¹	<20	470	31.1	153	129	39	287	54.1	286	7
Ba	barium	µg l ⁻¹	15.5	275	64	245	155					
Cd	cadmium	µg l ⁻¹	<0.02	0.26	<0.1	0.105	162	<0.1	0.41	<0.1	0.33	7
Cr	chromium	µg l ⁻¹	<0.2	16.5	0.7	3.8	162	<1	6.24	1.8	5.6	4
Cu	copper	µg l ⁻¹	<0.5	445	1.68	11.0	162	<1	700	9.5	442	10
F	fluoride	µg l ⁻¹	<100	1700	695	1520	256					
Hg	mercury	µg l ⁻¹	<0.02	0.705	0.057	0.360	168					
Fe	total iron	µg l ⁻¹	<5	6440	36.8	1690	162	<40	17500	189	5320	21
Mn	manganese	µg l ⁻¹	<0.2	2440	13.3	200	162	<3	178	<20	96.3	16
Ni	nickel	µg l ⁻¹	<1	49.4	<1	4.22	162	<1	9.65	<2.6	8.89	10
Pb	lead	µg l ⁻¹						<1	7.27	<1	6.05	7
Sb	antimony	µg l ⁻¹	<0.4	2.5	<0.4	1.3	135					
Se	selenium	µg l ⁻¹						<1	5.9	4.0	5.7	7
Sr	strontium	µg l ⁻¹						259	5580	707	5090	6
Zn	zinc	µg l ⁻¹	<1	420	13	99.8	162					

SECTION II.

UNDERSTANDING THE NATURAL QUALITY – CONTROLS AND PROCESSES

1. PERSPECTIVE

The Magnesian Limestone of Yorkshire and Northumbria forms one of the major aquifers of England and Wales. Groundwater from this aquifer is used for public, industrial and agricultural supply. The aquifer comprises limestone separated by marls and, at depth, evaporite deposits. This study is based on a representative set of 50 sites (56 boreholes) provided by the Environment Agency. The data cover the aquifer from Doncaster northwards to Sunderland. Industrial and agricultural processes are likely to have had an impact on water quality and it is unlikely that any waters are in use which have had no impact from human activity. However, natural geochemical processes are still considered to dominate the water chemistry and the most important effect on water quality is likely to be the dissolution of evaporite minerals. This study aims to identify water-quality variations due to natural geological processes having first identified the indicators of pollution.

2. BACKGROUND

2.1 Geology

The Upper Permian Magnesian Limestone is a cyclic sequence of limestones, marls and evaporites (Table II.2.1), reflecting alternate phases of transgression, regression and evaporation. A number of sub-basins were formed, separated by ridges and one such high separated the Northumbria Province to the north from the Yorkshire Province to the south.

At the base of the sequence, Marl Slate, a marine deposit composed of organic-rich siltstone and dolomite is overlain by Magnesian Limestone. In the Yorkshire province, the Lower Magnesian Limestone incorporating the Lower Permian Marl and Hampole beds passes into the Middle Permian Marl, whereas in the Northumbria province, Lower Magnesian Limestone passes directly into the Middle Magnesian Limestone. The Magnesian Limestones are dolomitic.

Downdip, the Lower and Middle Magnesian Limestones are overlain by anhydrite deposits which can be up to 40 m thick. These evaporite deposits pass laterally into secondary gypsum deposits updip and are almost entirely dissolved away at the outcrop where they pass laterally into the Middle Permian Marl. This latter formation comprises dolomitic mudstones and siltstones containing nodular, layered and massive gypsum and anhydrite.

The Middle Permian Marl is overlain by the Upper Magnesian Limestone, a white to grey dolomitic limestone. The limestone is very uniform and thinly bedded. This in turn passes up into another evaporitic deposit and marl.

The Upper Permian strata dip gently eastwards with only minor folding although the strata are faulted. Downdip, the Magnesian Limestone sequence is overlain by the Triassic Sandstones. Over most of the limestone outcrop, superficial deposits are thin or absent but these increase in thickness over the Upper Permian Marl and Triassic Sandstone (Aldrick, 1978).

2.2 Hydrogeology

The hydrogeology of the Magnesian Limestone aquifer is controlled by lithology and structure. The limestones form a multilayered aquifer with the marls functioning as leaky aquitards in between. Transmissivities in the range 6 to 4300 m² day⁻¹ have been recorded (Allen et al., 1997). Groundwater flow is predominantly in fractures although there is some intergranular storage and transmissivities are extremely variable depending on the degree of fracturing. Transmissivity is greatest near major faults and in areas of outcrop which have undergone collapse brecciation due to dissolution of gypsum in underlying horizons (Cooper, 1995). In addition, the fracturing may establish a hydraulic connection between the limestones (Aldrick, 1978). Caves have also been recorded in the Magnesian Limestone (Anon, 1974). If these persist below the water table they would significantly affect the flow regime.

Water levels in the Magnesian Limestones of Northumbria have shown a steady rise in the last 20 years due to changes in pumping regimes. During the period of the coalfield operations, the possible influence and leakage of water from the Magnesian Limestone were tested frequently and further data are available in this regard (Edmunds, 1975). Rising groundwater from the Coal Measures may affect the water quality in the Magnesian Limestone (Younger, 1994).

Table II.2.1 Summary of stratigraphy of the Permian Magnesian Limestones and their hydrogeological significance (thickness taken from Smith, 1974; Smith et al., 1986; Cooper and Burgess, 1993; Powell et al., 1992 and Grant, 1994). After Allen et al. (1997).

Stratigraphy				Hydrogeological Significance
Northumbria		Yorkshire		
Upper Permian Marl	30–40 m	Upper Permian Marl	30 m	Aquitard
Upper Magnesian Limestone	21–28 m	Upper Magnesian Limestone	10–35 m	Aquifer
Middle Permian Marl	10–50 m	Middle Permian Marl	up to 60 m	Leaky Aquitard
Middle Magnesian Limestone	up to 95 m	Lower Magnesian Limestone (incl. Lower Permian Marl and Hampole Beds where present)	up to 100 m	Aquifer (Lower Permian Marl - aquitard)
Lower Magnesian Limestone	20–50 m			
Marl Slate	few m	Marl Slate	1–9 m	
Basal Permian Sands (Yellow Sands)	0–60 m	Basal Permian Sands	0–15 m	Aquifer

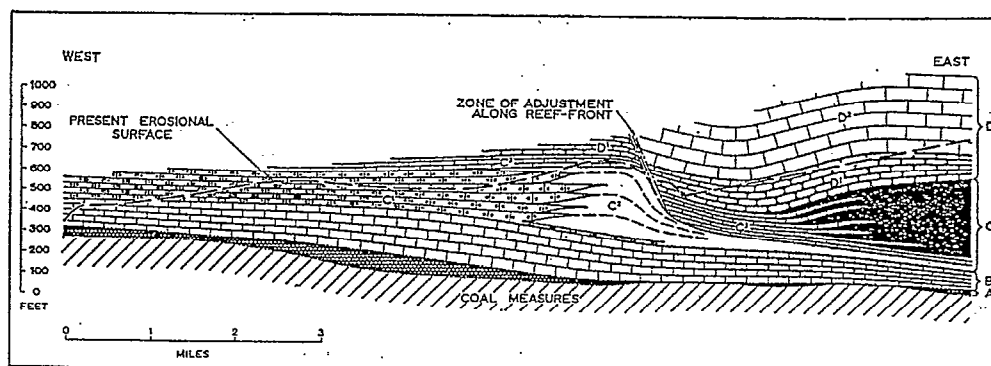


Figure II.2.1 Generalised horizontal section through the Magnesian Limestone of Northumbria.

3. DATA QUALITY AND HANDLING.

3.1 Source and Quality of Data.

This account describes data from 20 sites and 26 boreholes in the Magnesian Limestone of Yorkshire and 30 sites and 30 boreholes in Northumbria. Data are mainly from Environment Agency sources with some samples from the BGS archive. The data set from Yorkshire comprises mostly single samples for sites dating from the 1970s and 1980s. A few sites have a couple of samples from the 1990s. The Northumbria data set comprises several samples taken from sites in the 1990s. Only a few samples from the Yorkshire data set have sufficient data to allow the calculation of an ionic balance. However, where possible to calculate, all but one sample had ionic charge imbalances less than 3%. In the Northumbria data set, 66% of the samples had an ionic balance within 5% and 84% lay within 10%.

For production of statistical summaries of water-quality data, minima, maxima and median values have been calculated. Where median values are less than a given detection limit, the detection-limit values are given rather than actual values calculated by statistical analysis of the data distributions. Box plots are also given, where boxes define the ranges between the 25 and 75 percentiles and include the median concentrations. The 5 and 95 percentiles are given in the plots as filled circles.

In this document, as in the report series as a whole, the 95 percentile value has been taken for each element as an estimate of the upper limit of the 'baseline' concentration range. Values lying above this are largely those expected to be affected by pollution (see Appendix 1).

3.2 The Influence of Pollution.

The median concentrations for most elements (Table I.1) may be regarded as best estimates of the average unpolluted groundwater composition for each section of the aquifer; any effects of pollution can generally be found in the upper 50% of this group. An exception is nitrate. The influence of agricultural activities can be detected using the cumulative frequency plots (see below) and it is estimated that in the Yorkshire Magnesian limestone sources, some 60% of the groundwaters analysed in this study have significant contributions from agricultural nitrate. In Northumbria, the number is probably around 20%. The percentage of groundwaters with TOC above 2 mg l⁻¹ in the Northumbria data is also around 20% and can also be used as a good indicator of agricultural impacts.

4. HYDROGEOCHEMICAL CHARACTERISTICS.

The results are discussed in two groups corresponding to the Yorkshire and Northumbria sections of the aquifer. The groundwaters in the Magnesian Limestone of both Yorkshire and Northumbria are well buffered, with pH (field measured) having mean values of 7.4 and 7.3 respectively. The high alkalinities (mean of 320 mg l⁻¹ for Yorkshire and 368 mg l⁻¹ for Northumbria) result from the groundwaters being near saturation with carbonate minerals; there is no significant capacity for further dissolution of limestone.

The general hydrochemical characteristics can be followed and compared using the trilinear diagrams (Figures I.1 and I.2) and the box plots (Figures II.4.1-II.4.4 where, for convenience, the data are presented in the concentration order found in seawater), as well as in the statistical summary (Table I.1). Many of the analyses summarised in Table I.1 are likely to represent mixtures between groundwaters in the Upper, Middle and Lower horizons of the Limestone, corresponding to the sections penetrated by the drilling. After HCO₃, SO₄ is the main anion with median values in Yorkshire of 215 mg l⁻¹ and in Northumbria of 105 mg l⁻¹. This is a clear indication that the gypsum contained in the marls has been dissolved by the groundwater. This is more predominant in the Yorkshire aquifer than in Northumbria. Chloride concentrations are higher in the Yorkshire area than in Northumbria with median values of 90 mg l⁻¹ and 42 mg l⁻¹ respectively, the Cl probably being derived from traces of halite in the evaporite sequence.

The relative proportions of the principal cations (Na, Ca and Mg) can be seen in the trilinear plots (Figures I.1 and I.2). The predominant composition is groundwater with equimolar Mg and Ca, an expression of the dolomitic composition of the carbonate, in contrast to other limestone areas of England. Median nitrate (as N) values of 0.86 mg l⁻¹ in Northumbria indicate low levels of pollution from agricultural sources in contrast with the (limited) data from Yorkshire samples which indicate significantly higher levels of nitrate with a mean of 8 mg l⁻¹.

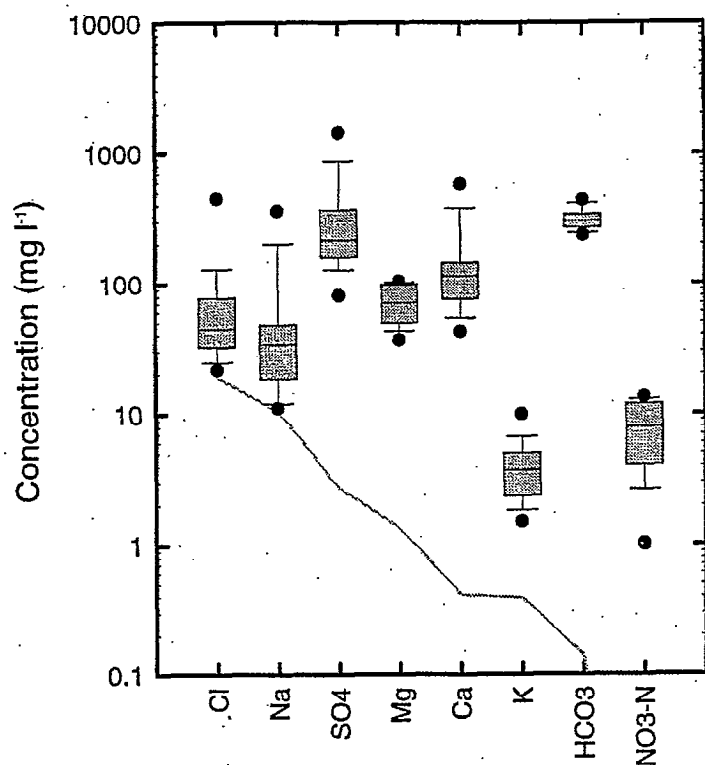


Figure II.4.1 Box plot showing the range of major ion concentrations in the Magnesian Limestone of Yorkshire.

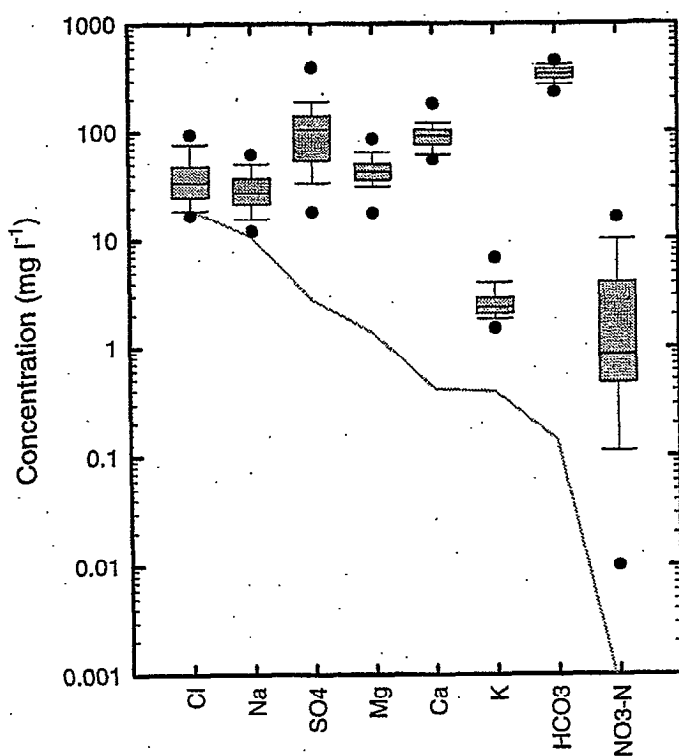


Figure II.4.2 Box plot showing the range of major ion concentrations in the Magnesian Limestone of Northumbria.

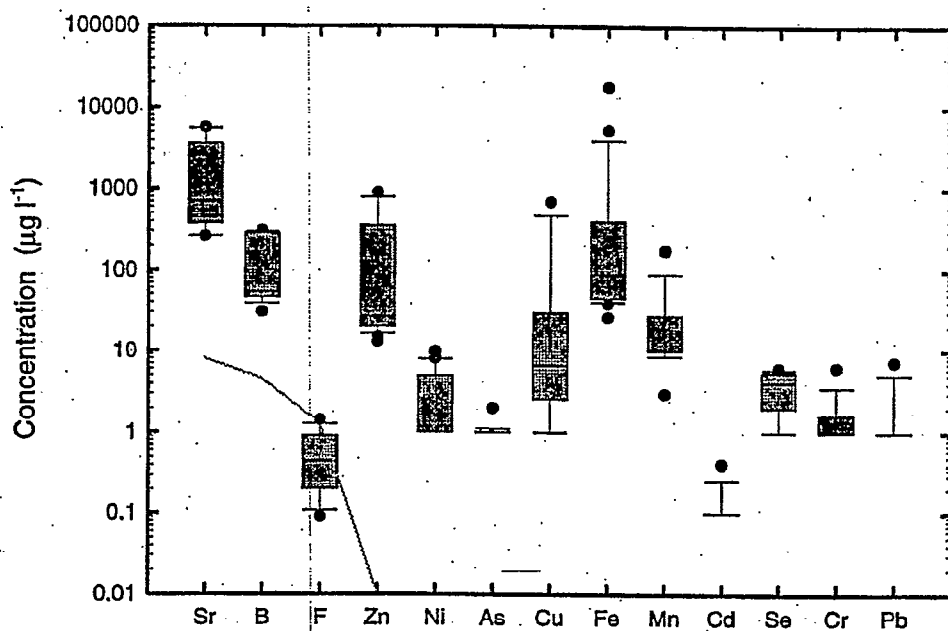


Figure II.4.3 Box plot showing the range of minor and trace element concentrations in the Magnesian Limestone of Yorkshire.

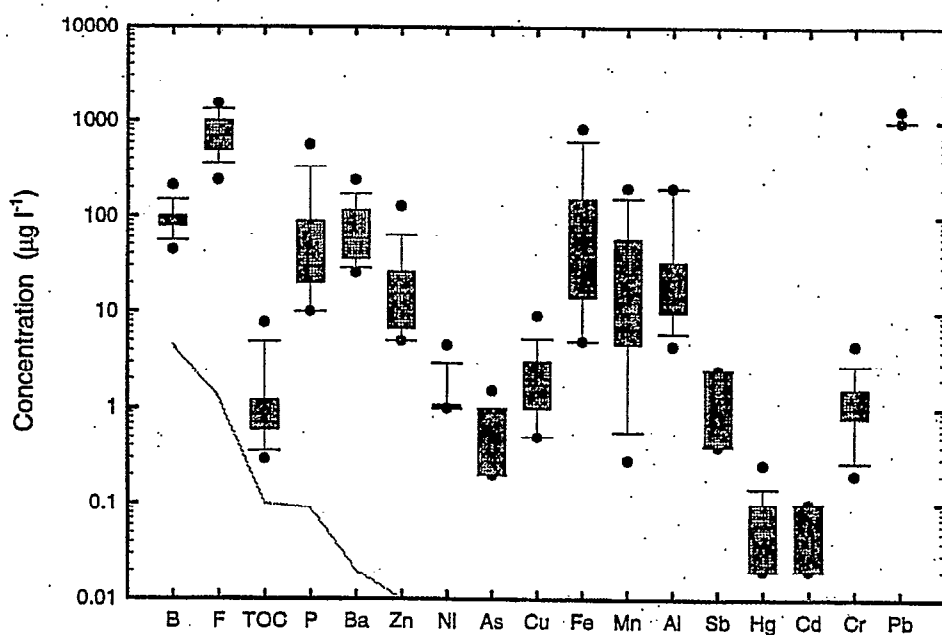


Figure II.4.4 Box plot showing the range of minor and trace element concentrations in the Magnesian Limestone of Northumbria.

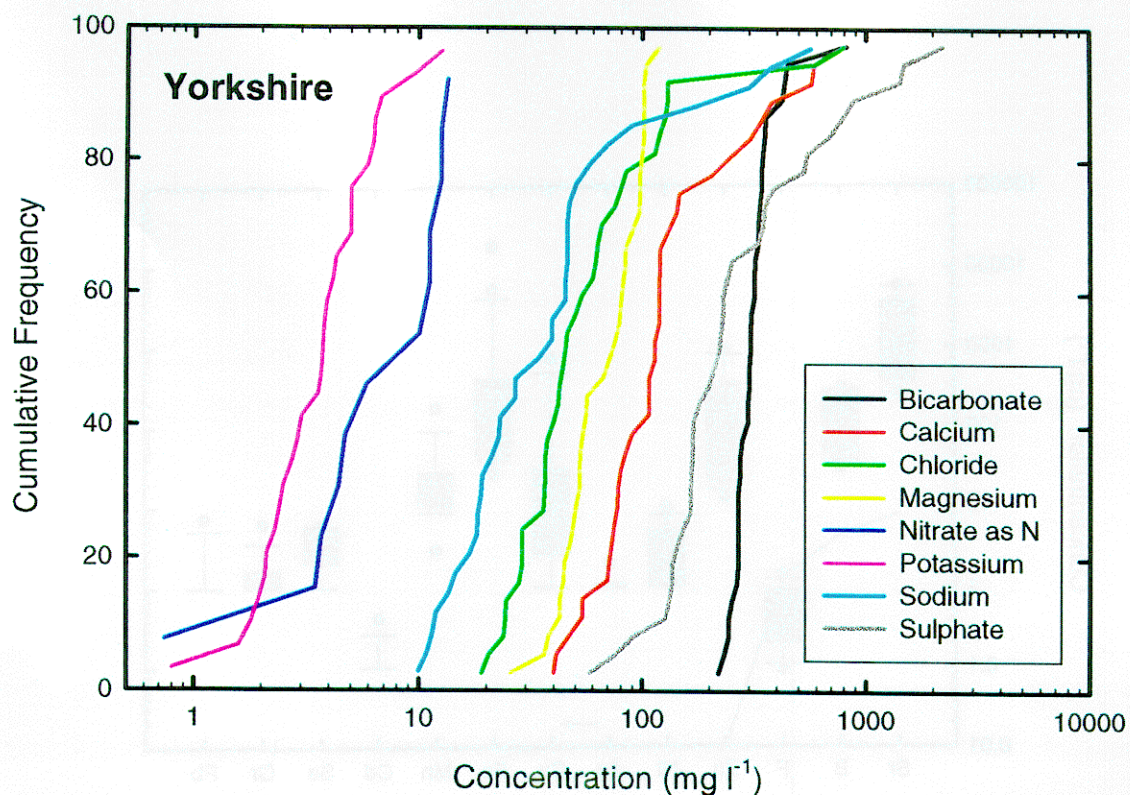


Figure II.4.5 Cumulative frequency diagram for major ions in groundwaters from the Magnesian Limestone of Yorkshire.

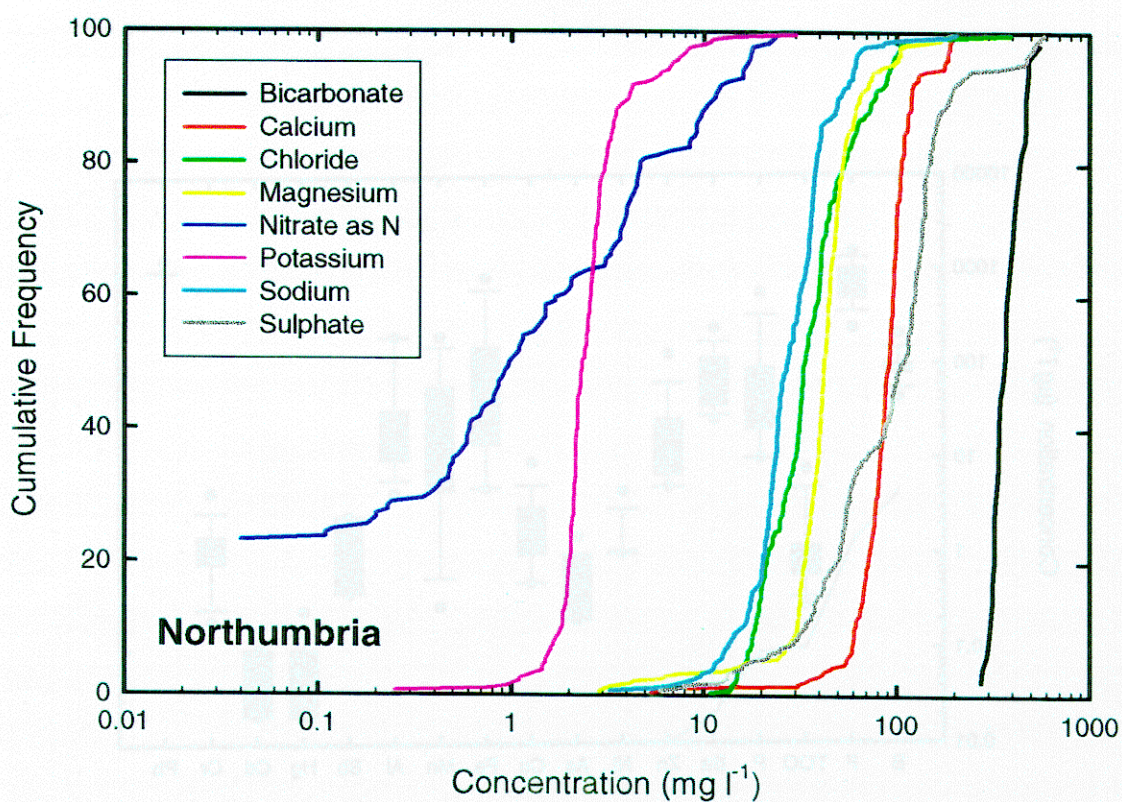


Figure II.4.6 Cumulative-frequency diagram for major ions in groundwaters from the Magnesian Limestone of Northumbria.

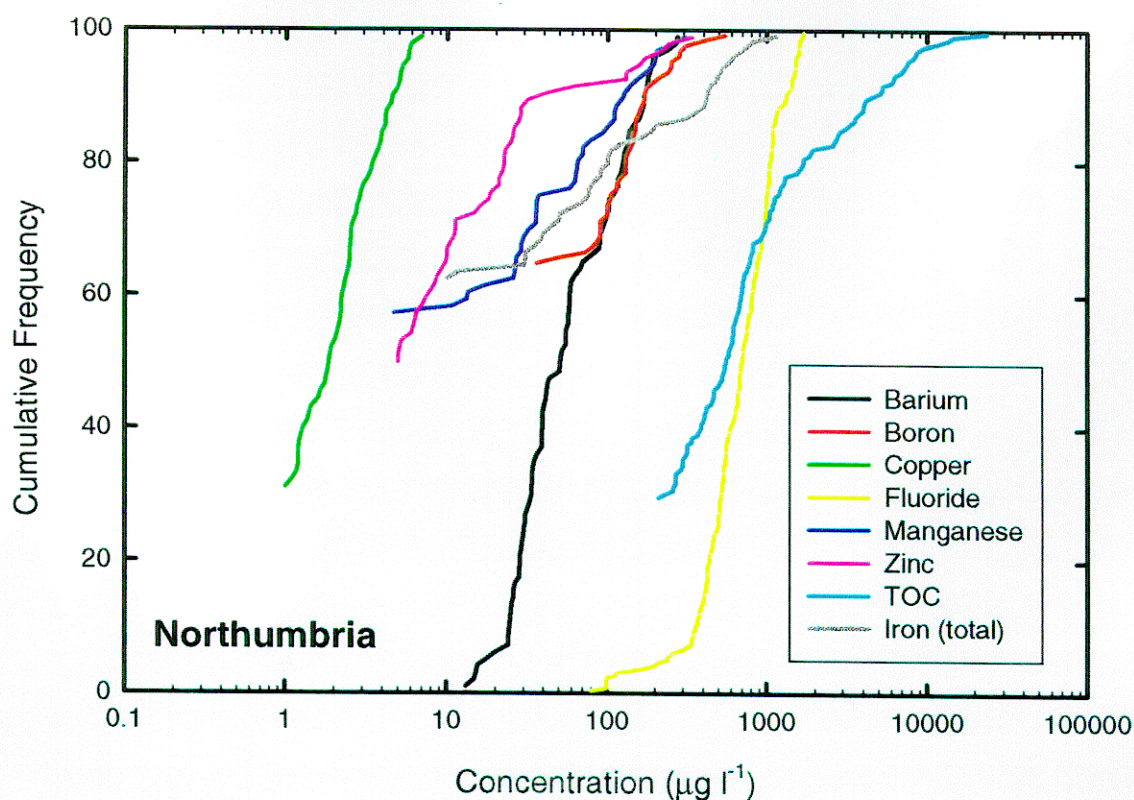


Figure II.4.7 Cumulative frequency diagram for minor and trace elements in groundwaters from the Magnesian Limestone of Northumbria.

The median concentrations of several trace elements are given in Table I.1 as well as in the box plots (Figures II.4.1 to II.4.4) and the cumulative-frequency diagrams (Figures II.4.5-II.4.7). The concentrations of most minor and trace elements are low with the exception of Fe, Mn and F. The median concentration of F in the Northumbria section is 0.7 mg l^{-1} and indicates that a source of F must exist within the formation probably as traces of fluorapatite in the carbonates. Selenium is detectable in the Yorkshire groundwaters (median $5.2 \text{ µg l}^{-1} \text{ Se}$) and warrants further investigation.

5. REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS

The chemistry of groundwaters in the Magnesian Limestone is predominantly affected by the dissolution of dolomite resulting in a $(\text{CaMg})\text{HCO}_3$ water. Dissolution of evaporite minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and/or anhydrite (CaSO_4) results in high levels of SO_4 in some groundwaters. These are generally samples from confined areas of the Magnesian Limestone where there is leakage from the overlying evaporite-rich marls. At outcrop, the evaporites have been mostly removed by solution.

No direct reliable measurements are available to demonstrate whether the groundwaters are oxidising or reducing but from the data for Fe and NO_3 , it is possible to make some deductions. The cumulative frequency plot for Northumbria shows a cut-off point where some 25% of the samples have $\text{NO}_3\text{-N}$ below detection limit: effectively zero nitrate, which is most likely to mark a distinction between reducing waters in which denitrification has occurred and oxidising waters. Without further fieldwork or more detailed examination of the data, it is not possible to show the spatial extent or geological control of redox conditions. The concentrations of Fe provide strong supporting evidence for the groundwaters being reducing. In the cumulative-frequency plot, the concentrations of total Fe exceeding 0.1 mg l^{-1} is also around 20% with upper concentrations approaching 1 mg l^{-1} in line with reducing conditions. In Yorkshire, the percentage of low-nitrate groundwaters is well below 10% and the majority are therefore aerobic.

5.1 Residence Times

No radionuclide studies (^{14}C , ^3H data) are available to estimate the groundwater residence time. The only indicators of residence time are the concentrations of contaminants such as nitrate.

5.2 Trends

The study has not identified any suitable data set to examine changes in groundwater chemistry with time in this aquifer.

5.3 Depth Variations

No geochemical logs, depth-sample data or studies recording water-quality variations with depth have been identified. It is clear that at depth the groundwater becomes saline. This is exemplified by the analysis of waters from the Basal Permian Sands from an upward-drilled borehole from the Carboniferous strata at Horden [NZ 460437], quoted by Edmunds (1975) where the total mineralisation is $58,000 \text{ mg l}^{-1}$.

6. SUMMARY

The median concentrations given in Table I.1 of Section I may be regarded as the best single value for baseline. Two sets of values are given, one for the Yorkshire area and the other for Northumbria. The upper baseline value is defined by the 95 percentile. Values in excess of this are likely to be due to pollution. In the Yorkshire Magnesian limestone sources, around 60% of the groundwaters analysed in this study have significant contributions from agricultural NO_3^- . In Northumbria, the number is probably around 20%.

The major ion characteristics of the Magnesian Limestone aquifer are summarised in two Piper diagrams (Figures I.1 and I.2). The cations are dominated by Ca and Mg derived from the dolomitic limestone; the molar Mg/Ca ratios are generally close to 1 reflecting the influence of dissolution of the dolomitic limestones. The anions are dominated by HCO_3^- from carbonate minerals and SO_4^{2-} derived from gypsum. Sulphate concentrations tend to be higher in the Yorkshire groundwaters than in Northumbria, probably due to more extensive dissolution of gypsum. Chloride concentrations are generally low but occasional high values occur probably due to the dissolution of halite or the influence of formation waters from depth.

The concentrations of most minor and trace elements are low with the exception of Fe, Mn and F. The median concentration of F in the Northumbria section is 0.7 mg l^{-1} and indicates that a source of F must exist within the formation, probably as traces of fluorapatite in the carbonates. Selenium is detectable in the Yorkshire groundwaters (median $5.2 \text{ } \mu\text{g l}^{-1} \text{ Se}$).

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.

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 A1.2.1 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 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, $\delta^{18}\text{O}$, $\delta^2\text{H}$, F;
2. Acidity and redox status: **pH**, **HCO₃**, Eh, DO, Fe, As;
3. Radioactivity: ^3H , ^{36}Cl , ^{222}Rn ;
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, \bar{X} , is calculated as the sum of the data values X_i , divided by the number of values, n :

$$\bar{X} = \sum X_i / n$$

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

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

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

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)	mg l ⁻¹ to meq l ⁻¹
Calcium	(Ca ²⁺)	100	-	-	0.0499
Magnesium	(Mg ²⁺)	30	50	-	0.0823
Sodium	(Na ⁺)†	20	150	200	0.0435
Potassium	(K ⁺)	10	12	-	0.0256
Chloride	(Cl)	25	-	250	0.0282
Sulphate	(SO ₄ ²⁻)	25	250	250	0.0208
Aluminium	(Al ³⁺)	0.05	0.5	0.2	0.1112
Nitrate	(NO ₃ ⁻)†	25	50	50	0.0161
	(as N)	5.65	11.3	10	
Nitrate	(NO ₂ ⁻)†	-	0.1	3 P	0.0217
Ammonium	(NH ₄ ⁺)	0.05	0.5	1.5	0.0554
Iron	(Fe ³⁺)	0.05(Fe _T)	0.2 (Fe _T)	0.3(Fe _T)	0.0537
	(Fe ²⁺)				0.0358
Manganese	(Mn ²⁺)	0.02	0.05	0.1	0.0364
		(µg/l)	(µg/l)	(µg/l)	
Copper	(Cu ²⁺)	3000	-	1000	0.0315
Zinc	(Zn ²⁺)	5000	-	3000	0.0306
Phosphate	(HPO ₄ ²⁻)	400	5000	-	0.0208
Fluoride	(F ⁻)†	8-12°C 25-30°C	1500 700	1500 -	0.0526
Barium	(Ba ²⁺)	100	-	700	0.0146
Silver	(Ag ⁺)	-	10	-	0.0093
Arsenic	(As)†	-	50	10 P	-
Cadmium	(Cd ²⁺)†	-	5	3	0.0178
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	0.0097
Antimony	(Sb)	-	10	5 P	-
Selenium	(Se)†	-	10	10	-
Pesticides	(separately)	-	0.1	different for each compound	-
	(total)	-	0.5		-
Polycyclic	(PAH)	-	0.2		-
Aromatic					
Hydrocarbons	(CTC)	-	-	2	
Carbon	(TCE)	-	-	70 P	
tetrachloride	(°C)	12	25	-	
Trichloroethene		6.5-8.5	-	6.5-8.5	
Temperature	(µS cm ⁻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:

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

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:

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

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.

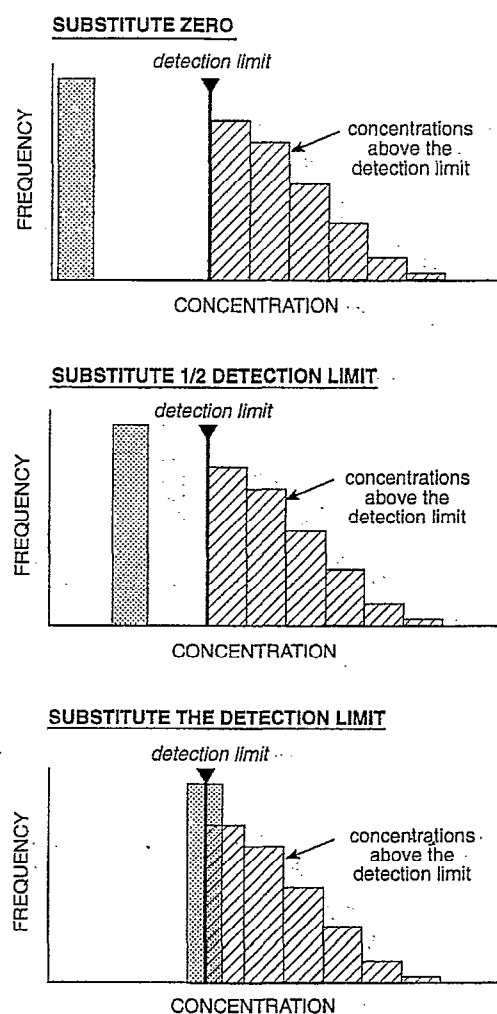


Figure A1.2.1 Illustration of the substitution method for estimating the mean (after Helsel and Hirsch, 1992).

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 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 (Ca+Mg)/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.

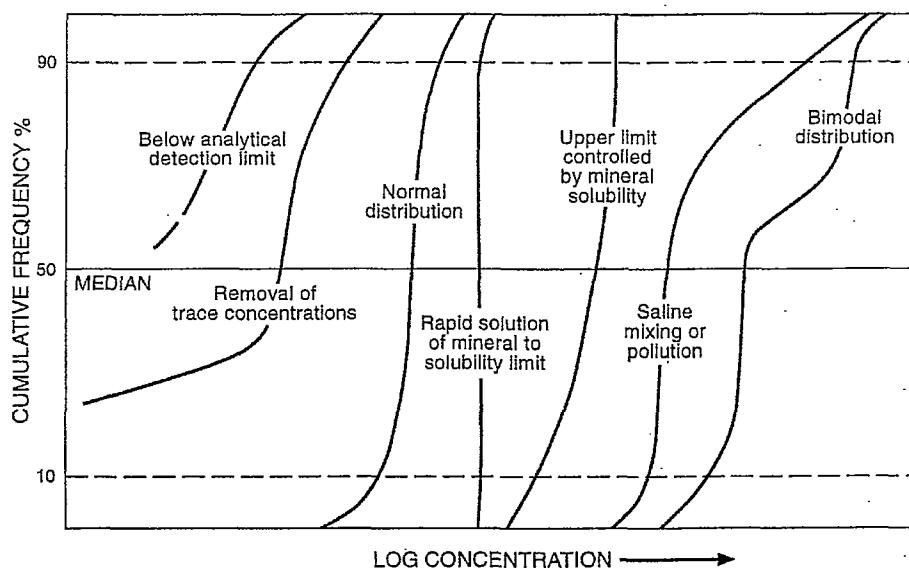


Figure A1.2.2. Illustration of the use of cumulative-frequency diagrams.

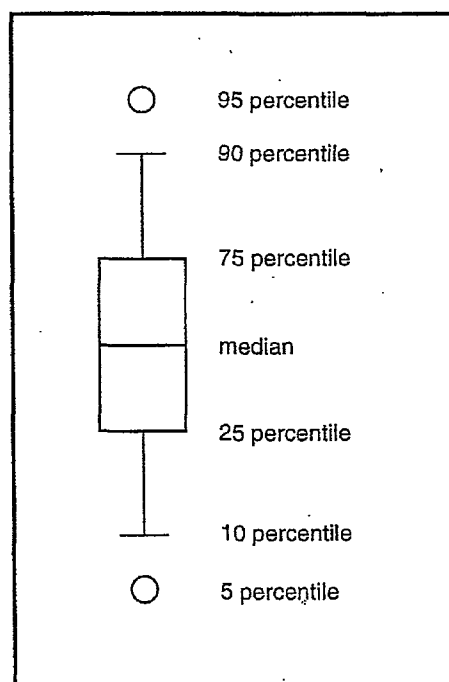


Figure A1.2.3. Key to the structure of the boxes in box plots.

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

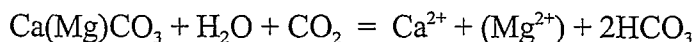
Some of the geochemical concepts and terminology used in the reports are included here as a reference. These terms will be added to in the nationwide report.

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:

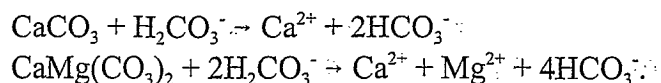


The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone. This process (**congruent dissolution**) yields Ca and Mg concentrations which are identical to those in the dissolving carbonate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

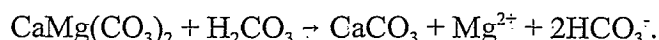
Congruent/incongruent reaction

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.

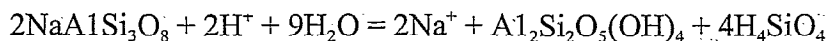
Examples of congruent reactions relevant to the Sherwood Sandstone aquifer are:



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 incongruent 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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