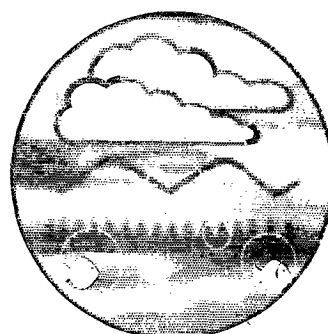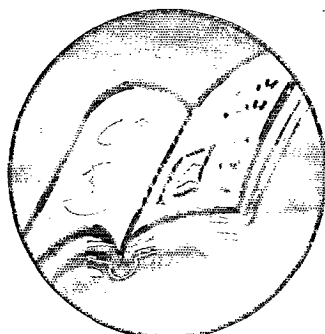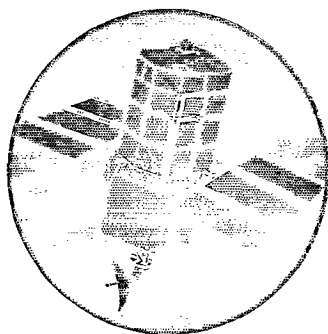# The Natural (Baseline) Quality of Groundwaters in England and Wales
The Permo-Triassic Sandstones of Cumbria, North-West England

Research and Development

Project Record
W6/i722/3

British Geological Survey

ENVIRONMENT AGENCY

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

The Permo-Triassic Sandstones of Cumbria, North-West England

R&D Project Record W6/i722/3

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Research Contractor:
British Geological Survey

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Research contractor
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R&D Project Record W6/i722/3

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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 the Appendix.

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 Vale of Eden forms a broad valley situated between the English Lake District and the western edge of the Pennines (Figure I.1). The aquifer comprises sedimentary rocks of Permian and Triassic age. The main aquifers are represented by the Permian Penrith Sandstone and the Triassic St Bees Sandstone, separated by the St Bees/Eden Shales. The Permo-Triassic rocks of the area represent an important aquifer in north-west England, supplying water for public supply, local industry and as a bottled mineral water.

The groundwaters are mainly of Ca-HCO$_3$ type, but other more evolved waters are present including Ca-Mg-SO$_4$, Na-Ca-Cl and Na-HCO$_3$ types (Figure I.2). The dominant water-rock interactions controlling water chemistry include the dissolution of minerals such as calcite, dolomite, gypsum/anhydrite or halite. It is likely that the upper parts of the sandstone aquifers have been decalcified and this has led to waters being undersaturated with respect to calcite. The waters are generally oxidising and concentrations of Fe and Mn are generally low (Tables I.1 and I.2). However, where reducing conditions exist in the confined parts of the aquifer Fe is relatively high. Some waters contain extremely high Fe and Mn but these are unfiltered and the high concentrations are considered to represent particulate matter. Trace metal concentrations are generally low reflecting low concentrations in the aquifer rocks as well as the neutral to alkaline conditions in the aquifer, but there is often a correlation between high Fe and Mn and high trace metal concentrations. This is most likely a consequence of the adsorption of metals onto Fe and Mn hydroxide surfaces. Local relatively high concentrations of metals such as Pb and Zn are found associated with high solute Fe and Mn and may relate to the incorporation of metals associated with the dissolution of Fe and Mn oxy-hydroxide phases under reducing conditions. Fluoride concentrations are low reflecting a lack of fluorite in the aquifer.

Concentrations of some solutes, particularly Fe and Mn vary significantly with time in some borehole waters, and this most likely relates to the incorporation of particulate matter. Most major elements show much less variation in general, although at some sites variations are significant.

KEYWORDS

Baseline quality, hydrochemistry, groundwater, Permian, Triassic, Sandstone, Cumbria.
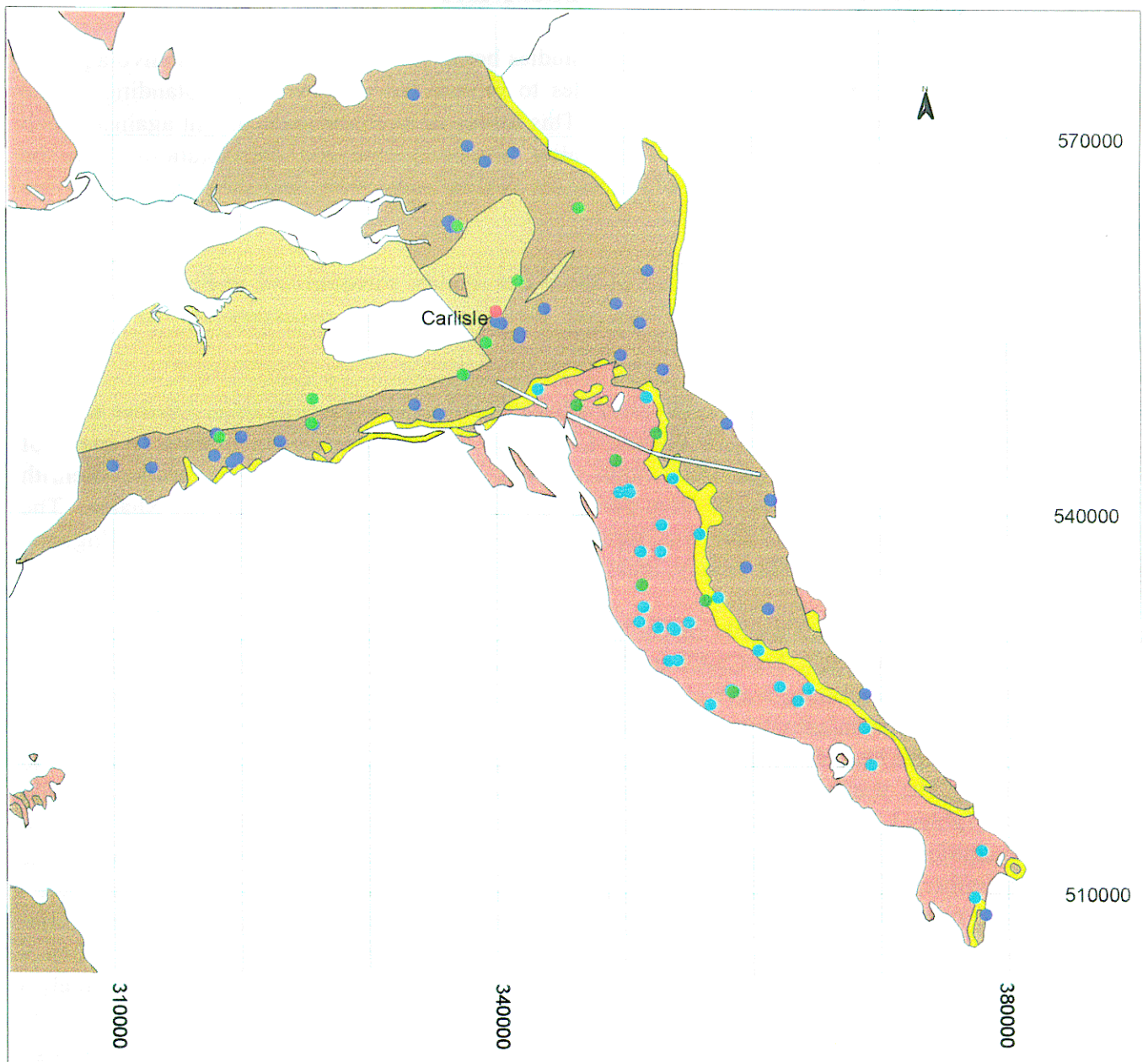
Figure I.1 Outcrop of Permo-Triassic rocks in north-west England showing sampling points.
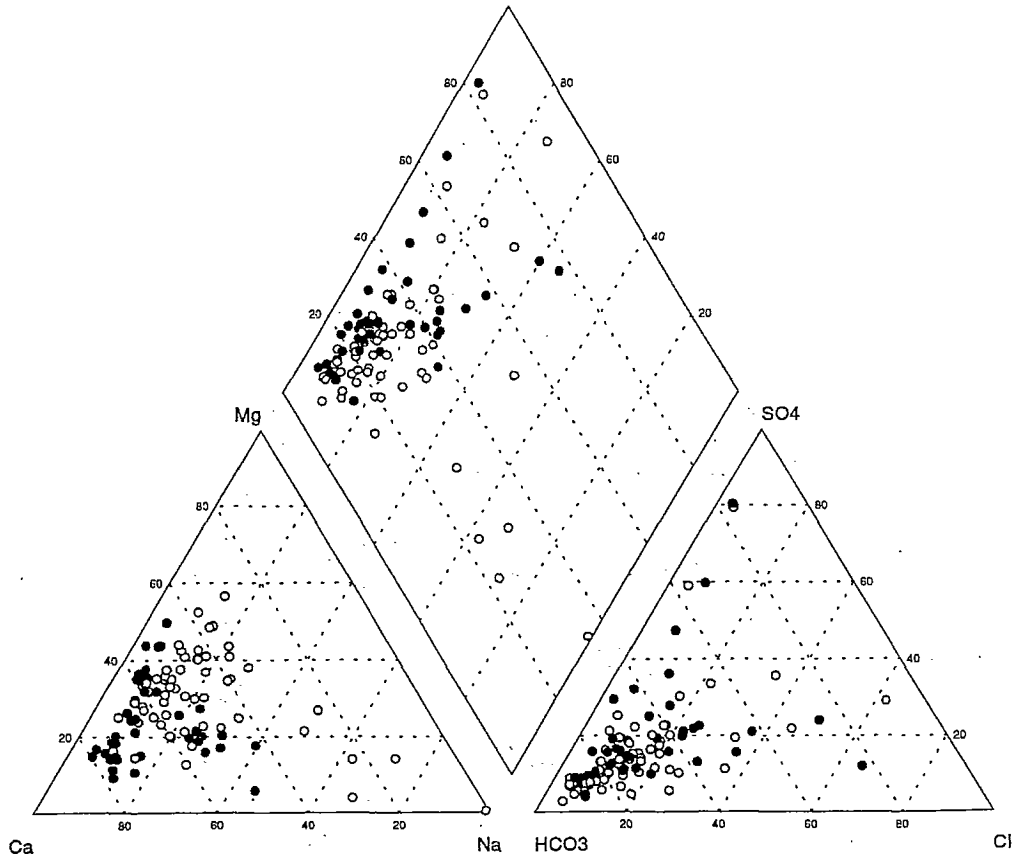
Figure I.2. Trilinear (Piper) diagram showing the groundwater types in the Permo-Triassic sandstones of Cumbria. Solid symbols represent groundwaters in the Permian aquifer and open symbols the Triassic aquifer.

Table I.1 Statistical summary of groundwater quality in the Permian Sandstones of the Carlisle Basin and the Vale of Eden. Estimates of the upper limit of baseline concentrations are calculated on the basis of the 95 percentile and correspond roughly with the upper change in slope (representing outlying chemical compositions) in the cumulative-frequency diagrams.

Determinand		Units	Min	Max	Median	Upper Baseline	n
Temp	temperature	°C	7	12.4	9.6	11.7	25
pH			6.6	8.01	7.3	7.8	40
Eh	redox potential	mV	220	360	280	357	4
SEC	conductivity	µS/cm	189	1423	411	953	40
Ca	calcium	mg/l	16	231.6	53.7	129	40
Mg	magnesium	mg/l	3	38.8	10	37.8	40
Na	sodium	mg/l	5	135	10	17.5	40
K	potassium	mg/l	1.08	8.5	2.1	4.84	40
Cl	chloride	mg/l	<5	283	16.1	32.7	40
SO$_4$	sulphate	mg/l	9.7	573.4	26.2	146.6	40
HCO$_3$	bicarbonate	mg/l	33	365	170	301	40
NO$_3$-N	nitrate as N	mg/l	<0.5	16.66	3.05	10.86	40
Al	aluminium	µg/l	<3	1030	<10	38.83	27
As	arsenic	µg/l	<0.1	233	<1	2.16	11
B	boron	µg/l	<7	<100	<100	<100	26
Ba	barium	µg/l	26	300	52	258	6
Be	beryllium	µg/l	<0.05	<0.05	<0.05	<0.05	6
Br	bromine	µg/l	<0.5	73	8.83	67.9	7
Cd	cadmium	µg/l	<10	<10	<10	<10	29
Co	cobalt	µg/l	<0.8	1	<0.8	<0.8	6
Cr	chromium	µg/l	<1	50.33	2.5	12.5	36
Cu	copper	µg/l	<0.5	157.5	10.45	85.5	39
F	fluorine	µg/l	<10	<100	12.5	<100	6
Fe	iron	µg/l	<30	16113	106.7	3179	40
I	iodine	µg/l	2	4	2	3.7	6
La	lanthanum	µg/l	<0.5	<0.5	<0.5	<0.5	6
Li	lithium	µg/l	1.8	3.6	2.9	3.5	6
Mn	manganese	µg/l	<0.2	1158	6.6	495	39
Mo	molybdenum	µg/l	<2	3	<2	<2	6
Ni	nickel	µg/l	<2.5	60.75	7.2	24.5	39
Pb	lead	µg/l	<1	220	15.7	83.8	35
Sc	scandium	µg/l	<0.05	<0.05	<0.05	<0.05	6
Si	silicon	µg/l	2730	6780	4038	6400	40
Sr	strontium	µg/l	53	3440	195	956	26
V	vanadium	µg/l	<0.2	<0.2	<0.2	<0.2	6
Y	yttrium	µg/l	<0.025	0.4	<0.025	0.29	6
Zn	zinc	µg/l	<2	318	21	172	39
Zr	zirconium	µg/l	<0.2	<0.2	<0.2	<0.2	6

Table I.2 Statistical summary of groundwater quality in the Triassic Sandstones of the Carlisle Basin and the Vale of Eden. Estimates of the upper limit of baseline concentrations are calculated on the basis of the 95 percentile and correspond roughly with the upper change in slope (representing outlying chemical compositions) in the cumulative-frequency diagrams.

Determinand		Units	Min	Max	Median	Upper Baseline	n
Temp	temperature	°C	6	17	10.3	13.2	37
pH			6.3	9.55	7.6	8.23	53
Eh	redox potential	mV	5	461	160	461	7
SEC	conductivity	µS/cm	245	2170	490	883	53
Ca	calcium	mg/l	1.1	458	46	92.8	53
Mg	magnesium	mg/l	0.3	59.7	19.1	38.2	53
Na	sodium	mg/l	5	212.7	17	66.1	53
K	potassium	mg/l	0.5	44.93	2.06	4.90	53
Cl	chloride	mg/l	7.6	83	19.7	43.6	53
SO$_4$	sulphate	mg/l	7.1	1080	24	92.3	53
HCO$_3$	bicarbonate	mg/l	61	430	229	385	53
NO$_3$-N	nitrate as N	mg/l	0.02	17.19	2.17	11.15	38
Al	aluminium	µg/l	<1.5	740	<5	96.6	34
As	arsenic	µg/l	<0.5	20	<2	15	21
B	boron	µg/l	<8	217.7	<100	144	34
Ba	barium	µg/l	27	460	112	440	8
Be	beryllium	µg/l	<0.05	<0.05	<0.05	<0.05	8
Br	bromine	µg/l	46	293	77.5	277	8
Cd	cadmium	µg/l	<10	<10	<10	<10	38
Co	cobalt	µg/l	<0.8	1	<0.8	<0.8	8
Cr	chromium	µg/l	<1	14	4	8.5	48
Cu	copper	µg/l	<0.2	180	12	104	53
F	fluorine	µg/l	<100	180	<100	176	8
Fe	iron	µg/l	<30	58500	260	28415	53
I	iodine	µg/l	2	36	3.5	20	8
La	lanthanum	µg/l	<0.3	<1	<0.5	<1	8
Li	lithium	µg/l	1	31	8.4	29	8
Mn	manganese	µg/l	<2.5	2145	30	1088	52
Mo	molybdenum	µg/l	<2	3	<2	2.6	8
Ni	nickel	µg/l	<2.5	170	8.5	34	53
Pb	lead	µg/l	<02	166	25	42	43
Sc	scandium	µg/l	<0.05	<0.05	<0.05	<0.05	8
Si	silicon	µg/l	1890	8400	5990	8120	53
Sr	strontium	µg/l	27	9746	177	2450	34
V	vanadium	µg/l	<0.3	2	0.55	1.6	8
Y	yttrium	µg/l	<0.05	0.4	<0.05	0.24	8
Zn	zinc	µg/l	<2	4600	24	493	53
Zr	zirconium	µg/l	<0.2	0.2	<0.2	<0.2	8

SECTION II.

UNDERSTANDING THE NATURAL QUALITY - CONTROLS AND PROCESSES

1.   PERSPECTIVE

This study is based on representative groundwater samples from the Permo-Triassic rocks from Cumbria comprising mainly boreholes in the Vale of Eden (Figure I.1). The Vale of Eden is a NW trending sedimentary basin situated between the English Lake District and the western edge of the Pennines. It forms a broad (c. 10 km) valley stretching c. 60 km from Kirkby Stephen in the south to Cumwhinton in the north, generally following the River Eden which is roughly coincident with the outcrop of the sedimentary Permo-Triassic rocks. The Permo-Triassic rocks of the area represent an important aquifer and although much of the public demand for water is met by surface water, groundwater is also used for public supply, local industry and as a bottled mineral water. The population density is relatively low and the main industries are based on agriculture, mineral resources (gypsum, anhydrite) and tourism.

This report provides a summary of the chemical compositions of groundwaters in the Eden Valley and Carlisle Basin and attempts to recognise likely baseline characteristics in the Permo-Triassic aquifer.

2. BACKGROUND

2.1 Geology

The Permo-Triassic basin of the Vale of Eden formed at the end of the late Carboniferous Hercynian Orogeny through reactivation of the Pennine fault. The present extent of outcrop defines the basin to the west and the eastern margin is largely defined by the Pennine fault. The stratigraphy of the Permo-Triassic is shown in Table II.2.1.

The Permo-Triassic Basin is narrow in the south but broadens out in the north towards and around Carlisle (Figure I.1). These Permo-Triassic rocks are surrounded to both the east and west by rocks of Carboniferous age. Older Palaeozoic sedimentary and igneous rocks are present further west in the Lake District and younger rocks are represented by doleritic Tertiary dykes. Surface water drainage is dominated by the River Eden, the tributaries of which drain the Pennines to the east and the Lake District in the west.

PERIOD	GROUP	FORMATION
TRIASSIC	Mercia Mudstone Series	Stanwix Shales
		Kirklinton Sandstone Formation
	Sherwood Sandstone Group	St Bees Sandstone Formation
		St Bees/Eden Shales Formation
PERMIAN		Penrith Sandstone and Brockram

Table II.2.1 Stratigraphy of the Vale of Eden and Carlisle Basin.

The Penrith Sandstone rests unconformably upon Carboniferous strata, and in the Vale of Eden dips approximately 8° to the north-east. Thicknesses of around 400 m are indicated from outcrop studies (Burgess & Wadge, 1974). The younger St Bees Shales form a sequence of red and chocolate coloured shales, mudstones, dolomitic beds and evaporite minerals: anhydrite and gypsum. The shales gradually pass into the Triassic St Bees Sandstone Formation comprising regularly bedded, waterlain, micaceous red sandstones, shales and marls. This formation forms the axial part of the Vale of Eden Syncline continuing northwards into Scotland. This is then succeeded by the Kirklinton Sandstone, a soft cross bedded sandstone similar to the Penrith Sandstone but characterised by the absence of shale bands and the scattered occurrence of beds of wind-rounded quartz grains. The younger Stanwix Shale is only present in northern Cumbria forming red to green grey mudstones with halite. Large parts of the Permo-Triassic sandstone are covered by a mantle of Glacial Drift deposits: boulder clay is the most extensive of these deposits but some sands and gravels also occur.

The valley floor soils are dominated by well drained brown earths whereas more acid soils are developed on the higher ground of the valley margins, particularly on the eastern margins.

2.2. Hydrogeology

The main aquifers are represented by the Permian Penrith Sandstone and the Triassic St Bees Sandstone, separated by the St Bees/Eden Shales. The Penrith Sandstone is largely aeolian in origin and is a medium to coarse grained red sandstone with occasional buff beds and false bedded. The groundwater development potential is substantial but demand is relatively low due to abundant surface water sources.

Groundwater transport within the Penrith sandstone is largely dependent on secondary permeability but the intergranular properties of the sandstone are important in controlling the release of water from storage. The permeability of the Penrith Sandstone varies significantly due to secondary silicification and cross bedding, which can affect borehole yields. Generally, borehole yields up to $45 \, l \, s^{-1}$ can be expected. The St Bees Sandstone also displays fracture flow and is strongly anisotropic, complicating groundwater movement. Potential groundwater yields are slightly less than in the Penrith Sandstone.

Rainfall in the area is relatively high and recharge to the aquifers is often inhibited by a thick mantle of till. Recharge takes place largely through areas of outcrop of the sandstone or where the till thins or is of a sandy nature.

2.3 Aquifer minerals

The Penrith Sandstone is generally composed of well rounded quartz grains often cemented with calcite and iron hydroxide minerals. Secondary coatings of silica on the quartz grains may lead to significant decreases in porosity. Coarse breccias (locally known as brockram) are found in the lower and upper parts of the formation and may contain clasts of Carboniferous limestone and sandstone and occasionally Lower Palaeozoic rocks.

Beds of dolomite and gypsum-anhydrite are present in the siltstones and sandstones of the Eden Shales. Carbonate and plant remains are also present in parts of the formation.

The St Bees Sandstone is similar to the Penrith Sandstone, but unlike the latter contains both feldspar and mica. The Stanwix shales also contain halite (NaCl).

3. DATA QUALITY AND HANDLING

There are two sets of data which have been used for this study: a) monitored data from the Environment Agency comprising 102 different sites and b) BGS data from geochemical study of 14 boreholes conducted in 1984 (Edmunds et al., 1989). Both data sets have been combined into an ACCESS database. Several chemical analyses were available from many of the EA sites and averages were calculated for statistical treatment of the data.

The BGS data set comprises six samples collected from the Permian Penrith Sandstone and eight from the Triassic Sandstone Formations, collected in 1985 Samples were collected by pumping except for Standingstone and British Sidac near Wigton and Edenhall which were artesian. The excellent quality of this data set is indicated by the ionic balances which vary from -1.8 to +3.7 %. The EA data set comprised data from boreholes in the Penrith St Bees and Kirklinton Sandstones. A total of 430 analyses from 102 boreholes were available collected over the period 1973 to 1998. Where all parameters were measured, ionic balances were generally good with only 9 analyses with balances greater than 10 % being discarded.

Statistical summaries of the data are shown in Tables I.1 and I.2 and details of the procedures used for its construction are given in the Guide. Concentrations of elements which were reported as below detection limit (DL) have been assigned a value equal to half of the detection limit for statistical purposes. Where the median value is less than the limit of detection, this has simply been reported as less than the quoted detection limit (Tables I.1 and I2). The 95th percentile value has been taken to be a reasonable estimate of the upper limit of the "baseline" concentration (Appendix 1).

4. HYDROCHEMICAL CHARACTERISTICS

The waters show a wide range of types based on major element compositions but are dominantly of Ca-HCO_3 or Ca-Mg-HCO_3 type. There are trends towards Ca-Mg-SO_4 and Ca-Na-Cl-HCO_3 types in both the Permian and Triassic aquifers (Figure I.2). Some Triassic groundwaters also show a distinct trend towards Na-HCO_3 type (Figure I.2). There is a small range in pH with most of the waters being slightly acid to alkaline. The waters generally have low conductivities although some high Cl or SO_4 is present in some samples (Figure II.4.1). Median concentrations of Na, Cl and HCO_3 are slightly higher in the Triassic sandstone waters, but SO_4 is similar (Table I.1 and 2, Figure II.4.1). Where the aquifer is overlain by Stanwix or Eden Shales, waters may contain high Ca and SO_4 (up to 495 and 1305 mg l^{-1} respectively) derived from dissolution of gypsum. However, many groundwaters collected from boreholes drilled through these shales have relatively low concentrations. High HCO_3 (up to 443 mg l^{-1}) is present in some groundwaters including those where the boreholes encountered brockram. Higher median concentrations of elements in Triassic groundwaters such as Si, Sr and Li and Na/Cl ratios indicate that in some waters silicate weathering has been more important. Several Triassic groundwaters also show a decrease in Ca and HCO_3 with an increase in Na at high pH, most likely as a consequence of calcite precipitation and ion exchange.

The groundwaters of the Carlisle and Eden Basins were considered to be, in general, relatively oxidising as reflected by low concentrations of Fe as well as high Eh and the presence of dissolved oxygen (Edmunds et al., 1989). Manganese concentrations are generally linked to those of Fe. High concentrations of Fe and Mn (up to 83000 and 5600 μg l^{-1} respectively) in the EA data set do occur in many samples from both aquifers, but temporal variations are extremely variable in these unfiltered waters (see Figure II.5.4). Such high concentrations are not likely to be in equilibrium with the redox conditions of the waters sampled and are considered to be caused by particulate matter being present during sampling. The BGS samples were filtered to avoid analysing the particulate fraction because many precipitates of Fe and Mn sesquioxides are known to adsorb large amounts of trace metals. In such circumstances the concentrations of many elements and their behaviour in the aquifer cannot be interpreted. Nitrate is present in waters where oxygen is present and concentrations can be relatively high: up to 19.4 mg l^{-1} as N; the anoxic waters contain nitrate at below detection limit implying that nitrate reduction has occurred. The reducing waters are typically down gradient and confined, and it is apparent that a redox boundary exists close to the confined/unconfined boundary. The relative enrichments in major elements compared to Cl are displayed in Figures II.4.2 and II.4.3 where it can be seen that Ca and HCO_3 show the highest levels of enrichment relative to those found in seawater.

Trace metals are expected to be low because of moderate to high pH and low concentrations in the aquifer. However, high concentrations of Pb, Cu, Zn were found in some waters. There is often a correlation between metal concentration and total Fe and Mn in individual borehole waters. This is most likely a consequence of these metals being adsorbed onto particulate matter which has not been filtered from the sample, making geochemical interpretation difficult. Cadmium is high in a few waters and although there is some correlation with other metals, it is difficult to establish definitively if this is affected by the presence of particulate matter or not.
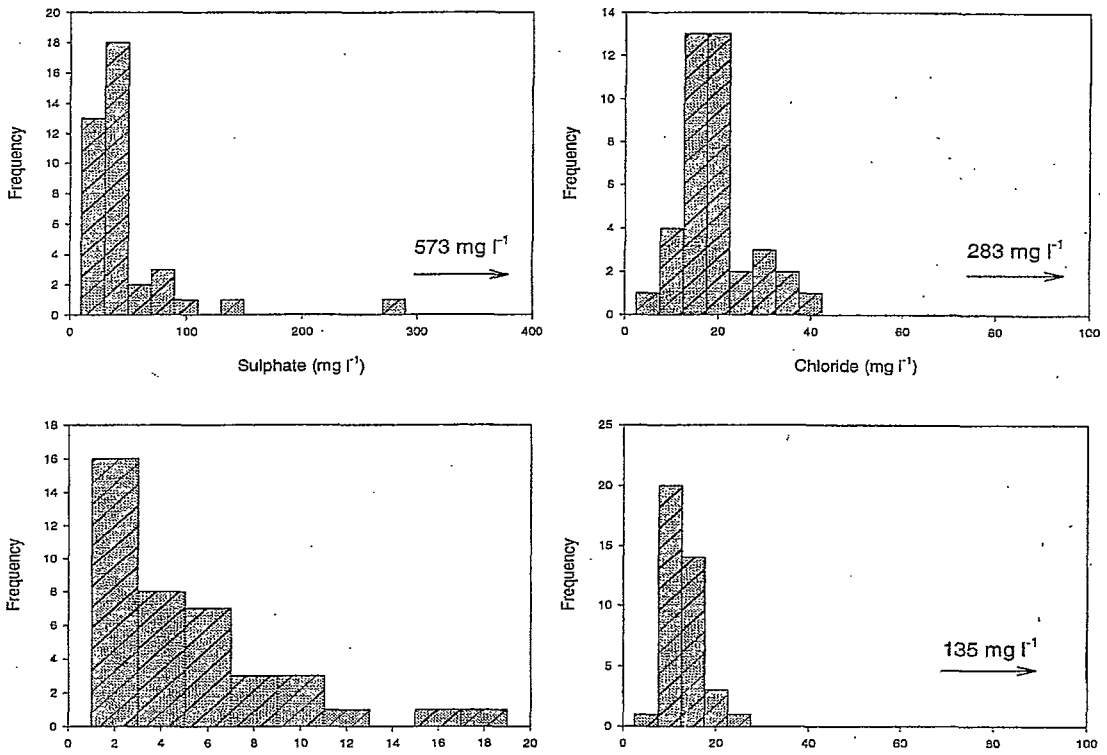
Figure II.4.1a. Histograms for sulphate, chloride, nitrate and sodium in Permian groundwaters.
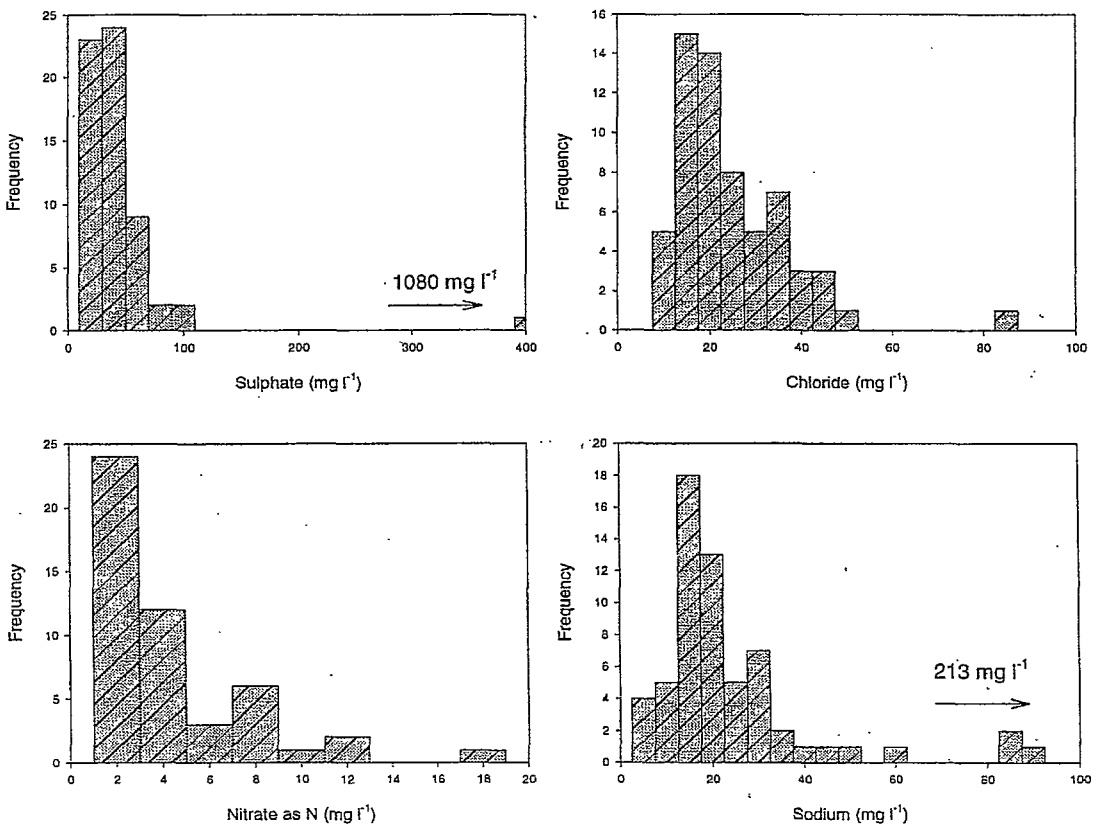
Figure II.4.1b Histograms for sulphate, chloride, nitrate and sodium in Triassic groundwaters.

Some waters contain relatively high Ba (> 400 µg l^{-1}), but where SO_4 is high concentrations are kept low due to saturation with respect to barite. Strontium is often low implying relatively little reaction with the rock but the high concentration in Tarraby is likely to be due to the presence of celestite or from high Sr barite in the Mercia Mudstone.

Lithium concentrations are higher in the deeper Triassic samples and may indicate a greater residence time in the aquifer. Arsenic was also detected in several samples at low concentrations, the highest being 20 µg l^{-1} at the Scott Leathers borehole and 15 µg l^{-1} at Tarraby. High Al in a few samples is considered to be due to particulate matter.

Fluoride is generally very low in the groundwaters indicating that fluorite is rare or absent in much of the aquifer. Bromide correlates poorly with Cl, and low Br/Cl ratios imply that halite dissolution has been important in the evolution of many of the groundwaters.

Figure II.4.2. Range of major ion concentrations in Permo-Triassic groundwaters from Cumbria.

Figure II.4.3. Range of minor and trace element concentrations in Permo-Triassic groundwaters from Cumbria.

5. REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS
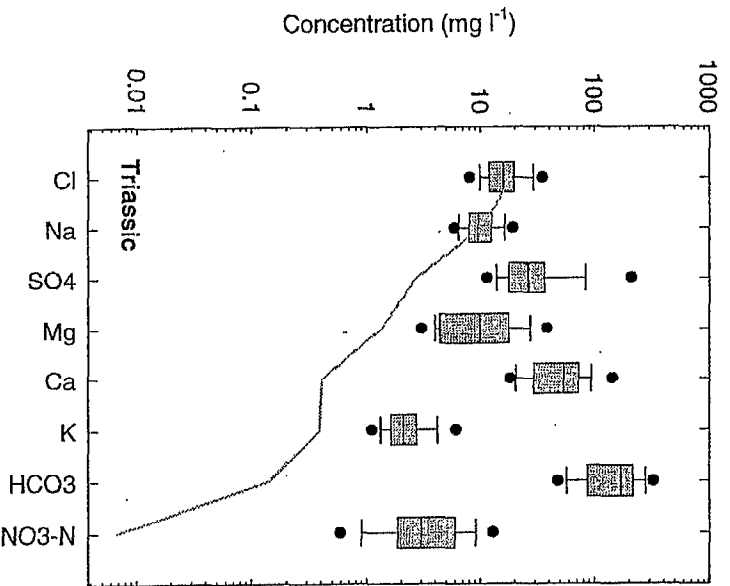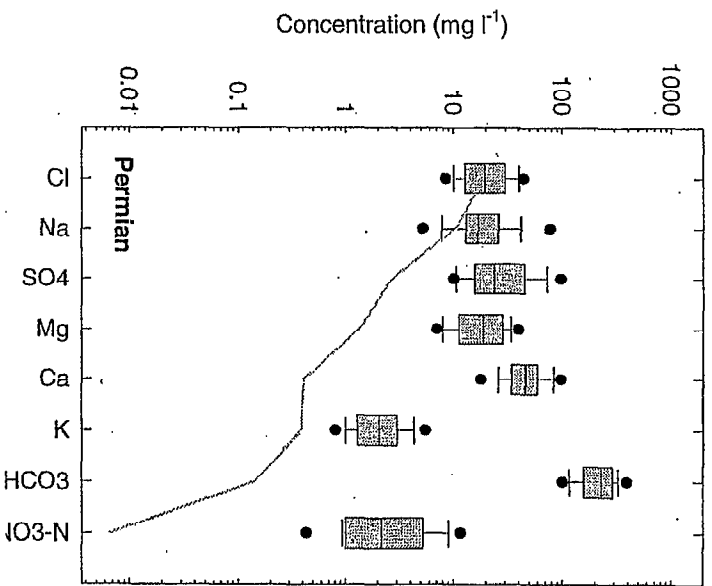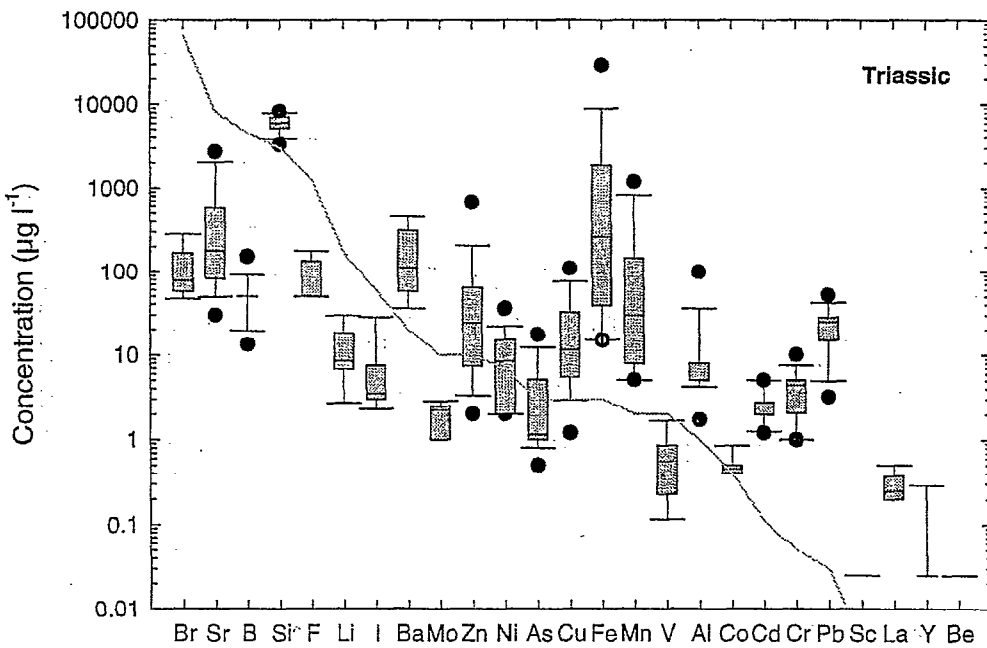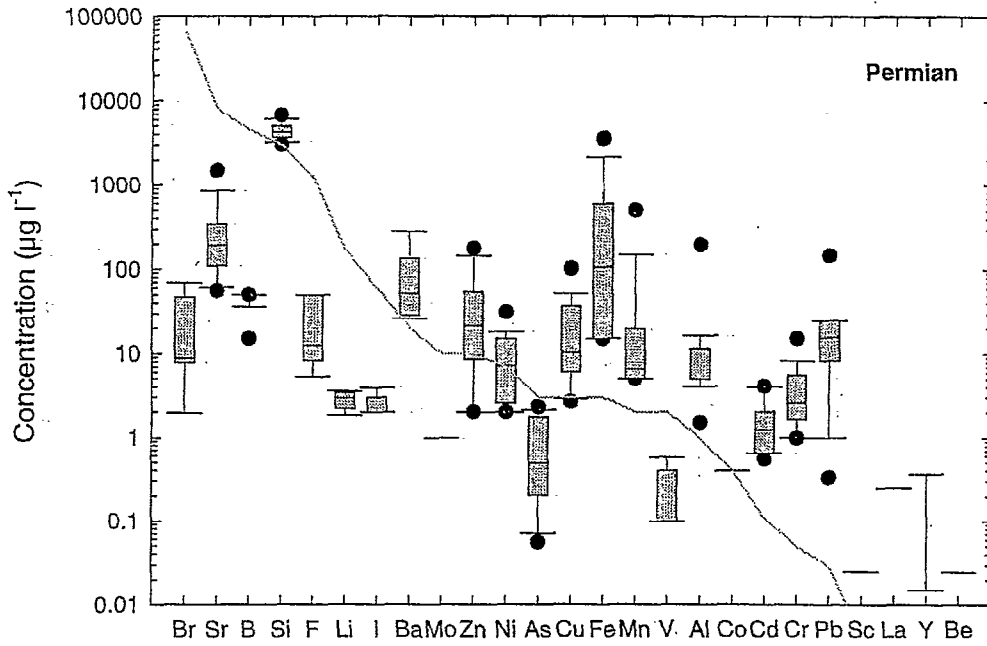
The higher T(°C) and conductivity in the Triassic sandstones is most likely a consequence of greater residence time since this correlates with depth of the boreholes where known. The presence of carbonate, particularly where brockram is present, helps to buffer the waters at neutral to alkaline pH. However, the fact that many waters are undersaturated with respect to calcite implies that silicate weathering and dissolution of salts also exert an important control on major element chemistry. Calcite dissolution is likely to take place in deeper parts of the aquifer which have not undergone decalcification.

There is trend towards increasing pH and Mg/Ca ratio in the deeper and more reducing waters implying that incongruent reaction of carbonate or ion-exchange has been an important control in the evolution of these groundwaters. This may lead in extreme cases to the evolution of waters of $Na-HCO_3$ composition. The $Na-HCO_3$ waters (Figure I.2) present in the Triassic aquifer are most likely formed in this way with ion-exchange of Ca for Na. The Stanwix shales, which contain halite, most likely provide slightly enhanced Na and Cl concentrations in some of the groundwaters which trend towards water of $Ca-Na-Cl-(HCO_3, SO_4)$ compositions. In addition there is another trend towards waters of $Ca-SO_4$ type where dissolution of gypsum/anhydrite has taken place. The presence of mineral phases which undergo rapid dissolution, such as halite and gypsum, has led to considerable variety in water types of the Carlisle basin and Eden Valley (Figure I.2). Several waters are undersaturated with respect to calcite demonstrating the absence of calcite to considerable depths probably as a function of decalcification in the upper parts of the aquifer. Buffering of the waters with respect to silica occurs quite rapidly and the bulk of the groundwaters are saturated with respect to chalcedony and quartz.

The relative distribution of major and trace elements are shown on cumulative frequency plots in Figures II.5.1 and II.5.2. Most major elements show a normal distribution and there are strong similarities between the Permian and Triassic groundwaters (Figure II.5.1). The low concentrations of Ca in the $Na-HCO_3$ type waters of the Triassic give rise to distinct tail at lower concentrations (Figure II.5.1).

Silicon shows a near-vertical profile (Figure II.5.2) indicating an upper limit of solubility by a silica (quartz/chalcedony) phase. Iron concentrations are variable and solute concentrations relate primarily to redox conditions in the aquifer with high Fe in the more reducing waters. In the oxidising waters Fe is removed from solution due to low solubility at high Eh and circumneutral pH. This exerts not only a strong influence on Fe and Mn but also on trace metals which are limited by adsorption of Fe and Mn oxy-hydroxide minerals. Barium is relatively high in some waters (up to 460 g l^{-1}), probably derived from feldspar or barite minerals in the aquifer matrix.

The regional variations between the two aquifers are illustrated in Figure II.5.3 for pH, Ca, Cl, Fe and NO_3. There is a tendency towards slightly higher pH in the Triassic sandstones. Higher than average concentrations of Ca and Cl (Figure II.5.3) appear to be associated with the central and northern area of the Triassic beds and most likely relate to dissolution of gypsum and halite in the aquifer matrix. High Fe is mostly present only in the Carlisle Basin. As mentioned previously, this is thought to be, at least in part, due to the incorporation of particulate matter. However, the presence of significant ferric hydroxide may be a consequence of high-Fe reducing groundwaters which have become oxidised near the surface. In contrast, high nitrate is mainly present in the Vale of Eden where the waters are oxidising.

Temporal trends for three elements; Cl, NO_3 and Fe are shown in Figure II.5.4. It is evident that some sites show significant variation for Cl whilst others much less. The reasons for this are unclear but may be related to different pumping regimes or large vertical differences in the chemistry of waters sampled. The behaviour of nitrate is different for different boreholes with some remaining relatively constant whilst others show fluctuations or trends, with some borehole waters showing an increase whilst others decrease. The behaviour of Fe (and also Mn) is very erratic at some sites and, as discussed previously, this may well be due to the presence of particulate matter present in the unfiltered waters.
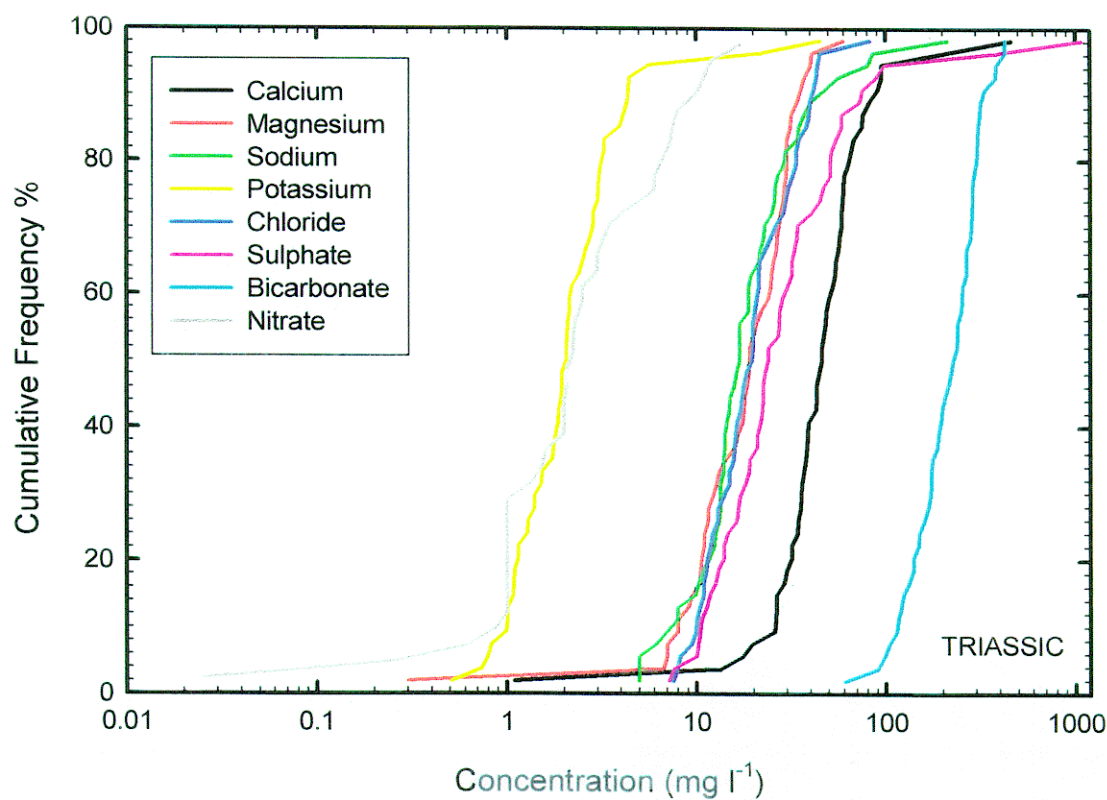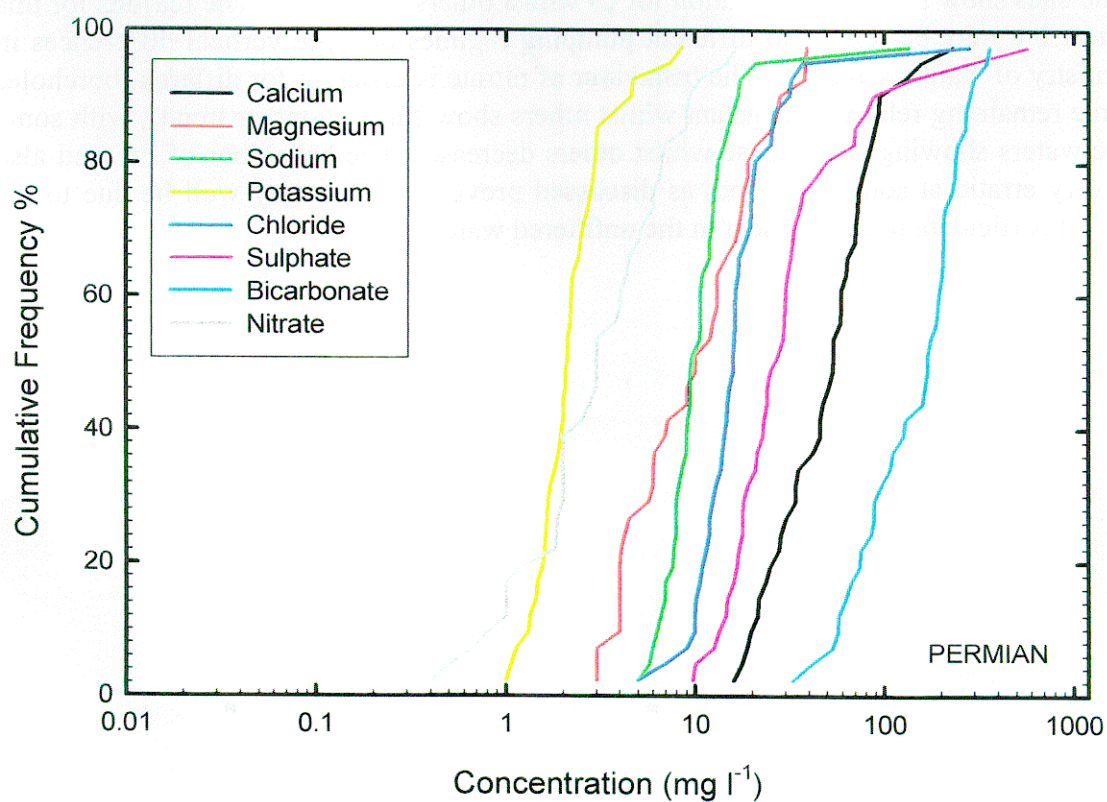
Figure II.5.1 Cumulative-frequency diagram for major ions in the groundwaters of Cumbria.
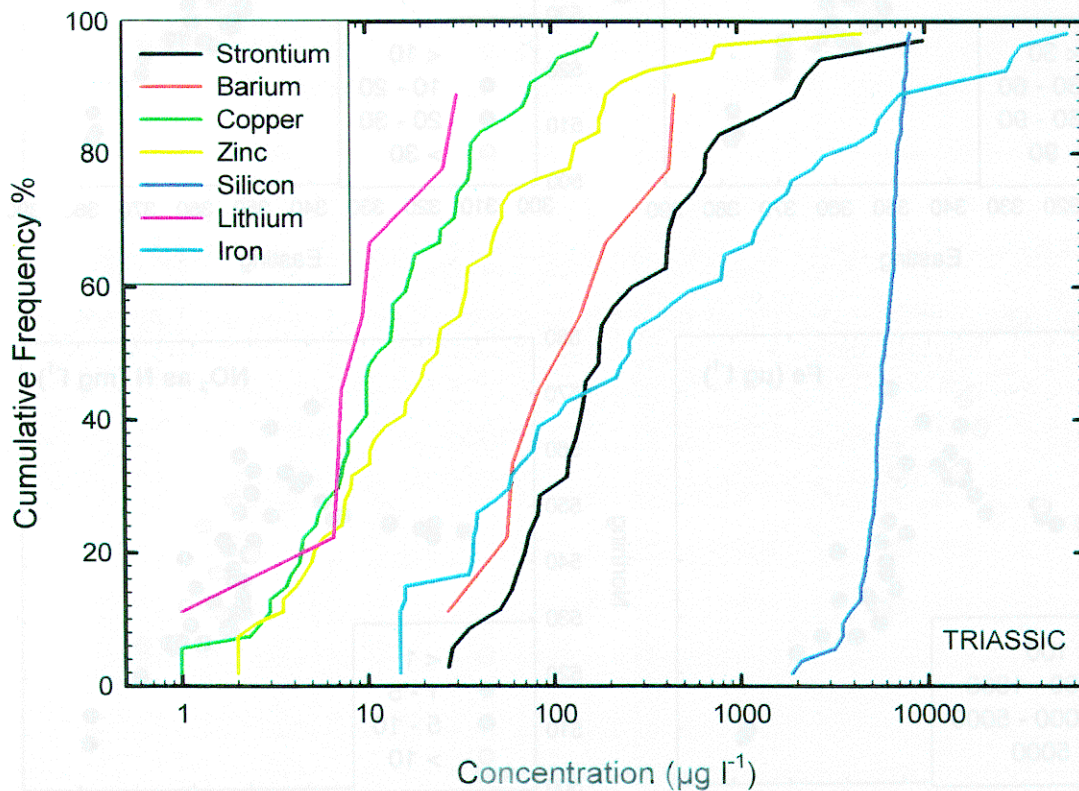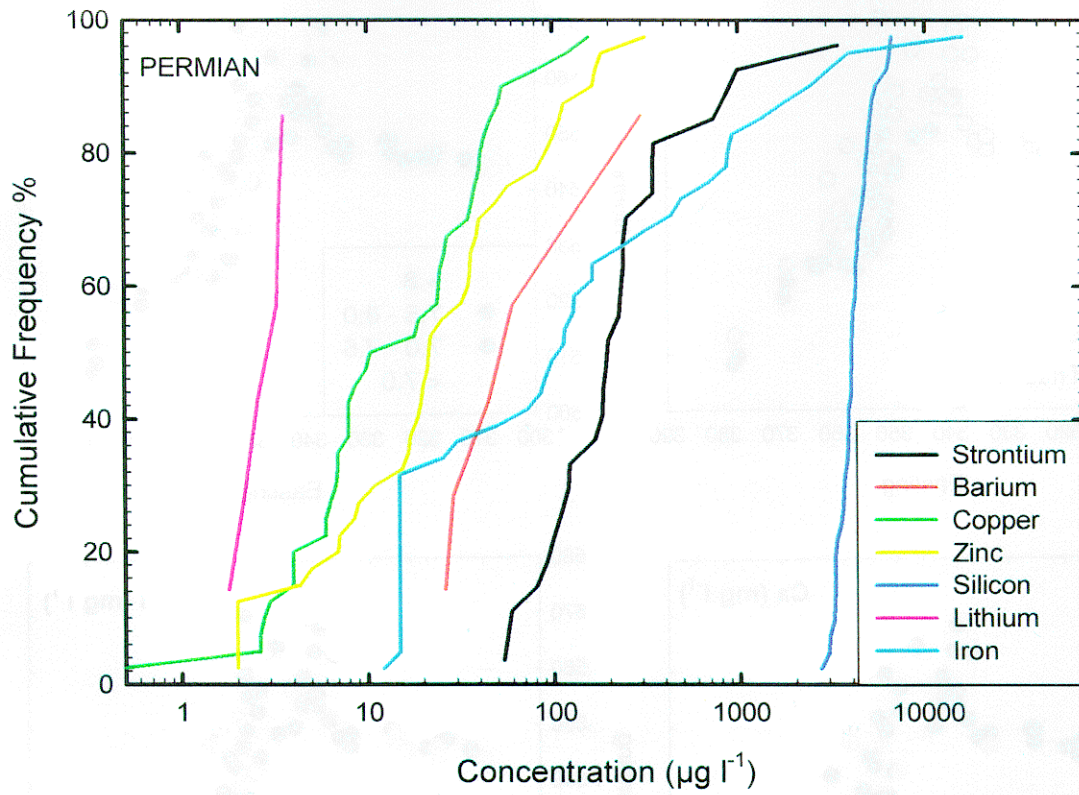
Figure II.5.2 Cumulative-frequency diagram for minor and trace elements in the groundwaters of Cumbria.
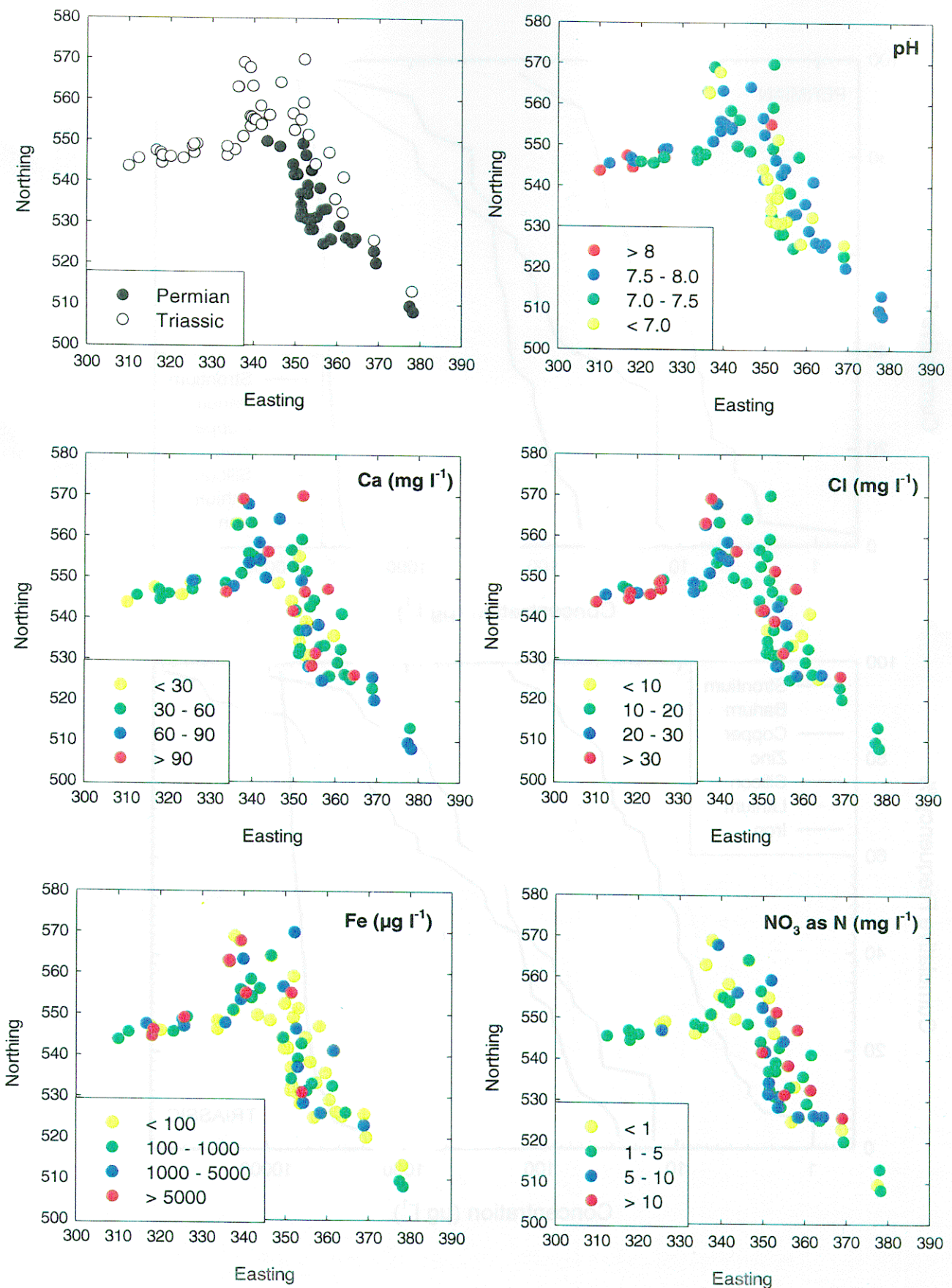
Figure II.5.3 Regional distribution of pH, Ca, Cl, Fe and NO₃ in the groundwaters of Cumbria.
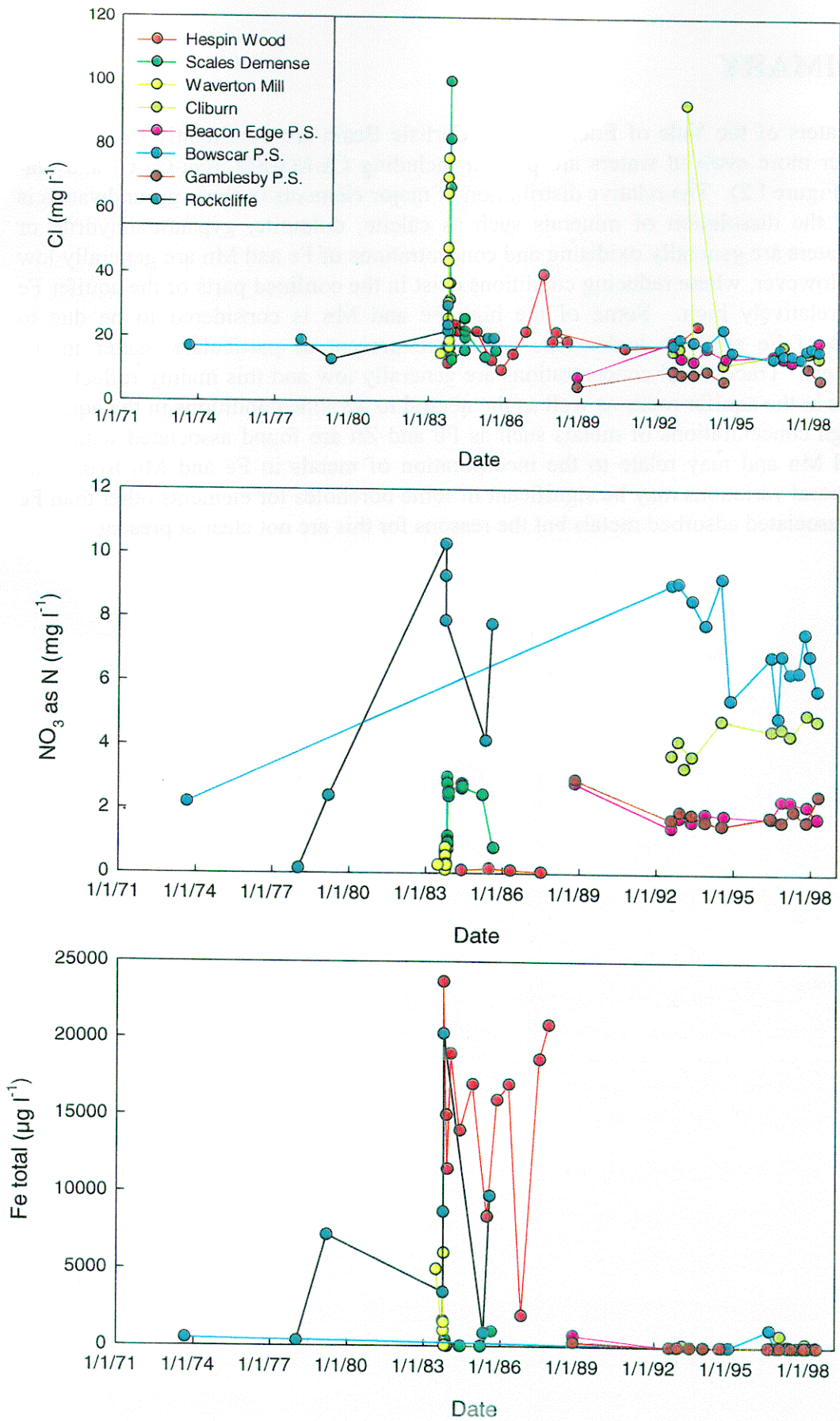
Figure II.5.4 Temporal trends for selected groundwaters in Cumbria showing Cl, SO₄ and Fe.

6. SUMMARY

The groundwaters of the Vale of Eden and the Carlisle Basin are dominantly of Ca-HCO$_3$ type, but other more evolved waters are present including Ca-Mg-SO$_4$, Na-Ca-Cl and Na-HCO$_3$ types (Figure I.2). The relative distribution of major elements in these groundwaters is controlled by the dissolution of minerals such as calcite, dolomite, gypsum/anhydrite or halite. The waters are generally oxidising and concentrations of Fe and Mn are generally low (Table I.1). However, where reducing conditions exist in the confined parts of the aquifer Fe and Mn are relatively high. Some of the high Fe and Mn is considered to be due to incorporations of Fe and Mn hydroxides which are present as particulate matter in the unfiltered waters. Trace metal concentrations are generally low and this mainly reflects low concentrations in the aquifer rocks as well as the neutral to alkaline conditions in the aquifer. Relatively high concentrations of metals such as Pb and Zn are found associated with high solute Fe and Mn and may relate to the incorporation of metals in Fe and Mn hydroxide phases. Temporal variations may be significant in some boreholes for elements other than Fe and Mn and associated adsorbed metals but the reasons for this are not clear at present.

7. SELECTED REFERENCES

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Edmunds, W.M., Brewerton, L.J., Shand, P. & Smedley, P.L. 1997 The natural (baseline) quality of groundwater in England and Wales. Part 1: A guide to the natural (baseline) quality study. *British Geological Survey Technical Report* **WD/97/54**.

Edmunds, W.M., Cook, J.M., Kinniburgh, D.G., Miles, D.L. & Trafford, J.M. 1989 Trace element occurrence in British groundwaters. British Geological Survey, Research Report, SD/89/3.

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 (^{3}H), 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:

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:	^3H, ^{14}C, $\delta^{18}O$, δ^2H, ^{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), SO_4, Br, TDS (total dissolved solids), Mg/Ca, $\delta^{18}O$, δ^2H, F;
2. Acidity and redox status: **pH**, **HCO_3**, Eh, DO, Fe, As;
3. Radioactivity: **^3H**, ^{36}Cl, ^{222}Rn;
4. Agricultural pollution: **NO_3**, **SO_4** **DOC** (dissolved organic carbon), K/Na, P, pesticides and herbicides;
5. Mining pollution: **SO_4**, **pH**, Fe, As, other metals, F, Sr;
6. Urban pollution: **Cl**, **HCO_3**, **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:

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

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

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	1500	1500	0.0526
		25-30°C	700	-	
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	
	(total)	-	0.5	each compound	
Polycyclic Aromatic	(PAH)	-	0.2	-	
Hydrocarbons	(CTC)	-	-	2	
Carbon	(TCE)	-	-	70 P	
tetrachloride	(°C)	12	25	-	
Trichloroethene		6.5-8.5	-	6.5-8.5	
Temperature	(µScm⁻¹ at	400	-	-	
pH	20°C)				
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:

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

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:

<1 <1 <1 <1 2 3 4   median is <1
<1 <1 1 2 3 3 4   median is 2

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.
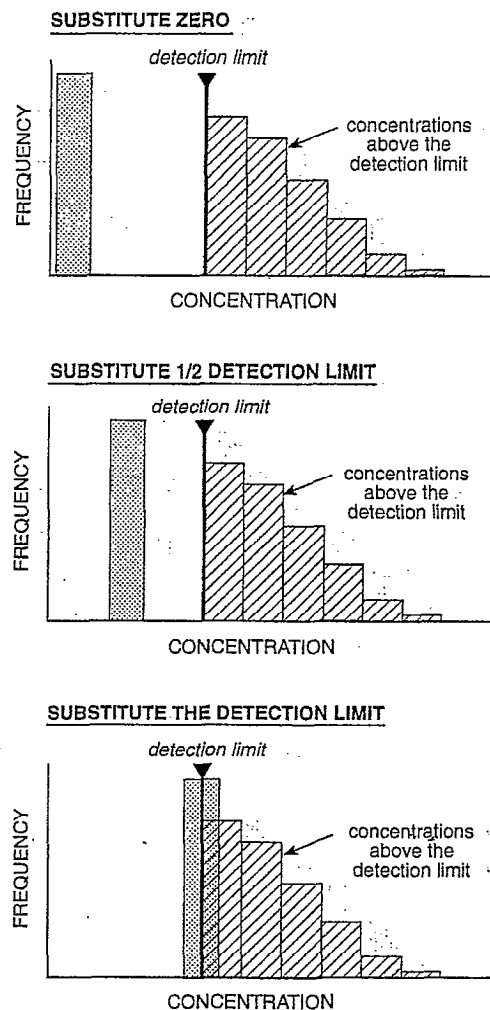
SUBSTITUTE ZERO

SUBSTITUTE 1/2 DETECTION LIMIT

SUBSTITUTE THE DETECTION LIMIT

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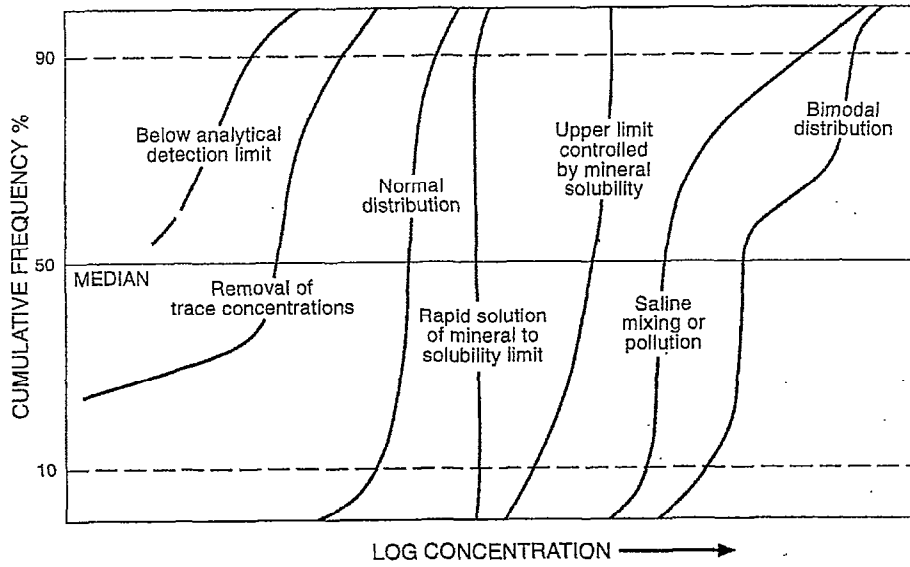
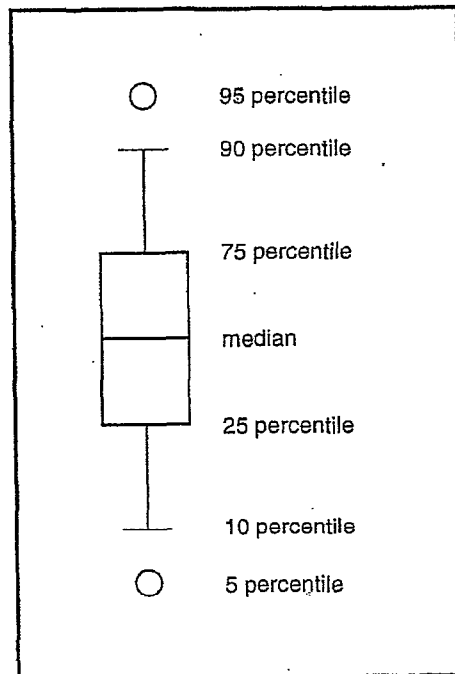**Figure A1.2.2. Illustration of the use of cumulative-frequency diagrams.**

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 (10–12 mg l^{-1} depending upon barometric and temperature conditions). Passing through the soil and the unsaturated zone, some of this O_2 will react as a result of microbiological processes and oxidation-reduction reactions. In the Chalk for example, almost all water reaching the water table 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:

$$Ca(Mg)CO_3 + H_2O + CO_2 = Ca^{2+} + (Mg^{2+}) + 2HCO_3$$
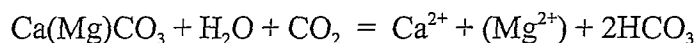
The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone. This process **(congruent dissolution)** yields Ca and Mg concentrations which are identical to those in the dissolving carbonate 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.
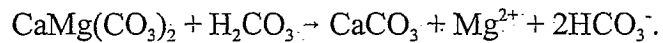
Congruent/incongruent reaction

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:

$$CaCO_3 + H_2CO_3^- \rightarrow Ca^{2+} + 2HCO_3^-$$
$$CaMg(CO_3)_2 + 2H_2CO_3^- \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-.$$
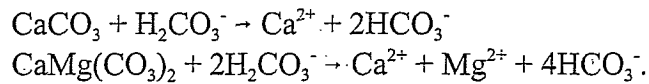
An incongruent reaction involving dissolution of primary dolomite and precipitation of secondary calcite, thought to be important in the confined Sherwood aquifer follows the form:

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

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:

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O = 2Na^+ + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4$$

A1.4. REFERENCES

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