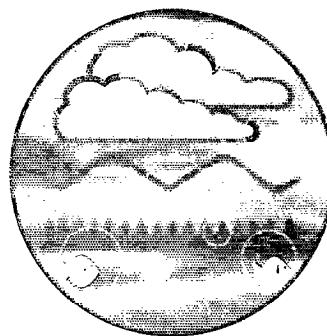
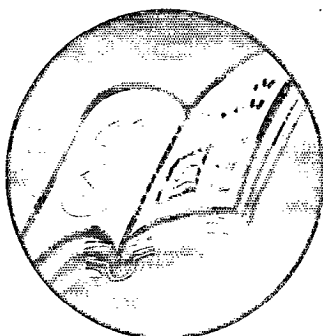
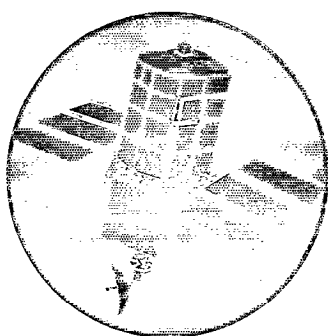


# **The Natural (Baseline) Quality of Groundwaters in England and Wales**

**The Chalk of Berkshire and the Chilterns**



## **Research and Development**

**Project Record  
W6/i722/6**



**British  
Geological  
Survey**



**ENVIRONMENT AGENCY**



All pulps used in production of this paper is sourced from sustainable managed forests and are elemental chlorine free and wood free

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

The Chalk of Berkshire and the Chilterns

R&D Project Record W6/i722/6

W M Edmunds and L J Brewerton

Research Contractor:  
British Geological Survey

Further copies of this report are available from:  
Environment Agency R&D Dissemination Centre, c/o  
WRc, Frankland Road, Swindon, Wilts SN5 8YF



tel: 01793-865000 .. fax: 01793-514562 .. e-mail: [publications@wrcplc.co.uk](mailto:publications@wrcplc.co.uk)

**Publishing Organisations:**

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

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

ISBN: 1 85705 104 1

© Environment Agency and Natural Environment Research Council 1997

All rights reserved. No part of this document may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior permission of the Environment Agency or the Natural Environment Research Council.

The views expressed in this document are not necessarily those of the Environment Agency or the Natural Environment Research Council. Its officers, servants or agents accept no liability whatsoever for any loss or damage arising from the interpretation or use of the information, or reliance upon views contained herein.

**Dissemination status**

Internal: Released to Regions

External: Released to Public Domain

**Statement of use**

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

# CONTENTS

## Page

List of Tables	ii
List of Figures	iii

## SECTION I: The Chalk of Berkshire and the Chilterns

EXECUTIVE SUMMARY	1
KEYWORDS	1

## SECTION II: Understanding the Natural Quality – Controls and Processes

1	PERSPECTIVE	5
2	BACKGROUND	6
2.1	Geology	6
2.2	Hydrogeology	7
2.3	Aquifer minerals and geochemical composition	7
2.4	Rainfall Chemistry	10
3	DATA QUALITY AND HANDLING	11
3.1	Source and quality of data	11
3.2	The influence of pollution	12
4	HYDROGEOCHEMICAL CHARACTERISTICS	13
5	REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS	14
5.1	Carbonate reactions	14
5.2	Redox reactions	15
5.3	Ion-exchange reactions	15
5.4	Trace element occurrence	16
5.5	Residence times	23
5.6	Depth variations	23
5.7	Saline water in the chalk	25
6.0	SUMMARY	26
7.0	SELECTED REFERENCES	27
	APPENDIX 1	29
A1.1	Introduction	29
A1.2	Methodology	32
A1.3	Geochemical Concepts	42
A1.4	References	44

## LIST OF TABLES

	Page
Table I.1 Statistical summary for groundwater from the Chalk of Berkshire and the Chilterns	3
Table II.2.1 Chemistry of rainfall (1977 - 1980) at Chilton, Berkshire compared with the composition of interstitial waters (0.6-3.0 m depth) beneath the soil zone, illustrating the effects of evapotranspiration and reactions in the near-surface environment	9
Table A1.1.1 Controls on the baseline chemistry of groundwaters	31
Table A.1.2.1 Determinands selected for baseline quality investigation. Determinands of health significance are given in bold	32
Table A1.2.2 Indicators of groundwater pollution	34
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)	35

## LIST OF FIGURES

## Page

Figure I.1	Trilinear (Piper diagram) illustrating the main features of groundwaters in the Chalk of Berkshire and the Chilterns. Unconfined groundwaters are shown as filled circles, confined groundwaters as open circles	2
Figure II.2.1	Schematic geological cross-section through the Berkshire Downs	6
Figure II.2.2	Model of the water-rock interactions in the chalk at the microscopic scale. Interstitial water (stippled) exchanges with fissure water	8
Figure II.2.3	Geological outcrop of the Chalk of Berkshire and the Chilterns with localities of boreholes used in this study	9
Figure II.3.1	Histograms of Cl, SO <sub>4</sub> and NO <sub>3</sub> -N in the Berkshire and Chilterns groundwaters	11
Figure II.5.1	Trilinear diagram showing the evolution of cation composition in groundwaters from the South Downs in relation to the Berkshire area	14
Figure II.5.2	Box plots for major ions in the groundwater of Berkshire and the Chilterns (unconfined and confined samples). For each element, the data within the 25th and 75th percentile range are highlighted with the median concentration. The outer bars show respectively the 5th and 95th percentile data limits. Maxima and minima are given as solid symbols	15
Figure II.5.3	Box plots for minor ions in the groundwater of Berkshire and the Chilterns arranged in the order of abundance in seawater (seawater line shown as reference). For each element, the data within the 25th and 75th percentile range are highlighted with the median concentration. The outer bars show respectively the 5th and 95th percentile data limits. Maxima and minima are given as solid symbols	16
Figure II.5.4	Cumulative-frequency diagram for major elements in the groundwaters of Berkshire and the Chilterns	17
Figure II.5.5	Cumulative-frequency diagram for minor elements in the groundwaters of Berkshire and the Chilterns	19
Figure II.5.6	Downgradient trends in the major-ion chemistry in the Chalk of Berkshire and the Chilterns	20
Figure II.5.7	Down gradient trends in Eh and redox-related elements in the Chalk of Berkshire and the Chilterns	21
Figure II.5.8	Downgradient trends in some minor and trace elements in the Chalk of Berkshire and the Chilterns	22
Figure II.5.9	Hydrogeochemical logs of Na, K, Ca, Mg and Sr in interstitial and depth-sampled waters from the Winterbourne bore borehole, Berkshire	24
Figure II.5.10	Interstitial water profile through the Upper, Middle and Lower Chalk from the saturated zone at Faircross, Berks	24
Figure II.6.1	Summary diagram to illustrate the principal hydrogeochemical processes taking place along flow lines in the Chalk	26
Figure A1.2.1	Illustration of the substitution method for estimating the mean (after Helsel and Hirsch, 1992).	37
Figure A1.2.2	Illustration of the use of cumulative-frequency diagrams.	40
Figure A1.2.3	Key to the structure of the boxes in box plots.	40

## 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.

This account describes chemical data from 65 boreholes in the Chalk aquifer of Berkshire and the Chilterns. Data from 169 samples from 32 sites on the unconfined Chalk and 101 samples from 33 sites on the confined Chalk are utilised. Data are compiled from Environment Agency (EA) and British Geological Survey (BGS) data files. It is estimated that of the Berkshire and Chilterns Chalk sources, some 80% of the groundwaters in the unconfined aquifer considered in this study, have significant contributions from agricultural sources (above  $5 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ ). Apart from this, the natural geochemical signature predominates.

Rainfall chemistry forms a major contribution for several ions (eg Cl, F, Mg) of the initial groundwater composition. However, the characteristic chemistry of chalk groundwaters is mainly established by water-rock reactions taking place in the top few metres of the unsaturated zone. Despite its purity, the small amount of other elements substituting in the calcites forming the Chalk have a disproportionate effect on controlling the water chemistry. The hydrogeochemistry of the Chalk as expressed in the major-ion chemistry is summarised in the trilinear plots (Figure I.1). The main feature is the distinctive low Mg composition (low Mg/Ca ratio) in the unsaturated zone and unconfined groundwaters and the evolution towards higher Mg/Ca ratios as the waters move downgradient into the confined aquifer, eventually increasing in Na (and Cl) concentrations at depth.

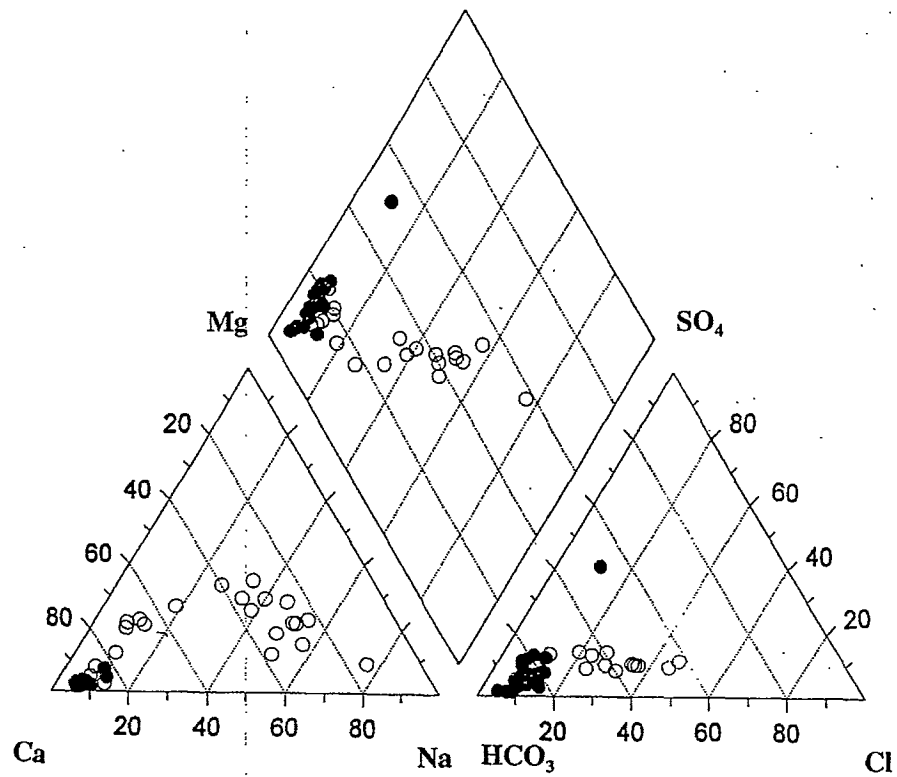
The main water-quality characteristics are controlled by the various reactions with the carbonate matrix, redox and ion-exchange reactions and mixing with slightly saline water at depth. The progressive reaction of the chalk sediment leads to release of a number of trace elements (notably Sr, F, Mn and Fe). Strontium in particular can be used as an indicator of the groundwater evolution and residence time. The report also contains detailed information on the occurrence and distribution of a number of other significant trace elements.

The area has also been the focus of research drilling to determine the physical and chemical properties of the chalk dual porosity system. These examples have proven that interstitial waters extracted from cores may differ in quality from waters taken by depth sampling or pumping.

### KEYWORDS

Baseline quality, hydrochemistry, groundwater, Chalk, Berkshire, Chilterns





**Figure I.1 Trilinear (Piper diagram) illustrating the main features of groundwaters in the Chalk of Berkshire and the Chilterns. Unconfined groundwaters are shown as filled circles, confined groundwaters as open circles.**

**Table I.1 Summary statistics for groundwater from the Chalk of Berkshire and the Chilterns.**

Determinand	Units	Unconfined Aquifer					Confined Aquifer				
		Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n
T	temperature °C	10.0	13.0	10.9	11.6	20	10.9	18.0	12.6	15.1	32
pH	(field measured)	6.80	8.43	7.16	7.36	20	7.00	8.24	7.40	7.79	33
Eh	redox potential mV	130	417	371	416	16	<50	445	80	381	30
DO	dissolved oxygen mg l <sup>-1</sup>	0.1	10.5	9	10.5	17	<0.1	10	0.2	9.18	32
SEC	conductivity µS cm <sup>-1</sup>	555	1100	683	887	12	636	1500	785	1410	21
Ca	calcium mg l <sup>-1</sup>	86	169	110	150	21	36	118	57	114	33
Mg	magnesium mg l <sup>-1</sup>	0.9	8.9	2.07	8.2	21	1.5	30	19	29.2	33
Na	sodium mg l <sup>-1</sup>	5.6	24	8.9	21.9	21	8.1	219	36	122	33
K	potassium mg l <sup>-1</sup>	0.6	5.3	1.5	4.3	21	1.1	10.2	6.8	9.88	33
Cl	chloride mg l <sup>-1</sup>	9	41	17	41	21	14.5	204	30	151	33
HCO <sub>3</sub>	bicarbonate mg l <sup>-1</sup>	221	341	289	330	18	267	349	303	324	24
SO <sub>4</sub>	sulphate mg l <sup>-1</sup>	2.5	197	13	125	21	13.5	68	33	55.8	33
NO <sub>3</sub> -N	nitrate (N) mg l <sup>-1</sup>	0.09	11.1	5.2	7.5	21	<0.02	7	<0.02	6.7	33
NH <sub>4</sub> -N	ammonium (N) µg l <sup>-1</sup>	<8	70	<8	69	13	<8	893	198	750	32
Al	aluminium µg l <sup>-1</sup>	<7	18	<7	2.8	20	<7	<7	<7	<7	33
As	arsenic µg l <sup>-1</sup>	<1	4	2	3.5	12	<1	5	3	4	22
B	boron µg l <sup>-1</sup>	<2	120	18	86.9	23	<2	1430	185	1180	36
Ba	barium µg l <sup>-1</sup>	1.5	100	60	100	21	18	146	90	124	33
C	cobalt µg l <sup>-1</sup>	<1.33	3.6	<1.33	1.87	8	<1.33	<1.33	<1.33	<1.33	11
Cd	cadmium µg l <sup>-1</sup>	<2	<2	<2	<2	8	<2	2.4	<2	<0.02	12
Cr	chromium µg l <sup>-1</sup>	<1	<1	<1	<1	2	<1	<2	<1	<1	4
Cu	copper µg l <sup>-1</sup>	<1.33	23	2.45	5.98	22	<1.33	29	1	13.1	35
F	fluoride µg l <sup>-1</sup>	60	350	150	326	17	<100	4800	1300	2360	33
Fe	total iron µg l <sup>-1</sup>	<1	4380	7	834	28	<1	2560	217	719	47
Fe(II)	ferrous iron µg l <sup>-1</sup>	<10	1900	<10	849	12	<10	1380	130	635	22
I	iodine µg l <sup>-1</sup>	3	10	5	9.5	11	4	54	18.5	49.3	26
Li	lithium µg l <sup>-1</sup>	<0.5	9	5	9	19	1.4	220	13.5	25	32
Mn	manganese µg l <sup>-1</sup>	<0.2	282	<10	81.6	28	<0.2	60	8	34.7	48
Mo	molybdenum µg l <sup>-1</sup>	<7	<7	<7	<7	4	<7	<7	<7	<7	2
Ni	nickel µg l <sup>-1</sup>	<2	11	<3	7.5	22	<3	7	<3	<3	37
P	orthophosphorus µg l <sup>-1</sup>	<3	6.5	<3	6.5	11	<3	278	3.2	12.7	22
Pb	lead µg l <sup>-1</sup>	<10	2	<10	<2.8	9	<2	<10	<10	<6.4	12
Rb	rubidium µg l <sup>-1</sup>	<50	<50	<50	<50	3	<50	<50	<50	<50	9
Si	silicon µg l <sup>-1</sup>	4100	10800	6500	10700	21	4700	10700	8200	10500	33
Sr	strontium µg l <sup>-1</sup>	40	1500	250	1400	21	180	6300	3600	6190	33
U	uranium µg l <sup>-1</sup>	0.24	1.7	0.28	1.37	6	0.01	0.6	0.03	0.23	19
Y	yttrium µg l <sup>-1</sup>	<0.2	<0.2	<0.2	<0.2	7	<0.2	<0.2	<0.2	<0.2	11
Zn	zinc µg l <sup>-1</sup>	<1.3	34	9.9	30	10	<1.3	414	21.3	207	15
	atrazine µg l <sup>-1</sup>	1	1		1	1					
TCE	trichloroethene µg l <sup>-1</sup>	4	4		4	1					
δ <sup>18</sup> O	oxygen-18 ‰	-6.2	-7.9	-7.3	-6.7	14	-6.6	-7.9	-7.2	-6.7	29
δ <sup>2</sup> H	deuterium ‰	-44	-49	-46	-45	14	-41		-47	-42	30
<b>Unfiltered</b>											
Fe	total iron µg/l	<0.01	0.53	<0.01	0.12	100	<0.01	2.41	0.11	1.74	50
Mn	manganese µg/l	<0.01	0.04	<0.01	0.02	101	<0.01	0.21	0.01	0.08	49

## **SECTION II.**

### **UNDERSTANDING THE NATURAL QUALITY – CONTROLS AND PROCESSES**

#### **1. PERSPECTIVE**

The Chalk of Berkshire has been extensively developed for public supply for over a century and has been well studied from the resources viewpoint in connection with river augmentation schemes (Owen and Robinson, 1978). There has also been a detailed investigation of the hydrogeochemical processes in this aquifer which serves as a framework for this baseline study (Edmunds et al., 1987). The area of this report covers the unconfined Chalk outcrop of the Chilterns and Berkshire Downs as well the confined Chalk aquifer lying in the Berkshire syncline, the western extension of the London Basin.

The area of outcrop is mainly agricultural land with lesser areas of woodland. Intensive farming has been practised in many areas since clearing of much of the natural grassland in the Downs during the 1950s. Since then, the area has undergone significant applications of artificial fertilisers and chemicals. The population density is relatively high and the demand for groundwater, especially from the Chalk outcrop and the Thames basin is intense. Industry is mainly light and concentrated in the area underlain by the confined aquifer, such as the Kennet valley, so that its influence on groundwaters is likely to be only of a local nature. The majority of the unconfined groundwaters sampled might be expected to show some evidence of human influence. The confined aquifer is less likely to have been seriously affected as the residence times of the groundwaters mainly pre-date the post-war or the industrial era.

## 2. BACKGROUND

### 2.1 Geology

The geological section (Figure II.2.1) shows that the Chalk is overlain by the Tertiary Reading Beds and itself overlies the Upper Greensand. The underlying Gault serves as a basal aquiclude.

The Upper Chalk is a soft, white, fine-grained limestone containing regularly spaced bands of nodular and tabular flints. Fissure flow predominates and, of the three subdivisions, the Upper Chalk is the most important in terms of water supply. The Chalk Rock at the base of the Upper Chalk frequently forms a preferential flow zone of less than 100 metres below ground surface. At outcrop, the Upper Chalk is often capped by clay-with-flints which reduces infiltration locally, but which results in increased surface run-off and recharge to the aquifer around the edge of the deposit. The Middle Chalk is very similar to the Upper Chalk, but contains a smaller number of flints. The hard, nodular Melbourn Rock at the base of the Middle Chalk may also form a preferential flow zone. The Lower Chalk contains no flints and the increase in clay content from the top to the bottom is reflected in the colour change from pale buff grey to dark blue grey. The Chilton Stone, a hard band within the Lower Chalk, forms a preferential flow zone which manifests itself on the scarp slope of the Berkshire Downs in a line of springs. The base of the Chalk is marked by a thick greenish-grey glauconitic marl.

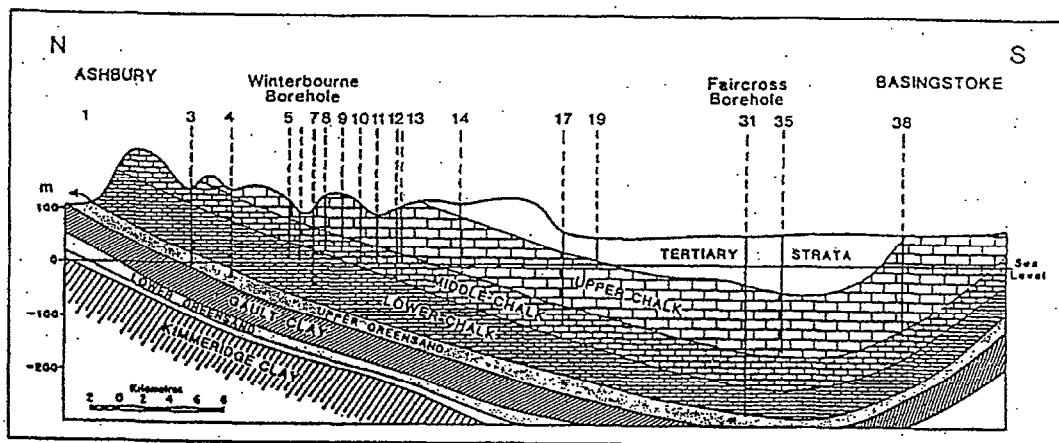


Figure II.2.1 Schematic geological cross-section through the Berkshire Downs.

## 2.2 Hydrogeology

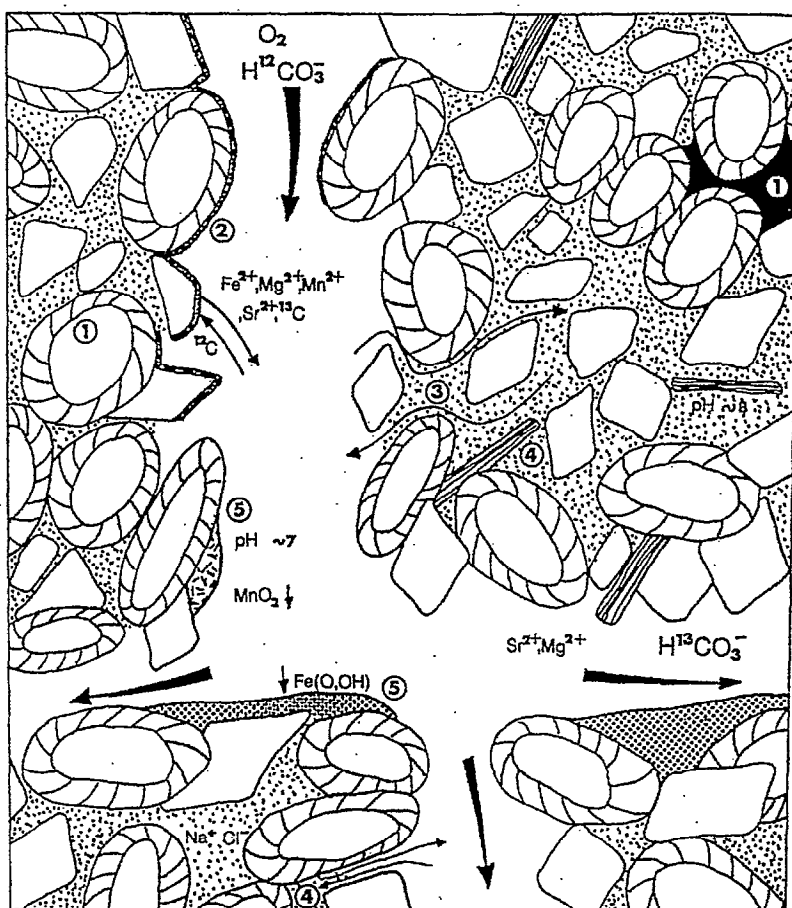
In the unconfined aquifer, the majority of fissures lie in the upper 60 metres of the Chalk and are well developed along the valley systems. There is a large lateral variation in transmissivity between  $50\text{--}2500\text{ m}^2\text{ d}^{-1}$  (Owen and Robinson, 1978). The high values are associated with the valleys and the transmissivity decreases rapidly away from these areas. The water table reflects the land surface in subdued form and shows seasonal fluctuations of up to 22 metres.

In the confined part of the aquifer, the density of fissures is less, although their vertical distribution is similar. Transmissivity values lie between  $270\text{--}450\text{ m}^2\text{ d}^{-1}$  (Owen and Robinson, 1978) and tend to decrease with increasing depth of burial. Lateral variation is not so pronounced. Fluctuations in pumping regimes and the barometric pressure affect the piezometric surface in the confined zone more than that at outcrop. Over the last 30 years, a limited long-term decline in the pressure surface of the confined aquifer has occurred south of Reading and east of Newbury.

Springs are rare on the dip slope of the Chalk of the Berkshire Downs; drainage is via a few major streams that gain their flow mainly by seepage from the aquifer and are characterised by intermittent sections in their upper reaches. On the scarp slope, springs are more common and tend to vary in stratigraphical position due to the intermittent hydraulic relationship between the Lower Chalk and Upper Greensand. Towards the east, the two formations appear to be separate aquifers, whereas in the west, where the Upper Greensand outcrop thins, they act more as a single aquifer.

## 2.3 Aquifer minerals and geochemical composition

The Upper and Middle Chalk are very pure carbonates comprising microfossil (coccolith) debris. The physical, chemical and mineralogical nature of the chalk at a microscopic scale is shown in Figure II.2.2. The Chalk has a dual porosity composed of micro/macro fissures and blocks. The packing of the coccoliths permits a very high intergranular porosity (in the range 20–45%) and this also gives rise to a very high specific surface area. This renders the chalk surfaces reactive. The matrix of the chalk, having a permeability several orders of magnitude higher than the fissures, acts as a potential reservoir for older water which has evolved on a geological timescale and which may affect the groundwater quality by slow exchange with water in the fissures.



1. Solid phase (mainly coccoliths and calcite platelets) comprising an 'impure' calcite with marine carbon isotopic ratios. Some pyrite is found at depth with minor amounts of clay (abundant in Lower Chalk).
2. Incongruent reactions on calcite surfaces releasing impurities (Fe, Mn, Mg, Sr, etc.) and  $^{13}\text{C}$ , resulting in a purer calcite being deposited.
3. Exchange of solutes by diffusion between matrix and micro or macro fissures.
4. Saline water diffuses from matrix at depth. Sodium is also released by exchange for calcium on the clays of marine origin.
5. Deposition of manganese and iron oxide minerals on fissure surfaces.

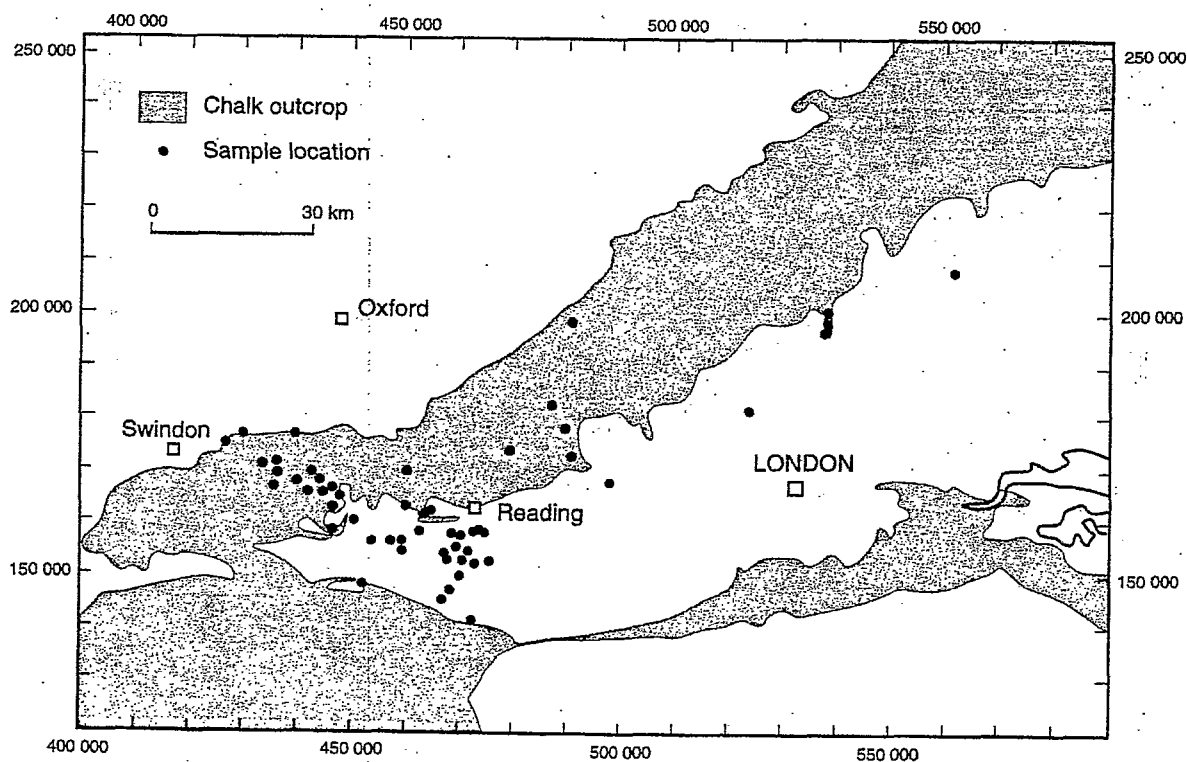
**Figure II.2.2 Model of the water-rock interactions in the chalk at the microscopic scale. Interstitial water (stippled) exchanges with fissure water.**

Despite the purity of the chalk, the small amount of other elements substituting in the calcite have a disproportionate effect on controlling the water chemistry. Small quantities of Mg, Mn, Sr and Fe are released during rapid (congruent) and slower (incongruent) reactions. The Upper Chalk contains between 1–2% of non-carbonate minerals (Morgan-Jones, 1977), whilst the Middle Chalk contains 3–6% and the Lower Chalk 5–12%. The most important non-carbonate minerals are quartz, montmorillonite, white mica and apatite, with kaolinite being found only in the Lower Chalk.

**Table II.2.1 Chemistry of rainfall (1975-1980) at Chilton, Berkshire compared with the composition of interstitial waters (0.6-3.0m depth) beneath the soil zone, illustrating the effects of evapotranspiration and reactions in the near-surface environment.**

Determinand	Rainfall 1975-1980 (mg l <sup>-1</sup> ) (688 mm yr <sup>-1</sup> )	Interstitial water (mg l <sup>-1</sup> ) (0.6-3.0m)	Determinand	Rainfall 1975-1980 (mg l <sup>-1</sup> ) (688 mm yr <sup>-1</sup> )	Interstitial water (mg l <sup>-1</sup> ) (0.6-3.0m)
Ba	nd	0.020	Mn	0.01	0.003
Ca	1.92	60.2	NO <sub>3</sub> -N	1.53	1.23
Cl	5.7	10.6	Na	2.64	4.12
F	0.096	nd	S	4.8	37.2
Fe <sub>total</sub>	0.055	0.009	Si	nd	1.82
HCO <sub>3</sub>	nd	121	Sr	nd	1.58
K	3.06	0.74	Zn	0.068	0.002
Mg	0.75	0.83			

nd: not determined



**Figure II.2.3 Geological outcrop of the Chalk of Berkshire and the Chilterns with localities of boreholes used in this study.**

## 2.4 Rainfall Chemistry

The chemistry of rainfall has a major impact on the initial groundwater composition for several elements. Long term data are available for the area at Chilton (1975–1980) taken from Cawse et al. (various AERE reports) and summarised for key elements in Table II.2.1. These values will be subject to evapotranspiration and higher concentrations of most elements will be expected as water infiltrates. The evapotranspiration effects can be estimated using the ratio of Cl in soil-moisture drainage to that in rainfall and data from a research site (natural grassland) also near Chilton are used to make the comparison (Edmunds et al., 1987). It is estimated that 370 mm of the 688 mm of rainfall (some 54% of the total) is effective as recharge at this site. The present day Cl concentration in the rainfall is around 5 mg l<sup>-1</sup> and under grassland approximately doubles on passing into the unsaturated zone due to evapotranspiration. Higher concentrations would be expected under woodland or forest. Baseline groundwater compositions would therefore be unlikely to exceed 20 mg l<sup>-1</sup> in this area. Table II.2.1 also identifies other significant changes which take place in the soil zone. The neutralisation of rainfall acidity and the gain of soil CO<sub>2</sub>, reacting with the carbonate, gives rise to high alkalinity within a short distance. The soil zone apparently acts as a sink for other elements such as iron, manganese and nitrate.



### 3. DATA QUALITY AND HANDLING

#### 3.1 Source and quality of data

This account describes chemical data from 65 boreholes in the Chalk aquifer of Berkshire and the Chilterns, the sites of which are shown in Figure II.2.3. Data are used from 169 samples taken from 32 sites on the unconfined Chalk and 101 samples from 33 sites on the confined Chalk. The data have been compiled from EA and BGS data files. The most detailed set of data is taken from the study (Edmunds et al., 1987) which was dedicated to using this as a model area for defining the baseline conditions in the Chalk aquifer. 94% of the data have ionic charge imbalances within 5%, the remainder of the data have balances within 7%. For production of water quality data, minima, maxima and median values have been calculated (Table I.1). Where median values are below a given detection limit, the detection limit values are substituted. The statistical data have also been summarised as histograms (Figure II.3.1). In Figure II.3.1 as well as some subsequent diagrams and Table I.1, the data have been subdivided into sets from the unconfined and confined aquifer.

The 95 percentile for each determinand has been taken as an estimate of the upper limit of the baseline concentration range. The 95 percentile is the point at which, for many determinands, there is a change in slope (tail) on the upper end of the cumulative-frequency distribution. Outliers above the 95 percentile are likely to be samples influenced by pollution or by anomalous in situ conditions. The 95 percentile therefore provides a useful guide for expected upper baseline compositions.

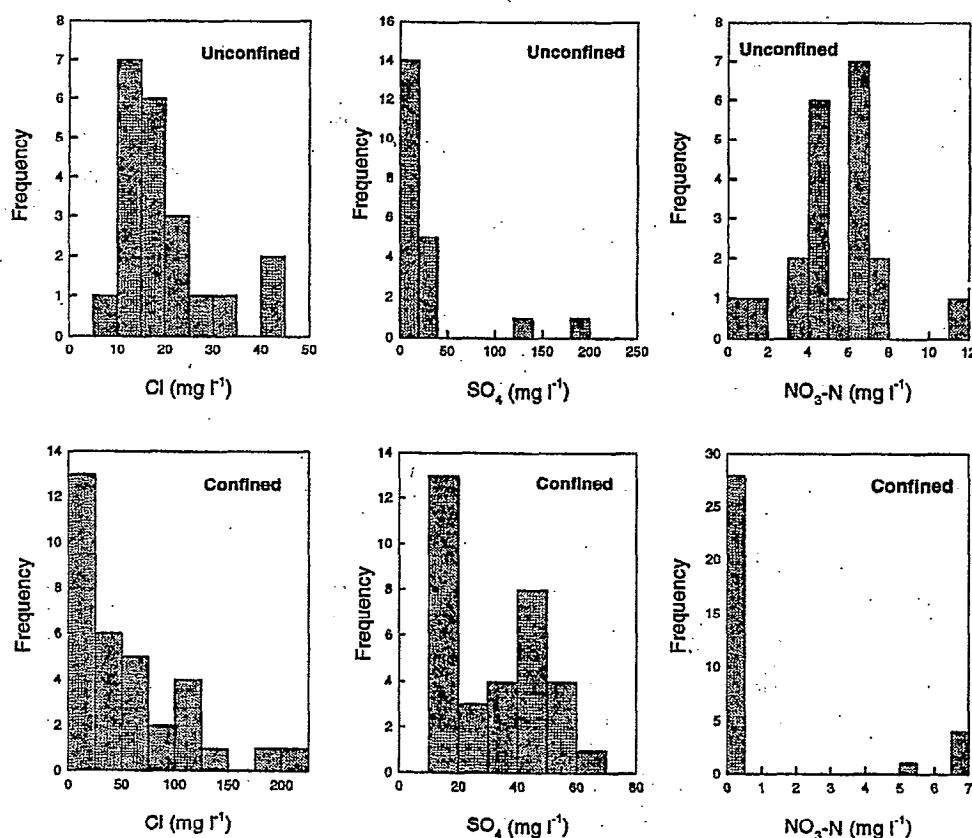


Figure II.3.1 Histograms of Cl, SO<sub>4</sub> and NO<sub>3</sub>-N in the Berkshire and Chilterns groundwaters.

### 3.2 The influence of pollution

The impact of pollution is considered to be restricted almost exclusively to the unconfined groundwaters. Median concentrations given in Table I.1 for most elements may be regarded as representative of the average unpolluted groundwater composition for the region; any effects of pollution will be found in the upper 50 percent of this group. An exception is nitrate. The influence of agricultural activities can be detected using the cumulative frequency plots (Figure II.5.4) and it is estimated that in the Berkshire and Chilterns Chalk sources, some 80% of the groundwaters in the unconfined aquifer considered have significant contributions (above  $5 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ ) from agricultural sources. Total organic carbon (TOC) above  $2 \text{ mg l}^{-1}$  might also provide a good indicator of agricultural impacts, although no data are available. The impacts from agriculture (in the unconfined Chalk) may also be seen in some other elements such as Cl (above  $20 \text{ mg l}^{-1}$ ) and  $\text{SO}_4$ , also above  $20 \text{ mg l}^{-1}$ . A few samples having Cl above  $100 \text{ mg l}^{-1}$ , mainly in the confined Chalk, are likely to contain a contribution from residual formation water (see below).

#### 4. HYDROGEOCHEMICAL CHARACTERISTICS

The hydrogeochemistry of the Chalk as expressed in the major ion chemistry can be examined using the trilinear plots (Figures I.1 and II.5.1). The main feature is the distinctive low Mg composition (low Mg/Ca ratio) in the unsaturated zone and unconfined groundwaters and the evolution towards higher Mg/Ca ratios as the waters move downgradient into the confined aquifer, eventually increasing in Na (and Cl) concentrations at depth.

The box plots (Figures II.5.2 and II.5.3) are used to illustrate the ranges of data in each section of the aquifer. The data are arranged for reference in order of their abundance in seawater. Cumulative frequency diagrams (Figures II.5.4 and II.5.5) provide information on the relative abundance of the major and minor elements in the groundwater and are used to provide insight into the natural processes as well as human influences (Appendix 1). The evolution of the groundwater chemistry from outcrop to depth along the flow line is shown in Figure II.5.6.

The mineral composition of the Chalk groundwater is established early in its history. Rainfall inputs are important for several elements (e.g. Cl, F,  $\text{SO}_4$ ) but then the mineral characteristics are established in the top few metres of the unsaturated zone. Rainfall acidity is quickly neutralised by reaction with the chalk as demonstrated by the results in Table II.2.1 and the reactivity of the soil water is greatly enhanced by the solubility of carbon dioxide produced biogenically in the soil zone. The  $\text{CO}_2$  partial pressure may vary from place to place depending on the soil type and depth and this will be reflected in the concentrations of  $\text{HCO}_3$  eventually found in the unconfined (carbonate-saturated) groundwaters. The relatively narrow range of bicarbonate concentrations (Figure II.5.2) implies that the initial soil  $\text{CO}_2$  concentrations were very similar across the region.

## 5. REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS

### 5.1 Carbonate Reactions

The main processes taking place in the Chalk and their effect on major element chemistry are summarised in Edmunds et al. (1987). The dominant chemical characteristics of the groundwater are rapidly determined during percolation through the soil zone and particularly at the soil-chalk interface. Congruent dissolution of the chalk occurs during infiltration through the unsaturated zone and saturation with calcite is typically attained within a few metres of the surface (Edmunds et al., 1992). Below this depth, chalk dissolution is greatly reduced. During this early evolution, the groundwater acquires a Ca-rich composition with Mg/Ca ratio close to that of the Chalk (Figure II.5.1). Once calcite saturation is reached, very little further increase in total mineralisation takes place. However, as groundwater moves downgradient, its composition is modified by several processes, especially the incongruent reaction of carbonate which releases  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and other trace elements to the groundwater. The process is summarised in Figure II.5.1 where the increase in Mg/Ca ratio indicates the changing maturity of the groundwater. The products of these reactions (including trace elements) can serve as a means of identifying the maturity of water pumped from individual boreholes.

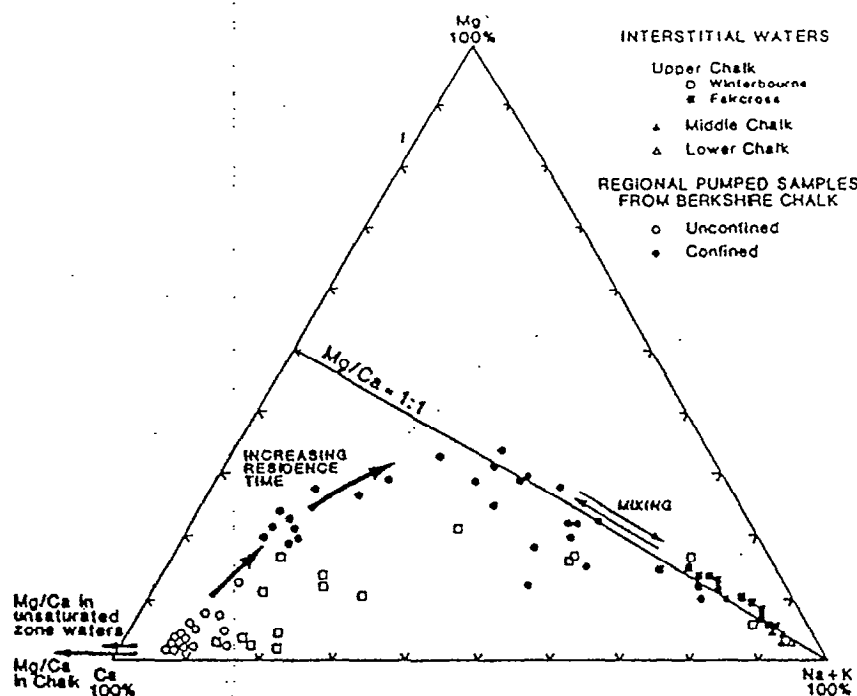


Figure II.5.1 Trilinear diagram showing the evolution of cation composition in groundwaters from the South Downs in relation to the Berkshire area.

## 5.2 Redox Reactions

The evolution of some redox-related elements and Eh are shown in Figure II.5.7. Dissolved-oxygen concentrations remain relatively high (median 9 mg l<sup>-1</sup>) in the unconfined aquifer indicating the virtual absence of pyrite or other minerals. A distinct redox boundary is found in the aquifer a short distance beyond the unconfined/confined boundary. Oxygen concentrations are reduced to zero. Reducing conditions allow Fe<sup>2+</sup> concentrations to increase and, beyond the redox boundary, NO<sub>3</sub>-N is rapidly reduced following the disappearance of oxygen. Reduced sulphur (H<sub>2</sub>S) may be detected but sulphate concentrations increase across the redox boundary; the reduction of sulphate to sulphide is only a very minor process in the Chalk aquifer.

## 5.3 Ion-Exchange Reactions

Cation-exchange reactions are relatively unimportant in the Chalk and at maximum amount to the equivalent of 30 mg l<sup>-1</sup> Na in the confined aquifer, the remaining increase in Na being accounted for by saline water. Several cations increase in concentration along the flow gradient as a result of the reaction of 'marine' clay minerals with the younger lower salinity groundwaters, e.g. K, NH<sub>4</sub>, Li (see trace elements below).

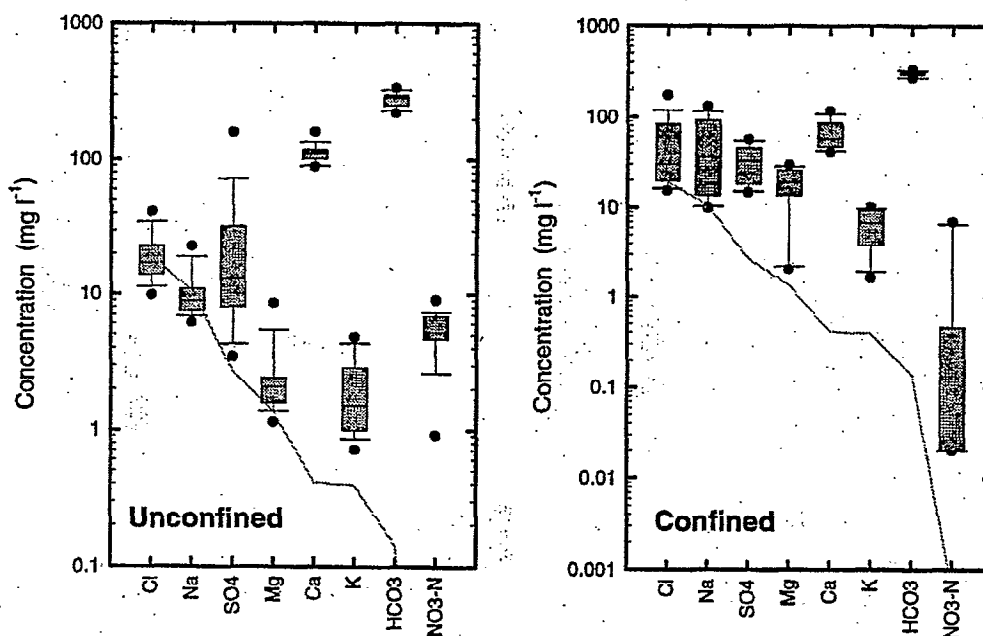


Figure II.5.2 Box plots for major ions in the groundwater of Berkshire and the Chilterns (unconfined and confined samples). For each element, the data within the 25th and 75th percentile range are highlighted with the median concentration. The outer bars show respectively the 5th and 95th percentile data limits. Maxima and minima are given as solid symbols.

### 5.3 Trace-Element Occurrence

The information for trace elements is summarised in Table I.1 as well as box plots (Figures II.5.2 and II.5.3), cumulative frequency diagrams (Figures II.5.4 and II.5.5) and the evolution downgradient in Figure II.5.8. The upper limit of concentration for some major elements may be controlled by the solubility products of various minerals. Once equilibrium is established, a maximum concentration should be reached which should remain constant, although precipitation and dissolution may continue under the dynamic conditions of the equilibrium. Several minor or trace elements which do not form discrete minerals may substitute in other minerals.

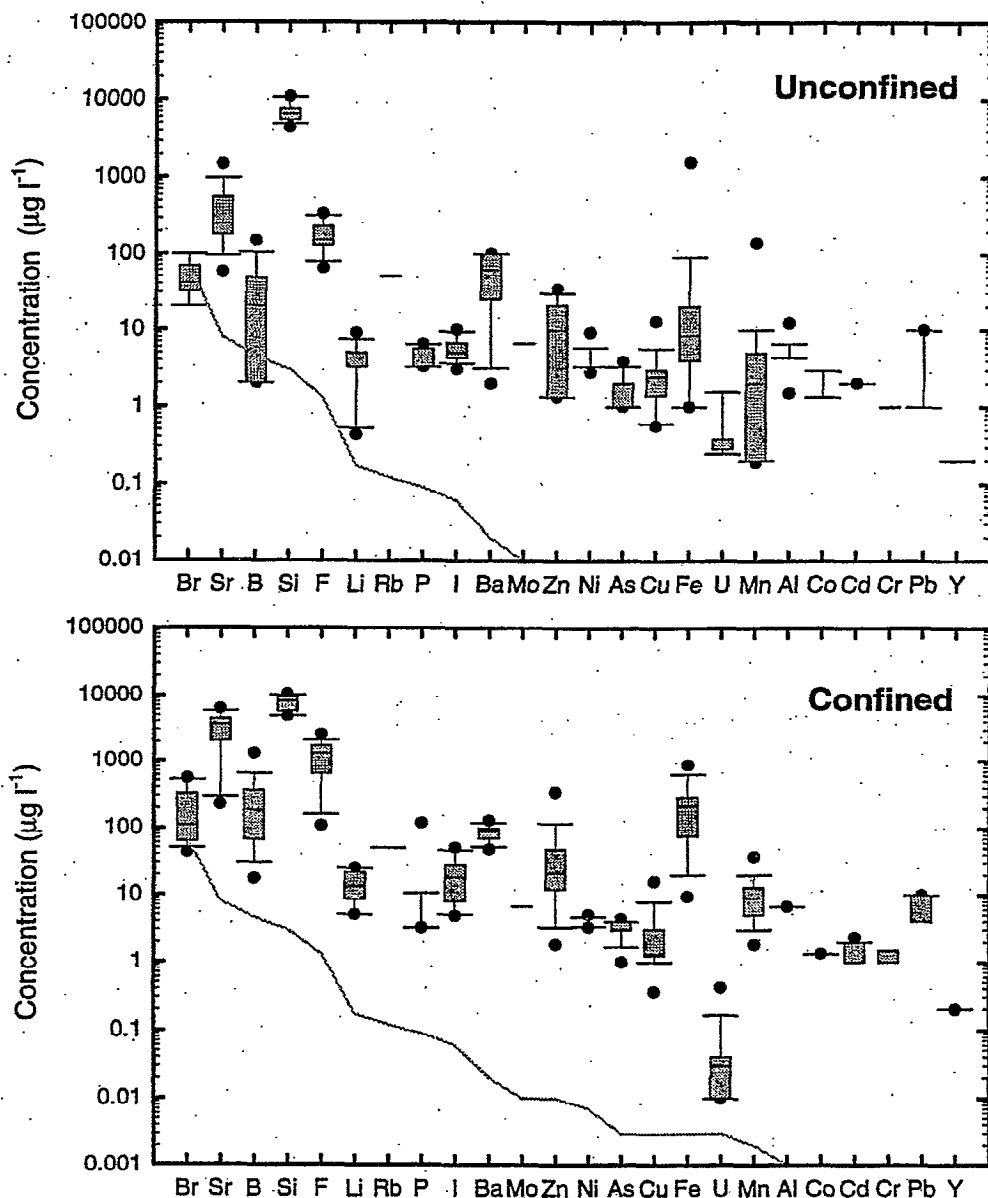
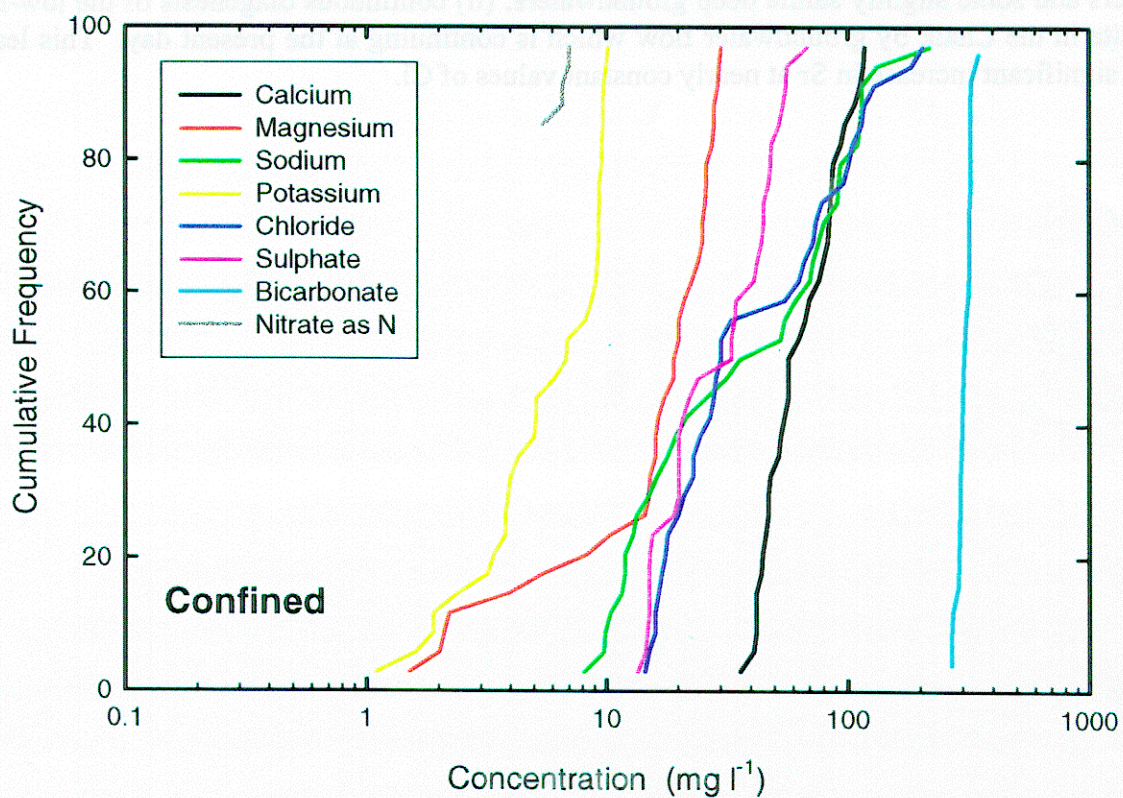
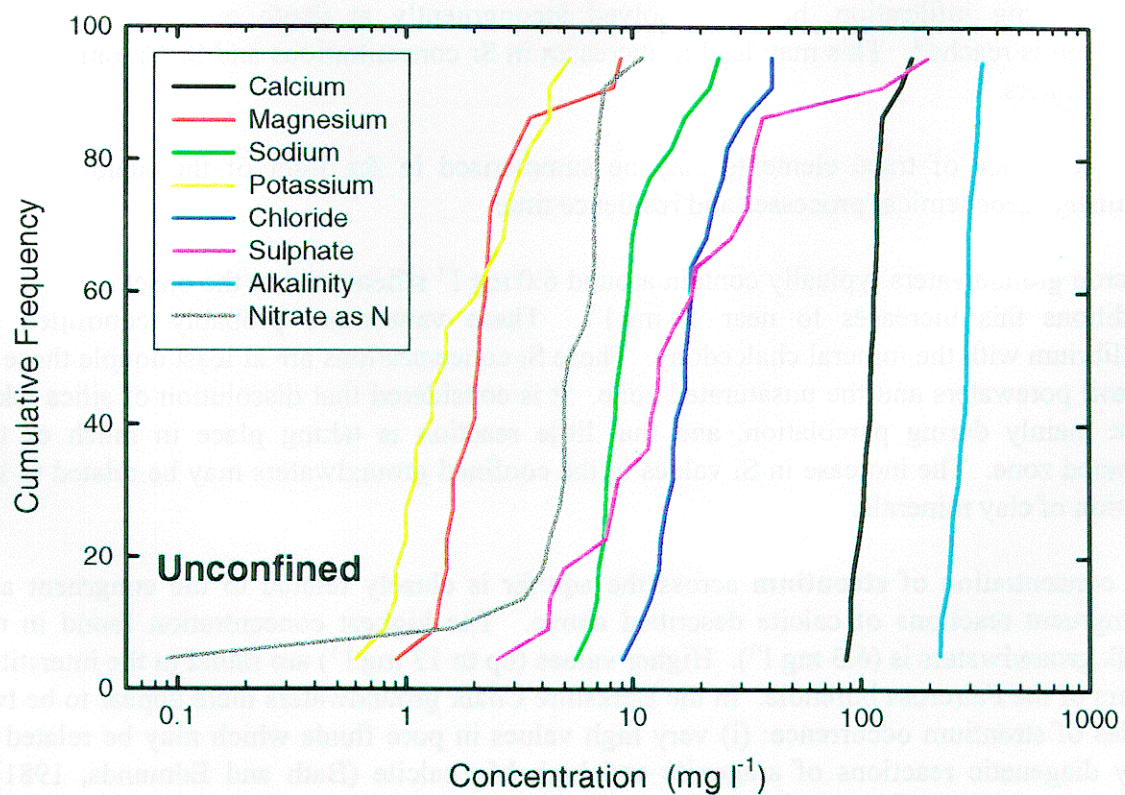


Figure II.5.3 Box plots for minor ions in the groundwater of Berkshire and the Chilterns arranged in the order of abundance in seawater (seawater line shown as reference). For each element, the data within the 25th and 75th percentile range are highlighted with the median concentration. The outer bars show respectively the 5th and 95th percentile data limits. Maxima and minima are given as solid symbols.





**Figure II.5.4 Cumulative-frequency diagram for major elements in the groundwaters of Berkshire and the Chilterns.**

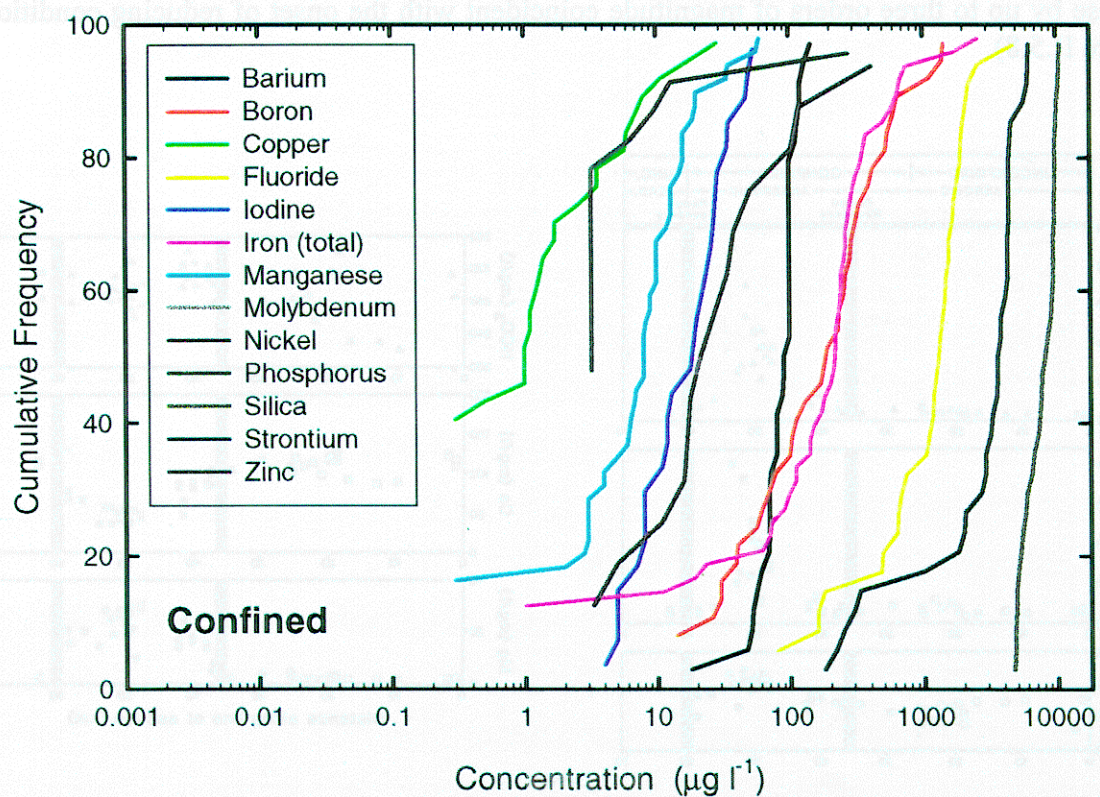
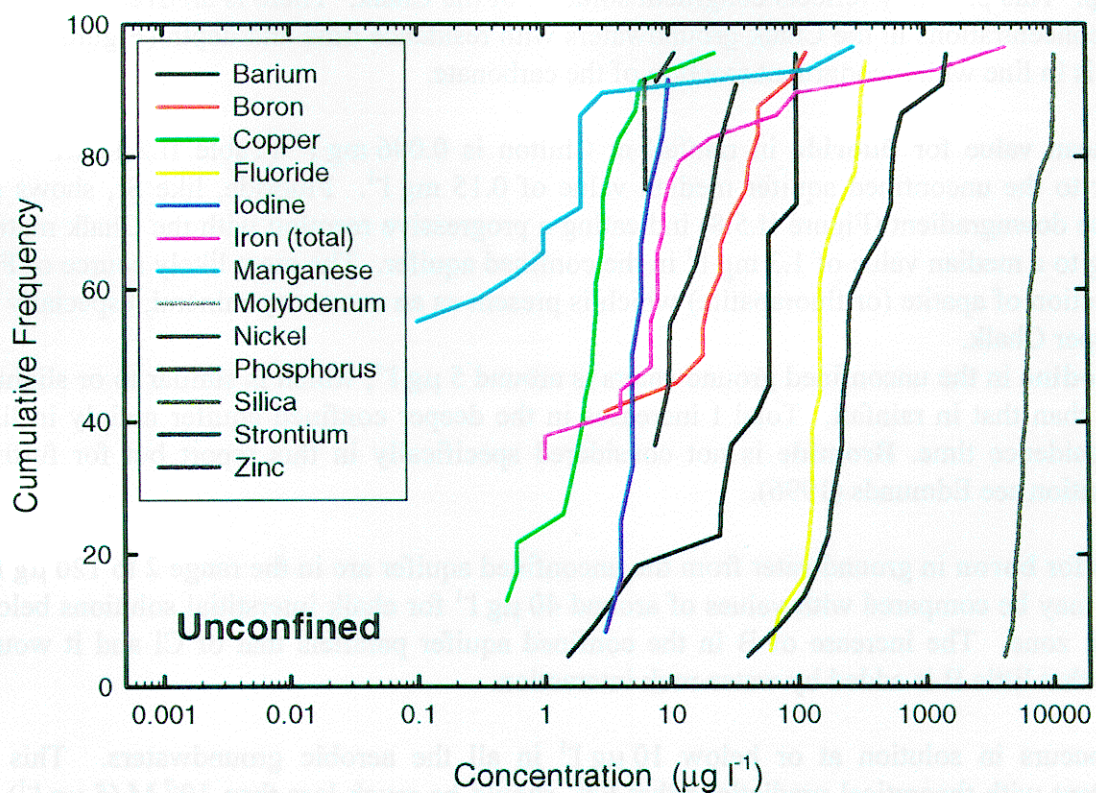
Thus, strontium an important minor constituent of calcite, is released congruently from calcite during infiltration, but is dissolved incongruently at depth even though calcite saturation is reached. This may lead to increases in Sr concentrations and Sr/Ca ratios in the groundwaters.

The occurrence of trace elements may be summarised in the light of the major-element chemistry, geochemical processes and residence time.

Outcrop groundwaters typically contain around 6.0 mg l<sup>-1</sup> **silicon** and at the onset of confined conditions this increases to near 10 mg l<sup>-1</sup>. These values are probably controlled by equilibrium with the mineral chalcedony. These Si concentrations are at least double those in the soil porewaters and the unsaturated zone. It is considered that dissolution of silica takes place mainly during percolation, and that little reaction is taking place in much of the saturated zone. The increase in Si values in the confined groundwaters may be related to the reaction of clay minerals.

The concentration of **strontium** across the aquifer is closely related to the congruent and incongruent reactions of calcite described above. The highest concentration found in the Chalk groundwaters is (6.3 mg l<sup>-1</sup>). Higher values (up to 13 mg l<sup>-1</sup>) are found in the interstitial waters of the Faircross borehole. In the Berkshire Chalk groundwaters there appear to be two modes of strontium occurrence: (i) very high values in pore fluids which may be related to early diagenetic reactions of aragonite and high Mg calcite (Bath and Edmunds, 1981). Strontium concentrations so derived are represented in this area by Faircross interstitial waters and some slightly saline deep groundwaters; (ii) continuous diagenesis of the low-Mg calcite in the Chalk by groundwater flow which is continuing at the present day. This leads to a significant increase in Sr at nearly constant values of Cl.





**Figure II.5.5** Cumulative-frequency diagram for minor elements in the groundwaters of Berkshire and the Chilterns.

Interstitial water immediately beneath soil at Chilton contains **barium** around  $20 \mu\text{g l}^{-1}$ , similar to the values found in most saturated zone groundwaters in the Chalk aquifer at outcrop. This probably reflects congruent solution of the Chalk. There is an overall increase in Ba concentrations in the Chalk groundwaters with residence time and depth (Figure II.5.8) which is in line with incongruent reaction of the carbonate.

The mean value for **fluoride** in rainfall at Chilton is  $0.096 \text{ mg l}^{-1}$  (Table II.2.1) which is similar to the unconfined aquifer median value of  $0.15 \text{ mg l}^{-1}$ . Fluoride, like Sr, shows an increase downgradient (Figure II.5.8) indicating a progressive reaction with the Chalk matrix leading to a median value of  $1.3 \text{ mg l}^{-1}$  in the confined aquifer. The most likely source of F is the reaction of apatite (or fluorapatite) which is present as an accessory mineral, especially in the Upper Chalk.

Total **iodine** in the unconfined groundwaters is around  $5 \mu\text{g l}^{-1}$ , which is similar to or slightly higher than that in rainfall. Total I increases in the deeper confined aquifer mainly in line with residence time. **Bromide** is not considered specifically in this report but for further information see Edmunds (1996).

Values for **boron** in groundwater from the unconfined aquifer are in the range  $2$  to  $120 \mu\text{g l}^{-1}$ , which may be compared with values of around  $40 \mu\text{g l}^{-1}$  for chalk interstitial solutions below the soil zone. The increase of B in the confined aquifer parallels that of Cl and it would appear that little B is added by water-rock interaction.

**Iron** occurs in solution at or below  $10 \mu\text{g l}^{-1}$  in all the aerobic groundwaters. This is consistent with theoretical predictions that  $\text{Fe}^{2+}$  should be much less than  $10^{-7} \text{ M}$  ( $5 \mu\text{g l}^{-1}$ ) in oxygenated waters at equilibrium with amorphous ferric hydroxide. Total Fe concentrations increase by up to three orders of magnitude coincident with the onset of reducing conditions (Figure II.5.8).

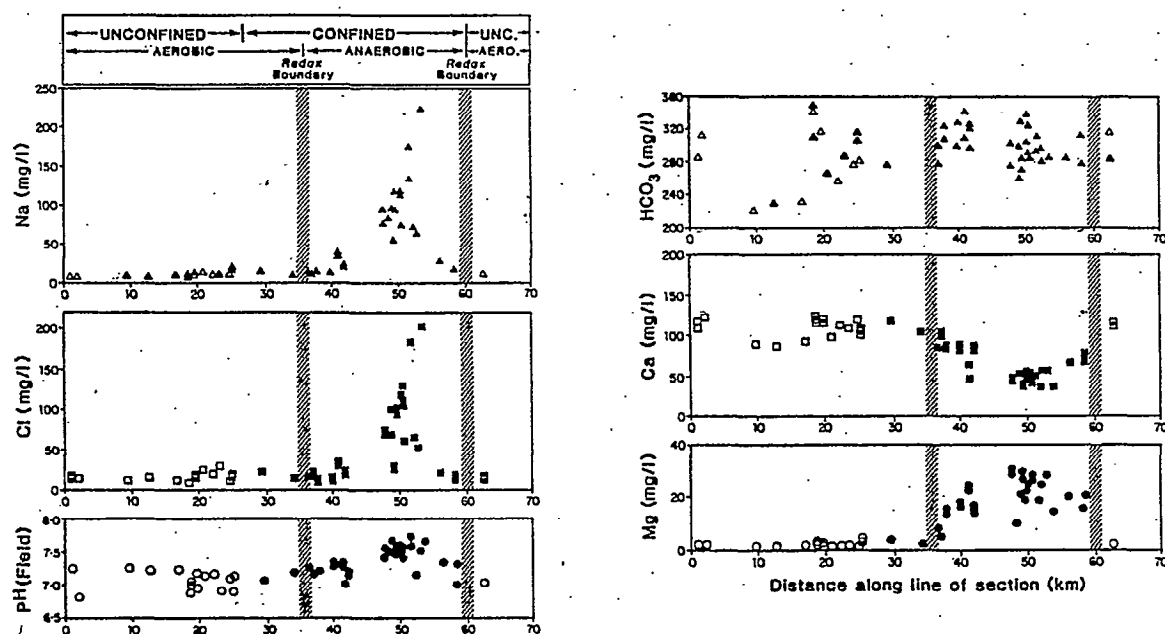
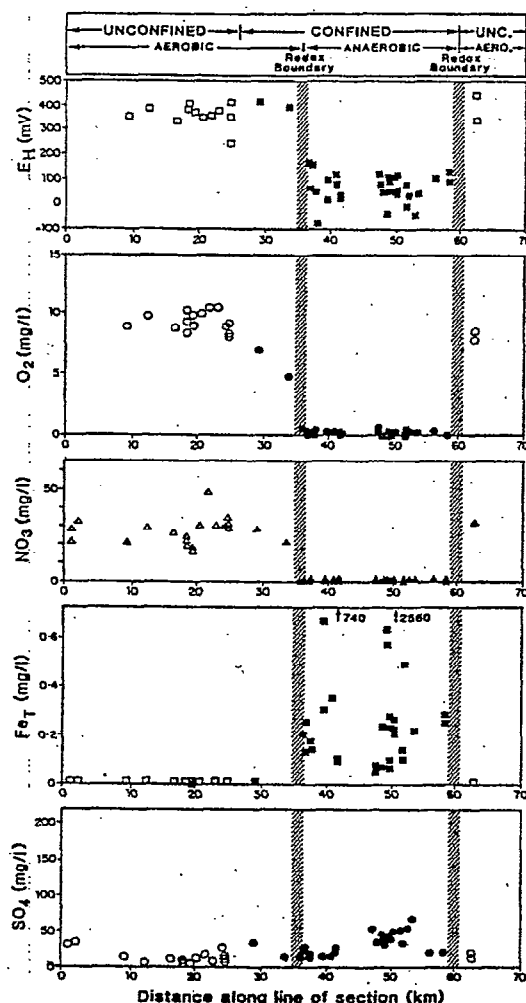


Figure II.5.6 Downgradient trends in the major-ion chemistry in the Chalk of Berkshire and the Chilterns



**Figure II.5.7 Down gradient trends in Eh and redox-related elements in the Chalk of Berkshire and the Chilterns.**

**Manganese** concentrations at outcrop are extremely low, usually below the detection limit of  $0.03 \mu\text{g l}^{-1}$ . Detectable Mn is found only beyond the redox boundary where concentrations are typically between 3 and  $20 \mu\text{g l}^{-1}$ . Manganese, which occurs at concentrations of  $100\text{--}200 \text{ mg kg}^{-1}$  in the solid Chalk, must be liberated during the dissolution of carbonate but, in view of the low dissolved concentrations, it must then be rapidly removed by oxidation. The removal of Mn and Fe from solution gives rise to the Mn dendrites and Fe(III) precipitates seen on Chalk surfaces.

**Copper** is present at concentrations up to  $7 \mu\text{g l}^{-1}$  in most groundwaters containing oxygen but Cu is at or below the detection limit of  $0.3 \mu\text{g l}^{-1}$  in nearly all of the reducing groundwaters. This distribution of Cu is geochemically consistent, since higher mobility would be expected under oxidising conditions. Wellhead contamination can be ruled out. It is possible that the Cu is derived from trace amounts present in the Chalk which could contain up to  $30 \text{ mg kg}^{-1}$ . In contrast to Cu, the **zinc** distribution does not show any clear relation to redox conditions. In three outcrop waters it is below the detection limits of  $2 \mu\text{g l}^{-1}$ , but otherwise is found at concentrations of  $3\text{--}30 \mu\text{g l}^{-1}$  throughout the aquifer, regardless of Eh. It correlates most closely with Fe and Mn and is likely to be derived from the Chalk which may contain up to  $35 \text{ mg kg}^{-1}$  Zn.



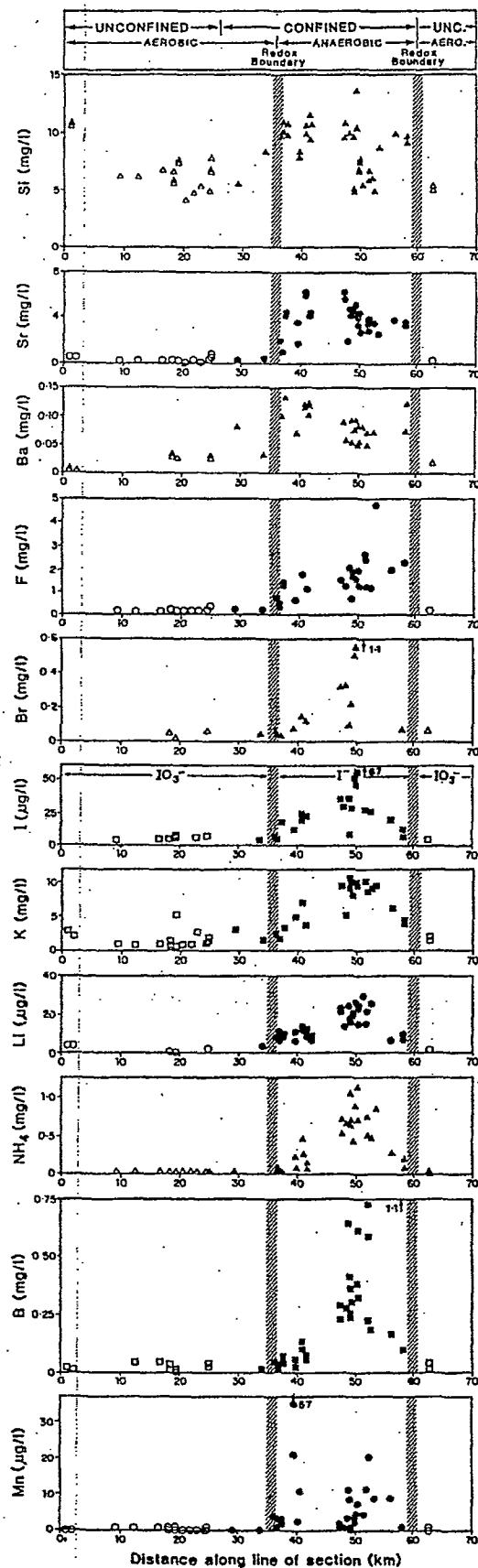


Figure II.5.8 Downgradient trends in some minor and trace elements in the Chalk of Berkshire and the Chilterns.

**Cadmium** was not found above the detection limit of  $0.3 \mu\text{g l}^{-1}$ , and is likely to be present at one or two orders of magnitude less than the Zn concentrations (with which it is geochemically associated). In an earlier (unpublished) BGS study, **arsenic** (as total As) was detected in 17% of all groundwaters sampled. The median value for groundwaters in the unconfined aquifer (containing  $\text{O}_2$ ) was found to be  $1 \mu\text{g l}^{-1}$  ( $2 \mu\text{g l}^{-1}$  in this study) as compared with  $3.4 \mu\text{g l}^{-1}$  ( $3 \mu\text{g l}^{-1}$  this study) in the confined anaerobic aquifer section. The higher total As in the anaerobic groundwater is consistent with the greater solubility of As(III)-species under the lower Eh conditions.

## 5.5 Residence Times

Water samples from the Chalk are generally mixtures of water flowing rapidly through the fracture system combined with small amounts of water from the matrix, the latter having a disproportionate effect on the quality (e.g. contribution of Cl and water of greater age). Additionally, the well-drilling operation penetrates water of different residence times (see Appendix 1). However, the waters sampled during this survey are predominantly of Holocene age, less than 10,000 yrs old. Their residence time has been determined using  $^{14}\text{C}$ , tritium and  $^4\text{He}$  (Edmunds et al., 1987). In the unconfined zone, quite high tritium values indicate that most groundwaters are recent but there are some low tritium waters at outcrop, (e.g. Chieveley) where the bulk of the water must be at least 30 years old; this demonstrates that considerable heterogeneity of age and therefore chemistry must exist in the Chalk reflecting physical characteristics of the aquifer (Owen and Robinson, 1978). Oxygen persists in the aquifer in most of the waters containing tritium but is absent in most waters having low or zero tritium values, indicating that oxygen is consumed within a few decades of residence in the aquifer.

## 5.6 Depth Variations

Various hydrogeophysical logs were produced for the Chalk of this area during the Thames Groundwater Scheme. These are available in published and unpublished form in the BGS archives. The area has also been the focus of research drilling to determine the physical and chemical properties of the chalk dual-porosity system. Two examples of depth variation are given (Figures II.5.9 and II.5.10) for the unconfined area at Winterbourne, Berkshire and the confined aquifer at Faircross (Edmunds et al., 1987). The results at outcrop from Winterbourne (Figure II.5.9) compare the water taken from depth samples with samples of interstitial waters extracted from cores and demonstrate the effect of the dual-porosity system on the water quality. There is apparent base-exchange occurring in water near to the top of the aquifer, and near the bottom of the formation, the rise in Na is probably due to traces of formation water (accompanied by Cl). Confirmation of this is provided by the increase in Mg and Sr relative to Ca: an indicator of the presence of longer-residence-time water deeper in the formation.

Data from the Faircross borehole provide a record of the water-quality changes through the complete confined sequence near to the centre of the Berkshire syncline (Edmunds et al., 1987). The record shown here (Figure II.5.10) demonstrates the increase in salinity with depth for the interstitial samples. Water used for public supply in the same area has elevated baseline salinity, for example at Mortimer PS.

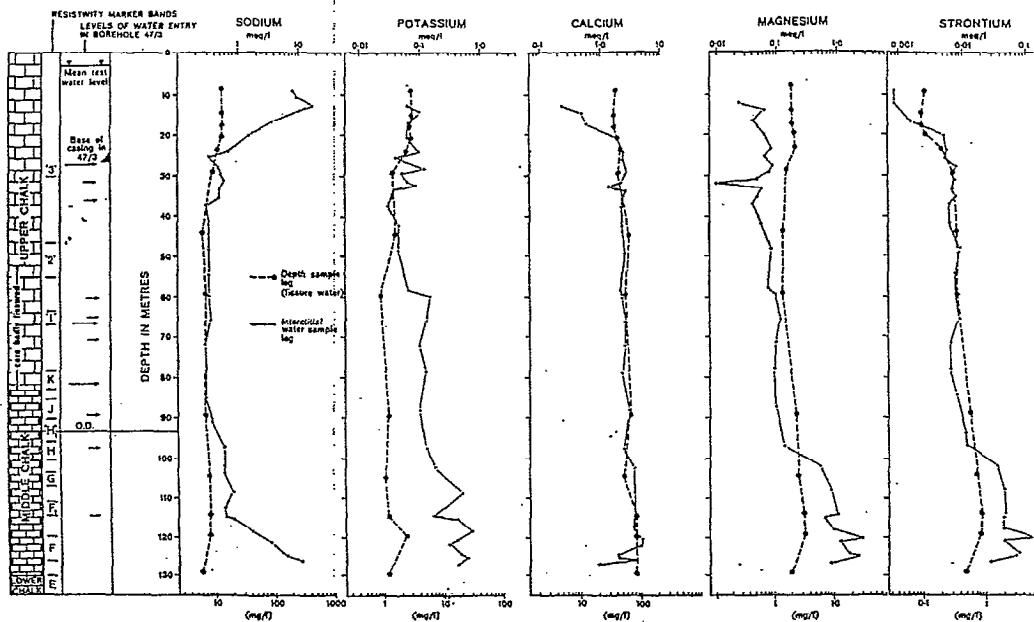


Figure II.5.9 Hydrogeochemical logs of Na, K, Ca, Mg and Sr in interstitial and depth-sampled waters from the Winterbourne bore borehole, Berkshire.

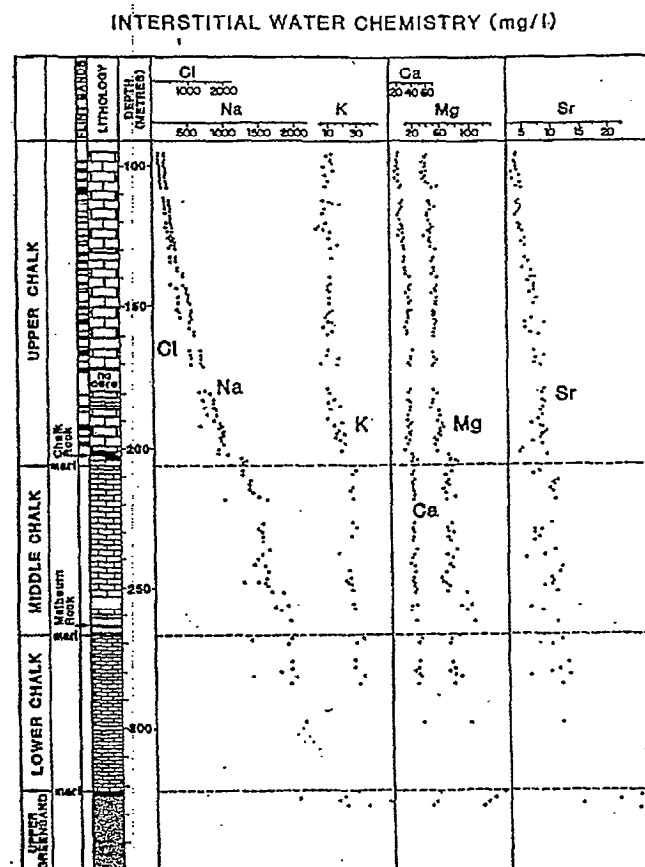


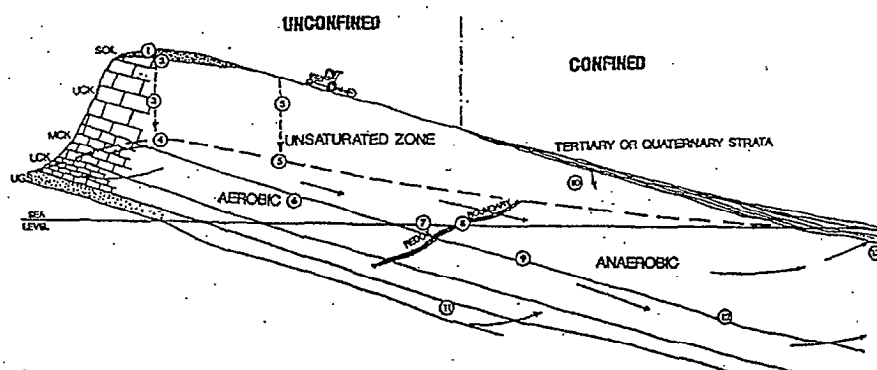
Figure II.5.10 Interstitial water profile through the Upper, Middle and Lower Chalk from the saturated zone at Faircross, Berks.

## 5.7 Saline Water in the Chalk

The Berkshire basin contains residual formation water which is considered to be of connate origin. This has been discussed in Bath and Edmunds (1981) using results from the Trunch borehole (Norfolk) which are then extrapolated to the inland location. At Faircross, the increase in Cl is from  $100 \text{ mg l}^{-1}$  to around  $2000 \text{ mg l}^{-1}$ , that is up to one fifth that of seawater. The profile is considered to reflect the extent of exchange of the original formation water by advection and diffusion since the Cretaceous period.

## 6. SUMMARY

The overall evolution of groundwater in the Chalk of Berkshire and the Chilterns is summarised in Figure II.6.1. The results from this study show that it is possible to understand in some detail how the baseline chemistry has evolved in the Chalk and that the results shown here probably hold for the whole of this area. There is evidence of human activity but the overwhelming amount of water-quality variation is the result of natural processes resulting from water-rock interaction.



- 1 Production of  $\text{CO}_2$  by microbiological activity in soil zone. Local acidic soils.
- 2 Dissolution reactions dominant at the soil/bedrock interface. Saturation with calcite attained, together with characteristic chalk water composition.
- 3 Residence times of water (deduced from tritium) in the unsaturated zone usually measured in decades (movement in matrix c.0.6  $\text{myr}^{-1}$ ). Limited carbonate dissolution.
- 4 At the water table increased solution reaction may occur due to fluctuation in water level (hydrochemical mixing).
- 5 The influence of pollution from agrochemicals may be seen in the unsaturated zone and shallow groundwater ( $\text{SO}_4$ ,  $\text{NO}_3^-$ ).
- 6 Incongruent reactions preferentially release Mg, Sr,  $^{13}\text{C}$ ,  $\text{Fe}^{2+}$  to groundwater; Ca,  $^{12}\text{C}$  to solid phase. Aerobic conditions (Eh ~350 mv).
- 7 Oxygen reacts with  $\text{Fe}^{2+}$  as incongruent reactions proceed and/or with pyrite or marcasite if present.
- 8 Redox boundary defined by complete reaction of oxygen. Nitrate is reduced rapidly once oxygen has completely reacted (denitrification). In the anaerobic aquifer (characterised by Eh, -50 to +100 mv)  $\text{Fe}^{2+}$  increases.
- 9 Exchange reactions with marine clays ( $2\text{Na}^+ - \text{Ca}^{2+}$ ) take place to a limited extent. These reactions also release  $\text{K}^+$  and  $\text{NH}_4^+$ .
- 10 Leakage of water from overlying sediments may locally influence water quality of the chalk (e.g. sulphate increase).
- 11 Albian Sands (Upper Greensand) may locally be in continuity with Chalk aquifer especially near the outcrop. The hydrochemistry of both formations is similar.
- 12 Residual saline connate or other formation water mixes with inflowing freshwater giving an increase in TDS especially Cl, Br, B.
- 13 Marine-groundwater interface. Zone of mixing and reaction.

**Figure II.6.1 Summary diagram to illustrate the principal hydrogeochemical processes taking place along flow lines in the Chalk.**



## 7. SELECTED REFERENCES

- Bath A. H., and Edmunds, W. M. 1981. Identification of connate water in interstitial solution of Chalk sediment. *Geochim. Cosmochim. Acta*, **45**, 1449-1461.
- Edmunds, W. M. and Bath, A. H. 1976. Centrifuge extraction and chemical analysis of interstitial waters. *Environ. Sci. Technol.*, **10**, 467-472.
- Edmunds W M, Cook J.M., Kinniburgh, D.G. Miles, D.L. and Trafford J.M. 1989. Trace element occurrence in British groundwaters. Research Rep. SD/89/3. British geol. Survey.
- Edmunds, W. M., Darling, W. G., Kinniburgh, D. G., Dever, L. and Vachier, P. 1992. Chalk groundwater in England and France: hydrogeochemistry and water quality. *Research report SD/92/2*, British Geological Survey.
- Edmunds, W. M., Cook, J. M., Darling, W. G., Kinniburgh, D. G., Miles, D. L., Bath, A. H., Morgan-Jones, M. and Andrews, J. N. 1987. Baseline geochemical conditions in the chalk aquifer, Berkshire, UK: a basis for groundwater quality management. *Appl. Geochem.*, **2**, 251-274.
- Edmunds, W.M. 1996. Bromine geochemistry of British groundwaters. *Min. Mag.*, **60**, 275-284.
- Morgan-Jones, M. 1977. Mineralogy of the non-carbonate material from the Chalk of Berkshire and Oxfordshire, England. *Clay Min.*, **12**, 331-344.
- Owen, M. and Robinson, V. K. 1978. Characteristics and yield of fissured chalk. In: *Thames Groundwater Scheme*. Inst. Civil Engineers, London.

## **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 ( $^3\text{H}$ ), 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.**

<b>(BIO)GEOCHEMICAL CONTROLS</b>	
<b>Soil Processes</b>	The biogeochemical reactions in the soil have a marked influence on groundwater chemistry. Acid-base reactions, nitrogen transformations and microbiological activity producing CO <sub>2</sub> are the most important.
<b>Aquifer Lithology</b>	Fundamental control by the host rock geochemistry e.g. carbonate versus non-carbonate rock and the degree of homogeneity.
<b>Mineralogy</b>	The mineral assemblage of the host rock, the relative abundance of individual minerals, solubilities, crystallinity and purity are primary controls.
<b>Physico-chemical Controls</b>	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.
<b>Residence Time</b>	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.
<b>SPATIAL VARIABILITY</b>	
<b>Between Aquifer</b>	Baseline conditions vary markedly from aquifer to aquifer due to stratigraphic and lithological variations.
<b>Within Aquifer</b>	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).
<b>RESIDENCE TIME</b>	
It is convenient to be able to distinguish water of different 'ages' using a variety of geochemical indicators:	
<ol style="list-style-type: none"> <li>1. Palaeowater: recharge originating during/before the last glacial era.</li> <li>2. Pre-Industrial Water.</li> <li>3. Pre-War (1940s).</li> <li>4. Modern Era.</li> </ol>	

## 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 <sub>4</sub> , Cl, NO <sub>3</sub> , HCO <sub>3</sub>
Minor determinands:	Organic carbon (TOC), Fe, <b>Mn</b> , <b>F</b> , <b>As</b> , P, <b>Al</b> , NH <sub>4</sub> , B, Cu, Zn, <b>Cd</b> , <b>Ni</b> , <b>Cr</b> , Co, <b>Pb</b> , <b>Ba</b> , Sr, <b>Sb</b> , <b>Be</b> , <b>Hg</b> , <b>Mo</b> , <b>U</b>
Residence-time indicators:	<sup>3</sup> H, <sup>14</sup> C, δ <sup>18</sup> O, δ <sup>2</sup> H, <sup>13</sup> 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  $5 \text{ mg l}^{-1}$  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  $2 \text{ mg l}^{-1}$ ). 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  $\text{NH}_4$ ); increases in  $\text{SO}_4$  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<sub>4</sub>**, Br, TDS (total dissolved solids), Mg/Ca,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , F;
2. Acidity and redox status: **pH**, **HCO<sub>3</sub>**, Eh, DO, Fe, As;
3. Radioactivity:  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{222}\text{Rn}$ ;
4. Agricultural pollution: **NO<sub>3</sub>**, **SO<sub>4</sub>**, **DOC** (dissolved organic carbon), K/Na, P, pesticides and herbicides;
5. Mining pollution: **SO<sub>4</sub>**, **pH**, Fe, As, other metals, F, Sr;
6. Urban pollution: **Cl**, **HCO<sub>3</sub>**, **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 <sup>-1</sup> )	MAC* (mg l <sup>-1</sup> )	GV* (mg l <sup>-1</sup> )	mg l <sup>-1</sup> to meq l <sup>-1</sup>
Calcium	(Ca <sup>2+</sup> )	100	-	-	0.0499
Magnesium	(Mg <sup>2+</sup> )	30	50	-	0.0823
Sodium	(Na <sup>+</sup> )†	20	150	200	0.0435
Potassium	(K <sup>+</sup> )	10	12	-	0.0256
Chloride	(Cl)	25	-	250	0.0282
Sulphate	(SO <sub>4</sub> <sup>2-</sup> )	25	250	250	0.0208
Aluminium	(Al <sup>3+</sup> )	0.05	0.5	0.2	0.1112
Nitrate	(NO <sub>3</sub> <sup>-</sup> )†	25	50	50	0.0161
	(as N)	5.65	11.3	10	
Nitrate	(NO <sub>2</sub> <sup>-</sup> )†	-	0.1	3 P	0.0217
Ammonium	(NH <sub>4</sub> <sup>+</sup> )	0.05	0.5	1.5	0.0554
Iron	(Fe <sup>3+</sup> )	0.05(Fe <sub>T</sub> )	0.2 (Fe <sub>T</sub> )	0.3(Fe <sub>T</sub> )	0.0537
	(Fe <sup>2+</sup> )				0.0358
Manganese	(Mn <sup>2+</sup> )	0.02	0.05	0.1	0.0364
		(µg/l)	(µg/l)	(µg/l)	
Copper	(Cu <sup>2+</sup> )	3000	-	1000	0.0315
Zinc	(Zn <sup>2+</sup> )	5000	-	3000	0.0306
Phosphate	(HPO <sub>4</sub> <sup>2-</sup> )	400	5000	-	0.0208
Fluoride	(F <sup>-</sup> )†	8-12°C 25-30°C	1500 700	1500 -	0.0526
Barium	(Ba <sup>2+</sup> )	100	-	700	0.0146
Silver	(Ag <sup>+</sup> )	-	10	-	0.0093
Arsenic	(As)†	-	50	10 P	-
Cadmium	(Cd <sup>2+</sup> )†	-	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 <sup>2+</sup> )†	-	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 Aromatic Hydrocarbons	(PAH)	-	0.2		
Carbon	(CTC)	-	-	2	
tetrachloride	(TCE)	-	-	70 P	
Trichloroethene	(°C)	12	25	-	
Temperature	(µScm <sup>-1</sup> at 20°C)	6.5-8.5 400	-	6.5-8.5 -	
pH					
Conductivity					

\*CEC : Council of the European Communities Directive 80/778  
 \*GL : Guide level  
 \*MAC : Maximum admissible concentration  
 \*WHO : World Health Organisation. Guidelines for drinking water quality. 1993  
 \*GV : Guide value  
 † : Inorganic constituents of health significance (WHO, 1993)  
 [additionally: asbestos, barium, beryllium, nickel, silver, - no guide value set]  
 P : Provisional value



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

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

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

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

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

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

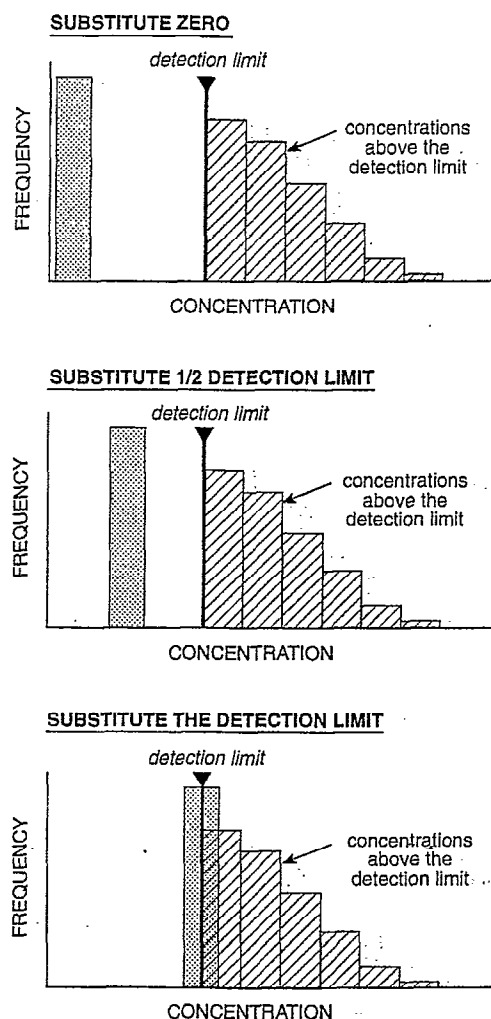
$$<1 <1 <1 <10 <10 <20 <20$$

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

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

The median is still <10.

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



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

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

#### **A1.2.6 Data Presentation**

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

## Tables

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

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

## Trilinear diagrams

The trilinear diagram and its projection onto a diamond-shaped diagram is used to summarise the major ion chemistry in each aquifer. Major ion data from each analysis, expressed as milliequivalents ( $\text{meq l}^{-1}$ ) 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  $\text{SO}_4/\text{Cl}$  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  $\text{HCO}_3$  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  $\text{HCO}_3$  (except where cation exchange occurs). The main changes of importance are in the  $\text{SO}_4$  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.

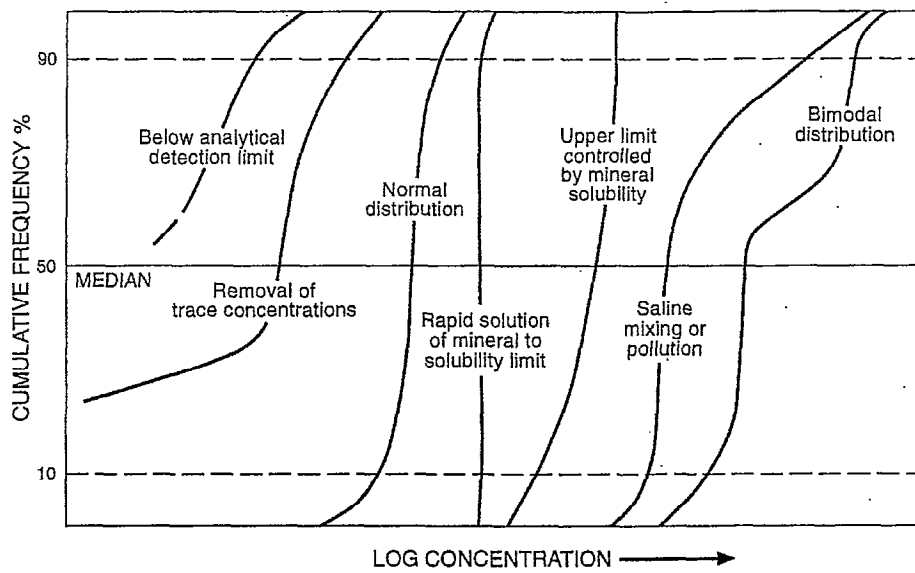
The form of the curve conveys information about the hydrogeochemistry and some of the information to be obtained is shown in Figure A1.2.2.

The most important concepts are:

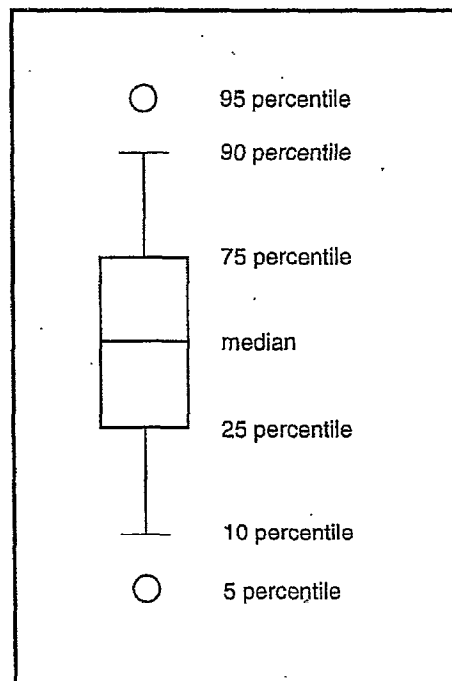
1. The median concentration is used as a single reference point for the element baseline which can be compared regionally or in relation to other elements.
2. Log-normal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence 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.  $\text{NO}_3$  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

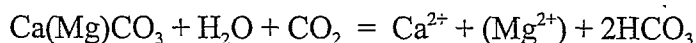
Some of the geochemical concepts and terminology used in the reports are included here as a reference. These terms will be added to in the nationwide report.

### *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  $\text{NO}_3$  and  $\text{O}_2$ ) 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  $\text{O}_2$  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  $\text{mg l}^{-1}$  dissolved  $\text{O}_2$ . Geochemical reactions (oxidation of traces of pyrite and release of ferrous iron ( $\text{Fe}^{2+}$ ) impurities from the Chalk) progressively remove the  $\text{O}_2$  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 ( $\text{Fe}^{2+}$ ) 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 ( $\text{H}_2\text{S}$ ) may also occur in extremely reducing conditions.

### *Carbonate reactions*

The concentrations of  $\text{H}^+$  (pH),  $\text{pCO}_2$ , Ca and Mg are closely related by the following reaction which represents the attack of rainwater on (impure) carbonate, assisted by  $\text{CO}_2$  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:

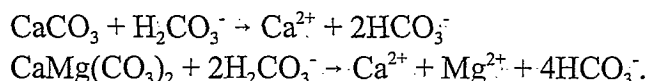


The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone. This process (**congruent dissolution**) yields Ca and Mg concentrations which are identical to those in the dissolving carbonate 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  $\text{Fe}^{2+}$ ,  $\text{Sr}^{2+}$ ) are slowly released, thereby raising the Mg/Ca and other trace element ratios.

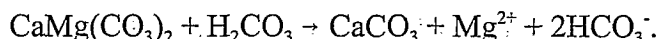
### *Congruent/incongruent reaction*

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.

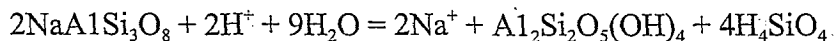
Examples of congruent reactions relevant to the Sherwood Sandstone aquifer are:



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

- Andrews, J. N., Edmunds, W. M., Smedley, P. L., Fontes, J-Ch., Fifield, L. K. and Allan, G. L. 1994. Chlorine-36 in groundwater as a palaeoclimatic indicator: the East Midlands Triassic aquifer (UK). *Earth and Planetary Science Letters*, **122**,159-172.
- Appelo, C. A. J. and Postma, D. 1994. *Groundwater, Geochemistry and Pollution*. A. A. Balkema. Rotterdam, 536 pp.
- Bath, A.H., Edmunds, W.M. and Andrews, J.N. 1979. Palaeoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer. International Symposium on Isotope Hydrology, Vienna. Vol. II. 545-568. IAEA-SM-228/27.
- Clark I. and Fritz, P. 1997. *Environmental Isotopes in Geology*, Lewis Publishers, New York, 328 pp.
- Edmunds, W. M. 1996. Indicators of rapid environmental change in the groundwater environment. In: Berger, A. R. and Iams, W. J. (eds), *Geoindicators: Assessing Rapid Environmental Change in Earth Systems*. pp.135-150. Rotterdam: A. A. Balkema.
- Edmunds, W. M., Brewerton, L. J. and Smedley, P. L. 1996. Natural quality of groundwaters in aquifers in England and Wales: a scoping study. *British Geological Survey Technical Report*, WD/96/46R
- Helsel, D. R. and Hirsch, R. M. 1992. Statistical methods in water resources. *Studies in Environmental Science*, 49. Elsevier.
- Hem, J. D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*. Water Suppl. Paper USGS 2254. US Govt Printing Office.
- Langmuir, D. 1997. *Aqueous Environmental Geochemistry*, Prentice-Hall, New Jersey, 600 pp.
- Piper, A. M. 1944 A graphic procedure in the geochemical interpretation of water analyses. *Trans. Am. Geophys. U.* **25**, 914-923.
- Shand, P., Edmunds, W. M., Wagstaff, S. and Flavin, R. 1994. The application of hydrogeochemical data and maps for environmental interpretation in upland Britain. *British Geological Survey Technical Report*, WD/94/57.
- WHO, 1993. *Guidelines for Drinking-Water Quality*, 2nd edition, Volume 1: Recommendations., WHO, Geneva, 188 pp.