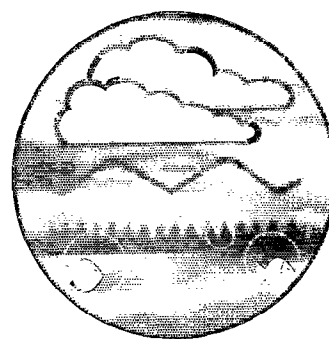
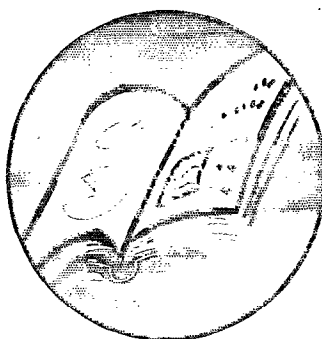
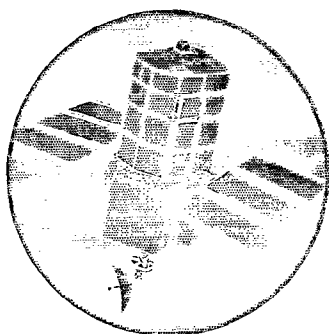


# **The Natural (Baseline) Quality of Groundwaters in England and Wales**

**The Chalk of the South Downs**



## **Research and Development**

**Project Record  
W6/i722/4**



**British  
Geological  
Survey**



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

The Chalk of the South Downs

R&D Project Record W6/i722/4

P Smedley and L J Brewerton

Research Contractor:  
British Geological Survey

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

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## **SECTION I. EXECUTIVE SUMMARY**

This document forms one of the regional studies being carried out on representative aquifers or parts of aquifers in England and Wales to provide an improved understanding of the natural baseline quality of groundwaters. It serves as a reference document against which current water quality and future trends (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 concerning the controls on water quality necessary for an informed interpretation of the hydrogeochemical data.

Representative analyses of groundwaters from pumped boreholes and springs in the South Downs area between Chichester and Lewes (Figure I.1) are used here as the basis for establishing the natural (baseline) water quality. These are compared with interstitial waters obtained from a deep borehole drilled at Sompting and from a shallow cored borehole drilled across the saline-freshwater interface near Lancing. With the exception of one site within the Chichester syncline, the chemical and isotopic characteristics show the water to be of low mineralisation, homogeneous and of recent origin and with chemistry which reflects the atmospheric inputs (Cl) as well as reactions at shallow depth between water and Chalk sediment. The waters are aerobic, although a small area of reducing groundwaters occurs beneath a confined section of the Chichester syncline. The South Downs groundwaters are less evolved compared with groundwaters in other regions in southern England. The water quality for the region is summarised in a Piper diagram (Figure I.2) and statistical summary (Table I.1).

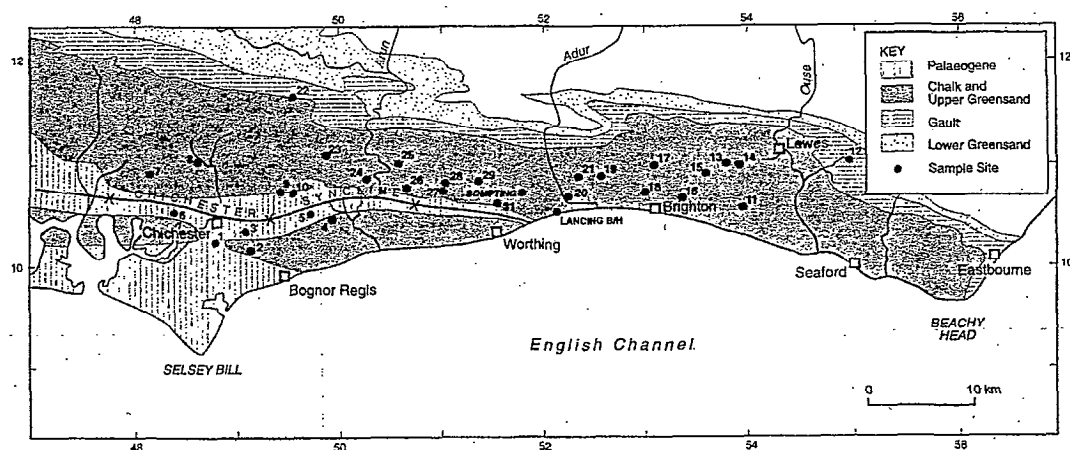
The influence of agricultural chemicals (using  $\text{NO}_3\text{-N}$  as an indicator) may be seen in around 30% of the boreholes but atrazine is detected in over 50% of the analyses, indicating the extent of human impacts on the region.

The chemistry of groundwaters in the South Downs can be described adequately in terms of:

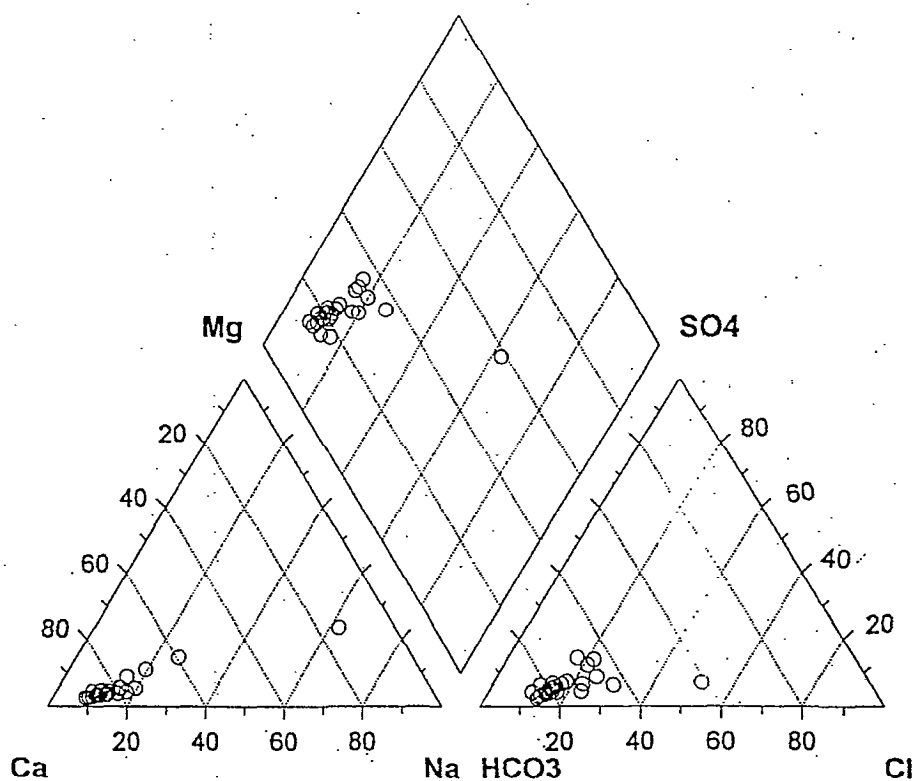
- initial rapid water-rock interaction;
- slight modification of the chemical composition by incongruent reaction with increasing residence time;
- mixing with small amounts of saline and chemically-evolved water from the matrix storage;
- mixing with seawater in localised instances near the coast.

### **KEYWORDS**

Baseline quality, hydrochemistry, groundwater, Chalk, South Downs



**Figure I.1 Geological map of the South Downs area with principle sites used in the baseline study.**



**Figure I.2 Trilinear (Piper diagram) illustrating the main features of groundwaters in the South Downs area.**

**Table I.1 Statistical summary of groundwater quality in the Chalk of the South Downs.**

Determinand			Units	Chichester Block					Worthing Block					Brighton Block				
				Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n
pH (field)				6.11	7.52	6.70	7.40	11	6.83	7.04	6.94	7.03	8	6.86	7.01	6.92	7.00	10
pH (lab)				7.1	7.9	7.4	7.6	329	0.44	10.3	7.4	7.7	1788	<7.4	8.1	7.5	7.8	1347
Eh	redox potential	mV		<30	495	190	414	11	<1	94	55	93.7	8	60	193	138	187	10
DO	dissolved oxygen	mg l <sup>-1</sup>		0.9	9.9	8.3	9.7	11	<0.1	66	7.9	46.2	8	7.1	10.4	9.25	9.99	10
SEC	conductivity	µS cm <sup>-1</sup>		512	1280	760	1140	11	636	775	697	768	8	544	696	590	691	10
Temp	temperature	°C		7.0	14.5	11.0	13.0	81	5.0	16.0	11.0	13.5	378	6.0		11.0	14.0	398
Ca	calcium	mg l <sup>-1</sup>		30.5	153	91	107	156	9.5	172	98.6	123	836	75	123	92	108	692
Mg	magnesium	mg l <sup>-1</sup>		1.32	30.5	1.8	2.98	156	<4	24.2	2.62	6.02	819	1.81	14.4	2.33	3.49	652
Na	sodium	mg l <sup>-1</sup>		4.7	153	10	13.7	165	0.2	254	17.9	84	2038	<0.1	117	14.2	26.6	753
K	potassium	mg l <sup>-1</sup>		<0.7	9.13	0.9	1.82	154	<0.7	15	1.2	2.3	819	<0.7	4.5	1.0	2.4	652
Cl	chloride	mg l <sup>-1</sup>		5	202	21	28.0	182	<33	638	34	175	2300	<23	212	28	47	828
HCO <sub>3</sub> (field)	bicarbonate	mg l <sup>-1</sup>		244	398	290	384	11	233	328	247	307	8	213	269	240	261	10
HCO <sub>3</sub> (lab)	bicarbonate	mg l <sup>-1</sup>		241	313	280	306	12	14.6	396	275	354	153	183	316	238	294	165
SO <sub>4</sub>	sulphate	mg l <sup>-1</sup>		<5	65.8	8	20	161	<1	88	17	36	910	<1	72	17	35	729
NO <sub>3</sub> -N	nitrate as N	mg l <sup>-1</sup>		<0.03	12.2	3.5	6.1	330	<0.2	40.9	6.5	8.5	1410	2.4	11.8	6.4	9.4	1358
NO <sub>2</sub> -N	nitrite as N	mg l <sup>-1</sup>		<0.003	0.02	<0.003	0.006	148	<0.003	2.6	<0.003	0.004	1145	<0.003	0.33	<0.003	0.003	1136
NH <sub>4</sub> -N	ammonium as N	mg l <sup>-1</sup>		<10	600	<30	20	320	<10	1100	<30	<30	3032	<10	360	<30	20	1756
	atrazine	µg l <sup>-1</sup>		<0.01	0.047	<0.01	0.011	219	<0.01	0.41	0.026	0.149	1238	<0.01	0.63	0.034	0.14	1259
Al	aluminium	µg l <sup>-1</sup>		<6	34.5	<6	31.1	11	<6	35.8	<6	27.5	8	<6	25.2	<6	15.2	10
B	boron	µg l <sup>-1</sup>		6.2	257	31	153	11	8.9	28.9	20.4	27.8	8	1.7	55.6	17.7	43.3	10
Ba	barium	µg l <sup>-1</sup>		11.1	84.4	19	81.2	11	8.8	1310	15.2	856	8	6.5	15.3	8.6	14.8	10
Be	beryllium	µg l <sup>-1</sup>		<0.07	0.28	<0.067	0.255	11	<0.07	0.35	<0.07	0.27	8	<0.07	0.3	<0.07	0.18	10
C	cobalt	µg l <sup>-1</sup>		<1.33	2.12	<1.3	1.77	11	<1.3	3.35	<1.3	2.50	8	<1.3	1.99	<1.3	1.32	10
Cd	cadmium	µg l <sup>-1</sup>		<2	3.35	<2	2.32	11	<2	2.34	<2	0.821	8	<2	2.25	<2	1.54	10
Cr	chromium	µg l <sup>-1</sup>		<2.7	5.74	<2.7	5.1	11	<3	5.46	<3	4.0	8	<3	4.22	<3	3.5	10
Cu	copper	µg l <sup>-1</sup>		<1.3	26.1	2.6	21	11	0.69	6.98	3.5	6.8	8	<1.3	12.6	1.65	9.7	10
F	fluoride	µg l <sup>-1</sup>		70	5900	100	3300	11	80	100	90	100	8	70	100	85	96	10

Determinand Units			Chichester Block					Worthing Block					Brighton Block				
			Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n
Fe <sub>total</sub>	total iron	µg l <sup>-1</sup>	<1	4370	4.6	2400	11	<1	54.6	4	37	8	<1	6.4	1.9	5.5	10
I	iodine	µg l <sup>-1</sup>	3	40.5	6.3	30	11	4	6.4	5.0	6.1	8	3.9	6	4.55	5.9	10
La	lanthanum	µg l <sup>-1</sup>	<1.3	1.44	<1.3	0.054	11	<1.3	2.44	<1.3	1.1	8	<1.3	<1.3	<1.3	<1.3	10
Li	lithium	µg l <sup>-1</sup>	<0.5	18.9	<1.7	12	11	<0.5	6.9	1.2	5.9	8	<0.5	3.9	0.2	2.8	10
Mn	manganese	µg l <sup>-1</sup>	<0.2	111	1	59	11	<0.2	0.6	0.15	0.53	8	<0.2	0.6	<0.2	0.48	10
Mo	molybdenum	µg l <sup>-1</sup>	<7	6.71	1.2	6.6	11	<7	12.0	<7	8.5	8	<7	5.75	<7	5.6	10
Ni	nickel	µg l <sup>-1</sup>	<3	41.8	1.7	26	11	<3	7.14	2.5	7.0	8	<3	4.87	<3	4.2	10
P <sub>total</sub>	total phosphorus	µg l <sup>-1</sup>	<33	250	55	170	11	<33	56.4	32	53	8	<33	57	29	51	10
Pb	lead	µg l <sup>-1</sup>	<10	21.7	<10	21	11	<10	15.5	<10	12	8	<10	18.3	<10	10	10
Si	silicon	µg l <sup>-1</sup>	3184	6890	4000	5900	11	3190	5710	4400	5500	8	3010	4190	3150	4150	10
Sr	strontium	µg l <sup>-1</sup>	202	6360	330	4300	11	204	311	240	300	8	182	234	193	230	10
Y	yttrium	µg l <sup>-1</sup>	<0.2	1.04	0.33	0.95	11	<0.2	1.06	0.62	1.0	8	<0.2	1.22	0.44	1.1	10
Zn	zinc	µg l <sup>-1</sup>	<1.3	181	16	120	11	<1.3	17.40	9.8	17	8	<1.3	15.6	3.23	11	10
Unfiltered samples																	
Al	aluminium	µg l <sup>-1</sup>						<7	<7	<7	<7	1					
As	arsenic	µg l <sup>-1</sup>	<0.1	0.8	<0.2	0.4	142	<0.2	1.6	<0.2	0.33	693	<0.2	3.3	<0.2	0.3	613
B	boron	µg l <sup>-1</sup>	<5	121	<100	57	142	<40	400	<100	130	698	<40	260	<100	110	592
Ba	barium	µg l <sup>-1</sup>	<5	43	12	30	142	<2	181	17	28	694	<2	39	11	17	591
Be	beryllium	µg l <sup>-1</sup>						<0.07	<0.07	<0.07	<0.07	1					
C	cobalt	µg l <sup>-1</sup>						<1.3	<1.3	<1.3	<1.3	1					
Cd	cadmium	µg l <sup>-1</sup>	<0.01	13	<0.5	<0.1	141	<0.1	4.8	<0.5	<0.3	693	<0.1	4.9	<0.5	<0.3	593
Cr	chromium	µg l <sup>-1</sup>	<0.4	2.76	<0.6	1.4	141	<0.4	21.4	<0.6	1.4	693	<0.4	19.2	<5	1.5	593
Cu	copper	µg l <sup>-1</sup>	<4	41	<26	11	140	<4	490	<26	34	719	<0.01	300	<26	12	622
F	fluoride	µg l <sup>-1</sup>	<50	950	78	120	137	<10	750	80	120	698	<10	620	69	140	588
Fe <sub>total</sub>	total iron	µg l <sup>-1</sup>						2.6	2.6	2.6	2.6	1					
Hg	mercury	µg l <sup>-1</sup>	<0.005	0.09	<0.005	0.024	142	<0.005	0.86	<0.005	0.025	694	<0.005	0.12	<0.005	0.022	589
I	iodine	µg l <sup>-1</sup>						5.2	5.2	5.2	5.2	1					
La	lanthanum	µg l <sup>-1</sup>						<1.3	<1.3	<1.3	<1.3	1					
Li	lithium	µg l <sup>-1</sup>						<0.5	<0.5	<0.5	<0.5	1					

Determinand Units			Chichester Block					Worthing Block					Brighton Block				
			Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n
Mn	manganese	µg l <sup>-1</sup>						0.1	0.1	0.1	0.1	1					
Mo	molybdenum	µg l <sup>-1</sup>						<7	<7	<7	<7	1					
Ni	nickel	µg l <sup>-1</sup>	<1	14	<2		4 141	<1	108	<5	9.1	693	<1	72	<2	4.5	593
P <sub>total</sub>	total phosphorus	µg l <sup>-1</sup>						36.8	36.8	36.8	36.8	1					
Pb	lead	µg l <sup>-1</sup>	<1	4	<4	<1	139	<1	30	<4	3.1	718	<1	17	<4	<1	621
Sb	antimony	µg l <sup>-1</sup>	<0.2	4	<0.4	<0.4	142	<0.4	2	<0.4	<0.4	693	<0.4	2.2	<0.4	<0.4	589
Si	silicon	µg l <sup>-1</sup>						4520	4520	4520	4520	1					
Sr	strontium	µg l <sup>-1</sup>						218	218	218	218	1					
Y	yttrium	µg l <sup>-1</sup>						0.38	0.38	0.38	0.38	1					
Zn	zinc	µg l <sup>-1</sup>	<5	157	<13		34 140	<5	370	<13	70	719	<5	170	<13	26	622



## **SECTION II.**

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

#### **1. PERSPECTIVE**

The Chalk aquifer of the South Downs covers an area of 700 km<sup>2</sup> and extends 90 km along the coast westwards from Eastbourne. It is an area with a high population density and which relies almost entirely on groundwater resources. The hydrogeology of the aquifer is generally well known and groundwater modelling has helped with the management of the resources in recent years (Headworth and Fox, 1986). Saline intrusion has been a problem at several locations along the coast (Monkhouse and Fleet, 1975), but this is considered to be mainly a near-surface problem since water of good quality is often found at depth in the aquifer. Apart from coastal saline intrusion, the groundwater is generally of good quality although with the constant threat of pollution, mainly from agrochemicals. To date there has been little published on the water quality across the South Downs area. In this baseline study of the groundwater, comparisons are made with the well-established controls on water quality in the London Basin to the north (Edmunds et al. 1987; 1992).

## **2. BACKGROUND**

### **2.1 Geology**

The geological structure of the South Downs has a marked impact on the hydrogeology of the area. A number of east-west folds cross the area. The most important, the Chichester syncline (Figure I.1), extends westwards from Worthing and shows the same asymmetry as the Wealden structures with a gently-dipping south limb ( $2-3^\circ$ ) and a steeply-dipping north limb. It is bounded to the south by an anticlinal structure, the Portsdown anticline, which becomes the Littlehampton anticline further east. Up to 160 m of Tertiary sediments and drift cover the Chalk surface near the syncline axis, preventing or restricting groundwater flow from north to south, but diverting the main flow to the east where it gives rise to abundant spring flow near the river Arun. The Chalk stratigraphy of the South Downs (Shephard-Thorn et al., 1997) is illustrated in Figure II.2.1 where the various stratigraphic names in modern use are compared with those commonly used by hydrogeologists (Upper, Middle and Lower Chalk).

### **2.2 Hydrogeology**

Groundwater flow is mainly from north to south, reflecting the surface topography, the geometry of the various formations and the variations in permeability. A perennial spring line exists to the north of the scarp slope, just above the base of the Lower Chalk (Headworth and Fox, 1986). Intermittent springs on the southern slopes also occur giving rise to 'bournes'. Spring discharges have also been identified along the coastal margin, especially near the wave-cut platform to the east of Brighton. The Palaeogene sediments of the Chichester syncline act as a confining layer and inhibit groundwater flow from north to south. The Quaternary deposits, particularly in the Sussex coastal plain control infiltration into the Chalk and shallow groundwater flow.

The hydrogeology is illustrated conceptually in Figure II.2.2 along a line of section near Worthing. Except in the west, the chalk aquifer forms the coastline and since the turn of the century, intrusion inland by up to 500 m of saline water has occurred and resulted in the abandonment of boreholes at Eastbourne, Bognor Regis, Littlehampton and Seaford. These have been replaced by sources further inland, although in later years one source, Eastbourne has been reinstated. Hydrogeophysical logging has revealed that the saline water moves inland along discrete horizons yet at the same time, freshwater may be moving seawards. Careful management of the aquifer in recent years has led to the optimum use of the coastal zone, restricting the pumping during times of lower water levels in summer (Headworth and Fox, 1986).

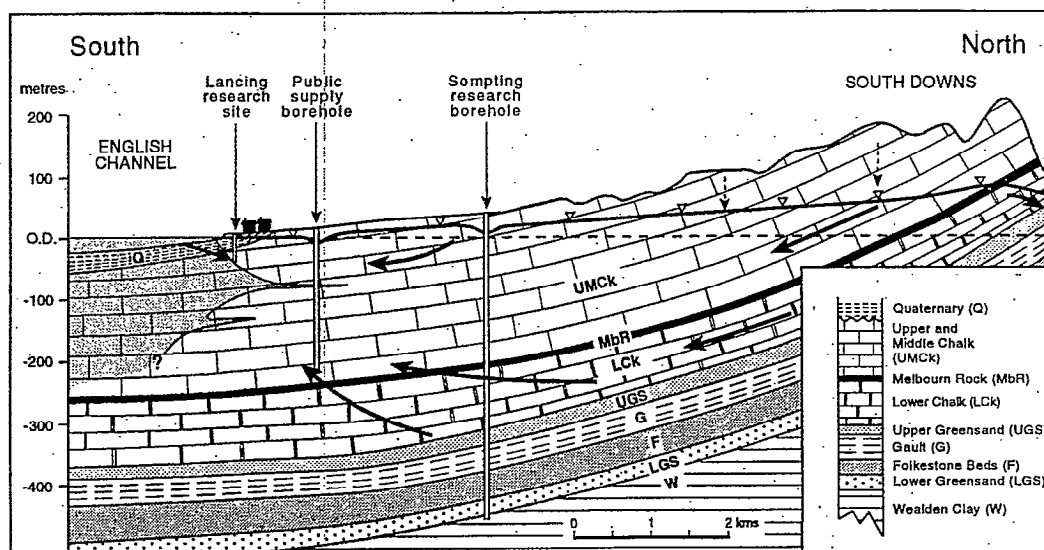


TRADITIONAL CHALK STRATIGRAPHY				SOUTHERN PROVINCE (Mortimore 1983, 1986)		
Stage	Fmn	Key Markers	Zone	Fmn	Member	BGS Lithostratigraphical members
CAMPANIAN			<i>Belemnites mucronata</i>	White Chalk Formation	PORTSDOWN	Portsmouth Chalk
			<i>Gonioteuthis quadrata</i>		CULVER	Spetisbury Chalk
			<i>Offaster pilula</i>			Tarrant Chalk
			<i>M.t.</i>		NEWHAVEN	Newhaven Chalk
SANTONIAN			<i>U.s.</i>			
			<i>Micraster corangulum</i>		SEAFORD	Seaford Chalk
CONIACIAN	Upper Chalk	Barrois Sponge Bed. Bedwell's Columnar Flint	<i>Micraster cortestudinarius</i>		LEWES	Lewes Chalk
			<i>Sternolaxis plana</i>			
TURONIAN	Middle Chalk	Top Rock Chalk Rock Spurious Chalk Rock	<i>Terebratulina lata</i>		RANSCOMBE	New Pit Chalk
			<i>Mytiloides labiatus</i>			Holywell Chalk
				Lower Chalk		Zig Zag Chalk
CENOMANIAN	Lower Chalk	Melbourn Rock Plenus Marls				West Melbury Chalk
		Jukes-Brown & Bed 7 Tenuis Limestone				
		Glauconitic Marl				

U.s. - *Uintacrinus socialis* Zone  
M.t. - *Marsupites testudinarius* Zone

(Not to scale)

Figure II.2.1 Comparison of classification systems for the Chalk of Sussex (after Mortimore, 1987).



**Figure II.2.2** Schematic cross-section through South Downs to show position of the Sompting and Lancing boreholes and the saline groundwater at shallow depths near the coast.

The detailed hydrogeology of the South Downs is described in Jones et al. (1997).

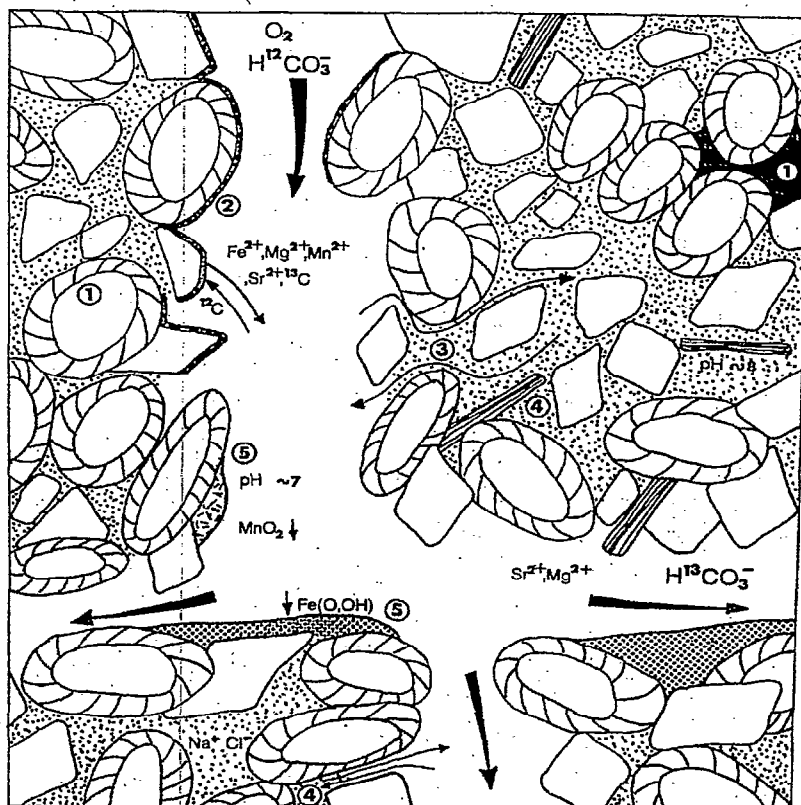
### 2.3 Aquifer Minerals and Geochemical Composition

The Upper and Middle Chalk are very pure carbonates comprising microfossil (coccolith) debris. The chalk has a dual porosity composed of micro/macro fissures and blocks. Packing of the coccolith material permits a very high intergranular porosity (in the range 20–45%) and this also gives rise to a very high specific surface area which enhances the potential for reaction of the chalk surfaces. In addition, the matrix of the chalk, having a permeability several orders of magnitude higher than in the fissures, acts as a 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. The microporosity and main mineralogical and geochemical features of the chalk are illustrated in Figure II.2.3.

Despite its purity, the small amount of other elements substituting in the calcites forming the chalk, have a disproportionate effect on the water chemistry. Small quantities of Mg, Mn, Sr and Fe are released during *congruent* (rapid) and *incongruent* (slower) reactions (see Appendix 1). The Upper Chalk contains 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.

## 2.4 Rainfall Chemistry

The influence of rainfall on the baseline water quality is likely to be important as the aquifer is near-coastal. The mean rainfall for the area is  $840 \text{ mm} \cdot \text{yr}^{-1}$  and the mean value for the Cl concentration in rain is  $7 \text{ mg l}^{-1}$  extrapolated from the Hartland Moor station in Dorset (UKAWRG, 1990). Using the data of Monkhouse et al. (1982) to obtain evapotranspiration for the area, a Cl concentration of  $17.4 \text{ mg l}^{-1}$  is estimated for recharge derived from rainfall, representing the probable natural concentration in groundwater.



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

### **3. DATA QUALITY AND HANDLING<sup>1</sup>.**

#### **3.1 Sources and Quality of Data**

This account describes chemical data from 81 boreholes in the Chalk aquifer of the South Downs. The data used comprise 3088 samples from 31 sites in the Brighton Block, 462 samples from 16 sites in the Chichester block and 5982 samples from 34 sites in the Worthing block. Data are compiled from Environment Agency and British Geological Survey (BGS) data files, including a comprehensive study by BGS (Edmunds et al., 1997), the sites of which are shown in Figure I.1. Ninety-five percent of the data considered have an ionic charge balance better than 10%, 88% of the data being within 5%. For production of water-quality data, minima, maxima and median values have been calculated. Where median values are below a given detection limit, the detection limit values are given. Box plots are also used to illustrate the data ranges (Figures II.4.3-4), where boxes define the ranges between the 25 and 75 percentiles. The 5 and 95 percentiles are also shown.

#### **3.2 The Influence of Pollution**

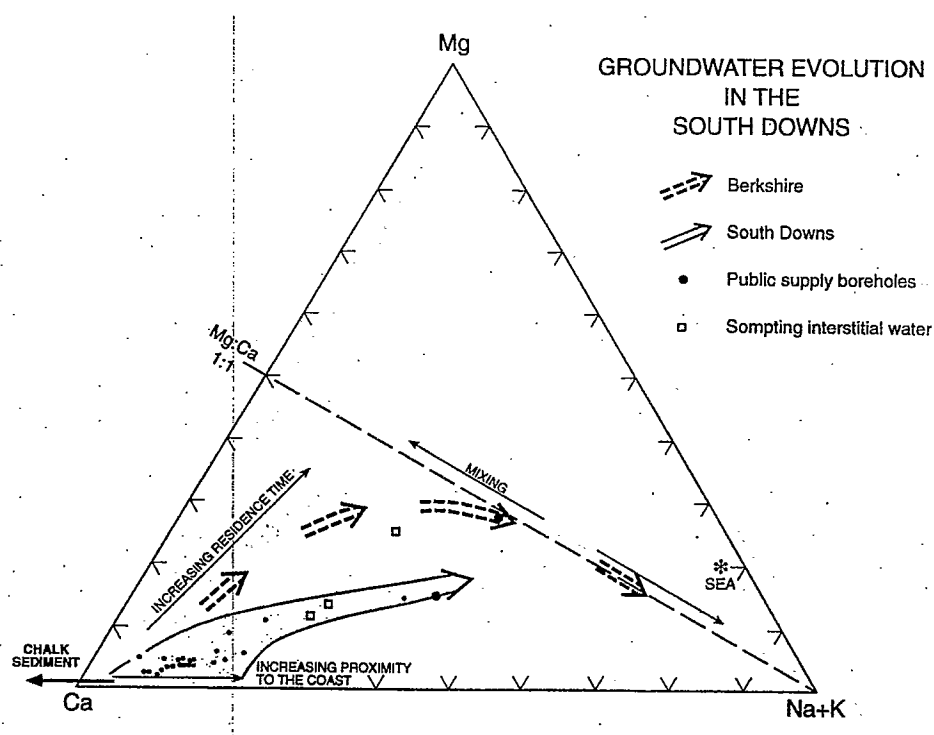
The median concentrations (Table I.1) for most elements may be regarded as best estimates of the average unpolluted groundwater composition for each of the Chalk Blocks; any effects of pollution will be found in the upper 50 percent of this group. An exception is  $\text{NO}_3\text{-N}$ . The influence of agricultural activities can be detected using the cumulative-frequency plots (Figures II.4.5-6) and it is estimated that in the South Downs Chalk sources, some 30% of the groundwaters included in this study have significant contributions of  $\text{NO}_3\text{-N}$  (above  $5 \text{ mg l}^{-1}$ ) from agricultural sources. In addition, atrazine is detected in over 50% of the groundwaters from the Worthing and Brighton blocks (Table I.1) and this illustrates the extent of migration of modern groundwater with an agricultural signature into the aquifer of the South Downs.

The 95 percentile values (Table I.1) are likely to represent the maximum limits of any baseline contributions and it is clear that for some determinands such as  $\text{NO}_3\text{-N}$ , these represent clear influence of human rather than natural impacts. For other species (e.g. F) this value represents contributions from geological sources.

The other potential contaminant is Cl from seawater intrusion. The median concentrations in all the blocks (Table I.1) are not significantly above the rainfall derived baseline value of  $17.4 \text{ mg l}^{-1}$  Cl. However, some of the higher values in the Worthing and Brighton (although not Chichester blocks, see below) are likely to reflect the influence of seawater.

## 4. HYDROGEOCHEMICAL CHARACTERISTICS

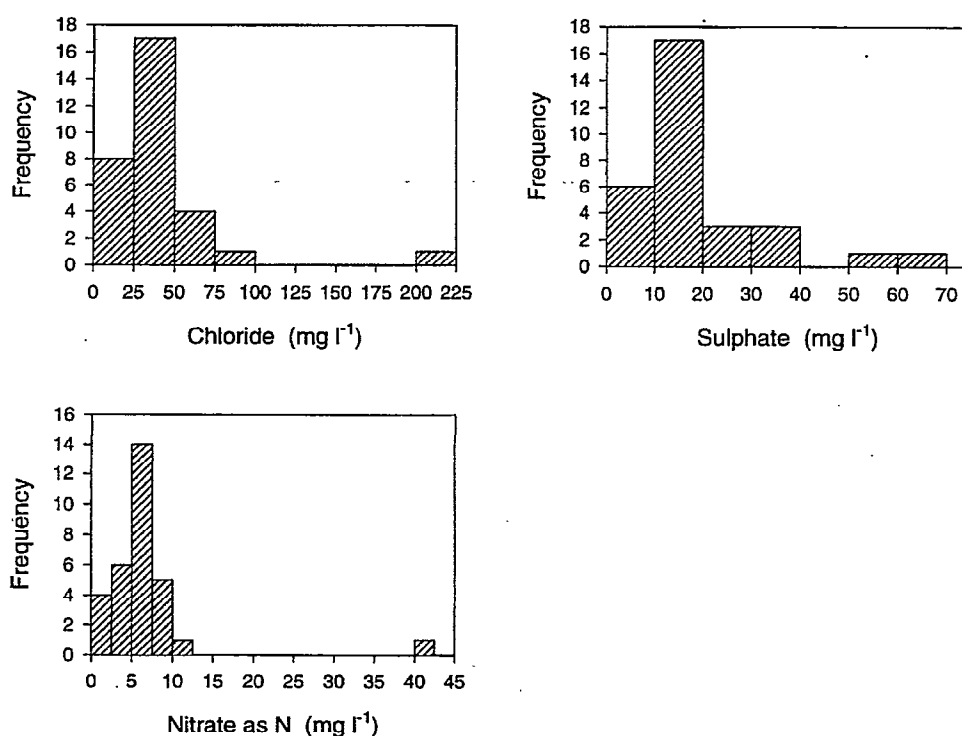
The mineral composition of the Chalk groundwater is established early in its history. Rainfall acidity is quickly neutralised by reaction with chalk sediment and the reactivity of the soil water is greatly enhanced by the solubility of carbon dioxide produced biogenically in the soil zone. The  $\text{CO}_2$  partial pressure may vary from place to place depending on the soil type and depth. 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 diminished. During early evolution in the aquifer, the groundwater acquires a Ca-rich composition with Mg/Ca ratio close to that of the Chalk as indicated in the trilinear diagram (Figure II.4.1). However, a small percentage of by-pass flow through open fractures may result in calcite-undersaturated water being transported to deeper levels in the unsaturated zone with the capacity for fissure enlargement, as demonstrated by studies using tritium (Foster and Smith-Carrington, 1980).



**Figure II.4.1** Trilinear diagram showing the evolution of cation composition in groundwaters from the South Downs in relation to the Berkshire area.

Groundwaters in the saturated zone beneath the South Downs have Mg/Ca ratios only slightly above those of the solid chalk as shown in the trilinear diagrams (Figures I.2, II.4.1), implying that their composition has evolved very little since infiltration. This provides indirect evidence of a short groundwater residence time. However, some groundwaters within the Chichester syncline have higher Mg/Ca ratio (as well as other characteristics described below) which indicate a degree of water-rock interaction where Mg has been preferentially released by incongruent solution from the Chalk. The direction of

hydrochemical evolution differs from that of the Berkshire Chalk due mainly to the higher Na concentrations in the rainfall in the coastal area, but the same trend of increasing Mg/Ca ratio is indicated.



**Figure II.4.2 Histograms for  $\text{Cl}$ ,  $\text{SO}_4$  and  $\text{NO}_3\text{-N}$  in the South Downs groundwaters.**

The field pH (median value 6.9) is rather below that measured in the laboratory (7.4) and indicates loss of  $\text{CO}_2$  between sampling and laboratory measurement. Saturation with respect to calcite calculated using the field pH data has been reached or slightly exceeded in the Chalk groundwaters of the South Downs area. The  $\text{HCO}_3$  concentrations in the groundwaters under conditions of equilibrium reflect the  $\text{pCO}_2$  of the open-system conditions established in the soil or the unsaturated zone. The  $\text{pCO}_2$  values in the South Downs waters range from 16 to 80 times greater than atmospheric values. Most groundwaters lie close to the mean concentration (30.6 times atmospheric) and this suggests similar recharge conditions across the outcrop of the Chalk.

The major ion hydrochemistry is summarised in the trilinear plot (Figure II.4.1) and Table 1. The histograms (Figure II.4.2) help to clarify the anion distribution, the outliers clearly identifying the gross contamination. The box plots (Figures II.4.3 and II.4.4) are used to express the relative enrichment or depletion of the elements relative to seawater. Most of the elements except  $\text{NO}_3\text{-N}$  show a log-normal distribution, indicating that the chemical characteristics are derived principally from a single source, in this case water-rock interaction rather than pollution. Sulphate and  $\text{NO}_3\text{-N}$  show a bimodal distribution, implying the extent of pollution. The upper 20% of samples show elevated concentrations of Sr, F and Zn, all of which may be related to chalk diagenesis and longer residence times (see below).

The cumulative frequency diagrams (Figures II.4.5 and II.4.6) link and compare the relative concentration distributions for both major and minor elements and also demonstrate several features relating to geochemical processes (see Appendix 1).

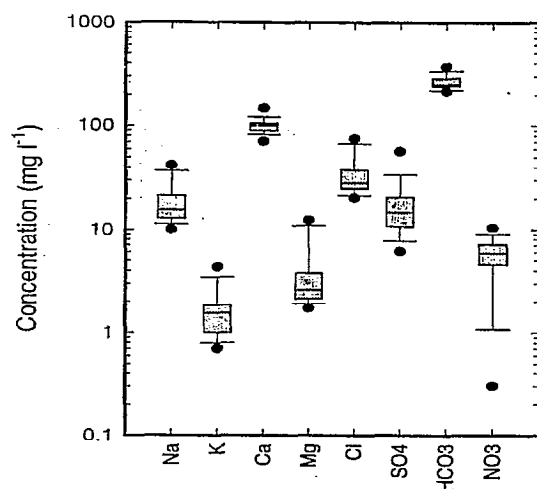


Figure II.4.3 Box plots for major ions in the groundwater of the South Downs. For each element, the data within the 25th and 75th percentile range are highlighted with the median concentration. The outer bars show respectively the 5th and 95th percentile data limits. Maxima and minima are given as solid symbols.

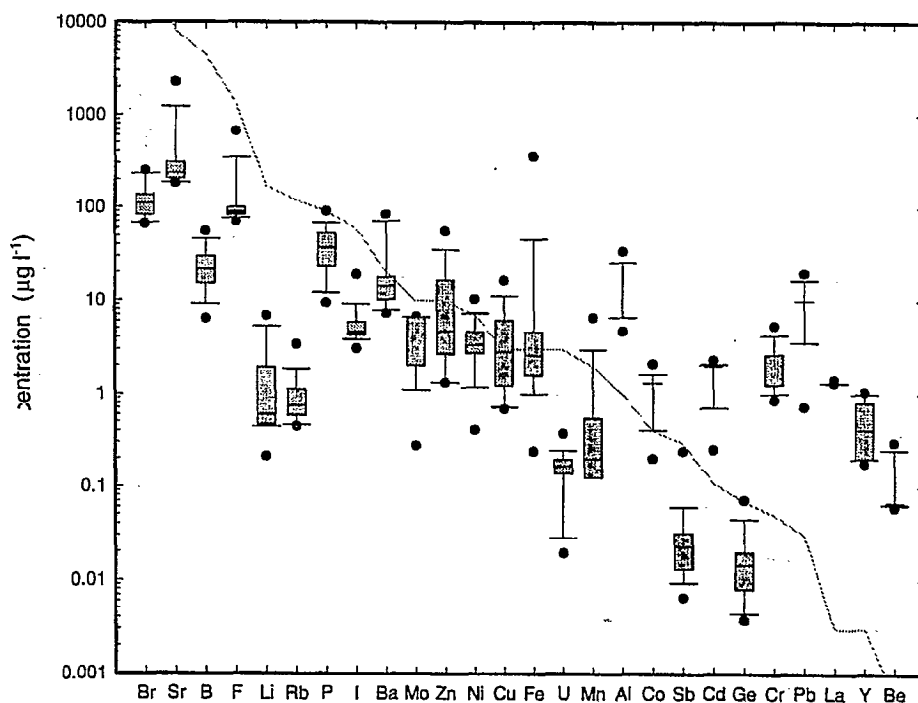
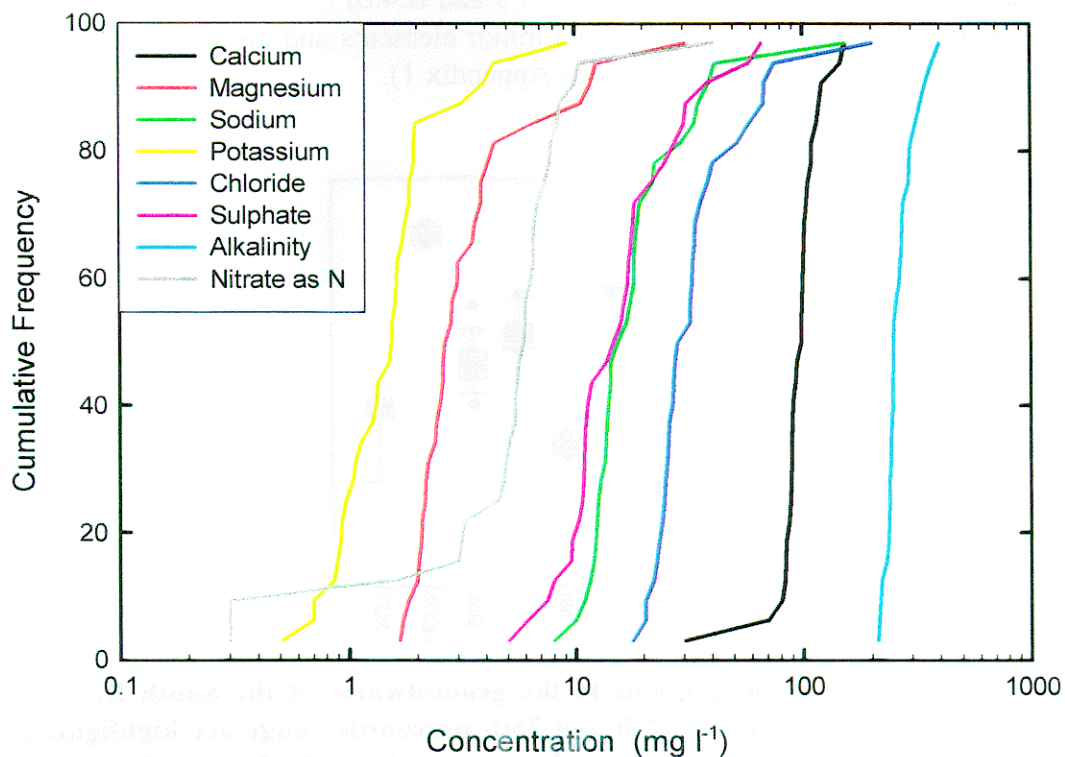
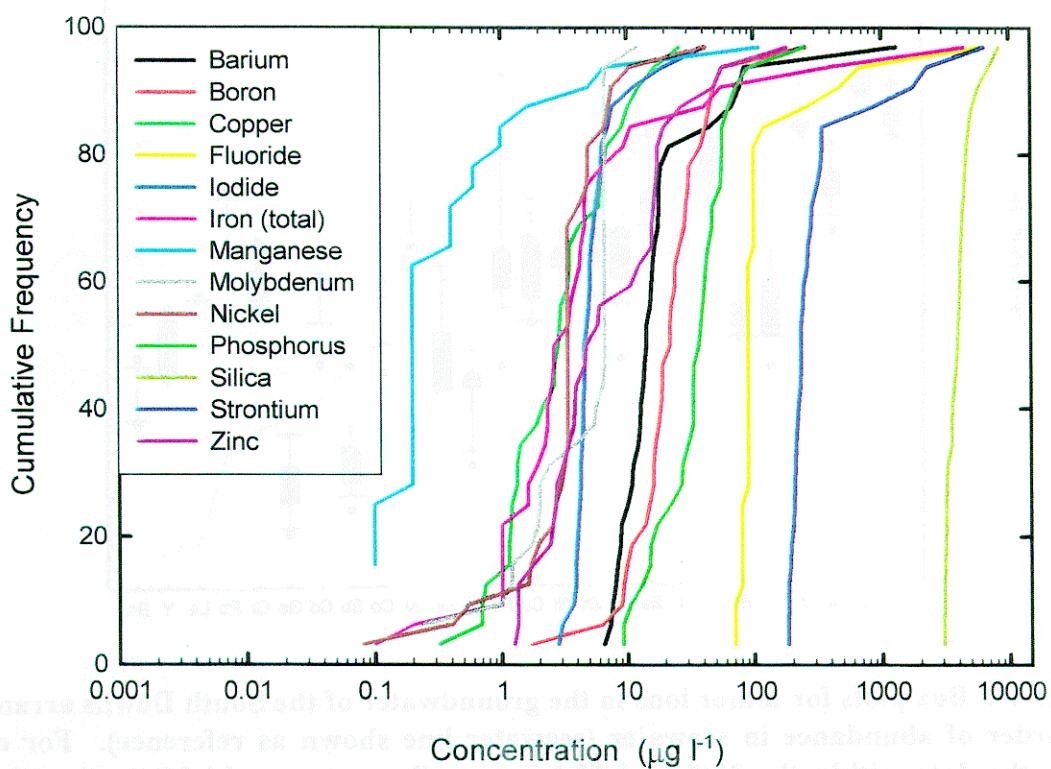


Figure II.4.4 Box plots for minor ions in the groundwater of the South Downs arranged in the order of abundance in seawater (seawater line shown as reference). For each element, the data within the 25th and 75th percentile range are highlighted with the median concentration. The outer bars show respectively the 5th and 95th percentile data limits. Maxima and minima are given as solid symbols.



**Figure II.4.5 Cumulative-frequency diagram for major elements in the groundwaters of the South Downs.**

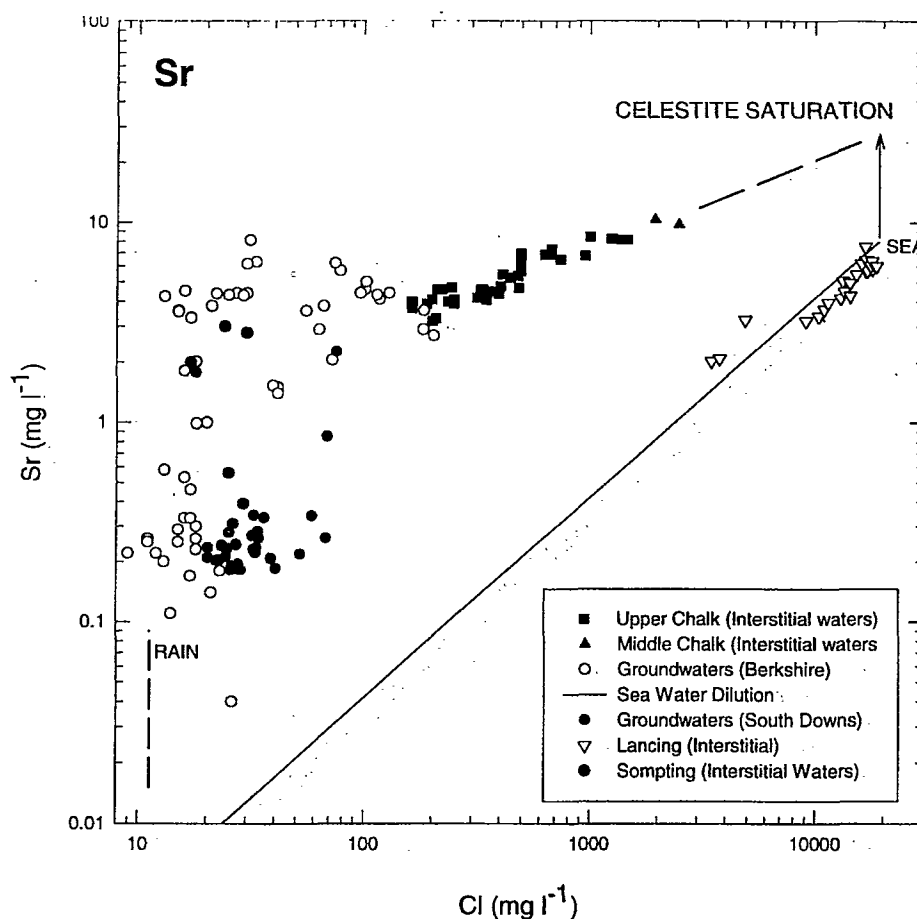


**Figure II.4.6 Cumulative-frequency diagram for minor elements in the groundwaters of the South Downs.**



## 5. REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS

Aerobic conditions prevail throughout most of the unconfined Chalk. This helps to maintain very low concentrations of dissolved Fe (typically less than  $5 \mu\text{g l}^{-1}$ ) and also favours the persistence of  $\text{NO}_3\text{-N}$  in the groundwater. It is likely that inorganic reactions are important in the gradual reaction and removal of oxygen in some parts of the aquifer. Iron ( $\text{Fe}^{2+}$ ), as well as  $\text{Mn}^{2+}$  and other trace elements are released from the impure chalk sediment during the initial reactions at outcrop and subsequently at much slower rates due to incongruent reactions. However, under the prevailing neutral pH and aerobic conditions, the Fe is oxidised and precipitates as oxides on the fracture surfaces.



**Figure II.5.1 Hydrogeochemistry of Sr in groundwaters from the South Downs area in relation to those from Berkshire (interstitial waters from the Upper and Middle Chalk as well as pumped groundwaters). Also shown are data from Sompting (interstitial waters) and interstitial waters from the borehole at Lancing.**

A region of reducing groundwaters is present within the confined Chalk aquifer of the Chichester syncline as indicated by values of  $<1 \text{ mg l}^{-1}$   $\text{NO}_3\text{-N}$  where denitrification has occurred. These groundwaters also have elevated concentrations of total dissolved Fe (maximum  $4.4 \text{ mg l}^{-1}$ ). Elsewhere, the oxidising conditions favour the persistence of  $\text{NO}_3$  and some other degradable pollutants.

The concentrations of trace elements and their relationships to the major elements, especially Cl, can be used to assist interpretation of Chalk groundwater evolution as well as providing information on baseline characteristics and potability. The median concentrations of a number of key minor and trace elements are included in Table 1. The box plot (Figure II.4.4) shows the overall concentration range of a wider spectrum of trace elements. Since the lithology of the aquifer is essentially uniform, the concentrations of trace elements will depend firstly on residence-time dependent water-rock interaction and secondly on redox conditions.

In the same way that Mg increases in the groundwater as a result of incongruent solution, high Sr concentration also provides a sensitive indicator of the presence of evolved groundwater (Figure II.5.1). The rather low and uniform Sr concentrations in the South Downs groundwater therefore indicate short residence times (Edmunds et al., 1997). Waters from the confined aquifer of the Chichester block with high Sr relative to Cl (Figure II.5.1) are likely to be the only groundwaters identified with long residence times (in excess of around  $10^3$  yr), in contrast to most groundwaters investigated which have residence times of the order of decades at most.

The baseline concentrations of transition metals (e.g. Cu, Ni, Zn) are generally low (Table I.1, Figures II.4.4 and II.4.6). The average 'baseline' concentration of Cu in the aerobic groundwaters is between  $1 \mu\text{g l}^{-1}$  and  $5 \mu\text{g l}^{-1}$  but several groundwaters have concentrations above  $10 \mu\text{g l}^{-1}$ . In the reducing environment, the Cu concentrations are significantly lower.

Like Sr, F concentrations are directly related to water-rock interaction, probably having been released from phosphatic minerals such as fluorapatite in the chalk. Groundwaters with high F (above  $0.25 \text{ mg l}^{-1}$ ) only occur in the Chichester syncline and suggest that they have had a longer residence time than other groundwaters in the South Downs area where the F is typically below  $0.1 \text{ mg l}^{-1}$ .

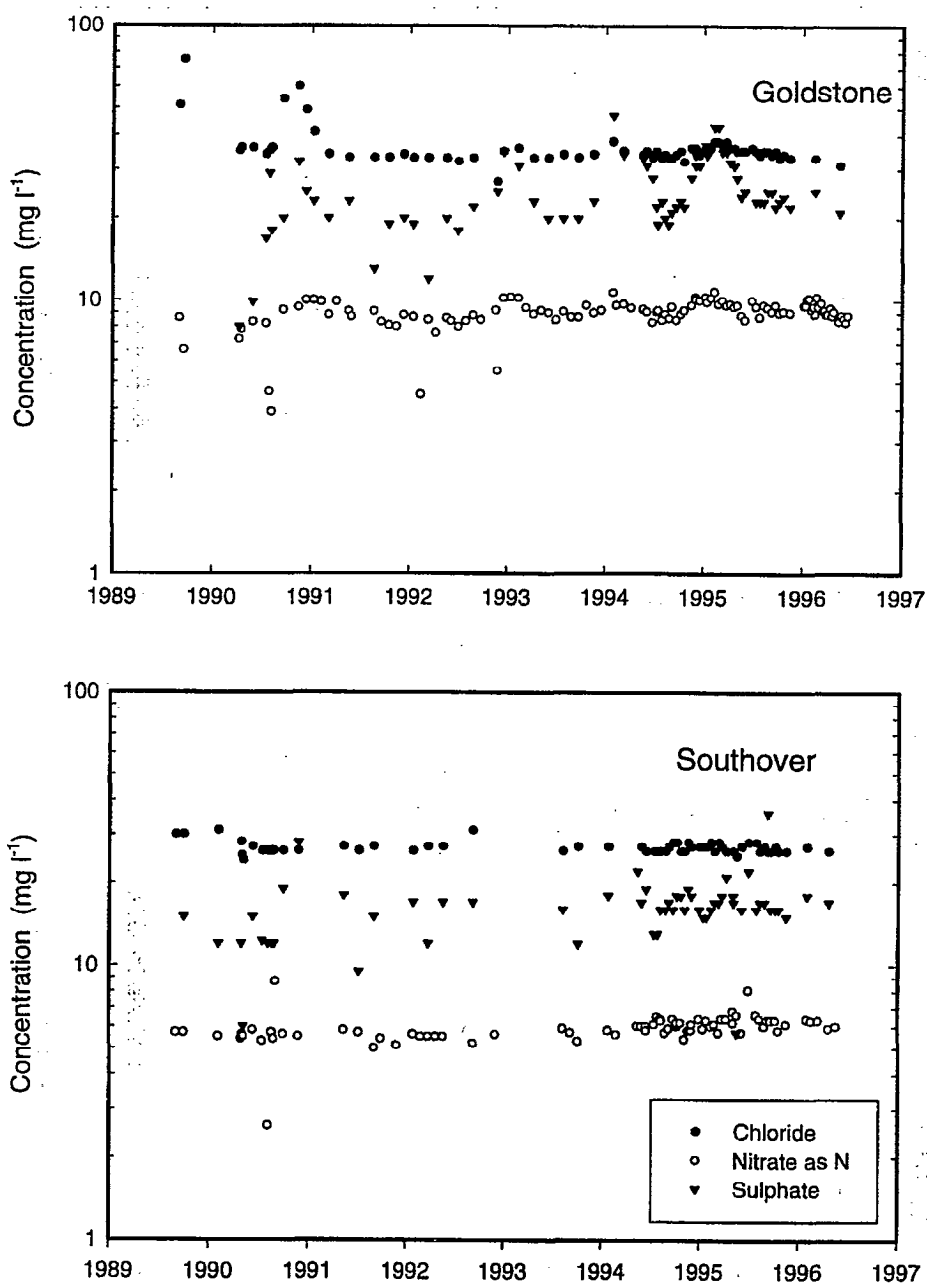
## 5.1 Residence Times

No work has been carried out on the age of groundwaters in the South Downs area but several indirect indicators of age may be cited. The range of stable isotope compositions is relatively narrow and the mean values of  $\delta^{18}\text{O}$  of  $-6.45 \text{ ‰}$  and  $\delta^2\text{H}$  of  $-38.6 \text{ ‰}$  are typical of those for recent meteoric waters for the southern UK (Darling et al., 1995). A single sample from Northmundham in the Chichester syncline area has a lighter  $\delta^{18}\text{O}$  isotopic composition ( $-7.7 \text{ ‰}$ ) which indicates a probable palaeowater (late Pleistocene) signature from water trapped at the present day. The geochemical evidence (Mg, Sr) discussed above relating to the release of impurities in the Chalk may also be used to indicate relative age. The presence of atrazine in many groundwaters is also a valuable additional indicator of residence time. Most of the groundwater currently being exploited is therefore considered to be modern.

## 5.2 Trends

Data for long-term (decadal scale) water-quality trends are not available for the region. Figure II.5.2 shows the temporal variation in water quality at two sites, Goldstone and Southover, in terms of the principal anions, Cl,  $\text{SO}_4$  and  $\text{NO}_3$ . Trends for Southover show a

very slight increase in  $\text{NO}_3$  and  $\text{SO}_4$  although Cl has remained almost constant over this 7-year period. At Goldstone, there is evidence of seasonality in the chemistry with higher concentrations of  $\text{SO}_4$  and  $\text{NO}_3$  in springtime. This is likely to relate to influxes of agricultural chemicals to the aquifer with new recharge inputs, although the source of these determinands is not identified as unequivocally agricultural.



**Figure II.5.2 Trends in the concentration of Cl,  $\text{SO}_4$ , and  $\text{NO}_3$ -N (1989-1996) from Goldstone and Southover boreholes.**

### **5.3 Depth Variations**

The variations in water quality with depth are complex, especially in the coastal areas. Freshwater may persist to the full saturated depth of the Chalk in some places but adjacent sites may exhibit salinity from modern seawater intrusion. A full discussion of the coastal salinity is given in Jones et al. (1997). Evidence has also been obtained from the Sompting borehole interstitial waters (Edmunds et al., 1997; Figure II.1.2) to suggest that the Chalk matrix may contain slightly saline formation waters or waters with an evolved chemical composition (Figure II.5.1). This residual water is also found at depth in the confined groundwaters in the Chichester syncline and is a feature of the Chalk elsewhere in England (Bath and Edmunds, 1981; Edmunds et al., 1992).

### **5.4 Saline Water in the Chalk**

The prevention and control of saline intrusion from modern seawater has been the prime management issue in the South Downs area (Headworth and Fox, 1986). The chemistry of modern saline water in the Chalk has been investigated by means of a cored borehole at Lancing (Edmunds et al., 1997). The salinity gradient is summarised in Figure 12 in relation to the Sr model. Modern saline water can be recognised easily by the simple dilution of Sr, in contrast with the older formation water, retained in the matrix at Sompting and elsewhere, where Sr is significantly enriched relative to Cl.

## 6. SUMMARY

The chemistry of groundwaters in the South Downs can be described adequately in terms of i) initial rapid water-rock interaction, ii) slight modification of the chemical composition by incongruent reaction with increasing residence time, iii) mixing with small amounts of saline and chemically-evolved water from the matrix storage and iv) mixing with seawater in localised instances near the coast.

Representative analyses of groundwaters from pumped boreholes and springs in the South Downs area between Chichester and Lewes are used here as the basis for establishing the natural (baseline) water quality. These are compared with interstitial waters obtained from a deep borehole drilled at Sompting and from a shallow cored borehole drilled across the saline-freshwater interface near Lancing. With the exception of one site within the Chichester syncline, the chemical and isotopic characteristics show the water to be of low mineralisation, homogeneous and of recent origin and with chemistry which reflects the atmospheric inputs as well as reactions at shallow depth between water and Chalk sediment. The waters are aerobic, although a small area of reducing groundwaters occurs beneath a confined section of the Chichester syncline. The South Downs groundwaters are less evolved compared with groundwaters in other regions in southern England.

The influence of agricultural chemicals (using  $\text{NO}_3\text{-N}$  as an indicator) may be seen in around 30% of the boreholes but atrazine is detected in over 50% of the analyses, indicating the extent of human impacts on the region.

The chemistry of groundwaters in the South Downs can be described adequately in terms of:

- initial rapid water-rock interaction;
- slight modification of the chemical composition by incongruent reaction with increasing residence time;
- mixing with small amounts of saline and chemically-evolved water from the matrix storage;
- mixing with seawater in localised instances near the coast.

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

## **A1.1 Introduction**

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

### **A1.1.1 Natural Groundwater Quality and the Baseline Concept**

Baseline concentrations of a substance in groundwater may be defined in several different ways. For the purpose of this study the definition is given as 'the concentration of a given element, species or chemical substance present in solution which is derived from natural geological, biological, or atmospheric sources'. Thus, an ideal starting point is to locate waters where there are no traces of human impact, essentially those from the pre-industrial era. To do this some attempt must be made to measure the residence times of groundwater. Measurement of the absolute age of groundwater presents many difficulties and the most widely used technique is the use of radiocarbon (Clark and Fritz, 1997). The interpretation of radiocarbon presents various problems, including the fact that it is a reactive tracer, intimately involved in reactions of the carbonate system; there is also the problem of mixed waters occurring due to pumping from boreholes which are open over large vertical intervals. By investigating the evolution of water quality along flow lines it may be possible to establish relative timescales using a combination of geochemical and isotopic methods. Indicators such as the stable isotope composition of water or palaeoclimatic indicators such as noble gases or chloride (Cl) may provide indirect evidence of residence time (Bath and Edmunds, 1978; Andrews et al., 1995). The identification (or absence) of marker species related to activities of the industrial era, such as total organic carbon (TOC), tritium ( $^3\text{H}$ ), 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> , <b>P</b> , <b>Al</b> , NH <sub>4</sub> , B, Cu, Zn, Cd, Ni, Cr, Co, <b>Pb</b> , <b>Ba</b> , Sr, Sb, <b>Be</b> , <b>Hg</b> , <b>Mo</b> , U
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> )†	25	50	50	0.0161
	(as N)	5.65	11.3	10	
Nitrate	(NO <sub>2</sub> )†	-	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	1500	1500	0.0526
		25-30°C	700	-	
Barium	(Ba <sup>2+</sup> )	100	-	700	0.0146
Silver	(Ag <sup>+</sup> )	-	10	-	0.0093
Arsenic	(As) <sup>†</sup>	-	50	10 P	-
Cadmium	(Cd <sup>2+</sup> )†	-	5	3	0.0178
Cyanide	(CN) <sup>†</sup>	-	50	100	-
Chromium	(Cr) <sup>†</sup>	-	50	50 P	-
Mercury	(Hg) <sup>†</sup>	-	1	1	-
Molybdenum	(Mo) <sup>†</sup>	-	-	70	-
Nickel	(Ni)	-	50	20	-
Lead	(Pb <sup>2+</sup> )†	-	50	10	0.0097
Antimony	(Sb)	-	10	5 P	-
Selenium	(Se) <sup>†</sup>	-	10	10	-
Pesticides	(separately)	-	0.1	different for each compound	-
	(total)	-	0.5		-
Polycyclic	(PAH)	-	0.2	-	-
Aromatic					
Hydrocarbons	(CTC)	-	-	2	-
Carbon	(TCE)	-	-	70 P	-
tetrachloride	(°C)	-	25	-	-
Trichloroethene		12	-	6.5-8.5	-
Temperature	(µScm <sup>-1</sup> at	6.5-8.5	-	-	-
pH	20°C)	400	-	-	-
Conductivity					

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

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

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

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

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

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

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

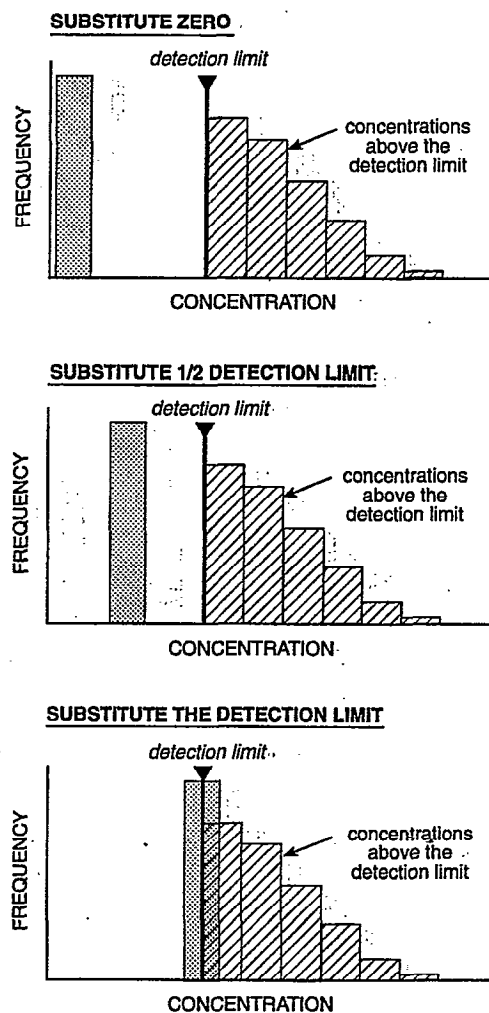
$$<1 <1 <1 <10 <10 <20 <20$$

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

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

The median is still <10.

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



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

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

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

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

## Tables

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

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

## Trilinear diagrams

The trilinear diagram and its projection onto a diamond-shaped diagram is used to summarise the major ion chemistry in each aquifer. Major ion data from each analysis, expressed as milliequivalents ( $\text{meq l}^{-1}$ ) 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  $\text{Mg/Ca}$  ratio). The molar  $\text{Mg/Ca}$  ratio of 1 may also be drawn as a reference line. This is useful since many groundwaters especially in carbonate aquifers trend towards this composition as water approaches equilibrium with calcite and dolomite (see Section A3). Waters with  $\text{Mg/Ca} > 1$  will usually indicate seawater mixing, a source within dolomitic or basic igneous rocks or weathering of Mg-rich minerals.

Some limitations of the plots should be pointed out:

1. The diamond field is of limited value since the  $\text{SO}_4/\text{Cl}$  ratio and the  $\text{Mg/Ca}$  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  $(\text{Ca}+\text{Mg})/\text{Na}$  ratios (but with carbonate mineral saturation being maintained).
2. In carbonate aquifers, the anion trilinear field is of limited value since waters quickly reach saturation with carbonate minerals and thereafter no increase can occur in  $\text{HCO}_3^-$  (except where cation exchange occurs). The main changes of importance are in the  $\text{SO}_4$  and  $\text{Cl}$  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.

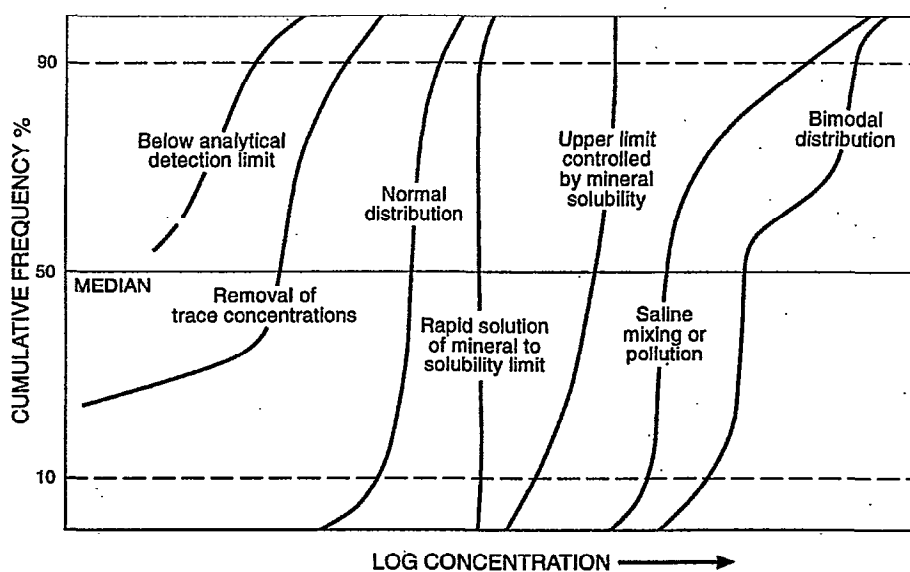
The form of the curve conveys information about the hydrogeochemistry and some of the information to be obtained is shown in Figure A1.2.2.

The most important concepts are:

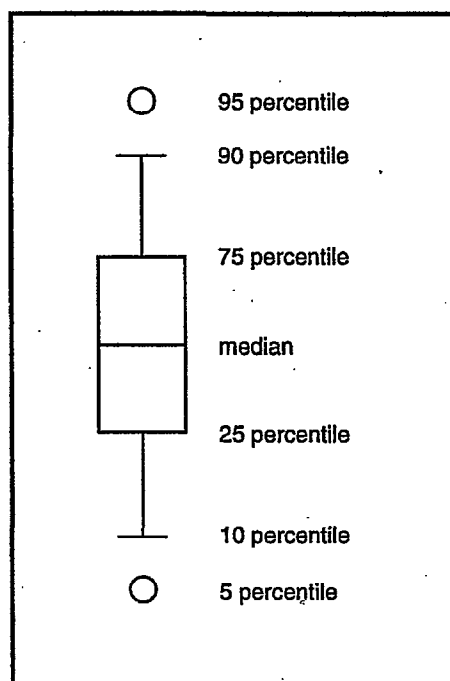
1. The median concentration is used as a single reference point for the element baseline which can be compared regionally or in relation to other elements.
2. Log-normal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence 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

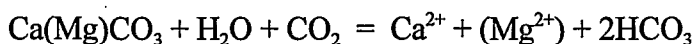
Some of the geochemical concepts and terminology used in the reports are included here as a reference. These terms will be added to in the nationwide report.

#### *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:

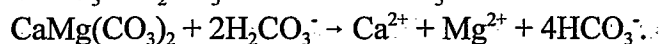
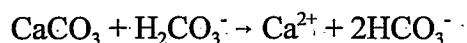


The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone. This process (**congruent dissolution**) yields Ca and Mg concentrations which are identical to those in the dissolving carbonate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

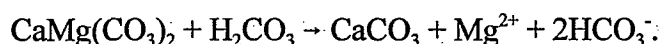
### ***Congruent/incongruent reaction***

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.

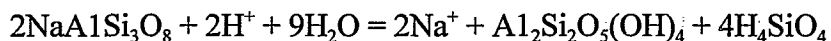
Examples of congruent reactions relevant to the Sherwood Sandstone aquifer are:



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:



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