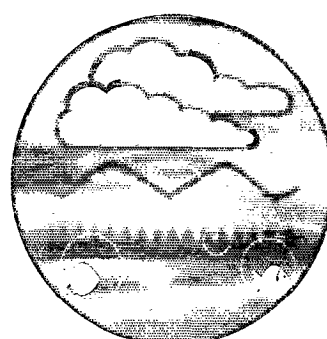
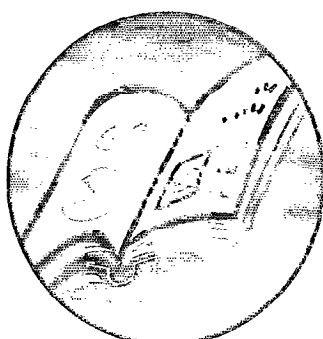
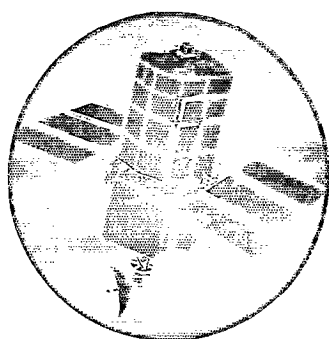


# **The Natural (Baseline) Quality of Groundwaters in England and Wales**

**The Chalk of Lincolnshire**



## **Research and Development**

**Project Record  
W6/i722/5**



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

The Chalk of Lincolnshire

R&D Project Record W6/i722/5

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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## 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 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. Concepts introduced in bold italics in Section II are referred to in Appendix 1.

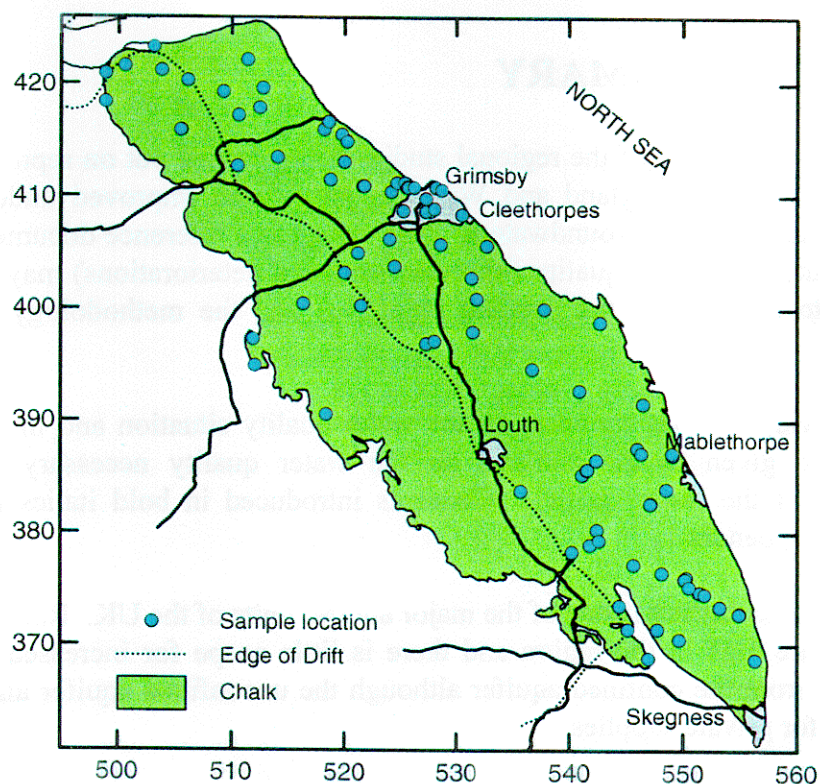
The Chalk of Lincolnshire is one of the major aquifer units of the UK. Rates of abstraction of groundwater are high in the region and there is little scope for increased licensing. Most abstraction is from the confined aquifer although the unconfined aquifer also provides some groundwater for private supplies.

The unconfined aquifer has suffered from diffuse pollution, principally by nitrate, resulting from arable agriculture over the last few decades. At many outcrop locations, groundwaters exceed acceptable limits for nitrate.

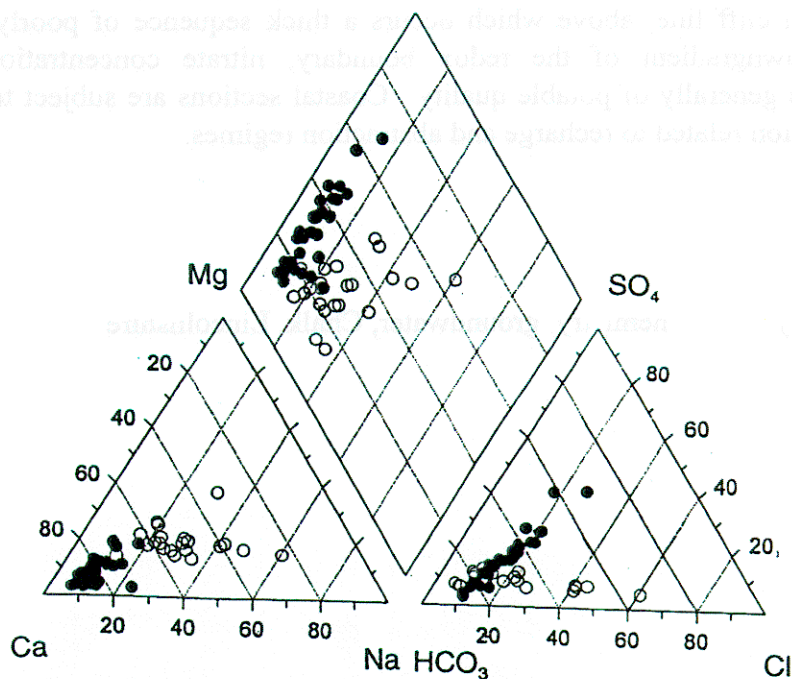
Down the groundwater flow gradient, notable changes in water chemistry occur, influenced particularly by a redox boundary which coincides approximately with the position of the buried Anglian cliff line, above which occurs a thick sequence of poorly permeable Drift deposits. Downgradient of the redox boundary, nitrate concentrations are low and groundwater is generally of potable quality. Coastal sections are subject to varying degrees of saline intrusion related to recharge and abstraction regimes.

## KEYWORDS

Baseline quality, hydrochemistry, groundwater, Chalk, Lincolnshire



**Figure I.1 Geological map of the Lincolnshire Chalk showing western edge of the Drift deposits and sample localities used in this report.**



**Figure I.2 Piper diagram for groundwaters from the unconfined (filled) and confined (open) parts of the Lincolnshire Chalk.**

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

Determinand	Units	Min	Max	Median	Upper baseline	n	Min	Max	Median	Upper baseline	n
		Unconfined aquifer					Confined aquifer				
Temp	°C	9.6	20.2	10.5	14.5	32	9.4	14.0	10.1	13.0	24
pH (field)		6.86	7.50	7.23	7.47	34	7.08	7.82	7.32	7.63	22
DO	dissolved oxygen	<0.1	9.9	6.7	9.2	29	<0.1	3.2	<0.1	3.1	20
Eh	redox potential	204	466	403	450	28	0	290	148	209	20
SEC	conductivity	514	961	692	888	41	456	4230	636	1743	52
Ca	calcium	83	161	115	157	41	4	211	82	144	51
Mg	magnesium	2.1	17.7	5.8	16.4	41	2.1	42.3	15.2	34.4	51
Na	sodium	8.8	31.6	15.4	30.0	41	8.4	542	34.4	235	51
K	potassium	1.1	22	2.0	5.6	34	2.21	10.6	4.41	8.7	22
Cl	chloride	17.4	75.4	35.4	55.5	42	11.0	1100	46.3	479	59
SO <sub>4</sub>	sulphate	7.3	157	50.9	130	41	<10	130	32.1	93.3	52
HCO <sub>3</sub>	bicarbonate	152	374	252	326	41	104	425	304	348	52
NO <sub>3</sub> -N	nitrate	1.5	23.8	9.1	18.2	34	<0.01	0.6	<0.01	0.4	22
NO <sub>2</sub> -N	nitrite	<0.002	0.061	<0.003	0.006	34	<0.002	0.50	<0.002	0.03	22
NH <sub>4</sub> -N	ammonium	<10	870	<30	10	41	<0.01	1650	0.3	776	52
TOC	organic carbon	<1	4.6	1.8	3.9	7	<1	2.6	0.2	2.6	29
Al	aluminium	<0.6	23	<40	3.7	34	<0.9	338	<40	77	22
As	arsenic	<2	10.7	<2	2.5	34	<2	62	16	35	22
As(III)	arsenic(III)	<2	<4	<4	<4	34	<2	42	9	32	22
B	boron	14	63	23	51	34	46	171	92	159	22
Ba	barium	14	268	68	143	34	59	186	101	147	22
Be	beryllium	<0.02	0.04	<0.02	<0.02	34	<0.02	<0.02	<0.02	<0.02	22
Br	bromine	67	227	119	177	34	40	1320	135	593	22
Cd	cadmium	<0.03	0.4	<0.07	0.2	34	<0.04	0.06	<0.07	<0.06	22
Co	cobalt	0.11	0.69	0.17	0.50	34	<0.01	1.9	0.43	1.8	22
Cr	chromium	<0.07	0.32	<0.22	0.28	34	<0.07	0.52	<0.22	0.31	22
Cs	caesium	<0.02	<0.04	<0.04	<0.04	34	<0.02	0.06	<0.04	<0.06	22
Cu	copper	<0.9	38	1.1	13.6	34	<0.4	40	0.07	14.6	22
F	fluoride	90	350	150	246	34	130	1110	230	390	22
Fe	iron	<6	760	<6	143	34	11	6790	757	5837	22
I	iodine	2.3	25.9	4.9	8.5	34	3.2	61	13.4	54	22
La	lanthanum	<0.004	0.03	<0.04	0.02	34	<0.005	0.07	<0.04	0.01	22
Li	lithium	0.97	8.1	2.5	5.1	34	3.6	8.5	5.1	8.2	22
Mn	manganese	<0.03	234	0.09	48	34	4	367	141	355	22
Mo	molybdenum	<0.11	0.53	0.16	0.44	34	<0.1	3.9	0.6	1.7	22
Ni	nickel	1.5	5.2	2.9	4.8	34	0.7	4.3	2.0	3.3	22
Pb	lead	<0.03	1.4	0.23	1.2	34	<0.03	0.96	<0.31	0.90	22
Rb	rubidium	0.34	3.4	0.59	1.25	34	0.5	3.0	1.1	2.8	22
Sb	antimony	<0.08	0.22	<0.09	0.19	34	<0.05	<0.09	<0.09	<0.09	22
Se	selenium	2294	5535	3470	4336	34	4380	6880	5880	6784	22
Si	silicon	189	602	313	453	34	377	1140	570	889	22
Sr	strontium	0.11	0.88	0.26	0.65	34	<0.04	0.29	<0.04	0.16	22
U	uranium	<0.004	0.04	<0.010	0.01	34	<0.004	0.05	<0.010	0.02	22
Zn	zinc	<1	359	5.4	191	34	<2	140	4.5	61	22
δ <sup>18</sup> O	oxygen-18	‰	-5.3	-8.0	-7.5	15	‰	-6.8	-7.7	-7.6	9
δ <sup>2</sup> H	deuterium	‰	-39	-55	-51	15	‰	-50	-54	-51	12

SEC: specific electrical conductance at 25°C. The upper baseline estimate is calculated on the basis of the 95 percentile and corresponds roughly with the upper change in slope (representing outlying chemical compositions) in the cumulative-frequency diagrams (Figures II.4.3 and II.4.4).



## **SECTION II.**

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

#### **1. PERSPECTIVE**

The Chalk aquifer of Lincolnshire is an important source of water supply for domestic, agricultural and industrial use. The area under consideration in this report extends between Barton-upon-Humber in the north-west to Skegness in the south-east and consists of the Wolds outcrop in the western part and the low-lying confined aquifer further east which is buried beneath a thick cover of Quaternary deposits of variable permeability. Agriculture is one of the main activities in the region and agricultural inputs to the unconfined aquifer have been significant in recent decades. Industry is mainly concentrated in the coastal sections (Immingham to Grimsby areas), much of it related to food processing. Southern Lincolnshire is dominated by agriculture and tourism.

This report provides a summary of the chemical compositions of groundwaters in the Lincolnshire Chalk and attempts to recognise likely baseline characteristics of those in the unconfined and confined sections.

## **2. BACKGROUND**

### **2.1 Geology**

The Chalk is a fine-grained (<10 µm) soft, pure limestone comprising around 98% CaCO<sub>3</sub> and formed dominantly by coccolithic fragments. Occasional marl bands and flint horizons also occur (Hancock, 1975). The Chalk of Lincolnshire and Yorkshire is generally more indurated than Chalk from southern England as a result of a greater degree of calcite cementation. Hardgrounds, representing former non-deposition surfaces, are abundant and are commonly phosphatised and/or glauconitised.

The Chalk is divided lithostratigraphically into four distinct formations, in order of decreasing age: the Ferriby Chalk, Welton Chalk, Burnham Chalk and the Flamborough Chalk (Wood and Smith, 1978). The Ferriby Chalk includes the Red Chalk at its base and is a slightly marly chalk with abundant iron oxide. Few flints occur in the Ferriby Chalk but the formation contains a hard shelly limestone band, the Totternhoe Stone. The overlying Welton Chalk is a more massive deposit with flint horizons. Its base is marked by a distinctive thick marker horizon of dark laminated marl known as the Black Band (Plenus Marl). The Burnham Chalk consists of thinly-bedded chalk horizons with abundant flint beds in the lowermost part. The topmost formation, the Flamborough Chalk is a thick (>300 m) well-bedded flint-free chalk with abundant stylolites and marl layers (Rawson, 1992).

The Chalk has a shallow north-easterly dip. Significant subaerial erosion of the Chalk occurred during the Quaternary and a west-east drainage system developed. The erosion produced numerous deep channels etched into the chalk below present-day valleys; these channels often contain thick infills of sand, gravel and clay. A thick sequence of superficial deposits overlies the Chalk in the eastern part of the study area, including Boulder Clay, fluvio-glacial sand and gravel, till, recent alluvium and estuarine deposits. A significant cliffline representing a fossil shoreline was eroded into the chalk during the Ipswichian interglacial period, against which Devensian deposits have subsequently banked up. The base of the Pleistocene deposits consists in large part of chalk rubble mixed with sand and gravel and known as the Chalk Bearings. These are largely representative of shoreline deposits.

Offshore, further deposits of Boulder Clay are usually thick and are overlain by Flandrian sediment largely of sandy composition. However, in the Immingham area of the Humber estuary, superficial deposit cover is thin and chalk occurs within 0.5 m of the sediment surface (McQuillin et al., 1969).

The Chalk is underlain by glauconitic sands of the Carstone and a series of largely impermeable clays of Lower Cretaceous age. The interface between the Carstone and the basal Red Chalk is gradational.

### **2.2 Aquifer Minerals**

The Chalk comprises predominantly low-Mg calcite, with small amounts of clay minerals (mainly illite and smectite) and fine-grained quartz. The clays and quartz usually compose around 1% of the matrix but are higher in the marl bands. Accessory apatite, glauconite and

authigenic pyrite are also present (Hancock, 1975). Pyrite occurs as either minute crystals or as nodules and is more common in the chalk marl facies. Some horizons in the Chalk are phosphatised, the collophane present being either nodular or granular.

## 2.3 Hydrogeology

The Chalk outcrops in the west between South Ferriby and Aby where it forms the undulating upland of the Lincolnshire Wolds at an elevation of up to 150 m above sea level. Eastwards of the Wolds, the Chalk is confined by impermeable Pleistocene deposits, including Boulder Clay. More permeable horizons in the Pleistocene sequence, notably the glacial sands and gravels, allow increased groundwater storage and throughflow. The fossil chalk cliffline forms a major barrier to groundwater flow from the unconfined to the confined aquifer (Allen et al., 1997):

The Chalk is likely to be in hydraulic continuity with the underlying Carstone. The argillaceous Lower-Cretaceous sediments below the Carstone form the base of the aquifer.

There is little surface drainage on the Wolds outcrop but on the confined aquifer, the Waithe Back, River Lud and the Great Eau flow eastwards and northeastwards over the drift deposits and discharge into the North Sea with no hydraulic connection to the confined chalk. Small chalk springs discharge along the interface between the chalk and drift outcrop, particularly along the buried cliffline, and in parts of the confined aquifer where artesian discharges occur through thin or permeable layers of drift. There are numerous public supply wells in the confined aquifer and significant industrial abstractions in the Grimsby and Killingholme areas. Licensed abstraction is around 200,000 m<sup>3</sup> day<sup>-1</sup> in north Lincolnshire but is much lower further south at less than 10,000 m<sup>3</sup> day<sup>-1</sup>. Many sources that were once artesian require pumping today as a result of reduced groundwater levels (Gray, 1950). Little scope exists for further groundwater development in the area (Allen et al., 1997).

Flow is principally via fractures with the high porosity of the Chalk matrix providing significant storage. Few porosity data exist for the Lincolnshire Chalk but Barker (1994) gave values of 20.6%, 14.8%, 20.5% and 29.2% respectively for the Ferriby, Lower Welton, Upper Welton and Burnham Chalk Formations. Porosity is significantly reduced in hardgrounds and marl bands. Permeability is greatest in the zone of present or past water-level fluctuation and decreases with depth as a result of overburden pressures.

There are few transmissivity values available for the unconfined chalk as most abstraction is from the confined aquifer. Confined transmissivities vary between 7 and 4350 m<sup>2</sup> day<sup>-1</sup>, values generally being higher in north Lincolnshire than further south (geometric mean values for north and south being 2347 m<sup>2</sup> day<sup>-1</sup> and 1376 m<sup>2</sup> day<sup>-1</sup> respectively, Allen et al 1997). The values reflect fracturing, developed particularly during the Quaternary sea-level fluctuations and the presence of overlying sand, gravel and Chalk Bearings. Most groundwater flow is concentrated via fractures in the upper 40 m of the chalk.

### **3. DATA QUALITY AND HANDLING**

Data used in this report are derived from both EA and BGS records. Not all water samples investigated have complete analytical results: many of the samples analysed by EA have only been analysed for selected determinands. Of the 65 samples with complete analyses, all had analytical charge imbalances of less than 3.7%.

Statistical summaries have been compiled for groundwaters from the confined and the unconfined (Wolds) sections of the aquifer. The median composition has been taken to represent a best estimate of the likely 'baseline' concentration for a given determinand and the 95 percentile is taken as an estimate of the expected upper limit of the baseline concentration (see Table I.1 and Appendix 1). Values above the 95 percentile limit are outlying concentrations that compose the upper tail of the data distribution in a cumulative-frequency diagram (Figures II.4.3 and II.4.4).



#### 4. HYDROGEOCHEMICAL CHARACTERISTICS

Much hydrogeochemical information was gathered and reported as part of the South Humberbank Salinity Research Project (University of Birmingham, 1978). Some of the observations and conclusions from that report are summarised here. Groundwaters are dominantly of Ca-HCO<sub>3</sub> type but increasing salinity in the coastal zone results from the greater influence of Na and Cl. Box plots showing the distributions of element concentrations are given in Figures II.4.1 and II.4.2 and cumulative frequency diagrams of selected determinands are given in Figures II.4.3 and II.4.4.

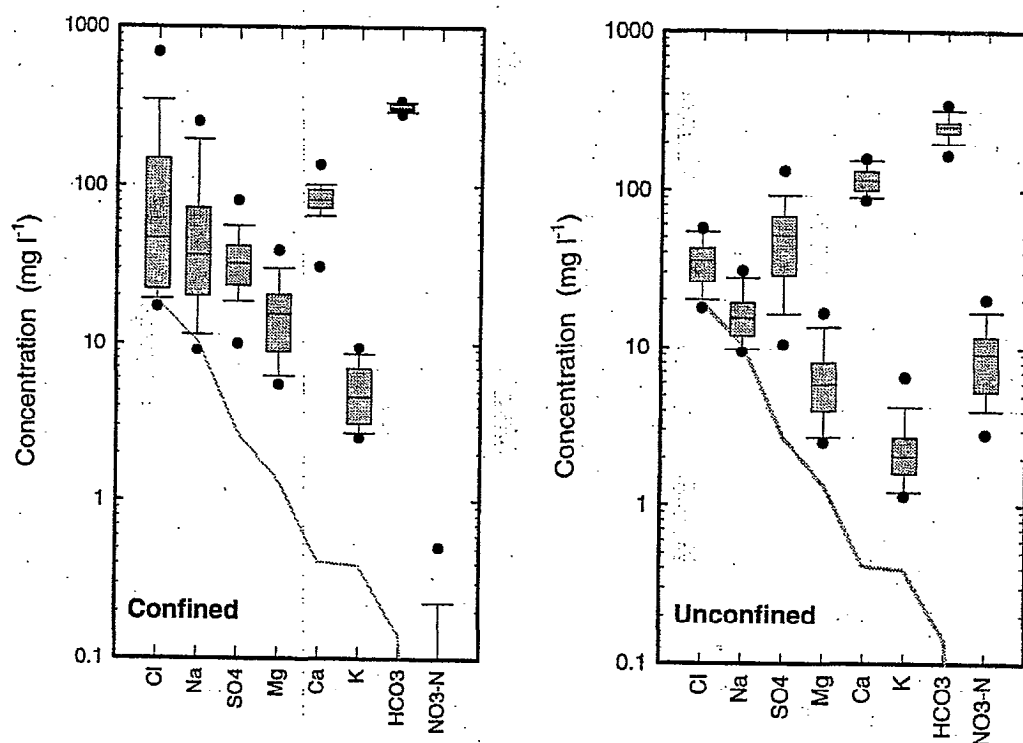


Figure II.4.1 Box plots for major ions from the unconfined and confined parts of the Lincolnshire Chalk.

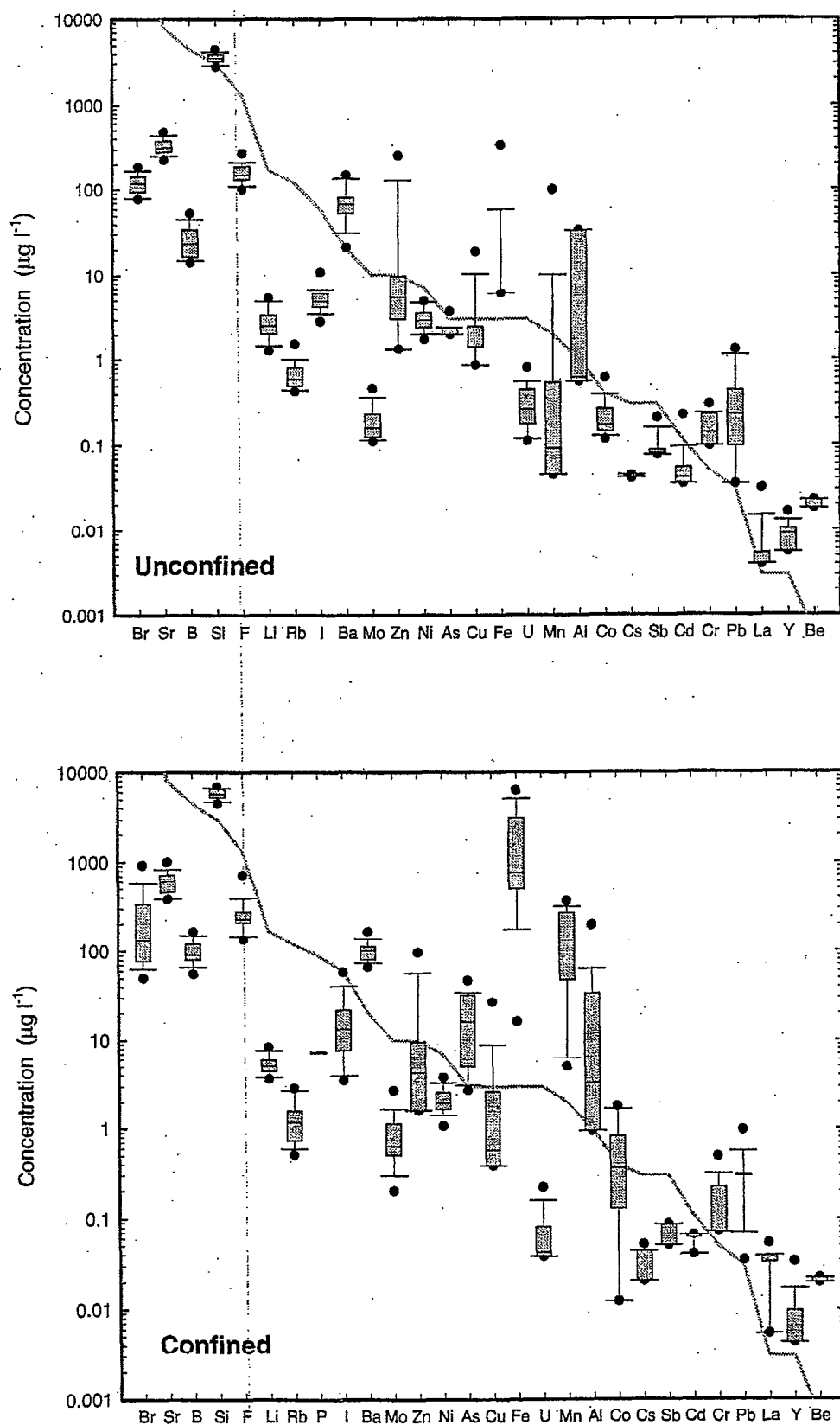
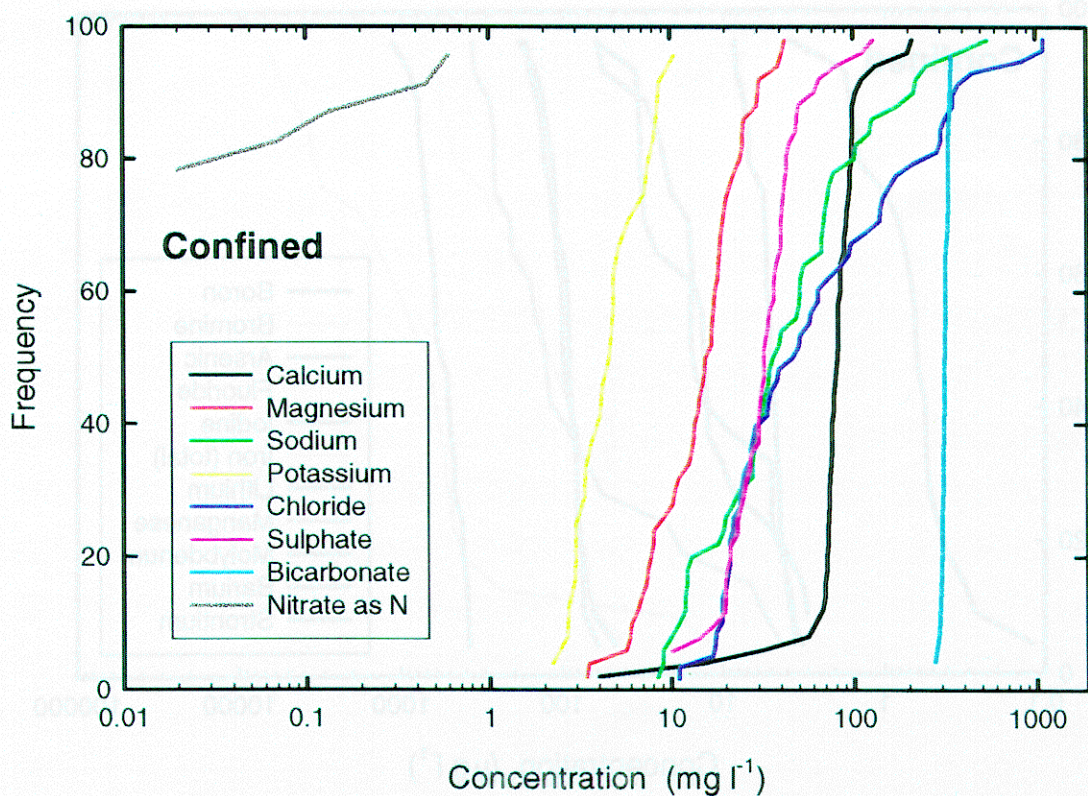
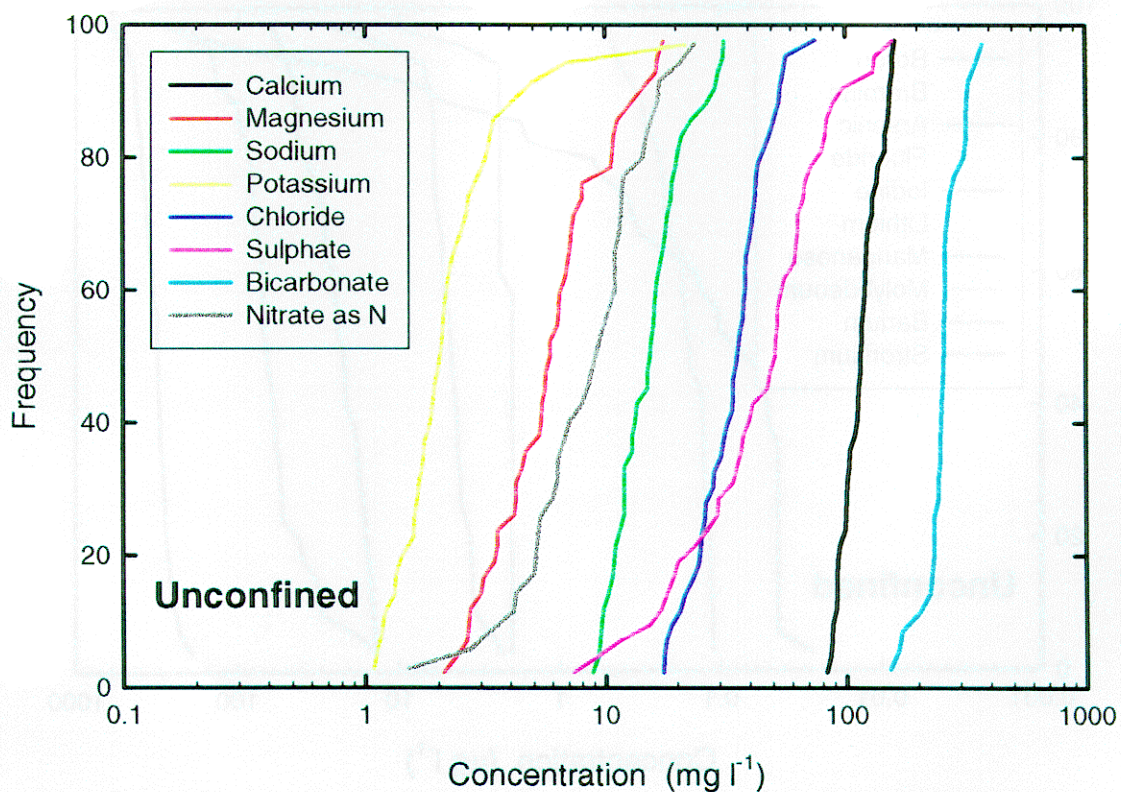


Figure II.4.2 Box plots for the trace ions for groundwaters from the unconfined and confined parts of the Lincolnshire Chalk.



**Figure II.4.3 Cumulative frequency diagram for the major elements from the unconfined and confined parts of the Lincolnshire Chalk aquifer.**



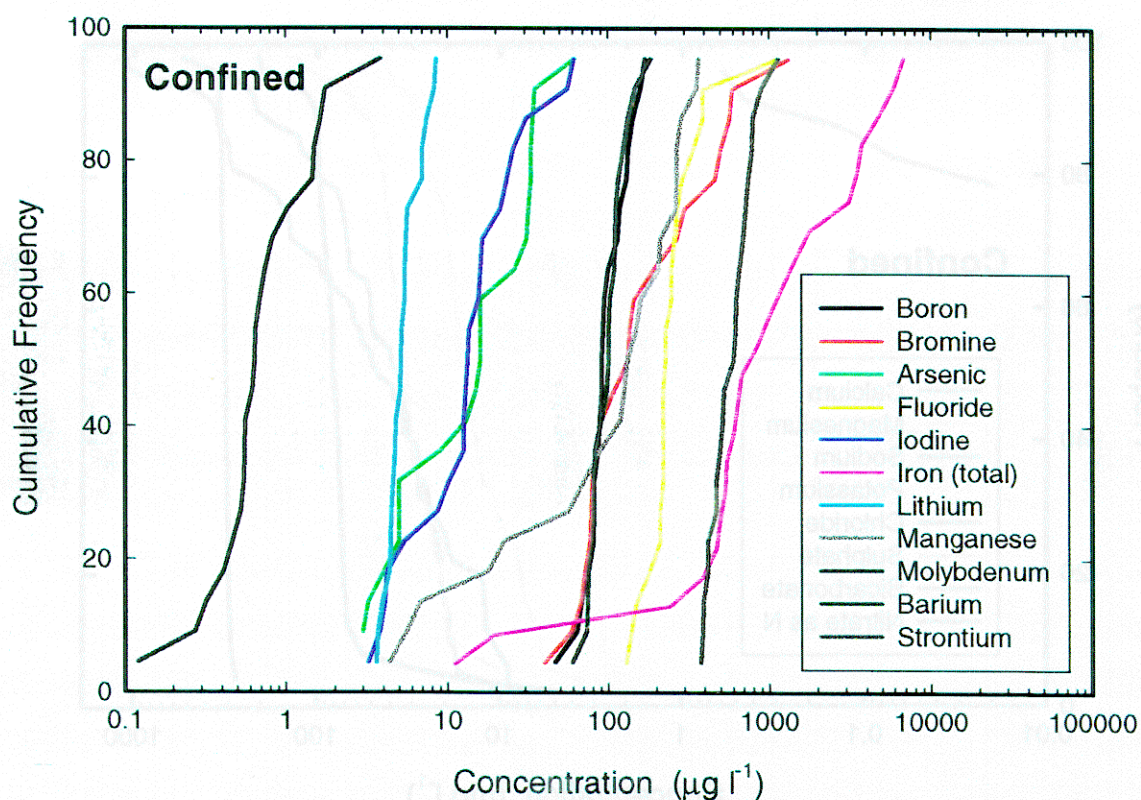
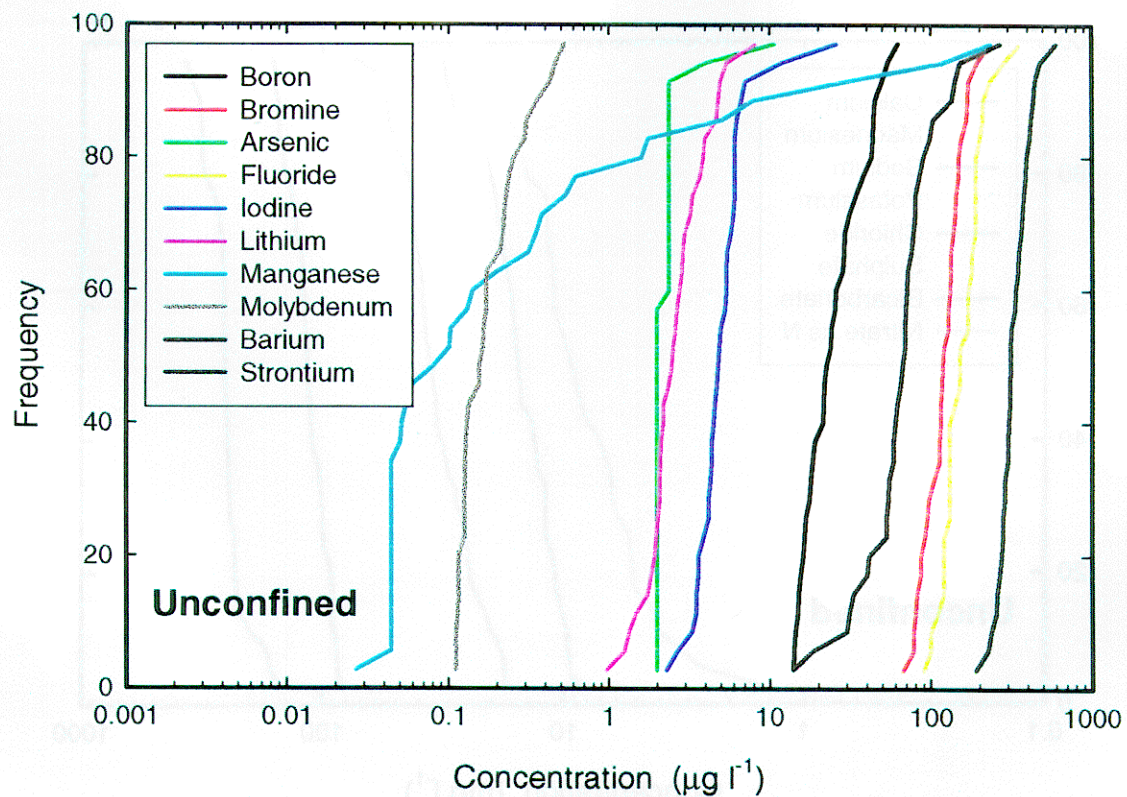


Figure II.4.4 Cumulative frequency diagram for selected trace ions from the unconfined and confined parts of the Lincolnshire Chalk aquifer.

## **5. REGIONAL CHARACTERISTICS AND GEOCHEMICAL CONTROLS**

### **5.1 Pollution Inputs**

Oxidising groundwaters from the outcrop area of the Wolds show the most prominent evidence of pollution from agricultural sources, with elevated concentrations of nitrate, Cl and SO<sub>4</sub> as a result. High SO<sub>4</sub> concentrations have been noted particularly in the unconfined aquifer north of the Caistor monocline and are believed to principally reflect inputs from agricultural chemicals (University of Birmingham, 1978). Nitrate concentrations reach up to 24 mg l<sup>-1</sup> in the unconfined aquifer (median 9 mg l<sup>-1</sup>, Table 1). Histograms showing the distribution of Cl, SO<sub>4</sub> and NO<sub>3</sub>-N are shown in Figure II.5.1. Median TOC (total organic carbon) concentrations are also higher in the unconfined groundwaters than those found in the confined aquifer further east (Table I.1). Industrial pollution is likely to be minor and restricted largely to the Grimsby-Killingholme areas.

### **5.2 Mineral Reactions**

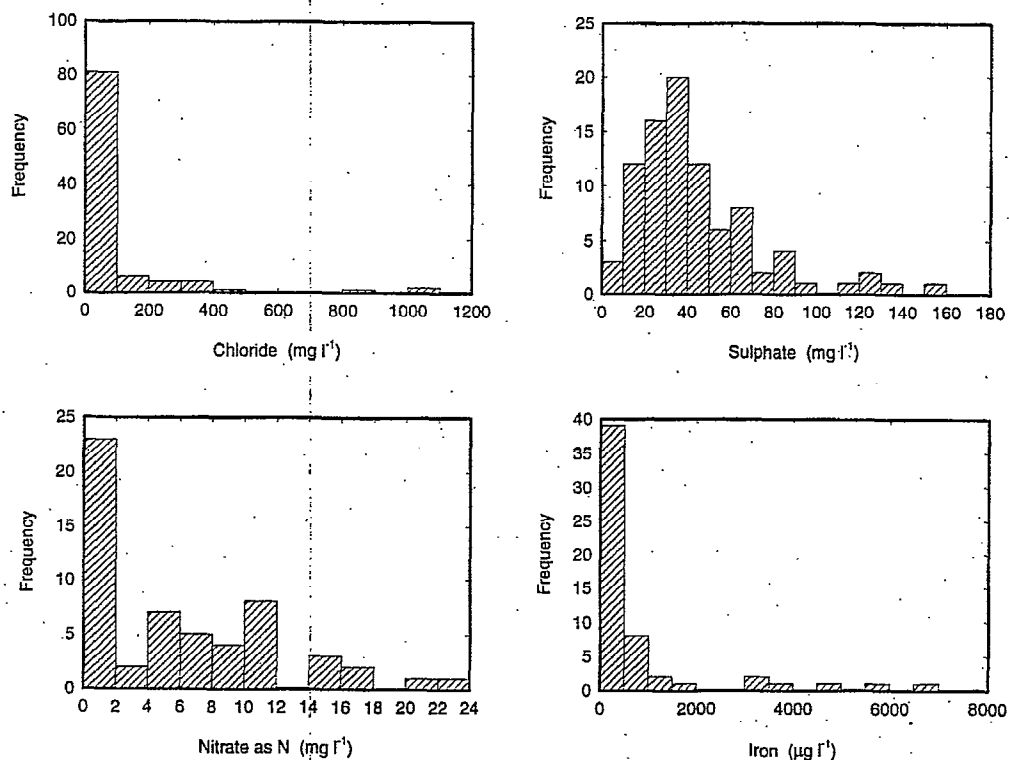
Mineral reactions in the Chalk are dominated by carbonate equilibria. Groundwaters are generally saturated or close to saturation with respect to calcite and dolomite and have strongly buffered pH values and relatively high alkalinity and hardness. Alkalinity concentrations increase downgradient in the aquifer with increasing carbonate reaction. Other important, though ancillary reactions include ion exchange with clays, particularly in the coastal zone where exchange is enhanced by increased ion activities. The most important clay minerals for ion exchange are thought to be smectite and illite, though some exchange with glauconite may also occur. Ion-exchange processes in the saline groundwaters have resulted in elevated concentrations of some trace elements such as F, Sr and possibly also NH<sub>4</sub><sup>+</sup>.

Additional reaction is also likely with pyrite, although concentrations of the mineral are low. Oxidation of pyrite in the aerobic unconfined aquifer leads to increases in SO<sub>4</sub> concentrations, though these are probably minor in relation to SO<sub>4</sub> derived from pollution and saline intrusion. Concentrations of transition metals from the oxidation process are unlikely to remain in solution in the oxidising groundwaters.

### **5.3 Redox Processes**

Groundwaters from the unconfined aquifer of the Wolds area are generally oxidising with high dissolved oxygen concentrations and redox potentials (median Eh: 403 mV, Table I.1). These usually have low Fe concentrations.

A redox boundary occurs in the aquifer at roughly the location of the buried fossil cliffline where Quaternary deposits are banked up against the Chalk and lead to confining conditions. Along this line, springs issue from the unconfined aquifer at surface. Down hydraulic gradient, springs issuing from the Chalk within the drift area are reducing, often with high Fe and Mn concentrations. The distribution of Fe in the Chalk groundwaters is shown in Figure II.5.1.



**Figure II.5.1 Histograms of Cl, SO<sub>4</sub>, NO<sub>3</sub>-N and Fe in groundwaters from the Lincolnshire Chalk.**

Distinct changes in NO<sub>3</sub> concentration occur across the redox boundary, with concentrations of <0.1–0.6 mg l<sup>-1</sup> in the confined aquifer downgradient of the boundary suggesting that some denitrification has occurred in the boundary zone over time. The confined groundwaters have higher concentrations of ammonium (NH<sub>4</sub>) than unconfined groundwaters from the outcrop Chalk and are likely to reflect mainly the influence of denitrification, although some of the NH<sub>4</sub> may result from ion-exchange on clay minerals in the saline groundwaters from the coastal zone (Section 5.2).

One distinct feature of some of the confined chalk groundwaters is relatively high As concentrations, reaching up to 62 µg l<sup>-1</sup> (median 16 µg l<sup>-1</sup>). These are most likely to be derived by desorption from pyrite in the chalk although dissolution from iron oxides which are themselves metastable in the reducing environment is also possible. The concentrations in the groundwaters are below the current EC MAC for As in drinking water but if the limit is reduced to 10 µg l<sup>-1</sup>, as is likely in future revisions of EC regulations, As may become a problem element for water supply and treatment.

## 5.4 Saline Mixing

Coastal parts of the Chalk aquifer show abundant evidence of saline intrusion. Salinity variations are evident both laterally and with increasing depth but the pattern is irregular as a result of lateral variations in Chalk permeability and drift cover. Saline groundwaters (with greater than ca. 100 mg l<sup>-1</sup> Cl) have been identified by the University of Birmingham study (1978) in three main coastal zones: the north-east zone from Barrow to Killingholme, a zone

around Grimsby and in the coastal area east of Louth where saline groundwaters extend some 10 km inland. Relatively fresh groundwater is found in the area of the Kirmington Fjord and between Humberston and Donna Nook (University of Birmingham, 1978).

## 5.5 Residence Time

The Lincolnshire Chalk groundwaters show evidence of increasing residence time with distance downgradient. This is indicated by the presence of recent pollutants in outcrop groundwaters, chemical evidence of progressive rock reaction, diminishing pollutant concentrations further eastwards, and the occurrence of time-dependent processes such as denitification at and beyond the redox boundary. However, few sites investigated in the confined aquifer show compelling evidence for the presence of palaeowater ( $\geq 10,000$  years old). Most stable-isotopic compositions analysed ( $^{18}\text{O}$ ,  $^2\text{H}$ ) are in the range for modern groundwaters (Table 1).

Tritium data collected in 1967 and 1973-1974 (reported by University of Birmingham, 1978) indicate the presence of tritiated and therefore young (post-1950s) groundwater in the outcrop and near-outcrop areas. Non-tritiated groundwater was observed in the coastal section of the aquifer north of Immingham and in the southern part, eastwards of Louth (southern Lincolnshire).

Radiocarbon results (Figure II.5.2 and University of Birmingham, 1978) indicate the presence of modern waters at outcrop and in the confined aquifer to the west of the Pyewipe-Grimsby areas. Some sites in the confined coastal zones give older radiocarbon model ages but those from the northern saline zone north of Immingham do not appear to show evidence for the presence of palaeowater, probably because the Quaternary deposits in the Humber Estuary are relatively thin and allow influx of modern estuarine water to the confined aquifer in this region as a result of prolonged pumping.

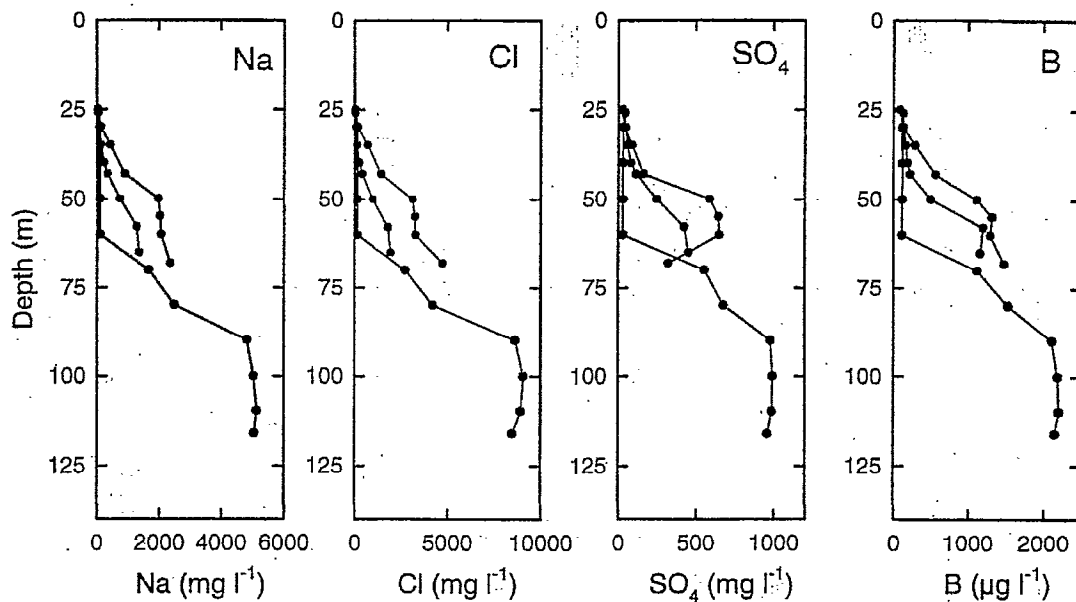
The only palaeowaters identified in the Lincolnshire Chalk are from the saline zone east of Louth. The University of Birmingham (1978) study identified old groundwater (2-3% modern carbon) in the Gayton boreholes as well as in the Theddlethorpe area (Figure II.5.2). Recent BGS radiocarbon data support the evidence for the presence of relatively old groundwater in the confined Chalk east of Louth (Marshchapel to Mablethorpe areas), with radiocarbon activity for some of less than 10% modern. Stable carbon isotope data also show evidence for a greater degree of reaction with the chalk, indicating longer residence time of groundwaters in this zone. In the saline zone east of Louth, chemical, isotopic and hydrogeological evidence suggests that groundwater flow rates are slow as recharge may be inhibited by the thickness of impermeable superficial deposits above the buried cliffline and by the paucity of fractures in the confined chalk at depth. The saline groundwaters east of Louth are therefore taken to be the oldest present in the Chalk aquifer.

## 5.6 Depth Variations

Since the Chalk is considered as a dual-porosity aquifer, the relative importance of fracture flow leads to high potential for rapid penetration of groundwater to depth and mixing of groundwaters of different ages and residence times. Distinct stratification of groundwater quality with depth is therefore not as likely as observed in aquifers dominated by granular flow.





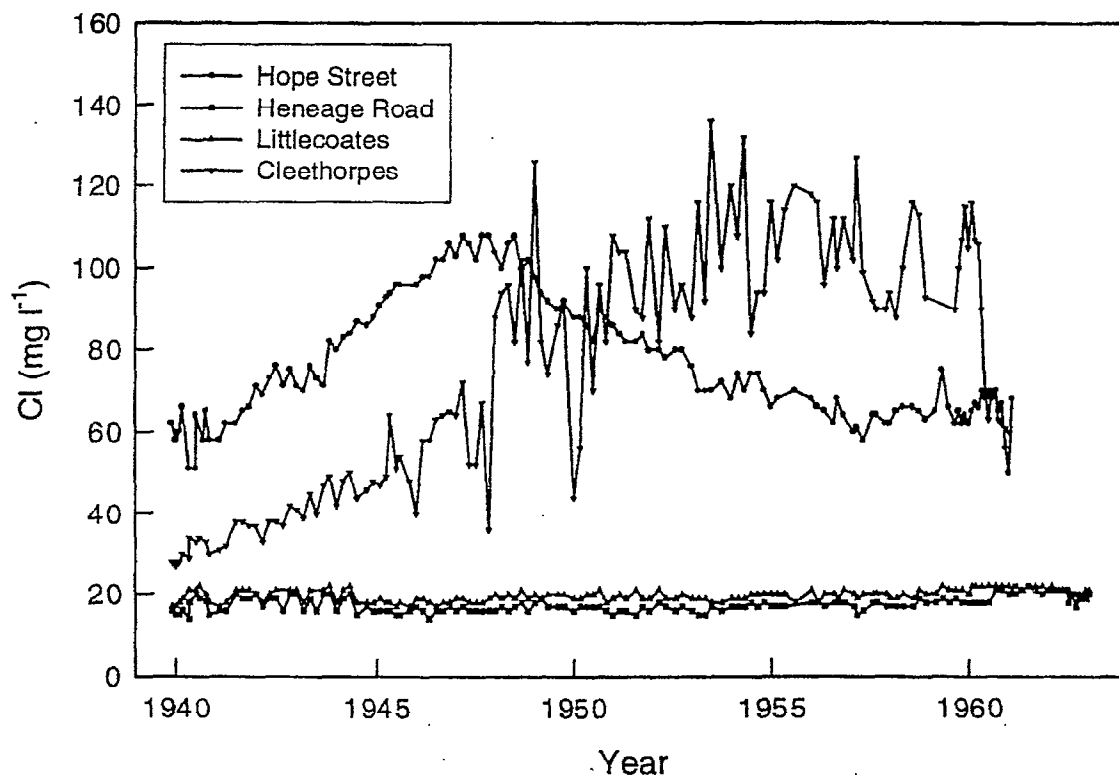


**Figure II.5.3** Variation with depth of selected chemical components in groundwater (depth samples) in three boreholes from Chalk in the Skegness area.

## 5.7 Temporal Trends

In the unconfined aquifer, time-series data indicate that there has been an increasing influence of agricultural pollution on groundwater quality, with increasing concentrations of nitrate in particular over the last few decades. Chloride concentrations in outcrop groundwaters also show some temporal variations. Concentrations were only occasionally above 30 mg l<sup>-1</sup> during the 1950s but became much more common in the 1970s (University of Birmingham, 1978) and are generally around 35–55 mg l<sup>-1</sup> today.

In the coastal aquifer, some groundwaters show evidence of saline intrusion with time, probably related mainly to groundwater abstraction rates. Notable variations in Cl concentration were found in groundwaters abstracted from some coastal boreholes during the 1940s to 1960s (e.g. Hope Street, Cleethorpes, Figure II.5.4). Groundwaters abstracted from boreholes in Grimsby (Heneage Road, Littlecoates) showed an unvarying 'baseline' freshwater Cl concentration of around 20 mg l<sup>-1</sup> or less between the 1940s and 1960s (Figure II.5.4). Concentrations at these sites today are 21 mg l<sup>-1</sup> and >25 mg l<sup>-1</sup> respectively and suggest that some change in water quality has occurred since the 1960s. This may relate to saline intrusion as the sites are near-coastal. However, groundwaters from these sites also contain relatively high nitrate concentrations and indicate that the Cl may be derived from diffuse agricultural pollutants at surface. Increases in Cl with time have also been observed in groundwaters from the Immingham area (University of Birmingham, 1978).



**Figure II.5.4 Temporal variation in Cl concentrations for groundwaters from coastal boreholes in north Lincolnshire.**

## 6. SUMMARY

Groundwaters from the Lincolnshire Chalk show a regional chemical variation affected significantly by the effects of mineral reaction, redox processes, pollution and saline intrusion. Groundwaters from the unconfined aquifer are aerobic and show evidence of pollution especially by agricultural chemicals. Elevated concentrations of nitrate,  $\text{SO}_4$  and Cl result and groundwater compositions are rarely truly representative of baseline conditions. Nonetheless, many determinands are considered unaffected by pollutant inputs (e.g. Ca, Mg, alkalinity, Fe, Mn, trace alkali metals, As) and can be considered as baseline concentrations.

In the confined aquifer, groundwaters are generally of good quality but with elevated concentrations of Fe (and some of Mn). Some of the confined groundwaters from southern Lincolnshire (south of Louth) have relatively high (baseline) concentrations of As (up to  $62 \mu\text{g l}^{-1}$ ) and may require future treatment (in the same way as Fe) if used for public supply given future changes in water-quality regulations.

In the coastal aquifer, saline intrusion is a significant influence with notable intrusion zones in the north-eastern coastal section, Grimsby area and the coastal belt east and south-east of Louth. Depth profiling indicates general increase in salinity with depth in coastal boreholes, but there is some evidence of modern saline water capping older generations of relatively fresh groundwater in the north-eastern coastal aquifer. There is little evidence of ancient palaeowater in the Lincolnshire Chalk but the oldest, most immobile groundwater appears to be in the near-coastal belt of south Lincolnshire (Somercotes to Skegness) where salinity is high, 1970s tritium concentrations are low,  $^{14}\text{C}$  shows the lowest percent modern carbon and flow modelling suggests negligible groundwater movement.

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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 A1.2.1 Determinands selected for baseline quality investigation. Determinands of health significance are given in bold.**

Physical/Chemical Parameters:	pH, Eh, DO, temperature
Major determinands:	Ca, Mg, Na, K, SO <sub>4</sub> , Cl, NO <sub>3</sub> , HCO <sub>3</sub>
Minor determinands:	Organic carbon (TOC), Fe, <b>Mn, F, As, P, Al, NH<sub>4</sub>, B, Cu, Zn, Cd, Ni, Cr, Co, Pb, Ba, Sr, Sb, Be, Hg, Mo, U</b>
Residence-time indicators:	<sup>3</sup> H, <sup>14</sup> C, $\delta^{18}\text{O}$ , $\delta^2\text{H}$ , <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: **<sup>3</sup>H**, **<sup>36</sup>Cl**, **<sup>222</sup>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) <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	
	(total)	-	0.5	each compound	
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:

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

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:

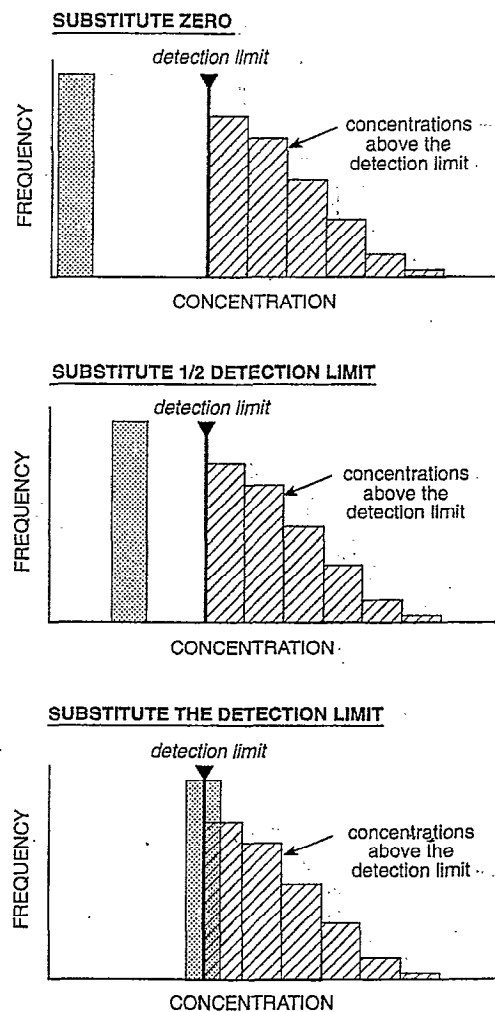
$$<1 <1 <1 <10 <10 <20 <20$$

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  $(\text{Ca}+\text{Mg})/\text{Na}$  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 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.

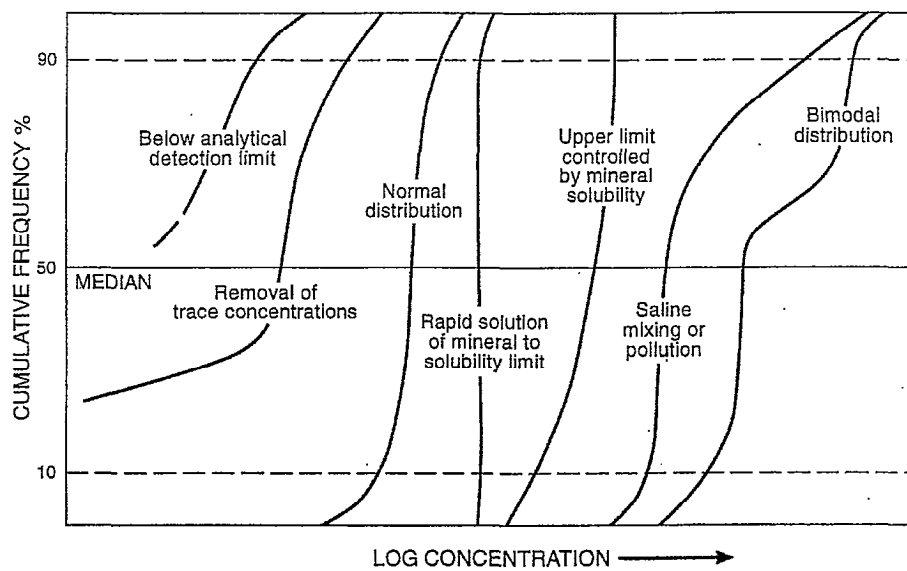
The form of the curve conveys information about the hydrogeochemistry and some of the information to be obtained is shown in Figure A1.2.2.

The most important concepts are:

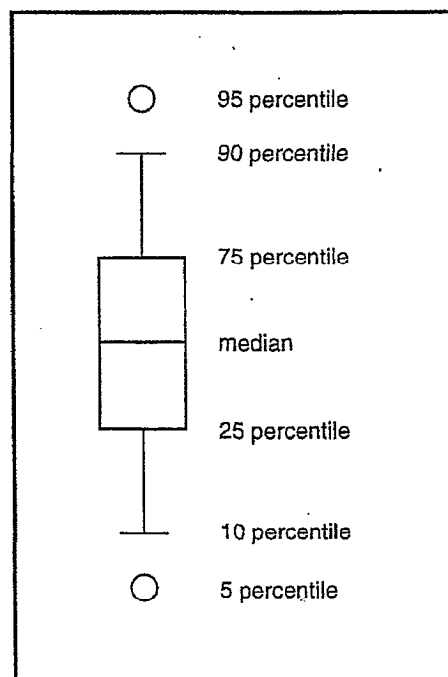
1. The median concentration is used as a single reference point for the element baseline which can be compared regionally or in relation to other elements.
2. Log-normal distributions are to be expected for many elements reflecting the range in recharge conditions, water-rock interaction and residence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

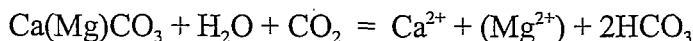
Some of the geochemical concepts and terminology used in the reports are included here as a reference. These terms will be added to in the nationwide report.

### *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:

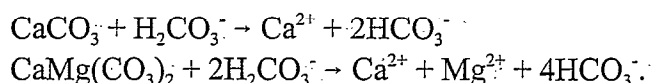


The above reaction is relatively rapid and it is probable that **saturation with respect to calcite** (effectively inhibiting rapid reaction) will occur in the unsaturated zone. This process (**congruent dissolution**) yields Ca and Mg concentrations which are identical to those in the dissolving carbonate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

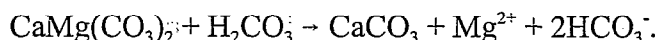
### *Congruent/incongruent reaction*

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.

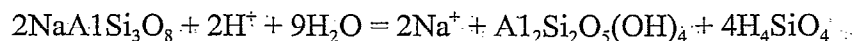
Examples of congruent reactions relevant to the Sherwood Sandstone aquifer are:



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

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**APPENDIX 2. Site locations and details of samples used in this study for regional interpretation and statistical analysis.**

Site and borehole name	EA/BGS Identifier	Grid reference		Data source	Date sampled	Total no. samples in database
Aby House Farm	961745	541780	378950	BGS	06/02/96	1
Alford Road, Mablethorpe	960439	548500	383920	BGS	15/03/96	1
Barnoldby le Beck No 1	961258	524460	403780	BGS	11/06/96	1
Barnoldby le Beck No 2	961257	524460	403780	BGS	11/06/96	1
Barrow No 1	961256	506100	420300	BGS	11/06/96	1
Barton No 1	961255	503800	421200	BGS	11/06/96	1
Beleau Springs	RO3BDTF402783	540230	378330	EA	04/12/95	68
Bilsby	961740	548090	376450	BGS	06/02/96	2
Birds Eye No 3, Grimsby	RO3BDTA280089	528000	408900	EA	03/07/95	22
Birdseye Walls	961517	528020	408920	BGS	24/07/96	1
Blacksmith Spring	961525	498900	420920	BGS	26/07/96	1
Bleak House Farm	961752	549080	386950	BGS	09/02/96	1
Brockhampton	961262	511450	422190	BGS	12/06/96	1
Carters Grimsby	RO3BDTA262108	526200	410800	EA	15/12/95	67
Cherry Valley Farm	961513	516340	300420	BGS	23/07/96	1
Ciba Geigy No 1, Grimsby	RO3BDTA247112	524700	411200	EA	15/12/95	23
Ciba Geigy No 2, Grimsby	RO3BDTA247113	524700	411200	EA	15/12/95	23
Claxby Spring	RO3BDTF451714	545100	371400	EA	04/12/95	68
Conways, Cleethorpes	RO3BDTA305084	530500	408400	EA	03/02/93	6
Croft Farm	961747	554930	372850	BGS	07/02/96	1
Dixon Ltd No 1	961518	531350	402750	BGS	24/07/96	1
Empty Sidings, Imming. Docks	RO3BDTA181159	518190	415970	EA	20/01/93	6
Ex Britag Barton On Humber	RO3BDTA031233	503100	423300	EA	11/12/95	68
Field Farm	961749	549650	370500	BGS	08/02/96	1
Flaxmill Cottages	961744	542430	380280	BGS	06/02/96	1
Fowlers, Theddlethorpe	RO3BDTF490871	549000	387100	EA	07/12/95	56
Fulstow No 2	961242	531440	397970	BGS	10/06/96	1
Goxhill No 2	961254	509300	419300	BGS	11/06/96	1
Grange Farm	961751	545980	387550	BGS	08/02/96	1
Greengate Farm	RO3BDTA006216	500600	421600	EA	02/10/95	23
Grimsby Exchange	RO3BDTA282108	528200	410800	EA	11/12/95	68
Grimsby Fish Meal No 2	RO3BDTA256109	525600	410900	EA	11/12/95	68
Grimsby Fish Meal No 3A	RO3BDTA256108	525600	410800	EA	11/12/95	68
Grove Farm	961523	532150	593880	BGS	25/07/96	1
Habrough No 2	961250	514050	413480	BGS	10/06/96	1
Healing No 2	961248	521730	410910	BGS	10/06/96	1
Healing No 5	961247	521640	410950	BGS	10/06/96	1
Heneage Road No 2	961244	527690	408670	BGS	10/06/96	1
Hop Farmaby	RO3BDTF426793	542600	379300	EA	27/11/95	23
Horkstow Garage Spring	961526	498900	418360	BGS	26/07/96	1
Hydro Fertilisers, Imm'ham	RO3BDTA198155	519800	415500	EA	15/12/95	23
Kirmondy Top Hall Spring	961516	518380	390530	BGS	23/07/96	1
Lake House Thoresthorpe	RO3BDTF456772	545600	377200	EA	07/12/95	11
Libbles Farm, Donna Nook	RO3BDTF427988	542700	398800	EA	13/06/95	11
Little London No 2	961249	518760	411470	BGS	10/06/96	1
Littlecoates No 2	961246	525260	408710	BGS	10/06/96	1
Littlecoates No 4	961245	527270	408690	BGS	10/06/96	1
Loco Bore, Imm'ham Dock	RO3BDTA202148	520200	414880	EA	11/12/95	50
Lowgate Farm	961748	553210	373400	BGS	07/02/96	1
Lt. Cawthorpe Spring	RO3BDTF357837	535700	383700	EA	04/12/95	68
Maltby le Marsh No 1	961738	547160	382660	BGS	05/02/96	1

Site and borehole name	EA/BGS Identifier	Grid reference		Data source	Date sampled	Total no. samples in database
Manor Farm Cottage Spring	961521	521480	400280	BGS	25/07/96	1
Middle Farm	961520	537800	400000	BGS	24/07/96	1
Mill House Farm	961750	547700	371430	BGS	08/02/96	1
Mill Lane Farm	RO3BDTF409927	540900	392700	EA	07/12/95	12
Mossops Marshchapel	RO3BDTA378000	537800	400000	EA	28/07/95	11
Mumby No 2	961733	551400	374670	BGS	05/02/96	2
Mumby No 3	961734	551420	374690	BGS	05/02/96	1
Neeves Farm, Theddlethorpe	RO3BDTF463871	546300	387100	EA	07/12/95	58
Normandy le Wold Spring	961515	512050	394900	BGS	23/07/96	1
Odessa, Beelsby	RO3BDTA200032	520000	403200	EA	30/07/93	16
Oxgangs Spring	961514	511900	397290	BGS	23/07/96	1
Pauls Malt, Grimsby	RO3BDTA273098	527300	409800	EA	19/06/92	29
Ready Mix Concrete	RO3BDTA257108	525700	410800	EA	11/12/95	68
Ross Autby House	RO3BDTA280971	528000	397100	EA	23/10/95	23
Ross Group Grimsby	RO3BDTA287106	528700	410600	EA	25/10/95	23
Ross Young's	961522	527300	396850	BGS	25/07/96	1
SCM Chem No 1 Stall'borough	RO3BDTA200133	520000	413100	EA	15/12/95	23
Scrub Holt Farm	961259	521180	404950	BGS	11/06/96	1
Sturdy Hill Farm	961753	541500	385590	BGS	09/02/96	1
Sturdy Hill Farm 2	960422	541550	385650	BGS	13/03/96	1
Sweet Briar Farm	961260	510610	417200	BGS	12/06/96	1
The White Bungalow	961524	536710	394610	BGS	25/07/96	1
Thornton Curtis No 2	961252	512500	417900	BGS	11/06/96	1
Thornton Curtis No 3	961253	512500	417900	BGS	11/06/96	1
Thurlby No 1	961737	550280	376020	BGS	05/02/96	2
Thurlby No 2	961736	550100	375900	BGS	05/02/96	2
Thurlby Exploratory	960413	550160	375890	BGS	12/03/96	1
Thurlby, Long Lane	960428	550480	375180	BGS	14/03/96	1
Timber Yard, Imm'm Dock	RO3BDTA186166	518580	416650	EA	02/10/95	17
Tioxide UK No 1, Grimsby	RO3BDTA253112	525550	411210	EA	23/11/95	67
Tioxide UK No 2, Grimsby	RO3BDTA253113	525480	411220	EA	15/12/95	23
Tioxide UK No 3, Grimsby	RO3BDTA253114	525350	411210	EA	15/12/95	67
Traves Farm, Chapel St L'ds	RO3BDTF549728	554900	372800	EA	27/11/95	69
Ulceby No 2	961251	510500	412700	BGS	10/06/96	1
United Biscuits, Grimsby	RO3BDTA242104	524200	410400	EA	02/04/92	10
Vines, Saltfleetby	RO3BDTF465915	546500	391500	EA	07/12/95	12
Walk Farm Manby	RO3BDTF423865	542360	386500	EA	07/12/95	12
Weelsby No 2	961243	528580	405760	BGS	10/06/96	1
Well Vale Spring, Alford	RO3BDTF444735	544400	373500	EA	04/12/95	68
Wellfarm Spring	961519	531820	400900	BGS	24/07/96	1
Welton Spring	RO3BDTF469688	546900	368800	EA	04/12/95	68
Westfield Farm	961261	512750	419650	BGS	12/06/96	1
Whitestacks, Ingoldmells	RO3BDTF563687	556300	368700	EA	07/12/95	58
Willowherb, Gt Carlton	961742	541100	385200	BGS	06/02/96	1
Woodland Poultry, Bradley	RO3BDTA240062	524000	406200	EA	23/10/95	23
Wooton Dale	RO3BDTA055159	505500	415900	EA	02/10/95	23
Wooton Dale Bottom	961527	505550	415900	BGS	26/07/96	1
YMCA, Cleethorpes	RO3BDTA327056	532700	405600	EA	28/07/95	11