IRON AND MANGANESE IN GROUND WATERS OF NORFOLK

A thesis submitted for the degree of Doctor of Philosophy of the University of London

By

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Abstract

This research is to study the source of the higher than acceptable levels of iron and manganese in Chalk ground water of Norfolk. Extensive literature survey was undertaken using the records of the Institute of Geological Sciences, the River Division of the Anglian Water Authority, and the Castle Museum in Norwich, for information on existing wells, boreholes and rock exposures in the study area of about 4,745 km^2.

Rock and water samples from the three main aquifers, the Glacial sands and gravels, the Crag and the Chalk, were chemically analysed for iron and manganese. The concentrations of other cations, anions, and of free carbon dioxide, which might influence the iron and manganese concentrations were determined in water samples.

From these analytical results and geological considerations, the following conclusions were reached: that the major sources of iron and manganese in ground waters of the area are the Glacial sands and gravels, and the Crag; that there is a seasonal variation in these concentrations; that the elements are distributed in ground waters according to water depth and to variations in the positions of the lithologies above the Chalk; and that a relationship may exist between iron and nitrate concentrations in the waters similar to that observed in soils.

The recommendations made in order to avoid ground waters with high iron and manganese content are as follows:

1. To locate areas where Chalk is either free from

overlying Glacial sands and gravels, and Crag or separated from sands and gravels by boulder clay.

2. To develop shallow well supplies in areas of Crag and Glacial sands and gravels that are not concealed by boulder clay.

3. To map the iron and manganese concentrations of the waters delineating areas of high 1.1 ppm - 10.0 ppm, moderate 0.64 ppm - 1.0 ppm and low 0.01 ppm - 0.1 ppm iron concentrations.

4. To determine the chemical oxidation states and mineralogy of the iron and manganese.

5. To investigate the relationship between iron and nitrate, and to establish what is responsible for this relationship.

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Mr. Peter Lawrence of the Norwich Castle Museum and Mrs. E. Lailey of the Institute of Geological Sciences made valuable information on rock exposures and existing wells and boreholes in Norfolk available to me. Peter also helped me during rock sampling. These various forms of assistance are appreciated.

Finally, I wish to thank all post graduate research students of the Department of Geology who have been of help to me.

Dedication

To:

My wife Boma and my children

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CHAPTER 1

INTRODUCTION

1.1. Aim and scope of work done

The purpose of this project is to determine the source, distribution, and migration of the high concentrations of iron (Fe) and manganese (Mn) in Chalk waters, within the operational area of the Norwich Water Division of the Anglian Water Authority in Norfolk.

In Norfolk, the Chalk is the principal aquifer and supplies almost ninety percent of all water for industrial and domestic use. However, iron levels and to some extent those of manganese in waters are such that waters are treated for their removal before being distributed for use.

1.1.1. Approach and method of investigation

As a first step, samples were taken from exposures of the three principal aquifer-rocks of the area - the Glacial sand and gravels, the Crag, and the Chalk. These were analysed for their iron and manganese content; based on the knowledge that the chemistry of ground waters is influenced by geology. In the second phase of the work, analyses of water samples from shallow wells and boreholes terminating within the Glacial sand and gravels, the Crag and the Chalk respectively were carried out. The aim of the analyses was to determine their relative content of iron and manganese and to find out the influence of the rock types on the chemistry of the ground waters. In addition the concentrations of other cations and anions as well as that of free carbon dioxide, which might influence the concentrations of iron and manganese in water, were determined.

Check sampling and analyses of Chalk water from selected locations were carried out. These were to determine any difference in relative concentrations of iron and manganese between the summer (1979) and the winter season (1979/80).

Recommendations are made based on a knowledge of the geology of the area and the results of chemical analyses, taking into account the influence of the geology and physical hydrology on these results.

1.2. A geographical description of the area

The study area is part of Norfolk in East Anglia and lies approximately between latitudes 52^{o} 20'N and 52^{o} 55'N and between longitudes 0^{o} 41'E and 1^{0} 46'E.

In the north and east it is bounded by the North Sea, in the south by the county of Suffolk and the River Waveney which also forms a boundary and in the west by the Fenlands.

It covers an area of approximately 4,745 square kilometres (see Fig. 1.1, in jacket at the back).

The greatest proportion of highlands in the area is in the north (i.e. north Norfolk), and the maximum elevation is about 99.7 metres (327 feet) above sea level.

Two ridges are prominent. The first runs in a northwest to southeast direction to as far south as Shipdham and Ovington. The second which is narrower runs in a northeast direction from Guist to the North Sea coast at Cromer; and it is called the Cromer Ridge. The rest of the area lies between sea level and 60.96 metres (sea level

and 200 feet) above sea level. Generally, the land slopes in a northwest to southeast, northwards to the sea from the Cromer Ridge, in a southwest to northeast, and in a west to east direction. Norwich at the centre almost sits in a depression. In the south, the region is low, fairly flat, and undulating. In the Tas catchment for example, ground levels range from about 9.8 metres (32 feet) above sea level at Shotesham Mill to a little over 60.96 metres (200 feet) along the higher parts of the watershed.

1.2.1. Drainage

The drainage of a greater part of the area is eastwards through the rivers Bure, Thurne, Wensum, Weveney, and the Yare.

The head waters of the River Thurne rise very little above sea level and very close to the coast. The river turns southwest to join the River Bure. In north Norfolk the Bure is the largest river. It rises near Melton Constable and terminates at its entry into Breydon Water. Further north are three small rivers: the Burn, the Stiffkey and the Glaven.

South of the area are three comparatively large rivers. These are the Wensum, the Yare and the Waveney. The Wensum has its source on the Chalk hills in the north; the Yare and its tributaries including the Tas, arise further south on less permeable land. At Norwich, the Yare is joined by the Wensum and continues as a single tidal river to Breydon Water. Here, the third river, the Waveney, joins from the south. The Waveney has little Chalk in its drainage from which it can draw water; as a result, its flow is very small in summer.

Most of the rivers of the area have cut their valleys into the Chalk. In addition to these surface valleys there are other concealed beneath the Pleistocene Crag and drift covers. These later ones are the buried valleys and channels, Fig. 1.2. Thus valley features in the Chalk may be divided into four types:-

1. Stream Valleys

These are valleys occupied by present-day rivers and streams. In spite of the considerable thickness of glacial materials, most stream valleys extend into the Chalk. However, the extreme headwaters of some of the rivers and streams flow in shallow depressions on the relatively impermeable Chalky boulder clay surface.

2. Dry Valleys

Most of these are restricted to the western area where the chalk is not overlain by boulder clay. They are thought to have been formed by fluvial processes at times when the water table was at higher levels than at present. They indicate that surface water erosion was important especially during glacial and periglacial periods.

3. Buried Valleys

These are preglacial forms which, due to infilling by Eocene London Clay, Lower Pleistocene Crag as well as by Middle and Upper Pleistocene glacial deposits, no longer have any expression on the land surface.

4. Buried Channels

These are known also as tunnel-valleys in Norfolk. They are deep, steep-sided features that are thought to have been formed by water flowing under pressure beneath Pleistocene ice sheets. Buried channels occur throughout most of Norfolk, and are also common else-

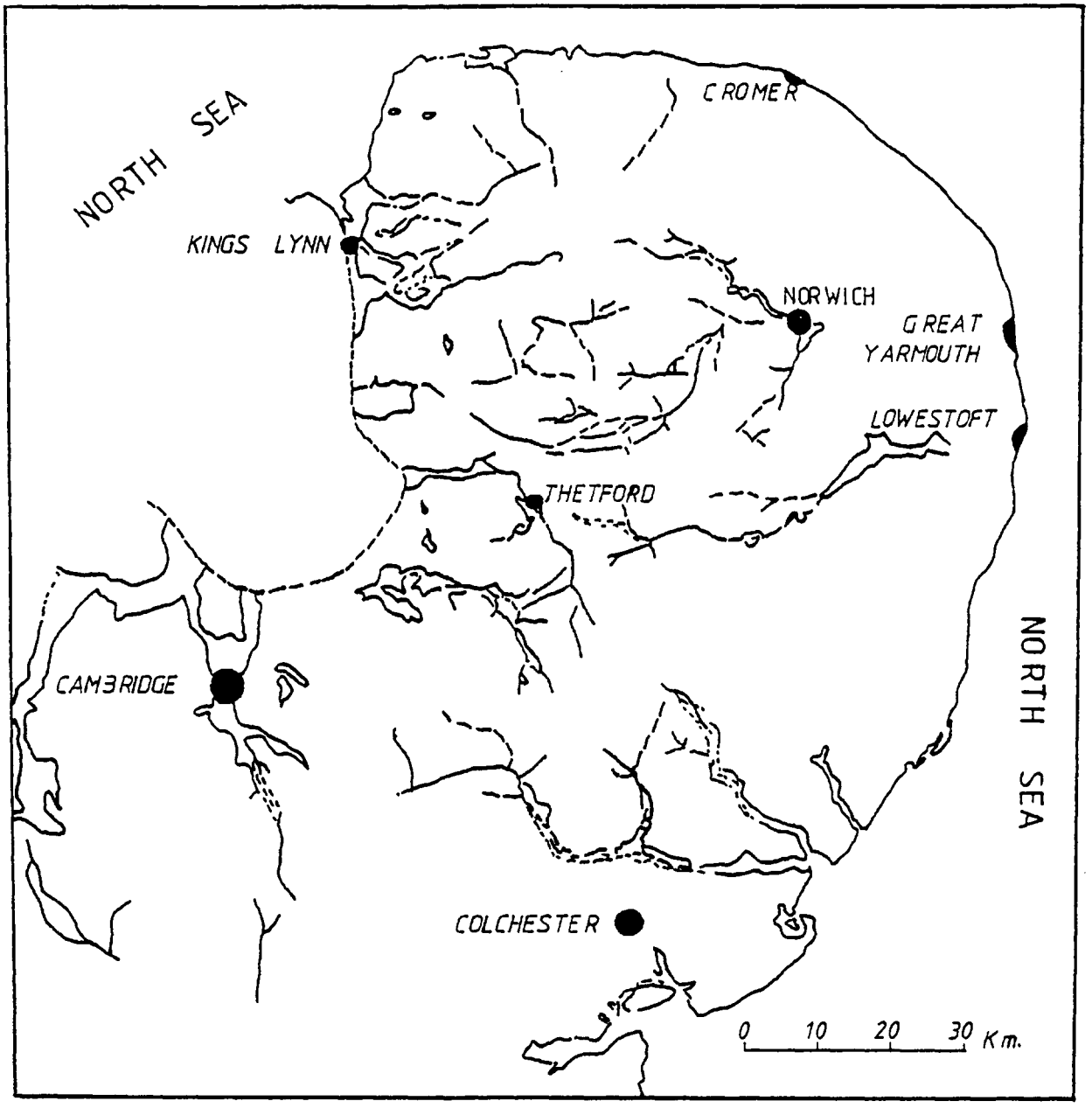


Fig. 1.2 Locations of buried tunnel-valleys in East Anglia (after Woodland,1970)

where in East Anglia (Woodland, 1969); (see Fig. 1.2). Those in the south tend to be oriented from west to east, cutting across the watershed whilst elsewhere they often occur beneath present-day stream valleys.

In general, present-day surface valleys often follow the courses of buried channels. This is possibly due either to the re-establishment of a preglacial drainage route imposed by the general topography of the area, or to the preferential erosion of the less resistant infill of unconsolidated materials.

1.2.2. Climate and Vegetation

The climate is a modified temperate region type with rain all the year round, but with the bulk coming during the winter season. The total annual precipitation in terms of rain and snow varies from year to year. An average of 645 mm was recorded for the period 1916 - 1950. For the hydrologic year April 1979 to March 1980, the average total precipitation based on records for three stations - Old Lakenham, Norwich Cemetery and Norwich Water Works - is 619.3 mm (see Fig. 1.3a). (Meteorological Office, Met. 0.8c). The present project was carried out within this period.

Normally, rainfall in Norfolk is higher on high ground, as for example, along the watershed with the Great Ouse river basin and part of the River Bure catchment. Here, a maximum of just over 700 mm was recorded for the period 1916 - 1950. Towards the south, rainfall is lower. In general, rainfall is high in the catchments of the non-tidal River Bure, the River Wensum and Tud, the non-tidal Yare and the Tas. Rainfall in the Waveney valley is somewhat lower and a narrow

strip of the North Norfolk coast and low lying area of Broadland are relatively dry (East Suffolk and Norfolk River Authority Report, 1971). The effect on river flows and ground water levels of a particular annual rainfall will vary according to the distribution of the rainfall between winter and summer and the rainfall in preceding years (see Fig. 1.3b). The steady rise of ground water levels during the corresponding period of high rainfall - November to March (Fig. 1.3a) is indicative of the fact that part of the high rainfall infiltrated underground into storage. The relative amount of infiltration through overlying strata into the Chalk could have been best determined conclusively using soil moisture deficit. Since data on soil moisture deficit are not available for the study area, it will suffice to assume, based on Figure 1.3b, that part of the effective rainfall infiltrated through overlying deposits. (See Fig. 1.4 for the distribution of observation wells).

Loss of water by evaporation takes place mainly by the action of transpiration by growing plants, but also from open water and wet or moist ground surfaces. All these processes are referred to by the general term evapo-transpiration. The balance of precipitation after deduction of evaporation is referred to as residual rainfall, and it is only this component which is available to provide all river flows and replenish ground water resources. Thus, in areas of high evaporation rates, the residual rainfall is low. East Anglia is included amongst areas of England and Wales having high potential evaporation. Potential evaporation is however higher in the summer than in winter, and in the study area, for at least part of every summer, the potential evaporation exceeds the rainfall.

When a saturated soil with good natural or artificial drainage is allowed to drain, part of the water is removed and replaced

with air. At the end of a period of drainage the water content remaining is approximately constant for the particular soil and this state is known as field capacity. Water can still be removed by the roots of growing crops and plants and when this happens, the amount by which the water content is reduced below field capacity is known as the soil moisture deficit. In Norfolk, the soil moisture deficit in most summers increases to a value which inhibits transpiration at the full potential rate. In consequence the actual seasonal evaporation usually falls below the potential evaporation. The combined effect of high evaporation and soil moisture deficit is that ground water recharge is delayed. Part of the early rainfall will first make up for the deficit and then saturate the top soil (the unsaturated zone), before actual downward flow to the ground water table to replenish ground water takes place.

Run-off in terms of river flow is known to be highest in places where more impermeable boulder clay is encountered, especially in the south of Norfolk. In the north, the catchments of the River Burn, the River Bure to as far as Ingworth, the River Ant and the upper part of the River Wensum to Fakenham Mill Gauging Station are covered by a more permeable type boulder clay or loam. The result is a greater infiltration and retention of rainfall, and low run-off. A flow or run-off of intermediate type is known for Costessey Mill Gauging Station, whose catchment includes both the permeable upstream of Fakenham Mill and less permeable land in the lower section (East Suffolk and Norfolk River Authority Report, 1971). The flow of rivers and the rate of infiltration in Norfolk are to a large extent controlled by the nature of the lithology covering the area, and not by the pattern of agricultural land use.

Table 1.1a. Total monthly rainfall for three stations in Norfolk

Data for 1979 in millimetres

Old Lakenham

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
61.7	*	85.5	62.0	65.2	47.7	19.0	54.9	18.5	34.0	57.3	92.2

Norwich Water Works

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
61.0	60.4	89.2	63.7	55.2	51.5	14.6	58.8	13.5	36.1	60.1	106.9

Norwich Cemetery

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
65.5	64.6	90.0	57.9	62.3	54.8	14.5	56.0	15.7	35.0	61.5	100.6

Data for 1980 in millimetres

Old Lakenham

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
45.9	57.9	48.2	22.7	*	79.2	45.6	23.6	31.3	*	*	*

Norwich Water Works

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
54.4	61.1	48.0	23.7	7.7	83.6	39.9	16.5	32.2	*	*	*

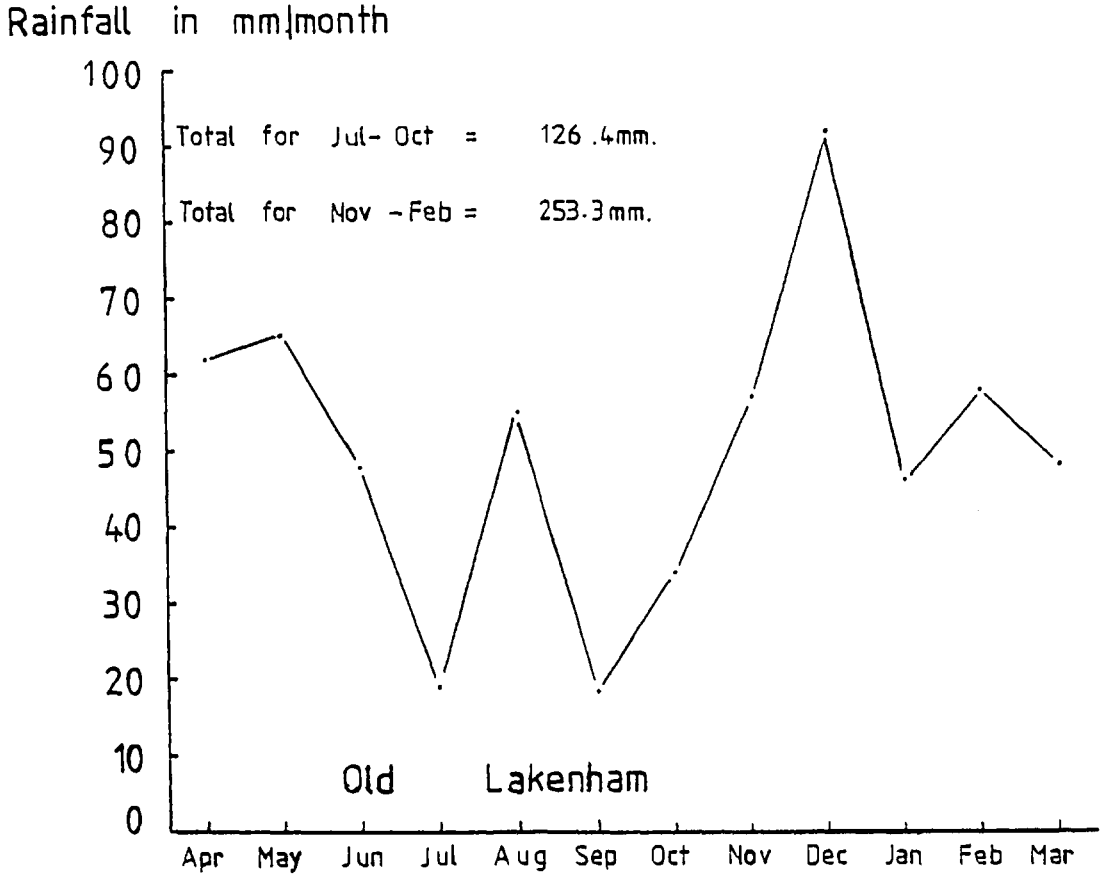
Norwich Cemetery

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
54.7	64.7	53.5	30.0	9.3	84.1	49.4	30.2	34.2	*	*	*

* = Data not available

Total average for the period July - October 1979 = 123.53 mm

Total average for the period November 1979 - February 1980 = 272.43 mm



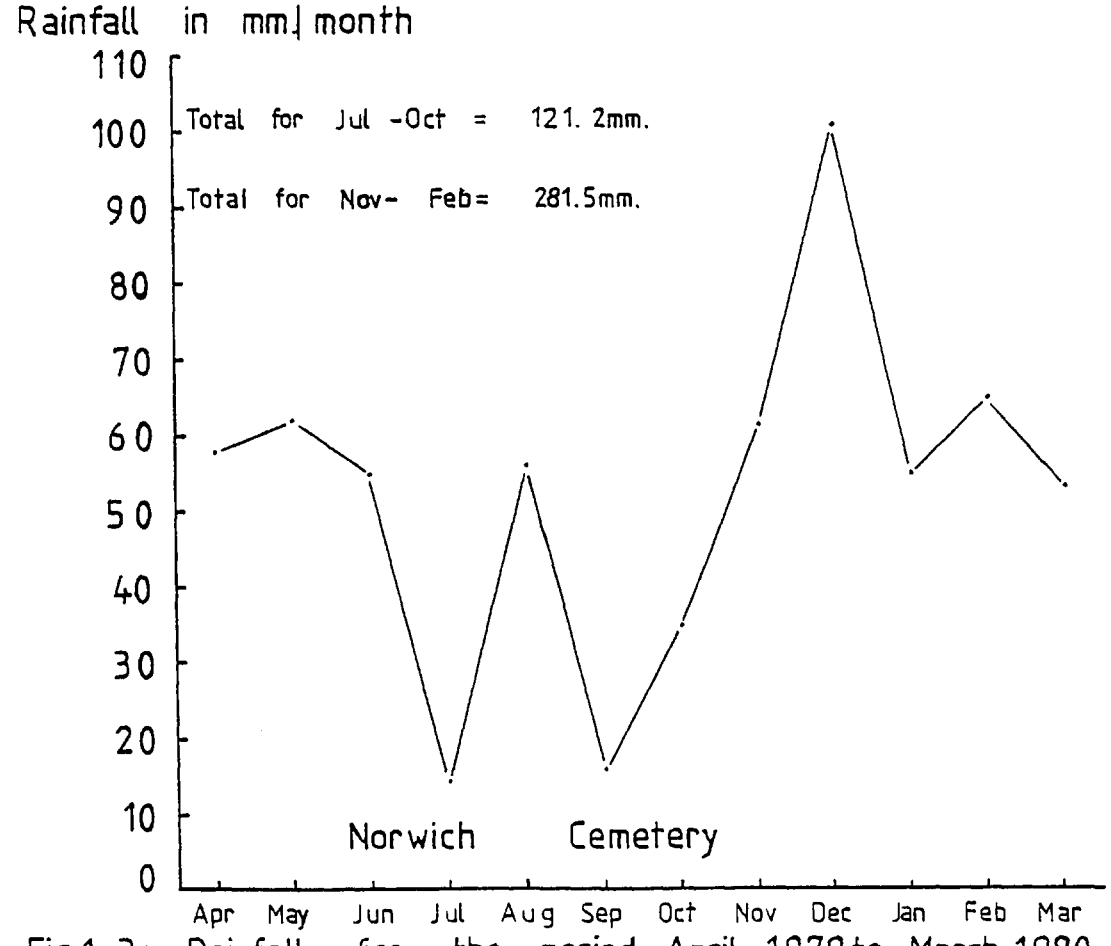


Fig.1. 3a Rainfall for the period April 1979 to March 1980 for two stations in the study area.

Table 1.1b. Monthly Ground Water Levels (metres O.D.N. ie. above sea level) from observation boreholes in parts of Norfolk (1979/1980)

Little Walsingham (the Old Mill) 1979 Chalk aquifer, Well

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
14.82	15.62	15.48	15.39	15.22	15.02	14.89	14.67	14.60	14.52	14.55	14.88
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
14.90	15.08	15.10	15.04	14.76	14.71	14.57	14.67	14.77	14.64	14.81	15.09

Guestwick (Abbey Farm) 1979 Chalk aquifer, Borehole

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
51.07	51.54	51.58	51.53	51.14	50.87	50.47	50.19	50.02	49.86	49.75	49.89
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
50.84	51.13	51.34	50.88	50.45	50.39	50.17	49.97	49.91	*	50.22	50.58

Knapton (No. 4, School Close) 1979 Chalk aquifer, Borehole

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
16.22	16.14	16.45	16.32	16.39	16.28	16.22	16.17	16.13	16.19	16.15	16.24
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
16.48	16.41	16.67	16.19	16.43	16.45	16.39	16.36	16.37	16.29	16.38	*

Neatishead (2-3, School Road) 1979 Chalk aquifer, Borehole

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
3.16	3.20	3.35	3.30	3.38	3.34	3.29	3.21	3.21	3.22	3.18	3.23
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
3.34	3.33	3.40	3.37	2.15+	1.98+	3.29	3.21	3.18	3.20	3.20	*

* = Data not available

\+ = Affected by irrigation pumping

Taverham (Beech Farm)						1979 Chalk aquifer, Borehole					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
8.19	8.49	8.50	8.58	8.41	8.36	8.16	8.23	8.00	8.00	8.00	8.23
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
8.44	8.55	8.47	8.20	8.19	8.35	8.27	8.19	7.99	8.01	8.16	8.20

Sprowston (Grange Farm)						1979, Chalk aquifer, Well					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
18.52	18.71	18.75	18.62	18.59	18.53	18.61	18.57	18.60	18.67	18.77	18.84
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
18.98	18.85	18.92	18.87	18.75	18.74	18.82	18.89	18.78	18.75	18.83	*

Gledeston (Green Bank)						1979 Crag aquifer, Well					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
5.86	6.33	6.33	6.36	6.07	5.95	6.11	6.01	5.78	5.50	5.20	5.63
1980						1980					
Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
5.84	5.96	6.18	5.95	6.12	6.09	5.85	5.83	5.77	5.73	5.72	6.11

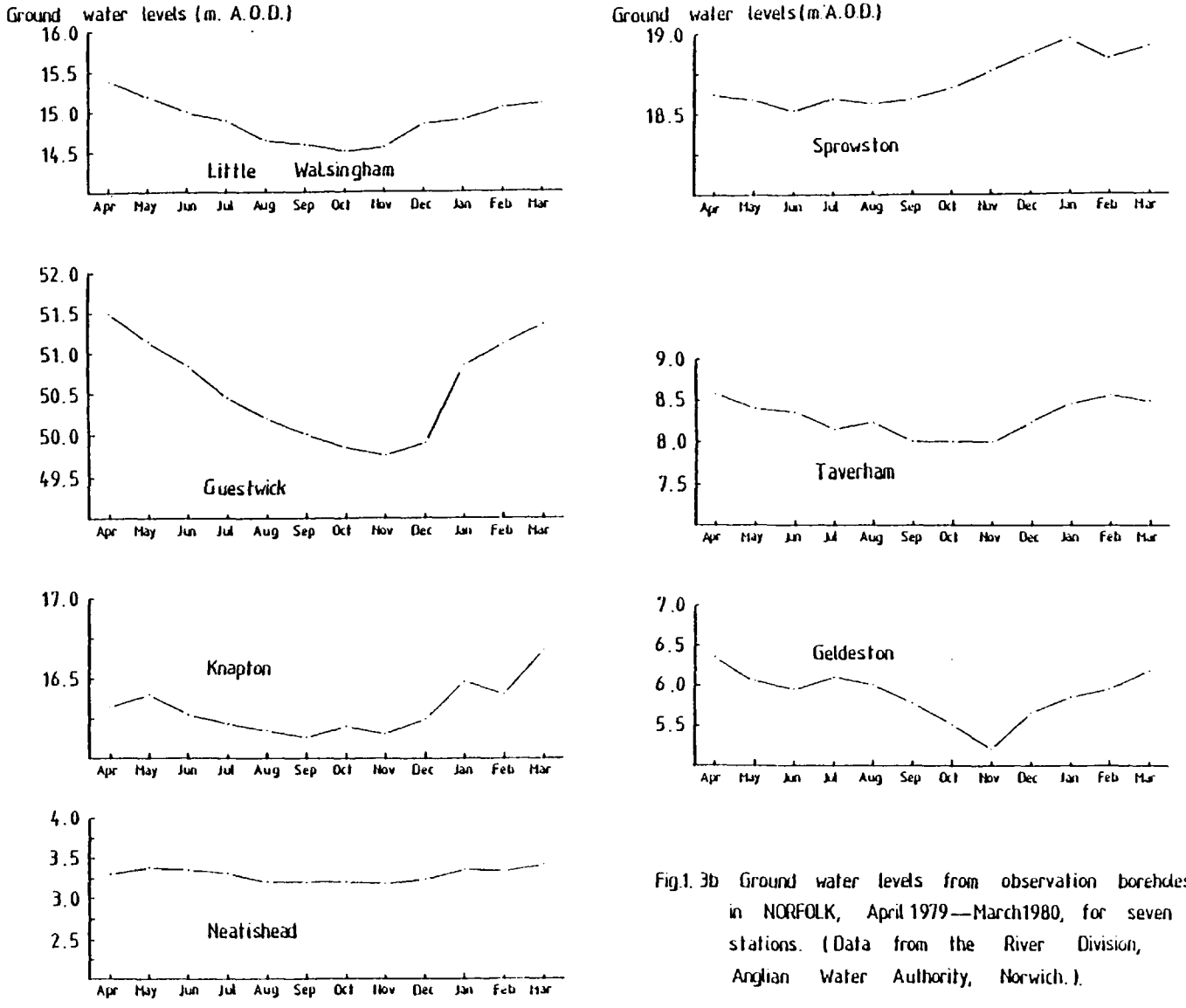


Fig.1. 3b Ground water levels from observation boreholes in NORFOLK, April 1979—March1980, for seven stations. (Data from the River Division, Anglian Water Authority, Norwich.).

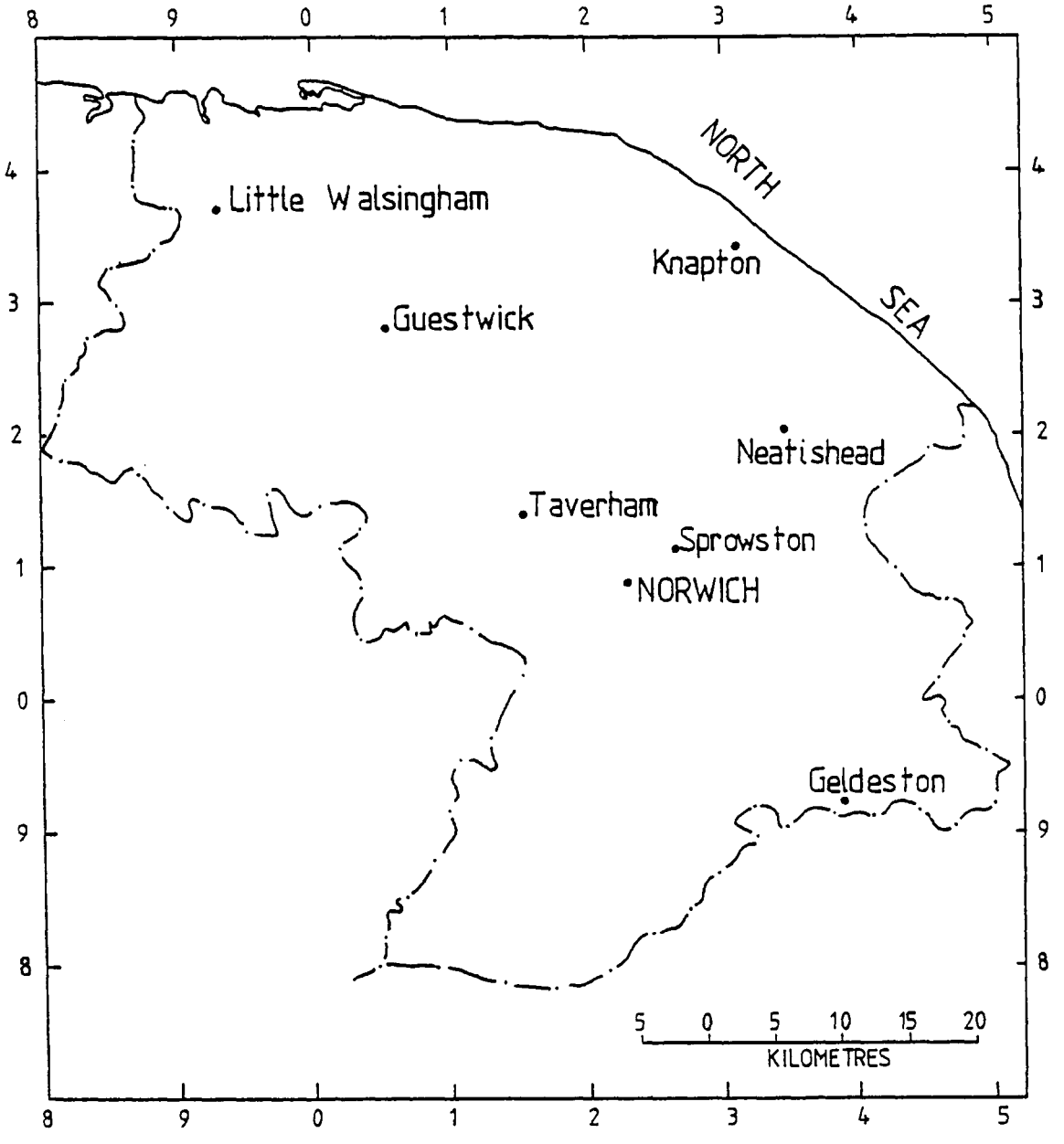


Fig.1.4 Locations of some ground water leveles observation boreholes in NORFOLK.

Most of the natural vegetation has given way to agriculture and to secondary forests called woodlands. Thus, the influence of vegetation on the quality of ground water in the region is expected to be minimal, since large-scale vegetal decay is known to contribute humic acids which enhance the leaching capability of infiltrating rain water. However, in flat, low lying areas of marshland with considerable primary and secondary vegetation, water logging results in increased vegetal decay and so makes organic acids available to infiltrating waters.

The main effect of agricultural fertilizers on ground water quality generally is a relative increase in nitrate concentrations (Young, C.P. and Gray, E., 1978) In the study area, this is not the case since the concentration of nitrate is low, using the World Health Organisation's recommended level as the standard. Nitrate concentrations in this part of Norfolk range between 0.01 ppm and 32 ppm. This is lower than the World Health Organisation's recommended maximum level of 45 ppm in drinking waters (Geneva, 1971).

1.3. Previous studies

Traditionally, most of the studies done on the Chalk and lower Pleistocene Crag have been descriptions and analyses from a palaeontological viewpoint. This results from the abundance of fossils they contain.

Several authors have, however, discussed the sedimentology of the Crag, among whom are Wood (1864) and Dixon (1979).

The whole of Norfolk and East Suffolk have been

investigated by the East Suffolk and Norfolk River Authority (1971). This study was part of a general consideration of water resources and demands of the area. In its report, the River Authority gives a description of the hydrogeochemistry of waters from the Chalk and overlying aquifers. In general, very little is known about the distribution and migration of chemical elements in the ground waters of Norfolk.

The rest of the thesis, in six chapters will deal with the following:

Chapter two, geology, hydrogeology and aquifer conditions of the area. The quality of ground water in this area is believed to have been influenced by the rock types and their relative positions one to another, the hydrogen ion concentrations pH and the redox potential of the environment. It is also suspected that the relative thickness and permeability of the various aquifers play a part in the water quality. Chapter three describes the rock and water sampling, as well as sample preparations for chemical analyses. The aquifer rocks are varied in their geochemistry. It is therefore necessary to determine which of them influences the quality of water most, with regard to iron and manganese concentrations. To do this, samples from the rocks were taken and prepared for analyses. Chapter four deals with the analyses of rock and water samples and presentation of the results. This chapter is a development from the one immediately before. Chapter five discusses the results from chapter four. The discussion is to state from field and laboratory analyses the elements' abundance in the rock types under consideration, and to offer an explanation to this distribution. The chapter also reviews the effects of Eh and pH on the distribution of iron and manganese in the waters. Chapter six considers in detail factors controlling the mobility of iron and manganese, and then a prediction is made of species of iron and manganese in solution based on a critical review of classical works on stability fields for the elements. Finally, in chapter seven, conclusions and recommendations are made based on deductions mainly from chapters four, five and six.

CHAPTER 2

GEOLOGY, HYDROGEOLOGY AND AQUIFER CONDITIONS

2.1. General Geology of the area

The regional geology of Norfolk (within which is the project area) is relatively simple stratigraphically and structurally.

The Chalk, a soft, white limestone underlies the whole area and crops out only over limited areas:

1. in the northwest
2. along the principal valleys around Norwich and
3. along the north Norfolk coast.

It is underlain by older Cretaceous and Jurassic formations which are not exposed within the area under consideration.

In the east, the Chalk is overlain along a coastal strip by Eocene strata, consisting mainly of the London Clay. Overlying the Eocene and overstepping it westwards is the Crag, a sequence of shelly sands and gravels of Lower Pleistocene age.

Virtually the entire area is covered by a blanket of superficial glacial deposits of Middle and Upper Pleistocene age. These are the:

1. Chalky boulder clay
2. Glacial sand and gravels and
3. Loam

As a result of this, the underlying Crag and Chalk are only exposed where subaerial erosion has removed the superficial glacial cover. The mantle of boulder clay covers most of the area except the north and east of Norwich.

Along the river valleys and estuaries, deposits of terrace gravels, alluvium, and peat occur, while beach deposits of shingle and sand are developed at certain localities along the coast line.

The table below gives the succession of formations in the area. However, the succession has been interrupted by erosion so a complete sequence is not found at every locality.

Table 2.1. A geological succession of Norfolk

Superficial Deposits

Series OR Epoch	Stage OR Age	Formation and Deposits	Isotopic Age (million years)
Recent			0 - 0.01
		Brown sand and shingles Alluvium Valley or terrace gravels	
Pleistocene	Upper and Middle		0.1 - 0.7
		Chalkey boulder clay Glacial sand and gravels Loam and brickearths	

Solid Formations

Series OR Epoch		Formation and Deposits	Isotopic Age (million years)
	Lower Pleistocene		0.7 - 1.8
		Leda myalis Bed	
		Cromer Forest-bed Series	
		Weybourne Crag	
		Norwich Crag	
	Pliocene	An Unconformity	Absent in Norfolk
Eocene			38 - 55
		London Clay	
		Woolwich Beds	
		Reading Beds	
Cretaceous			65 - 141
		Chalk	
		Gault Clay and Red Rock	
		Carstone	

2.2. Geology of the superficial deposits

The term superficial deposits is used here for all poorly consolidated materials which range in age from Middle Pleistocene to Recent.

2.2.1. Recent Deposits

These consist of blown sand and shingle and, alluvium and terrace gravels.

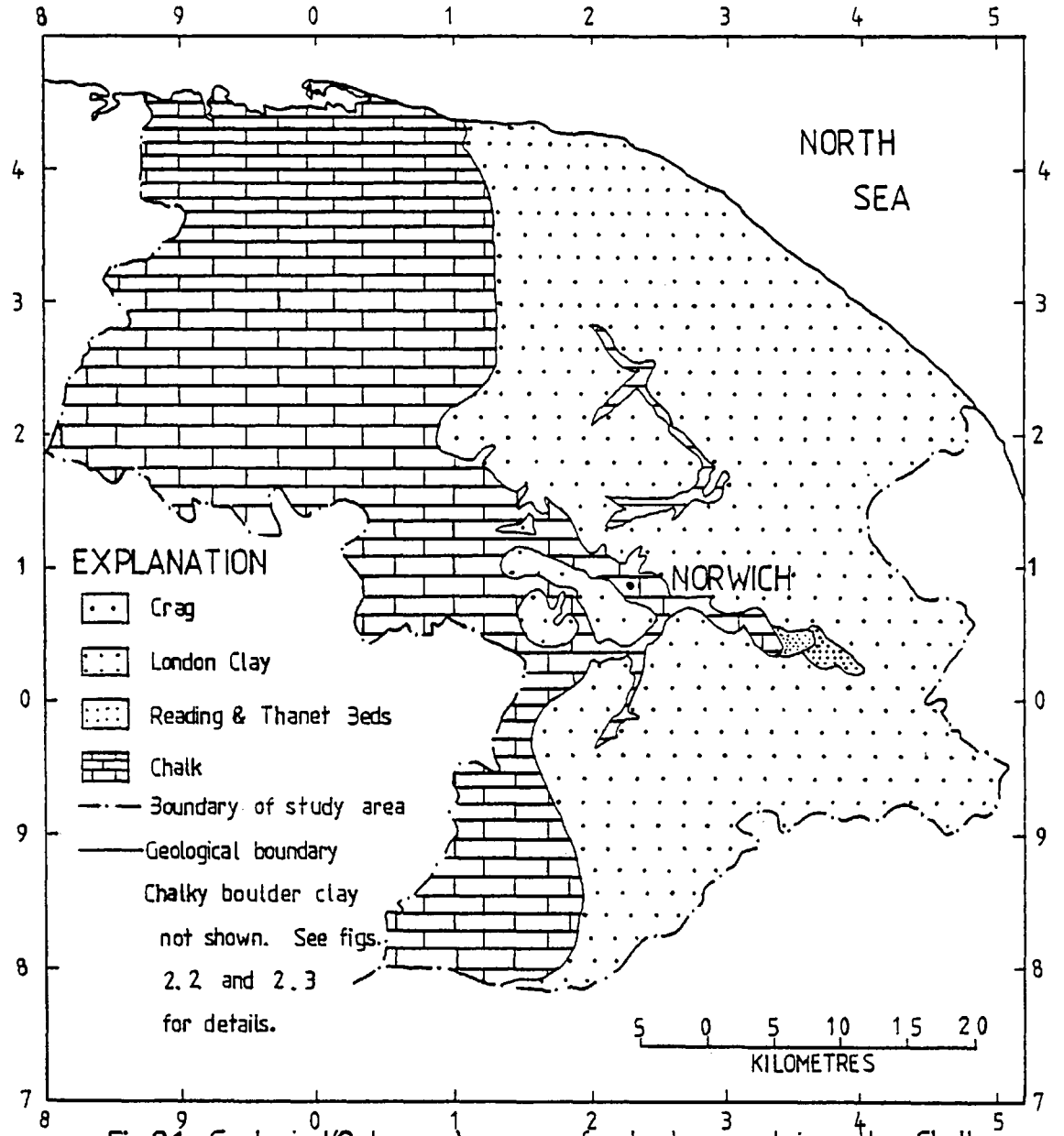


Fig.2.1 Geological(Outcrops) map of strata overlying the Chalk in the study area in NORFOLK.

Blown sand and shingle

At a number of localities along the coastline, blown sand and shingle have accumulated. Isolated deposits occur along the north Norfolk coast but on the east coast dunes of blown sand, which protect the marshes from inundation by the sea, extend over 30 km from Happisburgh to near Great Yarmouth. The southward drift of beach materials is an important feature in the development of the beach deposits south of Caistor-on-Sea.

Alluvium and terrace gravels

In the lower reaches of the valleys of the rivers Bure, Yare and Waveney and in the Broadlands area of Norfolk, are extensive alluvial covers. Similar deposits are found on the north Norfolk coast. The alluvium is a clay or silt or a mixture of these with some sand. It is rarely more than 1.5 m (5 ft) thick in the upper reaches of the valleys but, it exceeds this thickness where the alluvial tracts spread out near the coast.

Gravel deposits up to about 9 metres (30 feet) thick may underlie the alluvium and crop out along the sides of valleys beyond the alluvial plains.

2.2.2. Upper and Middle Pleistocene

These are glacial and interglacial deposits of varied lithology, thickness and distribution; they cover a large part of the solid formations of the study area.

Boulder Clay

In central Norfolk and other parts, this clay tends to be more sandy and chalky, especially in the extreme north, than, for example in south Norfolk and in Suffolk. Flints are common and, more rarely fragments of rocks from Scandinavia, Scotland and the Pennines are found, as well as more local Jurassic and Lower Cretaceous rocks. In addition, large masses of Chalk, one over 200 metres in length have been found contained within boulder clay in the cliffs along the north Norfolk coast. Isolated outcrops of boulder clay are found on Flegg and near Acle, resting on a sand called the Corton Beds. The thickness of the boulder clay varies, but under high ground it is often 36.6 (120 feet) to 45.7 metres (150 feet) and a thickness over 60.9 metres (200 feet) is known.

Sand and Gravels

Lithologically, these are highly varied, ranging from entirely gravel to entirely sand, and mixtures of the two often occur. The bulk of the gravel is of sub-rounded to angular flints, with chalk as rounded pebbles and pellets. Similarly the sands show great variation; they are yellow to brown in colour, may be clean and are usually ferriginous.

The high ground of Cromer ridge west of Overstrand is capped by sand and gravels, usually not more than 7.6 metres (25 feet) thick. Spreads of sand and gravel extend north and south from this high ground and overlie the boulder clays. These deposits extend as far south as the Norwich area.

Loam and brickearths

These, sometimes referred to as the North Sea Drift, underlie the Corton Beds. They consist of brown sandy clays and are widespread at the surface northeast of Norwich, where they are collectively called the Norwich Brickearths (see Fig. 2.3). South of the River Yare to the east of Norwich, the clay becomes rare and its extent into central Norfolk is uncertain.

2.3. Geology of the solid deposits

These consist of the Lower Pleistocene marine Crag, the Eocene London Clay and the Cretaceous Chalk.

2.3.1. The Lower Pleistocene Crag

The Crag in Norfolk consists of a series of marine deposits of Pleistocene age. It contains shelly sands, pebbly gravels and sand with thin seams of clay (see plate 2.1 next page). In the eastern part of Norfolk, approximately northeast of Norwich and in the main river valleys, Crag overlies the Chalk and the Eocene formations (see plate 2.2).

The upper beds, the Leda myalis Bed, the Cromer Forest-beds Series and the Weybourne Crag, occur mainly in the cliffs of the north Norfolk coast, and consist of clay, loams, sand and gravels.

The Chillesford Beds occur in east Norfolk. They consist

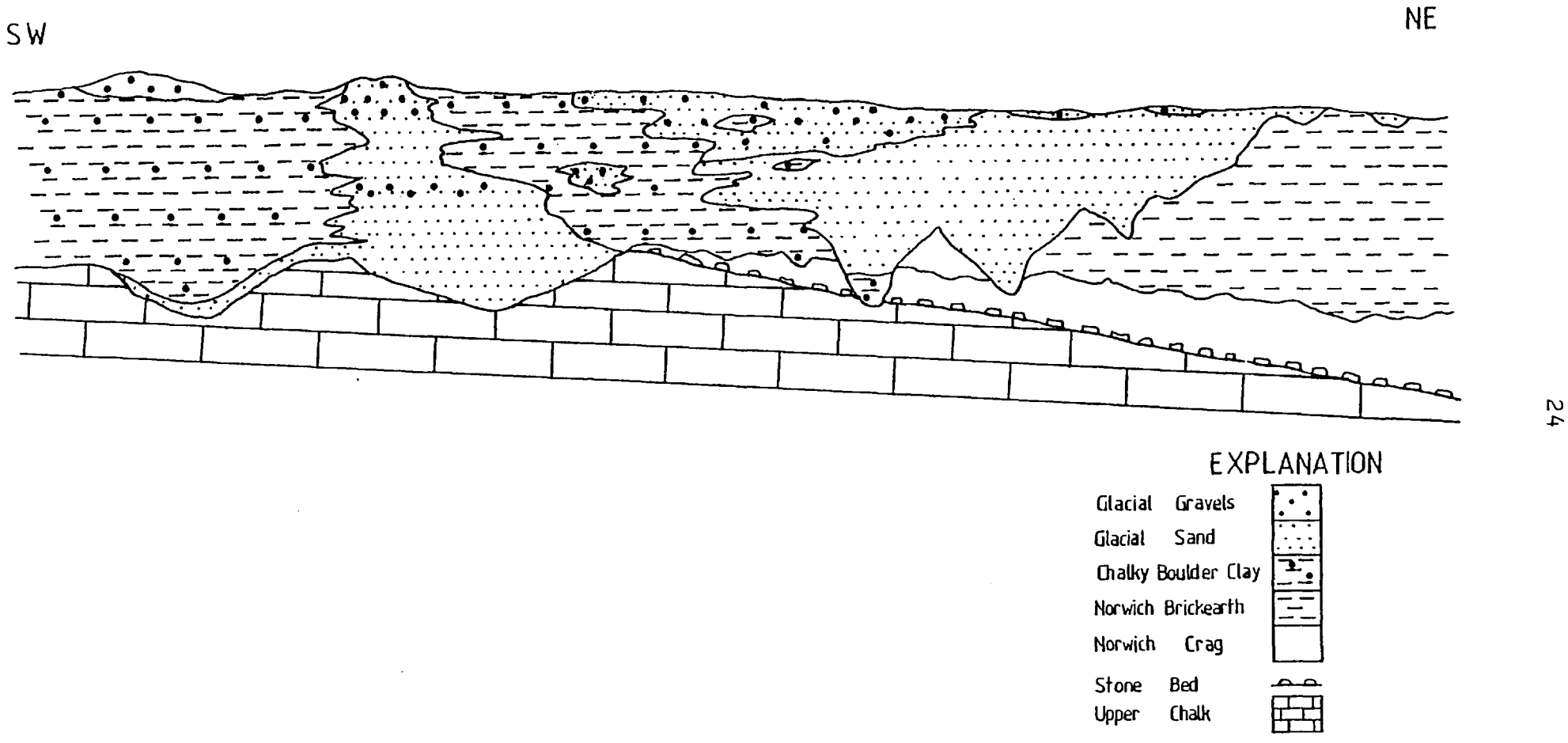


Fig. 2.3 Schematic section across the Chalky boulder clay ice front, showing the stratigraphy of Norwich area
(Modified from Nickless, 1971)



Plate 2.1a. The Pleistocene Crag:Caistor St. Edmund.
Showing:
Clay seams at the top.
Sands in the middle.
Gravels at the bottom.

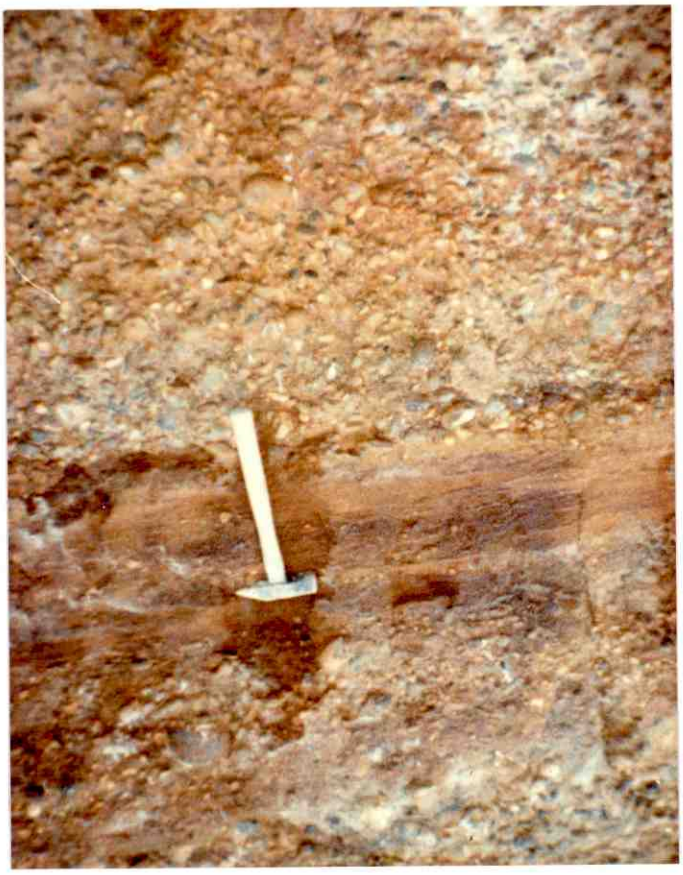


Plate 2.1b. The Pleistocene Crag: Caistor St. Edmund.
Showing:
Well cemented gravels at the top.
Sands, and clay seams in the middle and
Well cemented gravels at the bottom.



Plate 2.2. Showing the Crag directedly overlying partly weathered Chalk at Catton.

of fine micaceous sand overlian by micaceous clays: their total thickness is 7 metres and they overlie the Norwich Crag.

The Norwich Crag extends northwards from Bungay for about 35 km, and westwards for about 30 km from the coast. It is typically yellowish or reddish-brown in colour where it is exposed, but below the zone of exposure it is blue, green or greenish-blue. In places, especially towards the east coast, it is highly fossiliferous. One such place is at Bramerton, the type locality for the Norwich Crag. The Crag thins out westwards and thickens northwards and eastwards to a thickness of over 60.9 metres (200 feet).

Neither the Red Crag nor the Coralline Crag of Lower Plesitocene and Pliocene age occur within the study area, or in any place within Norfolk.

2.3.2. The Eocene London Clay, Woolwich and Reading Beds

London Clay

The London Clay is the highest division of the Eocene in Norfolk. It runs north to just south of Happisburgh. It is a blue-grey or brown impermeable clay containing, in places, interbedded concretionary masses of greyey limestone and nodules of pyrite. The thickness of this formation increases from zero in the west to about 48 metres at Lowestoft (results from borings). At Ludham a thickness of about 11.6 metres is known (Forbes, 1952).

Woolwich and Reading Beds

These underlie the London Clay and extend slightly westwards beyond it. They are of red and white sands with lenses of clay. A thickness of 14 metres of these was proved at Yarmouth and 23 metres at Lowestoft.

2.3.3. The Cretaceous Chalk

The Chalk, a soft, white limestone underlies the whole area and crops out only over limited areas:

1. in the northwest
2. along the principal valleys around Norwich and
3. along the north Norfolk coast.

It is underlain by older Cretaceous and Jurassic formations which are not exposed within the area under consideration.

In Britain, the Chalk has a variation in lithology on the basis of which it is subdivided into three, the Lower, the Middle and the Upper divisions.

The Upper Chalk

This division of the Chalk is the thickest in Norfolk and reaches a maximum thickness of about 305 metres (1000 feet) at the north Norfolk coast. Deep boreholes at Cromer and Matlaske indicated vertical thicknesses of 78 metres and 99.7 metres respecitvely. The highest Chalk zone recorded in England is at Trimmingham in northeast

Norfolk and within the study area.

The Upper Chalk has a hard bed, the Chalk Rock widely developed at its base. Flints occur throughout the division as nodules, tabular layers and as large cylinderical masses known as paramaudras. Flints are usually found along bedding planes or as fillings for joints.

As the majority of wells and boreholes penetrate the Chalk to less than 60 metres, the bulk of the ground water abstracted from the Chalk within the area flows through the Upper division.

The Middle Chalk

This division is about 30 metres thick where it crops out in the northwest of Norfolk and it thickens southwards. Throughout Norfolk, and so throughout the study area, its base is the Melbourne Rock, a very hard, yellowish, rocky Chalk which is 1.5 metres thick and is full of small nodules.

The Lower Chalk

The Lower Chalk is 17 metres thick where it is exposed near Hunstanton in northwest Norfolk and, like the Middle Chalk, thickens southwards. At its base in the northwest, is 5.5 metres of hard Chalk.

Below the Chalk, the Cretaceous is made up of the Gault clay, the Hunstanton Red Rock and the Carstone.

2.3.4. The boundary between the Chalk and overlying strata

The boundary between the Chalk and overlying strata is either sharp, in which case the overlying strata sits directly upon hard fissured Chalk, or gradational, in which case hard fissured rock is separated from the overlying strata by a transitional zone. Three materials occur at the Chalk contact viz: fine sand, coarse sand and gravels or putty chalk.

The contacts between Chalk and very coarse sands and gravels, and fine sands, occur where Glacial sands and gravels or Crag rest directly on the Chalk, as seen at the Caistor St. Edmund quarry in Norfolk. Here the contact is sharp, going from the sands or gravels into the Chalk. In one or two places contacts between sands and gravels or Crag, and the Chalk are gradational, separated by transitional zones of putty chalk. These occur in parts of the Tas catchment (Parvizi, 1977). Putty chalk contacts are most common where the Chalky boulder clay sits directly on the Chalk. Here the separating layer is neither all Chalk nor all boulder clay, but some mixture of the two becoming more chalky towards the Chalk surface below.

These two types of contacts viz. sharp or transitional, should have some influence both on the rate of infiltration of water into the Chalk and on the chemistry of the resulting Chalk waters. Where the boundary materials are coarse water will flow down into storage fast. Also, since such water will spend less time in contact with the overlying strata, the amount of leaching expected will be less than that for slower flows. Where the boundary materials are fine and are putty-like, relatively low permeability will result. Thus, the rate of

infiltration will be low, giving water flowing through them more time in contact with the strata. A greater amount of material will therefore be taken into solution. In these ways, the type of boundary between the Chalk and overlying strata affect the rate of infiltration and the quality of water in storage.

2.4. Geological Structures

After subsidence and the deposition of the Chalk, the area was raised as a landmass, and was acted upon by agents of denudation. It was also subjected to gentle tilting and "folding" at a later stage.

Just before the deposition of the Crag, the whole area became unstable, and movements of the sea floor controlled the nature and distribution of the next marine deposits, the Crag of East Anglia. This event perhaps coincided with the last stage of the opening of the North Sea (Ziegler, 1975).

The known major structures of the area are best expressed in the Chalk. Regionally, the Chalk shows an easterly dip of less than 1^{o}, which appears to increase beneath the Eocene cover in the east.

From south to north, there is a gradual change in the strike of the Chalk. In the south it is west south west, becoming due north and finally north north west in north Norfolk. In addition to these regional changes within the Chalk there are a series of south south west to north north east trending depressions, extending to depths greater than 45 metres below sea level and infilled by Crag materials.

Their southern extension is as far as Stowmarket. These have been interpreted as synclinal basins due to folding developed under conditions of continual subsidence during the deposition of Norwich Crag (Woodland, 1946). It is also possible that these depressions associated with the opening of the North Sea are features, possibly faults related to the predominantly E-W expansion of the North Sea and have since been excavated as troughs either by erosion or by collapse associated with Karst. There is also an apparent uniform plain, inclined gently eastwards from about 30 metres above sea level in the west to about 15 metres below sea level in the northeast; in the south, it is at sea level. In north Norfolk the plain undulates about the NE-SW trending Cromer Ridge, in a northwest to southeast direction. This undulating surface underlies the Weybourne Crag in the north and appears to be distinct from the surface overlain by the Norwich Crag, further south.

The inclined plain west of the depressions probably represents a peneplain developed in the Chalk during the Palaeogene-Pleistocene interval, and inundated by the Norwich Crag Sea. Its inclination may be partly due to downwarping towards the centre of the North Sea basin subsequent to its inundation.

2.5. Hydrogeological significance of deposits overlying the Chalk

The hydrogeological character of the area depends to a large extent on the glacial deposits. This is because of their influence on the quantity and quality of water they permit to infiltrate through

them into the underlying aquifers. In places, these deposits also produce semi-confined conditions in the Chalk. Thus, in general, aquifers in the area are confined, semi-confined and unconfined. Because of this influence, the distribution, thickness and lithological variations of the glacial deposits are of importance.

The study area can be divided into three broad zones based on variations in the composition of the glacial deposit - the Chalky boulder clay (see fig. 2.4 in jacket at the back).

1. Northeast of a line from Holt drawn through Saxthorpe, Norwich, and along the River Yare through Reedham and finally to Lowestoft, large areas of sands and gravels are exposed, especially along the Cromer Ridge and south of Holt to Norwich. In the northwest sands and gravels overlie Chalky boulder clay, but east of a line from Sheringham to Reepham they overlie sandy clay (the Contorted Drift) containing chalk fragments and lenses of sand and are thus permeable.

2. This is the area bounded to the east by the exposure of the Contorted Drift and to the south by a line through Bintree and Reepham. Here, the boulder clay has a chalky and less sandy matrix; it is thus light and only slightly permeable.

3. South of the Bintree to Reepham line and northwest and north of a line from Diss to Beccles is the third area. The boulder clay is dark and heavy, consisting mainly of clays with very little sand. It is less permeable than the boulder clay to the north.

The Chalk, which is the principal aquifer in the area, is almost entirely obscured by the boulder clay, the Lower Pleistocene

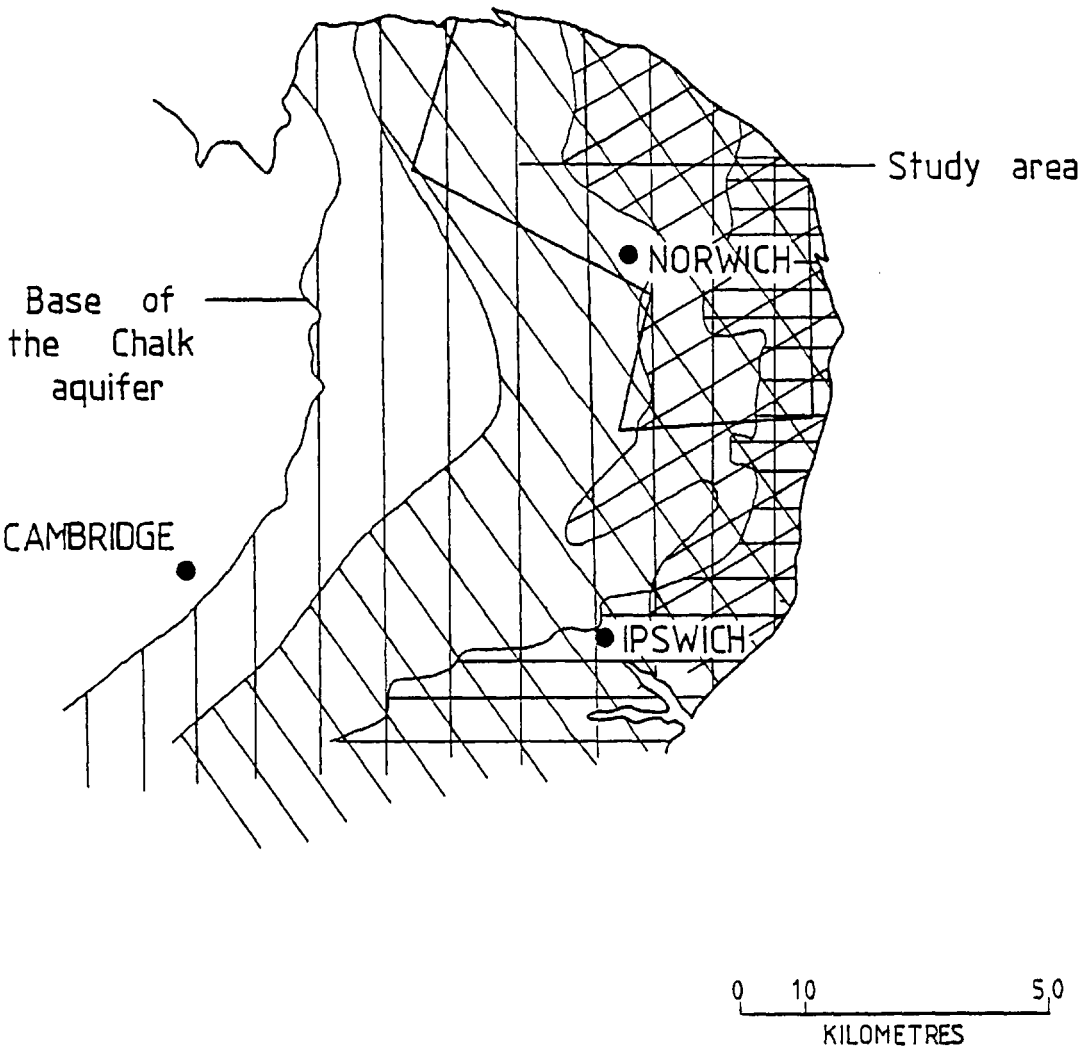
Crag, and the glacial sands and gravels. These last two deposits are in hydraulic continuity with the Chalk and to a large extent with each other, so that together they constitute a single aquifer over a greater part of the area.

Beneath the major topographic divides where the Chalky boulder clay directly overlies the Chalk, ground water in the Chalk aquifer is partially confined by the boulder clay. True confined conditions occur in the Chalk in the east, where the Eocene London Clay is the confining bed.

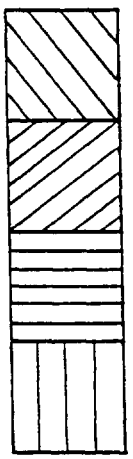
East of the western limit of the Eocene deposits (see fig. 2.5), the Crag is separated from the Chalk and forms the second most important aquifer.

Apart from these two, there are several minor aquifers which are of local importance. The Glacial sands and gravels overlying the boulder clay in the north provide some small supplies, while valley gravels have been partially developed in places. In the Waveney valley they have been developed for public water supply.

The ground water resources of the Chalk aquifer are derived from rain water infiltrating through overlying deposits, especially where these are considerably permeable, as for instance where the Crag as well as the Glacial sands and gravels directly overlie the Chalk. Some recharge is also derived from the west and southwest of the area where the Chalk is exposed (see Fig. 2.6). This is especially so for the Norwich area and the Tas catchment (Parvizi, 1977).



EXPLANATION (In descending order)



Glacial Drift

Norwich and Weybourne Crag

London Clay

Upper Chalk

Fig. 2.5 Location map of the Chalk and overlying deposits in East Anglia (after Parvizi, F., 1977)

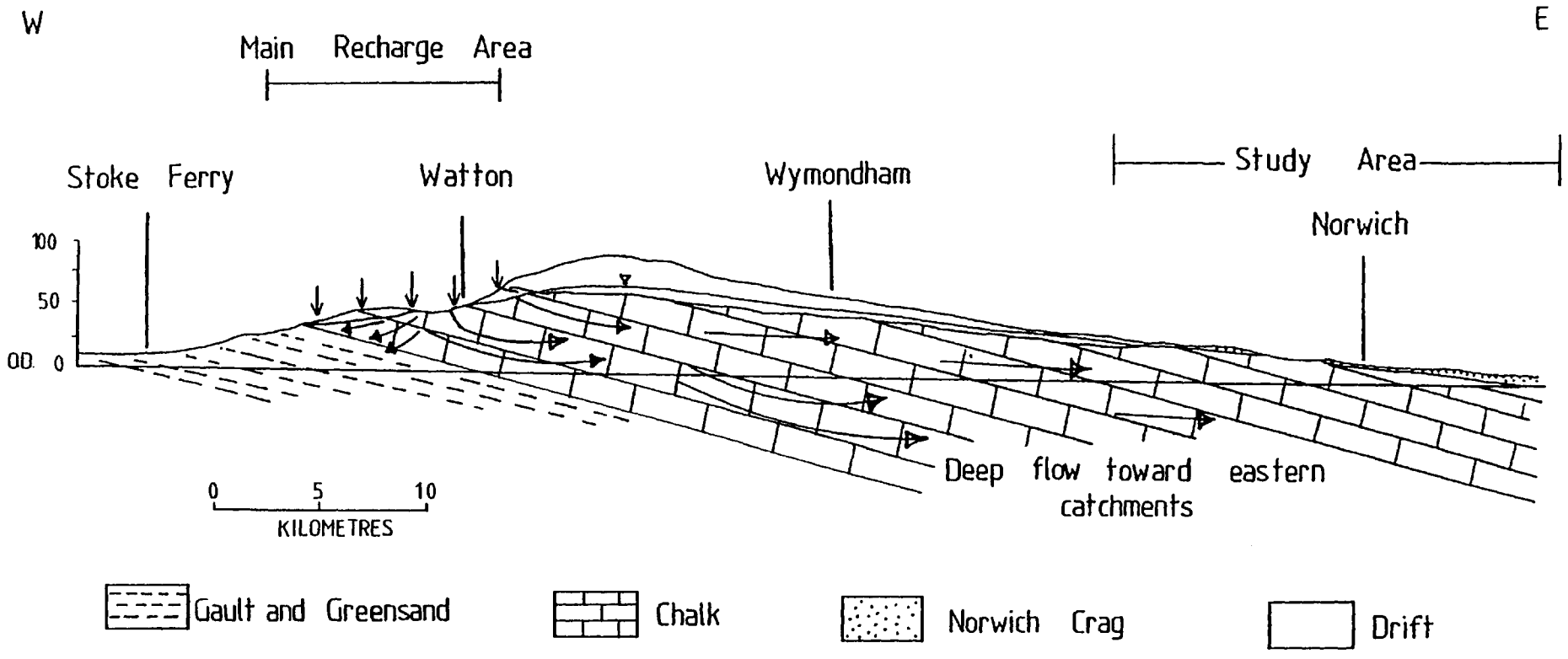


Fig. 2.6 A generalised section showing the position of the Chalk recharge zone in Norwich area (after Parvizi, F.,1977).

2.6. Hydrogeological properties of the three major aquifer rocks and the Chalky boulder clay

2.6.1. The Chalk

The Chalk is highly porous with a primary porosity of about 30%. Although the body of the rock has a relatively low permeability, it is traversed by fissures and solution holes, especially along the lines of old valleys. Its importance as an aquifer is due to these fissures which considerably increase its overall permeability. Thus, the yield from a borehole depends on the number, size and extent of the fissure systems it intersects (J. Ineson, 1959). These fissures represent bedding planes and joints and the results of faulting and shattering, and may develop along layers and sheets of flints. The interconnections of these fissures, which are often enlarged by solution, give the rock its high secondary permeability.

The fissures tend to close up with depth because of the weight of overlying strata, so that yields are often diminished in the lower horizon. The estimated infiltration into the Chalk formation north of the Cromer Ridge is 122.74 x 10^3 m^3/day. South of here in the Bure catchment infiltration west of the Eocene deposits is about 263.66 x 10^3 m^3/day. In the Pleistocene, where it overlies the Eocene this rate is about 45.46 x 10^3 m^3/day. In the southern part of the area, the Chalk is exposed in all valleys, but the exposure in the Waveney valley is small. In general, the average daily infiltrations of water into the Chalk are as follows: 181.84 x 10^3 m^3/day for the Wensum catchment, 177.29 x 10^3 m^3/day for the Yare and 100.01 x 10^3 m^3/day for the Waveney catchment (Ministry of Housing and Local

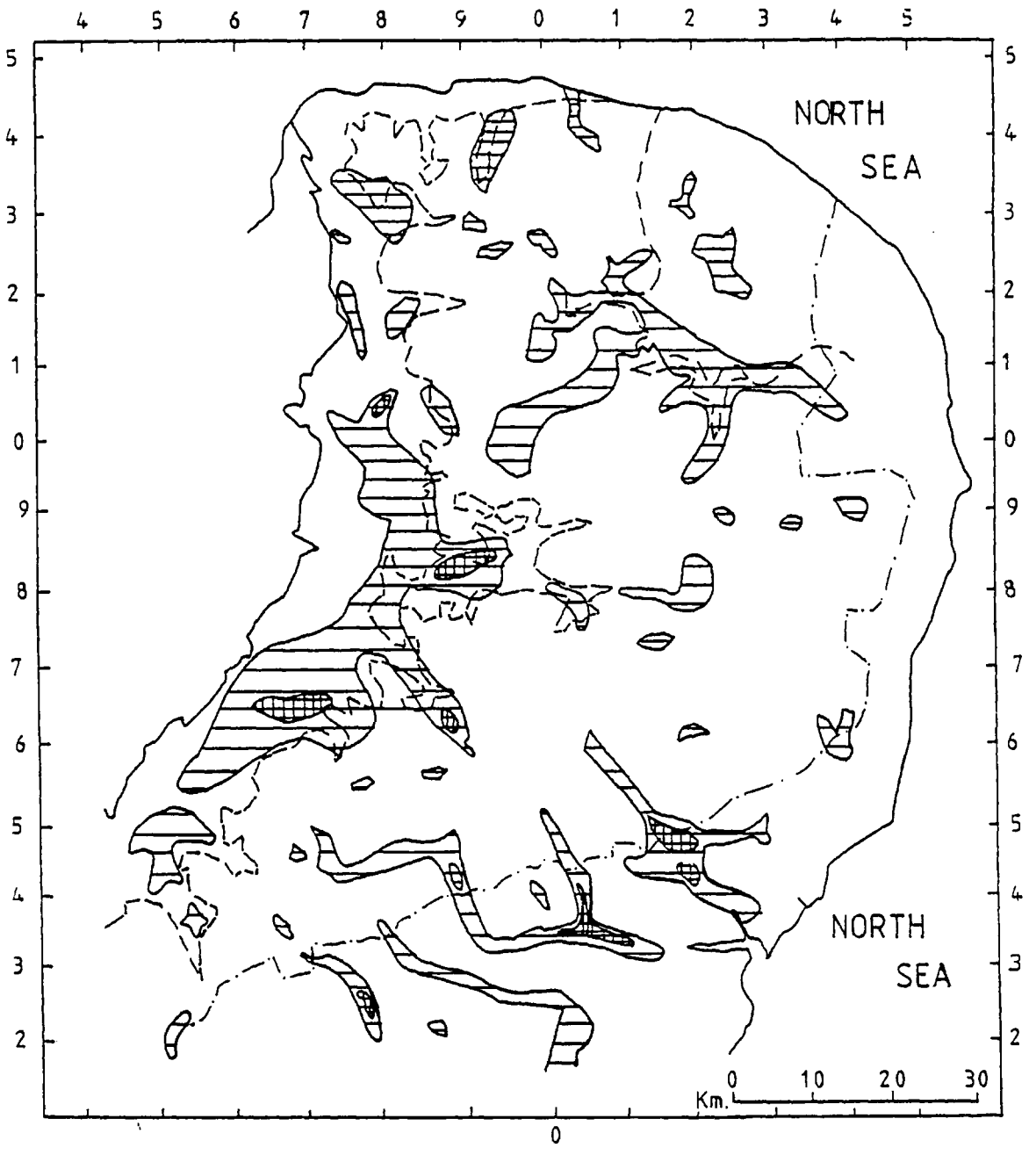
Government 1963).

Abstraction rates from Chalk boreholes in the east of the area exceed 5.46 x 10^3 m^3/day in a few cases. Usually the highest rates are between 2.18 x 10^3 m^3 and 3.27 x 10^3 m^3/day. For instance a borehole for public supplies at Thorpe St. Andrew yielded 16.1 x 10^3 m^3/day for a drawdown of only 15 metres. At Rushall, in the far south, the high yield of 4.4 x 10^3 m^3/day for a drawdown of 16 metres is associated with the existence of a buried channel. Poor yields, often of only a few cubic metres per day, are obtained from boreholes passing through considerable thickness of Eocene Clays or Chalky boulder clays to the underlying Chalk (see figs. 2.7 for values of transmissivities).

Generally, the Upper Chalk is softer and less fissured than the Middle and Lower Chalk.

2.6.2. The Crag

The major divisions of the Crag are lithologically similar and so may be treated as a single hydrological unit. The Crag is known to be in hydraulic continuity with the Chalk where it rests directly on the Chalk. In the Tas catchment rapid recharge rates of approximately 49 litres/sec. or 4,200 m^3/day were observed during pumping tests at the Rushall, Forncett St. Peter, and Carlton Rode sites. This rapid recharge is interpreted as being induced leakage from the overlying Crag sands (see Fig. 2.8a) (Foster, S.S.D. and A.S. Robertson, 1977). This induced leakage is also likely to occur during



EXPLANATION

Less than 34.09m^3/day/m.

34.09 – 68.19m^3/day/m

Greater than 68.19m^3/day/m

—— Base of Chalk

– – – Approx. boundary of Boulder clay.

—·—·— Base of London Clay

Fig. 2.7 Variations in the transmissivity of the Chalk in East Anglia (modified from Ineson, 1962.)

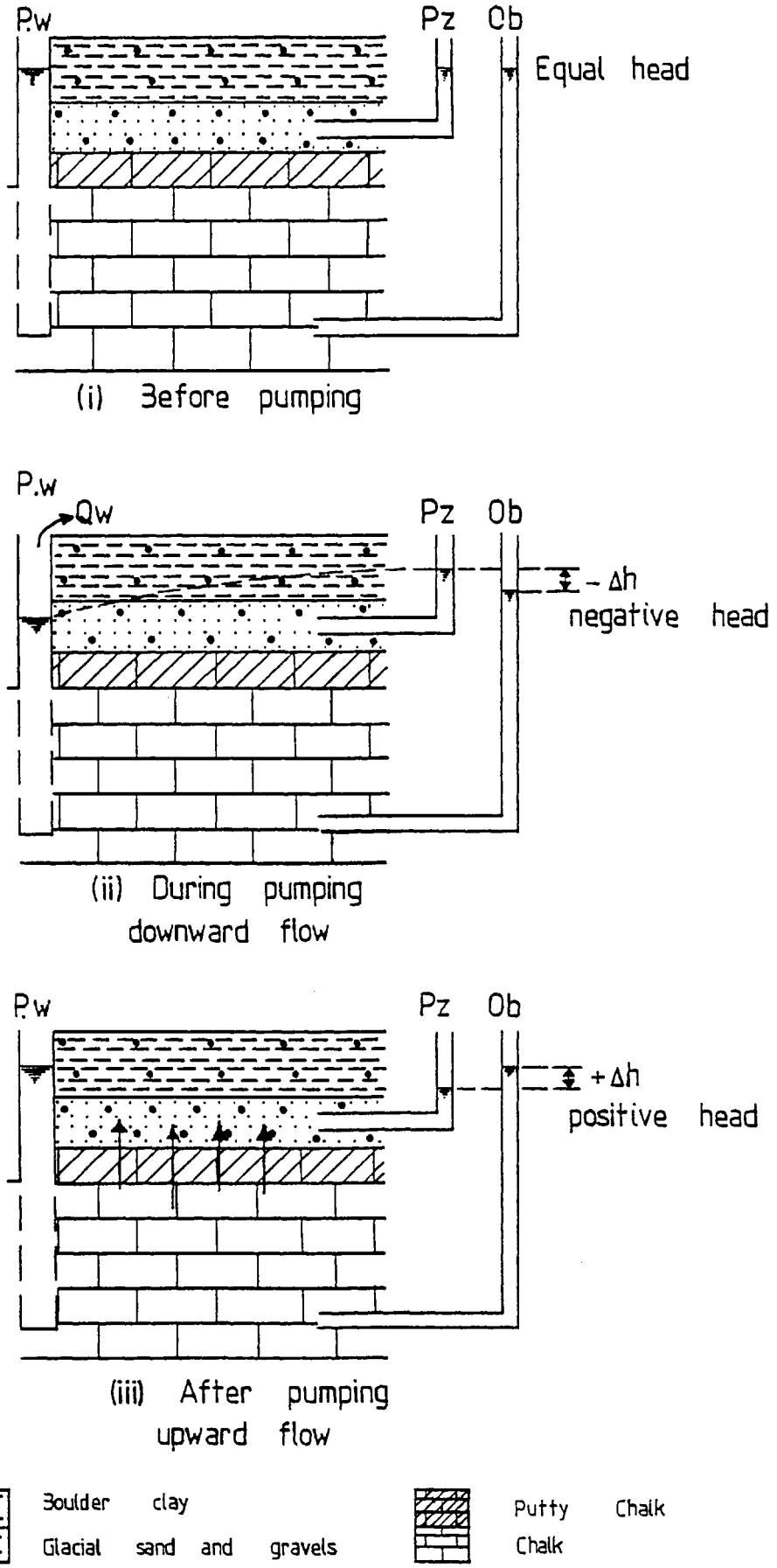


Fig. 2.8a Schematic model of the hydraulic behaviour of the Chalk and overlying strata during pumping. (after Parvizi, 1977)

fluctuations of water levels in markedly dry summers. The existence of leakage is confirmed by the behaviour of a piezometer in the Crag, which responds to pumping, but the response is smaller and less rapid in an adjacent Chalk observation well with the same pre-test water level. Generally, hydraulic continuity also exists between the Crag and the overlying Glacial sands and gravels as well as between the Chalk and the Glacial sands and gravels (Foster, S.S.D. and A.S. Robertson, 1977).

Much of the Crag consists of fine grained loose sands which create problems during the drilling and late development of boreholes. Even when properly constructed, possibly with graded filters or Johnson Well Screen, a borehole sunk into the finest sand will always have low yields because of the low permeability of such deposits. However, where coarse materials occur, high yields have been obtained from the Crag.

In the east, where the Crag reaches its maximum thickness, it has been developed for supplies because the Chalk water in this area is saline.

2.6.3. The Glacial sands and gravels

In the north of the area outcrops of Glacial sands and gravels occur overlying the boulder clay as, for example along the Cromer Ridge. These provide small supplies of water (East Suffolk and Norfolk River Authority, 1971).

The main deposits of glacial sands and gravels directly

overlie either the Crag or the Chalk and are generally known to be in hydraulic continuity with them. The sands and gravels are highly permeable where they are exposed and directly overlie the Chalk. Thus, during periods of abstraction, they are a recharge source for the Chalk (see fig. 2.8a), and are also considered to allow about 90% of the effective rainfall to infiltrate through them to lower aquifers (Foster, S.S.D. and A.S. Robertson, 1977; East Suffolk and Norfolk River Authority, 1971).

2.6.4. The Chalky boulder clay

This clay is important hydrogeologically because it controls the amount of water infiltrating to deep storage in the underlying aquifers. In places, especially along the main ground water divides, rest water levels in boreholes are within the boulder clay. As these levels are above those of the water in the Chalk where it crops out in the west of the area, they may have resulted from infiltration through the boulder clay.

Greater infiltration through the boulder clay occurs in the northwest where its matrix is more sandy than in the south of the area. Analyses of river hydrographs seem to support this (East Suffolk and Norfolk River Authority, 1971). Downing in Boulton and others, (1963), suggests that the average effective infiltration through the boulder clay is probably 101.6 mm per annum.

The boulder clay is of limited importance as an aquifer; it is rather an aquiclude. For instance, the boulder clay covering

central Norfolk does not yield water in any quantity. Shallow wells have yielded only very small quantities, usually for domestic and irrigational purposes. These are probably from thin gravelly beds, sand beds, or lenticular patches of Chalk debris within the clay. Yields depend on the thickness and lateral extent of the beds concerned. At Flegg, wells have yeilded 0.455 m^3/hour or 454.59 litres/hour (Ministry of Housing and Local Government Report, 1963).

2.6.5. Interpretation of water levels

The Chalk which is the major aquifer in the area, is overlain by strata of varying compositions. The interpretation of water levels measured in boreholes that penetrate these strata and enter the Chalk depends on the nature of the stratum directly above the Chalk. Since the Chalk can be directly overlain in places by Glacial sands and gravels, Crag, Chalky boulder clay or the London Clay, an attempt is made here to define the meaning of piezometric water level conditions that can be found in the area. The problem is that water levels in partially cased bores in the strata above the Chalk may represent the piezometric level of the Chalk water, or a water level independent of the Chalk water, or a mixture of the two.

A schematic diagram of piezometric water levels conditions is shown in figure 2.8b. Figure 2.8b(i) indicates a situation where the Glacial sands and gravels or the Crag (mainly sand and gravels) lies directly above the Chalk. These overlying materials are permeable, therefore they are in hydraulic continuity with the

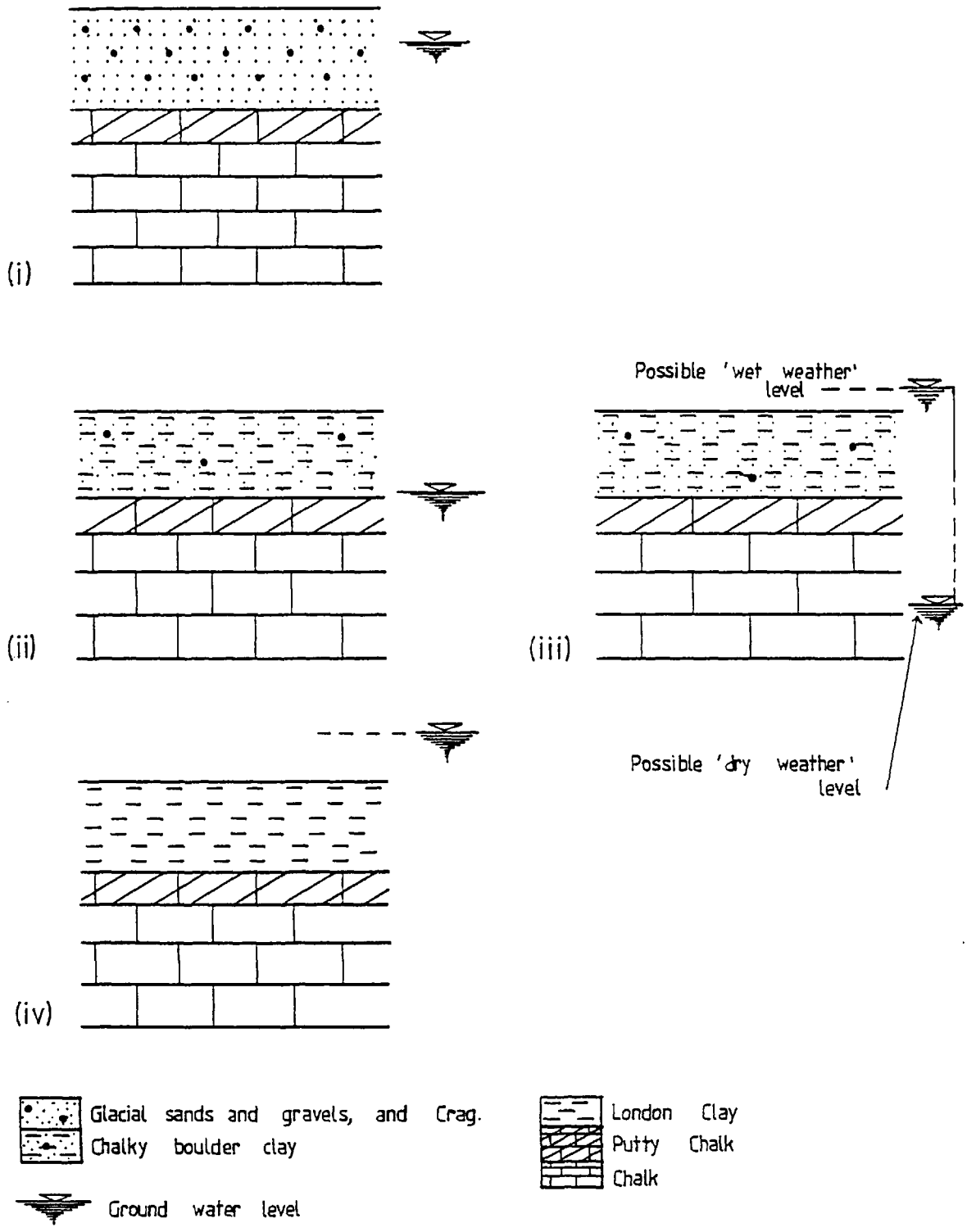


Fig. 2.8b A schematic model of piezometric water levels of the Chalk and overlying strata.

Chalk. Thus, water levels are expected to stand or rest within the overlying strata as in diagram. In this case, water within the aquifers may have been contributed both by direct infiltration from above, and from rising piezometric levels in the Chalk, especially where such an area is in lateral proximity to an area of Chalk recharge, as in the west of Norfolk. The amount of water contributed by direct infiltration through sands and gravels or Crag could be determined by calculations using soil moisture deficit values within the catchment. Periods of effective rainfall could be expected to be associated with a rise in water level that is most readily explained by surface recharge over the site rather than upward recharge from the Chalk beneath the site.

In figure 2.8b (ii) Chalky boulder clay sits directly on the Chalk. Here, the Chalk is partially confined by the relatively impermeable stratum above it. The degree of confinement of the Chalk depends on the type of boulder clay. Where the boulder clay has a sandy matrix as in the north and northwest of the area, piezometric water levels are expected to rise but only slightly above the Chalk surface. The water in the boulder clay may come largely from infiltration into the boulder clay, especially if the base of the boulder clay is at a higher elevation than exposed recharge surfaces of the Chalk in the vicinity. If the base of the boulder clay and Chalk recharge zones are at the same level, a test similar to that for 2.8b (i) will be necessary to determine whether or not the bulk of the water comes from infiltration. Where the boulder clay is less sandy, a higher degree of partial confinement results. Piezometric water levels may stand within the Chalk aquifer only during very dry

periods, when water levels must have fallen considerably (fig. 2.8b (iii)). In this case, most of the water present is Chalk water, although the downward drainage of any water in the boulder clay into the Chalk cannot be excluded as a possible mechanism. However, during periods of heavy precipitation, piezometric water levels may stand above the overlying boulder clay giving rise to artesian conditions as is observed at Bunwell (Norwich Water Division borehole). This condition may be due to upward movements of water from the Chalk aquifer, owing to relative increases in hydrostatic pressure. Here it is likely that the bulk of the water in the stratum above the Chalk comes from the Chalk.

Where the stratum above the Chalk is the London Clay as in the eastern part of the area (fig. 2.5), the Chalk aquifer is in true confinement. Piezometric water levels will definitely lie above the clay (fig. 2.8b (iv)), producing flowing (artesian) wells. There is however no field example within the study area of wells drilled through the London Clay into the Chalk.

In general, four possible piezometric water level conditions are expected in the study area:

1. water levels within overlying permeable strata, standing far above the Chalk surface, that may be supported by water from infiltration and water from the Chalk.

2. water levels within overlying relatively impermable layer, but only slightly above the Chalk surface, that

are probably mainly controlled by water pressure in the Chalk.

3. piezometric water levels within the Chalk aquifer itself, that are mainly Chalk water but may have some component derived from drainage of water from strata above and

4. piezometric water levels above impermeable clay stratum which overlies and distinctly confine the Chalk aquifer.

2.7. Ground water levels and seasonal fluctuations

The main ground water divide closely follow the topographic divide between the Norfolk and Suffolk River Division and the Great Ouse River Division, with the exception of the area to the northwest.

A further well-defined ground water divide occurs beneath the Cromer Ridge. Along this and the principal divide ground water levels reach their maximum elevation of more than 60 metres above sea level.

Except in the northwest and in the valleys, the rest water level of the Chalk ground water is usually above the Chalk surface: thus, the water table is found within the Crag or the Glacial sand and gravels. Beneath the major divides rest water levels are often above the base of the boulder clay and confined conditions may occur (Fig. 2.8 (ii) and (iii)).

Table 2.2. Infiltration rates within the study area

	Locality/Location	Estimated Infiltration Rate
1.	Bure Catchment	263.66 c 10^3 m^3/day
2.	Yare Catchment	177.29 x 10^3 m^3/day
3.	Tas Catchment	4.20 x 10^3 m^3/day
4.	Waveney Catchment	181.84 x 10^3 m^3/day
5.	North of Cromer Ridge	122.74 x 10^3 m^3/day
6.	Pleistocene deposits, east of the area	45.46 x 10^3 m^3/day
7.	Wells into Chalky boulder clay at Flegg	10.92 m^3/day (during pumping)
8.	Borehole into Chalk at Thorpe St. Andrew	
9.	Borehole into Chalk at Rushall	

(After East Suffolk and Norfolk River Authority, 1971)

The maximum ground water gradient of about 1 in 40 occurs north of the Cromer Ridge as the water table falls northwards, towards the coast. However, gradients of this magnitude are exceptional and between 1 in 200 and 1 in 700 are more typical. For instance, at Shotesham Mill in the Tas catchment the hydraulic gradient is about 1 in 460, the width of the valley being 1.61 km (Ineson and Downing, 1965).

In general, with the exception of the northwest and the north of the Cromer Ridge where the flow is toward The Wash and the North Sea coast respectively, the regional ground water flow is directed eastwards, following the topographical inclination.

Records from wells within the area show that the major seasonal fluctuations occur along the ground water divides, especially along the main divide with the Great Ouse River Division and beneath the Cromer Ridge.

These fluctuations are small, however, being about 3 metres to 5 metres per annum. In exceptionally dry years, fluctuations are large and 9 metres have been recorded in a well at Stanhoe. Over the rest of the area, the average seasonal fluctuation is less than 2 metres a year.

2.8 General factors influencing ground water chemistry

Elements have a tendency to move in a given chemical environment. This movement takes place when the element is incorporated as solid mineral matter, a gas, a melt, or in solution within a liquid.

The average composition of igneous rocks which are assumed to be the primary component of the earth's crust is given in table 2.3. A comparison of this composition with those of ground water, ocean water and sedimentary carbonates gives a general picture of the mobility of the common elements in water.

Table 2.3. The composition of two rock groups and two types of water in parts per million (ppm)

Element	Igneous Rocks	Sedimentary Carbonates	Sea Water	Portable Ground Water
Al	81,000	4,200	0.01	0.04
Fe	50,000	3,800	0.01	0.07
Ca	36,000	302,000	400	45
Na	26,000	400	10,500	35
K	26,000	2,700	380	2.50
Mg	21,000	47,000	1,350	11
Mn	1,000	1,100	0.002	0.02
Cl	200	150	19,000	16

After Davis, S.N. and R.J.M. De Wiest, 1967

Although aluminium and iron are the third and fourth most abundant elements respectively in igneous rocks, their mobility is very low, as reflected by their concentrations in sea water (see table 2.3). However, the movement of an element depends on three factors:

1. the solubility of its various compounds
2. the tendency of its ions to participate in ion exchange processes and
3. the extent to which organisms in water extract the element.

Solubility itself is controlled by five factors:

a. temperature
b. pressure
c. hydrogen and hydroxyl ions concentrations (pH)
d. redox potential (Eh) and
e. the relative concentrations of other substances in solution.

Ground water is continuously being replenished by infiltrating rain water. Thus, its composition is influenced by the geology and hydrology, as well as by physical, chemical and biological factors prevalent within the environment.

2.8.1. Rocks and soils

The chemical character of ground water is to a large extent related to the mineralogical composition of the surrounding rocks. The thickness of decomposed rock layers and soils are also controlled by the type of geology as well as climate.

Water takes minerals, carbon dioxide, oxygen and various organic acids (chiefly humic acid) and soluble solid substances into solution from rocks and soils as it flows through them to deeper layers.

Where the zone of aeration is highly permeable much chemical changes do not take place due to the rapid flow of the water through this zone. However, where the rocks and soils are less permeable the water spends longer time in contact with them and so greater chemical changes take place, and large amounts of materials are taken into solution. The chemical action of infiltrating water is affected by the amount of dissolved carbon dioxide it contains. This is particularly evident in limestone areas, where large solution holes and caverns are produced by carbon dioxide charged infiltrating waters.

The general chemical character of ground waters depend on major cations like sodium Na^{+}, potassium K^{+}, calcium Ca^{2+} and magnesium Mg^{2+}, and major anions such as bicarbonate HCO_3^{-}, carbonate CO_3^{2-}, sulphate SO_4^{2-}, and Cl^{-} as well as concentrations of other minor cations and anions (see table 2.4).

Usually, the minor constituents in waters form the critical indices for the chemical quality of the waters, just as iron Fe and manganese Mn are seen to do in the present study. In table 2.4 is a tentative general classification of the abundance of dissolved solids in potable water. Also as a general guide, limits of concentrations of certain elements (ions) commonly affecting the potability of water, as recommended by the World Health Organisation (WHO) Geneva, (1971) are given in table 2.5.

Table 2.4 Dissolved solids in potable water

Major Constituents	1.0 ppm to 1000 ppm
Sodium	Bicarbonate
Calcium	Sulphate
Magnesium	Chloride
Silica	
Secondary Constituents	0.01 ppm to 10.0 ppm
Iron	Carbonate
Strontium	Nitrate
Potassium	Fluoride
Boron	
Minor Constituents	0.001 ppm to 0.1 ppm
Aluminium	Manganese
Arsenic	Molybdenum
Barium	Nickel
Bromine	Phosphate
Cobalt	Selenium
Copper	Uranium
Iodine	Vanadium
Lead	Zinc
Lithium	

Adopted from Hydrogeology by Davis and De Wiest, 1967

Table 2.5 International standards for drinking water (after World Health Organisation, 1958 and 1971)

Substances or Characteristics	Highest desirable level (ppm)	Maximum permissible level (ppm)
Calcium, Ca^{2+}	75.00	200.00
Magnesium Mg^{2+}	50.00	150.00
Iron as Fe^{2+}	0.10	1.00
Manganese as Mn^{2+}	0.05	0.50
Copper Cu^{2+}	0.05	1.50
Zinc Zn^{2+}	5.00	15.00
Chloride Cl^{-}	200.00	600.00
Sulphate SO_4^{2-}	200.00	400.00
Sulphate, as ($MgSO_4$ and Na_2SO_4)	500.00	1000.00
Nitrate NO_3^{-}		45.00
Carbonate, as (Na_2CO_3 and K_2CO_3)		120.00
Total dissolved solids	500.00	1500.00
pH range	7.0 - 8.5	6.5 - 9.2

2.8.2. Rain Water

Rain water contains nitrogen and nitrogenous compounds, carbon dioxide, oxygen, sulphates and chlorides. The concentrations of these depend on various factors. For instance, distance from the coast

affects the concentrations of chloride from salt particles blown inland. In coastal regions the chloride content of rain water ranges from 3 ppm to 6 ppm, decreasing to about 1 ppm 100 km and 200 km inland and to about 0.3 ppm at about 800 km from the coast (Davis and DeWiest, 1970). In the study area, the chloride content of rain water at a distance of about 6.3 km from the North Sea coast is approximately 12,000 µg/l (12.0 mg/l i.e. 12.0 ppm) Peirson, Cawse, and Cambray, 1974), also see table 2.6. This measurement was carried out at Gresham, a station about 6.3 km south west of Cromer and about 30 km north north west of Norwich. This concentration agrees with the general concentration of chloride with distance from the coast, as stated by Davis and DeWiest. The degree of sulphate pollution of the atmosphere from industries, homes and other sources affects the concentrations of sulphates in rain waters.

In these ways, rain waters acquire some degree of salinity which accounts for only a very small percentage of dissolved substances in ground waters.

Table 2.6 Elemental concentrations in rain water (µg/l) for a station in Norfolk

Element	Station	Concentration
Sodium (Na)	Gresham	5,900 (5.9 ppm)
Chloride (Cl)	"	12,000 (12.0 ppm)
Manganese (Mn)	"	21 (0.021 ppm)
Iron (Fe)	"	440 (0.44 ppm)

Rainfall (mm/year) June 1972 to May 1973 = 476 mm

(After D.H. Peirson, P.A. Cawse and R.S. Cambray)

2.8.3. The velocity of infiltrating and circulating waters

The rate of infiltration of rain water and the rate of circulation of ground water affect the chemical quality of ground water itself. Velocity of movement generally decreases with depth but could be higher depending on the permeability of the lower strata. In limestone areas movement below the surface is usually faster because of caverns and solution holes present.

In the study area, the sands of the Crag and the Glacial sands and gravels are very fine. This means permeability will be low so that infiltrating rain water will be in intimate contact with the sands, thus, leaching the iron and manganese from them and enriching lower levels of the rock suite particularly where the Crag is also in contact with "putty" relatively impermeable Chalk (see table 2.2 for infiltration rates).

In conclusion, it may be necessary to consider the general flow equation here and show how its parameters influence water chemistry. The general equation is:

$$Q = \frac{Kxd^2hx}{dx^2} + \frac{Kyd^2hy}{dy^2} + \frac{Kzd^2hz}{dz^2} = \frac{S}{T} \cdot \frac{dh}{dt}$$

where Q = rate of charge of discharge (natural or artifical)

K = hydraulic conductivity

S = storativity, storage, coefficient of storage

T = transmissivity

h = total hydraulic head

$\frac{dh}{dt}$ = change in hydraulic head with time

$\frac{dh(x\text{-}y\text{-}z)}{d(x\text{-}y\text{-}z)}$ = change in total head in x, y, or z directions per unit distance in these directions.

These parameters are briefly considered below.

Hydraulic conductivity (K)

This is known as the coefficient of permeability, expressed in m/sec: it defines the ease with which a liquid may move through a porous medium and is approximately proportional to the square of the void diameter. For ground water purposes hydraulic conductivity is more meaningful because it takes into account the density and viscosity of the fluid. However, for our purpose, the definition as in permeability may be more useful. Permeability is a function of porosity, which in turn reflects the volume of water stored. Permeability itself is related to rate of flow, since rate of flow varies as permeability and hydraulic gradient $(\frac{dh}{dx})$.

For a given hydraulic gradient, a more highly permeable stratum will allow relatively rapid infiltration and percolation than a relatively less permeable stratum. This means that for the highly permeable stratum, the time taken for water to be in contact with aquifer materials will be shorter than in the case of a less permeable stratum of the same composition under the same hydraulic gradient. The result is that with the more permeable stratum there will be a tendency for less chemical materials to be leached from the rocks. Therefore water through it will have a relatively low concentration of mineral materials. It is obvious from the above that the concentration of chemical materials is a function of flow rate $(K\frac{dh}{dx})$, where $(\frac{dh}{dx})$, the hydraulic gradient, is the energy that sets the fluid into motion and keeps it flowing.

Storage, Storativity or Coefficient of Storage(s)

This is the volume of water that a permeable material (aquifer) will absorb into or release from storage per unit surface area per unit change in head. The quantity of water stored or released depends on the nature of aquifer materials.

In a saturated zone, the head creates pressure. This affects the arrangement of mineral grains as well as the density of the water in the voids. If the pressure increases, the mineral grains (skeleton) will tend to expand; if it drops, the mineral skeleton will tend to contract. In the same manner, the water will become more dense with an increase in pressure and expand to become less dense if the pressure drops.

Thus when the head drops in an aquifer, the aquifer skeleton compresses, reduces the effective porosity and so expels water. Additional water is released as the pore water expands due to the same drop in head.

For confined and unconfined aquifers, the storativity (S) is related to specific storage (Ss) and specific yield (Sy). Specific storage (Ss) is the amount of water per unit volume of a saturated formation that is stored or expelled from storage due to the compressibility of the mineral skeleton and the pore water. Specific yeild (Sy) is the ratio of the volume of water that drains from a saturated rock due to the attraction of gravity, to the total volume of the rock. In a confined aquifer, the head may decline, but the piezometric surface may remain above the unit or the confining stratum. Therefore when water

is released from storage, the entire aquifer can still remain saturated. In this case, the storativity is the product of the specific storage (Ss), the area of the aquifer affected (A), and the change in head (dh).

$$S = dQ = Ss.A.dh$$

For an unconfined aquifer, when the head falls and water is released from storage (dQ), the piezometric surface also falls and a certain amount of the aquifer material becomes unsaturated. Here, the storage or release of water (dQ) is a function of the specific yield (Sy) and specific storage (Ss). However, because of the dominant effect of the specific yield, it is usually regarded as equal to storativity (Fetter, C.W., 1980). In general, the storage of unconfined aquifers is taken as the sum of the specific yeild (Sy), and the product of the area of saturated zone (A), the specific storage (Ss) and the change in head (dh).

$$S = dQ = Sy + Ss.A.dh$$

From the above, it is likely that the influence of storage on the chemistry of water will be most apparent in unconfined aquifers where the piezometric surface fluctuates and where there is infiltration through the aquifer. Thus if the value for specific storage (S) is large, it follows that the aquifer is highly permeable, and so the velocity of flow will also be high. Therefore, water will tend to spend less time in contact with aquifer materials resulting in a small quantity of chemical materials being leached. Conversely, a low value of coefficient storage (S) will tend to give water more time in contact with aquifer materials, storage (S) will tend to give water more time in contact with aquifer materials,

since permeability and flow velocity will be low. This means a greater amount of chemical materials will be taken into solution. In conclusion therefore, a high value of storage can be expected to be associated with a low concentration of chemical materials and a low value of storage can be expected to be associated with a relatively high concentration of chemical materials in solution.

Transmissivity (T)

This describes the volume of water that passes through a saturated unit width of an aquifer under a unit hydraulic gradient in unit time i.e. m^3/day/m.

In this case, for a given hydraulic gradient an aquifer with a high transmissivity will allow a greater volume of water through it than one with a lower value of transmissivity. The effective parameter here is the volume of water, which also does the leaching of the aquifer rocks. It follows therefore that the more the quantity of water through a particular point at a given time, the more will be the amount of chemical elements taken into solution.

Total hydraulic head (h)

This is the manometric height of water above a given reference point. The height at which water stands in an aquifer depends on the nature of its materials which also controls the rate of water movement through the aquifer.

In an unconfined aquifer, the higher the hydraulic head, the more rock volume is in direct contact with ground water.

Changes in hydraulic head will tend to produce corresponding changes in pressure, especially in confined aquifers. These changes in pressure are supposed to affect water chemistry by causing the dissolution or release of carbon dioxide from water. When the pressure increases with rise in head, more carbon dioxide goes into solution and the pH may be considerably lowered, but when the pressure falls, carbon dioxide is released from solution and the pH may increase. However, in the research area, such changes in pH were not observed.

Rate of fall of hydraulic head $(\frac{dh}{dt})$

The rate of fall of head depends in part on the permeability of an aquifer.

A fast rate of head fall often reflects a high permeability and results in a low hydraulic gradient.

2.8.4. Carbon dioxide

Of the gases in water, carbon dioxide is the most important. The pH and so the chemical activities of ground waters of dissolution and precipitation, through the processes of hydration, hydrolysis, oxidation and chemical attack are controlled by the concentrations of dissolved carbon dioxide.

For instance, an increase in carbon dioxide will shift the carbon dioxide - carbonate - bicarbonate system, in such a way that more limestone will go into solution.

Carbon dioxide in ground water comes from two main sources:

1. the atmosphere and
2. the soil air.

Concentration of the gas in soil air is however from ten to more than one hundred times that in the atmosphere. On going into solution, carbon dioxide forms carbonic acid molecules which ionise to release hydrogen (H^+) ions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

By the presence of the hydrogen (H^+) ions, rain water acquires certain pH values ranging from 4.5 to 7.0 (A. Holmes, 1970).

Generally, the concentration of carbon dioxide in ground water is affected by changes in temperature and pressure, especially so in confined aquifers. The lower the temperature and the higher the pressure the more gas will go into solution.

2.8.5. Hydrogen (H^+) ion concentration (pH)

As seen from above, the pH of natural waters is most often controlled by the carbon dioxide-carbonate-bicarbonate system. As the solubility of carbon dioxide changes with temperature and pressure, the pH also changes. The pH of natural ground waters varies, and values as low as 3 in acid waters and as high as 10 in basic waters are encountered in nature. Low pH values in waters may be caused by humic acids from decaying vegetal matter in soils, leached down by infiltrating

rain water. They may also be due to the oxidation of sulphide minerals like pyrite with the release of hydrogen (H^+) ions

$$FeS_2 + H_2O + 7(O) \longrightarrow FeSO_4 + H_2SO_4$$

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

Ferrous sulphate may also undergo oxidation to release more hydrogen ions.

$$3FeSO_4 \longrightarrow 2F^{3+} + 3SO_4^{2-}$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

Low pH values could be due to the hydrolysis of iron and aluminium, and finally, they may be due to the solution of more carbon dioxide as a result of changes in temperature and pressure.

The pH of ground waters has a great effect on the mobility of many elements. Only a few ions such as sodium Na^+, potassium K^+, nitrate NO_3^- and chloride Cl^- remain in solution through the entire range of pH values found in normal ground waters. Most metalic elements are soluble as cations in acid ground waters but will precipitate as hydroxides or as basic salts with an increase in pH. Ferrous ions diminish rapidly as the pH value increases above 6, manganese ions are mostly precipitated at a pH of more than 10 (Davis and De Wiest, 1967).

2.8.6. Oxidation-Reduction Potential (Eh)

This, known also as redox-potential controls the oxidation

states of certain elements which in turn control their solubility and mobility.

Redox-potential (Eh) is a measure of the potential (i.e. the ability) of a chemical environment to either remove or donate electrons, for the oxidation or the reduction of ions within that environment. An example is the removal of an electron from a ferrous ion converting it to the ferric ion.

$$Fe^{2+} + 3H_2O \rightleftharpoons Fe^{3+} + 3OH^- + e^- + 3H^+$$

$\longrightarrow$ oxidation

$\longleftarrow$ reduction

In natural waters the presence or absence of uncombined oxygen is one of the primary causes of variations in Eh. The actual Eh at which oxidation or reduction takes place is a function of pH. Ground waters commonly tend to have low redox-potentials and are chemically reducing because they have usually been depleted in dissolved oxygen. In these low redox environments, the stable forms of iron and manganese are the ferrous (Fe^{2+}) and the manganous (Mn^{2+}) states respectively.

In general however, if a solution is more alkaline oxidation of iron to the ferric hydroxide takes place at a lower Eh. Thus, ferrous ions can be stable in ground waters at low pH values but will oxidise to ferric ions at higher pH values at a constant redox-potential.

Figure 2.9 shows the transition between the oxidised and reduced states of iron and manganese. The lower of the two lines shows the balance between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions in solution.

At every point along this line the concentrations of the two states of iron are equal. For all values of Eh and pH below the line, the concentration of ferrous ions is greater than that of ferric ions. The upper sloping line shows the relation between soluble divalent manganese (Mn^{2+}) and insoluble, precipitated tetravalent manganese MnO_2. Thus, in order to precipitate all the iron and manganese, the values of Eh and pH must be raised above those represented by the upper line (fig. 2.9).

However, the two sloping lines are not absolutely fixed. They can vary, depending on the relative concentrations of other substances in solution. For instance, the presence of high concentrations of sulphur and bicarbonate ions will shift the equilibrium lines in such a way as to precipitate ferric ions, thus reducing the concentration of ferrous ions in solution (Broom, M.E., 1966).

2.8.7. Biological factors

Recent hydrogeochemical research has shown the importance of micro-organisms mainly bacteria, in altering the chemical character of ground waters (Kuznetsov, S.I. (ed.), 1961). In addition to important modifications in the soil horizon and during early diagenesis of sediments, it is known that significant changes in water chemistry due to bacterial actions take place at great depths. Nutrients chiefly from the decomposition of surface plants, may be fed continuously by infiltrating surface water to the subsurface organisms. This may be true of many limestone aquifers where extensive cavernous zones exist as conduits.

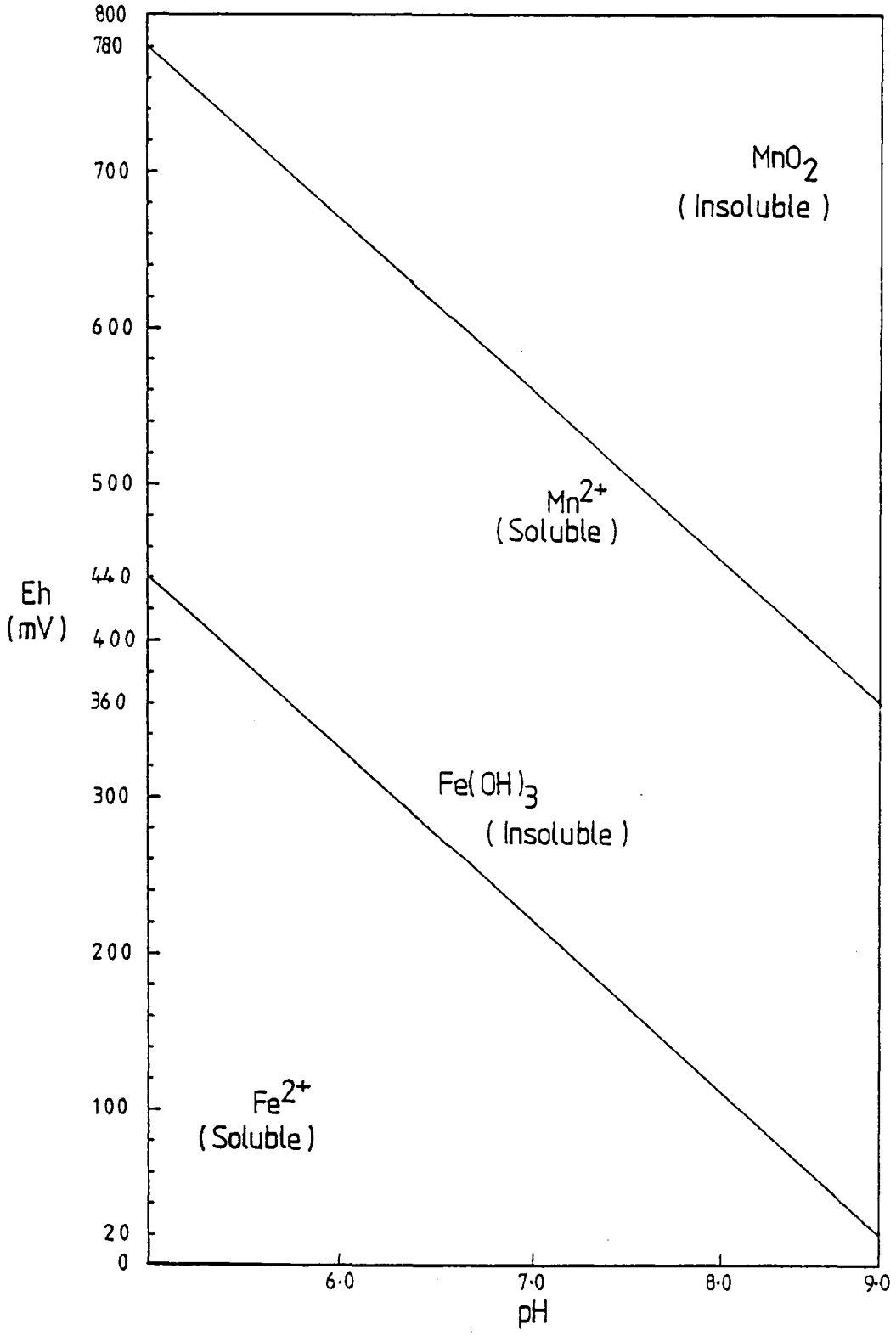


Fig. 2.9 Dissolved(Fe^{2+} and Mn^{2+}) and precipitated [$Fe(OH)_3$ and MnO_2] iron and manganese as functions of the variables pH and Eh.(after Rolf O. Hallberg and Rudolf Martinell, 1976.)

Organisms such as iron and manganese and sulphate-reducing bacteria are well known (Taylor, E.W. (ed.), 1949). Iron and manganese bacteria can produce high pH values in waters, thus facilitating the precipitation of higher valency forms of iron and manganese. These bacteria exploit the oxidation of iron and manganese in solution by absorbing electrons from them as sources of energy for their metabolism (Hallberg and Martinell, 1976). In this way, the soluble forms of iron and manganese are constantly depleted.

From what has been discussed, it is apparent that not just mineralogy, but the thickness and permeability of rocks and soils are also important. The chemistry of rain water being fairly constant, what is significant is its rate of infiltration. While high velocity is related to high permeability and low chemical action, low velocity is related to low permeability and high chemical activities. Hence chemical quality is in part related to permeability and spacial variations in quality may be a reflection of similar changes in permeability, i.e. strata types present. Carbon dioxide available in the atmosphere and soil air, and to some extent sulphide minerals, significantly control the pH of ground waters. pH, together with redox potential (Eh), control the solubility of minerals in ground waters. Eh is however controlled by the availability of dissolved oxygen, which is in turn controlled by the extent of water table fluctuation and permeability. Therefore chemical quality is also in part related to the position of an area in relation to neighbouring hydrological boundaries, e.g. close to or far from the water table; within or without an area through which water is being discharged. Though not fully understood, it is believed that bacteria play a significant role in the oxidation and reduction of iron and manganese in ground waters.

CHAPTER 3

SAMPLING AND SAMPLE PREPARATIONS

3.1. Introduction

In order to pursue the aim of the present project, and to test the validity of the proposition that the high iron and manganese concentrations in ground waters of the study area may have been derived largely from one of the three principal aquifer rocks, a sampling program for rocks and waters in the area was undertaken. This was to make rock and water samples available for chemical analyses in the laboratory. During the sampling for water, physical qualities of water considered relevant to the project were determined in the field. However, all water samples are taken from shallow wells and deep boreholes and do not include pore water.

All shallow wells sampled for water are brick, steel or concrete lined to their bottom, while all boreholes into the Chalk are cased (i.e. lined) with steel tubes into the top of the Chalk. This casing seals off both the Crag and Glacial sands and gravels, as well as the Chalky boulder clay.

3.2. Rock sampling

A list of known exposures of Glacial sands and gravel, Crag and Chalk within the study area was obtained from the Castle Museum in Norwich.

The exposures were numbered in order from north to south and from west to east, based on their national grid references (N.G. Refs.). With Weybourne Hope 110 438 and Overstrand 255 404 as an example, Weybourne Hope 110, is farther west than Overstrand 255, also Weybourne Hope 438 is farther north than Overstrand 404. Therefore Weybourne Hope is number one and Overstrand is number two (see appendix A, Table 3.1a, b and Figure 3.1). In a final numbering of sampled localities, the numbering of Chalk localities was tied up to that of the Crag and sands and gravel. This is because from a number of localities Chalk and Crag or Chalk and sands and gravels were taken together, with fewer localities of Crag and sands and gravel compared to Chalk.

Exposures of the rocks were found in pits and cliff faces (see appendix A, Table 3.1a). In all cases, digging was necessary to reach fairly fresh surfaces from which samples were taken. From each locality duplicate samples were taken, the distances and orientation between samples depending on the conditions of the exposures. In some cases, the second samples were taken from a few meters away from the first and in others they were taken several metres away. The second samples were taken either directly above or below the first, or horizontally along the same level.

In all, eighty one Crag and Glacial sands and gravels and, forty Chalk exposures were visited. Of these, only seventeen Crag and sands and gravels and twenty two Chalk localities could be sampled. This is because some of the localities have become completely obliterated, while others were so overgrown with vegetation sampling was not possible. Thus the random sampling method which resulted was dictated

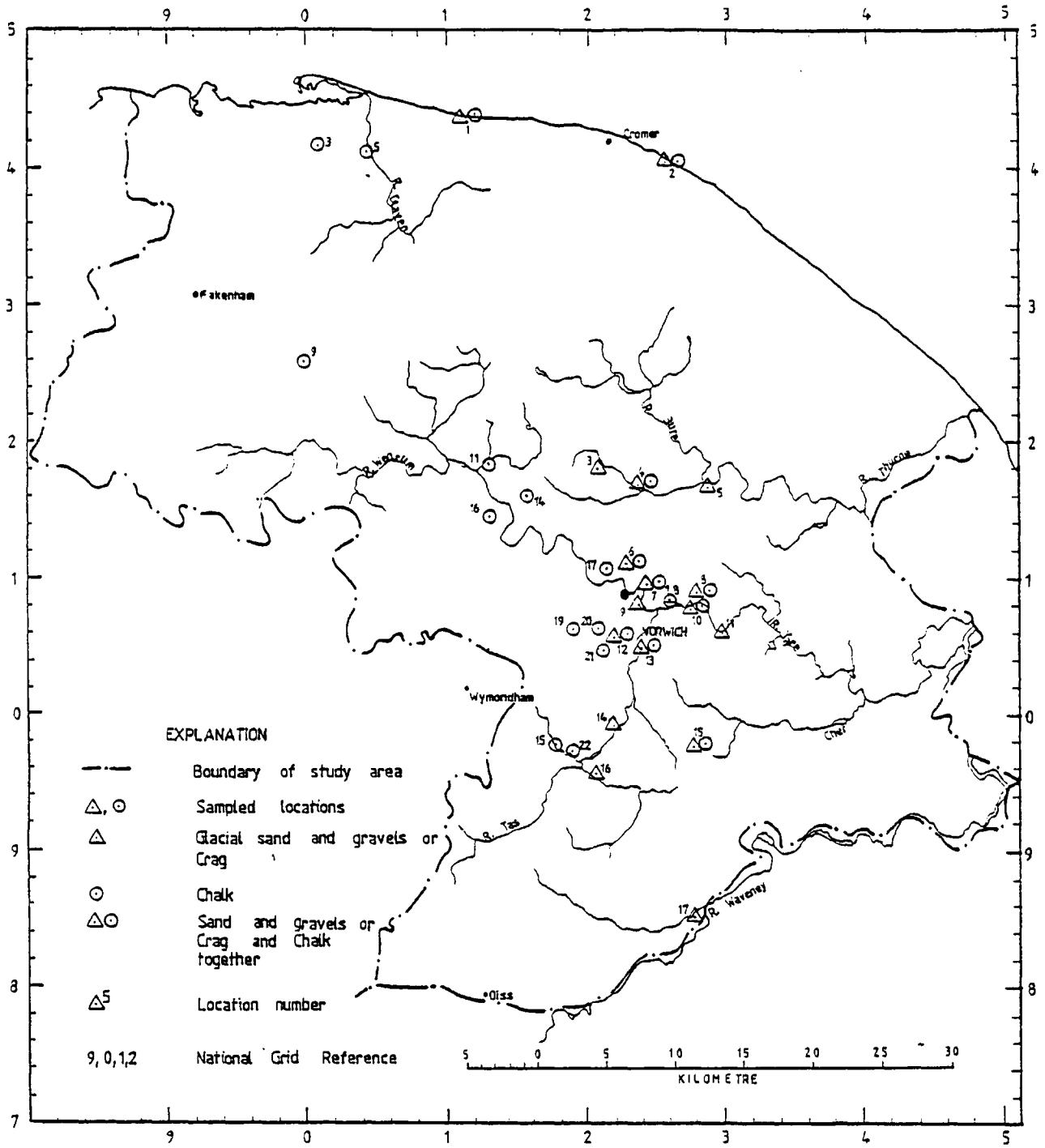


Fig.3.1 Sampled localities of Glacial sand and gravels, Crag and Chalk in NORFOLK

by the availability of good and accessible exposures.

3.3. Water Sampling

A compilation of known existing wells and boreholes was done with information from the Institute of Geological Sciences (I.G.S.) in London, and the River Division of the Anglian Water Authority in Norwich.

A total of one hundred and thirty shallow wells and boreholes were visited over the period of the research, making trips once a week. During each trip, a maximum of five samples were collected, one from each well or borehole. Of the total of one hundred and thirty, only ninety two wells and boreholes were sampled (see appendix A, Table 3.2 and fig. 3.2). This is because some boreholes are now disused and their pumps removed and, other wells and boreholes have been sealed off making sampling impossible.

Sampling was carried out in three stages. The initial samples were collected for a preliminary analysis, which excluded the four major metallic cations - sodium, potassium, calcium and magnesium. A second set of samples was collected from boreholes with samples having iron levels of 1.0 ppm and above, for an analysis of the four major cations. The third and final set of samples was from selected localities for iron and manganese determinations only. This is referred to as check analysis.

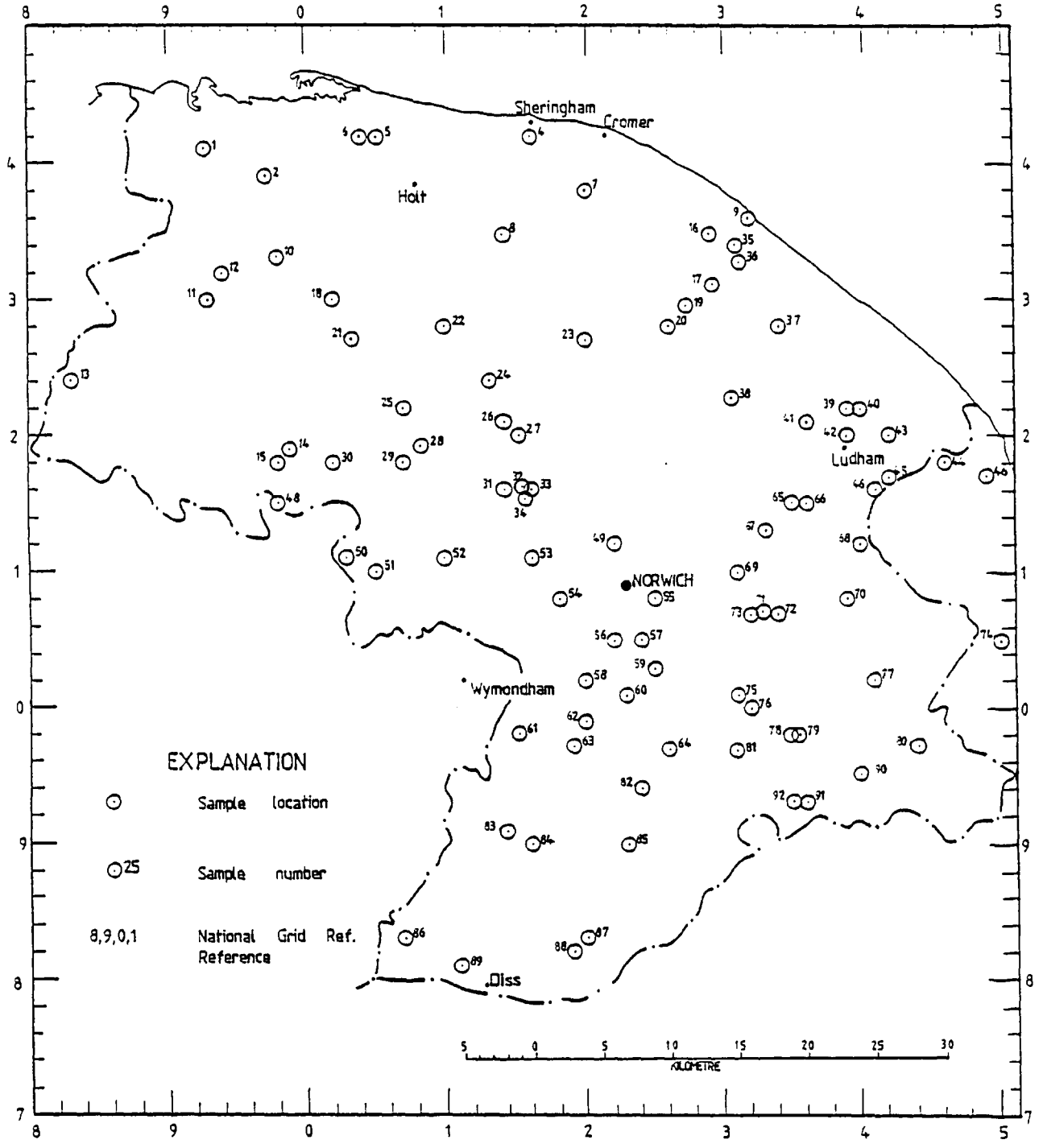


Fig.3.2 Locations of water samples

3.3.1. Sample containers and pre-sampling treatment

The American Association of Public Health (A.A.P.H.), (1969), Golterman (1971), and the Water Research Association of Britain (1973) have recommended that water samples be collected and stored in bottles made of pyrex, hard rubber, polyethylene or other inert materials. In the present study, high density polyethylene (clear plastic) bottles were used, to prevent:

1. contamination of the water samples by an otherwise reactive container,
2. large-scale loss of iron and manganese by absorption onto the walls of containers,
3. breakage of containers and the subsequent loss of samples, and
4. the escape of water vapour as is possible with low density polyethylene bottles. This, if allowed to happen may concentrate iron and manganese giving false readings (Water Research Association, Technical Memorandum No. 78, 1973).

The Water Research Association agrees that this sample bottle is also suitable for aluminium, cadmium, total chromium, copper, lead, nickel and zinc determination samples storage.

For each well or borehole sampled, two sample bottles were used. One is of 1 litre (1000 ml) capacity and the other a $\frac{1}{4}$ litre (250 ml) capacity bottle. The 1000 ml capacity bottle stored water for the determinations of free carbon dioxide, bicarbonate, chloride, nitrate and sulphate; sodium, potassium, calcium and magnesium. The

250 ml bottle stored acidified water for iron and manganese determinations.

Precautions were taken to minimise contamination of samples. One of these is the pre-sampling treatment of the sample bottles.

The bottles to be used were filled with an approximately 10% ($^{V}/_{V}$) hydrochloric acid for twenty four hours. They were emptied and washed thoroughly with distilled water. In addition, each bottle was washed three times over with the water to be sampled.

3.3.2. Sampling method

In collecting the water samples two basic methods were employed:

1. from taps and
2. by the use of a new galvanised bucket or a bottle and string.

With the taps, a number of situations were encountered:

a. There are taps specially provided for the purpose of raw water sampling; this is the case in all Norwich Water Division's pumping stations (see plates 3.1 a and b)

b. Bleed taps at the heads of wells and boreholes. This is generally peculiar to most private wells and boreholes.

c. Taps feeding overhead storage tanks.

d. Valved taps at the base of pressured storage tanks.

e. Taps at the end of pipes leading from wells and boreholes to animal watering areas.

The new and galvernised bucket and bottle were used in all cases to collect water from shallow wells where pumps have been removed or existing pump motors had broken down at the time of visit. Before water was taken from the taps, water was allowed to run for at least ten minutes, depending on whether the well or borehole was already in use (pumping) on arrival. Where the well or bore was not in use on arrival, water was allowed to run for a maximum period of twenty minutes. This was to achieve the following:

1. to ensure that water from the aquifer was sampled and

2. to prevent or reduce contamination of the samples by rust accumulation in the pipes and taps.

In addition to collecting water samples, in-situ measurements were made of temperature, of pH values, and of the percent saturation of dissolved oxygen (see Appendix A, table 3.3). For temperature determinations, a thermometer reading up to 50°C was employed, for pH values, a portable battery operated meter the dual pH electrodes (Electronic Instruments Ltd.) was used with a reproducibility to within $\pm$0.1 pH unit, while for the dissolved oxygen, a portable combined oxygen and temperature measuring, battery operated meter was used.

Repeat and check sampling were carried out. The repeat

sampling was to provide water for detailed analysis, and was restricted to water samples with iron levels 1.0 ppm and higher. The check sampling was undertaken during the winter months (December to February), to determine possible changes in iron and manganese concentrations in waters during this period of relatively higher precipitation (Dec. 1979 - Feb. 1980) (see table 1.1a and figure 1.3a.)

3.3.3. Water samples: preservation and storage

Prior to the fieldwork, a 900 ml, 1 in 3 solution of sulphuric acid (i.e. 300 ml of concentrated sulphuric acid to 600 ml of distilled water) was prepared, to acidify water samples in the field.

Part of this solution was added to a 250 ml of tap water in the laboratory, until a pH value of 2.14 (acid end) was reached. 0.5 ml of the acid solution was needed to do this, thus, to each of the water samples in the 250 ml bottles was added 0.5 ml of the acid solution at the time of collection.

Iron and manganese as well as many trace metals such as aluminium, cadmium, chromium, copper, lead and zinc may be lost from water samples by absorption onto the walls of sample containers. It has however been found that such losses are either eliminated or very much reduced by the acidification of the water samples. Therefore the acidification was to "fix" the samples in order to:

1. prevent loss of iron and manganese by sorption onto the walls of sample bottles.
2. prevent the loss of iron and manganese due to possible



Plate 3.1a. A raw water sampling point at Norwich Water Division's pumping station, Mundesley.



Plate 3.1b. A raw water sampling point, Norwich Water Division's pumping station, Royston Bridge.

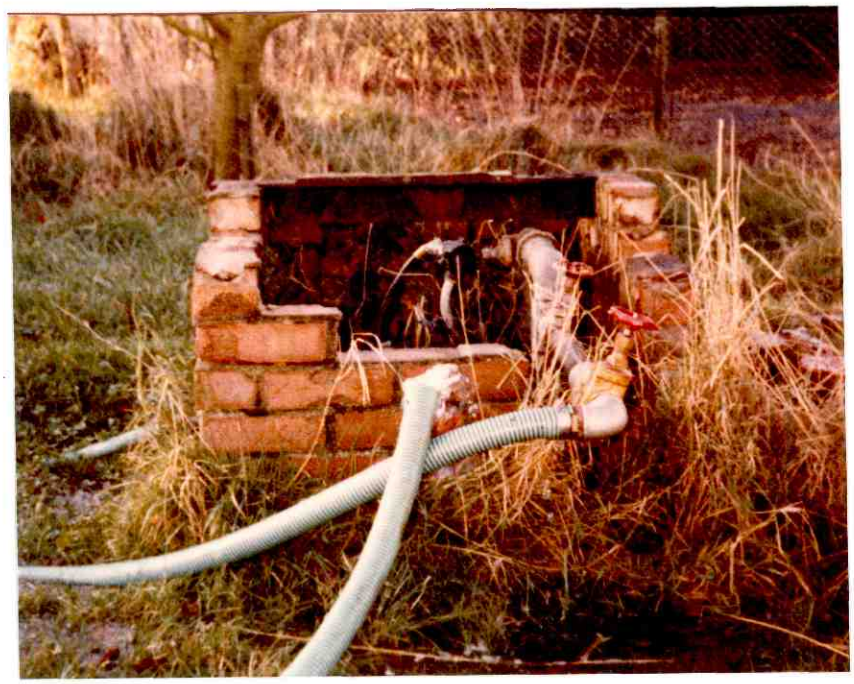


Plate 3.2. A water withdrawal point at the Wild Life Park, Great Witchingham. This was utilized for sampling the borehole.

oxidation of the divalent states to the insoluble trivalent and tetravelent states of the elements.

$$Fe^{2+} + (0) \longrightarrow Fe^{3+}$$

$$Fe^{3+} + 3(OH^{-}) \longrightarrow Fe(OH)_3 \uparrow \text{ Insoluble}$$

$$Mn^{2+} + 2(0) \longrightarrow MnO_2 \uparrow \text{ Insoluble}$$

3. dissolve available suspended colloidal and or particulate forms of iron, and

4. destroy any organic complexes which may not be measured by the analytical preocedure (International Standards for Drinking Water, Geneva, 1971 and Water Research Association Technical Memorandum No. TM83, 1973).

Samples in the 1000 ml bottles (unacidified) were stored in the refrigerator at a constant temperature of $4^{o}C$. This was to prevent a large-scale loss of free carbon dioxide, as well as nitrates. The method reduced the loss of free carbon dioxide, as the maximum variation between five in-situ determiantions of the gas in water and another set of five determinations using samples from the same source but stored for four days was only 0.3%.

3.4. Samples preparations for analyses

3.4.1. Rock samples

Most of the samples were wet when collected and so were air dried.

Shelly Chalk and shelly and gravelly Crag and sands and gravels were sieved through B.S. sieve mesh 30 to get rid of the very coarse materials. Each sample was then quartered and one part taken.

Each of the parts taken was crushed using the Tema Mill, to grain sizes passing 120 mesh B.S. sieve. In order to avoid contaminating subsequent samples, the Tema Mill was cleaned with acetone at the end of each milling.

Test tubes to be used for digesting were thoroughly washed with liquid soap, rinsed with tap water, then with de-ionised water and then left in an oven cupboard to dry. A 0.25 g portion of each sample from above was digested using 1 ml concentrated nitric acid (HNO_3) and heated for one hour and a half at a temperature of between 100^{o} and $110^{o}C$. This is done to take the rock into solution.

To the resulting solution, 9 ml of de-ionised water was added making a final solution of 10 ml. In order to ensure a thorough mixing of the solutions, each tube was shaken for one minute on the Whirlimixer. The solutions were thus ready for the determination of their iron and manganese concentrations.

3.4.2. Water samples

Apart from the cations required to be determined, there are others in solution which may negatively affect the analytical results. To prevent these other cations from interferring during analysis, precautions were taken.

To each 5 ml portion of the water samples for iron (Fe), manganese (Mn), and potassium (K^+) determinations, 1 ml of $^N/4$ (1:3 dilution) hydrochloric acid (HCl) was added. This solution was made up to 50 ml with distilled water. Also to each 5 ml portion of the water samples for sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) determinations, 1 ml of lanthanum chloride and 1 ml of $^N/4$ (1:3 dilution) hydrochloric acid were added. This solution was also made up to 50 ml with distilled water. The added acid either removes or substantially reduces any background disturbances on the analytical machine, while the lanthanium in the second solution stabilizes it especially with regard to calcium ions. At the end of these treatments, the fractions of the water samples were ready for analysis.

CHAPTER 4

ANALYSES AND RESULTS

4.1. Introduction

The chemical analyses were carried out at the Imperial College of Science and Technology in London and at the Heigham Works laboratory of the Anglian Water Authority in Norwich, East Anglia.

Seventy eight rock samples (thirty four of Crag and Glacial sands and gravels and forty four of Chalk), were chemically analyzed and in duplicate for their iron and manganese contents. Ninety two water samples were also analysed chemically for their iron and manganese as well as the major cations, anions and free carbon dioxide concentrations.

All analyses for the cations were by the method of the atomic absorption spectrophotometer (A.A.S.). The anions chloride (Cl^-) and bicarbonate (HCO_3^-) as well as the free carbon dioxide were determined by volumetric methods. The sulphate and nitrate were by an autoanalytical method based on colour measurements-colorimetry.

For iron and manganese (in water samples), the samples acidified in the field were used, while samples for the determination of the four major metallic ions - sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were non-acidified.

Samples for the anions and free carbon dioxide determinations were also unacidified. As a precaution, to ensure the operation went

satisfactorily during the analyses for cations, a blank and a standard sample preceded every set of four raw water samples thus:

Blank - Standard - Sample, Sample, Sample, Sample - Blank - Standard.

4.1.1. Chloride ion (Cl^-)

The concentration of this ion was determined by the Argentometric or silver nitrate method. A 100 ml of each of the unacidified water samples was titrated against silver nitrate solution (1 ml silver nitrate solution ≡ 1 mg Cl^-) using potassium chromate as a precipitation indicator. The end point is a tinge of red colour at the disappearance of the intial light green colour.

$$Ag^+ + Cl^- \longrightarrow \underset{\text{White precipitate}}{\underset{\downarrow}{AgCl}}$$

Excess Ag^+

$$\text{i.e. } 2Ag^+ + CrO_4^{2-} \longrightarrow \underset{\text{Red precipitate}}{\underset{\downarrow}{Ag_2CrO_4}}$$

Calculations

Volume of indicator used = 0.2 ml.

assuming: a ml as volume of silver nitrate used

given: 1 ml silver nitrate solution ≡ 1 mg Cl^- ion at end point,

(a - 0.2) ml silver nitrate solution used up. This is equivalent to (a - 0.2) mg Cl^-

i.e. the 100 ml raw water sample contain (a - 0.2) mg Cl^-

$\therefore$ 1000 ml will contain (a - 0.2) x 10 mg Cl^-

= (10a - 2) mg/l

= <u>(10a - 2) ppm</u>

4.1.2. <u>Bicarbonate ion (HCO_3^-)</u>

Using a pH meter to monitor the end point, 200 ml of each of the unacidified raw water samples was titrated against a 0.1N hydrochloric acid (HCl) solution until a pH value of 4.5 was reached. It is known that neutralization of the bicarbonate ion is complete only at a pH value of 4.5. Neutralization around pH 7 is known to occur only for strong acids and bases, which the bicarbonate and other very weak acid solutions involved here are not.

$$CO_3^{2-} + 2H^+ \longrightarrow HCO_3^- + H^+$$

$$HCO_3^- + H^+ \longrightarrow H_2CO_3 \quad \text{(at pH 4.5)}$$

<u>Calculations</u>

Assuming: Volume of 0.1N HCl used up = a ml

given: 1 ml 0.1N HCL $\equiv$ 5 mg HCO_3^- in 200 ml sample

$\therefore$ a ml 0.1N HCl $\equiv$ (5 x a) mg HCO_3 in 200 ml sample

i.e. 200 ml sample contain (5 x a) mg HCO_3^-

$\therefore$ 1000 ml sample will contain (5 x a) x 5 mg HCO_3^-

= 25a mg/l HCO_3^-

= <u>25a ppm HCO_3^-</u>

4.1.3. Free Carbon Dioxide (CO_2)

Free carbon dioxide is the amount of the gas present as dissolved carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

To determine the concentration of free carbon dioxide, phenolphthalein indicator and a pH meter to monitor the end point were used.

100 ml of each of the unacidified raw water samples was taken. 5 drops of the phenolphthalein indicator was added and titrated against $^N/_{44}$ sodium hydroxide (NaOH) solution until a violet red colour appeared. The titration was however continued until a pH value of 8.3 was reached. It is known that at pH values greater than 8.2, no carbon dioxide may be present in natural solutions.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$$

Calculations

Assuming: volume of $^N/_{44}$ NaOH solution used up = a ml

given: 1 ml $^N/_{44}$ NaOH ≡ 1 mg CO_2 in 100 ml sample

∴ a ml $^N/_{44}$ NaOH ≡ a mg CO_2 in 100 ml sample

i.e. 100 ml sample contain a mg CO_2

∴ 1000 ml sample will contain (a x 10) mg CO_2

= 10a mg/l CO_2

= 10a ppm CO_2

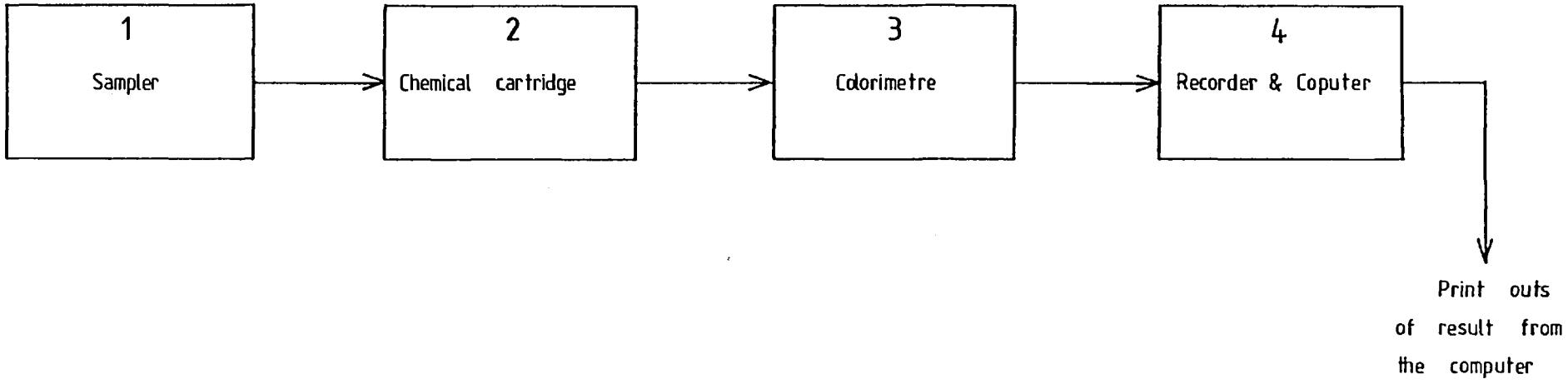


Fig. 4.1 A schematic flow diagram representation of the autoanalyser used for the determination of sulphate and nitrate ions.

4.1.4. Sulphate ion (SO_4^{2-})

This was determined using an autoanalyser, diagramatically shown in figure 4.1. The sampler holds the samples to be analyzed, the chemical cartridge is a compartment of chemical reactions. The colourimeter measures the turbidity of products from the chemical cartridge, while the fourth component records the measurements from (3) and gives a print out of results in milligram per litre (mg/l) on paper tapes. This computer, the last component (a Hewlett Packard 9815A System), operates by sampling and calculating results which are then printed out. It has the advantage of compensating for baseline drifts as well as changes in sensitivity during analyses when results are simultaneously calculated.

For the analysis of sulphate, a sulphate cartridge was fitted. In this case, sulphate (SO_4^{2-}) ions react with barium chloride ($BaCl_2$) in a 2% gelatine solution to produce a finely divided suspension of barium sulphate ($BaSO_4$). The turbidity of this suspension was measured at 505 nM.

The gelatine solution was to prevent barium sulphate from precipitating before it reached the third compartment, the colorimeter.

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$$

4.1.5. Nitrate ion (NO_3^-)

The same instrument for sulphate ion determinations fig. 4.1 was used for this, but with a nitrate cartridge in compartment (2).

In this case, nitrate (NO_3^-) ions were reduced to nitrite (NO_2^-) ions, using hydrazine catalised by copper. The produced nitrite diazotizes acidifed sulphanilamide that is simultaneously introduced. This diazotized sulphanilamide, then coupled with N - 1 - N. E.D.D. (N - 1 - Napthyl Ethylene diamine dihydrochloride) produces a purple coloured solution. The intensity of the purple colour is proportional to the concentration of the starting nitrate ions and was measured at 520 nM.

In conclusion, although iron and manganese exist in different forms in natural solutions, only their total concentrations have been analysed in the study area. This is so because of the available laboratory facilities and because, with the water industry in view, one is constrained to consider total instead of the different species in terms of the problems created by these elements in public water supply. However, the determination of the total iron and manganese, imposes a limitation to the understanding of the geochemistry of the elements, especially in considering the redox potentials of the ground waters. These problems will be discussed later in chapter six, where Eh-pH diagrams will be employed in predicting the species of iron and manganese possible in the ground waters.

The limit of detection for iron and manganese in rock samples was 0.01 ug/ml, with a precision (coefficient of variation) of 2% (i.e. $\pm$0.02). The limit of detection for iron was 0.01 ug/ml and for manganese and anions was 0.02 ug/ml in water samples, with a general precision of 0.5% (i.e. $\pm$ 0.005).

Table 4.1a Iron and manganese concentrations in the Glacial sand and gravels and the Crag of Norfolk

Locality No.	Sample No.	Average Concs. Iron (Fe) ppm	Iron (Fe) %	Average Concs. Manganese (Mn) ppm	Mang. (Mn) %
1	1	23000	2.30	2920	0.29
	2	19900	1.99	145.20	0.01
2	3	94000	9.40	1693	0.17
	4	103380	10.34	3793	0.38
3	5	9640	0.96	327.20	0.03
	6	13200	1.32	318.20	0.03
4	7	13840	1.38	177.20	0.02
	8	9860	0.98	88	0.008
5	9	17320	1.73	550.20	0.05
	10	25480	2.54	900	0.09
6	11	244360	24.43	7136	0.71
	12	21000	2.10	253	0.02
7	13	39900	3.99	432	0.04
	14	52000	5.20	738	0.07
8	15	54600	5.46	1970	0.19
	16	84800	8.48	1659.40	0.16
9	17	4140	0.41	20.40	0.002
	18	4480	0.45	20.80	0.002
10	19	16420	1.64	40	0.004
	20	20560	2.05	80	0.008
11	21	8560	0.86	232.40	0.02
	22	25780	2.58	400	0.04
12	23	22040	2.20	75.60	0.007
	24	15440	1.54	40.00	0.004
13	25	24520	2.45	436	0.04
	26	35880	3.58	80	0.008
14	27	7820	0.78	480	0.05
	28	13180	1.32	397	0.04
15	29	15180	1.52	40	0.004
	30	64840	6.48	359.40	0.04

Locality No.	Sample No.	Average Concs. Iron (Fe) ppm	Iron (Fe) %	Average Concs. Manganese (Mn) ppm	Mang. (Mn) %
16	31	14420	1.44	165.80	0.02
	32	14080	1.41	120	0.01
17	33	12080	1.21	129.40	0.01
	34	12420	1.24	137	0.01

Table 4.1b Iron and manganese concentrations in the Chalk of Norfolk

Locality No.	Sample No.	Average Concs. Iron (Fe) ppm	Iron (Fe) %	Average Concs. Manganese (Mn) ppm	Mang. (Mn) %
1	1	1714.20	0.17	266	0.03
	2	1447.80	0.14	228	0.02
2	3	860	0.09	181	0.018
	4	597.40	0.06	208	0.02
3	5	3060	0.31	220	0.02
	6	3640	0.36	230	0.02
4	7	5540	0.55	232.20	0.02
	8	5590.80	0.59	299.80	0.03
5	9	1000	0.10	196	0.019
	10	1540.20	0.15	164.20	0.016
6	11	1825.40	0.18	340.60	0.03
	12	1922	0.19	244	0.02
7	13	2136.40	0.21	216	0.02
	14	1099	0.11	202	0.02
8	15	1104	0.11	216.40	0.02
	16	840	0.08	187	0.018
9	17	1020	0.10	225.40	0.02
	18	2500.20	0.25	221	0.02
10	19	1885	0.19	320.20	0.03
	20	2142	0.21	361.40	0.036
11	21	3560	0.36	174	0.017
	22	3460	0.35	154.80	0.015
12	23	3052.40	0.30	240	0.02
	24	6005.60	0.60	259	0.026
13	25	563.20	0.06	195.60	0.019
	26	560	0.06	192	0.019
14	27	3608	0.36	140.20	0.01
	28	3590.20	0.36	151.40	0.015
15	29	5632.80	0.56	426.60	0.04
	30	4834	0.48	352.40	0.03

Locality No.	Sample No.	Average Concs. Iron (Fe) ppm	Iron (Fe) %	Average Concs. Manganese (Mn) ppm	Mang. (Mn) %
16	31	1902	0.19	140.40	0.016
	32	1343	0.13	164	0.016
17	33	1523.40	0.15	186.20	0.018
	34	1175.20	0.12	164	0.016
18	35	2885.80	0.29	352	0.035
	36	1836	0.18	297.20	0.029
19	37	3380.40	0.34	154.40	0.015
	38	1197.80	0.12	148	0.01
20	39	875.20	0.09	152.80	0.015
	40	915.20	0.09	156	0.015
21	41	1527	0.15	160.20	0.016
	42	1025.40	0.10	172	0.017
22	43	3254.40	0.32	320	0.03
	44	3082.40	0.31	270.60	0.027

Table 4.1c. Concentrations of iron and manganese in the Glacial sand and gravels, the Crag and the Chalk of Norfolk

Location No.	Average concentrations (ppm)			
	Glacial sands + gravels, + Crag		Chalk	
	Iron (Fe)	Manganese (Mn)	Iron (Fe)	Manganese (Mn)
* 1	21,450	659.42	1,581	246.26
* 2	98,690	2,534.25	728.7	194.03
3	11,420	322.66	3,350	224.94
* 4	11,850	125,05	5,565.4	263.66
5	21,900	703.76	1,270.1	179.40
* 6	10,500	243.19	1,873.7	288.29
* 7	45,950	564.68	1,617.7	208.88
* 8	69.700	1,807.69	972	201.16
9	4,310	19.99	1,760.1	223.19
* 10	18,490	56,57	2,013.5	340.08
11	17,170	304.88	3,510	164.12
* 12	18,740	54.99	4,529	249.32
* 13	30,200	79.98	561.6	193.78
14	10,500	436.52	3,599.1	145.69
* 15	40,010	39.99	5,233.4	387.68
16	14,250	141.03	1,622.5	151.74
17	12,250	133.15	1,349.3	174.74
18			2,360.9	323.44
19			2,289.1	151.16
20			895.2	154.39
21			1,276.2	165.99
22			3,168.4	294.26

* = Samples of Glacial sands and gravels or the Crag and Chalk taken from the same location.

All values for manganese (Mn) are geometric means.

Table 4.2 Physical and preliminary chemical results for water samples

Sample No.	Fe ppm	Mn ppm	SO_4^{2-} ppm	NO_3^- ppm	Cl^- ppm	HCO_3^- ppm	Free CO_2 ppm	pH	O_2 ppm	Temp °C
1	0.14	0.01	25.71	8.26	37.75	221.25	32.50	7.15	6.54	10.0
2	1.23	0.06	55.41	0.35	45.00	283.50	22.80	6.78	3.85	11.0
3	0.08	0.01	31.07	9.32	34.25	227.50	43.00	7.10	6.88	10.0
4	0.87	0.07	31.43	0.08	34.00	191.25	29.00	7.25	3.03	11.0
5	0.03	0.01	30.71	4.76	46.50	221.25	34.50	7.10	5.22	11.5
6	1.57	0.04	30.25	1.02	35.50	268.25	29.50	7.08	1.34	10.5
7	0.64	0.04	23.21	0.30	35.75	199.88	17.00	7.31	3.14	11.0
8	0.94	0.06	43.57	0.14	31.50	192.50	35.50	7.20	2.45	10.5
9	2.36	0.11	65.56	0.01	72.00	279.00	17.50	6.86	2.87	10.0
10	2.32	0.18	34.60	0.01	24.25	283.50	32.00	6.74	0.45	12.0
11	1.10	0.11	127.90	0.64	123.50	260.00	32.00	7.06	2.69	11.0
12	0.10	0.02	72.37	1.10	42.50	267.75	34.20	6.94	1.98	11.0
13	0.15	0.09	71.30	19.18	77.50	374.00	57.20	7.04	7.27	11.0
14	0.25	0.01	30.70	0.01	28.00	183.00	16.30	7.39	1.32	11.0
15	0.57	0.02	9.10	0.01	15.50	134.25	12.00	7.58	1.10	11.0
16	2.11	0.13	11.0	0.08	59.75	232.00	26.10	7.52	3.34	10.5
17	1.38	0.07	42.71	0.01	101.00	206.25	18.00	6.82	2.73	10.5
18	1.86	0.09	0.01	0.01	30.50	242.25	20.90	7.24	2.31	11.0
19	1.10	0.12	61.55	0.01	55.50	238.00	21.40	7.07	3.25	11.0
20	0.73	0.05	22.86	0.67	36.75	122.50	10.00	7.71	2.06	10.5
21	1.23	0.06	11.02	0.32	23.50	300.00	27.00	7.26	3.41	11.0
22	2.39	0.13	22.00	1.11	28.00	296.50	32.20	6.85	4.51	10.0
23	0.02	0.01	34.81	5.24	75.75	250.00	29.60	7.19	4.85	10.5
24	0.31	0.04	72.37	3.73	85.30	227.75	20.30	7.35	3.77	10.5
25	1.28	0.04	7.80	0.77	18.50	296.25	46.50	6.98	1.10	11.0
26	1.71	0.08	40.00	0.23	25.00	283.25	31.10	7.34	2.93	10.0
27	3.02	0.13	51.80	0.08	17.30	284.80	40.00	7.34	1.58	10.0
28	1.09	0.04	35.40	0.02	32.50	295.75	38.60	7.09	1.15	11.5
29	0.01	0.01	16.68	11.13	31.25	190.00	16.00	7.62	4.40	11.0
30	0.04	0.02	79.90	9.06	35.50	271.00	31.10	7.09	6.46	12.0
31	0.30	0.04	23.21	7.42	51.50	162.50	17.00	7.42	2.95	11.0
32	2.40	0.28	221.90	0.06	58.00	302.50	52.90	7.06	1.44	10.5
33	1.00	0.09	47.50	0.01	29.00	127.00	13.70	7.54	2.38	9.0

Sample	Fe ppm	Mn ppm	SO_4^{2-} ppm	NO_3^- ppm	Cl^- ppm	HCO_3^- ppm	Free CO_2 ppm	pH	O_2 ppm	Temp °C
34	0.17	0.04	90.40	14.18	28.50	94.50	32.20	6.71	6.77	10.0
35	0.75	0.09	49.20	0.08	49.50	184.00	17.90	7.40	1.13	10.0
36	1.52	0.01	66.10	3.84	65.50	235.25	20.60	7.36	2.86	11.0
37	0.46	0.03	64.36	0.01	128.50	216.00	17.50	7.25	2.64	11.0
38	4.86	1.39	108.90	0.08	49.00	284.25	50.00	7.18	1.35	10.0
39	0.22	0.11	426.00	19.34	90.50	69.00	70.00	6.39	3.58	13.0
40	0.13	0.08	172.50	18.99	147.00	29.50	55.40	6.31	6.59	11.5
41	0.13	0.02	54.60	16.61	35.50	140.00	25.50	6.88	5.27	12.0
42	0.77	0.08	37.14	20.00	44.50	186.50	18.00	7.28	3.40	10.5
43	0.11	0.17	126.70	17.75	113.50	161.25	58.10	6.84	1.32	11.5
44	0.34	0.03	207.80	19.08	121.00	236.00	35.40	7.02	5.01	10.5
45	0.10	0.01	135.70	32.00	105.25	142.00	27.70	7.01	6.17	11.0
46	0.81	0.63	137.40	13.71	95.50	318.00	69.20	6.87	1.93	12.0
47	0.23	0.05	133.00	19.80	87.00	178.75	33.70	6.94	6.78	12.0
48	0.19	0.07	48.80	1.39	25.50	201.25	17.00	7.39	2.64	11.0
49	0.16	0.03	77.30	4.03	32.50	267.00	34.35	7.18	3.51	11.5
50	1.80	0.07	5.60	0.01	34.50	333.00	40.00	7.16	1.98	11.0
51	1.38	0.06	9.10	0.01	24.00	322.00	51.20	7.15	1.54	11.0
52	0.65	0.02	277.40	0.05	16.50	222.50	21.60	7.33	4.61	11.5
53	0.12	0.03	11.40	6.23	36.25	142.75	20.60	7.33	5.51	11.0
54	0.01	0.01	84.52	7.12	43.00	245.00	30.00	7.22	3.91	11.0
55	0.11	0.01	74.51	13.60	58.50	211.00	20.60	7.15	5.57	10.5
56	0.12	0.02	32.40	7.01	36.00	274.75	43.50	7.26	4.23	10.5
57	0.03	0.02	66.77	5.65	39.75	274.75	33.80	6.96	4.43	10.5
58	1.71	0.09	32.10	0.06	26.75	342.50	68.00	7.21	1.67	10.5
59	0.23	0.06	64.80	16.47	31.00	254.50	32.80	7.29	2.37	12.0
60	0.68	0.11	42.20	4.05	32.50	318.50	53.85	7.03	3.34	10.5
61	0.02	0.01	24.60	0.59	25.00	315.50	20.00	7.68	3.68	13.0
62	1.85	0.09	18.60	0.04	29.50	347.25	67.00	7.16	2.37	10.0
63	0.58	0.10	117.50	0.36	67.00	349.75	80.00	6.96	2.25	10.0
64	6.02	0.15	8.70	0.01	30.50	328.75	37.00	7.42	2.03	10.0
65	1.06	0.14	47.90	0.01	75.50	200.50	20.00	7.48	2.42	11.0
66	0.26	0.03	105.40	17.79	76.65	167.50	36.30	7.09	2.93	10.0
67	1.29	0.15	12.80	0.91	31.50	173.50	15.00	7.37	2.20	11.0

Sample	Fe ppm	Mn ppm	SO_4^{2-} ppm	NO_3^- ppm	Cl^- ppm	HCO_3^- ppm	Free CO_2 ppm	pH	O_2 ppm	Temp °C
68	0.10	0.02	230.70	19.23	97.50	177.75	32.80	6.96	4.62	11.0
69	1.38	0.18	33.00	0.04	33.00	213.75	26.00	7.48	1.10	11.0
70	0.02	0.04	21.60	6.37	70.00	168.50	11.70	7.85	6.91	10.5
71	1.52	0.03	67.14	3.87	366.75	316.00	20.70	7.06	2.04	12.0
72	0.82	0.04	56.00	11.90	70.50	265.00	31.50	6.81	2.53	11.0
73	0.17	0.03	74.80	15.34	29.00	111.50	16.50	7.28	4.06	10.0
74	0.22	0.03	120.70	20.20	72.75	257.00	33.85	7.18	6.46	10.5
75	2.85	0.12	10.00	0.27	30.78	167.25	10.00	7.82	5.64	10.0
76	1.01	0.08	5.00	0.01	30.00	290.50	33.00	7.30	3.19	9.5
77	0.13	0.02	116.60	17.77	146.00	220.75	42.15	7.10	6.69	9.0
78	0.14	0.03	74.70	16.46	52.00	250.00	30.70	7.22	4.84	12.0
79	0.07	0.02	81.10	19.77	58.75	267.75	40.85	7.09	4.31	12.0
80	0.12	0.04	109.70	19.82	121.00	330.00	68.80	6.90	4.74	11.0
81	6.13	0.19	43.10	0.06	59.00	382.25	67.00	7.21	2.37	10.0
82	1.39	0.07	41.50	0.01	28.50	313.00	55.90	7.07	2.03	10.0
83	2.11	0.02	84.70	0.01	60.75	373.00	78.20	7.00	2.20	11.0
84	9.77	0.29	601.40	0.17	222.00	505.25	127.50	7.10	2.48	10.0
85	5.74	0.14	12.00	0.01	33.00	343.75	75.30	7.34	1.67	10.5
86	0.13	0.01	32.00	4.35	29.00	250.25	21.95	7.34	2.73	13.0
87	2.87	0.14	71.70	0.01	48.25	365.75	67.50	6.96	2.31	11.0
88	0.25	0.01	128.70	17.98	31.00	225.25	18.20	7.22	4.06	10.0
89	0.18	0.24	230.10	1.07	71.55	377.00	82.50	6.81	1.71	11.0
90	1.36	0.01	9.20	11.19	17.50	124.50	14.80	7.71	3.12	10.5
91	0.36	0.01	92.20	6.56	38.00	286.75	24.00	7.28	2.80	12.0
92	0.12	0.01	89.40	20.33	35.00	202.75	28.00	7.10	4.21	13.00

Sample	Locality Name	Fe	Mn	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^-	NO_3^-	HCO_3^-	CO_2	Cl^-	pH	Temp °C	O_2
2	Binham	1.23	0.06	18.0	3.90	126.0	5.1	55.41	0.35	283.5	22.8	45.0	6.78	11.0	3.85
6	Langham	1.57	0.04	28.0	2.70	109.0	5.7	30.25	1.02	268.2	29.5	35.50	7.08	10.5	1.34
9	Mundesley	2.36	0.11	40.0	3.5	120.0	12.6	65.56	0.01	279.0	17.5	72.0	6.86	10.0	2.87
10	Thursford	2.32	0.18	17.0	2.40	98.0	6.7	34.60	0.01	283.5	32.0	24.25	6.74	10.0	0.44
11	Fakenham	1.10	0.11	41.0	2.80	166.0	6.4	127.9	0.64	260.0	32.10	123.5	7.06	12.0	2.69
16	Trunch	2.11	0.13	37.0	3.25	78.0	9.4	11.0	0.08	232.0	26.10	59.75	7.52	10.5	3.34
17	Royston Bridge	1.38	0.07	61.0	3.75	75.0	12.4	42.71	0.01	206.2	18.0	101.0	6.82	10.5	2.73
18	Melton Constable	1.86	0.09	14.0	2.70	67.0	9.2	0.01	0.01	242.2	20.9	30.5	7.24	11.0	2.31
19	North Walsham	1.10	0.12	36.0	3.60	96.0	12.2	61.55	0.01	238.0	21.3	55.5	7.07	11.0	3.25
21	Foulsham	1.23	0.06	19.0	2.80	90.0	6.2	11.2	0.32	300.0	27.0	23.5	7.26	11.0	3.41
22	Wood Dalling	2.39	0.13	19.0	2.80	47.0	4.2	22.0	1.11	296.5	33.2	28.0	6.85	10.0	4.51
25	Reepham	1.28	0.04	9.0	1.75	43.0	4.2	7.80	0.77	296.2	46.5	18.5(	6.98	11.0	1.10
26	Brandiston	1.71	0.08	9.0	2.10	94.0	4.3	40.0	0.23	283.2	31.10	25.0	7.34	10.0	2.93
27	Haveringhand	3.02	0.13	8.0	2.00	101.0	4.5	51.80	0.08	284 7	40.0	17.3	7.34	10.0	1.58
28	Gt. Witchingham	1.09	0.04	25.0	2.40	62,0	5.5	35.4	0.02	295.7	38.6	32.5	7.09	11.5	1.15
32	Felthorpe	2.40	0.28	27.0	5.60	158.0	10.2	221.9	0.06	302.5	52.9	58.0	7.06	10.5	1.44
36	Edingthorpe	1.52	0.10	42.0	4.30	95.0	16.0	66.10	3.84	235.2	20.6	68.5	7.36	11.0	2.86
38	Tunstead	4.86	1.39	31.0	6.80	130.0	14.4	108.9	0.08	284.2	50.0	49.0	7.18	10.0	1.35
50	Matishall	1.80	0.07	15.0	2.00	47.0	5.6	0.01	0.01	333.0	40.0	34.5	7.16	11.0	1.98

Table 4.3 Detailed chemistry of water samples with iron levels higher than 1.0 ppm

Sample	Locality Name	Fe	Mn	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^-	NO_3^-	HCO_3^-	CO_2	Cl^-	pH	Temp °C	O_2
51	Matishall	1.38	0.06	11.0	1.65	85.0	4.3	9.10	0.01	322.0	51.20	24.0	7.15	11.0	1.54
58	Mulbarton	1.72	0.09	15.0	5.0	129.0	7.8	32.10	0.06	342.5	68.0	26.75	7.21	10.5	1.67
62	Newton Flotman	1.85	0.09	24.0	2.40	107.0	5.6	18.6	0.04	347.25	67.0	29.5	7.16	10.0	2.37
64	Shotesham	6.02	0.15	18.0	2.80	65.0	5.2	8.7	0.01	328.75	37.0	30.5	7.42	10.0	2.03
65	Ranworth	1.06	0.14	43.0	4.0	71.0	11.1	47.9	0.01	200.5	20.0	75.0	7.48	11.0	2.42
67	Woodbastwick	1.29	0.15	13.0	1.80	77.0	3.5	12.8	0.91	173.5	15.0	31.5	7.37	11.0	2.20
69	Witton	1.38	0.18	19.0	3.50	90.0	4.5	33.0	0.02	213.75	26.0	33.0	7.48	11.0	1.10
71	Brundall	1.52	0.03	239.0	14.0	115.0	35.0	67.15	3.87	316.0	20.7	336.7	7.48	12.0	2.04
75	Berghapton	2.85	0.12	21.0	3.30	61.0	3.6	10.0	0.27	167.25	10.0	30.78	7.06	10.0	5.64
76	Berghapton	1.01	0.08	17.0	2.40	119.0	4.5	5.0	0.01	290.5	33.0	30.0	7.82	9.5	3.19
81	Seething	6.13	0.19	41.0	7.50	99.0	19.0	43.10	0.06	282.25	67.0	59.0	7.30	12.0	2.37
82	Hempnall	1.39	0.07	13.0	3.70	85.0	3.9	41.5	0.01	313.0	55.9	28.5	7.21	10.0	2.03
83	Aslacton	2.11	0.02	31.0	3.30	110.0	10.0	85.7	0.01	373.0	78.2	60.75	7.07	11.0	2.20
84	Aslacton	9.77	0.29	88.0	5.50	310.0	42.4	601.4	0.17	505.25	127.5	222.0	7.00	10.0	2.48
85	Shelton	5.74	0.14	20.0	5.00	111.0	7.5	12.0	0.01	434.75	75.3	33.0	7.34	10.5	1.67
87	Rushall	2.87	0.04	34.0	3.50	132.0	9.6	71.70	0.01	365.95	67.5	48.35	6.96	11.0	2.31
90	Raveningham	1.36	0.01	10.0	5.20	38.0	8.3	9.2	11.9	124.5	14.80	17.50	7.71	10.5	3.12
13	Weasenham	0.15	0.09	42.0	4.00	202.0	6.6	71.0	19.8	374.0	57.20	77.5	7.04	11.0	7.27
47	Thurne	0.23	0.05	34.0	6.40	145.0	17.6	133.0	19.18	178.75	33.17	87.0	6.94	12.0	6.7

Table 4.4 Relative concentrations (ppm) of iron and manganese in summer and winter water samples (1979/80)

SUMMER SAMPLES					WINTER SAMPLES			
Sampling Date	Sample No.	Fe	Mn	pH	Sampling Date	Fe	Mn	pH
20.7.79	4	0.87	0.07	7.25	29.2.80	1.16	0.09	7.38
20.7.79	5	0.03	0.01	7.10	29.2.80	0.27	0.02	7.22
20.7.79	1	0.14	0.01	7.15	29.2.80	0.20	0.02	7.16
20.7.79	3	0.08	0.01	7.10	29.2.80	0.20	0.03	7.08
3.8.79	29	0.01	0.01	7.62	8.2.80	0.21	0.03	7.35
3.8.79	24	0.31	0.04	7.35	8.2.80	0.75	0.07	7.46
3.8.79	23	0.02	0.01	7.19	8.2.80	0.20	0.03	7.17
3.8.79	54	0.01	0.01	7.22	1.2.80	0.19	0.07	7.11
3.8.79	21	1.23	0.06	7.26	14.12.79	1.34	0.09	7.34
24.8.79	2	1.23	0.06	6.78	18.1.80	2.00	0.16	7.65
24.8.79	6	1.57	0.04	7.08	18.1.80	2.29	0.10	7.75
24.8.79	10	2.32	0.18	6.74	4.1.80	2.73	0.23	7.50
31.8.79	9	2.36	0.11	6.86	7.12.79	2.40	0.14	7.34
31.8.79	17	1.38	0.07	6.82	7.12.79	1.47	0.11	7.48
31.8.79	19	1.10	0.12	7.07	7.12.79	1.15	0.15	7.44
31.8.79	37	0.46	0.03	7.25	1.2.80	0.76	0.10	7.48
31.8.79	57	0.03	0.02	6.96	8.2.80	0.24	0.10	7.12
7.9.79	55	0.11	0.01	7.15	1.2.80	0.21	0.08	7.32
7.9.79	72	0.82	0.04	6.81	1.2.80	0.86	0.15	7.16
7.9.79	42	0.77	0.08	7.28	1.2.80	0.76	0.18	7.47
7.9.79	71	1.52	0.03	7.06	10.12.79	0.95	0.07	7.32
14.9.79	22	2.39	0.13	6.85	14.12.79	2.48	0.13	7.45
14.9.79	28	1.09	0.04	7.09	21.12.79	1.11	0.05	7.36
28.9.79	51	1.38	0.06	7.15	8.2.80	0.82	0.09	7.04
28.9.79	14	0.25	0.01	7.39	8.2.80	0.45	0.04	7.36
18.10.79	18	1.86	0.09	7.24	4.1.80	2.38	0.08	7.55
24.10.79	38	4.86	1.39	7.18	14.12.80	5.11	1.16	7.27

CHAPTER 5

DISCUSSION OF RESULTS

5.1. Introduction

The general theoretical aspects of the chemistry of natural ground waters have been discussed in Chapter Two. Results from the analyses of rock samples show that two of the three aquifer rocks contain higher iron and manganese concentrations than the third.

The background values of the chemical elements and radicals determined in the waters, reflect the composition of both the rocks and their hydrogeological environment. These values are however modified by the relative positions above the Chalk of the Glacial sands and gravels, the Crag and the Chalky boulder clay. These modifications amplify the influence of the different rock types on the chemical quality of the waters in the area.

In this project, the World Health Organisation's recommended drinking water standards (table 2.5) are taken as the threshold of measurement for chemical elements and radicals concentrations. Based on these standards, about 85.65% of all water samples analysed have iron concentrations higher than 0.1 ppm, while about 48.91% have manganese concentrations higher than 0.05 ppm. These two levels of concentrations are the highest desirable levels of the elements expected in drinking water as, recommended by the World Health Organisation (WHO), Geneva (1971) (see table 2.5). It is obvious from the above that most of the water from the project area could be considered unsuitable for direct domestic use with respect

to iron and manganese concentrations.

In general, natural waters contain less than 0.5 ppm of iron. But ground waters with pH values less than 8.2 may contain up to 10.0 ppm iron. It is not surprising therefore to obtain iron contents as high as between 4.86 and 9.77 ppm in the study area (table 4.2), since the pH values range between 6.31 and 7.85 (see fig. 5.1). Manganese concentration in natural ground waters is about 0.2 ppm or less. In this area however, two water samples have concentrations higher than 0.5 ppm, four contain less than 0.5 ppm, while the rest have levels of 0.2 ppm and less (see appendix B, tables 4.6d-e).

High iron concentrations in Chalk waters (borehole waters) are found where the Crag and Glacial sands and gravels directly overlie the Chalk aquifer (see samples Nos. 9, 16, 17, 18, 19, 25, 26, 27, 32, 33, 36, 38, 64, 65, 67, 69, 71, 75, 76, 85, 2, 6, 10, 11, 22, 28, 50, 51, 83, 84, 87, 58, 62, 82 and 90 of appendix C, table 5.1). This situation is however not hard and fast as sample Nos. 49, 12, 48, 23, 55 and 31 of the same appendix show low iron concentrations although the Crag and the Glacial sands and gravels are directly above the Chalk. The highest recorded concentrations, 4.86 ppm, 5.74 ppm, 6.13 ppm and 9.77 ppm are from water samples where the glacial sands and gravels, and the Crag directly overlie the Chalk aquifer and are in turn overlain by the chalky boulder clay or clay, sample Nos. 9, 16, 18, 38, 69, 75, 83, 10, 84 and 87 are examples.

Very low to almost negligible concentrations of iron were obtained from waters where:

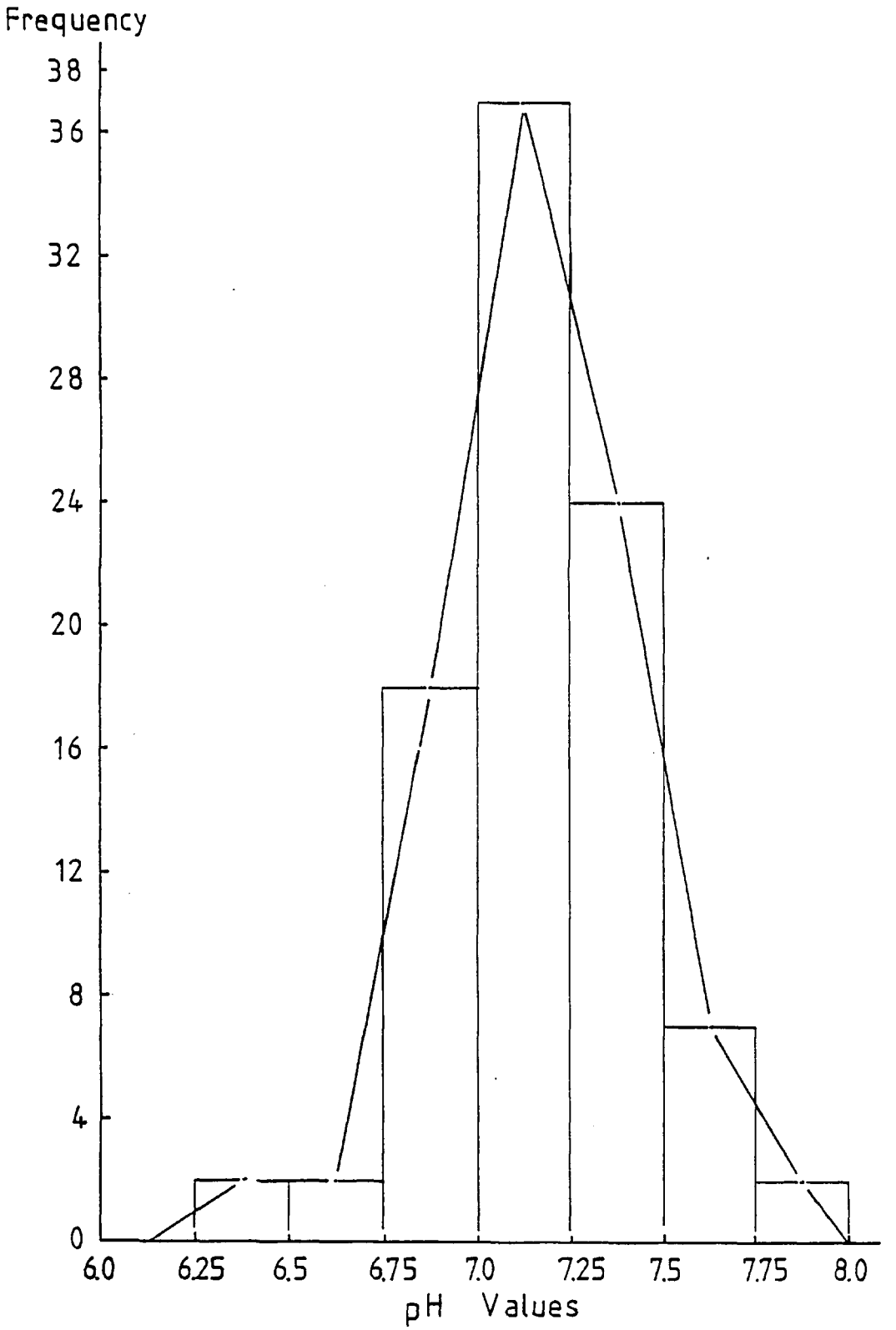


Fig.5.1 Frequency distribution of pH values in ground waters of the study area.

1. the Glacial sands and gravels is separated from the Chalk aquifer by the relatively impermeable boulder clay. Examples are sample Nos. 14, 29, 89, 24 and 57.

2. the Glacial sands and gravels, and the Crag are completely absent. Examples are sample Nos. 1, 3, 5, 13, 30, 61, 68, 53, 54, 56 and 92, and where

3. shallow wells tap water from the Glacial sands and gravels, the Crag, clay loam or alluvium and Chalk exposed at the surface. Examples are, sample Nos. 39, 40, 43, 44, 45, 47, 66, 70, 78, 88, 91, 73, 77 and 56 (see fig. 3.2 and appendix C, table 5.2).

A variation in the concentrations of iron and manganese between the summer (1979) and the winter (1979/80) was observed. In addition, a definite pattern of distribution of iron manganese in the ground waters of the area was also observed (fig. 5.2a and b).

5.2 Iron and Manganese concentrations in the three principal aquifer rocks

Table 4.1c shows the results of the analyses of samples of the Glacial sands and gravels, the Crag and the Chalk, while figures 5.3a and b are graphical comparisons of these results. There is a greater difference between concentrations for iron in the sands, gravels and Crag and that in the Chalk than for manganese between the Chalk and superficial deposits: median values of 18,490 ppm and 1,861 ppm iron and 243 ppm and 205 ppm manganese respectively are recorded. The almost

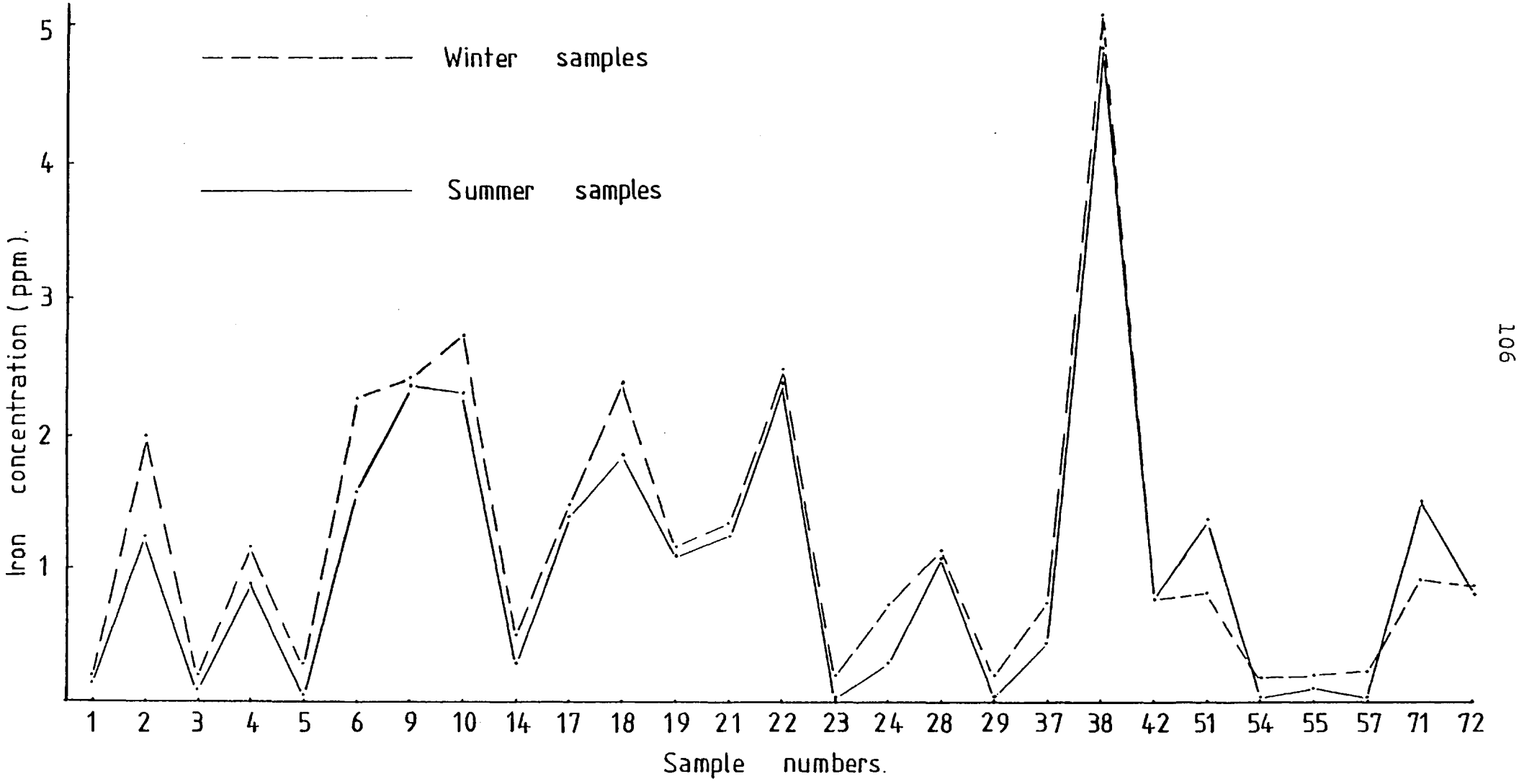


Fig. 5.2a Relative concentrations of iron in ground waters between the summer and the winter (1979/80).

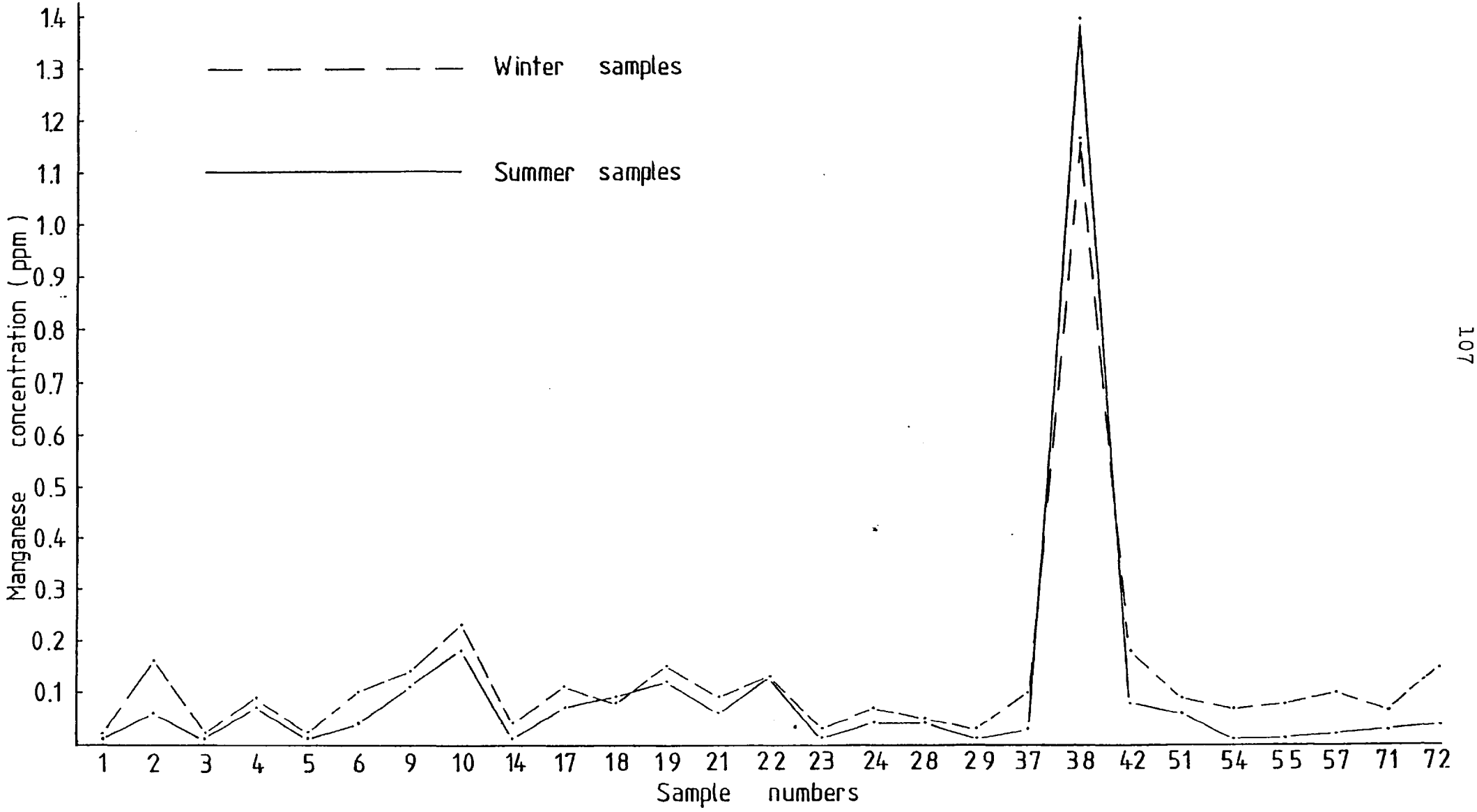


Fig. 5.2b Relative concentrations of manganese in ground waters between the summer and the winter (1979/80)

equal concentrations of manganese in the Chalk and Crag indicate that the ratio of manganese to iron is greater in the Chalk than it is in the Crag. Flints in the Chalk with high manganese encrustations are known in Norfolk. One Crag sample (sample No. 11) taken from a Crag-Chalk contact at Catton contains significantly high values of iron and manganese concentrations of 224,360 ppm and 7,136 ppm respectively. These are the highest recorded values for rock samples in the study area. These exceptionally high values may be due to the accumulation of materials leached from higher levels by infiltrating rain water. Such an accumulation is evident from the fact that in some places at Catton, the contact of Crag and Chalk (i.e. the base of the Crag) is marked by hard-pan situations - the sands and gravels cemented firmly together by oxides of iron. This condition is also known to occur at Caistor St. Edmund, where quarrying for sands, gravels and Chalk has exposed over a considerable distance the contact between the Crag and the Chalk.

The rock analyses have obviously confirmed that the Glacial sands and gravels, and the Crag contain higher iron and manganese concentrations than the Chalk.

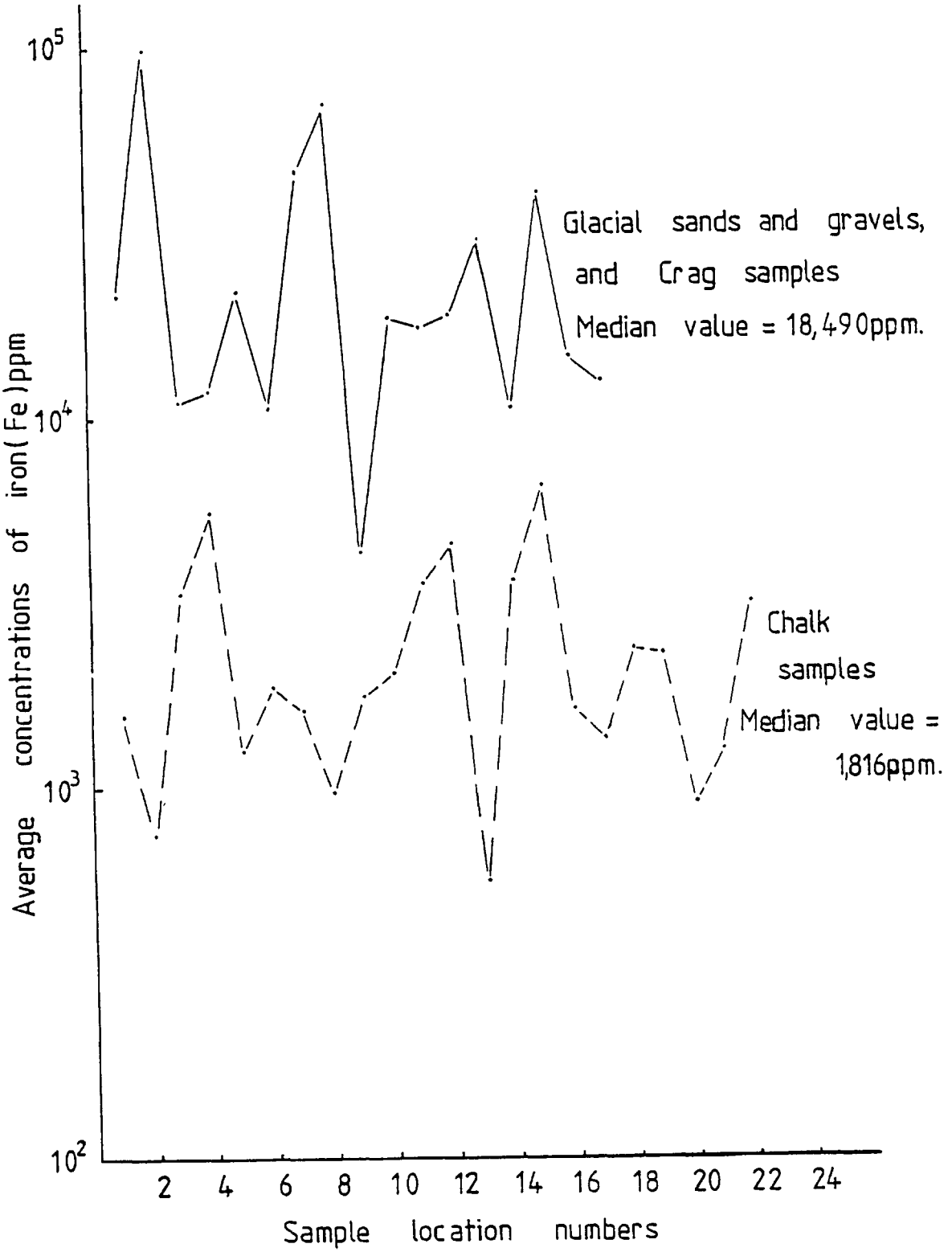


Fig. 5.3a Iron concentrations in the Glacial sands and gravels, the Crag, and the Chalk in NORFOLK.

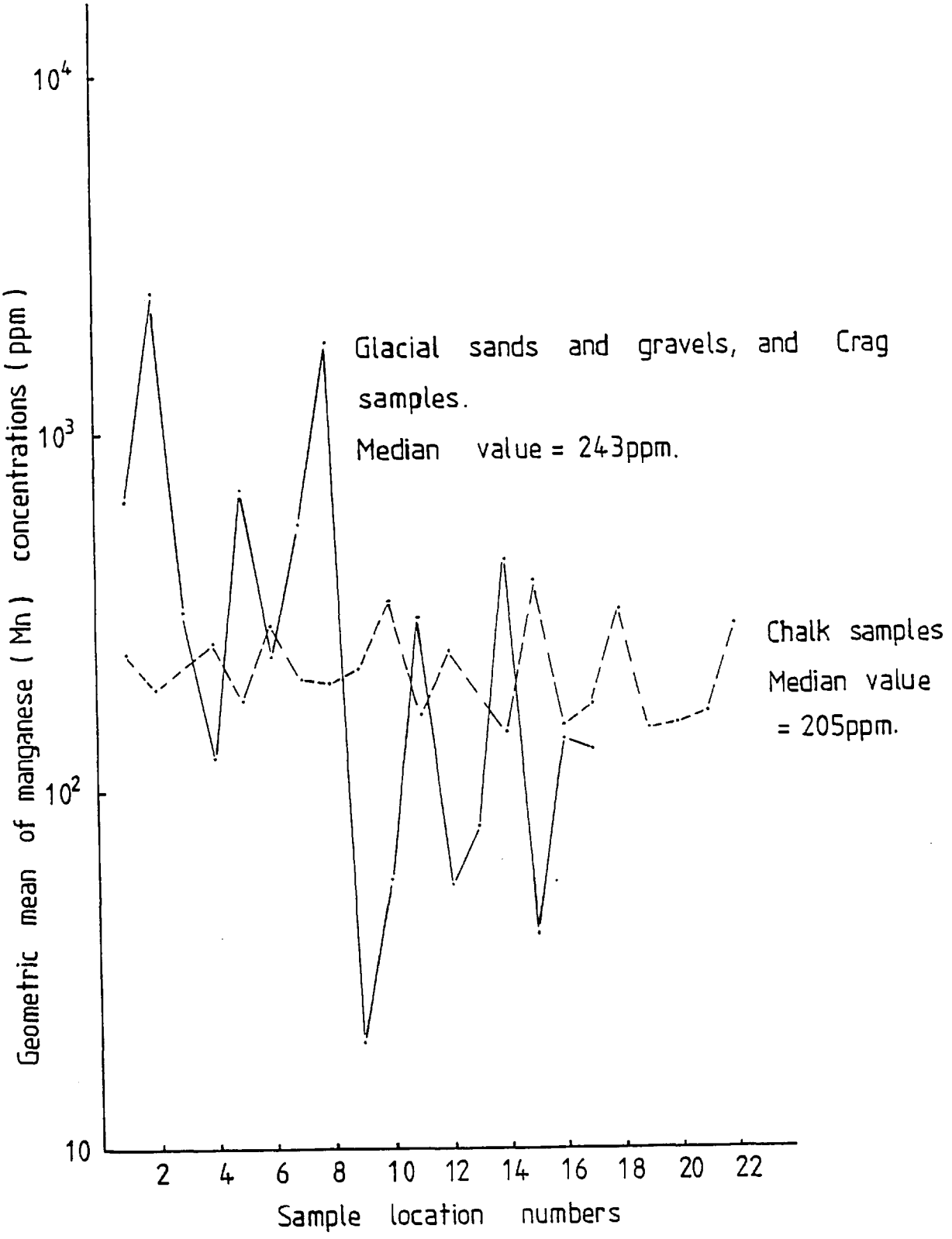


Fig. 5.3b Manganese concentrations in the Glacial sands and gravels, the Crag and the Chalk in NORFOLK.

5.3 Possible source of the Lower Pleistocene Crag Sea material and its iron content

The Crag is composed of:

1. fine grained ferruginous sands, calcareous in places and mixed with Chalk pebbles.
2. gravels which are ferruginous and also calcareous in places.
3. thin seams of clay within the sands (plate 2.1a).
4. marine fossils.

The sands and gravels must have been derived mainly from external sources, since the basal rock in Norfolk and its environs is the Chalk. Usually, sands and gravels are derived from the weathering of igneous and metamorphic (such as meta-igneous and quartzites) rocks as primary sources as well as from the reworking of unconsolidated detrital sediments from their major source. In the north of Britain, the Scottish highlands are of igneous rocks. However, these have no direct link with the Crag Sea basin, and the only other means by which materials from them could reach Norfolk is by the action of ice-sheets. Of course, it is known that by the Lower Pleistocene (when the Crag Sea deposited the Crag), glacial movements were unknown in Britain, West, R.G. (1968). Therefore one possible source of part of the sands and, the gravels of the Crag Sea is the continent of Europe. Ferruginous materials and the occasional pebbles associated with this rock - the Crag, as well as some sands, may have been derived mainly from within Britain. This is because deposits from which they could be derived are known to

exist within reasonable distances from Norfolk. Thus, it is probable that the Crag Sea materials were derived partly from within Britain and partly from the continent of Europe.

Sources inside Britain

Northwest of Norfolk in East Yorkshire and Lincolnshire are two of the most important iron producing fields of Britain. Here, many of the rocks of the Lower and Middle Jurassic as well as Lower Cretaceous are highly ferruginous. Examples are, the Frodingham ironstone of northwest Lincolnshire which is a shelly limonite (FeO (OH)) oolite about 7.92 metres thick; and the Cleveland ironstone. The main seam of the Cleveland deposit extends from west to east across the field and ranges in thickness from about 3.35 metres in the north to under 1.83 metres in the south of the worked area. In Yorkshire, the Dogger is ferruginous and sufficiently rich to be worked. The Gray Limestone series also contains a little impure ironstone in thin bands of 0.15 metres to 0.3 metres thick. The iron stones of this region are thus deposits of the Jurassic and the Cretaceous.

It is known that the Crag Sea was preceded by depressional movements and tilting towards the east, just after the earliest Eocene (Chatwin, 1954), probably coinciding with the final stage of the opening of the North Sea (Ziegler, 1975). It is likely this movement also affected parts of the region northwest of Norfolk, and so must have been responsible for the west to east trends of the Early Tertiary river systems of the region (Vernon Wilson, 1948).

According to Wingfield et al (1978), seismic profiling carried out within The Wash for the "Water Storage Feasbility Study" proved, the presence of several deep glacial filled valleys. These valleys together with those in Fenland have been interpreted by Gallois (1978) as part of a preglacial river system that was graded to a sea level which was about 100 metres below that of present day.

In East Yorkshire and Lincolnshire, there are no Tertiary and Lower Pleistocene deposits. It is therefore likely that these were periods of large-scale erosion, probably giving rise to undulating topography from which part of the Chalk, of the chalky boulder clays of Norfolk, were derived during the Middle Pleistocene. Part of the Tertiary and Lower Pleistocene erosion materials including ironstone and oxides of iron must have been deposited in the Crag Sea, which was now in its final stages of transgression.

Gallois, R.W. (1977) states that, "The Chalky Jurassic till (chalky boulder clay) made up entirely of Upper Jurassic and Cretaceous rocks derived from Lincolnshire and Norfolk, infill a topography cut into the solid deposits of West Norfolk." Further that the till is characteristically composed of:

1. Lower Cretaceous sandstone and ironstone
2. Red Chalk
3. Carstone
4. Flint
5. Upper Jurassic cementstone and shale
6. slightly sandy clay with fine and medium gravel-sized

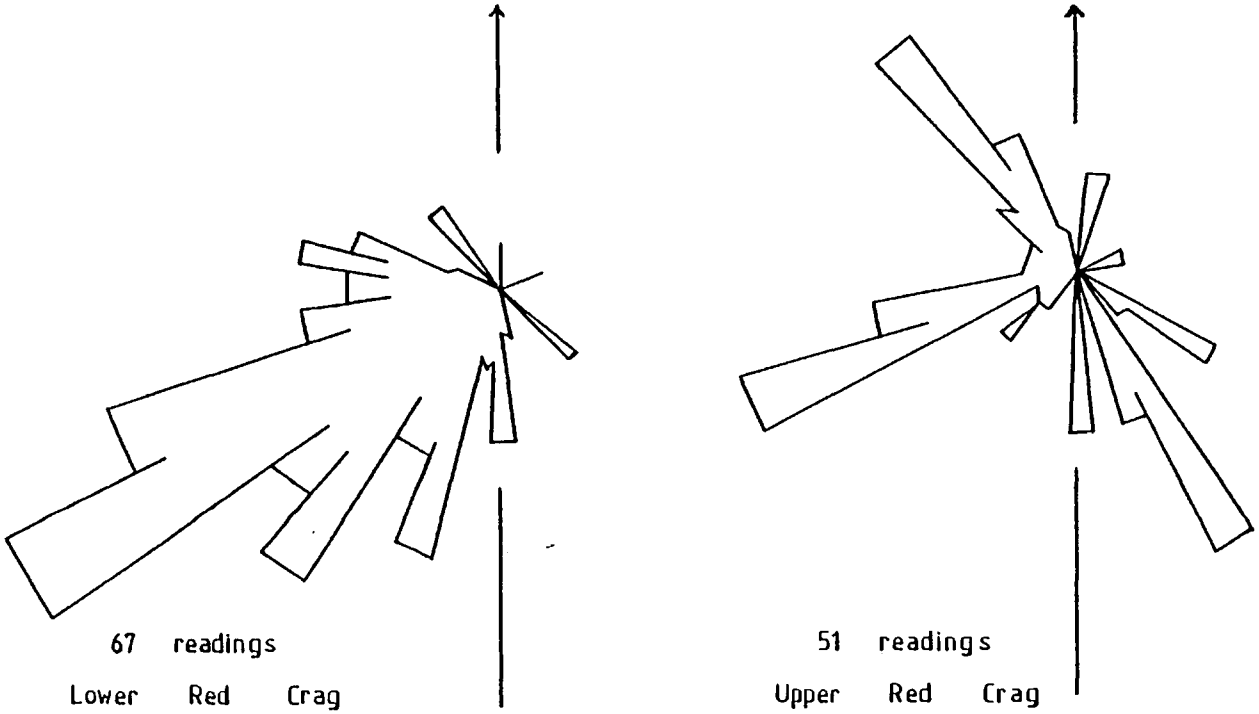


Fig.5.4a Rose diagrams of Crag palaeocurrent directions (after Dixon, R.G., 1979).

erratics of Chalk, and

7. rare farther travelled materials

Gallois further observed that the erratic content of the Chalky-Jurassic till of West Norfolk suggests derivation from the northwest; from the broad Upper Jurassic clay vale lying between the escarpments of the Lincolnshire Limestone and the Chalk.

From the above it is obvious that the Upper Jurassic and the Cretaceous of Lincolnshire must have been exposed by the long Tertiary and Lower Pleistocene erosion before the ice-flow. Therefore, the bulk of the Crag Sea deposits probably came from nearby, carried southwards to Norfolk by south trending sea currents along the North Sea coast (see fig. 5.4b). Since manganese usually occurs in association with iron (Jenne, E.A., 1967), the source of the iron-rich Crag Sea materials is probably the source of whatever manganese that is present in them.

Sources outside Britain

At the base of the Crag is the "Suffolk Bone Bed", which is persistent and of considerable thickness (a maximum of 0.6 metres) especially in Suffolk. This is probably derived from floating ice (Lyell and later observers).

West, R.G., (1968) also observed that estuarine silt of Pastonian (early Middle Pleistocene) age was pierced by ice-wedge cast of Beestonian (Middle Pleistocene) age (table 5.1) at West Runton,

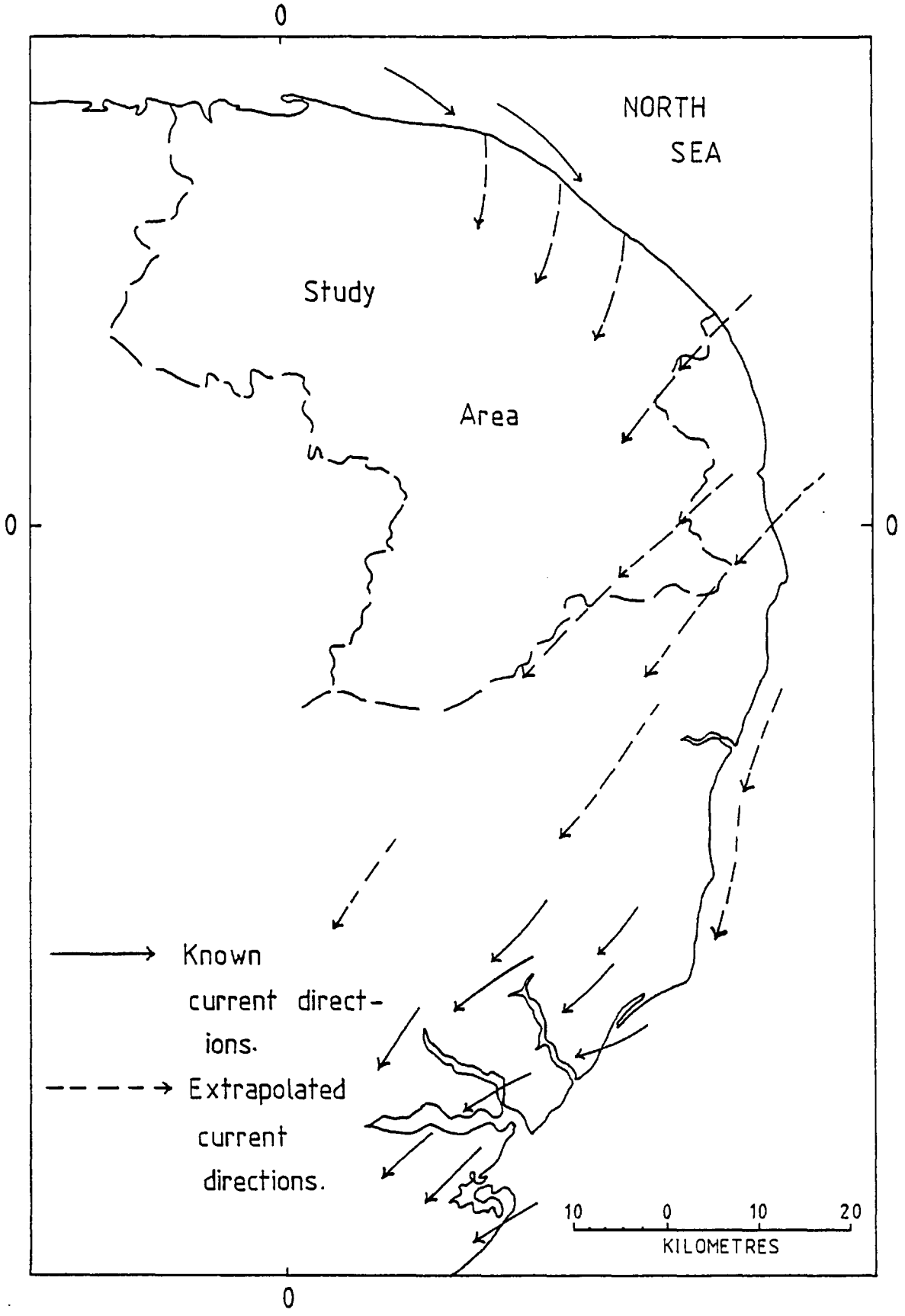


Fig. 5.4b Generalised current directions in the Lower Red Crag (Lower Pleistocene) facies (after Dixon, R.G.1979)

Table 5.1 Stages of the British Pleistocene (0.01 - 1.8m years)

Period	Series or Epoch		Stage	Climate
Quaternary	Holocene		Flandrian	t
	Pleistocene	Upper	Weichselian	c g p
			Ipswichian	t
			Gippingian	c g p
		Middle	Hoxnian	t
			Lowestoftian	c g p
			Cromerian	t
			Beestonian	c p
			Pastonian	t
		Lower	Baventian	c p
			Antian	t
			Thurnian	c
			Ludhamian	t

c = cold

p = permafrost known

g = glacial deposit known

t = temperate

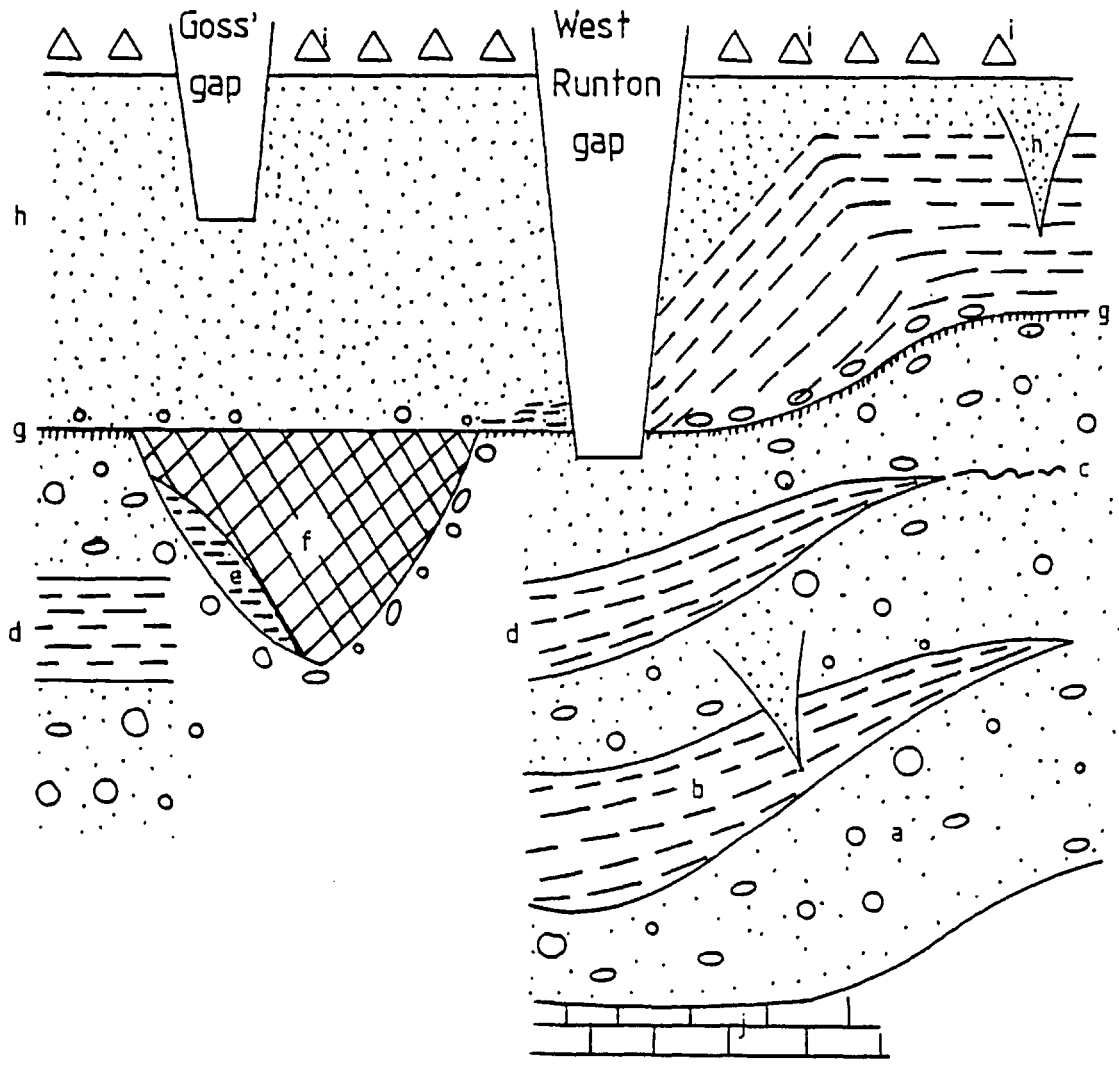
(After West, R.G. 1968)

on the north coast of Norfolk, and farther south and inland at Bungay (see fig. 5.5).

However, the Beestonian was a period when locally, ice had not reached this part of the country. The climate was only known to be cold (table 5.1). West, holds the opinion that parts of the Weybourne and Norwich Crag are of Pastonian (early Middle Pleistocene) and Beestonian age. The Beestonian was only permafrost in Britain, but a known glacial period in North West Europe. It is therefore likely that some, but certainly not all, Crag material came from the continent, as debris in floating ice.

Within the Norwich Crag at or near the base small pebbles are found in small proportions, with high proportions of medium quartz and quartzite pebbles at higher levels. Apart from what is stated above, 25% of quartz and quartzite of medium to large-size was recorded in a small count just below the soil, at the Pound Lane pit (N.G. Ref. 275 090), Thorpe St. Andrew. High proportions of quartz and quartzite can be seen beneath Norwich Brickearth at Catton brickworks (234 130) and Horsham St. Faiths (221 150). All these occurrences are at a similar stratigraphical level high in the Norwich Crag (Funnell, B.M., 1970).

Funnell, B.M., believes that the advent of large numbers of quartz and quartzite pebbles in Norfolk is probably indicative of an event of some considerable paleogeographical significance. Reid in Funnell, B.M. (1970), recorded approximately 40% quartz and quartzite pebbles from the Cromer Forest-bed series of Bacton, and suggests that the quartz and quartzite pebbles in both the Norwich Crag and the



EXPLANATION

a — Weybourne Crag (Beestonian/ Pastonian)

b — Estuarine silts (Pastonian) pierced by ice-wedge cast of Beestonian age

c — Sands and gravels, and a freshwater silt with actic plants (Beestonian)

d — Marl (Late Beestonian)

e — Muds and peats (Cromarian)

f — Weathered horizons (Cromarian 'soil')

g — Estuarine silts and sands(Cromarian), pierced by ice-wedge cast of Early Lowestoftian

h — Cromer Till (Lowestoftian)

i — Upper Chalk (Cretaceous)

Fig. 5.5 Schematic section of West Runton, about 450m long and 7m deep (after West, R.G. (1968).

the Cromer Forest-bed series originated from the Rhine drainage basin. This is not to say however that the proto-Rhine necessarily extended as far as the Norwich area. The pebbles may in this instance have been brought down by long-shore drifting. It does however indicate a change from an earlier regime when the pebbles consisted almost entirely of flint, perhaps derived locally from erosion of the Chalk (Funnell, B.M., 1970).

Cambridge, P.G. (Personal communications) believes that part of the Crag material must have come from the Belgian basin. This is based on scattered finds of iron-rich glauconite modules within the Crag. Glauconite nodules are the known sources of iron minerals in the Belgian basin. Dixon, (1979) also referred to the presence of glauconite nodules in the Red Crag. However, the glauconite nodules were either brought into the Crag Sea basin from the Belgian basin by long-shore drifts or they were deposited contemporaneously within both the Belgian and the Crag Sea basins. Glauconite is a hydrated potassium-iron silicate. Jarvis observed that iron is the major constituent of geothite, lepidocrocite, limonite and glauconite in the phosphatic chalks and hardgrounds of France, and that it is likely to be present in the montmorillitic portion of the mixed-layer clays. Parrron and Nahon also observed the in-situ weathering of glauconitic sediments, and the alteration of glauconite to ferruginous ŏoids consisting of Al-geothite or to a kaolinite- goethite mixture. This was part of a research program (IGCP Project 127) begun in 1970, on Mesozoic-Cenozoic "red-beds" of France and West Africa.

Glauconite is present in the uppermost Palaeogene Thanet

Beds of Herne Bay in Kent: Evernden et al, (1961) collected samples of pellets for dating the Palaeogene-Eocene rocks of East Kent. The samples were taken from the fresh sea-cliffs around the Thanet Dome. Glauconite is also found within the London Clay and, at the base of the Woolwich Beds. Jarvis, (1980), working on phosphatic chalks and hardgrounds of Santonian to early Campanian age in northern France, found that the hardgrounds are highly glauconitised. Thus, another possible source of glauconite was readily available and probably exposed at the time of the Crag Sea.

Apart from glauconite, pyrite and other minerals occur as diluents of both the hardgrounds and the phosphatic chalks. Sanford et al, (1975) working on radiometric dating of the base of the Niagaran (Silurian) near Hamilton, Ontario found the accumulations of phosphatic, glauconitic and ferruginous materials. Several localities in western New York are also known to contain accumulations of phosphatic nodules at the same horizon (Silurian) with the succeeding few metres of sedimentary rocks marked by the presence of iron minerals. These finds of glauconite in association with ferruginous materials seem to indicate a relationship between the presence of glauconite and iron minerals. Therefore, in places where it occurs in large quantities, glauconite could be a contributor of iron in such sediments.

If glauconite and other particular sources of iron were available for reworking they would still have to be transported to the Crag Sea. Strong currents which could have transported such grains are suspected to have existed. For in his study of sedimentary

facies of the Red Crag, Dixon, (1979) showed that there are two types of ripples - an upper small and a lower mega-ripple. The mega-ripple Dixon states are characteristic of fairly high intensity currents in the lower flow regime, where the resistance to flow is large, and sediment transport is intermittent, with sediments behaving as cohesionless (loose) grains. These mega-ripples are believed to be the result of unidirectional current streams, the dominant direction being a northeasterly trend (see fig. 5.4a & b). Thus for pebbles as large as those found within the Red Crag (50 mm to 300 mm long are known), the current strength and intensity must be high. This agrees with the findings of Funnell, (1970) that the quartz and quartzite pebbles must have been brought across the North Sea by long-shore drifting.

In conclusion, the materials of the Crag Sea, sands and gravels as well as the oxides, hydroxides, glauconite and pyrite they contain may have been derived from within and outside Britain. With a combination of a strong and intensive northeasterly current and a long-shore drift, it is possible to transport the pebbles of quartz and quartzite (gravels), the floating ice and some of the glauconite minerals from the continent of Europe, as well as iron oxide and iron-rich sediments from East Yorkshire and Lincolnshire coasts to the Crag Sea in Norfolk and Suffolk.

5.4 Hydrogeochemistry of the study area

Circulating meteoric ground waters of limestone areas are generally fairly constant in composition, being of calcium Ca^{2+}, manganesium Mg^{2+}, and bicarbonate HCO_3^- types. In the study area, calcium concentrations in the Chalk waters vary with a lowest of 38.0 ppm, a highest of 310.0 ppm and a median value of 94.0 ppm. When compared with waters from shallow wells (tapping the Glacial sands

and gravels, and the Crag aquifers) waters from the Chalk (limestone) aquifers contain slightly higher bicarbonate ion concentrations, 202.75 ppm from Crag and sands and gravels waters and 260.00 ppm from limestone waters (see fig. 5.6).

The geochemistry of cations such as iron, manganese, sodium, potassium, calcium and magnesium as well as anions such as bicarbonate, sulphate, chloride and nitrate, with reference to their concentrations, behaviour and sources are considered here.

5.4.1. Geochemistry of the cations

These are most likely to have been entirely derived from the solution of minerals within the rocks of the immediate environment.

Iron and Manganese (Fe and Mn)

These elements are considered together because thei. geochemistry is similar. However, emphasis is on iron, as 85.65% of all water samples analysed show iron concentrations higher than 0.1 ppm as against 48.91% with manganese concentrations higher than 0.05 ppm. Also, 39.13% of all water samples contain iron levels higher than 1.0 ppm as against only 2.09% with manganese concentrations higher than 0.5 ppm (see table 2.5). Concentrations if iron in the study area range between 0.01 ppm and 9.77 ppm, with a median value of 0.64 ppm, creating the most problem in waters of the area.

Iron is usually derived from iron-bearing minerals such as amphiboles, pyroxene and micas. In this area, the bulk of the iron and a small amount of the manganese in waters are believed to come from oxides, hydroxides and sulphide minerals within the Crag and, the Glacial sands and gravels (see table 4.1c; fig. 5.3 a & b). The occurrence of iron and manganese in these waters is haphazard, but two distinct patterns of distribution have emerged. The first is of higher concentrations in waters from boreholes into the Chalk, with the Crag or sands and gravels directly overlying the Chalk and, the second is of lower concentrations in waters from shallow wells (not into the Chalk), and from boreholes into the Chalk where the sands and gravels is separated from the Chalk or where both the sands and gravels and Crag are completely absent. Iron content in waters is high where the Crag and the Glacial sands and gravels are overlain by boulder clay. For instance, at Syleham with about 7.0 metres of boulder clay over the Crag and sands and gravels the concentration of iron in waters is about 6.0 ppm, with traces of manganese (East Suffolk and Norfolk River Authority, 1971). Also at Aslacton, where the overlying clay is both thick and dense, iron concentration of 9.77 ppm was recorded from a borehole at the Dale Farm (sample No. 84). Rushall (sample No. 87), Tunstead (sample No. 38), Bergh-Apton (sample No. 75), Wood Dalling (sample No. 22), and Bunwell (sample No. 83) are other examples. The boulder clay being dense and plastic is less permeable to both air and water and so is possibly easily water logged. This water logging may have produced high carbon dioxide concentration, and with perhaps organic acids persent, waters infiltrating through the clay acquire low pH values. These waters are now capable of leaching more iron from the underlying Crag than is normal. The amount of iron and manganese carried in solution to deeper levels will be

further increased by the thickness of ferruginous materials traversed. In two of the three samples from boreholes passing through the London Clay into the Chalk, Barton Turf (sample No. 41), Ludham (sample No. 42) and Seething (sample No. 81) iron levels are high, with low manganese concentrations (see appendix C, table 5.2). The high iron and the low manganese may be due to the presence of glauconite and pyrite. Glauconite, whose major constituent is iron - Jarvis, (1980) and, Parron and Nahon in Notholt, (1980), is known to be present in the London Clay - Everden et al, (1961).

A difference in the concentrations of iron and manganese between the summer of 1979 and the relatively wetter winter of 1979/80 was observed. During the final of the three stages of sampling for water, twenty seven of the seventy one boreholes and deep wells into the Chalk were sampled from December 1979 to February 1980. This was to make water available to determine any difference in iron and manganese concentrations with the seasons. The 1979/80 winter was wetter than the 1979 summer (fig. 1.3a). Analytical results show that there was a difference in elements concentrations between the two seasons (see table 4.4 and fig. 5.2a & b).

This difference in the concentrations of elements is attributed to the action of infiltrating rain water of the wetter winter, after the period of relatively dry summer. A plot of ground water levels from seven observation stations within the study area (figs. 1.3b and 1.4) indicate that a good part of the relatively high rainfall of the winter season, infiltrated underground. This means that the infiltrating rain water leached additional materials from overlying

sands and gravels, and Crag strata into Chalk waters.

Sodium (Na^+)

Sodium salts are very soluble and will not precipitate unless the concentration reaches several thousand parts per million (ppm). The saturation point for sodium chloride for instance is 264,000 ppm or 105,000 ppm Na^+ at 20°C (Davis and De Wiest, 1967).

Holden (1970), observed that most natural waters contain 30 ppm or less of sodium. Also Davis and De Wiest (1970) state that waters from pure limestone areas contain a range of 1.0 ppm to 20.0 ppm of sodium. In the study area eleven of thirty water samples analysed contain sodium in excess of the expected general level for a limestone area. The range of concentration here is between 8.0 ppm and 88.0 ppm with a median value of 21.0 ppm. One sample, (sample No. 71) has an exceptionally high level of 239 ppm of sodium. This is perhaps due to the intrusion of tidal water because of the location of the borehole at Brundal and the high chloride level obtained, the highest recorded for the project area (table 4.2).

Albite (Na-feldspar) is the main source of sodium. Upon attack by water containing carbon dioxide, albite decomposes to give silica, sodium carbonate and a clay mineral. Sodium is also derived from the atmosphere in association with salt spray near coastal areas. In Norfolk, however, sodium may be derived from connate sea water entrapped in strata during an earlier geological period, from rocks and minerals in the area, and some from the atmosphere washed down

by rain water in places close to the sea coast (see table 2.6).

Potassium (K^+)

Potassium occurs in the earth's crust in about the same quantity as sodium (table 2.3), but it is usually commonly less than ten percent of the concentration of sodium in ground waters (table 2.3, potable ground water), Davis and De Wiest, (1967). This relative immobility is due to a number of factors: such as the tendency of potassium to be absorbed or fixed in clays and clay minerals during weathering; and the fact that a good amount of potassium is concentrated by roots of vegetation. Most potassium-bearing minerals have higher resistance to weathering than sodium-bearing minerals.

The concentration of potassium in natural waters is usally 10.0 ppm and less (Davis and De Wiest, 1967). Holden, (1970) however, believes that it is usual to find up to 15.0 ppm of potassium in natural waters. A maximum value of 14.0 ppm was recorded for this area, with a range of between 1.65 ppm and 14.0 ppm and a median value of 3.3 ppm.

Common sources of potassium in nature are: the products of weathering of minerals such as orthoclase, microcline, nepheline, biotite and leucite. Possible sources in Norfolk are the clays and clay minerals.

Calcium (Ca^{2+})

This is the most abundant cation in many subsurface waters, as it is in the study area (see table 4.3).

In an environment with an abundant supply of hydrogen (H^+) ions, the solubility of calcium carbonate increases. One of the major sources of hydrogen ions in waters is the dissocation of carbonic acid, H_2CO_3.

$$CO_2 + H_2O \rightleftharpoons H_2CO_2 \qquad 1$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad 2$$

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad 3$$

From the equations above, an abundant supply of carbon dioxide is necessary to produce the required hydrogen ions. Water infiltrating through rocks and soils comes into contact with the carbon dioxide of the aeration zone, released by processes such as the respiration of plant roots and microorganisms as well as by microbiological decay of organic matter. Thus, such water becomes charged with much extra carbon dioxide and aquires a low pH value. It therefore leaches much calcium from calcium-rich minerals and from calcium carbonate in limestone areas. However, an increase in pH (the withdrawal of hydrogen ions or the removal of carbon dioxide from solution), will reverse the process of equation (3) above, then calcium carbonate will precipitate depleting the concentration of calcium ions in the solution. In this way, carbon dioxide is a critical factor with regard to the chemical quality of most natural ground waters, especially in limestone areas.

Most potable ground waters contain calcium up to between 10.0 ppm and 100.0 ppm (Davis and De Wiest, 1967), while waters from limestone areas may contain 160 ppm or more when carbon dioxide is under pressure, as in confined aquifers. The World Health Organisation, Geneva, (1971) has recommended 75.0 ppm and 200.0 ppm as the highest desirable and maximum permissible levels of calcium respectively in drinking waters (see table 2.5). Twenty eight of the thirty eight water samples analysed for calcium show concentrations higher than 75.0 ppm. Three samples contain over 160.00 ppm and two over 200.0 ppm. The range of concentration obtained is between 38.0 ppm and 310.0 ppm with a median value of 94.0 ppm. Since the environment is a limestone one with all the boreholes sampled abstracting water from the Chalk aquifer, it is not surprising to find this generally high calcium levels in the ground waters.

Calcium ions in ground waters are usually derived from limestone and dolomite; from calcium-bearing plagioclase, amphiboles, and pyroxene, as well as from gypsum and anhydrite.

The bulk of calcium in the study area definitely comes from the Chalk, a limestone. It is the bed-rock but also crops out at the surface over a large area in the west and northwest (fig. 2.4) as well as occurring as erratics, boulders and pebbles.

Magnesium (Mg^{2+})

Magnesium has a similar geochemistry to calcium, and its solubility (as magnesium carbonate) is also controlled by the

presence of carbon dioxide. But once in solution magnesium is not easily reprecipitated. This is reflected in the low magnesium-calcium (Mg/Ca) ratio of carbonates precipitated from natural waters.

Normal ground waters contain up to 40.0 ppm of magnesium though values higher than this have been observed (Holden, 1970), and values up to 100.0 ppm are known from magnesium-rich environments (Davis and De Wiest, 1967). The range of magnesium concentrations in the study area is between 3.5 ppm and 42.0 ppm with a median value of 6.6 ppm.

Magnesium is commonly derived from sources such as dolomite, olivine, biotite, hornblend, augite, and talc. Magnesium concentrations of the area are probably necessary to help balance the high chloride concentrations. The magnesium is probably derived mainly from connate sea water as well as from rocks and minerals in the area.

5.4.2. Geochemistry of the anions

Bicarbonate, sulphate and chloride are the major anions whilst nitrate is a secondary anion (table 2.4).

The anions are likely to be derived from the solution of minerals, but large amounts may come from non-litholigic sources. For instance, bicarbonate may come from carbon dioxide of the air and the soil due to soil processes. Chloride from salt blown inland from shorelines and sulphate from salt spray as well as from the oxidation-

reduction processes of independent minerals as well as sulphur dioxide gas.

Bicarbonate (HCO_3^-)

The carbonate (temporary) hardness of water is due to the presence of calcium and magnesium bicarbonates and carbonates in solution. The Chalk of the area is almost entirely calcium carbonate and is readily soluble in the presence of hydrogen (H^+) ions. Therefore the concentration of the bicarbonate ion is controlled by pH. At pH values above 8.2, bicarbonate ions dissociate into carbonates and hydrogen ions. $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ and at pH values less than 4.5 (i.e. increased H^+ ions concentration) bicarbonate ions are converted into carbonic acid molecules (Davis and De Wiest, 1970), $HCO_3^- + H^+ \rightleftharpoons H_2CO_3$. Recorded pH values of the study area are between 6.31 and 7.85. Since these values are above 4.5 and less than 8.2, bicarbonate ions predominate in the waters.

The concentration of hydrogen ions depends however on the dissociation of dissolved carbon dioxide (CO_2)

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$CO_3^{2-} + 2H^+ \rightleftharpoons HCO_3^- + H^+$$

The principal source of this carbon dioxide is the air in the soil root zone but it is also derived through the oxidation of organic matter by bacteria.

Organic matter + Bacteria + $O_2 \longrightarrow$ New cells + CO_2 + NH_3 + H_2O

In natural waters, bicarbonate ion concentrations range between 50 ppm and 400 ppm. All samples analysed contain bicarbonate concentrations of over 50 ppm, with one sample containing 505 ppm far above the maximum of 400 ppm. Generally, waters from beneath the heavier, less sandy boulder clay of the south have values of bicarbonate concentration between 200 ppm and 300 ppm and in places far exceed 300 ppm. For example boreholes at Bunwell (sample No. 83), Diss (No. 89), Seething (No. 81), and Aslacton (No. 84) have values of 373 ppm, 377 ppm, 382 ppm, and 505 ppm respectively. These high values are probably related to the high carbon dioxide content of the heavier soils derived from the boulder clay and solution of the chalk. (see equations 1, 2 and 3, page 128). However, in waters from shallow wells tapping the Crag and sands and gravels, the high bicarbonate values of between 90 ppm and 260 ppm correspond to carbon dioxide only. Sample Nos. 59, 70, 73, 78, 88, 91, and 92 (table 4.2) indicate this. Where the Crag, and sands and gravels are overlain by boulder clay (high CO_2 generation), the total bicarbonate concentration is much higher. For example at Syleham where 7 metres of boulder clay overlies the Crag, and sands and gravels, the bicarbonate concentration is 330 ppm.

In the north and northwest where the boulder clay is more sandy, the bicarbonate concentration is generally less than 300 ppm. This is probably due to the lighter relatively well oxygenated soil found here, derived from the sandy boulder clay.

Sulphate (SO_4^{2-})

The non-carbonate hardness of water is due entirely to the presence of calcium and magnesium sulphate in solution. Most sedimentary rocks contain less than 100ppm of sulphate and may contain less than 1 ppm, if waters pass through soils with sulphate reducing bacteria.

Common sources of sulphate in natural waters are: (1) the atmosphere, where it is probably from dust particles containing sulphate minerals from the oxidation of sulphur dioxide and hydrogen sulphide gases. (2) Hydrogen sulphides itself possible derived from bacterial reduction of organic matter especially in tidal flats. (3) The oxidation of sulphides in soils and water; in soils, the sulphides of the upper oxidised layers have largely been converted into sulphates which are gradually leached away by infiltrating water. (4) From the burning of natural fossil fuels like coal and petroleum oils. Since a lot of heating by means of coal fire and oil is done in the study area, this and the other two sources may be regarded as contributing to the sulphate concentrations in waters. However, the bulk of the sulphate in the area is derived from selenite - a mineral found in the boulder clay (East Suffolk and Norfolk River Authority, 1971). The concentration of sulphate varies according to the lithology of the deposits overlying the Chalk.

About 20 water samples have concentrations of sulphate higher than 100 ppm, with a general range of between 0.01 ppm and 601 ppm, with a median value of 49.2 ppm. In the north and northwest where the boulder clay is absent or has a sandy matrix, an average

value of about 35 ppm is known. But where the boulder clay is less sandy, as for example in the south, values increase to an average of over 100 ppm. South of the Waveney valley values commonly reach 300 ppm. This high concentration coincides with the occurrence of the more clayey, less chalky and less sandy boulder clay found in the area. (East Suffolk and Norfolk River Authority, 1971).

Beneath the Eocene (the London Clay), the saline waters of the Chalk show very high values of sulphate ion concentrations. For instance, water from a borehole into the Chalk at Lowestoft has a value of 2,800 ppm (East Suffolk and Norfolk River Authority, 1971).

Chloride (Cl^-)

Chloride salts are highly soluble therefore chloride is rarely removed from water except under freezing or evaporation conditions. Waters high in chloride are also high in sodium since sodium chloride is the main mineral in solution in highly mineralised waters.

Chloride ion concentration is usually a critical factor in waters for spray irrigation use. Shallow ground water in regions of heavy rainfall contains about 30.0 ppm or less of chloride ions. In the study area, seventy one of the ninety two water samples analysed contain chloride higher than 30.0 ppm, nineteen contain less than 30.0 ppm, the range of concentration is between 15.5 ppm and 366.0 ppm and the median value is 36.75 ppm.

However, over a large part of the area chloride concentrations of less than 100.0 ppm are found with an average of about

52.0 ppm for waters from boreholes into the Chalk and of 74.0 ppm for waters from shallow wells into the Crag (see fig. 5.6). One or two high values of concentrations are known. For example, from a borehole into the Chalk at Brundall (sample No. 71) a value of 366.0 ppm was obtained, from another at Aslacton (sample No. 84) 222.0 ppm as well as 146.0 ppm and 147.0 ppm from shallow wells into the Crag at Reedham (No. 77) and Catfield (No. 40) respectively.

Most chloride in ground waters is derived from chloride-bearing minerals like chloropetite and sodalite as primary sources. It is also derived from the precipitation the cyclic chloride lost from seas and oceans as spray. From ancient sea waters entrapped in sediments, and from intruding sea water into coastal or tidal aquifers. In the study area, however, in places where the Crag is exposed chloride concentrations are lower than where it is overlain by the boulder clay. At Catfield (Station Nurseries) sample No. 39 where the Crag is exposed, the value of chloride from a shallow well is 90.0 ppm. This compares with 147.0 ppm from Catfield (Long Acre, New Road) sample No. 40 where the Crag is overlain by the boulder clay.

The high value for Brundall (sample No. 71, table 4.3) may be associated with sea water intrusions. The recorded value for sodium, 239.0 ppm, the highest for the area may tend to confirm the above suggestion (see table 4.3).

Beneath the Eocene along the east coastal strip and in places around the synclinal area, concentrations of chloride in excess of an average of 250.0 ppm was recorded. It is thought that these high chloride waters are from connate sea waters entrapped in

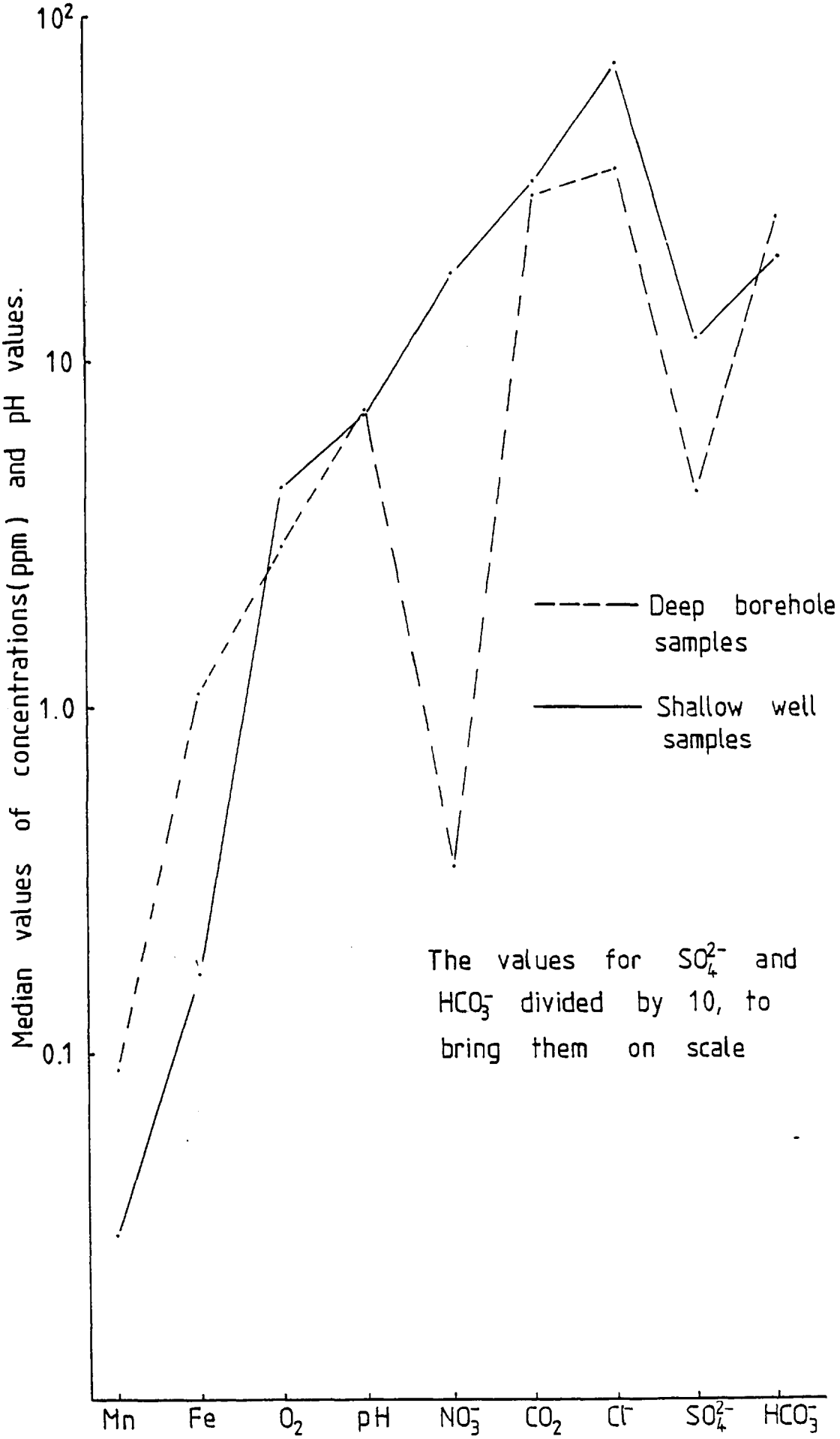


Fig.5.6 Comparison of waters from deep boreholes and shallow wells.

the strata during an earlier geological period, and from isolated intrusions of tidal sea water. Some of it could also have been derived from the atmosphere washed down by rain water, in places close to the sea coast (see table 2.6).

Nitrate (NO_3^-)

Compounds of nitrate are highly soluble and so nitrate is removed from water only through the activities of organisms and through evaporation.

Common nitrate concentrations in waters range between 0.1 ppm and 0.3 ppm in rain water. In normal ground waters, the concentration is between 0.1 ppm and 10.0 ppm of nitrate (George, W.O. and W.W. Hastings, 1957). The World Health Organisation (WHO) Geneva, (1971) has recommended a value of 45.0 ppm as the maximum permissible in drinking water (see table 2.5).

Nitrate is present in ground water throughout the study area in concentrations of between 0.01 ppm and 32.0 ppm. Twenty of the ninety two water samples analysed contain levels of higher than 10.0 ppm. A few of the lower values of concentrations are related to typically ferruginous waters from Chalk boreholes as for instance sample (Nos. 9, 27, 38, 64, 84 and 85) indicate (table 4.2). This is similar to an observation in soils (Koyama in Jenne, E.A., 1967). A few of the higher values of concentrations are also related to waters from Chalk boreholes and shallow wells with low iron contents; sample (Nos. 1, 5, 45, 57, 73, 80 and 90 are examples). From these examples

a relationship may exist between iron and nitrate concentrations in waters, in which lower iron concentrations may correspond to higher nitrate concentrations (see figs. 5.6 and 5.7). The nitrate levels in waters are however lower than the maximum recommended by the World Health Organisation (see fig. 5.8). Therefore, waters of the area are safe for direct use with regard to nitrate concentrations.

A satisfactory explanation has not been found for the relationship between the few high iron and the corresponding low nitrate concentrations, but it is believed that the low nitrate levels are due to the activities of sulphate - reducing bacteria, which are probably in association with iron - bacteria. These bacteria derive energy from the oxidation of organic compounds and in the process obtain oxygen from sulphate (SO_4^{2-}) ions. The result of this reduction produces nascent hydrogen (H) a strong reducing agent. This reacts with and reduces nitrates to nitrites through ammonia and to nitrogen (Smith, F., 1979, Norwich Water Division, Anglian Water Authority, personal communications). However, the author is of the opinion that the reduction of nitrates is a direct rather than an indirect biological action. At depths of 100 m and more reducing conditions are expected with very low dissolved oxygen concentrations. The bacteria, requiring oxygen for their metabolism, may have been involved in a process of reducing nitrates to nitrogen, thus setting oxygen free, which is then used, as a source of energy. In this way nitrate is depleted in solution.

Most nitrate in natural waters comes from organic sources of animal origin or from industrial and agricultural chemicals. When an organic material is decomposed through bacterial action, the complex protein change occurs through amino acids, ammonia, nitrites and finally to nitrates.

Some of the nitrates may be leached by percolating water and eventually reach the ground at low levels. Certain plants have bacteria living in their root nodules and fix nitrogen of the

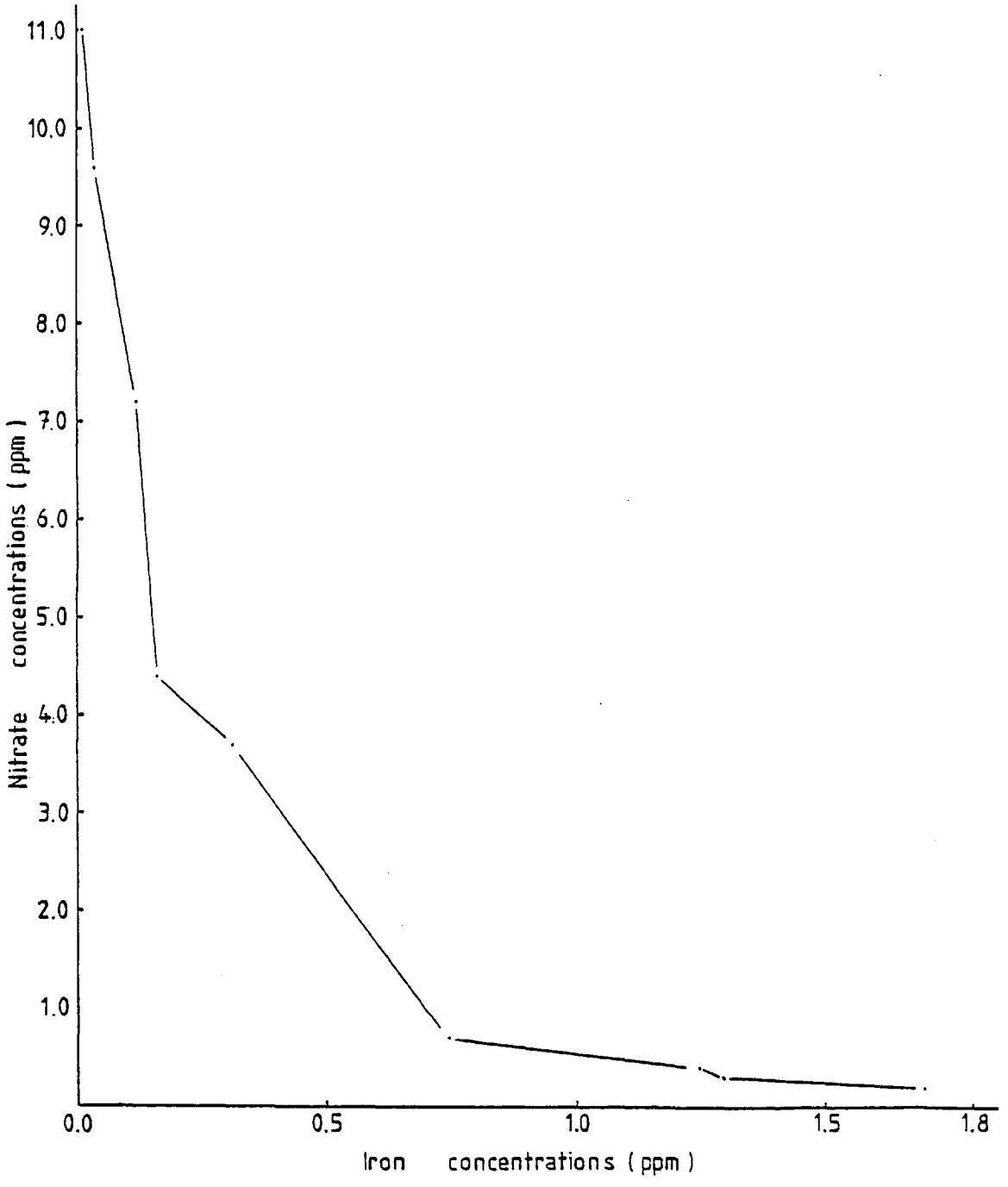


Fig.5.7 Showing a relationship between iron and nitrate concentrations in ground waters of the study area.

atmosphere, converting it to nitrates. The nitrates formed are usually in excess of the plants' needs, and so a surplus is available for leaching by infiltrating water. In the study area, nitrates are probably from organic and agricultural sources, because apart from the low levels in waters with high iron contents, nitrate concentrations are generally high.

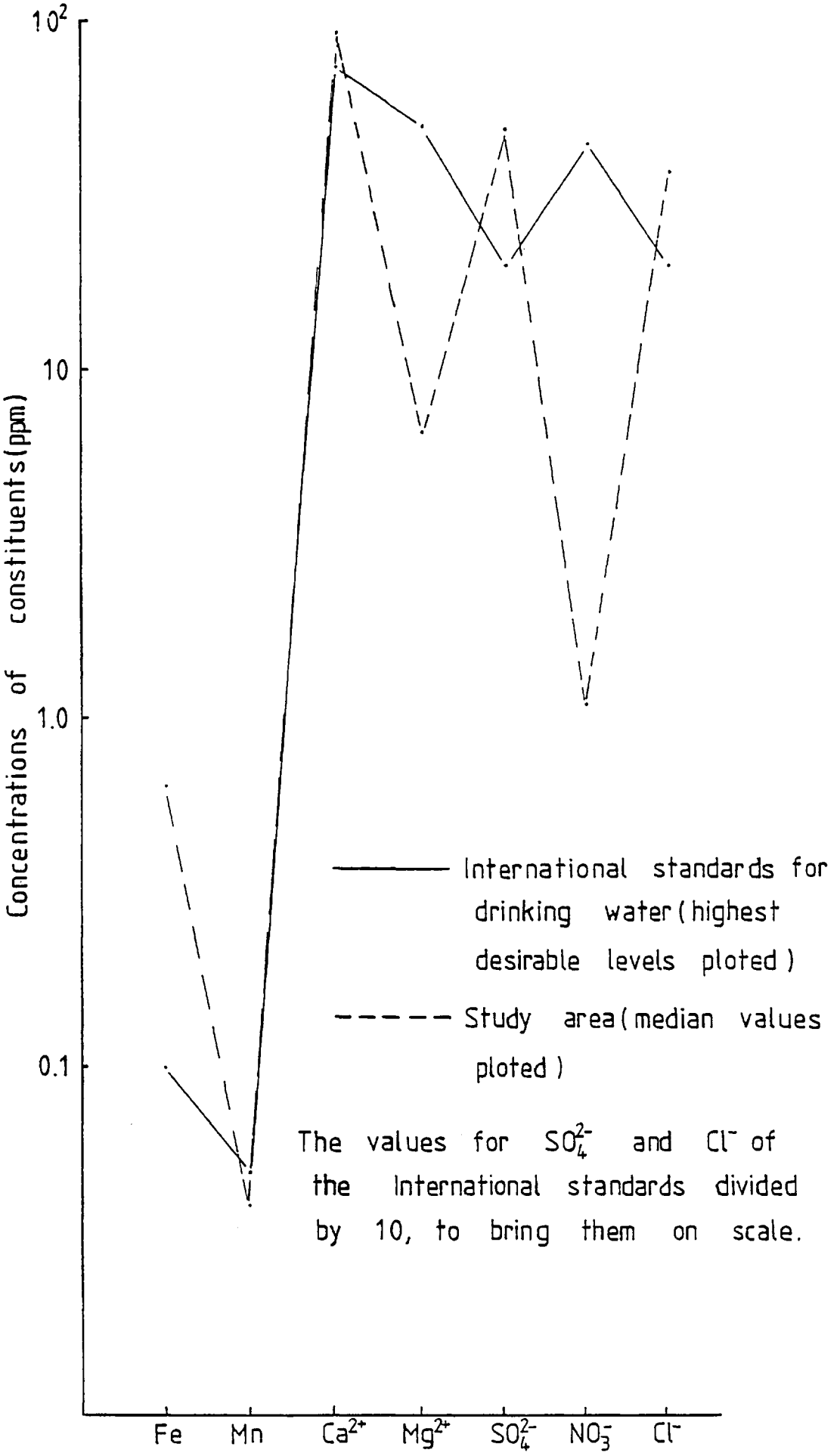


Fig. 5.8 Comparison of the median values of substances in waters of the study area with the Internation standards.

Chapter 6

The Distribution and chemistry of iron and manganese in the waters

6.1 Introduction

Having known from geology and chemical analyses the principal sources of iron and manganese in waters of the study area, it is necessary to go a step further to consider the observed pattern of distribution of the elements, and to try a prediction of species of the elements likely to be present in solution and in suspension, in terms of expected chemical processes. Also to be considered are the consequences of not measuring Eh, of only determining total iron and manganese and the likely hydrogeochemistry of the elements in a wider context, rather than for water supply purposes. The non-measurement of Eh means that: redox conditions within individual wells and boreholes are not known; the relationship between redox potential and element concentration cannot be determined; and the relationship between depth and redox conditions cannot be assessed. The wider aspect of the hydrogeochemistry of the elements to be looked at is the influence of hydrogen ion concentrations pH and redox potential Eh, as well as that of other ions like bicarbonate, chloride, fluoride and sulphate on their solubilities of the elements.

The major factors which control iron and manganese solubilities are pH, itself largely controlled by the availability of dissolved carbon dioxide in this environment, redox potential Eh, largelly controlled by the amount of dissolved oxygen present, bicarbonate and sulphate ions. Usually, activities of $10^{-3.0}$ mole/l (61 mg/l carbon dioxide) as bicarbonate and $10^{-4.0}$ mole/l (9.6 mg/l sulphate ions) are specified when the effects of these ions in solution on iron and manganese solubilities are considered. Measurements of pH in the study area show that waters from shallow wells (max 24 m from surface) generally have low pH values of 6.31 - 6.98 (mildly acid). This is consistent with the fact that in most near surface environments (especially with sands and gravels as in the study area), carbon dioxide is freely available. Waters from deep boreholes on the other hand have higher pH values of 7.00 - 7.85 (neutral to moderately basic). Also, most samples from shallow wells show higher concentrations of dissolved oxygen. No measurements were made of Eh, therefore an attempt will be made to theoretically calculate Eh values for use.

In order to be able to predict species of iron and manganese in the waters, stability-field diagrams based on Eh and pH have to be employed. However, in this work, simple diagrams of $Fe-H_2O$ and $Mn-H_2O$ systems will be considered. This is because only soluble species of iron and manganese are of interest.

According to Hem and Cropper (1959) in Barnes and Back, (1965), Jenne, (1968) and Hem (1977), the solubilities of iron and manganese are chiefly controlled by the behaviour of precipitated ferric hydroxide, the age and nature of surfaces of manganese dioxide, and the availability of dissolved oxygen.

Generally, manganese is more stable than iron. This is because manganese requires higher potential to be oxidised and precipitated, than iron. This means that at a given pH and Eh, iron will be precipitated more rapidly than manganese. Thus, manganese remains in solution and is precipitated later and in an environment with higher redox potential (Eh).

6.2 Eh - pH or stability-field diagrams

A stability-field diagram is a plot of Eh against pH, in which areas may be blocked out by thermodynamic, mass-law solubility and or electro-chemical calculations to show the conditions under which specific ionic and solid species are predominant. The diagrams are useful and convenient graphical means for the evaluation of factors that influence the solubilities of many elements including iron and manganese.

The intensity of oxidising or reducing conditions in an aqueous environment is represented by its redox potential Eh. The value of Eh is expressed in volts, in which increasing oxidising conditions are

represented by increasing positive values of Eh using a H^+ half cell potential as an arbitrary zero. In chemical equilibria in solutions, the redox potential is a function of the relative activities of oxidised and reduced species of the elements that are present. Also, at equilibrium, the degree of dissociation of say ferric or ferrous hydroxide is a function of the hydrogen (H^+) ion concentration (pH) of the solution. Thus, the stability-field diagram is a convenient way of representing the relationships mentioned above. Figures 6.1, 6.1a, 6.1b, 6.1c and 6.1d are such diagrams based on pH values measured at the time of water sampling, computed Eh values and total iron and manganese activities determined by water analyses.

6.2.1 Preparation of the diagrams

A basic or a framework diagram was first constructed (Fig. 6.1). This defines areas of stability and instability for water and the expected redox conditions of the study area.

The range of pH considered is from 0 to 14, and the range of Eh from -0.75 volt to 1.4 volts. For convenience, a standard temperature of 25°C is adopted. Standard potential E°, based on half redox reactions of unit activities in which either hydrogen gas or oxygen gas is evovled are used in the calculations for Eh for the basic diagram. The reactions are as follows:

Table 6.1 pH values and corresponding calculated Eh values at standard conditions of temperature and pressure

Hydrogen ion conc. (pH)	Calculated redox potential (Eh)	
	Upper Limit	Lower Limit
0	1.22	0.00
1	1.16	-0.06
2	1.10	-0.12
3	1.04	-0.18
4	0.98	-0.24
5	0.93	-0.30
6	0.87	-0.35
7	0.81	-0.41
8	0.75	-0.47
9	0.69	-0.53
10	0.63	-0.59
11	0.57	-0.65
12	0.51	-0.71
13	0.45	-0.77
14	0.39	-0.83

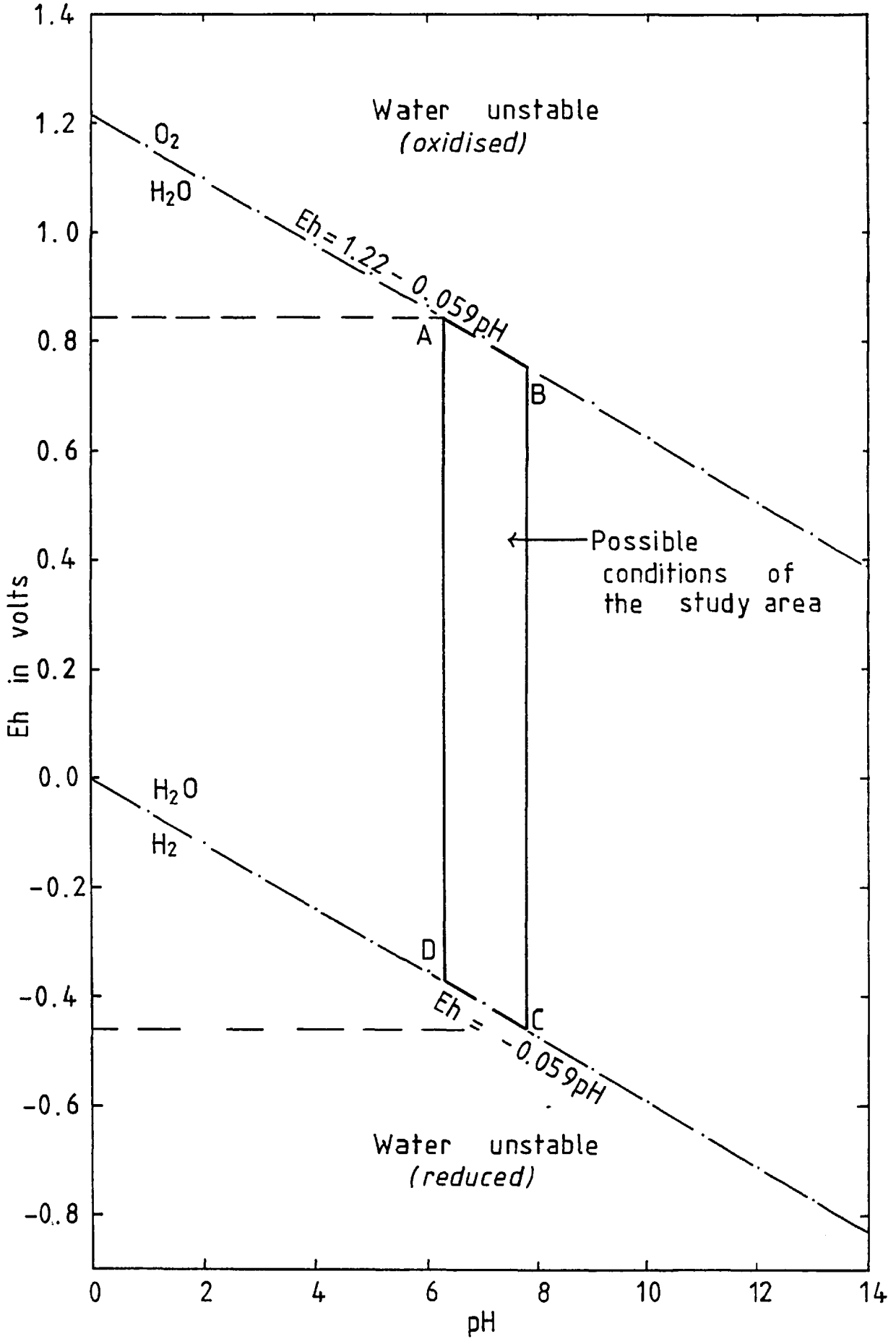


Fig. 6.1 Framework of the variation of oxidation potential with pH, and limits of Eh and pH of the study area at standard conditions: 25°C, 1 atmosphere pressure.

$$H_2 \rightleftharpoons 2H^+ + 2e^-, \quad E^o = 0.00 \text{ volt} \ldots\ldots (1)$$

$$H_2O \rightleftharpoons \tfrac{1}{2}O_2 + 2H^+ + 2e^-, \quad E^o = 1.23 \text{ volts} \ldots (2)$$

in which the potential for (1) is arbitrarily fixed at 0.00 volts, and all potentials greater than 0.00 volts (oxidising) are designated as positive and all potentials less than 0.00 (reducing) are designated negative.

These standard potentials were used in the Nernst equation to compute the expected theoretical Eh at varying pH values (see table 6.1). The Nernst equation relates standard oxidation potentials (E^o) for chemical half-reactions to equilibrium redox potentials (Eh) in the presence of known or assumed activities of particular ions. The equation if of the form:

$$Eh = E^o + \frac{RT}{nf} \ln \frac{A \text{ ox}}{A \text{ red}}$$

where

Eh = redox potential in volts or millivolts

E^o = standard potential (25°C, 1 atmosphere pressure for gases, and unit activities for solutes ions).

R = universal gas constant

T = temperature, °K

n = number of electrons transferred in half-reactions

f = Faraday constant, 21.3 kcal/mole.

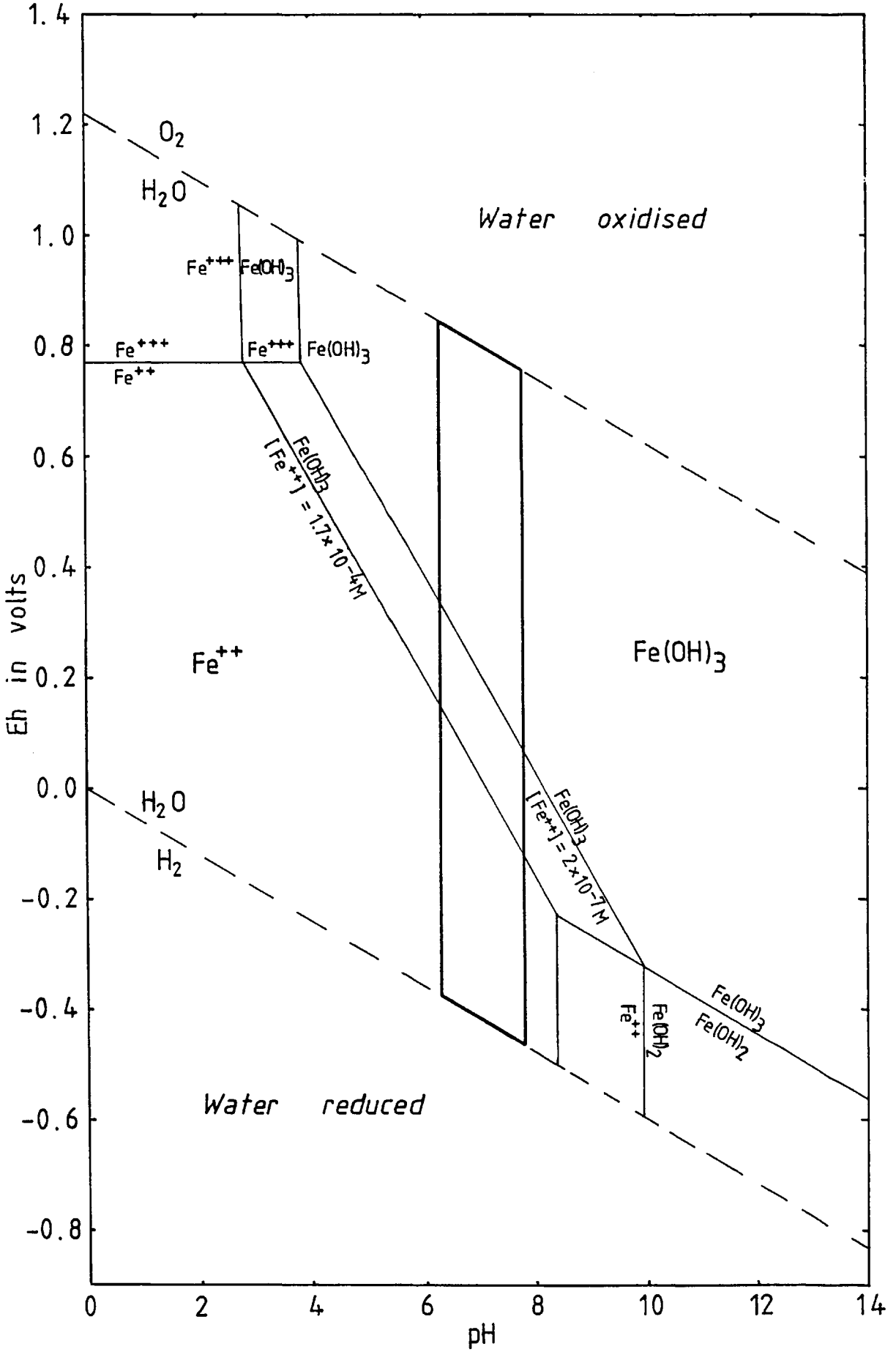


Fig. 6.1a Simplified stability-fields diagram for the system Fe–H_2O for total iron activities of 10^{-4} M (9.77mg/l) and 10^{-4} M (0.01mg/l) at 25°C.

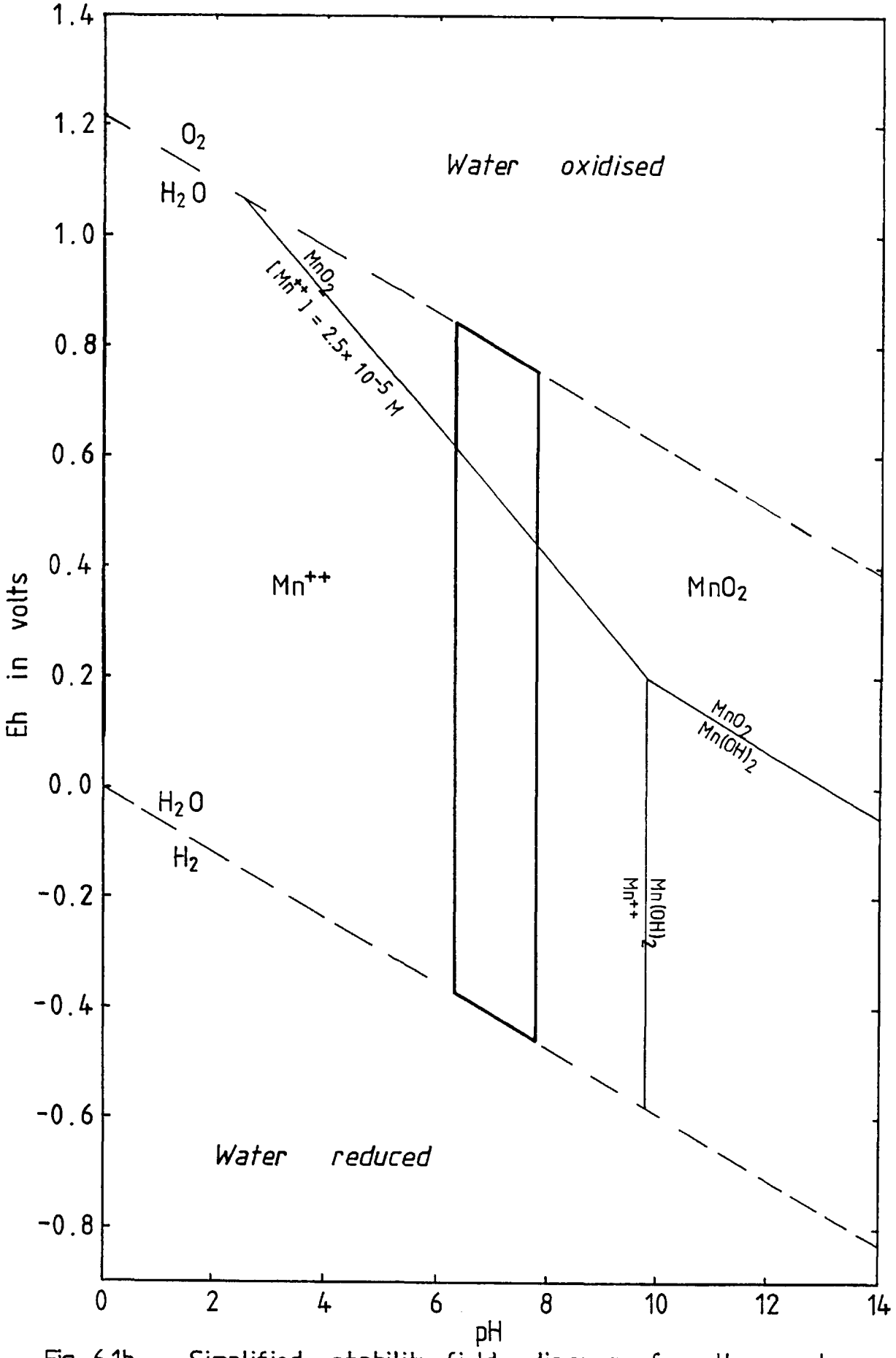


Fig. 6.1b Simplified stability-fields diagram for the system $Mn-H_2O$ for total manganese activity of 10^{-5} M (1.39mg/l Mn.) at 25°C.

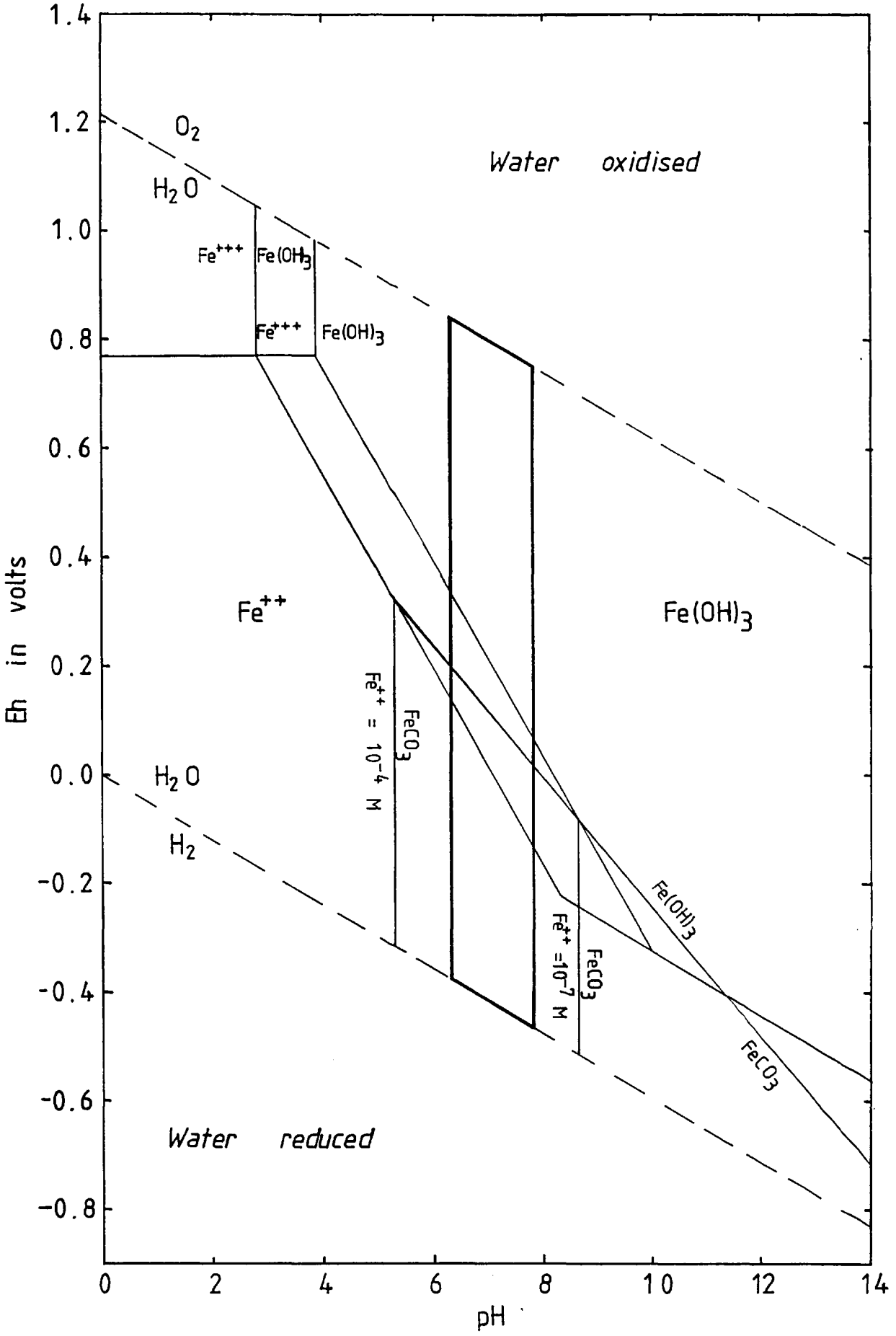


Fig.6.1c Simplified stability-fields diagram for the system $Fe-H_2O-CO_2$ for carbon dioxide activity of 8×10^{-3} M (505.25mg/l as HCO_3^-) at 25°C.

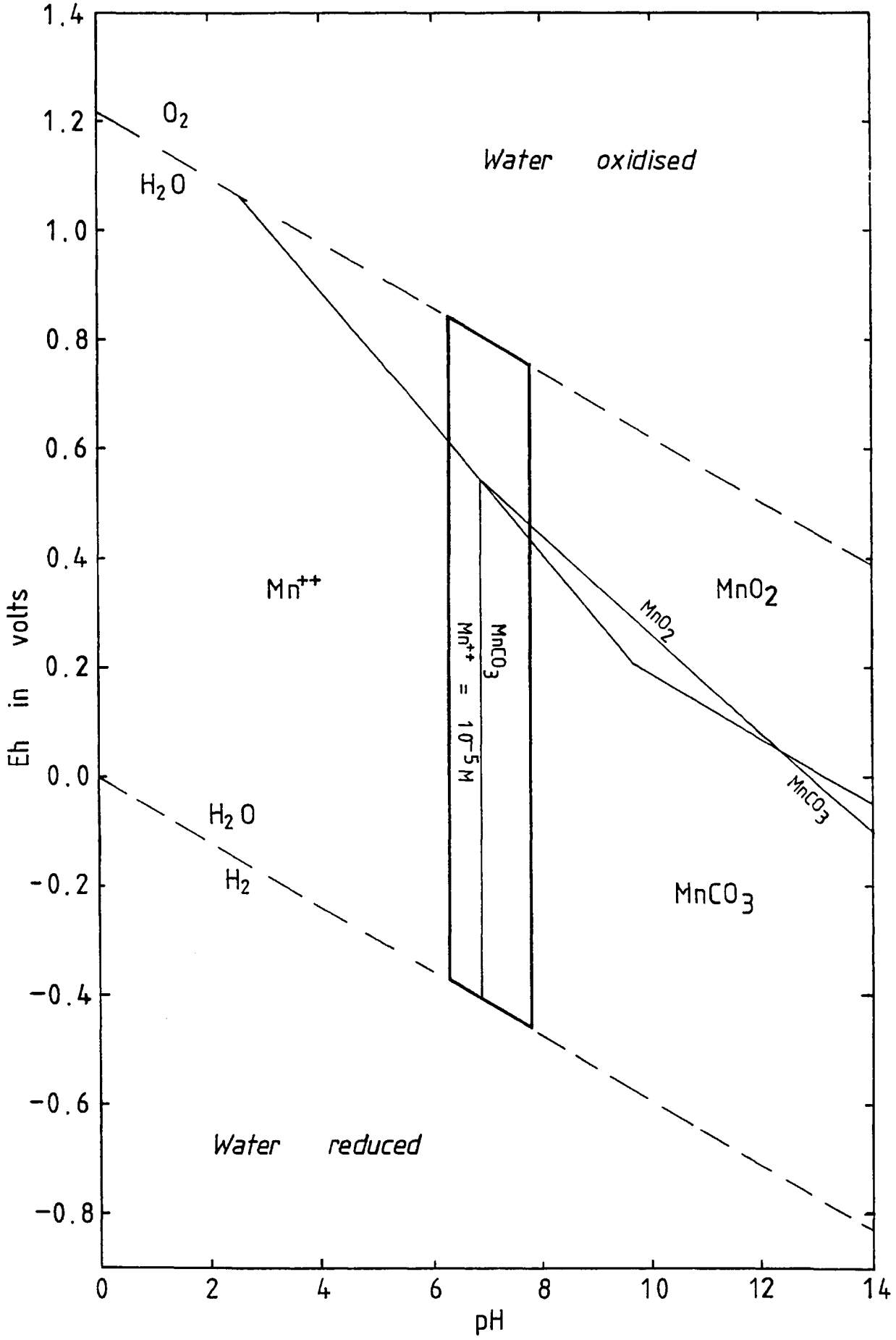


Fig. 6.1d Simplified stability-fields diagram for the system $Mn-H_2O-CO_2$, for carbon dioxide activity of 8×10 M(505.25mg/l as HCO_3^-) at 25°C.

The values for E^{o}, R, T and f could be obtained from standard tables.

$\log \frac{A\ ox}{A\ red}$ = natural logarithm of activities of species in half-reactions in mass-law form.

A ox = activity of oxidised form of ions

A red = activity of reduced form of ions.

The expression $\frac{RT}{f} \ln \frac{A\ ox}{A\ red}$ is numerically equal to $0.059 \log \frac{A\ ox}{A\ red}$

The Nernst equation could be written in a more general form, based on the following representative redox reaction.

$$aA + bB \rightleftharpoons cC + dD + ne^{-}$$

as,

$$Eh = E^{o} + \frac{0.0059}{n} \log \frac{[C]^{c}\ [D]^{d}}{[A]^{a}\ [B]^{b}}$$

in which C and D represent the oxidised forms and A and B represent the reduced forms of ions.

From calculations based on the first form of the Nernst equation, the water stability limits with respect to oxidation, forming oxygen gas and hydrogen ion, range from 1.22 volts at pH 0, to 0.39 volt at pH 14. Stability limits for the reduction of water to release hydrogen gas H_2, range from 0.00 volt at pH 0,

to -0.83 volt at pH 14 (see Fig. 6.1). Figures 6.1a and 6.1b were prepared using the two applications of the Nernst equation, and based on the iron activities of 1.7×10^{-4} mole/l (9.77 mg/l Fe) and 2×10^{-7} mole/l (0.01 mg/l Fe) as well as a manganese activity of 2.5×10^{-5} mole/l (1.39 mg/l Mn) respectively (see calculations below). The positions of the lines separating oxidised and reduced species of iron and manganese were determined by calculating the Eh for the pH values 0 and 10.

Based on a redox potential range of +1.40 volts down to -1.00 volt for an imaginary theoretical environment, the following divisions of the environment is suggested:

1.40 to 0.60 = strongly oxidising to oxidising

0.60 to 0.00 = oxidising to moderately oxidising

0.00 to -0.60= moderately reducing to reducing

-0.60 to -1.00= reducing to strongly reducing

6.2.2. Description of Diagram

The sloping upper and lower lines of fig. 6.1 are theoretically the limits within which water is chemically stable. Above the upper line (boundary) water is theoretically shown to be oxidised to produce oxygen gas, and below the lower line it is reduced to produce hydrogen gas. The parallelogram ABCD represents

probable pH and redox conditions of the area of study in Norfolk.

In addition to the above, figures 6.1a and b show conditions where soluble species of iron and manganese predominate and, conditions where solid species of hydroxides and oxides of the elements are stable and predominate.

Calculations for the preparation stability-fields diagrams Figs. 6.1a, b, c and d

Iron (Fe)

1. $Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$, $E^o = 0.77$ volt.
2. $Fe^{2+}\ 3H_2O \longrightarrow Fe(OH_3) + 3H^+ + e^-$, $E^o = 1.06$ volts.
3. $Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$
4. $Fe(OH)_2 + OH^- \rightleftharpoons Fe(OH)_3 + e^-$, $E^o = -0.56$

Total iron activities:

1.7×10^{-4} M (9.77 mg/l Fe).

2×10^{-7} M (0.001 mg/l Fe)

The Nernst equation is

$$Eh = E^o + \frac{0.059}{n} \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

Reaction 1:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-,\ E^o = 0.77 \text{ volt}$$

$$Eh = E^o + \frac{0.06}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$= 0.77 + 0.06 \log 1$

$= 0.77$

Therefore Eh = <u>0.77 volt</u>

In this case, the stability of iron is not controlled by pH.

<u>Reaction 2</u>

Total iron activity 1.7×10^{-4} M (9.77 mg/l Fe).

$Fe^{2+} + 3\ H_2O \longrightarrow Fe(OH)_3 + 3H^+ + e^-$, $E^o = 1.06$ volts.

$$Eh = E^o + \frac{0.06}{1} \log \frac{[Fe(OH)_3]}{[Fe^{2+}]} \frac{[H^+]^3}{[H_2O]}$$

$$= 1.06 + 0.06 \log \frac{[H^+]^3}{[Fe^{2+}]}, \quad [Fe(OH)_2] = 1, \quad [H_2O] = 1$$

$= 1.06 + 0.06 \log [H^+]^3 - 0.06 \log (1.7 \times 10^{-4})$

$= 1.06 + 0.06 \times 3 \times \log [H^+] - 0.06 (\log 1.7 + \log 10^{-4})$

$= 1.06 + 0.06 \times 3 \log [H^+] - 0.06 (0.2304 + (-4))$

$= 1.06 + 0.18 \log [H^+] + 0.23$

$= 1.06 + 0.23 + 0.18 \log [H^+]$

But $- \log [H^+] = pH$

Therefore Eh = <u>1.29 - 0.18 pH</u>

Reaction 2 for total iron activity of 10^{-7} M (0.01 mg/l Fe)

$$Eh = 1.06 + 0.06 \log [H^+]^3 - 0.06 \log 10^{-7}$$

$$= 1.06 + 0.06 \times 3 \times \log [H^+] + 0.42$$

$$= 1.06 + 0.42 - 0.18\ pH$$

Therefore $Eh = \underline{1.48 - 0.18\ pH}$

Reaction 3 was included simply to show how ferrous hydroxide could be obtained: it is not considered further.

Reaction 4:

$$Fe(OH)_2 + OH^- \rightleftharpoons Fe(OH)_3 + e^-,\ E^o,\ = 0.056 \text{ volt}$$

$$Eh = -0.56 + 0.06 \log \frac{[Fe(OH)_3]}{[Fe(OH)_2][OH^-]}$$

$$= -0.56 + 0.06 \log \frac{1}{[OH^-]}$$

Since $[H^+]\ [OH^-] = 10^{-14}$

$$\frac{1}{[OH^-]} = \frac{[H+]}{10^{-14}}$$

Therefore

$$Eh = -0.56 + 0.06 \log \frac{[H^+]}{10^{-14}}$$

$$= -0.56 + 0.06 \log [H^+] - 0.06 \log 10^{-14}$$

$$= 0.56 + 0.06 \log [H^+] + 0.84$$

Therefore

$$Eh = \underline{0.28 - 0.06\ pH}$$

Manganese (Mn)

The basic reactions considered are:

1. $Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$, $E^o = 1.51$ volts
2. $Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + 2e^-$, $E^o = 1.23$ volts
3. $Mn(OH)_2 + 2OH^- \rightleftharpoons MnO_2 + 2H_2O + 2e^-$, $E^o = -0.05$ volt

Total manganese activities:

2.5×10^{-5} M (1.39 mg/l Mn)

2×10^{-7} M (0.01 mg/l Mn)

Reaction 1:

$$Mn^{2+} \rightleftharpoons Mn^{3+} + e^-, \quad E^o = 1.51 \text{ volts}$$

$$Eh = E^o + \frac{0.06}{1} \log \frac{[Mn^{3+}]}{[Mn^{2+}]}$$

$$= E^o + 0.06 \log 1$$

Therefore $Eh = E^o =$ 1.51 volts

Reaction 2:

$$Mn^{2+} + 2\,H_2O \rightleftharpoons MnO_2 + 4H^+ + 2e^-, \quad E^o = 1.23 \text{ volts}$$

$$Eh = E^o + \frac{0.06}{2} \log \frac{[H^+]^4}{[Mn^{2+}]}$$

$$= E^o + 0.03 \log [H^+]^4 - 0.03 \log 10^{-5}$$

$$= 1.23 + 0.12 \log [H^+] + 0.15$$

$$= 1.23 + 0.15 - 0.12\ pH$$

Therefore $Eh = 1.38 - 0.12\ pH$

Reaction 3:

$$Mn(OH)_2 + 2OH^- \rightleftharpoons MnO_2 + 2H_2O + 2e^-, E^o = -0.05 \text{ volt}$$

$$Eh = E^o + \frac{0.06}{2} \log \frac{1}{[OH^-]^2}$$

$$= E^o + 0.03 \log \frac{[H^+]^2}{10^{-28}}$$

$$= -0.05 + 0.03 \times 2 \log [H^+] - 0.03 \log 10^{-28}$$

$$= -0.05 - 0.06 \text{ pH} + 0.84$$

Therefore $Eh = \underline{\underline{0.79 - 0.06 \text{ pH}}}$

From the calculations above, it is clear that a variety of forms of iron and manganese are possible, but these were not studied because of the total element concentration approach adopted. Also, it is clear from the diagrams that certain species of iron and manganese cannot occur in the environment found in wells and boreholes of the area of study.

Ferrous Carbonate ($FeCO_3$)

The basic reactions considered are:

1. $Fe^{2+} + CO_3^{2-} \rightleftharpoons FeCO_3$; $K = 10^{-10.5}$

Therefore $CO_3^{2-} = \frac{10^{-10.5}}{10^{-4}}$, (max. total iron activity= 10^{-4}M)

$$= \underline{10^{-6.5}}$$

2. $FeCO_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + H_2CO_3 + H^+ + e^-$

3. $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$; $K_1 = 10^{-6.4}$

$K_2 = 10^{-10.3}$

Maximum carbonate activity is:

8×10^{-3}M (505.25 mg/l as HCO_3^-)

Using free energy relations (i.e. energy of formation), the standard potential E^o for reaction (2) can be computed.

$FeCO_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + H_2CO_3 + H^+ + e^-$

$-161.1 \quad 3(-56.69) \quad -166.0 \quad -149.0 \quad 0$

$-331.17 \qquad\qquad -315.00$

Therefore $G^o = +16.17$ k cal $= 67.6$ KJ

but $\Delta G = nfE$

$\Delta G^o = nfE^o$

$E^o = \frac{\Delta G^o}{nf}$

$= \frac{67600}{96500}$

$= 0.7005$

Therefore $E^o =$ <u>0.70 volt</u>

<u>Reaction 2</u>:

$FeCO_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + H_2CO_3 + H^+ + e^-$,

$E^o = 0.70$ volt

$Eh = 0.7 + 0.06 \log [H_2CO_3][H^+]$

but $$\frac{[H^+]\ [HCO_3^-]}{[H_2CO_3]} = 10^{-6.4}$$

Therefore $$H_2CO_3 = \frac{[H^+]\ [HCO_3^-]}{10^{-6.4}}$$

$$= \frac{[H^+]\ \times 8 \times 10^{-3}}{10^{-6.4}}$$

$$= [H^+]\ \times 8 \times 10^{-3 + 6.4}$$

$$= [H^+]\ \times 8 \times 10^{3.4}$$

$$= 20{,}095.09\ [H^+]$$

$$Eh = 0.7 + 0.06 \log 20{,}095\ [H^+]^2$$

$$= 0.7 + 0.06 \log 20{,}095 + 0.06 \log [H^+]^2$$

$$= 0.7 + 0.258 - 0.12\ pH$$

Therefore Eh = <u>0.96 - 0.12 pH</u>

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-},\ K_2 = 10^{-10.3}$$

$$\frac{[H^+]\ [CO_2^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$

Therefore $$[H^+] = \frac{10^{-10.3}\ \times [HCO_3^-]}{[CO_3^{2-}]}$$

$$= \frac{10^{-10.3} \times 8 \times 10^{-3}}{10^{-6.5}}$$

$$= \frac{10^{-10.3} \times 10^{-2.1}}{10^{-6.5}}$$

$$= 10^{-6.8}$$

<u>pH = 6.8</u>

Manganese Carbonate, Rhodocrosite ($MnCO_3$)

The basic reactions considered are:

1. $Mn^{2+} + CO_3^{2-} \rightleftharpoons MnCO_3$; $K = 10^{-10.2}$

Therefore $CO_3^{2-} = \frac{10^{-10.2}}{10^{-5}}$, (max total Mn activity = 10^{-5} M)

$= \underline{10^{-5.2}}$

2. $MnCO_3 + 2H_2O \rightleftharpoons MnO_2 + H_2CO_3 + 2H^+ + 2e^-$

3. $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$; $K_1 = 10^{-6.4}$

$K_2 = 10^{-10.3}$

Maximum carbonate activity is:

8×10^{-3} M (505.25 mg/l as HCO_3^-)

$MnCO_3 + 2H_2O \rightleftharpoons MnO_2 + H_2CO_3 + 2H^+ + 2e^-$

$-195.4 \quad 2(-56.69) \quad -111.3 \quad -149.0 \quad 0$

$- \quad 308.78 \qquad -260.3$

Therefore $\Delta G^o = 48.48$ k cal $= 203.85$ kJ

$\Delta G^o = nfE^o$

$E^o = \frac{\Delta G^o}{nf}$

$= \frac{202840}{2 \times 96500}$

Therefore $E^o = \underline{1.05}$ volts

$$Eh = 1.05 + \frac{0.06}{2} \log [H_2CO_3][H^+]^2$$

$$[H_2CO_3] = \frac{[H^+][HCO_3^-]}{10^{-6.4}}$$

$$= \frac{[H^+] \times 8 \times 10^{-3}}{10^{-6.4}}$$

$$= [H^+] \times 8 \times 10^{3.4}$$

$$= 20{,}095.09\,[H^+]$$

$$Eh = 1.05 + 0.03 \log 20095\,[H^+]^3$$

$$= 1.05 + 0.03 \log 20095 + 0.03 \log [H^+]^3$$

$$= 1.05 + 0.129 - 0.09\ pH$$

Therefore $Eh = \underline{1.179 - 0.09\ pH}$

$$HCO_3^- \quad H^+ + CO_3^{2-},\ K_2 = 10^{-10.3}$$

$$[H^+] = \frac{10^{-10.3} \times 8 \times 10^{-3}}{10^{-5.2}}$$

$$= \frac{10^{-10.3} \times 10^{-2.1}}{10^{-5.2}}$$

$$= 10^{-7.2}$$

$$\underline{pH = 7.2}$$

6.3 The distribution and concentrations of iron and manganese in ground waters

The chemical analyses of waters from varying depths and lithologic areas in the environment show a general chemical stratification and zonation with respect to iron and manganese concentrations. Two types of zoning are apparent: zoning due to the depth of well or borehole from the surface and, zoning, for waters in the Chalk due to lithologies above the Chalk.

6.3.1 Distribution and concentration as detected by shallow wells and deep boreholes

On this basis, waters of the area can be divided into two broad zones, designated A and B which represent shallow wells and deep boreholes environments. The division is however not a sharp one since there is bound to be a median zone of transition within which mixing of waters from A and B is likely. However, because there are no distinct data to justify the creation of such a transition zone, it is ignored here. In general, all shallow wells have low concentrations of total iron and manganese, while deep boreholes show considerably higher concentrations.

The pH of the entire area range between 6.31 and 7.85. This is lower than the pH value of 8.5, above which iron may not be found in high concentrations in natural waters, and lower than the value 9.8 above which manganese may not be found in high concentrations.

Zone A

This zone goes down to a maximum of approximately 24 meters (72 feet) from the surface, and all shallow wells sampled belong to this grouping. The majority of these wells tap the glacial sands and gravels, and the Crag, while a few tap the Chalk (where it is exposed at the surface) and the Chalky boulder clay which overlie the Chalk, the Crag, and Glacial sands and gravels in places.

In general, waters from this zone contain little iron and manganese, having a range of concentration of between 0.01 ppm and 0.81 ppm and a median value of 0.17 ppm for iron and, between 0.01 ppm and 0.63 ppm and a median value of 0.03 ppm for manganese, as well as a comparatively low pH value of between 6.31 and 6.98. The A zone may be regarded as relatively stable and oxidizing. Much of the ground water circulated freely especially within the sands and the gravels of the Crag and glacial materials. It therefore would be high in dissolved oxygen concentration (see Fig. 5.6). This high oxygen means a high redox potential (Eh) for the

environment, thus, large amounts of iron and manganese cannot remain in solution (Broom, 1966), as they would be oxidised and precipitated from solution as solid species of hydroxide and oxides. In addition, because of the sufficient oxygen, iron bacteria oxidises ferrous ions into ferric and manganous ions into the tetravalent forms which precipitate as insoluble hydro-oxide and oxide (Galbraith, Williams and Siems, 1972; Hallberg and Martinell, 1976). These may serve to explain the comparatively low iron and manganese content of the waters here, though abstracted directly from the ferruginous Crag and Glacial sands and gravels. The low manganese may in addition be due to the fact that the Chalk and not the deposits above it contributes the greater amount of the manganese in the waters. Chemically therefore, zone A is one of oxidation.

In this zone however, leached organic matter in sediments like the heavy and less permeable boulder clay cover, as well as from decaying vegetal matter in marshy areas, may have caused local reducing conditions (low redox potential), and so given rise to a few local high iron and manganese contents in waters. Examples are Ellingham (sample No. 91), Flordon (sample No. 63) and Hemsby (sample No. 46) showing iron concentrations of 0.36 ppm, 0.58 ppm and 0.81 ppm respectively and, manganese concentrations of 0.1 ppm and 0.63 ppm.

Figures 6.1a, b, c and d represent the theoretical stability-fields for species of iron and manganese, while the parallelogram represents possible redox conditions for the field area. Based on Fig. 6.1a, nearly $\frac{2}{3}$ of the study area, lies within the zone of oxidation, where the stable form of iron is the precipitated ferric hydroxide. $\frac{1}{3}$ lies within the zone of soluble iron (moderately oxidising to moderately reducing). In theory, a number of workers have pointed out the existence of other soluble forms of iron, under varying pH and redox potentials.

The following are some of the suggested species according to Hem and Cropper, (1959) and Hem, (1970, 1972).

1. Fe^{3+}
2. $FeOH^{2+}$
3. $Fe(OH)_2^{+}$
4. Fe^{2+}
5. $FeOH^{+}$

The species no's. 2, 3, and 5 are complexes of ferric and ferrous iron. These species of iron are stable under pH values outside the limit of what obtains in the study area. The ferric ion Fe^{3+}, the ferric hydroxy complexes $FeOH^{2+}$ and $Fe(OH)_2^{+}$ are stable under pH values of between 2.4 and 4.8, while the ferrous hydroxide complex $FeOH^{+}$ is stable under pH values of 8.2 and above (Hem and Cropper 1959). This means that the only

soluble form of iron expected within the study area is the free soluble ferrous ion Fe^{2+}. Other forms of iron which might be considered in ground waters are ogranic complexes, ferric iron, inorganic complexes, soluble undissociated polymerised ferric hydroxides as well as anionic forms of iron $Fe(OH)_3^-$ and FeO_4^{2-}. Within the study area, organic complexes are likely, because according to work by Krumbein and Garrels, (1952) organic matter should be available for the range of pH and Eh under consideration. Soluble undissociated ferric hydroxide has been reported by Lamb and Jacques, (1938) in Hem and Cropper (1959). But the solubility of this 0.001 mg/l is far below the limit of detection. It is therefore not considered a possible contribution to the total iron observed. On the same basis, inorganic complexes like fluoride, carbonate, chloride and sulphate are not considered because their solubilities are very low, and concentrations as high as 100 mg/l are required for their effects to be of importance: Davison, (1979) and Hem, (1972). This level of concentration is far above what was observed in the study area. The anionic soluble forms of iron require such high pH and oxidation potentials that they are stable outside the limits of the study area.

From discussions so far, the expected forms of iron in solution within the environment of shallow wells are colloidal and particulate forms of ferric hydroxide, organic complexes and some amount of

free ions, probably due to one or two local reducing conditions. However, at pH above 5.05, the solubility of colloidal and particulate ferric hydroxide is known to be less than 0.01 mg/l. Therefore, its contribution to the amount of the iron in water will be small.

According to Hem, (1972) the soluble species of manganese theoretically expected in solutions are as follows:

1. Mn^{2+}
2. $MnOH^{+}$
3. $HMnO_2^{-}$
4. (MnO_4)
5. $MnSO_4$
6. $MnHCO_3^{+}$

However, the pH, Eh and levels of concentrations required for these species to be stable in solution and so be significant, rule out the possible availability of the bulk of them within the study area (see Fig. 6.1b). For example, $MnOH^{+}$ is stable at pH of 10 and above, $HMnO_2^{-}$, the anionic form is stable at pH of 12 and above, while $(MnO_4)^{-}$ another anionic form is stable at pH greater than 8 and a high Eh of 1.40 volts and over. The forms $MnSO_4$ and $MnHCO_3^{-}$ require concentrations of sulphate and bicarbonate ions of at least 2000 mg/l to form complexes of significant importance. Since these conditions of pH, Eh and levels of concentrations do not exist in the area of interest, Fig. 6.1b and Fig. 5.6b, these species could probably be regarded as not available.

This then means that the only available form of manganese is the manganous Mn^{2+} ion, and probably finely divided particles of manganese oxide. Manganese complexes with the inorganics chloride and fluoride are usually of negligible significance Hem, (1972). Thus, the expected species of manganese in the shallow wells environment are the free soluble manganous ions, which are probably in solution because the potential is not high enough to oxide and precipitate them, and finely divided particles of manganese dioxide MnO_2.

Zone B

This one is from approximately 24 metres to a maximum of about 137 meters below the surface, the maximum depth for boreholes sampled. All deep boreholes sampled, which also terminate within the Chalk belong to this group.

This zone is deficient in oxygen compared with zone A, so a lower redox potential (Eh) develops. The zone may correspond to the lower $\frac{1}{3}$ of Fig. 6.1a and the lower $\frac{3}{4}$ of Fig. 6.1b respectively, representing the probable conditions of the field area of study. As the ground water passes through zone A, most of its oxygen and so its oxidising potential is appreciably reduced by chemical reactions with ferrous and manganous ions. By the time the water moves to the lower part of the A zone,

it still contains enough carbon dioxide (carbonic acid) to have a low pH value but little oxygen. Thus more iron and manganese are leached from minerals, in the reduced states in the Glacial sands and gravels and the Crag, into solution and taken to the lower B zone.

Iron and manganese content of the B zone is therefore higher with a range of between 0.01 ppm and 9.77 ppm and a median value of 1.10 ppm, and between 0.01 ppm and 1.30 ppm with a median value of 0.09 ppm respectively. Apart from a few water samples with low iron and manganese concentrations, all samples showing iron concentrations of 0.64 ppm and manganese concentrations of 0.04 ppm (the median values for the area) and over, come from here. The presence of large amounts of iron in solution is governed by both the redox conditions and pH of the environment. Iron is most soluble in waters with low bicarbonate to iron ratios (HCO_3^-/Fe), and under reducing conditions. These conditions are found in combination in the B zone (see appendix C, table 5.1, and Fig. 6.1a). Therefore, with a relatively low redox potential (Eh) and a generally high iron and manganese content the B zone is one of reducing conditions, and may be unstable as mixing of waters and the diffusion of soluble materials from the A zone above may take place. The entire study area could be regarded as ranging from oxidising to reducing, with regard to the estimated conditions as shown in Fig. 6.1.

Since the B zone may be regarded as corresponding to the lower $\frac{1}{3}$ of Fig. 6.1a, it is probable that the bulk of the total detectable soluble iron in samples from this zone are in the ferrous forms. Thus, the principal species of iron in the B zone is the free ferrous Fe^{2+} form. However, since the lines separating the oxidised from the reduced forms of iron are not fixed, traces of ferric and ferrous complexes as well as organic and some inorganic complexes may be present in solutions.

The principal manganese species in the B zone is the free soluble manganous ion (see Fig. 6.1b). However, just as with iron, traces of manganese complexes as well as of colloidal and particulate forms of manganese oxides may be present. Although the area is a carbonate one, because of the very low solubilities of iron and manganese carbonates, their presence in solution will not play any significant role with regard to total iron content.

A comparision of figures 6.1a and 6.1b showsthat manganese is soluble over a larger area than iron, as the area for soluble manganous Mn^{2+} species is greater than that of the soluble ferrous Fe^{2+} species (see Figs. 6.1a and b).

6.3.2. Distribution and concentration as a function of geology (lithostratigraphy): This applies only to boreholes into the Chalk

On the basis of lithology, the Chalk ground waters of the area can be divided into two groups as well, X and Y (see Fig. 6.2).

Group X

This comprises all lithological conditions in which the Glacial sands and gravels, and the Crag directly overlie the Chalk. It is a grouping of high iron and manganese concentrations in Chalk waters with ranges of between 0.64 ppm and 9.77 ppm and, 0.02 ppm and 1.39 ppm respectively. In addition to their stratigraphical positions, the Glacial sands and gravels, and the Crag are in places completely overlain by the darker, denser type, less permeable boulder clay. It is likely that this situation induces reducing conditions within the strata directly below the boulder clay and so may result in more iron and manganese being taken into solution.

Group Y

Here, the boulder clay directly overlies the Chalk and stratigraphically separates the Glacial sands and gravels from the Chalk aquifer. The boulder clay

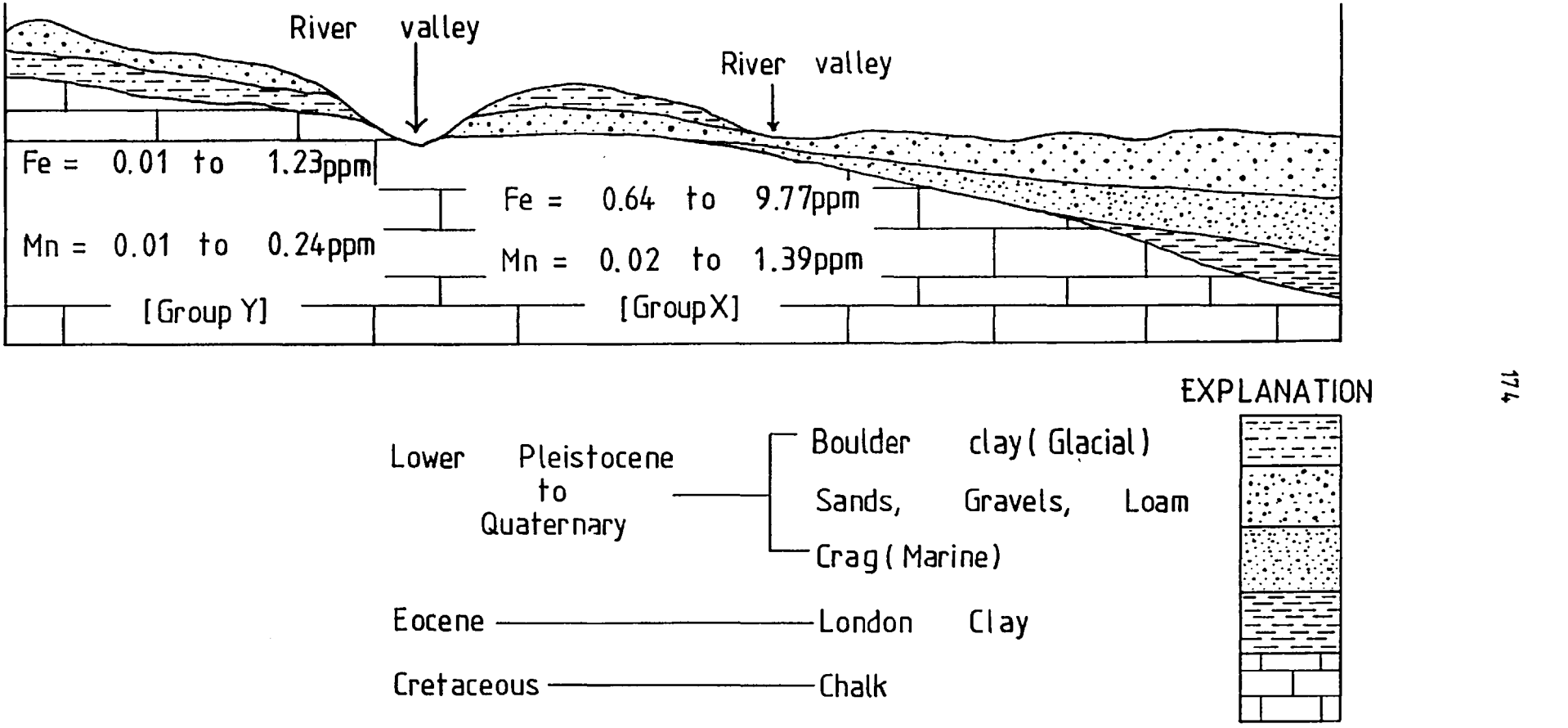


Fig. 6.2 A sketch showing the relationship between type of lithology above the Chalk and, Fe and Mn concentrations in Chalk ground waters.

is relativelv impermeable, and so cuts the Chalk aquifer off from a rapid supply of water from above (i.e. vertically).

Iron and manganese concentrations in waters of this grouping are lower than in the X grouping. The ranges of concentrations are between 0.01 ppm and 1.23 ppm and, between 0.01 ppm and 0.24 ppm iron and manganese respectively. Clays are known to adsorb iron onto their surfaces (Jenne, E.A., 1967), and that colloidal iron hydroxide is readily sorbed onto clay mineral surfaces (Follette and Fripiat and, Gastruche in Jenne, 1967). It is probable that this sorption onto clay and clay mineral surfaces also affects manganese in addition to scavenging , by surfaces, of precipitated ferric hydroxide and manganese oxides. It is therefore likely that iron and manganese taken into solution from minerals in the sands and gravels and the Crag, by infiltrating waters, are largely adsorbed before the waters finally infiltrate through the boulder clay to reach the Chalk aquifer. In addition to the above, some boreholes are sited in areas where there is neither Glacial sands and gravels, nor Crag. Thus, the source rocks for the greater part of iron and some of the manganese in waters are completely absent. The low iron and manganese levels in waters of group Y are therefore due to the relative stratigraphical positions of the sands and gravels and the boulder clay as well as the complete absence of the first material in places.

From what has been discussed, the X grouping may give rise to a mixed environment of oxidising and reducing conditions. If this is so, the species of iron and manganese in solutions will be a combination of those expected within the oxidizing environment of the shallow wells (zone A) and the reducing one of the deep boreholes (zone B). Therefore, free soluble ferrous ions, organic complexes of ferric hydroxide, colloidal forms of ferric hydroxide, free manganous ions and colloidal and particulate forms of manganese oxide,may be present in solutions. The Y group is different from the X. As well as creating possible reducing conditions in Chalk waters below, the overlying boulder clay also serves as a form of natural filter. It is therefore likely that all of iron and manganese species that infiltrate through this clay must be in solution. Thus, within the Chalk water below the boulder clay, the bulk of the low iron and manganese concentrations are the soluble ferrous and manganous forms.

In general, a comparision of Figs. 6.1a and 6.1c and of Figs. 6.1b and 6.1d will suggest that both ferrous carbonate $FeCO_3$ and manganese carbonate (rhodochrosite) $MnCO_3$ are the more stable solids than ferrous hydroxide and manganese hydroxide respectively. Fig. 6.1c indicates that at pH of about 5.3, Eh of about 0.32 volt and a ferrous ion activity of 10^{-4} M, ferrous carbonate will precipitate as the stable solid. But at a ferrous ion activity of 10^{-7} M, ferrous carbonate will precipiate at

a higher pH of about 8.6 and a lower Eh of about -0.08 volt. Similarly, Fig. 6.1d indicates that at pH of about 6.9 Eh of about 5.45 volts and a manganese Mn^{++} ion activity of 10^{-5} M, manganese carbonate will precipitate as the stable solid form.

Since the study area is a calcium carbonate (limestone) one, it is not surprising that the carbonates of iron and manganese may be more stable than their hydroxides.

6.3.3 Suggested mechanisms for iron and manganese migration into Chalk ground waters

From the stratigraphical positions of the Chalky boulder clay, the Glacial sands and gravels, the Crag and the Chalk, the bulk of iron and the little amount of manganese from rocks above the Chalk, have to be transported to the Chalk aquifer below. One of the possible means of transfer is by infiltrating rain waters aided by the redox conditions of the environment. Rain water, aided by carbon-dioxide of the atmosphere and the soil air is able to leach large amounts of iron and manganese from the surface to lower levels. Under reducing conditions, large amounts of the leached materials are retained in solution as the water infiltrates downward. Results of the analyses of water samples taken during the summer (1979) and the winter (1979/80) strengthen the concept of rain water transport. Samples taken during

the relatively wetter winter months (see Figs. 1.3a and b) show higher concentrations of iron and manganese (see Figs. 5.2a and b). Another possible means of transport is through rapid recharge of Chalk aquifers during the pumping of boreholes into the Chalk. Chalk rest water levels in parts of Norfolk are known to lie within the Glacial sands and gravels, and the Crag where these directly overlie the former (Figs. 2.8a and b); thus establishing a hydraulic continuity between the rock types (Foster, S.S.D. and A.S. Robertson, 1977). Avenues created at the sides of borehole pipes can also serve to transfer iron and manganese from their source rocks into Chalk aquifers. Finally, large-scale water level fluctuations during droughts or exceptionally dry summers can transport large quantities of materials already in solution to lower levels. Fluctuations as much as 9 meters are known in Norfolk (East Suffolk and Norfolk River Authority,1971).

6.4 Geochemical relationships between the major cations and anions in solution

The principal chemical characteristics of ground waters in the environment of study is shown by the ternary (trilinear) plot of fig. 6.3. Calcium and bicarbonate are the dominant major ions in solution. This fact agrees with expectations, since the principal aquifer from which much of the water samples were taken

Table 6.2 Percentage concentrations of cations and anions in ground waters of the area of study

Sample No.	$Na^+ + K^+$	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HCO_3^-	Cl^-
2	14.31	82.35	3.33	14.43	73.85	11.72
6	21.11	74.96	3.92	9.05	80.31	10.63
10	15.63	78.97	5.39	10.11	82.81	7.08
22	29.86	64.38	5.75	6.35	85.57	8.08
27	8.66	87.44	3.89	14.64	80.47	4.88
28	28.87	65.33	5.79	9.73	81.32	8.94
64	22.85	71.42	5.71	2.36	89.34	8.29
65	36.41	54.99	8.59	14.81	61.99	23.19
71	62.78	28.53	8.68	9.32	43.89	46.77
76	13.57	83.27	3.14	1.54	89.25	9.22
47	19.90	71.43	8.67	33.35	44.82	21.81
32	16.23	78.67	5.10	38.10	51.94	9.95
25	18.55	74.20	7.24	2.41	91.84	5.73
67	15.52	80.79	3.67	5.85	79.66	14.46
83	22.22	71.28	6.48	16.49	71.80	11.69
38	20.74	71.35	7.90	24.63	64.28	11.08
85	17.42	77.35	5.22	2.05	90.62	6.87
21	18.47	76.27	5.25	3.34	89.63	7.02
87	20.93	73.70	5.36	14.75	75.29	9.95
9	24.69	68.14	7.15	15.73	66.97	17.28
36	29.43	60.39	10.17	17.87	63.60	18.52
19	26.78	64.95	8.25	17.33	67.03	15.63

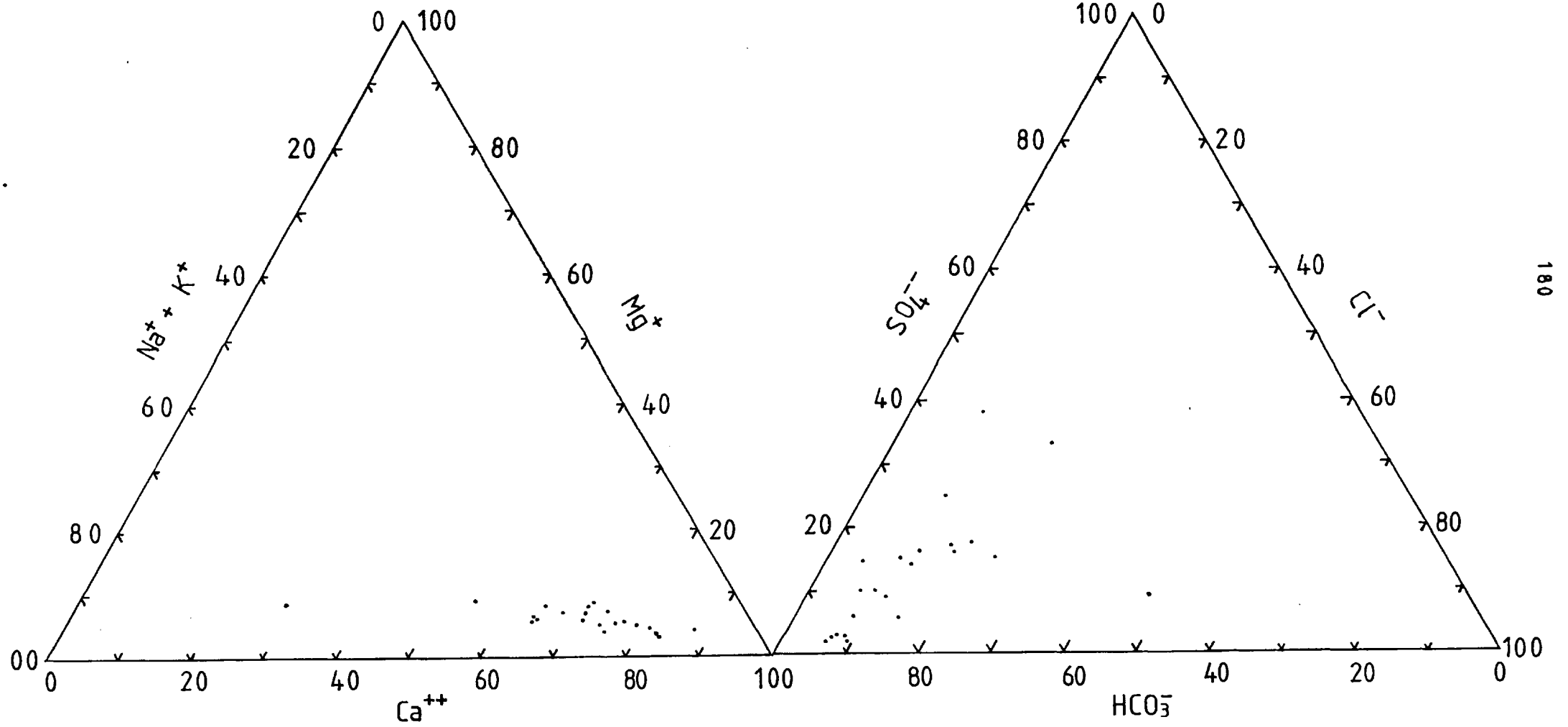


Fig. 6.3 Hydrochemical relationships between the major cations and anions in ground waters of the area of study.

for analyses is a calcium carbonate one. Concentrations of sodium, potassium and magnesium as well as chloride and sulphate ions are comparatively low. In one sample (No. 71), however, the concentration of the alkalis is higher (about 63%) than that of calcium, with a corresponding high chloride content of 47% (table 6.2). Two samples have concentrations of over 55% sulphate. The high alkalis and chloride are believed to be due to brackish water influence. In fact, the sample was taken at Brundall within the tidal flats area of the River Yare, east of Norwich. In general, the concentration of magnesium seems to remain fairly constant, at below 10% of the total concentration of the major elements. Since dolomitization is not known in the study area, the bulk of the magnesium must have been derived from circulating connate waters.

Ion-exchange processes seem to exist between calcium and the alkali metals (see table 6.3 and Fig. 6.4). As the percentage concentration of the alkalis increased, that of calcium decreased. Sodium and potassium (mainly sodium) involved in this process may have been derived from clay minerals within the environment saturated with these ions. According to work of Morgan-Jones and Eggboro, (1981), the increase in the alkalis over calcium should produce a corresponding increase in pH. However, Fig. 6.4, shows that such a relationship does not exist here.

The fact that changes in pH are not produced by the increase in alkali ions concentrations means that the pH of this environment is largely controlled by the carbon dioxide - carbonate-bicarbonate buffer system. Maintaining a fairly constant buffer is possible only with a rapid supply of dissolved carbon dioxide. In a limestone area with possible large scale fissures, caverns and solution holes, this is no problem. In one or two areas, the pH is high where calcium concentrations are high, and comparatively lower in others with lower calcium and high alkali concentrations. In areas with high calcium and high pH values, the supply of carbon dioxide may be rapid, resulting in an increase in both hydrogen (H^+) and bicarbonate (HCO_3^-) ions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + \ + HCO_3^-.$$

The hydrogen ion goes into chemical reaction with the aquifer rock releasing more calcium and bicarbonate ions.

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$

In this way, more calcium is taken into solution and the pH may rise. In areas with high alkalis and comparatively low pH values, as sodium and potassium replace calcium in solution, the equilibrium with regard to cations is disturbed. Since calcium is less soluble than the alkalis, it precipitates as calcium carbonate.

$$2\ Ca^{2+} + 2HCO_3^- \rightleftharpoons 2CaCO_3 + H_2O$$

This reaction may be seen to deplete the bicarbonate ion concentration, leaving behind a relatively higher concentration of hydrogen ions in solution. As the increase in

Table 6.3 A relationship between the alkali metals, calcium and pH in ground waters of the area of study

Sample No.	Na + K	Ca	pH
2.7	8.66	87.44	7.34
76	13.57	83.27	7.82
2	14.31	82.35	6.78
67	15.52	80.79	7.37
10	15.63	78.97	6.74
32	16.23	78.67	7.06
85	17.42	77.35	7.34
21	18.47	76.27	7.26
25	18.55	74.20	6.98
47	19.90	71.43	6.94
38	20.74	71.35	7.18
83	22.22	71.28	7.07
64	22.85	71.12	7.42
9	24.69	68.14	6.86
19	26.78	64.95	7.07
28	28.87	63.33	7.09
36	29.43	60.39	7.36
65	36.41	54.99	7.48
71	62.78	28.53	7.48

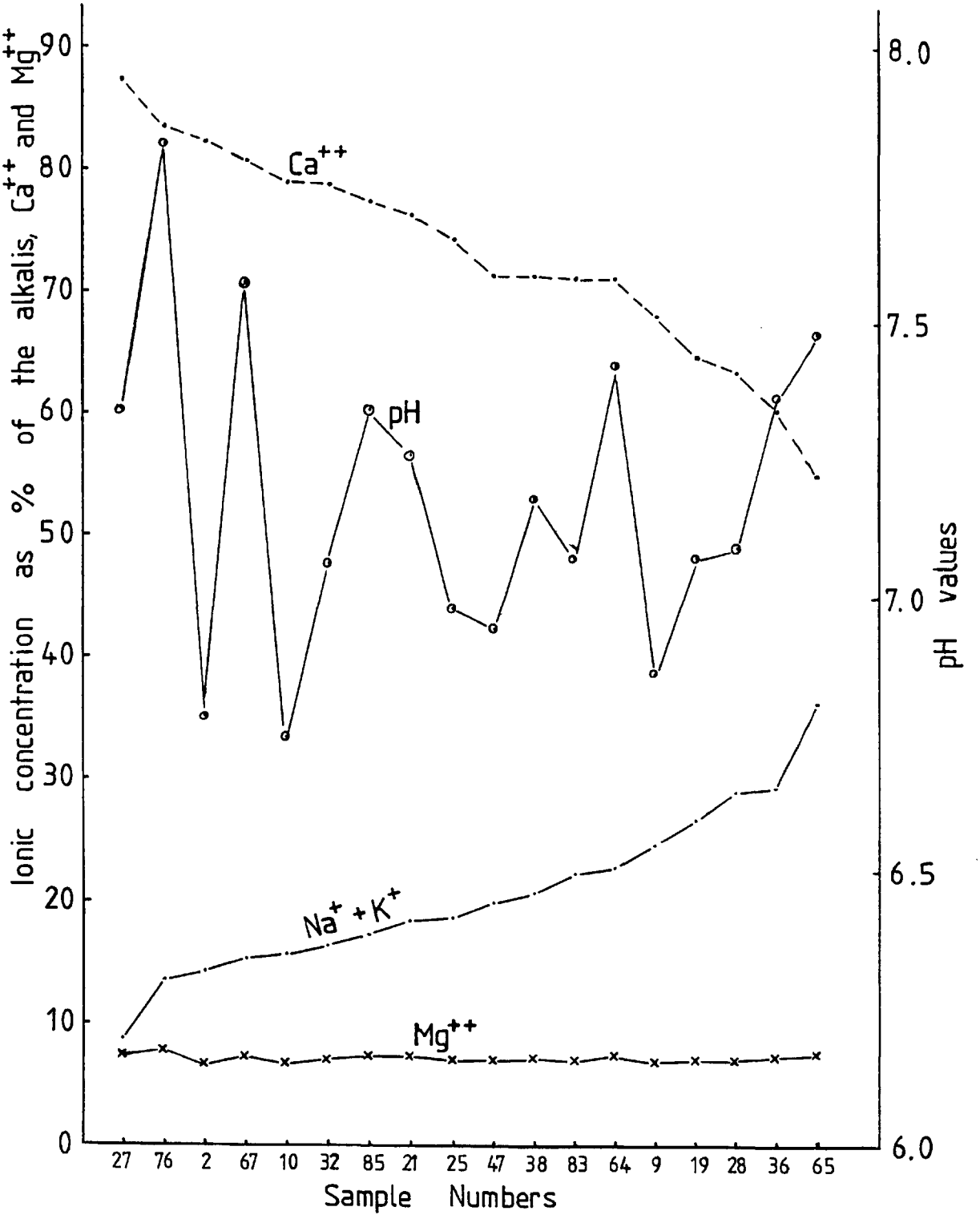


Fig. 6.4 Variations in the concentrations of calcium, magnesium and the alkali–metals in relation to pH.

pH of a solution depends on the concentration of bicarbonate ions, the reduction in bicarbonate thus results in a lowering of pH.

Based on what has been discussed, the pH of an environment is fixed by the relative concentration of bicarbonate (HCO_3^-) ions.

In conclusion this work has defined four basic facts concerning the geochemistry of the waters in the area.

1. A variation exists in both the distribution and the possible species of iron and manganese in solutions in the study area. These are dealt with under 6.3.1 and 6.3.2.
2. Eh - pH diagrams are extremely useful in the prediction of possible species of the elements in waters, however, their limitations must also be considered.
3. The approach using total iron and manganese values, although may be appropriate for water supply purposes, does have obvious limitations when interpreting the hydrogeochemistry of the area.
4. A relationship has been revealed between calcium and the alkali metals in terms of ion exchange processes. Calcium decreases as the concentration of the alkali metals increases.

Advantages of Eh - pH diagrams

1. Using measured pH and iron and manganese contents, the redox potential (Eh) of an environment can be estimated.

2. The diagrams serve as a useful device for illustrating and predicting the stability-fields of different minerals in aqueous environments.
3. They help to explain why certain compounds do not occur under certain geological conditions, for example the conditions under which permanganates are unstable and slowly decompose, liberating oxygen and precipitating pyrolusite, MnO_2.
4. Eh - pH diagrams go a long way towards explaining why certain elements do not occur together, although their ionic potentials indicate they should. Further, the diagrams help to explain why, when the elements do occur together they are associated in unequal amounts. Ferric hydroxide and manganese oxide should occur together in relatively equal proportions but in nature the reverse is the case. This is because iron is readily precipitated as hydrated ferric oxide, whereas managnese remains in solution longer and is eventually deposited under more oxidising conditions as comparatively iron-free manganese dioxide.

Limitations of Eh - pH diagrams

1. Eh - pH diagrams do not indicate the existence of organic complexes, colloidal and particulate suspensions.
2. In calculations for their preparations, equilibrium conditions are assumed. But it is known that in natural solutions such conditions are not possible as

changes in pH and Eh are constantly taking place.

3. The standard conditions of 25°C, 1 atmosphere for gases and unit activity for solutes are not attainable in normal ground waters. For example in the area of study, measured temperature was between 9°C and 12°C, the pressures of oxygen and carbon dioxide gases equal their partial pressures, and the maximum activities of iron and manganese were 1.7×10^{-4} and 2.5×10^{-5} respectively. However, conditions close to the standard may be attained in thermal environments.
4. The diagrams are prepared in terms of activities of solutes, which correspond to exact concentrations only in infinitely dilute solutions. This means that ionic-strength effects are not considered directly.
5. The use of boundary lines in these diagrams seem to give the impression that species of elements have fixed domains. But the lines are only equilibrium positions.
6. The choice of solute species in considering stability tends to limit the applicability of the diagrams to wider ranges of solubilities.
7. Many of the relationships used in preparing Eh - pH diagrams are half-reactions, while in natural systems chemical equilibria may appear to be established only through combining oxidation half-reactions with reducing ones.

These limitations in the preparation and use of stability-field diagrams notwithstanding, they provide a useful basis for the theoretical study of elemental chemistry. In fact, if carried further, these diagrams could be used to predict natural environments of possible mineralisation. The theoretical values of elemental chemistry based on Eh - pH diagrams have been intensively investigated by many workers. Barnes and Back (1965) as a group of such workers have found these theoretical values to be fairly reasonable and satisfactory.

Limitations of total iron and manganese determinations

In this study, as a result of available laboratory facilities, only total iron and manganese and not their soluble and particulate species in waters had been determined. This practice though useful in some sense, imposes limitations on the study of the chemical behaviour of the elements in solutions. Some of these limitations are as follows:

1. Both ferric hydroxide $Fe(OH)_3$ and ferrous hydroxide $Fe(OH)_2$ could exist with organic complexes and in colloidal and particulate forms. Manganese dioxide could also exist in

colloidal and particulate forms. The effect of these suspended materials is to slightly increase the concentrations of the elements in waters in a total iron and manganese determinations.

2. Analysis for total iron and manganese tends to mask the hydrogeochemistry of the elements and hence may make identification of the geological cause of problems associated with the elements much more difficult.
3. Values of redox potential (Eh) are usually calculated from soluble species of iron and manganese. Therefore calculations in this study based on total iron could give results slightly different from what is to be expected. However, since the concentrations of elements considered are low, and since the solubilities of the oxidised species are usually very low, the presence of the suspended species may not make a siginficant difference in the estimations of Eh values.

On the other hand, the determinations of only dissolved species which excludes collidal and particulate forms will serve only as an approximate index of iron and manganese activities. Therefore,when considered in the light of the statement above, the determinations of total elements in solutions could be considered useful.

CHAPTER 7

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

7.1 Summary and conclusions

Results of chemical analyses of rock and water samples from the three main aquifers, together with geological considerations have revealed the following:

1a) Of the three rocks, the Crag and the Glacial sands and gravels have higher levels of iron and manganese concentrations than the Chalk.

b) Iron and manganese concentrations are high in deep borehole waters from areas where the Crag and the Glacial sands and gravels directly overlie the Chalk aquifer.

c) Iron and manganese concentrations are low in deep borehole waters from areas where the Glacial sands and gravels are separated from the Chalk by the relatively impermeable Chalky boulder clay.

d) There is a low to negligible concentration of iron and manganese in deep borehole waters from areas where the Crag and the sands and gravels are completely absent from the strata.

These results show that the Crag and the Glacial sands and gravels are the sources of the higher than acceptable levels of iron and manganese concentrations in Chalk ground waters of the study area. The results also show that waters from deep boreholes through

strata with Crag and sands and gravels sitting directly on the Chalk will contain higher iron and manganese concentrations than waters from areas where either the sands and gravels are separated from the Chalk by boulder clay or both sands and gravels, and Crag are completely absent.

2a) Waters from shallow wells (a maximum depth of 24 metres from the surface) in any of the aquifers contain less iron and manganese than waters from deep boreholes (below 24 metres, to a maximum depth of about 137 metres).

b) Analytical results of waters taken during the wetter winter season (1979/80) show higher concentrations of the elements than waters taken during the summer (1979).

These results, together with those of 1b, 1c and 1d, show that a variation exists in the distribution of iron and manganese in ground waters of the area. This variation appears to be due to: the depth from which water is taken, the geology (lithology) of the environment and the relative amount of seasonal precipitation. In addition, the variation due to the amount of seasonal precipitation shows that the elements are transported from the Crag and the Glacial sands and gravels into Chalk waters below, mainly by infiltrating rain waters.

3a) A few water samples from both the shallow wells and the deep boreholes with high concentrations of iron, contain low concentrations of nitrate (NO_3^-), while a few others with low concentrations of iron contain high concentrations of nitrate (NO_3^-).

b) Waters from shallow wells, generally with lower

concentrations of iron than waters from the deep boreholes, show higher concentrations of nitrate than those of the deep boreholes.

These two observations suggest that an unexplained relationship may exist between iron and nitrate concentrations in the ground waters of the area, in which high iron concentrations may correspond to low nitrate concentrations. This situation is similar to that observed by Koyama in Jenne (1967), using soil samples in water under anaerobic conditions.

7.2 Recommendations for further studies

Two sets of recommendations are made for further studies, in order to avoid ground water with high iron and manganese concentrations; they are grouped under short and long term studies.

1. Short term studies

a) Geological investigations based on drilling within catchments and subcatchments of interest should be done, to locate :

ai) places where the Crag and the Glacial sands and gravels are absent, and

aii) places where the relatively impermeable Chalky boulder clay separates the Glacial sands and gravels from the Chalk aquifer (i.e. where the boulder clay directly overlies the Chalk). However, before a final decision is made on a location for a well or

a borehole, it will still be necessary to undertake pumping tests to determine water yield from such a location, so that yield is not sacrificed for good quality.

b) A series of large diameter shallow well supplies should be developed in areas where the Crag and the Glacial sands and gravels are exposed (i.e. where they are not overlain by the boulder clay). The large diameter of such wells will ensure adequate yields.

2. Long term studies

a) In this case, a detailed chemical survey of the Norwich Water Division's operational area (the research area) with reference to iron and manganese concentrations in Chalk waters, is recommended. This should be done on catchment or subcatchment basis. From such a survey, a map of elemental concentrations should be produced, delineating areas of high 1.1 ppm - 10.0 ppm, moderate 0.64 ppm - 1.0 ppm and low to negligible 0.01 - 0.1 ppm iron concentrations. The delineation should be based on iron because iron is the more problematic of the two elements in the area. As a rule, areas chosen for their low to negligible iron concentrations should be proved to have good transmissivity and storativity. In general, these recommendations are aimed at reducing the present and future costs of iron and manganese removal from waters of the area.

b) An investigation to determine the chemical oxidation states and the mineralogy of iron and manganese in the rocks and

ground waters should be undertaken. This is because in the present study, total concentrations of these elements, which may include their different oxidation states were determined in the waters.

c) The apparent relationship between iron and nitrate concentrations should be fully investigated to establish what is responsible for such a relationship and how the relationship can be used to advantage.

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APPENDIX A

Tables: 3.1a

3.1b

3.2

3.3

Table 3.1a Sampled exposures of the Glacial sand and gravels, and the Crag in Norfolk

Locality No.	Locality Name	Map Sheet No.	N.G. Ref.	Description of Locality
1	Weybourne Hope	131	110 438	Along the Coastal Cliff
2	Overstrand	131	255 404	Along the Coastal Cliff
3	Belaugh	147	209 178	In a pit, north of Old Hall
4	Frettenham	147	237 167	In a Lime Company's Old pit
5	Wroxham	147	286 166	East of Wroxham between the Beech Clump and the Dark Clump
6	Catton	161	229 109	At the Grove
7	Norwich	161	242 094	St. James' Park
8	Thorpe St. Andrew	161	275 090	In a pit along Pound Lane
9	Norwich	161	235 080	Gas Hill, along River-side Road
10	Whitlingham	161	273 078	Kirby Bedon, along Whitlingham Lane
11	Bramerton	161	295 060	At the Common
12	Norwich	161	220 057	Harford Bridge
13	Caistor St. Edmund	161	238 046	Chalk, Sands and Gravels Quarry
14	Newton Flotman	161	218 991	A small pit S.W. of Dairy Farm
15	Flordon	161	177 976	At the Common
16	Tasburgh	161	205 954	A pit along the river S. of Tasburgh Hill
17	Wortwell	175	280 850	An isolated hillside along the road to Homersfield from (off) the A143 Road.

Table 3.1b Sampled exposures of the Chalk in Norfolk

Locality No.	Locality Name	Map Sheet No.	N.G. Ref.	Description of Location
1	Weybourne Hope	131	110 438	Along the Coastal Cliff
2	Overstrand	131	255 404	Along the Coastal Cliff
3	Langham	131	009 417	N. of School, at junction of road from Langham to Marston
4	Frettenham	147	237 167	Lime Company's Old Pit
5	Glandford	131	943 411	In a pit, west of the road junction from Glandford to Bayfield Park
6	Catton	161	229 109	At the Grove
7	Norwich	161	242 094	St. James' Park
8	Thorpe St. Andrew	161	279 092	In a Pit along Pound Lane
9	Guist	147	000 256	At the Common
10	Whitlingham	161	273 078	Kirby Bedon, along Whitlingham Lane
11	Alderford	147	129 183	Swanning side of Common
12	Norwich	161	220 057	Harford Bridge
13	Caistor St. Edmund	161	238 046	Chalk, Sands and Gravel Quarry
14	Attlebridge	147	155 160	South of Spring Farm
15	Flordon	161	177 976	At the Common
16	Ringland	161	130 146	In a pit at the Church Farm
17	Lower Hellesdon	161	212 106	Along a steep face, behind a factory at the Industrial Estate
18	Norwich	161	260 085	Premises of Trustee Savings Bank along Thorpe Road
19	Cringleford	161	189 069	In an overgrown pit NE of Newfound Farm, across the road and towards Cringleford Wood
20	Eaton	161	208 063	In the cage along Newmarket Road.
21	Keswick	161	212 048	Beside the Lane, about 274 metres (300 yds) south of Old Mill

Locality No.	Locality Name	Map Sheet No.	N.G. Ref.	Description of Location
22	Flordon	161	189 972	In a pit south of Flordon Church

Table 3.2 Sampled walls and boreholes

Wells & Borehole Nos.	N.G. Ref	Locality Name	Ownership of Well or Borehole
1	933 408	Wighton (Pumping Station)	A.W.A.
2	967 385	Binham (Field House Farm)	R.H. Rounce (Private, P.)
3		Houghton St. Giles (Pumping Station)	A.W.A.
4	157 422	Sheringham (Pumping Station)	A.W.A.
5	049 418	Glandford (Pumping Station)	A.W.A.
6	042 415	Langham (Brakes Farm, Wiveton)	H.T. Harcourt & Sons
7	197 376	Metton (Pumping Station)	A.W.A.
8	144 353	Matlaske (Pumping Station)	A.W.A.
9	317 361	Mundesley (Pumping Station)	A.W.A.
10	981 333	Thursford (Brook Hill Farm, Fakenham)	G.E. & M.A. Cushing
11	928 303	Fakenham (Ross Foods Ltd., Old Holt Road)	Private
12	937 322	Fakenham (Thorpeland Hall Farm)	John N. Savory
13	826 236	Weasenham (Upper House Farm)	Overman & Co. Ltd.
14	987 190	Beetley (Pumping Station)	A.W.A.
15	977 179	Beetley (High House Farm)	S.D. Abram
16	292 349	Trunch (Millar's Farm)	V. Larke & Son
17	291 314	Royston Bridge (Pumping Station)	A.W.A.
18	024 304	Melton Constable (Tripples Farm)	Mr. E. Plumb
19	274 296	North Walsham (Pumping Station)	A.W.A.

A.W.A. = Anglian Water Authority

Wells & Borehole Nos.	N.G. Ref.	Locality Name	Ownership of Well or Borehole
20	257 283	North Walsham (Manor House Hotel)	Mr. Crowe
21	032 272	Foulsham (Pumping Station)	A.W.A.
22	098 275	Wood Dalling (Crab Tree Farm)	Messrs. A. & A. Clarke
23	201 273	Aylsham (Pumping Station)	A.W.A.
24	128 244	Sall (Pumping Station)	A.W.A.
25	071 216	Reepham (Woodrow Farm)	Stanley Simpson & Sons Ltd.
26	141 214	Brandiston (Church Farm)	K. H. Wells
27	148 202	Haveringland (Newstead Farm)	Frank W Allen
28	082 191	Great Witchingham (Wild Life Park)	Norfolk Wild Life Park)
29	068 178	Lyng (Pumping Station)	A.W.A.
30	019 181	Swanton Morley (The White House)	M.H.A. Boldero
31	139 157	Attlebridge (Old Hall Farm)	W.D. Oram
32	156 161	Felthorpe (Spring Farm)	P.J. Throssell
33	158 156	Felthorpe (Fir Covert Farm)	Kenneth H. Dye
34	159 156	Felthorpe (High Breck)	Mr. Mauncer
35	309 343	Knapton (Church Farm)	Norman May (Knapton) Ltd.
36	314 328	Edingthorpe (Hill Farm)	Clans Farms Ltd.
37	341 277	East Ruston (Pumping Station)	A.W.A.
38	306 226	Tunstead (Church Farm)	R & JM Place Ltd.
39	388 224	Catfield (Station Nurseries)	G.A. Bailey Ltd.

Wells & Borehole Nos.	N.G. Ref.	Locality Name	Ownership of Well or Borehole
40	398 217	Catfield (Long Acre, New Road)	Mrs. D.E. Puxley
41	363 205	Barton Turf (Irstead Lod.)	H.C. & R.A. King
42	385 200	Ludham (Pumping Station)	A.W.A.
43	421 199	Potter Heigham (Hall Farm)	C. Blaxell
44	462 182	Martham (Manor Farm)	William Bracey
45	416 171	Repps (Hall Farm)	Leonard J. Mitchell
46	487 168	Hemsby (Home Farm)	George E. Daniels
47	412 163	Thurne (Abbey Farm)	W.D. George
48	976 147	Dillington Hall (Dillington Hall Est,)	Private
49	223 120	Catton (Industrial Estate)	Coca Cola Bottlers Ltd.
50	034 109	Mattishall (Old Hall Farm)	Jesse Gogle
51	049 097	Mattishall (Pumping Station)	A.W.A.
52	103 108	Honingham (Greenacres Farm)	William Young Ltd.
53	157 109	Costessey (Dereham Road)	Harford Eng. Co. Ltd.
54	182 083	Colney (Pumping Station)	A.W.A.
55	253 084	Thorpe St. Andrew (Pumping Station)	A.W.A.
56	220 147	Norwich (Ipswich Road)	Milk Marketing Board
57	240 047	Caistor St. Edmund (Pumping Station)	A.W.A.
58	196 020	Mulbarton (V.L. Grey (Nurseries))	V.L. Grey
59	246 027	Stoke Holy Cross (Whiteford Hall Farm)	T.W. Humphrey
60	229 008	Swainsthorpe (Hall Farm)	J.H.D. Dickson

Wells & Borehole Nos.	N.G. Ref.	Locality Name	Ownership of Well or Borehole
61	150 977	Ashwellthorpe (Sampling Point)	A.W.A.
62	203 987	Newton Flotman (Birds Farm Mushroom)	Mrs. Hulman
63	187 873	Flordon (Birds Farm Mushroom)	Private
64	264 974	Shotesham (Kings Farm)	J & J Dunlop
65	351 147	Ranworth (Ranworth Farm)	F. Cator
66	364 146	Ranworth (Leit's Farm)	Jermy Bros.
67	326 132	Woodbastwick (Mousehold Heath Farm)	Heath Farms Ltd.
68	402 119	Acle (Fishley Hall)	William P. Molineux
69	314 097	Witton (Witton Hall)	H.T. Mack
70	385 082	Beighton (Cedar House)	John Arnold
71	326 071	Brundall (68 Station Road) Riverside	Harvey Eastwood Ltd.
72	340 068	Strumpshaw (Pumping station)	A.W.A.
73	318 069	Surlingham (Bixley Villa)	Reginald J. Clough
74	498 051	Burgh Castle (Breydon View, Market Road)	Frank N. Osborn
75	307 010	Bergh Apton (Church Farm)	A,A. Paraffit & Sons
76	323 997	Bergh Apton (Holy Lodge)	Michael Loyness
77	414 020	Reedham (Ferry Farm)	Reginald C. Mutten
78	347 983	Loddon (Lodge Farm,	F.J. & J.V. Haylock
79	347 983	Loddon (Lodge Farm,	F.J. & J.V. Haylock
80	442 970	Haddiscoe (Manor Farm)	Manor Farm Ltd.
81	312 967	Seething (Gerrins Farm)	A.J. Hewitt

Wells & Borehole Nos	N.G. Ref.	Locality Name	Ownership of Well or Borehole
82	240 944	Hempnall (Manor Farm)	G.H. Allen (Farms) Ltd.
83	138 911	Aslacton (Bunwell) Pumping Station	A.W.A.
84	155 901	Aslacton (Dale Farm)	Mrs. C.M. Thurgar
85	233 903	Shelton (Pine Lodge)	J. L. Smith
86	067 830	Fersfield (Sampoing Point)	A.W.A.
87	196 832	Rushall (Pumping Station	A.W.A.
88	194 821	Rushall (at the college)	Mrs. Debenham
89	108 807	Diss (Pumping Station)	A.W.A.
90	403 949	Raveningham (Grove Farm)	Wardes Farms
91	358 928	Ellingham (at the hall)	Col. Smith
92	355 926	Ellingham (Manor Farm)	R. B. Freland

Table 3.3 Details of water sampling

Sample No.	N.G. Ref.	Locality Name	Temp ^{o}C	pH	Dissolv. O_2%	Date Collected	Sampling Method
1	933 408	Wighton AWA	10.0	7.15	58.0	20.7.79	Sampling Tap (B.H.)
2	967 385	Binham	11.0	6.78	35.0	24.8.79	Bleed tap at head of Bore
3	932 356	Houghton AWA	10.0	7.10	61	20.7.79	Sampling Tap BH
4	157 422	Sheringham AWA	11.0	7.25	27.5	20.7.79	Sampling Tap BH
5	049 418	Glandford AWA	11.5	7.10	47.5	20.7.79	Sampling Tap BH
6	024 415	Langham AWA	10.5	7.08	12.0	24.8.79	Bleed Tap at head of BH
7	197 376	Metton AWA	11.0	7.31	28.5	13.7.79	Sampling Tap BH
8	144 353	Matlaske AWA	10.5	7.20	22.0	28.7.79	Sampling Tap BH
9	317 361	Mundesley AWA	10.0	6.86	25.5	31.8.79	Sampling Tap BH
10	981 333	Thursford	10.0	6.74	3.88	24.8.79	Tap at base of pressure
11	928 303	Fakenham Rose Foods	12.0	7.06	25.0	18.10.79	Pipe into storage tank BH
12	937 322	Fakenham Thorpeland Fm.	11.0	6.94	18.0	24.8.79	Bleed taps at head of BH
13	826 236	Weasenham	11.0	7.04	66.0	18.10.79	Bleed tap at head of BH
14	987 190	Beetley AWA	11.0	7.39	12.0	28.9.79	Sampling tap BH
15	977 179	Beetley	11.0	7.58	10.0	28.9.79	Bleed tap head of BH
16	292 349	Trunch	10.5	7.52	30.0	9.11.79	Tap on pressure tank BH
17	291 314	Royston Bge. AWA	10.5	6.82	24.5	31.8.79	Sampling tap BH

BH = Borehole

Sample No.	N.G. Ref.	Locality Name	Temp ^{o}C	pH	Dissolv. O_2%	Date Collected	Sampling Method
18	024 304	Melton Constable	11.0	7.24	21.0	18.10.79	Pipe into storage tank BH
19	274 296	N. Walsham AWA	11.0	7.07	29.5	31.8.79	Sampling tap BH
20	257 283	N. Walsham	10.5	7.71	18.5	27.7.79	Bleed tap at head of BH
21	032 272	Foulsham AWA	11.0	7.26	31.0	3.8.79	Sampling tap BH
22	098 275	Wood Dalling	10.0	6.85	40.0	14.9.79	Valve at base of pressure tank
23	201 273	Aylsham AWA	10.5	7.19	43.5	3.8.79	Sampling tap BH
24	128 244	Sall AWA	10.5	7.35	33.7	3.8.79	Sampling tap BH
25	071 216	Reepham	11.0	6.98	10.0	14.9.79	Bleed tap at head of BH
26	141 214	Brandiston	10.0	7.34	26.0	6.11.79	Tap on withdrawal pipe BH
27	148 202	Haveringland	10.0	7.34	14.0	6.11.79	Pressure tap head of BH
28	082 191	Gt. Witching-ham	11.7	7.09	10.5	14.9.79	Withdrawal hose at head of BH
29	068 178	Lyng AWA	11.0	7.62	40.0	3.8.79	Sampling tap BH
30	019 181	Swanton Morley	12.0	7.09	60.0	14.9.79	Bleed tap at head of BH
31	139 157	Attlebridge	11.0	7.42	26.8	13.7.79	Bleed tap on head of BH
32	156 161	Felthorpe (Spg. Farm)	10.5	7.06	13.0	1.11.79	Pipe into storage tank BH
33	158 156	Felthorpe (Fir Covert Farm)	9.0	7.54	20.6	8.11.79	Tap on pressure tank BH

Sample No.	N.G. Ref.	Locality Name	Temp °C	pH	Dissolv. O_2%	Date Collected	Sampling Method
34	159 156	Felthorpe (High Breck)	10.0	6.71	60.0	8.11.79	Withdrawal pipe (Well)
35	309 343	Knapton	10.0	7.40	10.0	25.10.79	Bleed tap Head of BH
36	314 328	Edingthorpe	11.0	7.36	26.0	25.10.79	Withdrawal Tap BH
37	341 277	E. Ruston AWA	11.0	7.25	24.0	31.8.79	Sampling tap BH
38	306 226	Tunstead	10 0	7.18	12.0	24.10.79	Withdrawal pipe BH
39	388 224	Catfield (Stn Nurs.)	13.0	6.39	34.0	24.10.79	Bucket and String (Well)
40	398 217	Catfield (Long Acre)	11.5	6.31	60.0	24.10.79	Bleed tap Well
41	363 205	Barton Turf	12.0	6.88	49.0	25.10.79	Bleed tap head of BH
42	385 200	Ludham AWA	10.5	7.28	30.5	7.9.79	Sampling tap BH
43	421 199	Potter Heigham	11.5	6.84	12.0	23.11.79	Bucket & String (Well)
44	462 182	Martham	10.5	7.02	45.0	19.10.79	Pipe into storage tank BH
45	416 171	Repps	11.0	7.01	56.0	7.9.79	Withdrawal pipe (Well)
46	487 168	Hemsby	12.0	6.87	18.0	19.10.79	Bleed tap (Well)
47	412 163	Thurne	12.0	6.94	63.0	19.10.79	Withdrawal Pipe (Well)
48	976 147	Dillington Hall	11.0	7.39	24.0	18.10.79	Withdrawal Tap (BH)
49	223 120	Catton	11.5	7.18	32.0	25.10.79	Bleed tap Head of BH
50	034 109	Matishall	11.0	7.16	18.0	28.9.79	Bleed tap Head of BH
51	049 097	Matishall AWA	11.0	7.15	14.0	28.9.79	Sampling Tap BH
52	103 108	Honingham	11.5	7.33	42.0	18.10.79	Withdrawal Pipe BH

Sample No.	N.G. Ref.	Locality Name	Temp ^{o}C	pH	Dissolv. O_2%	Date Collected	Sampling Method
53	157 109	Costessey	11.0	7.33	50.0	30.10.79	Service tap
54	182 083	Colney AWA	11.0	7.22	35.5	3.8.79	Sampling tap BH
55	253 084	Thorpe AWA	10.5	7.15	50.0	7.9.79	Sampling tap BH
56	220 047	Norwich MMB	10.5	7.26	38.0	30.10.79	Bleed tap head of BH
57	240 047	Caistor AWA	10.5	6.96	39.8	31.8.79	Sampling tap BH
58	196 020	Mulbarton	10.5	7.21	15.0	16.11.79	Withdrawal pipe BH
59	246 027	Stoke Holy X	12.0	7.29	22.0	5.11.79	Bottle & string well
60	229 008	Swainsthorpe	10.5	7.03	30.0	5.11.79	Bleed tap, head of BH
61	150 977	Ashwellthorpe AWA	13.0	7.68	35.0	12.10.79	Sampling tap BH
62	203 987	Newton Flotman	10.0	7.16	21.0	16.11.79	Tap on pressure tank BH
63	187 973	Flordon	10.0	6.96	20.0	5.11.79	Bleed tap head of BH
64	263 974	Shotesham	10.0	7.42	18.0	16.11.79	Bleed tap head of BH
65	357 151	Ranworth Ranworth Farm	11.0	7.48	22.0	30.11.79	Withdrawal pipe BH
66	364 146	Ranworth (Leist's Farm)	10.0	7.09	26.0	30.11.79	Bucket & string well
67	326 132	Woodbastwick	11.0	7.37	20.0	19.10.79	Bleed tap at head of BH
68	402 119	Acle	11.0	6.96	42.0	19.10.79	Withdrawal tap(well)
69	314 097	Witton	11.0	7.48	10.0	2.11.79	Withdrawal tap BH
70	385 082	Beighton	10.5	7.85	62.0	23.11.79	Bottle & rope(well)
71	326 071	Brundall	12.0	7.06	19.0	7.9.79	Withdrawal service or pipe

Sample No.	N.G. Ref.	Locality Name	Temp ^{o}C	pH	Dissolv. O_2%	Date Collected	Sampling Method
72	340 068	Strumpshaw	11.0	6.81	23.0	7.9.79	Sampling tap BH
73	318 069	Surlingham	10.0	7.28	36.0	23.11.79	Bucket & string (well)
74	498 051	Burgh Castle	10.5	7.18	58.0	31.10.79	Withdrawal service tap
75	307 010	Bergh Apton C. Farm	10.0	7.82	50.0	23.11.79	Tap base of pressure tank BH
76	323 997	Bergh Apton	9.5	7.30	28.0	23.11.79	Withdrawal pipe BH
77	414 020	Reedham	9.0	7.10	58.0	30.11.79	Bleed tap well
78	347 983	Loddon (House)	12.0	7.22	45.0	31.10.79	Withdrawal tap well
79	347 983	Loddon (The Farm)	12.0	7.09	40.0	31.10.79	Bucket & String Well
80	442 970	Haddiscoe	11.0	6.90	43.0	31.10.79	Bleed tap head of well
81	312 967	Seething	10.0	7.21	21.0	16.11.79	Pressure valve on head of BH
82	240 944	Hempnall	10.0	7.07	18.0	5.11.79	Bleed tap head of BH
83	138 911	Aslacton AWA	11.0	7.00	20.0	12.10.79	Sampling tap BH
84	155 901	Aslacton	10.0	7.10	22.0	7.11.79	Bleed tap head of BH
85	233 903	Shelton	10.5	7.34	15.0	7.12.79	Bleed tap head of BH
86	067 830	Fersfield AWA	13.0	7.34	26.0	17.10.79	Sampling tap
87	196 832	Rushall AWA	11.0	6.96	21.0	12.10.79	Sampling
88	194 821	Rushall	10.0	7.22	36.0	12.10.79	Bucket & chain well
89	108 807	Diss AWA	11.0	6.81	15.5	12.10.79	Sampling tap BH
90	403 949	Raveningham	10.5	7.71	28.0	26.10.79	Bleed tap head of BH

Sample No.	N.G. Ref.	Locality Name	Temp ^{o}C	pH	Dissolv. O_2%	Date Collected	Sampling Method
91	358 928	Ellingham	12.0	7.28	26.0	26.10.79	Bucket & chain well
92	355 926	Ellingham Manor Farm	14.0	7.10	40.0	26.10.79	Bucket & string well

APPENDIX B

Tables:

4.5a
4.5b
4.5c
4.5d

4.6a
4.6b
4.6c
4.6d
4.6e
4.6f

Appendix B

Determination of parts per million (ppm) equivalent of microgram per mille (μg/ml) of iron and manganese in the rock samples.

Dilution Factor (D.F.)

$$D.F. = \frac{\text{Final volume of solution}}{\text{Initial weight of sample digested}}$$

in this case, $\frac{10 \text{ ml}}{0.25\text{g}}$

$= 10 \times 4$

$= 40$

The parts per million (ppm)

If iron concentration were amg/l

the ppm equivalent = amg/l x D.F.(40)

= 40 a ppm

Explanation

Assuming: 0.25g sample in 10 ml gave 5 μg/ml iron (Fe)

i.e. In 10 ml, at a conc. of 5 μg/ml there was 50 μg Fe.

So in 0.25 g sample " " 50 μg Fe

∴ in 1.0g sample there will be $\frac{50 \times 1}{0.25}$ μg = 200 μg Fe

200 μg/g = 0.2 mg/g ≡ ppm (solid/solid)

To express this as a factor, will take the form

$$\frac{\text{conc. in lg}}{\text{conc. per mille}}$$

$$= \frac{200}{5} \text{ or } \frac{0.2}{0.005} = \underline{\underline{40}}$$

This is the same as $\frac{\text{Final volume of soln. in ml}}{\text{Initial weight in g}}$ (if no further dilution)

In general, mg/l in solution X D.F. = mg/g in sample = ppm (solid/solid)

Table 4.5a Concentrations of iron (Fe) in the Glacial sand and gravels, and the Crag of Norfolk

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
1	Weybourne	1a	23000.00	2.30
		1b	23000.00	2.30
		2a	19880.00	1.99
		2b	19920.00	1.99
2	Overstrand	3a	94400.00	9.44
		3b	93600.00	9.36
		4a	103400.00	10.34
		4b	103360.00	10.336
3	Belaugh	5a	9680.00	0.968
		5b	9600.00	0.96
		6a	13200.00	1.32
		6b	13200.00	1.32
4	Frettenham	7a	13800.00	1.38
		7b	13880.00	1.388
		8a	9840.00	0.98
		8b	9880.00	0.988
5	Wroxham	9a	17320.00	1.73
		9b	17320.00	1.73
		10a	25520.00	2.55
		10b	25440.00	2.54
*6	Catton	11a	244400.00	24.44
		11b	244320.00	24.43
		12a	20960,00	2.096
		12b	21040.00	2.10
7	Norwich (St. James' Pit)	13a	39840.00	3.98
		13b	39960.00	3.996
		14a	52000.00	5.20
		14b	52000.00	5.20

* Sample taken from Crag-Chalk contact (i.e. at the base of the Crag.

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
8	Thorpe St. Andrew	15a	54600.00	5.46
		15b	54600.00	5.46
		16a	84800.00	8.48
		16b	84800.00	8.48
9	Norwich (Gas Hill)	17a	4160.00	0.416
		17b	4120.00	0.41
		18a	4480.00	0.448
		18b	4480.00	0.448
10	Whitlingham	19a	16400.00	1.64
		19b	16440.00	1.64
		20a	20560.00	2.056
		20b	20560.00	2.056
11	Bramerton	21a	8520.00	0.85
		21b	8600.00	0.86
		22a	25840.00	2.58
		22b	25720.00	2.57
12	Norwich (Harford Bridge)	23a	22080.00	2.208
		23b	22000.00	2.20
		24a	15440.00	1.54
		24b	15440.00	1.54
13	Caistor St. Edmund	25a	24560.00	2.456
		25b	24480.00	2.448
		26a	35840.00	3.58
		26b	35920.00	3.59
14	Newton Flotman	27a	7840.00	0.78
		27b	7800.00	0.78
		28a	13200.00	1.32
		28b	13160.00	1.316

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
15	Flordon (Common)	29a	15200.00	1.52
		29b	15160.00	1.516
		30a	64800.00	6.48
		30b	64880.00	6.488
16	Tasburgh	31a	14360.00	1.436
		31b	14480.00	1.448
		32a	14080.00	1.408
		32b	14080.00	1.408
17	Wortwell	33a	12120.00	1.21
		33b	12040.00	1.20
		34a	12440.00	1.24
		34b	12400.00	1.24

Table 4.5b Concentrations of manganese (Mn) in the Glacial sand and gravels and the Crag of Norfolk

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
1	Weybourne	1a	2920.00	0.29
		1b	2920.00	0.29
		2a	154.60	0.01
		2b	144.80	0.01
2	Overstrand	3a	1720.00	0.17
		3b	1666.40	0.166
		4a	3800.00	0.38
		4b	3787.30	0.378
3	Belaugh	5a	325.60	0.03
		5b	328.80	0.03
		6a	316.40	0.03
		6b	320.00	0.03
4	Frettenham	7a	177.60	0.02
		7b	176.80	0.02
		8a	88.00	0.008
		8b	88.00	0.008
5	Wroxham	9a	560.40	0.056
		9b	540.00	0.05
		10a	880.00	0.008
		10b	920.00	0.09
6	Catton	11a	7160.00	0.716
		11b	7112.00	0.71
		12a	243.20	0.02
		12b	243.20	0.02
7	Norwich (St. James' Pit)	13a	432.00	0.04
		13b	432.00	0.04
		14a	732.00	0.07
		14b	744.00	0.07

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
8	Thorpe St.	15a	1964.00	0.196
		15b	1976.00	0.197
		16a	1638.00	0.164
		16b	1680.00	0.168
9	Norwich (Gas Hill)	17a	19.20	0.0019
		17b	20.00	0.002
		18a	19.60	0.0019
		18b	21.20	0.002
10	Whitlingham	19a	40.00	0.004
		19b	40.00	0.004
		20a	80.00	0.008
		20b	80.00	0.008
11	Bramerton	21a	228.40	0.023
		21b	236.40	0.024
		22a	400.00	0.04
		22b	400.00	0.04
12	Norwich (Harford Bridge)	23a	75.20	0.0075
		23b	76.00	0.0076
		24a	40.00	0.004
		24b	40.00	0.004
13	Caistor St. Edmund	25a	436.00	0.04
		25b	436.00	0.04
		26a	80.00	0.008
		26b	80.00	0.008
14	Newton Flotman	27a	480.00	0.048
		27b	480.00	0.048
		28a	394.00	0.039
		28b	400.00	0.04
15	Flordon (Common)	31a	161.60	0.016
		31b	170.00	0.017
		32a	120.00	0.01
		32b	120.00	0.01

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
16	Tasburgh	31a	161.60	0.016
		31b	170.00	0.017
		32a	120.00	0.01
		32b	120.00	0.01
17	Wortwell	33a	128.00	0.013
		33b	130.00	0.0131
		34a	136.80	0.014
		34b	137.20	0.014

Table 4.5c Concentrations of iron (Fe) in the Chalk of Norfolk

Locality No	Locality Name	Sample No.	Concentration in ppm	Concs. as %
1	Weybourne Hope	1a	1720.00	0.17
		1b	1708.00	0.17
		2a	1460.00	0.146
		2b	1435.00	0.14
2	Overstrand	3a	840.00	0.08
		3b	880.00	0.088
		4a	600.00	0.06
		4b	594.80	0.059
3	Langham	5a	3040.00	0.30
		5b	3080.00	0.30
		6a	3640.00	0.36
		6b	3640.00	0.36
4	Frettenham	7a	5540.00	0.55
		7b	5540.00	0.55
		8a	5977.60	0.597
		8b	6004.00	0.60
5	Glandford	9a	1000.00	0.10
		9b	1000.00	0.10
		10a	1520.00	0.15
		10b	1560.40	0.156
6	Catton	11a	1828.80	0.18
		11b	1828.00	0.18
		12a	1920.00	0.19
		12b	1924.00	0.19
7	Norwich (St. James' Pit)	13a	2136.00	0.21
		13b	2136.80	0.21
		14a	1104	0.11
		14b	1094.00	0.109

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
8	Thorpe St. Andrew	15a	1087.60	0.109
		15b	1120.40	0.11
		16a	840.00	0.08
		16b	840.00	0.08
9	Guist	17a	1000.00	0.10
		17b	1040.00	0.10
		18a	2480.00	0.248
		18b	2520.40	0.25
10	Whitlingham	19a	1880.00	0.188
		19b	1890.00	0.189
		20a	2142.00	0.21
		20b	2142.00	0.21
11	Alderford	21a	3560.00	0.356
		21b	3560.00	0.356
		22a	3440.00	0.34
		22b	3480.00	0.348
12	Norwich (Harford Bridge)	23a	3044.00	0.30
		23b	3060.80	0.306
		24a	6005.60	0.60
		24b	6005.60	0.60
13	Caistor St. Edmund	25a	563.20	0.056
		25b	563.20	0.056
		26a	560.00	0.056
		26b	560.00	0.056
14	Attlebridge	27a	3604.00	0.36
		27b	3612.00	0.36
		28a	3560.00	0.365
		28b	3620.00	0.36
15	Flordon (Common)	29a	5625.20	0.56
		29b	5640.40	0.56
		30a	4828.00	0.48
		30b	4840.40	0.48

Locality No.	Locality Name	Sample No.	Concentrations in ppm	Concs. as %
16	Ringland	31a	1902.00	0.19
		31b	1902.00	0.19
		32a	1326.00	0.13
		32b	1360.00	0.136
17	Lower Hellesdon	33a	1528.00	0.153
		33b	1518.80	0.152
		34a	1174.80	0.117
		34b	1175.60	0.117
18	Norwich (T.S. Bank)	35a	2881.60	0.288
		35b	2890.00	0.289
		36a	1836.00	0.18
		36b	1836.00	0.18
19	Cringleford	37a	3380.80	0.338
		37b	3380.00	0.338
		38a	1191.60	0.119
		38b	1204.00	0.12
20	Eaton	39a	870.40	0.087
		39b	880.00	0.088
		40a	915.20	0.09
		40b	915.20	0.09
21	Keswick	41a	1525.60	0.15
		41b	1528.40	0.153
		42a	1024.80	0.102
		42b	1026.00	0.102
22	Flordon (South of Church)	43a	3254.40	0.32
		43b	3254.40	0.32
		44a	3089.60	0.309
		44b	3075.20	0.307

Table 4.5d Concentrations of manganese (Mn) in the Chalk of Norfolk

Locality No.	Locality Name	Sample No.	Concentrations in ppm	Concs. as %
1	Weybourne Hope	1a	264.00	0.026
		1b	268.00	0.028
		2a	228.00	0.021
		2b	228.00	0.02
2	Overstrand	3a	180.00	0.108
		3b	182.00	0.018
		4a	208.00	0.02
		4b	208.00	0.02
3	Langham	5a	220.00	0.02
		5b	220.00	0.02
		6a	228.00	0.02
		6b	232.00	0.02
4	Frettenham	7a	224.00	0.02
		7b	240.40	0.02
		8a	288.00	0.028
		8b	311.60	0.03
5	Glandford	9a	196.00	0.019
		9b	196.00	0.019
		10a	164.00	0.016
		10b	164.40	0.016
6	Catton	11a	340.40	0.03
		11b	340.80	0.03
		12a	244.00	0.02
		12b	244.00	0.02
7	Norwich (St. James' Park)	13a	216.00	0.022
		13b	216.00	0.022
		14a	204.00	0.02
		14b	200.00	0.02

Locality No.	Locality Name	Sample No.	Concentrations	Concs. as %
8	Thorpe St. Andrew	15a	216.40	0.02
		15b	216.40	0.02
		16a	186.80	0.019
		16b	187.20	0.019
9	Guist	17a	224.40	0.02
		17b	226.40	0.023
		18a	219.20	0.02
		18b	222.80	0.02
10	Whitlingham	19a	320.00	0.03
		19b	320.40	0.03
		20a	364.00	0.036
		20b	358.80	0.035
11	Alderford	21a	172.80	0.017
		21b	175.20	0.017
		22a	153.20	0.015
		22b	156.40	0.016
12	Norwich (Harford Bridge)	23a	240.00	0.02
		23b	240.00	0.02
		24a	259.20	0.026
		24b	258.80	0.026
13	Caistor St. Edmund	25a	196.40	0.019
		25b	194.80	0.019
		26a	192.00	0.019
		26b	192.00	0.019
14	Attlebridge	27a	140.00	0.01
		27b	140.00	0.01
		28a	151.20	0.015
		28b	151.60	0.015
15	Flordon (Common)	29a	427.20	0.04
		29b	426.00	0.04
		30a	344.80	0.03
		30b	360.00	0.036

Locality No.	Locality Name	Sample No.	Concentration in ppm	Concs. as %
16	Ringland	31a	140.00	0.01
		31b	140.00	0.01
		32a	164.00	0.016
		32b	164.00	0.016
17	Lower Hellesdon	33a	185.60	0.018
		33b	186.80	0.018
		34a	164.00	0.016
		34b	164.00	0.016
18	Norwich (T.S. Bank)	35a	352.00	0.03
		35b	352.00	0.03
		36a	296.80	0.029
		36b	297.60	0.029
19	Cringleford	37a	156.00	0.01
		37b	152.00	0.01
		38a	148.40	0.01
		38b	147.60	0.01
20	Eaton	39a	153.20	0.01
		39b	152.40	0.01
		40a	156.00	0.01
		40b	156.00	0.01
21	Keswick	41a	160.00	0.016
		41b	160.40	0.016
		42a	172.00	0.017
		42b	172.00	0.017
22	Flordon (South of Church)	43a	320.00	0.03
		43b	320.00	0.03
		44a	268.40	0.026
		44b	272.80	0.027

Table 4.6a Boreholes and wells with iron (Fe) levels less than and equal to 0.1 ppm

Serial No.	Sample No.	Locality Name	N.G. Ref.	Fe conc. ppm
1	3	Houghton St. Giles	932 356	0.08
2	5	Glandford	049 418	0.03
3	12	Fakenham (Thorpeland)	937 322	0.10
4	23	Aylsham	201 273	0.02
5	29	Lyng	068 178	0.01
6	30	Swanton Morley	019 181	0.04
*7	45	Repps	416 171	0.01
8	54	Colney	182 083	0.01
9	57	Caistor	240 047	0.03
10	61	Ashwellthorpe	150 977	0.02
*11	68	Acle	402 119	0.10
*12	70	Beighton	385 082	0.02
*13	79	Loddon	347 983	0.07

* = Shallow Wells

Table 4.6b Boreholes and wells with iron (Fe) levels higher than 0.1 and equal to 1.0 ppm

Serial No.	Sample No.	Locality Name	N.G. Ref.	Fe conc. ppm
1	1	Wighton	933 408	0.14
2	4	Sheringham	157 422	0.87
3	7	Metton	197 376	0.64
4	8	Matlaske	144 353	0.94
5	13	Weasenham	826 236	0.15
6	14	Beetley	987 190	0.25
7	15	Beetley	977 179	0.57
8	20	North Walsham	257 283	0.73
9	24	Sall	128 244	0.31
10	31	Attlebridge	139 157	0.30
11	33	Felthorpe	158 156	1.00
* 12	34	Felthorpe	159 156	0.17
13	35	Knapton	309 343	0.75
14	37	East Ruston	341 277	0.46
* 15	39	Catfield	388 244	0.22
* 16	40	Catfield	398 217	0.13
17	41	Barton Turf	363 205	0.13
18	42	Ludham	385 200	0.77
19	43	Potter Heigham	421 199	0.11
20	44	Martham	462 182	0.34
* 21	46	Hemsby	487 168	0.81
* 22	47	Thurne	412 163	0.23
23	48	Dillington Hoe	976 147	0.19
24	49	Catton	223 120	0.16
25	52	Honingham	103 108	0.65
26	53	Costessey	157 109	0.12
27	55	Thorpe St. Andrews	253 084	0.11
28	56	Norwich (Milk M. Board)	220 027	0.12
* 29	59	Stoke Holy Cross	246 027	0.23
30	60	Swainsthorpe	229 008	0.68
31	63	Flordon	187 973	0.58

* = Shallow Wells

Serial No.	Sample No.	Locality Name	N.G. Ref.	Fe conc. ppm
32	66	Ranworth	364 146	0.26
33	72	Strumpshaw	340 068	0.82
*34	73	Surlingham	318 069	0.17
*35	74	Burgh Castle	498 051	0.22
*36	77	Reedham	414 020	0.13
*37	78	Loddon	347 983	0.14
*38	80	Haddiscoe	442 970	0.12
39	86	Fersfield (Kenninghall)	067 830	0.13
*40	88	Rushall	194 821	0.25
41	89	Diss	108 807	0.18
*42	91	Ellingham	358 928	0.36
*43	92	Ellingham	355 926	0.12

* = Shallow Wells

Table 4.6c Boreholes with iron (Fe) levels higher than 1.0 ppm

Serial No.	Sample No.	Locality Name	N.G. Ref.	Fe ppm
1	2	Binham	967 385	1.23
2	6	Langham	024 415	1.57
3	9	Mundesley	317 361	2.36
4	10	Thursford	981 333	2.32
5	11	Fakenham (Ross Foods Ltd.)	928 3-3	1.10
6	16	Trunch	292 349	2.11
7	17	Royston Bridge	291 314	1.38
8	18	Melton Constable	024 304	1.86
9	19	North Walsham	274 296	1.10
10	21	Foulsham	032 272	1.23
11	22	Wood Dalling	098 275	2.39
12	25	Reepham	071 216	1.28
13	26	Brandiston	141 214	1.71
14	27	Haveringland	148 202	3.02
15	28	Gt. Witchingham	082 191	1.09
16	32	Felthorpe	156 161	2.40
17	36	Edingthorpe	314 328	1.52
18	38	Tunstead	306 226	4.86
19	50	Matishall	034 109	1.80
20	51	Matishall	049 097	1.38
21	58	Mulbarton	196 020	1.71
22	62	Newton Flotman	203 987	1.85
23	64	Shotesham	264 974	6.02
24	65	Ranworth	351 147	1.06
25	67	Woodbastwick	326 132	1.29
26	69	Witton	314 097	1.38
27	71	Brundall	326 071	1.52
28	75	Bergh Apton	307 010	2.85
29	76	Bergh Apton	323 997	1.01
30	81	Seething	312 967	6.13
31	82	Hempnall	240 944	1.39
32	83	Aslacton (Bunwell)	155 901	9.77

Serial No.	Sample No.	Locality Name	N.G. Ref.	Fe ppm
33	84	Aslacton	155 901	9.77
34	85	Shelton	233 903	5.74
35	87	Rushall	196 832	2.87
36	90	Raveningham	403 949	1.36

Table 4.6d Boreholes and wells with manganese (Mn) levels less than and equal to 0.05 ppm

Serial No.	Sample No.	Locality Name	N.G. Ref	Mn ppm
1	1	Wighton	933 408	0.01
2	3	Houghton St. Giles	932 356	0.01
3	5	Glandford	049 418	0.01
4	6	Langham	024 415	0.04
5	7	Metton	197 376	0.04
6	12	Fakenham	937 322	0.02
7	14	Beetley	987 190	0.01
8	15	Beetley	977 179	0.02
9	20	North Walsham	257 283	0.05
10	23	Aylsham	201 273	0.01
11	24	Sall	128 244	0.04
12	25	Reepham	071 216	0.04
13	28	Gt. Witchingham	082 191	0.04
14	29	Lyng	068 178	0.01
15	30	Swanton Morley	019 181	0.02
16	31	Attlebridge	139 157	0.04
17	34	Felthorpe	159 156	0.04
18	37	East Ruston	341 277	0.03
19	41	Barton Turf	363 205	0.02
20	44	Martham	462 182	0.03
21	45	Repps	416 171	0.01
22	47	Thurne	412 163	0.05
23	49	Catton	223 120	0.03
24	52	Honingham	103 108	0.03
25	53	Costessey	157 109	0.03
26	54	Colney	182 083	0.01
27	55	Thorpe	253 084	0.01
28	56	Norwich M.M.B.	220 047	0.02
29	57	Caistor	240 047	0.02
30	61	Ashwellthorpe	150 977	0.01
31	66	Ranworth	364 146	0.03

Serial No.	Sample No.	Locality Name	N.G. Ref.	Mn ppm
32	68	Acle	402 119	0.02
33	70	Beighton	385 082	0.04
34	71	Brundall	326 071	0.03
35	72	Strumpshaw	340 068	0.04
36	73	Surlingham	318 069	0.03
37	74	Burgh Castle	498 051	0.03
38	77	Reedham	414 020	0.02
39	78	Loddon	347 983	0.03
40	79	Loddon	347 983	0.02
41	80	Haddiscoe	442 970	0.04
42	83	Aslacton (Bunwell)	138 911	0.02
43	86	Fersfield (Kenninghall)	067 830	0.01
44	88	Rushall	194 821	0.01
45	90	Raveningham	403 949	0.01
46	91	Ellingham	358 928	0.01
47	92	Ellingham	355 926	0.01

Table 4.6e Boreholes and wells with manganese levels higher than 0.05 and equal to 0.5 ppm

Serial No.	Sample No.	Locality Name	N.G. Ref.	Mn ppm
1	2	Binham	967 385	0.06
2	4	Sheringham	157 422	0.07
3	8	Matlaske	144 353	0.06
4	9	Mundesley	317 361	0.11
5	10	Thursford	981 333	0.18
6	11	Fakenham	928 303	0.11
7	13	Weasenham	826 236	0.09
8	16	Trunch	292 349	0.13
9	17	Royston Bridge	291 314	0.07
10	18	Melton Constable	024 304	0.09
11	19	North Walsham	274 296	0.12
12	21	Foulsham	032 272	0.06
13	22	Wood Dalling	098 275	0.13
14	26	Brandiston	141 214	0.08
15	27	Haveringland	148 202	0.13
16	32	Felthorpe	156 161	0.28
17	33	Felthorpe	158 156	0.28
18	35	Knapton	309 343	0.09
19	36	Edingthorpe	314 328	0.10
20	39	Catfield	388 224	0.11
21	40	Catfield	398 217	0.08
22	42	Ludham	385 200	0.08
23	43	Potter Heigham	421 199	0.17
24	48	Dillington Hoe	976 147	0.07
25	50	Matishall	034 109	0.07
26	51	Matishall	049 097	0.06
27	58	Mulbarton	196 020	0.09
28	59	Stoke Holy Cross	246 027	0.06
29	60	Swainsthorpe	229 008	0.11
30	62	Newton Flotman	203 987	0.09
31	63	Flordon	187 973	0.10

Serial No.	Sample No.	Locality Name	N.G. Ref.	Mn ppm
32	64	Shotesham	264 974	0.15
33	65	Ranworth	351 147	0.14
34	67	Woodbastwick	326 132	0.15
35	69	Witton	314 097	0.18
36	75	Bergh Apton	307 010	0.12
37	76	Bergh Apton	323 997	0.08
38	81	Seething	312 967	0.19
39	82	Hempnall	240 944	0.07
40	84	Aslacton	155 901	0.29
41	85	Shelton	233 903	0.14
42	87	Rushall	196 832	0.14
43	89	Diss	108 807	0.24

Table 4.6f Borehole and well with manganese levels higher than 0.5 ppm

Serial No.	Sample No.	Map Sheet No.	Locality Name	N.G. Ref.	Mn ppm
1	38	148	Tunstead	306 226	1.39
2	46	148	Hemsby	487 168	0.63

APPENDIX C

Tables: 5.1

5.2

Table 5.1 Ratios of bicarbonate ions and dissolved oxygen to iron

Sample Number	Fe Concs ppm	HCO_3^- Concs ppm	O_2 Concs ppm	HCO_3/Fe	O_2/Fe	Type of Device
1	0.14	221.25	6.54	1580.35	46.71	Borehole
2	1.23	283.50	3.85	230.48	3.13	Borehole
3	0.08	227.50	6.88	2843.75	86.00	Borehole
4	0.87	191.25	3.03	219.82	3.48	Borehole
5	0.03	221.25	5.22	7375.00	174.00	Borehole
6	1.57	268.25	1.34	170.86	0.85	Borehole
7	0.64	199.88	3.14	312.31	5.90	Shallow Well
8	0.94	192.50	2.45	204.79	2.60	Borehole
9	2.36	279.00	2.87	118.22	1.21	Borehole
10	2.32	283.50	0.45	122.20	0.19	Borehole
11	1.10	260.00	2.69	236.36	2.44	Borehole
12	0.10	267.75	1.98	2677.50	19.80	Shallow Well
13	0.15	374.00	7.27	2493.33	48.46	Borehole
14	0.25	183.00	1.32	732.00	5.28	Borehole
15	0.57	134.25	1.10	235.52	1.93	Borehole
16	2.11	232.00	3.34	109.95	1.58	Borehole
17	1.38	206.25	2.73	149.45	1.98	Borehole
18	1.86	242.25	2.31	130.24	1.24	Borehole
19	1.10	238.00	3.25	216.36	2.95	Borehole
20	0.73	122.50	2.06	167.81	2.82	Borehole
21	1.23	300.00	3.41	243.90	2.77	Borehole
22	2.39	296.50	4.51	124.06	1.88	Borehole
23	0.02	227.75	4.85	12500.00	242.50	Borehole
24	0.31	296.25	3.77	734.00	12.6	Borehole
25	1.28	283.25	1.10	231.44	0.86	Borehole
26	1.71	284.80	2.93	165.64	1.71	Borehole
27	3.02	295.75	1.58	94.30	0.52	Borehole
28	1.09	190.00	1.15	271.33	1.05	Borehole
29	0.01	271.00	4.40	19000.00	440.00	Borehole
30	0.04	162.50	6.46	6775.00	161.50	Borehole
31	0.30	162.50	2.95	541.66	9.83	Borehole
32	2.40	302.50	1.44	126.04	0.60	Borehole

Sample Number	Fe Concs ppm	HCO_3^- Concs ppm	O_2 Concs ppm	HCO_3/Fe	O_2/Fe	Type of Device
33	1.00	127.00	2.38	127.00	2.38	Borehole
34	0.17	94.50	6.77	555.88	39.82	Shallow Well
35	0.75	184.00	1.13	245.33	1.50	Borehole
36	1.52	235.25	2.86	154.77	1.88	Borehole
37	0.46	216.00	2.64	469.56	5.74	Borehole
38	4.86	284.25	1.35	58.48	0.27	Borehole
39	0.22	69.00	3.58	313.63	16.27	Shallow Well
40	0.13	29.50	6.59	226.92	50.69	Shallow Well
41	0.13	140.00	5.27	1076.92	40.54	Borehole
42	0.77	186.50	3.40	242.20	4.41	Borehole
43	0.11	161.25	1.32	1465.91	12.00	Shallow Well
44	0.34	236.00	5.01	694.11	14.73	Borehole
45	0.10	142.00	6.17	1420.00	61.70	Shallow Well
46	0.81	318.00	1.93	392.59	2.38	Shallow Well
47	0.23	178.75	6.78	777.17	29.48	Shallow Well
48	0.19	201.25	2.64	1059.21	13.89	Borehole
49	0.16	267.00	3.51	1668.75	21.93	Borehole
50	1.80	333.00	1.98	185.00	1.10	Borehole
51	1.38	322.00	1.54	233.33	1.11	Borehole
52	0.65	222.50	4.61	342.30	7.09	Borehole
53	0.12	142.75	5.51	1189.58	45.91	Borehole
54	0.01	245.00	3.91	24500.00	391.00	Borehole
55	0.11	211.00	5.57	1918.18	50.63	Borehole
56	0.12	274.75	4.23	2289.58	35.25	Borehole
57	0.03	274.75	4.43	9158.33	147.66	Borehole
58	1.71	342.50	1.67	200.29	0.97	Borehole
59	0.23	254.50	2.37	1106.52	10.30	Shallow Well
60	0.68	318.50	3.34	468.38	4.91	Borehole
61	0.02	315.50	3.68	15775.00	184.00	Borehole
62	1.85	347.25	2.37	187.70	1.28	Borehole
63	0.58	349.75	2.25	603.01	3.88	Shallow Well
64	6.02	328.75	2.03	54.61	0.33	Borehole
65	1.06	200.50	2.42	189.15	2.28	Borehole
66	0.26	167.50	2.93	644.23	11.27	Shallow Well

Sample Number	Fe Concs ppm	HCO_3^- Concs ppm	O_2 Concs ppm	HCO_3/Fe	O_2/Fe	Type of Device
67	1.29	173.50	2.20	134.49	1.70	Borehole
68	0.10	177.75	4.62	1777.50	46.20	Shallow Well
69	1.38	213.75	1.10	154.89	0.79	Borehole
70	0.02	168.50	6.91	8425.00	345.50	Shallow Well
71	1.52	316.00	2.04	207.89	1.34	Borehole
72	0.82	265.00	2.53	323.17	3.08	Borehole
73	0.17	111.50	4.06	655.88	23.88	Shallow Well
74	0.22	257.00	6.46	1168.18	29.36	Shallow Well
75	2.85	167.25	5.64	58.68	1.98	Borehole
76	1.01	290.50	3.19	287.62	3.16	Shallow Well
77	0.13	220.75	6.69	1698.07	51.46	Shallow Well
78	0.14	250.00	4.84	1785.71	34.57	Shallow Well
79	0.07	267.75	4.31	3825.00	61.57	Shallow Well
80	0.12	330.00	4.74	2750.00	39.50	Borehole
81	6.13	382.25	2.37	62.35	0.38	Borehole
82	1.39	313.00	2.03	225.18	1.46	Borehole
83	2.11	373.00	2.20	176.77	1.04	Borehole
84	9.77	505.25	2.48	51.71	0.25	Borehole
85	5.74	343.75	1.67	59.88	0.29	Borehole
86	0.13	250.25	2.73	1925.00	21.00	Borehole
87	2.87	365.75	2.31	127.44	0.80	Borehole
88	0.25	225.25	4.06	901.00	16.24	Shallow Well
89	0.18	377.00	1.71	2094.44	9.50	Borehole
90	1.36	124.50	3.12	91.54	2.29	Borehole
91	0.36	286.75	2.80	796.52	7.77	Shallow Well
92	0.12	202.75	4.21	1689.58	35.80	Shallow Well

Table 5.2 Strata logs and iron and manganese concentrations (ppm)

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from Surface (m)		
4	Sheringham	Sands and Gravels	8.85	8.85		
		Sandy Clay and pebbles	15.87	24.72		
		Crag	19.24	43.96		
		Upper Chalk	78.70	122.66	0.87	0.07
7	Metton	Sands and Gravels	1.83	1.83		
		Boulder Clay	14.80	16.63		
		Crag	14.03	30.66		
		Upper Chalk	60.78	91.44	0.64	0.04
8	Matlaske	Sands and Gravels	10.05	10.05		
		Clay	21.94	31.99		
		Crag	11.88	43.87		
		Upper Chalk	78.02	121.89	0.94	0.06
9	Mundesley	Sands and Gravels	10.05	10.05		
		Clay	19.81	29.86		
		Crag	11.27	41.13		
		Upper Chalk	57.91	99.04	2.36	0.11
16	Trunch	Boulder Clay	24.99	24.99		
		Crag	23.77	48.76		
		Upper Chalk	25.91	74.68	2.11	0.13
17	Royston Bridge	Silty Sands and Gravels	16.76	16.76		
		Crag	4.26	21.02		
		Soft Chalk and Clay	7.92	28.94	1.38	0.07
		Upper Chalk	108.81	43.89		

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from Surface (m)		
18	Melton Constable	Drift and Crag	43.89	43.89		
		Upper Chalk	14.63	58.52	1.86	0.09
19	N. Walsham	Drift	29.87	29.87		
		Crag	11.88	41.75		
		Upper Chalk	95.71	137.46	1.10	0.12
20	N. Walsham	Drift	18.29	18.29		
		Crag and Upper Chalk	35.05	53.34	0.73	0.05
25	Reepham	Drift / Crag	17.98	17.98		
		Upper Chalk	22.86	40.84	1.28	0.04
26	Brandiston	Drift	22.86	22.86		
		Crag	9.14	32.00		
		Upper Chalk	19.81	51.81	1.71	0.08
27	Haveringland	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	48.17	3.02	0.13
32	Felthorpe	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	29.87	2.40	0.28
33	Felthorpe	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	54.86	1.00	0.09
35	Knapton	Sands and Gravels	na	na		
		Boulder Clay	na	na		
		Crag	na	na		
		Upper Chalk	na	73.76	0.75	0.09
36	Edingthorpe	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	106.68	1.52	0.10

na = Data not available

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from surface(m)		
37	East Ruston	Drift	1.07	1.07		
		Crag	9.60	10.67		
		Upper Chalk	51.20	61.87	0.46	0.03
38	Tunstead	Boulder Clay	na	na		
		Sands & Gravels	na	na		
		Crag	na	na		
		Upper Chalk	na	60.96	4.86	1.39
49	Catton	Sandy Clay (N.E.B.)	3.65	3.65	0.16	0.03
		Crag	8.54	12.19		
		Upper Chalk	35.66	47.85	0.16	0.03
63	Flordon	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	19.81	0.58	0.10
64	Shotesham	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	45.42	6.02	0.15
65	Ranworth	Drift	6.09	6.09		
		Crag	41.15	47.24		
		Upper Chalk	7.01	54.25	1.06	0.14
67	Woodbast-wick	Drift	3.65	3.65		
		Crag	29.87	33.52		
		Upper Chalk	16.16	49.68	1.29	0.15
69	Witton	Clay & Loam	4.57	4.57		
		Crag	16.76	21.33		
		Upper Chalk	26.21	47.54	1.38	0.18
71	Brundall	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	21.34	1.52	0.03

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from Surface (m)		
72	Strumpshaw	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	na	0.82	0.04
75	Bergh Apton	Boulder Clay	na	na		
		Crag	na	na		
		Upper Chalk	na	53.34	2.85	0.12
76	Bergh Apton	Drift	na	na		
		Crag	na	na		
		Upper Chalk	na	27.43	1.01	0.08
85	Shelton	Drift	31.09	31.09		
		Crag	8.53	39.62		
		Upper Chalk	30.39	70.01	5.74	0.14
1	Wighton	Gravelly Clay	2.74	2.74		
		Gravelly Loam	1.83	4.57		
		Upper Chalk	22.86	27.43	0.14	0.01
2	Binham	Top Soil	na	na		
		Sand & Gravel	na	na		
		Upper Chalk	na	36.38	1.23	0.06
3	Houghton St. Giles	Gravelly Loam	3.36	3.36		
		Upper Chalk	42.54	45.90	0.03	0.01
5	Glandford	Topsoil	0.61	0.61		
		Upper Chalk	34.39	35.00	0.03	0.01
6	Langham	Boulder Clay	12.80	12.80		
		Sand & Gravel	na	na		
		Upper Chalk	na	na	1.57	0.04

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from Surface (m)		
10	Thursford	Sand & Gravel	3.04	3.04		
		Boulder Clay	4.57	7.61		
		Sand & Gravel	3.04	10.66		
		Boulder Clay	14.33	24.99		
		Sand & Gravel	7.92	32.91		
		Upper Chalk	24.99	57.90	2.32	0.18
11	Fakenham	Boulder Clay				
		Sand & Gravel	20.11	20.11		
		Upper Chalk	85.56	106.68	1.10	0.11
12	Fakenham	Sand & Gravel	na	na		
		Boulder Clay	na	na		
		Sand & Gravel	na	na		
		Upper Chalk	na	21.34	0.10	0.02
13	Weasenham	Boulder Clay	na	na		
		Upper Chalk	na	25.91	0.15	0.09
14	Beetley	Sand & Gravel	13.50	13.50		
		Boulder Clay	25.50	39.00		
		Upper Chalk	47.00	86.00	0.25	0.01
15	Beetley	Sand & Gravel / Boulder Clay / Sand & Gravel / Upper Chalk		39.62	0.57	0.02
21	Foulsham	Sand	8.00	8.00		
		Pebbly Clay	11.50	19.50		
		Sand	2.70	22.20		
		Boulder Clay	12.30	34.50		
		Upper Chalk	45.50	80.90	1.23	0.06

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from Surface(m)		
22	Wood Dalling	Boulder Clay	na	na		
		Sand & Gravel	na	na		
		Upper Chalk	na	42.67	2.39	0.13
28	Great Witching-ham	Boulder Clay	na	na		
		Sand & Gravel	na	na		
		Upper Chalk	na	41.15	1.02	0.04
29	Lyng (Skitfield)	Sand & Gravel / Boulder Clay	18.25	18.25		
		Upper Chalk	15.25	33.50	0.01	0.01
30	Swanton Morley	Drift / Soft Chalk	6.09	6.09		
		Upper Chalk	24.39	30.48	0.04	0.02
48	Dilling-ton Hall	Sand & Gravel	16.15	16.15		
		Boulder Clay				
		Sand & Gravel	9.75	25.90		
		Upper Chalk	27.12	53.03	0.19	0.07
50	Matishall	Boulder Clay	na	na		
		Sand & Gravel	na	na		
		Upper Chalk	na	42.67	1.80	0.07
51	Matishall	Top Soil / Clay	15.28	15.28		
		Sand	15.24	33.52		
		Upper Chalk	42.67	76.19	1.38	0.06
52	Honingham	Boulder Clay	na	na		
		Sand & Gravel	na	na		
		Upper Chalk	na	60.96	0.65	0.02
61	Ashwell-thorpe	Drift	na	na		
		Upper Chalk	na	na	0.02	0.01
83	Aslacton (Bunwell)	Chalky Clay	20.00	20.00		
		Sand (Buried Chnl)	8.00	28.00		
		Upper Chalk	32.00	60.00	2.11	0.02

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from surface (m)		
84	Aslacton	Boulder Clay	na	na		
		Sand & Gravel red	na	na		
		Upper Chalk	na	60.96	9.77	0.29
86	Fersfield (Kenninghall)	Drift	na	na		
		Upper Chalk	na	na	0.13	0.01
87	Rushall	Boulder Clay				
		Sand & Gravel				
		Upper Chalk			2.87	0.14
89	Diss	Sand & Gravel	na	na		
		Boulder Clay	na	na		
		Upper Chalk	na	na	0.18	0.24
23	Aylsham	Topsoil	1.10	1.10		
		Sand & Gravel & Flint	3.66	4.76		
		Upper Chalk	33.40	38.16	0.02	0.01
24	Sall	Sandy Clay	3.35	3.35		
		Sand & Gravel	5.33	8.68		
		Clay & Stones	3.97	12.65		
		Upper Chalk	63.55	76.20	0.31	0.04
53	Costessey	Clay & Sand	20.72	20.72		
		Upper Chalk	28.04	48.76	0.12	0.03
54	Colney	Drift	0.60	0.60		
		Upper Chalk	92.20	92.80	0.01	0.01
55	Thorpe St. Andrew	Sand & Gravel	2.43	2.43		
		Boulder Clay	7.63	10.06		
		Sand & Gravel	10.67	20.73		
		Upper Chalk	55.50	76.23	0.11	0.01
57	Caistor St. Edmund	Sand & Gravel	0.76	0.76		
		Boulder Clay	16.40	17.16		
		Upper Chalk	60.20	77.36	0.03	0.02

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from surface (m)		
58	Mulbarton	Boulder Clay, Sand & Gravel, Boulder Clay, Sand & Gravel, Upper Chalk	17.07	17.07		
		Upper Chalk	27.13	44.20	1.71	0.09
60	Swains-thorpe	Boulder Clay, Sand & Gravel	3.65	3.65		
		Upper Chalk	27.74	31.39	0.68	0.11
62	Newton Flotman	Sand & Gravel	na	na		
		Upper Chalk	na	70.10	1.85	0.09
82	Hempnall	Sand & Gravel	10.05	10.05		
		Boulder Clay	4.87	14.92		
		Sand & Gravel	3.35	18.27		
		Upper Chalk	18.28	36.58	1.39	0.07
90	Raveningham	Existing Well (Brick Shaft)	3.66	20.12		
		Boulder Clay	3.66	23.78		
		Sand & Gravel	25.60	49.38		
		Upper Chalk	27.16	76.54	1.36	0.01
41	Barton Turf	Drift	na	na		
		Crag	na	na		
		London Clay	na	na		
		Upper Chalk	na	59.44	0.13	0.02
42	Ludham	Drift	na	na		
		Crag	na	na		
		London Clay (Pyrite Nodule)	na	na		
		Upper Chalk	na	na	0.77	0.08

Sample No.	Locality Name	Strata Penetrated			Fe (ppm)	Mn (ppm)
		Lithology	Thickness (m)	Depth from Surface (m)		
81	Seething	Drift	na	na		
		Crag	na	na		
		London Clay (Pyrite Nodule)	na	na		
		Upper Chalk	na	30.48	6.13	0.19
31	Attlebridge	Crag	na	na		
		Upper Chalk	na	21.34	0.30	0.04
59	Stoke Holy Cross	Crag	na	na		
		Upper Chalk	na	9.14	0.23	0.06
34	Felthorpe	Drift	na	na		
		Crag	na	18.28	0.17	0.04
39	Catfield	Crag	7.62	7.62	0.22	0.11
40	Catfield	Drift	na	na		
		Crag	na	4.57	0.13	0.08
43	Potter Heigham	Crag	6.10	6.10	0.11	0.17
44	Martham	Drift				
		Crag		24.38	0.34	0.03
45	Repps	Drift	na	na		
		Crag	na	6.10	0.10	0.01
46	Hemsby	Drift	na	na		
		Crag	na	4.88	0.81	0.63
47	Thurne	Drift	na	na		
		Crag	na	3.66	0.23	0.05
66	Ranworth	Crag	9.14	9.14	0.26	0.03
70	Beighton	Drift	na	na		
		Crag	na	21.95	0.02	0.04
80	Haddiscoe	Sand	18.29	18.29	0.12	0.04
56	Norwich	Upper Chalk	76.19	76.19	0.12	0.02

Sample No.	Locality Name	Strata Penetrated			Fe	Mn
		Lithology	Thickness (m)	Depth from Surface (m)	(ppm)	(ppm)
68	Acle	Drift and Alluvium	3.66	3.66	0.10	0.02
73	Surlingham	Clay & Loam	3.66	3.66	0.17	0.03
74	Burgh Castle	Drift	11.58	11.58	0.22	0.03
77	Reedham	Alluvium	3.66	3.66	0.13	0.02
78	Loddon	Sand & Gravel	3.66	3.66	0.14	0.03
79	Loddon	Clay & Loam	3.66	3.66	0.07	0.02
88	Rushall	Boulder Clay	na	na		
		Sands & Gravel	na	na	0.25	0.01
91	Ellingham	Sand & Gravel	10.67	10.67	0.36	0.01
92	Ellingham	Topsoil	na	na		
		Upper Chalk	na	3.05	0.12	0.01

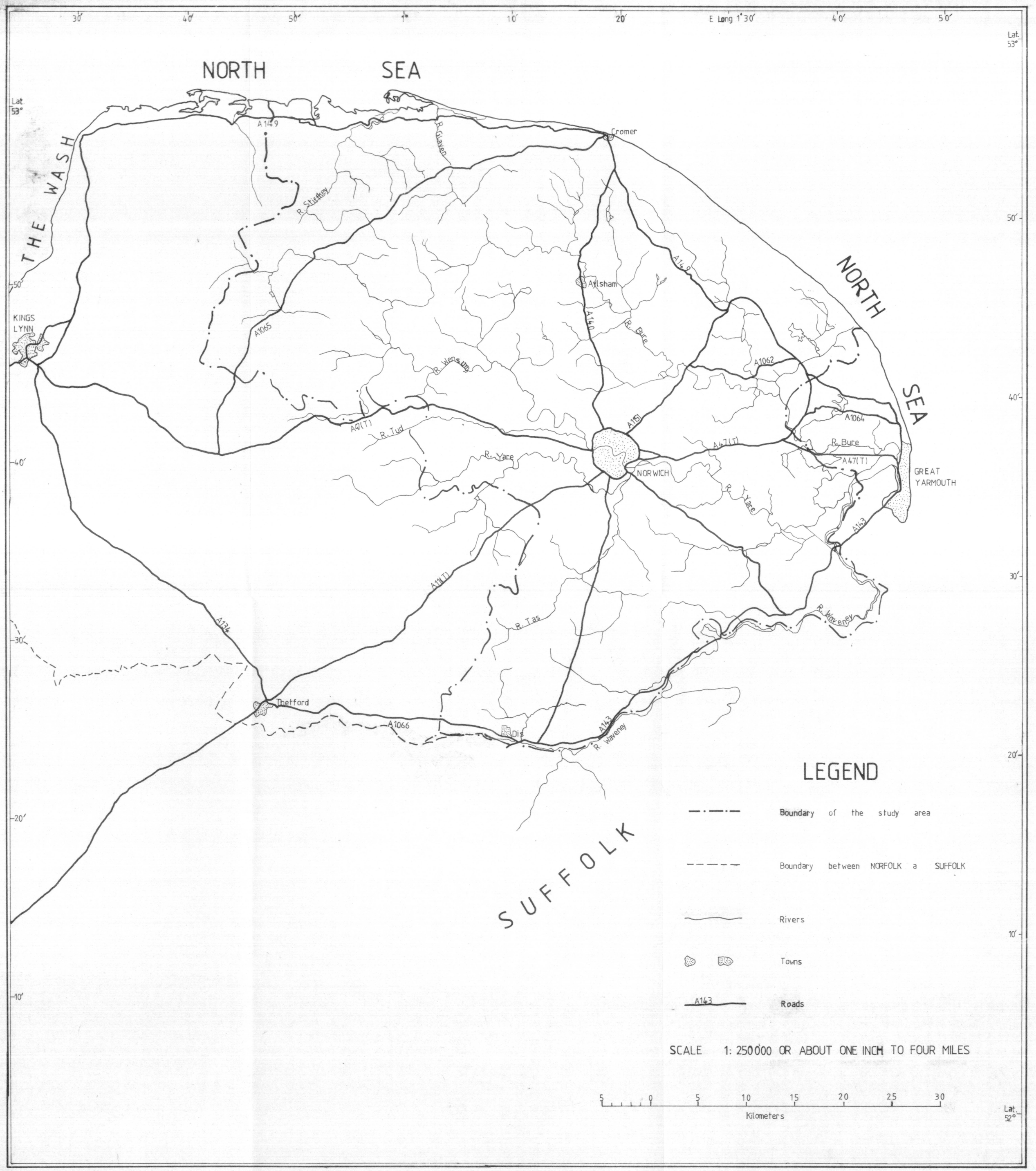
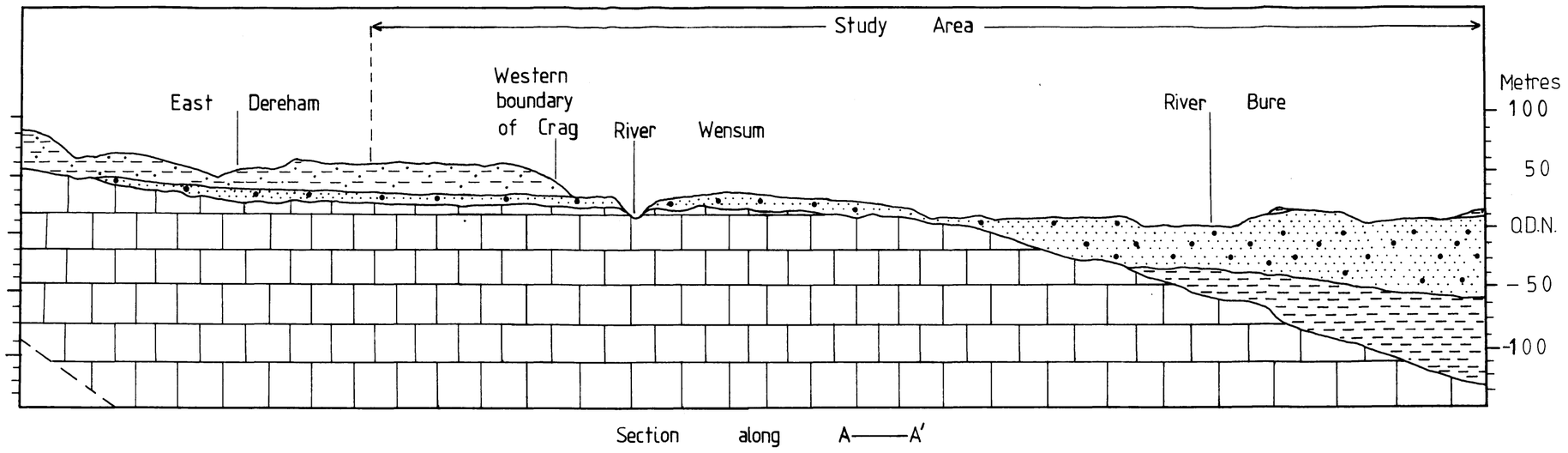
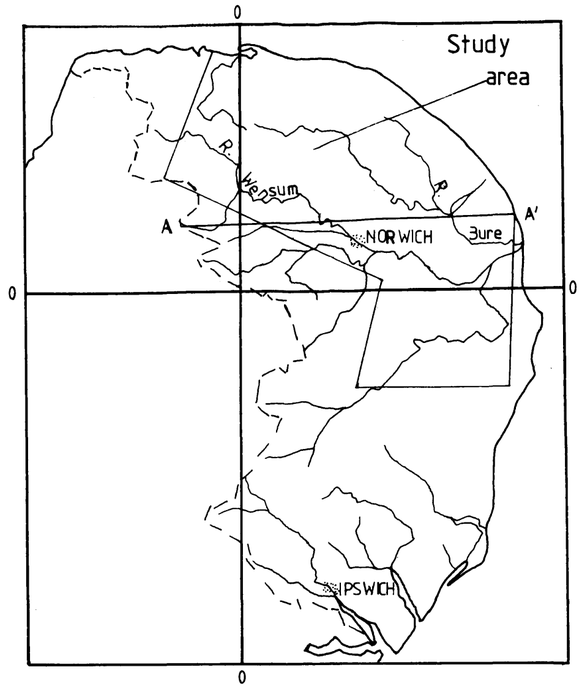


Fig.1.1 Showing Study Area In NORFOLK—EAST ANGLIA





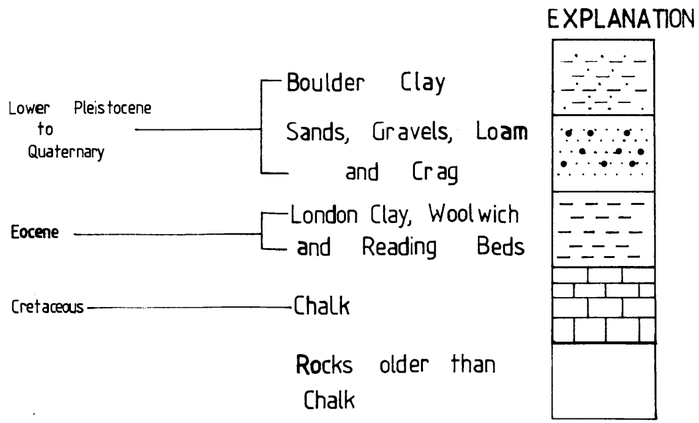


Fig. 2.2 A generalised geological section of NORFOLK including the study area (after E. Suffolk and Norfolk River Authority, 1971.)

Sheringham

Holt

Saxthorpe

Bintree

Reepham

NORTH SEA

NORWICH

Reedham

Lowestoft

Beecles

Dis

EXPLANATION

1 Boulder clay, less Chalky but sandy, with large areas of sands and gravels exposures

2 Boulder clay, chalky and less sandy.

3 Boulder clay, dark and heavy, mainly of clay with very little sand.

5 0 5 10 15 20

KILOMETRES

Fig. 2. 4 Showing the distribution of types of Chalky boulder clay.