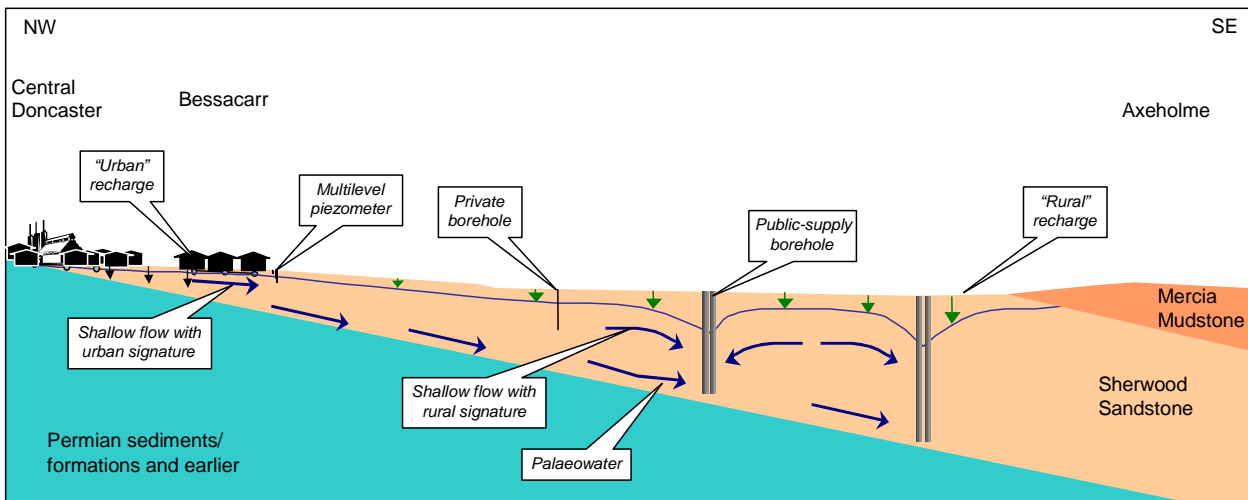




AISUWRS Work-package 4: Water quality of the Doncaster aquifer

Groundwater Systems and Water Quality Programme
Commissioned Report CR/04/026N



BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/04/026N

AISUWRS Work-package 4: Water quality of the Doncaster aquifer

M E Stuart, E J Whitehead and B L Morris

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Conceptual model of influences
on water quality in the Doncaster
aquifer

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Foreword

This report is the fourth in the UK series of the project “Assessing and Improving the Sustainability of Urban Water Resources and Systems” (AISUWRS) and is the result of collaborative work by the UK partners, the British Geological Survey and the Robens Centre for Public and Environmental Health of the University of Surrey. This 3-year urban water research project is partly funded by the European Community. It aims to develop an innovative modelling system of the urban water infrastructure which can inform decision support systems for cities that depend on underlying or nearby aquifers for their water supply.

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Summary

This interim report comprises the fourth in the UK series of the project “Assessing and Improving the Sustainability of Urban Water Resources and Systems” (AISUWRS). Doncaster is one of the three European urban areas being studied in this European Community 5th Framework Programme-Shared Cost Research Technological Development and Demonstration project. It comprises part of Deliverable D10 for project Work Package 4. The report assesses groundwater quality in the Triassic Sherwood Sandstone aquifer supplying the case study town of Doncaster, England. Available data from stakeholders, principally Yorkshire Water, and from the project’s tripartite sampling programme have been collated and analysed. An understanding of the characteristics of groundwater from both the upper and middle/lower parts of the aquifer is emerging and has informed the conceptual model of evolution of water quality. In this part of the Nottinghamshire-South Yorkshire Sherwood Sandstone outcrop, recharge processes are complicated by the presence of variable Quaternary superficial deposits, which appear to control both the ease with which recharge can occur and the hydrochemical characteristics of the resultant groundwater.

The data suggest that this complexity manifests itself in a degree of lateral variability of geochemical trends that is at least as great as that occurring with depth. The implication is that the degree to which the underlying saturated aquifer is affected by the contaminant load depends at least as much on local recharge conditions as the magnitude of the loading itself.

At this interim stage of the field programme, the study has succeeded in initial hydrochemical characterisation of the principal constituents of the groundwater circulating in the mains water supply to the study focus area, the wastewater in its sewer system, the underlying and surrounding shallow aquifer and the deeper aquifer. Assessment of the urban recharge indicators of chloride, sulphate, boron and zinc has shown that these are likely to be only partially successful in Doncaster, for the following reasons:

- the wastewater effluent load is relatively dilute
- pollution from other human activities (agriculture, mining) is present within the same catchments, generating similar contaminant types and loading profiles
- important relatively persistent contaminants found in urban wastewater such as sulphate and chloride also occur naturally and variably in the aquifer.

Further work will be needed to unravel this complex system sufficiently to inform the urban water models that are being developed, linked and operated as the principal task of the AISUWRS project.

1 Introduction

1.1 BACKGROUND

This report is the result of collaborative work by the British Geological Survey and the Robens Centre for Public and Environmental Health of the University of Surrey, who are the UK partners of the AISUWRS project. The 3-year urban water research project is partly funded by the European Community 5th Framework Programme for Shared Cost Research, Technological Development and Demonstration. The 5th Framework Programme was conceived to help solve problems and respond to major socio-economic challenges that the European Union is facing. Its objectives combine technological, industrial, economic, social and cultural aspects.

The project is one of a number of European research projects on integrated urban water management that are grouped as the CityNet cluster. The AISUWRS project aims to develop innovative new modelling techniques and a pilot decision support system (DSS) for cities that depend on underlying or nearby aquifers for their water supply. The objective is to assess and improve the sustainability of urban water resources and systems with the help of computer tools.

The project aims to use case studies of Doncaster in England, Rastatt in Germany, Ljubljana in Slovenia and Mt Gambier in Australia to test and develop an integrated suite of models for urban water-management purposes. As the case studies cover diverse hydrogeological and water-management settings, successful application of the models to these situations will be a test of the system's robustness for wider use in the many other cities in Europe and elsewhere that depend on local groundwater for public and private water supply.

1.2 OBJECTIVES OF THIS REPORT

The AISUWRS project is divided into three Work Areas (WAs) and 14 Work-Packages (WPs). This report is part of Deliverable D10 for the Doncaster part of WP4, Field Investigations. The objectives of this part of the work are to:

- evaluate groundwater-quality data collected during the first year of the project
- develop a conceptual model of the flow system
- determine if different elements of the flow system can be characterised by their chemical compositions
- characterise the chemical composition of shallow recharge beneath the city.

2 Groundwater-quality data

2.1 INTRODUCTION

The data presented in this report were obtained from a number of sources. Yorkshire Water (YW) and the Environment Agency (EA) kindly provided raw water quality data. Additional monitoring is a key fieldwork component of the case study. A network that the AISUWRS team are sampling has been progressively established during the first year of the project:

- (i) a number of privately owned boreholes in the Doncaster area
- (ii) wastewater from the sewerage system.
- (iii) five multi-level research boreholes drilled and installed in the project's focus area, which is the district of Bessacarr-Cantley.

The first set of data from this tripartite monitoring network is included in this report. The locations of the YW and project sampling points are shown in Figure 2.1.

2.2 PUBLIC SUPPLY BOREHOLES

YW operate 11 public-supply sites which form the Doncaster wellfield to the east of the town. The locations of these pumping stations are shown in Figure 2.1 and are labelled using the site-codes employed in Tables 2.2 to 2.4.

At each site there are two, or more commonly three, large diameter boreholes. These typically penetrate either close to the base or into the lowest third of the Triassic Sherwood Sandstone aquifer (with depths of 120 to 241 m). They are open hole or screened over the majority of their depths. A summary of borehole construction details for the sites in the central area and northern part of the wellfield is provided in Table 2.1; a fuller version forms Table 9 of Morris et al. (2003).

YW analyse raw water for a wide range of determinands (Table 2.2). Data were requested from YW for all these determinands for the last five years, except those where the dataset is small, in which case the whole set was requested.

2.3 ENVIRONMENT AGENCY MONITORING NETWORK

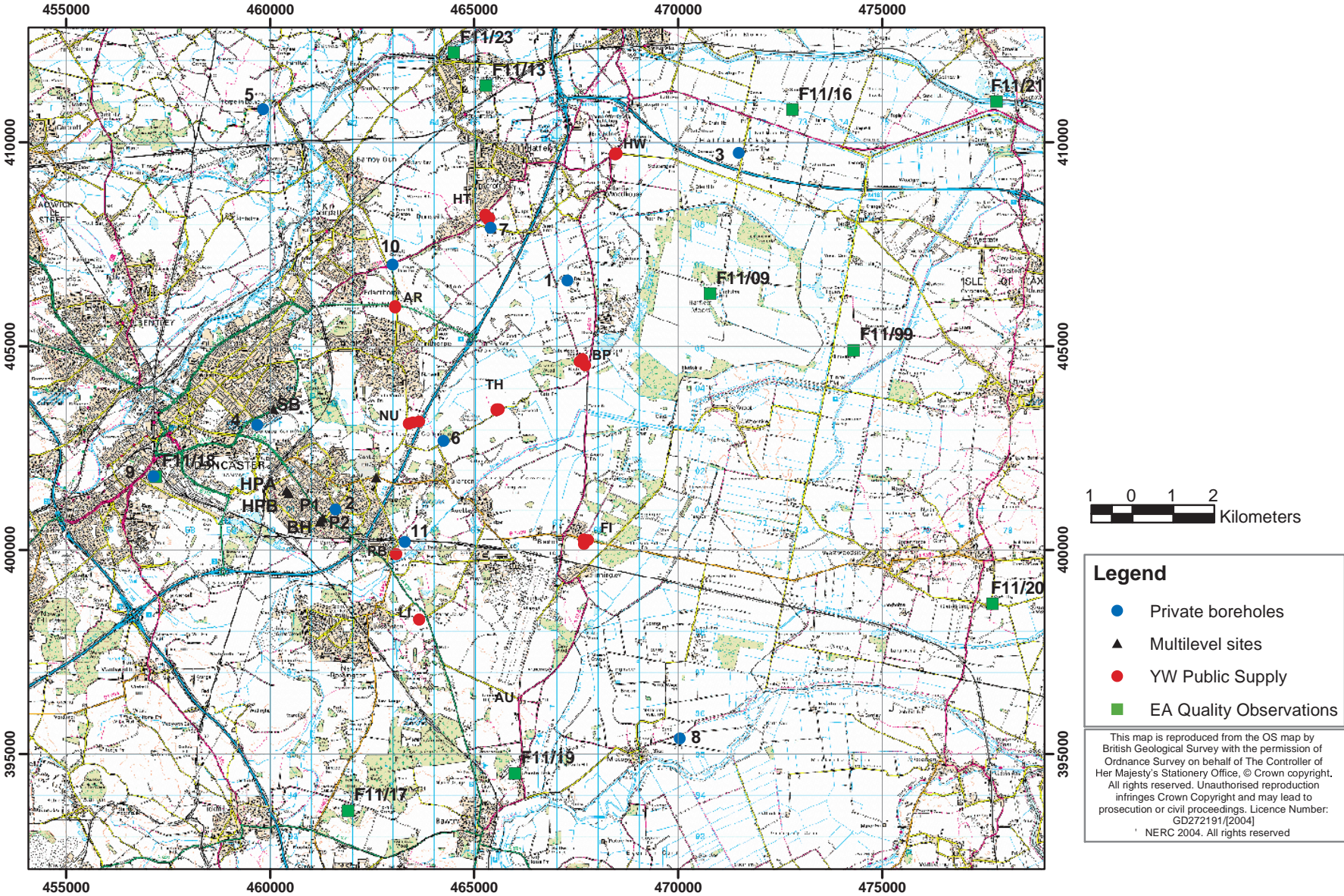
The EA maintains a database of groundwater quality. In the Doncaster area the majority of these data are supplied by YW from its public supply boreholes. Other sites are described in Table 2.3 and locations are shown in Figure 2.1. These are a mixture of farm and industrial boreholes ranging from almost entirely rural to periurban. There are no data in the database for over half these sites, and only 3 have any analyses for organic constituents. These are distant from the focus area or are otherwise unrepresentative (see 4.3.2) and inspection of the data indicates that their relevance to this project is marginal.

2.4 PRIVATE BOREHOLES

Unfortunately existing urban borehole/well sites are practically absent in Doncaster. Several privately owned boreholes in the general area are being sampled in order to provide additional regional chemistry information (Table 2.4). These sites were chosen by the following criteria:

- (i) they are relatively shallow boreholes with short uppermost plain casing lengths

Figure 2.1 Locations of public supply boreholes, EA groundwater quality monitoring network, private boreholes sampled and multi-level sites (labels from Tables 2.2 to 2.4).



- (ii) construction details and geological logs were mostly available
- (iii) Quaternary superficial cover at the sites is generally thin (Table 2.4).

Two sampling rounds were undertaken, in June and November 2003 and the network is scheduled to be reviewed before further sampling visits.

Table 2.1 Construction details for public water supply boreholes

Site	BH no	Construction date	Drilled depth (m)	Present depth (m)	Casing (mbgl)	Open hole diameter (mm)
AR	1	1964	176	176	30	375
	2	1967	168	168	30	375
	3	1967	168	168	30	375
BP	1	1969	231	176	30	375
	2	1974	137	137	30	375
	3	1974	137	137	36	375
FI	1	1955	184	148	38	914 then 838
	2	1955	1856	139	38.4	914 then 838
	3	1955	1856	138	37.6	914 then 838
HT	1	1927	137	135	31.1	600
	2	1931	137	137	36	750
HW	1	1965	241	241	30?	375
	2	1969	180	180	30?	375
	3	1969	180	180	34	375
LI	1	1964	167	160	40	600
	2	1980	120	120	59	600
NU	2	1927	152	152	33	825
	3	1980	120	120	45	600
	4	1980	120	120	45	600
RB	1	1933?	147	147	27	825
	2	1952?	145	148	27	825
TH	1	1934	155	159	32.9	600
	2	1934	182	182	31.1	750
	3	1980	121	121	45	825

Boreholes in proximity to or supplying Bessacarr-Cantley study area given in **bold**.

Table 2.2 Summary of determinand classes and data/metadata for Yorkshire Water raw water analyses for the Doncaster wellfield

Determinand class	Approx. no. in class	Example	No. of analyses per well since 1980 ¹
Taste and appearance	7	Colour, odour, taste	400 – 600
Temperature and pH	3	pH, temperature, turbidity	600 – 800
Major and minor inorganic constituents	22	Alkalinity	100 – 120
		Calcium, chloride, phosphate, sulphate	60 – 120
		Aluminium	60 – 80
		Boron	1 – 5
		Iron, manganese	400 – 600
		Nitrate	900 – 1100
		Nitrite	300 – 500
Trace heavy metals	8	Cadmium, lead, mercury, silver, zinc	10 – 40
Halogenated solvents	9	Trichloroethene, trihalomethanes	1 – 25
Petroleum hydrocarbons	4	MTBE, oil and grease, PAH	1 – 25 ²
Phenols	11	Chlorophenols, phenols	1 – 5
Pesticides ³	90	Atrazine, bentazone, isoproturon, MCPP	3 – 15
Other potentially toxic parameters	10	Arsenic, selenium, cyanide, fluoride, bromate, radioactivity	1 – 5
Microbiological	15	Total and faecal coliforms	150 per year
		Cryptosporidium, enterovirus, rotavirus	<25
Surfactants	1		1
Total organic carbon	1		40-100
Total all determinands	181		

¹ 11sites. ²Generally 1 – 5; extra sampling at HW due to fuel leak incident in catchment ³ since June 2000

Table 2.3 Environment Agency groundwater-quality monitoring sites (excluding YW sites)

GWCN Code	Name of site	B/H depth (m)	Easting	Northing	Inorganic data available	Organic data available	Most recent data
F11/09	Lindholme Hall	61	470780	406290			
F11/13	Hatfield Main Colliery	85	465290	411390	✓	✓	2001
F11/15	W.M. Darley, Thorne Brewery	137	468700	413400	✓		1986
F11/16	Redhouse Farm, Thorne	46	472800	410800			
F11/17	Yorkshire Bottle Co. Ltd, Bawtry	43	461910	393610	✓	✓	2001
F11/18	Peglers Ltd., Balby	30	457200	401800	✓		1992
F11/19	G.R. Stein Refractories Ltd	27	466000	394530			
F11/20	N.E. Pilkington Ltd , Graizelound	91	477700	398690	✓	✓	2001
F11/21	F.M.S. Farm Products	137	477800	411000			
F11/22	Eastoft Hall Borehole	146	480450	416330			
F11/23	Newfarm Chickens	31	464500	412200			
F11/98	Mill Lane, Crowle	107	478600	413300			
F11/99	Ninevah Farm		474300	404900			

Table 2.4 Private boreholes sampled for the AISUWRS project

Site no.	Site name	NGR	Depth (m)	Solid casing depth (m)	Drift thickness (m)
1	Beech Tree Nurseries	SE 6728 0661	30.5	17.7	up to 11*
2	Cantley Water Tower	SE 616 010	65.5	21.3	7.9
3	Crowtree Farm	SE 7148 0974	31.7	17.7	14.9
4	Doncaster Racecourse	SE 5968 0307	41.1	Not known	3.7
5	Elmstone Farm	SE 5983 1081	50.0	19.5	16.0 **
6	Gatewood Grange Farm	SE 6425 0268	76.2	Not known	7.8
7	Lings Farm	SE 6537 0791	12.0	Not known	Not known
8	Misson Quarry	SK 7004 9538	76.2	24.4	4.9
9	Peglers	SE 5714 0181	30.5	5.2	4.9
10	Sandall Common Farm	SE 630 070	63.4	17.4	4.6
11	Warning Tongue Borehole	SE 633 002	63.4	18.3	13.4

* drift/sandstone boundary poorly defined ** this value probably includes weathered sandstone

2.5 MULTI-LEVEL PIEZOMETERS

Five multi-level samplers were installed for the AISUWRS project in order to obtain depth profiles of urban groundwater chemistry (Table 2.5). At each site, a large diameter borehole was drilled and a number of piezometers were installed at different depths (Ruedi and Cronin, 2003). Most of the boreholes were drilled with air flush, however some mist was used at Haslam Park B. The piezometers are lined with plain casing throughout most of their length, with just 0.3 m interval of slotted casing used at the base of each. Bentonite seals hydraulically separate the piezometers from each other. Thus, samples of groundwater pumped from piezometers are known to originate from specific narrow depth intervals.

Two of the sampling sites (Haslam Park 1 and Haslam Park 2) were installed about 80 m apart, so that medium-scale variability in geology and hydrochemistry of the Sherwood Sandstone could be assessed. Two additional piezometers (P1 and P2, see Table 2.5) were installed in hand-augered holes to investigate very shallow groundwater, which appears to be perched upon low-permeability horizons within the Sherwood Sandstone.

Table 2.5 Multi-level samplers installed for the AISUWRS project

Site name	NGR	Approx. ground elevation at site (m AOD)	Piezometers installed at depths (mbgl)	Estimated drift thickness (m)
Sandall Beat (SB)	SE 6008 0345	9	16, 21, 26, 31, 36	6
Haslam Park 1 (HP1)	SE 6045 0139	9	10, 14, 21, 28, 35, 45, 60	0
Haslam Park 2 (HP2)	SE 6040 0146	9	10, 14, 19, 27, 35, 45, 60	1.6
McAuley High School (MHS)	SE 6259 0178	11	9, 14, 21, 28, 36, 45, 60	0.4
Bolton Hill (BH)	SE 6123 0070	5	16, 22, 28, 34, 39, 45, 51	0
P1 Bolton Hill	SE 6122 0070	5	3.15	0
P2 Bolton Hill	SE 6128 0079	5	1.30	0.5

The first round of sampling was undertaken in November 2003 and these data have been used for this report. Regular sampling of the multi-level piezometers will continue approximately every 3 months until late summer 2004.

2.6 SAMPLE COLLECTION AND ANALYSIS

2.6.1 Collection

For private-supply boreholes with in-situ pumps samples were collected directly from the pump outlet/sample tap after running the pump for a few minutes. For multi-level samplers and boreholes without pumps, samples were collected using either dedicated Waterra inertial pumps, or portable Whale[®] pumps connected in series or a suction-lift pump.

Hydrochemical samples were filtered through 0.45 μm cellulose nitrate membranes and collected in pairs in HDPE bottles, one being acidified to 1% with concentrated Aristar[®] nitric acid.

2.6.2 Field measurements

Dissolved oxygen (DO), redox potential (Eh), temperature and specific electrical conductivity (SEC) were measured during sample collection using a flow-through cell connected directly to the sample tap. Bicarbonate was determined by digital titrator.

2.6.3 Laboratory analysis

Measurements were made at BGS Wallingford. Cations, phosphorus and sulphate were determined on acidified sample splits by inductively-coupled plasma optical emission spectroscopy. On the unacidified splits, nitrogen species and chloride were measured by automated colorimetry, and bromide and fluoride by ion chromatography.

Results were reported using the normal limit of detection (LOD), which is derived from calculating the standard deviation (σ) of blanks about the mean blank value. The 6σ limit gives >99% confidence that the result can be distinguished from the blank and encompasses day-to-day variations in instrument noise. For the low concentrations of boron and phosphorus found, using this limit meant that a significant number were below the detection limit. For these determinands, data were also reported using the 3σ limit, which gives an increased number of quantifiable data, but is less statistically secure and also can mean that the limit of detection varies from day-to-day.

3 Development of conceptual model

3.1 GEOLOGICAL/GEOCHEMICAL SETTING: PREVIOUS STUDIES

3.1.1 Geological setting

Figure 3.1 indicates the regional geological setting in sketch section (from Morris et al 2003)

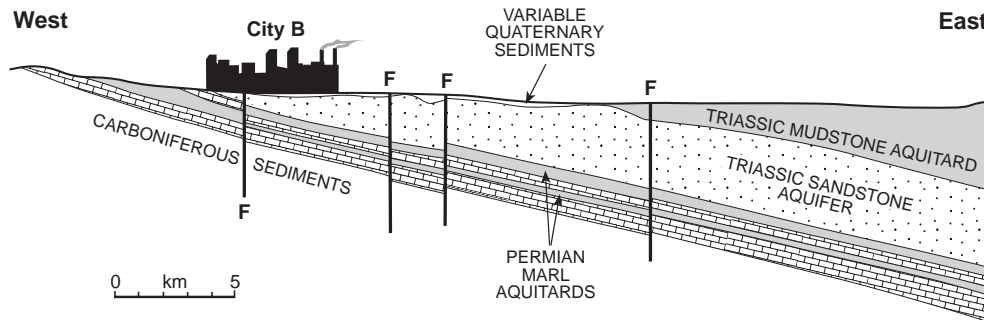


Figure 3.1 Sketch cross-section through the Doncaster aquifer

Key features of the aquifer's petrology are drawn from the regional memoir (Gaunt 1993) which describes the Sherwood Sandstone as mainly composed of quartz grains, with detrital and overgrowth silicate minerals. There are abundant clay and marl horizons and the sandstone is micaceous in parts. The red colouring is due to iron oxide present as sand coatings and in argillaceous fractions. The sandstone is poorly cemented and unconsolidated near the surface, but in parts contains a calcite cement. This cement may be gypsiferous in places and dolomite is an important accessory mineral.

3.1.2 Geochemical setting

The regional hydrogeochemical setting has been described by Smedley et al. (1993) who point out that unlike further south in Nottinghamshire, the Sherwood Sandstone Group west of the confining beds of the Mercia Mudstone Group is variably covered by Quaternary superficial deposits. Some of these deposits are semi-permeable or impermeable and produce additional locally confining conditions. Using regional reconnaissance sampling of well discharges, these authors observed that groundwater shows a distinct chemical evolution from west to east. The resultant regional hydrochemical setting has been interpreted as partly a response to anthropogenic contamination sources in the outcrop/subcrop area and partly a result of rock-water interaction, especially down-dip where the groundwater, confined beneath the Mercia Mudstone, comprises older water.

The evolution of groundwater chemistry is attributed to the strong influence of reactions with calcite and dolomite cements. In the unconfined aquifer, carbonate reaction is dominated by congruent dissolution of dolomite. There will also be progressive dissolution of gypsum, where present. Reaction with silicate minerals has a relatively minor effect compared with carbonate processes.

Previous more geographically extensive studies by Smedley et al. (1993) and Smedley and Brewerton (1997) provide a regional geochemical context to the outcrop/subcrop area between Doncaster and the Mercia Mudstone margin, which is the area the present project is exclusively concerned with.

Smedley and Brewerton (1997) in a study of the Sherwood Sandstone in the East Midlands region found that groundwater from boreholes in the unconfined aquifer show clear stratification with depth, revealing variations in the influence of pollution. In south

Yorkshire, concentrations of chloride, sulphate and nitrate are high at shallow depth and pumped groundwater appeared to be similar. Depth sampling showed that groundwater is often reducing at depth, with low nitrate, chloride and sulphate and containing a component of palaeowater with characteristically light stable-isotopic composition. This indicates that even in the unconfined aquifer, old pristine groundwater may be present at depth. Locally, Smedley et al. (1993) observed this effect at site BP, to the east of the present study area and tentatively concluded that agriculture and minor mine drainage influence were the sources of relatively high nitrate, sulphate and chloride contents in some of the public supply boreholes sampled. The patchy nature of the results was ascribed to:

- (i) local confinement and protection by low permeability superficial deposits; porewater evidence showed groundwater in places to be anaerobic
- (ii) depth stratification; decreasing redox potential and increasing residence time with depth was observed and palaeowater with depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and enriched $\delta^{13}\text{C}$ values was identifiable from depth sampling in BP

In their regional study, Smedley and Brewerton (1997) found nitrate to be distributed similarly to sulphate and potassium and also ascribed the distribution to diffuse pollution as a result of modern agricultural practice. Contamination of the semi-confined sources was shown to be less significant.

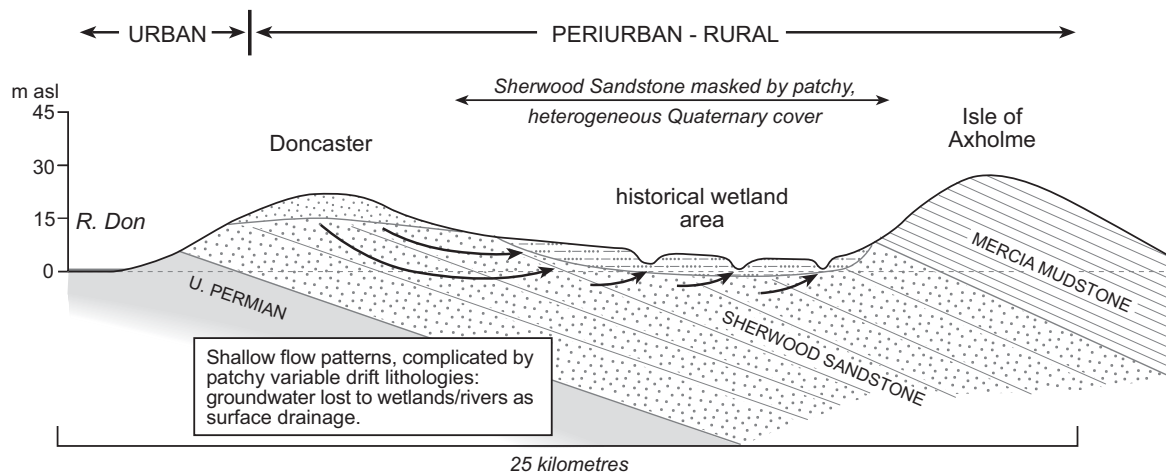
3.2 CONCEPTUALISATION OF FLOW SYSTEM

Figure 3.2 is a conceptualisation of the flow system as it has evolved in modern times. In the Sherwood Sandstone outcrop area east of present-day Doncaster and west of the Mercia Mudstone margin, it seems likely that pre-1900 flow patterns were both shallow and localised. The slightly elevated land below the present town and eastern suburbs is partly composed of Quaternary superficial deposits and groundwater recharge entering the subsurface is likely to have flowed only a limited distance eastwards to discharge to the River Torne, associated watercourses and wetlands on the eastern margin of the outcrop/subcrop zone. Until the turn of the 19th century this latter area was a wide fenland-type wetland, much of it less than 3 m above sea level and with eastward drainage constrained by higher land of the low Mercia Mudstone scarp of the Isle of Axholme. Unlike the main Sherwood Sandstone outcrop extending 60km to the south in Nottinghamshire there is negligible topography east of Doncaster to provide a head difference to drive down-dip flow beneath the Mercia Mudstone. In these circumstances palaeowaters would be expected in the aquifer both in the deeper aquifer at outcrop and close to the confined zone margin, which is what is observed (Smedley et al., 1993).

Post 1900, first mine dewatering then public supply, mineral washing and agricultural boreholes came into operation, and it is likely that the shallow flow cycles of lateral discharge to the wetlands west of the Isle of Axholme have become replaced by a progressively stronger vertical leakage component. In the last quarter of the 20th century, other groundwater uses have declined so that currently withdrawals for public supply, from the Doncaster wellfield, predominate. The late 20th century has therefore seen the development of a composite cone of depression, in effect replacing much lateral shallow drainage with downward leakage.

Today there is broadly radial flow towards this water-level depression, with the direction of groundwater flow from central Doncaster and Bessacarr broadly eastwards and south-eastwards towards a trough whose axis trends NNE-SSW from east of Hatfield through Finningley towards Austerfield.

① Pre-abstraction for public supply (c. 1900)



② As wellfield becomes established 1950 - 2000

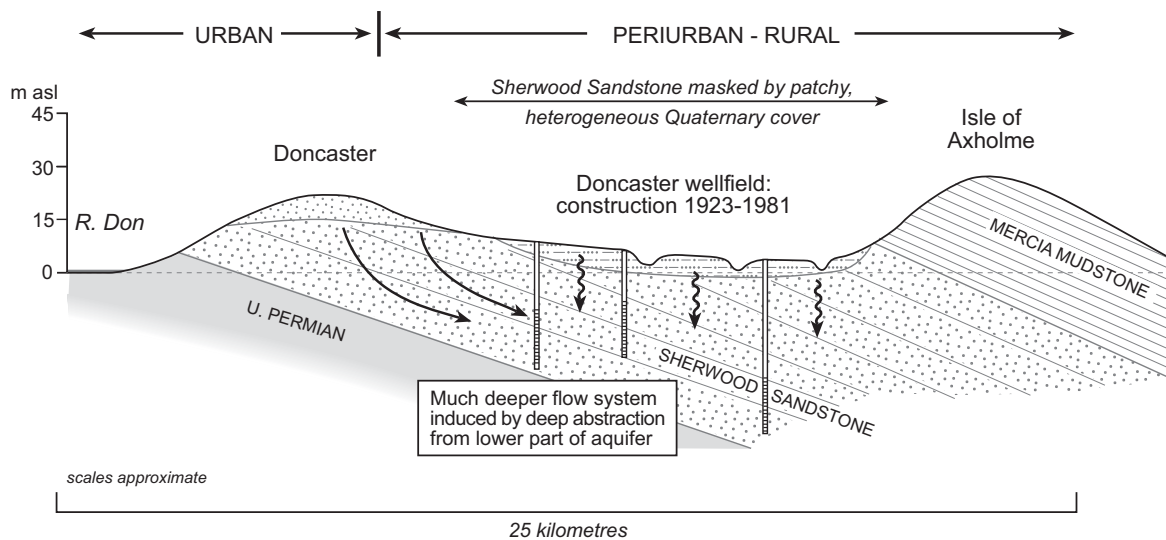


Figure 3.2 Influence of modern groundwater abstraction on groundwater flow

The pumping stations AR, NU, TH, NU and RB, which are located on the eastern margin of Doncaster and suburbs are therefore regarded as representative of local groundwater. These boreholes draw from the middle and lower part of the Sherwood Sandstone but are probably influenced by local effects on recharge, both urban and agricultural. A historic mine drainage/spoil influence is also likely from the presence of the former Markham Main coalmine at Armthorpe.

3.2.1 Local factors increasing flow system complexity

There are various lithological and sedimentary features that add complexity to local flow patterns. These are outlined below:

- (i) The uppermost, weathered zone of the Sherwood Sandstone in the Doncaster area is unconsolidated or poorly consolidated; an observation verified during the drilling and construction of the multi-level research boreholes. This weathering makes the

boundary between locally-derived superficial and bedrock deposits difficult to identify in many boreholes.

- (ii) The Sherwood Sandstone contains mudstone and mud-pellet conglomerate horizons, particularly at the top of the sequence and towards the east of the area, some of which appear to be persistent along the strike. Interpretations of pumping-test data have shown that such fine sediments can act as a semi-confining layer (Allen et al., 1997), or at least impede vertical flow components. The effects of these horizons in a dipping sequence are not documented but one result of abstraction-induced downward flows may be to focus lateral groundwater flow down-dip through the more permeable sandstone horizons rather than vertically through a given aquifer section.
- (iii) Quaternary superficial deposits overlying the Sherwood Sandstone over much of the study area can be laterally and vertically variable, with lithologies ranging from gravels to lacustrine clays. Locally some deep buried channels are also present (as described in Morris et al., 2003). Consequently, permeabilities can be widely variable and the less permeable silts and clays may both impede vertical recharge and cause local confinement of groundwater.

3.2.2 Factors affecting water quality

Some minor solute inputs may occur from non-local sources. For instance, recharging rainfall will historically have contained chloride, and also contributed other halogens. Modern rainfall also contributes sulphate and nitrate (Table 3.1).

Table 3.1 Rainfall quality at Jenny Hurn monitoring site (48163986) for 2001 (Precipitation-weighted mean provided by AEAT)

SEC ($\mu\text{S}/\text{cm}$)	Concentration (mg/l)							
	SO ₄	NO ₃	NH ₄	Na	Mg	Ca	Cl	K
30.3	2.8	2.3	0.98	0.90	0.15	0.41	2.1	0.08

The ease with which local recharge can occur also affects physicochemical parameters that influence groundwater inorganic content. For instance, under unconfined conditions, particularly at shallow depths where active recharge is taking place, groundwaters are oxidising with high dissolved oxygen (DO₂) content and redox potential (Eh). Where groundwaters are confined by the Mercia Mudstone, or locally by impermeable drift, conditions become reducing. This is marked by notably lower Eh readings and nitrate concentration. Although beyond this project's area of interest, the same effect has been noted by Smedley et al. (*op.cit*) further east in the Mercia Mudstone-confined zone, where the onset of reducing conditions beyond a redox boundary also leads to increased concentrations of iron and manganese and to a reduction in uranium concentration. These trends are reportedly less clearly defined in south Yorkshire than further south in the East Midlands as a result of local confinement (Smedley and Brewerton, 1997).

3.3 CONCEPTUALISATION OF WATER QUALITY SETTING

Figure 3.3. presents a simple conceptual model of the influences on water quality in the study area and includes the following elements:

- recharge with an urban signature enters the aquifer beneath central Doncaster and Bessacarr
- to the east of Doncaster, recharge occurs in a rural environment and agricultural chemicals especially fertilisers provide different sources of contamination, although there is overlap with the contaminant constituents of urban origin
- the characteristic ‘signatures’ of contaminated urban and rural recharge will be gradually diluted by mixing (through dispersion and diffusion) with older waters in the aquifer. Chemical processes such as denitrification and adsorption will also attenuate some contaminants
- the major public-supply sites abstract water that is a mixture of younger, contaminated shallow water and older uncontaminated (but still mineralised) water from greater depth.

3.4 POTENTIAL INDICATORS OF URBAN CONTAMINATION

Table 3.2 lists a number of potential indicators of pollution and their possible sources. After discussion the UK project partners chose a subset of these commonly encountered urban recharge indicators: chloride, sulphate, boron and zinc. *E. coli* and other faecal contamination indicator are discussed in a separate report describing the results of microbiological determinations (Rueedi et al., 2004).

Table 3.2 Possible contamination indicators

Determinand type	Determinand	Source	Activity type	Comment	
Major ions	Nitrate	Fertilisers Sewage	Rural Urban	Not conservative in reducing conditions	
	Chloride	Sewage	Urban		
		Road salt Mine drainage	Transport network Mining		
	Sulphate	Sewage	Urban		
		Mine drainage	Mining		
	Phosphate	Sewage Fertilisers	Urban Rural	Limited mobility in groundwater	
Potassium	Sewage Fertilisers	Urban Rural	Attenuated in soil zone		
Minor ions	Aluminium				
	Iron & manganese	Low redox	Natural/urban	High natural concentrations in areas of aquifer	
	Fluoride	Toothpaste	Natural/urban		
		Detergents	Urban		
	Boron	Mine drainage	Mining		
Metal working/processing		Industrial			
Trace metals	Cadmium	Metallurgy, pigments	Industrial	Very limited data available	
	Mercury	Batteries/landfill	Industrial		
	Zinc	Metal working/ landfill	Industrial		
Organics	Surfactants	Domestic and industrial cleaning	Urban		
	Solvents	Metal working, paints	Industrial	Very limited data available	
	Hydrocarbons	Fuel, heating oil	Urban, industrial		
	Phenols	Timber preservatives			
	Pesticides		Agricultural herbicides, fungicides and growth regulators	Rural	Potentially wide range of determinands - analysis very expensive
			Amenity herbicides	Urban and transport network	
			Rodenticides, mothproofers	Urban/industrial	
Timber preservatives					
Microbes	Faecal Coliforms				
	Clostridium	Urban wastewater	Urban		
	Viruses				

Determinands in bold selected for this study; note that pristine groundwater may also contain some or all of the above determinands as natural constituents.

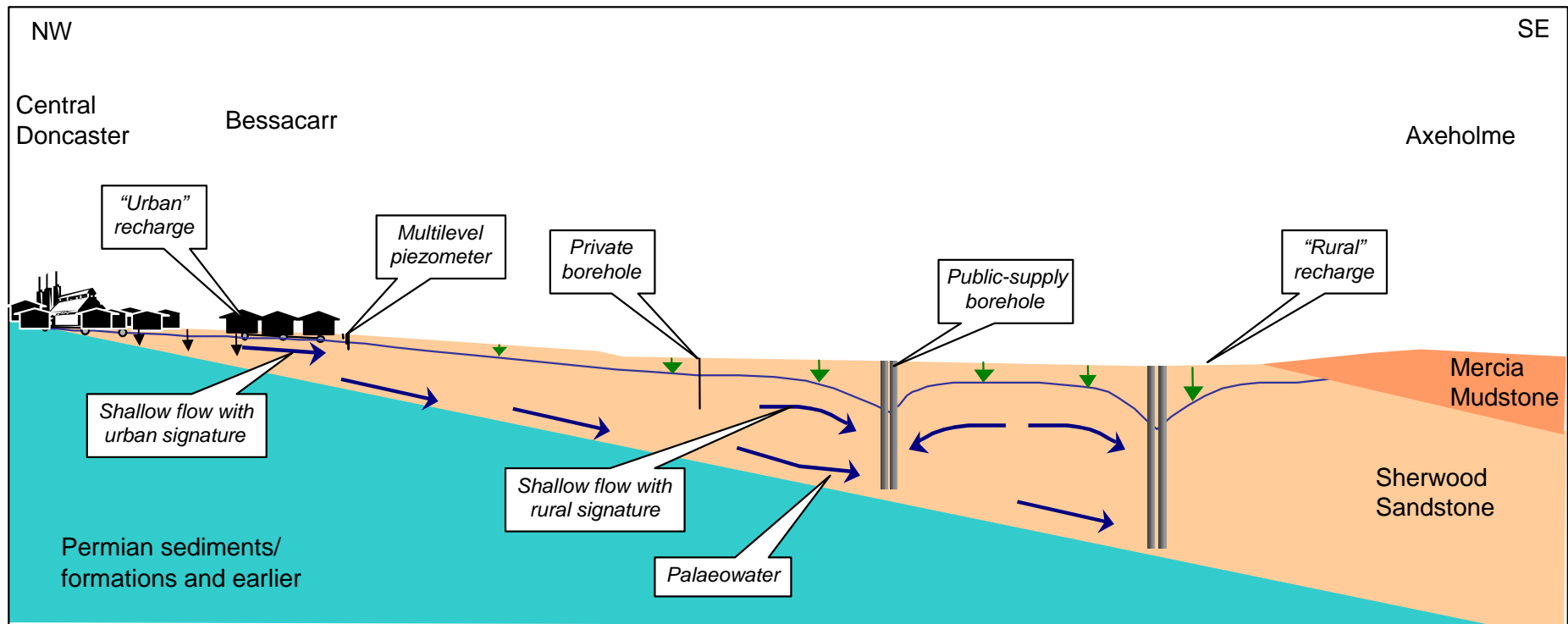


Figure 3.3 Schematic diagram illustrating the main features of the conceptual model

4 Inorganic monitoring results and discussion

4.1 RAW WATER DATA FROM PUBLIC SUPPLY BOREHOLES

4.1.1 Major ion chemistry

Raw water quality data from YW public supply boreholes are summarised in Tables 4.1 and 4.2. YW analyse for SEC, iron, manganese and nitrate in raw water much more frequently than for other major ions, so the data summaries in Table 4.1 are for a variable number of analyses. For the determinands shown in Table 4.2, the majority of the results are less than the detection limit, so no mean value has been calculated.

Of the sites considered in this report, these boreholes are likely to be yielding water with the least urban influence. Not only are the catchments, as delineated by the EA, in areas that are predominantly rural but also they are generally deeper than the other boreholes sampled. Nevertheless, these public supply boreholes are all open or screened over much of their depth and this design will draw in a mixture of water from different depths in the aquifer (Figure 4.1). Buckley and Talbot (1993) estimated that at HT2 about 40% of water moving to the pump was higher-conductivity water from the upper aquifer. So although boreholes at the same site may be of different depths this will not necessarily impact on the quality.

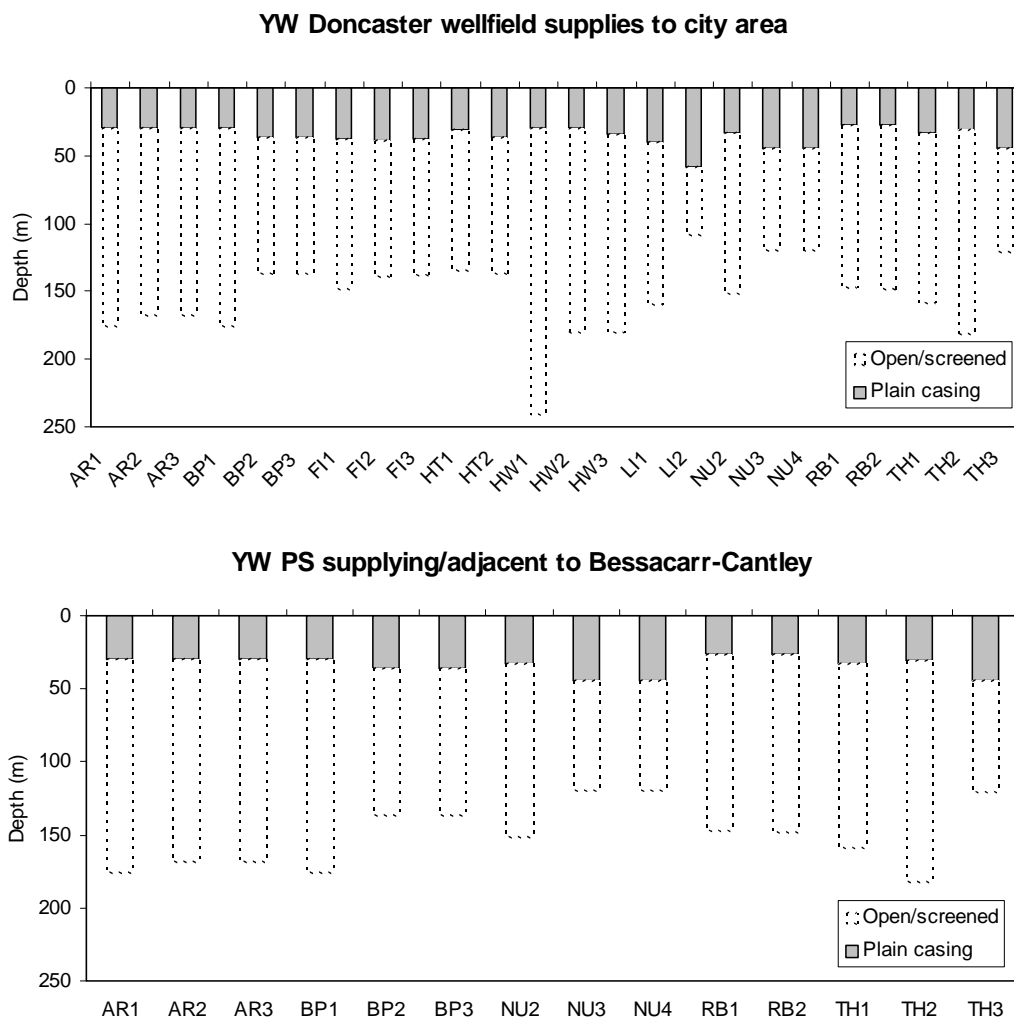


Figure 4.1 Designs of YW Doncaster wellfield supplies to the city area; in the vicinity of the study area, the boreholes tap the aquifer variously from 27-180m depth

Table 4.1 Range and mean concentrations of major and minor ions in raw and treated water from Yorkshire Water public supply boreholes since 1999

Site	BH	Depth (m)	SEC ($\mu\text{S/cm}$)			Na (mg/l)			K (mg/l)			Ca (mg/l)			Mg (mg/l)		
			Max	Min	Av	Max	Min	Av	Max	Min	Av	Max	Min	Av	Max	Min	Av
AR raw	1	176	537	259	401	-	-	14.1	-	-	2.4	-	-	40.3	-	-	17.9
	2	168	536	327	484	-	-	11.8	-	-	2.4	-	-	32.9	-	-	16.5
	3	168	563	369	478	-	-	14.6	-	-	2.9	-	-	45.4	-	-	20.1
BP raw	1	180	413	373	396	12.3	11.7	12.0	2.7	2.6	2.6	51.4	49.3	50.4	21.3	20.1	20.8
	2	137	598	365	365	14.4	12.3	13.2	2.4	1.9	2.2	53.5	50.6	51.9	21.2	20.0	20.6
	3	137	437	364	409	10.8	10.0	10.4	2.7	2.4	2.5	53.4	50.2	51.3	24.8	23.2	23.8
FI raw	1	148	445	298	357	12.8	11.4	11.9	2.2	2.2	2.1	44.4	41.1	42.6	17.2	15.4	16.3
	2	139	554	339	362	8.4	6.8	7.8	2.0	1.7	1.9	45.2	43.4	44.4	20.2	18.5	19.7
	3	138	565	337	430	13.9	7.6	12.3	2.3	1.8	2.1	51.7	45.7	49.9	23.1	18.6	21.9
HT raw	2	137	659	377	510	18.7	10.8	14.4	4.4	3.2	3.7	102	50.7	64.7	27.5	8.5	23.7
HW raw	3	180	533	364	431	14.9	11.0	12.7	3.5	2.9	3.2	55.8	49.2	51.3	22.9	19.7	21.3
LI raw	1	167	681	358	460	14.6	14.0	14.3	2.4	2.4	2.4	53.8	52.3	52.3	23.9	21.9	22.8
	2	120	571	305	361	12.1	9.5	10.9	2.1	1.7	1.9	44.4	36.7	40.9	19.3	16.2	18.1
NU raw	2	152	773	366	588	21.8	18.9	20.2	3.3	2.7	3.0	67.7	66.0	66.6	25.7	24.4	25.2
	3	152	1160	483	571	24.2	22.0	22.9	2.9	2.7	2.8	72.5	68.0	69.9	25.2	24.3	24.9
	4	120	865	408	528	23.4	19.1	20.5	3.0	2.6	2.8	67.3	52.0	55.7	25.1	22.5	23.8
RB raw	1	147	693	332	543	31.5	21.9	25.7	4.2	2.8	3.2	68.7	47.4	54.7	31.0	24.0	27.1
	2	145	884	350	586	57.6	13.8	32.6	3.7	2.7	3.1	65.9	38.2	55.8	33.2	21.3	27.9
TH raw	1	155	496	314	399	18.5	8.7	13.1	2.9	2.2	2.6	53.4	51.9	52.7	23.8	20.1	22.1
	2	180	737	358	428	18.5	8.1	10.0	2.9	2.2	2.7	58.9	51.3	53.8	25.5	19.9	22.5
	3	120	732	408	430	9.1	8.2	8.6	2.8	2.3	2.5	58.4	52.7	54.7	25.4	22.6	24.2
Nutwell final	-	-	607	359	456	17.9	10.9	14.9	2.9	2.3	2.7	63.0	49.5	54.4	26.9	21.5	23.0

Boreholes in proximity to or supplying Bessacarr-Cantley study area **bolded**. Max and min values not quoted where there is only one value

Table 4.1 continued

Site	BH	HCO ₃ (mg/l)			Cl (mg/l)			NO ₃ -N (mg/l)			SO ₄ (mg/l)			Fe (µg/l) [§]			Mn (µg/l)		
		Max	Min	Av	Max	Min	Av	Max	Min	Av	Max	Min	Av	Max	Min	Av	Max	Min	Av
AR raw	1	-	-	79	-	-	31.3	14.2	5.6	11.5	-	-	48.6	31	<7	8	113	<1.5	6.8
	2	-	-	104	-	-	19.9	14.4	8.3	12.6	-	-	31.0	20	<7	7	1.0	<1.5	0.9
	3	-	-	<i>644*</i>	-	-	29.9	19.5	8.8	14.4	-	-	42.0	22	<7	7	59	<1.5	2.3
BP raw	1	236	230	233	18.8	17.8	18.4	0.65	0.12	0.25	18.4	17.7	18.1	657	55	394	183	147	166
	2	233	204	216	28.8	25.5	27.0	8.4	<0.13	0.37	30.7	26.1	28.8	728	23	309	265	84	181
	3	253	244	250	16.8	14.5	15.8	8.5	0.12	0.42	25.3	23.6	24.3	832	279	494	133	17	121
FI raw	1	164	128	151	28.4	18.7	25.2	5.9	0.34	2.3	45.2	30.2	33.9	158	7	37	37	13	27
	2	230	203	215	19.7	18.8	19.3	7.6	0.15	0.46	8.5	7.5	8.1	1760	10	95	161	2.4	23
	3	202	176	193	28.9	19.0	25.9	8.3	0.34	5.0	34.3	8.2	27.3	476	12	75	54.1	4.0	21
HT raw	2	177	148	163	43.7	30.2	37.1	13.2	3.3	7.1	87.3	37.2	75.0	311	<7	12	23	<1.5	3.1
HW raw	3	152	135	148	36.2	28.9	31.5	9.9	5.8	8.2	70.9	40.4	47.0	96	<7	7	45	6.0	20
LI raw	1	138	136	137	34.6	32.3	33.1	11.8	5.6	10.4	66.3	37.2	60.5	145	<7	11	14.1	2.0	9.2
	2	135	122	131	25.5	18.5	23.1	11.4	1.9	7.7	40.4	22.7	33.3	706	<7	11	188	2.0	13
NU raw	2	223	193	204	84.3	62.5	71.0	8.95	4.7	5.8	38.2	29.7	34.2	862	10	71	167	32	113
	3	210	210	210	58.6	53.7	55.5	12.9	8.3	9.1	54.8	50.0	51.9	328	<7	49	138	49	78
	4	203	162	173	53.1	50.5	52.2	13.3	3.8	8.7	50.0	27.0	33.8	803	<7	31	462	5.0	60
RB raw	1	191	135	150	78.1	53.6	64.3	11.0	6.6	8.1	82.9	52.7	68.3	121	<7	10	66	1.7	6.7
	2	182	129	153	140	37.9	75.2	10.3	2.0	8.2	97.4	39.2	70.0	6300	<7	109	155	2.0	8.9
TH raw	1	210	170	195	51.8	20.7	31.6	9.3	0.1	2.0	38.2	24.5	30.3	416	<7	38	178	1	70
	2	231	170	211	52.8	20.6	25.5	10.6	0.1	2.0	63.3	21.8	35.6	364	<7	25	187	8.0	87
	3	246	218	237	25.7	19.4	21.5	8.5	1.6	2.1	49.1	19.8	25.7	856	<7	16	94	4.1	83
Nutwell final	-	240	180	211	41.0	25.9	34.1	10.1	0.49	4.26	45.5	27.1	36.4	48.0	<7	7	11.4	<1.5	1.2

* Data in *italics* apparently anomalous and not used.

§ It is not known if samples for Fe and Mn are filtered at the Yorkshire Water laboratory. If not the sporadic very high concentrations may be particulate in origin and therefore spurious.

Table 4.2 Maximum concentrations of infrequently analysed determinands in raw water from Yorkshire Water public supply boreholes since 1970

Site	As ($\mu\text{g/l}$)	Sb ($\mu\text{g/l}$)	F ($\mu\text{g/l}$)	Pb ($\mu\text{g/l}$)	Zn ($\mu\text{g/l}$)	B ($\mu\text{g/l}$)	PO ₄ ($\mu\text{g/l}$)
AR	6.4	2.1	500	45	30	50	130
BP	-	<1	80	<5	20	<50	<10
FI	5	<1	100	20	220	<50	60
HT	5.2	1.7	50	18	70	<50	60
HW	2.0	<1	125	<5	20	<50	40
LI	6.1	<1	80	<5	70	<50	40
NU	7.3	1.3	220	13	160	<50	10
RB	<5	<1	120	25	80	<50	110
TH	1.0	<1	120	16	100	<50	30

The data show a pattern consistent with the earlier studies referred to in the previous section where the west of the aquifer is characterised by its higher chloride, sodium and possibly sulphate concentration (chloride concentrations >30 mg/l are found in all boreholes at RB, HT and NU, and some at AR, LI and TH). One interpretation is that this may be due to a higher content of modern water in the western aquifer, which is thinner due to post-depositional tilting and erosion. To the southeast water contains a higher concentration of bicarbonate, and this interpretation would derive the bicarbonate presumably from a longer residence time in the full-thickness aquifer (bicarbonate concentrations of >200 mg/l are found in all boreholes at BP, and in at least one at FI, NU, and TH). AR, NU and LI are in a similar setting to RB and HW, and BP to FI (Figure 4.2).

There is limited evidence of local reducing conditions with iron and manganese detections and variable concentrations of nitrate in water from FI, NU and TH. This is consistent with the results from some of the multi-level piezometers as described in Section 4.4. The highest and most consistent concentrations of both iron and manganese are found at BP together with generally low nitrate concentrations.

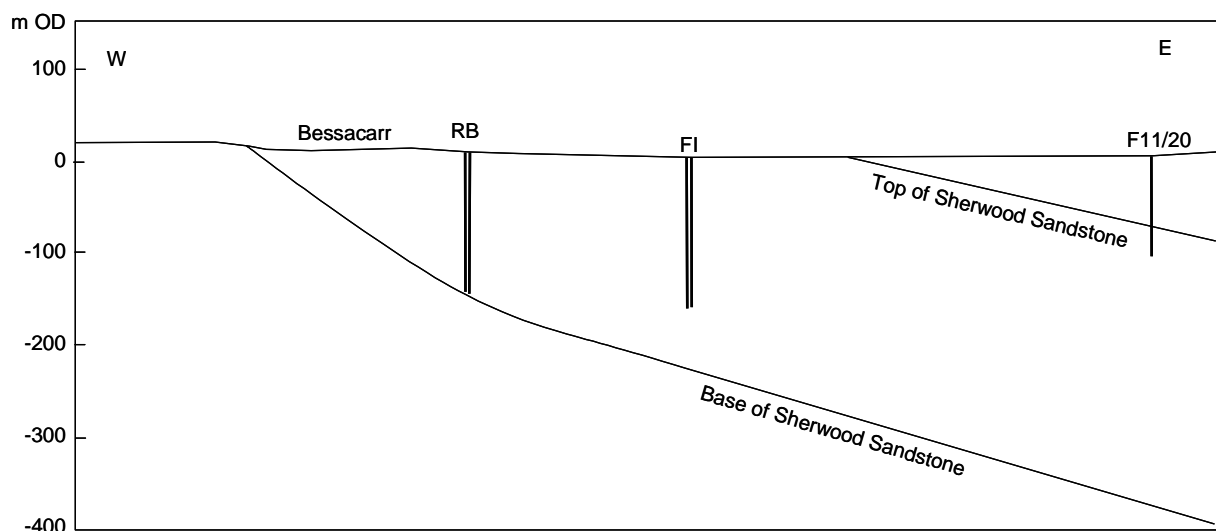


Figure 4.2 Sketch cross-section of central part of the aquifer showing examples from western PS sites where aquifer thickness is reduced by post-depositional tilting and eastern sites tapping full thickness aquifer (250m+)

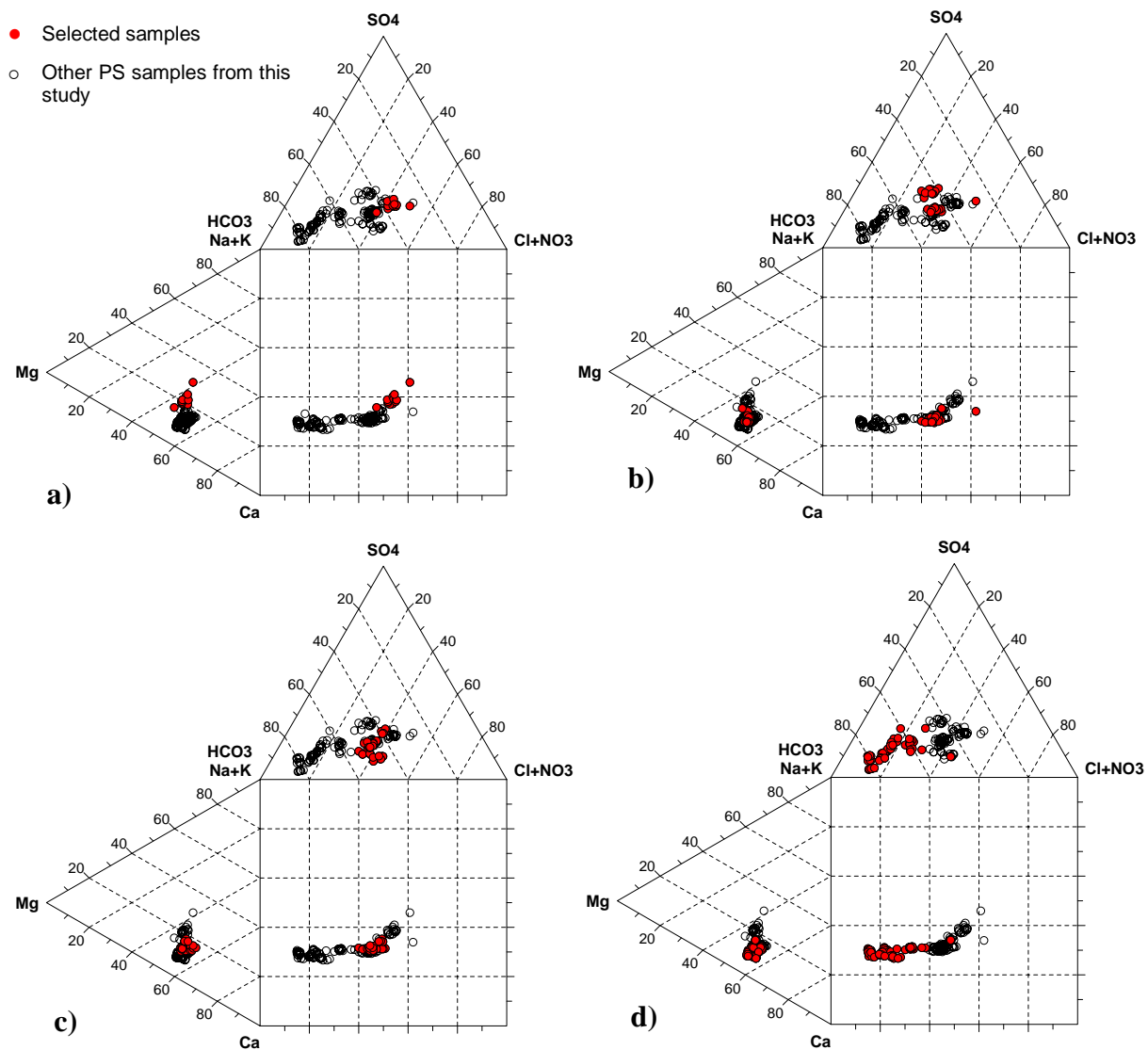


Figure 4.3 Durov plots showing geochemical evolution of water from Yorkshire Water public supply boreholes a) RB; b) AR, HT, HW; c) LI, NU; d) BP, FI, TH

Major-ion chemistry is summarised as Durov plots in Figure 4.3. While individual boreholes have a range of qualities, these plots show the water at RB as an end member of the distribution with the highest proportion of sodium, chloride and nitrate (Figure 4.3a) and the more reducing semi-confined water at BR, TH and FI at the other extreme dominated by calcium and bicarbonate (Figure 4.3d).

Although the 9 pumping stations that supply the city all abstract from the middle and lower Sherwood Sandstone aquifer, and are of the same general calcium-magnesium-bicarbonate-sulphate facies, the internal variability of water quality from the different pumping stations, as evidenced in Figure 4.3 and Table 4.1 is quite striking. It is clearly impractical to characterise as a single simple water type the 20 km strike section of outcrop Sherwood Sandstone aquifer that this wellfield taps. This observation has prompted a closer inspection (which is ongoing as part of the field programme) of the supply strategy to the Bessacarr-Cantley study area, with two objectives:

- (i) To characterise more closely groundwater in the immediate vicinity of the study area, in part to assess whether it is already subject to urban recharge influence and in part to

provide a baseline with which to compare the impact of contaminants in urban-derived recharge.

- (ii) To identify which pumping stations provide the groundwater to the water mains pipe network of the study area and in which proportions, in order to provide a 'mains standard average water quality' for the UVQ model and subsequently as a source term for solute transport modelling.

4.1.2 Treated water supplied to the Bessacarr-Cantley study area

The six Demand Management Areas (DMAs) in the study area receive a combined supply from AR, BP, NU, and TH pumping stations, blended at Nutwell Water Treatment Works. Data for these sites is highlighted in Table 4.1. The blend of these four raw waters will vary with time according to operational conditions. The water is treated for manganese removal, blended to manage nitrate, then put into supply after precautionary disinfection and plumbosolvency control stages. The resultant treated water blend is shown as an entry at the bottom of Table 4.1. This represents the typical water quality in the study area's mains supply and is a UVQ source term. Exceptionally, from November 2000, for about four months during the rehabilitation of the trunk main from Nutwell, the DMAs were supplied in approximately equal proportions with water from RB and FI.

The boreholes supplying Bessacarr-Cantley tap an aquifer with a saturated thickness of 104-222m which, depending on location, represents all or part of the middle and lower aquifer. The typical depth range for abstraction from screened or open-hole sections is approximately 32-150 mbgl. These boreholes at the four pumping stations supplying the water treatment works and RB are all located in the vicinity of the study area, with AR, NU and RB on the western side of the wellfield closest to Doncaster. Their locations and the key supply role to the study area of four of these five sites make them the most likely to be impacted by urban recharge effects. These five pumping stations will therefore become the main water supply reference points for further work in the AISUWRS field programme (Work Package 4).

4.1.3 Contaminants and potential urban indicators

The distribution of nitrate, which is widely and frequently analysed for regulatory purposes, is probably controlled by surface inputs and redox conditions in the aquifer. Previous studies (section 3.1.2) have shown that there is both local confinement by low-permeability deposits and decreasing redox potential with depth and that nitrate is absent or has low concentration where iron and manganese are significant. This may indicate either an element of denitrification (although there is little dissolved organic matter in the aquifer to drive this process) or the source water may predate pollution.

At several pumping station sites, e.g. FI and historically at HT, individual boreholes produce water with very different nitrate concentrations and sometimes large fluctuations. This may be due to one or more of the following explanations:

- land use in the individual borehole catchments of a pumping station is different. At HT, when two boreholes were operating, the catchment for borehole 1 extended under agricultural land whereas that for borehole 2 was predominantly under the village
- there are operational reasons, such as the borehole pumps are set at, and draw from, different depths
- there are interconnections between the boreholes in the aquifer
- there is a local redox boundary that can be reached by different pumping regimes.

Overall this suggests that the presence or absence of nitrate may not be a reliable delineator of contamination and especially of a particular provenance such as urban-derived recharge.

Sulphate concentration is variable over the wellfield. The highest concentrations are found in HT and RB (up to 75 mg/l) and the lowest in FI, TH and BP (generally 20 – 30 mg/l, but as low as 8 mg/l), but all sites show internal variation. This is greatest at LI and FI. It is not obviously related to Fe and Mn. Depth samples from BP1 (Smedley et al., 1993), show that sulphate is lowest in the profile from 60 – 90 mbgl, and Fe the highest from 62 – 108 mbgl. Chloride is high in NU and RB, and in the range 30 – 50 mg/l elsewhere. At BP1, HT2 and HT4 in 1993, downhole sampling showed that Cl decreased rapidly in the upper 50 m and was lowest at the base of the borehole (Smedley et al., 1993).

The less frequently analysed parameters are more difficult to interpret. Phosphate is present at low concentrations in groundwater from all boreholes except BP at 10 – 40 µg/l. Isolated higher concentrations (up to 130 µg/l) have been found at AR, RB, HT and FI. Phosphate can be derived from fertiliser applications to agricultural land and from urban wastewater (about 30 mg/l PO₄ in study area), but its ready adsorption to soil particles and other organic material is a strong attenuating factor.

Concentrations of fluoride are variable but are highest in groundwater from AR and NU. Arsenic and antimony are only occasionally detected above concentrations of <7 and <2 µg/l respectively. The highest concentrations of As and Sb were found at AR, HT and NU, and As was also found at LI. These elements appear to be present at higher concentrations in the western part of the aquifer. Boron has been infrequently analysed for. This was detected only once at a concentration close to the YW detection limit of 50 µg/l.

Smedley and Brewerton (1997) found little evidence of contamination by trace metals and the datasets from these production wells confirm this observation. Almost all analyses for Cd, Cu and Hg are below the limits of detection. Data for Pb and Zn are included in Table 4.2. Pb concentrations are highest at AR and RB. Zn is very variable and is highest in FI and NU.

The background concentrations of a range of anthropogenic organic compounds are very low with no evidence of significant urban impact on quality. There are a very few positive detections of trihalomethanes. These were all in groundwater from boreholes sampled during a two-day period in 1990 and may therefore be a laboratory artefact. There have been isolated detections of hydrocarbons at BP, oil and grease at RB, and phenols at NT. HW has been out of supply for some time as a precaution against a leaking underground storage tank problem at an adjacent fuel-filling station. Polyaromatic hydrocarbons, hexachlorobenzene, 2,4,6-trichlorophenol and ionic surfactants have never been detected.

Low concentrations of pesticides have been widely detected across the wellfield. The results can be considered to fall into four groups:

- triazine herbicides particularly at HT, but also at HW and FI – predominantly atrazine, which is presently still authorised for weed control in maize and orchards, but was previously used for road verges, railway lines and open areas until 1993
- agricultural pesticides at TH
- limited individual detections at AR and LI
- multiple detections of both agricultural and amenity pesticides at BP, NU and RB.

These results suggest that pesticides are probably present in the modern component of abstracted water from these boreholes. There is some evidence that these are related to catchment land use since significant detections of atrazine occurred in partly urban HT and RB and of purely agricultural compounds in BP, TH and NU which are more rural.

4.2 PRIVATE SUPPLIES AND ENVIRONMENT AGENCY MONITORING

4.2.1 Major-ion chemistry

The 11 private wells being monitored are located on the eastern and central zones of the Sherwood Sandstone outcrop. Major-ion chemistry for private supplies in the project monitoring network is summarised in Table 4.3. All of these boreholes apart from Cantley Water Tower and Warning Tongue Lane have higher electrical conductivities than the public supply boreholes in the vicinity, indicating a higher dissolved solids content. The distribution of major ion constituents appears unrelated to geographical position. In these boreholes the major ion constituents of the study area subset lie in the calcium-bicarbonate-sulphate hydrochemical type, within which they are as variable as the deeper aquifer waters sampled by the YW public supply boreholes (Figure 4.4). While anion chemistry is rather more variable, with higher proportions of sulphate and chloride than the deeper public-supply boreholes, a number of these wells, although rural, show possible local effects likely to be unrelated to urban recharge.

Reducing conditions are apparent at the rural sites of Beech Tree Nurseries and Elmstone Farm, as indicated by elevated Fe, Mn and sulphate and low nitrate. This is likely to be due to local confinement of the groundwater by superficial deposits or by low-permeability layers within the sandstone. The highest concentrations of Fe are found at Beech Tree Nurseries (22500 and 21100 $\mu\text{g/l}$). The redox status of groundwater from the rural site of Crowtree Farm is unclear as one set of data indicates oxidising conditions and the other reducing conditions.

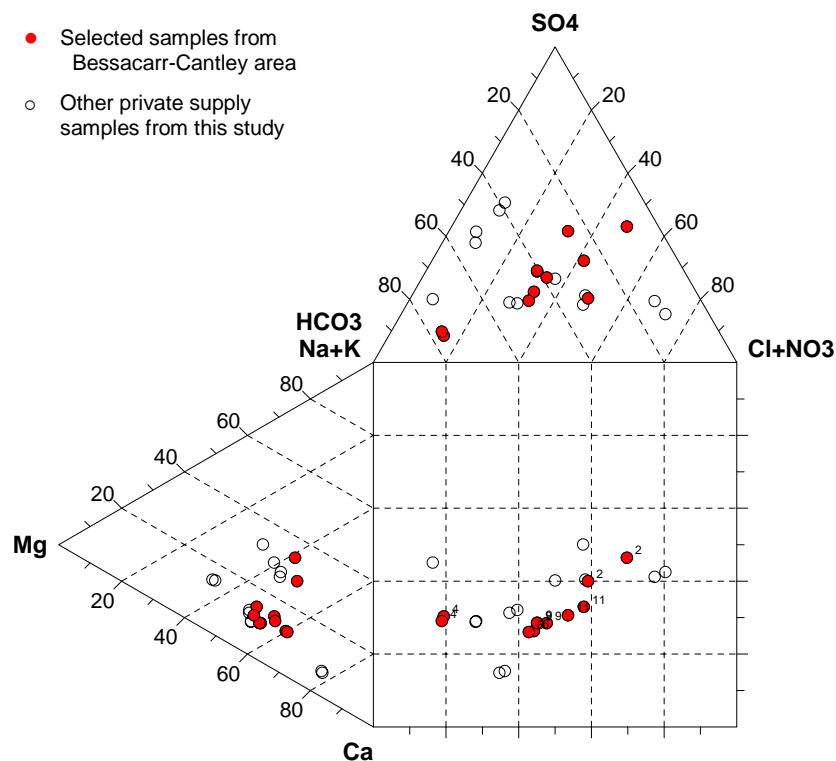


Figure 4.4 Durov plot showing composition of private supplies

Table 4.3 Mean quality data for private supplies and observation boreholes for June and November 2003

Site	Depth (m)	SEC (μ S/cm)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	HCO ₃ (mg/l)	Cl (mg/l)	NO ₃ -N (mg/l)	SO ₄ (mg/l)	Fe (μ g/l)	Mn (μ g/l)	Zn (μ g/l)	B (μ g/l)	Si (μ g/l)	Sr (μ g/l)	Br (μ g/l)
1. Beech Tree Nurseries	30.5	981	13.7	2.1	148	19.7	238	34.2	0.05	2289	21800	270	260	<80	8400	100	750
2. Cantley Water Tower	65.5	362	24.5	6.2	36.7	12.3	55.2	46.2	5.20	55.8	30	40	30	<80	6230	40	<30
3. Crowtree Farm	31.7	800	63.8	16.1	71.3	42.4	292	111.5	<0.06	89.2	630	40	10	150	2950	690	30
4. Doncaster Racecourse	41.1	379	11.1	1.4	40.9	14.5	163	16.6	0.16	15.3	200	80	10	<80	5690	30	<30
5. Elmstone Farm	50.0	1463	36.9	3.2	186	86.0	542	46.2	<0.06	323	730	1330	10	80	7170	680	170
6. Gatewood Grange Farm	76.2	696	18.7	2.2	85.5	24.3	203	46.2	8.76	71.8	50	340	10	<80	6010	40	40
7. Lings Farm	12.0	902	13.5	31.5	64.4	58.2	191	42.0	23.00	104	40	20	20	80	6120	220	90
8. Misson Quarry	76.2	1147	31.1	5.1	122	60.8	397	81.8	10.63	112	30	390	20	<80	5570	90	550
9. Peglers	30.5	801	16.6	4.8	87.1	36.0	207	42.3	12.95	113	20	10	30	80	5460	210	60
10. Sandall Common Farm	63.4	2930	147	9.8	213	89.6	201	538.5	18.75	205	10	30	10	100	7430	120	670
11. Warning Tongue Lane	63.4	198	10.1	5.3	47.5	22.0	76.8	29.9	6.74	91.1	40	20	320	<80	5260	40	40

Elevated concentrations of Sr are observed at Crowtree Farm (966 µg/l in the more reducing sample taken in Nov 2003) and Elmstone Farm (average concentration 680 µg/l). This may be indicative of longer residence time in the aquifer.

The concentrations of K in groundwater from the research site at Lings Farm are anomalously high (32 mg/l). One possibility is that this could be derived from tracing experiments carried out in other boreholes on the site, although details of this are not known and bromide concentrations (around 0.1mg/l) at this site are similar to others in the area. Monitoring at this site and several others in the network that are rural, relatively distant from the Bessacarr-Cantley study area, and may be displaying very local effects, are likely to be discontinued and the resources released for other analyses.

Based on these observations, it is recommended that for future monitoring five of the sites most remote from, or least representative of, the study area conditions be excluded from the monitoring network (Beech Tree Nurseries, Crowtree Farm, Elmstone Farm, Lings Farm and Misson Quarry).

4.2.2 Contaminants and potential urban indicators

Some sites in the aerobic parts of the aquifer contain very high concentrations of nitrate-N (23.0 mg/l at Lings Farm and 18.8 mg/l at Sandall Common Farm), but this is not ubiquitous; Doncaster Racecourse has a surprisingly low nitrate content considering its location immediately down-gradient of older districts of Doncaster and apparently shallow depth. As noted above, very high concentrations of potassium are found in Lings Farm and Sandall Common Farm.

Beech Tree Nurseries and Warning Tongue Lane contain high concentrations of zinc (260 and 320 µg/l respectively). This should be compared with the low zinc concentrations noted in the Bessacarr-Cantley wastewater samples to date (70-100 µg/l; see Table 4.6). The rural nature of the Beech Tree Nurseries and the fact that concentrations in excess of 100 µg/l are recorded for several of the YW public supply boreholes (FI, NU, TH; see Table 4.2) implies that naturally occurring zinc concentrations in groundwater can be of the same magnitude or higher than those in potential urban recharge. It is concluded that zinc will not prove to be a useful urban recharge indicator for this case-study setting.

Boron was detected close to the limit of detection at Crowtree Farm, Elmstone Farm, Lings Farm, Peglers and Sandall Common Farm in at least one of the replicates. This limit varied from 50 to 100 µg/l for the different sample batches and an average limit of 80 has been applied to these samples. Given that boron appears to be present at about 500 µg/l in local wastewater and is regarded as a relatively conservative contaminant, further effort is merited to establish whether it will be of real use as an indicator in this study.

Sandall Common Farm borehole also has a very high conductivity and elevated bromide (670 µg/l) and is thought to be influenced by drainage from Markham Main Colliery. Smedley and Brewerton (1993) similarly interpreted the salinity and high concentrations of bromide in the NU public supply borehole as indicative of coalmine drainage from this former mine, whose workings were located to the northwest and up-gradient of the pumping station. Beech Tree Nursery and Misson Quarry also contain elevated concentrations of bromide (750 and 550 µg/l respectively).

Pesticides were not analysed in this project but a study of shallow private boreholes in the vicinity of the Doncaster wellfield showed that the majority contained detectable pesticide concentrations (Goody et al., in press). The borehole samples were all in the rural part of the

wellfield or on the margins of the suburban area. The particular compounds detected were all consistent with the local land use:

- boreholes close to the railway line near RB contained high concentrations of atrazine (up to a maximum of 4.2 µg/l) plus propazine and terbutryn
- a borehole on a golf course contained benazolin, dicamba, MCPA, 2,4-D and atrazine, pesticides which can be used on turf and amenity grass
- boreholes on farms in agricultural production contained agricultural pesticides such as mecoprop, isoproturon, clopyralid and bentazone, although not necessarily those used in recent years around the site.

Apart from Peglers, none of the Environment Agency water quality monitoring sites is close to the Bessacarr study area. Analytical results from these unconfined-zone sites reveal various water-quality problems:

- groundwater from Hatfield Main (F11/13) has very high chloride concentration and may be impacted by mine drainage
- Yorkshire Bottle Co groundwater (F11/17) appears to have high trace metal concentrations (Cd, Cu, Ni, Pb and Zn), detectable polyaromatic hydrocarbons (anthracene, fluorene and phenanthrene) and nitrate. It seems unlikely that this represents a rural site
- Thorne Brewery groundwater (F11/15) has high conductivity and alkalinity.

Sulphate concentrations are high (180-280 mg/l) at all these sites. No boron analyses are available for these EA monitoring sites. These wells, which are presumably monitored for regulatory rather than regional assessment purposes, show localised effects unrelated to the objectives of this project and will not be considered further.

4.3 MULTI-LEVEL PIEZOMETERS

4.3.1 Major ions in pumped water

The major-ion profiles from the November 2003 sampling visit have been plotted in Figure 4.5 and the data summarised in Table 4.4. This is the first set of data collected from the piezometers and drilling effects may still be influencing the results.

The profiles for Na and K are similar at all the sites except McAuley High School (MHS), which has higher concentrations of Na near the top of the profile (Figure 4.5). Bicarbonate concentrations are also similar with the highest concentrations in all at about 20 m depth. At Haslam Park (HP1, HP2) it increases again in the lower part of the profile. Ca and Mg follow bicarbonate in a more muted profile. Dissolved oxygen and Eh measurements which are not shown show that the groundwater is predominantly oxidising. Iron and manganese suggestive of a transitional chemistry towards reducing conditions occur in some horizons, e.g. top of Haslam Park, 14m-depth zone at MHS.

Durov plots for the multi-level piezometer results are shown in Figure 4.6. These show a similar pattern to the private and public supply boreholes results, with some samples having major ion chemistry similar to the private boreholes where conditions are reducing (Figure 4.4), although nitrate concentrations are high. The shallower samples from P1, P2 and MHS9 (i.e. the 9 m deep piezometer at MHS) have a distinctly different composition, containing relatively more sodium and chloride.

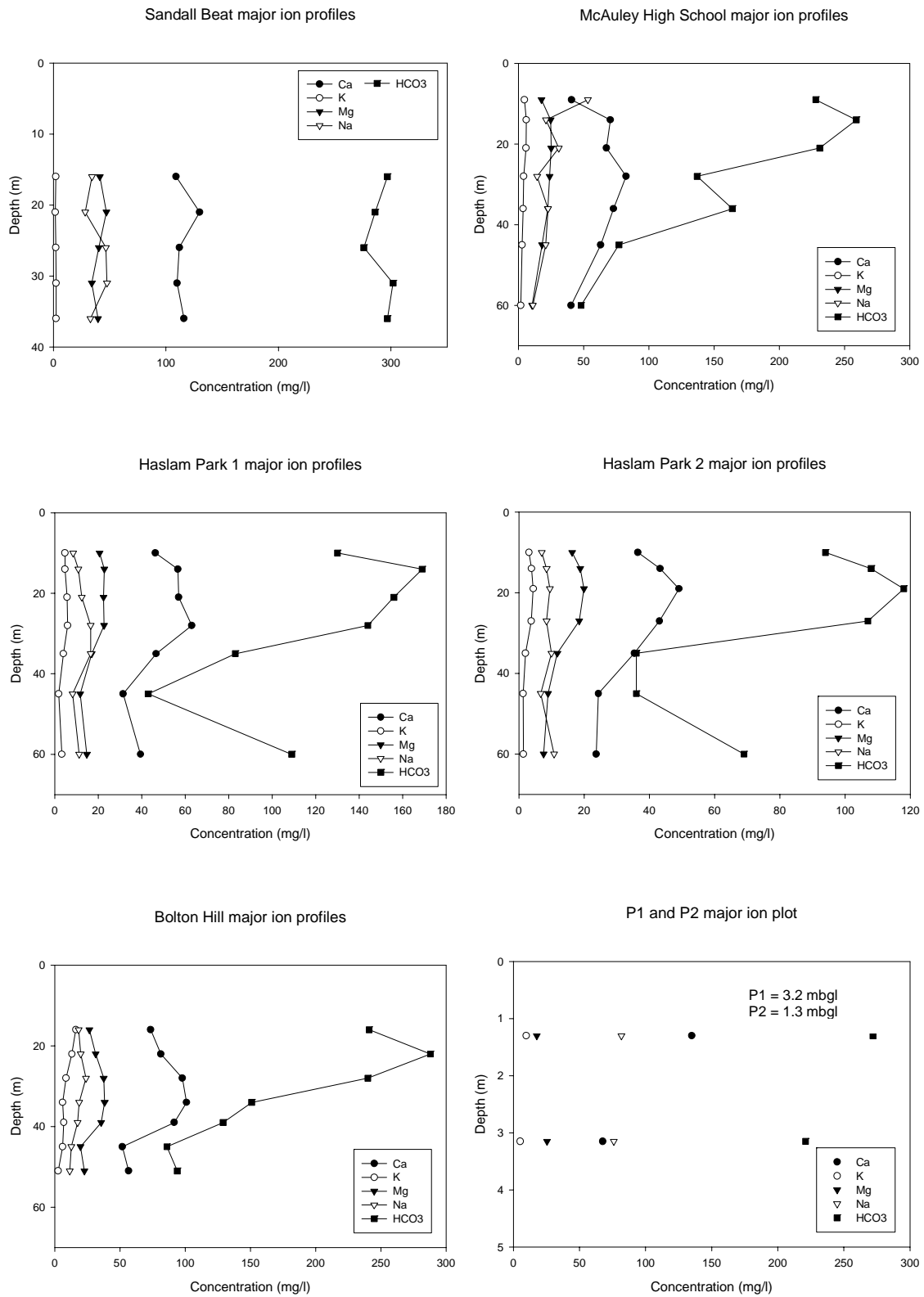


Figure 4.5 Major-ion chemistry profiles, except indicators, for multi-level piezometers for November 03

Table 4.4 Data for multi-level sampling sites, November 2003

Site	Depth (m)	SEC ($\mu\text{/cm}$)	Concentration (mg/l)								Concentration ($\mu\text{g/l}$)			
			Na	K	Ca	Mg	HCO ₃	Cl	TON	SO ₄	Fe	Mn	Zn	B
Sandall Beat (SB)	16	948	34.3	2.2	109	41.2	297	75.5	13.1	131	8	686	13	<100
	21	704	28.3	1.7	130	47.1	286	73.8	12.7	134	<5	521	16	<80
	26	1061	46.7	2.2	112	40.4	276	73.8	12.4	140	24	469	10	<100
	31	1061	47.7	2.3	110	34.2	302	39.5	7.82	165	6	288	10	<100
	36	814	32.9	2.4	116	39.7	297	61.4	10.4	149	30	299	12	<100
Haslam Park 1 (HP1)	10	480	8.5	4.7	46.3	20.6	130	26.4	4.26	52.8	649	18	10	<100
	14	567	10.9	4.7	56.6	22.8	169	32.5	5.47	59.7	<5	4	6	123
	21	567	12.5	5.7	57	22.4	156	32.5	5.94	70.8	7	3	6	137
	28	571	16.6	5.9	63	22.7	144	38.4	10.4	80.7	<5	3	7	137
	35	643	16.6	4	46.7	17	83	24.3	11.0	76.7	22	3	6	<100
	45	484	8.2	1.8	31.5	11.7	43	20.2	13.9	29.4	88	3	4	<100
	60	335	11.3	3.3	39.5	14.8	109	19.2	6.50	36.7	520	8	6	<100
Haslam Park 2 (HP2)	10	406	7	3.1	36.5	16.3	94	10.8	10.9	41.3	697	33	7	<80
	14	406	8.5	3.9	43.3	18.8	108	16.8	9.68	59.4	<5	15	6	100
	19	433	9.5	4.4	49.1	19.9	118	20	8.66	66.7	6	10	8	<80
	27	470	8.5	3.8	43.1	18.5	107	16.4	9.70	57	30	9	13	<80
	35	458	10	2	35.4	11.8	36	29.2	10.4	49.5	133	13	13	<80
	45	392	6.7	1.3	24.4	8.95	36	17.4	9.49	23.3	206	7	5	<80
	60	265	10.8	1.4	23.7	7.56	69	12.1	7.65	11.5	162	11	5	<80
McAuley High School (MHS)	9	597	53.2	4.7	40.8	17.8	228	19.6	6.87	35.9	29	9	7	100
	14	647	21.2	6	70.5	24.7	259	18.7	4.44	50.4	271	14	11	<80
	21	636	31	5.9	67.5	25.2	231	13.5	8.61	66.5	10	13	9	<80
	28	717	14.4	4	82.6	23.9	137	15	11.7	153	<5	20	9	<80
	36	717	22.7	3.7	72.9	22.6	164	19	7.31	130	9	12	9	<80
	45	698	20.9	2.9	63.1	18.2	77	25.3	17.7	107	11	16	7	95
	60	623	11.1	1.9	40.4	10.5	48	33.3	11.3	36.4	46	8	7	<80
Bolton Hill (BH)	16	529	18.4	16.2	73.5	26.6	241	27.7	3.95	90.9	71	7	9	88
	22	802	20	13.2	81.3	31.3	288	29.5	5.37	88.4	15	8	9	<80
	28	691	23.9	8.7	97.9	37.5	240	63.4	6.70	144	14	7	10	<80
	34	500	18.7	6	101	38.3	151	113	4.82	156	37	4	10	<80
	39	917	17.5	7	91.6	35.7	129	103	5.61	142	<5	8	8	<80
	45	567	12.8	6.1	51.9	19.8	86	41.7	8.17	77	6	7	6	<80
	51	604	11.5	2.6	56.6	22.7	94	45.8	9.86	76.3	46	3	8	86
Piezo 1 (P1)	3.15	1110	76	5.2	67.6	25.5	221	95.7	13.9	64.5	102	3	12	103
Piezo 2 (P2)	1.3	911	81.7	9.7	135	17.7	272	184	2.28	84.4	6200	1290	16	91

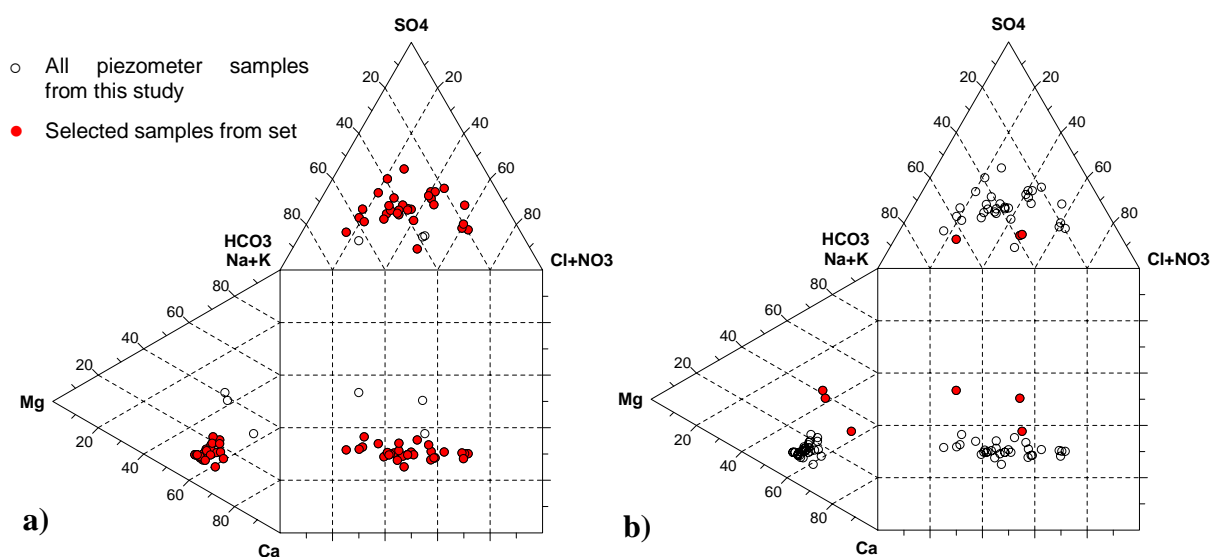


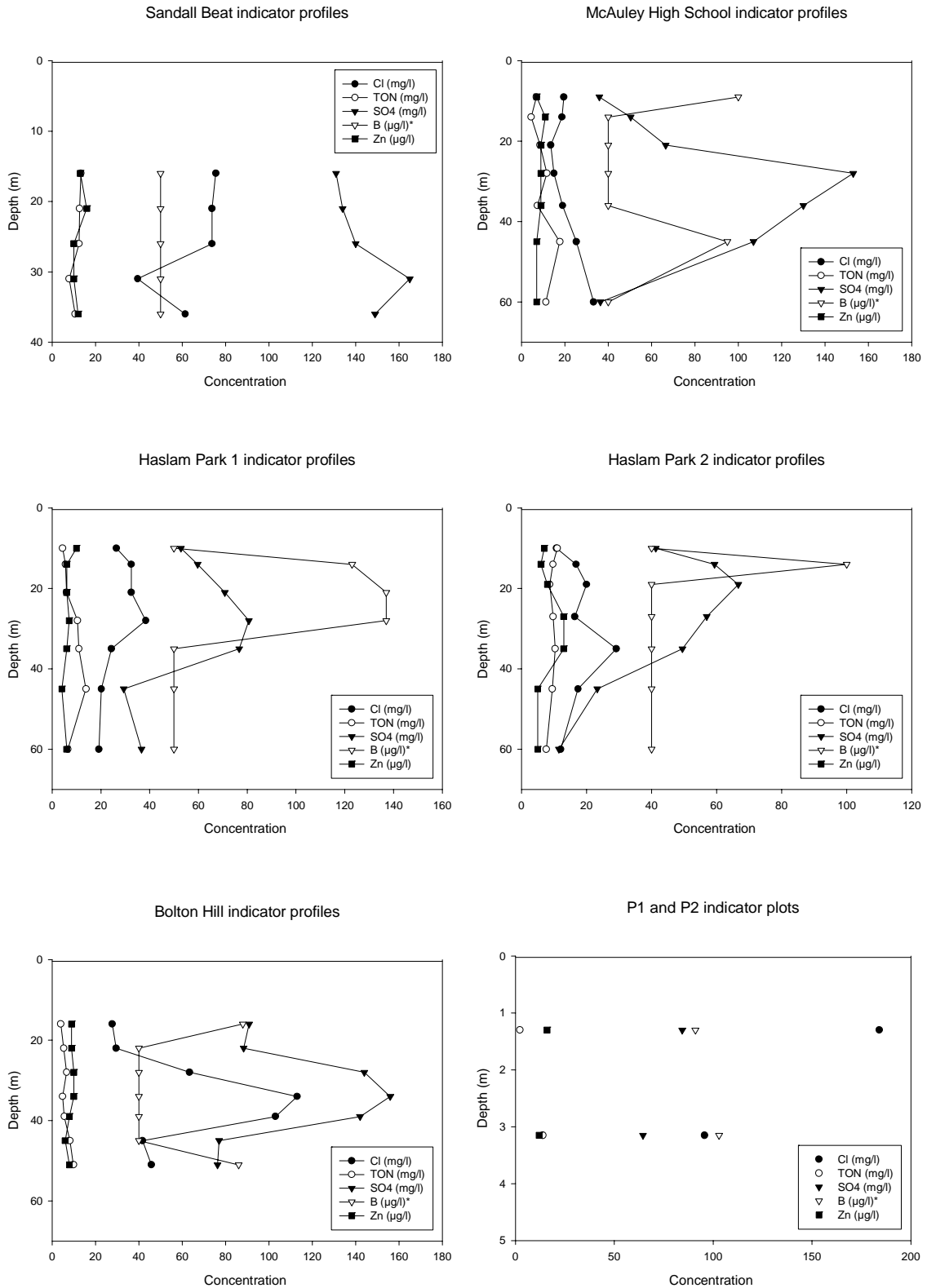
Figure 4.6 Durov plots for piezometers: a) shows the deeper samples; b) the results for P1, P2 and MHS9

4.3.2 Indicator parameters

Profiles of the indicator parameters are shown in Figure 4.7. Chloride profiles show little significant change with depth at the Sandall Beat, Haslam Park 2 and McAuley High School sites. At Bolton Hill, a peak is observed between about 30 and 40 mbgl, where concentrations rise from about 30 to 40 mg/l to over 100 mg/l and at Haslam Park 1 there is a smaller peak at about 30 m. These both coincide with elevated sulphate levels. High chloride concentrations were also observed in Sandall Beat, P1 (95.7 mg/l) and P2 (184 mg/l). These high concentrations at shallow depths are somewhat higher than the wastewater chloride concentration recorded in Table 4.3 and may be related to mine drainage, parkland fertiliser inputs or road salting.

Sulphate is one of the most variable parameters with depth, with a peak at about 30 m below ground level in BH, HP1 and MHS and a peak at about 20 m in the HP2 profile. These peaks tend to be about double the concentration observed in the shallower and deeper sample ports. The profile at SB is more subdued although the sulphate concentration is slightly elevated in the 31-mbgl sample zone. The consistent depth at which these high sulphate concentrations are observed in the multi-levels has no obvious explanation since the regional dip means that there is only minimal overlap of strata between the sites (apart from the Haslam Park dual multi-levels).

The nitrate profile from Sandall Beat shows high concentrations near the surface (12 to 13 mg/l between 16 and 26 mbgl) and an overall trend of diminishing concentrations with depth. Nitrate concentrations remain relatively stable with depth in Haslam Park B. However, at Haslam Park 1, McAuley High School and Bolton Hill the nitrate concentration increases with depth; in Haslam Park 1 the water contains 4.2 mg/l $\text{NO}_3\text{-N}$ at 10 mbgl, rising to 13.9 mg/l at 45 mbgl. Nitrate-N ($\text{NO}_3\text{-N}$) concentrations exceed 17 mg/l at 45 mbgl at McAuley High School.



*Boron concentrations of <limit of detection (LOD) are represented as 50% of LOD. This may exaggerate differences between detected and not detected concentrations

Figure 4.7 Indicator profiles for multi-level piezometers for November 03.

Data for the other potential indicators is inconclusive. Boron concentrations were mainly below or very close to the normal detection limit (100 µg/l). The results for boron were recalculated using a less conservative limit of detection (LOD), which gave more positive detections but an LOD which varied for each group of ten samples analysed and ranged from 50 µg/l for some private supplies to 100 µg/l for some samples from the multi-levels. The highest profile concentrations were in the upper part of the Haslam Park profiles and in P1. All profiles except Sandall Beat contained at least one positive detection of boron. The detection limits achieved for these samples are probably too high to discriminate urban-derived boron from background reliably even in the piezometers where evidence for infiltration of urban water is the most likely. A lower detection limit would be desirable for future samples. Zinc concentrations are in the range 70 to 160 µg/l with the highest concentrations in the upper levels in Sandall Beat and at mid-depth in Haslam Park 1.

4.3.3 Porewaters from core samples

Results for the analysis of the porewaters extracted from the multi-level piezometer at Haslam Park 2 during drilling are shown in Table 4.5. A sample of the drilling water that was spiked with LiCl is also included. The results for Li clearly demonstrate that the upper three samples have been invaded by drilling water. The major cations may have exchanged with Li making interpretation even more difficult and the results should therefore be considered as unreliable.

For the two remaining samples, from the core from 29.04 to 30.50 mbgl, the results can be compared to those obtained for pumped water from the 27 and 35 m samplers shown in Table 4.5. This comparison shows that for all analytes except nitrate and Zn the porewater data are 2 to 3 times higher. This may suggest that the multi-level samplers are not yet at equilibrium with porewater concentrations.

Table 4.5 Quality of extracted porewater and spiked drilling water for Haslam Park 2 cores

Mid-depth (m)	Concentration (mg/l)								(µg/l)				
	Na	K	Ca	Mg	HCO ₃	Cl	TON	SO ₄	Fe	Mn	Zn	B	Li
9.85	13.1	6.4	95	41.3	119	259	19.6	41.5	<5	6	17	200	15700
10.58	17.4	6.7	80.8	39.9	123	232	13.6	57.1	<5	2	13	200	11200
16.31	17.3	7.4	70.3	28	119	163	6.305	67.4	<5	<2	12	300	9390
29.51	23.1	8.7	73.7	24.1	97.6	88.5	13.9	95.1	<5	5	14	300	<4
30.20	21.9	7.4	71.3	23.2	99.1	71.5	13.4	97.5	10	<2	12	300	<4
Drilling water	40.9	4.3	43.5	13.1		1200	5.6	90.6	10	6	49	<100	227000

4.4 WASTEWATERS

Three wastewater samples were collected from sewers serving Bessacarr (Table 4.5) as part of the monitoring programme. Wastewater contains higher concentrations of Cl (60 – 80 mg/l), B (400 –600 µg/l), K (16–25 mg/l) and PO₄ (28000–33000 µg/l) than are seen in groundwater, as well of course as Na and very high ammonium concentrations. There will also be a high organic nitrogen loading but this was not measured. Other analysed inorganic constituents appear to be in the same general range as local groundwater.

Sulphate concentrations are also relatively high (80 – 100 mg/l). The analytical technique used (ICP-AES) measures total sulphur, which is reported as sulphate as this is the dominant S species in most natural waters. However in wastewater sulphur is likely to be present in reduced forms as well as sulphate.

Zinc is present at about 80 µg/l, copper at about 4 µg/l, and lithium at about 17 µg/l. Other trace metals are mainly below the limit of detection.

Two of these samples were also analysed for a limited range of organic compounds. Both samples contained concentrations of 1–5 µg/l of the haloforms chloroform and tribromomethane, presumably by-products of water chlorination, and one had 0.8 µg/l of tetrachloroethene. Both samples contained similar concentrations (0.1–0.2 µg/l) of the polyaromatic hydrocarbons acenaphthene, fluorene, naphthalene and phenanthrene. Phenol and methyl phenol were detected in both samples at 50–200 µg/l and sub µg/l traces of a range of other phenols were also detected. No BTEX were found in either sample.

Table 4.6 Data for wastewater sampling sites, November 2003

Site	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	NH ₄ -N (mg/l)	NO ₂ -N (mg/l)	TON (mg/l)	Cl (mg/l)	SO ₄ (mg/l)
Everingham Road	91.5	25.1	50.1	23.6	79.6	0.005	< 0.06	83.5	84.4
Warning Tongue Lane	119	18.7	49.3	23.4	40.4	0.007	< 0.06	69.9	102
Burnham Close	87.5	16.8	53.4	23.7	32.6	0.012	< 0.06	61.6	80.5

Site	[§] PO ₄ (µg/l)	Fe (µg/l)	Mn (µg/l)	Zn (µg/l)	Si (µg/l)	Sr (µg/l)	B (µg/l)	Cu (µg/l)	Li (µg/l)
Everingham Road	33400	26	15	69	5930	103	500	39	16
Warning Tongue Lane	31800	67	15	99	8600	98.8	400	57	19
Burnham Close	28100	110	17	76	7350	103	600	37	17

[§] BGS data reported as total P assumed to be PO₄

4.5 RAW WATER QUALITY COMPARED TO DRINKING WATER STANDARDS

The European Directive on the quality of water intended for human consumption (98/83/EC) defines the maximum admissible concentration (MAC) in drinking water for a wide range of parameters. These limits refer, of course, to water at the point of supply (i.e. post-treatment). However it is useful to compare raw water quality to these limits in order to investigate whether anthropogenic inputs will mean a requirement for increased water treatment in the future.

While nitrate (NO₃-N) concentrations are typically low in raw water from Yorkshire Water public-supply boreholes, the mean values from boreholes AR1 and AR2 are in excess of the drinking water standard (MAC=11.3 mg/l), while that at LI1 is approaching the MAC. Water from these higher-nitrate boreholes is blended with low-nitrate water from other boreholes prior to supply.

Nitrate-N concentrations exceeded the MAC at three of the private supplies sampled (Peglers, Sandall Common Farm and Lings Farm), and the concentration in the Misson Quarry sample is close to the limit. The concentration of 29.6 mg/l in the June 2003 sample from Lings Farm is more than double the MAC, while the November 2003 sample contained 16.2 mg/l. As the

Lings Farm borehole is the shallowest of the private supplies sampled, the water is likely to be younger than at other sites. The findings from the multi-level samplers (Section 4.4) show increasing nitrate concentrations with depth at three of the sites, and the MAC is exceeded at depths of 45 mbgl at two of these sites.

Nitrite (NO₂-N) concentrations at Gatewood Grange Farm and in two depth intervals in the piezometers at Sandall Beat multi-level site exceed the limit of 0.03 mgN/l. Ammonium concentrations are typically low, however the first (June 2003) sample from Beech Tree Nurseries contained 0.57 mg/l, above the drinking water standard of 0.39 mgN/l, although the November 2003 sample contained 0.48 mg/l.

For the major ions, sulphate is generally well below the MAC of 250 mg/l, except the values of 300 and 345 mg/l measured at Elmstone Farm. Magnesium is found in excess of the drinking water standard (50 mg/l) at four of the private supplies (Elmstone Farm, Lings Farm, Misson Quarry and Sandall Common Farm). Potassium concentrations exceed those acceptable in drinking waters at Crowtree Farm, Lings Farm, and in the 16 and 22 m deep piezometers at Bolton Hill. High chloride ion concentrations were observed in the samples from Sandall Common Farm (637 and 440 mg/l in Aug and Nov 2003 respectively).

These results indicate that nitrogen from both urban and non-agricultural sources may be making a significant contribution to nitrate concentrations in groundwater in the Doncaster area and this could cause problems for public water supplies in the future.

5 Evaluation of findings

5.1 INDICATOR PARAMETERS

The results from potential indicator parameters identified in Section 3.4 are summarised in Table 5.1.

CHLORIDE:

- (i) Chloride in wastewaters so far sampled is on average about twice that in local deep groundwater and that in mains water supplied to the study area, and about 60% more than that found in shallow groundwater in the vicinity.
- (ii) a corollary of this observation is that on the basis of results so far there is not a strong contrast in chloride content between shallow and deep groundwater in the vicinity of the study area.
- (iii) however there is significant overlap of maxima in both shallow and deep local groundwater, with public supply boreholes, monitored private boreholes away from the study area and multi-levels in Bessacarr-Cantley all revealing similar chloride concentrations to those found in autumn-sampled wastewater. Careful interpretation of results on a site-by-site basis is therefore indicated.
- (iv) several of the private monitored private boreholes have high chloride contents, for local point-source reasons. This can potentially distort the shallow aquifer characterisation; in fact pumped water from those wells which are local to the study area, both urban and rural, typically have chloride content <50mg/l, not dissimilar to the mean of that encountered in the multi-levels.
- (v) from the initial results of multi-level sampling, chloride seems to be indicating quality stratification.

These initial results indicate that chloride shows potential to act as an urban recharge indicator, although care is required in interpretation given the multiple potential sources in the urban environment (e.g. wastewater, road de-icing runoff, landfill leachate and industrial use of sodium hypochlorite), the overlap with naturally-occurring chloride content in the receptor aquifer and rural sources (from fertiliser) further afield.

SULPHATE

- (i) Sulphate concentrations in wastewaters sampled to date are also on average higher than those in local deep groundwater, typically more than twice as high, but like chloride there is overlap in maximum values.
- (ii) this difference is much less marked in shallow groundwaters in the vicinity, where sulphate is typically of the same order as that in the wastewater.
- (iii) unlike the chloride trend, waters from the upper part of the aquifer in the vicinity of the study area seem to have markedly higher sulphate content compared with deeper waters.
- (iv) initial results from the multi-levels indicate that these shallow aquifer sulphate concentrations can vary widely, both with depth and from site to site and again depth stratification can be observed.
- (v) as with chloride, some high sulphate results from the rural private well network need to be disregarded as local effects and not of urban recharge interest.

Table 5.1 Ranges and mean concentrations of potential urban recharge indicators

Indicator	Concentration												
	Groundwater						Inputs			Urban outputs			
	PS boreholes vicinity of study area		Private boreholes		ML Piezometers & P1, P2 (0-30 mbgl)		ML Piezometers (30-60 mbgl)		Precip- itation	WTW Supplied water**		Waste water	
	Mean [•]	Range	Mean*	Range*	Mean	Range	Mean	Range	Mean	Mean	Range	Mean	Range
Chloride (mg/l)	39	15-85	50	17-112	44	10-184	40	12-113	2.1	34	26-41	72	60-85
Sulphate (mg/l)	39	18-97	128	15-323	84	37-153	84	11-165	2.8	36	27-46	90	80-100
Boron (µg/l)	-	<50-50	-	<80-150	-	<80-140	-	<80-100	-	-	-	500	400-600
Ortho-phosphate [§] (µg/l)	14 [‡]	5-130 [‡]	-	100-500	-	300-600	-	300-600	-	620	<63-950	31000	28000- 33000
Zinc (µg/l)	-	<6-230	66	10-320	10	6-16	7	4-16	-	-	-	81	69-99
Potassium (mg/l)	2.6	1.9-2.9	7.8	1.4-32	5.8	1.7-16.2	3.2	1.3-7	0.08	2.7	2.3-2.9	20.2	17-25

The mean is not shown where the majority of the analyses are below the limit of detection

* Excluding Sandall Common Farm (local point source pollution from mine drainage suspected)

** Blended water supplied to study area from Nutwell water treatment works; mix of AR, BP, NU, TH,

• For illustrative purposes only, averages of individual well means were used for this complex dataset

§ BGS data for total P assumed to be PO₄

‡ Data period 4/1979-4/1990 inclusive; no later analyses available

Its value as an urban recharge indicator in Bessacarr-Cantley is not yet established. While the results show both stratification with higher concentrations in the shallow aquifer, it is quite possible that the sulphate may, at least in part, be of formation origin, from gypsiferous horizons within the Sherwood Sandstone. If so, the likelihood that gypsum is naturally present in some horizons may constrain its interpretative value, as it could easily mask or mimic the influence of wastewater recharge, especially as the wastewater/groundwater concentration ratio is not particularly high. Sulphate may also be derived from the use of ammonium sulphate fertilisers.

BORON

- (i) Although only sporadically measured, the few results available indicate low natural boron concentrations in groundwater from the Sherwood Sandstone, irrespective of depth. Results are almost universally less than current YW detection limits of 50-100 µg/l.
- (ii) in contrast boron concentrations in wastewater so far sampled, at about 500 µg/l are at least 5 times greater.
- (iii) initial values from the multi-levels are at or below minimum detection limits, and no stratification is observed.

In contrast to initial results from the case-study city of Rastatt, boron has proved so far to be a disappointing indicator. The detection limit of 80 to 100 µg/l which was obtained for the laboratory runs containing these samples was too high to discriminate small variations, but even if this were improved for future samples, these would be in the 0-100 µg/l range, implying that even if a pattern were detected, dilution/attenuation effects appear to be significant.

ZINC

- (i) Zinc concentrations in the wastewaters sampled so far are low at 100 µg/l or less
- (ii) this is well within the range for the relatively few analyses available for the deeper aquifer, but tends to be several times greater than that found in local private wells
- (iii) nevertheless, the multi-level initial results reveal only very low concentrations of less than 20 µg/l in the aquifer down to 60m depth.

Zinc does not look promising as an urban recharge indicator at this stage.

OTHER INDICATORS

Based on the above observations, it is proposed to assess whether another indicator could be introduced, replacing zinc and boron. Possible candidates include potassium, dissolved organic carbon (DOC) or dissolved organic nitrogen. An organic compound possibility might be the relatively persistent and soluble fuel additive MTBE (methyl tertiary butyl ether), although little is known about its background concentrations in UK aquifers.

5.2 OVERALL MAJOR-ION CHEMISTRY

Figures 5.1 to 5.3 gather together key results from YW pumping stations and the monitoring network for comparative purposes. These show that:

- (i) Local public supply boreholes can have quite variable major anion constituents that for parameters like TON and Cl seem to be related more to catchment activities than to the borehole depth (Figure 5.1). Thus TON, certainly with a high proportion of anthropogenic origin, is significantly higher in the deep AR borehole array than it is in the rather shallower TH boreholes, and these in turn have a similar TON to the shallower Cantley Water Tower borehole. There is a suggestion that a shallower screen/openhole top depth tends to result in higher TON, and this would be consistent with influence of infiltration of modern recharge influenced by catchment activities.
- (ii) Sulphate concentrations do not seem to fit in with depth-related, screen setting or rural/urban catchment patterns and this may imply a formation control at work, perhaps related to relative occurrence of local gypsiferous horizons.
- (iii) Major ion character for both shallow and deeper pumped aquifer waters is similar in type and variability (Figure 5.2). Groundwaters from RB and the nearby Cantley Water Tower are very similar in type, although the former is 145-147m deep and the latter only 65m deep. Similarly, at the other end of the data array, the low nitrate public supplies at BP and TH are similar to Doncaster Racecourse, despite the former being much deeper than the latter (120-180 m compared with 41 m deep).
- (iv) Nevertheless, some shallow waters do have a higher solute content, as indicated by the SEC measurements in Figure 5.3.
- (v) wastewaters monitored in the detailed study area have higher concentrations of major ion constituents than groundwaters in the same general area, but not conspicuously so (Figure 5.3). Using SEC as an indicator of total dissolved solids, groundwater mineralization can range from less than half to more than 80% that of wastewater.
- (vi) the character of the wastewater solute load is only moderately distinctive from nearby groundwater. For instance, while wastewater chloride concentrations appear to be about twice those in the nearby aquifer, sulphate concentrations are about twice those in the deeper aquifer but in the same general range for the shallow zone of the aquifer. The wastewaters have a much higher relative content of PO_4 , Na and K than the groundwaters, and this appears to be rapidly attenuated during infiltration, possibly by and/or ion-exchange.
- (vii) the presence of aerobic/anaerobic features in different aquifer locations may provide a surrogate indicator of the relative ease or otherwise with which urban recharge can occur.

5.3 RE-EVALUATION OF THE CONCEPTUAL MODEL

Although the water-quality data reviewed and collected for the AISUWRS project to date do not yet give a clear or consistent picture of the flow systems and hydrogeochemical processes occurring in the Sherwood Sandstone aquifer in the Doncaster area, a number of characteristics have emerged. The conceptual model clearly needs some revision; this will be undertaken in the final report on the fieldwork programme once all the data have been collected.

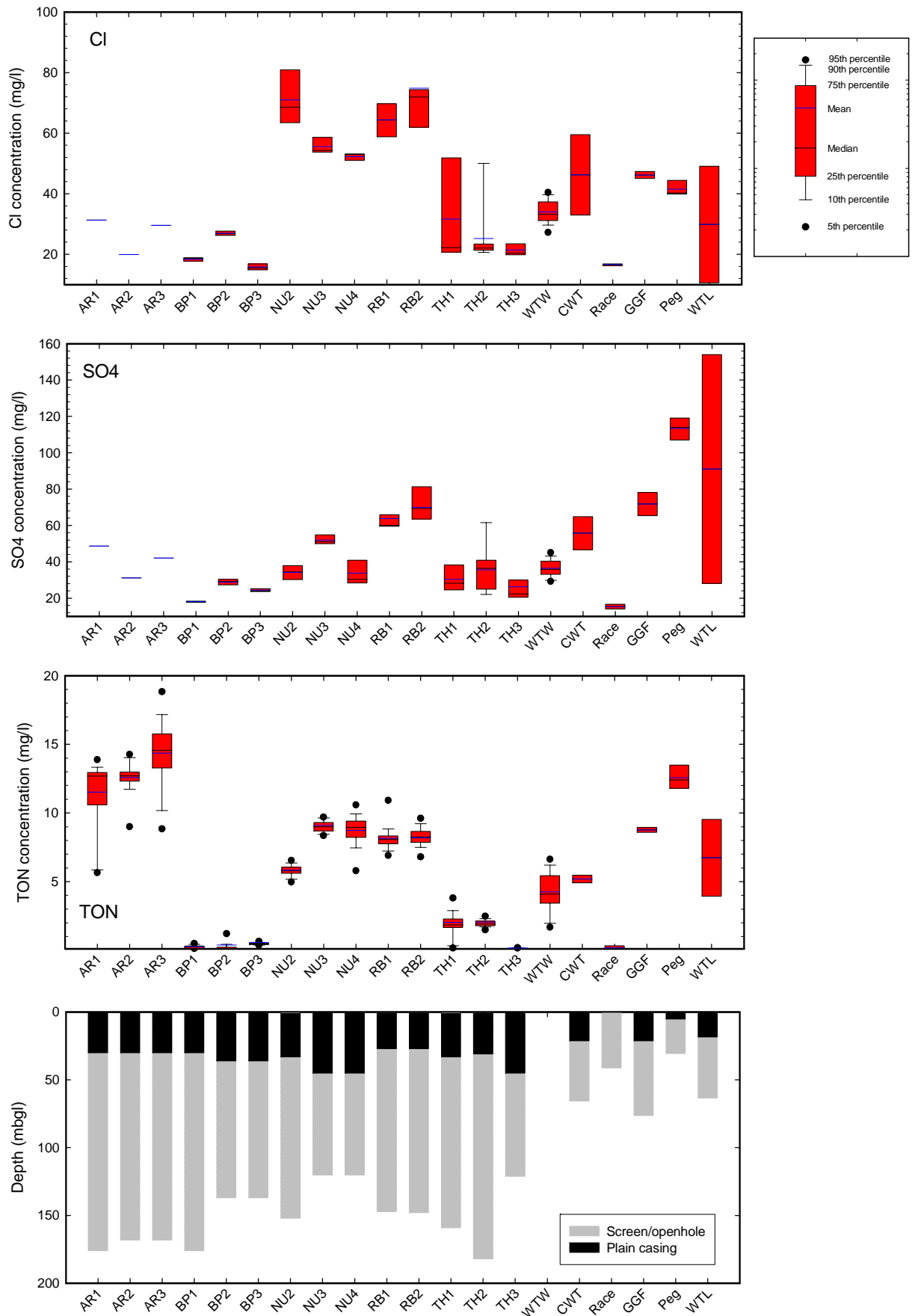


Figure 5.1 Comparison of key major constituents TON, SO4 and Cl for public supply and private boreholes in the general vicinity of Bessacarr-Cantley

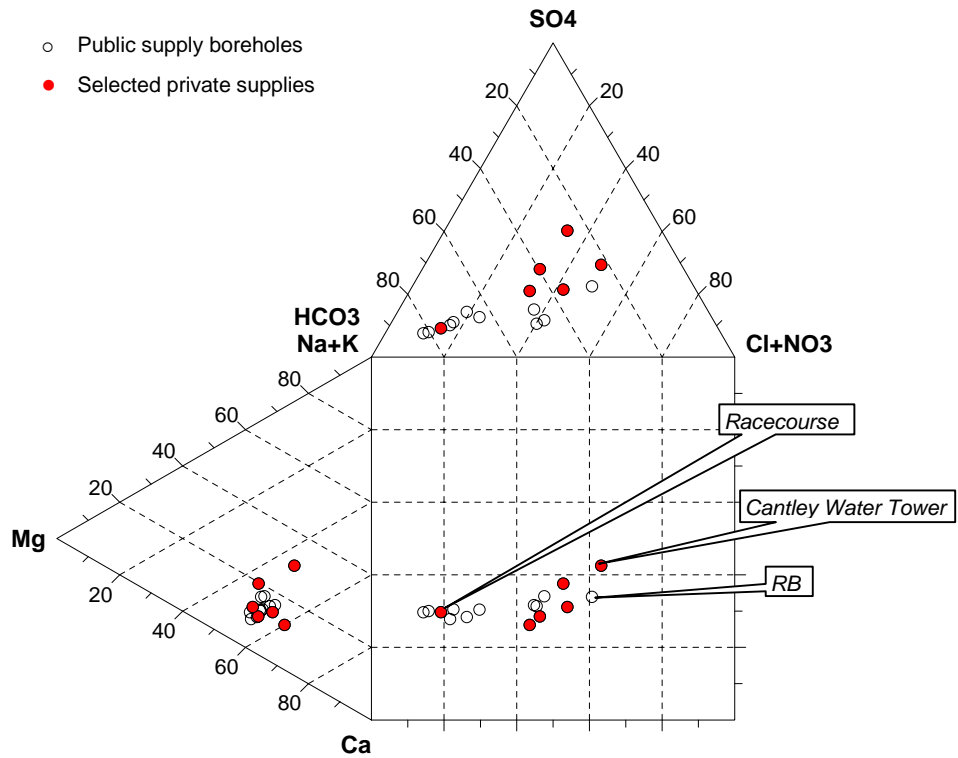


Figure 5.2 Durov plot of average water quality in public supply boreholes and private supplies for the Bessacarr-Cantley study area.

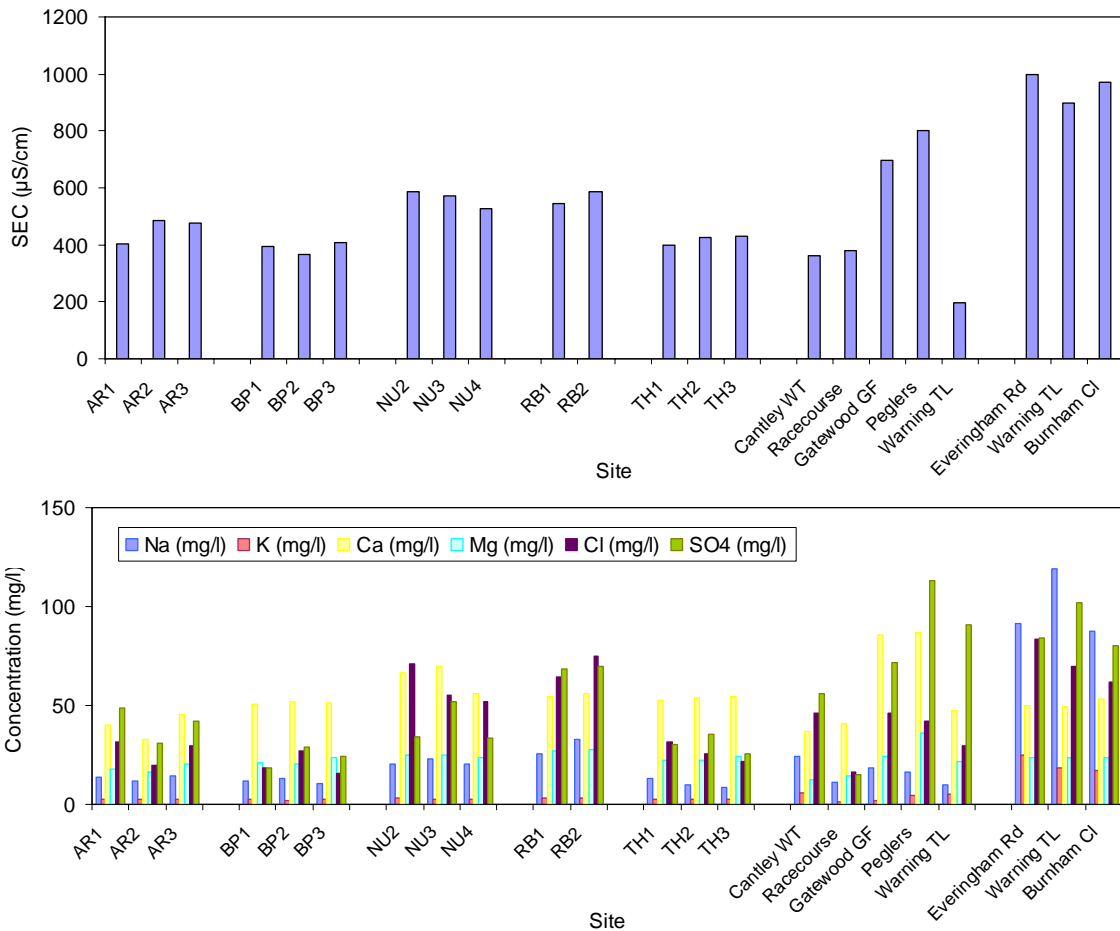


Figure 5.3 Comparison of electrical conductivity (SEC) and major constituents in public supply boreholes, private supplies and wastewater, Bessacarr-Cantley area.

6 Conclusions and recommendations

The main conclusions and recommendations from this phase of the programme are:

- (i) A developing programme of local groundwater monitoring has complemented an array of water quality data mainly derived from operational public water supply boreholes in the Doncaster wellfield operated by the project stakeholder Yorkshire Water.
- (ii) This monitoring array includes a set of local private supplies chosen to try to characterise the shallow Sherwood Sandstone east of Doncaster, and a local array for the focus area of the study (Bessacarr-Cantley district) comprising multilevel research boreholes and wastewater sampling sites.
- (iii) Data from the public supply boreholes and from the monitoring network have been evaluated in order to develop and then validate a conceptual model of the flow system and its likely effect on groundwater quality in the urban and periurban area.
- (iv) This conceptual model recognises that the Sherwood Sandstone east of Doncaster, as an intensively exploited unconfined aquifer with urban, rural, industrial, agricultural and mining activities at the land surface, is a complex system. The presence of variable Quaternary superficial deposits across the aquifer outcrop/subcrop adds to this complexity.
- (v) Initial interpretation suggests that there is significant variability both laterally across the aquifer system and with depth. No spatial pattern to the variability indicated by the datasets has yet been discerned.
- (vi) Initial wastewater sampling results indicate that while sewered waters have higher concentrations of major ion constituents than groundwaters in the same general area, the difference is not conspicuous, and the resulting effluent would be regarded as dilute in comparison with the groundwater receptor.
- (vii) These relatively small differences, for instance in chloride and sulphate indicator concentrations between wastewaters and the parent groundwater forming the supply to the study area will constrain their interpretative use in mass balance calculations later in the project.
- (viii) Consideration of the analytical results from the monitoring network indicate that a mid-term review of the monitoring strategy is required in order to concentrate effort on understanding processes in the Triassic aquifer in the immediate neighbourhood of the study area. This would imply some revision of the sampling programme, a closer focus on the 5 YW pumping stations either supplying the study area or located in its vicinity, and further inspection of data to assess whether an additional recharge indicator such as potassium, dissolved organic carbon or dissolved organic nitrogen can be identified to replace one or other from the present selection.
- (ix) The current minimum detection limits for boron do not permit discrimination of small variations in concentrations below 100µg/l; analysis by ICP-MS needs to be considered if B is to continue to be viewed as an urban recharge indicator.
- (x) Work continues to determine whether different elements of the flow system can be characterised by their chemical compositions, thereby allowing shallow recharge beneath the city to be characterised chemically.

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