

# Combined isotopic and modelling approach to determine the source of saline groundwaters in the Selby Triassic sandstone aquifer, UK

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**Abstract:** Groundwater abstraction from the Triassic Sherwood Sandstone aquifer in the Selby area, Yorkshire, UK, has caused decline of the water level in the aquifer and groundwater quality problems such as high chloride and sulphate concentrations. Geochemical and isotopic analysis of groundwaters and groundwater modelling of an approximately 25 × 30 km area around Selby was carried out to understand the groundwater flow conditions and identify the source of saline water. Isotopic compositions ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ ) of seawater sulphate, Coal Measures brine and Permian evaporite sources do not match that associated with salinity in the Selby wellfield. Rather, the source of saline groundwater in the Selby wellfield matches the isotopic composition of Triassic evaporites in the overlying Mercia Mudstones.

Steady-state groundwater flow modelling demonstrates that that majority of water abstracted from the Selby wellfield is balanced by recharge from the west of Selby at Brayton Barff, and from the Escrick and York moraines to the north. A small proportion of the abstracted water originates from leakage from the River Ouse through the confining layer as a result of drawdown in the Selby area. The development of a cone of drawdown centred on Selby has created a new E–W hydraulic gradient to the east of Selby, allowing water ingress from the east. Capture-zone analysis indicates that the four abstraction boreholes contaminated by saline water collect groundwater from the north to NE (i.e. from the direction of the boundary between the Sherwood Sandstone and the Mercia Mudstone), confirming that the source of salinity is likely to be the Mercia Mudstone evaporites.

Groundwater is an important water resource. In the UK, 80% of the total groundwater abstraction is from only two aquifers, the Cretaceous chalk (54%) and the Triassic sandstone (26%) (Owen *et al.* 1991). Incursion of saline waters into aquifers is a very common cause of lowered groundwater quality and, ultimately, loss of groundwater resources (Todd 1980). Marine incursion is the usual cause of increased groundwater salinity in coastal aquifers in hydraulic continuity with the sea, but in other situations a variety of sources of salinity can be involved. Brines from different sources often have similar chemistry (Tellam & Lloyd 1986; Tellam 1995), making distinction between different brine sources difficult from chemical analyses alone.

The town of Selby in East Yorkshire has a number of flour and feed mills and other industrial sites that have private abstraction wells in the Sherwood Sandstone aquifer. Abstraction at boreholes in the Selby wellfield wells has taken place for over 100 years at increasing rates, and in the 1970s some wells began to be affected by increases in salinity. This increase was severe enough in some cases to mean that wells were abandoned. In order to constrain the probable causes of increased salinity of these waters, a

dual approach has been adopted. Isotopic compositions of sulphate from wells affected by salinity increases have been compared with those of sulphate associated with different potential sources of salinity, as a possible 'fingerprint' of the source involved; and to test whether, and under what conditions, the sources identified might realistically contribute salinity at the Selby wellfield we have also modelled groundwater flows within the aquifer.

## Geology and hydrogeology of the Selby area

The geology of the study area is shown in Figure 1. Quaternary deposits ('drift') cover the Triassic Sherwood Sandstone, except for a small sandstone outcrop area at Brayton Barff. The area where drift is absent is relatively high ground. The ground elevation of the study area rises from 10 m AOD (metres above Ordnance Datum) in the SE to over 30 m AOD in the NW and at Brayton Barff. To the east of study area, the Sherwood Sandstone Group is overlain by the Triassic Mercia Mudstone Group (approximately 14 km from Selby town). The Sherwood

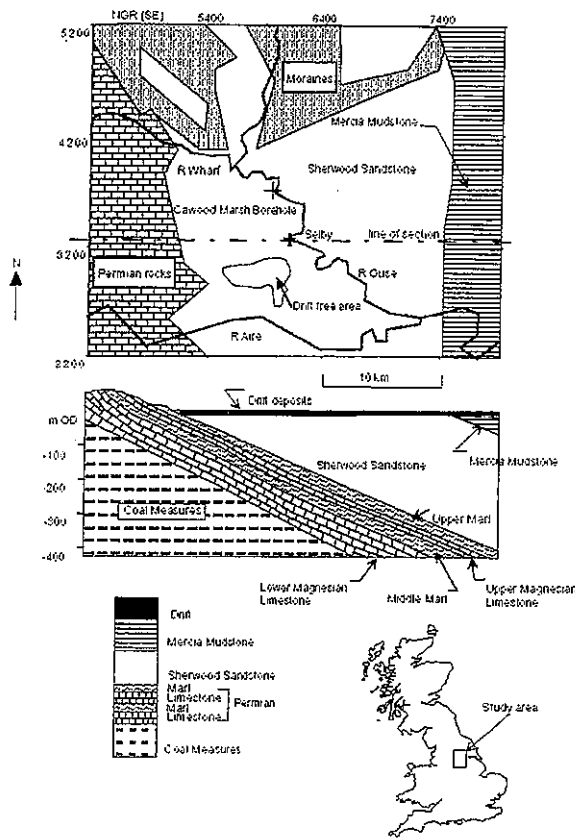


Fig. 1. Geological map and section for the Selby area, UK. NGR, national grid reference (data supplied by Environment Agency).

Sandstone is underlain by the Permian Marls and the Permian Magnesian Limestones, which crop out to the west of the study area. The Permian rocks themselves unconformably overlie Carboniferous Coal Measures strata and, until 2004, coal was deep-mined from these strata in the Selby coalfield.

The sandstone dips towards the east at a regional angle of about  $2^{\circ}$ – $4^{\circ}$  and increases in thickness from its feather-edge in the west to 400 m in the east. The thickness at Selby is around 180 m. The sandstone aquifer is confined below by the Upper Permian Marl. Pumping test transmissivity values for the sandstone aquifer in the York, Selby and Goole areas are  $50$ – $400$   $\text{m}^2 \text{day}^{-1}$ ; analysis of the trend of transmissivity data with borehole depth suggests hydraulic conductivity values in the range of  $1.8$ – $4$   $\text{m day}^{-1}$  (Allen *et al.* 1997). Hydraulic conductivity values estimated from core samples of the sandstone of the Yorkshire area range from  $0.18$  to  $2.2$   $\text{m day}^{-1}$  (Reeves *et al.* 1975; Lovelock 1977), which suggests that perhaps half of the flow into some of the more transmissive boreholes is via fractures. A significant proportion of this flow may occur via E–W

faults that are known to be present in the area (L. Brown pers. comm. 2003).

Recharge to the aquifer can take place as infiltration of precipitation through the drift (or directly into the sandstone at Brayton Barff) or by leakage from the rivers Aire and Ouse that cross the area. The majority of Quaternary drift covering the area is comprised of lacustrine clays and silts with low hydraulic conductivity, formed in pro-glacial and moraine and sea ice-dammed lakes during the Devensian glacial period (Cooper & Gibson 2003). However, to the north and west of the area (see Fig. 1) a complex pattern of sand and gravel deposits associated with the York (Askham) and Escrick moraines and intervening kames provides a far more permeable recharge pathway to the aquifer.

Owing to heavy abstraction in the Selby wellfield and in the Brayton Barff recharge zone, water levels have fallen significantly in recent decades (Fig. 2). The groundwater head dropped more than 8.0 m between 1984 and 1992. As a result, a huge cone of depression has been created by the abstraction at Selby, which appears to influence the groundwater flow direction within the whole study area. This hydrographic change has been accompanied by a dramatic increase in salinity (chloride and sulphate concentrations) in some of the wells within the Selby wellfield area.

## Sources of salinity

### Possible sources of salinity

The hydrogeology of the aquifer means that there are several possible sources for the salinity affecting the Selby wellfield: the brines and evaporites in the Permo-Carboniferous rocks below the Sherwood Sandstone Group; the

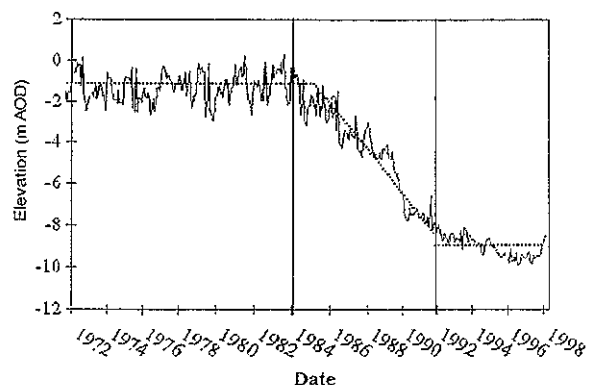


Fig. 2. Hydrograph of an observation borehole in Selby. m AOD, metres above Ordnance Datum.

brines and the evaporites in the Triassic sequence; and Quaternary or Recent marine incursion.

#### *Sources in Permo-Carboniferous rocks below the Sherwood Sandstone*

Upwards migration of brines from Permian evaporites or Coal Measures strata that underlie the Sherwood Sandstone (Fig. 1) have been invoked as possible sources of the saline waters (Aldrick 1976; Stagg 1995), possibly related to deep coal-mining activity and subsidence-related faulting. This migration is a possibility if the aquifer were in hydraulic continuity with groundwaters in the underlying strata, as depression of the groundwater head in the vicinity of the Selby wellfield could induce upconing of underlying denser brines.

Deep brines derived by dissolution of underlying Permian evaporites do occur in the Sherwood Sandstone further north in Cleveland, where hydraulic continuity is provided by fracturing of the intervening marl units (e.g. Bottrell *et al.* 1996). The Triassic and older sediments of the Selby area are affected by a series of ENE–WSW-trending faults that could possibly provide hydraulic continuity if permeable; none of these faults have sufficient throw to juxtapose Sherwood Sandstone directly against Permian evaporites. Strongly saline groundwater ‘formation water’ is also found in sandstones within the Carboniferous Coal Measures (e.g. Edmunds 1975; Sheppard & Langley 1984) and is a possible source of salinity in the Triassic aquifer. However, mine dewatering has reduced groundwater head in the underlying Coal Measures strata, which could act against any tendency for upward migration of brines.

#### *Sources in Triassic rocks*

Continental evaporite deposits are known from the Triassic Sherwood Sandstone; for example, elevated sulphate concentrations in the confined parts of the Birmingham aquifer are attributed to dissolution of gypsum and/or celestobarite that formed as authigenic phases under evaporative conditions (Jackson & Lloyd 1983; Hughes *et al.* 1999; cf. Sullivan & Koppi 1995). Much more significant deposits of evaporites occur within the overlying Mercia Mudstone, from which gypsum is worked commercially (Taylor 1983; Harvey & Stewart 1998). Saline groundwater could enter the Sherwood Sandstone from the Mercia

Mudstone in the eastern, confined part of the aquifer.

#### *Quaternary or Recent marine incursion*

The river Ouse is tidal within part of the area under study, but is not saline or brackish, so saline incursion into the aquifer by leakage of estuarine water is unlikely at the present day. However, infiltration of seawater into the eastern part of the aquifer could have taken place under higher sea-level conditions than at present during previous Quaternary interglacials.

#### **Isotope composition of sulphate as a tracer of source of salinity**

Sulphate molecules contain oxygen and sulphur, both of which exhibit measurable natural variation in their stable isotopic composition and can be used as a ‘fingerprint’ of different sulphate sources (e.g. Robinson & Bottrell 1997; Hughes *et al.* 1999). At environmental temperatures and near-neutral pH of most groundwaters, sulphate is resistant to isotopic exchange on timescales of several 100 000 years (Lloyd 1968). Only bacterial sulphate reduction can modify sulphate isotopic compositions markedly, so, provided groundwater redox potentials have remained sufficiently high to prevent this from occurring, sulphate isotopic compositions can act as a powerful tracer for different sulphate, and thus brine, sources. In the Selby aquifer redox potential ( $E_H$ ) measurements are not made as part of routine monitoring and were not made specifically for this study. However, a compilation of existing data for the Selby area groundwaters by Stagg (1995) shows that groundwater  $E_H$  has small positive values (+2 to more than +100 mV). Sulphate reduction typically occurs at  $E_H$  around –400 mV and thus sulphate in the Sherwood Sandstone groundwaters is unlikely to have been affected by sulphate reduction.

#### **Methods**

##### *Samples collected and analyses performed*

Permian marl evaporites were collected as chipping samples from an RJB Mining proving borehole at Cawood Marsh, North Yorkshire ([NGR SE5880 3718], see Fig. 1). Coal Measures water samples were collected at water ingress points into mines in the Selby coalfield. Groundwater samples were also collected from

boreholes into the Magnesian Limestone used for water supply at some mines, as well as observation and producing wells in the Sherwood Sandstone aquifer and the Selby wellfield, an observation well in the Mercia Mudstone and shallow monitoring wells in Quaternary drift deposits. Samples for  $\delta^{13}\text{C}$ -DIC (dissolved organic carbon) analysis were collected according to Bishop (1990) and DIC recovered as  $\text{SrCO}_3$  for analysis by the method of McCrea (1950). Evaporite-bearing marl and shale samples were leached with distilled water for 7 days to extract soluble ions. Anion concentrations of leachate and groundwater samples were measured using a Dionex DX-100 ion chromatograph. Cation compositions of groundwater samples were measured by ICP-OES (inductively coupled plasma-optical emission spectroscopy). Sulphate was recovered from leachates and groundwaters by precipitation as  $\text{BaSO}_4$  at pH 3 and approximately  $70^\circ\text{C}$  and analysed for  $\delta^{18}\text{O}$  (McCarthy *et al.* 1998) and  $\delta^{34}\text{S}$  (Halas *et al.* 1982) using a VG SIRA 10 isotope ratio mass spectrometer. Isotopic data are reported in standard delta ( $\delta$ ) notation as per mil (‰) deviations from the Cañon Diablo Troilite (CDT) standard for sulphur, Standard Mean Ocean Water (SMOW) standard for oxygen and Pee Dee Belemnite (PDB) for carbon.

### Groundwater modelling

**Model design.** In order to understand the present groundwater flow conditions and identify a saline water source, groundwater modelling was carried out using the MODFLOW code (McDonald & Harbaugh 1988), followed by particle-tracking analyses using the MODPATH code (Pollock 1989). The groundwater level of the sandstone aquifer in the Selby cone of drawdown dropped more than 8 m between 1984 and 1992 after which it stabilized (Fig. 2). There were not enough data available to construct a model to simulate the pre-1984 water-level conditions, so a steady-state model was developed to simulate the post-1992 conditions, using average water levels measured by the UK Environment Agency in 14 observation wells between 1992 and 1996. Preliminary modelling used two layers to represent the Quaternary drift and the Sherwood Sandstone Group, respectively. This modelling showed that, under steady-state conditions, the drift layer is not permeable enough to permit significant lateral flow and simply transmits recharge to the underlying sandstone. Hence, the further modelling work reported here did

not explicitly model flow in the drift layer, although Quaternary deposit characteristics were used to infer recharge rates to the sandstone.

An approximately 30 km E-W by 25 km N-S area of the aquifer was modelled; Figure 3 shows the model boundaries. The northern model boundary is where the highest groundwater levels are observed and is thought to be a groundwater divide, and hence is defined as a no-flow boundary. The eastern boundary represents the edge of the overlying Mercia Mudstone. In steady-state flow conditions, groundwater flow across this boundary will be very small, because of the deep confined nature of the aquifer to the east. Hence, it was assumed to be a no-flow boundary. In fact, a small amount of water is likely to have been drawn across this boundary from the confined zone during the period of transient drawdown prior to 1992. The western model boundary, and the lower boundary of the model, represent the contact between the Sherwood Sandstone and the underlying Upper Permian Marl. As the Upper Permian Marl has a relatively low permeability, and faults passing through it have insufficient throw to juxtapose the sandstone against the Upper Magnesian Limestone below, this boundary was assumed to be a no-flow boundary. The southern model boundary is defined by the position of the River Aire, and a constant head boundary, based on piezometric levels measured in Environment Agency observation wells, was assumed.

The topology of the top of the Sherwood Sandstone was obtained by kriging data from 70 boreholes penetrating the superficial deposits; the topology of its base was inferred from 35 boreholes penetrating to the base of the group, and from the position of its feather edge.

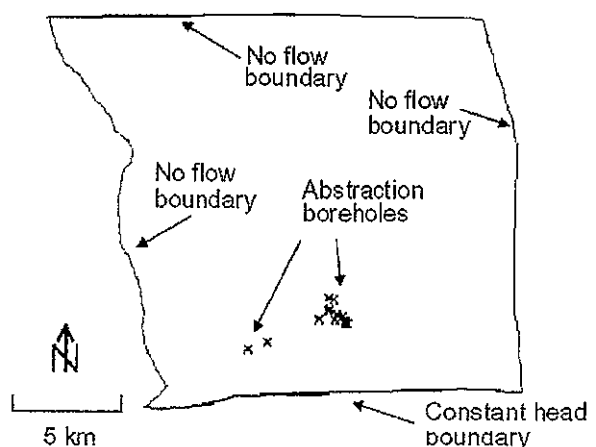
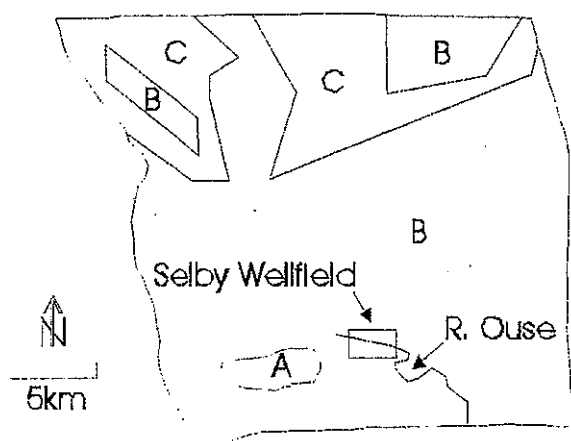


Fig. 3. Model boundary conditions.

These data indicate that the Sherwood Sandstone Group was up to 400 m thick in the eastern part of the modelled area. However, a plot of transmissivity v. effective aquifer thickness (i.e. borehole depth) shows that transmissivity tends to increase with thickness up to 100 m, but then remain approximately constant. Furthermore, a few very high transmissivities ( $>600 \text{ m}^2 \text{ day}^{-1}$ ), thought to be associated with fracturing, are seen in boreholes less than 100 m deep. These data suggest that most flow occurs in the upper 100 m of the aquifer (Allen *et al.* 1997), so the model layer thickness was restricted to a maximum of 100 m.

The characteristics of the Quaternary deposits overlying the sandstone were used to define three recharge zones, labelled A, B and C in Figure 4. Zone A is the area around Brayton Barff where the sandstone is not covered by drift. Here, it was assumed that all available water flows into the sandstone. A recharge rate of  $250 \text{ mm year}^{-1}$ , was calculated from rainfall minus actual evaporation data supplied by the UK Meteorological Office. In drift-covered areas recharge rates will depend on the permeability of the drift sequence, which controls the proportion of recharge lost to field drainage systems. Two zones were defined according to the nature of the superficial deposits, as described on geological maps and sheet memoirs (Edwards *et al.* 1950; Institute of Geological Sciences 1973) and seen in observation well logs supplied by the Environment Agency. In Zone C, in the northern sector of the modelled area, the superficial deposits consist of glacial sands and gravels associated with the



**Fig. 4.** Model recharge zones. Zone A, Brayton Barff recharge window (unconfined sandstone); Zone B, Vale of York glaciolacustrine deposits and till (mainly silts and clays); and Zone C, Escrick and York moraines and associated kame deposits (sands and gravels).

Escrick and York moraines and intervening kame deposits. In Zone B, which covers the majority of the study area, the superficial deposits comprise mainly glacio-lacustrine silts and clays with interbedded sands. River alluvium overlies these glaciolacustrine deposits in the river valleys. It was assumed that direct recharge was zero in Zone B, because of: (i) the low-permeability nature of the silt and clay deposits; and (ii) the extensive nature of the agricultural deep drainage, which has lowered the hydraulic head in much of the drift in the area to below that in the aquifer during the summer months. The recharge rate in Zone C (sands and gravels of the York and Escrick moraines) was found from model calibration to be  $16 \text{ mm year}^{-1}$ . Although this recharge rate seems low compared to that in the drift-free area at Brayton Barff ( $250 \text{ mm year}^{-1}$ ), it provides a significant proportion (33%) of the recharge because of the relatively large area of Zone C.

The rivers Wharf and Ouse cross the model area as shown in Figure 4. Over most of the modelled area, these rivers are floored by fine-grained alluvium, so their hydraulic connection with the aquifer is likely to be weak. However, in Selby the River Ouse has been dredged to allow navigation, and piezometric levels are well below river levels due to the cone of drawdown. Furthermore, chemical data discussed in the results section below (see Table 3 later) suggest that recharge from the overlying Quaternary drift deposits makes up, on average, 6% of abstracted water in the Selby wellfield. To incorporate this recharge into the model, river leakage via the drift was specified such that Ouse river water comprised 6% of the abstracted well water. The river conductance required was consistent with a hydraulic conductivity for the intervening drift layer of  $0.01 \text{ m day}^{-1}$ , assuming 10 m drift thickness and a 15 m-wide river channel. However, the sensitivity of the flow model and particle-tracking analyses to the magnitude of river leakage was low.

The hydraulic conductivity of the sandstone aquifer was assumed to be uniform and was used as a calibration parameter; a value of  $3 \text{ m day}^{-1}$  provided the best match when aquifer flowing thickness was restricted to 100 m. This value is consistent with aquifer transmissivity values measured in the area but higher than most core measurements, which suggests that fracture flow may be significant. Abstraction data for the Selby wellfield and the wells in the Brayton Barff area were supplied by the Environment Agency; these data show that

abstraction was approximately constant over the modelled period. Changes in hydraulic head at the northern and eastern boundaries over the modelled period were less than the seasonal variation (c. 0.5 m).

MODFLOW's performance is primarily dependent on the application of a sufficiently fine grid (Haitjema *et al.* 2001). In this model a finer grid spacing was used around wells than in other areas. The grid spacing ranged from 50 m close to wells to 500 m at the edge of the model. The total number of cells was 79 279 and the total model area was approximately 574 000 000 m<sup>2</sup>. Mesh-refinement exercises showed that this discretization was sufficiently fine.

### Model calibration

Calibration was performed using measured water levels in 14 observation boreholes penetrating the sandstone. In this study, sensitivity analyses to Zone C recharge and hydraulic conductivity were carried out to match the average water level values for the 1992–1996 period. Modelled *v.* target head values are shown in Figure 5, and the groundwater head contours and residuals are shown in map form in Figure 6. In general, mismatches between the observed and target values are less than 2 m, which is similar to the range of fluctuation seen in many of the boreholes for data collected between 1992 and 1996. Thus, it is considered that the model adequately represents the aquifer flow.

**Water budget.** The water budget for the steady-state model is summarized in Table 1. The sources of most inflow are recharge from the Brayton Barff outcrop area (40%), recharge through the York and Escrick moraines (33%),

leakage from the river Ouse in the Selby area where the groundwater heads are depressed (6%) and inflow from the constant head boundary in the SE where the hydraulic gradient is northwards as a result of the Selby abstractions (21%). The main discharges are well abstraction (92% of total discharge); the remaining discharge occurred across the constant head boundary in the SW, directly south of the Brayton Barff recharge area.

**Well capture-zone analysis.** To identify the source zones of the abstraction boreholes, capture-zone analysis was carried out using the MODPATH particle tracking code (Pollock 1989). The MODPATH code uses the cell-by-cell flow terms that are created by the MODFLOW simulation to determine particle movement directions and rates. Particle travel time analysis also requires a flowing (kinematic) porosity and a travel time to be specified. The flowing porosity of the Sherwood Sandstone is much lower than the total porosity (Allen *et al.* 1997). This is because a significant proportion of flow may be concentrated in fractures or faults, or relatively coarse-grained sandstone units that make up a low volumetric proportion of the sequence (Truss 2004). Here, a value of 5% was assumed. The particle travel time was specified as 100 years, on the grounds that abstraction has been going on for at least this length of time in the Selby wellfield.

## Results

### Groundwater chemistry

Groundwater chemical data are summarized in Table 2. The compositions of pumped waters from the Selby wellfield (Prefix P in Table 2) have been modelled in terms of mixtures of

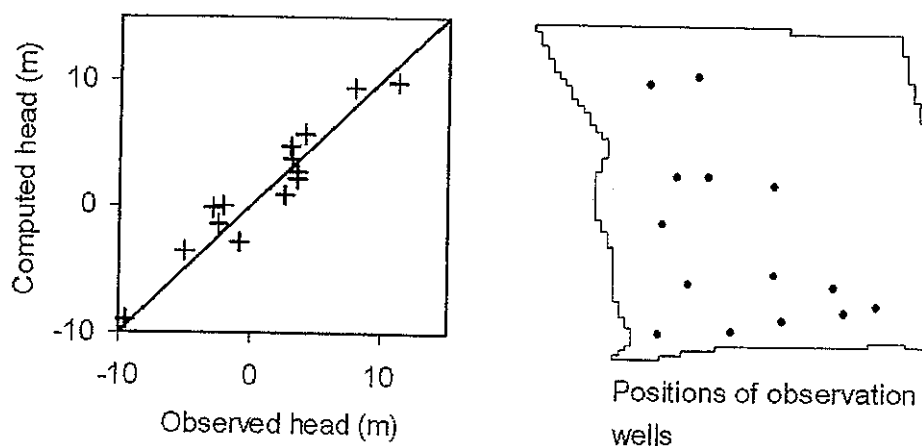


Fig. 5. Relationship between observed and computed hydraulic head, and positions of observation wells.

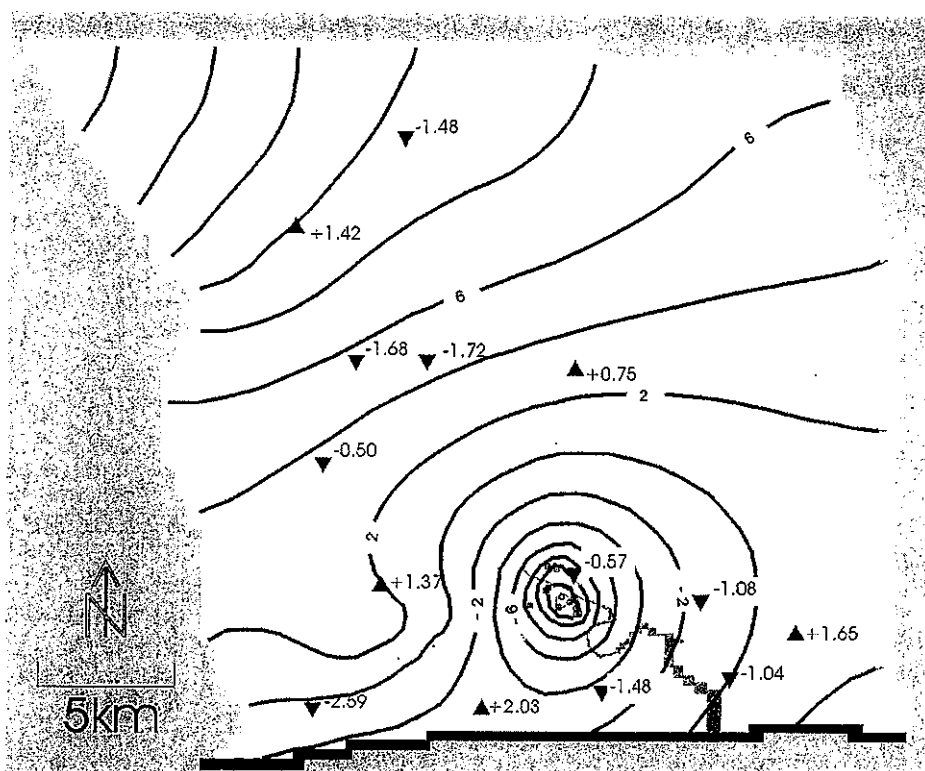


Fig. 6. Contour map of modelled hydraulic heads (m AOD) and differences from calibration targets (m, observed - computed).

Table 1. Water balance for steady-state model

Inflows	m <sup>3</sup> day <sup>-1</sup>	%	Outflows	m <sup>3</sup> day <sup>-1</sup>	%
Zone A (Brayton Barff)	5970	40	Abstraction	-13 590	92
Zone C (York and Escrick moraines)	4940	33	Southern boundary	-1220	8
Southern boundary	3090	21			
River Ouse	810	6			
Total	14 810	100		-14 810	100

three water types: aquifer water outside the cone of depression of the Selby wellfield; groundwater from wells in Quaternary drift; and Triassic evaporite brine. End-member compositions are based on representative analysed compositions of these water types (Table 2). Calculations used the NETPATH code (Plummer *et al.* 1991). The chemistry of many of the Selby wellfield waters can be explained as a simple mixture of aquifer water (sampled outside the wellfield area) and a small brine component supplying excess chloride and other components to affected wells (Table 3). However, drawdown resulting from heavy pumping abstractions in the Selby wellfield has markedly increased the head difference between drift water and Sherwood Sandstone aquifer in the wellfield area (Fig. 2). This has

induced water leakage from the overlying drift deposits into Sherwood Sandstone aquifer and some wells require a significant additional component of drift water to generate the observed compositions (Table 3). The model predicts the  $\delta^{13}\text{C}$  of the DIC in the calculated mixture, and this is compared with the analysed  $\delta^{13}\text{C}$  of the DIC in Table 3 as a test of model fit: the majority of predictions are in good to reasonable agreement with analysed compositions.

#### Sulphate stable isotopes

*Sherwood Sandstone.* Figure 7 shows sulphate isotopic compositions plotted against chloride concentration for abstraction wells in the Selby wellfield. Wells with low chloride exhibit a very

**Table 2.** Chemical analyses of water types and pumped waters from the Selby wellfield. All units are mg l<sup>-1</sup>, except pH

Site	N*	Na	Ca	K	Sr	Cl	HCO <sub>3</sub>	SO <sub>4</sub>	NO <sub>3</sub>	pH
Aquifer water	11	15	84	2	0.04	20	379	5	b.d.	7.3
Drift water	4	30	242	3	0.43	117	250	430	73	7.1
Brine	1 <sup>†</sup>	70 000	1900	140	28	105 000	24	3600	0.43	7.93
P1	1	101	154	7	1.06	576	296	173	10	7.2
P2	1	23	146	4	0.52	37	490	297	8	7.7
P4	1	9	93	2	0.10	39	338	133	3	7.3
P6	1	58	268	5	0.05	675	248	128	11	7.3
P7	1	105	188	6	0.38	576	372	298	5	7.6
P8	1	93	224	5	0.29	891	310	205	10	7.2
P10	1	9	74	2	0.18	67	323	22	1	7.3
P11	1	10	71	2	0.13	40	343	43	1	7.7
P12	1	10	58	2	0.02	69	249	10	5	7.5
P13	1	18	132	3	0.13	65	378	324	6	7.1

\* Number of sites from which representative analysis was taken.

<sup>†</sup> Brine from Brookhouse Farm borehole, Lower Mersey Basin (Tellam 1995). This brine is a high-concentration end-member of the saline waters in the Permo-Triassic sandstones of the Lower Mersey Basin aquifer: their source is the Mercia Mudstone Group evaporites. b.d., below limit of detection.

**Table 3.** Calculated water mixtures at Selby wells. Mixtures are based on representative analysed compositions of three water types: aquifer water outside the cone of depression of the Selby wellfield; groundwater from wells in Quaternary drift; and Triassic evaporite brine. Calculations used the NETPATH code (Plummer et al. 1991) and full details are given in Yoshida (2000). Note that the chemistry of sample P-8 is the only one requiring a large component of drift water, explaining the difference in its sulphate isotopic composition from the other high-chloride waters (P1, P6 and P7), which have zero or small drift-water component

Site	Predicted fraction in groundwater			Computed $\delta^{13}\text{C-DIC}$ ‰ V-PDB	Measured $\delta^{13}\text{C-DIC}$ ‰ V-PDB
	Aquifer water	Drift water	Brine		
P1	0.97	0.00	0.03	-16.7	-15.1
P2	0.98	0.00	0.02	-13.1	-13.0
P4	0.89	0.11	0.00	-16.9	-17.3
P6	0.92	0.00	0.08	-16.6	-15.8
P7	0.90	0.06	0.04	-17.0	-16.5
P8	0.76	0.17	0.05	-16.7	-14.7
P10	0.90	0.10	0.00	-17.0	-17.3
P11	0.91	0.09	0.00	-17.0	-17.3
P12	0.76	0.24	0.00	-17.5	-15.9
P13	0.62	0.38	0.00	-17.6	-15.2

wide range of sulphate isotopic compositions, but those with high chloride are all distinctly enriched in <sup>34</sup>S and <sup>18</sup>O. The wide range of sulphate isotopic compositions in low-chloride samples reflects a variety of sulphate sources in the aquifer and drift groundwaters, but only two samples overlap the isotopic signature of the saline waters (P4 and P12 for  $\delta^{34}\text{S}$  and P4 for  $\delta^{18}\text{O}$ ). Three of the saline water samples have  $\delta^{34}\text{S}$  in the range +17.2–+17.5‰ and  $\delta^{18}\text{O}$  in the range +14.6–+15.9‰; the fourth sample (P8) has  $\delta^{34}\text{S} = +8.5\text{‰}$  and  $\delta^{18}\text{O} = +13.7\text{‰}$ . The saline

water is thus associated with an isotopically heavy sulphate source, but one sample (P8 Fig. 7) has lighter compositions than the rest. The isotopic composition of this sample can be explained by mixing with a sulphate source with lighter  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ . The light sulphate source is likely to be the oxidation of pyrite as oxygenated water is drawn through the drift deposits, as this sample contains a significant drift-water component according to the mixing model calculations summarized above in Table 3. The isotopic composition of the group of



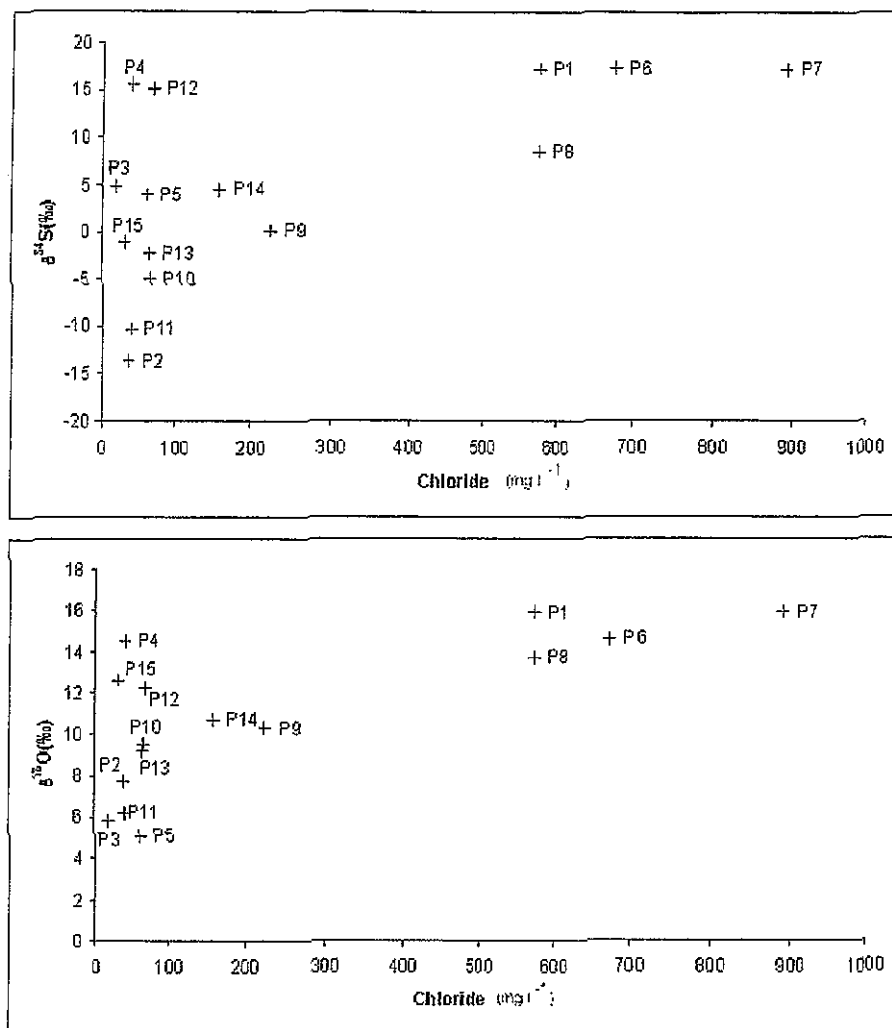


Fig. 7. Relationship between isotopic composition and chloride concentration for Sherwood Sandstone groundwater samples. (a)  $\delta^{34}\text{S}$  of sulphate and Cl concentration; and (b)  $\delta^{34}\text{S}$  of sulphate and chloride concentration.

three saline samples is thus taken to be indicative of the sulphate in the saline water source.

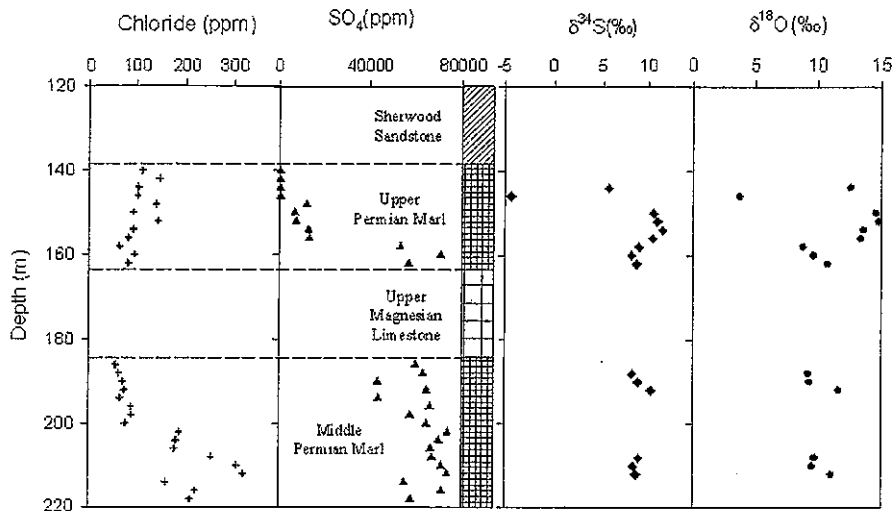
**Mercia Mudstone.** Table 4 presents the sulphate isotopic data from samples taken from the only well that intercepts Mercia Mudstone evaporite horizons in the study area. Table 4 also includes isotopic data on sulphate: in groundwater from an evaporite horizon in the Mercia Mudstone of the Cheshire Basin (Lymm Marina borehole) (Barker 1996); in groundwater from the sandstone sequence in the Mersey Basin (Gatewarth Observation borehole, Warrington, and data from Kimblin 1995); and solid samples from the Winsford Halite Mine and elsewhere in the Cheshire Basin (Taylor 1983; Hughes 1998).

**Permian Marl.** Figure 8 shows chloride and sulphate concentrations in Permian Marl drill-

chipping leachate samples. Chloride concentrations are generally low, except around 210 m in the Middle Permian Marl. Downhole geophysical logging of the Cawood Marsh borehole identified halite around 200–205 m and the origin of the elevated chloride is likely to be the halite. Much chloride will, however, have been lost by dissolution of halite into the drilling fluid before chippings could be sampled. Sulphate is low (similar to the overlying Sherwood Sandstone) in the uppermost 10 m of the Upper Permian Marl but increases substantially below this, reaching values of 50 000–70 000 ppm in the rock chippings. These high concentrations are found throughout the Middle Permian Marl. Figure 8 also shows  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of sulphate leached from the Permian marls. The upper, low-concentration samples show a wide variation in isotope composition from -4.3 to

**Table 4.** Isotopic compositions of sulphate in Mercia Mudstone groundwaters and evaporite minerals

Sulphate source	$\delta^{34}\text{S}\text{‰}$ CDT	$\delta^{18}\text{O}\text{‰}$ SMOW
Mercia Mudstone groundwater east of Selby (this study)	+17.3	+13.7
Sulphate associated with Traissic halite, Winsford Mine, Cheshire: Mean (SD) of six samples (Hughes 1998)	+17.9 (0.2)	+12.4 (0.2)
Gatewath borehole 160 m (Mercia Mudstone evaporite-derived brine present in the sandstone, Merseyside) (Barker 1996)	+16.6	+12.5
Lymm Marina borehole 160 m (Mercia Mudstone evaporite brine, Merseyside) (Barker 1996)	+15.5	+12.1
Mercia mudstone evaporitic gypsum (Taylor 1983)	+17.6	+13.9
Groundwater influenced by Mercia Mudstone evaporites Kimblin (1995)	+17.5	+13.7
	+17.9	+14.2

**Fig. 8.** Depth profiles of leachable chloride and sulphate from Permian marl units in the Cawood Marsh borehole and corresponding sulphate isotopic compositions. ppm,  $\text{mg kg}^{-1}$  in the solid phase.

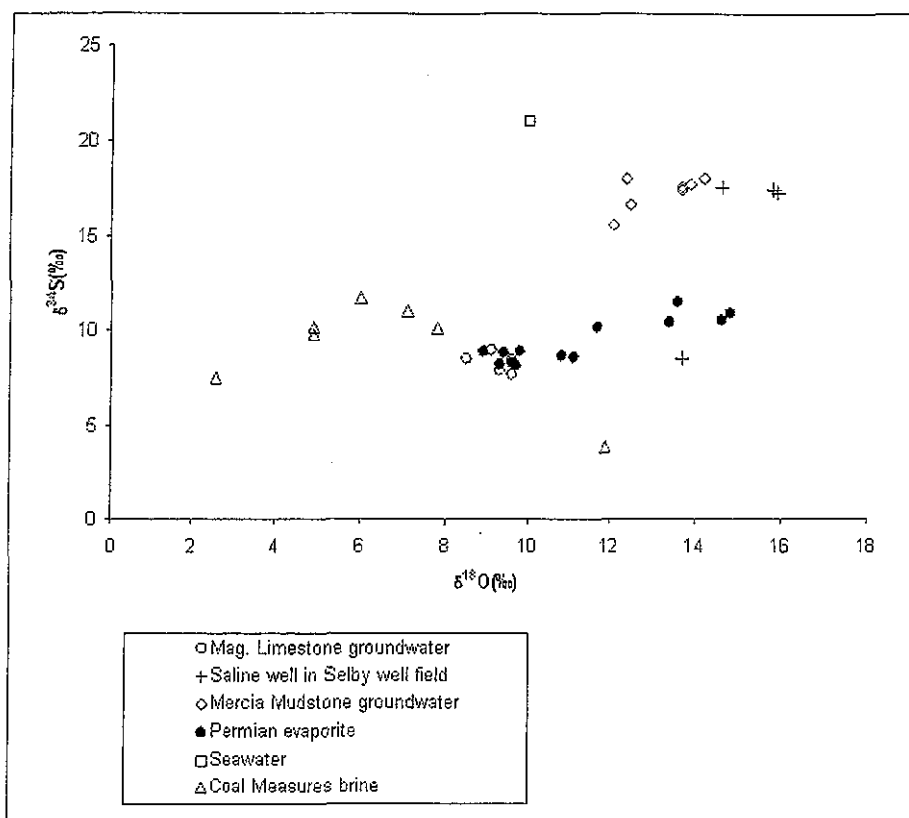
+11.5‰  $\delta^{34}\text{S}$  and from +3.8 to +14.8‰  $\delta^{18}\text{O}$ . The deeper, higher concentration samples have a much more restricted range of  $\delta^{34}\text{S}$  (+8.2–+10.2‰) and  $\delta^{18}\text{O}$  (+9.3–+11.7‰). As these compositions are associated with elevated chloride they are used below to represent the sulphate isotopic ‘fingerprint’ of this source of salinity.

*Coal Measures brines.* Mine-water samples collected between 650 and 750 m bgl in the Selby area have a range of concentrations: chloride ranges from 3 to 10  $\text{g l}^{-1}$  and sulphate from 54 to 57  $\text{g l}^{-1}$ . Figure 9 shows the sulphate isotopic composition of these mine-water samples:  $\delta^{34}\text{S}$  ranges from +3.9 to +11.7‰, while  $\delta^{18}\text{O}$  ranges from +2.6 to +11.9‰.

### Groundwater modelling

*Flow conditions.* Modelled head values (Fig. 6) suggest that the cone of drawdown beneath

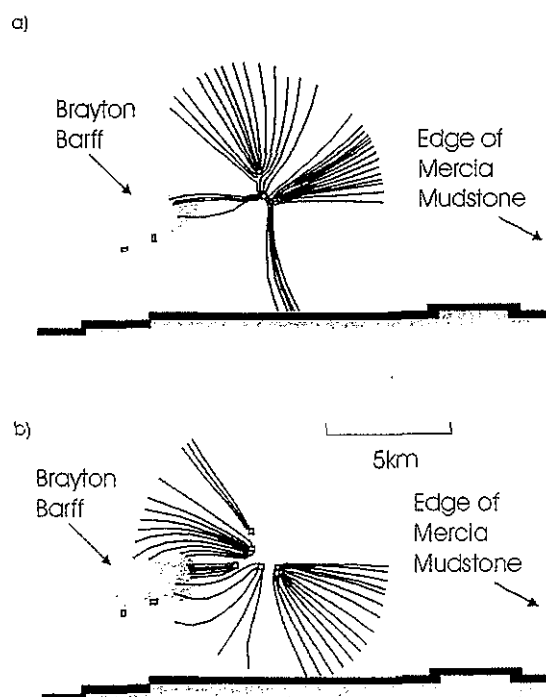
Selby has created an E–W hydraulic gradient to the east of Selby. This gradient is important from a contamination point of view, as it allows much older waters from the east of Selby to be drawn in, rather than simply flowing southwards to discharge into the River Aire, as would be the case under natural hydraulic conditions with no pumping. The modelled values also suggest the piezometric surface reached a minimum level of around –16 m AOD in the centre of the cone of drawdown. This is very close to the top of the sandstone, which suggests that the aquifer began to become unconfined in 1992. The influence of unconfined storage may explain why drawdown in the Selby wellfield appears to have stabilized at this time (Fig. 2). Drawdown will have occurred much more slowly once the aquifer became unconfined. The modal value for the confined storage coefficient measured in pumping tests for the Sherwood Sandstone in NE England is around  $10^{-3}$ , whereas the unconfined storage coefficient is typically 0.15–0.2



**Fig. 9.** Sulphate isotopic compositions of Selby wellfield groundwaters affected by salinity increase compared with sulphate isotopic compositions of the various possible salinity sources.

(Allen *et al.* 1997). Hence, the rate of increase in drawdown should reduce by two orders of magnitude once the top of the aquifer is reached.

**Well capture zones.** Several abstraction wells in the Selby wellfield have been contaminated by saline groundwater, with chloride levels reaching about  $900 \text{ mg l}^{-1}$  in the late 1990s. Capture zones for wells showing saline contamination are shown in Figure 10a; those for wells that had not shown saline contamination by 1996 are shown in Figure 10b. It is striking that three of the four wells showing contamination by saline water capture at least some water from the NE quadrant (the fourth contaminated well captures water mainly from the north). In contrast, uncontaminated wells do not capture any of their water from the NE quadrant. This distribution of capture zones strongly suggests that the source of the saline contamination lies to the north and east of the Selby wellfield.



**Fig. 10.** Hundred-year capture zone calculated for wells in the Selby wellfield. (a) Four wells affected by salinity increase; and (b) wells remaining uncontaminated.

## Discussion

### *Origin of salinity in the Selby wellfield*

Waters in the Sherwood Sandstone aquifer and Selby wellfield are oxidizing, with no evidence of sulphate reduction (Stagg 1995; Yoshida 2000); thus there is no risk of modification of sulphate isotopic compositions within the aquifer. The sulphate compositions can therefore be treated as conservative tracers of the origin of sulphate and, hence, the wellfield salinity. Figure 9 shows the  $\delta^{34}\text{S}$ - $\text{SO}_4$  and  $\delta^{18}\text{O}$ - $\text{SO}_4$  compositions of potential saline-water sources and the saline waters in the Selby wellfield. Three of the affected Selby wells show a tight grouping, but one has lighter  $\delta^{34}\text{S}$  as a result of mixing of drift water at the well (see Sherwood Sandstone, above, and Table 3). We thus take the isotopic compositions of the group as representative of sulphate associated with the source of salinity.

Sulphate in modern seawater has a  $\delta^{34}\text{S}$  of +20‰ and  $\delta^{18}\text{O}$  of +10‰ (e.g. Claypool *et al.* 1980). This is significantly different to the Selby wellfield saline-water composition (Fig. 9) indicating that the source of the saline water is not seawater. Hence, the origin is not modern or Quaternary seawater intrusion (which had closely similar values, according to Claypool *et al.* 1980).

The sulphur and oxygen isotope compositions of local Permian evaporite sulphate are +8–+11‰ and +9–+15‰, respectively. Groundwater samples taken from the Permian Magnesian Limestone aquifer have sulphate with  $\delta^{34}\text{S}$  between +7.7 and +8.5‰, and  $\delta^{18}\text{O}$  between +8.5 and +9.6‰. These are all significantly different to the saline waters (Fig. 9), implying that the origin of saline water is not in this case from the underlying Permian strata, as has happened in the Sherwood Sandstone further to the north in Cleveland (e.g. Bottrell *et al.* 1996).

Samples of Coal Measures brines contain sulphate with  $\delta^{34}\text{S}$  in the range +3.9–+11.7‰ and  $\delta^{18}\text{O}$  in the range +2.6–+11.9‰. These differ considerably from the saline water sulphate values (Fig. 9), and hence the source of saline water is not Coal Measures brine.

Triassic marine evaporite sulphate minerals have similar  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values to the saline waters in the Selby wellfield (Fig. 9). The isotope signatures of one groundwater sample taken from a borehole in the Mercia Mudstone reflect the local expression of this source and are also close to those of the Selby wellfield saline waters. Therefore, it is likely that the source of saline groundwater in the Selby area is inflow of

water influenced by the dissolution of evaporites present in the Mercia Mudstone. The Mercia Mudstone overlies the Sherwood Sandstone and crops out to the east of the Selby wellfield (Fig. 1). Groundwaters contaminated by leakage from the Mercia Mudstone could enter the catchment of the Selby wellfield as a result of the creation by abstraction of a westwards-directed hydraulic gradient. Alternatively, a Triassic evaporite sulphate isotopic 'fingerprint' could be present in evolved saline groundwaters in the deep confined aquifer (gained by long-term aquifer groundwater interaction with evaporite minerals in the sandstone sequence). Again, creation of a westwards head gradient would draw such waters into the Selby abstractions.

### *Flow pathway of saline water to affected wells*

The 100-year particle traces for wells showing saline contamination, based on the 1992–1996 steady-state condition (Fig. 10), are approximately 5 km long extending to the east and north of Selby. The direction of these traces suggests that the source of the saline contamination lies to the east and north of Selby, which is consistent with the identified Mercia Mudstone isotopic signature for sulphate. However, it is interesting to note that, despite the 100 year travel times, the flowlines still extend less than half the distance to the Mercia Mudstone feather edge. However, preferential flowpaths, such as E–W trending fault zones, are known to be present in the area but were not incorporated into the modelling. Hence, it is possible that saline waters from the confined zone of the Sherwood Sandstone could have been drawn into the Selby wellfield as a result of groundwater abstraction. Alternatively, the particle-tracking analysis may indicate that saline waters were present within the aquifer between Selby and the Mercia Mudstone feather-edge before pumping began.

## Conclusions

The isotopic composition of sulphate associated with salinity in affected wells casts doubt on the previously presumed source of saline contamination in the Selby wellfield. Rather than matching the Permian evaporite source, the sulphate isotopes point to a Triassic source for the salinity, probably from the Mercia Mudstones overlying the aquifer.

Groundwater modelling of the Selby area has

demonstrated that water sources of the Triassic Sherwood Sandstone aquifer are recharge, both via the unconfined aquifer at Brayton Barff and via the glacial moraine sediments in the north of the area. The areas covered by glacio-lacustrine sediments contribute relatively little. A small component of leakage from the River Ouse was incorporated in the model representation based on geochemical evidence. Calibration was achieved for steady-state conditions based on average piezometric levels between 1992 and 1996. It is probable that the reason that the deepening of the cone of drawdown slowed suddenly in 1996 was because the aquifer started to become unconfined in the wellfield area. The model also shows that the development of the cone produced an E–W hydraulic gradient in the Selby aquifer to the east of the wellfield. Well capture-zone analysis using MODPATH demonstrates that Selby wellfield boreholes that show saline contamination collect the groundwaters from the NE, whereas uncontaminated wells do not collect water from this quadrant. This is consistent with the Mercia Mudstone evaporite source indicated by the sulphur and oxygen isotope data.

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