

Factors controlling groundwater chemistry of the Triassic Sandstone aquifer in North Yorkshire UK

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ABSTRACT: It is important to understand groundwater conditions such as recharge, flow and hydrochemical process occurred within an aquifer for groundwater protection and groundwater resource management. Groundwater from the Triassic Sherwood Sandstone aquifer of North Yorkshire has been used for industrial purposes and domestic water supply. In order to understand the processes affecting groundwater chemistry and identify the sources of high chloride, sulphate and nitrate concentrations hydrochemical and isotopic measurements were carried out. Hydrochemical and isotopic measurements indicated that five groundwater types exist within the Sherwood Sandstone aquifer of study area. The results of hydrochemical and isotopic measurements showed that older groundwaters have different hydrochemical and isotopic characteristics from recent recharge water. It was also found that water-rock interactions are the dominant mechanism controlling the $\delta^{13}\text{C}$ composition of dissolved inorganic carbon, the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ composition of dissolved sulphate and the strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) in recent recharge water and old groundwater. Several abstraction boreholes within the Selby wellfield have been contaminated by saline water. The isotopic data of saline groundwater samples taken from these abstraction boreholes indicate that saline waters are derived from the dissolution of the Triassic evaporites within the Mercia Mudstone.

1 INTRODUCTION

In the UK 80% of the total groundwater abstraction is from only two aquifers, the Chalk (54%) and the Triassic Sandstone (26%) although the UK's varied geology has produced a wide range of recognised aquifers spanning the stratigraphic column from the Devonian to the Recent periods (Owen *et al.*, 1991). Groundwater from the Sherwood Sandstone aquifer of study area has been extracted for over 30 years. There are 16 abstraction boreholes in the Selby wellfield of study area and the total abstraction reached approximately 6,700 Trillion Cubic Meters Per Annum (TCMA) (1997). The abstraction from the wellfield has caused decline of the water level in the Triassic Sandstone aquifer and groundwater quality problems such as high chloride and sulphate concentrations. In an area of sandstone that is not covered by Quaternary drift deposits (glacial deposits), approximately 4 km south east of Selby, groundwater quality has been reduced by high nitrate. Groundwater gradients in the sandstone aquifer indicate a general groundwater movement from the topographically high area near the north west boundary towards the south east.

2 GEOLOGY AND HYDROGEOLOGY OF STUDY AREA

The geology of the study area is shown in Fig.1. The Sherwood Sandstone is covered by Quaternary drift deposits 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 to over 40 m AOD in the NW and at Brayton Barff. To the east of study area the Sherwood sandstone is overlain by the Mercia Mudstone (approximately 14 km from the Selby town). The Sherwood sandstone is underlain by the Permian Marls and the Permian Magnesian Limestones which crop out to the west of study area. The sandstone dips towards east at a regional angle of about 2-4 degree 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. The pumping test transmissivity values of the sandstone aquifer of the York, Selby and Goole area were 50-400 m^2/day (Allen *et al.* 1997). The hydraulic conductivity value estimated from core samples of the sandstone of the Yorkshire area ranges from 0.18 to 2.2 m/day (Lovelock 1977, Reeves *et al.* 1975). Due to heavy abstraction in the Selby wellfield, water levels have fallen significantly in recent decades. 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.

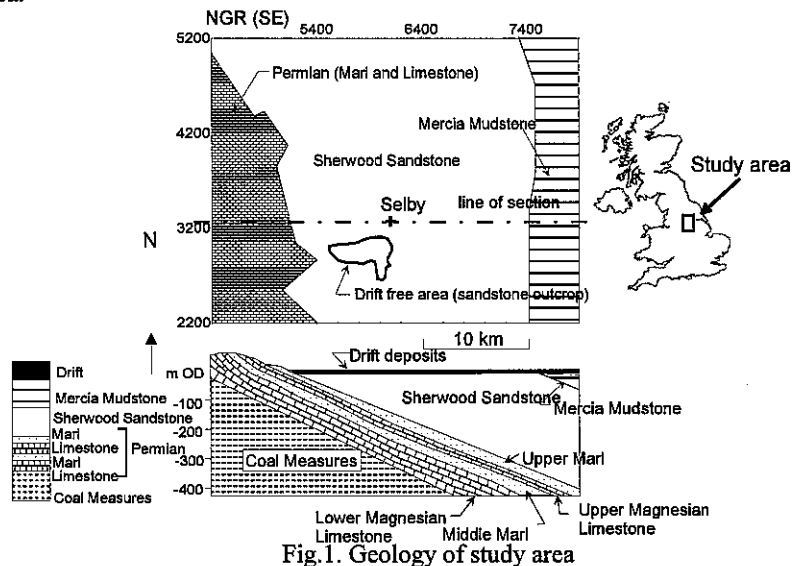


Fig. 1. Geology of study area

3 METHODOLOGY

3.1 Sample sites and sampling procedures

Fig.2 shows the sampling sites of the Sherwood Sandstone groundwaters. "P" indicates abstraction boreholes and "Obs" indicates the Environment Agency observation boreholes. Groundwater samples of the Selby wellfield were collected from 16 abstraction boreholes. The samples were taken directly from the rising main of the pump but in P-4 borehole the samples were collected from the water tank as direct sampling from a pump was not possible. In addition, groundwater samples were collected from the 11 Environment Agency observation boreholes. To collect water samples a submersible pump was installed at the sites. The pump was left running long enough to purge the borehole and flush the residual borehole water before taking a sample. These abstraction and observation boreholes are uncased. This means that the data analysed using these collected samples only show depth-integrated (mixed) groundwater chemistry.

3.2 Sample collection and analytical technique

Samples for anion and cation analysis were filtered through a 0.45µm membrane filter. In addition samples for cation analysis were acidified using 2% of HNO₃. Anions concentrations of samples were measured using Dionex DX-100 ion chromatograph. Relative standard deviations (RSD) were calculated as Cl (3.1%), SO₄ (3.3%), NO₃ (3.3%). Cation concentration analysis was carried out using ICP spectrophotometry. The following values of RSD were obtained; Na (4.0%), K (4.3%), Ca (4.4%), Mg (3.9%), Sr (5.1%).

The samples for carbon isotope analysis were collected using the method described by Bishop and Lloyd (1990), Bishop (1990). Samples were taken in 500ml well sealing polythene bottles which 50ml of a 400g/L SrCl₂ in 0.88M NH₄OH solution was added to precipitate SrCO₃. On return to the laboratory the samples were kept for one week to allow coarsening of the SrCO₃ precipitate. Then SrCO₃ sample was collected on a 0.45µm membrane filter and dried. SrCO₃ samples were converted to CO₂ gases by addition of phosphoric acid. CO₂ sample gases were then analysed on a VG SIRA-10 gas source ratio mass spectrometer. The error is estimated as ±0.2‰. Samples for strontium analysis were filtered in the field through a 0.45µm membrane filter and collected in a 50mL polythene bottle and acidified with 2% 6M redistilled HCl. The samples were stored at room temperature until the analysed. Sr of each sample was separated by ion-exchange techniques. The isotope ratio ⁸⁷Sr/⁸⁶Sr of the sample was measured using a VG 54E mass spectrometer. A total of 23 standards (NBS987 SrCl₂) were analysed. It gave a mean ratio of 0.71027 with RSD of 0.02‰. The samples for sulphur and oxygen isotope analysis were collected in 1L polythene bottle. On the return to the laboratory the sample was filtered and acidified by addition of HCl solution until the pH fell between pH2.5 and 3.0. 10%BaCl₂ solution was added

to precipitate all sulphate as BaSO₄ after heating to ~70°C. The BaSO₄ sample was then collected on a 0.45µm membrane filter and dried. Sulphur and oxygen isotope analysis was performed on the same BaSO₄ precipitates. Oxygen in sulphate was quantitatively converted to CO₂ gas for isotopic analysis by the reduction with graphite (McCarthy *et al.*, 1998). BaSO₄ precipitates were quantitatively converted to SO₂ gas for sulphur isotopic analysis by fluxing with a TMP (tri-sodium tri-metaphosphate) and reduction of SO₃ to SO₂ gas on copper wool (Halas *et al.*, 1982). All CO₂ and SO₂ sample gases were analysed on a VG SIRA-10 gas source ratio mass spectrometer. The estimated analytical uncertainty is δ³⁴S=±0.2‰, δ¹⁸O=±0.4‰.

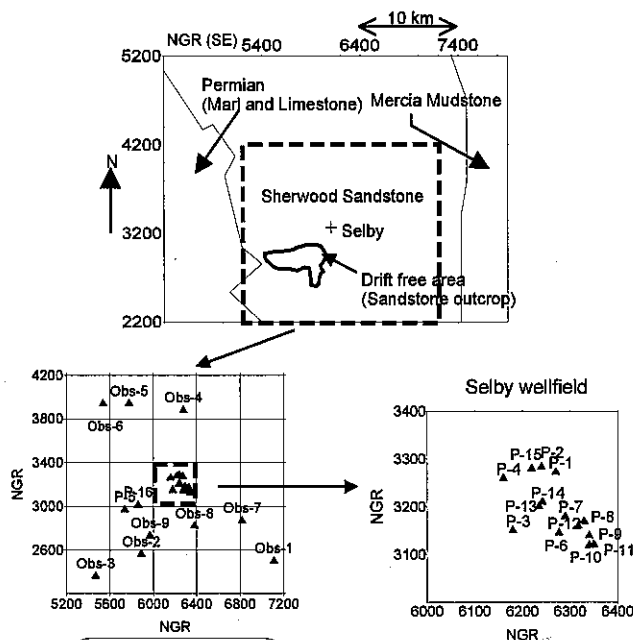


Fig.2. Location map of boreholes sampled for sandstone groundwater

4 RESULTS AND DISCUSSION

4.1 Hydrochemistry of fresh sandstone groundwaters

Fresh groundwaters are defined here as those containing less than 300mg/L Cl concentration. Saline groundwaters of the Sherwood Sandstone aquifer in the Selby wellfield are discussed separately.

4.1.1 Water types

The fresh groundwater samples collected in the study area are divided into groups or the water types, which are defined on the basis of chemistry and on the hydrogeological locations. This approach was used previously by Heathcote and Lloyd (1984) in the Chalk aquifer of southeast Suffolk, Tellam (1994) in the Triassic Sandstone aquifer of the Lower Mersey Basin and Tellam (1996) in the Triassic Sandstone aquifer of the Liverpool area. Major ions concentrations of groundwater samples are plotted on Fig.3.

Type 1A and 1B groundwaters

Type 1A groundwaters are characterised by low HCO₃⁻ <200 mg/L, high NO₃⁻ >50 mg/L. SO₄ concentration is between 70 mg and 150 mg/L and Cl concentration rises up to 110 mg/L (Fig.3). This low HCO₃⁻ indicates that the waters have low flow residence time, so little carbonate dissolution occurs. The saturation indices show these waters are undersaturated with respect to calcite and dolomite. High SO₄, Cl concentrations and especially high NO₃⁻ suggest that these waters are polluted by agrochemical pollutants such as fertilisers. These waters are situated on the sandstone outcrop area (lacking Quaternary drift deposits). These data all imply that Type 1A is recent recharged water. Type 1B waters have greater HCO₃⁻ than Type 1A groundwaters (Fig.3) and these waters are both undersaturated and saturated with respect to calcite. This suggests that Type 1B groundwaters are older

than Type 1A. These waters also have lower NO_3 , SO_4 , Cl concentrations than Type 1A waters. Thus Type 1B waters cannot be derived from Type 1A waters since Type 1A waters have higher NO_3 , SO_4 , and Cl concentrations. This suggests that Type 1A and Type 1B waters were recharged in different environment. In other words, Type 1B waters had lower NO_3 , SO_4 , and Cl concentrations at the time of recharge. Therefore it is likely that Type 1B waters were recharged when the area was less polluted and anthropogenic inputs of SO_4 , and NO_3 were lower. These waters occur close to the sandstone outcrop area.

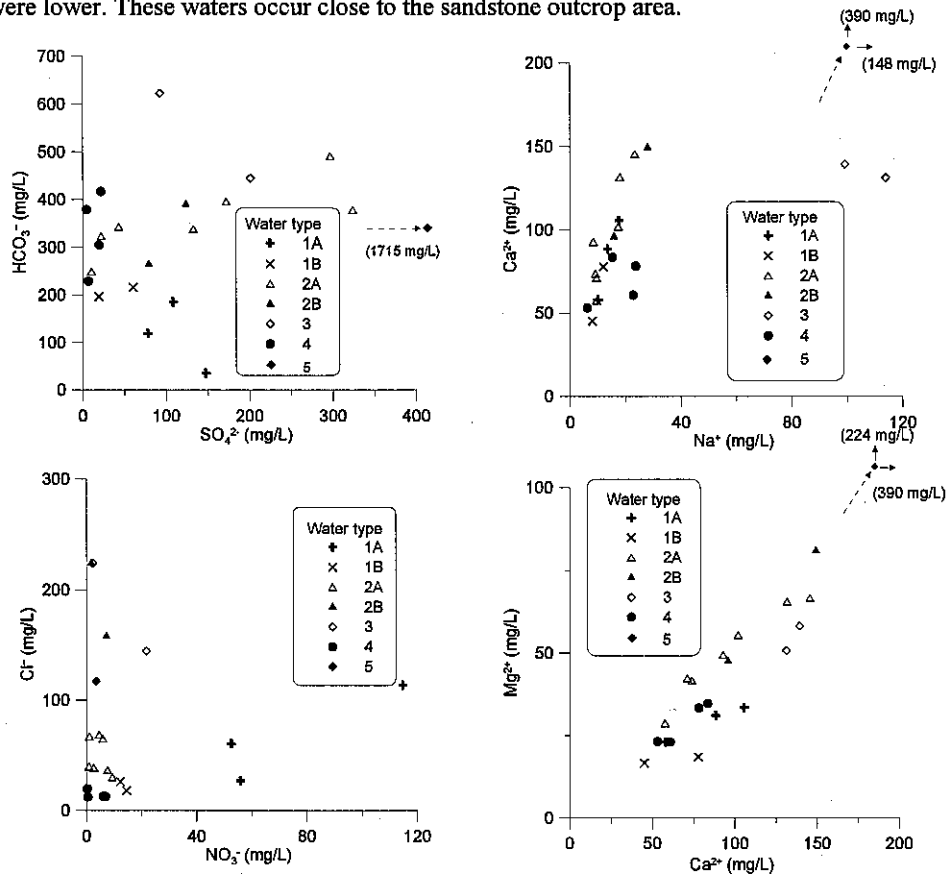


Fig.3. Major ions concentrations for groundwater samples

Type 4 groundwater

Type 4 waters contain low SO_4 , Cl and NO_3 concentrations. Ca concentration is between 50 and 60 mg/L and Mg concentration is 20 and 30 mg/L. These waters have higher HCO_3 concentration than that of Type 1B. The saturation indices show that the groundwaters are saturated with respect to calcite. This means that these waters have the time enough to contact with calcite to allow saturation. All these suggest that the waters are older than Type 1B. Type 4 waters occur in the hydrogeological situation which is below Quaternary drift deposit and away from sandstone outcrop.

Type 2A and 2B groundwaters

Type 2A waters have great variability of ion concentrations. These waters have a wide range of SO_4 concentration (between 50 and 300 mg/L). SO_4 concentration of these waters is generally higher than that of Type 4 water. Ca , Mg concentrations are also variable (Ca is 60 to 140 mg/L and Mg is 40 to 65 mg/L). NO_3 concentration of these waters is low. These waters are all found in abstraction boreholes of the Selby wellfield. Due to heavy pumping, the water level of the Sherwood Sandstone aquifer has declined and huge cone of depression has been created in this area. As the result the hydraulic potential head difference between the drift and the Sherwood Sandstone has been increased. Thus leakage (vertical flow) between drift and Sherwood sandstone has been induced. It seems therefore that these waters are the result of mixing of Type 4 (old

groundwaters) which have occupied this area with drift derived waters due to leakage induced from the overlying Quaternary drift deposits.

Fig.4 shows the relationship between SO₄ concentration and pumping rate of each borehole. The detailed interpretation of each borehole might be dubious as they have the different mixed nature and the complex pumping (on-off) regime. However it is clear that there is a general trend between SO₄ concentration and pumping rate which is higher pumping rate wells have low SO₄ concentration. It indicates that high pumping rate wells contain much higher proportion of Type 4 waters. For example, the highest pumping rate well (P-12) and Type 4 (old groundwaters) have similar ions concentrations. Pumping boreholes, which are not normally used have high SO₄ concentration. It may indicate that induced SO₄ rich waters from drift deposits have already occupied the shallow depth of Sherwood sandstone aquifer in this area.

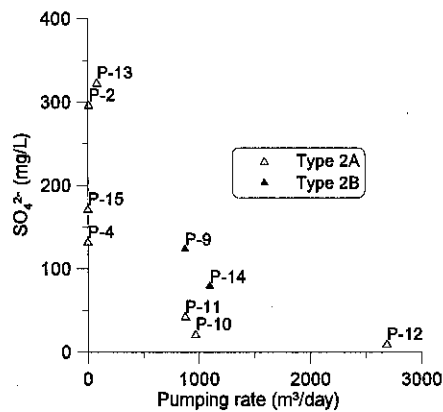
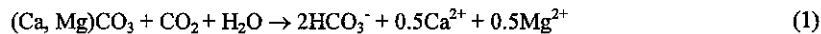


Fig.4. SO₄ concentration plotted against the pumping rate for Type 2 waters

The relatively high Mg/Ca ratios of these waters may reflect the presence of dolomite cement. Edmunds *et al.* (1982) and Kimblin (1995) found that the dolomite dissolution (Eq. (1)) is an important control on Mg/Ca ratios in the Triassic sandstone aquifers of East Midlands area and Northwest England. Type 2 waters are saturated to supersaturated with respect to calcite and dolomite.



Type 2B groundwaters are very similar to Type 2A except they have high Cl concentrations. Na/Cl equivalent ratios of these waters samples are less than unity (average ratios 0.17). These indicate that upconing saline groundwater contamination is occurring in these boreholes. SO₄ concentration of Type 2B seems to be higher comparing with that of same pumping rate of Type 2A wells (Fig.4). This suggests that Type 2B waters have an additional SO₄ source and it has possibly brought with upconing saline water. The detail of this SO₄ source is discussed in the Selby wellfield saline groundwaters section.

Type 3 groundwater

Type 3 waters are very similar to Type 2B waters except that they contain high Na, HCO₃ concentrations. These waters are found in the east of study area where is close to the boundary between Sherwood Sandstone and Mercia Mudstone. Na/Cl equivalent ratios (ion exchange indicator) of these waters are nearly unity to above unity, whereas those of Type 2B waters are less than unity. This indicates the source of Na, Cl of Type3 waters is not from upconing saline groundwaters and Na was released from the aquifer as the result of ion exchange. Appelo and Postma (1994) described this ion exchange takes place when fresh water flushes a saline water aquifer. Thus it seems that Type 4 groundwaters flushed the saline groundwater which previously occupied this area, possibly before the Mercia Mudstone had been removed by erosion. As this flushing was not completed, high Cl still remains in this area. This is one possible explanation of high Cl concentration of these waters. The same type of waters was observed in Triassic sandstone aquifer of the lower Mersey Basin (Tellam, 1994). High HCO₃ and ion exchange suggest that these waters are relatively old and groundwater flow rate of this area is low. Due to the limited availability of observation boreholes in this area the detailed areal distribution of these waters in study area can not be described.

Type 5 groundwater

Type 5 waters differ markedly from the other water types. Especially, they contain very high $SO_4 > 1700 \text{ mg/L}$. This is higher than Magnesian Limestone groundwaters. These waters are very similar to Magnesian Limestone groundwaters except high Mg concentration and high Mg/Ca ratios. It is known that Permian strata is extremely faulted. Thus it is likely that these waters are derived from the underlying Magnesian Limestone. The higher SO_4 suggests that the additional SO_4 is taken from the Permian evaporite dissolution. Groundwaters collected from surrounded boreholes are Type 4. It seems therefore that these waters are present only in a restricted area.

4.1.2 Isotope measurements

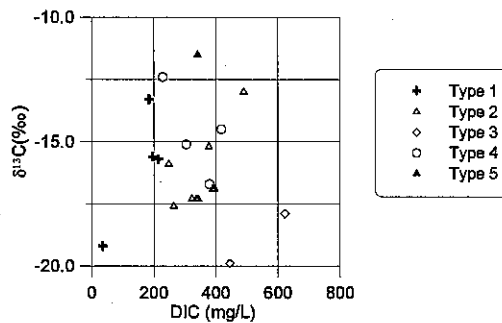


Fig.5. $\delta^{13}\text{C}$ plotted against DIC for Sherwood Sandstone groundwater samples

Fig.5 shows the plot of $\delta^{13}\text{C}$ against HCO_3 concentration. Type 1 waters (recharge waters) have the range of $\delta^{13}\text{C}$ composition between -13.3‰ and -19.2‰ . On the other hand Type 4 waters (old groundwater) have the restricted range of -12.4‰ to -16.7‰ . Type 2 waters have -13.0‰ to -17.9‰ but majority of samples have very restricted $\delta^{13}\text{C}$ range of -16.9‰ to -17.6‰ . Only one sample was collected from Type 5 waters, which has $\delta^{13}\text{C} = -11.5\text{‰}$. Type 3 waters have relatively light $\delta^{13}\text{C}$ values, which -17.9‰ and -19.9‰ . Recharge waters (Type 1 waters) have the relatively light $\delta^{13}\text{C}$ values and low HCO_3 concentration whereas old groundwaters (Type 4 waters) have heavy $\delta^{13}\text{C}$ and high HCO_3 concentration. It suggests that residence time of groundwaters controls $\delta^{13}\text{C}$ and hence calcite, dolomite dissolution within an aquifer dominates HCO_3 concentration. The sample of Type 5 waters had very heavy $\delta^{13}\text{C}$ and this indicates that $\delta^{13}\text{C}$ value of Type 5 waters is dominated by interaction with the Magnesian Limestone.

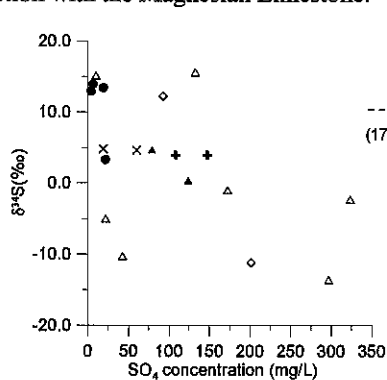


Fig.6. Sulphate - $\delta^{34}\text{S}$ against SO_4 concentration

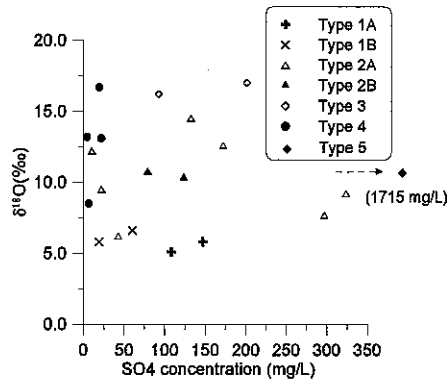


Fig.7. Sulphate - $\delta^{18}\text{O}$ against SO_4 concentration

Sulphur isotope values of sandstone groundwater samples were plotted against SO_4 concentration in Fig.6. Recharge water samples (Type 1A and Type 1B waters) have a similar S isotope composition (around $+5.0\text{‰}$) although major ion chemistry defined that Type 1A waters are recent recharge water and Type B waters are pre-pollution period recharge water. Type 4 waters defined as old groundwater have high $\delta^{34}\text{S}$ values and have a restricted range between $+12.9\text{‰}$ and $+13.9\text{‰}$ with one exception which had $+3.3\text{‰}$. Type 3 water samples have S composition of $+12.2\text{‰}$ and -11.2‰ . This higher $\delta^{34}\text{S}$ value is similar to those of Type 4 waters. Thus it is likely that Type 3 waters are derived from Type 4 waters. The lighter $\delta^{34}\text{S}$ value however indicates Type 3

waters might have another SO_4 source which has lighter $\delta^{34}\text{S}$ value. $\delta^{34}\text{S}$ values of Type 2 waters have the wide range between -13.5‰ and +15.6‰. The groundwater samples which had the lighter $\delta^{34}\text{S}$ value tend to contain high SO_4 concentration and samples which had the heavier S value tend to contain low SO_4 . This suggests that mixing with two ends members.

Fig.7 shows the plot of $\delta^{18}\text{O}$ against SO_4 for sandstone groundwater samples. The range of $\delta^{18}\text{O}$ composition varies from +5.1‰ to +17.0‰. Recharge waters (Type 1) have the lightest $\delta^{18}\text{O}$ composition and the restricted range of +3.1‰ to +6.6‰. Type 4 waters have the wide range between +8.5‰ and +16.7‰ although $\delta^{34}\text{S}$ compositions of these waters have a very restricted range. This may indicate that there was the variation in the recharge environment. $\delta^{18}\text{O}$ values of Type 3 waters are similar to those of Type 4 waters. This supports the hypothesis that Type 3 waters are derived from Type 4 waters. Type 2 waters have $\delta^{18}\text{O}$ in the range +6.2‰ to +14.5‰. These waters are thought to be the products of mixing of drift water and Type 4 groundwater and hence the wide range of $\delta^{18}\text{O}$ composition is thought to be the effect of this mixing.

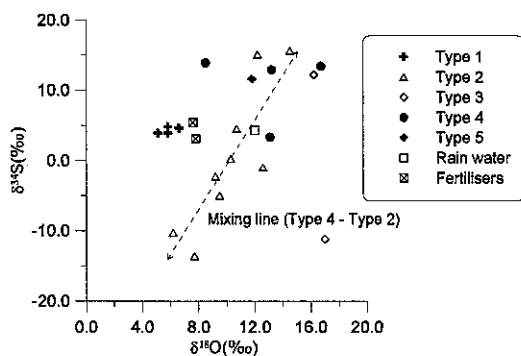


Fig.8. $\delta^{34}\text{S}$ against $\delta^{18}\text{O}$ for sandstone groundwater

Fig.8 shows the plot of $\delta^{34}\text{S}$ against $\delta^{18}\text{O}$ values for sandstone groundwater samples and the possible sources of SO_4 . As can be seen in Fig.8, the isotopic signatures of Type 1 waters (recent recharge waters) are close to those of fertilisers. The $\delta^{18}\text{O}$ value of rain water is heavier than those of Type 1 waters. This discrepancy can be explained as a result of ^{18}O depletion by the transformations caused by biochemical reactions in the soil zone. Thus the sulphate source of Type 1A (recent recharge water) seems to be the mixture of fertiliser and rainfall. However Type 1B waters have much less SO_4 concentration than Type 1A. This indicates that the main source of SO_4 of Type 1B water is rainfall rather than fertilisers. There are two possible sulphate sources of Type 4 waters. One source is rain water. The S isotope signatures of Type 4 waters (old groundwater) are much heavier than those of the present rainfall, but the signature of old recharge environment might have been close to those of Type 4 waters because of less anthropogenic activity. Very low SO_4 concentration of Type 4 waters supports this hypothesis. Tellam *et al* (1994) and Barker (1996) also interpreted the sulphate source of old groundwater of the sandstone aquifer of the Birmingham and Merseyside area by this hypothesis. The other possible source is sulphate derived from the sandstone itself, if isotopically heavy Triassic sulphate minerals (e.g. barite) were present (barite is known to be present in the Sherwood Sandstone of Birmingham area.).

The major ion chemistry of Type 2 and groundwater condition of the Selby wellfield, which is groundwater level declining due to the heavy abstraction, suggest that Type 2 water is the mixing product of induced water from upper drift layer and type 4 waters. The S isotope signatures also indicate the mixing of two ends member (Fig.8). The isotopic signature of the heavier $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ end member is similar to that of Type 4 waters and hence the source of heavier $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ seems to be from Type 4 water. There are two possible sources of sulphate of light end member. One is sulphate derived from weathering of drift deposits. The interpretation of sulphur isotope signatures of shallow drift waters shows this. The other source is waters from an old recharge environment.

In Fig.9, Sr isotope ratio is plotted against the reciprocal of Sr concentration. The recharge groundwaters (Type 1 waters) contain low Sr concentration and relatively high Sr isotope ratio with the exception of one sample which has high Sr concentration (0.237mg/L) and very high Sr ratio (0.714138). It is known that groundwater affected by agriculture fertilisers has very radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio = 0.715 (Bohlke and Horan, 2000). Thus it is most likely that this high Sr concentration and Sr isotope ratio sample acquired Sr from agricultural fertilisers. The rest of the Type 1 water samples also have relatively high Sr isotope ratio and are more radiogenic (higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) than rain water. This confirms that the source of Sr of these samples is

not rain water. Sr derived from the soil horizon has high Sr isotope ratios (Mattigod *et al.*, 1990, Bishop *et al.*, 1994) The source of Sr of Type 1 waters is therefore likely to be soil derived Sr with a possible fertiliser component. Type 4 waters (old groundwaters) have less radiogenic Sr isotope ratios (0.709082 and 0.709391). Surprisingly those values are similar to that of rainfall and modern sea water, but Sr concentration in rainfall (0.004 mg/L) is much less than those of Type 4 groundwaters (0.141- 0.357 mg/L). Therefore it is unlikely that atmospheric depositions are a major source of Sr in the Type 4 groundwaters. It is known that carbonate contain less radiogenic Sr (Bishop *et al.*, 1994). $\delta^{13}\text{C}$ isotopic data of the Sherwood Sandstone groundwater samples suggest that carbonate dissolution occurs within the sandstone aquifer. Thus it is likely that dissolution of carbonate controls the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Type 4 groundwaters and source of Sr is derived from carbonate.

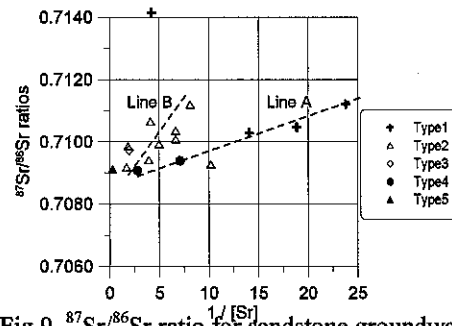


Fig.9. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for sandstone groundwater

In Fig.9, three of the Type 1 waters and Type 4 waters samples lie in a straight line (Line A). This indicates that i) three of Type 1 samples are relatively unaffected by fertiliser input, ii) Sr concentration increases with the residence time and Sr isotope ratio decreases with the residence time and iii) additional Sr derived by water rock interactions is more likely to be from unradiogenic carbonate minerals than from K-bearing clay minerals. Line B of Fig.9 indicates that Sr of Type 2 waters are mixtures of aquifer water (which has less radiogenic Sr) and a water with relatively radiogenic Sr, consistent with likely more radiogenic values for drift waters. Type 5 water sample had the ratio of 0.709121 which is similar to those of Type 4 waters. However the Sr concentration of Type 5 water is much higher than Type 4 water (3.341 mg/L and 0.141-0.357 mg/L respectively). This might imply that the source of Sr of Type 5 waters is not only from the sandstone but also from the Permian strata.

4.2 Origin of saline groundwaters of the Selby wellfield

Four abstraction boreholes have been contaminated by saline groundwater in the Selby wellfield. The chloride concentration has reached around 900mg/L. There are four possible saline water sources, which are a) modern or ancient sea water intrusion, b) Permian strata (Permian evaporite, Magnesian Limestone groundwater), c) Coal Measure brine, d) Mercia Mudstone evaporite.

Fig.10 shows the $\delta^{34}\text{S} - \text{SO}_4$ and $\delta^{18}\text{O} - \text{SO}_4$ compositions of potential saline water sources and saline waters of Selby wellfield. Only Coal Measures water samples collected from deep depth are included in this plot since more saline, brines are considered as providing an isotopic "fingerprint" for the Coal Measures brines as a source of sulphate to saline groundwater of the Sherwood sandstone aquifer. The sulphate of modern seawater has a $\delta^{34}\text{S}$ of +20‰ and a $\delta^{18}\text{O}$ of +10‰. This is significantly different to the saline water composition indicating that the origin of saline water is not seawater, hence the origin is not modern and ancient seawater intrusion (as in the case in the Humberside Chalk aquifer).

The sulphur and oxygen isotope compositions of Permian evaporite sulphate are +8.9‰ and +10.3‰, respectively. Groundwater samples taken from 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 significantly different to the saline waters implying that the origin of saline water is not from underlying Permian strata. Water samples considered typical of the Coal Measures brines contain sulphate with $\delta^{34}\text{S}$ in the range +3.9‰ to +11.7‰ and $\delta^{18}\text{O}$ in the range +2.6‰ to +11.9‰. These differ considerably from the saline water sulphate values, hence the source of saline water is not Coal Measures brine. Triassic marine evaporite sulphate has similar $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values to the saline waters. The isotope signatures of one groundwater sample with high SO_4 from evaporite dissolution taken from Mercia Mudstone reflect this source and are close to those of saline waters. Therefore it is likely that the source of saline groundwater in 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. Groundwaters contaminated by leakage from the Mercia Mudstone could enter the catchment of the Selby wellfield as a result of a local reversal of the regional eastward head gradient.

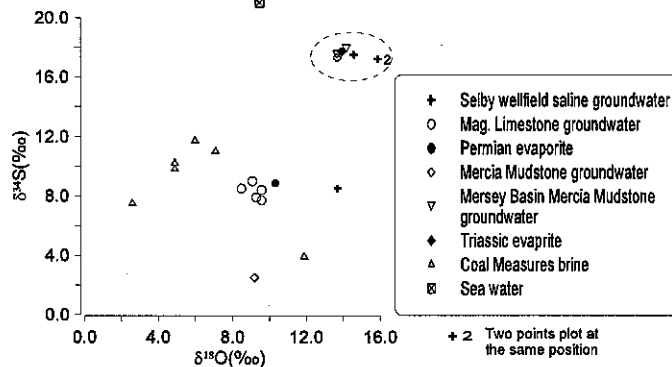


Fig. 10. $\delta^{34}\text{S}$ plotted against $\delta^{18}\text{O}$ for all samples

In Fig. 11, Sr isotope ratios of potential saline water sources and saline waters of Selby wellfield are plotted against their reciprocal of Sr concentrations. The Sr isotope ratios suggest that the Selby wellfield saline groundwater is the mixture of two end members which are drift water and Magnesian Limestone groundwaters or Mercia Mudstone groundwater, hence Coal Measures brine can be ruled out as a source of saline water. The strontium isotope ratio can not distinguish between Magnesian Limestone groundwater and Mercia Mudstone groundwater as a source of saline water. The sulphur isotope signatures however ruled out the Magnesian Limestone groundwater as a source of saline water. Thus it is highly likely that a source of saline water is the dissolution of evaporite derived from the Mercia Mudstone. Capture zone analysis of the abstraction boreholes contaminated by saline groundwater also showed that the groundwaters pumped in these boreholes are derived from the east or north-east, where the boundary between the Sherwood Sandstone and the Mercia Mudstone is located (Yoshida 2000, 2003).

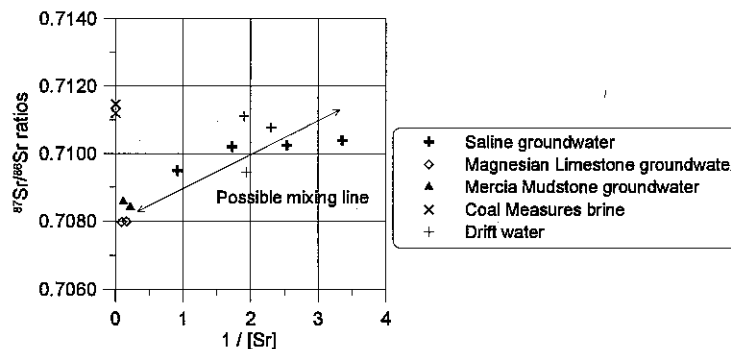


Fig. 11. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio against $1/[\text{Sr}]$ for saline groundwater samples and possible saline water sources

5 CONCLUSIONS

The major ion and isotope data of groundwater samples collected from the study area indicate that various groundwater types and mixing condition exist in the Sherwood Sandstone aquifer. The distributions of groundwater types are controlled by distribution of the drift deposits, pumping and faults.

In the sandstone outcrop area, groundwaters have been affected by agrochemical pollution. NO_3 concentration of these waters was close to or above the European Community (EU) drinking water MAC (50 mg/L NO_3). However in the surrounding area NO_3 concentration was very low. This shows that present recharge waters have not reached to this area. Old groundwaters contain low SO_4 , Cl and NO_3 concentrations and the isotope data remarkably differ from the recharge groundwaters. The groundwaters had heavier $\delta^{13}\text{C}$ values and higher HCO_3 concentrations than recharge waters. Those indicate that the reactions of calcite, dolomite dissolution have progressed than recharge waters. S isotopic signatures suggest that two possible SO_4 sources of

these groundwaters, which are rain water precipitated at old recharge environment and sulphate minerals (e.g. barite) within sandstone. In the Selby wellfield, the hydraulic potentials head difference between drift and Sherwood sandstone has been increased due to the pumping and the leakage between drift and the Sherwood Sandstone has been induced. As a result, groundwaters of the wellfield consist of mixing the residual aquifer waters and induced leakage waters from the overlying drift. S isotopic compositions of the Selby wellfield groundwater samples clearly show the mixing condition of two end members. Groundwaters of the heavier $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ member had low sulphate concentration whereas the lighter member generally had high sulphate concentration. The isotopic signature of the heavier member was close to old groundwaters and thus it is highly likely that the sulphate source is old groundwater. The sulphate source of the lighter member seems to be sulphate derived from weathering of drift deposits or water from old recharge environment in drift. Sr isotope data of these groundwater samples also indicate this mixing relationship between drift water and old groundwater. It was thought that the source of saline water was the dissolution of Permian evaporite. S isotope data of saline groundwater samples however ruled out the possibility and suggest that the source of saline water is the dissolution of the Triassic evaporite within the Mercia Mudstone Group. Study proved the usefulness of isotope analysis to identify hydrochemical processes occurring within an aquifer.

6 REFERENCES

- Allen, D.J., Brewerton, L.J., Coleby, L.M., Gibbs, B.R., Lewis, M.A., MacDonald, A.M., Wagstaff, S.J., and Williams, A.T. (1997). "The physical properties of major aquifers in England and Wales." BGS Technical Report WD/97/34.
- Appelo, C.A.J., and Postma, D. (1994). *Geochemistry, groundwater and pollution*. A.A. Balkema.
- Barker, A.P. (1996). "Isotopic studies of groundwater diagenesis." Unpubl. Ph.D. thesis, University of Leeds UK.
- Bishop, P.K. (1990). "Precipitation of dissolved carbonate species from natural waters for d^{13}C analysis - A critical appraisal." *Chemical Geology*. Vol. 80, pp. 251-259.
- Bishop, P.K., and Lloyd, J.W. (1990). "Chemical and isotopic evidence for hydrogeological processes occurring in the Lincolnshire Limestone." *Journal of Hydrology*. Vol. 121, pp. 293-320.
- Bishop, P.K., Smally, P.C., Emery, D., and Dickson, J.A.D. (1994). "Strontium isotopes as indicators of the dissolving phase in a carbonate aquifer: implications for ^{14}C dating of groundwater." *Journal of Hydrology*. Vol. 154, pp. 301-321.
- Bohlke, J.K., and Horan, M. (2000). "Strontium isotope geochemistry of groundwaters and stream affected by agriculture, Locust Grove, MD." *Applied Geochemistry*. Vol. 15, pp. 599-609.
- Edmunds, W.M., Bath, A.H., and Miles, D.L. (1982). "Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England." *Geochimica et Cosmochimica Acta*. Vol. 46, pp. 2069-2081.
- Halas, S., Shakur, A., and Krouse, H.R. (1982). "A modified method for SO_2 extraction from sulphates for isotopic analysis using NaPO_3 ." *Isotopenpraxis*. Vol. 18, pp. 11-13.
- Heathcote, J.A., and Lloyd, J.W. (1984). "Groundwater chemistry in south east Suffolk (UK) and its relation to Quaternary geology." *Journal of Hydrology*. Vol. 75, pp. 143-165.
- Kimblin, R.T. (1995). "The chemistry and origin of groundwater in Triassic sandstone and Quaternary deposits, northwest England and some UK comparisons." *Journal of Hydrology*. Vol. 172, pp. 293-315.
- Lovelock, P.E.R. (1977). "Aquifer properties of the Permo-Triassic sandstones of the United Kingdom." Bulletin of the Geological Survey of Great Britain No 56.
- McCarthy, M.D.B., Newton, R.J., and Bottrell, S.H. (1998). "Oxygen isotope composition of sulphate from coals: implications for primary sulphate sources and secondary weathering processes." *Fuel*. Vol. 77, pp. 677-682.
- Mattigod, S.V., Rai, D., and Fruchter, J.S. (1990). "Strontium isotopic characterisation of soils and coal ashes." *Applied Geochemistry*. Vol. 5, pp. 361-365.
- Owen, M., Headworth, H.G., and Morgan-Jones, M. (1991). "Groundwater in basin management." In: Downing, R.A. and Wilkinson, W.B. (eds) *Applied Groundwater Hydrology*. Clarendon Press, pp. 17-34.
- Reeves, M.J., Skinner, A.C. and Wilkinson, W.B., (1975). "The relevance of aquifer flow mechanisms to exploration and development of groundwater resources." *Journal of Hydrology*. 25, pp. 1-21.
- Tellam, J.H. (1994). "The groundwater chemistry of the Lower Mersey Basin Permo-Triassic Sandstone Aquifer system, U.K.: 1980 and pre-industrialisation-urbanisation." *Journal of Hydrology*. Vol. 161, pp. 287-325.
- Tellam, J.H. (1996). "Interpreting the borehole water chemistry of the Permo-Triassic sandstone aquifer of the Liverpool area, UK." *Geological Journal*. Vol. 31, pp. 61-87.
- Yoshida, K. (2000). "Groundwater vulnerability of the Triassic Sandstone aquifer in the Selby area, North Yorkshire." Unpubl. Ph.D. thesis, University of Leeds UK.
- Yoshida, K. (2003). "Groundwater modelling of the Triassic Sandstone aquifer in the Selby area, North Yorkshire, UK." Proc. Groundwater Problems Related to Geo-environment., AA Balkema, pp. 517-521.