

## **Sulphate isotope signatures in borehole waters from three urban Triassic Sandstone aquifers, UK**

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**Abstract** This paper outlines an investigation of the use of  $^{34}\text{S}$  and  $^{18}\text{O}$  data in provenancing sulphate in groundwaters of urban UK Triassic sandstone aquifers. The isotopic composition of potential S sources (precipitation, industrial acids, plating bath effluents, various building materials, public supply water, detergents, road salt, and geological materials) were determined. The isotopic data from pumped sampling in the Birmingham aquifer confirmed previous interpretations based on elemental concentrations, identifying natural and various anthropogenic sources. Detailed resolution of the anthropogenic sources was not possible, partly because of the common source of many man-made sulphur compounds in the aquifers studied (Triassic evaporites), and the mixed nature of the groundwater samples. However, the isotope data sets from Birmingham, Nottingham, and Liverpool all show that sulphide oxidation commonly occurs in the shallow subsurface; this has important implications for the attenuation of other pollutants. No sulphate reduction was apparent in any of the waters sampled from the three aquifers.

### **INTRODUCTION**

One characteristic of urban aquifers is the complexity of the distributions of potential sources of pollution. Sometimes sources can be deduced from the chemical composition of the waters, but in most cases much uncertainty remains because usually several sources exist for each chemical species present. However, by examining isotope compositions additional mass balances are introduced which may help in reducing this uncertainty. The isotopic composition of  $\text{SO}_4$  is considered here; although  $\text{SO}_4$  has the advantages of ubiquity and two elements for which isotopic determination can be carried out,  $\text{SO}_4$  isotopic ratios appear not to have been used in the urban context before. Sampling has been undertaken in the Triassic sandstone aquifers below Birmingham, Nottingham, and Liverpool, and potential source solutions and solids have also been analysed. This paper provides a brief overview of the results of these studies.

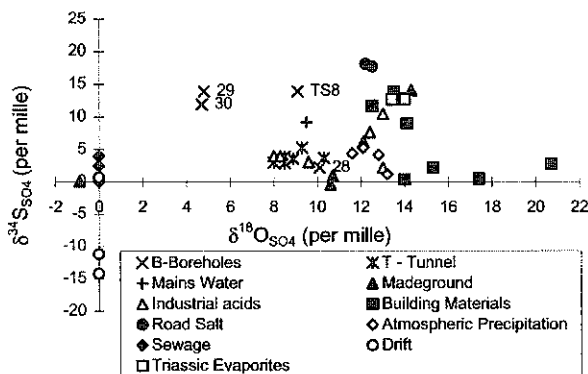
## METHODS

In all three aquifers, most groundwater samples were obtained from regularly pumped abstraction boreholes, and inflow to tunnels. Although all groundwater samples were analysed for major, minor, and trace determinands, and the results used in the interpretations, only the sulphate isotope signatures are reported here. For groundwater and other liquids, and for sulphate dissolved from solid samples,  $\text{SO}_2$  and  $\text{CO}_2$  produced from  $\text{BaSO}_4$  precipitates were analysed using a VG Sira-10 mass spectrometer. Sulphide was extracted by chromic acid reduction. Details are given in Hughes (1998).

## ISOTOPIC SIGNATURES OF POTENTIAL SULPHATE SOURCES

Figure 1 shows the  $\delta^{34}\text{S}_{\text{SO}_4}$  (SMOW) and  $\delta^{18}\text{O}_{\text{SO}_4}$  (CDT) signatures for a range of potential groundwater sulphate sources; although most of the samples were obtained during the Birmingham phase of the study, many are relevant to the other aquifers as well. All (de-icing) road salt and many building materials and industrial acids used in Birmingham's metalworking industries are derived from Triassic evaporite deposits mined in central England. Precipitation was sampled during the study at a site on the Birmingham University campus. For over 100 years the public ("mains") water supply for Birmingham has come from reservoirs in upland drainage basins in Wales, and has a very low dissolved content ( $\sim 80 \mu\text{S cm}^{-1}$  conductivity). Sewage data are from van Dover *et al.* (1992) (estimated  $\delta^{18}\text{O}_{\text{SO}_4}$ ). The tunnel samples are from tunnels in the centre of Birmingham, and represent the water quality at very shallow depths in the oldest part of the city. The S in the Quaternary ("drift") deposits from Birmingham is partly in sulphide form. Made ground (fill material) groundwaters were sampled using shallow boreholes. On Fig. 1, "boreholes" data refer to Group 3 waters (see below).

It is clear that although there is a wide range of signatures, discrimination in certain ranges may, in some cases, be difficult.



**Fig. 1**  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  data for potential S and  $\text{SO}_4$  sources. (Drift data points indicate  $^{34}\text{S}$  values only; sewage  $^{18}\text{O}$  are estimated.)

## THE BIRMINGHAM AQUIFER

### Outline hydrogeology

Birmingham is situated in the centre of England, has a population of around a million, and has been heavily industrialized since the seventeenth century. Figure 2 shows the bedrock geology of the Birmingham urbanized area. The main aquifer is the Triassic sandstone (maximum thickness ~200 m). The sandstone is quartz-dominated, fine to medium grained and sometimes pebbly, contains some feldspar and a few percent clays, is coloured red by haematite and other iron oxyhydroxide phases, and is often calcite cemented below the top 10–20 m (Ford & Tellam, 1994); gypsum is suspected to occur to the southeast of the Birmingham Fault (Jackson & Lloyd, 1983). The sandstone is underlain by a generally mudstone-dominated low permeability Carboniferous sequence. To the southeast of the northeast/southwest trending Birmingham Fault the sandstone is overlain by a thick mudstone sequence. Quaternary deposits—clays to sands of glacial and glacio-fluvial origins of 0–40 m in thickness—overlie the whole area, affecting recharge distributions and providing a relatively reactive substrate which includes clays, organic material, and pyrite. The sandstones have a permeability of around  $10^{-5}$  to  $10^{-4}$  m s<sup>-1</sup>, and a specific yield of around 15% (Knipe *et al.*, 1993). Typical groundwater velocities are tens to 100 m year<sup>-1</sup>.

The aquifer was extensively used for public water supply up until around 1900 when Birmingham established reservoirs in Wales; since then, almost all abstraction has been for industrial purposes. The dominant industry in Birmingham has been metal-working, and large quantities of sulphuric and other acids have been used in the city since at least the 1700s; groundwater abstraction reached a maximum in the 1960s, and since then groundwater levels have been rising. Fifty seven groundwater samples were obtained, almost all from industrial abstractions (mainly uncased 50–150 m deep wells pumping at, typically, 1 to 10 l s<sup>-1</sup>).

Current annual recharge to the aquifer in the area of Fig. 2 is about 460 l s<sup>-1</sup>, and this has not changed significantly since before industrialization due to the compensating effects of water-proofing and public water supply leakage (Knipe *et al.*, 1993).

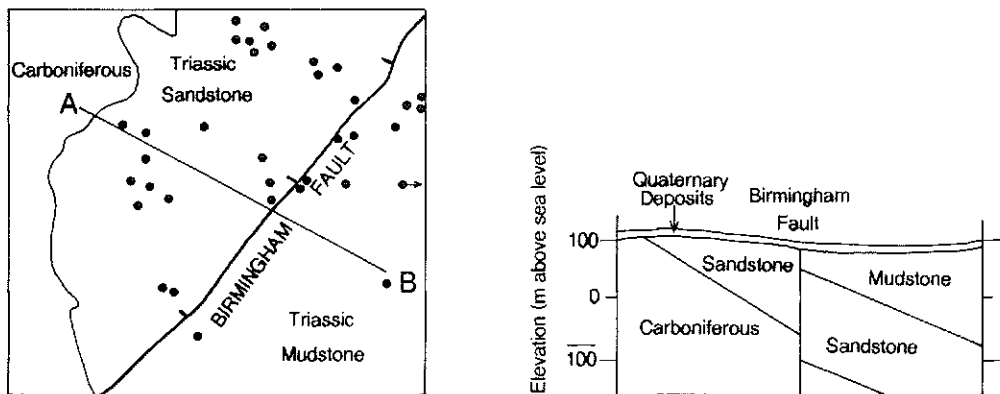


Fig. 2 The geological setting of the Birmingham aquifer. Sample locations are marked.

Inorganic groundwater quality as determined by sampling the deep high-abstraction boreholes is generally good, with only  $\text{NO}_3$  regularly approaching health limits (Ford & Tellam, 1994). The water quality in the deepest parts of the sandstone is excellent, and has been interpreted as being recharged before industrialization (Jackson & Lloyd, 1983). However, at some metal-working sites, high metal concentrations are present, and chlorinated solvents have been found at all sites where they have been used (Taylor & Rivett, 1999). Although all *borehole water samples* are oxidizing, there is little information as to redox status in the shallow more polluted zones of the aquifer.

### Groundwater sample isotope data

Figure 3 shows all the groundwater isotope data, and indications of the signatures for some of the potential sources (see Fig. 1 for ranges, which in some cases are large).

It is clear that the signatures for many of the sites which lie to the southeast of the Birmingham fault (referred to below as the “confined” sites) are heavy and approximate the Triassic evaporite signatures, thus confirming Jackson & Lloyd’s (1983) suggestion that the source of the sulphate in the confined aquifer is gypsum from the Triassic sequence. However, three or four of the confined sites have much lighter signatures suggesting another sulphate source; two of these sites are within 100 m of the Birmingham Fault, and the third is a shallow borehole in a sandstone unit within the mudstone sequence, suggesting respectively lateral and vertical flow from unconfined parts of the system dominated by surface sulphate inputs rather than geological sources.

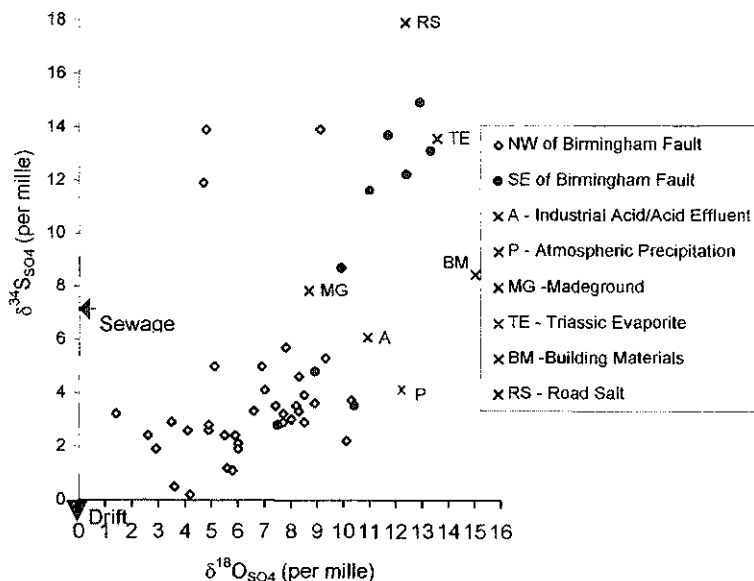


Fig. 3  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  data for the Birmingham groundwater samples, with mean values for some potential sources.

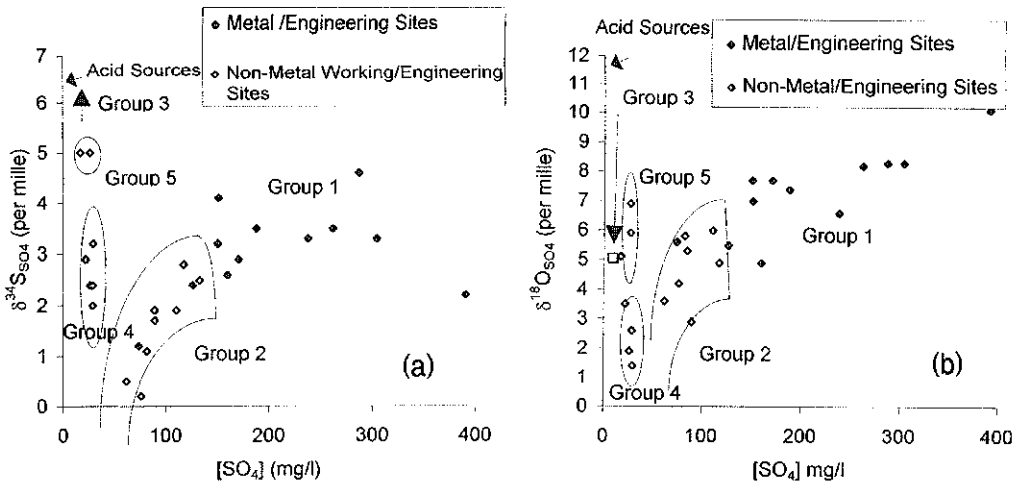


Fig. 4 (a)  $\delta^{34}\text{S}_{\text{SO}_4}$  and (b)  $\delta^{18}\text{O}_{\text{SO}_4}$  variation with  $\text{SO}_4$  concentration for the groundwater samples from the Birmingham aquifer.

The samples from the part of the aquifer to the northwest of the Birmingham Fault (confined area) can be split into five groups determined by isotope and  $\text{SO}_4$  concentrations (Fig. 4). The interpretation presented below assumes that there is a unique isotopic/concentration signature for each source.

Group 1 waters are from metalworking and engineering sites (Fig. 4), and are characterized by relatively heavy isotope signatures and high sulphate concentrations. This is consistent with a sulphate contribution from sulphuric acid and sulphuric acid derivatives. The effects of acid pollution are currently being investigated. The light/low concentration extreme of Group 1 merges with Group 2.

Group 2 waters are from non-metal-working industrial sites. Their isotopic signatures (Fig. 4) can be explained by a "mixing" trend between a relatively heavy "end member" source and a  $\sim 30 \text{ mg l}^{-1}$   $\text{SO}_4$  source with a relatively light signature of about  $-4$  and  $-1.5$  per mille  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ , respectively. This light source is consistent with the oxidation of Quaternary or made-ground deposit pyrite by recharge water. There are two, as yet unresolved, possibilities for the heavy "end member"; the Group 1 metal-working site waters or the "general" pollution signatures represented by the samples taken from the shallow tunnels in central Birmingham (Fig. 1). It is not possible to determine the origin of this general urban signature in detail, but it is consistent with  $\text{SO}_4$  inputs from a combination of precipitation, made ground/building materials, mains leakage, and sewage (Fig. 1).

Group 3 waters are present in the base of the aquifer, and on the basis of their very low Cl, low  $\text{SO}_4$ , and low  $^{14}\text{C}$  contents were interpreted as predominantly pre-industrial recharge waters by Jackson & Lloyd (1983). Calculations indicate that the sulphate isotope signatures of these waters can be derived by interaction of an assumed pre-industrial seawater dominated precipitation and (Quaternary deposit) pyrite.

Group 4 waters were obtained from industrial sites in dominantly residential areas. They may result from the same mechanism as Group 3 waters, but with a greater dominance of the light source. Alternatively, an origin involving mixing of Group 2 and 3 signatures may be feasible.

Group 5 waters are chemically similar to Group 4 waters and also from sites in dominantly residential area of the city, but their heavy  $^{18}\text{O}$  signatures indicate that aquifer gypsum must also be a sulphate source.

In none of the above interpretations has it been necessary to invoke sulphate reduction. This is consistent with the absence of reported sulphides in the groundwaters, but the lack of chemical and isotopic evidence does not prove that the process might not be of importance locally, especially where organic pollution is most severe.

## THE NOTTINGHAM AND LIVERPOOL AQUIFERS

A limited amount of sampling has also been undertaken in Nottingham and Liverpool. These cities, situated respectively about 80 km northeast and 160 km northwest of Birmingham, also stand on Triassic sandstone aquifers, but Quaternary deposits are thinner in Liverpool than in Birmingham, and are almost entirely absent in Nottingham. The industries using groundwaters in both cities are varied.

In the Nottingham aquifer, preliminary examination indicates that a three "end member" "mixing" scheme can explain the range of isotopic signatures. The end members in this case are a light source similar in composition to that deduced for the Birmingham study, aquifer gypsum, and a general urban source slightly heavier in  $^{34}\text{S}$  and slightly lighter in  $^{18}\text{O}$  than in the case of Birmingham.

In the case of Liverpool, Barker *et al.* (1998) report  $\delta^{34}\text{S}_{\text{SO}_4}/\text{SO}_4$  concentration and  $\delta^{18}\text{O}_{\text{SO}_4}/\text{SO}_4$  concentration mixing trends which imply a light isotopic end member. They were not able to identify the source, but suggested oxidation as one possibility. Taking a 30 mg l<sup>-1</sup> concentration as suggested for the Birmingham aquifer, the light isotopic end member will have a composition of around -16 to -20 per mille  $\delta^{34}\text{S}_{\text{SO}_4}$  and < -5 per mille  $\delta^{18}\text{O}_{\text{SO}_4}$ , rather lower than in the Birmingham area. The heavy end member was interpreted to be gypsum or a gypsum-derived product.

Although interpretations are at an early stage, it appears that oxidation reactions are of importance in all three aquifers, and that this is not strongly affected by the amount of Quaternary deposits present.

## CONCLUSIONS

The isotope data have confirmed the suggestions of previous authors that there is limited penetration of recent anthropogenically affected water into the confined parts of the aquifer, pre-industrial water is present in the deepest parts of the unconfined aquifer, and the metal-working industries cause local pollution (Jackson & Lloyd, 1983; Ford & Tellam, 1994). At specific sites isotope data have confirmed and in some cases revised earlier interpretations. Even greater resolution of sources would have been possible had there not been just one ultimate origin—Triassic evaporites—for many of the potential S sources.

In all three aquifers the isotopic data indicate that oxidation occurs in the shallow subsurface. This finding is important, as the shallow redox system may well affect the mobility of pollutants. In none of the aquifers studied is there any indication that sulphate reduction is occurring.

Work continues on refining the interpretation by integrating the isotope data set with those on other dissolved species and colloid distributions.

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## REFERENCES

- Barker, A. P., Newton, R. J., Bottrell, S. H. & Tellam, J. H. (1998) Processes affecting groundwater chemistry in a zone of saline intrusion into an urban sandstone aquifer. *Appl. Geochem.* **6**, 735–750.
- Ford, M. & Tellam, J. H. (1994) Source, type and extent of inorganic contamination within the Birmingham urban aquifer system, UK. *J. Hydrol.* **156**, 101–135.
- Hughes, A. J. (1998) Identification of natural and anthropogenic sources of sulphate in two UK aquifers using S and O isotopes. PhD Thesis Birmingham University, Birmingham, UK.
- Jackson, D. & Lloyd, J. W. (1983) Groundwater chemistry of the Birmingham Triassic sandstone aquifer and its relation to structure. *Quart. J. Engng Geol.* **16**, 135–142.
- Knipe, C. V., Lloyd, J. W., Lerner, D. N., & Greswell, R. B. (1993) *Rising Groundwater Levels in Birmingham and the Engineering Implications*. CIRIA Special Publ. 92, Construction Industry Research and Information Association, London.
- Taylor, L. & Rivett, M. O. (1999) Monitoring solvents in the Birmingham aquifer: 1987, 1998 and on to the next millennium. In: *Impacts of Urban Growth on Surface Water and Groundwater Quality* (ed. by J. B. Ellis) (Proceedings of IUGG 99 Symposium HS5, Birmingham, July 1999). IAHS Publ. no. 259 (this volume).
- van Dover, C., Grassie, J. F., Fry, B., Garritt, R. H. & Starczak, V. R. (1992) Stable isotope evidence for entry of sewage-derived organic material into a deep-sea food web. *Nature* **360**, 153–156.