# Migration and attenuation of agrochemical pollutants: insights from isotopic analysis of groundwater sulphate

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## Abstract

Existing hydrochemical and hydrogeological models of pollution migration and attenuation in the Lincolnshire Limestone aquifer of eastern England have been examined in the light of the results of a groundwater sulphate sulphur isotope investigation. This has allowed the distinction of different sources of sulphate and their relative importance in different parts of the aquifer. The principal sources are $^{34}$S-depleted inputs, derived from the oxidation of pyrite within both the aquifer matrix material and the overlying mudstone deposits, and $^{34}$S-enriched anthropogenic inputs which are derived from acid rain fallout augmented by agrochemicals.

Groundwaters sampled over the outcrop zone of the aquifer have sulphate $\delta^{34}$S dominated by contemporary acid rain inputs in the recharge waters. A down-dip decrease in the $^{34}$S content of groundwater sulphate over the unconfined and shallow confined areas of the aquifer is indicative of a progressive increase in the significance of pyrite-derived sulphate in the system. The contribution of sulphate from this source is large and indicates that pollution front penetration (previously based on total sulphate concentrations) is more restricted than previously thought. Moreover, the extent of pyrite oxidation is greater than can be accounted for by dissolved $O_2$ and the additional component corresponds to that which would be expected from reduction of nitrate using pyrite as the electron donor. We suggest that this mechanism is responsible for denitrifica-

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tion in the aquifer, but that it will be ultimately limited by pyrite availability near fissure surfaces where the reaction takes place. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Nitrate pollution of groundwaters by agrochemicals poses a serious threat to groundwater resources in Britain, Europe and North America. In areas of intensive agriculture, aquifer recharge can be contaminated with nitrate at concentrations well above requirements for safe drinking water, presenting problems for present and future aquifer management. Nitrate and other pollutants in an aquifer may be dispersed by mixing with older, unpolluted groundwater or attenuated via a variety of mechanisms. In the case of nitrate, bacterial nitrate reduction provides a potential natural remediation mechanism in anoxic zones of an aquifer.

Sulphate is a ubiquitous component of groundwaters, being derived from a variety of sources. Potentially, these sources may be distinguished by differences in their stable sulphur isotopic compositions. In this study we utilize this approach to distinguish between anthropogenic (''acid rain'' and agrochemical sources) sulphate and sulphate derived by pyrite oxidation in a limestone aquifer. These data are then used to re-examine models of dispersion and attenuation of pollutants within the aquifer and to infer mechanisms of bacterial denitrification that are taking place.

### 1.1. Geology and hydrogeology

The area selected for study lies immediately to the north of Sleaford, Lincolnshire and encompasses approximately 200 km$^2$ of the unconfined and confined mid-Jurassic Central Lincolnshire Limestone aquifer (Fig. 1). The limestone is approximately 20 m thick in this area and is comprised of a variety of carbonate lithologies (Ashton, 1977). These lithologies are dominantly either relatively pure oolitic deposits containing 90–95% $CaCO_3$ or argillaceous deposits which contain < 36% $CaCO_3$. In this area the limestone strikes north–south and has a slight regional dip to the east. East of the limestone outcrop the formation is confined between a series of low permeability mudstones (Fig. 1). The dip is modified in the northern and central parts of the study area by a north–south trending strike–parallel fault system and associated minor faults (Fig. 1).

Recharge to the aquifer is dominated by the infiltration of excess precipitation through the soils of the limestone outcrop (Peach, 1984) as there are no influent streams in this area. Over the area of the western unconfined zone the direction of groundwater flow is largely controlled by the regional dip of the limestone to the east. The fissure dominated secondary porosity of the limestone results in high transmissivities (commonly > 1000 m$^2$ day$^{-1}$) and low storativity (generally < $5 \times 10^{-3}$) (Peach, 1984). These factors combine to ensure that large areas of the western unconfined system are hydraulically inactive, except over the late winter and early spring recharge period
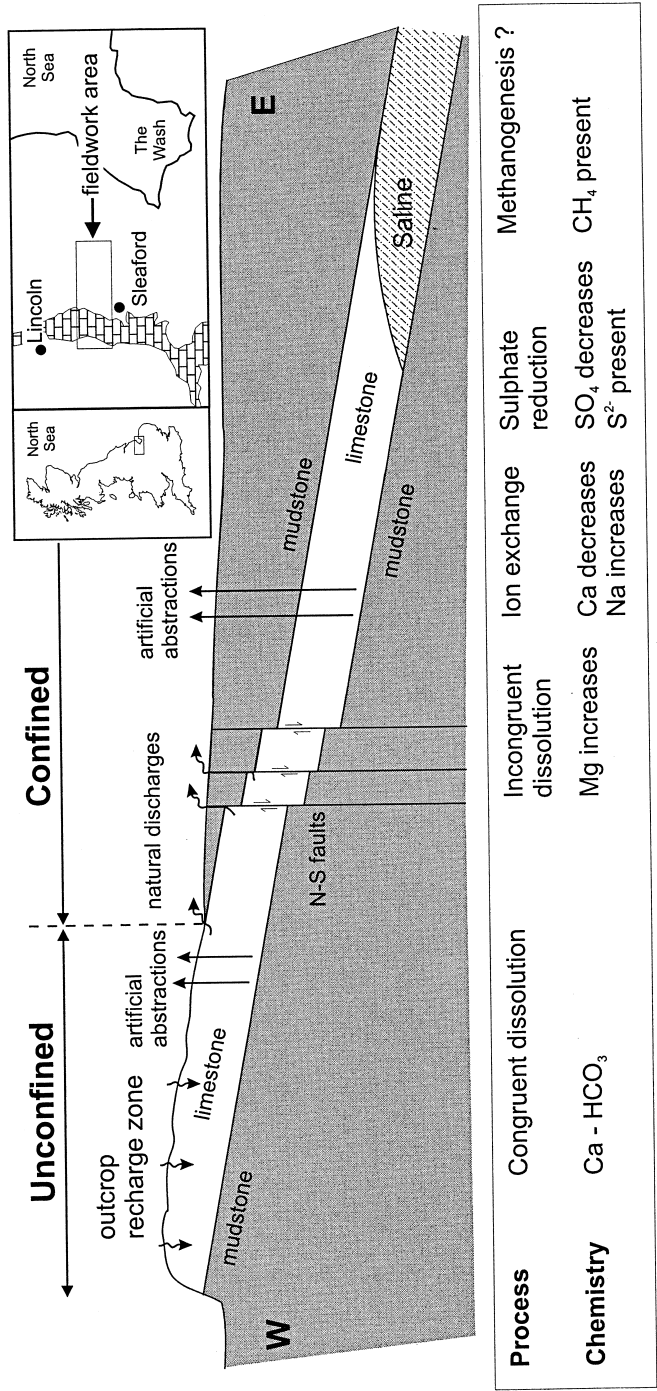
Fig. 1. Schematic cross section of the Lincolnshire limestone aquifer.

during which large volumes of groundwater may be rapidly transferred down-dip in the direction of the confined zone. This produces a marked seasonal variation in the saturated thickness of the aquifer (Smith, 1979; Rushton and Rathod, 1980).

Down-gradient of the boundary between the unconfined and the confined zones, local elements of the structural geology combine with bulk changes in transmissivity and a concentration of discharge points to modify the established pattern of groundwater flow to the east. In the comparatively shallow areas of the confined aquifer, transmissivities are frequently in excess of 1000 $m^2$ $day^{-1}$ and storativities vary from $5 \times 10^{-3}$ to $5 \times 10^{-5}$ (Peach, 1984). In the deeper parts of the confined zone, down-dip of the strike fault system, an easterly hydraulic gradient is re-established and flow is once again predominately down-dip but transmissivities are generally less than 50 $m^2$ $day^{-1}$ and groundwater flow velocities are consequently low. Groundwater discharge from the system is concentrated in an area of the eastern outcrop and the shallow confined zone, occurring as both spring discharges and abstraction from a number of wells for private and public water supply.

## 1.2. Hydrochemistry

The hydrochemistry of the Lincolnshire Limestone has been extensively investigated. A classic series of down-gradient, evolutionary hydrochemical zones and the occurrence of a widespread nitrate contamination problem have been well-described (Lamont, 1959; Downing and Williams, 1969; Edmunds, 1973, 1976; Lawrence et al., 1976; Smith-Carington et al, 1983; Edmunds and Walton, 1983; Marsh and Lloyd, 1984; Lawrence and Foster, 1986; Bishop and Lloyd, 1990a,b; Smalley et al., 1994). Hydrochemistry in the unconfined and shallow confined zones of the aquifer reflects the interaction between the recharge water and the carbonate aquifer. Congruent carbonate dissolution dominates in the unconfined zone and incongruent dissolution reactions become more important in the confined zone. The combination of these processes results in the overall domination of the groundwater chemistry by calcium and bicarbonate. The gradual down-dip increase in significance of the incongruent carbonate dissolution reaction is marked by evolution of groundwater strontium and inorganic carbon isotopic composi-tions toward those of the aquifer matrix material, a modest decline in calcium concentra-tions and an increase in magnesium concentrations. Superimposed on this evolution in carbonate chemistry, a ''pollution front'', characterised by elevated concentrations of sulphate and nitrate, has migrated down-dip (Edmunds and Walton, 1983; Bishop and Lloyd, 1990a,b). Declining concentrations of nitrate in the groundwaters of the shallow confined zone have been linked to a combination of nitrate reduction and diffusion exchange between mobile fissure waters and matrix pore-waters (Lawrence and Foster, 1986; Wilson et al, 1990).

In the deep confined zone, sharply declining concentrations of calcium and increasing concentrations of sodium and magnesium result from an increase in the significance of ion exchange. Sulphate concentrations decline rapidly as a result of sulphate reduction under the more reducing conditions (Edmunds and Walton, 1983; Bottrell et al., 2000). Mixing with saline groundwaters at the eastern margin of this zone ultimately causes additional large increases in sodium concentration and an increase in the concentration of chloride.

## 2. Sampling and analytical methods

Using the most recent hydrochemical classification of the groundwaters in the fieldwork area (Bishop and Lloyd, 1990a,b) samples from each of several hydrochemical zones were taken on a monthly basis from October 1989 to October 1990. All the data reported here are from up-gradient of the zone influenced by sulphate reduction identified by Bottrell et al. (2000). The locations of the wells sampled are given in Table 1. Additionally, samples of rainwater falling on the limestone outcrop area and samples of water recharging the aquifer from the base of the soil were collected. Samples of the various sulphur minerals present in the aquifer and confining beds and of agrochemical sulphate sources were also collected and analysed.

Measurements of pH, redox potential, temperature and alkalinity were made at each well head using standard techniques (Lloyd and Heathcote, 1985). Major and minor cation concentrations were determined by use of inductively coupled plasma spectroscopy (ICP) on samples that had been acidified by addition of hydrochloric acid. Sulphate, nitrate and chloride concentrations were determined by a combination of gravimetric analysis and ion chromatography. Aqueous sulphate was recovered by precipitation from acidified solutions as $BaSO_4$ at pH = 2.5 and 70°C. Crushed samples of gypsum and agrochemicals were dissolved in a heated 1 M solution of sodium chloride and, after filtration, $BaSO_4$ recovered as described above. Reduced sulphur minerals were processed by reaction with acidified chromous chloride solution, with the resulting hydrogen sulphide being trapped by reaction with copper acetate solution (Newton et al., 1995). Sulphur dioxide for sulphur isotope analysis was prepared from the $BaSO_4$ precipitates using the method of Halas et al. (1982) and from the copper sulphide precipitates using the method of Robinson and Kusakabe (1975). The sulphur dioxide gases were purified by standard vacuum-cryogenic techniques and analysed on a VG Isogas SIRA 10 gas source mass spectrometer. Raw data were corrected using standard techniques and sulphur isotopic compositions reported in delta notation as parts

Table 1

Locations of wells sampled, mean isotopic compositions and results of sulphate source modelling

| Well | Distance down-dip (km) | Mean sulphate $\delta^{34}S$ (‰) | Standard deviation (‰) | Mean sulphate conc. (mg l$^{-1}$) | $n$ | Anthropogenic sulphate (mg l$^{-1}$) | Pyrite-derived sulphate (mg l$^{-1}$) |
|---|---|---|---|---|---|---|---|
| Leadenham Landfill | 0 | −0.41 | 1.00 | 123.1 | 0.84 | 103.4 | 19.6 |
| Heath Farm | 1.4 | 0.36 | 0.78 | 119.8 | 0.88 | 105.4 | 14.4 |
| High Dyke | 2.8 | −1.55 | 1.35 | 111.6 | 0.77 | 85.9 | 25.7 |
| Temple Bruar | 4.2 | −3.54 | 0.63 | 125.9 | 0.66 | 83.1 | 42.8 |
| Pot Shot Wood | 5.9 | −1.03 | 1.94 | 112.8 | 0.80 | 90.2 | 22.6 |
| Slate House Farm | 7.3 | −6.50 | 1.87 | 166.3 | 0.47 | 78.1 | 88.2 |
| Ashby 11 B | 7.8 | −6.79 | 1.06 | 125.0 | 0.46 | 57.5 | 67.5 |
| Digby Exploratory | 10.8 | −10.82 | 1.08 | 165.0 | 0.24 | 39.6 | 125.4 |
| Kirkby Green Exploratory | 11.3 | −12.30 | 0.73 | 133.0 | 0.19 | 25.3 | 107.7 |
| Evedon | 12.4 | −11.59 | 0.83 | 111.6 | 0.19 | 21.2 | 90.4 |
| Dorrington Foraky | 12.9 | −13.22 | 1.99 | 97.2 | 0.09 | 8.7 | 88.4 |
| Digby Fen Exploratory | 13.1 | −14.20 | 1.17 | 97.6 | 0.03 | 2.9 | 94.7 |

per thousand (‰) variation relative to the Canon Diablo Troilite (CDT) standard. Statistical analysis of determinations performed on an internal standard (IAEA OGS-1 and chalcopyrite Cp-1) indicates that the results are accurate to within $\pm 0.16‰$ ($2\sigma$).

## 3. Results and discussion

### 3.1. Sulphate sources

Sulphate in groundwaters circulating through sedimentary rocks may be naturally derived from the dissolution of soluble sulphate minerals, the oxidation and solution of reduced sulphur minerals or from a variety of both organic and inorganic atmospheric and soil sources which are combined in recharge to the system.

#### 3.1.1. Agrochemicals

The majority of the limestone outcrop area is under an arable cropping regime which has become progressively more intensive over the last 50 years. Consequently, agricultural fertilizer inputs to the soil have been high over this period. The currently applied Triplesuperphosphate (TSP) and NPK fertilizers have a range of isotopic compositions, from $+1$ to $+10‰$ (Table 2). However, these modern fertilizers have much lower sulphate content than older Singlesuperphosphate (SSP) and ammonium sulphate (AS) fertilizers which were previously in extensive use (Jollans, 1985). These older fertilizers were manufactured using sulphuric acid, which in Britain came from two sources, coal coking and ore smelting. To constrain the isotopic compositions of these older agrochemical inputs, we have analyzed archive samples of SSP manufactured from coking acid ($+5.4‰$, Table 2) and smelter acid used in AS manufacture ($\sim +0.4‰$, Table 2).

Table 2
Sulphate S isotopic compositions of sulphur sources

| Source material | $\delta^{34}S$ (‰) | No. of samples | Standard deviation (‰) |
|---|---|---|---|
| Pyrite (reduced limestone, Brauncewell Quarry) | $-14.9$ | 6 | 5.2 |
| Pyrite (reduced limestone, LH core, mass-weighted mean) | $-14.3$ | 42 | 9.8 |
| Pyrite (Kirton Cementstones) | $-27.6$ | 6 | 4.8 |
| Pyrite (Upper Estuarine mudstones) | $-15.4$ | 2 | 0.8 |
| Gypsum (Upper Estuarine mudstones) | $-15.2$ | 1 | – |
| Fertilizers | | | |
| SSP (from coking acid) | $+5.4$ | 1 | – |
| AS (from smelter acid) | $+0.4$ | 2 | 0.2 |
| TSP | $+8.5$ | 2 | 0.3 |
| NPK 0–16–36 | $+1.0$ | 1 | – |
| NPK 4–25–25 | $+3.1$ | 1 | – |
| NPK 20–10–10 | $+10.3$ | 1 | – |

### 3.1.2. Rainfall and recharge waters

These were sampled during the recharge episode of the winter of 1990/1991. Recharge waters were collected using two large ($15 \, m^2$) lysimeters previously installed under different arable fields more than 1 year ago. Bulk atmospheric deposition was collected at the same site. The water collectors were wrapped in heavy gauge black polythene to inhibit algal growth and had an acidified Cu solution added as a biocide. The bulk deposition and recharge samples are considered to comprise sulphate from two principal diffuse sources of anthropogenic sulphate: ''acid rain'' and fertilizers. A series of large coal-fired power stations in the Trent valley to the west of the area gives rise to atmospheric sulphur deposition or ''acid rain''. This comprises a variety of solid, liquid and gaseous phase oxidised sulphur compounds which are deposited upon the soils of the outcrop area by either dry or wet fallout processes. Inputs from this source can be expected to be supplemented by sulphate derived from the application of fertilisers to the outcrop soils (Smith-Carington et al., 1983) as sulphate from fertilizers is readily leached from the soil (e.g., Robinson and Bottrell, 1997). In each case the accumulated sulphate is leached into the groundwater system by the annual passage of recharge through the outcrop soils and unsaturated zone. The isotopic composition of sulphate in recharge waters from two lysimeters (mean $+2.5‰$, s.d. $0.64‰$) is identical to that of the bulk deposition $+2.4 \pm 0.4‰$ (Table 3). This probably arises due to the low sulphate content of modern fertilizers, making ''acid rain'' sulphate the dominant input source (though some fertilizers are isotopically similar to the ''acid rain'' inputs). In the past, the use of more sulphate-rich fertilizers may have made this source more significant; however, the isotopic compositions of those fertilizers are rather similar to the ''acid rain'' sulphate (Table 2) and though sulphate loading in recharge may thus have been higher in the past, its isotopic composition will have been broadly similar.

### 3.1.3. Aquifer sulphate sources

Where exposed in quarry workings, the Lincolnshire Limestone is generally yellow-buff coloured on weathered fracture surfaces but characteristically blue/grey where unoxidised within the centres of blocks between fractures or in cores recovered from throughout the deep confined zone of the aquifer. The blue/grey colouration derives in part from the presence of pyrite in the unoxidized limestones and analyses were made of
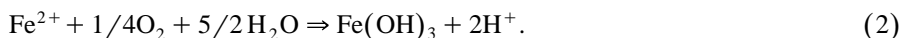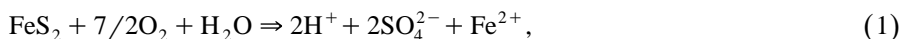
Table 3
Anion and sulphate S isotopic compositions of bulk deposition and lysimeter samples

|  |  | Dec. 1990 | Jan. 1991 | Sampling date | |
|---|---|---|---|---|---|
|  |  |  |  | Feb. 1991 | Mar. 1991 |
| Bulk deposition | $\delta^{34}S$ (‰) | $+2.8$ | $+2.0$ | insufficient | insufficient |
|  | $SO_4^{2-}$ (mg l$^{-1}$) | 75 | 76 | 74 | 81 |
| Lysimeter 1 | $NO_3^-$ (mg l$^{-1}$) | 81 | 89 |  |  |
|  | $\delta^{34}S$ (‰) | $+2.5$ | $+3.0$ | $+1.7$ | $+2.1$ |
|  | $SO_4^{2-}$ (mg l$^{-1}$) | 121 | 112 | 108 | 112 |
| Lysimeter 2 | $NO_3^-$ (mg l$^{-1}$) | 146 | 137 |  |  |
|  | $\delta^{34}S$ (‰) | $+2.6$ | $+3.7$ | $+2.3$ | $+1.9$ |

pyrite content and isotopic composition on samples from Brauncewell Quarry and on samples spaced at $\sim 0.4$ m intervals throughout a core collected from the deep confined zone at Long Holt (LH) (Bottrell et al., 2000). Though there is a range of pyrite isotopic compositions in both sets of data, they give very closely similar average isotopic compositions at $-14$ to $-15$‰ (Table 2). The Kirton Cementstones form a distinctive, clay-rich unit near the middle of the limestone sequence which acts as an aquitard. Pyrite isotopic data from this unit are presented separately (Table 2) as they are strongly biased to more $^{34}$S-depleted compositions ($\sim -28$‰).

The mudstones of the Upper Estuarine Series that overlies the aquifer also contain pyrite with an isotopic composition of $\sim -15$‰ (Table 2). Deposits of gypsum are found at the boundary between the Lincolnshire Limestone and the overlying mudstones. The gypsum occurs as infrequent secondary infill deposits within an iron-stained oxidative weathering horizon, comprising limonite, ferrihydrite and jarosite, at the base of the mudstones. The clear association of the gypsum with the weathering horizon suggests that it is associated with the oxidative weathering of pyrite within the mudstone and the generation of an acidic sulphate enriched leachate:

$$FeS_2 + 7/2 O_2 + H_2O \Rightarrow 2H^+ + 2SO_4^{2-} + Fe^{2+}, \tag{1}$$

$$Fe^{2+} + 1/4 O_2 + 5/2 H_2O \Rightarrow Fe(OH)_3 + 2H^+. \tag{2}$$

Upon migration into the limestone, the solution rapidly becomes saturated with respect to gypsum:

$$H^+ + SO_4^{2-} + CaCO_3 + 2H_2O \Rightarrow CaSO_4 \cdot 2H_2O + HCO_3^-. \tag{3}$$
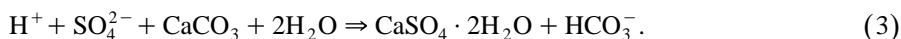
This is confirmed by the near-identical sulphur isotope signatures of the gypsum ($-15.2$‰) and the mudstone pyrite ($-15.4$‰) (Table 2). Since there is little or no isotopic fractionation on oxidation of pyrite to sulphate (Nakai and Jensen, 1964; Toran and Harris, 1989) the gypsum formed retains the original pyrite isotopic composition.

## 3.2. Groundwater sulphate

Mean sulphate concentrations and isotopic compositions for the well waters over the monitoring period are given in Table 1 and their variation down-dip in the aquifer plotted in Fig. 2. Over the area of the western limestone outcrop, average concentrations are constrained to values that vary from 110 mg $l^{-1}$ to 125 mg $l^{-1}$. Further down-dip, concentrations initially increase from this level, peaking at 166 mg $l^{-1}$ close to boundary of the limestone outcrop, before gradually falling back to values of $\sim 100$ mg $l^{-1}$. Sulphate isotope compositions (Fig. 3) also show down-dip variation. Over the area of the western unconfined zone, to within a distance of 2 km of the eastern margin of the outcrop, the sulphate $\delta^{34}$S exhibits a narrow range of values that are close to 0‰. Down-gradient of this zone, and throughout the shallow confined zone, $\delta^{34}$S becomes progressively more negative, ultimately reaching values approaching $-15$‰. The down-gradient evolution of sulphate isotopic composition is very pronounced and the straight line fit to the groundwater data in Fig. 3 has $R = 0.96$, significant at the 99.9% confidence level.
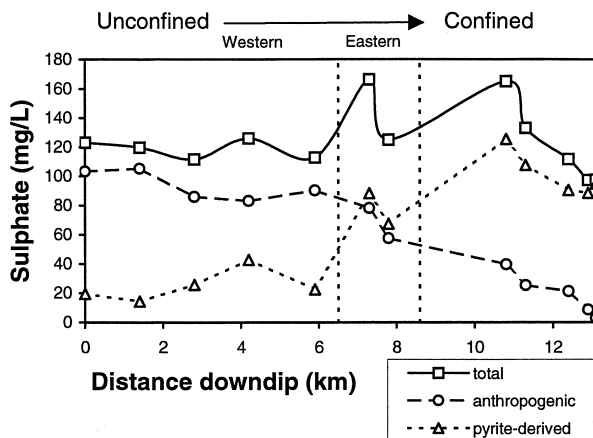
Fig. 2. Down-dip variation in sulphate concentrations in groundwaters of the Lincolnshire Limestone. The anthropogenic and pyrite-derived sulphate concentrations are those calculated using the isotope mass balance model detailed in the text.

In the deep confined zone, at a point which coincides with a precipitous decline in sulphate concentrations, this trend is abruptly reversed and sulphate becomes strongly $^{34}$S-enriched, with some values reaching in of excess of $+30‰$ as a result of sulphate reduction (Bottrell et al., 2000). Only the part of the aquifer up-gradient of this influence is considered in this work.

Groundwaters in the western outcrop area are characterized by sulphate isotopic compositions consistently slightly more $^{34}$S-depleted than the recharge water (by $\sim 3.5‰$, mean outcrop area groundwater sulphate $\delta^{34}S = -1‰$ vs. $2.4‰$ for the recharge waters). The limestones contain pyrite, and quarry exposures show abundant
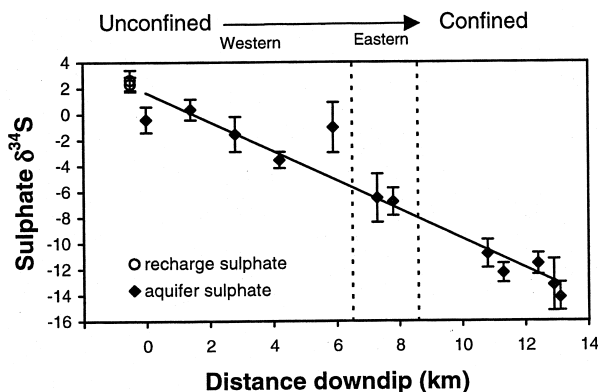


Fig. 3. Down-dip variation in sulphate isotopic compositions in groundwaters of the Lincolnshire Limestone. Data for recharge waters from lysimeters are plotted for comparison. Error bars give one standard deviation based on monthly samples over 1 year.

evidence for oxidation reactions adjacent to fissure surfaces, so addition of [34]S-depleted sulphate via pyrite oxidation (Reaction 1) is the likely cause of this change. Over the area of the western unconfined zone, the groundwater sulphate budget is dominated by anthropogenic inputs from recharge waters with slight addition of sulphate from pyrite oxidation.

The gradual down-dip decrease in groundwater sulphate [34]S content in the eastern outcrop and confined zones indicates that sulphate derived from pyrite oxidation becomes progressively more important in this part of the aquifer. On the basis of this evidence, the aquifer may be partitioned into two zones in which the up-gradient outcrop zone is dominated by the impact of anthropogenic sulphate inputs whilst the down-gradient, shallow confined zone is characterised by mixing between isotopically heavy pollution sulphate and isotopically light natural sulphate in which the latter becomes increasingly more significant. This down-gradient trend appears to confirm, therefore, the concept of a front of sulphate enriched polluted groundwater migrating down-dip into a portion of the aquifer in which natural pre-pollution groundwaters predominate.

### 3.3. Pollution front migration

Migration of the pollution front in the Lincolnshire Limestone may be modelled by use of a simple two end-member mixing model. In order for such a model to be appropriate it must be possible to:

1. rationalise the significant sulphate inputs into two representative end-member values;
2. establish that sulphate is not removed from the system.

In general, sinks for sulphate within aquatic systems are limited to redox transformations and precipitation as sulphate minerals (Francois and Gerrard, 1986). None of the sampled groundwaters are saturated with respect to any of the common sulphate minerals (e.g., gypsum, Reaction (3)) and our modelling is restricted to the areas of the aquifer up-dip of the influence of bacterial sulphate reduction. In this simple system there are two sources of groundwater sulphate (anthropogenic sources in recharge water and sulphate derived by pyrite oxidation) and no sinks, thus mixing is described by:

$$C_g \cdot \delta^{34}S(SO_4)_g = C_a \cdot \delta^{34}S(SO_4)_a + C_p \cdot \delta^{34}S(SO_4)_p, \qquad (4)$$

where:

| | |
|---|---|
| $C$ | concentration |
| $\delta^{34}S(SO_4)$ | sulphate sulphur isotope composition |
| g | total groundwater sulphate |
| a | anthropogenic sulphate component |
| p | component from pyrite oxidation. |

Since:

$$C_g = C_a + C_p, \qquad (5)$$

then,

$$\delta^{34}S(SO_4)_g = (n)\left(\delta^{34}S(SO_4)_a\right) + (1-n)\left(\delta^{34}S(SO_4)_p\right), \tag{6}$$

where $n$ = proportion of anthropogenic sulphate.

The consistent isotopic composition of the samples of sulphate in recharge waters indicate that anthropogenic sulphate inputs have a value of $+2.5‰$ (average value from eight measurements, s.d. is 0.58‰). This value is thought to be representative not only of the current pollution inputs to the system but also of that which historically would have been generated by application of more sulphate-rich fertilizers to the outcrop soils (see Table 2 and discussion above). The similarity of the pyrite sulphur signatures in both the pure limestone matrix material and the mudstone and shales of the overlying confining strata indicate a value of $-15.0‰$ for the natural inputs of sulphur to the system. This value is chosen in preference to the lighter compositions of the pyrite in the Kirton Cementstones as limestone predominates in the aquifer and there is field evidence for greater weathering of the limestone and overlying mudstone relative to the Kirton Cementstone.

Using this model yields the results detailed in Table 1 and Fig. 2, which indicate the following points.

### 3.3.1. Predominance of anthropogenic inputs over the area of the western unconfined zone

Between 66% and 88% of the sulphate in the outcrop groundwaters is derived from anthropogenic sources (Table 1). Thus, the unconfined zone is dominated by modern, polluted groundwaters as proposed by Bishop and Lloyd (1990a). This predominance can be attributed to the low specific yield of the limestone, the resulting limited porewater–fissure water interaction (Smith-Carington et al., 1983) and the regular flushing of the system by the annual passage of pollution-sulphate dominated recharge. Under these circumstances pre-existing ''natural'' groundwaters will have been rapidly displaced from the system by modern recharge.

### 3.3.2. Occurrence of small but significant amounts of pyrite-derived sulphate in the unconfined zone

Despite the predominance of pollution-derived sulphate over the area of the western unconfined zone, a significant proportion of the total sulphate, between 12% and 34% (14 to 43 mg $l^{-1}$), is derived from pyrite oxidation (Wells 1–4, Table 1). Given that the pyrite is restricted in occurrence to the unexposed interiors of the limestone blocks, this indicates a significant degree of interaction between the fissure waters and the aquifer matrix material. The anomalously large component of pyrite oxidation sulphate component at the Temple Bruar well (Table 1) may well be an anthropogenic effect, attributable to the impact of deep excavations within the limestone in the vicinity of the well.

### 3.3.3. There is an abrupt increase in the concentration of pyrite-derived sulphate at eastern margin of the unconfined zone

This increase takes place over a down-dip distance of 1.9 km between Pot Shot Wood, Slate House Farm and Ashby II B wells and coincides with the transition from

unconfined to confined conditions within the aquifer. Large variations in groundwater head levels (in excess of 10 m) occur at the eastern boundary of the unconfined zone resulting in the annual saturation and dewatering of a locally significant section of the limestone and overlying mudstones (Harley, 1979). This leads to the generation of a zone of enhanced oxidative weathering (described from quarry exposure and trial pits, above) from which the sulphate derived from pyrite oxidation will be actively flushed on an annual basis. At the Slate House Farm well, the increase in natural sulphate concentration augments established concentrations of anthropogenic sulphate and results in a marked peak in total sulphate concentration.

### 3.3.4. Progressive increase in the concentration of natural sulphate and a corresponding decline in anthropogenic sulphate concentrations

In the confined zone, concentrations of pyrite-derived sulphate peak at 125 mg $l^{-1}$ before declining to 90–95 mg $l^{-1}$ further down-dip. Over the same area, concentrations of anthropogenically derived sulphate progressively decline, ultimately approaching zero. The progressive increase in significance of pyrite-derived sulphate indicates that the down-gradient decline in concentrations of pollution-derived sulphate can be attributed to mixing between comtemporary groundwaters and older pre-pollution groundwaters which contain approximately 100 mg $l^{-1}$ of naturally derived sulphate. This result confirms the general model of ''pollution front migration'' but indicates that the penetration of the front is far more restricted than would otherwise be suggested by consideration of the total sulphate concentrations alone. The peak in total sulphate was formerly considered to represent older polluted waters from recharge contaminated with sulphate-rich AS and SSP fertilizers (e.g., Edmunds and Walton, 1983) but this is not the case. The restricted penetration of the pollution front is likely the result of the combined effects of dispersion and the generation of lateral flowpaths within the confined zone in response to abstraction and down-gradient decreases in transmissivity.

### 3.4. Groundwater–aquifer matrix interactions

In the unconfined zone, around 20 mg $l^{-1}$ of sulphate is derived from pyrite oxidation sources (ignoring the Temple Bruar well affected by building works). In this zone, oxidation of pyrite in the limestones is observed to give rise to secondary oxidized iron minerals, so the overall mass balance of pyrite oxidation by dissolved oxygen will be:

$$FeS_2 + 15/4O_2 + 7/2H_2O + 4CaCO_3 \Rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4HCO_3^- + 4Ca^{2+}.$$
(7)
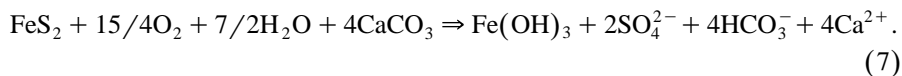
According to the stoichiometry of this reaction, water saturated with a normal atmosphere ($\sim 300$ $\mu$mol $l^{-1}$ $O_2$) would be capable of producing 160 $\mu$mol $l^{-1}$ (16 mg $l^{-1}$) $SO_4^{2-}$ in solution. This is a little less than the observed addition of sulphate, but dissolved gas isotope ratio studies of Lincolnshire Limestone groundwaters (Wilson et al., 1990) indicate 20–50% additional air component by entrainment which would account for the difference. In this zone pyrite oxidation is probably limited by $O_2$ availability and is the dominant sink for dissolved $O_2$.

In the shallow confined zone, increasingly significant concentrations of pyrite-derived sulphate enter the groundwater system. In this zone, groundwater carbon and strontium isotope compositions shift toward those of the aquifer carbonate (Bishop and Lloyd, 1990a; Smalley et al., 1994). This has previously been linked to widespread incongruent dissolution and dissolution/reprecipitation of the primary carbonate material within the limestone (Bishop and Lloyd, 1990a; Smalley et al., 1994). The association between the effects of carbonate dissolution and pyrite oxidation observed in the groundwaters of this zone could be explained by reaction (7) which will also release limestone-derived bicarbonate and $Sr^{2+}$ (substituted for $Ca^{2+}$ in calcite) into the groundwater. However, we do not believe that this is the case for the following three reasons.

(1) Available $O_2$ will have largely been depleted by pyrite oxidation in the unconfined zone as described above.

(2) In the shallow confined zone, changes in groundwater C and Sr isotopic compositions are accompanied by increases in Mg and Sr concentrations and Mg/Ca and Sr/Ca (Bishop and Lloyd 1990a), which must be the result of dissolution/reprecipitation reactions as reaction (7) would cause stoichiometric dissolution of Mg and Sr from calcite, and therefore not affect Mg/Ca and Sr/Ca ratios.

(3) the increases in Mg and Sr concentrations are not accompanied by significant increases in Ca concentrations (Bishop and Lloyd 1990a), as would be expected from reaction (7).

The next available oxidizing agent for pyrite oxidation is nitrate, available in abundance as a result of agrochemical pollution. Nitrate reduction utilizing pyrite as an electron donor is thermodynamically feasible and may be bacterially mediated (e.g., Robertson et al., 1996):

$$5FeS_2 + 14NO_3^- + 4H^+ \Rightarrow 5Fe^{2+} + 10SO_4^{2-} + 7N_2 + 2H_2O. \qquad (8)$$
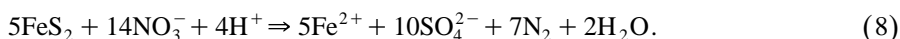
This reaction consumes $H^+$ and has thus been considered not to be feasible in carbonate aquifers where pH is buffered at values $> 7$. However, there is evidence that nitrate reduction does indeed occur. Dissolved gas $N_2/Ar$ increases (from $\sim 38$ to $\sim 55$) and $N_2-\delta^{15}N$ changes (to more $^{15}$N-depleted compositions) down-gradient in the aquifer, consistent with denitrification (Wilson et al., 1990). There is also a mass imbalance for nitrate compared with that expected from simple mixing/dispersion processes (Lawrence and Foster, 1986) indicative of nitrate loss by other processes. We confirm this by comparing attenuation of nitrate with the anthropogenic sulphate component in the groundwaters. Nitrate concentrations fall very rapidly to zero in the shallow confined zone as a result of bacterial denitrification, whereas simple mixing-dispersion (for which we use anthropogenic sulphate as a tracer) would cause significant nitrate to be transported into the deeper confined aquifer (Fig. 4).

In the Lincolnshire Limestone $O_2$ and $NO_3^-$ concentrations, both decline in the shallow confined zone (Edmunds and Walton, 1983) and we suggest that nitrate reduction by pyrite oxidation may be feasible if the $Fe^{2+}$ generated in reaction (8) undergoes oxidation by dissolved $O_2$ (reaction 2) giving the overall reaction:

$$20FeS_2 + 52NO_3^- + 5O_2 + 42H_2O \Rightarrow 20Fe(OH)_3 + 40SO_4^{2-} + 28N_2 + 24H^+.$$
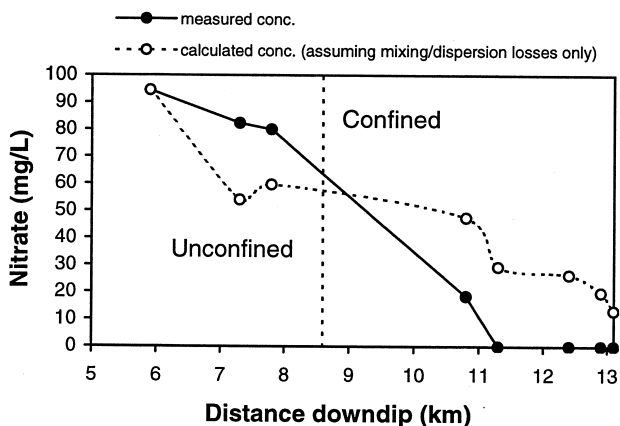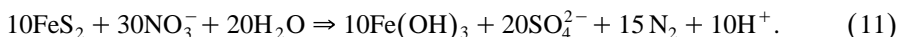
$$(9)$$
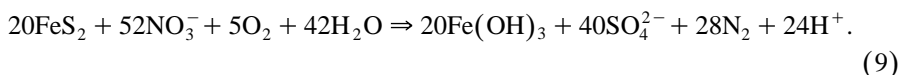
Fig. 4. Attenuation of nitrate pollution by bacterial denitrification evidenced by the precipitous decline in nitrate concentrations in the shallow confined zone compared to those predicted on the basis of mixing dispersion alone. The mixing dispersion values were calculated using the dispersion of the anthropogenic component sulphate in the system and assuming that the input $NO_3^-/SO_{4\ anthropogenic}^{2-}$ is equivalent to that observed at the Pot Shot Wood borehole in the unconfined zone.

Alternatively, bacterial iron oxidation by nitrate reduction has been shown to occur (Straub et al., 1996) with a stoichiometry consistent with:

$$10Fe^{2+} + 2NO_3^- + 24H_2O \Rightarrow 10Fe(OH)_3 + N_2 + 18H^+, \tag{10}$$
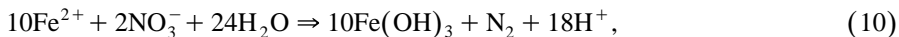
which would give an overall reaction:

$$10FeS_2 + 30NO_3^- + 20H_2O \Rightarrow 10Fe(OH)_3 + 20SO_4^{2-} + 15N_2 + 10H^+. \tag{11}$$

Both of these reactions are net generators of $H^+$ and may locally overcome the consumption of $H^+$ by carbonate dissolution. This might occur in carbonate-free weathered crusts on fissure surfaces where a chemically zoned environment like that depicted in Fig. 5 could develop. The existence of such crusts is consistent with the findings of Greswell et al. (1998) who identified high porosity coatings on fissure surfaces which could be inhabited by bacteria. Oxidation of $Fe^{2+}$ by $O_2$ nearer the fissure surface (or up-flow in the fissure flow network) would ensure an anoxic microenvironment deeper in the crust where nitrate reduction by pyrite cound take place. Indeed, Lawrence and Foster (1986) found that nitrate-reducing bacterial activity was localized in weathered crusts on fissure surfaces. Bacterial activity is very likely to be restricted to the fissure surfaces, as studies of sulphate reduction (Bottrell et al., 2000) and nitrate reduction (Lawrence and Foster, 1986) have shown that porethroat diameters in the limestone are too small to allow bacterial colonization of the aquifer matrix. Thus, unless limestone dissolution by the excess acidity produced in reactions 9 and/or 11 keeps pace with the utilization of pyrite in the matrix, the surface colonized by nitrate reducing bacteria will ultimately become depleted in pyrite, removing the availability of an electron donor. Reaction 9 consumes 20 mol of pyrite (2397 g) to yield 24 mol of $H^+$ (which would be capable of dissolving a maximum of 2400 g $CaCO_3$) and reaction 11 would yield 20 mol of $H^+$ for the same 20 mol of pyrite (equivalent to a maximum
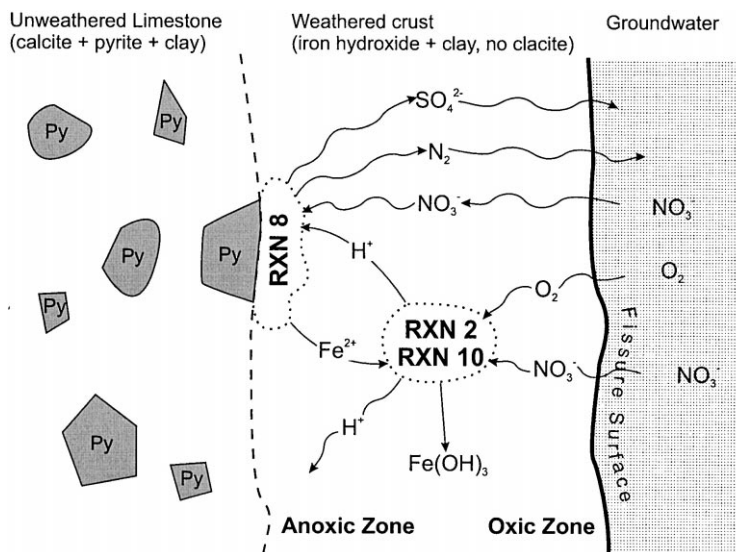
Fig. 5. Conceptual chemical model for the coupled reduction of nitrate and oxygen on fissure surfaces in the shallow confined zone using pyrite as an electron donor.

2000 g $CaCO_3$ dissolution). Since pyrite only comprises ∼ 1% by mass of the limestone, a pyrite-depleted carbonate crust will develop, restricting the potential for denitrification utilizing pyrite as an electron donor. The development of such crusts can explain the dominance of pyrite oxidation by $O_2$ (and lack of $NO_3^-$ reduction by pyrite) in the more weathered limestones of the outcrop zone; pyrite oxidation by $O_2$ does not require bacteria (Singer and Stumm, 1970) and dissolved $O_2$ can diffuse past the pyrite-depleted zone to oxidize pyrite deeper in the aquifer matrix blocks.

In the shallow confined zone, pyrite-derived sulphate concentrations increase from ∼ 20 to ∼ 120 mg $l^{-1}$ (Table 1, Fig. 2), which, by the stoichiometry of nitrate reduction, would correspond to a reduction of ∼ 87 mg $l^{-1}$ $NO_3^-$. This is slightly larger than the 60 mg $l^{-1}$ nitrate loss observed (in 1979) by Edmunds and Walton (1983) but consistent with the nitrate concentrations we observe in recharge waters (∼ 85–140 mg $l^{-1}$, Table 3). The highest concentrations of pyrite-derived sulphate occur at the Digby Exploratory well (125 mg $l^{-1}$, Table 1), before falling again to around 90 mg $l^{-1}$ still further down-dip (Fig. 2). This peak in the concentration of sulphate derived by pyrite oxidation may arise from abstraction for water supply in this region of the aquifer, drawing in relatively oxidizing and nitrate-rich waters from up-dip and increasing pyrite oxidation rates (and hence pyrite-derived sulphate concentrations) relative to older waters further down-dip unaffected by abstraction. The decline in pyrite-derived sulphate in this deep portion of the aquifer might also reflect generation of sulphate in earlier times when nitrate concentrations in recharge waters were lower (and hence generation of sulphate by nitrate reduction was less significant). The fact that pollution-derived sulphate concentrations fall markedly over the same interval (Fig. 2) suggests that this may indeed be the case.

## 4. Conclusions

Over the area of the western limestone outcrop, anthropogenic inputs from acid rain and agrochemicals predominate, confirming the established view that this portion of the aquifer is dominated by inputs of contemporary recharge. In this zone, the amount of sulphate added from pyrite oxidation corresponds well with available $O_2$ in the groundwater and $O_2$ availability may limit rapid pyrite oxidation here. At the eastern margin of the unconfined zone, inputs of pyrite-derived sulphate become increasingly significant. Since there is inadequate dissolved $O_2$ to sustain this pyrite oxidation, nitrate reduction is the presumed mechanism. This fits with previous models based on dissolved gas analysis and studies of core porewater nitrate and microbial populations. The extent of pyrite oxidation observed corresponds well with that expected from recharge nitrate concentrations. Since nitrate reduction using pyrite as an electron donor is a proton-consuming reaction, it has often been considered not to be viable in carbonate aquifers; we conclude that it probably takes place on microenvironments where consumption of protons by carbonate dissolution is inhibited and protons are available from Fe(II) oxidation.

The gradual decline in concentrations of anthropogenically derived sulphate over the same area to concentrations close to zero indicates that the ''pollution front'' penetration of the system is more strongly restricted than previously thought. However, pollution attenuation processes are restricted to the confined zone and, by comparison, in the up-gradient areas of the aquifer, the matrix pore-waters must contain a large proportion of anthropogenically derived sulphate, and thus have become effectively saturated with modern polluted groundwaters.

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