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Sulphur cycling in the drinking water catchment area of Torgau–Mockritz (Germany): insights from hydrochemical and stable isotope investigations

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Abstract:

The hydrochemical composition of groundwater and the isotopic composition of sulphur compounds in sediments (δ^{34}S of sulphide, inorganic sulphate) and groundwater (δ^{34}S, δ^{18}O of dissolved sulphate) have been investigated to reveal the reasons for elevated concentrations of dissolved groundwater sulphate in the drinking water catchment area of Torgau–Mockritz (Germany).

The three most important anthropogenic sources of sulphate identified in this study are historic atmospheric sulphate deposition, predominantly of anthropogenic origin, inorganic fertilization, and dissolution of gypsum from waste dumps. Owing to their overlapping isotopic range, no clear differentiation between the individual anthropogenic sources is possible. Sulphate from the oxidation of sedimentary sulphides, however, was recognized by its negative sulphur isotope signature ($\delta^{34}\mathrm{S} < -5‰$).

The mobilization of sulphate from different soil sulphur species is closely connected with variable isotopic fractionations, resulting in a wide isotopic variation range for the sulphate entering the saturated zone. Generally, sulphur and oxygen isotope ratios of the dissolved groundwater sulphate range from −19 to +37‰ (Vienna Cañon Diablo troilite) and from −2 to +19‰ (Vienna standard mean ocean water), respectively. Sulphate from the majority of groundwater samples can be assigned to anthropogenic sources. Sulphate from sulphide oxidation is especially present in samples from the upper sampling level and the groundwater surface. Sulphate concentrations above 700 mg $\mathrm{l^{-1}}$ are mostly caused by the oxidation of sulphide. Sulphate that occurs in low and moderate concentrations dominantly originates from anthropogenic sources.

δ^{34}S distribution patterns were used to locate the sources for the elevated sulphate concentrations in the raw water. It was shown that the sulphate is not mobilized in the immediate vicinity of the production wells. Rather, it originates in an area ~1·5 km west of the intake. The main mobilization mechanism there is the oxidation of reduced sedimentary sulphur species.

Beyond its local significance, this study presents a general example how changes in the sulphur cycle indicate major, anthropogenically induced alterations of the hydrochemical situation in catchment areas. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS groundwater; drinking water; sulphate; sulphur isotopes; oxygen isotopes; sulphide oxidation

INTRODUCTION

The waterworks of Torgau–Mockritz in eastern Germany (Figure 1), as part of the water company Fernwasserversorgung Elbaue–Ostharz, is one of the biggest suppliers of drinking water in the densely populated industrial region surrounding the major cities of Leipzig and Halle. Owing to a lower drinking water demand after German unification, the water production rate of the Torgau–Mockritz waterworks was drastically reduced in the mid 1990s. Simultaneously, a significant elevation of the sulphate concentration was observed

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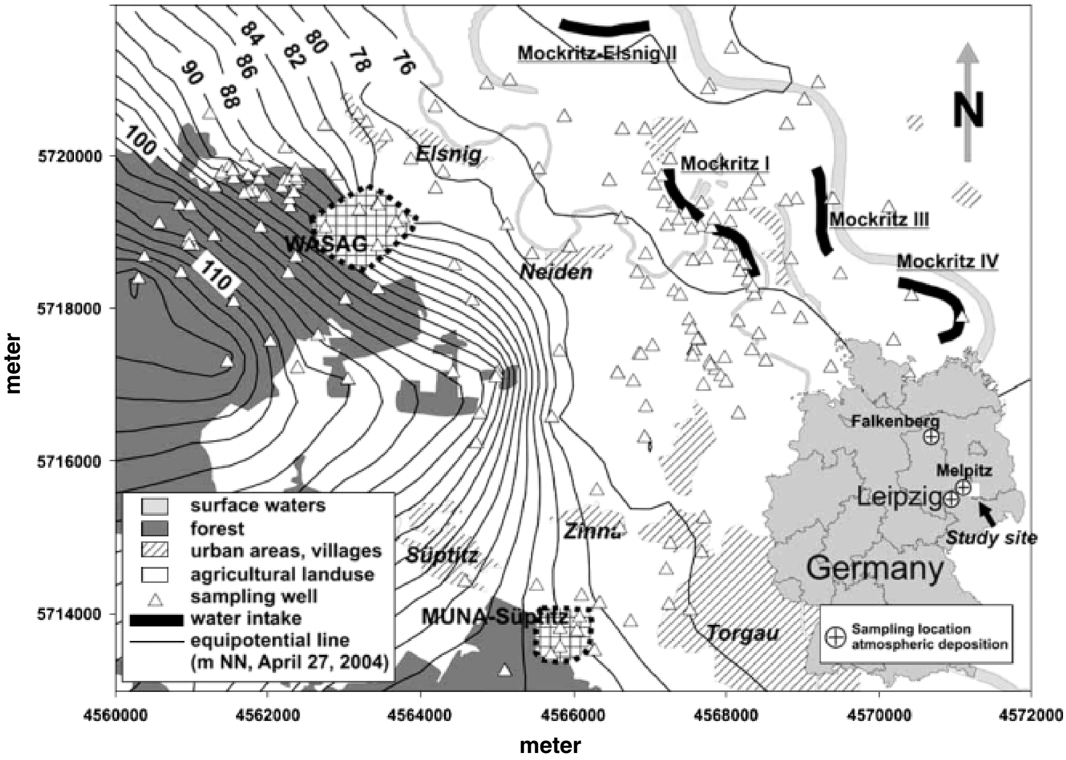

Figure 1. Overview of the study area (coordinates: Kraus-Krueger, Bessel-ellipsoid)

in the raw water that was collected from certain production wells, especially in the Mockritz I water intake (Figure 1).

Nowadays, the main goal of many water companies is to manage their water resource according to the principles of sustainability. Regarding those principles, and owing to the low toxicity of dissolved sulphate, the sulphur cycle seems to play just a secondary role. However, changes in the sulphur cycle indicated by rising sulphate concentrations point to a major alteration of the general hydrochemical and hydrological situation in the watershed.

Despite the low toxicity of sulphate, its presence deteriorates the quality of the drinking water. High sulphate concentrations influence the water hardness, cause corrosion in water pipelines, and impair the taste of the drinking water. According to the EU Drinking Water Directive, sulphate is considered as an indicator parameter with a parametric value of 250 mg l^{-1}. These quality aspects put economic constraints on the water companies to take measures keeping the sulphate concentration in the collected drinking water as low as possible.

Transformation and redox processes connected with the sulphur cycle in catchment areas have been investigated in many studies (e.g. Kölle *et al.*, 1983; Hendry *et al.*, 1989; Strebel *et al.*, 1990; Bottrell *et al.*, 1991, 2000; Dowuona *et al.*, 1993; Robertson *et al.*, 1996; Moncaster *et al.*, 2000; Dogramaci *et al.*, 2001), using a variety of hydrochemical and stable isotope methods.

The general objective of this research paper is to determine the reasons for the elevated sulphate concentrations in the raw water produced by means of hydrochemical stable environmental isotope investigations. The assessment is focused on the evaluation of the relevant sulphate sources and of possible sulphur pathways by examining the hydrochemical composition of the groundwater and the isotopic composition of dissolved and sedimentary sulphur compounds in soils and groundwater.

REGIONAL SETTING

The drinking water catchment area of Torgau–Mockritz, situated in the northwestern part of Saxony in Germany, northwest of the city of Torgau and west of the River Elbe (Figure 1), covers an area of ~100 km^2. For collecting drinking water, the water company presently operates three of the four existing water intakes. The two intakes close to the River Elbe (Mockritz III and IV in Figure 1) do not produce sulphate-rich drinking water, since they exclusively collect low-mineralized bank filtrate from the River Elbe. The Mockritz I water intake, however, is strongly affected by high sulphate concentrations, because it receives its raw water from the western groundwater inflow. Owing to the reduced production rate, the northernmost water intake Mockritz–Elsnig II is no longer operated.

In 1930, the waterworks were originally built to supply water for nearby ammunition and explosive factories (WASAG, MUNA-Süptitz; see Figure 1), which were destroyed during World War II. After 1945, drinking water was produced at a very low rate in order to contribute to the regional water supply. Between 1968 and 1981, the technical production capacity of the water works was progressively increased from 30 000 to 124 000 $\text{m}^3\ \text{day}^{-1}$. The highest production of $\sim 36 \times 10^6\ \text{m}^3\ \text{year}^{-1}$ was realized in the mid 1980s. From 1989 to 1995, the production was reduced to $10 \times 10^6\ \text{m}^3\ \text{year}^{-1}$.

The catchment area is mainly used for agriculture. Forest use is limited to the southwestern and western border of the area. The general groundwater flow direction is from the upland in the west to the River Elbe in the east, as demonstrated by the equipotential lines in Figure 1.

Geologically, the area is divided into two different sections: a Holocene flood plain in the eastern part and a very heterogeneously structured moraine area in the western part. Situated in a wide glacial erosion basin, the aquifer in the flood plain predominantly consists of sands and gravels of variable grain size and reaches a thickness of about 50–60 m. Generally, the flood plain is covered by meadow loam of variable thickness and low permeability and underlain by Tertiary clay. Locally, where the loam cover is missing, coarse-grained silts to fine-grained sands of much higher permeability conceal the aquifer instead. The moraine area is characterized by complicated stratigraphic sequences consisting of pushed moraines, including uplifted fragments of Tertiary layers. Despite the large number of drill holes, the geological situation in the moraine area and in the transition zone between flood plain and moraine area has not been clarified satisfactorily yet.

The study area is situated in the central European climatic changeover range between temperate maritime and continental climate. The average precipitation amounts to 587 mm year^{-1}. The mean annual temperature is 9·0 °C. Although the mean groundwater recharge rate in the moraine area ranges from 110 to 130 mm year^{-1}, a smaller rate of ~80 mm year^{-1} was postulated for the flood plain (Nestler *et al.*, 2004).

In the study area, more than 100 groundwater sampling locations have been installed since the early 1970s (Figure 1). Most of the wells have two or three sampling levels. This dense network of sampling wells was set up for monitoring the groundwater quality in the inflow of the water intakes and for assessing possible groundwater contamination in the outflow of the former ammunition and explosives production sites. For this study, 27 additional sampling wells along hypothetical flow paths were installed, especially where they provide access to the groundwater surface. Numerous samples from the groundwater surface were also collected during the drilling work.

ANALYTICAL METHODS AND SAMPLING

Groundwater samples from a total of 256 sampling wells were taken after three well volumes had been purged and the field parameters measured at the wellhead had stabilized. Samples for the measurements of sulphate concentrations were filtered on site through a 0·45 μm membrane. The sulphate concentration analysis was performed by ion chromatography. Groundwater samples for sulphur and oxygen isotope analysis were stabilized with chloroform and zinc acetate. Dissolved sulphate was recovered by precipitation as $BaSO_4$ at 70 °C after the pH of the solution was adjusted to 2·5. For the preparation of the sulphate from inorganic fertilizers, 10 g of the respective fertilizer material was dissolved in 100 Ml deionized water. The solution was filtered and then the sulphate precipitated as $BaSO_4$, as explained above.

Soil samples were collected in the course of the drilling work for installing new groundwater sampling wells. The soil samples were immediately transferred into gas-tight plastic bags that were thoroughly flushed with nitrogen before closing. Inorganic sulphate from soil was extracted by shaking 150 g of dried unground soil sample with 1000 ml deionized water for 18 h. The supernatant liquid was centrifuged and then filtered through a 0·45 µm membrane. Again, the sulphate was precipitated as $BaSO_4$.

Inorganic sulphur compounds from sediment samples were recovered by a two-step distillation method (Canfield *et al.*, 1986; Fossing and Jorgensen, 1989). Initially, sediment samples were reacted with 6 M hydrochloric acid in a distillation apparatus under permanent nitrogen gas flow. Acid volatile sulphur (AVS) was liberated as H_2S, precipitated as ZnS and subsequently converted to Ag_2S by addition of 0·1 M $AgNO_3$ solution.

After complete extraction of AVS, the supernatant acidic solution was removed from the reaction apparatus. Subsequently, the remaining sediment sample was boiled for 2 h after addition of acidified $CrCl_2$ solution (Canfield *et al.*, 1986; Fossing and Jorgensen, 1989). The H_2S resulting from the conversion of FeS_2 and S^0 (chromium reducible sulphur (CRS)) was carried with the N_2 gas flow into a zinc acetate trap and then converted to ZnS and Ag_2S as described above.

Sulphur isotopic compositions were measured after conversion of $BaSO_4$ or AgS_2 to SO_2 using the continuous flow combustion technique coupled with isotope-ratio mass spectrometry (delta S, Finnigan MAT). Sulphur isotope measurements were performed with an analytical error of the measurement of ±0·3‰ and results are reported in δ notation ($\delta^{34}S$) as parts per thousand (‰) deviation relative to the Vienna Cañon Diablo troilite (VCDT) standard. For normalizing the $\delta^{34}S$ data, the IAEA-distributed reference materials NBS 127 ($BaSO_4$) and IAEA-S1 (Ag_2S) were used. The assigned values were 20·3‰ (VCDT) for NBS 127 and −0·3‰ (VCDT) for IAEA-S1. Oxygen isotope analysis on $BaSO_4$ samples was carried out by pyrolysis at 1450 °C in a TC/EA connected to a delta plus XL mass spectrometer (Finnigan MAT) with an analytical precision of ±0·5‰. The results of oxygen isotope measurements are expressed in δ notation ($\delta^{18}O$) as parts per thousand (‰) deviation relative to Vienna standard mean ocean water (VSMOW). The normalization of oxygen isotope data of sulphate was carried out using the reference material NBS 127 with an assigned $\delta^{18}O$ value of 9·3‰ (VSMOW).

RESULTS AND DISCUSSION

Sources of dissolved sulphate in the study area

The essential basis for the description of the sulphur cycle in drinking water catchment areas by means of stable isotopes is the exact knowledge of the isotopic composition and the local and regional relevance of the present sources of dissolved sulphate. Generally, natural and anthropogenic sulphate sources can be distinguished in the catchment area of Torgau–Mockritz.

Possible natural sources of sulphate are sulphides in deeper sequences of the aquifer and sulphate-rich brines from the underlying Palaeozoic Zechstein aquifer. Investigations of the hydrodynamics in the catchment area by Trettin *et al.* (2002) showed that there is no evidence for an infiltration of such. Hence, the highly mineralized brines can be ruled out as a source of sulphate.

The anthropogenic sulphur input occurs from diffuse sources and from point sources. Diffuse sources are the application of inorganic fertilizers and atmospheric sulphur deposition. Even though the atmospheric deposition contains a natural component, those natural emissions are likely to be two to three orders of magnitude lower than the anthropogenic component in highly industrialized regions (Whelpdale, 1992). Therefore, the atmospheric deposition in the study area is considered as an anthropogenic source, neglecting the natural component. Point sources are expected in the closer vicinity of gypsum waste dumps. Those dumps were deposited during the operation of former ammunition and explosives factories.

Isotopic composition of sedimentary sulphides

Of the 60 soil samples that were prepared for the isotopic analysis of reduced inorganic soil sulphur, only nine samples contained AVS. The AVS content in those samples was approximately two orders of magnitude lower than the respective CRS content. The term 'sedimentary sulphide' used throughout the following discussion only refers to the CRS fraction, which is predominantly composed of disulphide. Elemental sulphur normally contributing to the CRS fraction only occurs in traces and can hence be neglected (Nestler *et al.*, 2004).

Generally, the δ^{34}S values of sedimentary sulphides from all depths of the saturated zone scatter in a wide range between −48 and −5‰ (VCDT). The frequency distribution of all samples analysed (Figure 2) does not show a significant maximum. However, Figure 2 reveals a systematic behaviour of the δ^{34}S values depending on the sampling depth. For sedimentary sulphide samples from the depth range between 5 and 40 m below the groundwater surface, a relatively uniform isotopic composition between −30 and −20‰ (VCDT) was observed. This isotopic range is typical for sulphides formed in marine Tertiary sediments (Knöller, 2000; Strauch *et al.*, 2003, Knöller *et al.*, 2004). The Quaternary sediments of the aquifer are glacial formations that mainly consist of displaced, mixed, and redeposited Tertiary material. Therefore, a Tertiary age of formation of the major portion of the sulphides in the depth range below 5 m seems very likely. Sulphides present in a depth range of 0 to 5 m below groundwater surface in areas that are covered by fine-grained silt or clay show a much larger scattering of their δ^{34}S values (−48 to −5‰).

The oxidation of sedimentary sulphide is accompanied by no (Nakai and Jensen, 1964; Taylor *et al.*, 1984b) or at most by a minor sulphur isotopic fractionation (Toran and Harris, 1989) between sulphide and the newly formed sulphate. Hence, a tight correspondence between the sulphur isotopic compositions of sulphide and dissolved sulphate is expected. Since all sulphide samples showed δ^{34}S values lower than −5‰ (VCDT), sulphate that comes from sulphide oxidation should also have a clearly negative sulphur isotope signature (<−5‰).

The oxygen isotope composition of dissolved sulphate depends strongly on the mechanism of sulphide oxidation (Taylor *et al.*, 1984a,b; Van Everdingen and Krouse, 1985; Toran and Harris, 1989; Taylor and Wheeler, 1994; Van Stempvoort and Krouse, 1994). If pyrite is oxidized in aerobic conditions by dissolved O_2, only 12·5% of the oxygen in the newly formed sulphate is derived from water. 100% oxygen from water is incorporated into the sulphate molecule if the oxidation is carried out in anoxic conditions by ferric iron.

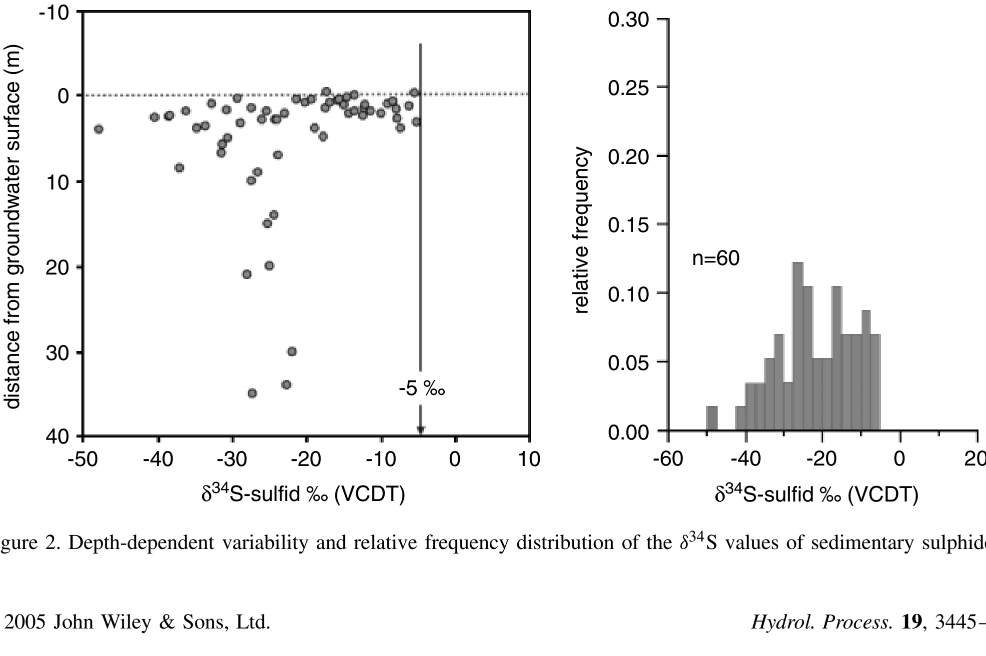

Figure 2. Depth-dependent variability and relative frequency distribution of the δ^{34}S values of sedimentary sulphides

The two oxygen sources show a large difference in their isotopic compositions. Whereas atmospheric oxygen has a δ^{18}O value of 23·5‰ (Kroopnick and Craig, 1972), the oxygen isotopic composition of water is typically negative, in our case showing a mean value of approximately −9‰ (Trettin *et al.*, 2002). Taylor and Wheeler (1994) suggested the following equation for calculating the relative proportions of oxygen derived from water and air:

$$\delta^{18}O_{SO_4{}^{2-}} = X_{O_2}\ (\delta^{18}O_{O_2} + \varepsilon_{O_2}) + X_{H_2O}\ (\delta^{18}O_{H_2O} + \varepsilon_{H_2O}) \qquad (1)$$

where X_{O_2} and X_{H_2O} are the relative proportions of oxygen from air and water respectively, and ε_{O_2} and ε_{H_2O} are the enrichment factors for incorporation of oxygen from air and water respectively.

The enrichment factors scatter widely under different environmental conditions, with ε_{O_2} of 0 to −11·4‰ and ε_{H_2O} of 0 to 9·7‰ (Van Stempvoort and Krouse, 1994). Taylor *et al.* (1984a,b) postulated ε_{O_2} of −11·2‰ (mediated by *Thiobacillus ferrooxidans*, aerobic conditions, pyrite submersed) and an ε_{H_2O} of 4·0‰ (abiological, anaerobic oxidation, pyrite submersed). Considering the predominant environmental conditions in the investigation area, the values by Taylor *et al.* (1984a,b) appear to be the ones that are most suitable for our study.

Equation (1) yields a theoretical range for δ^{18}O-$SO_4{}^{2-}$ (12·5 to 100% incorporation of oxygen from water) of −5 to +10‰ (VSMOW). However, Toran and Harris (1989) observed that, under natural conditions, the incorporation of oxygen from water varies between 35 and 80% with a maximum at ∼60%. This narrows the range of the expected oxygen isotope data to −2 to +6‰.

Isotopic composition of atmospheric sulphur deposition

In eastern Germany, the relevance of the atmospheric sulphur deposition as a source of sulphate changed considerably within the last two decades. Before 1990, deposition rates often exceeded 16 g m^{-2} $year^{-1}$ (Richter and Meissner, 2003). After German reunification in 1990, the industrial and domestic sulphur emission rate decreased continuously, leading to a significant reduction in atmospheric sulphur deposition. Since 1996, a very stable annual deposition rate of 0·1 to 0·3 g m^{-2} has been observed (Richter and Meissner, 2003).

The annual sulphur uptake of plants ranges from 0·1 to 0·4 g m^{-2} (Bloem, 1998). Prior to the reduction of the deposition rate the positive balance of sulphur input and plant uptake yields an immense surplus of sulphur in the unsaturated soil zone. This surplus was partly transported with the seepage water into the saturated zone, but most of it was accumulated in the soil matrix in the form of different soil sulphur species, such as inorganic soil sulphate, reduced inorganic sulphur, organic sulphate, and carbon-bound sulphur (CS; Richter, 2003; Schmalz *et al.*, 2003; Nestler and Grischek, 2004). Presently, the negative sulphur balance between input and uptake leads to a consumption of the accumulated soil sulphur pool in the topsoil.

The investigation of the isotopic composition of the sulphate component in the atmospheric sulphur deposition was carried out at three different stations in eastern Germany in the period from 1999 to 2001. One of the stations (Melpitz) is located only a few kilometres west of the study area. The data obtained in the observation period are only representative of the isotopic composition of the recent deposition. Owing to the lack of direct measurements, the estimation of isotope data of the more relevant historic deposition is much more difficult. These data have to be derived indirectly from the isotopic composition of the historic deposition sources of which sulphur-rich lignite is the most important.

Generally, no significant differences in the isotopic composition of the sulphate were observed between the three locations or between deposition forms (total deposition, wet-only deposition). Table I gives an overview of the mean isotopic composition of the sulphate deposition at the different stations. Mean δ^{34}S values of the wet and total deposition are in a very narrow range between 4 and 5‰ (VCDT). The standard deviation is better than 2·6‰. The oxygen isotope data show a slightly larger variability, with values between 11 and 13·4‰ (VSMOW) for both deposition forms. Owing to the large standard deviation of 4‰, the 2‰ difference between δ^{18}O of the total and the wet-only deposition is not significant. The temporal variations of δ^{34}S and δ^{18}O of the wet-only deposition at the station Leipzig are shown in Figure 3.

Table I. Average plus/minus standard deviation of the isotopic composition of different forms of the atmospheric sulphate deposition at three different stations in eastern Germany (observation period January 1999–December 2001)

	Falkenberg	Leipzig	Melpitz
δ^{34}S-mean$_{\text{wet-only}}$ (‰ VCDT)	4.4 ± 1.3 $n = 35$	4.0 ± 1.5 $n = 35$	4.6 ± 2.6 $n = 30$
δ^{34}S-mean$_{\text{total}}$ (‰ VCDT)	4.3 ± 1.1 $n = 12$		
δ^{18}O-mean$_{\text{wet-only}}$ (‰ VSMOW)	13.4 ± 3.8 $n = 35$	13.2 ± 3.8 $n = 35$	12.2 ± 3.7 $n = 30$
δ^{18}O-mean$_{\text{total}}$ (‰ VSMOW)	11.2 ± 4.1 $n = 12$		

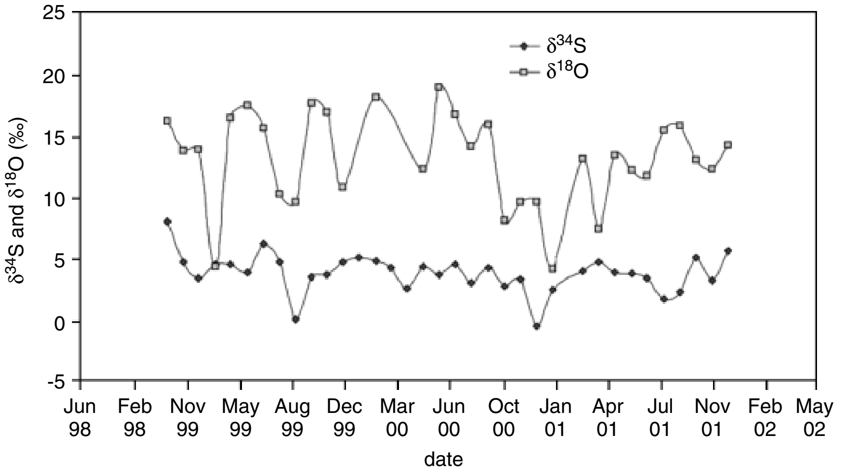

Figure 3. Temporal variation of the isotopic composition of the atmospheric sulphate deposition at the Leipzig station

The composition of the total deposition strongly influences its sulphur and oxygen isotope signatures. The small isotopic differences between the different deposition forms in the recent investigation are due to the large portion of the wet-only deposition in the total deposition. The recent ratio $S_{\text{tot}}/S_{\text{wet-only}}$ is 1·1 (Gauger *et al.*, 2000). For historic atmospheric sulphur deposition, this ratio is much larger (average of 3·3; Richter and Meissner, 2003). Before 1990, the total deposition consisted of 70% dry deposition and 30% wet deposition. The dry deposition is related to the combustion of fossil fuels (power plants with no or insufficient filtering systems, domestic heating), especially of lignite. Despite the considerable equilibrium and kinetic isotope effects during the transformation of gaseous SO_2 to dissolved sulphate (e.g. Saltzman *et al.*, 1983), δ^{34}S values of historic dry deposition are expected to be in the same range as the δ^{34}S values of the total sulphur in the lignite. Depending on the oxidation mechanism, the sulphate can be enriched in ^{34}S (heterogeneous oxidation) or depleted in ^{34}S (homogeneous oxidation) relative to the initial SO_2. However, assuming that most deposited SO_2 will eventually be converted to sulphate in the soil zone (given those high deposition rates) and that sulphate from the wet deposition formed by early atmospheric oxidation of SO_2 mixes well with that formed later, the net isotope effect will be very small. Therefore, the isotopic sulphur composition of sulphate from historic atmospheric deposition can be derived indirectly from the isotopic composition of the lignite sulphur.

The lignite that was combusted during the years of the highest pollution came from three different lignite seams of the central German lignite district (main seam Borna, upper seam Böhlen, seam Bitterfeld). δ^{34}S values of the total sulphur in lignite samples from those seams varied between 4·7 and 11·9‰ (VCDT) (Knöller, 2000). Since most of the historic deposition consisted of sulphur from lignite combustion, the $\delta^{34}S$ values of the historic deposition were most likely higher than those of the recent deposition.

No estimate of the oxygen isotope data of sulphate from the historic deposition can be made. However, different research papers that discuss the behaviour of the oxygen isotopes during the atmospheric oxidation of SO_2 (Holt *et al.*, 1981, 1982, 1983; McCarthy *et al.*, 1998) suggest a similar range of the $\delta^{18}O$ in recent and historic deposition.

According to our own measurements, to literature data, and to the estimation of the isotopic composition of the historic deposition, $\delta^{34}S$ values between −1 and +10‰ (VCDT) and $\delta^{18}O$ values between 6 and 18‰ (VSMOW) for the atmospheric sulphate input into the catchment area of Torgau–Mockritz can be assumed.

Isotopic composition of inorganic fertilizers

Sulphate-containing inorganic fertilizers can contribute considerably to the sulphate input into catchment areas with predominant agricultural use. In most cases, the application of sulphate-containing fertilizers did not aim at the attenuation of possible sulphur deficiencies, but rather on the supply of basic plant nutrients, especially nitrogen or phosphorus. For example, between 1977 and 1989, ammonium sulphate (average sulphur content 24%) was used for nitrogen fertilization in large areas of the investigation site. In the same period of time superphosphate (average sulphur content 12%) was applied for phosphorus fertilization. The application of those fertilizers further increased the sulphur surplus in the soil zone that was already achieved by the high atmospheric deposition rate.

In the same way as for the atmospheric deposition, not only the recent fertilizer input has to be considered. Owing to the storage capacity of the soil zone, the historic fertilizer input of recent decades can also play an important role in the sulphur budget of the catchment area. For that reason, the isotopic composition of a variety of recently used fertilizers was investigated and the results compared with isotope data of fertilizers that were applied in the 1970s and 1980s.

The $\delta^{34}S$ values of fertilizer sulphate are shown in Table II. Generally, the data for the recently used fertilizers vary in a wide isotopic range between −1 and +12‰ (VCDT). The only exception is the fertilizer HydroSulfan ($\delta^{34}S$: 22‰), which has been on the market since 1996. $\delta^{18}O$ values show a much smaller variation, between 10 and 15‰ (VSMOW). Basically the same range is covered by the historically applied fertilizers. The observed isotopic variation range of ammonium sulphate fits very well into the frequency maximum of world-wide fertilizer samples (0 to 10‰) postulated by Mizota and Sasaki (1996).

The isotopic composition of sulphate in fertilizers is determined by the composition of the raw materials used and by the production technique. In the former East Germany, the major part of inorganic fertilizers was

Table II. $\delta^{34}S$ data of recently and historically applied inorganic fertilizers

Data after Mallén (2000)			Data this study		
Fertilizer	Year of production	$\delta^{34}S$ (‰ VCDT)	Fertilizer	Year of production	$\delta^{34}S$ (‰ VCDT)
$(NH_4)_2SO_4$ gypsum technique	1938	10·9	Ferrogranul	1999	4·4
$(NH_4)_2SO_4$ gypsum technique	1988	11·3	Kieserit	1999	9·5
$(NH_4)_2SO_4$ mixed	1985	8·9	HydroUreaS	1999	7·1
$(NH_4)_2SO_4$ saturation techn.	1996	2·8	Solumas	1999	10·1
$(NH_4)_2SO_4$ saturation techn.	1997	−0·8	HydroSulfan	1999	22·0
Superphosphate	1980	8·3	Tripel	1999	12·3
Kamex	1996	9·8	KAS	1999	5·0
K 40/50	1996	9·8	SSA	1999	5·1
AmSupKa 5-10-16	1996	4·2	SSA fine	1999	1·5
NPK 20-8-8 + 3	1996	9·1	SSA coarse	1999	0·2

produced using salt minerals from the Zechstein evaporitic sequence by the so-called gypsum technique. δ^{34}S values of those sulphate minerals (mostly anhydrite) vary between 10 and 14‰ (VCDT) (Claypool *et al.*, 1980). Mallén (2000) showed that ammonium sulphates produced by the gypsum technique indeed reflect this isotopic range (Table II). If the ammonium sulphate is produced by the so-called saturation technique, during which ammonia is introduced into sulphuric acid, the raw material for the production of sulphuric acid determines the isotope signature of the fertilizer. In the former East Germany, isotopically relatively light sulphidic ore (δ^{34}S: ~0‰) was used for the production of sulphuric acid. Therefore, ammonium sulphate from the saturation technique shows clearly lower δ^{34}S values than ammonium sulphate from the gypsum technique.

Because ammonium sulphate from the gypsum technique and superphosphate was exclusively applied in the catchment area before 1996, a sulphur isotopic range of the historic fertilization between 8 and 12‰ (VCDT) can be assumed. Since the end of the 1990s, deliberate sulphur fertilization has been practiced to compensate the sulphur deficiencies in the topsoil resulting from the recent negative balance between atmospheric input and plant uptake. For that purpose, combined nitrogen/sulphur fertilizers, such as SSA and HydroUreaS, have been applied, so that the recent fertilizer input has 2 to 5‰ lower δ^{34}S values than the historic input.

Since no stock farming is practiced in the investigation region, the application of organic fertilizers is not considered as a relevant source of sulphate.

Isotopic composition of sulphate from gypsum waste dumps

Gypsum waste dumps that can act as point sources of sulphate are present at two different locations in the study area. One dumpsite is situated in the northwestern part of the catchment area (WASAG) and the other is at its southern border (MUNA-Süptitz). Both sites are related to the operation of neutralization facilities of former explosive factories. In the course of the production process, large amounts of sulphuric acid were used to stabilize the explosives. The sulphuric acid used was neutralized with CaO and the resulting gypsum was deposited on the respective waste dumps.

To investigate the isotopic composition of the sulphate that can be mobilized from the gypsum dumps, the dissolved groundwater sulphate present in the immediate body of the waste dump was analysed isotopically, not the solid gypsum. This approach provides the opportunity to obtain an integrated isotope signal for the dump.

In the WASAG area, dump-influenced groundwater showed very high sulphate concentrations between 1000 and 1500 mg l^{-1}. For δ^{34}S of the dissolved sulphate, a range between 7 and 10‰ (VCDT) was observed. Oxygen isotope values were less variable, with a rather constant value of 6‰ (VSMOW). Despite the large amount of gypsum deposited and the relatively high solubility, no significant influence of the dump on the quality of the raw water produced is expected. This is partly due to the low groundwater table leaving most of the dump body in unsaturated conditions where the gypsum solution is only of minor importance. On the other hand, the existing groundwater flow dynamics exclude the transport of the mobilized sulphate into the water intakes of the catchment area (Trettin *et al.*, 2002).

An even smaller influence on the regional sulphur cycling seems to come from the gypsum waste dump at the MUNA-Süptitz site. Sulphate concentrations in the dump groundwater are not or are only slightly elevated (250 to 400 mg l^{-1}, compared with 200 to 290 mg l^{-1} in the surroundings) and the isotopic composition of the dissolved dump sulphate does not differ from the sulphate in the groundwater inflow into the dump area.

Comparison of the isotopic compositions of different sulphate sources

The results of the investigation of the isotopic compositions of diffuse and point sources of sulphate in the catchment area are summarized in Table III. It is apparent that the isotopic ranges of the individual anthropogenic input sources overlap. Hence, a clear isotopic distinction between the anthropogenic sources is not possible. For that reason, the three sources, i.e. atmospheric deposition, fertilization, and gypsum

Table III. Variation ranges of the isotopic compositions of different sources of sulphate

Sulphate source	δ^{34}S (‰ VCDT)	δ^{18}O (‰ VSMOW)
Atmospheric deposition	-1 to $+10$	6–18
Inorganic fertilizers	-1 to $+12$	10–15
Gypsum waste dumps	7–10	6
Oxidation of sulphides	<-5	-2 to $+6$

waste dumps, are considered as a single anthropogenic source for the further discussion of the origin of the groundwater sulphate.

However, a clear isotopic distinction can be made between the anthropogenic input and the sulphate from sulphide oxidation. Oxidation sulphate shows significantly lower δ^{34}S and δ^{18}O values.

Sulphur transformation in the soil zone

The high sulphur input in recent decades and the limited plant uptake have resulted in an enormous sulphur surplus in the soil zone. Even though the opposite trend has been encountered in the top layers within the last few years, the large surplus is still present in deeper horizons of the unsaturated soil zone (Richter, 2003; Nestler *et al*., 2004).

The input sulphur is stored in the soil matrix in the form of different soil sulphur species, of which the most important are inorganic soil sulphate, carbon-bound organic sulphur, and sedimentary sulphides (Richter, 2003; Nestler *et al*., 2004). On a regional scale, organic ester sulphates only play a marginal role (Knöller and Trettin, 2003; Schmalz *et al*., 2003).

The fate of the inorganic sulphate in the soil zone is determined by two major processes, sorption and desorption. Even though some uncertainties regarding the isotope effects related to those processes are still being discussed, various research papers suggest only minor isotopic fractionations of less than 1‰ for both sulphur and oxygen (e.g. Nriagu, 1974; Van Stempvoort, 1989; Van Stempvoort *et al*., 1990; Mayer, 1993; Mayer *et al*., 1995). For that reason, a tight correspondence between the isotopic compositions of the sulphate input and the inorganic soil sulphate leaving the unsaturated zone is expected.

The isotopic sulphur composition of inorganic soil sulphate was measured in 152 soil samples from the unsaturated and the saturated zone. The δ^{34}S values vary within a very large range (-42 to $+18$‰). The frequency distribution shown in Figure 4 reveals a frequency maximum of around 5‰. This maximum corresponds with the mean δ^{34}S value of the anthropogenic sulphur input. From this correspondence it can be concluded that the inorganic soil sulphate is predominantly formed from the contribution of the different anthropogenic sources. The vertical isotopic distribution, also illustrated in Figure 4, shows clear differences in the isotopic composition of inorganic soil sulphate between the saturated and unsaturated zones. Above the mean groundwater table, in the unsaturated zone, only minor variations in the δ^{34}S values are visible. The soil sulphate there seems exclusively to derive from external anthropogenic sources. Below the groundwater table, the variability of the δ^{34}S data increases sharply. This is most likely due to the increasing influence of isotopically light sulphate from the oxidation of sedimentary sulphides. In some samples in the saturated zone, oxidation sulphate comprises the inorganic soil sulphate completely. For the examination of the isotopic composition of the soil sulphate in the saturated zone, not only does the vertical transport component have to be considered, but also a lateral component resulting from groundwater flow. Given a sufficient equilibration time (several hours, according to the method for the complete extraction of inorganic soil sulphate described above in the Analytical methods and sampling section), the isotope data of the soil sulphate and groundwater sulphate are identical within an uncertainty range resulting from the small isotope effects during the sulphate sorption/desorption.

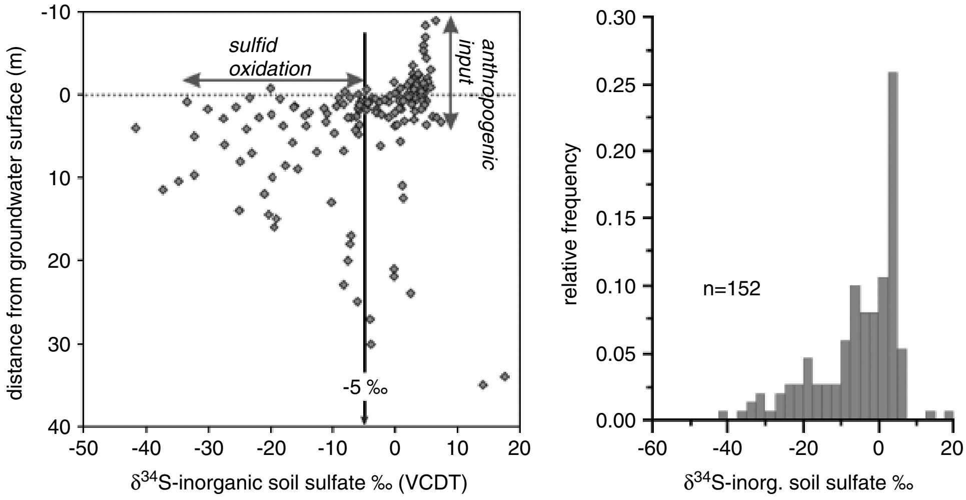

Figure 4. Depth-dependent variability and relative frequency distribution of the δ^{34}S values of inorganic soil sulphate from the unsaturated and saturated zones

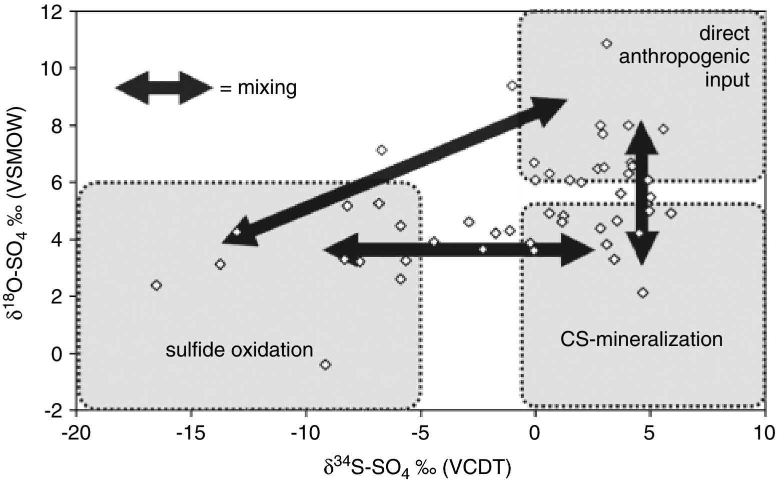

Figure 5. Sulphur and oxygen isotopic composition of inorganic soil sulphate from the unsaturated and saturated zones

The oxygen isotope composition of the inorganic soil sulphate was determined for 50 soil samples. Generally, δ^{18}O values range from −0·5 to +12‰ (VSMOW) (Figure 5). In contrast to the depth-dependent isotopic distribution of the sulphur, no differences exist between the δ^{18}O values in the saturated and unsaturated zones. In resemblance to the distribution of the sulphur isotopes, one would expect that, above the groundwater surface, δ^{18}O values similar to those of the anthropogenic input would be present, whereas below the groundwater surface the variability would increase due to the contribution of isotopically lighter oxidation sulphate. However, δ^{18}O values typical for sulphide oxidation were also observed in the unsaturated zone, where no sulphides occur. For such low δ^{18}O values (<5‰) a further process has to be taken into consideration.

According to Mayer (1993; Mayer *et al.*, 1995), the mineralization of carbon-bound organic soil sulphur creates similar low oxygen isotope values to those of sulphide oxidation (δ^{18}O-SO_4^{2-}: −2 to +5‰). From the observation of oxygen isotope values of less than 6‰ in the unsaturated zone, it can be concluded that not all the inorganic soil sulphate comes directly from anthropogenic sources but some sulphate results from the mineralization of CS. The CS itself was most likely primarily formed from anthropogenic sulphur.

The incorporation of sulphur into soil organic matter is not accompanied by an isotopic fractionation. For that reason, secondary CS and primary anthropogenic sulphur input show a similar sulphur isotopic composition. The reverse process, however, can produce an isotopic shift between CS and the resulting sulphate of up to −5‰ (Mayer, 1993; Mayer *et al.*, 1995). Such an isotopic shift was not observed in the case of the study area. This observation agrees with the finding of Norman *et al.* (2002), who report a much smaller isotope effect during the CS mineralization than −5‰. Whereas soil sulphate from direct anthropogenic input and sulphate from CS mineralization can be distinguished by their oxygen isotope compositions, the δ^{34}S values cover the same range and hence do not enable the distinction between the two types of sulphate.

Inorganic soil sulphate can originate in three different processes, i.e. direct anthropogenic sulphur input, mineralization of CS, and oxidation of reduced inorganic sulphur. The combined examination of both sulphur and oxygen isotopes allows the assignment of the individual sulphate samples to one of these processes (Figure 5). However, mixing of sulphate in the soil zone is a common process that influences the isotopic composition of the sulphate and, hence, makes it more difficult to relate the sulphate to a particular process.

The hydrolysis of organic ester sulphates is a further possible process that can contribute to the inorganic soil sulphate pool. During this process a significant sulphur isotope fractionation of up to −10‰ between the resulting inorganic sulphate and the initial organic sulphate is observed (Mayer, 1993). Considering the fact that (at most) only one new oxygen atom has to be incorporated into the inorganic sulphate molecule during the hydrolysis, and knowing that the formation of ester sulphates from the primary anthropogenic input is not accompanied by any isotope fractionation (Mayer *et al.*, 1995), the δ^{18}O values of the newly formed inorganic sulphate are expected to be in the same range as the initial input. Assuming the specified isotopic range of the anthropogenic input, the hydrolysis of ester sulphates would produce an inorganic sulphate with δ^{34}S values of approximately −5‰ and δ^{18}O values of approximately 10‰. As shown in Figure 5, no inorganic soil sulphate sample plots in that region. This suggests a minor relevance of the hydrolysis to the sulphur transformations in the soil zone of the catchment area.

Isotopic composition of dissolved groundwater sulphate

The investigation of the spatial distribution of the sulphate concentration yielded a very heterogeneous pattern (Herlitzius *et al.*, 2001). Although at the majority of the sampling locations only moderate sulphate concentrations (up to 250 mg l^{-1}) were measured, some locally restricted zones showed values of more than 1000 mg l^{-1}. In the catchment area of Torgau–Mockritz, three areas with significantly elevated sulphate concentrations were observed: one in the central study area west of the Mockritz I water intake, one close to the gypsum waste dump at the WASAG site, and one at the southern border in the vicinity of the village of Süptitz. The elevated sulphate concentrations are especially apparent at the groundwater surface and in the upper sampling level. In the middle and lower aquifer levels the sulphate concentrations did not exceed values of ~400 mg l^{-1} (Herlitzius *et al.*, 2001).

The isotopic composition of the dissolved groundwater sulphate was used to estimate the local and regional relevance of the different sulphate sources and mobilization processes. $\delta^{34}S\text{-}SO_4{}^{2-}$ was analysed for more than 500 individual groundwater samples from 256 sampling wells. $\delta^{18}O\text{-}SO_4{}^{2-}$ was measured in almost 400 samples. The variation ranges of both isotope species (mean values for the single sampling wells) are shown as frequency distributions in Figure 6.

δ^{34}S values of the individual samples range from −19 to +37‰ (VCDT). A significant frequency maximum exists between 2·5 and 5‰. A smaller variation range between −2 and +19‰ (VSMOW) was observed for $\delta^{18}O\text{-}SO_4{}^{2-}$. A significant frequency maximum is evident between 4 and 8‰. The positions of the frequency maxima for δ^{34}S and δ^{18}O give a first hint at the predominant origin of the groundwater sulphate. Whereas the sulphur isotope data clearly suggest the dominance of a primarily anthropogenic source, the oxygen isotope

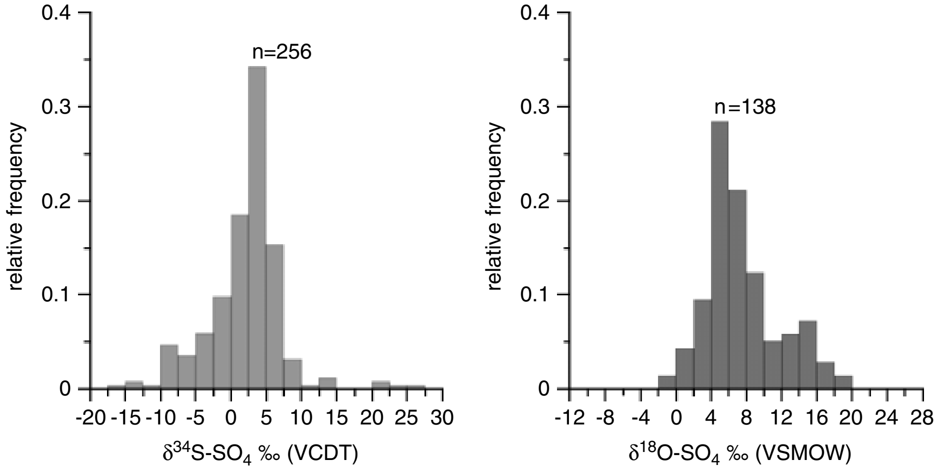

Figure 6. Relative frequency distribution of δ^{34}S and δ^{18}O of dissolved groundwater sulphate (calculation based on mean values for the individual sampling wells)

data indicate that CS mineralization and sorption/desorption of inorganic soil sulphate are the key mobilization processes contributing considerably to the groundwater sulphate pool on the regional scale of the catchment area.

More detailed information on the origin of the groundwater sulphate is derived from the δ^{34}S–δ^{18}O plot in Figure 7. The diagram also shows the specified isotopic ranges for the different sources and mobilization mechanisms. Most samples can be assigned to the isotopic range that is typical for the direct downward transport of sulphate from the anthropogenic input. Furthermore, a considerable number of samples plot in the sulphide oxidation range. Fewer samples are found in the isotopic ranges of the mineralization of organic soil sulphur. Between the single sampling levels, no clear differentiation is possible. Every rectangle in Figure 7 contains a different number of data points from each possible level. However, sulphide oxidation

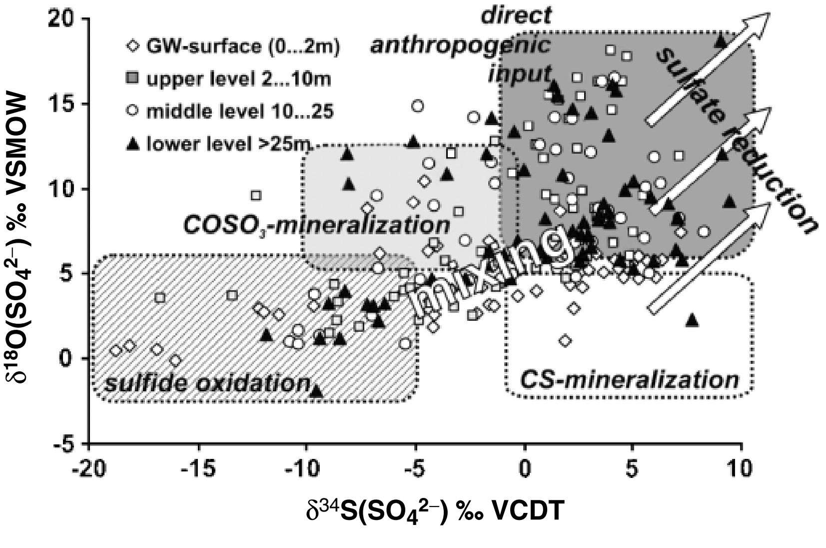

Figure 7. Isotopic composition of dissolved groundwater sulphate (mean values for the individual sampling wells)

and CS mineralization predominantly affect the sulphate at the groundwater surface and in the upper sampling horizon.

The coupled investigation of δ^{34}S and δ^{18}O does not always enable the definite assignment of the sulphate samples to a certain source or process. Owing to the dynamic flow regime in the entire catchment area (Trettin *et al.*, 2002), mixing of dissolved groundwater sulphate of different origins is a very widespread process. Mixing processes can significantly influence the isotopic composition of the sulphate. For example, a mixture of sulphate from sulphide oxidation and direct anthropogenic input, which is very common, especially at the groundwater surface, suggests a sulphate that originates in the hydrolysis of organic sulphates. Owing to the same mobilization environment, mixing of sulphate from CS mineralization and direct anthropogenic input also seems very likely.

A further process that can change the original isotope signature of the sulphate is bacterial (dissimilatory) sulphate reduction. Usually, a considerable enrichment of ^{34}S (e.g. Harrison and Thode, 1958; Rees, 1973; Chambers and Trudinger, 1979; Canfield and Thamdrup, 1994; Canfield *et al.* 1998; Canfield, 2001) and up to a certain level of ^{18}O ($\sim$20‰ (VSMOW)), depending on the δ^{18}O of the surrounding water (Fritz *et al.*, 1989) in the residual sulphate, is observed during this process. In several wells, especially from the lower level, hydrochemical parameters and the simultaneous occurrence of low sulphate concentrations (10–20 mg l^{-1}) and high δ^{34}S (37·2‰) and δ^{18}O (19·2‰) values pointed to the occurrence of bacterial sulphate reduction.

The sulphur–oxygen isotope plot can only give a qualitative picture of the relevance of the different sulphate sources. It is more important to find out what source is responsible for the high sulphate concentrations. For this reason, the sulphate concentrations were plotted versus δ^{34}S and versus δ^{18}O-$SO_4{}^{2-}$ (Figure 8). The isotopic range typical for oxidation of reduced sedimentary sulphur is displayed by a grey rectangle in both diagrams. Figure 8 clearly illustrates the concentration-dependent isotope differentiation. Samples with very high sulphate concentrations (>700 mg l^{-1}) are almost exclusively confined to the sulphide oxidation range. The highest concentrations are mostly found at the groundwater surface and in the upper sampling level. However, some of the samples with high concentrations show positive δ^{34}S values. Those samples were taken in the immediate vicinity of the northwestern gypsum waste dump, so that the sulphate there can undoubtedly be related to the dissolution of gypsum. Medium-high concentrations (300–700 mg l^{-1}) occurring in all sampling levels either plot in the range for anthropogenic sources or in the oxidation range. Low and moderate concentrations, mostly present in the middle and lower aquifer levels, are dominated by sulphate from anthropogenic sources.

An isotope differentiation depending on the sulphate concentration, as observed in the $SO_4{}^{2-}$ –δ^{34}S plot, is less apparent in the $SO_4{}^{2-}$ –δ^{18}O plot in Figure 8. This is partly due to the extremely variable δ^{18}O input signal of the anthropogenic sources. On the other hand, sulphide oxidation and CS mineralization produce sulphate with comparable oxygen isotope signatures. Only the coupled examination of δ^{34}S and δ^{18}O makes it possible to distinguish between the two processes. Looking at the δ^{18}O data only, CS mineralization seems possible as a source for very high sulphate concentrations. However, considering the negative δ^{34}S values, this possibility can be excluded.

Figure 9 shows the correlation between δ^{34}S and δ^{18}O of the dissolved sulphate in samples with very high sulphate concentrations (>700 mg l^{-1}). Only half of the samples can clearly be assigned to sulphide oxidation. For three samples, their origin is dissolution of gypsum. Several data points show isotope signatures that were specified for the hydrolysis of organic ester sulphates. According to a detailed soil investigation in the study area by Schmalz *et al.* (2003), hydrolysis does not play a significant role as a mobilization process of sulphate on a regional scale, but it cannot be excluded as a local phenomenon. Another process that could possibly cause an isotopic composition of the dissolved sulphate similar to that produced by hydrolysis is sulphide oxidation by autotrophic denitrification. Preliminary results from laboratory experiments (unpublished results) reveal that the oxidation of sulphide by nitrate leads to a preferred incorporation of nitrate-oxygen into the newly formed sulphate molecule. In the study area, δ^{18}O-NO_3^- values between 7 and 22‰ (VSMOW) were measured (Knöller and Trettin, 2003). Whereas sulphate produced by nitrate reduction is expected to show the same high oxygen isotopic range as the nitrate, δ^{34}S values would be in tight correspondence with the negative values of

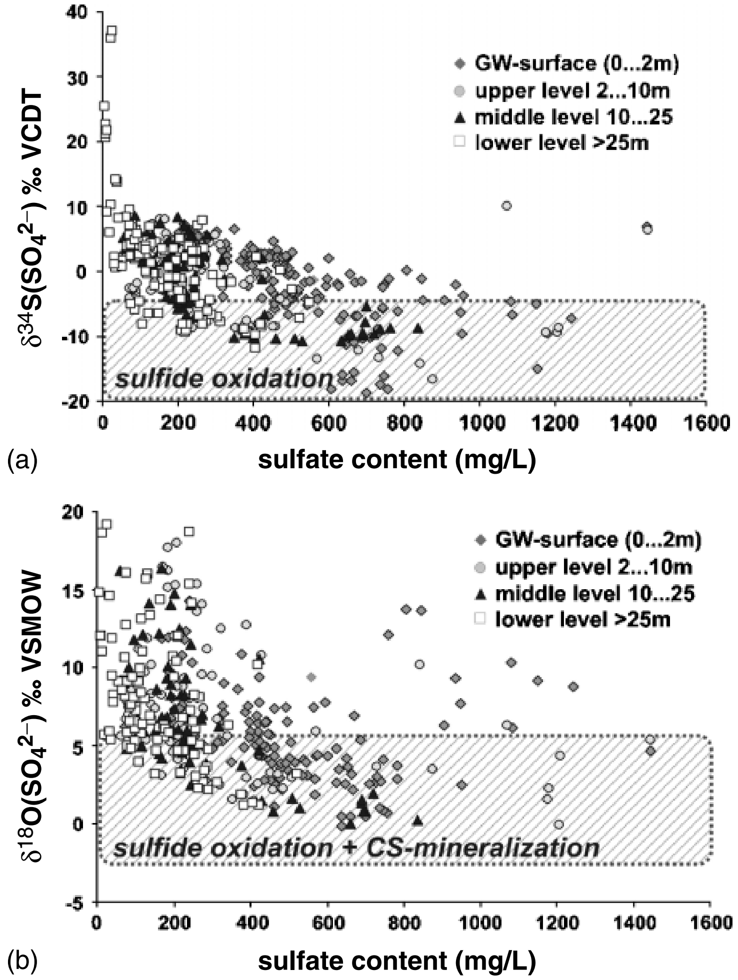

Figure 8. Relationship between sulphate concentrations and (a) $\delta^{34}S$ and (b) $\delta^{18}O$-SO_4^{2-} of groundwater samples from all sampling levels

sedimentary sulphides. This combination results in an isotopic composition of sulphate that fits exactly in the range specified for the hydrolysis of organic ester sulphates. The given environmental conditions from which the samples concerned were collected add more creditability to the suggested hypothesis. All samples with high sulphate concentrations, high $\delta^{18}O$, and negative $\delta^{34}S$ come from locations at the groundwater surface where dissolved groundwater nitrate and sedimentary sulphide are present (Schmalz *et al.*, 2003).

Regional distribution patterns of $\delta^{34}S$ of the dissolved groundwater sulphate

The high density of sampling locations in the study area for which $\delta^{34}S$ values were determined enables the construction of regional isotope distribution maps. By means of such distribution maps it is possible to estimate the local and regional relevance of the different sulphate sources on the sulphur dynamics of the catchment area. Figure 10 shows the distribution of the mean $\delta^{34}S$ data in the upper sampling level (groundwater surface to 10 m below). The map reveals a very heterogeneous regional distribution of the sulphur isotopic composition of the dissolved sulphate. Despite the heterogeneity, the upper groundwater horizon of the aquifer is dominated by sulphate with slightly positive $\delta^{34}S$ values originating in anthropogenic sources. However, in the central part of the study area, an extended range exists that is occupied by isotopically

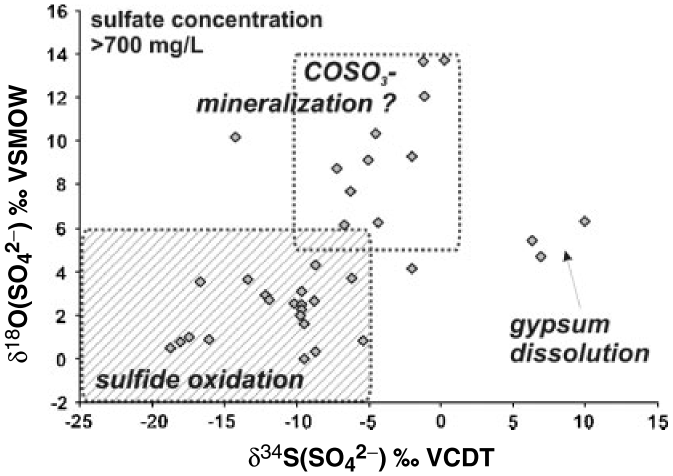

Figure 9. Isotopic composition of dissolved groundwater sulphate in samples with high (>700 mg l^{-1}) sulphate concentrations

negative sulphate from the oxidation of reduced sedimentary sulphur. That zone approximately occupies the same area as a zone of elevated sulphate concentrations in the central part of the study area postulated by Herlitzius *et al.* (2001). In the case of this so-called central sulphate zone, the high sulphate concentrations are connected with negative δ^{34}S values, pointing to sulphide oxidation as sulphate source.

In a zone of elevated sulphate concentrations in the northern study area (northern sulphate zone), congruence between isotope data and sulphate content does not exist. δ^{34}S values for samples with higher sulphate concentrations (>350 mg l^{-1}) range from −13 to +10‰, indicating the coexistence of several sources of sulphate in that area. According to the isotope data range, direct input from anthropogenic sources, sulphide oxidation, and, as mentioned above, dissolution of gypsum from waste dumps have to be taken into consideration. However, the question of why the direct input from anthropogenic sources produces higher sulphate concentrations than elsewhere in the study area remains unclear. An accidentally or purposefully higher application of inorganic fertilizers could be one possible reason for such a local phenomenon.

In the southern study area, elevated sulphate concentrations were detected at two different locations. The southernmost of those locations is situated on the gypsum waste dump of the MUNA-Süptitz site, so that the sulphate was derived from the dissolution of gypsum. For the other location, south of the central sulphate zone, no point source can be specified. Again, this location has to be considered as a local phenomenon that was possibly caused by a higher fertilizer application.

The sulphur isotope distribution in the middle and lower sampling levels is less heterogeneous and the dominance of isotopically slightly positive sulphate from anthropogenic sources is more pronounced than in the upper level. Whereas the central sulphate zone with its typical negative δ^{34}S values is still present in the middle level, only a few sampling locations of the lower level in the immediate vicinity of the Mockritz I water intake show isotopic evidence for the presence of sulphate from sulphide oxidation.

Figure 11 shows the distribution of δ^{34}S values in a vertical profile of a cross-section that roughly follows the hypothetical flow path from the moraine area to the Mockritz I water intake and crosses the central sulphate zone. The location of the cross-section is given in Figure 10. Again, extended regions of the profile are dominated by isotopically slightly positive sulphate that was derived from anthropogenic sources. At the western border of the flood plain, approximately marked by zero on the x-axis in the plot of Figure 11, an area close to the surface dominantly contains isotopically negative sulphate from sulphide oxidation. This characteristic sulphate moves progressively into deeper horizons of the aquifer with decreasing distance to the Mockritz I water intake and finally reaches the filter range of the production wells.

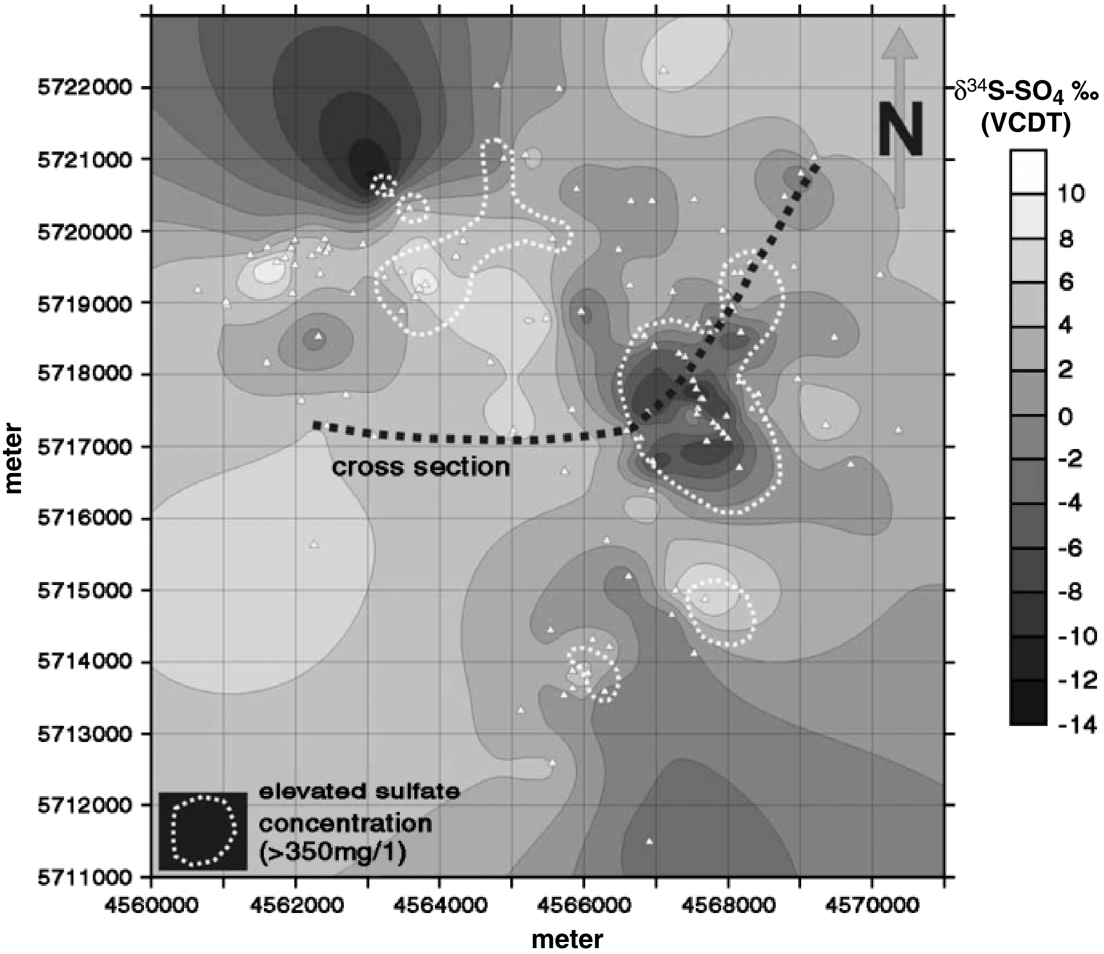

Figure 10. Regional distribution of the sulphur isotopic composition of dissolved groundwater sulphate in the upper sampling level (coordinates: Kraus-Krueger, Bessel-ellipsoid)

The isotopic difference between the dissolved sulphate in the upper aquifer level of the surroundings of the Mockritz I water intake and in the production well itself clearly indicates that the sulphate contained in the raw water produced does not originate in the immediate vicinity of the intake; rather, it is mobilized in the western flood plain and is transported laterally into the filter range.

One possible mobilization mechanism in the western flood plain is the process of autotrophic denitrification. Groundwater flowing from the moraine area into the flood plain contains dissolved nitrate up to 180 mg l^{-1} from fertilization (Schmalz *et al.*, 2003). In the western part of the flood plain the nitrate-bearing groundwater meets sediments that contain a considerable amount of sedimentary sulphides that can easily be oxidized. Besides the transport with the groundwater flow, nitrate-rich water (up to 300 mg l^{-1}) is led from the moraine area into the flood plain by a drainage channel system. The local infiltration of those drainage waters contributes additionally to the mobilization of sulphate from sedimentary sulphides. The occurrence of denitrification is confirmed by a quick decrease of the nitrate concentrations on the further flow path (Schmalz *et al.*, 2003). However, hydrochemical investigations showed that the nitrate input does not supply enough oxidation potential to produce a sulphate concentration of more than 1000 mg l^{-1}. Therefore, another oxidation mechanism, such as the oxidation by dissolved oxygen and subsequent oxidation by ferric iron,

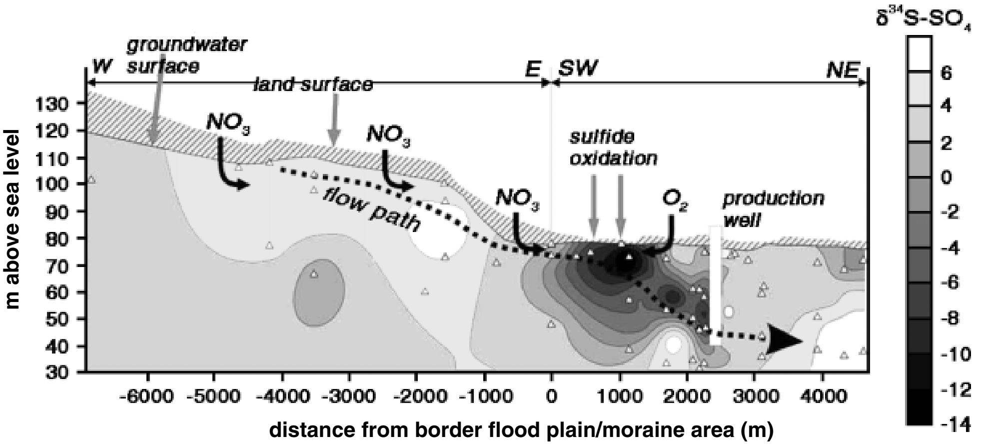

Figure 11. Distribution of δ^{34}S of dissolved sulphate in a cross-section through the central study area (for position see Figure 10)

has to be considered. In the immediate vicinity of the oxidation area (Figure 11) the meadow loam cover is missing locally. Depending on water table fluctuations, oxygen can migrate through those areas with higher permeability into sulphide-bearing sediment layers, thus causing oxidation of the sedimentary sulphides.

SUMMARY AND CONCLUSIONS

The examination of the hydrochemical composition of groundwater and isotopic composition of sedimentary and dissolved sulphur compounds was successfully applied to reveal the details of the sulphur cycling in the catchment area of Torgau–Mockritz. The focal points of this investigation were the identification of the relevant sources of sulphate and their locally and temporally variable contributions to the sulphate load of the groundwater, the characterization of sulphur transformation and transport processes, such as sulphide oxidation, sulphate mixing, or sulphate reduction, and the recognition of superposition of various processes.

Three major anthropogenic sources of sulphate, i.e. recent and historic atmospheric sulphur deposition, recent and historic application of inorganic fertilizers, and point emissions from gypsum waste dumps, were identified in the study area. Owing to their similar isotopic compositions, an isotopic distinction between the individual sources is almost impossible. However, anthropogenic sources can clearly be distinguished from sulphate that is contributed by the oxidation of sedimentary sulphides.

The sulphate input into the groundwater is predominantly realized by diffuse vertical transport. Point sources, such as waste dumps, only have a limited local influence on the sulphate dynamics in the catchment area. On a regional scale, the groundwater is dominated by isotopically slightly positive sulphate from the mobilization of inorganic soil sulphate (direct downward transport of anthropogenic input) or by the mineralization of CS. However, larger parts of the central catchment area are affected by isotopically negative sulphate from sulphide oxidation.

Despite the widespread regional occurrence of sulphate from anthropogenic sources, the highest sulphate concentrations are mostly connected to sulphate from sulphide oxidation. Exceptions are present in the form of local emissions from two gypsum waste dumps. Other mobilization processes only produce low to intermediate sulphate concentrations.

The dynamic groundwater flow regime is responsible for an extensive mixing in all horizons of the aquifer. This mixing has a considerable influence on the isotopic sulphate composition and, consequently, complicates the assignment of the dissolved sulphate to particular sources. Alterations of the original isotopic sulphate composition by bacterial sulphate reduction were only observed at a few locations in the lower sampling level. A widespread regional influence of the reduction process can hence be excluded.

Sulphate responsible for the elevated sulphate concentration in the raw water collected at the Mockritz I water intake is positively derived from the oxidation of sedimentary sulphides. Since no sulphide is present in the immediate vicinity of the water intake, *in situ* oxidation can be ruled out. The regional δ^{34}S distribution pattern enabled the localization of the relevant oxidation zone ~1·5 km west of the intake. The sulphide oxidation in the oxidation zone is caused by the infiltration of nitrate-rich groundwater and drainage water into sulphide-bearing sediments and the subsequent autotrophic denitrification and by the local infiltration of dissolved oxygen.

The localization of the oxidation zone and the characterization of the relevant mobilization processes provide the basic knowledge for developing a successful remediation strategy. A reduction of the sulphate load in the raw water produced can be achieved by active or by passive measures. Active measures aimed at suppressing the oxidation process could include the considerable reduction of fertilizer input in the moraine area or the installation of a drainage channel system that leads the nitrate-rich water around the sulphide-bearing sediments. These measures are either very expensive or politically difficult to enforce. More practicable are passive measures aimed at reducing the portion of the sulphate-rich groundwater from the west in the raw water produced. This reduction could be realized by a more constant production regime in combination with an increased production rate. The increased production rate would result in a higher inflow of low-mineralized bank filtrate from the River Elbe into the filter range of the production wells.

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REFERENCES

Bloem EM. 1998. *Schwefel-Bilanz von Agrarökosystemen unter besonderer Berücksichtigung hydrologischer und bodenphysikalischer Standorteigenschaften*. PhD thesis, Technical University of Braunschweig.

Bottrell SH, Smart PI, Whitaker F, Raiswell R. 1991. Geochemistry and isotope systematic of sulfur in the mixing zone of Bahamian blue holes. *Applied Geochemistry* **6**: 97–103.

Bottrell SH, Moncaster SM, Tellam JH, Lloyd JW, Fisher QJ, Newton RJ. 2000. Controls on bacterial sulphate reduction in a dual porosity aquifer system: the Lincoln limestone aquifer, England. *Chemical Geology* **169**: 461–470.

Canfield DE. 2001. Isotope fractionation by natural populations of sulfate-reducing bacteria. *Geochimica et Cosmochimica Acta* **65**: 1117–1124.

Canfield DE, Thamdrup B. 1994. The production of ^{34}S-depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* **266**: 1973–1975.

Canfield DE, Raiswell R, Westrich JT, Reaves CM. Berner RA. 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology* **54**: 149–155.

Canfield DE, Thamdrup B, Fleischer S. 1998. Isotope fractionation and sulfur metabolism by pure and enrichment cultures of elemental sulfur disproportionating bacteria. *Limnology and Oceanography* **43**: 253–264.

Chambers LA, Trudinger PA. 1979. Microbial fractionation of stable sulphur isotopes: a review and critique. *Geomicrobiology* **1**: 249–293.

Claypool GE, Holser WT, Kaplan IR, Sakai H, Zak I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* **28**: 199–260.

Dogramaci SS, Herczeg AL, Schiff SL, Bone Y. 2001. Controls on δ^{34}S and δ^{18}O of dissolved sulfate in aquifers of the Murray basin, Australia and their use as indicators of flow processes. *Applied Geochemistry* **16**: 475–488.

Dowuona GN, Mermut AR, Krouse HR. 1993. Stable isotope geochemistry of sulfate in relation to hydrogeology in southern Saskatchewan, Canada. *Applied Geochemistry* **8**: 255–263.

Fossing H, Jorgensen BB. 1989. Measurement of bacterial sulfate reduction in sediments: evaluation of a single step chromium reduction method. *Biogeochemistry* **8**: 205–222.

Fritz P, Basharmal GM, Drimmie RJ, Ibsen J, Qureshi RM. 1989. Oxygen isotope exchange between sulphate and water during bacterial sulfate reduction. *Chemical Geology (Isotope Geoscience Section)* **79**: 99–105.

Gauger T, Köble R, Anshelm F. 2000. *Kritische Luftschadstoff-Konzentration und Eintragsraten sowie ihre Überschreitung für Wald und Agrarökosysteme sowie nahe waldfreie Ökosysteme—Teil 1: deposition loads 1987–1989 und 1993–1995*. Report 29785079, Institute for Navigation, University of Stuttgart.

Harrison AG, Thode HG. 1958. Mechanism of the bacterial reduction of sulphate from isotope fractionation studies. *Transactions of the Faraday Society* **54**: 84–92.

Hendry MJ, Krouse HR, Shakur MA. 1989. Interpretation of oxygen and sulfur isotopes from dissolved sulfates in tills of southern Alberta, Canada. *Water Resources Research* **25**: 567–572.

Herlitzius J, Grischek T, Knöller K, Nestler W. 2001. Studium natürlicher Stoffumwandlungsprozesse in der Torgauer Elbaue als Beitrag zur Beschaffenheitsprognose für den Grundwasserabstrom von Altlasten (Study of natural attenuation processes in the River Elbe basin near Torgau as a contribution for the prognosis of groundwater quality at contaminated sites). In *Altlasten 2001—Neue Verfahren zur Sicherung und Sanierung*, Burkhardt G, Egloffstein T, Czurda K (eds). ICP Eigenverlag Bauen und Umwelt: Karlsruhe; 120–135.

Holt BD, Kumar R, Cunningham PT. 1981. Oxygen-18 study of the aqueous-phase oxidation of sulfur dioxide. *Atmospheric Environment* **15**: 557–566.

Holt BD, Kumar R, Cunningham PT. 1982. Primary sulfates in atmospheric sulfates: estimation by oxygen isotope ratio measurements. *Science* **217**: 51–53.

Holt BD, Cunningham PT, Engelkemeir AG, Graczyk DG, Kumar R. 1983. Oxygen-18 study of the nonaqueous-phase oxidation of sulfur dioxide. *Atmospheric Environment* **17**: 625–632.

Knöller K. 2000. *Anwendung stabiler Umweltisotope zur Bewertung hydrochemischer Zustände und Prozesse in Folgelandschaften des Braunkohlebergbaus*. PhD thesis, UFZ Report 33/2000.

Knöller K, Trettin R. 2003. *Isotopenanalytische Bewertung des Sulfathaushaltes in landwirtschaftlich genutzten Wassergewinnungsgebieten*. UFZ-Report 20/2003.

Knöller K, Fauville A, Mayer B, Strauch G, Friese K, Veizer J. 2004. Sulfur cycling in an acid mining lake and its vicinity in Lusatia, Germany. *Chemical Geology* **204**: 303–323.

Kölle W, Werner P, Strebel O, Böttcher J. 1983. Denitrifikation in einem reduzierenden Grundwasserleiter. *Vom Wasser* **61**: 125–147.

Kroopnick P, Craig H. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science* **175**: 54–55.

Mallén G. 2000. *Isotopenanalytische Charakterisierung hydrodynamischer und biogeochemischer Prozesse im Uferfiltrat und landseitigen Grundwässern der Torgauer Elbtalwanne unter besonderer Berücksichtigung der Herkunft und Umwandlungen von Kohlenstoff- und Schwefelspezies*. PhD thesis, UFZ Report 9/2000.

Mayer B. 1993. *Untersuchungen zur Isotopengeochemie des Schwefels in Waldböden und neu gebildetem Grundwasser unter Wald*. PhD thesis, University of Munich.

Mayer B, Fritz P, Prietzel J, Krouse HR. 1995. The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. *Applied Geochemistry* **10**: 161–173.

McCarthy MDB, Newton RJ, Bottrell SH. 1998. Oxygen isotopic composition of sulphate from coals: implication for primary sulphate sources and secondary weathering processes. *Fuel* **77**: 677–682.

Mizota C, Sasaki A. 1996. Sulfur isotope composition of soils and fertilizers: differences between Northern and Southern Hemispheres. *Geoderma* **71**: 77–93.

Moncaster SJ, Bottrell SH, Tellam JH, Lloyd JW, Konhauser KO. 2000. Migration and attenuation of agrochemical pollutants: insight from isotopic analysis of groundwater sulphate. *Journal of Contaminant Hydrology* **43**: 147–163.

Nakai N, Jensen ML. 1964. The kinetic isotope effect in the bacterial reduction and oxidation of sulfur. *Geochimica et Cosmochimica Acta* **28**: 1893–1912.

Nestler W, Grischek T (eds). 2004. *Handbuch Wasserversorgung und Sulfatbelastung des Grundwassers unter land- und forstwirtschaftlich genutzten Flächen*. German Federal Ministry for Education and Science (BMBF): Berlin.

Nestler W, Herlitzius J, Macheleidt M, Willms M, Knöller K, Trettin R, Schmalz V, Richter G. 2004. Case study Mockritz—Fallbeispiel Mockritz. In *Handbuch Wasserversorgung und Sulfatbelastung des Grundwassers unter land- und forstwirtschaftlich genutzten Flächen*, Nestler W, Grischek T (eds). German Federal Ministry for Education and Science (BMBF): Berlin; 178–243.

Norman AL, Giesemann A, Krouse HR, Jäger HJ. 2002. Sulphur isotope fractionation during sulphur mineralization: results of an incubation–extraction experiment with a Black Forest soil. *Soil Biology and Biogeochemistry* **34**: 1425–1538.

Nriagu JO. 1974. Fractionation of sulfur isotopes by sediment adsorption of sulfate. *Earth and Planetary Science Letters* **22**: 681–692.

Rees CE. 1973. A steady-state model for sulphur isotope fractionation in bacterial reduction processes. *Geochimica et Cosmochimica Acta* **37**: 1141–1162.

Richter G. 2003. *Verlagerung von Sulfat in Böden und Ableitung von Empfehlungen zur Steuerung des Eintrags in das Grundwasser*. PhD thesis, UFZ Report 15/2003.

Richter G, Meissner R. 2003. Schwefel in der Atmosphäre. In *Sulfat im Grundwasser*, Nestler W, Grischek T (eds). BMBF-Eigenverlag: Berlin; 56–64.

Robertson WD, Russell BM, Cherry JA. 1996. Attenuation of nitrate in aquitard sediments of southern Ontario. *Journal of Hydrology* **180**: 267–281.

Saltzman ES, Brass GW, Price DA. 1983. The mechanism of sulfate aerosol formation: chemical and sulfur isotopic evidence. *Geophysical Research Letters* **10**: 513–516.

Schmalz V, Grischek T, Herlitzius J, Gruner T, Worch E. 2003. Effect of pyrite oxidation on dynamic sulphate concentrations in an alluvial aquifer. In *Geochemical Processes in Soil and Groundwater*, Schulz HD, Hadeler A (eds). Wiley–VCH: Weinheim; 326–342.

Strauch G, Knöller K, Gläßer W. 2003. Sulfate reduction in lignite mining dumps. In *Geochemical Processes in Soil and Groundwater*, Schulz HD, Hadeler A (eds). Wiley–VCH: Weinheim; 343–355.

Strebel O, Böttcher J, Fritz P. 1990. Use of isotope fractionation of sulfate-sulfur and sulfate-oxygen to assess bacterial desulfurication in a sandy aquifer. *Journal of Hydrology* **121**: 155–172.

Taylor BE, Wheeler MC. 1994. Sulfur and oxygen isotope geochemistry of acid mine drainage in the Western United States. In *Environmental Geochemistry of Sulfide Oxidation*, Alpers CN, Blowes DW (eds). *American Chemical Society Symposium Series* 550. ACS: Washington, DC; 481–514.

Taylor BE, Wheeler MC, Nordstrom DK. 1984a. Isotope composition of sulfate in acid mine drainage as measure of bacterial oxidation. *Nature* **308**: 538–541.

Taylor BE, Wheeler MC, Nordstrom DK. 1984b. Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. *Geochimica et Cosmochimica Acta* **48**: 2669–2678.

Toran L, Harris RF. 1989. Interpretation of sulfur and oxygen isotopes in biological and abiological sulfide oxidation. *Geochimica et Cosmochimica Acta* **53**: 2341–2348.

Trettin R, Knöller K, Loosli HH, Kowski P. 2002. Evaluation of the sulfate dynamics in groundwater by means of environmental isotopes. *Isotopes in Environmental and Health Studies* **38**: 103–119.

Van Everdingen RO, Krouse HR. 1985. Isotope composition of sulphates generated by bacterial and abiological oxidation. *Nature* **315**: 395–396.

Van Stempvoort DR. 1989. *The use of stable isotope techniques to investigate the sulphur cycle in upland forests of central and southern Ohio*. PhD thesis, University of Waterloo.

Van Stempvoort DR, Krouse HR. 1994. Controls of δ^{18}O in sulfate. Review of experimental data and application to specific environments. In *Environmental Geochemistry of Sulfide Oxidation*, Alpers CN, Blowes DW (eds). *American Chemical Society Symposium Series* 550. ACS: Washington, DC; 447–480.

Van Stempvoort DR, Reardon EJ, Fritz P. 1990. Fractionation of sulfur and oxygen isotopes in sulfate by soil sorption. *Geochimica et Cosmochimica Acta* **54**: 2817–2826.

Whelpdale DM. 1992. An overview of the atmospheric sulfur cycle. In *Sulphur Cycling on the Continents: Wetlands, Terrestrial Ecosystems and Associated Water Bodies*, Howarth RW, Stewart JWB, Ivanov MV (eds). *SCOPE* 48. Wiley: Chichester; 5–26.