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The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils

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Abstract—The isotope compositions of sulfate in bulk precipitation near Munich (Germany) and of seepage water and soil sulfate in five acid forest soils representative of southern Germany were determined in order to ascertain the sources and dynamics of sulfur. While the δ^{34}S-values of inorganic sulfate in soil solution and solid phases were found to be nearly identical to those of precipitation sulfate, a depletion of several per mil was observed for the δ^{18}O-values of sulfate within the uppermost 30 cm of the investigated soils. Mineralization of carbon-bonded sulfur to SO_4^{2-} in the forest floor and humic mineral soil horizons is the only known process which can explain the observed shifts in $\delta^{18}O_{sulfate}$. The fact that this ^{18}O-depleted sulfate recharges the groundwater under forests must be considered, when sulfur and oxygen isotope data of sulfate are used for interpretations of the past geochemistry of groundwater systems.

Since the δ^{34}S-values of precipitation sulfate were barely altered during percolation through the soils, sulfate mobilities were inferred from a lysimeter experiment with undisturbed soil cores from the same sites, using the stable isotope composition of the irrigation sulfate as a tracer. Fifteen cores of each of the five forest soils, were repeatedly irrigated over 20 months with ^{34}S- and ^{18}O-enriched sulfate in three different treatments (35, 63, and 131 kg S ha^{-1} respectively). Despite the fact that the mean residence time of the seepage water was of the order of only a few months, the throughput of irrigation sulfate did not exceed 34% for all soils and irrigation treatments during the experiment. The low recovery of irrigation sulfate in the seepage water implies mean residence times for sulfur in the uppermost 60 cm of the forest soils of the order of decades, much longer than previously suggested.

INTRODUCTION

Due to increased SO_2 emissions primarily from burning fossil fuels, atmospheric sulfur deposition in the northern hemisphere increased in this century until the early 1980s (Husar *et al.*, 1992). Consequently, sulfate is today the predominant anion associated with atmospheric deposition in many regions of Europe and North America (e.g. Führer *et al.*, 1988; Binkley *et al.*, 1989). The biogeochemical response of soils, lakes, and streams to this elevated input of sulfate has been the subject of numerous studies in the past two decades (e.g. Likens *et al.*, 1977; Ulrich and Pankrath, 1983; Reuss and Johnson, 1986). As a result of this work it was concluded that nutrient transport in soils is strongly regulated by the mobility of anions in soil solution (e.g. Reuss and Johnson, 1986).

Much consideration has been given to the influence of acid deposition on sulfur cycling (e.g. Richter *et al.*, 1983). It was shown that increased inputs of SO_4^{2-} may accelerate leaching of acidic cations (H^+ and Al^{3+}), base cations, and nutrient elements and subsequently acidify terrestrial and aquatic systems (e.g. Reuss and Johnson, 1986). Therefore, the extent of atmospheric SO_4^{2-} retention in the soil is of

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crucial importance to cationic nutrient transport, acidification processes, and aluminium mobilization. Possible retention mechanisms in aerated acid forest soils include microbial sulfate immobilization (Fitzgerald *et al.*, 1982), sulfate adsorption on sesquioxides and clay minerals (Rajan, 1978) and precipitation of aluminium hydroxy sulfate minerals (Nordstrom, 1982; Khanna *et al.*, 1987). Sulfate adsorption and $Al_x(OH)_y(SO_4)_z$ precipitation are strongly dependent on the pH value of the soil solution; sulfate adsorption is negligible above pH 6.5 and typically increases with decreasing soil pH below this value. Dependent upon the presence of other mobile anions, retention of SO_4^{2-} in the soil can reduce the mobility of acidifying cations and thus diminish stream acidification (Mitchell *et al.*, 1992).

As a consequence of a drastic reduction of sulfur emissions and sulfate deposition in Central Europe over the past 10 years (Umweltbundesamt, 1992), the stability of soil sulfur pools has recently become a matter of concern. Possible mobilization mechanisms in aerated acid forest soils include the conversion of organic soil sulfur to inorganic forms (SO_4^{2-} under aerated conditions), a process which is referred to as mineralization (e.g. David and Mitchell, 1987). The decomposition of both major forms of organic sulfur, the mineralization of carbon-bonded sulfur and the hydrolysis of organic sulfates, are microbially mediated and occur presumably in the forest floor and humic mineral soil. In the subsoil, desorption can supply SO_4^{2-} to the soil solution (Singh, 1984). This process is dependent upon the degree to which the soil has previously adsorbed sulfate, and the concentration of sulfate in incoming solutions relative to the concentration with which the soil was equilibrated before (Johnson and Todd, 1983), changes in soil pH, and the reversibility of sulfate adsorption. The release of previously stored sulfur in the soil, which in some cases also occurs by dissolution of sulfate minerals and salts, involves cation leaching and further leads to acidification of soils and adjacent water bodies.

The use of stable isotopes in studies of biogeochemical cycles has increased rapidly over the past 20 years, because stable isotope data can contribute both source-sink (tracer) and process information. The sulfate ion is unique in this respect since it contains in the $\delta^{34}S$- and $\delta^{18}O$-value both types of information. The latter isotope ratio is expected to shift during redox reactions (process information), whereas $\delta^{34}S$-values are believed to vary only slightly during sulfur transformations under aerated conditions (e.g. Krouse *et al.*, 1991) and, therefore, should be a suitable tracer.

In this study, we analyzed the stable isotope composition of sulfate ($\delta^{34}S$- and $\delta^{18}O$-values) in precipitation, seepage water sulfate, and soil sulfate to gain a better understanding of sources and transformations of sulfur in five different acid forest soils, representative of southern Germany. Additionally, a long-term irrigation experiment with undisturbed soil cores was conducted using ^{34}S- and ^{18}O-enriched sulfate as tracer. The purpose of this experiment was to determine how the stable isotope composition of sulfate can be used to ascertain the mobility of sulfate in the biogeochemical soil sulfur cycle and whether it provides clues to processes therein.

MATERIALS AND ANALYTICAL METHODS

Precipitation

Bulk precipitation was sampled in a Hellmann collector at the GSF Research Centre 1 km north of the Munich city limit (Fig. 1) between April 1990 and December 1991 in four week intervals. Sulfate concentrations, $\delta^{18}O$-values of the precipitation water, as well as $\delta^{34}S$- and $\delta^{18}O$-values of precipitation sulfate were analysed as described below in order to determine the isotopic composition of SO_4^{2-} and its variability in bulk precipitation in southern Germany.

Soil profile investigations

Five soil profiles with different parent materials and different pedogeneses were selected within 300 km from the precipitation station north of Munich (Fig. 1). Two soils were derived from quartz-rich sandy deposits (Bamberg, Ferro-orthic Podzol; Steinach, Dystric Cambisol). Two Orthic Luvisols (Stalldorf and Höglwald) were derived mainly from loess, whereas the Dystric Cambisol (Nationalpark) was derived from gneiss debris. Forest floor, A- and B-horizons were sampled to a depth of 60 cm, air-dried (35°C), passed through a 2 mm sieve and ground prior to analyses. Bulk densities, organic carbon contents, total nitrogen contents, and pH in 0.01 M $CaCl_2$ were determined by standard techniques. Total sulfur was determined by a LECO sulfur analyzer SC 132 for forest floor samples, and an alkaline oxidation method followed by Johnson–Nishita reduction (Tabatabai and Bremmer, 1970) for mineral soil horizons. Sulfur contents were calculated from sulfur concentration, fine earth density, coarse fragment percentage, and thickness of a given horizon. Phosphate extractable SO_4^{2-} was analysed from sieved unground aliquots after 18 h extraction with 0.016 M KH_2PO_4 using a 5 : 1 solution : soil ratio. Sulfate concentrations in the extractants were determined by ion chromatography using a DIONEX 2020i analyser. Organic sulfur was calculated as the difference between total sulfur and inorganic SO_4–S, since reduced inorganic sulfur forms were found to be negligible.

In order to determine the isotopic composition of soluble sulfate in the different soil horizons, SO_4^{2-} was extracted from an aliquot of each horizon (typically 1 kg) with 0.1 M LiCl (solution : soil = 5 : 1). Samples were suspended in the LiCl solution for several days and agitated in an ultrasonic bath for 5 min prior to centrifugation and membrane filtration (0.45 μm). Although LiCl solutions may only extract part of the adsorbed sulfate in acidic soil horizons, $\delta^{34}S$- and $\delta^{18}O$-values for the extracted sulfate are considered to represent total inorganic sulfate, since isotope fractionation during sulfate sorption is negligible for S- and O-isotopes (Van Stempvoort *et al.*, 1990).

Lysimeter experiments

Seventy-five cylindrical soil cores (0.3 m diameter, 0.6 m length) were taken from the five study sites. Fifteen cores of

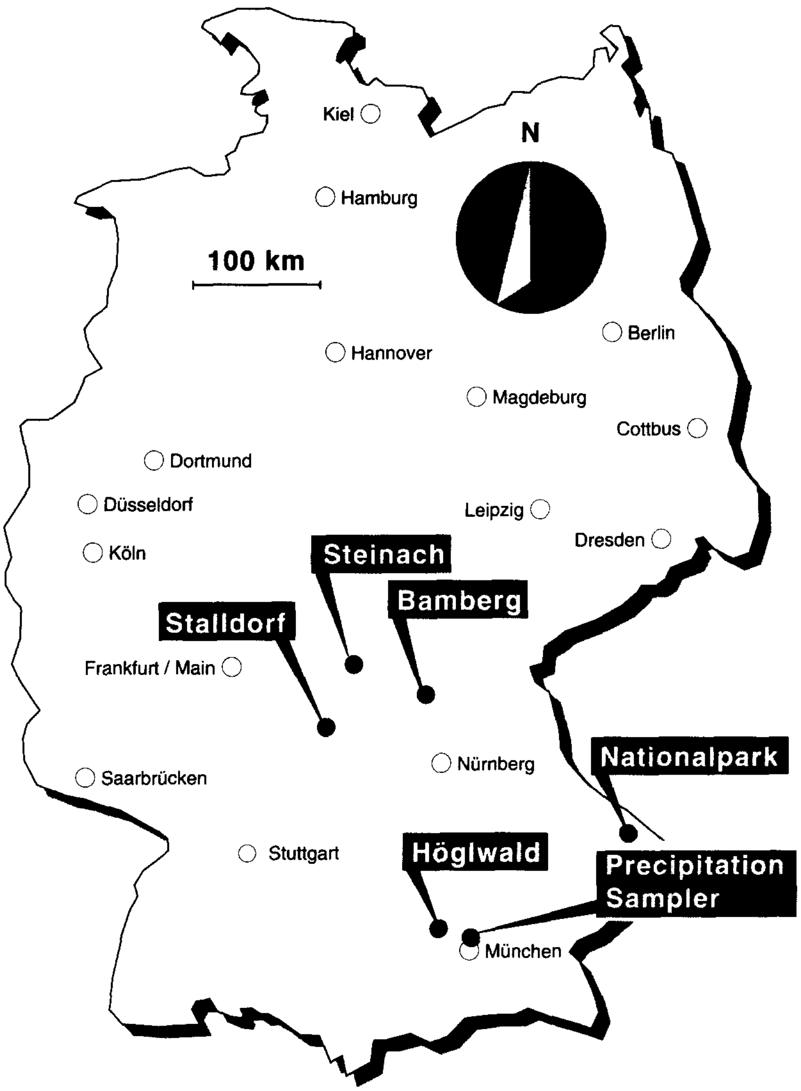

Fig. 1. Map of Germany showing the locations of the precipitation station 1 km north of Munich city limits and of the five investigated soil profiles.

each soil were each fitted with a 2 l sampling bottle and allowed to drain freely (Fig. 2). The lysimeters were reburied at the Höglwald experimental site and covered with a rain shield to exclude precipitation yet maintain natural light and temperature conditions. Although structural disturbances of the cores during excavation, lysimeter construction, and reburial were minimized, an increased mineralization of organic matter was unavoidable.

Starting three months after reburial of the cores, the lysimeters were artificially irrigated during a period of 20 months at a rate of 508 mm a^{-1}, which is the long-term mean value of canopy throughfall at the Höglwald site (Pröbstle and Kreutzer, 1991). This was done in the frost free period 3 to 4 times a week with either 250 or 500 ml solution volumes, corresponding to daily showers of 3.5 or 7.1 mm, respectively. Mean evaporation losses were about 20% for each soil type since the leachate volumes varied normally between 77 and 83% of the applied irrigation volumes. The irrigation solutions were made up to be chemically equivalent to mean canopy throughfall at selected sites in Germany with low (Höglwald, spruce site), moderate (Solling, beech site), and high (Solling, spruce site) atmospheric sulfur deposition (Bredemeier, 1987; Göttlein and Kreutzer, 1991). They comprised three different SO_4^{2-} concentrations corresponding to 23 (experimental treatment I), 42 (treatment II), and 87 kg SO_4-S ha^{-1} a^{-1} (treatment III). The irrigation SO_4^{2-} was derived from Silurian gypsum of the Salina Formation (Ontario, Canada) and was used as a tracer because of its high δ^{34}S-values (+28.0‰) and δ^{18}O-values (+14.7‰). The δ^{34}S-value of the irrigation SO_4^{2-} differed by more than 25‰ from those of seepage water sulfate in the investigated soils at the beginning of the experiment.

When each lysimeter had been irrigated with 2 l (usually after 1–2 weeks), seepage water was collected and SO_4^{2-} concentrations were measured. The remaining water was bulked for each lysimeter to 5 to 20 l samples, representing sampling intervals of 1 to 4 months. The isotope composition of sulfate was determined on the bulk samples in order to yield sufficient $BaSO_4$ for isotope analysis. Since it was found that there was very little variability in the seepage water SO_4^{2-} contents within the five lysimeters of a given treatment and soil, only mean SO_4^{2-} concentrations were determined as the experimental irrigations progressed. Sulfur fluxes in the lysimeters were studied by input–output balances calculated as the product of mean SO_4^{2-} concentrations and water volumes divided by the corresponding

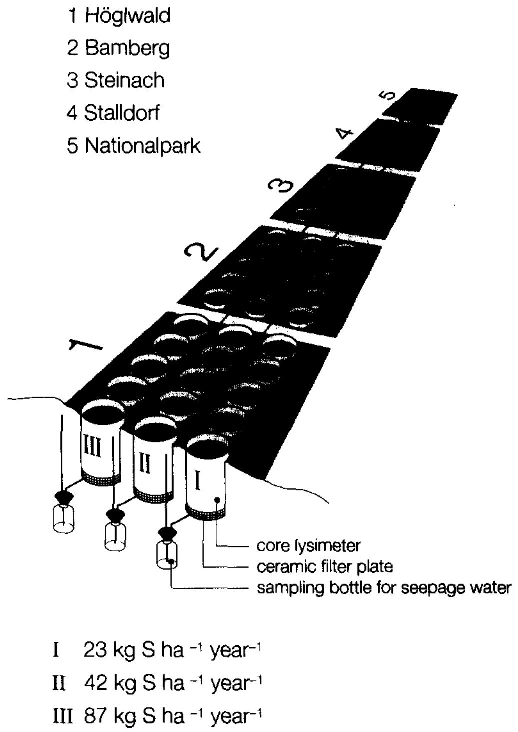

Fig. 2. Schematic setup of the irrigation experiment. Three sets of five lysimeters per soil were irrigated over 20 months with SO_4–S concentrations equivalent to 35, 63, and 131 kg S ha^{-1} in treatment I, II, and III, respectively.

time interval. Isotope and mass balance equations were used to calculate the amounts of pedogenic and irrigation sulfur in the lysimeter outflow (Mayer *et al.*, 1993).

The mean residence times of the irrigation water in the lysimeters were inferred from a Br^- tracer test. Sulfate and bromide concentrations were determined by ion chromatography with an overall precision of ±1% using a DIONEX 2020i analyser. Sulfate from precipitation or seepage water samples with $[SO_4^{2-}]$ <20 mg l^{-1} was extracted quantitatively from the water using ion exchange techniques (Baker ANGA 542) and recovered with 150 ml 1 M NaCl solution. This purified and concentrated sulfate solution was precipitated with 0.5 M $BaCl_2$ solution as $BaSO_4$ and acidified below pH 4 to remove potentially co-precipitated $BaCO_3$. Sulfate from water samples with $[SO_4^{2-}]$ >20 mg l^{-1} was precipitated directly without using ion exchange techniques. Finally, the barium sulfate precipitate was washed several times with deionized water, filtered and dried for subsequent isotope ratio determinations.

Isotope measurements

The SO_2 for $\delta^{34}S$ measurements was obtained by high temperature reaction of $BaSO_4$ with V_2O_5 and SiO_2 in a weight ratio of 1 : 10 : 10 (Yanagisawa and Sakai, 1983). For $\delta^{18}O$-measurements on sulfate, CO_2 was produced through the thermal decomposition of $BaSO_4$ with pure graphite (17 : 6 weight basis) in molybdenum foil under vacuum at more than 1000°C, followed by a conversion of CO to CO_2 in a discharge chamber (Holt, 1991). For $\delta^{18}O$-measurements on water, standard equilibration techniques were used (Epstein and Mayeda, 1953). Isotope compositions are reported on the usual δ-scale in parts per thousands:

$$\delta_{\text{sample}}\ (‰) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

where R is the $^{34}S/^{32}S$ or the $^{18}O/^{16}O$ abundance ratio. The standard for sulfur isotope measurements is Cañon Diablo Troilite (CDT) and for oxygen isotope measurements Vienna Standard Mean Ocean Water (V-SMOW). The overall reproducibilities for gas preparations and mass spectrometric determinations were ±0.2‰ for $\delta^{34}S$-values and ±0.5‰ for $\delta^{18}O$-values in sulfate, and ±0.15‰ for $\delta^{18}O$-values in water. Precision in estimating sulfate concentrations gravimetrically from $BaSO_4$ was ±0.2 mg which typically represented less than 5% of the total weight of $BaSO_4$, but up to 30% of some precipitation samples.

RESULTS AND DISCUSSION

Soil properties

Chemical and physical soil properties are summarized in Table 1. All soils were characterized by a strong accumulation of humus with a wide carbon : nitrogen ratio (27 : 31) in the forest floor. The organic carbon contents of the forest floor varied between 348 and 530 mg g^{-1} for the five soils. The soils differed markedly in texture and their sesquioxide contents. They were carbonate free in the uppermost 60 cm. The pH values in the forest floor and the organo-mineral topsoil varied between 2.9 and 3.7. In the subsoil, the pH gradually increased to values between 3.9 and 4.5, and even to 5.0 for the Stalldorf soil. Whereas the sandy soils, Steinach and Bamberg, had sulfur contents of about 500 kg ha^{-1} in the uppermost 60 cm of the profile, the Dystric Luvisols Höglwald and Stalldorf were intermediate with about 1000 kg S ha^{-1} compared to a number of forest soils throughout the world (Mitchell *et al.*, 1992). The Dystric Cambisol Nationalpark with more than 2000 kg S ha^{-1} had the highest amount of sulfur stored in the uppermost 60 cm of its profile. Between 50 and 70% of the sulfur in the soil profiles was organically bound, preferentially as carbon-bonded sulfur (Prietzel *et al.*, 1994).

Isotopic composition of precipitation sulfate

$\delta^{34}S$-values and $\delta^{18}O$-values for precipitation sulfate sampled between April 1990 and December 1991 north of Munich are given in Table 2. The observed range of $\delta^{34}S$-values for sulfate in bulk precipitation was 7.4‰. The maxima (+3.5‰) and the minima (−3.9‰) are generally identified with high sulfate concentrations but exhibit no seasonal trend. They seem to reflect $\delta^{34}S$-values of temporarily active local pollutant sources with different sulfur isotope compositions. At sulfate concentrations below 1 mg l^{-1}, the $\delta^{34}S$-values varied only between +1.9 and +2.8‰. This is in good agreement with $\delta^{34}S$-values for throughfall sulfate in remote areas of southern Germany (Mayer, 1993), having a mean $\delta^{34}S$-value

Table 1. Chemical and physical properties of the investigated soils

	Depth (cm)	Clay (weight%)	pH ($CaCl_2$)	C_{org} (mg g^{-1})	S_{tot} (μg g^{-1})	Inorganic SO_4-S (μg g^{-1})	S_{tot} content (kg ha^{-1})	Sesquioxide content (kmol ha^{-1})
Nationalpark (Dystric Cambisol)								
O	7–0	n.d.	3.1	348	1865	5	239	n.d.
A(e)h	0–4	26	3.3	106	514	16	174	238
AhBv	5–20	29	4.1	41	316	75	538	1391
B(s)v	21–48	13	4.4	23	316	172	1136	3059
Bv	49–60	13	4.4	9	180	97	244	793
Höglwald (Orthic Luvisol)								
O	4–0	n.d.	3.1	382	2190	0	115	n.d.
A(e)h	0–5	21	3.2	46	328	0	169	159
Ahl	6–10	15	3.7	15	94	10	53	169
Al	11–35	19	4.0	8	105	48	392	1030
Bt	36–50	31	3.8	2	98	52	221	885
Btv	51–60	25	4.0	2	40	24	58	598
Stalldorf (Orthic Luvisol)								
O	4–0	n.d.	3.4	419	2274	0	119	n.d.
Ah	0–3	20	3.2	89	577	0	169	77
Al	4–20	13	3.6	12	97	7	213	568
Bt	21–50	15	3.9	5	86	13	341	1147
Btv	51–60	34	5.0	4	170	23	244	515
Bamberg (Ferro-orthic Podzol)								
O	7–0	n.d.	2.9	367	1856	1	205	n.d.
Ahe	0–10	0	3.2	15	60	0	84	107
Bhs1	11–25	1	4.3	7	47	22	99	400
Bhs2	26–40	1	4.5	3	37	24	78	284
BvCv	41–60	2	4.4	1	16	3	44	240
Steinach (Dystric Cambisol)								
O	4–0	n.d.	2.9	530	2491	0	147	n.d.
Aeh	0–11	5	3.0	23	74	0	86	54
Bv	12–46	9	4.0	8	48	9	190	515
IISdBv	47–60	15	3.9	3	54	15	92	186

n.d. = not determined.

Table 2. Summary of precipitation amounts, gravimetrically determined SO_4^{2-} concentrations, $\delta^{34}S$ and $\delta^{18}O$-values of precipitation sulfate, and $\delta^{18}O$-values of precipitation water at the GSF Research Centre, 1 km north of the city limit of Munich between April 1990 and December 1991

Sampling period	Precipitation (mm)	$[SO_4^{2-}]$ (mg l^{-1})	$\delta^{34}S$ (‰)	$\delta^{18}O(SO_4^{2-})$ (‰)	$\delta^{18}O(H_2O)$ (‰)
09.04.90–07.05.90	81.2	3.8	0.0	10.5	−10.7
07.05.90–04.06.90	98.3	4.5	−3.9	–	−6.3
04.06.90–02.07.90	157.6	3.5	−0.6	11.0	−8.8
02.07.90–29.07.90	58.3	0.5	2.2	–	−8.2
29.07.90–27.08.90	97.8	4.1	3.5	13.5	−5.6
27.08.90–24.09.90	126.8	2.5	0.3	11.7	−8.2
24.09.90–22.10.90	36.8	1.5	−1.9	–	−10.1
22.10.90–19.11.90	85.9	2.5	−0.9	8.4	−11.6
19.11.90–17.12.90	47.9	3.0	0.3	9.5	−13.1
17.12.90–14.01.91	92.7	2.0	–	–	−11.3
11.03.91–08.04.91	56.0	3.3	3.2	–	−10.5
08.04.91–06.05.91	70.3	6.6	0.8	9.1	−12.3
06.05.91–03.06.91	128.0	10.7	1.8	11.8	−10.8
03.06.91–01.07.91	173.8	0.8	2.4	–	−8.9
01.07.91–29.07.91	82.9	1.3	2.1	–	−8.2
29.07.91–26.08.91	135.6	4.4	3.4	13.7	−7.4
26.08.91–23.09.91	32.8	<0.5	–	–	−6.5
23.09.91–21.10.91	40.4	<0.5	–	–	−9.7
21.10.91–18.11.91	66.6	0.5	1.9	–	−15.7
18.11.91–16.12.91	19.1	0.6	2.8	–	−14.5

(–) insufficient sample for analysis.

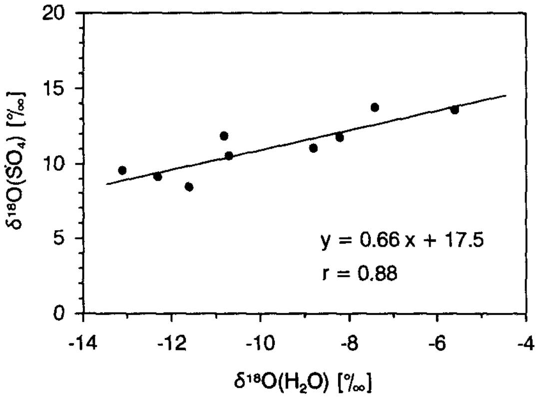

Fig. 3. Correlation between the $\delta^{18}O$-values of precipitation sulfate and precipitation water in bulk precipitation 1 km north of the Munich city limits between April 1990 and December 1991.

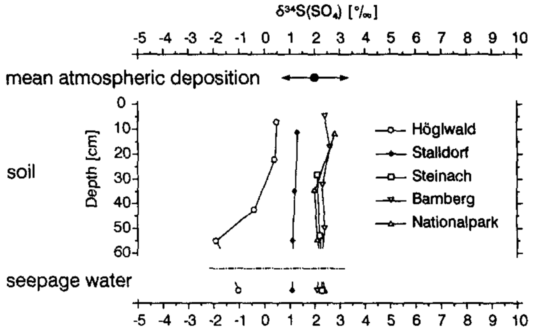

Fig. 4. $\delta^{34}S$-values for deposition sulfate derived from long-range transport, inorganic soil sulfate after LiCl extraction, and initial seepage water sulfate in 60 cm depth for the five investigated forest soils.

of +2.0 ± 1.3‰ ($n = 22$). This value represents sulfate in atmospheric deposition in southern Germany derived from long-range transport. It can be considered also as the mean $\delta^{34}S$-value of deposition sulfate at the five investigated sites, where local emissions of pollutants are minor.

The $\delta^{18}O$-values for sulfate in bulk precipitation varied between +8.4 and +13.7‰ during the observation period (Table 2). The $\delta^{18}O$-values of the precipitation water and sulfate reached their maxima in the summer months. Linear correlation of $\delta^{18}O$-values for sulfate with those of bulk precipitation water north of Munich (Fig. 3) was significant ($r = 0.88$, $n = 9$, $p = 0.05$) and follows the linear regresssion:

$$\delta^{18}O_{\text{sulfate}} = (0.66 \pm 0.14)\delta^{18}O_{\text{water}} + (17.48 \pm 1.39).$$

This correlation indicates the direct influence of the isotopic composition of water oxygen on the isotopic composition of the oxygen in the sulfate ion. Since SO_2 dissolved in water hydrolyses rapidly to HSO_3^- (Eigen *et al.*, 1961; Beilke and Gravenhorst, 1978), and HSO_3^- isotopically equilibrates with liquid water in large excess, the $\delta^{18}O$-value of the SO_2 is not reflected in the $\delta^{18}O$ of the oxidized sulfate (Holt *et al.*, 1981a). Therefore, the $\delta^{18}O$ of three of the oxygen atoms in the sulfate product are expected to be strongly controlled by the $\delta^{18}O$ of the H_2O. Indeed, Holt *et al.* (1981a) observed that the $\delta^{18}O$ of SO_4^{2-} varied with the $\delta^{18}O$ of the water with a slope close to 0.75 in SO_4^{2-} samples prepared by Fe^{3+}-catalysed aqueous oxidation of SO_2 in air with water in large excess. Holt *et al.* (1981b) also found a slope of 0.60 when SO_2 was oxidized by H_2O_2 in aqueous solution. Our data indicate that probably both H_2O and H_2O_2 are involved in the aqueous oxidation of SO_2 to SO_4^{2-} in the atmosphere of southern Germany.

From the mean annual $\delta^{18}O$-values (mass weighted) for precipitation water (1978–1991) at the station north of Munich (−10.4‰), a mean annual $\delta^{18}O$-value for precipitation sulfate of +10.6 ± 2.9‰ can be calculated using the above regression line. The average maximum in $\delta^{18}O_{\text{sulfate}}$ is expected in August at +12.7 ± 2.9‰ and the mean minimum in February at +8.0 ± 3.4‰, corresponding to monthly mean $\delta^{18}O$-values for precipitation water of −7.2 and −14.4‰, respectively (Trimborn, personal communication).

Isotopic composition of soil and seepage water sulfate

Depth profiles for $\delta^{34}S$-values of inorganic sulfate in the five forest soils are given in Fig. 4. The $\delta^{34}S$-values of inorganic soil sulfate generally fall in the range of those of precipitation sulfate derived from long-range transport. In four of the five soils, the $\delta^{34}S$-values for inorganic sulfate in the soil are constant throughout the profiles. Only for the Luvisol Höglwald a trend to slightly depleted $\delta^{34}S$-values was observed with depth (Fig. 4). This is indicative of a second sulfur source, having a more negative $\delta^{34}S$-value than precipitation sulfate. Since the Luvisol Höglwald is a translocated mixture of loess and tertiary freshwater sediments (molasse), the second source is most likely sedimentary sulfate (possibly derived from pyrite oxidation) from the molasse, whose proportion in the soil profile increases with depth. For all soils, the $\delta^{34}S$-values of inorganic sulfate in 50–60 cm depth were nearly identical to the $\delta^{34}S$-values of seepage water sulfate from the lysimeters prior to irrigation (Fig. 4). This supports findings of Van Stempvoort *et al.* (1990), indicating that sulfur isotope fractionation between adsorbed and aqueous sulfate in soils is negligible.

Whereas the $\delta^{34}S$-values for inorganic sulfate in solution and solid phase were nearly identical with those of the precipitation sulfate, the $\delta^{18}O$-values of sulfate in the deeper mineral soil were markedly depleted relative to those of the mean atmospheric

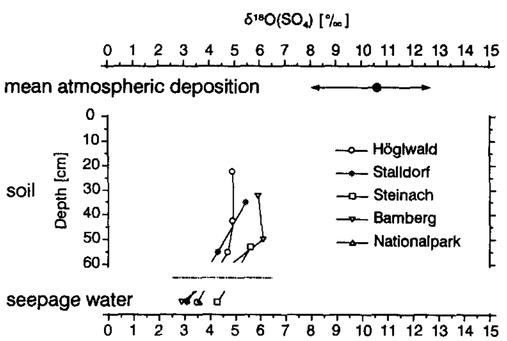

Fig. 5. δ^{18}O-values for deposition sulfate, inorganic soil sulfate after LiCl extraction, and initial seepage water sulfate in 60 cm depth for the five investigated forest soils.

input (Fig. 5). The δ^{18}O-values of the extracted sulfate varied between +4.3 and +5.4‰ in the Luvisols Höglwald and Stalldorf ($n = 5$) and between +5.6 and +6.1‰ in the sandy soils Bamberg and Steinach ($n = 3$). This documents a depletion of 4.5 to 6.3‰ with respect to the δ^{18}O-value of mean deposition sulfate, which was even more pronounced in the seepage water sulfate at 60 cm depth prior to irrigation (Fig. 5).

The marked depletion of the δ^{18}O-values in sulfate within the uppermost 20 to 30 cm of the investigated soil profiles can neither be explained by conservative percolation of sulfate, since oxygen atoms do not readily exchange between H_2O and SO_4^{2-} under environmental conditions (Chiba and Sakai, 1985), nor by soil sorption, which does not fractionate sulfate oxygen significantly (Van Stempvoort *et al.*, 1990). In both cases, deposition sulfate would retain its isotope integrity for δ^{18}O (mean value +10.6‰). Therefore it is proposed that the depleted δ^{18}O-values in seepage water sulfate originate from sulfate, which is formed by mineralization of organic soil sulfur.

The end products of the decomposition of organic sulfur compounds depend upon the nature of the mineralized sulfur compound, the microorganisms involved, and the environmental conditions (e.g. Freney, 1967). For the oxidation of carbon-bonded sulfur to SO_4^{2-}, there are several different reaction pathways described in the literature (e.g. Freney and Stevenson, 1966). Sulfur in amino acids and proteins is broken down to form H_2S (Germida *et al.*, 1992) and other gaseous forms of sulfur. Under aerobic conditions, the former will rapidly oxidize to SO_4^{2-}. If carbon-bonded sulfur is released from its organic moeity prior to oxidation, then similar ^{18}O-contents can be expected for mineralized sulfate, as for sulfate generated by biological and abiological oxidation experiments with reduced inorganic sulfur in the laboratory (Lloyd, 1968; Schwarcz and Cortecci, 1974; Taylor *et al.*, 1984a). The newly formed sulfate can acquire oxygen from soil water (negative δ^{18}O-values depending upon location) and atmospheric O_2, which has a δ^{18}O-value of +23.5 ± 0.3‰ (Kroopnick and Craig, 1972). As summarized by Toran and Harris (1989), between 45 and 75% water oxygen is generally incorporated during the biological oxidation of inorganic reduced sulfur, whereas between 60 and 90% were found for abiotic oxidation. No significant isotope fractionation is expected for the incorporation of water oxygen, whereas for the incorporation of molecular oxygen, an isotope fractionation between −4.3 and −11.4‰ is assumed (Lloyd, 1967; Taylor *et al.*, 1984a). Existing field data (Taylor *et al.*, 1984b; Van Everdingen and Krouse, 1985, 1988) confirm the results of laboratory experiments, covering the overlap (45 to 90% incorporation of water oxygen) between biological and abiotic experiments. With typical δ^{18}O-values of −10.0‰ for the investigated soils (negligible evaporative enrichment) and Lloyd's (1967) enrichment factors [$\varepsilon(H_2O) = 0.0$‰ and $\varepsilon(O_2) = -8.7$‰] and incorporation of 60 to 70% water oxygen, mineralized SO_4^{2-} from carbon-bonded sulfur would have slightly negative δ^{18}O-values (−2.6 to −0.1‰). These values have to be considered only as rough estimates due to variations in $\varepsilon(H_2O)$, $\varepsilon(O_2)$, and $\delta^{18}O(O_2)$ under given environmental conditions, the potential role of oxygen sources other than H_2O and O_2, and the particular oxidation pathway of reduced organic sulfur compounds (Van Stempvoort and Krouse, 1994). Nevertheless, a depletion in the order of 10‰ compared to the δ^{18}O-values of atmospheric sulfate is not unrealistic for mineralized SO_4^{2-} from carbon-bonded sulfur compounds.

A similar depletion can not be expected if organic sulfates are hydrolysed to SO_4^{2-}. Dependent upon arylsulfatase or alkylsulfatase enzymes being predominant (Fitzgerald, 1976; Cloves *et al.*, 1977), at least three oxygen atoms of the newly formed sulfate are carried over from the previously immobilized deposition SO_4^{2-}. Therefore, a depletion of only 2 to 3‰ in $\delta^{18}O_{\mathrm{sulfate}}$ can be expected for SO_4^{2-} derived by hydrolysis of organic sulfates (Mayer *et al.*, 1992). Consequently, the mineralization of carbon-bonded sulfur remains the only process, which explains the observed depletion of the $\delta^{18}O_{\mathrm{sulfate}}$-values of about 5‰ in the uppermost 30 cm of the investigated aerated forest soils. Most probably, the soil sulfate is a mixture of residual atmospheric SO_4^{2-} and hydrolyzed organic sulfates with high δ^{18}O-values and SO_4^{2-} formed by mineralization of carbon-bonded sulfur with low δ^{18}O-values.

Irrigation experiment

Water movement. The mean residence time of the seepage water under the experimental conditions, inferred from the bromide tracing test, was about 1 (Bamberg) and 3 months (Steinach) for the sandy soils, between 5 and 6 months for the Luvisols (Höglwald, Stalldorf) and between 7 and 9 months for the Cambisol Nationalpark (Mayer, 1993).

Sulfate concentrations in seepage water. Mean sulfate concentrations in the seepage water of the five lysimeters per soil type and irrigation treatment showed generally no (treatment I and II) or little effects (treatment III) on the sulfate concentration in the irrigation solutions (Fig. 6). The SO_4^{2-} concentrations in the lysimeter outflow of the Cambisol Nationalpark remained essentially constant during the observation period of 20 months. Even for the soils Höglwald, Steinach, and Bamberg changes in SO_4^{2-} concentrations in the lysimeter outflow were negligible for irrigation treatment I and II. However, after 11 months, the highest $[SO_4^{2-}]$ irrigation solution (treatment III) resulted in increasing sulfate concentrations in the seepage water. For all treatments, the sulfate concentration for Stalldorf decreased significantly from the initial value due to export of high amounts of water soluble sulfate in the B horizon of this soil profile.

Isotopic composition of seepage water sulfate. Dependent upon soil type and irrigation solution, the δ^{34}S-values in the seepage water increased between 2.0 and 15.5‰ during 20 months of experimental sulfur deposition. Generally the smallest shifts were observed with treatment I, whereas the shifts increased with higher SO_4^{2-} concentrations in the irrigation solution (Fig. 7). Assuming minor sulfur isotope fractionation during sulfur transformations in aerobic forest soils (e.g. Krouse *et al.*, 1991), the percentage of irrigation sulfate in the lysimeter outflow of each core was evaluated by a simple mixing model, in which a δ^{34}S-value of +28.0‰ represents 100% irrigation sulfate, whereas the other extreme of 100% pedogenic sulfur is represented by the δ^{34}S-values of the initial seepage water sulfate. In none of the investigated soils did the δ^{34}S-values of seepage water sulfate exceed +10‰ in treatment I, +14‰ in treatment II, and +16‰ in treatment III. Therefore, irrigation sulfate constituted always less than 50% of the seepage water sulfate for all investigated soils and irrigation treatments during the 20 months of the experiment. This indicates that more than 50% of the seepage water sulfate was derived from pedogenic sources throughout the entire experiment, although the mean transit time of the seepage water was of the order of only a few months.

In Fig. 8, δ^{34}S-values are plotted against δ^{18}O-values of sulfate for 91 seepage water samples of the sandy Cambisol Steinach. The sulfate isotope composition of all samples falls along the mixing line between irrigation sulfate and initial seepage water sulfate. This is also true for the other four investigated soils (not shown), although the trends are not as clearly pronounced due to the lower percentages of irrigation sulfate in their lysimeter outflows. The higher the SO_4^{2-} concentration in the irrigation water, the more irrigation sulfate was mixed with the initial pedogenic sulfate. Nevertheless, this admixing was much slower than expected indicating that a considerable part of the irrigated sulfate was retained in the soil. The hypothesis that all irrigation sulfate was immobilized as carbon-bonded sulfur and remineralized to SO_4^{2-} is not true. In that case, the δ^{18}O-values for SO_4^{2-} would have remained constant (Fig. 8).

Mass and isotope balances for seepage water sulfate. The mean recoveries of irrigation SO_4^{2-} in the lysimeter outflow for each soil and irrigation treatment, calculated from the sulfate concentrations and the percentage of irrigation sulfate for continuous seepage water samples, are given in Table 3. The throughput of irrigation sulfate did not exceed 34% of the applied sulfur for any of the investigated soils and irrigation treatments. A slightly higher throughput of irrigation sulfate was found for the coarse grained soils Bamberg and Steinach with their low sulfur status in all three treatments (16 to 34%), than for the Luvisols Höglwald and Stalldorf (11 to 22%) with their intermediate soil sulfur pools. For the loamy Cambisol Nationalpark with the highest amount of sulfur stored in the profile, only 4–5% of the irrigation sulfate was exported with the seepage water in all experimental treatments. This indicates that a considerable amount of irrigation sulfate was retained in the soil (more retention corresponds to a larger soil sulfur pool) and did not percolate conservatively through the acid forest soils.

CONCLUSIONS

From the similarity of δ^{34}S-values of sulfate in precipitation, seepage water, and solid phases it can not be concluded that sulfur transformations in the investigated forest soils do not occur. The observed depletion of the δ^{18}O-values of sulfate between the atmospheric input and the subsoil is evidence for intense biological cycling of sulfur, which includes bioassimilation of sulfate by soil microorganisms and vegetation and subsequent mineralization of organic sulfur compounds in the soil. Even though immobilization and mineralization occur concurrently and therefore do not affect the sulfur pools in the soil significantly, microbial processes seem to be more important for the mobility of sulfur than is generally assumed. A considerable part of the seepage water and soil sulfate in the mineral soil must be derived from the mineralization of carbon-bonded sulfur, which represents between 40–60% of the total sulfur in the forest soils. Although other authors have found a similar depletion of δ^{18}O-values between precipitation and runoff sulfate (e.g. Caron *et al.*, 1986; Gélineau *et al.*, 1989), it is concluded from the current study that depletions occur in the uppermost 30 cm of acid forest soils due to the mineralization of carbon-bonded soil sulfur. The attempt to quantify the percentage of mineralized sulfate *vs* unreacted irrigation sulfate (Gélineau *et al.*, 1989; Van Stemp-

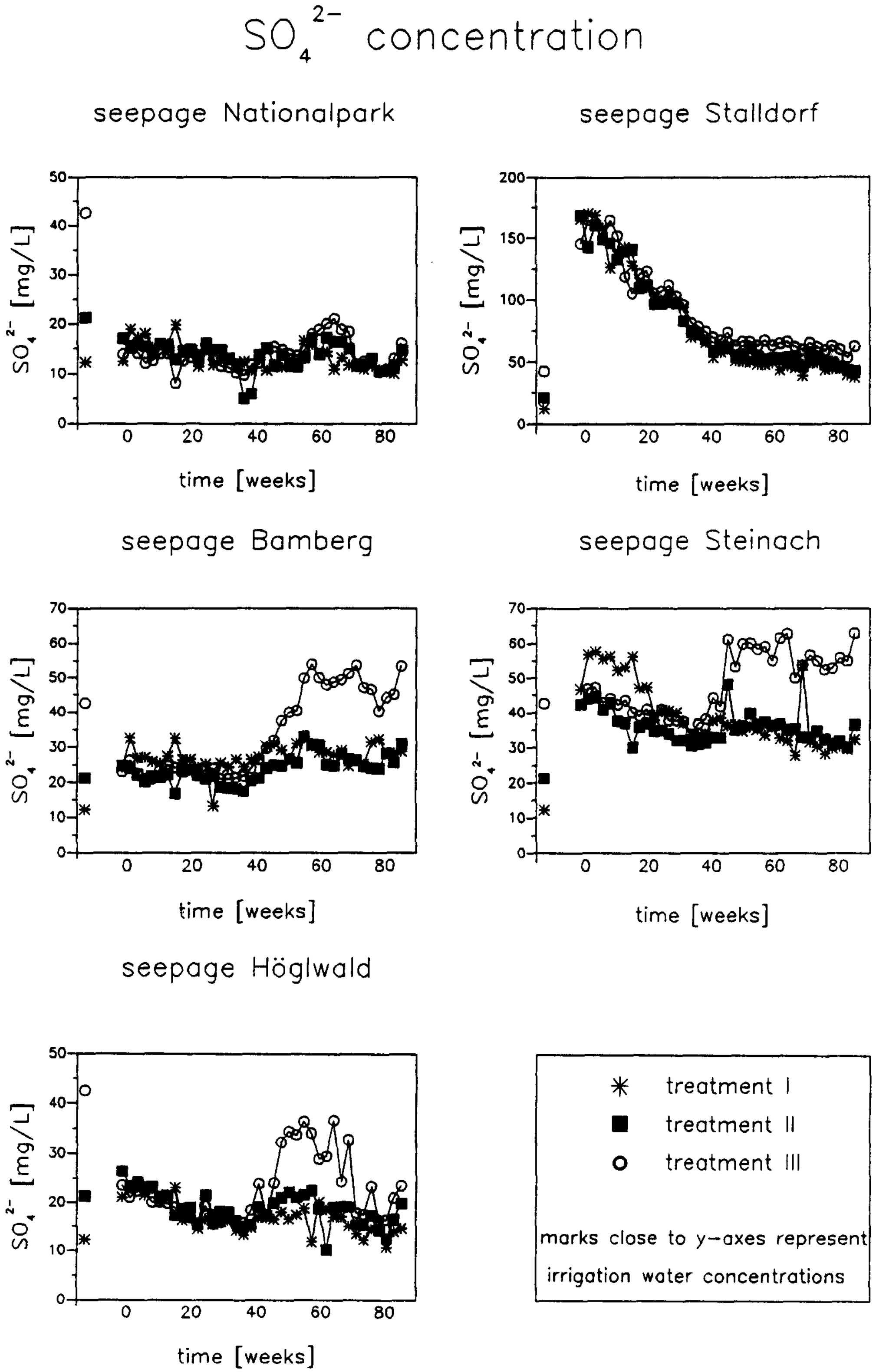

Fig. 6. Mean SO_4^{2-} concentrations in seepage water (five lysimeters per soil and irrigation treatment) during 20 months of artificial irrigation.

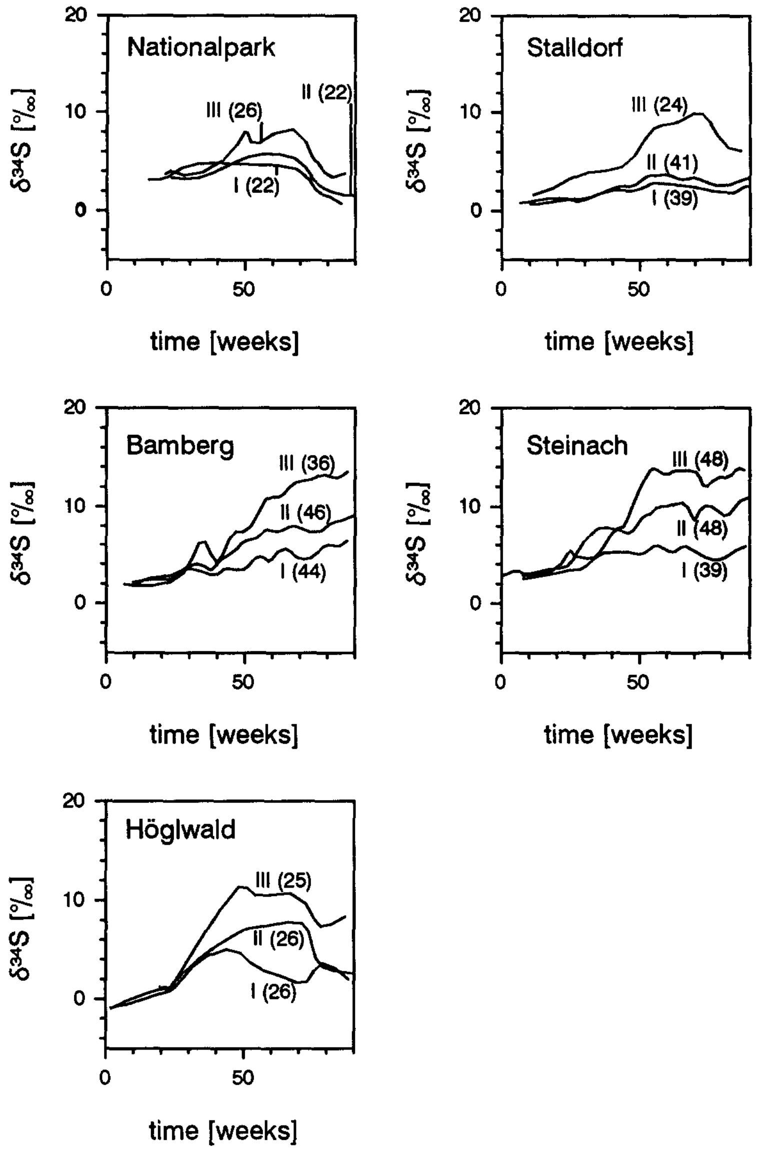

Fig. 7. Smoothed curves of δ^{34}S-values of seepage water sulfate *vs* time (five lysimeters per soil and irrigation treatment). I, II, and III indicate the treatments with the number of analyses in brackets.

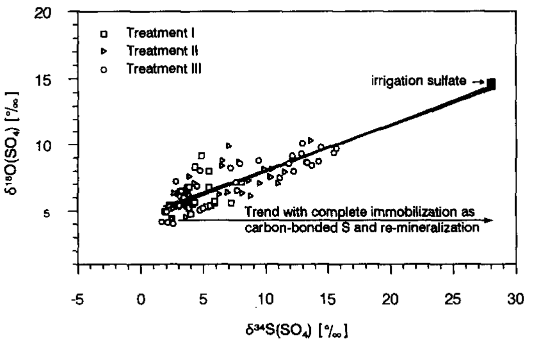

Fig. 8. δ^{18}O- *vs* δ^{34}S-values of seepage water sulfate for the three different treatments of the Dystric Cambisol Steinach during 20 months of artificial irrigation with ^{34}S- and ^{18}O-enriched sulfate.

voort *et al.*, 1992) is jeopardized, because the degradation pathways are poorly understood and δ^{18}O-values for mineralized sulfate depend upon the mineralized organic sulfur compounds (carbon-bonded sulfur or organic sulfate). Nevertheless, the fact that ^{18}O depleted sulfate arising from biological cycling of sulfur in the topsoil, recharges the groundwater under forests must be considered in interpretations of the isotope geochemistry of groundwater sulfate.

In contrast to the δ^{18}O-values of sulfate, which are significantly shifted by assimilatory sulfate reduction and subsequent reoxidation, the δ^{34}S-values of precipitation sulfate were not significantly altered as the sulfate percolated through the soils, unless a second source of sulfur contributed sulfur with a different isotopic composition (Höglwald). Therefore, the

Table 3. Mean recovery of irrigation SO_4^{2-} in the lysimeter outflow (number of lysimeters in brackets) for each soil during 20 months of experimental irrigation in three different treatments determined by mass and isotope balances

		Recovery (%)	
	Treatment I ($35\ kg\ S\ ha^{-1}$)	Treatment II ($63\ kg\ S\ ha^{-1}$)	Treatment III ($131\ kg\ S\ ha^{-1}$)
Nationalpark	5 ± 3(4)	4 ± 1(4)	4 ± 2(5)
Höglwald	14 ± 6(5)	14 ± 3(5)	14 ± 3(5)
Stalldorf	14 ± 3(5)	11 ± 2(5)	22 ± 3(3)
Bamberg	16 ± 9(5)	16 ± 3(5)	22 ± 6(5)
Steinach	24 ± 9(5)	29 ± 8(5)	34 ± 2(5)

$\delta^{34}S$-values of any applied sulfur compound can be used as a suitable tracer for studying sulfur transport and transformations under aerated conditions, if it differs significantly (>20‰) from those of naturally occurring sulfur in the system. In a controlled lysimeter experiment with ^{34}S- and ^{18}O-enriched sulfate irrigation, the throughput of labeled sulfate during the irrigation period of 20 months was only between 4 and 34% dependent upon soil and irrigation solution (Table 3), although the mean residence time of the seepage water was in the order of a few months. This indicates that the mean residence time of sulfur in the investigated forest soils must be at least in the order of years (Bamberg, Steinach) or several decades (Nationalpark). Besides inorganic retention processes like adsorption, organic transformations of sulfur seem to be important in regulating sulfur fluxes in soils, as indicated by the depleted $\delta^{18}O$-values of sulfate in the deeper mineral soil. Therefore, reactions responding to elevated sulfur inputs to the acid forest soils are delayed by the high sulfur retention capacity of the investigated soil. This means, however, that the reduction of sulfur deposition in recent years in Central Europe will not result in an immediate decrease of sulfur export with the seepage water from forest ecosystems. Depending on chemical, physical, and biological soil properties, a continued export of previously stored sulfur by desorption of sulfate (if reversible) and mineralization of organic sulfur must be expected and SO_4^{2-} will further enhance the movement of basic and acidic cations. This effect can delay the recovery of forest landscapes from deposition effects for many years.

Stable isotopes in the sulfate ion can provide information which cannot be discerned solely through the study of the distribution and fluxes of sulfur species. Whereas the $\delta^{34}S$-value can be used as a tracer under aerated conditions, if the applied sulfur differs in its isotopic composition significantly from the background sulfur, $\delta^{18}O$-values can be an indicator of microbial sulfur transformations, especially if they involve reduction and oxidation processes. The assimilatory reduction of sulfate to carbon-bonded sulfur and its subsequent mineralization is the only known process which can alter the $\delta^{18}O$-value of sulfate under aerated conditions. Therefore, isotope ratios for both sulfur and oxygen in the sulfate ion should be analysed along with concentration and flux measurements in a complete study of sulfur cycling in ecosystem research.

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