

## STABLE SULFUR ISOTOPES IN FOREST SPRING WATERS FROM THE FICHTELGEBIRGE (GERMANY)

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The potential role of processes discriminating S isotopes, for example dissimilatory  $\text{SO}_4^{2-}$  reduction and mineralization, in determining  $\text{SO}_4^{2-}$  concentrations was studied in forest spring water. S-isotope composition of sulfate from atmospheric input and forest springs representing a wide range of  $\text{SO}_4^{2-}$  concentrations was investigated in the Fichtelgebirge (NE Bavaria, Germany).  $\delta^{34}\text{S}$  values in atmospheric input ranged from +3.7 to +5.7‰. In spring waters with  $\text{SO}_4^{2-} > 150 \mu\text{mol l}^{-1}$   $\delta^{34}\text{S}$  values were between +4 and +5‰, whereas  $\delta^{34}\text{S}$  values increased up to +7.2‰ below  $150 \mu\text{mol l}^{-1}$   $\text{SO}_4^{2-}$ .  $\text{SO}_4^{2-}$  mineralization seemed to have no effect on isotopic composition since all  $\delta^{34}\text{S}$  values of spring water were higher than input values. Dissimilatory  $\text{SO}_4^{2-}$  reduction occurred in springs with  $\text{SO}_4^{2-} < 150 \mu\text{mol l}^{-1}$ . Spatial heterogeneity in forest soils or flow paths has to be invoked to explain increased  $\delta^{34}\text{S}$  values since  $\text{NO}_3^-$  concentrations would not allow for  $\text{SO}_4^{2-}$  reduction to occur.

**Keywords:** Forest hydrochemistry; natural variations; spring waters; sulfate reduction; sulfur 34

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## INTRODUCTION

Sulfate is the dominant anion in surface waters draining acidified forested regions like the Fichtelgebirge (Germany). Stable isotopes of *S* have proved to be a useful tool in identifying processes of *S* biogeochemistry on a watershed scale [1]. Sulfate that appears in forest runoff may have undergone numerous influences such as the biological processes of sulfide oxidation,  $\text{SO}_4^{2-}$  immobilization,  $\text{SO}_4^{2-}$  mineralization, volatilization,  $\text{SO}_4^{2-}$  reduction (desulfurisation), or physico-chemical processes like precipitation, solubilization, adsorption and desorption. Of these only immobilization, mineralization and reduction are processes potentially associated with changes in sulfur isotopic composition of  $\text{SO}_4^{2-}$  [2, 3]. Thus, the isotopic signature of  $\text{SO}_4^{2-}$  can potentially be used to determine the source and fate of sulfate in forest runoff [4–6] when sources can be identified [7].

Water chemistry in the Fichtelgebirge has been studied on a regional scale [8, 9] and on plot level [10, 11]. The regional pattern of sulfate output in forest springs shows increased sulfate in the eastern and northeastern spurs of the Fichtelgebirge [9]. Two factors contribute to this finding. (1) Increased sulfur deposition from Bohemia (Czech Republic) in the more easterly parts and (2) decreasing precipitation and seepage in the eastern lee-side. Lowest sulfate concentrations occur in the central part of the Fichtelgebirge for which theoretical models postulated low deposition rates [12]. However, sulfate output with forest runoff shows a wide concentration range in the Fichtelgebirge [9] spanning from < 20% to > 200% of throughfall sulfate concentrations [*e.g.*, 13]. This range, especially the low  $\text{SO}_4^{2-}$  concentrations ( $< 50 \mu\text{mol l}^{-1}$ ), cannot be explained by spatial differences in sulfur deposition and precipitation volume alone. Soil internal *S*-cycling must be considered here. For another site in the Fichtelgebirge it was shown that dissimilatory  $\text{SO}_4^{2-}$  reduction could significantly contribute to total *S* retention in the catchment [14].

The objective of this study was to test whether stable isotopes of *S* can elucidate processes in the cycling of deposited  $\text{SO}_4^{2-}$  in a set of 11 springs representative of the Fichtelgebirge, an acidified forested region in NE Bavaria (Germany).

## MATERIALS AND METHODS

### Study Sites and Hydrochemistry

The study was conducted in the Fichtelgebirge (50°5' N, 11°50' E), NE Bavaria, Germany (Durka *et al.*, 1994). The mountainous area is mainly covered by spruce (*Picea abies* [L.] KARST.) forests growing on luvic cambisols developed on granitic and phyllitic bedrock. Peat soils have developed locally. Pyrite is not present in the soils. From a total number of 300 forest springs under investigation [9, 10, 15] 11 springs with catchments dominated by spruce forests (Tab. I) were selected. The sites were named A, B, C, ... L in increasing order of  $\text{NO}_3^-$  concentration in runoff. The sites were originally selected to represent the total observed range of  $\text{NO}_3^-$  concentrations in spring water [10, 11], but sulfate concentrations cover the whole range of  $\text{SO}_4^{2-}$  concentrations as well. Water chemistry and flow rates were established by approximately monthly samples from July 1991 to December 1992. The ratio of maximal discharge to minimal discharge of monthly measurements is referred to as 'highflow/baseflow-ratio'. Chemical analyses were performed by DIONEX ion analyzer for anions and by VG-Plasma Quad PQ2 TurboPlus ICP-MS and GBC FS 3000 ICP-OES for cations. Annual atmospheric sulfate deposition was estimated by extrapolation of measurements of throughfall sampled between 15 April and 15 December 1992 with ten funnels per site using an anion exchange resin technique [9].

### Isotopic Analyses

Spring water was sampled in November 1991, March and May 1992, some additional samples were taken in March 1994. Throughfall deposition was collected in November 1991 on a plot 50 m uphill of the springs in open funnels. The original sample volume of 2 to 15 l was reduced to 200 ml by evaporation. Dissolved organic substances were extracted by charcoal filtration. Barium sulfate was gained by precipitation of inorganic  $\text{SO}_4^{2-}$  with  $\text{BaCl}_2$  in small excess.  $\text{BaSO}_4$  was converted to  $\text{Ag}_2\text{S}$  using Kiba's reduction procedure [16]. Dried  $\text{Ag}_2\text{S}$  was sealed in evacuated quartz vials together with  $\text{V}_2\text{O}_5$  and

TABLE I Physical and hydrological characteristics of investigated forest springs in the Fichtelgebirge (Germany)

Sites	Gauss-Krüger longitude	coordinates latitude	Altitude [m a.s.l.]	Mean discharge [ $l s^{-1}$ ]	Highflow/ baseflow-ratio	Seepage [mm] <sup>#</sup>	$SO_4^{2-}$ - deposition $mmol m^{-2} a^{-1} \pm std.err.$
A	4491 <sup>500</sup>	5538 <sup>600</sup>	630	0.08	100	500	70 ± 8
B	4488 <sup>975</sup>	5534 <sup>375</sup>	705	0.08	30	500	89 ± 10
C	4490 <sup>550</sup>	5546 <sup>975</sup>	920	0.36	400	700	79 ± 10
D	4486 <sup>575</sup>	5549 <sup>325</sup>	720	0.71	20	550	83 ± 10
E	4498 <sup>950</sup>	5538 <sup>250</sup>	715	0.28	250	500	72 ± 15
F	4488 <sup>050</sup>	5546 <sup>625</sup>	765	0.09	30	700	86 ± 10
G	4489 <sup>900</sup>	5547 <sup>400</sup>	870	0.51	100	700	74 ± 8
H	4498 <sup>875</sup>	5538 <sup>725</sup>	830	0.12	100	500	92 ± 15
I	4490 <sup>975</sup>	5558 <sup>200</sup>	645	1.02	80	400	74 ± 6
K	4498 <sup>500</sup>	5539 <sup>275</sup>	870	0.13	120	500	75 ± 8
L	4502 <sup>425</sup>	5560 <sup>450</sup>	720	0.20	300	250	102 ± 12

<sup>#</sup> from [26].

reacted at 1000°C in a muffle oven to form SO<sub>2</sub>. In a Finnigan MAT Delta S gas isotope mass spectrometer, equipped with a dual inlet system, the ion current of masses 64 and 66 was measured and the δ<sup>34</sup>S values calculated against the international standard CDT (Canyon Diablo Troilite).

Isotope ratios are denoted as δ values, calculated according to the following equation:

$$\delta^{34}\text{S} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000[\text{‰}] \quad (1)$$

$R_{\text{sample}}$  and  $R_{\text{standard}}$  are the <sup>34</sup>S/<sup>32</sup>S ratios of the samples and standards, respectively.

## RESULTS AND DISCUSSION

For the 11 springs investigated, volume weighted mean concentrations of SO<sub>4</sub><sup>2-</sup> ranged from 26 to 458 μmol l<sup>-1</sup> (Tab. II). Sulfate concentrations in spring water of the Fichtelgebirge previously studied ranged from 5 to 955 μmol l<sup>-1</sup> with mean 180 μmol l<sup>-1</sup> [9, 10]. Thus, apart from extreme outliers found in previous studies, the investigated springs represent the total observed concentration range. Over an annual cycle SO<sub>4</sub><sup>2-</sup> concentrations were quite constant except in springs C and G which showed increased concentrations in autumn and winter (Fig. 1). All springs, however, showed a clear seasonal course of discharge with highflow conditions in winter and spring. Baseflow conditions are reached between July and October. Discharge under highflow conditions consists preferentially of water of short residence time, whereas baseflow discharge is of longer residence time. Qualitatively, therefore, the ratio of maximal discharge to minimal discharge ('highflow/baseflow-ratio') can be used as an inverse measure of mean residence time of water in soil and aquifer (Tab. I). SO<sub>4</sub><sup>2-</sup> concentration was correlated to highflow/baseflow-ratio ( $r = 0.659$ ,  $P < 0.001$ ). The lowest SO<sub>4</sub><sup>2-</sup> concentrations were observed in springs with lowest highflow/baseflow-ratio, *i.e.*, longest residence time. This indicates that either physico-chemical or biotic interactions of SO<sub>4</sub><sup>2-</sup> in the soil and aquifer act in a time dependent way.

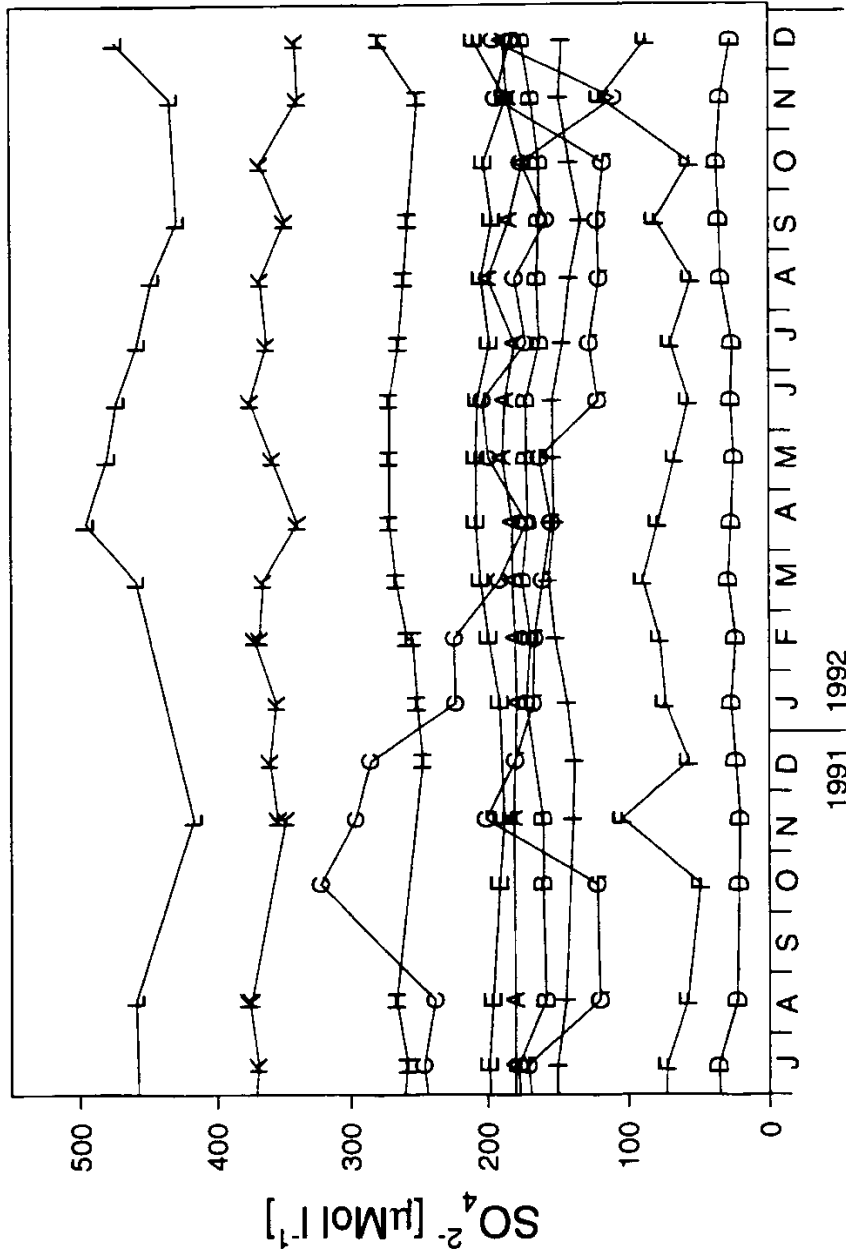


FIGURE 1 Seasonal course of  $\text{SO}_4^{2-}$  concentration in 11 forest springs.

TABLE II Hydrochemistry of investigated forest springs. Volume-weighted means of monthly samples 6'91 – 12'92

Sites	pH	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl	Mg [μmol l <sup>-1</sup> ]	Ca [μmol l <sup>-1</sup> ]	K	Na	Al
A	5.12	191	9	46	35	105	38	215	10
B	5.22	170	22	51	79	89	34	109	6
C	3.82	179	43	55	35	50	12	88	70
D	5.69	26	53	62	27	42	20	113	2
E	4.97	223	53	53	44	126	38	180	9
F	4.50	86	98	64	19	61	22	134	20
G	4.10	160	167	373	42	80	26	426	93
H	4.51	269	191	153	65	159	51	239	31
I	5.28	150	225	92	85	98	27	137	5
K	4.32	353	274	167	53	152	43	219	128
L	4.48	458	361	115	112	235	62	218	77

### Atmospheric Input

Sulfate sulfur isotope ratios of throughfall deposition and runoff as a function of SO<sub>4</sub><sup>2-</sup> concentrations are shown in Figure 2. Sulfur isotope ratios of throughfall SO<sub>4</sub><sup>2-</sup> ranged from δ<sup>34</sup>S = +3.7 to +4.5‰. Additional snow samples were higher, ranging from δ<sup>34</sup>S = +5.0 to

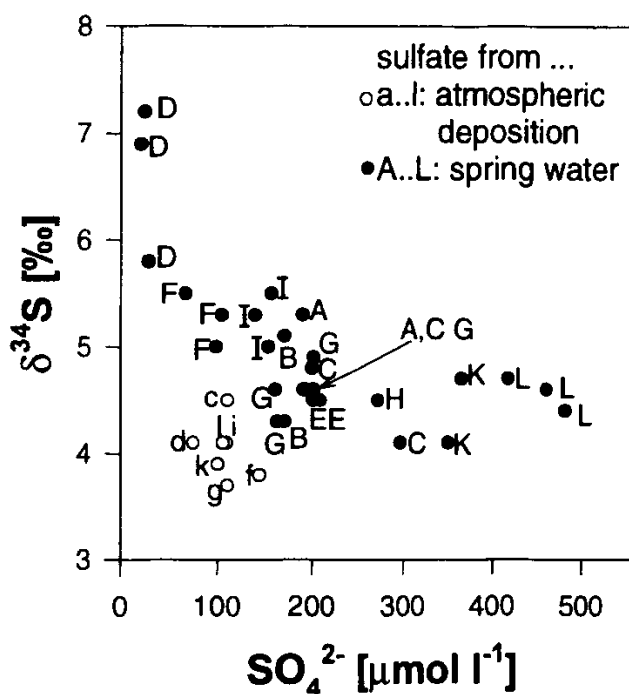


FIGURE 2 SO<sub>4</sub><sup>2-</sup> - S isotope ratios as function of sulfate concentration in throughfall and runoff in springs A to L. Data from runoff are denoted by capital letters, throughfall data by small ones.

+ 5.7‰. Isotope ratios are in good agreement with those from two North Bohemian catchments at a distance of app. 150 km, where mean  $\delta^{34}\text{S}$  ratios of throughfall were + 5.3 and + 7.1‰ (range + 3 to + 9‰ [17]). Isotope ratios were considerably higher than those reported from the Black Forest (SW-Germany: throughfall  $\text{SO}_4^{2-}$ : + 1.6‰ [6]). Emissions from brown coal power stations in the Czech republic are a major source for  $\text{SO}_4^{2-}$  immissions in the Fichtelgebirge, especially in winter with easterly winds [18]. Thus, high isotope ratios in deposited  $\text{SO}_4^{2-}$  as reported here reflect the source of S by burning [19] in contrast to low isotope ratios in the Black Forest which reflected biogenic S gas emissions [6]. Geogenic source of S can be excluded as potential sources since all sites have granitic or phyllitic bedrock.

### Spring Water

Sulfate sulfur isotope ratios of spring water ranged from + 4.1 to + 7.2‰ (Fig. 2). For  $\text{SO}_4^{2-}$  concentrations higher than  $150 \mu\text{mol l}^{-1}$ ,  $\delta^{34}\text{S}$  values were rather constant at + 4 to + 5‰. Below  $150 \mu\text{mol l}^{-1}$   $\text{SO}_4^{2-}$ ,  $\delta^{34}\text{S}$  values increased up to + 7.2‰ with decreasing  $\text{SO}_4^{2-}$ .

The processes possibly changing  $\text{SO}_4^{2-}$  concentrations and sulfur isotope ratios are depicted in Figure 3. Throughfall deposition with mean  $\text{SO}_4^{2-}$  concentrations of  $150 \mu\text{mol l}^{-1}$ , and  $\delta^{34}\text{S} \approx + 4\text{‰}$  is

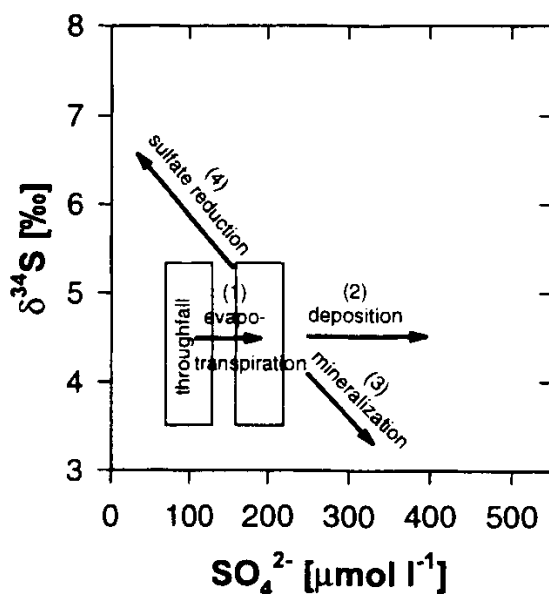


FIGURE 3 Processes active in changing sulfur isotope ratios.



entering the system. Two processes may increase  $\text{SO}_4^{2-}$  concentrations without changes in isotopic signature: (1)  $\text{SO}_4^{2-}$  is concentrated by a factor of about 2 in the soil solution by evapotranspiration. This effect should be equal at all sites since all sites are spruce forests of approximately equal age. (2) Luff-lee effects lead to variation in precipitation volume and seepage with high precipitation in the western part of the Fichtelgebirge and low precipitation in the east. This results in highly different  $\text{SO}_4^{2-}$  concentrations in spring water since total *S* deposition is rather constant (Tab. I). High  $\text{SO}_4^{2-}$  concentrations at the most northeastern site L are due to this fact together with higher absolute sulfate deposition.

Two processes are associated with isotopic discrimination and therefore may alter isotopic signature of spring water  $\text{SO}_4^{2-}$  (3). Mineralization of organic *S* will increase  $\text{SO}_4^{2-}$  concentration and decrease values of the soil  $\text{SO}_4^{2-}$  pool. (4) Dissimilatory reduction of  $\text{SO}_4^{2-}$  on the other hand will decrease  $\text{SO}_4^{2-}$  concentration and increase  $\delta^{34}\text{S}$  values. On a site in the Fichtelgebirge similar to ours, soil sulfur, which is substrate for mineralization, was found to have  $\delta^{34}\text{S}$  values of +1‰ in the organic litter horizon  $\text{O}_{\text{lf}}$  increasing with depth up to +5‰ in the mineral soil [20]. Mineralization is accompanied by high discrimination. For example a change in  $\delta^{34}\text{S}$  by -3.4‰ for  $\text{SO}_4^{2-}$  from mineralization of five soils from forests in southern Germany was reported [2]. Thus, if mineralization were active,  $\text{SO}_4^{2-}$  with very low isotope ratios (< 3‰) would be added to the soil sulfate pool and  $\delta^{34}\text{S}$  values should be below those of precipitation. However, since all spring water samples are higher in  $\delta^{34}\text{S}$  than the precipitation samples, mineralization seems to have no effect on isotope ratios in the cases investigated. In the springs D and F,  $\text{SO}_4^{2-}$  concentrations were clearly below concentration of atmospheric input ( $\text{SO}_4^{2-} < 150 \mu\text{mol l}^{-1}$ ), given the increase in soil  $\text{SO}_4^{2-}$  due to evapotranspiration. Thus,  $\text{SO}_4^{2-}$  was retained on its way from precipitation through soil and aquifer, along with an increase in sulfur isotope ratio. Springs A, B and I similarly have slightly increased  $\delta^{34}\text{S}$  values. Residence time seems to play an important role in this process (Fig. 4), since  $\delta^{34}\text{S}$  is correlated to highflow/baseflow-ratios ( $r = -0.510$ ,  $P = 0.004$ ). Highest  $\delta^{34}\text{S}$  values were found at lowest highflow/baseflow-ratios indicating high mean residence times. High residence times would allow for both biotic and abiotic processes to act on  $\text{SO}_4^{2-}$  in the soil solution.

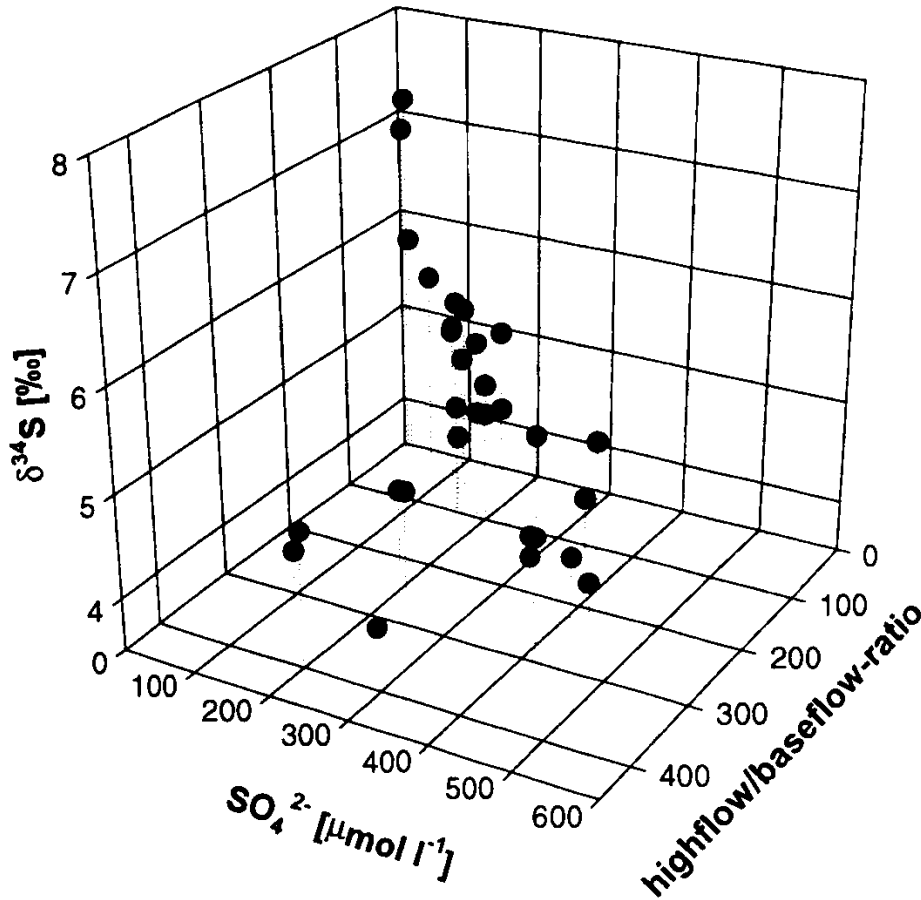


FIGURE 4  $\text{SO}_4^{2-}$  - S isotope ratios as function of sulfate concentration and highflow/baseflow-ratio.

Decreasing  $\text{SO}_4^{2-}$  concentration and increasing  $\delta^{34}\text{S}$  values suggest that dissimilatory reduction of  $\text{SO}_4^{2-}$  may be active here. From the same region similar  $\delta^{34}\text{S}$  values were reported as a result of dissimilatory reduction [14]. However it was not possible to quantify  $\text{SO}_4^{2-}$  reduction because the discrimination factor is unknown for field conditions [14].

Dissimilatory sulfate reduction should only occur at low redox potential when essentially no nitrate is available ( $\text{NO}_3^- < 20 \mu\text{mol l}^{-1}$  [4]), because the latter is used as oxygen source prior to sulfate. Springs D and F have  $53$  and  $98 \mu\text{mol l}^{-1}$   $\text{NO}_3^-$  (Tab. II), which should be used through denitrification before  $\text{SO}_4^{2-}$  reduction can start. Other springs are lower in  $\text{NO}_3^-$  without concurrent decrease of  $\text{SO}_4^{2-}$  concentration and increase of sulfur isotope ratio. Furthermore, only in spring A with lowest  $\text{NO}_3^-$  concentrations a marked influence of denitrification could be detected using natural isotopes of N and O

([11] and unpublished data). Thus, dissimilatory  $\text{SO}_4^{2-}$  reduction, which has been shown to occur, cannot easily explain increased  $\delta^{34}\text{S}$  values. Rather,  $\text{SO}_4^{2-}$  in spring water must have been mixed from two different sources. (1)  $\text{SO}_4^{2-}$  with high  $\delta^{34}\text{S}$  which has undergone dissimilatory reduction after  $\text{NO}_3^-$  has been denitrified and (2) unreduced  $\text{SO}_4^{2-}$  which was leached together with  $\text{NO}_3^-$ . These two potential sources of  $\text{SO}_4^{2-}$  could reflect spatial heterogeneity in the soil or aquifer system. Heterogeneity could be manifested either as horizontal heterogeneity of soil patches, which are either waterlogged or aerated or as vertical heterogeneity in the soil leading to flow paths in different soil horizons with oxidizing or reducing conditions. Further investigations should combine variation of  $\delta^{34}\text{S}$  values on catchment scale and among soil horizons.

Other possible mechanisms that decrease  $\text{SO}_4^{2-}$  concentration in soil are immobilization, adsorption and precipitation. Immobilization of  $\text{SO}_4^{2-}$  (assimilatory  $\text{SO}_4^{2-}$  reduction) cannot explain increased  $\delta^{34}\text{S}$  values of soil  $\text{SO}_4^{2-}$ , because preferential uptake of  $^{34}\text{SO}_4^{2-}$  should lead to decreased  $\delta^{34}\text{S}$  values of the remaining  $\text{SO}_4^{2-}$  [3, 21, 22]. Adsorption of  $\text{SO}_4^{2-}$  is a main process of reversible sulfur storage in forest soils [23], but it does not explain increasing  $\delta^{34}\text{S}$  values, since adsorption does not fractionate  $\text{S}$  isotopes [24]. In very acid soils like those in our study, precipitation of Al-hydroxosulfates like basaluminite, alunite or jurbanite is considered as a potential mechanism for sulfate storage [13, 25]. However, isotopic discrimination was found to be  $< 1\%$  in  $\text{SO}_4^{2-}$  precipitation [2].

## CONCLUSIONS

Our data suggest that in the Fichtelgebirge dissimilatory  $\text{SO}_4^{2-}$  reduction is an active process in reducing  $\text{SO}_4^{2-}$  concentration in forest springs. In springs having  $\text{SO}_4^{2-}$  below  $150 \mu\text{mol l}^{-1}$ ,  $\delta^{34}\text{S}$  values are increased relative to deposition due to dissimilatory  $\text{SO}_4^{2-}$  reduction. However, most of the springs investigated are higher in  $\text{SO}_4^{2-}$  ( $> 150 \mu\text{mol l}^{-1}$ ), and neither dissimilatory  $\text{SO}_4^{2-}$  reduction nor  $\text{SO}_4^{2-}$  mineralization play a major role. Physico-chemical processes possibly acting on sulfate, like adsorption/desorption and precipitation of Al hydroxysulfates do not change its isotopic composition.

The relevance of dissimilatory  $\text{SO}_4^{2-}$  reduction on spring water sulfate concentrations has to be considered on a regional scale. Mean  $\text{SO}_4^{2-}$  concentrations in forest springs of the area are  $167 \mu\text{mol l}^{-1}$  [9]. Depending on geological substrate, they are differentiated, with mean  $\text{SO}_4^{2-}$  being 147 and  $197 \mu\text{mol l}^{-1}$  in watersheds with phyllitic and granitic bedrock, respectively [9, 10]. Geology may act indirectly on sulfate, for example *via* soil types or flow paths. Springs below  $150 \mu\text{mol l}^{-1}$   $\text{SO}_4^{2-}$  for which dissimilatory  $\text{SO}_4^{2-}$  reduction may be important, comprise 53% and 32% of the springs in phyllitic and granitic catchments, respectively. Thus, in many forested watersheds on phyllitic bedrock dissimilatory  $\text{SO}_4^{2-}$  reduction potentially is an important process in the Fichtelgebirge. Future studies on dissimilatory  $\text{SO}_4^{2-}$  reduction should focus on springs on the lower range of sulfate concentrations.

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