

# Processes Affecting Oxygen Isotope Ratios of Atmospheric and Ecosystem Sulfate in Two Contrasting Forest Catchments in Central Europe

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Sulfate aerosols are harmful as respirable particles. They also play a role as cloud condensation nuclei and have radiative effects on global climate. A combination of  $\delta^{18}\text{O}-\text{SO}_4$  data with catchment sulfur mass balances was used to constrain processes affecting S cycling in the atmosphere and spruce forests of the Czech Republic. Extremely high S fluxes via spruce throughfall and runoff were measured at Jezeri (49 and 80 kg S ha<sup>-1</sup> yr<sup>-1</sup>, respectively). The second catchment, Na Lizu, was 10 times less polluted. In both catchments,  $\delta^{18}\text{O}-\text{SO}_4$  decreased in the following order: open-area precipitation > throughfall > runoff. The  $\delta^{18}\text{O}-\text{SO}_4$  values of throughfall exhibited a seasonal pattern at both sites, with maxima in summer and minima in winter. This seasonal pattern paralleled  $\delta^{18}\text{O}-\text{H}_2\text{O}$  values, which were offset by  $-18\%$ . Sulfate in throughfall was predominantly formed by heterogeneous (aqueous) oxidation of  $\text{SO}_2$ . Wet-deposited sulfate in an open area did not show systematic  $\delta^{18}\text{O}-\text{SO}_4$  trends, suggesting formation by homogeneous (gaseous) oxidation and/or transport from large distances. The percentage of incoming S that is organically cycled in soil was similar under the high and the low pollution. High-temperature  $^{18}\text{O}$ -rich sulfate was not detected, which contrasts with North American industrial sites.

## Introduction

Stable isotopes have often provided independent constraints on processes governing fluxes of chemicals in the atmosphere, biosphere, and hydrosphere (1). The critically ill forest ecosystems of Central Europe, especially those in Poland, Czech Republic, and Germany, have been thoroughly investigated by means of sulfur isotopes (2–4), while oxygen

isotopes in sulfates have remained an under-exploited tool (5). For example, in acidified spruce ecosystems, a time-series of canopy throughfall  $\delta^{18}\text{O}-\text{SO}_4$  data has never been reported. Elsewhere, oxygen isotopes in sulfates have been used to apportion rainfall sulfate between natural and anthropogenic origins, and to trace sulfate formation pathways (6, 7).

Processes controlling the behavior of sulfur and oxygen isotopes in environmental sulfates are decoupled. Atmospheric oxidation of  $\text{SO}_2$  causes only relatively small fractionations in sulfur isotopes (8), but it causes large fractionations in the oxygen isotope values (9). The  $\delta^{18}\text{O}$  value of sulfate is determined by the oxidation mechanism, while source variation and mixing also influence the O isotope composition of sulfate (10).

The resulting sulfate aerosols are potentially harmful as respirable particles and play a role as cloud condensation nuclei. Despite much investigation, uncertainties remain regarding oxidation processes of  $\text{SO}_2$  (11). Resolving the relative contributions of gas and aqueous-phase oxidative pathways is crucial because these pathways influence the lifetime of S species.  $\text{SO}_2$  oxidation is relatively slow in the gas phase, and more rapid in the aqueous phase (12). Better quantification of sulfate formation processes may provide information on atmospheric S budgets and on radiative effects of sulfate on global climate. It has been unclear whether prevailing  $\text{SO}_2$  oxidation pathways differ along a sharp pollution gradient, and to what extent different S oxidation pathways will prevail in wet and dry deposition in forests. Our first objective was to compare the  $\delta^{18}\text{O}-\text{SO}_4$  time-series of atmospheric inputs between two contrasting sites, to evaluate their dependence on the magnitude of dry and wet deposition, and to link wet and dry deposition with  $\text{SO}_2$  oxidation pathways. We selected one spruce die-back-affected catchment, and one relatively unpolluted catchment in the Czech Republic, and monitored  $\delta^{18}\text{O}-\text{SO}_4$  values of spruce throughfall, open-area precipitation, and runoff for a 2-year period. There was a unique 10-fold difference in the amounts of anthropogenic sulfur received by the two sites (13).

Our second objective was to quantify the contribution of primary high-temperature sulfate to total deposited S by means of  $\delta^{18}\text{O}-\text{SO}_4$ . It has been shown at North American sites that such high-temperature sulfate (1000 °C) carries distinctly high  $\delta^{18}\text{O}$  values, higher than secondary sulfate formed at lower temperatures from industrial  $\text{SO}_2$  (6). Knowledge of the relative amounts of primary and secondary sulfates is needed to refine control strategies. Such knowledge can be used to infer the relative importance of local versus distant pollution sources. It is also needed to determine whether  $\text{SO}_2$  control is related to decrease in sulfate deposition in a linear fashion (6). Wet scrubbers are not as effective in removing primary sulfate as they are at removing  $\text{SO}_2$ . If primary sulfates are important, new methods may be needed to effectively remove sulfuric acid mist.

We further constructed an annual S mass balance for both the polluted and the relatively unpolluted catchments. Information on S fluxes served as a constraint for the interpretation of  $\delta^{18}\text{O}-\text{SO}_4$ . We examined the relationships between  $\delta^{18}\text{O}-\text{SO}_4$  and  $\delta^{18}\text{O}-\text{H}_2\text{O}$  in order to assess the importance of aqueous oxidation of  $\text{SO}_2$  in various sample types. We further compared  $\delta^{18}\text{O}-\text{SO}_4$  values of rain and salt efflorescence on castellated sandstones in search of a proxy that would give the same isotope information as the costly monitoring of water solutes. Finally, we discuss re-setting of the atmospheric  $\delta^{18}\text{O}-\text{SO}_4$  signal by soil processes. Iso-

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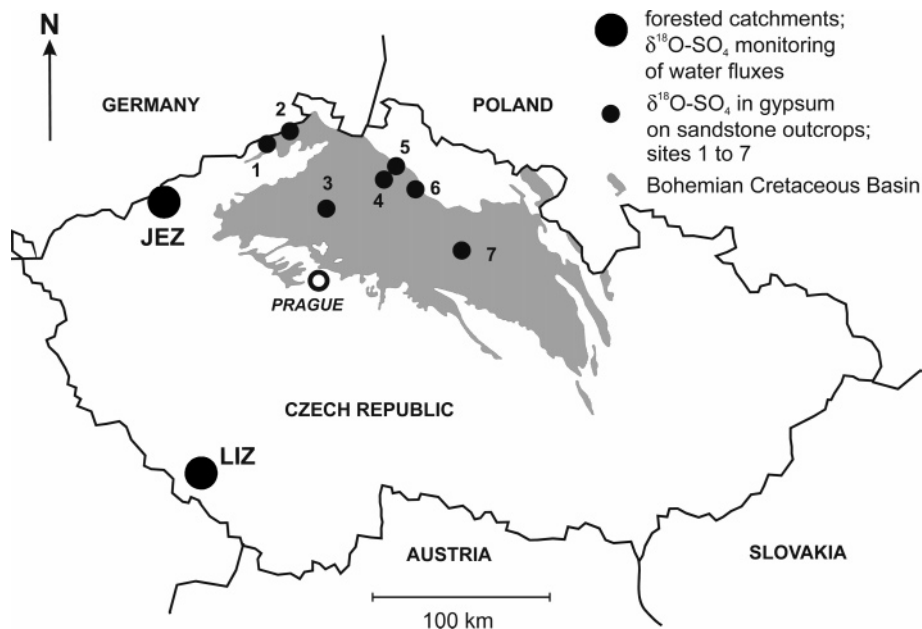


FIGURE 1. Study sites.

TABLE 1. Study Site Characteristics

site	JEZ	LIZ
location	50°32' N, 13°28' E	49°04' N, 13°41' E
elevation (m a.s.l.)	475–924	828–1024
mean slope (deg)	10	8
catchment area (ha)	261	99
bedrock	two-mica gneiss	sillimanite-biotite paragneiss
sulfur content in bedrock (wt.%)	<0.003	<0.001
soil type	distric cambisol	distric cambisol
vegetation (%)	spruce 11; clearings 63; beech 26	spruce 63; clearings 37
prevailing wind direction	west	west
mean temperature (°C)	+ 5.0	+ 4.9
annual precipitation (mm)	934	905

pically selective organic S cycling in soil, if observed at the study sites, should be considered in predictions of the rate of retreat from acidification (14).

## Methods

**Study Sites.** The industrially polluted catchment Jezeri (JEZ; Figure 1, Table 1) is situated in the Northern Czech Republic. It incorporates damaged spruce and healthy beech ecosystems of the Krusne Mts., facing a coal mining area with a cluster of power stations. Die-back of Norway spruce at JEZ occurred in 1970–1997; small patches of surviving spruce are 10–50 years old. The relatively unpolluted catchment Na Lizu (LIZ; Figure 1, Table 1) is situated 165 km south of JEZ near the Czech–Austrian border. The catchment is covered by undamaged 80-year old Norway spruce. Biogeochemistry of both catchments has been studied in detail (4, 8, 13, 15). Nationwide sulfur pollution peaked in 1987 (13). At that time, S deposition rates at JEZ were 10 times higher than those at LIZ (130 and 13 kg S ha<sup>-1</sup> yr<sup>-1</sup> in spruce stands, respectively; 15). Since 1987, industrial S emission rates decreased by 90% (5). Czech coal-fired power stations were subject to desulfurization in 1995–1998.

Sulfate oxygen isotopes on rocks were studied at seven sites in the Bohemian Cretaceous Basin, mainly castellated sandstone outcrops (Figure 1; <0.001 wt. % S in the rock). Pollution level at these sites varied, decreasing with increasing distance from JEZ and with decreasing elevation. Typical S deposition rates were 25 kg S ha<sup>-1</sup> yr<sup>-1</sup> in 1994 and 12 kg S ha<sup>-1</sup> yr<sup>-1</sup> in 2000 (13).

**Sampling and Analysis.** Samples of open-area precipitation and spruce canopy throughfall at JEZ and LIZ were collected monthly in water years 2000–2001. Samples of runoff were taken next to the gauging station once a month. In each catchment, two rain collectors were installed 5 m apart in an open field. A network of 9 samplers in a 10 × 10 m grid was used to collect spruce throughfall. One composite sample each of open-area precipitation, throughfall, and runoff was analyzed for sulfate concentration and δ<sup>18</sup>O–SO<sub>4</sub> monthly. Catchment-level S mass balances were calculated from water fluxes and sulfate concentrations. In clearings, precipitation samples were taken for δ<sup>18</sup>O–H<sub>2</sub>O analysis from June 2002 to June 2003. To prevent isotope fractionation, rainwater was collected under light oil. Salt crusts were scraped off sandstone outcrops (Figure 1). Gypsum and alums were identified by X-ray diffraction, dissolved in HCl and sulfate-precipitated as BaSO<sub>4</sub>.

Sulfate concentrations in waters were determined on a DIONEXDX-100 ion chromatograph. BaSO<sub>4</sub> was precipitated from waters by adding BaCl<sub>2</sub>. BaSO<sub>4</sub> was reacted at 950 °C with C to form CO<sub>2</sub> and analyzed for oxygen isotope composition inherited from sulfate (16). Isotope composition of H<sub>2</sub>O was calculated from an equilibrium isotope exchange equation for the H<sub>2</sub>O–CO<sub>2</sub> system (17). Isotope ratios were measured on a Finnigan MAT 251 mass spectrometer. The results were expressed in δ values, as a per mil (‰) deviation of the <sup>18</sup>O/<sup>16</sup>O ratio in the sample from the <sup>18</sup>O/<sup>16</sup>O ratio of a standard (SMOW). The reproducibility of δ<sup>18</sup>O–SO<sub>4</sub> and δ<sup>18</sup>O–H<sub>2</sub>O determinations was better than 0.4 and 0.1‰,

**TABLE 2. Sulfur Deposition Trends at the Two Catchments (in kg S ha<sup>-1</sup> yr<sup>-1</sup>)**

	JEZ			LIZ		
	1994	2000	2001	1994	2000	2001
open area precipitation	20.8	8.1	7.4	6.4	4.5	3.4
spruce canopy throughfall	66.7	49.3	49.5	9.0	11.0	6.5
throughfall/open area precipitation ratio	3.2	6.1	6.7	1.4	2.4	1.9
catchment input	33.7	16.1	16.1	8.2	9.1	5.6
catchment output	63.7	80.4	38.0	14.1	10.6	10.2
catchment mass balance	-30.0	-64.3	-21.9	-5.9	-1.5	-4.5
precipitation totals (mm yr <sup>-1</sup> )	982	945	708	911	770	707

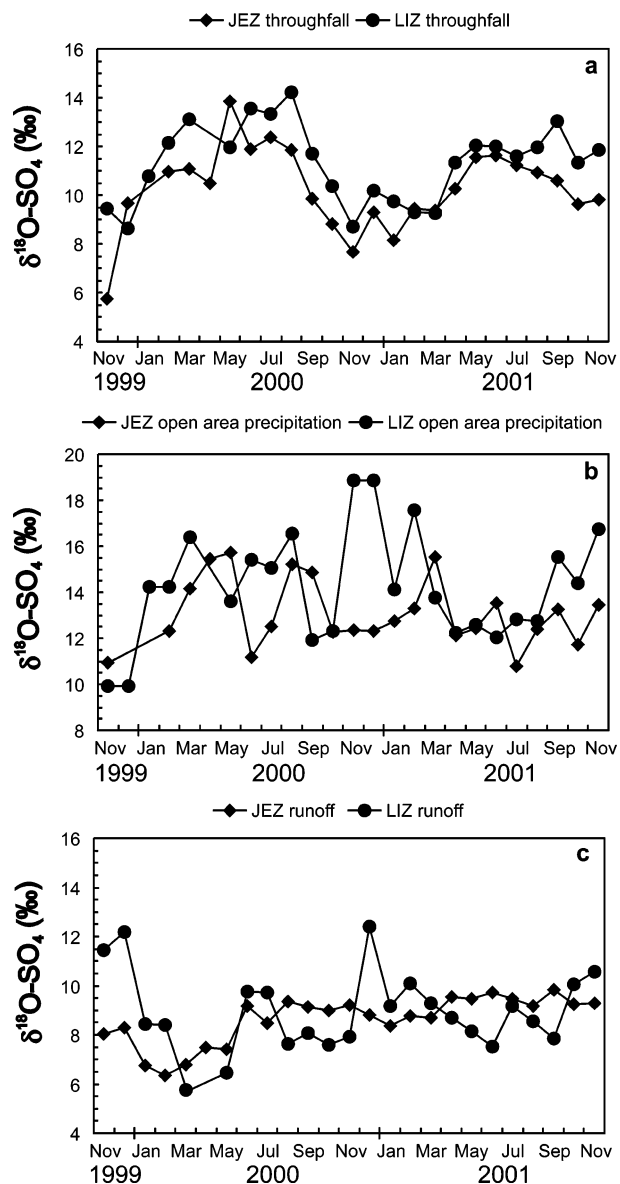
respectively. Statistical analysis of  $\delta^{18}\text{O}$  values (ANOVA) was performed using JMP from SAS Institute (18).

**Results and Discussion**

**Sulfur Deposition Trends.** In 2000–2001, JEZ still exhibited an extremely high atmospheric S deposition underneath spruce canopy (49 kg S ha<sup>-1</sup> yr<sup>-1</sup>; Table 2). This annual S deposition rate was 26% lower compared to that at the beginning of the systematic monitoring in 1994 (15). Table 2 compares previously published S depositions from 1994 (15) with data from 2000–2001. In 1994, spruce stands at LIZ received 7 times less S than those at JEZ. Six to seven years later throughfall at LIZ was on average 5.6 times lower than that at JEZ. Between 1994 and 2001, open-area deposition decreased at JEZ from 21 kg S ha<sup>-1</sup> yr<sup>-1</sup> to one-third of that amount. Over the same period, open-area deposition at LIZ decreased from 6.4 kg S ha<sup>-1</sup> yr<sup>-1</sup> to one-half. Overall, S flux via open-area precipitation was significantly lower than S flux via spruce throughfall (Table 2). This was due to lower surface roughness of clearings compared to forests, and weaker air filtering effect (1). Between 1994 and 2001, catchment-level atmospheric inputs decreased from 33.7 to 16.1 kg S ha<sup>-1</sup> yr<sup>-1</sup> at JEZ, and from 8.2 to 5.6 kg S ha<sup>-1</sup> yr<sup>-1</sup> at LIZ (Table 2). Decreases in S industrial emissions were accompanied by greater absolute and relative declines in atmospheric S deposition at the more polluted site (17.6 kg S ha<sup>-1</sup> yr<sup>-1</sup>; 52%), and slower decline at the less polluted site (2.6 kg S ha<sup>-1</sup> yr<sup>-1</sup>; 32%).

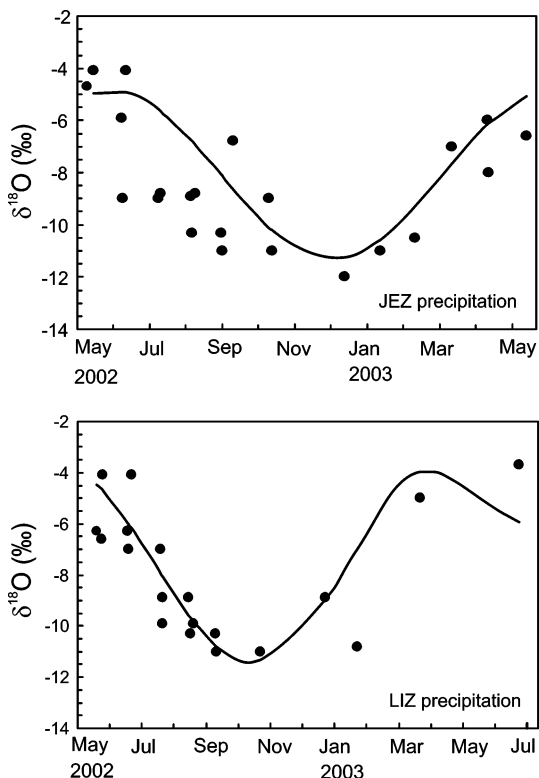
**Sulfur Export from Catchments.** In 2000, a record high catchment output via surface runoff was measured at JEZ (80.4 kg S ha<sup>-1</sup>; Table 2). The sulfur mass balance for JEZ in 2000 was extremely negative (-64.3 kg S ha<sup>-1</sup>). It was shown previously that weathering rates of sulfides in JEZ orthogneiss (<0.003 wt. % S) are low, and therefore atmospheric deposition represents the main S input (13). Table 2 shows that the amount of exported S at JEZ is highly dependent on precipitation. A dry year 2001 followed a wet year 2000. The S output in the dry year 2001 was much lower (38.0 kg S ha<sup>-1</sup>) than in the wet year 2000 (80.4 kg S ha<sup>-1</sup>). High net export of S from JEZ, recorded already in the 1990s, was caused by gradual release of pollutant S that had accumulated in the ecosystem over the period of industrial build-up (1950–1987; 13, 15). Export of S from LIZ was much lower than that from JEZ (ca. 10 kg S ha<sup>-1</sup> yr<sup>-1</sup> in 2000–2001; Table 2). Sulfur mass balance at LIZ (-1.5 to -4.5 kg S ha<sup>-1</sup> yr<sup>-1</sup> in 2000–2001) indicated conditions close to a steady state.

**Sulfate Oxygen Isotopes in Throughfall.** The  $\delta^{18}\text{O}-\text{SO}_4$  values of spruce canopy throughfall at JEZ and LIZ closely paralleled each other (Figure 2a). They exhibited a clear-cut seasonality, with maxima in summer and minima in winter. The pattern was close to a sinusoid. The difference between seasonal maxima and minima in  $\delta^{18}\text{O}-\text{SO}_4$  values was 8‰. The same difference between seasonal maxima and minima (8‰) was recorded also for the  $\delta^{18}\text{O}-\text{H}_2\text{O}$  values (Figure 3). Overall, the  $\delta^{18}\text{O}-\text{H}_2\text{O}$  curve was offset relative to the  $\delta^{18}\text{O}-\text{SO}_4$  curve by 18‰ toward negative values. The negative offset



**FIGURE 2. Between-site comparisons of  $\delta^{18}\text{O}-\text{SO}_4$  values for two types of catchment input (open area precipitation, spruce throughfall) and runoff.**

of 18‰ existed in both summer and winter. Such parallel seasonal curves for sulfate-O and water-O isotopes are typical of a heterogeneous (aqueous) pathway of sulfate formation (11, 19). Heterogeneous oxidation of  $\text{SO}_2$  involves dissolution of  $\text{SO}_2$  in droplets, hydration and oxidation of  $\text{HSO}_3^-$  (aq) to  $\text{HSO}_4^-$  (aq). During heterogeneous oxidation, both  $\text{SO}_2$  (g) and  $\text{HSO}_3^-$  (aq) equilibrate rapidly with water. The  $^{18}\text{O}$  content of the resulting sulfate is controlled by the O isotope composition of the associated rainwater (9).



**FIGURE 3.**  $\delta^{18}\text{O}-\text{H}_2\text{O}$  values of precipitation in clearings at JEZ and LIZ.

Therefore, sulfates formed in this manner exhibit a positive correlation between  $\delta^{18}\text{O}-\text{SO}_4$  and  $\delta^{18}\text{O}-\text{H}_2\text{O}$  (19). In contrast, homogeneous (gaseous)  $\text{SO}_2$  oxidation to sulfate does not lead to positive correlation of the  $^{18}\text{O}$  contents in sulfate and water (20). Heterogeneous formation of sulfate prevailed in the atmospheric inputs into forests at both JEZ and LIZ throughout the year. This finding is interesting in light of previously published conclusions that heterogeneous atmospheric oxidation of  $\text{SO}_2$  prevails in winter and that homogeneous oxidation of  $\text{SO}_2$  prevails in summer (12). Those conclusions were based on anomalously high  $^{17}\text{O}$  contents in sulfates in winter, which were linked to aqueous-phase  $\text{SO}_2$  oxidation. An  $^{17}\text{O}$  study at JEZ and LIZ could show whether there is less aqueous  $\text{SO}_2$  oxidation in summer, as the literature from low S-deposition areas may suggest.

The  $\delta^{18}\text{O}-\text{SO}_4$  value of throughfall at LIZ was systematically higher than that at JEZ, on average by  $1\text{‰}$  ( $p < 0.05$ ; Figure 2a). It is generally accepted that throughfall represents total S deposition in spruce forests and that the interchange of S between rainfall and the foliage is small (21). Throughfall S consists of wet-deposited sulfate-S and dry-deposited  $\text{SO}_2$ -S. The dry-deposited  $\text{SO}_2$  is oxidized to sulfate in situ during precipitation events. The wet-deposited portion of total S deposition via throughfall is about equal to the amount of S measured in open-area precipitation (21). In 2000–2001, 84% of total S in forests was dry-deposited  $\text{SO}_2$ -S at JEZ, and 54% at LIZ (cf. Table 2). Conversely, the contribution of wet-deposited  $\text{SO}_4$ -S to the throughfall S flux at JEZ was very small (16%), while that at LIZ was nearly one-half (46%). These 46% of wet-deposited  $\text{SO}_4$ -S at LIZ were so high that they were expected to show seasonality in  $\delta^{18}\text{O}$ . The presence or absence of seasonal  $\delta^{18}\text{O}-\text{SO}_4$  signal in wet deposition was investigated in clearings.

**Sulfate Oxygen Isotopes in Open-Area Precipitation.** Time-series of  $\delta^{18}\text{O}-\text{SO}_4$  values of open-area precipitation at JEZ and LIZ are given in Figure 2b. In contrast to throughfall, no systematic temporal trends are seen. These  $\delta^{18}\text{O}-\text{SO}_4$  values do not reflect seasonality of ambient water, and thus

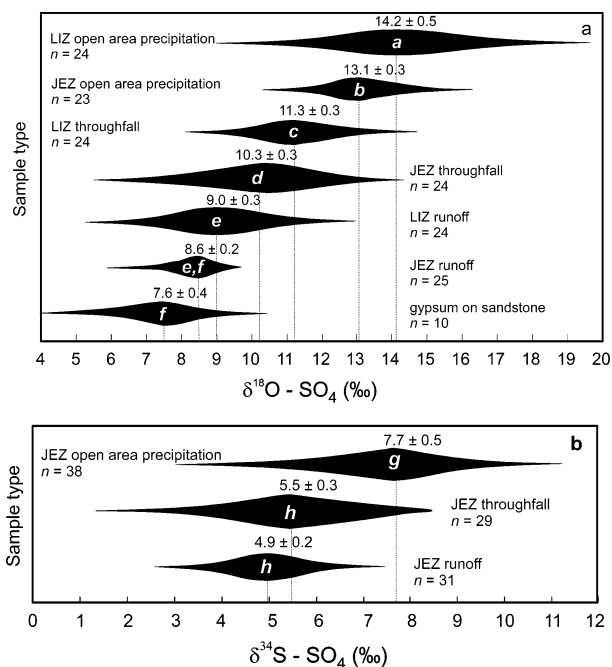
are likely a result of homogeneous (gaseous)  $\text{SO}_2$  to  $\text{SO}_4$  conversion (11, 20). The homogeneous oxidation of  $\text{SO}_2$  is characterized by the presence of gaseous  $\text{SO}_3$  as an intermediate. In the homogeneous process oxidation precedes hydration, whereas in the previously described heterogeneous process hydration precedes oxidation. Clearly, data in Figure 2b can be a result of mixing of sulfate from various sources and various distances. With an atmospheric mean residence time of about 4 days (8), sulfate at a receptor site can be a mixture of local and transported sulfate formed by different oxidation mechanisms.

Recent literature (22) admits heterogeneous  $\text{SO}_2$  oxidation for sites with no relationships between  $\delta^{18}\text{O}-\text{SO}_4$  and  $\delta^{18}\text{O}-\text{H}_2\text{O}$  (lack of two offset seasonal patterns) when the sampled air mass scavenged various aged aerosols that had originated from different precipitation events. If so, the erratic  $\delta^{18}\text{O}-\text{SO}_4$  pattern at JEZ and LIZ in Figure 2b would indicate distant sources for wet-deposited sulfate.

The absence of systematic  $\delta^{18}\text{O}-\text{SO}_4$  trends in open-area precipitation (Figure 2b) is surprising in light of LIZ throughfall data (Figure 2a) and S mass balances (Table 2). With a nearly 50% contribution of wet-deposited sulfate, which has erratic  $^{18}\text{O}$  contents, it would have seemed unlikely that the total S flux via throughfall at LIZ would form a clear seasonal pattern. Yet, a seasonal  $\delta^{18}\text{O}-\text{SO}_4$  throughfall curve was observed at LIZ (Figure 2a).

During homogeneous oxidation  $\text{SO}_2$  may be oxidized by  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , or OH radicals (9). Air oxygen ( $\text{O}_2$ ) has a high  $\delta^{18}\text{O}$  value of  $+23.5\text{‰}$ , while atmospheric water has a negative  $\delta^{18}\text{O}$  value ( $-4$  to  $-12\text{‰}$  at our sites; 5). The isotopic composition of sulfate-O will depend on the composition of the oxidant (20).  $\text{H}_2\text{O}_2$  and OH are expected to be richer in water oxygen than in air oxygen, leading to sulfate of lower  $\delta^{18}\text{O}$ . In contrast,  $\text{O}_2$  and  $\text{O}_3$  lead to higher  $\delta^{18}\text{O}-\text{SO}_4$  values (9, 20). In case of ozone, the  $\delta^{18}\text{O}$  value can be even higher than that of  $\text{O}_2$  (11). Ozone is known to cause high  $\delta^{18}\text{O}$  values of atmospherically formed nitrate (23). An interplay of seasonally different oxidants could generally be invoked to account for seasonality in  $\delta^{18}\text{O}-\text{SO}_4$  values of atmospheric deposition, however it would not resolve the discrepancy between  $^{18}\text{O}$  systematics at LIZ and the mass flux constraint (ca. 50% of input with erratic  $^{18}\text{O}$  still permitting a distinct seasonality for spruce throughfall S). One possible explanation could involve a different oxygen isotope composition of sulfate derived from fog and rain. Capture of fog droplets is more intense in forests than in clearings, and heterogeneous (aqueous)  $\text{SO}_2$  oxidation in fog is quite likely (4). Both JEZ and LIZ are upland sites (900 m a.s.l.) with relatively abundant fogs in autumn and winter. The weakness of this explanation is that in summer horizontal deposition is insignificant relative to rain, and yet Figure 2a shows a continuation of the systematic trends in summer. This hypothesis is testable, it would require  $\delta^{18}\text{O}-\text{SO}_4$  monitoring of a lowland forested site where horizontal deposition is insignificant in all four seasons.

**Role of High-Temperature Industrial Sulfate.** There is abundant evidence that primary, high-temperature sulfate formed in the stacks of coal-fired power stations brings into the troposphere isotopically heavy sulfate oxygen (20). The high-temperature-burning ( $1000\text{ °C}$ ) incorporates into the sulfate atmospheric  $\text{O}_2$  ( $+23.5\text{‰}$ ). We hypothesized that at JEZ, which is close to 11 power stations with a combined thermal output of 14 000 MW, primary sulfate would be detectable by high  $\delta^{18}\text{O}-\text{SO}_4$ , especially in comparison with LIZ. The assumed relationship  $\delta^{18}\text{O}_{\text{JEZ}} > \delta^{18}\text{O}_{\text{LIZ}}$  for atmospheric sulfate should be more pronounced in open-area precipitation than in spruce throughfall, since the proportion of throughfall sulfate that is derived from dry-deposited  $\text{SO}_2$  can only be low-temperature (“secondary”) sulfate. Figure 2b shows that the polluted site JEZ does not have higher



**FIGURE 4. Statistical evaluation of mean  $\delta^{18}\text{O}-\text{SO}_4$  (a) and  $\delta^{34}\text{S}-\text{SO}_4$  (b) values. Standard errors and ranges of values are also given;  $n$  = number of samples. Sample types denoted by a different letter are statistically different at the  $p < 0.05$  level. The  $\delta^{34}\text{S}-\text{SO}_4$  values are from ref 15.**

$\delta^{18}\text{O}-\text{SO}_4$  values of open-area precipitation than LIZ. In contrast, a  $\delta^{18}\text{O}_{\text{LIZ}} > \delta^{18}\text{O}_{\text{JEZ}}$  relationship was observed for rainfall sulfate during 17 out of 24 months. The mean  $\delta^{18}\text{O}-\text{SO}_4$  value at LIZ was 14.2‰, and that at JEZ was 13.1‰. The difference between these two open-area precipitation values was statistically significant ( $p < 0.05$ ). We conclude that, contrary to expectations, sulfate oxygen at the less polluted site LIZ was isotopically heavier than sulfate oxygen at the highly polluted site JEZ. Although only 5 km from the nearest power station, JEZ did not receive significant amounts of primary high-temperature sulfate. This situation contrasts with a number of industrial sites in North America, where high-temperature sulfate was isotopically identified (6, 20). Sulfate deposited in open areas at the polluted JEZ is consistent with transport from distant sources.

**Within-Catchment Comparisons of  $\delta^{18}\text{O}-\text{SO}_4$ .** The polluted site JEZ and the less polluted site LIZ exhibited the same within-catchment systematics in  $\delta^{18}\text{O}-\text{SO}_4$  values (Figure 4a;  $p < 0.05$ ). At both sites,  $\delta^{18}\text{O}-\text{SO}_4$  decreased in the following order: open-area precipitation > spruce throughfall > runoff. Mean  $\delta^{18}\text{O}-\text{SO}_4$  values were 13.1, 10.3, and 8.6‰ (JEZ), and 14.2, 11.3 and 9.0‰ (LIZ) for open-area precipitation, throughfall, and runoff, respectively. Within each site, the difference between clearings and forests in the mean input  $\delta^{18}\text{O}-\text{SO}_4$  was similar (2.8‰ at JEZ and 2.9‰ at LIZ). This was rather surprising. We would have expected a larger difference between  $\delta^{18}\text{O}-\text{SO}_4$  values of clearings and forests at the more polluted site JEZ compared to LIZ because of the higher addition of  $^{18}\text{O}$ -poor newly formed sulfate combining S from the abundant dry-deposited  $\text{SO}_2$  and O from  $^{18}\text{O}$ -deficient water. At the same time, lower  $\delta^{18}\text{O}-\text{SO}_4$  values of throughfall compared to open-area precipitation (Figure 4) demonstrate addition of newly formed low- $^{18}\text{O}$   $\text{SO}_4$  incorporating rainwater during  $\text{SO}_2$  in situ oxidation on vegetation surfaces.

**S-O Isotope Correlations.** Figure 4b gives ranges of  $\delta^{34}\text{S}-\text{SO}_4$  values at JEZ (15). The same sequence of open-area

**TABLE 3. Isotope Composition of Sulfate of Salt Efflorescence Taken from Castellated Sandstones (Bohemian Cretaceous Basin, Czech Republic)**

site number <sup>a</sup>	site	$\delta^{18}\text{O}-\text{SO}_4$ (‰)	$\delta^{34}\text{S}-\text{SO}_4$ (‰)
1	Tisa	8.0	4.5
2	Hrensko	8.3	3.9
		7.3	2.7
3	Jestrebice	7.4	3.3
4	Prihrazy	7.3	3.7
		7.9	4.1
5	Kacanovy	7.7	3.1
6	Prachov	8.1	
7	Ceska Trebova <sup>b</sup>	4.2	2.1
		9.9	4.6

<sup>a</sup> In Figure 1. <sup>b</sup> Non-castellated.

precipitation > spruce throughfall  $\geq$  runoff for both  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of sulfate is fortuitous. The  $\delta^{34}\text{S}-\text{SO}_4$  values of throughfall are lower than those of open-area precipitation due to scavenging of low- $\delta^{34}\text{S}$  coal-derived  $\text{SO}_2$  by the needles. It has been previously shown that during aqueous  $\text{SO}_2$  oxidation high- $\delta^{34}\text{S}$  sulfur is accumulated in the resulting sulfate, leaving the residual  $\text{SO}_2$   $^{32}\text{S}$ -enriched (8). The reason for this fractionation is that the heavy isotope  $^{34}\text{S}$  accumulates in a liquid rather than in a gas. In contrast, the lower  $\delta^{18}\text{O}-\text{SO}_4$  of throughfall compared to open-area precipitation is related to prevalence of heterogeneous  $\text{SO}_2$  oxidation on needles, and prevalence of homogeneous  $\text{SO}_2$  oxidation in open areas.

**Long-Term vs Short-Term Isotope Record of Air-Borne Sulfate Oxygen.** Gypsum and alum sampled in the form of salt efflorescence were sometimes believed to contain a long-term record of  $\delta^{34}\text{S}-\text{SO}_4$  and  $\delta^{18}\text{O}-\text{SO}_4$  of atmospheric deposition (24). This record would be mass-weighted, since seasons with higher S deposition fluxes dominate the isotope signature of salts. To compare a long-term isotope record with our 2-year time series of monthly water solutes, we analyzed salt crusts from seven sites (Figure 1; Table 3). The  $\delta^{18}\text{O}-\text{SO}_4$  values of the solid samples ranged between 4.2 and 9.9‰, with the mean value of 7.6‰. The salt crusts contained isotopically lighter sulfate oxygen than any type of atmospheric inputs observed at JEZ and LIZ ( $p < 0.05$ ). The mean  $\delta^{18}\text{O}-\text{SO}_4$  value for the salts was 2.7‰ lower compared to throughfall at JEZ, and as much as 6.6‰ lower compared to open-area precipitation at LIZ. We conclude that sulfate oxygen data from salt efflorescence may not simply reflect long-term  $\delta^{18}\text{O}-\text{SO}_4$  values of rainfall. Paired sampling of salt efflorescence and rainfall at a single site are needed to confirm this conclusion. Upward movement of groundwater that brings sulfate isotopically different from deposition may represent one explanation of the observed  $^{18}\text{O}$  systematics in gypsum.

**Biogeochemical Cycling of S in Catchments.** Isotopically, sulfate leaving the forest catchments via surface runoff was different from sulfate of atmospheric input (Figure 4). The  $\delta^{18}\text{O}-\text{SO}_4$  values of runoff (means of 9.0 and 8.6‰ at LIZ and JEZ, respectively) were significantly lower than those of local atmospheric input ( $p < 0.05$ ). This difference could be a result of physicochemical and biogeochemical processes taking place within the ecosystem, mainly in soils, and/or mixing of rainwater with groundwater (1, 7, 25, 26). Seasonally, the  $\delta^{18}\text{O}-\text{SO}_4$  value of runoff varied less than atmospheric input at both sites. This observation was consistent with a relatively long residence time of S in the catchment, long enough to dampen out the seasonality of throughfall. The mean residence time of sulfate O in the catchment may be

shorter than that of S. The difference in these two residence times is represented by temporal S storage in an organic form.

Because adsorption and desorption of inorganic sulfate has only a negligible effect on O isotopes (25), the negative shift of  $\delta^{18}\text{O}-\text{SO}_4$  from atmospheric input to runoff must be mainly a result of biogeochemical S cycling in the upper soil horizons. This finding agrees well with previous detailed studies of S isotopes in Czech catchments which estimated that as much as 50% of sulfate in the runoff was supplied by mineralization of organic S (13, 15). In a previous study at JEZ, we found a simultaneous decrease in sulfate  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in lysimeter solutes relative to spruce throughfall  $\text{SO}_4$ , indicative of mineralization of organic S (15). Mixing with sulfate containing bedrock S, which is isotopically heavy, was not detected in soil solutes at JEZ (15).

We note that at sites where S isotope systematic shows a substantial contribution of bedrock weathering to runoff sulfate,  $\delta^{18}\text{O}-\text{SO}_4$  of runoff is low also due to the fact that most of oxygen in sulfate produced by sulfide weathering is derived from  $^{18}\text{O}$ -deficient water (26).

It is not known whether organic S cycling in forest soils is equally important at extremely polluted and extremely unpolluted locations (27–29). A comparison of  $\delta^{18}\text{O}-\text{SO}_4$  between JEZ and LIZ provides a new insight into this question: The  $\delta^{18}\text{O}-\text{SO}_4$  data for runoff from these two sites were statistically indistinguishable. Given that the “extra” isotopically light oxygen in runoff sulfate was predominantly derived from ambient water via mineralization of organic S, the less polluted site LIZ should exhibit a significantly lower  $\delta^{18}\text{O}-\text{SO}_4$  of runoff if the percentage of atmospheric S that had been organically cycled was higher than at JEZ. Since the found  $\delta^{18}\text{O}-\text{SO}_4$  of runoff was indistinguishable between the two sites, we conclude that the percentage of organically cycled S may be similar at the opposite ends of the strong 10-fold pollution gradient. LIZ is used here as a reference regardless of the small net retention of deposited S (ca 5 kg S ha<sup>-1</sup> yr<sup>-1</sup>).

**Identification of Gaps in Understanding  $\delta^{18}\text{O}-\text{SO}_4$  Trends.** In summary, the found sulfate oxygen isotope systematics were surprising in three aspects: (i) the nearly 50% contribution of wet deposited sulfate to LIZ throughfall should smear out the  $\delta^{18}\text{O}-\text{SO}_4$  seasonal pattern, while it did not; (ii) the difference between mean  $\delta^{18}\text{O}-\text{SO}_4$  values of open-area precipitation and throughfall was similar at both sites, while it should be larger at JEZ; (iii) open-area precipitation at JEZ should contain more  $^{18}\text{O}$ -rich high-temperature industrial sulfate than LIZ, while it did not. Processes controlling these patterns merit further study.

## Acknowledgments

Czech Granting Agency is thanked for financial support (526/06/1589.). Karel Zak of the Czech Geological Survey refined the methodology of sulfate oxygen extraction.

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*Received for review April 27, 2006. Revised manuscript received October 13, 2006. Accepted November 1, 2006.*

ES0610028