Sulfur isotope dynamics in two Central European watersheds affected by high atmospheric deposition of SO$_x$

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Abstract—Sulfur fluxes and $\delta^{34}S$ values were determined in two acidified small watersheds located near the Czech–German border, Central Europe. Sulfur of sulfate aerosol in the broader region (mean $\delta^{34}S$ of 7.5‰ CDT) was isotopically heavier than sulfur of airborne SO$_2$ (mean $\delta^{34}S$ of 4.7‰). The annual atmospheric S deposition to the Jezeří watershed decreased markedly in 1993, 1994, and 1995 (40, 33, and 29 kg/ ha · yr), reflecting reductions in industrial S emissions. Sulfur export from Jezeří via surface discharge was twice atmospheric inputs, and increased from 52 to 58 to 85 kg/ha · yr over the same three-year period. The $\delta^{34}S$ value of Jezeří streamflow was 4.5 ± 0.3‰, intermediate between the average atmospheric deposition (5.4 ± 0.2‰) and soil S (4.0 ± 0.5‰), suggesting that the excess sulfate in runoff comes from release of S from the soil. Bedrock is not a plausible source of the excess S, because its S concentration is very low (<0.003 wt.%) and because its $\delta^{34}S$ value is too high (5.8‰) to be consistent with the $\delta^{34}S$ of runoff. A sulfur isotope mixing model indicated that release of soil S accounted for 64 ± 33% of sulfate S in Jezeří discharge. Approximately 30% of total sulfate S in the discharge were organically cycled. At Načetín, the same sequence of $\delta^{34}S_{IN} > \delta^{34}S_{OUT} > \delta^{34}S_{SOIL}$ was observed. The seasonality found in atmospheric input (higher $\delta^{34}S$ in summer, lower $\delta^{34}S$ in winter) was preserved in shallow (<10 cm) soil water, but not in deeper soil water. $\delta^{34}S$ values of deeper (>10 cm) soil water (4.8 ± 0.2‰) were intermediate between those of atmospheric input (5.9 ± 0.3‰) and Načetín soils (2.4 ± 0.1‰), again suggesting that remobilization of soil S accounts for a significant fraction (roughly 40 ± 10%) of the S in soil water at Načetín. The inventories of soil S at both of these sites are legacies of more intense atmospheric pollution during previous decades, and are large enough (740 and 1500 kg S/ha at Jezeří and Načetín, respectively) to supply significant sulfur fluxes to runoff for several more decades. The ongoing release of this stored soil S may significantly delay the recovery of water quality under declining atmospheric S deposition. Analysis of possible scenarios that would result in different S isotope composition of rainfall, runoff and soil suggested that biologic S isotope fractionation must be involved. Mineralization of organic soil S was recorded in two opposite but complementary vertical isotope trends: while soil water had lower $\delta^{34}S$ values in deeper horizons, bulk soil had higher $\delta^{34}S$ values in deeper horizons. *Copyright © 2000 Elsevier Science Ltd*

1. INTRODUCTION

Elevated atmospheric inputs of SO$_x$ into watersheds are detrimental, because they accelerate the depletion of nutrient basic cations from soils, and raise the concentrations of acidic cations (H$^+$, Al^{3+}) in soil porewaters and surface waters (Johnson, 1984; Driscoll and Schecher, 1988; Kirchner, 1992; Kirchner and Lydersen, 1995). In geochemical studies of forested watersheds, dissolved soil S has often been modeled as a conservative compound (see Mitchell and Fuller, 1988 for critical review). Consequently, models that predict time-scales of acidification reversal have focused on adsorption/desorption of inorganic sulfate in soil (e.g., Cosby et al., 1985). With the advent of stable isotope studies, the importance of biota in S cycling in forest ecosystems has become increasingly recognized. Sulfur transport pathways have been isotopically studied in the atmosphere (Krouse and Grinenko, 1991; Ohizumi et al., 1997), wet and dry deposition (Hesslein et al., 1988; Mayer et al., 1995a; Heaton et al., 1997), trees (Gebauer et al., 1994; Yang et al., 1996), soil water (Novák et al., 1995; Zhang et al.,

1998), soil (Fuller et al., 1986; Giesemann et al., 1995) and surface discharge (Stam et al., 1992). Sulfur isotope signatures ($\delta^{34}S$) can be used to identify natural and anthropogenic S sources, if the isotopic separation among them is large enough (Fry, 1989). Krouse (1986) proposed mixing models for the identification of point sources of atmospheric pollution. Finley et al. (1994) used $\delta^{34}S$ values to estimate the proportion of atmospheric and bedrock-derived S in watershed discharge. Nriagu and Glooschenko (1992) and de Caritat et al. (1997) studied $\delta^{34}S$ values of receptor surfaces on a regional basis. Sulfur fluxes were isotopically studied to obtain an insight into processes of S transport (van Stempvoort et al., 1992; Mayer et al., 1995b). Although most physicochemical processes in the environment (e.g., dissolution of bedrock sulfides/sulfates and adsorption/desorption of inorganic sulfate on soil particles) are associated with little or no S isotope fractionation (van Stempvoort et al., 1990), there are four processes that have been shown to fractionate S isotopes: conversion of SO$_2$ to SO$_4^{2-}$ in the atmosphere (Saltzman et al., 1983), bacterial SO$_4^{2-}$ reduction in anaerobic soils (Kaplan and Rittenberg, 1964), release of H$_2$S by some chloroplasts (Winner et al., 1981; Krouse et al., 1984), and maturation of organic S in the soil (Gebauer et al., 1994; Novák et al., 1996).

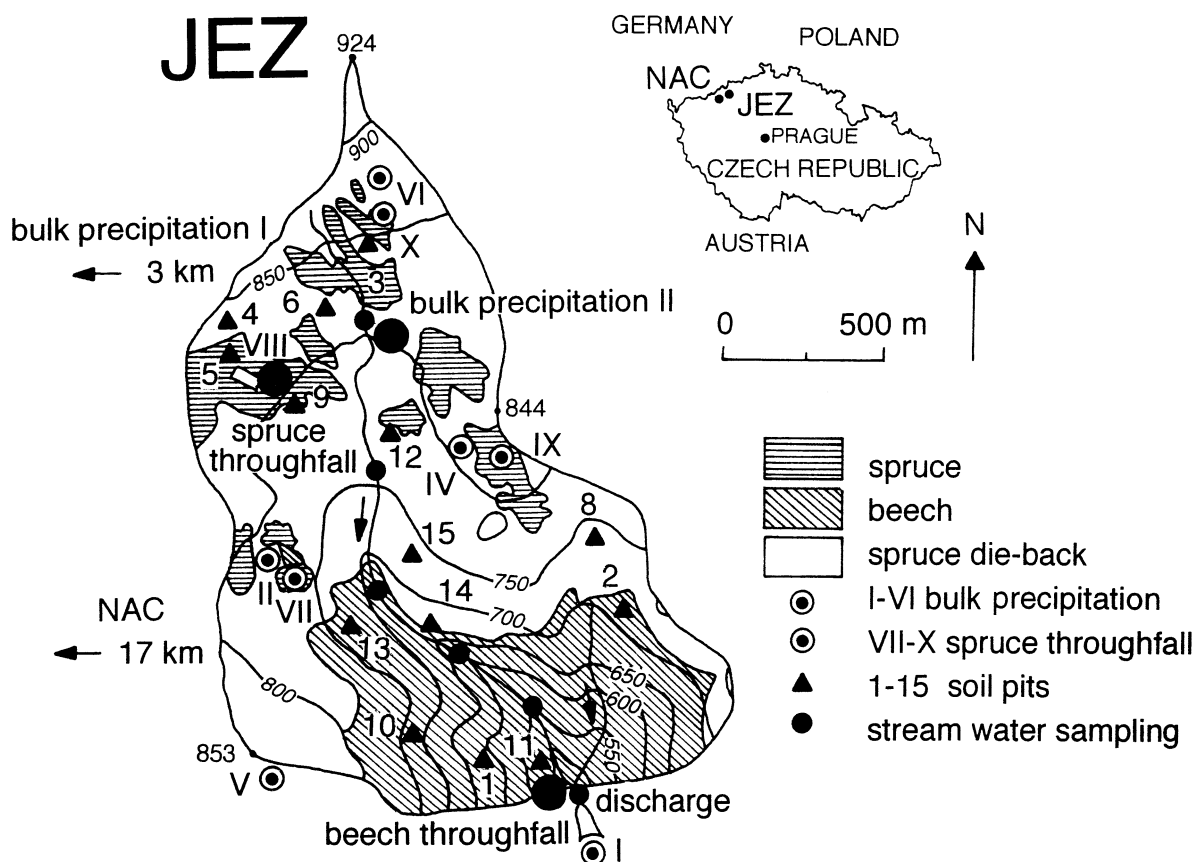*Author to whom correspondence should be addressed (novak@cgu.cz).

Fig. 1. A sketch of the JEZ watershed. ● represent the main sampling sites (JEZ data in Figs. 2 to 5, 8 and 10). "Bulk Precipitation I" and "Bulk Precipitation II" are replicate samplings at two different sites located 3 km apart. Roman numerals I–X denote auxiliary sampling sites used to assess the elevational gradient in atmospheric S input into the watershed. Arabic numerals are related to soil data in Table 5.

In heavily industrialized regions, such as the "Black Triangle" of the northern Czech Republic, southeastern Germany, and southern Poland, 98% of S is emitted in the form of SO_2. The rates of oxidation of SO_2 to SO_4^{2-} in the atmosphere vary seasonally. Sulfur enters the forested watersheds as both wet deposition (SO_4^{2-}) and dry deposition (primarily SO_2). The contribution of dry deposited S to the total deposition of S is smaller in open areas ("bulk precipitation") than underneath tree canopies ("throughfall"). Leaching of S from within foliage tissues by rain is negligible; however, low-δ^{34}S hydrogen sulfide may be released into the atmosphere (Krouse et al., 1984). In peaty soils bacterial sulfate reduction produces low-δ^{34}S S^{2+} (Bottrell and Novák, 1997; Novák et al., 1999). In aerated forest soils evidence for significant cycling of incoming SO_4^{2-}-S through an organic S pool was first obtained by comparing δ^{18}O values of throughfall sulfate with those in soil water (van Stempvoort et al., 1992; Mayer et al., 1995a). From lower δ^{18}O values in soil water than in input the importance of newly formed, "secondary" sulfate in the soil was inferred. In contrast, δ^{34}S of the "secondary" sulfate was indistinguishable from throughfall and appeared to be insensitive to mineralization. Novák et al. (1996) showed that, at 18 spruce-forested watersheds with contrasting precipitation, temperature, pollution, and bedrock, δ^{34}S of bulk soil increased with increasing

depth; they suggested that this positive S isotope shift was caused by mineralization of organic S.

Here we report on the isotope systematics of bulk precipitation, throughfall, soil water, and stream water at two heavily polluted sites in the northern Czech Republic. Fourteen different S fluxes were isotopically monitored for 3 yr, and the isotopic compositions of soil and bedrock S pools were measured. In all, 510 δ^{34}S measurements were used to fingerprint the individual S pools and fluxes, and to evaluate the seasonality in watershed inputs and outputs. Our measurements demonstrate that sulfate-S in soil water and stream water is isotopically lighter than atmospheric S deposition, and suggest that this negative isotopic shift is due to release of fractionated S from the soils.

2. MATERIALS AND METHODS

2.1. Study Sites

The two study sites, Jezeří (JEZ) and Načetín (NAC), are situated in the Krušné hory Mts. (Erzgebirge), a heavily industrialized part of the northern Czech Republic at the border with Germany (Fig. 1 and Table 1). JEZ is located 120 km north-west of Prague, and NAC is 17 km west of JEZ. The nearest major air pollution sources, coal-burning power plants and chemical plants, are located to the south of the main mountain range in the Most Basin, an Upper Eocene/Lower Miocene

Table 1. Characteristics of the JEZ watershed and the NAC research plot (Northern Czech Republic).

	JEZ	NAC
Location	50°38′N, 13°29′E	50°35′N, 13°15′E
Elevation (m a.s.l.)	490–924	760–780
Mean inclination (°)	4.0	2.5
Aspect	South	West
Area under study (ha)	261	25
Bedrock	Two-mica orthogneiss	Two-mica orthogneiss
Soil type	Mostly Dystric Cambisol	Dystric Cambisol
Vegetation	Spruce (11%), beech (26%) clearings (63%)	Spruce
Prevailing wind direction	West	West
Mean temperature (°C)	+6.0	+5.5
Annual precipitation (mm)	940	890
Sulfur deposition (kg/ha · yr)	56	48

graben. Soft coal containing up to 3% S is being exploited in 12 extensive (10 to 30 km^2 each) open pit mines. The 80 km long and 5 km wide mountain plateau of the Krušné hory (800 to 900 m elevation), which runs parallel to the basin, was first affected by massive spruce die-back in the early 1970s. As of 1999, 500 km^2 of spruce forests suffered from defoliation, with most of the dead trees having been clear-cut. Industrial SO$_2$ emissions in the whole Czech Republic decreased between 1990 and 1997 from 1900,000 to 700,000 tons/yr., i.e., by 60%. During the observation period (November 1992 to January 1996), however, atmospheric SO$_2$ loads on the mountain plateau of the Krušné hory did not reflect this improvement in emission rates. The mean SO$_2$ concentrations in the atmosphere were 56, 49, and 135 μg/m^3 in winter 1993 to 94, 1994 to 95, and 1995 to 96, respectively. During the 3-yr observation period, the health status of the spruce stands further deteriorated, with crown thinning at NAC, but few trees actually died. In the two years (1996 to 1997) following the observation period, another 1600 ha of spruce and 2100 ha of birch perished due to atmospheric pollution.

The 261-ha JEZ watershed (Pačes, 1985; Černý, 1995; Novák and Přechová, 1995) is situated on the southern slope of the Krušné hory Mts. facing the Most Basin. The watershed spans an elevation gradient of 430 m. The bedrock is formed by base-poor two-mica orthogneiss containing <0.003 wt.% S. The 60- to 90-cm deep soil is represented by Dystric to Eutric Cambisols to Orthic Podzols. In the early 1970s, Norway spruce *(Picea abies)* died back on 63% of the watershed's area, mostly above 700 m elevation; the dead spruce stands were harvested before 1988. The lowermost segment of the watershed (26%, between ca. 490 and 600 m elevation) is covered by a 140-year-old stand of European beech *(Fagus sylvatica).* Small patches of 10- to 100-year-old Norway spruce remain in the upper segment of the watershed (above 700 m elevation), covering 11% of the studied area. A heterogeneous mixture of birch *(Betula* sp*.)* and Mountain ash *(Sorbus aucuparia)* is presently invading the clearings.

In the 400-ha NAC watershed (Dambrine et al., 1993, Černý, 1995), we studied a 25 m^2 plot underneath the canopy of a 100-year-old stand of Norway spruce. The site lacks surface discharge, and is located on a mountain plateau (ca. 770 m elevation) that gently slopes west. Whereas JEZ is only five km from the nearest major source of air pollution, NAC is more remote from the basin (18 km) and relatively less polluted. Bedrock, soil, and precipitation at NAC are similar to JEZ (Table 1). The herbaceous layer is dominated by *Deschampsia flexuosa, Calamagrostis villosa, Vaccinium myrtillus, Athyrium alpestre, Poa* sp., and *Gallium* sp.

In both watersheds, soils are highly acidified, typically with pH$_{H_2O}$ of 3.2 to 4.3, pH$_{KCl}$ of 2 to 4, exchangeable acidity of 14 to 4 meq 100 g^{-1}, cation exchange capacity of 18 to 4 meq 100 g^{-1}, base saturation of 23 to 8%, and acid neutralizing capacity of 0 to 70 meq HCl kg^{-1} (Petřík, 1993). The mean residence time of organic C, inferred from enhanced ^{14}C from nuclear testing, is 4.0, 200, 750, and 1600 yr for the L/F horizon, 0 to 5, 5 to 10, and 10 to 20 cm depths, respectively (Harrison, *personal communication*).

2.2. Sampling Scheme

At JEZ we monitored sulfate concentration ([SO$_4^{2-}$]) and sulfur isotope composition (δ^{34}S) in the atmospheric input (Bulk Precipitation I, Bulk Precipitation II, Spruce Throughfall, and Beech Throughfall; *large solid circles* in Fig. 1) surface discharge (*small solid circle* at the watershed outlet) and vertical profiles through bulk soil (*solid triangles*). Water samples were taken monthly between November 1992 and January 1996. Soils from 15 one-meter deep soil pits were sampled in 1996. Stream water was also sampled over a 350 m elevation gradient in December 1992 (6 sites, step of 300 m; *small solid circles* in Fig. 1). Bulk precipitation was sampled at six different elevations (470 to 895 m) in January and April 1994 (sites I–VI in Fig. 1). Spruce throughfall was sampled at four different elevations (780 to 872 m) in January and April 1994 (sites VII–X).

Bulk Precipitation I was sampled 3 km west of JEZ, at an elevation of 890 m on a deforested southern slope similar to JEZ. Bulk Precipitation II was sampled in the upper segment of JEZ at an elevation of 803 m. At both sites, two samplers were installed 5 m apart in an open field; each pair was pooled to yield a single composite sample. Spruce throughfall was sampled in the upper segment of JEZ at an elevation of 798 m in a 30-year-old Norway spruce stand. A single composite sample was obtained from a network of 9 samplers in a regular 10 × 10 m grid underneath the closed spruce canopy. An identical network of 9 samplers was used to sample beech throughfall near the JEZ watershed outlet, at 493 m elevation. Deposition samplers were polyethylene (PE) funnels (area 122 cm^2), fitted to PE 1 L bottles placed 120 cm above the ground. In winter (December–March) plastic vessels (area 380 cm^2) with PE bags replaced the funnels to collect snow. The auxiliary sampling sites I–X were equipped with either two samplers (open area, I–VI) or a regular 10 × 10 m network of 9 samplers (spruce stands, VII–X).

JEZ discharge was sampled at the watershed outlet, which was equipped with a gauging station for continuous flow measurements. One liter of stream water was taken at the end of each 1-month sampling period. The isotope inventory of soil S was taken by analyzing soil from three depth intervals (O+A, Bv, and B/C for Dystric and Eutric Cambisols; O+A, Bsv, and B/C for Cambic Podzols) in 15 soil pits evenly distributed in the watershed (560 to 840 m a.s.l.; Fig. 1). Sulfur isotope composition was measured on a composite of 40 samples of mostly unweathered bedrock (10 kg in all), collected from widely distributed points in the watershed.

At NAC we monitored bulk precipitation, spruce throughfall and soil water at monthly intervals over the same 3-yr period. NAC bulk precipitation samples were collected at a forest opening 150 m south of the Norway spruce stand using two samplers (5 m apart), and NAC spruce throughfall was collected in the mature spruce stand using 25 samplers placed in a regular 10 × 10 m grid, identical to those at JEZ. For analysis, 5 composite samples were prepared by pooling water yields from 5 samplers in each of the 5 rows. The coefficient of variation of S yields between rows was <30%. For δ^{34}S analyses, 10 samples from rows 2 and 3 were pooled to produce a composite sample. Zero tension (gravitational) lysimeters and Prenart suction lysimeters

(Beier and Hansen, 1992) were installed at NAC in 1988 and 1989, respectively. NAC soil water was sampled by two replicate zero-tension lysimeters under the forest floor (soil water 0 cm I and II, analyzed separately), and by zero-tension lysimeters at depths of 10, 30, and 70 cm below the soil surface (one analysis per depth). Prenart suction lysimeters were also used to sample soil water at depths of 30 and 90 cm; yields from 2 suction cups were combined at each depth. For brevity, suction soil water is marked with an asterisk throughout this paper. NAC soil was sampled in a 90-cm deep pit; composite samples of horizons O+A, Bv, and B/C were prepared by mixing soil from 3 facets of the pit.

Sulfate δ^{18}O values of NAC spruce throughfall and soil water (30* and 90* cm) were determined for January 1993, June 1994, and June 1995.

At 8 meteorological stations located at distances of 10 to 500 km from JEZ, airborne SO_2 and aerosol sulfate were analyzed for δ^{34}S. Twenty samples represented 1 to 10 months of exposure of pretreated filters to ambient air 2 m above the ground. A solution of KOH in triethanol-amine was used to pretreat Whatman 541 filter paper for the capture of SO_2, and untreated 0.45 μm microfilters were used to capture aerosol sulfate.

2.3. Analytical Techniques

Samples of bulk precipitation, canopy throughfall, stream water and soil water were filtered and kept at 2°C. Water flux was measured by weighing the sampler contents. Conductivity, pH, and alkalinity were measured within 48 h of collection using a Radelkis conductivity electrode, Radiometer GK 2401C combined pH electrode, and automated Gran titration, respectively. Chemical analysis was performed on a Shimadzu LC 6A liquid chromatograph (SO_4^{2-}, Cl^-, NO_3^-), a Perkin-Elmer 2090 Hitachi spectrophotometer (NH_4^+), a Perkin-Elmer AA 3100 spectrometer (cations in bulk precipitation) and a Perkin-Elmer ICP Plasma II spectrometer (cations in throughfall). Sulfur for δ^{34}S measurements was precipitated from water as $BaSO_4$ and converted to SO_2 in a vacuum line (Yanagisawa and Sakai, 1983). $BaSO_4$ was mixed with V_2O_5 and SiO_2 (weight ratio of 1 : 10 : 10), heated to 980°C over a period of 10 min and kept for another 10 min to achieve quantitative thermal decomposition. SO_2 was trapped in a glass ampule by liquid nitrogen and sealed. Total S was extracted from bulk soil by digestion with Eschka's mixture of Mg and Na_2CO_3 (wt. ratio 2:1; Novák et al., 1994). One gram of dried, sieved (<2 mm) and homogenized soil was mixed with 3.5 g of Eschka's mixture and thermally decomposed in a crucible at 800°C for 90 min. The contents of the crucible were dissolved in 30 mL of DDW and treated with 17 mL of concentrated HCl; CO_2 was removed by boiling for 5 min. The sample was filtered using Whatman 541 filter paper, pH was adjusted to 2.5, and $BaSO_4$ was precipitated by adding 10 mL of 10 wt.% $BaCl_2$ solution. All δ^{34}S analyses were performed on a Finnigan MAT 251 mass spectrometer with a reproducibility of 0.2‰ (waters) and 0.3‰ (soils). The results were expressed in the usual notation as a per mil deviation of the ^{34}S/^{32}S ratio in the sample from the Canon Diablo Troilite (CDT) standard.

Bedrock samples from JEZ were ground to <0.1 mm. Two hundred grams of the whole-rock sample were subjected to Johnson-Nishita distillation in a 250 mL three-neck bottle (Johnson and Nishita, 1952). The sample was treated with Cr^{2+} in a N_2 atmosphere for 45 min at boiling temperature; S was extracted from accessory sulfides as H_2S, trapped in Zn-acetate, converted to Ag_2S, thermally decomposed at 800°C in a vacuum line, and analyzed for δ^{34}S.

Filters containing aerosol sulfate were treated in an ultrasonic bath with DDW. A few drops of H_2O_2 were added, the solution kept overnight, the remaining H_2O_2 destroyed by UV radiation, the solution acidified and $BaSO_4$ precipitated by addition of $BaCl_2$. By this procedure, S from up to 140 microfilters that had been exposed to ambient air for 1-day periods was extracted into a DDW volume of <50 mL. Airborne SO_2-S was obtained as $BaSO_4$ in 2 L of a thorin solution following colorimetric S determination. $BaSO_4$ was filtered, rinsed with DDW and processed as above.

Sulfate oxygen for stable isotope analysis was reacted at 950°C with carbon to form CO_2 in a vacuum line (Longinelli and Craig, 1967) and the δ^{18}O values measured on a Finnigan MAT 251 mass spectrometer with a reproducibility of 0.3‰ relative to Standard Mean Ocean Water (SMOW).

For the calculation of soil S pool size the <2 mm fraction was used.

The fraction of inorganic sulfate S was determined for the combined O+A soil horizon samples. Thirty grams of sieved dry soil were extracted with 100 mL of 16.1 mM solution of $NaH_2PO_4 \cdot H_2O$ overnight, and the fraction of inorganic sulfate S was determined gravimetrically as $BaSO_4$.

2.4. Statistical Evaluation

Statistical analysis of sulfate concentrations and δ^{34}S values was performed using JMP from SAS Institute. The Tukey-Kramer HSD was applied to test for differences in means. For time series data, the trend and seasonal amplitude are reported as means ± standard error estimated via nonlinear fitting techniques. The fitting equation was y = k + b * t + a cos (t + θ), where t was time and the fitted parameters k, b, a, and θ were, respectively, an intercept, the linear trend with time, the amplitude of the seasonal cycle, and a phase shift.

3. RESULTS

3.1. Water Chemistry

Both JEZ and NAC are chronically acidified watersheds. Chemical composition of bulk precipitation was dominated by SO_4^{2-} (61% of the anion charge), NO_3^- (27% of the anion charge), H^+ (35% of the cation charge), and NH_4^+ (31% of the cation charge). Basic cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) constituted 26% of the cation charge. Mean pH in bulk precipitation, beech and spruce canopy throughfall was 4.2, 4.3, and 3.5, respectively. The pH value of JEZ surface discharge was 5.4. Ca^{2+}, Na^+, and Mg^{2+} were the dominant cations and SO_4^{2-} was the dominant anion in discharge. At NAC the elemental fluxes were generally lower than at JEZ. Nitrate and ammonia fluxes in spruce throughfall were of similar magnitude. Aluminum concentration in NAC soil water increased between the depths of 0 and 90 cm by a factor of 22.

3.2. Comparisons of [SO_4^{2-}]

Sulfate concentrations ([SO_4^{2-}]) increased markedly from bulk precipitation, to throughfall, and to stream water, and also increased systematically down the soil profile at NAC (Fig. 2a). There was approximately a 10-fold difference in [SO_4^{2-}] between bulk precipitation (low) and JEZ discharge (high). Box plots in Figure 2a also depict the ranges of [SO_4^{2-}] for all 14 types of measured S solutes. ANOVA revealed statistically significant ($p < 0.05$) differences in [SO_4^{2-}] among the sampled S solutes, and the Tukey-Kramer HSD test found seven groups of S fluxes that differed significantly in their mean S concentrations (Table 2).

3.3. Comparisons of δ^{34}S

The δ^{34}S values generally decreased from bulk precipitation, to throughfall, and to stream water, and also decreased down the soil profile at NAC (Fig. 2b). Box plots in Figure 2b show that ranges in δ^{34}S values were greater than 3‰ for 13 out of 14 monitored S solutes. The Tukey-Kramer HSD test for mean δ^{34}S values (Table 2) revealed statistically significant differences ($p < 0.05$) among three groups of S solutes, with no overlap between bulk precipitation and spruce throughfall. The δ^{34}S values of bulk precipitation at JEZ I, JEZ II, and NAC (7.0, 7.7 and 7.9‰, respectively) were not statistically different. The δ^{34}S values of spruce throughfall were also statisti-
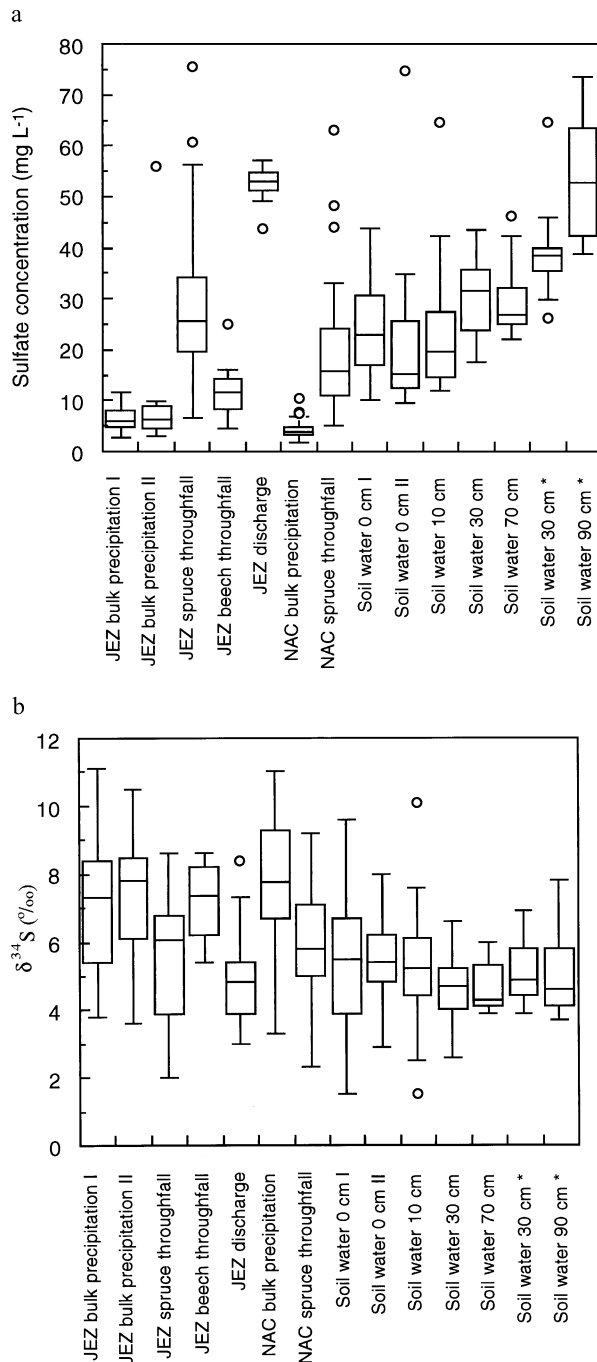
a

b

Fig. 2. Box plots of sulfate concentrations (a) and $\delta^{34}S$ ratios (b). The box encloses 50% of the data, the whiskers 90% of the data, the horizontal bar is the median, ○ are outliers. Roman numerals I and II denote replicate sampling, * indicate the use of suction lysimeters.

cally indistinguishable between JEZ and NAC (5.5 and 5.9‰, respectively).

3.4. Seasonality in Watershed Inputs/Outputs

Sulfate concentrations in the atmospheric inputs into JEZ were lower than in the output by surface discharge (Fig. 3a,b).

$[SO_4^{2-}]$ in bulk precipitation was relatively low (<10 mg/L), similar between JEZ I, JEZ II, and NAC, and showed little seasonality (Fig. 3a,c). Beech throughfall (<20 mg SO_4^{2-}/L) was intermediate between bulk precipitation and spruce throughfall in concentration and variability (cf. Fig. 3a,b). Sulfate concentrations in spruce throughfall at JEZ exhibited strong seasonality, amounting to ~20 mg SO_4^{2-}/L in summer and up to 100 mg SO_4^{2-}/L in winter (Fig. 3b). The seasonal amplitude (JMP, SAS) of 20.8 ± 4.8 mg/L was greater than twice the standard error corresponding to an approximate statistical significance of $p < 0.05$. For 2 to 3 winter months $[SO_4^{2-}]$ was higher in spruce throughfall than in JEZ discharge. Sulfate concentrations in spruce throughfall at NAC exhibited less distinct seasonality than at JEZ (Fig. 3c). $[SO_4^{2-}]$ of JEZ discharge showed only small seasonal fluctuations (amplitude of 2.3 ± 0.6 mg SO_4^{2-}/L).

The $\delta^{34}S$ values of JEZ spruce throughfall showed distinct seasonality, ranging up to 8‰ in summer and down to 2‰ in winter (Fig. 4a; amplitude of 1.5 ± 0.5‰). A similar, but less distinct, seasonal pattern was observed in spruce throughfall at NAC (Fig. 4b; amplitude of 1.0 ± 0.3‰). Bulk precipitation had higher $\delta^{34}S$ than spruce throughfall at both NAC and JEZ (cf. Fig. 4a,b), but showed no clear seasonality. Beech throughfall $\delta^{34}S$ values (Fig. 4c) were higher than the $\delta^{34}S$ values of spruce throughfall and did not show clear seasonality.

The $\delta^{34}S$ values of bulk precipitation at JEZ I and NAC (but not at JEZ II) decreased gradually over time (regression trends -1.8 ± 0.6 and -1.0 ± 0.4‰ per year, respectively; $p < 0.05$). At the same time, $[SO_4^{2-}]$ of these two types of samples lacked any trends. Spruce throughfall at JEZ showed an inverse relationship between $[SO_4^{2-}]$ and $\delta^{34}S$ ($r = 0.40$, $p < 0.05$); high winter-time sulfate concentrations were accompanied by low $\delta^{34}S$ values, and low summer-time sulfate concentrations were accompanied by high $\delta^{34}S$ values (Fig. 5a). At NAC, spruce throughfall $\delta^{34}S$ values declined through time (trend 1.0 ± 0.4‰ per year, $p < 0.05$), in parallel with bulk precipitation $\delta^{34}S$ values. The $\delta^{34}S$ values of JEZ discharge (Fig. 5b) varied between 3 and 8‰, with a small, but statistically significant, seasonal fluctuation (amplitude of 0.7 ± 0.3‰). Relative to other S constituents, the variability in $\delta^{34}S$ of the discharge contrasted with its relatively constant sulfate concentrations (Fig. 5b).

3.5. Sulfate Isotope Composition of Soil Water

In Figure 6, sulfate concentrations and $\delta^{34}S$ values from all lysimeters deeper than 10 cm below the soil surface are plotted. The atmospheric input into the soil is represented by NAC spruce throughfall. Sulfate concentrations of soil water deeper than 10 cm were generally higher than those in spruce throughfall (mean differences ranged from 5 to 36 mg/L, depending on depth, and were statistically significant at $p < 0.05$ in paired-sample t-tests). In contrast, the $\delta^{34}S$ values of the same soil water samples were lower than $\delta^{34}S$ of spruce throughfall (by 1.4 to 1.7‰, depending on depth; statistically significant at $p < 0.01$ in paired-sample t-tests).

Shallow soil waters (0 cm I, 0 cm II and 10 cm) exhibited fluctuations similar to spruce throughfall, with minima in $\delta^{34}S$ in winter 1994, 1995, and 1996 (Fig. 7a). Deeper soil water (30* and 90* cm) lacked seasonality in $\delta^{34}S$ (Fig. 7b).

Table 2. Means $\pm$ SE for [SO_4^{2-}] and $\delta^{34}S$. Different letters denote means found to be significantly different by the Tukey-Kramer HSD test.

	[SO_4^{2-}]								$\delta^{34}S$			
	Mean $\pm$ SE	Tukey-Kramer groups							Mean $\pm$ SE	T-K groups		
JEZ bulk precipitation I	6.1 $\pm$ 0.6	a							7.0 $\pm$ 0.4		b	c
JEZ bulk precipitation II	5.3 $\pm$ 0.4	a							7.7 $\pm$ 0.5			c
JEZ beech throughfall	11.7 $\pm$ 1.2	a	b						7.3 $\pm$ 0.3		b	c
JEZ spruce throughfall	32.2 $\pm$ 3.8					e	f		5.5 $\pm$ 0.3	a		
JEZ discharge	52.7 $\pm$ 0.5							g	4.9 $\pm$ 0.2	a		
NAC bulk precipitation	4.4 $\pm$ 0.3	a							7.9 $\pm$ 0.4			c
NAC spruce throughfall	20.3 $\pm$ 2.2		b	c					5.9 $\pm$ 0.3	a	b	
NAC soil water 0 cm I	25.7 $\pm$ 3.7			c	d	e	f		5.5 $\pm$ 0.5	a	b	
NAC soil water 0 cm II	21.6 $\pm$ 2.7		b	c	d				5.5 $\pm$ 0.3	a		
NAC soil water 10 cm	23.3 $\pm$ 2.1			c	d	e			5.3 $\pm$ 0.3	a		
NAC soil water 30 cm	30.9 $\pm$ 2.0				d	e	f		4.6 $\pm$ 0.3	a		
NAC soil water 30 cm*	36.5 $\pm$ 2.1						f		4.9 $\pm$ 0.3	a		
NAC soil water 70 cm	29.6 $\pm$ 2.0			c	d	e	f		4.6 $\pm$ 0.2	a		
NAC soil water 90 cm*	51.5 $\pm$ 2.4							g	4.9 $\pm$ 0.2	a		

* Suction lysimeters.
I, II-replicate sampling.

Isotope compositions of sulfate oxygen ($\delta^{18}O$) were determined for spruce throughfall and soil water at 30* and 90* cm ($n = 9$, Table 3). Mean $\delta^{18}O$ values were 7.4, 3.6, and 6.8‰ SMOW, respectively. The $\delta^{18}O$ value of all soil water samples was lower than $\delta^{18}O$ of spruce throughfall, with the lowest value at the shallower of the two depths (30* cm) each sampling month.

3.6. Elevational Gradient in Atmospheric Inputs and Streamwater at JEZ

The stream draining JEZ exhibited an increase in $\delta^{34}S$ values from 2.8 to 5.6‰ with increasing elevation, whereas [SO_4^{2-}] was slightly higher at lower elevations (53 vs. 47 mg/L at the lowermost and topmost sampling point). The trend of more concentrated streamwater sulfate downstream was confirmed by Havel et al. (1996). Groscheová et al. (1998) found an up-slope decrease in $\delta^{34}S$ values of spruce throughfall and an up-slope increase in $\delta^{34}S$ values of bulk precipitation. In this study, the lowest $\delta^{34}S$ value of bulk precipitation (5.4‰) was measured at the lowest elevation, the highest (14.5‰) at the highest elevation. Our data and those by Groscheová et al. (1998) are consistent.

3.7. Regional Variability in $\delta^{34}S$ of Airborne S Species

Sampling of air-borne SO_2 and sulfate aerosol focused on winter months (Table 4). $\delta^{34}S$ values averaged 4.7 and 7.5‰ for SO_2 and sulfate aerosol, respectively. Both chemical species of sulfur were characterized by large variability in $\delta^{34}S$ (from -2.4 to $+11.6$‰ for SO_2, and from $+3.1$ to $+16.9$‰ for sulfate aerosol). The highest $\delta^{34}S_{aerosol}$ value was measured at Churáňov, a relatively unpolluted site located in the Southern Czech Republic (atmospheric deposition of 10 kg S/ha · yr), the lowest in the heavily polluted north of the Czech Republic (site TP 54, ca. 10 km SE of JEZ; atmospheric deposition of 50 kg S/ha · yr). The highest $\delta^{34}S$ value of SO_2 was measured also at the relatively unpolluted Churáňov, the lowest $\delta^{34}S$ value of

SO_2 was measured in Libuš near Prague, a site characterized by a medium level of atmospheric pollution (20 kg S/ha · yr). During the course of this study, $\delta^{34}S$ values of SO_2 were measured at another 27 meteorological stations in the Czech Republic ($n = 79$). Two thirds of annual S deposition at these sites occur between October and March ("winter"), one third between April and September ("summer"). The mean $\delta^{34}S$ value of SO_2 in the northern half of the region, which includes both JEZ and NAC, was 0.3 and 4.1‰ in winter and summer, respectively. The mean $\delta^{34}S$ value of SO_2 in the southern half of the region was 0.2 and 2.5‰ in winter and summer, respectively. The mass weighted mean annual $\delta^{34}S$ value of SO_2 was similar in the most polluted north (1‰) and the relatively unpolluted south (0.9‰).

3.8. Soil and Bedrock S

Dystric Cambisol, Eutric Cambisol, and Cambic Podzol were represented in a 2.1:1:1 area ratio at JEZ. Samples of the organic (O+A) and mineral soil horizons (B and B/C) exhibited decreasing concentration of total S ([S]) and increasing $\delta^{34}S$ value with an increasing depth (Table 5). [S] averaged 0.12, 0.04, and 0.03% dry weight and $\delta^{34}S$ values averaged 2.6, 5.2, and 5.3‰ in the O+A, B, and B/C soil horizons, respectively. The differences were statistically significant ($p < 0.05$) between O+A and the mineral soil horizons (B, B/C) for both [S] and $\delta^{34}S$. The amount of total S stored in each horizon (Table 5) was primarily controlled by the volume % of the <2 mm soil fraction and the horizon's thickness. The amount of S stored in O+A was lower than in mineral soil (B+B/C) in all soil types below the elevation of 820 m (cf. Table 5 and Fig. 1). The fractions of inorganic sulfate and organic S in the O+A soil horizon were 8 and 92%, respectively. Similar to JEZ, NAC forest soil exhibited a decrease in [S] (from 0.23 to 0.05 wt.%) and an increase in $\delta^{34}S$ (from 2.0 to 2.5‰) with increasing soil depth (Table 5). The orthogneiss bedrock at JEZ was analyzed for $\delta^{34}S$ on 40 combined samples; it had an extremely low S concentration (<0.003 wt.%), with a $\delta^{34}S$ value of 5.8‰.
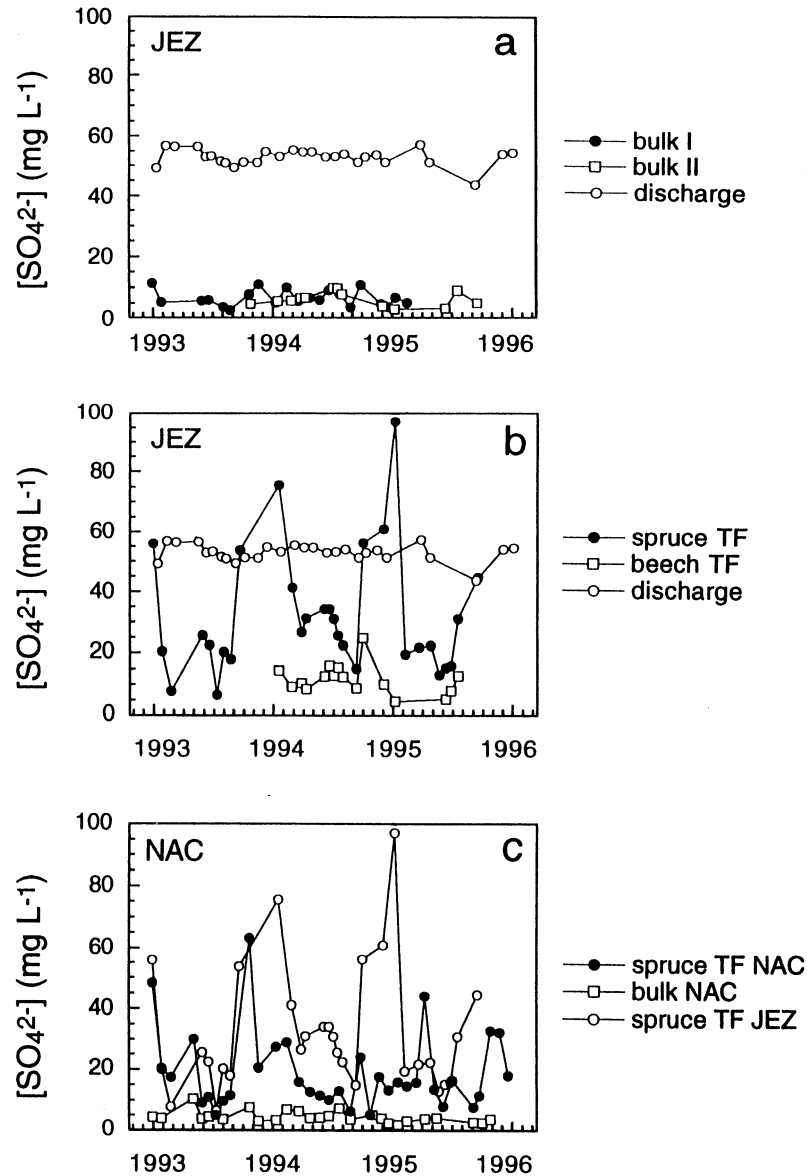
Fig. 3. Sulfate concentrations ([SO_4^{2-}]) in JEZ and NAC waters. TF, throughfall. Major ticks on the x-axis represent January 1.

3.9. Sulfur Mass and Isotope Budgets

3.9.1. JEZ sulfur mass budgets

Annual atmospheric deposition into JEZ (in kg S/ha · yr) was calculated from the precipitation total and [SO_4^{2-}] measured under each type of vegetation cover, weighted by the distribution of vegetation types within the watershed (Havel et al., 1996). Atmospheric deposition into JEZ was 40, 33, and 29 kg S/ha · yr in the hydrological years 1993, 1994, and 1995, respectively. These three years were marked by increasing water fluxes in precipitation (769, 998, and 1039 mm, respectively) and runoff (288, 337, and 474 mm, respectively). Sulfur export from JEZ via stream water, calculated from hydrological fluxes (Fig. 8) and [SO_4^{2-}], totalled 52, 58, and 85 kg S/ha in hydro-

logical years 1993, 1994, and 1995, respectively, mirroring the increase in runoff, rather than the decline in S inputs, over the period. The average mass-balance deficit over the 3-yr period was 32 ± 13 kg S/ha · yr, or 48 ± 12% of sulfur export (mean ± SE).

3.9.2. JEZ sulfur isotope budgets

The S isotope values of the annual watershed inputs and outputs were calculated as the mass-weighted mean $\delta^{34}S$

$$\delta^{34}S_{mean} = \frac{\Sigma \, \delta^{34}S_i m_i}{\Sigma \, m_i},$$

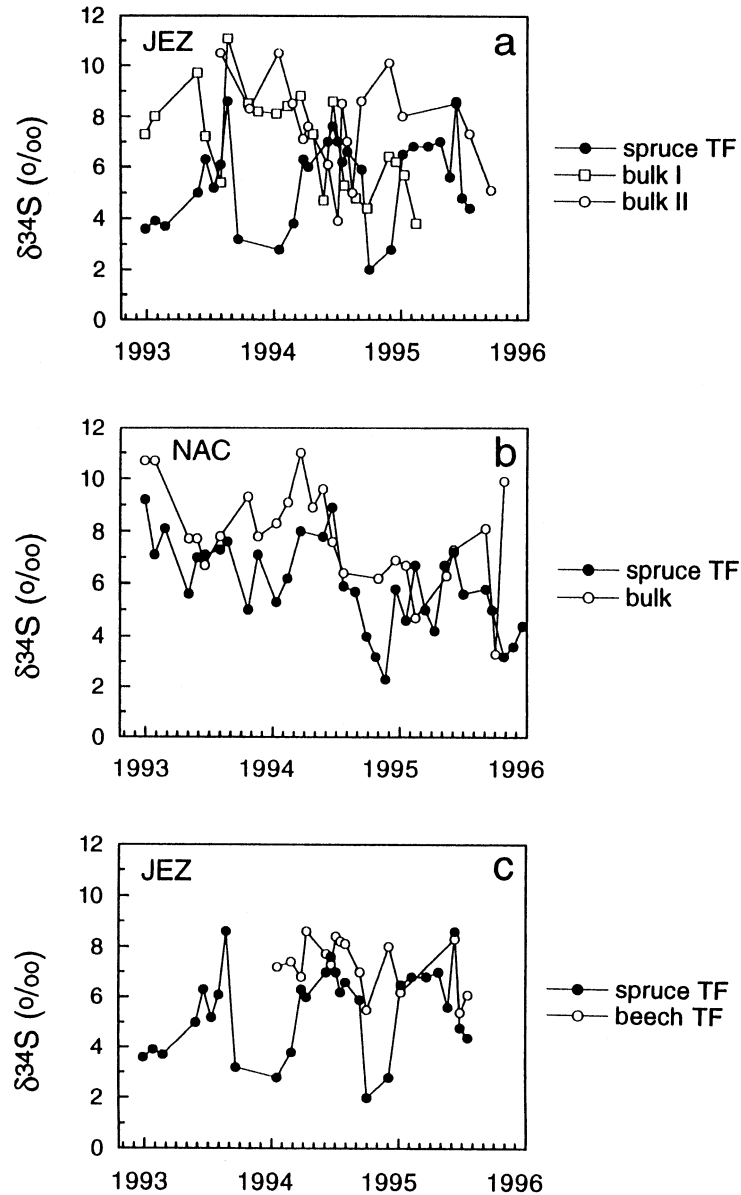where $\delta^{34}S_i$ (in ‰) relates to the i-th contribution to the

Fig. 4. $\delta^{34}S$ ratios in JEZ and NAC waters. TF, throughfall. Major ticks on the x-axis represent January 1.

watershed-level S isotope value, m_i is the mass of the *i-th* sulfur contribution. Uncertainties were calculated by first-order, second-moment error propagation.

The $\delta^{34}S_{mean}$ of annual atmospheric input into JEZ was calculated from bimonthly deposition $\delta^{34}S$ measurements during 1995 at 17 sites within the watershed (Groscheová et al., 1998), weighted by the mass of S deposited per unit area at each site and the watershed area corresponding to each site's vegetation type and elevation band. These measurements yield a mean watershed input of $5.4 \pm 0.2‰$ ($\pm$SE). The longer-term $\delta^{34}S$ measurements at three sites (one each for bulk precipitation, spruce throughfall, and beech throughfall; *large solid circles* in Fig. 1) would give a higher mean watershed input $\delta^{34}S$ of $6.7 \pm 0.3‰$. We believe that Groscheová et al.'s more widely dispersed measurements are more representative of the

average watershed inputs. The $\delta^{34}S_{mean}$ of annual export from JEZ via stream water was calculated from S mass flux and $\delta^{34}S$ values. The calculated $\delta^{34}S_{mean}$ for the JEZ output was 4.9 ± 0.2, 4.6 ± 0.2, and $4.3 \pm 0.7‰$ (means $\pm$ SE) for the hydrological years 1993, 1994, and 1995, respectively, and averaged $4.5 \pm 0.3‰$ for the three years combined.

3.9.3. Sulfur storage in the JEZ soil and its $\delta^{34}S$ value

The total amount of S stored in the JEZ soils, calculated from Table 5, was 740 kg S/ha. Thus the mass-balance deficit of 32 ± 13 kg S/ha·yr would deplete the soil S reservoir by roughly $4.3 \pm 1.7\%$ per year. The mass-weighted isotope value of the soil S reservoir (Table 5) was $4.0 \pm 0.5‰$, substantially lower than the $\delta^{34}S_{mean}$ of atmospheric inputs. The $\delta^{34}S_{mean}$ of
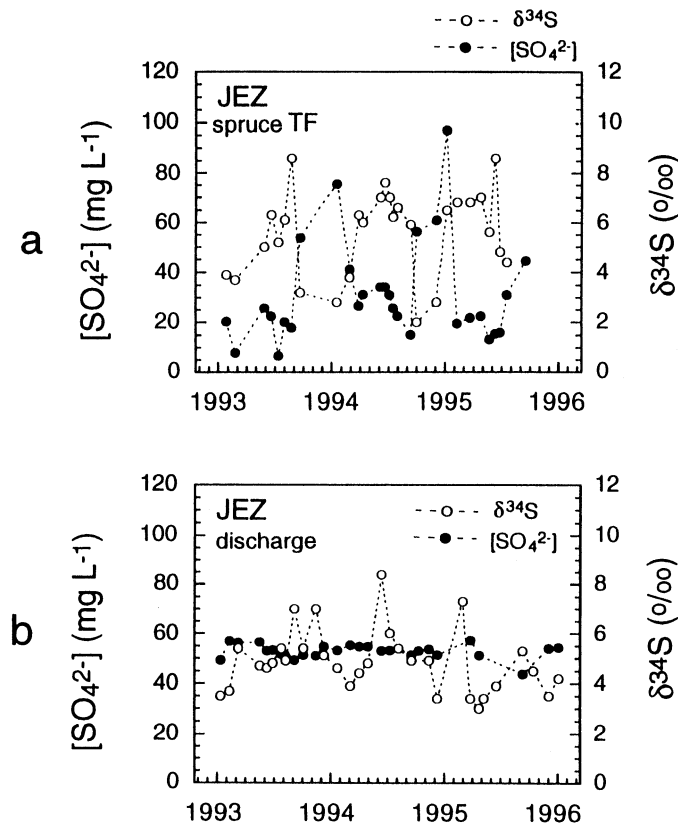
Fig. 5. Comparisons of sulfate concentrations ($[SO_4^{2-}]$) and $\delta^{34}S$ ratios for spruce throughfall (a) and surface discharge (b) at JEZ. TF, throughfall. Major ticks on the x-axis represent January 1.

stream water lies between the $\delta^{34}S_{mean}$ of atmospheric deposition and the soil S pool.

3.9.4. Annual S deposition at NAC

Precipitation totals at NAC increased from 755 to 921 to 1292 mm/yr between the hydrological years 1993, 1994, and 1995. Annual S depositions in the NAC spruce stand were 38, 34, and 31 kg/ha in 1993, 1994, and 1995, respectively. Annual mean $\delta^{34}S$ values of atmospheric input for the same three years were 6.5 ± 0.5, 6.0 ± 0.5, and $4.5 \pm 0.3‰$ in the spruce stand, averaging $5.9 \pm 0.3‰$ over the whole period.

4. DISCUSSION

4.1. Controls on Atmospheric Deposition

The proximity of the cluster of coal-burning power plants provides the key to understanding the S isotope dynamics in the atmospheric inputs into both upland study sites. Air pollution increases dramatically in winter (November-March), with the rise in electrical demand and power plant output. The $\delta^{34}S$ value of industrial emissions originating in the Most Basin is relatively low, reflecting the mean $\delta^{34}S$ value of local coal. The mean $\delta^{34}S$ of the coal was measured on 50 samples from all stratigraphic levels of the coal seam (Mach et al., 1999; Bouška et al., 1997). The mean $\delta^{34}S$ of the coal is 1.6‰ (median 2.0, SE 1.1‰), lower than the regional average $\delta^{34}S$ of airborne

SO$_2$ in Table 4 (4.7‰). Sulfate aerosols are isotopically heavier across the region (average of 7.5‰, Table 4) indicating that the SO_2-to-SO_4^{2-} conversion in the atmosphere discriminates against the lighter isotope ^{32}S, as proposed by Saltzman et al. (1983). In Saltzman's model, homogeneous reactions (fractionation factor $\alpha < 1$) are more important in warmer months, whereas in cooler months heterogeneous oxidation ($\alpha > 1$) predominates.

The seasonality in sulfate concentrations ($[SO_4^{2-}]$) and $\delta^{34}S$ values of spruce canopy throughfall at both JEZ and, to a lesser extent, NAC (Figs. 3, 4, and 5) is a result of scavenging of low-$\delta^{34}S$ sulfur dioxide from ambient air by the spruce canopy. The large surface area of spruce needles intercepts large amounts of SO_2. Low-$\delta^{34}S$ sulfur dioxide prevails in dry deposition, which is more abundant in winter, whereas high-$\delta^{34}S$ sulfate prevails in wet deposition, which dominates in summer. The percentage of dry deposition in total S deposition can be estimated from the difference between spruce throughfall and bulk precipitation. Dry deposition makes up 75% of atmospheric S deposition in spruce stands at JEZ and 61% at NAC. NAC, which is the more remote site from the Czech pollution sources, experienced dramatic spruce crown thinning during the observation period. Between 1992 and 1996, the leaf area index in the NAC spruce stand decreased from 4.7 to 2.9. This is reflected in lower $[SO_4^{2-}]$, indistinct seasonality in $\delta^{34}S$ values, and convergence of the $\delta^{34}S$ values of spruce through-
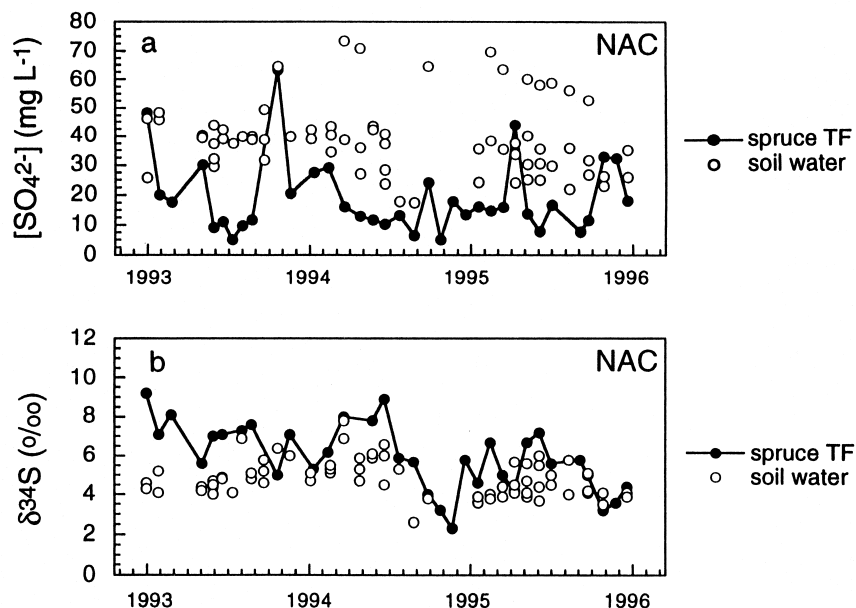
Fig. 6. Change in sulfate concentrations [SO_4^{2-}] (a) and $\delta^{34}S$ values (b) between atmospheric inputs (i.e., spruce throughfall) and soil water collected deeper than 10 cm under soil surface at NAC.

fall toward those of bulk precipitation toward the end of the observation period. Beech stands had a smaller foliar area than spruce, particularly in the winter, with a correspondingly smaller dry deposition flux (27% of S is dry deposited). [SO_4^{2-}] and $\delta^{34}S$ of beech throughfall were thus intermediary between spruce throughfall and open area precipitation.

It is important to note that [SO_4^{2-}] in open area precipitation (dominated by wet deposition) at both JEZ and NAC was very low (<10 mg/L). [SO_4^{2-}] of bulk precipitation was equally low in clearings adjacent to a spruce stand receiving as much as 126 kg S/ha · yr (elevation 782 m at JEZ, Northern Czech Republic) and in clearings in relatively unpolluted watersheds in the Southern Czech Republic (Fottová, 1992) where the annual S deposition under spruce is 12 times lower than at JEZ. This also illustrates the dominant role of dry-deposited S in Central European forest ecosystems.

Most watershed-level $\delta^{34}S$ studies lack seasonality of atmospheric inputs and/or differences in the $\delta^{34}S$ values between bulk precipitation and throughfall (Hesslein et al., 1988; Stam et al., 1992). A slightly isotopically heavier S in throughfall compared to bulk precipitation was reported by van Stempvoort et al. (1992). Nriagu et al. (1987) observed in a pristine part of Canada isotopically lighter sulfur in atmospheric sulfate during the growing season, resulting from biogenic S emissions. In Central Europe biogenic emissions have little influence on the overall seasonal $\delta^{34}S$ pattern due to the extremely high industrial emissions. Mayer et al. (1995a) reported seasonality in $\delta^{34}S$ values of atmospheric SO_2 in Germany. A 4‰ increase in $\delta^{34}S$ values of SO_2 from spring to summer was interpreted as reflecting seasonal changes in S sources. This interpretation agrees well with the situation described for JEZ and NAC in this paper. Similarly, Zhang et al. (1998) found throughfall $\delta^{34}S$ values to be slightly higher during the growing season and slightly lower in the dormant season at the Hubbard Brook Experimental Watershed (northeastern USA).

4.2. Sources of Sulfate in Streamwater and Soil Water

4.2.1. Streamwater S sources at JEZ

Sulfate concentrations in streamwater at JEZ were relatively high and showed little variation through time (Fig. 3), suggesting that they are substantially decoupled from atmospheric inputs. In addition to atmospheric S, the exported S may also contain inorganic sulfate desorbed from the soil, bedrock S, and organically cycled S. Mineralized sulfate is typically derived from the labile fraction of organic S, whereas a minor proportion of incoming S is converted to refractory humic compounds with a residence time on the order of centuries (cf., van Stempvoort et al., 1992). The behavior and fate of sulfur in the JEZ watershed is constrained by the following observations:

(i) S export by surface discharge in the hydrological years 1993, 1994, and 1995 was nearly twice the atmospheric input,

(ii) [SO_4^{2-}] in stream water increased down-slope,

(iii) [SO_4^{2-}] in stream water discharge has been decreasing steadily since the onset of hydrochemical monitoring in 1978,

(iv) the bedrock is extremely low in S, and the S pool in above-ground biomass is small compared to the soil S pool, partly due to clear-cutting following spruce die-back,

(v) leaching of dissolved and particulate organic S compounds to the bottom of the solum is significant (Novák and Přechová, 1995), and

(vi) $\delta^{34}S$ of surface discharge is lower than $\delta^{34}S$ of atmospheric input, but higher than the average $\delta^{34}S$ of the soil S pool.

We hypothesize that the excess sulfate in runoff from JEZ is derived from S stored in the soils during previous decades of very high atmospheric deposition. Atmospheric S loads in the JEZ area are directly proportional to the soft coal output in the Most Basin (Fig. 9). The mining started in the 1860s, intensified after World War II, peaked in 1988 and has been steadily
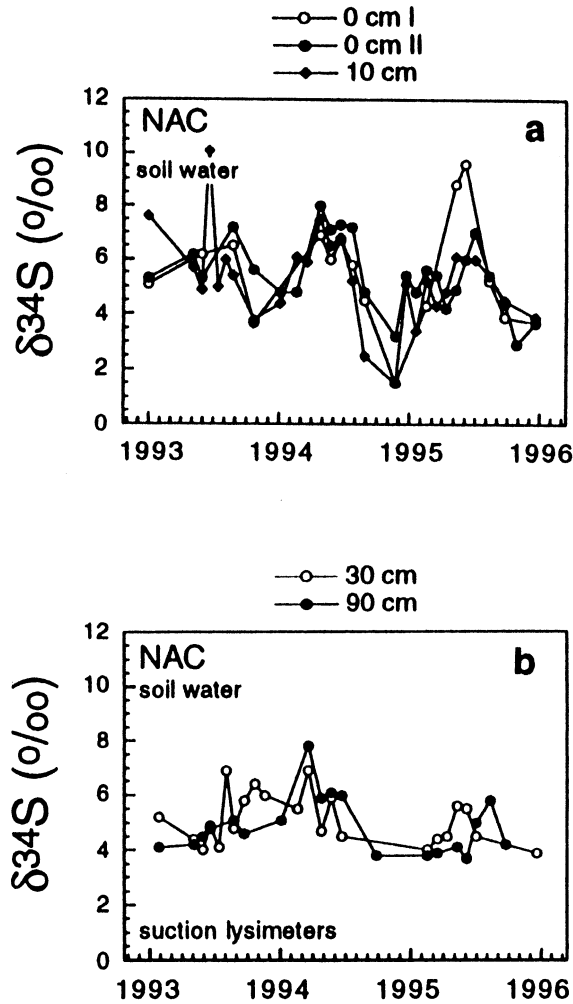
Fig. 7. Time series of δ^{34}S ratios for shallow (a) and deep (b) NAC soil water. Roman numerals I and II denote replicate sampling.

decreasing ever since. It is reasonable to assume that we are now seeing a delayed release of S deposited during the period of extremely high industrial pollution.

Sulfur stable isotope values can be used to constrain the sources of sulfate in the surface discharge and also the mean residence time for sulfur in JEZ. Figure 10 shows that δ^{34}S of bulk precipitation was higher than δ^{34}S of surface discharge for most of the 3-yr observation period. The mass-weighted δ^{34}S value of the atmospheric inputs into JEZ was either 6.7 ± 0.3‰ or 5.4 ± 0.2‰, depending on the measurements used (see section 3.9.2); by contrast, the δ^{34}S of the surface discharge over the 3-yr period was 4.5 ± 0.3‰. The discharge δ^{34}S can be viewed as a mixture of two isotopically different S sources. The isotopically heavier S source is atmospheric deposition. There are two candidates for the second unknown S source: bedrock and soil. Bedrock can be eliminated based on its high δ^{34}S value (5.8‰) and minimal content of accessory S minerals (<0.003% S by weight). The only alternative is soil S, which, indeed, meets the condition for the second source for the mixing, i.e., is isotopically lighter (4.0 ± 0.5‰) than the resulting discharge. The fraction of soil-derived S in the mixture can be estimated from the mixing equation,

$$\delta^{34}S_{OUT} = f\, \delta^{34}S_{SOIL} + (1 - f)\, \delta^{34}S_{IN}, \ or$$

$$f = \frac{\delta^{34}S_{OUT} - \delta^{34}S_{IN}}{\delta^{34}S_{SOIL} - \delta^{34}S_{IN}}$$

where the subscripts IN, OUT, and SOIL denote atmospheric inputs, stream water outputs, and soil S, and f is the fraction of S_{SOIL} in S_{OUT} ($0 < f < 1$). This mixing relationship implies that soil-derived S accounts for 64 ± 33 (mean ± SE) % of streamwater sulfate. This estimate is consistent with the 48% input-output deficit in the whole-watershed mass balance over the three years of this study (see section 3.9.1). The soil S pool at JEZ (740 kg S/ha) is sufficient to supply the average mass-balance S deficit (32 ± 13 kg/ha·yr) for at least 20 yr.

If we assume that the input-output mass balance is correct, with the excess of outputs over inputs coming from the soil sulfur pool (and thus that $f = 0.48$), we can use the equation above to estimate the average isotopic composition of soil-derived sulfate; this calculation yields $\delta^{34}S_{SOIL} = 3.6 ± 0.8‰$. This soil-derived sulfate in discharge can be interpreted as a mixture of S derived from organic soil (O+A horizons) and mineral soil (B+B/C horizons) at JEZ, with δ^{34}S = 2.5 ± 0.2 and 5.0 ± 0.6‰, respectively (Table 5). From the mixing

Table 3. Isotope composition of sulfate oxygen in spruce throughfall and soil water collected by suction lysimeters. Comparison between δ^{34}S and δ^{18}O ratios.

Date	Sample type	[SO_4^{2-}] (mg L^{-1})	$\delta^{34}S_{CDT}$ (‰)	$\delta^{18}O_{SMOW}$ (‰)
January 26, 1993	Spruce throughfall	20.1	7.1	8.7
	Lysimeter 30-cm depth	45.8	5.2	4.6
	90-cm depth	48.3	4.1	8.6
June 21, 1994	Spruce throughfall	10.2	8.9	6.4
	Lysimeter 30-cm depth	37.3	4.5	5.2
	90-cm depth	40.9	6.0	7.2
June 5, 1995	Spruce throughfall	7.9	7.2	7.0
	Lysimeter 30-cm depth	30.7	5.5	1.1
	90-cm depth	58.2	3.7	4.5
Mean	Spruce throughfall	12.7	7.7	7.4
	Lysimeter 30-cm depth	37.9	5.0	3.6
	90-cm depth	49.1	4.6	6.8

Table 4. Isotope composition of air-borne SO_2 and sulfate aerosol throughout the Czech Republic.

Site	Location	Sampling period	δ^{34}S (‰) SO$_2$	δ^{34}S (‰) Aerosol
Churáňov	40°04′N, 13°37′E	November, December 1992	+0.2	+16.9
		January, February 1993	+11.6	+10.4
		March, April 1993		+5.0
Karlov	49°58′N, 13°53′E	November, December 1992	+8.2	+4.7
		March 1993	+6.2	
		February 1994	+6.0	
Libuš	50°00′N, 14°27′E	November, December 1992	−2.4	+5.8
		March 1993		+11.2
		April 1993		+6.8
		March 1994	+7.6	
Bílý Kříž	49°45′N, 18°30′E	November 1990 to March 1991, November 1991 to March 1992		+6.0
Pec pod Sněžkou	50°41′N, 15°44′E	November, December 1992	−0.1	+6.6
Horní Jiřetín	50°35′N, 13°32′E	February 1993		+4.4
Vernéřov	50°24′N, 13°14′E	February 1993		+9.6
TP 54	50°30′N, 13°45′E	February 1993		+3.1

equation above, we can calculate that organic horizons and mineral horizons sources contribute approximately equally to the soil-derived sulfate, with 55 ± 33% of the soil sulfate flux coming from the organic horizons. Although this calculation cannot precisely partition the soil-derived sulfate in discharge between the different soil horizons, it suggests that neither one dominates.

4.2.2. Soil water S sources at NAC

The δ^{34}S values of NAC soil water samples were systematically lower than throughfall, by 1.4 ± 0.4, 1.6 ± 0.4, 1.5 ± 0.5, and 1.7 ± 0.3‰ at depths of 30, 30*, 70, and 90* cm, where asterisks indicate suction lysimeters (because this isotopic shift is calculated from paired throughfall and lysimeter samples, that is, samples from the same months, it differs

slightly from the average δ^{34}S values shown in Table 2). The mass-weighted δ^{34}S value of the NAC soil profile was 2.4 ± 0.1‰, roughly 2‰ lighter than the soil porewaters. The observation that δ^{34}S$_{input}$ > δ^{34}S$_{soil\ water}$ > δ^{34}S$_{bulk\ soil}$ suggests that the S in soil water may be a mixture of fast seepage "primary" (atmogenic) sulfate S and "secondary" soil-derived sulfate S. The fraction of soil-derived S in the mixture can be estimated from the mixing equation,

$$\delta^{34}S_{SW} = f\,\delta^{34}S_{SOIL} + (1 - f)\,\delta^{34}S_{TF}, \ or$$

$$f = \frac{\delta^{34}S_{SW} - \delta^{34}S_{TF}}{\delta^{34}S_{SOIL} - \delta^{34}S_{TF}}$$

where the subscripts SW, TF, and $SOIL$ denote soil water, throughfall, and soil S, and f is the fraction of S_{SOIL} in S_{SW}

Table 5. Sulfur storage and δ^{34}S values in soils at JEZ (pits 1–15) and NAC (pit 16).

Soil type	Area (ha)	Pit No.[a]	Horizon	S conc. (wt.%)	δ^{34}S (‰)	Thickness (cm)	vol.% of fraction < 2 mm	Density (kg m^{-3})	S pool (kg)
Eutric	35	1, 10, 11	O+A	0.03	2.2	8	89.6	380	2 960
Cambisol (JEZ)			Bv	0.02	3.3	18	49.6	1160	7 230
			B/C	0.01	4.6	53	63.4	840	9 850
Dystric	133	2, 8, 13,	O+A	0.14	2.7	6.5	93.6	330	36 900
Cambisol (JEZ)		14, 15	Bv	0.02	4.2	11.5	68.3	740	15 500
			B/C	0.02	3.8	45	71.0	650	55 000
Eutric	29	6, 9 12	O+A	0.05	2.6	10	87.2	550	6 900
Cambisol (JEZ)			Bv	0.02	6.2	14	71.6	780	4 540
			B/C	0.01	6.7	37	87.2	430	4 030
Cambic	62	3, 4, 5	O+A	0.12	2.8	14	91.0	310	28 000
Podzol (JEZ)			Bsv	0.02	6.7	22	64.0	760	13 500
			B/C	0.02	6.4	28	77.0	380	10 100
Dystric	25	16	O+A	0.23	2.0	6	96.0	190	6 620
Cambisol (NAC)			Bv	0.06	2.4	6	87.5	480	4 280
			B/C	0.05	2.5	78	92.0	280	27 500

[a] For sampling sites see Figure 1.
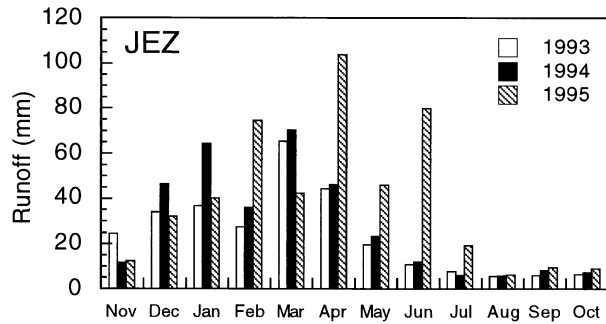
Fig. 8. Water runoff from JEZ between hydrological years 1993 and 1995.

Fig. 10. Comparison of $\delta^{34}S$ of present-day atmospheric input in the clearings prevailing on the southern slope of the Krušné hory Mts. (bulk I + II) and $\delta^{34}S$ of JEZ output by surface discharge. Roman numerals I and II denote replicate sampling.

$(0 < f < 1)$. From this mixing equation, we calculate that soil-derived S accounts for 37 ± 11, 40 ± 10, 40 ± 12, and $43 \pm 8\%$ of the soil water sulfate in the lysimeters at 30, 30*, 70, and 90* cm depths, respectively. Consistent with our observations at JEZ, this calculation indicates that a substantial fraction of S in soil porewaters is "secondary" soil-derived sulfate rather than "primary" atmogenic sulfate.

Our lysimeters sample soil water concentrations but do not measure seepage fluxes, so we cannot directly calculate a mass balance for S at NAC. However, we can infer the total seepage flux, and the net flux from soil pools, from the isotope mixing model presented above. If we take $40 \pm 10\%$ as the fraction of soil-derived S in the soil water sulfate, the remaining $60 \pm 10\%$ must be the throughfall flux over the lysimeters at NAC (35 ± 5 kg/ha · yr; Table 3). Thus, the seepage S flux is approximately $1/(1-f)$ times the throughfall flux, or 58 ± 13 kg/ha · yr, and the flux from the soil pool is approximately $f/(1-f)$ times the throughfall flux, or 23 ± 10 kg/ha · yr. The soil S pool at NAC (1500 kg/ha; Table 5) is large enough to supply this flux for roughly 60 yr.

4.2.3. Organic and inorganic S pools in soils

For interpreting the roles of organic and inorganic forms of S in watershed soils, it would be useful to know their isotopic
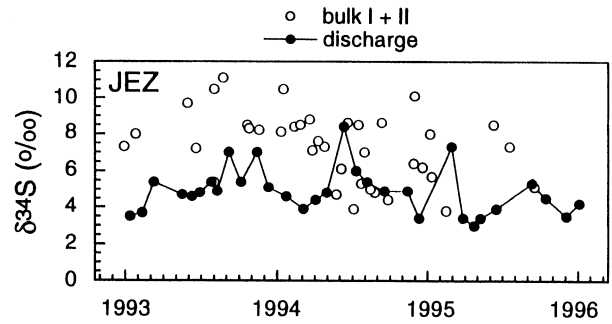
values. These are not known at JEZ, but Table 6 gives $\delta^{34}S$ values of individual S forms in soil for NAC along with four different spruce-forested sites in Europe. Similar to NAC, Aheden, Skogaby, and Aubure have a 100-yr or longer history of spruce vegetation. $\delta^{34}S$ speciation in soil of these four sites is similar in that:

(i) $\delta^{34}S_{organic}$ is higher than (or equal to) $\delta^{34}S_{total}$,

(ii) $\delta^{34}S_{inorganic}$ is lower than (or equal to) $\delta^{34}S_{total}$,

(iii) the shallowest soil depth (0 to 5 cm) has always the lowest $\delta^{34}S$ of both organic and total S compared to deeper soil layers (5 to 10, 10 to 20 cm).

NAC, the most polluted site in Table 6, contains the highest proportion of organic S (95%) in the topmost soil layer (0 to 5 cm), very close to that at JEZ (92 to 96%, see below). In general, the $\delta^{34}S_{organic} > \delta^{34}S_{inorganic}$ trend, with both values increasing below the soil depth of 5 cm, indicates that isotopically selective interconversions between organic and inorganic S forms take place as atmogenic sulfur moves downward in the soil profile.

Organic S is mineralized via two different pathways: the C-bonded S is mineralized biologically (during oxidation of organic C by soil microorganisms in their quest for energy), and the ester-bonded S is mineralized biochemically (through
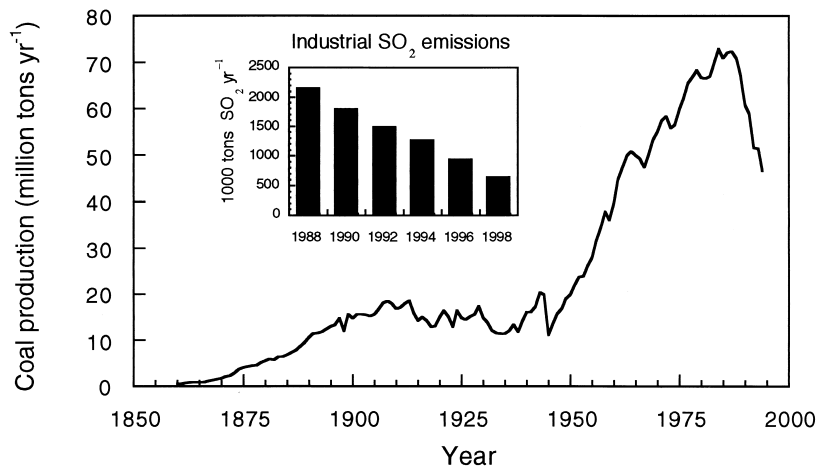

Fig. 9. Trends in annual soft coal production in the Northern Czech Republic (Most Basin). Inset, nationwide industrial emissions of SO_2.

Table 6. Isotope composition of organic and inorganic sulfur in *Picea abies* soils at five sites along a North-South European transect (*Adapted from Novák, 1999*).

Site[a]	Depth (cm)	Organic S (%)	$\delta^{34}S_{organic}$ (‰)	Inorganic S (%)	$\delta^{34}S_{inorganic}$ (‰)	Content of S_{total} ($\mu g\ g^{-1}$)	$\delta^{34}S_{total}$ (‰)
Aheden	0–5	86	5.4	14	5.4	100	5.4
	5–10	68	8.2	32	3.8	100	6.8
	10–20	59	6.6	41	4.1	100	5.6
Skogaby	0–5	76	6.4	24	4.0	230	5.8
	5–10	67	10.2	33	4.5	100	8.3
	10–20	47	8.8	53	6.2	100	7.4
Načetín	0–5	95	2.2	5	1.6	1500	2.2
	5–10	88	4.7	12	3.2	500	4.5
	10–20	53	7.8	47	3.6	400	5.5
Aubure	0–5	84	1.6	16	0.1	330	1.4
	5–10	56	5.3	44	2.3	100	4.0
	10–20	11	12.1	89	3.9	100	4.8
Monte di Mezzo[b]	0–5	94	n.d.	6	n.d.	430	1.0
	5–10	83	−0.3	17	2.7	330	0.2
	10–20	81	−0.7	19	0.9	330	−0.4

[a] Aheden − Sweden (64°13′N, 19°30′E), Skogaby − Sweden (56°33′, 13°13′), Načetín = NAC, Aubure − France (48°12′N, 7°11′E), Monte di Mezzo − Italy (41°45′N, 14°53′E). Inorganic = free + adsorbed sulfate S, organic = ester + C-bonded S; n.d. = not determined.

[b] Spruce planted on agricultural land in 1958.

enzymatic catalysis external to the cell membrane driven by the need for the end product). Inorganic sulfate is the main end product in both cases (McGill and Cole, 1981). NAC soil contains 2, 1, and 0% of ester-bonded S, and 93, 87, and 53% of C-bonded S at the depths of 0 to 5, 5 to 10, and 10 to 20 cm, respectively (unpublished data by Novák complementary to Table 6). $\delta^{34}S$ of ester-bonded S is 1.4 and 2.3‰ between 0 and 5 and 5 to 10 cm, which is lower than the $\delta^{34}S$ of inorganic sulfate. This agrees well with the data by Zhang et al. (1998) who also found isotopically lighter S in soil ester sulfates than in inorganic sulfates. The small abundance of esters in the NAC soil, however, indicates that the role of S storage in the C-O-S bonds of esters is probably minor.

In an incubation experiment, in which $^{35}SO_4^{2-}$ was applied on the soil surface, the relative contribution of chemically reacted (mostly organic) radiotracer to total activity increased with depth, constituting 8 and 40% of inorganic $^{35}SO_4^{2-}$ activity in the organic (AE) and mineral (Bvs) soil horizon at JEZ, respectively, after 13 weeks (Novák and Přechová, 1995). JEZ soil under spruce contained 78% of organic S, 18% of inorganic sulfate S, and 4% of reduced inorganic S (combined data for the organic and mineral soil horizons to a depth of 35 cm).

At JEZ, sulfur in the organic soil horizons at the beginning of the observation period (November 1992) was made up by 96% organic S and 4% inorganic S (Novák and Přechová, 1995). At the end of the observation period (June 1996; this study) the $S_{organic}$-to-$S_{inorganic}$ ratio was 92:8. This indicates that slightly more S of that released from the organic soil horizon to the stream was derived from the organic than the inorganic pool. In conjunction with the mixing model results presented in section 4.2.1, this implies that organically cycled S from the humus layer contributed at least half of the soil-derived sulfate in the JEZ discharge. Thirty or more percent of total S in discharge was organically cycled.

4.3. Origins of Isotopically Light Soil S Pools

Why is JEZ soil S isotopically lighter than sulfur of the atmospheric deposition? We propose two different mecha-

nisms, that are not mutually exclusive. First, the average $\delta^{34}S$ of atmospheric inputs to the watershed was lower in previous decades, when more of the watershed was covered with spruce forest more efficiently intercepting dry deposition with low $\delta^{34}S$ values. Only with the die-back of the original spruce stands has bulk precipitation, with its higher $\delta^{34}S$, become a major S input to the watershed. To the extent that this mechanism explains the low $\delta^{34}S$ of the JEZ soils, it also constrains their S residence time, since it indicates that a sizable proportion of S exported via stream in the 1990s is derived from a sulfur reservoir older than the time of defoliation, i.e., older than 20 yr (1975 to 1995). Such scenario, however, does not apply to NAC with continuous spruce growth.

Second, biologic fractionation can lower the $\delta^{34}S$ of the soils at JEZ and NAC. During assimilation, isotopically lighter S is preferentially incorporated into the organic matter (cf., Krouse et al., 1992). Such fractionation fits the pattern observed at JEZ: the $\delta^{34}S$ value of the organic soil horizons is the lowest in the system (2.4 ± 0.2‰, which is 30 ± 0.3‰ lower than $\delta^{34}S_{input}$). With increasing depth, $\delta^{34}S_{soil}$ increases, approximately to the value of atmospheric input (5.0 ± 0.6‰ vs. 5.4 ± 0.2‰). The sites in Table 6 show similar fractionation effects, with $\delta^{34}S_{total}$ in the organic horizon lower than the average $\delta^{34}S_{input}$ (on average by 2.3‰; Novák, 1999). Fuller et al. (1986) explained lower $\delta^{34}S$ of organic soil S compared to atmospheric input at Hubbard Brook by a biologic fractionation. Similarly, lower $\delta^{34}S$ of soil and vegetation compared to atmospheric input was interpreted by van Stempvoort et al. (1992) as a result of isotope selectiveness of assimilation. In addition to assimilation, mineralization of organic compounds also contributes to S isotope redistribution (Gebauer et al., 1994; Novák et al., 1996; Zhang et al., 1998; Alewell and Gehre, 1999). The resulting "secondary" sulfate S is isotopically lighter than the residual organic S, which largely remains in situ.

At NAC, the presence of secondary, biologically cycled sulfate in soil water (>10 cm depth) is documented by lower sulfate $\delta^{18}O$ in soil water compared to spruce throughfall (Table 3). This negative $\delta^{18}O$ trend is caused by formation of

new sulfate incorporating mineralized sulfur (Mayer et al., 1995a). Importantly, $\delta^{34}S$ of soil water (>10 cm depth) paralleled this negative $\delta^{18}O$ trend. The NAC soil profile shows opposite but complementary patterns in bulk soil (higher $\delta^{34}S$ values in deeper horizons) and soil water (lower $\delta^{34}S$ values in deeper horizons). In summary, mineralization-related S isotope redistribution at NAC is evidenced by the $\delta^{18}O$ analogy between atmospheric deposition and soil water, the opposite but complementary vertical S isotope trends in soil and soil water and the $\delta^{34}S_{organic} > \delta^{34}S_{inorganic}$ pattern in Table 6.

The observation period of this study was unique in that it represented a sequence of 3 yr with increasing precipitation totals. The response of JEZ to higher rainfall corroborates the scenario of mobilization of previously stored, pollution-derived soil S. Over the 3 yr, the rates of both industrial pollution and atmospheric deposition of S into the watershed decreased, but over the same period the increased water fluxes remobilized an increasing amount of S from the watershed. As annual S export from JEZ increased, its integrated $\delta^{34}S$ value (4.9, 4.6, and 4.3‰) converged toward that of the humus layer soil reservoir (2.6‰) indicating the importance of organically cycled S in discharge sulfate.

A number of other watersheds in Europe and North America are now experiencing declining industrial S pollution, and also have S exports that exceed present-day atmospheric inputs (Driscoll et al., 1998). The reasons for the high S export may be site-specific. The Hubbard Brook Experimental Watershed, NH, USA, is similar to JEZ in the presence of an elevational gradient and stratified vegetation (broad-leaves in the lower, conifers in the upper part). In contrast to the much more polluted JEZ, $[SO_4^{2-}]$ at Hubbard Brook decreases downstream. Fuller et al. (1986) suggested the existence of a localized S source in the upper part of Hubbard Brook, such as enhanced capture of S from ambient air by conifers at high elevations. We have shown this process to play a key role in JEZ. Because JEZ stream water $[SO_4^{2-}]$ exhibits an opposite elevational gradient than Hubbard Brook, the processes controlling $[SO_4^{2-}]$ in stream water along the slope may not be identical in both watersheds. Yet, there are two aspects in which the $\delta^{34}S$ features of JEZ and NAC are consistent with those of the Hubbard Brook (Zhang et al., 1998): compared to the atmospheric input, Hubbard Brook also exhibited lower $\delta^{34}S$ of stream water and lower $\delta^{34}S$ in deep soil water.

5. CONCLUSIONS

Stable isotopes were used to follow the transport pathways and biogeochemical transformations of sulfur in the industrially polluted part of Central Europe. The summer "background" $\delta^{34}S$ values of SO_2 in the atmosphere were higher than the $\delta^{34}S$ values of coal-derived S emissions which polluted the air mostly in winter. The $\delta^{34}S$ values of sulfate aerosol were higher than both $\delta^{34}S$ of coal-derived S emissions and atmospheric SO_2 suggesting discrimination against ^{32}S during the atmospheric SO_2-to-SO_4^{2-} conversion. Because of the isotope selectiveness of atmospheric oxidation of SO_2, care must be taken when ascribing a specific, isotopically distinct pollution source to sulfur found in damaged ecosystems. Clearings and forests at JEZ and NAC received atmospheric S of contrasting isotope composition (Fig. 2b). The $\delta^{34}S$ values of bulk precipitation in

the clearings were higher than the $\delta^{34}S$ values in spruce stands. In addition, seasonality was observed in spruce throughfall, with $\delta^{34}S$ values as low as 2‰ in winter and as high as 8‰ in summer. Enhanced scavenging of low-$\delta^{34}S$ sulfur dioxide by the foliage was responsible for both these phenomena. The sulfur isotope composition of soil water was indistinguishable from atmospheric input in the humus layer, but was significantly lower in the solum (Fig. 6b). The $\delta^{18}O$ values were also lower in the soil water sulfate than in sulfate deposited from the atmosphere. JEZ surface discharge had lower $\delta^{34}S$ value than present-day atmospheric deposition into the whole watershed (Fig. 10). At both sites $\delta^{34}S_{IN} > \delta^{34}S_{OUT} > \delta^{34}S_{SOIL}$. The soil S pool was not only the isotopically lightest potential source for S in watershed output (bedrock had a high $\delta^{34}S$), but also exhibited a vertical trend (higher $\delta^{34}S$ in deeper soil horizons) which complemented the opposite trend observed in soil water (lower $\delta^{34}S$ in deeper soil horizons). Analysis of possible scenarios that would result in different S isotope composition of rainfall, discharge and soil suggested that a biologic S isotope fractionation is involved. The candidates were uptake of atmospheric S by vegetation and mineralization of the C-S bond in the soil. Using the isotope mass balance approach, the proportion of the soil derived S to sulfate in watershed output was estimated as 64 ± 33 and $40 \pm 10\%$ for JEZ and NAC, respectively. We propose that the extremely negative watershed S input/output budget (output $\gg$ input) was caused by delayed removal of S accumulated over the decades-long period of heavy industrial pollution. The anthropogenic S was stored largely in an organic form in the humus layer. Approximately 30% of total sulfate S in the discharge were organically cycled.

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