

# Isotopic evidence for processes of sulfur retention/release in 13 forested catchments spanning a strong pollution gradient (Czech Republic, central Europe)

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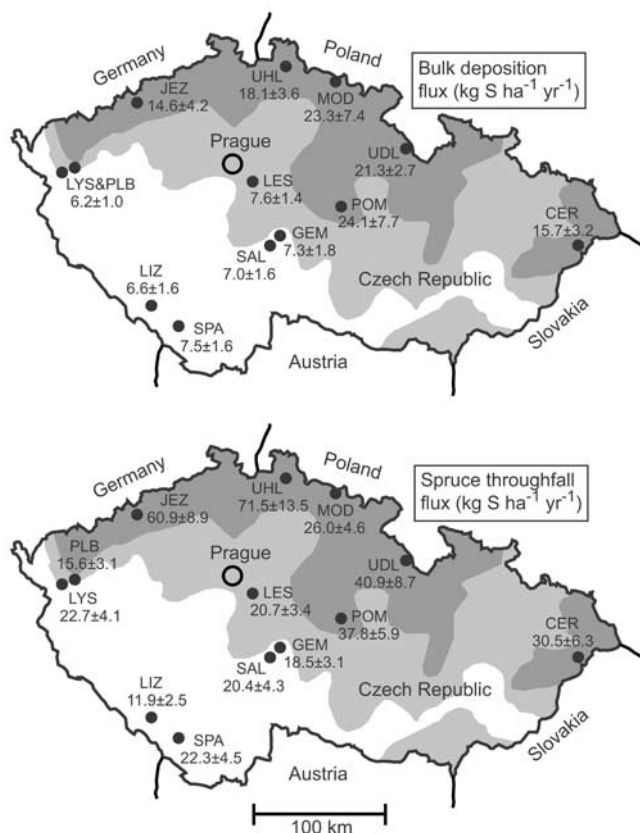
[1] Sulfur isotope systematics were studied in 13 small catchments in the Czech Republic, similar in topography (V-shaped valley) and vegetation (Norway spruce). The sites differed in elevation, rainfall, bedrock, soil type and S pollution. Across the sites,  $\delta^{34}\text{S}$  values decreased in the order: bulk deposition > runoff > spruce throughfall > C-horizon soil > A/B-horizon soil > O-horizon soil > bedrock (means of 5.5, 4.8, 4.7, 4.6, 4.2, 3.1 and 1.5‰, respectively). Some of the sites had a net export of S, while others accumulated S. Sites exporting S were located in the polluted north where atmospheric S input started to decrease in 1987. Sites retaining S were located in the relatively unpolluted south. Sulfur isotope composition of runoff depended on whether the catchment accumulated or released S. Sites releasing S had runoff  $\delta^{34}\text{S}$  values lower than deposition. In contrast, sites retaining S had runoff  $\delta^{34}\text{S}$  values higher than deposition. Across the sites, the  $\delta^{34}\text{S}$  values of runoff were not correlated with  $\delta^{34}\text{S}$  values of bedrock, indicating that the contribution of bedrock to S in runoff was negligible. The  $\delta^{34}\text{S}$  values of runoff were strongly positively correlated with the  $\delta^{34}\text{S}$  values of soil. Sulfur present in the C-horizon of soils was mainly derived from atmospheric deposition, not bedrock. Sulfur isotope mass balances were constructed for each catchment, making it possible to quantify the difference between  $\delta^{34}\text{S}$  values of the within-catchment source/sink of S and runoff S. Sulfur isotope mass balances indicated that the sink for the retained S at unpolluted sites and the source of the released S at polluted sites were isotopically fractionated by the same amount relative to runoff S. Inorganic and organic processes were considered as possible causes for this observation. Biological S cycling involves a variety of reactions, some of which fractionate S isotopes. In contrast, adsorption/desorption of inorganic sulfate in soil and weathering of S-containing minerals do not fractionate S isotopes. Therefore the within-catchment source/sink of S must be largely a result of biological S cycling. Organic S cycling played an important role over a wide range of atmospheric S inputs from 13 to 130 kg S ha<sup>-1</sup> yr<sup>-1</sup>.

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## 1. Introduction

[2] The Black Triangle, comprising the northern Czech Republic, southeastern Germany and southwestern Poland, has been one of the most polluted industrial regions of the world [Cerny and Paces, 1995; Wesselink et al., 1995;

Alewell et al., 1997; Vile et al., 2000; Jedrysek et al., 2002; Knoller et al., 2004]. Between 1975 and 1995, sulfur emissions from burning of high-sulfur coal in two dozen power plants contributed to massive spruce die-back on an area of more than 1000 km<sup>2</sup> [Innes, 1993; Hunova et al., 2004; B. Moldan, unpublished data, 2004]. Since 1987, i.e., in less than 20 years, industry restructuring and installation of scrubbers in power plants have reduced industrial S emission rates by more than 90% [Dostalova et al.,



**Figure 1.** Spatial variability of sulfur bulk deposition and spruce throughfall fluxes ( $\text{kg S ha}^{-1} \text{yr}^{-1}$ ,  $\pm 1$  standard error) for the 13 study catchments. Shading indicates approximate regions of average S deposition  $<15$ ,  $15\text{--}25$ , and  $>25 \text{ kg S ha}^{-1} \text{yr}^{-1}$  (white, light gray, and dark gray, respectively), according to Fiala *et al.* [1998]. Both bulk deposition and spruce throughfall are highest in the north (JEZ, UHL and UDL) and lowest in southwest (LYS, PLB, LIZ, SPA, SAL, GEM and LES). LYS and PLB share the same bulk deposition collector.

2004]; by comparison, elsewhere in Europe and Northern America, industrial emission rates have decreased by 40 to 60% over the past 30 years [Ambuster *et al.*, 2003; Likens *et al.*, 2002; Eimers and Dillon, 2002; Moldan *et al.*, 2004]. In addition to the temporal gradient of easing pollution, a sizable geographical S pollution gradient has been reported in Central Europe [Fottova, 2003]. In 1987, a record high annual atmospheric S deposition of  $130 \text{ kg S ha}^{-1} \text{yr}^{-1}$  occurred in the northern Czech Republic [Cerny, 1993], while ecosystems in the Southern Czech Republic, just 150 km southward, received only *ca.*  $13 \text{ kg S ha}^{-1} \text{yr}^{-1}$ , i.e., 10 times less [Santrösch *et al.*, 1988]. Here we discuss the fate of anthropogenic S in 13 forested catchments in the Czech Republic spanning this sharp deposition gradient.

[3] Currently, many catchments in the industrial world are losing more S via stream water than they are receiving from atmospheric S inputs [Mitchell *et al.*, 2001; Hruska and Kram, 2003; Schulz *et al.*, 2004; Novak *et al.*, 2005a]. Net sulfate export from catchments delays the recovery of acid-

impacted surface waters [Prechtel *et al.*, 2001; Prietzel *et al.*, 2001]. The excess S exported from forested catchments may originate from desorption of soil sulfate, mineral weathering or mineralization of organic S [Driscoll *et al.*, 1998]. If the excess S in stream discharge is derived from bedrock weathering, it will persist for the indefinite future, but if it is derived from release of stored pollutant S, it will gradually decline as the S stored in the catchment is slowly depleted. A S isotope mass balance can constrain the origin of the excess S in stream water, assuming that the mixing end-members are isotopically distinct [Finley *et al.*, 1994; Novak *et al.*, 1995; Mayer *et al.*, 1995, 2001; Alewell and Giesemann, 1996; Morth *et al.*, 1999]. We measured S fluxes and isotope compositions of bulk deposition, spruce/beechn canopy throughfall, and stream discharge over a 12-month period in 13 small catchments. The  $\delta^{34}\text{S}$  values of three main soil horizons and fresh bedrock in each catchment were known. Our first objective was to evaluate whether S fluxes and S pools within the catchments had contrasting isotope compositions. Our second objective was to construct sulfur mass balances and sulfur isotope mass balances for individual catchments for the hydrological year 1997. We used these mass balances to study the relationship between net retention/release of S and the pollution level. We further investigated whether S isotope composition of the discharge depended on net accumulation/release of S from the catchment. Using S isotopes, we identified the sink for the retained S and the source of the released S at individual sites. The relationship between the S isotope systematics and S mass balances across our 13 catchments allowed us to test whether the sinks for the retained S were the same as the sources of the released S.

## 2. Material and Methods

### 2.1. Study Sites

[4] Nine of the 13 study sites (JEZ, UHL, MOD, UDL, CER, SPA, LIZ, LYS and PLB) are located in the mountainous border regions of the Czech Republic. Four sites (LES, GEM, SAL and POM) are located in a highland southeast of Prague (Figure 1) [Fottova, 2003]. The sites are similar in topography (V-shaped valleys) and, for the past 200 years, also in vegetation (predominantly Norway spruce, *Picea abies*). Elevation, aspect, annual precipitation, bedrock, soil type and the stage of pedogenesis all vary among the sites (Table 1). Between 1975 and 1995, most mature spruce stands at JEZ, UDL and UHL, situated in the industrial north, died back owing to atmospheric pollution and were harvested (Table 2). By 1997, the clearings began to be regenerated by European birch (*Betula verrucosa*) and mountain ash (*Sorbus aucuparia*) [Peters *et al.*, 1999]. Intact Norway spruce stands covering 100% of the catchment's surface area survived at SAL and PLB. At LES and JEZ, undamaged European beech (*Fagus sylvatica*) stands covered a significant portion of the catchment's area (42 and 29%, respectively), mostly at lower elevations. At the remaining nine sites, more than 60% of the area was still covered by closed-canopy spruce stands (Table 2). Anthropogenic S deposition greatly exceeded other atmospheric sources; the contribution of sea-spray derived S to total

Table 1. Study Site Characteristics

Site	Location	Elevation (m a.s.l.)	Mean slope, deg	Aspect	Catchment Area, ha	Bedrock	Soil Type	Prevailing Wind Direction	Mean Temperature, °C	Annual Precipitation, mm
CER Cervik	49°27' N, 18°23' E	640–961	15	east	185	flysh-istebnan sandstone	dystric cambisol	west	+6.2	1155
GEM Anenský potok	49°34' E, 15°05' E	480–540	5.5	north	27	sillimanite-biotite paragneiss	dystric cambisol	west	+6.9	644
JEZ Jezerní	50°32' N, 13°28' E	475–924	10	south	261	two-mica gneiss	dystric cambisol	west	+5	934
LES Lesní potok	49°58' N, 14°49' E	400–495	3.5	north	70	biotite granite	dystric cambisol	west	+7	613
LIZ Na Lizu	49°04' N, 13°41' E	828–1024	8	east	99	sillimanite-biotite paragneiss	dystric cambisol	west	+4.9	905
LYS Lysina	50°03' N, 12°40' E	829–949	6	east	27	leucocratic granite	spodo-dystric cambisol	west	+5	934
MOD Modry potok	50°42' N, 15°42' E	1010–1554	13	south-east	262	muscovitic mica-schist	cambic podzol	west	+2.9	1666
PLB Pluhuv Bor	50°04' N, 12°46' E	690–804	6.5	east	22	serpentinite	eutrophic cambisol	west	+6	934
POM Polomka	49°47' N, 15°45' E	512–640	6.5	north	69	migmatite-orthogneiss, paragneiss	dystric cambisol, stagno-gleyic cambisol	west	+6.3	695
SAL Salacova Lhota	49°31' N, 14°59' E	557–744	5.5	south	168	sillimanite-biotite paragneiss	dystric cambisol, stagno-gleyic cambisol	west	+6	572
SPA Spalencec	48°55' N, 13°59' E	795–858	3.5	west	53	granulite gneiss	dystric cambisol	west	+5.5	816
UDL U dvou loucek	50°13' N, 16°29' E	880–950	6	south-west	33	two-mica gneiss	spodo-dystric cambisol, cambic podzol	west	+5	1308
UHL Uhlirská	50°49' N, 15°08' E	780–870	2.5	south	187	granite	spodo-dystric cambisol, cambic podzol	west	+4	1231

atmospheric S was between 2 and 14%, and the natural S deposition in pre-industrial times did not exceed  $2 \text{ kg ha}^{-1} \text{ yr}^{-1}$  [Novak *et al.*, 2001b]. In 1997, mean water fluxes in streams draining the catchments ranged between  $0.5 \text{ L s}^{-1}$  (GEM), and  $136 \text{ L s}^{-1}$  (MOD; mean of  $30 \text{ L s}^{-1}$  across the sites). On the basis of  $\delta^{18}\text{O}$  values of water inputs and outputs, the mean residence time of atmospheric water in the catchments was between 0.5 and 1.5 years [Buzek *et al.*, 1991, 1995]. The contribution of the rainfall component to stream runoff was about 20% and soil water contributed on average 40%, while the rest of stream runoff was formed by groundwater (data for LYS and JEZ). Detailed descriptions and/or hydrochemical mass balances for individual sites were given by Paces [1985], Kram and Hruska [1994], Novak *et al.* [1995], Cerny [1995], Kram *et al.* [1997], Fottova and Skorepova [1998], Hruska *et al.* [2002], Fottova [2003], and Shanley *et al.* [2004]. Stable S isotope systematics were previously reported by Novak *et al.* [1995, 1996, 2000, 2001a], and Groscheova *et al.* [1998]. Soil incubation experiments using the artificial radioisotope  $^{35}\text{S}$  were performed by Novak and Prechova [1995] and Novak *et al.* [2004]. Sulfate oxygen isotope data were reported by Novak *et al.* [2005b].

## 2.2. Sampling

[5] Each of the 13 catchments were monitored monthly beginning 1 November 1996 and ending 31 October 1997 (hydrological year 1997). Cumulative samples of bulk deposition (13 sites), spruce canopy throughfall (13 sites) and beech canopy throughfall (two sites, JEZ and LES) were complemented by monthly grab samples of runoff (13 sites). Two samplers installed 5 m apart in a clearing were used to sample bulk (i.e., open canopy) deposition. A single composite sample was prepared for analysis by combining these two samples. For the collection of spruce throughfall (all sites), and beech throughfall (JEZ and LES), an array of nine samplers in a regular  $10 \times 10 \text{ m}$  grid underneath the closed forest canopy was used [Mayer and Ulrich, 1974]. The nine throughfall samples were combined to yield a single composite sample. The samplers were polyethylene (PE) funnels ( $122 \text{ cm}^2$ ) fitted to PE 1-L bottles placed 120 cm above the ground. Snow (circa November to March) was sampled using plastic vessels ( $380 \text{ cm}^2$ ) with PE bags. About 1 L of stream water was taken at the catchment outlet at the end of each monthly interval.

[6] Sulfur concentrations and  $\delta^{34}\text{S}$  values of soils from 6 catchments (CER, JEZ, LIZ, LYS, PLB and SAL) are taken from Novak *et al.* [1996]. The soils were sampled in 1994. S concentration and isotope values were measured in three separate soil pits for each of three soil horizons (O, A/B, C). Soil from horizons Oi, Oe, and Oa, representing on average the top 12 cm of the profiles, was pooled by mass. The thickness of the A/B and C horizons averaged 30 and 40 cm, respectively. The distance between the three soil pits in each catchment was at least 50 m. For JEZ, S concentration and  $\delta^{34}\text{S}$  data from another 12 soil pits were from Novak *et al.* [2000]. Soil horizons O, A/B and C were sampled in each pit in 1997. For the current paper, soil horizons O, A/B and C were sampled in the seven remaining catchments (GEM, LES, MOD, POM, SPA, UDL and

**Table 2.** Fluxes and Isotopic Compositions of S at Study Catchments, Water Year 1997

Site	Flux Type <sup>a</sup>	Area, %	Water Flux, mm yr <sup>-1</sup>	SO <sub>4</sub> -S, mg L <sup>-1</sup>	S Flux, kg ha <sup>-1</sup> yr <sup>-1</sup>	δ <sup>34</sup> S, ‰ <sup>b</sup>
CER	bulk dep	15	1505 ± 354	1.05 ± 0.24	15.7 ± 3.2	4.4 ± 0.3
	spruce TF	85	1088 ± 341	2.81 ± 0.91	30.5 ± 6.3	3.6 ± 0.4
	avg dep <sup>c</sup>	100	1151 ± 343	2.39 ± 0.75	29.3 ± 6.2	3.7 ± 0.4
	runoff	100	971 ± 356	6.14 ± 0.05	59.7 ± 21.7	3.1 ± 0.2
GEM	bulk dep	6	638 ± 160	1.14 ± 0.07	7.3 ± 1.8	5.1 ± 0.3
	spruce TF	94	337 ± 82	5.49 ± 0.74	18.5 ± 3.1	4.5 ± 0.3
	avg dep	100	355 ± 87	5.02 ± 0.67	17.8 ± 3.0	4.5 ± 0.3
	runoff	100	61 ± 13	16.09 ± 1.41	9.9 ± 2.9	4.5 ± 0.2
JEZ	bulk dep	3	705 ± 94	2.07 ± 0.51	14.6 ± 4.2	6.0 ± 0.2
	spruce TF	7	577 ± 92	10.55 ± 1.67	60.9 ± 8.9	3.5 ± 0.4
	beech TF <sup>d</sup>	90	380 ± 69	5.28 ± 1.20	20.1 ± 5.8	5.4 ± 0.3
	avg dep	100	404 ± 64	5.64 ± 1.11	22.8 ± 5.5	5.0 ± 0.2
	runoff	100	315 ± 67	17.91 ± 0.57	56.5 ± 12.8	3.4 ± 0.2
LES	bulk dep	5	621 ± 133	1.22 ± 0.09	7.6 ± 1.4	5.6 ± 0.2
	spruce TF	53	324 ± 78	6.39 ± 0.85	20.7 ± 3.4	4.5 ± 0.3
	beech TF	42	381 ± 68	1.75 ± 0.13	6.7 ± 1.0	5.6 ± 0.2
	avg dep	100	363 ± 75	3.90 ± 0.38	14.2 ± 2.1	4.8 ± 0.2
	runoff	100	159 ± 32	25.28 ± 1.21	43.3 ± 9.0	4.3 ± 0.3
LIZ	bulk dep	37	825 ± 151	0.80 ± 0.13	6.6 ± 1.6	4.8 ± 0.3
	spruce TF	63	417 ± 103	2.86 ± 0.56	11.9 ± 2.5	4.6 ± 0.3
	avg dep	100	568 ± 120	1.75 ± 0.27	9.9 ± 2.1	4.6 ± 0.2
	runoff	100	387 ± 43	3.85 ± 0.29	14.9 ± 2.6	4.7 ± 0.3
LYS	bulk dep	30	649 ± 106	0.96 ± 0.06	6.2 ± 1.0	5.2 ± 0.3
	spruce TF	70	482 ± 93	4.70 ± 0.51	22.7 ± 4.1	5.4 ± 0.4
	avg dep	100	532 ± 93	3.33 ± 0.28	18.8 ± 3.1	5.4 ± 0.4
	runoff	100	326 ± 97	6.07 ± 0.21	19.8 ± 5.7	5.4 ± 0.2
MOD	bulk dep	38	2506 ± 869	0.86 ± 0.11	23.3 ± 7.4	6.6 ± 0.6
	spruce TF	62	1649 ± 313	1.58 ± 0.15	26.0 ± 4.6	6.2 ± 0.2
	avg dep	100	1974 ± 504	1.29 ± 0.15	25.4 ± 5.5	6.5 ± 0.3
	runoff	100	1633 ± 528	1.38 ± 0.03	22.6 ± 6.9	5.9 ± 0.1
PLB	bulk dep	0	649 ± 106	0.96 ± 0.06	6.2 ± 1.0	5.2 ± 0.3
	spruce TF	100	408 ± 67	3.82 ± 0.39	15.6 ± 3.1	5.0 ± 0.4
	avg dep	100	408 ± 67	3.82 ± 0.39	15.6 ± 3.1	5.0 ± 0.4
	runoff	100	222 ± 82	11.38 ± 0.54	25.3 ± 9.6	5.1 ± 0.5
POM	bulk dep	7	847 ± 131	2.85 ± 1.09	24.1 ± 7.7	4.3 ± 0.2
	spruce TF	93	648 ± 111	5.83 ± 1.34	37.8 ± 5.9	4.2 ± 0.3
	avg dep	100	661 ± 111	5.57 ± 1.29	36.8 ± 5.9	4.2 ± 0.3
	runoff	100	320 ± 89	16.41 ± 0.55	52.5 ± 14.8	4.1 ± 0.3
SAL	bulk dep	0	489 ± 137	1.44 ± 0.20	7.0 ± 1.6	5.4 ± 0.3
	spruce TF	100	308 ± 74	6.62 ± 0.97	20.4 ± 4.3	3.5 ± 0.2
	avg dep	100	308 ± 74	6.62 ± 0.97	20.4 ± 4.3	3.5 ± 0.2
	runoff	100	170 ± 14	5.06 ± 0.37	8.6 ± 1.1	4.5 ± 0.1
SPA	bulk dep	5	1242 ± 215	0.60 ± 0.07	7.5 ± 1.6	5.2 ± 0.4
	spruce TF	95	552 ± 108	4.04 ± 0.94	22.3 ± 4.5	3.8 ± 0.1
	avg dep	100	587 ± 113	3.67 ± 0.83	21.6 ± 4.3	3.8 ± 0.1
	Runoff	100	397 ± 56	3.54 ± 0.06	14.1 ± 2.0	5.5 ± 0.3
UDL	Bulk dep	87	1480 ± 311	1.44 ± 0.22	21.3 ± 2.7	5.6 ± 0.3
	Spruce TF	13	972 ± 196	4.21 ± 0.86	40.9 ± 8.7	5.0 ± 0.2
	Avg dep	100	1414 ± 294	1.69 ± 0.26	23.9 ± 3.1	5.4 ± 0.2
	Runoff	100	1187 ± 290	3.19 ± 0.10	37.8 ± 8.8	5.2 ± 0.2
UHL	Bulk dep	85	1379 ± 305	1.31 ± 0.12	18.1 ± 3.6	7.7 ± 0.4
	Spruce TF	15	1316 ± 309	5.43 ± 0.69	71.5 ± 13.5	7.1 ± 0.7
	Avg dep	100	1369 ± 306	1.91 ± 0.16	26.1 ± 4.8	7.4 ± 0.2
	Runoff	100	1058 ± 227	4.70 ± 0.16	49.7 ± 11.5	6.8 ± 0.2

<sup>a</sup>TF denotes throughfall.

<sup>b</sup>Sulfur isotope values are mass-weighted averages, and reported as means ± standard errors.

<sup>c</sup>Average deposition values calculated by area-weighting deposition for each vegetation type (spruce, beech, or bulk deposition in clearings).

<sup>d</sup>Beech throughfall fluxes are assumed to also apply to areas of spruce dieback at JEZ.

UHL) in 1998. Each entire soil horizon was collected at 10 different locations throughout the catchment, the samples pooled by horizon and a subsample taken for analysis. The δ<sup>34</sup>S values of bedrock are from M. Novak et al. (Temporal variation in δ<sup>34</sup>S values, S fluxes and mass balances in 13 Central European forest catchments, manuscript, in preparation, 2005) (hereinafter referred to as Novak et al., manuscript in preparation, 2005). An average whole rock δ<sup>34</sup>S value was obtained by pooling 10 kg of samples

from bedrock and boulders that had been collected at ~30 locations throughout each catchment.

### 2.3. Analytical Procedures

[7] Water samples (bulk deposition, spruce throughfall, beech throughfall, and runoff) were filtered and kept at 2°C. Water fluxes via bulk deposition and throughfall were measured by weighing the sampler contents. Runoff fluxes were measured by means of a gauging station. Sulfate

concentrations were determined on a Shimadzu LC 6A liquid chromatograph. Sulfur for  $\delta^{34}\text{S}$  determinations was precipitated from water as  $\text{BaSO}_4$  and converted to  $\text{SO}_2$  [Yanagisawa and Sakai, 1983]. Total S was extracted from sieved (<2 mm), dried and homogenized soils by digestion with Eschka mixture, precipitated as  $\text{BaSO}_4$  and converted to  $\text{SO}_2$  [Chakrabarti, 1978; Novak et al., 1994]. The concentration of S in soils was determined gravimetrically following the Eschka digestion. The  $\delta^{34}\text{S}$  values of waters and soils were determined on a Finnigan MAT 251 mass spectrometer with a reproducibility of 0.3‰. The results were expressed as a per mil deviation of the  $^{34}\text{S}/^{32}\text{S}$  ratio in the sample from the Canon Diablo Troilite (CDT) standard. Ten kilograms of bedrock and boulders from each catchment (Novak et al., manuscript in preparation, 2005) were ground to <0.1 mm, and a 200-g split was subjected to Johnson-Nishita distillation [Johnson and Nishita, 1952]. The sample was treated with  $\text{Cr}^{2+}$  in a  $\text{N}_2$  atmosphere for 45 min [Canfield et al., 1986]. All sulfide S present in the rock was quantitatively converted to  $\text{H}_2\text{S}$  and trapped in Zn-acetate; the resulting  $\text{ZnS}_2$  was converted to  $\text{Ag}_2\text{S}$ , oxidized to  $\text{SO}_2$  and analyzed for  $\delta^{34}\text{S}$  [Hall et al., 1988]. The reproducibility of the entire bedrock S extraction procedure was 0.4‰ (Novak et al., manuscript in preparation, 2005). Annual sulfate fluxes via atmospheric deposition and stream runoff were calculated from monthly sulfate concentrations and water fluxes. Deposition fluxes from different ground cover types (spruce throughfall, beech throughfall, and bulk deposition) were area-weighted to calculate average deposition for each catchment. Reported  $\delta^{34}\text{S}$  values are mass-weighted averages. First-order, second-moment error propagation was employed throughout the analysis; uncertainties are reported as  $\pm 1$  standard error in all cases.

### 3. Results and Discussion

#### 3.1. Sulfate Deposition

[8] Spruce throughfall was richer in S than bulk deposition sampled in nearby clearings by a factor of 1.1 (MOD) to 4.2 (JEZ; Table 2). Across the 13 sites, the average S enrichment factor for spruce throughfall relative to bulk deposition was 2.6. Thus if half of a typical catchment in the Czech Republic were covered by spruce, while the other half had been clearcut following pollution-related die-back, more than 70% of atmospheric S input into the catchment would still occur via the surviving spruce stand. Conifer forests intercept more airborne sulfur dioxide than clearings because of their greater surface roughness, which is related to the leaf area index and the shape of the needles. The enhancement of S deposition under forests is stronger close to industrial sources, because about 98% of industrial S is emitted in the form of  $\text{SO}_2$ , a gas which is scavenged by foliage [Kellog et al., 1972]. The efficiency of  $\text{SO}_2$  scavenging is affected by local aerodynamics and tree density. The windward margin of a closed-canopy forest intercepts large quantities of  $\text{SO}_2$ , deflecting most of the remaining  $\text{SO}_2$  upward. As a result, the uppermost branches in the tree canopy capture more S than lower branches [Fowler et al., 1990; Krouse et al., 1984]. Sulfur dioxide is oxidized on needle surfaces to sulfate and neutralized by  $\text{Ca}^{2+}$  leached from plant tissues [Ferm and Hultberg, 2004]. In small

amounts, S compounds can also enter the stomata, or be released by the stomata [Krouse et al., 1984]. During transport, several per cent of  $\text{SO}_2$  per hour are oxidized to sulfate, which then dominates wet deposition [Novak et al., 2001b].

#### 3.2. The Continuing Pollution Gradient

[9] In 1997, dry-deposited S (estimated from the difference of fluxes between canopy throughfall and bulk deposition) formed up to 76% of total S deposition underneath spruce (JEZ). The contribution of dry-deposited S to total S deposition in spruce stands averaged 56% across the 13 Czech sites (Table 2). This was much higher than, for example, the 15% contribution of dry deposited S to total S deposition in southern Sweden [Forsius et al., 2001], or the 21% contribution of dry deposited to total S over the 34 years of observations at Hubbard Brook [Likens et al., 2002]. Overall, the highest catchment-scale atmospheric S inputs in the present study (37 and 29  $\text{kg S ha}^{-1} \text{ yr}^{-1}$ , Table 2) occurred at POM and CER, sites with few clearings. However, much higher atmospheric S inputs were observed in patches of surviving spruce farther north (Figure 1). The highest spruce throughfall S fluxes were recorded at UHL and JEZ (72 and 61  $\text{kg S ha}^{-1} \text{ yr}^{-1}$ ). Even though these 1997 values followed 10 years of steadily decreasing pollution in central Europe, they were still higher than the highest annual S depositions ever measured in the northeastern United States [Howarth et al., 1992]. The lowest atmospheric S deposition rates in the present study (i.e., in water year 1997) occurred in the western Czech Republic, upwind from recent major industrial polluters (LYS and PLB with 6  $\text{kg S ha}^{-1} \text{ yr}^{-1}$  in clearings; Figure 1). Data in Figure 1 reveal a sharp continuing pollution gradient: In 1997, the ground surface underneath spruce at UHL received 12 times more S than the ground surface in clearings at LYS. Within a single vegetation type (spruce), the pollution gradient was seven-fold (markedly polluted UHL versus relatively unpolluted LIZ). Within a single site (over a distance of tens of meters), the S input gradient was the largest at JEZ (4.2 times more S deposited in spruce forests than in clearings).

#### 3.3. Isotope Composition of S Input

[10] Figure 2 contrasts S fluxes and  $\delta^{34}\text{S}$  values in bulk deposition and spruce throughfall across the 13 sites. As a result of scavenging of  $\text{SO}_2$  by the tree canopy, spruce throughfall fluxes were significantly higher than bulk deposition (Figure 2a). By contrast, at almost all of the 13 catchments, average mass-weighted  $\delta^{34}\text{S}$  values were lower in spruce throughfall than in bulk deposition, i.e., sulfur in spruce throughfall was enriched in the lighter isotope  $^{32}\text{S}$  (Figure 2b). All data points in Figure 2a lie above the 1:1 line, whereas nearly all data points in Figure 2b lie below the 1:1 line. Across the 13 sites, the  $\delta^{34}\text{S}$  value of spruce throughfall was 0.7‰ lower than that of bulk deposition (4.7 and 5.5‰, respectively; Table 2). The underlying process was again related to elevated dry deposition of  $\text{SO}_2$  in the canopies of conifers. Local coal contains isotopically relatively light S (mean of 1.6‰ [Mach et al., 1999]) and its combustion releases

low- $\delta^{34}\text{S}$   $\text{SO}_2$  to the atmosphere [Novak *et al.*, 2001a]. A large portion of this isotopically light  $\text{SO}_2$  is captured by spruce canopies as dry deposition. The remaining  $\text{SO}_2$  is converted to sulfate by atmospheric oxidation and washed out from the air by rain. The isotope selectivity of this reaction depends upon kinetics, some steps are associated with a negative effect, while other steps cause a positive effect. Field evidence implies that the negative effect is larger than the positive effect. The heavier isotope  $^{34}\text{S}$  is preferentially concentrated in the resulting liquid phase ( $\text{SO}_4$ ), while the residual gaseous phase ( $\text{SO}_2$ ) becomes enriched in the lighter isotope  $^{32}\text{S}$  [Saltzman *et al.*, 1983]. The magnitude of the overall isotope fractionation is 0 to 4‰ [Novak *et al.*, 2001a]. The wet-deposited sulfate has higher  $\delta^{34}\text{S}$  values than dry-deposited  $\text{SO}_2$ , resulting in isotopically heavier bulk deposition S compared to canopy throughfall S.

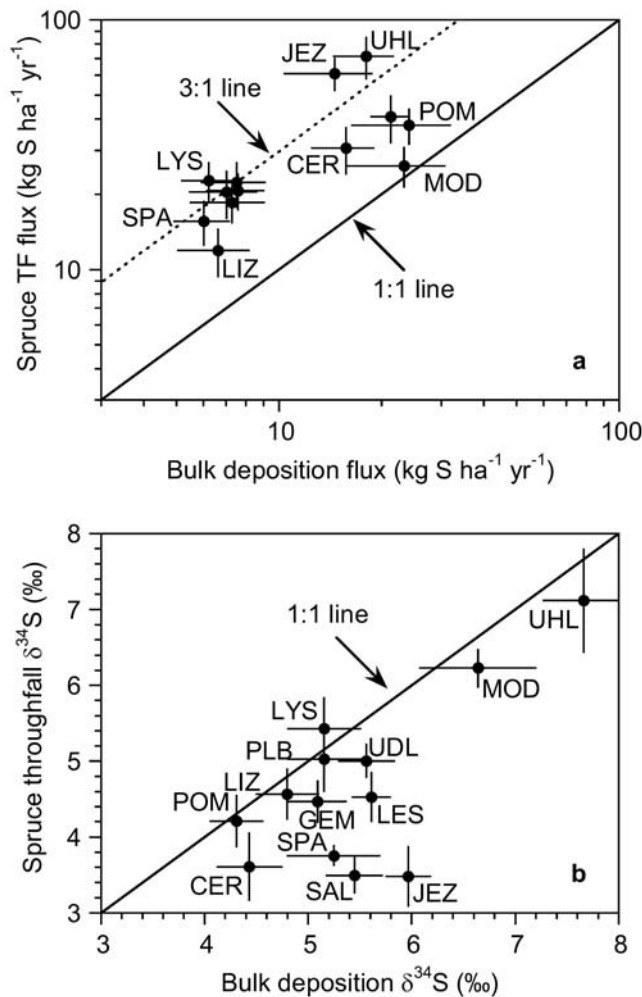
### 3.4. Comparison of S Inputs and Outputs

[11] Catchment outputs of S via surface runoff in the hydrological year 1997 are given in Table 1. The lowest runoff flux,  $9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ , was measured at SAL. The largest runoff flux,  $60 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ , was observed at the easternmost catchment CER, followed by JEZ, POM and UHL ( $56$ ,  $53$  and  $50 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ , respectively). At JEZ, we had monitored S runoff fluxes between 1994 and 1996 [Fottova and Skorepova, 1998; Peters *et al.*, 1999; Novak *et al.*, 2000], arriving at a time series of extremely high annual outputs of  $52$ ,  $58$  and  $85 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ . It appears that the  $56 \text{ kg S ha}^{-1}$  exported from JEZ in 1997 was not anomalous, following earlier years of even higher S exports. Runoff may not be the only S output from forest catchments. Highly polluted catchments with aerated soils can release additional S back to the atmosphere in the form of biogenic gaseous emissions [Andreae and Jaeschke, 1992]. Incubations of JEZ soil labeled with  $^{35}\text{S}$  and  $^{34}\text{S}$  showed that, following precipitation events, dissimilatory sulfate reduction in anaerobic domains can release as much as  $13 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  in the form of  $\text{H}_2\text{S}$  [Novak *et al.*, 2001a, 2004].

[12] Comparisons of average S deposition fluxes and  $\delta^{34}\text{S}$  values with those of runoff are shown in Figure 3. Sulfur fluxes for individual catchments plot on both sides of the 1:1 line (Figure 3a). Similarly, the  $\delta^{34}\text{S}$  values of individual sites plot on both sides of the 1:1 line (Figure 3b). Some of the study sites exhibited a net export of S, while other sites were still accumulating S. Some of the sites exported isotopically lighter S (lower  $\delta^{34}\text{S}$ ) than they were currently receiving from the atmosphere. Other sites exported isotopically heavier S (higher  $\delta^{34}\text{S}$ ) compared to current atmospheric S deposition.

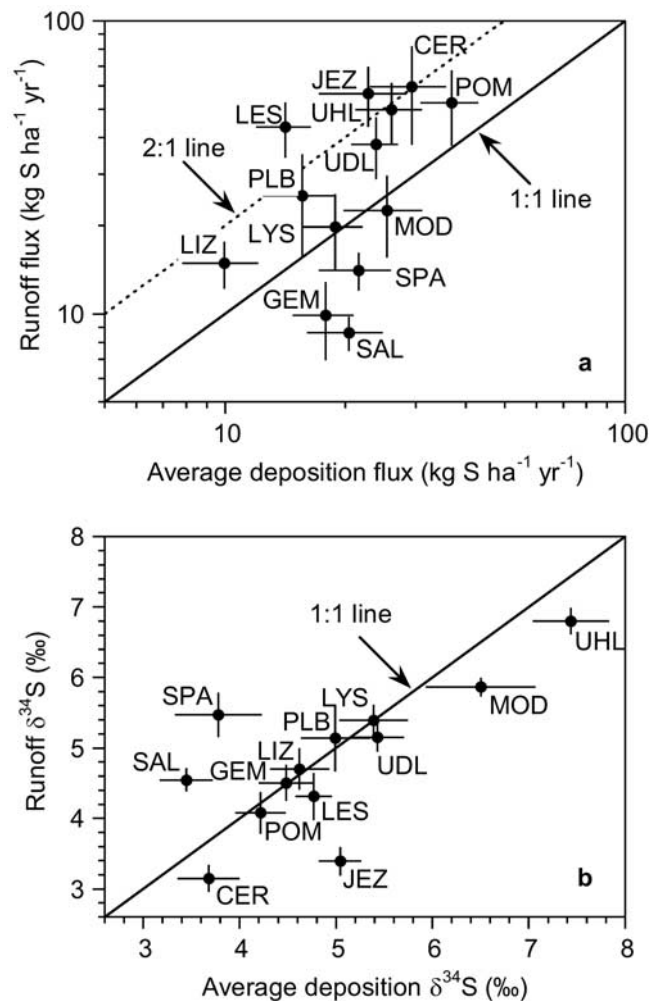
### 3.5. Links Between Site Histories and S Budgets

[13] In the Czech Republic, the simplest dividing line between contrasting S pollution histories is an east-west line through the center of the country, with an extremely polluted north and a relatively unpolluted south. A number of confounding factors exist, such as the presence of small but locally important point sources of pollution in otherwise unpolluted regions, or higher precipitation totals and S



**Figure 2.** Bulk deposition and spruce throughfall fluxes of sulfate, and their isotopic compositions. Spruce throughfall fluxes are correlated with bulk deposition (open canopy) fluxes, but are higher by roughly a factor of 3 (dotted line). Spruce throughfall is isotopically lighter than bulk deposition by approximately 0.5‰, except at SPA, SAL, and JEZ, where it is lighter by roughly 2‰. Error bars are  $\pm 1$  standard error.

fluxes close to mountain peaks relative to lowlands. Comparing Figures 1 and 3, one can see that the sites releasing S are situated in the polluted north. By contrast, the unpolluted sites in the south, which have not experienced the same drastic decrease in S deposition after 1987 as those in the north [Kopacek *et al.*, 2001], were continuing to retain S. Sites releasing the largest amounts of S tend to have low runoff  $\delta^{34}\text{S}$  values relative to deposition (e.g., JEZ, LES, CER and UHL; Figure 3). In contrast, sites retaining the largest amounts of S tend to have high runoff  $\delta^{34}\text{S}$  values relative to deposition (SPA and SAL). This implies that the source of S in sites releasing S must be isotopically lighter than the input, in order to produce a low- $\delta^{34}\text{S}$  output, and that one or more S-retaining processes at sites that are net sinks of S must favor light isotopes, in order to produce a high- $\delta^{34}\text{S}$  output. For a more specific evaluation of the



**Figure 3.** Average deposition and runoff fluxes of sulfate, and their isotopic compositions. Runoff sulfate fluxes are generally 1–2 times average deposition fluxes, except at JEZ and LES (runoff flux >2 times deposition flux) and at GEM, SPA, and SAL (runoff flux  $\approx$ 0.5 times deposition flux). The isotopic composition of runoff equals that of average deposition, within error, at roughly half the sites. Runoff is isotopically lighter than average deposition at CER, JEZ, LES, MOD, and UHL (predominantly sites at which runoff S fluxes are significantly higher than average deposition). Runoff is isotopically heavier than average deposition at SAL and SPA (where runoff S fluxes are significantly lower than average deposition). Error bars are  $\pm 1$  standard error.

sink/source relationships, we took an isotope inventory of individual S pools within the catchments.

### 3.6. S Concentrations and $\delta^{34}\text{S}$ Values of Bedrock and Soil

[14] The bedrock of the 13 studied catchments was formed by common lithologies, typically orthogneisses, paragneisses and granitoids (Table 1). The average S concentration in fresh bedrock was only 0.004 wt. %

(Table 3). None of the sites had S-rich rocks, such as black shales or evaporites. The whole rock  $\delta^{34}\text{S}$  values varied widely, ranging between  $-13.6$  and  $+12.4\text{‰}$  (Table 3). Sulfur concentrations and  $\delta^{34}\text{S}$  values of forest soils varied with depth at all sites. In general, S concentrations decreased and  $\delta^{34}\text{S}$  values increased with increasing soil depth (Table 3 [cf. Novak *et al.*, 1996, 2000]). Although catchment soils are notoriously heterogeneous, the amount of total S stored in each horizon is primarily controlled by the proportion of the <2 mm soil fraction, horizon thickness and density. In a detailed study at JEZ, we found that the organic and mineral soil horizons stored comparable amounts of S [Novak *et al.*, 2000]. Many studies have shown that the S in the O horizon in Dystric Cambisols and similar soils is predominantly organic S (95% at JEZ), with the proportion of organic S decreasing in the lower horizons [Mitchell *et al.*, 1992]. The  $\delta^{34}\text{S}$  values of organic S studied at five different sites by Novak *et al.* [2003] were isotopically nearly identical to total S in the O horizon, while sulfate S was isotopically lighter than organic S. At 18 different forested catchments, some of which are in the current study, we found significant increases in  $\delta^{34}\text{S}$  values from organic to mineral soil [Novak *et al.*, 1996]. The same trend was confirmed along a north-south European transect [Novak *et al.*, 2003]. There is now a general agreement that the positive downward  $\delta^{34}\text{S}$  shift in forest soils is caused by ageing of organic S, specifically by removal of isotopically light secondary sulfate-S resulting from mineralization of organic matter [Gebauer *et al.*, 1994; Novak *et al.*, 1996; Zhang *et al.*, 1998; Mitchell *et al.*, 2001; Norman *et al.*, 2002]. The residual high- $\delta^{34}\text{S}$  organic S remains in situ. Deep soil solutes, sampled by lysimeters, exhibit lower  $\delta^{34}\text{S}$  values than both the atmospheric inputs and shallow soil solutes [Novak *et al.*, 2000]. The positive  $\delta^{34}\text{S}$  shift downward in soil substrate and the negative  $\delta^{34}\text{S}$  shift downward in soil solutes are complementary isotope effects, diagnostic of mineralization of organic S. Older organic carbon and nitrogen behave similarly to S, exhibiting positive  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  shifts with increasing soil depth due to mineralization [Balesdent *et al.*, 1993; Nadelhoffer and Fry, 1988; Novak *et al.*, 2003].

### 3.7. The $\delta^{34}\text{S}$ Correlations Among S Pools and Fluxes

[15] Site-to-site Spearman rank correlations among  $\delta^{34}\text{S}$  values of catchment fluxes and pools are given in Table 4a. Across the 13 sites, the  $\delta^{34}\text{S}$  values of average mass-weighted deposition were strongly correlated with runoff and the O soil horizon. The  $\delta^{34}\text{S}$  values of runoff were strongly correlated with all three soil horizons (O, A/B and C). The  $\delta^{34}\text{S}$  values of all three soil horizons were strongly correlated with one another, possibly indicating a common S source, despite the isotopic fractionation effect associated with maturation of organic S. The  $\delta^{34}\text{S}$  values of the soil horizons were not correlated with the  $\delta^{34}\text{S}$  values in bedrock. Isotopes may be the only unambiguous tool to test the origin of S in the soil. Until the advent of stable isotope studies, no method existed to test whether C-horizon sulfate S is residual oxidized S from bedrock sulfides [Howarth *et al.*, 1992]. On the basis of our data from 13 catchments, we suggest that sulfate S present in the C

**Table 3.** Sulfur Isotope Mass Balance and Composition of Potential Catchment Sources/Sinks, Water Year 1997

Site	Soil Horizon															
	Soil Horizon O		A/B		Soil Horizon C		Bedrock		Average Deposition		Runoff		Internal Source/Sink			
	S, wt %	$\delta^{34}\text{S}$ , ‰	S, wt %	$\delta^{34}\text{S}$ , ‰	S, wt %	$\delta^{34}\text{S}$ , ‰	S, wt %	$\delta^{34}\text{S}$ , ‰	S Flux, $\text{kg ha}^{-1} \text{yr}^{-1}$	$\delta^{34}\text{S}$ , ‰	S Flux, $\text{kg ha}^{-1} \text{yr}^{-1}$	$\delta^{34}\text{S}$ , ‰	S Flux, $\text{kg ha}^{-1} \text{yr}^{-1}$	$\delta^{34}\text{S}$ , ‰		
CER	0.09	1.7 ± 0.8	0.05	2.5 ± 1.4	0.04	4.7 ± 2.1	0.03	2.4	29.3 ± 6.2	3.7 ± 0.4	59.7 ± 21.7	3.1 ± 0.2	30.4 ± 22.2	2.6 ± 0.6		
GEM	0.11	1.3 ± 0.6	0.01	3.3 ± 1.1	0.005	4.5 ± 1.4	0.002	-5.1	17.8 ± 3.0	4.5 ± 0.3	9.9 ± 2.9	4.5 ± 0.2	-8.0 ± 3.1	4.5 ± 0.6		
JEZ	0.16	1.4 ± 0.4	0.02	2.4 ± 0.9	0.01	3.6 ± 1.6	<0.003	5.8	22.8 ± 5.5	5.0 ± 0.2	56.5 ± 12.8	3.4 ± 0.2	33.7 ± 16.2	2.3 ± 0.7		
LES	0.05	2.2 ± 0.6	0.01	3.0 ± 1.1	0.005	2.1 ± 1.4	<0.001	3.4	14.2 ± 2.1	4.8 ± 0.2	43.3 ± 9.0	4.3 ± 0.3	29.2 ± 8.0	4.1 ± 0.5		
LIZ	0.12	2.4 ± 0.5	0.03	2.9 ± 0.7	0.04	2.8 ± 0.9	<0.001	3.2	9.9 ± 2.1	4.6 ± 0.2	14.9 ± 2.6	4.7 ± 0.3	4.9 ± 2.5	4.9 ± 0.9		
LYS	0.13	3.2 ± 0.6	0.02	3.3 ± 1.6	0.01	3.9 ± 1.3	<0.001	-13.6	17.7 ± 3.1	5.4 ± 0.4	19.8 ± 5.7	5.4 ± 0.2	2.1 ± 5.9	5.4 ± 3.1		
MOD	0.13	4.8 ± 0.6	0.02	5.1 ± 1.1	0.02	6.6 ± 1.4	0.01	3.7	25.4 ± 5.5	6.5 ± 0.3	22.6 ± 6.9	5.9 ± 0.1	-2.9 ± 4.5	11.5 ± 42.2 <sup>a</sup>		
PLB	0.12	4.2 ± 1.0	0.02	5.1 ± 0.8	0.02	5.2 ± 1.0	<0.001	n.d. <sup>b</sup>	15.6 ± 3.1	5.0 ± 0.4	25.3 ± 9.6	5.1 ± 0.5	9.7 ± 7.5	5.3 ± 1.5		
POM	0.08	1.7 ± 0.6	0.01	4.7 ± 1.1	0.01	4.7 ± 1.4	<0.001	1.5	36.8 ± 5.9	4.2 ± 0.3	52.5 ± 14.8	4.1 ± 0.3	15.7 ± 16.7	3.8 ± 1.1		
SAL	0.1	3.1 ± 0.1	0.04	3.6 ± 0.8	0.02	3.8 ± 0.7	0.003	12.4	20.4 ± 4.3	3.5 ± 0.2	8.6 ± 1.1	4.5 ± 0.1	-11.8 ± 3.5	2.7 ± 0.4		
SPA	0.06	3.6 ± 0.6	0.01	4.0 ± 1.1	0.01	4.9 ± 1.4	<0.001	5.6	21.6 ± 4.3	3.8 ± 0.1	14.1 ± 2.0	5.5 ± 0.3	-7.5 ± 3.9	0.6 ± 1.8		
UDL	0.15	5.3 ± 0.6	0.01	6.5 ± 1.1	0.01	6.2 ± 1.4	0.001	-3.3	23.9 ± 3.1	5.4 ± 0.2	37.8 ± 8.8	5.2 ± 0.2	14.0 ± 8.6	4.7 ± 0.7		
UHL	0.09	5.3 ± 0.6	0.01	7.1 ± 1.1	0.01	6.3 ± 1.4	0.004	2.1	26.1 ± 4.8	7.4 ± 0.2	49.7 ± 11.5	6.8 ± 0.2	23.6 ± 7.1	6.1 ± 0.4		

<sup>a</sup>Input and output S fluxes at MOD nearly balance, nearly dividing by zero in the estimation of the  $\delta^{34}\text{S}$  of the internal source/sink. Thus the estimate is large and highly uncertain.

<sup>b</sup>The concentration of S in bedrock at PLB was too low to permit  $\delta^{34}\text{S}$  to be measured.

horizon of soils that are developed on common S-poor rocks ( $\leq 40$  ppm S, Table 3) is mainly derived from the atmosphere.

### 3.8. S Isotope Systematics of Potential Mixing End-Members for Runoff

[16] Statistically significant differences existed among the S isotope compositions of several S fluxes and pools, averaged across the 13 sites (Table 4b). Sulfur in bulk deposition was isotopically significantly heavier than all other S fluxes and pools, with the exception of some of the bedrock. Sulfur in the O horizon of the soils was isotopically significantly lighter than all other S fluxes and pools, again except some bedrock. Sulfur in runoff was isotopically similar to the average atmospheric deposition and the C soil horizon. At the same time, S in runoff was isotopically significantly lighter than S in bulk deposition and significantly heavier than S in the O and A/B horizons. Sulfur in the A/B and C horizons was statistically indistinguishable. In general,  $\delta^{34}\text{S}$  values decreased across the sites in the order (mean  $\delta^{34}\text{S}$  values in brackets): bulk deposition (5.5‰) > runoff (4.8‰)  $\geq$  spruce throughfall (4.7‰)  $\geq$  soil (4.6, 4.2 and 3.1‰ for the horizons C, A/B and O, respectively) > bedrock (1.5‰).

### 3.9. Delayed Export of Atmospheric S From Catchments

[17] We have previously seen that  $\delta^{34}\text{S}$  values of runoff were positively correlated with those of the average atmospheric deposition (Table 4a). For many years, runoff of sulfate originating from instantaneous rainfall was considered to form a major proportion of stream runoff (see *Mitchell and Fuller* [1988] for a review). Recently, this traditional view has been challenged by studies using activities of the cosmogenic isotope  $^{35}\text{S}$  in catchment inputs and outputs [*Michel et al.*, 2000; *Kester et al.*, 2003; *Novak et al.*, 2004]. These studies have shown that the residence time of the incoming S in non-alpine catchments exceeds several months. We will further consider such delayed atmospheric S to be one mixing end-member for runoff

generation. What other S mixing end-members play a role in runoff generation at the 13 studied catchments?

### 3.10. Role of Soil and Bedrock S in Runoff Generation

[18] Sulfur isotope compositions are used in Figure 4 to constrain the role of within-site sources in S runoff generation. The  $\delta^{34}\text{S}$  value of runoff, as we have already seen in Table 4a, was strongly correlated with all three soil horizons. Figure 4a shows a systematic offset relative to a 1:1 relationship between  $\delta^{34}\text{S}$  of the O horizon and runoff. Across the sites, S in the O horizon was isotopically lighter than S in runoff by an average of 1.7‰. The isotopic offset between the deeper A/B horizon and runoff was smaller (0.7‰; Figure 4b), while that between the C horizon and runoff (0.3‰; Figure 4c) was statistically insignificant (Table 4b). The  $\delta^{34}\text{S}$  values of the O horizon were lighter than deposition by almost 2‰, suggesting that the reactions between deposited S and the O horizon were associated with an isotope effect. This  $\sim 2\%$   $\delta^{34}\text{S}$  offset from atmospheric input to O-horizon S may have been caused by isotope fractionation upon assimilation (uptake) of sulfate S by spruce, previously documented across an east-west European transect [*Novak et al.*, 2001b]. It is not well known whether S uptake by fine roots also fractionates S isotopes. Our preliminary data from JEZ indicate statistically insignificant differences among  $\delta^{34}\text{S}$  values of fine soil, fine roots and mycorrhizae (means of 2.2, 2.6 and 3.1‰, respectively; number of replicates  $n = 3$ ).

[19] Figure 4d clearly shows that, across the sites, the  $\delta^{34}\text{S}$  values of bedrock did not correlate with runoff. The scatter in Figure 4d contrasts with clear-cut positive correlations between  $\delta^{34}\text{S}$  values in runoff and each of the soil horizons (Figures 4a–4c, Table 4a), as discussed above. Sulfur isotope data from our 13 catchments thus imply that whereas the bedrock S contribution to runoff was negligible, soil S, largely of anthropogenic origin, was a major component of runoff. Most previous studies have focused on one or just a few catchments, with the usefulness of the isotope data depending on whether or not the  $\delta^{34}\text{S}$  of bedrock was sufficiently different from the  $\delta^{34}\text{S}$  of the



**Table 4a.** Site-to-Site Rank (Spearman) Correlations Among  $\delta^{34}\text{S}$  of Catchment Fluxes and Pools<sup>a</sup>

	Bulk Deposition	Spruce Throughfall	Average Deposition	Runoff	O Horizon Soils	A/B Horizon Soils	C Horizon Soils	Bedrock
Bulk deposition		0.311	<b>0.649</b>	0.490	0.507	0.314	0.256	0.364
Spruce throughfall	0.311		<b>0.775</b>	<b>0.753</b>	<b>0.701</b>	<b>0.610</b>	0.528	-0.518
Average deposition	<b>0.649</b>	<b>0.775</b>		<b>0.577</b>	<b>0.578</b>	0.429	0.434	-0.301
Runoff	0.490	<b>0.753</b>	<b>0.577</b>		<b>0.864</b>	<b>0.692</b>	<b>0.615</b>	-0.089
O horizon soils	0.507	<b>0.701</b>	<b>0.578</b>	<b>0.864</b>		<b>0.795</b>	<b>0.685</b>	-0.021
A/B horizon soils	0.314	<b>0.610</b>	0.429	<b>0.692</b>	<b>0.795</b>		<b>0.830</b>	-0.217
C horizon soils	0.256	0.528	0.434	<b>0.615</b>	<b>0.685</b>	<b>0.830</b>		-0.210
Bedrock	0.364	-0.518	-0.301	-0.089	-0.021	-0.217	-0.210	

<sup>a</sup>Bold indicates significance level  $p < 0.05$ .

atmospheric input [Bottrell and Novak, 1998; Mitchell et al., 2001]. Studies employing data from multiple catchments with various bedrock  $\delta^{34}\text{S}$  values, such as this one, maximize the diagnostic power of S isotopes for distinguishing between natural (bedrock-derived) and pollutant (atmospherically derived) S in discharge. We suggest that Figure 4d can be generalized to common igneous and metamorphic bedrock types whose S contribution to runoff is also negligible. In contrast, S-rich bedrocks, such as sulfidic black shales and coal, can yield a result different from ours (Figure 4d), with bedrock S forming a measurable portion of the S in stream discharge [e.g., Wieder, 1989; Bailey et al., 2004].

### 3.11. S Isotope Mass Balances for Forested Catchments

[20] In all, nine catchments had positive mass balances (net release of S), with five over  $10 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ , while the remaining four sites had negative mass balances (net accumulation of S; Figure 3). Table 3 also summarizes the sulfur isotope mass balances for each of the 13 catchments, including the associated uncertainties. The isotope mass balances use S input-output budgets from Figure 3. In Table 3, the internal (within-site) sources of S are expressed as positive values, and internal sinks as negative values. The isotope mass balances allow us to infer the isotopic composition of the catchments' internal S sources/sinks (Table 3). If the output flux ("out") is a mixture of deposition ("in") and an unknown within catchment source/sink ("x"), then

$$Q_x = Q_{\text{out}} - Q_{\text{in}}, \quad (1)$$

where Q denotes S fluxes (the internal source  $Q_x$  is negative if the catchment is a net sink for S). The isotope mass balance is

$$\delta_x Q_x = \delta_{\text{out}} Q_{\text{out}} - \delta_{\text{in}} Q_{\text{in}}, \quad (2)$$

where  $\delta$  denotes  $\delta^{34}\text{S}$  values. These two equations can be re-arranged to yield the composition of the missing source or sink,

$$\delta_x = (\delta_{\text{out}} Q_{\text{out}} - \delta_{\text{in}} Q_{\text{in}}) / (Q_{\text{out}} - Q_{\text{in}}). \quad (3)$$

[21] The missing S sources or sinks had  $\delta^{34}\text{S}$  values ranging from 0.6‰ (SPA) to 6.1‰ (UHL). At MOD the measured S input and output fluxes nearly balanced leading to a nearly divide-by-zero situation in equation (3).

### 3.12. An Isotope Source/Sink Model for Catchment S

[22] If the sulfur of the internal source or sink is isotopically lighter than deposition S, we would expect runoff S to be isotopically lighter than deposition S in catchments that are net exporters of S, and we would expect runoff S to be isotopically heavier than deposition S in catchments that are net retainers of S. This analysis can be made quantitative by rewriting equations (1) and (2) in the following form:

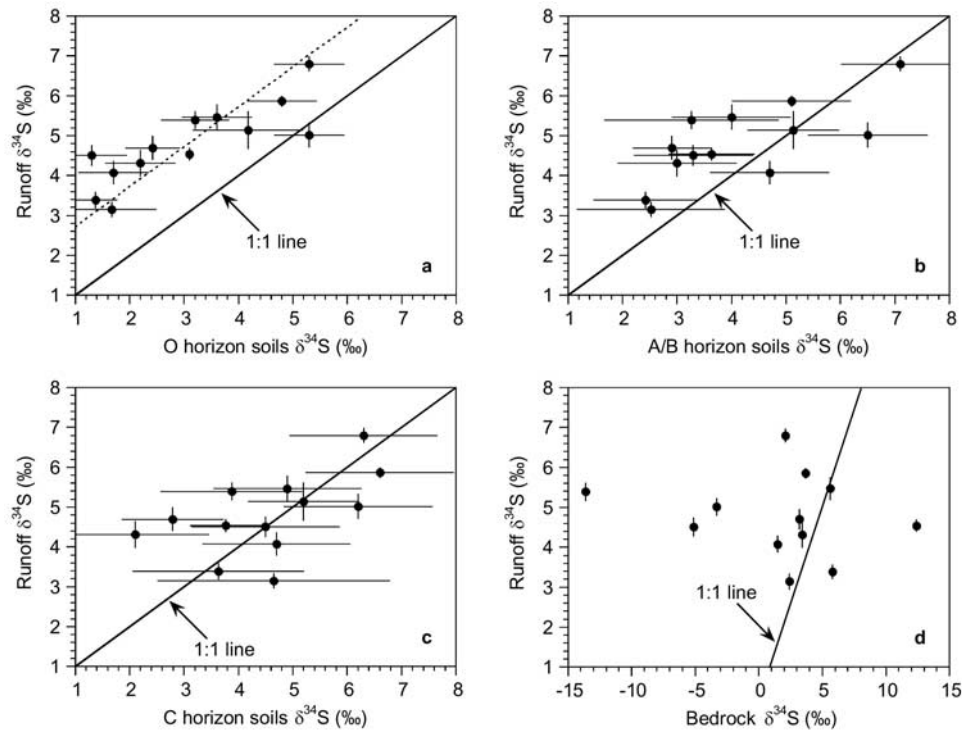
$$(\delta_{\text{out}} - \delta_{\text{in}}) = (\delta_x - \delta_{\text{out}})(Q_{\text{out}} - Q_{\text{in}}) / Q_{\text{in}}. \quad (4)$$

[23] Equation (4) implies that if the internal source or sink is consistently isotopically different from runoff, then a graph with the isotopic shift between input and output ( $\delta_{\text{out}} - \delta_{\text{in}}$ ) on the y axis, and  $(Q_{\text{out}} - Q_{\text{in}}) / Q_{\text{in}}$  on the x axis,

**Table 4b.** Differences Between Mean  $\delta^{34}\text{S}$  of Catchment Fluxes and Pools<sup>a</sup>

	Bulk Deposition	Spruce Throughfall	Average Deposition	Runoff	O Horizon Soils	A/B Horizon Soils	C Horizon Soils	Bedrock
Bulk deposition		<b>-0.8 ± 0.2</b>	<b>-0.6 ± 0.2</b>	<b>-0.7 ± 0.2</b>	<b>-2.4 ± 0.3</b>	<b>-1.3 ± 0.3</b>	<b>-0.9 ± 0.3</b>	-4.0 ± 1.8
Spruce throughfall	<b>0.8 ± 0.2</b>		0.2 ± 0.1	0.1 ± 0.2	<b>-1.6 ± 0.3</b>	-0.6 ± 0.3	-0.1 ± 0.3	-3.2 ± 2.0
Average deposition	<b>0.6 ± 0.2</b>	-0.2 ± 0.1		-0.1 ± 0.2	<b>-1.8 ± 0.3</b>	<b>-0.8 ± 0.3</b>	-0.4 ± 0.3	-3.4 ± 2.0
Runoff	<b>0.7 ± 0.2</b>	-0.1 ± 0.2	0.1 ± 0.2		<b>-1.7 ± 0.2</b>	<b>-0.7 ± 0.3</b>	-0.3 ± 0.3	-3.3 ± 1.9
O horizon soils	<b>2.4 ± 0.3</b>	<b>1.6 ± 0.3</b>	<b>1.8 ± 0.3</b>	<b>1.7 ± 0.2</b>		<b>1.0 ± 0.2</b>	<b>1.5 ± 0.3</b>	-1.6 ± 1.9
A/B horizon soils	<b>1.3 ± 0.3</b>	0.6 ± 0.3	<b>0.8 ± 0.3</b>	<b>0.7 ± 0.3</b>	<b>-1.0 ± 0.2</b>		0.4 ± 0.2	-2.6 ± 1.9
C horizon soils	<b>0.9 ± 0.3</b>	0.1 ± 0.3	0.4 ± 0.3	0.3 ± 0.3	<b>-1.5 ± 0.3</b>	-0.4 ± 0.2		-3.0 ± 1.9
Bedrock	4.0 ± 1.8	3.2 ± 2.0	3.4 ± 2.0	3.3 ± 1.9	1.6 ± 1.9	2.6 ± 1.9	3.0 ± 1.9	

<sup>a</sup>Units are ‰, means ± standard errors. Table entries are signed differences calculated as column variable minus row variable. For example, spruce throughfall is isotopically lighter on average than bulk deposition. Thus the average of spruce throughfall  $\delta^{34}\text{S}$  minus bulk deposition  $\delta^{34}\text{S}$  (first row, second column) is negative, whereas the average bulk deposition  $\delta^{34}\text{S}$  minus spruce throughfall  $\delta^{34}\text{S}$  (second row, first column) is positive. Bold indicates differences that have significance level  $p < 0.05$  by two-tailed t test.

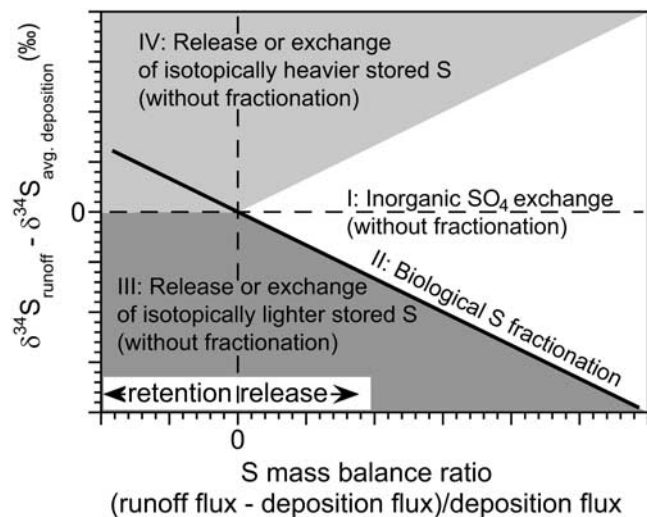


**Figure 4.** Site-to-site correlations between  $\delta^{34}\text{S}$  in runoff and  $\delta^{34}\text{S}$  of soils and bedrock. The  $\delta^{34}\text{S}$  of runoff is strongly correlated with all three soil horizons, but not with bedrock (see Table 3). The  $\delta^{34}\text{S}$  of O horizon soils is correlated with runoff, but is isotopically lighter, by an average of  $1.72 \pm 0.23$  per mil (mean  $\pm$  standard error) across the 13 sites. The dotted line in Figure 4a indicates this average isotopic offset. The isotopic difference between soils and runoff is smaller in the A/B horizons (averaging  $0.69 \pm 0.28$  per mil), and is not statistically significant in the C horizon (averaging  $0.25 \pm 0.32$  per mil). No error bars are shown for bedrock  $\delta^{34}\text{S}$ ; these were measured on a single composited sample, and thus uncertainty estimates are unavailable.

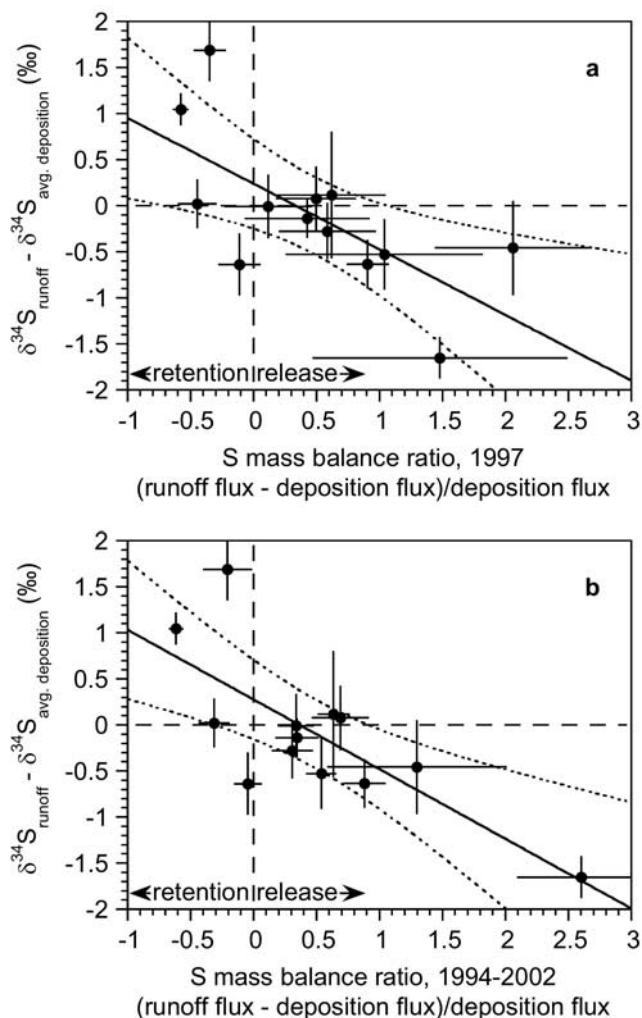
will form a straight line with an intercept of zero and a slope of  $(\delta_x - \delta_{\text{out}})$ , the fractionation of the internal source/sink relative to runoff. Figure 5 depicts a conceptual diagram of this relationship, as one of four alternative scenarios.

[24] Scenario I is non-fractionating S exchange between deposition, catchment pools, and runoff. Typically, this scenario would correspond to the prevalence of abiotic adsorption/desorption of atmospherically derived sulfate in soils. *Van Stempvoort et al.* [1990] showed that abiotic physico-chemical adsorption/desorption of sulfate produces no isotopic fractionation. If sulfate were adsorbed and re-released without organic cycling,  $\delta^{34}\text{S}$  values similar to those of atmospheric inputs would be expected in runoff. Scenario I is represented by a horizontal line in Figure 5. In this purely inorganic scenario mean annual  $\delta^{34}\text{S}$  values of atmospheric input did not change over time.

[25] Scenario II is biological fractionation during organic S cycling in soil. Isotope selectivity of some organic reactions involving S has been documented by *Krouse et al.* [1992], *Gebauer et al.* [1994], *Novak et al.* [1996, 2000, 2001b], *Norman et al.* [2002], and others. If the internal sulfur source or sink is biologically fractionated with respect to runoff, we expect the catchments to fall along a downward-sloping line, in accordance with equation (4).



**Figure 5.** Conceptual diagram illustrating sulfur isotope patterns expected for four alternative scenarios of S retention and release in catchments (see text for explanation).



**Figure 6.** Sulfur isotopic shift between average deposition and runoff in 1997, as a function of the net release or retention of sulfur at 13 Czech catchments in (a) 1997 and (b) 1994 through 2002. Error bars are  $\pm 1$  standard error. Net catchment source or sink of sulfur, calculated from mass balance between deposition and runoff fluxes, is expressed as a ratio to the deposition flux. Plotted in this way, the data are expected to fall along a single mixing line if the internal catchment source or sink in each catchment is isotopically fractionated by the same amount relative to runoff (see text). The slope of the regression line indicates the average  $\delta^{34}\text{S}$  of the internal source or sink, relative to the  $\delta^{34}\text{S}$  of average deposition (see text). Thin dotted lines indicate 95% confidence envelope for the regression line.

[26] In scenario III, if old pollutant S were isotopically lighter than today's atmospheric input, and were stored in the catchment and gradually released via runoff, the catchments could fall within the lower gray polygon of Figure 5. No within-catchment fractionation is invoked in this inorganic scenario.

[27] In scenario IV, if old pollutant S were isotopically heavier than today's atmospheric input, and were stored in

the catchment and gradually released via runoff, the catchments could fall within the upper gray polygon of Figure 5. No within-catchment fractionation is invoked in this inorganic scenario.

[28] On a mass basis, most pollution in central Europe occurred after 1950. We have no evidence that  $\delta^{34}\text{S}$  of industrial S emissions was changing from the 1950s to the 1990s. A minor though statistically significant shift toward lower  $\delta^{34}\text{S}$  of deposited S occurred in the northern part of the Czech Republic between 1993 and 1996 [Novak *et al.*, 2001a], which might argue against scenario III, however, most of the S stored within the catchments probably comes from the period prior to 1993 (soil S pool size  $\gg$  yearly atmospheric S input [Novak *et al.*, 2000]).

[29] Figure 6 shows the relationship between the isotopic shift from deposition to runoff ( $\delta_{\text{out}} - \delta_{\text{in}}$ ) and the catchment mass balance ratio  $(Q_{\text{out}} - Q_{\text{in}}) / Q_{\text{in}}$  for the 13 study catchments. Catchment S mass balances from 1997 were used to calculate the x axis of Figure 6a, whereas a nine-year-long time series of S mass balances from 1994–2002 was used in Figure 6b [Fottova, 2003]. Either data set was consistent with a downward-sloping line, i.e., consistent with scenario II. The data therefore suggest that biological processes that fractionate S isotopes controlled the retention/release of S across the 13 catchments. The slope of the line was statistically significant at a confidence level of  $>99\%$  in both figures, and was consistent between the two figures ( $0.71 \pm 0.24$  in Figure 6a and  $0.76 \pm 0.20$  in Figure 6b). The intercept was not statistically significant in either figure, consistent with equation (4). To the extent that the catchments conform to a single mixing line, equation (4) implies that the internal source or sink in each catchment was isotopically fractionated by the same amount ( $-0.7\text{‰}$ ) relative to runoff. This implies that the mechanisms of retention/release of S are not site-specific. Rather, it suggests that organic S cycling of atmospheric, mainly pollutant S, occurring predominantly in the O and A/B soil horizon, plays a significant role across the sites. Collectively, these results suggest that catchments that were previously extremely polluted are releasing S from the same reservoir in which S is still being accumulated in low-pollution areas. This reservoir, complex in nature, is dominated by organic soil S, but may also include adsorbed sulfate which itself was formed during oxidation of organic S.

[30] The exact contribution of primary atmospheric sulfate desorbed from soil Al and Fe sesquioxides to runoff is not known. This is because of large uncertainties in soil horizon thickness and stoniness in the studied catchments (for within-site elevation spans, which affect the horizon thickness, see Table 1 [cf. Huntington *et al.*, 1988]). At JEZ, where a soil mass inventory was taken using 15 soil pits, runoff contained about 60% of S cycled in soil and 40% of unaltered atmospheric S [Novak *et al.*, 2000]. The export of secondary sulfate containing organically cycled S from catchments is hydrology-driven, just like the export of desorbed atmospheric sulfate. More mineralized S (secondary sulfate) and desorbed atmospheric S (primary sulfate) are released in wet years than in dry years. Dry warm summers result in enhanced rates of S mineralization supplying more sulfate for export by subsequent storm flow. This essentially

climatic control of catchment S dynamics has been recently described for Canadian catchments [Eimers and Dillon, 2002]. In a similar manner, it may operate at the Czech sites. At JEZ, for example, a warm, dry year in 1998 (570 mm of annual precipitation) was followed by a wetter year in 1999 (950 mm). Over the same period, S export increased dramatically from 40 to 65 kg ha<sup>-1</sup> yr<sup>-1</sup>, despite decreasing air pollution.

### 3.13. Comparison of the Model With Isotope Data on $\delta^{34}\text{S}$ of S Forms in Soil

[31] The single S source and sink makes our model rather simplified. In the future, a more detailed model may be developed using multicompartment soil S reservoirs. With the exception of JEZ [Novak *et al.*, 1995, 2000], the abundance of individual S forms in forest soils and their isotope systematics has not been studied in the Czech catchments. However, S speciation in a number of European spruce forest soils exhibits common features [Mayer *et al.*, 2001; Novak *et al.*, 2003]: (1) sites near industrial S emission sources have higher O horizon S<sub>total</sub> pool than unpolluted sites; (2) 75–95% of O horizon S is formed by organic C-bonded S, and the proportion of organic C-bonded S tends to increase with atmospheric S loads; (3) with an increasing soil depth the proportion of organic S decreases while that of inorganic sulfate S increases; and (4) ester-sulfate S is mostly less abundant than inorganic sulfate S, making up <20% of total S.

[32] Sulfur isotope speciation in soil appears to be more site-specific than concentration patterns. Most sites exhibit increasing  $\delta^{34}\text{S}$  values of organic C-bonded S with an increasing depth, and these values are similar to the  $\delta^{34}\text{S}$  values of total soil S [Novak *et al.*, 1996, 2003]. At most sites,  $\delta^{34}\text{S}$  values of organic S are higher than  $\delta^{34}\text{S}$  values of inorganic soil sulfate [Chae and Krouse, 1987; Schoenau and Bettany, 1989; Mayer *et al.*, 1995; Novak *et al.*, 2003]. The  $\delta^{34}\text{S}$  values of ester-sulfate S are higher than  $\delta^{34}\text{S}$  values of C-bonded S at relatively unpolluted sites, but lower than  $\delta^{34}\text{S}$  values of all other S forms in soil at heavily polluted sites [Novak *et al.*, 2003]. At historically polluted sites where  $\delta^{34}\text{S}$  values of spruce throughfall, soil S forms and lysimeter solutes are known, the following isotope systematics prevails:  $\delta^{34}\text{S}_{\text{lysimeters}} \leq \delta^{34}\text{S}_{\text{adsorbed sulfate in soil}} < \delta^{34}\text{S}_{\text{organic C-bonded S}} < \delta^{34}\text{S}_{\text{spruce throughfall}}$ . It appears that S of inorganic sulfate adsorbed in soils is isotopically systematically lighter than both organic C-bonded S and atmospheric input. These limited data on soil S isotope speciation are consistent with our catchment-level isotope systematics at sites releasing S in two respects: (1) both lysimeter solutes and runoff tend to contain isotopically lighter sulfate S, and (2) atmospheric sulfate S is isotopically heavier than sulfate leaving the soil profile. Both features corroborate the prevalence of secondary sulfate, containing organically cycled S, in soils and runoff.

## 4. Conclusions

[33] We constructed S isotope mass balances for 13 forested catchments spanning a 10-fold S deposition gradient in Central Europe. From 1987, the year of maximum industrial S emission rates, to 1997, the year of intensive S

isotope monitoring, anthropogenic S emission rates decreased by 50% owing to industry restructuring and installation of scrubbers in coal-burning power plants. In 1997, we found that catchments with a history of extreme pollution were releasing 1–3 times more S than the contemporary atmospheric S input, whereas relatively unpolluted catchments were still accumulating S. Using nearly 500  $\delta^{34}\text{S}$  determinations of individual S pools and fluxes we were able to show that the excess S in runoff at the polluted sites was not bedrock-derived, but instead was older pollutant S which had been temporarily stored in soil. Isotopes provided evidence that weathering of common rocks, such as gneisses and granitoids, supplies a negligible amount of S to stream runoff. Across the sites, the  $\delta^{34}\text{S}$  values of runoff were strongly correlated with the soil O horizon, whose S was predominantly organic, and always isotopically lighter than S in runoff. The sulfur isotopic composition of the discharge depended on whether the catchment accumulated or released S. The  $\delta^{34}\text{S}$  values of runoff were lower than the  $\delta^{34}\text{S}$  of average atmospheric deposition at sites releasing S, and higher than the  $\delta^{34}\text{S}$  of the input at sites accumulating S. The sink for the retained S and the source of the released S was isotopically fractionated by the same amount relative to runoff. It has been known from previous studies that inorganic adsorption/desorption of sulfate does not fractionate S isotopes [Van Stempvoort *et al.*, 1990], whereas biological S cycling is isotopically selective [Novak *et al.*, 1996, 2001b]. Thus the within-catchment source/sink of S was mainly organically cycled soil S. We developed a model to show that the sink and source of S within the catchment was the same along a steep pollution gradient. The mechanisms of S storage in these forest catchments were not site-specific, but rather organic cycling played an important role over a wide range of atmospheric S inputs (13 to 130 kg S ha<sup>-1</sup> yr<sup>-1</sup>). Using isotopes, we had previously demonstrated the importance of organic S cycling at two sites in the highly polluted northern Czech Republic (JEZ, NAC [Novak *et al.*, 2000]). Sulfur isotope data from our 13 catchments show that these conclusions are applicable across a considerably wider pollution gradient.

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