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Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living *Sphagnum* along a NW–SE transect across Europe

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Abstract. At five European sites, differing in atmospheric S inputs by a factor of 6, and differing in S isotope signatures of these inputs by up to 14‰ (CDT), we investigated the direction and magnitude of an assimilation-related δ^{34}S shift and the relationship between atmospheric deposition and S retention in selected ecosystem compartments. Bulk precipitation and spruce throughfall were collected between 1994 and 1996 in the Isle of Mull (Scotland), Connemara (Ireland), Thorne Moors (England), Rybárenská slat' and Oceán (both Czech Republic) and analyzed for sulfate concentrations and δ^{34}S ratios. Eighteen replicate samples per site of living *Sphagnum* collected in unforested peatlands and 18 samples of spruce forest floor collected near each of the peatlands were also analyzed for S concentrations and δ^{34}S ratios. Assimilation of S was associated with a negative δ^{34}S shift. Plant tissues systematically preferred the light isotope ^{32}S, on average by 2‰. There was a strong positive correlation between the non-marine portion of the atmospheric S input and total S concentration in forest floor and *Sphagnum*, respectively (R = 0.97 and R = 0.85). Elevated S inputs lead to higher S retention in these two organic-rich compartments of the ecosystem. It follows that equal emphasis must be placed on organic S as on adsorption/desorption of inorganic sulfate when studying acidification reversal in ecosystems. The sea-shore sites had rainfall enriched in the heavy isotope ^{34}S due to an admixture of sea-spray. The inland sites had low δ^{34}S reflecting δ^{34}S of sulfur emitted from local coal-burning power stations. *Sphagnum* had always lower S contents and higher δ^{34}S ratios compared to forest floor. The within-site range of δ^{34}S ratios of *Sphagnum* and forest floor was wide (up to 12‰) suggesting that at least six replicate samples should be taken when using δ^{34}S as a tracer.

Introduction

Behavior of sulfur isotopes during biogeochemical processes has been the focus of numerous studies (Giesemann et al. 1995a, b; Yang et al. 1996; Heaton et al. 1997; de Caritat et al. 1997; Zhang et al. 1998; Alewell et al. 1999; Novák et al. 2000). By the end of the 1980s it was well established that sources of pollution often have a distinct δ^{34}S signature which can be used to follow the transport pathways and residence times of sulfur in terrestrial ecosystems (Krouse et al. 1984). However, several isotope-fractionating processes affect sulfur in the system atmosphere – biosphere – bedrock and may hamper the use of δ^{34}S ratios as a tracer. The δ^{34}S signature of atmospheric input can be altered by processes redistributing isotopes within the ecosystem. Isotope effects of several successive biogeochemical reactions may be difficult to decouple. For such cases, Fritz and Fontes (1980) introduced the term ‘overall’ fractionations. Two processes suspected to cause ‘overall’ sulfur fractionations are assimilation of sulfur by plants and mineralization of organic S in the soil (Krouse & Grinenko 1991). While there is a general agreement that S mineralization in the soil does redistribute S isotopes (Fuller et al. 1986; Gebauer et al. 1994; Novák et al. 1994; Mayer et al. 1995, Novák et al. 1996; Zhang et al. 1998; Driscoll et al. 1998, Novák et al. 1999; Novák et al. 2000), evidence for the existence of δ^{34}S shifts related to sulfur assimilation by plants remains inconclusive (Manskaya & Drozdova 1968; for discussion of the topic see also van Stempvoort et al. 1992; Mayer et al. 1995).

One approach toward evaluation of the direction and magnitude of an assimilation-related δ^{34}S shift is to compare sulfur isotope composition of atmospheric input and biological S pools at a number of different sites. If all sites consistently exhibited enrichment in the abundance of one of the isotopes (^{32}S or ^{34}S) upon assimilation, we would conclude that assimilation redistributes S isotopes. Such approach has been rarely used because of the need to generate relatively large data sets by long-term monitoring of atmospheric deposition and by replicate sampling of organic material, both under an array of atmospheric and bedrock S isotope signatures.

Another problem often encountered when using δ^{34}S ratios as a tracer in terrestrial ecosystems is the heterogeneity in δ^{34}S ratios in a particular compartment of the ecosystem. In ombrotrophic peatlands, as well as in the uppermost soil horizons on common types of bedrock (such as granites and gneisses with S contents <0.05 wt. %; *cf.* also Likens & Bormann 1995), atmogenic S dominates over geogenic S. There is no *a priori* reason for a sizable scatter in δ^{34}S ratios in these biogenic materials, supposing constant δ^{34}S ratio of atmospheric input (for example in pristine areas) and absence of the dissimilatory sulfate reduction which may strongly fractionate (Kaplan & Rittenberg 1964).

To further explore the potential of δ^{34}S ratios as an environmental tracer, we isotopically analyzed S fluxes and S pools at five sites along a NE–SW transect across western and central Europe, spanning S deposition levels differing by a factor of 6. The sulfur fluxes studied included bulk (open area) precipitation and spruce canopy throughfall; the sulfur pools studied were living *Sphagnum* and spruce forest floor.

Our objectives were: (i) to evaluate the existence/non-existence of sulfur isotope fractionation accompanying assimilation; (ii) to determine whether or not elevated sulfur inputs result in higher retention in the organic-rich sulfur pools (*Sphagnum* and spruce forest floor); and (iii) to show that in a specific terrestrial ecosystem the δ^{34}S ratio of one type of biogenic material, such as moss or humus, may represent a rather wide range of values.

Study sites

The Isle of Mull (480 km^2; Jermy & Crabbe 1978), is situated in a pristine area 3 km off the Western coast of Scotland (Figure 1; Table 1). Both moss and forest floor samples were taken in the Ross of Mull, a sparsely populated south-western peninsula with no industries. Bog pools were dominated by *Sphagnum cuspidatum/recurvum* with *S. auriculatum* and *S. palustre* also present. *Carex limosum, Utricularia* spp. and *Menyathes trifoliata* were common. *Sphagnum* samples were taken between Loch Scridan, Sidhean Riabhach and Cnoc ant-Suidhe. The peatland is known as Ann Grosan Gleann Moor. Forest floor samples were collected in two Norway spruce plantations located 2 to 6 km east of Loch Scridan. The plantations were 30 years old. A bulk precipitation collector was placed near Loch Scridan, throughfall was collected in the eastern spruce plantation.

Connemara (1400 km^2; Whilde 1994) was the second of the two study sites affected by the proximity of the Atlantic Ocean. The National Park Connemara is situated in pristine western Ireland between the Galway and Clew Bays. It is sparsely inhabited and remote from industrial pollution sources. The bog is 90% *Sphagnum* covered, with evergreen dwarf shrubs and tussock-forming grasses, sedges and rushes. In addition to *Sphagna* mentioned in Mull, the species sampled included *S. papillosum*, *S. magellanicum*, *S. capillifolium* and *S. tenellum*. The climate at Connemara is mild and moist, the number of wet days exceeds 230 per year. *Sphagnum* was sampled near the western-most tip of the mainland, southeast of Clifden and southwest of Glendollagh Lough, forest soil underneath 30-year old plantations of Norway spruce 15 km east of the bog. Rain and spruce throughfall collectors were installed in a sparsely populated area 20 km east of the bog.

Thorne Moors (19 km^2; Caufield 1991) is situated south-west of the city of Goole in South Yorkshire, England. The distance from the North and Irish Sea is 55 and 130 km, respectively. Thorne Moors is Britain's largest raised bog. Colonized by *Sphagnum* 3000 years ago, the moor accumulated 7 m of peat

Table 1. Characteristics of the study sites.

	Mull	Connemara	Thorne Moors	Rybárenská slat’	Oceán
Country	Scotland, U.K.	Ireland	England, U.K.	Czech Republic	Czech Republic
Location	56°18′ N, 6°17′ W	53°24′, 10°00′ W	53°42′ N, 0°52′ W	49°03′ N, 13°30′ E	50°21′ N, 12°42′ E
Elevation	30 m a.s.l.	30 m a.s.l.	10 m a.s.l.	1050 m a.s.l.	900 m a.s.l.
Area studied	78 km^2	70 km^2	80 km^2	60 km^2	15 km^2
Bedrock	Granite, gneiss, basalt	Amphibolite	Lacustrine clay	Granite	Granite
Soil type under spruce	Dystric Cambisol	Dystric Cambisol	Stagnogley	Dystric Cambisol	Dystric Cambisol
Prevailing wind direction	South-west	South-west	West	West	West
Nearest pollution sources	None	None	Yorkshire power plants	City of Plzeň	North Bohemian power plants
Mean annual temperature	+8.8 °C	+10.0 °C	+9.6 °C	+3.7 °C	+4.8°C
Annual precipitation	1632 mm	1213 mm	654 mm	1105 mm	1029 mm
Distance from sea	Max. 3 km	Max. 3 km	55 km	560 km	390 km
Distance between peat bog and spruce stand	12 km	15 km	33 km	9 km	4 km

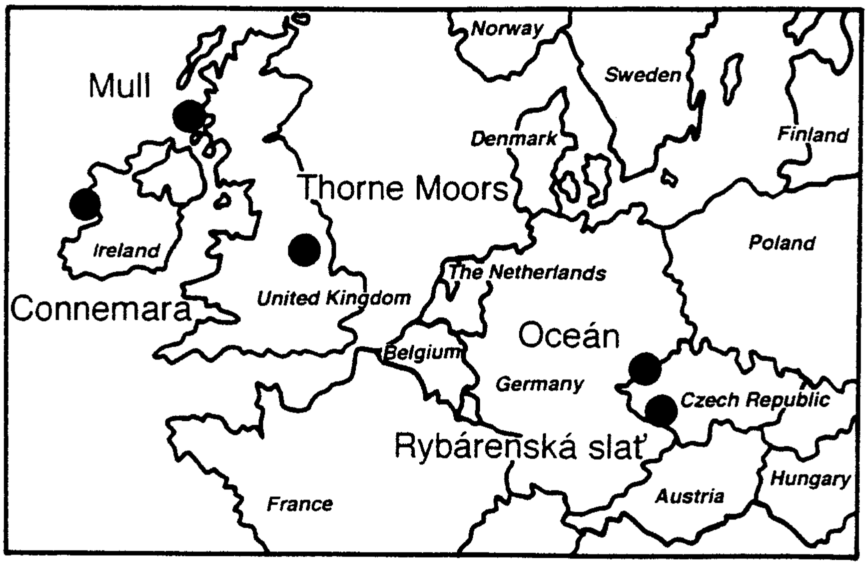

Figure 1. Study sites.

standing up to 10 m over the surrounding countryside. Due to peat mining, Thorne Moors today is nowhere deeper than 2.5 m. The following species of *Sphagna* were identified: *S. cuspidatum*, *S. imbricatum*, *S. compactum* and *S. plumulosum*. *Sphagnum* samples were taken in the National Nature Reserve in the central part of the bog and its close vicinity. A bulk precipitation collector was installed directly in the bog.

Since no spruce plantations exist near Thorne Moors, spruce throughfall deposition was taken 60 km northwest of the bog at Harewood Estate, West Yorkshire. Between the two sites two coal-burning power stations equipped with desulfurization units are located. The distance of Harewood Estate from the North and Irish Sea is 88 and 97 km, respectively. Forest floor samples were taken in mature Norway spruce stands in Scotton Common, Warren Wood and Market Rasen in the surroundings of Gainsborough, Lincolnshire (30 km south of Thorne Moors).

The Rybárenská slat’ bog (134 ha; Dohnal et al. 1965) is situated west of the village of Modrava in the Šumava National Park, southern Czech Republic. Further north air pollution worsens dramatically, the major Czech industrial sources of S emissions are located 150 km north of Rybárenská slat’. In the bog *S. girgensohnii Russ.* predominates over *S. fallax v. Klinggr.* and *S. subsecundum Nees*. The bog is surrounded by healthy mature spruce forests. Bulk precipitation and spruce throughfall were collected directly at the bog. Forest floor samples were taken north of Modrava, between Filip’s Glasworks and Čeněk’s Sawmill.

The Oceán bog (116 ha; Dohnal et al. 1965) is located in the Krušné hory Mts., northern Czech Republic, one of the most polluted regions of the world. The mountains overlook a coal basin with 11 major coal-burning power stations. Sulfur dioxide emissions peaked in 1987 (820,000 tons yr^{-1}). Soft coal currently exploited contains 2 to 4% S. After 1970, more than 400 km^2 of spruce monocultures died back in this area. The Oceán bog is situated on the mountain-top plateau 30 km northwest of the main cluster of power stations. The bog is surrounded by mature spruce stands showing symptoms of crown thinning and yellowing. *Sphagnum* samples were taken in open segments of the bog where also bulk precipitation was measured. *S. riparium Angstr.* dominated over *S. fallax v. Klinggr.*, *S. girgensonii Russ.* and *S. russowii Warnst*. Forest floor samples were taken between the town of Nejdek (4 km south-east of the bog) and Oceán.

Sampling

Bi-monthly cumulative sampling of atmospheric deposition was carried out using a simplified protocol of the GEOMON Monitoring Network (Fottová & Skořepová 1998). Sampling of bulk precipitation started on April 1, May 22, March 3, May 23 and May 5, 1994 in Mull, Connemara, Thorne Moors, Rybárenská slat’ and Oceán, respectively. Sampling of spruce throughfall started on August 21, May 21, June 21, May 23 and May 5, 1994 in Mull, Connemara, Thorne Moors, Rybárenská slat’ and Oceán, respectively. The sampling lasted for 26 months in Rybárenská slat’ and Oceán (both bulk and throughfall), 18 months in Thorne Moors (throughfall), and 12 months in Mull (bulk and throughfall), Connemara (bulk and throughfall) and Thorne Moors (bulk). Bulk precipitation was sampled in an open area into a 200-mm-diameter polyethylene funnel set 1.1 m above ground level. The collector was allowed to drain into a 5-L can wrapped in a light-proof black polyethylene bag and containing 5 mL of 200 g L^{-1} $Cu(NO_3)_2$ in 50% v/v nitric acid. Throughfall was collected underneath the canopy of a 20–40 year old spruce tree into collectors identical to those used for bulk precipitation. Cupric nitrate added to inhibit biological activity in the collected rainwater was substituted with thymol in the second year of monitoring at Rybárenská slat’ and Oceán. Also at the two Czech sites, the funnels were replaced with 265-mm-diameter bottomless PE buckets fitted to large (1.5 by 0.8 m) polyethylene bags to collect snow between December and April.

Samples of living *Sphagnum* (100 g; 2–3 cm long capitula tips) and forest floor (250 g; 0–3 cm below soil surface) respectively, were taken at 18 locations situated at least 200 m apart within each of the five sites. The samples were placed into ZipLoc bags and transported into the laboratory. The collection dates were: April 1–3, 1994 (Mull), May 21–23, 1994 (Connemara), March 3–June 21, 1994 (Thorne Moors), April 6, 1994 (Rybárenská slat’) and April 9, 1994 (Oceán).

At each of the five sites a pit was dug out in the spruce forest and 2 kg of mineral soil were taken from the rooting depth of the trees (C soil horizon). The depth intervals sampled were: 34–40 cm (Mull), 40–50 cm (Connemara), 45–60 cm (Thorne Moors), 65–80 cm (Rybárenská slat’), and 40–64 cm (Oceán).

Analytical methods

On return to the laboratory the volume of water samples was measured. Following filtration a sub-sample was taken to be analyzed for sulfate and chloride using a Dionex DX-100 (Irish and UK samples) and a Shimadzu LC 6A (Czech samples) ion chromatograph. Up to 50 mL of hydrogen peroxide were added to the remaining sample to oxidize organic material. Sulfate in water samples was concentrated by a combination of evaporation to half the original volume with the use of ion exhange columns. The water pH was adjusted to approximately 3 before adding $BaCl_2$ to the hot sample to precipitate $BaSO_4$. *Sphagnum* samples were dried at 105 °C and milled to a powder using a blender. Soil samples were sieved (<2 mm), dried at 105 °C and homogenized in a planetary mill. An aliquot of both types of solid samples was analyzed for sulfur content using a LECO SC-132 sulfur analyzer. Total sulfur for stable isotope analysis was recovered from *Sphagnum* samples by combustion in a Parr oxygen bomb apparatus and converted to $BaSO_4$. The $BaSO_4$ precipitates resulting from all *Sphagnum* samples plus the Irish and UK water samples were converted to SO_2 by flushing with $Na_3(PO_3)_3$ at 930 °C (Halas et al. 1982) in vacuum and their sulfur isotope ratios measured on a VG SIRA 10 mass spectrometer. Total sulfur for stable isotope analysis was recovered from soil samples by thermal decomposition with Eschka’s mixture at 850 °C (Novák et al. 1994) and converted to $BaSO_4$. Barium sulfate precipitates resulting from all soil samples plus the Czech water samples were converted to SO_2 in a vacuum line at 980 °C using the method of Yanagisawa and Sakai (1983; mixing of $BaSO_4$ with V_2O_5 and SiO_2 in a 1:10:10 wt. ratio) and the sulfur isotope ratios were measured on a Finnigan MAT 251 mass spectrometer. 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 CDT standard. Analytical uncertainty was $\leq 0.3‰$ for each preparatory procedure in combination with any of the two mass spectrometers employed.

Ash content in the forest floor was calculated as loss on ignition at 550 °C over a period of four hours. Soil characteristics of the combined unhomogenized, but sieved (<2 mm), O + A horizons were determined according to Houba et al. (1989). These soil characteristics included: pH_{CaCl_2}, pH_{KCl}, cation exchange capacity, exchangeable H^+, Ca^{2+}, Mg^{2+} and K^+. The amount of inorganic free and adsorbed SO_4^{2-}-S contained in *Sphagnum* and forest floor was calculated as the difference between two gravimetric Eshka's mixture sulfur determinations, one on untreated solid samples and one on the solid residue following overnight extraction of 5 g of the sample with 100 mL 16.1 mM $NaH_2PO_4 \cdot 2H_2O$.

The sea-spray sulfate component in precipitation was calculated from total SO_4^{2-} concentrations using Cl concentrations and the known Cl/SO_4^{2-} ratio in sea-water (7.1). The pollutant portion of atmospheric deposition at individual sites was calculated by subtracting the sea-spray component from total deposition.

Statistical analyses were performed using the JMP IN package by SAS (Sall & Lehman 1996). Once the difference in mean sulfur concentrations or $\delta^{34}S$ ratios was found to be statistically significant (one-way, five-level ANOVA, *F*-test; $p < 0.05$), comparisons for each pair of means were performed using the Student's *t* with LSD.

For forest floor and *Sphagnum*, we calculated a minimum number of replicates needed for a satisfactory estimation of the true mean $\delta^{34}S$ ratio according to Cochran and Cox (1957). The chosen width of the $1 - \alpha$ confidence interval was ±1‰. The 'true' mean was calculated from our 18 replicate samples. Normality of the data was verified using the Shapiro-Wilk test. The recommended number of observations (n) was calculated from the formula

$$n \geq \left(\frac{2\sigma z(\alpha/2)}{\Delta} \right)^2$$

where σ is the standard deviation, z is the critical value of normal distribution corresponding to $\alpha/2$ (1.96 for the chosen $\alpha = 0.05$), and Δ is the width of the confidence interval (2‰).

Results and discussion

Atmospheric deposition

Generally, sulfur in bulk precipitation, measured in an unforested area, is dominated by wet-deposited sulfate (Johnson & Lindberg 1992). Sulfur in spruce throughfall may contain, due to a large surface area of the canopy, a considerable additional amount of S derived from dry-deposited SO_2. Direct uptake or leaching of sulfate by spruce canopy bears little effect on sulfur fluxes because the amount of sulfur exchanged with the canopy and leached from the needles is negligible (Fowler et al. 1989). Sulfate concentrations in bulk precipitation were mostly below 10 mg L^{-1} at all five sites (Figure 2 *top left*). Inland sites (whose upwind distance from the sea was $>$100 km) had the lowest mean SO_4^{2-} concentrations in bulk precipitation: 2.5 mg L^{-1} (Rybárenská slat') and 3.9 mg L^{-1} (Oceán). The amount of sulfur washed out from the atmosphere at Oceán, which is located in the vicinity of large coal-burning power stations, was very low in open areas. Sulfate concentrations in spruce throughfall were the highest at the industrially polluted sites Thorne Moors and Oceán, at times reaching 70 mg L^{-1} (Figure 2 *top right*). It appears that at polluted, spruce die-back affected sites, such as Oceán, forest soil receives high S loads prior to defoliation, but immediately after defoliation S deposition drops dramatically. The sudden decrease in S inputs into the already acidified soil occurs even without reduction in industrial S emissions and is entirely due to less efficient scavenging of SO_2 following pollution-induced defoliation.

Sea-shore sites (Mull, Connemara) differed strikingly in their $\delta^{34}S$ ratios of atmospheric deposition from the other three sites (Figure 2 *bottom*). The between-site $\delta^{34}S$ pattern was similar for bulk precipitation and spruce throughfall. While the $\delta^{34}S$ ratios of atmospheric deposition fluctuated around 15‰ at both sea-shore sites, Mull and Connemara, the $\delta^{34}S$ ratios at Thorne Moors, Rybárenská slat' and Oceán were much lower, mostly around 5‰. Air-borne sulfur at the former two sites was influenced by sea-spray whose high $\delta^{34}S$ ratio was identical to that of sea water (21‰; Rees 1970). It folllows from Figure 2 (*bottom*) that even at sites very near the shore (hundreds of m), such as Mull and Connemara in this study, sulfur input from the atmosphere is not purely derived from sea-water and its $\delta^{34}S$ is a result of mixing of sea-water sulfur with a non-marine component characterized by a lower $\delta^{34}S$ (*cf.*, McArdle & Liss 1995). The $\delta^{34}S$ ratio of the non-marine component can be calculated using the known sea-salt contribution in precipitation. The $\delta^{34}S$ ratio of the non-marine component was 10.7 and 12.3‰ for Mull and Connemara, respectively. The lowest $\delta^{34}S$ ratios (mean of 4.2, and 3.2‰ for bulk precipitation and throughfall, respectively) were those of Thorne Moors, even though the distance of Thorne Moors from the sea (55 km) is shorter than in case of the Czech sites (400 km). The non-marine S component in Thorne Moors precipitation was characterized by a lower $\delta^{34}S$ ratio (2.4‰) than that in Rybárenská slat' (3.3‰) and Oceán (5.2‰).

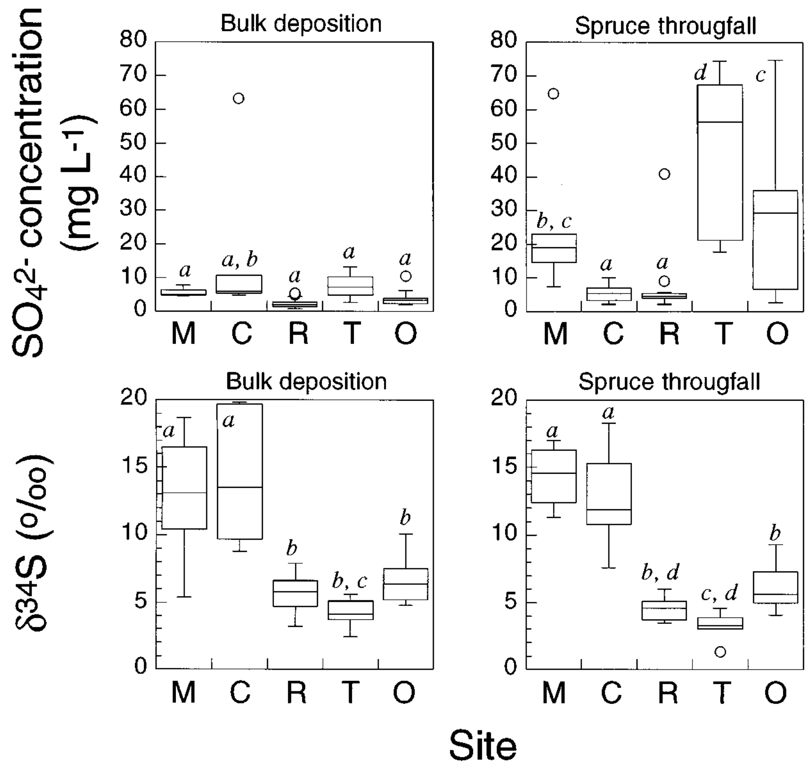

Figure 2. Boxplots of sulfate concentrations (*top*) and δ^{34}S ratios (*bottom*) of atmospheric input. The box encloses 50% of the data, the whiskers 90% of the data, the horizontal bar is the median, open circles are outliers. M-Mull, C-Connemara, R-Rybárenská slat', T-Thorne Moors, O-Oceán. The differences in means were statistically significant (one-way ANOVA, F-test, $p < 0.05$). Different letters denote means found to be statistically different by the Student's *t* with LSD.

The $\delta^{34}S_{INPUT}$ time series are in Figure 3. One striking feature of δ^{34}S time series in recently published studies is a tendency toward lower values of throughfall (TF) compared to bulk precipitation (BULK). This tendency is especially seen in winter: For example, Zhang et al. (1998) reported $\delta^{34}S_{TF}$ of 4.9 and $\delta^{34}S_{BULK}$ of 5.9‰ at Hubbard Brook, northeastern U.S.; Novák et al. (1995) found $\delta^{34}S_{TF}$ of 3.0 and $\delta^{34}S_{BULK}$ of 8.0‰ at CER, and $\delta^{34}S_{TF}$ of 4.0, and $\delta^{34}S_{BULK}$ of 10.0‰ at NAC, two sites in the Czech Republic. In this study, we compared *flux-weighted* long-time mean $\delta^{34}S_{TF}$ and $\delta^{34}S_{BULK}$ ratios at five sites situated along the NW–SE European transect. Across the sites, the flux-weighted mean $\delta^{34}S_{TF}$ ratio was on average by 1.1‰ lower than the $\delta^{34}S_{BULK}$ ratio. The individual flux-weighted mean $\delta^{34}S_{TF}$ and $\delta^{34}S_{BULK}$ ratios were: 14.9 vs. 13.7‰ (Mull), 13.6 vs. 17.8‰ (Connemara), 4.7 vs.

Table 2. Annual atmospheric deposition of sulfur at the study sites. The difference between spruce throughfall and bulk precipitation represents dry deposition (mainly SO_2).

Site	Bulk precipitation ($kg\ S\ ha^{-1}\ yr^{-1}$)	% of marine-derived component	Spruce throughfall ($kg\ S\ ha^{-1}\ yr^{-1}$)	% of marine-derived component
Mull	31.4	29.2	55.6	78.2
Connemara	60.6	63.1	23.1	58.2
Rybárenská slat’	9.1	14.3	19.4	7.6
Thorne Moors	14.5	10.4	56.9	10.4
Oceán	11.8	9.5	66.7	2.4

5.8‰ (Rybárenská slat’), 3.4 vs. 4.3‰ (Thorne Moors), and 6.2 vs. 6.7‰ (Oceán). Thus four of the five sites exhibited a $\delta^{34}S_{TF} < \delta^{34}S_{BULK}$ relationship. We conclude that the existence of some general mechanism driving the $\delta^{34}S_{TF}$ and $\delta^{34}S_{BULK}$ ratios apart cannot be ruled out. Such mechanism may be linked with seasonal variation in the intensity of biological (Nriagu et al. 1987) or abiotic (Saltzman et al. 1983) processes affecting $\delta^{34}S$ in the atmosphere. It is difficult to compare our result with literature data, because none of the previous studies (van Stempvoort & Wills 1991; Stam et al. 1992; Gebauer et al. 1994; Giesemann et al. 1995a; Mayer et al. 1995; Heaton et al. 1997; Pichlmayer & Seibert 1997; Alewell & Gehre 1999) give flux-weighted $\delta^{34}S$ data.

Annual rates of sulfur deposition at each site differed between open and forested locations (Table 2). Bulk atmospheric deposition increased from Rybárenská slat’ to Oceán, Thorne Moors, Mull and Connemara, respectively. Atmospheric deposition underneath spruce canopy increased from Rybárenská slat’ to Connemara, Mull, Thorne Moors and Oceán, respectively. Sulfur dioxide originating from industries was partly scavenged by foliage before oxidation to SO_4^{2-} in the atmosphere could proceed. As a result, the forested part of Oceán exhibited the highest atmospheric deposition of sulfur of all sites (66.7 kg ha^{-1} yr^{-1}). Sulfur dioxide deposition at Thorne Moors (Harewood) remained nearly as high (56.9 kg S ha^{-1} yr^{-1}), despite desulfurization of the nearby power stations. Similar to these industrially polluted sites was atmospheric deposition in coastal areas (60.6 kg S ha^{-1} yr^{-1} in an open location in Connemara, and 55.6 kg S ha^{-1} yr^{-1} in a spruce stand in Mull). Sulfur at the coastal sites was largely sea-derived (Table 2), contributing to ecosystem acidification only in the short-run by means of the salt effect (Reuss & Johnson 1986).

Table 2 also shows that the proportion of dry-deposited S can be extremely high at industrially polluted sites, reaching 70% at Oceán.

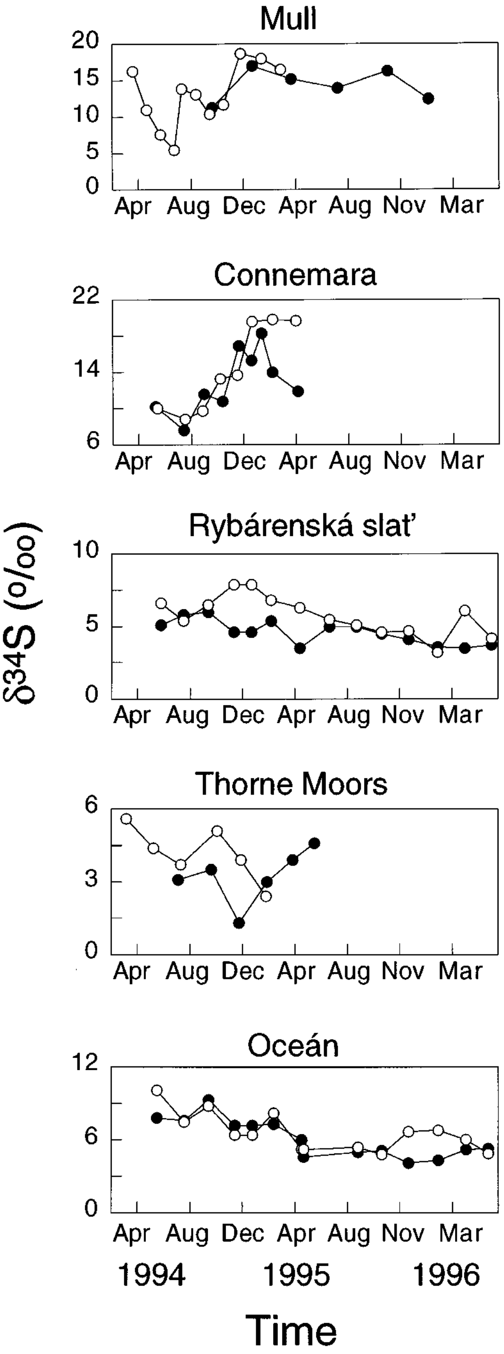

Figure 3. Time series of δ^{34}S ratios. Solid circles represent spruce throughfall, open circles represent bulk precipitation.

Table 3. Soil characteristics. O + A horizon in spruce stands.

Site	pH_{CaCl_2}	pH_{KCl}	CEC* (mmol/100g)	$H^+_{exch.}$ (mmol/100g)	$Ca^{2+}_{exch.}$	$Mg^{2+}_{exch.}$ (mmol/100g)	$K^+_{exch.}$
Mull	4.05	3.90	68.0	15.5	4.56	2.68	2.68
Connemara	3.60	3.50	52.5	52.0	4.00	3.22	0.67
Thorne Moors	3.10	3.00	19.4	20.0	1.40	0.82	0.20
Rybárenská slat’	5.35	5.20	16.1	12.0	8.00	0.90	0.10
Oceán	3.20	3.15	48.0	63.0	6.10	0.25	0.34

*cation exchange capacity
exch. = exchangeable

Organic-rich materials

Living *Sphagnum* had lower concentrations of total S than forest floor soil at all five sites (Figure 4). Mean S concentrations in living *Sphagnum* were: 0.10, 0.12, 0.13, 0.14 and 0.25 wt. % at Mull, Connemara, Rybárenská slat’, Thorne Moors and Oceán, respectively. The ash content in *Sphagnum* was low ($<$1% dry mass). Similar to *Sphagnum*, forest floor had the lowest S concentrations at Mull (0.19 wt. %), and the highest S concentrations at Oceán (0.24 wt. %). Forest floor, for which characteristics are summarized in Table 3, contained silicate and sesquioxide particles (11, 9, 34, 24 and 37 wt. % at Mull, Connemara, Rybárenská slat’, Thorne Moors and Oceán, respectively) which ‘diluted’ the organic contents. Figure 5 gives the relationship between ash content and S concentration in forest floor samples. Pearson’s correlation coefficients (R) were high for Rybárenská slat’ and Oceán (0.92 and 0.78, respectively). When a correction for ash contents was applied, S concentrations in forest floor increased from sea-shore to inland sites in a fashion similar to *Sphagnum* (0.23, 0.22, 0.29, 0.36 and 0.39 wt. % at Mull, Connemara, Rybárenská slat’, Thorne Moors and Oceán, respectively).

The δ^{34}S ratios for *Sphagnum* and forest floor are in Figure 6. In comparison with Figure 4, the general patterns are inversed: sites with relatively low S concentrations in organic-rich materials had high δ^{34}S ratios and *vice versa*. These patterns were primarily driven by two factors: (i) the distance from the sea, and (ii) the fact that pristine sea-shore sites accumulate relatively little S even if the input of marine sulfate may be large. Sea-shore sites (Mull and Connemara) exhibited a considerable proportion of isotopically heavy sea-spray derived S in organic-rich materials (mean δ^{34}S of 12.7 and 10.2‰ in *Sphagnum* and forest floor, respectively, for Mull; the corresponding values for Connemara were 14.7 and 13.2‰). The lowest δ^{34}S ratio was found in forest floor near Thorne Moors (2.6‰). The low δ^{34}S ratios at the three inland sites (Thorne Moors, Rybárenská slat’ and Oceán) were statistically

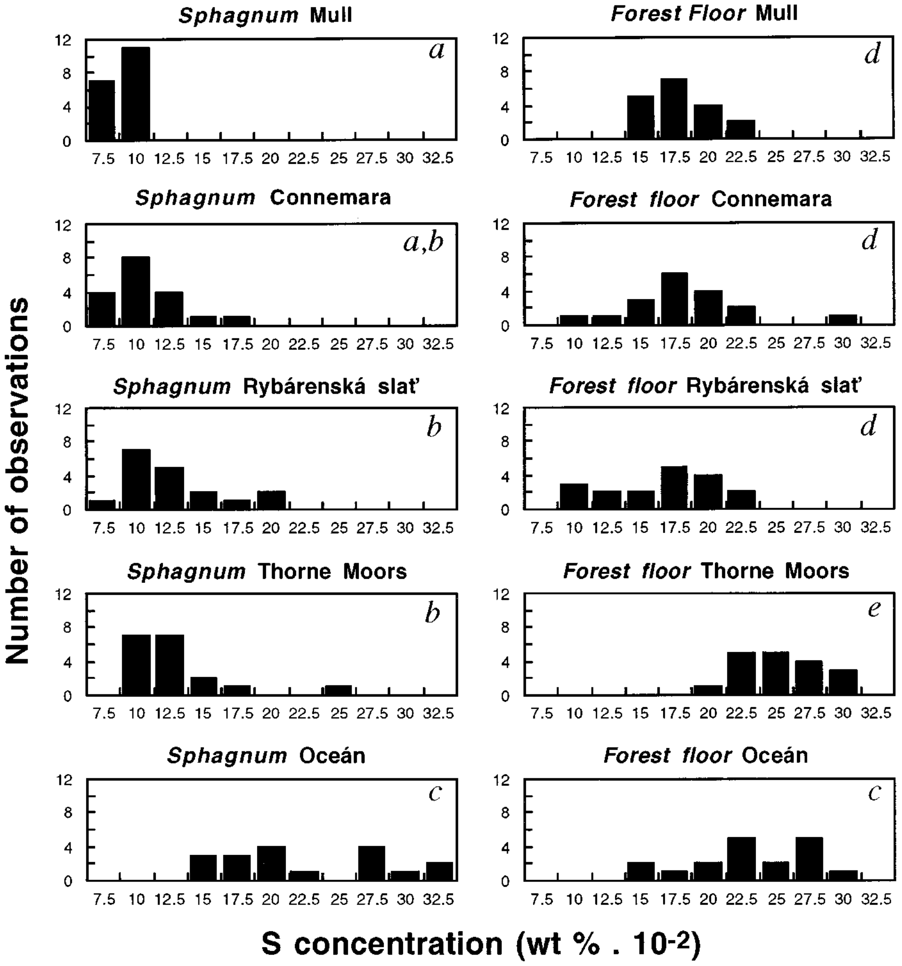

Figure 4. Histograms of S concentrations in organic-rich materials. Number of observations = 18 per site and sample type. Different letters denote means found to be statistically different.

indistinguishable (Figure 6). Interestingly, mean δ^{34}S ratios were higher for *Sphagnum* than for forest floor at all five sites, on average by 2.8‰. Of these two somewhat arbitrarily selected types of organic-rich material, the one systematically accumulating more S (forest floor) had always lower δ^{34}S ratios.

In contrast to forest floor samples, which were derived from a single species (*Picea abies*), a number of different species of *Sphagnum* were sampled. Between-site differences in δ^{34}S of *Sphagnum* might be caused by inclusion of different species at individual sites. Therefore, we identified all isotopically analysed *Sphagnum* species at two sites, Rybárenská slat' and

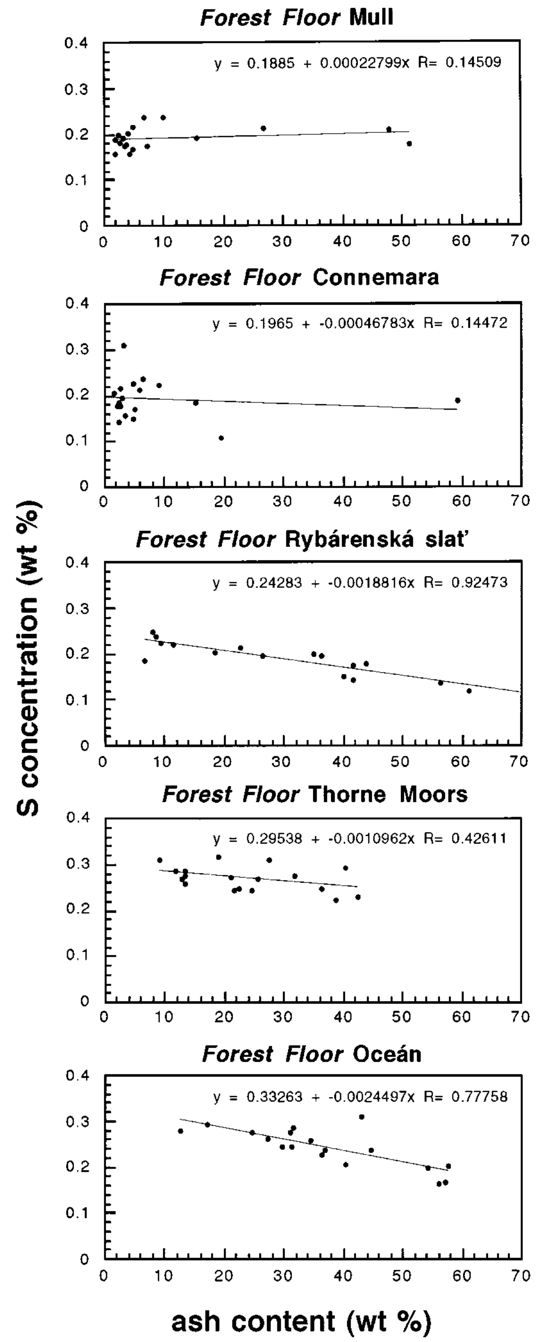

Figure 5. Relationship between ash content and S concentrations in forest floor samples.

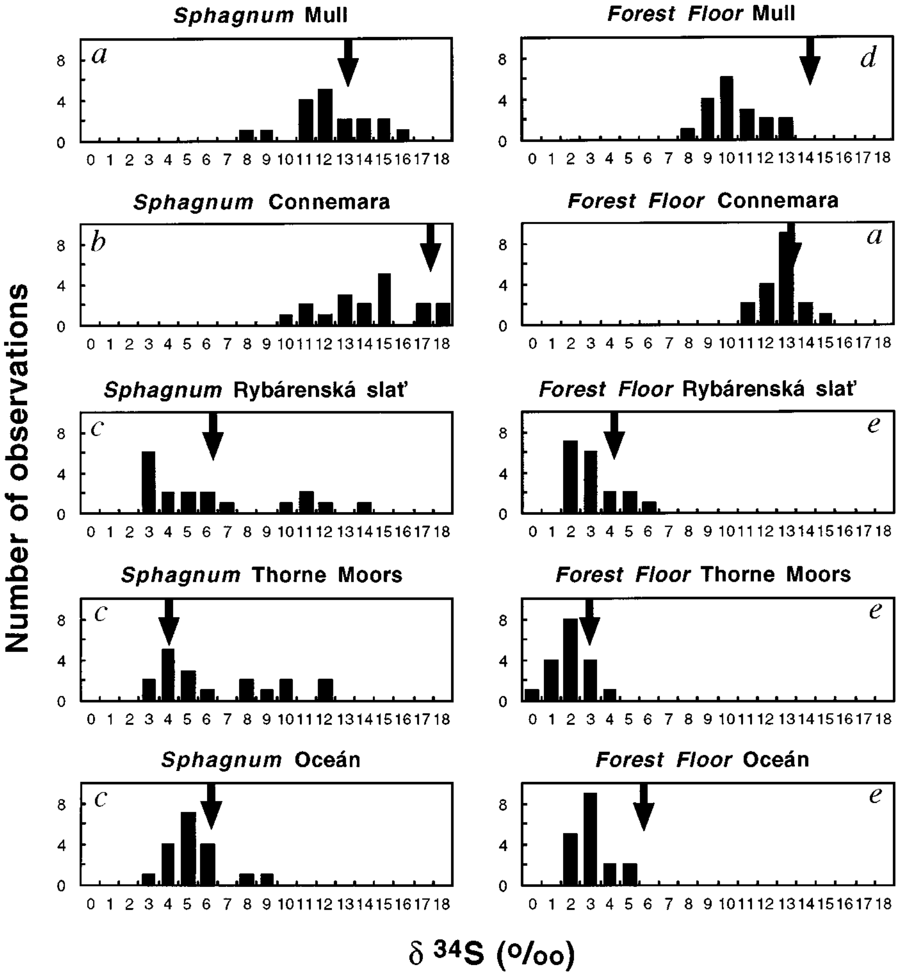

Figure 6. Histograms of δ^{34}S ratios of the organic-rich materials. Number of observations = 18 per site and sample type. Different letters denote means found to be statistically different. The down arrows represent flux-weighted mean δ^{34}S ratios of atmospheric deposition (bulk precipitation *left*, spruce throughfall *right*).

Oceán (Table 4), and tested for an effect of species on δ^{34}S. We found no statistically significant effect of the species on δ^{34}S (ANOVA, *F*-test, $p >$ 0.05).

The range of δ^{34}S ratios depicted in Figure 6 differed between the two types of samples within each site even though the number of observations was identical (n = 18). At each of the five sites, the range of δ^{34}S ratios was larger for *Sphagnum* than for forest floor, on average by 4.4‰. Table 5

Table 4. *Sphagnum* species sampled at the two peat bogs in the Czech Republic and their δ^{34}S ratios (‰).

Sample ID	Species	δ^{34}S	Sample ID	Species	δ^{34}S
	Rybárenská slat’			Oceán	
R1	*S. girgensohnii Russ.*	7.2	O1	*S. fallax v. Klinggr.*	5.5
R2	*S. girgensohnii Russ.*	11.7	O2	*S. fallax v. Klinggr.*	5.8
R3	*S. girgensohnii Russ.*	6.3	O3	*S. riparium Angstr.*	4.7
R4	*S. fallax v. Klinggr.*	5.2	O4	*S. riparium Angstr.*	5.9
R5	*S. subsecundum Nees*	3.8	O5	*S. girgensohnii Russ.*	5.5
R6	*S. girgensohnii Russ*	3.7	O6	*S. russowii Warnst.*	6.6
R7	*S. fallax v. Klinggr.*	4.9	O7	*S. riparium Angstr.*	5.3
R8	*S. subsecundum Nees*	3.9	O8	*S. riparium Angstr.*	4.7
R9	*S. riparium Angstr.*	12.9	O9	*S. fallax v. Klinggr.*	9.3
R10	*S. nemoreum Scop.*	14.6	O10	*S. fallax v. Klinggr.*	5.7
R11	*S. girgensohnii Russ.*	5.5	O11	*S. russowii Warnst.*	4.1
R12	*S. girgensohnii Russ.*	10.6	O12	*S. fallax v. Klinggr.*	8.3
R13	*S. girgensohnii Russ.*	3.4	O13	*S. girgensohnii Russ.*	6.0
R14	*S. girgensohnii Russ.*	4.9	O14	*S. girgensohnii Russ.*	6.7
R15	*S. girgensohnii Russ.*	11.2	O15	*S. girgensohnii Russ.*	3.7
R16	*S. girgensohnii Russ.*	6.1	O16	*S. riparium Angstr.*	4.9
R17	*S. girgensohnii Russ.*	3.7	O17	*S. riparium Angstr.*	5.6
R18	*S. fallax v. Klinggr.*	3.7	O18	*S. riparium Angstr.*	6.4

gives the minimum number of replicates needed to estimate the true mean δ^{34}S ratio within ±1‰ with a 95% probability. The chosen width of the confidence interval (±1‰, i.e., 2‰) is nearly one order of magnitude greater than the reproducibility of the mass spectrometric determinations (±0.2 to 0.3‰). Across the five sites, the minimum number of replicates averaged 6 for forest floor and 27 for *Sphagnum*. At specific unpolluted sites, the minimum number of replicates could be as high as 9 for forest floor and as high as 52 for *Sphagnum*. It appears that forest floor is more suited for studies aimed at identification of sources of pollution at the ecosystem level than *Sphagnum*. The within-site variability of up to 12‰ along with Table 5 show that the interpretive significance of δ^{34}S data based on the usual triplicate sampling of various ecosystem compartments may be quite low.

Table 5. The smallest number of observations needed for the estimated mean δ^{34}S ratio to fall within ±1‰ of the true mean with a 95% probability.

Site	Number of observations forest floor	Number of observations *Sphagnum*
Mull	9	18
Connemara	3	20
Rybárenská slat’	7	52
Thorne Moors	4	36
Oceán	3	8
Mean	6	27

Isotope effect of S assimilation

It has been shown by Gebauer et al. (1994) that sulfur in spruce needles is sensitive to the time of exposure to ambient air and its δ^{34}S ratio changes with age. It follows that spruce needles *per se* may be a problematic medium for studying the effect of assimilation on δ^{34}S. In the following paragraph we suggest that the difference between δ^{34}S of atmospheric deposition and forest floor can be viewed as an ‘overall’ fractionation (*sensu* Fritz & Fontes 1980) and used as an estimate of the magnitude of the assimilation-related δ^{34}S shift. It will be a *minimum* estimate because its magnitude is lowered by a small isotope effect of mineralization that has an opposite direction compared to assimilation (see below). We will show that the direction of the assimilation-related δ^{34}S shift is consistent at all study sites. Similarly, the direction of the mineralization-related δ^{34}S shift, which is opposite, is consistent at a variety of S loads and soil types (Novák et al. 1996).

At all study sites (Table 6), mean δ^{34}S ratios of spruce forest floor were lower than those of local atmospheric input via canopy throughfall, on average by 2.0‰. Soil may contain bedrock-derived sulfur which could influence its δ^{34}S ratio (Turk et al. 1993; Finley et al. 1995). However, Table 6 shows that the found negative δ^{34}S shift cannot be caused by adding of isotopically light S from bedrock to isotopically heavier S of the atmospheric input: Sulfur at the spruce rooting depth was isotopically heavier compared to the forest floor (at Mull, Connemara, Rybárenská slat’ and Thorne Moors even heavier than S in the atmospheric input), and could not act as an end-member for S mixing. Total S in forest floor of the five sites investigated contained on average 97.6 wt. % of organic S, and 2.4% of inorganic sulfate-S (Table 7). The age of organic S in forest floor is not known but its upper limit is indicated by the time elapsed since the needles grew on the tree.

Table 6. Comparisons between mean δ^{34}S ratios of the C soil horizon ('deep soil'), spruce throughfall and forest floor (left), and between bulk (open area) precipitation and living *Sphagnum* (right). The deep soil represents spruce rooting depth. Mean δ^{34}S ratios of spruce throughfall and bulk precipitation were flux-weighted over a one- to two-year period.

Site	Mean δ^{34}S (‰)				
	Deep soil	Spruce throughfall	Forest floor	Bulk precipitation	*Sphagnum*
Mull	15.1	14.9	10.2	13.7	12.7
Connemara	14.7	13.6	13.2	17.8	14.7
Rybárenská slat'	5.3	4.7	3.6	5.8	6.8
Thorne Moors	7.2	3.4	2.6	4.3	6.9
Oceán	5.9	6.2	3.5	6.7	5.8

The mean age of organic carbon in partly decomposed needles of the forest floor, inferred from enhanced ^{14}C from nuclear testing, is 4 years (Novák et al. 2000; data for the Northern Czech Republic). As mentioned before, the time elapsed between the actual S uptake and sampling was associated with additional isotope changes. With an increasing age of spruce needles and spruce litter, δ^{34}S ratios tend to increase (Gebauer et al. 1994; Novák et al. 1996). The reasons are longer exposure to air-borne S (the heavier end-member in the system) in case of needles, and mineralization in case of soil (heavier residual organic S remains *in situ* while lighter S is preferentially mineralized and removed). Thus our measured negative δ^{34}S shift of 2‰ from the atmospheric input to forest floor represents a minimum estimate of the actual assimilation-related S isotope effect.

Sulfur accumulated by *Sphagnum* in unforested locations had δ^{34}S ratio on average by 0.7‰ lower than bulk (open area) precipitation (Table 6). Apparently, assimilation of S by *Sphagnum* also exhibits a negative δ^{34}S shift. Its magnitude is smaller in comparison with spruce. However, data in Table 6 do not reflect the true isotope effect of S assimilation by *Sphagnum*. The reasons are twofold: (i) bulk precipitation is not a good measure of the atmospheric input into a *Sphagnum* peatland, and (ii) part of the sulfate taken up by *Sphagnum* always comes from surface bog water enriched in ^{34}S as a result of bacterial sulfate reduction (residual SO_4^{2-}-S becomes isotopically heavier, while the product, isotopically light S^{2-}, is removed; Bottrell & Novák 1998). Atmospheric S input into an open *Sphagnum* peatland, in fact, may be closer to spruce canopy throughfall than to bulk precipitation due to an underestimation of dry deposition of SO_2 into *Sphagnum* plants by plastic

Table 7. Percentage of total S released from *Sphagnum* and forest floor samples by 16.1 mM solution of $NaH_2PO_4 \cdot H_2O$.

Site	% of S released from *Sphagnum*	% of S released from forest floor
Mull	36.7	1.6
Connemara	15.3	0.0
Rybárenská slat’	34.2	3.4
Thorne Moors	21.5	3.3
Oceán	39.8	3.7
Mean	29.5	2.4

collectors (Fowler, pers. commun.). It has been shown previously that dry-deposited SO_2 may have a different $\delta^{34}S$ ratio than wet-deposited sulfate, the difference in Central Europe is up to 5‰ (dry-deposited S isotopically lighter; Novák et al. 1995, 2000).

Krouse et al. (1992) compiled all available data on $\delta^{34}S$ ratios of co-existing sulfate and organic S in plants. Their conclusion is consistent with ours in that organic S was isotopically lighter than sulfate-S by up to 6‰, on average by 2‰.

The existence of a negative assimilation-related $\delta^{34}S$ shift also provides explanation for our previous data from the watershed Jezeří in the Northern Czech Republic (Novák et al. 2000). In 15 soil pits we found isotopically systematically lighter soil S compared to $\delta^{34}S$ of atmospheric input which was monitored for a period of three years.

S retention in organic-rich materials

Plots of annual rates of atmospheric S deposition vs. mean S concentrations in forest floor and *Sphagnum* are given in Figure 7. Only the pollutant portion of total atmospheric deposition was used, i.e., atmospheric inputs were corrected by means of Cl concentrations for the marine component. Sulfur concentrations were corrected for ash content. Strong positive correlation (R = 0.97) was observed between S input into spruce stands and S retention in forest floor. Both variables were the highest at the inland, industrially polluted sites (Oceán and Thorne Moors). When total (pollutant plus marine) atmospheric deposition was used in an analogy to Figure 7 *top* instead of the mere pollutant portion of the atmospheric deposition, the positive correlation input – retention became somewhat less strong (R = 0.60), but still existed. When throughfall was used as a better approximation of S input into *Sphagnum*

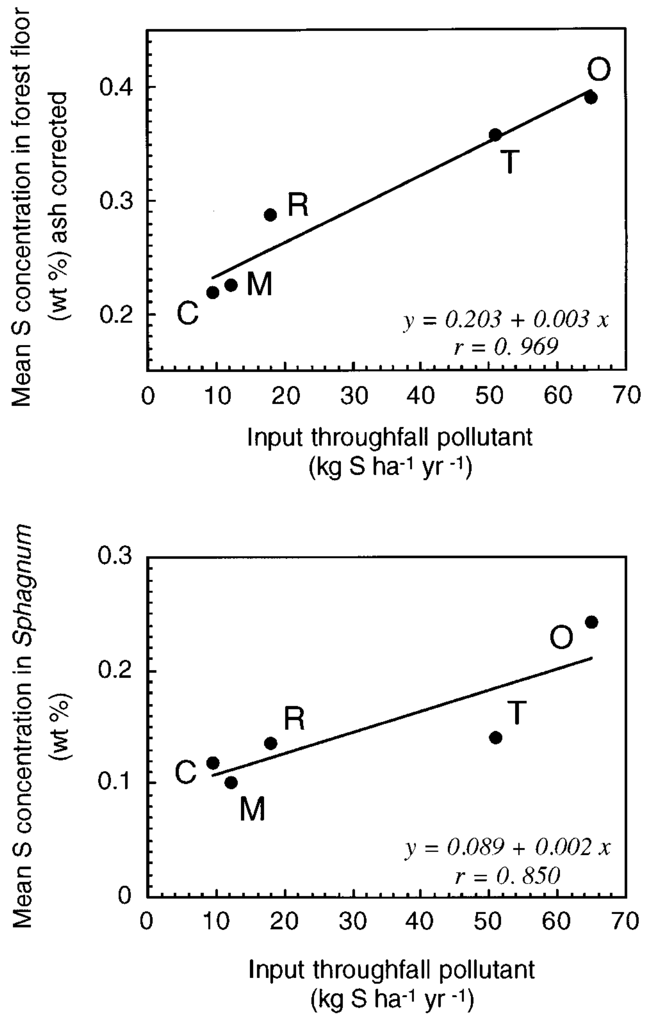

Figure 7. Relationship between annual rates of atmospheric deposition of acidifying S and mean S concentration in forest floor (*top*) and *Sphagnum* (*bottom*).

peatlands than bulk precipitation (Figure 7 *bottom*), the positive correlation input – retention was strong (R = 0.85). From these results it follows that in acidification studies equal stress must be put on biological uptake of atmogenic sulfate as on reversibility of sulfate adsorption in soils. This principle is now being increasingly recognized (Mayer et al. 1995; Driscoll et al. 1998; Mörth et al. 1999; Alewell & Gehre 1999), even though it was previously believed that high S inputs do not augment organic S in forest ecosystems (Johnson 1984; Houle & Carignan 1992).

In the early years of soil acidification studies it was acknowledged that biological effects may delay the onset of base removal from soils, however, stress was put on the fact that on death and decomposition of plants, the sulfhydroxyl groups are oxidized to SO_4^{2-}, so that, effectively, all input becomes SO_4^{2-} in the soil (Reuss & Johnson 1986). It was shown at a variety of forest soils that with increasing soil depth the amount of adsorbed inorganic sulfate also increases (Moldan & Černý 1994). However, Autry et al. (1990) found, also at a number of soil types, that adsorbed sulfate constituted substantially less of the total S than did organic S, irrespective of depth. Autry et al. (1990) concluded that organosulfur formation can be viewed as the primary mechanism for S retention in forest soils. Watwood et al. (1988) found that organic S formation can be occuring at high rates which are masked by rapid mobilization of the organic S to yield sulfate. There is increasing evidence that S accumulated in watersheds during the period of maximum industrial pollution (1960–1980) is relased via stream water following a reduction in S immisions (Driscoll et al. 1998; Alewell et al. 1999). An isotope mass balance may constrain the proportion of organically cycled S in stream-water sulfate. At some watersheds, as much as 60% of all exported sulfate contains organically cycled S (Gélineau et al. 1989; Novák et al. 2000). At two Central European sites with easing pollution in the vicinity of Oceán, we found that the percentage of soil sulfur in the output depends on hydrological conditions, i.e., steepness of the slope. Under inclination of 6°, the water output contained 60% of soil S, while under inclination of 2° remobilization of soil S accounted for only 40% of S in the output (Novák et al. 2000).

Identification of S sources

Mixing models by Krouse (1980) provide a tool to estimate the number and character of S sources affecting a receptor site. For the forest floor samples from Thorne Moors and Oceán (Figure 8 *bottom right*), the $\delta^{34}S$ vs. S concentration^{-1} plots show no variation. Such pattern indicates a single dominant pollution source with $\delta^{34}S$ = const. and sulfur concentration [S] = const. At both these sites the source are local coal-burning power stations whose S isotope signature fully overprints that of regional background. Both the S concentration and S isotope composition of power station emissions are constant at time scales comparable to the mean age of the sampled material ($\sim$4 years). The $\delta^{34}S$ signature of Yorkshire coal is not known, however that for Czech coals is well constrained. Mach et al. (1999) measured $\delta^{34}S$ ratios of 70 samples of coal from all stratigraphical levels in the Northern Czech Republic, arriving at a mean value of 2‰. This $\delta^{34}S$ signature of the pollution source differs from $\delta^{34}S$ of the forest floor (3.4‰) by only 1.4‰.

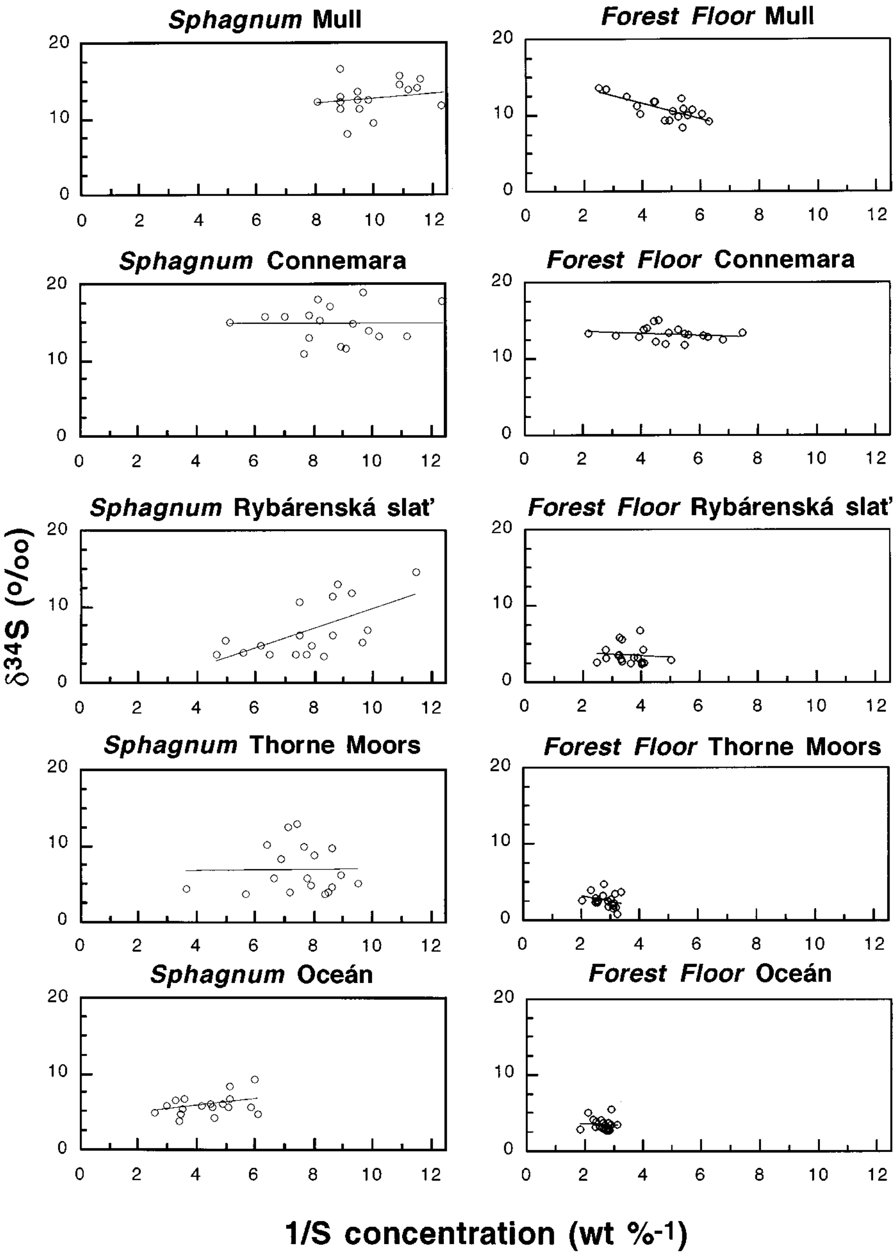

Figure 8. Graphs of S concentration^{-1} vs. δ^{34}S for the organic-rich materials. According to Krouse (1980), data points form a line when only two sources of S dominate (see text for further explanation).

If mixing of S from one source with [S] = const. and δ^{34}S = const. (regional background), and a second (anthropogenic or natural) source with variable [S] and constant δ^{34}S occurs, observations at the receptor site are arrayed along a straight line and the intercept with the vertical coordinate gives δ^{34}S ratio of the variable source (Krouse 1980). As seen in Figure 8 (forest floor), a two-source scenario suffices mainly for Connemara and Mull. The strong variable source at these sites (δ^{34}S of 15 and 13‰, respectively; Figure 8) is rich in isotopically heavy sea-spray S. The regional background is affected by adjacent mainland and has a lower δ^{34}S ratio. Neither the graph for *Sphagnum* nor the one for forest floor at Rybárenská slat' in Figure 9 forms a straight line. More than two S sources must be invoked to account for such cluster of points. For *Sphagnum* at each site, uptake of ^{34}S enriched surface bog water represents one additional mixing end-member.

Conclusions

Assimilation of atmospheric S by Norway spruce (*Picea abies*) is associated with an isotope effect. A comparison of δ^{34}S ratios of atmospheric input (canopy throughfall) and ecosystem S pools (forest floor) has shown a systematic shift toward lower δ^{34}S, on average by 2‰. Assimilation of S discriminates against the heavier isotope ^{34}S. This isotope effect must be considered when trying to ascribe sulfur found in damaged trees, and ecosystems in general, to specific pollution sources. Sea-shore sites accumulated less S in *Sphagnum* and in spruce forest floor than inland industrially polluted sites, even though the total atmospheric S loads were equally high ($\approx$60 kg S ha^{-1} yr^{-1}). The amount of S accumulated in these organic-rich S pools was directly proportional to the amount of non-marine S supplied by atmospheric deposition. Therefore, equal emphasis must be placed on organic S as on adsorption/desorption of inorganic sulfate when studying the acidification reversal in ecosystems. In areas of Central Europe affected by spruce decline, the atmospheric S input drops dramatically immediately following defoliation (the terminal stage of spruce die-back). Up to 70% of S input in industrially polluted spruce stands is formed by dry-deposited SO_2, which, after defoliation, is no longer captured by needles (Table 2). Living *Sphagnum* had higher δ^{34}S ratios than forest floor due to incorporation of isotopically heavy sulfate S resulting from dissimilatory sulfate reduction. Small-scale roughness of *Sphagnum* plants is higher compared to the smooth surface of bulk precipitation collectors and the amount of dry-deposited SO_2 in open peatlands is unclear. Realistic estimates of atmospheric S input into open peatlands are methodologically complicated and remain a challenge for the future. Forest floor soil is more suited for tracing the pathways of pollutants

S in terrestrial ecosystems than *Sphagnum* thanks to smaller within-site variability in δ^{34}S. When organic-rich materials were sampled in 18 replicates, the within-site range of the δ^{34}S ratios measured was up to 12‰. The use of δ^{34}S ratios as a tracer in environmental studies is possible only upon well replicated sampling. The minimum number of replicates needed to estimate the true δ^{34}S ratio of forest floor within ±1‰ (α = 0.05) averaged 6, but could be as high as 9 at unpolluted sea-shore sites. In case of *Sphagnum*, the minimum recommended number of replicates averaged 27, but could be as high as 52.

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